## APPLICATION OF CHEMICAL PRESSURE TO RARE EARTH PYROCHLORES

## THE EFFECT OF CHEMICAL PRESSURE ON THE MAGNETIC GROUND STATES OF RARE EARTH PYROCHLORES

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# Lay Abstract

Rare earth pyrochlores have the chemical formula  $R_2B_2O_7$ , where R is a magnetic rare earth element and B is a non-magnetic element. Materials of this type are widely studied because they have a propensity to exhibit exotic magnetic properties. In this thesis, we study the effect of varying the size of the non-magnetic B site atom, which is termed chemical pressure. As B is made larger or smaller, the crystal lattice expands or contracts, mimicking the effect of externally applied pressure. High-pressure synthesis techniques were used to prepare  $R_2B_2O_7$ compounds with B site cations that are typically too small (germanium), too large (lead), or too unstable (platinum) under ambient pressure conditions. Our characterizations of these highpressure materials have revealed that their magnetism is remarkably sensitive to the application of chemical pressure.

## Abstract

The rare earth pyrochlore oxides, with formula  $R_2B_2O_7$ , are a chemically versatile family of materials that exhibit a diverse array of magnetic phenomena. In this structure the R and Bsite cations each form a corner-sharing tetrahedral network, a motif that is prone to intense geometric magnetic frustration. As a consequence of their magnetic frustration, rare earth pyrochlores are observed to host a number of remarkable states such as spin ice and spin liquid states. In this thesis we endeavor to explore the phase diagrams of the rare earth pyrochlores through the lens of chemical pressure. Chemical pressure is applied by varying the ionic radius of the non-magnetic B site cation, which either expands or contracts the lattice, in analogy to externally applied pressure. We apply positive chemical pressure by substituting germanium at the B site and negative chemical pressure by substituting lead at the B site. We also consider the effect of platinum substitution, which has nominally negligible chemical pressure effects. In the ytterbium pyrochlores, we find that positive chemical pressure tunes the magnetic ground state from ferromagnetic to antiferromagnetic. Remarkably, we also find that the ytterbium pyrochlores share a ubiquitous form to their low temperature spin dynamics despite their disparate ordered states. In the terbium pyrochlores, we find that positive chemical pressure promotes ferromagnetic correlations - the opposite effect of externally applied pressure. Our studies of platinum pyrochlores reveal that platinum, while non-magnetic, is able to facilitate superexchange pathways. Thus, the magnetic ground states of the platinum pyrochlores are significantly altered from their titanate analogs. The work in this thesis highlights the delicate balance of interactions inherent to rare earth pyrochlore magnetism and shows that chemical pressure is a powerful tool for navigating their phase spaces.

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# Preface

This is a stapled paper thesis. It contains seven published or submitted articles. The surrounding material is meant to provide background and place the work into a broader context. All of the original research is found in the seven publications.

**Publication I**: "XY antiferromagnetic ground state in the effective S = 1/2 pyrochlore  $Yb_2Ge_2O_7$ ", Alannah M. Hallas, Jonathan Gaudet, Murray N. Wilson, Timothy J. Munsie, Adam A. Aczel, Matthew B. Stone, Rafael S. Freitas, Angel M. Arevalo-Lopez, J. Paul Attfield, Makoto Tachibana, Christopher R. Wiebe, Graeme M. Luke, and Bruce D. Gaulin. Physical Review B **93**, 104405 (2016).

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**Publication II**: "Universal dynamic magnetism in Yb pyrochlores with disparate ground states", Alannah M. Hallas, Jonathan Gaudet, Nicholas P. Butch, Makoto Tachibana, Rafael S. Freitas, Graeme M. Luke, Christopher R. Wiebe, and Bruce D. Gaulin . Physical Review B: Rapid Communications **93**, 100403(R) (2016).

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**Publication III**: "Incipient ferromagnetism in  $Tb_2Ge_2O_7$ : Application of chemical pressure to the enigmatic spin-liquid compound  $Tb_2Ti_2O_7$ ", Alannah M. Hallas, Jinguang G. Cheng, Angel M. Arevalo-Lopez, Harlyn J. Silverstein, Yixi Su, Paul M. Sarte, Haidong D. Zhou, Eun Sang Choi, J. Paul Attfield, Graeme M. Luke, and Christopher R. Wiebe. Physical Review Letters **113**, 267205 (2014).

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Publication IV: "Magnetic frustration in lead pyrochlores", Alannah M. Hallas, Angel M. Arevalo-Lopez, Arzoo Z. Sharma, Timothy J. Munsie, J. Paul Attfield, Christopher R. Wiebe, and Graeme M. Luke. Physical Review B 91, 104417 (2015).

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**Publication V:** "Relief of frustration in the Heisenberg pyrochlore antiferromagnet  $Gd_2Pt_2O_7$ ", Alannah M. Hallas, Arzoo Z. Sharma, Yipeng Cai, Timothy J. Munsie, Murray N. Wilson, Makoto Tachibana, Christopher R. Wiebe, and Graeme M. Luke. Physical Review B **94**, 134417 (2016). Reproduced from Ref. [5] with permission, copyrighted by the American Physical Society. **Publication VI**: "Phase competition in the Palmer-Chalker XY pyrochlore  $Er_2Pt_2O_7$ ", Alannah M. Hallas, Jonathan Gaudet, Nicholas P. Butch, Guangyong Xu, Makoto Tachibana, Christopher R. Wiebe, Graeme M. Luke, and Bruce D. Gaulin. Submitted to Physical Review Letters (2017) [6].

**Publication VII**: "Experimental insights into ground state selection of quantum XY pyrochlores", Alannah M. Hallas, Jonathan Gaudet, and Bruce D. Gaulin. Invited Review to appear in the Annual Review of Condensed Matter Physics (2017) [7].

In the course of my doctoral studies, I have had many opportunities to work collaboratively on projects that resulted in publications. On these papers I do not appear as the primary author, nor are they included in this thesis. However, several of these works share strong connections with the themes of this thesis and are listed here for completeness.

**Publication VIII**: "Magnetic dilution and domain selection in the XY pyrochlore antiferromagnet  $Er_2 Ti2 O_7$ ", Jonathan Gaudet, Alannah M. Hallas, Dalini D. Maharaj, Connor R.C. Buhariwalla, Edwin Kermarrec, Nicholas P. Butch, Timothy J.S. Munsie, Hanna A. Dabkowska, Graeme M. Luke, and Bruce D. Gaulin. Physical Review B **94**, 060407(R) (2016) [8].

**Publication IX**: "Experimental evidence for field-induced emergent clock anisotropies in the XY pyrochlore  $Er_2 Ti_2 O_7$ ", Jonathan Gaudet, Alannah M. Hallas, Jacque Thibault, Nicholas P. Butch, Hanna A. Dabkowska, and Bruce D. Gaulin. Physical Review B **95**, 054407 (2017) [9].

**Publication X**: "Effect of chemical pressure on the crystal electric field states of erbium pyrochlore magnets", Jonathan Gaudet, Alannah M. Hallas, Alexander I. Kolesnikov, and Bruce D. Gaulin. Submitted to Physical Review B (2017) [10].

Chapter

# Introduction

Magnetic materials are ubiquitous in our modern world. Their rich phenomenology is key to many technologies, such as hard drives, which rely on giant magnetoresistance (2007 Nobel Prize in Physics), or magnetic resonance imaging, which utilizes superconducting magnets (2003 Nobel Prize in Physiology or Medicine). On the more fundamental side, the limits of magnetic phenomena are far from known, and new discoveries have the potential to astonish, such as the spin texture of a skyrmion [11]. Furthermore, the intrinsic range of spin dimensionalities (Ising, XY, Heisenberg) leads magnetism to play a special role in the field of statistical mechanics [12]. This was particularly evident with the awarding of the 2016 Nobel Prize in Physics for the theoretical discovery of topological phases and phase transitions. The pioneering works that led to this award are magnetic models for XY spins in 2D (the Kosterlitz-Thouless transition [13]) and Heisenberg spins in 1D (Haldane chains [14]).

The array of magnetic phenomena introduced in the previous paragraph have diverse microscopic origins. Yet, there is a unifying feature: in each case, the underlying crystal structure provides an essential ingredient for the remarkable phenomenology that emerges. For example, the Dzyaloshinkii-Moriya interaction, which is necessary to obtain skyrmions, can only occur when the bond between the magnetic ions has a broken inversion symmetry. Indeed, there is often a strong interplay between lattice and magnetic degrees of freedom. One research topic where this is especially true is highly frustrated magnetism. In this field, crystal lattice geometries are constructed with the deliberate intention of inhibiting conventional magnetic order. As a result, geometrically frustrated materials have been found to exhibit a wealth of exotic ground states and behaviors. The work undertaken in this thesis is the synthesis and characterization of new geometrically frustrated materials. The introduction begins in Section 1.1 with an overview of conventional magnetism in solid state materials. Then Section 1.2 describes how geometric frustration is disruptive to conventional magnetic order and can give rise to exotic phenomena. Section 1.3 introduces the pyrochlore lattice, a canonical crystalline architecture for 3-dimensional geometric frustration. The sections that follow give an overview of rare earth magnetism on the pyrochlore lattice, starting with the single ion properties in Section 1.4 and then the collective magnetic phenomena in Section 1.5. Section 1.6 summarizes the magnetic properties of the most well-studied family of frustrated pyrochlores: the rare earth titanates. Finally, Section 1.7 outlines the remainder of this thesis.

#### 1.1 Magnetism in Condensed Matter

The topic of this thesis is the remarkable collective phenomena that can be observed in magnetically frustrated solid state systems. While the materials we will ultimately discuss are exotic magnets, it is illustrative to begin with some description of conventional magnetism. To determine whether a material is magnetic, one can simply count the electrons in its constituent ions. Unpaired electrons carry a magnetic dipole moment, while paired electrons do not. A simple example of a material where all the electrons are paired is the ionic salt NaCl, where sodium is in its 1+ oxidation state (Na<sup>+</sup> = [Ne]) and chlorine is in its 1- oxidation state (Cl<sup>-</sup> = [Ar]). Such a material will have a diamagnetic response to an external magnetic field, but for simplicity we will refer to ions or compounds with no unpaired electrons as non-magnetic. If unpaired electrons are found, such as in NiO (Ni<sup>2+</sup> = [Ar] $3d^8$ ) or CrO<sub>2</sub> (Cr<sup>4+</sup> = [Ar] $3d^2$ ), then a magnetic material has been identified (Figure 1.1(a,b)). There is, however, a significant difference between these two binary compounds:  $CrO_2$  is a ferromagnet, whereas NiO is an antiferromagnet. Thus, below  $T_C = 386$  K, the spins of the unpaired electrons in CrO<sub>2</sub> align parallel to one another [15], as shown in Figure 1.1(c). A very different ordered state occurs in NiO, where below  $T_N = 523$  K the  $Ni^{2+}$  moments adopt an anti-parallel configuration in alternating [111] planes [16], as shown in Figure 1.1(d).

To understand why some materials are ferromagnets while others are antiferromagnets we can consider the nearest neighbour Heisenberg Hamiltonian,

$$\mathcal{H} = -2\sum_{i>j} J\mathbf{S}_{i} \cdot \mathbf{S}_{j},\tag{1.1}$$

where J is the material dependent exchange integral. If J is positive, then the energy will be



Figure 1.1: (a,b) The magnetism in  $\text{CrO}_2$  and NiO originates from unpaired *d* electrons. (c) Below  $T_C = 386$  K,  $\text{CrO}_2$  orders ferromagnetically, while (d) NiO orders antiferromagnetically below  $T_N = 523$  K. The inverse magnetic susceptibility,  $\chi^{-1}$  for an unfrustrated (e) ferromagnet and (f) antiferromagnet.

minimized for a parallel spin alignment whereas if J is negative it will be minimized for an anti-parallel alignment. However, predicting the sign and magnitude of J for a given material is a highly non-trivial task. In the case of NiO, there is very little direct exchange via the overlap of the nickel 3d orbitals. Instead, the exchange is primarily mediated by the oxygen anions, where their 2p orbitals hybridize with the partially filled 3d orbitals giving rise to superexchange. In cases such as this, the semi-empirical Goodenough-Kanamori rules can be used to predict the sign and magnitude of J based on structural considerations [17, 18]. For NiO, the Ni–O–Ni bonds have an angle of 180° and the Goodenough-Kanamori rules predict an antiferromagnetic ordered state, which is indeed what is observed. The case of CrO<sub>2</sub> is more complex than one might initially suspect for a binary transition metal oxide. Phenomenological considerations would lead one to predict that CrO<sub>2</sub> is a Mott insulating antiferromagnet, when in fact it is a ferromagnetic half-metal [19]. The metallic nature of CrO<sub>2</sub> is now understood to originate from a highly unusual band structure, a secondary consequence of which is ferromagnetism mediated by itinerant d electrons [15].

In general, determining the magnetic structure of a material requires neutron diffraction.

However, a broad classification of a material's magnetic state can be achieved with magnetic susceptibility,

$$\mathbf{M}_{\mathbf{i}} = \chi_{\mathbf{i}\mathbf{j}}\mathbf{H}_{\mathbf{j}},\tag{1.2}$$

where  $\chi$  is the proportionality constant for the induced magnetization, **M**, from an applied magnetic field, **H**. Magnetic susceptibility measurements yield distinct responses for various magnetic states. At temperatures much higher than the characteristic interaction energy,  $k_BT > |JS^2|$ , the system is in a disordered paramagnetic state, where thermal fluctuations dominate. In this regime, disregarding possible crystal electric field effects, the susceptibility should inversely scale with temperature, as can be derived with mean field theory,

$$\chi = \frac{C}{T - \theta_{CW}},\tag{1.3}$$

which is known as the Curie-Weiss law. It is conventional to plot the inverse quantity,  $\chi^{-1}$ , giving a linear temperature dependence, examples of which are shown in Figure 1.1(e,f). The Curie-Weiss constant,  $\theta_{CW}$ , gives the characteristic energy scale of the magnetic interactions,

$$\theta_{CW} = \frac{2S(S+1)}{3k_B} \sum_{n} z_n J_n,$$
(1.4)

where  $z_n$  is the number of *n*th nearest neighbours and  $J_n$  is the corresponding exchange constant. As  $\theta_{CW}$  depends on J, it will be negative for an antiferromagnet and positive for a ferromagnet. As  $k_B T$  becomes comparable to  $|JS^2|$ , deviations from Curie-Weiss behavior are expected as the result of developing short-range spin correlations. In a conventional magnet, one finds that the magnetic ordering temperature,  $T_C$  or  $T_N$ , is not very different from  $|\theta_{CW}|$ . Below this temperature, the spins in the system will spontaneously break rotational symmetry as they adopt a long-range ordered state. In this thesis we will be interested in materials where magnetic order is suppressed far below the characteristic temperature scale of the magnetic interactions – systems that are "frustrated".

#### **1.2** Magnetic Frustration

The term "frustrated" describes a system in which the pairwise interactions cannot all be satisfied simultaneously. This phenomenon can be trivially illustrated by considering antiferromagnetic Ising spins on the vertices of an equilateral triangle, as shown in Figure 1.2(a). The first two spins can arbitrarily be chosen to adopt "up" and "down" alignments, respectively. Then,



Figure 1.2: Lattice architectures prone to geometric magnetic frustration. In 2-dimensions (a) the triangular lattice, (b) the Kagome lattice, and (c) the  $J_1 \sim J_2$  square lattice. In 3-dimensions (a) the pyrochlore lattice and (b) the face centered cubic lattice.

the third spin has two opposing constraints, as it cannot align anti-parallel with both its neighbours simultaneously. Thus, the magnetism is frustrated and because it is imposed by the lattice architecture, it is called geometric frustration. Should this triangular lattice be distorted from equilateral to isosceles, then the frustration would be partially relieved as the competing interactions would no longer be identical in strength. This contrived example illustrates a key aspect of geometric magnetic frustration – that triangular motifs are particularly prone to frustration. Thus, in real materials, crystalline lattices composed of edge and corner sharing triangles are desirable for frustration, such as the triangular and Kagome lattices shown in Figure 1.2(a,b). However, even a square lattice can be frustrated provided the exchange couplings between nearest and next-nearest neighbours are both antiferromagnetic and of comparable magnitude,  $J_1 \sim J_2$  (Figure 1.2(c)). Expanding into 3-dimensions, the most frustration prone architectures are those built up of tetrahedra, such as the pyrochlore and the face centered cubic lattices (Figure 1.2(d,e)). The pyrochlore lattice is the focus of this thesis and will be discussed at length in the sections that follow.

The most basic experimental identification of a frustrated material comes from magnetic susceptibility. The ratio of the magnetic ordering temperature and the Curie-Weiss temperature can be parameterized as a frustration index [20],

$$f = \frac{|\theta_{CW}|}{T_{N,C}}.$$
(1.5)

The condition for magnetic frustration is loosely defined by Ramirez *et al.* as f > 10 [20]. In the temperature range between  $T_{N,C}$  and  $|\theta_{CW}|$ , the system is strongly correlated but only on short length scales, a state sometimes referred to as cooperative paramagnetism [21]. If the system does ultimately achieve magnetic order, some compromise must be reached in the competing interactions. Returning to the example of antiferromagnetic moments on a triangular lattice, one could imagine orienting the spins at  $120^{\circ}$  with respect to each of their nearest neighbours. Such a state globally satisfies the antiferromagnetic constraints, as there is zero net magnetization, and is in fact found in many real materials [22]. However, in some cases, no such compromise can be reached. For example,  $YbMgGaO_4$ , which has a 2-dimensional triangular lattice of Yb<sup>3+</sup> and a frustrated index of f > 67, does not appear to magnetically order at any temperature [23, 24]. In this material non-magnetic Mg<sup>2+</sup> and Ga<sup>3+</sup> are randomly distributed over a single crystallographic site, leading some to speculate about the role of disorder in preventing magnetic order [25]. This illustrates another important facet of magnetically frustrated materials: the interactions are often precariously balanced such that effects that would otherwise be negligible (weak disorder, further neighbour interactions, etc.) can take on an important role.

The holy grail in the field of magnetic frustration is the quantum spin liquid (QSL). The QSL is a superposition state in which the spins are strongly entangled and quantum fluctuations prohibit magnetic order [26]. In the sense that a liquid is a correlated but disordered state, all frustrated materials have a spin liquid (or cooperative paramagnet) regime above their magnetic ordering temperature. However, in a QSL, magnetic order is suppressed even at T = 0 K. Numerous microscopic models have been shown to support QSL ground states on various lattice types [27]. Yet, there are no conclusive experimental realizations of a QSL state. Indeed, it remains to be shown whether such a definitive identification is even possible [26]. An absence of magnetic order to the lowest measurable temperatures, along with persisting spin dynamics, is a necessary but not sufficient criterion. The defining theoretical signature of a QSL state is the



Figure 1.3: (a) The A and B sites of the pyrochlore structure each form an independent network of corner sharing tetrahedra, a canonically frustrated motif. (b) The 8-fold oxygen environment about the A site cation forms a distorted cube. (c) The 6-fold oxygen environment about the B site cation forms a distorted octahedron.

entanglement entropy, but this is not an experimentally measurable quantity [27]. Nonetheless, there are a number of promising QSL candidates. One of the most notable candidate materials is Herbertsmithite, which has a Kagome lattice of S = 1/2 Cu<sup>2+</sup> cations. This material has a Curie-Weiss temperature of  $\theta_{CW} = -241$  K and does not order or freeze to at least 50 mK [28]. Thus, Herbertsmithite has a frustration index in excess of f > 5000, where of course f is infinite for a quantum spin liquid. Furthermore, the inelastic neutron scattering spectra of Herbertsmithite has been interpreted as a spinon continuum, strengthening its QSL candidacy [3].

#### **1.3** The Pyrochlore Lattice

Our discussion of geometric frustration thus far has focused on 2-dimensional lattices. In 3dimensions, the most successful platform for the study of magnetic frustration is the corner-sharing tetrahedral architecture, dubbed pyrochlore. Pyrochlore lattices can be found in two common crystal structures, one of which is called pyrochlore and the other is the spinel structure. Both of these structures have the space group  $Fd\bar{3}m$ . The name pyrochlore comes from the isostructural naturally occurring pyrochlore mineral,  $(Na,Ca)_2Nb_2O_6(OH,F)$ , and literally translates to "fire green". In the pyrochlore structure, which has the chemical formula  $A_2B_2O_7$ , both the A and B sites with Wyckoff positions 16c and 16d each independently form a network of corner-sharing tetrahedra, as shown in Figure 1.3(a). In the spinel structure,  $AB_2O_4$ , there is only one pyrochlore sublattice, which is the B site at Wyckoff position 16d. In this thesis we will only be concerned with the  $A_2B_2O_7$  pyrochlores. However, much of the phenomenology we will discuss is also directly applicable to the spinel lattice.

Before discussing magnetic frustration on the  $A_2B_2O_7$  pyrochlore lattice, we will first address structural considerations. As already mentioned, the A and B sites in this lattice each form a network of corner sharing tetrahedra. The oxygen anions are split over two crystallographically distinct sites, which can be written as  $A_2B_2O_6O'$ . The O' oxygen, one per formula unit, sits at the 8b Wyckoff site, which is at the geometric center of the A sublattice tetrahedra. The O oxygen, six per formula unit, are positioned on the 48f Wyckoff site. The coordinates of these oxygen anions contain the only adjustable position in the entire structure, their x position. This x coordinate can take values between 0.3125 and 0.375. When x = 0.3125, the 6-fold coordinate oxygen environment around the A site is precisely cubic. When x = 0.3125, the 6-fold coordinate oxygen environment around the B site is a regular octahedron. In actual materials, the x coordinate takes an intermediate value and thus the oxygen environments about both A and B are distorted from an ideal cube and octahedron, respectively, which is shown in Figures 1.3(b,c).

A remarkable attribute of the pyrochlore oxides is the size of their stability field. Compounds with the  $A_2B_2O_7$  pyrochlore structure number over 150 [29]. These materials can be further subdivided into the 3+/4+ family,  $(A^{3+})_2(B^{4+})_2O_7$ , and the 2+/5+ family,  $(A^{2+})_2(B^{5+})_2O_7$ . It is worth emphasizing that due to the presence of electronegative oxygen, the oxidation states of the metal cations that occupy the A and B sublattices are, in general, well-defined. The known elements that can occupy either of these sublattices are highlighted in the periodic table of Figure 1.4. The materials discussed in this thesis are those in which the A site is occupied by a rare earth cation and thus all belong to the 3+/4+ family. Within this family, the possible B site cations are the Group 14 elements, from silicon to lead, and transition metals in the 3d, 4d, and 5d blocks. Rare earth pyrochlores number well over 50 [29]. In the next sections we will discuss the magnetic properties of these rare earth pyrochlores, starting first with their single ion properties and then moving to their collective magnetic phenomena.

### **1.4 Single Ion Anisotropy**

An overarching topic in this thesis will be that different rare earth ions on the pyrochlore lattice can have markedly different single ion properties. This in turn has significant implications for the ground state magnetism [30]. As compared to magnetic elements elsewhere on the periodic table, the rare earths have a very well-defined hierarchy of energy scales. The rare earths are heavy, and thus they have a large spin-orbit coupling constant,  $\lambda \propto Z^4$ , of order 1 eV. Next the

Н	$(A^{3+})_2(B^{4+})_2O_7$ and $(A^{2+})_2(B^{5+})_2O_7$															He	
Li	Be												С	N	0	F	Ne
Na	Mg											Al	Si	Р	S	Cl	Ar
K	Ca	Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe
Cs	Ba	La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	Tl	РЬ	Bi	Ро	At	Rn

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 1.4: The elements that can occupy the pyrochlore lattice,  $(A^{3+})_2(B^{4+})_2O_7$  or  $(A^{2+})_2(B^{5+})_2O_7$ , in some combination are highlighted on this periodic table according to their oxidation state, where 2+ is shown in teal, 3+ in blue, 4+ in red, and 5+ in pink.

crystal electric field acts on an energy scale of approximately 100 meV. The final energy scale is the exchange interactions, the magnitude of which is set by orbital overlap. In the rare earths, it is the f electron orbitals that are partially filled, and they are far more spatially localized than the partially occupied d orbitals in magnetic transition metals. Thus, orbital overlap is quite minimal and consequently the exchange interactions are relatively weak, on the order of 0.1 - 1 meV. In this section, where we discuss single ion properties, we will deal with the first two of these effects, the spin orbit coupling and the crystal electric field.

There are two components to the angular momentum of the electrons in an atom, the orbital angular momentum,  $\mathbf{L}$ , and the spin angular momentum,  $\mathbf{S}$ , which can be combined in (2L + 1)(2S + 1) ways. However, these components are not wholly distinct, but rather are coupled via the spin-orbit interaction. Consequently, the quantity that must be conserved is the total angular momentum,  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ , and not  $\mathbf{L}$  and  $\mathbf{S}$  independently. J can take values from |L - S| to L + S. The spin-orbit interaction, which goes as

$$\langle \lambda \mathbf{L} \cdot \mathbf{S} \rangle = \frac{\lambda}{2} [J(J+1) - L(L+1) - S(S+1)], \qquad (1.6)$$

splits these (2L + 1)(2S + 1) levels into well-defined J manifolds, each with a degeneracy of 2J + 1. It follows that the energy separation between the J manifold and the J - 1 manifold is

 $\lambda J$ . It is worth emphasizing that in the absence of spin-orbit coupling all the (2L+1)(2S+1)levels would be degenerate. Now, in the specific case of rare earth magnetism, we can clearly see that since  $\lambda$  is large, we will typically be left with a well-isolated ground state J manifold.

We can now use Hund's rules to understand which of the J manifolds, which go from |L - S| to L + S, will be the ground state for a given ion. Hund's first rule is to maximize the spin angular momentum, S, in accordance with the Pauli exclusion principle. Thus, we will singly occupy each electron level with parallel spins before doubly occupying any level. Next, Hund's second rule is to maximize the orbital angular momentum, L. Thus, we will preferentially fill the maximum  $m_l$  states (+3, then +2, etc. for f orbitals). These first two rules both serve to minimize Coulomb repulsion. The third and last of Hund's rules is to minimize the spin-orbit energy by choosing J = L + S if the shell is more than half filled, and J = L - S if the shell is less than half-filled. In Figure 1.5, these rules have been followed to find J for six rare earth ions, which are the magnetic ions that will be considered in the forthcoming chapters. The calculated magnetic moment,  $\mu_{calc}$  for each of these cations is also given,

$$\mu_{calc} = g_J \sqrt{[J(J+1)]} \mu_B, \qquad (1.7)$$

where  $g_J$  is the Landé g-factor given by

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}.$$
(1.8)

The experimentally determined magnetic moments for each of these rare earths differs from the calculated value by less than 5%, demonstrating the applicability of simple Hund's rules arguments to these ions. This is not uniformly true across the periodic table. For example, in the 3d transition metals, which are much lighter than the 4f rare earths, the spin-orbit coupling,  $\lambda$ , is not sufficiently large to isolate a single J manifold. Consequently, Hund's third rule is not applicable and these elements are instead found to be best described by J = S. Amongst the 4f elements there are also a couple examples of poor agreement with Hund's rules, particularly samarium and europium. In these two rare earths, the ground state J manifold is not sufficiently separated from the first excited manifold.

In this section, we have thus far addressed spin-orbit coupling and the applicability of Hund's rules to the rare earths. For each of the elements we will be concerned with in this thesis ( $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Gd^{3+}$ ,  $Tb^{3+}$ ,  $Er^{3+}$ , and  $Yb^{3+}$ ), we have a well-isolated spin-orbit ground state comprised of 2J + 1 levels. The next energy scale we will consider is the crystal electric field. The crystal

	3	2	1	0	-1	-2	-3		$\mu_{calc}$
$Pr^{3+}(4f^2)$	╀	ϯ						L = 5, S = 1, J = 4	3.58 µ <sub>B</sub>
$Nd^{3+}(4f^{3})$	≁	≁						L = 6, S = 3/2, J = 9/2	$3.62\ \mu_B$
$\mathrm{Gd}^{3+}(4f^{7})$	_	≁	←	1	≁	╋	≁	L = 0, S = 7/2, J = 7/2	7.94 μ <sub>B</sub>
${ m Tb}^{3+}(4f^{8})$	₽	←	←	ϯ	ϯ	←	╀	L = 3, S = 3, J = 6	9.72 μ <sub>B</sub>
${\rm Er}^{3+}(4f^{11})$	₽	+↓	<b>†</b> ↓	†↓	←	←	≁	L = 6, S = 3/2, J = 15/2	9.59 μ <sub>B</sub>
$Yb^{3+}(4f^{13})$	<b>↑</b> ↓	<b>†</b> ↓	<b>↑</b> ↓	+↓	+↓	+↓		L = 3, S = 1/2, J = 7/2	4.54 μ <sub>B</sub>

Figure 1.5: Hund's rules determination of the total angular momentum, J, for the six rare earths that will be discussed in this thesis.

electric field is simply the electric field that originates from the surrounding atoms in the crystal. For the pyrochlore oxides, this crystal field most strongly originates from the oxygen anions. This electric field lifts the degeneracy of the 2J + 1 levels, which in turn determines the single ion anisotropy of the ion in question. There is one important consideration we have not yet touched upon, which is whether the total electronic count is odd (Nd<sup>3+</sup>, Gd<sup>3+</sup>, Er<sup>3+</sup>, and Yb<sup>3+</sup>) or even (Pr<sup>3+</sup> and Tb<sup>3+</sup>). In cases of an odd electron count, the total spin is a half integer and Kramers theorem applies, which is that every energy level must be at least doubly degenerate [31]. Taking  $Er^{3+}$  as an example, this means that the 2J + 1 = 16 levels will be split by the crystal electric field into eight doublets. In the case of integer spin systems, Kramers theorem does not apply, and the 2J + 1 levels can be maximally split in accordance with the site symmetry. For Tb<sup>3+</sup>, the 2J + 1 = 13 levels are split into 4 doublets and 5 singlets. Thus, for these non-Kramers systems, there exists the possibility of obtaining a non-magnetic singlet ground state. This is in fact realized for thulium in Tm<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [32].

The rare earth site in the pyrochlore lattice has a  $D_{3d}$  point group symmetry, the symmetry elements of which are a 3-fold rotation axis, an inversion center, two 2-fold rotation axis and a mirror plane. The 3-fold rotation axis defines the z axis which will interchangeably be referred to as the local [111] axis. This is the axis which connects the rare earth to its two apical O' oxygens (Figure 1.3(b)). The two 2-fold axes define the local x and y axes and also the mirror plane. These three local axes are orthonormal to one another. The crystal electric field Hamiltonian for an ion with  $D_{3d}$  point symmetry is

$$\mathcal{H}_{CEF} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^3 \hat{O}_4^3 + B_6^0 \hat{O}_6^0 + B_6^3 \hat{O}_6^3 + B_6^6 \hat{O}_6^6, \tag{1.9}$$

where the operators  $\hat{O}_2^0$ ,  $\hat{O}_4^0$ , etc. are written in the Stevens operator formalism, which express the crystal field interaction in terms of total angular momentum operators [33]. The terms  $B_2^0$ ,  $B_4^0$ , etc. are the crystal electric field parameters that approximate the Coulomb potential from the neighbouring atoms. These parameters can be experimentally determined using inelastic neutron scattering, as will be discussed in detail in **Chapter 2** and **Chapter 5**. Once the six crystal electric field parameters have been determined, the exact composition of the crystal field wavefunctions can be written in the  $m_J$  basis, where  $m_J$  can take values from -J to J. Due to the point group symmetry at the rare earth site, a Stevens operator acting on  $|m_J\rangle$  can only give  $|m_J\rangle$ ,  $|m_J \pm 3\rangle$  and  $|m_J \pm 6\rangle$ . Thus the ground state wave function will take the approximate form

$$\left|\phi_{0}^{\pm}\right\rangle = a\left|m_{J}\right\rangle \mp b\left|m_{J}\pm3\right\rangle \mp c\left|m_{J}\pm6\right\rangle\dots$$
(1.10)

where a, b, and c are the eigenvectors. The anisotropic g-tensors for the ground state doublet can then be directly computed as

$$g_z = 2g_J \left| \left\langle \phi_0^{\pm} \right| J_z \left| \phi_0^{\pm} \right\rangle \right| \quad \text{and} \tag{1.11}$$

$$g_{\perp} = g_J |\langle \phi_0^+ | J_+ | \phi_0^- \rangle| = g_J |\langle \phi_0^- | J_- | \phi_0^+ \rangle|$$
(1.12)

Ising spin anisotropy is obtained in cases where  $g_z$  is greater than  $g_{\perp}$ . Conversely, when  $g_{\perp}$  is larger than  $g_z$ , the spin anisotropy will be XY-like. The Ising axis is the local [111] axis and the the XY plane is perpendicular to this axis. It is noteworthy that both of these spin anisotropies are explicitly defined with respect to local, *not global*, coordinates. Thus, Ising-like spins on the pyrochlore lattice are not collinear and XY spins are not coplanar.

## **1.5** Magnetism on the Pyrochlore Lattice

Having now detailed the structural properties of the pyrochlore lattice and the single ion physics, we can at last begin to consider magnetic frustration on this lattice. One of the canonical examples of frustration is to consider antiferromagnetically coupled Ising spins on the vertices of a tetrahedron, as shown in Figure 1.6(a), with some arbitrary global Ising axis. This is indeed



Figure 1.6: (a) An antiferromagnetic global Ising orientation is a frustrated motif on the pyrochlore lattice, (b) while with local Ising anisotropy it is not frustrated. (c) Ferromagnetic Ising spins on a pyrochlore lattice are frustrated.

a frustrated motif, for after two of the four spins have been placed, the third and fourth will necessarily not satisfy one of their pairwise interactions. However, this example is also unphysical, for as was just described in the previous section, the Ising axis in the pyrochlores is along the local [111] axis, which is the axis that points into or out of the center of a tetrahedra. If we reconsider the stated problem, antiferromagnetically coupled Ising spins on the pyrochlore lattice, now with the spins constrained to the appropriate Ising axis, we see something remarkable: this is *not* a frustrated motif! This spins adopt a so-called all-in/all-out structure, as shown in Figure 1.6(b). This state has been experimentally observed in several materials, including FeF<sub>3</sub> [34] and Sm<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [35].

For Ising spins on the pyrochlore lattice, it is in fact those with ferromagnetic coupling that are frustrated. The best arrangement that these ferromagnetically coupled spins can achieve is a two-in/two-out configuration, displayed in Figure 1.6(c). This spin state is frustrated because there are too many equivalent ways this arrangement can be achieved. Even on a single tetrahedra, a two-in/two-out configuration can be achieved in six unique ways. When the system size is increased to that of a macroscopic sample, the degeneracy is infinite [36]. Harris *et al.* realized that this degeneracy maps precisely onto the proton disorder in water ice, which was first studied by Pauling [37,38]. Thus, this ferromagnetic Ising pyrochlore state was dubbed "spin ice". As with water ice, spin ice has an extensive ground state degeneracy of

$$S = \frac{Nk_B}{2}\log(3/2),$$
 (1.13)

where N is the number of spins. The spin ice state was experimentally discovered in the pyrochlores  $Ho_2Ti_2O_7$  and  $Dy_2Ti_2O_7$  [38, 39]. The nearly infinite Ising anisotropy in these systems originates from crystal electric field effects. The ferromagnetic coupling does not

originate from the exchange interactions, as was initially believed, but rather from long-range dipolar interactions [40]. Both of these rare earths have very large moments, ~  $10\mu_B$ , which gives a ferromagnetic dipolar interaction of approximately 2 K, much larger than the nearest neighbour exchange interaction. Thus, these systems are examples of dipolar spin ice, a so-called classical spin liquid state [41]. An interesting side note is that in 1956, Anderson wrote down a model for antiferromagnetically coupled Ising spins on the pyrochlore lattice, where he used a global Ising axis. While this model is unphysical it turns out to give an analogous result to the problem of spin ice, an extensive ground state degeneracy [42].

Moving beyond Ising spins, we next consider Heisenberg spins on the pyrochlore lattice. This scenario generates the inverse result of the Ising case, where antiferromagnetically coupled Heisenberg spins are highly frustrated while the ferromagnetically coupled ones are unfrustrated [43]. While a detailed overview of the Heisenberg pyrochlore antiferromagnet is beyond the scope of this thesis, numerous works have predicted the existence of quantum spin liquid states within this framework [21, 43, 44]. It remains to be seen whether the conditions of these models can be borne out in a real material. Lastly, in the intermediate case, a highly degenerate ground state is also found for the XY pyrochlore antiferromagnet. However, unlike the case of the Heisenberg pyrochlore antiferromagnet or the Ising pyrochlore ferromagnet, this degeneracy is sub-extensive. Fluctuation driven long range order can be achieved in this model [45, 46], ie. order-by-disorder [47]. Finally, an XY pyrochlore with ferromagnetic coupling would order into a canted ferromagnetic state [48].

## 1.6 The Titanate Pyrochlores

The most well-studied family of rare earth pyrochlores to date is the titanates,  $R_2$ Ti<sub>2</sub>O<sub>7</sub>, where non-magnetic Ti<sup>4+</sup> has the noble gas electron configuration of [Ar]. The popularity of this family has a couple likely origins. First, the groundbreaking discovery of the spin ice state was originally made in Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [38]. More generally, however, is that the titanates can be readily synthesized by conventional solid state synthesis and grown as large single crystals via the optical floating zone technique [49–51]. The availability of large single crystals of the  $R_2$ Ti<sub>2</sub>O<sub>7</sub> pyrochlores has allowed enormous advancement in the understanding of their magnetic properties. The  $R_2$ Ti<sub>2</sub>O<sub>7</sub> series can be grown over a wide range of rare earths, from Sm<sup>3+</sup> (4f<sup>5</sup>) to Lu<sup>3+</sup> (4f<sup>14</sup>). Three of these members have non-magnetic ground states: Eu<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [52], Tm<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [32], and Lu<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. The former two do possess unpaired electrons and are paramagnetic at high temperatures, but they are non-Kramers ions with singlet crystal electric field ground states. The latter simply has

	Anisotropy	Free moment	$\theta_{CW}$	$T_N, T_C, \text{ or } T_f$	Ground State
$\mathrm{Sm}_2\mathrm{Ti}_2\mathrm{O}_7$ [35]	Ising	$1.5 \ \mu_B$	$-0.3 { m K}$	0.3 K	All-in/All-out
$Gd_2Ti_2O_7$ [53]	Heisenberg	7.9 $\mu_B$	$-9~\mathrm{K}$	1 K	Partial order
$\mathrm{Tb}_{2}\mathrm{Ti}_{2}\mathrm{O}_{7}~[54]$	Ising	$9.7 \ \mu_B$	$-19 \mathrm{K}$	_	Spin liquid?
$Dy_2Ti_2O_7$ [39]	Ising	10.6 $\mu_B$	$+0.5 {\rm K}$	$\sim 1 {\rm K}$	Spin Ice
$Ho_2Ti_2O_7$ [38]	Ising	$10.4 \ \mu_B$	$+1.9 { m K}$	$\sim 1 \text{ K}$	Spin Ice
$\mathrm{Er}_{2}\mathrm{Ti}_{2}\mathrm{O}_{7}$ [46]	XY	$9.5 \ \mu_B$	$-22 \mathrm{K}$	1.2 K	XY AFM
$Yb_2Ti_2O_7~[55]$	XY	$4.5 \ \mu_B$	$+0.6 {\rm K}$	$0.25~{ m K}$	Canted FM

Table 1.1: Magnetic properties of the rare earth titanate pyrochlores,  $R_2 Ti_2 O_7$ .

a filled electron shell. The magnetism of the remaining seven rare earth titanates have all been well-studied and are summarized in Table 1.1.

Of the different combinations of spin anisotropy and couplings described in the preceding section, examples of almost all can be found amongst the rare earth titanates. Here, we will give a cursory overview of these seven materials, leaving a more detailed treatment to the introductory remarks in the relevant chapters.  $Sm_2Ti_2O_7$  has antiferromagnetically coupled Ising spins and is thus, unfrustrated. As would be expected, it orders at  $T_N = |\theta_{CW}| = 0.3$  K into the all-in/all-out spin structure [35].  $Gd_2Ti_2O_7$ , which is a good approximation to a Heisenberg antiferromagnet, has a perplexing partially-ordered state below  $T_N = 1$  K. In this state, only  $\frac{3}{4}$  of the Gd<sup>3+</sup> moments adopt an ordered configuration, while the remaining  $\frac{1}{4}$  remain dynamic [53]. The origin and exact nature of this state is not fully understood [56,57]. Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is perhaps the most enigmatic of these rare earth titanates, with an absence of magnetic order to at least 60 mK [54]. There are a number of factors that complicate a simple understanding of this material, including a low lying first excited crystal field level ( $\sim 1 \text{ meV}$ ) [58], sample dependence due to strong sensitivity to disorder [59], and remarkable field-induced phenomenology [60]. As discussed in the previous section, the Ising ferromagnets  $Ho_2Ti_2O_7$  and  $Dy_2Ti_2O_7$  are both realizations of the dipolar spin ice state.  $Er_2Ti_2O_7$ , on the other hand, is an antiferromagnetic XY pyrochlore with a relatively high magnetic ordering transition at  $T_N = 1.2$  K [46]. The degeneracy breaking that gives rise to  $Er_2Ti_2O_7$ 's long range magnetic order is a compelling candidate for an order-by-disorder mechanism [61]. Last is Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, where much like Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, sensitivity to disorder and sample dependence have hindered the categorization of this material's magnetic ground state [62, 63]. The most recent works point towards a growing consensus that the ground

state of  $Yb_2Ti_2O_7$  is a canted ferromagnet, with a number of unresolved peculiarities [55, 64–67].

## 1.7 Overview

In this thesis we explore the rare earth pyrochlore phase space using chemical pressure.

- **Chapter 2** contains three papers, where we discuss the effects of positive chemical pressure on rare earth pyrochlore magnetism, which is achieved via germanium substitution.
- In **Chapter 3** we present one paper on the lead pyrochlores, which are at the edge of the stability field for the pyrochlore structure, and thus the limit of negative chemical pressure.
- **Chapter 4** features two papers where we study the properties of the platinum pyrochlores and find that platinum has a profound effect on the magnetic properties on these systems, despite being non-magnetic.
- In Chapter 5 we present a review article on the XY pyrochlores, in which we unify the behaviors of this family with respect to phase competition.
- Chapter 6 contains concluding remarks.

Chapter

# Germanium Pyrochlores

From an empirical standpoint, the introductory survey of rare earth titanate pyrochlores has revealed that these materials live in a rich phase space for complex magnetic phenomena. However, due to the unique attributes of the various rare earth cations, it is difficult to unify the properties of a large subset of these systems onto a single phase diagram. For example, the strength of the dipolar interactions range from unimportant (*e.g.* Ce [68]) to dominant (*e.g.* Dy [40]), the crystal electric field anisotropy can go from Ising (*e.g.* Ho [38]) to Heisenberg (*e.g.* Gd [69]), and the exchange interactions themselves can be highly anisotropic (*e.g.* Yb [70]). The convolution of these effects is directly responsible for the rich complexity of rare earth pyrochlore magnetism.

In this thesis, we attempt to experimentally create a framework for understanding the rich phase spaces of the rare earth pyrochlores. Our approach has been to consider multiple systems with the same rare earth cation A site and varying non-magnetic B sites. In this approach, the magnetic properties intrinsic to the rare earth A site are left largely unaltered. Then, the primary tuning parameter is the changing ionic radius of the non-magnetic B site cation, which in turn varies the cubic lattice parameter, a. Within the pyrochlore structure the distance between two adjacent rare earth cations is:

$$d = \sqrt{2}a/2. \tag{2.1}$$

Thus, chemical substitution of the B site can be thought of as exerting an isotropic, internal pressure on the lattice. When the radius of the B site cation is reduced, the lattice is compressed, bringing the rare earth ions closer together. This is considered a positive chemical pressure. Conversely, if the radius of the B site cation is increased, then the lattice and the distance between neighbouring rare earths is expanded, corresponding to a negative chemical pressure.



Figure 2.1: The relative ionic radii of the the non-magnetic B site cations, germanium, titanium, and tin in their 4+ oxidation state, as well as the rare earth A site cation ytterbium in its 3+ oxidation state.

Within the  $Fd\bar{3}m$  pyrochlore structure, the positions of both the A and B site cations, as well as the apical oxygens, are constrained by symmetry. The second oxygen, however, has a single adjustable parameter: its x coordinate. This oxygen x coordinate need not vary linearly with chemical pressure, an effect which could have implications for both the crystal electric field and the superexchange pathways. Although we will proceed with the naive picture that chemical pressure acts as a uniform, isotropic pressure, this previously mentioned fact should be kept in mind.

In the realm of magnetic frustration, the titanate breed of rare earth pyrochlores have been the most extensively characterized [30] and thus, provide a natural starting point for studies with chemical pressure. The titanate pyrochlores can be stabilized with rare earths from Sm<sup>3+</sup>  $(4f^5)$  to Lu<sup>3+</sup>  $(4f^{14})$  [29]. For this set of rare earths, there are many other possible B sites, such as molybdenum,  $Mo^{4+}$ , and iridium,  $Ir^{4+}$ . However, the majority of these B site cations are themselves magnetic, which complicates the objective of understanding the rare earth magnetism. In ambient pressure conditions, the only other non-magnetic B site besides titanium,  $Ti^{4+}$ , compatible with most of these rare earths is tin,  $\operatorname{Sn}^{4+}$  [29]. The ionic radius of tin, r = 69 pm, is 14% larger than that of titanium, as shown in Figure 2.1. Tin substitution then provides a negative chemical pressure, enlarging the cubic lattice parameter, a, by approximately 3%. Sideby-side comparisons of these tin pyrochlores with their titanate analogs, highlights the delicate balance inherent to rare earth magnetism. For example,  $Er_2Ti_2O_7$  orders antiferromagnetically at a relatively high temperature,  $T_N = 1.2$  K [46,71], while  $\text{Er}_2\text{Sn}_2\text{O}_7$  does not magnetically order down to at least 100 mK [72, 73]. Likewise, the cooperative paramagnet  $Tb_2Ti_2O_7$  has no conventional magnetic order down to at least 70 mK [54], while  $Tb_2Sn_2O_7$  adopts an ordered spin ice-like state at 0.87 K [74].

The objective of the work undertaken in this chapter was to explore the phase space of

the rare earth pyrochlores by expanding the range of materials with non-magnetic B-sites. To do so, we synthesized a collection of germanium, Ge<sup>4+</sup>, based pyrochlores. Under ambient conditions,  $R_2$ Ge<sub>2</sub>O<sub>7</sub> forms in the lower-symmetry tetragonal pyrogermanate phase, due to the large size mismatch between the A and B site cations [75]. However, using high pressure techniques, Shannon and Sleight reported the first rare earth germanate pyrochlores,  $R_2$ Ge<sub>2</sub>O<sub>7</sub> in 1968 [76]. Germanium, with an ionic radius of r = 53 pm, is 11% smaller than titanium, as shown in Figure 2.1, which contracts the cubic lattice parameter, a, by approximately 2%. Thus, with respect to titanium, germanium provides an effective positive chemical pressure. To date, germanium is the smallest B site cation that has been successfully combined with a rare earth Asite to form a pyrochlore lattice. The germanate pyrochlores are particularly attractive because they can be stabilized with high pressure synthesis techniques all the way from  $\mathrm{Gd}^{3+}$  (4f<sup>7</sup>) to  $Lu^{3+}$  (4 $f^{14}$ ), giving a large overlap with the titanate family. Furthermore, due to the large size mismatch between germanium and the rare earths, the germanate pyrochlores are less prone to site-mixing disorder, i.e. errant A site cations sitting on the B sublattice, and vice-versa. This is attractive in light of the extreme sample dependence in several rare earth titanates, notably  $Yb_2Ti_2O_7$  [62, 63] and  $Tb_2Ti_2O_7$  [59, 60], which has been attributed to off-stoichiometry and site-mixing.

While the high pressure synthesis of the germanate pyrochlores dates back to 1968 [76], their magnetic characterization began in earnest less than 10 years ago, starting with  $Dy_2Ge_2O_7$ and Ho<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> [77]. These two materials adopt a dipolar spin ice state at low temperature, in similitude with their titanate and stannate variants. In each of the Dy and Ho pyrochlores, the transition to the spin ice state is marked by a broad peak in specific heat, as shown in Figure 2.2(a) [77]. The entropy release associated with this transition falls short of the expected Rln(2) for an isolated ground state doublet by the exact amount calculated by Pauling for water ice [37]. In the case of Ho<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, the spin ice correlations were also verified via powder neutron diffraction, which is shown in Figure 2.2(b) [78]. Thus, while substitution of the Bsite does enhance the strength of the nearest neighbour exchange interaction, the spin ice state remains robust (Figure 2.2(c)). An interesting side note, however, is that due to their contracted lattice parameters, the germanate spin ices should host a higher density of monopolelike excitations [79]. Two other germanate pyrochlores, Er<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> [80, 81] and Gd<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> [82], have also been investigated in parallel to the work conducted in this thesis.  $Er_2Ge_2O_7$  and  $Gd_2Ge_2O_7$  both order antiferromagnetically at  $T_N = 1.4$  K, with similar phenomenology to their titanate analogs. These above examples illustrate cases where positive chemical pressure induced



Figure 2.2: Dipolar spin ice states are obtained for each of  $\text{Ho}_2B_2\text{O}_7$  and  $\text{Dy}_2B_2\text{O}_7$  with B = Ge, Ti, Sn, as evidenced by (a) magnetic heat capacity and (b) neutron scattering. (c) The dipolar spin ice phase diagram with the estimated interaction strength for each material. Figures reproduced from Ref. [77] and [78], copyright held by the American Physical Society.

by germanium substitution does not drastically alter the low temperature magnetic properties.

The published works contained in this chapter describe the low temperature magnetism of two germanate pyrochlores,  $Yb_2Ge_2O_7$  and  $Tb_2Ge_2O_7$ . Throughout these works, we draw comparisons to their titanate and stannate analogs, allowing their properties to be understood in a broader context. In both cases, we show that chemical pressure upsets the delicate balance of magnetic interactions, resulting in a pronounced effect on the low temperature magnetism. The following publications are contained in this chapter:

**Publication I:** "XY antiferromagnetic ground state in the effective S = 1/2 pyrochlore  $Yb_2Ge_2O_7$ ", Alannah M. Hallas, Jonathan Gaudet, Murray N. Wilson, Timothy J. Munsie, Adam A. Aczel, Matthew B. Stone, Rafael S. Freitas, Angel M. Arevalo-Lopez, J. Paul

Attfield, Makoto Tachibana, Christopher R. Wiebe, Graeme M. Luke, and Bruce D. Gaulin. Physical Review B **93**, 104405 (2016).

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Publication II: "Universal dynamic magnetism in Yb pyrochlores with disparate ground states", Alannah M. Hallas, Jonathan Gaudet, Nicholas P. Butch, Makoto Tachibana, Rafael S. Freitas, Graeme M. Luke, Christopher R. Wiebe, and Bruce D. Gaulin . Physical Review B: Rapid Communications 93, 100403(R) (2016).

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**Publication III**: "Incipient ferromagnetism in  $Tb_2 Ge_2 O_7$ : Application of chemical pressure to the enigmatic spin-liquid compound  $Tb_2 Ti_2 O_7$ ", Alannah M. Hallas, Jinguang G. Cheng, Angel M. Arevalo-Lopez, Harlyn J. Silverstein, Yixi Su, Paul M. Sarte, Haidong D. Zhou, Eun Sang Choi, J. Paul Attfield, Graeme M. Luke, and Christopher R. Wiebe. Physical Review Letters **113**, 267205 (2014).

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# 2.1 Preface to Publication I: Tuning the ground states of the ytterbium pyrochlores with chemical pressure

In this manuscript, we present a thorough characterization of the ground state magnetism of the pyrochlore Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. Interest in the ytterbium pyrochlores, and in particular, Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, grew immensely following work that showed its microscopic spin Hamiltonian could support a unique quantum spin liquid state known as quantum spin ice [70]. While quantum spin ice may be part of the story, subsequent studies have shown that many samples of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> order into a splayed ferromagnetic state at low temperature [55, 64–67]. However, this state is not without its peculiarities, one of which is the substantial sample dependence alluded to earlier. Levels of defects that would be negligible in most materials can dramatically alter or suppress magnetic order in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [62, 63]. Recently, this sample dependence has been reconciled as originating from multi-phase competition [83, 84]. The anisotropic exchange parameters of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are believed to place it close to the boundaries of two or more competing classical phases [83,84]. Then, it is plausible that small levels of defects and natural sample variation could slightly shift the anisotropic exchange parameters, altering the low temperature state. The experimentally determined anisotropic exchange parameters for Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> do indeed place it in a splayed ferromagnetic,  $\Gamma_9$ , ordered state [70,85–87]. The proximate competing phase is thought to be the antiferromagnetic  $\Gamma_5$  ( $\psi_2$  or  $\psi_3$ ) state [83,84]. This competing ground state could be stabilized by the application of positive chemical pressure, as can be obtained via germanium substitution [83].

The first experimental investigation of the magnetic properties of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> identified an ordering transition at  $T_N = 600$  mK [88]. In our manuscript we expand on this earlier work with a thorough characterization of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>'s magnetically ordered state. First, we present an inelastic neutron scattering study that was carried out to determine the crystal electric field scheme of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. We find that Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> has a well-separated ground state doublet, primarily composed of  $m_J = \pm 1/2$ , giving rise to an effective S = 1/2 description for the Yb<sup>3+</sup> moments and XY crystal field anisotropy. Next, we present muon spin relaxation measurements, which confirm the presence of magnetic order below  $T_N = 600$  mK. The ordered state in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is quasistatic on the muon timescale and exhibits persistent spin dynamics, characteristic of a geometrically frustrated system. Finally, we performed neutron diffraction measurements and using symmetry analysis, we found that the magnetic ground state of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> belongs to the  $\Gamma_5$  manifold. This result confirms that  $\Gamma_5$  is the competing proximate phase of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and gives us a broader understanding of the ytterbium pyrochlore phase space.

The antiferromagnetic  $\Gamma_5$  ground state we find for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> sets it apart from the other ytterbium-based pyrochlores, Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [55, 64–67] and Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [48, 89], both of which have ferromagnetic low temperature states. Instead, the ground state properties of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> make for an interesting comparison to Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. These two materials, Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, share XY anisotropy and a ground state belonging to the  $\Gamma_5$  ( $\psi_2$  or  $\psi_3$ ) manifold [46]. In the case of Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, neutron polarimetry measurements on a single crystal sample have shown that the ordered state is pure  $\psi_2$  [90]. This observation has sparked a great deal of interest because  $\psi_2$ and  $\psi_3$  are degenerate at the mean field level [61]. One intriguing possibility is that the ground state selection may arise from an order-by-disorder mechanism [46, 61, 91]. However, there is a compelling alternative scenario for the ground state selection in Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> that relies on the presence of a low-lying excited crystal field level [92–94]. In this mechanism, the energy difference between  $\psi_2$  and  $\psi_3$ ,  $\delta E$ , varies as the inverse fourth power of the separation between the ground state and the first excited crystal field level,  $\Lambda$  [94],

$$\delta E \propto \frac{1}{\Lambda^4}.\tag{2.2}$$

If the  $\Gamma_5$  degeneracy is lifted in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, the virtual crystal field mechanism is far less plausible. In Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> the crystal field splitting to the first excited level,  $\Lambda = 81$  meV is more than an order of magnitude larger than in Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>,  $\Lambda = 6.5$  meV [46]. Thus, Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> may be an unambiguous example of ground state selection by order-by-disorder. However, at present it is not known whether one of  $\psi_2$  or  $\psi_3$  is uniquely selected in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. Neutron polarimetry experiments that could resolve this question have not yet been attempted due to the lack of large single crystal samples. However, of all the germanate pyrochlores, Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is the most promising for development in this area, as it is the closest to ambient pressure stability. Indeed, there are even reports of small (1 mm<sup>3</sup>) single crystals of pyrochlore phase Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> from hydrothermal crystal growth [95].

#### Author Contributions:

- Experimental Concept: A.M. Hallas, C.R. Wiebe, G.M. Luke, B.D. Gaulin
- Sample Preparation: A.M. Hallas, A.M. Arevalo-Lopez, J.P. Attfield, M. Tachibana, C.R. Wiebe
- Heat Capacity Measurements: R.S. Freitas
- Neutron Scattering Experiments: A.M. Hallas, J. Gaudet, A.A. Aczel, M.B. Stone, B.D. Gaulin
- *µSR Experiment*: **A.M. Hallas**, M.N. Wilson, T.J. Munsie, G.M. Luke
- Data Analysis: A.M. Hallas, J. Gaudet, G.M. Luke, B.D. Gaulin
- Manuscript: A.M. Hallas, J. Gaudet, B.D. Gaulin

## XY antiferromagnetic ground state in the effective $S = \frac{1}{2}$ pyrochlore Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>

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We report neutron scattering and muon spin relaxation measurements ( $\mu$ SR) on the pyrochlore antiferromagnet Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. Inelastic neutron scattering was used to probe the transitions between crystal electric field levels, allowing us to determine the eigenvalues and eigenvectors appropriate to the  $J = \frac{7}{2}$  Yb<sup>3+</sup> ion in this environment. The crystal electric field ground state doublet in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> corresponds primarily to  $m_J = \pm \frac{1}{2}$  with local XY anisotropy, consistent with an  $S_{eff} = \frac{1}{2}$  description for the Yb moments.  $\mu$ SR measurements reveal the presence of an ordering transition at  $T_N = 0.57$  K with persistent weak dynamics in the ordered state. Finally, we present neutron diffraction measurements that reveal a clear phase transition to the  $\mathbf{k} = (000) \Gamma_5$  ground state with an ordered magnetic moment of  $0.3(1)\mu_B$  per Yb ion. We compare and contrast this phenomenology with the low-temperature behavior of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, the prototypical  $S_{eff} = \frac{1}{2}$  XY pyrochlore magnets.

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#### I. INTRODUCTION

Magnetic frustration arises for systems in which the lattice geometry precludes the simultaneous satisfaction of all pairwise magnetic interactions. Cubic pyrochlore oxides, with the composition  $A_2B_2O_7$ , present exemplary three-dimensional realizations of lattices that can be subject to strong geometric magnetic frustration when either the *A* or *B* site is occupied by a magnetic cation [1]. The sublattices produced by the *A* and *B* site cations form two interpenetrating networks of cornersharing tetrahedra. The topicality of the pyrochlore lattice for the study of magnetic frustration is, in part, due to the ease with which numerous magnetic and nonmagnetic cations can be substituted onto the *A* and *B* sites of the lattice [2]. As a result, a plethora of magnetic pyrochlores have been investigated, revealing a diverse array of exotic magnetic ground states.

Rare-earth titanates and stannates of the form  $R_2B_2O_7$ , where *R* is a rare-earth ion and nonmagnetic *B* is either Ti<sup>4+</sup> or Sn<sup>4+</sup>, have been of great experimental interest. Both of these families can be synthesized using a wide range of rare-earth ions. However, while it is straightforward to grow large single crystals of the titanate  $R_2Ti_2O_7$  series, the stannate  $R_2Sn_2O_7$ series exists only in powder form at present. More recently, the rare-earth germanate family,  $R_2Ge_2O_7$ , has presented a new avenue to investigate the physics of magnetic pyrochlores. The germanate family is relatively unexplored, as they can only be grown under high pressures, and have thus far only been obtained as small polycrystalline samples [3]. The germanate pyrochlores, due to the small ionic radius of Ge<sup>4+</sup>, have contracted lattice parameters with respect to their titanium and tin analogs, and thus have so far been studied in the context of chemical pressure [3-5].

The diversity of magnetic ground states observed across the  $R_2B_2O_7$  series, with B = Ge, Ti, or Sn, can be primarily attributed to two sources. First, the moment size and anisotropy differ significantly, depending upon which rare-earth element sits at the A site. These single-ion properties are determined by the crystal field splitting of the (2J + 1) multiplet arising from the partially filled 4 f shell at the  $R^{3+}$  site. Second, the relative strength and nature of the magnetic interactions that exist between the  $R^{3+}$  moments can vary greatly. Furthermore, due to strong spin-orbit coupling in the 4f series, the exchange interactions between the  $R^{3+}$  moments are anisotropic, and the form of these interactions is determined by the point group symmetry at the  $R^{3+}$  site [6]. In simple terms, these combinations can generate ferromagnetically or antiferromagnetically coupled Ising, XY, or Heisenberg spins decorating a network of corner-sharing tetrahedra, and the diversity of ground states that these combinations imply.

While a range of magnetic ground states exist in the rareearth pyrochlores, we limit ourselves henceforth to discussion of those rare-earth pyrochlores with XY anisotropy, specifically the Yb<sup>3+</sup> and Er<sup>3+</sup> pyrochlores. The crystal electric field states for Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are well understood [7–9], while those corresponding to Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are less well determined [10,11]. However, it is clear that both the Yb<sup>3+</sup> and Er<sup>3+</sup> ions in  $R_2$ Ti<sub>2</sub>O<sub>7</sub> give rise to XY-like magnetic anisotropy. This XY anisotropy implies that the eigenfunctions describing the ground state doublet have large contributions from  $m_J = \pm \frac{1}{2}$ . Provided that the ground state doublet is well separated from the first excited crystal field level, this results in an  $S_{\text{eff}} = \frac{1}{2}$ quantum description for the magnetic degrees of freedom.

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effects suggest that the same should be true for all of  $Yb_2B_2O_7$ and  $Er_2B_2O_7$  with B = Ge, Ti, and Sn.

Yb2Ti2O7 and Yb2Sn2O7 both possess Curie-Weiss constants that are ferromagnetic and weak [8,12,13]. These two materials have also both been found to order into a canted ferromagnetic state at low temperatures [13-16]. However, there are exotic characteristics to such states, at least in the case of Yb2Ti2O7, for which single-crystal studies are required. For example in the "ordered" state of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> there is persistent anisotropic diffuse scattering [17,18] and no evidence of well defined spin wave excitations in zero magnetic field [19,20]. Further single-crystal inelastic neutron scattering measurements of Yb2Ti2O7 in its field-induced polarized state have been used to estimate its microscopic spin Hamiltonian [21,22]. Interestingly, the heat capacity anomalies in  $Yb_2Ti_2O_7$ are known to be sample dependent, with sensitivity to the presence of weak quenched disorder at the 1% level [23,24]. This sample dependence also extends to the ground state properties, as observed with both  $\mu$ SR and neutron scattering [14,15,19,20,25,26].

 $Er_2Ti_2O_7$  is an interesting contrast to the ytterbium systems. Er2Ti2O7 is known to possess a relatively large, antiferromagnetic Curie-Weiss constant [10,12] and undergoes a continuous phase transition to a noncoplanar  $\psi_2$  antiferromagnetic ordered state at  $T_N = 1.2$  K [27–29]. However, in contrast to Yb2Ti2O7, there are well-defined conventional spin wave excitations in  $\text{Er}_2\text{Ti}_2\text{O}_7$  below  $T_N$  [30]. Its microscopic spin Hamiltonian has also been estimated from inelastic neutron scattering [31], and the selection of the  $\psi_2$  ground state is argued to arise due to an order-by-quantum disorder mechanism [27,31–35]. The corresponding order-by-disorder spin wave gap has been measured with inelastic neutron scattering [36]. An alternate energetic argument for ground state selection of the  $\psi_2$  state has also recently been made [37,38]. In striking contrast to Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, the  $\psi_2$  ground state in Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is not obviously sensitive to quenched disorder and does not display sample dependence. It has even been shown to accommodate magnetic dilution consistent with three-dimensional percolation theory [39].

In this paper, we turn our attention to a member of the germanate pyrochlore family,  $Yb_2Ge_2O_7$ , wherein  $Ge^{4+}$  on the B site is nonmagnetic and the magnetism is carried by  $Yb^{3+}$  on the A site. We first present our inelastic neutron scattering measurements, which establish the eigenvalues and eigenfunctions for the crystal field levels appropriate to  $Yb_2Ge_2O_7$ . This firmly establishes the XY nature of the  $Yb^{3+}$ moments in their g tensor anisotropy. We next show  $\mu$ SR measurements that establish a phase transition at  $T_N = 0.57$ K to a conventional long-range ordered state with weak dynamics. Finally we present elastic neutron scattering measurements which reveal the ordered state in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> to be the  $\mathbf{k} = (000) \Gamma_5$  antiferromagnetic structure with an ordered moment of  $0.3(1)\mu_B$ . As both Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are antiferromagnetically coupled systems with ordered states in the  $\Gamma_5$  manifold,  $S_{\rm eff} = \frac{1}{2}$  degrees of freedom, and XY anisotropy, we compare and contrast these two pyrochlores.

#### **II. EXPERIMENTAL METHODS**

The cubic pyrochlore phase of  $Yb_2Ge_2O_7$  cannot be stabilized at ambient pressure using conventional solid state

synthesis. Thus, powder samples of Yb2Ge2O7 were synthesized using a belt-type high pressure apparatus. Stoichiometric quantities of Yb<sub>2</sub>O<sub>3</sub> and GeO<sub>2</sub>, pre-reacted into the tetragonal pyrogermanate phase, were sealed in gold capsules and reacted at 1300 °C under 6 GPa of pressure. The resulting product was thoroughly ground and powder x-ray diffraction was used to confirm the  $Fd\bar{3}m$  pyrochlore structure for each 400 mg batch. Our Rietveld refinements of the x-ray patterns gave a lattice parameter of 9.8284(2) Å, in agreement with previous reports [5,40]. While scaling up materials synthesized under high pressure is cumbersome, such samples do present some inherent advantages. First, high pressure synthesis gives a high degree of control over the stoichiometry [4]. Furthermore, the large ionic radii difference between  $Yb^{3+}$  and  $Ge^{4+}$ , which necessitates high-pressure synthesis, also significantly reduces the probability of site mixing [3]. This is particularly attractive in light of the sensitivity that the magnetism in some pyrochlores has shown to subtle variations in stoichiometry and so-called "stuffing" [23,41,42].

Muon spin relaxation ( $\mu$ SR) measurements on Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> were carried out at the TRIUMF Laboratory. A 300 mg pressed pellet of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, mixed with 20% silver powder to improve thermalization, was attached to a silver coated cold finger with Apiezon N-grease. Measurements between 25 mK and 2 K were carried out in a dilution refrigerator, both with zero external field and in fields up to 0.5 T. In  $\mu$ SR measurements, 100% spin polarized muons are implanted one at a time in a sample, where the muon spins evolve in the local magnetic environment. As the muons decay, with an average lifetime of 2.2  $\mu$ s, they emit a positron preferentially in the direction of the muon spin. Two opposing sets of detectors, in the forward and backward direction from the sample relative to the muon beam, detect the emitted positrons. The asymmetry spectrum, which is directly proportional to the muon polarization, is described by A(t) = [F(t) - B(t)]/[F(t) + B(t)], where F(t)and B(t) are the numbers of positrons detected in the forward and backward directions respectively, scaled by their counting efficiencies. Fits to the  $\mu$ SR data were performed using MUSRFIT [43].

The inelastic neutron scattering measurements on  $Yb_2Ge_2O_7$  were performed on the SEQUOIA spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory. A 2.7 gram powder sample of  $Yb_2Ge_2O_7$  was sealed in an aluminum sample can under a helium atmosphere. Using a standard orange Institut Laue-Langevin (ILL) cryostat, measurements were performed at 2 K with an incident energy of 150 meV, giving an elastic energy resolution of  $\pm 2.8$  meV. The energy resolution improves at higher energies and is approximately 1.4 meV for energy transfers of 80 meV and 1 meV for energy transfers of 120 meV. This configuration was also used for measurements on an identical empty can, which serves as a background.

Magnetic neutron diffraction measurements on  $Yb_2Ge_2O_7$ were carried out with the fixed incident energy triple axis spectrometer HB1A at the High Flux Isotope Reactor at Oak Ridge National Laboratory. The same 2.7 gram sample of  $Yb_2Ge_2O_7$  was mounted in an oxygen free copper sample can under a helium atmosphere. The incident neutron beam has a wavelength of 2.37 Å, which is selected by a double pyrolitic graphite monochromator. Energy analysis of the scattered beam employs a pyrolitic graphite analyzer crystal, giving an elastic energy resolution of approximately 1 meV. Elastic diffraction measurements were carried out using both a <sup>3</sup>He insert and a dilution insert, with base temperatures of 300 and 50 mK, respectively, and a maximum temperature of 10 K. Representational analysis of the diffracted intensities were performed using SARAH REFINE [44] and FULLPROF [45].

#### **III. RESULTS AND DISCUSSION**

#### A. Determination of the crystal electric field eigenvalues and eigenfunctions via inelastic neutron scattering

Figure 1(a) shows the inelastic neutron scattering spectrum for  $Yb_2Ge_2O_7$  collected at 2 K for energy transfers up to



FIG. 1. (a) Inelastic neutron scattering spectrum of  $Yb_2Ge_2O_7$ measured at 2 K with a neutron beam of incident energy 150 meV. A background spectrum, measured on an empty can, has been subtracted from the data. Crystal field excitations at 80.7, 84.2, and 123.3 meV are indicated by the blue, yellow, and green arrows, respectively. (b) An integrated cut of the same data over the range  $Q = [5.4, 6.0] \text{ Å}^{-1}$ . The fit to the data is achieved using a Hamiltonian, given by Eq. (1), which approximates the Coulomb potential generated by the crystal electric field due to the neighboring oxygen atoms.



FIG. 2. The Q dependence of the first two crystal electric field levels in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, indicated by the blue and yellow arrows respectively. The decrease in intensity as a function of Q is consistent with the magnetic form factor for Yb<sup>3+</sup>.

150 meV. The excitations corresponding to transitions between crystal electric field (CEF) levels can be assigned based on two criteria: (i) They should be dispersionless, i.e., without Qdependence, and (ii) their intensity should be maximal at the lowest Q values and should fall off according to the magnetic form factor of Yb<sup>3+</sup>. Following these criteria, three crystal field excitations can be identified in Fig. 1(a) at 80.7, 84.2, and 123.3 meV. The Q dependence for the first two transitions is shown in Fig. 2 and is consistent with the  $Yb^{3+}$  magnetic form factor. The valence shell of  $Yb^{3+}$  contains 13 f electrons which, following Hund's rules, gives a spin orbit ground state with total angular momentum  $J = \frac{7}{2}$  and a 2J + 1 = 8fold degeneracy. The local oxygen environment surrounding each Yb<sup>3+</sup> cation produces a crystal electric field that lifts the ground state degeneracy. However, from its odd electron count, it follows that Yb<sup>3+</sup> is subject to Kramer's theorem and, consequently, the crystal electric field can produce at most four doublets. Thus, the three crystal field doublets observed in Fig. 1(a) and the ground state doublet account for the full manifold of the  $Yb^{3+}$  crystal electric field transitions.

The eight oxygens that surround each Yb<sup>3+</sup> cation form a cube that is distorted along one of its body diagonals, where this direction forms the local [111] axis. Defining the  $\hat{z}$  axis along this [111] local axis, the local environment has a threefold symmetry, as well as an inversion symmetry, giving a point group symmetry  $D_{3d}$ . Following the Stevens' operator formalism, we use the following Hamiltonian to approximate the Coulomb potential generated by the crystal electric field due to the neighboring oxygen atoms [46–48]:

$$\mathcal{H}_{\text{CEF}} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^3 \hat{O}_4^3 + B_6^0 \hat{O}_6^0 + B_6^3 \hat{O}_6^3 + B_6^6 \hat{O}_6^6,$$
(1)

where the CEF parameters,  $B_n^m$ , have been fit using our inelastic neutron scattering data of Fig. 1(a). To do so, the scattered intensity is computed in the same way as in Ref. [7] using the CEF parameters of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> as an initial guess. This calculation is compared by a least squares refinement

TABLE I. The crystal electric field (CEF) eigenvalues and eigenvectors for Yb<sup>3+</sup> at the *A* site of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. The first column displays the CEF eigenvalues of the system, while the corresponding eigenvectors are given in each row in terms of the  $m_J$  basis.

E (meV)	$\left -\frac{7}{2}\right\rangle$	$\left -\frac{5}{2}\right\rangle$	$ -\frac{3}{2}\rangle$	$ -\frac{1}{2}\rangle$	$ \frac{1}{2}\rangle$	$ \frac{3}{2}\rangle$	$\left \frac{5}{2}\right\rangle$	$\left \frac{7}{2}\right\rangle$
0	0	0.13	0	0	-0.91	0	0	0.40
0	-0.40	0	0	-0.91	0	0	-0.13	0
80.7	0.90	0	0	0.36	0	0	-0.24	0
80.7	0	-0.24	0	0	0.36	0	0	0.90
84.2	0	0	-1	0	0	0	0	0
84.2	0	0	0	0	0	$^{-1}$	0	0
123.3	0.05	-0.93	0	-0.05	-0.21	0	0.23	-0.17
123.3	0.17	0.23	0	-0.21	0.05	0	0.93	0.05

to the experimental result [in this case, an integrated cut over  $Q = [5.4, 6.0] \text{ Å}^{-1}$ , as shown in Fig. 1(b)]. The CEF parameters are varied until good agreement is obtained with the experimental data. The resulting fit is shown in Fig. 1(b) where a Lorentzian function has been added at 73 meV to phenomenologically capture the scattered intensity produced from a nonmagnetic contribution, likely phonon or multiple phonon scattering. The nonmagnetic origin of this feature can be deduced from the lack of Q dependence, as shown in Fig. 2, as well as the temperature dependence, as was shown for Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [7].

The resulting CEF parameters are  $B_2^0 = 1.08$  meV,  $B_4^0 = -6.32 \times 10^{-2}$  meV,  $B_4^3 = 3.02 \times 10^{-1}$  meV,  $B_6^0 = 9.25 \times 10^{-4}$  meV,  $B_6^3 = 4.66 \times 10^{-2}$  meV, and  $B_6^6 = 3.10 \times 10^{-3}$ meV. The corresponding eigenfunctions and eigenvalues obtained with the above CEF parameters are given in Table I. As is the case for Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, the CEF ground state is primarily composed of  $m_J = \pm \frac{1}{2}$ . As well, the first, second, and third excited states of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> are predominantly made up of  $m_J = \pm \frac{7}{2}, m_J = \pm \frac{3}{2}$ , and  $m_J = \pm \frac{5}{2}$ , respectively. In fact, the crystal electric field scheme of  $\tilde{Y}b_2B_2O_7$  appears to be relatively unperturbed by substitution of the nonmagnetic B site from Ti<sup>4+</sup> to Ge<sup>4+</sup>. Each of the excited crystal field states in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is shifted upwards in energy approximately 5% from the corresponding level in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. This can be understood intuitively in terms of the reduction in the lattice parameter going from Ti<sup>4+</sup> to Ge<sup>4+</sup>. The reduced lattice parameter leads to a contraction of the oxygen atoms about the Yb<sup>3+</sup> cations and, as a result, Yb<sup>3+</sup> feels a larger crystal electric field, leading to a stronger splitting of the levels.

The anisotropic g tensors for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, obtained from the fit shown in Fig. 1(b), are  $g_{\perp} = 3.5(2)$  and  $g_z = 2.1(1)$ , where z corresponds to the local [111] axis. The uncertainties on the g tensors have been obtained by comparing the best-fit results with and without the phonon contribution around 73 meV and with and without a sloping background taken along the full energy range. The resulting g-tensor anisotropy corresponds to XY anisotropy and can be quantified by taking their ratio, giving  $g_{\perp}/g_z = 1.7(2)$ . For comparison, the value obtained for the same ratio with Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is 1.9(2) [7], indicating that the XY anisotropy may be slightly stronger in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> as compared to Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>.



FIG. 3. The results from muon spin relaxation measurements performed on Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> between 25 mK and 2 K. (a) Several representative asymmetry spectra for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> in which the background asymmetry has been subtracted. The fits to the data are indicated by the solid lines. The asymmetry is fit by a dynamical Lorentzian Kubo-Toyabe function. (b) The longitudinal field decoupling at 25 mK in fields between 0.01 and 0.5 T. The fits, as indicated by the solid lines, are given by a dynamical Lorentzian Kubo-Toyabe function. (c) The fitted values for the internal field distribution, *a*, an adjustable parameter in the dynamical Lorentzian Kubo-Toyabe function. The field distribution forms an order parameter which plateaus below 200 mK, and shows the onset of magnetic order at  $T_N = 0.57$  K.

#### B. Static magnetism revealed by muon spin relaxation

We employed muon spin relaxation ( $\mu$ SR) measurements to further characterize the low-temperature magnetism in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. Figure 3(a) shows some representative asymmetry spectra for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> in zero external field between 0 and 2  $\mu$ s. A background asymmetry contribution was fit to a slowly relaxing temperature-independent exponential and then subtracted from the presented data. This background asymmetry contribution comes from muons that land outside the sample, either in the admixed silver, the silver sample holder, or the cryostat.

At sufficiently high temperatures, when a system is in its paramagnetic regime, there will only be a small relaxation due to nuclear dipole moments; at such temperatures, the spins in the sample are rapidly fluctuating and the dynamics are faster than the muon time window. In Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> we see that at 2 K the asymmetry is only weakly relaxing, indicating that the
sample is within its paramagnetic regime. At 1 K, there is a slight increase in the relaxation, indicating that electronic spin correlations are beginning to develop. Upon cooling towards the Néel temperature, the relaxation further increases due to slowing fluctuations as the electronic correlations grow stronger [Fig. 3(a)]. As Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is cooled below the Néel temperature, the asymmetry takes on a two-component form, with a sharp drop in the early time asymmetry followed by a slow relaxation at longer times.

The data at all temperatures are well described in terms of a dynamical Lorentzian Kubo-Toyabe function [49]. This function, which is appropriate for a system with a Lorentzian distribution of internal fields, *a*, appropriately captures the physics in a system with slow or fast dynamics. The temperature evolution of *a*, as shown in Fig. 3(c), provides a clear order parameter corresponding well with the observed Néel temperature from ac susceptibility and heat capacity,  $T_N = 0.57$  K [5]. The internal field distribution plateaus below 200 mK at approximately 12  $\mu$ s<sup>-1</sup>, which corresponds to 0.1 T.

The asymmetry spectra for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> differs from the canonical spectra for a system with static magnetic order in two key aspects. First, the long-time component is not fully time independent, but instead has a weak exponential relaxation. This indicates that, below the Néel temperature, Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> remains weakly dynamic. A persistent relaxing signal, while not fully understood, is a common feature of magnetically frustrated systems [50]. Second, no long-lived precessing signal could be resolved in the asymmetry spectra. However, a lack of oscillations does not preclude static magnetic order. In fact, the absence of oscillations is frequently observed for pyrochlores with long range magnetic order, such as Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [51] and Tb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [52,53]. A lack of oscillations can be attributed to an inhomogeneous internal field distribution, which can, in part, be explained by having multiple muon stopping sites. Similarly, the minimum in Kubo Toyabe function can be "wiped out" by multiple field distributions, as would be expected for multiple muon stopping sites [54]. As the pyrochlore structure contains two inequivalent oxygen sites, and positively charged muons stop at the most electronegative positions, at least two inequivalent stopping sites can be expected in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>.

We also performed  $\mu$ SR measurements on Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> with an externally applied magnetic field. In our measurements, the external field is applied parallel to the initial muon polarization direction, i.e., longitudinal geometry. In the case of static (or quasistatic) magnetism, the external field can be increased until it overwhelms the static internal fields produced by the sample. When this happens, the muon spins will respond more strongly to the external field and become effectively "decoupled" from the sample, resulting in a reduced relaxation rate. For Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, at 25 mK in fields between 0.01 and 0.5 T, the asymmetry decouples in the expected manner for a dynamic Lorentzian Kubo-Toyabe, with the magnitude of the external field imposed as a constraint [Fig. 3(b)]. While applying a longitudinal field effectively decouples the majority of the relaxation, as in the zero field case, there remains a weak long time relaxation, so-called persistent spin dynamics. Thus, both the zero field and longitudinal field measurements on Yb2Ge2O7 are consistent with quasi static magnetic order on the muon timescale.

# C. Measurement of the magnetic structure by elastic neutron diffraction

Magnetic neutron diffraction was employed to determine the magnetic ground state of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. Our initial measurements surveyed a broad region of *Q*-space between 0.5 and 2.5 Å<sup>-1</sup>. Comparison of data sets collected at 50 and 900 mK revealed the formation of magnetic Bragg peaks on cooling into the ordered phase. All magnetic Bragg peaks were observed to form on allowed positions for nuclear reflections in the pyrochlore lattice. Figure 4 shows four of the measured Bragg positions at 50 and 900 mK. In each case, the peak has been fit to a Lorentzian peak shape function where the only independent adjustable parameter between 50 and 900 mK is the peak area. The peak centers and the background (denoted by the dashed line) were jointly refined. The peak widths were fixed according to the width of the (222) nuclear peak, which is the largest nuclear reflection.

Below the Néel transition in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, the largest intensity gain is observed on the (111) position [Fig. 4(a)]. The intensity gain from 900 to 50 mK, in arbitrary units of counts normalized by monitor, is  $3.1 \pm 0.7$ . The (002) position, which does not contain a nuclear reflection, is also devoid of a magnetic reflection [Fig. 4(b)]. The next magnetic reflections occur at (220) and (113), which have intensity gains of  $1.8 \pm 1.0$ 



FIG. 4. Neutron diffraction of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> over regions of *Q*-space corresponding to the (a) (111), (b) (002), (c) (220), and (d) (113) nuclear-allowed Bragg positions. Data collected below  $T_N$  (50 mK) is shown in blue and above  $T_N$  (900 mK) in red. The Bragg peaks are fit by Lorentzian functions in which the peak position and the background (indicated by the dashed black line) are jointly refined. The peak widths were fixed by fitting the (222) nuclear reflection. Thus, for each Bragg reflection, the only independent adjustable parameter is the peak area. The intensity gain on cooling into the Néel state is indicated on each panel, denoted as  $\Delta I$ , except in the case of (002) where no reflection is observed. The relative intensities of the observed magnetic Bragg reflections in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> correspond to a  $\Gamma_5$  ordered state.

TABLE II. Powder averaged magnetic Bragg intensities for each of the irreducible representations allowed for Yb<sup>3+</sup> on the 16*d* site of the  $Fd\bar{3}m$  pyrochlore lattice with a propagation vector of  $\mathbf{k} = (000)$ . Despite having multiple basis vectors,  $\Gamma_5$  and  $\Gamma_7$  have only one entry because the powder diffraction patterns are identical for each of their basis vectors. The six basis vectors of  $\Gamma_9$  likewise produce only two unique powder patterns. We also consider an optimized linear combination of  $\Gamma_9$ . The final row gives the experimentally observed magnetic intensities. In all cases, the intensities have been normalized relative to the most intense reflection in that pattern.

	(111)	(002)	(220)	(113)	(222)	(004)
$\Gamma_3(\psi_1)$	0	0	0.99	1	0	0
$\Gamma_{5}(\psi_{2,3})$	1	0	0.68	0.37	0	0
$\Gamma_7(\psi_{4,5,6})$	1	0.74	0.34	0.37	0	0
$\Gamma_9(\psi_{7,9,11})$	1	0.55	0.26	0.45	0.21	0.11
$\Gamma_9(\psi_{8,10,12})$	0.17	0.38	0.18	1	0.58	0.31
Γ <sub>9</sub> (L.C.)	1	0.22	0.10	0.37	0.40	0.21
Experiment	$1\pm 0.2$	0	$0.6\pm0.3$	$0.4\pm0.3$	0	0

and  $1.3 \pm 0.9$ , respectively [Figs. 4(c) and 4(d)]. The (113) Bragg peak, which is centered at 2.13 Å<sup>-1</sup> has a large sloping background because it is immediately adjacent to the large (222) nuclear reflection, centered at 2.23 Å<sup>-1</sup>. The (222) and (004) positions were also carefully measured and showed no intensity gain below the Néel temperature. A summary of the experimental intensities, given as a fraction of the intensity of (111), is shown in Table II.

Magnetic Bragg peaks were only found on positions allowed for nuclear scattering by the pyrochlore lattice. Thus, the magnetic reflections in Yb2Ge2O7 can be indexed with a propagation vector of  $\mathbf{k} = (000)$ . The possible magnetic structures for Yb<sup>3+</sup> on the 16d site of the  $Fd\bar{3}m$  pyrochlore lattice, with propagation vector  $\mathbf{k} = (000)$ , can be described by four possible irreducible magnetic representations:  $\Gamma_{Mag} = \Gamma_3^1 +$  $\Gamma_5^2 + \Gamma_7^3 + \Gamma_9^6$  [55,56]. These irreducible representations can be expressed in terms of their basis vectors  $(\psi_1, \psi_2, \dots, \psi_{12})$ . The  $\Gamma_3(\psi_1)$  structure is the so-called "all-in, all-out" state, a noncoplanar antiferromagnetic structure in which the moments are oriented along their local (111) axes. The  $\Gamma_3$  ( $\psi_1$ ) structure was first experimentally realized in FeF<sub>3</sub> [57] and has subsequently been found in various other systems [58-60]. The  $\Gamma_5$  manifold has two basis vectors,  $\psi_2$  and  $\psi_3$ , and has been observed in the XY antiferromagnets Er2Ti2O7 and Er2Ge2O7 [27,61]. Linear combinations of the  $\Gamma_7$  manifold, composed of  $\psi_4, \psi_5$ , and  $\psi_6$ , are often referred to as the Palmer-Chalker ground state [62]. The Palmer-Chalker ground state is found in Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, which is a realization of a Heisenberg pyrochlore antiferromagnet with dipolar interactions [56]. There are six basis vectors that make up the  $\Gamma_9$  manifold. Linear combinations of these six basis vectors can give noncollinear ferromagnetic structures related to the spin ice state, such as the splayed ferromagnetic state found in  $Yb_2Sn_2O_7$  [13].

The simulated relative intensities for each of these representations are listed in Table II. In the case of  $\Gamma_5$  and  $\Gamma_7$ , the powder diffraction patterns for their specific basis vectors are, in general, identical. Thus, we do not distinguish between  $\psi_2$  and  $\psi_3$ , nor do we distinguish between  $\psi_4$ ,  $\psi_5$ , and  $\psi_6$ . The six basis vectors that make up  $\Gamma_9$  produce two distinct powder diffraction patterns, as indicated in the table. Finally, a linear combination of the  $\Gamma_9$  basis vectors can also be considered. While there is poor agreement between  $\Gamma_9$  and the experimental data, the linear combination presented in Table II is the one that most closely fits the experimental data:  $\Gamma_{Mag} = 0.038(\psi_{7,9,11}) + 0.021(\psi_{8,10,12})$ . Inspection of this table reveals excellent agreement between the experimental results and the  $\Gamma_5$  manifold.

Rietveld refinement of all measured Bragg reflections, as summarized in Table II, was used to determine the size of the ordered moment in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. All structural parameters for the pyrochlore  $Fd\bar{3}m$  lattice and the scaling factor were determined from a refinement of the 900 mK data set, which is well above  $T_N$ . The 50 mK data set was then refined with a  $\Gamma_5$  magnetic structure where only the magnitude of the ordered moment was allowed to freely vary. The  $\psi_2$  and  $\psi_3$ basis vectors which comprise  $\Gamma_5$  generate identical powder neutron diffraction patterns and identical magnetic moment sizes, and thus we do not distinguish between the two within our Rietveld refinement. The resultant Rietveld refinement for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> at 50 mK is shown in Fig. 5(a). The best agreement with the measured data, as indicated by a minimization of  $R_{\rm Bragg}$ , was obtained for an ordered moment of 0.3(1)  $\mu_{\rm B}$ [Fig. 5(b)].

In order to obtain a measurement of the order parameter in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, we tracked the (111) Bragg peak, which is the largest magnetic reflection. Figure 6 shows the intensity of (111) as a function of temperature, where the zero has been set by the average intensity between 1 and 5 K, well above the Néel temperature. The order parameter in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> correlates directly with the sharp anomaly in the heat capacity, which is peaked at  $T_N = 0.57$  K. While the order parameter in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> appears quite conventional, this is not generically true in the ytterbium pyrochlores. The order parameter in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, which plateaus below  $T_c = 240$  mK, continually decreases well above  $T_c$ , to at least 700 mK [16].

## D. Comparison to relevant XY pyrochlore magnets

The antiferromagnetic  $\Gamma_5$  structure we have determined for  $Yb_2Ge_2O_7$  below  $T_N = 0.57$  K belongs to the same ground state manifold as  $\text{Er}_2\text{Ti}_2\text{O}_7$  below its  $T_N = 1.2$  K transition. However, Er2Ti2O7 was identified as uniquely displaying the  $\psi_2$  state, with a rather large ordered moment of  $\mu_{ord} =$  $3.01\mu_B$  [27]. For our powder sample of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, we cannot distinguish  $\psi_2$  from  $\psi_3$  within  $\Gamma_5$  [inset of Fig. 5(b)], and the ordered moment within this structure at low temperatures is small,  $\mu_{ord} = 0.3(1)\mu_B$ . We note that a large ordered moment of  $1.06(7)\mu_B$  has recently been reported for the antiferromagnetic ground state of Yb2Ge2O7 [61], but this estimate arose from measurements on a much smaller volume of sample, and no net magnetic scattering (i.e., difference between high and low temperature) is shown for the strongest magnetic Bragg peak, (111). In any case, this large ordered moment estimate for Yb2Ge2O7 is inconsistent with our results [Fig. 5(b)].

Order-by-quantum disorder has been proposed as the mechanism for the selection of the  $\psi_2$  ground state for Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [27,31–35], based on understanding the microscopic spin Hamiltonian derived from spin wave measurements [31].



FIG. 5. (a) Rietveld refinement of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> at 50 mK. All structural and scaling parameters were fixed from a refinement of the 900 mK dataset, as indicated by the red curve. Thus, in the magnetic refinement, indicated by the blue curve, the only adjustable parameter is the moment size. (b) Goodness of fit of the magnetic structure refinement for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, as measured by the minimization of  $R_{\text{Bragg}}$ , as a function of the magnitude of the ordered moment.  $R_{\text{Bragg}}$  is the sum of the weighted residuals for only the magnetic Bragg reflections. The best agreement between is given by an ordered moment of  $0.3(1)\mu_B$ . The inset shows the spin alignments given by the  $\psi_2$  and  $\psi_3$  states.

This mechanism predicts a gap in the spin wave spectrum due to breaking the continuous symmetry which exists between the  $\psi_2$  and  $\psi_3$  ground states within  $\Gamma_5$ . Indeed, this spin wave gap has been measured in  $Er_2Ti_2O_7$  [36]. However, an alternative mechanism for ground state selection based on virtual transitions to excited crystal field levels has also been proposed for Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [35,37,38]. This alternative mechanism relies on the presence of low energy crystal field levels, as the probability for such virtual transitions go as the inverse square of the energy required for the transitions out of the ground state. This is a plausible scenario for Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, as the lowest lying crystal field levels in Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are at 6.3 and 7.3 meV [27]. However, it is not a plausible scenario for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, as we have just determined that the lowest crystal field transition occurs at 80.7 meV, more than an order of magnitude higher in energy than was the case for Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. In this regard, Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is a stronger candidate for



FIG. 6. The relative intensity of the (111) magnetic Bragg reflection as a function of temperature. The intensity is given relative to the average intensity between 1 and 5 K, which is set to zero. The order parameter correlates well with the heat capacity anomaly, shown in red on the right-hand axis. The upturn below 100 mK in the heat capacity corresponds to a nuclear Schottky anomaly.

exhibiting an ordered state selected by a thermal or quantum order-by-disorder mechanism.

We emphasize that it does not follow that the  $\Gamma_5$  antiferromagnetic ground state we observe in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> arises from an order-by-disorder mechanism. It has been shown that a  $\Gamma_5$ state in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> could be predicted purely on the basis of the phase diagram for Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> obtained from its anisotropic spin exchange Hamiltonian [63]. Indeed, as  $\Gamma_5$  is constituted by both  $\psi_2$  and  $\psi_3$ , it is not clear that a selection is even being made, which would necessitate an order-by-disorder scenario. Dun *et al.* claim that fits to the heat capacity below  $T_N = 0.57$  K are consistent with the presence of an emerging spin wave gap of 24  $\mu$ eV, but no such gap has been directly measured. Nonetheless, the absence of low lying crystal field excitations in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> implies that there could be significant differences between the antiferromagnetic ground states in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, despite their similarities.

#### **IV. CONCLUSIONS**

To conclude, we have synthesized relatively large volumes of the pyrochlore magnet Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> using high-pressure synthesis techniques. This has enabled studies of both the crystal field excitations of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, using inelastic neutron scattering, and the low-temperature ground state of this system, using magnetic neutron diffraction and  $\mu$ SR techniques. Our inelastic neutron scattering measurements allow us to determine the eigenvalues and eigenfunctions associated with the splitting of the (2*J* + 1) manifold of states appropriate to Yb<sup>3+</sup> in the Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> environment. We find an XY nature to the single-ion ground state wave function, as expressed in  $g_{\perp}/g_z = 1.7(2)$ , and a large 80.7 meV gap to the first excited state. The ground state doublet is primarily comprised of  $m_J = \pm \frac{1}{2}$ , supporting a picture of  $S_{\text{eff}} = \frac{1}{2}$  Yb<sup>3+</sup> moments.

 $\mu$ SR measurements show quasistatic magnetic order on the muon time scale to set in below  $T_N = 0.57$  K. Our elastic neutron scattering measurements show the ground state to be a  $\Gamma_5$ , **k** = (000), antiferromagnetic state, with a relatively small ordered moment of  $0.3(1)\mu_B$  at low temperatures. We hope that this characterization of the single ion and ground state properties of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> motivates a full understanding of the structure and dynamics of this exotic pyrochlore magnet, and helps guide a thorough understanding of its fascinating phase behavior.

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# 2.2 Preface to Publication II: Revealing the ubiquitous dynamic magnetism of the ytterbium pyrochlores

We continue the investigation of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> in the second paper of this chapter, with an inelastic neutron scattering study. In contrast to the inelastic neutron scattering measurements used to determine the crystal electric field in the previous paper, the present study was preformed at lower temperatures, including below  $T_N = 600$  mK, and at lower energy transfers, ~ 1 meV, characteristic of rare earth collective spin excitations. The intention of this experiment was to characterize the spin wave excitations in the  $\Gamma_5$  ordered state of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. Then, based on known differences in the spin wave spectra of  $\psi_2$  and  $\psi_3$  [61], we hoped to distinguish precisely which state Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is ordering into. However, this plan did not come to fruition as the measured spin excitations of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> bear no resemblance to what is expected for a  $\Gamma_5$  ( $\psi_2$  or  $\psi_3$ ) antiferromagnet. Instead, we find that the spin excitations resemble gapless, over-damped ferromagnetic spin waves. Thus, the spin excitations of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> are highly unconventional, which is particularly mysterious given the conventional appearance of its magnetic ordering transition in ac susceptibility [88], heat capacity [1,81], and neutron diffraction [1,81].

The spin excitations of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> appear to be fundamentally at odds with an antiferromagnetic ordered state, which in and of itself is a novel result. Furthering the significance of this result is our observation that the excitation spectrum of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> shares a common form with those of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, despite their markedly different ordered states. Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [55, 64–67] and Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [48,89] both order into splayed ferromagnetic states at low temperatures, whereas Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is an XY antiferromagnet [1,81]. Yet, these three materials share a ubiquitous form to their spin excitations, with the greatest spectral intensity centered towards Q = 0 and extending out in a broad continuum without any apparent coherent propagation. It is important to note that although the observed spin excitations are more ferromagnetic in character they still do not have the expected form for a splayed ferromagnetic ordered state [55]. In fact, the absence of conventional spin waves in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> has been a long-standing puzzle [55, 86, 96–98]. It is remarkable that this trend extends to Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> with its antiferromagnetic ordered state.

Our examination of the magnetic specific heat unveils further commonalities between these three ytterbium pyrochlores,  $Yb_2B_2O_7$  (B = Ge, Ti, Sn). In each case the transition to magnetic order is marked by a sharp specific heat anomaly at  $T_N$  or  $T_C$ . At a higher temperature, which we label as  $T^*$ , there is a second broad specific heat anomaly. In each of these materials, approximately 80% of the spin entropy is connected with the higher temperature broad specific heat anomaly, rather than the sharp, low temperature anomaly. Comparing the temperature dependence of the inelastic neutron scattering with the magnetic specific heat reveals that the unconventional spin excitations do not form at  $T_N$  or  $T_C$ , but are instead correlated with  $T^*$ . For example, in the case of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, the excitations develop in the vicinity of  $T^* = 2$  K and then do not appreciably evolve at lower temperatures, including upon passing through  $T_N = 600$  mK. Despite the fact that these ytterbium pyrochlores have different dipole ordered states, it is clear that the shared form of their spin dynamics must also share a microscopic origin. Understanding the origin of these unconventional spin dynamics is likely key to a comprehensive understanding of the exotic magnetism of the ytterbium pyrochlores and is deserving of further attention.

# Author Contributions:

- Experimental Concept: A.M. Hallas, B.D. Gaulin, C.R. Wiebe, G.M. Luke
- Sample Preparation: A.M. Hallas, M. Tachibana
- Heat Capacity Measurements: R.S. Freitas
- Neutron Scattering Experiment: A.M. Hallas, N.P. Butch, B.D. Gaulin
- Data Analysis: A.M. Hallas, J. Gaudet, B.D. Gaulin
- Manuscript: A.M. Hallas, J. Gaudet, B.D. Gaulin

## Universal dynamic magnetism in Yb pyrochlores with disparate ground states

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The ytterbium pyrochlore magnets,  $Yb_2B_2O_7$  (B = Sn, Ti, Ge) are well described by  $S_{eff} = 1/2$  quantum spins decorating a network of corner-sharing tetrahedra and interacting via anisotropic exchange. Structurally, only the nonmagnetic *B*-site cation, and hence primarily the lattice parameter, changes across the series. Nonetheless, a range of magnetic behaviors is observed: the low-temperature magnetism in  $Yb_2Ti_2O_7$  and  $Yb_2Sn_2O_7$  has a ferromagnetic character, while  $Yb_2Ge_2O_7$  displays an antiferromagnetically ordered Néel state at low temperatures. While the static properties of the ytterbium pyrochlores are distinct, inelastic neutron scattering measurements reveal a common character to their exotic spin dynamics. All three ytterbium pyrochlores show a gapless continuum of spin excitations, resembling overdamped ferromagnetic spin waves at low *Q*. Furthermore, the specific heat of the series also follows a common form, with a broad, high-temperature anomaly followed by a sharp low-temperature anomaly at  $T_C$  or  $T_N$ . The novel spin dynamics we report correlate strongly with the broad specific heat anomaly *only*, remaining unchanged across the sharp anomaly. This result suggests that the primary order parameter in the ytterbium pyrochlores associated with the sharp anomaly is "hidden" and not simple magnetic dipole order.

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The pyrochlores, with chemical composition  $A_2B_2O_7$ , are exemplary realizations of systems that often exhibit strong geometric magnetic frustration when either the *A* or the *B* site is occupied by a magnetic ion. Recently, the pyrochlore Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has attracted significant interest owing to its rich low-temperature physics. Within Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, magnetic Yb<sup>3+</sup> sits at the *A* site and nonmagnetic Ti<sup>4+</sup> resides at the *B* site, each forming a network of corner-sharing tetrahedra. The ability to grow large, high-quality single crystals of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has made it an ideal system for investigation of its microscopic Hamiltonian [1–5]. These studies suggest that anisotropic exchange is the dominant driver for its low-temperature physics. The resulting microscopic Hamiltonian is also the basis for proposals that Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> could realize a quantum spin ice state at low temperatures [5–10].

The low-temperature phase behavior in real specimens of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is complex and subject to strong sample dependencies. The specific heat of polycrystalline samples synthesized by conventional solid-state techniques contains a sharp anomaly [11]. Meanwhile, single-crystal samples grown using zone melting techniques display broader anomalies with lower transition temperatures, multiple transitions, and sometimes no obvious transition [12–14]. Furthermore, a host of magnetometry, neutron scattering, and muon spin relaxation measurements have shown evidence of an ordered ferromagnetic state below  $T_C = 265$  mK in some samples of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [7,11,15–17] but not in others [10,14,18]. This strong sample dependence, especially in single-crystal samples, is attributed to quenched disorder at the 1% level [12,13]. Perhaps moving towards a consensus, recent work on stoichiometric powders of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has revealed long-range splayed ferromagnetic correlations in which the moments are canted towards the local (111) direction [17]. There is, however, a longstanding mystery in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, which is not subject to these sample dependencies [17]: the absence of conventional spin waves below  $T_C$  [10].

The interesting physics of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> provided the initial impetus for the study of Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, in which the nonmagnetic *B* site has been substituted with Sn<sup>4+</sup>. The larger ionic radius of Sn<sup>4+</sup> increases the lattice parameter of Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> by approximately 3%. Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> undergoes an ordering transition at  $T_C = 150$  mK to a splayed ferromagnetic state [19] in which the moments are canted away from ferromagnetic alignment along (111) but in the opposite direction from Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. Despite this transition in Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> being marked by a relatively sharp anomaly in the specific heat [19,20], there is an absence of conventional spin-wave excitations below  $T_C$ , as in the case of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [21].

Entering the fray most recently is Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, where the *B* site is now occupied by nonmagnetic Ge<sup>4+</sup>. The smaller ionic radius of germanium reduces the lattice parameter by 2% compared to Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. In the first report on Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, nonlinear ac susceptibility measurements showed an ordering transition at  $T_N = 0.57$  K with an antiferromagnetic character [22]. Subsequent neutron diffraction measurements have identified the antiferromagnetic k = 0 ordered state in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> as belonging to the  $\Gamma_5$  manifold [23,24]. In the  $\Gamma_5$  ordered state, the four moments on each tetrahedron are oriented perpendicular to the local (111) axes, a state markedly different from those observed in the other ytterbium pyrochlores.

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FIG. 1. Specific heat of the ytterbium pyrochlores,  $Yb_2B_2O_7$  (B = Ge, Ti, and Sn), where in each case a broad high-temperature anomaly precedes a sharp low-temperature anomaly. The upturn at the lowest temperatures is due to a nuclear Schottky anomaly.

There are a number of distinguishing magnetic properties for these three ytterbium pyrochlores,  $Yb_2B_2O_7$  (B = Sn, Ti, Ge), as described above. However, there are commonalities as well. Neutron spectroscopy of Yb2Ti2O7 and Yb2Ge2O7 has revealed that their crystal electric field schemes are largely the same [24,25]. Due to their well-separated ground-state doublets, both systems are well-described in terms of  $S_{\rm eff} =$ 1/2 quantum spins with local XY anisotropy. Similar crystalfield phenomenology is expected for Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>. Perhaps most striking, however, is the similarity of the low-temperature specific heats of these three materials (Fig. 1). In each case, there is a broad specific heat anomaly at high temperatures that precedes a sharp low-temperature anomaly [11,19]. This sharp,  $\lambda$ -like specific heat anomaly heralds the onset of long-range magnetic correlations as detected by neutron diffraction in Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [19] and Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> [24]; longrange correlations are also found in Yb2Ti2O7, but with an onset temperature higher than  $T_C$  [17]. Furthermore, in each case, the total integrated magnetic entropy is consistent with  $R \ln (2)$ , the expected value for a well-separated ground-state doublet.

In this paper, we present a new detailed study of the dynamic properties of  $Yb_2Ge_2O_7$  via inelastic neutron scattering. We then compare these results to those for  $Yb_2Ti_2O_7$  and  $Yb_2Sn_2O_7$  and discover a ubiquitous character to their exotic magnetic excitations. In each case, this excitation spectrum correlates strongly with *only* the broad, high-temperature specific heat anomaly. This is a striking result, as these three materials do not share a common ordered magnetic dipole state. Thus, it may be the case that the primary order in the ytterbium pyrochlores associated with the sharp, low-temperature anomaly is "hidden," to use an analogy to the enigmatic hidden-order state displayed by URu<sub>2</sub>Si<sub>2</sub> [26].

Experimental details are given in the Supplemental Material [27]. Figure 2 shows the inelastic neutron scattering spectra,  $S(Q,\omega)$ , for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> collected at temperatures ranging from 0.05 to 10 K, above and below both specific heat



FIG. 2. Temperature dependence of the inelastic scattering,  $S(Q,\omega)$ , of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> measured at (a) 0.05 K, (b) 0.9 K, (c) 1.8 K, (d) 4 K, (e) 7 K, and (f) 10 K. In each case, the background was subtracted using an empty can measurement. All six data sets have been normalized by counting time and scaled over an identical logarithmic intensity range.

anomalies. At all temperatures, we observe an intense phonon mode originating from the (222) Bragg position at 2.3  $\text{\AA}^{-1}$ . However, we attribute all other inelastic signal to a magnetic origin. At 50 mK the inelastic scattering in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> forms a continuum of spin excitations that is gapless within the resolution of our measurement (0.09 meV). These diffusive excitations are maximally intense approaching Q = 0 and resembles overdamped ferromagnetic spin waves ( $E \propto Q^2$ ) at the lowest wave vectors. Integration of the elastic scattering reveals the formation of magnetic Bragg reflections between 50 and 900 mK that give an ordered moment consistent with previous diffraction measurements [24] (see Supplemental Material [27]). Yet there is little or no temperature dependence to the spin-excitation spectrum across  $T_N$ , between 50 mK and 1.8 K. At 4 K, there is a small decrease in the inelastic intensity, particularly at low Q, while at 7 and 10 K the scattering is significantly reduced at all values of Q. Furthermore, the signal is shifted lower in energy, softening towards the elastic line. These spin excitations in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> are clearly exotic in two respects: (i) they correlate in temperature not with the sharp specific heat anomaly at  $T_N = 0.57$  K but, instead, with the broad specific heat anomaly centered at 4 K; and (ii) they are far removed from resolution-limited spin-wave excitations, which would be expected for any ordered state.

It is illuminating to compare our lowest temperature inelastic neutron scattering measurements on Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> to those on



FIG. 3. Inelastic scattering,  $S(Q,\omega)$ , of (a) Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, (b) Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, (c) Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, and (d) Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. For each sample the measurement was taken at a temperature of 100 mK or lower and an empty can background was subtracted. In the cases of the ytterbium pyrochlores, Yb<sub>2</sub>B<sub>2</sub>O<sub>7</sub>, measurements were performed on powder samples. The measurement on Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, which was taken on a single-crystal sample, has been powder averaged over the (*HHL*) scattering plane. The intensity ranges have been selected such that the inelastic scattering at  $Q = 1.2 \text{ Å}^{-1}$  saturates the scale.

its fellow XY pyrochlores. Neutron diffraction measurements have found that the ordered state in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> belongs to the  $k = 0, \Gamma_5$  irreducible representation, the same ground-state manifold to which  $Er_2Ti_2O_7$  belongs [28]. While  $\Gamma_5$  does contain two basis vectors,  $\psi_2$  and  $\psi_3$ , the powder diffraction patterns for these two states are identical and, thus, cannot be distinguished in polycrystalline Yb2Ge2O7. Regardless, the spin-wave spectra arising from these two states contain only subtle differences [29]. Thus, whether Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> orders into  $\psi_2$ ,  $\psi_3$ , or a linear combination of the two, we would expect the spin-wave spectra to strongly resemble those of Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. However, comparing the inelastic scattering profiles of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> [Fig. 3(a)] and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [Fig. 3(d)], both in their ordered states, it is clear that this is not the case. In Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, the sharp, Goldstone-like spin waves arise from the (111) Bragg peak at 1.1  $\text{\AA}^{-1}$ , with an absence of scattering around Q = 0, typical for a conventional antiferromagnet. Conversely, the excitations in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> are extremely diffusive and maximally intense approaching Q = 0, typical of a disordered ferromagnet.

We instead find that the excitations in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> strongly resemble those of  $Yb_2Ti_2O_7$  [Fig. 3(b)] and  $Yb_2Sn_2O_7$ [Fig. 3(c)]. This is a remarkable result, as these three ytterbium pyrochlores do not share an ordered state. In fact, Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> orders antiferromagnetically, while Yb2Sn2O7 orders ferromagnetically and Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> shows related ferromagnetism. The diffusive spin excitations, centered at Q = 0, share a common form in each of these materials and appear to simply scale in energy across the series. Although this excitation spectrum is ferromagnetic in appearance, it is gapless at all wave vectors and does not resemble the gapped spin-wave spectrum expected to arise due to anisotropic exchange within a splayed ferromagnetic ordered state [17]. Furthermore, for all three materials, the excitations evolve in temperature only in the range of the broad specific heat anomaly and do not obviously acknowledge the presence of the sharp low-temperature specific heat anomaly [17,21]. This is quite distinct from the low-temperature properties of Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, where a single specific heat anomaly marks its transition to the  $\psi_2$  antiferromagnetic state, and this directly correlates with the evolution of well-defined spin-wave excitations [28,30,31] and a spin-wave gap [32].

In order to further compare the inelastic scattering spectra of  $Yb_2B_2O_7$  (B = Ge, Ti, and Sn) we have taken several integrated cuts through the normalized data over selected Qranges. For each interval, the same general Q dependence is observed in the three materials. At the lowest values of Qthe intensity is primarily quasielastic, but at larger values of Q the spectral weight begins to shift to higher energies. The bandwidth of the spin excitations is smallest in Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and the most extended in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. The top of the bandwidth for  $Yb_2B_2O_7$  (B = Ge, Ti, and Sn), which occurs in the interval between  $Q = [1.3, 1.5] \text{ Å}^{-1}$ , is 0.9, 0.69, and 0.48 meV, respectively [Fig. 4(c)]. This continuum of scattering appears to be arcing towards the (222) Bragg reflection, and accordingly, over this Q interval the intensity shifts back towards the elastic line. It is, however, important to note that the (222) nuclear Bragg reflection is intense for each of these materials, and thus, phonon scattering partially obscures this region.



FIG. 4. Integrated scattering intensity of Yb<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (B = Ge, Ti, and Sn) as a function of energy transfer over the Q intervals (a) 0.3–0.5 Å<sup>-1</sup>, (b) 0.5–0.7 Å<sup>-1</sup>, (c) 1.3–1.5 Å<sup>-1</sup>, and (d) 1.9–2.1 Å<sup>-1</sup>. The intensities have been normalized by scaling the simulated relative intensities on the largest nuclear Bragg reflection, (222).



FIG. 5. Relationship between the lattice parameter and the magnetism temperature scales in  $Yb_2B_2O_7$  (B = Ge, Ti, and Sn). The temperature at which the heat capacity anomalies appear, as well as the energy bandwidth of the inelastic scattering, scales linearly with the lattice parameter.

In Fig. 5 we plot the energy bandwidth for the spin excitations, as defined above, as well as the temperatures for the two specific heat anomalies in  $Yb_2B_2O_7$  (B = Ge, Ti, and Sn) as a function of their lattice parameter. We find a remarkably linear correspondence between the bandwidth and the lattice parameter, as well as the temperature of the broad heat capacity anomaly, which we attribute to the formation of these excitations. It is interesting to note that even the temperature of the sharp heat capacity anomaly tracks quite well with this dependence, despite having no apparent role in the observed continuum of diffusive magnetic scattering. It is also worth noting that since we observe magnetic Bragg reflections for  $Yb_2Ge_2O_7$  in a  $\Gamma_5$  ordered state, there should be some signature of this in the inelastic signal as well. We conjecture that these spin waves are in fact present but are overwhelmed by the intensity of the continuum of magnetic scattering. While only approximately 0.3(1)  $\mu_{\rm B}$  of the ytterbium moment is involved in this ordered state of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> [24], it appears that the majority of the ytterbium moment contributes to the ferromagnetic-like continuum of scattering.

The universality of the nature of the spin-excitation spectrum in Yb<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (B = Ge, Ti, and Sn), as well as in the form of the specific heat, strongly suggests that the prevailing order is *not* driven primarily by magnetic dipole correlations. The spin-excitation spectrum itself, as measured by inelastic neutron scattering, is a measure of magnetic dipole fluctuations on an appropriate energy scale. Thus, there are two key observations suggesting that magnetic dipole order is not the primary order parameter in Yb<sub>2</sub>B<sub>2</sub>O<sub>7</sub>. First,  $S(Q,\omega)$  shows little or no temperature dependence on a scale related to the ordering temperature in any of these materials. Second, the form of  $S(Q,\omega)$  is the same across the series despite different magnetic dipole ordered ground states. A similar scenario appears to be realized in a different pyrochlore magnet,  $Tb_{2+x}Ti_{2-x}O_{7+y}$  with x = 0.005, in which the low-temperature thermodynamic phase transition does not obviously correlate with its magnetic neutron order parameter [33]. In  $Tb_{2+x}Ti_{2-x}O_{7+y}$  with x = 0.005 it has been speculated that this order originates from multipolar correlations. However, the well-separated ground-state doublet in Yb<sub>2</sub>B<sub>2</sub>O<sub>7</sub> precludes the possibility of a multipolar scenario. Hence, we draw an association with "hidden" order.

Finally, it is worth emphasizing that it is not just the shared form of these excitations that is exotic. The spin excitations are highly exotic in their own right: a gapless continuum of scattering, unrelated to the magnetic dipole ordered state of each material. Especially in Yb2Ge2O7, where the ordered state is a  $\Gamma_5$  antiferromagnet, it is clear that these excitations, which resemble overdamped ferromagnetic spin waves, have little relation to the dipole ordered state. Furthermore, while Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is renowned for sample dependence and sensitivity to weak disorder [12,13], these dynamic properties stand in stark contrast; the spin excitations are robust, appearing in both powder and single-crystalline samples, as well as in nonstoichiometric samples [17]. As we associate these excitations with the broad specific heat anomaly, which accounts for approximately 80% of the  $R \ln(2)$  entropy, our results should prompt a refocusing of theoretical studies which attempt to explain the magnetism of the Yb pyrochlores. It is apparent that these unconventional excitations hold the key to a comprehensive understanding of this exotic family of quantum magnets.

To conclude, new neutron scattering measurements on Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> reveal the same exotic form of the spin dynamical properties,  $S(Q,\omega)$ , as have been observed in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>. This is despite the fact that, below  $T_N = 0.57$  K, the magnetic dipole ordered phase in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is a  $\Gamma_5$ antiferromagnet, rather than splayed ferromagnetism, as in Yb2Ti2O7 and Yb2Sn2O7. In all three of the ytterbium pyrochlores,  $S(Q, \omega)$  evolves on a temperature scale set *only* by the broad, high-temperature specific heat anomaly. This broad, high-temperature feature in the specific heat carries with it approximately 80% of the  $R \ln (2)$  entropy in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> and is associated with most of the dipole moment and spectral weight probed by neutron scattering. This strongly suggests that the topical ground states in the  $Yb_2B_2O_7$  (B = Ge, Ti, and Sn) series are perhaps more exotic than previously thought, with a dominant "hidden" order parameter at the lowest temperatures.

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# SUPPLEMENTAL MATERIAL: Ubiquitous Nature of the Magnetic Excitations in the Ytterbium Pyrochlores

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## EXPERIMENTAL METHODS

The sample of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> under study in this paper was prepared by a high-pressure, high-temperature technique, the details of which can be found in Ref. [1]. Heat capacity measurements were made in the dilution refrigerator option of a Quantum Design Physical Property Measurement System using a standard semi-adiabatic heat pulse technique. For the inelastic neutron scattering measurements, the 2.7 gram powder sample of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> was loaded into an oxygen-free copper sample can and sealed with indium in a helium atmosphere. Previous diffraction measurements under this configuration have revealed a conventional order parameter with  $T_N = 0.57$  K, confirming that the sample is being successfully cooled to dilution temperatures [1]. A second unsealed empty can was utilized for background measurements.

The inelastic measurements on Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> were performed on the time-of-flight Disc Chopper Spectrometer (DCS) at the National Institute for Standards and Technology (NIST) Center for Neutron Research. The sample was measured in an Oxford Instruments ICE Dilution insert in a standard orange ILL cryostat over a temperature range of 0.05 K to 20 K. A wavelength of 5 Å was used for all measurements which gives a Q-space coverage of 0.15 Å<sup>-1</sup> to 2.3 Å<sup>-1</sup> and an energy resolution of 0.09 meV. The data presented on Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> were also collected on the DCS at NIST and have been previously published in Refs. [2] and [3]. In all cases, the error bars correspond to one standard deviation from the measured average.

# TEMPERATURE DEPENDENCE OF THE MAGNETIC NEUTRON SCATTERING IN $Yb_2Ge_2O_7$

In Figure 1(a) we show an integrated cut over the elastic channel of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, defined as  $\pm 0.05$  meV. At 900 mK and 1.8 K the scattering is purely structural in origin, and does not change between these two temperatures. How-



FIG. 1. (a) Temperature dependence of the elastic scattering of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> as measured on the Disc Chopper Spectrometer at NIST. The elastic scattering is taken as integrated cut between  $\pm 0.05$  meV. Between 0.05 K and 900 mK, there is a clear formation of magnetic Bragg reflections consistent with the k = 0,  $\Gamma_5$  ordered state. Temperature dependence of the inelastic scattering over Q intervals of (b) 0.3 - 0.5 Å<sup>-1</sup> and (c) 1.3 - 1.5 Å<sup>-1</sup>. We observe no temperature dependence in the inelastic scattering between 0.05 K and 1.8 K, the same temperature range over which magnetic Bragg reflections are observed to form. Instead the temperature evolution of the inelastic signal correlates with the broad specific heat anomaly at approximately 4 K.

ever, upon cooling to 50 mK, below the Néel transition at  $T_N = 0.57$  K, we see a significant enhancement on the Bragg positions. The locations for this enhancement are 1.1 Å<sup>-1</sup>, 1.8 Å<sup>-1</sup> and 2.1 Å<sup>-1</sup> corresponding to the (111), (220), and (113) Bragg positions, respectively. The relative intensities for these peaks is consistent with an antiferromagnetic k = 0,  $\Gamma_5$  ordered state, as reported in previous diffraction studies [1, 4]. The refined ordered moment is consistent with our previous diffraction study, 0.3(1)  $\mu_{\rm B}$ . It is worth mentioning that these previous diffraction measurements of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> were in fact elastic with an energy resolution of  $\pm 0.5$  meV or worse. Our energy resolution, as shown in Fig 1(a), is  $\pm 0.05$  meV, an order of magnitude better. Thus, we can see that our sample of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is successfully cooling into its ordered Néel state.

In Figure 1(b) and (c), we show the temperature dependence of the inelastic scattering in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. The spin dynamic properties of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> do not evolve between 0.05 K and 1.8 K, the temperature range over which the Néel ordering is observed to take place as evidenced by the formation of magnetic Bragg reflections coincident with a sharp specific heat anomaly. Instead the temperature evolution of these spin excitations is correlated with the broad specific heat anomaly centered at approximately 4 K. On the negative energy transfer side we see a clear increase in the intensity with temperature, consistent with detailed balance.

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# 2.3 Preface to Publication III: Effects of positive chemical pressure on a putative spin liquid

In the final paper of this chapter, we turn to the terbium family of pyrochlores and, in particular,  $Tb_2Ge_2O_7$ . The terbium pyrochlores are perhaps the least well-understood of the rare earth pyrochlore family, although not for lack of effort [30]. These introductory remarks will expand upon some of the contributing factors that impede the understanding of these fascinating materials.  $Tb_2Ti_2O_7$ , an Ising antiferromagnet [99], was one of the first rare earth pyrochlores to have an in depth investigation of its low temperature magnetism [54]. As discussed in the introduction, Ising antiferromagnetism on the pyrochlore lattice should lead to a non-frustrated long range ordered state (all-in/all-out) [100, 101]. Indeed, the spin model that successfully accounts for the spin ice states in  $Ho_2Ti_2O_7$  and  $Dy_2Ti_2O_7$  would predict a transition to this state in  $Tb_2Ti_2O_7$  with a Néel temperature of 1 K [40, 102]. The remarkable experimental discovery made in 1999 is that  $Tb_2Ti_2O_7$  does not magnetically order or freeze down to temperatures as low as 50 mK [54,103]. In the intervening years, this spin liquid state has attracted significant experimental and theoretical attention, but still remains somewhat mysterious.

There are a number of confounding factors that inhibit a simple categorization or understanding of Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>'s ground state. One of these factors is that the first excited crystal field is separated from the ground state by only 1 meV [99]. This is a significantly smaller separation than the other rare earth pyrochlores discussed thus far. For example, the first excited crystal field level in the ytterbium pyrochlores occurs at approximately 70 meV, and thus can be completely disregarded in the low-energy Hamiltonian [104]. In  $Tb_2Ti_2O_7$ , the low lying crystal field level plays an important role in enhancing quantum fluctuations and would thus have to be included in any successful theory [102]. Furthermore,  $Tb^{3+}$  is a non-Kramers ion, and thus its J manifold contains both doublet and singlet levels, making the analysis of its crystal electric field Hamiltonian more challenging [105–108]. A second complicating factor is the coupling between magnetic and lattice degrees of freedom, as evidenced by a large magneto-elastic response [109-113]. The complexities of Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>'s low temperature magnetism are further exacerbated by a pronounced sensitivity to off-stoichiometry leading to sample dependence in the low temperature magnetism [59]. How all these puzzle pieces fit together is not exactly clear, although one intriguing possibility is that that the low temperature state of  $Tb_2Ti_2O_7$  is related to quantum spin ice [114]. Other contending theories are proximity to competing phases [115] and quadrupolar order [116]. The reality is likely some intertwining of these effects and possibly

others.

Studies with pressure, both externally applied and chemical, have shed some light on the phase diagram of Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. An external hydrostatic pressure of 7.1 GPa, induces long range antiferromagnetic order in Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> with a Néel temperature of  $T_N = 2.1$  K [117]. Even applied pressures as small as 1.5 GPa are sufficient to induce partial ordering. Although these pressures are amongst the largest that can be applied in experiments of this type, they are still small in terms of the overall lattice compression. The maximum pressure applied in this work, 8.6 GPa, reduces the cubic lattice parameter by only 1% [117]. Negative chemical pressure, which has been studied with tin substitution, also results in long range magnetic order. Tb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> orders at  $T_C = 0.87$  K into a so-called ordered spin ice state in which the moments have a net ferromagnetic canting away from the local Ising axis in their two-in/two-out motif [74]. These two studies highlight the precarious nature of the spin liquid state in Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. Positive applied pressure and negative chemical pressure both push the system to magnetic order, although in the former case it is antiferromagnetic and in the latter it is ferromagnetic. This would tend to support the notion that Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> lays near the boundary of competing phases.

Our contribution to this enigmatic situation was to explore the effect of positive chemical pressure via germanium substitution. In this paper, we characterized the low temperature magnetism of Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> with susceptibility, heat capacity, and polarized neutron diffraction. Our specific heat measurements show that like both  $Tb_2Ti_2O_7$  [99,105–107] and  $Tb_2Sn_2O_7$  [105,106],  $Tb_2Ge_2O_7$  has a low-lying excited crystal field level that is likely disruptive to magnetic order. Our polarized neutron scattering shows that upon cooling from 25 K and 3.5 K,  $Tb_2Ge_2O_7$ develops short range antiferromagnetic correlations, much like  $Tb_2Ti_2O_7$  over the same temperature range [30]. However, at much lower temperatures, these short range antiferromagnetic correlations give way to ferromagnetic correlations. Magnetic susceptibility measurements provide further evidence that the low temperature state of  $Tb_2Ge_2O_7$  is dominated by ferromagnetic interactions. Thus, we find that externally applied and positive chemical pressure, which both act to compress the crystal lattice, are having utterly disparate effects on the ground state magnetism of  $Tb_2Ti_2O_7$ . Given all the complicating factors we discussed in the previous paragraphs, it is perhaps not surprising that the effect of chemical pressure cannot be naively understood in the terbium pyrochlores. Much remains to be understood about the low temperature magnetic ground state of  $Tb_2Ge_2O_7$ , which while undoubtedly distinct from that of  $Tb_2Ti_2O_7$ , appears to be rich in its own complexities.

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- Susceptibility Measurements: J.G. Cheng, H.D. Zhou, E.S. Choi
- Heat Capacity Measurements: H.J. Silverstein
- Neutron Scattering Experiments: A.M. Hallas, H.J. Silverstein, Y. Su, P.M. Sarte, A.M. Arevalo-Lopez, C.R. Wiebe
- Data Analysis: A.M. Hallas, J.G. Cheng, H.D. Zhou, C.R. Wiebe
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# Incipient Ferromagnetism in Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>: Application of Chemical Pressure to the Enigmatic Spin-Liquid Compound Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>

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After nearly 20 years of study, the origin of the spin-liquid state in  $Tb_2Ti_2O_7$  remains a challenge for experimentalists and theorists alike. To improve our understanding of the exotic magnetism in  $Tb_2Ti_2O_7$ , we synthesize a chemical pressure analog:  $Tb_2Ge_2O_7$ . Substitution of titanium by germanium results in a lattice contraction and enhanced exchange interactions. We characterize the magnetic ground state of  $Tb_2Ge_2O_7$  with specific heat, ac and dc magnetic susceptibility, and polarized neutron scattering measurements. Akin to  $Tb_2Ti_2O_7$ , there is no long-range order in  $Tb_2Ge_2O_7$  down to 20 mK. The Weiss temperature of -19.2(1) K, which is more negative than that of  $Tb_2Ge_2O_7$  reveals that liquidlike correlations dominate in this system at 3.5 K. However, below 1 K, the liquidlike correlations give way to intense shortrange ferromagnetic correlations with a length scale similar to the Tb-Tb nearest neighbor distance. Despite stronger antiferromagnetic exchange, the ground state of  $Tb_2Ge_2O_7$  has ferromagnetic character, in stark contrast to the pressure-induced antiferromagnetic order observed in  $Tb_2Ti_2O_7$ .

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Geometrically frustrated pyrochlores  $R_2M_2O_7$  exhibit a diverse array of exotic magnetic behaviors [1]. The ground states in these materials are dictated by a complex, and often delicate balance of exchange, dipolar, and crystal field energies. Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is one of the most remarkable of these frustrated pyrochlores; strong antiferromagnetic exchange and Ising-like spins led to predictions of an antiferromagnetic Néel state below ~1 K for this material [2]. However, experimental studies revealed a lack of static order or spin freezing in Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> down to 70 mK [3,4], and more recently 57 mK [5]. Subsequently, enormous efforts have been undertaken to uncover the origin of the spin-liquid state in Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>.

A further complication in  $\text{Tb}_2\text{Ti}_2\text{O}_7$  is the coupling of the magnetic and lattice degrees of freedom [6–9]. It has been suggested that hybridized magnetoelastic excitations may be responsible for the suppression of magnetic order in  $\text{Tb}_2\text{Ti}_2\text{O}_7$  [10]. Another theoretical construct that attempts to account for the lack of static order in  $\text{Tb}_2\text{Ti}_2\text{O}_7$  is a quantum spin ice state [11–15]. A third proposed scenario is that the non-Kramers doublet ground state of  $\text{Tb}_2\text{Ti}_2\text{O}_7$  is split into two nonmagnetic singlets through a symmetry reducing structural distortion [16–18].

Other studies sought to uncover the origin of the spinliquid state in Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> by focusing on mechanisms of its destruction, such as external pressure [19], magnetic fields [18,20,21], and a combination of the two [22]. Partial antiferromagnetic order is induced in Tb2Ti2O7 with external hydrostatic pressures of 8.6 GPa, resulting in a 1% compression of the lattice [19]. Another means of destroying the spin-liquid state is chemical pressure: substitution of the nonmagnetic titanium cation for a valence isoelectronic cation with a different ionic radius. Substitution of titanium in Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> for the larger tin cation allowed exploration of negative chemical pressure [23]. In Tb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, reduced antiferromagnetic exchange results in an "ordered spin ice" state at 0.87 K [23,24]. In this two-in, two-out state, the spins are oriented  $13.3^{\circ}$  to the local  $\langle 111 \rangle$  axes. This ground state can be partially understood by a model of Heisenberg spins with finite ferromangetic exchange and  $\langle 111 \rangle$  anisotropy [25]. However, this can only be reconciled with the apparent antiferromagnetic nearest neighbor exchange in  $Tb_2Sn_2O_7$  if a tetragonal distortion is considered [26], for which there is currently no evidence.

More recently, the study of chemical pressure in the pyrochlores has focused on substitution of Ti<sup>4+</sup> for the much smaller Ge<sup>4+</sup>. Germanium substitution results in a lattice contraction and enhanced exchange interactions [27]. Study of the germanate pyrochlores has revealed that some frustrated ground states are stable against the application of chemical pressure while others are not. For example, the spin ice state is robust in the holmium pyrochlores Ho<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (B = Ge, Ti, Sn) [27–29]. Conversely, quantum fluctuations in the effective S = 1/2 Yb<sup>3+</sup> cation are very sensitive to chemical pressure. Consequently, the ytterbium pyrochlores Yb<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (B = Ge, Ti, Sn) each have markedly different magnetic ground states [30].

To gain a better understanding of the exotic magnetism in  $Tb_2Ti_2O_7$  we synthesized a positive chemical pressure analog:  $Tb_2Ge_2O_7$ . We characterized the magnetic ground state of  $Tb_2Ge_2O_7$  with specific heat, magnetic susceptibility, and polarized neutron scattering measurements. Akin to  $Tb_2Ti_2O_7$ , there is no long-range order in  $Tb_2Ge_2O_7$  down to 20 mK. However, the liquidlike correlations in  $Tb_2Ge_2O_7$  give way to intense short-range ferromagnetic interactions below 1 K.

When reacted under ambient pressure, Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> has a tetragonal pyrogermanate structure [31]. We prepared  $Tb_2Ge_2O_7$  in the cubic pyrochlore phase using a hightemperature, high-pressure technique. Stoichiometric quantities of Tb<sub>2</sub>O<sub>3</sub> and GeO<sub>2</sub> were reacted at 1000 °C and 8 GPa using a multianvil press. Batches of approximately 60 mg, prepared from a common precursor, were heated in rhenium capsules to produce a total of 320 mg of polycrystalline sample. Room temperature powder neutron diffraction measurements were made on the general materials diffractometer at the ISIS neutron facility. Rietveld fits to the diffraction pattern of Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> with GSAS confirmed the Fd3m pyrochlore phase and the absence of pyrogermanate impurities [Fig. 1(a)]. The room temperature lattice parameter was refined to a value of 9.9617(1) Å. This corresponds to a reduction from  $Tb_2Ti_2O_7$ and  $Tb_2Sn_2O_7$  of ~2% and ~5%, respectively (Table I).

Off stoichiometry and site mixing are known to have a significant impact on the magnetic properties of  $Tb_2Ti_2O_7$  [33,34] and other pyrochlores [35]. These issues are most severe in the case of single crystals grown with the optical floating zone technique [35]. A key advantage of the study of germanium pyrochlores is that the large size mismatch between the rare earth and germanium cations should preclude the possibility of site mixing. Rietveld refinement of the powder neutron diffraction pattern indicates ideal stoichiometry and the absence of site mixing in  $Tb_2Ge_2O_7$ . The *A* and *B* sites of the lattice have an occupation of 1.00(5) by  $Tb^{3+}$  and  $Ge^{4+}$ , respectively.



FIG. 1 (color online). (a) Neutron diffraction pattern of  $Tb_2Ge_2O_7$  from the 90° detector bank confirming the pyrochlore structure (Fd3m). Asterisks mark the reflections from vanadium and unreacted precursors. (b) The dc susceptibility of  $Tb_2Ge_2O_7$  where the black line is a Curie-Weiss law fit. Demagnetizing field effects were found to be negligible. Inset: inverse susceptibility below 2 K.

The inverse dc susceptibility of Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> provides no evidence of long-range order down to 0.5 K [Fig. 1(b)]. A Curie-Weiss fit between 100 and 300 K yields an antiferromagnetic Weiss temperature of  $\theta_{CW} = -19.2(1)$  K. Fits over an identical temperature range for Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [32] and Tb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [23] give Weiss temperatures of -17.5 and -12.5 K, respectively. The more negative Weiss temperature for Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is indicative of stronger antiferromagnetic exchange that results from a reduced Tb-Tb distance. The susceptibility of Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> begins to deviate from Curie-Weiss behavior below 70 K. This is similar to Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [32], in which the deviation is attributed to the onset of developing short-range magnetic correlations [3].

The heat capacity of  $Tb_2Ge_2O_7$  contains two low temperature anomalies centered at 5.5 and 1.2 K

TABLE I. Comparison of lattice and magnetic parameters in the  $Tb_2B_2O_7$  (B = Sn [23,24], Ti [32], Ge) pyrochlores.

	a (Å)	$\theta_{\rm CW}$ (K)	$\mu_{\rm eff}~(\mu_B)$	D <sub>nn</sub> (K)
$Tb_2Sn_2O_7$	10.426	-12.5	9.68	1.91
Tb <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	10.149	-17.5(3)	9.56	2.06
Tb <sub>2</sub> Ge <sub>2</sub> O <sub>7</sub>	9.9617(1)	-19.2(1)	9.87(3)	2.19(1)



FIG. 2 (color online). The heat capacity of  $Tb_2Ge_2O_7$  contains anomalies at 1.2 and 5.5 K, which strongly resemble the anomalies in the heat capacity of  $Tb_2Ti_2O_7$  (inset, reproduced from Ref. [32]). The application of 0.02 and 0.05 T fields does not alter these features.

(Fig. 2). These features bear a significant qualitative resemblance to the low temperature heat capacity of Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, which exhibits two peaks centered at 6 and 1.5 K (inset of Fig. 2). Gingras et al. interpret the peak at 6 K in Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> as a remnant of the first excited state doublet [32]. The anomaly at 1.5 K in Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is attributed to the buildup of short-range magnetic correlations. While the corresponding peak in  $Tb_2Ge_2O_7$  is sharper, there is no evidence for the onset of long-range order at 1.2 K. We thus speculate that Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> has a crystal field scheme that resembles that of Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, resulting in similar heat capacity anomalies. In  $Tb_2Ti_2O_7$ , approximately -6 K of the Weiss temperature is due to crystal field effects [32], 2 K is related to longrange dipolar contributions, and the remaining -13.5 K is due to magnetic exchange. The dipolar interaction, approximated as  $D_{nn} = 5/3(\mu_0/4\pi)\mu^2/r_{nn}^3$  in pyrochlores, does not significantly vary with lattice parameter (Table I). Given that the crystal fields and dipolar contributions are similar to those of Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, we suggest that the increased magnitude of the Weiss temperature in Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> results from enhanced antiferromagnetic exchange. However, a definite conclusion on this matter will require a detailed investigation of the crystal electric field of Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>.

We measured the ac susceptibility of Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> down to 20 mK with frequencies ranging from 41 to 511 Hz and in dc fields up to 0.05 T. In zero field, the real component of the susceptibility  $\chi'$  contains no evidence of an ordering transition down to 20 mK in Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> [Fig. 3(a)]. The imaginary component of the susceptibility  $\chi''$  is also free of anomalies and has an increasing magnitude with decreasing temperature [Fig. 3(b)]. The application of external dc fields as small as 0.01 T to Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> induces a broad peak in  $\chi'$  [Fig. 3(a)]. As the external dc field is increased, the peak flattens and shifts to higher temperatures. At constant field strength, this feature is independent of frequency



FIG. 3 (color online). The (a) real  $\chi'$  and (b) imaginary  $\chi''$  components of the ac susceptibility of Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. At zero field, there is no peak in the susceptibility down to 20 mK. (c) Small external dc fields induce a frequency independent peak that shifts to higher temperatures with increasing field.

[Fig. 3(c)]. There is no corresponding peak or significant difference in  $\chi''$ . If this field-induced feature in Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> had antiferromagnetic origins, an increasing field would suppress the peak to lower temperature. The field enhancement of this peak combined with its frequency independence suggest that it is ferromagnetic in character. This feature may be related to the formation of short-range spin correlations in Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>.

The related pyrochlores Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Tb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> have been extensively characterized with ac susceptibility [14,36-38]. In Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, frequency dependent peaks at 350 and 140 mK are attributed to defect freezing [4] and a quantum spin ice state [14], respectively. In Tb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, the ordering transition at 850 mK is marked by a frequency independent feature in both the real and imaginary parts of the ac susceptibility [38]. With an external magnetic field, this feature of Tb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> is reduced in magnitude while shifting to higher temperatures. Although no peak is observed in the zero-field susceptibility of Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, the behaviors otherwise more closely resemble Tb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>. It is possible that at the lowest temperatures  $Tb_2Ge_2O_7$  is approaching an ordering transition that is not accessible experimentally. A further similarity between Tb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and  $Tb_2Ge_2O_7$  is the increasing magnitude of the imaginary susceptibility below 1 K, which has been attributed to increasing ferromagnetic correlations in  $Tb_2Sn_2O_7$  [38].

We carried out polarized neutron scattering measurements on Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> using the DNS spectrometer, which is operated by the Heinz Maier-Leibnitz Zentrum at Garching. Measurements were taken at 100 mK, 3.5 K, 25 K, and 100 K using a dry-type dilution insert and a toploading closed cycle refrigerator with an incident wavelength of 4.2 Å. *XYZ*-polarization analysis allows the magnetic scattering to be separated from the nuclearcoherent and spin-incoherent components. The scattering of Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> at 25 and 100 K is well fit by the square of the magnetic form factor for Tb<sup>3+</sup> [Fig. 4(a)]. Thus, the scattering at these temperatures is mainly paramagnetic. However, the deviations from the magnetic form factor are more pronounced at 25 K compared to 100 K due to the development of short-range correlations.

At 3.5 K, the magnetic diffuse scattering in Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> strongly deviates from the magnetic form factor. There is an upturn in the scattering at low Q and a hump in the scattering centered at 1.1 Å<sup>-1</sup> [Fig. 4(a)]. These two features have competing origins. The upturn at low Q is related to short-range ferromagnetic correlations. The hump at 1.1 Å<sup>-1</sup> is related to liquidlike correlations. A



FIG. 4 (color online). Magnetic diffuse scattering of  $Tb_2Ge_2O_7$  at (a) 100 K, 25 K, 3.5 K, and (b) 100 mK. The scattering at 25 and 100 K has been offset 6 and 12 counts/s respectively for clarity. The ferromagnetic Bragg peak positions (111) and (200) are indicated by the dashed lines. The black lines are the fits to data, as described in the text.

coexistence of short-range ferromagnetic and liquidlike correlations has also been observed in Tb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> at 1.2 K, above its ordering temperature [24]. The fit to the data was achieved by combining a Lorentzian function and an antiferromagnetic nearest-neighbor spin correlation function. The Lorentzian function  $I(Q) = (A/\pi)(\kappa/(\kappa^2 + Q^2))$ fits the short-range ferromagnetic correlations [39]. The liquidlike scattering is modeled by  $I(Q) \approx \sin(Qr_{ij})/Qr_{ij}$ , where  $r_{ij}$  is the distance between spins at sites *i* and *j* [3]. The value of  $r_{ij}$  was refined to 3.65(6) Å, which agrees well with the Tb-Tb nearest neighbor distance of 3.52 Å in Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. The antiferromagnetic contribution to the scattering, which is responsible for the maximum at Q =1.1 Å<sup>-1</sup> and the minimum at Q = 2.1 Å<sup>-1</sup>, is strongly reminiscent of the scattering in Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> at 2.5 K [3].

The Q dependence of the magnetic diffuse scattering changes significantly between 100 mK and 3.5 K [Fig. 4(b)]. The decreased error bar size at 100 mK is due to significantly longer counting times. The spectral weight at 100 mK is increasing at low-Q values, towards Q = 0. The contribution from the liquidlike correlations, which were prominent at 3.5 K, are dwarfed by the low-Q scattering. Thus, at 100 mK the magnetism in Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is dominated by short-range ferromagnetic correlations. This low-Q scattering is fit to a Lorentzian function between 0.3 and 0.7 Å<sup>-1</sup>. From this fit, a mean correlation length can be estimated by  $\kappa^{-1}$  as 3.6(9) Å, close to the Tb-Tb distance. Another feature at 100 mK is the presence of developing intensity at 1.08 and 1.26  $\text{\AA}^{-1}$  [Fig. 4(b)]. These positions are the ferromagnetic Bragg peak positions (111) and (200). The (111) reflection is an allowed structural Bragg peak, but the (200) reflection is not. Examining the ~60 hours of data collected at 100 mK reveals no change in intensity at these positions as a function of time. We thus consider two viable origins for this additional intensity: (i) an imperfect polarization analysis is giving rise to a residual signature from the nuclear channel, or (ii) at 100 mK, Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is approaching ferromagnetic order that is static on the neutron time scale. The absence of an ordering transition down to 20 mK in the ac susceptibility precludes the possibility of static order. While ac susceptibility can probe dynamics up to the kilohertz scale, neutrons are sensitive to dynamics on the order of terahertz.

It is worth noting that the 8.6 GPa of external pressure found to induce antiferromagnetic order in  $Tb_2Ti_2O_7$ corresponds to a 1% difference in the lattice parameter [19]. Substitution of  $Ti^{4+}$  by  $Ge^{4+}$  represents a 2% reduction in the lattice parameter. Our results show that, despite enhanced antiferromagnetic exchange,  $Tb_2Ge_2O_7$ does not order antiferromagnetically, nor is it even dominated by antiferromagnetic interactions. Thus, chemical pressure does not mimic the effects of external isotropic pressure in  $Tb_2Ti_2O_7$ . Chemical substitution of  $Tb_2Ti_2O_7$ radically alters the magnetic ground state. This result further emphasizes the delicate balance of exchange, dipolar, and crystal field interactions in these pyrochlores. Consideration of the similarities and differences between  $Tb_2Ti_2O_7$  and  $Tb_2Ge_2O_7$  should be useful for achieving a complete understanding of the origin of their collective paramagnetic states. To that end, a thorough study of  $Tb_2Ge_2O_7$ 's crystal field scheme will prove valuable. The local oxygen environment of terbium, which dictates the crystal electric field, is altered by germanium substitution. Our heat capacity measurements indicate qualitative similarities in the crystal fields of  $Tb_2Ge_2O_7$  and  $Tb_2Ti_2O_7$ . However, it is possible that the significant differences in the magnetism of these two materials are related to subtle differences in the crystal field scheme and, consequently, the single ion anisotropy.

In conclusion, our results reveal a lack of long-range order in  $Tb_2Ge_2O_7$  down to 20 mK. Magnetic diffuse neutron scattering measurements reveal that  $Tb_2Ge_2O_7$  does not share a spin-liquid ground state with  $Tb_2Ti_2O_7$ . Instead,  $Tb_2Ge_2O_7$  is dominated by short-range ferromagnetic correlations with a length scale characteristic of the Tb-Tb distance. A field induced peak with ferromagnetic character is observed in the ac susceptibility.  $Tb_2Ge_2O_7$  represents an exciting new avenue to probe the exotic phase diagram of the terbium pyrochlores. Characterization of the crystal field scheme of  $Tb_2Ge_2O_7$  and a muon spin relaxation investigation of its dynamics will allow additional valuable comparisons to be drawn.

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# Chapter 3

# Lead Pyrochlores

In the previous chapter, we considered the germanium pyrochlores - the rare earth pyrochlores with the smallest non-magnetic B site achieved thus far. In this chapter, we delve into the opposite limit with the lead pyrochlores - where lead is the largest ionic radius B site cation thus far found to be compatible with the pyrochlore structure [29]. Thus, with respect to any other rare earth pyrochlore family, lead acts as a negative chemical pressure. For example, substitution of tin with lead results in a 2.5% lattice expansion. In both germanium and lead pyrochlores, high pressure synthesis techniques are required, which on its surface might be counterintuitive. However, the purpose that pressure serves in these two cases is different. As previously discussed, high pressure is required in the germanates to compensate for the large ionic radii difference between the A and B site cations, which in ambient pressure would give rise to a lower symmetry structure [75]. In the case of the lead pyrochlores, the A and B site cations are far more similar in size, as shown in Figure 3.1, and thus, prone to site-mixing. High pressure promotes site-ordering of the rare earth and lead cations onto independent sublattices. An additional challenge of synthesizing lead pyrochlores is that at elevated reaction temperatures, lead will readily reduce from its 4+ oxidation state to a 2+ oxidation state. This problem can also be countered with high pressure synthesis as this technique requires a sealed environment, which naturally provides control over the reaction conditions [118]. Unlike the germanium pyrochlores, which once prepared are very stable, the lead pyrochlores readily degrade and reduce when heated above  $300^{\circ}$ C [118].

Due to the large ionic radius of lead, the pyrochlore structure can only be stabilized with the lighter (larger ionic radii) rare earths, from lanthanum  $(4f^0)$  to gadolinium  $(4f^7)$ . For the heavier (smaller ionic radii) rare earths, from terbium upwards, a disordered fluorite structure is



Figure 3.1: The relative ionic radii of the the non-magnetic B site cations, titanium, tin, and lead in their 4+ oxidation state, as well as the rare earth A site cation gadolinium in its 3+ oxidation state.

obtained [118]. In the disordered fluorite structure both the A and B site cations are randomly distributed over a single crystallographic site that forms a face-centered cubic lattice. The disordering in this fluorite structure also extends to the anion sublattice, such that the oxygens are randomly distributed over eight equivalent crystallographic sites. These structural differences relieve geometric frustration, which is why fluorite materials have not been a focus of study in the field of frustrated magnetism. The pyrochlore and disordered fluorite structures can be distinguished via x-ray diffraction, where the pyrochlore structure will have superlattice reflections originating from the site-ordering of the A and B sublattices that will be absent in the case of a disordered fluorite structure. The lead pyrochlores we will discuss are indeed pyrochlores, in the sense that they are predominantly site-ordered and do exhibit the expected superlattice reflections. However, the proximity to the disordered fluorite phase must be kept in consideration as it indicates a propensity for defect formation. Indeed, as can be seen in Figure 3.2(a), the computed energy cost of forming a cation antisite defect (swapping of A onto the B sublattice and vice-versa) is the lowest for the  $R_2 Pb_2 O_7$  pyrochlores of any family [119]. Note that in this figure, the red dots are compounds that do not exist and the vellow dots represent compounds prepared under high pressure. Likewise, these lead pyrochlores are also the most prone to oxygen Frenkel pair defects [119], where a vacancy of the 48f oxygen site will be compensated by an errant oxygen at the 8a site, in the center of the B sublattice tetrahedra (Figure 3.2(b)).

For the lead pyrochlore family there is very little direct comparison possible with the titanate and germanate pyrochlores. The only rare earth that is stable amongst all these families is gadolinium, all the way from  $Gd_2Ge_2O_7$  to  $Gd_2Pb_2O_7$ . More relevant points of comparison for the lead pyrochlores are the stannate (Sn<sup>4+</sup>) pyrochlores, as well as the zirconate (Zr<sup>4+</sup>) and halfnate (Hf<sup>4+</sup>) pyrochlores. Recently, a great deal of progress has been made in the growth of single crystalline samples of the zirconate and halfnate pyrochlores using the optical floating



Figure 3.2: Contour map of defect formation energies for (a) cation anti-site defects and (b) anion Frenkel pair defects. Each of the dots represents a specific A and B site combination where black represents ambient pressure pyrochlores, yellow is high pressure pyrochlores, red is defective fluorite, and green is non-cubic phases. The rare earth lead pyrochlores,  $R_2Pb_2O_7$ , have the lowest energy barrier to forming defects of either type. Reproduced from Ref. [119] with permission, copyrighted by John Wiley and Sons.

zone technique [120–122]. As was the case for the titanates, the availability of single crystals has proven a boon to the detailed investigation of their magnetic properties [123–125]. These studies have revealed that the lighter (larger ionic radii) rare earths are no less fascinating than the heavier rare earths we surveyed in the previous chapter. For example, Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> has a remarkable low temperature state in which unfrustrated all-in/all-out Ising antiferromagnetic order [126,127] is accompanied by low energy spin ice-like excitations [124]. The origin of this state appears to lie in the dipolar-octupolar nature of the Nd<sup>3+</sup> ground state crystal field doublet [127,128]. Another remarkable state is found in  $Pr_2Zr_2O_7$ , which was originally interpreted as a quantum spin ice state [123], but has more recently been described as disorder-induced quantum spin liquid [129]. The negative chemical pressure induced by substitution of lead at the *B* site is an intriguing opportunity to study the effect of weakened exchange on these exotic ground states. The following publication is contained in this chapter:

Publication IV: "Magnetic frustration in lead pyrochlores", Alannah M. Hallas, Angel M. Arevalo-Lopez, Arzoo Z. Sharma, Timothy J. Munsie, J. Paul Attfield, Christopher R. Wiebe, and Graeme M. Luke. Physical Review B 91, 104417 (2015).
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# 3.1 Preface to Publication IV: A new family of lead-based magnetically frustrated pyrochlores

In this work, we present a comprehensive structural and bulk magnetic characterization of four high-pressure lead pyrochlore materials,  $R_2Pb_2O_7$  with R = La, Nd, Pr, and Gd. The first of these four materials,  $La_2Pb_2O_7$ , is non-magnetic and primarily serves as a lattice standard for our low temperature specific heat measurements. The latter three compounds each carry a magnetic moment. We characterize the low temperature magnetic states of each of Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>, Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> using magnetization techniques and heat capacity. Neither Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> nor Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> exhibits Curie-Weiss behavior over a wide temperature range due to low-lying crystal electric field levels. However, the magnetization data for both materials is consistent with the powder averaged response for spins with [111] Ising anisotropy. In the case of Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>, there appears to be long-range magnetic order below  $T_N = 0.4$  K. The ordered state in this Ising antiferromagnet is very likely the all-in/all-out structure, as has subsequently been observed in each of Nd<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (B = Zr [126, 127], Sn [130], and Hf [131]). Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>, on the other hand, does not undergo long-range magnetic ordering down to at least 0.4 K. Instead, the specific heat of this material shows a broad anomaly centered near 1.2 K, much like its familial analogs Pr<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (B = Zr [123], Sn [132], and Hf [133]). The low temperatures correlations in these materials are surely related to spin ice but whether that state is indeed the sought-after quantum spin ice is an open question [115]. Lastly, we find that Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> orders antiferromagnetically at  $T_N = 0.8$  K. Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> remains the stand-alone member of this family to exhibit a two-stage ordering transition into a partially ordered state [53,69]. The other members of the gadolinium pyrochlore family, Gd<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (B = Ge [82], Sn [134], Pt [5,82]), have a single stage transition to an antiferromagnetic ordered state at or above 1 K. In the case of Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, neutron diffraction performed on an isotopically enriched sample revealed that the ordered state is the  $\Gamma_7$  Palmer-Chalker state [135], the expected ground state for a Heisenberg antiferromagnet with dipolar interactions [136].

As discussed in the introduction of this chapter, an important corollary of lead being the largest pyrochlore B site cation is a propensity for site disorder. Given that far smaller levels of disorder have been found to play a pivotal role in some titanate pyrochlores [59, 62, 63], the lead pyrochlores provide insight in the limit of large defect concentrations. To characterize the level of defects, we performed structural refinements on all samples using laboratory x-ray diffraction, as well as powder neutron diffraction in the case of  $Pr_2Pb_2O_7$ . This revealed a high degree of site order for A = La, Nd, and Pr, on the order of 95%. The end member,  $Gd_2Pb_2O_7$ , has a significantly reduced degree of site ordering, as evidenced by the near extinction of its superlattice peaks. Our refinements indicate approximately 60% site ordering in this material, very close to the limit of full site disorder. It is remarkable that at this level of disorder,  $Gd_2Pb_2O_7$  undergoes long range magnetic order at  $T_N = 0.8$  K with only minimal evidence for glassiness. One interesting avenue worthy of further exploration is a systematic study of how the degree of site ordering varies with the magnitude of the applied pressure during synthesis. The samples in this published work were prepared under 2 GPa of applied pressure at 900°C, then later prepared in a different press at 6 GPa and 1000°C, while the original report of their synthesis by A. W. Sleight used 0.3 GPa and  $700^{\circ}$ C [118]. Thus, it is clear that these lead pyrochlores can be obtained over a wide range of conditions. However, the optimal conditions for minimizing defect formation is an open problem.

# <u>Author Contributions:</u>

- Experimental Concept: C.R. Wiebe, G.M. Luke
- Sample Preparation: A.M. Arevalo-Lopez, J.P. Attfield
- Susceptibility Measurements: A.M. Hallas, T.J. Munsie, G.M. Luke
- Heat Capacity Measurements: A.Z. Sharma, C.R. Wiebe
- Data Analysis: A.M. Hallas, C.R. Wiebe, G.M. Luke
- Manuscript: A.M. Hallas, C.R. Wiebe, G.M. Luke

# Magnetic frustration in lead pyrochlores

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The rich phase diagrams of magnetically frustrated pyrochlores have maintained a high level of interest over the past 20 years. To experimentally explore these phase diagrams requires a means of tuning the relevant interactions. One approach to achieve this is chemical pressure, that is, varying the size of the nonmagnetic cation. Here, we report on the family of lead-based pyrochlores  $A_2Pb_2O_7$  (A = Pr, Nd, Gd), which we have characterized with magnetic susceptibility and specific heat. Lead is the largest known possible *B*-site cation for the pyrochlore lattice. Thus, these materials significantly expand the phase space of the frustrated pyrochlores. Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> has an absence of long-range magnetic order down to 400 mK and a spin-ice-like heat capacity anomaly at 1.2 K. Thus, Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> is a candidate for a quantum spin ice state, despite weaker exchange. Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> transitions to a magnetically ordered state at 0.41 K. The Weiss temperature for Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> is  $\theta_{CW} =$ -0.06 K, indicating close competition between ferromagnetic and antiferromagnetic interactions. Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> is a Heisenberg antiferromagnet that transitions to long-range magnetic order at 0.81 K, in spite of significant site mixing. Below its ordering transition, we find a  $T^{3/2}$  heat capacity dependence in Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>, indication of a ground state that is distinct from other gadolinium pyrochlores. These lead-based pyrochlores provide insight into the effects of weakened exchange on highly frustrated lattices and represent further realizations of several exotic magnetic ground states which can test theoretical models.

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## I. INTRODUCTION

Magnetic frustration occurs when it is impossible to satisfy all pairwise magnetic interactions simultaneously and is typically a consequence of the underlying lattice geometry. The canonical example of magnetic frustration is antiferromagnetic Ising spins placed on the vertices of an equilateral triangle; in this scenario, only two of the three spin pairs can be antiparallel, resulting in magnetic frustration. Most structures studied in the context of magnetic frustration are composed of triangular motifs [1]. Some examples of frustrated lattice geometries include the kagome, honeycomb, and perovskite lattices. However, there is perhaps no lattice better suited to the study of magnetic frustration than the pyrochlore lattice [2]. Pyrochlores, with formula  $A_2B_2O_7$ , are composed of two interpenetrating networks of corner-sharing tetrahedra. The vertices of one tetrahedral network are occupied by the  $A^{3+}$ cations while the second network is occupied by the  $B^{4+}$ cations. This corner-sharing tetrahedral arrangement is subject to extreme frustration when occupied by a magnetic ion. It is fortunate for the study of magnetic frustration that a large fraction of the cations which can occupy the pyrochlore lattice are, in fact, magnetic.

The most well-characterized family of frustrated pyrochlores are the rare-earth titanate pyrochlores,  $R_2$ Ti<sub>2</sub>O<sub>7</sub> [2]. The *B*-site cation, Ti<sup>4+</sup>, has a closed valence shell and is thus nonmagnetic. By varying the *A*-site rare-earth cation, many unique and exotic magnetic ground states have been uncovered in this family. The spin ice state, a magnetic analog for the proton arrangement in water ice, is observed for R = Ho [3], Dy [4]. When the rare-earth site is occupied by R = Tb, there is an absence of conventional long-range magnetic order down to 70 mK, leading Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> to be considered a spin liquid candidate [5,6]. Long-range order may also be absent in the case of the apparent quantum spin liquid R = Yb [7,8]. A detailed investigation of the Hamiltonian of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has justified the label "quantum spin ice" [9]. However, the lowtemperature magnetism of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> remains controversial, due to sample variation [10,11] and conflicting reports [12,13]. Even the titanate pyrochlores that transition to long-range magnetic order, R = Gd, Er, have exotic properties. In the case of Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, one proposed scenario is that the transition to long-range magnetic order is selected by thermal fluctuations (i.e., order-by-disorder) [14–16]. In Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, an uncommon example of Heisenberg spins on a pyrochlore lattice [17], the antiferromagnetic ground state is a complex multi-k structure with a two-stage ordering [18,19].

The plethora of exotic magnetism discovered in the titanate pyrochlores was further expanded through substitution of titanium for other nonmagnetic cations of varying size, i.e., chemical pressure [20,21]. Studies with chemical pressure have allowed investigation into the phase space for these frustrated materials. In the pyrochlores, variation of the nonmagnetic *B*-site cation has two main consequences. First, the change in ionic radii introduces a positive or negative chemical pressure. This results in differences in the distances between magnetic *A*-site cations, allowing an effective tuning of the exchange interaction [22]. The second consequence

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of substituting the *B*-site cation involves subtle changes to the local oxygen environment surrounding each magnetic cation [23]. These differences, although structurally small, can result in large differences to the single-ion properties which determine the crystal electric field and, consequently, the anisotropy.

In the case of some rare-earth cations, the magnetic ground state is robust under the application of chemical pressure. For example, the spin ice state that was first observed in Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> persists at negative chemical pressure (Ho<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [24,25]) and positive chemical pressure (Ho<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> [26,27]). In other cases, chemical pressure can radically alter the magnetic ground state. For example, in the ytterbium-based pyrochlores, Yb<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (B = Sn, Ti, Ge), the interactions between ytterbium moments are very sensitive to changes in chemical pressure [28]. Consequently, each of these pyrochlores have a markedly different magnetic ground state ranging from ferromagnetic order in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> [28]. Different magnetic ground states are also observed in the terbium-based pyrochlores, Yb<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (B = Sn, Ti, Ge) [6,30,31].

Even more extreme differences in chemical pressure can be achieved through the substitution of lead onto the B site of the pyrochlore lattice. Using high-pressure synthesis techniques, the pyrochlore stability field was expanded in 1969 by Sleight to include the plumbates [32]. Pb<sup>4+</sup>, with an ionic radius of 77.5 pm, is the largest B-site cation to be successfully incorporated into the pyrochlore structure [32]. However, the very large ionic radii of lead imposes limitations on possible A-site rare-earth cations. Only the largest of the rare earths have been successfully prepared:  $A_2Pb_2O_7$  (A = Pr, Nd, Gd). In fact, the only rare earth which can be prepared on both a titanate and plumbate lattice is gadolinium. Instead, the stannate,  $A_2 Sn_2 O_7$ , and zirconate,  $A_2Zr_2O_7$ , pyrochlores are a more direct point of comparison. Each of the above-mentioned rare earths can be combined with tin and zirconium onto the pyrochlore lattice.

The praeseodymium pyrochlores,  $Pr_2Sn_2O_7$  and  $Pr_2Zr_2O_7$ , play host to the so-called dynamic or quantum spin ice states [33,34]. Much like the dipolar spin ice state, the  $Pr^{3+}$  moments are locally arranged into a two-in/two-out configuration. However, the  $Pr^{3+}$  moments are subject to stronger quantum fluctuations and remain dynamic down to the lowest measured temperatures, 200 mK [33]. This state is of significant experimental [33–35] and theoretical interest [36–41] as it may permit the propagation of monopole excitations. Neutron scattering measurements of single-crystal  $Pr_2Zr_2O_7$  have revealed a large inelastic signal, absent of pinch points, suggesting quantum fluctuations of magnetic monopoles [34].

There has been comparatively little study of the neodymium-based pyrochlores. Long-range ordering has been observed in Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> using heat capacity [42] and magnetic susceptibility [20]. Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> has a negative Weiss temperature,  $\theta_{CW} = -0.31$  K [20]. However, until recently, the ground state of this material had not been determined. Recent magnetic neutron diffraction measurements have revealed that the exact magnetic ground state in Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> is an antiferromagnetic q = 0 state [43].

Gadolinium pyrochlores are unique in two respects. (i) First, gadolinium has a spin-only total angular momentum (S = 7/2, L = 0). As a result, the single ion anisotropy of Gd<sup>3+</sup> is small compared to other magnetic rare earth cations. (ii) Second, gadolinium pyrochlores have the largest size range for nonmagnetic *B*-site cations, ranging from the smallest (Ge<sup>4+</sup> [21]) to the largest (Pb<sup>4+</sup> [32]). However, only the intermediate-sized members, Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, have been magnetically characterized until now [17,44– 46]. Both Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> are candidates for the Palmer-Chalker ground state, a four-sublattice Néel state [47]. Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> does appear to be a good experimental realization of this state [48]. However, the exact ground state of Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has remained experimentally elusive [18,19,49].

With a diverse array of magnetic behavior, the frustrated pyrochlores have maintained a high level of interest over the past 20 years. An expanded knowledge of their phase diagrams will improve understanding of these unique ground states, and may allow the discovery of new ground states. Here, we report on the synthesis and characterization of the lead-based pyrochlores,  $A_2Pb_2O_7$  (A = Pr, Nd, Gd).

#### **II. EXPERIMENTAL METHODS**

Polycrystalline samples of  $A_2Pb_2O_7$  (A = La, Nd, Pr, Gd) were synthesized from stoichiometric amounts of  $A_2O_3$  and PbO<sub>2</sub> reacted in a gold capsule. The high-pressure synthesis was carried out in a Walker-type multianvil press at 2 GPa and 900 °C. Room-temperature x-ray powder diffraction was performed with a D2-phaser diffractometer using Cu K $\alpha$  radiation. Rietveld analyses of the x-ray diffraction patterns were performed using FULLPROF [50]. Powder neutron diffraction measurements on a 90 mg sample of Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> were made on the General Materials Diffractometer (GEM) at the ISIS neutron facility. Rietveld analysis of the neutron diffraction patterns were performed with GSAS.

The susceptibility and magnetization measurements were made using a Quantum Design MPMS magnetometer equipped with a <sup>3</sup>He insert. The dc magnetic susceptibility measurements were made in fields of 1000 Oe between 0.5 K and 300 K. The ac magnetic susceptibility measurements were carried out with an ac driving field of 3.5 Oe, over a frequency range of 1 Hz to 1000 Hz. Specific-heat measurements were carried out using a Quantum Design physical property measurement system (PPMS) equipped with a <sup>3</sup>He insert. The magnetic component of the specific heat was isolated by subtracting the specific heat of a nonmagnetic lattice equivalent, La<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>.

#### **III. CRYSTAL STRUCTURES**

The crystal structures of the powder  $A_2Pb_2O_7$  (A = La, Nd, Pr, Gd) samples were investigated by room-temperature powder x-ray diffraction. The crystal structure was determined by Rietveld refinement of the diffraction patterns using the space group  $Fd\bar{3}m$  (Fig. 1). Lattice parameters for  $A_2Pb_2O_7$  (A = La, Nd, Pr, Gd), listed in Table I, were in agreement with prior investigations [32]. The lattice parameters for the plumbate pyrochlores follow a linear relation with A site ionic radii. The marked peak in each diffraction pattern at



FIG. 1. (Color online) Room-temperature powder x-ray diffraction patterns and structure refinements of  $A_2$ Pb<sub>2</sub>O<sub>7</sub>, where A = (a)La, (b) Nd, (c) Pr, and (d) Gd. Patterns for the observed (red marks), calculated (black lines), and difference (blue lines) are shown. The ticks indicate the positions of the Bragg reflections for the  $Fd\bar{3}m$ space group.

 $2\theta = 25.6^{\circ}$  corresponds to the (222) pyrochlore reflection from the Cu K $\beta$  wavelength.

Lead is the largest known possible *B*-site cation for the pyrochlore lattice. As a result, the *A*-site to *B*-site ratio,  $A^{3+}/B^{4+}$ , in the lead pyrochlores are among the smallest. Consequently, much like zirconium-based pyrochlores, nonnegligible site mixing between the *A* and *B* sites is expected to be likely [52]. To determine the exact level of site mixing in the lead pyrochlores, we have performed room-temperature neutron diffraction on Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> (Fig. 2). Rietveld analysis revealed the presence of mixing between Pr<sup>3+</sup> and Pb<sup>4+</sup> on the order of 8%. This is also evidenced by the reduced size of the (111) superlattice peak at  $2\theta = 14^{\circ}$  with decreasing rare-earth size (Fig. 1). The pyrochlore superlattice peaks arise due to *A*-and *B*-site ordering, and vanish in the case of random site

TABLE I. Ionic radii for A = Pr, Nd, Gd and B = Ti, Sn, Pb, and the resultant pyrochlore lattice parameter. The lattice parameters for the stannate pyrochlores are taken from [51].

Cation	Pr (0.99 Å)	Nd (0.98 Å)	Gd (0.94 Å)
Ti (0.61 Å) Sn (0.69 Å) Pb (0.78 Å)	10.600 Å 10.872 Å	10.567 Å 10.834 Å	10.18 Å [44] 10.454 Å 10.729 Å





FIG. 2. (Color online) Rietveld refinement of the roomtemperature TOF diffraction pattern of Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> measured on the GEM diffractometer. The observed (red marks), calculated (black lines), and difference (blue lines) patterns are shown. The ticks indicate the positions of the Bragg reflections for the  $Fd\bar{3}m$  space group. The weighted profile *R* factor for the fit is  $R_{wp} = 4.14\%$ .

occupancy. The detailed results of the structural refinement of  $Pr_2Pb_2O_7$  are presented in Table II.

 $Gd_2Pb_2O_7$  has an *A*-site to *B*-site ratio of 1.36, the smallest of any pyrochlore [2]. From inspection of the x-ray diffraction pattern, it is apparent that the (111) superlattice peak at  $2\theta = 14^\circ$  is nearly extinct in  $Gd_2Pb_2O_7$  [Fig. 1(d)]. However, neutron diffraction of  $Gd_2Pb_2O_7$  is made difficult by the high neutron absorption cross section of gadolinium. Instead, we used x-ray refinements to investigate the degree of site mixing in  $Gd_2Pb_2O_7$ . Refinements in which the *A*-site and *B*-site occupancies are allowed to freely vary give 61% order of

TABLE II. Selected parameters for the refinement of the neutron diffraction pattern of  $Pr_2Pb_2O_7$ .

Atom	Site	(x,y,z)	Occupancy	$U_{\rm iso}({\rm \AA}^2)$
Pr/Pb	16 <i>d</i>	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	0.924(7)/0.076(7)	0.0071(9)
Pb/Pr	16 <i>c</i>	(0, 0, 0)	0.924(7)/0.076(7)	0.0026(4)
01	8b	$(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$	0.91(1)	0.006(1)
O2	48f	$(0.342, \frac{1}{8}, \frac{1}{8})$	1.0	0.0085(4)

the *A* and *B* sites (39% site mixing), close to the random occupancies (50%) expected for the defect-fluorite structure. For comparison, x-ray refinements of the other three lead pyrochlores we investigated,  $A_2Pb_2O_7$  (A = La, Nd, Pr), each gave 96% order (4% site mixing), which agrees well with the neutron refinements.

## IV. MAGNETIC PROPERTIES: Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>

Figure 3 shows the magnetic susceptibility of  $Pr_2Pb_2O_7$ measured in a field of 1000 Oe. The susceptibility of Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> is free of anomalies down to 0.5 K. The inverse susceptibility has a large negative curvature with increasing temperature, likely due to a large splitting of the crystal electric field levels. Consequently, the region over which the Curie-Weiss law can be applied is limited to low temperatures, between 0.5 K and 5 K (Fig. 3 inset). The effect of low-lying crystal fields is to limit the quantitative validity of the Curie-Weiss analysis; however, we proceed with the intention of drawing comparisons with other praeseodymium pyrochlores. The fit gives a Weiss temperature of  $\theta_{CW} = -0.74(1)$  K, indicating net antiferromagnetic interactions. The Weiss temperatures in Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and Pr<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> are 0.32 K [20] and -1.41 K [34], respectively. However, the temperature regions which exhibit Curie-Weiss behavior differs significantly between these three compounds. As a result, it is difficult to draw comparisons on the basis of the Weiss temperature. The strength of the nearest-neighbor dipolar interactions, which can be approximated in pyrochlores by

$$D_{\rm nn} = \frac{5\mu_0}{3 \times 4\pi} \frac{\mu^2}{r_{nn}^3},\tag{1}$$

when  $\mu$  is estimated from the low temperature susceptibility, is only 0.11 K in Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>. Thus, the magnetism in Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> is dominated by exchange interactions.

The higher temperature magnetic susceptibility of  $Pr_2Pb_2O_7$  is dominated by single-ion physics, due to a large crystal electric field splitting. The 9-fold degenerate state of  $Pr^{3+}$  is split into three non-Kramers doublets and three singlets



FIG. 3. (Color online) The temperature dependence of the magnetic susceptibility (red) and inverse susceptibility (blue) of  $Pr_2Pb_2O_7$ measured with a field of 1000 Oe. Inset: Low-temperature inverse susceptibility with a Curie-Weiss law fit between 0.5 K and 5 K.



FIG. 4. (Color online) The magnetization of  $Pr_2Pb_2O_7$  as a function of applied field between 0 T and 7 T at 0.5 K and 1.8 K. The dashed line marks half the effective moment value, 1.25  $\mu_B/Pr$ .

[20]. From the Curie-Weiss fit between 0.5 and 5 K, we calculate an effective magnetic moment of 2.53(1)  $\mu_B$ , a value not significantly different from that found in Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and Pr<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> [20,34]. However, this moment falls short of the 3.58  $\mu_B$  free-ion moment for a pure  $|J = \pm 4\rangle$  state, suggesting a mixing of  $|J = \pm 1\rangle$  and  $|J = \mp 2\rangle$  terms [20]. Thus, Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> has a doublet ground state with Ising moments pointing along the local (111) trigonal axes.

The magnetization of  $Pr_2Pb_2O_7$ , shown in Fig. 4, does not saturate in a field of 7 T at 0.5 K. This behavior deviates strongly from the Brillouin function for J = 4,

$$B_J(x) = \frac{2J+1}{2J} \operatorname{coth}\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \operatorname{coth}\left(\frac{x}{2J}\right), \quad (2)$$

where

$$x = \frac{g_J \mu_B J B}{k_B T},\tag{3}$$

due to significant interactions between the  $Pr^{3+}$  moments at these temperatures and deviations from isotropic crystal field levels. The magnetization of  $Pr_2Pb_2O_7$  appears to be approaching a saturation value of ~1.25  $\mu_B = \frac{\mu_{eff}}{2}$ . A saturation value of half the effective moment in powder samples is a hallmark of (111) Ising anisotropy, as observed in other praseodymium pyrochlores [53,54]. In general, the magnetization of  $Pr_2Pb_2O_7$ closely resembles that of  $Pr_2Zr_2O_7$ , which also fails to saturate by 7 T [54].

The heat capacity of  $Pr_2Pb_2O_7$  contains a broad anomaly centered at 1.2 K (Fig. 5). This feature does not resemble the sharp anomalies which typically signify long-range ordering, nor does it fit to a Schottky model. Instead, the peak in the heat capacity of  $Pr_2Pb_2O_7$  bears a resemblance to those observed in spin ice, attributed to a condensation of thermally activated monopole pairs [34]. Much like  $Pr_2Zr_2O_7$ , the peak is broader than those observed in the dipolar spin ices [4]. This broadening is attributed to monopole quantum dynamics in  $Pr_2Zr_2O_7$ , and is likely also at play in  $Pr_2Pb_2O_7$ .

The lattice contribution to the specific heat was subtracted by using the specific heat of nonmagnetic  $La_2Pb_2O_7$ .



FIG. 5. (Color online) The specific heat of  $Pr_2Pb_2O_7$  and non-magnetic  $La_2Pb_2O_7$ . Inset: Low-temperature lattice subtracted specific heat.

Calculation of the entropy for the lattice subtracted specific heat,  $\Delta S = \int \frac{C_p}{T} dT$ , gives a value which exceeds the maximum value for an Ising system,  $R \ln(2)$ . However, there are other known contributions to the specific heat of Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>. The hyperfine splitting of the nuclear levels of  $Pr^{3+}$  produces a nuclear Schottky anomaly with significant intensity below 1 K. Furthermore, the crystal field scheme of Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> has not been measured, but there is likely a low-lying crystal field contributing to the specific heat, as evidenced from changes in the curvature close to 10 K. However, to subtract this contribution would require a more precise knowledge of the low-lying crystal field levels. Since these contributions to the specific heat of Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> cannot be accurately determined, a realistic calculation of the magnetic entropy is not possible. It is interesting to note that the lowest crystal fields in Pr<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> and Pr<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> occur at energies an order of magnitude higher [34,55]. Thus, Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> represents an interesting opportunity to investigate the impact of a low-lying crystal field on a dynamic spin ice state.

## V. MAGNETIC PROPERTIES: Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>

The magnetic susceptibility of Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>, shown in Fig. 6, contains no anomalies down to 0.5 K. Between 0.5 K and 15 K, the inverse susceptibility is well fitted by the Curie-Weiss law. Before proceeding, we should note that much like Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>, the crystal electric field is likely impacting the analysis. The Weiss temperature calculated from this fit is  $\theta_{CW} = -0.069(4)$  K, indicating weak net antiferromagnetic interactions. A Curie-Weiss fit over the same temperature range in Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> gives a Weiss temperature of -0.31 K [20]. Thus, the change from the stannate to the plumbate results in a very close competition of antiferromagnetic and ferromagnetic interactions. It is worth noting that the calculated dipolar interactions in Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> and Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> are 0.11 K and 0.12 K, respectively. Thus, the changing strength of the dipolar interaction alone cannot account for the change in the Weiss



FIG. 6. (Color online) The magnetic susceptibility of  $Nd_2Pb_2O_7$  measured with an applied field of 1000 Oe. The left axis gives the direct susceptibility (red) and the right axis gives the inverse susceptibility (blue). The Curie-Weiss fit between 0.5 K and 15 K is given by the blue line.

temperature. The decreased Weiss temperature in  $Nd_2Pb_2O_7$  is thus indicative of decreased exchange interactions.

The calculated effective magnetic moment for Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>, from the Curie-Weiss fit, is 2.55(7)  $\mu_B$ . This value falls short of the free-ion value of 3.62  $\mu_B$  for  $|J = \pm 9/2\rangle$ , indicating the mixing of  $|J = \pm 3/2\rangle$  terms. Above 20 K, the susceptibility deviates from Curie-Weiss behavior due to low-lying crystal field levels. The 10-fold degenerate ground state of Nd<sup>3+</sup> (J =9/2) is split into five symmetry-protected Kramers doublets. Figure 7 shows the magnetization of Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> at 0.5 K and 2 K. At both temperatures, the magnetization is similar to that of a Brillouin function for J = 9/2. The magnetization saturates at 1.26  $\mu_B/Nd^{3+}$ , half the value of the effective moment. Again, this is a consequence of local (111) Ising anisotropy and powder averaging.



FIG. 7. (Color online) The magnetization of  $Nd_2Pb_2O_7$  as a function of applied field between 0 T and 7 T at 0.5 K and 2 K. The solid blue and red curves give the Brillouin function for 0.5 K and 2 K, respectively.



FIG. 8. (Color online) Magnetic specific heat of  $Nd_2Pb_2O_7$  measured in zero field, 3 T, and 9 T between 0.4 K and 40 K. Inset: Scaled in view of the low-temperature zero-field specific heat of  $Nd_2Pb_2O_7$ .

The magnetic specific heat of  $Nd_2Pb_2O_7$  is shown in Fig. 8. In zero field, the magnetic component of the specific heat increases below 3 K. Below 0.5 K, the specific heat begins to strongly increase, with its maximum occurring at 0.41 K. However, only a single data point could be collected below the peak's maximum. This peak, which is likely due to longrange magnetic ordering, shifts upwards in temperature and broadens with an externally applied field. A field of 3 T shifts the maximum to 2.5 K, while a field of 9 T further increases it to 8 K. The magnetic origin of this peak is most easily verified by integrating out the entropy, which should give  $R \ln 2$  for an Ising system. However, this cannot be done with our zero-field measurement, in which the decreasing side of the anomaly is outside our measurement range (Fig. 8). Integration of  $C_p/T$ between 0.4 K and 40 K for the 3 T and 9 T data sets yields 0.95*R* ln 2 and 0.96*R* ln 2, respectively (Fig. 9).



FIG. 9. (Color online) Calculated magnetic entropy of Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> measured in zero field, 3 T, and 9 T between 0.4 K and 40 K. The dashed line indicates the expected value,  $R \ln (2)$ , for an Ising system.

Long-range order was also found in Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, which has both a sharp peak in its heat capacity [42] and a cusp in its susceptibility [20] at 0.9 K. It is interesting to note that the ordering temperature in Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> is reduced from Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> by a factor of two. Recent neutron scattering measurements of Nd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> have confirmed that the ordered state is the k = 0antiferromagnetic all-in/all-out state [43]. Neutron scattering will also be required to determine the consequence of net ferromagnetic interactions on the magnetic ground state of Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>.

## VI. MAGNETIC PROPERTIES: Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>

Figure 10(a) shows the low-temperature magnetic susceptibility of  $Gd_2Pb_2O_7$  measured in 1000 Oe. A magnetic ordering transition is signaled by a cusp in the susceptibility at 0.8 K. There is a slight splitting of the field-cooled and zero-field-cooled susceptibility below the transition at 0.8 K indicating a small amount of irreversibility. The susceptibilities of the related pyrochlores,  $Gd_2Ti_2O_7$  and  $Gd_2Sn_2O_7$ , both contain



FIG. 10. (Color online) (a) The low-temperature magnetic susceptibility of  $Gd_2Pb_2O_7$  measured with an applied field of 1000 Oe. Below the magnetic ordering transition at 0.8 K there is a splitting between the zero-field-cooled and field-cooled susceptibility. (b) The high-temperature magnetic susceptibility of  $Gd_2Pb_2O_7$ . The left axis gives the direct susceptibility (red) and the right axis gives the inverse susceptibility (blue). The Curie-Weiss law fit is given by the blue line.



FIG. 11. (Color online) The magnetization of  $Gd_2Pb_2O_7$  as a function of applied field between 0 T and 7 T at temperatures between 0.5 K and 50 K. The solid curves show the Brillouin function for J = 7/2 at each corresponding temperature.

magnetic ordering anomalies close to 1.0 K [44]. They too both exhibit a degree of irreversibility below these transitions. The maximum FC/ZFC splitting measured in  $Gd_2Pb_2O_7$  is 0.03 emu/mol  $Gd^{3+}$ , very similar to the magnitude of the splitting in  $Gd_2Ti_2O_7$  [44]. Conversely, in  $Gd_2Sn_2O_7$ , the FC/ZFC splitting is an order of magnitude larger [44].

The high-temperature magnetic susceptibility of  $Gd_2Pb_2O_7$ up to 300 K is shown in Fig. 10(b). Between 10 K and 300 K the inverse susceptibility is strikingly linear, fitting well to Curie-Weiss behavior. The Weiss temperature is -7.38(6) K, indicating dominant antiferromagnetic interactions. The Weiss temperatures for  $Gd_2Ti_2O_7$  and  $Gd_2Sn_2O_7$  are -9.9(1) K and -8.6(1) K, respectively [44]. As anticipated, the substitution of the larger Pb<sup>4+</sup> cation appears to have weakened the antiferromagnetic exchange in  $Gd_2Pb_2O_7$ .

The Curie-Weiss fit of Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> can also be used to extract an effective moment, yielding 7.67(1)  $\mu_{\rm B}$  [Fig. 10(b)]. This calculated moment is close to the expected 7.94  $\mu_{\rm B}$  free-ion moment. In Gd<sup>3+</sup>, the isotropic spin, S = 7/2, is the only contribution to the total angular momentum, J. Consequently, the 8-fold degeneracy of the ground state is only marginally lifted by the crystal electric field, on the order of a fraction of a kelvin [17]. The high degree of linearity in the inverse susceptibility between 10 K to 300 K suggests there are no well-separated crystal field levels in Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>, supporting the picture described above.

The magnetization of  $Gd_2Pb_2O_7$  is shown in Fig. 11 at temperatures ranging from 0.5 K to 50 K. At 10 K and higher, the magnetization fits well to the Brillouin function for J = 7/2, which describes a system of paramagnetic, non-interacting moments. At 0.5 K, where the Brillouin function fails completely, the magnetization approaches a saturation value on the order of the free-ion  $Gd^{3+}$  moment by 7 T.

The magnetic specific heat of  $Gd_2Pb_2O_7$  is shown in Fig. 12. The magnetic specific heat increases below 10 K and peaks at 0.81 K. Extrapolating  $C_{mag}/T$  to 0 J/mol K<sup>2</sup> gives an integrated entropy of 17.1 J/mol K (Fig. 12 inset). This value



FIG. 12. (Color online) Magnetic specific heat of  $Gd_2Pb_2O_7$  measured in zero field between 0.4 K and 20 K. Inset: Integrated entropy of  $Gd_2Pb_2O_7$ , giving the expected value,  $R \ln 8$ , for Heisenberg-like spins.

corresponds to  $0.99R \ln 8 = 0.99R \ln (2S + 1)$ . This is the expected value for  $Gd^{3+}$  (S = 7/2), which, with very small single-ion anisotropy, has Heisenberg-like spins. Anomalies related to magnetic ordering are also observed in  $Gd_2Ti_2O_7$  and  $Gd_2Sn_2O_7$  at approximately 1 K. The maximum amplitude of the anomaly in  $Gd_2Pb_2O_7$  is 8.7 J/mol K. This is similar in magnitude to that of  $Gd_2Ti_2O_7$ , whereas the anomaly in  $Gd_2Sn_2O_7$  has a maximum amplitude of 120 J/mol K [44]. However, in  $Gd_2Ti_2O_7$ , there is a second anomaly at 0.75 K and the ordering in this compound occurs in two distinct stages [44,46]. Thus, the heat capacity anomaly of  $Gd_2Pb_2O_7$  does not strongly resemble either of its group members.

The temperature dependence of the magnetic specific heat of Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>, below the ordering temperature, reveals further differences from the other gadolinium pyrochlores (Fig. 13). Conventional ungapped antiferromagnetic spin wave excitations give rise to a  $C_{\text{mag}} \propto T^3$ . However, the specific heat below the ordering transition in both Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> is better parametrized by  $C_{\text{mag}} \propto T^2$  [44,56]. In Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, the specific heat is found to decrease exponentially below 350 mK [57]. This behavior in Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> is attributed to conventional antiferromagnetic gapped magnons and can be theoretically reconciled with linear spin-wave theory [57]. However, the  $C_{\text{mag}} \propto T^2$  dependence in Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, which is ungapped down to 100 mK, remains a mystery [56].

A least-squares fit to the heat capacity of Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> between 0.35 K and 0.75 K to  $C_{\text{mag}} \propto T^{\eta}$  gives  $\eta = 1.49(3)$ . Thus, the specific heat of Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> below 0.8 K is well described by a  $C_{\text{mag}} \propto T^{3/2}$  power law, as shown in Fig. 13. In an ordered ferromagnet, spin wave excitations make a  $C_{\text{mag}} \propto T^{3/2}$  contribution to the specific heat. However, a ferromagnetic ground state cannot be reconciled with the overwhelmingly negative (antiferromagnetic) Curie-Weiss temperature in Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>. Determination of the magnetic ground state of Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> will require neutron diffraction, which is made challenging by the high neutron absorption cross section of gadolinium. While the exact ground state remains


FIG. 13. (Color online) Power-law fits to the low-temperature specific heat of Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>. The least-squares refinement gives a  $C_{\text{mag}} \propto T^{3/2}$  dependence (red curve).

unknown at present, it is clear that it is markedly different from those of  $Gd_2Ti_2O_7$  and  $Gd_2Sn_2O_7$ . In the absence of neutron diffraction or muon spin relaxation microscopic magnetic measurements we cannot rule out spin glass freezing. However, the sharpness of the transition seen in our bulk dc susceptibility and specific-heat measurements, along with a lack of frequency dependence in ac susceptibility (not shown), make spin glass ordering highly unlikely in  $Gd_2Pb_2O_7$ . This is particularly noteworthy given the significant degree of site mixing.

#### VII. CONCLUSIONS

We have reported on the crystallographic and magnetic properties of the lead-based pyrochlores  $A_2Pb_2O_7$  (A = La, Pr, Nd, Gd) (Table III). We have explored a region of phase space in a family of materials known to have a rich collection of ground states. Lead is the largest *B*-site cation which can occupy the pyrochlore lattice. Consequently, lead substitution on the pyrochlore lattice results in an effective weakening of the exchange interaction. As a result, magnetic ordering is suppressed to lower temperatures in each case. Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> has strong Ising (111) anisotropy and an absence of long-range magnetic order down to 500 mK. Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> has a spin-icelike anomaly in its heat capacity centered at 1.2 K. Thus, Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> is a candidate for a quantum spin ice state, despite

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TABLE III. Comparison of lattice parameters and selected magnetic parameters in the  $A_2$ Pb<sub>2</sub>O<sub>7</sub> (A =La, Nd, Pr, and Gd pyrochlores).

	a (Å)	$\theta_{\mathrm{CW}}\left(\mathrm{K}\right)$	$\mu_{\mathrm{eff}}\left(\mu_{\mathrm{B}} ight)$	Anisotropy
La <sub>2</sub> Pb <sub>2</sub> O <sub>7</sub>	10.9682(4)			
$Pr_2Pb_2O_7$	10.8721(9)	-0.74(1)	2.53(1)	Ising
Nd <sub>2</sub> Pb <sub>2</sub> O <sub>7</sub>	10.8336(4)	0.15(1)	2.47(1)	Ising
$Gd_2Pb_2O_7$	10.7292(8)	-7.38(6)	7.67(1)	Heisenberg

weakened exchange and mild disorder. Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> also has strong (111) Ising anisotropy. However, Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> transitions to long-range magnetic order at 0.41 K. The small, negative Weiss temperature of Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> indicates it may lie on the border between ferromagnetism and antiferromagnetism. Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> is a good approximation to Heisenberg spins on the pyrochlore lattice. However, due to the very similar ionic radii of gadolinium and lead, Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> has a significant level of site mixing. Despite this structural disorder, magnetic ordering in Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> at 0.81 K is signaled by a cusp in the susceptibility and a lambda-like specific-heat anomaly. Unlike Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> the ordering in Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> occurs in a single stage. Furthermore, a  $T^{3/2}$  dependence is observed in the low-temperature specific heat, a value which is typically associated with the spin wave contribution in a conventional ferromagnet. Thus, it is unlikely that Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> is adopting the antiferromagnetic Palmer-Chalker ground state. To that end, neutron diffraction of Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> is recommended. In general, these lead-based pyrochlores provide insight into the effects of weaker exchange on highly frustrated ground states.

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# Chapter 4\_

## Platinum Pyrochlores

We have now explored the effect of chemical pressure on the pyrochlore lattice in the positive (germanium) and negative (lead) limits. In this final chapter of original research we consider the effect of platinum substitution at the B site. As was the case for both the germanates and the plumbates, the successful synthesis of the platinate pyrochlores has primarily been achieved using high pressure conditions. For the platinum pyrochlores, it is *not* the relative ionic radii of the A and B site cations that necessitates external pressure. Indeed, since platinum has an ionic radius intermediate to those of titanium and tin (Figure 4.1), it should lie well within the ambient pressure stability range for the pyrochlore structure. However, the platinum containing reactant, PtO<sub>2</sub>, readily decomposes at the elevated temperatures that are required to prepare rare earth pyrochlore phases. Once PtO<sub>2</sub> has reduced to platinum metal it is inert, as implied by the name "noble metal". High pressure conditions suppress the decomposition of PtO<sub>2</sub> to sufficiently high temperatures, allowing the pyrochlore phase to be obtained. Once prepared,



Figure 4.1: The relative ionic radii of the non-magnetic B site cations, titanium, platinum, and tin in their 4+ oxidation state, as well as the rare earth A site cation erbium in its 3+ oxidation state.



Figure 4.2: Periodic table highlighted to show the three groups of non-magnetic B site cations (red) that can be combined with a rare earth cation (blue) to form a pyrochlore structure.

the  $R_2Pt_2O_7$  pyrochlores are stable against decomposition up to 1000°C and are thus, highly metastable phases [137].

The first reports on the synthesis of the platinate pyrochlores,  $R_2 Pt_2 O_7$  with various rare earths at the R site, occurred in 1968. The first of these reports came from Hoekstra and Gallagher, who performed their synthesis using stoichiometric quantities of PtO<sub>2</sub> and rare earth oxide,  $R_2O_3$ , reacted at relatively high pressure and temperature, 4 GPa and 1200°C [137]. The second report, from Sleight, used a very modest pressure of 0.3 GPa at 700°C, but included a large quantity of potassium chlorate, KClO<sub>3</sub>, a strong oxidizing agent [138]. As the desired phase is successfully obtained using both sets of reaction conditions, it tends to suggest that the stability range under which the platinate pyrochlores can be obtained is quite large. It may well be the case that the platinate pyrochlores can be prepared at ambient pressure, provided the conditions can be kept sufficiently oxidizing. Indeed, small flux grown single crystals of  $R_2Pt_2O_7$ pyrochlores have been reported under oxygen pressures of only 12 atm = 0.001 GPa [139]. In the works contained in this chapter, the samples were powders prepared using the high pressure method. However, of the three families of pyrochlores that are discussed in this thesis, the platinate pyrochlores are likely the most accessible as large single crystals, given their position in the pyrochlore stability field [29].

Platinum makes for an interesting counterexample to the chemical pressure narrative we have followed thus far. As shown in Figure 4.1, platinum with an ionic radius of r = 62.5 pm, is only slightly larger than titanium. Substitution of titanium by platinum expands the cubic lattice parameter, a, by less than 0.5%, significantly smaller than the effects of germanium (-2%) and lead (+2.5%) substitution. Thus, one might naively expect that substitution of titanium by platinum would have a quite subtle effect on the ground state magnetism. However, this is not the case and the explanation for "Why?" underscores the ways in which chemical pressure does not always provide an adequate framework. To begin this explanation we refer to Figure 4.2, which is a periodic table where only the elements that are both non-magnetic and able to occupy the pyrochlore B site in combination with some subset of the rare earths are highlighted. It can be seen that the non-magnetic B sites fall in three distinct groups. The first is the Group 4 transition metals: titanium, zirconium, and hafnium. In their 4+ oxidation states, each of these cations has a noble gas electron configuration, those of [Ar], [Kr], and [Xe] respectively. The second group is the Group 14 p-block metals: germanium, tin, and lead. In their 4+ oxidation states, each of these cations has a filled d shell. For example, lead, the B site cation that was the subject of our previous chapter, has an electron configuration of  $[Xe]5d^{10}$ . The last group of non-magnetic B site cations are the so-called noble metals: palladium and platinum, which are located in Group 10. In their 4+ oxidation states, these cations have partially filled d shells, with  $[Kr]5d^6$  and  $[Xe]5d^6$  electron configurations, respectively.

It is immediately apparent that  $Pt^{4+}$  is a very different cation from  $Ti^{4+}$ , despite their similar ionic radii. First of all, Pt<sup>4+</sup> is significantly heavier than Ti<sup>4+</sup> and has more than quadruple the number of electrons. This is sure to have an impact on the chemical nature of the bonding. Perhaps more important, platinum does not have a closed shell electron configuration. Within the octahedral oxygen environment of the pyrochlore B site, the five d electron orbitals are split into a lower  $t_{2g}$  band and an upper  $e_g$  band. The six d electrons in  $Pt^{4+}$  completely fill the  $t_{2g}$  band, leaving the  $e_g$  band empty. As platinum is a very heavy atom, spin-orbit coupling can be expected to further split these levels, but  $Pt^{4+}$  remains non-magnetic. Thus, we can proceed with the simplified picture of a filled  $t_{2g}$  band with a large energy separation to an empty  $e_g$  band. These empty  $e_g$  orbitals are important because they are spatially extended and can facilitate superexchange. It is important to recall that 4f orbitals are spatially contracted and thus, superexchange amongst rare earths tends to be quite weak. Thus, new exchange pathways are likely to play a prominent role in the ground state selection. The pathways facilitated by the  $Pt^{4+}$  5d orbitals are not available for the other two groups of B site cations, and in particular Ti<sup>4+</sup>. Thus, platinum dramatically upsets the delicate balance of interactions, far more than chemical pressure alone would lead one to expect. The following publications are contained in this chapter:

Publication V: "Relief of frustration in the Heisenberg pyrochlore antiferromagnet Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>", Alannah M. Hallas, Arzoo Z. Sharma, Yipeng Cai, Timothy J. Munsie, Murray N. Wilson, Makoto Tachibana, Christopher R. Wiebe, and Graeme M. Luke. Physical Review B 94, 134417 (2016).

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**Publication VI**: "Phase competition in the Palmer-Chalker XY pyrochlore  $Er_2Pt_2O_7$ ", Alannah M. Hallas, Jonathan Gaudet, Nicholas P. Butch, Guangyong Xu, Makoto Tachibana, Christopher R. Wiebe, Graeme M. Luke, and Bruce D. Gaulin. Submitted to Physical Review Letters (2017) [6].

### 4.1 Preface to Publication V: Relief of magnetic frustration through a novel exchange pathway

In this paper, we characterize the magnetic ground state of the platinate pyrochlore  $Gd_2Pt_2O_7$ . In gadolinium, the orbital angular momentum is quenched (i.e. L = 0). Consequently the spin-only moment (S = 7/2) is highly isotropic, making gadolinium the best (and only) realization of Heisenberg anisotropy amongst the magnetic rare earths. Heisenberg pyrochlore antiferromagnets first came to prominence following theoretical work that predicted an infinite ground state degeneracy and, hence, the possibility for spin liquid physics [21,43,44]. However, subsequent work by Palmer and Chalker showed that the ground state degeneracy of such a system would be lifted by finite dipolar interactions [136]. On the experimental front, investigations of gadolinium pyrochlores have revealed an exotic partially ordered state in  $Gd_2Sn_2O_7$  [53], and the first experimental realization of the so-called Palmer-Chalker state in  $Gd_2Sn_2O_7$  [135].  $Gd_2Pt_2O_7$  is intermediate to these two materials in terms of its lattice parameter.

Although  $Gd_2Pt_2O_7$  was originally synthesized in 1968 [137, 138], our work is the first characterization of its magnetic properties. We performed magnetic susceptibility, heat capacity, and muon spin relaxation ( $\mu$ SR) measurements on this material, all of which reveal a transition to long-range magnetic ordering at  $T_N = 1.6$  K. The ordered state in  $Gd_2Pt_2O_7$  is antiferromagnetic, as evidenced by the form of the susceptibility, which peaks at  $T_N = 1.6$  K, as well as the negative Curie-Weiss temperature,  $\theta_{CW} = -9.4$  K. The peak at  $T_N = 1.6$  K in specific heat is remarkably sharp, indicating a first order transition. The first order nature of this transition is verified by the observation of thermal hysteresis in susceptibility. Fits to the very low temperature specific heat, well below  $T_N$ , suggest the presence of a gapped spin excitation spectrum, with a fitted gap of  $\Delta = 0.25$  meV. Finally, within its ordered state, oscillations can be resolved in the muon decay asymmetry of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> establishing the presence of quasi-static internal fields. Direct determination of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>'s ordered state via neutron diffraction was not attempted due to the massive neutron absorption cross-section of gadolinium. However, the magnitude of the internal fields in Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>, as measured by  $\mu$ SR are nearly identical to those of Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [140]. Thus, its quite likely that Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> shares the Palmer-Chalker ground state of Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [135].

The Néel temperature of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>,  $T_N = 1.6$  K, is a striking 160% larger than Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, which order at 1 K or lower [134]. Given the low energy scales of rare earth magnetism, an enhancement of this magnitude is certainly noteworthy. These three materials have similar Curie-Weiss temperatures,  $\theta_{CW} \approx -9$  K, indicating comparable interaction strengths. Thus, the enhanced  $T_N$  of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> corresponds to a marked 38% decrease in its frustration index,  $f = \frac{|\theta_{CW}|}{T_N}$ . Both dipolar interactions and crystal electric field effects can be ruled out as the origin of this enhancement. The energy scale of the dipolar interactions can be estimated as

$$D = \frac{5}{3} \left(\frac{\mu_0}{4\pi}\right) \frac{\mu^2}{r_{nn}^3},$$
(4.1)

where  $\mu$  is the magnetic moment of the gadolinium and  $r_{nn}$  is their nearest neighbour distance [40,141]. The strength of the dipolar interaction is approximately 1 K in the gadolinium pyrochlores, far smaller in magnitude than the exchange interactions, as indicated by the Curie Weiss temperature. Furthermore, the small lattice parameter shifts, going from titanium to platinum to tin at the *B* site, only negligibly modify the strength of this interaction. Likewise, substitution of the *B* site is unimportant for the crystal electric field phenomenology of the gadolinium pyrochlores. Due to gadolinium's quenched orbital angular momentum, the degeneracy of the 2J + 1 = 8-fold ground state multiplet is left intact. Thus, with dipolar and crystal field effects ruled out, the source of the enhanced Néel temperature in Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> is unambiguously exchange-based. We propose that the exchange pathways opened by the hybridization between the oxygen 2p orbitals and the platinum 5d orbitals are responsible for the partial relief of frustration in Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>. The proposed superexchange pathway, Gd-O-Pt-O-Gd, has a very large multiplicity. It is not a generic result that such further neighbour exchange will act to promote magnetic ordering, as we will see in the next paper [6, 142]. Thus, we conclude that platinum substitution provides a novel mechanism for tuning the frustration in the rare earth pyrochlores.

#### Author Contributions:

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- Heat Capacity Measurements: A.Z. Sharma, C.R. Wiebe
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- Data Analysis: A.M. Hallas, G.M. Luke
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#### Relief of frustration in the Heisenberg pyrochlore antiferromagnet Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>

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The gadolinium pyrochlores  $Gd_2B_2O_7$  are among the best realizations of antiferromagnetically coupled Heisenberg spins on a pyrochlore lattice. We present a magnetic characterization of  $Gd_2Pt_2O_7$ , a unique member of this family. Magnetic susceptibility, heat capacity, and muon spin relaxation measurements show that  $Gd_2Pt_2O_7$ undergoes an antiferromagnetic ordering transition at  $T_N = 1.6$  K. This transition is strongly first order, as indicated by the sharpness of the heat capacity anomaly, thermal hysteresis in the magnetic susceptibility, and a nondivergent relaxation rate in  $\mu$ SR. The form of the heat capacity below  $T_N$  suggests that the ground state is an anisotropic collinear antiferromagnet with an excitation spectrum that is gapped by 0.245(1) meV. The ordering temperature in  $Gd_2Pt_2O_7$ ,  $T_N = 1.6$  K, is a substantial 160% increase from other gadolinium pyrochlores, which are all known to order at 1 K or lower. We attribute this enhancement in  $T_N$  to the *B*-site cation, platinum. Despite being nonmagnetic, platinum has a filled 5*d*  $t_{2g}$  orbital and an empty 5*d*  $e_g$  orbital that can facilitate superexchange. Thus, the magnetic frustration in  $Gd_2Pt_2O_7$  is partially "relieved," thereby promoting magnetic order.

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#### I. INTRODUCTION

The pyrochlore oxides  $A_2B_2O_7$  are the paragon of geometric magnetic frustration in three dimensions [1]. Each of the A-site and B-site sublattices forms a network of corner sharing tetrahedra. This geometry is highly susceptible to magnetic frustration when either the A or B site is occupied by a magnetic cation. The rare earth pyrochlores are a very interesting subset of these materials, with an astonishing diversity of magnetic ground states and behaviors. This diversity can, in part, be attributed to the different single ion anisotropies realized by the different rare earth cations. Pyrochlores with terbium, dysprosium, or holmium occupying the A site exhibit Ising spin anisotropy [2–4], while pyrochlores with ytterbium or erbium have XY spin anisotropy [3,5]. Among the magnetic rare earth pyrochlores, it is gadolinium alone that provides a good realization of Heisenberg anisotropy on the pyrochlore lattice. This is because gadolinium has a largely isotropic spin only total angular momentum. A number of gadolinium based pyrochlores have now been synthesized and studied,  $Gd_2B_2O_7$ with B = Ti, Sn, Zr, Hf, and Pb [6–9]. Each of these systems undergoes an antiferromagnetic ordering transition at 1 K or lower.

Heisenberg pyrochlore antiferromagnets have attracted significant interest, beginning with calculations that predicted an infinite ground state degeneracy and, hence, the possibility for spin liquid phenomena [10–12]. However, it was subsequently shown by Palmer and Chalker that a Heisenberg antiferromagnet with dipolar interactions would order into a four-sublattice state with ordering vector k = (0,0,0) [13]. Investigating these predictions in the gadolinium pyrochlores via neutron scattering is made challenging due to the very high neutron absorption cross section of gadolinium. In the case of Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [14] and Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [15], this challenge has been overcome by synthesizing samples with isotopically

enriched gadolinium. The ordered state in  $Gd_2Sn_2O_7$  is indeed the k = (0,0,0) "Palmer-Chalker" state [15]. However, the situation in  $Gd_2Ti_2O_7$  is far more complicated.

In Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, there are two closely separated magnetic ordering transitions, at  $T_{N1} = 1.0$  K and  $T_{N2} = 0.75$  K [16–18]. Despite these two transitions. Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> remains in a state that is only partially ordered down to the lowest measured temperatures. In this partially ordered state, 3/4 of the spins participate in long-range order while the other 1/4 remain in a paramagnetic regime, with short range correlations. Identifying the precise nature of this partially ordered state has proven difficult, as two states, referred to as "1-k" and "4-k," are both consistent with most experimental observations [19]. In the 1-k structure, the disordered sites are confined to the triangular layers perpendicular to [111], and the ordered sites reside on the kagome layers with a single propagation vector  $k = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . Conversely, the 4-k structure is a superposition of four  $k \in \{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$ , with all of the disordered sites confined to share a tetrahedron. The diffuse scattering below  $T_{N2}$  has been the primary means of attempting to distinguish between 1-k and 4-k. Earlier studies interpreted the diffuse scattering as supporting a picture of 4-k [20], but more recently this data have been reanalyzed and deemed consistent with only the 1-k structure [19]. The nature of the state intermediate to  $T_{N1}$ and  $T_{N2}$  is still not definitively known, but a recent theoretical study has shown that thermal fluctuations should select the 4-k structure [21].

In this work we turn our attention to the magnetism of an overlooked gadolinium pyrochlore  $Gd_2Pt_2O_7$ . While the synthesis of the platinum pyrochlores was first reported nearly 50 years ago [22–24], their magnetic characterization has only recently begun [25]. We investigated the low temperature magnetism of  $Gd_2Pt_2O_7$  using magnetometry, heat capacity, and muon spin relaxation techniques. These probes reveal a transition to an antiferromagnetically ordered ground state in  $Gd_2Pt_2O_7$ . Remarkably, this transition occurs at  $T_N = 1.6$  K, a substantial enhancement from the other gadolinium-based pyrochlores, which are all found to order at 1 K or lower. We discuss the role of nonmagnetic platinum in the relief of frustration in this Heisenberg pyrochlore antiferromagnet.

#### **II. SYNTHESIS AND EXPERIMENTAL DETAILS**

The stability of the pyrochlore lattice  $A_2B_2O_7$  can be predicted by the ratio of the ionic radii of the A and Bsite cations. The pyrochlore structure is often stable for  $1.4 < R_A/R_B < 2.0$  [26]. Given that the ionic radii of Gd<sup>3+</sup> and Pt<sup>4+</sup> give a ratio of 1.7, a Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> pyrochlore would appear obtainable. Hindering the formation of the pyrochlore phase, however, is the low decomposition temperature of PtO<sub>2</sub>, only 450 °C, which makes reaction by conventional solid state synthesis impossible. High pressure can be used to suppress the decomposition of PtO<sub>2</sub> to sufficiently high temperature, allowing reaction into the pyrochlore phase. Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> pyrochlore was prepared from stoichiometric quantities of  $Gd_2O_3$  and  $PtO_2$  using a belt-type high pressure apparatus at 6 GPa and 1000 °C. Small amounts of platinum metal and unreacted Gd<sub>2</sub>O<sub>3</sub> were removed from the reacted product using a solution of boiling aqua regia. The  $Fd\bar{3}m$  pyrochlore structure was verified using powder x-ray diffraction with a copper  $K_{\alpha 1}$  target, giving a monochromatic beam of x-rays with wavelength  $\lambda = 1.5406$  Å. Rietveld refinement of the measured x-ray diffraction pattern was performed using FullProf [27].

The bulk magnetic properties of  $Gd_2Pt_2O_7$  were studied with magnetometry and heat capacity measurements. The dc susceptibility was measured using a Quantum Design SQUID magnetometer equipped with a <sup>3</sup>He insert, allowing measurements to be performed between 0.5 and 300 K. The heat capacity measurements were collected on warming in a Quantum Design Physical Properties Measurement System with a <sup>3</sup>He insert, giving a base temperature of 0.4 K.

Muon spin relaxation ( $\mu$ SR) measurements on Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> were performed at the TRIUMF laboratory in Vancouver, Canada. A 250 mg sample of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> was combined with 100 mg of silver powder, to improve thermal equilibration and mechanical stability, and then pressed into a 3/8 in. pellet, which was affixed to a silver cold finger using Apiezon N-grease. The  $\mu$ SR measurements were taken at the M15 surface muon beam line using the Pandora spectrometer and dilution refrigerator, which gives a base temperature of 25 mK and 0.39 ns time resolution. In a  $\mu$ SR experiment [28], 100% spin polarized muons are implanted in the sample, one at a time, and come to rest at Coulomb potential minima. These muons precess in the local magnetic environment and then decay, after an average lifetime of 2.2  $\mu$ s, emitting a positron preferentially in the muon spin direction. Histograms of the muon decay events are measured in forwards F(t)and backwards B(t) detectors. The muon decay asymmetry is then given by A(t) = [F(t) - B(t)]/[F(t) + B(t)], which is proportional to the muon spin polarization function. The resulting asymmetry spectra were fitted using the muSRfit software package [29].



FIG. 1. The x-ray powder diffraction pattern and Rietveld refinement for Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> measured at T = 300 K with a copper  $K_{\alpha 1}$ wavelength,  $\lambda = 1.5406$  Å. The measured data are given by the black points, the fitted curve by the red line, and the difference by the blue curve. The allowed nuclear Bragg peak positions are indicated by the yellow marks. The goodness of fit for the refinement into the Fd3mspace group is  $\chi^2 = 1.74$ . The inset is an enhanced view of the low intensity peaks between 42.5° and 72.5° in 2 $\theta$ , showing the absence of any impurity peaks.

#### **III. POWDER X-RAY DIFFRACTION**

The x-ray powder diffraction pattern and Rietveld refinement for Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> is shown in Fig. 1. All of the observed Bragg reflections can be indexed into the  $Fd\bar{3}m$  space group. The fitted profile describes the data well, giving a goodness of fit  $\chi^2$  of 1.74. The results of this fit are summarized in Table I. The only adjustable atomic coordinate within the pyrochlore structure is the oxygen x position, which refined to a value of 0.354(1). The lattice constant for Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> is a = 10.2626(2) Å, which agrees well with previous reports [22–24].

It is interesting to note that, due to the similar ionic radii of  $Ti^{4+}$  and  $Pt^{4+}$ , the lattice parameters of  $Gd_2Pt_2O_7$  (10.26 Å) and  $Gd_2Ti_2O_7$  (10.19 Å [30]) are quite similar, differing by only 0.7%. Thus, one might naively expect the magnetic properties of  $Gd_2Pt_2O_7$  to quite closely resemble those of

TABLE I. Structural parameters from the Rietveld refinement of the x-ray diffraction pattern for Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>. The only adjustable atomic coordinate is the first oxygen's *x* position. The lattice parameter refines to a value of a = 10.2626(2) Å and the goodness-of-fit  $\chi^2$  is 1.74.

Atom	Wyckoff	x	у	z	$B_{\rm iso}$ (Å <sup>2</sup> )
Gd	16 <i>d</i>	0.5	0.5	0.5	0.53(5)
Pt	16 <i>c</i>	0	0	0	0.12(4)
0	48f	0.354(1)	0.125	0.125	1.8(9)
$\mathbf{O}'$	$8\dot{b}$	0.375	0.375	0.375	2.1(3)

Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. However, there are several distinguishing structural properties of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> worth considering. First, Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> has a significantly larger oxygen *x* coordinate than its titanate analog, corresponding to a less distorted oxygen environment about the gadolinium site. Second, in other nonmagnetic *B*-site pyrochlores of the form Gd<sub>2</sub>B<sub>2</sub>O<sub>7</sub>, with B = Ti [30], Sn [31], Zr [32], Hf [8], and Pb [9], the *B*-site cation has a closed shell electron configuration. Platinum differs in this regard, with a [Xe]5d<sup>6</sup> valence shell, leading to a filled  $t_{2g}$  orbital and an empty  $e_g$  orbital. We will discuss this difference further, in the context of the magnetic properties of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>, below.

#### IV. MAGNETIC SUSCEPTIBILITY

The dc magnetic susceptibility of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> measured in a 0.1 T applied field is shown in Fig. 2. At high temperature, the susceptibility is well described in terms of the Curie-Weiss law. Fits between 50 and 300 K give an antiferromagnetic Curie-Weiss temperature  $\theta_{CW}$  of -9.4(1) K. The fitted effective paramagnetic moment  $\mu_{eff}$  is 7.830(5)  $\mu_B$ , close to the 7.94  $\mu_B$  free-ion moment. As Gd<sup>3+</sup> has seven *f* electrons (i.e., a half-filled *f* electron shell), the orbital angular momentum is quenched, L = 0, resulting in an isotropic spin-only total angular momentum of S = J = 7/2. Thus, crystal electric field effects are expected to be relatively unimportant, as it is the anisotropic orbital angular momentum that is primarily responsible for splitting the 2J + 1 = 8-fold ground state multiplet. Consequently, the Curie-Weiss temperature can



FIG. 2. The dc magnetic susceptibility of  $Gd_2Pt_2O_7$  measured in an H = 0.1 T applied field. The high temperature data, between 50 and 300 K, is well described by the Curie-Weiss law, which is given by the red curve. Upper inset: The low temperature dc susceptibility, between 0.5 and 5 K. An antiferromagnetic ordering transition is observed at 1.6 K, as signaled by the cusp and the bifurcation of the field-cooled and zero-field-cooled susceptibility. Lower inset: Fieldcooled measurements taken on warming and cooling show a thermal hysteresis of 30 mK below the maximum of the transition.

be realistically interpreted as a measure of the exchange interactions, as opposed to crystal field effects as in many other rare earth pyrochlores.

At 1.6 K, Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> undergoes an antiferromagnetic ordering transition, marked by a sharp cusp in the susceptibility (Fig. 2 upper inset). Taken with the Curie-Weiss constant, we can then determine the frustration index for Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>,  $f = \theta_{\rm CW}/T_N \approx 6$ , which corresponds to only moderate frustration [33]. Below  $T_N = 1.6$  K, there is a bifurcation of the zero-field-cooled and field-cooled susceptibilities, indicative of glassy dynamics or domain effects. A similar effect is observed in both Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, which has an antiferromagnetic Palmer-Chalker ground state [15,17], and in Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, which has an antiferromagnetic  $\psi_2$  ground state [34,35]. Conversely, there is a negligibly small field-cooled/zero-field-cooled splitting in Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, which has a highly unusual partially ordered state [19]. Lastly, within the field-cooled protocol, measurements were performed passing through the anomaly at  $T_N = 1.6$  K on warming and cooling (Fig. 2 lower inset). Below  $T_N = 1.6$  K, there is a thermal hysteresis of 30 mK, significantly larger than the instrumental resolution. This is clear evidence that this magnetic ordering transition is first order.

#### V. HEAT CAPACITY

The magnetic heat capacity of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>, shown in Fig. 3, also shows a magnetic ordering transition at  $T_N = 1.6$  K. This sharp transition appears first order, with its maximum at 58.6 J/mol Gd K. The calculated magnetic entropy, determined by integrating  $C_{\text{mag}}/T$  up to 15 K, gives the full *R* ln 8



FIG. 3. The low temperature magnetic heat capacity of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>, showing a first order phase transition at  $T_N = 1.6$  K. The lattice contribution, while very small below 15 K, was subtracted using the heat capacity of nonmagnetic isostructural Lu<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>. Inset: The low temperature heat capacity, between 0.4 and 2 K on a logarithmic scale. Below 0.75 K, the heat capacity is well described by an exponential decay, given by the red curve, indicating the presence of a gap in the spin excitation spectrum. The fitted value of the gap is  $\Delta =$ 0.245(1) meV.

entropy, as expected for J = 7/2. Notably there is only a single transition in Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>, unlike Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, where there are two distinct ordering transitions [16–18]. Instead, the specific heat of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> more strongly resembles that of Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, which also has a single sharp anomaly [17].

More can be learned about the ordered state in Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> by considering the magnetic heat capacity below  $T_N$ , a probe of the spin excitations arising from the ordered state. It is worth noting that gadolinium does have a nuclear contribution to its heat capacity. However, it only becomes substantial below 200 mK [36], which is outside the measured range in this study and thus we need not consider it. Below  $T_N$ , the heat capacity in Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> does not follow a  $C_{\rm mag} \propto T^3$ dependence, as would be expected for conventional ungapped antiferromagnetic spin waves. Nor does it follow a  $C_{\rm mag} \propto T^2$ dependence, which is the unusual temperature dependence observed in Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [37]. Instead, the lowest temperature magnetic heat capacity of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> can be well parametrized by  $C_{\text{mag}} \propto (1/T^2)e^{-\Delta/T}$ , which is the expected form for a gapped spin wave spectrum in a collinear antiferromagnet with anisotropy. The fitted value of the gap  $\Delta$  is 0.245(1) meV. This once again mirrors the situation in  $Gd_2Sn_2O_7$ , where the ordering temperature  $T_N = 1.0$  K and the magnitude of the spin wave gap  $\Delta = 0.121(1)$  meV is much smaller than in Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> [36].

#### VI. MUON SPIN RELAXATION

The muon decay asymmetry in  $Gd_2Pt_2O_7$  in a very small 10 G longitudinal field is shown above and below  $T_N = 1.6$  K in Fig. 4. The purpose of the 10 G field was to decouple any



FIG. 4. The muon decay asymmetry  $Gd_2Pt_2O_7$  out to 6  $\mu$ s at 25 mK and 2 K. Below  $T_N = 1.6$  K, the relaxation rate steeply increases such that the early time asymmetry falls outside of our time window at 25 mK. The fits to the data are given by an exponential decay. Inset: The early time asymmetry, below 0.3  $\mu$ s, where oscillations can be resolved at 25 mK. The fit at 25 mK is the sum of two cosine functions with frequencies of 0.21(1) and 0.49(2) T.

relaxation due to nuclear dipole moments from the sample or silver sample holder. Below  $T_N = 1.6$  K, the initial asymmetry is dramatically reduced. This indicates that very fast relaxation occurs within the first 10 ns, which is the deadtime that follows the initial muon implantation and is thus outside of our time window. Fast relaxation like this is commonly observed in materials with very large magnetic moments, such as other gadolinium-based systems [38,39]. Thus, passing through the magnetic ordering transition, the relaxation rate of the front end rapidly increases.

Examining more closely the early time, the first 0.3  $\mu$ s, shown in the inset of Fig. 4, we observe an oscillatory component to the asymmetry below  $T_N$ . An oscillating muon decay asymmetry is a hallmark of static magnetic order. The muon decay asymmetry in Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> at 25 mK fits to an exponential relaxation and two damped cosines:

$$A(t) = A_1 e^{-\lambda_1 t} \cos(\gamma_\mu B_1 t + \phi) + A_2 e^{-\lambda_2 t} \cos(\gamma_\mu B_2 t + \phi) + A_3 e^{-\lambda_3 t}.$$
 (1)

The fits at 25 mK indicate that the internal field strength at these two muon stopping sites are  $\mu_0 H_1 = 0.21(1)$  T and  $\mu_0 H_2 =$ 0.49(2) T. Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> share phenomenologically similar  $\mu$ SR spectra in their ordered states, both with two oscillation frequencies of similar magnitude, suggesting they may adopt the same magnetic structure [39]. The application of a longitudinal magnetic field at 25 mK partially decouples the fast relaxing asymmetry at H = 0.1 T, and fully decouples it at H = 1 T, as would be expected for conventional static order.

The long time asymmetry of Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> is well described by a single exponential relaxation function (Fig. 4). The relaxation rate  $\lambda$  as a function of temperature is peaked at  $T_N = 1.6$  K [Figure 5(a)] but does not diverge. A divergent relaxation rate at  $T_N$  is expected for a second order transition, and the absence of such a divergence is then a further demonstration of the first order nature of this magnetic phase transition [40]. Below  $T_N$ , there is a residual relaxation rate of approximately 0.3  $\mu s^{-1}$  that persists to the lowest measured temperature. In a conventional magnetic ordering transition, the relaxation rate well-below  $T_N$  should approach zero. Experimental evidence, however, would suggest that a nonzero relaxation rate at the lowest measured temperatures is a characteristic feature of magnetically frustrated materials. This effect is attributed to persistent spin dynamics. In particular, persistent spin dynamics have been observed in other frustrated gadoliniumbased systems [38,41], including Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [39], as well as other pyrochlores with long-range magnetic order, such as Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [42] and Tb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [43,44]. The enigma of persistent spin dynamics has been has highlighted in Gd<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, where the gapped excitation spectrum arising from a well-ordered magnetic state is at odds with a nonzero longitudinal relaxation that persists to the lowest measured temperature, and cannot be accounted for theoretically [45]. One recent proposal associates persistent spin dynamics with excitations within spin loop substructures [46]. While an understanding of persistent spin dynamics is far from complete, they are, regardless, ubiquitous in geometrically frustrated systems. The persistent spin dynamics in Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> are not fully decoupled



FIG. 5. Temperature dependence of two fit parameters, (a) the relaxation rate  $\lambda$  and (b) the fraction of the initial asymmetry, for the fits to the muon decay asymmetry in Gd<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>. The relaxation rate is peaked at  $T_N = 1.6$  K, while the initial asymmetry falls off sharply at  $T_N = 1.6$  K, which is marked by the dashed red line. The initial asymmetry in the magnetically ordered state is 1/3 of the total asymmetry, as marked by the dashed blue line, where the remaining 2/3 asymmetry is relaxing so fast that it falls outside of our time window.

by even an H = 1 T field, which is far larger than the magnitudes of the internal fields.

Finally, we can consider the amount of asymmetry that rapidly relaxes outside of our time window, or "lost asymmetry," as a function of temperature. In Fig. 5(b) we plot the initial asymmetry, expressed as a fraction of the full asymmetry. The full asymmetry is defined by the value of the initial asymmetry in the paramagnetic regime at 2 K and above, which is  $a_0 = 0.072(1)$ . This initial asymmetry is small as a result of the small sample size, leading a significant fraction of the muons to stop in the silver cold finger. Below  $T_N = 1.6$  K, the initial asymmetry falls off precipitously. At the lowest temperatures, between 1 K and 25 mK, only 1/3 of the initial asymmetry is detected, where the remaining 2/3 is part of the rapidly relaxing front end, and falls outside our time window. This division of the muon decay asymmetry into 1/3 and 2/3components is the result of the isotropic environment produced in a powder sample, where directional averaging gives a 1/3contribution longitudinal to the initial muon spin direction and a 2/3 transverse contribution. The 1/3 component gives the long time relaxation. The 2/3 contribution accounts for both the oscillating component and the rapidly relaxing front end. The front end relaxes within the first 10 ns, indicating a relaxation rate in excess of 100  $\mu$ s<sup>-1</sup>.

#### VII. DISCUSSION AND CONCLUSIONS

In many regards,  $Gd_2Pt_2O_7$  strongly resembles its sister compound  $Gd_2Sn_2O_7$ : the clear antiferromagnetic transition in its susceptibility, the strongly first order heat capacity transition, and gapped spin wave spectrum. In fact, these



FIG. 6. Schematic views of the local environments of (a) gadolinium and (b) platinum in  $Gd_2Pt_2O_7$ , where the gadolinium cations are given in blue, the platinum cations in yellow, and the oxygen anions in red. (a) Gadolinium sits in an eightfold coordinate oxygen environment with six nearest neighbor platinum cations. (b) Looking along the [111] crystallographic direction, the Gd–O–Pt–O–Gd exchange pathways can be clearly observed.

signatures all suggest that  $Gd_2Pt_2O_7$  is a good candidate for the Palmer-Chalker ground state [13,15]. However, the determination of the magnetic structure in  $Gd_2Pt_2O_7$  will likely have to await a neutron diffraction measurement, which would require a sample prepared with isotopically enriched gadolinium.

There are, however, several distinctive properties in  $Gd_2Pt_2O_7$  that bear consideration. In particular, the Néel ordering transition  $T_N = 1.6$  K is substantially increased over the values of 1 K or lower, as seen in other Gd-pyrochlores. As the lattice parameters of  $Gd_2B_2O_7$  (B = Ti, Pt, Sn) are all quite similar, the difference in the dipolar interaction is likely negligible. Instead, we attribute this enhancement to the nonmagnetic platinum which occupies the *B* site. The empty platinum 5*d*  $e_g$  orbitals open additional, and apparently important, superexchange pathways. We propose that this

superexchange pathway would likely involve the gadolinium 5*d* orbitals, as the 4*f* orbitals are too spatially localized. The superexchange pathway would then proceed from Gd–O–Pt–O–Gd. Of the eight oxygens surrounding each gadolinium, all except for the axial oxygens are shared with nearest neighbor platinum cations. The six nearest neighbor platinums form a hexagon surrounding gadolinium in the plane perpendicular to the local (111) axis, as can be seen in Fig. 6(a). Referring to Fig. 6(b), it can be seen that while Gd1 shares an oxygen with Gd2 and Gd6, it does not with Gd3, Gd4, or Gd5. Thus, our proposed superexchange pathway Gd–O–Pt–O–Gd would then be relevant for each of these three Gd sites, which is repeated for each of the six platinum nearest neighbors.

While this proposal remains speculative, corroborative evidence comes from the other Pt pyrochlores  $Yb_2Pt_2O_7$  and  $Er_2Pt_2O_7$ , where the ordering temperatures are respectively higher and lower than what would be expected from the lattice parameter trend [25]. The exact effect of this additional superexchange pathway would be dependent on the anisotropic exchange parameters, which vary a great deal from system to system. In  $Yb_2Pt_2O_7$ , the net effect is to enhance ferromagnetic order, while in  $Er_2Pt_2O_7$  the net effect is to suppress antiferromagnetic order [25]. In the present case of  $Gd_2Pt_2O_7$ , the effect is to *enhance* antiferromagnetic order. Thus, the detailed manifestation of this superexchange pathway in the platinum pyrochlores remains an open question, which could possibly be addressed using density functional theory.

In summary, we have found that replacement of the *B* site in the gadolinium pyrochlores with platinum results in an effective reduction in the geometric magnetic frustration.  $Gd_2Pt_2O_7$  undergoes a strongly first order antiferromagnetic

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transition at  $T_N = 1.6$  K. While the energy scales of rare earth magnetism are small as compared to transition metal systems, it is worth highlighting that this is a substantial 160% enhancement from other gadolinium pyrochlores. This reduction in frustration can be understood in terms of the superexchange pathway via the empty 5*d*  $e_g$  orbitals in nonmagnetic platinum. This study therefore offers a fresh insight into the phenomena of geometric magnetic frustration by exploring an alternative mechanism through which the frustration can be tuned.

*Note added.* Recent work has shown that the exchange interactions in  $Gd_2Sn_2O_7$  are highly anisotropic and sensitive to further neighbor correlations, and hence, likely strongly perturbed by platinum substitution [47].

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## 4.2 Preface to Publication VI: Experimental insights into ground state selection of quantum XY pyrochlores

The XY pyrochlores are known to live in a rich phase space [84]. This was previously discussed in **Chapter 2** of this thesis, where we reported on the ytterbium pyrochlore family and in particular, Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. We demonstrated that the application of positive chemical pressure through germanium substitution traverses the ytterbium pyrochlores from the ferromagnetic  $\Gamma_9$ state to the antiferromagnetic  $\Gamma_5$  state [1,2]. In this paper, which is the final piece of original research in this thesis, we report on the erbium pyrochlore family and  $\text{Er}_2\text{Pt}_2\text{O}_7$ . As has already been discussed in the context of  $\text{Gd}_2\text{Pt}_2\text{O}_7$ , chemical pressure is not the primary effect of platinum substitution. Instead the larger effect appears to be a reconfiguration of the exchange pathways. The partially filled 5*d* shell of platinum allows hybridization with oxygen 2*p* orbitals, enhancing further neighbour exchange. However, whether this enhanced exchange will enhance or suppress order is dependent on the precise values of the anisotropic exchange parameters and is thus, strongly material dependent. Therefore, the effect of platinum substitution on the ground state magnetism for a given rare earth is somewhat unpredictable.

The work contained in this manuscript is a detailed neutron scattering study on  $\text{Er}_2\text{Pt}_2\text{O}_7$ . The neutron absorption cross-section of erbium, while non-negligible, is reduced by a factor of 300 from gadolinium, making neutron scattering measurements possible. Previous bulk characterization had shown that  $\text{Er}_2\text{Pt}_2\text{O}_7$  orders antiferromagnetically at  $T_N = 0.3$  K [142]. Thus, platinum substitution in the erbium pyrochlores leads to a striking suppression of  $T_N$ , in contrast to the situation in the gadolinium pyrochlores. The Néel temperature of  $\text{Er}_2\text{Pt}_2\text{O}_7$  is a 75% reduction from that of  $\text{Er}_2\text{Ti}_2\text{O}_7$ , which we reiterate is a near lattice match for  $\text{Er}_2\text{Pt}_2\text{O}_7$ . We performed powder neutron diffraction measurements on  $\text{Er}_2\text{Pt}_2\text{O}_7$  above and below its Néel transition and used symmetry analysis to determine that its ordered state is the  $\Gamma_7$  Palmer-Chalker state. Thus, not only is magnetic order suppressed in by platinum substitution, but also a change of ground state is induced from  $\text{Er}_2\text{Ti}_2\text{O}_7$ 's  $\Gamma_5$  ground state. In fact,  $\text{Er}_2\text{Pt}_2\text{O}_7$  is the first XY pyrochlore to display a  $\Gamma_7$  Palmer-Chalker ground state.

We also conducted an inelastic neutron scattering experiment on our powder sample of  $\text{Er}_2\text{Pt}_2\text{O}_7$ . This measurement was motivated by the form of  $\text{Er}_2\text{Pt}_2\text{O}_7$ 's specific heat, which contains a sharp anomaly at  $T_N = 300$  mK and a higher temperature broad anomaly centered at  $T^* = 1.5$  K. This form is reminiscent of the ytterbium pyrochlores, which as we detailed in **Chapter 2** have an unconventional form to their low temperature spin excitations. Given

these similarities, we sought to determine whether unconventional spin excitations would also be present in  $\text{Er}_2\text{Pt}_2\text{O}_7$ . Our inelastic neutron scattering measurements reveal that  $T^* = 1.5$  K marks the temperature scale on which strong quasi-elastic short range spin correlations form. Passing below  $T_N = 300$  mK, this spectral intensity segregates into resolution limited Bragg peaks and a sharp flat band of excitations. These spin excitations appear to be gapped from the elastic line by approximately 0.1 meV. Although it is challenging to assess the conventionality of spin excitations in a powder sample, it is still clear that the spin excitations of  $\text{Er}_2\text{Pt}_2\text{O}_7$  are more conventional than those observed in the ytterbium pyrochlores. Linear spin wave calculations provide a good description of this flat band but also predict a dispersive higher energy mode that is not observed in the experimental data. One possibility is that the quasiparticles associated with this higher energy mode decay due to the enhanced quantum fluctuations originating from phase competition. A more pronounced version of this phenomenology has recently been discussed in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [87] and may be applicable to all XY pyrochlores with intense phase competition.

It has recently been reported that, in addition to  $\text{Er}_2\text{Pt}_2\text{O}_7$ , another erbium pyrochlore,  $\text{Er}_2\text{Sn}_2\text{O}_7$ , orders into the  $\Gamma_7$  Palmer-Chalker state below 100 mK [143]. A fourth erbium relative,  $\text{Er}_2\text{Ge}_2\text{O}_7$ , is known to possess a  $\Gamma_5$  ground state [81], as is also observed in  $\text{Er}_2\text{Ti}_2\text{O}_7$  [46]. Thus, it is clear that the erbium pyrochlores reside at the boundary between  $\Gamma_5$  and  $\Gamma_7$ , which are both antiferromagnetic XY states. This is fully consistent with the theoretically predicted phase diagram for XY pyrochlores [84]. We interpret the suppression of  $T_N$  and the multiple heat capacity anomalies in  $\text{Er}_2\text{Pt}_2\text{O}_7$  as signatures of phase competition. This scenario would imply that the anisotropic exchange parameters of  $\text{Er}_2\text{Pt}_2\text{O}_7$  naturally place it close to the  $\Gamma_5/\Gamma_7$  phase boundary. The intense short-range correlations that develop at  $T^* = 1.5$  K are U(1) fluctuations as the system is unable to select between these ordered states until a much lower temperature when it selects  $\Gamma_7$ . The fitted exchange parameters for  $\text{Er}_2\text{Pt}_2\text{O}_7$  from linear spin wave calculations are consistent with proximity to the  $\Gamma_5/\Gamma_7$  phase boundary.

#### Author Contributions:

- Experimental Concept: A.M. Hallas, C.R. Wiebe, G.M. Luke, B.D. Gaulin
- Sample Preparation: A.M. Hallas, M. Tachibana
- Neutron Experiments: A.M. Hallas, J. Gaudet, N.P. Butch, G. Xu, B.D. Gaulin
- Data Analysis: A.M. Hallas, J. Gaudet, B.D. Gaulin
- Spin Wave Calculations: J. Gaudet
- Manuscript: A.M. Hallas, J. Gaudet, B.D. Gaulin

#### Phase Competition in the Palmer-Chalker XY Pyrochlore Er<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>

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We report neutron scattering measurements on  $\text{Er}_2\text{Pt}_2\text{O}_7$ , a new addition to the XY family of frustrated pyrochlore magnets. Symmetry analysis of our elastic scattering data shows that  $\text{Er}_2\text{Pt}_2\text{O}_7$ is the first XY pyrochlore to order into the k = 0,  $\Gamma_7$  magnetic structure (the Palmer-Chalker state), at  $T_N = 0.38$  K. This contrasts with its sister XY pyrochlore antiferromagnets  $\text{Er}_2\text{Ti}_2\text{O}_7$  and  $\text{Er}_2\text{Ge}_2\text{O}_7$ , both of which order into  $\Gamma_5$  magnetic structures at much higher temperatures,  $T_N = 1.2$  K and 1.4 K, respectively. In this temperature range, the magnetic heat capacity of  $\text{Er}_2\text{Pt}_2\text{O}_7$  contains a broad anomaly centered at  $T^* = 1.5$  K. Our inelastic neutron scattering measurements reveal that this broad heat capacity anomaly sets the temperature scale for strong short-range spin fluctuations. Below  $T_N = 0.38$  K,  $\text{Er}_2\text{Pt}_2\text{O}_7$  displays a gapped spin wave spectrum with an intense, flat band of excitations at lower energy and a weak, diffusive band of excitations at higher energy. The flat band is well-described by classical spin wave calculations, but these calculations also predict sharp dispersive branches at higher energy, a striking discrepancy with the experimental data. This, in concert with the strong suppression of  $T_N$ , is attributable to enhanced quantum fluctuations due to phase competition between the  $\Gamma_7$  and  $\Gamma_5$  states that border each other within a classically predicted phase diagram.

The low temperature magnetism of the rare-earth pyrochlore oxides,  $R_2B_2O_7$ , has become synonymous with complexity and exotic ground states. Both of these are natural consequences of magnetism on the pyrochlore lattice, which is comprised of two site-ordered networks of corner-sharing tetrahedra. This is the canonical threedimensional crystalline architecture for geometric magnetic frustration, in which competing interactions can preclude or hinder the formation of a classically ordered state. The diversity in the phenomenology of the rare-earth pyrochlores is attributable to the different anisotropies and interactions exhibited by the rare-earth ions that can occupy its magnetic sublattice, which conspire to produce a veritable zoo of magnetic behaviors [1].

A particularly interesting sub-group of the rare-earth pyrochlores are those that exhibit XY spin anisotropy [2], which is obtained when the rare-earth site is occupied by either erbium (Er) or ytterbium (Yb). This XY label is garnered on the basis of their crystal electric field phenomenology, where in both cases, the ground state is an isolated doublet protected by Kramers' theorem, allowing an effective S = 1/2 description [3–5]. The anisotropic exchange Hamiltonian, with a form determined by the symmetry of the crystal lattice, provides an appropriate starting point for understanding the ground states of many XY pyrochlores [6–8]. Within the nearest neighbor version of this model, certain sets of exchange parameters can give rise to exotic states such as quantum spin ice [6, 9] or various spin liquids [10, 11], while other sets of exchange parameters are predicted to stabilize classically

ordered states [8].

The phase diagram that encompasses the region of parameter space believed to be relevant to the XY pyrochlores contains four distinct k = 0 ordered states [8, 15]:  $\psi_2$  non-coplanar antiferromagnet,  $\psi_3$  coplanar antiferromagnet,  $\Gamma_7$  antiferromagnet (the Palmer-Chalker state [16]), and  $\Gamma_9$  splayed ferromagnet. Of these states, all but  $\Gamma_7$  have been experimentally observed in the XY pyrochlores. This XY family is made up of  $Yb_2B_2O_7$ and  $Er_2B_2O_7$  with B = Ge, Ti, and Sn, where: (i) The order-by-disorder candidate  $Er_2Ti_2O_7$  orders into  $\psi_2$  [17] (ii) 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> have as-of-vet unidentified ordered states within  $\Gamma_5$  ( $\psi_2$  or  $\psi_3$ ) [12, 18] and (iii) Both Yb<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> [19, 20] and some samples of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [21-25] order into the  $\Gamma_9$  splayed ferromagnetic state. This ensemble of magnetic ground states supports the picture of a rich phase space.

In this Letter, we present a comprehensive neutron scattering study of  $\text{Er}_2\text{Pt}_2\text{O}_7$ , a recent addition to the XY family of pyrochlores [5, 14]. Through magnetic symmetry analysis, we find that  $\text{Er}_2\text{Pt}_2\text{O}_7$  orders into the  $\Gamma_7$  Palmer-Chalker state, the first XY pyrochlore shown to possess this ground state. The Néel ordering temperature,  $T_N = 0.38$  K, is a 75% reduction from those of its closest sister pyrochlore antiferromagnets:  $\text{Er}_2\text{Ti}_2\text{O}_7$  and  $\text{Er}_2\text{Ge}_2\text{O}_7$ . Given that the lattice parameter of  $\text{Er}_2\text{Pt}_2\text{O}_7$  differs by less then 0.5% from its titanate analog, it is surprising that the transition temperature is so substantially reduced. This dramatic reduction in  $T_N$  occurs despite minimal structural modifications and a larger Curie-Weiss





FIG. 1. Low temperature heat capacity of the three sister XY antiferromagnets:  $\text{Er}_2\text{Ge}_2\text{O}_7$  [12],  $\text{Er}_2\text{Ti}_2\text{O}_7$  [13], and  $\text{Er}_2\text{Pt}_2\text{O}_7$ , filled in circles from [14] and open circles from our study. The latter two samples magnetically order with  $T_N = 1.4$  K and 1.2 K, respectively. In this temperature range,  $\text{Er}_2\text{Pt}_2\text{O}_7$  exhibits a broad heat capacity anomaly centered at  $T^* = 1.5$  K with a strongly suppressed  $T_N$ . The vertical dashed lines indicate the temperatures that correspond with the inelastic scattering spectra that are presented in Figure 3.

temperature, as given in Figure 1. Our inelastic neutron scattering measurements reveal that strong quasi-elastic spin fluctuations develop in  $Er_2Pt_2O_7$  at a temperature well-above  $T_N$ , around  $T^* = 1.5$  K. This is coincident with the  $T_N$ 's of both  $\text{Er}_2\text{Ti}_2\text{O}_7$  and  $\text{Er}_2\text{Ge}_2\text{O}_7$ , and a broad peak in its own magnetic heat capacity, as shown in Figure 1. Below  $T_N = 0.38$  K,  $Er_2Pt_2O_7$ 's spin wave spectrum contains a narrow band of low energy spin excitations that are gapped by  $0.18 \pm 0.02$  meV from the elastic position and a diffusive band at higher energy. Spin wave calculations show that the spin excitation spectrum of  $Er_2Pt_2O_7$  should contain dispersive higher energy branches that are strikingly absent from the experimental data. We conclude that the origin of the suppressed  $T_N$ and the unusual spin dynamics is strong phase competition between the  $\Gamma_7$  and  $\Gamma_5$  states.

 $\rm Er_2Pt_2O_7$  can be synthesized in the cubic  $Fd\bar{3}m$  pyrochlore structure, in powder form only, using highpressure techniques. We investigated the low temperature magnetic state of our 1.2 gram sample of  $\rm Er_2Pt_2O_7$  using both elastic and inelastic neutron scattering techniques. Elastic measurements were performed on the cold neutron triple-axis spectrometer SPINS and time-of-flight inelastic measurements were performed on the Disc Chopper Spectrometer [26], both located at the National Institute for Standards and Technology's Center for Neutron Research. Further details of the synthesis and experimental methods can be found in the Supplemental Material.

The magnetically ordered state of  $Er_2Pt_2O_7$  can be



FIG. 2. Rietveld refinement of Er<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> at 0.06 K, where the magnetic scattering has been isolated by subtracting the 8 K data set. The data (red points) is refined against the  $\Gamma_7$  magnetic structure, the resulting fit is given by the black curve and the residual is given by the blue curve. The inset shows the unsubtracted elastic scattering at 0.06 K and 8 K. (b) The spin configuration of Er<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> in its Palmer-Chalker ( $\Gamma_7$ ) ground state. (c) The intensity of the (111) and (002) magnetic Bragg peaks as a function of temperature normalized by the average high and low temperature values. A power law fit, given by the yellow curve, gives a critical exponent of  $\beta = 0.35 \pm 0.03$ .

characterized by the Bragg scattering, which we isolate by integrating over the elastic channel ( $\pm 0.05 \text{ meV}$ ) in the time-of-flight data. As shown in the inset to Figure 2(a), additional Bragg scattering forms upon cooling from 8 K to 0.06 K due to long range magnetic ordering. These magnetic Bragg peaks are resolution limited, corresponding to a minimum correlation length of  $132 \pm 9$  Å. A new Bragg reflection is observed to form on the (002) position, as well as enhanced intensity on the (111), (220), and (113)positions. These magnetic reflections can all be indexed with the propagation vector k = 0. The possible k = 0magnetic structures for  $Er^{3+}$  at the 16*d* crystallographic position in the  $Fd\bar{3}m$  space group are described by four irreducible representations:  $\Gamma_{\rm mag} = \Gamma_3^1 + \Gamma_5^2 + \Gamma_7^3 + \Gamma_9^6$ , where the superscript denotes the number of basis vectors for the given representation, which are labeled  $\psi_1, \psi_2, \dots, \psi_{12}$  [27]. Both  $\Gamma_3$  and  $\Gamma_5$  can be immediately ruled out, as the (002) magnetic reflection is symmetry forbidden in both



FIG. 3. The inelastic neutron scattering spectra for  $\text{Er}_2\text{Pt}_2\text{O}_7$  at (a) 8 K, (b) 1.5 K, (c) 0.5 K, (d) 0.3 K, and (e) 0.06 K. Each data set has had an empty sample can background subtracted. At  $T^* = 1.5$  K, the center of the broad specific heat anomaly, short range correlations are building up at 1.1 Å<sup>-1</sup>; these correlations grow more intense down to 0.5 K. Below  $T_N = 0.38$  K, the spectral weight segregates into magnetic Bragg peaks and a gapped spin wave excitation.

of these representations, while (002) is very intense in our measured pattern. Furthermore, bulk characterization indicates the ordered state of  $\rm Er_2Pt_2O_7$  is antiferromagnetic [14], and  $\Gamma_9$  is ferromagnetic. Thus, on qualitative grounds alone, one could deduce that  $\rm Er_2Pt_2O_7$  orders into the  $\Gamma_7$  irreducible representation.

To definitively determine the ordered state of  $Er_2Pt_2O_7$ , we have performed a Rietveld refinement, the result of which is shown in Figure 2(a). The magnetic Bragg scattering was isolated by subtracting a high temperature, 8 K, data set from the 0.06 K data set. All structural and instrumental parameters were fixed according to a refinement of the 8 K data set. Thus, the only parameter allowed to vary for the magnetic refinement at 0.06 K is the size of the ordered moment. Magnetic refinements were attempted with each of the k = 0 representations, and the best agreement,  $\chi^2 = 2.22$ , was obtained with  $\Gamma_7$ , validating our earlier qualitative assessment. Fixing the scale of the magnetic scattering according to the structural component allows us to determine the size of the ordered moment, which is  $3.4(2) \ \mu_{\rm B}$  at 0.06 K. This ordered moment is approximately 90% of the total moment that was recently determined for the crystal field ground state of  $\text{Er}_2\text{Pt}_2\text{O}_7$ ,  $\mu_{\text{CEF}} = 3.9 \ \mu_{\text{B}}$  [5]. The normalized intensity of the (111) and (002) Bragg peaks as a function of temperature are plotted in Figure 2(c). Fitting a narrow temperature range below  $T_N = 0.38$  K to a power law gives the critical exponent  $\beta = 0.35 \pm 0.03$ , consistent with conventional 3D XY universality [28].

In the  $\Gamma_7$  ordered state of  $\text{Er}_2\text{Pt}_2\text{O}_7$ , all spins lie in the plane perpendicular to the local  $\langle 111 \rangle$  axes, that connect the vertices of a tetrahedron to its center. The three basis vectors in the  $\Gamma_7$  manifold are denoted as  $\psi_4$ ,  $\psi_5$ , and  $\psi_6$ . These three basis vectors are connected by cubic symmetry transformations, meaning that they are necessarily degenerate and that an equiprobable distribution of all domains will be present in zero magnetic field. Thus, we can arbitrarily proceed by visualizing  $\psi_4$ , which is pictured in Figure 2(b). On each tetrahedron, there are two pairs of anti-parallel oriented spins, and all spins are aligned parallel to one of the tetrahedron's edges.

In Figure 3 we present the inelastic neutron scattering spectra for  $\text{Er}_2\text{Pt}_2\text{O}_7$  at 8 K, 1.5 K, 0.5 K, 0.3 K and 0.06 K. These temperatures span the range of both specific heat anomalies displayed by  $\text{Er}_2\text{Pt}_2\text{O}_7$  and are indicated by the dashed vertical lines in Figure 1. Each of these data sets has had an empty sample can background subtracted from it. We can associate the broad specific heat anomaly at  $T^* = 1.5$  K to short range quasi-elastic spin fluctuations, giving rise to a diffuse feature centered at 1.1 Å<sup>-1</sup>. These short range correlations grow more intense upon cooling to 0.5 K. The majority of the diffuse scattering at these temperatures, above  $T_N$ , is elastic within our 0.09 meV resolution.

As Er<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> is cooled through its Néel ordering transition at  $T_N = 0.38$  K the diffuse scattering segregates into sharp magnetic Bragg reflections, a narrow inelastic mode centered near 0.2 meV, and a higher energy broad distribution of spin excitations. The upper broad band of excitations is centered at 0.6 meV as can be seen by integrating over our full Q range, as presented in Figure 5(a). However, this upper band of scattering lacks apparent structure as seen in Figure 3(e). The lower band of spin excitations is gapped from the nlastic line by  $0.18 \pm 0.02$  meV. This gap is essentially constant at all wave-vectors, due to the fact that the band itself is so narrow in energy, with a bandwidth of only 0.1 meV. A dispersionless band of excitations, such as this, has been observed in a number of highly frustrated magnetic systems: for example, the "weathervane mode" predicted for two-dimensional Kagome systems [29], and observed in  $KFe_3(OH)_6(SO_4)_2$  [30], as well as the singlet-triplet excitations of the frustrated Shastry-Sutherland system,  $SrCu_2(BO_3)_2$  [31].

We have performed classical spin wave calculations to further investigate the spin excitations of  $\text{Er}_2\text{Pt}_2\text{O}_7$ . The



FIG. 4. Comparison of the (a) measured spin wave spectrum of  $\text{Er}_2\text{Pt}_2\text{O}_7$  at 60 mK with the (b) calculated spin wave spectrum with  $J_1 = 0.10 \pm 0.05$ ,  $J_2 = 0.20 \pm 0.05$ ,  $J_3 = -0.10 \pm 0.03$ , and  $J_4 = 0$  meV. The calculation captures the lower flat band, indicated by the white dashed line, but predicts a dispersive higher energy mode absent in the measurement.

powder averaged spin wave spectra were calculated using the anisotropic exchange Hamiltonian [6, 8] and further details can be found in the Supplemental Material. We used the experimentally derived exchange parameters for  $\mathrm{Er}_{2}\mathrm{Ti}_{2}\mathrm{O}_{7}$  as an approximate starting point:  $J_{1}=0.10$ ,  $J_2 = -0.06, J_3 = -0.10, \text{ and } J_4 = 0 \text{ meV}$  [7]. From these values, we carried out a least squares refinement and the best agreement with our experimental spectra for  $Er_2Pt_2O_7$  occurs with  $J_1 = 0.10 \pm 0.05$ ,  $J_2 = 0.20 \pm 0.05$ ,  $J_3 = -0.10 \pm 0.03$ , and  $J_4 = 0$  meV. The calculated spin wave spectrum for this set of parameters is presented in Figure 4, where it is presented side-by-side with the lowest temperature experimental data set. This calculated spectra provides a very good description of the low energy flat band, as can be further appreciated by the integrations presented in Figures 5(b) and (c). However, there is a striking discrepancy at higher energies: the computed spin excitation spectrum contains an intense, dispersive mode that is not observed in the experimental data (Fig. 4(a)) and 5(c)). It is important to emphasize that this intense, dispersive upper band is present in the computed spectra for the entire range of exchange parameters considered in our study. As our exchange parameters for  $Er_2Pt_2O_7$ place it relatively close to the phase boundary between  $\Gamma_5$  and  $\Gamma_7$ , it is possible that enhanced quantum fluctuations due to phase competition are responsible for the breakdown of the quasiparticles associated with this spin wave branch. Similar phenomenology has recently been investigated in  $Yb_2Ti_2O_7$  [32]. Fruitful comparisons can also be made with  $Gd_2Sn_2O_7$ , which also possesses a Palmer-Chalker ground state below  $T_N = 1$  K [27] but with Heisenberg spins rather than XY anisotropy. In addition to a sharp flat band at low energy, the spin wave spectrum of  $Gd_2Sn_2O_7$  contains at least two additional sharp branches at higher energies [33]. Thus the breakdown of this upper spin wave branch is not a generic attribute of Palmer-Chalker magnets, evidencing that



FIG. 5. Integrated scattered intensity of  $\text{Er}_2\text{Pt}_2\text{O}_7$  as a function of energy transfer over the the full measured Q range, from 0.2 Å<sup>-1</sup> to 2.2 Å<sup>-1</sup>. The gray shaded region indicates the elastic resolution. Below  $T_N$ , at 0.06 K, the spin excitations are gapped by  $0.18 \pm 0.02$  meV and a weak second band is observed at 0.6 meV. (b) The Q dependence of the lower flat band at T = 0.06 K, showing good agreement with the spin wave calculation given by the solid line. (c) Integrations over several representative Q intervals. The spin wave calculation provides a good fit to the flat lower band but predicts a second intense branch not observed in the experimental data.

Er<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> experiences stronger quantum effects.

The ensemble of Er<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>'s ground state magnetic properties are remarkable, given that it is structurally so similar to Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. Indeed the lattice parameters of these two sister compounds differ by less than 0.5%. far smaller than the 2% difference with the third sister, Er<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>, whose magnetic properties are largely unchanged from Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [12, 34]. Comparing Er<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, we find its Néel ordering temperature is reduced by a factor of three, from 1.2 K to 0.38 K, and the ordered state itself is altered from  $\Gamma_5$  to  $\Gamma_7$ . Moreover, the spin wave gap of  $0.18 \pm 0.02$  meV is more than triple the  $0.053 \pm 0.006$  meV order-by-disorder spin wave gap observed in  $Er_2Ti_2O_7$  [35]. Despite the lower band being very narrow, the full bandwidth of the inelastic scattering in Er<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>, 0.6 meV, is still considerably larger than that of Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, 0.4 meV [36]. Such observations eliminate simple energetic arguments for Er<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub>'s anomalously low  $T_N$ . Two considerations are important to understand these surprising differences: (i) The partially occupied platinum 5d orbital can facilitate superexchange pathways that are inaccessible in closed shell titanium [14, 37], and (ii) The XY pyrochlores live in a rich phase space where modest changes in anisotropic exchange parameters can have a large effect on ground state selection [8]. Indeed, this paradigm predicts that proximity to competing classical phases should manifest as a suppressed

ordering temperature [8]. Thus, our observations strongly implicate that  $\rm Er_2Pt_2O_7$  resides in a region of exchange parameter space where it is subject to strong  $\Gamma_5$ - $\Gamma_7$  phase competition.

Related phenomenology has previously been observed in the ytterbium family of pyrochlores, including both broad and sharp specific heat anomalies, where the spin dynamics develop well-above  $T_N$  or  $T_C$  [23, 38–41]. However, for the ytterbium pyrochlores, this competition is between the ferromagnetic  $\Gamma_9$  state and the antiferromagnetic  $\Gamma_5$  state [8, 40, 42]. In the case of  $\text{Er}_2\text{Pt}_2\text{O}_7$ , it is two antiferromagnetic states,  $\Gamma_5$  and  $\Gamma_7$ , that compete. Thus, we interpret the short-range order at  $T^*$  as originating in the spins fluctuating between these two XY states, without breaking the continuous U(1) degeneracy. Then at a lower temperature,  $T_N$ , a single manifold is uniquely selected. Conversely, no such broad anomaly or unusual spin dynamics are observed in  $Er_2Ti_2O_7$  [36], which orders at a much higher temperature and for which phase competition is certainly less important [8].

We have shown that  $\text{Er}_2\text{Pt}_2\text{O}_7$  is the first realization of a Palmer-Chalker ( $\Gamma_7$ ) ground state amongst the XY pyrochlores, with  $T_N = 0.38$  K and an ordered moment of 3.4(2)  $\mu_{\text{B}}$ . The spin dynamics develop well-above the ordering temperature, near  $T^* = 1.5$  K, the origin of the broad specific anomaly. The dramatically suppressed ordering temperature and change of ground state in  $\text{Er}_2\text{Pt}_2\text{O}_7$  can be understood in the context of strong phase competition. Multiphase competition is already understood to be important within the ytterbium family of pyrochlores and our work shows that this premise can equally be expanded into the erbium pyrochlores.

Note added: Following the submission of this paper, a related manuscript on another erbium XY pyrochlore,  $\text{Er}_2\text{Sn}_2\text{O}_7$ , appeared on the arXiv [43]. This material is also found to possess a Palmer-Chalker ground state with  $T_N = 0.1$  K. Evidence is also found for frustration induced by phase competition, consistent with our arguments on its relevance to erbium pyrochlores.

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#### SUPPLEMENTAL MATERIAL: Phase Competition in the Palmer-Chalker XY Pyrochlore $Er_2Pt_2O_7$

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#### EXPERIMENTAL METHODS

 $\mathrm{Er}_{2}\mathrm{Pt}_{2}\mathrm{O}_{7}$  can be synthesized in the cubic  $Fd\bar{3}m$ pyrochlore structure, in powder form only, using highpressure techniques. Unlike the rare earth germanium and lead pyrochlores, it is not the relative size of the A and B site cations that necessitates the use of high-pressure synthesis [1, 2]. In fact, the ionic radii of platinum is intermediate to titanium and tin, and is thus well within the ambient pressure stability range for the formation of a pyrochlore phase with many rare earths. Rather, it is the low decomposition temperature of  $PtO_2$  which necessitates the use of high-pressure. Stoichiometric quantities of  $Er_2O_3$  and  $PtO_2$  were reacted in gold or platinum capsules at 6 GPa and 1200°C for two hours, then rapidly quenched to room temperature before releasing the pressure. Small quantities of unreacted Er<sub>2</sub>O<sub>3</sub> and Pt-metal were removed by repeated washings in aqua regia. Each batch of Er<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> was x-rayed to verify phase purity and the total resultant sample was 1.2 grams. The room temperature lattice parameter (a = 10.13 Å) and Curie-Weiss temperature  $(\theta_{\rm CW} = -24.7 \text{ K } [3])$  for our sample are consistent with previous reports [4–6].

Elastic neutron scattering measurements were carried out on the cold neutron triple-axis spectrometer SPINS at the National Institute for Standards and Technology's Center for Neutron Research (NCNR) [7]. These measurements were performed with a monochromatic neutron beam of wavelength 4.04 Å, giving an energy resolution of 0.34 meV at the elastic line. Inelastic neutron scattering measurements were performed on the time-of-flight Disc Chopper Spectrometer (DCS) at the NCNR [8]. An incident neutron beam of 5 Å was used, corresponding to a maximum energy transfer of 3.3 meV, with an energy resolution of 0.09 meV. Both experiments were performed with an ICE dilution insert in a standard orange ILL cryostat over a temperature range of 60 mK to 8 K. To facilitate thermal equilibration at low temperatures, the sample was wrapped in a piece of copper foil and sealed in a copper sample can with 10 atmospheres of helium. All error bars correspond to one standard deviation. The DCS data were reduced and visualized using the DAVE software package [9]. The magnetic symmetry analysis was performed with SARAh [10] and Rietveld refinements were carried out using FullProf [11].

#### ORDER PARAMETER

We used the SPINS spectrometer to measure the scattered elastic neutron intensity at the center of the (111) and (002) Bragg peaks, the results of which are shown in Figure 2(c) of the main manuscript. All data were collected on warming from base temperature, allowing two minutes to equilibrate at each temperature. Our order parameter indicates the formation of a statically ordered state below  $T_N = 0.38$  K, consistent with the heat capacity measured in Ref. [6]. In a narrow temperature range below  $T_N$ , the data is well fit to a power law dependence,

$$I \propto \left(\frac{T_N - T}{T_N}\right)^{2\beta} \tag{1}$$

where  $\beta$  is the critical exponent. A fit between 0.38 K and 0.32 K, given by the yellow curve in Figure 2(c) gives  $\beta = 0.35 \pm 0.03$ , consistent with conventional 3D XY universality [12], as well as the  $\beta$  extracted for Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [13]. However, over a wider temperature range, the form of this order parameter is somewhat unusual for its lack of curvature.

#### SPIN WAVE CALCULATION

As described in the text, we fit the exchange parameters of  $\text{Er}_2\text{Pt}_2\text{O}_7$  using an anisotropic exchange Hamiltonian. The nearest-neighbor anisotropic exchange Hamiltonian has been extensively employed to describe the magnetism in other pyrochlore magnets [14–16] and is defined as:

$$\mathcal{H}_{ex} = \sum_{\langle ij \rangle} J^{\mu\nu}_{ij} S^{\mu}_i S^{\nu}_j.$$
 (2)



FIG. 1. Evolution of the powder averaged spin excitation spectrum as a function of  $J_2$  where  $J_1 = 0.11$  meV,  $J_3 = -0.10$  meV, and  $J_4 = 0$  meV. A phase transition between  $\Gamma_5$  and  $\Gamma_7$  occurs when  $J_1 = J_2$ . The set of exchange parameters displayed in (a) are those that describe  $\text{Er}_2\text{Ti}_2\text{O}_7$ . The best qualitative agreement for  $\text{Er}_2\text{Pt}_2\text{O}_7$  is shown in (e), in close proximity to the  $\Gamma_5/\Gamma_7$ phase boundary.

The sum  $\langle ij \rangle$  runs over all nearest-neighbor bonds.  $S_i$  is the magnetic moment operator of an  $\mathrm{Er}^{3+}$  atom located at site *i* and is composed of three components:  $S_x$ ,  $S_y$ and  $S_z$ . Due to the symmetry of the pyrochlore lattice, the exchange coupling matrix,  $J_{ij}^{\mu\nu}$ , can be reduced to four independent exchange parameters [17]. The exchange parameters are defined as  $J_1$  (XY term),  $J_2$ (Ising term),  $J_3$  (symmetric off-diagonal term) and  $J_4$ (Dzyaloshinskii-Moriya term).

To fit the exchange parameters of  $Er_2Pt_2O_7$ , we used the base temperature, T = 0.06 K, data set shown in Figure 4(a) of the main manuscript, where an empty can data set has been subtracted. The fitted data have also been corrected for the absorption of  $Er^{3+}$  in cylindrical geometry. We parameterized the exchange couplings by fitting the scattered intensity as a function of energy transfer for three different integrations in momentum transfer, Q. The intervals in momentum transfer, Q, used for these three integrations are 0.3 to 0.6  $\text{\AA}^{-1}$ , 1.0 to 1.3  $\text{\AA}^{-1}$  and 1.7 to 2.0  $\text{\AA}^{-1}$ , as shown in Figure 5(c) of the main text. We further constrained the spin wave calculation by fitting an energy integration from 0.1 to 0.3 meV, which corresponds to an integration over the flat mode. The resulting integration is shown in Figure 5(b) of the main text and shows the intensity of the flat mode as a function of the momentum transfer, Q. Note that the small peak near 2.1  $Å^{-1}$  corresponds to crossing the phonon branch extending out of (222), which is the most intense nuclear Bragg reflection.

The linear spin wave calculation was performed using the program SpinW [18] with the anisotropic exchange Hamiltonian of Equation 2 in the Supplemental Material. The exchange parameters  $J_1$ ,  $J_2$ , and  $J_3$  were freely varied, but  $J_4$  were kept fixed to 0 as this term has been found to be negligible for all other known XY pyrochlore magnets [14, 15, 19]. The best agreement with our measured data was obtained with  $J_1 = 0.10 \pm 0.05$ ,  $J_2 = 0.20 \pm 0.05$ ,  $J_3 = -0.10 \pm 0.03$ . The calculated spin wave spectra for this set of exchange parameters is shown in Figure 4(b) of the main text and quantitative comparison is shown in Figure 5(b,c). The energy and momentum transfer dependence of the flat mode is well captured by our model. However, the high energy spin wave branches predicted by the spin wave calculation are not observed in our base temperature inelastic neutron scattering data set. The most striking difference occurs at low Q where a relatively intense and dispersive spin wave branch is expected to be present, but is not visible in our data. Instead, a broad and weak continuum of scattering is observed in higher energy.

It is interesting to note that the experimentally determined exchange parameters for  $\text{Er}_2\text{Ti}_2\text{O}_7$  differ from those of  $\text{Er}_2\text{Pt}_2\text{O}_7$  only in their  $J_2$  value. The computed spin wave spectra for these two materials are shown in Figure 1(a) and 1(e), respectively. In the nearest-neighbor anisotropic exchange phase space, the transition from  $\Gamma_5$ to  $\Gamma_7$  occurs when  $J_2$  becomes larger than  $J_1$ . Thus, in the remaining panels of Figure 1 we have simulated the spin excitation spectrum as a function of increasing  $J_2$  keeping all other exchange parameters fixed at the values determined for  $\text{Er}_2\text{Ti}_2\text{O}_7$  and  $\text{Er}_2\text{Pt}_2\text{O}_7$ . The relatively flat lower band appears over the entire Palmer-Chalker phase space with dispersive higher energy modes of increasing band width.

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# Chapter 5

## The XY Rare Earth Pyrochlores

## 5.1 Preface to Publication VII: Experimental review on XY pyrochlores

The rare earth pyrochlores live in a rich and fascinating magnetic phase space. Throughout this thesis, the desirability of chemically expanding the families of these exotic magnets has been emphasized, with the aim of exploring their phase diagrams. Here, in the final work of this thesis, the advantage to this approach is made evident. This work is a review article in which we summarize the ground state magnetic properties of two families of XY pyrochlores,  $Er_2B_2O_7$  and  $Yb_2B_2O_7$  with (B = Ge, Ti, Pt, and Sn). Two of these materials were the specific subjects of papers in this thesis:  $Yb_2Ge_2O_7$  in **Chapter 2** and  $Er_2Pt_2O_7$  in **Chapter 4**. Having a larger subset of these materials to consider allows us to find commonalities and draw strong connections with theoretical works.

The objective of this review was to concisely summarize the extensive experimental literature, including our own work, on XY pyrochlore magnets. We begin by elucidating the origin of XY spin anisotropy, which arises as the consequence of a material's crystal electric field phenomenology. On this basis, we can narrow the XY pyrochlore family down to those  $R_2B_2O_7$  materials that have erbium or ytterbium at the R site. We next introduce the anisotropic exchange Hamiltonian, a minimal model that can account for many of the observed properties of the XY pyrochlores [84]. The experimental parameterization of this Hamiltonian can be achieved using inelastic neutron scattering to map out the spin wave dispersions. However, such an approach generally requires single crystal samples, which, for the XY pyrochlores, are only currently available in the titanates,  $Er_2Ti_2O_7$  and  $Yb_2Ti_2O_7$ . For these two materials, this approach has been successfully implemented [61, 70, 86, 87, 93]. Taking these experimentally determined exchange parameters as a starting point, theoretical works have explored the nearby phase space, revealing a rich phase diagram [84]. We next enumerate the experimentally determined magnetic ground states for each of the  $\text{Er}_2B_2\text{O}_7$  and  $\text{Yb}_2B_2\text{O}_7$  pyrochlores (B = Ge, Ti, Pt, and Sn) with respect to this theoretical phase diagram. Both the experimental and theoretical understanding of the XY pyrochlore phase space tend to support a picture of strong phase competition. A key discussion in our review is what we believe to be the experimental signatures of phase competition: multiple heat capacity anomalies, unconventional spin dynamics, and pronounced sensitivity to disorder and applied pressure. We next discuss other families of XY materials for which phase competition could be relevant. In particular, we highlight the transition metal fluoride pyrochlore, NaCaCo<sub>2</sub>F<sub>7</sub>, which is known to possess spin dynamics from both the  $\Gamma_5$ manifold and a collinear antiferromagnetic state [144]. Our review concludes by posing a handful of open questions that future experimental work could aim to address. The following publication is contained in this chapter:

**Publication VII**: "Experimental insights into ground state selection of quantum XY pyrochlores", Alannah M. Hallas, Jonathan Gaudet, and Bruce D. Gaulin. Invited Review to appear in the Annual Review of Condensed Matter Physics (2017) [7].

#### Author Contributions:

- Concept: A.M. Hallas, J. Gaudet, B.D. Gaulin
- Figures: A.M. Hallas
- Manuscript: A.M. Hallas, J. Gaudet, B.D. Gaulin

## Experimental Insights into Ground State Selection of Quantum XY Pyrochlores

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#### Keywords

geometric frustration, quantum magnetism, pyrochlores, phase competition, XY anisotropy, neutron scattering

#### Abstract

Extensive experimental investigations of the magnetic structures and excitations in the XY pyrochlores have been carried out over the last decade. Three families of XY pyrochlores have emerged: Yb<sub>2</sub>B<sub>2</sub>O<sub>7</sub>, Er<sub>2</sub>B<sub>2</sub>O<sub>7</sub>, and, most recently,  $AA'Co_2F_7$ . In each case, the magnetic cation (either Yb, Er, or Co) exhibits XY anisotropy within the local pyrochlore coordinates, a consequence of crystal field effects. Materials in these families display rich phase behavior and are candidates for exotic ground states, such as quantum spin ice, and exotic ground state selection via order-by-disorder mechanisms. In this review, we present an experimental summary of the ground state properties of the XY pyrochlores, including evidence that they are strongly influenced by phase competition. We empirically demonstrate the signatures for phase competition in a frustrated magnet: multiple heat capacity anomalies, suppressed  $T_N$  or  $T_C$ , sample and pressure dependent ground states, and unconventional spin dynamics.

#### **1. INTRODUCTION**

Cubic pyrochlore oxides of the form  $A_2B_2O_7$  display a broad range of physical properties, in direct relation to their chemical diversity. The A and B sites of this lattice can each host many chemical elements, leading to families that involve over 150 compounds. Pyrochlores can exhibit insulating, metallic, and even superconducting states (1). The experimental intrigue with pyrochlore magnetism began in earnest with the discovery of a spin glass state in  $Y_2Mo_2O_7$ , unexpected in a structurally well-ordered material (2). From that point on, pyrochlore oxides have been of great interest to physicists and at the forefront of new magnetic and electronic phenomena, including: cooperative paramagnetism in  $Tb_2Ti_2O_7$  (3), the anomalous Hall effect in  $Nd_2Mo_2O_7$  (4,5), giant magnetoresistance in  $Tl_2Mn_2O_7$  (6), and, most recently, possible topological states in  $A_2 Ir_2 O_7$  (7). Insulating rare earth pyrochlores in particular have attracted enormous attention as they represent an archetype for 3-dimensional geometrically frustrated magnetism. The A and B sites of the pyrochlore lattice each independently form a network of corner-sharing tetrahedra, as drawn in Figure 1(a), an architecture that is prone to frustration when occupied by a magnetic cation. The whole series of rare earth cations, most of which are magnetic, can reside on the A site of the lattice. These rare earth pyrochlores have been lauded for their diverse magnetic properties, which can be attributed to the combination of varied magnetic anisotropies and interactions that conspire to produce a wealth of exotic ground states (8).

**Frustration:** The inability of a system to satisfy all of its pairwise constraints simultaneously.

The rare earth pyrochlores were propelled into the spotlight when the classical spin ice state was discovered in  $Ho_2Ti_2O_7$  (9, 10), and soon after in  $Dy_2Ti_2O_7$  (11). The spin ice state has a residual entropy analogous to that of proton disorder in water ice (12), which in both cases is the result of an extensive ground state degeneracy. The requirements for spin ice physics are the connectivity of the pyrochlore lattice, local Ising anisotropy, and net ferromagnetic interactions (9). The dipolar interaction between Ising moments on the pyrochlore lattice is ferromagnetic at the nearest neighbor level (13, 14). Consequently, provided antiferromagnetic exchange interactions are sufficiently weak, large Ising moments



#### Figure 1

(a) The A (blue) and B (red) sites of the pyrochlore lattice,  $A_2B_2O_7$ , each form a network of corner-sharing tetrahedra, a motif prone to magnetic frustration. (b) XY anisotropy on the pyrochlore lattice is achieved when the A site is occupied by either erbium or ytterbium, as indicated by the blue highlighting, with the possible non-magnetic B sites highlighted in red. The faded blue and red squares reflect all known  $A^{3+}$  and  $B^{4+}$  cations that can be found on the pyrochlore lattice in some combination.

 $(\sim 10 \ \mu_B)$  on the pyrochlore lattice, in and of themselves, have the ingredients for spin ice physics. Ten years after its discovery, the spin ice state was understood to possess emergent magnetic monopole excitations (15–17), generating a new level of interest. However, the spin ice states found in Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Dy<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are predominantly governed by classical physics, in part because their crystal field ground state doublets are almost purely made up of maximal  $m_J$  (18–20). Thus, a route to enhancing quantum effects is to consider rare earths where contributions from smaller  $m_J$  states are non-negligible, thereby inducing XY rather than Ising anisotropy. This is achieved in nature when the rare earth site is occupied by either ytterbium or erbium (**Figure 1(b)**), the subjects of this review.

The incorporation of XY degrees of freedom has important implications for the spin ice state. In the classical spin ices, which have large Ising moments, the magnetic interactions are dipolar augmented by relatively weak exchange (13, 14). If the magnitude of the rare earth moment is reduced, dipolar interactions become less important and exchange interactions, correspondingly, more important. Then, anisotropic exchange terms can couple effective  $S = \frac{1}{2}$  moments, which will promote quantum fluctuations, particularly in the case of a ground state composed of minimal  $m_J$ . A possible resulting state is referred to as quantum spin ice. One of the most exciting revelations has been that the quantum spin ice problem maps onto an emergent quantum electrodynamics, whose elementary excitations include not only magnetic monopoles, but also electric monopoles and gauge photons (21–28). In this realm, theory is out-pacing experiment, for a robust experimental realization of quantum spin ice remains elusive. Amongst the rare earth pyrochlores, several candidate materials have been identified as possessing many of the requisite ingredients, including: Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (29), Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (30), and Pr<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (31). While quantum spin ice ground states in these materials remain tantalizingly close, recent experimental studies show rich low temperature phenomenology including strong sensitivity to quenched impurities (32–34), which complicates a simple categorization of their ground states.

Another example of quantum XY phenomenology is found in the degeneracy-breaking that results in long range magnetic order in  $\text{Er}_2\text{Ti}_2\text{O}_7$ . In the mean field limit of its spin Hamiltonian, there is a degeneracy between two ordered, non-collinear XY states, termed  $\psi_2$ and  $\psi_3$ . Linear combinations of these two states continuously span the XY plane, giving a U(1) degeneracy. Thus, it was at first perplexing when  $\text{Er}_2\text{Ti}_2\text{O}_7$  was observed to undergo a continuous phase transition into a pure  $\psi_2$  state (35,36). The selection of this ground state is believed to be driven by thermal and quantum fluctuations, i.e. order-by-disorder. Despite the mean field U(1) degeneracy, the spin excitations of  $\psi_2$  and  $\psi_3$  contribute differently to the free energy. This can occur either at finite temperature via a thermal order-by-disorder mechanism (37–40), or via quantum fluctuations at zero temperature, hence quantum orderby-disorder (41–43). While theoretical ideas on order-by-disorder date back more than 60 years (44, 45),  $\psi_2$  ground state selection in  $\text{Er}_2\text{Ti}_2\text{O}_7$  remains one of the most compelling candidates for its experimental realization. However, an alternative mechanism that relies only on energetic selection by virtual crystal field transitions has also been shown to break the U(1) degeneracy in  $\text{Er}_2\text{Ti}_2\text{O}_7$  (46–48).

This introduction has highlighted several fascinating aspects of the effective  $S = \frac{1}{2}$  quantum XY pyrochlores, such as ground state selection by order-by-disorder and quantum spin ice. Here, we will focus our attention on the prevalence for low temperature magnetism that appears to be influenced by the presence and proximity of competing phases. We compare and contrast the properties of two XY families,  $Er_2B_2O_7$  and  $Yb_2B_2O_7$ , with varying non-magnetic B site cations, and conclude that many of their exotic properties stem

Effective S = 1/2: In the case of an isolated ground state doublet, the system can be projected into a pseudo-spin  $\frac{1}{2}$ basis. from strong phase competition, in agreement with recent theoretical suggestions (40, 49, 50).

#### 2. ORIGIN OF XY ANISOTROPY

A unique attribute of rare earth magnetism is the hierarchy of energy scales, where spinorbit coupling, the crystal electric field, and exchange interactions each have characteristic energies that are typically separated by an order of magnitude or more. The spin anisotropy of the rare earth pyrochlores is derived from crystal electric field effects. Thus, we begin by elucidating the origin of XY anisotropy and justify the application of the XY label to the vtterbium and erbium pyrochlores. As a consequence of their seven f electron orbitals, magnetic rare earths typically have large values for their total angular momentum J, as compared to magnetic elements elsewhere on the periodic table. Furthermore, as rare earth ions are relatively heavy, the spin-orbit coupling,  $\lambda$ , is usually sufficiently large to isolate a spin-orbit ground state that is comprised of 2J + 1 degenerate levels. Within a crystalline environment, the 2J + 1 levels of the spin-orbit ground state are then split by the crystal's electric field – an effect that is on the order of 100 meV and typically much smaller than  $\lambda J$ . Thus, the crystal electric field of the rare earths can often be successfully treated as a perturbation from spin-orbit coupling. This is in contrast to transition metal systems, where a perturbative approach fails because the strength of the spin-orbit coupling is comparable or smaller than the crystal electric field splitting.

The crystal electric field, which lifts the 2J+1 degeneracy of the spin-orbit ground state, depends on the point-group symmetry at the rare earth site and originates most strongly from the oxygen anions. In the pyrochlore lattice, the rare earth cation sits at the center of an eight-fold coordinate oxygen environment that forms a distorted cube, compressed along its diagonal (1), as shown in **Figure 2(a)**. The axis along which the cube is compressed is the one that connects the oxygens at the centers of adjacent tetrahedra. This axis is the local z axis and is commonly referred to as the local [111] direction. The symmetry at the rare earth site is given by the  $D_{3d}$  point group, which has two-fold and three-fold rotation axes and an inversion center, defined with respect to the [111] axis. In these coordinates, a spin with Ising anisotropy will be oriented along its local [111] direction. Likewise, a spin with XY anisotropy will be constrained to lay in the plane perpendicular to [111], as shown in **Figure 2(b)**, where the local x and y axes are defined by the two-fold rotation axes. A peculiar aspect of the pyrochlore lattice, and one worth emphasizing, is that both of these anisotropies are explicitly defined with respect to a local direction, not a global one. Thus, Ising spins are not parallel to one another and XY spins do not share a common plane.

#### Kramer's theorem:

Every energy level of a time reversal symmetric system with half integer spin must be at least doubly degenerate (53).

> XY anisotropy is achieved on the pyrochlore lattice when the rare earth site is occupied by either ytterbium or erbium. Both of these cations, Yb<sup>3+</sup> and Er<sup>3+</sup>, have an odd number of f electrons, and accordingly their crystal electric field levels cannot be split beyond a doublet, as required by Kramer's theorem. Yb<sup>3+</sup> with  $J = \frac{7}{2}$  has its lowest energy spin-orbit manifold comprised of four doublets, while Er<sup>3+</sup> with  $J = \frac{15}{2}$  has eight doublets. Transitions between the crystal electric field levels can be directly probed by inelastic neutron scattering. Taking Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> as examples, **Figures 2(c)** and **2(d)** show inelastic neutron scattering maps where the crystal field transitions are indicated by the black arrows on the right hand side. As the crystal electric field is a single ion property, crystal field excitations lack dispersion and their intensities fall off with Q according to the single ion magnetic form factor. While we only show crystal field schemes for Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, the general features can be expanded to their respective families (51,52,54).



Figure 2

(a) The rare earth site (blue) of the pyrochlore lattice is enclosed by eight oxygen anions (yellow), which form a distorted cube. (b) Spins with XY anisotropy are constrained to lie in the plane perpendicular to the local [111] axis. Inelastic neutron scattering measurements of (c) Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and (d)  $\text{Er}_2\text{Ti}_2\text{O}_7$ , used to determine their crystal electric field schemes. The black arrows indicate the positions of the crystal electric field transitions. The crystal electric field Hamiltonian, given in Eqn. 1, is used to fit the experimentally measured spectra for (e) Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (51) and (f)  $\text{Er}_2\text{Ti}_2\text{O}_7$  (52).

In particular, the ytterbium pyrochlores typically have their ground states separated from their first excited crystal field state by  $\sim 800$  K, while the erbium pyrochlores have their ground states separated from their first excited states by  $\sim 80$  K.

The crystal field eigenstates and eigenvalues can be determined by fitting the experimental neutron scattering spectra with the crystal electric field Hamiltonian (56),

$$\mathcal{H}_{CEF} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^3 \hat{O}_4^3 + B_6^0 \hat{O}_6^0 + B_6^3 \hat{O}_6^3 + B_6^6 \hat{O}_6^6,$$

which is based upon the point group symmetry at the rare earth site,  $D_{3d}$ , and is written in the Stevens operator formalism (55). The values of the six crystal electric field parameters  $(B_2^0, B_4^0, etc.)$  can be systematically varied to achieve the best agreement with the experiential spectra. The result of such fittings are shown in **Figures 2(e)** and **2(f)** for Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, respectively. A more detailed treatment of these types of analyses applied to pyrochlore materials can be found elsewhere (18,20,51,57,58). The result, however, is that for all the Yb and Er pyrochlores that have been measured to date, the anisotropic *g*-tensors for their ground state doublets have a larger perpendicular component,  $g_{\perp}$ , than parallel,  $g_{\parallel}$ (**Table 1**). Hence, their spin anisotropy is XY-like (51,52,54,57,59–62). The values of the *g*-tensors in the crystal electric field ground state are substantially reduced from the free ion value - corresponding to a reduced magnetic moment. Furthermore, the ground state Stevens Operators: Formalism that uses the Wigner-Eckart theorem to express the crystal field interaction in terms of angular momentum operators (55).

(1)

#### g-tensor: A

generalization of the magnetic g-factor that, when coupled with its total angular momentum, defines the magnetic moment of an atom. eigenfunctions of the Yb and Er pyrochlores have large components of  $m_J = \pm \frac{1}{2}$ , which favors quantum fluctuations.

#### 3. GROUND STATE PHASE DIAGRAM OF XY PYROCHLORES

Due to their crystal electric field phenomenology, the XY pyrochlore magnets  $Yb_2B_2O_7$  and  $Er_2B_2O_7$  have well-isolated ground state doublets. Consequently, their low temperature magnetism is well described by an effective  $S = \frac{1}{2}$  system with a reduced magnetic moment and an anisotropic XY g-tensor. A minimal model that can describe many of their observed magnetic properties is the anisotropic nearest-neighbor exchange Hamiltonian (40):

$$\mathcal{H}_{ex} = \sum_{\langle i,j \rangle} J_{ij}^{\mu\nu} S_i^{\mu} S_j^{\nu}.$$
<sup>(2)</sup>

This Hamiltonian permits anisotropic exchange between the three spatial coordinates of each spin,  $S_j^{\mu}$ , resulting in an exchange matrix (rather than the more typical exchange constant) defined, in principle, by nine different components,  $J_{ij}^{\mu\nu}$ . However, the point group symmetry of the rare earth site in the pyrochlore lattice reduces the number of independent exchange parameters to just four (84). Depending on the values of these four exchange parameters, the anisotropic exchange Hamiltonian can support the stabilization of a spin liquid ground state (85–87) as well as the emergence of classical (9,13) or quantum spin ice ground states (21,22,24–28).

The experimental determination of a real material's exchange parameters is a problem that is well-suited to the technique of inelastic neutron scattering. First, the spin wave dispersions of a single crystal can be mapped out along different crystallographic directions, a task that is increasingly straightforward given the capabilities of modern time-of-flight neutron instrumentation. Then, using linear spin wave theory derived from the Hamiltonian of **Equation 2**, a fit of the experimental spectra can be performed until a set of exchange parameters and g-tensor components have been found that yield good agreement (30). In principle, this approach can be applied within the long range ordered state of a material at low temperatures. However, if the material displays a disordered ground state in zero magnetic field or if the ordered state is complicated and not completely understood, linear

#### Table 1 Ground state magnetic properties for the ytterbium and erbium pyrochlores.

	$a^{\mathrm{a}}$	$\theta_{CW}$	$g_\perp/g_\parallel$	$T^*$	$T_C$ or $T_N$	Ordered State
	(Å)	(K)		(K)	(K)	
$Yb_2Ge_2O_7$	9.8 (63)	0.9(64)	1.7(54)	3.7(65)	0.6(66)	$\psi_2 \text{ or } \psi_3 \text{ AFM } (54,66)$
$Yb_2Ti_2O_7$	10.0(67)	0.8~(68)	1.9(51)	2.5(68)	0.25(68)	$\Gamma_9  {\rm FM^b}  (69,70)$
$Yb_2Pt_2O_7$	10.1(71)	0.9(72)	—	2.4(72)	0.30(72)	Undeterm. FM $(72)$
$Yb_2Sn_2O_7$	10.3(73)	0.5(74)	_	1.8(75)	0.15(76)	$\Gamma_9  { m FM}  (76,77)$
$\mathrm{Er}_{2}\mathrm{Ge}_{2}\mathrm{O}_{7}$	9.9(63)	-22(78)	3.3(52)	_	1.4 (66)	$\psi_2 \text{ or } \psi_3 \text{ AFM}^{c} (66)$
$\mathrm{Er}_{2}\mathrm{Ti}_{2}\mathrm{O}_{7}$	10.1(67)	-22 (79)	1.6(52)	—	1.2(80)	$\psi_2 \text{ AFM } (36)$
$\mathrm{Er}_{2}\mathrm{Pt}_{2}\mathrm{O}_{7}$	10.1(71)	-22 (72)	28(52)	1.5(72)	0.30(72)	$\Gamma_7 \text{ PC AFM (81)}$
$\mathrm{Er}_{2}\mathrm{Sn}_{2}\mathrm{O}_{7}$	10.4(73)	-14 (74)	54(52)	4.3(82)	0.11(83)	$\Gamma_7 \text{ PC AFM (83)}$

<sup>a</sup>Measured at room temperature and truncated at one decimal places; <sup>b</sup>The low temperature magnetism of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is sample dependent, as we elaborate on in Section 4.2; <sup>c</sup>This work concluded the ground state of  $\text{Er}_2\text{Ge}_2\text{O}_7$  is  $\psi_3$  based on an incorrect assumption, as we elaborate in the main text.

neutron scattering: A technique where one or both of the incident and scattering neutron

determined by its

Time-of-flight

energies are

speed.



#### Figure 3

The measured (top row) and computed (bottom row) spin wave spectra along various crystallographic directions for (a) Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> at H = 5 T, adapted with permission from Ref. (30) and (b) Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> at H = 3 T, adapted with permission from Ref. (41), copyrighted by the American Physical Society. The fits to the experimental spectra, which were obtained using inelastic neutron scattering, allow the determination of the anisotropic exchange couplings in the microscopic spin Hamiltonian.

spin wave theory can still successfully be applied in the field polarized state of the material, where its magnetic moments are tending to follow the magnetic field.

The success of this approach relies on the availability of large single crystal samples, which restricts its use to a select few materials. Amongst the family of XY pyrochlores, the titanates have provided the most successful platform for the growth of large single crystals (88–90). Several groups have estimated the anisotropic exchange couplings for  $Yb_2Ti_2O_7$  and  $Er_2Ti_2O_7$  with inelastic neutron scattering (30, 41, 47, 91, 92). Still, this is not a completely straightforward exercise, as there are six strongly coupled parameters to be fit, if the components of the g-tensor are to be adjusted in addition to the four exchange terms. Figure 3 shows an example of an analysis of this type for  $Yb_2Ti_2O_7$  (30) and  $Er_2Ti_2O_7$  (41). The precise values of the exchange parameters for  $Yb_2Ti_2O_7$  vary amongst different groups, but there is consensus that its exchange parameters, at least at the mean field level, should lead to a k = 0,  $\Gamma_9$  splayed ferromagnetic ordered state, as shown in Figure 4 (30, 40, 50, 91–93). Experimentally, a splayed ferromagnetic ground state has indeed been observed for some samples of  $Yb_2Ti_2O_7$  (69, 70, 94–96). However, this state displays a number of peculiarities, one of which is that low levels of quenched disorder drastically impacts the formation of long-range magnetic order (33, 97–99). The exchange parameters for  $\text{Er}_2\text{Ti}_2\text{O}_7$  place it within the antiferromagnetic  $\Gamma_5$  manifold ( $\psi_2$  or  $\psi_3$ , shown in **Figure 4**) at the mean field level, but it has been shown that order-by-disorder and virtual crystal field transitions will select  $\psi_2$  (37,39,41–43,46–48,100). It is interesting to note that order-by-disorder can select  $\psi_3$  for exchange parameters different than those of  $Er_2Ti_2O_7$  (43, 101), but  $\psi_2$  is uniformly favored by current models of virtual crystal field transitions (48). Experimentally, differentiating between the  $\psi_2$  and  $\psi_3$  states is very challenging as their diffraction patterns are identical. They can, however, be distinguished via polarized neutron scattering measurements on a single crystal, and this has been used to confirm that the ordered phase of  $\text{Er}_2\text{Ti}_2\text{O}_7$  is a pure  $\psi_2$  state (36).



#### Figure 4

The classical ground state phase diagram for pyrochlores with anisotropic exchange, where  $J_4 = 0$  - adapted from Ref. (40) with permission, copyrighted by the American Physical Society. This phase diagram contains four classically ordered states - the spin configurations of which are presented on two tetrahedra. The exchange parameters determined for Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (30) and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (41) place these two materials in the  $\Gamma_9$  and  $\psi_2$  regions, respectively.

Palmer-Chalker State: Named after the authors of Ref. (102), which showed that  $\Gamma_7$  is the ground state for a Heisenberg pyrochlore antiferromagnet with dipolar interactions. Taking the experimentally determined exchange parameters of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> as a starting point, theoretical studies have explored the ordered phases that are expected classically within a subspace of exchange parameters relevant for the XY pyrochlores (40, 43, 50). The resulting phase diagram is rich, revealing the possibility of stabilizing various magnetic structures, as shown in **Figure 4** (40). This phase diagram contains four k = 0 magnetic structures, where the spin configuration of each is shown around the perimeter. In addition to the ferromagnetic  $\Gamma_9$  phase found for parameters appropriate to Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and the antiferromagnetic  $\psi_2$  phase for Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, there are two additional antiferromagnetic states:  $\psi_3$ , which is part of the  $\Gamma_5$  manifold, and  $\Gamma_7$ , the socalled Palmer-Chalker state (102). All these magnetic structures can be obtained within a narrow range of exchange parameters, suggesting that phase competition could exist within the family of XY pyrochlores (40,50). This scenario would imply that a change of magnetic ground state amongst the Yb and Er pyrochlores would require only modest changes to the anisotropic exchange parameters, as might be induced by chemical or external pressure.

Chemical pressure can be realized by substituting a non-magnetic constituent for an element of varying size. In the case of the XY titanate pyrochlores, this leads to the replacement of titanium on the *B* site by germanium, tin, or platinum (**Figure 1(b)**). As reported in **Table 1**, the magnetic structures of most of these chemical pressure analogs have already been determined. For the ytterbium pyrochlores, no change of magnetic ground state is obtained by incorporation of tin (76,77), but an antiferromagnetic  $\Gamma_5$  phase is obtained for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> (54,66). For the erbium pyrochlores, germanium substitution also results in a  $\Gamma_5$  ( $\psi_2$  or  $\psi_3$ ) ground state (66). The effect of a magnetic field on the powder diffraction pattern of Er<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> has been argued to indicate a pure  $\psi_3$  state (66). However, the domain selection arguments upon which this determination is based have been found to
be incorrect (103–105). Thus, while it is possible that  $\text{Er}_2\text{Ge}_2\text{O}_7$  has a  $\psi_3$  ground state, it remains to be definitively shown. For  $\text{Er}_2\text{Pt}_2\text{O}_7$  and  $\text{Er}_2\text{Sn}_2\text{O}_7$ , powder neutron diffraction studies have uncovered  $\Gamma_7$  Palmer-Chalker ground states but with significantly reduced  $T_N$ 's from the other erbium pyrochlores (81,83). This suppression of magnetic order could originate from phase competition between the  $\Gamma_5$  and  $\Gamma_7$  states (40,62,81). Moreover, the ensemble of states observed within these two XY pyrochlore families confirms the proximity of the  $\Gamma_5$ ,  $\Gamma_7$ , and  $\Gamma_9$  states in their phase space and empirically validates the scenario of strong phase competition. This stands in contrast to the classical spin ice pyrochlores,  $\text{Ho}_2\text{Ti}_2\text{O}_7$  and  $\text{Dy}_2\text{Ti}_2\text{O}_7$ , where germanium and tin substitution at the *B* site leaves the ground state properties largely unchanged (74, 106–108).

# 4. EXPERIMENTAL SIGNATURES OF PHASE COMPETITION IN THE XY PYROCHLORES

The variety of ground states observed amongst the XY pyrochlores, combined with a theoretically-derived phase diagram based on anisotropic exchange, leads one to suspect that phase competition is likely important in these materials. In this section, we describe several experimental observations that could be manifestations of this phase competition. We first demonstrate that the ytterbium based XY pyrochlores possess unconventional spin dynamics that are clearly linked with a broad feature in their specific heat, rather than the sharp anomalies they display at  $T_C$  or  $T_N$ . We argue that the origin of these unconventional dynamics is the proximity of nearby ordered phases and the competition between them. We further demonstrate the sensitivity of the ground state in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> to both weak quenched disorder and hydrostatic pressure, and argue that this too has a natural explanation in phase competition.

# 4.1. UNCONVENTIONAL SPIN DYNAMICS

A summary of heat capacity measurements performed on the ytterbium and erbium pyrochlores is shown in Figure 5. Over the temperature range displayed, the lattice contribution is negligible, and the heat capacity is dominated by the magnetic component. There is a striking similarity in the form of the specific heat for all the ytterbium pyrochlores, as well as  $\text{Er}_2\text{Pt}_2\text{O}_7$ , which consists of a sharp lambda-like anomaly at  $T_C$  or  $T_N$  and a broad, higher temperature anomaly at a temperature we label as  $T^*$  (66, 68, 72, 75, 76). Two compounds order above 1 K,  $Er_2Ti_2O_7$  and  $Er_2Ge_2O_7$ , and interestingly, these are also the only two that do not display broad specific heat anomalies (66, 80). Lastly,  $Er_2Sn_2O_7$  displays only a broad specific heat anomaly (82), as there is no reported data that extends below its  $T_N = 0.11$  K ordering transition (83), where we assume a sharp peak exists. Our conjecture is that the presence of a broad specific heat anomaly, coincident with a suppression of magnetic ordering to lower temperature, is an experimental signature of phase competition in the XY pyrochlores. It is worth noting that these broad specific heat anomalies do not have the characteristic form of a Schottky anomaly, as would be expected if their origin was the thermal depopulation of a crystal field level. As discussed in Section 2, the crystal electric field splittings in the Yb and Er pyrochlores are on the order of  $\sim 800$  K and  $\sim 80$  K, respectively, far above the energy scale for these broad specific heat anomalies. Furthermore, the combined entropy release of the sharp and broad anomalies is  $R \cdot \ln(2)$  (65,72). Thus, the entropy release associated with these broad specific heat anomalies is related to spin



The low temperature heat capacity of the (a)  $Yb_2B_2O_7$  pyrochlores (B = Ge (66), Ti (68), Pt (72), Sn (75,76)) and the (b)  $Er_2B_2O_7$  pyrochlores (B = Ge (66), Ti (80), Pt (72), Sn (82)).

degrees of freedom within the isolated ground state doublet.

The fact that Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> displays no such broad anomaly and orders at relatively high temperature indicates that phase competition is less relevant to its ground state selection. This is consistent with the placement of  $Er_2Ti_2O_7$  in the classical anisotropic exchange phase diagram, relatively far from the phase boundaries of the  $\Gamma_9$  and  $\Gamma_7$  ordered phases (Figure 4). In contrast, each of the ytterbium pyrochlores exhibits a broad specific heat anomaly, which we propose is connected with phase competition. For the ytterbium pyrochlores, we expect the most intense phase competition to arise between the ferromagnetic  $\Gamma_9$  state and the antiferromagnetic  $\Gamma_5$  state – a scenario that is consistent with the placement of  $Yb_2Ti_2O_7$  in the XY phase diagram (Figure 4) and also with the fact that the ground states of the ytterbium pyrochlores are known to span these two states (Table 1). Lastly, we suggest that the broad specific heat anomalies observed in  $Er_2Sn_2O_7$  and  $Er_2Pt_2O_7$  also originate from phase competition, but between the  $\Gamma_5$  and the  $\Gamma_7$  ordered phases. These phases and the boundary between them correspond to net antiferromagnetic interactions, consistent with the Curie-Weiss temperatures in the Er pyrochlores (**Table 1**). It is also empirically supported by the fact that both  $\text{Er}_2\text{Ti}_2\text{O}_7$  and  $\text{Er}_2\text{Ge}_2\text{O}_7$  order into the  $\Gamma_5$ phase, while  $Er_2Pt_2O_7$  orders into the  $\Gamma_7$  phase.

To better understand what is physically transpiring in the XY pyrochlores at the temperature of the broad specific heat anomaly,  $T^*$ , we consider evidence from inelastic neutron scattering. We take Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> as our representative example because it has the greatest degree of temperature separation between its broad and sharp heat capacity anomalies. In **Figure 6**, we present the temperature dependence of the low energy inelastic neutron scattering spectra of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> and compare it with the heat capacity. In contrast to the inelastic neutron scattering measurements shown in Section 2, these measurements probe far smaller energy transfers (~ 1 meV) at lower temperatures. Thus, they are sensitive to the collective spin dynamics, as opposed to the single ion excitations. Between 10 K and 4 K, there is a significant buildup of correlations centered towards Q = 0, a ferromagnetic zone center. This broad band of excitations decays in intensity as it extends outwards in Q, but without apparent coherent propagation. These spin excitations form at ~ 4 K, well above  $T_N$ , and are thus the origin of the broad specific heat anomaly. The



(a-d) The evolution of the spin dynamics in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> as a function of temperature measured by inelastic neutron scattering, adapted with permission from Ref. (65). (e) The temperatures at which the inelastic neutron scattering spectra were measured are indicated in reference to the specific heat. The broad band of ferromagnetic-like excitations form well above  $T_N$ , in the temperature range of the broad specific heat anomaly,  $T^*$ .

confluence of  $T^*$  with a change in form of the spin dynamics is a shared feature amongst all the Yb-based pyrochlores that have been measured thus far, and also  $\text{Er}_2\text{Pt}_2\text{O}_7$  and  $\text{Er}_2\text{Sn}_2\text{O}_7$  (65,70,75,81,83,109). That is to say, in all the XY pyrochlores that display both broad and sharp specific heat anomalies, the excitations develop some coherence at  $T^*$ , a temperature well-above  $T_C$  or  $T_N$ .

As Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is further cooled to 0.9 K and 0.06 K, below  $T_N$ , there is little significant redistribution of the spectral weight. Despite ordering into the  $\Gamma_5$  antiferromagnetic representation manifold, there is no corresponding response in the spin dynamics (within an energy resolution of ~0.09 meV). Once again, this insensitivity of the spin dynamics to long range magnetic order is shared amongst all the ytterbium pyrochlores (65, 70, 75). In **Figure 7** we present the low temperature inelastic neutron scattering spectra for the three ytterbium pyrochlores and  $\text{Er}_2\text{Ti}_2\text{O}_7$ . Of all the neutron inelastic spectra shown in **Figure 7**,  $\text{Er}_2\text{Ti}_2\text{O}_7$  is the only XY pyrochlore where the formation of the spin wave excitations coincides with the observation of long range magnetic order (110). A striking difference is observed between the low temperature inelastic spectra of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> and  $\text{Er}_2\text{Ti}_2\text{O}_7$ , despite the fact that both order into a  $\Gamma_5$  manifold. Instead of spin waves originating from the antiferromagnetic zone center, as observed in  $\text{Er}_2\text{Ti}_2\text{O}_7$ , Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> has its largest spectral weight near Q = 0, a ferromagnetic zone center (65).

Finally, comparing the low temperature inelastic neutron spectra of the three ytterbium pyrochlores in **Figure 7**, it is clear that they all share a common form for their spin excitation spectra. In each Yb pyrochlore, the zero field spin excitations are very unconventional, displaying a broad continuum of gapless excitations to temperatures as low as



Comparison of the low temperature (below  $T_C$  or  $T_N$ ) spin dynamics among the (a) ytterbium pyrochlores and (b)  $\text{Er}_2\text{Ti}_2\text{O}_7$  as measured by inelastic neutron scattering. Experimental details for each of these data sets can be found in the corresponding original publication: (a)  $\text{Yb}_2\text{Ge}_2\text{O}_7$  (65), (b)  $\text{Yb}_2\text{Ti}_2\text{O}_7$  (70), (c)  $\text{Yb}_2\text{Sn}_2\text{O}_7$  (75), and (d)  $\text{Er}_2\text{Ti}_2\text{O}_7$  (110). Note that  $\text{Yb}_2\text{Ge}_2\text{O}_7$  and  $\text{Er}_2\text{Ti}_2\text{O}_7$  share the same antiferromagnetic ordered state.

60 mK. The only substantial difference is the energy band-width of the spin excitations, which reduces as expected with increasing lattice parameter (65). The anisotropic exchange parameters for Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> should result in a  $\Gamma_9$  ferromagnetic ordered state at the mean field level (30, 91, 92), and this expectation has been partially fulfilled in some samples of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (69, 70, 94–96). Thus, at zero magnetic field, well defined spin waves and a relatively large spin wave gap are predicted to emerge at  $T_C$  (40, 70, 92). However, the zero field spin excitations reflect a far more disordered state. The evolution of this continuum of scattering at zero field into dispersing magnons at high field has recently been investigated in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (92). In magnetic fields up to 9 T, the intensity from two-magnon processes is strongly underestimated by a non-interacting spin-wave model, suggesting the presence of strong quantum fluctuations that persist even in high magnetic fields. At lower fields, there is an overlap between one and two-magnon states leading to strong renormalization effects and quasi-particle breakdown in zero field (92, 111, 112). Thus, the measured spin excitation spectrum of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> bears little resemblance to that predicted within the low temperature mean field ordered state.

# 4.2. SENSITIVITY TO DISORDER

Within the family of XY pyrochlores, only the titanates, Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, have long existed as large single crystals. Thus, for these two materials, comparisons can be made between polycrystalline materials, prepared by solid state synthesis, and single crystals, grown by the floating zone technique. This comparison has revealed that the magnetic ground state of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has a fascinating dependence on quenched disorder. This unusual sample dependence was first reported in early heat capacity studies (97, 113), and can be broadly summarized as polycrystalline samples possessing sharper heat capacity anomalies at relatively high  $T_C$ 's, while single crystal samples possess much broader anomalies, sometimes multiple peaks, and with considerably lower  $T_C$ 's (97,99,113–115). Subsequent characterization with neutron diffraction has revealed the likely origin of this effect: floating zone single crystals grown from stoichiometric precursors have a small concentration of anti-site defects. Specifically, a small fraction of Yb<sup>3+</sup> cations, on the order of 1%, can be stuffed onto the *B* site, leading to a net off-stoichiometry, Yb<sub>2+x</sub>Ti<sub>2-x</sub>O<sub>7- $\delta$ </sub> (98), which is necessarily accompanied by oxygen defects (116,117). Very recently, a systematic investiga-



The effect of quenched disorder on the magnetic properties of (a)  $Yb_2Ti_2O_7$ , adapted with permission from Ref. (33), copyrighted by the American Physical Society and (b)  $Er_2Ti_2O_7$ , adapted with permission from Ref. (121).  $Yb_2Ti_2O_7$  exhibits a pronounced sensitivity to small levels of off-stoichiometry while the long-range order of  $Er_2Ti_2O_7$  is robust to disorder.

tion of off-stoichiometry in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has been carried out, as shown in **Figure 8(a)** (33). It is clear that small levels of quenched disorder give a large and pronounced suppression of  $T_C$ , consistent with earlier studies, but now with the off-stoichiometry being introduced in a controlled manner. This same work also employed the traveling solvent floating zone method to successfully grow a stoichiometric single crystal of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> that exhibits a sharp heat capacity anomaly and a high  $T_C$ , also shown in **Figure 8(a)** (33). This sample variability, which is most conveniently demonstrated by heat capacity, has also been appreciated with muon spin relaxation ( $\mu$ SR) and neutron scattering, where some samples display the signatures of long range magnetic order (69, 70, 94–96, 114) and others do not (68, 91, 99, 118–120).

The sensitivity to quenched disorder observed in  $Yb_2Ti_2O_7$  is not seen in the low temperature phase behavior of  $Er_2Ti_2O_7$  (80). This is particularly interesting given that one would expect roughly the same type and concentration of disorder to be present in samples of each. To our knowledge, no sample dependence or variation between polycrystalline and single crystal samples of  $Er_2Ti_2O_7$  has been reported. In fact, systematic studies of magnetic dilution in  $Er_2Ti_2O_7$ , where  $Er^{3+}$  is substituted with non-magnetic  $Y^{3+}$ , show that dilution gradually suppresses  $T_N$ , consistent with the expectations of three dimensional percolation theory (Figure 8(b)) (121). However, while it has been shown that the  $\Gamma_5$  state is robust to disorder (104), there are theoretical proposals that magnetic dilution may induce a transition from  $\psi_2$  to  $\psi_3$ , without additional suppression of  $T_N$  (101, 122). Regardless, the insensitivity of the  $\Gamma_5$  magnetically ordered state in  $\text{Er}_2\text{Ti}_2\text{O}_7$  to impurities is consistent with the idea that it is far-removed from competing XY phases (40). Likewise, the astounding sensitivity of the ground state magnetism of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> to low levels of disorder or off-stoichiometry is qualitatively understood by its proximity to competing XY phases (40, 50). Indeed, small changes in stoichiometry could slightly vary the anisotropic exchange terms, which would naturally be expected to have a larger impact in the presence of proximate phases.

Floating Zone Crystal Growth: A crucible-free, melt based technique that can produce large, high quality single crystals.



Muon spin relaxation measurements showing that a sample of  $Yb_2Ti_2O_7$  that does not exhibit long range magnetic order at (a) ambient pressure can have magnetic order induced by the application of a modest (b) applied pressure of 19.7 kbar. (c) The resulting phase diagram for this sample of  $Yb_2Ti_2O_7$  showing how pressure can be used as a tuning parameter from splayed ferromagnet to quantum spin liquid. Adapted from Ref. (120) with permission.

# 4.3. SENSITIVITY TO APPLIED HYDROSTATIC PRESSURE

A corollary to the sensitivity of  $Yb_2Ti_2O_7$ 's ground state to quenched disorder, which can be thought of as inducing a chemical pressure, is that applied pressure may also be expected to have a disproportionate effect on ground state selection. The only other pyrochlore titanate with pronounced sensitivity to low levels of disorder and off-stoichiometry,  $Tb_2Ti_2O_7$  (32, 123), shows long range order induced out of its enigmatic spin liquid state by the application of external pressure (124, 125). Thus, a natural question that arises is, what effect would externally applied pressure have on a sample of  $Yb_2Ti_2O_7$  that does not exhibit the signatures of static magnetic order? The answer to this question is given in Figure 9(a) and (b), which presents the zero field muon decay asymmetry as a function of temperature for a stoichiometric powder sample of  $Yb_2Ti_2O_7$  in ambient pressure and at P = 19.7 kbar (120). With zero applied hydrostatic pressure, the form of the  $\mu$ SR time dependence displays little variation with temperature, maintaining a weak exponential falloff for all temperatures, above and below  $T_C$ , indicating a magnetically disordered ground state. However, with a hydrostatic pressure of 19.7 kbar, the  $\mu$ SR signal changes dramatically passing through  $T_C = 0.265$  K. There is a rapid relaxation of the muon polarization at early times, indicative of static internal fields and a magnetically *ordered* state. Complementary neutron diffraction measurements revealed that at P = 12 kbar this same sample of  $Yb_2Ti_2O_7$  undergoes a phase transition to a weakly-splayed ferromagnetic state (120).

These measurements on Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are summarized in a temperature-pressure phase dia-

gram, Figure 9(c) (120). For this sample, even the smallest applied pressure, P = 1.4 kbar, results in a long range ordered state. However, why the ground state selection of  $Yb_2Ti_2O_7$ should be so sensitive to applied pressure remains a mystery, likely interconnected to the

#### Muon spin relaxation: A

technique that uses spin polarized muons as a local probe of the distribution and dynamics of internal magnetic fields in materials.

mystery that surrounds why small levels of stuffing and other defects are so effective at disrupting what would otherwise be a simple ordered state: a splayed ferromagnet. The leading contenders to resolve these mysteries are that pressure, either applied or chemically-induced by impurities, shifts terms in the anisotropic exchange Hamiltonian of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, pushing the system from one phase to a nearby competing ordered structure within its classical phase diagram, as illustrated in **Figure 4** (40,50). Another factor is that the low level of Yb<sup>3+</sup> ions that sit at defect sites in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> will still carry magnetic moments, but due to the changed oxygen environment, will have Ising rather than XY anisotropy (51). Such defect moments may well be surprisingly effective in frustrating even simple ferromagnetic order. Of course, both of these effects could be relevant, possibly in combination with other factors.

# 5. XY PYROCHLORES BEYOND THE RARE EARTHS

The availability of large single crystals allows significantly more sophisticated measurements and analyses to be performed, which generally advances the physical understanding of a given material. As has been established in the prior sections, the ability to grow large single crystals of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has allowed the determination of their microscopic spin Hamiltonians. Such studies have thus far not been possible for the germanium, platinum, and tin based pyrochlores. The synthesis barrier to overcome in the case of the  $A_2$ Ge<sub>2</sub>O<sub>7</sub> and  $A_2$ Pt<sub>2</sub>O<sub>7</sub> pyrochlores is quite high, as these materials are prepared under high pressure conditions (of order GPa) (63,71). In the case of the  $A_2$ Sn<sub>2</sub>O<sub>7</sub> pyrochlores, the dilemma is the volatility of SnO<sub>2</sub> at high temperatures, which renders the melt-based techniques utilized in the titanate pyrochlores unsuitable. However, progress has recently been made with flux growth techniques - resulting in millimeter sized crystals of  $A_2$ Sn<sub>2</sub>O<sub>7</sub> pyrochlores (126).

Beyond the rare earth pyrochlores, and indeed beyond oxides, recent progress has been made in the growth of fluoride pyrochlores,  $AA'B_2F_7$ . In these fluoride pyrochlores, the magnetic ions are 3d transition metals that sit on the B site and the nonmagnetic A/A'site has mixed occupancy to preserve charge neutrality. A handful of these fluoride materials have recently been synthesized, such as NaCaNi<sub>2</sub>F<sub>7</sub>, NaSrMn<sub>2</sub>F<sub>7</sub>, and NaCaFe<sub>2</sub>F<sub>7</sub>, and there is great promise for expansion of this family (127–130). These materials present an exciting opportunity as they incorporate magnetic cations that are not generally accessible with oxide pyrochlores. Furthermore, the magnetic ions are transition metals, rather than rare earths, and hence the exchange interactions are stronger and the characteristic temperature scales are higher. Moreover, these new fluoride pyrochlores are grown using the floating zone method and are thus readily available as large single crystals.

While detailed investigations of this new family have only recently begun, already there have been interesting developments for XY phenomenology with NaCaCo<sub>2</sub>F<sub>7</sub>, where the magnetism originates from Co<sup>2+</sup> in an effective  $S = \frac{1}{2}$  state (132). This material undergoes a spin freezing transition at  $T_f = 2.4$  K due to weak exchange disorder arising from the random distribution of Na<sup>+</sup> and Ca<sup>2+</sup> on the A sublattice (127). Elastic neutron scattering measurements and simulations for NaCaCo<sub>2</sub>F<sub>7</sub>, shown in **Figure 10(a)** and **(d)**, reveal that within this frozen state, clusters of spins achieve short range order within the XY ( $\Gamma_5$ ) manifold (131), and are argued to form a mosaic of  $\psi_2$  and  $\psi_3$  (133). However, the inelastic spectra at energy transfers of  $\Delta E = 1.25$  meV is described by a combination of XY and collinear antiferromagnetic spin configurations, as shown in **Figure 10(b)** and **(e)**. At still higher energy transfers,  $\Delta E = 4.75$  meV, the spectra can be described by



The top row shows inelastic neutron scattering maps of NaCaCo<sub>2</sub>F<sub>7</sub> at various energy transfers, (a) Elastic,  $\Delta E = 0.00 \text{ meV}$ , (b)  $\Delta E = 1.25 \text{ meV}$ , and (c)  $\Delta E = 4.75 \text{ meV}$ , all with an integration of ±0.17 meV. The bottom row shows calculated spectra that are consistent with the experimental data, indicating static short range order in the XY  $\Gamma_5$  manifold and excitations consistent with both  $\Gamma_5$  and a collinear antiferromagnetic state. Adapted from Ref. (131) with permission, copyrighted by the American Physical Society.

a collinear antiferromagnetic model alone (Figure 10(c) and (f)). Ultimately, the spin freezing transition in NaCaCo<sub>2</sub>F<sub>7</sub> preempts the breaking of the  $\Gamma_5$  degeneracy and the formation of a long range ordered state (131). However, the coexistence of dynamics from the XY ( $\Gamma_5$ ) manifold and those originating from a collinear antiferromagnet indicate that phase competition may also be a factor in this material.

In this review we have focused our attention on the cubic pyrochlore lattice. However, other exciting avenues exist to investigate XY anisotropy with related crystalline architectures. One such class of materials is the rare earth chalcogenide spinels,  $CdR_2Se_4$  and  $CdR_2S_4$ , where the rare earth cation R again forms a 3D network of corner-sharing tetrahedra (134). In a reversal from the case of the rare earth pyrochlores, erbium in this geometry has local Ising anisotropy, resulting in a spin ice state (135). However, it has been predicted that a dysprosium variant,  $CdDy_2Se_4$ , would realize XY spin anisotropy (43), making it a good candidate to explore the types of phenomenology discussed here, possibly including phase competition. A little further afield, another direction for future work is the so-called "tripod kagome" systems,  $R_3Mg_2Sb_3O_{14}$  and  $R_3Zn_2Sb_3O_{14}$ , where R is a rare earth cation (136–138). This chemical formula can be thought of in terms of a doubling of the pyrochlore lattice, where a quarter of the rare earth sites are replaced by antimony. The resulting structure is a two-dimensional kagome lattice of rare earth cations. Detailed investigations of these materials have only recently begun. However, the ytterbium and erbium variants of this family may retain the XY anisotropy of the pyrochlore parent compounds, and in this regard would make interesting case studies.

Kagome Lattice: A two-dimensional lattice made up of corner sharing triangles and a canonically frustrated architecture.

# 6. SUMMARY AND FUTURE ISSUES

#### SUMMARY POINTS

- 1. The nature of their crystal electric field ground states imparts the erbium and ytterbium pyrochlores with XY spin anisotropy and effective  $S = \frac{1}{2}$ .
- 2. Many of the observed properties of the ytterbium and erbium pyrochlores can be attributed to the combination of anisotropic exchange and XY spin anisotropy. The general form of the nearest neighbor anisotropic exchange Hamiltonian produces a rich phase diagram, and competition between phases is likely key to understanding their exotic low temperature properties.
- 3. The experimental signatures of phase competition are multiple heat capacity anomalies, suppressed  $T_N$  or  $T_C$ , and anomalous spin dynamics.
- 4. Many of the peculiarities of ground state selection in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, including extreme sample and pressure dependence, can be qualitatively understood within the scenario of phase competition.
- 5.  $Er_2Ti_2O_7$ , with a single relatively high temperature heat capacity anomaly, appears insensitive to phase competition and correspondingly, is robust to weak disorder.

#### **FUTURE ISSUES**

- 1. Can phase competition within the anisotropic exchange model quantitatively account for all the exotic features observed in the XY pyrochlores, including their multiple heat capacity anomalies?
- 2. What is the origin of the unconventional spin excitations observed in the ytterbium XY pyrochlores?
- 3. With the prediction of emergent quantum electrodynamics, the physical properties of quantum spin ice are remarkable. Are any of these emergent properties, such as photon-like excitations, manifest in the XY pyrochlores?
- 4. Could strong phase competition result in a quantum spin liquid state, and what would the experimental signatures of this spin liquid be?
- 5. Can order-by-disorder be uniquely distinguished as the ground state selection mechanism in Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>?

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# Chapter 6

# Conclusions and Future Directions

This thesis has examined the effect of chemical pressure on the magnetic ground states of the rare earth pyrochlores,  $R_2B_2O_7$ . A common element to the works presented is that, in each case, powerful high pressure synthetic techniques were used to stabilize compositions that cannot be obtained, for various reasons, using conventional solid state synthesis. Specifically in these works, high pressure synthesis was used to prepare a suite of germanium, lead, and platinum based rare earth pyrochlores. Our work is amongst the first magnetic characterizations of these families of materials. Germanium and lead are respectively the smallest and largest *B* site cation that can be incorporated onto the pyrochlore structure with a rare earth at the *R* site. Thus, as the lattice parameter scales with the ionic radius of *B*, these materials exist at the edges of the pyrochlore stability field. The rare earth pyrochlores are often found to inhabit a rich phase space and thus, it is instructive to venture to its extreme edges to build an experimental phase diagram. Once a phase space is mapped out for a given rare earth, *R*, fruitful comparison can be drawn with theory.

In **Paper I** and **Paper II** we present a detailed investigation of  $Yb_2Ge_2O_7$ , which is a positive chemical pressure analog to  $Yb_2Ti_2O_7$  and  $Yb_2Sn_2O_7$ . We show that the effect of positive chemical pressure is to transition the ground state from ferromagnetic to antiferromagnetic, in agreement with theoretical works [83]. Despite their different ordered states, there is a striking similarity to the form of the low temperature spin dynamics amongst these three ytterbium pyrochlores. Stranger still is that in each case these excitations have a highly unusual form and temperature dependence. The shared form of these excitations undoubtedly points to a shared microscopic mechanism - a fact that may ultimately shed some light on this interesting phenomenology. In **Paper III** we investigated  $Tb_2Ge_2O_7$ , which is a positive chemical pressure analog of Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. This comparison is particularly interesting because Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has previously been studied with externally applied pressure, which is found to induce antiferromagnetic order out of a putative spin liquid state [117]. A markedly different result is obtained with positive chemical pressure: the low temperature state of Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> has ferromagnetic character. Thus, chemical pressure and externally applied pressure are having intriguingly different effects in the terbium pyrochlores. This result, along with many others, exemplifies the complexity inherent to terbium pyrochlores due to many intertwined effects, such as a low-lying crystal electric field level [99, 102], coupling of lattice and magnetic degrees of freedom [109–113], and sensitivity to disorder [59]. In fact, sensitivity to astonishingly small levels of off-stoichiometry is a shared attribute between Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [63]. It would be interesting to probe whether a fragile low temperature magnetic state (*ie.* sample dependence) is also at play in Tb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> and Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>.

**Paper IV** reports the first detailed characterization of the magnetic properties of the lead based pyrochlores,  $R_2Pb_2O_7$  (R = Pr, Nd and Gd). As lead is the largest *B* site cation compatible with the pyrochlore structure,  $R_2Pb_2O_7$  pyrochlores have a strong propensity for site mixing. As just mentioned, nearly undetectable levels of site mixing have been identified as important to the presence or absence of long-range magnetic order in several well-studied titanate pyrochlores. Thus, it is interesting to examine the effect of site mixing in a larger limit. In the cases of Nd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> and Gd<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub>, site-mixing does not prohibit the formation of a magnetically ordered state, indicating a robustness to disorder for these rare earth cations. The low temperature magnetic properties of Pr<sub>2</sub>Pb<sub>2</sub>O<sub>7</sub> indicate some spin ice-like character, in similitude with other praseodymium pyrochlores.

In Paper V and Paper VI we investigate the effect of platinum substitution on rare earth magnetism in the materials  $Gd_2Pt_2O_7$  and  $Er_2Pt_2O_7$ . Platinum is a close ionic radius match with titanium, and thus these materials do not incur substantial chemical pressure with respect to their titanate analogs. Nonetheless, we do find that their magnetic ground states are substantially altered. In the case of  $Gd_2Pt_2O_7$ , we measure a transition to long-range antiferromagnetic order at a Néel temperature of  $T_N = 1.6$  K, an impressive 60% enhancement from the 1 K Néel temperatures seen in most other gadolinium pyrochlores. Being able to eliminate chemical pressure, crystal electric field effects, and dipolar interactions as the source of this enhancement we conclude that it must originate from the details of the orbital overlap, *ie.* the exchange interactions. A likely scenario is that non-magnetic platinum is able to facilitate superexchange through its empty  $5d e_g$  orbitals. In  $Er_2Pt_2O_7$ , we find that this additional exchange pathway

is responsible for a 75% suppression of  $T_N$  from that of  $\text{Er}_2\text{Ti}_2\text{O}_7$ . Moreover, our neutron scattering measurements confirm a change of ground state, with  $\text{Er}_2\text{Pt}_2\text{O}_7$  ordering into the  $\Gamma_7$ Palmer-Chalker state, the first XY pyrochlore found to possess this ground state. We interpret the suppression of  $T_N$  in  $\text{Er}_2\text{Pt}_2\text{O}_7$  as originating from phase competition between the neighbouring  $\Gamma_5$  and  $\Gamma_7$  states. Many of these ideas are explored in more detail in the final work of this thesis, **Paper VII**, which is a review article on the XY pyrochlores with a focus on experimental works and phase competition.

The clear benefit of high pressure techniques is that they allow the synthesis of materials that cannot otherwise be obtained. In many cases, these materials will reside at the edges of the stability field for a given magnetic cation, meaning that they are particularly useful in mapping out the phase space. The most apparent disadvantage of high pressure techniques is that it is not a straightforward endeavor to obtain single crystalline samples. As magnetism is inherently anisotropic, not being able to measure the directional dependence of, for examples, spin wave excitations, is a distinct disadvantage. Indeed, while many questions remain to be answered about the materials we've investigated in this thesis, most of them are best suited to experiments on single crystal samples. For example, the question of whether Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> is ordering into the  $\psi_2$  or  $\psi_3$  basis state is an interesting and open question. Another example is the determination of these materials microscopic Hamiltonians, which in the cases of  $\text{Er}_2\text{Ti}_2\text{O}_7$  and Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, was achieved by fitting the spin waves in the field polarized state [61,70]. Recently, there have been reports of single crystals of stannate pyrochlores grown using flux methods [145]. Similar methodology may prove promising for the germanate, plumbate, and platinate pyrochlores. Developments in this area would certainly lead to new and exciting possibilities.

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