Geometrical frustration, phase transitions and dynamical order

The $Tb_2M_2O_7$ compounds (M = Ti, Sn)

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GRENOBLE 1

Outline

1. Introduction
2. The $Tb_2M_2O_7$ compounds (M = Ti, Sn)
3. $Tb_2Ti_2O_7$: sample study
4. Crystal field levels
5. Conclusions

Outline

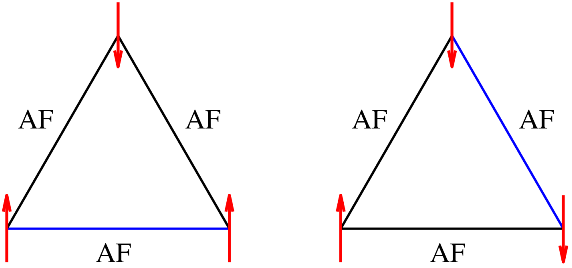
1. Introduction
   - geometrical frustration
   - connectivity and degeneracy
   - spin ice
2. The $Tb_2M_2O_7$ compounds (M = Ti, Sn)
3. $Tb_2Ti_2O_7$: sample study
4. Crystal field levels
5. Conclusions

Introduction

geometrical frustration

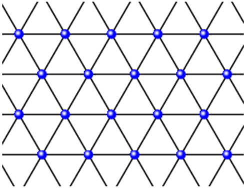
- impossibility to satisfy simultaneously all the magnetic interactions
- frustration index : $f = |\theta_{CW}| / T_{\mathrm{c}}$; frustration if $f \gtrsim 5$
  θ_{CW} : Curie-Weiss temperature
  T_{c} : transition temperature

- example of 2D Ising antiferromagnets

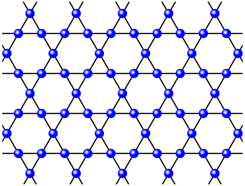


Introduction
geometrical frustration

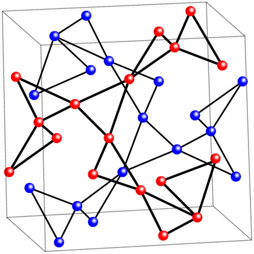
- triangular lattice



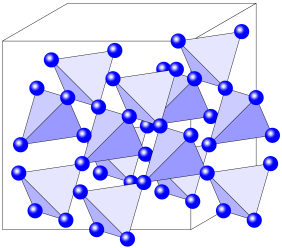
- Kagomé lattice

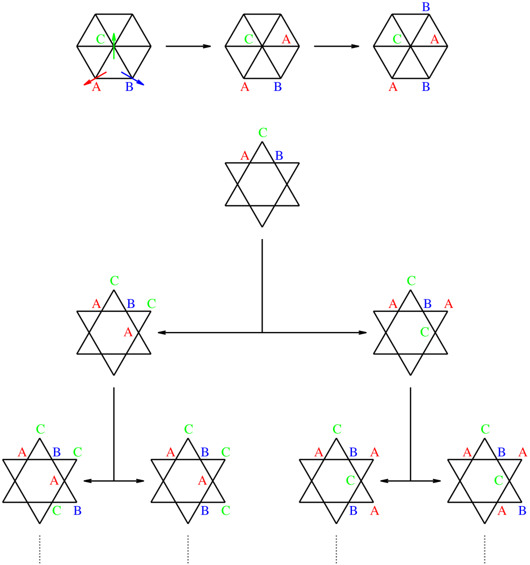


- garnet lattice



- pyrochlore lattice

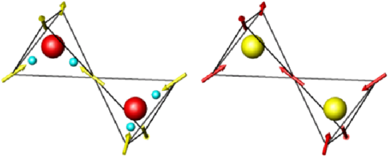




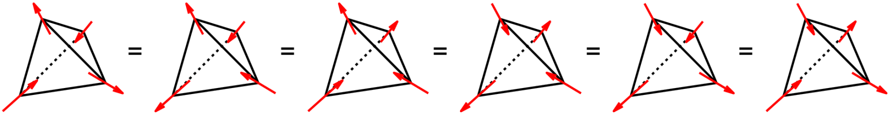
low connectivity
=
large degeneracy

Introduction
spin ice

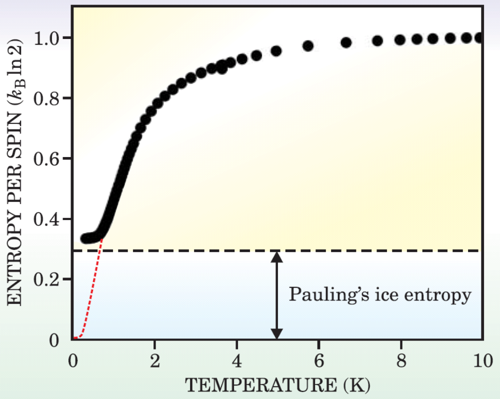
- water ice (on the left) and spin ice (on the right) : analogy between protons displacement vectors and magnetic moments



- water ice = each oxygen with two protons close and two protons away (Pauling)
- spin ice = two spins in, two spins out → six equivalent configurations



entropy of the spin ice compound $Dy_2Ti_2O_7$



source : Moessner and Ramirez, Physics Today 2006

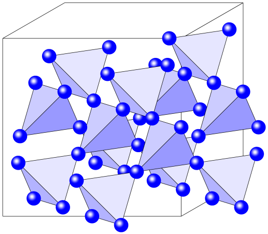
→ non vanishing entropy for $T \to 0$

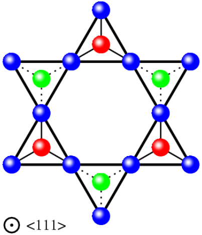
Outline

The $Tb_2M_2O_7$ compounds (M = Ti, Sn)

the pyrochlore structure

- on the left : pyrochlore structure = three dimensional arrangement of corner-sharing tetrahedra
- on the right : projection of the pyrochlore structure on the (111) plane



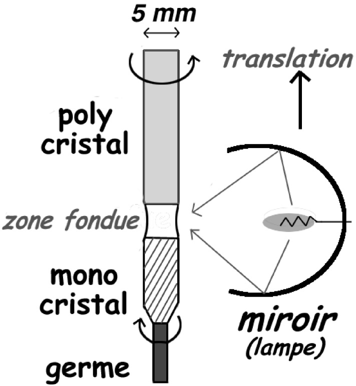


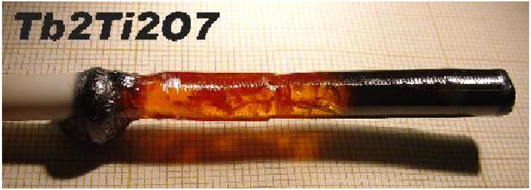
space group $Fd\bar{3}m$

compounds	lattice parameter
$Tb_2Ti_2O_7$	10.149 Å
$Tb_2Sn_2O_7$	10.426 Å

The $Tb_2M_2O_7$ compounds (M = Ti, Sn)

general points : $Tb_2Ti_2O_7$



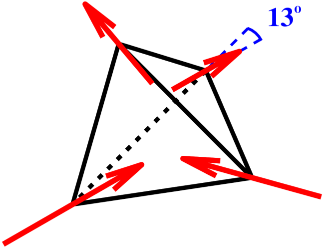


Christophe Marin
(CEA-Grenoble/Inac/SPSMS)

- Curie-Weiss temperature $\theta_{\mathrm{CW}} = -18.4(5)$ K (AF interactions)
- no obvious magnetic transition
- frustration index $f \to \infty$

- Curie-Weiss temperature $\theta_{\rm CW} = -12$ K (AF interactions)

  Matsuhira *et al.*, J. Phys. Soc. Jpn. **71** (2002)
- magnetic transition at $T_{\rm c} = 0.88(1)$ K
- frustration index $f \simeq 14$



neutron diffraction :
→ ordered spin ice
→ magnetic moments with both ferro and antiferromagnetic components

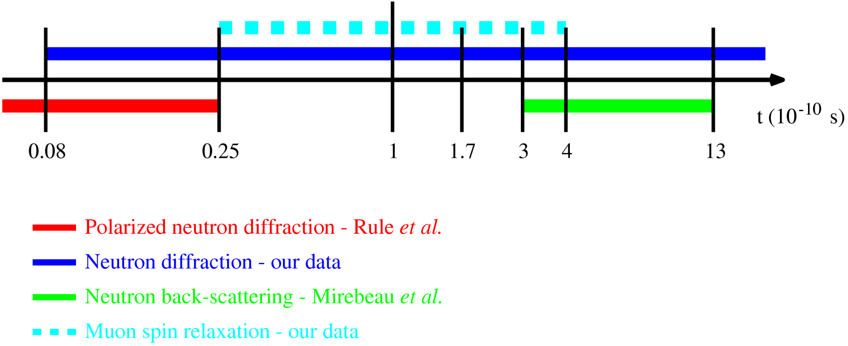
Mirebeau *et al.*, Phys. Rev. Lett. **94** (2005)

Dalmas de Réotier *et al.*, Phys. Rev. Lett. **96** (2006)

The $Tb_2M_2O_7$ compounds (M = Ti, Sn)

general points : $Tb_2Sn_2O_7$

fluctuation times in the ordered phase

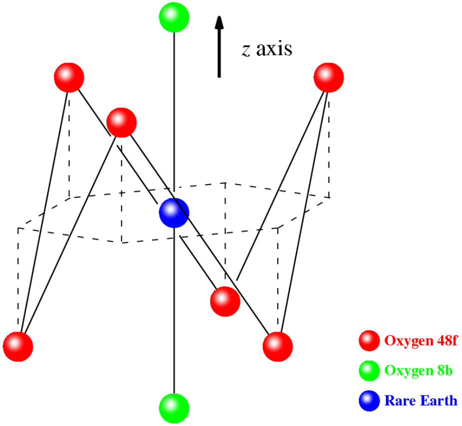


+ no relaxation in our neutron spin echo data (IN11 at ILL) : $\tau > 10^{-8}$ s

→ complex spin dynamics mechanism characterized by different fluctuation times : static at low Q and dynamic at high Q ?

The $Tb_2M_2O_7$ compounds (M = Ti, Sn)

Tb environment

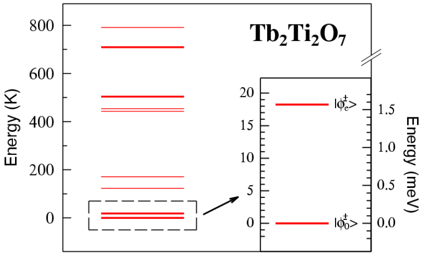


- spin angular momentum : $S = 3$
- orbital angular momentum : $L = 3$
- total angular momentum : $J = 6$
- Landé factor : $g_J = 3/2$

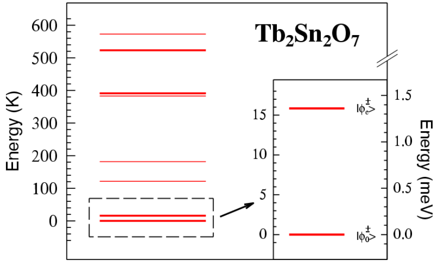
	d_{8b} (Å)	d_{48f} (Å)
$Tb_2Ti_2O_7$	2.197	2.502
$Tb_2Sn_2O_7$	2.257	2.517

with d the distance between the oxygen and the rare earth trigonal symmetry with main axis ∥ to ⟨111⟩ (local symmetry ≡ $\bar{3}m$)

$$\mathcal{H}_{tri}^{CF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + B_6^0 O_6^0 + B_6^3 O_6^3 + B_6^6 O_6^6$$



Gingras *et al.*, Phys. Rev. B **62** (2000)



Mirebeau *et al.*, Phys. Rev. B **76** (2007)

two lowest energy levels ≡ doublets

The $Tb_2M_2O_7$ compounds (M = Ti, Sn)

energy levels

$Tb_2Ti_2O_7$

$$
\begin{aligned}
|\phi_0^\pm\rangle &= -0.958|\pm 4\rangle \pm 0.129|\pm 1\rangle - 0.121|\mp 2\rangle \mp 0.226|\mp 5\rangle \\
|\phi_e^\pm\rangle &= -0.937|\pm 5\rangle \pm 0.241|\pm 2\rangle - 0.078|\mp 1\rangle \mp 0.241|\mp 4\rangle
\end{aligned}
$$

→ ground state magnetic moment : $\mu^{\mathrm{CF}} = 5.1\ \mu_{\mathrm{B}}$

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$\rightarrow$ ground state magnetic moment : $\mu^{\mathrm{CF}} = 5.1\ \mu_{\mathrm{B}}$

$Tb_2Sn_2O_7$

$$
\begin{aligned}
|\phi_0^\pm\rangle &= 0.922|\pm 5\rangle \mp 0.243|\pm 2\rangle + 0.016|\mp 1\rangle \mp 0.301|\mp 4\rangle \\
|\phi_e^\pm\rangle &= \pm 0.938|\pm 4\rangle - 0.156|\pm 1\rangle \pm 0.019|\mp 2\rangle - 0.309|\mp 5\rangle
\end{aligned}
$$

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The $Tb_2M_2O_7$ compounds (M = Ti, Sn)

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→ ground state magnetic moment : $\mu^{\mathrm{CF}} = 6.0\ \mu_{\mathrm{B}}$

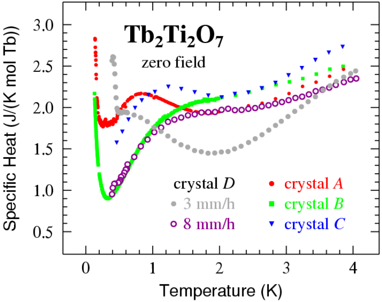
swap of $|m_z\rangle$ state mainly contributing to $|\phi_0^\pm\rangle$ and $|\phi_e^\pm\rangle$, depending on the B_6^0 parameter

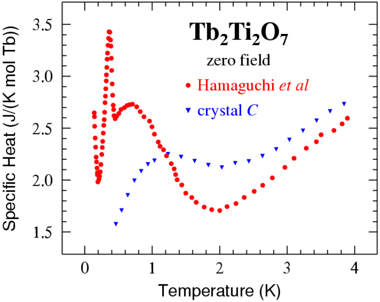
Outline

$Tb_2Ti_2O_7$: sample study

sample dependence of some properties

crystals	initial powders	growth rate, flow
A, *B*	$TiO_2 + Tb_4O_7$	8 mm/h, argon
C	$TiO_2 + Tb_2O_3$	7 mm/h, oxygen
D	$TiO_2 + Tb_4O_7$	3 & 8 mm/h, argon

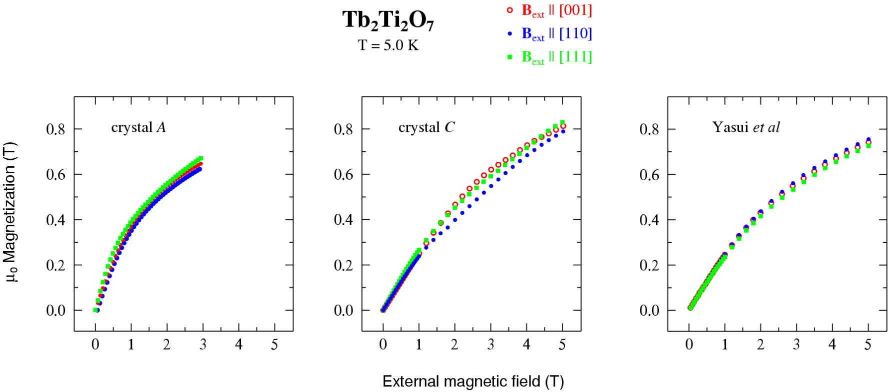




- crystal growth rate dependence of specific heat + possible well defined anomaly at 0.4 K   Hamaguchi *et al.*, Phys. Rev. B **69** (2004)

$Tb_2Ti_2O_7$: sample study

sample dependence of some properties

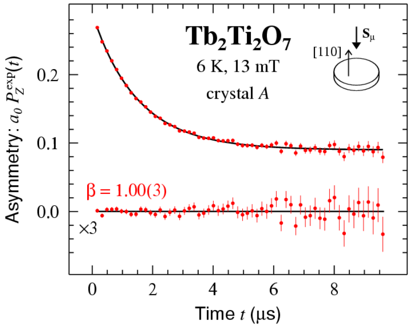


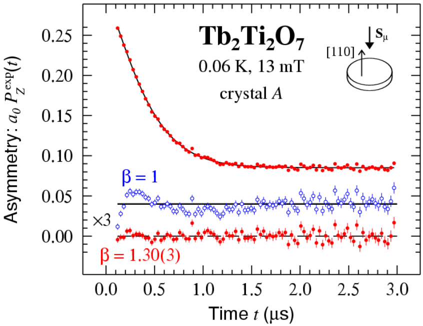
- same sample as Hamaguchi *et al.* Yasui *et al.*, J. Phys. Soc. Jpn. **71** (2002)
- some weak differences between samples

$Tb_2Ti_2O_7$: sample study

sample dependence of some properties

- muon = magnetic local probe (μSR measurements from ISIS)

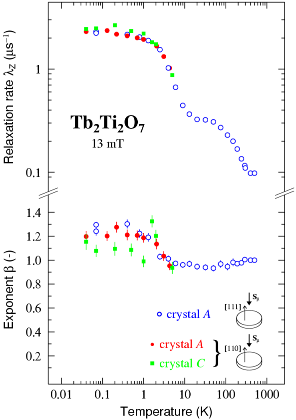


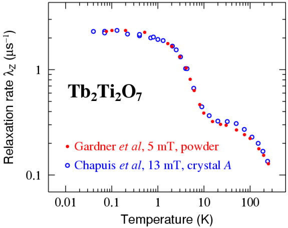


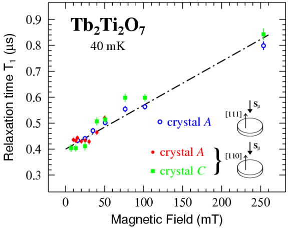
- counts rate : $N(t) = N_0 \exp(-t/\tau_\mu)[1 + a_0 P_Z(t)]$
- asymmetry : $a_0 P_z(t) = a_s \exp[-(\lambda_Z t)^\beta] + a_{bg}$
- at 6 K : $\beta = 1.00(3)$; and at 0.06 K : $\beta = 1.30(2)$

$Tb_2Ti_2O_7$: sample study

sample dependence of some properties





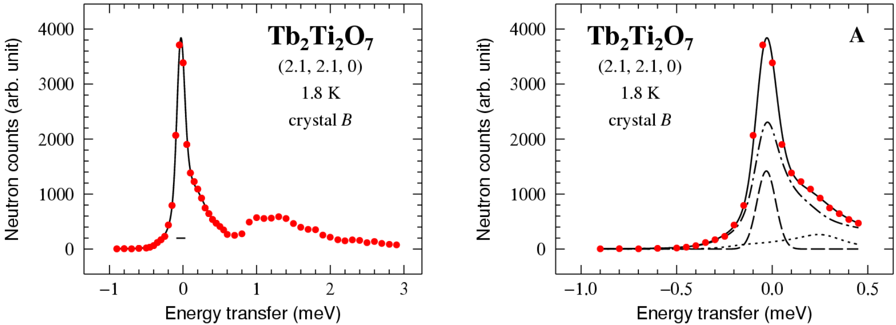


- no sample dependence of the relaxation rate λ_Z
- sample dependence of the exponent β needs to be checked

$Tb_2Ti_2O_7$: sample study

characteristic temperatures

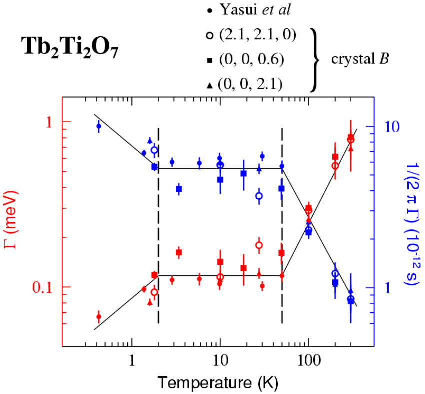
- inelastic neutron scattering measurements from IN12 at ILL

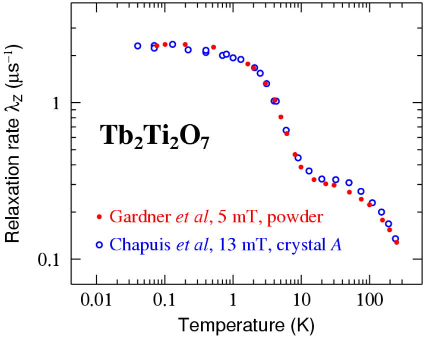


- $I(Q,\omega) = |F(Q)|^2 R \otimes \left[\frac{\hbar\omega}{1-\exp(-\hbar\omega/k_B T)} \left\{ L_q(\omega,\omega_0,\Gamma,A_L) + L_{inel}(\omega,\omega_0,\delta,\sigma_{inel},A_{inel}) \right\} \right] + G_{inc}(\omega,\omega_0,\sigma_{inc},A_{inc}) + C_{bg}$
- weakly inelastic contribution only for $T \leq 10$ K and relative high Q

$Tb_2Ti_2O_7$: sample study

characteristic temperatures

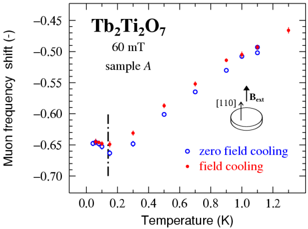


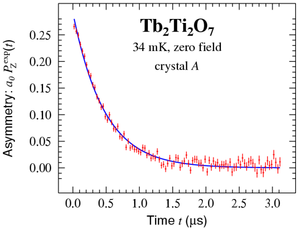


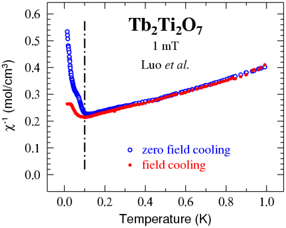
- $\lambda_Z \propto T \int \mathcal{A}(Q) \frac{\chi(Q)}{\Gamma(Q)} d^3Q$
- from inelastic neutron scattering and muon spin relaxation : two characteristic temperatures = 2 and 50 K

$Tb_2Ti_2O_7$: sample study

characteristic temperatures







Luo *et al.*, Phys. Lett. A **291** (2001)

- low temperature μSR spectra (from PSI) : no oscillation
- susceptibility : anomaly at around 0.1 K

→ magnetic transition or not ?

→ nature of the lowest temperature phase ?

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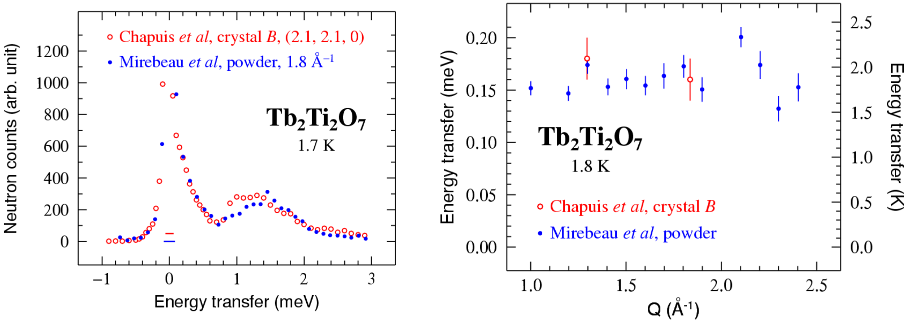
2. The $Tb_2M_2O_7$ compounds (M = Ti, Sn)
3. $Tb_2Ti_2O_7$: sample study
4. Crystal field levels
    - inelastic neutron scattering
    - entropy variation study
5. Conclusions

Crystal field levels
inelastic neutron scattering



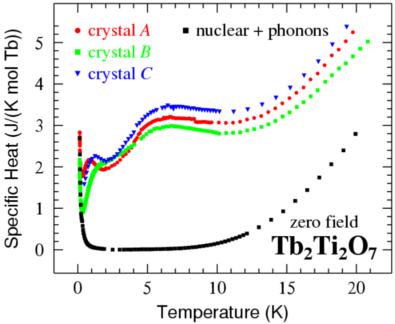
- for $Tb_2Ti_2O_7$, our data are consistent with the ones of Mirebeau *et al.* and Yasui *et al.*

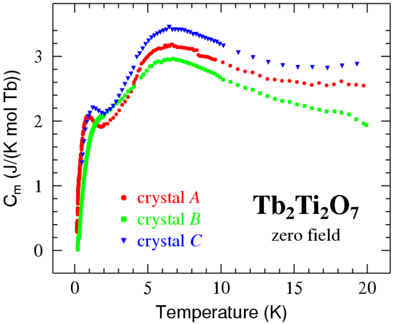
  Mirebeau *et al.*, Phys. Rev. B **76** (2007)　　Yasui *et al.*, J. Phys. Soc. Jpn. **71** (2002)

- weakly inelastic contribution : energy level at $\simeq 2$ K
- similar results for $Tb_2Sn_2O_7$ are obtained by Mirebeau *et al.*

Crystal field levels

entropy variation study





- on the left, total specific heat, nuclear and phonons contributions
  - nuclear contribution from Zeeman splitting ($\Delta_{\mathrm{N}} = 82(5)$ mK) $\rightarrow \mu_{\mathrm{SH}} = 4.5(7)\ \mu_{\mathrm{B}}$
  - phonons from non magnetic and isostructural compound
- on the right, magnetic specific heat

Crystal field levels

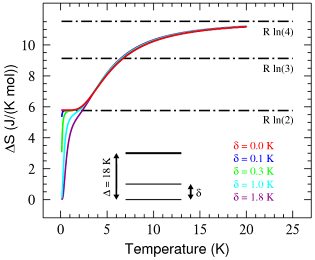
entropy variation study

2 doublets

$$\langle E \rangle = \frac{0 + 2\Delta \exp(-\beta\Delta)}{2 + 2\exp(-\beta\Delta)} = \frac{\Delta \exp(-\beta\Delta)}{1 + \exp(-\beta\Delta)}$$

2 singlets and 1 doublet

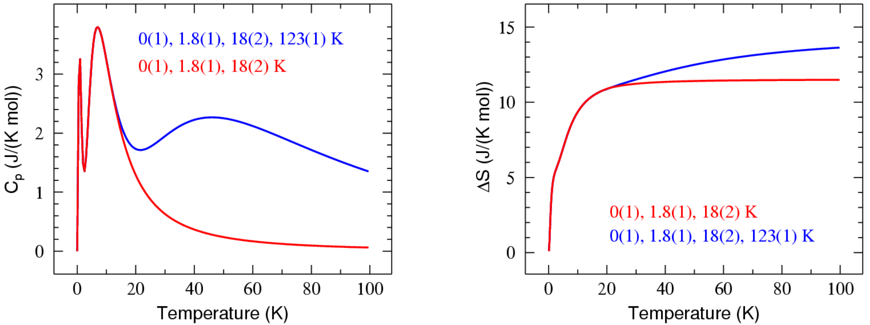
$$\langle E \rangle = \frac{0 + \delta \exp(-\beta\delta) + 2\Delta \exp(-\beta\Delta)}{1 + \exp(-\beta\delta) + 2\exp(-\beta\Delta)}$$



- $C_v = d\langle E \rangle / dT$
- $\Delta S = \int \frac{C_v}{T} dT$
- ΔS calculated between 200 K down to 0.13 K

Crystal field levels

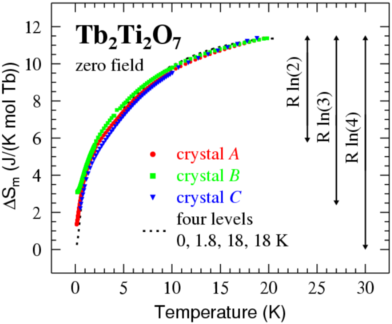
entropy variation study

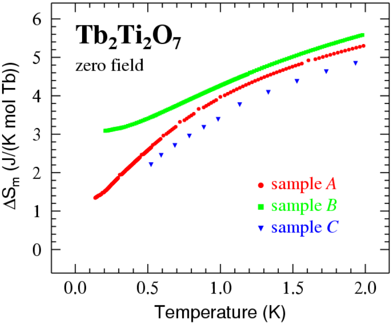


- for 0 K $\leq T \leq$ 20 K, no influence of higher energy levels
- similar results for $Tb_2Ti_2O_7$ and $Tb_2Sn_2O_7$

Crystal field levels

entropy variation study

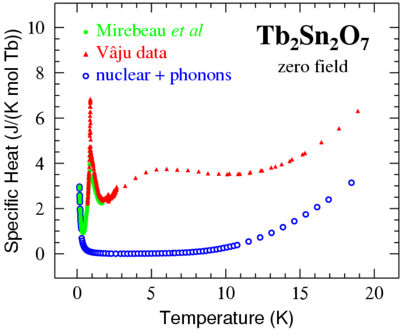


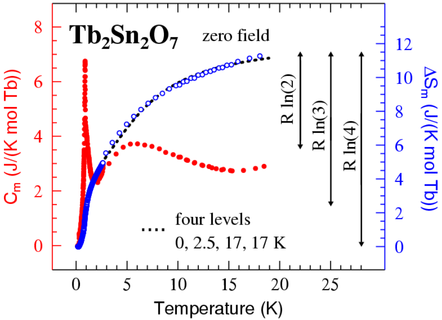


- on the left, magnetic entropy variation : $\Delta S_{\rm m}(0 \rightarrow 20K) \; > \; R\ln(2)$
  $\rightarrow$ ground state splitting
- on the right, at low temperature : $\Delta S_{\rm m}(T = 0K) = R\ln(4)$?

Crystal field levels

entropy variation study





- ΔS_m reaches $R\ln(4)$ at 20 K
- splitting observed by Mirebeau *et al.* with inelastic neutron scattering

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2 The $Tb_2M_2O_7$ compounds (M = Ti, Sn)

3 $Tb_2Ti_2O_7$: sample study

4 Crystal field levels

5 Conclusions
- summary
- outlook

Conclusions

summary

$Tb_2Ti_2O_7$

- sample dependence of specific heat, magnetization and μSR (?) $\rightarrow$ a detailed structural study is required
- but sample independence of inelastic neutron scattering results
- characteristic temperatures $T \simeq 2$ K and 50 K : μSR and inelastic neutron scattering are consistent
- from muon frequency shift and susceptibility, possible transition at $\simeq 0.1$ K : what is the nature of the lowest temperature phase ?

Conclusions

summary

$Tb_2Ti_2O_7$

- sample dependence of specific heat, magnetization and μSR (?) $\rightarrow$ a detailed structural study is required
- but sample independence of inelastic neutron scattering results
- characteristic temperatures $T \simeq 2$ K and 50 K : μSR and inelastic neutron scattering are consistent
- from muon frequency shift and susceptibility, possible transition at $\simeq 0.1$ K : what is the nature of the lowest temperature phase ?

$Tb_2Sn_2O_7$

- low temperature spin dynamics characterized by different fluctuation times
- order of magnitude depending on Q : 10^{-11} s / 10^{-9} s and $> 10^{-8}$ s

Conclusions

summary

$Tb_2M_2O_7$

$\simeq$ 2 K splitting of the ground state : deduced from inelastic neutron scattering ; consistent with the tetragonal distortion along [001] and now, confirmed by entropy variation study

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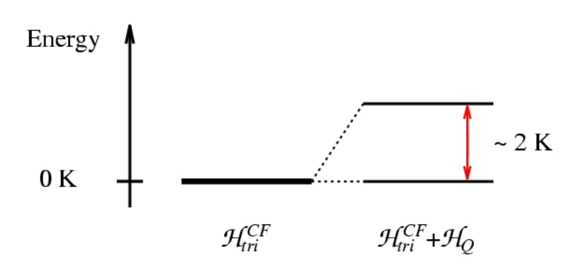
new energy levels scheme



Conclusions
outlook

$Tb_2Ti_2O_7$

- μSR measurements on sample C to know the behaviour of the exponent β versus the temperature
- specific heat measurements in dilution on sample C to compare with other samples : $\Delta S \to R\ln(4)$?
- understand X-Ray and neutron diffraction patterns

Conclusions

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- μSR measurements on sample C to know the behaviour of the exponent β versus the temperature
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$Tb_2Sn_2O_7$

- the magnetic moment has both ferromagnetic and antiferromagnetic components : what are consequences on the spin dynamics ?
- static at low Q and dynamic at high Q ?
- why no oscillations have been observed in μSR spectra at low temperature ?

Thanks

the jury

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And thank you for your attention...