

Dy₂Ti₂O₇ Spin Ice: A Test Case for Emergent Clusters in a Frustrated Magnet

Taras Yavors'kii,¹ Tom Fennell,² Michel J. P. Gingras,^{1,3} and Steven T. Bramwell^{2,4}

¹*Department of Physics and Astronomy, University of Waterloo, Ontario, N2L 3G1, Canada*

²*London Center for Nanotechnology, 17-19 Gordon Street, London, WC1H 0AH, United Kingdom*

³*Department of Physics and Astronomy, University of Canterbury, Private Bag 4800, Christchurch, New Zealand*

⁴*Department of Chemistry, University College of London, London, WC1H 0AJ, United Kingdom*

(Received 23 July 2007; revised manuscript received 7 May 2008; published 16 July 2008)

Dy₂Ti₂O₇ is a geometrically frustrated magnetic material with a strongly correlated spin ice regime that extends from 1 K down to as low as 60 mK. The diffuse elastic neutron scattering intensities in the spin ice regime can be remarkably well described by a phenomenological model of weakly interacting hexagonal spin clusters, as invoked in other geometrically frustrated magnets. We present a highly refined microscopic theory of Dy₂Ti₂O₇ that includes long-range dipolar and exchange interactions to third nearest neighbors and which demonstrates that the clusters are purely fictitious in this material. The seeming emergence of composite spin clusters and their associated scattering pattern is instead an indicator of fine-tuning of ancillary correlations within a strongly correlated state.

DOI: 10.1103/PhysRevLett.101.037204

PACS numbers: 75.10.Hk, 05.50.+q, 75.40.Cx, 75.40.Mg

Geometrically frustrated magnetic materials have in recent years furnished many new paradigms for the exploration of novel condensed states of matter. Examples include spin ice behavior [1–11], collective paramagnetism or spin liquid behavior [12], spin glassiness in stoichiometrically pure materials [13] and an anomalous Hall effect [14]. Frustration is detrimental to the development of conventional periodic arrangements of magnetic moments at low temperatures [15]. As a consequence, at temperatures that are small compared to the scale of the leading interactions, highly frustrated systems typically form collective dynamical states [16]. Most commonly, the massive degeneracy of such “cooperative paramagnetic” states is ultimately resolved by specific material-dependent perturbative effects. This is the origin of the diversity of experimentally observed phenomena [15].

Among the many systems that exhibit geometric frustration [15], all the above phenomena have been observed in materials with magnetic moments (spins) residing on a network of corner sharing tetrahedra, or pyrochlore lattice. This arrangement is found, for example, in the rare earth titanates $R_2\text{Ti}_2\text{O}_7$, with magnetic rare earth ions ($R^{3+} = \text{Ho}, \text{Dy} \dots$), and in the spinels like $AB_2\text{O}_4$ ($A = \text{Zn}, \text{Cd}$), with magnetic transition metal ions ($B = \text{Fe}^{3+}, \text{Cr}^{3+}$). In this paper we are concerned with Dy₂Ti₂O₇, a spin ice [1–3]. In this material, the local spin correlations are characterized by the ice rule: two spins point in and two spins point out of every tetrahedron [1–3]. The strongly correlated spin ice regime (analogous to the spin liquid or collective paramagnetic regime in geometrically frustrated antiferromagnets [16]) extends from 1 K down to the lowest measured temperatures (≈ 100 mK).

Given the many phenomenologies exhibited by frustrated materials, the recent idea [17] that there may be an organizing principle that describes the spin correlations in

spin liquid states is very appealing. Using inelastic neutron scattering data, it was shown in Ref. [17] that the spatial correlations of magnetic excitations in the spinel ZnCr₂O₄ are well described by a model of strongly bound hexagonal spin clusters that are uncorrelated with respect to each other. Subsequently, similar evidence of such clusters was obtained in CdFe₂O₄ [18], CdCr₂O₄ [19] and Y_{0.5}Ca_{0.5}BaCo₄O₇ [20], lending weight to the idea that the clusters may effectively be emergent objects. In most cases it is numerically or analytically rather intractable to examine these systems by detailed microscopic calculations. However, Dy₂Ti₂O₇ [2] provides an exception, as we show here [21].

In Ref. [7], we and collaborators showed that the well-established microscopic “standard dipolar spin ice model” (s-DSM, defined below [3,22,23]) describes the spin correlations in the spin ice state of Dy₂Ti₂O₇ with only modest success. The original objective for the present study was to understand the reason for the differences between theory and experiment. To do so, we examined two models of the spin-spin correlations in Dy₂Ti₂O₇ by calculating the Fourier image, $I(\mathbf{q})$, of the spin correlation function and comparing it to the energy-integrated neutron scattering structure factor [7]. The Dy³⁺ ion in Dy₂Ti₂O₇ has a Kramers doublet as single-ion crystal-field ground state [24] that, for each site i , is well approximated by a classical Ising degree of freedom, $s_i = \pm 1$, defined along its local [111] trigonal axis \hat{z}_i [22]. We calculate $I(\mathbf{q})$ using [7]:

$$I(\mathbf{q}) = \frac{[f(l\mathbf{q})]^2}{N} \sum_{ij} \langle s_i s_j \rangle (\hat{z}_i^\perp \cdot \hat{z}_j^\perp) e^{i\mathbf{q} \cdot \mathbf{r}_{ij}}, \quad (1)$$

where $\langle \dots \rangle$ denote thermally averaged $\langle s_i s_j \rangle$ correlations between the Ising spins at sites i, j ; \hat{z}_i^\perp is the component of the quantization direction at site i perpendicular to the

scattering vector \mathbf{q} , N is the number of spins and $f(|\mathbf{q}|)$ is the Dy^{3+} magnetic form factor [25]. For comparison with experiment, $I(\mathbf{q})$ is adjusted by an overall scale factor and a slowly varying linear-in- $|\mathbf{q}|$ background. The experimental diffuse neutron scattering, measured in the elastic approximation in the (hhl) plane (from Ref. [7]), is shown in Fig. 1(a). As previously observed [7], in addition to structural Bragg peaks [e.g., (004), (222)] and bright broad

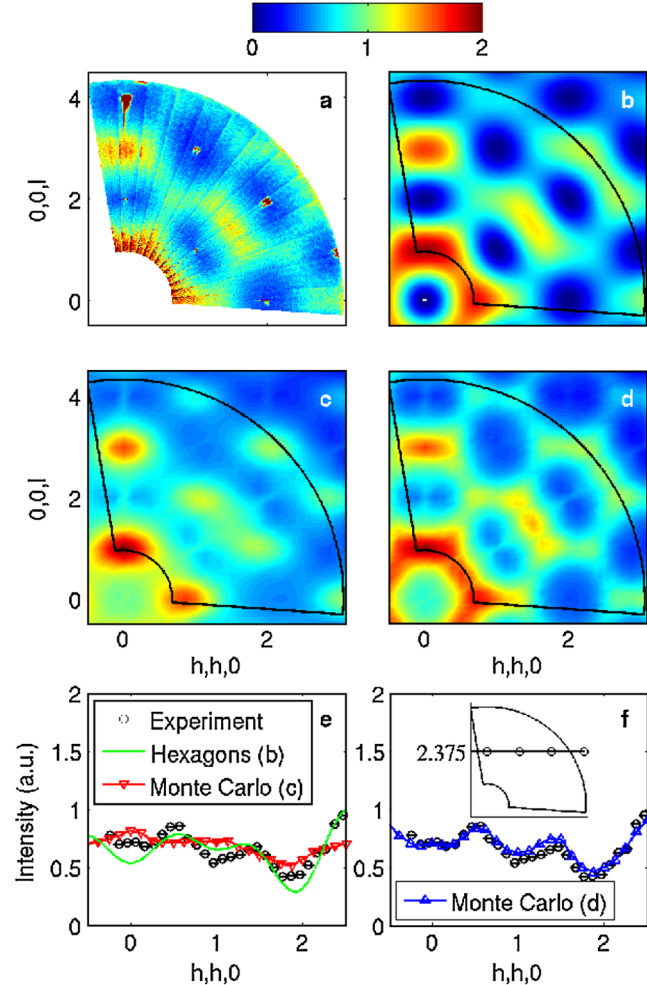


FIG. 1 (color online). Neutron scattering intensity $I(\mathbf{q})$ of $\text{Dy}_2\text{Ti}_2\text{O}_7$ as a function of the wave vector. (a) Experimental elastic scattering intensity at 300 mK [7] in the (hhl) planes of the reciprocal space is notably amassed along the hexagonal zone boundaries. (b) $I(\mathbf{q})$ calculated using the model of uncorrelated hexagonal spin clusters (see text). (c) $I(\mathbf{q})$ obtained from MC simulations on the s-DSM of $\text{Dy}_2\text{Ti}_2\text{O}_7$ [22] describes the main experimental features, but is inadequate in reproducing the ZBS [7]. (d) The g-DSM allows for an excellent match between the theoretical and experimental $I(\mathbf{q})$, and allows us to identify that correlations beyond 3rd nearest neighbors are the microscopic origin behind the ZBS. (e, f) Quantitative comparison of the experimental (a) and theoretical (b),(c),(d) data along a cut through the reciprocal space chosen to emphasize the mismatch with the s-DSM. Panels (c),(d),(e),(f) produced by MC simulations of $8192 = 8^3 \times 16$ spins.

features at (001), (003) and $(\frac{3}{2}, \frac{3}{2}, \frac{3}{2})$, the experimental $I(\mathbf{q})$ is further decorated by hexagonal loops of diffuse scattering running along the Brillouin zone boundaries.

The first model of correlations we examine is phenomenological and based on postulating an ansatz for $\langle s_i s_j \rangle$ in (1). We assume that $\langle s_i s_j \rangle$ can be viewed as generated by static clusters that remain uncorrelated between themselves. Each cluster is a zero-magnetization hexagonal loop of spins that circulate perpendicular to the loop normal. These clusters are the discrete equivalent of the “emergent” clusters used to describe the inelastic $I(\mathbf{q})$ in ZnCr_2O_4 [17] [see Fig. 1(c) in Ref. [17]]. Taking into account that all spins on a pyrochlore lattice can be grouped into nonoverlapping hexagons without breaking the ice rules, that hexagon normals have four possible orientations, and that each hexagon has two possible senses of “spin circulation” around the normal, $I(\mathbf{q})$ can then be calculated using Eq. (1). Figure 1(b) shows $I(\mathbf{q})$ calculated using the spin cluster scattering function. This model describes the experimental data quite well. The selection of hexagonal clusters as effective degrees of freedom in $\text{Dy}_2\text{Ti}_2\text{O}_7$ does not incorporate any microscopic information about the host material, and could be viewed as another example [17] of emergent composite spin clusters in frustrated systems.

The second approach we use to determine $\langle s_i s_j \rangle$ is microscopic. The s-DSM was previously shown to account fairly well for the spin ice phenomenology of $\text{Dy}_2\text{Ti}_2\text{O}_7$ [3,22,26]. It comprises the magnetostatic dipole interaction, which gives a ferromagnetic nearest-neighbor coupling, that competes with a weaker antiferromagnetic nearest-neighbor exchange interaction J_1 . Sufficiently strong antiferromagnetic J_1 would lead to long-range order [22,23]. It is the interplay between the properties of the spin ice manifold and the symmetry and long-range nature of the dipolar interaction that leads to a correlated spin ice state over an extended temperature range [22,23,27]. Surprisingly, the s-DSM is much less successful than the simple phenomenological cluster model at describing $I(\mathbf{q})$.

Monte Carlo (MC) simulations have shown [7] that the s-DSM correctly describes the location and relative intensity of the strong $I(\mathbf{q})$ features, but fails to reproduce the hexagonal zone boundary scattering (ZBS), Fig. 1(c). We interpret this as a sign that the s-DSM is incomplete and needs to be extended [11,28].

$\text{Dy}_2\text{Ti}_2\text{O}_7$ displays a number of phase transitions and other structured response in an applied magnetic field \mathbf{H} [2,4–6,8–11]. Independently of the disagreement between Figs. 1(a) and 1(c), the necessity to adjust the s-DSM was previously also suggested by the observation that, while it qualitatively explains the in-field transitions, the s-DSM does not correctly predict their temperatures [28], unless properly adjusted by perturbative exchange couplings beyond J_1 . Here, we consider a generalized dipolar spin ice model (g-DSM) of $\text{Dy}_2\text{Ti}_2\text{O}_7$ that includes second J_2 and third J_3 nearest-neighbor exchange couplings:

$$\mathcal{H} = \sum_{i>j} s_i s_j \left\{ \sum_{\nu=1}^3 J_\nu \delta_{r_{ij}, r_\nu} \hat{z}_i \cdot \hat{z}_j + D r_1^3 / r_{ij}^3 [\hat{z}_i \cdot \hat{z}_j - 3(\hat{z}_i \cdot \hat{r}_{ij})(\hat{z}_j \cdot \hat{r}_{ij})] \right\} - g \langle J^z \rangle \mu_B \sum_i s_i (\hat{z}_i \cdot \mathbf{H}). \quad (2)$$

Here, i, j span the sites of the Dy^{3+} ions, r_{ij} and \hat{r}_{ij} is the length and direction of the vector separation between spin pairs. $D = \mu_0 (\langle J^z \rangle g \mu_B)^2 / (4\pi r_1^3) = 1.3224 \text{ K}$ is the strength of the dipolar interaction at nearest-neighbor distance $r_1 = a\sqrt{2}/4$, as obtained from the estimate $\langle J^z \rangle = 7.40$ [29] within the ground state doublet of Dy^{3+} in $\text{Dy}_2\text{Ti}_2\text{O}_7$, and from the size $a = 10.124 \text{ \AA}$ [26] of the cubic unit cell of the material. $g = 4/3$ is the Dy^{3+} Landé factor, μ_B is the Bohr magneton, and J_ν is the exchange coupling of spins at distance r_ν . In reality, there should be two different 3rd nearest-neighbor exchange couplings. We take them equal, which, as shown below, provides a consistent description of $\text{Dy}_2\text{Ti}_2\text{O}_7$. By doing mean-field theory (MFT) calculations of $I(\mathbf{q})$ in the paramagnetic regime [30] we checked that the conclusions about $I(\mathbf{q})$ are not sensitive to $\sim 50\%$ deviations of the two J_3 from equality.

Rather extensive MC simulations were used to investigate whether the g-DSM can provide a consistent description of the phenomenology of $\text{Dy}_2\text{Ti}_2\text{O}_7$ both for $\mathbf{H} = 0$ [2,4,5] and $\mathbf{H} \neq 0$ [2,6,8–10] regimes. MC simulations were performed on system sizes of $1024 = 4^3 \times 16$ spins with periodic boundary conditions, treating the long-range dipolar interaction by the Ewald method [23]. For each set of parameters in (2) and each temperature, 10^5 MC steps per spin for equilibration followed by an additional 10^6 steps per spin for production were performed. The simulations exploited both single spin-flip and loop-update [23] Metropolis algorithms, the latter being a generalized algorithmic MC version of the dynamics of the hexagonal cluster degrees of freedom discussed above (cf. Fig. 1 [23]). Finite size effects were found to be insignificant for the discussion below.

Three groups of experimental data about $\text{Dy}_2\text{Ti}_2\text{O}_7$ are used to determine the J_ν in (2). First, we consider the temperature-driven ferromagnetic ordering of $\text{Dy}_2\text{Ti}_2\text{O}_7$ for \mathbf{H} nearly along the [112] direction [9,28]. For fixed D , the transition is controlled by J_3 only [28]. Mapping the MC critical temperature, obtained as location of the maximum in magnetic heat capacity C_m , to the experimental estimates of 0.34, 0.28(1), and 0.26(1) K, obtained by specific heat [2], susceptibility [9] and magnetization [10] measurements, we conclude that $0.019 \text{ K} \leq J_3 \leq 0.026 \text{ K}$. Second, we examine $C_m(T)$ data in $\mathbf{H} = 0$ [2,4,5] for constraining J_1, J_2 , as $C_m(T)$ is only weakly sensitive to the allowed small variation of J_3 . We determine optimal J_1, J_2 by minimizing the root mean square (rms) deviation σ of experimental vs theoretical temperature curves for $C_m(T)/T$. The function $\sigma(J_1, J_2)$ at $J_3 = 0.025 \text{ K}$ is plotted in Fig. 2 using Ref. [4] data. The two panels illustrate that $\sigma(J_1, J_2)$ has a stable minimum even if determined over two different temperature intervals. Third, we exploit an empirical equation $H_c = 0.90(1) + 0.08 T$,

$T \leq 0.36 \text{ K}$ [6,8] for the line of phase transitions in $\text{Dy}_2\text{Ti}_2\text{O}_7$ for \mathbf{H} along [111]. We obtain values of H_c at several temperatures as positions of maxima on MC $C_m(\mathbf{H})$ curves, and vary J_1 and J_2 to match the experimental $H_c(T)$. This, the above $\mathbf{H} = 0$ analysis, and an additional observation that at $\mathbf{H} = 0$ a magnetic phase transition, if any, can occur only at $T_c < 300 \text{ mK}$ [3,7] cf. Fig. 1(a), yields: $3.26 \text{ K} \leq J_1 \leq 3.53 \text{ K}$; $-0.20 \text{ K} \leq J_2 < 0 \text{ K}$. Our value for J_2 is consistent with the value $J_2 = -0.1 \text{ K}$ reported in Ref. [11] from fitting (2) with $D = 1.41 \text{ K}$, $J_1 = 3.72 \text{ K}$, $J_3 = 0.03 \text{ K}$ (Ref. [28]) to the experimental $C_m(\mathbf{H})$ for \mathbf{H} along [111].

To verify whether the experimental $I(\mathbf{q})$ in Fig. 1(a) can be described by (2), we perform MC simulations of the optimized g-DSM at 300 mK. We find that the g-DSM with J_ν couplings within the above allowed limits is consistent with the experimental scattering pattern in Fig. 1(a), but requires even stronger restriction on J_2 : $-0.16 \text{ K} \leq J_2 \leq -0.10 \text{ K}$. For instance, the theoretical pattern at $J_1 = 3.41 \text{ K}$, $J_2 = -0.14 \text{ K}$, $J_3 = 0.025 \text{ K}$ [Figs. 1(d) and 1(f)] reproduces the experimental one [Fig. 1(a)] extremely well. As seen from Figs. 1(c)–1(f), the small adjustments to the initial s-DSM [22] do result in a redistribution of the scattering response, with intensities that now capture correctly both major features of the experimental pattern, and the weaker ZBS. The characteristic features on the experimental $I(\mathbf{q})$ for $\text{Dy}_2\text{Ti}_2\text{O}_7$, first described above as arising from hexagonal spin clusters, can therefore be “straightforwardly” described within a conventional microscopic treatment of the static spin-spin correlation function [31].

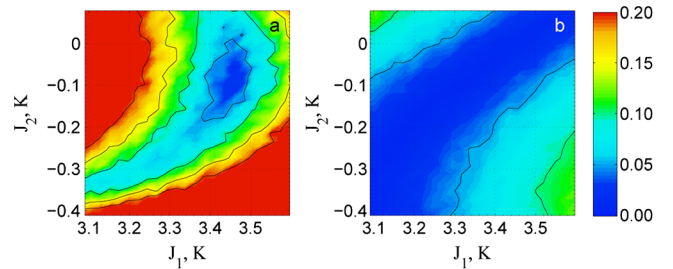


FIG. 2 (color online). rms deviation σ of Monte Carlo vs experimental [4] specific heat data in the $J_1 - J_2$ plane at fixed value of $J_3 = 0.025 \text{ K}$. The isolines are drawn at $\sigma = 0.05, 0.10, 0.15$ and $0.20 \text{ J mol}^{-1} \text{ K}^{-2}$ outward. The two functions σ [(a), obtained for the $T_1 = 0.7 \text{ K} - 1.49 \text{ K}$ temperature interval, and (b), for $T_2 = 1.5 \text{ K} - 2.8 \text{ K}$] yield candidate solutions (delineated by inner isolines) in overlapping parts of the $J_1 - J_2$ plane. The determination of the J_ν couplings in the Hamiltonian (2) of $\text{Dy}_2\text{Ti}_2\text{O}_7$ is obtained via a fitting to several bulk experimental thermodynamic data, akin to the procedure illustrated here (see text).

Having now a credible microscopic model in hand, are we able to explain the success of the phenomenological fit [Fig. 1(b)]? To answer this question, we examine the direct space $\langle s_i s_j \rangle$ correlations behind the reciprocal space patterns in Figs. 1(b)–1(d). We intimate that the picture of independent clusters is equivalent to a correlation function truncated beyond third nearest-neighbor distance (i.e., outside the hexagonal cluster). The $\langle s_i s_j \rangle$ obtained from MC simulations on both the s-DSM [Fig. 1(c)] and optimized g-DSM [Fig. 1(d)] are very similar at short distances. If truncated beyond third nearest-neighbor distance, the Fourier transform of each produces a pattern close to that of experiment [Fig. 1(a)]. We conclude that the difference between the two MC $I(\mathbf{q})$ patterns [Figs. 1(c) and 1(d)] is caused by correlations *beyond* third neighbors. For the tuned g-DSM, the long-range part strongly reinforces the ZBS arising from the short range part, contributing the *majority* of this scattering. This contradicts the notion of independent hexagons, which underlie the calculation of $I(\mathbf{q})$ in Fig. 1(b), since correlations between hexagons are of the same order as the correlations defining the hexagons. Thus, weakly interacting clusters are not an appropriate microscopic description of $\text{Dy}_2\text{Ti}_2\text{O}_7$, nor are they here an effective organizing principle. Rather, the ZBS is caused by subsidiary (J_2 and J_3) interactions that are largely inconsequential to the formation of the strongly correlated spin ice regime [22,23,27]. We further confirmed the fine-tuned nature of the ZBS using MFT to calculate $I(\mathbf{q})$ in the paramagnetic regime [30]. Finally, we note that independent hexagonal clusters, unlike the s-DSM and g-DSM, fail to predict the “pinch point” scattering characteristic of a spin ice manifold, which is discernible in the experiment.

We finally comment on the broader consequences that the observed complementarity of the phenomenological and microscopic interpretations of neutron scattering patterns might have for other systems. Our results support the idea expressed in Ref. [17] that clusterlike scattering (CLS) may be common among highly frustrated magnets and establish here a microscopic mechanism by which it can arise. However, by considering $\text{Dy}_2\text{Ti}_2\text{O}_7$ as a test case, we have shown that the CLS does not necessarily imply the emergence of “real” clusters [32], nor a new organizing principle. Instead, the CLS is the property of a strongly correlated liquidlike state and a consequence of the sensitivity of frustrated systems to perturbations [16]. Our study also shows how neutron scattering can allow one to fully interpret CLS provided sufficiently accurate data and a computationally tractable theoretical microscopic model are available.

We thank our collaborators in Ref. [7], particularly B. Fåk and O. Petrenko, for their role in obtaining the neutron data. We acknowledge useful discussions with C. Broholm, M. Enjalran, C. Henley, S.-H. Lee, H. Molavian, O. Tchernyshyov, and A.-M. Tremblay. Support for this work was provided by NSERC, the CRC

Program (Tier I, M. G.), the CFI, the OIT, and the CIFAR. M. G. acknowledges the U. of Canterbury (UC) for financial support and the hospitality of the Department of Physics and Astronomy at UC.

-
- [1] M. J. Harris *et al.*, Phys. Rev. Lett. **79**, 2554 (1997).
 - [2] A. P. Ramirez *et al.*, Nature (London) **399**, 333 (1999).
 - [3] S. T. Bramwell and M. J. P. Gingras, Science **294**, 1495 (2001).
 - [4] R. Higashinaka and Y. Maeno, Phys. Rev. B **68**, 014415 (2003).
 - [5] Z. Hiroi *et al.*, J. Phys. Soc. Jpn. **72**, 411 (2003).
 - [6] T. Sakakibara *et al.*, Phys. Rev. Lett. **90**, 207205 (2003).
 - [7] T. Fennell *et al.*, Phys. Rev. B **70**, 134408 (2004).
 - [8] H. Aoki *et al.*, J. Phys. Soc. Jpn. **73**, 2851 (2004).
 - [9] R. Higashinaka and Y. Maeno, Phys. Rev. Lett. **95**, 237208 (2005).
 - [10] H. Sato *et al.*, J. Phys. Condens. Matter **18**, L297 (2006).
 - [11] Y. Tabata *et al.*, Phys. Rev. Lett. **97**, 257205 (2006).
 - [12] J. S. Gardner *et al.*, Phys. Rev. Lett. **82**, 1012 (1999).
 - [13] B. D. Gaulin *et al.*, Phys. Rev. Lett. **69**, 3244 (1992).
 - [14] Y. Taguchi *et al.*, Science **291**, 2573 (2001).
 - [15] *Frustrated Spin Systems*, edited by H. T. Diep (World Scientific, Singapore, 2004); A. P. Ramirez, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier Science, Amsterdam, 2001), Vol. 13; J. E. Greedan, J. Alloys Compd. **408–412**, 444 (2006).
 - [16] J. Villain, Z. Phys. B **33**, 31 (1979).
 - [17] S.-H. Lee *et al.*, Nature (London) **418**, 856 (2002).
 - [18] K. Kamazawa *et al.*, Phys. Rev. B **70**, 024418 (2004).
 - [19] J.-H. Chung *et al.*, Phys. Rev. Lett. **95**, 247204 (2005).
 - [20] W. Schweika *et al.*, Phys. Rev. Lett. **98**, 067201 (2007).
 - [21] Unlike Ref. [17], we base our study on elastic, rather than inelastic, neutron scattering data, Ref. [7].
 - [22] B. C. den Hertog and M. J. P. Gingras, Phys. Rev. Lett. **84**, 3430 (2000).
 - [23] R. G. Melko and M. J. P. Gingras, J. Phys. Condens. Matter **16**, R1277 (2004).
 - [24] S. Rosenkranz *et al.*, J. Appl. Phys. **87**, 5914 (2000).
 - [25] P. J. Brown, in *International Tables for Crystallography*, edited by A. J. C. Wilson (D. Reidel Pub. Co., Dordrecht, Holland, 1983–1993), Vol. C, Chap. 4.4.5, p. 391.
 - [26] H. Fukazawa *et al.*, Phys. Rev. B **65**, 054410 (2002).
 - [27] S. V. Isakov *et al.*, Phys. Rev. Lett. **95**, 217201 (2005).
 - [28] J. P. C. Ruff *et al.*, Phys. Rev. Lett. **95**, 097202 (2005).
 - [29] The Dy^{3+} dipole moment was obtained by diagonalizing the crystal-field (CF) Hamiltonian for $\text{Dy}_2\text{Ti}_2\text{O}_7$, using the CF parameters taken from Ref. [24] for $\text{Ho}_2\text{Ti}_2\text{O}_7$ but rescaled for $\text{Dy}_2\text{Ti}_2\text{O}_7$.
 - [30] M. Enjalran and M. J. P. Gingras, Phys. Rev. B **70**, 174426 (2004).
 - [31] Examining models (2) with couplings J_ν close to those used in Fig. 1(d), we find evidence that the model exhibits a transition to long-range ordered state at a temperature as low as 60 mK, unlike 180 mK found in Ref. [23].
 - [32] A similar view is expressed in C. Henley, Phys. Rev. B **71**, 014424 (2005).