Far-from-equilibrium monopole dynamics in spin ice

C. Paulsen^{1*}, M. J. Jackson¹, E. Lhotel¹, B. Canals¹, D. Prabhakaran², K. Matsuhira³, S. R. Giblin⁴ and S. T. Bramwell⁵

Condensed matter in the low-temperature limit reveals exotic physics associated with unusual orders and excitations, with examples ranging from helium superfluidity¹ to magnetic monopoles in spin ice^{2,3}. The far-from-equilibrium physics of such low-temperature states may be even more exotic, yet to access it in the laboratory remains a challenge. Here we demonstrate a simple and robust technique—the ‘magnetothermal avalanche quench’—and its use in the controlled creation of non-equilibrium populations of magnetic monopoles in spin ice at millikelvin temperatures. These populations are found to exhibit spontaneous dynamical effects that typify far-from-equilibrium systems and yet are captured by simple models. Our method thus opens new directions in the study of far-from-equilibrium states in spin ice and other exotic magnets.

The normal way of controlling the temperature of a system is to connect it thermally to a second body with a much larger thermal mass, which then acts as a thermal reservoir. If it is desired to force thermal excitations out of equilibrium by a rapid temperature quench, then the simplest strategy would be to heat the sample, and then abruptly remove the heating so that the sample is cooled rapidly by the reservoir. However, direct heating of the sample will also tend to heat the reservoir, and this becomes a particular problem in low-temperature devices: for example, in a ³He–⁴He dilution refrigerator it may entail heating of the mixing chamber, and ultimately limit the speed of any thermal quench that can be practically achieved. Our technique gets round this problem by using the natural tendency of magnets to undergo magnetothermal ‘avalanches’ at low temperature^{4–7}. It is illustrated in Fig. 1 and discussed further in Supplementary Section 1.4. The essential principle is that magnetic work done on the sample is abruptly converted into internal heat, which causes a sudden increase in temperature inside the sample (T_{int}). The sample then finds itself at a relatively high temperature but connected to a cold thermal bath. The ensuing quench is as efficient and rapid as possible as it involves minimal heating of the sample environment, which remains at the reservoir temperature, T .

Magnetothermal avalanches typically occur at low temperature ($T < 1$ K), a regime also notable for the occurrence of exotic magnetic states based on long-range interactions, quantum effects and magnetic frustration^{8–14}. Hence, the avalanche quench technique could be generally used to drive such systems out of equilibrium. We focus on the case of spin ice, a nearly ideal realization of a magnetic ice-type or vertex model⁸. The far-from-equilibrium physics of vertex models is a subject of great intrinsic interest¹⁵, so to access it

in an experimental system would open up numerous opportunities for the study of new physics.

In spin-ice materials such as Dy₂Ti₂O₇ and Ho₂Ti₂O₇, the frustrated pyrochlore lattice geometry and local crystal field combines with a self-screening dipole–dipole interaction to give a local ‘ice rule’ that controls low-energy spin configurations^{8,16,17}. Simply stated, the minimum-energy state corresponds to two spins pointing into and two spins pointing out of each tetrahedron of the pyrochlore lattice, which stabilizes a degenerate and disordered magnetic ground state. Thermally generated defects (that is, three spins in and one out, or three out and one in) in the disordered ice rules manifold take the form of effective magnetic monopoles^{2,3,18}. At low temperatures these defects are thermally activated with density in zero applied field varying as $2\exp(\mu/kT)$, where μ is the monopole chemical potential ($\mu/k \approx -4.5$ K for Dy₂Ti₂O₇). The monopole description replaces the conventional description based on the spin degrees of freedom, with a model of a symmetric magnetic Coulomb gas with magnetic charge ($\pm Q$). However, the Coulomb gas is unusual in that the magnetic monopoles are connected by a network of ‘Dirac strings’¹⁸.

Below about 0.6 K, certain degrees of freedom in spin ice fall out of equilibrium on experimental timescales^{19–21}. This has been discussed in terms of intrinsic kinetic effects²², slowing down of the monopole hop rate^{18,23,24}, and the trapping of monopoles on extrinsic defects²³, and it is likely that all such factors play a role. However, the degree of non-equilibration has not hitherto been brought under experimental control. It was theoretically shown that a fast thermal quench in the ‘dipolar spin ice’ model could create monopole-rich states at low temperature²⁵. This same study also identified the important effect of ‘non-contractible’ monopole-antimonopole pairs, for which annihilation is itself a thermally activated process that would lead to a dynamical arrest at low temperature.

The clear importance of the rate at which the sample is cooled ($r = dT/dt$) on the subsequent relaxation at low temperature is illustrated in Fig. 2. Three of the curves shown in this figure followed the conventional cooling protocol to prepare the sample. First, the sample was first heated to 900 mK for approximately 1 min in zero magnetic field (and the measured magnetization was $M = 0$). The sample was then cooled at three different rates as shown in the inset. After a total cooling/wait period of 3,000 s, the sample temperature was regulated to the measuring temperature (that is, 300 mK for the curves shown in Fig. 2a) for another 600 s. Then, a 5 mT field was applied, the clock was reset and the ensuing relaxation of the magnetization recorded at constant temperature.

¹Institut Néel, C.N.R.S.—Université Joseph Fourier, BP 166, Grenoble 38042, France, ²Clarendon Laboratory, Physics Department, Oxford University, Oxford OX1 3PU, UK, ³Kyushu Institute of Technology, Kitakyushu 804-8550, Japan, ⁴School of Physics and Astronomy, Cardiff University, Cardiff CF24 3AA, UK, ⁵London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, 17–19 Gordon Street, London WC1H 0AJ, UK.

*e-mail: carley.paulsen@grenoble.cnrs.fr

Figure 1 | The avalanche quench technique used to produce a residual population of monopoles in the spin ice $\text{Dy}_2\text{Ti}_2\text{O}_7$. Through the application of magnetic fields, the internal sample temperature T_{int} is raised to approximately 900 mK and then rapidly quenched, while the temperature of the cryostat mixing chamber T_{mix} remains below 200 mK. **a**, The time (t) dependence of $T_{\text{mix}}(t)$ compared with that of the applied field $H(t)$ and the measured sample magnetization $M(t)$. **b–g**, Illustrations showing the behaviour of the sample, where its internal temperature $T_{\text{int}}(t)$ was estimated by means of separate control experiments, as described in Supplementary Section 1.4. These illustrations describe the sequence of processes to which the sample is subjected. **b**, Before the procedure begins, the sample is first magnetized to $-2.5\mu_{\text{B}}$ per Dy atom in a field of -0.2 T, and the temperature of the mixing chamber and sample is stabilized to 75 mK. **c**, At time $t = 0$, the field is rapidly reversed from -0.2 to $+0.2$ T at a rate of 0.55 T s^{-1} . The magnetization follows, albeit with some delay. The magnetic Zeeman energy $\Delta M \cdot H$ released from the spins rapidly heats the interior of the sample to $T_{\text{int}} \sim 900$ mK, and the heat then leaks out of the sample to the mixing chamber, as seen as a spike in the temperature T_{mix} on our thermometer. **d**, T_{mix} remains below 200 mK, so the sample cools very quickly, limited only by thermal conduction to the Cu sample holder. We estimate cooling to be as fast as 0.07 K s^{-1} at 500 mK. **e**, At $t = 8$ s, the field is then removed, and the sample avalanches again with less energy (against its internal field). Nevertheless, we estimate that the temperature inside the sample again approaches 900 mK. **f**, The heat is again swiftly evacuated to the mixing chamber and M approaches 0. **g**, The result of the fast magnetothermal quench is to freeze in a very large, non-equilibrium density of defects, or monopoles.

Figure 2 | Relaxation of the magnetization M versus time t . A magnetic field of 5 mT was applied at $t = 0$, having beforehand prepared the $t = 0$ state by either conventional cooling in zero field or by an avalanche quench (Fig. 1). The inset in **a** shows the evolution of the measured temperature during conventional cooling with different cooling rates (blue, $r \approx 0.3 \text{ mK s}^{-1}$; black, $r \approx 4 \text{ mK s}^{-1}$ and green, $r \approx 17 \text{ mK s}^{-1}$). **a**, Comparison of the subsequent magnetic relaxation $M(t)$ after conventional cooling (same colour scheme) with that for the avalanche quench (red curve). Note that because the measuring field was so small, there was absolutely no heating of the sample when this field was applied, and the relaxation was at constant temperature. **b**, Pairs of conventional cooling (blue, $r \approx 0.3 \text{ mK s}^{-1}$) and avalanche quench (red) relaxation curves measured at fixed temperatures ranging from 600 to 200 mK. The faster the cooling rate, the faster the relaxation, and clearly the avalanche quench protocol is the fastest. The trend becomes very marked below 300 mK.

It is seen in Fig. 2 that the faster the cooling rate, the faster the magnetic response.

Also shown in the figure are relaxation data taken after the sample was prepared using the magneto-thermal avalanche quench protocol outlined in Fig. 1. According to the model of ref. 3, $\mathbf{J} = \partial \mathbf{M}(t)/\partial t$ is the monopole current density, and as monopole dynamics are in the diffusive limit, a larger current density $\mathbf{J}$ directly implies a larger monopole density ρ . In the simplest scenario

Figure 3 | Simulation of non-equilibrium effect. a, b, Magnetization M (**a**) and monopole density ρ (**b**) versus time t , from a kinetic Monte Carlo simulation of nearest-neighbour spin ice—a 16-vertex model, similar to that studied in refs 15,25. The inset shows the time t^* needed to reach the magnetization $M(t^*) = M(T, t = \infty)/10$ as a function of the density of monopoles ρ at $t = 0$, which depends itself on the simulated cooling rate (K). The line ($\propto 1/\rho(t=0)$) is a guide to the eye. The numerical system assumes single-spin-flip dynamics with periodic boundary conditions on a pyrochlore lattice of size $L \times L \times L$ face-centred-cubic unit cells with 16 spins per unit cell ($L = 8$ in this figure). The model is thermally quenched by reducing the temperature in equal logarithmic steps, from 1 K to 300 mK, in zero applied magnetic field. The logarithmic decrement, from right to left is $K = 1.0001, 1.001, 1.01, 1.1$ and 2. A field of 10 mT is then applied at $t = 0$ and $M(t)$ is monitored until it reaches its asymptotic, cooling-rate-independent, value. The microscopic parameters for the simulation are those of $\text{Dy}_2\text{Ti}_2\text{O}_7$ (from ref. 18). Each $M(t)$ curve corresponds to an average of 100 independent cooling scenarios. Time is given in units of Monte Carlo steps (MCS), with 1 MCS being associated with a stochastic sampling of the whole sample. (Note that similar simulations with the dipolar spin-ice model reproduce the same behaviour. See Supplementary Section 1.5.)

$\mathbf{J} \propto \rho$, but the precise relation (unimportant here) depends on the density dependence of the monopole mobility. Thus, referring to Fig. 1, we conclude that both conventional and avalanche cooling

Figure 4 | Scaling of the relaxation. **a**, The normalized avalanche quench relaxation M (normalized) = $M(T, t)/M(T, t = \infty)$ measured from 700 to 75 mK in a 5 mT field. The dashed line is the 450 mK curve with the time scaled (that is, the log curve shifted to the left) in such a way that M (normalized) = $1 - 1/e$ occurs at 1 s. The arrows indicate similar scaling for other curves. The scale factor represents an average relaxation time τ and is shown in the inset as a function of temperature down to 400 mK. **b**, The results of the scaling for all of the curves in **a**. For $T > 0.4$ K, all of the curves can be more or less superimposed as shown. However, at lower temperature, the curves cannot be scaled, indicating that there is a change in the dynamic behaviour, and τ for these curves cannot be so simply defined. Inset, Average relaxation time τ derived from the scale factor used to collapse the M versus t curves in **a**, shown as a function of temperature down to 400 mK (the line is guide to the eye).

protocols result in the creation of non-equilibrium monopole populations. However, Fig. 2 shows how the avalanche quench leads to significantly faster relaxation than the fastest conventional protocol, and hence we may infer that it stabilizes a proportionately larger monopole density. Furthermore, the difference between the two protocols becomes more obvious at lower temperature as seen in Fig. 2b. Note that, although there are differences in the relaxation curves, both cooling protocols lead to the same final magnetization after application of a field, suggesting that the final state is an equilibrium state. The data presented here were obtained with the field applied along the [111] direction. Our results are qualitatively similar when the applied field was perpendicular to the [111] axis and along the [001] axis (see Supplementary Section 1.3).

Remarkably, we found that the dependence of the relaxation on the cooling rate is captured by the most simple model of spin ice: the nearest-neighbour spin-ice model (simulations of the dipolar model¹⁷ are reported in Supplementary Section 1.6). Figure 3 shows the results of a kinetic Monte Carlo simulation of nearest-neighbour spin ice—a 16-vertex model, similar to that studied in refs 15, 25. The numerical system assumes single-spin-flip dynamics with periodic boundary conditions and was thermally quenched by reducing the temperature in equal logarithmic steps. It is clear that it qualitatively reproduces experiment. In addition, the simulation correlates the rate of the relaxation of $M(t)$ with the $t = 0$ monopole density (Fig. 3, inset), which is itself related to the dT/dt cooling rate of the sample: the faster the cooling rate, the more monopoles, and the more monopoles the faster the initial relaxation. As anticipated, the relaxation rate is roughly inversely proportional to the initial monopole density (see Fig. 3b and Supplementary Sections 1.3–1.4). The general agreement between theory and experiment suggests that this is true for the real material as well.

The qualitative success of the nearest-neighbour spin-ice model also shows that the avalanche quench has realized intrinsic non-

equilibrium behaviour in spin ice. Although extrinsic defects can influence the dynamics of spin ice at low temperature²³, it is clear that they do not cause the behaviour we observe (see Supplementary Section 1.3). The irrelevance of extrinsic defects to our experiments are consistent with creation of monopole-rich states, in which the monopole density far exceeds that of extrinsic defects.

Close inspection of the experimental curves (Fig. 2b), reveals an intriguing behaviour of the avalanche quench magnetization at long times. All of the conventional cooling protocols lead to a monotonic, roughly exponential evolution of $M(t)$, typical of systems whose initial state is not too far from equilibrium. In contrast, the avalanche quench leads to a non-monotonic $M(t)$ that initially increases, but later reaches a maximum before finally decreasing towards the final equilibrium state. In thermodynamics the magnetization is an increasing function of field, so the behaviour following avalanche quenching suggests that the magnetic system is exploring states that are sufficiently far from equilibrium for oscillatory behaviour to occur. It therefore seems that the avalanche quench puts the monopole gas far-from-equilibrium in this sense, whereas the conventional cooling leads to near-equilibrium behaviour. Interestingly, a similar overshoot appears in the simulations for small system sizes when considering open boundary conditions, but it disappears in the thermodynamic limit.

The overshoot of the magnetization may plausibly be explained in terms of the larger non-equilibrium monopole population of the avalanche-quench-prepared sample as compared with the conventionally cooled sample. Immediately after the field is applied, the avalanche-quench-cooled sample does not need to create new monopoles (a process that becomes exceedingly slow at low temperatures owing to the high energy barrier for their creation) and existing monopoles are free to hop between tetrahedra within the constraints of the ice rules, leaving behind Dirac strings of overturned spins. The magnetization grows, and the process is so efficient

that the magnetization can even overshoot the thermal equilibrium value. However, at longer times, the lower entropy of the strings and finite temperature will favour collapsing strings and an eventual rearrangement of the spins towards true thermodynamic equilibrium.

A final interesting property of the monopole-rich state is illustrated in Fig. 4. It is shown in Fig. 4b that, above 0.4 K, the relaxation curves $M(t)$ collapse when scaling the time axis, whereas below 0.4 K they do not. This reveals a basic change of dynamical regime at $T < 0.4$ K, which may indicate either a change in the microscopic spin or monopole dynamics, or an approach towards a different equilibrium state. The latter is consistent with a recent specific-heat study that has suggested the onset of ordering correlations in this temperature range²⁶, and also with neutron scattering evidence that reveals a gradual departure from pure spin-ice correlations (although no tendency to order) as $\text{Dy}_2\text{Ti}_2\text{O}_7$ is cooled to 0.3 K (refs 27, 28). On the other hand, the ‘dual electrolyte’ of the monopole model shows a striking change of dynamics exactly in this temperature range, which is associated with the Wien effect for magnetic monopoles^{29–31}. Future work will be aimed at distinguishing these possibilities, more closely connecting our results with intrinsic far-from-equilibrium dynamics of a 16-vertex model¹⁵ and applying the avalanche quench technique to other magnetic systems.

Received 27 August 2013; accepted 27 November 2013;
published online 19 January 2014

References

- Allen, J. F. & Misener, A. D. Flow phenomena in liquid helium II. *Nature* **142**, 633–634 (1938).
- Castelnovo, C., Moessner, R. & Sondhi, S. L. Magnetic monopoles in spin ice. *Nature* **451**, 42–45 (2008).
- Ryzhkin, I. A. Magnetic relaxation in rare-earth oxide pyrochlores. *J. Exp. Theor. Phys.* **101**, 481–486 (2005).
- Paulsen, C. & Park, J.-G. *Quantum Tunnelling of Magnetization-QTM'94* 189–207 (Kluwer Academic, 1995).
- Paulsen, C., Park, J.-G., Barbara, B., Sessoli, R. & Caneschi, A. Studies of hysteresis in Mn_{12}Ac . *J. Mag. Mag. Mater.* **140**, 1891–1892 (1995).
- Subedi, P. *et al.* Onset of a propagating self-sustained spin reversal front in a magnetic system. *Phys. Rev. Lett.* **110**, 207203 (2013).
- Slobinsky, D. *et al.* Unconventional magnetization processes and thermal runaway in spin-ice $\text{Dy}_2\text{Ti}_2\text{O}_7$. *Phys. Rev. Lett.* **105**, 267205 (2010).
- Harris, M. J., Bramwell, S. T., McMorro, D. F., Zeiske, T. & Godfrey, K. W. Geometrical frustration in the ferromagnetic pyrochlore $\text{Ho}_2\text{Ti}_2\text{O}_7$. *Phys. Rev. Lett.* **79**, 2554–2557 (1997).
- Lee, S. H. *et al.* Emergent excitations in a geometrically frustrated magnet. *Nature* **418**, 856–858 (2002).
- Ross, K. A., Savary, L., Gaulin, B. D. & Balents, L. Quantum excitations in quantum spin ice. *Phys. Rev. X* **1**, 021002 (2011).
- Chang, L.-J. *et al.* Higgs transition from a magnetic Coulomb liquid to a ferromagnet in $\text{Yb}_2\text{Ti}_2\text{O}_7$. *Nature Commun.* **3**, 992 (2012).
- Kraemer, C. *et al.* Dipolar antiferromagnetism and quantum criticality in LiErF_4 . *Science* **336**, 1416–1419 (2012).
- Fennell, T., Kenzelmann, M., Roessli, B., Hass, M. K. & Cava, R. J. Power-law spin correlations in the pyrochlore antiferromagnet $\text{Tb}_2\text{Ti}_2\text{O}_7$. *Phys. Rev. Lett.* **109**, 017201 (2012).
- Kimura, K. *et al.* Quantum fluctuations in spin-ice-like $\text{Pr}_2\text{Zr}_2\text{O}_7$. *Nature Commun.* **4**, 1934 (2013).
- Levis, D. & Cugliandolo, L. F. Out-of-equilibrium dynamics in the bidimensional spin-ice model. *Euro. Phys. Lett.* **97**, 30002 (2012).
- Bramwell, S. T. & Gingras, M. J. P. Spin ice state in frustrated magnetic pyrochlore materials. *Science* **294**, 1495–1501 (2001).
- Melko, R. G. & Gingras, M. J. P. Monte Carlo studies of the dipolar spin ice model. *J. Phys. Condens. Matter* **16**, R1277 (2004).
- 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).
- Snyder, J. *et al.* Low-temperature spin freezing in the $\text{Dy}_2\text{Ti}_2\text{O}_7$ spin ice. *Phys. Rev. B* **69**, 064414 (2004).
- Matsuhira, K. *et al.* Spin dynamics at very low temperature in spin ice $\text{Dy}_2\text{Ti}_2\text{O}_7$. *J. Phys. Soc. Jpn* **80**, 123711 (2011).
- Yaraskavitch, L. R. *et al.* Spin dynamics in the frozen state of the dipolar spin ice material $\text{Dy}_2\text{Ti}_2\text{O}_7$. *Phys. Rev. B* **85**, 020410(R) (2012).
- Bramwell, S. T. Generalized longitudinal susceptibility for magnetic monopoles in spin ice. *Phil. Trans. R. Soc. A* **370**, 5738–5766 (2012).
- Revell, H. M. *et al.* Evidence of impurity and boundary effects on magnetic monopole dynamics in spin ice. *Nature Phys.* **9**, 34–37 (2013).
- Bovo, L., Bloxson, J. A., Prabhakaran, D., Aeppli, G. & Bramwell, S. T. Brownian motion and quantum dynamics of magnetic monopoles in spin ice. *Nature Commun.* **4**, 1535 (2013).
- Castelnovo, C., Moessner, R. & Sondhi, S. L. Thermal quenches in spin ice. *Phys. Rev. Lett.* **104**, 107201 (2010).
- Pomaranski, D. *et al.* Absence of Paulings residual entropy in thermally equilibrated $\text{Dy}_2\text{Ti}_2\text{O}_7$. *Nature Phys.* **9**, 353–356 (2013).
- Yavorskii, T., Fennell, T., Gingras, M. J. P. & Bramwell, S. T. $\text{Dy}_2\text{Ti}_2\text{O}_7$ spin ice: A test case for emergent clusters in a frustrated magnet. *Phys. Rev. Lett.* **101**, 037204 (2008).
- Fennell, T. *et al.* Neutron scattering investigation of the spin ice state in $\text{Dy}_2\text{Ti}_2\text{O}_7$. *Phys. Rev. B* **70**, 134408 (2004).
- Bramwell, S. T. *et al.* Measurement of the charge and current of magnetic monopoles in spin ice. *Nature* **461**, 956–959 (2009).
- Giblin, S. R., Bramwell, S. T., Holdsworth, P. C. W., Prabhakaran, D. & Terry, I. Creation and measurement of long-lived magnetic monopole currents in spin ice. *Nature Phys.* **7**, 252–258 (2011).
- Kaiser, V., Bramwell, S. T., Holdsworth, P. C. W. & Moessner, R. Onsager's Wien effect on a lattice. *Nature Mater.* **12**, 1033–1037 (2013).

Acknowledgements

S.R.G. would like to acknowledge the support of the European Community—Research Infrastructures under the FP7 Capacities Specific Programme, MICROKELVIN project number 228464. M.J.J. was supported by the French ANR project CHIRnMAG.

Author contributions

Experiments were conceived and designed by C.P. and E.L. and performed by C.P., E.L., S.R.G. and M.J.J. The data were analysed by C.P., E.L., S.R.G., M.J.J., B.C. and S.T.B. Contributed materials and analysis tools were made by K.M., D.P. and B.C. The paper was written by S.T.B., C.P., E.L., S.R.G. and B.C. with feedback from all authors.

Additional information

Supplementary information is available in the [online version of the paper](#). Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to C.P.

Competing financial interests

The authors declare no competing financial interests.