Spin fluctuations in the magnetically ordered phase of frustrated pyrochlore systems

P. Bonville*, I. Mirebeau† and J.-P. Sanchez**

*CEA, CE Saclay, DSM/Service de Physique de l’Etat Condensé, 91191 Gif-sur-Yvette, France
†CEA, CE Saclay, Laboratoire Léon Brillouin, 91191 Gif-sur-Yvette, France
**CEA, CE Grenoble, DSM/Service de Physique Statistique, Magnétisme et Supraconductivité, 38054 Grenoble, France

Abstract. Two geometrically frustrated pyrochlore stannates, undergoing long range magnetic order below 1 K, were investigated at very low temperature. Anomalies in the behaviour of hyperfine quantities are found, by $^{155}$Gd Mössbauer spectroscopy in Gd$_2$Sn$_2$O$_7$ and by low temperature specific heat measurements in Tb$_2$Sn$_2$O$_7$. They are interpreted in terms of fluctuations of the correlated Gd or Tb spins, using a model two-level system (the nuclear spins) submitted to a randomly fluctuating (hyperfine) field.

Keywords: 4f pyrochlore systems, spin fluctuations, geometrically frustrated magnetism
PACS: 31.30.Gs; 75.50.Lk; 76.30.Kg; 76.80.+y, 76.75.+i

1. INTRODUCTION

Geometrical frustration in magnetic systems occurs, for instance, in crystallographically ordered kagomé or pyrochlore lattices, where the building unit is resp. a triangle and a tetrahedron, and where the units are loosely bound, in general sharing an apex only (see Ref.[1] for a review). The simple example of Heisenberg (isotropic) spins on a triangle, coupled by antiferromagnetic (AF) exchange, illustrates the impossibility for this system to reach a collinear Néel type ground state. Frustration also plays a role in the case of Ising spins, but for ferromagnetic interactions, leading to the so-called “spin-ice” ground state [2], as found in the pyrochlore Ho$_2$Ti$_2$O$_7$. Geometrical frustration is expected to prevent the onset of long range magnetic order (LRO) down to the lowest temperature, but extra interactions like the dipolar coupling in the AF Heisenberg case, or a finite anisotropy in the case of spin-ices, can lift the large degeneracy of the ground state and stabilize a magnetic LRO state.

We focus here on two frustrated pyrochlore stannates undergoing LRO below around 1 K, Gd$_2$Sn$_2$O$_7$ [3] and Tb$_2$Sn$_2$O$_7$ [4]. We report on indirect experimental evidence, through the measurement of hyperfine quantities, that fluctuations of the correlated spins persist in the LRO phase, at least down to the 0.1 K range. Before we present the data, we will develop the model which mimics the real situation, i.e. a nuclear spin submitted to a randomly fluctuating electronic (hyperfine) magnetic field [5].
2. TWO-LEVEL SYSTEM DRIVEN BY A RANDOMLY REVERSING FIELD

We consider a (nuclear) spin 1/2, whose levels are split by a magnetic field, and we assume that two time scales govern the dynamics of the system: a relaxation time $T_1$, which maintains the equilibrium populations of the two levels, and a time $\tau$ associated with fluctuations of the field. At low temperature in the LRO phase, $T_1$ can be viewed as a magnon driven spin lattice relaxation time. We wish to calculate the steady state average populations of the two levels as a function of the ratio $T_1/\tau$, which in turn allows to obtain two hyperfine quantities of interest: the effective hyperfine temperature $T_{hf}$ and the hyperfine (nuclear) specific heat $C_{hf}$. When $\tau \gg T_1$, i.e. the common case, the hyperfine levels have time to reach thermal equilibrium in the interval between two reversals of the field; then $T_{hf} = T$ and $C_{hf} = C_{Sch}$, where $C_{Sch}$ is the regular Schottky anomaly associated with the hyperfine splitting $\Delta_{hf}$. Conversely, when $T_1 \gg \tau$, the hyperfine levels are completely out of equilibrium, the steady state populations of the two levels are equal, and $T_{hf}$ is infinite. For a finite value of the ratio $T_1/\tau$, it turns out that the problem is analytically solvable, and the details of the calculation can be found in Ref. [5]. The steady state population $p_g$ of the ground level writes:

$$p_g(T) = \frac{1}{2} \left( 1 + \frac{1}{1 + 2\frac{T_1}{\tau}} \tanh \frac{\Delta_{hf}}{k_B T} \right),$$

(1)

the hyperfine temperature being related to $p_g$ by: $p_g(T) = \left( 1 + \exp(-\frac{\Delta_{hf}}{k_B T_{hf}(T)}) \right)^{-1}$. Then, when $k_B T > 2\Delta_{hf}$, one obtains: $T_{hf} \simeq T(1+2\frac{T_1}{\tau})$, which means that the out of equilibrium hyperfine system is warmer than the lattice, and:

$$C_{hf} = \frac{1}{1 + 2\frac{T_1}{\tau}} C_{Sch} + \alpha \frac{\Delta_{hf}}{\frac{d}{dT}(\frac{T_1}{\tau})},$$

(2)

where $\alpha$ is a dimensionless coefficient of order unity. Our estimations show that the second term in this expression is much smaller than the first one, with the reasonable assumption that $T_1/\tau$ varies slowly with temperature. Then, the hyperfine specific heat is reduced by a factor $1 + 2\frac{T_1}{\tau}$ with respect to the expected Schottky anomaly, but does not change its shape. This implies an apparent reduction of the hyperfine field $H_{hf}$ giving rise to the nuclear level splittings.

These two remarkable effects, the warming up of the hyperfine levels and the reduction of the Schottky nuclear anomaly, can be observed when it occurs that the nuclear relaxation time $T_1$ is of the same magnitude as the reversal time $\tau$; the latter corresponds to a spin-flip time since, for rare earths, the hyperfine field is proportional to the magnetic moment to a very good approximation.
Gd$_2$Sn$_2$O$_7$ shows magnetic order below 1 K and its AF $k$=0 magnetic structure corresponds to that expected for a Heisenberg pyrochlore antiferromagnet where the degeneracy is lifted by a sizeable dipolar interaction [6]. The $^{155}$Gd Mössbauer spectrum at 0.027 K is shown in Fig. 1 left. It is a LRO spectrum with a hyperfine field $H_{hf} \simeq 30$ T, and with a sizeable hyperfine quadrupolar interaction. The ground nuclear spin $I_g = 3/2$ is then split into two quasi-doublets separated by about 0.015 K. Thus, below 0.1 K, the line intensities of the Mössbauer transitions depend on temperature through the Boltzmann populations of the hyperfine levels, and the absolute temperature can be determined by fitting the spectrum. It is clear in Fig. 1 left that the hyperfine temperature (0.09 K) is higher than the lattice temperature (0.027 K). According to section 2, this points to the presence of Gd spin fluctuations, at 0.027 K, with a time scale $\tau$ of the same order as the nuclear spin-lattice time $T_1$: $T_1 / \tau \simeq 1$. Since no relaxational effects are observed in the Mössbauer spectrum, this implies that $\tau$ is longer than the hyperfine Larmor period for $^{155}$Gd $\tau_L \sim 3 \times 10^{-8}$ s. Muon spin resonance ($\mu$SR) measurements carried out at 0.02 K in zero field and longitudinal geometry [7] show an oscillating time decay due to the precession of the $\mu^+$ spin in the dipolar field $H_{dip}$ from the Gd moments. The pulsation associated with the precession is $\Delta = \gamma_\mu H_{dip}$, where $\gamma_\mu = 851.6$ Mrad s$^{-1}$ T$^{-1}$ is the $\mu^+$ gyromagnetic ratio. Actually, one observes two pulsations: $\Delta=190$ and 380 Mrad s$^{-1}$, corresponding probably to two muon stopping sites. No damping at short times is observed, and this allows to set a lower limit for $\tau$.

For this purpose, we computed the $\mu^+$ depolarisation $P_z(t)$ in the presence of a dipolar field perpendicular to the initial $\mu^+$ polarisation direction and randomly reversing with a frequency $\nu$. We used the stochastic theory developed in Ref. [8], which assumes the

```
3. THE VERY LOW TEMPERATURE $^{155}$GD MÖSSBAUER SPECTRUM IN GD$_2$SN$_2$O$_7$
```
field jumps have a stationary and Markovian character. In the slow relaxation regime ($\nu < 2\Delta$), one obtains a damped oscillatory behaviour:

$$P_z(t) = \exp\left(-\frac{\nu^2}{2} t\right) \left(\cos \delta t + \frac{\nu^2}{2\delta} \sin \delta t\right),$$

(3)

where $\delta = \sqrt{\Delta^2 - \nu^2/4}$. Setting $\beta = \nu^2 \Delta$, this signal can be viewed as a damped cosine function with a reduced pulsation $\Delta' = \Delta \sqrt{1 - \beta^2}$ and a phase shift $\varphi$ such that $\tan \varphi = \beta / \sqrt{1 - \beta^2}$. In the limiting case $\nu = 2\Delta$, one gets: $P_z(t) = \exp(-\frac{\nu^2}{2} t) (1 + \frac{\nu^2}{2\beta} t)$.

In the fast relaxation regime ($\nu > 2\Delta$), an expression analogous to (3) holds, with the trigonometric functions replaced by hyperbolic ones, and with $\delta = \sqrt{\nu^2/4 - \Delta^2}$. In this case, an exponential-like decay is obtained. In the extreme narrowing limit, when $\nu \gg 2\Delta$, a true exponential decay occurs: $P_z(t) = \exp(-\lambda_z t)$, with $\lambda_z = \frac{\Delta^2}{\nu}$. This latter formula differs by a factor 2 from the usual expression for $\lambda_z$ in the paramagnetic phase, i.e. in the presence of randomly distributed fluctuating fields.

The behaviour of $P_z(t)$ is sketched in Fig. 1 right, for $\Delta = 380 \text{ Mrad s}^{-1}$ and for fluctuation frequencies ranging from 1 to 300 MHz. It can be seen that the upper limit of the fluctuation frequency which allows the full undamped oscillations to be observed amounts to about 10 MHz. The lower limit for $\tau$ is then $10^{-7}$ s, which is compatible with the Mössbauer data.

For Gd materials, the small hyperfine interaction precludes the observation of the nuclear Schottky anomaly in the currently attainable temperature range for specific heat measurements (T > 0.05 K).

4. LOW TEMPERATURE SPECIFIC HEAT IN TB$_2$Sn$_2$O$_7$

TB$_2$Sn$_2$O$_7$ orders magnetically below 0.87 K, according to a k=0 “ordered spin-ice” structure [4], i.e. the Tb$^{3+}$ magnetic moments lie close to the four threefold <1 1 1> axes within a tetrahedron in the “two in-two out” configuration, like in a regular spin-ice. The local saturated Tb$^{3+}$ moment is found to be 5.9(1) $\mu_B$/Tb. The rare-earth magnetic (4f) specific heat (the lattice contribution is negligible below 5 K) is shown in Fig. 2 left. Apart from the $\lambda$-like anomaly at $T_C$, a nuclear Schottky tail is observed in the LRO phase below 0.4 K. It can be accounted for by a hyperfine field of 180 T acting on the $I = 3/2$ spin of the isotope $^{159}$Tb, the hyperfine quadrupolar contribution being very small. Since the hyperfine constant for Tb is 40(3) T/$\mu_B$ [9], the corresponding magnetic moment is $m=4.50(3)$ $\mu_B$/Tb [10] (see solid lines in Fig. 2 left). This value is remarkably smaller than the value 5.9 $\mu_B$ found in the neutron diffraction experiments [4], which we interpret, in the frame of the model developed in section 2 as a clue to the presence of spin fluctuations. Indeed, the high temperature tail of the nuclear Schottky anomaly is proportional to $\Delta_{hf}^2$, i.e. to $m^2$. Hence, an overall depletion of the specific heat according to expression (2) leads to a reduction of the derived moment by the factor $\sqrt{1 + 2\frac{\mu_{hf}^2}{m^2}}$. In the present case, this yields: $T_1/\tau \simeq 0.4$. Fluctuations of the correlated Tb spins in the LRO phase were also inferred from $\mu$SR data [11, 12]. Contrary to Gd$_2$Sn$_2$O$_7$, no oscillations are observed, and the time decay of the $\mu^+$
spin depolarisation is exponential, which corresponds to the extreme narrowing limit of expression $\overline{3}$. From the measured low temperature value $\lambda_z \simeq 2.3 \text{ MHz}$ and a value $\Delta \sim 100 \text{ Mrad s}^{-1}$, $\tau$ is estimated at $10^{-10} \text{ s}$ $\overline{11}$.

In the parent compound Tb$_2$Ti$_2$O$_7$ which, contrary to Tb$_2$Sn$_2$O$_7$, does not order down to 0.05 K, a Schottky upturn in the specific heat has nevertheless been observed below 0.3 K $\overline{15}$. It corresponds approximately to a hyperfine field of 115 T, i.e. to a Tb moment value of 2.9 $\mu_B$, which is also strongly reduced with respect to the crystal field ground state value of $\simeq 5 \mu_B$ $\overline{16, 17}$. This is very likely to be due to moment fluctuations, associated with the strong short range dynamic spin correlations which persist down to the lowest temperature in the spin-liquid Tb$_2$Ti$_2$O$_7$.

5. SUMMARY AND CONCLUSIONS

Anomalies in the hyperfine quantities were detected in the LRO phase of some rare-earth based frustrated pyrochlore systems. They strongly suggest that spin fluctuations of the correlated moments persist in the magnetically ordered phase, down to very low temperature, with frequencies in the range 10 MHz - 10 GHz. The mechanism underlying these fluctuations could be a tunneling between degenerate spin configurations. However, these observations demand that the two time scales, the nuclear relaxation time $T_1$ and the spin-flip time $\tau$, be of the same order of magnitude, which is strongly material dependent. For example, no anomaly in the hyperfine temperature is observed in Gd$_2$Ti$_2$O$_7$ $\overline{5}$, whereas this material is likely to behave similarly to Gd$_2$Sn$_2$O$_7$. The nuclear Schottky upturn in Yb$_2$Ti$_2$O$_7$ $\overline{13}$ corresponds exactly to the hyperfine field of 114 T measured by $^{170}$Yb Mössbauer spectroscopy $\overline{14}$ (see Fig.2 right), although spin fluctuations have been evidenced in the low temperature short range ordered phase of this material $\overline{14}$.
ACKNOWLEDGMENTS

We are grateful for useful discussions with P. Dalmas de Réotier and J.A. Hodges.

REFERENCES

1. A.P. Ramirez, ”Geometrical frustration”, in Handbook of magnetic materials 13, edited by K.H.J. Buschow, Elsevier, 2001, pp. 423–520
2. M.J. Harris, S.T. Bramwell, D.F. McMorrow, T. Zeiske, K.W. Godfrey, Phys. Rev. Lett. 79, 2554–2557 (1998).
3. A.S. Wills, M.E. Zhitomirsky, B. Canals, J.P. Sanchez, P. Bonville, P. Dalmas de Réotier, A. Yaouanc, J.Phys.: Condens.Matter 18, L37-L42 (2006)
4. I. Mirebeau, A. Apetrei, J. Rodríguez-Carvajal, P. Bonville, A. Forget, D. Colson, V.N. Glazkov, J.P. Sanchez, O. Isnard, E. Suard, Phys. Rev. Lett. 94, 246402 (2005)
5. E. Bertin, P. Bonville, J.P. Bouchaud, J.A. Hodges, J.P. Sanchez, P. Vulliet, Eur. Phys. J. B 27, 347–354 (2002)
6. S.E. Palmer, J.T. Chalker, Phys. Rev. B 62, 488 (2000)
7. P. Bonville, J.A. Hodges, E. Bertin, J.P. Bouchaud, P. Dalmas de Réotier, L.P. Regnault, H.M. Ronnow, J.P. Sanchez, S. Sosin, A. Yaouanc, Hyperfine Interactions 156-157, 103–111 (2004)
8. S.K. Dattagupta, Hyperfine Interactions 11, 77 (1981)
9. B.D. Dunlap, “Relativistic effects in hyperfine interactions”, in Mössbauer effect methodology 7, edited by I.J. Gruverman, Plenum Press, 1971, pp.123–145
10. A moment value of 3.38µB/Tb has been erroneously stated in Ref.[4].
11. P. Dalmas de Réotier, A. Yaouanc, L. Keller, A. Cervellino, B. Roessli, C. Baines, A. Forget, C. Vâju, P.C.M. Gubbens, A. Amato, P.J.C. King, Phys. Rev. Lett. 96, 127202 (2006)
12. F. Bert, P. Mendels, A. Olariu, N. Blanchart, G. Collin, A. Amato, C. Baines, A.D. Hillier, Phys. Rev. Lett. 97, 117203 (2006)
13. H.W.J. Blöte, R.F. Wielinga, W.J. Huiskamp, Physica 43, 549–568 (1969)
14. J.A. Hodges, P. Bonville, A. Forget, A. Yaouanc, P. Dalmas de Réotier, G. André, M. Rams, K. Krolas, C. Ritter, P.C.M. Gubbens, C.T. Kaiser, P.J.C. King, C. Baines, Phys. Rev. Lett. 88, 077204 (2002)
15. R. Siddhartan, B.S. Shastry, A.P. Ramirez, A. Hayashi, R.J. Cava, S. Rosenkranz, Phys. Rev. Lett. 83, 1854 (1999)
16. M. J. P. Gingras, B. C. denHertog, M. Faucher, J. S. Gardner, S. Dunsinger, L. J. Chang, B. D. Gaulin, N. P. Raju, J. E. Greedan, Phys. Rev. B 62, 6496 (2000)
17. I. Mirebeau, P. Bonville, M. Hennion, Phys. Rev. B 76, 184436 (2007)