Geometrical Frustration in the Ferromagnetic Pyrochlore $Ho_2Ti_2O_7$

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We report a detailed study of the pyrochlore $Ho_2Ti_2O_7$, in which the magnetic ions (Ho^{3+}) are ferromagnetically coupled with $J \sim 1$ K. We show that the presence of local Ising anisotropy leads to a geometrically frustrated ground state, preventing long-range magnetic order down to at least 0.05 K. However, unlike in the case of a frustrated *antiferromagnet*, this disorder is principally static. In a magnetic field, the ground-state degeneracy is broken and ordered magnetic phases are formed which display an unusual history dependence due to the slow dynamics of the system. These results represent the first experimental evidence for geometrical frustration in a *ferromagnetic* system. [S0031-9007(97)04147-1]

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The concept of a macroscopically degenerate ground state was first introduced by Pauling [1] to describe the proton disorder in ice. There are now a number of model magnetic systems on simple lattices that have disordered, macroscopically degenerate ground states. These all contain antiferromagnetic interactions that are frustrated by the geometry of the lattice. A well-known example is the pyrochlore lattice, where the frustration arises from the fact that the spins occupy the vertices of a network of linked tetrahedra, and no spin configuration exists that simultaneously satisfies all of the interactions between the spins [2]. The antiferromagnetic Heisenberg model on this lattice is expected to form a fluctuating "spin liquid" state at low temperatures.

At first sight, it would appear obvious that geometrical frustration cannot occur when the interactions are purely ferromagnetic, since the geometry of the lattice alone cannot cause frustration. However, we have discovered that this conclusion is untrue, and that, in certain cases, strong frustration can arise through the combination of ferromagnetic coupling and single-ion anisotropy. We consider a ferromagnetic pyrochlore with Ising anisotropy directed along the ⟨111⟩-type directions, which connect a spin with the center of its tetrahedron. The ground state of such a single tetrahedron of spins is shown in Fig. 1(a), which is characterized by the simple arrangement of two spins "in" and two spins "out." The pyrochlore lattice may be mapped directly onto the ice lattice [3], and our "two in, two out" condition is then identical to the "ice rule" which controls the proton ordering [1,4]. Our ground state is therefore expected to be highly degenerate like that of ice, so that it is disordered right down to 0 K. However, unlike the dynamic disorder that occurs in an antiferromagnetic spin liquid, this disorder is purely static. For ease of discussion, we refer to the above model of a ferromagnetic pyrochlore with local Ising anisotropy as the "spin ice model."

In the course of a systematic study of rare earth titanate pyrochlores, we have discovered that $Ho_2Ti_2O_7$ (with space group $Fd\bar{3}m$) approximates well to the spin ice model. $Ho_2Ti_2O_7$ is an insulator, and only the Ho^{3+} ions are magnetic, occupying the trigonal 16*c* sites which form a pyrochlore lattice. The crystal field on these sites splits

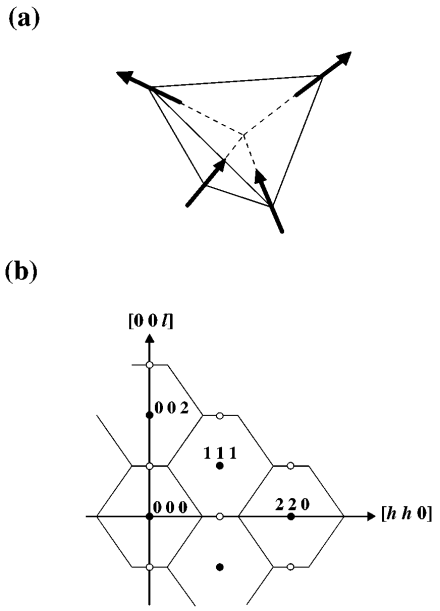

FIG. 1. (a) The ground state of a single tetrahedron of spins containing ferromagnetic interactions and local Ising anisotropy. The dashed lines show the anisotropy axes. (b) Schematic plot of reciprocal space for the pyrochlore lattice. The full circles show the positions of Bragg peaks for a $q = 0$ magnetic structure, while the open circles show the *X* points.

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the Ho^{3+} $^5I_8$ free ion ground state so that the lowest level is a doublet composed almost entirely of the $m_J = |\pm 8\rangle$ free ion states. This results in strong easy-axis anisotropy of the order of 50 K along the $\langle 111 \rangle$ axes, which point towards the center of every tetrahedron of spins. Indeed, magnetization data obtained between 1.8 and 300 K in a wide variety of fields may be described by a model containing purely Ising anisotropy. The Curie-Weiss temperature is $\theta \approx +1.9$ K, which indicates ferromagnetic coupling between the Ho^{3+} ions with $J \sim 1$ K. However, we have found no evidence of a magnetic transition down to at least 0.05 K using muon spin resonance (μSR) measurements [5]. We have performed Monte Carlo calculations to confirm that these observations are consistent with the spin ice model. For instance, we find that the bulk susceptibility of $Ho_2Ti_2O_7$ is described by the spin ice model down to the limit of our experimental measurements at 1.8 K, while no long-range order occurs in the Monte Carlo calculations down to at least $T/J = 10^{-4}$ [6].

In this Letter, we concentrate on neutron scattering results from $Ho_2Ti_2O_7$, showing that they can be understood in terms of the spin ice model. No magnetic long-range order is observed down to temperatures of at least 0.35 K in zero magnetic field, but instead, short-range ferromagnetic correlations are observed. However, upon applying a field, there is a spectacular restoration of magnetic order: Two ordered phases are observed that have an unusual history dependence suggestive of the slow dynamics of the spin ice model.

Our measurements were performed using the TAS7 triple-axis neutron spectrometer at Risø National Laboratory, Denmark. The spectrometer was operated in the elastic mode, with pyrolytic graphite crystals for both monochromator and analyzer, using neutrons of energy 4.9 meV. This produced an energy resolution of 0.23 meV (FWHM). Contamination of the incident beam by higher-order components was reduced by a cooled Be filter. We used a single crystal of $Ho_2Ti_2O_7$, placed in a ^{3}He sorption refrigerator inside a 9 T cryomagnet. The crystal was aligned with the $[1\bar{1}0]$ direction vertical, parallel to the direction of the applied magnetic field. The scattering plane therefore contained (hhl) wave vectors.

The magnetic scattering in *zero field* was characterized by scanning the wave-vector transfer over several Brillouin zones at sample temperatures of 0.35, 1.8, and 42 K. No significant change was observed in the intensities of any of the Bragg peaks while initially cooling the crystal from 300 to 0.35 K, so we conclude they are all nuclear in origin, and that no phase transition to a magnetically ordered state occurs in zero field. Instead, strong magnetic diffuse scattering was detected in the 0.35 and 1.8 K scans. In particular, we observed broad scattering centered at the $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ position, and as a ridge beginning at the (000) point and extending along the $\mathbf{c}^*$ axis to the (001) point. This distribution of scattering is consistent with our Monte Carlo calculations of the neutron scattering cross section from the spin ice model. The ridge of scattering sharpens upon cooling down to 0.35 K, showing that, while the ferromagnetic order is on a scale of one to two nearest-neighbor distances at 1.8 K, it increases to between three and four distances at 0.35 K.

The *field-dependent* behavior of $Ho_2Ti_2O_7$ is both dramatic and unusual. At all temperatures available to us (0.35 to 50 K), we found that, upon applying a field of the order of 0.1 T, strong magnetic Bragg peaks appeared at the (002), (111), and (220) positions. The positions of these Bragg peaks in reciprocal space are illustrated in Fig. 1(b). They indicate that a long-range ordered magnetic structure is formed with the same unit cell as the chemical structure; we therefore refer to it as the $q = 0$ phase. To illustrate, in Fig. 2(a) we show the field dependence of the (002) Bragg peak, with the abrupt onset of magnetic ordering.

Also apparent in Fig. 2 is the history dependence of the magnetic structure at low temperatures. We observed that, if the field was removed, the (002) magnetic Bragg intensity did not decrease quite to zero, but dropped to the small but finite fraction of about 2% of the saturation intensity. If the sample was then heated to a temperature of 1 K in zero field, this residual intensity disappeared. Magnetic long-range order is clearly frozen into the sample at low temperatures by applying a field and then removing it. In this respect, the behavior is reminiscent of a spin-freezing transition below which nonreversible behavior occurs, rather like in a spin glass. We have observed

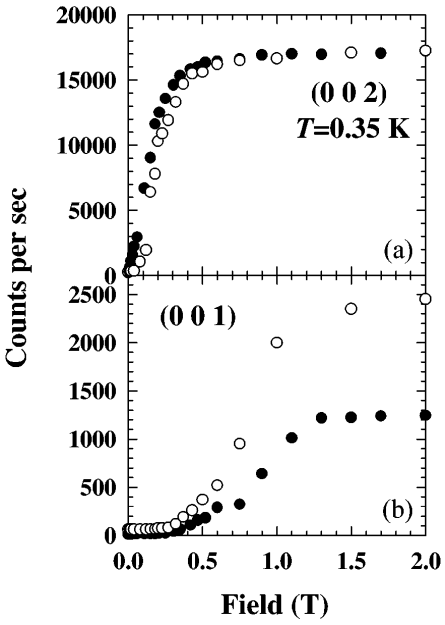

FIG. 2. Magnetic field dependence of the scattering from $Ho_2Ti_2O_7$ at a sample temperature of 0.35 K, at (a) the (002) position, and (b) the (001) position. The measurements shown by the full circles were made after cooling from high temperatures in zero field, while the open circles show the behavior after an initial field of 0.5 T was applied and then removed before beginning the measurements. This reveals the field-dependent behavior of the frozen-in magnetic order.

similar irreversible effects in μSR and low-field susceptibility measurements [5].

In addition to the $q = 0$ Bragg reflections, very complex field-dependent behavior was observed at other positions in reciprocal space, as illustrated in Fig. 2(b): At a temperature of 0.35 K, strong but broad magnetic scattering appears centered on the (001) and (110) positions, but its onset is at much higher fields than for the $q = 0$ Bragg peaks. Pronounced hysteresis was also observed for these two peaks, as illustrated in Fig. 2(b) for the (001) position. In addition, the widths in the wave vector and the intensities of the two peaks are sensitive to both temperature and history. At 0.35 K, the peaks are several times broader in wave vector than the resolution of the spectrometer, indicating that the correlations are rather short ranged. However, upon heating to 1.4 K, a dramatic increase in their intensities occurs, together with a concomitant decrease in their widths to below the experimental resolution. We illustrate this effect in Fig. 3, where we show measurements of the intensities at all 5 positions: (002), (111), (220), (001), and (110), in a constant magnetic field of 2 T, as the sample was heated from 0.35 up to 2 K. It can be seen that, while the $q = 0$ peaks remain independent of temperature, the scattering at the (001) and (110) positions has a maximum at a temperature of about 1.4 K, and then decreases to zero at higher temperatures. A modification to the $q = 0$ structure must become stable at 1.4 K. This involves a breaking of the face-centered symmetry so that the magnetic unit cell is larger than the chemical unit cell. Since the (001) and (110) positions are X points of the Brillouin zone, we refer to this second structure as the $q = X$ phase.

We now consider the possible magnetic structures that could give rise to these two ordered phases. The pyrochlore lattice can be considered as four interpenetrating sublattices of magnetic ions, so that each tetrahedron contains an ion from each sublattice. A $q = 0$ structure indicates that the spins occupying the same sublattice are either ferromagnetically ordered with respect to one another or are completely disordered. This means that a $q = 0$ structure may be completely defined by specifying the ordered spin arrangement on a single tetrahedron. However, a $q = X$ structure breaks the four-sublattice symmetry, so that the spin arrangement on every tetrahedron in the unit cell is different.

A structure refinement using the observed intensities of the (002), (111), (113), and (220) magnetic Bragg peaks reveals that the $q = 0$ phase is constructed from the ground state of a single tetrahedron of spins [shown in Fig. 1(a)], i.e., the two spins in, two spins out configuration. A schematic view of this structure is shown in Fig. 4(a). The ordered moment on every spin in the structure was determined as $4.6(5)\mu_B$, which is about half of the total moment of $10\mu_B$ available to each Ho^{3+} ion. This structure is noncollinear and can only arise when there is very strong $\langle 111 \rangle$ axial anisotropy in the system. This is apparent when the energetics of ordering are considered: A

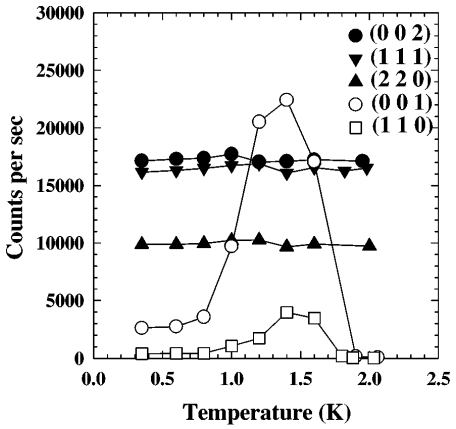

FIG. 3. The observed intensity at the (002), (111), (220), (001), and (110) positions while heating in an applied field of 2 T. Symbols for the $q = 0$ peaks are full, while those for the (001) and (110) peaks are open.

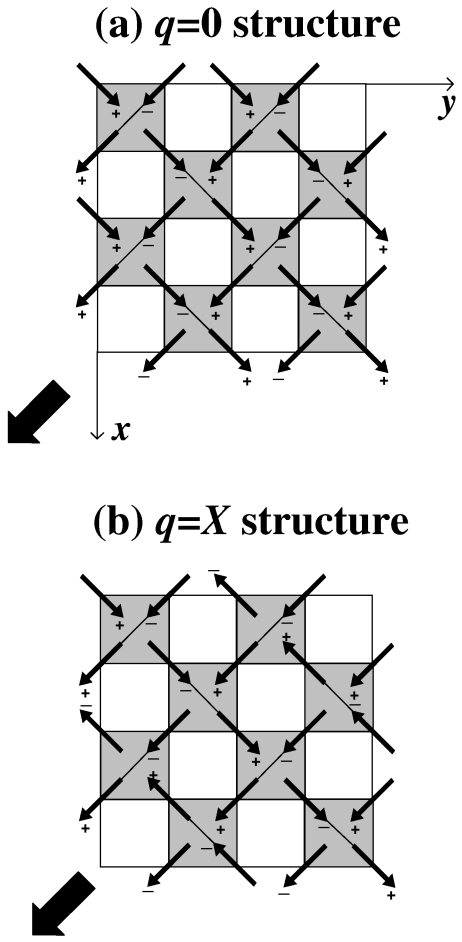

FIG. 4. (a) The $q = 0$ magnetic structure observed in $Ho_2Ti_2O_7$, projected down the z axis. The tetrahedra appear as squares in this projection and are shown in grey. The component of each spin parallel to the z axis is indicated by a "+" and "−" sign. This structure is a long-range version of the ground-state configuration for a single tetrahedron. The direction of the magnetic field is indicated by the bold arrow. (b) A schematic plot of the $q = X$ magnetic structure.

field of the order of 0.3 T is required to stabilize the $q = 0$ phase, which is roughly equivalent to the exchange energy $J \sim 1$ K. Thus, the structure is achieved by ordering the net magnetization on each tetrahedron while maintaining the ground-state configuration, because overcoming the single-ion anisotropy ($\sim$50 K) requires much higher fields of order 15 T.

As can be seen from Fig. 4(a), the $q = 0$ structure is ferromagnetic and results in a net magnetization directed along one of the fourfold crystallographic axes; we have chosen this to be the x axis in the figure. This net moment is at an angle of 45° to the applied field direction. The structure of the $q = X$ phase (which only forms as a true long-range structure at temperatures about 1.4 K) is considerably more complex than that of the $q = 0$ phase, since there is an increased number of sublattices, each of which now has a different ordered moment per spin. The restricted number of Bragg peaks accessible in our experiment has meant that we are unable to obtain a unique solution to the $q = X$ structure, but an approximate solution consistent with our observations is illustrated in Fig. 4(b). This structure involves antiferromagnetic ordering of the moments in chains transverse to the applied magnetic field. This results in a change in the direction of the net magnetic moment towards the field direction, and is achieved by spins in alternating chains undergoing 180° spin flips relative to the $q = 0$ structure. Since the dynamics of the spin ice model are slow, it is not surprising that this is a highly metastable process, and requires a certain amount of thermal energy to be achieved on a long-range length scale.

We now address the interesting question of the dynamics of ordering in $Ho_2Ti_2O_7$, and its context in our understanding of spin glassiness. This is especially pertinent in the light of recent experimental work on frustrated antiferromagnets. One very intriguing observation is that chemically ordered materials such as many oxide pyrochlore antiferromagnets form spin glass phases [7,8]. On the other hand, the quasi-two-dimensional system $SrCr_{8-x}Ga_{4+x}O_{19}$ (SCGO) [9] and the fluoride pyrochlores $CsNiCrF_6$ and $CsMnFeF_6$ [10] appear to have fluctuating ground states. This is contrary to the received wisdom that a spin glass requires both frustration *and* chemical disorder, because the oxide pyrochlores are chemically *ordered*, but form spin glasses, while SCGO and the fluoride pyrochlores contain chemical *disorder*, but do not form spin glasses [2].

Our results from $Ho_2Ti_2O_7$ make it clear that single-ion anisotropy can play a major part in the process of spin freezing. SCGO and the fluoride pyrochlores are generally thought to have relatively isotropic interactions, consistent with the Heisenberg model. The frustrated Heisenberg model is unlike that of a spin glass, because it does not have infinite energy barriers separating its degenerate ground states, and so remains fluctuating even at the lowest temperatures. The energy barriers can be introduced by adding local planar anisotropy, but instead of a spin glass phase, a long-range ordered state is formed through the action of thermal fluctuations [11]. The spin ice model also has energy barriers, but according to our experimental and Monte Carlo results does not suffer from thermal degeneracy breaking. Many of the antiferromagnetic oxide pyrochlores (such as $Tb_2Mo_2O_7$ [2,8]) contain a large orbital moment and so are also expected to contain strong single-ion anisotropy, similar to that in $Ho_2Ti_2O_7$. We suggest that the spin freezing observed in these compounds is at least partly due to single-ion anisotropy, which introduces large energy barriers between ground states.

In conclusion, the spin ice model shows that strong geometrical frustration can arise in the presence of dominant ferromagnetic interactions and axial single-ion anisotropy. While this may be a surprising result, it sheds new light on the unusual dynamical properties that have recently been observed in frustrated systems.

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[6] If we keep the Ising anisotropy in the Hamiltonian but change the sign of the interactions to *antiferromagnetic*, we observe a phase transition to a long-range ordered state at $T_N \sim |J|$. Thus, axial anisotropy has the remarkable effect that *ferromagnetic interactions experience stronger frustration than antiferromagnetic*.

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