Magnetic Density of States at Low Energy in Geometrically Frustrated Systems

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Using muon-spin-relaxation measurements we show that the pyrochlore compound $Gd_2Ti_2O_7$, in its magnetically ordered phase below ~ 1 K, displays persistent spin dynamics down to temperatures as low as 20 mK. The characteristics of the induced muon relaxation can be accounted for by a scattering process involving two magnetic excitations, with a density of states characterized by an upturn at low energy and a small gap depending linearly on the temperature. We propose that such a density of states is a generic feature of geometrically frustrated magnetic materials.

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The study of geometrically frustrated materials (GFMs) is a subject at the forefront of research in condensed matter physics not only because of their own interest but also because the concept of the frustration of the interactions plays a role for understanding the physics of, e.g., ice, cholesteric crystals, and metallic glasses; see, for instance, Ref. [1] for a discussion.

Magnetic materials based on lattices with triangular motifs and nearest-neighbor antiferromagnetic exchange interaction belong to the family of GFMs. They are, in the absence of further terms in the expression of their energy, believed to remain disordered and fluctuating down to zero temperature [2]. The absence of magnetic order stems from their highly degenerate ground state. It is only upon inclusion of perturbations such as exchange interactions extending beyond nearest-neighbor magnetic ions or dipole coupling that magnetic ordering may appear. Experiments on Kagomé, garnet, and pyrochlore structure compounds support these general predictions [1].

A fingerprint for the geometrical frustration of a material is the shift towards low energy of the spectral weight of excitations [1]. The first convincing experimental proof has been obtained in a Kagomé-like magnetic material, where the low temperature specific heat [3] is found to be dominated by singlet excitations arising from correlated spins, rather than from individual spins. This enhanced density of spectral weight at low energy could be linked with the persistence of spin dynamics observed at low temperature in many systems, as magnetic excitations are continuously available from zero energy. This behavior has been evidenced in the Kagomé compounds $SrCr_{9p}Ga_{12-9p}O_{19}$ with $0.39 \leq p \leq 0.89$ [4,5], for which a spin-glass transition is detected at $T_g = 4p$ K, in Kagomé-like systems [6,7], in the garnet $Gd_3Ga_5O_{12}$ [8–10] with $T_g = 0.15$ K, and in the pyrochlore compounds $Y_2Mo_2O_7$ ($T_g = 22$ K) [11], $Tb_2Mo_2O_7$ ($T_g = 25$ K) [11]. It was also observed in the spin liquid $Tb_2Ti_2O_7$ [12–14], for which there is no evidence of a transition down to 0.07 K [15]. The spin dynamics becomes approximately temperature independent below about T_g for the spin-glass systems, except for the two molybdates for which it occurs in the temperature range $T/T_g < 0.05$, and for $Tb_2Ti_2O_7$ which displays a temperature independent relaxation below about 1 K. Appreciable spin dynamics is also found in $Yb_2Ti_2O_7$ below the temperature at which the specific heat presents a sharp anomaly [16–18]. In compounds where the fluctuations have been studied by the muon-spin-relaxation (μSR) technique, the muon-spin-lattice relaxation function is usually found to be a stretched exponential, i.e., $P_Z^{\mathrm{sl}}(t) = \exp[-(\lambda_Z t)^{\alpha}]$ with $\alpha \neq 1$.

More unconventional is the spin dynamics recently observed by Mössbauer spectroscopy, down to 30 mK, in $Gd_2Sn_2O_7$ which shows long-range ordering below 1 K [19], and which was confirmed by μSR measurements down to 20 mK [20,21]. This anomalous spin dynamics cannot arise from conventional magnons, since their population vanishes at low temperature. In order to further investigate these zero temperature fluctuations, we performed μSR measurements in the parent compound $Gd_2Ti_2O_7$, for which single crystals are available. This compound undergoes a first magnetic transition at $T_{c1} \simeq 1$ K, followed by a second one at $T_{c2} \simeq 0.75$ K [22]. We report the results of specific heat and μSR measurements in this material, and propose to account for the observed persistent spin dynamics in GFMs in terms of an unconventional density of states at low energy.

A $Gd_2Ti_2O_7$ polycrystalline rod was prepared by mixing, heating, and compacting the constituent oxides Gd_2O_3 and TiO_2 of respective purity 5N and 4N5. A single crystal was then grown by the traveling solvent floating zone technique using a Crystal System Inc. optical furnace with a velocity of 8 mm per hour. Oriented platelets were cut from the crystal and subsequently annealed under oxygen pressure to ensure optimized physical properties. The

top panel of Fig. 1 shows the result of specific heat measurements performed using a dynamic adiabatic technique. The two phase transitions are observed at $T_{c1} = 1.02$ K and $T_{c2} = 0.74$ K, respectively, in agreement with recent single crystal measurements [23]. The peak at T_{c2} is found much sharper than previously reported [22–24]. Its shape suggests that the lower phase transition is first order. Although we do not have any experimental evidence, it is possible that at this lower magnetic transition corresponds a structural transition which could be induced through magneto-elastic coupling. Anyhow, the magnetic transitions do not relieve the frustration since in the following we do report the observation of persistent spin dynamics, a fingerprint of geometrical magnetic frustration. At low temperature, up to ~0.55 K, the specific heat divided by temperature C_p/T is proportional to T. Such a behavior was also found for $Gd_2Sn_2O_7$ [24] and Kagomé-like compounds [3], but it is not a general rule for GFMs since a T^2 dependence is reported for $Er_2Ti_2O_7$ [25]. The entropy release reaches $\simeq 90\%$ of $R \ln 8$ only near 5 K.

The μSR measurements (see Ref. [26] for an introduction to this technique) were performed at the Low Temperature Facility (πM3 beam line) of the Swiss Muon Source (Paul Scherrer Institute, Villigen, Switzerland). As expected, the μSR spectra in the paramagnetic phase are well described by a single exponential relaxation function; i.e., they are proportional to $P_Z^{\exp}(t) = \exp(-\lambda_Z t)$, where λ_Z is the spin-lattice relaxation rate. Z labels the direction of the initial muon beam polarization. Below T_{c1}, the observed oscillations, due to spontaneous precession of the muon spin (see inset of Fig. 2), are a signature of the long-range order of the magnetic structure, consistent with the observation of magnetic Bragg reflections by neutron diffraction [27,28]. Surprisingly, even at 20 mK, a stretched exponential decay of the spin-lattice relaxation channel is observed, superposed on the damped wiggles (Fig. 2). This implies that excitations of the spin

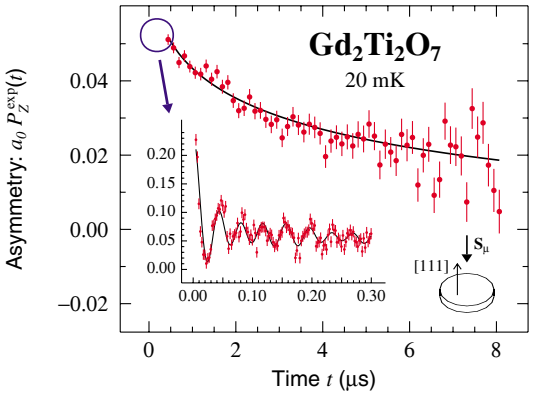

FIG. 1 (color online). μSR spectrum recorded in zero field at 20 mK in a single crystal of $Gd_2Ti_2O_7$ with the initial muon beam polarization parallel to the [111] crystal direction. The main frame displays the time spectrum up to 8 μs, and the inset magnifies the short time behavior. The latter is characterized by wiggles which are damped out at the earliest time displayed in the main frame. The wiggles correspond to the spontaneous precession of the muon spin in two local fields of respective magnitude $B_1 = 194(1)$ and $B_2 = 149(1)$ mT. As expected, the spin-lattice relaxation channel, most easily seen in the main frame, accounts for ~1/3 of the spectrum and the wiggles for ~2/3, this being temperature independent as is also the total asymmetry. The amplitude of the B_1 component is approximately 4 times as large as that of B_2.

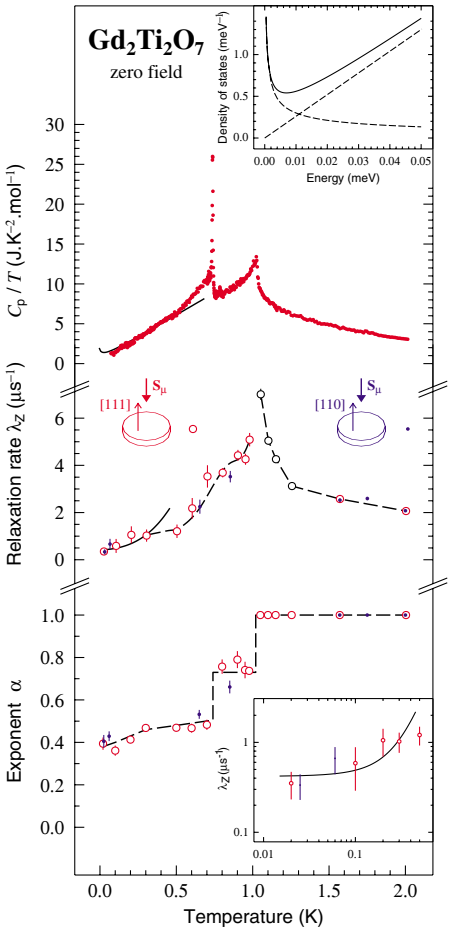

FIG. 2 (color online). In $Gd_2Ti_2O_7$, low temperature dependence of specific heat over temperature C_p/T per mole of Gd (top panel), of the muon-spin-lattice relaxation rate λ_Z (middle panel), and of the exponent α (bottom panel) of the stretched exponential decay. The muon data were measured in a single crystal, with different orientations relative to the muon polarization $\mathbf{S}_\mu$, as shown, and the anisotropy of λ_Z was found to be negligible. The dashed lines for $\lambda_Z(T)$ and $\alpha(T)$ are guides for the eye. The lower inset shows, on a double logarithmic scale, the weak temperature dependence of $\lambda_Z(T)$ at low temperature. The full lines give the predictions for C_p/T and λ_Z computed with $b_\mu = 0.03$ meV$^{-1/2}$, $b_{sh} = 26$ meV^{-2} per Gd atom and $a = 0.1$ (see text). The upper inset shows the density of magnetic excitations $g_m(\epsilon)$ at 50 mK, with its two components as dashed lines. The gap is: $\Delta \simeq 5 \times 10^{-4}$ meV. The upturn at low energy is responsible for the finite value of λ_Z as $T \to 0$.

system are present, inducing spin-lattice relaxation of the muon levels. In Fig. 1 are displayed the thermal variations of the two parameters accounting for this channel, λ_Z, and the stretched exponent α.

Approaching T_{c1} from above, λ_Z increases, reflecting the slowing down of the paramagnetic fluctuations. As expected, it drops when crossing T_{c1}, but it remains roughly temperature independent below 0.5 K with a value $\lesssim 1\ \mu s^{-1}$. So the persistent spin dynamics known to exist in GFMs with no long-range magnetic order is also present in a magnetically ordered compound. Interestingly, α is not far from $1/2$ for $T < T_{c2}$ and jumps to $\sim 3/4$ for $T_{c2} < T < T_{c1}$. It is expected to be equal to 1 for a homogeneous spin system, as found in the paramagnetic state. A value $\alpha = 1/2$ suggests that relaxation stems from only a small fraction c of the spins [29], fluctuating with a correlation time τ_c and distributed at random in the lattice. These spins create a field distribution at the muon site which is known to have a squared Lorentzian shape [30], with a width Δ_{Lor}. A recent neutron diffraction study of $Gd_2Ti_2O_7$ [28] has shown that $1/4$ of the Gd magnetic moments are only partially ordered in the low temperature phase, and we tentatively attribute the relaxation channel with $\alpha = 1/2$ to a fraction of these spins. Our measurements at 0.1 K with a longitudinal field (not shown) yield $\tau_c = 0.7(2)$ ns and the relationship $\lambda_Z = 4\Delta_{\mathrm{Lor}}^2 \tau_c$ yields a width $\Delta_{\mathrm{Lor}} = 18(5)$ mT. According to Uemura *et al.* [31], $\Delta_{\mathrm{Lor}} = \sqrt{\pi/2} c \Delta_{\mathrm{max}}$, where Δ_{max} is the field width if all the Gd moments were contributing to the muon relaxation. Using the scaling between Δ_{max} and the rare earth moment which was successfully used for $Tb_2Ti_2O_7$ [12] and $Yb_2Ti_2O_7$ [17], we deduce $c \lesssim 10\%$. We note that a significant distribution in the spin fluctuation times has been observed, by the neutron spin echo technique, in $Gd_2Ti_2O_7$ [32] and in $Tb_2Ti_2O_7$ [13]. This backs our observation that only a fraction of the Gd^{3+} ions relax the muon spin, whereas the remaining part does not because it is characterized by fluctuation times either too short or too long.

Our specific heat and μSR measurements show therefore that, in the long-range order phase of $Gd_2Ti_2O_7$, magnetic excitations with a nonvanishing density at low energy are present. These excitations lead to a T^2 behavior for the specific heat and to a muon spin-lattice relaxation rate which is quasi-independent of temperature. In fact, below 0.5 K a fit of $\lambda_Z(T)$ to a power law gives $\lambda_Z(T) \propto T^\beta$ with $\beta \simeq 1/3$. This is a negligible temperature dependence relative to power laws observed for usual ferromagnets ($\beta = 2$) and conventional antiferromagnets ($\beta = 5$) [21]. In the following, we aim at determining the density of magnetic excitations responsible for the observed thermal behaviors of C_p and λ_Z.

First of all, assuming these excitations to obey Bose-Einstein statistics like conventional magnons, it is easy to derive that, if their density of states per volume unit $g_m(\epsilon)$ is proportional to ϵ^q, then $C_p \propto T^{q+1}$. Hence $g_m(\epsilon) \propto \epsilon$ accounts for the T^2 behavior of C_p. Second, for the muon relaxation rate, if one considers a direct process with a single excitation, then energy conservation with $\epsilon = \epsilon_\mu \simeq 0$ ($\epsilon_\mu = \hbar\omega_\mu$, ω_μ being the muon angular frequency) leads to $\lambda_Z \propto T$, which is in disagreement with the experimental data for $Gd_2Ti_2O_7$ and other frustrated systems mentioned in the introduction. The relaxation process to consider next involves a *two-excitation scattering (Raman process)*. Within the harmonic approximation, energy conservation implies that only the component of the spin-spin correlation tensor parallel to the magnetization, $\Lambda^{\parallel}(\mathbf{q}, \omega_\mu = 0)$, is probed [33]. Thus, $\lambda_Z \propto \int C(\mathbf{q}) \Lambda^{\parallel}(\mathbf{q}, \omega_\mu = 0) \mathrm{d}^3\mathbf{q}$, where $C(\mathbf{q})$ accounts for the interaction of the muon spin with the lattice spins and the integral extends over the Brillouin zone. For antiferromagnets with two collinear sublattices, the muon relaxation rate due to a Raman magnon process has been derived assuming for simplicity no orientation dependence for $\epsilon(q)$ and $C(q)$:

$$\lambda_Z = \frac{8(2\pi)^3 \mathcal{D}\hbar}{15} \frac{(B_e + B_a)^2}{(B_e + B_a)^2 - B_e^2} \int_\Delta^\infty n(\epsilon/k_B T) \times [n(\epsilon/k_B T) + 1] g_m^2(\epsilon) \mathrm{d}\epsilon, \quad (1)$$

where $\mathcal{D} = (\mu_0/4\pi)^2 \gamma_\mu^2 g^2 \mu_B^2$, $n(\epsilon/k_B T)$ is the Bose-Einstein occupation factor, and Δ the energy gap of the excitations at zero energy. B_e and B_a are, respectively, the exchange and anisotropy fields; a mean-field estimate for B_e is 10 T and, with reference to another Gd compound [34], we take $B_a = 0.2$ T. Equation (1) contains two population factors standing for the creation and annihilation of an excitation, a density of states being associated with each of them. The expression given by Eq. (1) assumes a muon site of high symmetry, e.g., the octahedral or tetrahedral interstitial sites of a face centered cubic lattice. For a muon site of lower symmetry, as expected in the case of the pyrochlores, Eq. (1) is essentially modified by a multiplicative factor η which depends on the actual site and is in the range between 1 and ~ 10. We took $\eta = 7$ in the calculation below.

As a first step, let us assume λ_Z to be temperature independent. The density of states must be $g_m(\epsilon) = b_\mu \epsilon^{-1/2}$ [35]. It must also be assumed that $\Delta = a k_B T$; i.e., the gap at zero energy is proportional to temperature. If a is of order 1 or lower, it can be shown that $\lambda_Z \propto b_\mu^2/a^2$ and that $g_m(\epsilon)$ is essentially probed for $\Delta \leq \epsilon \lesssim 3\Delta$. Therefore, the $\epsilon^{-1/2}$ dependence for $g_m(\epsilon)$ holds only in a very restricted energy interval. As stated above, the T^2 dependence of C_p implies that $g_m(\epsilon)$ is linear with energy, and this must prevail for $\epsilon \gtrsim 3\Delta$. Combining the two regimes, we obtain: $g_m(\epsilon) = b_\mu \epsilon^{-1/2} + b_{\mathrm{sh}} \epsilon$. The numerical calculations show that $a \leq 0.1$ is compatible with the C_p/T and λ_Z data. The predictions of the model with $a = 0.1$ are shown in Fig. 1. As expected, the model predicts λ_Z to be independent of T at low temperature. Note that a

further refinement of the model, namely, a slight change in the value of the exponent in the former term of $g_m(\epsilon)$ ($-0.5 \rightarrow -0.4$), allows us to improve the fit of $\lambda_Z(T)$ at low T for the specific case of $Gd_2Ti_2O_7$. This change affects the details in the shape of $g_m(\epsilon)$, but not its main features: the upturn at small energy and the existence of a gap proportional to the temperature.

The calculated C_p/T shown in Fig. 1 is T linear as expected, but shows an upturn below about 40 mK, caused by the $\epsilon^{-1/2}$ dependence of the density of states. This signature could be searched for in very low temperature specific heat measurements performed on a sample enriched with Gd isotopes having zero nuclear moment, thus showing no nuclear Schottky anomaly. The computed curve for λ_Z above $\sim$0.4 K overestimates the measured values. This could indicate that a fraction of the density of states, in the region where the dependence $g_m(\epsilon) \propto \epsilon$ prevails, arises from singletlike states [3] which do not contribute to the relaxation.

In summary, we have shown that, in GFMs, a nonvanishing muon-spin-lattice relaxation at low T, with a weak temperature dependence, if any, is the signature of a low energy upturn in the density of magnetic states. This density is characterized by a gap varying linearly with temperature, leading to an accumulation of states at low energy (see the upper inset of Fig. 1). This is a rare feature, which is also observed in BCS superconductors. We propose that the gap is due to the dipole interaction between magnetic moments, which breaks rotational invariance. However, its increase with T is unexpected. It is usually temperature independent or, for superconductors, decreases as temperature is increased [36]. A linear thermal increase strongly suggests that the thermal energy exceeds the energy involved in the excitation scattering process. Indeed, an analytical classical calculation performed for a triangular planar model with nearest-neighbor antiferromagnetic interactions and dipole interactions predicts a gap proportional to T with $a = 0.2$ for one of the phases [37].

As pointed out at the beginning of this Letter, persistent and weakly temperature spin dynamics has been observed for a large number of GFM, included magnetically ordered powder samples of $Gd_2Ti_2O_7$ [17], $Gd_2Sn_2O_7$ [10,21], and $Er_2Ti_2O_7$ [38]. A combined analysis of $C_p(T)$ and $\lambda_Z(T)$ is always possible, resulting in g_m with a gap linear in temperature.

The possibility for a GFM to order magnetically at finite temperature, although it is predicted to remain disordered down to zero temperature, was discovered theoretically a long time ago [39], as ''order from thermal disorder.'' The gap we infer here is a consequence of the same mechanism. It appears if rotational invariance is broken. This naturally occurs because of the presence of the dipole interaction.

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