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Lucile Savary, Kate A. Ross, Bruce D. Gaulin, Jacob P. C. Ruff, and Leon Balents

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Order-by-Quantum-Disorder in $Er_2Ti_2O_7$

Lucile Savary,[1] Kate A. Ross,[2] Bruce D. Gaulin,[2,3,4] Jacob P. C. Ruff,[2,5] and Leon Balents[6]

[1] *Department of Physics, University of California, Santa Barbara, California 93106-9530, U.S.A.*
[2] *Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, L8S 4M1, Canada*
[3] *Canadian Institute for Advanced Research, 180 Dundas St. W., Toronto, Ontario, M5G 1Z8, Canada*
[4] *Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario, L8S 4M1, Canada*
[5] *The Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.*
[6] *Kavli Institute for Theoretical Physics, University of California, Santa Barbara, California, 93106-4030, U.S.A.*

Here we establish the systematic existence of a $U(1)$ degeneracy of *all* symmetry-allowed Hamiltonians quadratic in the spins on the pyrochlore lattice, at the mean-field level. By extracting the Hamiltonian of $Er_2Ti_2O_7$ from inelastic neutron scattering measurements, we then show that the $U(1)$-degenerate states of $Er_2Ti_2O_7$ are its classical ground states, and *unambiguously* show that quantum fluctuations break the degeneracy in a way which is confirmed by experiment. The degree of symmetry protection of the classical $U(1)$ degeneracy in $Er_2Ti_2O_7$ is unprecedented in other materials. As a consequence, our observation of order-by-disorder is unusually definitive. We provide further verifiable consequences of this phenomenon, and several additional comparisons between theory and experiment.

Models with frustrated interactions often display an "accidental" ground state degeneracy in the classical limit. Within mean field theory (MFT), the classical degeneracy extends to one of the free energy, even for quantum spins. Theoretically, quantum or thermal fluctuations may lift this degeneracy and thereby select and stabilize an ordered state. This phenomenon is called "order-by-disorder" (ObD) [1–3], and has been discussed theoretically for more than three decades.

While ObD could therefore be expected to arise fairly frequently, it has so far escaped indisputable experimental detection, to a large extent because of the difficulty of distinguishing fluctuation effects from those of weak interactions that explicitly break the degeneracy at the mean-field level (see Supp. Mat. [4] for a discussion of ambiguities in the most accepted experimental claims [5–7] of ObD). Hence, to unambiguously identify ObD in a material, we need both a detailed knowledge of the material's Hamiltonian and a proof that a mean field degeneracy exists which is *robust* to weak perturbations. We provide both here for the rare earth pyrochlore $Er_2Ti_2O_7$, and confirm the ObD physics through confrontation of the theoretically-predicted order with experimental observations.

Prior work identified $Er_2Ti_2O_7$ as an "XY" antiferromagnet with an ordered ground state [8–15] in zero field. ObD was actually already insightfully suggested for it long ago [8, 9], but based on an ad-hoc model which led to several significant conflicts with experiment, and as such $Er_2Ti_2O_7$ has been regarded as a long-standing puzzle. Recently ObD was revisited [15], but our model and theory go well beyond existing work and resolve all the prior enigmas. Relation to prior work on this material will be returned to at the end of the paper.

We proceed as follows. First, we prove that, at the mean-field level, *any* symmetry-allowed Hamiltonian for *any* system of effective $S = 1/2$ spins on the pyrochlore lattice, quadratic in the spins, possesses a $U(1)$ degeneracy, which can *only* be broken by fluctuations or disorder. We next extract the parameters of the nearest-neighbor model for $Er_2Ti_2O_7$ from the fits of linear spin wave theory with single-crystal high-field inelastic neutron scattering, show that MFT describes $Er_2Ti_2O_7$ well, and that the $U(1)$ degeneracy of its model applies to its zero-field ordered phase. We then calculate the splitting due to quantum fluctuations, and show that the selected state is compatible with zero-field measurements. We also predict correspondingly a spin-wave gap of ≈ 260 mK (and other effects) which may be measured in future experiments.

General $U(1)$ degeneracy: We project the Hamiltonian to that of effective $S = 1/2$ quantum spins describing the magnetic doublet of each rare earth ion on the pyrochlore lattice. The most general form of H involving two-spin interactions is $H = \frac{1}{2}\sum_{i,j} J_{ij}^{\mu\nu} S_i^\mu S_j^\nu$, where S_i^μ is the μ^{th} component of the spin on the site i, in the *global* $(\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}})$ basis. (Implicitly, the $J_{ij}^{\mu\nu}$ are of course constrained by crystal symmetry – see Refs. 16 and 17 for details of the constraints for nearest-neighbor exchange.) The mean field (variational) free energy $F_{\text{MF}} = F_0 + \langle H - H_0 \rangle$, where H_0 and F_0 are the Hamiltonian and free energy for a fiducial system of decoupled spins with applied Zeeman fields, is

$$F_{\text{MF}} = \frac{1}{2}\sum_{i,j} J_{ij}^{\mu\nu} m_i^\mu m_j^\nu + \frac{1}{\beta}\sum_i \Big[(\tfrac{1}{2} - |\mathbf{m}_i|) \ln\left(\tfrac{1}{2} - |\mathbf{m}_i|\right) + (\tfrac{1}{2} + |\mathbf{m}_i|) \ln\left(\tfrac{1}{2} + |\mathbf{m}_i|\right) \Big], \quad (1)$$

where $\beta = 1/(k_B T)$, where T is the temperature and k_B is Boltzmann's constant, and where $\mathbf{m}_i = \langle \mathbf{S}_i \rangle$, $m_i^\mu = \langle S_i^\mu \rangle$ and thus $|\mathbf{m}_i| \leq 1/2$. The entropic part of the free energy, i.e. the last term of Eq. (1), is obviously independent of the orientation of the magnetization $\mathbf{m}_i$. Now consider the Ansatz

$$\mathbf{m}_j^0(\alpha) = \rho\, \text{Re}\left[e^{-i\alpha} \left(\hat{\mathbf{a}}_j + i\hat{\mathbf{b}}_j \right) \right], \quad (2)$$

where $\rho \in [0, 1/2]$, $\alpha \in [0, 2\pi[$, and $\hat{\mathbf{a}}_j$ and $\hat{\mathbf{b}}_j$ are the *local*

x and y unit vectors, respectively (see Supp. Mat. [4]), which depend only upon which of the four sublattices the site resides. In words, Eq. (2) describes translational invariant states (no unit cell enlargement) where all spins make the same angle with their local x-axis. (Note that this spin configuration carries no total net moment.) This is the Γ_5 manifold of ground states first identified in Ref. 8 for $Er_2Ti_2O_7$. Now, let $\Phi = \rho\, e^{i\alpha} = \Phi_1 + i\Phi_2$, $\Phi_1, \Phi_2 \in \mathbb{R}$. Up to an unimportant constant, the free energy for the Ansatz Eq. (1) as a function of Φ reads

$$F^0_{\rm MF}[\Phi] = a\Phi^2 + a^*(\Phi^*)^2 + b|\Phi|^2, \qquad a \in \mathbb{C}, b \in \mathbb{R}, \quad (3)$$

since Eq. (1) is quadratic in the spins. Cubic symmetries then impose that $a = a^* = 0$, so that $F^0_{\rm MF}$ depends on $|\Phi|$ only, i.e. solely on $|\mathbf{m}^0_i|$. Indeed, under the three-fold rotation along the [111] axis, one finds $\alpha \to \alpha + 2\pi/3$, or

$$\Phi \to e^{2i\pi/3}\Phi \quad \Rightarrow \quad a = 0, \qquad (4)$$

since $F^0_{\rm MF}$ should remain invariant under the above transformation. Thus, within MFT, the degeneracy is present for arbitrary two-spin interactions [18]. Similar arguments show that the leading order term splitting the degeneracy in the free energy and consistent with cubic symmetry is

$$F_6 = -c\,(\Phi^6 + (\Phi^*)^6), \qquad (5)$$

with some real constant c. Since there is no general argument to make c vanish, we conclude that the $U(1)$ degeneracy is an artifact of the approximations introduced so far. In MFT, it is, however, remarkably robust: *six spin interactions* would be required to induce a term of the form of Eq. (5). In $Er_2Ti_2O_7$ (and indeed most other rare earth pyrochlores), this is entirely negligible [14][19]. Spin-lattice coupling may generate effective four-spin interactions [20], which also cannot split the degeneracy. This leaves only fluctuations – i.e. ObD – to determine the splitting coefficient c.

Local minimum: By expanding about the degenerate states described by Eq. (2), we find that for arbitrary (symmetry preserving) exchange parameters, the states in Eq. (2) are extrema of the free energy (see Supp. Mat. [4]). Whether or not they are global minima, i.e. whether or not they constitute ground states of the problem, depends on the parameters $J^{\mu\nu}_{ij}$. We now proceed to the extraction of the latter from experiment, and lift any potential suspense: for parameters relevant to $Er_2Ti_2O_7$, these are the lowest-energy states.

$Er_2Ti_2O_7$ Hamiltonian: The effective $S = 1/2$ description applies to $Er_2Ti_2O_7$ below about 74 K [8, 21]. Nearest-neighbor exchange dominates, for which the Hamiltonian takes the form [17]

$$\begin{aligned} H = \sum_{\langle ij \rangle} \Big[& J_{zz} \mathsf{S}^z_i \mathsf{S}^z_j - J_\pm (\mathsf{S}^+_i \mathsf{S}^-_j + \mathsf{S}^-_i \mathsf{S}^+_j) \\ & + J_{\pm\pm} \left[\gamma_{ij} \mathsf{S}^+_i \mathsf{S}^+_j + \gamma^*_{ij} \mathsf{S}^-_i \mathsf{S}^-_j \right] \\ & + J_{z\pm} \left[\mathsf{S}^z_i (\zeta_{ij} \mathsf{S}^+_j + \zeta^*_{ij} \mathsf{S}^-_j) + i \leftrightarrow j \right] \Big], \end{aligned} \qquad (6)$$

where the sans serif characters S^μ_i denote components of the spins in the *local* pyrochlore bases, where γ is a 4×4 complex unimodular matrix, and $\zeta_{ij} = -\gamma^*_{ij}$ [17]. J_{zz}, $J_\pm$, $J_{z\pm}$ and $J_{\pm\pm}$ are related to the $J^{\mu\nu}_{ij}$ (for nearest-neighbor i and j) through basis rotations, and the resulting linear combinations between the said parameters, as well as the explicit expression of γ and the local bases used in Eq. (6) are given in the Supp. Mat. [4].

To determine the four exchange constants and the two components of the g-tensor specific to $Er_2Ti_2O_7$, we fit inelastic neutron scattering data with the structure factor obtained from linear spin wave theory in high field applied to the Hamiltonian Eq. (6). This method was described at length in Ref. 17 (esp. in its Appendix C). Experiments were carried out on a single crystal of $Er_2Ti_2O_7$ grown at McMaster University by the floating zone technique [22]. Inelastic neutron scattering by the time-of-flight method was performed at the NIST Center for Neutron Research using the Disk Chopper Spectrometer [23]. The incident wavelength of 5 Å afforded an energy resolution of 0.09 meV. Two orientations of the crystal were used such that the vertical axes, i.e. the crystallographic directions parallel to the applied field, were $[1\bar{1}0]$ and [111]. Using two field orientations allowed an exceptionally comprehensive study of the high-field spin-wave spectra. Furthermore, the understanding of the zero-field spectra from the ordered state was also enhanced by access to the two inequivalent scattering planes normal to the field directions. In all color contour plots herein, the last two panels represent scattering within the plane normal to [111]. All others include scattering vectors normal to $[1\bar{1}0]$.

Spin wave spectra arising in the polarized quantum paramagnetic state at $H = 3$ T and $T = 30$ mK were fit to the general anisotropic exchange model of Eq. (6) by matching the dispersions in several directions using a least squares method. The full structure factor $S(\mathbf{Q}, \omega)$ was not fit to the data, but followed directly from the Hamiltonian extracted from the fit to the dispersions. Within the linear spin wave approximation and the nearest-neighbor model, we find $g_z = 2.45 \pm 0.23$ and $g_{xy} = 5.97 \pm 0.08$ (Ref. 12 finds $g_z = 2.6$ and $g_{xy} = 6.8$), and in 10^{-2} meV

$$\begin{aligned} J_{\pm\pm} &= 4.2 \pm 0.5, \qquad & J_\pm &= 6.5 \pm 0.75, \\ J_{zz} &= -2.5 \pm 1.8, \qquad & J_{z\pm} &= -0.88 \pm 1.5 \quad . \end{aligned} \qquad (7)$$

Note that these parameters include the nearest-neighbor component of the dipolar interactions, and that weaker further neighbor components *cannot* break the $U(1)$ degeneracy, as shown above.

The above parameters Eq. (7) place $Er_2Ti_2O_7$ in a region of the $J_{zz} - J_\pm - J_{z\pm} - J_{\pm\pm}$ phase diagram far from spin ice. Notably, in sharp contrast to $Yb_2Ti_2O_7$ [17], the interactions $J_\pm$ and $J_{\pm\pm}$ involving the local XY components of the spins are dominant. Here conventional magnetic order is expected at low temperature [24], and Curie-Weiss MFT is a good starting point. Within the latter, we obtain the $U(1)$ degenerate manifold as

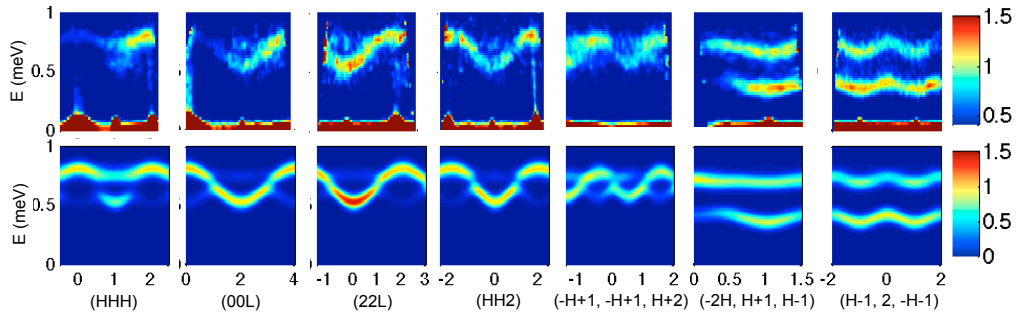

FIG. 1. The measured $S(\mathbf{Q},\omega)$ at $T = 30$ mK, $H = 3$ T sliced along several directions. The first five columns show $S(\mathbf{Q},\omega)$ in the HHL plane, with the field applied along $[1\bar{1}0]$, while the last two columns show $S(\mathbf{Q},\omega)$ for the field along [111]. Top row: measured $S(\mathbf{Q},\omega)$. Bottom row: calculated $S(\mathbf{Q},\omega)$, based on an anisotropic exchange model with six free parameters (see text) that were extracted by fitting to the measured dispersions.

the zero-field ordered states. Other predictions of MFT compare well with experiment. MFT predicts a continuous ordering transition at $T_c^{\rm MF} = 2.3$ K which implies a fluctuation parameter $f = T_c^{\rm MF}/T_c \approx 2.1$, given the experimental transition temperature $T_c = 1.1$ K [11]. This parameter is much smaller here than in typical systems with strong fluctuations (c.f. $f = 13$ for $Yb_2Ti_2O_7$ [17]). Likely $f \neq 1$ can be attributed to the usual *thermal* fluctuation effects neglected in MFT. The zero temperature field-induced transition (for a $\langle 110\rangle$ field) with $H_c^{\rm MF} = 1.74$ T, agrees perfectly with the experimental value $H_c = 1.7 \pm 0.05$ T [25].

Zero-point fluctuations: Neglecting the tiny six spin couplings, only zero-point quantum fluctuations can break the degeneracy of a clean crystal at low temperature. We show below that they do, though weakly, find the preferred states, and quantitatively estimate the energy splitting of the degenerate manifold.

In the spin wave approximation, the energy of the zero-point fluctuations per unit cell is given by

$$\epsilon_0^{sw} = V_{\rm BZ}^{-1} \sum_{i=1}^{4} \int_{\mathbf{k}\in \rm BZ} \omega_{\mathbf{k}}^i/2, \qquad (8)$$

where the sum runs over the four spin wave modes (see Ref. 17), and where $V_{\rm BZ}$ is the volume of the Brillouin zone. The spectrum $\omega_{\mathbf{k}}^i$ of states described by Eq. (2) depends on the angle α (the structure factor is shown for different values of α on Fig. 8 of the Supp. Mat. [4]); Therefore ϵ_0^{sw} depends on α as well. Performing the integration in Eq. (8) numerically for different values of the phase α, we indeed find that zero-point fluctuations break the $U(1)$ degeneracy, and that the six equivalent values $\alpha = n\pi/3$ $(n = 0, 1, \ldots, 5)$ are the minima of ϵ_0^{sw} as illustrated in Figure 2. The energy splitting fits well, up to a constant, to $\epsilon_0^{sw} = -\lambda/2 \cos 6\alpha$ $(c = 32 N_{u.c.}\lambda$ in Eq. (5) at $T = 0$, where $N_{u.c.}$ is the number of unit cells), with $\lambda = 3.5 \times 10^{-4}$meV. The six $\alpha = n\pi/3$ states are equivalent, i.e. related to one another by cubic symmetries, but differ in the absolute orientation of the spins. A zero-field cooled sample would be expected to form a

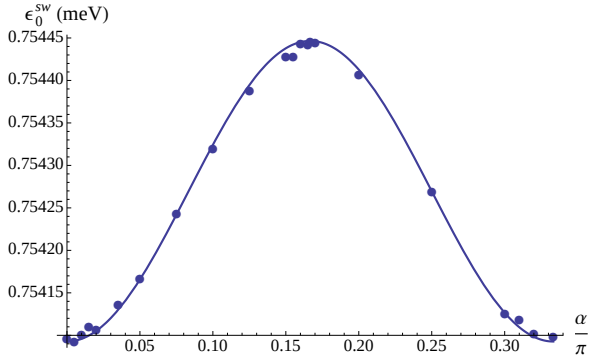

FIG. 2. Zero-point fluctuation energy ϵ_0^{sw} in the classically degenerate manifold parametrized by α. The peak-to-peak energy is $\lambda \approx 3.5\,10^{-4}$ meV.

multi-domain state with an equal volume fraction of each state. Indeed, we find that an equal superposition of the spectra of all six domains compares well with the experimental zero field neutron spectrum (see Supp. Mat. [4]).

Implications: The first prediction of the ObD calculation is a definite set of six zero-field ground states, with $\alpha = n\pi/3$, selected by the *positive* coefficient λ. These are exactly the ψ_2 states identified in Ref. 8. General symmetry arguments predict *either* these ψ_2 states or the alternative sequence that would be selected were $\lambda < 0$, with $\alpha = \pi/6 + n\pi/3$, which are denoted ψ_1 states in Ref. 8. The crucial experiment to distinguish the two was already noted in the latter reference and in Ref. 26: a magnetic field applied along $\langle 110\rangle$ to a zero-field cooled sample should lead, due to domain alignment, to a sharp *increase* of the (220) Bragg peak intensity for the ψ_2 states, but a sharp *decrease* of intensity for the ψ_1 states (see Supp. Mat. [4]). A sharp increase is consistently observed in several experiments [8, 11, 26]. Here – see Figure 3– we make an extensive comparison of theory (Supp. Mat. [4]) to experimental intensity versus field at *five* Bragg peaks including (220), which gives strong evidence for the correctness of the ψ_2 ground state and

the Hamiltonian parameters [27]. The ψ_2 state was also found by a sophisticated neutron spherical polarimetry study [10].

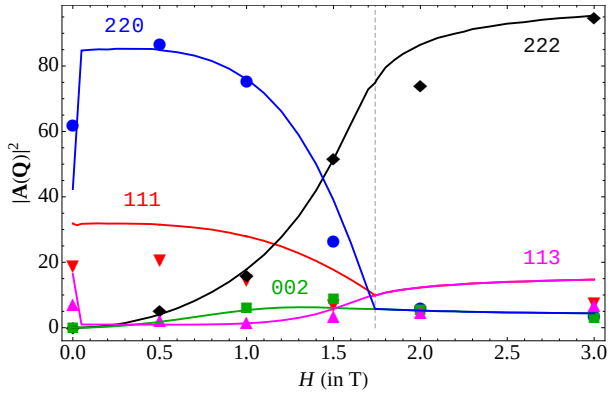

FIG. 3. Evolution of the Bragg peak intensities with a field $\mathbf{H} \parallel [\bar{1}10]$. The experimental data points from Ref. 11 are overplotted on the theoretical curves (the overall vertical scale of experiment was adjusted by hand) obtained when all six domains occupy an equal fraction of the volume in zero field. The experimental values for (111) and (113) are suppressed by instrumental complications, which are *partially* compensated for here by a multiplication factor of 1.3 (see Supp. Mat. [4] for more details). The dashed vertical line shows the critical field $H_c^{\rm MF} = 1.74$ T obtained within MFT.

The second consequence of our ObD scenario is the existence of a pseudo-Goldstone mode which acquires a small gap at low temperature. It is important to emphasize that the exchange Hamiltonian in Eq. (6) has only discrete (point group) symmetries, so the appearance of a Goldstone-like mode should be surprising! Though surprise has been expressed only recently [15], the existence of such a mode is apparent from multiple reports of a large T^3 low temperature specific heat [8, 11, 13, 28, 29] in $Er_2Ti_2O_7$. The pseudo-Goldstone mode is also explicitly visible in our zero field inelastic neutron scattering spectra. One can estimate the specific heat by Debye theory, $C_V^{T^3} = 4N_{u.c.}\,\sigma\,T^3$, where $N_{u.c.}$ is the number of unit cells in the system, and

$$\sigma = \frac{k_B^4\,\pi^2\,a^3}{120\,\overline{v}^3}. \tag{9}$$

Here a is the usual cubic lattice spacing, and $\overline{v}$ is the geometric mean spin wave velocity (see Supp. Mat. [4]). Using the theoretical value for $\overline{v}$ one obtains $\sigma_{\rm th} \approx 3.6\ {\rm J}\cdot{\rm K}^{-4}\cdot{\rm mol}^{-1}$. The experimental value from Ref. 11 (extracted in the Supp. Mat. [4]) is $\sigma_{\rm exp} = 4.6$ in the same units, comparable with theory.

Evidently the gap is not visible in current experiments. We now estimate it using field theory. Consider the effective (Euclidean) action of a system at $T = 0$ with slow space and time variations of the angle α:

$$\mathcal{S} = \int \frac{d^3r}{v_{u.c.}}d\tau \left[\sum_\mu \frac{\kappa_\mu}{2}\left(\partial_\mu\alpha\right)^2 + \frac{\eta}{2}\left(\partial_\tau\alpha\right)^2 - \frac{\lambda}{2}\cos 6\alpha\right], \tag{10}$$

where $v_{u.c.}$ is the volume of the unit cell, and the parameters κ_μ, η are obtained from spin wave theory (see Supp. Mat. [4]). Expanding the cosine above, we find that the gap Δ to the spin waves is

$$\Delta = \sqrt{18\lambda/\eta} = \sqrt{27\lambda\left(J_\pm + J_{zz}/2\right)} \approx 0.02\ {\rm meV}. \tag{11}$$

This is below the 0.09 meV resolution of the inelastic neutron scattering data reported in Ref. 11, but is certainly experimentally accessible. The gap should also be manifest in a crossover from T^3 to activated magnetic specific heat for $T \lesssim \Delta/k_B$ (see Supp. Mat. [4]). A nuclear Schottky anomaly below 200 mK [28] makes a direct observation challenging, but extrapolation of specific heat data from Ref. 11 *does* suggest a gap of approximately the right magnitude (Supp. Mat. [4]).

From Eq. (10), one may also extract the lengths $\xi_\mu = \sqrt{\kappa_\mu/(18\lambda)}$, which describe the width of domain walls between symmetry-related ψ_2 states. We obtain $\xi_1 = 1.86\,a = 18.71$ Å and $\xi_2 = 2.44\,a = 24.55$ Å for $Er_2Ti_2O_7$. Confrontation of domain wall theory with experiments will be addressed in a future publication.

Relation to prior theoretical work: Early theoretical work had conjectured the existence of order-by-disorder in $Er_2Ti_2O_7$, based upon a classical Heisenberg model with easy-plane single-ion anisotropy, which exhibits an *extensive* degeneracy [8, 9] very different from the $U(1)$ degeneracy discussed here. This model is microscopically inaccurate (as noted in Refs. 14 and 26), and moreover the extensive degeneracy obtained within it is not robust. The use of a general Hamiltonian, the finding of the robust degeneracy, and the extraction of the parameters of $Er_2Ti_2O_7$ are essential ingredients for the new and definitive conclusions we draw in this work.

Discussion: The measurement of the gap via neutrons or thermodynamics is a remaining experimental challenge, but higher resolution experiments are needed. Neutron scattering data on field-cooled materials which are expected to contain single domains, i.e. single α's, would allow a wonderful synergy of theory and experiment and show proof of high control on this interesting material. The interesting field evolution of the lineshape of the Bragg reflections [11] will be returned to in a future publication. We have achieved a conclusive and detailed understanding of the magnetism of $Er_2Ti_2O_7$, and most importantly shed light on a material where order-by-disorder physics is unambiguously at play.

After completion of this paper, a theoretical preprint [30] appeared, which reaches some of the same conclusions regarding $Er_2Ti_2O_7$.

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