Magnetization and susceptibility studies on single crystals of the pyrochlore \( \text{Ho}_2\text{Ti}_2\text{O}_7 \) are reported for the first time. Magnetization isotherms are shown to be qualitatively similar to that predicted by the nearest neighbor spin-ice model. Below the lock-in temperature, \( T^* \approx 1.97 \text{ K} \), magnetization is consistent with the locking of spins along \([111]\) directions in a specific two-spins-in, two-spins-out arrangement. Below \( T^* \) the magnetization for \( B\|[111] \) displays a two step behavior signalling the breaking of the ice rules.
Materials containing antiferromagnetically coupled magnetic moments which reside on geometrical units, such as triangles, that inhibit the formation of a collinear ordered state, often display phenomena known broadly as geometrical frustration \[^{[1]}\]. A pyrochlore lattice with corner-sharing tetrahedra of magnetic ions running through it, is an ideal system for studying geometrical frustration. The discovery by Harris et al. \[^{[2]}\] that a magnetic pyrochlore with ferromagnetic interactions and strong single ion anisotropy could be just as frustrated as the analogous antiferromagnets is counterintuitive \[^{[3,4]}\]. The prototypical example of these ferromagnetic compounds is Ho\(_2\)Ti\(_2\)O\(_7\) \[^{[5,6]}\], however this has been questioned recently \[^{[7]}\]. Such materials are termed spin-ices because their physics maps directly onto the historic problem of proton disorder in hexagonal ice.

The magnetic ground state of the ferromagnetic pyrochlore with Ising anisotropy along the [111] axis consists of two spins pointing in and two spins pointing out of the individual tetrahedra \[^{[6]}\]. This is identical to the lattice formed by the mid-points of the oxygen-oxygen bonds in ice \[^{[3]}\]. This resulted in the “spin-ice” label, and is one of two conditions required for this class of materials, the other being a zero-point entropy close to (1/2) ln(3/2) which has been measured in Dy\(_2\)Ti\(_2\)O\(_7\), and is identical to the proton ordering in real ice. The discovery of spin-ice prompted considerable research by other groups \[^{[7,9,10]}\], however until recently neither Dy\(_2\)Ti\(_2\)O\(_7\) nor Ho\(_2\)Ti\(_2\)O\(_7\) have been shown to meet these two criteria. Due to the neutron absorbing nature of dysprosium, neutron scattering measurements on Dy\(_2\)Ti\(_2\)O\(_7\) to investigate the nature of the magnetic ordering have yet to be performed. Recently, Bramwell et al. reported the first low temperature \(C_m\) results on Ho\(_2\)Ti\(_2\)O\(_7\) \[^{[8]}\]. In these data a maximum is seen in the magnetic contribution, \(C_m\), to the specific heat at 1.97 K which we will refer to as the blocking temperature. Their data, heat capacity and neutron diffraction, clearly shows that Ho\(_2\)Ti\(_2\)O\(_7\) requires a spin-ice model that includes longer-range, dipolar interactions when discussing its properties down to 300 mK.

To investigate the bulk magnetic properties of Ho\(_2\)Ti\(_2\)O\(_7\), we have performed both a.c. and d.c. magnetization measurements on single crystals. These are the first single crystal measurements, with fields as large as 9 T applied along the three principle cubic crystallographic axes [100], [110] and [111], of this geometrically frustrated materials. These data are in excellent qualitative agreement with calculations \[^{[3]}\]; in particular a step is seen below the lock-in temperature, \(T^*\) when the magnetic field is applied along the [111] axis. Unlike the predictions, there is little difference in the low temperature saturation magnetization for the different crystal orientations.

The single crystals were synthesized using the floating-zone method described elsewhere \[^{[11]}\]. Polycrystalline samples of Ho\(_2\)Ti\(_2\)O\(_7\) were prepared by firing, in air, stoichiometric amounts of high purity (> 99.99%) Ho\(_2\)O\(_3\) and TiO\(_2\) for several days with intermittent grindings to ensure a complete reaction. The polycrystalline material is then used to grow large (> 1 cm\(^3\)) single crystals in an infrared image furnace with the aid of a small seed crystal. A small piece of the resulting large single crystal was ground up for characterization by X-ray powder diffraction (XRD). The impurity content is less than 3% (limit of our XRD) and the room temperature cubic lattice parameter is 10.102(2) Å.

Magnetization measurements between 1.8 and 300 K were performed in a fully calibrated Quantum Design PPMS system inside a 9 T superconducting magnet. The zero field susceptibility measurements used a 10 Oe AC field at a frequency of 1000 Hz. The high field magnetization measurements were made with a DC extraction technique.

Previous magnetic measurements on Ho\(_2\)Ti\(_2\)O\(_7\) have been interpreted in different ways \[^{[12,13]}\]. We will discuss our results within the framework of a ground-state spin one-half doublet \(S = 1/2\) with an effective \(g\) value of \(g_\parallel = g\) and \(g_\perp = 0\) where parallel is the [111] direction corresponding to the direction of the applied field. We will use the standard form \[^{[14]}\]

\[
\chi(T) = \frac{(g\mu_B)^2}{k_B T} S(S + 1) \left[ 1 + \frac{\theta}{T} \right], \theta = S(S + 1) J/3,
\]

where \(J\) is the effective interaction between the Ho spins. As noted by others \[^{[15]}\], \(\theta\) is going to be the sum of the exchange, dipole, and crystal field contributions. We do not attempt to extract these individual contributions to \(\theta\). The results of the AC zero field susceptibility measurements are shown in Fig. \[^{[1]}\]. For \(T > 10\) K, the data are consistent with that expected for \(g = 20\) and weak ferromagnetic interactions as previous report \[^{[12]}\]. In the range 3-10 K, the data can be described well using \(\theta = -1.8\) K which corresponds to an antiferromagnetic interaction, in agreement with the results of Siddharthan et al. \[^{[7]}\]. Jana et al. \[^{[13]}\] and other have already noted that the Curie-Weiss temperature is very dependent on the range of temperatures studied, this is undoubtedly due to crystal field contributions to the effective interaction. Rosenkranz et al. \[^{[16]}\] have shown that the lowest crystal field excitation is at \(\sim 200\) K. If we fit our high temperature, \(T > 200\) K, DC magnetization data, (Fig. \[^{[2]}\]), with \(B||[111]=1\) kOe, we find \(\theta \approx +1.6\) K, in agreement with others \[^{[12]}\]. From these results, we conclude that the Ho moments can indeed be considered as \(S = 1/2\) spins, with \(g = 20\) and weak, but dominant ferromagnetic interactions in the paramagnetic state. It
should be noted there that this net ferromagnetic interaction between Ho spins is a combination of antiferromagnetic exchange interactions and ferromagnetic dipolar coupling.

Although not shown here, it can be shown that \( C_{\text{en}} \) is also well described by the nearest neighbor spin-ice model at temperatures above 1K. Using the data from Bramwell et al. we have calculated the magnetic entropy \( \Delta S_m \) by integrating \( C_{\text{en}} / T \) and the results are shown in the inset of Fig. 3. The error bars represent the estimated uncertainty in the entropy, mainly due to the fit of hyperfine component. The solid line is the entropy expected from Harris et al. \( \Delta S_m \) behavior is remarkably similar to that observed in Dy\(_2\)Ti\(_2\)O\(_7\) where the application of a 1 T magnetic field nearly recovers the missing \((1/2)R \ln(3/2)\) of entropy expected for a spin 1/2 system \((R \ln 2)\). This is in sharp contrast to a previous report \( ^{2} \), and is consistent with Ho\(_2\)Ti\(_2\)O\(_7\) being a spin-ice compound.

One naively expects magnetic ordering for \( T < |\theta| \). However, the geometric frustration leads to the absence of magnetic order at least down to 0.05 K. \(^3\) Though long-range magnetic order does not appear, the magnetic interactions can lead to short-range local ordering. Measurements of the DC magnetization as a function of magnetic field are shown in Fig. 3. Before each of these measurements, the temperature was raised to 10 K in zero applied field before returning to the desired temperature and applying a magnetic field. For \( T > 2 \) K, the curves for \( B[|111]\) and \( B[|100]\) are identical, while for \( T \lesssim 2 \) K drastically different behavior is observed. The data for the \( B[|110]\) orientation is rather interesting. While the other two orientations show identical behavior for \( T > T^* \), suggestive of isotropic magnetization, the \( B[|110]\) data is rather different. Also, for \( T < T^* \) the \( B[|110]\) data does not differ appreciably from the 4 K data. In other words, the locking of the spins that we believe to occur for \( T < T^* \) seems to have little effect on the behavior when \( B[|110]\) is expected. It should be noted that when \( B[|110]\), two of the four spins are perpendicular to the field and cannot order. In the other directions all spins have a component of their moment in the field direction. In general the data can be explained by the spins having strong Ising anisotropy along the [111] axis. Below \( T^* \sim 1.9 \) K \( T \) the spins lock into a specific set of [111] direction so that a tetrahedron has the two-spins-in, two-spins-out configuration. From Monte Carlo calculations of the nearest neighbor spin-ice lattice \(^4\), it was shown that the degeneracy breaking occurs via a two step process for \( B[|111]\). First the spin pointing along the [111] direction is aligned with the field leading to an average moment in the field direction of \((1+1/3+1/3+1/3)/4=1/3\) followed by a breaking of the two-spins-in two-spins-out ice rules with an average moment of \((1+1/3+1/3+1/3)/4=1/2\) at higher fields. This predicted behavior yields a plateau at 3.33 \( \mu_B \)/Ho atom followed by saturation at 5.00 \( \mu_B \)/Ho atom for the case \( g = 20 \). Our data for \( B[|111]\) clearly shows a plateau at \( \sim 3.3 \mu_B/\text{Ho} \) appearing as temperature is lowered, which agrees well with the predicted behavior. However, the saturation magnetization is approximately 20% higher than calculated. For \( B[|100]\) and \( B[|110]\), the data at \( T = 1.8 \) K qualitatively agree well with the predicted behavior \(^5\). In particular, for \( T < T^* \), the field required to reach saturation is significantly less for \( B[|110]\) as for \( B[|111]\). It is seen that, in stark contrast to the predicted behavior of a saturation moment of 5.78 \( \mu_B/\text{Ho} \) for \( B[|110]\) and 4.08 \( \mu_B/\text{Ho} \) for \( B[|111]\), the measured saturation moment of 5.9 \( \mu_B/\text{Ho} \) is close to the value expected for \( B[|110]\) and is nearly independent of direction, though it requires a higher field than reached in the current experiment to say for certainty that saturation has been achieved for \( B[|110]\). We have no definitive explanation for the lack of anisotropy in the measured saturation moment, perhaps the influence of the dipolar interaction, which is not taken into account by Harris et al. \(^6\), plays a role. We should also point out that the calculations of Harris et al. \(^7\) are at \( T/J = 0.1 \sim 0.3 K \), which is much lower than our lowest temperature, but the qualitative agreement is good since both temperatures are below \( T^* \). This is the same conclusion of a different simulation that shows a single step like feature followed by saturation for \( B[|111]\) and an identical saturation moment (though a much different \( M \) versus \( B \) curve) for a different field direction \(^8\).

We have performed the first measurements of the magnetization on Ho\(_2\)Ti\(_2\)O\(_7\) single crystals along various crystalline directions. The magnetization results can be explained by \( S = 1/2 \) spins with \( g = 20 \) which lock in along the [111] direction at \( T^* \approx 1.97 \) K, and the results of applying the field along the different crystalline axes are explained qualitatively by a Monte Carlo calculation of the spin-ice model with nearest neighbor interactions only \(^9\). In particular, the observation of a plateau in the magnetization as a function of applied magnetic field for \( B[|111]\) at \( T < T^* \) as predicted \(^5\), has been observed for the first time. Contrary to predicted behavior \(^5\), it was found that the saturation magnetic moment of \( \sim 5.9 \mu_B/\text{Ho} \) is nearly independent of the orientation of the crystalline axes relative to the applied field. The magnetization and heat capacity measurements are both consistent with an interaction strength of \( J \approx 7.2 \sim 7.4 \) K between the Ho magnetic moments.

In conclusion, above \( T^* \) the spins have a preferred orientation along the [111] direction due to single ion anisotropy revealed by the reduced saturated moment in the system. From magnetization measurements below 2 K the moments on a single tetrahedron have a specific two-spins-in, two-spins-out configuration and the moments cannot overcome an energy barrier to another configuration. This result is consistent with neutron scattering work which finds the Ho spins in a two-spins-in, two-spins-out configuration and recent specific heat results \(^4\).

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FIG. 1. AC susceptibility times temperature versus inverse temperature on a Ho$_2$Ti$_2$O$_7$ single crystal for magnetic field applied along the [111] axis. The horizontal line is the expected value for $g = 20$. The other line is a fit described in the text.

FIG. 2. The inverse static susceptibility in an applied field of 1 kOe as a function of temperature. The line is a Curie-Weiss fit as described in text. The inset shows the magnetic entropy $\Delta S_m$ as a function of temperature $T$ for Ho$_2$Ti$_2$O$_7$ at 0 T and 1 T. The solid line corresponds to the expected values of the nearest neighbor spin-ice model as discussed in the text. The dashed lines represent the recovery of $(1/2)R\ln(3/2)$ of the expected $R\ln 2$ entropy as discussed in text.

FIG. 3. Magnetization as a function of applied magnetic field along the listed crystalline directions for Ho$_2$Ti$_2$O$_7$ at various temperatures. A plateau is clearly observed in the data for $B||[111]$ as the temperature is lowered below $T^* \simeq 2$ K.
Cornelius and Gardner, Fig. 2
Cornelius and Gardner, Fig. 3

$M (\mu_B / H_o)$ vs $\mu_o H$ (T)

- $T=4.0$ K
- $T=2.0$ K
- $T=1.8$ K

$B || [111]$ (solid circle)
$B || [100]$ (solid star)
$B || [110]$ (solid square)