Magneetoelastic excitations in the pyrochlore spin liquid Tb$_2$Ti$_2$O$_7$

T. Fennell, M. Kenzelmann, B. Roessli, H. Mutka, J. Ollivier, M. Ruminy, U. Stuhr, O. Zaharko, L. Bovo, A. Cervellino, M. K. Haas, and R. J. Cava

1 Laboratory for Neutron Scattering, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
2 Laboratory for Developments and Methods, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
3 Institut Laue Langevin, BP 156, 6, rue Jules Horowitz, 38042, Grenoble Cedex 9, France
4 London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, 17-19 Gordon Street, London, WC1H 0AH, UK
5 Swiss Light Source, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
6 Department of Chemistry, Princeton University, Princeton NJ 08540, USA

(Dated: May 24, 2013)

At low temperatures, Tb$_2$Ti$_2$O$_7$ enters a spin liquid state, despite expectations of magnetic order and/or a structural distortion. Using neutron scattering, we have discovered that in Tb$_2$Ti$_2$O$_7$ an excited crystal field level is coupled to a transverse acoustic phonon, forming a new hybrid excitation. Magnetic and phonon-like branches with identical dispersion relations can be identified, and the hybridization vanishes as Tb$_2$Ti$_2$O$_7$ crosses over from the correlated, or spin liquid, state to the high temperature paramagnetic phase. We suggest that Tb$_2$Ti$_2$O$_7$ is aptly named a “magnetoelastic spin liquid” and that it is the hybridization of the excitations which suppresses both magnetic ordering and the structural distortion.

Experimental classification of spin liquids [1] is problematic - absence of broken symmetry is not definitive and topological properties [2] are not experimentally accessible. One possibility is to study the excitations, which are often predicted to be exotic fractional quasiparticles such as spinons [3] or monopoles [4]. Despite the absence of broken symmetries, propagating bosonic excitations are predicted in certain models [5-8]. For example, in a quantum spin ice (QSI), a magnetic excitation which has a linear dispersion is expected [6,7]. The QSI state can be described by a theory of emergent electrodynamics, of which this mode is the photon [6].

Spin liquids are typically sought in frustrated magnets, but although the Tb$^{3+}$ ions in Tb$_2$Ti$_2$O$_7$ form a pyrochlore lattice and are coupled antiferromagnetically, common ingredients for frustration, at first sight Tb$_2$Ti$_2$O$_7$ should not be frustrated. The trigonal crystal field at the rare earth site splits the free ion term to give an $E_g$ doublet groundstate. The first excited state, at 1.5 meV, is also an $E_g$ doublet [9]. Classically, the resulting anisotropy combined with antiferromagnetic interactions should ensure long-range order at $T \sim 1$ K [10]. Instead, a magnetically disordered phase with spin dynamics, usually called a spin liquid, exists down to 0.05 K.

One proposed explanation for the absence of magnetic order in Tb$_2$Ti$_2$O$_7$ is that three-body exchanges caused by virtual crystal field excitations via the low-lying excited state, renormalize the antiferromagnetic exchange, making Tb$_2$Ti$_2$O$_7$ a type of QSI [11]. The existence of the full emergent phenomenology of the QSI state in the Hamiltonian of Ref. [11] remains to be clarified, and recent experiments [12,15] have debated the existence of a magnetization plateau expected to signify the QSI state predicted in Tb$_2$Ti$_2$O$_7$ [16]. Recent neutron scattering experiments show that the spin correlations have a power-law form, often associated with ice-rule constraints on the pyrochlore lattice [17].

The theory of Ref. [11] is based on the unperturbed pyrochlore structure and crystal field doublets, but because Tb$^{3+}$ ($f^8$ and $7F_6$) is a non-Kramers ion, its degenerate electronic states are susceptible to structural distortions, as in the canonical cooperative Jahn-Teller transition in TbVO$_4$ [18]. Indeed, much experimental evidence points to the relevance of magnetoelastic effects and proximity to a magnetically ordered groundstate [19-23]. In an alternative theory, a hypothetical tetragonal distortion splits the doublets into singlets [24]. While such a splitting has been observed in extraordinarily pure powder samples, no clear splitting has been observed in “normal” crystals of Tb$_2$Ti$_2$O$_7$, motivating the suggestion that the spin liquid state of Tb$_2$Ti$_2$O$_7$ involves frustration of both spin and structural degrees of freedom [25]. We contend that the electronic and structural excitations of Tb$_2$Ti$_2$O$_7$ are mixed into hybrid fluctuations which we call magnetoelastic modes (MEMs), and this is at the origin of the combined absence of magnetic order and structural distortion in Tb$_2$Ti$_2$O$_7$. Here we characterize a MEM, and demonstrate that it has both magnetic and phononic characters, which are visible at different wavevectors.

We used the same single crystal of Tb$_2$Ti$_2$O$_7$ as in Ref. [17]. Further details of its characterization are to be found in the supplementary material [26]. Using the time-of-flight (TOF) spectrometer IN5 [27] at the Institut Laue Langevin, we surveyed a four-dimensional volume of $S(Q,\omega)$. We measured at 0.05, 5 and 20 K using $\lambda = 4$ Å, and additionally at 0.05 K using $\lambda = 2$ and 7 Å. Using the triple-axis spectrometers (TAS) TASP (in combination with the neutron polarimetry device MuPAD) and EIGER at the SINQ, Paul Scherrer Institut,
we investigated the polarization and temperature dependence of the MEM respectively. In the polarized neutron scattering experiment, we measured non-spin flip (NSF) and spin flip (SF) cross sections with the neutron polarization parallel to the scattering vector \( \mathbf{Q} \), such that all excitations appear in the NSF channel and nuclear scattering in the SF channel. Data from the TAS experiments can be compared with cuts through the TOF spectra by scaling.

The known magnetic neutron scattering response of \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) consists of elastic diffuse scattering [17, 28, 29], quasielastic scattering [24, 30], and crystal field excitations (CFEs) [31]. Fig. 1 and 2 show overviews of the inelastic scattering, with lower resolution extending to higher energy transfer, and with higher energy resolution around the first CFE, respectively. We concentrate here on the MEM, which is a new feature. It is the weak but sharp mode extending out of the \((2, 2, 0)\) position, between the two intense CFEs (Fig. 1a-d). A similar mode is visible at \((1, 1, 1)\) (Fig. 1f), and the topmost part of the dispersion can be distinguished in nearby zones. Strong excitations are also visible at \((0, 0, 8)\) (Fig. 1c), \((3, 3, 7)\) and \((5, 5, 5)\), but while those in low zones have their propagation vector \((\mathbf{k})\) parallel to the scattering vector \((\mathbf{Q})\), these have \( \mathbf{k} \perp \mathbf{Q} \).

The interaction of the MEM with the first CFE, which is pulled up in energy where the two meet, can be seen in Fig. 2a. Despite the steep dispersion of the MEM, there is no branch reaching down to \( h\omega = 0 \), below the CFE (Fig. 2a, b, c). Examination of the intensity throughout the iso-energy volume \( S(\mathbf{Q}, h\omega = 0.65 \text{ meV}) \) shows no sharp features cut through it (Fig. 2b). The MEM therefore has a gap of \( \sim 1.5 \text{ meV} \) (20 K). A single broad, asymmetric peak is formed where the modes intersect, but, away from \((2, 2, 0)\), two components can be distinguished in the CFE (Fig. 2f). The MEM does not interact with the second CFE, as its dispersion passes just below it (Fig. 1f).

MEMs can be observed at small wavevectors, typical of magnetic excitations. At \((2, 2, 0)\), we have determined explicitly that the MEM has a magnetic contribution by using polarized neutron scattering. As shown in Fig. 3a, all the scattering occurs in the spin flip channel, indicating that in fact there is no measurable nuclear contribution at this position. The intensity of the MEM is almost independent of energy until it approaches the second CFE where it may increase (Fig. 3b), in contrast to typical antiferromagnetic excitations which decrease in intensity with increasing energy.

Because magnetic neutron scattering is due to spin components perpendicular to \( \mathbf{Q} \), and the wavevector \( \mathbf{k} \) of the mode is parallel to \( \mathbf{Q} \), the MEM is a transverse mode (i.e. the spin fluctuations are perpendicular to its direction of propagation). In comparison, the excitations at large wavevectors are similar to transverse acoustic phonons - they appear at large wavevectors (the phonon cross section depends on \( |\mathbf{Q}|^2 \)), they are gapless (within the energy resolution of this setting of the spectrometer), their intensity decreases with \( h\omega \) (Fig. 3b), and...
FIG. 2. Interaction of the MEM with the first crystal field excitation, and gap of the MEM. At (2,2,0), the MEM intersects with the first crystal field excitation (a, this is the same view as Fig. 1a, but with better energy resolution). The MEM can be seen above the crystal field level. The MEM is faintly visible in the perpendicular direction (b), where some intensity concentrated around (h,h,0) is integrated in the cut. No sharp feature can be found extending below the crystal field level, as can also be seen in an intensity map at $E = 0.75$ meV (dashed line in b), i.e. in the gap (c). Constant-$Q$ cuts (d, at positions indicated by dashed lines in panel a) show a two-component lineshape for the crystal field excitation far away from (2,2,0) and a single, broad, asymmetric, peak where the MEM meets the crystal field level.

they are intense when $k \perp Q$. However, if we compare the transverse magnetic mode at (2,2,0) with the transverse phonon-like mode (0,0,8) (which is to say along (h,h,0) and (h,h,8) respectively), we see that the upper parts of their dispersions overlap precisely (Fig. 3c), suggesting they have a common origin, and that these are therefore mixed modes carrying both magnetic and structural fluctuations. We observe the magnetic part at small wavevectors, where the magnetic form factor of Tb$^{3+}$ is large, and the phononic part at large wavevectors, where the phonon cross section is large.

In Fig. 3, we show the temperature dependence of the MEM at (2,2,0). Its intensity collapses in the range 20 – 50 K, again quite unlike a conventional phonon, which would become stronger at higher temperature. The detailed structure of interacting modes and split-
The coupling could be allowed if the inversion symmetry of the Tb$^{3+}$ site was lost, and since we observe no sign of a global symmetry lowering across the onset of the magnetoelastic coupling at $T \sim 20$ K (see also supporting material [30]), this must be a local [24, 33] or dynamical effect. Possible mechanisms could be inhomogeneous strain [21], or magnetically induced charge redistribution associated with certain spin configurations [34, 35]. In the former, inhomogeneous strains would be expected to build up as the excited state is depopulated [18, 30], and in the latter, the relevant spin configurations would also appear as the spins become more anisotropic. Either mechanism would therefore enhance the coupling below the temperature scale of $5-20$ K. Lattice vibrations now carry spin fluctuations, and relaxation of a spin configuration can generate structural fluctuations. Since an acoustic phonon is involved, passage of a hybrid fluctuation might be expected to reconfigure both spins and strains over long distances, frustrating the development of long-ranged magnetic or structural ordering.

We may hope for an emergent gauge theory for Tb$_2$Ti$_2$O$_7$, which must now contain a propagating bosonic excitation. Various theories of frustrated magnetism support dispersive excitations despite the absence of long-range magnetic order. In particular, in a quantum spin ice, the photon mode looks superficially much like our MEM, and we speculate that the theory of a magnetoelastic spin liquid will ultimately resemble a quantum spin ice, with vibronic fluctuations replacing the quantum tunneling fluctuations. Furthermore, we point out that since the MEM carries both transverse electric dipole and spin fluctuations, it can already be regarded as a type of emergent photon. The praseodymium pyrochlores [37] which are currently attracting interest as quantum spin ices also have non-Kramers doublet groundstates. Higher-order multipolar moments are implicated in these materials, which we note because the mechanism of the hybridization we observe appears somewhat similar to a system such as UO$_2$, where mixing of quadrupolar and dipolar fluctuations renders an entire branch of quadrupolar excitations visible to magnetic neutron scattering [38] (though UO$_2$ has both quadrupolar and dipolar order). Magnetoelastic modes may be relevant in these other pyrochlores and should be distinguished in the future identification of quantum spin ice photons.

In conclusion, we have observed a magnetoelastic mode in the spin liquid phase of Tb$_2$Ti$_2$O$_7$. This mode is formed by the hybridization of the first excited crystal field level and the transverse acoustic phonons. The hybridization of the excitations disappears in the paramagnetic regime. The existence of the magnetoelastic mode implies that the spin liquid phase of Tb$_2$Ti$_2$O$_7$ supports a propagating bosonic spin excitation. We suggest that the coupling we have observed is at the origin of the anomalous magnetoelastic behavior of Tb$_2$Ti$_2$O$_7$.
We thank X Thonon (ILL), M Zolliker and M Bartkowiak (PSI) for operation of dilution refrigerators; S Fischer and W Latscha for additional cryogenic support on EIGER; and A Buller for assistance with cutting the sample. We are pleased to acknowledge discussions with O Benton, AT Boothroyd, ST Bramwell, MJP Gingras, A Gukasov, H Kadowaki, P McClarty, C Ruegg and N Shannon. Neutron scattering experiments were carried out at the high flux reactor of the Institut Laue Langevin in Grenoble, France, and the continuous spallation neutron source SINQ at the Paul Scherrer Institut at Villigen PSI in Switzerland, and work at PSI was partly funded by the Swiss National Science Foundation grant “Quantum Frustration”.

Supplementary Information

In Ref. 25 it was suggested that Tb$_2$Ti$_2$O$_7$ samples are of variable quality, having only the approximate stoichiometry Tb$_{2+x}$Ti$_{2-x}$O$_y$, and that different properties vis-a-vis the spin liquid state or magnetic order result. A similar conclusion about samples of Yb$_2$Ti$_2$O$_7$ was drawn in Ref. 39. Because of the recently highlighted sample dependence we present some further characterizations of our sample by synchrotron powder x-ray diffraction and heat capacity measurements, and also refer briefly to a single crystal neutron diffraction experiment. We suggest that the results will provide a guide as to which Tb$_2$Ti$_2$O$_7$ samples would be expected to show a MEM and associated magnetoelastic spin liquid, as compared to the ordered groundstate found in Ref. 25. The following information contains: i: Background; ii: Sample details; iii: Heat capacity measurements; iv: X-ray diffraction measurements; v: Discussion and Summary.

i: Background. Long-ranged magnetic order, and/or a splitting of the groundstate doublet into two singlets are highly plausible in Tb$_2$Ti$_2$O$_7$, but have only been observed in certain powder samples, depending on very fine control of the stoichiometry. 25. In that work, a well-developed peak appears in the heat capacity at $T \sim 0.5$ K, and inelastic neutron scattering clearly shows a new crystal field excitation at 0.1 meV. In other works, the sample (which may be a powder or a crystal) shows a poorly developed peak in the heat capacity, or no peak at all 40,47. Furthermore, there are variable reports of spin freezing at $T \sim 0.4$ K observed by ac-susceptibility, $\mu$SR or neutron spin echo measurements 9. In Ref. 25, it was suggested that Tb$_2$Ti$_2$O$_7$ samples are of variable quality, having only the approximate stoichiometry Tb$_{2+x}$Ti$_{2-x}$O$_y$. A spin liquid state was attributed to samples with $x < x_c = -0.0025$, and long range order was found for larger values of $x$.

Despite this sample dependence, all neutron scattering studies of Tb$_2$Ti$_2$O$_7$ in the literature which use large single crystals are in agreement where different studies and spectrometers can be compared. Apart from resolution effects, energy cuts through the quasielastic scattering of single crystals appear identical in Refs. 24, 30, and our high resolution data is also closely comparable. Intensity maps of the quasielastic scattering in Ref. 24 are identical to similar cuts through our high resolution data at casual levels of comparison. Diffuse scattering at high temperature 28 and low temperature 24, 29, 30, appears identical to that which we have measured in our previous work 17, when the use of polarization analysis is taken into account. The form of the first crystal field excitation along $(0,0,1)$ reported by Rule et al. 29 and again by Gaulin et al. 48 also appears identical to that measured in our sample.

We therefore suppose that the magnetoelastic spin liquid behaviour we have described is a generic property of “normal” samples of Tb$_2$Ti$_2$O$_7$ (i.e. those which have previously been described as spin liquids). We suggest that the results presented below will provide a guide as to which Tb$_2$Ti$_2$O$_7$ samples would be expected to show a MEM and associated magnetoelastic spin liquid, as compared to the ordered groundstate found in Ref. 25.

ii: Sample details. Our sample is a large single crystal ($\sim 7$ g) grown by the floating zone method. Post-growth, the crystal was mainly dark red in colour, with some black regions. Annealing under argon converted the crystal completely to the dark red colour. We cut small pieces from one end of the crystal and used them for specific heat, synchrotron powder x-ray diffraction and single crystal neutron diffraction experiments. Although these pieces do not come from the very heart of the boule, they do come from the same part which we use for our neutron scattering experiments. Furthermore, although we are using very small pieces to characterize a large crystal, experiments on the full crystal volume (for example our time of flight spectroscopy, or the neutron Laue diffraction used for alignment of the sample) do not reveal any multiple Bragg peaks which could be suggestive of serious inhomogeneity.

iii: Heat Capacity. The specific heat of a small piece of the crystal was measured between 0.35 K and 50 K with a Quantum Design Physical Properties Measurement System (PPMS), equipped with a $^3$He option, using a heating-relaxation method. An addenda measurement was made to evaluate the background of Apiezon Grease N and this contribution was subtracted from the data. The heat capacity of our sample, reported in Supporting Fig. 1 most closely resembles that of Refs. 44 or 46. In particular, no sharp features are present in the low temperature regime, below 0.5 K, and there is no sign of a phase transition associated with the onset of the magnetoelastic coupling at $T \sim 30$ K. Different pyrochlores present different lattice contributions, making an accurate subtraction difficult to evaluate at relatively high temperature, above 10 K, which would be needed to properly estimate the presence of a tail in the magnetic specific heat extending above 10 K. Nevertheless, there is no sign of a
phase transition associated with the onset of the magnetoelastic coupling, nor at low temperature, supporting our suggestion that the magnetoelastic spin liquid develops without global symmetry breaking, and is stable at all temperatures below $T \sim 20$ K in normal samples of Tb$_2$Ti$_2$O$_7$.

$iv$: Powder X-ray diffraction. Two tiny fragments from the crystal were ground in an agate pestle and mortar, then mixed with an approximately equal volume of silicon powder and ground together to obtain a uniform powder. This mixture was loaded into a 0.3 mm glass capillary. The silicon serves primarily to disperse the Tb$_2$Ti$_2$O$_7$ in the beam, while minimizing absorption, but also provides a convenient calibrant for wavelength and lattice parameters ($a_{Si} = 5.431194$ Å, NIST powder diffraction standard 640c). We measured the diffraction pattern of the mixture at room temperature, using the high resolution powder diffractometer of the Materials Science Beamline at the Swiss Light Source. The diffractometer operates in Debye-Scherrer geometry, using a Mythen microstrip detector and capillary spinner. The incident wavelength was 0.620474(3) Å (i.e. 19.98 keV) with the 2θ range extending from 2° to 120°. Discernible peaks were visible to the highest scattering angles, and accounting for typical peak widths, there are around 270 effectively independent reflections (i.e. separated by 1.0 × FWHM).

The work of Ross et. al. on Yb$_2$Ti$_2$O$_7$ suggests that rare earth pyrochlore crystals may be susceptible to small levels of disorder, in which some titanium ions are lost and are replaced during crystal growth by rare earth ions, and that this may be diagnosed by accurate measurements of the lattice parameter \[39\]. In the work of Taniguchi et al. \[25\], small variations of Tb$_2$Ti$_2$O$_7$ of the type Tb$_{2+\epsilon}$Ti$_{2-\epsilon}$O$_6$ were studied, and the dependence of the lattice parameter on $x$ was reported. From our x-ray diffraction measurements and the profile refinements discussed below, we find that the lattice parameter of our sample is 10.1544 Å, which implies a stoichiometry of Tb$_{2.013}$Ti$_{1.987}$O$_{6.99}$. When compared to the reported lattice parameter trend. In Ref. \[25\] it is reported that $x$ may vary by ±0.002 from the nominal value, which forms the main limitation for our determination of $x$ in this way. Literature values of the lattice parameter of Tb$_2$Ti$_2$O$_7$ are clustered around 10.154 Å, but outlying values do exist and could cast doubt on this assignment of composition \[30\]–\[33\].

The powder diffraction data were modeled and fitted using the Rietveld method, as implemented in the package FullProf \[54\]. Preliminary refinements were performed in which the absorption coefficient was estimated from the quantitative phase analysis and updated between cycles of refinement of all other parameters, until the phase proportions were stable. The data were subsequently corrected for absorption by the sample and capillary, and the background contribution from an empty capillary was subtracted. These corrected data were used for the final refinements.

Using the Le Bail, a structureless profile match was performed. The profile matching showed that the shape of the Bragg peaks due to the silicon is well modeled by a pseudo-Voigt form, but that the Bragg peaks of Tb$_2$Ti$_2$O$_7$ are best described by a pure Lorentzian. Asymmetry effects are only important for $2\theta < 11.5^\circ$, and were refined independently for the two phases. Subsequently we used a conventional Rietveld refinement of a crystallographic model incorporating two phases (i.e. Tb$_2$Ti$_2$O$_7$ and silicon). In general, we refined two capillary offset corrections, linearly interpolated background, profile parameters, and thermal parameters for both phases. We found that anisotropic thermal parameters lead to some, or all, thermal ellipsoids becoming non-positive definite, and no marked increase in fit quality, so we retained isotropic thermal parameters throughout. For Tb$_2$Ti$_2$O$_7$, we also refined the free positional parameter of the 48/4 oxygen site, and the lattice parameter. The lattice parameter of silicon was held fixed; the wavelength and zero-shift of 2θ were derived from an independent refinement of the silicon standard; and the asymmetry parameters from the profile matching were used. All models were then refined freely to convergence.

We have compared a model of stoichiometric Tb$_2$Ti$_2$O$_7$ (model I) with one with refinable occupancy of the 16d sites, Tb$_2$Ti$_{2-x}$O$_6$O$_{6-x/2}$ (with oxygen loss only from the 48f sites) (model II). The atom positions are summarized in Table I. We found that the we do not have sufficient sensitivity to the defect population to provide any improvement on the estimate derived from the lattice parameter. We illustrate the refinements in Supporting Fig. 2 and summarize the refinements in Table II.

We also investigated the crystal structure by single crystal neutron diffraction, which may have enhanced contrast for lighter elements, and also allowed us to compare the structure at room temperature, and in the magnetoelastic regime. We used the TRICS diffractometer at the PSI, and a small sample of size 3 × 3 × 0.5 mm cut from the main crystal. We found that our refinements were dominated by extinction corrections, and that models with small levels of defects consistent with the (x-ray) lattice parameter could not be distinguished statistically from the stoichiometric model. We also found that the cubic symmetry is unmodified between room temperature and 5 K, so no structural change accompanies the onset of the magnetoelastic spin liquid at $T \sim 20$ K. The periodicity of the excitations measured at low temperatures further suggests that no distortion occurs between 5 K and 0.05 K.

$iv$: Discussion and Summary. By virtue of the lattice parameter determination, our powder x-ray diffraction measurements suggest that there is a degree of replacement of Ti$^{4+}$ by Ti$^{3+}$ at the level of 0.7 ± 0.1 %, or Tb$_{2.013}$O$_{6.992}$Ti$_{1.987}$. Neither our x-ray
or neutron diffraction measurements are able distinguish the defect level more precisely in a crystallographic structure refinement, but are also consistent with this level of defects. The defect population is lower than that found by Ross et al. when comparing stoichiometric powders and crystals of Yb$_2$Ti$_2$O$_7$ (2.3%) [39]. It is just outside the window of compositions studied by Taniguchi et al. [25], and they do not report heat capacity measurements for $x > 0.005$, concluding instead that the spin liquid occurs only for $x < x_c$ and long range order occurs for all $x > x_c$ ($x_c = -0.0025$). This picture is not completely compatible with this work, which suggests that the spin liquid typically studied in Tb$_2$Ti$_2$O$_7$ single crystals by neutron scattering is a property of “lightly stuffed” samples with additional rare earth ions. The study of ultrapure powders does not extend far to the “stuffed” side of ideality, even to where our sample lies, so we suggest that there is a narrow dome of stability for the ordered phase observed in Ref. [25], with disordered phases on either side. It would be very interesting to establish if the disordered phases are the same. We expect that the MEM detailed here will exist in all other normal single crystal samples so far studied, and that they are to be found on the “lightly stuffed” side of the ideal stoichiometry. Comparisons of crystallographic data at room temperature and 5 K, specific heat data in the range 0.35-50 K, and the periodicity of the excitations at 0.05 K show no evidence of a structural phase transition throughout the temperature range we study.

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**Supplementary Information Fig. 1.** Heat capacity of the Tb$_2$Ti$_2$O$_7$ single crystal. Throughout the full measured temperature range there is no sharp feature associated with a phase transition (a, compared to Y$_2$Ti$_2$O$_7$). In particular, the low temperature part of the specific heat (b) of our Tb$_2$Ti$_2$O$_7$ sample shows no clear upturn or any development of the peak which is associated with magnetic ordering in certain Tb$_{2+x}$Ti$_{2-x}$O$_y$ samples [25].

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*[tom.fennell@psi.ch] Began this work at Institut Laue Langevin, BP 156, 6, rue Jules Horowitz, 38042, Grenoble Cedex 9, France
† Now at Air Products and Chemicals Inc., Allentown PA 18195 USA

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Supplementary Information Fig. 2. Refinement of models I and II against powder x-ray diffraction data. The similarity in quality of the crystallographic refinements and Lebail extraction implies that the fit cannot be significantly improved.

| Atom | Wykoff Position | x    | y    | z    | Ideal Occupancy |
|------|-----------------|------|------|------|-----------------|
| Tb   | 16c             | 0    | 0    | 0    | 0.08333         |
| Ti   | 16d             | 0.5  | 0.5  | 0.5  | 0.08333         |
| O    | 48f             | x    | 0.125| 0.125| 0.25000         |
| O    | 8a              | 0.125| 0.125| 0.125| 0.04167         |

**TABLE I.** Atom positions of the spacegroup Fd\(\overline{3}m\) used in the structural refinements. These correspond to the second origin setting given in the International Tables of Crystallography. Nominally \(x = 0.42\), and occupancies are normalized to multiplicity of a general site (192).

| Model | \(R_p\) (%) | \(R_{wp}\) (%) | \(R_{exp}\) (%) | \(\chi^2\) | \(a\) |
|-------|-------------|----------------|-----------------|-----------|-------|
| I     | 6.54        | 9.26           | 5.26            | 3.1       | 10.15529(1) |
| II    | 6.6         | 9.18           | 5.26            | 3.05      | 10.15529(1) |

| Atom  | x    | y    | z    | \(B_{iso}\) | Occupancy |
|-------|------|------|------|--------------|-----------|
| Tb    | 0    | 0    | 0    | 0.700(3)     | 0.08333   |
| Ti    | 0.5  | 0.5  | 0.5  | 0.568(7)     | 0.08333   |
| O\(_{48f}\) | 0.42203(20) | 0.125 | 0.125 | 0.850(41) | 0.25 |
| O\(_{8a}\) | 0.125 | 0.125 | 0.125 | 1.076(76) | 0.04167 |

| Model | \(R_p\) (%) | \(R_{wp}\) (%) | \(R_{exp}\) (%) | \(\chi^2\) | \(a\) |
|-------|-------------|----------------|-----------------|-----------|-------|
| I     | 6.54        | 9.18           | 5.26            | 3.05      | 10.15529(1) |
| II    | 6.6         | 9.18           | 5.26            | 3.05      | 10.15529(1) |

| Atom  | x    | y    | z    | \(B_{iso}\) | Occupancy |
|-------|------|------|------|--------------|-----------|
| Tb    | 0    | 0    | 0    | 0.685(3)     | 0.08333   |
| Ti    | 0.5  | 0.5  | 0.5  | 0.731(10)    | 0.081(0)  |
| Tb    | 0.5  | 0.5  | 0.5  | 0.731(10)    | 0.002(0)  |
| O\(_{48f}\) | 0.42129(20) | 0.125 | 0.125 | 0.757(40) | 0.249(0) |
| O\(_{8a}\) | 0.125 | 0.125 | 0.125 | 1.132(77) | 0.04167 |

**TABLE II.** Parameters for models I and II when refined against the powder x-ray diffraction data.
