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# Spin liquid and spin ice under high pressure: a neutron study of $R_2Ti_2O_7$ ( $R = Tb, Ho$ )

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## Abstract

The rare earth titanates show unusual types of short range magnetic order, known as spin liquid and spin ice states, which arise from the geometrical frustration of the pyrochlore lattice. We have investigated the effect of applied pressures on these magnetic states by means of powder neutron diffraction, up to 8 GPa. In the spin liquid  $Tb_2Ti_2O_7$ , pressure induces a long range antiferromagnetic order, coexisting with the spin liquid state below the Néel temperature ( $T_N = 2.1$  K). The onset of long range order coincides with a strong decrease of the diffuse intensity, due to a gradual transfer from the liquid to the ordered state as the temperature decreases. The short range correlations are also modified under pressure, even above  $T_N$ . In contrast, in  $Ho_2Ti_2O_7$  the spin ice state remains stable under pressure, as was checked up to 6 GPa, and down to 1.4 K. The short range correlations are unaffected here. The possible origins of this behaviour are discussed.

## 1. Introduction

The cubic pyrochlore lattice is fully frustrated for antiferromagnetic (AF) first-neighbour interactions, so that in the absence of any perturbation no transition is expected, and the magnetic moments fluctuate down to  $T = 0$ , in a spin liquid state involving strong short range dynamical correlations [1, 2]. In practice, the degeneracy of the ground state is generally lifted by a perturbation, like further neighbour interactions, anisotropy, chemical disorder, thermal or quantum fluctuations. The pyrochlore lattice is also frustrated for ferromagnetic first-neighbour interactions, in the presence of local Ising anisotropy, leading to the spin ice state [3].

In  $R_2Ti_2O_7$ , the magnetic R cations on a pyrochlore lattice show several unusual magnetic behaviours.  $Yb_2Ti_2O_7$  shows a surprising first-order transition towards a short range ordered state [4].  $Er_2Ti_2O_7$  and  $Gd_2Ti_2O_7$  order below 2 K in complex antiferromagnetic structures [5, 6], and in  $Gd_2Ti_2O_7$  some Gd moments may remain paramagnetic below the

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ordering transition.  $\text{Ho}_2\text{Ti}_2\text{O}_7$  and  $\text{Dy}_2\text{Ti}_2\text{O}_7$  with strong single-ion anisotropy are spin ices in spite of a weak AF exchange interaction ( $J_{\text{nn}} = -0.5$  K for Ho) due to the influence of dipolar interactions [7, 8].

$\text{Tb}_2\text{Ti}_2\text{O}_7$  is especially intriguing, since it remains a spin liquid down to at least 0.07 K, 200 times at least below the Curie–Weiss constant ( $\theta_{\text{CW}} \sim -19$  K) [9] which set the typical scale of the magnetic interactions. Spin glass-like irreversibilities are observed below 0.07 K [10], but magnetic moments still fluctuate even below [9, 11]. At high temperature, the Tb ions bear almost the full effective paramagnetic moment expected for the free ion ( $9.6 \mu_{\text{B}}$ ). The single-ion ground state is a doublet with magnetic moment evaluated to  $5 \mu_{\text{B}}$ , separated from the first excited state by an energy splitting  $\Delta$  of 18 K [12]. Recent analysis of the liquid-like correlations suggest that the magnetic moments may evolve from Heisenberg to Ising behaviour with decreasing temperature [11, 13]. The near neighbour interaction ( $J_{\text{nn}} = -0.9$  K) is much stronger than in the Gd, Dy or Ho compounds. The contributions of exchange, crystal field (CF) and dipolar energies to  $\theta_{\text{CW}}$  were evaluated to be  $-14$ ,  $-6$  and  $1.2$  K respectively [12]. Given these values for the interactions,  $\text{Tb}_2\text{Ti}_2\text{O}_7$  is expected to order in a  $\mathbf{k} = 0$  antiferromagnetic structure, at about 1.1 K [12]. Therefore, the absence of magnetic order is highly surprising.

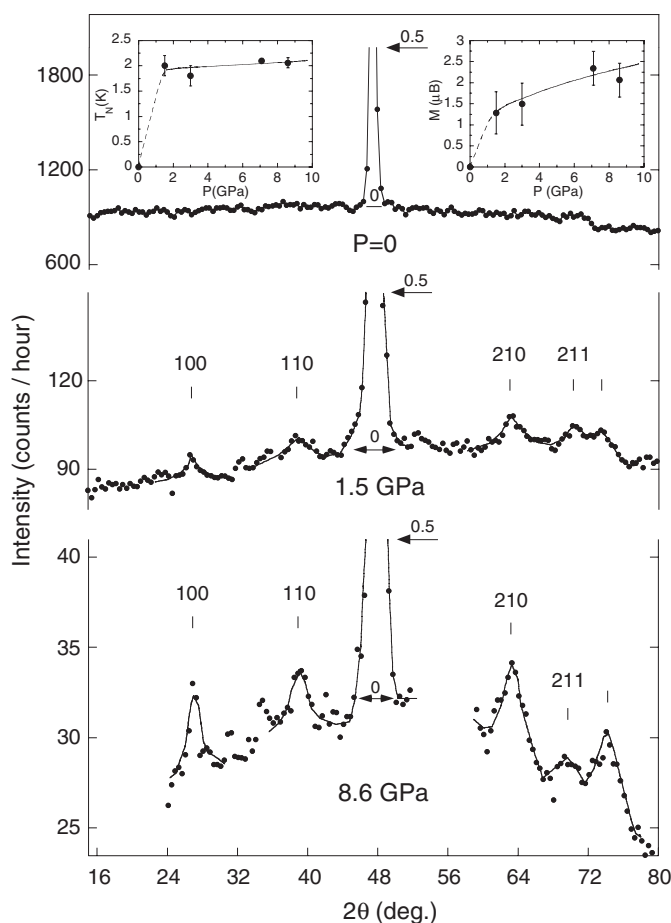
If this abnormal spin liquid and the dipolar spin ice states arise from some special balance between exchange, CF and dipolar interactions, one could expect to change this balance with isotropic pressure, since these magnetic interactions depend on interatomic distances in a different way. Pressure (either isotropic or anisotropic) could also induce a structural distortion which changes the crystal symmetry, lifting the degeneracy of the pyrochlore lattice. We have applied high pressure to  $\text{Tb}_2\text{Ti}_2\text{O}_7$  and  $\text{Ho}_2\text{Ti}_2\text{O}_7$  as a possible way to destabilize the spin liquid or dipolar spin ice regime and to induce long range magnetic order. The first results on  $\text{Tb}_2\text{Ti}_2\text{O}_7$  were published in [14].

## 2. Samples and experiment

The Tb and Ho powder samples were characterized by neutron diffraction at ambient pressure and room temperature. They are free from impurities and show no evidence of magnetic order at ambient pressure. The magnetization of the Tb sample was also measured on a SQUID magnetometer. The neutron diffraction spectra were refined in the space group  $Fd\bar{3}m$ , yielding a lattice constant of 10.104 Å (Ho) and 10.149 Å (Tb) at  $P = 0$ . The positional parameter of the  $O'(8b)$  oxygen was found as 0.328 (Tb), reflecting the trigonal symmetry of the oxygen environment of R ions [15]. High pressure data were recorded on the powder diffractometer G6-1 of the LLB, a spectrometer especially adapted for high pressure powder neutron diffraction [16]. The neutron wavelength was 4.741 Å. We used the Kurchatov-LLB pressure cells with sapphire anvils [17]. The NaCl pressure transmitting medium provides a quasi-hydrostatic pressure, with a non-uniform component estimated to be less than 5%. The pressure was measured with a precision of  $\pm 0.1$  GPa. The measurements on  $\text{Tb}_2\text{Ti}_2\text{O}_7$  were at  $P = 0$  and at five pressures between 1.5 and 8.6 GPa, and those on  $\text{Ho}_2\text{Ti}_2\text{O}_7$  were at  $P = 0$ , 5 and 6 GPa. The cell was inserted in a helium cryostat and spectra were recorded down to 1.4 K. A spectrum measured in the paramagnetic range (50 K) was subtracted to extract the magnetic correlations.

## 3. Spin liquid $\text{Tb}_2\text{Ti}_2\text{O}_7$

At  $P = 0$  a broad diffuse scattering starts to develop in  $\text{Tb}_2\text{Ti}_2\text{O}_7$  below the structural Bragg peaks. The large damped oscillations show the onset of short range antiferromagnetic



**Figure 1.**  $\text{Tb}_2\text{Ti}_2\text{O}_7$ . Raw neutron diffraction spectra for three pressure at  $T = 1.4$  K. The intensity scales are chosen to show the magnetic peaks as compared with the 111 structural peak. The half-intensity of the 111 peak is shown at the centre of the figure. Insets: the Néel temperature  $T_N$  (left) and the magnetic moment  $M$  at 1.4 K (right), versus pressure. From [14].

correlations, with a first maximum at the position of the 111 structural peak. The liquid-like correlations develop below about 50 K. Under applied pressure drastic changes are observed in the magnetic spectra:

- (i) new Bragg peaks appear showing the onset of long range antiferromagnetic order;
- (ii) the  $q$  and  $T$  dependences of the liquid-like correlations are strongly modified.

We detail these effects below.

### 3.1. Onset of long range order: pressure induced crystallization of the spin liquid

Figure 1 shows raw diffraction spectra at 1.4 K for several pressures, focusing of the region around the 111 structural peak. The scales were adjusted to allow a direct comparison of the spectra. At  $P = 0$ , only the 111 Bragg peak is observed. At 1.5 GPa, small Bragg peaks start to emerge from the diffuse background. At 8.6 GPa, these peaks are now clearly seen, with an intensity reaching up to 30% of that of the 111 peak. Concomitantly, the diffuse background

shows a stronger modulation. The presence of the diffraction peaks clearly shows the onset of a magnetically ordered phase, which develops with increasing pressure. The pressure induced phase disappears when heating. Plotting the intensity of the peaks versus  $T$  (inset figure 4) allows one to determine the Néel temperature  $T_N$ . As shown in the inset of figure 1,  $T_N$  is almost pressure independent:  $T_N = 2.1 \pm 0.05$  K.

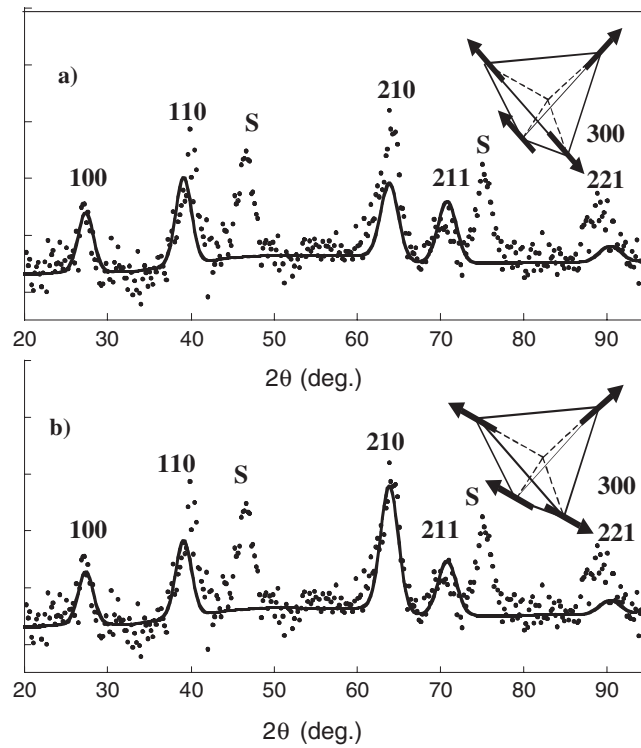
The ordered structure has a simple cubic unit cell (lattice parameter  $a$ ), derived from the chemical one of  $Fd\bar{3}m$  symmetry via a propagation vector  $\mathbf{k} = 100$  or  $110$ . There is no magnetic contribution in the structural peaks. Two extra magnetic peaks can be indexed in a much larger cell, of lattice parameter  $4a$ . This second family of peaks evolves with pressure and temperature like the cubic peaks, and therefore is attributed to a long wavelength modulation of the main structure. To study the spin arrangement precisely, the peak intensities of the main structure were refined using the Rietveld method and the Fullprof program [18]. The cubic cell of lattice parameter  $a$  contains four Tb tetrahedra, and the translations compatible with either  $100$  or  $110$  propagation vectors impose that two tetrahedra have the same orientations and two have reversed spin orientations. Then the question remains of the local spin arrangement within one tetrahedron. Using group theory (the program Basireps), we found four irreducible representations for the symmetry elements which leave the propagation vector (either  $100$  or  $110$ ) invariant within the space group  $Fd\bar{3}m$ . Then we tested systematically all variants, assuming that all Tb moments have identical length and are situated along the principal axis of the same family (of either  $100$ ,  $110$  or  $111$  type). Due to the high symmetry, most variants yield extinctions of some Bragg peaks and only one (obtained with  $\mathbf{k} = 100$ ) yields a reasonable agreement with the data (figure 2(a)). It corresponds to spins along the  $110$  axis. We also tested by trial and error other spin arrangements which cannot be obtained by the above method and found a close variant with spins along the  $111$  axis, yielding a slightly better agreement with the data (figure 2(b)). The spin arrangement of this ‘best solution’ for the whole unit cell is shown in figure 3.

Obviously, the variant proposed is oversimplified since it neglects the second family of peaks which should be taken into account via a larger unit cell and multi- $\mathbf{k}$  structure. (The real unit cell should contain at least 76 spins!) As for the main structure, we did not explore more complex variants with either lower symmetry or inequivalent Tb moments. Nevertheless, several important points remain:

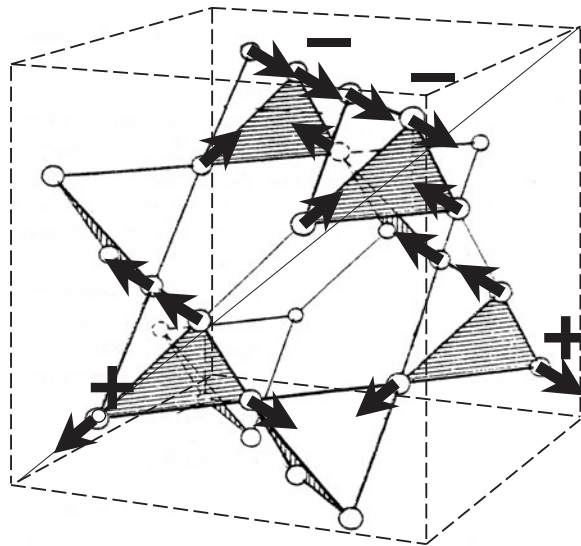
- (i) the magnetic structure differs from the previous ones found in other pyrochlores, with either  $\mathbf{k} = 0$  or  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  propagation vectors [5, 6, 19];
- (ii) in one tetrahedron the magnetization does not compensate (the  $100$  peak is observed);
- (iii) the local arrangement inside one tetrahedron should be complex (non-collinear and non-symmetric) to produce intensity on all possible peaks of the cubic lattice.

In particular, spin arrangements along the local anisotropy  $111$  axis, based either on pyr-FeF<sub>3</sub> [19] or on the spin ice structure [3], are excluded from this model.

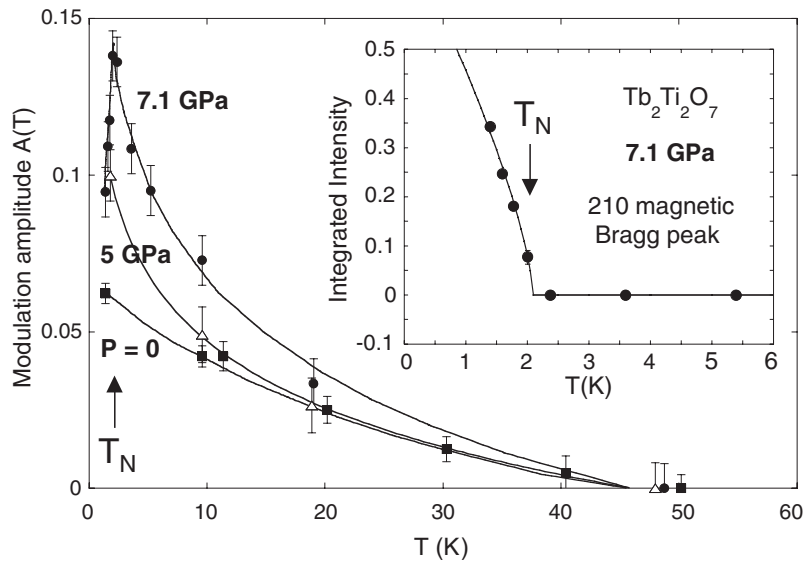
The magnetic structure is independent of pressure within the accuracy of the measurements. The average ordered moment increases with pressure (inset of figure 1) and decreases with temperature as the square root of the intensity of the magnetic peaks. Within the above model we find a maximum value of  $2.4 \mu_B$  at 7–8 GPa and 1.4 K. This ordered moment does not depend much on the precise spin arrangement (all other models yield values between 2 and  $3 \mu_B$ ), and remains well below the local free ion value of  $9 \mu_B$ , and below the  $5 \mu_B$  value calculated in [12] taking the crystal field energy into account. This reduced moment value is connected with the persistence of the spin liquid phase below  $T_N$ , as discussed below.



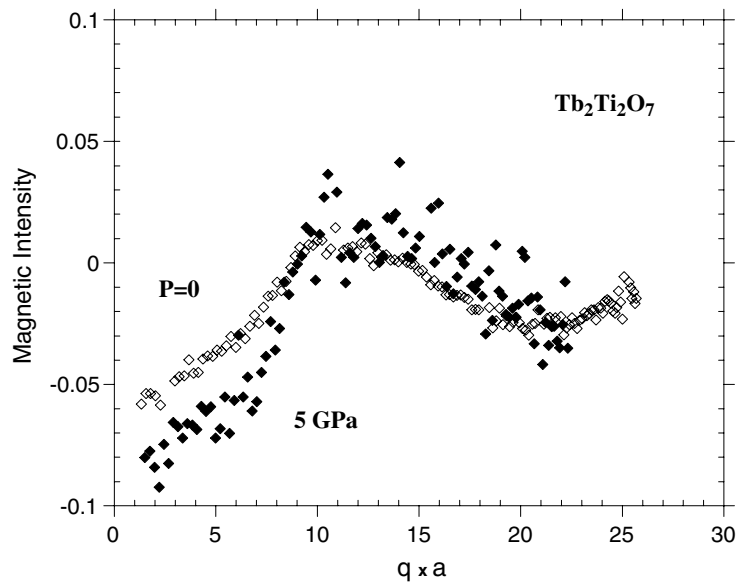
**Figure 2.**  $\text{Tb}_2\text{Ti}_2\text{O}_7$ . Magnetic neutron diffraction spectra at 1.4 K. The solid curve is the refined profile corresponding to the local spin arrangement drawn in the insets, with spins either along the 110 axis (a) or along the 111 axis (b). Reflections with  $hkl$  indices belong to the  $\mathbf{k} = 100$  or 110 set; reflections with S belong to the second set with  $\mathbf{k} = \frac{1}{4}\frac{1}{4}\frac{1}{4}$ .



**Figure 3.**  $\text{Tb}_2\text{Ti}_2\text{O}_7$ . Magnetic structure corresponding to the refinement of figure 2(b).



**Figure 4.**  $Tb_2Ti_2O_7$ . The temperature dependence of the modulation amplitude  $A(P, T)$  for  $P = 0, 5$  and  $7$  GPa. In the inset, the variation of the intensity of the 210 magnetic Bragg peak versus temperature is shown.



**Figure 5.**  $Tb_2Ti_2O_7$ . Magnetic scattering in the spin liquid state at  $P = 0$  and  $5$  GPa.

### 3.2. Change in the spin liquid state under pressure above $T_N$

Under pressure, the short range magnetic correlations are strongly modified (figure 5). In particular, one observes a much stronger decrease of the diffuse intensity at low  $q$  values in the pressure data, suggesting an enhancement of the antiferromagnetic character of the first-neighbour spin correlations. The modulation amplitude  $A(P, T)$  of the diffuse scattering, defined experimentally as  $I_{\min} - I_{\max}$  in our experimental  $q$  range, is expected to be proportional

to the thermal average of the near neighbour correlations.  $A$  increases with decreasing temperature, and this effect becomes more pronounced with increasing pressure. The onset of long range order at  $T_N$  coincides with a sharp kink of  $A$ , which starts to decrease steeply below  $T_N$  (figure 4).

Taking off the  $P = 0$  data, we note that data at different pressures and temperatures all superimpose when divided by the modulation amplitude,  $A$ . This evinces a thermal and spatial decoupling of the magnetic modes:  $S(q, T) = A(T)S(q)$  predicted by theory [20, 21]. The correlation length does not increase and remains roughly constrained to first neighbours, in contrast with expectations for a second-order transition. The change in the  $q$  dependence between  $P = 0$  and high pressure data is more intricate but also more interesting as it may be the precursor of the transition in the spin liquid state. It is shown in figure 6, where the diffuse intensity scaled to  $A(T)$  is plotted versus the scattering vector  $qa$  in reduced units. The maximum of the diffuse peak, centred at  $P = 0$  at the 111 peak position ( $qa = 10.9 \pm 0.1$ ), shifts under pressure to a higher  $qa$  value of  $12.6 \pm 0.3$ . Under pressure, the diffuse intensity is well fitted by a simple law expected for a pair of AF coupled spins [23]. We also fitted the data with calculated neutron cross sections for the pyrochlore lattice with first-neighbour AF interactions. The calculations involve either Monte Carlo simulations [20] or an exact solution of the infinite component spin vector model [21]. As in experiment, the peak position of the calculated curves is governed by the first-neighbour distance, although the peak is sharper than the experimental one.

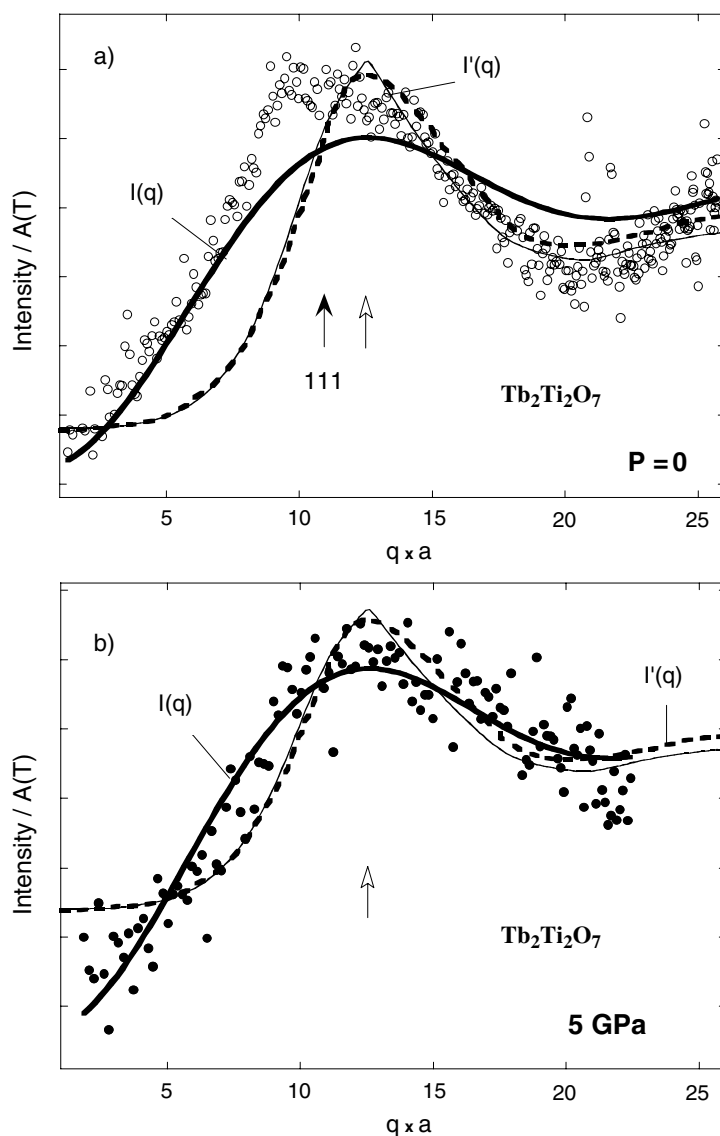
### 3.3. Nature of the mixed solid–liquid phase below $T_N$

Below  $T_N$ , the decrease of the modulation amplitude mirrors the increase of the Bragg intensity, showing that the ordered phase develops at the expense of the spin liquid one. The facts that  $T_N$  is almost pressure independent and that the liquid phase persists down to at least 1.4 K ( $0.7T_N$ ) suggest that the transition is of first order and that the two phases may coexist in an inhomogeneous way. In this picture, it would consist of small ordered regions growing with decreasing temperature or increasing pressure, inside the liquid phase. In a rough approximation, by considering the decrease of the diffuse intensity between  $T_N$  and 1.4 K, we evaluate the relative volume of the ordered regions to be 33–40% at high pressure. This yields a value of the ordered moment within this regions of about  $4 \mu_B$ , rather close to the predicted value of  $5 \mu_B$ . Further measurements with a dilution cryostat will allow study of the ordered moment well below  $T_N$  to see whether the spin liquid phase could persist down to  $T = 0$ .

## 4. Spin ice $\text{Ho}_2\text{Ti}_2\text{O}_7$

In  $\text{Ho}_2\text{Ti}_2\text{O}_7$ , neutron diffraction data at  $P = 0$  also evince short range magnetic correlations with damped oscillations. But here the first maximum is centred at  $0.6 \text{ \AA}^{-1}$ , yielding a typical distance  $d = 10.5 \text{ \AA}$  close to  $a$ , which shows that correlations involve at least second-neighbour distances (figure 7). In  $\text{Ho}_2\text{Ti}_2\text{O}_7$  single crystal [7] and  $\text{Ho}_2\text{Sn}_2\text{O}_7$  powder [22], the peculiar shape of the diffuse scattering was accounted for by dipolar interactions, together with a weak AF near neighbour exchange. The amplitude of modulation of the first oscillation strongly increases with decreasing temperature, like in  $\text{Tb}_2\text{Ti}_2\text{O}_7$ . But here, we do not observe any onset of long range magnetic order up to 6 GPa and down to 1.4 K. Moreover the  $q$  dependence of the diffuse intensity remains unchanged by pressure, and we do not see any shift in the position of the first modulation (inset figure 8). The temperature dependence of the correlations is also unaffected by pressure, as shown in figure 8 where the amplitudes of modulation measured at  $P = 0, 5$  and 6 GPa for several temperatures all collapse onto a single curve. Clearly, the dipolar spin ice state is stable under pressure.

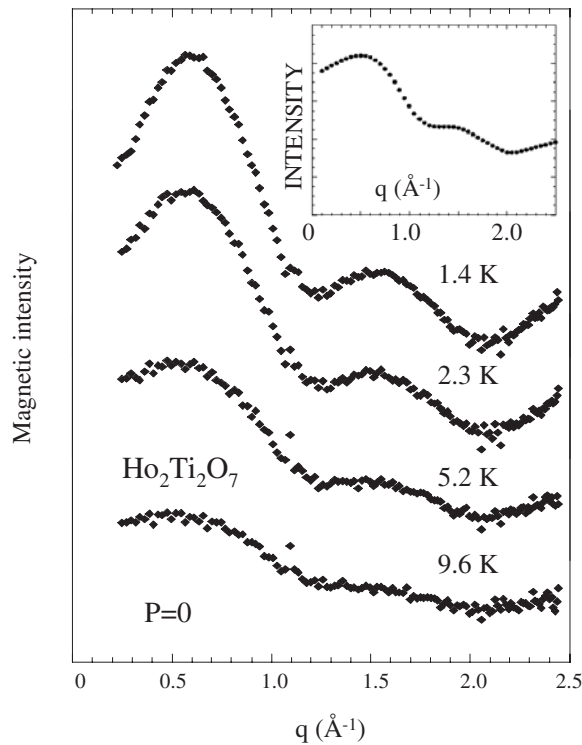




**Figure 6.**  $\text{Tb}_2\text{Ti}_2\text{O}_7$ . Diffuse magnetic intensity of the spin liquid state, scaled to the modulation amplitude, versus scattering vector  $qa$  in reduced units: at  $P = 0$  (a) and 5 GPa (b). The thick solid curve is a fit with  $I(q) = -B(T)f^2(q) \sin(qR_1)/(qR_1) + c(T)$  where  $R_1 = a/\sqrt{8}$  is the first-neighbour distance and  $f(q)$  is the magnetic form factor of  $\text{Tb}^{3+}$ .  $B$  is proportional to the modulation amplitude  $A$ , and  $c$  is a small background. Fits with functions calculated in [20] (thin curve) and [21] (dashed curve) are also shown. Black and white arrows point to the 111 and first-neighbour peaks respectively.

## 5. Discussion

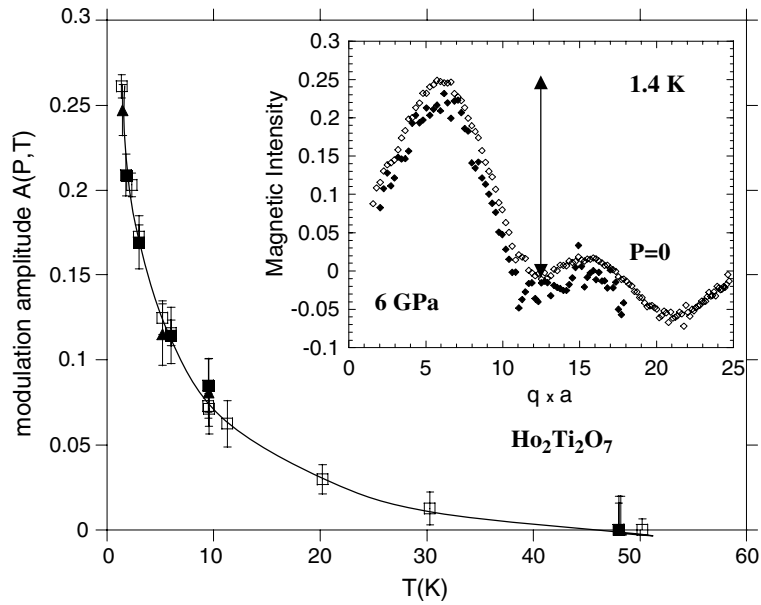
Obviously the spectacular pressure induced transition found in  $\text{Tb}_2\text{Ti}_2\text{O}_7$  raises more questions than it answers. First of all, the type of order is very surprising. The propagation vector of the ordered structure differs from that previously observed in other pyrochlores [5, 6, 19].



**Figure 7.**  $\text{Ho}_2\text{Ti}_2\text{O}_7$ . Diffuse intensity at  $P = 0$  for several temperatures. In the inset, magnetic scattering calculated assuming dipole interactions only, from [22], is shown.

Neither was it predicted by theoretical models, which predict a  $\mathbf{k} = 0$  structure [13]. Secondly, the microscopic mechanism by which pressure induces the magnetic order is not known. Last but not least, we have observed a change in the short range correlations well above the transition (up to temperatures 20 times  $T_N$ ), in the spin liquid phase where spins fluctuate with a high fluctuation rate (in the THz range). This may be the signature of a pressure induced effect at a local scale, preliminary to the Néel order. It suggests that pressure not only modifies the dipolar interactions (of typical energy scale 1 K) but also affects the balance between near neighbour exchange and crystal field energies (with higher energy scales). This is also supported by the fact that the dipolar spin ice  $\text{Ho}_2\text{Ti}_2\text{O}_7$  (with lower exchange energy and Ising anisotropy) is not affected by pressure. For  $\text{Tb}_2\text{Ti}_2\text{O}_7$  one should take into account the presence of low lying energy levels for the  $\text{Tb}^{3+}$  ion. The energy splitting  $\Delta$  between the ground and first excited states ( $\Delta \sim 18$  K) is much lower than for the other  $\text{R}_2\text{Ti}_2\text{O}_7$  compounds ( $\Delta$  above 100 K) and of the order of  $\theta_{\text{CW}}$ . This peculiar feature of  $\text{Tb}_2\text{Ti}_2\text{O}_7$  seems to be uniquely responsible for its ‘giant magnetostriction’ [24], if we note that the elastic constants and the electron–lattice interaction do not change substantially within the series. It could also play a role in the stabilization of the spin liquid state at  $P = 0$  [13]. All these indices reveal a strong coupling between lattice and spin degrees of freedom in  $\text{Tb}_2\text{Ti}_2\text{O}_7$ .

More precisely, two different mechanisms could be suggested to explain the pressure induced order in  $\text{Tb}_2\text{Ti}_2\text{O}_7$ , depending on the existence, or non-existence, of a broken symmetry in the crystal lattice. First of all, assuming an isotropic effect on the magnetic interactions (hydrostatic pressure), one could propose that at  $P = 0$ , exchange, crystal field and dipolar interactions are naturally balanced in such a way as to suppress the Néel order by making



**Figure 8.**  $\text{Ho}_2\text{Ti}_2\text{O}_7$ . Modulation amplitude versus temperature at  $P = 0, 5$  and  $6$  GPa. In the inset the magnetic scattering at  $P = 0$  and  $6$  GPa is shown.

quantum fluctuations significant. Noticing that  $\theta_{\text{CW}}/\Delta \sim 1$ , one could speculate that quantum fluctuations arising from the transverse part of the exchange and dipolar interactions, neglected in [13] are at play in  $\text{Tb}_2\text{Ti}_2\text{O}_7$  and reintroduced via quantum fluctuation process to high order in  $\theta_{\text{CW}}/\Delta$ . Applying pressure might destroy this delicate balance, inducing Néel order. On the other hand, one could also release frustration via an anisotropic effect (uniaxial pressure, or isotropic pressure inducing a structural distortion). A pressure induced local distortion of some tetrahedra, of the order of  $\Delta a/a \sim 5 \times 10^{-3}$ , might be enough to yield local variations of the near neighbour exchange  $\Delta J_{\text{nn}}/J_{\text{nn}} \sim 1\text{--}3\%$ . In a rough estimation, the ordering temperature arising from the non-compensated bonds would be  $T_{\text{N}} \sim \theta_{\text{CW}} \Delta J_{\text{nn}}/J_{\text{nn}} \sim 0.2\text{--}0.6$  K, taking only the exchange contribution to  $\theta_{\text{CW}}$ . In [25], a spin-driven Jahn–Teller distortion, by which the lattice spontaneously distorts to gain exchange energy, was proposed as a mechanism to relieve the frustration in the pyrochlore lattice. It could drive a spin–Peierls transition, possibly followed at a lower temperature by a Néel transition. This mechanism may be naturally at play at  $P = 0$  in some pyrochlore compounds with 3d magnetic ions, such as the  $\text{ZnV}_2\text{O}_4$  spinel [26] or the itinerant magnet  $\text{YMn}_2$  [27]. For rare earth ions with more localized 4f shells, such an intrinsic mechanism is unlikely, but a somewhat similar one may be induced by pressure.

Up to now we have not observed any structural distortion induced by pressure in  $\text{Tb}_2\text{Ti}_2\text{O}_7$ , which means that, if it exists, it is either local (random  $\Delta a/a \sim 10^{-2}$ ) or very small ( $\Delta a/a \sim 10^{-3}$ ). We have now started new experiments on oriented single crystals, with either isotropic pressure, or uniaxial stress, or a combination of the two, using a dilution cryostat to search for magnetic order down to the 100 mK range. Our preliminary results are very surprising. They suggest that neither a fully hydrostatic pressure (up to about 3 GPa at least) nor a uniaxial stress (of the order of 0.3 GPa) is sufficient to induce magnetic order, but that the combination of the two can do it.

Clearly, more theoretical and experimental work is necessary to fully understand this new transition. Still, such measurements open the possibility to create new types of order, by

tuning the magnetic order with pressure, and perhaps to induce some kind of dimerization in the spin liquid phase. This might provide a new insight into a wide range of systems combining frustration with a magnetic instability.

### Acknowledgments

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