Magnetic orders in $\text{Tb}_2\text{Sn}_2\text{O}_7$ under high pressure: from ordered spin ice to spin liquid and antiferromagnetic order.

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We have studied the $\text{Tb}_2\text{Sn}_2\text{O}_7$ frustrated magnet by neutron diffraction under isotropic pressure of 4.6 GPa, combined with uniaxial pressure of 0.3 GPa, in the temperature range 0.06 K<T<100 K. Magnetic order persists under pressure but the ordered spin ice structure stabilized at ambient pressure below 1.3 K partly transforms into an antiferromagnetic one. The long range ordered moment at 0.06 K is reduced under pressure, which is interpreted by a pressure induced enhancement of the spin liquid fluctuations. Above the ordering transition, short range spin correlations are affected by pressure, and ferromagnetic correlations are suppressed. The influence of pressure on the ground state is discussed considering both isotropic and stress effects.

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Original orders can be found in geometrically frustrated magnets, with magnetic ground states showing similarities with the liquid, ice, and glassy states of matter. Among them, the spin ices attract increasing attention. Their magnetic ground state can be mapped to that of real ice$^{[1, 2]}$ and possesses the same entropy$^{[3]}$. Whereas in many magnets antiferromagnetic (AF) first neighbor interactions are geometrically frustrated, in spin ices this occurs for ferromagnetic (F) interactions, when combined with the local Ising-like anisotropy of the magnetic moments. In pyrochlore spin ices $\text{R}_2\text{Ti}_2\text{O}_7$, where the rare earth ion $\text{R}$ is Dy or Ho, the effective ferromagnetic interaction between $\text{R}$ moments results from AF superexchange and F dipolar interactions. The strong crystal field anisotropy of the Dy$^{3+}$ or Ho$^{3+}$ moments constrains the moments to lie along the <111> local axes connecting the center of each tetrahedron to its corners.

The Terbium pyrochlores show a more complex but even richer behavior, due to the smaller anisotropy of the Tb$^{3+}$ ion$^{[4, 5]}$, and to the fact that superexchange and dipolar interactions between near-neighbor Tb$^{3+}$ ions nearly compensate. $\text{Tb}_2\text{Sn}_2\text{O}_7$ (TSO) is an intriguing example of an ordered spin ice$^{[6]}$. Contrary to classical spin ices which do not order at large scale, here the four tetrahedra of the unit cell have identical moment orientations, yielding long range order (LRO) below $T_\text{f}=1.3(1)$ K. An strong increase of the correlation length and ordered magnetic moment occurs at $T_\text{c}=0.87(2)$K, together with a peak in the specific heat. The nature of this LRO, and its coexistence with spin fluctuations in the ground state is highly debated$^{[7, 8, 9, 10, 11, 12]}$.

Whereas TSO shows an ordered ground state, the sibling compound $\text{Tb}_2\text{Ti}_2\text{O}_7$ (TTO) does not order at ambient pressure, showing liquid like fluctuations down to 50 mK$^{[13]}$. Recent theories$^{[14]}$ suggest that quantum fluctuations are responsible for its ground state. These different ground states arise from the lattice expansion induced by Ti/Sn substitution. Taking compressibility$^{[13, 12]}$ into account, substitution of Ti for Sn corresponds to a negative chemical pressure of 12-15 GPa.

In TTO, the spin liquid (SL) ground state is strongly suppressed under pressure and long range AF order is induced$^{[17]}$. Further single crystal measurements showed that this effect mainly arises from the lattice distortion induced by a uniaxial stress, allowing one to tune the ordered magnetic moment and Néel temperature by the stress orientation$^{[18]}$.

Here we report the first measurements of TSO under pressure. We studied the pressure induced state in a powder sample, both in the paramagnetic region up to 100 K and in the ordered spin ice region down to 0.06 K. Considering the pressure behavior of TTO, two scenarios could be a priori predicted for the effect of pressure in TSO: i) a "melting" of the spin ice long range order (LRO), due to the decrease of the lattice constant, yielding a spin liquid state similar to that in TTO at ambient pressure ii) a change from the spin ice LRO with F ordered moment to another LRO structure of AF character, as in TTO under stress. These two behaviors should be connected with the nature (isotropic or uniaxial) of the applied pressure.

By combining a high isostatic pressure of 4.6 GPa with a uniaxial stress of 0.3(1) GPa, we find that the ordered spin ice structure partly transforms into an AF one. Both orders coexist at 0.06 K but their transition temperatures slightly differ. The LRO moment at 0.06 K is reduced with respect to its ambient pressure value, suggesting that the spin liquid ground state is favored by pressure. In the paramagnetic region, short range order (SRO) between Tb moments is also affected by pressure. The ferromagnetic correlations are suppressed, whereas AF first neighbor correlations remain unchanged. The pressure induced ground state is discussed considering the influence of an isostatic compression and stress-induced lattice distortion separately.

A $\text{Tb}_2\text{Sn}_2\text{O}_7$ powder sample was inserted in a sapphire anvil cell, with an isostatic pressure component $P_\perp=4.6(1)$ GPa. High pressure neutron diffraction patterns were recorded at the diffractometer G6-1 of the Laboratoire Léon Brillouin$^{[19]}$, with an incident neutron wavelength $\lambda=4.74$ Å. Two experimental set-ups were used. In one set-up, the sample was mixed with a pressure transmitting medium (40 vol% NaCl), yielding a uniaxial component $P_\parallel=0.2$ GPa along the axis of the pressure cell. The cell was inserted in a helium cryostat and diffraction patterns were recorded at
The analysis of the k=0 structure, quoted F for simplicity (Fig. 1 top left), has 4 identical tetrahedra in the cubic cell. The local spin structure in a tetrahedron was described by the same irreducible representation of the space group I4\_1/amd as at ambient pressure \[6\]. To refine this structure, the only parameters are the ordered Tb moment \( M_F \) (the same for all Tb ions, determined by absolute calibration) and its canting angle \( \alpha \) with respect to the [111] local anisotropy axis. The refinement at 0.06 K (R= 1%) yields \( M_F = 3.3(3) \mu_B \) and \( \alpha = 28(1)^\circ \) to be compared with the ambient pressure values \( M_F = 5.9(1) \mu_B \) and \( \alpha = 13^\circ \). So, under pressure the Tb moments in the k=0 structure decrease and turn away from their local easy axis. The magnetization evaluated to 37% of \( M_F \) or 2.2 \( \mu_B \)/Tb at 1 bar [8] is reduced to 0.4(1) \( \mu_B \) under pressure.

The analysis of the k=(0,0,1) structure is more intricate. Here, in the cubic unit cell, two tetrahedra have identical orientations of the magnetic moments, and two tetrahedra have reversed orientations. This structure has no ferromagnetic component. To determine the possible local spin structures inside a tetrahedron (Fig. 1 top right), we first searched for
structures described by an irreducible representation of the I41/amd space group, as for TSO at ambient pressure. A possible structure (R=12%) is given by model 1, which involves two couples of Tb moments of 2.6(1)μB with canting angles of 27(1)° and 33(1)°. Slightly better models were found by relaxing the symmetry constraints and/or the relative values of the moments in a tetrahedron. Model 2 (R=6%) is derived from that proposed for TTO under pressure, with moments directions along <110> axes, and one AF pair of Tb moments, which could be favored by a stress along a [110] axis [18]. Model 3 (R=3%) assumes that all moments have the same value (2.8(1)μB), 2 moments have canting angles of 28(1)°, and the other two make an AF pair. Actually, the small number of magnetic peaks and the numerous possible models do not allow us to draw a definite conclusion. Importantly, whatever the solution considered, the average Tb moment keeps at 2.7(2)μB at 0.06 K.

We now discuss the influence of pressure on the SRO, as measured just above the transition. Difference patterns at 1.5 K with respect to T= 100 K clearly show magnetic SRO, as broad modulations of the intensity versus the momentum transfer (Fig. 3a). The SRO intensity Imag changes under pressure, as shown in Fig. 3b. This change was analyzed in a semi-quantitative way. At ambient pressure, Imag was fitted by the expression Imag = F(q)I(q) + L(q) + C where F(q) is the magnetic form factor of the Tb3+ ion, L(q) is a Lorentzian function and C a constant background. The liquid-like function I(q)=μ1 sin(qR)/qR accounts for correlations between first neighbor Tb pairs at a distance R1. It has two maxima in the measured q-range, as also seen in TTO [13]. The negative γ1 value shows that first neighbor Tb pairs are AF coupled, and its temperature dependence (Fig. 4) reflects the increasing correlations as temperature decreases. The Lorentzian term L(q) accounts for ferromagnetic correlations, expected when approaching the transition towards the ordered spin ice, and actually observed below [10, 11]. The Lorentzian term enhances the magnetic intensity at low q’s, shifts the position and damps the intensity of the two maxima. Under pressure, the γ1 value remains unchanged, whereas the Lorentzian term vanishes (Fig. 3b). The fit of the SRO under pressure is slightly improved by inserting third neighbor correlations between Tb moments (with ferromagnetic γ3), noticing that second neighbor Tb pairs are absent in the pyrochlore structure [20]. The suppression of the Lorentzian term by pressure suggests that the critical fluctuations associated with the ordered spin ice transition vanish, as the F ordered moment decreases and AF order is stabilized.

The nature of the pressure induced ground state may be un-
nderstood by referring both to TSO at ambient pressure and TTO under pressure and stress. At 0.06 K the ordered moment M per Tb ion, considering both F and AF structures, can be calculated as $M^2 = M_F^2 + M_{AF}^2$, yielding $M = 4.3(3) \mu_B$. Taking into account the long period structure, the ordered moment of which is evaluated to $1.3(2) \mu_B$ by comparing the intensity of the q=1.01 Å$^{-1}$ peak to those of the (201) or (200) peaks, one gets a value of $4.5(3) \mu_B$. So the pressure induced ordered moment is strongly reduced with respect to the ambient pressure value of $5.9(1) \mu_B$. We attribute this effect to the enhancement of the spin liquid fluctuations, which should naturally wash out the magnetic order.

We therefore conclude that the applied pressure favors both SL and AF orders at the expense of the ordered spin ice. To understand this result, one needs to consider the effects of isotropic and uniaxial pressure components separately. An isotropic pressure of 4.6 GPa induces an average compression of the lattice $\Delta V/V$ of about 2% [10]. This favors the SL rather than the ordered spin ice, as under chemical pressure when Sn is replaced by Ti of smaller ionic radius. Compressing the lattice enhances the AF superexchange with respect to the F dipolar interaction. The effect of the uniaxial component of 0.3 GPa depends on stress orientation with respect to the crystal axes, and a powder average must be performed. In TTO single crystal [18], a stress along a [110] axis induces AF order with ordered moment at 0.1 K up to 3.9 $\mu_B$ and $T_N$ of 1.8 K. The [110] stress relieves the geometrical frustration by inducing 3 different bond lengths in the distorted tetrahedron. This is not the case for stresses along [111] or [100] axis, which have a much smaller effect: a [111] stress yields an ordered moment of 0.4(1) $\mu_B$ and $T_N$ value of 0.7(1) K.

To evaluate the effect of the stress on the powder sample, noticing that the smallest angle between [110] and [111] axes is 35°, we assume that only stresses closer to a [110] axis may induce AF order. In a powder sample, the probability of finding a [110] type axis in a cone of angle $\theta$ is simply given by $P(\theta) = 6(1-\cos \theta)$, for $\theta \leq 30°$. Taking for instance $\theta = 20°$, we find that 36% of the grains should experience an efficient stress. We therefore conclude that both SL and AF orders are favored by pressure, but in different ways. With the above assumptions, the AF structure involves only the well-oriented grains (36%), with a strong AF moment $M_{AF} = 4.7 \mu_B$, and a total one of 5.4 $\mu_B$, whereas the other grains stabilize SL and ordered spin ice states.

Our results bring strong evidence that the magneto elastic coupling responsible for the pressure-induced AF order in TTO is also at play in TSO. The high sensitivity of the magnetic interactions to a pressure induced distortion allows one to tune ordered spin ice, spin liquid and AF orders through pressure and stress. This coupling also plays a role at ambient pressure. In TTO, a spontaneous distortion was observed, likely precursor of a Jahn-Teller transition [21]. Recent results [22] suggest that this distortion is also present in TSO and could help to stabilize the ordered spin ice state. As shown in ref [22], a quadratic distortion corresponding to an energy scale $D_Q = 0.2$ K can account for the canting angle $\alpha = 13°$, still unexplained. One naturally expects this distortion to increase under stress. This could explain both the increase of the canting angle in the F structure, (a distortion $D_Q = 0.4$ K yields $\alpha = 26°$ close to the experimental value), and the onset of the AF structure.

The pressure induced tunability of TTO and its strong spin lattice coupling allow one to consider it as a "soft" spin ice, contrary to model spin ices. In Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ magnetic correlations are insensitive to pressure down to 1.4 K and up to 6 GPa [23], although their high field magnetization is slightly decreases under uniaxial pressure [24] and isotropic pressure may tune the charge of the magnetic monopoles [25].

In conclusion, we have shown that applying pressure in Tb$_2$Sn$_2$O$_7$ allows one to destabilize the ordered spin ice state and induce spin liquid and antiferromagnetic orders. This onset occurs through two different mechanisms, which evidence the effect of isotropic compression on the energy balance of magnetic interactions, and the influence of pressure induced distortion on the magnetic exchange, respectively.

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[1] S. T. Bramwell et al. Phys. Rev. Lett. 87, 047205 (2001).
[2] S. T. Bramwell, M. J. P. Gingras Science 294, 1495 (2001).
[3] A. P. Ramirez, A. Hayashi, R.J. Cava, R. Siddharta, B. S. Hasting, Nature 399, 333 (1999).
[4] M. J. P. Gingras et al. Phys. Rev. B 62, 6496 (2000).
[5] I. Mirebeau, P. Bonville, M. Hennion Phys. Rev. B. 76, 184436 (2007).
[6] I. Mirebeau et al. Phys. Rev. Lett. 94, 246402 (2005).
[7] F. Bert et al. Phys. Rev. Lett. 97, 117203 (2006).
[8] P. Dalmas de Réotier et al. Phys. Rev. Lett. 96, 127202 (2006).
[9] K. C. Rule et al. Phys. Rev. B 76, 212405 (2007).
[10] Y. Chapuis et al. J. Phys. Cond. Mat. 19, 446206 (2007).
[11] I. Mirebeau et al. Phys. Rev. B 78, 174416, (2008).
[12] S. R. Giblin et al. Phys. Rev. Lett. 101, 237201 (2008).
[13] J. S. Gardner et al. Phys. Rev. Lett. 82, 1012, (1999).
[14] H. R. Molavian, M. J. P. Gingras, and B. Canals, Phys. Rev. Lett. 98, 157204 (2007).
[15] R. S. Kumar et al., Appl. Phys. Lett. 88, 031903 (2006).
[16] A. Apetrei, I. Mirebeau, I. Goncharenko and W. Crichton, J. Phys. Cond. Mat. 19, 376208 (2007).
[17] I. Mirebeau et al. Nature 420, 54 (2002).
[18] I. Mirebeau, I. N. Goncharenko, G. Dhallene and A. Revcolevski, Phys. Rev. Lett. 93, 187204 (2004).
[19] I. N. Goncharenko, High Press. Res. 24, 193 (2004).
[20] J. E. Greedan, J. N. Reimers, C. V. Stager and S. L. Penny, Phys. Rev. B 43, 5682 (1991).
[21] F. Bert et al. Phys. Rev. Lett. 99, 237202, (2007).
[22] K. C. Rule and P. Bonville J. of Phys., Conf. Series, 145, 012027 (2009); P. Bonville et al. unpublished.
[23] I. Mirebeau and I. N. Goncharenko. Physica B 350, 250, (2004).
[24] M. Mito et al., J. Mag. Mag. Mat. 310, e432, (2007).
[25] C. Castelnovo, R. Moessner, S. L. Sondhi, Nature 451, 44, (2008).