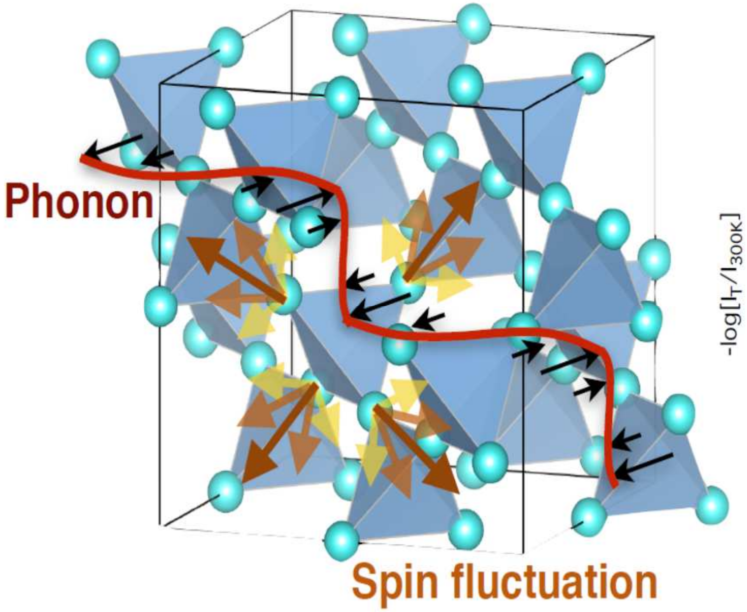
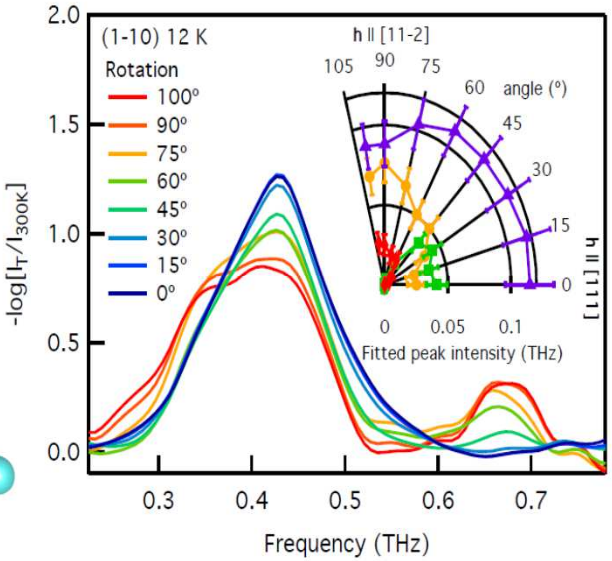
THz PROPERTIES OF COMPLEX MAGNETIC PHASES: ELECROMAGNONS AND BEYOND



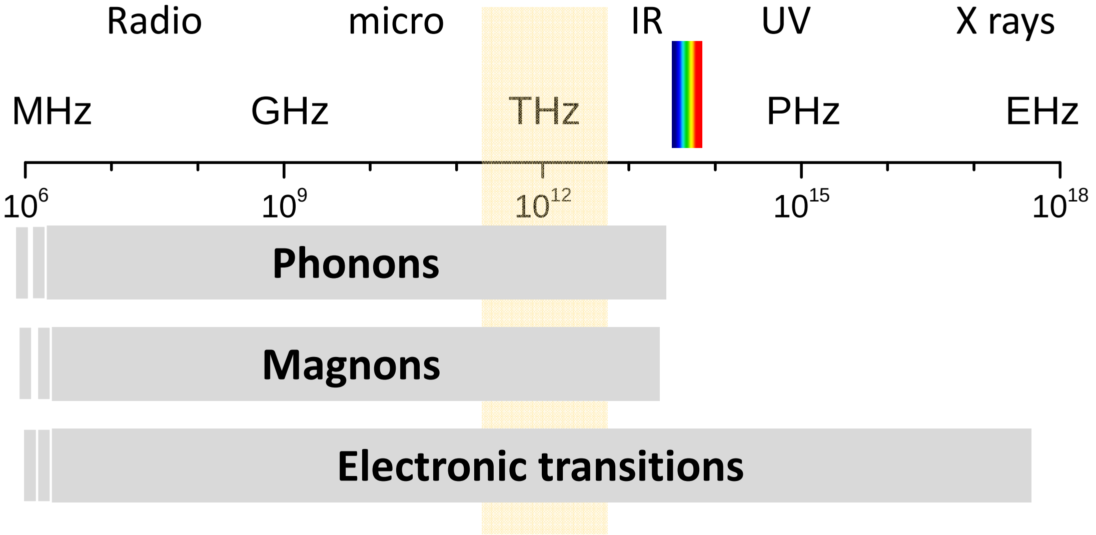


1. THz properties of complex magnetic phases
2. Multiferroics: hybride excitations in hexagonal manganites
3. Frustrated magnets: hybride excitations in the quantum spin ice $Tb_2Ti_2O_7$
4. Perspectives

S. DE BRION

1. THz properties in condensed matter

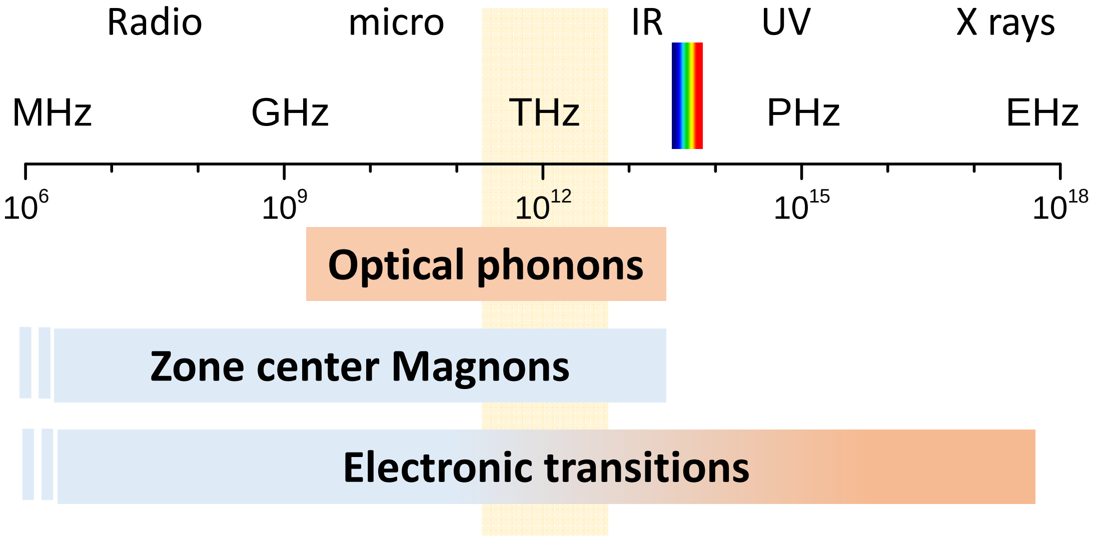
1 THz ≈ 33 cm^{-1} ≈ 300 µm ≈ 4 meV ≈ 50 K



ORDERED PHASES
(ATOMIC /ELECTRIC / MAGNETIC)
HAVE CHARATERICS EXCITATIONS IN THE THz RANGE

1. THz properties in condensed matter

1 THz ≈ 33 cm^{-1} ≈ 300 µm ≈ 4 meV ≈ 50 K



Radio micro IR UV X rays

MHz GHz THz PHz EHz

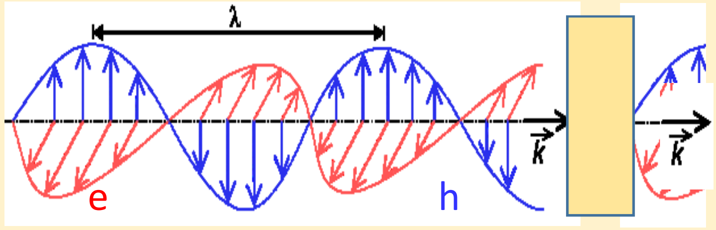
10^6 10^9 10^{12} 10^{15} 10^{18}

Optical phonons

Zone center Magnons

Electronic transitions

THz SPECTROSCOPY



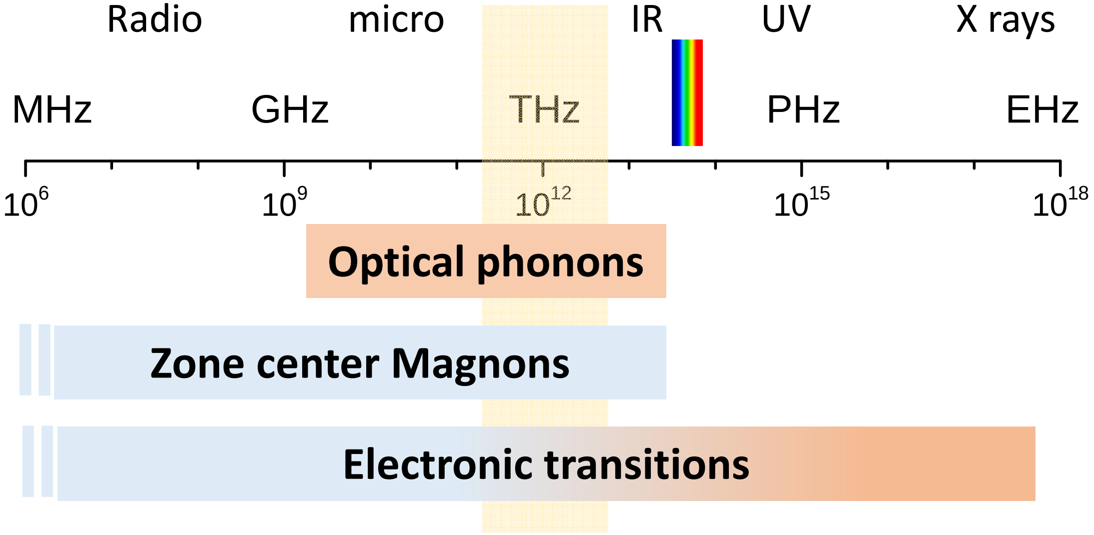
sample

Electric field to probe electric charges

Magnetic field to probe magnetic moments

1. THz properties in condensed matter

1 THz ≈ 33 cm^{-1} ≈ 300 µm ≈ 4 meV ≈ 50 K



SIGNATURES OF COMPLEX PHASES :

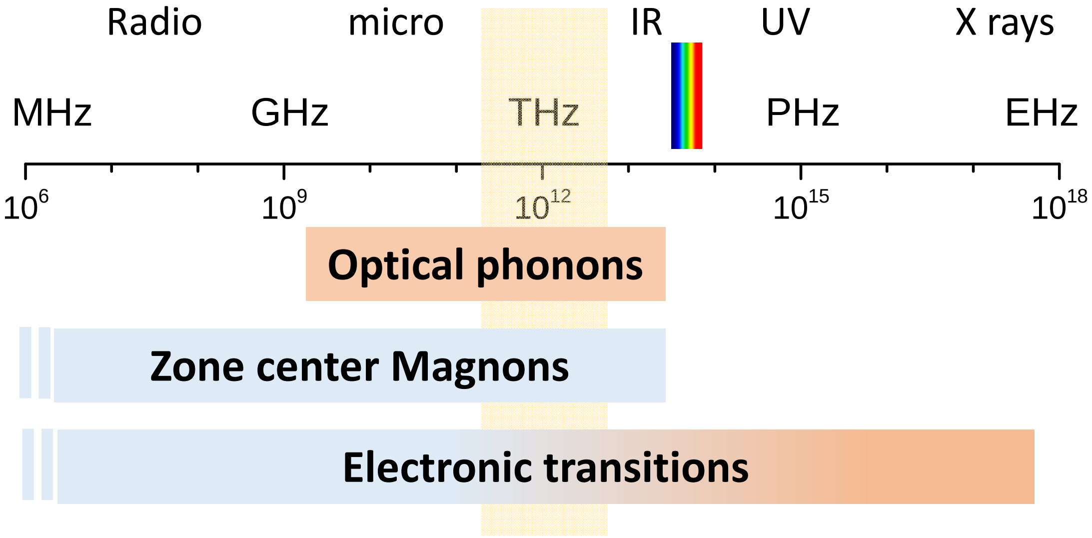
FERRO –ELECTRIC ORDER (phonons)
MAGNETIC ORDER (magnons)
MULTIFERROICS (electro-magnons)
1 DIM CHARGE/MAGNETIC ORDER (sliding modes)
…

⟷

NEW HYBRIDE EXCITATIONS :
production and manipulation

Magnetic phonon
Electric magnon
phononic electronic transition
….

1. THz properties in condensed matter



Optical phonons

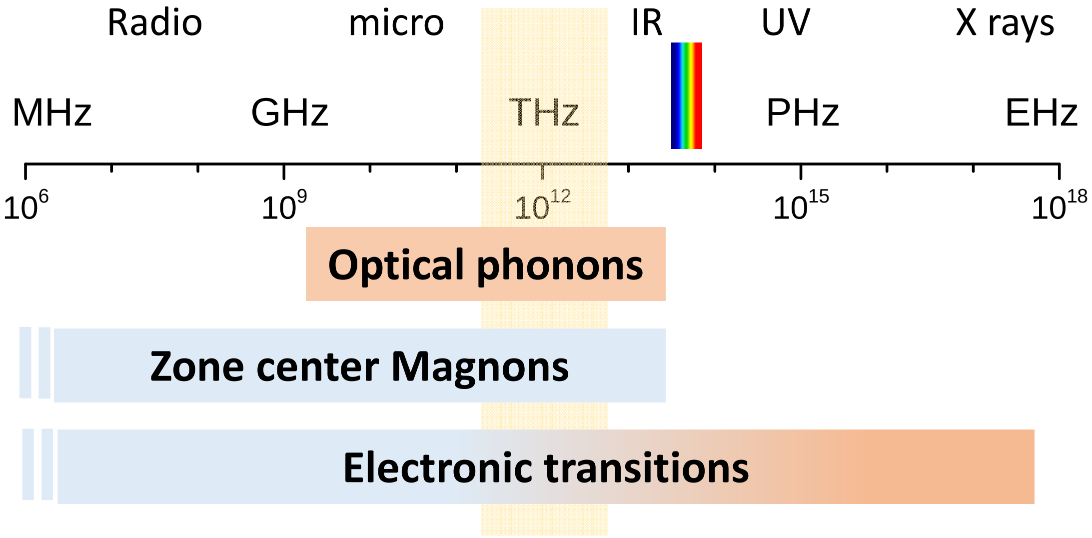
Zone center Magnons

Electronic transitions

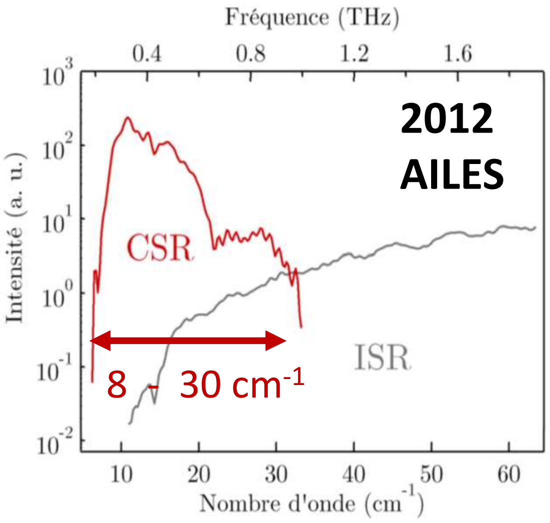
COMPLEX PHASES WITH SEVERAL DEGREES OF FREEDOM:
lattice, charge, spin ….

THz SPECTROSCOPY as a function of T, P
WITH A INTENSE , STABLE THz SOURCE on AILES@SOLEIL

1. THz properties in condensed matter



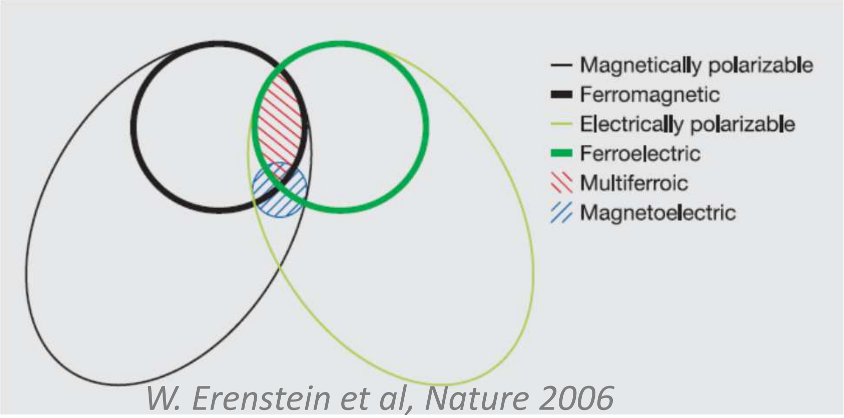
SOLEIL SYNCHROTRON



COMPLEX PHASES WITH SEVERAL DEGREES OF FREEDOM

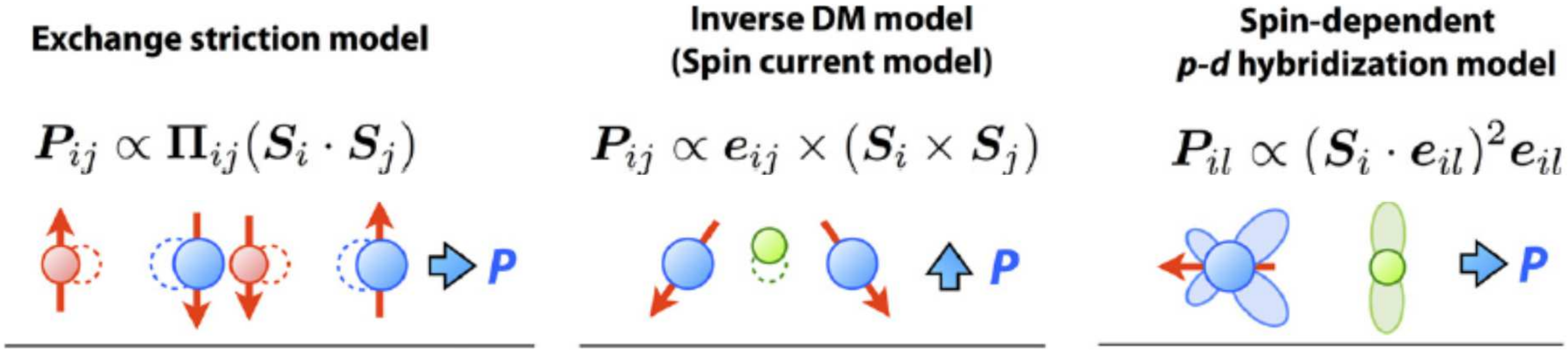
THz SPECTROSCOPY as a function of T, P WITH A INTENSE , STABLE THz SOURCE on AILES@SOLEIL

2. THE CASE OF MULTIFERROICS



W. Erenstein et al, Nature 2006

Type II multiferroics: ferroelectric order induced by the magnetic order



Exchange striction model

$$\boldsymbol{P}_{ij} \propto \boldsymbol{\Pi}_{ij}(\boldsymbol{S}_i \cdot \boldsymbol{S}_j)$$

Inverse DM model (Spin current model)

$$\boldsymbol{P}_{ij} \propto \boldsymbol{e}_{ij} \times (\boldsymbol{S}_i \times \boldsymbol{S}_j)$$

Spin-dependent *p-d* hybridization model

$$\boldsymbol{P}_{il} \propto (\boldsymbol{S}_i \cdot \boldsymbol{e}_{il})^2 \boldsymbol{e}_{il}$$

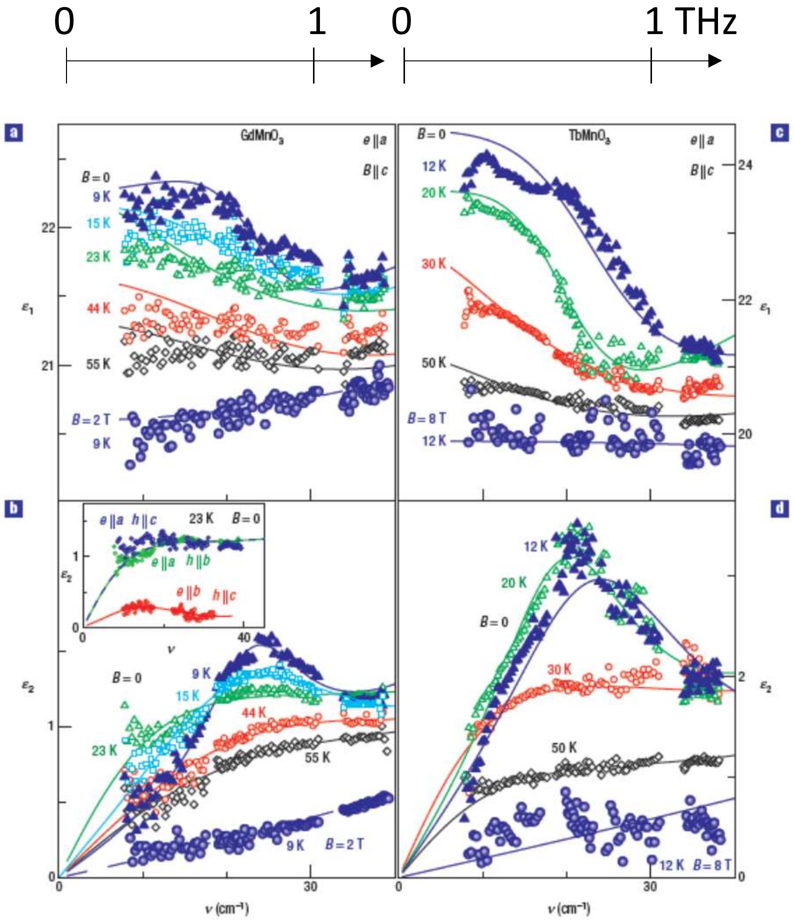
Y. Tokura et al, Rep. Prog. Phys. 2014

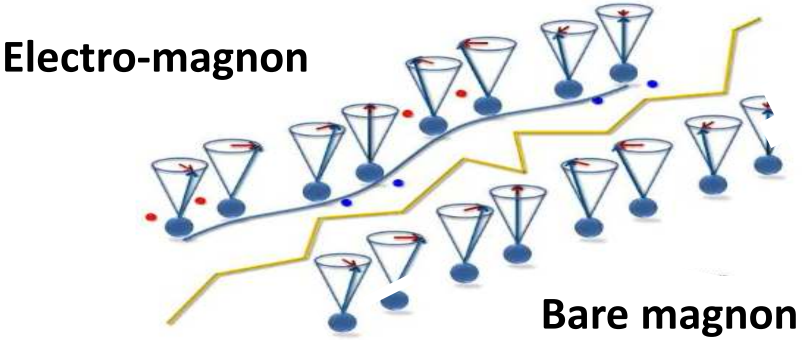
RESPONSIBLE FOR ELECTRIC POLARISATION AND NEW DYNAMICAL ELECTRO-MAGNETIC EFFETCS

2. Electro-magnons in multiferroics

A. PIMENOV et, Nature Physics 2006
Orthorhombic RMnO$_3$

Magnon dressed with electric charges thanks to magneto-electric coupling

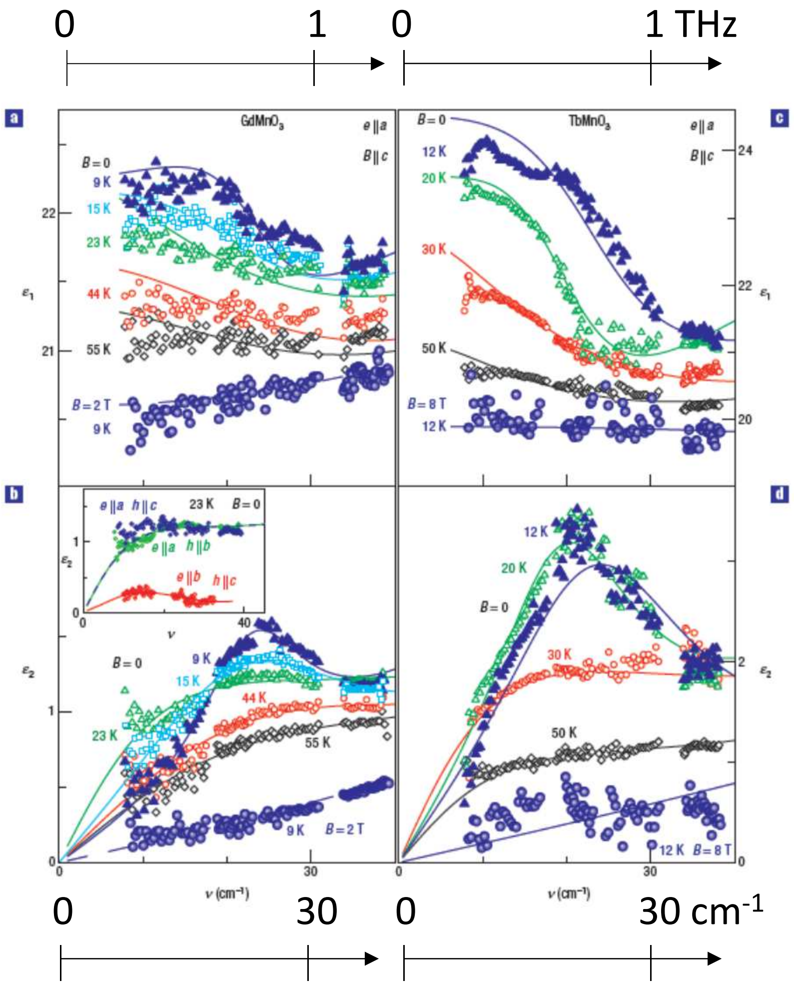




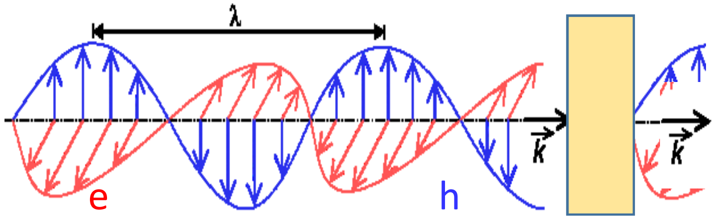
A magnon that is excited by the electric field of the THz wave

2. Electro-magnons in multiferroics

A. PIMENOV et, Nature Physics 2006
Orthorhombic RMnO$_3$



THz/FIR wave :

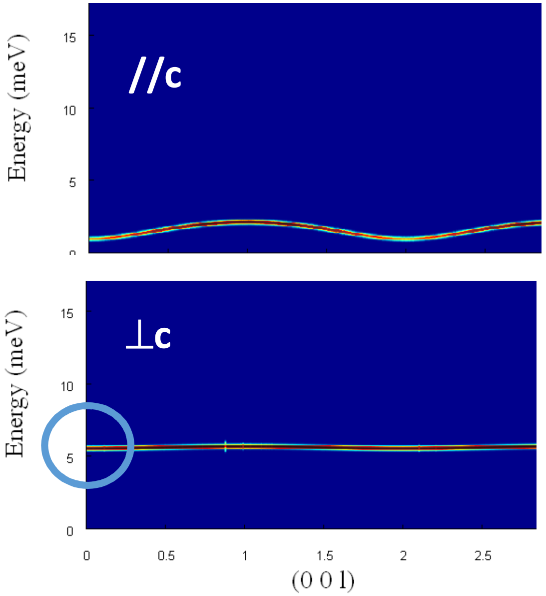


THz magneto-dielectic response: $\varepsilon_{ij}^{k}\ \mu_{i'j'}^{\ k'}$ = $(N_{ij}^{k})^{2}$
Refractive index : N_{ij}^{k}

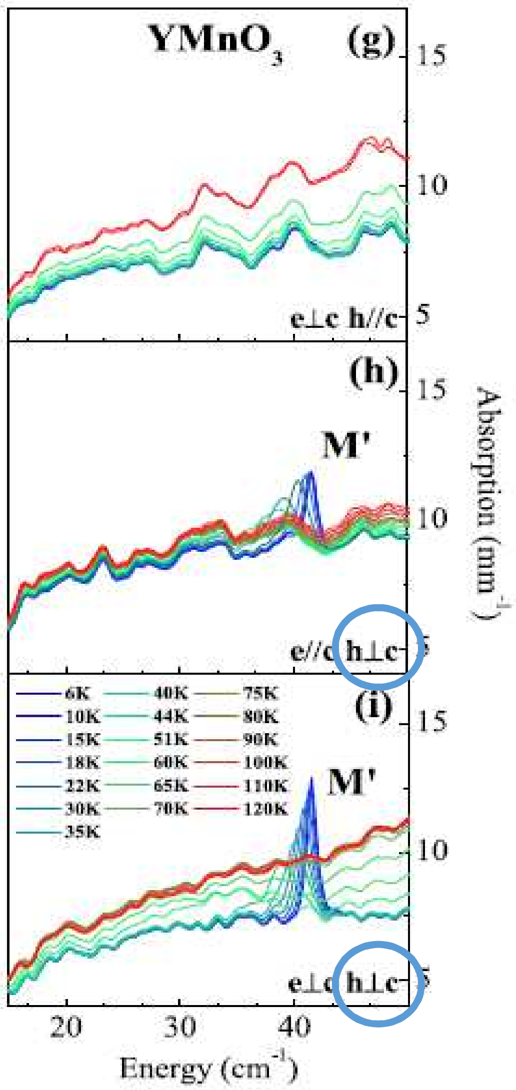
THz absorbtion : T = I / I_0 ≈ exp (– α_{ij}^{k} d)
Absorbance : Abs= - Log (T) ≈ α_{ij}^{k} d

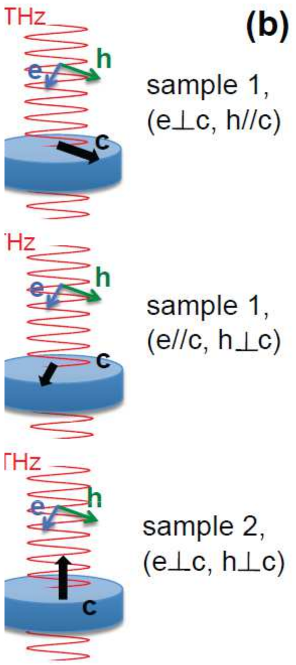
THz SPECTROSCOPY on h-RMnO3 at AILES@SOLEIL

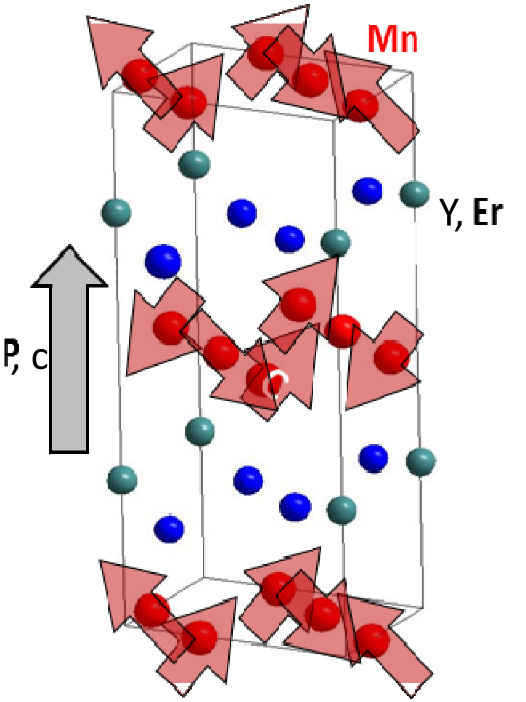
2. THz Properties of hexagonal manganites : $YMnO_3$



Mn Spin wave calculation

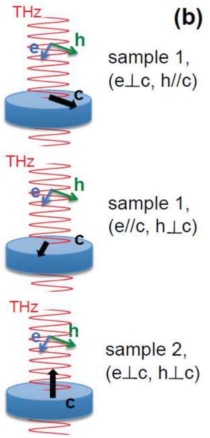


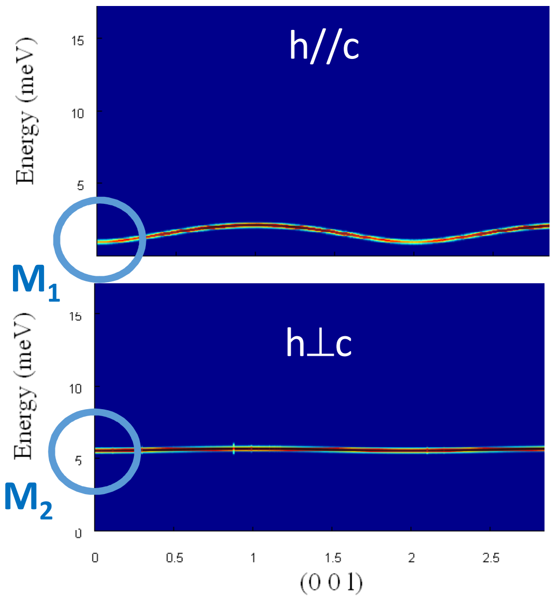


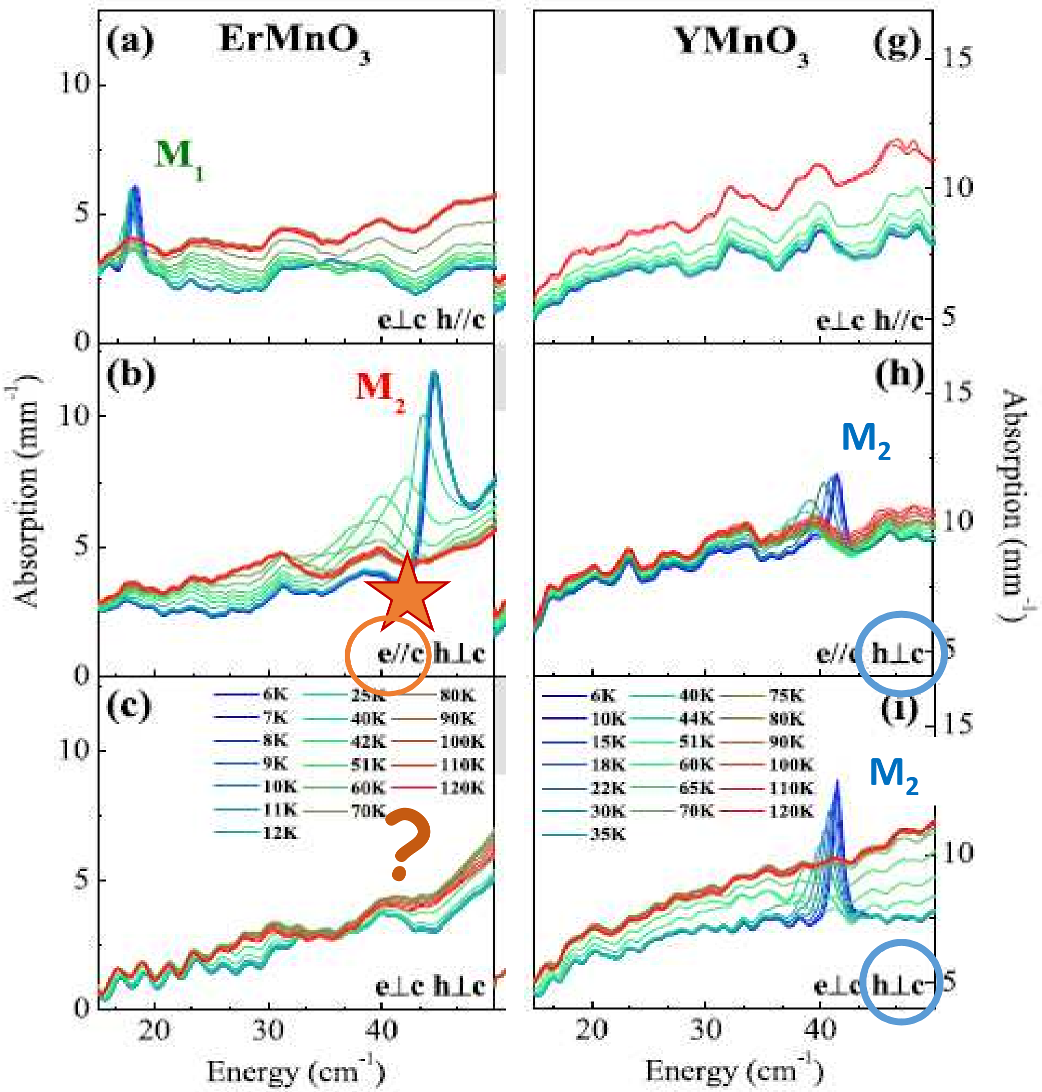


Axial
magnetic / electric system

2. Hexagonal manganites : $ErMnO_3$

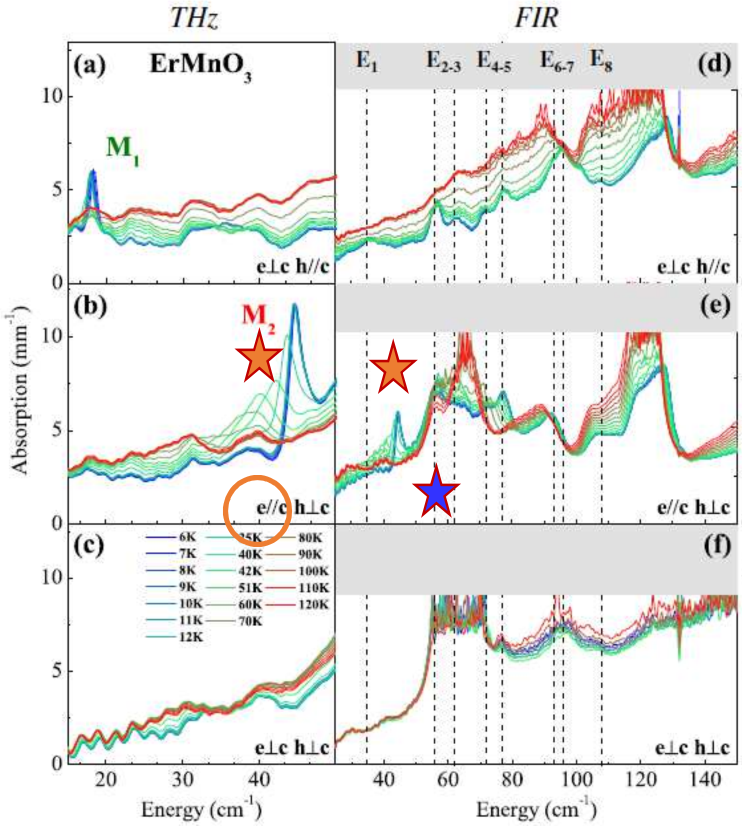




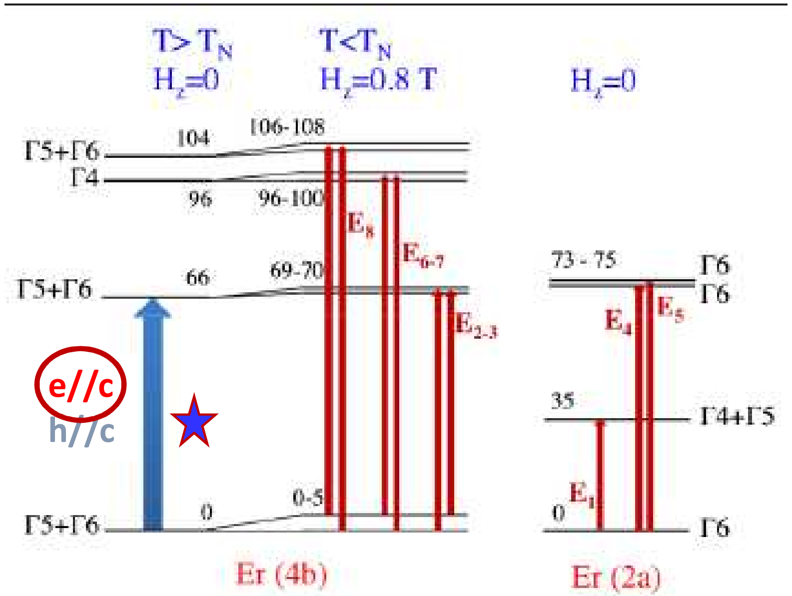


2. Hexagonal manganites : $ErMnO_3$

THz measurements



Er Crystal field excitations

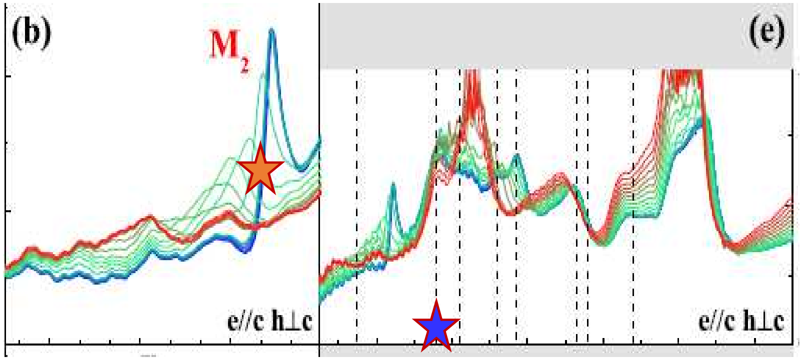


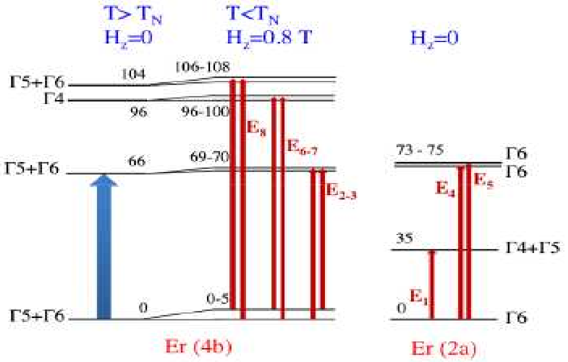
Er/Mn dynamical coupling : electroactive magnon
Mn MAGNON / Er CRYSTAL FIELD HYBRIDE EXCITATION

L. CHAIX et al PRL ***112****, 137201(2014)*

2. ELECTRO ACTIVITY OF A MAGNON IN h-ErMnO3

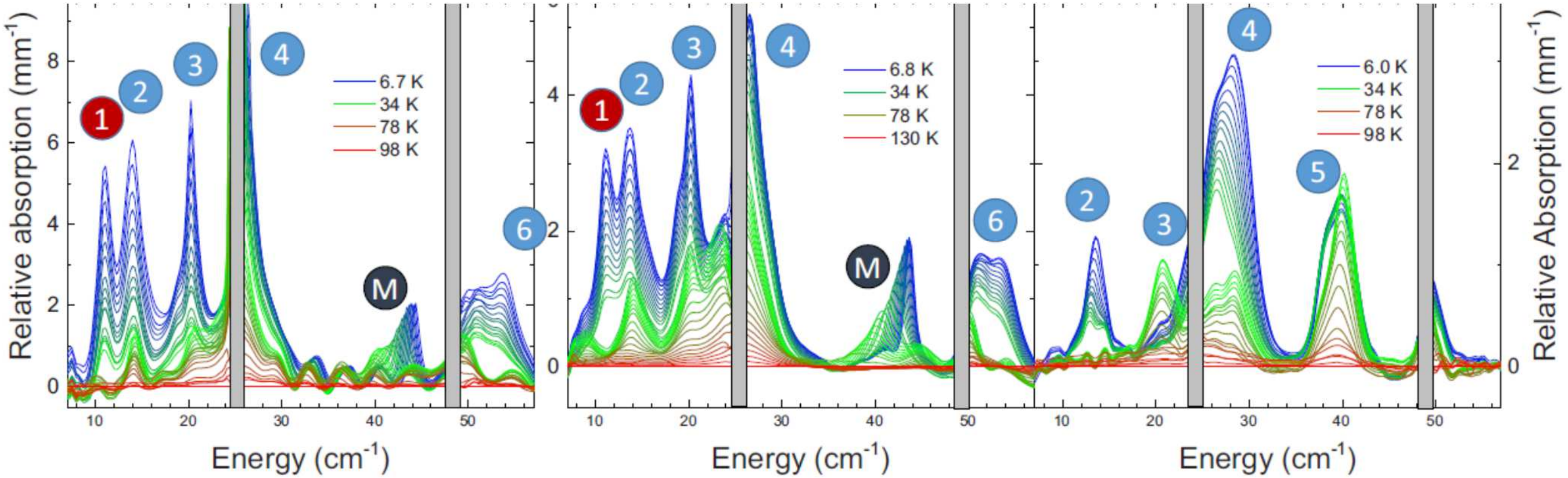
L. Chaix et al PRL 2014



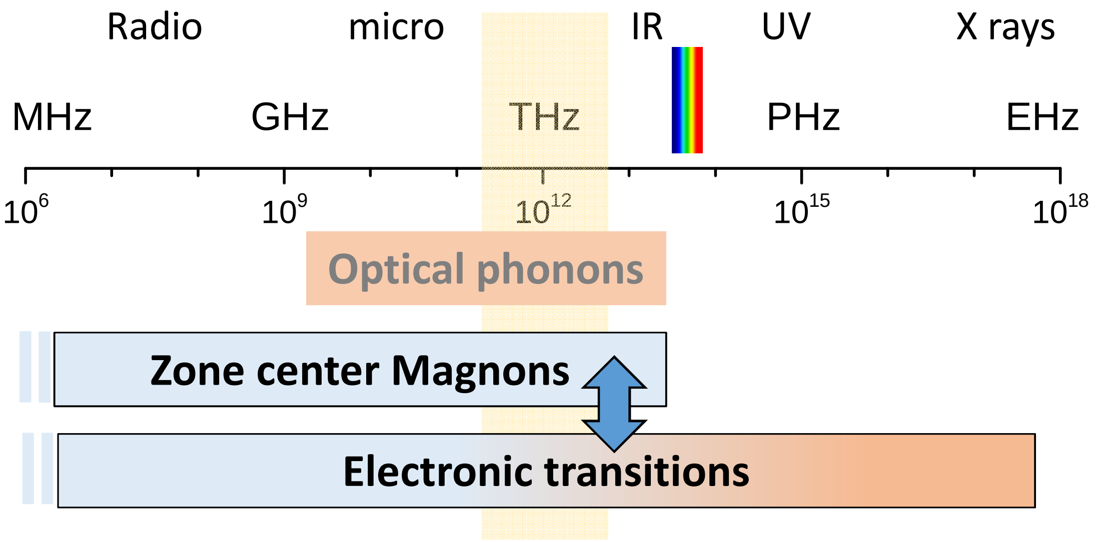


GENERAL TREND IN RARE EARTH MANGANITES ? h-HoMnO$_3$

X. Fabrèges et al PRB 2019



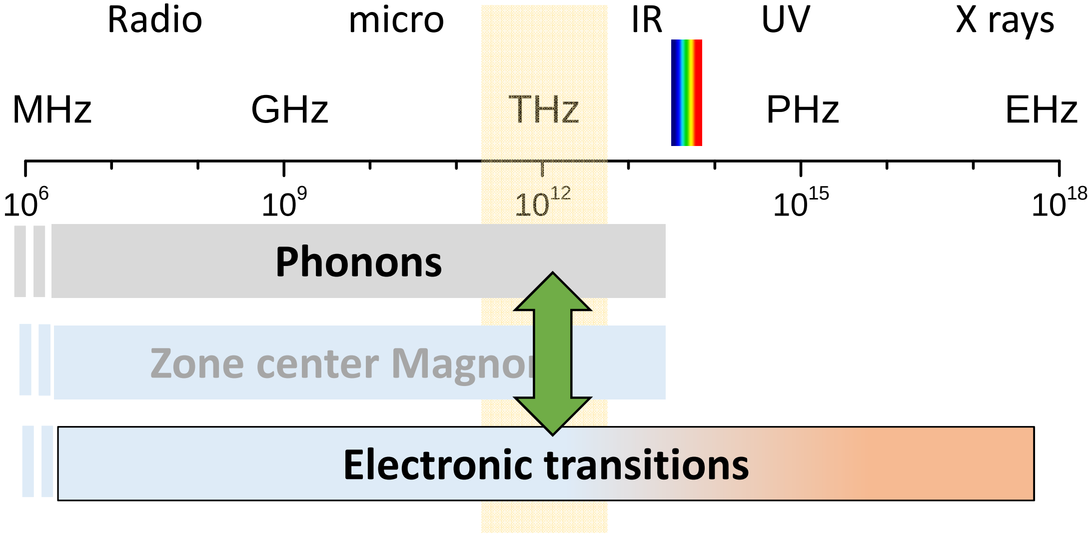
2. THz properties of hexagonal manganites RMnO3



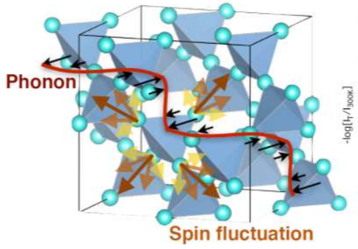
COUPLING MECANISMS between RARE EARTH 4f / 3d TRANSITION ELEMENTS :
Different Crystal Field excitations, different hybridization process

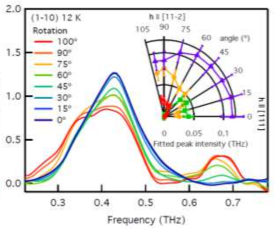
energy matching + symmetry requirement+ interacting strength

3. Other coupling mechanism



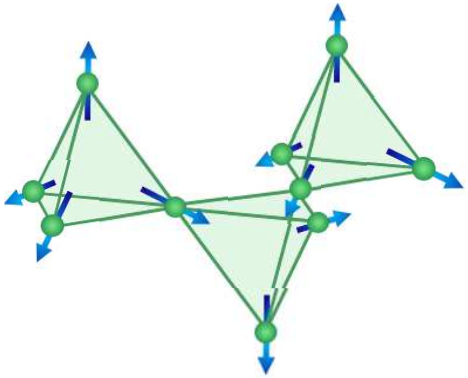
SIGNATURE OF A COMPLEX MAGNETIC PHASE :
the quantum spin ice $Tb_2Ti_2O_7$





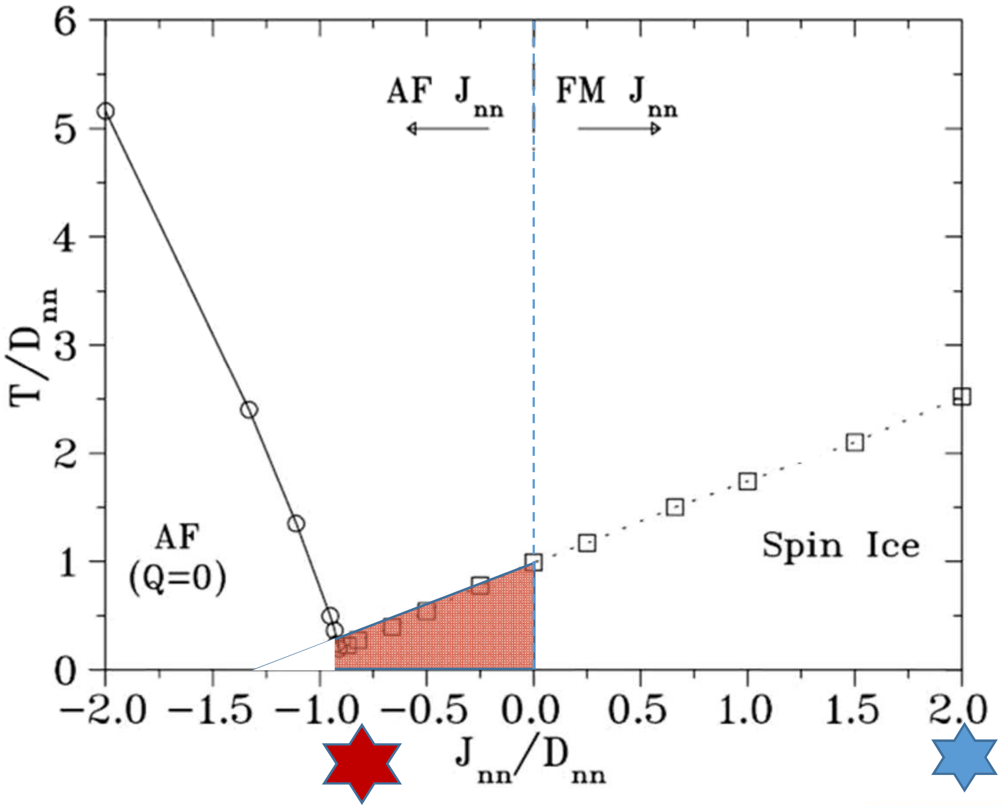
E. Constable & al PRB (R) 95 (2017)
Y. Alexanian & al on going work

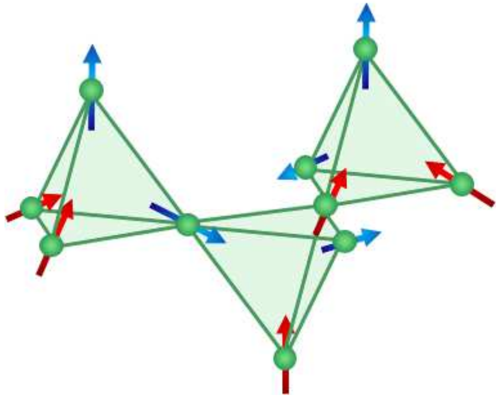
3. Ising spin Phase diagram



« All in – All out »
long range order

B.C. den Hertog & M.J.P.Gingras, PRL 84 (2000)





« 2 in – 2 out »
degenerate state

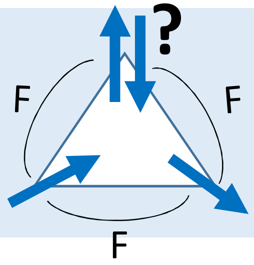
$Tb_2Ti_2O_7$

(Weak) Ising

No long range order down to 50 mK !!!

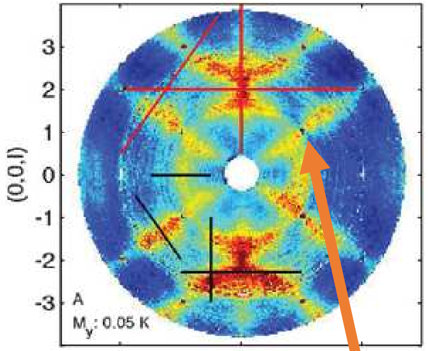
$Dy_2Ti_2O_7$ $Ho_2Ti_2O_7$

Spin ice



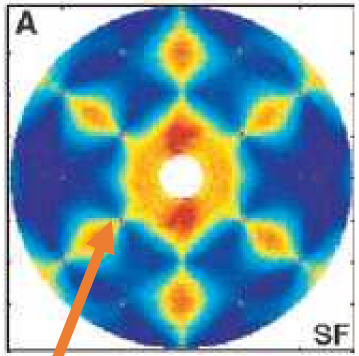
3. TTO Similarities with spin ices

$Tb_2Ti_2O_7$



T.Fennell & al, PRL 109 (2012)

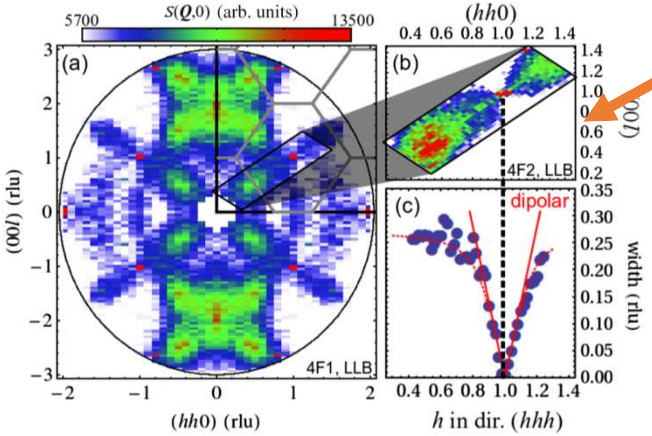
$Ho_2Ti_2O_7$



T.Fennell & al, Science 326 (2009)

Pinch points

$Tb_2Ti_2O_7$

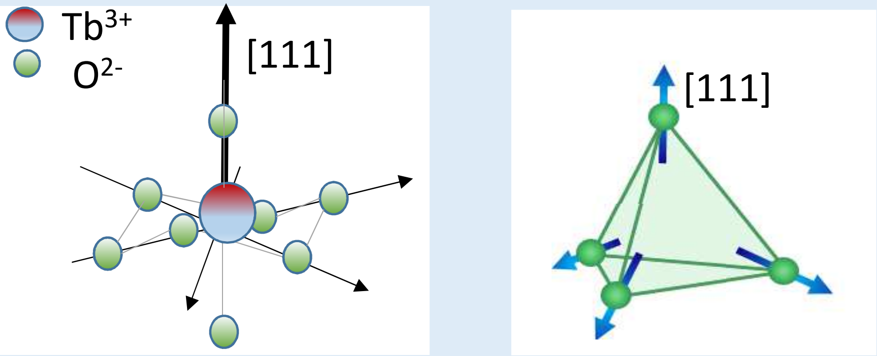


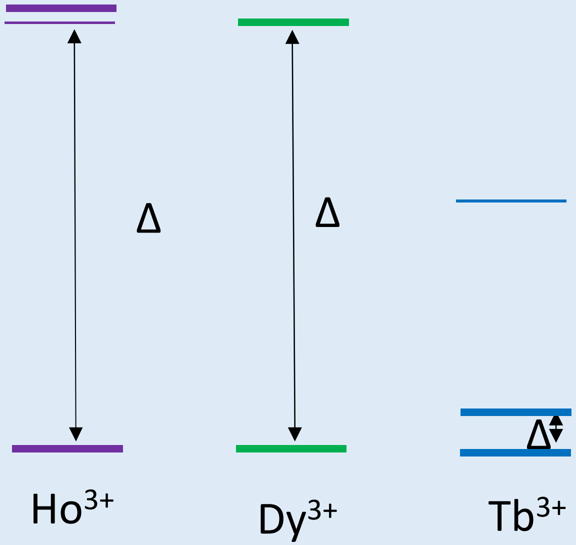
S. Guitteny& al, PRL 111 (2013)

The ground state shows diffuse scattering with « pinch points », suggesting that it is a Coulomb phase…

3. TTO peculiarities: Crystal Electric Field (CEF)

Crystal Field electronic levels in local D3d symmetry





For Ho, Dy

$\Delta \approx 300$ K

Ising spins

For Tb

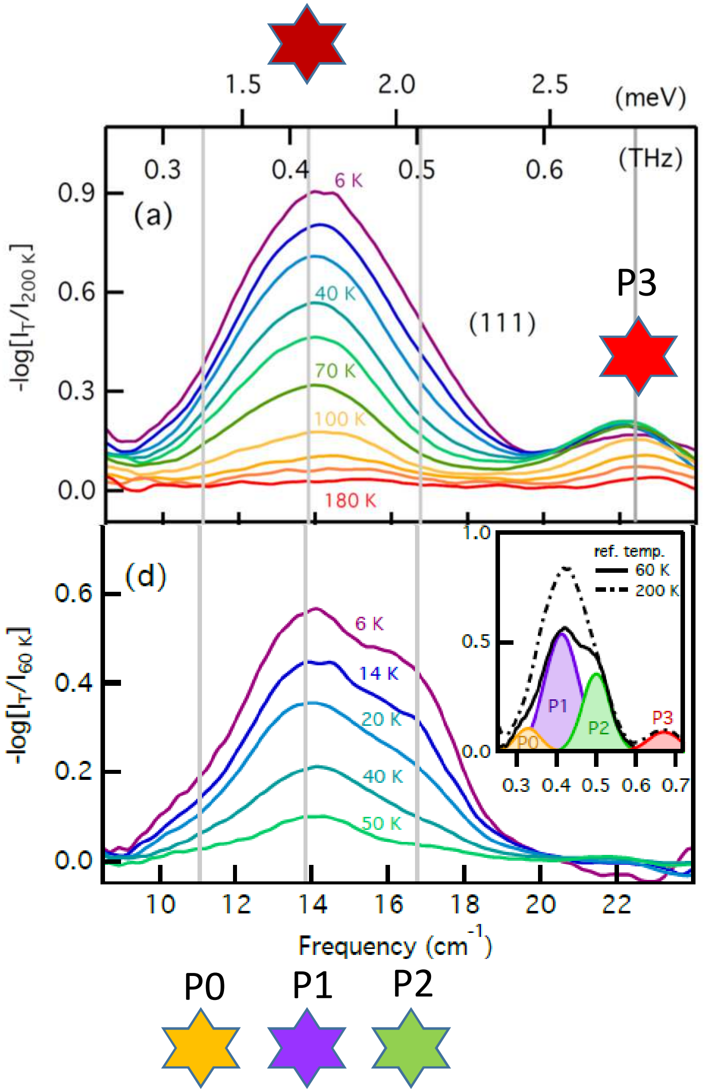
$\Delta \approx 20$ K ≈ 0.4 THz

Weak Ising

⇩

THz spectroscopy

3. TTO THz spectra



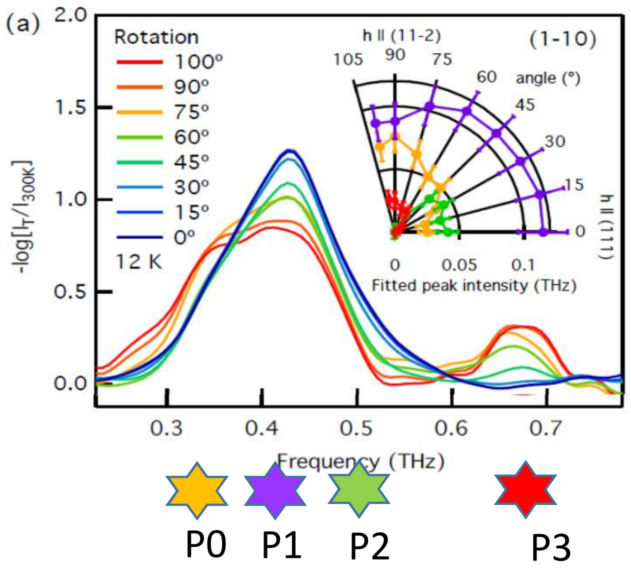
Absorption peak at ~ **0.42 THz (14 cm^{-1})** that develops at low temperatures in agreement with the first excited CEF level

P3

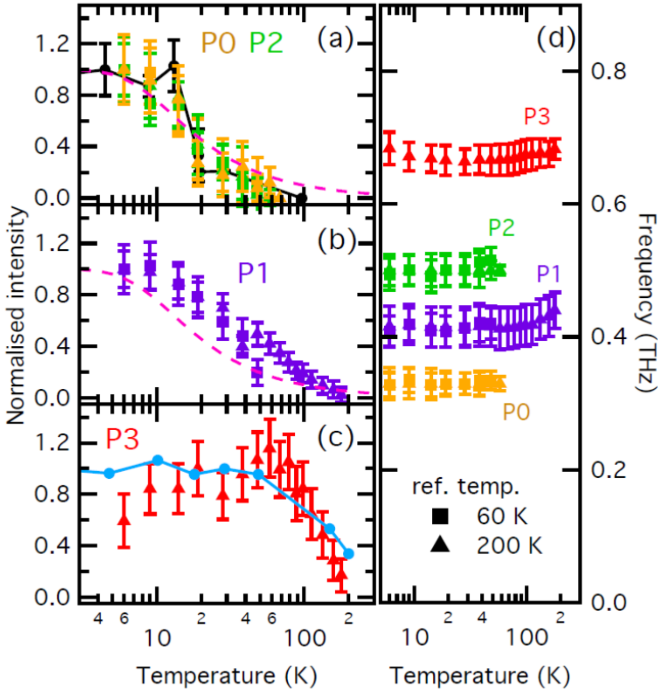
Additionnal peak below 200 K :
0.67 THz (22 cm^{-1})

3 peaks visible below 50 K :
P0 **0.33 THz (11 cm^{-1})**
P1 **0.41 THz (14 cm^{-1})**
P2 **0.50 THz (17 cm^{-1})**

3. TTO THz spectra



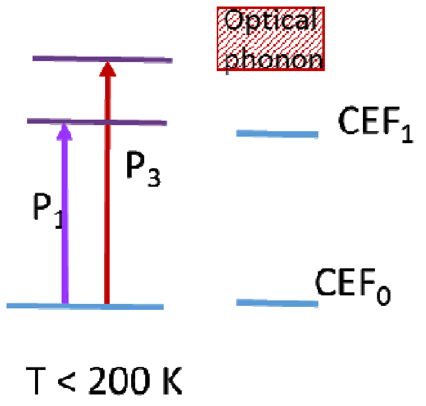
strong anisotropy in the intensity profile

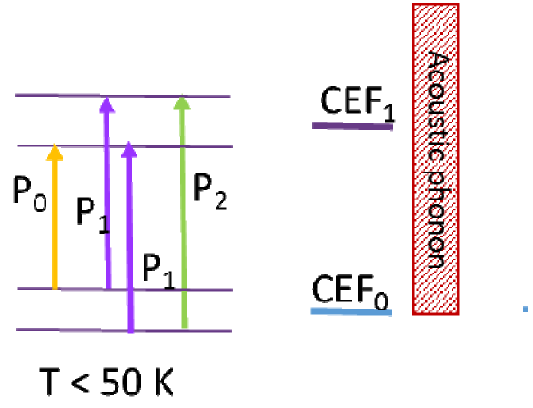


Two temperature scale:

200 K for P3

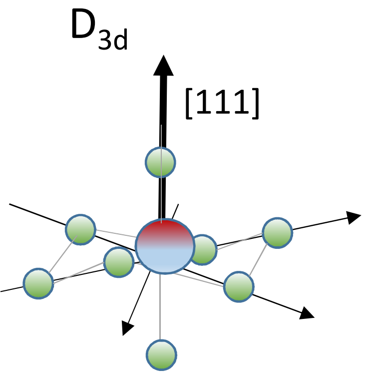
50 K for P0-P2





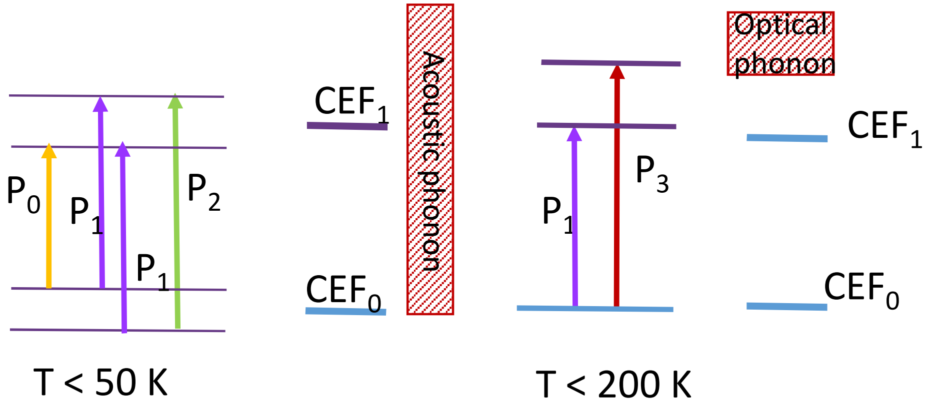
ORIGIN : CEF / PHONON COUPLINGS (double vibronic process)

3. TTO vibronic process: calculations



One site Hamiltonian :

$$\hat{\mathcal{H}} = \sum_{k,q} \underbrace{B_q^k \hat{O}_q^k}_{\text{Cristal field}} + \underbrace{D_q^k(T)\hat{O}_q^k}_{\text{Vibronic coupling}}$$



Symmetry analysis :

CEF$_1$ and CEF$_2$
of E_g symmetry

Acoustic phonon: $T_{1u\downarrow D_{3d}}$ = $A_{2u} \oplus E_2$
Coupling to E_g CEF states through $\hat{O}_2^k$ k = 1, 2

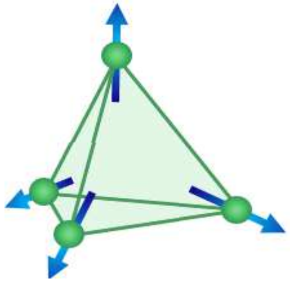
Vibronic coupling through quadrupolar operators
$\hat{O}_0^2$ of A_{1g} symmetry
$\hat{O}_2^k$ k = 1, 2 of E_g symmetry

Optical phonon: $T_{2u\downarrow D_{3d}}$ = $A_{1u} \oplus E_2$
Coupling to Eg CEF states through $\hat{O}_2^k$ k = 1, 2 and $\hat{O}_0^2$

3. TTO THz response : calculations

4 sites Hamiltonian :

$$\widehat{\mathcal{H}} = \sum_{i=1}^{4}\left(\sum_{k,q}\underbrace{B_q^k\hat{O}_q^k}_{\text{Cristal field}} + \underbrace{D_q^k(T)\hat{O}_q^k}_{\text{Vibronic coupling}}\right)_i$$



CEF eigenstates and energies

$$\chi_{\alpha\beta} = \sum_{kl}\frac{P_k - P_l}{(\hbar\omega_{kl} - \hbar\omega)^2 + \Gamma_{lk}^2}\left[i\Gamma_{lk} + (\hbar\omega_{kl} - \hbar\omega)\right]\hat{J}_{kl}^{\beta}\hat{J}_{lk}^{\alpha}$$

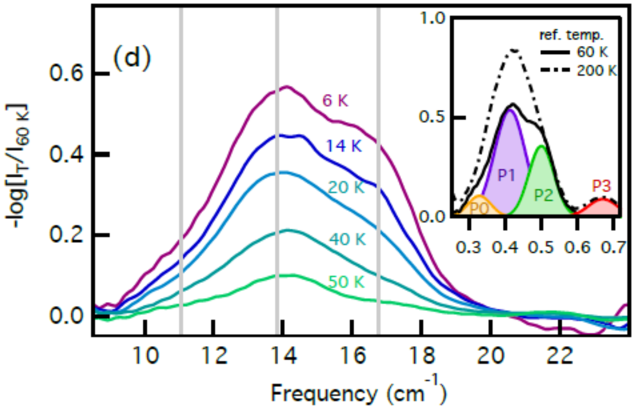
magnetic susceptibility

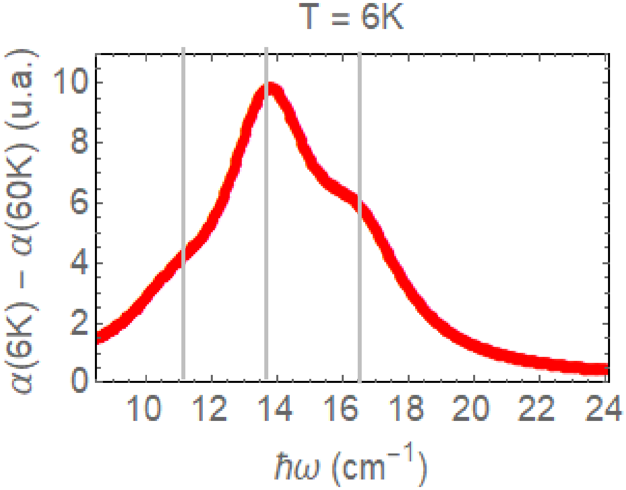
+

Maxwell equation in anisotropic medium

THz absorption

$$\alpha(\omega) \cong \frac{\omega}{c}\left[Im(\chi_{||\,||}) + Im(\chi_{\perp\,||})\right]_{o,e}$$





$D_2^1 = 0.097\ cm^{-1}$

$D_2^2 = 0.032\ cm^{-1}$

$D_2^{-1} = D_2^{-2} = 0$

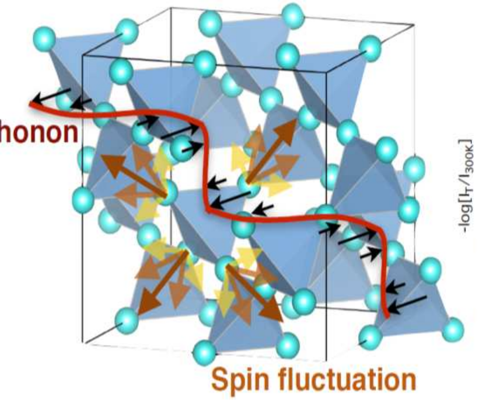
Splitting (2.8 cm^{-1}) of CEF$_0$ and CEF$_1$

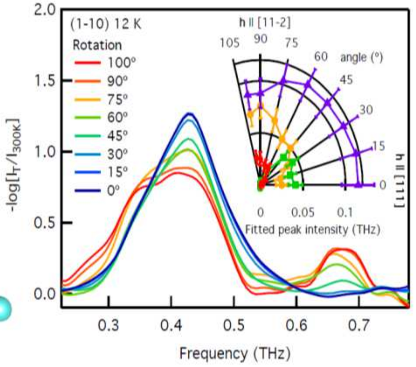
$D_2^0 =\ - 0.2\ cm\text{-}1$

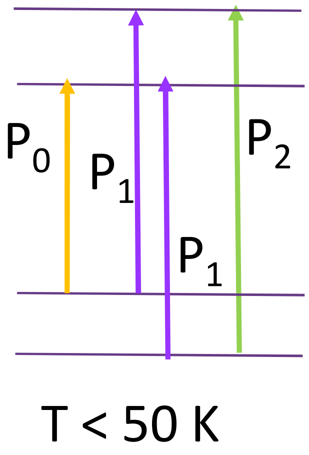
Shift of CEF$_1$ (1.0 cm^{-1})

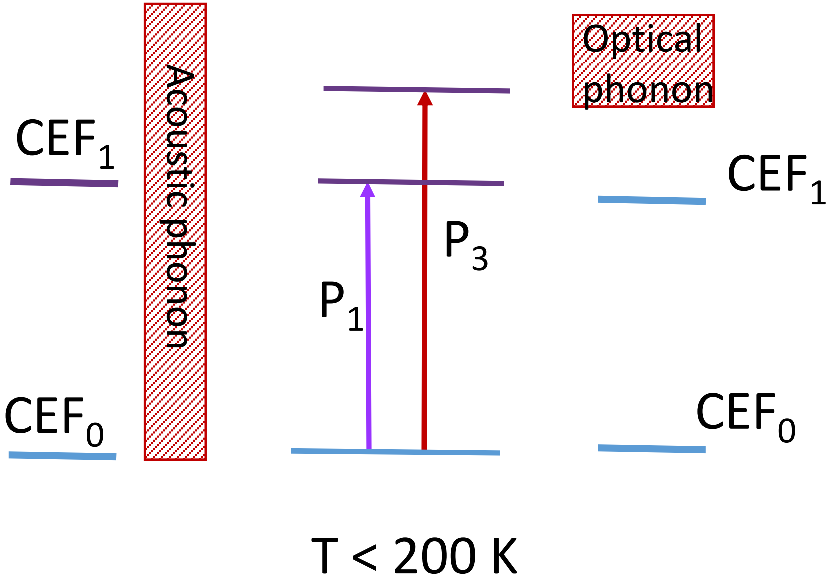
$\Gamma_{lk} = 1.65\ cm^{-1}$

3. TTO double vibronic process









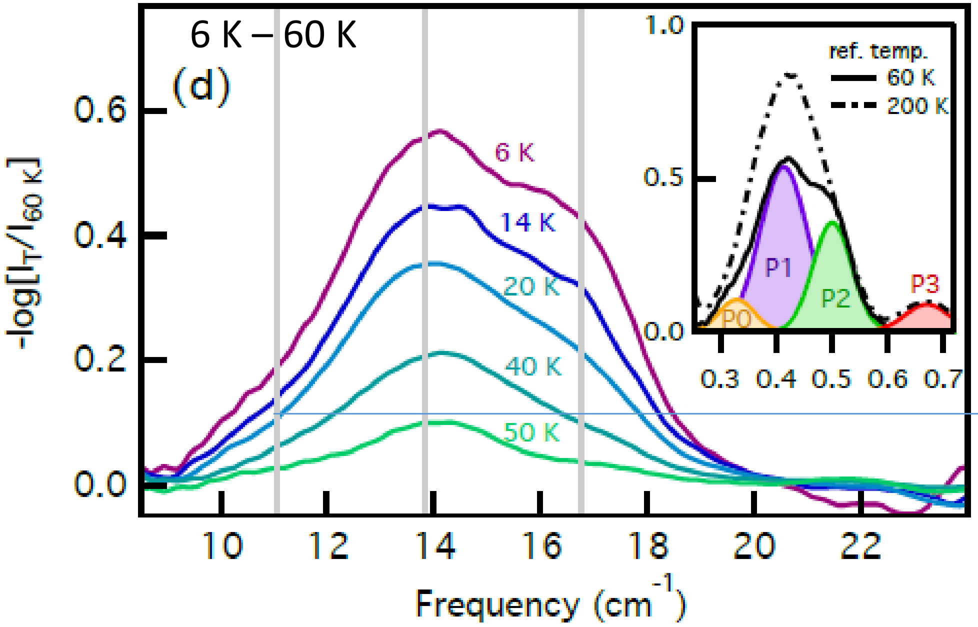
The ground state is a collective vibronic state built on CEF_0 + CEF_1 acoustic phonon +optical phonon.

These couplings only occur in TTO due to adequate energy maching and strong quadrupolar effects.

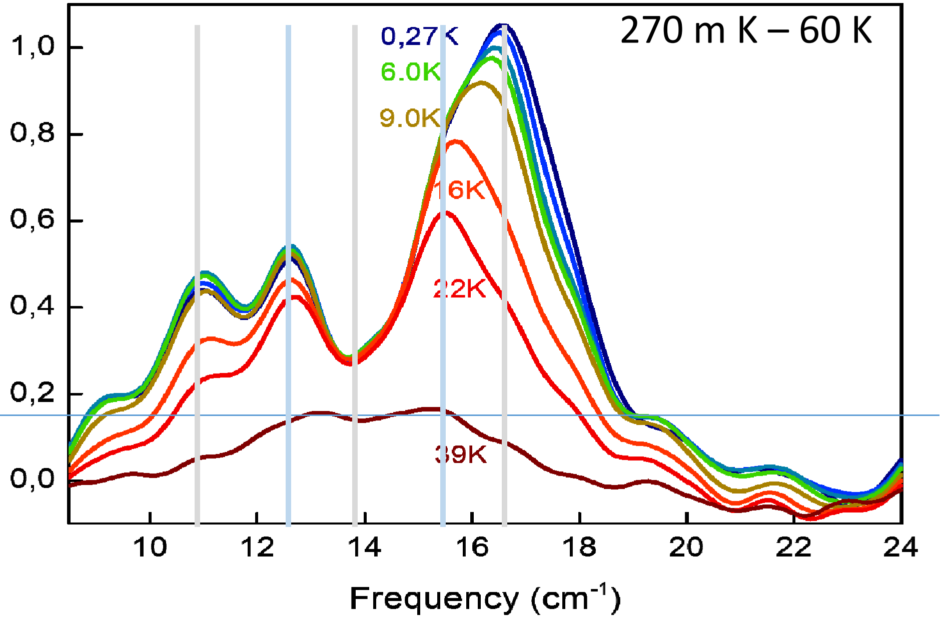
Does these couplings persist at lower temperature deep into the fluctuating spin phase ?

3. TTO THz response below 10 K

Sample #1 Spin liquid

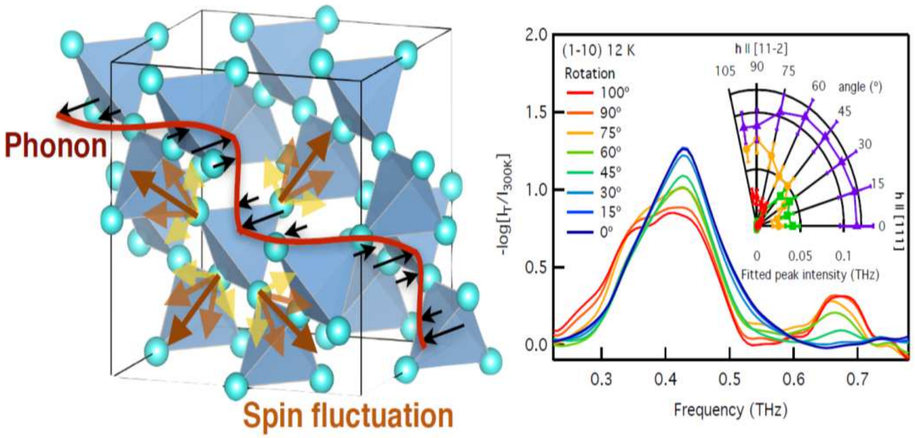


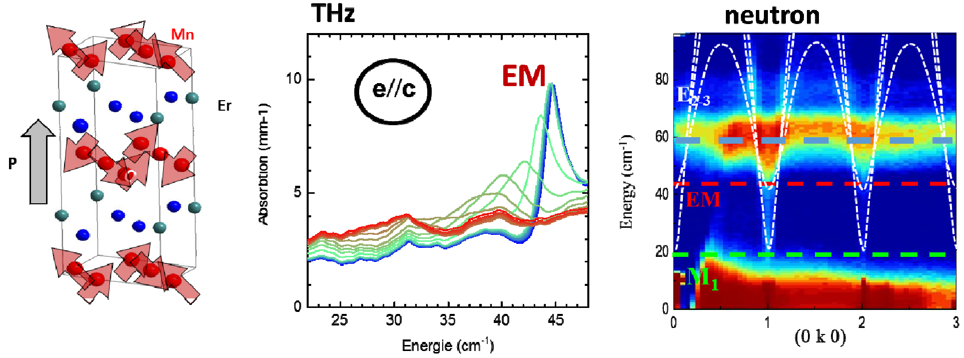
Sample #2 quadrupolar phase T_Q= 400 mK



The vibronic coupling strength is sample dependent :
Corelation with fluctuating spins / quadrupolar order? Ongoing work…

THz PROPERTIES OF COMPLEX MAGNETIC PHASES





Tb Pyrochlore : a quantum spin ice
With strong dynamical spin-lattice coupling

Hexagonal manganites : Type I multiferroic
with rare earth/ manganese
magneto-electric couplings

Y. ALEXANIAN
L. CHAIX
E. CONSTABLE *
* TU Wien -Austria

R. BALLOU
A. CANO
S. DE BRION
P. LEJAY
E. LHOTEL
J. ROBERT
V. SIMONET

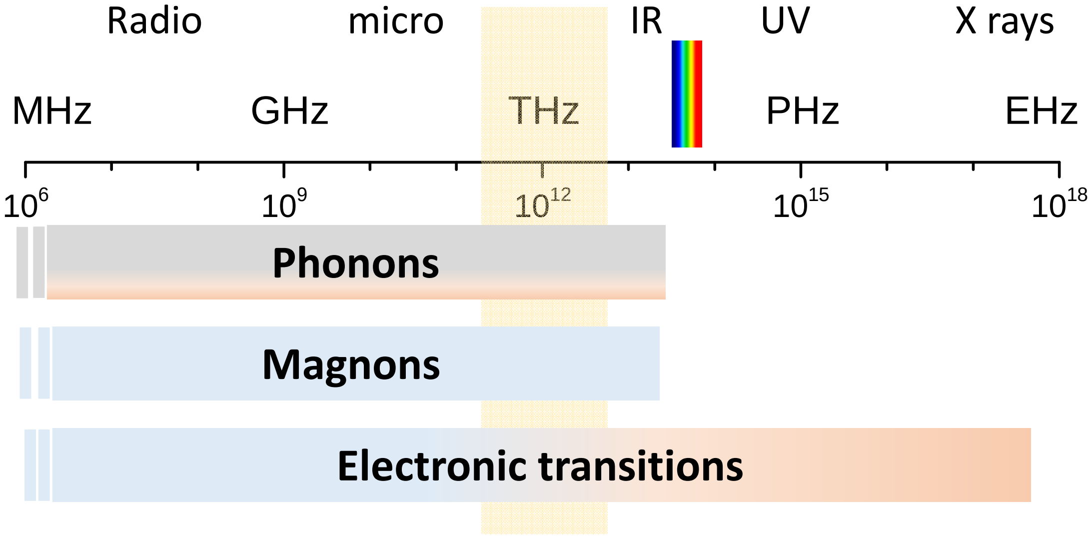
J.-B. BRUBACH
P. ROY

B. LANGEROME
M. VERSEILS

C. DECORSE
L. PINSARD-GAUDART

X. FABREGES
S.PETIT

4. Perspectives :
probing hybride excitations in the THz range



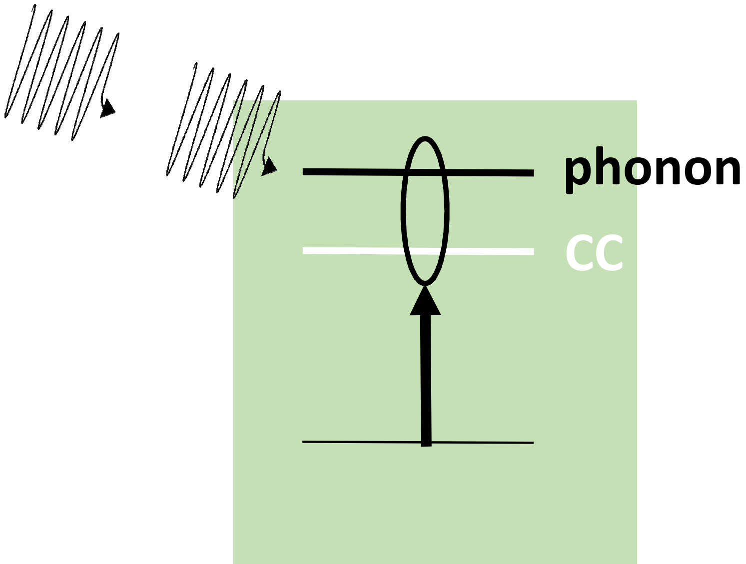
ELECTRO-
MAGNETIC
PROBE

SIGNATURES OF COMPLEX PHASES ⟷ **HYBRIDE EXCITATIONS: PRODUCTION AND MANIPULATION**

SAMPLE ENVIRONMENT T, H, P + THz SOURCES

4. PUMP PROBE EXPERIMENTS

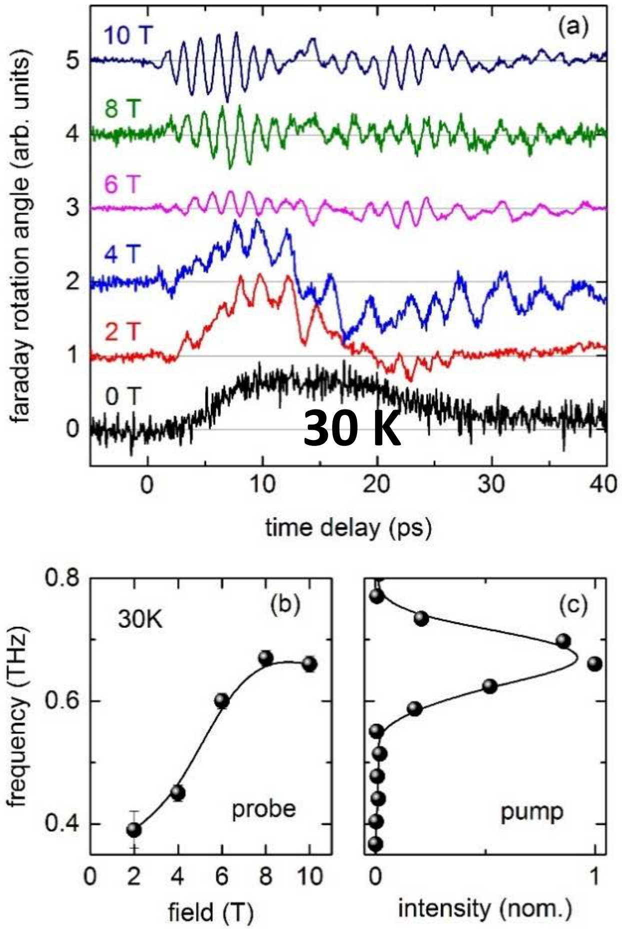
INTENSE THZ SOURCE



PUMP on one component to alter the hybridisation process …

$Tb_2Ti_2O_7$ TELBE 2017

E. constable et al



THz PROPERTIES OF COMPLEX MAGNETIC PHASES

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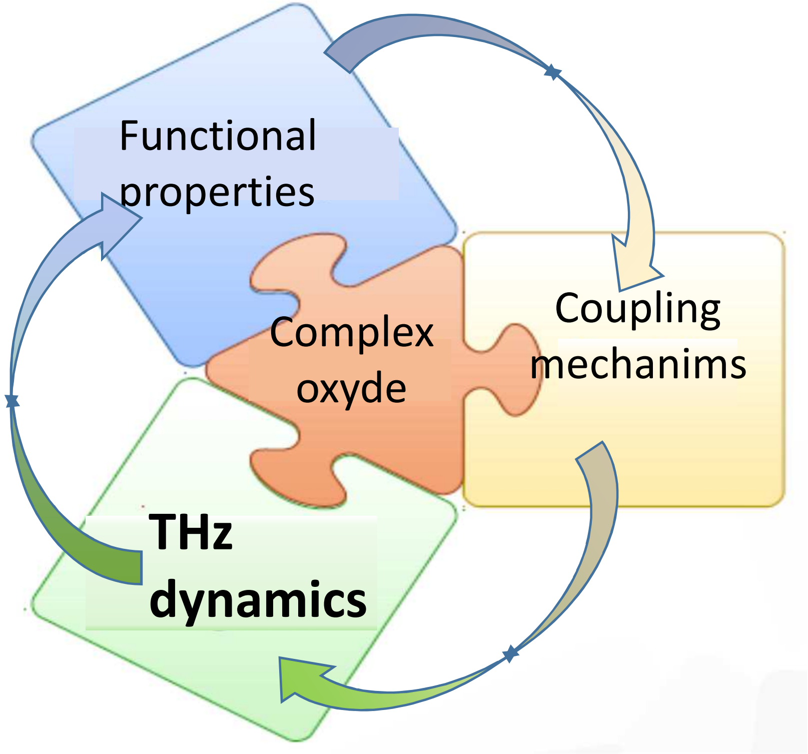
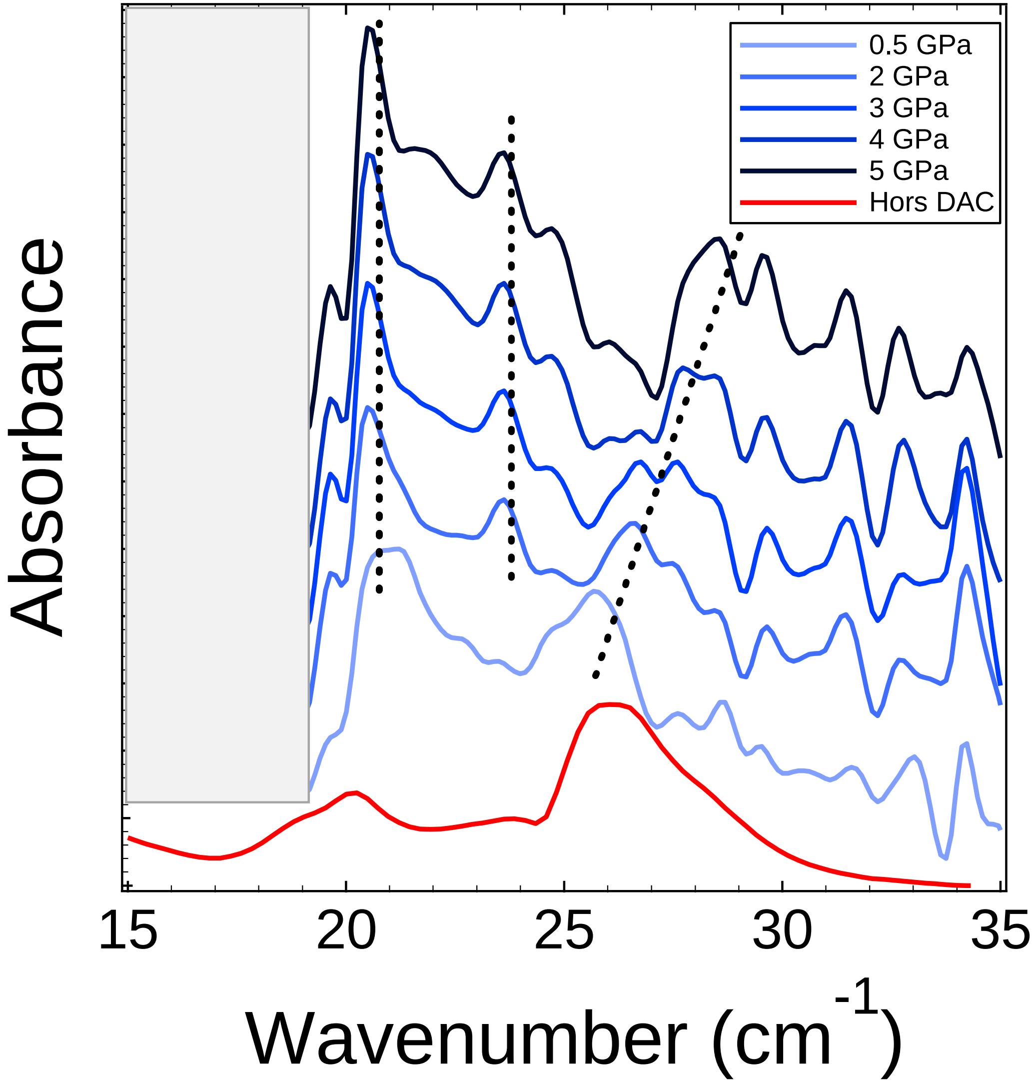


Functional properties

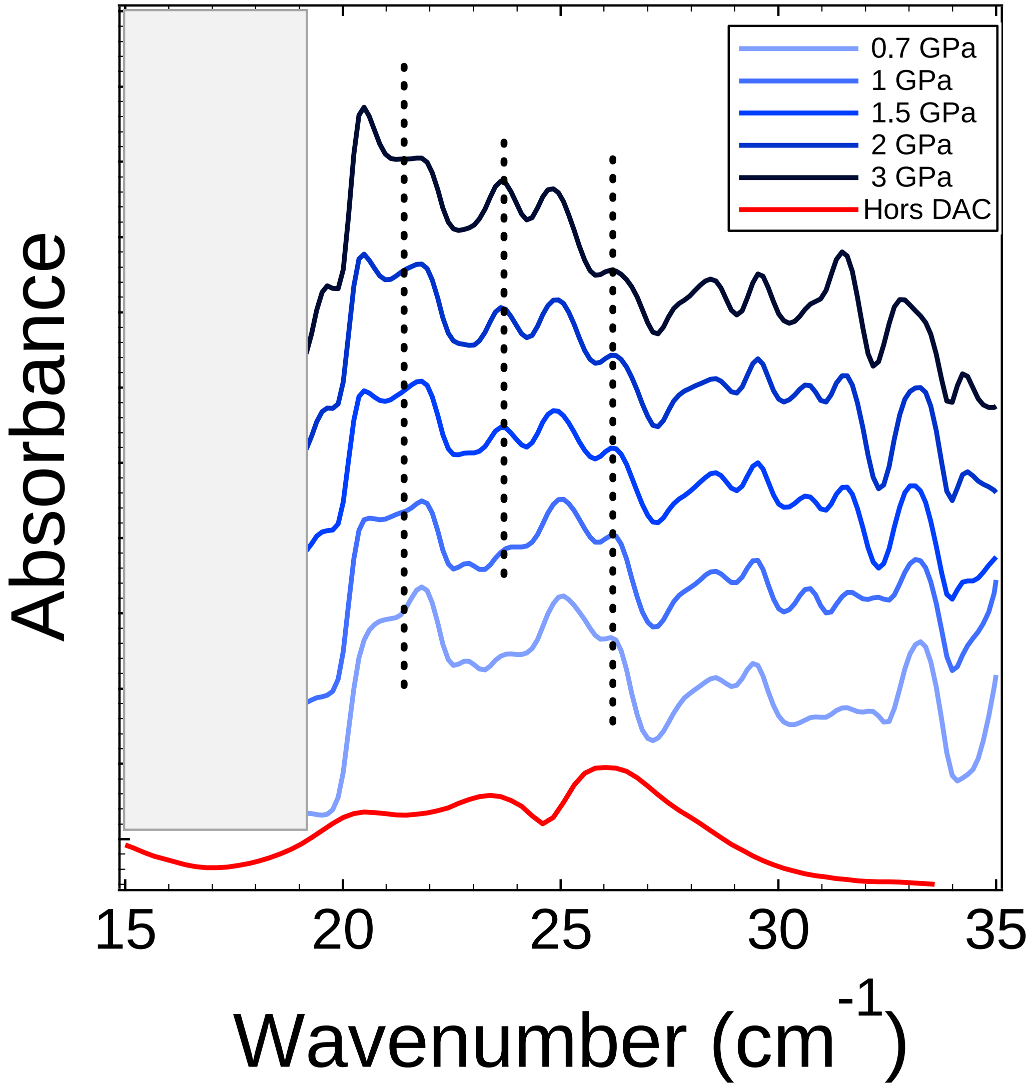
Complex oxyde

Coupling mechanims

THz dynamics



$HoMnO_3$
30K/100K



$HoMnO_3$
45K/100K

multiferroic hexagonal manganites h-RMnO3

Type I multiferroics :

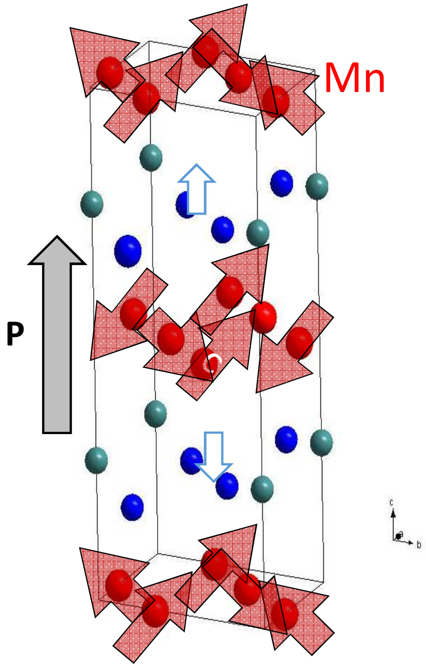
Ferroelectric T_C≈ 800 K P63*cm*

Antiferromagnetic

T_N ≈ 80 K Mn^{3+}

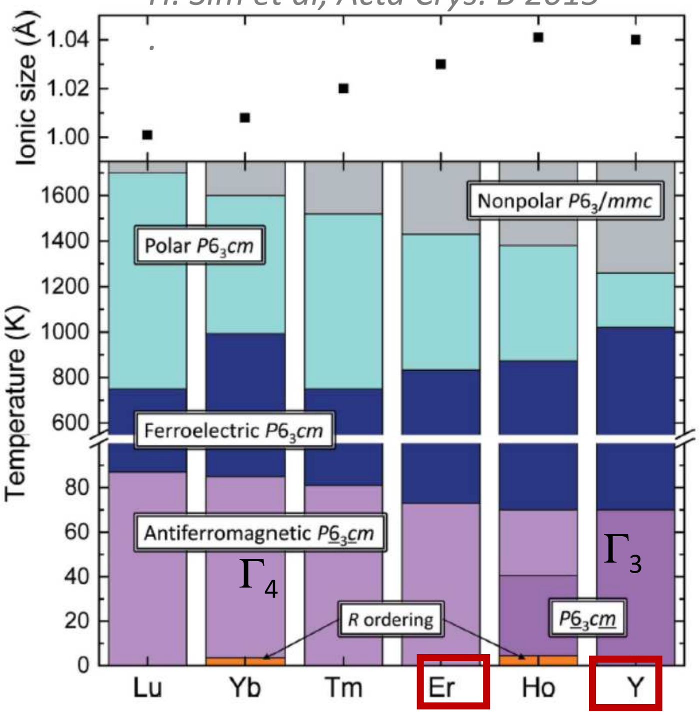
+ magnetic R at lower temperature

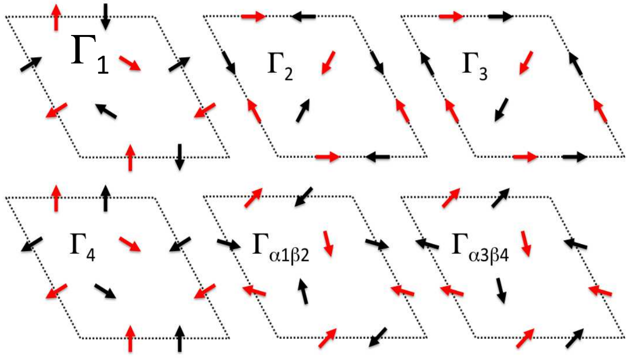
Two sites 2a and 4b



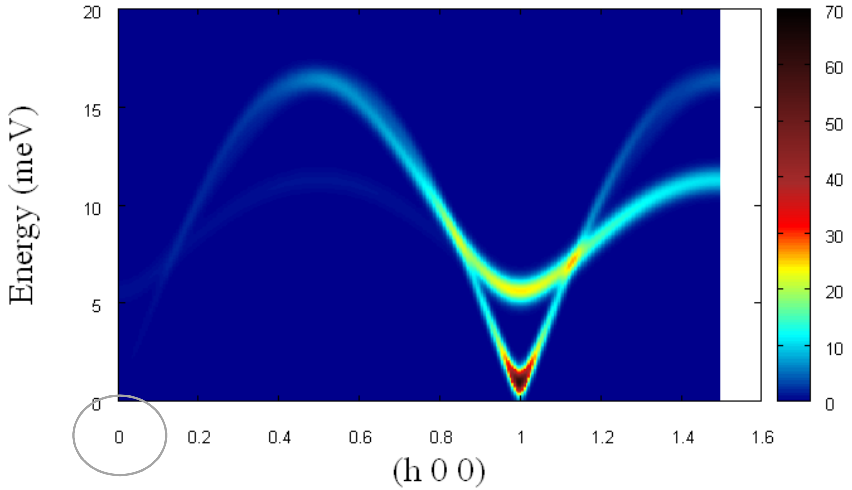
Axial magnetic/electric system

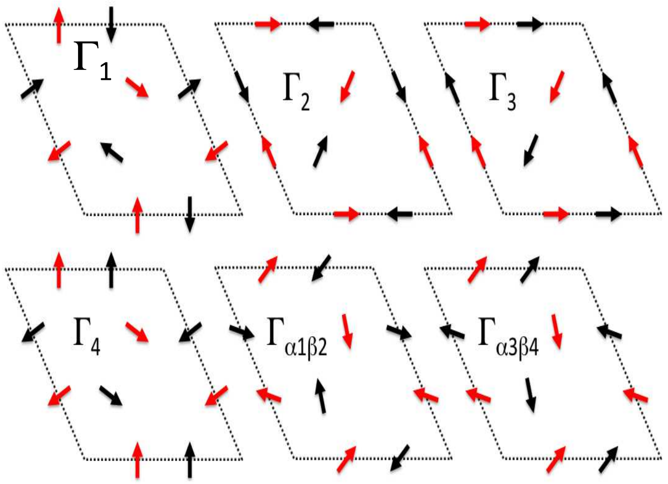
H. Sim et al, Acta Crys. B 2015



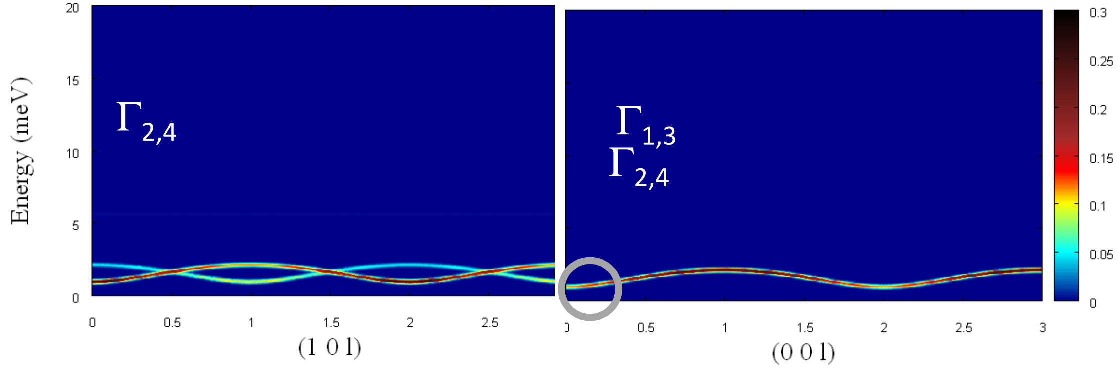


Mn Spin wave calculations / Γ point

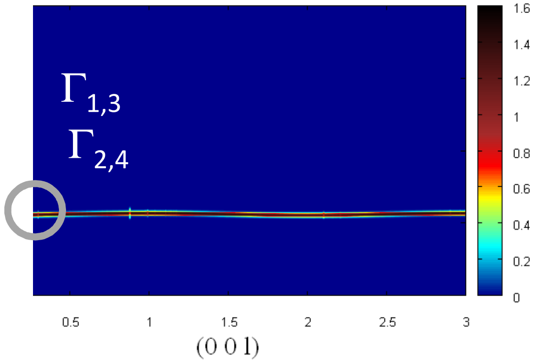




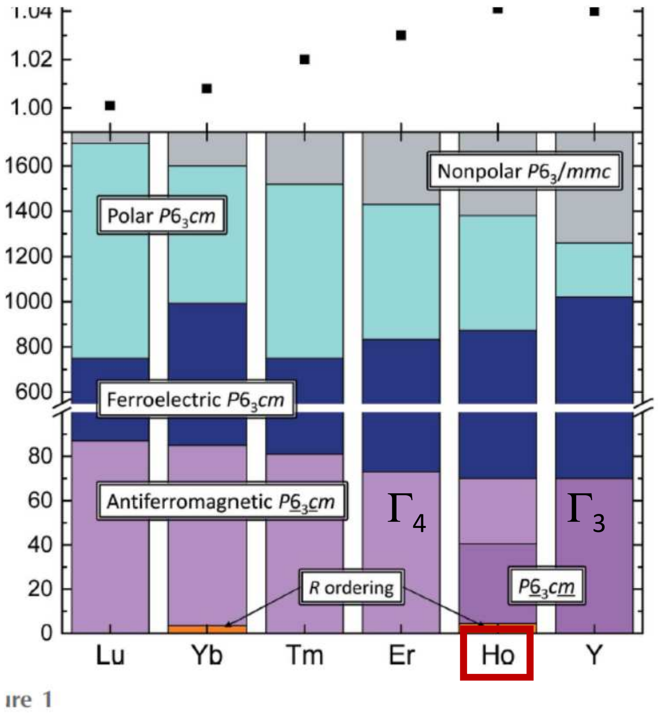
spin fluctuations // c



spin fluctuations ⊥ c



GENERAL TREND IN RARE EARTH MANGANITES ?
h-HoMnO$_3$



H. Sim et al, Acta Crys. B 2015

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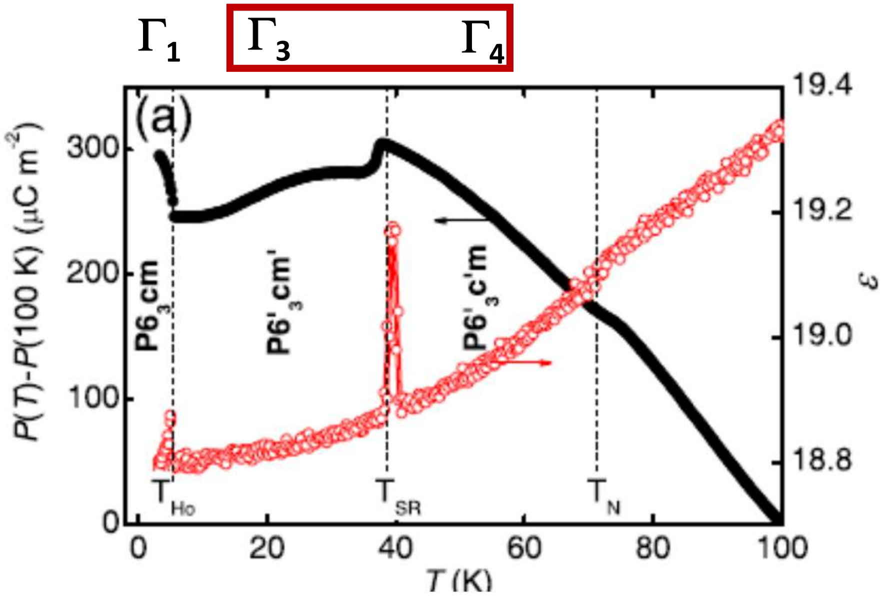
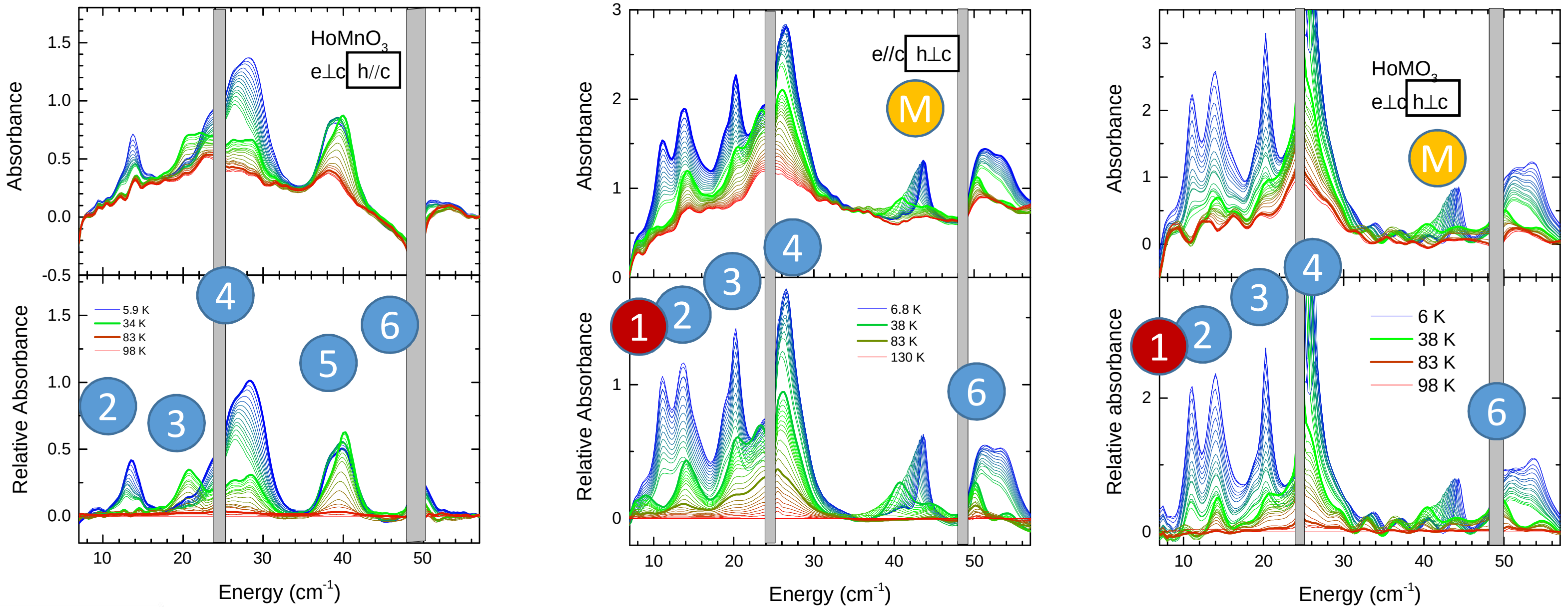


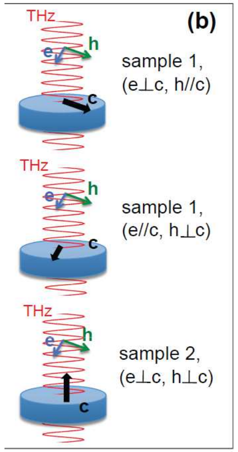
Hur et al PRB 2009 e// c

h-HoMnO$_3$

T_N= 75 K T_{SR}= 37 K

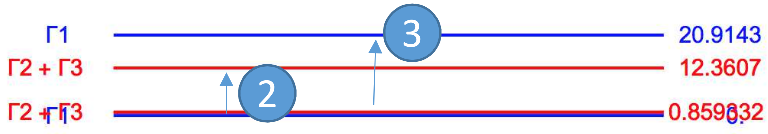
THz spectroscopy on HoMnO$_3$



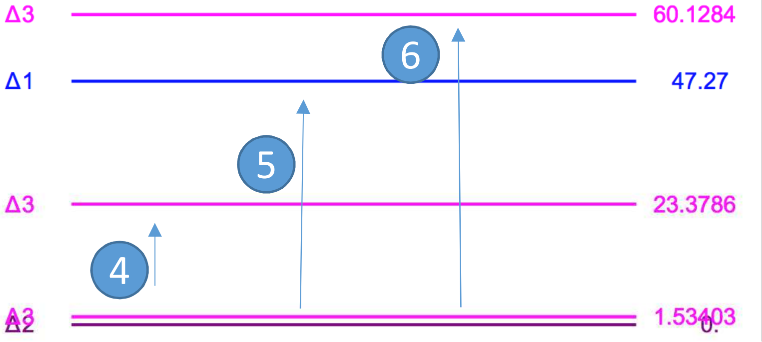


THE WHOLE SPECTRUM IS OF MAGNETIC ORIGIN (h involved only)
Mn Magnon around 40 cm-1 + Ho CF excitations
LARGE CHANGES AT T$_{SR}$!

HoMnO$_3$ CF CALCULATIONS



Ho Site 4b



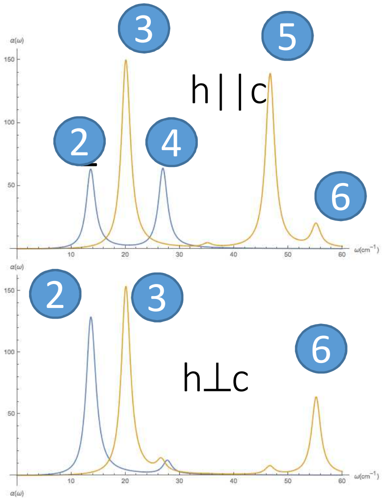
Ho Site 2a

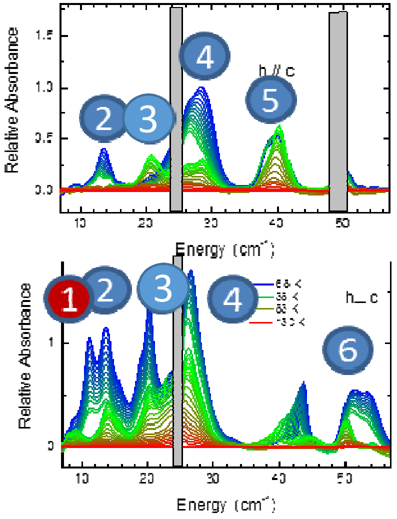
2 transitions for Ho(4b)

② ③

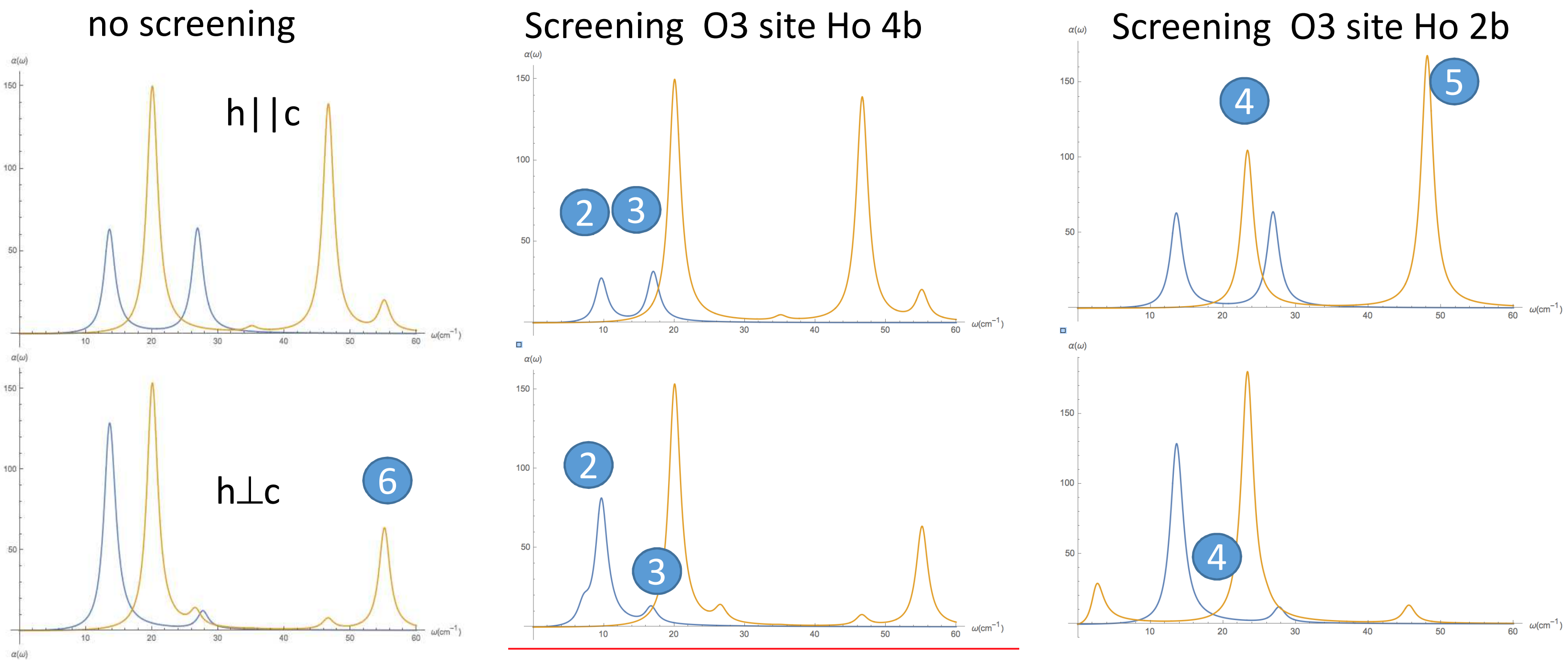
3 transitions for Ho (2a)

④ ⑤ ⑥





CF CALCULATIONS : Oxygen screening effects



no screening

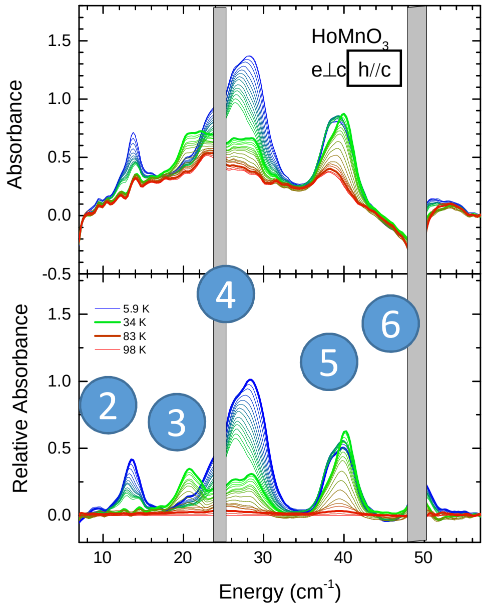
Screening O3 site Ho 4b

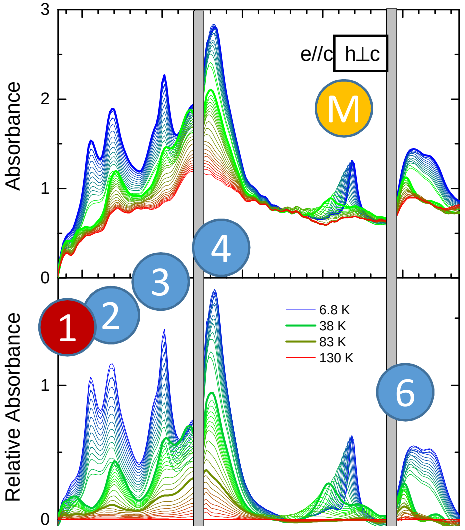
Screening O3 site Ho 2b

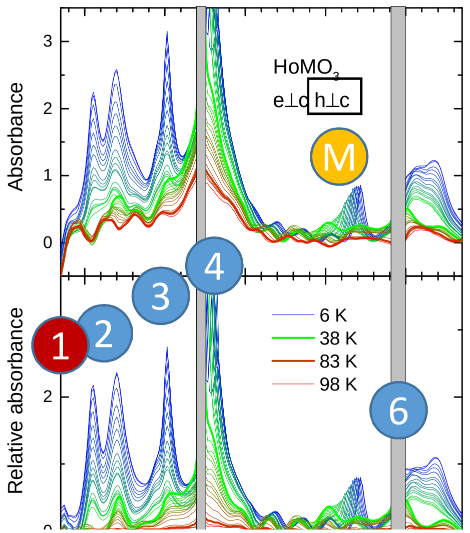
Shift in energy + change in sprectral weight

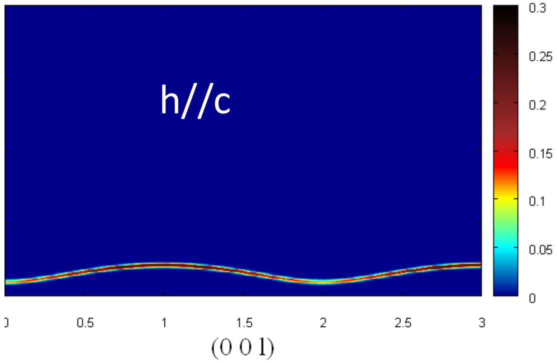
LARGE CHANGES in Ho CF excitations AT T_{SR} explained by Oxygen related effects

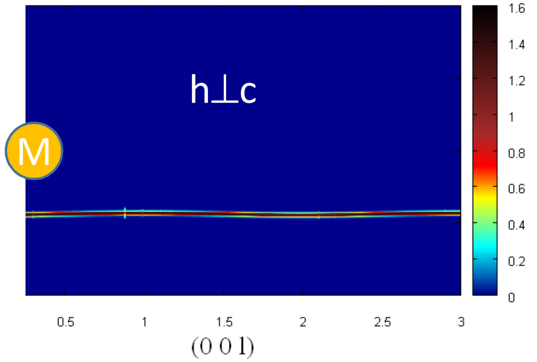
THz spectroscopy on $HoMnO_3$







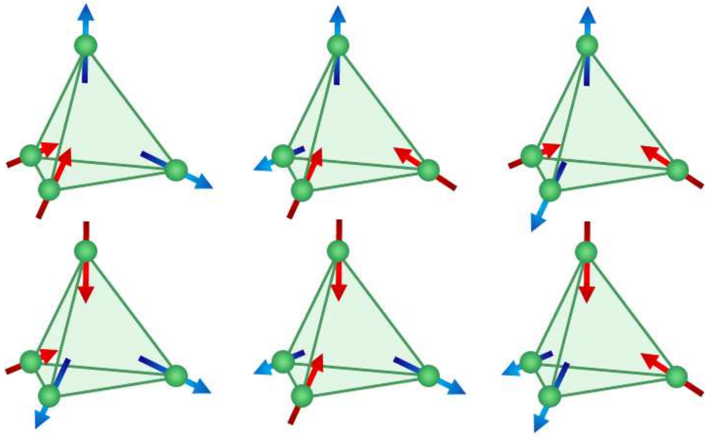




Where are the magnons ?
OK M
But 1 has the wrong selection rules !

⇨ **Hybridization Mn spin wave / Ho CF**

1. Spin ices

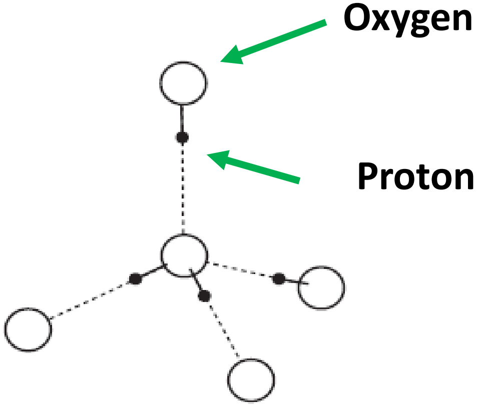


Extensive degeneracy
Finite entropy

« 2 in – 2 out »

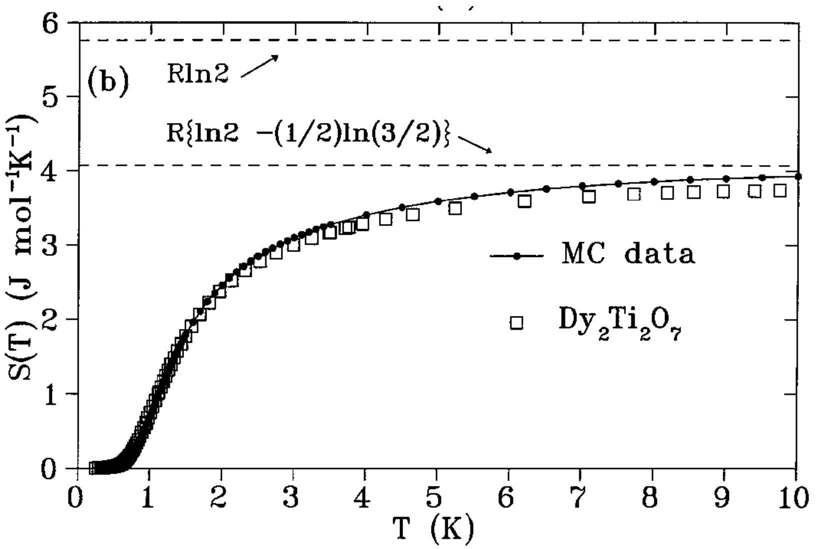
« ice rule »

Local order of protons in water ice
« 2 close - 2 far » from Oxygen



Oxygen

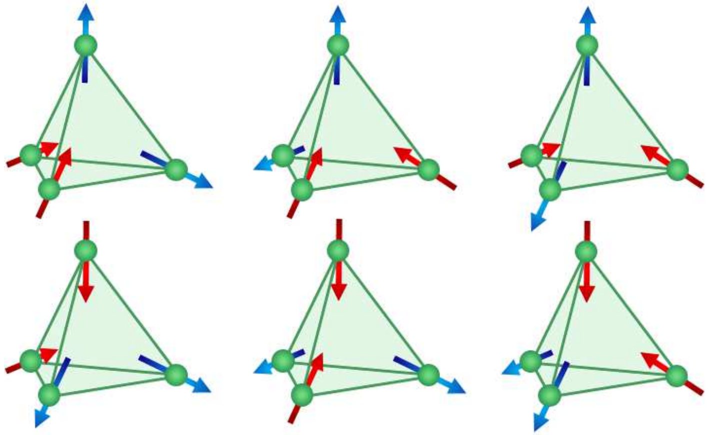
Proton



J.S.Gardner, M.J.P.Gingras, J.E.Greedan, Phys.Rev.Mod 82 (2010)

1. Spin ices

No long range order but strong spin correlations



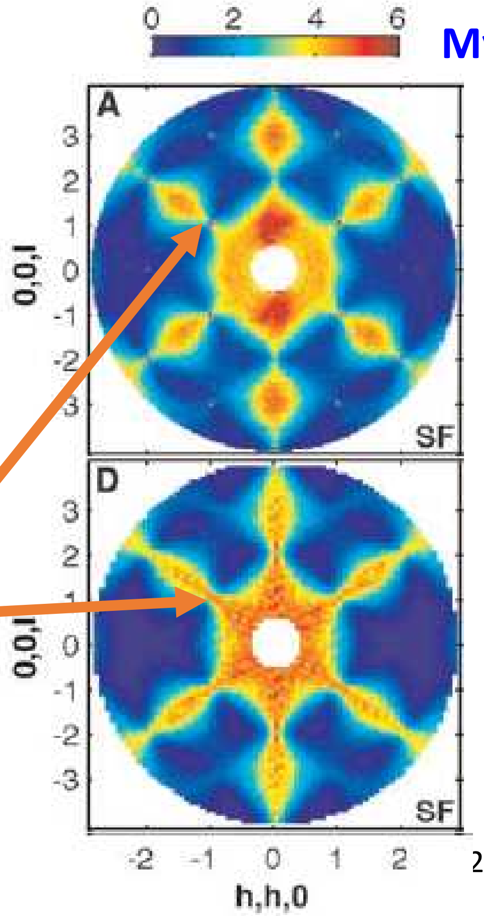
Ice rule :

two in – two out

div **B**=0   Coulomb phase

Power law spin correlations

Pinch points



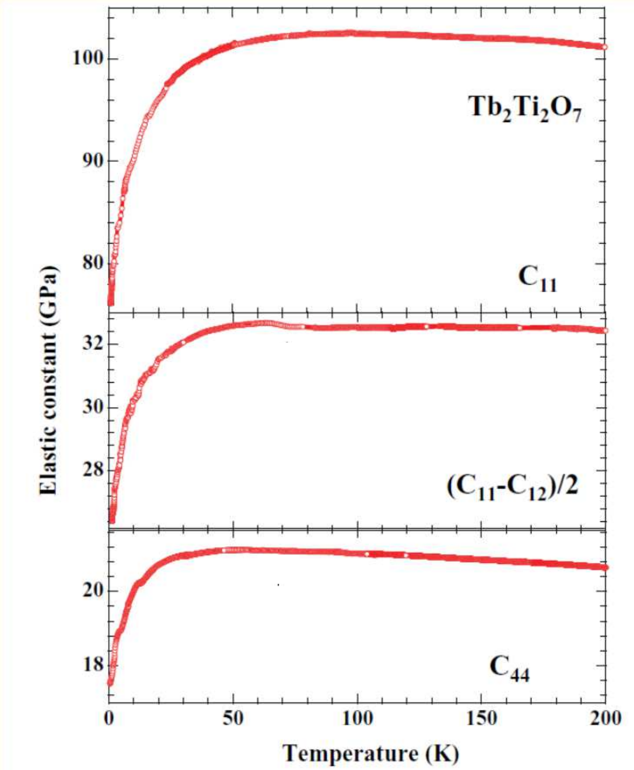
$Ho_2Ti_2O_7$

26 (2009)

Neutron diffuse scattering
T.Fennell & al, Science 326 (2009)

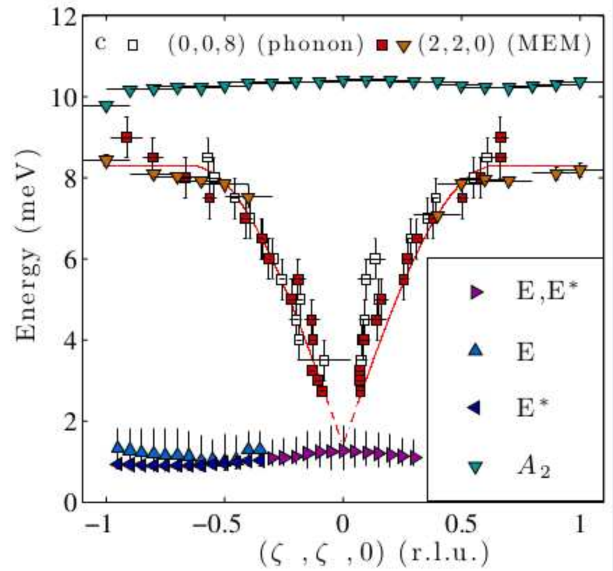
1. TTO peculiarities: lattice effects

Nakanishi et al, PRB 2011



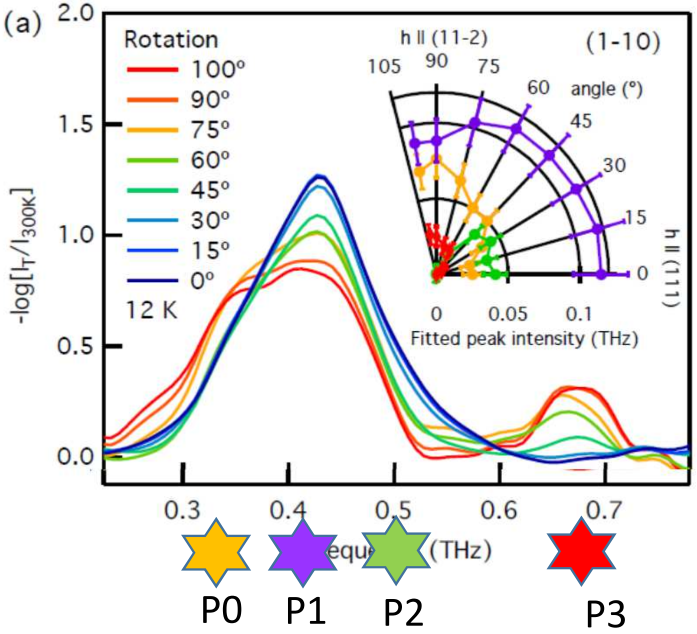
Giant softening
with no lattice distortion

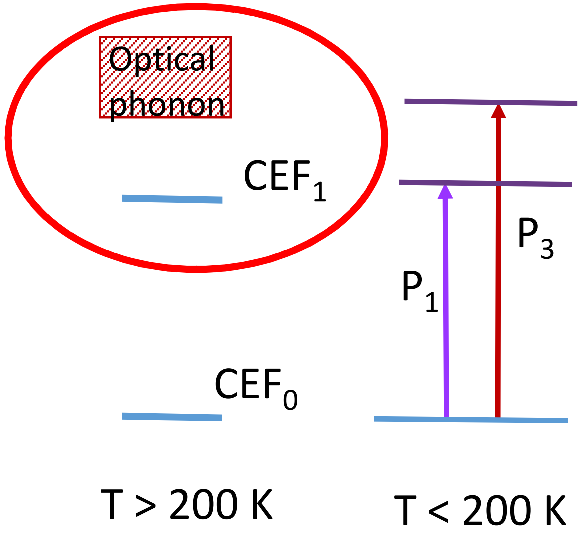
Fennell et al, PRL, 112 (2014)

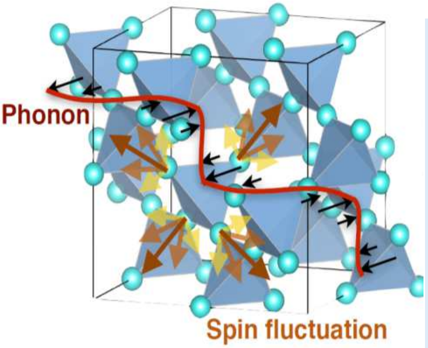


Magneto-elastic mode (MEM)
with the same dispersion as the
transverse acoustic phonon

3. TTO High Temperature vibronic process T < 200 K



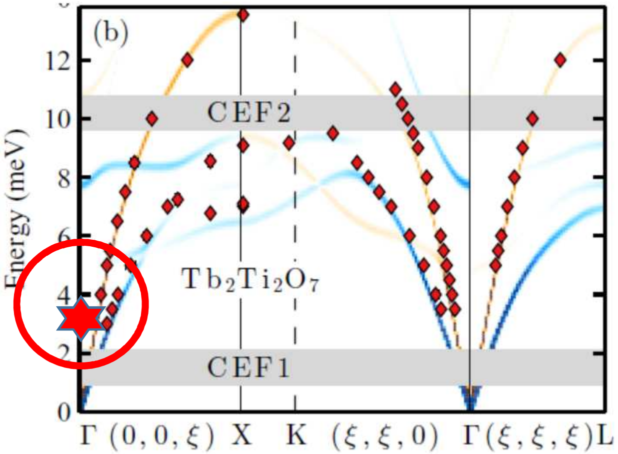




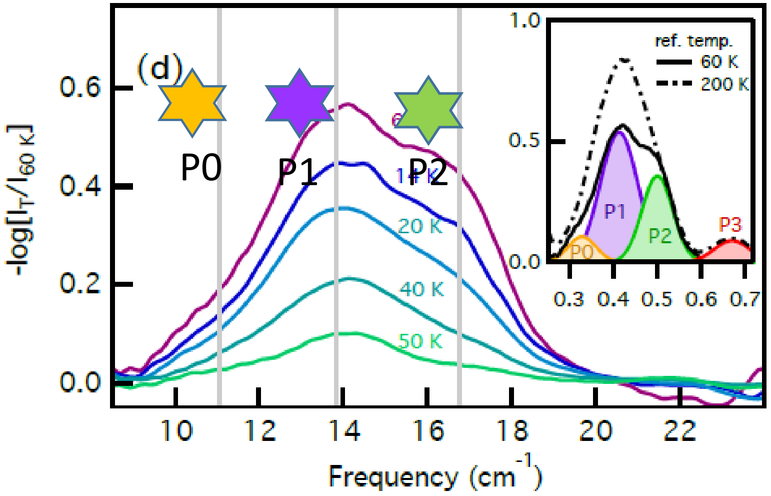
coupling
with a (silent) optical phonon
only CEF_1 is affected.

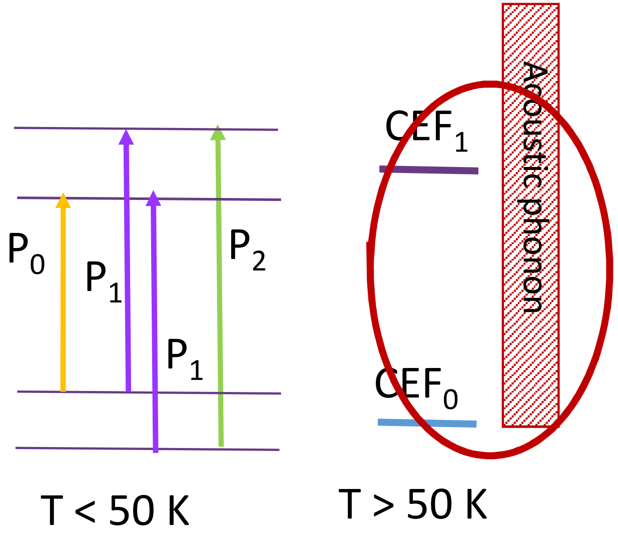
The lowest optical phonon is calculated at 4.6 meV=37 cm^{-1} close to P3 at 22 cm^{-1} (2.78 meV).

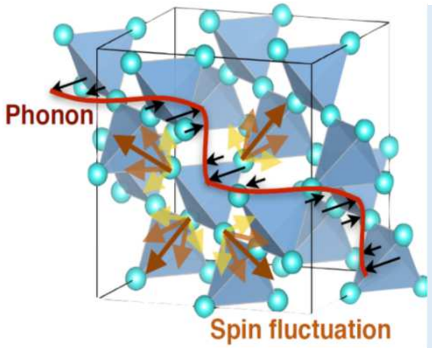
Ruminy et al, PRB, 93 (2016)



3. TTO low temperature vibronic process T < 50 K





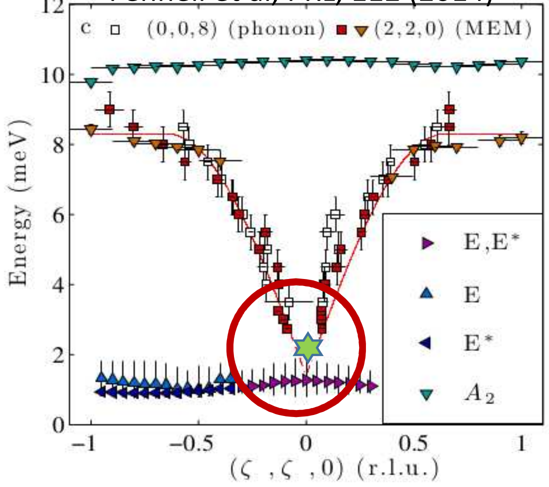


CEF_0 and CEF_1 degeneracy lifted with similar amplitude

P2 matches the MEM
(CEF_1 / acoustic phonon coupling).

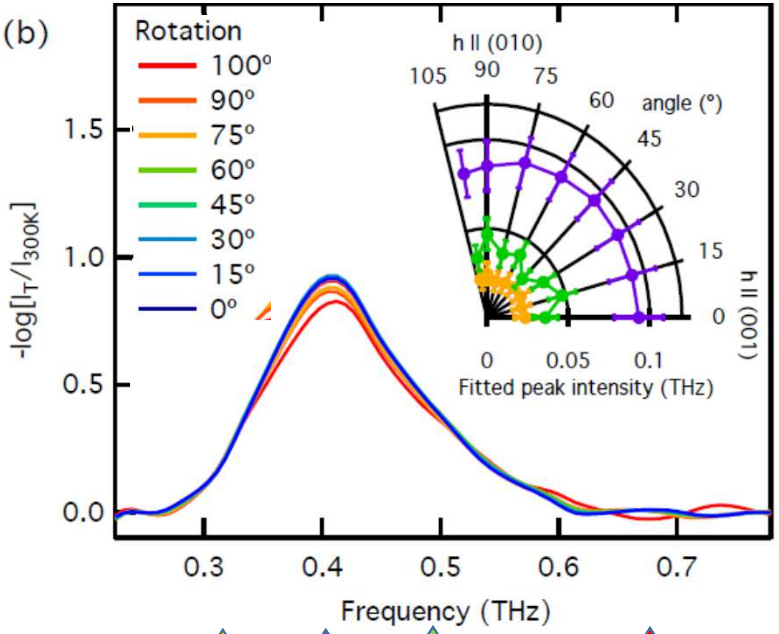
MAGNETO-ELASTIC COUPLING OCCURS ALSO WITH THE GROUND STATE.

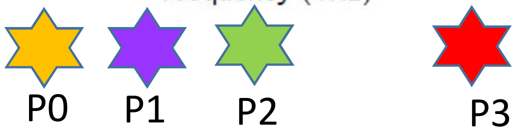
Fennell et al, PRL, 112 (2014)



$Tb_2Ti_2O_7$ THz SPECTRA: ANGULAR DEPENDENCE

Rotation around the 4-fold [100] axis at 12 K



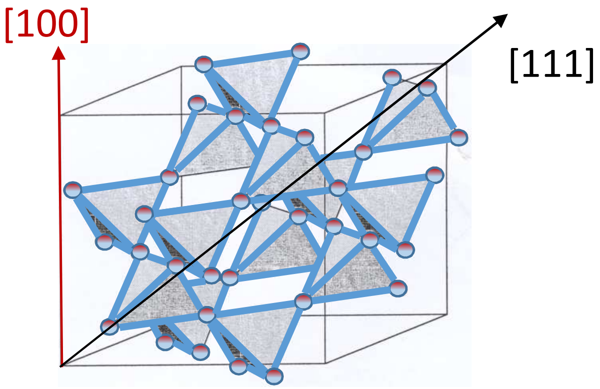


[100] 4-fold axis:

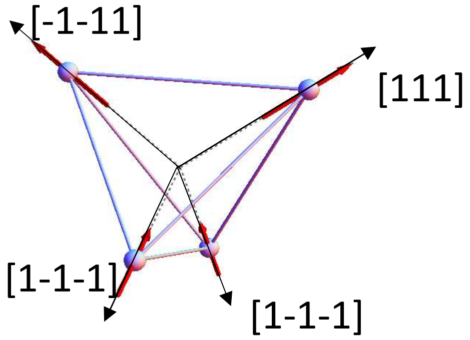
P3 absent

P1 strongest

Global cubic symmetry



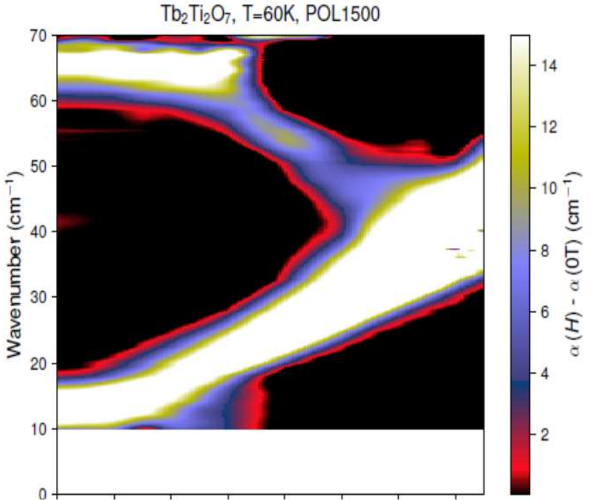
Multiaxial Ising system



TTO THz spectra under magnetic field

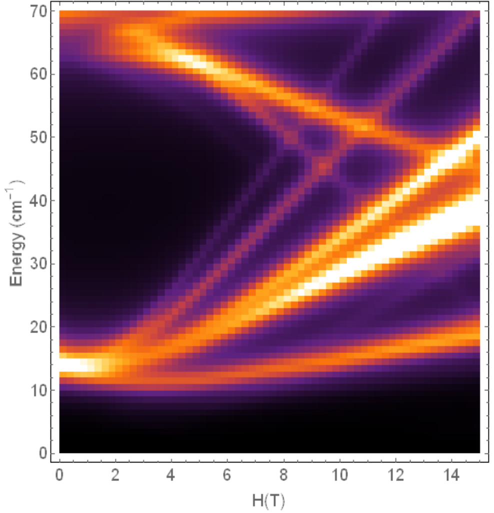
NICPB
Tallinn
K. Amelin
&al

60 K
0 – 14 T



Calculation
Néel

60 K
0 – 14 T



Hamiltonien:

$$\hat{H} = \sum_{i=1}^{4}\left(\sum_{k,q} B_q^k\,\hat{O}_q^k - \frac{g_J \mu_B}{k_B}\boldsymbol{H}\cdot\hat{\boldsymbol{J}} + D_2^1\hat{O}_2^1 + \; D_2^2\hat{O}_2^2)\right)_i$$

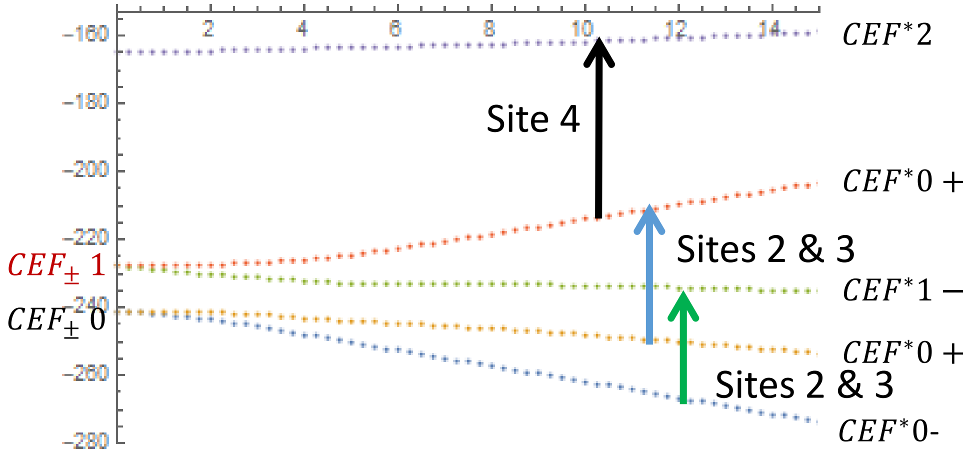


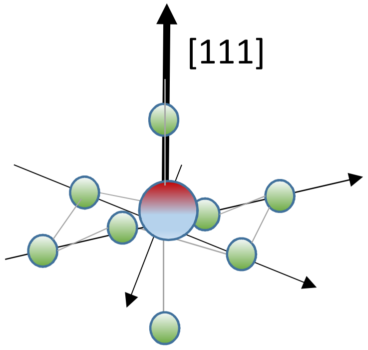
Diagramme des niveaux d’énergie pour les sites 2, 3 et 4 (champ statique H // [111]

Vibronic process

in the local D3d symmetry:

Coupling for phonons and CEF states with same symmetry and opposite parity via quadrupolar operators

$$\mathcal{H}_{\mathrm{ME}} = \sum_{\gamma\gamma'} \zeta_{2E_u\gamma\gamma'} \underbrace{(a^\dagger_{E_u\gamma} + a_{E_u\gamma})}_{\text{phonons}} \langle r^2 \rangle \sum_{m=1,2} \sum_{\substack{s=\pm \\ x=0,1}} \sum_{\substack{s'=\pm \\ x'=0,1}} \underbrace{|\psi^x_s\rangle\langle\psi^x_s|\, f_{E_g\gamma'}(\mathcal{C}^m_2)\, |\psi^{x'}_{s'}\rangle\langle\psi^{x'}_{s'}|}_{\text{Electronic states}}$$



Quadrupolar Wyborne operators

Acoustic phonon:

$$T_{1u\downarrow D_{3d}} = A_{2u} \oplus E_u$$

Coupling to Eg CEF states through $\mathcal{C}^m_2 \pm \mathcal{C}^{-m}_2 \ (m = 1, 2)$

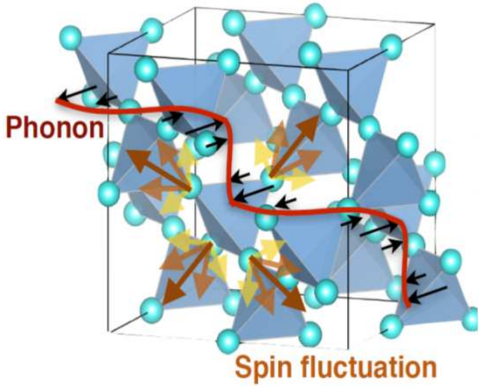
Optical phonon:

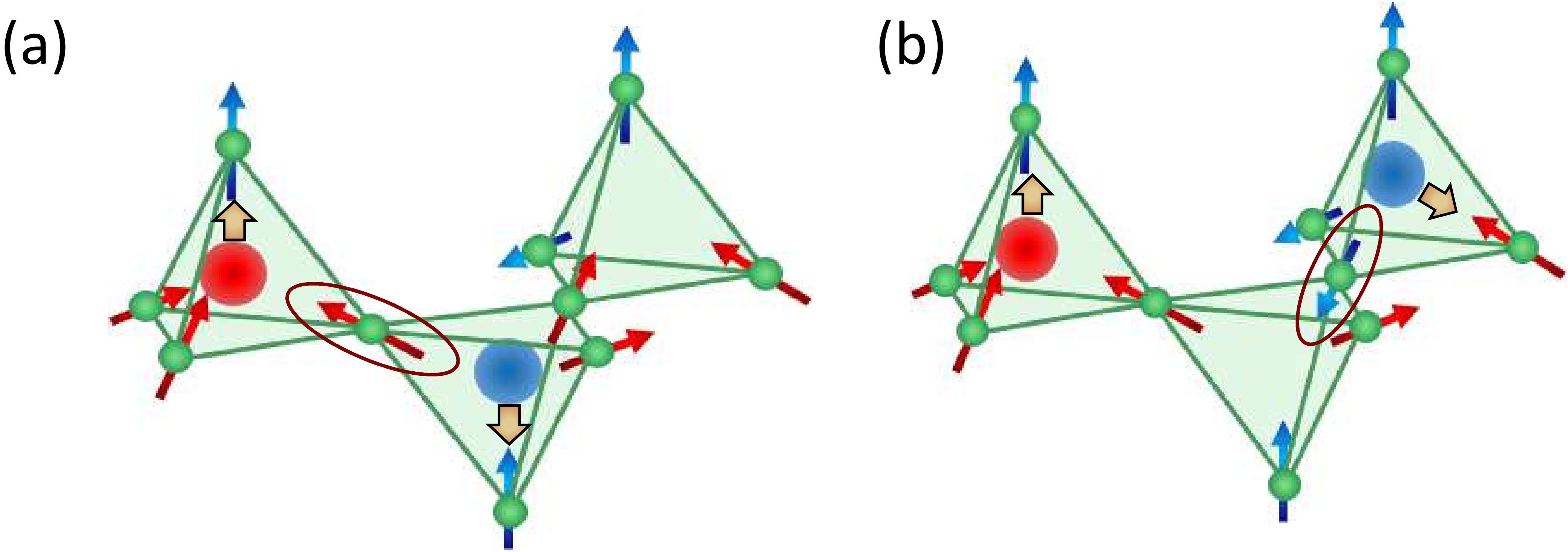
$$T_{2u\downarrow D_{3d}} = A_{1u} \oplus E_u$$

Coupling to Eg CEF states through $\mathcal{C}^m_2 \pm \mathcal{C}^{-m}_2 \ (m = 1, 2)$ and C^2_0

$\mathcal{D}_{3d}$	$\bar{3}$m	$\mathfrak{C}_1$	$\mathfrak{C}_2$	$\mathfrak{C}_3$	$\mathfrak{C}_{\bar{1}}$	$\mathfrak{C}_{\bar{2}}$	$\mathfrak{C}_{\bar{3}}$	Basis Vectors – Invariants
A_{1g}	Γ^+_1	1	1	1	1	1	1	C^2_0 $\vec{E}^2 - \vec{B}^2$
A_{2g}	Γ^+_2	1	-1	1	1	-1	1	[illegible]
E_g	Γ^+_3	2	0	-1	2	0	-1	$\mathcal{C}^m_2 \pm \mathcal{C}^{-m}_2 \ (m = 1, 2)$ (J_x, J_y)
A_{1u}	Γ^-_1	1	1	1	-1	-1	-1	$E \cdot B$
A_{2u}	Γ^-_2	1	-1	1	-1	1	-1	Z
E_u	Γ^-_3	2	0	-1	-2	0	1	(X, Y)

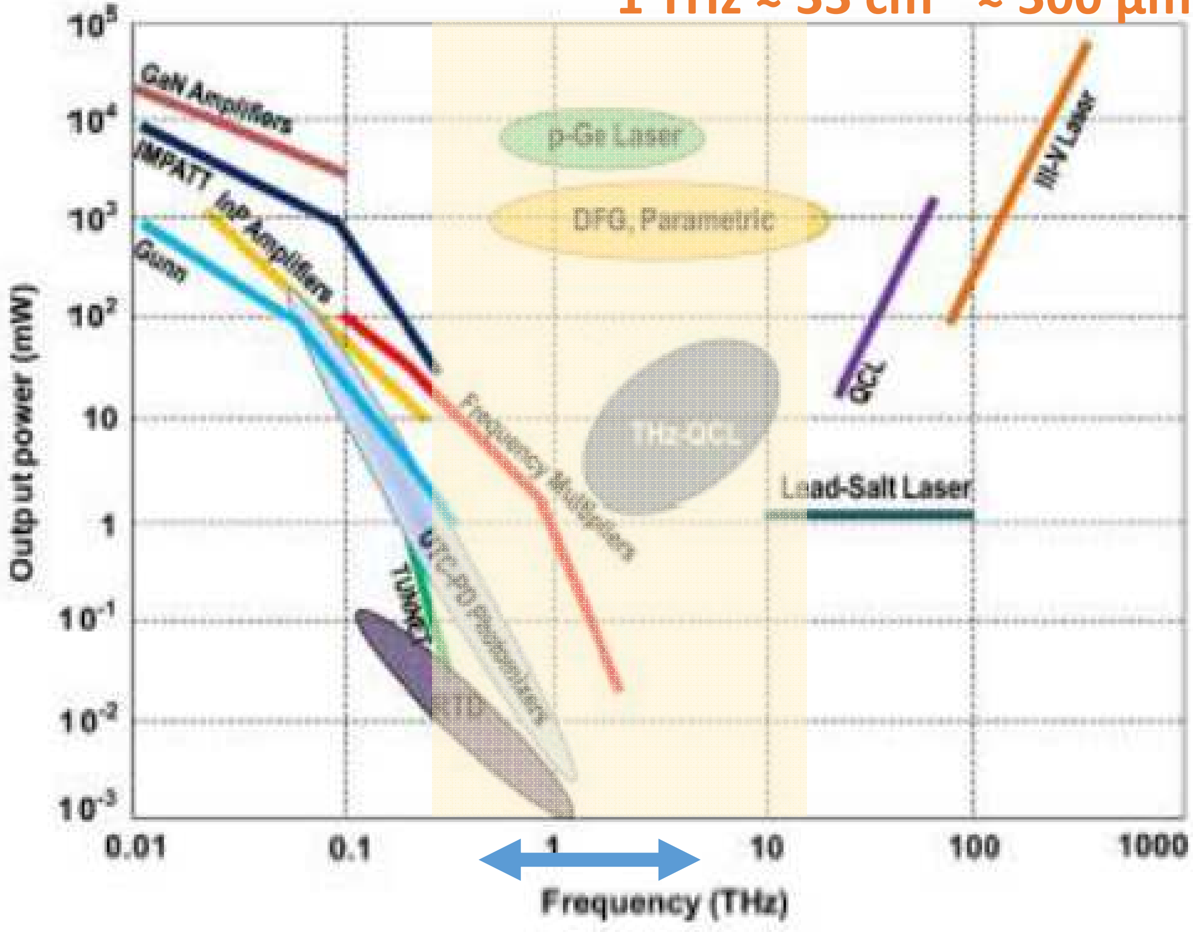
and




(a)
(b)

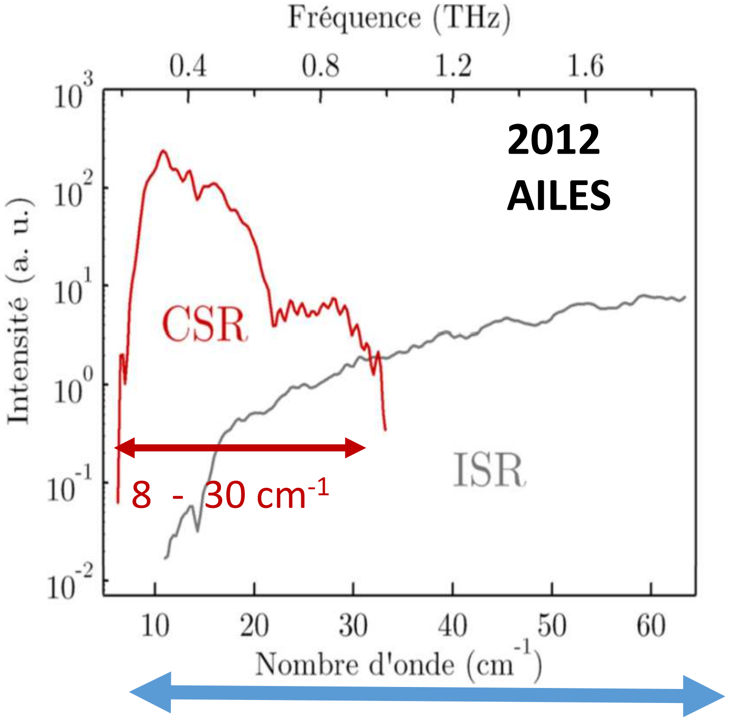
1. THz SPECTROSCOPY

1 THz ≈ 33 cm^{-1} ≈ 300 µm ≈ 4 meV ≈ 50 K



The THz GAP

SOLEIL SYNCHROTRON



SYNCHROTRON :

AILES@SOLEIL

THz spectroscopy in multiferroic HoMnO3

N.P. ARMITAGE et al , PRL 2017
TDS laser source

X. FABREGES et al, in press
SYNCHTROTRON SOURCE AILES@SOLEIL