Liquid-Gas Critical Behavior in a Frustrated Pyrochlore Ferromagnet

M. J. Harris,[1] S. T. Bramwell,[2] P. C. W. Holdsworth,[3] and J. D. M. Champion[1,2,3]
[1]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, United Kingdom*
[2]*Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom*
[3]*Laboratoire de Physique, Ecole Normale Supérieure, 46 Allée d'Italie, F-69364, Lyon Cedex 07, France*
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The newly discovered frustrated pyrochlore ferromagnet ("spin ice") is investigated using Monte Carlo simulations. The ground state is disordered and infinitely degenerate, but in an applied magnetic field the degeneracy is broken and ordering can occur. We find that the degree of degeneracy breaking is highly dependent on the field direction, and one direction in particular leads to a complete and spontaneous lifting of the degeneracy. We show that this occurs via a new type of magnetic phase transition that does not involve a change in symmetry, and is related to the liquid-gas transition. These results are relevant to a wide number of pyrochlore compounds. [S0031-9007(98)07616-9]

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The pyrochlore lattice [Fig. 1(a)] represents a model system in statistical physics for probing the effects of strongly competing interactions. In geometrical terms, it presents the strongest frustration possible for any known lattice with *antiferromagnetic* interactions [1], but a surprising recent discovery is that *ferromagnetic* interactions can also experience strong frustration [2,3]. This cannot occur with Heisenberg spins, but only when there is strong single-ion anisotropy along the $\langle 1\,1\,1\rangle$ axes of the pyrochlore lattice. In particular, when the anisotropy is infinite (corresponding to pure Ising anisotropy), no magnetic order can form on the lattice right down to 0 K [3].

In Fig. 1(b), we show the ground state of a single tetrahedron of spins with ferromagnetic coupling and local Ising anisotropy along the $\langle 1\,1\,1\rangle$ axes, which connect each spin with the center of the tetrahedron. The ground state is characterized by the simple arrangement of two spins "in" and two spins "out." Topologically, it is identical to the problem of cation ordering on the pyrochlore lattice considered by Anderson [4], which can be mapped directly onto the problem of proton ordering on the cubic ice lattice. Pauling [5] showed that the ground state of ice is composed of a macroscopic number of degenerate states, and is thus geometrically frustrated. For ease of reference, the frustrated pyrochlore ferromagnet is thus referred to as the "spin ice" model [2].

It can also be shown [4] that the uniaxial Ising pyrochlore antiferromagnet maps onto the ice model, and so must in turn map onto the spin ice model [3]. Both pyrochlores therefore exhibit a macroscopic ground-state degeneracy at all temperatures down to 0 K. A direct mapping between the spin ice model and the Ising antiferromagnet has recently been obtained [6] without resort to the ice model. However, we shall continue to discuss the frustrated ferromagnet with reference to it, since the literature on ice reveals some further interesting features which may not have been anticipated simply by considering the spin models.

The first point is that the protons in the ice ground state are effectively frozen due to the large energy barriers associated with rearrangements [7]. These slow dynamics translate directly to the spin ice model, resulting in spin freezing reminiscent of a spin glass but without the chemical disorder that is usually thought to be a necessary component of the spin-glass state. The second interesting property of ice that we shall mention in passing is that its ground-state degeneracy is lifted by doping with small

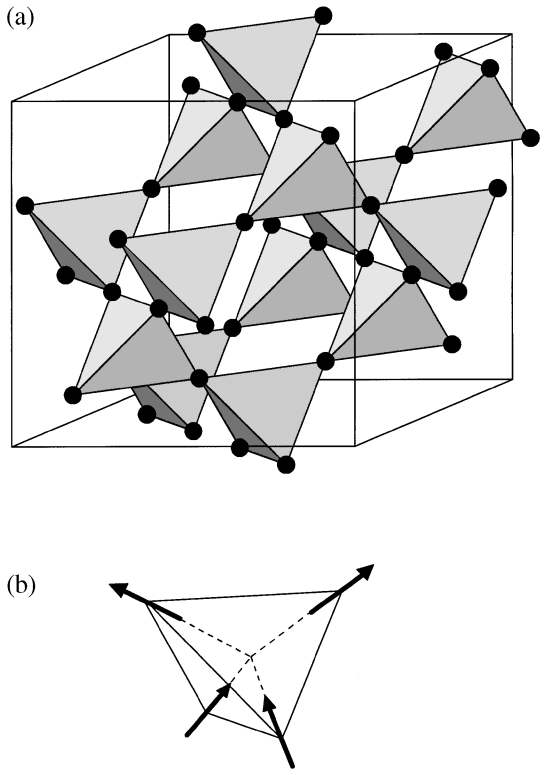

FIG. 1. (a) A schematic plot of the pyrochlore lattice. The spots show the positions of the magnetic ions. (b) The ground state of a single tetrahedron of spins with ferromagnetic exchange and local Ising anisotropy.

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amounts of alkali cations. This breaks the ice rules locally so that ferroelectric order can occur [8]. We thus expect that, by doping spin ice with nonmagnetic ions, long-range order may be stabilized.

While this model is amusing from a conceptual point of view, it is also of immense practical value, because a large number of pyrochlore oxides contain single-ion anisotropy associated with the $\langle 1\,1\,1\rangle$ axes of the lattice. This is especially true where the magnetic ion is a rare earth with a large orbital moment, such as in $Ho_2Ti_2O_7$ [2], $Dy_2Ti_2O_7$, and $Yb_2Ti_2O_7$ [9], which are known to offer good realizations of the spin ice model. Other prominent examples are a number of pyrochlore manganates such as $Y_2Mn_2O_7$, $Sc_2Mn_2O_7$, and $Lu_2Mn_2O_7$, which exhibit the latterly mysterious property that, while the exchange is strongly ferromagnetic, transitions to spin-glass rather than ordered phases are observed [10].

In this Letter, we present an exploration of the properties of the spin ice model using Monte Carlo simulations, paying particular attention to those accessible to experiment. We find that, while no magnetic order occurs in zero magnetic field, ordered phases occur when a field is applied, consistent with experimental work on $Ho_2Ti_2O_7$ [2]. But the most important result is our discovery of a new type of magnetic phase transition, analogous to that in a fluid system.

A classical Ising Hamiltonian was used in the Monte Carlo calculations:

$$\mathcal{H} = -\frac{1}{2} J \sum_{i,j} \mathbf{S}_i^{\mathbf{z}_i} \cdot \mathbf{S}_j^{\mathbf{z}_j} - \sum_i \mathbf{H} \cdot \mathbf{S}_i^{\mathbf{z}_i}, \qquad (1)$$

where the first summation is over nearest neighbors, $\mathbf{H}$ is the magnetic field, and $\mathbf{S}_i^{\mathbf{z}_i}$ is the spin on the ith magnetic ion, which has its own Ising axis denoted $\mathbf{z}_i$. There are four distinct Ising axes (one for each site on the basic tetrahedron) directed along the $\langle 1\,1\,1\rangle$ directions towards the center of each tetrahedron.

The Monte Carlo calculations were carried out using the MCMAG program [11], which utilizes the standard Metropolis spin-flipping algorithm. To collect thermodynamic data, a lattice size of $10 \times 10 \times 10$ cubic unit cells was used, with a total number of spins $N = 16\,000$. The simulation lengths were generally 10^5 Monte Carlo steps per spin (MCS/spin), including 2×10^4 equilibration steps. This was found to be sufficient to achieve equilibration for all temperatures considered here: some longer simulations with 10^6 MCS/spin and 10^5 equilibration steps were performed as a consistency check, and no significant differences were observed with the shorter simulations.

In zero magnetic field, no transitions were observed to ordered states at any temperature, consistent with both the ice mapping and experimental work on $Ho_2Ti_2O_7$ [2]. However, novel behavior is revealed when a magnetic field is applied. In Fig. 2 we show the magnetization per spin calculated when a field is applied along the three symmetry directions: [1 0 0], [1 1 0], and [1 1 1]. These

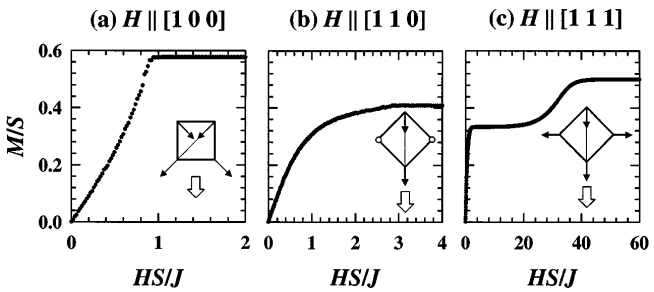

FIG. 2. The magnetization, M, per spin for the spin ice model, calculated at a temperature of $T/J = 0.1$, with a magnetic field, H, applied along the three symmetry directions of the pyrochlore lattice: (a) [1 0 0], (b) [1 1 0], and (c) [1 1 1]. Beneath each magnetization curve is shown a view of a single tetrahedron of spins looking down its 4_1 axis, thus appearing as a square in projection. The black arrows represent the projections of spins ordered by the maximum field applied in each case, while the open circles represent spins unaffected by the field and thus disordered. The white arrows show the projections of the field directions.

directions correspond to the 4_1, 2, and $\bar{3}$ symmetry axes, respectively, of the pyrochlore space group, $Fd\bar{3}m$. Note that the magnetic field is given in dimensionless units of HS/J. It can be seen in each case 2(a)–2(c) that the application of a field results in the selection of magnetic order from the macroscopically degenerate ground state, such that there is a component of magnetization along the field direction. What is interesting is that the degree of degeneracy breaking is strongly dependent on the direction along which the field is applied. This becomes clear when we study the schematic diagrams in Fig. 2 showing a single tetrahedron of spins with the full field applied along [1 0 0], [1 1 0], and [1 1 1]. Note that the tetrahedron is shown in projection as a square. In case 2(a), when the field is applied along [1 0 0], all four spins on the basic tetrahedron order so that each has a component of magnetization along the field direction, and the degeneracy is completely broken. The saturated magnetization per spin is $3^{-1/2} \approx 0.578$, which is the theoretical maximum for this field direction. The structure formed is the $q = 0$ structure observed in $Ho_2Ti_2O_7$ [2]. In case 2(b), when the field is applied along [1 1 0], we see that the local Ising axes for two out of the four spins are perpendicular to the applied field, so that they cannot order at all. The only spins that *can* order are those two that have anisotropy axes with a component along the field direction. The maximum net magnetization per spin is now $6^{-1/2} \approx 0.408$. We emphasize that the two-spins-in, two-spins-out rule is preserved in cases 2(a) and 2(b). More complex behavior is seen in 2(c), where the field is applied along the [1 1 1] axis. Here, we find that, since there is one spin on each tetrahedron with its anisotropy axis parallel to the field, this spin orders first, the other three remaining only partially ordered until the field is strong enough to overcome the exchange. At this point the two-spins-in, two-spins-out

rule can be broken, so that an ordered arrangement of one spin in, three spins out occurs, as shown in the figure. The saturated magnetization per spin is now $\frac{1}{2}$, and the degeneracy breaking is a *two-stage process*.

Figure 2(a) gives a hint of our most important result, which is that the degeneracy breaking for fields along the [1 0 0] direction occurs via a cooperative phase transition. The magnetization has a positive curvature until a field of $HS/J = 0.9$ is reached, where there is an abrupt change to full, saturated order. This behavior is characteristic of a field-induced phase transition, in complete contrast to the behavior of a paramagnet, even though in both cases the degeneracy is completely broken by the field. There is an interesting system-size effect: for small system sizes ($N \leq 16$), the magnetization curve has a *negative* curvature for all H, like that of a paramagnet, while, for $N \geq 128$, it has a positive curvature until saturation, and is almost independent of the system size. This suggests that the phase transition is controlled by very short-ranged fluctuations, with a correlation length of the order of only one unit cell ($N = 16$). They are therefore not *critical* fluctuations, in the sense of a second-order phase transition.

In Fig. 3, we show the heat capacity, c_H, obtained on cooling in several different magnetic fields applied along the [1 0 0] direction. The curves are characterized by a broad peak, or Schottky anomaly, at $T/J = 0.25$, which can be seen most clearly in the zero-field result ($HS/J = 0$). This reflects isolated spin flips. In finite small fields ($HS/J < 1.5$), a sharp spike appears at lower temperatures to the Schottky anomaly, marking the cooperative phase transition. As the field is increased, so the phase transition temperature increases, and the spike becomes less pronounced. For $HS/J > 1.5$ the spike disappears completely and is replaced by a broad feature that merges with—but is considerably stronger than—the Schottky anomaly. A clear change in behavior has occurred: the spike in c_H indicates a *first-order* phase transition, which changes into a continuous ordering process for $HS/J > 1.5$.

In Fig. 4 we show the phase diagram for fields applied along the [1 0 0] direction, obtained from the behavior of c_H. We find a line of first-order phase transitions separating two phases with the same symmetry but different magnetization. The line terminates at a temperature of $T_c/J \approx 0.16$, and at all higher temperatures the system can move continuously from one state to another without going through a phase transition, as shown by the dashed path. This marks a critical point. Ignoring the trivial time-reversal symmetry of the magnetic field, Fig. 4 is identical to the pressure-temperature phase diagram of a liquid-gas system. In this case, when $T < T_c$, the order parameter is $\langle \phi \rangle = \rho_L - \rho_G$, where ρ_L and ρ_G are the densities of the liquid and gas phases, respectively. By analogy, the order parameter in spin ice is $\langle \phi \rangle = m_L - m_G$, where m_L and m_G are the magnetizations of the phases above and below the critical line, respectively. In the inset of Fig. 3, we show the order parameter $\langle \phi \rangle$ obtained on heating in a field of $HS/J = 0.1$, with a clear first-order jump marking the phase transition at $T/J \approx 0.015$.

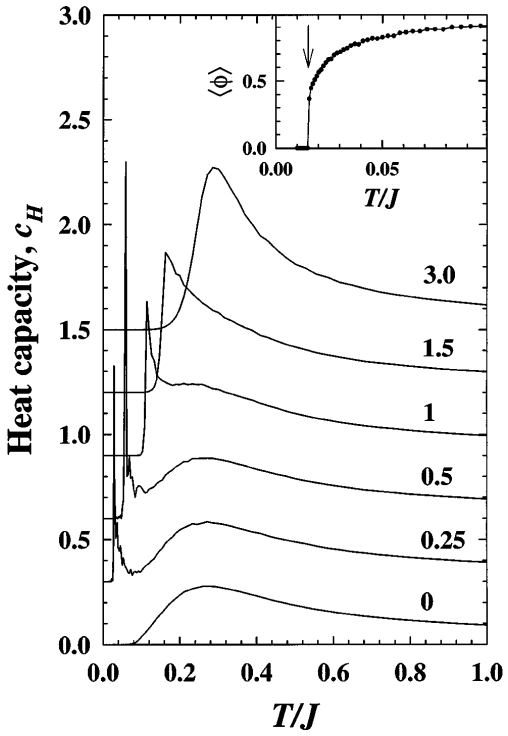

FIG. 3. The heat capacity at constant field, c_H, calculated with various fields applied along the [1 0 0] direction. The inset shows the order parameter, $\langle \phi \rangle$, calculated with $HS/J = 0.1$. The arrow indicates the first-order jump at the transition temperature.

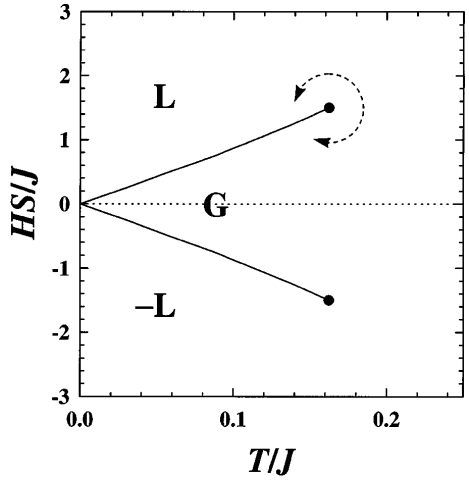

FIG. 4. The phase diagram for the spin ice model with the magnetic field applied along the [1 0 0] direction. The full line shows the line of field-induced first-order phase transitions, terminating in a critical point at $T_c/J \approx 0.16$. The letters "L" and "G" refer to the "liquid" and "gas" phases, respectively. The dashed path shows a way of converting from one state to another continuously.

The phase diagram of the conventional Ising ferromagnet contains a line of first-order phase transitions along the $H = 0$ line, terminating at a critical point. The phases above and below the line of transitions represent phases with magnetization up and down, respectively. The analogy typically made between the liquid-gas transition and the magnetic transition is then purely one of symmetry: the two magnetization directions represent the two fluid phases, with magnetization up the liquid, and magnetization down the gas [12]. In our case, the analogy is much more physical, with the scalar value of the magnetization mapping directly onto the fluid density. As in the fluid system, the symmetry breaking is between the low and high density (magnetization) configurations of phase space. We have two phases, one with high entropy and high enthalpy for fields below the coexistence line, and the other with low entropy and low enthalpy above it. But both have broken magnetic symmetry, i.e., a finite magnetization. The analogy breaks down when we consider the dynamics, since our model is essentially discrete and cannot have liquidlike dynamics, in spite of its macroscopic ground-state degeneracy. This is in marked contrast to the case of the Heisenberg antiferromagnet on the pyrochlore lattice, which was recently shown to be a classical "spin liquid" [13]. Instead, the analogy between our spin ice model and a fluid system is purely thermodynamic.

One might be tempted to ask why the [1 0 0] direction is so special, since fields applied along the other two symmetry axes do not result in a thermodynamic phase transition. The [1 0 0] field direction is unique because symmetry is broken completely: a single state is selected from an infinitely degenerate manifold, and the system transforms from a state of high entropy to a state of zero entropy. At temperatures above the Schottky anomaly there is sufficient thermal energy for this process to be continuous, while, below the Schottky anomaly, spin flips are exponentially unlikely, and the process is discontinuous. The possibility of a phase transition between two magnetic states with the same symmetry has been predicted from general Landau theory arguments [14], and we believe that our work is the first realization of such a phase transition. The up-down symmetry is maintained by reversing the magnetic field and each half of the phase diagram is directly analogous to the liquid-gas phase transition. The point at $T = H = 0$ in Fig. 4 is thus a triple point.

In conclusion, the predictions of this paper are eminently suitable for experimental tests using any one of a number of rare earth pyrochlores. Since the magnetic moments of rare earth ions such as Ho^{3+} are large, the critical point should be accessible using a relatively small magnetic field, probably less than 1 T in magnitude. The downside of using ions with such large magnetic moments is that dipolar coupling and demagnetization effects due to sample shape will be important. For example, very complex behavior was observed in the recent neutron scattering study of $Ho_2Ti_2O_7$ [2], part of which was due to these effects, although the overall features were consistent with the spin ice model.

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