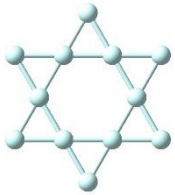
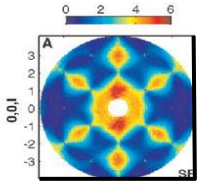
Orphée
Laboratoire Léon Brillouin

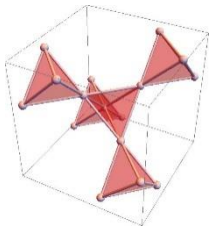
SQL workshop, Budapest 2025

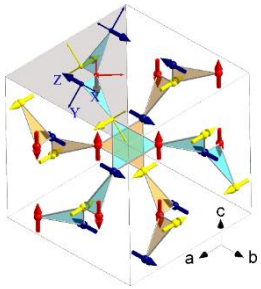
High entropy materials as a platform to explore frustrated magnets

F. Damay









ICMMO

F. Vayer, C. Decorse, D. Bérardan, N. Dragoe
(powder samples synthesis and characterizations)

LLB

S. Petit
(INS, modelling)

ILL

C. Colin (D1B)
S. Rols (Panther)

PSI

J. Embs (Focus)

Institut Néel

E. Lhotel
(LT magnetisation measurements)

Pyrochlores synthesis, an old story

$A_2B_2O_7$

rare earth ion (RE^{3+})
dodecahedral site

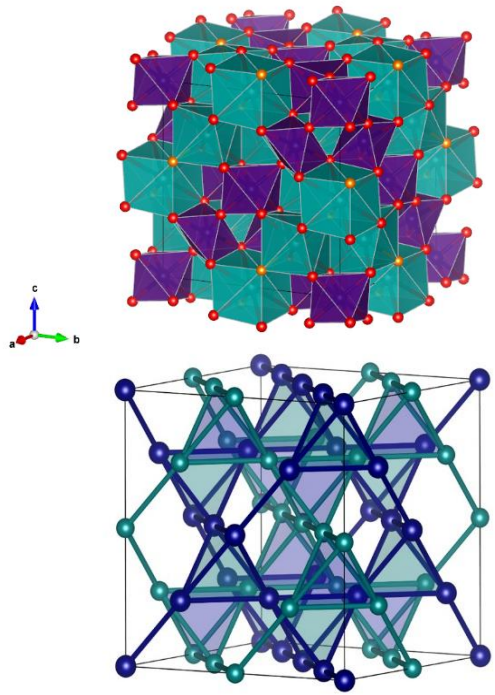
tetravalent cations (B^{4+})
octahedral site

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La /Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

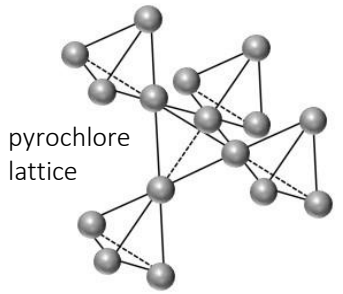
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

limited to A^{3+}/B^{4+}

Gd site A Ti site B Ge site B (under pressure)



A and B pyrochlore lattices



pyrochlore lattice

Stability criterion
$1.46 \leq r_A/r_B \leq 1.78$

- $r_A/r_B \leq 1.46$ fluorite + vacancies
- $r_A/r_B \geq 1.78$ other structures

Quite a flexible structure!
Many compositions possible…
…but most have been investigated

M.A. Subramanian, *Prog. Solid St. Chem*, **15**, 55-143 (1983). F. Vayer, *thèse de doctorat de l'Université Paris-Saclay* (2023). C. Decorse, *Habilitation à diriger des recherches* (2024).

Disorder – an original tool to design new materials

In 2004, first high-entropy alloys (at least 5 cations on a given crystallographic site)

Free enthalpy of formation

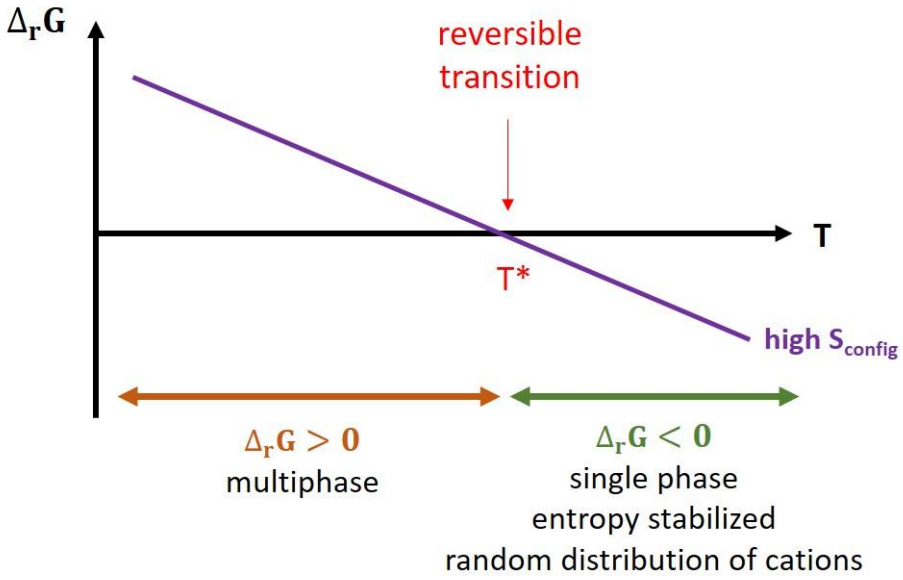
$$\Delta G = \Delta H - T\Delta S$$

$\Delta H < 0$

Classical route

$\Delta H > 0$

Classical route fails
Stabilisation possible through the $T\Delta S$ term ($\Delta G < 0$ at high T, METASTABLE at RT)



High Entropy compounds ($\Delta s_{config} = R\ln(N) \geq 1.61R$)
Entropy Stabilized compounds ($T\Delta S > \Delta H$)

★ disorder(s) and cocktail effect
★ stabilization of unusual geometries/valencies/structures

Very large range of
NEW compounds
NEW unexpected properties

Cantor *et al.*, Mater. Sci. and Eng. **A : 375-377** (2004)
Yeh *et al.*, Adv. Eng. Mater. **6** (2004)
Rost *et al.*, Nat. Commun. **6** (2015)

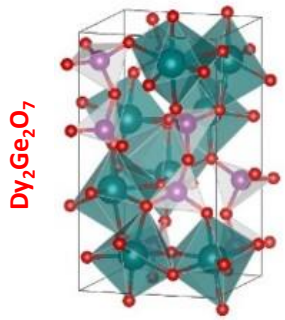
Entropy-stabilized pyrochlores

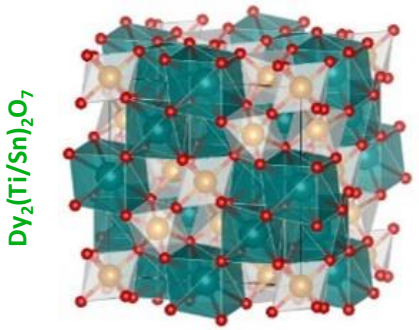
Design of an entropy-stabilized compounds with a pyrochlore structure

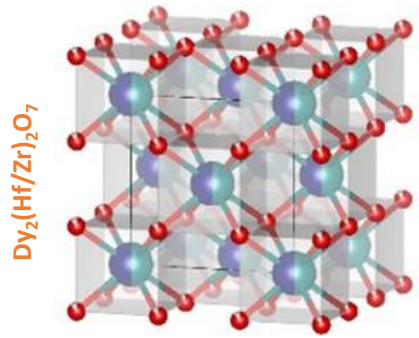
Some criteria

- preserve the A lattice, HEOx on the B site
- not the same structure/coordination in the parent compounds
- $r_{(avg)B}$ in the pyrochlore structure stability range
- equimolar mixture on B
- (*isovalent and non-magnetic cations to start with*)

Parent compound	r_B	r_A/r_B	Structure	Magnetic behaviour
$Dy_2Ge_2O_7$	0,53	1,94	tetragonal or pyrochlore*	- spin ice
$Dy_2Ti_2O_7$	0,605	1,70	pyrochlore	spin ice
$Dy_2Sn_2O_7$	0,69	1,49	pyrochlore	spin ice
$Dy_2Hf_2O_7$	0,71	1,45	fluorite	-
$Dy_2Zr_2O_7$	0,72	1,43	fluorite	-
$Dy_2(TiZrHfGeSn)_2O_7$ (equimolar mixture on B site)	$r_{(avg)B}$ 0,651	1,58	?	?







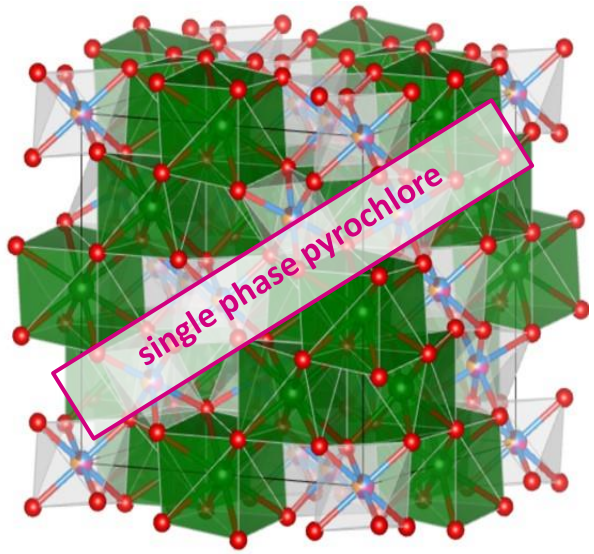
F. Vayer, *thèse de doctorat de l'Université Paris-Saclay* (2023). C. Decorse, *Habilitation à diriger des recherches* (2024)

Entropy-stabilized pyrochlores

Synthesis at sufficiently high T (1600 °C) + quenching

1st entropy stabilized pyrochlore : $Dy_2(TiZrHfGeSn)_2O_7$

- single phase compound
- reversible transition between single phase HT and multiple phases at LT proves the entropy stabilization



$A_2B_2O_7$	a (Å)	T_{freeze} (K)	Ground state
$Dy_2Ge_2O_7$	9,93	0,83	spin ice
$Dy_2Ti_2O_7$	10,10	1,2	spin ice
$Dy_2(TiZrHfGeSn)_2O_7$	10,30	?	? in progress!
$Dy_2Sn_2O_7$	10,40	1,2	spin ice

Robustness of the spin ice ground state in Dy pyrochlores

This new route offers rich perspectives for the design of original materials

- possibility to extend to all REs by changing the cations mixture
- multiplication of possibilities using mixtures of alliovalent cations

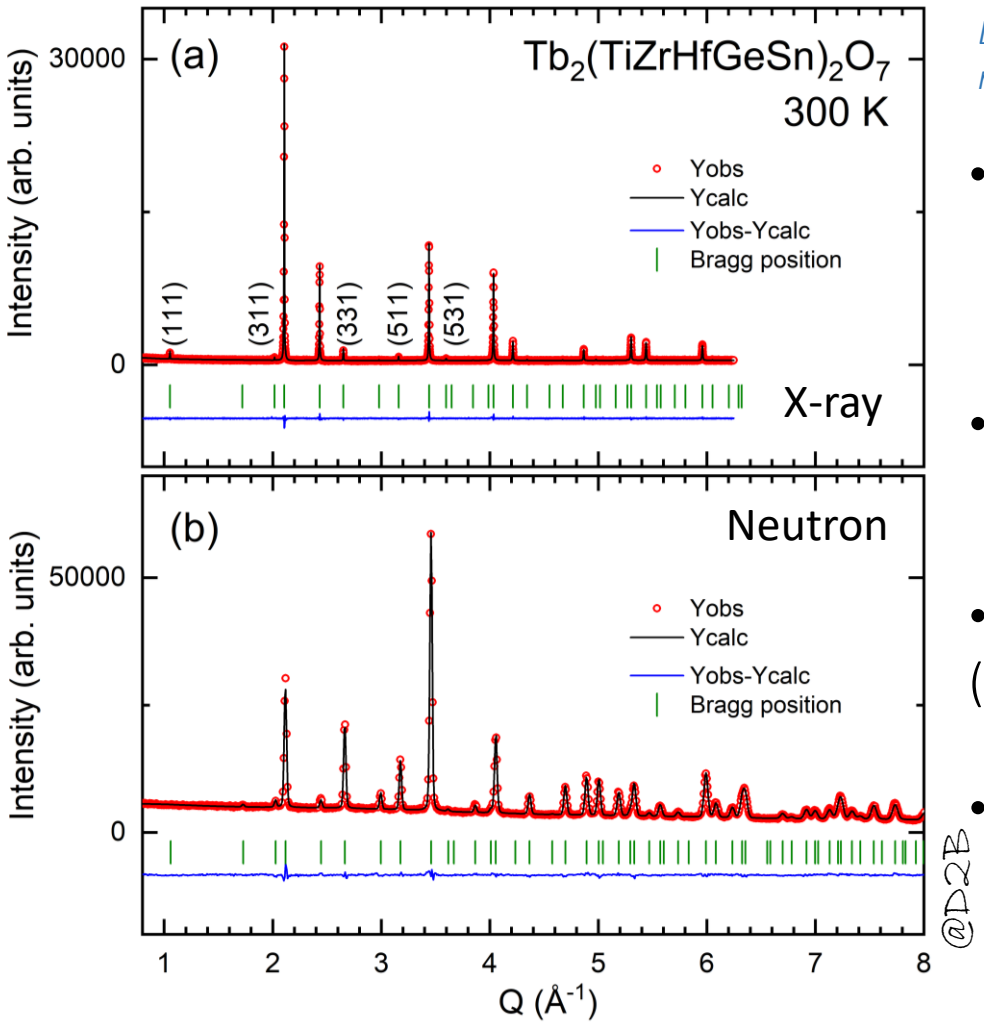
$...Nd_2(TiZrHfScNb)_2O_7$ | $Tb_2(TiZrHfGeSn)_2O_7$

New hints on the enigmatic ground state of $Tb_2Ti_2O_7$?

F. Vayer, *thèse de doctorat de l'Université Paris-Saclay* (2023). C. Decorse, *Habilitation à diriger des recherches* (2024)

$Tb_2(Ti_{0.2}Zr_{0.2}Hf_{0.2}Ge_{0.2}Sn_{0.2})_2O_7$
Entropy-stabilized pyrochlore

Crystal structure characterizations



Tb on the A-site of the pyrochlore structure

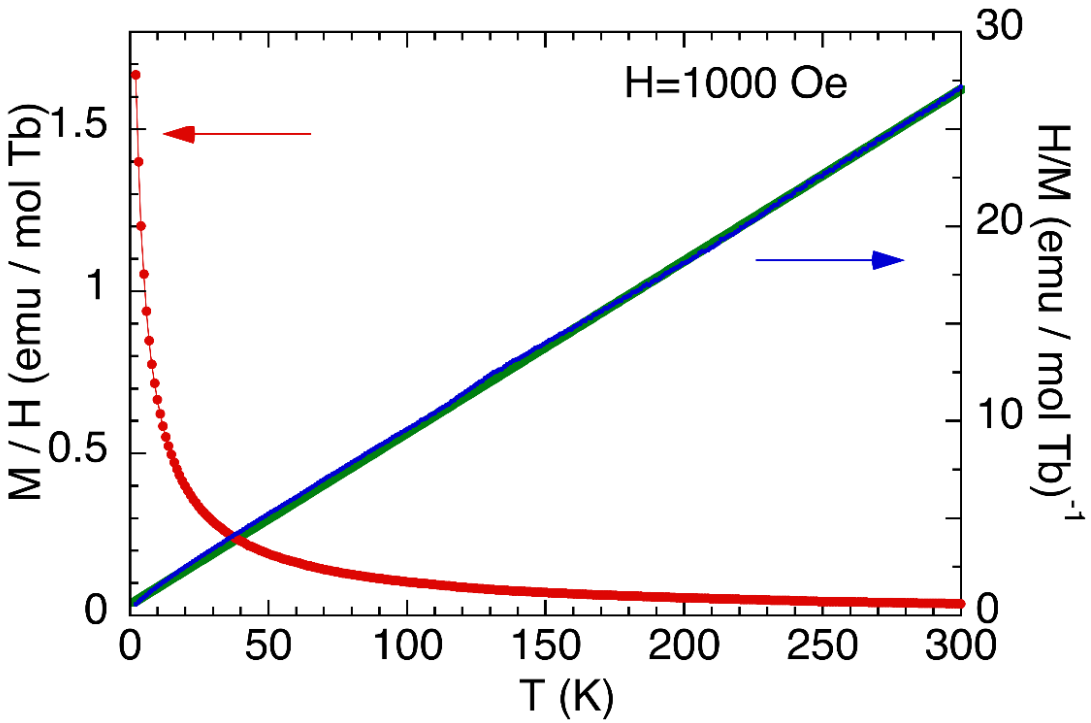
Disorder introduced on the B site with 5 non-magnetic cations (Ti^{4+}, Zr^{4+}, Hf^{4+}, Ge^{4+} and Sn^{4+})

- **Single phase cubic *Fd-3m***
  a = 10.3287(10) Å at RT
  Confirmed stoichiometry
- **Debye-Waller** parameter large on O (> 1 Å^2) - position disorder
- **Antisite** (RE <-> B) disorder possible (as *b* for Tb, Hf, Ti are similar)
- **No broadening**, or short range structural disorder signature

F. Vayer et al., Communications Materials | (2024) 5:162

$Tb_2(Ti_{0.2}Zr_{0.2}Hf_{0.2}Ge_{0.2}Sn_{0.2})_2O_7$
Entropy-stabilized pyrochlore

Magnetization measurements

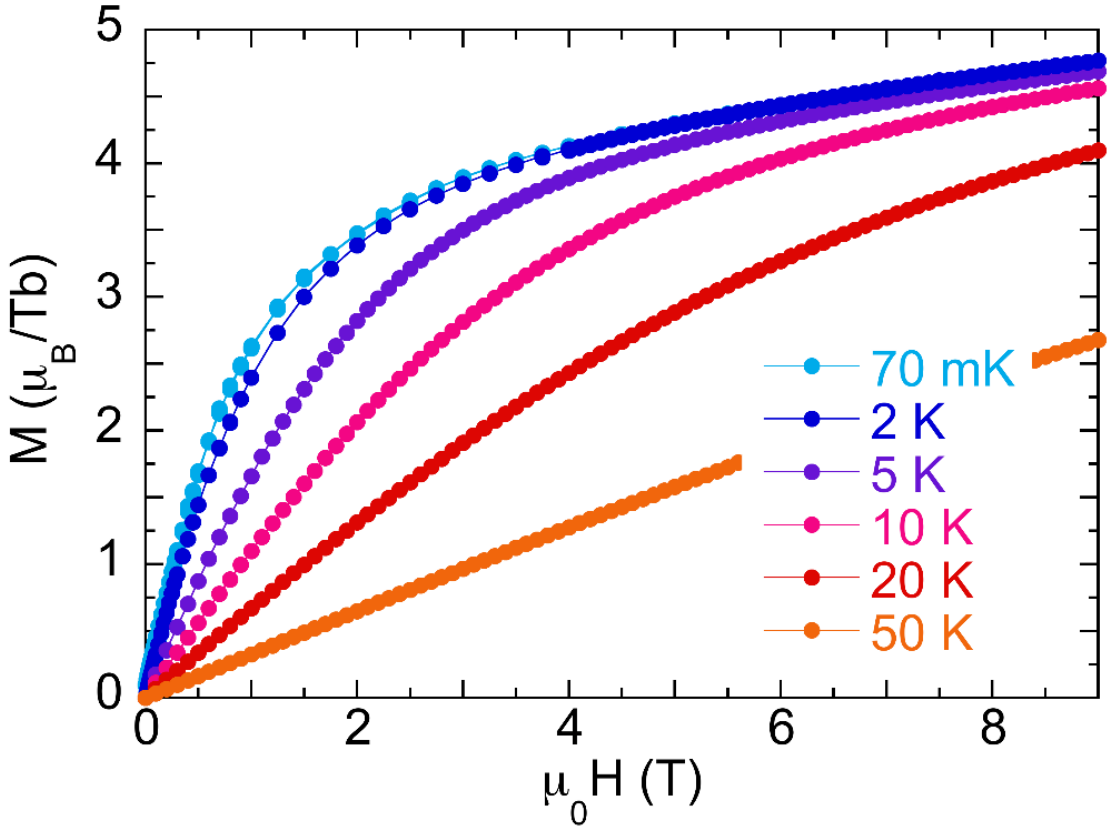


- No ordering down to 2 K
  Almost linear behaviour above 20 K, like in other Tb pyrochlores
- θ_{CW} = -6.4 K (≈ Tb_2ScNbO_7), M_{eff} = 9.5 μ_B ($g_J J$ = 9 μ_B for Tb^{3+})

$$\theta_{CW} = \theta_0 + \theta_{CW}^{CEF}, \text{ if } \theta_{CW}^{CEF} \approx -6 \text{ K}, \theta_0 \approx -0.5 \text{ K}$$

Weak AFM interactions

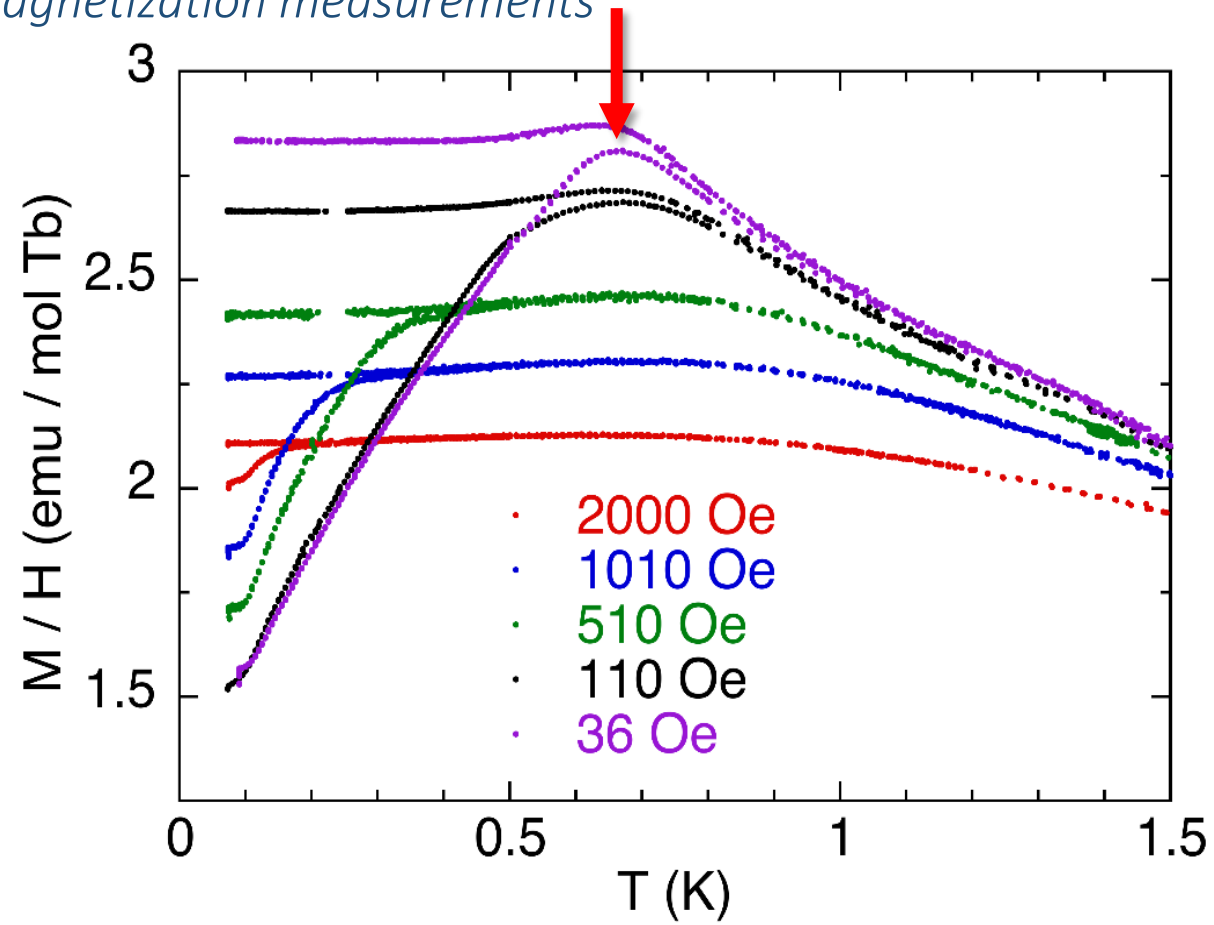
Magnetization measurements



- No saturation in 70 mK, 9 T
- $M_{max} \approx 4.75\ \mu_B$/Tb, like $Tb_2Ti_2O_7$ or $Tb_2Nb_2O_7$

$Tb_2(Ti_{0.2}Zr_{0.2}Hf_{0.2}Ge_{0.2}Sn_{0.2})_2O_7$
Entropy-stabilized pyrochlore

Zfc-fc magnetization measurements



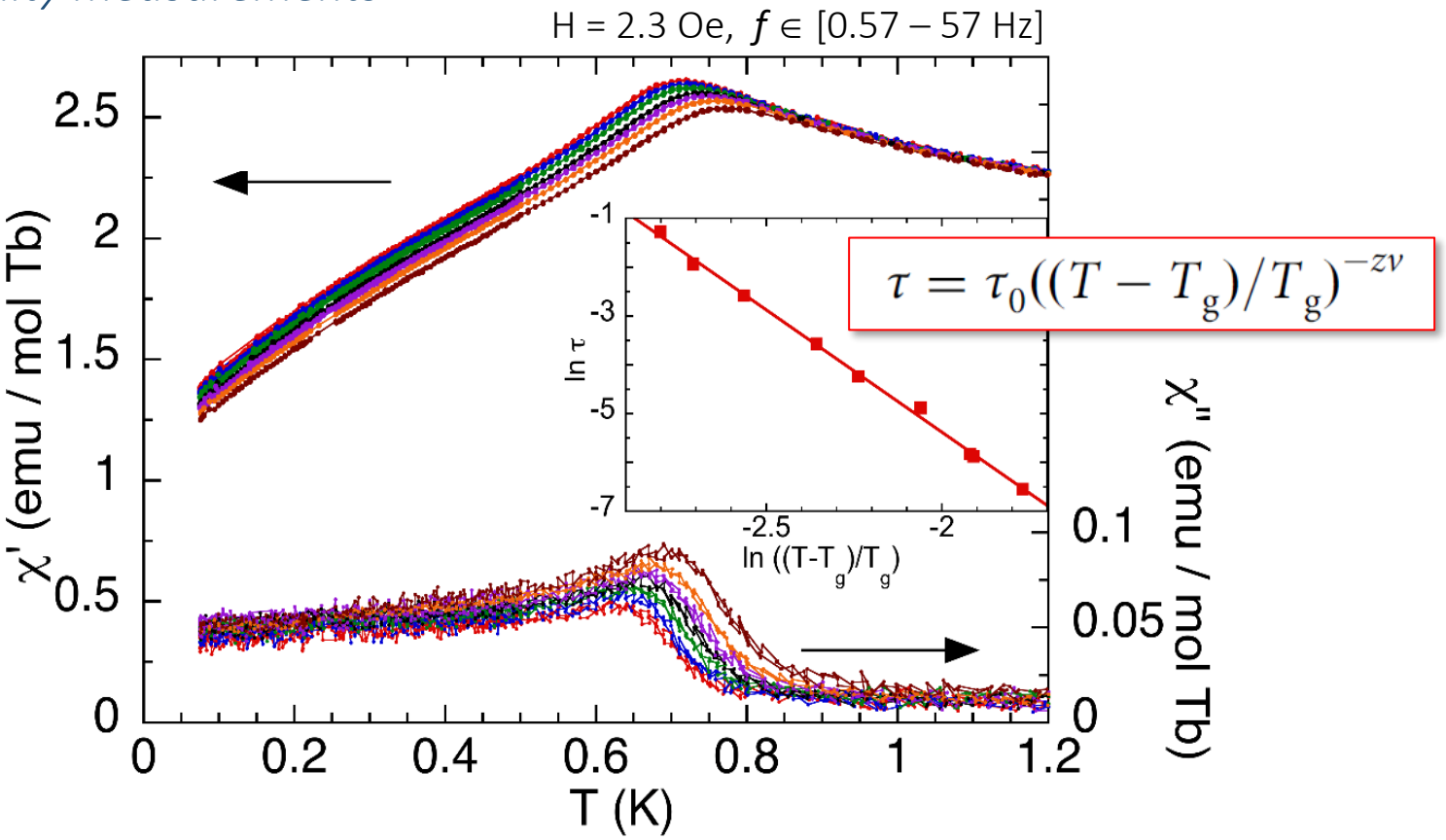
- Maximum a T ≈ 0.65 K, irreversibility ≈ 0.8 K
- Broadening when H increases, irreversibility suppressed for H > 0.5 T

→ Spin freezing, r ≈ 50 % (r = 1-M_{ZFC}/M_{FC})

like Tb_2ScNbO_7

$Tb_2(Ti_{0.2}Zr_{0.2}Hf_{0.2}Ge_{0.2}Sn_{0.2})_2O_7$
Entropy-stabilized pyrochlore

Ac susceptibility measurements

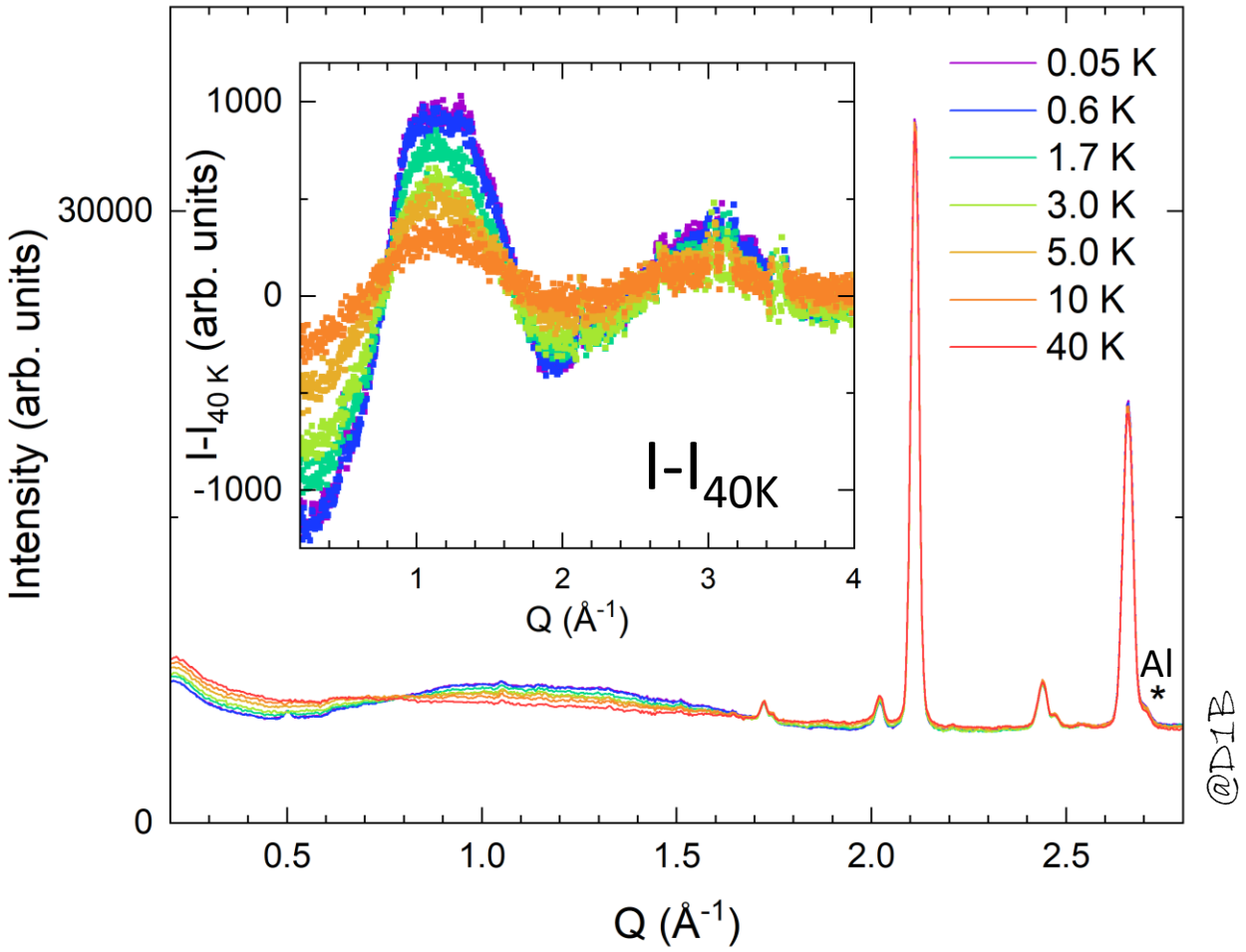


- Frequency dependence of χ' and χ''
- Described by a scaling law
- Similar parameters in other disordered Tb pyrochlores ($Tb_2Hf_2O_7$ and Tb_2ScNbO_7)

$\tau_0 = 2.10^{-7} \pm 5.10^{-8}$ s, $T_g = 0.675 \pm 0.05$ K and $zv = 5 \pm 1$

$Tb_2(Ti_{0.2}Zr_{0.2}Hf_{0.2}Ge_{0.2}Sn_{0.2})_2O_7$
Entropy-stabilized pyrochlore

Neutron powder diffraction

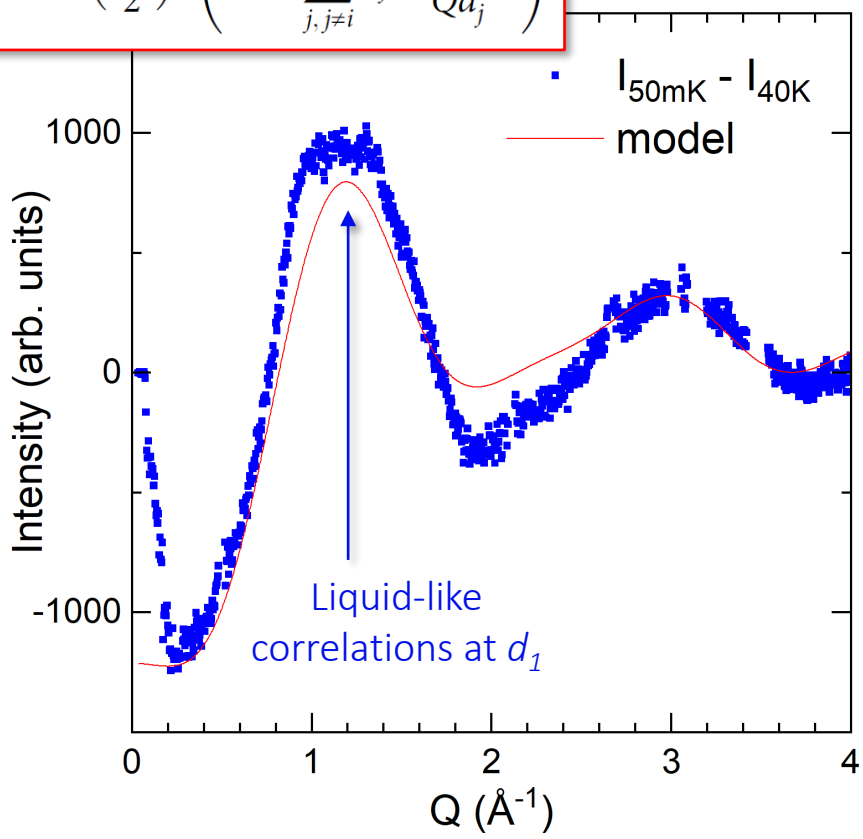


- No long range ordering down to 50 mK
- Strong diffuse scattering signal

$Tb_2(Ti_{0.2}Zr_{0.2}Hf_{0.2}Ge_{0.2}Sn_{0.2})_2O_7$
Entropy-stabilized pyrochlore

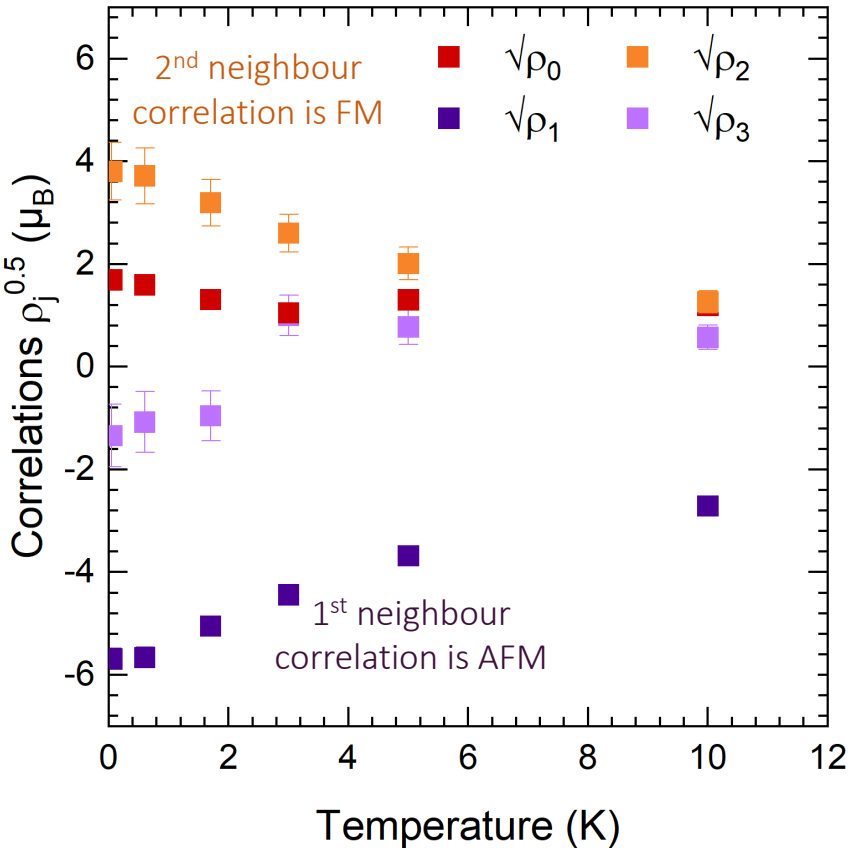
Correlated spin modelling of the magnetic diffuse scattering

$$I_M = N\left(\frac{\gamma r_0}{2}\right)^2 \left(\rho_0 + \sum_{j,j\neq i} \rho_j \frac{\sin(Qd_j)}{Qd_j}\right)$$



General shape of the diffuse scattering reproduced by the modelling

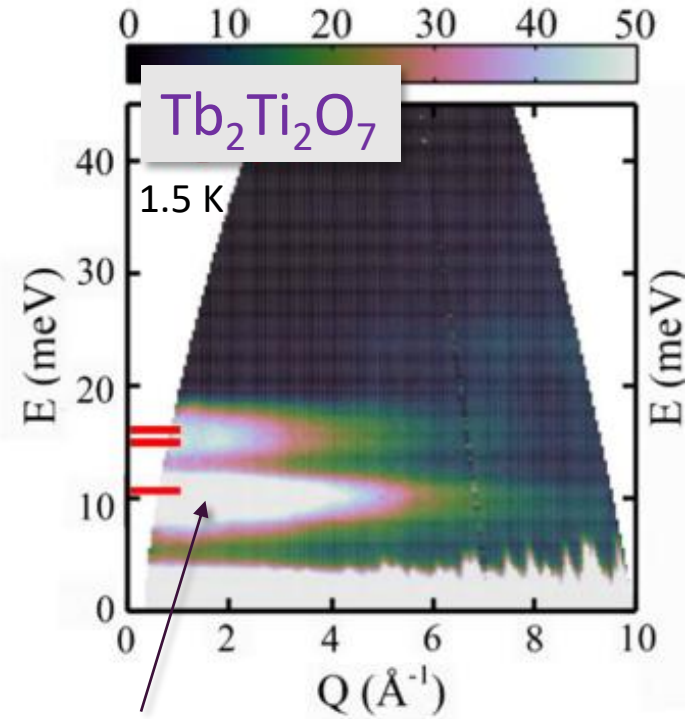
Evolution with T of the correlated moments



Similar diffuse scattering features to $Tb_2Ti_2O_7$

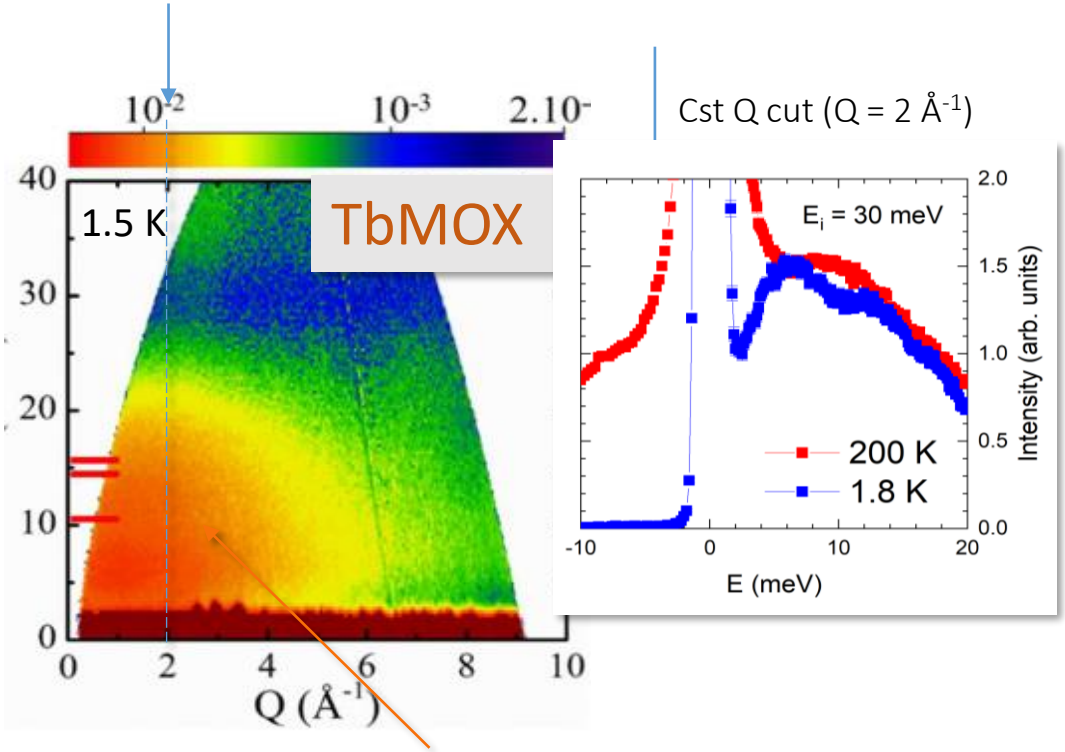
$Tb_2(Ti_{0.2}Zr_{0.2}Hf_{0.2}Ge_{0.2}Sn_{0.2})_2O_7$
Entropy-stabilized pyrochlore

Probing CEF excitations by inelastic neutron scattering (0 – 40 meV)



Several discrete and flat levels below 20 meV*

*Ruminy, Magnetoelastic effects in rare earth Titanate Pyrochlores, Thèse de Doctorat, ETH Zurich, (2016).

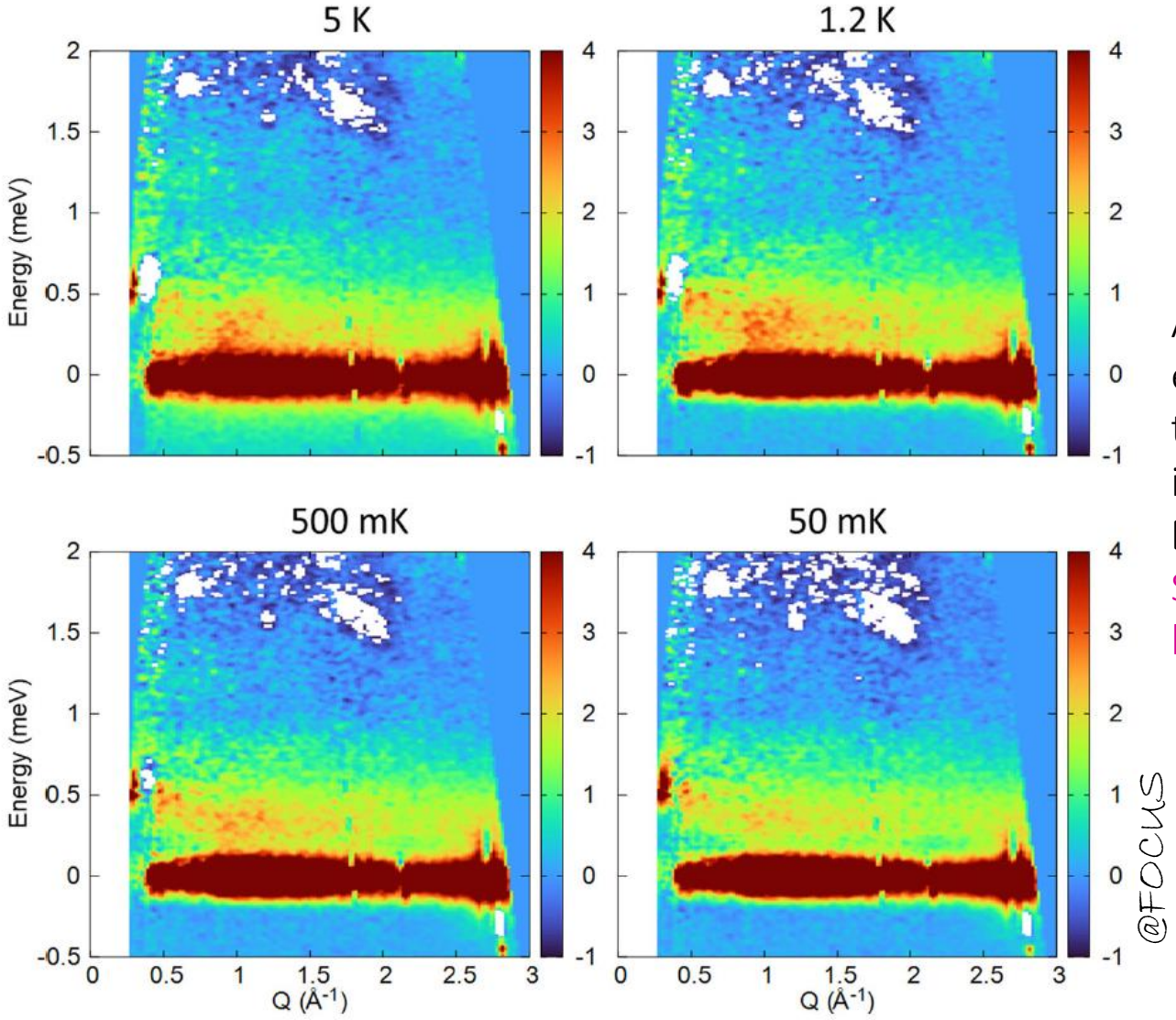


Broad signal between 4 and 40 meV
Reflects the distribution of oxygen positions around Tb ions

@Panther

$Tb_2(Ti_{0.2}Zr_{0.2}Hf_{0.2}Ge_{0.2}Sn_{0.2})_2O_7$
Entropy-stabilized pyrochlore

Probing CEF excitations by inelastic neutron scattering (0 – 2 meV)



At low E, a quasi elastic signal transforms into an inelastic flat level at
E ≈ 0.37 meV
Strikingly **narrow** level (Γ = 0.25 meV)

$Tb_2(Ti_{0.2}Zr_{0.2}Hf_{0.2}Ge_{0.2}Sn_{0.2})_2O_7$
Entropy-stabilized pyrochlore

Modelling (CEF part)

Stevens parameters

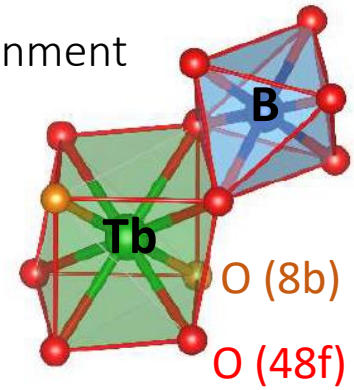
Stevens operators

CEF Hamiltonian $$H_{CEF} = \sum_{n,m} B_{n,m} O_{n,m}$$

For a pyrochlore A site (D_{3d} symmetry) : B_{20}, B_{40}, B_{43}, B_{60}, B_{63}, B_{66} only are non zero

Simple approach to estimate B_{nm} : the point charge model

Tb environment
D_{3d}



To model B-site entropy : oxygen coordinates are shifted by an isotropic shift parameter δ, away from their actual values.

δ ≈ Debye-Waller parameter

Importantly : random δ on the 8 oxygen atoms introduce a symmetry breaking of the local D_{3d} symmetry.
All B_{nm} now allowed, D_{3d} symmetry fulfilled only in average

Using the point charge approximation, CEF enery levels and corresponding neutron scattering spectrum can be calculated vs δ

Modelling (magnetic interactions part)

Magnetic diffuse scattering implies magnetic interactions between Tb moments :

$$\mathcal{H}_{mag} \approx \sum_{<i,j>} g^{zz} I_i^z I_j^z$$

Owing to the non-Kramers nature of the Tb^{3+} ions

z // <111>, g^{zz} the magnetic coupling

To keep the approach simple, a mean field approximation is used, involving a local molecular field H

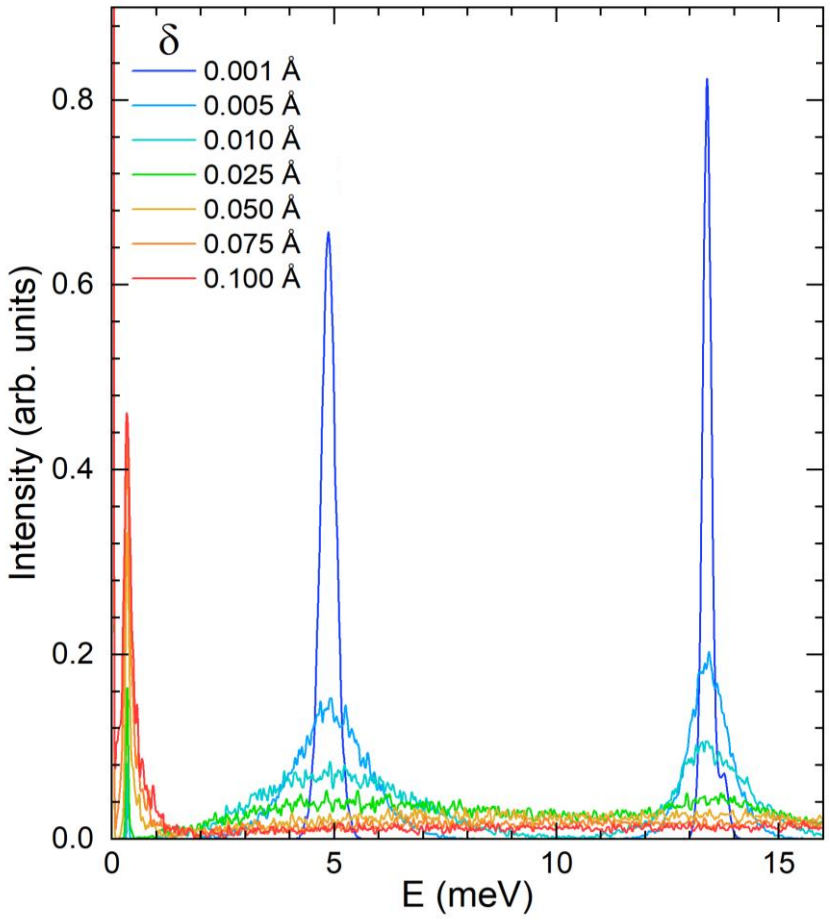
Modelling (CEF + magnetic interactions)

$$\mathcal{H} \approx \mathcal{H}_{CEF} + HI_i^z$$

This model only has two parameters, the molecular field H and the oxygen position shift δ

Modelling (CEF + magnetic interactions)

Calculations CEF spectra vs. δ for H = 0.45 K



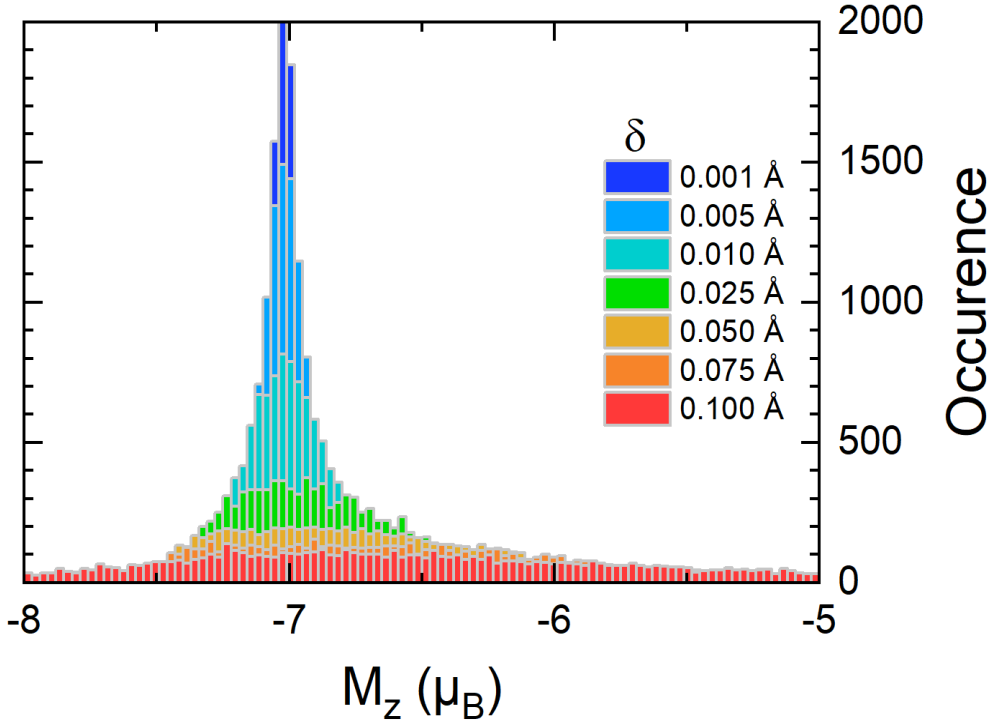
H = 0.45 K leads to a split ground state with a first level at 0.4 meV

- With increasing δ (disorder), clear broadening of the CEF levels at high energy
- Spectral weight of the low E mode (at 0.4 meV) is zero if δ = 0
- Spectral weight of 0.4 meV mode increases with increasing δ, without broadening or E shift

Disorder must be present to visualize this mode!

Modelling (CEF + magnetic interactions)

Distribution of moment value vs. δ for H = 0.45 K



The distribution of Tb^{3+} moment values broadens also with δ, but remains peaked around 7 μ_B up to δ = 0.05 Å.

Nearly uniform distribution of local moments!

This simple modelling reproduces rather well experimental findings!

Can we go further….?

More complex modelling……introducing quadrupole interactions

In $Tb_2Ti_2O_7$, quadrupolar interactions are a key ingredient to the understanding of the ground state

A simplified way to tackle quadrupolar interactions is to use a projection of the Hamiltonian on a subspace formed by the two states ↑ and ↓ of a pseudo spin ½ (σ_i). This approach only works for the ground doublet, which is the one of interest here. At the mean field level :

$$\mathcal{H}' \approx \sum_i h\sigma_i^z + \sum_i h_\perp \sigma_i^x$$

Longitudinal molecular field due to magnetic interactions

Transverse effective field

$$h_\perp = (\bar{h}_\perp + \delta h_\perp)$$

Quadrupole -quadrupole interactions

Net effect of random deviations out of D_{3d} symmetry

The *z* component of the pseudo spin is directly related to the local magnetic moment M_z

$$M_z = g_J \langle I_i^z \rangle \approx 7\,\mu_B,$$

More complex modelling……introducing quadrupole interactions

Diagonalization of $\mathcal{H}'$ shows that there are two eigenstates separated by :

$$\Delta = \sqrt{h^2 + h_\perp{}^2}$$

Corresponding neutron spectrum :

$$S(\omega) \approx \mu^2/4 \left\{ \frac{h^2}{h^2 + h_\perp{}^2} \delta(\omega) + \frac{h_\perp{}^2}{h^2 + h_\perp{}^2} \delta(\omega - \Delta) \right\}$$

Complementary spectral weight — Elastic — Inelastic

Peak at finite Δ whose spectral weight depends on $h_\perp$

Physical understanding of the low energy peak and its behaviour with δ

$Tb_2(Ti_{0.2}Zr_{0.2}Hf_{0.2}Ge_{0.2}Sn_{0.2})_2O_7$
Entropy-stabilized pyrochlore

More complex modelling……introducing quadrupole interactions

Approximations

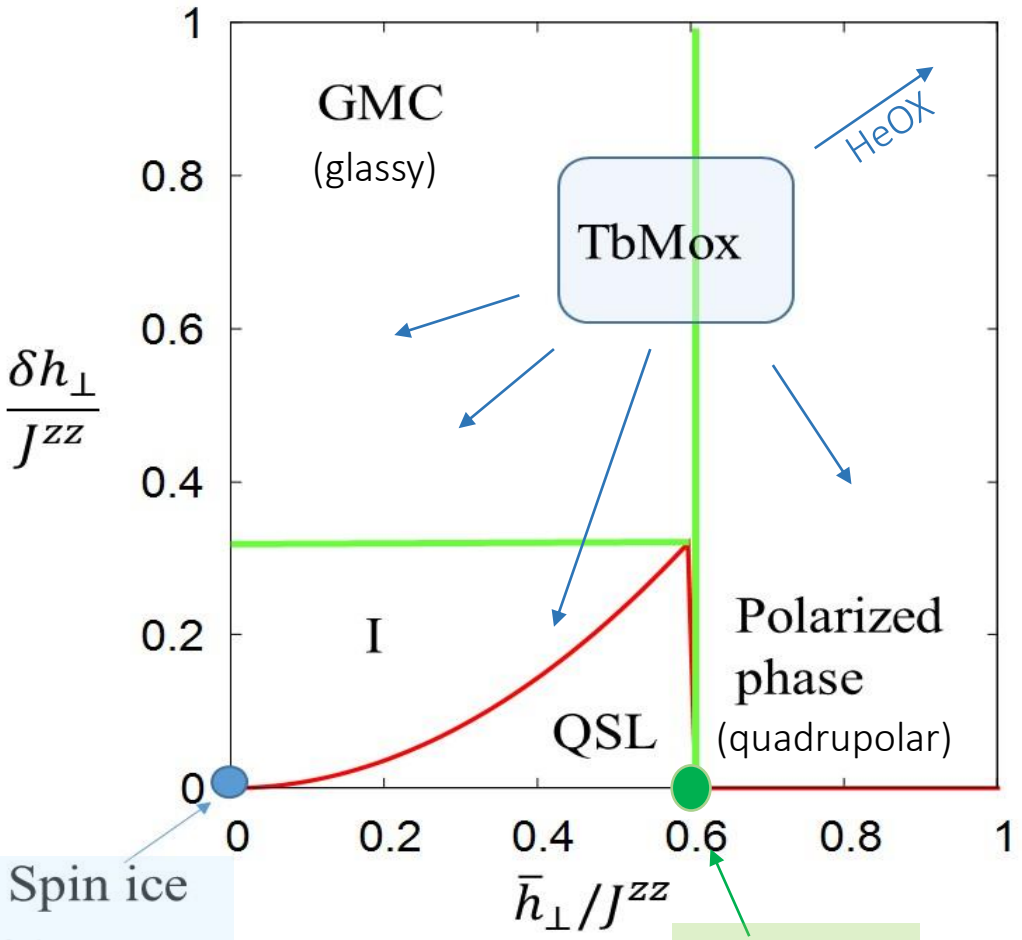
$\Delta = \sqrt{h^2 + h_\perp{}^2}$ = 0.37 meV

$\delta h_\perp$ = 0.25 meV ($\approx \Gamma$)

$h \approx J^{zz} \approx$ 0.32 meV ($\sqrt{\rho_1} = 6\,\mu_B$)

$$\frac{\delta h_\perp}{J^{zz}} \sim 0.8, \frac{\bar{h}_\perp}{J^{zz}} \sim 0.6$$

Disorder and quadrupolar effects of same order of magnitude



Spin ice

$\bar{h}_\perp = \delta h_\perp = 0$

(?) $Tb_2Ti_2O_7$

Benton et al., *Phys. Rev. Letters* **121**, 037203 (2018)
Savary et al., *Phys. Rev. Letters* **118**, 087203 (2017)

Conclusions

- A new, entropy-stabilized terbium pyrochlore!
- Like in $Tb_2Ti_2O_7$: AF interactions and a narrow low energy flat mode

- Compositional disorder leads to random shifts of oxygen atoms

- Disorder
  - does not impact Tb^{3+} magnetic moment
  - broadens high energy CEF levels
  - increases low energy excitation mode intensity

- **High entropy provides a tunable and smooth disorder : promising to achieve QSL phases!**

F. Vayer et al., Communications Materials | (2024) 5:162

Thank you for your attention!