Phase Transition and Thermal Order-by-Disorder in the Pyrochlore Quantum Antiferromagnet 
$\text{Er}_2\text{Ti}_2\text{O}_7$: A High-Temperature Series Expansion Study

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Several rare earth magnetic pyrochlore materials are well modeled by a spin-$1/2$ quantum Hamiltonian with anisotropic exchange parameters $J_s$. For the $\text{Er}_2\text{Ti}_2\text{O}_7$ material, the $J_s$ were recently determined from high-field inelastic neutron scattering measurements. Here, we perform high-temperature ($T$) series expansions to compute the thermodynamic properties of this material using these $J_s$. Comparison with experimental data show that the model describes the material very well including the finite temperature phase transition to an ordered phase at $T_c \approx 1.2$ K. We show that high temperature expansions give identical results for different $q=0_{xy}$ order parameter susceptibilities up to $8^{th}$ order in $\beta \equiv 1/T$ (presumably to all orders in $\beta$). Conversely, a non-linear susceptibility related to the $6^{th}$ power of the order parameter reveals a thermal order-by-disorder selection of the same non-collinear $\psi_2$ state as found in $\text{Er}_2\text{Ti}_2\text{O}_7$.

Order-by-disorder (ObD) is a beautiful concept of central importance in the field of frustrated magnetism. Saddled with large accidental degeneracies, a subset of states, those that support the largest quantum and/or thermal fluctuations, may be selected to form true long-range order, thus turning on its head the conventional wisdom of “less fluctuations lead to more order”. While ObD has been discussed theoretically for over thirty years, and proposed to be at play in a number of experimental settings, most recently in cold atom systems, convincing demonstrations of ObD in real materials have remained scarce. The main reason for the paucity of confirmed ObD material examplars is that the classical degeneracies are typically not sufficiently symmetry-protected to rule out that some weak energetic perturbations are responsible for stabilizing the observed long-range order. An exception is the long-range order found in the $XY$ pyrochlore antiferromagnet $\text{Er}_2\text{Ti}_2\text{O}_7$. Two groups have recently put forward a strong case for a robust highly protected classical degeneracy in that system, hence making the case for ObD much more compelling than in any previous examples.

FIG. 1: The pyrochlore lattice can be described as a face-centered cubic lattice of elementary tetrahedra units. In $\psi_2$ (left) and $\psi_3$ (right), each elementary tetrahedron has the shown spin configuration with moments along the local $x$ and $y$ axis for $\psi_2$ and $\psi_3$, respectively.

In an $XY$ pyrochlore such as $\text{Er}_2\text{Ti}_2\text{O}_7$, the ordered moments lie on average in an $xy$ plane perpendicular to their local [111] cubic direction. At the classical level, energetics further require a vanishing net magnetic moment on each elementary tetrahedron of the pyrochlore lattice. Particularly interesting is the fact that among all classically degenerate ground states that satisfy such zero tetrahedral moment configuration, the material orders at a critical temperature $T_c \approx 1.2$ K in a ground state that breaks a discrete symmetry within the local [111] $xy$ plane – the so-called $\psi_2$ basis state of the $\Gamma_5$ irreducible representation (see Fig. 1). Since the original determination of the long-range order in $\text{Er}_2\text{Ti}_2\text{O}_7$, two rather puzzling questions had been identified: Firstly, how could the system order into a state that does not minimize the dipolar interactions, the so-called...
Palmer-Chalker state \([10]\) which has each spin in its local \(xy\) plane? Secondly, what mechanism may lead to the \(\psi_2\) selection, as opposed to the other \(\psi_3\) basis vector of the two-dimensional \(T_5\) manifold (see Fig. 1), or even an arbitrary superposition of \(\psi_2\) and \(\psi_3\) arising from a spontaneous \(XY\) (\(U(1)\)) global symmetry breaking?

Earlier studies had shown thermal \([6, 11, 12]\) and quantum \([12]\) ObD selecting a \(\psi_2\) state in a simplified pyrochlore antiferromagnetic XY model. More recent work found that anisotropic exchange can efficiently compete with dipolar interactions and lower the energy of \(T_5\) below that of the Palmer-Chalker state. Building on these results, Savary et al. \([5]\) showed that the classical degeneracies within \(T_5\) are in fact immune to anisotropic bilinear spin-spin interactions of arbitrary form and range, leaving quantum ObD (q-ObD) as essentially \([13]\) the only plausible mechanism explaining the \(\psi_2\) low-temperature state in \(\text{Er}_2\text{Ti}_2\text{O}_7\). A similar conclusion was reached in Ref. \([9]\). The possible occurence of ObD in \(\text{Er}_2\text{Ti}_2\text{O}_7\) represents a potentially significant result in the field of highly frustrated magnetism.

While the arguments of Ref. \([5]\) as per the symmetry-protection of degeneracy are compelling, there is still reason to worry whether the ordering mechanism in \(\text{Er}_2\text{Ti}_2\text{O}_7\) has indeed been fully unveiled. In particular, one may ask whether the model of Ref. \([5]\) describes accurately the thermodynamic behavior of \(\text{Er}_2\text{Ti}_2\text{O}_7\) close to the transition and predict a \(T_c \sim 1.2\) K in accord with experiment. For example, since this was not investigated in Ref. \([5]\), a concern one might have is whether the model, for ignoring the long-range part of the dipole-dipole interactions \([15]\) and other perturbations, does display a thermal ObD at \(T_\xi\) in the correct \(\psi_2\) state, rather than \(\psi_3\), which would then be inconsistent with experiments. \([16]\) Conversely, one may ask whether the experimentally observed \(\psi_2\) state at low \(T\) is the true ground state of the material or a metastable relic of the thermal ObD at \(T_\xi\). \([17]\) Finally, the recent observation that there exists a tendency for rare-earth ions (e.g. \(R=\text{Er}^{3+}\)) in \(\text{R}_2\text{Ti}_2\text{O}_7\) pyrochlores to occupy the \(T_5^{4+}\) site at the 1% level, \([18]\) hence generating effective random magnetic interactions, also raises concerns whether a plausible q-ObD at low temperatures smoothly merges to its thermal variant at \(T_c\).

The concerns above can only be alleviated by directly addressing, as we do in this paper, whether the model of Ref. \([5]\) describes well the thermodynamic behavior of \(\text{Er}_2\text{Ti}_2\text{O}_7\) above \(T_c\). To do so, we use high-temperature expansions (HTE) and crystal-field theory to study the magnetic specific heat and susceptibility of the model. We also calculate order-parameter susceptibilities for \(\psi_2\) and \(\psi_3\), finding that the model displays a continuous phase transition at a \(T_c \approx 1.2\) K close to the experimental value. By calculating a non-linear susceptibility, we show that \(\psi_2\) order is indeed selected by thermal ObD. These results imply that the long-range part of the dipolar interactions neglected in Ref. \([5]\) are not important above \(T_c\). \([15]\) and that the model of Ref. \([5]\) is quantitatively accurate. We are thus rather confident that ObD, both thermal and quantum, cooperate in \(\text{Er}_2\text{Ti}_2\text{O}_7\) to select \(\psi_2\) over the whole temperature range \(0 < T \leq T_c\).

Model & method — In a number of pyrochlore oxides \([19]\), the single-ion crystal-field magnetic doublet ground state is separated from the lowest excited crystal-field energy level by an energy gap \(\Delta\) that is large compared to the microscopic interactions, \(\mathcal{H}_{\text{mic}}\), between the ions. This is the case for \(\text{Er}_2\text{Ti}_2\text{O}_7\) for which \(\mathcal{H}_{\text{mic}} \sim 1\) K while \(\Delta \approx 75\) K. In such a case, one can use an effective spin-1/2 Hamiltonian \(\mathcal{H}\) with bilinear anisotropic couplings, \(J_s\), to describe the interactions between ions, and where \(\mathcal{H}\) is the projection of \(\mathcal{H}_{\text{mic}}\) onto the Hilbert space spanned by the single-ion ground doublets. On symmetry grounds, the nearest-neighbor \(\mathcal{H}\) can be parametrized by four exchange parameters as follows:

\[
\mathcal{H} = \sum_{\langle i,j \rangle} \left\{ J_{zz} S_i^z S_j^z - J_{\pm} (S_i^z S_j^+ + S_i^- S_j^+) + J_{\pm}[\gamma_{ij} S_i^+ S_j^z + \gamma_{ij}^* S_i^- S_j^-] + J_{\pm}[\zeta S_i^+ (S_j^- + \zeta S_j^+) + i \leftrightarrow j] \right\}
\]

Here, \(\langle i, j \rangle\) refers to nearest-neighbor sites of the pyrochlore lattice, \(\gamma_{ij}\) is a \(4 \times 4\) complex unimodular matrix, and \(\zeta = -\gamma^*\) \([5, 20]\). The \(\hat{z}\) quantization axis is along the local \([111]\) direction, and \(\pm\) refers to the two orthogonal local directions. The \(J_s\) were determined from fits to inelastic neutron scattering spectra in the field polarized state. \([5, 21]\) The magnetic properties of the system are described by the Zeeman Hamiltonian, \(\mathcal{H}_Z = -g_l \mu_B \sum_i J_i \cdot \vec{B}\) added to \(\mathcal{H}\), where \(J\) is the \(J = 15/2\) angular momentum operator of \(\text{Er}^{3+}\), \(\vec{B}\) is the applied magnetic field, \(\mu_B\) is the Bohr magneton and \(g_l = 6/5\) is the \(\text{Er}^{3+}\) Landé factor. \([22]\) In this paper we investigate the thermodynamic properties of \(\mathcal{H}\) above and near \(T_c\), using HTE. \([23]\)

We have computed series for the following quantities: (1) log of the partition function, \(\ln Z\), from which heat capacity and entropy are readily calculated; (2) uniform susceptibility as a linear response to a static applied external magnetic field; (3) linear order parameter susceptibilities, \(\chi_{xx}\) and \(\chi_{yy}\), corresponding to \(\psi_2\) and \(\psi_3\) order, respectively; and (4) non-linear (4\textsuperscript{th} and 6\textsuperscript{th} order) order parameter cumulants associated with \(\psi_2\) and \(\psi_3\) long-range order. We discuss below the reason for calculating non-linear susceptibilities from these cumulants. \([17]\)

Demonstrating the validity of \(\mathcal{H}\) — We first show evidence that the Hamiltonian \([1]\) is consistent with a phase transition to long-range order in the \(xy\) components of the spins at a critical temperature \(T_c \sim 1.2\) K. To do so, we calculate high temperature series expansions for the \(xy\) order-parameter susceptibilities. We apply a field along the local \(x\) \((y)\)-axis at all sites, and calculate the linear response order-parameter susceptibility, \(\chi_{xx}(\chi_{yy})\). Detailed expressions can be found in the supplementary material \([17]\). As discussed in Refs. \([5, 9]\), there is an emergent continuous symmetry in the model \([1]\), which is only weakly lifted by higher order effects beyond classical ground state energetics. In the notation of Ref. \([5]\), this classical degeneracy can be parameterized by a continuous angle \(\alpha\). Then, \(\chi_{xx}\) is the susceptibility for \(\alpha = 0\) order (i.e. \(\psi_2\) order) while \(\chi_{yy}\) is the
susceptibility for $\alpha = \pi/6$ order (i.e. $\psi_3$ order). We find that the two linear susceptibilities have identical high temperature series expansions to the order calculated ($8^{th}$ order in $\beta$). We believe that this result is true to all orders and the selection of order within the $\Gamma_5$ manifold must therefore only be manifest in non-linear order parameter susceptibilities. We return to this matter later. We study the singularities of the order-parameter susceptibility using d-log Padé approximants. Various estimated $T_c$ and critical exponents $\gamma$ from near diagonal d-log Padé values, expressed in the form of $(L, M; T_c, \gamma)$ sets, are $(3, 4; 1.26, 1.21)$, $(4, 3; 1.25, 1.71)$, $(3, 3; 1.33, 1.19)$ and $(2, 4; 1.28, 1.14)$ where $T_c$ is in Kelvin. Although the convergence is not excellent for this short series, we nevertheless conclude that the transition temperature is $T_c = 1.2 \pm 0.1$ K. Given the large uncertainty in $T_c$ we cannot make a reliable estimate for $\gamma$, but its $\gamma = 1.3 \pm 0.4$ value is consistent with $\gamma$ values known for 3-dimensional spin models. A plot of the order parameter susceptibility ($\chi_{xx} = \chi_{yy}$) versus temperature is shown in the inset of Fig. 2.

Next, we turn to a calculation of the specific heat, $C(T)$, and its comparison with experiments. We have calculated specific heat using both Numerical Linked Cluster (NLC) methods and HTE. The two methods agree well at $T > 2$ K. At lower temperatures, the HTE method is better as it allows us to analyze the behavior near the phase transition, where the correlation length diverges. Since we expect the system to display a three-dimensional $XY$ universality class, for which the specific heat exponent $\alpha$ is known to be very close to zero, we bias the analysis of the specific heat series to have a log singularity at $T_c$. The biased analysis shows good convergence with several approximants found to be very close to each other. A representative plot is shown together with experimental data in Fig. 2 where an excellent agreement with experimental data is seen. The phonon contributions are clearly seen to be negligible below 2 K. The magnetic entropy above $T_c$ can be found in the supplementary material. Its value at $T_c$ is reduced from the infinite temperature value by less than 50 percent, not atypical of 3-dimensional critical points.

We now turn to the uniform magnetic susceptibility, which has been measured up to 300 K. As shown in Fig. 4, this data shows a crossover from a high temperature Curie constant of $11.5$ emu/mol·K to a low temperature Curie constant of $2.48$ emu/mol·K, reflecting the evolution of the material from a $J = 15/2$ system to an effective spin-$1/2$ system. To understand this susceptibility data, we use HTE to calculate the susceptibility for the effective spin-$1/2$ model with $g_{zz}$ and $g_{zz}$ $g$-tensor components from Ref. [5], but also the full single-ion susceptibility, $\chi_{s,i}$, obtained by including all the crystal-field states of the crystal-field Hamiltonian of Er$_2$Ti$_2$O$_7$. The latter is obtained by treating the infinitesimal magnetic field $B$ that couples to the non-interacting rare-earth ion with second order (degenerate) perturbation theory. The single-ion susceptibility ($\chi_{s,i}$) then takes

![Figure 2: Thermodynamic behavior of model compared to experimental data. The main panel shows specific heat data for Er$_2$Ti$_2$O$_7$ compared with Padé approximants for the high temperature series expansions biased to have a logarithmic singularity at $T_c$. The experimental data are from Dalmas de Réotier et al. and Sosin et al. The inset shows plots of the order parameter susceptibility ($\chi_{xx} = \chi_{yy}$) calculated from high temperature expansions for various dlog Padé approximants (see text).](image-url)
the form:

\[ \chi_{\text{s.i.}} = gL^2 \mu_0^2 \mu_B^2 N_A \sum_n \beta [E_n^{(1)}]^2 e^{-\beta E_n^{(0)}} e^{-\beta E_n^{(0)}}. \]

(2)

Here \( E_n^{(0)} \) is the energy of the \( n \)-th state of \( H_{\text{CF}} \) while \( E_n^{(1)} \) and \( E_n^{(2)} \) are the first and second order perturbation theory coefficient of the energy of the \( n \)th state, respectively. [30, 31] \( N_A \) is the Avogadro number and \( \mu_0 \) the vacuum permeability.

The inset of Fig. 3(a) shows a comparison of the measured susceptibility with \( \chi_{\text{s.i.}} \). The agreement at high temperatures is apparent. The increasing disagreement between the experimental \( \chi \) and the calculated \( \chi_{\text{s.i.}} \) as \( T \) is reduced is caused by the progressive development of antiferromagnetic correlations which decrease the uniform susceptibility. The main plot shows that below about 70 K, \( \chi_{\text{s.i.}} \) deviates significantly from the measured values. Also shown in Fig. 3(a) and Fig. 3(b) are comparisons with the susceptibility calculated by HTE for the projected spin-1/2 model (1) taken alone. The latter saturates to a Curie law \( C_{\text{HTE}}/T \) form with \( C_{\text{HTE}} = 2.48 \) emu/mol · K at high temperatures. The HTE expansion considers AF correlations within...
the low-energy Hilbert space spanned by the single-ion crystal-field doublets of interacting Er$^{3+}$ ions. These HTE calculations ignore the residual $T \lesssim 10$ K temperature-independent contribution coming from the excited crystal-field states, which is the so-called van Vleck susceptibility, $\chi_{vV}$. [30, 31] To compare experimental data with model calculations, we thus need to add $\chi_{vV}$ to the HTE calculation results. As seen in Fig. 4(b), one obtains a very good agreement with the experimental data once $\chi_{vV}$ is added.

**Thermal ObD into $\psi_2$** — Having demonstrated that the model in Eq. (1) describes the thermodynamic properties of the material above $T_c$, we now turn to the central question of thermal ObD at $T_c$. We have already shown that the linear order-parameter susceptibility fails to distinguish between $\psi_2$ and $\psi_3$ order upon approaching $T_c$ from the paramagnetic phase. To further address this issue, we need to calculate non-linear order-parameter susceptibilities constructed from equal-time 4th and 6th power cumulants of the $\psi_2$ and $\psi_3$ order parameters in HTE. We find that the 4th power cumulant is also identical for the two cases. However, the 6th power of the order parameter does distinguish between $\psi_2$ and $\psi_3$ order (see Table VI in the supplementary materials [17]).

The necessity to compute a non-linear susceptibility that is 6th order in the order-parameter to reveal the selection of $\psi_2$ vs $\psi_3$ can be understood on the basis that a 6th order effective “potential”, $V(\psi) \sim g_\delta \cos(6\psi)$, where $g_\delta < 0$ and $g_\delta > 0$ selects $\psi_2$ and $\psi_3$, respectively, in the Ginzburg-Landau free-energy is dynamically generated by thermal and quantum fluctuations. [5, 13] Starting at order $\beta^4$, the 6th non-linear order susceptibility for $\psi_2$ order (or $\alpha = 0$) gets larger than for $\psi_3$ for every $\beta^\alpha (\alpha \geq 4)$ order considered. [17] This 6th order susceptibility exposes a thermal order-by-disorder that coincides with the pattern of order selected at $T = T_c$ in the works of Savary et al. [5] and Zhitomirsky et al. [9] (whose model is slightly different from the one we study).

**Conclusion** — We have shown that the nearest-neighbor spin Hamiltonian [1], with exchange parameters determined from inelastic neutron scattering, [5] describes the thermodynamic properties of Er$_2$Ti$_2$O$_7$ at $T > T_c$, including the continuous phase transition at $T_c$ rather adequately. This was demonstrated through detailed comparison of calculated and experimental specific heat ($C(T)$) and uniform susceptibility ($\chi(T)$) data. While the nearest-neighbor part of the dipolar interactions is implicitly incorporated in the model, [15] it lacks such terms beyond nearest neighbors. In spite of that, the thermodynamic properties are described quite well. Similar conclusions were recently reached about a nearest-neighbor model determined by inelastic neutron scattering for the material Yb$_2$Ti$_2$O$_7$ [20, 25, 26].

We have also shown that in the paramagnetic phase, the linear order-parameter susceptibility does not reveal the lifting of the $\Gamma_5$ manifold degeneracy. The selection of $\psi_2$ order is only evinced through a non-linear susceptibility with 6th order in the order-parameter. The thermal order-by-disorder identified in this paper was found to occur in the $\psi_2$ state, in agreement with experiments [4, 5] and with the quantum order-by-disorder calculations of Refs. [5, 3]. We thus conclude that the material Er$_2$Ti$_2$O$_7$ presents a unique and convincing case of co-operating quantum and thermal order-by-disorder in a frustrated quantum antiferromagnet.

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It is possible in principle to have a different low-temperature state stabilized by q-ObD than the state found at $T \lesssim T_c$ that is selected by thermal ObD. For example, a double-transition sequence paramagnetic $\rightarrow \psi_2 \rightarrow \psi_3$ is observed in a classical Heisenberg pyrochlore antiferromagnet model with “indirect” Dzyaloshinskii-Moriya interactions. G.-W. Chern, arXiv:1008.3038 (2010).

See Supplementary Material.

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The numerical values of those $J_s$ couplings are, (in Kelvin): $J_\pm = 0.754 \pm 0.087$, $J_{\pm\pm} = 0.487 \pm 0.058$, $J_{zz} = -0.290 \pm 0.21$ and $J_{z\pm} = -0.102 \pm 0.18$. The two largest couplings are of the XY type and the physics is thus very different from spin ice (see for example Ref. [20]).

The components of $\mathbf{J}$ entering in $\mathcal{H}_Z$ projected in the ground doublet are expressed as $J^{\alpha}_{\mathbf{i}} = g_{\alpha\beta}S^{\beta}_{\mathbf{i}}$ where $\alpha, \beta$ are cartesian components and sum over repeated indices is implied. $g_{\alpha\beta}$ are the elements of the $g$-tensor with principal axes along the local $x, y$ and $z$ directions with eigenvalues $g_{xx} \equiv g_{yy} = 5.97$ and $g_{zz} = 2.45$ from Ref. [5].

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The addition of pseudo-dipolar or indirect Dzyaloshinskii-Moriya interactions, such as those considered in Ref. [13], renormalize the critical value of the magnetostatic dipolar interaction at which thermal ObD to $\psi_2$ occurs in Ref. [12] despite the ground state being Palmer-Chalker. [10]

A Monte Carlo study of a classical Heisenberg antiferromagnet model that interpolates between a face-centered cubic lattice and a pyrochlore found that the thermal order-by-disorder always overcomes the energetic selection down to the lowest temperature. [C. Pinettes, B. Canals, and C. Lacroix, Phys. Rev. B 66, 024422 (2002).]

We thank B. Gaulin, K. Ross and J. Ruff and K. Rule for correspondence on this matter.
SUPPLEMENTAL MATERIAL

This section provides supplemental material to the main part of our paper. Firstly, we discuss the hypothetical situation when the thermal order-by-disorder can lead to a different long-range ordered state than the quantum order-by-disorder. Secondly, we provide some details regarding the high-temperature series expansion, in particular in regards to the order parameter linear and non-linear susceptibilities. Then we show the results for the temperature dependence of the magnetic entropy, $S(T)$, corresponding to the magnetic specific heat $C(T) =TdS/dT$ presented in the body of the paper. Finally, we provide tables for the high-temperature series expansion of various quantities of interest and referred to in the main text.

Metastability of States Selected by Thermal Order-by-Disorder

One may ask whether the long-range ordered state that is selected at the critical temperature differs from the zero-temperature ground state selected by quantum fluctuations. In case, thermal and quantum ObD are different, there is a possibility of metastability of the thermal ObD state at low temperatures. Thus, the concern here has to do with the kinetics in the real material rather than thermodynamics. Unlike natural proteins, extensively degenerate systems may lack funneled free-energy landscapes. As a result, configuration-space pathways and dynamical access to states may play a role in the specific long-range ordered phases experimentally realized. Ref. [5] finds a zero-point energy stabilization ($\delta E_0$) of $\psi_2$ compared to $\psi_3$ of merely $\delta E_0 \sim 0.3 \text{ } \mu\text{eV}$ (a factor 1/30 of the reported smallest anisotropic exchange. [5]). One may then ask whether the neglected interactions beyond nearest neighbors, in particular the dipolar interactions of magnitude $10 \text{ } \mu\text{eV} \sim 30\delta E_0$, [15] may have instead led to a $\psi_3$ ground state via quantum ObD. Meanwhile, thermal ObD, not considered in Ref. [5], may in fact be responsible for a transition into $\psi_2$ at $T_c$, both in the material and in an amended version of the model of Ref. [5] that would incorporate interactions neglected therein. [16] Following such a thermal ObD into $\psi_2$ in the material, a lower temperature ordering into $\psi_3$, or even in the Palmer-Chalker state, may be dynamically inhibited, similar to what is found in Monte Carlo simulations of a pyrochlore $XY$ antiferromagnet with weak dipolar interactions. [12, 32, 33] In such a scenario, the model of Ref. [5] would seemingly predict the correct low-temperature state of $\text{Er}_2\text{Ti}_2\text{O}_7$ — but for the wrong reasons. To rule out the possibility of metastability of $\psi_2$ at low temperatures, one could cool down to a high-field phase and gradually lower the field at low temperatures to assess whether $\psi_2$ is still realized. To our knowledge, such an experiment has not been carried out. [34]

Notes on High Temperature Series Expansion for $\text{Er}_2\text{Ti}_2\text{O}_7$

We consider the Hamiltonian

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_Z + H_x + H_y,$$

(3)

Here $\mathcal{H}_e$ is the exchange Hamiltonian defined in terms of local spin variables and exchange constants $J_{zz}, J_{z\pm}, J_{\pm}$ and $J_{\pm\pm}$. The next term $\mathcal{H}_Z$ is the Zeeman term arising from the applied external field $B$ which, for a field along $[111]$, can be written in terms of local spin variables as

$$\mathcal{H}_Z = -B \left[ g_{zz}S_0^z - \frac{1}{3}g_{zz}(S_1^z + S_2^z + S_3^z) \right]$$

$$- \frac{2\sqrt{2}}{3}g_{xy}S_1^x + \frac{2\sqrt{2}}{3}g_{xy}(S_2^x + S_3^x) - \sqrt{2}g_{xy}(S_2^y - S_3^y)].$$

(4)

Here the subscripts 0, 1, 2 and 3 denote different sublattices and one needs to sum over all sites. The last two terms in the Hamiltonian are auxiliary field terms introduced for computational purposes.

$$H_x = -h_x \sum_i S_i^x$$

(5)

and

$$H_y = -h_y \sum_i S_i^y.$$  

(6)

All spins are defined in their local basis.
High temperature series expansions are calculated for the logarithm of the zero-field partition function $\ln (Z_0)$, with $Z_0$ given by

$$Z_0 = \text{Tr} \exp (-\beta H_e).$$  \hfill (7)

From $\ln (Z_0)$, the entropy and specific heat series follow by simple differentiation.

The zero field uniform susceptibility is calculated as the second derivative of the free energy with respect to the applied external magnetic field, $B$, with $h_x = h_y = 0$.

$$\chi = -\frac{1}{N \beta} \frac{\partial^2}{\partial B^2} \ln (Z(B)) \bigg|_{B=0}. \hfill (8)$$

In calculating $\chi$ from this equation, one obtains only the contribution from the interacting ions assumed to be in their single-ion crystal field ground states and neglecting any contribution from excited crystal field levels. To reach quantitative agreement with experiments, one needs to incorporate the residual low-temperature contribution to the susceptibility coming from the excited crystal field states. This is the so-called van Vleck susceptibility. [30, 31]

To calculate the order-parameter susceptibility for $\psi_2$, we set $B = h_y = 0$ and calculate the second derivative of the free energy with respect to $h_x$.

$$\chi_{xx} = -\frac{1}{N \beta} \frac{\partial^2}{\partial h_x^2} \ln (Z(h_x)) \bigg|_{h_x=0} \hfill (9)$$

Similarly, for $\psi_3$, order we set $B = h_x = 0$ and take second derivative of free energy with respect to $h_y$.

$$\chi_{yy} = -\frac{1}{N \beta} \frac{\partial^2}{\partial h_y^2} \ln (Z(h_y)) \bigg|_{h_y=0} \hfill (10)$$

Evidently the series for $\chi_{xx}$ and $\chi_{yy}$ are identical.

Non-linear susceptibilities do not appear to have linked-cluster property. Instead, higher order zero field cumulants were calculated by Linked cluster expansion. These are analogous to equal-time structure factors (rather than zero-frequency susceptibilities). Setting $B = h_x = h_y = 0$, we define for $\alpha = x$ or $\alpha = y$ the order-parameter operator

$$M_\alpha \equiv \sum_i S_i^\alpha. \hfill (11)$$

Then, the cumulants, $C_{n,\alpha}$, are:

$$C_{2,\alpha} \equiv \langle M_\alpha^2 \rangle, \hfill (12)$$

$$C_{4,\alpha} \equiv \langle M_\alpha^4 \rangle - 3\langle M_\alpha^2 \rangle^2, \hfill (13)$$

and

$$C_{6,\alpha} \equiv \langle M_\alpha^6 \rangle - 15\langle M_\alpha^4 \rangle \langle M_\alpha^2 \rangle + 30\langle M_\alpha^2 \rangle^3. \hfill (14)$$

Here, one should note that the bare moments $\langle M_\alpha^4 \rangle$ and $\langle M_\alpha^6 \rangle$ do not satisfy linked cluster property but the $C_{n,\alpha}$ cumulants do. Since $\langle M_\alpha^2 \rangle$ and $\langle M_\alpha^4 \rangle$ are identical term by term, the difference $\langle M_\alpha^2 \rangle - \langle M_\alpha^6 \rangle$ is equal to the difference in the cumulants, $\langle C_{6,\alpha} \rangle = \langle C_{6,\alpha} \rangle$. 

The magnetic entropy function, $S(T)$, is shown in Fig. 4. We show the partial sums of the series from order 8 to order 12 as well as a few Pade approximants. At the critical temperature the entropy per mole in units of the perfect gas constant $R$ is around 0.4. In other words, it is reduced from the infinite temperature value, $S_\infty = R \ln(2)$, by less than fifty percent. This is not unusual compared to typical three-dimensional phase transitions to long-range order. This indicates that the system is not highly frustrated with the development of a strongly correlated regime above $T_c$. A similar conclusion was reached in Ref. [5] on the basis of a comparison between the mean-field critical temperature of the model, $T_{c}^{mf} \sim 2.3$ K, and the experimentally observed $T_c = 1.2$ K.

High-Temperature Series for Various Quantities

In this section, we provide the reader with tables of coefficients for the high-temperature series of quantities of interest. Unless stated otherwise, the high-temperature series of a quantity, $Q(T)$, as a function of inverse temperature $\beta \equiv 1/T$ (with temperature $T$ in Kelvin), is expressed in the form

$$Q(T) = \sum_{n=0}^{n_{\text{max}}} a_n \beta^n.$$  

(15)
TABLE I: \( \ln(Z) \) (per spin) series with only the two largest \( J \) (in Kelvin); \( J_{\pm} = 0.754 \), \( J_{\pm\pm} = 0.487 \), \( J_{zz} = 0 \) and \( J_{z\pm} = 0 \). The label \( E \pm m \) means \( 10^{\pm m} \).

| Order \( n \) | Expansion coefficient \( a_n \) |
|-------------|-----------------|
| 0           | +0.693147181 \( E +00 \) |
| 1           | +0.000000000 \( E +00 \) |
| 2           | +0.0604263750 \( E +00 \) |
| 3           | +0.802114625 \( E -01 \) |
| 4           | -0.218372147 \( E +00 \) |
| 5           | -0.863347964 \( E -01 \) |
| 6           | +0.158902388 \( E +00 \) |
| 7           | +0.120287973 \( E +00 \) |
| 8           | -0.958592054 \( E -01 \) |
| 9           | -0.118324998 \( E +00 \) |
| 10          | +0.361281401 \( E -01 \) |
| 11          | +0.728830750 \( E -01 \) |
| 12          | +0.335017563 \( E -01 \) |

TABLE II: \( \ln(Z) \) (per spin) series with all four \( J \) (in Kelvin); \( J_{\pm} = 0.754 \), \( J_{\pm\pm} = 0.487 \), \( J_{zz} = -0.290 \) and \( J_{z\pm} = -0.102 \). The label \( E \pm m \) means \( 10^{\pm m} \).

| Order \( n \) | Expansion coefficient \( a_n \) |
|-------------|-----------------|
| 0           | +0.693147181 \( E +00 \) |
| 1           | +0.000000000 \( E +00 \) |
| 2           | +0.0619951125 \( E +00 \) |
| 3           | +0.604908776 \( E -01 \) |
| 4           | -0.257221456 \( E +00 \) |
| 5           | -0.662731421 \( E -01 \) |
| 6           | +0.223356105 \( E +00 \) |
| 7           | +0.103109973 \( E +00 \) |
| 8           | -0.200436766 \( E +00 \) |
| 9           | -0.120572677 \( E +00 \) |
| 10          | +0.186373242 \( E +00 \) |
| 11          | +0.113320221 \( E +00 \) |
| 12          | -0.155050053 \( E +00 \) |

TABLE III: Order parameter susceptibility \( \chi_{xx} = \chi_{yy} \) per spin with all four \( J \) (in Kelvin); \( J_{\pm} = 0.754 \), \( J_{\pm\pm} = 0.487 \), \( J_{zz} = -0.290 \) and \( J_{z\pm} = -0.102 \). The label \( E \pm m \) means \( 10^{\pm m} \).

| Order \( n \) | Expansion coefficient \( a_n \) |
|-------------|-----------------|
| 0           | +0.250000000 \( E +00 \) |
| 1           | +0.565500000 \( E +00 \) |
| 2           | +0.856772872 \( E +00 \) |
| 3           | +0.105521359 \( E +01 \) |
| 4           | +0.130532942 \( E +01 \) |
| 5           | +0.181908741 \( E +01 \) |
| 6           | +0.253686031 \( E +01 \) |
| 7           | +0.320904312 \( E +01 \) |
| 8           | +0.386983904 \( E +01 \) |
TABLE IV: Second order order-parameter $C_{2,x}$ cumulant per spin with all four $J_s$ (in Kelvin); $J_{\pm} = 0.754$, $J_{\pm\pm} = 0.487$, $J_{zz} = -0.290$ and $J_{z\pm} = -0.102$. Each coefficient is the same for the second order $C_{2,y}$ cumulant to the last digit shown. The label $E \pm m$ means $10^{\pm m}$.

| Order $n$ | Expansion coefficient $a_n$ |
|-----------|----------------------------|
| 0         | +0.250000000000 $E +00$    |
| 1         | +0.565500000000 $E +00$    |
| 2         | +0.936030375000 $E +00$    |
| 3         | +0.107532105831 $E +01$    |
| 4         | +0.12306642254 $E +01$     |
| 5         | +0.179517883700 $E +01$    |
| 6         | +0.263550433751 $E +01$    |
| 7         | +0.325196289151 $E +01$    |
| 8         | +0.374996212319 $E +01$    |

TABLE V: Fourth order order-parameter $C_{4,x}$ cumulant per spin with all four $J_s$ (in Kelvin); $J_{\pm} = 0.754$, $J_{\pm\pm} = 0.487$, $J_{zz} = -0.290$ and $J_{z\pm} = -0.102$. Each coefficient is the same for fourth order $C_{4,y}$ cumulant to the last digit shown. The label $E \pm m$ means $10^{\pm m}$.

| Order $n$ | Expansion coefficient $a_n$ |
|-----------|----------------------------|
| 0         | -0.125000000000 $E +00$    |
| 1         | -0.113100000000 $E +01$    |
| 2         | -0.532304971875 $E +01$    |
| 3         | -0.172896459338 $E +02$    |
| 4         | -0.43748147843 $E +02$     |
| 5         | -0.961820514195 $E +02$    |
| 6         | -0.196495861437 $E +03$    |
| 7         | -0.381391503061 $E +03$    |
| 8         | -0.704597614446 $E +03$    |

TABLE VI: Sixth order order-parameter $C_{6,x}$ cumulant and $C_{6,y}$ cumulant per spin with all four $J_s$ (in Kelvin); $J_{\pm} = 0.754$, $J_{\pm\pm} = 0.487$, $J_{zz} = -0.290$ and $J_{z\pm} = -0.102$. The label $E \pm m$ means $10^{\pm m}$. The last column shows the difference between the two cumulants. Note the increasing difference with increasing $\beta^n$ order.

| Order $n$ | Expansion coefficient $a_n$ ($C_{6,x}$-cumulant) | Expansion coefficient $a_n$ ($C_{6,y}$-cumulant) | Difference |
|-----------|-----------------------------------------------|-----------------------------------------------|------------|
| 0         | +0.250000000000 $E +00$                        | +0.250000000000 $E +00$                        |            |
| 1         | +0.480675000000 $E +01$                        | +0.480675000000 $E +01$                        |            |
| 2         | +0.42466147875 $E +02$                         | +0.42466147875 $E +02$                        |            |
| 3         | +0.243939243681 $E +03$                        | +0.243939243681 $E +03$                        |            |
| 4         | +0.104714406827 $E +04$                        | +0.104714406827 $E +04$                        | +0.00130123 |
| 5         | +0.36600012391 $E +04$                        | +0.365997458485 $E +04$                        | +0.02553906 |
| 6         | +0.11053363334 $E +05$                        | +0.110532277550 $E +05$                        | +0.1085784  |
| 7         | +0.300260377288 $E +05$                        | +0.300256729522 $E +05$                        | +0.3647766  |
| 8         | +0.752398706312 $E +05$                        | +0.752389652239 $E +05$                        | +0.9054073  |
TABLE VII: Uniform susceptibility series per spin with all four $J_s$ (in Kelvin); $J_{\pm} = 0.754$, $J_{\pm\pm} = 0.487$, $J_{zz} = -0.290$ and $J_{z\pm} = -0.102$. The $g$-tensor values are $g_\perp = 6.05$ and $g_{zz} = 2.5$. The infinitesimal applied field is along the [111] cubic direction. The label $E \pm m$ means $10^{\pm m}$. To convert into a susceptibility in emu/mol·K units, the given values have to be multiplied by $N_\Lambda \mu_B^2/k_B \approx 0.375$ where $N_\Lambda$, $\mu_B$ and $k_B$ are the Avogadro number, Bohr magneton and Boltzmann constant, respectively, all expressed in CGS units.

| Order $n$ | Expansion coefficient $a_n$ |
|-----------|-----------------------------|
| 0         | $+0.662125000 \ E +01$     |
| 1         | $-0.988978150 \ E +01$     |
| 2         | $+0.683472045 \ E +01$     |
| 3         | $-0.163940184 \ E +01$     |
| 4         | $+0.131075702 \ E +01$     |
| 5         | $-0.379184574 \ E +01$     |
| 6         | $+0.103613852 \ E +01$     |