Cooperative Paramagnetism in the Geometrically Frustrated Pyrochlore Antiferromagnet $Tb_2Ti_2O_7$

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Neutron scattering, muon spin relaxation, and dc susceptibility studies have been carried out on polycrystalline $Tb_2Ti_2O_7$, a pyrochlore antiferromagnet in which the Tb^{3+} moments reside on a network of corner-sharing tetrahedra. Unlike other geometrically frustrated systems, $Tb_2Ti_2O_7$ remains paramagnetic down to $\sim$0.07 K, rather than ordering into a conventional Néel or spin-glass-like state, despite the fact that short-range antiferromagnetic correlations (AFC) develop at $\sim$50 K. At the first AFC wave vector, its low-lying, relatively flat magnetic excitation spectrum softens partially below 30 K. [S0031-9007(98)08346-X]

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The combination of antiferromagnetism and certain lattice symmetries based on triangles results in phenomena known broadly as *geometrical frustration* [1]. These local symmetries preclude the occurrence of two-sublattice Néel ordering, as it is not possible to satisfy the antiferromagnetic (AF) coupling with mutually antiparallel near-neighbor spins on such lattices. Antiferromagnetically coupled spins residing on a network of corner sharing tetrahedra can occur in cubic pyrochlores which are often constituted by the chemical formula $A_2B_2O_7$, where the *A* site is occupied by a trivalent rare-earth ion with eightfold oxygen coordination and the *B* site by a tetravalent transition metal ion with sixfold oxygen coordination [2]. The *A* and *B* sites individually form infinite interpenetrating sublattices of corner-sharing tetrahedra, and if either the *A* or *B* site is occupied by a magnetic atom with an AF nearest-neighbor interaction, then a high degree of frustration must be present.

Theoretical arguments have been made which lead to large ground state degeneracies for both discrete [3] and continuous spin symmetries [4,5] on the pyrochlore lattice. For near-neighbor AF interactions, long-range order is suppressed, with incoherent, local ordering of the spin configurations on a tetrahedron subject to the constraint $\Sigma_i \mathbf{S}_i = 0$, where the sum is over those spins on a single tetrahedra. Villain [5] coined the term "cooperative paramagnetism" to describe such a state at low temperatures.

Experimentally, however, it has been found that such systems do not typically remain paramagnetic, but either order into a noncollinear antiferromagnetic state, as in the case of FeF_3 [6], or enter a spin-glass-like state. This latter possibility is more common, occurring in the chemically ordered pyrochlores $Y_2Mo_2O_7$ [7], $Tb_2Mo_2O_7$ [8], and $Y_2Mn_2O_7$ [9], as well as the disordered pyrochlore $CsNiCrF_6$ [10] and the well-studied disordered kagomé system $SrCr_{9p}Ga_{12-9p}O_{19}$ [11]. In this Letter we report on elastic and inelastic neutron scattering (INS), muon spin relaxation (μSR), and susceptibility studies of the chemically ordered pyrochlore $Tb_2Ti_2O_7$. These results show that despite the onset of AF short-range order at $\sim$50 K, this material remains paramagnetic at least to temperatures $\sim$0.07 K. In addition, INS shows incomplete soft mode behavior in the low-lying magnetic excitation spectrum below about 30 K.

Other related low temperature states have recently been studied in the pyrochlore rare-earth titanates. Counterintuitively, *ferromagnetic* exchange and strong anisotropy lead to a geometrically frustrated state referred to as "spin-ice" in $Ho_2Ti_2O_7$ [12]. A nonmagnetic (i.e., singlet) ground state is also possible, and has been shown to exist in $Tm_2Ti_2O_7$ [13].

$Tb_2Ti_2O_7$ is an insulator which crystallizes in the cubic, face centered space group $Fd\bar{3}m$ with lattice parameter $a = 10.15(1)$ Å at 300 K, and only the Tb^{3+} ions on the *A* site possess a magnetic moment. Polycrystalline samples of $Tb_2Ti_2O_7$ were prepared by firing, in air at 1350 °C, stoichiometric amounts of Tb_2O_3 and TiO_2 for several days with intermittent grindings to ensure a complete reaction.

Figure 1 shows the inverse susceptibility of $Tb_2Ti_2O_7$, measured in a 0.01 T applied magnetic field. A fit of the high temperature regime to a Curie-Weiss form $\chi^{-1} \sim T - \theta_p$, yields an AF Curie-Weiss temperature of $\theta_p \sim -19$ K and a paramagnetic moment of $9.4\mu_B$, which compares favorably with the free ion value $^7F_6$, appropriate to Tb^{3+}. No anomalies or history dependencies are observed in the susceptibility at low temperatures,

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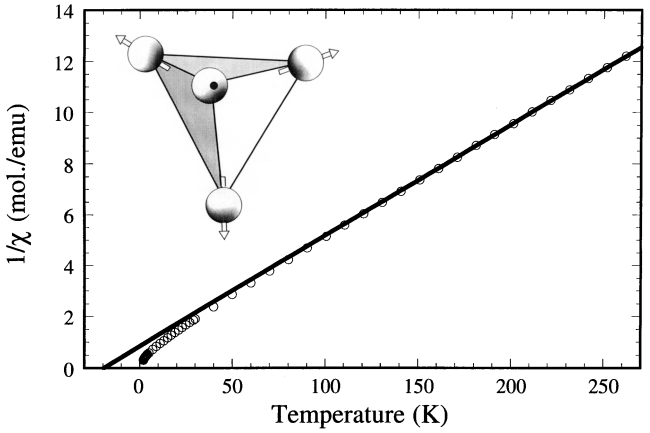

FIG. 1. The temperature dependence of the inverse susceptibility for $Tb_2Ti_2O_7$, along with a fit of the high temperature regime of this data to a Curie-Weiss form (see text). The inset shows the assumed local arrangement of moments on a single tetrahedron, based on the noncollinear FeF_3 magnetic structure.

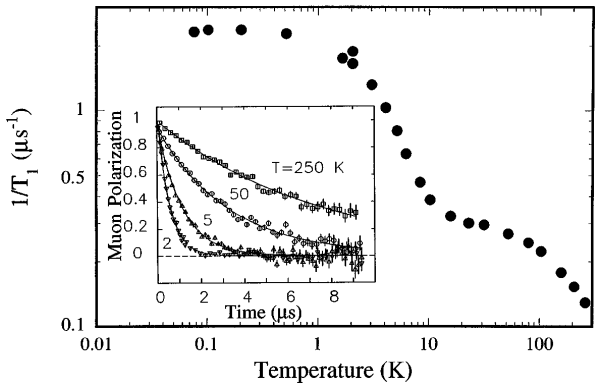

FIG. 2. The variation with temperature of the muon spin relaxation rate $1/T_1$ for $Tb_2Ti_2O_7$ in a longitudinal applied field of 0.005 T. The inset shows the single exponential relaxation of the muon polarization at various temperatures. The flat low temperature relaxation rate corresponds to a Tb^{3+} fluctuation rate of 0.04 THz, which is a good measure of the effective exchange constant.

indicating the absence of a transition to a long-range ordered or spin-glass-like state above 2 K.

Susceptibility measurements were also carried out on dilute $Tb_{0.04}Y_{1.96}O_7$ to investigate the nature of the ground state in isolated Tb^{3+} within the pyrochlore environment. As with $Tb_2Ti_2O_7$, a strongly temperature-dependent signal was observed to the lowest temperatures measured, $\sim$2 K, indicating a magnetic ground state for Tb^{3+} in this material. This is consistent with crystal-field calculations [14] which show a magnetic ground state doublet and doublet first excited state to be relevant for Tb^{3+} in this environment. These same calculations give a ground state doublet for $Ho_2Ti_2O_7$ and a nonmagnetic singlet for $Tm_2Ti_2O_7$, consistent with experimental observations [12,13].

The low temperature paramagnetic behavior of $Tb_2Ti_2O_7$ is confirmed by μSR measurements at TRIUMF (see Fig. 2). Details of the method can be found elsewhere [15]. Large rapidly fluctuating internal magnetic fields, which characterize a paramagnet, are evidenced by the single exponential muon spin relaxation in a small longitudinal magnetic field observed at all temperatures (see inset of Fig. 2). Furthermore, a large paramagnetic frequency shift was observed in transverse magnetic fields at all temperatures. The muon frequency shift tracks the dc susceptibility down to 2 K, indicating the muon is not perturbing the magnetic system in any significant way. These observations along with the smooth monotonic increase of $1/T_1$ down to 70 mK establishes that $Tb_2Ti_2O_7$ remains paramagnetic down to very low temperatures. In the fast fluctuation limit, which is appropriate here, the spin relaxation rate [16], $1/T_1 = 2\Delta^2\tau$, where $\Delta^2/\gamma_\mu^2 = \langle H_i^2 \rangle$ is the second moment of the internal magnetic field H_i, τ is the mean correlation time for fluctuations in H_i, and γ_μ is the muon gyromagnetic ratio. Taking $\Delta/\gamma_\mu = 0.70(6)T$ from studies of the isostructural compound $Tb_2Mo_2O_7$ [15], one can estimate the spin fluctuation rate [17]. For example, on the low temperature plateau below 2 K we estimate $(1/\tau)$ saturates at about 0.04 THz. Generally, a temperature-independent fluctuation rate is a measure of an effective exchange constant.

Powder neutron diffraction measurements were carried out on the C2 diffractometer at the NRU reactor at the Chalk River Laboratories (CRL). Measurements were performed between 2.5 and 100 K employing a Si(1,1,3) monochromator and 3.52 THz neutrons, with a PG filter in the incident beam to remove higher order contamination. Results at 2.5 K are shown in the top panel of Fig. 3. Sharp, resolution limited nuclear Bragg peaks are superimposed on diffuse magnetic scattering, reminiscent of that seen from $Tb_2Mo_2O_7$ [8]. Data sets at 2.5 and 50 K, in which the diffraction pattern taken at 100 K has been subtracted, are shown in the bottom panel of Fig. 3. This net intensity has been corrected for the $|\mathbf{Q}|$ dependence due to the Tb^{3+} magnetic form factor [18], and can be directly compared with models of short-range AF order, which clearly begins to set in by 50 K.

The net intensities at 2.5 and 50 K are compared to a calculation of the scattering expected from spin correlations extending over a single tetrahedron only. We have chosen to calculate the scattering expected from the local, four-sublattice, AF structure displayed by FeF_3 [6], shown schematically in the inset of Fig. 1. This local magnetic structure is not unique, but is consistent with the $\Sigma_i \mathbf{S}_i = 0$ constraint, and has the moments at the eightfold coordinated Tb^{3+} site aligned along the eight [1,1,1] cubic symmetry directions. As will be discussed, INS provides clear evidence for substantial single-ion anisotropy in the Tb^{3+} moments. The form of the scattering from a polycrystal displaying such a local magnetic structure

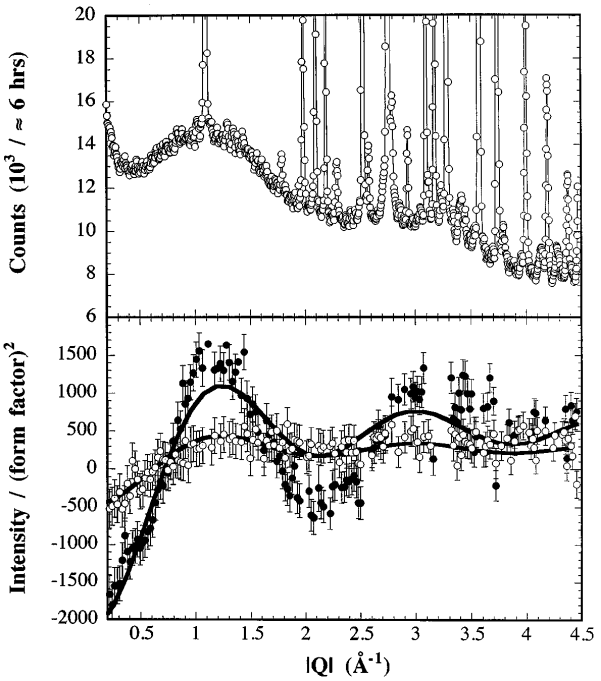

FIG. 3. Top panel: A neutron diffraction pattern from $Tb_2Ti_2O_7$ at 2.5 K is shown. Bottom panel: The difference between diffraction patterns taken at (i) 2.5 K (closed symbols) and (ii) 50 K (open symbols) and that taken at 100 K. The solid lines are fits of the net intensity to the scattering expected from spins correlated over a single tetrahedron only (see text).

is [19]

$$I(Q) \sim \Sigma_{i,j} < S_i \cdot S_j > \frac{\sin(Qr_{i,j})}{Qr_{i,j}} \sim \frac{\sin(Qr_{i,j})}{Qr_{i,j}} \quad (1)$$

if spins are correlated over nearest neighbors and consequently one value of $r_{i,j}$ (the distance between spins at sites i and j), only. The fit of the model to the data is shown as the solid lines in the bottom panel of Fig. 3. It provides a good description of the diffuse scattering, correctly accounting for the positions of the peaks and valleys. Interestingly, the inclusion of spin correlations beyond nearest neighbor and using, for example, the FeF_3 local structure produces another broad peak in the calculated net intensity intermediate between those at ~1.2 and ~3.1 Å^{-1}, as observed [8] in $Tb_2Mo_2O_7$, where magnetic moments at the Mo^{4+} site can mediate longer-range spin correlations. We therefore conclude that spins in $Tb_2Ti_2O_7$ are correlated over a single tetrahedron only, down to at least 2.5 K.

INS measurements were carried out on the same sample, now mounted in a closed cycle refrigerator. Measurements were performed on the C5 triple axis spectrometer at CRL in constant scattered energy mode with $E'/h = 3.52$ THz and a PG filter in the scattered beam, as well as with $E'/h = 1.2$ THz and a cooled Be filter in the scattered beam. Low energy-resolution measurements revealed the presence of dispersionless magnetic modes at $\hbar\omega \sim 2.4$ and 3.5 THz, which are crystalline electric field levels.

Lowering $E'/h = 1.2$ THz allowed for higher energy resolution (~0.09 THz FWHM) measurements and typical constant $|\mathbf{Q}|$ scans at 0.7, 1.2, and 2.2 Å^{-1} at 12 K are shown in the top panel of Fig. 4. The energy of the modes at 0.7 and 2.2 Å^{-1} are nearly identical, while there is a pronounced decrease in the integrated intensity of the mode at 2.2 Å^{-1} compared with that at 0.7 Å^{-1} consistent with that expected due to the Tb^{3+} magnetic form factor. The energy of these modes clearly dips near 1.2 Å^{-1}, and Gaussian fits to these and similar data at a variety of $|\mathbf{Q}|$'s bear this out as is seen in the lower panel of Fig. 4. At this temperature, the energy of this mode dips by roughly 10%, at the wave vector corresponding to the first maximum in the magnetic structure factor (see Fig. 2).

This incomplete softening of a well-defined excitation has not been previously observed in geometrically frustrated magnets, or in chemically disordered spin glasses. Similar magnetic behavior has been observed in the amorphous ferromagnet Co_4P [20]. The minimum in the magnetic excitation spectrum goes away with increasing temperature roughly on the scale of θ_p and by 30 K it is no longer evident as seen in the bottom panel of Fig. 4,

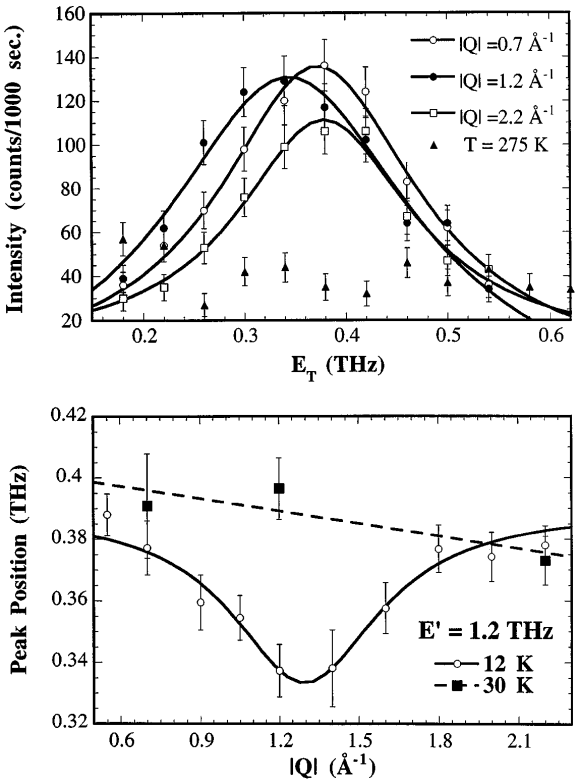

FIG. 4. Top panel: Constant $|\mathbf{Q}|$ scans at 12 K are shown. The inelastic peak at 1.2 Å^{-1} is centered at a lower energy than those at 0.7 or 2.2 Å^{-1}. Bottom panel: The dispersion of the magnetic excitation spectrum at 12 and 30 K is shown. At 12 K a clear minimum in the excitation spectrum is seen near the first maximum in the magnetic structure factor (see Fig. 3).

even though the excitations themselves are still well defined. On further increasing the temperature, the mode weakens in intensity and has merged into the background by 100 K.

A gapped magnetic excitation spectrum with weak dispersion is known to exist in a variety of singlet ground state systems such as Haldane [21] and spin-Peierls [22] materials wherein the first excited states form a triplet, as well as in systems for which the first excited state is another singlet, as occurs, for example, in praseodymium intermetallics [23]. In the pyrochlores, such a singlet ground state occurs in the Tm^{3+} based titanate, $Tm_2Ti_2O_7$ [13]. However, for temperatures below the gap energy, such systems display distinctive temperature-independent susceptibilities and an absence of elastic magnetic neutron scattering in the paramagnetic state. The softening of the gapped excitation spectrum we report here for $Tb_2Ti_2O_7$ is particularly intriguing given that such a nonmagnetic ground state is ruled out by both the present experimental study and by theoretical calculations [14].

The gapped magnetic excitation spectrum is then attributed to Ising-like anisotropy in the spin Hamiltonian, as would be expected due to orbital contributions to the Tb^{3+} magnetic moment in its crystalline environment. The present measurements indicate an anisotropy gap of $\sim$0.38 THz or 18 K. Employing our local FeF_3 structure [6], it is possible to think of the dip in the excitation spectrum as a collective tumbling of spin orientations on loosely correlated tetrahedra from one such local ground state to another. A magnetic excitation with such a characteristic has been discussed theoretically [24]. We speculate that further softening of this mode, requiring larger exchange relative to the competing energy scales in the problem, including the anisotropy gap and perhaps dipolar energies, would precipitate a transition to either a noncollinear ordered magnetic state or a spin glass state. This does not occur in $Tb_2Ti_2O_7$, leaving it a cooperative paramagnet to low temperatures. In light of this the low temperature plateau in the muon spin relaxation rate and corresponding field fluctuation rate are determined by the effective coupling between the correlated tetrahedra of Tb^{3+} spins.

In conclusion, our results point to the persistence of the paramagnetic state down to 0.07 K, even though AFC develops as high as 50 K, being the result of competition between the near-neighbor exchange and anisotropic energy scales on the pyrochlore lattice. Thus, correlated tetrahedra are only weakly coupled and continue to fluctuate, as demonstrated directly in the nonzero, low temperature $1/\tau$ values measured by μSR. The low-lying magnetic excitation spectrum displays an anisotropy gap of $\sim$18 K, which undergoes incomplete softening at the wave vector characterizing the AF short range order.

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[1] For recent reviews, see A. P. Ramirez, Annu. Rev. Mater. Sci. **24**, 453 (1994); *Magnetic Systems with Competing Interactions,* edited by H. T. Diep (World Scientific, Singapore, 1994).
[2] M. A. Subramanian, G. Aravamudan, and G. V. Subba Rao, Prog. Solid State Chem. **15**, 55 (1983).
[3] P. W. Anderson, Phys. Rev. **102**, 1008 (1956).
[4] J. N. Reimers *et al.,* Phys. Rev. B **43**, 865 (1991); J. T. Chalker *et al.,* Phys. Rev. Lett. **68**, 855 (1992).
[5] J. Villain, Z. Phys. B **33**, 31 (1979).
[6] G. Ferey *et al.,* Rev. Chim. Miner. **23**, 474 (1986).
[7] M. J. P. Gingras *et al.,* Phys. Rev. Lett. **78**, 947 (1997).
[8] B. D. Gaulin *et al.,* Phys. Rev. Lett. **69**, 3244 (1992).
[9] J. N. Reimers *et al.,* Phys. Rev. B **43**, 3387 (1991).
[10] M. J. Harris *et al.,* Phys. Rev. Lett. **73**, 189 (1994)
[11] A. P. Ramirez, Phys. Rev. Lett. **64**, 2070 (1990); B. Martinez *et al.,* Phys. Rev. B **50**, 15 779 (1994); C. Broholm *et al.,* Phys. Rev. Lett. **65**, 3173 (1990).
[12] M. J. Harris *et al.,* Phys. Rev. Lett. **79**, 2554 (1997).
[13] M. P. Zinkin *et al.,* J. Phys. C **8**, 193 (1997).
[14] M. Faucher (unpublished).
[15] S. R. Dunsiger *et al.,* Phys. Rev. B **54**, 9019 (1996).
[16] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).
[17] This is reasonable as the behavior of Tb^{3+} moments in the paramagnetic regime are measured to be roughly the same. In $Tb_2Mo_2O_7$ one can measure the magnitude of H_i directly since spin freezing is observed.
[18] G. H. Lander *et al.,* Phys. Rev. B **8**, 3237 (1973).
[19] E. F. Bertaut and P. Burlet, Solid State Commun. **5**, 279 (1967).
[20] H. A. Mook, N. Wakabayashi, and D. Pan, Phys. Rev. Lett. **34**, 1029 (1975).
[21] R. M. Morra *et al.,* Phys. Rev. B **38**, 543 (1988).
[22] O. Fujita *et al.,* Phys. Rev. Lett. **74**, 1677 (1995), and references contained therein.
[23] For example, J. A. Blanco, R. M. Nicklow, and D. Schmitt, Phys. Rev. B **56**, 11 666 (1997).
[24] P. Chandra and P. Coleman, Int. J. Mod. Phys. B **3**, 1729 (1989).