PARADIGM LOST – Where the Missing Entropy Goes in Spin Ice

"Absence of Pauling's Residual Entropy in Thermally Equilibrated $Dy_2Ti_2O_7$", D. Pomeransky, L.R. Yaraskavitch, S. Meng, K.A. Ross, H.M.L. Noad, H.A. Dabkowska, B.D. Gaulin, and J.B. Kycia, *Nat. Phys*., **9**, 353 (2013)

Recommended with a Commentary by A. P. Ramirez and B. S. Shastry,

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Collective effects in insulating magnets have played a central role in the development of classical statistical physics. The detailed microscopic understanding of magnetic solids allows high accuracy at the Hamiltonian level, which in turn advances statistical predictions of physical properties.

Among the most successful of statistical tools is mean field theory (MFT). Thus the development of geometrically frustrated magnets – an entire class of magnets for which MFT fails – has posed interesting challenges for theorists. Prior to 1997, however, one statistical, i.e. thermodynamic, state had been known to exist but never observed in magnets. This was the ice state proposed by Pauling to explain the entropy missing from calorimetric studies of water. Harris et al, recognized (1) that the orientation of the H_2O molecule can be mapped onto an Ising spin and that the rare-earth pyrochlore lattice provides a mapping for Paulings' ice state. This so-called "spin ice" model gained credence with the discovery, in the spin sublattice of the pyrochlore $Dy_2Ti_2O_7$, of missing entropy (2) within 10% of Pauling's estimated value. This observation introduced a new type of magnetic thermodynamic state, one that was completely frozen in space and time but possessing neither long-range correlations of conventional ordered magnets nor the quenched disorder of spin glass. In spin ice, like other geometrically frustrated magnets, disorder arises from the incompatibility of the spin interactions with the geometry of the lattice.

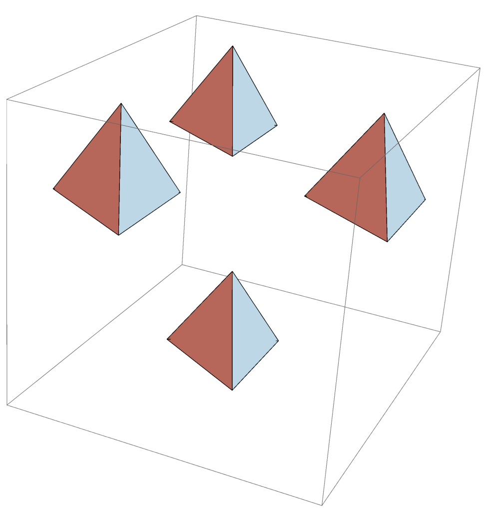

Figure 1. The pyrochlore lattice can be built up with a basis of four tetrahedra as seen in the side view here. We populate this lattice with Ising spins on the corners, pointing either in or out of each tetrahedron along the local axis pointing to the center.

After the initial discovery in $Dy_2Ti_2O_7$, missing entropy was also observed in several other pyrochlore-based Ising magnets. A not-too-recent specific heat measurement of $Dy_2Ti_2O_7$ by Pomaranski et al., however, found that this entropy is partially recovered when the sample is allowed to equilibrate over a timescale that reaches over 15 hours at the not-too-low temperature of 0.34K (3).

Thus, the putative spin ice state is at best a metastable configuration of the system of Ising spins on a pyrochlore lattice.

The existence of an ordered state was, indeed, predicted shortly after the initial, short time-scale, measurement of $Dy_2Ti_2O_7$ by two groups (4, 5). The nature of the spin configuration can be understood from the two figures shown here. First a simple argument from (4), considers a convenient decomposition of the pyrochlore lattice into a unit cell with a basis consisting of a tetrahedron of tetrahedra, as in Fig. 1. This figure displays only the “up” tetrahedra, the remaining “down” tetrahedra of the pyrochlore structure being defined in the process. The Ising spins on this lattice interact with the exchange and dipolar terms. By enumerating the 65,536 (i.e. 2^{16}) states of this cluster of spins, one can evaluate the total energy exactly. The ground state turns out to be 12-fold degenerate. One configuration is shown in Fig. 2, and the other 11 are related to this state by symmetry operations. These ground states satisfy the local Bernal-Fowler ice rules operative for each tetrahedron, namely having two spins pointing in and two spins pointing out. This configuration is extendable to the whole lattice (4), which thus acquires a long ranged ordered ground state, while satisfying the local ice rules on every tetrahedron. Thus, the true ground state of spin ice is only finitely degenerate, a situation that is far from the thermodynamically large degeneracy of Pauling’s model. Moreover, single spin flip simulations of this model tend to get stuck in one of the many locally ice-like but globally excited states of the Pauling manifold, suggesting that the experimental situation will consist of domains small enough to suppress rapid growth of long-range correlations but with inter-domain barriers that are eventually surmountable.

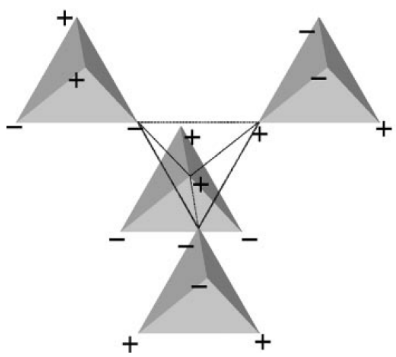

Figure 2. In the ground state (found originally by enumeration of clusters of 16 sites), each tetrahedron satisfies the Ice rules i.e. two spins point in and two point out, and yet the crystal has true long ranged order. The nature of the order is visualized in the top view here (from R. Siddharthan et. al, Phys. Rev. B63, 184412 (2001)).

It is of interest, therefore, to ask by what relaxation process do the spins ultimately reach their ordered configuration in the experiment by Pomoranski et al? One might suppose that generalized Orbach spin lattice processes come into play, these might be very slow indeed. If on the other hand this process involves quantum tunneling, then the “spin ice” compounds might be even more interesting than originally thought, and these results might provide a guide for complementary studies of water ice.

1) M.J. Harris, S.T. Bramwell, D.F. McMorrow, T. Zeiske, and K.W. Godfrey, *Phys. Rev. Lett*., **79**, 2554 (1997).

2) A. P. Ramirez, A. Hayashi, R.J. Cava, R. Siddharthan, and B.S. Shastry, *Nature*, **399**, 333 (1999).

3) D. Pomeransky, L.R. Yaraskavitch, S. Meng, K.A. Ross, H.M.L. Noad, H.A. Dabkowska, B.D. Gaulin, and J.B. Kycia, *Nat. Phys.*, **9**, 353 (2013)

4) R. Siddharthan, B.S. Shastry, and A.P. Ramirez, *Phys. Rev. B*, **63**, 184412 (2001)

5) R.G. Melko, B. C. den Hertoh, and M.J.P. Gingras, *Phys. Rev. Lett.*, **87**, 067203 (2001)