Sample independence of magnetoelastic excitations in the rare earth pyrochlore \( \text{Tb}_2\text{Ti}_2\text{O}_7 \)

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Recent experimental results have emphasized two aspects of \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) which have not been taken into account in previous attempts to construct theories of \( \text{Tb}_2\text{Ti}_2\text{O}_7 \): the role of small levels of structural disorder, which appears to control the formation of a long-range ordered state of as yet unknown nature; and the importance of strong coupling between spin and lattice degrees of freedom, which results in the hybridization of crystal field excitons and transverse acoustic phonons. In this work we examine the juncture of these two phenomena and show that samples with strongly contrasting behavior vis-a-vis the structural disorder (i.e. with and without the transition to the ordered state), develop identical magnetoelastic coupling. We also show that the comparison between single crystal and powder samples is more complicated than previously thought - the correlation between lattice parameter (as a measure of superstoichiometric \( \text{Tb}^{3+} \)) and the existence of a specific heat peak, as observed in powder samples, does not hold for single crystals.

I. INTRODUCTION

The rare earth pyrochlor\(\text{es}^{11} R_2\text{Ti}_2\text{O}_7 \) \( R = \text{Gd-Yb} \) are well known as model systems for the study of frustrated magnetism\(\text{s}^{12} \). Although \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) has been studied as long and intensively as other members of the series such as the spin ices \( \text{ Dy}_2\text{Ti}_2\text{O}_7 \) and \( \text{ Ho}_2\text{Ti}_2\text{O}_7 \), it remains a much less tractable mystery. The low temperature state of \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) was originally thought to have only very short-range correlations amongst its spins\(\text{s}^{13} \), which themselves continued to fluctuate down to the lowest temperatures measured\(\text{s}^{13} \), often leading to the designation of \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) as a spin liquid. Theories of \( \text{Tb}_2\text{Ti}_2\text{O}_7 \), which have aimed to explain the existence and properties of this state face a three-pronged problem: how does ostensibly unfrustrated \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) evade long-range magnetic order; why is there no cooperative Jahn-Teller transition, despite a non-Kramers doublet ground state; and does the state support any interesting emergent phenomena?

Much theoretical progress has been made on the subject of spin liquids\(\text{s}^{14-16} \), in particular in the area of quantum spin ices\(\text{s}^{17-19} \). The idea that \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) is closely related to spin ices, with an additional quantum ingredient, is a long-running thread in the study of \( \text{Tb}_2\text{Ti}_2\text{O}_7 \)\(\text{s}^{20-22} \) and is a good reason for continued interest in it, particularly given recent progress in the development of generalized Hamiltonians for rare earth pyrochlo\(\text{res}^{23,24,27} \). However, there is currently no theoretical consensus on the low temperature state of \( \text{Tb}_2\text{Ti}_2\text{O}_7 \)\(\text{s}^{21,22,29} \), and indeed it may not be possible to form one while certain experimental issues remain unresolved.

\( \text{Tb}_2\text{Ti}_2\text{O}_7 \) is known to have antiferromagnetic inter-
actions \( \theta_{\text{CW}} \approx -13 \text{ K} \), and a non-Kramers doublet ground state which produces an Ising-like moment that points “in” or “out” of the tetrahedra. This is the first aspect of the \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) puzzle - with antiferromagnetic coupling, such moments should order in the unfrustrated “all-in-all-out” state. Although the crystal field scheme has been investigated several times, the exact composition of the doublet is still discussed\(\text{s}^{30-32} \). A static distortion resulting in a single-ion singlet ground-state\(\text{s}^{33-35} \), the second possibility in the puzzle, has never been accepted since the ground state apparently does retain a permanent magnetic moment on the terbium ions and no departure from cubic symmetry can be detected\(\text{s}^{36-38} \). The original picture of very short-range spin correlation\(\text{s}^{39} \), spin fluctuations on the timescale of probes such as \( \mu\text{SR} \)\(\text{s}^{40-42} \), neutron spin echo and susceptibility\(\text{s}^{43,44} \), and a large quasielastic contribution to the neutron scattering\(\text{s}^{45-47} \) has given way to a Coulomb phase with power-law correlation\(\text{s}^{48} \) and propagating excitations\(\text{s}^{49} \), and/or a mesoscopically ordered spin ice state\(\text{s}^{50-52} \). The evolution and dynamics of this state are rather unclear. The spin correlations of the spin liquid phase begin to build up below \( T \sim 40 \text{ K} \) and at first are isotropic and short-range\(\text{s}^{53} \), becoming anisotropic and complex by \( T = 1.7 \text{ K} \). An enhancement of the mesoscopic spin ice correlations has been observed below 0.275 K\(\text{s}^{54} \) by neutron scattering, but other freezing transitions have also been found at temperatures of 0.1 K\(\text{s}^{55} \), 0.15 K\(\text{s}^{56} \), 0.2 K\(\text{s}^{57} \), and 0.35 K\(\text{s}^{58} \) by techniques including ac-susceptibility and \( \mu\text{SR} \). Similarly, the presence or absence of a magnetization plateau with field applied along [111], a feature whose existence\(\text{s}^{59,60} \) or ab-
ence\cite{25} could vindicate certain theories of $\text{Tb}_2\text{Ti}_2\text{O}_7$, has been debated\cite{25,62,60}.

These last two points concerning the low temperature state, particularly the various temperatures for freezing transitions, suggest there is sample dependence in $\text{Tb}_2\text{Ti}_2\text{O}_7$. In fact, this is most pronounced as the presence (absence) of a specific heat peak\cite{25,62,60,63} which is thought to be due to a transition to a long range ordered state of unknown character at $T \approx 0.5$ K. The sample dependence in $\text{Tb}_2\text{Ti}_2\text{O}_7$ is sometimes suggested to be due to differences between single crystal and powder samples, with the former being variable and the latter reproducible\cite{62}.

A similar situation exists in $\text{Yb}_2\text{Ti}_2\text{O}_7$, in which powder samples have extremely sharp heat capacity anomalies, while crystals have at best weak and broad anomalies\cite{64,65}. This difference was suggested to be due to “light stuffing” of rare earth ions (i.e. substitution of $\text{Yb}^{3+}$ at the $\text{Ti}^{4+}$ site to give a stoichiometry like $\text{Yb}_{2+x}\text{Ti}_{2-x}\text{O}_y$) due to the evaporation of a small amount of titanium during the growth of a single crystal from nominally stoichiometric powders\cite{64}. This process is attributed to the high temperatures used during crystal growth, and can only produce an excess of rare earth ions, since titanium is preferentially evaporated. Because lower temperatures are employed during powder synthesis, the evaporation of titanium is not thought to be a problem, so that the stoichiometry of the starting materials is preserved, and either rare earth-depleted or rare earth-rich (stuffed) powder samples can be produced. The role of this effect in $\text{Tb}_2\text{Ti}_2\text{O}_7$ was studied by synthesizing powder samples of $\text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{y-y'}$, and a strong effect was indeed observed as a function of $x$\cite{62}; the heat capacity peak was absent for small negative values, and suddenly appears around $x = -0.005$. For larger $x$, including $x \approx 0$, a strong heat capacity peak occurs at $T \approx 0.5$ K. It is accompanied by a very clear splitting of the quasielastic scattering into a new sharp mode at 0.1 meV, and a small, presumably magnetic, Bragg peak at $k = (1/2, 1/2, 1/2)$. Further studies show that the mesoscopic correlations are present in all samples, but the resolution limited Bragg peak only occurs in association with the heat capacity peak\cite{62}.

Interestingly, the small size of the Bragg peak shows it cannot be due to the ordering of the full moment of the $\text{Tb}^{3+}$ ground state doublet, so the nature of the order parameter remains unknown. Recently it has been suggested to be due to a quadrupolar transition\cite{66,67}, but since the long range order associated with the heat capacity anomaly has so far not been directly determined, we will refer to it as a “hidden order” throughout the rest of the paper.

There is also (at least) one more important factor in the physics of $\text{Tb}_2\text{Ti}_2\text{O}_7$ which must be understood - the lattice. It is well known that there is a strong spin lattice coupling in $\text{Tb}_2\text{Ti}_2\text{O}_7$, as manifested in elastic constant\cite{11}, dielectric constant\cite{70}, anisotropic strain\cite{11}, thermal conductivity\cite{71} and thermal Hall effect\cite{72} which all become anomalous exactly at the onset of the spin liquid regime at $10 < T < 40$ K. Pressure induced magnetic order\cite{23} and field induced lattice modification\cite{23} also indicate the coupling. Most recently, the interaction was shown to give rise to hybridization between crystal field excitons and transverse acoustic phonons, forming a so-called magnetoelastic mode (MEM), suggesting that pure spin models cannot capture the physics of $\text{Tb}_2\text{Ti}_2\text{O}_7$, since the basic degrees of freedom of $\text{Tb}_2\text{Ti}_2\text{O}_7$ would not be accurately incorporated\cite{49,63}. The fate of the magnetoelastic coupling at the ordering transition is not known, though such a coupling can be very important in quadrupolar systems.

In our previous study of the MEM, we used a single crystal with no heat capacity peak, implying a level of defects sufficient to destroy the hidden order state. In the garnet $\text{Tb}_3\text{Ga}_5\text{O}_{12}$ (TGG), which also supports a thermal Hall effect\cite{73}, superstoichiometric terbium ions have recently been advanced as a source of magnetic phonon scattering underlying the effect\cite{22}, and one might therefore ask if the spin-phonon interaction we observed in $\text{Tb}_2\text{Ti}_2\text{O}_7$ is actually due to disorder. In this work, we compare crystals with (without) the specific heat anomaly, implying, by the logic of Ref.\cite{62} the absence (presence) of structural disorder, and show that in the range $1.5 < T < 50$ K all the crystals develop the same magnetoelastic excitation spectrum. Although we suggest that the various low temperature behaviors of $\text{Tb}_2\text{Ti}_2\text{O}_7$ all emerge from the same microscopic degrees of freedom, which are formed by the magnetoelastic hybridization, we do not directly investigate their behavior at low temperature in this work. We also find that the comparison of the single crystal sample compositions with the study of the composition dependent properties\cite{62} is not as simple as we expected, suggesting that other structural effects may be involved in controlling the ordering transition.

II. EXPERIMENTAL METHODS

A. Crystal growth

We discuss three different single crystals. Sample MH1 is our original sample, grown at Princeton and discussed in Refs.\cite{15} and \cite{63}. Samples EP2 and EP3 were grown at PSI, and have not previously been reported.

As grown $\text{Tb}_2\text{Ti}_2\text{O}_7$ crystals contain dark/black regions, and annealing of $\text{Tb}_2\text{Ti}_2\text{O}_7$ crystals under oxygen converts them to a state which is uniform black/dark in color. This is thought to be due to the formation of $\text{Ti}^{4+}$ defects, as in $\text{Pr}_2\text{Zr}_2\text{O}_7$ where transparent green crystals are thought to be ideal and brown/black crystals to be contaminated with $\text{Pr}^{4+}$ Annaling under argon converts both as-grown or oxygen annealed $\text{Tb}_2\text{Ti}_2\text{O}_7$ crystals to a uniform transparent reddish-orange. This may be contrasted with pyrochlores such as $\text{Ho}_2\text{Ti}_2\text{O}_7$ or $\text{Dy}_2\text{Ti}_2\text{O}_7$, where annealing under oxygen is used to produce transparent crystals of characteristic color.\cite{72}
The exact conditions of growth for sample MH1 are not known, but prior to neutron scattering experiments it was annealed under flowing argon to eliminate dark patches and produce a large reddish-orange boule. For the growth of sample EP2 and EP3, polycrystalline Tb$_2$Ti$_2$O$_7$ was prepared by a solid state reaction. Starting materials of Tb$_4$O$_7$ and TiO$_2$ with 99.99% purity were mixed and ground, followed by heat treatment at 900 – 1150 °C in air, for at least 100 hours with several intermediate grindings. The phase purity of the resulting powder was confirmed using a conventional laboratory powder x-ray diffractometer. This material was hydrostatically pressed in the form of rods of 7 mm diameter and ≈ 60 mm length. The rods were subsequently sintered at 1150 °C for 15 hours. The crystal growth was carried out using an optical floating zone furnace (FZ-T-10000-H-IV-VP-PC, Crystal System Corp., Japan) with four 1000 W halogen lamps as a heat source. The growth rate was 10 mm hr$^{-1}$, with both rods (feed and seed rod) rotated at 25 rpm in opposite directions to ensure homogeneity of the melt. During growth, 2.5 bar pressure of argon-oxygen mixture (50:50) was applied. The obtained crystals were post-annealed for 48 hours at 1150 °C in argon.

B. Heat capacity

The specific heat of small pieces of each 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 heat-relaxation method. An addenda measurement was made to evaluate the background of Apiezon Grease N and this contribution was subtracted from the data. Differing lattice contributions in different pyrochlores make an accurate estimation of magnetic contributions to the specific heat above T $\sim$ 10 K difficult to evaluate.

C. Neutron scattering

The neutron scattering experiments performed on sample MH1 to investigate the magnetoelastic mode were described in Ref. 63 and involved both time of flight and triple axis spectroscopy. We also report some new measurements in which the crystal, held in a copper clamp holder, was mounted in a dilution refrigerator and cryomagnet. To confirm the existence, dispersion and temperature dependence of the magnetoelastic mode in samples EP2 and EP3 we used the thermal neutron triple axis spectrometer EIGER at SINQ, PSI. The crystals, which were aligned such that the scattering plane contains wavevectors of type $(h, h, l)$, were mounted on aluminium holders in a standard helium cryostat. We used a PG002 monochromator, analyzer and filter, and operated EIGER with fixed $E_f = 14.68$ meV (i.e. $k_f = 2.662$ Å$^{-1}$). The magnetoelastic mode can be readily located by constant energy scans in the otherwise featureless part of the spectrum between the intense first and second crystal field excitations (i.e. at energies of 4 - 7 meV), and in constant wavevector scans at positions such as (1.5, 1.5, 0).

D. X-ray diffraction

Fragments from each crystal were mixed with silicon powder and ground together in an agate pestle and mortar to obtain uniform powders. These mixtures were loaded into 0.3 mm glass capillaries. 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 at 22.5 °C, NIST powder diffraction standard 640c). We measured the diffraction pattern of the mixture using the high resolution powder diffractometer of the Materials Science Beamline at the Swiss Light Source (SLS). The diffractometer operates in Debye-Scherrer geometry, using a Mythen microstrip detector, capillary spinner, and 2θ range extending from 2° to 120°. Sample MH1 was measured in a previous experiment in which the incident wavelength was $\lambda = 0.620474(3)$ Å (i.e. $E = 19.98$ keV), and sample EP2 and EP3 were measured in a second experiment using a wavelength of $\lambda = 0.4959$ Å (i.e. $E = 25$ keV). All measurements were made at room temperature, which is maintained constantly at 24 deg C at the SLS. The powder diffraction data were modeled and fitted using the Rietveld method, as implemented in the package FullProf.$^{22}$

Details of the refinements for sample MH1 were presented in Ref. 63. Notably, we found that while the shape of the Bragg peaks due to the silicon was well modeled by a pseudo-Voigt form, as expected for this diffractometer, the Bragg peaks of Tb$_2$Ti$_2$O$_7$ were best described by a pure Lorentzian. This effect is somewhat less pronounced with a shorter wavelength, but nonetheless, a pure Lorentzian lineshape gives the best description for the Tb$_2$Ti$_2$O$_7$ samples (the difference being that the FWHM of the pseudo-Voigt becomes negative in certain angular ranges, while for the Lorentzian it does not). 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 linearly interpolated background, profile parameters, and isotropic thermal parameters for both phases. For Tb$_2$Ti$_2$O$_7$, we also refined the free positional parameter of the 48f oxygen site, and the lattice parameter. The lattice parameter of the silicon standard (defined at 22.5 deg C) was corrected for thermal expansion at the temperature of the experimental hutch (24 deg C) and then held fixed, while the wavelength and zero-shift of 2θ were refined. Asymmetry corrections were applied up to 2θ = 25° and refined, but capillary offset parameters could not be stably refined. All models were refined freely to convergence.
We can therefore conveniently investigate their existence without recourse to low temperature sample environment equipment. In Fig. 2A we show constant energy scans along the \((h, h, 0)\) direction at \((2, 2, 0)\) with an energy transfer of 5 meV, at 1.5 K. We see that in all three crystals, a steeply dispersing, longitudinal excitation exists (i.e. as we scan along \((h, h, 0)\) we cut through the dispersion surface twice, resulting in a double peak). That the dispersion is the same in all the samples is confirmed in Fig. 2B, where we show the full structure of the excitation spectrum as it was presented in Ref. 63 along with a limited number of points obtained from various scans through the excitations of the new samples. We can also follow the temperature dependence of the hybrid modes, and show in Fig. 3 that the three samples are essentially identical in this respect. The comparison of heat capacity and neutron scattering experiments shows directly that the hybrid modes are robust against the sample dependence which affects the low temperature state.

Given the strong connection between stoichiometry and form of heat capacity advanced in the work of Taniguchi et al.\(^{62}\) and the expectation that the stoichiometry of a pyrochlore can be diagnosed by accurate lattice parameter measurements,\(^{62–64}\) we use the lattice parameters obtained from the x-ray diffraction in this way. In Ref. 63 we used the \(x\)-dependence of the lattice parameter of \(\text{Tb}_{2+ \delta} \text{Ti}_{2- \gamma} \text{O}_7\) reported in Ref. 62 to establish the stoichiometry of sample MH1 (\(\text{Tb}_{2.013} \text{Ti}_{1.987} \text{O}_{6.99}\)). Following a correction of the lattice parameter calibration\(^{63}\) and correction for thermal expansion of the silicon standard, we now find that samples MH1 \((a = 10.15533(1) \ \text{Å})\) is \(\text{Tb}_{2.02} \text{Ti}_{1.98} \text{O}_{6.99}\), sample EP2 \((a = 10.15782(1) \ \text{Å})\) is \(\text{Tb}_{2.04} \text{Ti}_{1.96} \text{O}_{6.98}\), and sample EP3 \((a = 10.14873(1) \ \text{Å})\) is \(\text{Tb}_{1.97} \text{Ti}_{2.03} \text{O}_{7.03}\). The MEM also exists in the data presented in Ref. 49 where the lattice parameter is reported to be \(a = 10.1528(5) \ \text{Å}\), suggesting a composition of essentially \(\text{Tb}_{2} \text{Ti}_{2} \text{O}_7\) (i.e. \(x = 0.0004\)). Fig. 4 shows the extrapolated lattice parameter trend of Ref. 50 and indicates how these samples fall on it. A new lattice parameter trend was recently reported, which we also show, and by comparison with this our samples would have composition \(\text{Tb}_{2.029} \text{Ti}_{1.971} \text{O}_{5.986}\) (MH1), \(\text{Tb}_{2.051} \text{Ti}_{1.946} \text{O}_{6.973}\) (EP2), and \(\text{Tb}_{1.963} \text{Ti}_{2.037} \text{O}_{7.019}\) (EP3) respectively. The lattice parameters of the nominally stoichiometric powder used for the crystal growth of samples EP2 and EP3, as well as a separate powder sample prepared by the same method, are clustered in the range \(a = 10.1525(4)\). Although not shown on Fig. 3, they all fall at \(x \approx 0\).

Fig. 4 also shows the window of compositions investigated in Ref. 62 and the proposed phase diagram of the hidden order. We see that there appears to be considerable variation in the lattice parameter of nominally stoichiometric single crystals, far outside the window investigated in powder samples. Furthermore, the sample which shows the heat capacity anomaly (EP3) does not fall within the window of stoichiometry expected by comparison with the powder samples (either in terms of lat-

III. RESULTS

The heat capacities of the three samples are identical down to 4 K, as shown in Figs. 1A and 1B. At temperatures in the range \(10 < T < 40 \ \text{K}\) where the magnetoelastic coupling develops, the heat capacities show that there is no sign of any symmetry breaking phase transition associated with the coupling. At low temperatures, below 2 K, sample MH1 and EP2 exhibit the very broad peak at \(T \approx 1 \ \text{K}\) which is typically attributed to the formation of the so-called spin liquid state in \(\text{Tb}_{2} \text{Ti}_{2} \text{O}_7\). Sample EP3 shows a more pronounced dip in the heat capacity at \(T \approx 2 \ \text{K}\), and the broad peak which appears below this suddenly gives way to a very sharp peak in the heat capacity at \(T \approx 0.46 \ \text{K}\). This sharp feature is very similar to those observed in powder samples of \(\text{Tb}_{2+ \delta} \text{Ti}_{2- \gamma} \text{O}_7\) with \(0 < x < 0.005\) where the temperature, sharpness and height of the peak are maximum for \(x = 0.005\). By comparison, the height of the peak in sample EP3 suggests \(0.0025 < x < 0.005\).

On cooling, the hybrid excitations develop in the temperature range \(10 < T < 40 \ \text{K}\), and then remain essentially unchanged to temperatures as low as 0.05 K.\(^{63}\)
FIG. 2. Existence and dispersion of MEMs in three crystals of Tb$_2$Ti$_2$O$_7$. The mode is found in all the crystals using longitudinal constant energy scans along the (h, h, 0) axis at (2, 2, 0) with energy transfer $E = 5$ meV (panel A). Constant energy scans ($E = 5$, 7 meV) and constant wavevector ($\zeta = -0.5$) show that the dispersion relation of the MEM is the same in all three crystals (panel B). (Data for MH1 shows the full structure of the excitation spectrum, including the MEM and first and second crystal field excitons, as already presented in Ref. 63, EP2 peak positions are reflected to positive $\zeta$ for clarity. The line in B is a guide to the eye for the dispersion relation of the form $\hbar \omega = a \sim |k| |\pi|$ for $0.7 < |k| < 0.7$ and $\hbar \omega = a$ for $0.7 < k < 1)$. $a = 8.25$ meV, the approximate zone boundary energy, and the crossover to a wavevector-independent section is due to the fact that at $\zeta = \pm 0.75$, the plotted dispersion relation runs along the Brillouin zone boundary.)

Another question related to the stoichiometry of the sample is the homogeneity. In Fig. 5 we compare the intensity of the MEM with the intensity of the second crystal field excitation (i.e. the mode at 10.2 meV in Fig. 2) in constant wavevector scans. We have measured such scans at (1, 1, 0, 1, 0, 0) in MH1 and EP2, and (1, 1, 5, 0) in EP2 and EP3. The measurements of MH1 were made at 0.07 K, while those of EP2 and EP3 were at 1.5 K, but it can be seen from Fig. 5 that the intensity of the MEM does not change below 10 K. In both cases, when the peaks from the crystal field excitation are scaled together, the MEM also scales. This result suggests that both excitations exist in the same volume fraction of all the crystals. The background scattering in these experiments seems to come mainly from the sample itself, so the almost identical signal to noise ratio seen in Fig. 2 is also to be expected in the case that the MEM exists throughout the sample. However, comparison with another signal originating uniquely from the sample, as

FIG. 3. Temperature dependence of magnetoelastic mode intensities in three crystals of Tb$_2$Ti$_2$O$_7$. (Intensities from different crystals are scaled to match at 5 K. The dashed line is $n_0 - n_1$ (scaled), where $n_0$ and $n_1$ are the thermal population factors of the ground and excited states, respectively, of a two-level system with $\Delta = 1.4$ meV.)

FIG. 4. Lattice parameter trends and stoichiometry estimates for various Tb$_2$Ti$_2$O$_7$ crystals. The measured lattice parameters are used to obtain the composition by comparison with lattice parameter trends 52–55, 62, 80. Although all the crystals are nominally stoichiometric ($x = 0$), their lattice parameters imply a considerable range of compositions, so the lattice parameter trends have been extrapolated as required. The MEM, which was originally reported in sample MH1 in Ref. 63 and is here reported in EP2 and EP3, is also clearly visible in the data of Ref. 62, measured using sample “CEA”. The vertical dashed lines indicate the window of stoichiometry studied in powders in Ref. 62 and the phase diagram for spin liquid (SL) and hidden order (HO) found in this window is also shown. The composition and temperature dependence of the heat capacity peaks observed in Ref. 62 are indicated by open (red) diamonds, and can be read from the bottom and right axes respectively.
determining the low temperature state of Tb actions advanced as the origin of certain magneto-phonon inter-

superstoichiometric terbium ions in TGG have been ad-

coupling is not a consequence of such disorder. Although

MEM also scales exactly.

We have observed that the magnetoelastic coupling

which results in the hybridization of crystal field exci-
tons and transverse acoustic phonons in Tb$_2$Ti$_2$O$_7$ is an

intrinsic feature, which does not depend on the sample -
crystals with and without the heat capacity anomaly

have the same magnetoelastic excitation spectrum. This

may not seem surprising, since the hybridization devel-
opds at a much higher temperature than the heat capac-
ity features attributed to the formation of the spin-liquid
state or transition to hidden order. However, these low-
temperature phenomena must derive from low-energy de-
grees of freedom which emerge in a state whose basic
structure always incorporates the magneotelastic coupl-
ing, and this is the first important aspect of our observ-
ings. Secondly, while the presence (absence) of a heat
capacity peak is associated with the absence (presence)
of structural disorder, we show that the magnetoelastic
coupling is not a consequence of such disorder. Although

superstoichiometric terbium ions in TGG have been ad-

vanced as the origin of certain magneto-phonon inter-
action, if structural disorder is indeed responsible for
determining the low temperature state of Tb$_2$Ti$_2$O$_7$ sam-

ples, it does not mediate the magnetoelastic coupling. It

will be very interesting to examine the fate of the magne-
toelastic excitations at the ordering transition in samples

such as EP3.

The remaining question is to understand the differ-
ence between samples MH1, EP2, and EP3. Our first

observation is that according to their lattice parameters,
one of our nominally stoichiometric samples lie within
the small compositional window around $x = 0$ where the
heat capacity peak is expected (though the the lattice
parameter reported in Ref. [9] places that sample within
the window).

Although all the crystals are nominally stoichiome-

tic, we see considerable variation amongst them, even

even between EP2 and EP3 which were grown by the same

method in the same laboratory (and whose lattice pa-
tameters were measured consecutively in the same x-

ray diffraction experiment, and which were synthesized

from powders verified to have lattice parameters agree-

ing within $1 \times 10^{-4}$). Other values of the lattice pa-

ter parameter of nominally stoichiometric Tb$_2$Ti$_2$O$_7$ crystals or

powders can be found in the literature clustered around

10.154 Å [13] and also some which actually lie outside

the range of Fig. 1 such as 10.12 Å [12] or 10.1694 Å [32].

At face value, this implies a surprisingly large range of

off-stoichiometry, even amongst powders where the evap-

oration of titanium during synthesis is not thought to be

problematic.

Our second surprising observation is that the lattice

parameter comparison implies a negative value of $x$ for

sample EP3, i.e. terbium depletion during growth. This

is not compatible with the light stuffing mechanism, which

depends on the evaporation of titanium during crystal

growth, so can only produce superstoichiometric rare

earth ions. Rare earth depletion during crystal growth is

not possible by this mechanism (as mentioned above,

rare earth depletion is only possible in a powder sample

by control of starting material stoichiometry and lower

synthesis temperatures). Because of the incompatibility

of rare earth depletion and stuffing during crystal

growth, factors other than this must be at play in or-
der to have “$x < 0$” in a single crystal, and the change of

lattice parameter between starting material and crystal

implies that they are associated with the growth pro-
cess. For example, oxygen deficient defect clusters have

recently been detected in Dy$_2$Ti$_2$O$_7$ [33] and, if present

in Tb$_2$Ti$_2$O$_7$ crystals in variable density, could perhaps

modify the lattice parameter differently to the stuffing.

It will be interesting to compare the microstructure of

crystals with and without the heat capacity anomaly.

Overall, we get the impression that determining sto-

ichiomtery of single crystals by comparison with pub-
lished lattice parameter trends is more complicated than

we had proposed in Ref. [33] which is now born out by

the existence of two different lattice parameter trends

in the literature [32,33]. Comparing lattice parameters

measured under different experimental conditions may

be more complicated than first suggested, requiring exact

specification of the temperature and accurate wavelength
calibration, which may not be possible retrospectively.

However, these effects are taken into account in the com-

parison of our crystals with the known lattice parameter

trends.

Very recently, a study was reported of a single crystal
in which regions with different concentration of defects (covering essentially the full phase diagram of Ref. [62]) could be identified by measuring the lattice parameter and specific heat of many small pieces cut along the length of the boule.[63]. It was suggested that large single crystals studied by neutron scattering may not be homogeneous. Although our heat capacity samples were cut from our crystals adjacent to the (much larger) pieces used for neutron scattering experiments, there exists the possibility that they are inhomogeneous.

We first note that the single crystal described in Ref. [53] has a strong color gradient from red-orange to transparent accompanying the concentration gradient, while our crystals are each uniformly colored. Secondly, in Fig. 5 we showed that the volume fraction of the crystal which supports the MEM is the same as that supporting the crystal field excitation. An oft-cited advantage of neutron scattering is its sensitivity to the full volume of large samples, and since the crystal field spectrum is a universal property of all Tb$_2$Ti$_2$O$_7$ samples,[33] we think it is justifiable to assume that the intensity of the crystal field excitation derives from the entire sample, and by virtue of its identical volume fraction, so does the MEM. The crystal field excitation betrays no sign of sample dependence or inhomogeneity: in all the samples it has the same energy, identical Voigt peak shape, and identical width (1.7±0.2 meV, close to the estimated resolution limit (1.3 – 1.5 meV) of the spectrometer). The MEM then is a property of Tb$_2$Ti$_2$O$_7$, robust to the levels of off-stoichiometry currently discussed.

More generally, we point out that single crystals studied by neutron scattering are highly similar, so far as data in the literature from different experiments can be compared. For example, although different studies have employed different energy resolution/integration, or different wavevector resolution/detail, or polarization analyses, the diffuse scattering measured in crystals or different wavevector resolution/detail, or polarization analysis and high resolution were employed to show that the quasielastic contribution contains a propagating mode.[19] other unpolarized studies measure the total, which again is quite comparable.[19][20] Sadly the heat capacities of all these samples have not been reported, and this makes it extremely interesting to pursue studies of samples explicitly shown to have the heat capacity anomaly, in order to establish the fate of all these features at the transition. Even if the true groundstate of pure Tb$_2$Ti$_2$O$_7$ is a quadrupolar ordered state, there remain the questions of how a strongly correlated but disordered phase survives in the dipole sector, and, given that the ordered phase is destroyed by very small levels of disorder, does it support any of the interesting types of effect which may appear when a manifold of frustrated groundstates is perturbed by small levels of disorder.[87,88]

V. CONCLUSION

We have shown that the contrasting types of low temperature ($T < 0.6$ K) states observed in different single crystals of Tb$_2$Ti$_2$O$_7$ - both hidden order and spin liquid - emerge from a higher temperature (1.5 < $T < 40$ K) state in which the same magnetoelastic excitation spectrum develops in all the samples. We have shown that the comparison between single crystal samples and powders implies that other structural effects in addition to stuffing of terbium at the titanium site may also be involved in controlling the lattice parameter and eventual ordering behavior of the sample.

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