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Lifting of the ground-state degeneracy by crystal-field interactions in the pyrochlore $Tm_2Ti_2O_7$

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Abstract. The results of susceptibility and neutron inelastic scattering measurements on the pyrochlore compound $Tm_2Ti_2O_7$ are presented. The crystal-field ground state of the Tm^{3+} ion has zero spontaneous magnetization, and a virtually dispersionless crystal-field excitation is observed. It is concluded that the crystal-field interaction dominates the exchange interaction in $Tm_2Ti_2O_7$, lifting the expected degeneracy of the frustrated ground state.

Obtaining detailed information about the spin structure and excitations of frustrated magnetic systems with highly degenerate ground states remains a challenging experimental and theoretical problem. In this paper an additional consideration is illustrated: that the ground-state degeneracy may be partially, or even completely, lifted by the single-ion interaction of the magnetic ion with the crystalline electric field from its non-magnetic neighbours. This can lead to an absence of magnetic order unrelated to the inherent frustration.

The 16c and 16d sites of the $Fd\bar{3}m$ space group each form a sublattice of corner-sharing tetrahedra. In the pyrochlore compounds one (or both) of these sites may be occupied by a magnetic ion leading to intense frustration, due entirely to the geometry of the structure, if the exchange interaction between the magnetic ions is antiferromagnetic. Diffuse magnetic neutron scattering has been observed in powder diffraction experiments on several rare-earth pyrochlores, for example $Tb_2Mo_2O_7$ [1], $Y_2Mn_2O_7$ [2], and $Y_2Mo_2O_7$ [3], as well as in single-crystal experiments on the related compounds $CsNiCrF_6$ [4] and $CsMnFeF_6$ [5]. This scattering has been interpreted as arising from spin-glass-like short-range-ordered magnetic structures characteristic of frustrated systems, in qualitative agreement with Monte Carlo [6] and mean-field calculations [7] in which only the bare Heisenberg exchange is included in the Hamiltonian.

In real systems the crystal-field term describing the interaction of the magnetic ion with the crystalline electric field due to its neighbours can radically change the nature of both the ground state and the excitations in an otherwise frustrated system. If the crystal-field level splittings are much larger than the exchange between the magnetic ions, and the crystal-field ground state is a singlet, a collective frustrated ground state no longer exists—the ground state will simply consist of single-ion crystal-field ground states, the excitations of which may be weakly coupled by the exchange interaction to give an exciton-like dispersion relation. On the basis of the susceptibility and neutron inelastic scattering experiments discussed in this paper, it is suggested that this is the case in at least one

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pyrochlore compound, $Tm_2Ti_2O_7$, in which the magnetic Tm^{3+} ions constitute one of the corner-sharing tetrahedral sublattices.

The trigonal $\bar{3}m$ environment of the Tm^{3+} ion can be considered as a perturbation of the cubic $m3m$ symmetry considered in detail by Lea *et al* [8], for which the ground state is a singlet (either A_{1g} or A_{2g}) with $\langle J_z \rangle = 0$ for all possible values of the crystal-field parameters. The lowest-lying excited state coupled to the ground state by a dipole matrix element is a triplet for all possible crystal-field parameters (either the triplet T_{2g}, which occurs twice in the irreducible representation of $D^{(6)}$, and splits into the doublet E_g and the singlet A_{1g} under the perturbation, or the triplet T_{1g}, which occurs once in the irreducible representation, and splits into $E_g + A_{2g}$). The calculation of the susceptibility from second-order perturbation theory is straightforward, and, assuming the singlet–triplet level scheme, leads to an expression of the form

$$\chi = \frac{1}{1 + 3e^{-\beta\Delta}} \left[a + be^{-\beta\Delta} + c\beta e^{-\beta\Delta} \right]. \tag{1}$$

The constants a, b, and c are related to the matrix elements

$$M_{nm} = \mu_B g(JLS) \langle n | J_z | m \rangle$$

and

$$N_{nm} = \frac{e^2}{8mc^2} \langle n | \sum_i \left(x_i^2 + y_i^2 \right) | m \rangle$$

by $a = |M_{01}|^2 / \Delta - N_{01}$, $b = 2N_{22} - N_{11} - |M_{01}|^2 / \Delta$, and $c = |M_{22}|^2$. The singlet–triplet energy gap is Δ, and $\beta = 1/k_B T$.

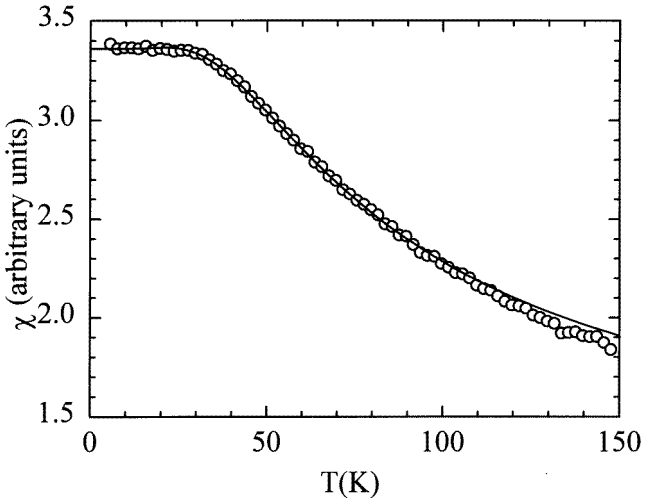

Figure 1. The a.c. magnetic susceptibility of $Tm_2Ti_2O_7$ measured in a applied field of 10 kHz and 2.5 G. The solid line is a fit to the data between 0 and 60 K of equation (1), with $a = (3.36 \pm 0.01) \times 10^{-5}$, $b = (9 \pm 2) \times 10^{-6}$, $c = (2.3 \pm 0.1) \times 10^{-3}$ and Δ fixed to the value of 10.64 meV obtained from the neutron scattering measurements.

Figure 1 shows the a.c. magnetic susceptibility of $Tm_2Ti_2O_7$. The solid line is a fit of equation (1) to the data, treating the quantities a, b, and c, as adjustable parameters, but with the gap fixed to the value $\Delta = 10.64$ meV obtained from the neutron scattering

measurements presented below. Significant deviations are only apparent above 100 K, where the presence of higher-energy crystal-field states, neglected in the calculation of equation (1), reduces the susceptibility. Were the value of $\langle J_z \rangle$ in the ground state non-vanishing, the low-temperature susceptibility would be dominated by a $\chi \sim 1/T$ Curie law term rather than the observed weak temperature dependence. Figure 1 is therefore clear evidence of a vanishing spontaneous magnetic moment in the crystal-field ground state.

Inelastic neutron scattering experiments were performed on a single crystal of $Tm_2Ti_2O_7$ measuring approximately $6 \times 6 \times 6$ mm on the E3 triple-axis spectrometer at Chalk River Laboratories. Two spectrometer configurations were employed: a low-energy-transfer configuration using the (002) reflection from a pyrolitic graphite (PG002) monochromator and analyser with a pre-analyser graphite filter to reduce contamination from higher-order reflections, and a high-energy configuration using the (113) reflection from a silicon monochromator, a PG002 analyser, and no filter. Energy transfers in the range 0–54 meV were available, with an energy resolution of ≈1.5 meV FWHM. In addition, two-axis scans with a PG002 monochromator and no analyser were performed to investigate possible diffuse magnetic scattering. All measurements were performed in a helium cryostat at a sample temperature of 1.5 K.

Constant-$\boldsymbol{q}$ scans were taken along the $[\zeta\ \zeta\ 0]$ and $[0\,0\,\eta]$ symmetry directions, with fixed scattered neutron energies of 14.5 meV and 31.0 meV in the low- and high-energy transfer configurations respectively. Figure 2 shows a typical scan.

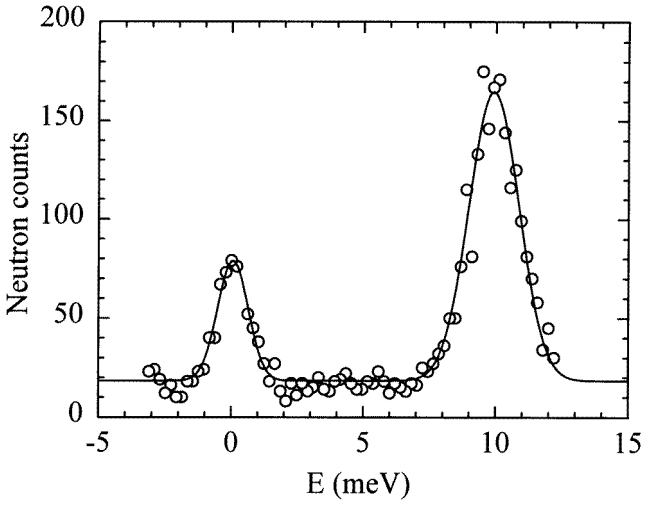

Figure 2. A constant-$\boldsymbol{q}$ scan for $\boldsymbol{q} = (1.34, 1.34, 0)$. The solid line is a fit to the data of a sum of two gaussians. The scattering centred at zero energy transfer arises from incoherent scattering, that at 10.6 meV from a crystal-field excitation of the Tm^{3+} ion.

The intensity of the quasi-elastic scattering centred at zero energy transfer is independent of $\boldsymbol{q}$ to within experimental uncertainty, and extensive two-axis scans showed no evidence of the diffuse magnetic scattering expected if the system possessed the short-range magnetic order observed in other pyrochlore compounds, and expected if the ground state were highly degenerate. In figure 3 the dispersion relation $E(\boldsymbol{q})$ of the crystal-field excitation at 10.6 meV, extracted from scans like that of figure 2, is plotted. Scans up to the maximum available energy transfer of 54 meV failed to reveal higher-energy excitations;

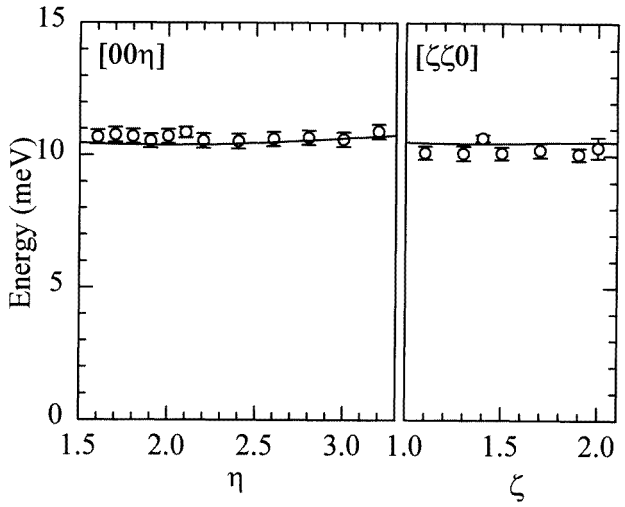

Figure 3. The energy of the lowest-lying crystal-field excitation in $Tm_2Ti_2O_7$ as a function of wavevector transfer, $\boldsymbol{q}$. The solid line is a fit to the data of an exciton dispersion relation (equation (4)) discussed in the text.

further experiments would therefore be required to determine the crystal-field parameters completely. Symmetry considerations discussed earlier imply that the excited state should consist of a narrowly split singlet and doublet state. The splitting was not directly observable in the present experiment, probably because the energy resolution was insufficient.

The excitation of figure 3 is virtually dispersionless, consistent with a very small exchange interaction. A somewhat more quantitative estimate of the strength of the exchange relative to that required for collective ordering can be obtained by considering the collective excitations of a system in which the ground crystal-field term is a singlet and the exchange is weak. This dispersion can be calculated in the pseudospin representation [9], leading to a relation of the form

$$E(\boldsymbol{q}) = \left\{\Delta\left[\Delta - 4\alpha^2\mathcal{J}(\boldsymbol{q})\right]\right\}^{1/2} \tag{2}$$

where $\alpha = \langle 0\,|J_z|\,1\rangle$ is the dipolar matrix element coupling the crystal-field ground state to the first excited state, Δ is the splitting between the two states, and $\mathcal{J}(\boldsymbol{q})$ is the Fourier transform of the exchange interaction. It is convenient to define the parameter

$$A \equiv \frac{4\mathcal{J}(0)\alpha^2}{\Delta} \tag{3}$$

proportional to the ratio of the effective exchange energy to the crystal-field splitting. The dispersion (equation (2)) can then be written

$$E(\boldsymbol{q}) = \Delta\left[1 - A\gamma(\boldsymbol{q})\right]^{1/2} \tag{4}$$

where $\gamma(\boldsymbol{q}) \equiv \mathcal{J}(\boldsymbol{q})/\mathcal{J}(0)$. Whether the ground state of the system is determined by the exchange or crystal-field interactions then depends on the value of the parameter A. For example, the excitations of a system with ferromagnetic exchange exhibit a continuous transition from exciton to spin-wave character as A increases from zero. At a critical value $A_f = 1$, $E(q = 0) = 0$ at $T = 0$, and there is a transition to a ferromagnetic ground state, analogous to the soft-mode model of structural phase transitions, with the parameter

A playing the role of temperature. The critical value of A for which a collective ground state is stabilized by an antiferromagnetic exchange interaction depends on the detailed geometry of the system, but is of order -1. While such mean-field concepts cannot be applied directly to a frustrated system in which the ground state does not possess long-range order, it is nevertheless anticipated that a transition to a collective ground state will not occur for $A \gtrsim -1$. A fit to the data of the dispersion relation of equation (4) is shown in figure 3 and yields $\Delta = 10.64 \pm 0.06$ and $A = -0.07 \pm 0.04$ indicating an effective antiferromagnetic exchange that is too weak to result in collective magnetic behaviour by more than an order of magnitude. No significance is attached to the precise value of A obtained from the fit, since the reduced χ^2 of 1.15 is only marginally better than the value obtained with the constraint $A = 0$ (i.e. a flat dispersion) of 1.26. The actual dispersion relation has a branch for each of the four magnetic ions in the primitive unit cell, which are weakly split by the exchange interaction. The experimental resolution of the present experiment is insufficient to resolve the splitting, and so the energies shown in figure 3 are effectively averages over the branches, weighted by the $\boldsymbol{q}$-dependent structure factor for each branch. This may explain the fact that the mean energy of the excitation measured in the $[\zeta\,\zeta\,0\,]$ direction is approximately 4% lower than that measured in the $[00\eta]$ direction. An upper bound of $A \gtrsim -0.2$ is obtained by requiring the total variation in the dispersion to be comparable to that of the data.

It is concluded that the expected frustrated ground-state degeneracy in this system is completely lifted, and both the static and dynamic magnetic properties are dominated by crystal-field effects. This result is significant in the context of the future investigation of magnetic frustration in these and other compounds. In particular the desirability of avoiding systems in which the magnetic ions have singlet ground states, unless there is reason to believe that the exchange is large compared with the splitting of crystal-field levels, is pointed out.

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References

[1] Gaulin B D, Reimers J N, Mason T E, Greedan J E and Tun Z 1992 *Phys. Rev. Lett.* **69** 3244
[2] Reimers J N, Greedan J E, Kremer R K, Gmelin E and Subramanian M A 1991 *Phys. Rev.* B **43** 3387
[3] Greedan J E, Reimers J N, Stager C V and Penny S L 1991 *Phys. Rev.* B **43** 5682
[4] Harris M J, Zinkin M P, Tun Z, Wanklyn B M and Swainson I P 1994 *Phys. Rev. Lett.* **73** 189
[5] Steiner M, Krasnicki S, Dachs H and Wallpach R V 1983 *J. Phys. Soc. Japan. (Suppl.)* **52** 173
[6] Reimers J N 1992 *Phys. Rev.* B **45** 7287
[7] Zinkin M P and Harris M J 1995 *J. Magn. Magn. Mater.* **140–144** 1803
[8] Lea K R, Leask M J M and Wolf W P 1962 *J. Phys. Chem. Solids* **23** 1381
[9] Cooper B R 1972 *Magnetic Properties of Rare Earth Metals* ed R J Elliott (London: Plenum)