Bulk magnetization of the heavy rare earth titanate pyrochlores—a series of model frustrated magnets

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Abstract. We describe magnetization measurements on the heavy rare earth titanate pyrochlores $R_2Ti_2O_7$, where R = Gd, Dy, Ho, Er, Yb, in the temperature range 1.8–300 K, and the field range 0–70 000 Oe. In these materials magnetism arises from the rare earth ions, while Ti is non-magnetic. Analysis of the low field susceptibility versus temperature curves shows that $Gd_2Ti_2O_7$ has antiferromagnetic coupling ($\theta \approx -9$ K), which suggests that it is an example of a frustrated antiferromagnet on the pyrochlore lattice. $Er_2Ti_2O_7$ is likewise found to have a large negative Curie–Weiss temperature, $\theta \approx -22$ K, which we argue is indicative of antiferromagnetic coupling. $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$ and $Yb_2Ti_2O_7$ are found to have weak ferromagnetic coupling ($\theta \approx 2$ K, 1 K and 1 K respectively) which may be largely dipolar in origin. Fitting of the high field magnetization versus field curves suggests a strong $\langle 1, 1, 1 \rangle$ single ion anisotropy that identifies these three materials as possible realizations of the ferromagnetic 'spin ice' model.

1. Introduction

The tetrahedral pyrochlore lattice is a particularly common structural motif in solid compounds [1]. For example, it describes the metal positions in the pyrochlore oxides $M_2M'_2O_7$ (e.g. $Hg_2Nb_2O_7$ [2]), the B site positions in the spinel structure AB_2O_4 (e.g. $ZnFe_2O_4$ [3]), the transition metal positions in the ternary fluorides $AMM'F_6$ (e.g. $CsMnFeF_6$ [4]) and the M′ positions in the MM'_2 Laves phase C15 structure (e.g. $MgCu_2$ [5]). The lattice (figure 1) consists of a face-centred cubic array of corner-linked tetrahedra. Magnetic spins placed on the lattice are highly frustrated when coupled antiferromagnetically to nearest neighbours, as was first noticed by Anderson [6] and investigated in greater detail by Villain [7]. In recent years there has been increasing interest in the frustration properties of pyrochlore compounds. In particular the oxides $Y_2Mo_2O_7$ [8] and $Tb_2Mo_2O_7$ [9] appear to be chemically ordered spin glasses, while the fluorides $CsNiCrF_6$ [10] and YMn_2 [11] show spin-liquid-like behaviour. An obstacle in pyrochlore research, however, is that these systems are far from being ideal model magnetic materials, containing either delocalized electrons in the case of the molybdates or YMn_2, or chemical disorder in the case of the fluorides. In an effort to remedy this situation we began a detailed magnetic study of the rare earth titanate pyrochlores [12, 13]. These materials are chemically ordered electrical insulators containing a single magnetic ion (the rare earth) placed on a pyrochlore lattice [14, 15]. For all the trivalent rare earth ions except Gd^{3+} one expects single ion anisotropy to be important. In recent publications [12, 16, 17] we showed how local axial single ion anisotropy in the pyrochlore structure can reverse the roles of ferromagnetic and antiferromagnetic exchange with regard to frustration, such that the ferromagnet is frustrated

and the antiferromagnet is not. The frustrated ferromagnetic pyrochlore maps onto the problem of proton ordering in ice, and hence we have termed it 'spin ice' [12, 16]. Neutron scattering and μsr experiments have shown $Ho_2Ti_2O_7$ to be a realization of this model [12]. Our interpretation of these results is underpinned by extensive characterization of the magnetic properties of $Ho_2Ti_2O_7$ and other rare earth titanates. This includes a susceptibility study of polycrystalline samples in the temperature range 1.8–300 K, and field range 0–70 000 Oe, which we report in detail here. We have measured the magnetization of polycrystalline samples of $R_2Ti_2O_7$, with R = Gd, Dy, Ho, Er, Yb. The material with R = Tm was omitted from our study as this has been shown to have a singlet ground state [18]. Similarly we avoided studying $Tb_2Ti_2O_7$ as it has been the subject of a concurrent investigation by workers at McMaster university [19].

The heavy rare earth titanates were originally described by Roth [20], and a detailed crystal structure determination of $Er_2Ti_2O_7$ by Knop *et al* [14] serves as a benchmark structural study for the whole series. This compound is cubic, space group $Fd\bar{3}m$, with the Er^{3+} ion occupying the positions (0, 0, 0), (1/4, 1/4, 0), (0, 1/4, 1/4) and (1/4, 0, 1/4) and equivalent positions in the unit cell related by the face centring operation. The symmetry of the Er^{3+} sites is trigonal, with two oxide ions diametrically opposed at 2.185 Å along the threefold $\langle 1, 1, 1 \rangle$ axis, and six others forming a puckered hexagon perpendicular to this axis at 2.471 Å. Blöte *et al* [15] reported a detailed heat capacity study of several of the series and related phases at temperatures down to the millikelvin range. The heavy rare earth phases investigated included $Dy_2Ti_2O_7$, Ho_2GaSbO_7, $Er_2Ti_2O_7$, Er_2GaSbO_7, $Yb_2Ti_2O_7$ and Yb_2GaSbO_7. Magnetic susceptibilities of $Dy_2Ti_2O_7$, $Er_2Ti_2O_7$, $Yb_2Ti_2O_7$ and Yb_2GaSbO_7 were also reported by these authors, while Bongers and Van Meurs [21] reported magnetization measurements on Ho_2GaSbO_7 and Dy_2GaSbO_7 (as well as ferromagnetic R_2CrSbO_7), and Cashion *et al* [22] determined the susceptibilities of $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$, $Tb_2Ti_2O_7$ and $Gd_2Ti_2O_7$. Several of the rare earth titanates investigated in these early studies showed effects arising from magnetic coupling at temperatures of the order of 1 K; we will describe these results in more detail in the discussion, section 3. Very recently Raju *et al* [23] reported magnetization and specific heat measurements on $Gd_2Ti_2O_7$. An ordering transition was found at 0.97 K, which was suggested to result from further neighbour interactions.

Our polycrystalline samples were prepared by the method described by Knop *et al* [14], and confirmed to be single phases by powder x-ray diffraction. The refined lattice parameters at ambient temperature were 10.1561(1) Å ($Gd_2Ti_2O_7$), 10.1171(1) Å ($Dy_2Ti_2O_7$), 10.0831(1) Å ($Ho_2Ti_2O_7$), 10.068(1) Å ($Er_2Ti_2O_7$) and 10.024(1) Å ($Yb_2Ti_2O_7$). Magnetic susceptibility measurements were made using a Quantum Design SQUID magnetometer at the Royal Institution of Great Britain. The samples were contained in a gel cap positioned in a cylindrical plastic tube with identical gel caps placed above and below the sample to ensure a uniform magnetic environment. Three measurements were made on each sample: high field (0–70 000 Oe) magnetization, low field ($\sim$10 Oe) susceptibility and field-cooled (FC) versus zero-field-cooled (ZFC) susceptibility. For the magnetization measurements samples of typically a few mg were used, which were immobilized in diamagnetic tape to prevent sample movement in the field; the contribution of the tape to the observed magnetization was estimated to be negligible. For the low field susceptibility measurements samples of typically $\sim$30 mg were used. The field-cooled versus zero-field-cooled susceptibility measurements involved cooling the sample to 1.8 K in zero field, applying a weak magnetic field (typically 10 Oe), measuring the susceptibility whilst warming to 20 K, cooling to 1.8 K and re-measuring the susceptibility whilst warming. With such a low measuring field, the absolute value of the field on this instrument was known only to $\pm$10%. Therefore, to estimate absolute susceptibilities, data above $T \approx 50$ K were measured in an applied field of 500 Oe (accurate to $\pm$10 Oe). The low field data were then scaled to fit the higher field data at $\sim$50 K. This procedure corrects
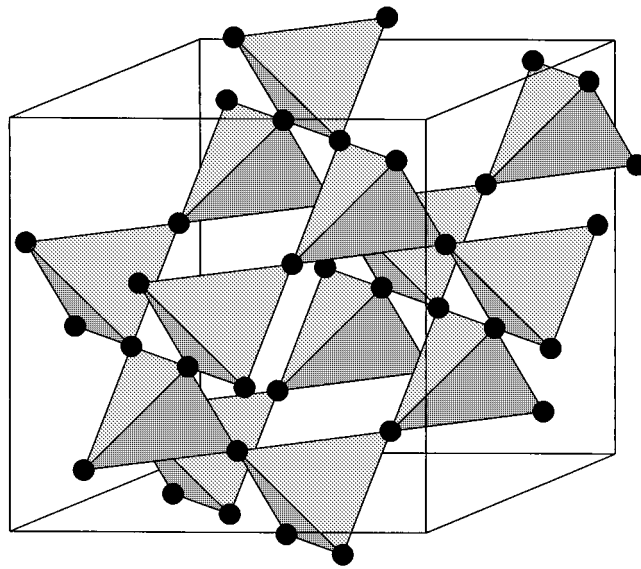
Figure 1. The lattice occupied by the rare earth ions in the cubic pyrochlore structure.

for the uncertainty in the applied field of 10 Oe, but assumes negligible nonlinearity in the susceptibility between 0 and 500 Oe at 50 K. The validity of this assumption has been explicitly confirmed in several cases.

2. Results

2.1. $Gd_2Ti_2O_7$

The susceptibility (defined as the ratio of magnetization to field) was measured in a field of 500 Oe between 50 and 300 K, and initially analysed assuming $\chi = C/(T - \theta)$ where $C = \mu^2/8$ in cgs units. A linear regression analysis of χ^{-1} versus T gave $\theta = -11.8(4)$ K and $\mu = 7.35(2)$ μ_B. The inverse susceptibility plot showed some negative curvature at high temperature, consistent with a small Van Vleck temperature independent paramagnetism. Fixing the temperature independent term to the value 6×10^{-4} that produced linearity in the reciprocal susceptibility versus temperature plot led to revised estimates of $\theta = -8.95(6)$ K and $\mu = 7.224(3)$ μ_B. The large negative Curie–Weiss temperature is presumably due to antiferromagnetic exchange coupling, while the estimated magnetic moment is consistent with the value $\mu = 7.94$ μ_B for the free ion ${}^8S_{7/2}$ ground state of Gd^{3+}. The possible Van Vleck paramagnetism would arise from crystal-field-induced mixing of the $J = 7/2$ ground state with higher states in the J manifold. The susceptibility between 1.8 K and 50 K was measured in an applied field of 10 Oe, and showed no anomalies that would indicate a magnetic transition, nor any difference between field-cooled and zero-field-cooled susceptibility; the inverse susceptibility in this range is plotted in figure 2(a). The magnetization versus field isotherm at 1.8 K shows a much slower approach to saturation than the theoretical Brillouin function for the free ion with $J = S = 7/2$, as shown in figure 2(b). This is also consistent with significant antiferromagnetic exchange.

These results are consistent with those of Cashion *et al* [22], who reported $\theta = -11.7$ K and $\mu = 7.8$ μ_B, and no magnetic ordering above 1 K. They also agree with those of Raju *et al* who found $\theta = -9.6$ K, $\mu = 7.7$ μ_B and an ordering transition at 0.97 K [23].
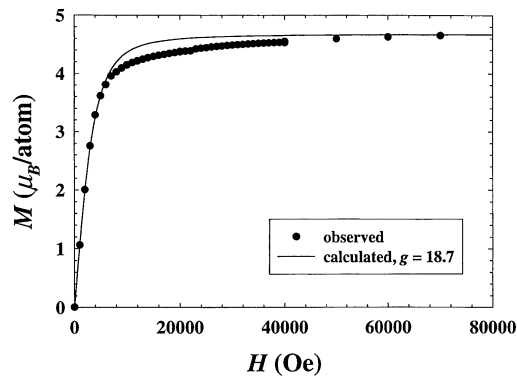
(a)

(b)
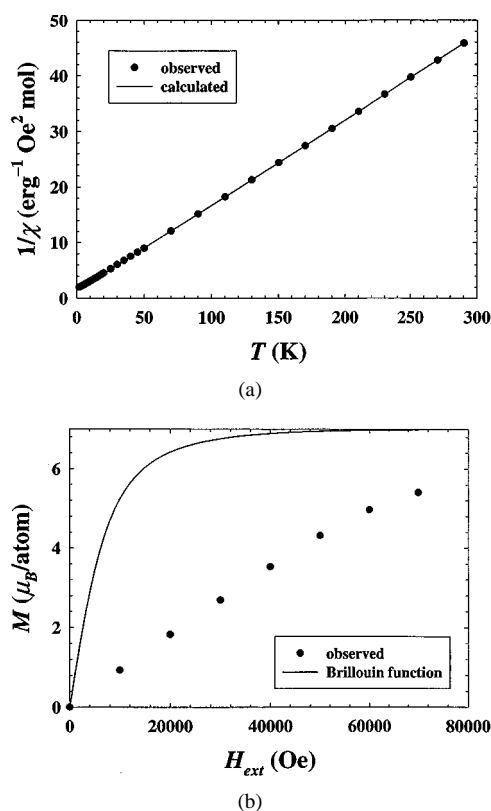
Figure 2. (a) Inverse susceptibility versus temperature for $Gd_2Ti_2O_7$. The susceptibility data (circles) have been corrected for a temperature independent paramagnetic term of 6×10^{-4} erg Oe^{-2} mol^{-1}. The full line is a fit to the data between 70 K and 300 K, corresponding to $\theta = -8.95(6)$ K and $\mu = 7.224(3)$ μ_B. (b) Magnetization versus applied field H_{ext} for $Gd_2Ti_2O_7$ at $T = 1.8$ K. The circles represent the experimental data, and the full line the Brillouin function prediction for $S = 7/2$.

2.2. $Ho_2Ti_2O_7$

The susceptibility, measured in a field of 500 Oe between 50 and 300 K, was analysed in the same way as described for $Gd_2Ti_2O_7$, described above. The negative curvature of the high temperature reciprocal susceptibility versus temperature curve was consistent with a Van Vleck paramagnetism of about 4×10^{-3} erg Oe^{-2} mol^{-1}. After applying this correction, the Curie–Weiss plot of the susceptibility measured in a field of 10 Oe between 20 and 50 K gave $\theta = 0.59(9)$ K and $\mu = 9.15(3)$ μ_B (figure 3(a)). Without the Van Vleck correction, the following values were obtained: $\theta = 0.15(8)$ K and $\mu = 9.27(3)$ μ_B. These values are consistent with weak ferromagnetic coupling and are close to either the free ion moment for the $^5I_8$ state of Ho^{3+}, $\mu = 10.61$ μ_B, or the value expected for an $m_J = \pm 8$ doublet ground state, $\mu = 10.00$ μ_B, as described below. Analysis of single crystal samples [24] has shown that in $Ho_2Ti_2O_7$ there is an extremely large demagnetizing field correction that reduces the observed value of the Curie–Weiss temperature in a manner that depends on the sample shape. It is not possible to estimate this correction precisely for polycrystalline samples, but for approximately spherical samples the correction is about 1.4 K, which, when applied to the powder, would adjust the estimated Curie–Weiss temperature to about 2 K. This is consistent
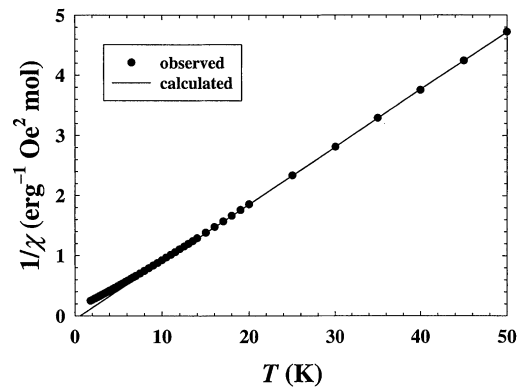
(a)

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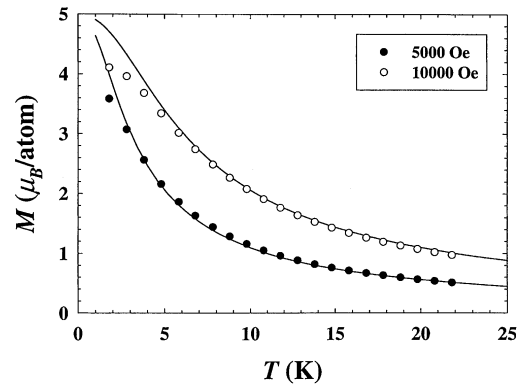
(c)

Figure 3. (a) Inverse susceptibility versus temperature for $Ho_2Ti_2O_7$. The susceptibility data (circles) have been corrected for a temperature independent paramagnetic term of 4×10^{-4} erg Oe^{-2} mol^{-1}. The full line is a fit to the data between 20 K and 50 K, corresponding to $\theta = 0.59(9)$ K and $\mu = 9.15(3)$ μ_B. (b) Magnetization versus applied field H_{ext} for $Ho_2Ti_2O_7$ at $T = 1.8$ K. The circles represent the experimental data, and the full line the powder-averaged theoretical expression for an effective spin one-half doublet with $\langle 1, 1, 1 \rangle$ anisotropy (1), and $g = 18.7$. (c) Magnetization versus temperature for $Ho_2Ti_2O_7$ at applied fields $H_{ext} = 5000$ Oe (closed circles) and $H_{ext} = 10\,000$ Oe (open circles). The full line represents the calculated magnetization for the theoretical expression for an effective spin one-half doublet with $\langle 1, 1, 1 \rangle$ anisotropy 1), and $g = 20.0$.

with the value of 1.9 K derived from single crystal measurements [24]. Below $T = 2.5$ K a very slight difference in the field-cooled and zero-field-cooled susceptibility was observed, with the field-cooled susceptibility being, unusually, very slightly *less* than the zero-field-cooled susceptibility. This again has been confirmed by single crystal measurements.

The high field magnetization at 1.8 K could not be described by the free ion Brillouin function for $J = 8$, but rather, was observed to saturate at roughly half the theoretical maximum magnetization. Such behaviour is indicative of substantial single ion anisotropy, as would be expected for Ho^{3+}, with $L = 6$, $S = 2$. The simplest anisotropy that one can consider is local easy-axis anisotropy, with the easy axes directed towards the centre of the elementary tetrahedron, that is, along the four $\langle 1, 1, 1 \rangle$ directions of the cubic cell. Ignoring exchange coupling, the partition function factorizes into a product of single-ion partition functions, and so the problem of calculating the thermally averaged and powder-averaged magnetization reduces to a single ion problem. We assume that the ground state is an effective spin one-half doublet ($S = 1/2$), with effective g value determined by the mixing of the m_J states by the crystal field. We assume that $g_\parallel = g$ and $g_\perp = 0$, where $\parallel$ and $\perp$ denote parallel and perpendicular to the applied field respectively. It is straightforward to show that with powder averaging, the thermally averaged magnetization of this two state model is then given by the expression:

$$\langle \mu \rangle / \mu_B = \frac{(kT)^2}{g\mu_B H^2 S} \int_0^{g\mu_B HS/kT} x \tanh(x) \, \mathrm{d}x \tag{1}$$

which can be integrated numerically. This expression was found to describe the data quite well with $g \approx 18.7$ (figure 3(b)), which is close to the maximum possible value $g = 20$ which would arise if the ground state were a pure $m_J = \pm 8$ doublet, with $g_J = 1.25$. Further data were recorded as a function of temperature in the range 1.8–25 K, at two fields of 5000 Oe and 10 000 Oe. Fitting of this data above 5 K gave a good fit with $g = 20$, but a clear deviation at low temperature. Thus it was not possible to find a g-value that exactly described the data over the whole (H, T)-range, but it is safe to conclude that, to a reasonable approximation, the ground state is a doublet with almost the maximum possible moment ($g = 20$). The fit is shown in figure 3(c).

The assignment of Ho^{3+} in $Ho_2Ti_2O_7$ as an $m_J = \pm 8$ doublet is the same as that of Blöte *et al* [15] for Ho^{3+} in the related compound Ho_2GaSbO_7, based on specific heat and susceptibility measurements. The Curie–Weiss temperature and moment we have measured in $Ho_2Ti_2O_7$ are consistent with those reported by Cashion *et al* [22], $\theta = 0$ K, $\mu = 10.03 \, \mu_B$. Note that these measurements were performed on a single crystal, and yet no demagnetizing correction was applied, which leads to a systematic correction to θ of about 1.4 K (for a spherical sample) as discussed above [24]. The susceptibility was found to have a maximum at 1.3 K.

2.3. $Dy_2Ti_2O_7$

The magnetization data for $Dy_2Ti_2O_7$ were analysed in the same way as for $Gd_2Ti_2O_7$ (above). A Van Vleck paramagnetism of 2×10^{-3} erg Oe^{-2} mol^{-1} was deduced from the analysis of the high temperature susceptibility measured in a field of 500 Oe, 50–300 K, which, when applied to the susceptibility measured in 10 Oe, 10–20 K, gave the following parameters: $\theta = -0.20(1)$ K and $\mu = 9.590(6) \, \mu_B$ (figure 4(a)). Without the Van Vleck correction the following parameters were obtained: $\theta = -0.24(1)$ K and $\mu = 9.615(5)$. The fitted Curie–Weiss temperature is indicative of very weak antiferromagnetic coupling; however, it is more likely to be ferromagnetic, for, when the correction for demagnetizing effects ($\sim$1.4 K, see above) is applied, one obtains $\theta \approx 1$ K. No difference between field-cooled and zero-field-cooled magnetization was observed down to 1.8 K. The fitted moment is close to the free ion
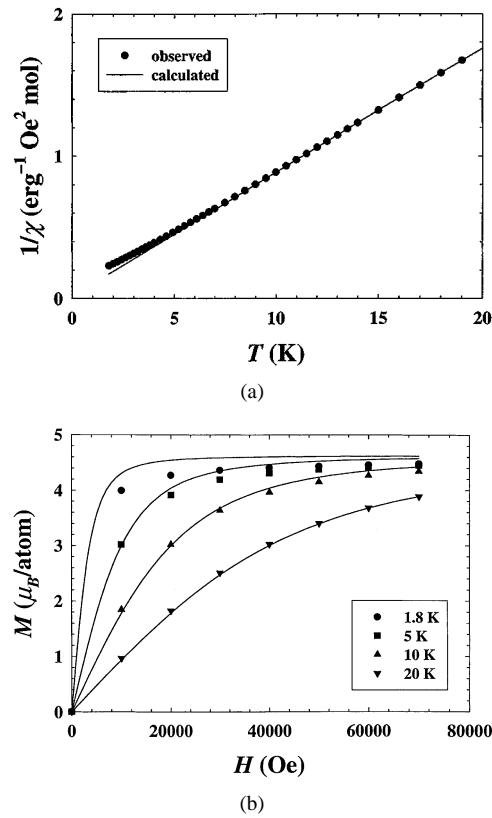
Figure 4. (a) Inverse susceptibility versus temperature for $Dy_2Ti_2O_7$. The susceptibility data (circles) have been corrected for a temperature independent paramagnetic term of 2×10^{-4} erg Oe^{-2} mol^{-1}. The full line is a fit to the data between 10 K and 20 K, corresponding to $\theta = -0.20(1)$ K and $\mu = 9.590(6)$ μ_B. (b) Magnetization versus applied field H_{ext} for $Dy_2Ti_2O_7$ at temperatures $T = 1.8$ K, 5 K, 10 K and 20 K. The symbols represent the experimental data, and the full line the theoretical expression for an effective spin one-half doublet with $\langle 1, 1, 1 \rangle$ anisotropy (1), and $g = 18.5$.

value $\mu = 10.61$ μ_B expected for the $^6G_{15/2}$ ground term of Dy^{3+}, as well as to the value $\mu = 10.00$ μ_B, for a ground state $m_J = \pm 15/2$ doublet, with $g_J = 4/3$. As with Ho^{3+}, this ion, with $J = 15/2$, $S = 5/2$, is expected to be anisotropic. This expectation was borne out by the behaviour of the high field magnetization at 1.8 K which saturated at a value of about half the expected maximum. Magnetization versus field isotherms, in fields of up to 7 T, were measured at several temperatures between 1.8 K and 20 K, and fitted by expression (1) above. A reasonably good fit to all the data, shown in figure 4(b), was obtained with effective g-factor $g = 18.5(1)$. This value is slightly reduced from the value $g = 20$, which would arise if the ground state were a pure $m_J = \pm 15/2$ doublet, with $g_J = 4/3$. Therefore, it is likely that there is some admixture of other terms in the m_J manifold, albeit small.

These results for $Dy_2Ti_2O_7$ may be compared to those of Blöte *et al* [15], who found that the weak field susceptibility had a maximum at 0.9 K, and decreased to almost zero at 0.4 K. Hence, they argued that the g-tensor must be extremely anisotropic, in which case the observed magnetic moment could best be explained in terms of an $m_J = \pm 15/2$ doublet, as we have confirmed. The specific heat was found to exhibit a broad Schottky anomaly in this

temperature range, but no singularity. Integration of the specific heat gave an estimate of the magnetic entropy change to be about three-quarters of the expected $R \ln(2)$ for the Kramers doublet of Dy^{3+}. Such behaviour is fully consistent with the behaviour of the spin ice model, as discussed further in section 3, although in the case of $Dy_2Ti_2O_7$ the ferromagnetic coupling is rather weak. The Curie–Weiss temperature and moment that we have measured for $Dy_2Ti_2O_7$ are consistent with those reported by Cashion *et al* [22]: $\theta = -0.65(1)$ K and $\mu = 9.96\,\mu_B$. These authors reported a maximum in the susceptibility at 1.3 K, which is slightly higher than that found by Blöte *et al* [15]. Very recently, Ramirez *et al* [25] reported a Curie–Weiss temperature $\theta = -0.5$ K which is also consistent with our value, before the application of the demagnetizing factor correction.

2.4. $Yb_2Ti_2O_7$

For $Yb_2Ti_2O_7$, the effective magnetic moment $\mu_{eff} \approx \sqrt{(8\chi T)}$ was found to be temperature dependent, falling from $\sim 4\,\mu_B$ at ambient temperature to $\sim 3\mu_B$ at liquid helium temperatures. This is consistent with the free ion moment $\mu = 4.54\,\mu_B$ of Yb^{3+} at ambient temperature, and the settling of the ions into a Kramers doublet ground state at low temperature, with slightly reduced moment. Analysis of the high temperature susceptibility (50–300 K, 500 Oe) as for $Gd_2Ti_2O_7$ gave a rather large Van Vleck temperature independent paramagnetism of 2.9×10^{-3} erg Oe^{-2} mol^{-1}; with this correction the effective magnetic moment was less temperature dependent, being roughly $3\,\mu_B$ over the whole temperature range. However, the possibility of temperature dependence arising from the thermal population of excited states makes the validity of the Van Vleck correction dubious. Fortunately it did not make much difference to the derived Curie–Weiss temperatures. Thus, including the Van Vleck correction gave the following parameters for the analysis of the low field susceptibility (5–11 K, 10 Oe): $\theta = +0.59(1)$ K and $\mu = 3.335(4)\,\mu_B$ (figure 5(a)). The latter is somewhat below the value $\mu = 4.00\,\mu_B$ expected for an $m_J = \pm 7/2$ doublet ground state, with $g_J = 1.143$. Neglecting the Van Vleck correction gave $\theta = +0.49(1)$ K and $\mu = 3.385(6)\,\mu_B$. The demagnetizing field correction to the Curie–Weiss temperature for $Yb_2Ti_2O_7$ (see above) should be about 0.18 K, which would increase θ slightly to about 0.7 K. No splitting between field-cooled and zero-field-cooled susceptibility was observed. With $L = 3$, $S = 0.5$, Yb^{3+} would be expected to be strongly anisotropic, as is the case for Ho^{3+} and Dy^{3+}. The high field magnetization over several temperatures between 1.8 and 10.8 K was fitted with equation (1). However, it was not possible to find a single g-value that described the experimental data over the whole temperature and field range. The best compromise was $g = 7.2$ as shown in figure 5(b). This value of g is close to the value $g = 8.0$ that would arise if the ground state were a pure $m_J = \pm 7/2$ Kramers doublet, and corresponds to a moment $\mu = 3.75\,\mu_B$ which is slightly higher than that obtained from the low field susceptibility $\mu \approx 3.4\,\mu_B$ (see above). However, in view of the relatively poor fit of the magnetization to equation (1), it is possible that there is a significant perpendicular g-value in this material. A full understanding of the magnetism of Yb^{3+} in $Yb_2Ti_2O_7$ awaits a study of the crystal field levels, the results of which must reproduce the magnetic moments we have reported here.

$Yb_2Ti_2O_7$ was previously studied by Blöte *et al* [15], who measured the specific heat and susceptibility down to 50 mK. The susceptibility in the range 2 to 3.5 K was analysed to give $\theta = 0.4$ K, $\mu = 2.1\,\mu_B$. Although the value of θ is consistent with our value, the moment reported by Blöte *et al* is significantly less. To check the origin of this discrepancy, we re-measured the susceptibility of our sample on two separate occasions, but could find no systematic difference from the original measurements. Blöte *et al* [15] also reported that the specific heat of $Yb_2Ti_2O_7$ showed a distinct anomaly at 0.214 K, indicative of a magnetic
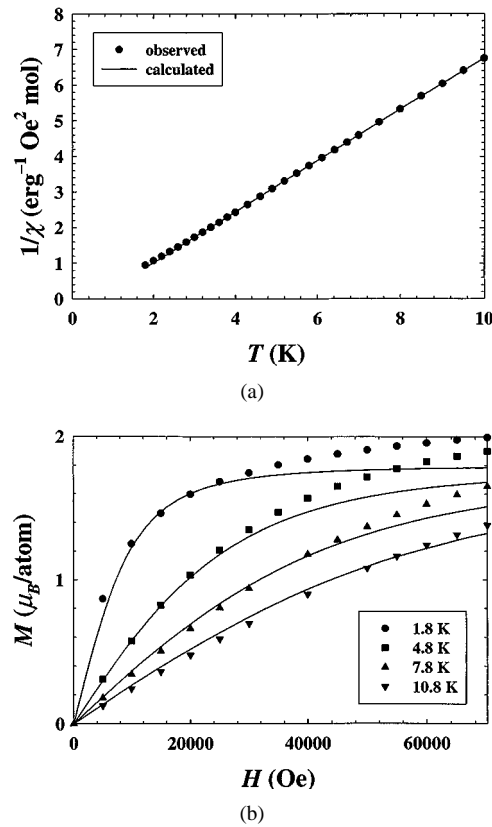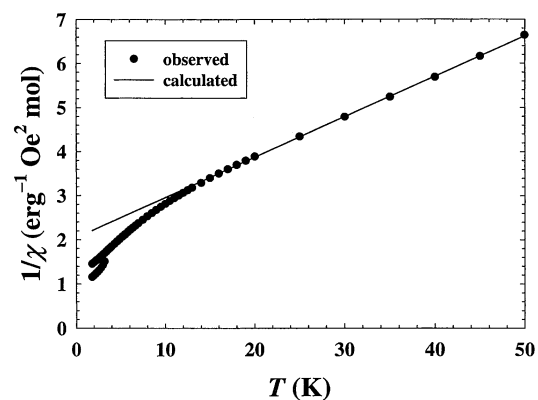
Figure 5. (a) Inverse susceptibility versus temperature for $Yb_2Ti_2O_7$. The susceptibility data (circles) have been corrected for a temperature independent paramagnetic term of 2.9×10^{-3} erg Oe^{-2} mol^{-1}. The full line is a fit to the data between 10 K and 20 K, corresponding to $\theta = 0.59(1)$ K and $\mu = 3.335(4)$ μ_B. (b) Magnetization versus applied field H_{ext} for $Yb_2Ti_2O_7$ at temperatures $T = 1.8$ K, 4.8 K, 7.8 K and 10.8 K. The symbols represent the experimental data, and the full line the theoretical expression for an effective spin one-half doublet with $\langle 1, 1, 1 \rangle$ anisotropy (1), and $g = 7.2$.

ordering transition. This feature was superimposed on a broad, Schottky-like hump, centred around 2 K. Analysis of the specific heat gave an entropy of $R \ln 2$, and an exchange constant that corresponds to a Curie–Weiss temperature of 3.6 K. This estimate seems rather large. In any case, considering these and our own results shows that the ratio of the ordering temperature to the Curie–Weiss temperature is quite small. We return to discuss this point in section 3.
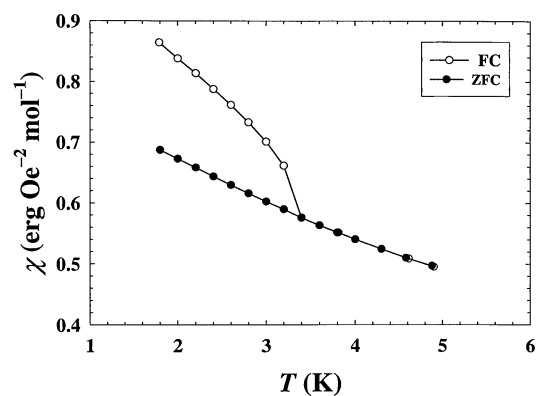
2.5. Er₂Ti₂O₇

Analysis of the high temperature reciprocal susceptibility (50–300 K, 500 Oe) for $Er_2Ti_2O_7$ showed no evidence of Van Vleck temperature-independent paramagnetism. Fitting this data to the Curie–Weiss expression gave $\theta = -15.93(3)$ K, $\mu = 8.936(4)$ μ_B. A similar analysis of the low temperature, low field susceptibility (20–50 K, 10 Oe) gave $\theta = -22.3(3)$ K, $\mu = 9.34(9)$ μ_B (figure 6(a)). The Curie–Weiss temperature indicates either substantial antiferromagnetic coupling, or the thermal population of an excited state. The fitted moment is close to both the free ion value 9.58 μ_B for the free ion ${}^3I_{15/2}$ ground term of Er^{3+}, and the
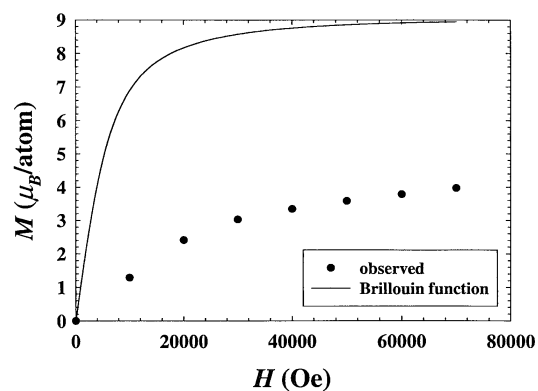
Figure 6. (a) Inverse susceptibility versus temperature for $Er_2Ti_2O_7$. The full line is a fit to the data between 20 K and 50 K, corresponding to $\theta = -22.3(3)$ K, $\mu = 9.34(9)$ μ_B. The field-cooled–zero-field-cooled splitting at low temperature is shown more clearly in figure 6(c). (b) Magnetization versus applied field H_{ext} for $Er_2Ti_2O_7$ at temperature $T = 1.8$ K. The circles represent the experimental data, and the full line the free ion Brillouin function for $J = 15/2$. (c) Susceptibility of $Er_2Ti_2O_7$ measured in a field $H_{ext} = 10$ Oe, versus temperature. The curves illustrate the splitting between the field-cooled (FC) and zero-field-cooled (ZFC) susceptibilities. The data points are represented by circles and the lines are a guide to the eye. Note that FC and ZFC data are coincident above $T \approx 3.2$ K and so can barely be distinguished by eye.

value $\mu = 9.0\,\mu_B$ for an $m_J = \pm 15/2$ doublet with $g_J = 1.2$. With $S = 1.5$ and $L = 6$, Er^{3+} would be expected to be significantly anisotropic. The high field magnetization (figure 6(b)) confirmed this, approaching saturation at a value of approximately half the free ion maximum $\mu = 9\,\mu_B$. However, in the case of strong exchange coupling, an analysis according to equation (1) would be meaningless. Thus we cannot tell whether $Er_2Ti_2O_7$ has dominant uniaxial or planar anisotropy.

Blöte *et al* measured the specific heat of $Er_2Ti_2O_7$ down to 50 mK, and observed a sharp anomaly at 1.25 K. Our recent neutron diffraction study [13] has confirmed that this marks a magnetic ordering transition. On the basis of ac-susceptibility measurements Blöte *et al* [15] suggested that weak ferromagnetism may play a role in this compound, which is consistent with our observation of deviations from Curie–Weiss behaviour. They also quoted unpublished work of Van Geuns, who found $\theta = -22$ K, which is very close to our value, but argued that this was too large to be due to exchange interactions. Their analysis of the specific heat confirmed this, giving an exchange constant which would correspond to a θ of only 1.8 K. It was thus suggested that the Curie–Weiss behaviour reflected the existence of a low lying crystal field level at about $10\ \mathrm{cm}^{-1}$ (14 K) above the ground level. We have recently located two low lying crystal field levels, but at 6–8 meV (70–90 K) above the ground level, using neutron scattering. It seems unlikely that this alone can account for the large Curie–Weiss temperature. A full understanding of the magnetic properties of $Er_2Ti_2O_7$ must await a more detailed study of the crystal field levels.

The field-cooled versus zero-field-cooled susceptibility plot for $Er_2Ti_2O_7$ showed an extraordinary splitting below about 3 K, which is shown in figure 6(c). We have also observed this strange phenomenon in Er_2Sn2O_7, but in no other titanates, and it seems likely to be a real effect, and not an artifact of the measuring technique. An understanding of this unusual feature awaits further experimentation.

3. Discussion and conclusions

Of the five heavy rare earth titanate phases that we have characterized, two ($Gd_2Ti_2O_7$ and $Er_2Ti_2O_7$) have predominantly antiferromagnetic coupling, and three ($Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$ and $Yb_2Ti_2O_7$) have predominantly ferromagnetic coupling. $Gd_2Ti_2O_7$ appears to behave as an isotropic antiferromagnet above 1.8 K, with $\theta \approx 9$ K. The value of θ is significantly greater than the transition temperature of 0.97 K, reported in a recent study [23], confirming the presence of frustrated interactions in this material. $Er_2Ti_2O_7$ orders magnetically at 1.25 K, which is also much lower than the Curie–Weiss temperature, $\theta = -22.3$ K. Although it has been suggested that the large value of θ is due to crystal field effects [15], our results do not rule out the possibility that it is due in large part to exchange coupling, which would make $Er_2Ti_2O_7$ a frustrated antiferromagnet with strong single ion anisotropy.

The rare earth ions in $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$ and $Yb_2Ti_2O_7$ all appear to be highly anisotropic. On the basis of quite good fits to equation (1), it was concluded that $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ have ground state doublets, which are separated from other states by energies much greater than the weak ferromagnetic coupling. The anisotropy assumed here is Ising-like, as equation (1) applies to the case of zero perpendicular *g*-value, $g_\perp = 0$. The quantization axis is the local $\langle 1, 1, 1 \rangle$ axis that points towards the centre of the elementary tetrahedral plaquette of the pyrochlore lattice. Therefore, both compounds should be realizations of the 'spin ice' model, that is, an Ising ferromagnet on the pyrochlore lattice, in which the Ising spins are constrained parallel to the local $\langle 1, 1, 1 \rangle$ axes. The ground state of a single tetrahedral plaquette in this model is shown in figure 7. The 'two spins in, two spins out' condition is analogous to the rule that controls the proton ordering in ice [12, 16]. Thus, if the arrows in figure 7 represent
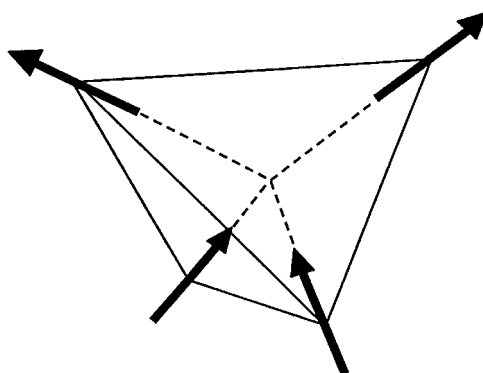
Figure 7. Single tetrahedral plaquette of the spin ice model [12, 16], illustrating the ordering rule that two spins must point into, and two out of, each tetrahedron along the cubic $\langle 1, 1, 1 \rangle$ axes.

proton displacement vectors, and the centre of the tetrahedron locates an oxide ion, one has the local 'H_2O' coordination in ice. There are an infinite number of ways that the ice rules can be satisfied on the lattice as a whole, and hence the ground state of ice, or equivalently of spin ice, is macroscopically degenerate, and no order should occur. $Ho_2Ti_2O_7$ has been shown to possess several characteristics of the spin ice model, in particular an absence of order down to at least 50 mK, and field-induced ordered states that preserve the local $\langle 1, 1, 1 \rangle$ anisotropy [12]. For $Dy_2Ti_2O_7$, as mentioned in section 2, Blöte *et al* [15] estimated the spin entropy by integrating the specific heat between 0.27 and 1.37 K and found that some of the expected entropy $R \ln 2$ was missing. It is now possible to understand this as the residual entropy of the icelike ground state [27]. Very recently, Ramirez *et al* [25] reported a careful experimental determination of the numerical value of this residual entropy, and found it to be almost exactly equal to that predicted by Pauling for ice [26]. This interesting result is fully consistent with the data presented here.

In the case of $Yb_2Ti_2O_7$, the fit of the magnetization to equation (1) is not very convincing, so that, while it seems likely that $\langle 1, 1, 1 \rangle$ is the local quantization axis, it is possible that there is a significant deviation from $g_\perp = 0$. Furthermore, for $Yb_2Ti_2O_7$, the low temperature transition observed by Blöte *et al* [15] precludes true spin ice behaviour. However, as discussed above, $Yb_2Ti_2O_7$ does have ferromagnetic interactions, a Schottky-like heat capacity (above the transition) and a large ratio of θ to the transition temperature, which are all suggestive of spin ice. Recently we found that a ferromagnetic model derived from spin ice, by allowing the moments to cant off their spin ice $\langle 1, 1, 1 \rangle$ axes, has all these attributes, including the ordering transition at low temperature [27]. It is therefore possible that $Yb_2Ti_2O_7$ is a realization of the latter. Another possibility is that the dominant anisotropy in $Yb_2Ti_2O_7$ is easy plane rather than easy axis, in which case one also expects an ordering transition for finite anisotropy [28].

A final point of interest about $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ is to what extent the observed ferromagnetic coupling in these compounds arises from the dipolar interaction. As both materials have approximately the same magnetic moment and unit cell constants, the dipolar coupling must have roughly the same value in each. Assuming $\mu \approx 10\ \mu_B$ gives a near-neighbour dipolar energy of 2.4 K, corresponding to a Curie–Weiss temperature $\theta \approx 3.2$ K. Because of the discrete anisotropy this behaves in exactly the same way as a near-neighbour ferromagnetic exchange, favouring a spin ice ground state. Blöte *et al* [15] calculated a dipolar sum over 14 430 nearest neighbours for the net ferromagnetic configuration that we now understand to be a '$q = 0$' ordered state of the spin ice model (illustrated in [12]).

Assuming $g = 20$, their calculation gives a dipolar energy of 1.92 K, that corresponds (again in the classical approximation) to a Curie–Weiss temperature $\theta \approx 2.6$ K. This is slightly larger than the coupling found experimentally in both $Ho_2Ti_2O_7$ (2K) and $Dy_2Ti_2O_7$ (~ 1 K). Thus, although we have firm evidence that both materials do *not* form the $q = 0$ state down to 50 mK in zero field [12, 26], it seems likely that the observed ferromagnetic coupling is largely dipolar in origin. The difference between $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$ is likely to arise from the presence of weak superexchange in addition to the dipole interactions.

References

[1] Wells A F 1975 *Structural Inorganic Chemistry* 4th edn (Oxford: Oxford University Press)
[2] Sleight A W 1968 *Inorg. Chem.* **7** 1704
[3] Schiessl W *et al* 1996 *Phys. Rev.* B **53** 9143
[4] Babel D, Pausewang G and Viebahn W 1967 *Z. Naturf.* b **22** 1219
[5] Friauf J B 1927 *J. Am. Chem. Soc.* **49** 3107
[6] Anderson P W 1956 *Phys. Rev.* **102** 1008
[7] Villain J 1979 *Z. Phys.* B **33** 31
[8] Gingras M J P, Stager C V, Raju N P, Gaulin B D and Greedan J E 1997 *Phys. Lett.* **78** 947
[9] Gaulin B D, Reimers J N, Mason T E, Greedan J E and Tun Z 1992 *Phys. Rev. Lett.* **69** 3244
[10] Harris M J, Zinkin M P, Tun Z, Wanklyn B M and Swianson I P 1994 *Phys. Rev. Lett.* **53** 189
[11] Ballou R, Lelièvre-Berna E and Fåk B 1996 *Phys. Rev. Lett.* **79** 2554
[12] Harris M J, Bramwell S T, McMorrow D F, Zeiske T and Godfrey K W 1997 *Phys. Rev. Lett.* **79** 2554
[13] Harris M J, Bramwell S T, Zeiske T, McMorrow D F and King P J C 1998 *J. Magn. Magn. Mater.* **177** 757
[14] Knop O, Brisse F, Castelliz L and Sutarno 1965 *Can. J. Chem.* **43** 2812
[15] Blöte H W J, Wielinga R F and Huiskamp H 1969 *Physica* **43** 549
[16] Bramwell S T and Harris M J 1998 *J. Phys.: Condens. Matter* **10** L215
[17] Harris M J, Bramwell S T, Holdsworth P C W and Champion J D M 1998 *Phys. Rev. Lett.* **81** 4496
[18] Zinkin M P, Harris M J, Tun Z, Cowley R A and Wanklyn B M 1996 *J. Phys.: Condens. Matter* **8** 193
[19] Gardner J S *et al* 1999 *Phys. Rev. Lett.* **82** 1012
[20] Roth R S 1956 *J. Res. Natl Bur. Stand.* **56** 17
[21] Bongers P F and Van Meurs E R 1967 *J. Appl. Phys.* **38** 944
[22] Cashion J D, Cooke A H, Leask M J M, Thorp T L and Wells M R 1968 *J. Mater. Sci.* **3** 402
[23] Raju N P, Dion M, Gingras M J P, Mason T E and Greedan J E 1999 *Phys. Rev.* B **59** 14 489
[24] Bramwell S T and Harris M J 1997 unpublished
[25] Ramirez A P, Hayashi A, Cava R J, Siddharthan R and Shastry B S 1999 *Nature* **399** 333
[26] Pauling L 1935 *J. Am. Chem. Soc.* **57** 2680
[27] Champion J D M, Holdsworth P C W, Harris M J and Bramwell S T 1999 unpublished
[28] Bramwell S T, Gingras M J P and Reimers J 1994 *J. Appl. Phys.* **75** 5523