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Two geometrically frustrated magnets studied by neutron diffraction

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Abstract

In the pyrochlore compounds, $Tb_2Ti_2O_7$ and $Tb_2Sn_2O_7$, only the Tb^{3+} ions are magnetic. They exhibit quite abnormal—and, in view of their chemical similarity, strikingly different—magnetic behaviour, as probed by neutron diffraction at ambient and applied pressure. $Tb_2Ti_2O_7$ is a cooperative paramagnet (''spin liquid''), without long-range order at ambient pressure; however, it does become ordered under pressure. By contrast, $Tb_2Sn_2O_7$ enters an ''ordered spin ice'' state already at ambient pressure. We analyse a simple model which already clearly exhibits some of the qualitative features observed experimentally. Overall, comparing these two compounds emphasizes the power of small perturbations in selecting low-temperature states in geometrically frustrated systems.

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Keywords: Spin liquid; Spin ice; Neutron diffraction

1. Introduction

Geometrical frustration (GF) [1] is now widely studied in solid state physics, as it seems to play a key role in original phenomena recently observed in new materials. Examples include the large anomalous Hall effect in ferromagnetic pyrochlores or spinels [2], the unconventional superconductivity observed in water substituted Na_xCoO_2 with triangular Co sheets [3], or the interaction between electric and magnetic properties of multiferroics materials [4].

What is GF? Most simply, it occurs when the specific geometry of the lattice prevents magnetic interactions from being satisfied simultaneously. In insulating systems such as the rare earth pyrochlores, the impossibility of a simple Néel ground state due to GF offers the possibility of finding a large variety of alternative, magnetic and non-magnetic, short-or long-ranged ordered states. In the most extreme case, paramagnetic behaviour persists down to the lowest temperatures, leading to an extended cooperative paramagnetic, or spin liquid, regime, in which only short-range correlations result [5].

Ferromagnetic interactions on the pyrochlore lattice may also be frustrated, namely when the exchange is dominated by a strong anisotropy which forces the spins in a tetrahedron to point along their local, non-collinear easy axes [6]. This leads to the spin ice state, whose degeneracy can be mapped onto that of real ice [6], leading to approximately the same entropy in the ground state [7].

In real compounds, the eventual choice of the stable magnetic state depends on a subtle energy balance between the frustrated first neighbour exchange energy term and perturbation terms of various origins (longer range interactions, anisotropies, quantum fluctuations, etc.). It is of course also determined by thermodynamic parameters, such as temperature, pressure or magnetic field. Counter intuitively, thermal fluctuations can even induce order when ordered states permit softer fluctuations than generic disordered ones. This effect is known as order by disorder [8] and is commonly encountered in frustrated magnetism. It has been well studied by Monte-Carlo simulations, and also received some experimental confirmation [9]. Pressure can change the nature of, and balance between different terms in the Hamiltonian, as they can depend on interatomic distances in different ways. An applied field adds Zeeman energy, and can, for

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example, stabilize a subset of the original ground states, at times resulting in magnetization plateaus.

In this paper, we study a well-known pyrochlore $Tb_2Ti_2O_7$, which we investigated by neutron diffraction under extreme conditions of temperature (down to 0.1 K) and applied pressure (up to 8.7 GPa). We review one of its most fascinating properties, namely its ability to "crystallize" or order magnetically under pressure and we propose a new theoretical approach which accounts for some important peculiarities of this effect. We also compare $Tb_2Ti_2O_7$ to its sibling compound $Tb_2Sn_2O_7$, very recently studied, which behaves as an "ordered spin ice". Both compounds have a fully chemically ordered structure, the pyrochlore structure of cubic $Fd\bar{3}m$ space group, where the Tb^{3+} magnetic ions occupy a GF network of corner sharing tetrahedra. Although they differ only by the nature of the non-magnetic ion (Ti/Sn), they show very different magnetic ground states. The comparison sheds some light on how to select the ground state through very small perturbations, one of the most prominent characteristics of GF.

2. $Tb_2Ti_2O_7$: a spin liquid orders under applied pressure

$Tb_2Ti_2O_7$ is a famous example of a spin liquid, investigated by numerous groups, where short-range correlated Tb spins fluctuate down to 70 mK at least [10], that is more than 300 times below the typical energy scale of the magnetic interactions (the Curie–Weiss constant θ_{CW} of -19 K, where the minus sign corresponds to AF interactions). The persistence of these fluctuations was checked by muon relaxation [10], at the timescale of the muon probe of about 10^{-6} s. At shorter timescales, inelastic neutron scattering showed a quasielastic signal, whose energy linewidth strongly decreases below about 1 K, indicating a stronger slowing down in this temperature range [11]. Coexisting with the spin liquid phase, spin glass-like irreversibilities and anomalies of the specific heat were recently observed in the range 0.1–0.8 K [12]. Using high-pressure powder neutron diffraction [13], we observed two interesting phenomena induced by pressure [14]: (i) the onset of antiferromagnetic long-range order below a Néel temperature T_N of about 2 K; (ii) the enhancement of the magnetic correlations in the spin liquid phase above T_N. Just below T_N, the ordered phase coexists with the spin liquid in a mixed solid–liquid phase, whose relative contributions vary with pressure and temperature. The magnetic Bragg peaks of the simple cubic lattice can be indexed from the crystal structure of $Fd\bar{3}m$ symmetry, taking a propagation vector $\mathbf{k} = (1, 0, 0)$. It means that in the cubic unit cell with four Tb tetrahedra, two tetrahedra are identical and two have reversed moment directions. A longer wavelength modulation of this structure, involving a much larger unit cell, was also observed in the powder data.

What is the pressure induced ground state? More fundamentally what is the role of pressure? To answer these questions, we performed single crystal neutron diffraction down to very low temperatures (0.14 K), combining hydrostatic pressure with anisotropic stress [15]. We showed that both components play a role in inducing the long-range order, and that the ordered moment and Néel temperature can be tuned by the direction of the stress. A stress along a [1 1 0] axis, namely along the direction of the first neighbour distances between Tb^{3+} ions, is the most efficient in inducing magnetic order (Fig. 1).

FullProf refinements of the single crystal data allowed a determination of the magnetic structure with better precision, especially the local spin structure within a Tb tetrahedron. The structure corresponding to the best refinement ($R_F = 14\%$ is given in Table 1). The bond 1–4 along the axis of the stress, which should be reinforced, has AF collinear spins. This corresponds to a natural expectation for AF first neighbour exchange. The orientation of

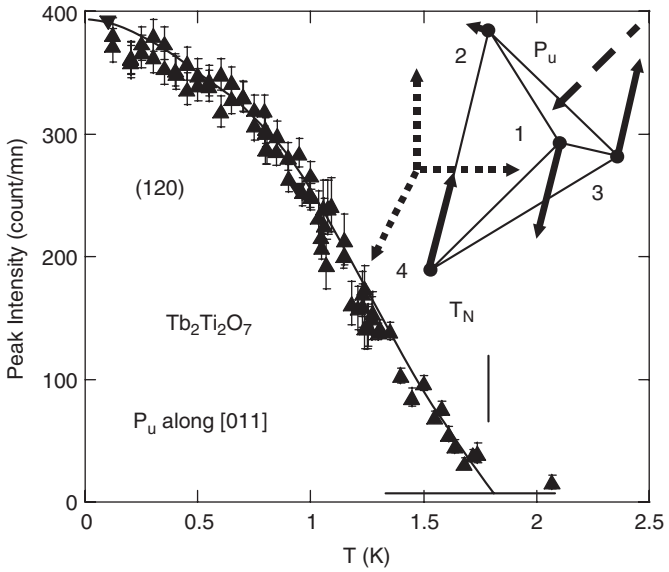

Fig. 1. $Tb_2Ti_2O_7$: an antiferromagnetic ordered state with $\mathbf{k} = (1, 0, 0)$ propagation vector is induced under pressure. Here an isotropic pressure $P_i = 2.0$ GPa is combined with uniaxial pressure $P_u = 0.3$ GPa along [0 1 1] axis. The variation of the peak intensity of the magnetic Bragg peak (1 2 0) shows the Néel temperature. The local spin structure in a tetrahedron has non-compensated magnetization.

Table 1
Orientation of the magnetic moments in one tetrahedron in the pressure induced state of Fig. 1, deduced from the refinement of the magnetic structure

Site	x	y	z	M
1	0.5	0.5	0.5	[1 0 −1]
2	0.25	0.25	0.5	[1 0 1]
3	0.25	0.5	0.25	[−1 0 1]
4	0.5	0.25	0.25	[−1 0 1]

The stress component is along [0 1 1]. The atomic coordinates x, y, z, are expressed in the cubic unit cell containing four tetrahedra. Two tetrahedra are identical and two have reversed spin orientations.