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AC susceptibility and heat capacity studies of the geometrically frustrated pyrochlores terbium titanium tin oxides and holmium titanates

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AC SUSCEPTIBILITY AND HEAT CAPACITY STUDIES OF THE
GEOMETRICALLY FRUSTRATED PYROCHLORES

$\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ AND $\text{Ho}_{2-x}\text{R}_x\text{Ti}_2\text{O}_7$

by

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A thesis submitted in partial fulfillment
of the requirements for the

**Master of Science Degree in Physics
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College of Sciences**

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University of Nevada, Las Vegas
December 2009**

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THE GRADUATE COLLEGE

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AC Susceptibility and Heat Capacity Studies of the Geometrically Frustrated Pyrochlores $\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ and $\text{Ho}_{2-x}\text{R}_x\text{Ti}_2\text{O}_7$

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ABSTRACT

AC Susceptibility And Heat Capacity Studies Of The Geometrically Frustrated Pyrochlores $\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ And $\text{Ho}_{2-x}\text{R}_x\text{Ti}_2\text{O}_7$

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Materials with a geometrically frustrated magnetic pyrochlore lattice have been of interest due to their unusual ground states. $\text{Tb}_2\text{Ti}_2\text{O}_7$ is known for having a spin liquid ground state which does not transition to a long-range ordered state down to at least 50 mK. $\text{Ho}_2\text{Ti}_2\text{O}_7$ has a macroscopically degenerate spin ice ground state which resembles that of the proton ordering in water ice. Heat Capacity measurements of $\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ were done down to 0.36 K and AC magnetic susceptibility measurements of $\text{Ho}_{2-x}\text{Y}_x\text{Ti}_2\text{O}_7$ and $\text{Ho}_{2-x}\text{La}_x\text{Ti}_2\text{O}_7$ were done for frequencies from 10 Hz to 10 kHz down to 1.8 K, both in magnetic fields up to 9 T. These experiments were performed in an effort to further understanding of the factors that lead to their unusual behavior and to study the effects of introducing disorder through doping with nonmagnetic elements. Determination of the effect of an external field on the hyperfine crystal field at the Tb sites was done. In addition, unusual behavior in the ac susceptibility of the Ho samples at lower temperatures was observed.

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CHAPTER 1

INTRODUCTION

Geometric Frustration

Most magnetic systems spontaneously transition to a state of long range magnetic order at some critical temperature. The type of ordering (ferromagnetic, antiferromagnetic, ferrimagnetic, etc.) depends on the type of interactions between the spins. Systems with competing magnetic interactions may resist this ordering. A material that exhibits these competing interactions is said to be frustrated. Frustration in systems is common, but cases where the competing interactions are of the same magnitude make the frustration very strong, which can lead to unusual and complex phenomena such as highly degenerate ground states.

Geometric frustration arises when incompatibilities between the spin interactions and the symmetry of the lattice itself do not allow all neighboring spins to satisfy the dominant magnetic interaction. The simplest case of this is illustrated by a triangle of antiferromagnetically coupled Ising spins, shown in Figure 1, first studied by G.H. Wannier in 1950 [1]. The spins can only point up or down, and will preferentially orient anti-parallel to each other. Two of the spins can easily orient in opposite directions and satisfy the interaction, but the last spin cannot. Both orientations conflict equally with one of the first two spins, so there is no preferred lowest energy orientation for the third spin. This causes a highly degenerate ground state.

This frustration can sometimes be relieved by making one orientation more favorable. Placing the frustrated material in an external magnetic field causes the spins pointing in same direction of the field to have lower energy than those pointing against the field, by:

$$\Delta E = B \cdot \mu - (-B \cdot \mu) = 2(B \cdot \mu) \quad (1.1)$$

where B is the external field and μ is the magnetic moment of a single spin. Also, because geometric frustration depends on lattice symmetries, one would expect perturbations to the lattice to relieve the frustration. Non hydrostatic pressure would cause unequal distances between competing pairs of spins and therefore affect the relative strengths of the rival interactions. Hydrostatic pressure will shorten the average distances between spins and can possibly change the nature of the interactions. Randomly doping the material with atoms of slightly different size or replacing the magnetic atoms with non magnetic ones would also be expected to break the lattice symmetries.

As geometrically frustrated magnets are ideal models for complex phenomena ranging from protein folding to nuclear fragmentation to financial systems, this work allows a direct experimental probe of extremely complex models that are applicable to a broad range of disciplines. The experimental tools allow for precise adjustment of the magnetic interactions and allow rigorous experimental testing of theory in these model systems.

Magnetic Order

Above a critical temperature, magnetic systems with either ferromagnetic or antiferromagnetic interactions will be in a paramagnetic state. There is no long range order because thermal fluctuations overpower the magnetic interactions, leading to randomly oriented spins. Below a certain temperature, called the Curie temperature, T_C , for ferromagnetic systems and the Néel temperature, T_N , for antiferromagnetic systems, the thermal fluctuations will no longer be strong enough to disrupt the magnetic interactions and the system will usually spontaneously transition to an ordered state.

In a ferromagnet, the neighboring spins favor orienting parallel to each other, so the bulk material has a net magnetic moment. Using the mean field approximation,

in which it is assumed that each magnetic atom experiences a field proportional to it the material's magnetization, the temperature at which the system orders can be estimated from from the Curie-Weiss law at temperatures above T_C :

$$\chi = \frac{C}{(T - T_C)} \quad (1.2)$$

where $\chi = M/H$ is the magnetic susceptibility of the paramagnetic phase, T_C is the critical temperature, C is the Currie constant:

$$C = \frac{Np^2\mu_B^2}{3k_B T} \quad (1.3)$$

and p is the effective number of Bohr magnetons:

$$p = g[J(J + 1)]^{\frac{1}{2}} \quad (1.4)$$

where N is the total number of atoms, J is the angular momentum quantum number, and g is the Landé factor:

$$g = 1 + \frac{j(j + 1) + s(s + 1) - l(l + 1)}{2j(j + 1)} \quad (1.5)$$

This only works for temperatures well above T_C , and it can be seen from a graph of the inverse susceptibility versus temperature that it diverges from a straight line as it approaches T_C . The exchange integral, J_{ex} , which gives a measure of the strength of the exchange interactions, can usually be approximated from T_C using:

$$J_{ex} = \frac{3k_B T_C}{2zS(S + 1)} \quad (1.6)$$

where z is the number of nearest neighbors, and S is the magnetic spin. This assumes that farther neighbors and dipole interactions are negligible [9].

In an antiferromagnet, the spins favor orienting antiparallel to each other. This can be viewed as two interpenetrating ferromagnetic lattices of the same ion that have a strong antiferromagnetic interaction between them. This gives an equation analogous to the Curie-Weiss Law for antiferromagnets:

$$\chi = \frac{C}{T + T_N} \quad (1.7)$$

Note that this formula is very similar to equation (1.2) for ferromagnets. Typically, one combines equations (1.2) and (1.7) and fits experimental data to

$$\chi = \frac{C}{T - \theta} \quad (1.8)$$

where values for the Weiss Temperature θ can be positive (ferromagnetic) or negative (antiferromagnetic), depending on the type of magnetic interaction.

Typically, values of T_N and T_C are on the order of $|\theta|$. In systems that display frustration, the magnetic ordering temperature can be much lower than that of $|\theta|$. Defining a frustration parameter f as the ratio of $|\theta|$ to the ordering temperature ($T_{mag} = T_N$ or T_C), one can get an idea of the degree of frustration. A material having $f > 1$ corresponds to frustration. A value of $f > 10$ cannot be described by mean-field theory, indicating a more complicated state. This can be considered a benchmark for strong geometric frustration [10]. Table 1 gives values of f for some materials that are strongly frustrated and some materials that would be considered “normal” for comparison.

Dipole and exchange effects from farther neighbors often account for this difference. Another odd effect of frustration is that for strongly frustrated magnetic systems, the susceptibility follows ideal linear Curie-Weiss behavior much more closely for temperatures well below the expected Néel temperature as shown in Figure 2.

Below the ordering temperature for both cases, the magnetization diverges from

this simple behavior. The magnetization goes to infinity for the Curie-Weiss law at T_C , and more complex behavior takes over for lower temperatures. For antiferromagnets, the magnetization has its maximum value at T_N , where there is a well defined cusp. This feature is matched by a peak in the heat capacity, corresponding to a dramatic change in magnetic entropy that marks the transition as well.

Spin Interactions

The interactions between spins on different lattice sites are what give rise to spontaneous magnetic order. The purely quantum-mechanical exchange field is often what dominates these interactions. This effect arises from the Pauli exclusion principal, which prevents identical fermions from being in the same state. The wavefunctions of the neighboring spins overlap and must be anti-symmetric under an exchange of coordinates. This keeps parallel spins from being near each other, because the probability of finding them goes to zero as they approach the same position, and therefore the Coulomb repulsion is lessened. There is then a difference in energy between parallel and antiparallel spins. This can be represented by an energy term $-2J\mu_1 \cdot \mu_2$, where J is the exchange integral, given by:

$$J = \int d^3r_1 d^3r_2 \frac{\Psi_1^*(1)\Psi_2^*(2)\Psi_1(2)\Psi_2(1)}{r_{12}} \quad (1.9)$$

In a solid, the Coulomb interactions are more complex due to repulsion between electrons and attraction to neighboring nuclei, so J can be positive, indicating ferromagnetic interactions that favor parallel alignment, or J can be negative, indicating antiferromagnetic interactions that favor antiparallel alignment. The exchange energy for a solid can be represented by the Heisenberg model:

$$H^{ex} = - \sum_i \sum_{i \neq j} J_{ij} S_i \cdot S_j \quad (1.10)$$

where S_i and S_j are the total spins of the atoms at sites i and j [13, 14]. The exchange interaction depends on the overlap of wavefunctions, so the interactions beyond the nearest neighbor are often negligible.

The spins can also be treated as classical dipoles, which interact with each other and can create another preferred spin alignment. The dipole-dipole interactions are proportional to $1/r^3$, so they are longer range than the exchange interaction. In a solid, atoms farther than nearest neighbor must be taken into account. This can make calculations complicated and whether the exchange or dipole interactions dominate depends on the system. The dipole-dipole interaction energy is given by:

$$H^{dip} = \frac{1}{2}(g\mu_B)^2 \sum_{i,j} \left\{ \frac{S_i \cdot S_j}{r_{ij}^3} - 3 \frac{(S_i \cdot r_{ij})(S_j \cdot r_{ij})}{r_{ij}^5} \right\} \quad (1.11)$$

Structure of $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$

In the compounds terbium titanate and holmium titanate, the rare earth ions form a magnetic pyrochlore lattice, shown in Figure 3. This lattice of corner sharing tetrahedrons, essentially a three dimensional triangular lattice, is highly frustrated. Both of these compounds show unusual ground states. The Tb^{3+} ions in $\text{Tb}_2\text{Ti}_2\text{O}_7$ are antiferromagnetically coupled [6], and the Ho^{3+} ions have an effective ferromagnetic coupling [4]. The rare earth ions have relatively large dipoles due to unpaired localized f electrons and relatively small overlap of wavefunctions, so the dipole interaction energy is of the same magnitude as the exchange energy, unlike in transition metals where the dipole-dipole interaction is negligible. Both ions have moments of about $10\mu_B$, but coordination with the O^{2-} ions surrounding the Tb^{3+} ions in $\text{Tb}_2\text{Ti}_2\text{O}_7$ reduces its permanent moment to just over $5\mu_B$ [4, 7].

Both have highly anisotropic crystal fields which force the spins to point either directly into or out of the tetrahedra in the $\langle 111 \rangle$ direction, making them effectively Ising spins. This has been shown from a combination of magnetic susceptibility mea-

surements, inelastic neutron-scattering measurements, heat capacity, and theoretical crystal field calculations [4, 7]. The single ion ground states are doublets, with the first excited state about 220 K above for $\text{Ho}_2\text{Ti}_2\text{O}_7$ [8] and only 15-20 K above for $\text{Tb}_2\text{Ti}_2\text{O}_7$ [7].

The ground state of $\text{Tb}_2\text{Ti}_2\text{O}_7$ appears to be a spin liquid. In this state, which is also called a cooperative paramagnet, there is no transition to long range magnetic order despite the development of strong short range interactions. This ground state was theoretically predicted for a pyrochlore lattice, but $\text{Tb}_2\text{Ti}_2\text{O}_7$ was the first compound to show promise of staying completely disordered all the way to zero Kelvin. The spins remain randomly oriented and dynamic down to the lowest temperatures measured, which is at least 50 mK, even though AF correlations develop below ≈ 50 K and $\theta \approx -18$ K [6].

The ground state of $\text{Ho}_2\text{Ti}_2\text{O}_7$ is a spin ice. It has an arrangement analogous to the proton ordering in water ice, with two spins on each tetrahedron pointing in, and two out, which leads to the largest possible moment on every local tetrahedron, shown in Figure 4. This is because, despite susceptibility measurements indicating AF interactions, the strong dipole interaction leads to an overall ferromagnetic interaction. This large zero temperature degeneracy is equivalent to the frozen in residual entropy in water ice discovered by Pauling [4].

While the residual entropy is difficult to recover in water ice, the application of a magnetic field was used successfully to release the entropy in spin-ice for $\text{Ho}_2\text{Ti}_2\text{O}_7$ [4] and for $\text{Dy}_2\text{Ti}_2\text{O}_7$ [15]. In other words, a magnetic field can be used to destroy the spin-ice state by breaking the large degeneracy that arises from the spin ice rules (2 spins in, 2 spin out of each tetrahedron).

In this thesis I will study the way in which the frustration is relieved in magnetically frustrated pyrochlore systems. This will include both spin liquid and spin ice states that are disturbed by chemical substitution and/or applied magnetic fields. By

its nature, geometric frustration is highly dependent on the physical structure of the crystal lattice. Substitutions of different atoms at random sites in the lattice would be expected to break the symmetries that the degenerate states rely on and relieve the frustration. Replacing some of the titanium sites in $\text{Tb}_2\text{Ti}_2\text{O}_7$ with larger tin atoms distorts the lattice, altering the positions of the magnetic terbium ions. Replacing some of the holmium atoms in $\text{Ho}_2\text{Ti}_2\text{O}_7$ with chemically similar, but non-magnetic, lanthanum and yttrium atoms will create holes in the magnetic lattice, effectively isolating some individual spins from neighbors. Various amounts of these dopants were substituted into these compounds. Subsequent, heat capacity and ac magnetization measurements were performed at various applied magnetic field strengths and temperatures in order to measure the strength of the frustration in the altered lattices, and to investigate the nature of the frustration by testing the conditions under which the materials have frustration relieved in the form of long range ordering.

CHAPTER 2

EXPERIMENTAL PROCEDURE

Polycrystalline samples of $\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ for $x = 0, 0.05, 0.1, 1$, and 2 , as well as $\text{Ho}_{2-x}\text{R}_x\text{Ti}_2\text{O}_7$ for $\text{R} = \text{La}$ with $x = 0.1, 0.4, 1.7$ and $\text{R} = \text{Y}$ with $x = 1.3, 1.5$, and 1.8 , were all obtained from an outside source. They were made by firing stoichiometric amounts of the appropriate oxides at high temperatures for several days with intermittent grindings as described elsewhere [17].

All measurements were performed in a Quantum Design PPMS, shown in Figure 5. Using various optional parts, the system can be configured to perform heat capacity, magnetization, and resistivity measurements in a temperature range of 0.36 K to 400 K and in magnetic fields up to 9 T.

Temperature is maintained through a balance of resistive heating and evaporative cooling of liquid helium. Liquid ^4He boils at 4.18 K at atmospheric pressure, but by pumping on it to reduce pressure the boiling point is lowered and the system can reach 1.8 K. A separate self-contained ^3He system, shown in Figure 6, can be used to reach temperatures down to 0.36 K. The boiling point of ^3He is 3.2 K, so the ^4He system is used to first liquefy the ^3He , and then it is pumped on in order to reach lower temperatures. ^3He is much rarer than ^4He , so the ^3He system is sealed so that the gas can be continuously reused.

A magnetic field is provided by a superconducting solenoid around the sample chamber, inside the same helium reservoir used for the ^4He cooling. A persistent current up to 46.7 A is sustained in the solenoid to generate the large magnetic fields.

Heat Capacity Measurement

The heat capacity of the samples is measured using a quasi-adiabatic thermal relaxation technique. The samples are ground and pressed into pellets. They are

then secured to an alumina stage with Apiezon N grease in order to assure good thermal contact. The stage is supported by platinum wires connected to a resistive heater and a thermometer, all inside a removable copper puck, shown in Figure 7. In order to ensure that the wires are the only significant thermal link to the stage, the sample chamber is evacuated to a pressure of about 0.01 mTorr using a turbo-pump. The sample puck is brought to thermal equilibrium at the desired temperature, and then a heat pulse is sent along the wires to the resistive heater on the underside of the stage. The temperature is continuously measured as the stage cools back to base temperature. The temperature rise is kept small, at about 2% of the base temperature, in order to resolve sharp peaks in the data and to make sure that the heat capacity does not vary significantly over the measurement. The change in temperature with time is fit to a simple exponential model given by:

$$C_{total} \left(\frac{dT}{dt} \right) = -K_W(T - T_o) + P(t) \quad (2.1)$$

where C_{total} is the total heat capacity of the sample and platform, K_W is the thermal conductance of the supporting wires, T_o is the base temperature of the puck, and P is the heater power. The solution is exponential with characteristic time-constant τ equal to C_{total}/K . This assumes that the coupling between the stage and sample is perfect, but if it is not close enough then a model which fits to two time constants is needed:

$$C_{platform} \left(\frac{dT_p}{dt} \right) = -K_W(T_p - T_o) + K_g(T_s - T) \quad (2.2)$$

$$C_{sample} \left(\frac{dT_s}{dt} \right) = -K_g(T_s - T_p) \quad (2.3)$$

where K_g is the thermal conductance between the sample and platform. The heat capacity of the stage and grease alone is measured beforehand, so it can be subtracted from the total found from the fit to find the sample heat capacity. The simpler model

is used when measuring with no sample or for a very small sample, because the two-tau model diverges for 100% sample coupling.

This technique measures heat capacity at constant pressure, not constant volume. The change in volume of solids with pressure and temperature is small (at least for the temperatures measured in the current study), so C_p and C_v are considered equivalent in our results.

The heat capacities of all $\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ samples were measured to the lowest temperature possible, about 0.4 K, and in magnetic fields from 0 to 9 Tesla.

Magnetic Measurements

The PPMS functions as both a DC magnetometer and as an AC susceptometer. A set of copper drive and detection coils is inserted within the superconducting magnet, shown in Figure 8. The sample is moved through the coils using a servo motor and the induced signal in the detection coils is analyzed. The detection coils are arranged in a first order gradiometer configuration with two sets of counter-wound copper wires connected in series separated by several centimeters. A larger AC drive coil surrounds them both, which is also surrounded by and connected in series with a counter-wound compensation coil that reduces interaction with materials outside the coils. The AC Magnetization option for the PPMS is not compatible with the ^3He option, so the minimum temperature achievable is 1.8 K.

During DC measurements the sample is put in a constant persistent field, H , using the superconducting magnet, creating a moment, M , in the sample. It is then moved quickly through the detection coils and a signal is induced according to Faraday's Law. The magnetic susceptibility is calculated as:

$$\chi = \frac{M}{H} \tag{2.4}$$

For AC measurements, a small alternating field, dH , is applied to the sample chamber

using the drive coil, while a large constant field can still be applied by the superconducting magnet. The amplitude and phase of the sample’s response is received by the detection coils and compared with the drive signal. The change in the samples moment, dM , is found from this. The AC susceptibility is then calculated by:

$$\chi_{AC} = \frac{dM}{dH} \quad (2.5)$$

This is the local slope of the sample’s magnetization curve. The ideal sample response signal is 90° out of phase with the drive signal in accordance with Faraday’s law, but other factors lead to deviations. Therefore, the AC susceptibility can also be described by a real component, χ' , that is in phase with the ideal response and an imaginary component, χ'' , that is 90° out of phase with the ideal response. These values are indicative of the “stiffness” of the spins, or their resistance to flipping with the changing field.

The DC magnetizations of all the $\text{Ho}_{2-x}\text{R}_x\text{Ti}_2\text{O}_7$ samples were measured in a 0.1 Tesla persistent field down to the lowest temperature. Their AC susceptibilities were then measured in a 1 Tesla persistent field with a 10 Oe oscillating field at frequencies from 10 Hz to 10 kHz at temperatures from about 100 K down to 1.8 K as well. When spins ‘slow down’ (spin relaxation times can be as fast 10^{-14} s), our ac susceptibility measurements allow the exploration of time scales from 10^{-1} to 10^{-4} s. When combined with collaborators who perform neutron scattering, we can span time scales to 10^{-14} s allowing a wide dynamic measurement range.

CHAPTER 3

RESULTS AND ANALYSIS

Sn substitution in $\text{Tb}_2\text{Ti}_2\text{O}_7$

The magnetic heat capacities of all the $\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ samples from about 3 K to the lowest measured temperatures and at various applied field strengths are shown in Figures 9 through 13. Non-magnetic $\text{Y}_2\text{Ti}_2\text{O}_7$ was used to estimate the lattice contribution to the total heat capacity, and it was found that the lattice contribution was very small compared to the dominating magnetic contribution at these temperatures. The errors in the heat capacity measurements are on the order of 0.1%, which is smaller than the data points in the graphs.

In Figure 9, the zero applied field graph shows the spin liquid behavior of the pure $\text{Tb}_2\text{Ti}_2\text{O}_7$ sample down to our lowest applied temperature, as no features corresponding to coordination between the spins or a sharp feature indicating a transition to long range order are seen. All the other graphs show an upturn below 1 K that increases with applied field, which is believed to be part of a nuclear Schottky peak. This is caused by static Terbium electron spins reacting to the applied field, creating a very large internal field to which the Tb nuclear moments react. This shows that many Tb spins are static as they line up with each other, which means that the applied field breaks the spin liquid state [18]. A sharper feature at about 0.8 Kelvin in Figure 13 indicates that the pure $\text{Tb}_2\text{Sn}_2\text{O}_7$ transitions to what may be a type of a long range ordered spin ice state in zero field, even though there is evidence of slow magnetic fluctuations persisting that are similar to the spin liquid state [19].

The strong internal field splits the degenerate ground state by an energy gap .

The heat capacity for such a two level magnetic system is given by:

$$C = Nk \left(\frac{\Delta E}{kT} \right)^2 \frac{e^{\left(\frac{\Delta E}{kT}\right)}}{\left(1 + e^{\left(\frac{\Delta E}{kT}\right)}\right)^2} \quad (3.1)$$

In the high temperature limit, the trailing edge of the Schottky peak can be approximated by:

$$C \approx \frac{A}{T^2} \quad (3.2)$$

where, for nuclear spins:

$$A = \frac{Nk}{3} \left(\frac{I+1}{I} \right) \left(\frac{\mu_N B_{hyp}}{k} \right)^2 \quad (3.3)$$

with I as the nuclear spin of the magnetic atom, which is 3/2 for our Terbium, μ_N is a nuclear magneton, and B_{hyp} equal to the hyperfine magnetic field at the site of the magnetic atom. If there is a low temperature upturn in our heat capacity data, we can attribute it to the appearance of this nuclear entropy. It is important to note that this will only occur when the nuclear moments experience large static (at least on the order of heat capacity measurements which are typically many seconds) magnetic fields from the electron magnetic moments. This gives us a thermodynamic measurement of static magnetic moments that are typically involved in short or long-range magnetic order that can be determined by neutron scattering measurements. As our measurements are relatively easy to perform, they are a very useful ‘first step’ measurement to lead the way in performing more time and infrastructure intensive nuclear scattering measurements.

A , and therefore B_{hyp} , can be found by a least squares fit to the data below 1 K to:

$$C = \frac{A}{T^2} + bT^2 + cT \quad (3.4)$$

where the T^2 and T terms account for the non-nuclear (namely magnetic and lattice

as the systems in question are insulators) contributions. The hyperfine field was calculated from A , using equation (3.3). The results of these fits and calculations are collected in Tables 2 and 3, and shown in Figures 14 through 18. Errors are taken from the least squared fits from equation (3.4). In general, all the doped samples showed an increase in the hyperfine field up to about a 2 T applied field, where it then seemed to almost level off at just below 20 T, and then increased very slowly from there. The pure $\text{Tb}_2\text{Ti}_2\text{O}_7$ sample showed a fairly steady increase to about 22.5 T without leveling off. The $\text{Tb}_2\text{Sn}_2\text{O}_7$ sample showed what could be two plateaus; one from 2 to 3 T applied fields and another from 6 T on, although their significance is unknown.

La and Y substitution in $\text{Ho}_2\text{Ti}_2\text{O}_7$

The graphs of the imaginary part of the AC susceptibility divided by the DC magnetization versus temperature for each applied oscillating frequency show peaks which correspond to the temperature for which the applied frequency becomes larger than the actual spin frequency. These peaks occur because at lower frequencies the spins can more easily keep up with the changing magnetic field, and so will be more in phase with the drive field, going to just the DC response in the extreme low frequency limit. In the opposing limit, a frequency that is too high will result in the spins not having enough time to come into alignment with the oscillating field, reducing the magnitude of the in phase AC response.

In order for a single spin in one of the sample's two-in-two-out magnetic tetrahedra to flip, it must overcome the energy barrier between the degenerate ground state and the first-excited state. This is expected to result in Arrhenius, or thermally activated, behavior which is described by the equation:

$$t = t_o e^{\left(\frac{\Delta}{T_{peak}}\right)} \quad (3.5)$$

where t_o is the characteristic time between spin flips of the sample, t is the inverse of the AC drive coil frequency f , the peak temperature at that frequency is T_{peak} , and Δ is the energy barrier between states in Kelvin. Rearranging equation (3.5) gives:

$$\frac{1}{T_{peak}} = \frac{-1}{\Delta} \ln f + \frac{1}{\Delta} \ln t_o \quad (3.6)$$

From this equation, one would expect that a graph of inverse peak temperature versus the natural log of the input frequency would give a straight line whose slope could be used to determine the energy difference between the ground and first excited states, as in Figure 19.

An example of the utility of AC susceptibility measurements can be seen in past measurements of the spin ice compound $\text{Dy}_2\text{Ti}_2\text{O}_7$ [20]. These results in Figure 20 clearly show multiple relaxation processes. The ‘high temperature’ process at about 15 K has an energy barrier of about 191 K and is due to single spin flips being promoted to the first excited crystal field level. The low temperature process at about 2 K only has an energy barrier of about 8.9 K and is believed to be due to a cooperative effect involving multiple spin flips.

The results of the AC susceptibility measurements for the spin-ice $\text{Ho}_{2-x}\text{R}_x\text{Ti}_2\text{O}_7$ samples are shown in Figures 21 through 26.

All the χ_{AC}/χ_{DC} graphs show a larger peak at from 10 K to 20 K, and a smaller peak below 5 K, though the smaller peak could not be distinguished well due to either becoming lost in the tail of the larger peak or quickly shifting out of our temperature range. The Y doped samples showed that the larger peak increases in intensity and shifts to steadily higher temperatures with increasing drive field frequency, while the La doped samples showed a very different trend, even for samples that had similar ratios of Ho to non-magnetic atoms. All three La samples showed an initial decrease in peak intensities with rising frequencies, while the peak did not seem to shift at all.

Then the two samples that were least highly doped with $x = 0.4$ and $x = 0.1$ showed a very abrupt shift to higher temperature and reversed direction to start increasing with rising frequencies.

The larger peaks were fit to a Gaussian function in order to find their centers. The graphs of the peak temperatures versus the logarithm of the applied field frequency are shown in Figure 27. All errors are taken from the least squares fits to the Gaussian function. None of these graphs entirely show the Arrhenius behavior we were expecting. A value of about 270 K for the energy barrier was found in reference [8] using neutron spin echo (NSE) data which probes much higher frequencies (10^7 to 10^{11} Hz), but no parts of the data we obtained could be fit to obtain a similar value for Δ . Instead, large ranges of the frequencies showed no clear dependence of the peak temperatures on the resonant frequencies. The yttrium samples show plateaus of unchanging behavior up to about 120 Hz, then what looks like a linear trend that appears to be the expected Arrhenius behavior for the rest of the higher frequency range. Fits to the data for $Y = 1.3, 1.5$, and 1.8 showed values for Δ of $98.8 \text{ K} \pm 3.5 \text{ K}$, $94.5 \text{ K} \pm 3.6 \text{ K}$, and $92.17 \text{ K} \pm 6.0 \text{ K}$ respectively. This difference from the NSE data may be due to the presence of the other process with a similar time scale which caused the smaller peak. There appears to be no evidence of thermally activated behavior in the lanthanum samples for the entire range of frequencies. In the $\text{La} = 1.7$ sample, the peak temperature remains relatively constant, but the $\text{La} = 0.4$ and 0.1 samples show a sudden jump to another temperature at about 500 Hz, which then remains constant again. This difference in the highly doped La samples is because the larger La ions exert more chemical pressure on the lattice, forming a coexisting a non-pyrochlore phase for $x > 0.4$ [8]. The regions where the peaks become independent of temperature may be due to slower quantum relaxation processes, which essentially need zero activation energy, which become dominant at lower temperatures where the thermal process freezes.

CHAPTER 4

CONCLUSIONS

The most surprising results of the heat capacity measurements of the $\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ samples were that, despite the large amount of structural disorder introduced, none of the doped samples showed any abrupt transitions to a long range magnetic ordered state at any temperatures or fields in our measurement ranges. The upturns in the data at low temperatures for the applied fields do confirm that the spin liquid state is broken, though. In order to produce these upturns, at least some of the Tb spins must be static over the time scale of the measurements, which are on the order of seconds. This means that long range order does occur at low temperatures, but it develops slowly from short range order instead of from a collective phase transition. It is also noteworthy that an applied field of 2T makes the pure $\text{Tb}_2\text{Ti}_2\text{O}_7$ behave very similarly to $\text{Tb}_2\text{Sn}_2\text{O}_7$ [21]. The magnetic lattice likely transitions to a spin ice state like that of $\text{Ho}_2\text{Ti}_2\text{O}_7$ with correlations over single tetrahedrons, but still no translational symmetry over the entire lattice.

Though the results from the $\text{Ho}_{2-x}\text{R}_x\text{Ti}_2\text{O}_7$ samples do not necessarily match earlier NSE measurements, the differences can be explained by processes that are not active at the much higher frequencies that those techniques must be used. Further work would need to be done in order to better understand the exact nature of the new processes that these results reveal. The results from these different samples are very similar, despite very large substitutions of holes in the magnetic lattices which effectively isolate individual spins from each other. The frustrated spin-spin interactions are very robust, with little change in the crystal field and spin dynamics, especially in the Y doped samples.

While single crystal neutron measurements may be better for directly measuring the dynamics of individual spins in the lattice, bulk measurements like heat capacity

and AC susceptibility which can indirectly probe similar properties are much easier, faster, and cost effective. This makes them excellent compliments to each other, so that areas of likely interest can be identified using easier techniques, which can then be more thoroughly analyzed at a neutron source.

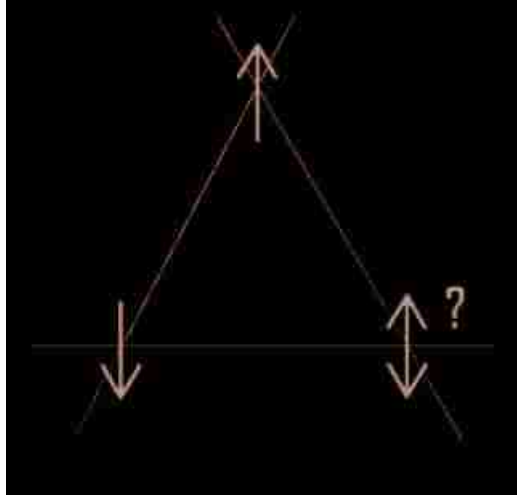


Figure 1 A triangular lattice with antiferromagnetically coupled Ising spins at its corners. The interaction between the two spins at the top and left are satisfied, but the third cannot be satisfied with both of the others at the same time, making neither state energetically favorable.

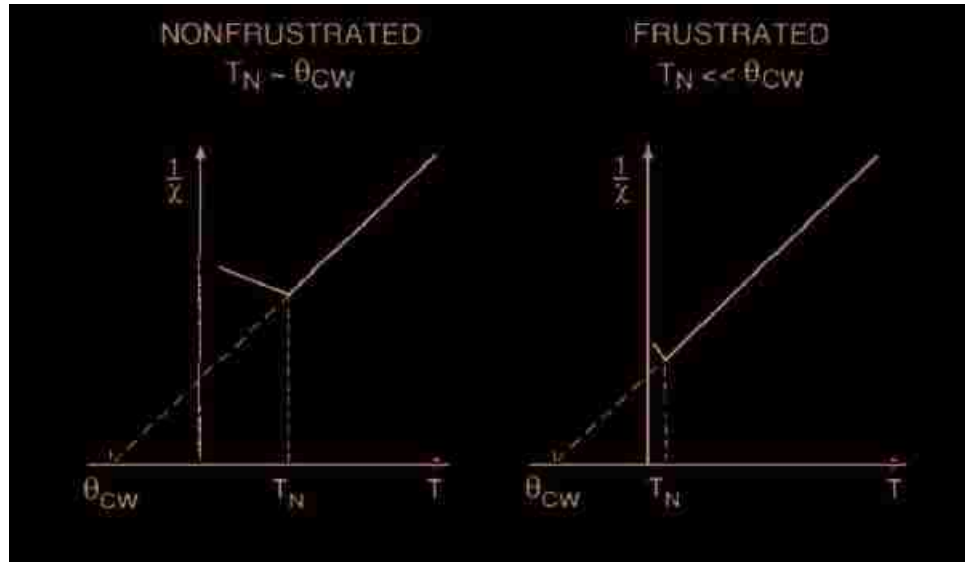


Figure 2 Taken from Ref. [10]. The graph on the left shows the expected behavior of a nonfrustrated antiferromagnetic material, which diverges from linear Curie-Weiss behavior near its ordering temperature, T_N , which is about equal to its projected Curie-Weiss Temperature, θ_{CW} . The graph on the right represents a strongly frustrated material with the same θ_{CW} , which stays linear until it orders at a much lower temperature.

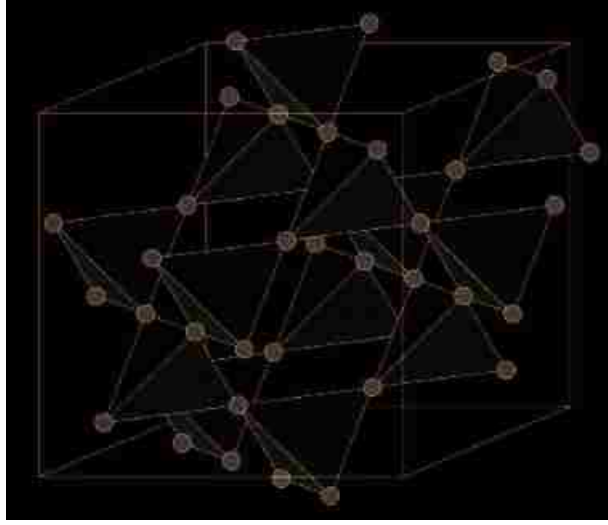


Figure 3 Taken from Ref. [16]. The pyrochlore lattice is an arrangement of corner sharing tetrahedra. In $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$, magnetic atoms sit on each corner and their spins are confined to point directly into or out of each tetrahedron.

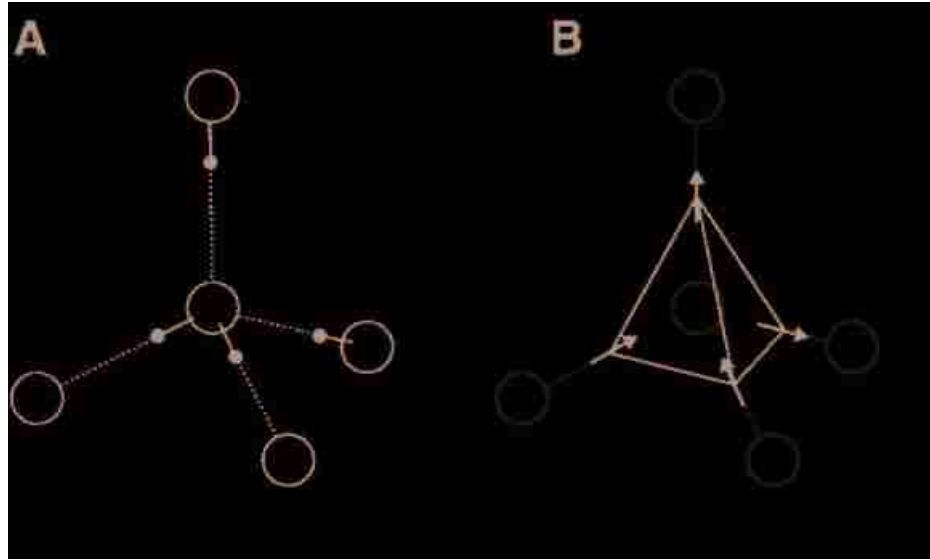


Figure 4 Taken from Ref. [4]. **(A)** shows the proton ordering in water ice, with two hydrogen atoms nearer each oxygen and two farther. **(B)** shows a single tetrahedron from the $\text{Ho}_2\text{Ti}_2\text{O}_7$ lattice showing the same arrangement, but with the hydrogen atoms replaced by vectors at the corners representing the direction of the spins.

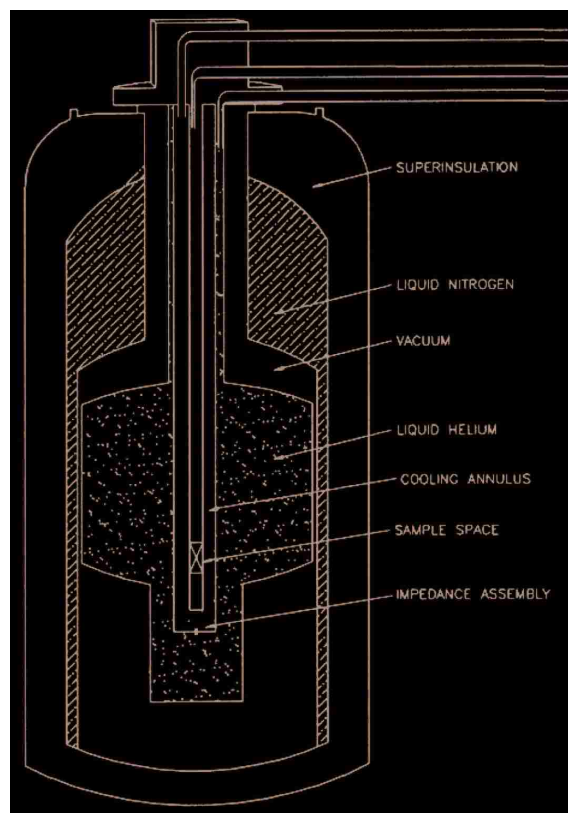


Figure 5 A Quantum Design Physical Property Measurement System, with an interior view of the dewar.

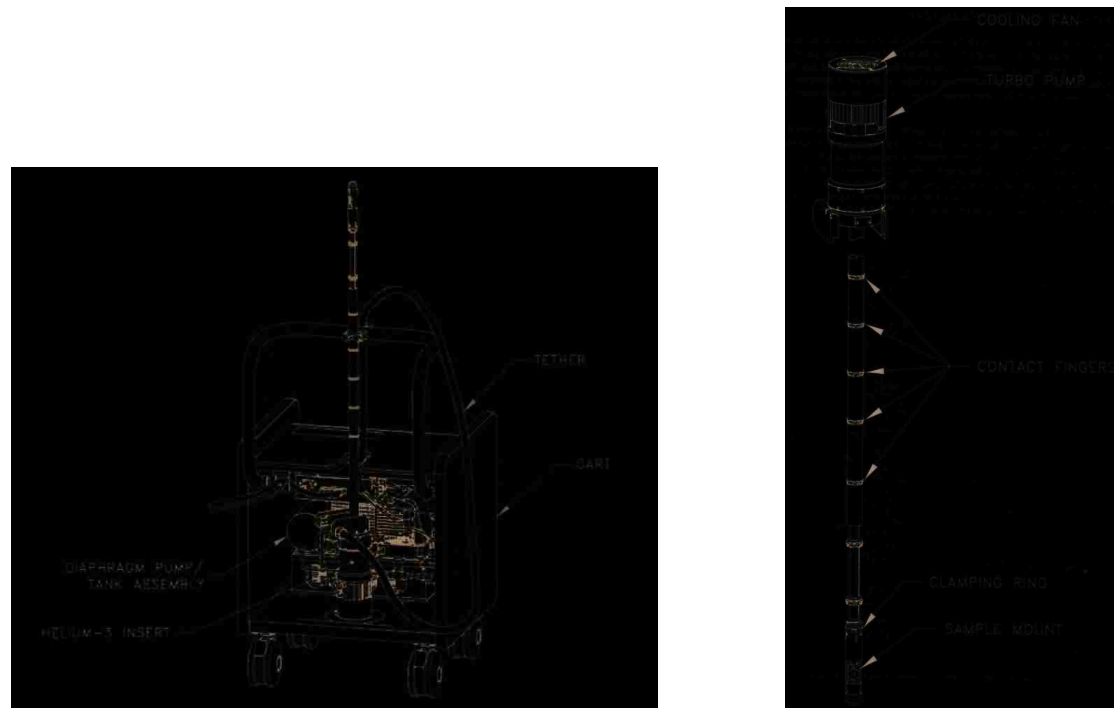


Figure 6 The Helium 3 insert, which allows the system to reach 0.36 Kelvin by pumping on a self enclosed liquid helium reservoir.



Figure 7 A Helium 3 Heat Capacity Puck. The left image shows the placement of the heater and the thermometer on the underside of the stage on which the sample is placed.

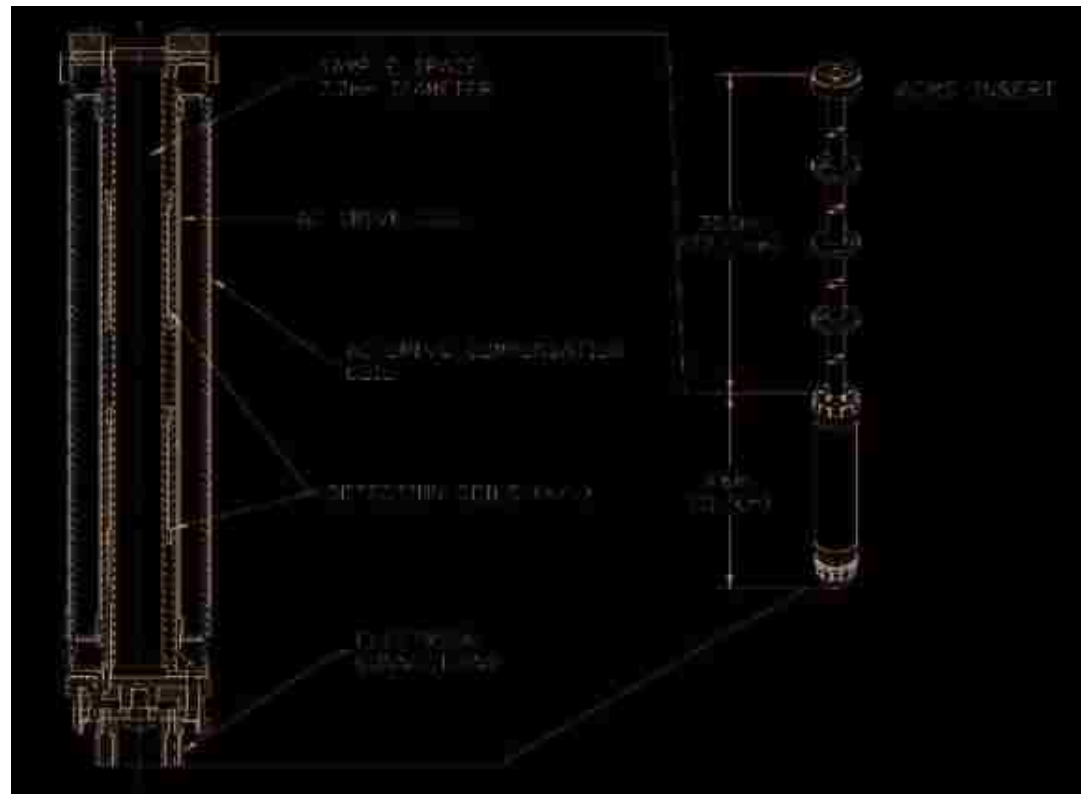


Figure 8 The drive and detection coils for the PPMS ACMS Option. They reside within the larger superconducting magnet.

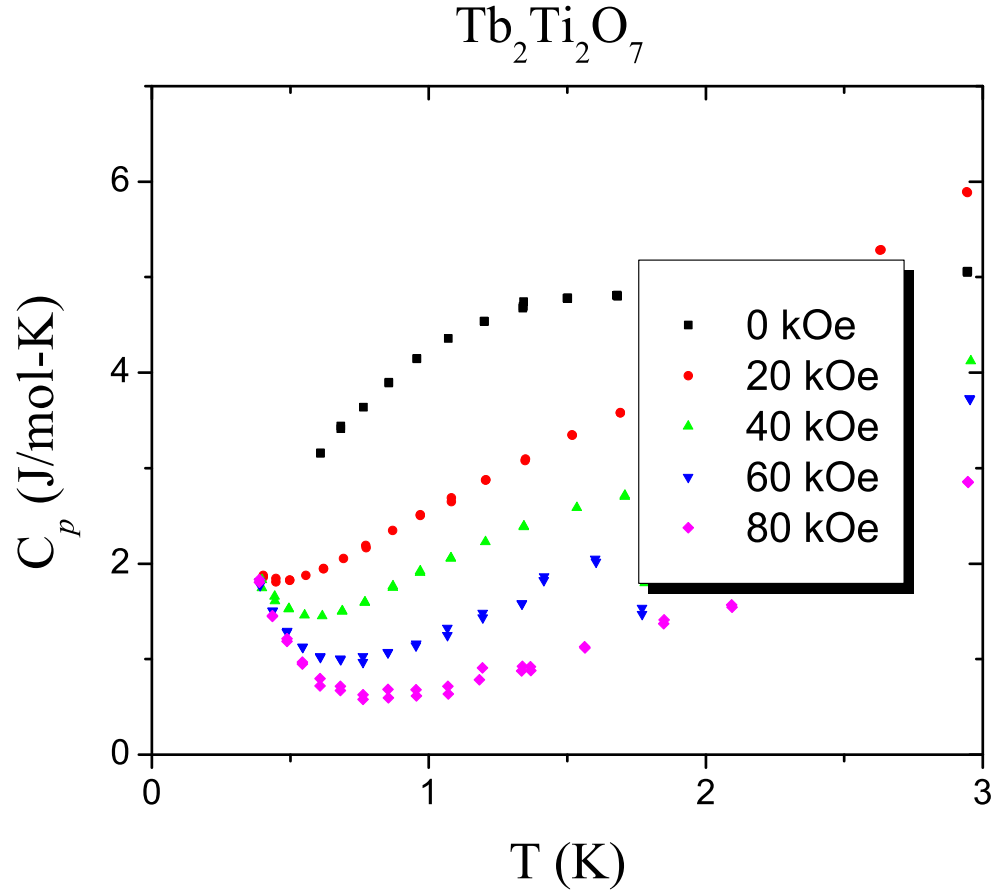


Figure 9 The magnetic heat capacity of the undoped terbium titanate for several applied fields. The zero field measurement shows an absence of correlated behavior for its spins, which is broken with the introduction of an applied field. No sharp transition to long range order is seen at any field. Errors are on the order of 0.1%, which is smaller than the data points.

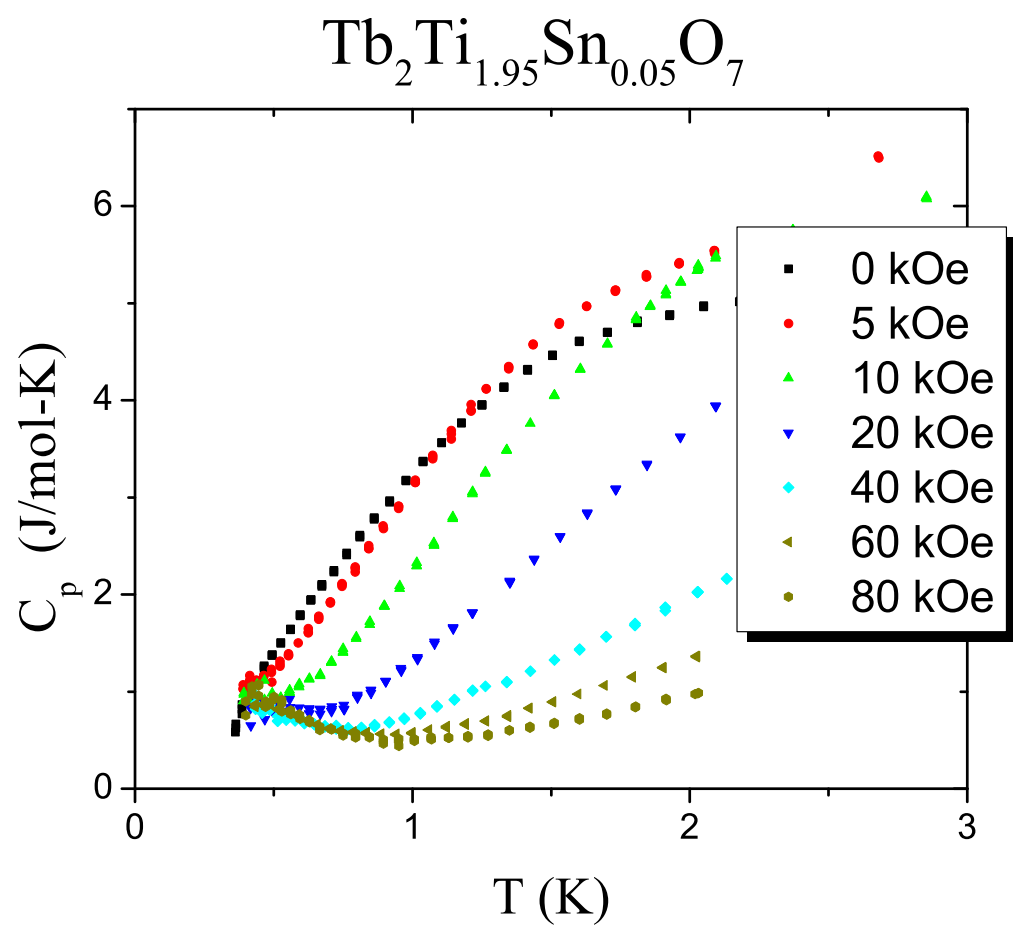


Figure 10 The magnetic heat capacity of $\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$ at several applied fields. No sharp transition to long range order is seen.

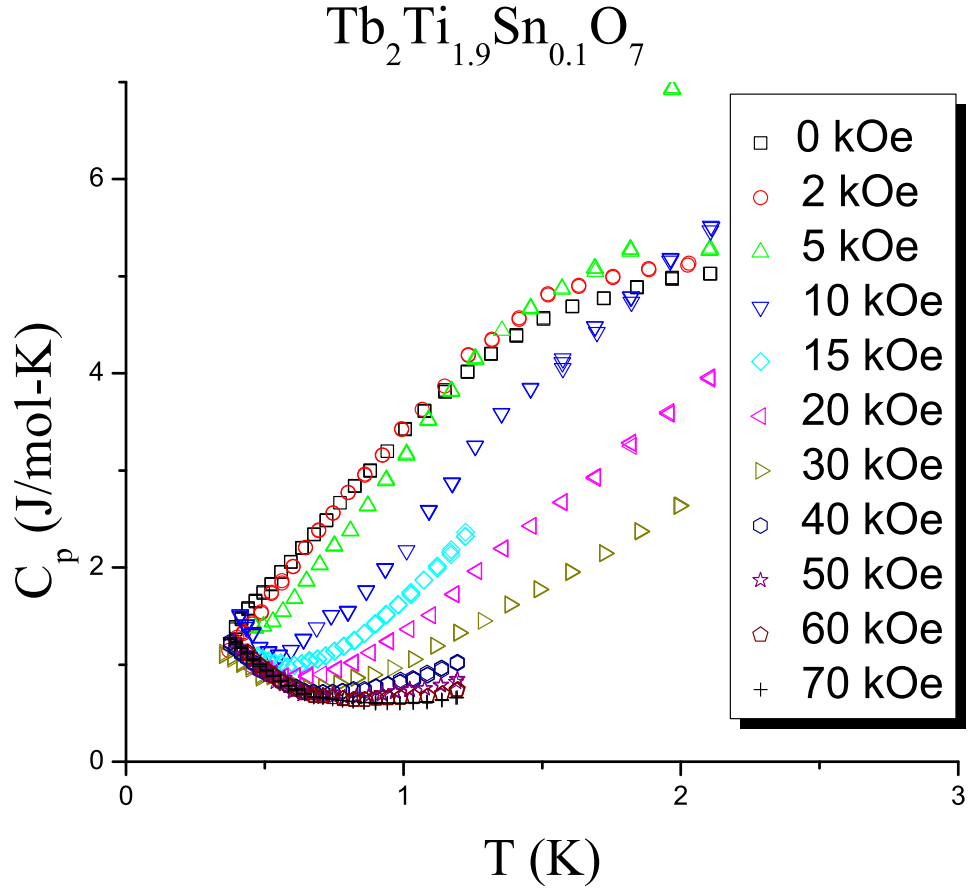


Figure 11 The magnetic heat capacity of $\text{Tb}_2\text{Ti}_{1.9}\text{Sn}_{0.1}\text{O}_7$ at several applied fields. No sharp transition to long range order is seen.

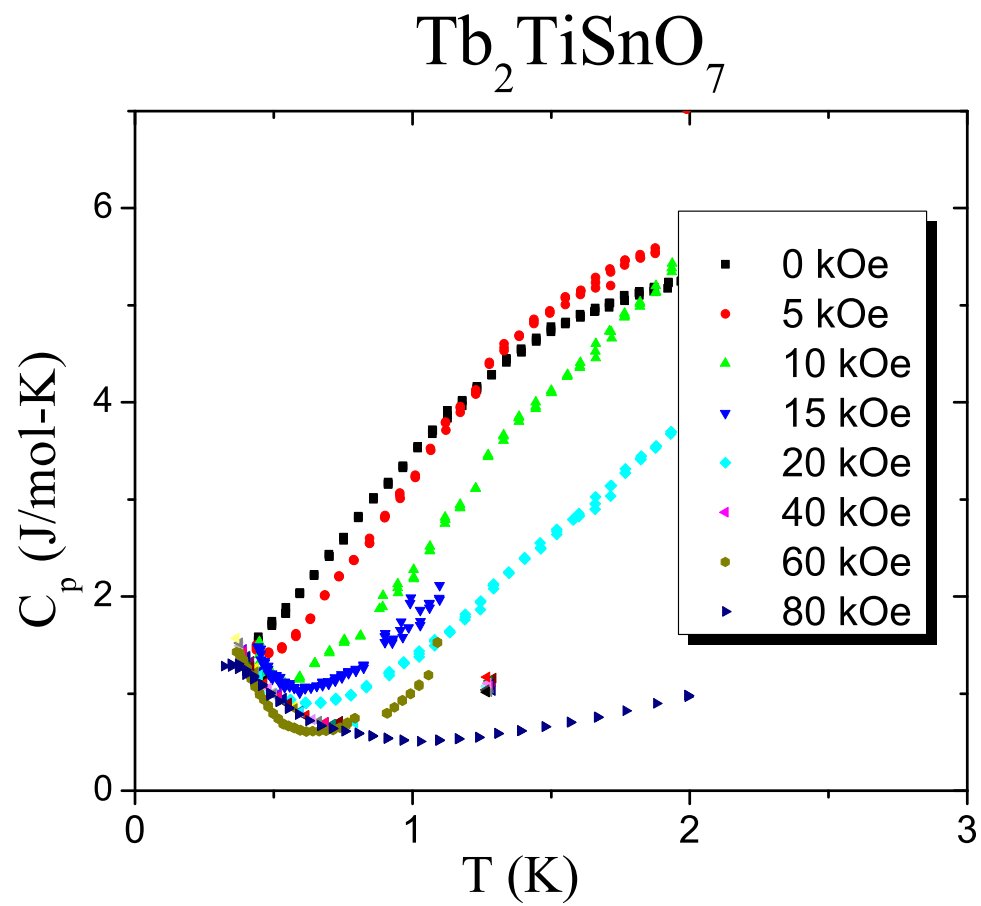


Figure 12 The magnetic heat capacity of $\text{Tb}_2\text{TiSnO}_7$ at several applied fields. No sharp transition to long range order is seen.

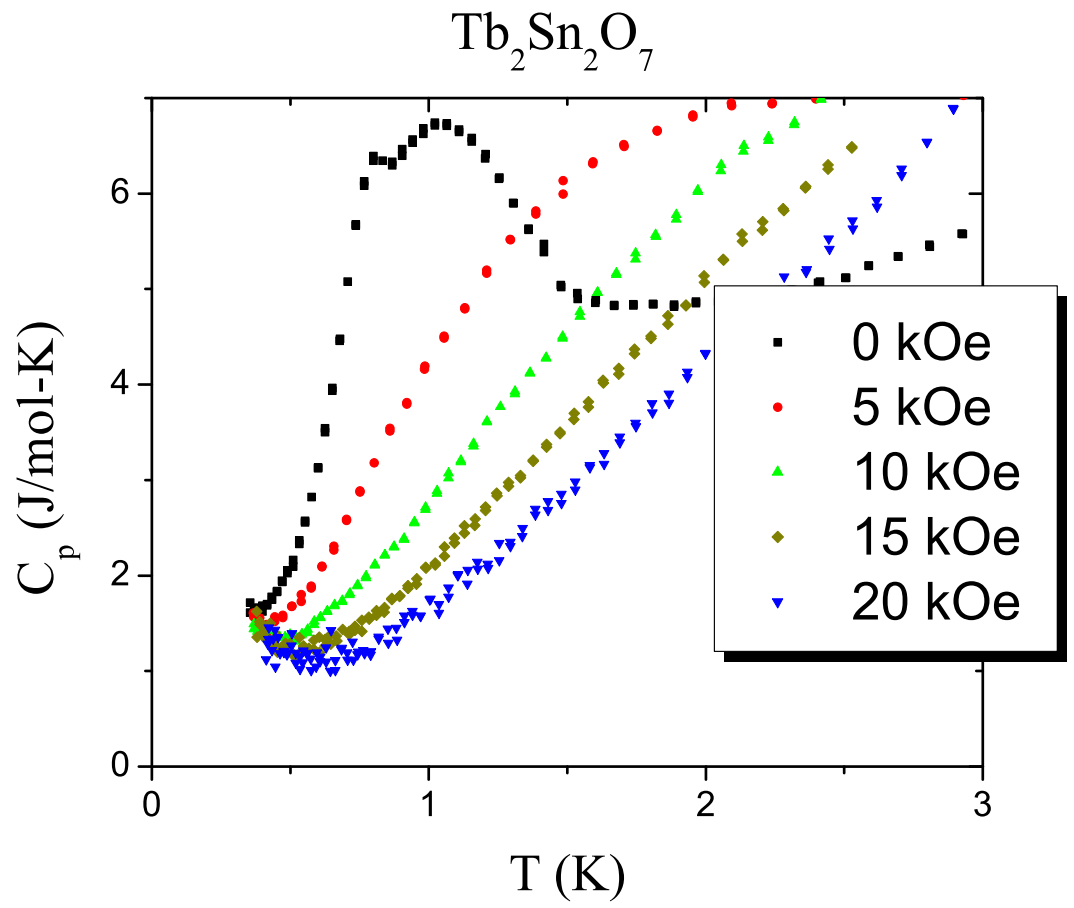


Figure 13 The magnetic heat capacity of $\text{Tb}_2\text{Sn}_2\text{O}_7$ at several applied fields. No sharp transition to long range order is seen.

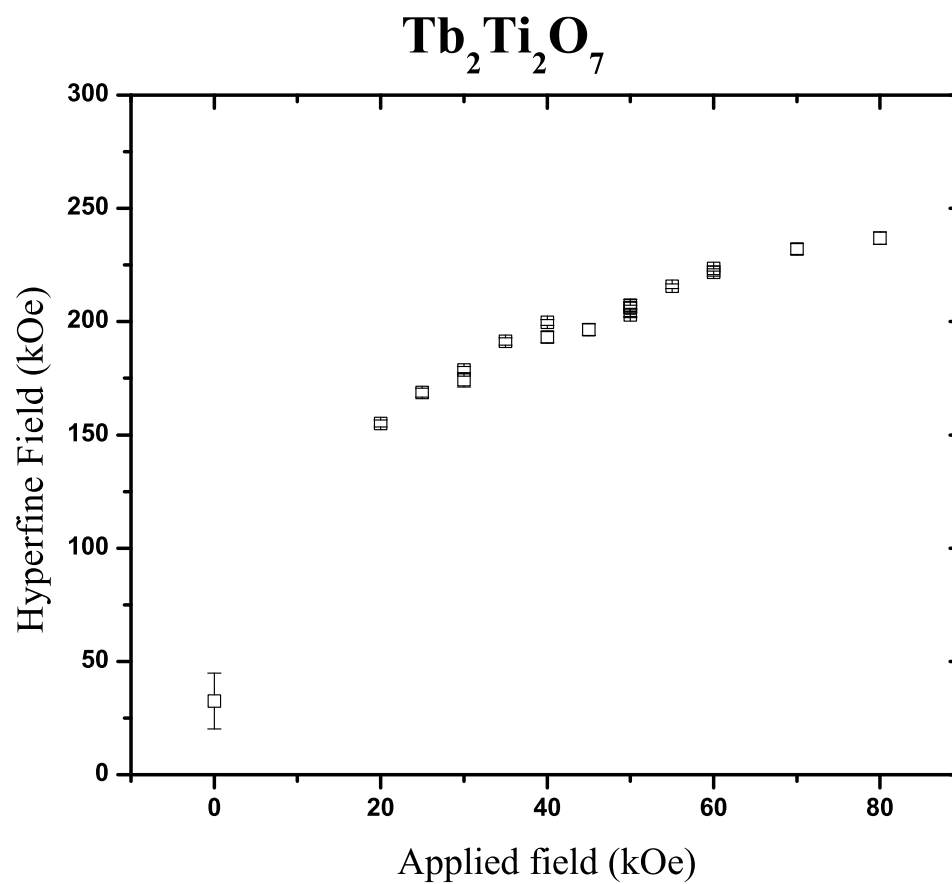


Figure 14 The hyperfine field at the terbium sites for the pure Tb₂Ti₂O₇ as it varies with the applied field.

$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$

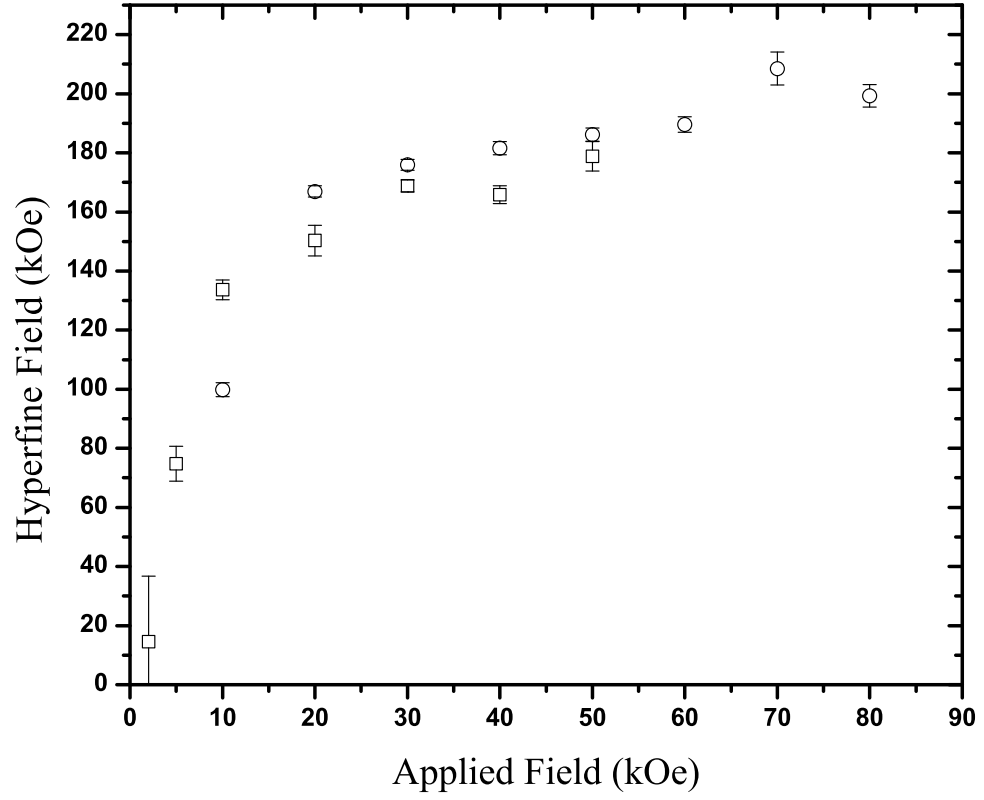


Figure 15 The hyperfine field at the terbium sites for $\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$ as it varies with the applied field.

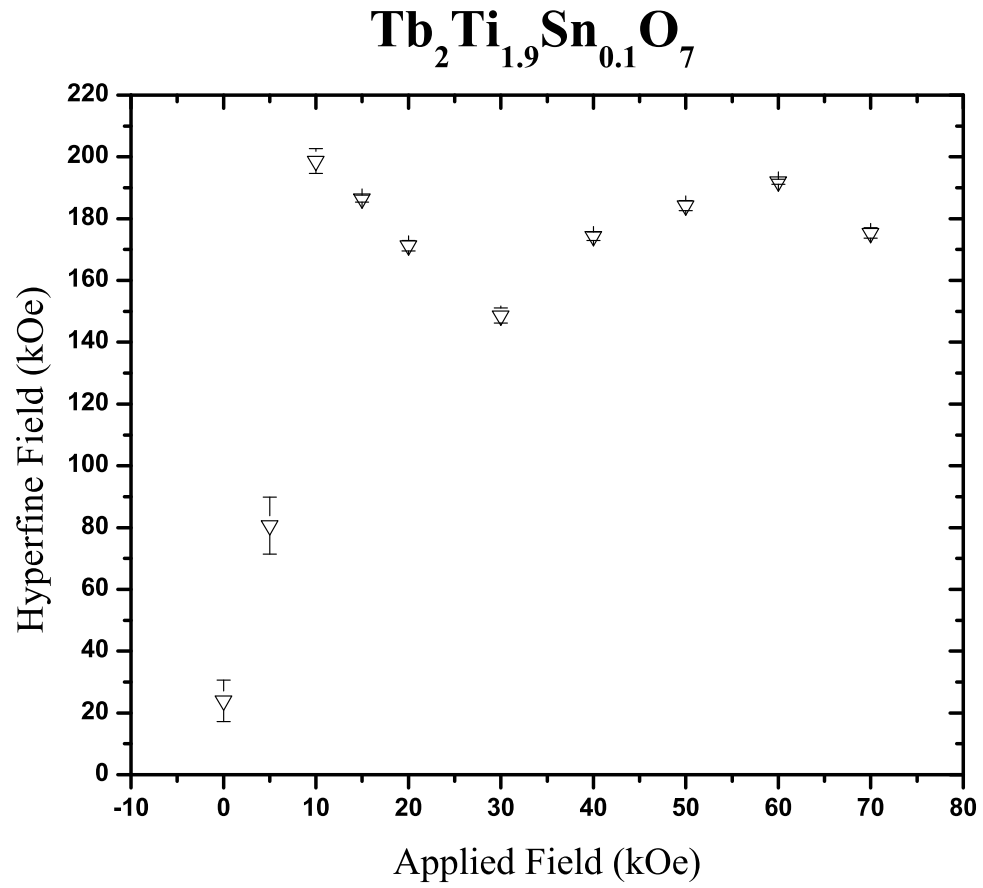


Figure 16 The hyperfine field at the terbium sites for $\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$ as it varies with the applied field.

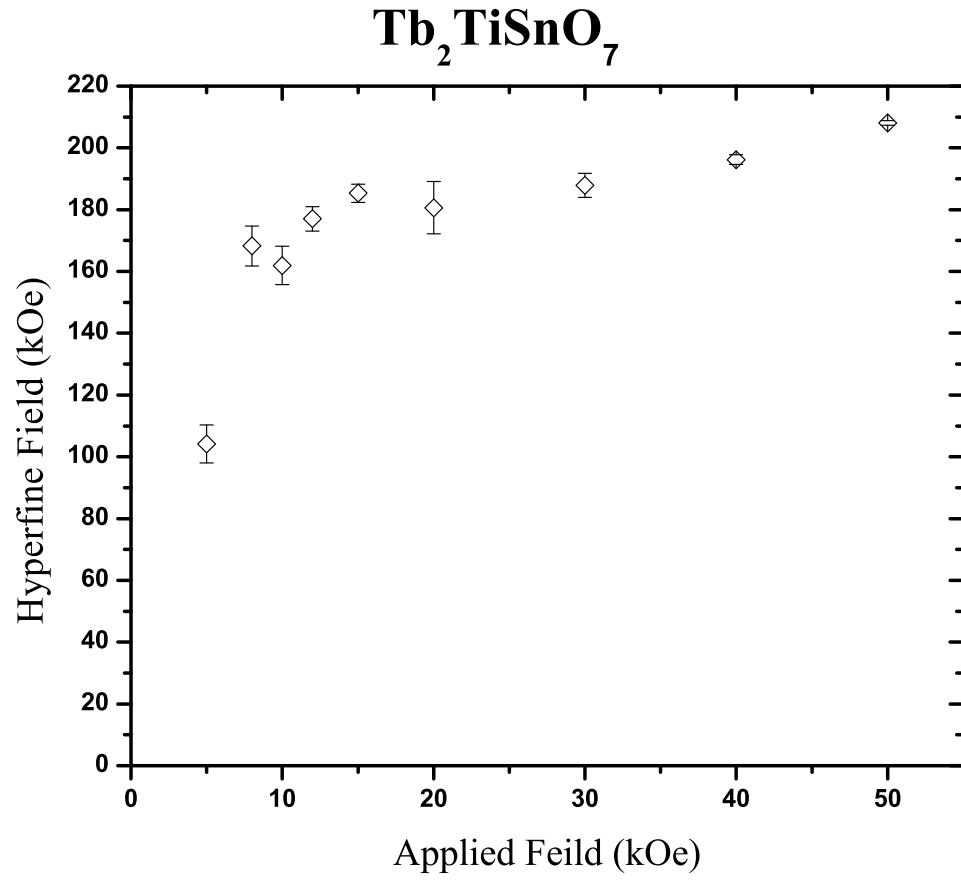


Figure 17 The hyperfine field at the terbium sites for $\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$ as it varies with the applied field.

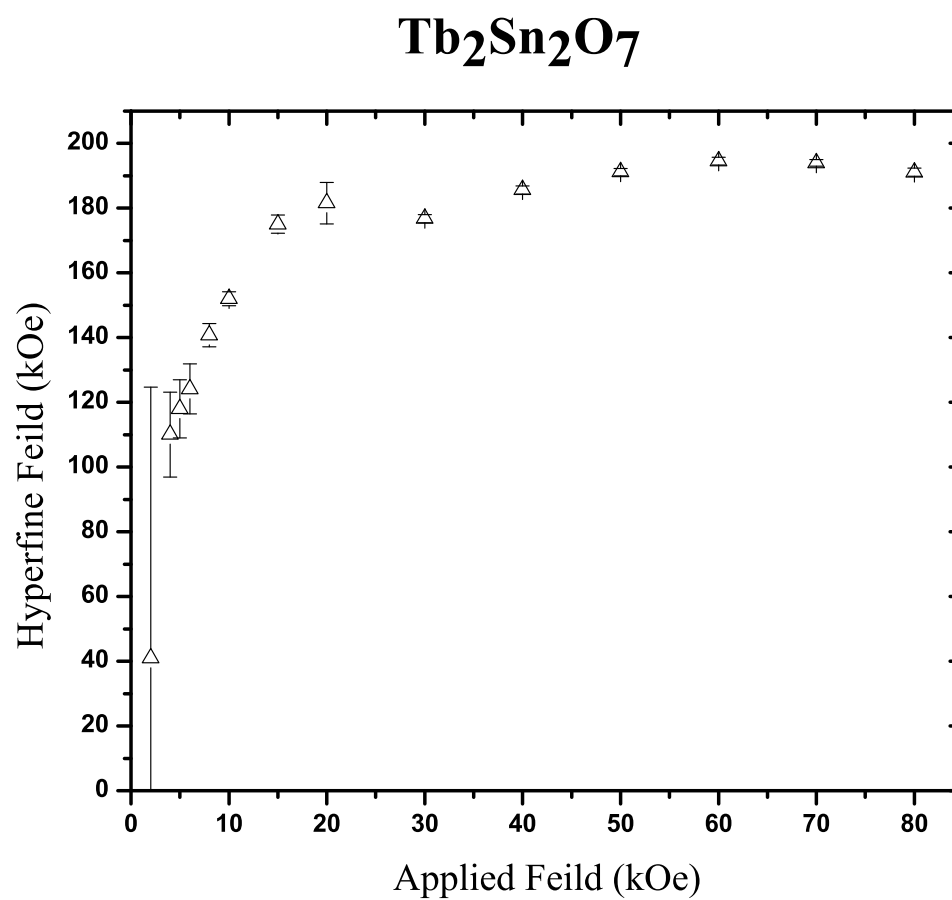


Figure 18 The hyperfine field at the terbium sites for Tb₂Sn₂O₇ as it varies with the applied field.

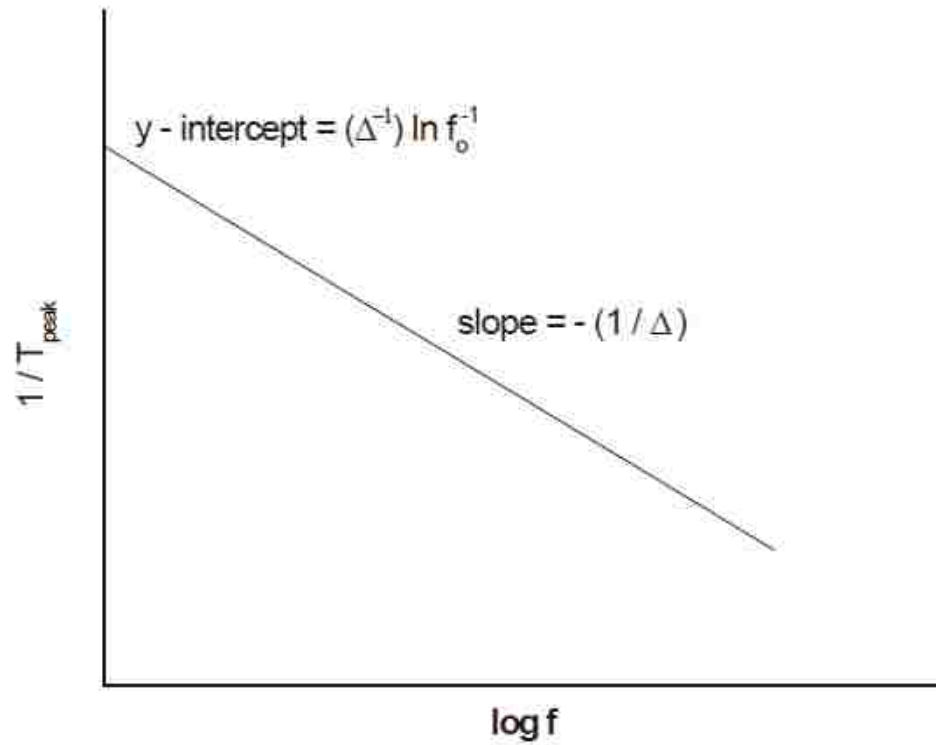


Figure 19 The expected response due to thermally activated behavior. The graph of the logarithm of applied frequency versus the inverse of the peak temperature should conform to a straight line. When fit to equation 3.6, the slope of the line should equal the inverse of the energy barrier, and the y-intercept can be used to calculate the characteristic time between the spins.

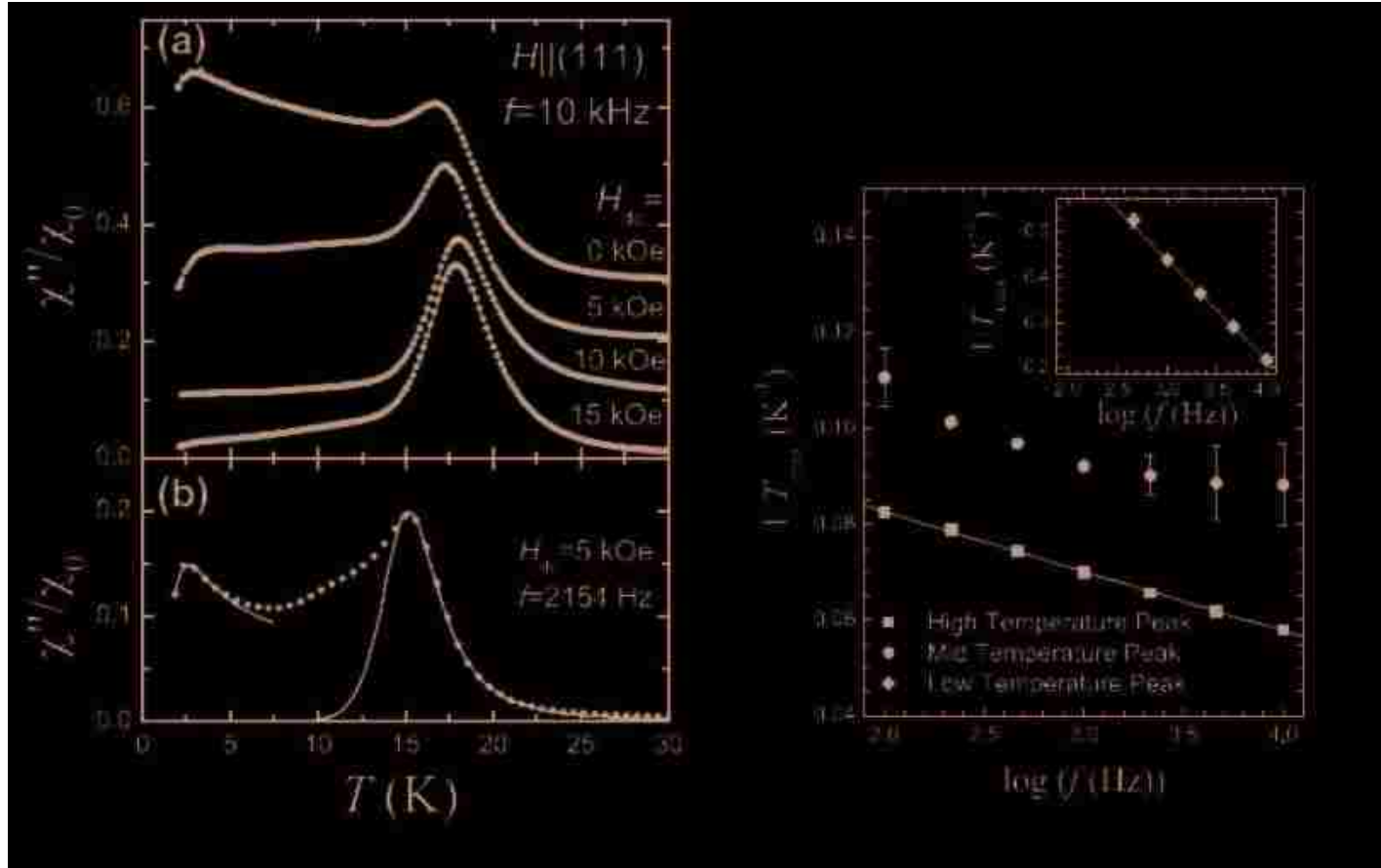


Figure 20 Taken from Ref. [20]. (left) (a) The normalized imaginary AC susceptibility versus temperature for $\text{Dy}_2\text{Ti}_2\text{O}_7$ for different applied DC fields. (b) The solid lines show peaks from two separate processes at about 2 K and 15 K. A third peak exists between them, but it is difficult to separate. (right) The inverse of the maximum peak temperature versus the $\log f$. The linear fits give values of 191 K and 8.9 K for the high and low temperature peaks, respectively.

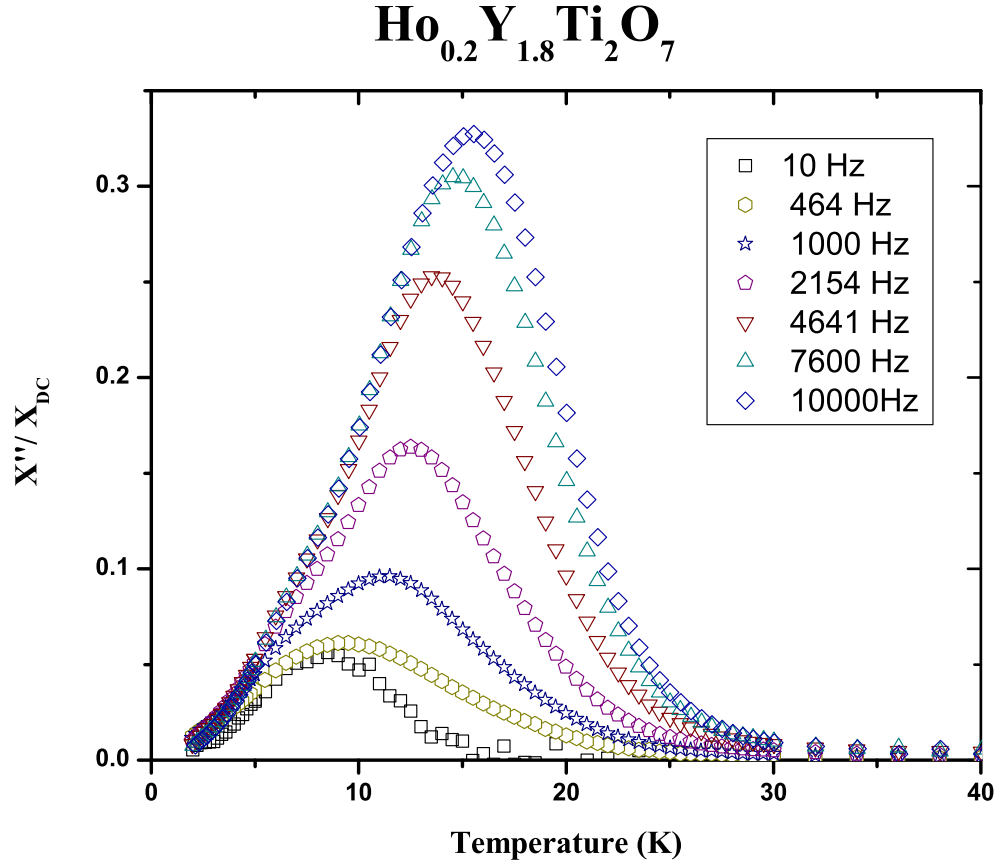


Figure 21 The AC susceptibility of Ho_{0.2}Y_{1.8}Ti₂O₇ divided by its DC magnetization for some of the frequencies that were investigated from 10 Hz to 10 kHz. There appears to be a smaller peak at about 5 Kelvin, but it is lost in the larger one. The large peak grows in magnitude and shifts left with higher frequency.

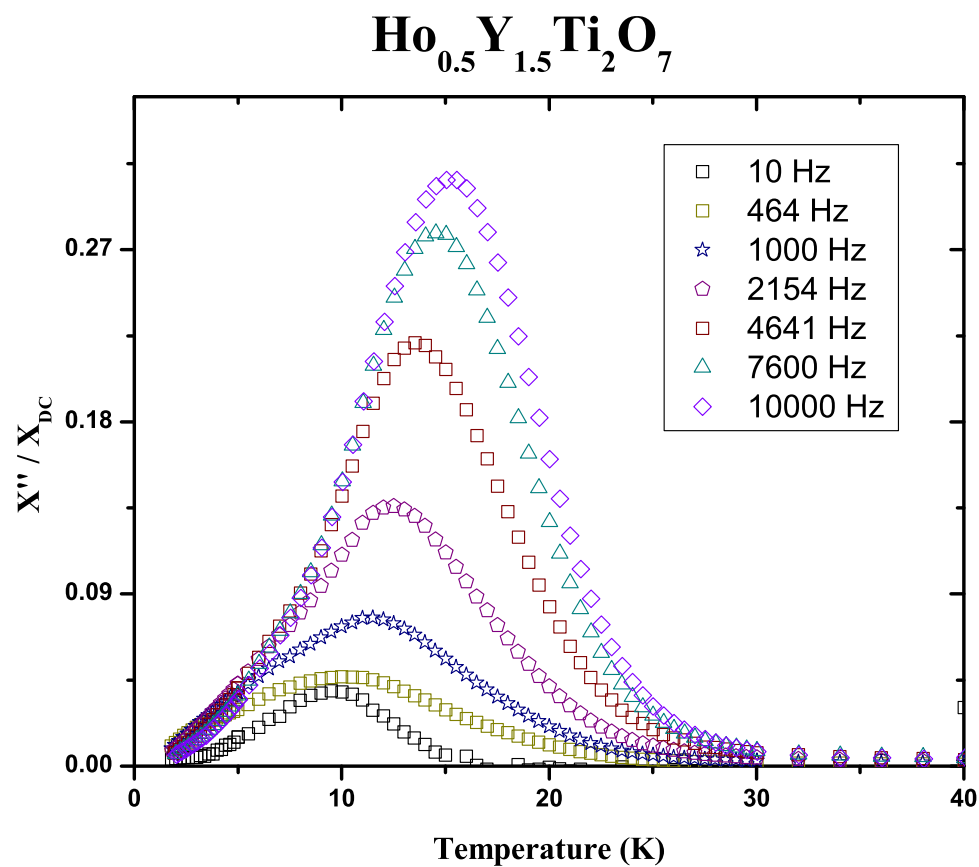


Figure 22 The AC susceptibility of $\text{Ho}_{0.5}\text{Y}_{1.5}\text{Ti}_2\text{O}_7$ divided by its DC magnetization for some of the frequencies that were investigated from 10 Hz to 10 kHz. There appears to be a smaller peak at about 5 Kelvin, but it is lost in the larger one. The large peak grows in magnitude and shifts left with higher frequency.

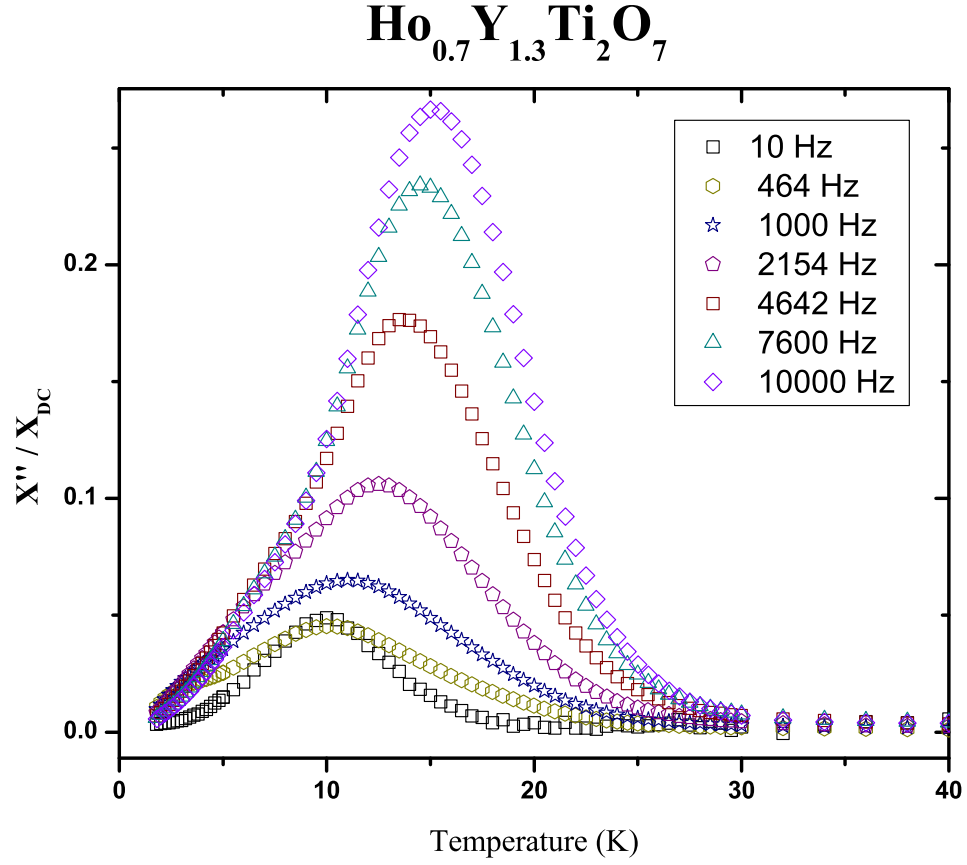


Figure 23 The AC susceptibility of Ho_{0.7}Y_{1.3}Ti₂O₇ divided by its DC magnetization for some of the frequencies that were investigated from 10 Hz to 10 kHz. There appears to be a smaller peak at about 5 Kelvin, but it is lost in the larger one. The large peak grows in magnitude and shifts left with higher frequency.

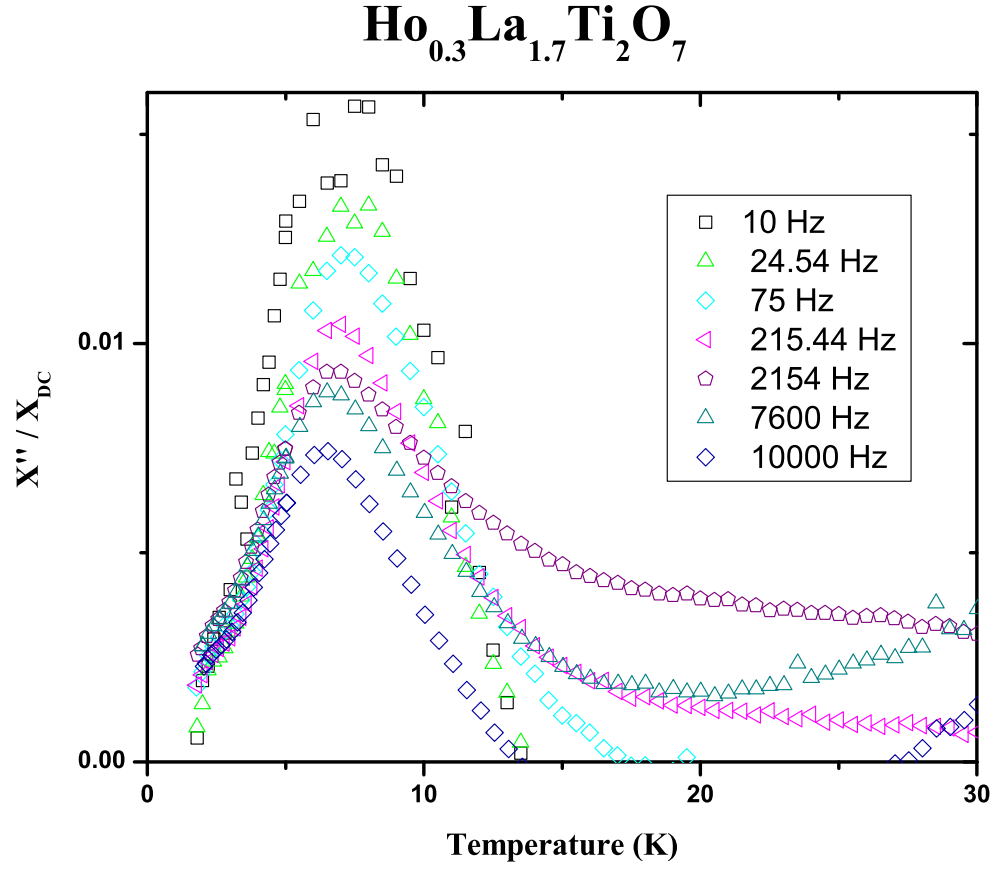


Figure 24 The AC susceptibility of Ho_{0.3}La_{1.7}Ti₂O₇ divided by its DC magnetization for some of the frequencies that were investigated from 10 Hz to 10 kHz. A smaller peak at about 5 Kelvin is lost in the larger feature. Unlike the Y doped samples, the larger peak gets smaller with increasing frequencies, and it shows no clear trend to higher or lower temperatures.

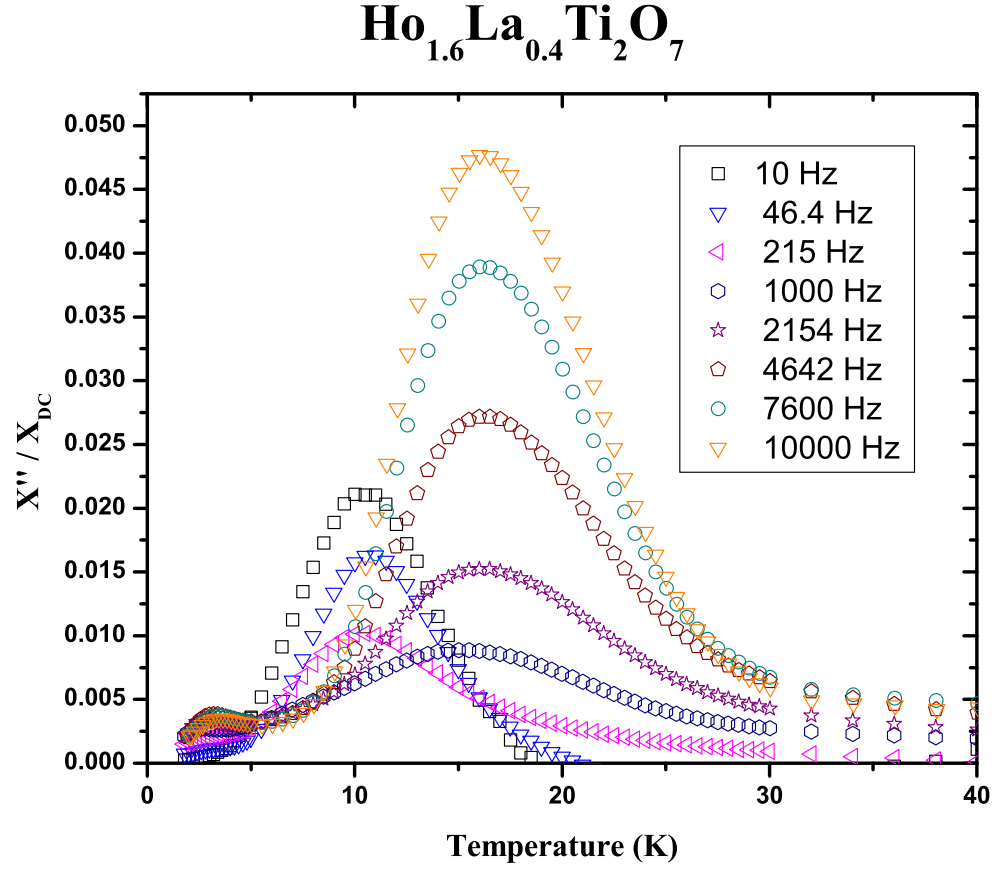


Figure 25 The AC susceptibility of Ho_{1.6}La_{0.4}Ti₂O₇ divided by its DC magnetization for some of the frequencies that were investigated from 10 Hz to 10 kHz. A smaller peak can be seen below 5 Kelvin, but it moves out of the observable range at lower frequencies. There is still only one larger peak. It seems to remain at a constant temperature of about 10 K and decreases with increasing frequency, and then moves to a higher constant temperature of about 18 K and increases again with farther increasing frequency.

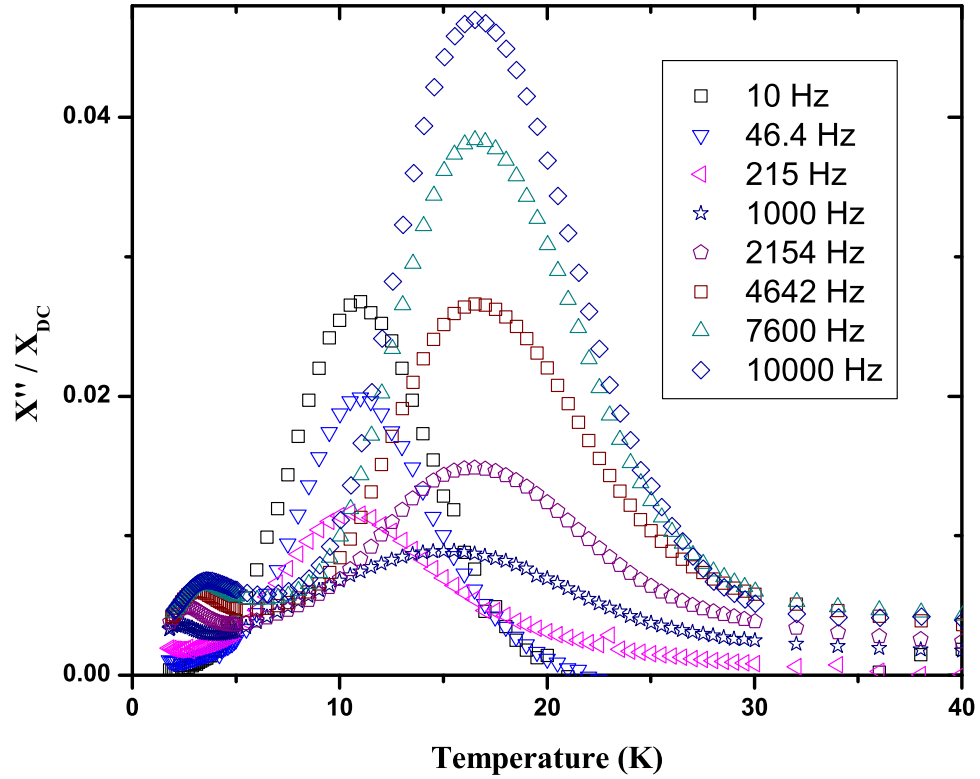
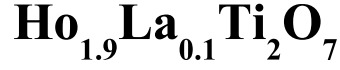


Figure 26 The AC susceptibility of $\text{Ho}_{1.9}\text{La}_{0.1}\text{Ti}_2\text{O}_7$ divided by its DC magnetization for some of the frequencies that were investigated from 10 Hz to 10 kHz. A smaller peak can be seen below 5 Kelvin, but it moves out of the observable range at lower frequencies. There is still only one larger peak. It seems to remain at a constant temperature of about 10 K and decreases with increasing frequency, and then moves to a higher constant temperature of about 18 K and increases again with farther increasing frequency.

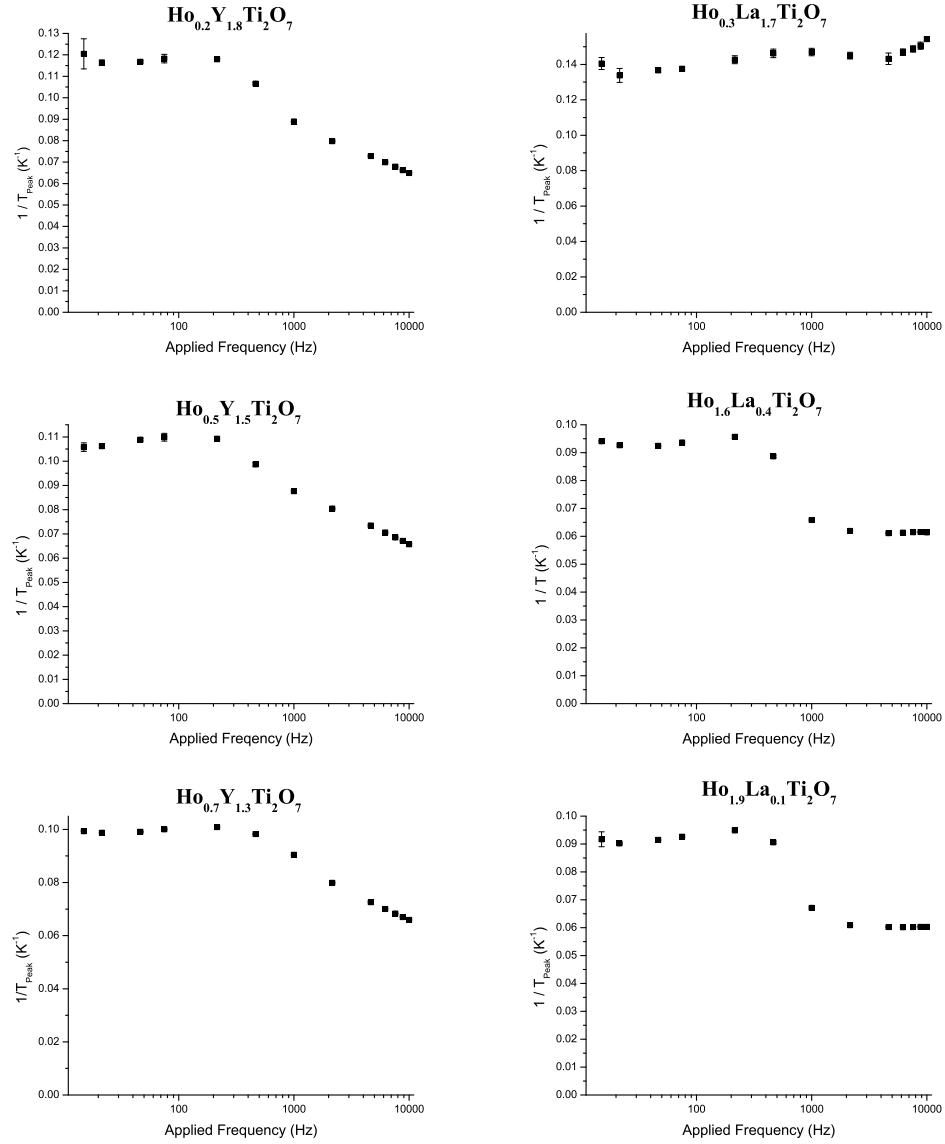


Figure 27 Graphs of the applied frequency on a logarithmic scale versus the inverse peak frequency for all six holmium titanate samples. None of the samples seem to conform to the expected Arrhenius behavior. All samples show regions where frequency appears entirely independent of the temperature.

Compound	θ (K)	T_{mag} (K)	f	Reference
ZnCr ₂ O ₄	-390	16	24	[10]
K ₂ IrCl ₆	-32	3.1	10	[10]
Fe ₂ F ₃	-240	15	16	[10]
CsNiFeF ₅	-210	4.4	48	[10]
Tb ₂ Ti ₂ O ₇	-18	< 0.050	> 360	[6]
Ho ₂ Ti ₂ O ₇	2	< 0.050	> 40	[4]
MnO	-610	116	5	[9]
FeF ₂	117	79	1.5	[9]
Fe	1840	1043	1.75	[11]
Gd	334	293	1.1	[12]

Table 1 Frustration parameters for some strongly frustrated materials with frustration parameters $f = |\theta|/T_{\text{mag}}$ greater than 10, and some more conventional materials for comparison. Tb₂Ti₂O₇ and Ho₂Ti₂O₇ have not been observed to transition to long range order down to the lowest observed temperatures.

Sample ($\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$)	Applied Field (kOe)	A (K-J/mol)	A error	B_{hyp} (kOe)	B_{hyp} error
$\text{Tb}_2\text{Ti}_2\text{O}_7$	0	0.0053	0.00403	32.51035	12.36007
$\text{Tb}_2\text{Ti}_2\text{O}_7$	20	0.12059	0.00241	155.07413	1.54958
$\text{Tb}_2\text{Ti}_2\text{O}_7$	25	0.14273	0.00329	168.7102	1.94443
$\text{Tb}_2\text{Ti}_2\text{O}_7$	30	0.16	0.00285	178.6256	1.59088
$\text{Tb}_2\text{Ti}_2\text{O}_7$	30	0.15235	0.00557	174.30303	3.18631
$\text{Tb}_2\text{Ti}_2\text{O}_7$	35	0.18343	0.003	191.25768	1.56401
$\text{Tb}_2\text{Ti}_2\text{O}_7$	40	0.19985	0.00248	199.63459	1.23866
$\text{Tb}_2\text{Ti}_2\text{O}_7$	40	0.18715	0.00478	193.18732	2.4671
$\text{Tb}_2\text{Ti}_2\text{O}_7$	45	0.19362	0.00499	196.49831	2.53209
$\text{Tb}_2\text{Ti}_2\text{O}_7$	50	0.20665	0.00237	203.00251	1.16408
$\text{Tb}_2\text{Ti}_2\text{O}_7$	50	0.21284	0.00786	206.02045	3.80408
$\text{Tb}_2\text{Ti}_2\text{O}_7$	50	0.2134	0.00213	206.2913	1.02952
$\text{Tb}_2\text{Ti}_2\text{O}_7$	50	0.21537	0.00272	207.2413	1.30867
$\text{Tb}_2\text{Ti}_2\text{O}_7$	55	0.23315	0.00222	215.62615	1.02657
$\text{Tb}_2\text{Ti}_2\text{O}_7$	60	0.25032	0.00264	223.42485	1.17818
$\text{Tb}_2\text{Ti}_2\text{O}_7$	60	0.24652	0.00371	221.72251	1.66841
$\text{Tb}_2\text{Ti}_2\text{O}_7$	70	0.26993	0.00566	232.01138	2.43245
$\text{Tb}_2\text{Ti}_2\text{O}_7$	80	0.2813	0.00651	236.84737	2.74063
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$	2	0.00107	0.00324	14.60749	22.11601
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$	5	0.02808	0.00444	74.83112	5.91614
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$	10	0.08963	0.00449	133.69354	3.34868
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$	20	0.11327	0.00783	150.29383	5.19467
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$	30	0.14292	0.00341	168.82246	2.01401
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$	40	0.13786	0.00503	165.80699	3.02484
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.05}\text{O}_7$	50	0.16047	0.00916	178.88776	5.10566
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.1}\text{O}_7$	0	0.00287	0.0016	23.9235	6.66857
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.1}\text{O}_7$	2	-0.02614	0.00356	--	--
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.1}\text{O}_7$	5	0.03261	0.00748	80.64159	9.24868
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.1}\text{O}_7$	10	0.19799	0.00801	198.70342	4.01943
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.1}\text{O}_7$	15	0.17437	0.00215	186.47456	1.14963
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.1}\text{O}_7$	20	0.14705	0.00288	171.24434	1.67693
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.1}\text{O}_7$	30	0.1108	0.00368	148.64612	2.46849
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.1}\text{O}_7$	40	0.15235	0.00238	174.30303	1.36147
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.1}\text{O}_7$	50	0.1703	0.00302	184.28544	1.634
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.1}\text{O}_7$	60	0.18477	0.00161	191.955	0.8363
$\text{Tb}_2\text{Ti}_{1.95}\text{Sn}_{0.1}\text{O}_7$	70	0.15422	0.0029	175.3695	1.64885

Table 2 The results of the fit of the low temperature heat capacity of $\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ for $x = 0, 0.05$, and 0.1 to a high temperature Schottky peak and the calculation of the hyperfine field. B_{hyp} was not calculated for poor fits that resulted in negative values for A. Errors are the standard deviation of the parameter.

Sample ($\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$)	Applied Field (kOe)	A (K-J/mol)	A error	B_{hyp} (kOe)	B_{hyp} error
$\text{Tb}_2\text{TiSnO}_7$	0	-1.00E-04	0.00334	--	--
$\text{Tb}_2\text{TiSnO}_7$	2	-0.01846	0.00448	--	--
$\text{Tb}_2\text{TiSnO}_7$	5	0.05436	0.00643	104.11743	6.15779
$\text{Tb}_2\text{TiSnO}_7$	8	0.14195	0.01093	168.24858	6.47748
$\text{Tb}_2\text{TiSnO}_7$	10	0.13153	0.01008	161.95566	6.20586
$\text{Tb}_2\text{TiSnO}_7$	12	0.15714	0.00702	177.02194	3.9541
$\text{Tb}_2\text{TiSnO}_7$	15	0.17222	0.00549	185.32137	2.95382
$\text{Tb}_2\text{TiSnO}_7$	20	0.16365	0.01539	180.65156	8.49443
$\text{Tb}_2\text{TiSnO}_7$	30	0.17696	0.00741	187.85435	3.93309
$\text{Tb}_2\text{TiSnO}_7$	40	0.19302	0.00308	196.19361	1.56532
$\text{Tb}_2\text{TiSnO}_7$	50	0.21709	0.00157	208.0672	0.75237
$\text{Tb}_2\text{Sn}_2\text{O}_7$	0	-0.13799	0.04676	--	--
$\text{Tb}_2\text{Sn}_2\text{O}_7$	0	-0.20213	0.02439	--	--
$\text{Tb}_2\text{Sn}_2\text{O}_7$	2	0.0084	0.03441	40.92827	83.82986
$\text{Tb}_2\text{Sn}_2\text{O}_7$	4	0.06077	0.01448	110.08505	13.11528
$\text{Tb}_2\text{Sn}_2\text{O}_7$	5	0.06978	0.0106	117.96392	8.95971
$\text{Tb}_2\text{Sn}_2\text{O}_7$	6	0.07728	0.00965	124.14158	7.75082
$\text{Tb}_2\text{Sn}_2\text{O}_7$	8	0.09936	0.00506	140.76332	3.58425
$\text{Tb}_2\text{Sn}_2\text{O}_7$	10	0.11587	0.00331	152.00897	2.17118
$\text{Tb}_2\text{Sn}_2\text{O}_7$	15	0.1537	0.005	175.07359	2.84765
$\text{Tb}_2\text{Sn}_2\text{O}_7$	20	0.16533	0.01166	181.57646	6.4029

Table 3 The results of the fit of the low temperature heat capacity of $\text{Tb}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ for $x = 1$ and 2 to a high temperature Schottky peak and the calculation of the hyperfine field. B_{hyp} was not calculated for poor fits that resulted in negative values for A. Errors are the standard deviation of the parameter.

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