First order metamagnetic transition in Ho$_2$Ti$_2$O$_7$ observed by vibrating coil magnetometry at milli-Kelvin temperatures

C. Krey, S. Legl, S. R. Dunsiger, M. Meven, J. S. Gardner, J. M. Roper, and C. Pfleiderer

1 Technische Universität München, Physik-Department E21, D-85748 Garching, Germany
2 Technische Universität München, Forschungsneutronenquelle FRM II, D-85748 Garching, Germany
3 Department of Physics, Indiana University, Bloomington, IN 47408, USA
4 Los Alamos National Laboratory, Los Alamos, USA

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We report vibrating coil magnetometry of the spin ice system Ho$_2$Ti$_2$O$_7$ down to $\sim 0.04$ K for magnetic fields up to 5 T applied parallel to the [111] axis. History dependent behavior emerges below $T^*_m \sim 0.6$ K near zero magnetic field, in common with other spin ice compounds. In large magnetic fields we observe a magnetization plateau followed by a hysteretic metamagnetic transition. The temperature dependence of the coercive fields as well as the susceptibility calculated from the magnetization identify the metamagnetic transition as a line of first order transitions terminating in a critical endpoint at $T^*_m \approx 0.37$ K, $B_m \approx 1.5$ T. The metamagnetic transition in Ho$_2$Ti$_2$O$_7$ is strongly reminiscent of that observed in Dy$_2$Ti$_2$O$_7$, suggestive of a general feature of the spin ices.

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Metamagnetism (MMT), where a paramagnet undergoes a first order phase transition to a ferromagnetic (FM) state in high magnetic fields with a discontinuous jump in the magnetisation, is a pervasive phenomenon in systems based on rare earth or transition metals. However, despite striking similarities in the magnetization of a wide range of MMTs their microscopic origin may be radically different (see e.g. [1–6]). A prominent example of such a MMT has been reported recently for Dy$_2$Ti$_2$O$_7$, where the transition is preceded by a plateau in the magnetization and a critical end-point is located at $T^*_m \sim 0.36$ K and $B_m \sim 0.9$ T for fields strictly parallel to a (111) axis [7–8]. It has been argued that the MMT in Dy$_2$Ti$_2$O$_7$ reflects directly the nature of the spin excitations from the zero-field spin state [9]. The magnetic ions in Dy$_2$Ti$_2$O$_7$ reside on the vertices of a pyrochlore lattice of corner sharing tetrahedra in the presence of strong local (111) crystalline anisotropy and effective ferromagnetic interactions, leading to geometric frustration. The ground state is characterized by a residual entropy quantitatively comparable to the value of water ice [10–12]. This reflects spin disorder at low temperature such that two spins are constrained to point outward and two spins in towards the center of a tetrahedron [11–13].

The MMT in Dy$_2$Ti$_2$O$_7$ has been explained in terms of an entropy reduction which takes place in two steps [14]. First, the system partially magnetizes retaining the two-in, two-out state, in which one of the four spins on each tetrahedron has a component of the moment antiparallel to the field. Second, as the field increases further, the nearest-neighbor spin ice model predicts an ice-rule breaking spin flip to the three-in, one-out (one-in, three out) state [15] [16]. Recent theoretical work suggests that the spin-flips related to the second step may be viewed as emergent magnetic monopoles that condense at the MMT [17] [17]. This scenario was subsequently found to be consistent with the entropy reduction inferred from the magnetocaloric effect [8] [18], as well as the evolution of the spin relaxation time in the ac susceptibility [19] [20], at least above 1 K. The strong temperature dependence of the specific heat below 1 K [21], the heat transport [22] and finally magnetization avalanches in low magnetic fields [23] are also thought to be consistent with magnetic monopoles. On a microscopic level, evidence for magnetic monopoles in Dy$_2$Ti$_2$O$_7$ has been inferred from the observation of lines of reversed spins between monopole pairs (cf. Dirac strings) using neutron scattering [21].

A second candidate for emergent magnetic monopoles is Ho$_2$Ti$_2$O$_7$. The experimental situation in Ho$_2$Ti$_2$O$_7$ is, however, much less clear. Neutron scattering at low temperatures reveals pinch-points in the structure factor consistent with power law correlation functions [24] [25]. However, neutron spin echo and neutron backscattering experiments [26–28] suggest intrinsic spin relaxation times much faster than for Dy$_2$Ti$_2$O$_7$, raising the question how this may be reconciled in terms of magnetic monopoles. Further, the specific heat displays large nuclear hyperfine contributions [29], which manifest themselves as a Schottky anomaly, complicating a comparison with the predictions for spin ice behaviour. The magnetization of Ho$_2$Ti$_2$O$_7$ for a field along [111] reported so far down to 0.5 K [30] [31] showed a non-linear increase around 2 T reminiscent of Dy$_2$Ti$_2$O$_7$ (distinct from discussions of a liquid-gas transition for fields along [100] [32]). In general, the magnetic phase diagram of Ho-based compounds may show strong effects below 0.5 K due to hyperfine interactions as e.g., for the transverse field Ising magnet LiHoF$_4$ [33]. Hence, detailed measurements below 0.5 K are needed to explore the putative equivalence between Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ quantitatively.
The observation of history dependencies and dynamics on long timescales in Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ in previous studies imposes strong experimental constraints. First, tiny sample movements in the applied magnetic field must be avoided; they might change the magnetic state. Second, the sample must be rigidly anchored thermally, since changes of the magnetization may cause large associated entropy release and uncontrolled local heating effects. Third, as the magnetic properties are sensitive to the precise field value and orientation [34, 35] a uniform applied field is essential.

All of these requirements are met by the vibrating coil magnetometer (VCM) [36, 37] we used to measure the magnetization of Ho$_2$Ti$_2$O$_7$. Data reported in the following between 0.04 K and $\sim$ 1.8 K correspond to the properties for field parallel to [111] within a few tenths of a degree. For larger misalignments ($\sim\pm 2^\circ$) we found that the features of interest tend to broaden and shift, with additional hysteretic features suggesting complexities beyond the scope of our study. All temperature dependent data were recorded while continuously heating at a rate of 5 mK/min, where zero-field cooled properties and field-cooled properties are distinguished. Likewise, all measurements as a function of magnetic field followed the zero-field cooled properties with respect to zero field.

The Ho$_2$Ti$_2$O$_7$ single crystal studied was grown by means of optical float zoning at LANL in an argon atmosphere at 5 mm/hr. Single crystal neutron diffraction at HEIDI (FRM II) establish a room temperature lattice constant of $a=10.13(2)$ $\text{Å}$ consistent with previous studies [38]. A psi scan of the (555) reflection confirms the homogeneity and high quality of the sample. Demagnetising fields were accounted for by approximating the disc shaped single crystal as an ellipsoid ($7.3 \times 4.8 \times 1.2$ mm$^3$) with a demagnetising factor $N=0.75$ ([111] direction perpendicular to the plane) [39, 40]. The edges of the sample were wedge shaped, which may result in a distribution of internal fields over a small volume fraction. This does not affect the main conclusions reported here.

Shown in Fig. 1(a) is the temperature dependence of the magnetization of Ho$_2$Ti$_2$O$_7$ for $B = 0.01$ T along [111]. With decreasing temperature the low-field magnetization increases gradually, characteristic of a paramagnetic state. Below a temperature $T^*_0 \sim 0.6$ K the zfc/fc and fc/fh data begin to show pronounced differences. While the former rapidly decreases to a very low value, the latter remain constant. This behaviour is strongly reminiscent of other spin ices, where $T^*_0$ is roughly 0.6-0.75 K for A$_2$B$_2$O$_7$ (A= Dy, Ho; B= Ti, Sn) [30, 41, 42], i.e., $T^*_0$ is not proportional to the rare earth exchange coupling $J$ [43]. The microscopic origin of the history dependence shares many features of magnetic blocking, but is not understood. For instance, Monte Carlo simulations predict a 1st order transition at 0.18K [44] which has never been observed experimentally. Interestingly, however, an exponential slowing down of the spin relaxation has been reported in solid paramagnets which proceeds via energy levels caused by crystalline or hyperfine splitting of the ground state of the ion [45].

As a function of magnetic field the history dependence below $T^*_0$ is connected with strong hysteresis with respect to $B = 0$, followed by a metamagnetic increase at a field $B^*_m \sim 1.5$ T, which becomes distinctly hysteretic at low temperatures. This is illustrated in Fig. 2, where typical data are shown as a function of internal magnetic field, $B_{\text{int}}$, given by $\mu_0 H + M$. Data at 1.8 K shown in Fig. 2(a) are in excellent agreement with Refs. [30, 31]. The variation of the magnetization near $B = 0$ and around 1.5 T becomes much steeper below $T^*_0 = 0.7$ K as shown in

![Image](https://example.com/image.png)
FIG. 2: (Color online) Magnetic field dependence of the low temperature magnetization of Ho$_2$Ti$_2$O$_7$. With decreasing temperature, hysteresis emerges at $B = 0$ and around 1.5 T. The susceptibility calculated from the magnetization is shown on the right hand side of each panel. At the metamagnetic transition it increases strongly with decreasing temperature.

FIG. 3: (Color online) Magnetization of Ho$_2$Ti$_2$O$_7$ as a function of internal magnetic field after correction of the demagnetising fields, following field sweeps of protocol (B). For $T < T_0^*$ the initial change of the magnetization is zero within experimental sensitivity and followed by a very pronounced increase with increasing field. (a) Magnetic field dependence in sweeps of type B1. (b) through (d) magnetization in field cycles of sweep types B1, B2 and B3 (e) magnetization in field cycles of sweep types A4 and A5.

There are several regimes: essentially no hysteresis is observed at 0.7 K within the accuracy of our set-up. At $T = 0.4 K < T_0^*$, shown in Fig. 2(c), sizeable hysteresis may be seen with respect to zero field, while the magnetization at the second step rises non-hysteretically, but more steeply than at 0.7 K. Finally, as shown in Fig. 2(d), hysteresis exists with respect to both $B = 0$ and $B_m = 1.5$ T for 0.1 K.

In order to track the width of the hysteresis loop we define coercive fields $B_0^-$, $B_0^+$ and $B_m^-$ (see Fig. 2(d)). Shown in Fig. 2(b) are the coercive fields $B_0^-$, $B_0^+$, which increase strongly below $T_0^*$ with decreasing temperature and appear to level off around ±0.2 T as $T \rightarrow 0$. In contrast, the hysteretic behaviour at high fields appears at $T_m^* = 0.37$ K, well below $T_0^*$ (Fig. 2(c)).

No conventional long range thermodynamic ordering transition is reported as a function of temperature at $B = 0$, despite the appearance of strong hysteresis. Specifically, there is no development of magnetic Bragg peaks. Rather, the notion of strong magnetic blocking is beautifully illustrated by the initial field dependence of the magnetization for $T < T_0^*$ after zfc. Shown in Fig. 3(a) is the magnetization in the first field sweep after zero-field cooling (referred to as B1). Up to field values exceeding the coercive fields seen in field sweeps (B2), (B3) the magnetization is unchanged and trapped in the zfc state. The peculiar field dependence, specifically the negative slope of the magnetization at intermediate fields is reminiscent of Dy$_2$Ti$_2$O$_7$ (Fig. 3(b) through (e)), where it has been interpreted as evidence of monopole avalanches [23]. However, similar features have also been reported in mesoscopic spin systems [40]. In view of the enormous sensitivity to the precise orientation of the sample and the large demagnetising factor, as well as a small distribution of internal fields at its fringes, a detailed account of possible magnetization avalanches is beyond the scope of our study.

Two arguments establish that the hysteresis at $B_m$ is connected with a thermodynamic phase transition, in contrast to the behaviour in zero field. First, the inverse susceptibility at $B_m$ calculated from the magneti-
zation essentially displays a Curie dependence and vanishes within experimental accuracy at $T_m^\ast = 0.37(0.01)$ K and $B_m^\ast = 1.52(0.01)$ T as shown in Fig.[1(d)]. This is characteristic of a critical point at $(T_m^\ast, B_m^\ast)$. Moreover, the hysteresis observed for $T < T_m^\ast$ provides evidence that this critical point is located at the end of a line of first order transitions. Interestingly, $T_m^\ast$ is found to be very close to the value for Dy$_2$Ti$_2$O$_7$.[7]. By contrast, theory predicts scaling of $B_m^\ast$ with the effective exchange coupling $J_{\text{eff}}$.[18, 37]. Given $J_{\text{eff}} = 5D/3 + J/3$, where $D$ is the dipolar coupling between the rare earth moments, $J$ is the dipolar coupling between the rare earth moments, $J_{\text{eff}}$ is located midway in the hysteretic range or at the field of the peak of $dM/dB$ we find $dB_m/dT \approx 0.2$ T/K. In this case the expected entropy release at $B_m$ exceeds the entropy associated with Kagomé ice by an unphysically large factor of 3.65. Hence the latter prescription must be inappropriate.

Second, following the Clausius-Clapeyron equation (CC), $dB_m/dT = -\Delta S/\Delta M$, the transition at $B_m$ is connected with a strong entropy reduction of a thermodynamic phase transition subject to the value of $dB_m/dT$. Because the transition at $B_m$ is hysteretic determination of the phase boundary using CC depends on the choice of $dB_m/dT$. As a first step it is instructive to suppose Kagomé ice behaviour for $B < B_m$. In this case a rigorous calculation predicts an entropy reduction of $0.672 \cdot 10^{-1}$ mol$^{-1}$-ion.[18]. The corresponding value of $dB_m/dT = 0.073$ T/K, as shown by the solid black line passing through $(T_m^\ast, B_m^\ast)$ in Fig.[1] is perfectly consistent with our data and follows the cross-over line for $T > T_m^\ast$. However, the phase boundary would lie asymmetrically with respect to $B_m^\ast$ and $B_m$. If we assume instead that $B_m$ is located midway in the hysteretic field range or at the field of the peak of $dM/dB$ we find $dB_m/dT \approx 0.2$ T/K. In this case the expected entropy release at $B_m$ exceeds the entropy associated with Kagomé ice by an unphysically large factor of 3.65. Hence the latter prescription must be inappropriate.

Strong support for the assumption of Kagomé ice behaviour for $B < B_m$ may be seen in the magnetization, which forms a very well defined plateau at $3.55 \mu_B$ Ho$^{-1}$ (cf Fig.[2(a)]). This is quantitatively in excellent agreement with theoretical prediction. Moreover, above $B_m$ the magnetization assumes a well-defined value of $5.20 \mu_B$ Ho$^{-1}$ for $T \to 0$ characteristic of a three-in/one-out spin configuration. Thus the magnetization of Ho$_2$Ti$_2$O$_7$ is quantitatively comparable with that of Dy$_2$Ti$_2$O$_7$ and consistent with the dipolar spin ice model. The temperature dependence of $B_m^\ast$ and $B_m^\ast$ and the magnetization provide unambiguous evidence of a first order transition with a large entropy reduction. Experimental determinations of the residual entropy of the Kagome ice state inferred from the specific heat in Dy$_2$Ti$_2$O$_7$ for $B < B_m$ are scattered between $0.44(8) - 0.8(1)$ J K$^{-1}$ mol$^{-1}$-Dy.[16, 39], consistent with the value inferred from the magnetization, $0.5 J K^{-1} mol^{-1}$-Dy.[7]. The temperature dependence of the entropy release in the magnetocaloric effect in Dy$_2$Ti$_2$O$_7$[8] is attributed to magnetic correlations.[50].

We finally show in Fig.[4] the magnetic phase diagram of Ho$_2$Ti$_2$O$_7$ for the [111] axis inferred from our magnetization data. In zero field Ho$_2$Ti$_2$O$_7$ enters a spin ice state with strong spin blocking below $T_0^\ast$. A moderate field stabilises a magnetization plateau characteristic of Kagomé ice. Further increasing the field results in a line of first order metamagnetic phase transitions up to a critical endpoint at $T_m^\ast = 0.37$ K and $B_m^\ast = 1.52$ T. This line of transitions separates Kagomé ice from the spin polarised 3-in/1-out configuration. While the critical field for $T \to 0$ scales experimentally with the $J_{\text{eff}}$, in agreement with theory, $T_0^\ast$ and $T_m^\ast$ appear to be material independent for Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$. The tuning parameter for these energy scales remains to be explored.

In conclusion, the remarkable analogy we observe between the properties of Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ establishes the field induced liquid-gas like transition, interpreted in terms of the condensation of magnetic monopoles, as a more generic phenomenon within spin ice systems. However, given the importance of dipolar interactions and the resultant power law correlations.[25] as an essential prerequisite for a description of the excitations in terms of magnetic monopoles, it also seems clear that further Ising like compounds not based on Ho or Dy, which have similar classical magnetic moments, must be investigated. In this way, the strength of the dipolar coupling could be controllably tuned. Perhaps most remarkably, the phase boundaries appear to be independent of the strength of the hyperfine interactions, which are much stronger in Ho$_2$Ti$_2$O$_7$. It is important to note that the dc magnetization is a measure of the zero
frequency response of the system. Subleading transverse interactions $J_{\perp}$, which are material dependent and could lead for instance to differing quantum tunnelling amplitudes between spin-ice states are predicted to affect the finite frequency response [51]. A complete description of the excitations in terms of magnetic monopoles must account for such differences.

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SUPPLEMENTARY MATERIAL FOR: FIRST ORDER METAMAGNETIC TRANSITION IN HO$_2$TI$_2$O$_7$ OBSERVED BY VIBRATING COIL MAGNETOMETRY AT MILLI-KELVIN TEMPERATURES

In this supplement we present a detailed account of the precise temperature and field history used in our measurements and the terminology used to refer to specific temperature and field sweeps in the main text.

Temperature dependence

We distinguish two types of temperature sweeps, namely zero-field cooled/field heated (zfc/fh) and field-cooled/field heated (fc/fh). In both cases data were recorded while heating the sample continuously at a rate of 5 mK/min. Data denoted as zfc/fh were recorded after initially cooling the superconducting magnet system and cryostat from room temperature, to guarantee the absence of any remanent magnetic fields. To record data denoted as fc/fh, we recooled the sample to base temperature after the zfc/fh measurement was completed (at roughly 1.5 K), keeping the magnetic field unchanged. Data were then recorded again while continuously heating.

Field dependence: Protocol A

For field sweeps following protocol (A) the empty VCM was at first demagnetised and the sample cooled in zero magnetic field to $T = 1.8$ K. Data were subsequently recorded in three field sweeps as follows: (A1) $0 \rightarrow +5$ T, (A2) $+5$ T $\rightarrow -5$ T, and (A3) $-5$ T $\rightarrow +5$ T. At the final field of $+5$ T the temperature was changed. At each subsequent temperature two field sweeps were carried out, namely (A4) $+5$ T $\rightarrow -5$ T and (A5) $-5$ T $\rightarrow +5$ T.

At temperatures above 0.1 K all data were recorded while sweeping the field continuously at 15 mT/min. Below 0.1 K, to avoid heating effects due to eddy currents, data were recorded in a step mode, holding the magnetic field constant while recording the magnetisation.

Field dependence: Protocol B

For measurements following protocol (B) the empty VCM was at first demagnetised and the sample subsequently cooled in zero magnetic field from room temperature directly to the temperature of interest. Data were then recorded in a sequence of three field sweeps: (B1) $0 \rightarrow +5$ T, (B2) $+5$ T $\rightarrow -5$ T, and (B3) $-5$ T $\rightarrow +5$ T. For the next set of measurements following protocol (B) the sample was removed from the VCM and the empty VCM again demagnetised.

At temperature below 0.1 K and for all sweeps of type (B1) data were recorded in a step mode. All other data were recorded while sweeping the field continuously at 15 mT/min. No differences were observed between (A4), (A5) and (B2), (B3), respectively.

| sweep # | field values | condition |
|---------|--------------|-----------|
| protocol (A) | A1 $0 \rightarrow 5$ T | zfc to 1.8 K |
|          | A2 $+5$ T $\rightarrow -5$ T |
|          | A3 $-5$ T $\rightarrow +5$ T |
|          | A4 $+5$ T $\rightarrow -5$ T | field-cooled |
|          | A5 $-5$ T $\rightarrow +5$ T | field-cooled |
| protocol (B) | B1 $0 \rightarrow +5$ T | zfc from ambient |
|          | B2 $+5$ T $\rightarrow -5$ T |
|          | B3 $-5$ T $\rightarrow +5$ T |

TABLE I: Summary of protocol (A) and (B) used in measurements as a function of magnetic field. Zero-field-cooled and field-cooled starting conditions are denoted as zfc and fc, respectively.