COOPERATIVE MAGNETIC RELAXATION IN GEOMETRICALLY FRUSTRATED RARE-EARTH PYROCHLORES

A Thesis in
Physics
by
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We report thermodynamic measurements on the cooperative paramagnet \(\text{Tb}_2\text{Ti}_2\text{O}_7\) and the stuffed spin ices \(\text{Ho}_2(\text{Ho}_x\text{Ti}_{2-x})\text{O}_{7-x/2}\) and \(\text{Dy}_2(\text{Dy}_x\text{Ti}_{2-x})\text{O}_{7-x/2}\), where \(0 \leq x \leq 0.67\). For \(\text{Tb}_2\text{Ti}_2\text{O}_7\), AC susceptibility data taken down to \(T = 1.8\) K and in applied magnetic fields up to \(H = 9\) T show the expected saturation maximum in \(\chi(T)\) and also an unexpected low frequency dependence (<1 Hz) of this peak, suggesting very slow spin relaxations are occurring. Measurements on samples diluted with nonmagnetic \(\text{Y}^{3+}\) or \(\text{Lu}^{3+}\) and complementary measurements on pure and diluted \(\text{Dy}_2\text{Ti}_2\text{O}_7\) strongly suggest that the relaxation is associated with dipolar spin correlations, representing unusual cooperative behavior in a paramagnetic system.

For the stuffed spin ices \(\text{Ho}_2(\text{Ho}_x\text{Ti}_{2-x})\text{O}_{7-x/2}\) and \(\text{Dy}_2(\text{Dy}_x\text{Ti}_{2-x})\text{O}_{7-x/2}\), \(0 \leq x \leq 0.67\), magnetization data show an increasingly antiferromagnetic effective interaction with increased stuffing \(x\), with Ising like single spin ground states. Although heat capacity measurements down to \(T = 0.4\) K yield the expected residual entropy for \(x = 0\), surprisingly, despite the changing magnetic interactions, the total entropy per spin in \((\text{Ho}_x\text{Ti}_{2-x})\text{O}_{7-x/2}\) remains at the spin ice value for all \(x\), while the entropy per spin in \(\text{Dy}_2(\text{Dy}_x\text{Ti}_{2-x})\text{O}_{7-x/2}\) approaches the Ising value of \(S = R\ln2\) for \(x \geq 0.3\). AC susceptibility measurements confirm different low temperature states in \(\text{Ho}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}\) and \(\text{Dy}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}\), showing a disordered spin freezing in \(\text{Ho}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}\), and a partial freezing in \(\text{Dy}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}\) coexisting with behavior seen in some cooperative paramagnets and spin liquids.
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Chapter 1

Introduction and Theory

1.1 An Overview of this Thesis

Magnetism is widely exploited in contemporary technologies. From simple compasses, to electrical generators, to computers, magnetism literally powers the world. The practical applications of magnetism all stem from research into the basic properties of magnetism and magnetic materials, and new research into magnetic systems continues to provide us with new technology, and, most importantly, advances our knowledge of the physical world.

This thesis reports low temperature thermodynamic experiments on two systems of geometrically frustrated magnets: the cooperative paramagnet Tb$_2$Ti$_2$O$_7$ and the stuffed spin ice Ln$_2$(Ti$_{1-x}$Ln$_x$)O$_{7-x/2}$, where Ln = Ho or Dy and x = 0 – 0.67. This first chapter gives an overview of some basic theory describing the thermodynamic properties of magnets, while chapter two discusses magnetic frustration and presents data illustrating basic features of frustrated magnetic systems. Next, chapter three describes the experimental techniques used in this work. We then move on in chapters four to recounting previous results for Tb$_2$Ti$_2$O$_7$ and present our experimental results and conclusions. Chapter five follows in a similar manner, with a discussion on the stuffed spin ices.
1.2 The Basics of Magnetism for an Experimental Physicist

Magnetic materials contain ions with magnetic moments, meaning that these ions respond to a magnetic field. This work is chiefly concerned with electronic magnetic moments created by the total angular momentum of an electron, which in general consists of both the orbital and spin angular momentum. The orbital angular momentum arises from the electron’s periodic motion around a nucleus, while spin angular momentum is an intrinsic property of electrons (and certain other particles) that can be derived from relativistic considerations. Colloquially, the total magnetic moment of a particle is referred to as its spin. Thus, magnetic materials contain spins that can interact with external magnetic fields and with other spins in the material.

Magnetic interactions fall into four basic groups: paramagnetism, diamagnetism, ferromagnetism, and antiferromagnetism. Paramagnetism is the property of an ion or material to align to an applied magnetic field, while diamagnetism is the property of an ion or a material to counteract an applied field. Ferromagnetism and antiferromagnetism refer to spins aligning either parallel or opposite to their neighboring spins, which can lead to collective behavior of the spins in the material.

Diamagnetic behavior results from Lenz’s Law, which tells us that for a current loop encircling a magnetic field, any change in the magnetic flux through the loop will create a current in the loop opposing the change in flux. Hence, the orbital motion of electrons around a nucleus causes all atoms to show some degree of diamagnetism in response to a change in any external field. Hence, even insulating materials with no open shells exhibit diamagnetism. Additionally, perhaps the best known examples of
diamagnetic behavior have been made when applying magnetic fields to superconductors, where demonstrations such as a magnet levitating over a piece of superconducting material are well known.

As stated above, paramagnets easily align their spins to an applied magnetic field. Considering a system of \(N\) free spins in an applied field, we can describe the system as a canonical ensemble with a partition function given by Equation 1.1:

\[
Z = \sum_i e^{\beta \mu_i \cdot H}, \tag{1.1}
\]

where \(\mu_i\) is the magnetic moment of ion \(i\), and \(\beta\) is the Boltzmann constant \(k_B\) times the system’s temperature \(T\) \([1][2]\). We define the magnetic moment in the \(j\) direction in Equation 1.2:

\[
\mu_j = g_{jk} S_k \mu_B. \tag{1.2}
\]

Here, \(g_{jk}\) is the Landé g-factor (or spectroscopic splitting factor), \(S_k\) is the total angular momentum of a single ion, \(\mu_B\) is the Bohr magneton, and \(j\) and \(k\) represent spatial directions \([3]\). Equation 1.2 uses the Einstein summation convention, meaning that we must take the sum over the repeated index \(k\).

From the partition function in Equation 1.1, we can derive the thermal averages of all the macroscopic properties of the spin system. For example, we can find the average magnetization \(M\) of the system by taking the derivative of the natural logarithm of the partition function with respect to the field and dividing by \(-\beta\). With proper normalization, this yields the average component of \(M\) along \(H\), which is proportional to the Brillouin function as shown in Equation 1.3:
For small fields \((H \ll T)\), we can expand \(M\) as a power series in \(H\), yielding Curie’s Law, Equation 1.4:

\[
M = N\mu_B gS \left[ \frac{2S+1}{2S} \coth \left( \frac{2S+1}{2S} \mu_B gSH\beta \right) - \frac{1}{2S} \coth \left( \frac{1}{2S} \mu_B gSH\beta \right) \right]. \tag{1.3}
\]

This law predicts a \(T^{-1}\) dependence of the susceptibility at high \(T\) and small \(H\), which has been confirmed experimentally. Also, one can define the effect moment by Equation 1.5:

\[
\chi = \frac{M}{H} = \frac{N\mu_B^2 g^2 S(S+1)}{3k_B T}. \tag{1.4}
\]

and determine the value from simple fits to experimental data. The effective moment is important in determining whether or not spins will act as free spins or whether some correlation between spins is occurring. It also gives clues about the effect of the crystalline electric field on the spins, since the crystal field should partially lift the degeneracy of the angular momentum multiplet of each spin. Thus, the correct value used for \(S\) must correspond to the total angular momentum of the crystal field level an electron is in at a given temperature. In the case of some transition metals, the crystal field is strong enough to quench the orbital angular momentum, meaning that only the spin angular momentum will be the valid quantity to use in Equation 1.5 when analyzing experimental results.
1.3 Magnetic Ordering

Magnetic ordering due to spin-spin interactions occurs when the interactions are strong enough to dominate the other energies present in the system. As stated above, ferromagnetic or antiferromagnetic interactions can exist between neighboring spins. Ferromagnetic interactions occur when the lowest interaction energy between the spins occurs when they align parallel to each other, while antiferromagnetic interactions occur when the spins obtain their lowest interaction energy by pointing opposite to each other.

Magnetic interactions between spins are primarily due to the magnetic dipole field set up by each spin and quantum mechanical exchange, with exchange typically being the more predominant of the two. The dipole energy simply comes from treating a spin as a magnetic dipole, yielding an energy decreasing with distance as $r^{-3}$ that depends greatly on the magnitude of the spin. While the exchange interactions result from quantum mechanical considerations of the indistinguishable nature of electrons. In other words, if one considers two H atoms brought close enough together, the electronic wave functions of each atom will mix, making it impossible to assign a specific electron to a specific nucleus. In general, the exchange of electrons between two nuclei will bond atoms together. However, the electrons must follow the Pauli Exclusion Principle, and their atomic states are also subject to the Stark splitting of the crystalline electric field. These restrictions on the exchange of electrons between ions can give rise to magnetic ordering.

Since exchange interactions are due to orbital mixing, they are generally short range, but in most cases, they are stronger and more influential than any dipolar spin-spin interactions present. In addition, the exchange interaction does not need to be direct,
meaning that a nonmagnetic intermediate ion can exist between two magnetic ions and
share electrons with both. This situation is termed superexchange. Other types of
exchange interactions exist, and the interested reader can find their descriptions in a solid
state or magnetism textbook [3][4][5][6].

Even though exchange involves the overlap of electronic wave functions, we can
often write the exchange Hamiltonian for spin i quite simply as Equation 1.6:

\[
H_i = -2\sum_j J_{ij} S_i \cdot S_j ,
\]

(1.6)

where \( J_{ij} \) is the exchange constant representing the exchange interaction between spin i
and spin j. The negative sign implies that if \( J_{ij} \) is positive, the lowest interaction energy
between the spins is ferromagnetic. Similarly, if the exchange constant is negative, then
antiferromagnetic interactions exist.

Since the summation in Equation 1.6 is over all the spins in the material, we
cannot exactly solve for the exchange energy. However, we can reasonably approximate
the energy with the mean field approximation, in which we truncate the sum over j to
being a sum only over the first nearest neighbors to spin i. This method interprets the
interactions on spin i by its j nearest neighbors as an effective magnetic field on spin i.
Surprisingly, this rather gross approximation sometimes yields results that agree rather
well with experimental data. In fact, adding the mean field energy into Equation 1.1,
determining the magnetization, and expanding as before yeilds Equation 1.7:

\[
\chi = \frac{N\mu_B^2 g^2 S(S+1)}{3k_B(T - \theta_M)},
\]

(1.7)
which is the Curie-Weiss Law. The Weiss Temperature $\theta_W$ estimates the temperature at which a magnetic transition will occur, and equals Equation 1.8:

$$\theta_W = \frac{2zJS(S+1)}{3k_B}.$$  \hfill (1.8)

Here, $J$ is the effective magnetic interaction with one nearest neighbor, and $z$ is the coordination number, or rather the number of nearest neighbors per spin.

We again emphasize that the mean field theory is a gross approximation and does not absolutely predict the transition temperature. However, the Weiss Temperature usually is very good at predicting whether the average magnetic interactions are ferromagnetic or antiferromagnetic. Moreover, quick experimental determination of $\theta_W$ is possible from high temperature, low field magnetization measurements by plotting the inverse magnetic susceptibility versus $T$ and performing a linear fit. Figure 1.1 shows a
A cartoon illustrating the determination of $\theta_w$ from the x-intercept of the fit. Note, that the slope of the linear fit also allows determination of the effective moment per spin.

1.4 Spin Relaxation and the Time Scale of the Measurements

A spin relaxes when it aligns with an external field due to the torque created by the interaction between the spin and field. For a thermodynamical system of $N$ identical, non-interacting (or very weakly interacting) spins, the response of the magnetization of the system to a static (DC) magnetic field is Equation 1.9:

$$\hbar \frac{dM}{dt} = -g\mu_B S \times H.$$  \hfill (1.9)

If the direction of the field is taken as the $z-$direction, then the equilibrium magnetization $M_0$ will also be in the $z-$direction. However, if we apply an additional field along the $z-$direction that is strong enough to create a different macroscopic state, then once we remove this additional field, the system must relax back to its original equilibrium, which will require some finite length of time. If we apply the additional field periodically at a frequency corresponding to a length of time quicker than the relaxation time of the spin system, then the spins will remain in a non-equilibrium state. Measurements made on the system at the same frequency as the perturbing field will then yield a magnetization less than $M_0$. Quantitatively, adding a small sinusoidal perturbing field $H_1$ to Equation 1.9 results in the well known Bloch equations [7]. For the case above, the Bloch equations reduce to Equation 1.10:

$$\hbar \frac{dm_z}{dt} = g\mu_B (M \times H)_z + \frac{Z_0 H_1 \cos \omega t - m_z}{T_1},$$ \hfill (1.10)
where $\chi_0$ is the static susceptibility, $\omega$ is the frequency of the perturbing field, $T_1$ is the longitudinal relaxation time of the system, and $m_z$ is the component of the magnetization in the $z$–direction [3]. Note that Equation 1.10 is actually an approximation, since only the static susceptibility is present.

By its derivation, the Curie-Weiss Law deals with spins in thermal equilibrium, or in other words, it tells us the static or DC susceptibility $\chi_{DC}$ of a material. The law is valid when $\chi_{DC}$ equals the isothermal susceptibility $\chi_T$, which is the susceptibility when the spins and, for our purposes, the lattice in which they are imbedded are at the same temperature. If we assume that the spins and the lattice are two separate thermodynamical systems able to transfer energy between each other by spin-phonon coupling, than an adiabatic susceptibility $\chi_S$ can be defined as the susceptibility when no heat is exchanged between the spin and lattice systems. The importance in the difference between these two limiting susceptibilities and how spin freezing is defined becomes apparent once the time over which a measurement becomes comparable to the relaxation time of the spin system. One way we can realize such a measurement is by performing AC susceptibility experiments, in which we apply to the material a small field with a sinusoidally varying magnitude with time in addition to any other external field. The dynamics of this technique are discussed above and are governed by Equation 1.10 if the measurement is performed with longitudinal fields. AC susceptibility experiments are usually carried out over a relatively low frequency range from $0.01 \text{ Hz} < f < 10,000 \text{ Hz}$. Higher frequency ranges can be investigated using techniques such as electron paramagnetic resonance EPR [8], muon spin resonance $\mu$SR [9], or neutron scattering[10]. We emphasize again that in all these dynamic experiments, we effectively
make measurements at the same frequency as the perturbing probe. Therefore, we are able to see non-equilibrium dynamics and must recognize whether the spins are completely freezing, or if they are just relaxing fast too slowly to be observed by the experiment.

We can make a quantitative interpretation of the difference between the isothermal and adiabatic susceptibilities by using the Casimir - du Pré relations \([11]\) given in Equations 1.11 and 1.12:

\[
\begin{align*}
\chi' &= \chi_S + \frac{\chi_T - \chi_S}{1 + \omega^2 \tau_1^2}, \\
\chi'' &= \frac{(\chi_T - \chi_S)\omega \tau_1}{1 + \omega^2 \tau_1^2}.
\end{align*}
\]

These equations consider \(\chi\) to be a complex quantity, with a real part \(\chi'\) that is in phase with an external field oscillating of angular frequency \(\omega\), and an imaginary part \(\chi''\) that is \(90^\circ\) out of phase with the field. The spin lattice relaxation time is given by \(\tau_1\). It should be pointed out that these relations assume that the time rate of change of heat flowing from the spin system to the lattice is directly proportional to the difference in temperatures of the spin and lattice systems. In addition, one could derive these two equations from Equation 1.10, where it will than be obvious that \(T_1\) is the same as the spin – lattice relaxation time \(\tau_1\). Figure 1.2 gives a graphical representation of the relations and shows the phasor representation of \(\chi\). Note that \(\chi''\) is much smaller than \(\chi'\) and peaks as \(\chi'\) rapidly decreases. In addition, to the Casimir - du Pré relations, the components of \(\chi\) must also follow the Kramers - Kronig relations \([12][13]\).

The assumption that the lattice and spins are two separate thermodynamic systems is valid when there are large differences in time scales between spin - spin and spin -
lattice relaxation. This is typically the case at low temperatures, where the spin-spin relaxation time can be many orders of magnitude higher than the spin-lattice relaxation time. The large difference in the relaxation times relates to the density of states of each system and to the amount that their energies overlap. Additionally, the lattice only directly affects the orbital angular momentum, since the spin angular momentum exists in a different space, and the spin angular momentum only interacts with the lattice through the spin–orbit coupling. Thus, the spin angular momentum is usually well separated from the lattice phonons, allowing spin-spin relaxation to occur independent of any spin–lattice relaxation [14].

Figure 1.2: The real and imaginary parts of the complex susceptibility versus the frequency of the applied field. The isothermal and adiabatic susceptibilities occur at the lowest and the highest frequencies, respectively. The phasor representation of the complex susceptibility is also shown. The angle $\phi$ is the phase difference between the excitation field and the magnetic response of the sample.
Turning again to the Casimir – du Pré relations, we see that their theory assumes that heat transfer occurs between the spin and lattice systems, however no details are given about the mechanisms behind any heat transfer. From the discussion above, it is obvious that spin – spin relaxation occurs due to the exchange and the dipolar interactions between spins. However, spin – lattice relaxation must involve coupling of the electronic angular momentum to phonons. The way that this spin – phonon coupling occurs is by a periodic modulation of the electronic orbits due to the phonons dynamically changing the crystal field environment of the magnetic ions. The energy changes from the modulation of the crystal field then project on to the total angular momentum by the spin - orbit coupling, allowing the spin system to relax to the lattice. The three most common processes used to describe spin – lattice relaxations are the direct, Orbach, and Raman processes, and are illustrated in Figure 1.3. The direct process simply consists of the creation of a single phonon by a single spin – lattice relaxation. Hence, the phonon must have exactly the same energy as the difference in energy between two of the spin’s states. The Orbach process is a two stage process in which a phonon with the same magnitude as
the energy of the first excited crystal field state is absorbed by the spin. The spin’s transition rules then permit it to relax to a state lower in energy than its initial state by emitting a phonon different from the initial one absorbed. The Raman process consists of a spin absorbing a phonon such that it enters a virtual intermediate energy state. The spin then spontaneously decays and emits a phonon.

Though the discussion above is brief, we do have enough information about the different relaxation processes to predict the temperatures at which each process will dominate. For example, since the Raman process has no restriction on the energy of the incoming phonon, the entire phonon spectrum is available to it. Thus, the Raman process should dominate at high temperatures. On the other hand, the direct and Orbach processes can only utilize phonons with energies located in narrow bands, allowing a somewhat more accurate prediction of the temperatures at which each process should dominate. For example, because the direct process involves phonons with the lowest energy, it should be prevalent only at the lowest temperatures. Likewise, since the Orbach process needs phonons capable of exciting spins into their first excited states, the process should be most prevalent at temperatures corresponding to the energy of the crystal field splitting. For any further detailed derivations and analyses of the different spin – lattice relaxation processes the interested reader is referred to a comprehensive review of the subject by Stevens [14].
Chapter 2
Frustrated Systems

2.1 Magnetic Frustration

Common sense suggests that every physical system should be capable of finding some single ground energy state - a macroscopic state with the lowest overall energy. The Third Law of Thermodynamics quantifies this supposition by requiring that the entropy of a system go to zero as the temperature approaches zero \[1\][2]. In a classical sense, this means that once there is not enough heat, or other energy, present in a closed thermodynamic system to excite its constituents out of their individual ground energy states, a single macroscopic ground state for the entire system should form. However, observations show that some thermodynamical systems apparently have several macroscopic states possessing its expected ground state energy. Such systems are said to have multiple degenerate macroscopic ground states, meaning that even at \( T = 0 \) it is possible for the system to switch between different states. If the degenerate ground states arise from an inability to simultaneously minimize all interactions between the particles in the system, then the system can be classified as being frustrated.

This dissertation concerns Geometrically Frustrated Magnets (GFM), which are magnetic systems unable to reach a single ground energy state, due to the relative locations of their magnetic moments on a regular crystal lattice \[16][17][18][19\]. In other words, the frustration arises from an incompatibility between the geometry of the
spin arrangement and the local spin-spin interactions, resulting in the formation of many
degenerate macroscopic ground states. It is important to note that other types of
magnetic frustration occur. For example, a class of materials called spin glass exists,
which also contain frustrated magnetic interactions. Since studies on spin glasses under
the context of frustration started long before studies on many now recognized GFM, it is
valuable to compare experimental results on GFM to results on spin glasses.

2.2 Spin Glasses

Spin glasses must contain two basic properties: disorder (or randomness) and
frustration. Disorder refers to spins not being located at distinct positions on a lattice
(structural disorder), or it can mean that the magnetic interactions between spins are not
all the same and do not occur in a regular, periodic fashion (bond disorder). Figure 2.1
contains two cartoons illustrating the differences between bond and structural disorder in
a spin glass. The disorder in the magnet then causes frustration, meaning that frustration
alone is not enough to create a spin glass. More examples of disorder and frustration in
spin glasses can be found in Mydosh’s comprehensive text on spin glasses [20].
We can view the energy topology of a spin glass as numerous local energy minima separated by many different large energy barriers, which impede relaxation between the different minima. Thus, the barriers obstruct the formation of a macroscopic ground state, resulting in a number of nearly energy equivalent macroscopic ground states. As a result, a spin glass exists in a metastable state, since its constituents seemingly can not overcome the large energy barriers and form a global ground state. In actuality, the many large energy barriers cause the spin glass to relax into lower energy states over extremely long time scales (>>100 s) and with a large distribution of relaxation times. For comparison, a typical ferromagnet in a conventional long range ordered state without different magnetic domains would relax into its ground state with a much narrower distribution of relaxation times.

Despite their slow spin relaxation, spin glasses have a number of magnetic experimental signatures. However, they share many of these signatures with other magnetic systems, meaning that experiments showing evidence for glassiness do not
necessarily indicate that the measured material is a spin glass. It is therefore important to perform a variety of experiments on a material with glassy properties before labeling it as a spin glass, especially if the material’s structure is well ordered. As will be discussed further below, a number of similarities exist between experimental data for spin glasses and geometrically frustrated magnets. As such, we next discuss some experiments valid for both types of systems. The discussion below will mainly focus on results for spin glasses, and we will reserve comparison of these results to data taken on geometrically frustrated magnets for the next section.

Perhaps the hallmark experiment to perform on a spin glass, is to make two measurements of the magnetization $M$ as a function of temperature at very low fields ($H \sim 0.01$ T) - first after initially cooling the material in zero applied magnetic field (ZFC) and then after initially cooling the sample in the measurement field (FC). Since the spin glass exists in a metastable state, we will see a bifurcation in the resulting $M(T)$ data at the glass temperature created by the different initial states of the ZFC and FC measurements. Figure 2.2 shows an example of this phenomenon. The ZFC magnetization curves have a lower magnitude below the glass temperature due to both the self averaging of the spins while cooling and the slow relaxation times of the spins after applying field. In fact, if we perform a ZFC magnetization experiment on a spin glass by measuring $M$ as a function of time at a temperature below the glass transition, then once we apply the field $M$ will slowly change from $M = 0$ to the value that would have been obtained if we had used the FC procedure. The time over which this will happen, though, can be paraphrased from Mydosh’s book as being, “[greater than] the average lifetime of a graduate student [which] is only about $10^8$ s [20].”
AC magnetic susceptibility experiments also lend great insight in determining if a material is a spin glass. Since we can make these measurements at various frequencies, we can probe the distribution of spin relaxation times in a spin glass. For example, \( \chi(T) \) will peak around the glass transition, however, the actual temperature where this peak occurs greatly depends on the frequency of the measurement and shifts to higher temperatures with increasing frequency. Additionally, the imaginary component of the susceptibility peaks around the same temperature, indicating that the spins are decoupling from the lattice due to the time scales of the spin-lattice relaxation processes.

Figure 2.2: Magnetization versus temperature curves at \( H = 5.9 \) Oe from experiments on the spin glass \( CuMn \). The percentages in the figure represent the atomic percentage of Mn relative to copper in the alloy. Curves (a) and (c) are from data taken after cooling in the applied magnetic field (FC), while curves (b) and (d) are from measurements made after cooling the material with no applied field (ZFC). This figure is reproduced from Reference [21]. (Copyright 1979 by the American Physical Society.)
This indicates that the spins are absorbing energy from the oscillating field. Figure 2.3 shows AC susceptibility data on the spin glass Eu$_{0.2}$Sr$_{0.8}$S taken at H = 0 and H$_{AC}$ ≈ 0.1 Oe. Different symbols represent different measurement frequencies, as described in the figure caption. Although not shown in this figure, application of even a static magnetic field as small as H ~ 0.01 T can be sufficient to disturb the spin glass state. In AC susceptibility measurements, the peak in χ′(T) will decrease in magnitude and broaden in temperature as the field is increased. Also, the temperature of the maximum will
decrease in accordance with either the de Almeida-Thouless line (for an Ising spin glass in a field) or the Gabay-Toulouse line (for transverse spin freezing with weak irreversibility in a non-Ising spin glass) [20][23][24]. The fact that such a small external field can affect the spin glass is surprising, since the effective temperature of the applied field is often orders of magnitude smaller than the glass temperature.

2.3 Geometrically Frustrated Magnets

This dissertation is chiefly concerned with Geometrically Frustrated Magnets (GFM), in which the regular arrangement of the spins on a crystal lattice creates frustration. Figure 2.4 shows a simple gedankenexperiment illustrating geometrical frustration. We perform the experiment by imagining an equilateral triangle with Ising spins located at its vertices. The spins are constrained to the plane of the page and allowed to point either up or down. If we now turn on effective ferromagnetic (FM) interactions between the spins, we see that all three spins can simultaneously minimize their bipartite interactions by pointing in the same direction. However, if we turn on antiferromagnetic (AFM) interactions between the spins, then only two of the three interactions can be simultaneously satisfied, resulting in frustration. For the AFM Ising triangle, there are six different spin configurations with the lowest energies, meaning that there are six global ground states, as compared to the two global ground states in the ferromagnetic triangle. Thus, if this situation is repeated an infinite number of times, the spins will form a lattice of side sharing triangles with antiferromagnetic nearest neighbor interactions, and there will be no single well defined macroscopic ground state.
It is important to note that Ising spins are not necessary for a geometrically frustrated system. In fact, a large degree of frustration exits on the pyrochlore lattice when 3-D AFM Heisenberg spins are located at the corners of corner sharing tetrahedra. Figure 2.5 shows various geometrically frustrated magnetic lattices. The triangle and kagome lattices are two dimensional, while the face-centered cubic, pyrochlore, and garnet lattices are three dimensional. It is interesting, but not surprising, that all of these lattices contain triangular arrangements of spins: the triangular lattice consisting of side sharing triangles, the garnet and kagome lattices consisting of corner sharing triangles, and the FCC lattice consisting of side sharing tetrahedra. The pyrochlore lattice is comprised of spins forming corner sharing tetrahedra, and materials with its structure are the focus of this thesis.

The many degenerate ground states available to a frustrated magnet can create a situation in which the spins are free to fluctuate, at temperatures well below the equivalent temperature of their nearest-neighbor interactions. This means that like spin
glasses, magnetization versus temperature measurements are key to the initial characterization of the material. Specifically, if we fit low field \((H < 0.1 \, \text{T})\), high temperature \((T \sim 10^2 \, \text{K})\) \(M(T)\) measurements on a GFM to the Curie-Weiss law (Equation 1.7) and determine the value of the Weiss temperature \(\theta_w\) (Equation 1.8), we will see that \(M(T)\) follows the Curie-Weiss law down to temperatures well below \(\theta_w\). Figure 2.6 shows an example of a Curie-Weiss fit on unpublished \(\chi^{-1}(T)\) data for the GFM Ba\(_2\)Sn\(_2\)ZnGa\(_4\)Cr\(_6\)O\(_{22}\) (published data for this material can be found in References [25] and [26]). The line represents a linear fit to the data at \(T > 100 \, \text{K}\), and the Weiss temperature and effective moment (Equation 1.5) obtained from the fit are indicated.

Figure 2.5: Examples of various possible geometrically frustrated magnetic lattices, labeled with their corresponding three dimensional space groups. The two drawings at the top illustrate two dimensional frustrating lattice geometries, while the bottom drawings depict three dimensional frustrated lattice geometries. This figure is reproduced from Reference [15]. (Copyright 1996 by Gordon & Breach.)
Clearly, this material follows the Curie-Weiss law well below the determined magnitude of its Weiss temperature of $|\theta_W| = 251.9$ K.

Geometrically frustrated magnets are also widely studied using AC susceptibility experiments, since the frustration can yield rather slow spin relaxation times. However, it is not prudent to generalize about the features observed in these experiments, since GFM can show a wide range of features in $\chi$. It is relatively safe to say, however, that evidence for short range spin correlations appears in measurements on many different GFM, and it is not uncommon to see frequency dependent peaks in $\chi(T)$ similar to those seen in spin glasses (although the response of the peaks to an external magnetic field can be quite different). Heat capacity data taken on GFM also often show peaks corresponding to

Figure 2.6: Unpublished magnetization data showing inverse DC susceptibility versus temperature of the geometrically frustrated magnet $\text{Ba}_2\text{Sn}_2\text{ZnGa}_4\text{Cr}_6\text{O}_{22}$, at $H = 50$ Oe. The line shows a linear fit to the high temperature data, which yielded the values for $\theta_W$ and $p$ in the Curie-Weiss law. $\text{Ba}_2\text{Sn}_2\text{ZnGa}_4\text{Cr}_6\text{O}_{22}$ is a Q-S ferrite, in which the magnetic Cr ions form kagome layers.
short range spin correlations. Some example AC susceptibility and specific heat data can be found in References [27][28][29][30][31][32].

We also should not overlook that much work exists examining faster spin relaxations in geometrically frustrated magnets. Specifically, neutron scattering and muon spin resonance experiments can tell a great deal about the local correlations between spins and the nature of any magnetic ordering that may be present.
3.1 Introduction

Various experiments were used to determine the magnetic properties of the materials studied for this dissertation. This chapter gives descriptions of these measurement techniques, which included magnetization, AC magnetic susceptibility, and heat capacity experiments. We performed all of these experiments in commercially available equipment manufactured by Quantum Design, Inc. [33], and, additionally, we performed AC susceptibility experiments down to $T = 60 \text{ mK}$ using a custom made instrument thermally anchored to the mixing chamber of a He$^3$/He$^4$ dilution refrigerator.

3.2 Magnetization

As previously discussed, the bulk magnetic response of a material a long time after changing external parameters to the system (i.e. magnetic field, temperature, pressure...) is the static (DC) magnetization $M$ of the material. For this work, we performed magnetization measurements using a Quantum Design, Inc., Magnetic Property Measurement System (MPMS). The system’s main components consist of an insulated liquid He dewar, a long cylindrical insert (probe), a control cabinet, a rotary vane vacuum pump, and a desktop computer. The probe contains the sample chamber, impedance, cooling valves, electrical heaters, and measurement circuits. It sits at the
center of the dewar, submerged in liquid He, and a superconducting magnet surrounding
the sample chamber can apply persistent fields up to \( H = 7 \) T with a uniformity of 0.01% 
over the length the measurement. Control of the sample chamber temperature is made by
regulating the flow of liquid/gaseous He into the cooling annulus using automated valves
and electrical heaters. In this way, the temperature of the sample chamber can be
precisely varied between \( T = 1.8 \) K – 400 K at rates from \( 10^{-3} \) – \( 10^{1} \) K / s and kept stable
within ± 0.5%. The sample chamber is kept in vacuum (~ 0.001 Torr), and samples are
inserted into it through an airlock that can be purged with He from the bath.

We generally will mount a sample in a clear plastic drinking straw inside of a
gelatin capsule. Since most of the materials measured were powders, the small magnetic
susceptibility of the gelatin capsule provided a convenient means to contain the sample.
The powder did not fill the volume of the capsule, so cotton was packed on top of the
powder to keep it at the bottom of the capsule. We then position the gelatin capsule at
the center of the straw and tie it into place with clear Nylon thread. Since we measured
materials containing large spins, the magnetic background from the straw, thread, cotton,
and capsule was at most two orders of magnitude smaller than the measured moment of
the sample, the background due to the sample mounting technique could be safely
neglected.

We would then take the straw and connect its top to the end of a long thin rod
using a combination of Kapton and masking tapes. The rod consisted of two pieces, a top
piece made from thin walled stainless steel tubing, and a smaller length of non-magnetic
thin walled brass tubing. (The straw was attached to the brass section of the rod.) When
inserted into the sample chamber, the top of the rod was anchored to a stepper motor that
moved the rod vertically. A light coat of vacuum grease on the rod and a sliding seal at the top of the airlock allow vertical movement of the rod while keeping the sample chamber under vacuum.

To perform magnetization measurements, the MPMS uses a superconducting quantum interference device SQUID inductively coupled to a tank circuit. A measurement is made by smoothly pulling a small sample (<0.1 cm³) through four loops of wire, while a DC magnetic field is applied. The wire loops are configured to form a ≈ 3 cm long second order gradiometer, meaning that the top and bottom loops are wound in one direction, while the two middle loops are wound in the opposite direction (i.e. if the top and bottom loops are wound clockwise, then the two middle loops would be wound counter-clockwise). The coil set is designed to reject the uniform field created by the magnet to within 0.1%, making the detector insensitive to any drift in the magnetic field. A schematic of the pickup loops is shown in Figure 3.1. By Faraday’s Law, the change in magnetic flux created by pulling the magnetic sample through the wire loops will induce a voltage in the loops as in Equation 3.1:

\[ E = -\frac{d\phi_m}{dt}. \]  

Here, \( E \) is the induced electric motive force (EMF), \( \phi_m \) is the magnetic flux, \( t \) is time, and the negative sign is due to Lenz’s Law. The EMF causes an electric potential, so \( E \) has units of Volts.

The EMF induced by the sample’s magnetic moment creates a current that is then inductively coupled through a transformer to the SQUID circuit. The current induced by the sample changes the magnetic flux in the SQUID circuit, and a feedback circuit then
acts to counteract the change of flux by producing an opposing magnetic field. The current the feedback circuit creates is fed across a resistor, and the voltage across the resistor is recorded, providing an accurate measurement of the sample’s magnetic moment. This procedure allows the instrument to determine changes as small as $10^{-7}$ emu (1 emu = 1 electromagnetic unit = 1 erg/G) of the moment in the sample chamber as the sample rod is extracted. 

Figure 3.1: A schematic of the pickup coils in a Quantum Design, Inc. Magnetic Property Measurement System. The superconducting coils are arranged in a second order gradiometer configuration, meaning that the outer two coils are wound in one direction and the inner two coils are wound in the opposite direction. The sample is attached to a rod that is pulled through the coils by a motor located at the top of the cryostat. The illustration is of longitudinal pickup coils, which means that the magnetic moment is measured along the direction of the magnetic field.
3.3 AC Magnetic Susceptibility down to \( T = 1.8 \) K

The susceptibility \( \chi \) of a sample to a magnetic field is determined by many factors including temperature, frequency, and magnitude of the applied field. One method of measuring a sample’s AC susceptibility is by applying a small oscillating magnetic field \( H_{ac} \) to the sample, effectively measuring the slope of \( M(H) \), i.e. Equation 3.2:

\[
\chi_{ac} = \frac{\partial M}{\partial H} , \tag{3.2}
\]

where \( H \) is any static magnetic field that may be present. If we place the samples inside of a coil of wire (i.e. a solenoid), the small oscillating magnetic field will change the sample’s magnetization, changing the magnetic flux enclosed by the coil. Thus, we again can use Faraday’s Law (Equation 3.1) to determine the susceptibility. However, in contrast to the MPMS, the machine does not use a SQUID circuit. Instead, the electrical potential across each coil is directly read by a voltmeter that locks in at the frequency of \( H_{ac} \). The voltage signal is then transformed via Faraday’s Law into a measurement of the samples magnetic moment.

To perform these experiments, a Quantum Design, Inc., Physical Property Measurement System (PPMS) with the AC Magnetic Susceptibility option (ACMS) installed was used to measure \( \chi \) between \( T = 1.8 - 350 \) K, in static magnetic fields up to \( H = 9 \) T. Temperature control and changes to the magnetic field were performed using methods analogous to those used with the MPMS.

The main components of the PPMS are similar to those of the MPMS, although the PPMS can accommodate a broader range of experiments. This is accomplished through use of a plug at the bottom of the sample chamber that offers twelve electrical
connections to the top of the instrument. A sample can then be either mounted on a ≈ 2.5 cm diameter brass puck, which plugs into the bottom of the sample chamber, or mounted to a PPMS option that plugs into the bottom of the sample chamber.

The ACMS option has a PPMS insert that plugs into the bottom of the sample chamber, containing five concentric coils. A schematic of the instrument is shown in Figure 3.2. One of the coils, called the primary, applies the oscillating field, while two other coils, called the secondaries, measure the response. The remaining two coils are proprietary to the ACMS, and are used to record and subtract out any spurious magnetic signals induced in the PPMS sample chamber. They are located between the two secondary coils. We prepared a sample for measurement by securing it in a plastic drinking straw via the same method as for the MPMS, and then attached the straw to a non-magnetic plastic rod. The rod connected to a drive motor on top of the PPMS
sample chamber, which moved the sample vertically between the centers of the two secondaries. The oscillating field $H_{ac}$ was then applied once the sample reached the proper position. During a measurement, the sample was also centered between all 4 pickup coils, and $H_{ac}$ was applied to measure any background signal. A computer then used an algorithm to combine the different measurements, subtract out any background signals, and convert the remaining voltage into a measurement of the sample’s moment due to $H_{ac}$. The ACMS measured the response voltage in phase and $90^\circ$ out of phase, independently detecting the real and imaginary parts, $\chi'$ and $\chi''$, of $\chi$.

Although, the determination of the dynamic susceptibility by these means may seem complex, the system is a simple mutual inductance bridge using a lock-in amplifier to read the voltage across the bridge. The main reason for the lengthy procedure used by the ACMS is to make an accurate measurement, and indeed the ACMS can measure a moment in the $10^{-7}$ emu range. In Section 3.5, we will discuss AC susceptibility experiments performed on a dilution refrigerator. The instrument used in this case consists of a mutual inductance bridge with the sample fixed inside one of the secondary coils. $\chi$ is then determined more directly than in the ACMS.

### 3.4 Heat Capacity

To measure the heat capacity of samples to temperature below $T = 0.4$ K, we employed the Heat Capacity Option for a Quantum Design, Inc., PPMS in conjunction with the Quantum Design, Inc., He$^3$ insert. The He$^3$ insert is a closed cycle He$^3$ refrigerator, utilizing a turbo pump along with a backing diaphragm pump to circulate
He$^3$. In order to get to temperatures below $T = 1.8$ K, we thermally isolated the sample from the sample chamber by evacuating the chamber down to $10^{-6}$ Torr using a turbo pump. Additionally, no direct physical link exists between the sample and the sample chamber while the sample is mounted to the insert.

The Heat Capacity Option uses a semi-adiabatic heat pulse technique to determine the heat capacity with an accuracy of $< 5 \%$, and a resolution of $10^{-8}$ J/K at $T = 2$ K. The sample platform consists of a thin 3×3 mm square sheet manufactured out of either epoxy or sapphire, and is suspended by thin wires attached to its corners. The wires supplied power to a heater, and allowed the resistance of a resistor fixed to the underside of the platform to be monitored. A schematic of the sample platform is shown in Figure 3.3. To make a measurement, the heater added heat to the sample, while the resistor was used to track the sample’s temperature. The evacuation of the sample chamber via a turbo pump allowed the wires attached to the platform to be the dominant pathways for heat transportation between the sample and the He$^3$ insert. Since we precisely knew the thermal conductivity of the wires, the time it took for the sample’s temperature to relax back to its initial value after being heated can be measured and used to derive the heat capacity. Normalizing by the number of mols then yields the molar specific heat $c$ in Equation 3.3:

$$c = \frac{1}{n} \frac{dQ}{dT}. \quad (3.3)$$
We measured both single crystal samples and powder samples, with the powder samples being pressed into a hard pellet prior to measurement, and when using the He\textsuperscript{3} insert, a magnetic field along the plane of the sample could be applied by the superconducting magnet of the PPMS. A sample would be attached to the sample platform with a small amount of Apeizon N grease, with the heat capacity of the grease and the platform having been previously determined during an addenda measurement.

Since we used a thermal relaxation technique, it was important to make sure that the sample thermally relaxes to the sample platform much quicker than the platform relaxes across the wires to the He\textsuperscript{3} insert. To that end, the surface area of the sample

Figure 3.3: A schematic of the sample puck used with the Heat Capacity option of a Quantum Design, Inc., PPMS. The left side of the figure shows a top view of the sample platform. The four wires are soldered on the bottom of the platform to a heater and a resistor (shown as dashed lines). The right side shows a side view of the platform, meant to illustrate that it is suspended by the wires over a hole going straight through the sample puck. (Some artistic license has been taken in the drawing of these schematics.)
touching the platform had to be as large as possible. Also, the sample had to be very thin, in order to minimize thermal gradients within the sample. For powder samples, we thoroughly mixed Ag powder with the sample prior to pressing it into a pellet. The Ag helped to bind the pellet together and facilitated thermal relaxation between the crystals in the powder. Since the heat capacity of Ag is well known, we were able to subtract it out from the total heat capacity as if it were another addendum.

3.5 AC Susceptibility Experiments Performed on a Dilution Refrigerator

3.5.1 The AC Susceptibility Instrument

We measured the dynamic susceptibility down to $T = 60$ mK using a custom mutual inductance bridge mounted in a LHe sample can anchored to the bottom of a He$^3$/He$^4$ dilution refrigerator, and a static field up to $H = 9.5$ T was applied to the sample using a superconducting magnet situated in the dilution refrigerator’s LHe dewar. (The LHe sample can is discussed in more detail below.) The mutual inductance bridge consists of a superconducting primary coil enclosing two identical secondary coils. The primary coil applied an alternating magnetic field along the secondary coils using a sinusoidal AC current supplied by a circuit driven with a function generator. The secondary coils were connected in series, such that the direction of their windings was opposite to each other. Ideally, in the absence of a sample the voltage read across the connected secondary coils will be zero, since any magnetic field applied to both coils creates the same EMF in each coil, but with opposing polarities. The sample was fixed in
one of the secondary coils, ideally making any voltage read across the secondary coils be due to the magnetic response of the sample to the field of the primary coil.

The coils were wound using a DC electric motor connected to a standard drill chuck. The speed of the motor was controlled with a rheostat placed between the motor and its power supply, and a mechanical counter attached to the output shaft tracked the number of revolutions. Wire was pulled across a table from spools that could freely rotate parallel to the table. The wire was threaded through a 3/8 inch stainless steel nut, and then through a small hole drilled in a thin Teflon sheet. The Teflon sheet was held vertical with a vise. The nut’s weight provided tension for the wire, and a large hole was cut in the center of the table to allow any excess wire to hang. From the Teflon, the wire was fed on to the coil form while being watched under a microscope. A blunt wooden stick was used to guide the wire into forming smooth, tightly packed coils. The coils were started by securing the free end of the wire to the chuck and making approximately ten turns of wire by hand positioned outside of the length of the coil.

The secondaries were wound on a cylindrical Mylar form created by coating a thin 1.5 – 2 inch long sheet of Mylar with Stycast 1266 and then wrapping it around a 0.0125 inch diameter, 1.5 inch long Teflon mandrel. Great care was required to wrap only two to three layers of Mylar around the Teflon in order to achieve a smooth surface free of air bubbles. Additionally, after the Stycast dried, the remaining edge across the form had to be carefully trimmed away. Once the form was ready, 0.5 inch diameter Teflon end caps were installed, and the wire secured to the mandrel as described above. The winding of the coil could then begin. After laying the first layer of wire, a thin coat of Stycast 1266 was applied to the coil and allowed to dry. It was extremely important
that the first layer was as flawless as possible, and that only the wire that had already
been laid down was coated with epoxy.

Once the epoxy dried, the rest of the coil was wound by building successive
layers of wire on top of each other. Care had to be taken whenever a new layer of wire
was started, as the wire would not simply change direction at the end caps, and it had to
be painstakingly guided into position using the wooden stick. After approximately the
first ten windings of a new layer, the wire would start to fall into place more
automatically. When the entire coil was wound, it was coated with Stycast 1266 and
allowed to dry. Thicker gauge wire was then soldered to the small leads on the secondary
coils, and the joint was covered with GE varnish or epoxy to enhance the structural
stability.

The primary coil was wound in a similar manner. However, since the diameter of
the coil had to be large enough to enclose the secondaries, the primary was wound on a
harder nonmagnetic base. A plastic drinking straw was inserted into the chuck, and the
coil was wound directly on to it. Again, the first layer was coated in Stycast 1266 to help
hold the form. Unfortunately, the properties of the wire made it quite springy, and the
coil could unwind even after the epoxy had dried. (The epoxy was necessary though, in
order to hold the coil at least weakly together.) Subsequent layers were then wound, and
epoxy was applied over the whole coil. Once the Stycast dried, thick layers of electrical
tape were used to make endcaps. It was important to tightly wrap some extra wire at the
end of the coil, and cover it with the tape endcap. This ensured that the coil did not
accidentally unwind.
For this thesis, we built an instrument with two 1 cm long, 0.3 cm inner diameter secondary coils wound in opposite directions on the same Mylar form. Winding the coils on the same form ensured the coils were concentric and eliminated a pair of solder joints. A simple half loop of wire was used between the coils to transition from one winding direction to the other and created a separation between the coils of 0.2 cm. We used 7 layers of 44 AWG Cu wire coated with Formvar insulation to make secondary coils containing 1019 turns of wire each. We wound a 3.4 cm long, 0.5 cm diameter primary coil with 848 turns using 4 layers of insulated superconducting wire (T_c = 9.8 K). All of our coils were found to have inductances of 1-2 mH.

In order to fix the secondary coils within the primary coil, the secondary coils were glued with GE varnish into a drinking straw cut to fit the outer diameter of the secondary coils. We then wrapped some nylon fishing line around the secondary coil assembly to match the inner diameter of the primary, and used GE varnish to glue the line to the straw. The complete secondary coil set was then inserted into the primary coil, making sure that the coil set was concentric with the primary coil and that the secondary coils were far away from the ends of the primary. GE varnish was then applied to fix the secondary coil set in place.

We used a gelatin capsule designed for dispensing drugs to rats (Harvard Apparatus, catalog number 72-1690) to hold the sample, allowing us to measure either powder or solid samples. The capsules had outer diameters slightly less than 3 mm, and lengths of \( \approx 8 \text{ mm} \), which fit quite well into a secondary coil. We would size the sample so that it would fill about half of the capsule, and use cotton to fill the remaining empty space. The end containing cotton was glued to the end of a wooden stick with GE
varnish, and four pin holes were poked into the capsule just above the joint once the varnish had dried. As will become clear in the next section, the stick was used to position the sample within one of the secondaries.

3.5.2 The LHe Sample Can and Mounting the Instrument

To ensure thermal equilibrium during the experiment, we constructed a sample can in order to submerge the entire instrument in a bath of liquid He. Since we were using an AC magnetic field for the experiment, we needed to construct most of the can out of a non-metallic and non-magnetic material. To this end, we designed a can that was machined from a solid cylinder of Stycast 1266. The cylinder was molded in a Teflon tube and was built in increments of m ~ 100 mg, to prevent excess heating by the exothermic reaction of the epoxy’s curing process. A collar made out of naval brass was permanently glued to the epoxy can with more Stycast 1266, and a naval brass endcap with a flange for making an In o-ring could be attached to the collar using bolts, and provide a leak-tight seal. The top of the endcap screwed on to a thermally conducting rod anchored to the mixing chamber of a He³/He⁴ dilution refrigerator, which allowed the sample can to be positioned inside the superconducting magnet in the refrigerator’s LHe dewar. Pictures of the bottom half of the sample can and of the sample can attached to the dilution refrigerator are shown in Figure 3.4. The finished sample can had an outer diameter of 3.5 cm, an inner diameter of 2.5 cm, and was approximately 12.5 cm long without the endcap attached.
Figure 3.4: The LHe sample can used to perform AC susceptibility experiments on a He³/He⁴ dilution refrigerator. The picture on the left shows the entire sample can attached to the dilution refrigerator, and the pictures on the right show top and side views of the bottom half of the sample can. All of the pictures have different scales.
The endcap also contained feed-throughs for electrical connections and the He supply line. The feed-throughs were made by passing 0.0625 inch diameter copper tubing through holes drilled through the top of the endcap. The tubing was then soldered into place, and caps were made out of Stycast 1266 per page 104 of Reference [34]. Each feed-through had 2 – 4 wires running through it, to which experimental leads could be connected. Ultra-high purity He was supplied at P = 5 psi to the sample can by a thin capillary thermally anchored to each stage of the dilution refrigerator. The capillary was passed through the LHe feed-through on the endcap, and a solder joint was made between the capillary and the top of the feed-through.

The underside of the endcap was also threaded so that a naval brass heat exchanger could be screwed into it concentric with the rod connected to the mixing chamber. The base of the heat exchanger consisted of a 1.5 inch long, 0.5 inch diameter spindle, with thin 0.75 inch diameter endcaps. The spindle had a 0.5 inch long body between the endcaps, with smaller diameter threaded sections protruding from the top and bottom. We created a clamp by cutting a piece off of the body, and then reattaching it to the spindle with two small screws. We used the clamp to anchor 0.5 inch wide, thin Cu foil to the heat exchanger, and then tightly wound the foil around the heat exchanger’s body many times. To help prevent eddy currents from being produced in the heat exchanger by the experiment, the side of the foil facing the spindle was covered with Saran wrap. After enough foil was wound, three pieces of dental floss were used to tie it in place. The completed heat exchanger was then tightly screwed into the bottom of the endcap.
The experiment was held by a 0.125 inch thick, 2.5 inch long, 0.75 inch wide rectangular Delrin stage. A threaded hole at the top of the stage allowed it to be screwed into the bottom of the heat exchanger. The stage had a 1.875 inch long, 0.5 inch wide rectangular hole in which the instrument could sit, and holes drilled along the length of the stage were used to tie the instrument into place with waxed dental floss.

The AC susceptibility coil set was mounted on the sample stage as shown in Figure 3.5. We placed the sample in the lower secondary coil such that the wooden stick varnished to the rat capsule rested on the sample stage, allowing us to vertically position the sample within the coil. Also, since the outer diameter was only slightly less than the inner diameter of a secondary coil, the capsule was held centered along the coils’ lengths. As is obvious from the picture, the coil set was initially tied securely to the sample stage.
with waxed dental floss. We then used a syringe to inject some GE varnish along the side and bottom of the coil set to fix it in place. Care was taken to ensure that the instrument, and thus the sample, was vertically aligned with respect to the dilution refrigerator. We insulated the wires running to the coils using shrink wrap and secured them with floss, trying to tie them in such a way as to prevent undue stress on the solder joints. Additionally, we kept in mind that the wires and joints would expand and contract due to the dramatic temperature changes during the experiment.

3.5.3 Performing the Measurements

We made measurements using two Stanford Research Systems SR-830 lock-in amplifiers and a SR-560 low-noise preamplifier. A schematic of the electrical circuits used for the experiment is given in Appendix A.1. One SR-830 was used to drive the circuit supplying power to the primary coil and to determine the current flowing through the circuit. The circuit was made such that the primary coil acted as an inductor in a series L-R circuit.

The second lock-in amplifier was used in conjunction with the SR-560 preamplifier to read the voltage across the secondaries. Since, we placed the sample inside only one of the secondary coils, we could use the other secondary coil to cancel out any spurious background signals detected by the circuit. Ideally, the background subtraction would be automatic, since both secondary coils were made with the same dimensions, but wound in different directions. Thus, the only signal detected should be due to the sample. However, due to slight difference in their geometries, we found that
the secondary coils were balanced within 1.3% at room temperature. However, we were able to compensate for this mismatch during the calibration process discussed below.

We used custom ANSI C code to control the experiment and record the data using a personal computer. We made measurements by applying a sine wave at $V_{\text{rms}} = 5$ V to the primary circuit, resulting in an alternating field of $H_{\text{ac}} < 1$ Oe being applied to the sample. Depending on the sample and the sample environment, the field would typically induce an EMF of $E \sim 10^{-5}$-$10^{-4}$ V at $f = 1$ kHz. We ran the preamplifier at a gain of 10 to increase this signal by an order of magnitude before sending it to the lock-in. The derivation for converting the voltage read by the lock-in to susceptibility is given in Appendix A.2.

The instrument needed to be calibrated for each sample measured, since the susceptibility depended on the filling factor of the secondary coil containing the sample (see Appendix A.2). We accomplished this by performing experiments measuring $\chi(H)$ of the sample with the ACMS and the dilution refrigerator, at the same temperatures. We then normalized the susceptibility obtained in the dilution fridge into absolute units by scaling to the ACMS data. The voltage read across the secondary coils had a slight DC offset, so the dilution refrigerator data was fit to the ACMS data using Equation 3.4:

$$\chi_{\text{ACMS}} = A\chi_{\text{DF}} + B, \quad (3.4)$$

where $A$ and $B$ are constants. Obviously, since there are two fitting parameters, two data points had to be used, and we used points corresponding to the maximum and minimum values of $\chi(H)$ for a given temperature. Calibrations performed in this manner were found to be accurate to the magnitude of ACMS data within 10%, with the largest error
occurring at the largest maximum in \( \chi(H) \). We note that the parameter B was not used when calculating \( \chi'' \), since the induced voltage across the secondaries corresponding to the imaginary part of the susceptibility did not depend on any DC offset to the signal.
Chapter 4

Slow Spin Relaxation in the Cooperative Paramagnet Tb$_2$Ti$_2$O$_7$

4.1 Introduction

Although, an ideal geometrically frustrated magnet may never order, at low temperatures, many different interactions between the spins and their environment become more relevant. These interactions may lift the degeneracy of the ground state, causing an ordered state to form or creating energy barriers preventing fluctuations between degenerate ground states. Such lifting of the degeneracy may explain why some geometrically frustrated magnets eventually order or freeze into certain macroscopic configurations. There are, however, geometrically frustrated magnets that appear to have persistent magnetic fluctuations down to $T \sim 0$. Such materials have been dubbed either spin liquids or cooperative paramagnets [35]. The term spin liquid refers to materials containing spins with small magnitudes, meaning that the spins in the magnet should be treated quantum mechanically [32][36]. Cooperative paramagnets contain big spins, such as magnetic lanthanides, in which the large total angular momentum available may allow classical descriptions of the spin dynamics. Tb$_2$Ti$_2$O$_7$ has been shown to be a cooperative paramagnet through experiments demonstrating the presence of persistent spin fluctuations to temperatures below $T = 50$ mK despite the onset of nearest neighbor antiferromagnetic correlations at $T \approx 50$ K [29][37][38].
This chapter reports experimental studies of the dynamic susceptibility of Tb$_2$Ti$_2$O$_7$ in static magnetic fields as large as $H = 9$ T, closely following a previously published article by the author [28]. Surprisingly, these measurements show uncommonly slow spin relaxations ($f < 1$ Hz) occurring in addition to the maximum in $\chi$ due to magnetic saturation at low temperatures and high fields. Furthermore, we performed systematic high field studies on magnetically dilute variants of the system, created by randomly replacing some Tb$^{3+}$ with either non-magnetic Y$^{3+}$ or Lu$^{3+}$, which indicate that the slow spin relaxations are a cooperative effect, despite the highly polarized paramagnetic state of the material. We also performed similar experiments on both pure and similarly diluted samples of the isostructural spin ice Dy$_2$Ti$_2$O$_7$. Despite the presence of large energy barriers to spin flipping in spin ice, as discussed in the next chapter, the experimental results are analogous to those for Tb$_2$Ti$_2$O$_7$. These measurements suggest that the observed slow relaxations are due to correlations created by the large dipolar interactions between the magnetic lanthanides on the lattice, which would be unusual for a highly polarized paramagnetic material.

### 4.2 Previous Experimental Results

Tb$_2$Ti$_2$O$_7$ has a pyrochlore lattice with the large $S = 6$ Tb$^{3+}$ cations forming a sub-lattice of corner sharing tetrahedra. (Remember, $S$ represents the total angular momentum unless otherwise stated.) We show a schematic of the sub-lattice formed by the lanthanides in Figure 4.1. The crystalline electric field created by the distorted cube if O$^{2-}$ anions surrounding each Tb is believed to split the $S = 6$ single ion multiplet in to a
S \approx \pm 4\text{ ground state doublet separated from a } S \approx \pm 5\text{ a first excited state doublet by } \Delta \approx 19\text{ K}\[31][39][40][41][42].\text{ Both of these crystal field states are predicted to have strong }\langle 111\rangle\text{ anisotropy, meaning the spins point along an axis connecting the center of each magnetic tetrahedron}\[31][43].\text{ The close spacing of the two doublets permits crystal field transitions even at low temperatures, and may allow the states to mix under the presence of magnetic fields available to modern laboratories.}

Previous magnetization measurements found an effective antiferromagnetic interaction between spins of } \theta_W \approx -18\text{ K}\[31][37][39][40][41][42].\text{ This contrasts with neutron scattering data showing short range correlations developing below } T \approx 50\text{ K, and Muon spin resonance and neutron spin echo data showing that spin fluctuations persist down to } T \approx 50\text{ mK}\[29][37][38].\text{ The neutron scattering experiments also show that the}
spin-spin correlations persist over lengths equivalent to the size of a single magnetic tetrahedron down to at least $T = 2.5$ K [29][37][39]. Since the spins continue to fluctuate well below $\theta_W$ and reside on a lattice capable of causing frustration, Tb$_2$Ti$_2$O$_7$ is generally considered to be a geometrically frustrated magnet with a cooperative paramagnet state.

Though the above experiments do not find evidence of magnetic order, neutron scattering measurements on samples at high pressure show AFM long range order coexisting with dynamical states [44], and time-of-flight neutron scattering data taken at ambient pressure but at high magnetic fields also show evidence of long range order capable of supporting spin waves at $T = 400$ mK [45]. Also, magnetization data show a transition into a spin glass state at $T \approx 300$ mK [46], and AC susceptibility experiments performed in a dilution refrigerator at $H = 0$ also show a frequency dependent peak in $\chi(T)$ characteristic of a spin glass transition near the same temperature [29][47][48]. However, neutron spin echo experiments show that the majority of spins remain fluctuating on time scales as slow as $10^{-9}$ s, and that the apparent glassy freezing is likely due to defects in the samples [29].

4.3 Experiment

Polycrystalline samples of (Tb$_x$M$_{1-x}$)$_2$Ti$_2$O$_7$ and (Dy$_x$M$_{1-x}$)$_2$Ti$_2$O$_7$, with M = Lu or Y, and $1 \geq x \geq 0.01$, were prepared using standard solid state synthesis techniques and determined to be single phase through X-ray diffraction. We used the MPMS SQUID magnetometer to measure the magnetization in fields up to $H = 7$ T, and we measured the AC susceptibility in static fields up to $H = 9$ T over $f = 10 – 10,000$ Hz using the ACMS
option for the PPMS. A collaborator took additional lower frequency AC susceptibility data with a MPMS outfitted with an AC SQUID capable of making accurate measurements at $f < 10$ Hz and in static fields up to $H = 7$ T. All of the AC susceptibility data were independent of the magnitude of the excitation field ($H_{ac} = 0.5 - 10$ Oe), and we found no difference between zero field cooled and field cooled data over the temperature range studied ($T = 1.8$ K - 300 K). We also obtained even lower frequency AC susceptibility data as a function of temperature $[dM/dH]_{dc}(T)$ by taking the derivative with respect to field of data from magnetization measurements made as a function of field, at a number of different temperatures. Since the MPMS makes measurements on time scales of $\sim 100$ s, we effectively found the AC susceptibility for $f < 0.01$ Hz by using this technique.

4.4 Results

Magnetization data for each sample at $H = 0.1$ T were used to make fits over $T = 210 - 300$ K to the Curie-Weiss Law. The fits yielded effective magneton values for all samples equivalent to the expected values of $p = 9.5 \pm 0.5$ for free $\text{Tb}^{3+}$ and $p = 10.5 \pm 0.5$ for free $\text{Dy}^{3+}$. The Weiss temperatures for the $(\text{Tb}_x\text{M}_{1-x})_2\text{Ti}_2\text{O}_7$ samples were found to be $\theta_W = -17.9 \pm 0.3$ K for $x = 1$ and $\theta_W = -7.4 \pm 0.4$ K for $x = 0.01$, and compare well to previously reported values \cite{31,37}. We found Weiss temperatures for the $(\text{Dy}_x\text{M}_{1-x})_2\text{Ti}_2\text{O}_7$ samples of $\theta_W \approx 1$ K, which are also consistent with previous reports \cite{49}. (The small magnitude of $\theta_W$ for the $(\text{Dy}_x\text{M}_{1-x})_2\text{Ti}_2\text{O}_7$ samples makes it difficult to resolve any changes in the effective interactions for the different samples.)
Figure 4.2: The real and imaginary parts of the AC susceptibility of Tb$_2$Ti$_2$O$_7$ for various frequencies at applied fields of $H = 0$, 5, and 9 T. This figure is reproduced from Reference[28]. (Copyright 2006 by the American Physical Society.)

Figure 4.2 shows the real and imaginary parts of the AC susceptibility of undiluted Tb$_2$Ti$_2$O$_7$ from ACMS data taken at various excitation frequencies and applied DC magnetic fields. For $H = 0$, $\chi'$ displays paramagnetic behavior by monotonically rising with an increasing slope as the temperature is decreased. The data can be fit to a combination of the Curie-Weiss formula and the Van Vleck term, which takes into account the susceptibility due to transitions between the closely space crystal field levels [50]. For the data taken in a field, a maximum in $\chi'$ occurs at $T \approx 20$ K for $H > 3$ T, which shifts to higher temperatures at higher fields. This peak corresponds to the magnetic saturation of the Tb$^{3+}$ cations at low temperature due to the strong magnetic
field. A maximum in $\chi''$ also occurs at temperatures matching the fall in $\chi'$, in agreement with the Kramers–Kronig relations [13]. Interestingly, despite the application of a relatively strong field, the magnitude of the peak in $\chi''$ increases for lower frequencies, indicating that spin relaxation occurs at time scales as slow as $\tau = 0.1$ s. The susceptibility does not go to zero for $T \sim 0$ due to the crystal field levels of the Tb$^{3+}$ cations permitting transitions between different states. This means that the Van Vleck susceptibility is dominating the low temperature, high field magnetic response, causing the nearly temperature independent susceptibility at low temperatures seen in the $H = 9$ T data [50]. Appendix C further explains the Van Vleck susceptibility.

To investigate further the slow spin relaxation, we took susceptibility data down to $f \sim 0.01$ Hz using the AC SQUID and the MPMS magnetization measurements described above. The top panel of Figure 4.3 shows $\chi(T)$ at $H = 5$ T, while the bottom panel shows typical data used to obtain $[dM/dH]_{dc}$. We find that the maximum in $\chi(T)$ shifts to lower temperatures and has a higher magnitude at lower frequencies. In addition, the high field temperature independent susceptibility for $T < 15$ K is not seen in data taken at $f < 5$ Hz.

Figure 4.4 compares $\chi'(T)$ at $f = 10$ Hz and $[dM/dH]_{dc}$ for (TbxM1-x)2Ti2O7 and (DyxM1-x)2Ti2O7, where $M = Y$ or Lu. Diluted samples with $x = 0.01$ and $x = 0.05$ were used for the (TbxM1-x)2Ti2O7 and (DyxM1-x)2Ti2O7 systems, respectively, with data for (TbxM1-x)2Ti2O7 shown in the top panels and data on (DyxM1-x)2Ti2O7 shown in the bottom panels. From left to right, the panels show the susceptibility of the pure, Y diluted, and Lu diluted materials. For $x = 0$, the single ion magnetic saturation peak seen in the data for both the Tb and Dy samples has a larger magnitude and occurs at lower
Figure 4.3: The magnetic susceptibility of Tb$_2$Ti$_2$O$_7$ at H = 5 T. The top panel includes low frequency AC measurements from the MPMS, higher frequency measurements from the PPMS at higher frequency, and [dM/dH]$_{dc}$ obtained from magnetization data, as described in the text. The bottom panel shows the measured magnetization M(T) at various magnetic fields used to determine [dM/dH]$_{dc}$ (H increases from bottom to top). A high degree of polarization can be seen in M(T) at the fields where slow relaxation is occurring. This figure is reproduced from Reference[28]. (Copyright 2006 by the American Physical Society.)
temperatures in the lower frequency data. While for both the Y and the Lu diluted sets of samples, the peaks show no such frequency dependence. In addition, in contrast to the data for the Tb samples, the low temperature susceptibility at high field goes to zero for the Dy samples, indicating that the Van Vleck term in the susceptibility is not important.

Figure 4.4: Comparison of the ac magnetic susceptibility at $f = 10$ Hz and $[dM/dH]_{dc}$ for both $(\text{Tb}_x\text{M}_{1-x})_2\text{Ti}_2\text{O}_7$ and $(\text{Dy}_x\text{M}_{1-x})_2\text{Ti}_2\text{O}_7$, as described in the text. Note that the dependence is virtually eliminated for the highly dilute samples. The dip in the $H = 0$ AC data of the diluted Dy samples is a consequence of simple single-ion relaxation studies previously, which unlike the frequency dependence we observe, follows an Arrhenius law [30]. This figure is reproduced from Reference [28]. (Copyright 2006 by the American Physical Society.)
4.5 Discussion

We now consider possible reasons for the slow spin relaxation implied by the low frequency behavior of the magnetic saturation peak. We first consider that the slow spin relaxation implies entrance into some novel spin glass state. However, the strong fields used in the experiments, the lack of a divergence between ZFC and FC magnetization data, and the weakening of the frequency dependence for \( f > 100 \) Hz would rule out this explanation. The weakening high frequency behavior also rules out thermal relaxation of single spins as observed in \( \text{Dy}_2\text{Ti}_2\text{O}_7 \) at low fields [30][51].

Another possibility is that the slow spin relaxation occurs due to a sufficiently infrequent spin-phonon interaction. However, the 50% difference in mass between Y and Lu should cause a dramatic difference in the phonon spectrum, which depends on the non-magnetic ion substituted into the lattice. The change in the spectrum would presumably affect the spin-phonon interaction responsible for the slow relaxation, causing a difference in the frequency dependence of the susceptibility of the Y and Lu diluted samples. Since we observed no substantial differences in the susceptibility of the differently diluted materials, and since the mass of Lu is quite similar to the mass of Tb, we can rule out that a spin phonon interaction occurring at a sufficiently infrequent rate causes the observed slow relaxation.

Next, we consider whether the observed phenomena are associated with the onset of long range order, since recent neutron scattering measurements have shown evidence of magnetic long range order in \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) at high magnetic fields [45]. However, the ordered state observed in these experiments occurs at much lower temperatures than the
slow spin relaxation reported here. In addition, since we observe that the slow relaxation is coincident with the single moment saturation peak in the susceptibility, and since we see the same type of relaxation in data for Dy$_2$Ti$_2$O$_7$, we believe that the source of the slow relaxation lies within the highly polarized paramagnetic state of these rare-earth pyrochlores.

Finally, we consider if the relaxation is associated with the crystal field level structure of Tb$_2$Ti$_2$O$_7$. We saw in the data that the close spacing of these energy levels leads to a significant contribution of Van Vleck terms to the susceptibility. However, since similar relaxation is observed in data taken on the diluted spin ice (Dy$_x$M$_{1-x}$)$_2$Ti$_2$O$_7$, which has a much different crystal field level scheme than the Tb materials [43][49][52], attributing the cause of the slow relaxation to single ion transitions between crystal field levels is discounted.

While all of the above explanations appear incorrect, the disappearance of the frequency dependence of the susceptibility with non-magnetic dilution suggests that the slow spin relaxation is due to the formation of correlations between spins. We find it surprising to observe an effect due to these correlations in the susceptibility of a paramagnet, especially in the spin ice, where spins freeze only at much lower temperatures. However, it is well known that the rare earth pyrochlores have large spins and sizable long range dipolar interactions (E$_{dip}$ $\sim$ 1 K), which play a strong role in determining the low temperature properties [52][53][54]. In addition, previous studies have hypothesized the existence of a cooperative state at lower fields [55]. Since these both systems are highly polarized in the dc fields considered, we may be observing the formation of correlated domains of spins highly polarized along the field, with a few
spins oppositely polarized (canted) to the field direction, due to the dipolar interactions of groups of polarized spins competing with the external field. This means that there will be large energy barriers to switching the direction of these few canted spins, making the relaxation between spin states very slow. Slow dynamics have been observed in ferromagnetic cluster system (though at faster time scales than observed here), and have also been linked with domain dynamics in ferromagnets [56]. Consistent with this explanation, we ruled out demagnetization effects (discussed in Appendix B) causing the relaxation by performing measurements on different shaped samples, which showed that the sample shape only alters the magnitude of the peaks in the susceptibility and not the temperature at which they occur.

4.6 Conclusion

The observation that strong magnetic fields may induce slow spin relaxation contradicts normal intuition that a strong field would hasten relaxation to an equilibrium state. Indeed, the data presented in this chapter suggest a new form of collective behavior in the rare earth titanates and further indicate the importance of understanding the effects of magnetic fields on frustrated magnets. While this relaxation may be possible in any strongly correlated paramagnetic system, the effects are particularly important to geometrically frustrated systems, since they remain paramagnetic down to temperatures much lower than the relative strengths of their spin-spin interactions.
Chapter 5

Stuffed Spin Ice

5.1 Introduction

One of the oldest known frustrated systems is ice. When H₂O freezes, the O²⁻ lie in positions similar to the sites on a wurzite lattice, with each O²⁻ surrounded by four H⁺ with a somewhat tetrahedral coordination. The tetrahedral coordination distorts in the sense that two of the H have longer O-H bonds than the other two, meaning that macroscopically there is a periodic arrangement of the O²⁻ ions and a disordered arrangement of H⁺. Since two possible bond lengths exist for each O²⁻, one may assume that ice has two degrees of freedom, resulting in a measured molar entropy $S$ given by Equation 5.1:

$$S = R \ln 2,$$  \hspace{1cm} (5.1)

where $R$ is the ideal gas constant. However, there are actually 16 different ways to arrange four H around each O, with only 6 yielding the lowest energy per O. Bernal and Fowler were the first to recognize the disorder of the H in ice, leading them to write a set of “ice rules” describing the structure [57].

Experimentally, we can determine the entropy of a material by measuring its specific heat as a function of temperature by the procedure discussed in Section 3.4. Performing the integral in Equation 5.2:
from $T = 0$ to high temperatures then yields the total entropy of the material. (Here, we define the specific heat as in Equation 3.3.) When heat capacity experiments from $T = 15\, -\, 273$ K were performed on ice in the early 20th century to determine its entropy, $S$ was found to fall short of the entropy of Equation 5.1, resulting in what has been termed “residual entropy [58],” which is the assumed entropy of the system associated with the configurational disorder at $T = 0$. Following these results, Pauling calculated the entropy of ice using Bernal’s and Fowler’s ice rules, finding that it should fall 29% short of $S = R \ln 2$, which agrees well with the experimental results [59]. Certain geometrically frustrated magnets can also possess a residual entropy as $T \sim 0$ [60][61]. In fact, a direct analogy exists between the magnetic entropy present in certain rare earth pyrochlores and the entropy of ice [49][62][63]. These materials have been dubbed “spin ice,” since the spins freeze into positions analogous to the configuration of the H\textsuperscript{+} in ice [62].

In this chapter we report magnetization, susceptibility, and heat capacity measurements on materials known as stuffed spin ice (SSI), created by replacing some of the non-magnetic Ti\textsuperscript{4+} in Ho\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} or Dy\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} spin ice with either Ho or Dy, respectively. Stuffing the lattice with more magnetic cations increases the number of nearest neighbors per Ln, presumably increasing the magnetic connectivity of the lattice. The SSI studied here have the formula Ln\textsubscript{2}(Ln\textsubscript{x}Ti\textsubscript{2-x})O\textsubscript{7-x/2}, where Ln = Ho or Dy and $x = 0 \sim 0.67$. Both stuffed spin ices show increasing antiferromagnetic interactions with stuffing, while the effective moment per Ln remains constant. Surprisingly, for the Ho stuffed spin ice we find that the total magnetic entropy remains around the spin ice value

\[
S = \int \frac{C}{T} dT \quad (5.2)
\]
for all x, while in the Dy stuffed spin ice, the magnetic entropy increases with x. Much of the data presented in this chapter on the Ho SSI has already been published [64], and a manuscript on the data for Dy SSI is being prepared [65].

5.2 Previous Experimental Results

Spin ices, such as Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ have a pyrochlore lattice with the general formula A$_2$B$_2$O$_7$ (see Figure 4.1), with the magnetic lanthanides sitting on the A-sites forming a magnetic sub-lattice of corner sharing tetrahedra. Previous magnetization data show effective ferromagnetic nearest neighbor interactions of $\theta_W \approx 1$ K for both materials [49][63], which both theory and experiment indicate to originate in the large dipolar interactions ($E_{\text{dip}} \approx 1$ K) between the big spins ($S = 8$ for Ho$^{3+}$ and $S = 15/2$ for Dy$^{3+}$) [53][66][67]. Neutron scattering experiments and theoretical calculations show that for both materials the crystal field splits the single ion multiplet into a ground state doublet separated from the first excited state by $\Delta \approx 200$ K, resulting in well defined Ising spin states pointing either into or away from the center of each magnetic tetrahedron [43][52]. The geometric frustration, effective ferromagnetic interactions, and Ising ground states cause the lowest energy per tetrahedron to occur when two spins point into and two spins point out of each tetrahedron, resulting in many degenerate ground states [49][62]. Macroscopically, the local constraints on the spins lead to the same residual ground state entropy in ice [49], and heat capacity experiments confirm that the spins freeze into an ice like state at $T_{\text{ice}} \approx 2$ K [63][68]. Figure 5.1 shows a comparison between the local ordering in ice and spin ice.
In the absence of a DC magnetic field, the AC susceptibility of spin ice has a frequency dependent peak beginning at $T \approx 2$ K for $f = 10$ kHz, corresponding to the spins freezing into the ice state, with $\chi'(T) \sim 0$ by $T = 0.7$ K for frequencies down to $f = 0.5$ Hz \[69][70][71]. The low frequency maximum in $\chi'(T)$ corresponds well to magnetization data, which show a bifurcation in $M(T)$ for $\text{Dy}_2\text{Ti}_2\text{O}_7$ at $T = 0.6$ K between ZFC and FC data taken at $H = 500$ Oe [71]. Though such a bifurcation in $M(T)$ of a frustrated material usually indicates a spin glass transition (see Section 2.2), the bifurcation persists in fields up to $H = 0.5$ T, highly unusual for a canonical spin glass transition [20]. Also, AC susceptibility measurements yielding $\chi''(f)$ do not show the broad range of spin relaxation times expected in a spin glass, but rather show a single characteristic spin relaxation time [71].

The AC susceptibility of $\text{Dy}_2\text{Ti}_2\text{O}_7$ also has a frequency dependent maximum at $T \approx 16$ K, in addition to the maximum at $T_{\text{ice}}$ [30][51][70][72]. $\chi''(f)$ data exploring this high temperature peak are also characteristic of single spin relaxation, but resulting from
relaxation across the large energy barriers created by the crystal field, not spin-spin correlations [30][51][70][72]. Surprisingly, as the temperature is lowered, the spin relaxation at $T \approx 16$ K changes from simple Arrhenius type behavior corresponding to thermal relaxation over the crystal field energy barriers, to almost temperature independent relaxation at $T \approx 13$ K, and then back to strongly temperature dependent relaxation around $T_{\text{ice}}$ [30]. Though the reason behind the slow rate at which the higher temperature spin relaxation in Dy$_2$Ti$_2$O$_7$ occurs is still unclear, it is intriguing that a similar peak is absent from the AC susceptibility of Ho$_2$Ti$_2$O$_7$. However, there are signs of high temperature spin relaxation at higher frequencies do occur in neutron spin echo measurements on Ho$_2$Ti$_2$O$_7$ [73]. While this spin relaxation at high temperatures is quite interesting, our studies on stuffed spin ice focus on its lower temperature properties.

5.3 Experiment

Polycrystalline samples of Ho$_2$(Ho$_x$Ti$_{2-x}$)O$_{7-x/2}$ and Dy$_2$(Dy$_x$Ti$_{2-x}$)O$_{7-x/2}$, where $0 \leq x \leq 0.67$, were synthesized using previously published techniques [64][74]. We performed magnetization measurements on each sample down to $T = 1.8$ K and in fields up to $H = 7$ T with the MPMS, and we measured the AC susceptibility of each sample down to $T = 1.8$ K and up to $H = 9$ T using the ACMS. The AC experiments were performed at frequencies spanning $f = 10 - 10000$ Hz with a $H_{\text{ac}} = 1$ Oe excitation field. Additional AC susceptibility measurements were performed on $x = 0.67$ samples down to $T = 85$ mK and in fields up to $H = 9$ T in the dilution refrigerator.
Measurements on the heat capacity of each sample were made down to $T = 0.4$ K using the He$^3$ insert for the PPMS, in fields up to $H = 1$ T. The $\text{Ho}_2(\text{Ho}_x\text{Ti}_{2-x})\text{O}_{7-x/2}$ samples were first pressed into 1 cm diameter pellets and then cut to fit the heat capacity sample platform. To reduce possible demagnetization effects, we cut the samples into rectangular pieces with heights and widths much smaller than their lengths. We then mounted a sample on the sample platform, such that its length was along the axis of any applied field. (The plane of the sample platform is parallel to the applied field when using the He$^3$ insert.) Typical samples had a length of 2 mm and both a height and width of 1 mm, resulting in a mass of $m \approx 5$ mg. For the $\text{Dy}_2(\text{Dy}_x\text{Ti}_{2-x})\text{O}_{7-x/2}$ samples, Ag powder was added prior to pressing the samples into pellets, in order to facilitate thermal equilibrium and help hold the sample together. (The $\text{Ho}_2(\text{Ho}_x\text{Ti}_{2-x})\text{O}_{7-x/2}$ pellets did not require any Ag, because they were pressed using much more force.) Each pellet contained approximately 50% Ag by weight, and, after pressing, each sample was prepared for measurement in the same way as the Ho samples.

5.4 Results

In pure spin ice ($x = 0$), the Ti sit solely on the B-sites of the $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore lattice, creating another sub-lattice of corner sharing tetrahedra identical to the magnetic sub-lattice. The two sub-lattices are offset by an amount equal to the length of a side of a tetrahedron, resulting in each Ln cation having 6 Ln nearest neighbors and 6 Ti nearest neighbors. For Ho SSI, it was found that Ti mixed on to the pyrochlore A sites for $x > 0.3$, resulting in the material being best described as a disordered fluorite lattice, in which
the Ho and Ti are randomly distributed over the A and B sites of the original pyrochlore lattice. At \( x = 0.67 \), this results in a possibly frustrated Ho sub-lattice of side sharing tetrahedra [74]. Figure 5.2 shows a cartoon illustrating the substitution of one Ln ion for a Ti on the pyrochlore lattice and a graph showing the percentage of Ti that occupies a pyrochlore A-site as a function of stuffing. From the figure, it is obvious that the Ti mainly remains on the pyrochlore B-sites for \( Dy_2(Dy_xTi_{2-x})O_{7-x/2} \), which leads to the Dy materials being best described by the pyrochlore lattice, for all \( x \).

Curie-Weiss fits to magnetization measurements on each sample between \( T = 10 \) – 20 K at \( H = 0.1 \) T yielded the effective moments and Weiss temperatures. Figures 5.3

Figure 5.2: The percentage of A-sites on the \( A_2B_2O_7 \) pyrochlore lattice containing Ti\(^{4+} \), as more Ho or Dy is stuffed into the lattice (lines are guides to the eye). The drawing within the graph illustrates the effect of stuffing on the A and B-sites of the pyrochlore lattice, in which the circled B-site has its Ti replaced by a lanthanide. Parts of this figure are reproduced from Reference [64]. (Copyright 2006 by Nature Publishing Group.)
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and 5.4 show that $\theta_W$ becomes increasingly AFM with stuffing for both the Ho and Dy samples, and we found that the effective moment of each sample agreed with the values for either a single Ho$^{3+}$ or Dy$^{3+}$ ion. It is noticeable that an antiferromagnetic $\theta_W$ was obtained for the $x = 0$ Dy sample. However, since the magnitude of $\theta_W$ is quite small, and since it is very sensitive to range of the fit, its negative value is likely a result of experimental error. In addition, because the experimental procedure was consistent, and we performed all of the fits over the same temperature range, the qualitative interpretation that $\theta_W(x)$ becomes more AFM with increasing $x$ remains valid.

Figures 5.3 and 5.4 also show that the saturated magnetization at $T = 2$ K for each set of samples is constant at $M_{\text{sat}} \approx 5.25 \, \mu_B/Ln$ for all $x$, which is about one half the value expected for saturated Ho or Dy ions and in agreement with previous results for the pure spin ice materials [71][75]. In addition, Figure 5.4 shows that the $T = 2$ K $M(H)$ curves for the Dy samples have similar shapes, or rather that the curves all approach saturation in a similar manner. Since the data saturate to the same values seen in the pure spin ices for each value of $x$, these results suggest Ising like single ion ground states in the Dy SSI materials. Similarly, the $M(H)$ data in Figure 5.3 suggest that the Ho SSI also retains Ising like single ion states for all values of stuffing.
Figure 5.3: (a) The Weiss temperature and saturation magnetization (T = 2 K, H = 5.5-7 T) plotted versus x for the various Ho₂(HoxTi₂-x)O₇-x/2 samples. The Weiss temperature was determined from fits to the Curie-Weiss law; the estimated uncertainty in the magnetization is ±5% based on the uncertainty in sample mass. (b) The inverse dc magnetic susceptibility versus temperature for x = 0 and 0.67. The lines are fits to the data used to determine $\theta_W$, as described in the text; the effective moment $\mu$ obtained from these fits is within 2% of the accepted value for Ho. This figure is reproduced from Reference [64]. (Copyright 2006 by Nature Publishing Group.)
Figure 5.4: Magnetization data for Dy$_2$(Dy$_x$Ti$_{2-x}$)O$_{7-x/2}$, $0 \leq x \leq 0.67$. (a) The Weiss Temperature $\theta_W$ as a function of stuffing $x$ was obtained from fits to data taken in a field of $H = 0.1$ T. Examples of the fits are shown in (b). (c) $M(H)$ at $T = 2$ K for each value of $x$. 
Figure 5.5 shows heat capacity data for $\text{Ho}_2(\text{Ho}_x\text{Ti}_{2-x})\text{O}_{7-x/2}$, along with the fits used to subtract out the lattice contribution to the specific heat. We performed the fitting by scaling polynomial fits to heat capacity data on the structurally similar non-magnetic materials $\text{Lu}_2(\text{Lu}_x\text{Ti}_{2-x})\text{O}_{7-x/2}$, for $x = 0, 0.3, \text{and } 0.67$. In addition, the hyperfine interactions in Ho materials give rise to a large Schottky peak associated with hyperfine contributions to the specific heat that was visible in the temperature range we measured. We subtracted this peak from the data using fits made to previously published work [66]. After subtracting out the lattice and hyperfine contributions, we used the resulting
magnetic specific heat to determine the total magnetic entropy from Equation 5.2 by assuming that \( S = 0 \) at \( T = 0 \), which is valid since there was no significant contribution to the entropy below the temperature range of our measurements. Panel (c) in Figure 5.5 shows \( S(T) \) for the \( x = 0 \) and \( x = 0.67 \) samples at fields of \( H = 0 \) and 1 T, illustrating the climb in \( S(T) \) with temperature for large values of \( c/T \), and that \( S(T) \) stabilizes at some total value once \( c/T \sim 0 \). For \( x = 0 \) and \( H = 0 \) the entropy rises to the spin ice value, in agreement with previously published work \cite{66,68}. The total value of the magnetic entropy at \( T = 22 \) K for each value of \( x \) is shown in panel (b) of Figure 5.5, where every point represents the average of at least two separate measurements on different samples for each value of \( x \). Surprisingly, the entropy at \( H = 0 \) remains at the spin ice value for all \( x \), within the \( \pm 10\% \) uncertainty caused by the uncertainty in the sample mass. At \( H = 1 \) T, the total entropy grows towards \( S = R \ln 2 \) for \( x = 0 \), and again stays at a constant value for all \( x \).

To contrast with the \( \text{Ho}_2(\text{Ho}_x\text{Ti}_{2-x})\text{O}_{7-x/2} \) data, we show specific heat data for \( \text{Dy}_2(\text{Dy}_x\text{Ti}_{2-x})\text{O}_{7-x/2} \) in Figure 5.6. The left panel shows the specific heat after subtracting out the contributions due to the Ag used in preparing the sample for measurement. The lattice contributions were again subtracted out by scaling data on \( \text{Lu}_2(\text{Lu}_x\text{Ti}_{2-x})\text{O}_{7-x/2} \), \( x = 0, 0.3, \) and 0.67, using the same procedure as in the \( \text{Ho}_2(\text{Ho}_x\text{Ti}_{2-x})\text{O}_{7-x/2} \) data. Unlike the Ho samples, the Schottky peak due to hyperfine interactions does not appear in these measurements, resulting in a simpler determination of the magnetic specific heat by merely subtracting out the lattice contributions. As shown in the inset to the left panel, we again obtain the total magnetic entropy by integrating the magnetic specific heat and assuming \( S = 0 \) at \( T = 0 \). The right panel in Figure 5.6 shows the total magnetic entropy
as a function of stuffing for Dy\textsubscript{2}(Dy\textsubscript{x}Ti\textsubscript{2-x})O\textsubscript{7-x/2} at H = 0 and 1 T, along with the H = 0 total magnetic entropy for Ho\textsubscript{2}(Ho\textsubscript{x}Ti\textsubscript{2-x})O\textsubscript{7-x/2}. Again, the points in this figure are the average of multiple measurements for each value of x, and the error primarily depends on the uncertainty in the sample mass. The two error bars shown represent the typical uncertainty for each point. Clearly, for x < 0.3, the total entropy for the Dy materials monotonically increases away from the spin ice value towards S = R\ln 2, and then remains constant, within error, up to x = 0.67. Application of a magnetic field restores some of the residual entropy in the x = 0 sample, in agreement with previous results [63]. For higher x, the total entropy in a H = 1 T field stays at the x = 0 value.

To further investigate these systems, AC susceptibility experiments were performed on x = 0.67 samples of both materials. The data were independent of the AC
excitation field used, which was $H_{ac} < 1$ Oe for all of the measurements. For the Ho case, the large hyperfine effects seen in the specific heat will not appear in the AC susceptibility measurements, yielding a clearer picture of the electronic magnetism in the sample. Additionally, since low temperature AC susceptibility measurements have been previously performed on Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$, data on the $x = 0.67$ sample can be compared to a good base set of data [69][71].

Figure 5.7 shows the real part of the H = 0 AC susceptibility versus temperature for Ho$_{2.67}$Ti$_{1.33}$O$_{6.67}$ ($x = 0.67$) at various frequencies. The data are calibrated using $\chi'(H)$ data from the ACMS, with an estimated error of ± 1% in calibration. While
paramagnetic behavior occurs at high temperature, below $T = 2$ K a frequency dependent peak in the susceptibility forms, with maxima occurring at $T \approx 1.4$ K for $f = 10$ Hz and $T \approx 1.7$ K for $f = 1$ kHz. This peak is quite similar to the peak seen in $\chi'(T)$ for $\text{Ho}_2\text{Ti}_2\text{O}_7$, although its magnitude is much smaller. The presence of the frequency dependent maximum indicates a possible spin freezing at the measurement frequencies and at temperatures corresponding to the magnitude of $\theta_W$ shown in Figure 5.3. After the maximum, the susceptibility tends towards zero as $T \sim 0$ for each frequency measured. The inset to Figure 5.7 shows a corresponding frequency dependent peak in $\chi''(T)$ at the same temperatures, as expected from the Kramers – Kronig relations.

Next, Figure 5.8 shows $\chi'(T)$ and $\chi''(T)$ at $H = 0$ for $\text{Dy}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}$ for various measurement frequencies. The data here are again calibrated using $\chi'(H)$ data from the ACMS, with an estimated error in the calibration of $\pm 1\%$. As in the data for $\text{Ho}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}$, $\chi'(T)$ shows a frequency dependent peak ending the high temperature paramagnetic behavior. The peak develops at $T < 2.5$ K and reaches a maximum at $T \approx 1.7$ K for $f = 10$ Hz and at $T \approx 1.9$ K for $f = 100$ Hz., indicating that spins are freezing at these temperatures. The inset shows that for $T > 0.75$ K, $\chi''(T)$ has a corresponding frequency dependent maximum, again indicating that at least some of the spins are freezing. However, in contrast with the $\text{Ho}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}$ data, $\chi'(T)$ retains a strong frequency dependence and does not appear to go to zero as $T \sim 0$. Though unusual, this behavior occurs in some spin glasses and in some geometrically frustrated magnets which display cooperative paramagnetic behavior at low temperatures [20][47].
Next, we examine the effects of an applied magnetic field on SSI at low temperatures. Figure 5.9 shows the real part of the AC susceptibility versus temperature of Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$ for various excitation frequencies and DC magnetic fields. Examining the far left panel of the figure, at $H = 0$, $\chi'(T)$ displays peaks at $T = 1.7$ K in the $f = 10$ Hz data and at approximately $T = 2$ K in the $f = 1$ kHz data. At temperatures below the peak, $\chi'(T)$ decreases at a much slower rate than seen for Dy$_2$Ti$_2$O$_7$, where $\chi'(T)$ approaches
zero below $T = 0.5$ K\[69][71].  As the magnetic field is increased, the magnitude of the peak diminishes, while its frequency dependence appears to be substantially affected only in the $H = 2$ T data.  The frequency dependence of the temperature of the peak is indicative of a spin glass, however the fact that the peak does not shift in temperature and is not substantially broadened by even a field of $H = 1$ T appears to rule out a typical spin glass state at low temperatures.

Figure 5.9: The field dependence of the real part of the AC susceptibility versus temperature of Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$ for various measurement frequencies. Each panel shows data taken at a different applied magnetic field ($H = 0 \rightarrow 2$ T, from left to right).

Figure 5.10 shows $f = 50$ Hz $\chi'(H)$ data for Ho$_{2.67}$Ti$_{1.33}$O$_{6.67}$ at $T = 0.3$ K and 1.8 K, while increasing the magnetic field at 0.01 T/min and 0.1 T/min, respectively. The data show typical behavior for magnetic saturation at $T = 1.8$ K and a diminished susceptibility at $T = 0.3$ K. The small value of $\chi'(H)$ at low fields for $T = 0.3$ K reflects the spin freezing occurring below $T = 1.7$ K. Unfortunately, we were not able to take data at more temperatures. However, we will next show $\chi(H)$ data on Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$ at various low temperatures.
χ′(H) and χ″(H) for Dy2.67Ti1.33O6.67 at T ≤ 1.8 K and f = 50 Hz are plotted in Figure 5.11, where we made measurements while sweeping the field at a rate of 0.001 T/min to ensure equilibrium conditions. The data show two peaks forming in χ′(H) at lower temperatures, with corresponding peaks occurring in χ″(H). For H < 3 T, χ′(H) decreases and flattens out with decreasing temperature, until the temperature becomes low enough for another peak to form in χ′(H). The imaginary part of the susceptibility rises and falls at the two peaks in χ′(H) and plateaus in between.
The insets to Figures 5.10 and 5.11, show the magnetization versus field of each sample obtained by integrating $\chi'(H)$. At $T = 1.8$ K the data saturates at $M \sim 5 \mu_B$, in agreement with the data in Figures 5.3 and 5.4. At lower temperatures, $M(H)$ saturates at a slower rate, which is consistent with the AFM spin-spin interactions becoming more important. Furthermore, $M(H)$ of Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$ at $T = 0.2$ K and 0.085 K, does not even reach $M = 2\mu_B$/Dy by $H = 1.5$ T, and the AC susceptibility is going towards zero at

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Figure 5.11: The $f = 50$ Hz AC susceptibility versus applied DC field of Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$, at various temperatures. Data was taken while sweeping the field at a rate of 10 Oe/min. The inset shows $M(H)$ for $T \leq 1.8$ K, determined by integrating $\chi'(H)$. Note the log scale on the inset’s vertical axis.
higher fields. This means that more than half of moment in Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$ may be frozen out at these temperatures due to spin-spin interactions. This is in stark contrast to data for Dy$_2$Ti$_2$O$_7$ and other spin ice materials, which show $M \sim 4 \mu_B$ by $H = 1.5$ T at $T = 0.25$ K [69][71].

5.5 Discussion

We now discuss the data on the Ho and Dy SSI materials and start by looking at the similar behavior in the DC magnetization results in Figures 5.3 and 5.4. The increasingly AFM behavior of $\theta_W$ with increasing x seen for both the Ho and Dy samples suggest that the alteration of the lattice with stuffing does not drastically change the interactions between the magnetic cations on the A-sites because of the higher level of Ti disorder in the Ho materials, as seen in Figure 5.2. Rather, we conclude that the magnetic interactions between the A and B-sites are antiferromagnetic, and that increasing the number of such pairs creates a more AFM $\theta_W$ at larger x. Additionally, as previously discussed, the $M(H)$ data suggest that the single ion ground state remains Ising like in both the Ho and Dy SSI, since the saturated magnetization remains constant for all values of stuffing.

Moving on to the heat capacity data in Figures 5.5 and 5.6, the $T \approx 2$ K peaks in the specific heat are broader at higher values of stuffing for both Ho$_2$(Ho$_x$Ti$_{2-x}$)O$_{7-x/2}$ and Dy$_2$(Dy$_x$Ti$_{2-x}$)O$_{7-x/2}$. Broad peaks in $c(T)$ can indicate the presence of short range correlations between spins, and since the peak in our data appears wider for larger x, it is possible that the additional AFM interactions from stuffing lead to more correlations.
developing between spins. This is reasonable since AFM coupled Ising spins with [111] anisotropy on the pyrochlore lattice can form the all in, all out (Q = 0) long range ordered state \([53][62]\). However, the fact that the entropy approaches \(S = R \ln 2\) for \(\text{Dy}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}\) but not for \(\text{Ho}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}\) can not be explained using the heat capacity data alone.

To clarify the reasons behind the difference between the total entropy for \(\text{Ho}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}\) and \(\text{Dy}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}\), we turn to the AC susceptibility data in Figures 5.7 and 5.8, where we see that the low temperature susceptibilities of the two materials are somewhat different. For \(\text{Ho}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}\), the maximum in \(\chi'(T)\) is followed by a steady drop to \(\chi'(T) \approx 0\) at \(T \approx 0\) indicating that most (if not all) of the spins in the material freeze at low temperature, while the frequency dependence of the temperature of the maximum suggests an absence of long range magnetic order. This situation is quite similar to \(\chi'(T)\) for \(\text{Ho}_2\text{Ti}_2\text{O}_7\), where the large energy barriers in the material cause the Ho to freeze into the disordered spin ice state \([30][51][70][72]\). However, in our case \(\chi'(T) \approx 0\) only as \(T \approx 0\), not at a finite temperature as in pure spin ice \([69]\). This may indicate that the additional magnetic interactions and the disorder in the lattice alter the spin relaxation pathways in \(\text{Ho}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}\) permitting the spins to fluctuate down to much lower temperatures, yet still show a complete freezing as \(T \approx 0\). Since the total entropy remains around the ice value, we therefore conclude that \(\text{Ho}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}\) freezes below \(T \approx 2\) K into a disordered state showing both glassy and ice like properties analogous to pure spin ice.
Turning now to Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$, Figure 5.8 shows that the maximum in $\chi'(T)$ for Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$ also has some frequency dependence, however, contrary to the data for Ho$_{2.67}$Ti$_{1.33}$O$_{6.67}$ the susceptibility seemingly does not approach zero as $T \sim 0$. Also, the frequency dependence of $\chi'(T)$ strongly persists down to $T \sim 0$ for Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$. As previously stated and discussed more below, such behavior occurs in some spin glasses and cooperative paramagnets (i.e. spin liquids) [20][31][41][47]. Next, we see in Figure 5.11 that two maxima in $\chi'(H)$ for Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$ at low temperatures with a corresponding plateau in $\chi''(H)$. As seen in the inset to the figure, the peak at higher field, followed by the decrease to $\chi'(H) = 0$ at high fields is due to the field completely saturating single spins. However, the peak in $\chi'(H)$ at lower temperatures obviously does not represent single spin saturation, since a finite susceptibility remains at fields above the peak. One possible explanation is that the low field maximum in $\chi'(H)$ seen at low temperatures represents the energy due to the field beginning to dominate the interactions between spins. Such a situation has been seen in AC susceptibility data on GGG, in which a broad peak develops in $\chi'(H)$ at low temperatures, corresponding to the field quenching the short range AFM order between spins [76]. Taking this interpretation of the low field maximum in $\chi'(H)$ together with the fact that $\chi'(T)$ retains a finite value $T \sim 0$, leads us to conclude that Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$ may have a cooperative paramagnet type state at low temperatures among at least some of its spins.

Our data also compare well to results from studies on different cooperative paramagnets and spin liquids. For example, specific heat and susceptibility data on the cooperative paramagnets Tb$_2$Ti$_2$O$_2$ and Tb$_2$Nb$_2$O$_7$, which both have a pyrochlore lattice,
show that the expected total entropy per Tb is recovered at temperatures corresponding to the effective magnetic interactions, while their susceptibilities remain finite as T ~ 0 \cite{20,31,41,47}. This compares well with our data in Figure 5.6, which show the total entropy per Dy in Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$ rapidly rising at T \approx 4 K, approaching the expected value for an Ising system of S = R ln2, and our data in Figure 5.8, which show a finite susceptibility for Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$ as T ~ 0. Additionally, frequency dependent peaks in $\chi'(T)$ similar to those seen in Figures 5.8 and 5.9 indicative of a spin glass type freezing are seen in data on Tb$_2$Ti$_2$O$_7$, and the spin liquids Gd$_3$Ga$_5$O$_{12}$ (GGG) \cite{77,78} and SrCr$_{0.9}$Ga$_{12-9p}$O$_{19}$ (SCGO) \cite{79,80}. Furthermore, susceptibility, neutron scattering, and Muon spin resonance data on Tb$_2$Ti$_2$O$_7$ and SCGO show the persistence of spin fluctuations even after partial spin freezing occurs \cite{29,37,38,81,82,83}.

5.6 Conclusion

Though we have not proven that Dy$_{2.67}$Ti$_{1.33}$O$_{6.67}$ is a cooperative paramagnet, creating a liquid like state by adding competing interactions to an ice state is quite intriguing, and any sensitivity of such a transformation to the Ti disorder in Ho$_{2.67}$Ti$_{1.33}$O$_{6.67}$ is curious. Subsequent studies involving AC susceptibility and neutron scattering measurements on both powders and single crystals of Ho$_2$(Ho$_x$Ti$_{2-x}$)O$_{7-x/2}$ and Dy$_2$(Dy$_x$Ti$_{2-x}$)O$_{7-x/2}$ for different values of x need to be performed before any solid conclusions can be made. Nevertheless, the energy scales involved in these materials allow probing of their properties by many different techniques, and further experiments
on these materials will undoubtedly shed light into the development of correlations and order within materials.


33. Quantum Design, Inc. 6325 Lusk Boulevard, San Diego CA 92121.


48. B.G. Ueland, unpublished.
65. B.G. Ueland et al., manuscript in preparation.
67. R.G. Melko et al., cond-mat/0308282.
Appendix A

AC Susceptibility Measurements on a Dilution Refrigerator

A.1 Schematic of the Electrical Circuits Used for AC Susceptibility Measurements

Figure A.1: The electrical circuits used to measure the AC susceptibility as described in Section 3.12.3. For most of the measurements, the secondaries were connected to a preamplifier located before the secondary lock-in amplifier. All experimental connections between the dilution refrigerator and external instruments were made using coaxial cables with BNC connectors. The resistances used in the primary circuit were $R_1 = 48.2 \, \Omega$ and $R_2 = 1.085 \, k\Omega$, and the ground for the primary circuit was taken at the shield of the BNC connector supplying the AC voltage. The reference phase for the secondary lock-in was taken between one of the $R_2$ resistors and the primary circuit’s ground.
A.2 Procedure for Converting the Measured Voltage to Susceptibility

Converting the voltage signal received by the secondary lock-in amplifier into a measure of magnetic susceptibility relies on Faraday’s Law (Equation 3.1). Labeling the secondary coil containing the sample as coil 1 and the empty secondary coil as coil 2, we can write the induced EMF in the circuit in CGS units as Equation A.1:

$$E = -\frac{1}{c}\left(\frac{d\phi_1}{dt} + \frac{d\phi_2}{dt}\right), \quad (A.1)$$

where the magnetic flux $\phi$ going through each coil is equal to the magnitude of the magnetic field along the axis of the coil times the coil’s cross sectional area. Since both secondaries have equal dimensions, we can label the number of turns of wire in each secondary as $N_s$ and the cross sectional area of each as $A_s$. Remembering that we can write the magnetic field $B$ inside of each coil as Equation A.2:

$$B = H + 4\pi M, \quad (A.2)$$

then the total EMF induced in the secondary circuit by an external magnetic field $H$ is Equation A.3:

$$E = -\frac{1}{c}\left(\frac{d(H + 4\pi M)}{dt}N_sA_s + \frac{dH}{dt}(-A_s)N_s\right), \quad (A.3)$$

where the negative sign in front of the cross sectional area for coil 2 results from the coils being wound in opposite directions. We can easily see from Equation A.3 that balancing the secondary coils cancels out any EMF induced by a field simultaneously present in
both coils. Hence, when we apply an alternating field to the coils, only the response of
the magnetization of the sample in coil 1 produces an EMF, yielding Equation A.4:

\[ E = - \frac{4\pi}{c} N_s A_s \frac{dM}{dt}. \]  \hspace{1cm} \text{(A.4)}

We then rewrite Equation A.4 as Equation A.5 using the definition for the susceptibility
of a magnet in a small field:

\[ E = - \frac{4\pi}{c} N_s A_s \frac{d(f\chi H)}{dt}, \]  \hspace{1cm} \text{(A.5)}

where \( f \) is called the filling factor of the coil and depends on the volume of the coil
occupied by the sample.

Next, we use the infinite solenoid approximation and Ampere’s Law to derive the
field \( H \) created by the primary coil. We start by defining \( n \) as the number of turns per
unit length of the coil and \( j \) as the current in each loop of wire. This leads to
Equation A.6:

\[ H = \frac{4\pi}{c} nj. \]  \hspace{1cm} \text{(A.6)}

If we assume that \( j \) changes periodically in time at an angular frequency \( \omega \), then \( H \) will
also be time dependent and we can again rewrite Equation A.5, yielding Equation A.7:

\[ E = -\left( \frac{4\pi}{c} \right)^2 N_s A_s nf \chi \frac{d(j\exp(i\omega t))}{dt} \]  \hspace{1cm} \text{(A.7)}

followed by Equation A.8:

\[ E = -i \left( \frac{4\pi}{c} \right)^2 N_s A_s nf \chi \omega \exp(i\omega t). \]  \hspace{1cm} \text{(A.8)}
Now, we write $E$ as a time dependent quantity with the same frequency as $H$ giving Equation A.9:

\[ E = V \exp(i\omega t), \quad (A.9) \]

which leads to Equation A.10:

\[ V = -i\left(\frac{4\pi}{c}\right)^2 N_s A_s n f j \omega. \quad (A.10) \]

Finally, writing $V$ and $\chi$ as complex variables and equating real and imaginary parts gives Equations A.11 and A.12:

\[ \chi' = -\left(\frac{c}{4\pi}\right)^2 \frac{V''}{N_s A_s n j \omega f}, \quad (A.11) \]

\[ \chi'' = \left(\frac{c}{4\pi}\right)^2 \frac{V'}{N_s A_s n j \omega f}. \quad (A.12) \]
Appendix B

Demagnetization Effects

The purpose of this appendix is to introduce the concept of demagnetization effects on magnetic samples and show their relevance to the experiments performed for this thesis.

When an external magnetic field $H$ polarizes a uniform magnetic material, the magnetization of the sample creates an internal field $[H' - H]$ that, in general, changes the effective field acting on the material. Following the discussion given in Morrish [6], for a uniform ferromagnetic material with an ellipsoidal shape lying with its long axis along the external field, we can picture north and south magnetic poles appearing on opposing sides of the sample as in Figure B.1. Mathematically, for a sample with magnetization per unit volume $M$, Equation B.1 gives the correct internal field as:

$$H' = H - DM,$$  \hspace{1cm} (B.1)

where $D$ is a tensor describing a shape dependent demagnetization factor, and tables listing the values of $D$ for different shapes are available [6].

For our purposes, we will consider two shapes: a sphere and a long thin ellipsoid of revolution. The case of a sphere may apply to our powder samples, because we can consider the particulates to be micron sized spherical crystals. However, in practice it may be more practical to look at the bulk shape of the powder while it is measured. Since previous studies disagree on the proper treatment for the demagnetization effects in a powder sample, we will simply consider here a large single crystalline sphere. Also, we
examine the case of a long ellipsoid aligned with its long axis along the magnetic field, since it may apply to the needle shaped pressed powder samples measured by our experiments on the stuffed spin ices. We will also assume for both cases that the magnetization per ion is $M = 10 \mu_B$/ion, since it represents the upper limit for the lanthanides considered in this thesis, and that the magnetization is uniform throughout the samples. These assumptions will give us an idea of the maximum affects of the demagnetization field on our results.

Figure B.1: A cartoon of the demagnetization effect for an ellipsoid with uniform magnetization $M$ lying along an external field $H$. The polarization of the ellipsoid creates magnetic poles at either end of the sample, which in turn create an effective internal field $[H' - H]$.

Appendix II in Morrish [6] tells us that for a spherical magnet $D = 4\pi/3$, and for a long ellipsoid having a 2 to 1 ratio between its major and minor axes, which was typical for both susceptibility and heat capacity measurements on the pressed stuffed spin ice samples, $D = 2.18$. If we consider 1 mol of Ho, completely saturated by a magnetic field, the magnetization is $M \approx 56000$ emu. Next, using the fact that each sample contained at
most $10^5$ mols of the magnetic lanthanide, gives us a maximum magnetization of $M \approx 0.56$ emu. Then using the average volume of a sample as $V \approx 0.2 \times 0.1 \times 0.1 = 0.002 \text{ cm}^3$, we get a normalized magnetization of $M \approx 280 \text{ emu} / \text{cm}^3$. Substituting this number and the values of $D$ into Equation B.1 gives us $D_{sp} = 1173$ Gauss and $D_{nc} = 610$ Gauss, for the sphere and thin needle cases, respectively, for fully saturated samples (i.e. at very high fields).

From these maximum limiting results, we see that correcting for demagnetization effects would have been sensible, if we were more interested in precisely determining the magnetic fields at which we were measuring. Additionally, since we used pressed powder samples an ambiguity existed as to which value of $D$ and which sample volume to use, thus we decided it would be more prudent to present uncorrected data. As it stands, the results for $\text{Tb}_2\text{Ti}_2\text{O}_7$ were mainly qualitative in nature, and we measured samples of different shapes to show that the sample’s shape did not qualitatively change our results. For the stuffed spin ices, our discussion on the field effects was limited to the effects of a $H = 1 \text{ T}$ field on the heat capacity of the samples and the saturation magnetization value of each sample. For the saturated magnetization the demagnetization effect would have changed the applied field by $\approx 13\%$ between the $x = 0$ and $x = 0.67$ SSI samples (this number mainly comes from the $\approx 13\%$ difference in densities between the $x = 0$ and $x = 0.67$ SSI samples). Since we were more concerned about the saturated moment, and not the field at which saturation occurred, the demagnetization effect does not change our discussion.

In practice, we found that demagnetization effects could change our derived values for $\theta_W$ at most $\approx 15\%$, if we considered the pressed powder samples as having
uniformly magnetized needle like shapes. However, since we estimated the error in the mass of each sample as \( \approx 5\text{-}10\% \) (due to the mass of each sample be comparable to the precision of the scale), and since the samples were polycrystalline, as discussed above, we decided not to show data after performing a demagnetization correction. Additionally, the change in \( \theta_w \) as a function of \( x \) was much larger than 15\%.
Appendix C

The Van Vleck Susceptibility

The Van Vleck susceptibility \([4][50]\) is responsible for the temperature independent susceptibility observed in \(\text{Tb}_2\text{Ti}_2\text{O}_7\) at low temperatures and high fields. It derives from the interaction between an electron orbiting the nucleus of an atom and an externally applied magnetic field. Treating the interaction as a perturbation, we can write Equation C.1:

\[
\Delta E_n = \mu_B H \langle n | L + g_0 S | n \rangle + 
\sum_{m \neq n} \frac{| \langle n | \mu_B H \left( L + g_0 S \right) m \rangle |^2}{E_n - E_m} + \frac{e^2}{8mc^2} H^2 \langle n | \sum_{i} \left( x_i^2 + y_i^2 \right) n \rangle. \tag{C.1}
\]

The first term in this equation gives the change in energy of an electron in state \(n\), due to the Zeeman splitting of its angular momentum multiplet. We can find the susceptibility due to the remaining two terms by taking the second derivative with respect to field. If we take \(n = 0\), we see that the last term in the equation yields a susceptibility solely due to the orbital motion of the electron, which is the Larmor diamagnetic susceptibility present in all atoms. Next, taking the second derivative of the middle term and normalizing by sample size yeilds Equation C.2:

\[
\chi_{VV} = \frac{N}{V} 2\mu_B^2 \sum_n \left| \langle 0 | \left( L_z + g_0 S_z \right) n \rangle \right|^2 \frac{1}{E_n - E_0}, \tag{C.2}
\]
which is the Van Vleck susceptibility. Clearly, the Van Vleck susceptibility stems from electrons switching between different orbital states, or rather between the different crystal field levels created by the Stark splitting inside of a material. As is the case for Tb$_2$Ti$_2$O$_7$, if two crystal field levels with different total angular momentum lay close enough that at low temperatures an applied magnetic field can still excite electrons between them, the Van Vleck term will yield an apparently temperature independent paramagnetic susceptibility.
Appendix D

Data on the Stuffed Pyrochlore $\text{Tb}_2(\text{Tb}_x\text{Ti}_{2-x})\text{O}_{7-x/2}$, $0 \leq x \leq 0.67$

This appendix contains preliminary data taken on the stuffed pyrochlore $\text{Tb}_2(\text{Tb}_x\text{Ti}_{2-x})\text{O}_{7-x/2}$. Data were taken in the MPMS, PPMS, and dilution refrigerator, and we used the He$^3$ insert to make the heat capacity measurements.

Figure D.1: The Weiss temperature $\theta_W$ and effective moment $p$ as a function of stuffing $x$ in $\text{Tb}_2(\text{Tb}_x\text{Ti}_{2-x})\text{O}_{7-x/2}$. The parameters were obtained from fits on $H = 0.1$ T magnetization data to the Curie Weiss law, over $T = 7 – 14$ K. (These data were taken by M.L. Dahlberg.)
Figure D.2: Magnetization versus field data on $\text{Tb}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}$ at $T = 2$ K. (These data were taken by M.L. Dahlberg.)
Figure D.3: The magnetic specific heat versus temperature of $\text{Tb}_2(\text{Ti}_{2-x}\text{Tb}_x)\text{O}_{7-x/2}$ at $H = 0$ and 1 T. All data were taken upon cooling in the applied magnetic field. Lattice contributions were subtracted out by scaling to data on non-magnetic $\text{Lu}_2(\text{Lu}_{x}\text{Ti}_{2-x})\text{O}_{7-x/2}$, $x = 0$, 0.3, and 0.67. (Hyperfine contributions should not become important until below $T = 400 \text{ mK}$ [31].)
Figure D.4: The magnetic specific heat divided by temperature versus temperature of $\text{Tb}_2(\text{Ti}_{2-x}\text{Tb}_x)\text{O}_{7-x/2}$ at $H = 0$. Lattice contributions were subtracted out by scaling to data on non-magnetic $\text{Lu}_2(\text{Lu}_{x}\text{Ti}_{2-x})\text{O}_{7-x/2}$, $x = 0$, 0.3, and 0.67. (Hyperfine contributions should not become important until below $T = 400$ mK [31].)
Figure D.5: The magnetic specific heat divided by temperature versus temperature of Tb$_2$(Ti$_{2-x}$Tb$_x$)O$_{7-x/2}$ at $H = 1$ T (field cooled). Lattice contributions were subtracted out by scaling to data on non-magnetic Lu$_2$(Lu$_x$Ti$_{2-x}$)O$_{7-x/2}$, $x = 0$, 0.3, and 0.67. (Hyperfine contributions should not become important until below $T = 400$ mK [31].)
Figure D.6: The integrated magnetic entropy versus temperature of $\text{Tb}_2(\text{Ti}_{2-x}\text{ Tb}_x)\text{O}_{7-x/2}$ at $H = 0$. Lattice contributions were subtracted out by scaling to data on non-magnetic $\text{Lu}_2(\text{Lu}_{x}\text{ Ti}_{2-x})\text{O}_{7-x/2}$, $x = 0$, 0.3, and 0.67.
Figure D.7: The integrated magnetic entropy versus temperature of $\text{Tb}_2(\text{Tb}_x\text{Ti}_{2-x})\text{O}_{7-x/2}$ at $H = 1$ T (field cooled). Lattice contributions were subtracted out by scaling to data on non-magnetic $\text{Lu}_2(\text{Lu}_x\text{Ti}_{2-x})\text{O}_{7-x/2}$, $x = 0, 0.3,$ and $0.67$. 

\[ S \left[ \frac{J}{\text{mol}_{\text{Tb}} \text{K}} \right] \]

\[ \text{Temperature} \left[ \text{K} \right] \]
Figure D.8: The real part of the $H = 0$ AC susceptibility of $\text{Tb}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}$ versus temperature for various measurement frequencies. Open symbols represent data taken in the ACMS, while closed circles represent data taken in the dilution refrigerator. These data were calibrated assuming $\chi'(H = 5 \text{ T}, T = 1.8 \text{ K}) = 0$ (see Section 3.5.3).
Figure D.9: The real part of the $f = 50$ Hz AC susceptibility of $\text{Tb}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}$ versus field at various temperatures, and field sweeping rates. These data were calibrated assuming $\chi'(H = 5 \text{ T}, T = 1.8 \text{ K}) = 0$ (see Section 3.5.3).
Figure D.10: The real part of the $f = 50$ Hz AC susceptibility of $\text{Tb}_{2.67}\text{Ti}_{1.33}\text{O}_{6.67}$ versus field at $T = 0.3$ K and 0.2 K, taken after initially zero field cooling or field cooling the sample. These data were calibrated assuming $\chi'(H = 5 \text{ T}, T = 1.8 \text{ K}) = 0$ (see Section 3.5.3).
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