Spin fluctuations in the magnetic phase of frustrated pyrochlores: evidence and controversy

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Abstract. We give here the experimental evidences for the presence of spin fluctuations in the magnetically (long range) ordered phase of some frustrated rare earth based pyrochlore systems, together with recent data that seem to contradict this picture.

1. Introduction
Geometrical frustration of exchange interactions occurs in special lattices where the geometry prevents all pairwise couplings to be satisfied altogether [1, 2]. For instance, in a triangular lattice with magnetic ions at the corners interacting via antiferromagnetic (AF) couplings, the ground state cannot be a Néel-like collinear arrangement. In three dimensions, the pyrochlore lattice formed of tetrahedra linked by their corners shows the same property (see Fig.1 right). The pyrochlore compounds have formula R$_2$M$_2$O$_7$, where R is a rare earth and M a transition or sp metal. To these examples of “frustrating geometry”, one can add the two-dimensional kagomé lattice, made of corner-sharing triangles (see Fig.1 left), the rare earth lattice in the garnets R$_3$Ga$_5$O$_{12}$, and the B lattice in the spinels AB$_2$O$_4$, which is a pyrochlore lattice. In all these systems, in the presence of AF Heisenberg-like (isotropic) interactions, the ground state must be such that $\sum_{i=1,n} S_i=0$, where $S_i$ is the spin of the $i$th ion in a unit “plaquette” (a triangle, a tetrahedron, … according to the lattice) and the sum runs over the spins of a plaquette. This has two consequences: for the lattices with “loose connectivity”, i.e. those where the plaquettes are linked through their corners, the ground state has a very large degeneracy because there are many ways of arranging the spins on the whole lattice such that the above condition is fulfilled [3]. Hence long range order (LRO) of the magnetic moments is in principle impossible, and the system should remain in a fluctuating “spin liquid” phase down to the lowest temperature. For the pyrochlore lattice, another kind of frustration was discovered in the case of ferromagnetic (F) interactions: if the spins are Ising-like, i.e. constrained by the crystal field anisotropy to lie along the ternary $<111>$ axes, then the magnetic system is frustrated. This frustration is similar to the structural frustration of protons in ice, hence the name of “spin ice” for such materials like Ho$_2$Ti$_2$O$_7$ or Dy$_2$Ti$_2$O$_7$ [4, 5], which show no LRO and present a ground state with large degeneracy. In both types (F or AF), degeneracy can be lifted by second order interactions with respect to exchange, like the dipole-dipole coupling or a finite crystal field anisotropy, resulting eventually in the onset of magnetic LRO with specific structures. Although well characterised by the presence of magnetic Bragg peaks in the neutron diffraction spectra, the
LRO seems to be concomitant with spin fluctuations, as witnessed by various local techniques like Mössbauer spectroscopy, μSR or inelastic neutron scattering. However, recently, the presence of spin fluctuations in the LRO phase has been questioned by new experimental evidence. In this work, we will first give two examples of “true” spin liquids, the Yb and Gd gallium garnets, where Mössbauer spectroscopy has been used to measure the thermal dependence of the spin fluctuation frequency down to the 100 mK range. Next, we will describe the evidences for the presence of fluctuations in the magnetic LRO phase of the pyrochlore stannates Gd$_2$Sn$_2$O$_7$ and Tb$_2$Sn$_2$O$_7$. Finally, we will discuss the recent data which seem to be at odds with this picture.

2. The spin liquids Yb and Gd garnets
The Yb and Gd Gallium garnets do not show magnetic ordering of the Yb$^{3+}$/Gd$^{3+}$ ions down to very low temperature. A small specific heat anomaly is observed at 0.054 K in the Yb garnet [6], but it does not seem to be due to LRO. The Mössbauer experiments, resp. on $^{170}$Yb and $^{155}$Gd, were carried out down to the 50 mK range. In the Yb garnet [7], no resolved hyperfine field spectrum is observed down to the lowest temperature; spin fluctuations are clearly present, and the spectrum narrows on heating, which means that their frequency increases. In the Gd garnet, the spectrum at 0.04 K (not shown) is a “static” hyperfine field spectrum [8], and increasing the temperature yields original relaxational lineshapes with increasing frequencies (Fig.2 left). The spectra in both garnets were fitted using a lineshape appropriate for a fluctuating hyperfine field [10] because, although no LRO is present, the magnetic moments are short range correlated. Figure 2 left shows the thermal variation of the spin fluctuation frequency $1/\tau$: in Yb$_3$Ga$_5$O$_{12}$, the fluctuations were taken to be isotropic, and a T-linear law is approximately obeyed above 0.09 K, in agreement with theoretical predictions [3]. In Gd$_3$Ga$_5$O$_{12}$, where the fluctuations seem to be of planar type [8], the fluctuation frequency obeys a $T^2$ law. In both compounds, the fluctuation rate saturates below about 0.1 K; in Gd$_3$Ga$_5$O$_{12}$, the lower limit $(1/\tau)_{LF}$ of the Mössbauer “relaxational window” is reached at about 0.1 K, but the saturation was observed by μSR down to 20 mK [9]. Tunneling of the short range correlated “spin clusters” could be at the origin of this saturation, whereas thermally excited fluctuations dominate above 0.1 K.

Contrary to the Yb and Gd garnets, in most pyrochlore materials, magnetic LRO settles, but at a temperature much lower than the exchange energy, which is a signature of frustration [1].

3. Degeneracy lifting and LRO due to dipolar coupling in Gd$_2$Sn$_2$O$_7$
Our first example of magnetic ordering due to degeneracy lifting is the stannate Gd$_2$Sn$_2$O$_7$, which, although a close realisation of a Heisenberg antiferromagnet, shows a transition at 1 K.
to a LRO phase [11]. The associated AF $q=0$ magnetic structure is precisely that predicted to occur in pyrochlore compounds with isotropic AF exchange when the degeneracy is lifted by dipolar interactions [12]. The $^{155}$Gd Mössbauer spectrum at 27 mK, shown in Fig.3 left, corresponds to combined magnetic and quadrupolar hyperfine interactions, with a hyperfine field $H_{hf} \simeq 30$ T and a hyperfine splitting $\Delta_{hf} \simeq 15$ mK. It shows the peculiar feature that the hyperfine temperature, which can be fitted to the spectrum since $k_BT \sim \Delta_{hf}$, is 90(20) mK, i.e. it is higher than the lattice temperature. Thus the hyperfine levels are not at thermal equilibrium, which can be interpreted as due to the presence of hyperfine field fluctuations, i.e. of fluctuations of the Gd$^{3+}$ moment [13]. Indeed, as sketched in Fig.3 right, if the hyperfine (nuclear) relaxation time $T_1$ is much longer than the spin flip time $\tau$, then the hyperfine levels have an infinite temperature ($p_g=0.5$, green line in Fig.3 right). When $T_1 \sim \tau$, these levels are still out of equilibrium (black line in Fig.3 right), and it can be shown [13] that their spin temperature is $T_{hf} \simeq T \left(1 + 2T_1/\tau\right)$, higher than the lattice. So we are led to the conclusion that the correlated Gd spins undergo fluctuations in the LRO phase with a time scale $\tau$ of the same order of magnitude as the hyperfine relaxation time $T_1$. It is to be noted that $\tau$ is longer than $\tau_L \simeq 30$ ns which is the hyperfine Larmor period for $^{155}$Gd. Observation of oscillations in the $\mu$SR decay in $\text{Gd}_2\text{Sn}_2\text{O}_7$ [14] shifts the lower limit for $\tau$ to 1 $\mu$s.

These spin fluctuations deep in the LRO phase could be concomittant with, for instance, soft spin-wave modes or peculiarities in the spin-wave spectrum. This was proved by very low temperature specific heat measurements [15, 16] which showed without ambiguity that the excitations in the LRO phase of $\text{Gd}_2\text{Sn}_2\text{O}_7$ are conventional gapped spin waves. A confirmation came from inelastic neutron scattering [17], which detected a $q$-independent excitation with energy 1.5 K above the ground state. The spin wave gap is thus $\Delta_{SW} \simeq 1.5$ K, and the spin fluctuations evidenced by Mössbauer spectroscopy at 27 mK, as well as the unexpected non-zero
muon relaxation rate observed down to 20 mK [14], do not seem to be linked with some anomaly in the spin-wave spectrum.

4. Degeneracy lifting and LRO due to finite anisotropy in Tb$_2$Sn$_2$O$_7$

The Tb$^{3+}$ ion in Tb$_2$Sn$_2$O$_7$ is subjected to the crystal electric field, and its ground state is a doublet [18] which has Ising anisotropy. Neutron diffraction reveals a transition to magnetic LRO at 0.87 K, with the development of ferromagnetic correlations just above the transition [19]. The $q=0$ long range magnetic structure is shown in Fig.4 right. It has been called the “ordered spin ice” structure because in each tetrahedron, the moment configuration “two spins in - two spins out” reproduces that of the ground state in the spin ice [5]. In this case, it is thought that the degeneracy lifting leading to LRO is brought about by the finite crystal field anisotropy. The spontaneous saturated LRO moment is 5.9(1) $\mu_B$, to which must be “added” a short range ordered component of 3.3(3) $\mu_B$, yielding a magnitude of 6.6(2) $\mu_B$ for the local Tb moment [20]. A ferromagnetic LRO component of 2.2 $\mu_B$/Tb is present along <100>.

The specific heat was also measured in Tb$_2$Sn$_2$O$_7$ down to 0.15 K. It is shown in Fig.4 right: deep in the LRO phase, one observes a clear turn-up below 0.4 K. It corresponds to the Schottky anomaly arising from the hyperfine splitting of the I=3/2 nuclear spin of $^{159}$Tb, with a hyperfine field value of 180(5) T. The hyperfine constant of Tb$^{3+}$ can be estimated as $C=38(3)$ T/$\mu_B$, taking into account the values measured in insulators [21] and the relativistic calculations [22, 23]. We then obtain a Tb moment of 4.7(5) $\mu_B$ from the nuclear Schottky anomaly. This moment value is markedly lower than the neutron derived one, and this can also be interpreted as caused by spin fluctuations in the LRO phase [13], with a relaxation time $\tau$ of the same order of magnitude as the nuclear relaxation time $T_1$.

This dynamic behaviour is supported by the unexpected results of $\mu$SR measurements [24] which, contrary to Gd$_2$Sn$_2$O$_7$, did not detect any oscillations of the $\mu^+$ decay in the LRO phase, nor any anomaly of the $\mu^+$ relaxation rate at the transition. High resolution inelastic neutron scattering [20] in Tb$_2$Sn$_2$O$_7$ depict a rather complex situation at low temperature, with different correlation lengths and time scales. Nevertheless, they present evidence for spin fluctuations with a characteristic time of 1 ns at 90 mK. This dynamic picture has been questioned in a $\mu$SR work where muons are not implanted in the sample, but in a nearby Ag plate [25]. Therefore, they
are sensitive not to the local fields, but to the field created by the bulk magnetisation. In zero field cooling, no oscillation is observed in the $\mu^+$ decay at 0.35 K, as expected for a domain compensated ferromagnet, but an oscillation appears after field cooling with 0.25 T. From these data and FC/ZGC susceptibility data, the authors conclude that their results “rule out a purely dynamical ground state” in Tb$_2$Sn$_2$O$_7$.

5. Discussion and conclusions
The situation in the Gd and Tb pyrochlore stannates is therefore puzzling as to the dynamic behaviour in the magnetic LRO phase. The problem is not restricted to the stannates since some titanates also present seemingly contradictory experimental data: Er$_2$Ti$_2$O$_7$ shows AF LRO at 1 K [26], but no oscillations of the $\mu$SR decay can be detected in the LRO phase [27]. The hyperfine relaxation time, found to be of the same magnitude as the spin fluctuation time in the stannates, would be unusually short, especially in Tb$_2$Sn$_2$O$_7$ ($\sim 10^{-8}$ s). The indirect Suhl-Nakamura nuclear spin-spin interaction [28] could perhaps account for this fast relaxation, especially for Tb which is monoisotopic. Finally, the presence of a tetragonal distortion at low temperature in the Tb pyrochlores [29] could contribute to enhance the spin fluctuations by mixing the wave functions and allowing transitions forbidden in the pure trigonal symmetry.

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