Relief and generation of frustration in pyrochlore magnets by single-ion anisotropy

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We show that a strongly anisotropic classical Heisenberg magnet on the pyrochlore lattice can be mapped onto an Ising model with an exchange constant of the opposite sign. This mapping can be applied to the recently discovered ''spin ice'' $Ho_2Ti_2O_7$ [Harris *et al.*, Phys. Rev. Lett. **79**, 2554 (1997)], a pyrochlore ferromagnet which—counterintuitively—is frustrated. We describe the implications of this mapping for the ordering properties of the magnets at low temperatures. Finally, we extend this discussion to the ordering properties of Heisenberg pyrochlore antiferromagnets of any anisotropy strength. [S0163-1829(98)50214-7]

I. INTRODUCTION

Both theoretical and experimental studies have found antiferromagnets on strongly geometrically frustrating lattices to display a number of effects which set them apart both from spin glasses and from conventional unfrustrated magnets.[1] In particular, they tend to have an unusually large number of degrees of freedom in the ground state, and the formation of a simple magnetically ordered state near the Curie-Weiss temperature is often prevented by the frustration: the magnets remain in a ''cooperative paramagnetic'' phase[2] down to much lower temperatures; most of them eventually freeze. These properties are particularly pronounced when the spins reside on a lattice consisting of corner-sharing triangles and tetrahedra.

A lattice on which the effects of frustration are especially severe is the pyrochlore lattice (Fig. 1), which is made up of a network of corner-sharing tetrahedra. An Ising antiferromagnet on this lattice has an extensive entropy at $T=0$,[3] while a pure Heisenberg antiferromagnet—which has an extensive number of degrees of freedom in the ground state[4]—has recently been shown to remain in a liquidlike state all the way down to zero temperature: there is a T-independent magnetic correlation length of only around two nearest-neighbor distances, and the dynamics slows down without freezing as T is lowered towards zero.[5]

The most recent surprise in this field was the experimental discovery by Harris *et al.* of frustration in the *ferromagnet* $Ho_2Ti_2O_7$.[6] They found no evidence of a magnetic ordering transition in neutron scattering and muon spin resonance experiments down to a temperature of 0.05 K, with the Curie-Weiss constant of the magnet being almost 40 times as large at 1.9 K. This is surprising since ferromagnets are generally considered to be intrinsically unfrustrated. Harris *et al.* ascribed the occurrence of frustration in this magnet to the presence of strong single-ion anisotropy, with an anisotropy constant D, determined to be roughly -50 K, whereas J is only around -1 K. The easy axes are directed towards the center of the tetrahedron on the corner of which the spin is located. They showed that the ferromagnetic model maps onto the ice model, the ground states of which are characterized by two spins pointing into and two out of each tetrahedron,[6] and named this magnet spin ice, due to the similarity of these rules to the ice rules of proton ordering.[7] Bramwell and Harris independently pointed out the relationship with the antiferromagnetic model.[8]

In this paper, we show that such a strongly anisotropic classical Heisenberg model on the pyrochlore lattice can be mapped onto an Ising pseudospin model. Since the anisotropy directions are not collinear, it turns out that the exchange constant of the Ising model is opposite in sign to that of the Heisenberg model—which explains how a ferromagnet can be frustrated. We then discuss the properties of these magnets which can be deduced from this new description. Finally, we address the ordering properties of Heisenberg antiferromagnets for any anisotropy strength.

II. THE MAPPING

The Hamiltonian for a classical Heisenberg magnet with easy axis anisotropy is given by

$$H=\frac{D}{2}\sum_{K,\kappa}(\hat{\mathbf{d}}_\kappa\cdot\mathbf{S}_{K,\kappa})^2+J\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j\,. \tag{2.1}$$

Here, J is the exchange constant (bond energy), with $J<0$ for a ferromagnet. $D<0$ is the strength of the easy axis anisotropy. The easy axes are specified by the unit vectors $\hat{\mathbf{d}}_\kappa$. κ runs from 1 to 4 as there are four easy axes directions, one for each corner of the tetrahedron. These easy axes, which point from the center of the tetrahedron to the corner on which the spin is located, are the $\langle 111\rangle$ directions. $\mathbf{S}_{K,\kappa}$ de-

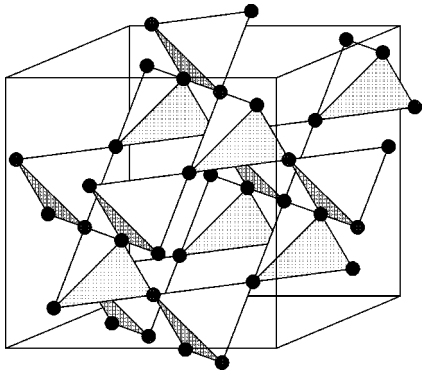

FIG. 1. The pyrochlore lattice, consisting of two interpenetrating face-centered-cubic sublattices of tetrahedra.

notes the spin on the corner labeled by κ of the tetrahedron labeled by K. The summation $\langle i,j\rangle$ runs over nearest-neighbor bonds only. Each spin belongs to two tetrahedra, and therefore the first term includes a factor of 1/2. These two tetrahedra, which belong to two different sublattices (Fig. 1), are inequivalent, and we label them type A and B in the following.

The mapping proceeds as follows. For strong anisotropy, $|J/D|\ll 1$, so that the first term fixes the spins to point along the easy axes at temperatures below $|D|$. The second term can then be treated as a perturbation, which determines the direction of the spins along their easy axes.

From the relative orientations of the axes it follows that the spins can only enclose two angles, α_+ and α_-, with $\cos\alpha_+ = 1/3$ and $\cos\alpha_- = -1/3$. Therefore, $\alpha_+ = 70.5°$ and $\alpha_- = 109.5°$. This means that a pair of spins can have two different energies: $E_+ = J/3$ or $E_- = -J/3$. If we assign Ising pseudospin variables T_i to the spins $\mathbf{S}_i$, choosing $T=1$ for a spin pointing out of a tetrahedron of type A (and therefore into one of type B) and $T=-1$ for a spin pointing inwards, we obtain the Hamiltonian (N being the total number of spins in the system)

$$H = DN - \frac{J}{3}\sum_{\langle i,j\rangle} T_i T_j . \tag{2.2}$$

The first term in Eq. (2.2) is a constant, which can be ignored. The crucial feature of the new Hamiltonian is that the sign of the exchange interaction has changed: a ferromagnetic Hamiltonian becomes an antiferromagnetic one and vice versa. In addition, the anisotropy turns a Heisenberg model into an Ising model.

Note that the Ising spins are pseudospins. The directions of their axes in pseudospin space are not constrained by the symmetry of the crystal to be along the $\langle 111\rangle$ directions.

The fact that the Heisenberg magnet is best described by an Ising model with an exchange constant of opposite sign opens up unusual ways of probing the Ising model experimentally. For example, as described below, the ground states minimize the total pseudospin per tetrahedron for the Heisenberg ferromagnet and maximize it for the antiferromagnet. Magnetic fields and neutrons, of course, couple to the real spin, for which the converse is true: different ground states of the antiferromagnetic Ising model can have different net magnetic moments.

III. THE FRUSTRATED FERROMAGNET

For the anisotropic ferromagnet, the ground states follow from those of the antiferromagnetic Ising model on the pyrochlore lattice:[3,9] the system can minimize its energy by maximizing the number of pairs of spins on each tetrahedron with one spin pointing in and one out. We see that there is no way of making all the pairs satisfy this condition: the ferromagnet is frustrated. A ground state, displayed in Fig. 2 for a single tetrahedron, has two spins pointing into and two out of every tetrahedron, which corresponds to zero net pseudospin. There is an infinite number of such ground states—in fact, the system has a finite entropy per spin down to $T=0$.[3] It does not order at any finite temperature, as was indeed found

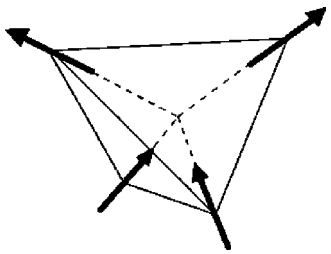

FIG. 2. A ground-state spin configuration for a single tetrahedron with ferromagnetic interactions and strong single-ion anisotropy. For an antiferromagnet, the spins point either all in- or all outwards. The dashed lines are the easy axes.

experimentally and as a theoretical consequence of the ice model by Harris *et al.*

The parameters for the experimental system $Ho_2Ti_2O_7$ yield $|J/D|\sim 1/50\ll 1$. Moreover, due to the large magnetic moment of the Ho^{3+} ions, the assumption of classical spins is well satisfied. Our Ising Hamiltonian therefore represents an accurate description of the experimental system. The main weakness of the model is the omission of dipolar interactions, which may be significant due to the combination of a small exchange constant and a high magnetic moment.

In addition, even small perturbations can act to lift the large ground-state degeneracy. Experimentally, a small magnetic field was found to induce long-range magnetic order. This is due to the fact that each tetrahedron—despite the sum of its pseudospins being zero—has a net magnetic moment along a $\langle 100\rangle$ direction, so that the zero-field ground states with a maximal projection of these magnetic moments along the field direction are selected by the field.[6]

The dynamics is the potentially most interesting aspect of this magnet. Unlike in the case of the Heisenberg pyrochlore antiferromagnet,[5] the ground states of the frustrated ferromagnet are separated by large energy barriers. In the absence of quantum tunneling, and with thermal tunneling between ground states exponentially suppressed for temperatures below $|D|$, the dynamics of the magnet is found to display a rich variety of freezing properties[6] the discussion of which lies beyond the scope of the work presented here.

IV. THE RELIEVED ANTIFERROMAGNET

Another important consequence of the mapping presented above is that strong anisotropy in a pyrochlore Heisenberg antiferromagnet relieves frustration: once the dominant term in the Hamiltonian is satisfied, the exchange is described by a ferromagnetic Ising model, which is not frustrated. Of course, the geometric frustration of the antiferromagnetic interactions cannot actually be removed, but the anisotropy lifts the internal ground-state degeneracy resulting from the frustration completely so that the resulting system appears unfrustrated.

Indeed, this result holds for *all* values of the anisotropy, even when $|J/D|$ is not small. There is a state which separately minimizes the anisotropy energy and the antiferromagnetic exchange term in the Hamiltonian. This state is described by long-range order in the pseudospin variables: $T_i \equiv 1$. In this state, all spins point into the tetrahedra of type A and out of those of type B—or vice versa.

Such a state has been known for a long time to occur in the pyrochlore antiferromagnet FeF_3, which is one of the few antiferromagnets on this lattice which exhibit long-range order.[10,11] However, the anisotropy in this magnet, estimated at $E_{\rm anis}<0.1$ K,[12] is too weak to account for an ordering temperature around 15 K. In fact, in Monte Carlo simulations, we have verified that ordering for $|D/J|\ll 1$ occurs at an ordering temperature T_c, proportional to D, around $|T_c/D|\simeq 0.5$. Reimers and co-workers[4,11] have proposed that four-sublattice long-range order arises from ferromagnetic third-nearest-neighbor interactions. The resulting ground state has two internal and three global degrees of freedom; the weak anisotropy can then induce the $T_i\equiv 1$ state by acting as a symmetry-breaking field.

It would appear that the dynamics of such a relieved antiferromagnet should be simply described by spin-wave excitations around the unique long-range ordered state at low temperatures. For large $|D/J|$, however, this is not the case. If the system is cooled down quickly or in an applied magnetic field to the magnetic ordering temperature, which is of order J, it will be trapped in a metastable state, at $T\sim|D|$, which is separated from the ground state by large energy barriers. For this reason, Bramwell and Harris predict spin freezing to be present nonetheless.[8]

By contrast, for small $|D/J|$, freezing does not occur because of the nature of the ground state of the isotropic Heisenberg antiferromagnet: long-range correlations are absent, and there are neither internal nor free energy barriers which the system has to surmount as the temperature is lowered through J down to the ordering temperature below $|D|$.[5] This rules out weak anisotropy on its own as the origin of the glassiness observed in almost disorder-free Heisenberg antiferromagnets.[13,14]

In summary, we have presented a mechanism whereby single-ion anisotropy can generate and relieve geometric frustration. Our discussion has concentrated on the special properties which follow from the simultaneous change in sign of the magnetic interaction and the mutation of the nature of the spin. The most interesting open questions arising from this mapping are those relating to the dynamics of such anisotropic magnets. Due to the high energy barriers erected by the strong anisotropy between the large number of states which are very close in energy, the low-temperature dynamics of both ferro- and antiferromagnet is rather unconventional, as was indeed observed in the original experiments on $Ho_2Ti_2O_7$.[6]

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