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**LETTER TO THE EDITOR**

# Frustration in Ising-type spin models on the pyrochlore lattice

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**Abstract.** We compare the behaviour of ferromagnetic and antiferromagnetic Ising-type spin models on the cubic pyrochlore lattice. With simple 'up–down' Ising spins, the antiferromagnet is highly frustrated and the ferromagnet is not. However, such spin symmetry cannot be realized on the pyrochlore lattice, since it requires a unique symmetry axis, which is incompatible with the cubic symmetry. The only two-state spin symmetry which *is* compatible is that with four local ⟨1 1 1⟩ anisotropy axes, which direct the spins to point in or out of the tetrahedral plaquettes of the pyrochlore lattice. We show how the local 'in–out' magnetic anisotropy reverses the roles of the ferro- and antiferromagnetic exchange couplings with regard to frustration, such that the ferromagnet is highly frustrated and the antiferromagnet is not. The in–out ferromagnet is a magnetic analogue of the ice model, which we have termed the 'spin ice model'. It is realized in the material $Ho_2Ti_2O_7$. The up–down antiferromagnet is also an analogue of the ice model, albeit a less direct one, as originally shown by Anderson. Combining these results shows that the up–down spin models map onto the in–out spin models with the opposite sign of the exchange coupling. We present Monte Carlo simulations of the susceptibility for each model, and discuss their relevance to experimental systems.

The pyrochlore lattice antiferromagnet is an enigmatic subject of current research [1]. Its tetrahedral geometry leads to intense frustration of the magnetic bonds, and a number of unusual effects which challenge our understanding of cooperative phenomena. Most notably, many pyrochlore compounds show spin-glass transitions in the apparent absence of chemical disorder. This is in direct contradiction to well established theory, and currently has no accepted explanation. In contrast, the pyrochlore lattice *ferromagnet* would seem at first sight unfrustrated and conventional. However, in a recent publication [2] we have shown that the pyrochlore material $Ho_2Ti_2O_7$ is geometically frustrated, even though the coupling between the magnetic $Ho^{3+}$ ions is *ferromagnetic*. In this letter we show, in detail, how local magnetic anisotropy reverses the roles of the ferro- and antiferromagnetic exchange couplings with regard to frustration, such that the ferromagnet is highly frustrated and the antiferromagnet is not.

The pyrochlore lattice (figure 1) consists of a corner-linked array of tetrahedral plaquettes. In figure 2 we show the ground states of a single tetrahedron of spins with various combinations of exchange coupling and axial anisotropy. Ising spins on a single plaquette are unfrustrated when the coupling is ferromagnetic (figure 2(a)), but fully frustrated when the coupling is antiferromagnetic (figure 2(b)). Thus the ferromagnet has a phase transition to a long-range ordered state at a temperature $T$ of the order of the exchange coupling $J$, while the antiferromagnet has no phase transition down to absolute zero [3]. The

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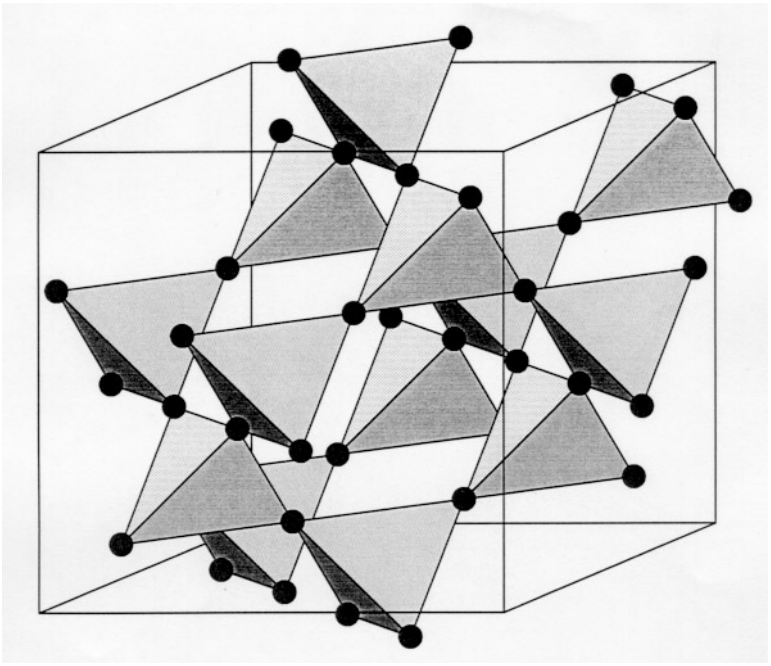

**Figure 1.** The cubic pyrochlore lattice.

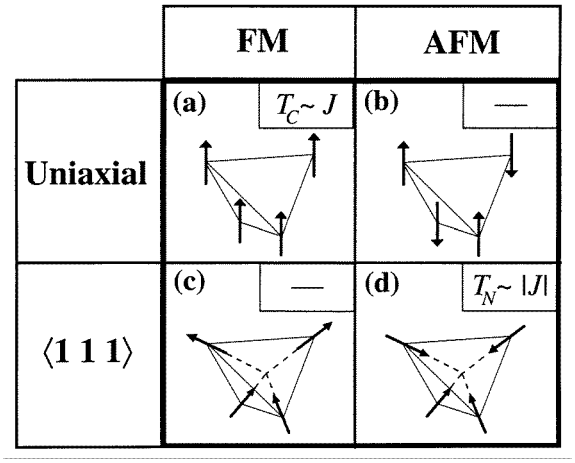


**Figure 2.** The ground states of a single tetrahedron of spins with various combinations of exchange coupling (FM = ferromagnetic, AFM = antiferromagnetic) and uniaxial or ⟨1 1 1⟩ Ising anisotropy. The ordering temperatures for each are shown in the inset boxes. Note that only the uniaxial ferromagnet and ⟨1 1 1⟩ antiferromagnet display transitions at finite temperature.

antiferromagnetic ground state of a single tetrahedron consists of two 'up' spins and two 'down' spins. There are an infinite number of ways in which such configurations can be arranged on the lattice, and so the ground state manifold is said to be macroscopically degenerate, with residual entropy at $T = 0$. Although Ising-like anisotropy is common in nature, the uniaxial anisotropy assumed in figures 2(a) and (b) is unphysical as it requires

a unique crystalline axis, which is not available in the cubic pyrochlore lattice. The only Ising-like anisotropy consistent with this symmetry is that in which the easy axes point along the cubic $\langle 1\,1\,1\rangle$-type directions into the centre of the tetrahedron. The antiferromagnetic ground state is now unique, consisting of alternate tetrahedra with four spins 'in' or four spins 'out' (figure 2(d)). This is the ordered spin structure observed in the pyrochlore $FeF_3$ [4]. The degeneracy is thus broken, and there is a phase transition into this state at $T \sim J$. However, with ferromagnetic coupling (figure 2(c)), the ground state of the tetrahedron has two spins 'in' and two spins 'out'. It is easily shown that these stack to form a disordered, macroscopically degenerate ground state, and we have verified by Monte Carlo simulation [5] that there is no ordering transition at any temperature. The pyrochlore with ferromagnetic coupling and $\langle 1\,1\,1\rangle$ anisotropy is thus much more strongly frustrated than the antiferromagnet with $\langle 1\,1\,1\rangle$ anisotropy. The ordering temperatures for each of the four combinations of exchange coupling and anisotropy (henceforth referred to as models (a)–(d)) are shown in figure 2.

A two-state antiferromagnetic model equivalent to model (b) was previously considered by Anderson [6], who showed that it maps onto the cubic ice model. The essence of Anderson's mapping is that spin states represent proton positions; however, there is no direct correspondence between spin *direction* and proton position. We show here that the ferromagnetic model (c) also maps onto the ice model, but in this case there *is* a direct correspondence between spin direction and proton position. Our mapping is thus rather more transparent than Anderson's and for this reason it is convenient to describe it first.

To see how the mapping works, we observe, following Anderson, that the cubic ice structure is generated by placing an oxygen atom at the centre of every elementary pyrochlore lattice tetrahedron. The vertices of every tetrahedron on the pyrochlore lattice lie at the mid-points of the oxygen–oxygen contacts. In the cubic ice structure, the hydrogen atoms are displaced from these mid-points so that every hydrogen–oxygen bond forms both a shorter covalent bond and a longer hydrogen bond with an oxygen. The displacement of each hydrogen atom from the mid-point of the oxygen–oxygen contact may be represented by an arrow, as shown in figure 3. The hydrogen ordering is then controlled by the Bernal–Fowler 'ice rules', which require that two arrows point into, and two out of, each tetrahedron, so that every oxygen atom has two adjacent hydrogens, forming a water molecule [7]. If the arrows are replaced by spins, one obtains exactly the frustrated ferromagnetic model (c); for simplicity we refer to this as 'spin ice'. It is formally a non-trivial case of the 16-vertex

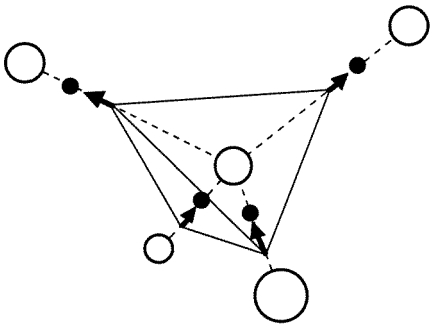

**Figure 3.** Local proton arrangement in ice, showing oxygen atoms (large white circles) and hydrogen atoms (small black circles), and with the displacement of the hydrogen atoms from the mid-points of the oxygen–oxygen bonds marked by arrows.

model of statistical mechanics [8], and reduces to the ice model at zero temperature. The ice model in three dimensions has a macroscopically degenerate *disordered* ground state, because the ice rules are insufficient to define long-range order (in the absence of an applied electric field) [7]. The model has been solved exactly in two dimensions, as has a non-trivial extension of it, the Baxter 8-vertex model, and these form two of the key exact results discovered in statistical mechanics in recent years [9]. They are well known to map onto ferromagnetic Ising models with 2- and 4-spin interactions; however these are physically unrealistic. We believe that the spin ice model is the first vertex model to be discovered that is physically realizable. One interesting feature of ice is that the hydrogen atoms effectively freeze at low temperatures (due to the large energy barriers associated with rearrangements), so that a disordered structure with very slow dynamics is formed. This is to some extent reminiscent of a spin glass. We note, however, that there are sixfold rings in the ice structure which allow hydrogen atoms to tunnel from one site to another in a closed loop without any cost in energy, as long as they do so simultaneously. Since this process is by necessity highly correlated and involves six atoms moving in concert, we imagine that it may be rather unlikely in general, and the dynamics will be controlled by large energy barriers. We note further that a similar argument will carry over to the pyrochlore lattice, which also contains sixfold rings of spins which can flip with zero energy cost.

Combining our mapping of spin ice (figure 2(c)) onto the ice model, with Anderson's mapping of the ice model onto the Ising antiferromagnet (figure 2(b)), shows that spin ice is effectively a realization of the latter. Anderson's mapping exploits the fact that the oxide lattice of cubic ice is bipartite, such that adjacent lattice sites belong to distinct but identical Bravais sublattices. An up spin (for example) then represents 'proton in' on one sublattice, and 'proton out' on the other; and vice-versa for a down spin. Thus, one finds that the up-down spins of model (b) are equivalent to the in–out spins of model (c), so long as the sign of the exchange coupling is reversed. There is obviously a similar correspondence between model (a) and model (d).

In order to explore the consequences of these diagonal mappings, we show, in figure 4,

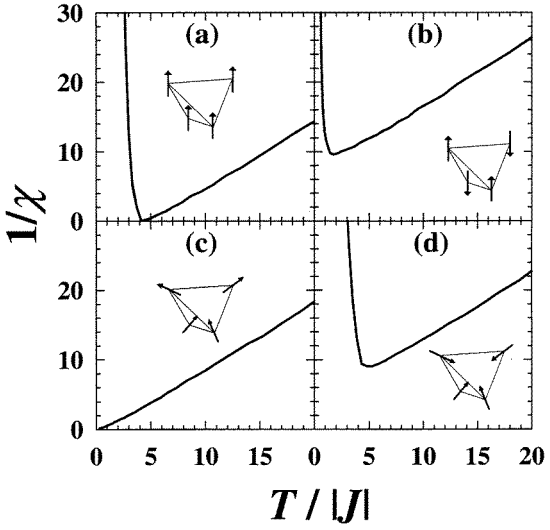


**Figure 4.** The inverse susceptibility, $1/\chi$, as a function of temperature for the four combinations of exchange coupling and anisotropy shown in figure 2.

the reciprocal susceptibility, $1/\chi$, versus temperature $T$ for each model, calculated by the Monte Carlo method [5]. The susceptibility is defined as $\chi = (\langle M^2 \rangle - \langle M \rangle^2)/T$, where $M$ is the magnetization per spin, and in order that a meaningful comparison can be made, the parameters $J$ and $S$ have been chosen so that each model has the same Curie–Weiss temperature and moment.

Referring to figure 4, a number of conclusions may be drawn. Firstly, the unfrustrated models (a) and (d) show evidence of the expected phase transition at $T/|J| = 4$. Model (a) shows behaviour typical of a conventional ferromagnet, in that the reciprocal susceptibility deviates only slightly from linear Curie–Weiss behaviour, before approaching zero at a finite temperature. The reciprocal susceptibility of the frustrated spin ice model, (c), in contrast, deviates strongly from Curie–Weiss behaviour below $T/J = 10$, and approaches zero only at $T = 0$. The divergence of the susceptibility at this point is reminiscent of the behaviour of a paramagnet, in that it reflects the presence of a significant number of magnetized states in the degenerate ground state manifold. These magnetized states may be selected by an applied field. The $q = 0$ state is the state most strongly selected, and the observation of such a field-induced ordering pattern in the material $Ho_2Ti_2O_7$ constitutes the main evidence that the latter material is a realization of spin ice [2]. Although one expects equivalent thermodynamics from the frustrated antiferromagnet, model (b), in this case there are no magnetized states in the ground state manifold, and consequently, the susceptibility does not diverge. The reciprocal susceptibility curve of model (b) in fact shows a distinct minimum at $T/|J| \approx 5$ which corresponds to the settling of the spins into their local ground states. The similarity of this feature to the ordering signatures of models (a) and (d) is most surprising, and suggests the intriguing possibility that the disordered ground state of model (b) may be accessed by a process which bears some similarity to a thermodynamic phase transition.

The diagonal relationships between the four magnetic models of figure 2 are the main result of this letter. They strictly apply to the case of two-state Ising-type spins, and are thus relevant to experimental systems such as $Ho_2Ti_2O_7$, in which the single-ion ground state is a doublet [2]. The relationships do not apply directly to a more general Heisenberg Hamiltonian with exchange coupling $J$ and anisotropy $D$, although Moessner [10] has recently proposed that they should be regarded as the first term in a perturbation expansion in the small parameter $(J/D)$. Recent experimental work has highlighted the fact that many oxide pyrochlores display spin glass transitions even when the level of defects is immeasurably small [11]. This suggests that the spin freezing transition is a more universal property of the pyrochlore Hamiltonian, rather than arising from a combination of frustration and chemical disorder, as has long been thought [12]. Our results suggest that at least one mechanism for spin freezing in pyrochlore magnets is the slow spin dynamics associated with Ising anisotropy along the cubic $\langle 1\,1\,1 \rangle$ axes. In the case of ferromagnetic coupling this is clearly a fundamental property of the spin ice model, but we believe that these results also carry over to the case of antiferromagnetic coupling. This is because of the large energy barriers between ground states which occur in the $\langle 1\,1\,1 \rangle$-axis Ising Hamiltonian, whatever the sign of the exchange coupling.

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## References

[1] Ramirez A P 1994 *Ann. Rev. Mater. Sci.* **24** 453

Schiffer P and Ramirez A P 1996 *Commun. Condens. Matter Phys.* **18** 21
Harris M J and Zinkin M P 1996 *Mod. Phys. Lett.* B **10** 417
[2] Harris M J, Bramwell S T, McMorrow D F, Zeiske T and Godfrey K W 1997 *Phys. Rev. Lett.* **79** 2554
[3] Liebmann R 1986 *Statistical Mechanics of Periodic Frustrated Ising Systems* (Berlin: Springer)
[4] Ferey G, de Pape R, Leblanc M and Pannetier J 1986 *Rev. Chim. Miner.* **23** 474
[5] Our calculations were carried out using the MCMAG Monte Carlo program developed by P Lacorre. The results shown correspond to a lattice of 432 spins, with 20 000 MCS/spin and 5000 equilibration steps.
[6] Anderson P W 1956 *Phys. Rev.* **102** 1008
[7] Pauling L 1960 *The Nature of the Chemical Bond* 3rd edn (Ithaca, NY: Cornell University Press) pp 465–8
[8] Lieb E H and Wu F Y 1972 *Phase Transitions and Critical Phenomena* ed C Domb and M S Green (New York: Academic) pp 332–490
[9] Baxter R J 1982 *Exactly Solved Models in Statistical Mechanics* (New York: Academic)
[10] Moessner R 1998 *Phys. Rev.* B at press
[11] Reimers J N, Greedan J E, Kremer R K, Gmelin E and Subramanian M A 1991 *Phys. Rev.* B **43** 3387
Greedan J E, Reimers J N, Stager C V and Penny S L 1991 *Phys. Rev.* B **43** 5682
Gaulin B D, Reimers J N, Mason T E, Greedan J E and Tun Z 1992 *Phys. Rev. Lett.* **69** 3244
Gingras M J P, Stager C V, Raju N P, Gaulin B D and Greedan J E 1997 *Phys. Rev. Lett.* **78** 947
[12] Fischer K H and Hertz J A 1991 *Spin Glasses* (Cambridge: Cambridge University Press)
Mydosh J A 1993 *Spin Glasses: An Experimental Introduction* (London: Taylor and Francis)