Er$_2$Ti$_2$O$_7$: Evidence of quantum order by disorder in a frustrated antiferromagnet


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Er$_2$Ti$_2$O$_7$ has been suggested to be a realization of the frustrated (111) $XY$ pyrochlore lattice antiferromagnet, for which theory predicts fluctuation-induced symmetry breaking in a highly degenerate ground state manifold. We present a theoretical analysis of the classical model compared to neutron scattering experiments on the real material, both below and above $T_N = 1.173(2)$ K. The model correctly predicts the ordered magnetic structure, suggesting that the real system has order stabilized by zero-point quantum fluctuations that can be modeled by classical spin wave theory. However, the model fails to describe the excitations of the system, which show unusual features.

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An important aspect of condensed matter is the separation of energy scales, such that the minimization of one set of interactions may result in the frustration of another. A paradigm is the frustrated antiferromagnet, in which the local magnetic couplings between ions are frustrated by the crystal symmetry that the ions adopt. However, a systematic study of the rare earth pyrochlore titanates R$_2$Ti$_2$O$_7$ has shown that local antiferromagnetic bond frustration is neither a necessary, nor a sufficient condition for magnetic frustration. Rather, it arises from the interplay, in the context of the crystal symmetry, of the principal terms in the spin Hamiltonian. In the case of R$_2$Ti$_2$O$_7$, the main terms are single-ion anisotropy, exchange and dipolar coupling. Depending on the balance of these factors, one observes spin ice behavior ($R = $Ho, Dy), spin liquid behavior ($R = $Tb), and dipole induced partial order ($R = $Gd).

Such behavior is best classified in the domain of ordered spin systems that transform as the third order IR of the crystal group. There is thus a clear motivation to study models based on other simple anisotropies and their realization in the titanate series. In this paper we study one such model the (111) $XY$ model antiferromagnet and its realization Er$_2$Ti$_2$O$_7$.

We consider the Hamiltonian

$$H = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - D \sum_i (\vec{S}_i \cdot \hat{d}_i)^2,$$ \hspace{1cm} (1)

where the classical spins $\vec{S}_i$ populate a face centered cubic array of corner sharing tetrahedra: the pyrochlore lattice. The spins are confined to easy $XY$ planes by a local $d_i = (111)$ anisotropy $D < 0$ and are coupled antiferromagnetically by exchange $J < 0$. This model was first studied in Ref. 8, where a discrete, but macroscopically degenerate, set of ground states was identified. At finite temperature thermal fluctuations were found to select an ordered state by the mechanism that Villain called “order by disorder” and a first order phase transition was observed in numerical simulations. The propagation vector of the ordered state was found to be $k = 0, 0, 0$ (henceforth “$k = 0$”), but the basis vectors of the magnetic structure were not determined. We have recently discovered that the ground state degeneracy is more extensive than suggested in Ref. 8; that there exists a continuous manifold of $k = 0$ ground states and that there may even be disordered states with continuous internal degrees of freedom.

The possible basis states of the $k = 0$ manifold were identified by group theory methods. They transform as linear combinations of the basis vectors of four irreducible representations (IR’s), labeled $\Gamma_{3,5,7,9}$. The $XY$ anisotropy energy is minimized only by (a) linear combinations of the two basis vectors $\psi_{3,2}$ that transform as the second order IR $\Gamma_5$, (b) the discrete set of symmetrically equivalent basis vectors $\psi_{3,5}$ that transform as the third order IR $\Gamma_7$ (see Fig. 1). Monte Carlo simulations confirmed that the first order transition at $T_N / J = 0.125$ selects $k = 0$ order. An analysis of the distribution of bond energies suggested that immediately below $T_N$ there remains a continuous degeneracy in the $k = 0$ manifold. As $T \to 0$, the spins were found to settle gradu-
FIG. 1. Upper inset: tetrahedral basis projected down [001], from left to right: $\psi_1, \psi_2, \psi_3, \pm$ denotes how spins tilt out of the plane (they lie parallel to the opposite triangular face of the tetrahedron). Graph: size dependence of the simulated specific heat for $N=16L^3$ spins. Lower inset: experimental low temperature specific heat vs $T^3$ (powder sample). A turn up low at temperature, attributed to hyperfine effects (Ref. 9), is barely visible with this choice of scale.

ally into the magnetic structure defined by $\psi_2$ belonging to the continuously degenerate IR $\Gamma_5$. (Note that $\psi_2$ is the only noncoplanar structure among $\psi_1, \pm$.) Both the initial selection of $k=0$ and the final selection of $\psi_2$ must be order by disorder processes as the ground state manifold is macroscopically degenerate.

To understand this ground state selection, we analyze the $D/J \rightarrow \infty$ model (i.e., spins confined to local $XY$ planes). We expect that for the preferred ground state a spin wave analysis should expose the presence of zero frequency modes over an extensive region of the Brillouin zone.\textsuperscript{15} This is indeed the case: we calculate the quadratic Hamiltonian for small displacements away from a given ground state, which we symmetrize and diagonalize to find the normal mode spectrum.\textsuperscript{12}

Applying this procedure to the state $\psi_2$ gives eigenvalues

$$\lambda(q) = 4J\{ 1 \pm \cos(q \cdot \hat{a}/2) \},$$

$$\lambda(q) = 4J\{ 1 \pm \cos(q \cdot (c-\hat{b})/2) \},$$

(2)

where $\hat{a}, \hat{b}, \hat{c}$ are the basis vectors of the primitive rhombohedral unit cell. Hence, there are branches with $\lambda(q) = 0$ over planes in the Brillouin zone, for which $q \cdot \hat{a} = 0$ and $q \cdot (c-\hat{b}) = 0$. The same procedure when applied to other selected ground states yields a microscopic number of zero modes at specific points in the zone. This difference gives the mechanism for the order by disorder selection of $\psi_2$. In this approximation the amplitude of the soft modes diverges, giving a dominant contribution to the entropy.\textsuperscript{15}

Evidence of the soft modes exists in the specific heat, as each contributes less than $\frac{1}{2}k_B$. As there are $O(L^2)$ modes, the quantity $\frac{1}{2}C_N/Nk_B$ should scale as $1/L$ at low temperature, as confirmed in Fig. 1. We note that the entropy contribution to the free energy from the soft modes scales as $N^{23}$ and so is not extensive. While this could mean that the ordering within the $k=0$ manifold occurs at a temperature-dependent system size that goes to zero in the thermodynamic limit, no such effect was detected in the system sizes we have studied.

Disordered states are occasionally formed in the simulations, by the rotation of columns of spins with infinite length out of an ordered state. This suggests that, starting from the $\psi_2$ state, one can introduce $O(L^2)$ independent column defects, all perpendicular to a given plane. Our calculation, giving $O(L^2)$ soft modes is compatible with this description and is analogous to the case of the Heisenberg kagomé antiferromagnet.\textsuperscript{15} For the latter, fluctuations out of a coplanar spin configuration can be described equivalently in terms of soft propagating modes and localized zero energy excitations.

The material Er$_2$Ti$_2$O$_7$, which orders magnetically at $\sim 1.2$ K, has been suggested to approximate the $\langle 111 \rangle$ $XY$ antiferromagnet.\textsuperscript{10,11} To test this we have determined its magnetic structure by powder neutron diffraction using the POLARIS diffractometer (ISIS). The magnetic reflections observed below $T_N = 1.2$ K index with a propagation vector of $k=0$. As the transition is continuous (see below), the system is expected to order under only one of the nonzero IR’s of the Er site representations: $\Gamma_3, \Gamma_5, \Gamma_7, \Gamma_9$, as defined above.

Refinement of the magnetic structure\textsuperscript{15} showed that only the two basis vectors $\psi_1, \psi_2$ of $\Gamma_5$ were consistent with the magnetic intensity (see Figs. 1, 2). Single crystal diffraction data collected on the instruments E2 (HMI, Berlin) and PRISMA (ISIS), allowed us to distinguish between the two structures. The measurements were performed on a ($\sim 8$ mm$^3$) crystal at temperatures down to 0.13 K. In order to suppress the formation of multidomains due to the cubic symmetry, a magnetic field was applied along the $[1 1 0]$ direction. Below $T_N$, we found that a field of 0.5 T caused the $(2,2,0)$ magnetic Bragg peak to increase from 260 counts to 500 counts, while the other peaks remained approximately unchanged. This increase in the $(2,2,0)$ by a factor of 1.9 $\pm 0.2$ is consistent with the formation of a monodomain of the $\psi_2$ ground state. We can conclude that the zero field ordering pattern is also described by $\psi_2$, in agreement with the theory.
The ordered moment at 50 mK (where ordering is essentially complete) is $3.01 \pm 0.05 \mu_B$ per atom. A CEF analysis, following Ref. 18, predicts a single-ion Kramers doublet ground state with the wave function $-0.5428 | -\frac{1}{2} \rangle - 0.2384 | -\frac{3}{2} \rangle + 0.5628 | \frac{1}{2} \rangle + 0.3876 | \frac{3}{2} \rangle - 0.426 | \frac{5}{2} \rangle$. This corresponds to moments of $3.8 \mu_B$ and $0.12 \mu_B$ perpendicular and parallel to (111). In an antiferromagnet, zero-point quantum fluctuations significantly reduce the ordered moment from the single-ion value. The observed moment of $3.01 \mu_B$, thus, agrees well with quasi-classical ordering of local XY-like moments with a magnitude fixed by the CEF.

The dominant perturbation to the model Hamiltonian in Er$_2$Ti$_2$O$_7$ are dipole-dipole interactions and one might speculate that these are the true cause for the $\psi_3$ ordering. In the Heisenberg pyrochlore antiferromagnet, provided the ratio of dipolar energy to near neighbor exchange is less than a critical value, $J_{dd}/J_{nn} \leq 5.7$, the ground state is an energetically selected $k=0$ state: the $\psi_3$ basis (Fig. 1). As this state is also a ground state for the (111) XY model, it is clear that in the present case it will be stabilized by dipolar interactions. We expect Er$_2$Ti$_2$O$_7$ to have $J_{dd}/J_{nn} \leq 5.7$, and thus $\psi_3$ order, contrary to observation. With a moment of $3 \mu_B$ the near neighbor dipolar interaction has a magnitude $-0.32$ K per spin for $\psi_3$ and $+0.06$ K per spin for $\psi_1$. It is therefore a substantial fraction of $T_N$. However, zero point quantum fluctuations also stabilize the ground state of an antiferromagnet and will favor the softer $\psi_2$ state.21

We are therefore drawn to the conclusion that the most likely cause of the observed $\psi_2$ order in Er$_2$Ti$_2$O$_7$ is its stabilization by zero-point quantum fluctuations, the effect of which is captured by our classical spin wave calculation. However, the close agreement of experiment and theory does not extend to the excitations of the system, as we now discuss.

In our model, the density of classical spin wave states, $g(\lambda)$ is a constant, a result that is incompatible with the experimental specific heat, which shows a $T^3$ dependence up to $\sim 1$ K (inset, Fig. 1). Furthermore, in contradiction with theory,8 the ordering transition was found to be continuous within experimental precision. The evolution of the magnetic Bragg peaks near the critical temperature $T_N = 1.173(2)$ K obeys a standard power law with the critical exponent $\beta = 0.33(2)$, characteristic of the 3D-XY model (inset, Fig. 2).22 This observation of a conventional $\beta$ provides a counter example to the idea that pyrochlore antiferromagnets represent a new universality class, analogous to Kawamura's chiral universality class for triangular lattice antiferromagnets.24

To investigate the excitations further, the dynamics of Er$_2$Ti$_2$O$_7$ have been investigated by inelastic neutron scattering. Measurements were carried out on the spectrometers PRISMA (ISIS), RITA (Risø National Laboratory), and IN14 (ILL). For a powder sample, excitons25 were found at 6.3 and 7.3 meV [Fig. 3(a)]. Their dispersion can be fitted to $E(Q) = \sqrt{\Delta^2 - 2a|J_0(Q)|\Delta}$ with $\Delta = 6.38(1)$ meV, $a \sqrt{J_0(0)} = 0.35(1)$ meV$^{1/2}$ for the lower level and $\Delta = 7.39(1)$ meV, $a \sqrt{J(0)} = 0.21(1)$ meV$^{1/2}$ for the upper level. Here, $J(Q)$ is the Fourier transformed exchange and $a$ is related to the matrix elements that connect the ground and excited states.26,27 The values of $\Delta$ compare with the CEF predictions of 6.4 and 8.8 meV,17 while $J(0)/k_B$ is implied to be at least 1.5 K. Dispersed excitons are also observed in Tb$_2$Ti$_2$O$_7$.4

In the lower energy scale, data from an image-furnace grown single crystal ($\sim 250$ mm$^2$) reveal a shoulder of scattering on the elastic line extending out to $\sim 1$ meV ([Fig. 3(b)]). This shoulder, which does not appear to obey a strong wave vector dependence [Fig. 3(b)], gradually weakens upon heating above $T_N$. High resolution scans on PRISMA ($T = 0.08$ K) and on a powder sample on the IRIS spectrometer at ISIS [inset, Fig. 3(b)] resolved the shoulder into a peak at 0.4 meV, with a width outside the instrumental resolution.

One possible explanation, that this peak is a very low lying CEF level, as invoked by Blöte et al.9 to explain the anomalously large Curie-Weiss temperature $\theta = -22$ K is not consistent with the predicted CEF scheme.17 A more natural explanation is that it is a weakly dispersed optical magnon mode. Evidence for a gapped magnon spectrum is provided by the IRIS data [inset, Fig. 3(b)], which is at the level of background between 0.03 meV ($\sim 0.3$ K) and 0.2 meV ($\sim 2$ K), indicating an absence of magnons in this range. However, there is a problem with this interpretation:
the $T^3$ specific heat (inset, Fig. 1) requires a density of un-gapped excited states that increases quadratically with energy up to at least $\sim$1 K. One possible way out of this conundrum is to invoke the existence of a hidden branch of excitations that do not couple directly to neutrons. It is interesting to note that frustrated, quasi-two-dimensional SrCr$_x$Ga$_{1-x}$O$_{19}$ and (H$_2$O)Fe$_3$(SO$_4$)$_2$(OH)$_6$ have $T^2$ specific heats despite the absence of conventional magnons.$^{28,29}$

A final point of interest is that the other erbium pyrochlores Er$_2$GaSbO$_7$ and Er$_2$Sn$_2$O$_7$ apparently do not order down to 50 mK.$^{30}$ It is possible that in this family there is a kind of quantum critical point where as a function of the energy up to at least 8 $T^3$.

**References**

14. These are a subset of the nine IRs, $\Gamma_1 \ldots 9$, that describe all possible $k=0$ spin configurations in the crystallographic space group $Fd\bar{3}m$. The numbering follows the scheme defined in O. V. Kovalev, *Representations of the Crystallographic Space Groups*, ed. 2 (Gordon and Breach Science Publishers, Switzerland, 1993).

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20. Modeling of the dispersion would require a full and very accurate knowledge of the CEF wave functions (Ref. 25).