Tetragonal distortion in Tb$_2$Ti$_2$O$_7$ seen by neutron scattering

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Abstract. Inelastic neutron spectra performed at 0.4 K in a single crystal of Tb$_2$Ti$_2$O$_7$, with a magnetic field applied along the [110] direction, confirm the presence of a tetragonal lattice distortion from the nominal cubic symmetry, previously evidenced below 20 K in high resolution x-ray experiments. The signature of the distortion is an inelastic line at very low energy ($\simeq 0.04$ THz), which is also present in the powder inelastic neutron spectra of Tb$_2$Sn$_2$O$_7$.

1. Introduction
The geometrically frustrated pyrochlore Tb$_2$Ti$_2$O$_7$ has interesting, non-classical low temperature behaviour, remaining in a dynamic spin-liquid state down to at least 0.02 K [1, 2, 3]. The crystal field (CF) interaction acting on the Tb$^{3+}$ ion ($J=6$, $g_J=1.5$) has threefold symmetry and is expected to play a fundamental role in the low temperature properties. Its level scheme for Tb$_2$Ti$_2$O$_7$ has been determined by inelastic neutron scattering in powder samples [4, 5]. The two lowest CF states are doublets separated by about 20 K (0.4 THz). One peculiarity of the pyrochlore lattice, made of corner sharing tetrahedra, is that there are 4 distinct threefold axes per tetraedron, namely the $[111]$, $[\bar{1}\bar{1}1]$, $[1\bar{1}\bar{1}]$ and $[\bar{1}1\bar{1}]$ axes. At low temperature, the non-Kramers Tb$^{3+}$ ion is extremely anisotropic along such an axis at low magnetic field, i.e. the Tb moment lies along, say, [111] whatever the orientation of the field. For larger fields, the Tb$^{3+}$ ion acquires a finite anisotropy due to mixing with excited CF states.

Recently, high resolution x-ray measurements on single crystal Tb$_2$Ti$_2$O$_7$ have revealed cubic-to-tetragonal structural fluctuations below 20 K [6], i.e. the local symmetry at a Tb site suffers a tetragonal distortion along a cubic [001] axis, away from the [111] threefold symmetry axis. Therefore, the degeneracy of the low lying CF doublets can be expected to be lifted by a small amount. Then, at low temperature, a low energy inelastic line should show up in the neutron spectra. This was indeed observed in the powder inelastic spectra of Tb$_2$Ti$_2$O$_7$ [5], where an ill-resolved, quasielastic excitation appears in the collective paramagnetic state (at 1.6 K) at an energy 0.03-0.04 THz. This could not be indexed as a transition within the trigonal symmetry CF level scheme. More clearly, single crystal inelastic neutron spectra in Tb$_2$Ti$_2$O$_7$ with a magnetic field [7] display, at 0.4 K and at large Q values, an excitation with sizeable intensity which is progressively resolved from the quasi-elastic scattering as the field increases. Its energy is weakly field dependent and ranges from 0.035 THz in zero field to 0.06 THz at 3 T.
In the following, we will examine constant Q cuts of the inelastic spectra in Tb$_2$Ti$_2$O$_7$ from Ref.[7] and show that they can be interpreted, in first approximation, using a hamiltonian including the nominal trigonal CF interaction along [111], as determined in Ref.[5], to which is added a small tetragonal distortion along [001] and an effective Zeeman interaction taking into account the applied field and a molecular field.

2. Experimental Details
The single crystal sample of Tb$_2$Ti$_2$O$_7$ was grown by the floating zone image furnace techniques as described earlier [8]. It conforms to the cubic spacegroup of $Fd\overline{3}m$ with lattice parameter 10.12(7) Å at 300K. Time of flight (TOF) neutron scattering was performed with both high and low energy resolution using the Disk Chopper Spectrometer (DCS) at NIST, USA. With over 900 detectors, DCS can measure a wide range of Q and $\omega$ space simultaneously with a resolution between 1.97 and 0.017 meV for incident neutron wavelengths between 1.8 and 9 Å [10].

3. The single crystal inelastic spectra in Tb$_2$Ti$_2$O$_7$
Constant Q energy scans at 0.4 K in Tb$_2$Ti$_2$O$_7$ with a field of 1 T and 3 T applied along [110] are represented in the upper panels of Figs.1a and b respectively. An isolated excitation is observed near 0.05 THz for both field values, followed by a structured pattern which is well resolved into 4 peaks for $H$=3 T. For a field applied along [110], the Tb sites can be divided into two types: those where the ternary axis is at an angle $\theta_m = \arcsin 1/\sqrt{3}=35.3^\circ$ (α sites) from H and those where it is perpendicular to H (β sites). This has important consequences as to the Tb moment magnitude and the Zeeman splitting because of the strong anisotropy of the Tb$^{3+}$ ion.

The cross section for inelastic neutron scattering from a rare earth state $|i\rangle$ to a state $|j\rangle$, separated by an energy $E_{ij}$, in a single crystal is written [11]:

$$I_{ij}(Q, E) \propto p_i \sum_{m,n} (\delta_{mn} - Q_m Q_n) \langle i| J^\dagger_m |j\rangle \langle j| J_n |i\rangle \delta(E - E_{ij}),$$

(1)

Figure 1. Constant Q energy scans in Tb$_2$Ti$_2$O$_7$ single crystal at $T = 0.4$ K with a field of 1 T (a) and 3 T (b) applied along [110]. Upper panels: experimental data for $Q \simeq (002)$ Å$^{-1}$. The quasi-elastic line has been subtracted for the 1 T scan. Lower panels: calculation using expression (1) and hamiltonian (3), with $D_Q = 0.19$ K. The labels α and β refer to the two types of Tb sites (see text).
where \( p_i \) is the population of the initial state \(|i\rangle\), \( \mathbf{Q} \) is the unit vector in the direction of the scattering vector and \( m \) and \( n \) scan the coordinates \( x, y \) and \( z \). In order to interpret the above spectra, we start with the trigonal symmetry CF hamiltonian \( \mathcal{H}_{\text{trig}} \) with axis \( OZ \) along the cubic [111] axis (see e.g. Ref.[5] and Fig.2) to which we add a small tetragonal term of the form: \( \mathcal{H}_Q = D_Q J_z^2 \), where \( OZ \) is the cubic [001] axis and \( D_Q \) is the tetragonal distortion parameter. Such a procedure holds if the tetragonal term is a perturbation with respect to the main trigonal one, which is verified \( \textit{a posteriori} \) by the fact that the splitting due to the distortion is about 10% of the first excitation energy of the trigonal CF. In the OXYZ frame where \( OZ \) is the ternary axis and the plane YOZ is chosen such that it contains the z-axis, this tetragonal term can be written:

\[
D_Q J_z^2 = D_Q \left[ \frac{2}{3} J_Y^2 + \frac{1}{3} J_Z^2 - \frac{\sqrt{2}}{3} (J_Y J_Z + J_Z J_Y) \right].
\]

We add to the CF hamiltonian a Zeeman term including the applied field \( \mathbf{H} \) and an exchange/dipole field, whose magnitude and orientation are free parameters for each type of site (\( \alpha \) or \( \beta \)). The total hamiltonian then writes:

\[
\mathcal{H} = \mathcal{H}_{\text{trig}} + D_Q J_z^2 + g_J \mu_B \mathbf{J} \cdot (\mathbf{H} + \mathbf{H}_{\text{ex}}^{\alpha, \beta}).
\]

Diagonalisation of (3) allows to compute the neutron inelastic spectra from expression (1) by summing over the rare earth states. Comparison with the data at different fields yields the small value \( D_Q = 0.19 \text{K} \) for the tetragonal parameter. The degeneracy lifting of the ground doublet in zero field is 0.044 THz = 2.14 K, and the position and relative intensity of the lowest energy inelastic line observed in \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) [5] are well accounted for. For the single crystal in-field spectra in \( \text{Tb}_2\text{Ti}_2\text{O}_7 \), this \( D_Q \) value accounts for this same line arising from the \( \beta \) sites only (first line labelled \( \beta \) in the lower panels of Fig.1). Indeed, for the \( \beta \) sites, the applied field is perpendicular to the local ternary axis, i.e. it is along a hard magnetic axis if one neglects the tetragonal distortion, and it is still close to it if the latter is taken into account. Then the Zeeman splitting is weak and the ground doublet splitting is mainly due to the distortion term. On the contrary, the Zeeman splitting for the \( \alpha \) Tb sites strongly depends on the field, and the corresponding line (first line labelled \( \alpha \) in the lower panels of Fig.1) shifts to higher energy as the field increases. In order to better reproduce the spectra, one needs to introduce a molecular field for each site, which adds to the applied field. For instance, for the 3 T spectra, the \( \alpha \) molecular field is 0.2 T and is antiparallel to the applied field, while for \( \beta \) sites, it is 1 T and almost antiparallel to \( \mathbf{H} \). The energies of the levels for both types of Tb sites are shown in Fig.3, illustrating the large difference in the distortion/Zeeman splittings of the two sites. Our

![Figure 2. Coordination axes indicating the OXYZ frame. Here OZ coincides with the crystallographic [111] axis and the [001] axis resides within the YOZ plane. The position of the magnetic field for the two types of Tb sites is also indicated.](image-url)
Figure 3. Energy level schemes ($E < 0.6 \text{ THz}$) for $\alpha$ and $\beta$ sites in Tb$_2$Ti$_2$O$_7$ for an applied field of 3 T applied along [110] and molecular fields as described in the text. The number at the right of each level is its energy with respect to the ground level. At 0.4 K, the latter alone is populated, and for $E < 0.6 \text{ THz}$, three transitions appear for the $\beta$ sites, but only two for the $\alpha$ sites, the $4^{th}$ level lying higher in energy.

spectral simulations also show that the intensity of the first $\beta$ line decreases very rapidly if the molecular field at the $\beta$ site departs more than by $20^\circ$ from the direction perpendicular to the local axis.

4. Conclusion

The origin of a low energy inelastic line appearing at low temperature in the neutron scattering spectra of Tb$_2$Ti$_2$O$_7$, both in powder and single crystal samples, has been unraveled. It arises from a tetragonal distortion from the nominal trigonal symmetry of the Tb$^{3+}$ crystal field interaction. This distortion had been previously detected below 20 K in single crystal Tb$_2$Ti$_2$O$_7$ by x-ray diffraction measurements. We have modelled the inelastic neutron scattering spectra using a Hamiltonian which includes the trigonal CF interaction along [111], a small tetragonal distortion along [001] and a Zeeman term for the case of the spectra with a magnetic field applied along the crystallographic [110] axis. The correspondence between the calculated crystal field excitations and the neutron scattering data is reasonably good. In particular, there is good agreement for the energy and intensity of the lowest transition ($\simeq 0.04 \text{ THz or 2 K in zero field}$), which corresponds to the splitting of the ground doublet by the tetragonal distortion with a parameter $D_Q = 0.19 \text{ K}$. This low energy inelastic line is also present in the low temperature inelastic neutron data of Tb$_2$Sn$_2$O$_7$, which suggests that the quadratic distortion also occurs in this compound.

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