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Order in the Heisenberg pyrochlore: The magnetic structure of $Gd_2Ti_2O_7$

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The rare-earth pyrochlore material $Gd_2Ti_2O_7$ is considered to be an ideal model frustrated Heisenberg antiferromagnet with additional dipolar interactions. For this system there are several untested theoretical predictions of the ground state ordering pattern. Here we establish the magnetic structure of isotopically enriched $^{160}Gd_2Ti_2O_7$, using powder neutron diffraction at a temperature of 50 mK. The magnetic structure at this temperature is a partially ordered, noncollinear antiferromagnetic structure, with propagation vector $\mathbf{k}=\frac{1}{2}\frac{1}{2}\frac{1}{2}$. It can be described as a set of "$q=0$" ordered kagomé planes separated by zero interstitial moments. This magnetic structure agrees with theory only in part, leaving an interesting problem for future research.

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Lattices based on triangular motifs with antiferromagnetic nearest-neighbor exchange are, in the absence of further terms in the Hamiltonian, expected to be geometrically frustrated as all the interactions between coupled spins cannot be simultaneously minimized. This situation is at an extreme in magnets based on the pyrochlore lattice, a face centred cubic array of corner linked tetrahedra. Some thirty years ago Villain considered the problem of the Heisenberg antiferromagnet on the pyrochlore lattice and argued that it would be a "cooperative paramagnet" that remained disordered and fluctuating down to zero temperature.[1] This has subsequently been confirmed by both numerical and analytical calculations.[2–5] However, one question has remained: do the dipolar interactions that must be present in a real pyrochlore material play a decisive role in its low temperature physics? In order to answer this question, interest has turned recently to the material $Gd_2Ti_2O_7$, perhaps the only known pyrochlore material that is sufficiently free of anisotropy and quenched disorder to realistically approximate a dipolar Heisenberg system.

Confounding expectations, $Gd_2Ti_2O_7$ was found to have an ordering transition at 0.97 K, a temperature that is comparable to the Curie-Weiss temperature, 9.6 K.[6] To understand this transition, two recent theoretical studies are particularly important, both of which developed the methodology of Reimers *et al.*[3] The first, by Raju *et al.*,[6] considered a Heisenberg antiferromagnet with dipolar coupling and showed that this does not completely lift the ground state degeneracy to second order in the expansion of the free energy, but rather stabilizes a degenerate set of periodic states with *h h h* propagation vectors. It was therefore suggested that the transition observed in $Gd_2Ti_2O_7$ might be provoked by thermal or quantum fluctuations, or alternatively by extra energy terms in the spin Hamiltonian. The second study, by Palmer and Chalker,[7] in contrast, showed that the fourth order term in the free energy expansion would select, from the degenerate *h h h* set, an ordered state with propagation vector $\mathbf{k}=0$. In order to test these predictions we have now determined the ordered magnetic structure of $Gd_2Ti_2O_7$ by powder neutron diffraction techniques.

Natural Gd is almost opaque to neutrons due to the high absorption cross section of ^{155}Gd and ^{157}Gd, so for neutron studies one must use the isotope ^{160}Gd. Isotopically enriched $^{160}Gd_2Ti_2O_7$ was prepared from $^{160}Gd_2O_3$ and TiO_2. Stoichiometric quantities were mixed, ground, pressed into a pellet and fired at 1200–1400 K for ~100 h. The grinding, pressing and firing processes were repeated several times. Powder neutron diffraction data were collected using the POLARIS high intensity diffractometer at the ISIS pulsed neutron facility. The sample was contained in a vanadium can with ^{4}He exchange gas and mounted in an Oxford Instruments dilution refrigerator. Data were collected for 17 h above and below the ordering transition ($T_c\sim1$ K) at 5 K, 500 mK, and 50 mK. A refinement of the pattern at 5 K showed the sample to be phase pure. Below $T_c\sim1$ K new reflections were observed that could be indexed with a magnetic propagation vector of $\mathbf{k}=\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The continuous evolution of these reflections as a function of temperature showed the transition to be second order. Given this observation, representational analysis can be used to facilitate magnetic structure determination.[8–11]

We define $G_{\mathbf{k}}$ as the little group of symmetry elements that leave the propagation vector $\mathbf{k}$ invariant. The magnetic representation, Γ_{Gd}, of the Gd site (16*c* in $Fd\bar{3}m$), can be decomposed in terms of the irreducible representations (IR's) of $G_{\mathbf{k}}$. These are listed in Table I along with their associated basis vectors. The application of $G_{\mathbf{k}}$ to the four Gd positions of the tetrahedron of the asymmetric unit results in two orbits. When applied to 0,0,0 it generates only the position 0,0,0—orbit 1. When applied to another seed position, say $\frac{3}{4},\frac{1}{4},\frac{1}{2}$, it generates the remaining 16*c* sites: $\frac{3}{4},\frac{1}{4},\frac{1}{2}$ $\frac{1}{4},\frac{1}{2},\frac{3}{4}$ and $\frac{1}{2},\frac{3}{4},\frac{1}{4}$—orbit 2.

These two orbits can be understood in terms of a description of the pyrochlore lattice as a set of two dimensional kagomé lattice sheets (the (1 1 1) planes) decorated by interstitial spins which serve to link the sheets. These form "up" and "down" pointing corner-sharing tetrahedra. If the lattice is described in this way, then orbit 2 describes the three atoms that make up the triangular motif of a particular

TABLE I. Nonzero IR's and associated basis vectors ψ_ν for the space group $Fd\bar{3}m$ with $\mathbf{k}=\frac{1}{2}\frac{1}{2}\frac{1}{2}$ calculated using the program SARA*h*-Representational Analysis (Refs. 10 and 11). The labeling of the propagation vectors and the IRs follows the scheme used by Kovalev in his tabulated works (Ref. 12).

Orbit 1:					Orbit 2:										
IR	BV	Atom 1			IR	BV	Atom 2			Atom 3			Atom 4		
		m_x	m_y	m_z			m_x	m_y	m_z	m_x	m_y	m_z	m_x	m_y	m_z
Γ_3	ψ_1	1	1	1	Γ_2	ψ_4	1	1	0	0	1	1	1	0	1
Γ_5	ψ_2	1	$\bar{1}$	0		ψ_5	0	0	1	1	0	0	0	1	0
	ψ_3	1	1	$\bar{2}$	Γ_4	ψ_6	1	$\bar{1}$	0	0	1	$\bar{1}$	$\bar{1}$	0	1
					Γ_6	ψ_7	1	1	0	0	$\bar{1}$	$\bar{1}$	$\bar{1}$	0	$\bar{1}$
						ψ_8	0	0	1	$\bar{1}$	0	0	0	$\bar{1}$	0
						ψ_9	0	0	0	0	$\bar{1}$	1	$\bar{1}$	0	1

kagomé sheet and orbit 1 is the unique atom present in the interstitial site. The decomposition of the magnetic representation Γ_{Gd} for orbits 1 and 2 are

$$\Gamma_{\mathrm{Gd}}^{\mathrm{orbit\ 1}}=0\Gamma_1^{(1)}+0\Gamma_2^{(1)}+1\Gamma_3^{(1)}+0\Gamma_4^{(1)}+1\Gamma_5^{(2)}+0\Gamma_6^{(2)},$$

$$\Gamma_{\mathrm{Gd}}^{\mathrm{orbit\ 2}}=0\Gamma_1^{(1)}+2\Gamma_2^{(1)}+0\Gamma_3^{(1)}+1\Gamma_4^{(1)}+0\Gamma_5^{(2)}+3\Gamma_6^{(2)}. \quad (1)$$

Landau theory states that in simple systems, a continuous magnetic ordering transition should involve only one IR becoming critical. However, in this case the same IR's are not present in the decomposition of Γ on the different sites. For such a situation the only restriction that symmetry affords is the constraint that each site, or orbit, orders under a single IR with its own set of basis vectors. From the decompositions (1), there are two magnetic representations for orbit 1 and three representations for orbit 2 (see Table I). Permutation of these results in six allowed combinations of basis vectors, to be tested against the experimental data.

Magnetic structure factors were calculated using the GENLES routine of the GSAS suite,[13] while the orientations of the magnetic moments were controlled and refined separately by the simulated annealing-based program SARA *h*–Refine for GSAS.[10] The χ^2 and R_{wp} values for each refinement are shown in Table II. It is clear that, among the six possibilities, there are only two candidates for the magnetic structure; all the other combinations can be immediately discarded. We refer to these candidate structures as (i) and (ii), see Table II. While both involve the basis vector ψ_6 for orbit 2, they differ in that, for orbit 1, structure (i) involves ψ_1 while structure (ii) involves the two basis vectors ψ_2 and ψ_3. The basis vector ψ_6, which refers to the kagomé planes, in fact corresponds to the "$q=0$" spin structure observed in ordered kagomé antiferromagnets.[14] For the interstitial site, structure (i), with the basis vector ψ_1, corresponds to a spin pointing parallel to the [1 1 1] direction which is perpendicular to the kagomé plane. Structure (ii), with basis vectors ψ_2 and ψ_3, correspond to a spin lying with any orientation in a plane parallel to the kagomé sheet. We note that powder neutron diffraction cannot distinguish this orientation. Three dimensional visualizations of the two possible structures are shown in Fig. 1. In both cases the interstitial spins are ferromagnetically aligned within their planes, and alternating planes are antiferromagnetically aligned.

Both structures (i) and (ii) fit well to the data, but there is an important difference at ≈ 3.1 Å (see Fig. 1). Here, structure (i) predicts more intensity than structure (ii), while experiment suggests that the reflections at this *d* spacing (for example $\frac{3}{2},\frac{3}{2},\frac{5}{2}$) are systematically absent. Thus neither structures (i) nor (ii) are satisfactory. A further fit was made which assigned zero moment to the interstitial site, structure (iii). This is plausible, since a planar antiferromagnetic structure on the kagomé sheets gives a zero mean field at the interstitial site.

Structure (iii), with zero interstitial moment was found to improve the fit to experiment by, most importantly, removing the peak at 3.1 Å (see Fig. 1). The final refined profile is shown in Fig. 2 and goodness of fit parameters are listed in Table II. We therefore conclude that structure (iii), with zero interstitial moment, is fully consistent with the experimental data. It should be noted that the current diffraction experiment cannot shed any light on whether the fourth moment is zero as a result of static or fluctuating disorder.

In high symmetry crystals powder neutron diffraction does not give an unambiguous determination of the magnetic structure, because there is always the possibility of a multi-*k* structure. In the present case, multi-*k* structures can be

TABLE II. Goodness of fit parameters χ^2 and R_{wp} for each of the six alternative combinations of IR's, for the data measured on the A and C detector banks of POLARIS. The last line indicates the fit that considers ordering only in orbit 2. The IR's corresponding to models (i), (ii), and (iii) are indicated.

Label	Orbit		A Bank		C Bank	
	1	2	χ^2	R_{wp}	χ^2	R_{wp}
	Γ_3	Γ_2	43.44	0.0876	11.68	0.0424
(i)	Γ_3	Γ_4	3.844	0.0261	2.720	0.0205
	Γ_3	Γ_6	13.17	0.0483	5.168	0.0282
	Γ_5	Γ_2	40.76	0.0849	11.62	0.0423
(ii)	Γ_5	Γ_4	2.838	0.0224	2.494	0.0196
	Γ_5	Γ_6	11.66	0.0454	4.957	0.0276
(iii)	0	Γ_4	2.977	0.0229	2.186	0.0184

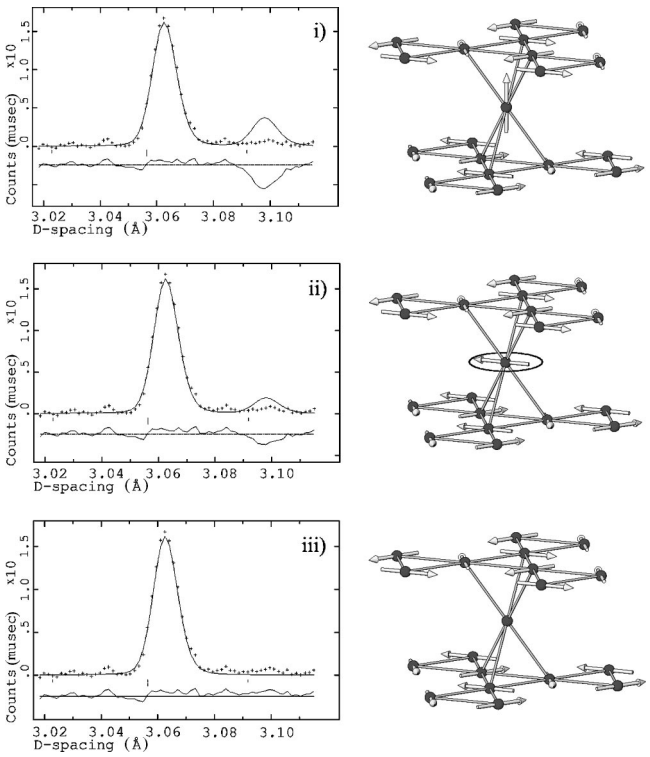

FIG. 1. The intensity of the magnetic reflection as a function of the different structural models (i), (ii), (iii) defined in the text, for the spin at position (0,0,0).

formed by contributions from any of the four equivalent arms of the star of **k**. However, recent investigations of $Gd_2Ti_2O_7$ by Mössbauer spectroscopy[15] suggest that all the magnetic spins lie in planes perpendicular to the [1 1 1] direction below the ordering temperature. ESR measurements on the system above T_c have also indicated that the spins lie preferentially in the (1 1 1) plane.[16] These observations rule out a multi-*k* structure as the latter would always have a finite spin component parallel to [1 1 1].

Our result that $\mathbf{k}=\frac{1}{2}\frac{1}{2}\frac{1}{2}$ agrees with the prediction of Raju *et al.*[6] These authors considered a dipolar Heisenberg Hamiltonian with coupling parameters appropriate to $Gd_2Ti_2O_7$. They showed that, to quadratic order in the Landau expansion of the free energy, the ground state consisted of a degenerate manifold of magnetic structures with *h h h* propagation vectors. It was therefore suggested that thermal or quantum fluctuations, or additional terms in the Hamiltonian, might operate to select a single ordered state in the real material, with one particular value of *h*. Palmer and Chalker extended this calculation to the fourth order term, and found it to be minimized by setting moments of equal magnitudes on each site of the elementary tetrahedron. A general state was constructed by combining three basis vectors of the type ψ_6 (in our notation). Each of these basis vectors has three coplanar and one zero moment, as described above, but differ in the choice of $\langle 1\,1\,1\rangle$ plane. The condition of equal moments was found to restrict the possibilities to a single ground state with $h=0$, with the four spins in a $\langle 1\,0\,0\rangle$ plane, contrary to our findings.

There are two possible explanations for the disagreement

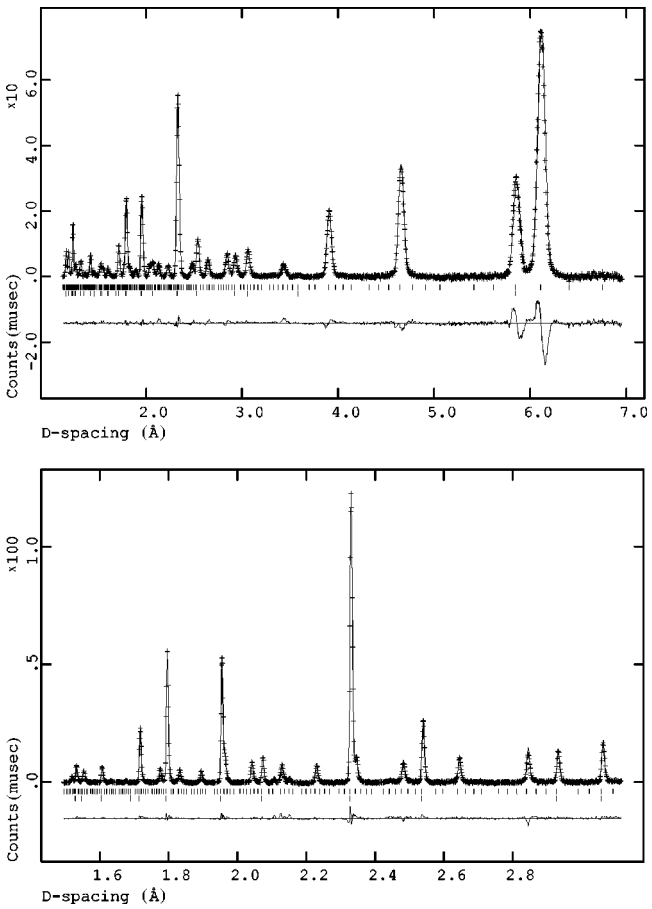

FIG. 2. The final refined magnetic profiles for data collected from the A and C detector banks of the POLARIS instrument from $Gd_2Ti_2O_7$ at 50 mK (nuclear reflections are marked by the lower line of ticks).

between experiment and theory. The first is that the real material has additional terms in the spin Hamiltonian, such as further neighbor exchange, that overcome the fourth order terms in the free energy expansion. The influence of such terms was considered in a rather general sense by Reimers *et al.*[3] and it would be interesting to develop the latter study in the present context. From an experimental perspective, the Hamiltonian could be investigated by studying relatives of $Gd_2Ti_2O_7$ such as $Gd_2Sn_2O_7$ and Gd_2SbGaO_7, where additional energy terms might have a different weighting. The second, and perhaps more intriguing explanation, is that quantum fluctuations, neglected in the classical theory, play a role in determining the ordering pattern. However, the refined value of the ordered moment of $Gd_2Ti_2O_7$ is 6.73 ± 0.05 μ_B, which is comparable with the maximum expected value of 7.0 μ_B. This suggests that quantum mechanical fluctuations out of the ground state are not very important in this spin $S=\frac{7}{2}$ system.

In conclusion, the model dipolar Heisenberg antiferromagnet $^{160}Gd_2Ti_2O_7$ is partially ordered at 50 mK in a pattern that consists of "$q=0$" kagomé planes plus a zero interstitial moment. It would be interesting to determine whether this moment exhibits a freezing transition at some finite temperature. The partial order of chemically pure

$Gd_2Ti_2O_7$ contrasts with the behavior of Heisenberg antiferromagnets with small amounts of quenched chemical disorder, such as $CsNiCrF_6$ (Ref. 17) and $Y(Sc)Mn_2$.[18] These materials show spin freezing transitions in the absence of long range order and spin correlations characteristic of the pure Heisenberg system.[5,17,18] Thus our results support the idea that quenched chemical disorder is a strongly relevant perturbation in the pyrochlore system that is responsible for the glassy ground states often observed.[19] The theory of Raju *et al.*[6] encompasses the experimental behavior of $Gd_2Ti_2O_7$ in that it predicts an *h h h* propagation vector. We note that, in symmetry terms, *h h h* is an equivalence line in the Brillouin zone, such that all possible ordering wavevectors share the IR's and basis vectors that we have enumerated in Table I. The selection of $h=\frac{1}{2}$ might be specific to this material or might be more general; this question remains to be answered. The higher order theory of Palmer and Chalker[7] does not agree with our result. It remains an interesting challenge, both experimental and theoretical to understand the origin of this disagreement.

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