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# Titanium pyrochlore magnets: how much can be learned from magnetization measurements?

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## Abstract

We report magnetization data for several titanium pyrochlore systems measured down to 0.5 K. The measurements, performed on single crystal samples in fields of up to 7 kOe, have captured the essential elements of the previously reported phase transitions in these compounds and have also revealed additional important features overlooked previously either because of the insufficiently low temperatures used, or due to limitations imposed by polycrystalline samples. For the spin-ice pyrochlores  $\text{Dy}_2\text{Ti}_2\text{O}_7$  and  $\text{Ho}_2\text{Ti}_2\text{O}_7$ , an unusually slow relaxation of the magnetization has been observed in lower fields, while the magnetization process in higher fields is essentially hysteresis-free and does not depend on sample history. For the  $XY$  pyrochlore  $\text{Er}_2\text{Ti}_2\text{O}_7$ , the magnetic susceptibility shows nearly diverging behaviour on approach to a critical field,  $H_C = 13.5$  kOe, above which the magnetization does not saturate but continues to grow at a significant rate. For the Heisenberg pyrochlore  $\text{Gd}_2\text{Ti}_2\text{O}_7$ , the magnetic susceptibility shows a pronounced change of slope at both transition temperatures,  $T_{N1} = 1.02$  K and  $T_{N2} = 0.74$  K, contrary to the earlier reports.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

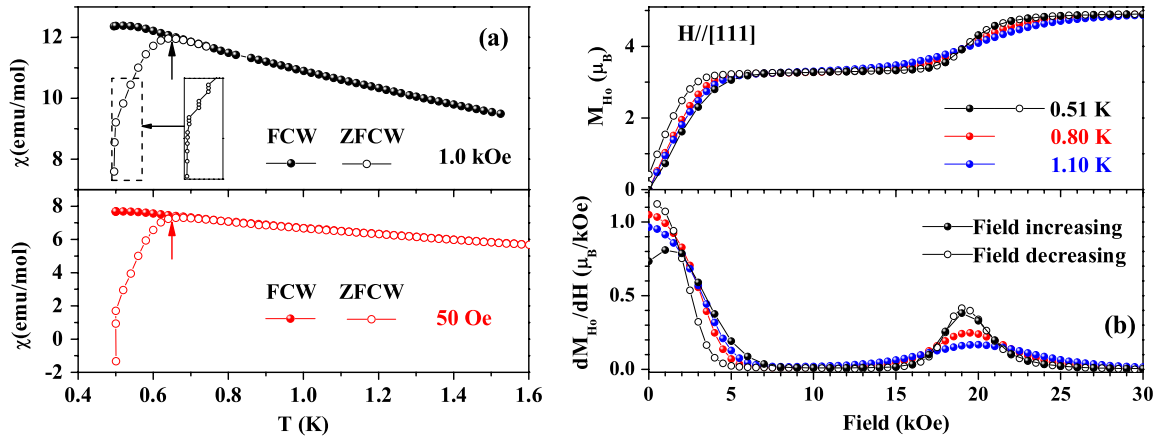
Since the publication ten years ago of a paper on the bulk magnetization of the heavy rare earth titanate pyrochlores [1], significant progress has been made in the understanding of the magnetic properties of the various members of this family [2]. This progress is due to the utilization of both advanced experimental techniques (such as, for example, diffuse neutron scattering with polarization analysis [3]) and modern numerical and theoretical methods. Despite often being perceived as simple and straightforward, magnetization measurements capture nicely the physics of titanium pyrochlores. We revisit and extend the bulk magnetization studies of the spin-ice systems  $\text{Dy}_2\text{Ti}_2\text{O}_7$  and  $\text{Ho}_2\text{Ti}_2\text{O}_7$ , an  $XY$  antiferromagnet  $\text{Er}_2\text{Ti}_2\text{O}_7$ , and a Heisenberg pyrochlore  $\text{Gd}_2\text{Ti}_2\text{O}_7$ , by performing the measurements (i) on high quality single crystals, (ii) down to 0.5 K. The magnetization values, the rate of their change with applied field, and especially the anisotropy observed, all give real insights into the nature of the magnetic ground states and the field-induced transitions in the titanium pyrochlores. Particular

attention is paid to sample history dependence, as well as to the time dependence of the magnetization, as unusually slow relaxation processes are discovered at low temperatures.

Given the nature of this special issue of *Journal of Physics: Condensed Matter* on geometrically frustrated magnetism, an extensive general introduction to the pyrochlore systems is omitted. Instead, after a brief description of the experimental details, we proceed to the presentation of the results and compare them to previously published data where necessary.

## 2. Experimental procedures

Single crystals of the pyrochlore magnets were grown by the floating zone technique, using an infrared image furnace [4]. Small thin plates of a characteristic size  $2 \times 2 \times 0.5$  mm<sup>3</sup> (typically containing the (110)-plane) were cut from the original larger samples. The plates were mounted in such a way that the magnetic field was applied in the sample plane in order



**Figure 1.** (a) Temperature dependence of the magnetic susceptibility of  $\text{Ho}_2\text{Ti}_2\text{O}_7$  single crystal measured on warming for field cooled (solid symbols) and zero field cooled (open symbols) samples. Each point is obtained by averaging three consecutive measurements, each of them typically taking 1–2 min. The inset emphasizes a pronounced time dependence of the zero field cooled susceptibility for  $T_C < 0.65$  K (marked by arrows) by showing raw data in a selected region. (b) Field dependence of the magnetization measured for increasing and decreasing magnetic field (shown by solid and open symbols, respectively). The  $dM/dH$  curves obtained from the magnetization curves at different temperatures show that temperature effects are most pronounced at both ends of a plateau.

to minimize demagnetization effects<sup>1</sup>. The principal axes of the samples were determined using the x-ray diffraction Laue technique; the crystals were aligned to within an accuracy of  $2^\circ$ . In this paper we report the magnetization data for a field applied along the [111] axis, which is an ‘easy-axis’ direction for the spin-ice systems  $\text{Ho}_2\text{Ti}_2\text{O}_7$  and  $\text{Dy}_2\text{Ti}_2\text{O}_7$  and a ‘hard-axis’ direction for the  $XY$  antiferromagnet  $\text{Er}_2\text{Ti}_2\text{O}_7$ .

Magnetization measurements were made down to 0.5 K in applied magnetic fields of up to 7 kOe using a Quantum Design magnetic properties measurement system SQUID magnetometer along with an i-Quantum  $^3\text{He}$  insert. The magnetization was measured both as a function of temperature in a constant magnetic field and as a function of applied field at constant temperature.

### 3. Experimental results and discussion

#### 3.1. Spin-ice compounds $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Dy}_2\text{Ti}_2\text{O}_7$

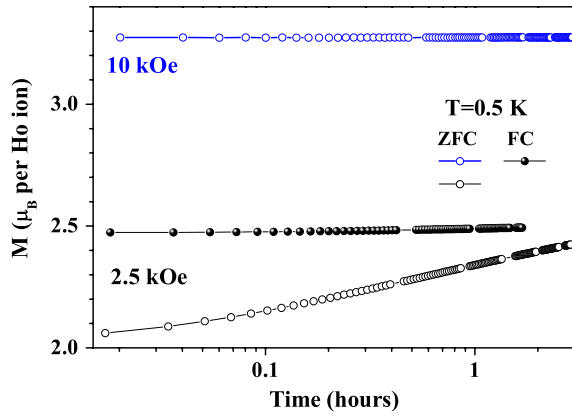
The temperature and field dependence of the magnetization of  $\text{Ho}_2\text{Ti}_2\text{O}_7$  is shown in figure 1. Below a temperature of approximately 0.65 K the magnetic susceptibility of  $\text{Ho}_2\text{Ti}_2\text{O}_7$  is very sensitive to the sample history, as the  $\chi(T)$  curves for field cooled (FC) and zero field cooled (ZFC) samples differ significantly, particularly for lower applied fields. Below  $T_C = 0.65$  K, the ZFC susceptibility shows a pronounced time dependence—it continues to grow with time even when the temperature remains constant. Moreover, if the applied field is as weak as 50 Oe, the susceptibility measured at  $T = 0.5$  K is initially negative. It grows rapidly with temperature and time and joins the FC susceptibility at  $T_C$  (see figure 1(a)). A natural explanation of the observed phenomenon is linked to the presence of a small, typically less than 5 Oe, frozen field always present in a cryomagnet. Therefore a ZFC protocol

is in fact a cooling in a very weak field of opposite polarity to the main applied field. It is still surprising to observe, at temperatures near 0.5 K, a process of magnetization reversal on a time scale of several minutes.

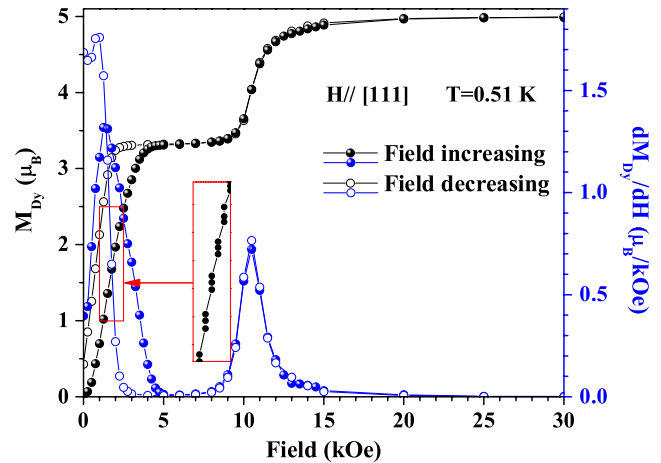
For  $\text{Ho}_2\text{Ti}_2\text{O}_7$ , we have previously reported magnetization curves for all three principal directions of an applied magnetic field at temperatures down to 1.6 K [5]. Lowering the temperature to 0.5 K makes the plateau for  $H \parallel [111]$  much more pronounced (see figure 1(b)). Comparing the results obtained for increasing and decreasing applied fields, one has to conclude that the magnetization process in higher fields is essentially hysteresis-free, while a significant hysteresis is evident in a field of less than 5 kOe. As can be seen in figure 2, the magnetization has a pronounced time dependence in weaker magnetic fields. For example, if the field applied to a ZFC sample is rapidly raised to 2.5 kOe and stabilized, the first measurement immediately after field stabilization gives  $2.02 \mu_B/\text{Ho}$  ion, while measurements 30 and 120 min later give  $2.28$  and  $2.40 \mu_B/\text{Ho}$  ion respectively. Technical limitations do not allow us to maintain a constant sample temperature ( $T < 0.51$  K) for more than 3 h. However, it is very likely that after several hours, the measurements would return a value very close to the FC magnetization of  $2.50 \mu_B/\text{Ho}$  ion. The magnetization shows no significant time dependence in fields of more than 5 kOe or at temperatures above 0.65 K.

The low-temperature magnetization process in the spin-ice compound  $\text{Dy}_2\text{Ti}_2\text{O}_7$  has been extensively studied previously. For  $H \parallel [111]$  there is an agreement between our data shown in figure 3 and the data originally reported by Sakakibara’s group [6]. In common with what is observed for  $\text{Ho}_2\text{Ti}_2\text{O}_7$ , the magnetization process in  $\text{Dy}_2\text{Ti}_2\text{O}_7$  also consists of four distinct regions: (i) a sharp rise in fields below 5 kOe; (ii) a plateau (often labelled as the Kagome ice state) in intermediate fields, (iii) a further sharp rise in a field of 10.5 kOe for  $\text{Dy}_2\text{Ti}_2\text{O}_7$  and 19.0 kOe for  $\text{Ho}_2\text{Ti}_2\text{O}_7$ ; (iv) another plateau in higher fields. The second plateau, which is sometimes

<sup>1</sup> Although irregular sample shapes prevent accurate calculations of demagnetization fields, our estimates show that the difference between applied and effective fields does not exceed 3–4%.



**Figure 2.** Time dependence of the magnetization of a  $\text{Ho}_2\text{Ti}_2\text{O}_7$  single crystal for a field applied along the [111] direction at  $T = 0.5$  K. FC and ZFC measurements are shown by solid and open symbols, respectively. The change in the ZFC signal at 2.5 kOe over a period of nearly 3 h is 20%, while the changes in the FC signal at 2.5 kOe and the ZFC signal at 10 kOe are 0.8% and 0.07%, respectively.



**Figure 3.** Field dependence of the magnetization  $M$  as well as of the  $dM/dH$  curves for  $\text{Dy}_2\text{Ti}_2\text{O}_7$ . Each point is obtained by averaging three consecutive measurements. The inset emphasizes a pronounced time dependence of the magnetization for lower fields by showing raw data in a selected region.

referred to as the saturation magnetization, is associated with a state where the spin-ice rules are broken by the force of the applied field. Hysteretic behaviour and pronounced time dependence of magnetization at lower temperatures are only seen in the first low field region (see inset in figure 3). The time and history dependence is significant only at  $T < T_C \approx 0.65$  K, the same temperature as has been reported previously as a bifurcation point between the FC and ZFC powder magnetization data [7]. According to the latest reports [8], on lowering the temperature to  $\sim 0.1\text{--}0.2$  K, pronounced non-equilibrium processes are observed, culminating in the appearance of sharp magnetization steps accompanied by similarly sharp peaks in the temperature of the sample. The low-temperature behaviour is ascribed to the field-driven motion of the magnetic monopole excitations [8]. It would be interesting to check if the observed time dependence at intermediate temperatures in both  $\text{Dy}_2\text{Ti}_2\text{O}_7$  and  $\text{Ho}_2\text{Ti}_2\text{O}_7$  could also be described in terms of monopole movement [9].

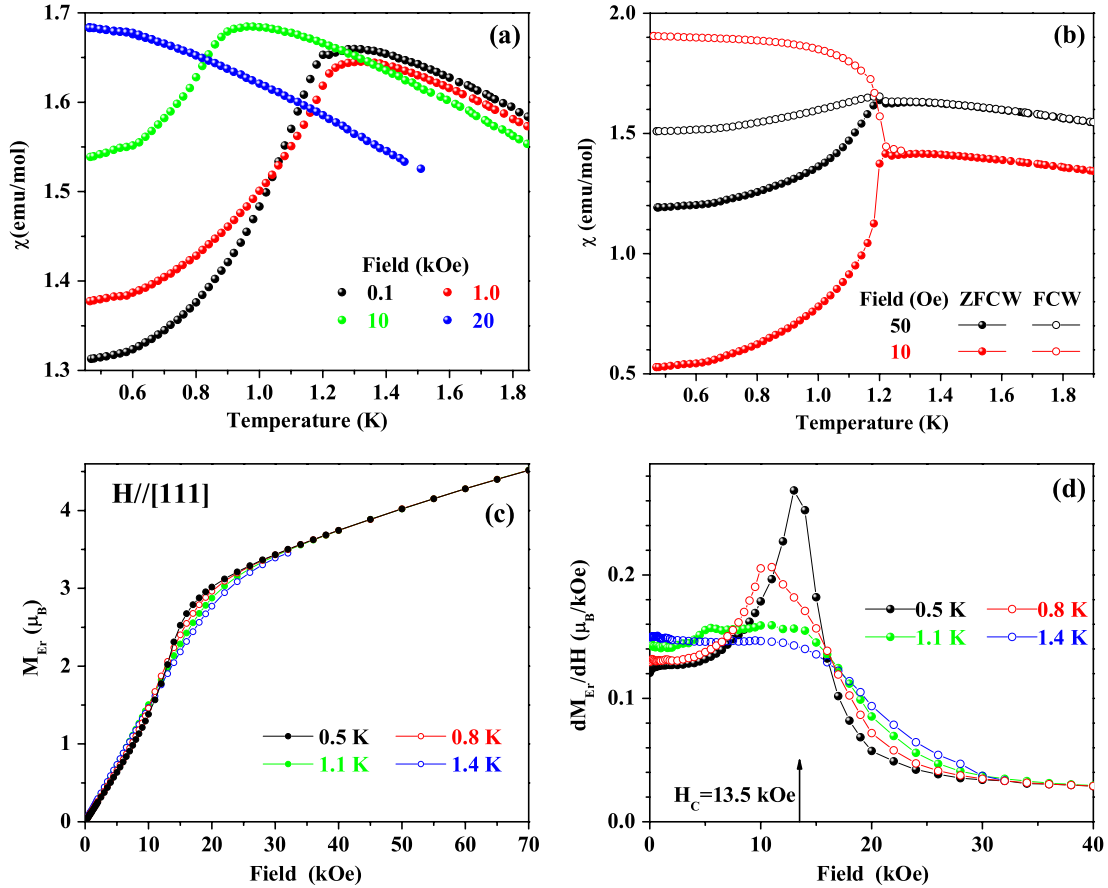
### 3.2. XY antiferromagnet $\text{Er}_2\text{Ti}_2\text{O}_7$

In  $\text{Er}_2\text{Ti}_2\text{O}_7$ , the ordering temperature of  $T_N = 1.2$  K is marked by a change of slope in the temperature dependence of the magnetic susceptibility (see figure 4). The anomaly moves to lower temperatures and becomes less pronounced in higher fields, disappearing completely above 15 kOe, in agreement with the heat-capacity measurements [10, 11]. For applied fields between 100 Oe and 20 kOe, no appreciable history dependence has been seen. For the weaker applied fields, such as 10 and 50 Oe, however, the FC and ZFC susceptibility curves differ significantly (see figure 4(b)). This difference is likely to be associated with the movement of magnetic domain walls in the sample.

Magnetization curves measured in  $\text{Er}_2\text{Ti}_2\text{O}_7$  at different temperatures are shown in figure 4(c) alongside their derivatives in figure 4(d). After the initial, nearly linear growth in lower fields, the magnetization starts to increase much

more rapidly around a critical field  $H_C$ , reaching a value of  $3 \mu_B/\text{Er}$  ion at 20 kOe. Then the magnetization continues to increase but at an appreciably lower rate of  $0.03 \mu_B \text{ kOe}^{-1}$  per Er ion. The high field part of the magnetization appears to be temperature independent, while the influence of temperature is evident around a transition field  $H_C$ , which is itself temperature dependent and amounts to 13.5 kOe at  $T = 0.5$  K if defined as the maximum in the  $dM/dH(T)$  curves. The value of the critical field is in perfect agreement with the heat-capacity results [11]. Both the diverging behaviour seen in the  $dM/dH(T)$  curves at  $H_C$  and a considerable increase in the magnetization above  $H_C$  are further proof that at this field a critical phase transition takes place, most likely quantum in nature [10], rather than a trivial magnetization saturation.

Although the magnetic properties of  $\text{Er}_2\text{Ti}_2\text{O}_7$  are highly anisotropic [11], the magnetization curves for a field applied along [110] and [100] directions (not shown in this paper) appear to demonstrate a field dependence that is functionally similar to the [111] direction, with a diverging susceptibility around a critical field. This result is difficult to reconcile with the recent neutron diffraction measurements for a field applied along [110] [12], where it is claimed that the Er moments have different magnitudes and are aligned along the field at  $H_C$ , with their values reaching a minimum at this field. An alternative explanation is that this second-order transition takes place at a field above which the magnetization process is accompanied by a canting of the magnetic moments off their local ‘easy-planes’ [11]. It remains to be seen whether an appropriate description of the magnetization process in  $\text{Er}_2\text{Ti}_2\text{O}_7$  can be achieved in the framework of a classical spin system (perhaps by adding a strong easy-plane anisotropy to the exchange Hamiltonian [13, 14]) or if a full quantum-mechanical treatment is required. Despite the large overall magnetic moment on the Er ions, a quantum influence cannot be ruled out, as the single-ion crystal-field ground state of  $\text{Er}^{3+}$  in  $\text{Er}_2\text{Ti}_2\text{O}_7$  is a Kramers doublet [15] with strongly different magnetic moments perpendicular and parallel to the



**Figure 4.** Temperature (upper panels) and field (lower panels) dependence of the magnetization of a single crystal of  $\text{Er}_2\text{Ti}_2\text{O}_7$  for a field applied along the [111] direction. The  $\chi(T)$  curves shown in panel (a) have been measured on warming for ZFC samples. In panel (b) the results for FC and ZFC samples obtained in weak applied fields are contrasted. Panel (d) shows the  $dM/dH$  curves around a critical field which is temperature dependent and amounts to  $H_c = 13.5$  kOe at 0.5 K.

local (111) axis, which could be effectively described as an  $S = 1/2$  system.

### 3.3. Heisenberg antiferromagnet $\text{Gd}_2\text{Ti}_2\text{O}_7$

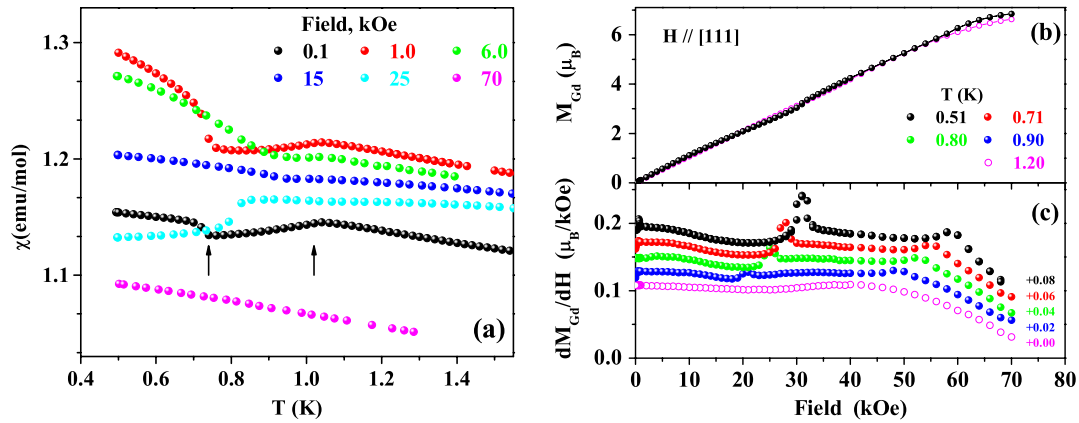
Figure 5(a) shows the temperature dependence of the magnetic susceptibility of  $\text{Gd}_2\text{Ti}_2\text{O}_7$  measured for different fields applied along the [111] axis. The compound orders magnetically at  $T_{N1} = 1.02$  K and undergoes a further transition at  $T_{N2} = 0.74$  K [16, 17]. Both these transitions are clearly visible in the  $\chi(T)$  curves in low applied field, contrary to the previously published results [18]. Remarkably, the susceptibility increases with increasing temperature for  $T_{N2} < T < T_{N1}$ , while the tendency is opposite for  $T > T_{N1}$  and  $T < T_{N2}$ . In intermediate magnetic fields either one or two anomalies can be seen in the  $\chi(T)$  curves depending on which part of the  $H$ - $T$  phase diagram has been traversed [17], while for magnetic fields above 60 kOe no transition is visible.

Figure 5(b) shows the field dependence of the magnetization of  $\text{Gd}_2\text{Ti}_2\text{O}_7$  measured for  $H \parallel [111]$  above and below the ordering temperature. In the highest available field of 70 kOe, at which point the magnetization is still growing at a considerable rate, a magnetic moment of  $6.8 \mu_B/\text{Gd}$  ion is reached, close to a maximum value of  $7 \mu_B$  expected for a state with  $S = 7/2$  and  $L = 0$ . If a saturation field

is defined as the maximum in the  $dM/dH(T)$  curve (see figure 5(c)), then its value is 59 kOe at  $T = 0.5$  K. Apart from the saturation field,  $H_{ST}$ , another field-induced transition is evident at a field of  $H_{ST}/2$ , in agreement with the previously reported heat-capacity measurements [17]. The nature of this transition remains uncertain, as neither of the two proposed models (a canting of the magnetic moments away from their local ‘easy-planes’ [19] or a collinear three spins up one spin down structure [20]) seem to fit all the experimental results. Given that the zero field magnetic structure of  $\text{Gd}_2\text{Ti}_2\text{O}_7$  is still a matter for debate [21], it is not surprising that a theoretical description of the magnetization process in this compound is still unavailable.

## 4. Summary

In conclusion, we report magnetization measurements performed at temperatures down to 0.5 K for the highly frustrated pyrochlore systems  $\text{Ho}_2\text{Ti}_2\text{O}_7$ ,  $\text{Dy}_2\text{Ti}_2\text{O}_7$ ,  $\text{Er}_2\text{Ti}_2\text{O}_7$  and  $\text{Gd}_2\text{Ti}_2\text{O}_7$  for a field applied along the [111] cubic axis. In each case unusual phenomena associated with field-induced phase transformations have been observed and commented upon. The use of high quality single crystal samples allowed for much more accurate and reliable data collection.



**Figure 5.** Temperature (left) and field (right) dependences of the magnetization of a  $\text{Gd}_2\text{Ti}_2\text{O}_7$  single crystal for  $H \parallel [111]$ . The arrows indicate two transition temperatures,  $T_{N1} = 1.02$  K and  $T_{N2} = 0.74$  K reported from the specific heat measurements in zero field [17]. The  $dM/dH$  curves obtained from the magnetization curves at different temperatures have been offset by the specified values for clarity.

## Acknowledgments

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