Low-temperature muon spin rotation studies of the monopole charges and currents in Y doped Ho$_2$Ti$_2$O$_7$

L. J. Chang$^1$, M. R. Lees$^2$, G. Balakrishnan$^2$, Y.-J. Kao$^3$ & A. D. Hillier$^4$

$^1$Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan, $^2$Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom, $^3$Department of Physics and Center of Quantum Science and Engineering, National Taiwan University, Taipei 10607, Taiwan, $^4$STFC Rutherford Appleton Laboratory, ISIS Facility, Didcot OX11 0QX, United Kingdom.

In the ground state of Ho$_2$Ti$_2$O$_7$ spin ice, the disorder of the magnetic moments follows the same rules as the proton disorder in water ice. Excitations take the form of magnetic monopoles that interact via a magnetic Coulomb interaction. Muon spin rotation has been used to probe the low-temperature magnetic behaviour in single crystal Ho$_2$-xY$_x$Ti$_2$O$_7$ (x = 0, 0.1, 1, 1.6 and 2). At very low temperatures, a linear field dependence for the relaxation rate of the muon precession $\dot{\varphi}(B)$, that in some previous experiments on Dy$_2$Ti$_2$O$_7$ spin ice has been associated with monopole currents, is observed in samples with $x = 0$, and 0.1. A signal from the magnetic fields penetrating into the silver sample plate due to the magnetization of the crystals is observed for all the samples containing Ho allowing us to study the unusual magnetic dynamics of Y doped spin ice.

In the spin ice materials R$_2$Ti$_2$O$_7$ (R = Ho, Dy)$^{10}$ a large (∼10 $\mu_B$) magnetic moment on the R$^{3+}$ ions giving a strong, but at low temperature almost completely screened dipole-dipole interaction, together with a local Ising-like anisotropy leads to an effective nearest-neighbour frustrated ferromagnetic interaction between the magnetic moments. The organizing principles of the magnetic ground state in spin ice, or “ice rules”, require that two R$^{3+}$ spins should point in and two out of each elementary tetrahedron in the R$_2$Ti$_2$O$_7$ pyrochlore lattice$^{2,4-7}$. Excitations above the ground state manifold, which locally violate the ice rules, can be viewed as magnetic monopoles of opposite “magnetic charge” connected by Dirac strings$^{8-10}$. Evidence of magnetic monopoles in spin ice has recently been observed in several experiments$^{11-13}$.

Given the existence of magnetic monopoles, it is logical to consider the nature of the magnetic charges and any associated currents or “magnetricity”. Bramwell et al. used transverse-field muon spin-rotation (TF-μSR) to investigate the magnitude and dynamics of the magnetic charge in Dy$_2$Ti$_2$O$_7$ spin ice$^{14}$. In these experiments the equivalence of electricity and magnetism proposed in Ref. 8 was assumed and Onsager’s theory$^{15}$, which describes the nonlinear increase with applied field in the dissociation constant of a weak electrolyte (second Wien effect), was applied to the problem of spin ice. It was argued that in spin ice, if the magnetic field $B$ is changed, the relaxation of the magnetic moment $\nu_m$ occurs at the same rate as that of the monopole density and so in the weak field limit, $\nu_m(B)/\nu_m(0) = \kappa(B)/\kappa(0) = 1 + b/2$, where $\kappa$ is the magnetic conductivity and $b = \mu_0 Q^2 B/8nk_b T^2$ with a magnetic charge $Q^2$. At low temperature, the fluctuating local fields lead to a de-phasing of the muon precession and an exponential decay in the oscillatory muon polarization as a function of time $t$

$$A(t) = \nu_0 \cos(2\pi vt) \exp(-\lambda t),$$

(1)

where $\nu_0$ is the initial muon asymmetry, $\nu = \gamma_\mu B/2\pi$ is the frequency of the oscillations, and $\gamma_\mu$ is the gyromagnetic ratio. With $\nu_m(B)/\nu_m(0) = \lambda(B)/\lambda(0)$ one can directly infer the magnetic monopole charge. These measurements have proven intriguing and controversial. Dunsiger et al.$^{16}$ contend that the TF-μSR data never takes a form where $\lambda \propto \nu$ (see however$^{17}$). It has also been suggested that the magnetic field at any muon implantation site in Dy$_2$Ti$_2$O$_7$ is likely to take a range of values up to 0.5 T$^{16,18,19}$. If this is the case it is difficult to understand how the fields of 1–2 mT used in Ref. 14 could lead to a precession signal. Both Dunsiger et al.$^{16}$ and later Blundell$^{17}$ have suggested that the signals seen in the μSR data in Ref. 14 originate from outside the sample. In their reply to this suggestion, Bramwell et al.$^{21}$ acknowledged that their experiments exploited both muons implanted in the sample (interior muons) and muons decaying outside the sample (exterior muons), with the aim of separating near and
far field contributions to the signal. They went on to note that the signal at higher temperatures is dominated by muons implanted in the silver backing plate. This possibility was not discussed in their original paper. Nevertheless, they continued to insist that the signal at low temperature (0.4 > T > 0.07 K) cannot be explained by exterior muons and that the Wien effect signal originates from muons within the sample or muons sufficiently close to the surface of the sample so as to probe the monopolar far field.

**Results**

Fig. 1 shows a TF-μSR time spectrum collected at 150 mK in a field of 2 mT for a pure Ho$_2$Ti$_2$O$_7$ sample. These results are representative of the data collected during this study.

For all the samples containing Ho, a nearly T independent $\lambda(T)$ is observed at low-temperature. As the temperature is raised there is a rapid increase in $\lambda(T)$ at some crossover temperature $T_{CR}$. This $T_{CR}$ increases from ~0.4 K for the crystals with $x = 1.6$ and 1.0 (data not shown) to 0.5 K for the samples with $x = 0.1$ and 0.0. Above $T_{CR}$ the relaxation rate decreases with increasing temperature and has a similar T dependence for all four samples containing Ho that were studied. For two samples ($x = 0.1$ and 1.6) we also collected field-cooled-cooling data. In both cases a divergence between the zero-field-cooled warming (ZFCW) and the field-cooled cooling (FCC) curves appears at $T_{CR}$. For pure Y$_2$Ti$_2$O$_7$ a temperature independent relaxation rate is measured for the whole temperature range (0.05 to 5 K) studied.

In order to better understand the origins of these signals we have also collected relaxation data as a function of temperature in 2 mT for the pure Ho$_2$Ti$_2$O$_7$ sample discussed above, covered with a silver foil 0.25 mm thick. This thickness of foil is expected to stop all the muons before they reach the sample. Muons implanted in silver have a negligible relaxation and so any relaxation must result from a combination of the externally applied field and/or field lines originating from the sample penetrating into the silver. The $\lambda(T)$ curve obtained in this way is very similar to the signal from the pure Ho$_2$Ti$_2$O$_7$ shown in Fig. 2a and demonstrates that at least some of the signal comes from fields within the silver, but that these fields are the result of the magnetic properties of the sample (see Supplementary information).

As a next step we then investigated the magnetic field dependence of the muon relaxation rate. Fig. 3 shows $\lambda(B)$ for a sample with $x = 0$ at selected temperatures. Studies were also made for samples with $x = 0.1, 1, 1.6$ and 2. Following Bramwell et al., linear fits to the $\lambda(B)$ data were made at each temperature. Using the gradient and intercept extracted from each fit, the effective magnetic charge $Q_{eff}$ was obtained from $Q_{eff} = 2.1223 m^{1/3} T^{2/3}$, where $m = (d\lambda(B)/dB)/\lambda_0^{14}$. For samples with $x = 0$ and 0.1 the resulting values of $Q_{eff}$ range from 4.5 to 7.5 $\mu_B$A$^{-1}$ in the temperature regime in which Onsager's
theory is expected to be valid, but increase rapidly as the temperatures increase outside this range (see Fig. 4).

At high temperature, a linear field dependence for $\lambda(B)$ is also observed for the two samples with a much higher yttrium doping ($x = 1$ and 1.6) but the calculated $Q_{\text{eff}}$ is always greater than $\sim 10 \mu B^{-1}$. For $x = 1$ and 1.6 in the low-temperature regime $T < T_{\text{CR}}$ there is no systematic linear field dependence in $\lambda(B)$ and no signal that can be associated with magnetricity.

We have also looked for a linear magnetic field dependence in $\lambda(B)$ for the pure Ho$_2$Ti$_2$O$_7$ sample covered in a thick (0.25 mm) silver foil. At higher temperatures $T > T_{\text{CR}}$ we observed a linear behaviour leading to a large $Q_{\text{eff}}$ (i.e. $Q_{\text{eff}} > 10 \mu B^{-1}$), but at low temperatures $T < T_{\text{CR}}$ we found no signature of magnetricity and could not obtain reliable linear fits to the $\lambda(B)$ data or physically acceptable values for $Q_{\text{eff}}$.

**Discussion**

We can draw a number of important conclusions from our work. Our results indicate that at higher temperatures, as suggested previously,[25,26,27] the dominant contribution to the $\lambda(T)$ signal arises from stray fields from the magnetized spin ice that penetrate into the silver sample plate. The observation of a signal in a sample covered with silver, for the pure Ho$_2$Ti$_2$O$_7$ sample covered in a thick (0.25 mm) silver foil, is consistent with the suggestion made in Ref. 21 that the Wien effect signal may arise from impurities, dislocations, and surface effects on the low-temperature dynamics of spin ice.

Returning to the question of magnetricity in spin ice we note that in our $\mu$SR data the low-temperature signal that has previously been observed for the two samples with a much higher yttrium doping ($x = 1$ and 1.6) but the calculated $Q_{\text{eff}}$ is always greater than $\sim 10 \mu B^{-1}$. For $x = 1$ and 1.6 in the low-temperature regime $T < T_{\text{CR}}$ there is no systematic linear field dependence in $\lambda(B)$ and no signal that can be associated with magnetricity.

We have also looked for a linear magnetic field dependence in $\lambda(B)$ for the pure Ho$_2$Ti$_2$O$_7$ sample covered in a thick (0.25 mm) silver foil. At higher temperatures $T > T_{\text{CR}}$ we observed a linear behaviour leading to a large $Q_{\text{eff}}$ (i.e. $Q_{\text{eff}} > 10 \mu B^{-1}$), but at low temperatures $T < T_{\text{CR}}$ we found no signature of magnetricity and could not obtain reliable linear fits to the $\lambda(B)$ data or physically acceptable values for $Q_{\text{eff}}$.

**Figure 3** | Magnetic field dependence of the muon relaxation rate $\lambda(B)$ for pure Ho$_2$Ti$_2$O$_7$ at three different temperatures. The values for $m = (\dot{\lambda}(B)/dB)/\lambda_0$ and the effective magnetic charge $Q_{\text{eff}}$ shown in Figure 4 have been obtained from the straight line fits to the data.

**Figure 4** | $Q_{\text{eff}}$ versus $1/T$ for samples of Ho$_{1-x}$Y$_x$Ti$_2$O$_7$ with $x = 0$ and 0.1. The vertical dashed lines indicate the high and low temperature limits between which the Onsager theory is expected to be valid[43] and the horizontal line marks the value for $Q_{\text{eff}} = 4.6 \mu B^{-1}$. The inset shows $m(T)$ for the same data; the solid line shows $m = Q_{\text{eff}} / T^2$ with $Q_{\text{eff}} = 5 \mu B^{-1}$. Also shown in both plots are the data of Bramwell et al. from Ref. 14.
interpreted as a signature of magnetoreactivity is seen in the x = 0 and 0.1 samples and is not observed in the more dilute Ho2−xYxTi2O7 materials. Within the T range indicated by the dashed lines in Fig. 4, where the theory presented by Bramwell et al. is expected to be valid, the value of Q_{ag} agrees with expectations. Following Blundell et al. we also plot m versus T. We see that the expected m ∝ T only holds for the same narrow T range. Our experiments, including two separate runs on pure Ho2Ti2O7 carried out three months apart, demonstrate the reproducibility of the data (see Fig. 2a). A realignment of the Ho2Ti2O7 disks between runs also shows that the results are not particularly sensitive to the exact details of the sample geometry. Our results for the samples with a higher Y content and with the thick Ag foil demonstrate that the behaviour cannot be attributed to instrumental effects. The samples were made at Warwick and are Ho rather than Dy based pyrochlores, eliminating the possibility of material specific effects.

In summary, transverse-field pSR experiments on Ho2−xYxTi2O7, including measurements on non-magnetic Y2Ti2O7 and a sample of Ho2Ti2O7 covered in thick silver foil, suggest that the major signal in the $\chi(T)$ response comes from stray fields due to the sample magnetization penetrating into the silver sample plate. The results for Ho2Ti2O7 are comparable with those observed for Dy2Ti2O7. The low-temperature $T < T_C$ field linear field dependence in $\chi(B)$ is only observed in samples with x = 0 and 0.1. In this low-temperature regime the value of Q_{ag} agrees quantitatively with the theory presented in Ref. 14. The low-temperature hysteresis in $\chi(T)$ for the magnetically dilute material (x = 1.6) appears inconsistent with the current understanding of monopoles in spin ice.

**Methods**

Single crystals of Ho2−xYxTi2O7 (x = 0, 0.1, 1.6 and 2) were grown in an image furnace using the floating zone technique. The single crystal disks were glued on to a silver plate and covered with a thin (0.01 mm) sheet of silver foil to improve thermal conductivity. The plate was then attached to the cold stage of an Oxford Instruments He3 He dilution refrigerator. Transverse-field muon spin-rotation experiments were performed using the MuSR spectrometer at the ISIS pulsed muon facility, Rutherford Appleton Laboratory, UK. The magnetic field was applied along the [001] direction, perpendicular to the initial direction of the muon spin polarization which was along the [110] axis. Measurements were carried out as a function of applied field at fixed temperature and as a function of temperature in a fixed magnetic field. See Supplementary information for full details of the measurement protocols.

1. Ramirez, A. P., Hayashi, A., Cava, R. J., Siddharthan, R. & Shastry, B. S. Zero-point entropy in 'spin ice'. Nature 399, 333–335 (1999).
2. Harris, M. J., Bramwell, S. T., McMorrow, D. F., Zeiske, T. & Godfrey, K. W. Geometrical frustration in the ferromagnetic pyrochlore Ho2Ti2O7. Phys. Rev. Lett. 79, 2554–2557 (1997).
3. Bramwell, S. T. & Gingras, M. J. P. Spin ice state in frustrated magnetic pyrochlore materials. Science 294, 1495–1501 (2001).
4. Bramwell, S. T., & Harris, M. J. Frustration in Ising-type spin models on the pyrochlore lattice. J. Phys.: Condens. Matter 10, L215–L220 (1998).
5. den Hertog, B. C. & Gingras, M. J. P. Dipolar interactions and origin of spin ice in Ising pyrochlore magnets. Phys. Rev. Lett. 84, 3430–3433 (2000).
6. Yavorskii, I., Fennell, T., Gingras, M. J. P. & Bramwell, S. T. Dy2Ti2O7–spin ice: a test case for emergent clusters in a frustrated magnet. Phys. Rev. Lett. 101, 037204 (2008).
7. Isakov, S. V., Moessner, R. & Sondhi, S. L. Why spin ice obeys the ice rules. Phys. Rev. Lett. 95, 217201 (2005).
8. Castelnovo, C., Moessner, R. & Sondhi, S. L. Magnetic monopoles in spin ice. Nature 451, 42–45 (2008).
9. Ryzhkin, I. A. Magnetic relaxation in rare-earth oxide pyrochlores. J. Exp. Theor. Phys. 101, 481–486 (2005).
10. Jaubert, L. D. C. & Holdsworth, P. C. W. Signature of magnetic monopole and Dirac string dynamics in spin ice. Nature Phys. 5, 258–261 (2009).
11. Fennell, T. et al. Magnetic Coulomb phase in the spin ice Ho2Ti2O7. Science 326, 415–417 (2009).
12. Morris, D. J. P. et al. Dirac strings and magnetic monopoles in the spin ice Dy2Ti2O7. Science 326, 411–414 (2009).

Acknowledgements

This work was supported by the EPSRC, United Kingdom (EP/I007210/1) and the National Science Council, Taiwan (NSC 101-2122-M-006-010-MYS). Some of the equipment used in this research was obtained through the Science City Advanced Materials project: Creating and Characterizing Next Generation Advanced Materials project, with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF). We would like to thank Stephen Blundell, Steve Bramwell, Claudia Castelnovo, and Sean Giovin for useful discussions.

Author contributions

L.J.C. and M.R.L. conceived of the project. G.B. prepared the samples. A.D.H., L.J.C. and M.R.L. carried out the experiments. M.R.L., M.R. and Paul, D. M. single crystal growth of rare earth titanate pyrochlores. J. Phys.: Condens. Matter 10, L723–L725 (1998).

Competing financial interests: The authors declare no competing financial interests.

License: This work is licensed under a Creative Commons Attribution 3.0 Unported License. To view a copy of this license, visit http://creativecommons.org/licenses/by/3.0/

How to cite this article: Chang, L. J. et al. Magnetic relaxation in rare-earth oxide pyrochlores. J. Phys.: Condens. Matter 10, L723–L725 (1998).