

Spin ice and other frustrated magnets on the pyrochlore lattice

B. Sriram Shastry

Indian Institute of Science, Bangalore 560042, India

Abstract

The recent identification of the dysprosium titanate compound $\text{Dy}_2\text{Ti}_2\text{O}_7$ as a “Spin ice”, i.e. the spin analog of regular entropic ice of Pauling, has created considerable excitement. The ability to manipulate spins using magnetic fields gives a unique advantage over regular ice in these systems, and has been used to study the recovery of entropy. Predicted magnetization plateaus have been observed, testing the underlying model consisting of a competition between short-ranged super exchange, and long-ranged dipolar interactions between spins. I discuss other compounds that are possibly spin ice like: $\text{Ho}_2\text{Ti}_2\text{O}_7$, and the two stannates $\text{Ho}_2\text{Sn}_2\text{O}_7$, $\text{Dy}_2\text{Sn}_2\text{O}_7$.

© 2003 Published by Elsevier Science B.V.

Keywords: Spin ice; Zero-point entropy; Ice rule; DTO

1. Introduction

The recent realization that $\text{Dy}_2\text{Ti}_2\text{O}_7$ (DTO) is a spin analog of regular (I_h) ice, has caused considerable excitement. Ice has fascinated several generations of physicists in view of its apparent violation of the third law of thermodynamics, by virtue of having an entropic ground state. The calorimetry experiment of Giauque and Stout [1] in 1936 was indeed one of the first triumphs of experimental low-temperature physics, and theory followed experiment rapidly. The model of Pauling explained the origin of the entropy, as arising from the rearrangements of protons on the two possible locations on each H–O–H bond, subject to the Bernal Fowler ice rule of two close protons and two far protons for each oxygen on the wurtzite structure. DTO not only provides a spin realization of the two-fold variable on each bond, it further gives one the handle of the Zeeman coupling between spins and the magnetic field, this energy reduces the degeneracy, and the expected entropy recovery have stimulated considerable activity in the community. In this talk I will give a quick review of the basic phenomena and discuss the modelling of the system. I will discuss the basic model that has been proposed by us, and tested against various experiments,

most sensitively the magnetization plateaus seen recently. I will also mention some unresolved issues, mainly the predicted long-ranged order in the true ground state that has evaded observation by neutron scattering. After summarizing the situation of some other candidates for spin ice behaviour, most notably holmium titanate and the stannates, I briefly discuss the dynamical susceptibility that has been used to probe the nature of precursor spin liquid, i.e. the state that the spin ice melts into, it appears to be nontrivial in its correlations.

2. Basic phenomenon and history

Early data [1] showed the surprising feature of entropy in the ground state, although crystallographic transitions prevented the cooling of I_h ice in the wurtzite structure to very low temperatures. Bernal and Fowler pointed out the importance of minimizing dipolar energy in the proximity of each oxygen by formulating the famous “ice rule”, i.e. the rule that two protons are close by and two are further from each oxygen so that there is a six-fold manifold of states that dominate the configuration space. Pauling made the connection with experiments by estimating the global entropy arising from these local ice rules—the configurations on a single

E-mail address: bss@physics.iisc.ernet.in (B.S. Shastry).

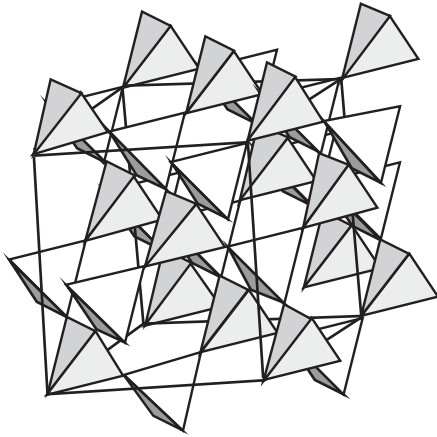


Fig. 1. The pyrochlore lattice.

oxygen influence the neighbours so there is a highly non-trivial many-body problem here. Pauling’s estimate of the ground-state entropy as $R \frac{1}{2} \log(\frac{3}{2})$ turns out to be an inspired approximation in that numerical computation of the entropy yield estimates that are close. In the world of models, this led to the celebrated two-dimensional ice model, where the combinatorial problem was solved exactly by Lieb [2] using *Bethe’s Ansatz*. Anderson [3] showed that the identity between the spinel B site sublattice and the wurtzite structure leads to an interesting connection with the configurational entropy in magnetite.

Harris et al. [4] showed in 1997 that the pyrochlore compound $\text{Ho}_2\text{Ti}_2\text{O}_7$ (HTO) (Fig. 1) could be considered as “spin ice” by noting the absence of LRO in neutron scattering and from μSR data. Moessner [5] emphasized the fact that ferromagnetism plus a non-collinear using type easy axis arrangement can lead to frustration, which is commonly associated with *anti-ferromagnetism*.

In a definitive experiment in 1999 Ramirez et al. [6] showed that the entropy of DTO has a shortfall from the expected $R \log(2)$ by an amount that is very close to the Pauling value, thus establishing it as the first clear spin ice system. In Fig. 2 we see that the entropy in zero-field powder DTO saturates nicely, and a finite field, as small as 0.5 T releases some of the entropy. We return to discuss the details of “entropy recovery” later.

The currently popular basic model to describe the spin ice system was formulated in Siddharthan et al. [7]. It consists of local ising variables pointing along or against the local easy axis found in each case by joining the sites to the centre of either of the two tetrahedra it belongs to. These local moments interact via the long-ranged magnetic dipole–dipole interaction in addition to the short-ranged superexchange interaction J , which provides the single parameter of the theory. The values of the local moment are large for DTO ($J = 15/2$ and $p =$

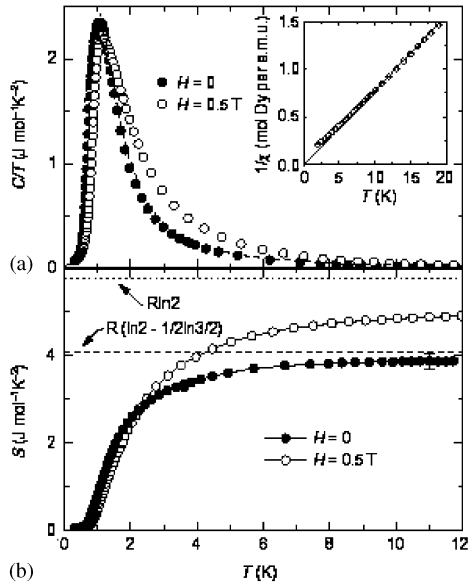


Fig. 2. The specific heat and integrated entropy from Ref. [6].

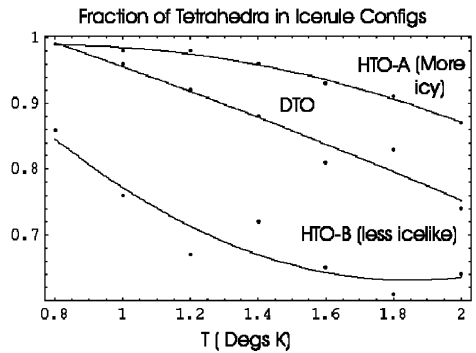


Fig. 3. The fraction of tetrahedra in ice ruled configurations for three values of superexchange $J = 1.9, 1.24, 0.52$ for curves from bottom up. The middle curve corresponds to DTO, and the other to two possible parameters for HTO.

$gJ\mu_B = 10\mu_B$) so the dipolar interaction energy is ~ 2.3 K for nearest neighbours. The dipolar interaction is long ranged but not a source of divergences in this problem, since all the interesting physics is away from zero momentum (i.e. ferromagnetic region). An interesting point is that the ice rule configurations are increasingly important at lower temperatures, in Fig. 3 we plot the fraction of tetrahedra in the ice rule configuration for three different values of J taken from a crude Monte Carlo sampling. It is in fact easy to see that the six configurations allowed by the ice rule possess a net magnetic moment that points along or antiparallel to the three crystallographic axes, so at low temperature one expects a renormalization of the effective moment by a factor of $\frac{2}{3}$, and hence the uniform susceptibility by

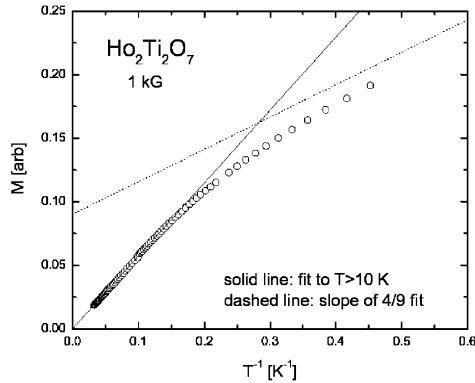


Fig. 4. The low-temperature susceptibility of HTO follows a Curie law but the Curie constant renormalizes to $\sim \frac{4}{9}$ below the ice rule scale of temperature.

$\frac{4}{9}$. Data from Lawes and Ramirez [10] on susceptibility is consistent with this expectation, as seen in Fig. 4.

The agreement between experiments and theory on specific heat is quite good with the basic model [7,8], and one can fine-tune the basic model by adding superexchange at further neighbour distance to improve the agreement further [9]. We note that the most stringent test is the behaviour of the magnetization versus magnetic field for different directions of the field. The prediction of Siddharthan et al. [11] of magnetization plateaux for fields along $\langle 111 \rangle$ direction represent the best test, since the plateau at ~ 1 T corresponds to some tetrahedra breaking the ice rule configurations, and going into a three-in one-out configuration. Recent experiments by Matsuhira et al. [12] bear out this prediction very well, as seen in Fig. 5. The onset of the second plateau is sharp at low temperatures, and can be used to *experimentally define the ice rule energy scale*. It should be regarded as the fingerprint of the ice rule physics. This scale arises from the competition between the (known) ferromagnetic dipolar energy and the (unknown) antiferromagnetic superexchange. In Fig. 6 we show the range over which the ice rule scale changes by changing the exchange J , this can be used (with linear extrapolation) to *deduce J* if we know the location of the plateau. The values of the magnetic moment at the first and second plateau are easy to understand, the saturation values are $\frac{1}{3}$ and $\frac{1}{2}$ of the maximum.

The problem of entropy recovery in the presence of a uniform magnetic field was alluded to earlier. While the first experiment on this in Ref. [6] was on powder samples, the Monte Carlo data [11] already gave indications of considerable fine structure in the specific heat depending upon the direction of the field relative to the symmetry axes. For example, a double peak structure was predicted for fields along $\langle 1, -1, \sqrt{2} \rangle$ direction which looks rather close to the double peak seen very recently in experiments [12].

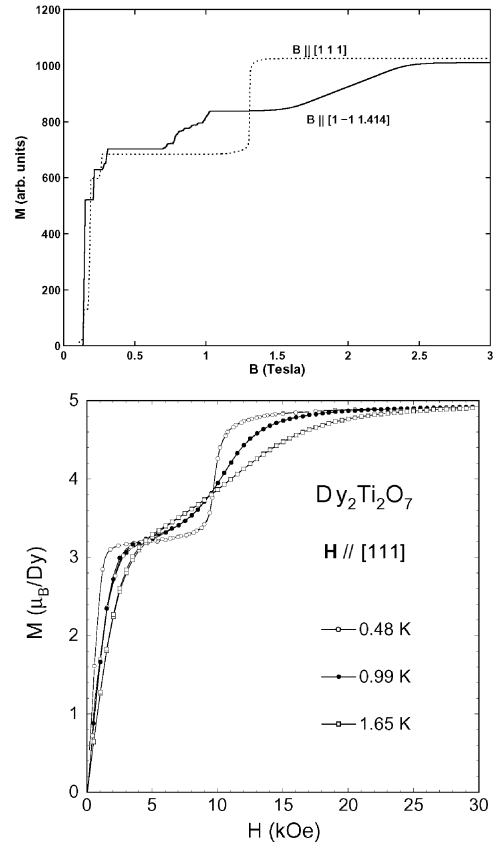


Fig. 5. Top is the theoretical prediction [11], the dotted curve should be compared with the one below from experiment [12].

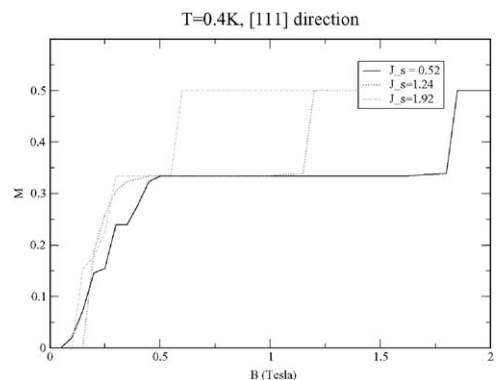


Fig. 6. Three values of J and the resulting range of the plateau. the values of J are 1.92, 1.24, 0.52 from left to right.

We next mention holmium titanate HTO, where Ho^{3+} has an identical magnetic moment as Dy^{3+} , and hence the same dipolar interaction, but possibly different exchange J . Initial experiments [6] showed a rising specific heat down at ~ 0.5 K, at which point the system

fell out of equilibrium. One can interpret this in one of two possible ways. It is imaginable [7,9,11] that the system undergoes a transition to a long-range ordered (LRO) state which is anyway predicted by theory (see below), and that the slow dynamics hides this transition. One has to then explain the difference between DTO and HTO as possibly arising from differences in the ice rule scale, or equivalently J , so that HTO would have a much lower ice rule temperature (hence larger $|J|$) whereas DTO with a higher ice rule temperature would be stuck in a subset of configurations that would prevent it from undergoing a transition to a state with lower free energy. The other view point [14] ascribes the difference in behaviour to the significant hyperfine coupling constants in HTO, as known from early work of Blote et al. [13]. Subtracting the nuclear component makes the data for HTO look similar to DTO, and the recent first principles calculations of the hyperfine constants of these two compounds [16] lend weight to this view point, as does the absence of LRO as indicated by neutron scattering [14,15] and other experiments at low temperatures ~ 50 mK.

Staying with the issue of LRO, we mention that even in the case of DTO one expects LRO at low enough temperatures. Siddharthan et al. [9,11] were the first to show, by explicit enumeration of ground states for finite clusters, that the model for DTO should have LRO of a certain type. This has been collaborated by Melko et al. [17], who use a loop algorithm to equilibrate the system rather than single spin flips, and find the same structure, with a transition at ~ 0.2 K. In contrast, neutron scattering [18] sees no signs of LRO down to low temperatures ~ 50 mK! Therefore it seems to me that DTO and possibly HTO may yet have a surprise in store at low temperatures.

Turning to other possible spin ice compounds, the stannates $M_2Sn_2O_7$ with $M = Dy, Ho$ have been recently proposed [19]. These have small differences in lattice constants, and hence slightly different dipolar as well as superexchange interactions, and should be useful in fixing several details of the models.

Finally on the topic of spin ice, I would like to mention two very recent and nice experiments on the AC susceptibility of DTO. Schiffer et al. [20] and Matsuhira et al. [21] have found that the Curie type divergence of the low field susceptibility (as in Fig. 4) is in fact cut off at a low temperature ~ 15 K that depends upon the frequency of the probe field, resulting in two maxima, one at a higher temperature ~ 18 K and the other at a lower temperature ~ 1.5 K. Each of these maxima is frequency dependent, and from the Arrhenius dependence of these we can extract a characteristic energy scale ϵ_c corresponding to these peaks. The higher one yields an energy scale ~ 220 K, very nearly the crystal field splitting seen in Ref. [7], and the lower one give

~ 10 K, presumably a multiple of the ice rule energy scale. The real as well as imaginary parts of the susceptibility show the same features, and these seem to be consistent above ~ 10 K with a dynamical susceptibility $\chi_0/(1 - i\omega\tau)^\alpha$, where $\chi_0 \sim 1/T$ and α departing from the Debye value of unity, and further being rather temperature dependent, with $\alpha \sim 0.544$ at 17 K and $d\alpha/dT \sim 0.06/K$. Thus the non Debye relaxation with temperature dependent α , and the origin of the relaxation rate $\tau \sim \tau_0 \exp(\epsilon_c/kT)$ demand a fundamental understanding that is missing at the moment.

Acknowledgements

It is a pleasure to acknowledge my collaborators: Art Ramirez and Gavin Lawes at Los Alamos National Lab, and Rahul Siddharthan at IISc/ENS Paris.

References

- [1] W.E. Giaque, J.W. Stout, *J. Chem. Phys.* 1 (1933) 515.
- [2] E.H. Lieb, *Phys. Rev. Lett.* 18 (1967) 1046.
- [3] P.W. Anderson, *Phys. Rev.* 102 (1956) 1008.
- [4] M.J. Harris, et al., *Phys. Rev. Lett.* 79 (1997) 2554.
- [5] R. Moessner, *Phys. Rev. B* 57 (1998) 5587.
- [6] A.P. Ramirez, A. Hayashi, R.J. Cava, R. Siddharthan, B.S. Shastry, *Nature* 399 (1999) 333.
- [7] R. Siddharthan, B.S. Shastry, A. Ramirez, A. Hayashi, R.J. Cava, S. Rosenkranz, *Phys. Rev. Lett.* 83 (1999) 1854.
- [8] B.C. den Hertog, M. Gingras, *Phys. Rev. Lett.* 84 (2000) 3430.
- [9] R. Siddharthan, Ph.D. Thesis, IISc Bangalore, July 2000.
- [10] G. Lawes, A. Ramirez, 2002, to be published.
- [11] R. Siddharthan, B.S. Shastry, A. Ramirez, *Phys. Rev. B* 63 (2001) 184412 cond-mat 0009265.
- [12] K. Matsuhira, Z. Hiroi, S. Takagi, T. Sakakibara, *J. Phys.: Condens. Mater.* 14 (2002) L559; H. Fukazawa, R.G. Melko, R. Higashinaka, Y. Maeno, M. Gingras, *Phys. Rev. B* 65 (2002) 054410.
- [13] H. Blote, R. Wielinga, W. Huiskamp, *Physica* 43 (1969) 549.
- [14] S. Bramwell, et al., *Phys. Rev. Lett.* 87 (2001) 47205.
- [15] H. Kadowaki, Y. Ishii, K. Matsuhira, Y. Hinatsu, *Phys. Rev. B* 65 (2002) 144421.
- [16] Y. Jana, D. Ghosh, *Phys. Rev. B* 61 (2000) 9657; Y. Jana, D. Ghosh, *J. Magn. Magn. Mater.* 248 (2002) 7.
- [17] R. Melko, B.C. den Hertog, M. Gingras, *Phys. Rev. Lett.* 87 (2001) 67203.
- [18] T. Fennell, et al., 2001, to be published, cond-mat 0107414.
- [19] K. Matsuhira, Y. Hinatsu, K. Tenya, T. Sakakibara, *J. Phys.: Condens. Mater.* 12 (2000) L649.
- [20] J. Snyder, J. Slusky, R. Cava, P. Schiffer, *Nature* 413 (2001) 48.
- [21] K. Matsuhira, Y. Hinatsu, T. Sakakibara, *J. Phys.: Condens. Mater.* 13 (2001) L737.