Field induced ground states in Tb$_2$Ti$_2$O$_7$ spin liquid

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Abstract. We have studied the field induced magnetic structures ($H$//[110]) in Tb$_2$Ti$_2$O$_7$ in a wide temperature ($0.2<T<270$ K) and field ($0<H<7$ T) range, by combining polarized and unpolarized neutron diffraction in a single crystal. Below 2 K and above 2 T, two structures with $k=0$ and (0,0,1) propagation vectors are simultaneously observed. Their analysis yields a precise description of the field induced ground states. The $k=0$ structure with net magnetization shows spin-ice like local order, but with Tb moments of very different magnitudes. The $k=(0,0,1)$ AF-like structure is stabilized in a finite ($H,T$) range and attributed to magnetostriction.

1. Introduction

In pyrochlore spin ices R$_2$Ti$_2$O$_7$ (R=Dy, Ho), the spin ice degeneracy can be lifted by a magnetic field $H$, leading to original magnetic transitions which depend on the orientation of $H$ with respect to the local <111> anisotropy axes [1, 2, 3]. With $H$//[110], the lattice separates into $\alpha$ and $\beta$-chains [4, 5], having different angles between $H$ and the local Ising axes.

In Tb$_2$Ti$_2$O$_7$, the crystal field anisotropy [6, 7] is weaker than in model spin ices, and ferromagnetic (F) and antiferromagnetic (AF) first neighbor interactions nearly compensate. This leads to a rich variety of magnetic behaviors, from an unconventional spin liquid in zero field [8, 9] to antiferromagnetic order induced by pressure [10] and/or magnetic field [11, 12].

Up to now, the complex field induced magnetic structures were not thoroughly studied in Tb$_2$Ti$_2$O$_7$. We have combined high accuracy neutron diffraction experiments in a wide temperature ($0.2<T<270$ K) and field ($0<H<7$ T) range to investigate them in detail. The use of short wavelength neutrons allows us to measure many Bragg peaks (from 200 to 400) for each ($H,T$) set, and to solve the magnetic structures unambiguously. We report here the complete evolution of the field induced magnetic states, up to 7 T. We used both polarized and unpolarized neutrons; the polarized neutron technique, newly used for such compounds, allows small magnetic moments to be measured with a great accuracy. It is especially interesting for low fields ($H<1$ T) and high temperatures ($T>5$ K). The polarized neutron data were analyzed within the local susceptibility approach [13] and will be fully described elsewhere [14, 15].

2. Experimental

A single crystal of Tb$_2$Ti$_2$O$_7$ was grown by the floating-zone technique. We checked the crystal structure by neutron diffraction (434 reflections measured at 50 K in zero-field) and we refined it within the $Fd\bar{3}m$ space group, in agreement with previous results [11].

The neutron diffraction studies were performed on the diffractometer Super-6T2 at the Orphée reactor of the Laboratoire Léon Brillouin [16]. The field $H$ was applied along [110]. We used unpolarized neutrons of wavelength $\lambda_n=0.90$ Å, collecting about 200 reflections for each ($H,T$) set,
for 10 temperatures between 0.3 K and 50 K and 7 fields between 0 and 7 T. We also used polarized neutrons of incident wavelength $\lambda_n = 0.84 \text{ Å}$ and polarization $P_0 = 0.91$. We collected flipping ratios at 200 to 400 Bragg peaks for each $(H, T)$ set, for 8 temperatures between 5 and 270 K, in a field of 1 T. The programs FULLPROF [17] and CHILSQ [18] were used to refine the magnetic intensities and flipping ratios, respectively.

3. $k=0$ ferromagnetic-like structure

In zero magnetic field, Tb$_2$Ti$_2$O$_7$ is in a spin liquid state [8], so the Bragg peaks, indexed in the face centered cubic (fcc) lattice, have a purely nuclear origin. When applying a magnetic field, the integrated intensity of the Bragg peaks first increases, evidencing a magnetic contribution with $k=0$ propagation vector (Fig. 1). It corresponds to a ferromagnetic (F)-like structure having the same cubic unit cell as the nuclear one, and a net magnetization. This increase of the Bragg intensities is linear up to about 1 T, then it shows different behaviors according to the peak considered. Especially, the onset of the magnetic (200) and (2-20) peaks [12], which correspond to peculiar nuclear extinctions, due to Fd$\bar{3}$m extinction and specific Tb position respectively, reflects a non-collinear F structure.

Figure 1. Tb$_2$Ti$_2$O$_7$: Field dependence of the integrated intensities of some fcc Bragg peaks at selected temperatures.

In the F-like structure with $k=0$ propagation vector, the 4 Tb tetrahedra of the cubic cell are identical. In order to solve this structure, one needs to determine the magnitudes and orientations of the 4 Tb moments in a given tetrahedron. The polarized neutron data (5$< T <$270 K, $H=1$ T) were analyzed within the local susceptibility model [13], and the magnetic moments were derived from the local susceptibility parameters [15]. Unpolarized neutron data (0.2$< T <$50 K, $H$ up to 7 T) were analyzed by refining the 4 Tb moments independently. The results obtained with both techniques perfectly overlap (Fig. 2a).

3.1. Temperature dependence in a field $H=1$ T along [110]

With a field $H \parallel [110]$, the Tb ions separate into $\alpha$ and $\beta$-chains [4, 5]: those in $\alpha$-chains have their local $<111>$ easy axis close to $H$ (35.3°), whereas those in $\beta$-chains have their easy axis perpendicular to $H$. The temperature evolution of the magnetic moments and magnetic structure is sketched in Fig. 2 for a field of 1 T along [110]. At 270 K, all induced moments have the same value. With decreasing $T$, $\alpha$ and $\beta$-moments field induced moments start to have very different values, with much stronger moments in the $\alpha$-chains (Fig. 2a).

From the moment values, one can deduce the temperature dependence of the net magnetization, which perfectly agrees bulk magnetization (inset Fig. 2a). Below 2 K, due to a misorientation of 5° of the field with respect to [110], the $\alpha$- and $\beta$-moments each split into two values: $\alpha_1$ and $\alpha_2$ are very close, while $\beta_1$ and $\beta_2$ show a sizeable difference (Fig. 2a).

As to the moment orientations, the experimental determination of the angles of the $\alpha$- and $\beta$-moments with the field $H$ (Fig. 2b) and with their local $<111>$ easy axis (Fig. 2c) shows that $\alpha$- and $\beta$-moments are close to field axis at high temperature, then reorient along their local $<111>$ easy axis with decreasing...
Figure 2. \( \text{Tb}_2\text{Ti}_2\text{O}_7 \): \( k=0 \) F-like structure induced by \( H=1 \text{ T} \parallel [110] \). (a): temperature dependence of the Tb moments from unpolarized (● for \( \alpha \) -chains and ○ for \( \beta \) -chains) and polarized (■ for \( \alpha \) -chains and □ for \( \beta \) -chains) neutron data. The two types of \( \alpha \) and \( \beta \)-moments are due to the 5° misorientation of \( H \) with respect to [110]. The thick red lines are a crystal field calculation with \( H \) applied at 35.3° (resp. 90°) from the local \( <111> \) for \( \alpha \) (resp. \( \beta \) ) sites. Inset: magnetization \( M \) versus temperature: (▲) from neutron data, (△) from bulk measurements of Ref. [7]. Thin solid lines are guides to the eye; (b) and (c): temperature dependence of the angles of the moments with local \( <111> \) axis and field, respectively, determined by unpolarized (open symbols) and polarized (solid symbols) neutron data; (d), (e), and (f): evolution of the F-like structure with temperature. The Tb moments shown by arrows were multiplied by \( T \) to compensate for the Curie-Weiss behaviour of the susceptibility.

The temperature dependence of the magnetic moments mainly results from the crystal field (CF) anisotropy of the Tb ion. Calculations of the \( T \)-dependence of the F \( \alpha \)- and \( \beta \)-moments with a field of 1 T // [110] were performed with the trigonal crystal field scheme deduced from inelastic neutron scattering data [7] (red lines in Fig. 2a) and the moment magnitudes agree very well with experiment. In the model, the applied field was assumed to lie exactly along [110], so the two \( \beta \)-moments deduced from experiment must be averaged for comparison with the calculation.

The trigonal crystal field model correctly predicts the orientation of the \( \alpha \)-moments, but fails for the \( \beta \) ones in the low temperature state. Indeed, for \( H \) perpendicular to the \( <111> \) easy axis, the \( \beta \)-moments should lie along \( H \), contrary to experiment below 2 K (see Fig. 2b). This discrepancy may be due to the onset of a tetragonal distortion below 10 K [19], which tilts the easy axis away from \( <111> \).

Figure 2. Tb\(_2\)Ti\(_2\)O\(_7\): \( k=0 \) F-like structure induced by \( H=1 \text{ T} \parallel [110] \). (a): temperature dependence of the Tb moments from unpolarized (● for \( \alpha \)-chains and ○ for \( \beta \)-chains) and polarized (■ for \( \alpha \)-chains and □ for \( \beta \)-chains) neutron data. The two types of \( \alpha \) and \( \beta \)-moments are due to the 5° misorientation of \( H \) with respect to [110]. The thick red lines are a crystal field calculation with \( H \) applied at 35.3° (resp. 90°) from the local \( <111> \) for \( \alpha \) (resp. \( \beta \) ) sites. Inset: magnetization \( M \) versus temperature: (▲) from neutron data, (△) from bulk measurements of Ref. [7]. Thin solid lines are guides to the eye; (b) and (c): temperature dependence of the angles of the moments with local \( <111> \) axis and field, respectively, determined by unpolarized (open symbols) and polarized (solid symbols) neutron data; (d), (e), and (f): evolution of the F-like structure with temperature. The Tb moments shown by arrows were multiplied by \( T \) to compensate for the Curie-Weiss behaviour of the susceptibility.

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3.2. Field dependence in the ground state

At the lowest temperature ($T=0.33$ K), the F-like structure in low field ($H=1$ T) has a local spin arrangement very close to that of a spin ice, with 2 spins pointing in and 2 out of a given tetrahedron (Fig. 3a). With increasing the field, all moments progressively reorient towards $H$, as shown in Fig. 3b for the F-like spin structure at the highest field ($H=7$ T). The quality of the refinement is shown in Fig. 3c.

In the low field ground state, we find very different moments for the $\alpha$- and $\beta$-chains. These moment values become comparable in high fields. The $\alpha$-moments in the ground state saturate at low fields (Fig. 4a), reaching values around 6 $\mu_B$ as predicted by crystal field calculations [7], whereas the $\beta$-moments increase much more slowly with increasing the field (Fig. 4c). The $\alpha$- and $\beta$-moments seem to be systematically closer to their local easy axis at 0.33 K than at higher temperatures, whatever the field value (Fig 4b and 4d). Then the variation of the moment angles with the field remain basically unchanged in the temperature range 0.65-2.4 K.

One also notices from Fig. 4a, that the $\alpha$-moments at 0.33 K are systematically below those at 0.65 K, 0.95 K and 1.5 K, which merge into a single curve. This reentrant behavior at the lowest temperature is connected with the onset of a $k=(0,0,1)$ antiferromagnetic (AF)-like structure, as described below.

4. $k=(0,0,1)$ antiferromagnetic-like structure

For temperatures below 2 K, new types of Bragg peaks of the simple cubic lattice appear when the magnetic field is increased above 2 T. They are indexed in the space group $Fd\bar{3}m$ with $k=(0,0,1)$ and correspond to an AF-like structure having no net magnetization. Indeed, in the unit cell two Tb tetrahedra are identical, and the other two have reversed moment orientations. This second structure was refined independently of the F-like one, assuming that it also involves the whole sample. Results are shown in Fig. 5. In this structure, the AF $\beta$-moments alone have sizeable values, the AF $\alpha$-moments being negligible (0.2(2) $\mu_B$ typically). At $T=0.33$ K, the AF $\beta$-moments remain oriented at $10(5)^\circ$ from their local $<111>$ axis and are perpendicular to the field (90(5)$^\circ$), up to the highest field $H=7$ T. The AF-like structure (Fig. 5a) is stabilized in a limited field range, as shown by the field dependence of the AF peaks at 0.33 K (Fig. 5b), which presents a clear maximum around 5 T. This maximum is also seen in the field dependence of the AF $\beta$-moments (Fig. 5d). The range of stability of the AF-like structure can be determined by plotting the integrated neutron intensities either versus temperature at constant field.
Figure 4. \(\text{Tb}_2\text{Ti}_2\text{O}_7\): \(k=0\) F-like structure induced by a field \(H\parallel[110]\). (a): \(H\)-dependence of the F \(\alpha\)-moments. At 0.33 K, a reentrant behavior is observed for \(H > 2\) T. (b): angles of the F \(\alpha\)-moments versus \(H\). When \(H\) increases, the moments rotate from their local \(<111>\) easy axis (red arrow) towards \(H\) (blue arrow). (c): \(H\)-dependence of the F \(\beta\)-moments. (d): angles of the F \(\beta\)-moments versus \(H\).

(Fig. 5c), or versus field at constant temperature (Fig. 5d). The transition line deduced from these plots agrees at low field (below 1.5 T) with that previously determined [12], but starts to depart from it at higher field.

The Lorentzian shape of the AF peaks (inset Fig. 5f) shows that the AF-like structure extends over a finite length. The correlation length (Fig. 5f) shows a maximum versus field and reaches 70 Å for \(H=4\) T. One naturally expects the AF-like structure to disappear at high field, by extending over shorter and shorter length scales, since the Zeeman energy should ultimately align all moments along the field.

5. Nature and origin of the field induced ground states
Here we briefly discuss the nature and coexistence of F-like and AF-like structures in the field induced ground states (GS) of \(\text{Tb}_2\text{Ti}_2\text{O}_7\), and we speculate about the origin of the AF-like structure. Below 2 T, the GS consists of a long range ordered \(k=0\) structure, with field induced moments both on \(\alpha\) and \(\beta\) chains. In low field, the local structure is akin to the well known “2 in-2 out” spin ice structure, but with moments of very different magnitudes. The presence of non-zero moments in the \(\beta\)-chains contrasts with observations of the field induced \(k=0\) structure of model spin ices [5]. The values of the magnetic moments are quantitatively explained by a calculation taking the Tb CF anisotropy [7] into account, noticing that it is much weaker than in spin ices. \(\text{Tb}_2\text{Ti}_2\text{O}_7\) provides an original example of different moments induced by the field at identical crystallographic sites in the homogeneous and highly symmetric pyrochlore lattice. With increasing \(H\) or \(T\), the moments reorient and the \(k=0\) structure evolves from an ordered spin ice to a field aligned structure, as the local susceptibility transforms from Ising-like to isotropic. This change is a CF effect and is directly probed by the local susceptibility approach [14, 15].

Above 2 T and below 2 K, the GS is a superposition of two modes with \(k=0\) and \((0,0,1)\), the latter extending over a finite length scale. The \(k=(0,0,1)\) AF-like structure, which involves negligible \(\alpha\) moments and smaller \(\beta\) moments than in the F-like structure for the same fields, has no net magnetisation.
Figure 5. Tb$_2$Ti$_2$O$_7$: $\mathbf{k}=(0,0,1)$ AF-like structure induced by a field $\mathbf{H}/[110]$ ($T<2$ K, $H>2$ T). (a): magnetic structure at 0.33 K in $H=7$ T. (b): $H$-dependence of the integrated intensities (in arb. unit.) of selected AF Bragg peaks. In the inset, refinement at $H=7$ T and $T=0.33$ K, with $R_F=7\%$. (c): $T$-dependence of the integrated intensity (in arb. unit.) of the (112) AF peak. The lines are extrapolated to find the AF transition points, shown by arrows. (d): $H$-dependence of the AF $\beta$-moments. Lines are guide to the eye, dotted lines are extrapolated to determine the transition points. The AF $\alpha$-moments (not plotted) are below 0.2 $\mu_B$. (e): ($H, T_{AF}$) transition line: $\bullet$ and $\Delta$ as determined in figure (c) and (d) respectively, from our measurements, $\square$ from Ref. [12]. (f): $H$-dependence of the AF correlation length at $T=0.33$ K. In the inset, the (112) peak for several fields. Solid lines are fits to a Lorentzian peak shape, the dashed line is the resolution peak shape.

It is stabilized in a “pocket” of the ($H, T$) phase diagram, ranging from 2 T to 10-15 T at $T=0$, and reaching about 2 K at 6-7 T. Such a limited field induced AF region was also observed in the well known GGG (Gd$_3$Ga$_3$O$_{12}$) highly frustrated magnet [20].

The onset of the $\mathbf{k}=(0,0,1)$ AF-like structure is connected with the appearance of well defined spin-waves [12], and with a field broadening of the nuclear Bragg peaks [14]. These features suggest a symmetry breaking through a lattice distortion. We also notice that this structure is similar to that induced in Tb$_2$Ti$_2$O$_7$ by a stress along the same [110] direction [11]. This suggests a magnetostriction effect. An AF order induced by magnetostriction was recently observed in a quasi 2-D magnetic system [21]. Here, taking into account the value of the bulk modulus [22] and of the magnetostriction [23] in Tb$_2$Ti$_2$O$_7$, we evaluate that a field of 7 T induces an average isotropic magnetostriction comparable to that due to a pressure of 0.03 GPa. This is well below the stress applied to induce the AF long range order (0.2 GPa), but may be comparable to spontaneous stresses, inducing AF order over a finite length scale of 50 Å in Tb$_2$Ti$_2$O$_7$ powder [24]. Moreover, the anisotropic magnetostriction coefficients being much larger than the isotropic ones, the field orientation, as well as the stress orientation [11], should play a role in stabilizing the AF structure.

6. Summary
In conclusion, we determined the field induced magnetic structures in Tb$_2$Ti$_2$O$_7$ by combining polarized and unpolarized neutron diffraction, in a wide range of temperature and applied field. The low field ground state is a non-collinear ferromagnetic structure, with the local spin ice configuration, but with
Tb moments of very different magnitudes. With increasing field, the Tb moments reorient from the spin ice easy axes to the field direction. In the high field ground state, an antiferromagnetic-like structure is observed together with the ferromagnetic one. The AF-like structure involves smaller moments, is stable in a limited ($T, H$) range and extends over a finite length scale. It is attributed to magnetostriction.

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