DISSERTATION

FRUSTRATION DRIVEN EMERGENT PHENOMENA IN QUANTUM AND CLASSICAL MAGNETS

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In partial fulfillment of the requirements For the Degree of Doctor of Philosophy Colorado State University Fort Collins, Colorado Spring 2021

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ABSTRACT

FRUSTRATION DRIVEN EMERGENT PHENOMENA IN QUANTUM AND CLASSICAL MAGNETS

Frustrated and quantum magnets remain a fascinating and broad area of physics with applications ranging from information science to commercial applications. The wide breadth of possible behavior, caused through the combination of frustration, anisotropy, and many-body physics allow for a large number of exotic phenomena to be realized within these systems. In this dissertation, I cover work on three compounds which all exhibit unusual properties in their low temperature magnetic phases. For Fe₃PO₄O₃, the low temperature static magnetic structure shows partial magnetic ordering, where the system orders commensurately along the c-axis and retains a well-defined ordering wavevector in magnitude but not direction within the *ab*-plane. Within a simple Heisenberg J_1 - J_2 model, Luttinger-Tisa ground state calculations show the existence of a quasi-degenerate well of lowest energy states coinciding with the rings of scattering observed in neutron diffraction. Taken with polycrystalline data, a small correlation size in the *ab*-plane suggests a large number of topological defects present in Fe₃PO₄O₃. A few possible magnetic textures which could produce the observed behavior in $Fe_3PO_4O_3$ are discussed. In the antiferromagnetic pyrochlore Yb₂Ge₂O₇, continuum excitations were previously found through neutron scattering below this material's long range magnetic ordering temperature. By comparing field polarized inelastic neutron scattering data to linear spin wave theory we extract the four unique exchange parameters and placeYb₂Ge₂O₇ within a classical phase diagram. We find Yb₂Ge₂O₇ lies in close proximity to the boundary between an antiferromagnetic and ferromagnetic state leads to a phenomenon known as phase competition, where the excitations are poorly defined because of the influence of the neighboring state. Finally non-equilibrium dynamics in CoNb₂O₆ show the existence of a frozen state existing within its commensurate antiferromagnetic long range ordered state. This frozen state introduce aging effects at low temperatures in $CoNb_2O_6$, complicating its behavior. Following quenches of a magnetic field transverse to all moments in this material, we observe a relaxation below its field-induced phase transition into the commensurate antiferromagnetic state. Quenches of a transverse field exhibit a scaling behavior as a function of quench rate remarkably similar to a Kibble Zurek mechanism, although in our experiments, this behavior can be traced back to systematic effects. Each of these materials exemplify distinct unusual behaviors possible in low temperature quantum and frustrated magnetism.

ACKNOWLEDGEMENTS

I would like to thank many people who helped me throughout my Ph.D process. I would first like to thank my wonderful wife Megan, who was willing to support and believe in me throughout this process. Her kindness and support has meant everything to me throughout my Ph.D. She has gotten me through the best and worst of times over the past 7 years and I am by far a better person with her by my side. My parents, Judy and Ramsey, have also been beacons of encouragement for as long as I can remember, and my life would not be the same without their support. They are always there to offer anything they can to help. I hope this document in some way makes up for the years of love and support you have given me. I would like to acknowledge Hayden George and Leif Hoover for being some of the best friends one can ask for. Endless stream of memes aside, being friends with you both is and will always be my esteemed honor and pleasure. Thanks to all the CSU physics graduate students from 2016 for keeping us all sane through classes and research, in particular Alec Iverson and Chris Slone for always being ready to hangout and have a beer. I would also like to acknowledge the rest of Rosslab, who always look out for each other, and are there for whatever. In particular Gavin Hester, Danielle Yahne, and Steffen Säubert. Gavin, thanks for always being there with an answer to a question, a voice of support, or even just an offer for a round of Among us to take off some stress. Danielle, thank you for always lending an ear or a hand. You have been one of the most supportive colleagues I have had the pleasure of working with. Playing board games with you and Kevin over the weekend remains some of my favorite memories from the last few years. Steffen, thanks for being the outspoken extrovert who was always up for hanging out. It was for our own good, even if the rest of us didn't always feel like it. Traveling with you on the experiments and learning from you was always an enjoyment. Thanks to all my undergraduate professors, who not only fostered and developed my love for science, but encouraged me to apply to graduate school despite me being a mediocre student. Thank you to all the instrument scientists, Huibo Cao, Jose Rodriguez-Riviera, Feng Ye, Eun Sang Choi for your help running experiments and teaching me the ins and outs of the instruments, as well as

the support for future endeavors. Thanks to all of my collaborators and everyone in the frustrated magnetism community for fostering a supportive community to discuss and learn physics. You have all made entering this field feel approachable and interesting. Thank you to my committee members Prof. Matthew Shores, Prof. Kristen Buchanan, Prof. Marty Gelfand, and Prof. Jose de la Venta. Last I would like to thank my advisor Prof. Kate Ross. Working with you was an inspiration and an honor. Despite always being busy from being a new professor and a new mother, you have always tried to be available for discussion and teaching opportunities. You never made learning the subject of frustrated magnetism feel impossible or boring. Thanks for being one of the best advisors a student could ask for.

DEDICATION

I would like to dedicate this thesis to wife, Megan as well as my parents, Judy and Ramsey Sarkis. This work was only possible because of you.

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Chapter 1

Introduction

This chapter will provide a basic introduction to quantum magnetism in solid state materials, phase transitions, frustrated magnetism, and quasiparticle descriptions of low energy excitations. I reserve discussion on more in-depth and material specific topics for the specific material chapters. Details of experimental instrumentation, in particular neutron scattering, is reserved for Chapter 2. There are many resources one can find which cover condensed matter and magnetism extensively. In particular I used many books, [1, 2, 3, 4, 5, 6, 7, 8, 9, 10], lectures and class notes [11, 12, 13], and review papers [14, 15, 16, 17] as references.

1.1 Magnetism and Phase Transitions

For all magnetic materials at high temperatures, thermal fluctuations are strong enough to destroy the preference of magnetic spins to order, and the resulting state is known as a paramagnet. Within the paramagnetic phase a macroscopic description of magnetism can be described through two quantities, the magnetization M and magnetic susceptibility χ . The magnetization can be described as the response of the system's free energy to a magnetic field, H.

$$\boldsymbol{M} = -\left(\frac{\partial F}{\partial \boldsymbol{H}}\right) \tag{1.1}$$

while the magnetic susceptibility is defined as the response of the magnetization to an applied field.

$$\chi = \frac{\partial M}{\partial H} = -\frac{\partial^2 F}{\partial H^2}$$
(1.2)

While in the paramagnetic phase, random fluctuations of individual moments tend to cancel each other, leading to a net magnetization of zero without an applied field. Application of an external field breaks the continuous rotational symmetry and favors a particular direction for the moments to

align, creating a non-zero macroscopic magnetization. An estimate to the form of the paramagnetic susceptibility in some insulating materials can be made at low applied fields (or high temperature) through the treatment of non-interacting magnetic moments [4]. This leads to the Curie form of the paramagnetic susceptibility

$$\chi_C = \frac{C}{T} \tag{1.3}$$

where $C = \frac{n\mu_{eff}^2}{2k_B}$ is known as Curie's constant and T denotes temperature. A positive susceptibility corresponds to a tendency for classical spins to align with the applied field, and is constructed around systems with unpaired electrons (magnetic). Another term present in materials with closed electron shells is diamagnetism. The diamagnetic susceptibility can be formed classically through the application of Lenz's law, which shows a magnetic field will create circular current of electrons which form their own magnetic field, opposing the applied field. Following this form and treating magnetic moments as current loops with Larmor precession, one can arrive at the Langevin diamagnetic susceptibility

$$\chi_{dia} = -\frac{\mu_0 n Z e^2}{6m_e} \langle r^2 \rangle \tag{1.4}$$

where Ze is the electron charge of Z electrons undergoing Larmor precession, m_e is the mass of the electron, μ_0 is the permeability of free space, and $\langle r^2 \rangle$ represents the mean square of the perpendicular distance of the electron from the applied field axis. In the case of Langevin susceptibility $\langle r^2 \rangle$ was taken for a spherically symmetric charge distribution. One can note that in the case of diamagnetism, the negative susceptibility indicates the preference for spins to oppose the field classically. While diamagnetism is present in all materials, magnetic contributions, such as paramagnetism and ferromagnetism are often much larger in magnitude and dominate the behavior of the magnetic susceptibility in these systems.

Most magnetic materials feature a key characteristic temperature scale, below which the system spontaneously breaks the rotational symmetry of the paramagnetic state and orders into a longrange ordered state. Such a description separates two distinct phases of the magnetic system, separated by a phase transition. Classically, the phase transition is characterized by its transition temperature, T_c , and the onset of an order parameter. Such transitions can either be *first-order*, where (at T_c) the order parameter itself features a discontinuity, or higher order, where powers of the derivatives of the order parameter are discontinuous (at T_c).

A phenomenological model for *second-order* phase transitions was developed by Lev Landau based on the concept of spontaneous symmetry breaking and the Free Energy's response to a complex scalar order parameter ψ [18, 19]. Near the transition, Landau hypothesized that the Free Energy could be Taylor series expanded into powers of the order parameter

$$F = F_0 + \alpha |\psi|^2 + \gamma (\nabla \psi)^2 + \beta |\psi|^4$$
(1.5)

where α , β , and γ are temperature dependent constants. The choice of order parameter depends on the inherent symmetry of the system, and for magnetic systems the order parameter is most often the local magnetic moment M. To be time-reversal symmetric, only even powers of M(or gradient of M) are allowed. The two phases are separated by a critical value (temperature), below which the order parameter becomes non-zero. For magnetic systems the spontaneously broken symmetry is rotational symmetry. Above the transition the state is paramagnetic, with the individual spins randomly oriented and the average magnetic moment of the system being zero, $\langle M \rangle = 0$. Below the transition, specific orientations are favored and, even though fluctuations can still be present, the average magnetic moment will become non-zero, $\langle M \rangle \neq 0$. The utility of Landau theory in regards to condensed matter phase transitions relies on its connections to group theory, which remains a powerful tool in understanding crystalline systems [5, 20]. Symmetries present in a crystal define its crystal space group and the ordered magnetic state will always be a subgroup of the crystal space group. This requirement greatly reduces the possible states and parameters available and gives a tractable approach for the determination of a magnetic structure. While Landau theory cannot explain certain exotic ordering, such as topologically ordered or spin liquid states where no symmetry was broken, it remains an important model describing classical and quantum phase transitions.



Figure 1.1: Example phase diagram for a quantum phase transition. At zero-temperature, a QCP separates an ordered and quantum disordered state. At finite temperatures a region remains where quantum fluctuations dominate the behavior. For higher temperatures the system is a paramagnet.

Analogous to a classical or thermal phase transition, where *thermal fluctuations* tune between two phases of a system at a critical temperature, a quantum phase transition is a zero-temperature phase transition at a critical value of a non-thermal parameter, such as external pressure or magnetic field [10, 14]. In this case *quantum fluctuations* diverge and drive the transition between an ordered and disordered state. Magnetic systems, most notably the transverse field Ising model, have remained paradigmatic examples of systems exhibiting quantum phase transitions. While experimentally T = 0 is not physically realizable, the properties of the quantum phase transition can remain at low but finite temperatures near the critical point. Thermal and quantum fluctuations, $\hbar\omega$, is greater than the thermal fluctuations, k_BT , the system is expected to retain its quantum critical behavior. An example phase diagram of a system exhibiting a quantum phase transition to a quantum control parameter is shown in Fig. 1.1.

Quantum phase transitions show that many interesting effects can take place when quantum effects become important. In many materials, the rough classical approaches to magnetism are not

sufficient to describe their properties, particularly at low temperatures, and an approach using the quantum nature of magnetism within a condensed matter framework are required.

1.2 Quantum Magnetism

In condensed matter systems, the atoms form into vast networks which can either be periodic (crystals), irregular (liquids/amorphous) or even somewhere in between (liquid crystals). Magnetism in condensed matter arises from unpaired electrons in the system. Magnetism can arise in either localized electron systems, where the electrons are confined to their parent nucleus, or itinerant electron systems, where the electron is unbound from the parent nuclei. The subject of itinerant magnetism is a fascinating and complicated one, but will not be addressed in this work. Instead, I will focus on insulating magnetic materials with localized electrons.

For localized electrons, at a single-ion level, the interaction of an electron with its parent nucleus is broken up into two components: the orbital angular momentum of the electron (m_l) , and the intrinsic spin angular momentum of the electron (m_s) . The orbital momentum represents the electrons being localized to specific orbitals around the nucleus. These orbitals were originally classified by the names sharp (s : l = 0, principal (p : l = 1), diffuse (d : l = 2), and fundamental (f: l = 3) [21]. For a given l, the components of m_l range from $m_l = -l, -l+1, ..., l-1, l$. The intrinsic spin angular momentum of an electron is $s = \frac{1}{2}$ such that m_s is two-valued canonically: $m_s = \pm \frac{1}{2}$. These momenta combine through spin-orbit coupling to produce a new good quantum number describing the angular momentum, J, with 2J+1 degenerate m_J states. Through the spin-orbit coupling, anisotropy in magnetic properties can develop, which are often important in describing the behavior of the magnetic system [22]. The spin-orbit coupling scales with the number of protons as Z^4 , making the scale of the interaction far more dominant in heavier magnetic systems [1]. If the repulsion of valence electrons can be assumed to be much larger than the spin-orbit coupling, the formation of the total angular momentum J is performed through the use of Hund's rules. Hund's rules state that the ground state of a free ion is the that which maximizes spin S following Pauli-exclusion and then maximizes orbital momentum L, through which the system reduces Coulomb repulsion. The orbital and spin components combine to form the total angular momentum through spin-orbit coupling J = |L - S| for an orbital that is equal to or less than half-full and J = |L + S| for an orbital that is more than half-full. The associated effective magnetic dipole moment of the electron, μ_{eff} , is given by

$$\mu_{eff} = -g_J \mu_B \sqrt{J(J+1)} \tag{1.6}$$

where μ_B is the Bohr magneton and g_J is the Landé g-factor, which is given by

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$
(1.7)

when $g_L = 1$, and $g_S = 2$. In the presence of a magnetic field, B, the degeneracy of the total angular momentum states is lifted due to Zeeman splitting.

$$H_Z = -\boldsymbol{\mu}_{eff} \cdot \boldsymbol{B} \tag{1.8}$$

In condensed matter systems, the electrons differ from the free-ion picture above through additional interactions with neighboring atoms, which depend on the symmetries of the system. The first effect of neighboring atoms is described by the crystal electric field the magnetic ion feels from neighboring non-magnetic atoms, while the second are interactions from neighboring magnetic ions including exchange and dipolar interactions.

1.2.1 Crystal Electric Field

Effects from coordination to ligands in condensed matter systems can distort orbitals of the magnetic ion. The distortion of orbitals causes the degenerate orbitals to split in energy according to the symmetry of the ligands surrounding the magnetic ion. A good approximate treatment of the crystal field is often well-represented by an electrostatic approach, where the ligands are treated as negatively charged ions and stationary point charges. This tends to work best for localized

systems where the bonding can be described as highly ionic. Using this method, one can model a rough approximation of covalency within the system by screening or varying the charge value of the anion [23]. A better treatment of covalency in the bonding, such as needed for the 3*d* ions, is better described through the more robust ligand field theory [24, 25], where crystal field theory is combined with molecular orbital theory.

For the 3*d* transition metal ions, the crystal electric field is often the strongest interaction and splits the orbital *d*-states according to the symmetry of the ligand field around the transition metal ion. A couple examples related to materials covered later are shown in Fig. 1.2. The *d*-orbitals (l = 2) form into five orbitals: d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$, d_{z^2} . In an octahedral environment, with ligand charges along the Cartesian axes, one can see that the d_{z^2} and $d_{x^2-y^2}$ orbitals will lie along the axes closer to the ligands. This will raise the energy of these orbitals compared to d_{xy} , d_{xz} , and d_{yz} which do not lie directly along the bonding axes and are thus further away from the ligands. In the case of a trigonal bipyramidal coordination, the d_z^2 orbital is the only one that lies completely on the axes, making it the highest energy orbital. The two orbitals contained in the *xy*-plane (d_{xy} and $d_{x^2-y^2}$) have one side of the orbital along the ligand axes, making them higher energy than the two out of plane orbitals $d_x z$ and $d_y z$. In crystalline environments, most 3*d* ions orbital angular momentum is quenched, such that only the spin angular momentum remains. The effect of the spin-orbit interaction can restore some degree of the orbital angular momentum, but is usually ignored in initial calculations.

For rare-earth magnets, the localized 4f ions are shielded by the 5s and 6s shells. Because of this, the spin-orbit coupling is often a much stronger interaction and thus the crystal electric field can be described as a perturbation on the 2J + 1 total angular momentum states that lifts their degeneracy [17, 26]. The form of the crystal electric field Hamiltonian depends on the point group symmetry at the rare-earth ion site. One of the most widely-used formulations of the crystal electric field Hamiltonian is given by the Steven's notation [26, 27]. Following the Stevens notation, the crystal electric field Hamiltonian is



Figure 1.2: Examples of crystal field effects on the *d*-orbitals in 3*d* transition metal ion for an octahedral (CoNb₂O₆) and trigonal bipyramidal (Fe₃PO₄O₃) symmetry of the ligand field. For octahedral coordination, the d-orbitals split into the triply degenerate t_{2g} and doubly degenerate e_g orbitals.

$$H_{CEF} = \sum_{n,m} B_n^m \hat{O}_n^m \tag{1.9}$$

where B_n^m are coefficients that depend on the angular momentum quantum numbers n and m, and \hat{O}_n^m are Stevens operators, which are operators made up of combinations of either the total angular momentum J in the case of rare earths, or the coupled momentum L for 3d transition metals. The symmetry of magnetic ion dictates which coefficients are zero; for instance, if inversion symmetry is present at the magnetic ion site all n = odd coefficients are zero.

Crystal field excitations represent single-ion excitations, rather than collective, and are thus local excitations. A quantitative description of the splitting between the crystal field states can be made by measuring the the excitations directly, which show up as flat dispersion-less excitations that decay in intensity for larger momentum transfers, following the form factor of the ion inquestion.

1.2.2 Exchange Interaction

Unpaired spins in condensed matter systems are coupled through through an interaction known as the exchange interaction. The source of the exchange interaction is most easily described by a two electron picture [2]. When brought together, Pauli exclusion will give rise to a S = 0 spin singlet state and a S = 1 spin triplet state. Because the overall wavefunction must remain antisymmetric with respect to exchange, the spatial wavefunctions describing the singlet and triplet states differ. The Hamiltonian of such a system is given by

$$H = \frac{1}{4}(E_s + 3E_t) - (E_s - E_t)\mathbf{S}_1 \cdot \mathbf{S}_2$$
(1.10)

where E_s and E_t represent the energies of the singlet and triplet states respectively. From this Hamiltonian, we see the first term just gives an overall shift to the ground state energy, while the second term gives the exchange interaction. The energy difference between the singlet and triplet energies, $E_s - E_t$, can be calculated from an exchange integral

$$E_{s} - E_{t} = \int \psi_{1}^{*}[\boldsymbol{x}_{1}]\psi_{2}^{*}[\boldsymbol{x}_{2}]\hat{H}\psi_{1}^{*}[\boldsymbol{x}_{2}]\psi_{2}^{*}[\boldsymbol{x}_{1}]d^{3}x_{1}d^{3}x_{2}$$
(1.11)

where $\psi_i[x_i]$ is a single particle wavefunction of one electron at position x_i . Dropping the first term and defining this exchange integral as J, known as the exchange constant, we arrive at the following Hamiltonian for the exchange interaction between two electrons.

$$H = -J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 \tag{1.12}$$

While this was constructed for a two electron system, the exchange interaction can be generalized into a full ensemble of interaction spins. For an ensemble of pair-wise interacting spins, the simplest general form of the above exchange interaction is given by the isotropic Heisenberg exchange Hamiltonian

$$H_{Heisenberg} = -J \sum_{\langle ij \rangle} S_i \cdot S_j \tag{1.13}$$

where $\langle ij \rangle$ denotes a sum over nearest neighbor interactions. In principle the exchange integral can be either positive or negative depending on the specific system being investigated. For J >0 the exchange favors a state with parallel spins or ferromagnetic order while J < 0 favors an antiparallel or antiferromagnetic arrangement of spins.

In stark contrast to Heisenberg exchange interactions, which favor either the parallel or anti parallel spin configurations, anti-symmetric exchange produced through spin orbit coupling favors

spins to orienting orthogonally. Originally introduced by Igor Dzyaloshinskii in 1958 and formulated in terms of the spin orbit coupling later in 1960 by Toru Moriya, this form of exchange is most commonly referred to as the Dzyaloshinskii-Moriya Interaction (DMI)[28, 29]. The form of the DMI Hamiltonian is given by:

$$H_{DM} = \sum_{\langle ij \rangle} \boldsymbol{D}_{ij} \cdot [\boldsymbol{S}_i \times \boldsymbol{S}_j]$$
(1.14)

where the D_{ij} is the orientation vector, which has both its magnitude and direction constrained by the lattice symmetry. It remains a key interaction in many systems with unusual or frustrated interactions due to its direct competition with a Heisenberg-like interaction. Aside from being a contributing factor to the creation of incommensurate magnetic structures, the DMI has been linked to magnetic topological textures known as skyrmions as well as the generation of the magnetoelectric effect in some multiferroics.

Spin-orbit coupling can lead to anisotropy in exchange as well as single ion properties, and is often found in real materials. Heavier ions such as the rare earth lanthanides feature strong spin orbit coupling, and can show strong anisotropy in their properties. Such anisotropy can be often play an important role in exotic and unusual magnetic systems and can force characteristic behavior to the ground states in these materials. One type of anisotropy found is Ising anisotropy, where the local zz coupling is large and the other two components are either much smaller or zero.

The Ising Model

The Ising model can be regarded as one of the most ubiquitous models in physics. Much like the harmonic oscillator, its prevalence is aided by the fact that many problems can be mapped onto the Ising model. Adaptations of the Ising model remain an important tool in the fields of phase transitions and critical phenomena [10], magnetism [2, 9, 10], quantum information science [10], neuroscience [30], and much more. The Ising model is given by

$$H_{Ising} = -J \sum_{\langle i,j \rangle} \sigma_i^z \sigma_j^z - h \sum_i \sigma_i^z$$
(1.15)

where σ_i^{α} ($\alpha = x, y, z$) are Pauli spin matrices and *h* represents an external magnetic field. As a two-valued scalar model, it has been solved analytically in one dimension and two dimensions. The solution of the 1D Ising model was original performed by Ernest Ising himself in his 1925 thesis [31], while the solution for the 2D case was first shown by Lars Onsager using a transfer matrix method [32]. While not analytically solved, numerical solutions to the Ising model in 3D have been performed [33, 34], and above 4D, the Ising model can be described by a mean-field picture [35]. The Ising model is amenable to both classical and quantum formulations of spin- $\frac{1}{2}$ systems, and the Ising model can be regarded as a special occurrence of the more generalized Potts model with q = 2 [36, 37].

Sources of Exchange in Condensed Matter

Physically, the exchange interaction is generated through a few possible mechanisms. The exchange interaction can be coupled via direct overlap of the electron orbitals, known as direct exchange, or mediated by a shared ligand, as in superexchange. In the case of superexchange, a qualitative description of the form of the superexchange can be found through the Goodenough-Kanamori rules [38, 39, 40]. Another variation between two separate oxidation states of a magnetic atom is double exchange, where a superexchange between two oxidation states favors a ferromagnetic interaction to allow for electron hopping between two strongly Hund's-coupled ions. Although not discussed in the context of this dissertation, metallic systems can also realize exchange through the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction which can couple localized moments through conduction electrons.

Other Magnetic Interactions

While for many magnetic systems exchange interactions can be the dominant term in the Hamiltonian, there are in principle other magnetic interactions present, which may be necessary for an accurate depiction of the magnetic properties. Most commonly, dipolar coupling of spins can be an important term in the Hamiltonian. Unlike exchange, which are generally very short ranged interactions, dipolar interactions fall off as $1/r^3$, making them much longer ranged. The

long range nature of the dipolar interaction makes its implementation difficult for most models. The strength of the dipolar interaction depends on the size of the magnetic moments as well as the distance between atoms. Such dipolar effects are particularly prominent for rare earth systems, where along with large moments, rare earths systems feature weak exchange. On the other hand, strong orbital overlap in many 3d transition ions-based molecules ensure these systems are often exchange dominated, though dipolar terms cannot necessarily be neglected.

While implementation of higher order couplings, such as quadrupolar coupling, remain difficult in condensed matter systems, they can play a crucial role in the low energy behavior of certain systems[41]. These high order couplings can become important due to symmetry effects suppressing dipolar behavior and in the case of $Ce_2Sn_2O_7$ spin orbit coupling and crystal field effects show a dipole-octopole form to the ground state local moments [42].

1.3 Magnetic Order and Excitations

Most magnetic systems exhibit a conventional magnetic order below their characteristic ordering temperature. While many order into co-linear ferromagnet or antiferromagnetic ground states, competing interactions, anisotropies, or disorder can lead to more unconventional ground states, including spin-liquid ground states discussed below.

Long-range order of the magnetic system allows for an additional Bragg condition to be met in scattering events. For probes which are sensitive to magnetic order, such as the neutron, the magnetic Bragg condition is

$$\lambda = \frac{4\pi}{|\mathbf{Q}|} \sin(\theta) \tag{1.16}$$

where |Q| is the momentum transfer of the probe, λ is the wavelength of the probe, and θ is the scattering angle. Similar to crystalline unit-cells being described by lattice vectors, long-range magnetically ordered systems can have their order characterized by an ordering wavevector, also known as a propagation vector, k. The ordering wavevector notation is identical to the reciprocal lattice notation

$$\boldsymbol{k} = (k_{a^*} \ k_{b^*} \ k_{c^*}) \tag{1.17}$$

where $k_{a^*}, k_{b^*}, k_{c^*}$ represent components of the ordering wavevector along the three reciprocal lattice vectors of the Bravais lattice. Compared to the crystalline unit cells, the magnetic structure can repeat over larger periods allowing for fractional states to exist. For instance, a simple cubic antiferromagnetic order is a combination of two opposing ferromagnetic superlattices. Thus it repeats for every two nuclear unit cells and for a magnetic structure repeating along the *a**-axis can be represented by $\mathbf{k} = (0.5 \ 0 \ 0)$. *Commensurate* magnetic structures are simple magnetic structures with a rational ratio between the nuclear and magnetic unitcells. These include more conventional orderings like ferromagnets and antiferromagnets. *Incommensurate* magnetic structures feature no simple relation between the nuclear and magnetic unit cells, with a prime example being chiral magnetic order. In the case of chiral order, its ordering wavevector can be taken to be $\frac{2\pi}{\lambda}$, where λ is known as its helical pitch length, the distance a structure takes to repeat or wind. Some examples of common magnetic orders and their corresponding ordering wavevectors are shown in Fig. 1.3. For each example, nuclear atoms decorate the vertices of the 2D Bravais lattice with magnetic Bragg reflections shown in red.

Excitations and Quasi-Particles

For conventional long-range ordered magnets, the basic low energy excitations are described by spin waves. In a classical picture for the simplest case of a Heisenberg ferromagnet, the spins order into one of two degenerate sublattices (in zero-field). The ground state of such a system is one where all spins are aligned along an easy axis with maximal magnetization. Small excitations reduce the overall magnetization by reducing a single moment away from its maximal value. Without anisotropy, such a state is a linear combination of all states within a plane of equivalent z-component, where the moment is free to precess around its equilibrium point, shown in Fig. 1.4.

One of the more fantastic aspects of condensed matter physics is the analogues of exotic particles that can exist within the framework of condensed matter systems, known as quasi-particles. Similar to the quantum field theory approach to a particle/wave, as an excitation of an underlying quantum field, these quasi-particles are simply descriptions of excitations found within various



Figure 1.3: Examples of conventional magnetic ordering along with Bragg reflections described by an ordering wavevector in reciprocal space for rectangular 2D lattice. Commensurate magnetic structures that have a simple relation to the nuclear unitcell include ferromagnets, ferimagnets, and antiferromagnets. Incommensurate magnetic structures which do not have any simple relation to the nuclear unit cells include sine/cosine and helical magnetic order.



Figure 1.4: (a) Ground state of 1D ferromagnet. (b) Classical description of spin-wave excitation in 1D ferromagnet. Figure based on Ref. [43]

condensed matter systems. The quasi-particle formalism has been successful in describing the properties of many condensed matter systems. The depiction of an electron hole quasi-particle as a positively charged electron for example, has remained one of the more successful quasi-particle theories, guiding a large area of semiconductor physics [2].

For magnetic systems, quasi-particles known as magnons arise naturally from second quantization of a spin-wave excitation described above [6, 8, 9]. Analogous to the phonon formalism of vibrations of atoms in a lattice, spin-waves can be formulated in terms of spin raising and lowering operators which change the value of a single spin by one. Compared to phonons, the energies associated with magnons are smaller, on the order of 1 meV rather than 10s to 100s of meV for phonons. Because it describes a single spin-flip, the magnon is described by S = 1, and thus follows bosonic relations. In the limit of small deviations from the ground state, a convenient representation of spin raising and lowering operators as bosonic creation/annihilation operators, known as the Holstein-Primakoff transformation, is used [8, 9, 44, 45, 46].

$$\hat{S}_{i}^{+} = (2S - \hat{a}_{i}^{\dagger} \hat{a}_{i})^{1/2} \hat{a}_{i}$$
$$\hat{S}_{i}^{-} = \hat{a}_{i}^{\dagger} (2S - \hat{a}_{i}^{\dagger} \hat{a}_{i})^{1/2}$$
$$\hat{S}_{i}^{z} = S - \hat{a}_{i}^{\dagger} \hat{a}_{i}$$
(1.18)

The Holstein-Primakoff transformation's utility lies in making a semi-classical approximation. For large spin $(S \gg \frac{1}{2})$, one can expand the operators in terms of 1/S. Within this approximation, one can keep only terms to leading order of S for the linear (harmonic) spin-wave approximation and the resulting quadratic Hamiltonian can be diagonalized via Fourier transform. In the case of the 1D Heisenberg ferromagnet such an approximation leads to

$$H = -JNS^2 + 4JS\sum_k \sin^2\left(\frac{k}{2}\right)\hat{a}_k^{\dagger}\hat{a}_k \tag{1.19}$$

where the summation is carried over the Brillouin zone. A similar approach for the 1D quantum *antiferromagnet* involves the formation of a bipartite lattice and an additional transformation of the

bosonic operators using a Bogoliubov transformation [47, 48]

$$H = -JNS^{2} + 2JS\sum_{k} |\sin(k)| (\hat{\alpha}_{k}^{\dagger}\hat{\alpha}_{k} + \frac{1}{2})$$
(1.20)

While the forms of the two look similar, it is important to note that in the limit of small-k, the Hamiltonian of the 1D Heisenberg ferromagnet is quadratic in k while that of the antiferromagnet is linear in k. Comparisons to calculated dispersions, such as in the case above, can provide important insight into the behavior of magnetic systems. While it may seem like the approximations above are too specific to accurately correspond to real materials, linear spin-wave approximations have been shown to be surprisingly well-suited for describing the low energy excitations in many magnetic materials.

The true power of condensed matter physics is that under the extensive possible quantum fields which can be realized within these systems, many quasi-particle analogues of exotic particles that have not been observed in nature can be found [7, 9]. The famous discovery of quasi-particles in dipolar spin-ice that behave like magnetic monopoles are a prime example of such exotic particles not observed elsewhere in nature [49, 50, 51]. Many more quasi-particles have been theorized to exist in the framework of many condensed matter systems. Alexei Kitaev's exactly solvable model on a honeycomb lattice, which remains one of the more popular model systems in the field of frustrated magnetism, was shown to host both Majorana fermion quasi-particles as well as quasi-particle excitations that are anyons, neither fermionic nor bosonic particles [52].

1.3.1 Frustrated Magnetism

Constraints placed on the magnetic moments can lead to situations where all interactions cannot be simultaneously satisfied. This leads to a frustration of magnetic interactions and has been shown to lead to a breadth of exotic phenomena [7]. Frustrated magnets can provide an avenue to avoid conventional Néel order, and many systems exhibit low frequency excitations that can be populated through both thermal and quantum fluctuations. The most clear case of magnetic frustration is geometric frustration on the triangular lattice with antiferromagnetic Ising interactions. For



Figure 1.5: (a) Examples of geometric frustration, where red lines show frustrated bonds. (left) The triangular plaquette with antiferromagnetic interactions. All bonds cannot be satisfied simultaneously, and there are multiple degenerate states which in a fully connected lattice create a macroscopic entropy. (right) The pyrochlore lattice is a natural 3D extension to the frustrated 2D triangular lattice. Now for each unit (tetrahedra) there are two frustrated bonds creating a larger associated entropy. (b) Configuration of water-ice. Hydrogen in water arrange themselves into a network of tetrahedra where two hydrogen are bonded to an oxygen (closer) and two hydrogen from other water molecules are coordinated with the oxygen (further). (c) Two forms of spins on a tetrahedra with an easy-axis anisotropy pointing into the center of each tetrahedra. For the all-in-all-out structure (left), all spins on a single tetrahedra together completely cancel out, leading to no net moment. Such a configuration is not geometrically frustrated with ferromagnetic interactions. The spin-ice analog of water ice (right). Spins form into a 2-in-2-out arrangement which is generated by ferromagnetic interactions.

a perfect equilateral triangle lattice, the interactions of spins decorating each vertex are equal in magnitude and antiferromagnetic. If the interactions between two spins are satisfied then the other interactions are frustrated, shown in Fig. 1.5a. For each triangular unit there are three degenerate ground states, leading to a macroscopic degeneracy in frustrated systems. A natural 3D lattice extension of the triangular lattice is realized in the cubic pyrochlore lattice, where a network of corner sharing tetrahedra connect magnetic ions. For the pyrochlore lattice with antiferromagnetic interactions, of the six nearest neighbor bonds two will be frustrated per unit tetrahedra forming a similar macroscopic degeneracy to the triangular lattice. An alternative route to frustration in the pyrochlore lattice is found through analogy to water ice. In hexagonal and cubic water ice, the water molecules form into a network of tetrahedra. The bond length of hydrogen to the oxygen in the water molecule is smaller than the coordination length between water molecules, leading to a 2-close-2-far structure, shown in Fig. 1.5b. Such a structure was found to have a residual entropy famously described by Linus Pauling [53]. With six out of the total 16 configurations energetically favorable, Pauling calculated the residual configurational entropy in water ice to be S = Nk_Bln($\frac{3}{2}$) \sim 3.4 J/(mol $\cdot K$), which was found to be in excellent agreement with measured values. Many magnetic rare earth ions form into non-colinear systems on the pyrochlore lattice, where spins lie along an easy axis, pointing into or out of the center of the tetrahedra. These systems, such as Ho₂Ti₂O₇ [54, 55, 56] and Dy₂Ti₂O₇ [51, 57, 58], were shown to follow a similar configuration arrangement of spins as water ice, known as *spin-ice* (Fig. 1.5c).

Aside from just geometric constraints, ratios of strengths of competing interactions such as between different forms of exchange interactions can also lead to frustration in magnetic systems. For the $J_1 - J_2$ Heisenberg antiferromagnet on a square lattice in the infinite limit [59], frustration can develop over a balance of interactions, shown in Fig. 1.6. For $J_1 > 2J_2$, the ground state is a simple Néel state, where nearest-neighbor spins are anti-aligned at the cost of second-neighbors being aligned. For $J_1 < 2J_2$, the ground state is now a decoupled colinear ordered ground state, where the second neighbor spins are anti-aligned at the cost of the nearest-neighbors being aligned. But when $J_1 = 2J_2$, competition between the two ordered states cause fluctuations to diverge



Figure 1.6: Simplest representation of exchange frustration on the J_1 - J_2 Heisenberg model on a square lattice. For ratio of $\frac{J_2}{J_1}$, different ground states are found. For $\frac{J_2}{J_1} < \frac{1}{2}$, the ground state is a standard Néel state. For $\frac{J_2}{J_1} > \frac{1}{2}$, the ground state becomes a striped state. However, when $\frac{J_2}{J_1} = \frac{1}{2}$, the ground state has strong competition between these two states, and strong fluctuations lead to a disordered state.

and the system cannot classically order down to 0 K. This shows us that near the phase boundary between the Néel and striped phase ($J_1 = 2J_2$), competition between two nearly degenerate ground states can also suppress classical Néel order entirely. This underlying process is referred to as *phase competition*, and remains a possible mechanism to realize exotic ground states, including a number of possible quantum spin liquids [60, 61]. As described in Ch. 4, phase competition plays a crucial role in the unusual dynamics found within the Yb-pyrochlores. It is also linked to the unusual behavior in Fe₃PO₄O₃, described in Ch. 3.

Spin Liquids

For most magnetic materials, the true ground state of the system will be a long range ordered state due to finite exchange couplings. The temperature scale of this ordering may be greatly suppressed by frustration, and in some cases as the temperature goes to zero a long range ordered state will not form. This spin liquid state is characterized as a correlated fluctuating system of spins with no conventional magnetic ordering down to T = 0 [7]. In the case of a classical spin liquid, classical (thermal) fluctuations tend to dominate, as would expect for "large spin" systems $(S \gg \frac{1}{2})$. Quantum fluctuations can become more dominant for "small spin" systems and

produce a quantum spin liquid state (QSL). In the case of a QSL, a large scale phase coherence or entanglement is allowed [62]. Possible applications of QSLs to topological quantum computing have also been proposed, motivating the search for such exotic phases [63].

In 1973, P.W. Anderson looked at a $S=\frac{1}{2}$ antiferromagnet on a triangular lattice [64], where he described the possible ground state as a resonating valence bond (RVB). A valence bond is described by a spin-singlet state, ψ_{ij} , of two $S=\frac{1}{2}$ spins at lattice sites *i* and *j*. A RVB state can then be described as a sum over tensor products of said valence bond states

$$\Psi_{RVB} = \sum_{i_1, j_1 \dots i_n, j_n} \alpha_{(i_1, j_1 \dots i_n, j_n)} |\psi_{(i_1, j_1)} \dots \psi_{(i_n, j_n)} \rangle$$
(1.21)

where the above wavefunction is summed across all possible orientations of dimer pairs. In the case of one unique ground state dimer configuration, this is known as a valence-bond solid (VBS). Just as there are many types of conventional magnetic order depending on the symmetry of the model, multiple types of spin liquids have been theorized within the framework of multiple models including SU(2), Z_2 , and U(1) spin liquids [65]. QSLs can also be further separated by the nature of their excitations, which can be either gapless or gapped. In the case of the latter, the ground states are described by a global topological order to their ground states [15]. While theoretically measures of entanglement entropy can define a spin liquid phase within a model framework, such a quantity is currently beyond experimental means as it is not an observable quantity. Aside from no signs of long range magnetic order down the lowest observable temperatures, identification of candidate materials can be found through the exotic excitations found in spin liquids. The simplest example of a quasi-particle associated with a spin liquid is found by looking at the excitation of a 2D RVB system, as well as excitations in 1D materials, known as spinons. For the RVB picture, this excitation is represented by the breaking of a single valence bond, and can be mapped to a two independent unpaired spins, making each a $S = \frac{1}{2}$ quasi-particle. Since in a QSL the system is long range entangled, there is no cost in energy for the two spins in the broken valence bond to independently propagate throughout the system. In some cases, a finite potential will

ensure that there is an energy cost associated with the two particles separating, a process known as *confinement*. This leads to a qualitatively different description of a dispersion relation than in the case of magnons above. Fractionalized quasi-particles are created in pairs (or more) and thus can take a wide range of values in momentum and energy. The resulting dispersion becomes a continuum within a range of energy and momentum space.

Experimentally there have been many candidate materials of spin liquids which show no signs of magnetic ordering down to 0.05 K and featuring continuum-like excitations hinting at fractionalization. Organic materials such as κ -(BEDT-TTF)₂Cu₂(CN)₃ [66] and EtMe₃Sb[Pd(dmit)₂]₂ [67] as well as inorganic materials like Herbertsmithite (ZnCu₃(OH)₆Cl₂) [68] remain some of the most famous and well studied candidate materials. α -RuCl₃ and YbMgGaO₄ have also been investigated heavily as possible QSL materials. In the case of α -RuCl₃, low temperature magnetic order was found [69], but application of a magnetic field could destabilize the order. It has been proposed to be "proximate" to a spin-liquid phase [15, 70, 71]. YbMgGaO₄ showed hallmarks of QSL behavior as well, though more recently disorder effects have been argued to mimic a QSL state [72]. Aside from disorder mimicking QSL behavior, a strong sensitivity to disorder has been proposed in many spin liquid models. With finite disorder present in all real material candidates, one may raise questions of the viability of finding true QSL states in real materials, however much theoretical work on QSLs have shown these states to be perturbatively stable, making them possible even in the face of disorder [16, 73, 74].

Within the full quantum mechanical formalism, magnetism in condensed matter systems can exhibit a large range of phenomena, ranging from the more conventional, for example long range Néel order, to the more exotic, such as quantum spin liquids. In order to measure the magnetic behavior in real systems, a number of experimental techniques are available. A few of these techniques will be discussed in the next chapter, with most dedicated to the technique of neutron scattering.

Chapter 2

Experimental Methods

2.1 Introduction

This chapter is dedicated to the experimental techniques I used over my Ph.D, as well as details about how each experimental technique can be used. The majority of the chapter details neutron scattering from its most basic form up to specific neutron scattering instrument types and how they work. Other characterization methods such as specific heat and magnetization are briefly mentioned as well.

2.2 Neutron Scattering

2.2.1 Neutron Properties

Neutron scattering is an experimental technique used widely by condensed matter physicists, chemists, biologists, and material scientists. Analogous to x-ray scattering, neutron scattering utilizes the wave-particle duality of the neutron as a probe of matter. For my research, neutron scattering allowed me to measure both the magnetic and nuclear structures in Fe₃PO₄O₃ and Yb₂Ge₂O₇ as well as probing the low energy excitations in Yb₂Ge₂O₇. There is an exhaustive amount of literature regarding this subject of which I will give a brief overview [75, 76, 77].

Because it is not charged, the neutron is able to penetrate matter, making it an excellent bulk probe of matter, unlike x-rays or electrons, which are more surface sensitive techniques. Furthermore, the lack of a Coulomb barrier means that neutrons are able to scatter directly off nuclei via the nuclear forces. Neutrons also contain an intrinsic spin- $\frac{1}{2}$ with a magnetic moment $\mu = -1.04\mu_B$. This allows it to interact with the electromagnetic force via magnetic fields. One of the most crucial axioms of neutron scattering is the validity of first-order perturbation theory in the *Born Approximation*. This approximation is adequate for nearly all neutron scattering due to the weak scattering nature of the neutrons. Neutron sources are produced in one of two ways at research facilities. The first way is through a nuclear reactor, where a large amount of neutrons are produced through nuclear fission with typical energies on the order of 1 MeV. The second way is through a spallation process, where protons are accelerated to high energies, stored in synchrotron rings (or not), and then slammed in pulses into a heavy metal target to produce pulsed showers of neutrons. In either case, primary moderation through deuterium (or other moderation source) immediately after creation, converts these high energy neutrons into thermal neutrons (E ~ meV)^{*}, which can be used for neutron scattering.

The De Broglie wavelength of thermal neutrons is comparable to the inter-atomic spacing found in many crystalline lattices, and thus is able to scatter off matter. Furthermore, the energy scales of thermal neutrons are on the same order of magnitude as many excitations found in condensed matter systems, such as excitations discussed in Ch 1. Thermal neutrons are non-relativistic and their kinetic energies can be described classically and related simply to the temperature via the equipartition theorem

$$E_{neutron} = \frac{\hbar^2 |\mathbf{k}|^2}{2m} \tag{2.1}$$

$$E_{neutron} = \frac{1}{2}m|\boldsymbol{v}|^2 = \frac{3}{2}k_BT$$
(2.2)

were k is the wavevector, \hbar is Planck's reduced constant, k_B is Boltzmann's constant, |v| is the velocity of the neutron, and T is the temperature. The ability of neutrons to efficiently thermally equilibrate within certain media allows neutron scattering facilities to tune the temperature and thus the neutron's wavelength distributions. Moderation produces a Boltzmann distribution of neutrons centered around a characteristic velocity (wavelength). Wavelengths greater than $\lambda \ge 5$ Å due to moderation through liquid hydrogen cooled down to T = 20 K, can be generated with large flux. This opens up neutron scattering to larger length scales, such as in molecules or polymers. Alternatively, neutrons can pass through an epithermal moderator such as heated pyrolytic graphite to achieve wavelengths down below $\lambda \le 1$ Å.

^{*}Here the term thermal neutrons is used to describe neutrons with kinetic energies of similar orders of magnitude to standard room temperatures.



Figure 2.1: (a) Depiction of scattering of neutrons off a sample with scattering angle 2θ . (b) Scattering triangle for elastic scattering on top ($|k_i| = |k_f|$), and inelastic scattering on bottom ($|k_i| \neq |k_f|$)

A neutron which scatters off matter can be described by two variables. The momentum transfer or scattering vector, denoted by Q, is a 3D vector given by the equation

$$Q = k - k' \tag{2.3}$$

where k is the wavevector of the incoming neutron and k' is the wavevector of the scattered wave. These three momenta form a "scattering triangle" represented in Fig 2.1. The second variable is the energy transfer of the neutron, denoted by the frequency ω .

$$\Delta E = E_f - E_i$$

$$\Delta E = \frac{\hbar^2}{2m} (|\mathbf{k'}|^2 - |\mathbf{k}|^2)$$

$$\Delta E = \hbar \omega$$

(2.4)

If the magnitudes of the two wavevectors are equal, the neutron did not transfer any energy. This process is known as *elastic* neutron scattering and is often used to probe static behavior. In the case where $|\mathbf{k}| \neq |\mathbf{k'}|$, the neutron and the sample transferred energy, a process referred to as *inelastic* neutron scattering (INS) which is sensitive to excitations of the sample.

In the next section, I will cover one of the most important descriptions of neutron scattering: the scattering cross-section following Ref. [75].

2.2.2 The Neutron Scattering Cross-Section

In neutron scattering, the quantity which is measured is the flux of neutrons scattered, also referred to as the scattering cross-section. The total number of scattered neutrons (normalized by the total flux of incoming neutrons), denoted by σ , is also referred to as the integrated or total scattering cross-section. Rather than the total cross section, the quantity that is of most interest is the spatial and time dependence of the scattering itself. To get the so called *partial differential* or *double differential* cross-section, we measure the flux of scattered neutrons of some small energy range [E,E+dE] over some small solid angle range [Ω , $\Omega + d\Omega$]. In its most general form, the partial differential cross-section for a neutron scattered by some potential V is given by

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k'}{k} \left(\frac{m}{2\pi\hbar}\right)^2 \sum_{\boldsymbol{s},\lambda} p_{\lambda} p_{\boldsymbol{s}} \sum_{\boldsymbol{s}'\lambda'} |\langle \boldsymbol{s}' \; \lambda' \; \boldsymbol{k}'| \hat{V} | \boldsymbol{s} \; \lambda \; \boldsymbol{k} \rangle|^2 \delta(E_{\lambda'} - E_{\lambda} + \hbar\omega)$$
(2.5)

where *s* is the spin state, λ is the system state, *k* describes the neutron state, \hat{V} is an operator describing the scattering potential, E_{λ} is the energy of the system, and $\hbar\omega$ is the energy transfer. All primed quantities represent the final states after the scattering event and all un-primed quantities represent the initial states. Eqn 2.5 describes the sum of every process by which the scattering system and neutron change from state (s, λ, k) to (s', λ', k') under conservation of energy. In this thesis, I will not consider polarized neutron scattering, since none of the experiments I employed in my research used the spin-polarization degree of freedom of the neutron.

Nuclear Scattering

Often the largest contribution to the cross-section is the scattering of neutrons directly off nuclei. Since neutron wavelengths are very large compared to the nuclei, we can approximate this scattering process by a Fermi pseudopotential:

$$V(r) = \frac{2\pi\hbar^2}{m} \sum_j b_j \delta(r - r_j)$$
(2.6)

here b_j is known as the scattering length of the atomic nucleus j. It is a constant which is in general dependent on both the element and isotope of nucleus j, as well as the orientation of the nuclear spin. The nuclear partial differential cross-section itself can be broken up into two contributions: *coherent* and *incoherent* scattering.

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{nuc} = \left(\frac{d^2\sigma}{d\Omega dE}\right)_{coh} + \left(\frac{d^2\sigma}{d\Omega dE}\right)_{inc}$$
(2.7)

where

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{coh} = \frac{\sigma_{coh}}{4\pi} \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_{j', j \neq j'} \int_{-\infty}^{\infty} \langle e^{-i\boldsymbol{Q}\cdot\boldsymbol{R}_{j'}(0)} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_{j}(t)} \rangle e^{-i\omega t} dt$$
(2.8)

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{inc} = \frac{\sigma_{inc}}{4\pi} \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_{j} \int_{-\infty}^{\infty} \langle e^{-i\boldsymbol{Q}\cdot\boldsymbol{R}_{j}(0)} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_{j}(t)} \rangle e^{-i\omega t} dt$$
(2.9)

and

$$\sigma_{coh} = 4\pi(\overline{b})^2$$

$$\sigma_{inc} = 4\pi(\overline{b^2} - (\overline{b})^2)$$
(2.10)

As we can see looking at Eqn 2.8, coherent scattering describes correlations between positions of different nuclei at different times and describes interference effects in a system. Eqn 2.9 shows that incoherent scattering only describes correlations of the positions of the same nuclei at different times. In any real sample b is not single valued across the entire system. Incoherent scattering describes the distribution of b values across the system and thus acts as an isotropic background

to the total scattering. We also see that scattering cross-sections describe different correlations in the system, and so convenient descriptions of correlation functions are needed. We define the *scattering function*, also referred to as the *dynamic structure factor*, for both coherent and incoherent scattering as

$$S(\boldsymbol{Q},\omega)_{coh} = \frac{1}{4\pi} \frac{1}{2\pi\hbar} \sum_{j \neq j'} b_j b_{j'} \int_{-\infty}^{\infty} \langle e^{-i\boldsymbol{Q}\cdot\boldsymbol{R}_{j'}(0)} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_{j}(t)} \rangle \langle e^{-i\omega t} dt$$

$$S(\boldsymbol{Q},\omega)_{inc} = \frac{1}{2\pi\hbar} \sum_{j} \int_{-\infty}^{\infty} \langle e^{-i\boldsymbol{Q}\cdot\boldsymbol{R}_{j}(0)} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_{j}(t)} \rangle \langle e^{-i\omega t} dt$$
(2.11)

such that the two components to the partial differential crossection are

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{coh} = \frac{k'}{k}S(\boldsymbol{Q},\omega)_{coh}$$

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{inc} = \frac{k'}{k}S(\boldsymbol{Q},\omega)_{inc}$$
(2.12)

Often the component of interest in nuclear scattering is the coherent scattering, which gives information about the sample's structure as well as coherent excitations in the lattice. For crystalline samples, the majority of this signal tends to be in the elastic regime due to strong Bragg scattering off crystalline atomic planes. For any periodic atomic structure, the Bragg condition is met when the scattering vector is equal to a reciprocal lattice vector and perpendicular to the associated atomic planes. For Bragg scattering, the partial differential scatting cross-section becomes

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{Bragg} = \frac{(2\pi)^3 N}{V} |F_{nuc}(\boldsymbol{Q})|^2 \delta(\boldsymbol{Q} - \boldsymbol{\tau}) \delta(\hbar\omega)$$
(2.13)

where τ is a reciprocal lattice vector and $F_{nuc}(Q)$ is the nuclear structure factor given by

$$F_{nuc}(\boldsymbol{Q}) = \sum_{j} b_{j} e^{i\boldsymbol{Q}\cdot\boldsymbol{r}_{j}} e^{-W_{j}(\boldsymbol{Q},T)}$$
(2.14)

The second exponential term above is known as the *Debye-Waller factor* and is discussed briefly below.
Debye-Waller Factor

For any material at non-zero temperature, there exists thermally induced motion of atomic nuclei. This thermal motion disrupts periodicity and attenuates the coherent scattering as a function of Q.

$$e^{-2W} = \langle e^{i\boldsymbol{Q}\cdot\boldsymbol{u}_i} \rangle^2 \tag{2.15}$$

where u_i is the displacement of the i^{th} nucleus and < ... > denotes a thermal averaging at temperature T. If we treat the nuclei under a harmonic approximation, we can describe the Debye-Waller factor as

$$W = \frac{1}{2} < (\boldsymbol{Q} \cdot \boldsymbol{u}_i)^2 >$$
(2.16)

We can express this in terms of creation and annihilation operators

$$W = \frac{1}{2} \sum_{\lambda} p_{\lambda} \sum_{i} \frac{\hbar}{2MN} \left[\frac{(\boldsymbol{Q} \cdot \boldsymbol{\epsilon}_{i})^{2}}{\omega_{i}} \right] < \lambda |a_{i}a_{i}^{\dagger} + a_{i}^{\dagger}a_{i}|\lambda >$$
(2.17)

where M is the mass of the nucleus, N is the total number of nuclei, and ϵ_i is the polarization vector of the i^{th} oscillator for state λ . Using the relation

$$<\lambda|a_i a_i^{\dagger} + a_i^{\dagger} a_i|\lambda> = <2n_i + 1>$$
(2.18)

We can average over all states and assume each state is independent to arrive at the expression for the Debye-Waller factor

$$2W = \frac{\hbar}{2MN} \sum_{i} \left[\frac{(\boldsymbol{Q} \cdot \boldsymbol{\epsilon}_{i})^{2}}{\omega_{i}} \right] < 2n_{i} + 1 >$$
(2.19)

Where n_i is the quantum number of the i^{th} quantum oscillator. Because the motion is considered to be random and uncorrelated, we see that the Debye-Waller factor will diminish the intensity of a Bragg peak, but will not broaden the profile of the Bragg peak.

Magnetic Scattering

The neutron can also interact with the electromagnetic field generated by unpaired electrons, where both the intrinsic spin and orbital angular momentum of the unpaired electrons contribute to the scattering. The dipole moment of the neutron, μ_N , interacting with the magnetic field of an electron, H_e , in the sample is given by the potential

$$V_{mag} = -\boldsymbol{\mu}_N \cdot \boldsymbol{H}_e \tag{2.20}$$

The neutron's magnetic dipole moment, μ_N , is given by

$$\boldsymbol{\mu}_N = -\gamma \boldsymbol{\mu}_N \boldsymbol{\sigma} = \frac{-\gamma e \hbar}{2m_N} \boldsymbol{\sigma}$$
(2.21)

where σ represents the Pauli spin operator of the neutron, γ is the neutron's gyromagnetic ratio (γ = 1.913). For a system of electrons, contributions to the magnetic field distribution that the neutron sees arise from both the spin and orbital components of unpaired electrons.

Inserting the interaction potential above into Eqn. 2.5 and evaluating the k, σ dependence of the matrix elements for unpolarized neutrons, the partial differential cross-section is given by

$$\left(\frac{d^2\sigma}{d\Omega dE}\right) = \frac{(\gamma r_0)^2}{4\mu_B^2} \frac{k'}{k} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\boldsymbol{Q}}_{\alpha} \hat{\boldsymbol{Q}}_{\beta}) \sum_{\lambda\lambda'} p_\lambda \langle \lambda | \boldsymbol{M}_{\alpha}^{\dagger}(\boldsymbol{Q}) | \lambda' \rangle \langle \lambda' | \boldsymbol{M}_{\beta}(\boldsymbol{Q}) \lambda \rangle | \delta(E_\lambda - E_{\lambda'} + \hbar\omega)$$
(2.22)

here r_0 is a constant known as the classical radius of the electron. In many crystalline systems, the orbital component of the electron spins is quenched, removing its contribution to the partial differential cross-section. In this case, the partial differential scattering cross-section simplifies to

$$\left(\frac{d^2\sigma}{d\Omega dE}\right) = (\gamma r_0)^2 \frac{k'}{k} (F(\boldsymbol{Q}))^2 e^{-2W(\boldsymbol{Q},T)} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\boldsymbol{Q}}_{\alpha} \hat{\boldsymbol{Q}}_{\beta}) S^{\alpha\beta}(\boldsymbol{Q},\omega)$$
(2.23)

where $F(\mathbf{Q})$ is the magnetic form factor, and the correlation function $S^{\alpha\beta}(\mathbf{Q},\omega)$ is the dynamic magnetic structure factor given by the time and momentum Fourier transform of the spin-spin

correlation function

$$S^{\alpha\beta}(\boldsymbol{Q},\omega) = \sum_{jj'} e^{-i\boldsymbol{Q}\cdot(\boldsymbol{R}_{j'}-\boldsymbol{R}_j)} \int_{-\infty}^{\infty} \langle S_j^{\alpha}(0) S_{j'}^{\beta}(t) \rangle e^{-i\omega t} dt$$
(2.24)

Here, S_j^{α} is the α component of the spin from atom j. Looking at Eqn 2.23, its behavior is governed by a few terms. The dynamic magnetic structure factor describes how the spins of the system react to the magnetic field produced by the neutron. The magnetic form factor acts as an envelope function, which tends to suppress scattering intensity for large Q. Since the spin-density only includes valence shell contributions from the unpaired electrons, this form factor is expected to fall off more quickly than its nuclear counterpart described above. The constant $(\gamma r_0)^2$ takes the place of the scattering length for nuclear scattering, and is typically of similar order of magnitude. This means that the strength of the magnetic cross-section is of similar order to that of the nuclear crosssection, allowing scattering experiments to observe both nuclear and magnetic scattering together. Finally the polarization factor, $(\delta_{\alpha\beta} - \hat{Q}_{\alpha}\hat{Q}_{\beta})$, enforces that only magnetic moments/fluctuations perpendicular to Q can couple to the neutron.

Detailed Balance Factor

When there is energy transfer, either the neutrons will lose energy to the system (positive energy transfer), or the neutron will gain energy from the system (negative energy transfer). In principle these two events will both happen while scattering off any scattering system at non-zero temperatures. These two channels will be related to each other by the *law of detailed balance*

$$S(\boldsymbol{Q}, -\omega) = S(\boldsymbol{Q}, \omega)e^{-\hbar\omega/k_BT}$$
(2.25)

Where $S(\mathbf{Q}, -\omega)$ describes the neutron gaining energy to the system, $S(\mathbf{Q}, \omega)$ describes the neutron losing energy to the system, and $\hbar\omega$ is the energy transferred. The law of detailed balance holds for any system in equilibrium and can be a good way to verify sample temperature in situ. Nega-

tive energy transfers are often directly measured in time-of-flight geometry instruments alongside positive energy transfers.

2.2.3 Neutron Instruments

In this section, I will discuss how different neutron instruments operate. The most simple class of neutron instruments are *diffractometers* which are insensitive to neutron energies and thus probe the energy integrated differential cross-section. Instruments capable of energy discrimination are usually referred to as *spectrometers*. There are many different neutron instruments, each specialized to a different area of neutron scattering. These include diffractometers, triple-axis spectrometers, time of flight spectrometers, neutron spin echo spectrometers, backscattering spectrometers, reflectometers, and more. For my research, I used the following instruments at the High Flux Iso-tope Reactor (HFIR) at Oak Ridge National Laboratory, The Spallation Neutron Source (SNS) at Oak Ridge National Laboratory, and the Reactor source at the NIST Center for Neutron Research (NCNR) at the National Institute for Standards and Technology-Gaithersburg:

- HB:3A: The Four-Circle Single Crystal Diffractometer at HFIR [78]
- MACS: The Multi-Axis Crystal Spectrometer at NCNR [79]
- CNCS: The Cold Neutron Chopper Spectrometer at SNS [80]
- CORELLI: The Elastic Diffuse Scattering Spectrometer at SNS [81]

Diffractometers

As stated above, diffractometers are among the simplest neutron instruments, as they are insensitive to neutron energies and thus integrate over all possible energies. In crystals, the resulting signal is overwhelmingly elastic due to the strong Bragg scattering, and as such diffractometers are used to probe the static structures of materials. A diagram of a diffractometer is shown in Fig. 2.2a. An incident neutron beam is made monochromatic, usually via Bragg reflection off a monochromator crystal. Neutron optics, such as filters and collimators are used to clean the beam profile. An



Detector bank

Figure 2.2: (a) Schematic diagram of a powder diffractometer. (b) Four-circle goniometer used for single crystal diffraction experiments. Any 3D rotation of the crystal can be made by a combination of four principle angles: $2\theta, \chi, \phi$, and ω .

example of a neutron filter is a fast neutron filter, which has a much higher crossection for higher wavelength neutrons and less for thermal neutrons. This allows for an effective screening of high energy neutrons while allows thermal neutrons through. Collimators primarily limit divergence of the neutron beam, which translates to resolution in reciprocal space. The monochromatic beam is then incident on a sample and scatters before being measured at a detector. For polycrystalline samples, the random orientations of microcrystallites cause Bragg diffraction in a full sphere at |Q|matching the Bragg condition. The magnitude of the momentum transfer is changed as the sample (or detector system) is rotated, denoted by the angle 2θ from the unscattered beam. Single crystal diffractometers generally feature specialized goniometers, such as a four-circle goniometer, in order to freely rotate the sample to all possible reflections. A depiction of a full χ circle goniometer is shown in Fig. 2.2b, such as the one located at HB-3A. Non-crystalline materials, such as polymers or liquids, usually require a more specialized diffractometer called a Small-Angle Neutron Scattering (SANS) instrument. These are specialized instruments which focus on small Q, for larger scale structures.

Triple-Axis Spectrometers

The simplest form of an instrument which is sensitive to the energy transfer of the neutron is the triple-axis spectrometer. Its named for the three independent axes of rotation which define the scattering, shown in Fig. 2.3a. The first axis is a monochromator crystal, which selects an initial neutron energy E_i . The second is the sample rotation through a plane in reciprocal space. Last is a second energy discriminating crystal, defined as the analyzer crystal. This crystal can be set for a final neutron energy E_f . One of the main benefits of triple-axis spectrometers lies in their flexibility. They can be adapted to be sensitive to the neutron polarization. They also can feature a host of complex sample environments to suit the needs of the user. They are one of the most approachable and conceptually simple neutron spectrometers, allowing for well-optimized data analysis. Triple-axis instruments focus their available flux to a specific point in reciprocal space (Q, ω) and are often used to map out phonon dispersions in a direction in reciprocal space, polarization experiments, and Bragg peak evolutions. This also means they are not generally suited for surveying large chunks of reciprocal space due to the limited detector coverage. They also usually feature a more coarse energy resolution compared to modern time of flight instruments. For the Multi-Axis Crystal Spectrometer (MACS), rather than one detector, it utilizes twenty separate detectors each with their own analyser for energy discrimination, shown in 2.3b. This allows MACS to overcome one of the largest downsides of standard triple-axis spectrometers. It also features a dedicated liquid hydrogen moderator, which thermally equilibrates incoming neutron flux of MACS, allowing for lower incident energies and better energy resolution than many other thermal triple-axis instruments.

Time of Flight Spectrometers

A powerful inelastic instrument which naturally utilizes the pulsed neutron beam from a spallation source (though does not require one), is a time of flight spectrometer. There are two designs of flight instruments, called direct geometry and indirect geometry. In a direct geometry time of flight spectrometer a pulse of neutrons are monochromated via a set of choppers, with the energy transfer determined through the time of flight of the scattered beam. In an indirect geometry time



Figure 2.3: (a) Schematic diagram of a triple-axis instrument. (b) Detector system for MACS adapted from [79]. MACS behaves as a triple axis with a 20 channel detector system, allowing for a much more efficient mapping of reciprocal space.



Figure 2.4: (a) Diagram of a typical time of flight instrument. An incident pulse of neutrons gets monochromated by a set of fermi choppers then scatters of the sample into detectors.

of flight spectrometer, a white beam of neutrons is incident on the sample and a final energy is selected (i.e. through analyzer crystals). A diagrammatic description of a typical direct geometry time of flight instrument is shown in Fig 2.4. An incoming neutron beam is guided down a path by a neutron waveguide, which are usually coated in neutron "supermirrors". The beam then encounters a number of choppers which rotate with their angular momentum axis aligned with the beam direction. These choppers can be used shape and control the neutron beam in a few ways: they can shape the pulse, cut out higher order containminations, monochromate, or create pulses out of continuous sources. For my research I only used direct geometry spectrometers. The key differences in time of flight geometry allow for, on average, finer energy resolution and also allows them to collect multiple energy transfers at once. Coupled with large detector coverages, they can also make excellent survey instruments of reciprocal-space. They are especially powerful instruments for mapping inelastic events across large ranges of reciprocal-space, such as energy dispersions in crystals.

Statistical Chopper

A less conventional class of instruments are statistical chopper spectrometers. These instruments rely on the cross-correlation technique to utilize much more of a neutron beam (up to 50% of a white beam source [82]), while retaining energy discrimination. This allows for a substantial increase in flux incident on the sample.

For a short-pulse neutron source, such as the Spallation Neutron Source, one can achieve the cross correlation technique by applying a psuedorandom modulation in time of the incident pulse. This changes the signal being measured at the detectors from the scattering function, $S(Q,\omega)$ to being dependent on the $S(Q,\omega)$ summed over a fixed time of flight. The true scattering function is then reconstructed by forming the cross-correlation of the data with the modulation of the initial pulse. For the pulsed source, the errors in the reconstructed $S(Q,\omega)$ are correlated only along the energy transfer and are not dependent on Q. This tends to more strongly adversely affect statistics relating to strongly localized objects in momentum space, such as Bragg peaks. Thus one can expect the correlation to favor diffuse scattering relative to the Bragg scattering. Combined with large detector coverage, cross correlation choppers allow one access to large volumes in reciprocal space with elastic discrimination [82, 83, 84].

2.3 Other Experimental Techniques

Aside from neutron scattering, several other experimental techniques were used throughout my Ph.D work. Our group's main motivation for utilizing these techniques was usually to characterize materials prior to a neutron scattering experiment, however through such techniques many important and interesting properties can be identified. In many regards, these techniques are intricate and robust areas of study which focus on specific properties of condensed matter systems and can be the subject of an entire Ph.D study.

2.3.1 Magnetometry

Magnetometry provides direct bulk measurements of a material's magnetic properties. It provides a measure for material properties characterization, including phase transitions and the form of the main exchange interactions for magnetic materials. Because it can easily be combined with cryogenics and high magnetic fields, one can measure a temperature and field dependence of the

magnetic susceptibility or magnetization within a sample. Typically, there are two regimes in which magnetometry is performed, either dc magnetometry or ac magnetometry. In the case of dc magnetometry, a static magnetic field is applied and one measures the equilibrium value of the magnetization within a sample as a function of temperature, field, time, ect. One can use a small applied field to approximate the dc-susceptibility as well. Ac magnetometry instead drives an ac magnetic field, which can be combined with a static dc field. Rather than directly measuring the equilibrium magnetization, ac magnetometry probes the slope of the magnetization (the susceptibility) directly. In the low frequency limit of the ac field, moments are able to follow the field and the susceptibility matches the dc-susceptibility. At higher frequencies, the magnetization may lag behind the driving field due to dynamic effects in the material. In this way, one measures two quantities for the ac susceptibility. The first is χ' , known as the longitudinal or real component of the susceptibility. It measures the component of the magnetization that is in-phase with the ac field. The second is the transverse or imaginary component of the susceptibility, χ'' , which measures the component that is out of phase with the ac field. This component indicates dissipative processes within the sample. In the most simple case for a conductive material, this can be thought of as eddy currents being generated. In the case of relaxation and irreversible processes, such as found in spin-glasses, one also finds a large χ'' . Ac susceptibility has remained one of the more important measurement techniques in classifying spin-glass systems [85, 86]. In my research I used magnetometry to measure the low temperature magnetization and susceptibility properties of $Yb_2Ge_2O_7$ and $CoNb_2O_6$.

Most modern magnetometers are superconducting quantum interference device (SQUID) magnetometers, due to their extreme sensitivity [87]. Along with a SQUID sensor, one may combine one of several operational techniques, such as DC-SQUID, or vibrating sample/coil magnetometry (VSM/VCM). SQUID magnetometers are instruments built off the Josephson effect [88, 89]. As schematically shown in Fig 2.5a, the device construction centers around two or more Josephson junctions connected in parallel within a superconducting loop [87, 90, 91]. Resistive shunts are added to prevent hysteretic behavior [92]. A bias current I_b is applied so that each Josephson junc-



ally has a frequency limited to a few Hz. The RSO option provides greater sensitivity, however the DC option allows for a larger sample scan range. In addition the two techniques allowed on the MPMS-XL, I also used a VSM option through Quantum Design's physical properties measurement system (PPMS). In vibrating sample magnetometry, a sample is mounted to an oscillating stage, which vibrates though a pickup coil. Its counterpart, the vibrating coil magnetometer operates similarly, except that instead of the sample being oscillated, it is the coil assembly. In the case of VCM, one can avoid the mechanical heating of the sample and can achieve lower temperatures, but are more complicated designs. As the sample is moved through a pick up coil (such as a SQUID), it changes the flux through the loop.

2.3.2 Specific Heat

Specific heat (C) is an intrinsic material property, which is a measure of the amount of energy required to raise the temperature of a material. It can be a direct measure of excited states of a material for a given temperature or energy range. In my research, I used heat capacity to measure the low temperature behavior of Yb₂Ge₂O₇ and CoNb₂O₆. For measuring heat capacity in solid materials, the most natural way is to measure the system under a constant pressure, and allow the material to expand, C_p . The opposite is true for gases, where it is most natural to hold the system under a constant volume and allow the pressure to change, C_v . These are related to each other through

$$C_p - C_v = 9\alpha\kappa VT \tag{2.26}$$

where α is the thermal expansion coefficient, κ is the compressibility, and V is the volume. Since all measurements I took were on solid materials, I will only discuss heat capacity under constant pressure, C_p .

A measure of specific heat is usually a combination of many contributions within the material, depending on the allowed excitations. In crystalline materials, two of the most common contributions are phonons and conduction electrons, whose general form of specific heat in 3D systems is given by

$$C_p = \alpha T + \beta T^3 \tag{2.27}$$

where α and β are material dependent constants, the electron contribution is the term linear in temperature, and the phonon contribution is cubic in temperature. These can be easily derived using the free electron (aka Sommerfeld) model, and Debye model respectively [93]. It should be noted that this form of the specific heat applies in "low" temperature limit, where the excited states of the phonons and electrons are not thermally saturated. In the high temperature limit, the heat capacity approaches the limit known as the Dulong-Petit law given by $C_v = 3R = 24.94$ J mol⁻¹ K⁻¹.

Magnetism also contributes to the specific heat of a sample in systems with unpaired electrons. Under an applied magnetic field, the angular momentum degeneracy is split into 2J+1 states, were J is the total angular momentum. At zero temperature only the lowest energy state is populated, but with thermal energy on order of the energy splitting between states, transitions between levels can occur giving a contribution to the specific heat. This is known as a Schottky anomaly and in a spin- $\frac{1}{2}$ system it is given by

$$C_m = nR[\frac{\Delta E}{k_B T}]^2 \frac{e^{\Delta E/k_B T}}{[1 + e^{\Delta E/k_B T}]^2}$$
(2.28)

where n is the number of moles of the magnetic species and R is the universal gas constant. The low energy excitations of magnetic systems, magnons, will also contribute to the specific heat of magnetic materials.

Specific heat can also be an excellent measure of entropy changes. A change in entropy can be estimated by integrating a heat capacity plot through the thermodynamic relationship

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT \tag{2.29}$$



Figure 2.6: Example specific heat signature of a phase transition seen in the ⁴He superfluid transition taken from [94]. Consecutive specific heat measurements show the superfluid transition λ =2.177 K.

Many magnetic systems show hallmarks of effective spin- $\frac{1}{2}$ behavior in their low temperature degrees of freedom, which can be estimated by a plateau in the entropy saturating near its characteristic value ($\Delta S = Rln(2)$ for spin- $\frac{1}{2}$).

Magnetic ordering into a long-range ordered state carries an entropy with it and is marked by a symmetry breaking phase transition, which the specific heat is sensitive to. At a phase transition, the specific heat diverges which manifests as an anomaly in the specific heat. This was most famously shown in Fig 2.6, the " λ " super-fluid transition in ⁴He [94]. Specific heat can be one of the most dramatic experimental signatures of phase transitions.

All specific heat measurements taken for my studies were performed using a Quantum Design Dynacool physical properties measurement system (PPMS). The sample is mounted on a calibrated puck and put into thermal contact with the sample stage using a conventional cryogenic grease (Apiezon grease). The sample stage is a microcalorimeter suspended by a series of thin insulating wires which are connected via thin electrical leads to the heater and thermometer. This puck is mounted under high-vacuum to be in thermal contact with the mixing chamber of a ${}^{3}\text{He}/{}^{4}\text{He}$ dilution refrigerator. Above 1.8 K, the instrument relies on conventional pumped ${}^{4}\text{He}$ cooling. This combination allowed for a continuous operating temperature range of 300 K down to 0.05 K.

Specific heat is generally determined using one of two methods. In the first method, known the quasi-adiabatic heat pulse method, a small heat pulse ($\sim 2\%$ sample temperature rise) is given to the stage once the temperature has been stabilized [95, 96]. The temperature of the sample is then monitored as it increases while the heater is on, and decreases back to the initial temperature once the heater is turned off. This is the usual method to collect heat capacity data, and can collect data over a large temperature range. The heat capacity an be extracted from the temperature of the stage

$$T_{stage} = T_0 + \Delta T e^{-t/\tau_1} \tag{2.30}$$

where T_0 is the initial temperature before the heat pulse, and the time constant τ_1 can be expressed as

$$\tau_1 = \frac{C_{stage} + C_{sample}}{K_1} \tag{2.31}$$

for the case where the sample to stage thermal conductance (K_2) is much larger than the stage and heat sink thermal conductance (K_1) . If this is not the case then the relation between the temperature change is

$$T_0 + Ae^{-t/\tau_1} + Be^{-t/\tau_2} \tag{2.32}$$

where the more gradual time constant τ_1 corresponds to the relaxation between sample/platform and the heat sink temperature bath, while the shorter time constant τ_2 corresponds to the relaxation between sample and the platform [97]. For the Quantum Design PPMS, the fitting process is described in Ref. [98]. In principle, if the material has a complicated heat relaxation response, such as a spin glass material, the correction to the equation above would be to add multiple sample dependent time constants, which correspond to multiple relaxation processes present in the material. Therefore one may expect a poorer fit of the pulse profile in such cases.

In the second method, known as the long pulse method, once the stage temperature has been stabilized, a larger heat pulse of set duration and heat ($\sim 200\%$ sample temperature rise) is applied to the sample. The sample temperature is then monitored as the heat decays and the sample equilibrates back to the initial temperature. The heat capacity is obtained through the time derivative of the temperature [99]. This technique is sensitive to the latent heat of first order transitions, and can be used for situations where the time constants relating to the sample relaxation begin to diverge. One is generally limited to a small temperature range of measurement, since one would not want to inject too large of a heat pulse in order to limit the effects of parasitic heating and other complications. While it can be a rather time consuming process depending on the rate of relaxation in the sample and the stage, for low temperature measurements it can be faster than the quasi-adiabatic technique.

In order to eliminate the contributions of the puck and grease, background specific heat measurements with no sample are subtracted from the overall specific heat measurement as outlined in [98]. This combined with a calibrated subtraction from the sample stage itself can allow for more precise measurements. These procedures, along with sophisticated design considerations to limit parasitic heating, can greatly enhance the sensitivity of modern heat capacity measurements. Even so, most heat capacity measurements still suffer from errors on the order of a few percent at low temperatures [96, 97, 100].

2.3.3 Electron Paramagnetic Resonance

This section describes a technique used by our collaborators in order to determine the *g*-tensor in $Yb_2Ge_2O_7$ (Ch. 4).

An excellent bulk probe for magnetism is electron paramagnetic resonance (EPR). This technique works similarly to nuclear magnetic resonance (NMR), except probes the spin of the electron rather than the nuclear spin [1, 101]. There are generally two types of EPR spectrometers which differ in function. The first and most common type is continuous wave EPR, where low power microwave radiation is continuously applied to the sample. The other type is pulsed EPR, which utilizes small pulses of high power microwave radiation. A standard continuous wave EPR setup is an X-band (8-12Ghz), with a static field $B_z = 3.5$ T. In a continuous wave EPR instrument, samples are placed within a resonator cavity, where a large electromagnet creates a homogeneous *z*-component field and a transverse oscillating magnetic field is supplied from the microwave bridge.

Through application of a static magnetic field, the Zeeman effect will split the degenerate states of the electron's angular momentum. For a spin only effect in a single spin carrier system, as is the case for most 3d transition ions where the orbital contribution is quenched, this gives

$$E = g\mu_B S_z B_0 \tag{2.33}$$

where B_0 is the strength of the static field applied along the spin z-axis, g is the Landé g-factor, μ_B is the Bohr magneton, and S_z is the z component of the spin angular momentum of the unpaired electron. The quantum eigenstates of the spin allow only discrete values for S in units of \hbar . The simplest case, a pure $S = \frac{1}{2}$, this gives two energy levels corresponding to the two eigenvalues of S_z ($\frac{1}{2}$ and $-\frac{1}{2}$).

$$E_{\pm} = \pm \frac{g\mu_B B_0}{2}$$
(2.34)

One can obtain a resonance condition for the difference between the energies

$$h\nu = g\mu_B B_0 \tag{2.35}$$

by stimulating the ion with electromagnetic radiation of frequency ν . Here g changes depending on the crystalline environment from its free value of $g_f \sim 2.0023$. Thus g acts as a tunable parameter in Eqn. 2.35, also referred to as the master equation of EPR. Furthermore, anisotropy can lead to different values for g depending on the principal directions of the anisotropy. This promotes g to a tensor (the g-tensor) whose characteristics can greatly influence the properties of the magnetic system. Detection of absorption depends on a difference in thermal populations of the two states involved in the resonance. For identical populations stimulated emission would cause the system to saturate and no detection of absorption would be possible. Generally thermal populations of the states are given by a simple Boltzmann factor, so a ratio between a lower energy state B and a higher energy state A would be

$$n_A/n_B = exp[-\frac{(E_A - E_B)}{k_B T}]$$
 (2.36)

One can also expect if the system fails to dump additional energy gained from absorption and is unable not restore the equilibrium populations, the absorption profile will eventually saturate as the populations become equally populated. A measure of the ability of a spin system to equilibrate is generally given by a characteristic time, T_1 , often denoted the *spin-lattice relaxation time* or longitudinal relaxation time.

The resonance condition is most commonly achieved through application of a time dependent field B_x , which is applied perpendicular to the static field B_0 . The time dependent magnetic field oscillates with a given frequency, ω ,

$$B_x(t) = B_1 \cos(\omega t) \tag{2.37}$$

A classical spin ensemble with magnetization along the z-direction, $M = M_0 \hat{z}$, subjected to such an oscillating field will precess according to the Bloch equations.

$$\frac{d\boldsymbol{M}}{dt} = \boldsymbol{M} \times g\mu_B \boldsymbol{B}_{eff}$$
(2.38)

where B_{eff} contains the contributions of both the static and oscillating fields. A second characteristic time, T_2 , describes the rate at which the transverse components of the magnetization return to zero. This is known as the *spin-spin relaxation time* or transverse relaxation time. Solving the Bloch equations show a lineshape that is Lorentzian (Fig. 2.7b) and dependent on T_2 for such a



Figure 2.7: Typical EPR spectra for an ideal S=1/2 particle in a magnetic field, where the signal is plotted as the first derivative of the absorption. The two eigenstates have their degeneracy lifted by the magnetic field with a splitting equal to $g\mu_B B_z$. The absorption is a Lorentzian lineshape such that its first derivative is plotted above.

homogeneous absorption, that is an absorption profile arising from one distinct magnetic species. In contrast, if one has a superposition of multiple magnetically distinct resonances, either through different orientations with respect to the field or a separate magnetic atom, one would expect such a inhomogeneous profile to be Gaussian in form.

Additional interactions, such as the hyperfine and dipolar interactions can modify the EPR spectrum, introducing new resonances and anisotropy into the profile. In an analogous manner to the electron spin shown above the nuclear spin states, *I*, will also undergo Zeeman splitting

$$E_N = -g_N \mu_N B_0 I_z \tag{2.39}$$

for a field applied along the z-direction. Here g_N and μ_N are the nuclear Landé factor and nuclear Bohr magneton respectively. Typically nuclear spectra appear at much lower frequency than electronic spectra and so one will not tend to directly probe the nuclear Zeeman transitions in an X-band spectrometer. The nuclear spins can couple to the electron spins through the hyperfine interaction

$$E_{hf} = \alpha \boldsymbol{S} \cdot \boldsymbol{I} \tag{2.40}$$

where α is the hyperfine coupling constant. The coupling strength depends on the overlap of the electron wavefunction with the nucleus. Aside from selection rules applying to EPR ($\Delta S_z = \pm 1, \Delta I_z = 0$) one can have forbidden transitions ($\Delta S_z = \pm 1, \Delta I_z = \pm 1$), which appear with suppressed intensity compared to allowed EPR transitions, but can greatly modify EPR spectra. The dipole-dipole nature of the moments can lead to highly anisotropic hyperfine interactions within materials, and can further modify the spectra observed.

2.4 Cryogenics

Many magnetic systems show interesting behavior at low temperatures, in particular rare-earth ions, whose limited spatial orbitals and shielding of valence shells lead to weak exchange interactions. In addition, much theory in condensed matter centers around low-energy effective theories, where only a subset of the degrees of freedom are relevant. Thus, reliably taking data while at extremely low temperatures is of great importance in studying these materials. Experimentally, one can reach different temperatures through different cryogenic processes. A good reference for low temperature methods is given by Pobell [100]. All cryogenics used during my Ph.D. were various closed-cycle refrigerators, discussed below. Aside from closed-cycle, there also exist cryogen-free methods to reach low temperature such as adiabatic demagnetization.

The most common low temperature cryostat is a standard ⁴He cryostat, where liquid helium is put in thermal contact with the sample. They generally operate continuously in a temperature range of 300 K down to 1.6 K, and are used for virtually all low temperature cooling methods below 10 K, as either the primary or precursor cooling method. They are usually combined with liquid nitrogen cooling for higher temperatures and pre-cooling (300 K to 77 K), which is not only far cheaper than helium, but has a latent heat of evaporation roughly 60 times that of helium. Since ⁴He has a boiling point of 4.2 K, in order to reach cooler temperatures a pumping technique is applied. Vapor pressure from higher energy ⁴He are pumped away leaving the remaining liquid a lower temperature. An analogous argument can be made for ³He, however this isotope is a fermion, unlike ⁴He, which behaves as a boson. Therefore we expect a difference in physics



Figure 2.8: x-T phase diagram for low temperature mixtures of ³He / ⁴He. The mixture undergoes a phase separation transition at the lowest temperatures for a large window of ⁴He concentration. T_F shows the Fermi temperature of the ³He. Adapted from Ref. [100]

between the two isotopes. In particular, ³He has much larger vapor pressure and lower boiling point, as well as a larger specific heat at low temperatures. This allows ³He to cool down to 0.3 K through conventional pumping techniques described above and can more efficiently cool a sample at low temperatures. Despite this, the main downsides to ³He, namely its smaller latent heat of evaporation and its extremely high cost, ensure that one usually chooses ⁴He cryostats unless a lower temperature or higher cooling power is needed.

2.4.1 ³He / ⁴He Dilution Refrigerator

A technique that has become a standard for ultra-low temperature measurements is use of a 3 He / 4 He dilution refrigerator [102]. While the first successful dilution refrigerator was designed in 1964 by the Kamerlingh Onnes Laboratorium [103], the technique was first suggested in the early 1950's by Heinz London. Since then design, improvements and refinements have allowed for an easily available method to achieve temperatures down to a few milikelvin. Aside from its low temperature functionality, dilution refrigerators can be designed to be largely unaffected by high magnetic fields, allowing for the study of magnetic field dependent properties of a material down to ultra low temperatures.

Unlike conventional evaporative cryogenics, dilution refrigerators utilize the enthalpy of mixing between the two helium isotopes, ³He and ⁴He. As a function of temperature and concentration of ³He, a mixture of ³He and ⁴He will form into different phases, shown in Fig. 2.8, where ³He concentration is defined as $c_3 = \frac{n_3}{(n_3+n_4)}$ with n_3 and n_4 being the number of ³He and ⁴He atoms respectively. The Lambda transition separating the superfluid transition gives way to a tricritical point at ~ 0.87 K for a mixture of 6.6% ³ and 93.4% ⁴He. Below this point the mixture separates into two phases, with one phase being rich in ³He (referred to as the concentrated phase), while the other is rich in ⁴He (dilute phase). If one removes ³He from the dilute phase, through pumping from the bottom of the mixing chamber (the dilute phase is denser and will sink to the bottom), osmotic pressure from the concentrated phase will diffuse ³He across the phase boundary into the dilute phase to restore equilibrium. This process is endothermic, leading to an effective cooling



Figure 2.9: Diagramatic representation of a dilution refrigerator system, with the Quantum Design probe insert for the PPMS. Figure adapted from Ref. [104] and Ref. [105].

of the mixing chamber. As the temperature decreases, the concentrated phase tends toward 100% 3 He, while the dilute phase tends toward a constant concentration of ~ 6% 3 He. This means there is theoretically no low temperature limit to this cooling technique, though practical experiment limits for the cooling power are around 2 mK.

A diagramatic representation of a commercial dilution refrigerator, such as the one designed by Quantum Design, is shown in Fig. 2.9. The dilute phase inside the mixing chamber is pumped to a still where it cools the concentrated phase through heat exchangers. When not in use, the mixture is stored into a tank to prevent loss. Most commercial dilution refrigerators are made to be inserts for larger conventional cryostats, which precool the inset and allow for a continuous operating temperature from 300 K down to several milikelvin.

Chapter 3

Partial Antiferromagnetic Helical Order in Single Crystal Fe₃PO₄O₃

3.1 Introduction

This chapter details some single-crystal neutron diffraction results on the insulating incommensurate antiferromagnet Fe₃PO₄O₃. A rare phenomena of partial magnetic ordering is observed in this compound below its ordering transition $T_N = 163$ K down to 4 K. The compound retains long-range antiferromagnetic order along the crystallographic *c*-axis, while exhibiting a wellordered ordering wavevector magnitude in the *ab*-plane with no directional preference. Combined with high-resolution powder data in the literature, restricting the size of correlations within the *ab*-plane, this strongly suggests a highly unusual structure to the static moments of Fe₃PO₄O₃. It shares striking similarities with the partially ordered high pressure phase of MnSi. A key difference between the two is that in Fe₃PO₄O₃ the interactions which produce such a state are frustrated antiferromagnetic interactions, rather than chiral ferromagnetic interactions in present in MnSi.

All collection and analysis of single-crystal neutron data, including any simulation related to the data were performed by myself, with supervision from my advisor Kate Ross and the instrument scientist at HB-3A, Huibo Cao. Luttinger-Tisza calculations of the second-neighbor Heisenberg Hamiltonian were performed by Ethan Coldren under the supervision of Prof. Martin Gelfand. Crystals of $Fe_3PO_4O_3$ were grown by Michael Tarne and Prof. James Neilson. Powder data from Michael Tarne, Prof. Kathryn Ross, and Prof. James Neilson were also crucial in guiding the direction of this project.

The rest of the chapter is outlined as follows: sections 3.2 to 3.4 contain introductory material covering skyrmions, B20 compounds, and previous literature on $Fe_3PO_4O_3$. Section 3.5 provides a clarifying description of real space images of magnetic spin textures. Section 3.6 reproduces

our published manuscript detailing single crystal neutron diffraction on $Fe_3PO_4O_3$, and the full reference can be found at Ref. [106]. Finally, section 3.7 describes conclusions and future outlook for $Fe_3PO_4O_3$.

3.2 Skyrmions

The first model of a skyrmion was proposed by Tony Skyrme in 1962 as a stable soliton solution of the nucleon[107]. It was later proposed that chiral magnetic skyrmion analogs to Skyrme's soliton could be found in magnetic materials[108], such that easy-axis magnetic systems with Dzyaloshinskii-Moriya interactions (DMI) could host magnetic skyrmions, where the DMI provides the stabilizing energy term to their solutions[109, 110]. A depiction of the two main types of topological magnetic skyrmion are shown in Fig. 3.1a, the Néel-type, which winds radially, and the Bloch-type, which winds azimuthally. While the magnetic skyrmion consists of a collection of chiral spins, it differs from more conventional magnetic vortices, such as at intersections between Néel type domain walls, as the skyrmion is a quasi-particle with its own non-trivial *topological* index. Historically, much theoretical work into magnetic skyrmions was centered around 2D structures, such as thin films and interfaces[111, 112]. For a 2D (or quasi-2D) material the skyrmion is described by a non trivial topological charge or *skyrmion number*, *Q*.

$$Q = \frac{1}{4\pi} \int d^2 \boldsymbol{r} \cdot \boldsymbol{m}(\boldsymbol{r}) \cdot (\partial_x \boldsymbol{m}(\boldsymbol{r}) \times \partial_y \boldsymbol{m}(\boldsymbol{r}))$$
(3.1)

where m(r) is the local magnetization. One can map the topological charge of a 2D surface of a sphere, shown in Fig.3.1b. In systems arising from a competition between ferromagnetic Heisenberg interactions and DMI, an estimate of the spin-helix length can be made with $4\pi J/D$, where J is the exchange constant and D is the DMI strength[113]. Typical strengths of J and D in transition metal ion structures give rise to skyrmions on the order of 0.1-100 nm, with larger skyrmions observed to decouple with the lattice. The first known bulk skyrmion was found in the B20 compound MnSi through neutron scattering off a well-ordered skyrmion super-lattice[114].



Figure 3.1: (a) Two types of stable skyrmion quasi-particles. Bloch-type skyrmion with an azimuthal winding of the moments (left), and the Néel-type skyrmion with a radial winding of the magnetic moments (right). (b) A 2D skyrmion winding of moments can be represented as the 2D surface of a sphere for each skyrmion type. Figure adapted from Ref. [118]

Because of their net local magnetization along an easy-plane for ferromagnetic materials, these objects can also be viewed experimentally through a Lorentz force atomic force microscope[115]. With properties fine tuned toward the next generation of magnetic storage, a new field of electronics focused on taking to account the skyrmion as an information carrier was started, known as *skyrmionics*[113]. Although there have been a few bulk materials to form skyrmion phases, some even at temperatures reaching up to 260 K[116], the need for room temperature (and higher) skyrmions for application purposes pushed much research into ferromagnetic heterostructures, after it was observed Ta/CoFeB/TaO_x heterostructures[117].

Although their low power, topological protection, and size make them ideal choices for ultra dense low power magnetic storage, ferromagnetic skyrmions have a few problems for spintronic applications. They feel a non-zero Magnus (Lorentz) force arising from driven spin-polarized currents, which alters the trajectory of the skyrmion and impedes their usefulness in skyrmionics[119, 120]. It was proposed that a two-sublattice picture, with opposing configurations cancelling the magnus effect for skyrmions would be a natural consequence of an antiferromagnetic skyrmion[121]. Another benefit for antiferromagnetic skyrmions would be faster dynamics well into the THz range, which would allow for ultra-fast memory[122]. The detection and manipulation of such skyrmions proves to be a difficult hurdle experimentally, though there have been recent successes with ferrimagnetic two-sublattice skyrmions[123, 124, 125].

3.3 The B20 Compounds

3.3.1 Chiral Magnetic B20 Compounds

Compounds which form into the structure B20 have become a quintessential example of incommensurate magnetic structures[126, 127]. The B20 compounds form in a cubic structure (Space group $P 2_1 3$), with relatively low symmetry. When a magnetic atom (usually a transition metal) resides in the B20 structure, the lack of inversion symmetry allows an anti-symmetrical exchange interaction known as the Dzyaloshinskii-Moriya Interaction (DMI), discussed in Sec. 1.2.2. The competition between ferromagnetic Heisenberg exchange and DMI results in chiral magnetic structures. The unusual magnetism in these compounds has been well-studied for decades, tracing back to the 1960s[128, 129]. While originally studied for their incommensurate chiral magnetic structures, these compounds returned to the scientific spotlight with the discovery of a skyrmion lattice phase in the chiral ferromagnet MnSi[114].

The phase diagrams of MnSi for high pressure and low applied fields were experimentally determined in Ref. [114, 130, 131], and are shown in Fig. 3.2a-b. With an applied magnetic field perpendicular to <1 0 0>, a small pocket "A"-phase is stabilized, and was shown to be separated from the conical phase by a 1^{st} order phase transition[132]. Experiments within the "A"-phase showed an unusual modulated magnetic structure with its moments perpendicular to the applied field[130]. It was later shown that within the "A" phase, MnSi could only be explained by a multi-k state with three ordering wavevectors perpendicular to the applied field that were 120°

apart from each other[114] which was shown to be a skyrmion phase[114, 133, 134]. Since the primary interactions in the B20 compounds are ferromagnetic, a typical technique to view the incommensurate magnetic structure is small-angle neutron scattering (SANS) centered around |Q| = 0. SANS data of MnSi taken by Muhlbauer, *et. al*[114], are shown in Fig. 3.2c-d. For their setup, Ref. [114] used a horizontal field magnet with field along < 100 >. The incommensurate peaks show a change from the zero-field helical state into a six-fold symmetric state that is distinct from the helical or conical states. This state was shown to be identical for any rotation of the crystal with respect to the field, implying that the features they observed were from an object disconnected from the lattice while maintaining an ordering wavevector perpendicular to the applied field.

3.3.2 Partial Order in the B20 Compounds

Contrary to this conventional incommensurate picture, where Bragg peaks will be observed at satellite wavevectors G + k around the magnetic zone centers, G, that correspond to the "parent" commensurate structure, there have been recent cases of interest, in which a well-defined *magnitude* for the incommensuration exists, but not a *direction*. This lack of a specific direction for the ordering wavevector has been termed "partial" or "unpinned" magnetic order [136, 137]. Aside from the interest garnered by their skyrmion hosting properties, the B20 compounds are also some of the only compounds observed to have partial order. This was first shown in MnSi before the discovery its of skyrmion phase by Pfleiderer, et al [136]. Above a critical pressure $p_c = 14.6$ kbar, MnSi enters a non-Fermi liquid phase as shown by resistivity[138, 139, 140] from 6 K down to milikelvin temperatures. Within this phase, Pfleiderer, *et al.* found a strange magnetic order. Neutron scattering in this phase shows broad scattering over a sphere of radius $Q = 0.043 \text{Å}^{-1}$. Longitudinal scans were found to be instrument resolution limited indicating a well-ordered wavevector magnitude with no preference of direction. The integrated intensity of the scattering was comparable to ambient pressure, showing that the total static magnetic moment within this phase is of similar order of magnitude. In MnSi, this was also seen in the correlated paramagnetic regime above its



Figure 3.2: (a) Magnetic field phase diagram of MnSi with field applied along <1 0 0>, adapted from [114]. The small "A"-phase stabilized at non-zero external fields corresponds with stable skyrmion lattice phase and is separated from the conical phase by a 1st order phase transition. (b) Pressure phase diagram for MnSi adapted from [131]. The dark green shaded area shows the region of partial order within the non-Fermi liquid phase. (c)-(d) SANS data on MnSi adapted from [114] taken within the helical ($T = 16 \ KB = 0 \ T$) and "A" phase ($T = 28 \ KB = 0.16 \ T$) respectively. In zero applied field, MnSi shows a helical diffraction pattern, while application of a field stabilizing the "A" phase shows a different structure decoupled from the nuclear structure. (e) SANS data taken on Fe_{1-x}Co_xSi within its "A" phase, adapted from [135]. After being zero-field cooled, a shell of scattering is observed as circles in reciprocal space slices.

ambient pressure transition [141]. Fe_{1-x}Co_xSi, another B20 compound, displays a similar shell when zero-field cooled [135] as shown in Fig. 3.2e.

In the case of MnSi, this partial helical order has been argued to be analogous to a "blue phase" of chiral liquid crystals, where the directors are arranged into double-twist cylinders that are not long range ordered. In MnSi, the analogous topological spin textures of the partially ordered phase are triple-twist cylinders, which are similar to skyrmions that are tightly packed, but not long range ordered [142, 143, 144]. Furthermore, in MnSi this phase appears to be energetically preferred compared to a well-ordered helix [145], and there is evidence that the combination of nearest-neighbor FM and DMI could stabilize such a state [142]. Although the case for a topologically non-trivial partial order in MnSi is compelling, it is not yet clear how general this kind of phase may be.

3.4 Polycrystalline Neutron Data on Fe₃PO₄O₃

High-resolution powder neutron diffraction was performed by Ross, *et al.*[146] at the general purpose powder diffractometer POWGEN, located at Oak Ridge National Laboratory. Below $T_N = 163$ K, powder neutron diffraction revealed anomalously broad magnetic peaks coinciding with resolution limited magnetic peaks, as shown in Fig. 3.3. These broad peaks were far broader than the instrument resolution and were fit by assuming a helical magnetic structures. At $|Q| \neq 0$, Bragg peaks are broken up into symmetry related peaks. To correctly reproduce the data, they needed to apply additional broadening to the calculated peaks such that within the *ab*-plane correlations were restricted to $\xi_{ab} \approx 100$ Å. Combined with resolution limited peaks along the *c*-axis, their data revealed a helical antiferromagnetic magnetic structure with "needle"" domains: short range correlations in the *ab*-plane and long range order (up to resolution limits) along *c*. With these two features included, Ref. [146] found no unique ordering wavevector which best reproduced the data, shown in Fig. 3.3 inset. Powder neutron diffraction was performed on polycrystalline samples of the disordered variant Fe_{3-x}Ga_xPO₄O₃ by Tarne, *et al.*[147, 148]. Magnetic substitution of Fe³⁺ ions with non-magnetic Ga³⁺ was shown to decrease both the helical winding length and



Figure 3.3: Adapted from [146]. (a) Powder neutron diffraction on Fe₃PO₄O₃ from Ross, *et al.* Broad magnetic features were fit using a combination of six helical peaks plus a correlation length in the *ab*-plane of $\xi_{ab} \approx 100$ Å. Shown in the inset, there was no unique wavevector choice which best fit experimental data. (b) Possible magnetic structure of Fe₃PO₄O₃ presented in the hexagonal unitcell, showing and example domain wall separating two domains.

correlation lengths associated with the broad magnetic peaks as the concentration of substitution, x, was increased. Ref. [147] found that these two quantities both decreased such that, within instrument resolution, they remained identical across the doping series. This strongly implies an intimate connection between the magnetic structure and the source of the unusual correlations reported in Ref. [146].

3.5 Visualizing Magnetic Textures

In our work presented in the following section, we propose three separate candidate magnetic textures to explain the combination of small correlations in polycrystalline experiments and partial order observed in single crystals. These candidate magnetic textures are presented in Fig. 3.8. Our Our depiction of these ideas for spin textures were similar to Lorentz TEM images of skyrmion and helical magnetic structures, shown in Ref. [115] and reproduced in Fig. 3.4a-b for clarity. For 2D materials, if one looks down at the magnetic plane in real space, helical magnetic structures



Figure 3.4: Lorentz TEM real space images of (a) helical and (b) skyrmion phases in Fe_{0.5}Co_{0.5}Si. Images adapted from Ref. [115] to show schematic representation of magnetic structures. (c) One possible ordering wavevector found in Fe₃PO₄O₃. Along *c* magnetic moments are offset by 180°, while within the *ab* plane moments rotate with a pitch length of $\lambda \sim 80$ Å. Contrast images can be described by a phase, ϕ , as the helical system winds.

can be viewed in contrasting peaks and troughs, with the ordering wavevector perpendicular to regions of constant phase (same contrast). In skyrmions one finds a completely different real space depiction, with a swirl of contrast on top of a constant contrast manifold. For Fe₃PO₄O₃, the magnetic structure is commensurate along *c* and thus one can realize such a depiction by looking down along the *c*-axis. Regions of darkest contrast (dark grey) represent one phase (say $\phi = 0$) while regions of lightest contrast (white/ light grey) represent a phase offset of π . An example of this phase description compared to an actual visualization of the magnetic structure is shown in Fig. 3.4c.

3.6 Single Crystal Neutron Diffraction: Published Work

This section reproduces our published work, *Partial antiferromagnetic helical order in singlecrystal Fe*₃ PO_4O_3 . The full reference and work can be found at [106] *.

3.6.1 Article Overview

Magnetic frustration in Fe₃PO₄O₃ produces an unusual magnetic state below $T_N = 163$ K, where incommensurate antiferromagnetic order is restricted to nanosized needle-like domains, as inferred from neutron powder diffraction. Here we show using single-crystal neutron diffraction that Fe₃PO₄O₃ does not exhibit a preferred ordering wavevector direction in the *ab*-plane despite having a well-defined ordering wavevector length. This results in the observation of continuous rings of scattering rather than satellite Bragg peaks. The lack of a preferred incommensurate ordering wavevector direction can be understood in terms of an antiferromagnetic Heisenberg model with nearest-neighbor (J_1) and second-neighbor (J_2) interactions, which produces a quasidegenerate manifold of ordering wavevectors. This state appears to be similar to the partially ordered phase of MnSi, but in Fe₃PO₄O₃ arises in a frustrated antiferromagnet rather than a chiral ferromagnet.

3.6.2 Research Article

Introduction

Incommensurate helical magnetic structures are of interest as potential generators of multiferroic or skyrmion phases [114, 149, 150]. Typically an incommensurate structure will have a well-defined pitch length, λ , producing an ordering wavevector magnitude $|\mathbf{k}| = 2\pi/\lambda$, and a well-defined ordering wavevector direction. Both properties can be measured through neutron

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diffraction experiments, where Bragg peaks will be observed at satellite wavevectors G + k around the magnetic zone centers G that correspond to the "parent" commensurate structure [†].

Contrary to this conventional picture, there have been recent cases of interest, notably in the B20 material MnSi, in which a well-defined *magnitude* for the incommensuration exists, but not a *direction*. This lack of a specific direction for the ordering wavevector has been termed "partial" or "unpinned" magnetic order [136, 137]. The B20 materials, e.g., MnSi, MnGe, FeGe, and $Fe_{1-x}Co_xSi$, host locally ferromagnetic (FM) helical phases which transform into skyrmion lattices under small applied fields [114, 116, 135, 151, 152]. The parent helical structures and field-induced skyrmion phases are long range ordered (LRO), with magnetic propagation vectors k that are welldefined in both magnitude and direction, manifesting as sharp satellite peaks in neutron diffraction experiments. The 6-fold symmetric arrangement of Bragg peaks are observed a small, constant reciprocal lattice distance away from magnetic zone centers. Due to the FM nature of the parent commensurate state, the commensurate zone centers include G = (0, 0, 0), so they can be most effectively studied via small-angle neutron scattering (SANS) [114]. However, this well-ordered skyrmion lattice phase can be disrupted such that the six incommensurate Bragg peaks become a spherical shell of scattering due to "partial order": MnSi displays this type of spherical structure factor in a high pressure phase with unusual electronic transport properties [136] as well as in the correlated paramagnetic regime above its ambient pressure transition [141], while $Fe_{1-x}Co_xSi$ displays a similar shell when zero field cooled [135]. In the case of MnSi, this partial helical order has been argued to be analogous to a "blue phase" of chiral liquid crystals, where the directors are arranged into double-twist cylinders that are not long range ordered. In MnSi, the analogous topological spin textures of the partially ordered phase are triple-twist cylinders, which are similar to skyrmions that are tightly packed, but not long range ordered [142, 143, 144]. Furthermore, in MnSi this phase appears to be energetically preferred compared to a well-ordered helix [145], and there is evidence that the combination of nearest neighbor FM and Dzyaloshinskii-Moriya (DM)

[†]In locally ferromagnetic incommensurate structures, those magnetic zone centers are the same as the nuclear zone centers, including G = (0, 0, 0), but for antiferromagnetic parent structures, the "parent" magnetic zone centers are not generally coincident with nuclear zone centers.



Figure 3.5: Magnetic sublattice formed by Fe^{3+} ions in $\text{Fe}_3\text{PO}_4\text{O}_3$, with structural unit cell (in the hexagonal setting of R3m) shown as gray lines. Here J_1 interactions are shown in orange and J_2 interactions are shown in blue.

interactions could stabilize such a state [142]. Although the case for a topologically non-trivial partial order in MnSi is compelling, it is not yet clear how general this kind of phase may be.

Here we report the first observation of a partially ordered helical state in a locally *antiferromagnetic* (AFM) spin structure arising in the insulating magnet $Fe_3PO_4O_3$. The state is characterized by incommensurate *rings* in the magnetic structure factor as measured by single-crystal neutron diffraction. Taken together with previous studies showing short correlation lengths in the plane of the ring, these results suggest a disordered state similar to the blue phase description of MnSi. However, compared to MnSi, the static partial order in $Fe_3PO_4O_3$ appears to be extremely stable, spanning temperatures from 163 K to 4 K (or below), with no external pressure or magnetic field required.

The magnetic properties of Fe₃PO₄O₃ were first investigated in the 1980's [153, 154], but study of the material has enjoyed renewed interest [146, 147, 155, 156] due to recent high-resolution neutron powder diffraction (NPD) measurements. These measurements revealed unusual magnetic correlations below an antiferromagnetic transition at $T_N = 163$ K [146, 147]. Fe₃PO₄O₃ forms a non-centrosymmetric lattice (spacegroup R3m, with room temperature lattice parameters of a =



Figure 3.6: (a) Single-crystal neutron diffraction intensity maps near $(h \ k \ l) = (0 \ 0 \ 1.5)$ at $T = 4 \ K$ in two planes of reciprocal space (top). k' refers to a length along the vector orthogonal to both a^* and c^* and normalized to be the same length as b* Calculation of the diffraction intensity expected for a resolution-limited ring of radius 98 Å in the hk'-plane and centered on $(h \ k \ l) = (0 \ 0 \ 1.5)$ (bottom). The ring is convolved with an anisotropic instrumental resolution ellipsoid that was determined via measurements of a nearby nuclear Bragg peak (see appendix). Insets show the non-convolved ring in each respective plane. (b) Integrated intensity of the ring as a function of temperature centered on $(h \ k \ l) = (\overline{2} \ 2 \ 0.5)$. (Inset) Single crystal Fe₃PO₄O₃ used for neutron diffraction. (c) Intensity along a^* for $(h \ k \ l) = (0 \ 0 \ 1.5)$ showing agreement between data and resolution calculation.
8.006 Å, c = 6.863 Å [153] in the hexagonal setting) with magnetic Fe³⁺ ions residing in a 3D network of triangular units shown in Fig. 3.5. Previous work on polycrystalline samples indicated strong antiferromagnetic interactions ($|\Theta_{CW}| > 1000$ K), and a frustration parameter f = $|\Theta_{CW}|/T_N \ge 6$ [146]. An incommensurate AFM state occurs below T_N [146, 153, 155], which occupies the full volume fraction of the material [156]. Analysis of Mössbauer spectra identified an easy axis along the crystallographic *a*-axis[155] with a corresponding ordered moment of 4.3 μ_B . Although DM interactions are allowed by symmetry in Fe₃PO₄O₃, many properties of the state below T_N seem to be captured by a simple Heisenberg model with competing nearest-neighbor (J_1) and second-neighbor (J_2) interactions [146, 147].

Neutron diffraction on polycrystalline powders revealed magnetic peaks which are extremely broad and oddly-shaped in reciprocal space coexisting with a resolution-limited peak [146]. Analogous neutron powder diffraction features were also observed in some samples of the multiferroic material BiFeO₃ [157, 158], but the shape of the pattern was highly sample dependent and the structure of the most ideal samples measured with high resolution neutron instrumentation were eventually understood to be a AFM magnetic cycloid structure [159]. In the case of Fe₃PO₄O₃, extremely high-resolution powder neutron diffraction could not resolve individual satellite peaks. This was explained by an AFM helical structure with the propagation vector residing in the *ab*plane and a pitch length of $\lambda = 86$ Å. Crucially, a "needle-like" correlation volume was required to reproduce the data, with short range *ab*-plane correlations ($\xi_{ab} \approx 100$ Å) and very long range correlations in the *c* direction. With the availability of single crystals, we can now demonstrate that the magnetic features previously identified in the powder samples do not correspond incommensurate Bragg peaks, but rather to incommensurate *rings* of intensity in the *ab* plane. Thus, a specific incommensurate wavevector direction is not selected in this material, and only partial AFM helical order exists.

Experimental Methods

Small single crystals of Fe₃PO₄O₃ (~0.3mm on a side, see Fig. 3.6b inset), were grown from powders of FePO₄ (\geq 99% phase purity) by chemical vapor transport using ZrCl₄ as the transport

agent (920 °C at source, 800 °C at sink, for 120 h) [148, 160]. The single crystals are a transparent dark red, and are typically $0.5 \times 0.3 \times 0.3$ mm in size. The single-crystal unit cell was confirmed using a Bruker D8 Advance Quest SCXRD and Photonic Science Laue diffractometer (a = 7.998 Å, c = 6.854 Å).

Results & Discussion

Single Crystal Neutron Diffraction

Neutron diffraction on a single crystal of Fe₃PO₄O₃ ($m \approx 0.3$ mg) was carried out on HB-3A, the four-circle neutron diffractometer at Oak Ridge National Laboratory, with an incident neutron wavelength $\lambda = 1.546$ Å from a Si-220 monochromator. The monochromator was set to doublyfocusing mode, in order to increase flux. An area detector allowed for efficient mapping of the intensity near the "parent structure" commensurate AFM wavevectors (e.g., (0 0 1.5) and related positions). Most of the data was taken at T = 4 K with background subtractions from T= 200 K scans. The magnetic scattering near ($\overline{2} \ 2 \ 0.5$) was measured as a function of temperature in 10 K steps up to 200 K.

Representative data at 4 K are shown in Fig. 3.6a, along with a simulation of a resolutionconvoluted ring of intensity centered around the commensurate reflection. The doubly-focusing monochromator at HB-3A produces broad resolution in the vertical direction. Depending on the specific orientation of the crystal in the four-circle diffractometer for each measured ring, this broadening shows up in different directions in reciprocal space. We modeled the instrumental resolution function as an ellipsoid with Gaussian intensity profiles, whose principal axes widths were obtained from measurements of nuclear Bragg peaks (also accounting for variations in the resolution as a function of scattering angle [161]). The resolution function was transformed using the four-circle diffractometer coordinate system formalism described in Busing, et al.[162] with appropriate modifications for the coordinate system at HB-3A. Further details can be found in the appendix. The observed diffraction patterns are consistent with a continuous ring of uniform intensity lying in the hk-plane. These rings are appear around each parent commensurate magnetic structure zone center, and as shown in Fig. 3.6b, they onset below the known AFM ordering transition. The rings produce two peaks in the kl-plane, from which we determined the radius of the ring to be |Q|=0.064(6) Å⁻¹, corresponding to a helical pitch length $\lambda = 98 \pm 12$ Å, which is in reasonable agreement with the pitch length determined from powder neutron diffraction (86 Å). A comparison in size of the scattering rings to the full Brillouin zone is shown in Fig. 3.7b. All five measured rings were found to be resolution limited in each dimension (see for example, Fig. 3.6 (c)). However, this does not contradict the previous determinations of correlation lengths which were made using very high-resolution powder diffraction. The best resolution at HB-3A with our setup was 0.0059 ± 0.00024 Å⁻¹, giving a maximum resolvable correlation length of 470 ± 21 Å, however the orientation of the resolution function was such that the resolution in the hk-plane was much coarser for typical reflections (appendix).

This measurement thus exposes a unique scattering structure factor in $Fe_3PO_4O_3$ which is analogous to the spherical shells observed in MnSi. In the case of $Fe_3PO_4O_3$, the presence of long range *commensurate* order along the *c*-axis produces a 2D ring of scattering in the *hk*-plane, rather than a spherical shell. The existence of these rings shows that $Fe_3PO_4O_3$ has "partial" magnetic order in the *ab*-plane.

Discussion

The lack of a preferred ordering wavevector direction in $Fe_3PO_4O_3$ can be understood on the basis of the frustrated Heisenberg model used in previous studies of $Fe_3PO_4O_3$. We determined the ground state ordering wavevectors via the Luttinger-Tisza (LT) method [163, 164, 165] within the frustrated AFM J_1 , J_2 Heisenberg Hamiltonian model

$$\mathcal{H} = J_1 \sum_{n.n.} S_i \cdot S_j + J_2 \sum_{n.n.n.} S_i \cdot S_j$$
(3.2)



Figure 3.7: (a) Luttinger-Tisza calculation of energies in the rhombehedral unit cell of $\text{Fe}_3\text{PO}_4\text{O}_3$ (but presented in the hexagonal setting) using $J_2/J_1 \sim 1.9$ taken from Ref. [147]. Cuts within the ring show six energy minima in the *hk*-plane centered around (*h k l*) = (0 0 1.5). Variations inside the well on the order of $10^{-3}J_1$ correspond to energy differences of T ~ 0.4 K.(b) 1st Brillouin zone (in hexagonal setting) showing the relative size of the ring of scattering compared to the full Brillouin zone.



Figure 3.8: Possible scenarios (depicted in direct space) of helical magnetic structures that can produce a circular ring in the magnetic structure factor. Lines represent the "crests" (zero phase angle) of an incommensurately modulated magnetic structure, with a distance of λ (pitch length) between each line. Dots represent skyrmions. Red arrows denote incommensurate modulation wavevector directions. (a) Short range helical domains, where every domain chooses an ordering wavevector direction at random. (b) A singledomain structure with a wavevector that is unpinned from the lattice and "meanders" through space (similar to the blue phase in liquid crystals). (c) A disordered skyrmion state, in which skyrmions maintain an average spacing of λ between neighbors but do not crystallize.

Where $S_i = \{S_i^x, S_i^y, S_i^z\}$ are spins associated with site *i* in the Fe³⁺ sublattice, and J_1 and J_2 are antiferromagnetic super-exchange couplings between nearest and second neighbor pairs of spins, respectively (shown in Fig. 3.5). When the "hard constraint" of the LT method is met (i.e., all spin lengths are found to be equal), this method provides an exact determination of classical spin ground states for isotropic models [166, 167].

Using the ratio of exchange interactions previously estimated for Fe₃PO₄O₃ ($J_2/J_1 \sim 1.9$ [147]) LT produces helical structures with ordering wavevectors consistent with the measured data. Examining the preferred ordering wavevectors in reciprocal space, a circular distribution of low energy configurations is obtained around the commensurate parent structure zone centers (Fig. 3.7a). Within the model there is indeed a subtle preferred orientation within this ring (resulting in six symmetry related ordering wavevectors); however, the difference in energy of these directions compared to the rest of the circle is ~ J₁/1000. Using an estimate of $J_1 > 319$ K based on $\theta_{CW} > 1000$ K, the energy barriers between minimum around the ring is at most 0.4 K: therefore, LT predicts an effectively degenerate manifold of ordering wavevectors. Although unlikely, due to the kinetic cost of reorienting correlated static spins, it may be possible that $Fe_3PO_4O_3$ would undergo a second transition below 1 K to lock into the weakly preferred wavevectors produced by LT.

Given this degeneracy of the ordering wavevectors, one may imagine several scenarios for a ring-like structure factor, some of which are depicted in Fig. 3.8. In the simplest case, short range helical domains with many topological defects (domain walls) between them could form a continuum of ordering directions with well-defined domain sizes (Fig. 3.8a). The second case is a single-domain structure that is free to vary in direction while maintaining its pitch length (Fig. 3.8b). The last case is a short range correlated state of topological spin textures, as in a disordered skyrmion [136] or "blue phase" [142], as proposed for partial order of MnSi. In this scenario, the average distance between the topological objects would be preserved, but they would not crystallize (Fig. 3.8c).

What remains to be understood in Fe₃PO₄O₃, which may help to distinguish between the above scenarios, is what limits the length scale of correlations within the *ab*-plane. The influence of site dilution reported in Ref. [147] offers a clue. Substituting non-magnetic gallium at the iron sites of Fe₃PO₄O₃ in powder samples of was found to cause both λ and ξ_{ab} decrease, and, intriguingly, these two lengths exhibited the same trend across the whole doping series [147]. This suggests that the source of the short range correlations is intrinsically tied to the microscopic origin of the incommensurate structure itself. A state like a disordered skyrmion phase would provide a natural connection between ξ_{ab} , the size of the coherent helical object (a skyrmion), and λ . In the case of a disordered skyrmion phase, one would expect that λ would equal approximately twice ξ_{ab} , the latter being defined as the radius of the correlated region. In contrast, in the case of Fe₃PO₄O₃, it appears that ξ_{ab} remains approximately equal to λ [147], suggesting a slightly different type of object in direct space. However, we note here that a quantitative determination of ξ_{ab} based on the diffraction peak profile shape relies on several assumptions when the peak shape is something other than a simple Lorentzian. For instance, in Ref. [147] the Scherrer formula was used with

shape factor K = 1, and though this should give the right order of magnitude, this precise value of K, and thus the precise value of ξ_{ab} is not quantitatively justified. Nevertheless, the quantitative values of λ and the *trends* in ξ_{ab} reported in Ref. [147] stand up to any choice of analysis, and strongly suggest an intrinsic connection between these length scales, as would be expected based on a disordered collection of topological objects.

Conclusions

In summary, we have carried out detailed single-crystal neutron diffraction measurements on $Fe_3PO_4O_3$, which has revealed a partially ordered helical phase; i.e., one with a well-defined ordering wavevector magnitude, but not direction, down to T = 4 K. Luttinger-Tisza calculations using the frustrated Heisenberg J_1 , J_2 model confirm that a specific direction for helical ordering wavevector is only very weakly preferred. This result is reminiscent of the partially ordered phase in MnSi, which was argued to be an analog to the blue phase found in liquid crystals. In $Fe_3PO_4O_3$, this unusual state appears to also be related to a disordered AFM skyrmion-like state. Determining the direct space nature of the unusual partially ordered state in $Fe_3PO_4O_3$ is thus an interesting open question.

The authors acknowledge useful discussions with R. Glaum relating to the synthesis of the single crystal samples, and with D. Reznik relating to the partially ordered state of MnSi. This research used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

For Appendices related to this work, please see Appendix A.

3.7 Conclusions and Outlook

Without accessibility to large single crystals, further experimental progress for $Fe_3PO_4O_3$ remains difficult. With the Dzyaloshinskii-Moriya interaction allowed by symmetry, characterizing its contribution remains an important step in determining the magnetic structure of $Fe_3PO_4O_3$. There has been little investigation into the dynamics of the system, which may be intimately connected to its unusual magnetic properties. As of the time of this work, the full details of the mag-

netic structure of $Fe_3PO_4O_3$ remain a mystery, however it remains a promising candidate to host a disordered skyrmion lattice. The combination of strongly insulating and antiferromagnetic parent structure prevents conventional techniques for identification of skyrmions, such as Lorentz transmission electron microscopy (Lorentz-TEM). The combination of nanoscale correlation sizes and low contrast of helical magnetic structure exceeds current instrumentation resolutions for the photoemission electron microscopy technique (PEEM). If $Fe_3PO_4O_3$ hosts such exotic quasi-particles, it would be the first observed material to host the highly sought after antiferromagnetic skyrmion in its bulk. Whatever the true nature of $Fe_3PO_4O_3$'s magnetic structure, its unusual partial magnetic order and dense topological defects make it a material worthy of more study.

Chapter 4

Phase Competition in Antiferromagnetic Pyrochlore Yb₂Ge₂O₇

4.1 Introduction

In this chapter, I cover work on single crystals of the rare earth pyrochlore antiferromagnet Yb₂Ge₂O₇. In highly anisotropic complex systems, such as the rare earth pyrochlore oxides, a unique determination of interactions can only be accomplished through characterization of single crystals. These rare earth pyrochlore oxides have been shown to host an extensive diversity of exotic phenomena. In particular the Yb-based pyrochlore oxides share similar polycrystalline properties, including broad featureless excitations within their magnetically ordered phases. This is despite $Yb_2Ge_2O_7$ being shown to order into an antiferromagnetic ground state, rather than the ferromagnetic ground state of Yb₂Ti₂O₇ or Yb₂Sn₂O₇. Using a combination of inelastic neutron scattering, electron paramagnetic resonance, specific heat, and magnetometry, we compare data to linear spin wave theory and numerical linked-cluster expansion calculations to extract the exchange parameters of Yb₂Ge₂O₇ within the anisotropic nearest neighbor model. Our parameters show Yb₂Ge₂O₇ most likely lies within the antiferromagnetic ψ_3 state classically, close to the phase boundary between the two antiferromagnetic states ψ_2 and ψ_3 , as well as the boundary between ψ_3 and the splayed ferromagnet state. This is opposite of Yb₂Ti₂O₇, which lies close to the same boundary, but on the ferromagnet side. The close proximity of these materials to a classical phase boundary in exchange space lends strong support to the theory that competition between neighboring phases is driving the unusual behavior of these materials.

Work on the magnetometry data, specific heat data, and inelastic neutron data presented here was performed by myself under supervision of my advisor Kate Ross and instrument scientist Jose A. Rodriguez-Rivera, with aid from Danielle Yahne, Steffen Säubert, and instrument scientist Daniel Pajerowski in the collection and analysis of the inelastic neutron data taken at CNCS. Coalignment of single crystals of Yb₂Ge₂O₇ was also done by myself. All theoretical work, including linear spin-wave theory, single-ion modeling, and numerical-linked cluster calculations were performed by Prof. Jeffery Rau at University of Windsor and Prof. Michel Gingras at University of Waterloo. All EPR data collection and analysis was completed by Prof. Stephen Hill and Jonathon Mabry at Florida State University. Crystals were grown by the group of Prof. Joe Kolis at Clemson University, with Duminda Sanjeewa growing the pure Yb₂Ge₂O₇ crystals and Matthew Powell growing the dilute Yb-doped Lu₂Ge₂O₇ crystals. The mansucript mentioned below was written by myself, Kate Ross, Jeff Rau, and Michel Gingras. While all groups efforts were instrumental in completion of this work, I would like to give extra thanks to Prof. Jeff Rau and Prof. Michel Gingras for their tremendous contributions.

The rest of the chapter is outlined as follows: sections 4.2 to 4.3 contain introductory material covering rare earth pyrochlores, the anisotropic nearest neighbor model for the pyrochlore lattice, and previous work on the Yb-pyrochlores, including literature on polycrystalline Yb₂Ge₂O₇. Section 4.4 reproduces our published manuscript detailing work on single crystals of Yb₂Ge₂O₇, and the full reference can be found at Ref. [168]. Finally section 4.5 describes conclusions and future outlook for Yb₂Ge₂O₇.

4.2 Rare Earth Pyrochlores

Pyrochlore oxides of the form $(A_2B_2O_7)$ represent an extensive family of materials with great diversity of electronic properties. The cubic pyrochlore lattice, space group $Fd\bar{3}m$ (227), consists of two interpenetrating networks of corner sharing tetrahedra, shown in Fig. 4.1a. The pyrochlore lattice is an ideal framework to host magnetic frustration, both in the form of geometric and exchange frustrations[22, 169, 170]. It also contains a remarkably large set of possible compounds, owing to the large number of possible A and B site combinations which can form into the pyrochlore lattice[171]. The rare-earth pyrochlore oxides, with a rare earth trivalent ion on the A site, further exemplify the diversity in material properties. A combination of



Figure 4.1: (a) The cubic pyrochlore lattice shown as two interpenetrating networks of corner sharing tetrahedra, the anions are not shown for clarity.(b) Single-ion anisotropy found on the pyrochlore lattice are depicted by the red Ising anisotropy, where spins lie along the local <1 1 1> for each site on the tetrahedra, and the green easy-plane XY anisotropy, where the spins lie within a plane perpendicular to the local <1 1 1>. (c) The D_{3d} point group symmetry of the octahedral coordination of oxygen anions (yellow) in the pyrochlore structure.

large spin-orbit coupling from the heavy rare-earths and crystal electric field effects from the surrounding oxygen ions can produce states featuring a breadth of novel phenomena. Some examples include dipolar spin-ice in Ho₂Ti₂O₇[54, 55, 56] and Dy₂Ti₂O₇[51, 57, 58], order by disorder in Er₂Ti₂O₇[172, 173, 174], Anomalous Hall in Nd₂Mo₂O₇[175, 176], cooperative paramagnetism in Tb₂Ti₂O₇[177, 178, 179], and multiple possible quantum spin liquid candidates such as Ce₂Zr₂O₇[180, 181] and Ce₂Sn₂O₇[182, 183]. Although the rare-earths strong spin-orbit coupling often lead to large total angular momentum states that behave classically ($J \gg \frac{1}{2}$), degeneracy lifting of the states due to crystal electric field effects can lead to large splitting between new effective states. For ions with a ground state doublet, such as is guaranteed for ions containing an odd number of electrons due to Kramer's theorem, the low temperature physics can be described by treating the magnetic ion as an effective pseudo-spin- $\frac{1}{2}$ with anisotropic effective bilinear coefficients[170].

4.2.1 Yb Pyrochlores

The Yb-pyrochlores (Yb₂B₂O₇) have proven to be an interesting sub-set of the rare-earth pyrochlores. Er^{3+} and Yb³⁺ exhibit an XY easy-plane single-ion anisotropy shown in Fig. 4.1b, where the spins prefer to align in a plane perpendicular to the local *z*-axis. This anisotropy differs from the more traditional uniaxial Ising-like single-ion anisotropy seen in many of the lanthanide group. As a result, the physics observed in Yb and Er compounds can strongly differ from the other lanthanide compounds. In particular, rare earth ions with XY anisotropy show smaller effective moments which allows for dipolar effects to becomes less prominent and exchange interactions to become the dominant terms in the Hamiltonian.

Anisotropic Nearest-Neighbor Model

Building off inelastic neutron scattering results of $Yb_2Ti_2O_7$ and $Er_2Ti_2O_7$, one particular minimalist model has been successful at recovering the low temperature behavior of many of the Yb and Er based pyrochlores. This model is the nearest-neighbor anisotropic effective spin- $\frac{1}{2}$ model[173, 184, 185, 186]

$$H = \sum_{\langle ij \rangle} \sum_{\mu\nu} J_{ij}^{\mu\nu} S_i^{\mu} S_j^{\nu} - \mu_{\rm B} \sum_{\mu\nu} B^{\mu} \sum_i g_i^{\mu\nu} S_i^{\nu}, \qquad (4.1)$$

where μ and ν run over the Cartesian directions (x, y, z), $J_{ij}^{\mu\nu}$ is the exchange tensor between spins at lattice sites *i* and *j*, $g_i^{\mu\nu}$ is the *g*-tensor for spin at site *i*, and B^{μ} is the μ component of the external magnetic field.

Following Ref. [184], for the pyrochlore lattice one can define a coordinate system such that centers of tetrahedra form into an FCC lattice (four sublattices). From the relative centers of each tetrahedra, one can define four lattice vectors linking each site on an individual tetrahedra to its center,

$$a_{0} = \frac{a}{8}(1\ 1\ 1)$$

$$a_{1} = \frac{a}{8}(1\ \overline{1}\ \overline{1})$$

$$a_{2} = \frac{a}{8}(\overline{1}\ 1\ \overline{1})$$

$$a_{3} = \frac{a}{8}(\overline{1}\ \overline{1}\ 1)$$
(4.2)

where *a* is the lattice constant of the pyrochlore unitcell. Symmetry reduces the possible exchange tensor values into just four independent exchange parameters (J_1, J_2, J_3, J_4) [184, 187]. These terms behave as follows: J_1 is an XY-like interaction with respect to the local bond, J_2 is an Ising-like interaction with respect to the local bond, J_3 is a pseudo-dipolar-like term, and J_4 is the Dzyaloshinskii-Moriya term. Noting that $J_{ij} = J_{ji}^T$, the exchange tensors for each pair of neighbors are

$$\boldsymbol{J}_{01} = \begin{pmatrix} J_2 & J_4 & J_4 \\ -J_4 & J_1 & J_3 \\ -J_4 & J_3 & J_1 \end{pmatrix}, \boldsymbol{J}_{02} = \begin{pmatrix} J_1 & -J_4 & J_3 \\ J_4 & J_2 & J_4 \\ J_3 & -J_4 & J_1 \end{pmatrix}, \boldsymbol{J}_{03} = \begin{pmatrix} J_1 & J_3 & -J_4 \\ J_3 & J_1 & -J_4 \\ J_4 & J_4 & J_2 \end{pmatrix}$$
$$\boldsymbol{J}_{12} = \begin{pmatrix} J_1 & -J_3 & J_4 \\ -J_3 & J_1 & -J_4 \\ -J_4 & J_4 & J_2 \end{pmatrix}, \boldsymbol{J}_{13} = \begin{pmatrix} J_1 & J_4 & -J_3 \\ -J_4 & J_2 & J_4 \\ -J_3 & -J_4 & J_1 \end{pmatrix}, \boldsymbol{J}_{23} = \begin{pmatrix} J_2 & -J_4 & J_4 \\ J_4 & J_1 & -J_3 \\ -J_4 & -J_3 & J_1 \end{pmatrix}$$

An alternative local basis to the one used above can be formed by coupling each local spin component such that the local z-direction for site i is aligned with the C_3 symmetry axis of the local CEF on site i. In this basis, the four exchange parameters follow the convention J_{zz} , J_{\pm} , $J_{\pm\pm}$, $J_{z\pm}$ and Eqn. 4.1 becomes,

$$H = \sum_{\langle ij \rangle} J_{zz} S_i^z S_j^z - J_{\pm} (S_i^+ S_j^- + S_i^- S_j^+) + J_{\pm\pm} (S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^-) + J_{z\pm} [S_i^z (S_j \zeta_{ij} + S_j^- \zeta_{ij}^*) + S_j^z (S_i \zeta_{ij} + S_i^- \zeta_{ij}^*)]$$
(4.4)

where γ_{ij} and ζ_{ij} are bond dependent phases which encode the change in coordinate frame across the sublattices

$$\zeta = \begin{pmatrix} 0 & -1 & e^{i\pi/3} & e^{-i\pi/3} \\ -1 & 0 & e^{-i\pi/3} & e^{i\pi/3} \\ e^{i\pi/3} & e^{-i\pi/3} & 0 & -1 \\ e^{-i\pi/3} & e^{i\pi/3} & -1 & 0 \end{pmatrix}, \gamma = -\zeta^*$$
(4.5)

the relation between the two sets of bases $(J_{zz}, J_{\pm}, J_{\pm\pm}, z_{\pm})$ and $J_1, J_2, J_3, J_4)$ are

$$J_{zz} = -\frac{1}{3}(2J_1 - J_2 + 2J_3 + 4J_4)$$

$$J_{\pm} = \frac{1}{6}(2J_1 - J_2 - J_3 - 2J_4)$$

$$J_{\pm\pm} = \frac{1}{6}(J_1 + J_2 - 2J_3 + 2J_4)$$

$$J_{z\pm} = \frac{1}{3\sqrt{2}}(J_1 + J_2 + J_3 - J_4)$$
(4.6)

As a function of these exchanges, the *classical* phase diagram shown in Fig. 4.2 contains four q = 0 ordered phases separated by several phase boundaries: three antiferromagnetic phases (the ψ_2 , ψ_3 and Palmer-Chalker states) and one splayed ferromagnet phase (SFM) [186, 188]. Quantum effects were found to distort the phase boundaries and introduce regions of no classical order shown in a log-polar plot in Fig. 4.2b.

Yb₂Ti₂O₇

Most famously, work on Yb₂Ti₂O₇ showed many hallmarks of a quantum spin-ice ground state in early experiments. While there was one group that reported an ordered ferromagnetic state [189], multiple other groups reported no obvious magnetic order down to 0.03 K[190, 191, 192] from neutron diffraction data. Magnetic ordering was expected from heat capacity, which showed a sharp low temperature anomaly at $T_N = 0.260$ K as well as a higher temperature broad bump[193, 194]. Inelastic neutron scattering below the sharp specific heat anomaly showed the existence of broad continuum-like excitations within the ordered magnetic state, rather than conventional spin wave excitations[192] (see Fig. 4.3). At temperatures below the broad higher temperature bump in Yb₂Ti₂O₇, multiple groups noticed rods of diffuse scattering along the <1 1 1> directions[192, 195], which became less intense as the temperature was driven lower, but persisted below the sharp heat capacity anomaly.

Sample dependence issues were observed in single-crystal studies, both in the specific heat[196], and the found exchange parameters[184, 197, 198]. It was also noted that single crystal samples of $Yb_2Ti_2O_7$ were yellow in color, whereas Yb^{3+} oxides are generally colorless. This has since been attributed to small deviations from perfect stoichiometry, where excess Yb^{3+} reside on the B-site,



Figure 4.2: Adapted from [186]. (a) Classical ground-state phase diagram for Eqn. 4.1, where J_4 has been set to zero. There are four q = 0 ground-states shown in (c). (b) Quantum fluctuations on top of the classical phase diagram shown in (a). Regions of white show where quantum fluctuations can destroy conventional order within linear spin-wave theory. Parameters are shown in a log polar plot. (c) Classical spin configurations of the four ground-states found in (a).



Figure 4.3: Adapted from Ref. [17]. Inelastic neutron scattering on polycrystalline samples of $Yb_2Ge_2O_7$, $Yb_2Sn_2O_7$, $Yb_2Ti_2O_7$, and $Er_2Ti_2O_7$. All the Yb-pyrochlores share unusual broad diffuse and featureless excitation spectra, while $Er_2Ti_2O_7$ spectra shows a more structured dispersion, characteristic of spin-wave like excitations.

i.e. a naturally "stuffed" pyrochlore[199]. It was shown that magnetic properties of Yb₂Ti₂O₇ were extremely sensitive to such disorder, down to deviations of order $\sim 1\%$. High-quality stoichiometric crystals grown showed clear-colorless optical properties and also showed good agreement with polycrystalline heat capacity measurements [199, 200].

A large body of work has since shown that $Yb_2Ti_2O_7$ indeed exhibits a weak magnet ordering into a Γ_9 splayed ferromagnetic ground state (Fig. 4.2) [189, 200, 201, 202, 203]. Stoichiometric crystals have also reported a field dependent re-entrant phase diagram[200, 203], which may arise from strong quantum effects. Despite magnetically ordering, the unusual zero-field excitations remain even in stoichiometric samples[204]. A conventional spin-wave spectrum develops for fields above 0.5 T in the [1 1 0] direction[192] and in this limit linear spin-wave theory is valid, and one can match fits to the field polarized dispersion to Eqn. 4.1 in order to extract the unique exchange parameters and determine the ground state of $Yb_2Ti_2O_7[184, 197, 198, 204]$.

Shown in Fig. 4.2a are two sets of exchange parameters for Yb₂Ti₂O₇ (Ross, *et al.*[184] and Robert, *et al.*[197]). Further exchange parameters from Thompson, *et al.*[198] and most recently Scheie, *et al.* on stoichiometric crystals[204] all show Yb₂Ti₂O₇ close to a classical phase boundary between the Γ_9 splayed ferromagnetic ground state and a Γ_5 antiferromagnetic ground state. One hypothesis for the unusual excitations within the ordered state is due to phase competition between FM and AFM phases[17, 186, 204, 205]. Scheie, et al. revealed strong evidence of phase competition in inelastic neutron scattering, diffuse elastic scattering, and domain wall structures of stoichiometric Yb₂Ti₂O₇[204]. In particular detailed fits to inelastic neutron scattering data show zero-field dispersions can be produced by a coexistence of ferromagnetic Γ_9 and antiferomagnetic Γ_5 phases.

Aside from Yb₂Ti₂O₇, experiments on polycrystalline variants of the other Yb pyrochlores Yb₂Sn₂O₇ andYb₂Ge₂O₇ show similarities to Yb₂Ti₂O₇'s unusual properties and have been reviewed by Hallas, *et al.*[17]. Polycrystalline zero-field inelastic neutron scattering show similar continuum excitations as observed in Yb₂Ti₂O₇, shown in Fig. 4.3. Due to difficulties in growth, single crystals of these other Yb-pyrochlore compounds remain elusive, despite a large interest. The Yb series of pyrochlores share similar heat capacity profiles, all showing a low temperature lambda-like anomaly indicating long-range order and a higher temperature broad Schottky-like anomaly which has been proposed to be the onset of short-range correlations in these materials (see Fig. 4.4c). These features were observed to be magnetic in nature, with the non-magnetic variants (Lu₂Ge₂O₇, ect) showing no signal in the specific heat below ~ 10 K. Neutron diffraction show that Yb₂Sn₂O₇ orders into the Γ_9 splayed ferromagnetic state below $T_C = 0.1$ K, similar to Yb₂Ti₂O₇[206, 207]. Yb₂Pt₂O₇ also shows an ordering into a ferromagnetic state below $T_C = 0.3$ K[208], and ¹⁹⁵Pt NMR studies show a field-induced gap which decreases with applied field as well as additional low-energy modes which develop below ~ 0.5 T[209].

4.3 Yb₂Ge₂O₇

Unlike Yb₂Ti₂O₇, the cubic pyrochlore phase of Yb₂Ge₂O₇ (room temperature lattice parameter a = 9.8297(7) [210]) is a metastable phase. The thermodynamically stable crystal structure is the tetragonal pyrogermanate[210, 211, 212, 213]. Recently, the pyrochlore structure was able to be synthesised as powder samples through a combination of high pressure and high temperature (1300°C, 6 GPa) [214, 215]. This has allowed neutron experiments on polycrystalline Yb₂Ge₂O₇ by Dun, *et al.*[216, 217] and by Hallas, *et al.*[214, 218]. Neutron diffraction showed a magnetic ordering at T_N = 0.57 K into a q = 0 antiferromagnetic state, in stark contrast to the other Yb pyrochlores which order ferromagnetically. Observation of weak magnetic Bragg peaks, most notably the absence of the (0 0 2) peak placed Yb₂Ge₂O₇ in the Γ_5 state, choosing either ψ_2 or ψ_3 (see Fig. 4.2). Both ψ_2 or ψ_3 have identical unpolarized neutron diffraction patterns, though in principle a polarized neutron experiment could discriminate these two states. Inelastic neutron data on powders of Yb₂Ge₂O₇ and Yb₂Sn₂O₇ taken below their respective ordering temperatures revealed a striking similarity to the broad diffuse scattering seen in Yb₂Ti₂O₇[218]. In the case of Yb₂Ge₂O₇, this gives evidence that the unusual excitations are not linked to the ground state, but some other mutual aspect. Given Yb₂Ti₂O₇'s close proximity to the phase boundary between the antiferromagnetic ψ_3 and ferromagnetic state, it was surmised that Yb₂Ge₂O₇ should lie in close proximity to the phase boundary on the antiferromagnetic side. Because of this proximity it has been proposed that phase competition is responsible for the unusual excitation spectra observed in the Yb pyrochlores.

4.4 Inelastic Neutron Scattering on Single Crystal Yb₂Ge₂O₇: Published Work

This section reproduces our published paper Unravelling competing microscopic interactions at a phase boundary: A single-crystal study of the metastable antiferromagnetic pyrochlore $Yb_2Ge_2O_7$. The full reference and work can be found at [168] *.

4.4.1 Article Overview

We report inelastic neutron scattering measurements from our newly synthesized single crystals of the structurally metastable antiferromagnetic pyrochlore $Yb_2Ge_2O_7$. We determine the four symmetry-allowed nearest-neighbor anisotropic exchange parameters via fits to linear spin wave theory supplemented by fits of the high-temperature specific heat using the numerical linkedcluster expansion method. The exchange parameters so-determined are strongly correlated to the values determined for the *g*-tensor components, as previously noted for the related Yb pyrochlore

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Yb₂Ti₂O₇. To address this issue, we directly determined the *g*-tensor from electron paramagnetic resonance of 1% Yb-doped Lu₂Ge₂O₇, thus enabling an unambiguous determination of the exchange parameters. Our results show that Yb₂Ge₂O₇ resides extremely close to the classical phase boundary between an antiferromagnetic Γ_5 phase and a splayed ferromagnet phase. By juxtaposing our results with recent ones on Yb₂Ti₂O₇, our work illustrates that the Yb pyrochlore oxides represent ideal systems for studying quantum magnets in close proximity to classical phase boundaries.

4.4.2 Research Article

Introduction

Phase competition in correlated electron systems is intimately linked to their novel behavior, such as high T_c superconductivity [219], colossal magnetoresistance [220], and the formation of quantum spin liquids (QSLs) [16]. Such complex systems with competing, or frustrated, interactions exhibit rich phase diagrams with many phase boundaries, as vividly illustrated by highly-frustrated magnets (HFM) [221]. Near phase boundaries —- regions of strongest competition —- quantum fluctuations can play an important role in shifting the phase boundaries, reducing the average order parameter, or potentially producing intrinsically quantum states such as QSLs or valence bond/plaquette order [59, 222, 223, 224, 225]. Finding materials that lie close to classical phase boundaries can thus provide invaluable insights into the effects of competing quantum many-body interactions, and result in the discovery of new phenomena. If a material, or family of materials, is thought to exhibit this phase competition, it is essential to determine precisely the nature of the microscopic interactions. To do so, the study of high-quality single crystals is crucial, since orientational averaging from polycrystalline (powder) samples can obscure important features, such as the excitation spectra.

In this work, we take advantage of the new availability of single crystals of the Yb pyrochlore Yb₂Ge₂O₇ to determine its microscopic exchange interactions and show that the Yb₂M₂O₇ family of pyrochlore oxides are exquisite materials for studying exotic phase boundary effects in HFM



Figure 4.4: (a,b) Sections of classical phase diagram for the anisotropic exchange model [Eq. (4.7)] relevant for (a) $Yb_2Ge_2O_7$ and (b) $Yb_2Ti_2O_7$. (c) Comparison of the specific heat of $Yb_2Ge_2O_7$ from a representative single crystal [210] and the powder sample studied in Ref. [216]. (d) Optical images of representative single crystals, adapted from Ref. [210].

systems. This knowledge should motivate future studies aimed at tuning these materials directly to the phase boundary, while also providing an important benchmark for improving our theoretical understanding of anisotropic exchange [226] in the now widely-studied class of Yb-based quantum magnets [227, 228, 229, 230, 231, 232, 233].

The rare-earth pyrochlore lattice materials beautifully exemplify the diversity of behaviors possible for competing interactions in frustrated effective spin- $\frac{1}{2}$ systems [17, 170]. At typical experimental temperature and energy scales, the angular momentum of the magnetic rare-earth ions can often be described as a pseudo-spin- $\frac{1}{2}$ with anisotropic exchange interactions [170]. Detailed inelastic neutron scattering (INS) studies on single crystals of rare-earth titanate pyrochlores [173, 184, 197, 198] have cemented the acceptance of a unifying minimal physical model [173, 184, 185] that underlies the behavior of many of these materials. This model is the nearest-neighbor (effective) spin- $\frac{1}{2}$ anisotropic exchange Hamiltonian for the pseudo-spins *S*,

$$H = \sum_{\langle ij \rangle} \sum_{\mu\nu} J_{ij}^{\mu\nu} S_i^{\mu} S_j^{\nu} - \mu_{\rm B} \sum_{\mu\nu} B^{\mu} \sum_i g_i^{\mu\nu} S_i^{\nu}, \qquad (4.7)$$

where μ and ν run over the Cartesian directions (x, y, z), $J_{ij}^{\mu\nu}$ is the exchange tensor between spins at lattice sites *i* and *j*, $g_i^{\mu\nu}$ is the *g*-tensor for spin at site *i*, and B^{μ} is the μ component of the external magnetic field.

For the pyrochlore lattice, symmetry allows four independent exchange parameters (J_1, J_2, J_3, J_4) [184, 187]. Varying these exchanges, the *classical* phase diagram contains four q = 0 ordered phases: three antiferromagnetic phases (the ψ_2, ψ_3 and Palmer-Chalker (PC) states) and one splayed ferromagnet phase (SFM) [186, 188]. The Yb pyrochlore oxides Yb₂Ti₂O₇, Yb₂Ge₂O₇ and Yb₂Sn₂O₇ are prime candidates for realizing strong phase competition described by this model. While Yb₂Ge₂O₇ has been found to order into a Γ_5 AFM ground state (ψ_2 or ψ_3) [216], both Yb₂Ti₂O₇ [189, 201, 202] and Yb₂Sn₂O₇ [206, 207] order into SFM states. This strongly suggests that these three materials lie close to a phase boundary between a Γ_5 phase and an SFM phase. To date, this has only been verified for Yb₂Ti₂O₇ [197, 198, 204, 234] due to the availability of large single crystals of that material.

In order to shed light on the evolution of this Yb series through the magnetic phase diagram and to assess the proximity of Yb₂Ge₂O₇ to a boundary with *any* potentially competing phase(s), we have studied a collection of single crystals which were recently grown hydrothermally [210]. We determined the exchange parameters for Yb₂Ge₂O₇ and found that it is (classically) as close to the SFM/ Γ_5 phase boundary as Yb₂Ti₂O₇, but now *within* the Γ_5 phase, with the leading quantum fluctuations predicted to select a ψ_3 state.

Experimental Methods

The cubic pyrochlore structure of Yb₂Ge₂O₇ (room temperature lattice parameter a = 9.8297(7) [210]) is a metastable phase. The thermodynamically stable crystal structure is the tetragonal pyrogermanate [210, 211, 212, 213], but the pyrochlore structure has been previously obtained as powder samples by high pressure and high temperature synthesis (1300°C, 6 GPa) [214, 215]. The growth of large single crystals that could readily be used for INS investigations is not yet possible under these extreme conditions, though Ho₂Ge₂O₇ and Dy₂Ge₂O₇ have been prepared very recently as small crystals under high pressure [235]. Meanwhile, a relatively low temperature hy-

drothermal synthesis (650°C) can stabilize the pyrochlore structure of Yb₂Ge₂O₇ and produce high quality single crystals of approximately $1 \times 1 \times 1$ mm³ size [210, 211]. Clear and colorless single crystals of cubic Yb₂Ge₂O₇ were synthesized by this method [Inset of Fig. 4.4d].

The temperature dependence of the specific heat, $C_p(T)$, measured on a 0.67 mg single crystal, was previously reported [210]; we reproduce it here for comparison to the powder data from [216, 217] [Fig. 4.4c]. A broad feature centered around 3.5 K, and a sharp peak at $T_N = 0.572(4)$ K, are observed. Such features have been argued to correspond to the onset of short-range spin correlations and long-range order, respectively, in Yb pyrochlores [214, 218, 236, 237]. The good agreement between the powder and the single crystal $C_p(T)$ data, the colorless appearance of the crystals, as well as the x-ray refinement results of Ref. [210], indicate that "stuffing" defects, or other non-idealities of the crystal structure that could produce a sample dependence of the physical properties [199, 238, 239], are negligible in our single crystals of Yb₂Ge₂O₇. Magnetic susceptibility data, $\chi(T)$, on the same single crystal (not oriented) were obtained using a vibrating sample magnetometer from 100 K down to 1.8 K, in a field of 100 Oe.

Continuous wave electron paramagnetic resonance (EPR) spectra were recorded from a 50 mg collection of micro-crystals[†] of 1% Yb doped Lu₂Ge₂O₇ (Lu_{1.98}Yb_{0.02}Ge₂O₇) which were synthesized in a similar manner as the Yb₂Ge₂O₇ crystals [210]. Several EPR spectra were taken at varying temperatures using a superheterodyne quasi-optical setup operating at 120 GHz, described in Ref. [240]. Data at different temperatures were taken in order to observe that the resonance peak positions in the dilute compound do not shift, thus eliminating any possible concerns of spin interactions affecting the determination of the *g*-tensor. INS data were collected using the Multi Axis Crystal Spectrometer (MACS) [241] at the NIST Center for Neutron Scattering, under an applied field up to 9 T, and the Cold Neutron Chopper Spectrometer (CNCS) at the Spallation Neutron Source in zero field [242]. Twenty-eight single crystals of Yb₂Ge₂O₇ (total mass ~ 160 mg) were co-aligned on an oxygen-free copper mount to orient the [*hhl*] plane horizontally and the

[†]This collection of relatively large (compared to powder samples) crystals represents a large sampling of random orientations, but does not exactly correspond to a powder average. We did not pulverize the crystals in order to avoid strain broadening of the g-tensor.



Figure 4.5: (a,b,d,e) Comparison of constant-energy slices (centered at energy *E* with an energy dependent energy resolution function B) of the 3 T field polarized spin-waves between Yb₂Ge₂O₇ at 1.8 K (left) and linear spin wave theory using the best fit J_1 - J_4 parameters within Eq. (4.7) (right). The overall intensity scale is consistent between panels, but arbitrary. Comparison between the (c) magnetic susceptibility and (f) specific heat and NLC calculations for the parameters listed in Table 4.1.

field vertically along the $[1\bar{1}0]$ direction. The overall mosaic spread of the crystal array was found to be $\leq 5^{\circ}$ (Appendix B). At MACS, INS data were taken throughout the [hhl] plane at a constant energy-transfer ($E = |E_f - E_i|$), using a fixed final energy of $E_f = 3.7$ meV and varying E_i , in a configuration that produces an energy resolution of 0.17 meV at the elastic line.

Although the sample was in a dilution refrigerator with base temperature of the mixing chamber reading 260 mK, comparison of our zero field base temperature data with data taken at 1.8 K suggests that the sample did not cool below this higher temperature (see discussion in Appendix B). We therefore assign a temperature of 1.8 K to our field-polarized INS measurements presented here. This higher temperature does not affect the spin wave dispersions in the field-polarized paramagnetic state; since the excitation energies are large relative to the temperature with the effects of the relevant Bose factor being negligible. Corresponding constant energy [hhl] slices are shown in Fig. 4.5, where each energy slice took approximately 5 hours. The 3 T data, with 9 T data used as a background subtraction, was used in conjunction with thermodynamic and EPR data

to determine the exchange parameters, as described below. The zero-field CNCS data collection parameters are described in Appendix B.

Results and Discussion

Results

First, we address the single-ion properties of Yb³⁺ in Yb₂Ge₂O₇. The site symmetry of Yb in Yb₂Ge₂O₇ is trigonal (D_{3d}). This results in two independent *g* factors: one in the local *xy* plane (g_{\pm}) and one along the local *z* direction (g_z). Studies of Yb₂Ti₂O₇ have shown that fitted *g*-tensor values and exchange parameters are strongly correlated when fitting field-polarized INS [198]. An unambiguous determination of the *g*-values, independent from the fitting of the exchange parameters, is thus essential. Guided by this lesson, we used EPR to directly measure the *g*-tensor of 1% Yb doped Lu₂Ge₂O₇ on a randomly oriented collection of micro-crystals.

The measurements were performed on a coarse powder of micro-crystalline material (1% Yb³⁺ in Lu₂Ge₂O₇) to avoid any sample degradation that might result from over-grinding to the degree usually necessary for powder EPR studies. Because of this, many sharp, albeit weak resonances corresponding to individual randomly oriented micro-crystals can be observed in between the extremes of the spectra; these resonances give the appearance of an increased noise level, but they are real signals from individual micro-crystals. The sample was remeasured multiple times after stirring to confirm a re-distribution of the stronger signals.

The principal components of the g-tensor were determined from the end-points of the 120 GHz EPR absorption profile. These end-points manifest as a first derivative in the recorded spectrum (see Fig. 4.6) due to the use of field modulation and lock-in detection method of the in-phase signal. For an axial spectrum ($g_x = g_y \neq g_z$), as expected on the basis of the local site symmetry at the Yb sites, sharp features in the first derivative spectrum are expected only at the onset and cessation of the absorption profile, i.e., the end-points of the spectrum. For the easy-plane case ($g_x = g_y > g_z$), a biased spectral intensity with a derivative lineshape is expected on the low-field end of the spectrum (absorption onset), with a dip at the high-field end (cessation of the absorption).

The low-field signal may be further biased in a loose powder due to torquing and preferential alignment of individual microcrystals. Therefore, we associate the strong derivative signal centered just above 2.0 T (frequency of 120.0 GHz) with g_x and $g_y = 4.20(5)$. A weak dip corresponding to the g_z component of the spectrum is harder to pick-out, as it rides on top of a broad signal spanning the g = 2.00 region that we ascribe to paramagnetic contaminants; the sharp signal exactly at g = 2.00, marked with an asterisk in Fig. 4.6, is also assigned to an impurity. Nevertheless, the sharp dip at the $g_z = 1.93(2)$ position persists to high temperatures and is consistent with signals observed each time the sample was re-measured. Error bars were determined from the linewidths of the observed signals (peak-to-peak linewidth in the case of the g_x/g_y signal). Finally, the fact that the resonance positions do not shift upon varying the temperature indicates that magnetic interactions do not influence the measurements, thus confirming that the EPR is in fact probing the isolated Yb sites in the diluted sample. By contrast, measurements performed on concentrated samples (100% Yb³⁺ in place of Lu³⁺) revealed broad EPR signals with strongly temperature dependent effective g-values, significantly shifted from the free-ion values due to the Yb-Yb exchange.

Our EPR results confirm the xy anisotropy of the g-tensor in Yb₂Ge₂O₇, expected from powder studies [214], but does not agree quantitatively with previous determinations of the g-values from INS [214]. We attribute this disagreement to an intrinsic ambiguity in the fitting of the INS CEF data in Ref. [214]. A similar ambiguity is likely to affect the determination of CEF parameters for other Yb-based materials. See Appendix B for details.

With the single-ion properties determined, the exchange interactions (J_1, J_2, J_3, J_4) can next be obtained using the high-field spectrum. In a field of 3 T applied along $[1\bar{1}0]$, Yb₂Ge₂O₇ is in a field-polarized paramagnetic state and spin-wave excitations can be observed via INS. Due to the coarseness of the energy resolution of our measurement compared to the bandwidth, the dispersion of the excitations could not be reliably fit in the conventional way (as energy versus momentum relations), as we show in Appendix B. Therefore, to constrain the exchange interactions, we instead fit the intensity profile in the [hhl] plane at fixed energy-transfer (constant *E*), taking into account the energy dependent energy resolution, as shown in Fig. 4.5. The expected intensity was computed



Figure 4.6: EPR spectra from a 50mg collection of 1% Yb-doped Lu₂Ge₂O₇ microcrystallites at different temperatures (arbitrary scale, offset for clarity). The *g*-tensor values are determined from the minimum and maximum of the broad EPR absorption, $g_{\pm} = 4.20(5)$, $g_z = 1.93(2)$, which are shown with the green and blue vertical lines. An unidentified $g \approx 2$ impurity is present (indicated by the star).

Local		Global		Global (Alt.)		Dual (Alt.)	
J_{zz}	=+0.128(95)	J_1	= -0.01(6)	J	= -0.01(6)	\tilde{J}	=+0.35(4)
J_{\pm}	=+0.138(6)	J_2	= -0.44(4)	K	= -0.43(7)	\tilde{K}	= -0.08(3)
$J_{\pm\pm}$	=+0.044(24)	J_3	= -0.37(6)	Γ	= -0.37(6)	$\tilde{\Gamma}$	= -0.02(7)
$J_{z\pm}$	= -0.188(18)	J_4	= -0.02(13)	D	= -0.03(2)	\tilde{D}	= -0.27(9)

Table 4.1: Best fit exchange parameters (in meV) for Yb₂Ge₂O₇, determined from fitting INS and C_p , in several different (equivalent) presentations: local [173], global [184] and alternate global and dual global forms [226]. Uncertainties in the last few digits are shown in parentheses.

using the model Eq. (4.7) via linear spin-wave theory, with the g-tensor values fixed to those determined by EPR, $[g_{\pm} = 4.20(5) \text{ and } g_z = 1.93(2)]$. Results were averaged in a small window out the scattering plane to account for the finite detector size. To further constrain the exchange parameters, we included in the fit the high-temperature part of the specific heat (5 K < T < 8 K) computed theoretically via a numerical linked-cluster expansion (NLC) [236, 237, 243]. Our best fit exchange interactions are given in Table 4.1, with Fig. 4.5 showing the good agreement between the calculations and the data using the best-fit parameters.

Discussion

The determined exchange parameters place Yb₂Ge₂O₇ (Table 4.1) very close to the (classical) boundary between the SFM and Γ_5 phases. They indicate that Yb₂Ge₂O₇ lies within the Γ_5 phase classically, with leading quantum corrections selecting the ψ_3 state. This is consistent with the magnetic structure below T_N , which was previously reported to be either ψ_2 or ψ_3 [216]. While the classical phase boundaries are known to shift due to quantum fluctuations [205, 234], the Γ_5 phase is expected *grow* due the presence of soft modes [205]. We therefore do not expect quantum corrections to affect our assignment of Yb₂Ge₂O₇ to the Γ_5 phase. However, our assignment of Yb₂Ge₂O₇ to ψ_3 is more tentative, given the uncertainties in our parameters (see Table 4.1) and their proximity to the boundary between the ψ_2 and ψ_3 phases. How the boundary between ψ_2 and ψ_3 changes as one goes beyond the classical approximation is less clear. One might expect that ψ_3 may be further stabilized at the expense of the ψ_2 due to additional soft modes that appear near



Figure 4.7: (a) Constant energy transfer slice (E = 0.3 meV) for Yb₂Ge₂O₇ in zero field at T = 1.8 K. "Rods" of scattering are visible along $\langle 111 \rangle$ directions as well as diffuse scattering at ($\overline{220}$). (b) Static (equal time) structure factor calculated using NLC at T = 1.8 K using our best fit parameters from the field-polarized spin waves (see Table 4.1), which also shows rods of scattering and intensity at (220)

the SFM phase boundary for the former [186, 244, 245, 246]. This expectation, combined with ψ_3 occupying more phase space near our best fit parameters, leads us to conclude that Yb₂Ge₂O₇ is more likely to be in the ψ_3 state.

By locating Yb₂Ge₂O₇ on the phase diagram, we confirm that changing the non-magnetic cation from Ti to Ge, which presumably alters the superexchange interactions by modifying distances and bond angles [226], is enough to push the Yb pyrochlores just across the SFM- Γ_5 phase boundary. Yet, the titanate and germanate are otherwise extremely similar. The close relationship between these compounds is apparent even in powder samples: despite the disparate ordered ground states, a striking similarity is observed in the *powder averaged* zero field excitation spectra of the Yb pyrochlores as probed by INS [218], with each material exhibiting a continuum of excitations.

One exciting potential explanation for the continuum is that the ordered phases in the $Yb_2M_2O_7$ family are "proximate" to an exotic QSL brought on by the phase competition. Near such bound-

aries, classical degeneracies are enhanced, which can lead to the appearance of classical spin liquids [55, 247, 248]. These are highly susceptible to quantum fluctuations [186, 205] and can potentially help stabilize a QSL state [249, 250, 251, 252, 253]. The effects of a nearby QSL in the Yb pyrochlores may explain unusual excitations such as the ones observed in powder samples [218], as has been proposed for the α -RuCl₃ Kitaev material [70, 254]. The nearby QSL phase may be accessible via the application of chemical or external pressure, or perhaps a combination of both, to the Yb pyrochlores. In Yb₂Ti₂O₇ external hydrostatic pressure was found to further stabilize the FM state [255]. This suggests that external pressure on Yb₂Ge₂O₇ could move the compound in the same general direction, i.e. towards the SFM phase, and thus towards the phase boundary.

Zero-field spin excitations of single crystal Yb₂Ge₂O₇ for temperatures below T_N collected at CNCS show broad and nearly featureless scattering, similar to polycrystalline INS reported in Ref. [218] (Appendix B). The zero-field data collected at MACS, with an attributed temperature T = 1.8 K, measures the correlations below the Schottky-like hump in the specific heat, a feature that coincides with the onset of significant structured paramagnetic scattering in Yb₂Ti₂O₇ [192, 195] and other Yb pyrochlores [17] (as well as some reports of other quantum coherent phenomenon [256, 257]). We find that quasi-elastic paramagnetic scattering in Yb₂Ge₂O₇ at 0 T and 1.8 K qualitatively matches that of Yb₂Ti₂O₇ in the same regime; "rods" of scattering are observed along the $\langle 111 \rangle$ directions [192, 195], with a broad peak near (220) [Fig. 4.7(a)]. A similar pattern is reproduced in the theoretical static structure factor computed via NLC (Fig. 4.7(b) using our best fit parameters). A detailed comparison of the zero-field excitations in Yb₂Ge₂O₇ and Yb₂Ti₂O₇ single crystals in their ordered states is worthy of future study.

Conclusions

In summary, we have presented single crystal neutron scattering data from Yb₂Ge₂O₇, the sister compound of the well-studied pyrochlore Yb₂Ti₂O₇. We have determined accurate values of the *g*-tensor of Yb₂Ge₂O₇, measured directly by EPR spectroscopy of 1% Yb-doped Lu₂Ge₂O₇. Fits to field-polarized INS and thermodynamic data, allow the determination of the four symmetryallowed nearest neighbor exchanges, placing Yb₂Ge₂O₇ exquisitely close to the classical phase boundary between the SFM and Γ_5 phase, just inside the Γ_5 phase, with the leading quantum effects predicting a ψ_3 ground state. The zero field paramagnetic scattering in Yb₂Ge₂O₇ shows the same qualitative features as Yb₂Ti₂O₇. Our work demonstrates the striking similarity between these two unconventional pyrochlores, and definitively locates Yb₂Ge₂O₇ on the phase diagram that has been so successful in describing a variety rare-earth pyrochlores [170, 186, 188]. Having established the proximity of Yb₂Ge₂O₇ to the SFM/ Γ_5 boundary, and perhaps the ψ_2/ψ_3 one [see Fig. 4.4a], one may now begin investigating how this affects the zero-field collective excitations of this compound [218]. Moreover, our work opens the door to tuning these Yb pyrochlores directly to the phase boundary, either by using external pressure [255] or chemical pressure (e.g. YbTi_{2-x}Ge_xO₇). Finally, we have shown that relatively small single crystal samples obtained by hydrothermal synthesis can be used for detailed INS measurements, paving the way for other such measurements on crystals that can be grown using similar methods.

This research was partially supported by the CIFAR Quantum Materials program. KAR and CLS acknowledge support from the Department of Energy award DE-SC0020071 during the preparation of this manuscript. Access to MACS was provided by the Center for High Resolution Neutron Scattering, a partnership between the National Institute of Standards and Technology and the National Science Foundation under Agreement No. DMR-1508249. This work was in part supported by Deutsche Forschungsgemeinschaft (DFG) under grant SFB 1143 and through the Würzburg-Dresden Cluster of Excellence on Complexity and Topology in Quantum Matter – *ct.qmat* (EXC 2147, project-id 39085490). The work at the University of Waterloo was supported by the Canada Research Chair program (M.J.P.G., Tier 1). A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by the National Science Foundation Cooperative Agreement No. DMR-1644779 and the state of Florida.

For Appendices related to this work, please see Appendix B.

4.5 Conclusions and Outlook

Here I presented the first experimental study of single crystals of the pyrochlore Yb₂Ge₂O₇. Motivated by the need for single-crystal studies to accurately quantify the interactions in these complex materials, this research provides a successful path forward for the study of small single-crystal pyrochlore materials, which have been readily grown in polycrystalline form. Single crystal studies of Yb₂Sn₂O₇, and other stannate pyrochlores would be a promising avenue of research. The complete determination of the exchange interactions in two similar compounds differing only by small structural changes may also provide an important benchmark toward building a working model of the how the effective exchange interactions are determined by structural characteristics in these complex systems. With the concrete placement of Yb₂Ge₂O₇ and Yb₂Ti₂O₇ on either side of a phase boundary in close proximity, one would be well motivated to try to tune towards the phase boundary through a disordered series Yb₂Ti_{2-x}Ge_xO₇. While such a material may not possess a spin liquid ground state due to disorder effects, it would pose an interesting avenue of research to test the effects of regions of strongest competition at the phase boundary. Alternatively pressure experiments of Yb₂Ge₂O₇ can provide a separate route to tune toward the phase boundary.

Chapter 5

Low Temperature Non-equilibrium Behavior in CoNb₂O₆

5.1 Introduction

In this section, I cover non-equilibrium work on single crystals of the Quasi 1D-Ising material $CoNb_2O_6$. As one of the few experimental realizations of the transverse field Ising model, work on $CoNb_2O_6$ has propelled theoretical progress in quantum magnetism. Now we focus experimental progress on $CoNb_2O_6$ to the burgeoning field of non-equilibrium dynamics, where much theoretical progress relies on the combination of tractable models and experimental guidance. Our transverse field ac susceptibility data show the emergence of an unusual frozen state in zero-field below $T_f = 1.2$ K. Measurements directly following a quench of the magnetic field show the existence of slow relaxations which onset near the in-field commensurate antiferromagnetic transition and are described by a logarithmic form. After quenches across the QCP and other in-field transitions, systematic effects from these relaxing populations produce a logarithmic scaling as a function of quench rate, which mimic a power-law over the window of measurements. Absence of an intrinsic power-law as a function of quench rate is surprising with measurements taken across the QCP, where such an effect is expected to result from a Kibble-Zurek mechanism.

Transverse field susceptibility measurements taken on $CoNb_2O_6$ were taken myself, with help from Steffen Säubert, Tim Reeder, and Kate Ross, with the help of Eun Sang Choi at the National High Magnetic Field Laboratory in Tallahassee. Analysis of the susceptibility data was done by myself, Matt Williams, Tim Reeder, and Kate Ross. All heat capacity measurements were collected and analyzed by myself. The manuscript in progress described below was written by myself and Kate Ross. The rest of the chapter is organized as follows: Sections 5.2 to 5.3 contribute introductory information covering non equilibrium behavior relating to the Kibble Zurek Mechanism, the transverse field Ising model, and previous literature on $CoNb_2O_6$. Section 5.4 covers unpublished work on transverse field ac susceptibility measurements on $CoNb_2O_6$, which is currently being prepared as a manuscript. These sections are laid out in the paper format. Finally, section 5.5 details concluding remarks and future outlook for $CoNb_2O_6$.

5.2 Novel Phenomena in Non-equilibrium Condensed Matter

The successes of classical thermodynamics throughout the 19th and 20th centuries allowed for a robust and comprehensive theoretical framework to be built and tested against hundreds of experimental observations. The description of systems which constitute equilibrium thermodynamic states has remained one of the great triumphs of condensed matter physics [258]. While nonequilibrium thermodynamics has had a storied history dating as far back as equilibrium thermodynamics [259, 260], it has recently had a resurgence driven by recent developments in theoretical and experimental approaches. This more recent body of work has shown non-equilibrium dynamics as a potential generator of novel phenomena, such as Kibble Zurek Mechanism scaling [261], and Many Body Localization [262, 263, 264]. Without the theoretical tools of equilibrium thermodynamics, much work in non-equilibrium has been driven by experimental observations centered around theoretically tractable models. With this in mind, we focus on materials which can realize the paradigmatic model of the transverse field Ising model (TFIM).

Transverse Field Ising Model

The consequence of adding a transverse field component to the Ising model allows for a much broader class of phenomena. The transverse field Ising model (TFIM) is given by

$$H = -J \sum_{\langle i,j \rangle} \sigma_i^z \sigma_j^z - h_x \sum_i \sigma_i^x - h_z \sum_i \sigma_i^z$$
(5.1)

while the first term is identical to the standard Ising model the second and third terms now represent coupling to a transverse field, and longitudinal field respectively. The TFIM is a paradigmatic model for quantum criticality and constitutes the simplest model which hosts a quantum critical point. In the limit $h_z \rightarrow 0$, this model can be exactly solved in 1D using a Jordan-Wigner transformation [265]. At T = 0 quantum fluctuations arising from the non-commutatibility of the transverse magnetization components can destroy conventional ferromagnetic order at a quantum critical point (QCP) $J = 2h_c$ [10, 266]. For transverse fields above h_c , fluctuations from the transverse field leave the system in a quantum disordered paramagnetic state, while for fields below h_c the exchange interaction dominates and the system remains in a ferromagnetically ordered state. Solutions to the 1D quantum TFIM model showed behavior consistent with a d + 1 dimensional classical Ising model [267], allowing for estimates of behavior near the critical point.

For 1D TFIM spin- $\frac{1}{2}$ systems, the basic excitations within the ordered state are domain walls formed between the two lowest energy configurations. Since each spin flip creates two domain walls or kinks, shown in Fig. 5.1a, the excitations fractionalize into two independent quasi-particles which are free to propagate. Above the QCP the excitations are represented by a single spin flip excitations. Due to the self-duality of the model, as one nears the QCP the gap closes and the lowest energy excitations above and below the QCP must be similar. Despite its relative simplicity, addition of a small longitudinal field to the the 1D transverse field Ising chain richly complicates its behavior, with the excitations described by an exotic E8 symmetry near the critical point [268, 269, 270, 271].

Despite being an emblematic model for decades, real world candidates for the TFIM have been rare. Candidate materials for the TFIM have dominant Ising exchange, usually achieved through strong spin-orbit coupling, as well as some coupling of the field transverse to all local Ising orientations. Also importantly, the interactions of the material must be small to allow experimentally feasible critical fields. Well-known candidate materials include the 3D dipolar LiHoF₄, and the and the quasi-1D CoNb₂O₆.



Figure 5.1: (a) 1D TFIM excitations for $h < h_c$, within one of the two ferromagnetically ordered states, where moving down shows the propagation of the domain walls. Spin flip excitations cause even number of domain walls. The domain walls cost no energy to propagate with no longitudinal field, and behave as two independent quasi-particles. (b) 1D TFIM excitations for $h > h_c$, in the quantum disordered paramagnetic state. Excitations represent a single spin flip quasi-particle.

5.2.1 Kibble Zurek Mechanism

In the 1976 Thomas Kibble proposed a model for cosmological strings in the early universe resulting from a spontaneously broken gauge field [272, 273]. The model centered around the idea that if a system rapidly switches between an isotropic high temperature phase and a symmetry-broken low temperature phase, the order parameter of a two-component Higgs-like scalar field need not be identical in regions disconnected from causality. Two regions separated enough cannot communicate and thus the order parameter is allowed to differ in the two regions due fluctuations in the Higgs-like field, with a domain wall connecting them. Wojciech Zurek recast Kibble's arguments into condensed matter systems by considering continuous phase transitions in superfluid ⁴He [274, 275, 276, 277]. With a two-component complex scalar field analog of the Higgs-field, superfluid helium defects (vortex lines) could be explained analogous to Kibble's formulation of early universe defects. A key argument of Zurek was a power-law scaling of defects as a function of annealing time (or quench rate) of a control parameter across the transition.

For a continuous phase transition, due to a vanishing gap at the critical point separating the isotropic higher temperature and low temperature symmetry-broken phases, the characteristic time scale (relaxation time) of the system will diverge [10]. This fact ensures that no quench across the phase transition will remain adiabatic throughout, no matter how slowly one varies its control parameter, λ . In the vicinity of the critical value of a control parameter, $\lambda_c = 0$, renormalization group theory states the correlation length, ξ , and the relaxation time of the system, ξ_{τ} will have an algebraic divergence

$$\xi \sim \lambda^{-\nu} \tag{5.2}$$

$$\xi_{\tau} \sim \lambda^{-z\nu} \tag{5.3}$$

where ν and z are the correlation length and dynamic critical exponents, respectively. Now if the control parameter is changed in time such that, $\lambda = t/\tau$, then at characteristic time \hat{t} in which the system becomes non-adiabatic, the relaxation time of the system is on the same order of the time scale at which the Hamiltonian is changed

$$\hat{t} = \xi_{\tau}|_{\hat{t}} \sim \left(\frac{\hat{t}}{\tau}\right)^{-z\nu} \tag{5.4}$$

$$\hat{t} \sim \tau^{z\nu/(1+z\nu)} \tag{5.5}$$

A depiction of such a process is shown in Fig. 5.2. The time set by \hat{t} splits the system into three phases; two adiabatic phases separated by one non-equilibrium phase. Depending on the rate that the control parameter is changed, a different characteristic time \hat{t} will describe when the system is thrown out of equilibrium. Looking at the correlation length's dependence with a linear ramp we have

$$\xi \sim \tau^{\nu/(1+z\nu)} \tag{5.6}$$

if we assume there is one defect per unit domain size of linear dimension, the density of defects, ρ , scales as

$$\rho \sim \tau^{-d\nu/(1+z\nu)} \tag{5.7}$$


Figure 5.2: Depiction of a quench of a control parameter of a system across a continuous phase transition. Near the critical point, the relaxation time diverges and produces a non-adiabatic phase for any finite quench rate. The green trajectories represent finite quenches through the critical regime across the continuous transition. At the crossing between the relaxation time and quench trajectory, two times separate the non-equilibrium phase from the two adiabatic phases.

or equivalently in terms of the quench rate of the control parameter, r_Q

$$\rho \sim r_Q^{d\nu/(1+z\nu)} \tag{5.8}$$

The above equation represents a key experimental signature for the Kibble-Zurek mechanism (KZM). If one observes a power law scaling of defects after a quench across a continuous phase transition, one can test the KZM for known critical exponents. While domain wall densities are a convenient variable to measure, KZM is expected to apply to all observables that depend on it. Looking at Eqn. 5.8, we see that despite being an inherently non-equilibrium effect, KZM can be described entirely by equilibrium properties of the system. This makes it a convenient bridging concept linking non-equilibrium dynamics to equilibrium properties in condensed matter is systems [261].

Experimental evidence for KZM has been found in a large variety of systems including superfluid He [278], cold ion chains [279], liquid crystals [280, 281], multiferroic vortices [282, 283], and Bose-Einstein condensates [284, 285]. Since its inception, Kibble-Zurek mechanism has since been generalized to quantum phase transitions [286, 287, 288] and experimental evidence for scaling from quantum phase transitions have been observed in cold gases [289, 290]. To this date, no KZM has been observed in quantum magnetic systems, where a magnetic field can provide a natural parameter to tune across a quantum phase transition. Due to strong spin-lattice coupling, typical relaxations in magnetic systems are fast (picoseconds). Thus, a fast quench of the field through the quantum critical region is needed to produce observable defect densities in the form of domain walls. Compared to conventional superconducting magnets, which are limited to slow quench rates ($< 10^{-3}$ T/min), buildup of defects through a KZM are expected to be too small to observe conventionally. Alternative magnets, such as high-field resistive magnets can reach magnetic field quench rates up to 10 T/min and fields up to 32 T. Ultra-fast field ramps can also be achieved through pulsed magnets, which can reach quench rates of $> 10^3$ T/min [291, 292]. These magnets, combined with systems containing slow relaxation processes, such as in weak spin-lattice coupled systems, can provide a possible avenue for non-equilibrium studies in quantum magnets.

5.3 CoNb₂O₆ TFIM Behavior

 $CoNb_2O_6$ has remained one of the more famous materials to display behavior consistent with the TFIM. Its quasi-1D behavior arises from a predominantly ferromagnetic interaction between Co^{2+} ions which are linked by through 90° superexchange with oxygen octahedra forming zigzag chains along the *c*-axis [293]. The material also has small but finite couplings between chains which cause $CoNb_2O_6$ to magnetically order at low temperatures into a 3D long range ordered state. While neutron scattering experiments under a transverse field show $CoNb_2O_6$ retains much of its quasi-1D behavior down to 0.05 K with the interchain interactions providing an effective longitudinal field term, [294], a multitude of studies on the low temperature behavior of $CoNb_2O_6$ show a much more complicated picture, with several low field induced phases for fields along the *a*



Figure 5.3: Transverse field-temperature phase diagram for single Ising 1D Ising chains approximated in $CoNb_2O_6$, showing low field renormalized classical behavior (red), quantum critical behavior (green), and quantum disordered behavior (blue). At low temperatures 3D order envelopes the 1D QCP of a single isolated chain.

and *c* axes [295, 296, 297] and slow dynamics [298, 299]. Heat capacity measurements and NMR also show the 1D QCP of an isolated chain at 5.25 T is overshadowed by the field induced 3D QCP due to the finite interchain couplings, shown in Fig. 5.3. While the (quasi) 1D TFIM behavior of $CoNb_2O_6$ makes it a promising candidate to explore new frontiers of nonequilibrium phenomena, its low temperature behavior may complicate its application.

5.4 Transverse Field AC Susceptibility on CoNb₂O₆

This section consists of a manuscript in preparation, entitled *Low Temperature Domain Wall Freezing and Non-Equilibrium Dynamics in the Transverse-Field Ising Model Material* $CoNb_2O_6$, which details our transverse field ac susceptibility measurements on $CoNb_2O_6$.

5.4.1 Article Overview

 $CoNb_2O_6$ is a rare realization of the transverse field Ising model (TFIM), making it a useful tool for studying both equilibrium and non-equilibrium many-body quantum physics. Despite a large body of work dedicated to characterizing this material, details of the ordered states in the presence of relatively weak transverse fields have not been discussed in detail. Here, we present a detailed study of $CoNb_2O_6$ via ac susceptibility measurements in order to further characterize its low temperature behavior in the presence of a transverse field. Specifically, we call attention to an unconventional freezing transition in zero-field below $T_f = 1.2$ K, occurring within the well-known commensurate antiferromagnetic (AFM) state that onsets at T_{N2} = 1.9 K. We performed a series of transverse-field quenches into this frozen state, which resulted in a slowly relaxing susceptibility, $\chi'(t)$, that followed a logarithmic decay within the time range measured. We discuss the frozen state in the context of the freezing of previously discussed "free" chains arising from domain walls between the four degenerate sublattices of the commensurate AFM state. We also attempted to observe Kibble-Zurek scaling by quenching the transverse field into the frozen state at different rates. This produced a null result; the behavior can be explained by coarsening of domains over the timescale of the quenches. The absence of a clear Kibble-Zurek scaling is itself is surprising, given the proposed ubiquity of the phenomenon for general second order phase transitions, including glass transitions.

5.4.2 Research Article

Introduction

Recently non-equilibrium condensed matter has become a prominent field of study as a generator of exotic phenomena, such as many-body localization [262, 263, 300] and Kibble-Zurek scaling [261, 274, 286]. While theory has been propitious in some areas, much progress in nonequilibrium relies heavily on the guidance of experiment. Thus experimental studies which are centered on tractable models are crucial for the growth of the field of non-equilibrium physics.

One of the archetypal models of condensed matter is the transverse field Ising model (TFIM) [10],

$$H = J \sum_{\langle i,j \rangle} \sigma_i^z \sigma_j^z - h_x \sum_i \sigma_i^x,$$
(5.9)

where σ_i^{α} ($\alpha = x, y, z$) are Pauli spin matrices, J is the exchange interaction strength, and h_x represents an external magnetic field transverse to the Ising (z) axis. This model can be exactly solved in 1D and features a quantum critical point at $J = 2h_x$ [10, 266]. The TFIM provides a robust theoretical framework to study quantum criticality and non-equilibrium many-body physics.

While real material analogs of the TFIM with critical fields accessible in current laboratory settings are rare, one celebrated example is the quasi-1D Ising material CoNb₂O₆. This material was extensively studied from the 1970's to 2000's, with the goal of characterizing its complex magnetic phase diagram in the presence of a magnetic field [295, 296, 301, 302, 303, 304, 305], though the *transverse* field behavior was not investigated until later [294]. The electronically insulating CoNb₂O₆ crystallizes into the orthorhombic Columbite space group Pbcn, with room temperature lattice parameters of a = 14.1475, b = 5.712, c = 5.045 [306]. The Co²⁺ sublattice is shown in Fig. 5.4a. Co²⁺ ions are linked by oxygen octahedra forming zigzag chains along the *c*-axis, with ~90° superexchange giving rise to ferromagnetic nearest neighbor interactions J_0 and a pronounced 1D behavior [293]. Staggered planes of isosceles triangles form in the *ab*-plane, with antiferromagnetic (AFM) interactions between chains estimated to be an order of magnitude smaller in than J_0 [307]. The shorter isosceles bond forms along the crystallographic *b* axis (J_1),

with the other two legs forming AFM (J_2) bonds resulting in geometric frustration. In zero-field, the system undergoes a phase transition at $T_{N1} = 2.9$ K into an incommensurate AFM (ICAFM) phase with temperature-dependent wavevector $q = (0 q_y 0)$. Below $T_{N2} = 1.9$ K, the system locks into a commensurate AFM (CAFM) phase with q = (0 0.5 0) via a first-order phase transition. Within the CAFM phase, neutron diffraction showed that CoNb₂O₆ has an ordered moment of $\mu \approx 3.2\mu_B$ [303] with the CAFM persisting down to 50 mK [308]. Heat capacity measurements show that magnetic contributions persist up to T = 25 K [296] and have an associated entropy of Rln2, supporting an $S_{\text{eff}} = \frac{1}{2}$ picture for the low temperature spin system [296, 309]. In the CAFM state, there are two distinct Ising spins canted $\pm 31^{\circ}$ away from the *c*-axis in the *ac*-plane. A series of papers by Kobayashi, et al. reported anisotropic domain coarsening within the basal plane at T= 1.5 K exhibiting an anomalously small growth exponent of n = 0.2 [298, 299].

More recently, $CoNb_2O_6$ has enjoyed renewed interest due to its application to the TFIM [271]. Neutron scattering under a transverse field (i.e. oriented along the *b* axis) revealed an emergent \mathbb{E}_8 symmetry [294], which describes the 1D transverse field Ising chain at the quantum critical point with small but non-zero longitudinal field [268, 269, 270, 271]. Transverse field heat capacity [309] and NMR [310] measurements revealed that the quantum phase transition for an isolated Ising chain in $CoNb_2O_6$ would be at 5.25 T, however, this is overshadowed by the 3D quantum phase transition at 5.45 T [308], due to weak but non-zero interchain couplings. While recently it has been argued that additional off-diagonal exchange terms are important in $CoNb_2O_6$, implying that the symmetry is not strictly Ising-like, the field-induced quantum critical point of such models still map onto the TFIM [311, 312]. Given how famous the material now is due to its behavior in a transverse field strengths. In order to use $CoNb_2O_6$ to experimentally investigate non-equilibrium properties of the TFIM, it is important to fully characterize its low temperature and low transverse field properties, particularly since the system exhibits slow relaxation in this regime.

Here, we report ac susceptibility measurements on CoNb_2O_6 taken down to a base temperature of T = 0.5 K. We used a transverse dc field geometry (Fig. 5.4 b) to measure the ac susceptibility



Figure 5.4: (a) Magnetic structure of CoNb_2O_6 . Nearest neighbors form zig-zag chains along c with ferromagnetic interactions (J_0) . Magnetic moments (arrows) illustrate the CAFM state. Second (J_1) and third (J_2) nearest neighbors (both antiferromagnetic) connect isosceles triangles in the *ab*-plane which stabilize 3D order at low temperatures. J_0 is roughly an order of magnitude larger than the other exchange interactions, making CoNb_2O_6 quasi-1D. (b) Diagram of the ac-susceptometer at the NHMFL, showing ac-field direction and plane of rotation for dc-field. The ac-field can be set at any angle with respect to the dc-field, within a single plane of rotation. For our experiments, the ac field was oriented along the c axis (31° from the Ising axes), and the dc field was oriented along the b axis (transverse to the Ising axes).

along the *c*-axis in various scenarios: 1) the zero-field ac susceptibility, 2) the ac susceptibility as a function of transverse field, and 3) the relaxation of the ac susceptibility in zero-field after ramping the transverse magnetic field to zero at various rates (r_Q) , spanning 0.1 to 10 T/min. For the zero-field data we find good agreement with prior measurements [296], including the presence of a freezing transition which onsets at $T_f \sim 1.2$ K in our sample. This freezing transition, which occurs within the commensurate ordered phase, is not usually discussed in studies of CoNb₂O₆, but appears to be present in several samples [296, 302, 307, 309]. The transverse-field dependence of the ac susceptibility at 0.5 K reveals several features which can be identified with transitions between different ordered states, culminating in the QCP at 5.45 T. Upon quenching the transverse field into the frozen state, we observe a relaxation in the real $(\chi'(t))$ and imaginary $(\chi''(t))$ components of the ac susceptibility, which is best described by a logarithmic decay. This contrasts with the power law relaxation of ac susceptibility (and neutron Bragg diffraction) that was found by Kobayashi, et al. at T = 1.5 K after longitudinal (*c*-axis) field quenches [298, 299], and points to the role of a disordered potential leading to modified coarsening behavior below T_F . Varying the quench rate (r_Q) of the transverse field, we also find a logarithmic dependence of χ' on r_Q . Though the scaling could also be fit well to a power law, which would suggest a connection to the Kibble-Zurek mechanism (KZM), we find that the dependence and can be attributed entirely to a systematic effect resulting from the relaxing population of domain walls over the course of the quench time. This highlights the care necessary in showing KZM behavior for experimental systems in which coarsening occurs on a similar timescale to the quench time [313, 314]. It appears that KZM is not evident in our measurements, which in itself is surprising given the ubiquitous nature of the mechanism for second order transitions [261, 274] and glass transitions [315, 316].

Experimental Methods

Small single crystals of $CoNb_2O_6$ (2 × 1 × 0.5 mm) were prepared via flux growth, following Ref. [317], using 1.5 g $CoNb_2O_6$ with 1 g Borax (Na₂B₄O₇) in a Pt crucible (1250 °C for 15 hrs then 750 °C for 12 hrs with temperature ramps of 1.2 K/hr). Representative samples were crushed and checked for phase purity with a powder x-ray powder diffractometer. Alignment and crys-



Figure 5.5: (a) Zero-field susceptibility of $CoNb_2O_6$ as a function of probe frequency. A frequencydependent hump is seen centered around $T_f \sim 1.2$ K (shown in inset), consistent with Ref. [296].(b) Single crystal heat capacity of $CoNb_2O_6$. A sharp peak at $T_{N1} = 2.9$ K coincides with the incommensurate AFM transition, while a broad shoulder at $T_{N2} = 1.9$ K coincides with the commensurate AFM transition. Heat capacity from Ref. [296] is also shown here in order to highlight the overall agreement between measurements. (inset) A small shoulder is observed in the heat capacity near 1 K, which could be due to the freezing transition observed in the zero-field susceptibility. (c) Dependence of τ_2 on temperature, which is a measure of the sample-to-stage relaxation processes. τ_2 becomes non-zero near the onset of the frequency dependent low transition found in zero-field ac susceptibility.

tallinity were checked with a Laue diffractometer, where the crystal was aligned within $\sim 0.5^{\circ}$. Two single crystals were used: Sample "A" (13.6 mg) and Sample "B" (8.2 mg), both cut into a cuboidal shape. The heat capacity of a representative single crystal grown in the same manner as samples A and B was taken on a Quantum Design Dynacool PPMS with dilution refrigerator insert using the thermal relaxation method.

Transverse field ac susceptibility data were taken at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee with ³He cryostat mounted in a 20 MW 31 T 50 mm bore resistive solenoid dc magnet [318]. The crystals were oriented such that the ac field was applied along the average moment direction (*c*-axis), while the dc field could be continuously oriented within the *bc*-plane, between the average Ising axis and the transverse direction (Fig 5.4b). The ability to change the angle *in situ* enabled us to more accurately align the dc field to the *b*-axis within the plane of rotation, by observing the symmetry of the ac signal as a function of rotation angle (Appendix C). The resistive magnet allowed for linear magnetic field ramps of the dc field with rates between 0.1-10 T/min (note that typical maximum ramp rates for a superconducting magnet is \leq 1 T/min, which is what motivated us to use a resistive magnet instead). The ac field had amplitude 1.65 Oe and frequencies ranging between f = 40 Hz to 10 kHz, with most dc field-dependent measurements at taken at 710 Hz. The dc field-dependent data were collected at T = 0.5 K with high temperature background scans taken at T = 10 K.

Results & Discussion

Temperature dependence of zero-field susceptibility

The zero-field ac susceptibility data is shown in Fig. 5.5a. A kink in the susceptibility at T_{N1} = 2.9 K coincides with the ICAFM transition. An abrupt decrease in susceptibility is observed at the CAFM transition, T_{N2} = 1.9 K. CoNb₂O₆ shows a pronounced frequency dependence below T_f = 1.2 K accompanying a small peak in the susceptibility. This feature was also observed by Hanawa, *et al.* in their ac susceptibility data, who attributed it to a metamagnetic (first order) transition and noted that it did not appear when measuring along the crystallographic *b*-axis [296]. The CAFM order is now known to persist to 0.05 K [308], so this frequency-dependent feature appears to signal a frozen state that co-exists with CAFM.

We performed heat capacity measurements on a small single crystal (1.55 mg) of CoNb_2O_6 in zero field from 4 K to 0.06 K (Fig. 5.5b-c). The specific heat capacity shows good agreement with the literature [296, 309]. A sharp anomaly corresponds to T_{N1} , while a low temperature shoulder corresponds to T_{N2} . A second smaller shoulder is also observed around 1 K, which may be related to the freezing transition discussed above. A high temperature broad shoulder was seen to be associated with the magnetic spin system and persists in the paramagnetic phase up to ~25 K [296], suggesting the presence of short range spin correlations up to this temperature. The thermal relaxation method allows one to analyze the relaxation curves in terms of a two-timeconstant model, where τ_1 is related to the heat capacity of the sample, and τ_2 is related to the heat flowing from within the sample to the sample platform and can be an indicator for slow relaxation within the sample [97, 319]. The onset of significant τ_2 at $T \sim 1.2$ K is consistent with slow



Figure 5.6: Typical ac susceptibility data taken at T = 0.5 K as a function of transverse field for real component (a) and imaginary component (b). A shoulder observed near 5.3 T (blue vertical line) in both real and imaginary components is consistent with the field induced transition between the paramagnetic and an "up up down" (UUD) ferrimagnetic phase identified in Ref. [308], which approximately corresponds to the TFIM QCP. A small hysteresis (history dependence) is evident at this phase boundary, but it is more pronounced below ~3.7 T (black dotted vertical line), which is a field-induced first-order transition into the ICAFM state [308]. The transition into the CAFM state around 3 T (red dot-dashed vertical line) is more difficult to observe in our susceptibility data, though it can be distinguished in the second derivative of $\chi'(H)$. A ramp rate dependent discontinuity around ~1.7 T (green dashed vertical line) represents the onset of the frozen phase.

thermal relaxation within the sample, as expected based on the freezing transition observed by ac susceptibility at the same temperature.

Previous studies of domain coarsening by Kobayashi, *et al.* have also shown slow relaxation in CoNb₂O₆ within the CAFM phase, but at temperatures above the freezing transition that we report [298, 299]. In those studies, the FM *c*-axis chains were treated as single super-spins (since J_0 is by far the dominant exchange interaction, the spins along each chain were assumed to have the same orientation), and the defects of the ordering of those super-spins within the *ab*-plane was investigated. The commensurate AFM state in CoNb₂O₆ has a four-fold degeneracy, so domains of this order populate randomly following a quench into the ordered state, with domain walls forming between them. Kobayashi, *et al.* proposed "free" domain walls which arise from chains within the commensurate AFM state that feel no net interaction with neighboring spins, due to the frustration of the isosceles triangular lattice formed by the chains. A relaxation in both correlation length in CoNb₂O₆'s *ab*-plane from neutron scattering and magnetic susceptibility as a function of time was also reported by Ref. [299] at T = 1.5 K, just above the T_f . They were able to fit both relaxations to a power law form with a growth exponent $n = 0.2 \pm 0.02$ over several decades of time. This is in contrast to predictions from standard coarsening models of a four-fold degenerate Ising system with curvature-driven domain growth, which give a growth exponent of n = 0.5 [320, 321], though within the ANNNI model deviations from this exponent have been predicted [322]. The low growth exponent found in CoNb₂O₆ above the freezing transition strongly suggests that the growth of domains in CoNb₂O₆ are restricted, possibly due to domain wall interactions. One possible source of this freezing transition then may be due to the freezing out of these "free" domain walls, restricting the domain wall growth even further.

However, another possibility is that the domain walls are pinned by disorder. A natural route to disorder in $CoNb_2O_6$ comes from the $CoO-Nb_2O_5$ binary phase diagram [323], which shows that $CoNb_2O_6$ is not a "line compound", i.e. there is a fairly wide range of stoichiometries (within ~ 1% of the ideal 1:1 molar ratio) that lead to the same average crystal structure (the columbite form). The relatively wide compositional space that stabilizes the columbite structure indicates a low enthalpy for defects relative to the concomitant gain in configurational entropy (e.g antisite disorder or vacancies). Thus, even for perfect stoichiometry, one could expect a relatively high defect density [324] [‡]. It is already known that $CoNb_2O_6$ can be extremely sensitive to small amounts of disorder [325, 326]; for instance, in $Mg_xCo_{1-x}Nb_2O_6$, less than 1% substitution (*x*=0.008) is enough to entirely suppress the CAFM state at low temperatures [326].

Transverse-field dependence of susceptibility

Typical ac susceptibility data taken as a function of field at constant temperature (0.5 K) is shown in Fig 5.6a. The data were taken after cooling in zero-field from 2 K to 0.5 K. Features in these data align well with phase transitions identified from neutron scattering data [308] and are indicated in the figure by vertical lines. A shoulder near 5.3 T shows the transition between

[‡]Care must also be taken to convert cobalt oxide precursors to a single type. When purchased from chemical suppliers they often contain a mixture of Co_3O_4 and CoO which, if uncorrected, can lead to inaccurate Co stoichiometry.

an ordered state and a field-polarized paramagnet, with a small accompanying hysteresis between ramps of increasing and decreasing field. The hysteresis is more dramatic below ~ 3.7 T, where Ref. [308] reported a the transition between a ferrimagnetic phase and a field-induced ICAFM phase. A discontinuity in the real and imaginary components of the susceptibility appears near 1.7 T, with the field value at which it occurs weakly depending on quench rate, possibly signifying the field-induced frozen state. Accompanying the development of a hysteresis, a slow relaxation is observed in the susceptibility (see Appendix C). The slow relaxation is seen for all fields below the ICAFM transition (3.7 T) but becomes more pronounced below the CAFM and freezing transitions (< 3 T). In the frozen state, it appears that it would persist well beyond our maximum measurement time (600 s after field is removed).

In zero-field following a field quench, our time-dependent ac susceptibility is best fit to a logarithmic relaxation form:

$$\chi'(t) = a \ln\left(\frac{t - t_0}{\tau}\right) + c \tag{5.10}$$

where *a* is a negative scale factor, t_0 is the onset time of the relaxation, τ is needed to make the argument of the logarithm dimensionless and may represent an intrinsic relaxation timescale, and *c* represents an offset that is partially due to a background contribution. The form shown in Eqn. 5.10 produces an unbounded χ' for infinite time and thus cannot represent the full relaxation curve. We treat it as an early-time approximation for the relaxation, similar to the intermediate time logarithmic relaxation proposed by Ref. [327]. Thus the *c* parameter also likely accounts for some of the late-time behavior of the relaxation. The functional form above provides a slightly better fit compared to a power law relaxation, and the power law fit gives a low exponent ($n = 0.1\pm0.03$), hinting at the appropriateness of a logarithmic relaxation for our data. The zero-field power law relaxation of ac susceptibility obtained in Ref. [299] was measured above the freezing transition (1.5 K, which is above T_f), and after different quench protocols compared to ours (they used temperature quenches and a *c*-axis field quench). We therefore do not necessarily expect the relaxation forms to agree, particularly if the frozen state is due to disorder.



Figure 5.7: (a) Relaxation in zero-field at T = 0.5 K after several quenches from a maximum field of 4 T at different rates, r_Q . Colors represent different r_Q , as quantified by the color bar. (inset) Zero-field relaxation of several quenches with $r_Q = 2$ T/min showing a history-dependence of the initial and final susceptibility, leading us to use the difference $\langle \chi'_d \rangle$ as a measure of the relaxation at a given r_Q (see Eqn. 5.11). (b) Zero-field relaxation of 4 T quenches with time shown on a semi-log scale, where time is shifted by a critical time " t_c " defined as the time during the quench when the field reaches 0.11 T. This produces straight lines, confirming the logarithm form of relaxation. (c) and (d) Log-log plots of $\langle \chi'_d \rangle$ vs r_Q for sample "A" (c) and sample 'B" (d). Different colors of the data points represent different sets of quenches, where between the quenches the sample was "reset" by warming past T_f . Fits of a logarithmic form (Eqn. C.4), which arises from purely systematic effects, as well as fits from a power law, which would potentially arise from KZM are shown for reference. Within the time window of our experiment, systematics due to relaxing populations during the quench are enough to reproduce the r_Q dependence.

Indeed, disorder has been predicted to lead to logarithmic coarsening in Ising systems [328], while other studies have proposed a crossover from a power law to a logarithmic form beyond a critical time related to the length scale separating impurities [321, 329]. Slow relaxations in many systems, most noticeably spin glass systems, have also been modeled through hierarchically constrained dynamics [330, 331, 332]. Such a dynamical structure has been shown to lead to either a stretched exponential [333, 334] or logarithmic [327] form of the relaxation.

Quench-rate dependence of susceptibility

One may think of the zero-field ac susceptibility as containing the response of the domain walls, as well as the intrinsic response of the CAFM ground state. Generally, we expect any signal which displays a relaxation over time to be attributed to the domain walls of the system (the non-equilibrium objects). However, one intriguing observation we have made is that the system shows the presence of aging effects, i.e. certain properties of the relaxation depend on the overall history since cooling into the frozen state, *even after* the transverse field is brought to 6 T, which is outside any ordered states, discussed in Appendix C (also see Fig. C.2d, Fig. C.4). While intriguing, this aging complicates the analysis of the quench rate dependence, since even identical repeated quenches lead to different offsets of the susceptibility, shown in Fig. 5.7a. To investigate the *trends* of the relaxation within the frozen state, we thus characterized the relaxation by the difference between its initial value and final value

$$\langle \chi'_D \rangle = \langle f \rangle - \langle l \rangle \tag{5.11}$$

where $\langle f \rangle$ describes the average of the first second of zero-field data after the quench and $\langle l \rangle$ is the average of last second of collected data (usually at 300s). This represents the initial density of defects due to each new quench. When $\langle \chi'_D \rangle$ is plotted as a function of quench rate (r_Q) , a clear trend is seen (Fig. 5.7c-d). In both samples A and B, this scaling with quench rate was observed for all sets of collected data, which include quenches from 6 T across the QCP as well as quenches from 4 T which do not cross the QCP. Thus, the scaling with r_Q is not due to the QCP. Rather, as we show in Appendix C, it seems to be due to a very low field transition around 0.11 T. When we shift each set of the zero-field data by the time this field was reached (t_c) , we see a collapsing of the data to one linear set when plotted as a log-log (Fig. 5.7b). The scaling with quench rate can be approximated by either a power law with exponent 0.26 \pm 0.04 (which would potentially indicate KZM, but with an unexpected scaling exponent), or by a logarithm. Despite the predicted ubiquity for KZM across phase transitions, it turns out that the logarithm fits better, particularly at low r_Q . Furthermore, the form of the logarithmic scaling can be completely understood to be a consequence of a systematic effect, namely the coarsening of domains during the quench (see appendix C). Another way to see this is that the fitting parameter *a* in Eqn. 5.10, which one could reasonably be expected to scale with defect density, is independent of r_Q (see Appendix C).

Conclusion

In summary, we have performed ac susceptibility measurements of the quasi-1D Ising material CoNb₂O₆ under transverse magnetic fields. At low temperatures (500 mK) we see evidence of several transverse-field-induced transitions at fields below the known QCP (at 5.3 T), some of which are similar to those which have been predicted theoretically [271] and observed in a prior study [308]. We have also observed and characterized a zero-field transition into an unconventional frozen state at $T_f = 1.2$ K, which is within the known commensurate antiferromagnetic state. This is consistent with earlier reports of extremely slow dynamics in this temperature range, but has not been discussed in detail before. Within this frozen state, the ac susceptibility shows a logarithmic relaxation over time in response to a dc transverse field quench. This form of relaxation is expected for coarsening of domains in the presence of disordered potentials, and this is an appealing explanation given prior work which successfully attributed some higher temperature behavior of CoNb₂O₆ to domain wall motion and coarsening [298, 299]. However, the presence of lattice disorder in our (and other's) samples of CoNb₂O₆ remains to be confirmed.

We investigated the effect on the ac susceptibility response of "quenching" a transverse field across the various field-induced phase transitions of $CoNb_2O_6$. While we do find a distinct depen-

dence of χ' on quench rate, similar to a power law that would be expected based on the KZM, it does not correspond to quenching across the QCP. Further, we find it can be attributed to a systematic effect resulting from coarsening during the quench, an analysis which surprisingly indicates a field-induced transition at 0.11 T. Thus, we observe no evidence for the KZM in quenches across the QCP, or across any of the field-induced transitions including the glass transition. This "null result" is somewhat surprising given the proposed ubiquity of KZM the phenomenon for second order transitions (and glass transitions), and the fact that we clearly observe non-equilibrium states generated by the quenches. However, we cannot rule out that the KZ scaling is being obscured by the aging effect we have observed.

Overall, our results emphasize the complexity of the dynamical behavior of the famous quasi-1D transverse field Ising model material, $CoNb_2O_6$ under a relatively weak transverse field. This transverse field regime has until now not been explored in detail experimentally, but appears to contain a wealth of intriguing phenomena related to the frustration of the isosceles triangular lattice, which is likely to be strongly influenced by additional quantum fluctuations produced by the transverse field.

This research was funded by Dept of Energy grant DE-SC0018972. Authors would like to acknowledge Prof. Tarun Grover for insightful conversations relating to the Kibble-Zurek mechanism and domain coarsening effects. The authors would also like to thank Prof. James Neilson for stimulating conversations on non-line compounds and disorder chemistry within crystalline materials. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by the National Science Foundation Cooperative Agreement No. DMR-1644779 and the state of Florida. Some figures were made using the 3D crystal modeling software VESTA [335].

For appendices related to this work, please see Appendix C.

5.5 Conclusions and Outlook

The application of the TFIM makes $CoNb_2O_6$ a popular material as a probe for nonequilibrium phenomena. A large body of research has shown $CoNb_2O_6$ also displays complex low temperature

behavior, which is emphasized in our work. In our zero-field ac susceptibility data, we observed a freezing transition at $T_f = 1.2 K$, within the commensurate antiferromagnetic state. Although we hypothesize disorder naturally present in CoNb₂O₆ is responsible for this behavior, further study characterizing this transition and the underlying mechanism responsible would be a worthy avenue of further research.

When we quench a transverse field across different field-induced phase transitions of $CoNb_2O_6$, we observed a prominent quench rate dependence of the susceptibility. While the exact values of the susceptibility were distorted by aging effects found below the freezing transition, a measure of the relaxation of the susceptibility (related to nonequilibrium domain walls) show a logarithmic scaling which mimic a power law over our observed quench rates. Such a scaling was able to be reproduced entirely through systematic effects of our experimental setup, rather than through a Kibble Zurek mechanism. The expectation for the Kibble Zurek mechanism within the TFIM makes its absence in our experiment somewhat surprising. With observed aging effects possibly masking any effects from a Kibble Zurek mechanism, one would be well motivated to attempt a similar experiment while avoiding such effects from the low temperature frozen state.

Chapter 6 Concluding Remarks

Frustrated and quantum magnetic systems can display a wide breadth of unconventional phenomena in their static and dynamic properties. I detailed work on three materials which show some of these unusual magnetic properties in their low temperature behavior, as observed through neutron scattering and ac susceptibility measurements. In particular, I focused on magnetic diffraction of the insulating magnetic iron compound $Fe_3PO_4O_3$, spin-wave dispersions within the pyrochlore oxide Yb₂Ge₂O₇, and magnetic susceptibility measurements of nonequilibrium dynamics in the quasi-1D Ising material CoNb₂O₆ under a transverse field.

While Fe₃PO₄O₃, the subject of Ch. 3, exhibits an antiferromagnetic transition at 163 K, it shows unusual low temperature behavior in the static magnetic structure as observed in both polycrystalline and single crystalline samples. Neutron diffraction of polycrystalline samples show the ordered state is an antiferromagnetic helical order, a consequence of a balancing of competing interactions. Previously it was shown that modeling powder diffraction required a small correlation length within the ab plane down to \sim 100 Å, far below instrument resolution. Through single crystal neutron diffraction performed at HB-3A at HFIR, we determined that the system does not prefer a single ordering wavevector, but instead a continuum of equal magnitude ordering wavevectors contained within the *ab* plane. Along the *c*-axis the entire system can be described by a single commensurate antiferromagnetic wavevector, showing long range order along c. Such a partially ordered state onsets at the antiferromagnetic transition of 163 K and persists down to at least 4 K. Due to the doubly focused monochromator, anisotropic instrument resolution for our single crystal data was enough to obscure the correlation lengths described in polycrystalline samples, which was observed not only in the pure compound but also magnetically diluted variants. While the dynamics within this system remain unknown, within the static regime three possible scenarios can reproduce the combined partial magnetic order observed in single crystals and small correlation lengths shown in polycrystalline samples. The most conventional possibility is that the system prefers to form small domains on the order of the correlation length, although such a system would be expected to have a high energy cost associated with the creation of many domain walls. Alternatively the system could form one coherent domain where the magnetic ordering wavevector is allowed to vary throughout the system. Materials which possibly show such behavior are extremely rare, as the magnetic structure would have to almost entirely decouple from the nuclear lattice system. Finally the system could form into a disordered skyrmion system. While all bulk materials showing skyrmions were seen to form ordered super-lattices, there is a close connection to these B20 compound materials and partial magnetic order, such as we observed in Fe₃PO₄O₃. Magnetic dilution of polycrystalline samples also show a promising trend between the helical pitch length and correlation length, which one would expect for a skyrmion. While the existence of skyrmions within Fe₃PO₄O₃ remains only speculative, its possibility remains a subject of great interest, as it would be the first bulk antiferromagnetic skyrmion material observed. The difficulty in producing larger single crystals remains an important obstacle in further characterization of this material, where both investigations of the dynamics and true magnetic structure through use of neutron polarimetry could provide insight to this system's unusual low temperature physics.

A description of the low temperature physics in the antiferromagnetic pyrochlore, $Yb_2Ge_2O_7$, was discussed in Ch. 4. In the pyrochlore lattice, geometric frustration is present as well as the possibility for exchange frustration. The Yb pyrochlore material $Yb_2Ti_2O_7$ has been an exceptional example of exotic effects arising from magnetic frustration. Below its long range ordering transition into a weak ferromagnet, $Yb_2Ti_2O_7$ shows unconventional continuum excitations in zero-field, reminiscent of fractionalized excitations. Subsequent inelastic neutron scattering on polycrystalline samples of $Yb_2Ge_2O_7$ and $Yb_2Sn_2O_7$ show similar unconventional dynamics below their respective long range ordering transitions. While $Yb_2Sn_2O_7$ orders into a weak ferromagnet similar to $Yb_2Ti_2O_7$, $Yb_2Ge_2O_7$ was found to order into an antiferromagnetic state. Such a difference in ground states displaying similar dynamics hinted toward an underlying mechanism for the behavior being phase competition between the ferromagnetic and antiferromagnetic states. Close proximity to a phase boundary has been proposed to enhance fluctuations and destabilize classical order, giving way to more exotic orders such as a possible quantum spin liquid state. $Yb_2Ti_2O_7$'s close proximity to the ferromagnetic/antiferromagnetic boundary lead to a theory that phase competition could be the underlying mechanism for the unusual excitations. Our work on single crystals of $Yb_2Ge_2O_7$ allowed for the unambiguous placement of $Yb_2Ge_2O_7$ within a classical phase diagram and shows definitively that $Yb_2Ge_2O_7$ also lies close to the ferromagnetic/antiferromagnetic phase boundary, as well as a boundary between two antiferromagnetic phases. One would be well motivated to similarly determine the placement of $Yb_2Sn_2O_7$, in order to confirm such behavior in $Yb_2Sn_2O_7$ arises from phase competition effects. With strong support for phase competition from two separate materials, one can now attempt a balance between the two in order to achieve a material tuned directly onto the phase boundary, and possibly realize a spin liquid state. Such tuning may be possible through pressure, either external or chemical. Now with two materials, presumably differing only by slight differences in bond angles, exchange pathways, etc, one can also attempt to build up a predictive model for low temperature magnetism within these highly anisotropic rare earth pyrochlores.

Finally a look into non-equilibrium magnetism of a material realization of the transverse Ising model was shown in Ch. 5. The possibility for non-equilibrium processes to generate new exotic forms of order has motivated a new push into understanding non-equilibrium systems centered around simple models, such as the transverse field Ising model. While a large body of work on CoNb₂O₆ have described its magnetic properties and application to the transverse field Ising model near its quantum critical point, the properties of CoNb₂O₆ in the low transverse field and low temperature limit have not been experimentally explained. Our ac susceptibility measurements show a development of slow relaxations which may be attributed to domain coarsening of the four degenerate sublattices within the commensurate antiferromagnetic state. These slow relaxations culminate in a frozen transition at $T_f = 1.2$ K, which has been observed by other groups, but not discussed in great detail. We attribute such a phase to a freezing of previously free domain walls due to disorder effects present in CoNb₂O₆. We expect due to the relatively large range of stoichiometries away from ideal which can retain the average Columbite structure in CoNb₂O₆ that all samples of $CoNb_2O_6$ have some disorder present, and clarifying the role of disorder is an important future avenue of research. Within the experimental limits a logarithmic scaling, which mimics a power-law, can be observed as a function of quench rate in our zero-field susceptibility. While one would expect a power-law scaling across the quantum critical point related to a Kibble-Zurek mechanism, we were able to reproduce this scaling as a systematic effect due to coarsening, for both quenches across the QCP (6 T \rightarrow 0 T) as well as quenches which do not cross the QCP (4 T \rightarrow 0 T). Due to the similarity of $CoNb_2O_6$ to the (quasi-1D) transverse field Ising model, it remains one of the best materials to study the effects of non-equilibrium dynamics in quantum magnetic materials. Although no evidence for Kibble-Zurek mechanism was found in our study, we cannot rule out the possibility that it was present but obscured by aging effects present within the frozen state discussed above. Repeating the search for the Kibble Zurek mechanism outside the frozen state of $CoNb_2O_6$ certainly warrants additional investigation.

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Appendix A

Appendices for Partial Antiferromagnetic Helical Order in Single Crystal Fe₃PO₄O₃

Neutron Structure Factor Simulation

Single crystal neutron diffraction was carried out on the four-circle diffractometer, HB-3A, at the High-Flux Isotope Reactor (HFIR) at Oak Ridge National Lab. This instrument features a full χ circle goniometer with a 4-800 K closed cycle helium refrigerator. The detector is a 2D scintillating Anger Camera. A silicon-wafer monochromator in Bragg geometry using (2 2 0) and (4 4 0) reflections provide an incident neutron wavelength of $\lambda = 1.546$ Å and peak intensity of 2.2 x 10⁷ neutrons cm⁻²s⁻¹. All experimental data reduction and analysis was done through use of the neutron scattering software Mantid[336].

Resolution Function Determination

The monochromator was set in double focusing mode to increase incident flux on sample. This produced a divergence in the k-space instrument resolution in the coincident with a y and z (horizontal and vertical) direction of the "lab frame" as defined by Busing, et al. [162]. As the four-circle diffractometer is positioned to access different reflections, the lab frame is related to the reciprocal lattice frame through a series of rotation transformations in conjunction with the orientation matrix (UB) defined by our crystal alignment.

$$\begin{pmatrix} 0\\0\\1 \end{pmatrix} = \Theta \Omega X \Phi U B \begin{pmatrix} h\\k\\l \end{pmatrix}$$
(A.1)

where Θ , Ω , X, and Φ are 3D rotation matrices corresponding to the four fundamental angles of the instrument, as described by Busing, et al. [162], U is the reflection matrix, and B is the crystal Cartesian matrix. For HB-3A there are two angles, ω and χ , are not defined precisely the same way as in Busing, et al. The correspondence is shown below:

$$\omega_{\text{Busing}} \to \omega_{\text{HB3A}} - \theta$$
 (A.2)

$$\chi_{\text{Busing}} \to \chi_{\text{HB3A}} + \pi$$
 (A.3)

The lab frame z-axis gives one of the principal axes of the instrument resolution ellipsoid, and the other two are oriented parallel and perpendicular to the scattering vector Q. Keeping the same conventions as Busing, et al.[162], for any 2θ angle, these are related to the lab frame coordinates through

$$\begin{pmatrix} Q_{\perp} \\ Q_{\parallel} \end{pmatrix} = \begin{bmatrix} \cos(\theta) & \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{bmatrix} \begin{pmatrix} x_{lab} \\ y_{lab} \end{pmatrix}$$
(A.4)

We can project the measured nuclear Bragg peaks into our principal axes using the inverse transform of Eq. A.1 in order to extract a measure of the instrument resolution along each of the principal axes. We assumed a Gaussian form and extracted the full width at half max (FWHM) for each of the principal axes. Figure A.1 shows example projections of the axes from experimental data from the nuclear reflection $(h \ k \ l) = (\bar{1} \ 0 \ 2)$. Note that the vertical focusing is achieved through stacking silicon wafers, which produces a non-Gaussian form to the 3rd principal axis. This will introduce small quantitative deviations of the simulated values from the experimental data, but gives good qualitative agreement. The width of the instrument resolution also intrinsically depends on the value of 2θ [161]. We corrected for this dependence when using the measured nuclear resolution function to model rings centered at various |Q| values.

We measured three separate nuclear peaks which were all located at nearly identical 2θ values and extracted the three principal ellipsoid FWHM for each nuclear peak in order to determine accurately the resolution limits. These are shown in Table A.1. With the exception of the 1st



Figure A.1: Gaussian approximated fits to nuclear peak (0 1 2). While the 3rd principal axis corresponding to the lab frame *z*-axis (vertical) is a non-Gaussian form, this approximation closely matches the FWHM values of the experimental data and works well to reproduce the observed data when convolved with rings (see main text and Fig. A.3).

Table A.1: Extracted nuclear peak FWHM and the corresponding limits on instrument resolutions. All errors are represented by 95% confidence bounds. With the exception of the 1st principal axis, instrument resolution is too coarse to probe the *ab*-plane correlation length associated with the magnetic scattering reported in [146].

	Principle Axis 1	Principle Axis 2	Principle Axis 3
	FWHM (\AA^{-1})	FWHM (\AA^{-1})	FWHM (\AA^{-1})
(0 1 2)	0.0053 ± 0.00025	0.038 ± 0.0068	0.10 ± 0.017
(102)	0.0060 ± 0.00023	0.039 ± 0.0059	0.099 ± 0.017
$(\bar{2} \ 0 \ 1)$	0.0064 ± 0.00022	0.040 ± 0.0062	0.098 ± 0.017
Average	0.0059 ± 0.00025	0.039 ± 0.0068	0.099 ± 0.017
ξ_{MAX}	470 ± 21 Å	71 ± 14 Å	28 ± 6 Å

principal axes, our resolution was too coarse to probe correlation lengths associated with previous powder neutron diffraction data (~ 100 Å) as reported in [146].

With the intrinsic widths of the resolution ellipsoid determined, now we can rotate the ellipsoid to magnetic reflection hkl indices. As a check that we were correctly reproducing this instrument resolution effect, we reproduced nuclear peaks by rotating the ellipsoid based on Eqn A.1 and taking a cut through various reciprocal lattice planes. Fig. A.2 shows good agreement with nuclear peak profiles seen experimentally and simulated within both the principal axes and in the (h k' l) frames. Here the reciprocal lattice direction k' represents a vector perpendicular to both a^* and c^* and normalized to be the same magnitude as b^* . Aside from qualitative agreement, we can check quantitative agreement as well by comparing cuts in various directions (Fig. A.2c).

Simulation Details

With the resolution ellipsoid correctly described, we then convolved it with a uniform ring in the hk-plane centered around a commensurate antiferromagnetic reflection seen in previously in neutron powder diffraction [146]. The radius of the ring was fixed at a value $r_{ring} = 0.064 \pm 0.006 \text{ Å}^{-1}$, which was determined experimentally via matching the distance between peaks of integrated cuts along the a^* -axis for several magnetic peaks. Figure A.3 shows a comparison of the simulated magnetic peaks with the experimental data around four additional commensurate magnetic reflections: $(h \ k \ l) = (2 \ 0 \ 0.5), (h \ k \ l) = (\overline{2} \ 2 \ 0.5), (h \ k \ l) = (0 \ 2 \ \overline{0.5}), and (h \ k \ l) = (\overline{1} \ 0 \ 0.5).$ For any reciprocal lattice point with $k \neq 0$, the hk indices will become non-integers due the use of the orthogonal vectors a^* and $b^{*'}$. High temperature (T = 200 K) background scans were taken at several peak positions and are feature-less with the exception of some $\frac{\lambda}{2}$ beam contamination from the $(\bar{2} \ 0 \ 1)$ nuclear peaks, as seen in Fig. A.3d. The nuclear contamination persists even with background subtraction due to thermal lattice contractions producing a slight mismatch between the two sets of data. The intensity variation seen in Fig. A.3a cannot be correctly reproduced by the simulation for this peak alone. Here it should be noted that without a unique magnetic structure determined, the polarization factor from neutron scattering was not taken into account for the simulation. While it seems the instrument resolution dominates the observed data for most reflections,



Figure A.2: (a) and (b) Simulation of Gaussian intensity profile resolution ellipsoids (bottom) vs experimental data (top) for nuclear peak $(h \ k \ l) = (\overline{1} \ 0 \ 2)$. In panel (a), the peak is shown in the principal axes frame, while in panel (b) is shown within the h, k', l frame. Colored dashes show the line cuts seen below. (c) Cuts comparing the data and simulation along the h and k' directions respectively.

Table A.2: Resolution limits on correlation lengths of magnetic peaks extracted from HB-3A. Limits are produced from integrated cuts of simulated magnetic peaks along the three orthogonal reciprocal lattice directions, a^* , $b^{*'}$, and c^* .

	ξ_{a^*} (Å)	$\xi_{b^{*\prime}}$ (Å)	ξ_{c^*} (Å)
(2 0 0.5)	57 ± 6	29 ± 1	163 ± 64
(0 0 1.5)	71 ± 10	28 ± 1	66 ± 9
(0 2 0.5)	213 ± 125	73 ± 10	43 ± 3
$(\bar{2} \ 2 \ 0.5)$	32 ± 2	59 ± 6	139 ± 43

the discrepancy between data and simulation for the reflection (2 0 0.5) could be attributed to the polarization factor.

The magnetic peaks appear to be resolution-limited in all directions. The FWHM of the simulated rings in different directions gives a bound on the correlation lengths for each magnetic feature. The correlation length radius is considered to be the HWHM of a Gaussian envelope in direct space and is related to the measured FWHM Gaussian in reciprocal space by

$$HWHM_{directspace} = \frac{4\ln 2}{FWHM_{reciprocal}}$$
(A.5)

Since the peaks are resolution-limited, we use the FWHM extracted from the simulation to recover limits on the correlation length from the instrument. These are recorded in Table A.2. The inferred error in the widths of the simulated ring was taken to be equal to the bin width in the simulation. With the exception of cuts along the a^* direction for magnetic reflection $(h \ k \ l) = (0 \ 2 \ 0.5)$, all correlation length limits in the hk-plane are consistent with previous powder estimates [146]. For $(0 \ 2 \ 0.5)$, we note an anomalously large correlation length, but its associated error is too large to reliably state that this is inconsistent with the previously reported powder data correlation lengths [146, 147].



Figure A.3: Simulation of Gaussian approximated resolution functions (bottom) vs experimental data (top) for magnetic peaks.(a) $(h \ k \ l) = (2 \ 0 \ 0.5)$, (b) $(h \ k \ l) = (\overline{2} \ 2 \ 0.5)$, (c) $(h \ k \ l) = (0 \ 2 \ 0.5)$, and (d) $(h \ k \ l) = (\overline{1} \ 0 \ 0.5)$. Note that the positions have moved away from their original h, k, l values due to re-binning data from k to k' for both (b) and (c). The data in (d) shows a central peak from higher order contamination of $(\overline{2} \ 0 \ 1)$ nuclear peaks.

Comparison to Fully Ordered IC State

For an incommensurate wavevector in the hk'-plane symmetry allows six peaks for Fe₃PO₄O₃. With the highly anisotropic instrument resolution, simulation of a well-ordered incommensurate state is crucial to distinguish the partial ordered state in Fe₃PO₄O₃. Fig. A.4 shows the six-peak simulations vs experimental data for two reflections centered around $(h \ k \ l) = (0 \ 0 \ 1.5)$ and $(h \ k \ l)$ = $(2 \ 0 \ 0.5)$. The peaks were chosen to be an incommensuration along $\pm a^*$, $\pm b^*$, and $\pm b^* \mp a^*$ in order to reproduce the lowest energy configuration chosen by LT in the main paper (Fig. 3.7a).

Both simulation and experimental data were normalized to distinguish relative intensities expected for each. The data for $(0\ 0\ 1.5)$ shows a large disparity in the intensity in the hk'-plane. The six-peak simulation can reproduce some out of plane features (hl/k'l-planes), as for $(2\ 0\ 0.5)$, but cannot accurately reproduce the in-plane features (hk'-plane). This is most striking in the center of the in-plane ring, furthest from large intensity edges. The large relative intensity on the section



Figure A.4: Comparison of a six-peak well-ordered IC magnetic state and experimental data centered around two commensurate peaks: $(h \ k \ l) = (0 \ 0 \ 1.5)$ and $(h \ k \ l) = (2 \ 0 \ 0.5)$ plotted along the hk' and hl planes. All data was normalized to show differences in relative features. The six-peak simulations cannot reproduce the features observed experimentally both within the hk' plane, and for $(0 \ 0 \ 1.5)$ the hl plane.

of the ring perpendicular to the elongated resolution seen near $(0 \ 0 \ 1.5)$ can be described by a stacking of intensities from many peaks near each other, but not for six peaks. Thus we conclude that Fe₃PO₄O₃ *cannot* be explained by a well-ordered IC magnetic state.

Appendix B

Appendices for Phase Competition in Antiferromagnetic Pyrochlore Yb₂Ge₂O₇

Magnetization

Magnetization on a small single crystal (m = 0.68 mg) of Yb₂Ge₂O₇ was performed using vibrating sample magnetometry (VSM) on a Quantum Design Dynacool PPMS. Three separate measurements were performed such that the field was aligned with each of the high symmetry directions of the pyrochlore lattice ([111], [110], [001]). Correct orientation was checked prior to and after measurement to rule out sample movement during the measurements. Magnetization versus field curves show a nearly isotropic response at T = 2 K and 10 K [Fig. B.1a,c]. The data are nearly in agreement with the expectations for the single-ion using the g-tensor values extracted from EPR [Fig. B.1d]. We also note that the saturated moment at 2 K, $\mu \sim 1.6\mu_{\text{B}}$, agrees well with previous literature [216]. The small deviations from the single ion model are likely attributable to the effect of exchange interactions, which are not negligible even relative to the maximum field strength.

Lower temperature (0.4 K) magnetization data with the field applied along [110] were collected using a Quantum Design MPMS SQUID magnetometer with ³He insert [Fig. B.1b]. A kink in the magnetization data reveal a phase transition into the field-polarized paramagnetic state around 0.4 T.

Details of INS measurements

Due to the difficulty in growing large (i.e., cm³ sized) single crystals of the metastable pyrochlore phase of Yb₂Ge₂O₇, we were restricted to small high-quality single crystals (1mm x 1mm x 1mm). To increase the sample volume for neutron scattering, we co-aligned 28 small single crystals in the *hhl* scattering plane ([110] direction vertical) for a total mass of 154 mg [Fig. B.2a]. The crystals were fixed in place using a fluorinated glue (CYTOP 807-M). A rocking scan was taken over a



Figure B.1: Magnetization vs magnetic field for a Yb₂Ge₂O₇ single crystal. (*a*) Data taken at T = 10 K for three high symmetry directions of pyrochlore lattice. (*b*) Data taken at T = 0.4 K, with field along [110]. (*c*) Data taken at T = 2 K. (*d*) Calculated single ion magnetization (using $g_z = 1.93$, $g_{\pm} = 4.20$) at T = 2 K.



Figure B.2: (a): MACS neutron sample mount with 28 co-aligned single crystals of Yb₂Ge₂O₇. (b): Example rocking scan taken at MACS across a (111) nuclear peak at $T \sim 6$ K.The peak is split into three peaks indicating a mosaic of $\leq 5^{\circ}$

(111) nuclear peak, shown in Fig. B.2b. We note a peak splitting consistent with a mosaic of $\leq 5^{\circ}$ over all 28 crystals.

At MACS, INS data were taken throughout the [hhl] plane at a constant energy transfer ($E = |E_f - E_i|$), using a fixed final energy of $E_f = 3.7$ meV and varying E_i . The monochromator was used in doubly-focused mode with no radial collimators or filters in the incident beam, and cooled BeO filters were used in the scattered beam before the detectors. This configuration produces an energy resolution of 0.17 meV at the elastic line [79]. At each E (which increased in 0.1 meV steps from 0 to 1.5 meV), the sample was rotated through 180° in 2° increments, counting for 1.66×10^5 monitor units (approximately 10 s) at each increment.

As mentioned in the main text, data taken in zero field at the base temperature of the dilution refrigerator (mixing chamber temperature reading 260 mK) during the INS measurement at MACS is indistinguishable from data taken at 1.8 K. One possibility is that the inelastic spectrum is basically insensitive to temperature below 1.8 K, which would be largely consistent with a previous powder study [218]. However, in our experiment the elastic scattering also does not show any dependence on temperature below T = 1.8 K, even though it is clear that AFM Bragg peaks should develop



Figure B.3: Nominal temperature dependence of neutron scattering data taken on MACS. (a) and (b) show a lack of additional intensity on expected AFM Bragg peak positions. A shift of the peaks is observed instead (resulting in a net-zero profile with some regions of negative and positive differences). (c) overlay of the intensity along [-1, -1, l] of the low energy excitations, E = 0.3 meV, at both temperatures (3 T data used as background subtraction).

below T_N (as has indeed been observed in the powder samples[216]). We can thus only conclude that the sample did not cool below T_N , potentially due to the large mass of the sample holder (necessary to hold the 28 co-aligned crystals), or weak thermal coupling between the small crystals and the sample holder. We thus assign a sample temperature of 1.8 K for our field-polarized INS data.

Figure B.3 shows the comparison between the T = 260 mK (nominal) and T = 1.8 K data.

Dispersion of 3 T data

Figure B.4 shows INS data presented as a typical spin wave dispersion plot, illustrating that the energy resolution is insufficient to uniquely resolve each spin-wave branch and thus it is not feasi-



Figure B.4: Yb₂Ge₂O₇ INS data presented as a typical spin wave dispersion plot along [h, h, -1]. The dispersion is constructed from the combination of several constant energy slices through the [hhl] plane.

ble to fit the dispersions themselves. Instead, we fit the intensity at several energies over the whole [hhl] plane.

Dispersion of zero-field data

A measurement of the zero-field, low temperature (60 mK) dynamic structure factor was performed on the cold neutron chopper spectrometer (CNCS) at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL), using an 8T magnet (8T field-polarized data was used as background subtraction for zero-field data) with dilution refrigerator insert. The same crystals and crystal mount were used in this experiment as in the MACS experiment in the main text, oriented with the [110] along the vertical field direction to access the horizontal [*hhl*] scattering plane. Data was taken throughout the [*hhl*] plane with an incident neutron energy of E_i = 2.5 meV, operated in high-flux mode which gave an energy resolution of 0.07 meV at the elastic line [80, 337]. The sample rotation method was used, where the sample was rotated 180° around the vertical in 2° steps. Data was collected at 0 T and 8 T (used for background subtraction) with data taken above the ordering transition (90 K) and below the ordering transition (60 mK reported at the mixing



Figure B.5: (a) Zero-field INS spectrum of Yb₂Ge₂O₇ at 60 mK, within the ordered state. All reciprocal space directions were integrated ± 0.1 r.l.u. in their respective perpendicular components (for example, the cut along [*hh*0] is integrated ± 0.1 r.l.u. in [001]). The excitations are broad and featureless, despite the ordered ground state, similar to powder INS data reported in Ref. [218].(b) comparison of (111) Bragg peak at 60 mK and 90 K showing added intensity from magnetic ordering. Plots were integrated from ± 0.1 meV and ± 0.1 r.l.u. in [001].

chamber). The clear temperature dependence of the (111) peak indicates that the sample cooled below the transition temperature (Fig. B.5b).

Below the ordering transition, the excitation spectrum remains broad and featureless across reciprocal space, shown in Fig. B.5a. The bandwidth of the excitations is approximately 1.25 meV. This is similar to polycrystalline INS data taken by Hallas *et al.* [218], who also reported broad diffuse dispersion below the ordering transition.

Details of fitting

Ambiguities in fitting crystal field parameters

In this section, we address in more detail why it was necessary to obtain additional information above and beyond the inelastic neutron scattering data, specifically EPR on a diluted sample (as described in Sec. 4.4.2), to determine the *g*-factors.

A commonly used and reliable approach to finding the g-factors in a rare-earth magnet, such as $Yb_2Ge_2O_7$, is through determination of the parameters that describe the crystal field potential via fitting to experimental data. Typically, in INS measurements, the data used would be the transition energies and intensities between different crystal field multiplets. However, two issues present

themselves in Yb₂Ge₂O₇. First, the energy scale of the crystal field is very large, with the gap between the ground and first excited doublet being ~ 80 meV [214]. At accessible experimental temperatures, one can thus only probe transitions from the ground doublet (which is essentially fully populated) to the excited doublets (which are unpopulated). Second, for the D_{3d} environment of Yb³⁺ in Yb₂Ge₂O₇, the J = 7/2 manifold is split into only four Kramers doublets. Given the overall absolute intensity scale is (typically) difficult to determine, this leaves only *five* pieces of information: three transition energies (ground to excited levels for the reason stated above) and two relative transition intensities. This is less than the *six* parameters needed to describe the crystal field; usually denoted B_{20} , B_{40} , B_{60} , B_{43} , B_{63} and B_{66} (see, e.g. Ref. [338] for details). Such fitting, for example as carried out in Ref. [339] for Yb₂Ti₂O₇ and in Ref. [214] for Yb₂Ge₂O₇, is thus underconstrained and generically cannot yield a unique best fit. We note that in some ytterbium magnets where the crystal field energy scale is smaller, neutron data at several different temperatures may be used to resolve this issue (see, for example, Ref. [232]).

To make this point explicit, we have performed a re-analysis of the fitting results of Ref. [214] to highlight the non-uniqueness of the fit. Due to some ambiguities due to a phonon subtraction near the crystal field levels, we do *not* attempt to directly refit their intensity as a function of energy. Instead, we determine sets of crystal field parameters that can reproduce the best fit transition energies (ground to excited) and relative intensities (which can be calculated using the best fit CEF parameters of Ref. [214]), to within 1% accuracy. The result of this fitting is shown in Fig. B.6, where one sees that a large number of crystal field parameters can produce nearly identical transitions and relative intensities as their best fit, but with wildly different *g*-factors. Indeed, the manifold of fits shown in Fig. B.6 is (piece-wise) one-dimensional, as one would expect when trying to fit six parameters with only five pieces of data. One thus cannot use inelastic neutron scattering data alone to determine the *g*-factors in Yb₂Ge₂O₇.

We stress here that the set of g-factors in Fig. B.6 does not exhaust all potential values of g_z and g_{\pm} relevant for Yb₂Ge₂O₇, since the phonon subtraction leaves a reasonable amount of uncertainty in properly assigning some of the transition energies and relative intensities. Indeed, our final g-



Figure B.6: Illustration of the non-uniqueness of the *g*-factors obtained from the fit reported in Ref. [214]. Each set of *g*-factors represents a set of six crystal field parameters (B_{kq}) with transition energies and relative intensities within 1% of the result computed using the best fit parameters of Ref. [214]. The color of each point show the variation of the Van Vleck contribution (χ_0) to the susceptibility. Several important limits are indicated: Γ_6 doublet (octahedron cage), Γ_7 doublet (cube cage), as well as pure $|\pm 1/2\rangle$, $|\pm 5/2\rangle$ and $|\pm 7/2\rangle$ doublets. The *g*-factors in the shaded region are not physical for a pure J = 7/2 manifold in a D_{3d} crystal field [226]

factors, determined in the diluted sample via EPR (see Sec. 4.4.2), do not belong to the manifold of fitted g parameters shown in Fig. B.6.

We also explored a joint fit between the high temperature susceptibility and the crystal field data (three transitions and two relative intensities), as an alternative to the EPR from the diluted samples. These fits were inconclusive due to both the phonon subtraction issue discussed above, and some variability depending on the temperature range used in fitting the high-temperature susceptibility. We do note that, while not determinative, these results are somewhat consistent with the g-factors determined by EPR, i.e. $(g_z, g_{\pm}) = (1.93, 4.20)$. However, the Curie constant that was obtained by fitting the susceptibility was somewhat insensitive to the aforementioned confounding factors and is consistent with the EPR value.

Fitting of the exchange parameters

In this section, we describe our fitting methodology to determine the four exchange constants J_{zz} , J_{\pm} , $J_{\pm\pm}$ and $J_{z\pm}$ (or, equivalently, in the global or dual bases). Throughout, we fix the *g*-factors to the ones found from EPR, that is $(g_z, g_{\pm}) = (1.93, 4.20)$ (for details, see Sec. 4.4.2). We consider data from two independent controlled "perturbative" regimes (high magnetic field or high temperature) to determine these four exchange constants.

First, is the inelastic response in the high-field partially polarized phase obtained by applying a B = 3 T magnetic field along $[1\bar{1}0]$ at T = 1.8 K. Theoretically, the inelastic response can be tractably calculated using standard linear spin-wave theory, as has been used in previous determinations of exchange constants in Yb₂Ti₂O₇ [184, 197, 198] and in Er₂Ti₂O₇ [173]. Due to experimental limitations (see Sec. B), instead of fitting the spin-wave *spectrum*, we consider the inelastic intensity as a function of wave-vector (in the [*hhl*] plane) within several fixed energy windows. Specifically, we consider the four energies E = 0.5 meV, 0.7 meV, 0.9 meV and 1.1 meV each averaged over an energy window with a resolution function that depends on the particular energy slice used (see Fig. B.7 for the precise form). To include the extent of the detectors out of the scattering plane, we also averaged over a window of [-0.28, +0.28] r.l.u. in the $[1\bar{1}0]$ direction (the effect of finite resolution in the scattering plane is negligible for our purposes). The magnetic



Figure B.7: Energy resolution functions at energy transfer ΔE for specified energy transfers $(\Delta E)_0$ used in the theoretical calculations to emulate the behavior of the experimental setup. Practically these functions can be modelled by a two-sided Gaussian, with energy dependent width for $\Delta E < (\Delta E)_0$.

form factor of Yb^{3+} was included in the fitting [340], though the temperature is not, as the thermal population factors are unimportant even in the lowest energy window considered. Further, given we fit within (somewhat) narrow energy windows, any thermal factors primarily affect the overall intensity scale, not the variation with wave-vector.

Second, we make use of the specific heat data at zero field, but at high temperatures. This high temperature regime can be readily accessed using series expansion techniques. For this purpose, we employ a numerical linked-cluster expansion [243, 341, 342] to third order (NLC-3) in the number tetrahedra [205, 236, 237]. This order in the expansion is sufficient for good convergence in the temperature range considered for typical exchange constants, yet sufficiently fast computationally to still be amenable to automated fitting. More specifically, we consider five temperatures in the range 5 K $\leq T \leq 8$ K (to minimize any phonon effects) with the specific heat of the non-magnetic analog Lu₂Ge₂O₇ subtracted [216]. For each comparison to experimental data (high-field



Figure B.8: Comparison of constant-energy slices (centered at energy E with an energy dependent energy resolution function, see Fig. B.7) of the 3 T field polarized spin-waves between Yb₂Ge₂O₇ at 1.8 K (left) and linear spin wave theory using the best fit exchange parameters within linear spin-wave theory (right). Overall intensity scale is consistent between panels, but arbitrary. For the 1.3 meV and 1.5 meV cuts we assume the energy resolution function is the same as the 1.1 meV case.

inelastic response or high-temperature specific heat), we evaluate a χ^2 value using estimates of the experimental errors, then sum these to obtain a total χ^2 value. This total χ^2 is then minimized to find the best fit (via standard Nelder-Mead simplex method implementation). To ensure that we find the global minimum, we repeat the fitting procedure $O(10^2)$ times from random initial points, typically taking each of the four exchanges $(J_{zz}, J_{\pm}, J_{\pm\pm}, J_{z\pm})$ to be chosen independently and uniformly in the range -0.2 meV to +0.2 meV. The best fit found is

$$J_{zz} = +0.128(95) \text{ meV}, \tag{B.1a}$$

$$J_{\pm} = +0.138(6) \text{ meV}, \tag{B.1b}$$

$$J_{\pm\pm} = +0.044(24) \text{ meV}, \tag{B.1c}$$

$$J_{z\pm} = -0.188(18) \text{ meV}, \tag{B.1d}$$

as given in Table I of the main text. Statistical uncertainties are estimated using standard techniques by computing the curvature of χ^2 about the best fit minimum. The uncertainties are most significant for the parameter J_{zz} . This is consistent with previous fits of experimental data in Yb₂Ti₂O₇ have also found J_{zz} to be constrained more loosely than the other fitted exchange parameters [198]. The curvature of χ^2 provide the full (Gaussian) covariance matrix which was then transformed to obtain the corresponding error estimates for the global, alternate global and alternate dual exchanges presented in Table I of the main text.

We note that two high energy slices of the experimental data were not included in the fitting – specifically those at 1.3 meV and 1.5 meV. These were excluded for three reasons, first that they were mostly featureless and thus did not provide much additional information. Second that the intensity showed evidence of some spurious experimental effects, such as not following the known lattice symmetries (potentially due to differences in absorption for different rotation angles). Third, due to the greater importance of anharmonic magnon interactions (renormalization and spontaneous decay) at high energies, the applicability of linear spin-wave theory becomes questionable. The effects of these interactions is likely even an issue at 1.1 meV, as the one-magnon and two-

magnon states overlap at this energy, and might account for some of the quantitative disagreements between the theory and experiment at this energy.

However, for completeness we include a comparison between the theory and experiment at all energies, as shown in Fig. B.8. It can be seen that while there are some differences, there is broad qualitative agreement for both the 1.3 meV and 1.5 meV energy slices.

Finally, we note that we also attempted determining the g-factors without the EPR data, using only the high-field inelastic neutron scattering data and the Curie constant obtained from the magnetic susceptibility. Including the Curie constant fixes $\bar{g}^2 \equiv g_z^2 + 2g_{\pm}^2$, giving the pair of g-factors in terms of a single angle, θ , as $g_z = \bar{g} \cos \theta$ and $g_{\pm} = \bar{g} \sin \theta / \sqrt{2}$. The fitting procedure described above was then carried out on the high-field inelastic neutron scattering data alone, on a grid to determine the value of θ having the lowest χ^2 . This was inconclusive, given the issues described above with temperature range dependence in determining the Curie constant and a large number of nearly equally good local minima. However, we do note that the g-factor values obtained via the EPR measurements is present among these local minima determined using susceptibility data.

Appendix C

Appendices for Low Temperature Non-equilibrium Behavior in CoNb₂O₆

Kibble-Zurek considerations in CoNb₂O₆

One goal of this study was to investigate the possibility of a Kibble-Zurek Mechanism (KZM) scaling in CoNb₂O₆. By quenching a control parameter through a continuous phase transition the system will inherently be driven out of equilibrium, a direct result of the divergence of the relaxation time near the critical point. This results in a non-zero density of defects which accumulate in the system for any finite quench rate. The density of defects, and all observables that depend on it, are predicted to scale as a power law with the quench rate, r_Q [261]. The density of defects, ρ , is predicted to scale as,

$$\rho \sim r_Q^{d\nu/(1+z\nu)} \tag{C.1}$$

where r_Q is the quench rate, d is the dimension, ν is the correlation length critical exponent, and z is the dynamical critical exponent. The interest in Kibble-Zurek scaling is two-fold. First, despite being an inherently non-equilibrium effect, which are typically challenging to describe, this phenomenon is described *entirely* by equilibrium properties (critical exponents). Second, the only requirement for Kibble-Zurek effects to occur is to cross a continuous phase transition at a finite rate, with the scaling relying only on the universality class of the system. While it was originally formulated by Kibble for defects in the early universe [272, 273], it was extended to condensed matter systems by Zurek, who proposed it in superfluid helium [274]. It has since been generalized to quantum phase transitions [286, 287, 288], and experimental evidence for the KZM has been found in many systems including superfluid He [278], cold ion chains [279], and Bose condensates [284, 285]. To this date, no scaling from a KZM due to a quantum phase transition has been observed in a magnetic system, where a magnetic field can provide a natural tuning parameter. Due to strong spin-lattice coupling, typical relaxations in magnetic systems are fast (picoseconds). However, the timescale for observation of defects is not limited by this spin-lattice relaxation; rather, it is limited by the coarsening time, which relies on the mobility of defects (to some extent set by the exchange interactions) and the dimension. Thus, one should expect that when defect motion is restricted, perhaps by disorder or frustration, KZ scaling could be readily observed over experimentally achievable timescales. To accurately assess the power law exponent, observation of the scaling over several orders of magnitude of the quench rate is desirable. Conventional superconducting magnets are limited to slow quench rates (< 10^{-3} T/min) do not offer a reasonable range. Alternatively, resistive magnets can reach much higher magnetic field quench rates; the 31 T magnet at NHMFL provided us a range between 0.1 and 10 T/min. Ultra-fast field ramps can also be achieved through pulsed magnets, which can reach quench rates of > 10^3 T/min [291, 292].

The combination of an appropriate range of magnetic field quench rates as well as the observed slow coarsening dynamics of $CoNb_2O_6$ suggests it would have been a good candidate for observation of KZM. What is less obvious is what type of scaling should observed in $CoNb_2O_6$. It is well-established that near the QCP $CoNb_2O_6$ displays hallmark behavior of the 1D TFIM with small but non-zero longitudinal field from the intrachain couplings [269, 270, 294]. In the case of defects being kinks along the Ising chains, scaling could be that of the QCP of the 1D Ising chain with an exponent of 0.5 [10, 343]. However, $CoNb_2O_6$ orders into a 3D magnetically ordered ground state with much of its coarsening behavior at T = 1.5 K attributed to domain walls within the *ab* plane [298, 299]. These defects would then perhaps be expected to scale according to the QCP of the 3D Ising model with an exponent of 0.75 [35, 344]. With a frozen state developing below T = 1.2 K, the system may be described better by a 3D random field/bond Ising model, where dramatically increased dynamical exponents can greatly reduced expected scaling exponents.

These predictions also are only inherently true for closed quantum systems, which we know $CoNb_2O_6$ is *not*. Recent theoretical work for 1D Ising systems show that coupling to a bosonic

bath greatly reduces the critical exponent down to 0.28 [345]. Experimental work on quantum simulators of the 1D TFIM have also estimated the value of the scaling exponent due to the KZM range between 0.2 and 0.33 [346]. Coarsening and the KZM have been further explored [314], with estimates that in d > 2, coarsening does not strongly affect the expected critical exponents [313].

Finally, we note that the scaling of the initial ac susceptibility with quench rate, parameterized by a in Equation 5.10, would likely be good indicator of defect density. But as discussed in Appendix C (and shown in Fig. C.4), we find that a does not depend on quench rate systematically; rather, it appears to display some aging effects, though not as clearly as the c parameter.

Transverse Field Susceptibility

For conventional ac susceptibility, one measures with the ac field in the same direction as the dc field. In contrast, for the susceptometer we used, the ac component was measured along the crystallographic *c*-axis, while the dc field could be applied anywhere in the *bc* plane by an *in situ* rotation of the ac coilset. The samples were loaded and aligned into the coilset with use of a laue diffractometer, limiting a possible rotation of the sample out of the *bc* plane to 1-2°. In order to accurately align the dc field to be transverse to the Ising axis (i.e. *b*), we first located the *c* axis by rotating the coilset under a 1 T dc field through a range of angles for which the direction of H_{ac} is approximately equal to that of H_{dc} , and once determined, set the coilset to 90° from there. Figure C.1a, taken at T = 0.5 K, shows an approximately symmetric signal around "108°", which identifies the coil angle of 108° as the *c*-axis direction. The several peaks observed around this position are likely may indicating different field-induced transitions as a function of angle (for fields near the Ising axis, the phase diagram is known to be highly complex: [296, 307]). The overall background from the coil is not symmetric, but this is likely due to details of the coil design and centering in the magnet.

In general, for ac susceptometers in a transverse field, an anisotropic background signal of the coil can develop, which can be both field-dependent and frequency-dependent [347]. For our setup, an estimate of the coil background was taken using a high temperature scan at 10 K, well-into the paramagnetic phase (Fig. C.1b). Interestingly, we note that even at the maximum field of 10 T
the imaginary component is still non-zero. This perhaps indicates that the system still exhibits frustration deep into the field polarized paramagnetic phase and could help to explain the aging effects we have observed. This background is subtracted from all ac susceptibility figures shown. In an attempt to separate any possible trends coming from aging effects compared to quench rate effects, we instituted the following protocol for our magnetic field quenches: after the system was reset (warmed to 1.8 K then cooled in zero-field), we ran a series of quenches from 0 T up to a maximum field (either 6 or 4 T) and then back down to 0 T. Each of the quenches was ran with an identical quench rate on the ramp up to the maximum field of 1 T/min, held at maximum field for 10 s, and then non-systematically changed to a value between 0.1 T/min and 10 T/min for the quench back to 0 T. The system was then reset again before another set of quenches. By doing the quenches "out of order" with respect to quench rate, we are able to separate any overall aging effects (i.e. effects that correlate with run number, which loosely represents time since cooling into the frozen state) from effects depending on the quench rate, r_Q .

After a magnetic field quench (i.e. when the dc field returns to zero), we observe a decay over time of the real and imaginary components of the susceptibility at T = 0.5 K, i.e. a non-equilibrium state is generated. This decay appears for all quenches to zero field, regardless of their starting field values (which were either 4 T or 6 T), indicating that the non-equilibrium state is not due to quenching through the QCP associated with the 1D TFIM (at 5.2 T) or the 3D QCP to the field-polarized paramagnet (at 5.5 T). To observe at what field the relaxation begins, we measured the susceptibility over time for many smaller intermediate magnetic field quenches (e.g. 4 T to 3 T, 3 T to 2 T etc.). A small relaxation on the order of the noise limit of our experiment is observed in the 4 T to 3 T quenches, shown in Fig. C.2a. The onset of appreciable relaxation occurs for quenches from 3 T to 2 T, across the previously-identified transition between the IAFM and CAFM ordered states at $B_{AFM} \sim 3$ T (Fig. C.2b). For the final fields above the freezing transition, relaxations show an overall aging effect such that progressive quenches are shifted down with run number (Fig. C.2c). For final fields below the anomaly at $B_f \sim 1.7 T$, which we have tentatively associated with a field boundary of the frozen phase, the relaxation gains a more complicated



Figure C.1: (a) Real component of ac susceptibility vs linear motor rotation angle taken under a 1 T dc field. A large peak near 108° shows the location of the average Ising axis (*c*), which is identified based on the symmetric peaks around it, which likely relate to field-induced phase transitions that are highly dependent on the field direction. (b) Example of transverse-field dependent susceptibility, with the background from coil shown, which was taken at 10 K for the real component (main figure) and imaginary component (inset) of the susceptibility. The background from the coil shows a frequency dependence as well as transverse field dependence but little to no quench-rate dependence at 710 Hz.



Figure C.2: (a-b)Representative ac susceptibility data taken at the end of intermediate quenches for various points in the phase diagram. Color scale represents r_Q . (a) 4 T to 3 T quenches showing a small relaxation barely larger than instrument noise limit, showing the approach to the CAFM state at 2.9 T. (b) 3 T to 2 T quenches show a clear relaxation well beyond noise limit that exhibit a decrease in signal with increasing run number. Small bumps in some relaxations are attributed to spurious experimental effects, since they are not present in repeated measurements. (c) Average susceptibility over last second of measuring time ($\chi'_{<l>}$) as function of quench run number for data in panel (b). Above the frozen transition, the system relaxes overall with each subsequent quench. (d) Average susceptibility over last second of measuring time as function of quench data for zero-field data showing aging effects within frozen state.

dependence on the quench rate, shown in the main paper by the zero-field relaxation (Fig. 5.7a). Looking at the average susceptibility at the last second of measurement time, shown in Fig. C.2d, we notice two different aging behaviors in the 4 T and 6 T quenches. For the 4 T quenches, the average final susceptibility increases with initial runs and then saturates, while the 6 T quenches increase with consecutive quenches. Any trend that appears as a function of run number (which was not correlated with quench rate, by design) strongly suggests aging effects are present, and we find that these are surprisingly *not erased* by going to 6 T (in the paramagnetic regime). This may be related to the presence of significant absorption up to 10 T, as indicated by the high χ'' (Fig. 5.5) at 6 T, and suggests that one needs to go to higher fields to reset the system.

In order to account for the aging effect, which mainly seemed to produce an offset to χ' , we looked at the difference of the first second and last second of the susceptibility, $\chi'(t)$ (Eqn. 5.11). This difference increases as a function of magnetic field quench rate, r_Q (as shown in Fig. 5.7b-c). The dependence can be understood to result from a systematic effect, described next.

Systematic effect

Due to the coupling between the spin system and the lattice, excess energy left over from the field quench (the Zeeman energy) will decay over time, i.e. this is ultimately an open quantum system. Another way to think of this is the domain coarsening effect. In CoNb_2O_6 at T = 0.5 K, this coarsening is very slow below ~ 3 T, and is measurable (in the form of the time-dependence of the ac susceptibility) over the timescale of minutes to hours. Since the decay of defects should also occur over the course of the quench time (i.e. while the dc field is still decreasing but not yet zero), care must be taken in analyzing any quench-rate-dependent behavior to account for this systematic effect. This is true for any open system such as ours where coarsening occurs on the same approximate timescale as the quench time.

We have analyzed the results of quenches as follows. During our experiments, the magnetic field was ramped linearly at a set quench rate from 6 T down to 0 T and from 4 T down to 0 T, as well as between intermediate field values, as described above. The quench rate, r_Q , is given by,

$$r_Q = \frac{dB}{dt}$$

$$r_Q = \frac{B_i - B_f}{t_i - t_f}$$
(C.2)

where the subscripts i and f refer to the initial and final parameters of the quench. Note that r_Q is defined to be positive for a decreasing field. Following the quench, the zero-field domain wall relaxation at intermediate times within the frozen state can be fit relatively well to three different forms: a stretched exponential, a power law decay, and a logarithmic function given by,

$$\chi'(t, B = 0) = a \cdot \exp\left[-\left(\frac{t-t_0}{\tau}\right)^{\beta}\right] + c$$
 (C.3a)

$$\chi'(t, B = 0) = a \cdot \left(\frac{t - t_0}{\tau}\right)^n + c \tag{C.3b}$$

$$\chi'(t, B = 0) = a \cdot \ln\left(\frac{t - t_0}{\tau}\right) + c \tag{C.3c}$$

respectively. In each of the forms, t_0 represents the time of relaxation onset, τ represents an intrinsic time (needed in theory to make the time arguments dimensionless, but absorbed into the other parameters for fitting purposes), a is a scale factor that one could expect to represent the initial population of defects generated by the quench, and c is an offset due to late-time behavior and/or background. For the stretched exponential, τ represents the average relaxation time and β represents the distribution of relaxation times. This form of relaxation is commonly found in glass systems [348, 349], and has also been found for hierarchically constrained dynamics [333]. A power law would instead indicate relaxations occurring on all time scales with growth exponent n describing the coarsening. Power law relaxation has been observed for CoNb₂O₆ at higher temperature above the glass transition where the exponent n was found to be -0.2 [298, 299, 326]. Meanwhile, the logarithmic relaxation function has also been proposed for hierarchical dynamics [327], and is often seen for domain coarsening in disordered models, such as the random field Ising model [350, 351].

To determine the best model for the decay, we compared χ^2 for fits of the three models to several relaxation curves. An example of best fits for the three functional forms are shown in Fig. C.3, where the best fit parameters used are shown in Table C.1. Note that the form of the power law and logarithmic decay functions have absorbed τ into the definition of the other parameters, a and c, as appropriate. For the sake of comparison to Ref. [298, 299], we note the data can be well-represented by a power law, but with a smaller exponent of n = -0.097(3) compared to the value reported in literature (n = -0.2). While the χ^2 for the three forms were comparable, in the end we chose the logarithmic form due to the reduced number of free parameters required to accurately fit the decay, and the very small exponent indicated by the power law fit.

From intermediate quench data (quenches ending at a non-zero field), the system only shows a sizeable decaying population below the CAFM transition, $B_{AFM} \sim 3$ T. Within the frozen state, best fit values of the parameters a and c show a large distribution of values, but remain largely insensitive to the quench rate of the magnet, shown in Fig. C.4. In comparing differences data (Eqn. 5.11), assuming the fit parameters of Eqn. 5.10 (the log relaxation form) do not change



Figure C.3: Example of least square best fits to zero-field relaxation for the following functional forms: Power law, Stretched exponential and Logarithmic decay.

Table C.1: Table of least squared fits to typical zero-field relaxation of the susceptibility of $CoNb_2O_6$ at T = 0.5 K taken after a 2 T/min quench from a peak field of 4 T. Best fit parameters are shown for three different forms of the relaxation: a logarithmic relaxation, a power law relaxation, and a stretched exponential relaxation. τ was absorbed into *a* and *c* for the power law and logarithmic forms respectively in order to reduce free parameters.

	Logarithmic	Power law	Stretched Exponential
	$a \cdot ln(t-t_0) + c$	$a \cdot (t - t_0)^n + c$	$a \cdot exp\left[-(\frac{t-t_0}{\tau})^{\beta}\right] + c$
a	-2.11(2)e-6	3.54(6)e-5	3.9(5)e-4
t_0	368.6(2)	365.3(4)	367(1)
С	3.02(1)e-5	-2.2(8)e-6	-1.2(3)e-4
\overline{n}	-	-0.097(3)	-
τ	-	-	124(8)
β	-	-	0.01(5)
χ^2	3.2e-6	2.3e-6	7.0e-6



Figure C.4: (a) Plots of best fit parameters a and c for least squares fit of Eqn. B2c as a function of quench run number, shown with psuedo-random r_Q protocol as a function of quench run number. Color overlays shown distinct sets of quenches: red is Q1 4 T, green is Q2 4 T, and blue is Q1 6 T. Parameters a and c both show weak trends in run number, suggesting aging. Parameter c also shows a general offset to the data for each individual quench set (each set started after warming past T_f and cooling back down in zero field). (b) Plots of best fit parameters a and c for least-squares fit of Eqn. B2c as a function of r_Q , where errors plotted are 95% confidence of the fitted parameters. Although the spread in values is much larger than the error plotted, they show no obvious dependence on ramp rate. With a large distribution of values across all fits, explicit estimates of values were not enforced in fitting Eqn. C.4, and instead the values were unbounded.



Figure C.5: Loglog plots of difference susceptibility (χ'_D) as a function of quench rate for quenches from a maximum field of 6 T (similar graphs in the main text are for a maximum field of 4 T). Fits to both a power law form and logarithmic form described in Eqn. C.4 are shown. Different colors of data points are associated with different 6 T quenches, where the system was reset in between. Despite crossing the QCP in CoNb₂O₆, no difference in scaling between the 6 T and 4 T data are observed, with the systematics still reproducing the scaling.

over the relevant field range (below B_c , as defined below), we find a best fit functional form to the systematics as a function of quench rate,

$$\chi'_{D,sys}(r_Q) = a \cdot \ln\left[\frac{B_c r_Q}{t_m + B_c r_Q}\right],\tag{C.4}$$

where t_m is the measurement time between $\langle f \rangle$ and $\langle l \rangle$, *a* is the same scale factor as in Eqn 5.10, and B_c is a fitting parameter describing the critical field at which relaxation starts. Least squares fitting of Eqn. C.4 to quench rate dependence of the difference susceptibility is shown in the main paper (Fig. 5.7b). Without explicit limits on the parameters *a* and B_c , the logarithmic decay due to systematic relaxation is enough to completely reproduce the data. While a KZM-like power law form can also fit the data reasonably well, we find that the logarithmic form produced from coarsening systematics better fits the observed scaling, in particular around the low quench rate regions. The can be seen for both quenches from a maximum field of 4 T (shown in the main paper) and in quenches from a maximum field of 6 T (Fig. C.5). While the best fit parameter *a* is in reasonable agreement to the fitted *a* values from the zero-field relaxation, the best fit B_c value is 0.11(7) T. This is far smaller than any transition that appears to relate to the onset of relaxation $(B_{ICAFM} = 3.7 T, B_{CAFM} = 3 T, B_f = 1.7 T)$. As a secondary check, the time associated with crossing this field is also the offset in time required to produce linear dependence of the susceptibility on a semi-log scale (Fig. 5.7b). These two analysis are thus consistently pointing to some relevance of this low field in the relaxation. We also note that constraining B_c near to be near either of the *expected* transitions, Eqn. C.4 does not accurately fit the data, and the relaxation is not linear on a semilog scale.

The meaning of this low B_c is not clear. While one would expect the form of the relaxation to change in the presence of a field, as well as across different phases, our results suggest only the *very* low field behavior is relevant to the zero field relaxation.