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Spin dynamics in geometrically frustrated antiferromagnetic pyrochlores

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Abstract

We have studied the spin dynamics of several antiferromagnetic pyrochlore oxides. These magnets are geometrically frustrated and only reach their ground states at temperatures much lower than that expected from mean field theory. Here we present data on the magnetic nature, especially the spin dynamics of $Tb_2Ti_2O_7$, $Gd_2Ti_2O_7$ and $Y_2Mo_2O_7$. In these systems the ground states are found to be very different. $Y_2Mo_2O_7$ freezes completely into a spin glass-like state, $Tb_2Ti_2O_7$ is a cooperative paramagnetic and remains dynamic down to 15 mK and $Gd_2Ti_2O_7$ enters a unique partially ordered state at $\sim$1 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Frustration occurs when different competing interactions of comparable strength prevent the global system from finding a unique state. The most frustrated physical systems have many equivalent minimum-energy configurations. In condensed matter science, a strongly frustrated system therefore has a high density of dispersionless, low energy excitations or soft modes, that correspond to fluctuations between these energetically equivalent configurations. Protein folding [1], exotic magnetic excitations in low dimensional systems [2, 3], high temperature superconductivity [4] and shape formation of nanoclusters [5] are all thought to be, at least in part, governed by frustration.

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The effects of these competing interactions are easily studied in magnetism where frustrated systems such as spin glasses have been studied for many decades. Geometrically frustrated magnets, where the spatial arrangement of atoms (geometry) competes with the other interactions between atomic spins (exchange, dipole, local anisotropy etc), has become an active area in condensed matter science, but only recently has the dynamics been investigated.

Geometric frustration leads to a variety of exotic, cooperative, spin states and has spawned new studies in several model magnets, such as *spin glass*, *spin liquid* and *spin ice* systems. A simple example of local geometrical frustration is the arrangement of three identical spins on an equilateral triangle: if the spins are constrained to point either up or down, and the energy of interaction between any two spins is minimized if the two point in opposite directions, then the individual interaction energies of all three pairings on the triangle compete and cannot be minimized simultaneously. However, the total energy of the triangle is the same for the six different spin configurations with two spins in one direction and one antiparallel to the others.

Experiments on geometrically frustrated magnets alone have shown a wide range of novel physical phenomena: the only transition metal based heavy fermion conductor [6]; glassy behaviour in the presence of minimal disorder [7, 8]; 'colossal' magnetoresistance [9]; superconductivity [10]; statistical mechanics equivalent to the proton disorder in water ice [11–13]; Berry phase effects on the anomalous Hall effect [14] and 'cooperative paramagnetic' behaviour [15].

The pyrochlore-type structure ($A_2B_2O_7$) is an ideal lattice to host geometrically frustrated spins [16]. It is composed of two sublattices of A and B sites, either of which can be magnetically frustrated if occupied by a magnetic species. These sublattices are structurally identical but are displaced by half a lattice constant from each other. They each comprise a face centred cubic array of corner linked tetrahedra. A three-dimensional analogue of the triangle, the tetrahedron is strongly frustrated for antiferromagnetic interactions.

In this paper we will review the spin dynamics in three very different antiferromagnetic pyrochlores. $Y_2Mo_2O_7$ freezes completely into a spin glass state at low temperatures. $Tb_2Ti_2O_7$ is a cooperative paramagnet and remains dynamic down to 15 mK although magnetic correlations begin to build up at 100 K, and $Gd_2Ti_2O_7$ enters a unique partially ordered state at $\sim$1 K where a subset of the spins remain dynamic, whilst the others enter a frozen long ranged ordered state.

2. Experimental details

Polycrystalline samples of the oxide pyrochlores were prepared by a conventional solid state reaction from rare-earth oxide and transition metal oxide starting materials, as described in [15]. The $Y_2Mo_2O_7$ requires the process to be performed in argon gas, but the Gd and Tb samples were made in air. Large, high quality, single crystals of $Tb_2Ti_2O_7$ have been successfully grown by the floating zone method under a controlled atmosphere in an optical image furnace. Details of this crystal growth are described elsewhere [17]. Room temperature x-ray powder diffraction confirmed that these oxide pyrochlores crystallize into the face centred cubic space group $Fd\bar{3}m$ with a lattice parameter of approximately 10.1 Å at 300 K depending on the metallic ions.

Neutron diffraction was performed on the single-crystal spectrometer, PRISMA, at the Rutherford Appleton Laboratory and neutron spin echo (NSE) experiments were performed on the IN11 machine at the Institut Laue-Langevin. The NSE experiments used the wide angle multidetector option available on IN11. The neutron wavelength was $\lambda = 5.5$ Å, and a $\mathbf{Q}$ range of 0.5 Å$^{-1} \leqslant \mathbf{Q} \leqslant 1.6$ Å^{-1} could be covered by two positions of the detector bank.

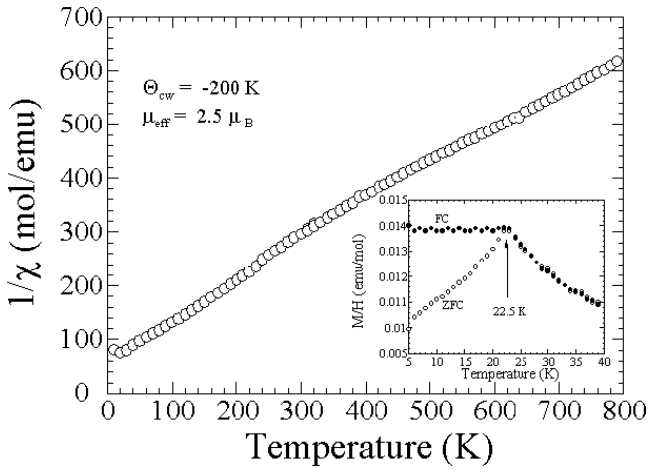

Figure 1. $Y_2Mo_2O_7$: dc susceptibility over a wide range of temperature (main figure) and close to the freezing temperature (inset).

3. Results and discussion

3.1. Frozen $Y_2Mo_2O_7$

Many geometrically frustrated magnets enter a disordered, frozen state as the temperature lowered. A glass-like state is seen for example in the pyrochlores $RE_2Mn_2O_7$ (RE = Y, Ho and Yb) [18] and $Tb_2Mo_2O_7$ [19]. Not much is known about the dynamics in these samples; however, it is believed that the glassy nature of many of these is a result of having two magnetic species in the compound and hence multiple exchange paths. The garnet ($Gd_3Ga_5O_{12}$) [20], the pyrochlore slab ($SrCr_{9p}Ga_{12-9p}O_{19}$) [21] and the corner sharing triangular systems ($(D_3O)Fe_3(SO_4)_2(OD)_6$) [22] also show a glass-like transition, but in these samples a finite amount of chemical disorder is always present. One property of many of these *glassy* systems is the persistence of some spin dynamics to the lowest experimental temperatures. This might be a common property of many geometrically frustrated systems, including the spin ice compounds [23] and ordered magnets [24]. It is consistent with the presence of zero modes and a degenerate ground state.

$Y_2Mo_2O_7$ has been studied using a wide range of techniques since it was shown by Reimers *et al* [25] to be a crystallographically well ordered compound with the characteristics of a spin glass. This is an unusual result because spin glass formation is believed to require the presence of some chemical disorder, in addition to magnetic frustration. Bulk magnetic susceptibility measurements show strong irreversible behaviour below the freezing temperature, $T_F = 22.5$ K (see figure 1), as reported earlier [26]. Muon spin relaxation [27] and neutron scattering [7] data confirm the rapid slowing down of the magnetic moments as one approaches T_F from above. These data also reveal the absence of long range order down to $\frac{1}{10}T_F \sim \frac{1}{100}\Theta_{CW}$. However, some small details in the spin dynamics are considered to be anomalous when compared to better established spin glass materials where a magnetic ion is substituted into a non-magnetic host [27, 28] suggesting a new type of spin glass. Curie–Weiss analysis requires relatively high temperature magnetization measurements in order to enter a truly paramagnetic state. Using data above 500 K, Θ_{CW} was found to be -200 K, indicating strong antiferromagnetic interactions and an effective moment of 2.55 μ_B, close to the effective moment of 2.8 μ_B expected for the $S = 1$ Mo^{4+} ion. XAFS [29] and NMR [30] have since shown that there

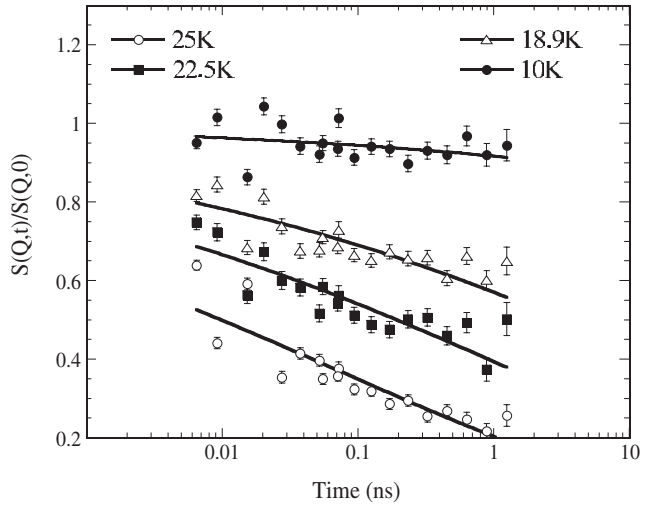

Figure 2. $Y_2Mo_2O_7$: the normalized intermediate scattering function at 10, 18, 22.5 and 25 K measured for a polycrystalline sample.

is indeed a small distortion in the magnetic sublattice of $Y_2Mo_2O_7$ that might provide the chemical disorder required to freeze the spins, although at a much lower temperature than that expected from the Curie–Weiss temperature.

The normalized intermediate scattering function, $S(Q, t)/S(Q, 0)$, for $Y_2Mo_2O_7$, determined by NSE experiments, is shown in figure 2 for temperatures close to T_F. The time independent $S(Q, t)/S(Q, 0)$ at 10 K of 1 indicates that the entire Mo^{4+} spin system is frozen in the frequency window measured by NSE experiments. However, there is a strong dynamical contribution to the signal above 10 K and below T_F. This agrees with muon data [27] and has been seen in other glassy systems. This ambiguity in T_F is a result of the different frequency windows probed by magnetization, muon spin relaxation and NSE experiments. One should also note that the flatness of these curves, at all temperatures, is indicative of multiple relaxation processes. Stretched exponential fits to $S(Q, t)/S(Q, 0)$ revealed that the relaxation times increase from 0.07 to 8×10^5 ns between 25 and 10 K while the exponent β was fixed at 0.18.

3.2. Liquid $Tb_2Ti_2O_7$

In this cooperative paramagnet, or spin liquid [31, 32], the spins are believed to remain fluctuating at extremely low temperatures. Recent studies by Yasui *et al* [33] suggest that $Tb_2Ti_2O_7$ enters an ordered, albeit glassy, state at a relatively high temperature, ∼1.5 K. Luo *et al* [34] have also reported history dependence in the low temperature magnetization of $Tb_2Ti_2O_7$. However, muon spin relaxation work confirms that the system remains dynamic down to 15 mK [15].

Figure 3 shows the inverse susceptibility of $Tb_2Ti_2O_7$ down to 0.5 K. The static susceptibility reveals no phase transition into either a conventional Néel ordered or glass-like state. Instead a deviation from a Curie–Weiss behaviour is seen below 100 K, an indication of short range correlations. At lower temperatures $1/\chi$ falls below the Curie–Weiss fit at a lower temperature. This characteristic is seen in many frustrated antiferromagnets [35].

$S(\mathbf{Q})$, the neutron scattering structure factor, is shown in figure 4. In the (hhl) plane, the face centred nuclear Bragg peaks can be seen at the all odd or all even reciprocal lattice points.

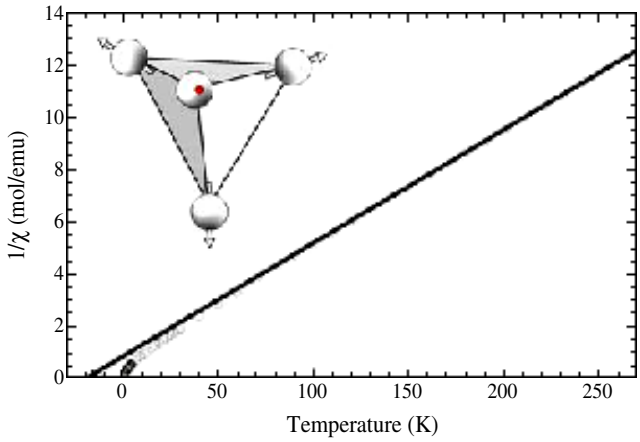

Figure 3. $Tb_2Ti_2O_7$: the inverse static susceptibility. Inset: one of several possible local units with minimal energy.

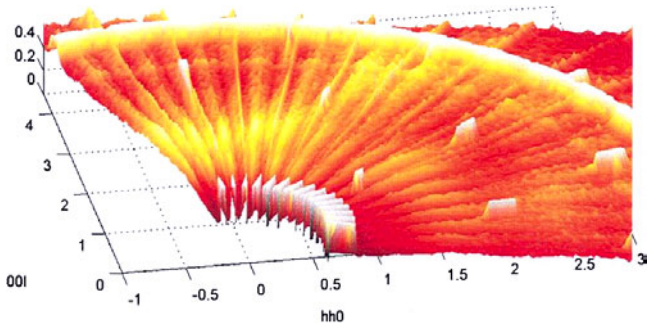

Figure 4. $Tb_2Ti_2O_7$: a contour plot of the neutron diffraction pattern over several Brillouin zones at base temperature. Nuclear Bragg reflections are seen as expected at the all even or all odd reciprocal lattice points. There is no indication of magnetic Bragg-like scattering, but extensive diffuse scattering is seen around the (0, 0, 2) position.

A significant amount of diffuse magnetic scattering can be seen at 50 mK, but magnetic Bragg-like peaks are absent in this plane. This lack of Bragg scattering is conclusive evidence that long range correlations do not form in the magnetic sublattice. Indeed, analysis of the diffuse scattering around the (0, 0, 2) reciprocal lattice point reveals that the spin–spin correlations only extend to nearest neighbours (∼5 Å). This type of neutron diffraction pattern is often seen in liquids (dynamic) or amorphous (static) materials where only short range correlations exist. Note that the diffuse scattering tells us nothing about the dynamics in the material.

Figures 5 and 6 show results that probe the spin dynamics of $Tb_2Ti_2O_7$. Inelastic neutron scattering from $Tb_2Ti_2O_7$ at 9 K is shown in figure 5. Here a well developed low level excitation is seen to partially soften at the wavevector corresponding to the first maximum in the magnetic structure factor. This mode bears a striking resemblance to the roton minimum seen in the excitation spectrum of liquid ^{4}He, a well studied quantum liquid that does not freeze at the lowest temperatures. The minimum in the magnetic excitation spectrum in $Tb_2Ti_2O_7$ goes away with increasing temperature and by 30 K it is a well defined low energy, dispersionless excitation [15, 31].

The high energy resolution technique, NSE study, was used to probe the slower dynamics in $Tb_2Ti_2O_7$. In figure 6 the normalized intermediate scattering function is shown for several

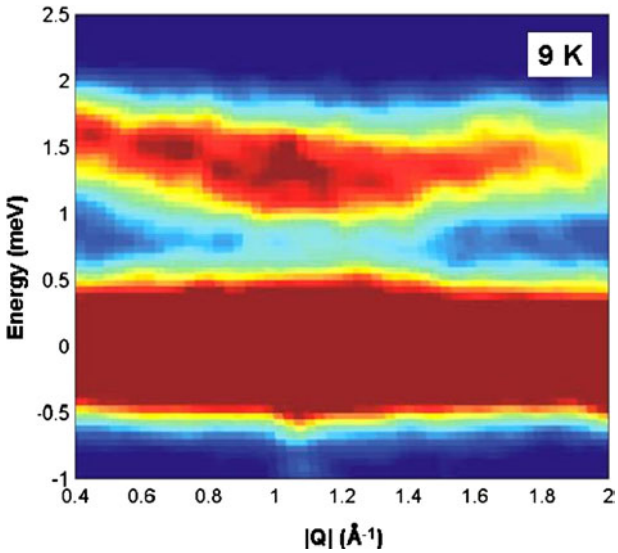

Figure 5. $Tb_2Ti_2O_7$: a contour plot of the first magnetic excitation as seen by inelastic neutron scattering. The partial softening seen here at 9 K goes by 30 K leaving a well defined dispersionless mode.

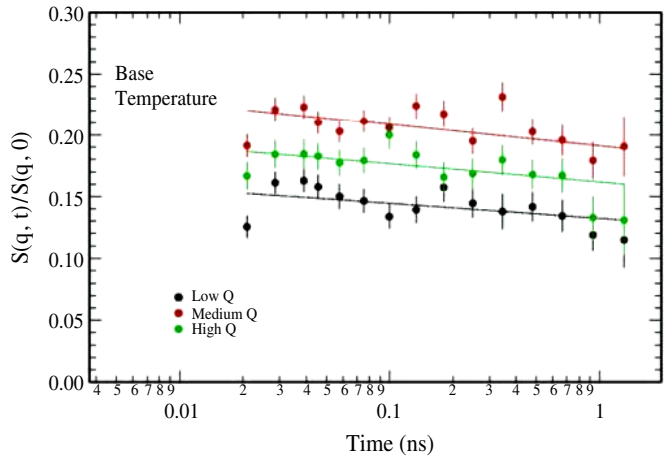

Figure 6. $Tb_2Ti_2O_7$: the normalized intermediate scattering function at base temperatures at 0.8, 1.1 and 1.4 Å, or low medium and high **Q**, respectively.

different **Q**'s between 0.5 and 1.6 Å, at 50 mK. Unlike the case already seen in figure 2, for $Y_2Mo_2O_7$, $S(Q, t)/S(Q, 0)$ never reaches 1 in the NSE time window and the signal is always relaxing, due to fluctuating moments in the system. At 50 mK, approximately 15% of the spin system has slowed into the NSE window (baseline of about 0.15), but it is still dynamic and relaxing very slowly. Like for $Y_2Mo_2O_7$, the flatness of the signal indicates the presence of multiple relaxation processes.

Inelastic neutron scattering and crystal field calculations provide very strong evidence for strong single-ion anisotropy along the $\langle 1, 1, 1\rangle$ direction at the Tb^{3+} site. Indeed, the diffuse magnetic scattering observed at low temperatures can be calculated assuming the local

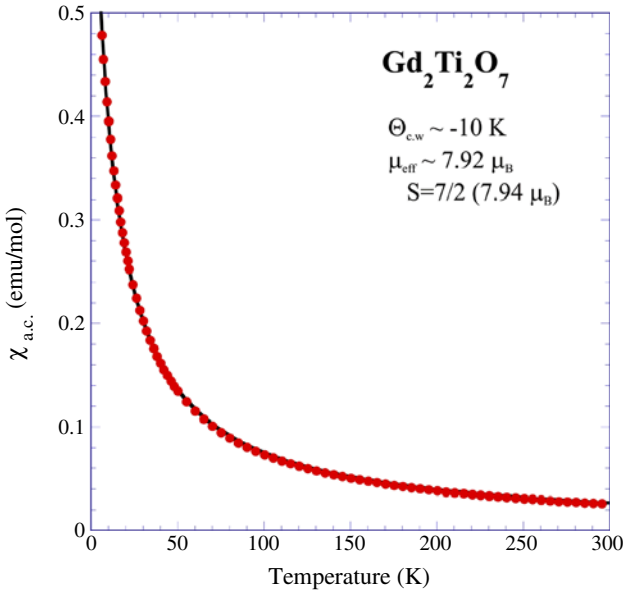

Figure 7. $Gd_2Ti_2O_7$: the temperature dependence of the magnetic susceptibility. Curie–Weiss behaviour describes the data well down to 2 K.

structure shown in the inset to figure 3. Here, each 'unit' is not unique, but is consistent with an antiferromagnetic exchange and strong anisotropy along the eight $\langle 1, 1, 1\rangle$ cubic directions. It is believed that $Tb_2Ti_2O_7$ would 'like' to enter a four-sublattice antiferromagnetically ordered state, similar to that seen in FeF_3 [36], but is prevented from reaching such a state due to competing interactions. This results in a continuum of energetically equivalent tetrahedra and the spins fluctuate between different, correlated configurations despite being coupled to neighbouring spins with an interaction energy much greater than the temperature.

3.3. Partially ordered $Gd_2Ti_2O_7$

The Gd^{3+} ion is a spin only ion with a $^8S_{7/2}$ ground state; thus crystal field splittings and anisotropy, which play a large role in the properties of the aforementioned Tb^{3+} materials, are not significant in this magnetic system. Figure 7 shows the static susceptibility down to 2 K. A Curie–Weiss fit describes the data well from 2 K to room temperature. The effective moment is within error of that expected for the Gd^{3+} ion and Θ_{CW} is -10 K. Raju *et al* [37] and Ramirez *et al* [38] have shown by means of the specific heat and magnetization that this insulating pyrochlore has a magnetic transition near 1 K. However, powder neutron scattering has shown that this transition corresponds to the ordering of only three spins per tetrahedron, the fourth remaining disordered down to 50 mK [39]. Such division of equivalent sublattices into ordered and disordered states is scarce among Heisenberg models [40], and this may be the only experimental example. Recent theoretical work [41] has shown that the partially ordered state is a property of the dipolar interaction but is strongly favoured by second-neighbour exchange. NSE has conclusively confirmed the presence of fluctuating moments at 110 mK [42]. In figure 8 we show $S(Q, t)/S(Q, 0)$ at several temperatures. Above T_C the normalized echo signal relaxes to zero, indicative of a paramagnet. Below this temperature the baseline is lifted to approximately 20%. These data suggest that $1/5$ of the spin system is

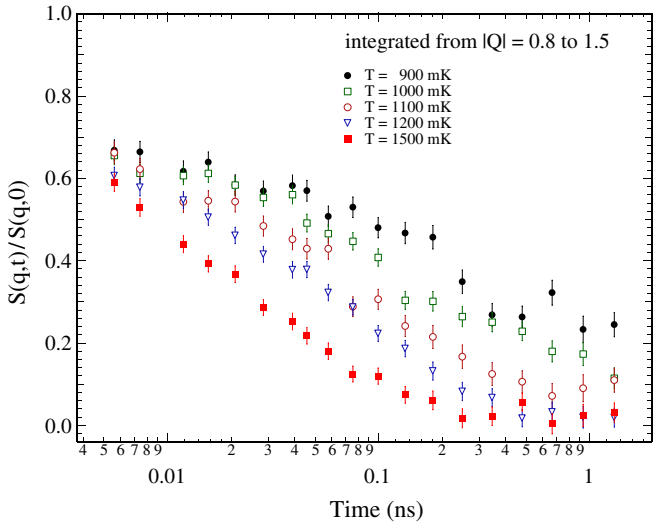

Figure 8. $Gd_2Ti_2O_7$: the normalized intermediate scattering function at several different temperatures around the 1 K transition.

frozen in the NSE window. Presumably this is the ordered component seen by means of neutron diffraction just below T_C. At all measurement temperatures, there is a very fast relaxation of 1/4 of the spin system, too fast for a neutron spin echo, and only 3/4 of the spin system is seen to relax. This is consistent with the magnetic structure determined by Champion *et al* [39] where one spin on every tetrahedron is disordered and the others freeze into ordered Kagomé sheets.

4. Conclusions

Our studies of $Y_2Mo_2O_7$, $Tb_2Ti_2O_7$ and $Gd_2Ti_2O_7$ reveal strong but different manifestations of geometrical frustration. $Y_2Mo_2O_7$ freezes, at $\frac{1}{10}\Theta_{CW}$, into a randomly oriented, spin glass-like state. The Heisenberg spin system, $Gd_2Ti_2O_7$, enters a partially ordered state at $\frac{1}{10}\Theta_{CW}$ with one of its four spins on every tetrahedron still fluctuating and the low temperature Ising system, $Tb_2Ti_2O_7$, remains dynamic down to 15 mK. The suppression of the ordering temperature in these systems is an indication of strong geometric frustration. Although good progress has been made, important questions still remain as to what microscopic features in the Hamiltonians are responsible for their differing ground states.

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