

## Field-induced partial order in the spin ice dysprosium titanate

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**Abstract.** Neutron scattering has been used to investigate the magnetic correlations in the spin-ice material dysprosium titanate, Dy<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. An isotopically enriched sample was used to minimise neutron absorption. In zero field no magnetic order was observed down to 50 mK but the magnetic diffuse scattering was in qualitative agreement with that expected for the disordered low-temperature state of dipolar spin ice. Application of a field of  $\approx 0.8$  T in the [100] direction led to long-range order. With the field applied in the [1 $\bar{1}$ 0] direction a coexistence of long-range ferromagnetic and short-range antiferromagnetic order was observed. This is attributed to the pinning of only half the spins by the field. The hysteresis loops in both field orientations displayed unusual steps and plateaus.

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Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Dy<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are regarded as good examples of spin-ice materials [1–3]. The magnetic rare earth ions occupy a pyrochlore lattice, a cubic array of corner-linked tetrahedra. In the near neighbour spin ice model the lattice is occupied by  $\langle 111 \rangle$  Ising spins that are coupled ferromagnetically to nearest neighbours [4]. The result is a disordered, macroscopically degenerate, ground state that is determined only by the rule that two spins must point into and two out of each tetrahedron. This “two in, two out” rule is analogous to the “ice rules” that control the proton arrangement in water ice, and so the near neighbour spin ice model maps exactly onto Pauling’s model of the proton disorder in water ice [4, 5]. The near neighbour spin ice model qualitatively describes much of the behaviour of the real materials, but for an accurate description the dipolar spin ice model has been developed [6]. In this model, the near neighbour ferromagnetic coupling between  $\langle 111 \rangle$  spins is dipolar in origin and it has been shown that the long range part of the dipolar coupling maintains a spin-ice

like disordered ground state even in the presence of an antiferromagnetic near neighbour super-exchange [6]. The dipolar spin ice model has been shown to give an accurate description of the zero field magnetic neutron scattering of Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [2] in the spin ice regime ( $T < 2$  K) as well as the specific heat of Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Dy<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> throughout the low temperature range (50 mK–20 K) [2, 6]. The dipolar coupling in Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Dy<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is of similar magnitude ( $D_{nn} \approx 2.35$  K for both Dy and Ho) while the antiferromagnetic exchange is weak in both cases (–1.2 K for Dy and –0.52 K for Ho) [2, 6]. The main difference between these two materials appears to arise from the nuclear spins. Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> has a single isotope (<sup>165</sup>Ho) and strong hyperfine coupling that complicates the spin ice freezing process below  $\approx 0.8$  K [2]. Dy<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, on the other hand, has much weaker hyperfine coupling that does not affect the dominant spin ice behaviour in the temperature range of interest. It might therefore be considered the simpler spin ice material. However, the natural mixture of Dy isotopes leads to significant neutron absorption (994 barn for 2200 ms<sup>–1</sup> neutrons). Thus, although neutron scattering should be the ideal microscopic probe of the spin correlations and dynamics of this system, the most significant experimental observations so far are bulk measurements [3]. To minimise the absorption problem we have prepared a single crystal of <sup>162</sup>Dy<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. In this paper we present the initial results of our neutron scattering study of this sample, in both zero and applied magnetic field.

### 1 Experimental

The absorption cross section of natural Dysprosium is  $\sigma_a = 994$  barn, the large value being due mainly to the presence of <sup>164</sup>Dy. Isotopically enriched Dy<sub>2</sub>O<sub>3</sub> with composition <sup>156</sup>Dy < 0.01%, <sup>158</sup>Dy < 0.01%, <sup>160</sup>Dy = 0.02%, <sup>161</sup>Dy = 0.47%, <sup>162</sup>Dy = 96.8%, <sup>163</sup>Dy = 2.21% and <sup>164</sup>Dy = 0.5% was prepared by Goss Scientific Instruments Ltd. Enrichment in <sup>162</sup>Dy was considered optimum as it has a high abundance and the dominant impurity is <sup>163</sup>Dy which has a slightly lower absorption cross section. Enrichment in <sup>163</sup>Dy would have led to <sup>164</sup>Dy as the dominant impurity. Through enrichment,

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the absorption cross section was reduced by a factor of five to  $208 \pm 13$  barn.

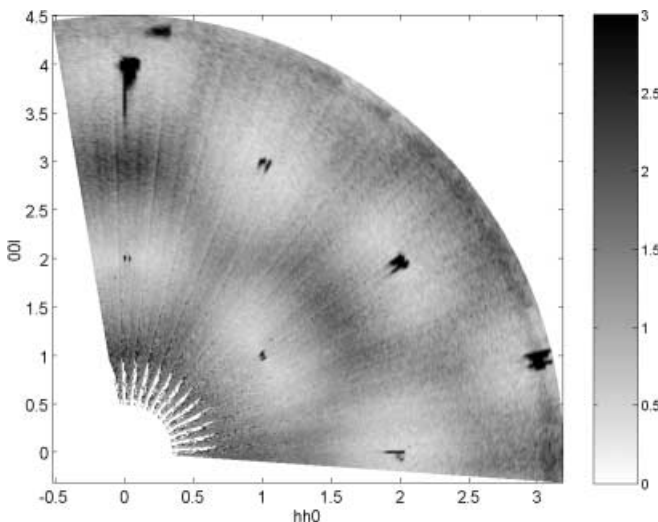
A single crystal of  $\text{Dy}_2\text{Ti}_2\text{O}_7$  was prepared from the isotopically enriched  $\text{Dy}_2\text{O}_3$  and  $\text{TiO}_2$  by the floating zone technique [8]. Neutron scattering was carried out at the ISIS facility on the indirect geometry spectrometer PRISMA. It was configured in the diffraction mode so that sixteen  $^3\text{He}$  tube detectors are used simultaneously. Rotation of the crystal allows a rapid mapping of a large section of reciprocal space, making PRISMA ideal for observing magnetic diffuse scattering.

In the first experiment the crystal was cooled by a  $^3\text{He}$  sorption refrigerator for measurements in zero applied magnetic field. It was aligned with  $[1\bar{1}0]$  vertical, such that the scattering plane contained  $(hhl)$  wavevectors. In the second experiment an Oxford instruments 7 T vertical field cryomagnet, with dilution refrigerator insert, was used. For the applied field measurements two field orientations were studied:  $[1\bar{1}0]$  as above and  $[100]$  corresponding to a  $(0kl)$  scattering plane. The data were normalised to monitor counts and vanadium to remove the characteristic flux profile of the spallation source. Since the sample is still significantly absorbing a correction for this was also applied.

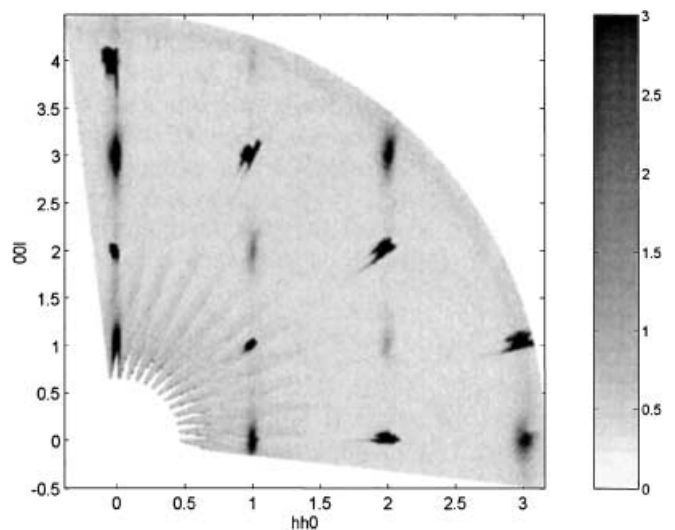
## 2 Results

With  $[100]$  vertical, a map of reciprocal space was made at the base temperature ( $\approx 70$  mK) in zero field. The diffuse scattering maxima observed agree with those predicted in the  $(hhl)$  scattering plane for the dipolar spin ice model. For example there is a diffuse feature at  $3, 0, 0$  in  $(hk0)$  and  $0, 0, 3$  in  $(hhl)$  [2]. On application of a field the diffuse scattering disappeared and was replaced by magnetic Bragg peaks at the  $Q = 0$  positions. A field of  $\approx 0.7$  T was sufficient to saturate these peaks.

This behaviour is readily explained as the applied field breaks the degeneracy of the six “two in, two out” spin configurations of the elementary tetrahedron. The pyrochlore lattice



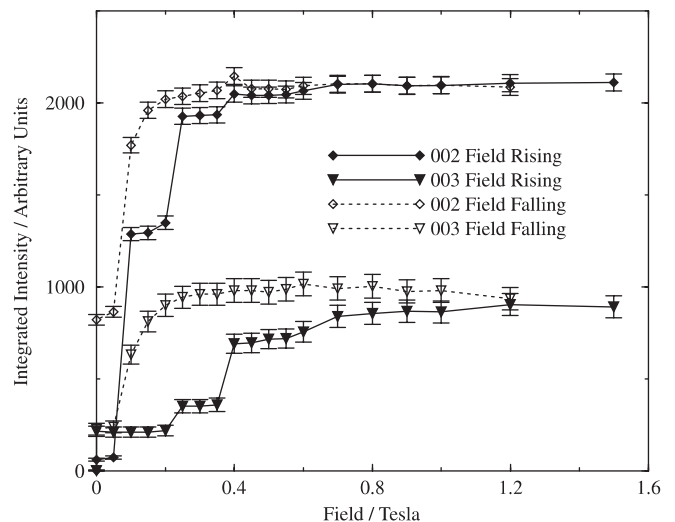
**Fig. 1.** Diffuse scattering in the  $(hhl)$  plane. In zero field at 270 mK no magnetic Bragg peaks are observed. All resolution limited intense features are of nuclear origin



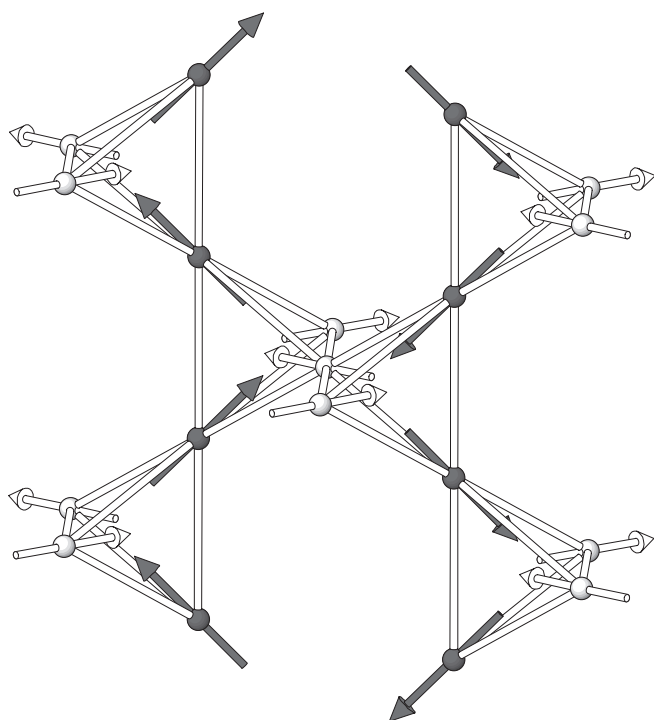
**Fig. 2.** Scattering in the  $(hhl)$  plane with a field of 1.5 T applied on  $[1\bar{1}0]$  at  $\approx 60$  mK. Magnetic Bragg peaks have appeared at positions such as  $2, 0, 0$  and the diffuse features observed in zero field at positions such as  $0, 0, 3$  have sharpened into features elongated on  $[00l]$

can be described as a face centred cubic lattice with a tetrahedral basis, and the degeneracy breaking means that every tetrahedron adopts the same “two in, two out” state with a net moment in the direction of the applied field,  $[100]$ . This non-collinear ferromagnetic structure allows the observed magnetic Bragg peaks at the  $Q = 0$  positions such as  $2, 0, 0$ . Interestingly the experimental magnetization did not develop smoothly, but in a series of steps. Hysteresis was observed on cycling the field.

The  $[1\bar{1}0]$  direction is a hard direction of magnetization [9]. In zero field, the magnetic scattering was observed to be diffuse, and characteristic of the disordered low temperature state of dipolar spin ice [2], see Fig. 1. Application of a small field ( $\approx 0.1$  T) in this direction again caused the appearance of the  $Q = 0$  Bragg peaks; however, unlike the



**Fig. 3.** Integrated intensity of the  $0,0,2$  magnetic Bragg peak and the  $0,0,3$  diffuse feature (scaled  $\times 3$  for this plot) as the field is scanned at  $\approx 70$  mK



**Fig. 4.** A fragment of the pyrochlore lattice illustrating the  $Q = X$  structure. The applied field is projected into the plane of the page and pins the unshaded spins into ferromagnetic chains. The *shaded spins* are not coupled to the field but are governed by the “ice rules”. The *shaded spins* may form two structures, either  $Q = 0$  with all shaded spin chains parallel or  $Q = X$  with shaded spin chains antiparallel. This degeneracy is not raised by the field

[100] direction, the diffuse scattering features did not disappear. As the field was raised up to 1.5 T the diffuse scattering sharpened around the  $Q = X$  positions such as 0, 0, 1 without becoming resolution limited. This is seen clearly in Fig. 2. Similar features have been observed in the neutron scattering of  $\text{Ho}_2\text{Ti}_2\text{O}_7$  [1, 7], adding strength to the idea that the true ground state of these systems is a  $Q = X$  structure that is dynamically inhibited from being accessed on experimental timescales [10]. Again the magnetization versus field curve was observed to have several sharp steps and plateaus (Fig. 3).

The formation of the  $Q = X$  structure is consistent with the spin ice rules [1]. In this field orientation, assuming perfect  $\langle 111 \rangle$  spins, only two of the spins of the tetrahedral basis have a component along the field direction. These form

“in-out”  $[1\bar{1}0]$  chains parallel to the field forcing the remaining two spins per tetrahedra into “in-out”  $[110]$  chains perpendicular to the field, as illustrated in Fig. 4. The perpendicular chains are not coupled to each other by the spin ice rules which, in the absence of any further neighbour coupling, would lead to two dimensional  $[110]$  Bragg sheets of scattering extended along  $[00l]$  in the scattering plane. The diffuse features in the experimental pattern are indeed extended along this direction, but the sharp build up of intensity around the  $Q = X$  points indicates a strong tendency to prefer  $Q = X$  short range ordering of the perpendicular rods (see Fig. 2). Neglecting interference between the scattering from the two spin sets (perpendicular and parallel to the field) one arrives at the conclusion that the  $Q = 0$  Bragg scattering arises from the parallel rods and the  $Q = X$  diffuse scattering arises from the perpendicular rods. However, it may be a crude approximation to separate the scattering in this way.

In conclusion, we have obtained accurate neutron scattering data for  $\text{Dy}_2\text{Ti}_2\text{O}_7$  that is in qualitative agreement with theoretical expectations for a spin ice material [1, 2, 4, 6]. It is of interest that, even in a relatively strong field along  $[1\bar{1}0]$ , the system remains only partially ordered. It is also noteworthy that the magnetic hysteresis loop shows several steps and plateaus. An understanding of these effects awaits a detailed study of the static and dynamic properties of the dipolar spin ice model [6] in an applied magnetic field.

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