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A comparison of the local magnetic susceptibility in rare earth pyrochlores

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Abstract

We report transverse field muon spin rotation studies of the rare earth pyrochlores $Gd_2Ti_2O_7$ and $Tb_2Ti_2O_7$. The paramagnetic shift in the observed precession frequency depends on the local spin susceptibility and probes the contact hyperfine and dipolar fields at the muon site within these materials. The results are compared with measurements of the bulk susceptibility. While no features associated with magnetic ordering are observed down to 0.015 K, hysteretic behavior develops in $Tb_2Ti_2O_7$ below $T = 1$ K, likely due to the formation of clusters of ferromagnetically correlated spins.

Keywords: Pyrochlore; Paramagnetic shift; Geometric frustration

The pyrochlore oxides, of general formula $A_2B_2O_7$, represent ideal systems for studying the effects of geometrical frustration where it is not possible to energetically satisfy all the magnetic interactions simultaneously. This results in a highly degenerate ground state, which is extremely sensitive to second order effects such as further neighbor interactions, disorder, anisotropy or thermal or quantum fluctuations. Consequently, one finds a wide variety of exotic ground states in isostructural compounds [1]. Magnetic analogues of water ice, so called 'spin ice', are currently of considerable interest. To date, the most extensively studied candidates are $Dy_2Ti_2O_7$ [2] and $Ho_2Ti_2O_7$ [3–5], which should behave as anisotropic quasi spin $\frac{1}{2}$ Ising systems at sufficiently low temperatures. By contrast, the $^8S_{7/2}$ ground state of the Gd^{3+} ion has no orbital contribution to its angular momentum. Crystal electric fields affect closed shells of S state ions only in a high order of

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perturbation theory and thus $Gd_2Ti_2O_7$ should be an excellent approximation to a classical Heisenberg antiferromagnetic system with nearest neighbor superexchange interactions. Dipole–dipole interactions then constitute the leading perturbation. The situation is less clear in $Tb_2Ti_2O_7$. The exchange interactions are thought to be highly anisotropic. However, it is still under debate whether the spins are Heisenberg or Ising-like [6]. An ab initio calculation of the crystal field parameters [7] finds that the lowest and first excited states are doublets comprised of large $J_Z = \pm 4$ and $J_Z = \pm 5$ components respectively with a splitting of ~ 18 K. The ground state is hence not well isolated and intersite interactions, which are of the same order of magnitude, may lead to significant mixing of energy levels. DC susceptibility measurements in the high temperature regime (> 200 K) yield a paramagnetic moment of $9.6\mu_B$, which compares favorably with the free ion value appropriate to Tb^{3+} in its $^7F_6$ ground state. This may be contrasted with a value of $5.1\mu_B$ extracted given isolated Tb^{3+} ions in the dilute system $(Tb_{0.02}Y_{0.98})_2Ti_2O_7$ below 30 K [7]. As the temperature is reduced, higher crystal field levels are depopulated, altering the magnitude of the moment. The Tb^{3+} moments are constrained to lie along the local $\langle 1\,1\,1 \rangle$ axis to a greater degree, making the g-tensor more anisotropic. In addition, the DC susceptibility deviates from Curie-Weiss behavior below ~ 100 K due to the build up of short range antiferromagnetic correlations.

Muon spin relaxation [8,9] experiments indicate that unlike other geometrically frustrated systems, $Tb_2Ti_2O_7$ displays neither conventional Néel order nor a glass-like state down to temperatures as low as ~ 0.015 K. Rather, in terms of the spin fluctuations the system appears essentially to remain dynamic at low temperatures. Most of the previous work has been done in a longitudinal field configuration, studying the spin-lattice relaxation rate T_1^{-1}. However, measurements of the local susceptibility provide another way to understand this system, probing the magnetism via measurements of the shift in the muon spin precession frequency relative to an applied transverse magnetic field. The frequency shift measures the real part of the dynamic susceptibility (χ') evaluated at $\omega = 0$. In a single crystal, where the spectrum is not broadened by a superposition of dipolar fields, the line width can be related to the imaginary part χ'' through the fluctuation–dissipation theorem.

μSR studies on pellets of polycrystalline $Gd_2Ti_2O_7$ and $Tb_2Ti_2O_7$ were performed at TRIUMF with the sample mounted in a ^{4}He flow cryostat for measurements between 3 and 295 K. Spectra were collected simultaneously on a silver reference and on the samples using a special cryostat insert described elsewhere [10]. The frequency shift is then given by $(\nu_{Sample} - \nu_{Silver})/\nu_{Silver}$. Measurements on a single crystal of $Tb_2Ti_2O_7$ were performed in an Oxford Instruments dilution refrigerator on the M15 beamline at TRIUMF at temperatures from 20 mK up to 6 K, with the cubic $\langle 1\,1\,1 \rangle$ direction parallel to the applied magnetic field.

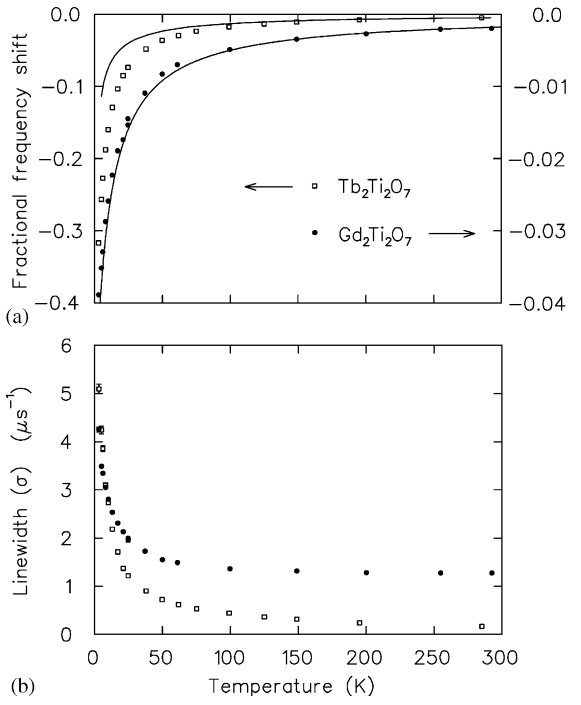

Fig. 1. (a) Paramagnetic frequency shifts and (b) line widths in $Tb_2Ti_2O_7$ and $Gd_2Ti_2O_7$ in an applied field of 0.09 T. The solid lines in (a) indicate the DC susceptibility measured in a field of 0.01 T, suitably scaled. Note the different vertical scales for the 2 materials in (a).

The temperature variation of the paramagnetic frequency shift in $Gd_2Ti_2O_7$ is shown in Fig. 1a. The rapidly damped sample spectra are fit to a single exponential envelope $P_Z(t) = A\exp(-\sigma t)\cos(2\pi\nu_{\mathrm{Sample}}t)$ between 0.05 and 2.5 μs; the silver reference to a single Gaussian between 0.05 and 4.5 μs. The frequency shifts are well described by a Curie–Weiss form $\chi_{\mathrm{mol}} \propto (T + 9.6)^{-1}$ and scale with the bulk DC susceptibility [11], demonstrating that the muon is not perturbing the magnetic system in any significant way.

In general, for a system of point dipoles and assuming axial symmetry, the frequency shift K in a polycrystalline paramagnet is given by [12]

$$K = -\frac{\chi_{\mathrm{mol}}}{N_A\mu_B}\left[\frac{(g_\parallel^2 + 2g_\perp^2)}{3g^2}A_c + \frac{(g_\parallel^2 - g_\perp^2)}{3g^2}A_{\mathrm{dip}}\right] + K_{\mathrm{bulk}}, \quad (1)$$

where $g_\parallel^2 + 2g_\perp^2 = g^2$ is the Landé factor. The first 2 terms are respectively the contact hyperfine and dipolar couplings associated with the interactions between the μ^+ and the rare earth moments. A_c is determined by the unpaired electron density at the muon site [13]. The third term $K_{\mathrm{bulk}} = 4\pi(\frac{1}{3} - N)\rho_{\mathrm{mol}}\chi_{\mathrm{mol}}$ describes contributions from demagnetization effects and the Lorentz sphere, where N is the demagnetization factor and ρ_{mol} is the molar density. The demagnetization factor depends on the shape of crystallites within the polycrystal, as well as that of the bulk. The powder samples of $Tb_2Ti_2O_7$ are disk shaped, while those of $Gd_2Ti_2O_7$ are more irregular. No correction has been applied to the data shown in Fig. 1a: the demagnetization factor is difficult to calculate in a powder but is typically of order 0.3, resulting in values of $K_{\mathrm{bulk}} \sim 1$–2% of the total observed shift.

In $Gd_2Ti_2O_7$, the shift is solely a measure of the local contact hyperfine field at the muon site, since the dipolar field contributes nothing in an isotropic powder material [14]. As may be seen in Eq. (1), this is only true given an isotropic g tensor. Experimentally, with very few exceptions, no anisotropy in g has been detected outside the experimental error for an S-state ion. Thus, the magnitude of the hyperfine field may be extracted by comparison with measurements of the bulk susceptibility and is found to be $A_c = 189(2)$ Oe/μ_B, comparable with values found in other rare earth oxides [15]. By contrast, in an isotropic system, the dipolar interaction contributes only to the line width of the precession signal. The line width in $Gd_2Ti_2O_7$ is shown in Fig. 1b. Above 100 K it is roughly temperature independent, consistent with rapidly fluctuating Gd moments in the paramagnetic regime. In addition, T_1^{-1} and the line width are approximately equal. Moriya has considered the relaxation of nuclei of magnetic ions, where the primary mechanism is due to the hyperfine interaction. In the paramagnetic regime, $T_1 \approx T_2$, given both the electron spin fluctuations and electron–nucleus coupling are isotropic [16]. It should be remembered that in the case of interacting, fluctuating moments, the line width may be significantly altered due to 'exchange narrowing' [17]. Below $\sim$4 K, the line width increases rapidly due to critical slowing down of the Gd spin fluctuations. This is consistent with experimental evidence from measurements of the AC and DC susceptibility, heat capacity [11] and neutron diffraction [18] data, which show that $Gd_2Ti_2O_7$ exhibits long range order at 0.97 K, with possibly as many as four ordered phases as a function of temperature and applied magnetic field [19].

Comparing isostructural rare earth titanates, the bulk DC susceptibility should scale as the square of the effective magnetic moment $p = g[J(J+1)]^{1/2}$ at high temperatures where spin–spin correlations may be neglected. For the free Gd^{3+} and Tb^{3+} ions, $p = 7.94$ and 9.72, respectively. The ratio of the Curie constants [7,11] squared in these two pyrochlores is found to be 1.43, close to the expected value of 1.5. However, the ratio of the precession frequency shift at 200 K is found to be a factor of 2 larger. By 3 K the shift in $Tb_2Ti_2O_7$ is almost a factor of 10 larger than that in $Gd_2Ti_2O_7$. In the former compound where $g_\parallel \neq g_\perp$, both dipolar *and* hyperfine fields contribute to the frequency shift. The system becomes progressively more anisotropic as the temperature decreases and only the lowest ground state doublet remains appreciably occupied. Measurements of the local paramagnetic shift on oriented single crystals would elucidate the anisotropic nature of the internal fields; contributions from dipolar and hyperfine interactions could also be separated. In

addition, the angular dependence of the frequency shift would provide information on the muon site [20]. It seems reasonable to assume the same site in both compounds. There are also increasingly significant hyperfine contributions to the line width, which has a faster temperature dependence than that observed in $Gd_2Ti_2O_7$, as may be seen in Fig. 1b.

Transverse field measurements were carried out at 285 and 3 K on the powder $Tb_2Ti_2O_7$ sample as a function of applied magnetic field. The fractional shift in the muon spin precession frequency is independent of field at high temperatures, as anticipated in the linear response regime. However, at 3 K, where short range correlations also predominate, the lowest doublet becomes fully magnetized and the fractional frequency shift increases linearly to zero in a relatively small field of 13.5 kOe. It is clear that there are two relevant energy scales in $Tb_2Ti_2O_7$: that associated with the crystal electric field energy splittings of tens of Kelvin, which is also comparable with the Curie–Weiss temperature and hence the classical exchange coupling $\mathcal{J}S(S+1)$. In addition, there is an energy scale where the Zeeman splitting of the lowest doublet becomes comparable with k_BT (at $\sim$1 K and $\sim$0.1 T).

It is interesting to note that in $Tb_2Ti_2O_7$ there is a subtle difference between the shift in the muon spin precession frequency and the bulk susceptibility χ below $\sim$75 K (see Fig. 1), which is *not* observed in the Gd compound. This discrepancy could arise either because of a muon induced effect or possibly a small impurity phase detected by bulk susceptibility, but which contributes nothing to local probe measurements [21]. Alternatively, the contact hyperfine and/or dipolar field could be temperature dependent. Similar changes in the anisotropic hyperfine couplings with temperature due to changes in crystal field level populations have been observed in the heavy fermion superconductor $CeCoIn_5$ above T_c [22]. A comparison with the frequency shift obtained from NMR measurements, where no potentially perturbing probe is introduced, would eliminate the ambiguity. It should be kept in mind that the few special cases where the muon is a significant perturbation such as $PrNi_5$ [23] are singlet ground state systems. The low lying first excited crystal electric field level at $\sim$25 K is perturbed downwards by 15 to 20 K and becomes significantly occupied. In $PrIn_3$ [24] by contrast, the first excited level, at $\sim$100 K, is more isolated and within the experimental accuracy, the crystal electric field levels are not noticeably affected by the implanted muon.

While the longitudinal field μSR measurements give no indication of a phase transition down to 75 mK in the powder sample [8] and 15 mK in the single crystal [9], experiments in a transverse field geometry of $\sim$0.9 kOe show history dependence below 1 K (see Fig. 2). The spectra taken in the dilution refrigerator were analyzed by fitting them to two oscillating signals between 0.01 and 1.5 μs with Gaussian and exponential envelopes. The former was used to model the silver background, the latter the sample. As shown, there is a difference of $\sim$5–10% in the inverse fractional frequency shift between spectra taken on cooling or warming. The total frequency shift of $\sim$50% observed at 0.5 K corresponds with a magnetic field of 5 kOe and hence the history dependence implies there is a static component to the internal field of $\sim$0.025–0.05 kOe. It is speculated that the sample is magnetized on cooling, inducing a small ferromagnetic component which persists on warming to 1 K. Note that such a small static field

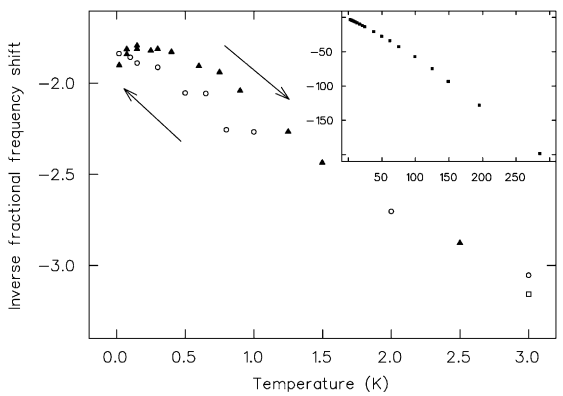

Fig. 2. Inverse fractional shift in the muon precession frequency relative to a silver reference versus temperature for $Tb_2Ti_2O_7$ in a transverse field of 0.09 T. The squares indicate data taken on a powder sample, the circles and triangles a [1 1 1] single crystal. Measurements taken on warming or cooling are given by the arrows.

would not have been picked up by previous T_1^{-1} measurements since they could easily be masked by the signal from the dynamic internal fields, which are known to be of the order of 10 kOe from studies of the isostructural compound $Tb_2Mo_2O_7$ [25], where the behavior of the Tb^{3+} moments in the paramagnetic regime is measured to be roughly the same. In $Tb_2Mo_2O_7$ one can measure the magnitude of the internal field directly since spin freezing is observed.

In an applied field of 1 T, a linear extrapolation of χ^{-1} has a positive intercept, suggestive of ferromagnetic correlations [26]. Yasui et al. [27] have observed a growth of the integrated intensity of elastic neutron scattering and hysteresis at $Q = (0, 0, 2.1)$, as the temperature decreases below 1.5 K. It should be pointed out that the muon probes the spin dynamics at its Larmor frequency: 1 kOe is equivalent to 0.056 μeV, well inside the resolution limited elastic peak. The neutron scattering measurements are therefore completely insensitive to the spin dynamics at these low energies. Finally, differences between the field cooled and zero field cooled susceptibility have been reported below 70 mK [28], indicative of spin glass-like behavior. One possible explanation for these results is that $Tb_2Ti_2O_7$ undergoes *partial* clustering at low temperatures, though the low temperature spin structure is a matter of debate [27,29,30]. Significant spin dynamics nevertheless persist.

Bulk susceptibility indicates that the isostructural compounds $Gd_2Ti_2O_7$ and $Tb_2Ti_2O_7$ have electronic moments of comparable size, where the Curie–Weiss temperature indicates the exchange couplings are also similar. However, the paramagnetic frequency shifts are an order of magnitude larger in $Tb_2Ti_2O_7$ due to a large dipolar contribution to the shift for the anisotropic Tb spin. History dependent behavior is observed below 1 K. However, this is a second order effect, since the major component of the μSR signal arises from persistent dynamics. The system remains in a 'cooperative paramagnetic' state [31] with only short range spin-spin correlations for all $T >$ 15 mK.

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