Eur. Phys. J. B **27**, 347–354 (2002)
DOI: 10.1140/epjb/e2002-00165-2

**THE EUROPEAN
PHYSICAL JOURNAL B**

Effective hyperfine temperature in frustrated $Gd_2Sn_2O_7$: two level model and ^{155}Gd Mössbauer measurements

E. Bertin[1], P. Bonville[1,a], J.-P. Bouchaud[1], J.A. Hodges[1], J.P. Sanchez[2], and P. Vulliet[2]

[1] Commissariat à l'Énergie Atomique, Service de Physique de l'État Condensé, 91191 Gif-sur-Yvette, France
[2] Commissariat à l'Énergie Atomique, Service de Physique Statistique, Magnétisme et Supraconductivité, 38054 Grenoble, France

Received 17 October 2001

Abstract. Using ^{155}Gd Mössbauer spectroscopy down to 27 mK, we show that, in the geometrically frustrated pyrochlore $Gd_2Sn_2O_7$, the Gd^{3+} hyperfine levels are populated out of equilibrium. From this, we deduce that the hyperfine field, and the correlated Gd^{3+} moments which produce this field, continue to fluctuate as $T \to 0$. With a model of a spin 1/2 system experiencing a magnetic field which reverses randomly in time, we obtain an analytical expression for the steady state probability distribution of the level populations. This distribution is a simple function of the ratio of the nuclear spin relaxation time to the average electronic spin-flip time. In $Gd_2Sn_2O_7$, we find the two time scales are of the same order of magnitude. We discuss the mechanism giving rise to the nuclear spin relaxation and the influence of the electronic spin fluctuations on the hyperfine specific heat. The corresponding low temperature measurements in $Gd_2Ti_2O_7$ are presented and discussed.

PACS. 76.80.+y Mössbauer effect, other γ-ray spectroscopies – 75.50.Ee Antiferromagnetics – 75.40.Gb Dynamic properties – 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion

1 Introduction

In geometrically frustrated magnetic systems, the interaction energies cannot be minimised at the same time for all pairs of spins [1]. A simple example is the two-dimensional triangular lattice with nearest-neighbour antiferromagnetic (AF) coupling of isotropic spins (the so-called Heisenberg antiferromagnet). An analogous situation in three dimensions is provided by the pyrochlore structure compounds with general formula $R_2M_2O_7$ where the rare earth (R) ions and the transition metal or *sp*-metal (M) ions each lie on an array of corner-sharing tetrahedra. A general prediction was made by Villain [2] about the ground state of a Heisenberg antiferromagnet on a tetrahedral lattice: as the temperature goes to zero, there is no long range ordering and the system remains in a collective paramagnetic state where spin fluctuations persist. The low temperature properties in frustrated systems may also be influenced by perturbations beyond the dominant nearest neighbour exchange interaction [3]. These include exchange with more distant neighbours [4–6], dipolar coupling [7], and anisotropy [8,9]. They may lead to the lifting of the degeneracy of the ground state and to the development of magnetic long range order.

The gadolinium based pyrochlore compounds $Gd_2Ti_2O_7$ and $Gd_2Sn_2O_7$, where the M sublattice is non-magnetic, possess the basic ingredients of a Heisenberg antiferromagnet. The Gd^{3+} ion has zero orbital moment ($L = 0$, $S = 7/2$) and thus presents a (quasi) isotropic response to an exchange or external field. Both compounds show a negative paramagnetic Curie-Weiss temperature θ_p indicative of AF coupling. Our values, $\theta_p = -9.9$ K for $Gd_2Ti_2O_7$ and -8.6 K for $Gd_2Sn_2O_7$, are similar to those of the literature [10,11]. Experimentally, however, it is known that the properties of the Gd^{3+} based pyrochlores do show some differences relative to those expected for the nearest neighbour AF Heisenberg model. For example, in $Gd_2Ti_2O_7$, specific heat data suggest that a phase transition occurs near 1 K [10] and below this temperature neutron diffraction data evidence magnetic Bragg peaks [12]. The details of the low temperature properties of the Gd^{3+} based pyrochlores are however quite complex. We show here that, in $Gd_2Sn_2O_7$, the Gd^{3+} spins are magnetically correlated and continue to fluctuate as $T \to 0$.

The evidence for the very low temperature spin fluctuations is provided by ^{155}Gd Mössbauer measurements, but not through the conventional approach based on the analysis of the Mössbauer line shape to obtain the relaxation rate. This approach is possible only when the fluctuation rate of the spins falls within the classical Mössbauer "relaxation window", which is centered around 100 MHz for ^{155}Gd. In the present case, the spins fluctuate at

---

[a] e-mail: `bonville@spec.saclay.cea.fr`

lower frequencies such that the hyperfine field associated with the Gd^{3+} spin appears static on the Mössbauer time scale. The very low temperature spin fluctuations were evidenced using a novel method, *i.e.* through the observation that the hyperfine levels of the ^{155}Gd nuclei are populated out of thermal equilibrium. We show that an out-of-equilibrium distribution can occur when the electronic spin flips persist at low temperature and when the nuclear relaxation time T_1 is longer than, or of the same magnitude as, the flipping time τ of the hyperfine field (of the electronic spin). Considering the nuclear spins as a two-level system driven by a randomly fluctuating field, we develop a stochastic model which yields an analytical expression for the probability distribution of the level populations. This quantity depends on the ratio T_1/τ of the two characteristic times of the system and it is directly linked to the effective hyperfine temperature provided by the very low temperature Mössbauer measurements.

We also propose a nuclear relaxation mechanism, linked with the scattering of electronic spin-waves, which could explain the short nuclear relaxation times suggested by the analysis and we discuss some implications of the presence of spin fluctuations on the magnitude of the hyperfine specific heat.

2 The low temperature ^{155}Gd Mössbauer measurements

The pyrochlore lattice corresponds to the cubic space group $Fd3m$ and the crystallographic unit cell contains 16 Gd^{3+} ions each with the same point symmetry $\bar{3}m$. Each Gd^{3+} ion has one of the four [111] directions as threefold symmetry axis. The Mössbauer transition of the ^{155}Gd isotope links the nuclear ground state, with spin $I_g = 3/2$ to the first excited state, with spin $I_e = 5/2$, at an energy $E_0 = 86.5$ keV. The Mössbauer spectra for $Gd_2Sn_2O_7$ and for $Gd_2Ti_2O_7$ were recorded in the range from 4.2 K down to 27 mK, in a ^{3}He-^{4}He dilution refrigerator coupled to a constant acceleration spectrometer and using a Sm(^{155}Eu)Pd$_3$ source. For ^{155}Gd, the velocity unit 1 mm s^{-1} corresponds to 69.8 MHz or to 3.35 mK.

At 4.2 K, in agreement with the literature [13,14], for each of the two compounds we observe a quadrupole hyperfine spectrum characteristic of the paramagnetic phase. The quadrupole splitting is -4 and -5.5 mm s^{-1} in $Gd_2Sn_2O_7$ and in $Gd_2Ti_2O_7$ respectively, corresponding respectively to a splitting of 13.5 and 18.4 mK between the $m = \pm 3/2$ and $m = \pm 1/2$ sublevels of the $I_g = 3/2$ ^{155}Gd nuclear ground state. As Gd^{3+} is an S-state ion, in these insulating compounds, the hyperfine quadrupole interaction is due only to the electric field gradient produced by the anisotropic distribution of lattice charges.

Below ~ 1 K, an additional magnetic hyperfine interaction is visible. Usually, the presence of a hyperfine field is linked with magnetic ordering, but short range correlated moments also yield a hyperfine field spectrum provided their fluctuation frequency is lower than a characteristic value of about 100 MHz for ^{155}Gd. The thermal evolution of the magnetic hyperfine parameters and the information they provide concerning low temperature magnetic properties will be discussed in a future publication. We mention here that, in each compound at any temperature below $\sim$1 K, the four moments of a tetrahedron have a common size and a common local direction (perpendicular to the appropriate [111] axis). Our results are coherent with a number of the features of the magnetic structure proposed for $Gd_2Ti_2O_7$ in reference [12], but differ in one aspect. Whereas reference [12] suggests that one of the sites of a tetrahedron experiences zero mean field, we find that a sizeable exchange field is present at each of the four sites.

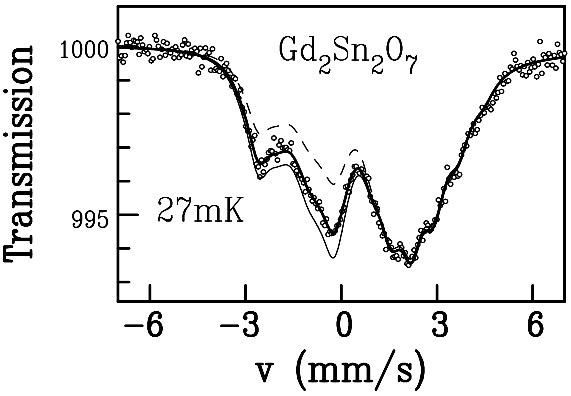

Fig. 1. ^{155}Gd Mössbauer absorption spectrum at 27 mK in $Gd_2Sn_2O_7$. The sample temperature is at most 33(2) mK (see text). The dashed line represents the expected theoretical spectrum at $T = 27$ mK, the thin solid line the expected spectrum for equipopulated hyperfine levels ($T > 0.2$ K) and the thick solid line passing through the experimental points the spectrum with a fitted effective temperature $T_{\text{eff}} = 90$ mK.

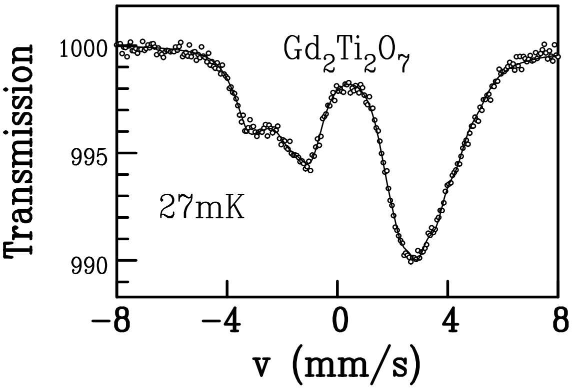

Fig. 2. ^{155}Gd Mössbauer absorption spectrum at 27 mK in $Gd_2Ti_2O_7$. The sample temperature is at most 33(2) mK (see text). The fitted line was obtained with an effective temperature of 36 mK.

In the following, we will focus on the data obtained at 27 mK, shown in Figure 1 for $Gd_2Sn_2O_7$ and in Figure 2 for $Gd_2Ti_2O_7$. For $Gd_2Sn_2O_7$, the fitted hyperfine field is 30 T, and the combined quadrupolar and magnetic interactions within the ground $I_g = 3/2$ nuclear state yield four hyperfine sublevels with energies 0, 0.05, 12.1 and 15.9 mK. Therefore, at a temperature not too high with respect to these splittings, the intensities of the Mössbauer absorption transitions originating from these levels should reflect their different populations. In other words, the effective hyperfine temperature can be obtained from the line intensities of the ^{155}Gd Mössbauer spectrum insofar that the temperature is below about 200 mK. The 27 mK spectrum in $Gd_2Sn_2O_7$ of Figure 1 was fitted with the temperature as a free parameter. Surprisingly, the best fit, shown as a thick solid line in Figure 1, yields an effective hyperfine temperature of 90 mK. Taking into account experimental uncertainties, this temperature falls in the range from 60 to 120 mK. Also represented in Figure 1 are the expected spectrum for $T = 27$ mK (dashed line) and the limiting high temperature ($T > 200$ mK) spectrum when the hyperfine levels are equi-populated (thin solid line). Thus, it is clear the difference between the measured effective hyperfine temperature and the sample temperature is outside statistical errors. In this analysis, lineshape effects that could lead to intensity deviations were fully accounted for: the dispersive correction [15] was included with $\xi = 0.027$, as was the Goldanskii-Karyagin effect shown to be present in the Gd pyrochlores [16] with an anisotropy coefficient $\epsilon = -1.5$.

We checked that the Mössbauer absorber, which is in the form of a powder mixed with General Electric varnish and glued onto a thin copper sheet, was correctly thermalised by carrying out two controls. First we performed a 27 mK measurement with the isotope ^{151}Eu ($I_g = 5/2, I_e = 7/2, E_0 = 21.6$ keV) in the insulating compound $EuAl_2Si_2O_8$ (Eu^{2+} charge state) in its saturated magnetically ordered state. As the hyperfine interaction is larger for $^{151}Eu^{2+}$ than for $^{155}Gd^{3+}$, Eu^{2+} compounds are better “Mössbauer thermometers” [17] than are Gd^{3+} compounds. From these measurements, we found that the ^{151}Eu hyperfine level temperature corresponds exactly to the sample temperature. Second, we performed, under identical experimental conditions as for the pyrochlores, a 27 mK ^{155}Gd Mössbauer measurement in the metallic Gd-based ferromagnet $GdCo_2B_2$ ($T_C = 26$ K). This compound was selected because the size of the quadrupole hyperfine interaction and the size and direction of the saturated hyperfine field relative to the principal axis of the electric field gradient [18] are close to those in the pyrochlores. We obtained a hyperfine level temperature of 33(2) mK, slightly higher than that of the sample. This difference could be due to the heating of the sample by the incident high energy γ-rays, so that a small temperature gradient exists between the sample and the carbon temperature probe. Such a heating would also occur for the ^{155}Gd measurements in the pyrochlores meaning that for a temperature probe value of 27 mK, the actual sample temperature could be 33(2) mK. We thus reach the conclusion that in $Gd_2Sn_2O_7$, the sample temperature is at most 35 mK, but that the hyperfine levels have an effective temperature of 90(30) mK; they are thus populated out of thermal equilibrium.

From the ^{155}Gd Mössbauer analysis of the 27 mK data in $Gd_2Ti_2O_7$ (Fig. 2), we find that the hyperfine field is 28.3 T, and the combined quadrupolar and magnetic interactions yield four hyperfine sublevels situated at 0, 0.02, 17.0 and 20.4 mK. In contrast to $Gd_2Sn_2O_7$, the measured effective hyperfine temperature is found to be 36 mK. As this is only very marginally higher than the sample temperature (33(2) mK), there is no clear experimental evidence that the hyperfine level temperature is different from that of the sample. The hyperfine levels can be said to be practically in thermal equilibrium. As the measurements in $Gd_2Sn_2O_7$ and in $Gd_2Ti_2O_7$ were carried out under exactly the same experimental conditions, the fact that there is at most only a small difference in the two temperatures for $Gd_2Ti_2O_7$, whereas there is a marked difference for $Gd_2Sn_2O_7$ reinforces the credibility of the anomalous hyperfine level temperature found for $Gd_2Sn_2O_7$.

Our interpretation of the non-Boltzmann population distribution in $Gd_2Sn_2O_7$ is based on the influence of spin dynamics. The hyperfine levels do not reach thermal equilibrium because the Gd^{3+} hyperfine field continues to fluctuate as $T \to 0$. In turn, this means the Gd^{3+} magnetic moments which are at the origin of the hyperfine fields continue to fluctuate as $T \to 0$. As shown in Section 4, this approach also entails that the hyperfine spin-lattice times are of the same magnitude as those associated with the fluctuations of the Gd^{3+} hyperfine field.

As described above, the quadrupole and magnetic hyperfine interactions in $Gd_2Sn_2O_7$ lift the degeneracy of the $I_g = 3/2$ ground state to leave two almost degenerate levels at 0 and 0.05 mK and two closely separated levels at 12.1 and 15.9 mK. To a first approximation, this resembles a two level system with an energy separation ~ 14 mK. In the next section we present a model of a spin 1/2 system driven by a randomly varying (hyperfine) field. Although the ^{155}Gd mixed nuclear levels in $Gd_2Sn_2O_7$ cannot be mapped exactly onto a spin 1/2 system, the main results of our calculation are not affected by the details of the nuclear wave-functions.

3 The model of a two-level system driven by a randomly varying field

In order to put on a more quantitative ground the concept of effective temperature due to the competition between nuclear relaxation with time scale T_1 and electronic spin flip, with time scale τ, we performed a model calculation on a two-level (nuclear) spin 1/2 system driven by a randomly time dependent (hyperfine) field.

We wish to calculate the steady state out-of-equilibrium distributions of the populations of the two levels. We show here that the problem of a two level system in a randomly flipping field is exactly soluble, and that the steady state probability distribution can be expressed in terms of the ratio $\mu = T_1/\tau$. A two level system need not necessarily be a spin 1/2 system. The low temperature properties of glasses, for example, are argued to be dominated by quasi degenerate local configurations, where an atom or molecule hops between two local equilibrium positions [19,20]. The difference of energies between these two positions plays the role of the Zeeman splitting for a spin 1/2. If these two level systems are strongly interacting, then the splitting field itself will have non trivial dynamics, and our calculation might be relevant to this situation as well.

Our calculation provides an exact solution for the steady state distribution of a non equilibrium, randomly driven system. For a two level system, it is justified to describe the relaxation dynamics in terms of a single relaxation time T_1. This comes from the fact that the Master evolution operator for the 'up' probability $P_{\mathrm{u}}(t)$ and 'down' probability $P_{\mathrm{d}}(t)$ has two eigenvalues – one is zero and corresponds to the Boltzmann equilibrium, and the second is $1/T_1$. Here we will consider a splitting field $H(t) = \pm H_0$, which changes its direction (or sign) randomly in time. We assume that the probability of switching per unit time is a constant $1/\tau$. Then the time interval t_f between two successive flips is distributed according to an exponential law of mean τ:

$$\rho(t_f) = \frac{1}{\tau}\,\mathrm{e}^{-t_f/\tau}. \tag{1}$$

We are interested in the distributions of the populations of the two levels, but it turns out that the calculation is easier if we use the magnetization $M(t)$:

$$M(t) = m_0\left[P_{\mathrm{u}}(t) - P_{\mathrm{d}}(t)\right], \tag{2}$$

where $\pm m_0$ is the intrinsic moment of the spin levels. This is due to the symmetry properties of the corresponding distributions (see Eq. (7) below). Within the time interval during which $H(t)$ is constant, we obtain an explicit expression for $M(t)$, that we denote by $M^+(t)$ or $M^-(t)$, depending on the sign of $H(t)$. Suppose $H(t)$ is positive between t_1 and t_2, and then negative between t_2 and t_3. Then we can write, for $t_1 \le t \le t_2$:

$$M^+(t) = M_0\left(1 - \mathrm{e}^{-(t-t_1)/T_1}\right) + M^-(t_1)\,\mathrm{e}^{-(t-t_1)/T_1} \tag{3}$$

and for $t_2 \le t \le t_3$:

$$M^-(t) = -M_0\left(1 - \mathrm{e}^{-(t-t_2)/T_1}\right) + M^+(t_2)\,\mathrm{e}^{-(t-t_2)/T_1}. \tag{4}$$

where $M_0 = m_0 \tanh\frac{m_0 H_0}{k_B T}$ is the Boltzmann magnetization of the system under a static magnetic field H_0. Since the times t_i are randomly distributed, we must determine the sequence of random magnetizations corresponding to the flipping times, $M^-(t_{2i+1})$ and $M^+(t_{2i+2})$. In the steady state, these quantities are identically distributed random variables M^- and M^+, with some probability distributions $\mathcal{P}_-(M^-)$ and $\mathcal{P}_+(M^+)$. Between two successive flips, M^+ and M^- are related by:

$$M^+ = M_0\left(1 - \mathrm{e}^{-t_f/T_1}\right) + M^-\mathrm{e}^{-t_f/T_1}, \tag{5}$$

and *vice versa.* Obviously, both M^+ and M^- will be in the interval $[-M_0, M_0]$. The stationarity of the probability distributions allows us to write the following equation:

$$\mathcal{P}_+\left(M^+\right) = \int_{-M_0}^{M_0} \mathrm{d}M^-\,\mathcal{P}_-(M^-)\int_0^{+\infty}\mathrm{d}t_f\,\rho(t_f) \times\delta\left[M^+ - \left(M_0\left(1-\mathrm{e}^{-t_f/T_1}\right) + M^-\mathrm{e}^{-t_f/T_1}\right)\right]. \tag{6}$$

For reasons of symmetry, $\mathcal{P}_+$ and $\mathcal{P}_-$ satisfy the following relation:

$$\mathcal{P}_-(M) = \mathcal{P}_+(-M), \tag{7}$$

so that we get an integral equation involving only one distribution. It will be useful to make the following changes of variables:

$$u = \mathrm{e}^{-t_f/T_1}, \qquad y = \frac{M^+}{M_0}, \qquad z = \frac{M^-}{M_0}\cdot \tag{8}$$

One therefore also has: $P_+(y) = M_0\,\mathcal{P}_+(M^+)$. The resulting integral equation is:

$$P_+(y) = \int_{-1}^{1}\mathrm{d}z\,P_+(-z\ )\int_0^1\frac{T_1\,\mathrm{d}u}{u} \times\frac{u^{T_1/\tau}}{\tau}\ \delta\left[y - ((1-u) + zu)\right]\cdot \tag{9}$$

Introducing the ratio $\mu = T_1/\tau$ of the relaxation time to the flipping time and using the properties of the δ distribution we find:

$$P_+(y) = \int_{-1}^{1}\mathrm{d}z\,\frac{P_+(-z)}{1-z}\int_0^1\mu\,\mathrm{d}u\,u^{\mu-1}\,\delta\left(u - \frac{1-y}{1-z}\right)\cdot \tag{10}$$

For the integral over u to be non-zero, we must have $\frac{1-y}{1-z} < 1$, or equivalently $z < y$. Changing z in $-z$, we obtain the resulting integral equation:

$$P_+(y) = \mu(1-y)^{\mu-1}\int_{-y}^{1}\frac{P_+(z)}{(1+z)^{\mu}}\mathrm{d}z\cdot \tag{11}$$

It is easily checked that the following beta-distribution is an exact solution of this integral equation:

$$P_+(y) = \frac{\Gamma\left(\frac{1}{2}+\mu\right)}{\Gamma\left(\frac{1}{2}\right)\,\Gamma(\mu)}\,(1-y)^{\mu-1}(1+y)^{\mu}, \tag{12}$$

where $\Gamma(x)$ is the usual Gamma function defined as: $\Gamma(x) = \int_0^{+\infty} t^{x-1}e^{-t}\mathrm{d}t$. Now we are interested in the distribution of magnetization $M(t)$ at *any* time t, not necessarily a flipping time. However, since the flip times are chosen at random, the distribution we have just computed is also that governing the magnetization observed at an arbitrary instant of time.

This distribution $P_+(y)$ must be used to compute the average populations of the energy levels, as will be done in the next section. Here, we just derive the mean distribution $P(y)$ of the (rescaled) magnetization, obtained by averaging over the periods of positive and negative H.

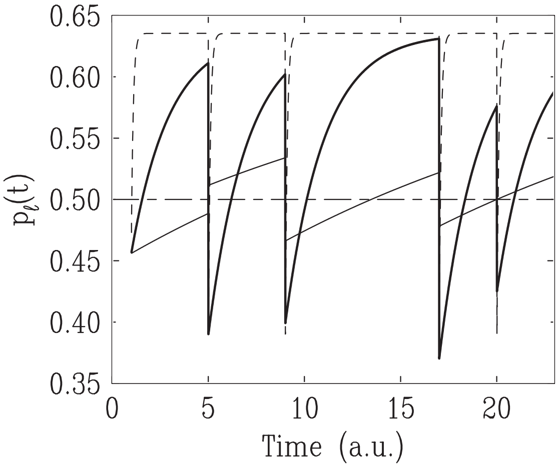

Fig. 3. Temporal evolution of the population $p_\ell(t)$ of the ground level of a nuclear spin 1/2 doublet as the hyperfine field reverses randomly in time, for three values of the ratio T_1/τ. The doublet splitting is $\Delta/k_B = 14$ mK and the sample temperature $T = 33$ mK. The reversals were arbitrarily chosen to occur at 5, 9, 17 and 20 a.u and the nuclear relaxation has an exponential form. Dashed line: $T_1 \ll \tau$; the hyperfine levels have time to thermalize between spin flips, and the time average of p_ℓ is the Boltzmann value p_ℓ^{B} (0.63); thick solid line: $T_1 \sim \tau$; the time average of p_ℓ is smaller than p_ℓ^{B} and it is a function of the ration T_1/τ; thin solid line (with straight segments): $T_1 \gg \tau$; the time average of p_ℓ tends to 0.50.

Since the two values of H are equally probable, we can write $P(y)$ as:

$$P(y) = \frac{1}{2}\left[P_+(y) + P_+(-y)\right] \tag{13}$$

$$= \frac{\Gamma\left(\frac{1}{2}+\mu\right)}{\Gamma\left(\frac{1}{2}\right)\Gamma(\mu)}(1-y^2)^{\mu-1}, \tag{14}$$

which is, of course, an even expression in y, leading to a zero mean value for the magnetization. For $\mu \to 0$, this distribution tends to two δ functions at ± 1, as it should. Interestingly, when $\mu < 1$, the points $y = \pm 1$ are still the most probable values of the magnetization. This comes from the fact that for long flip times, the magnetization has time to converge towards its asymptotic value. However, when the flips become too frequent (*i.e.* for $\mu > 1$), the most probable value of the magnetization is zero. For large μ, the distribution actually becomes Gaussian, with a width equal to $1/\sqrt{\mu}$.

4 Effective hyperfine temperature in $Gd_2Sn_2O_7$

In order to compare with experiment (Sect. 2), it is convenient to express the probability distribution found above in terms of an effective temperature. First, we present in Figure 3 a schematic representation of the time dependence of the population of the lowest energy level for the two limiting cases of rapid and slow nuclear relaxation with respect to the spin flip, and for the intermediate case where the two time scales T_1 and τ are of comparable magnitude. When T_1 is comparable to or larger than τ, the time-averaged population is reduced compared to the Boltzmann value. In this context it is important to emphasize the difference between spin states and energy levels. When the hyperfine field flips, the spin states exchange their energies, so that the two spin directions are equiprobable on average. This is not the case for the energy levels, as the level with the lowest energy remains the most probable on average.

We now calculate the steady state population of the lowest level. We can identify a spin state and an energy level only for a given value of the field $H(t)$. For instance, if $H(t) = +H_0$, the lowest energy level corresponds to the "up" state. The probability p_ℓ^+ to be in the lowest state when $H(t) = +H_0$ is therefore given by:

$$p_\ell^+ = \frac{1}{2}(1 + M^+) = \frac{1}{2}\left(1 + y\frac{M_0}{m_0}\right)\cdot \tag{15}$$

In a similar way, the probability to be in the lowest state when the field is $-H_0$ is given by:

$$p_\ell^- = \frac{1}{2}(1 - M^-) = \frac{1}{2}\left(1 - y\frac{M_0}{m_0}\right)\cdot \tag{16}$$

Therefore, the average population in the lowest level is obtained as:

$$\langle p_\ell \rangle = \frac{1}{2} + \frac{1}{4}\frac{M_0}{m_0}\int_{-1}^{1}\left[yP_+(y) - yP_-(y)\right]\mathrm{d}y. \tag{17}$$

Using the fact that $P_+(y) = P_-(-y)$, this expression can be transformed into:

$$\langle p_\ell \rangle = \frac{1}{2}\left[1 + \frac{M_0}{m_0}\int_{-1}^{1} yP_+(y)\,\mathrm{d}y\right]\cdot \tag{18}$$

Using the expression of $P_+(y)$ given by equation (12), we find:

$$\langle y \rangle_{P_+} = \frac{\Gamma\left(\frac{1}{2}+\mu\right)}{\Gamma\left(\frac{1}{2}\right)\Gamma(\mu)}\,\frac{\Gamma\left(\frac{3}{2}\right)\Gamma(\mu)}{\Gamma\left(\frac{3}{2}+\mu\right)} \tag{19}$$

$$= \frac{1}{1+2\mu}, \tag{20}$$

so that finally

$$\langle p_\ell \rangle(\mu, T) = \frac{1}{2}\left(1 + \frac{1}{1+2\mu}\tanh\frac{m_0 H_0}{k_B T}\right)\cdot \tag{21}$$

It is natural to define an effective temperature T_{eff} such that:

$$\langle p_\ell \rangle(\mu, T) = \frac{1}{1 + \exp(-\Delta/k_B T_{\text{eff}})}, \tag{22}$$

where $\Delta = 2m_0 H_0$ is the mean hyperfine splitting. Therefore, the following relation holds between T_{eff}, T and μ:

$$\tanh\frac{\Delta}{2k_B T_{\text{eff}}} = \frac{1}{1+2\mu}\tanh\frac{\Delta}{2k_B T}\cdot \tag{23}$$

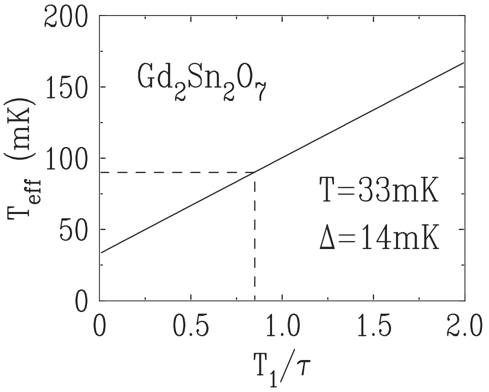

Fig. 4. Effective hyperfine temperature T_{eff} for a nuclear spin 1/2 system, with a splitting $\Delta/k_B = 14$ mK and for a temperature $T = 33$ mK, as a function of the ratio of the nuclear relaxation time T_1 to the electronic spin flip time τ. The dashed lines link the effective hyperfine temperature measured in Gd$_2$Sn$_2$O$_7$ to the T_1/τ value.

In the limit $k_BT > 2\Delta$, which is the temperature range of the experiments, the above relation reduces to a simple linear function:

$$T_{\text{eff}} \simeq 2T\mu + T. \tag{24}$$

In the other limit, when T goes to zero, we get from equation (23):

$$\tanh \frac{\Delta}{2k_BT_{\text{eff}}} \to \frac{1}{1+2\mu}\cdot \tag{25}$$

So, if μ does not tend to zero with T, T_{eff} remains finite, or even goes to infinity if μ diverges as $T \to 0$. As will be discussed in Section 5, this latter case is plausible because T_1 should increase and τ can remain finite as T tends to zero. The out-of-equilibrium two-level system should then show equipopulation at zero temperature. We note that the concept of an effective temperature in out-of-equilibrium systems has been recently discussed in [21], where the general situation of a continuous degree of freedom interacting with a multi-time scale random environment is considered.

The effective temperature as a function of $\mu = T_1/\tau$ is represented in Figure 4 for Gd$_2$Sn$_2$O$_7$, assuming a sample temperature of 33 mK and a nuclear sublevel splitting of 14 mK. The time scale ratio can be read off on the figure from the value of the measured hyperfine temperature T_{eff}; choosing the experimental mean value $T_{\text{eff}} = 90$ mK, we find: $T_1/\tau \sim 0.85$. Because the experimental accuracy with which T_{eff} can be measured decreases progressively as the temperature is increased, it is not possible to obtain reliable values for T_{eff} as a function of T, nor to obtain any information concerning the thermal dependence of the ratio μ.

Therefore, in the ground state of Gd$_2$Sn$_2$O$_7$ at very low temperatures, the Gd^{3+} magnetic moments are correlated and they fluctuate with a characteristic time which is close to the nuclear relaxation time. The fact that T_1 and τ are of the same magnitude is somewhat surprising, as in paramagnetic insulators the nuclear relaxation times at very low temperature are in the majority of cases quite long ($\sim 10^{-2} - 1$ s), whereas the electronic fluctuation times are rather in the μs range or shorter. However, in magnetically ordered (or short range correlated) materials at low temperature, the dominant hyperfine relaxation mechanism is the scattering of magnons by nuclear moments *via* the transverse part of the hyperfine interaction [22]. This mechanism yields nuclear relaxation frequencies proportional to the square of the hyperfine constant A, and can lead to short relaxation times, as measured for instance in antiferromagnetic CrCl$_3$ [23] where T_1 of ^{53}Cr is in the range $10^{-4} - 10^{-3}$ s in zero or low field at low temperature. As the hyperfine constant of ^{155}Gd is about 10 times bigger than that of ^{53}Cr, it is likely that the hyperfine relaxation frequencies fall in the MHz range in Gd$_2$Sn$_2$O$_7$. Further information concerning the fluctuation rate of the Gd^{3+} spins should be provided by our planned muon spin relaxation (μSR) measurements. Another possibility would be to perform ^{119}Sn Mössbauer absorption measurements in Gd$_2$Sn$_2$O$_7$. The Sn atom is non magnetic, but the Sn nucleus will experience a transferred hyperfine field arising from the Gd^{3+} moments, and this field will follow their fluctuations. Such an approach was successfully used in the spin-fluctuation compound UPd$_2$Sn [24], where we could measure the hyperfine field relaxation frequency in the 100 MHz range, corresponding to that of the U^{3+} moment, down to 50 mK.

Let us remark that for paramagnetic spins experiencing an exchange interaction, the spin fluctuations would occur at a rate $\frac{1}{\tau} \sim \frac{k_B|\theta_p|}{h}$; taking $\theta_p \sim -8$ K, (the experimental value for Gd$_2$Sn$_2$O$_7$) then $\frac{1}{\tau} \sim$100 GHz. Such fluctuation rates are well above the upper limit of the ^{155}Gd Mössbauer "relaxation window" ($\sim$ 1 GHz) and they would completely wipe out the hyperfine structure. As the low temperature fluctuations of the Gd^{3+} moments occur at frequencies below 100 MHz, they cannot be linked to paramagnetic relaxation. This confirms that the fluctuations concern Gd^{3+} moments that are correlated.

5 Influence of the electronic fluctuations on the hyperfine specific heat

We will compute here the steady state out-of-equilibrium hyperfine specific heat when electronic spin fluctuations are present. As a function of the ratio μ of the nuclear relaxation time to the electronic flip time, the average steady state populations $\langle p_\ell\rangle(\mu,T)$ and $1 - \langle p_\ell\rangle(\mu,T)$ of the two levels fulfil the relation:

$$2\langle p_\ell\rangle(\mu,T) - 1 = g(\mu)\left(2p_\ell^B - 1\right), \tag{26}$$

where p_ℓ^B is the Boltzmann population and $g(\mu)$ a reduction function given by equation (20):

$$g(\mu) = \frac{1}{1+2\mu}\cdot \tag{27}$$

The energy of the out-of-equilibrium two-level system being given by:

$$\begin{aligned} E(\mu,T) &= \langle p_\ell\rangle(\mu,T)E_1 + [1-\langle p_\ell\rangle(\mu,T)]\,E_2 \\ &= E_2 - \varDelta\langle p_\ell\rangle(\mu,T), \end{aligned} \tag{28}$$

the specific heat is readily obtained as:

$$C_p = g(\mu)C_p^{nuc} - \varDelta\left(p_\ell^B - \frac{1}{2}\right)\frac{\mathrm{d}\mu}{\mathrm{d}T}\frac{\mathrm{d}g}{\mathrm{d}\mu}, \tag{29}$$

where C_p^{nuc} is the standard (static) two-level Schottky expression:

$$C_p^{nuc} = k_B\left(\frac{\varDelta}{k_BT}\right)^2\frac{\exp(-\varDelta/k_BT)}{[1+\exp(-\varDelta/k_BT)]^2}\,\cdot \tag{30}$$

The first term in equation (29) leads, for finite μ, to a reduction of the nuclear specific heat with respect to the standard (static) Schottky result, since $g(\mu) < 1$. The sign of the second term depends on the sign of $\frac{\mathrm{d}\mu}{\mathrm{d}T}$ which is difficult to estimate because, in principle, both T_1 and τ should decrease as temperature increases. A reasonable assumption is that T_1, which is due to a thermally driven mechanism, varies with temperature more rapidly than τ, which is probably associated to a (tunneling) quantum mechanism. Then $\frac{\mathrm{d}\mu}{\mathrm{d}T} < 0$, and the second term in the expression of C_p leads to a further, but temperature dependent, reduction. Therefore, the specific heat associated with the hyperfine levels could be strongly reduced in the presence of electronic fluctuations. In particular, when the low temperature electronic fluctuations are very fast, *i.e.* when the ratio $\mu \gg 1$, the hyperfine specific heat vanishes, as both g and $\frac{\mathrm{d}g}{\mathrm{d}\mu}$ tend to zero when μ increases. To illustrate this point, Figure 5 presents the hyperfine specific heat (Eq. 29) divided by temperature, for the case $\frac{\mathrm{d}\mu}{\mathrm{d}T} = 0$, in the temperature range above the Schottky anomaly peak, and for increasing values of the ratio μ. Whatever the value of μ, the Schottky peak occurs at the same temperature ($\sim \varDelta/3$), but its height decreases as μ increases. Figure 5 shows that, as μ increases (*i.e.* as the electronic relaxation rate increases if T_1 is kept constant), the high temperature part of the hyperfine Schottky anomaly appears at lower temperature.

An issue of current interest in geometrically frustrated compounds concerns the possible existence of a missing electronic entropy [25]. Since the electronic entropy is deduced from the total measured specific heat by subtracting the hyperfine contribution, it is necessary to incorporate a correct assessment of the latter, as discussed in reference [26]. As shown here, the steady state out-of-equilibrium hyperfine specific heat appropriate for fluctuating spin systems may be smaller than the hyperfine specific heat due to the standard (static) Schottky anomaly. In such a case, the value of the electronic entropy obtained by subtracting the standard (static) Schottky anomaly contribution from the total measured value would be underestimated.

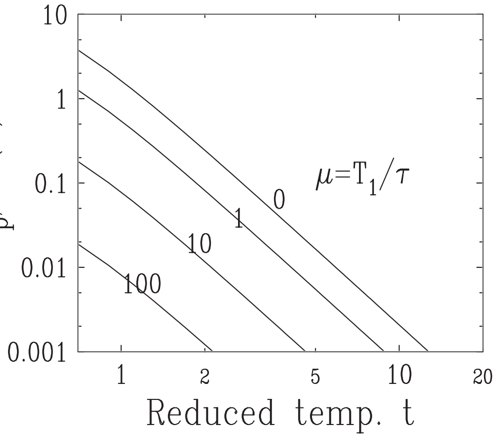

Fig. 5. Thermal variation of the hyperfine specific heat divided by the reduced temperature $t = \frac{k_\mathrm{B}T}{\varDelta}$ in the presence of electronic fluctuations, for increasing values of the ratio $\mu = T_1/\tau$ (see text), in the temperature range above the Schottky peak. Note the logarithmic scale on both axes.

In theory, all geometrically frustrated systems are potential candidates for a reduced hyperfine specific heat because such systems share the common property of persisting low temperature spin fluctuations. In practice, the amount of reduction (from no reduction to total removal) will depend on the ratio μ of the nuclear relaxation and electronic spin flip times. For the rare-earth pyrochlores quite different behaviours are observed. As shown here, in $Gd_2Sn_2O_7$ where $\mu \sim 0.85$, the hyperfine specific heat will be reduced at least by a factor 0.37. In $Yb_2Ti_2O_7$, where the low temperature spin flip time is ~ 1 μs [27], the hyperfine specific heat appears to be present with a value approaching its full possible size [28]. An essentially complete hyperfine specific heat appears also to be present in $Ho_2Ti_2O_7$ [26]. In $Dy_2Ti_2O_7$ however, the hyperfine specific heat appears to be considerably reduced: the Schottky anomaly calculated using the known hyperfine Dy^{3+} hyperfine parameters [29] is not present in the data of reference [25]. This absence of a hyperfine specific heat provides evidence that the electronic spin flips persist as $T \to 0$ in $Dy_2Ti_2O_7$. Considering the different pyrochlores relative to Figure 4, $Yb_2Ti_2O_7$, $Ho_2Ti_2O_7$ and $Gd_2Ti_2O_7$ are situated near the left hand side, $Gd_2Sn_2O_7$ is situated near the centre and $Dy_2Ti_2O_7$ is situated near or beyond the right hand side.

6 Conclusion

Collective electronic spin fluctuations have been evidenced by ^{155}Gd Mössbauer spectroscopy in the frustrated antiferromagnet pyrochlore $Gd_2Sn_2O_7$ at very low temperature (27 mK). These fluctuations show up in an unusual manner, *i.e.* through the out of thermal equilibrium populations of the ^{155}Gd hyperfine levels. We developed a model calculation which provides the stationary populations of a spin 1/2 system in the presence of a magnetic field which randomly reverses in time. With simple assumptions, we obtain an analytical expression for the level populations, or equivalently for the effective temperature of the system, as a function of the ratio of the nuclear relaxation time to the electronic flip time. Applying this calculation to the case of $Gd_2Sn_2O_7$, we find that the ratio of these two time scales is close to unity.

From an analogous study of $Gd_2Ti_2O_7$ we show that the hyperfine levels are populated at or close to thermal equilibrium. This difference compared to $Gd_2Sn_2O_7$ is probably not due to any difference in their basic properties: in both compounds, we find that the antiferromagnetic $Gd^{3+} - Gd^{3+}$ coupling has comparable strength, and that below ~1 K, the electronic moments are blocked (on the scale of ~100 MHz) along directions perpendicular to the appropriate local [111] axis. Rather, we propose that the hyperfine populations in $Gd_2Ti_2O_7$ are at, or near, thermal equilibrium because the electronic spin fluctuations are partially quenched under the influence of disorder. The presence of disorder in $Gd_2Ti_2O_7$ is suggested by the abnormally enhanced background signal in the X-ray diffraction patterns both for our and for other [30] samples. In $Gd_2Sn_2O_7$ there is no abnormal background signal.

Finally, we examine the consequence of electronic spin fluctuations on the hyperfine specific heat and show that it can be strongly reduced when the ratio of the nuclear relaxation time to the electronic flip time is comparable to or greater than unity.

We thank J.F. Lericque and N. Genand-Riondet for technical assistance and A. Forget for preparing the samples.

References

1. *Magnetic Systems with Competing Interactions*, edited by H.T. Diep (World Scientific, Singapore, 1994)
2. J. Villain, Z. Physik **33**, 31 (1979)
3. R. Moessner, J.T. Chalker, Phys. Rev. B **58**, 12049 (1998)
4. J.N. Reimers, J.E. Greedan, C.V. Stager, M. Björgvinssen, Phys. Rev. B **43**, 5692 (1991)
5. J.N. Reimers, A.J. Berlinsky, A.-C. Shi, Phys. Rev. B **43**, 865 (1991)
6. W.I. Kinney, W.P. Wolf, J. Appl. Phys. **50**, 2115 (1979)
7. S.E. Palmer, J.T. Chalker, Phys. Rev. B **62**, 488 (2000)
8. S.T. Bramwell, M.J.P. Gingras, J.N. Reimers, J. Appl. Phys. **75**, 5523 (1994)
9. R. Moessner, Phys. Rev. B **57**, R5587 (1998)
10. N.P. Raju, M. Dion, M.J.P. Gingras, T.E. Mason, J.E. Greedan, Phys. Rev. B **59**, 14489 (1999)
11. V. Bondah-Jagalu, S.T. Bramwell, Can. J. Phys. **79**, 1381 (2001)
12. J.D.M. Champion, A.S. Wills, T. Fennel, S.T. Bramwell, J.S. Gardner, M.A. Green, Phys. Rev. B **64**, 140407(R) (2001)
13. J.D. Cashion, D.B. Prowse, A. Vas, J. Phys. C: Solid State Phys. **6**, 2611 (1973)
14. H. Armon, E.R. Bauminger, A. Diamant, I. Nowik, S. Ofer, Nuclar Phys. A **233**, 385 (1974)
15. W. Henning, G. Baehre, P. Kienle, Phys. Lett. B **31**, 203 (1970)
16. H. Armon, E.R. Bauminger, A. Diamant, I. Nowik, S. Ofer, Solid State Comm. **15**, 543 (1974)
17. G.K. Shenoy, H. Maletta, Z. Physik **269**, 241 (1974)
18. I. Felner, Solid State Comm. **52**, 191 (1984)
19. P.W. Anderson, B.I. Halperin, C.M. Varma, Phil. Mag. **25**, 1 (1972)
20. S.A. Langer, A.T. Dorsey, J.P. Sethna, Phys. Rev. B **40**, 345 (1989); M. Huang, J.P. Sethna, Phys. Rev. B **43**, 3245 (1991)
21. L. Cugliandolo, J. Kurchan, J. Phys. Soc. Jpn **69**, 247 (2000)
22. T. Moriya, Prog. Theor. Physics **16**, 641 (1956)
23. A. Narath, A.T. Froholm, Jr., Phys. Rev. Lett. **17**, 354 (1966)
24. B. Chevalier, L. Fournès, P. Bonville, F. Gonzalez-Jimenez, J. Etourneau, Physica B **259-261**, 252 (1999)
25. A.P. Ramirez, A. Hayashi, R.J. Cava, R. Siddharthan, B.S. Shastry, Nature **399**, 333 (1999)
26. S.T. Bramwell, M.J. Harris, B.C. den Hertog, M.J.P. Gingras, J.S. Gardner, D.F. McMorrow, A.R. Wildes, A. Cornelius, J.D.M. Champion, R.G. Melko, T. Fennell, Phys. Rev. Lett. **87**, 047205 (2001)
27. J.A. Hodges, P. Bonville, A. Forget, A. Yaouanc, P. Dalmas de Réotier, G. André, M. Rams, K. Królas, C. Ritter, P.C.M. Gubbens, C.T. Kaiser, P.J.C. King, Phys. Rev. Lett. **88**, 077204 (2002)
28. H.W.J. Blöte, R.F. Weilinga, W.J. Huiskamp, Physica **43**, 549 (1969)
29. A. Almog, E.R. Bauminger, A. Levy, I. Nowik, S. Ofer, Solid State Comm. **12**, 693 (1973)
30. O. Knop, F. Brisse, L. Castelliz, Can. J. Chem. **47**, 971 (1969)