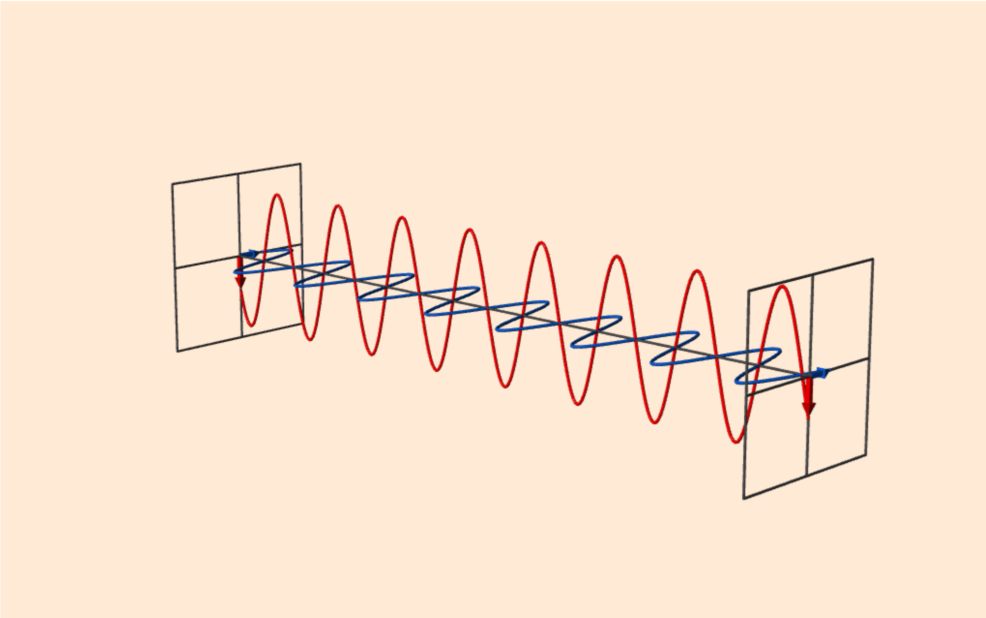
THZ DYMAMICS IN OXIDES

with Electro-magnetic waves

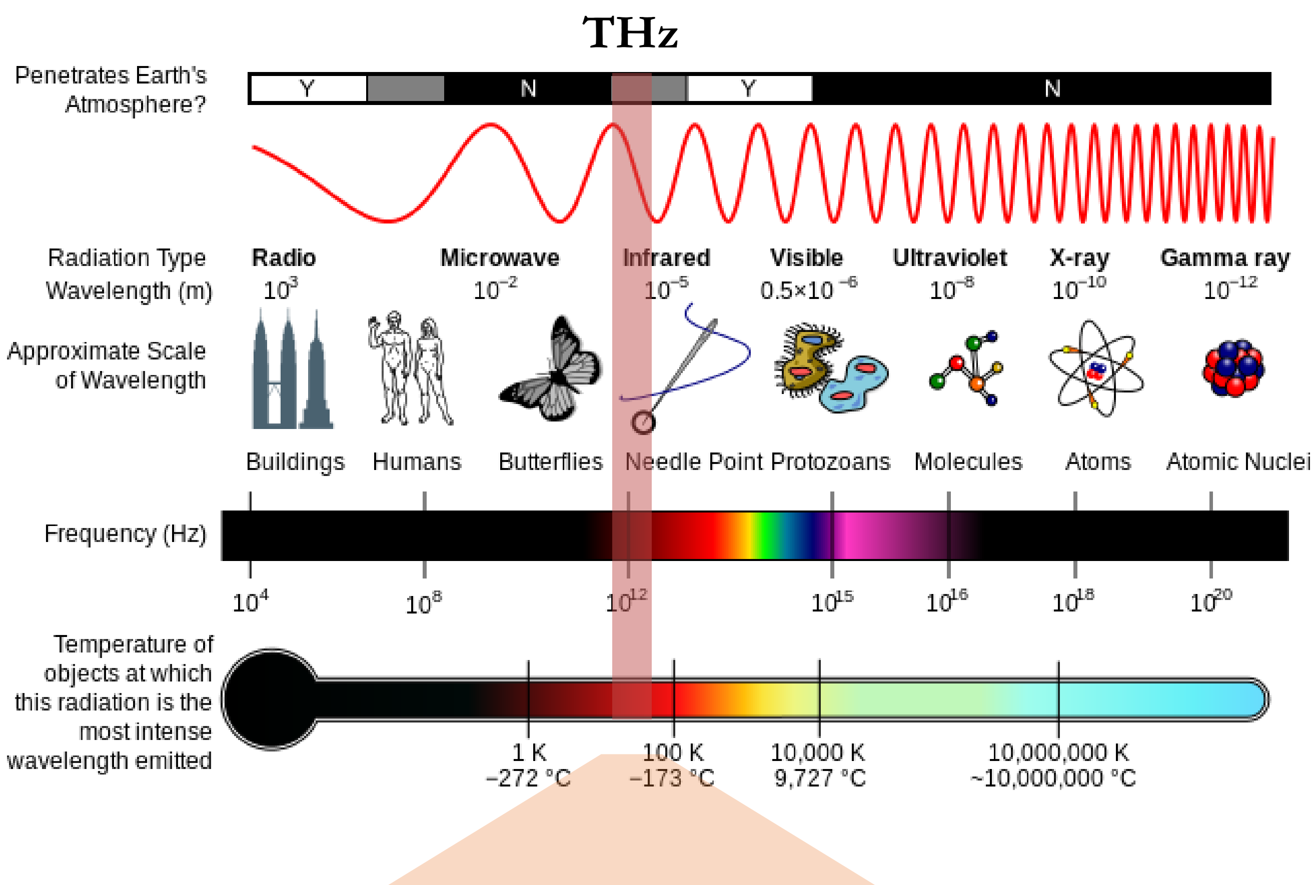


EMANIM

Electric and magnetic fields

S. DE BRION Aug 2023

The THz range in the electromagnetic spectrum

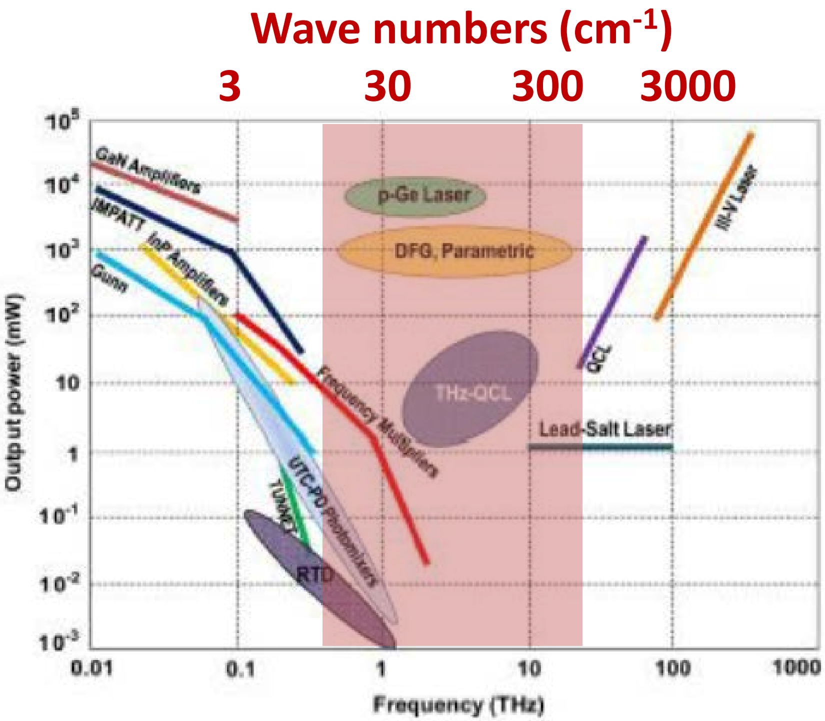


wikipedia

$1\ \text{THz} \approx 33\ \text{cm}^{-1} \approx 0.3\text{mm} \approx 4\ \text{meV} \approx 50\ \text{K}$

The THz gap

2011

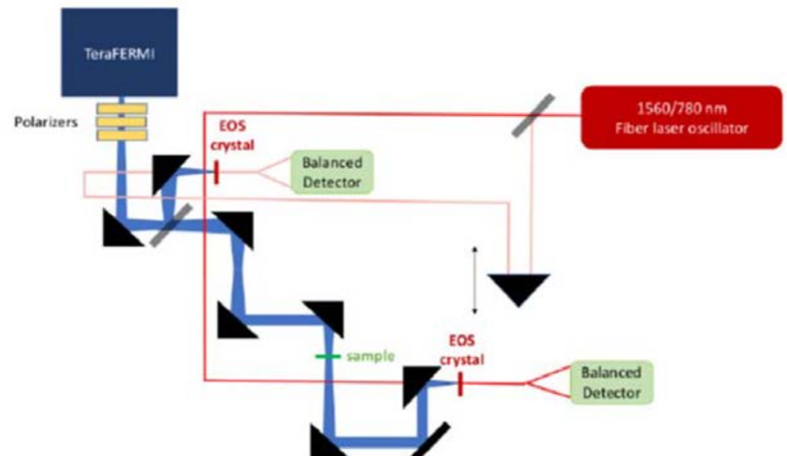


Electronics

Photonics

2023

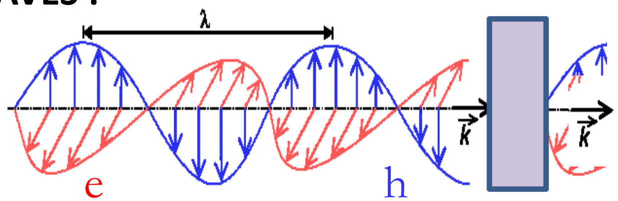
Time domain spectrometers
Synchroton base THz emission
FEL strong THz pulses



Time domain spectrometer at TeraFERMI

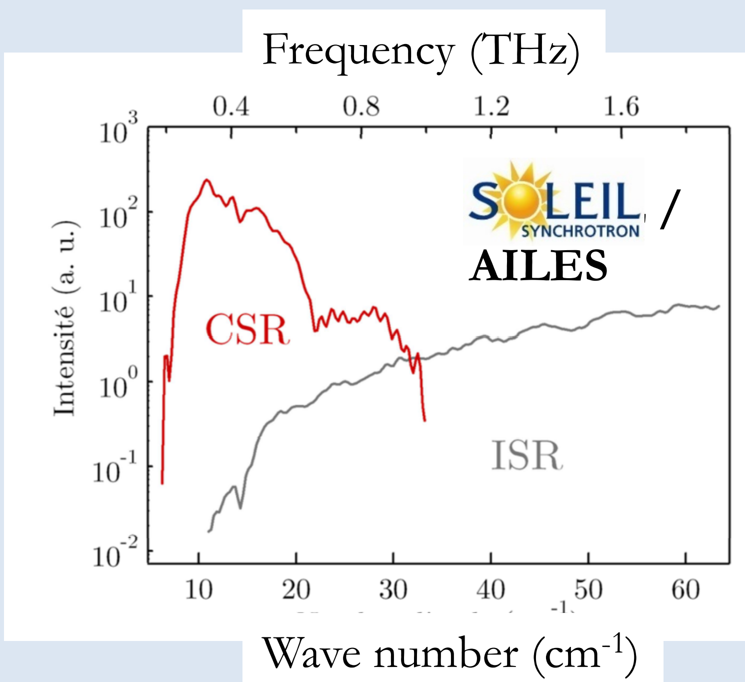
THz spectroscopy at SOLEIL@AILES

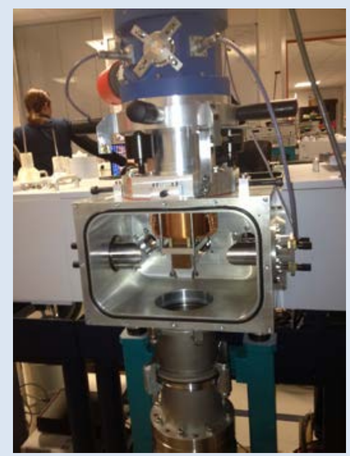
THz WAVES :



A probe for the dynamics of electric charges and magnetic moments at ~zero wave vector

SYNCHROTRON BASED SPECTROSCOPY:

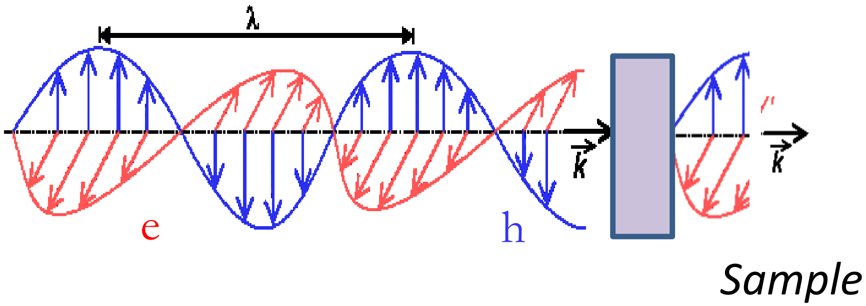




An intense,stable broadband THz source in a cryogenic environment

THz spectroscopy

THz wave :



Fourier transform spectroscopy

Transmission : $T = I / I_0 \approx \exp(-\alpha d)$

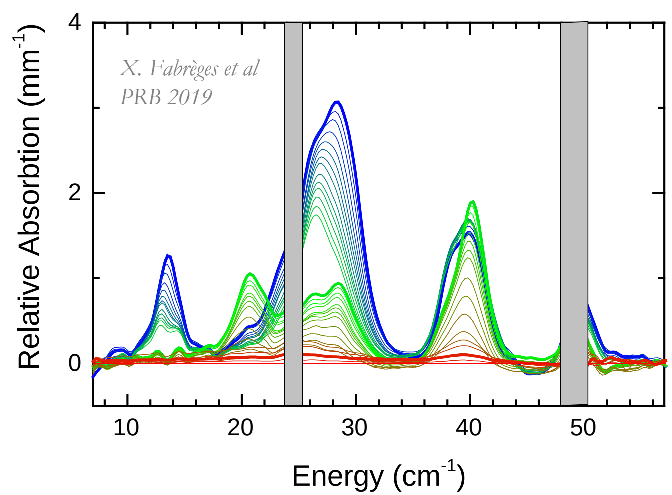
Absorbance : Abs= - Log (T) $\approx \alpha d$

Absorption $\alpha(\omega)$

⇩

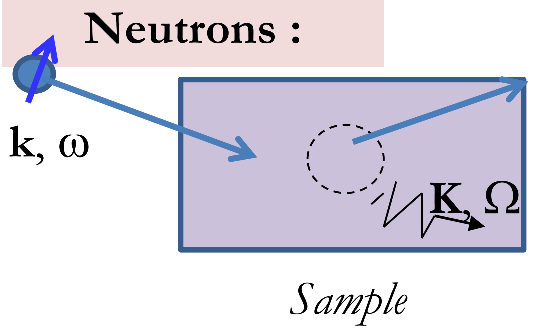
dissipative part of the susceptibility

$\chi_2(\omega, 0)$ **electric**/**magnetic** according to EM polarization and sample symmetry



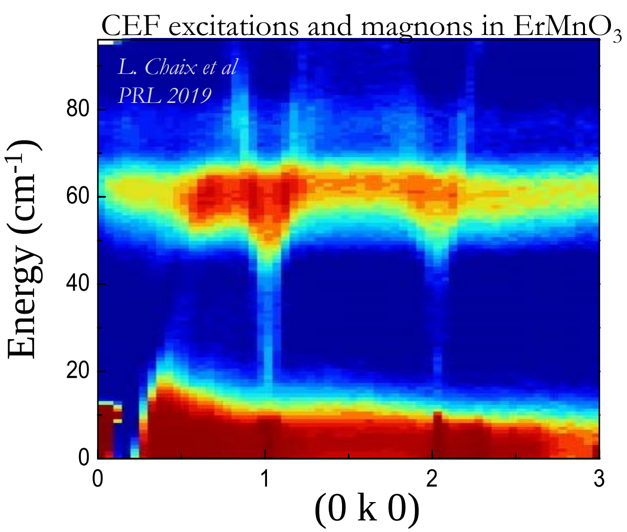
CF excitations in h- $HoMnO_3$

Ineslastic neutron scattering



$k = k' + K$

$\omega = \omega' + \Omega$



DISPERSION CURVES :

Position in energy Ω(**K**)

Intensity map I = form factor x dissipative part of the susceptibility

χ_2 (Ω, K) $\perp$ K

MAGNETIC AND ATOMIC PROBE :

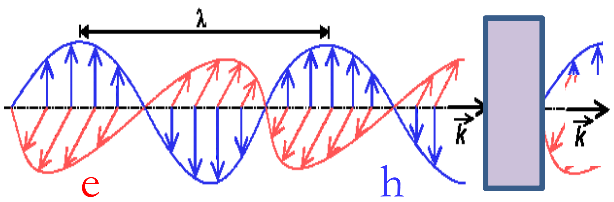
Low K → magnetic contribution

large K→ atomic contribution

Polarised neutron → magnetic /atomic contribution

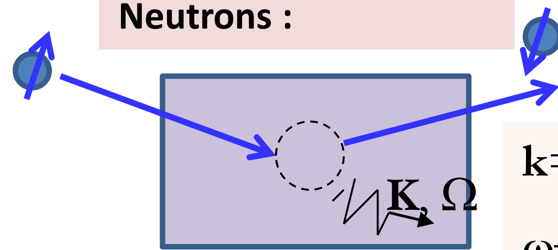
Electromagnetic waves versus Neutrons

THz wave :



Sample

Neutrons :



k=k'+K

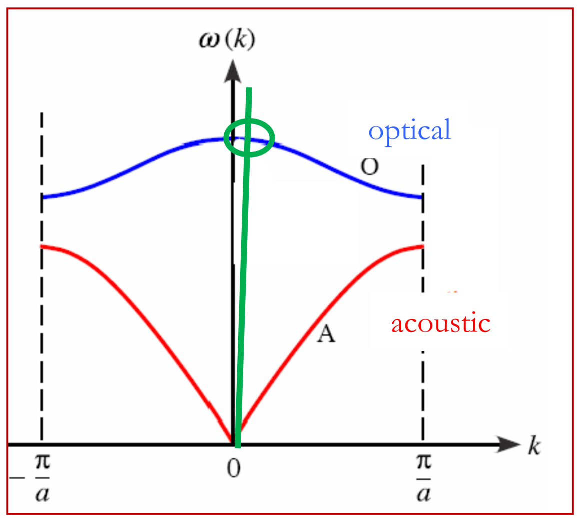
ω=ω'+Ω

Sample

ABSORBTION CURVES
Ω (K ≈ 0)
χ_2 (Ω, ≈ 0)

MAGNETIC AND ELECTRIC PROBE

Smaller sample
Increased energy resolution

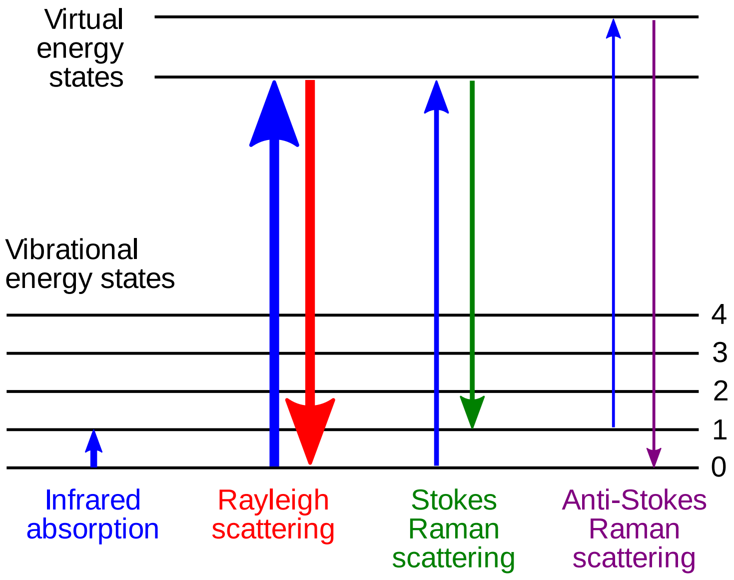


DISPERSION CURVES
Ω(K)
χ_2 (Ω, K) ⊥ K

MAGNETIC AND ATOMIC PROBE

Whole reciprocal space

RAMAN spectroscopy



Indirect probe:

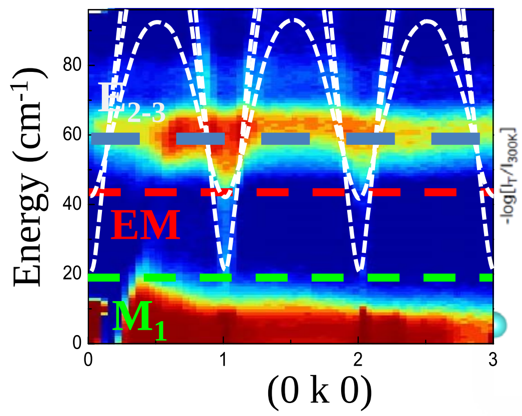
High energy excitation

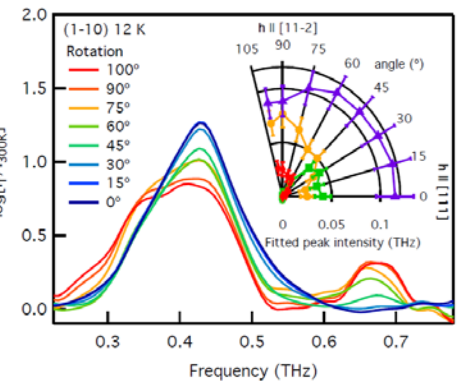
Indirect process

Different selection rules (phonons, etc…)

THz: close to Rayleigh scattering

THZ DYMAMICS IN OXIDES

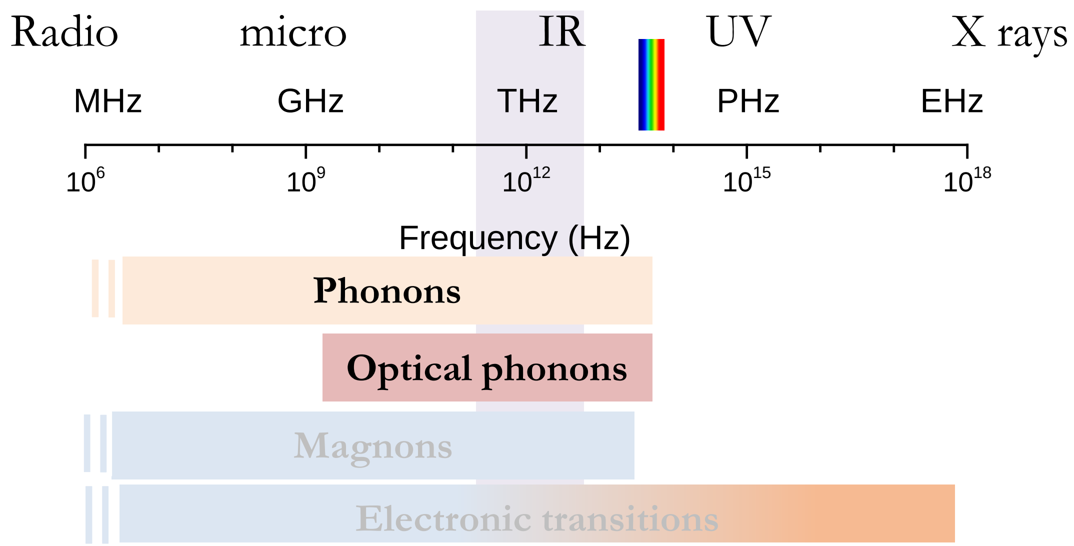




1. Phonons
2. Magnons
3. Crystal field excitations
4. Examples of more complex excitations

1. THz properties in oxides

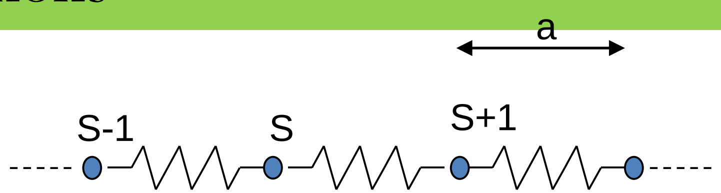
1 THz ≈ 33 cm^{-1} ≈ 300 μm ≈ 4 meV ≈ **50 K**

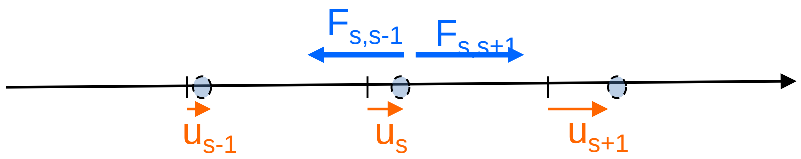


SINGLE ATOMS (MAGNETIC / ELECTRIC)
AND **ORDERED PHASES** (ATOMIC /ELECTRIC / MAGNETIC)
HAVE CHARATERICS EXCITATIONS IN THE THz RANGE

1. Phonons

Mono atomic chain :





Dispersion law: $$\omega = \sqrt{\frac{4C}{M}}\left|\sin\left(\frac{ka}{2}\right)\right|$$

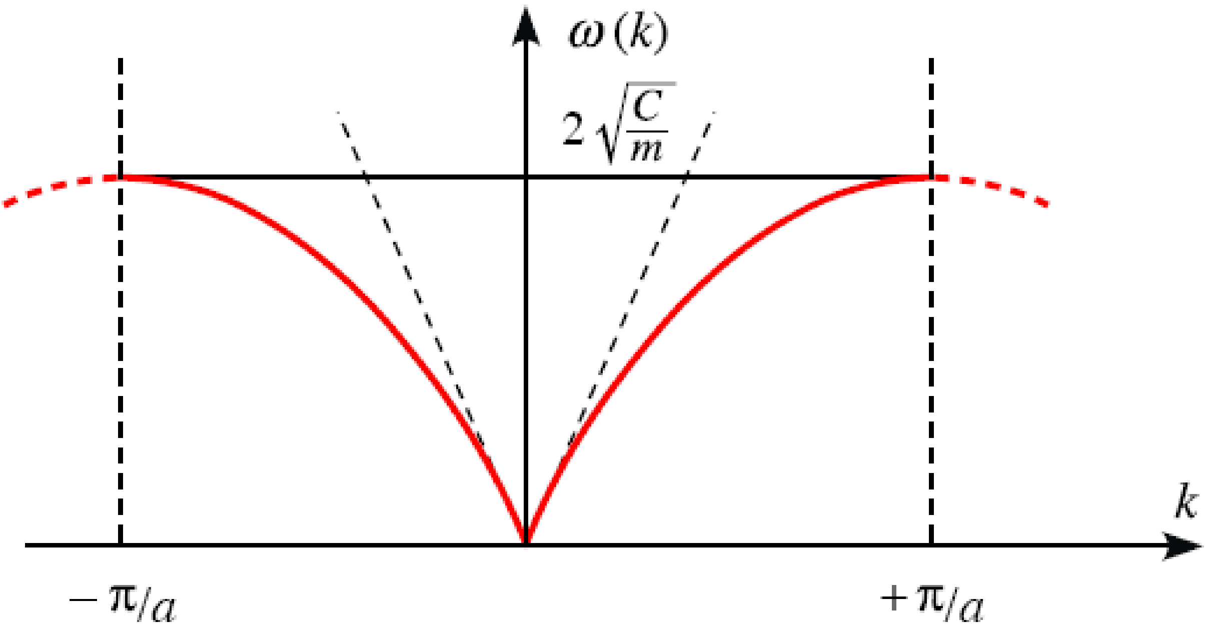
•Small k, large wave length (zone center):

Atoms vibrate in phase.

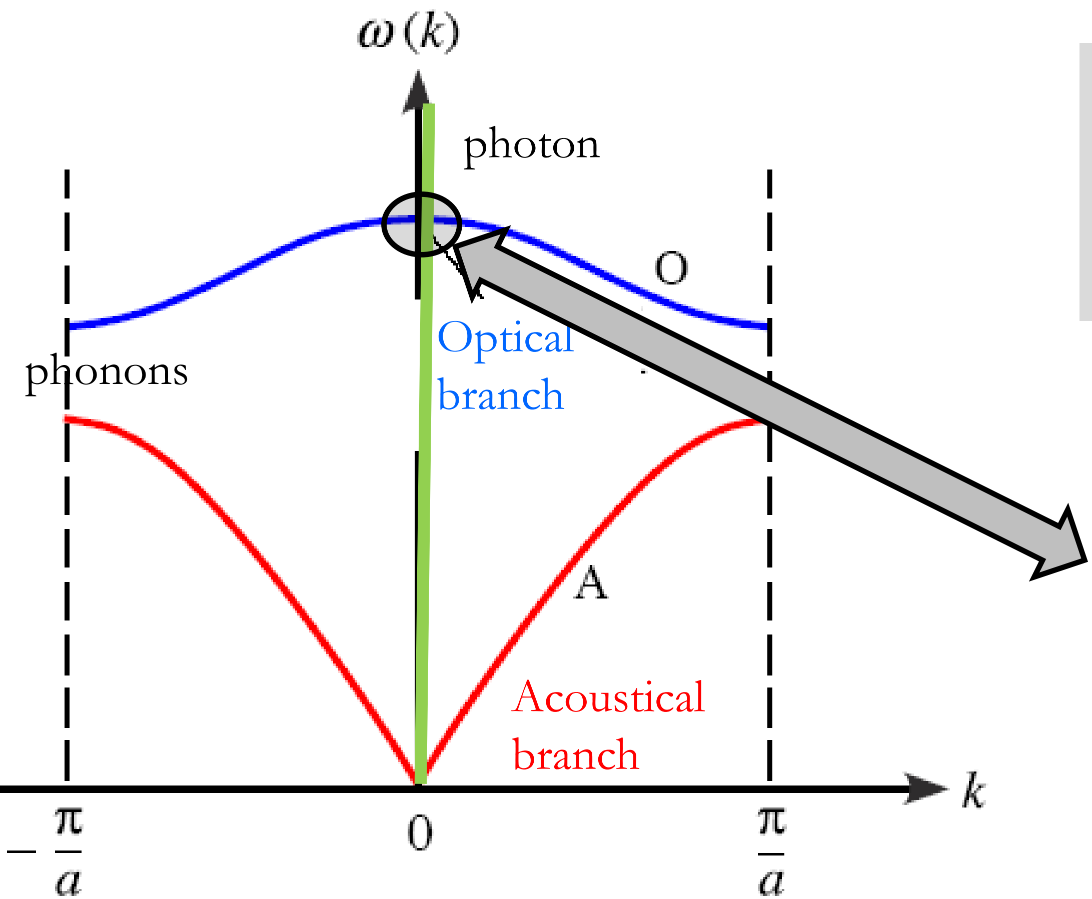
$$\omega = v_s k v_s = a\sqrt{\frac{C}{M}}$$

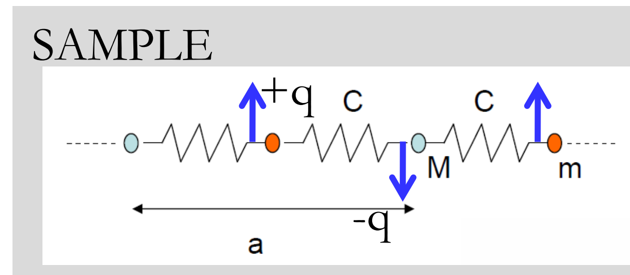
• Brillouin zone boundary : atoms vibrate out of phase.

$$\omega = \omega_{\max} \quad = 2\sqrt{\frac{C}{M}}$$



1. PHONONS



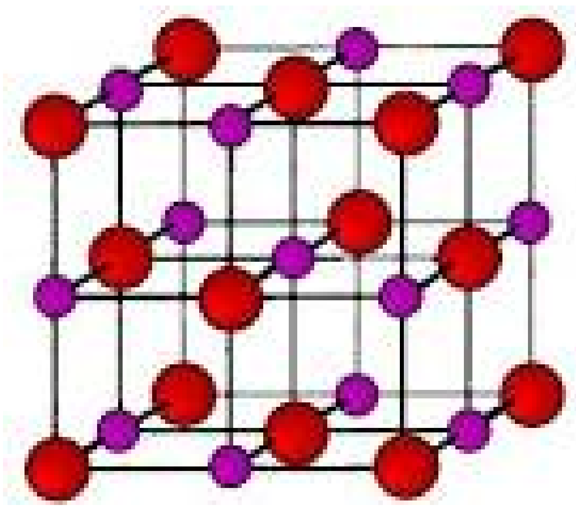


Several branches
Dispersion in the energy range 0 - Θ_{Debye}

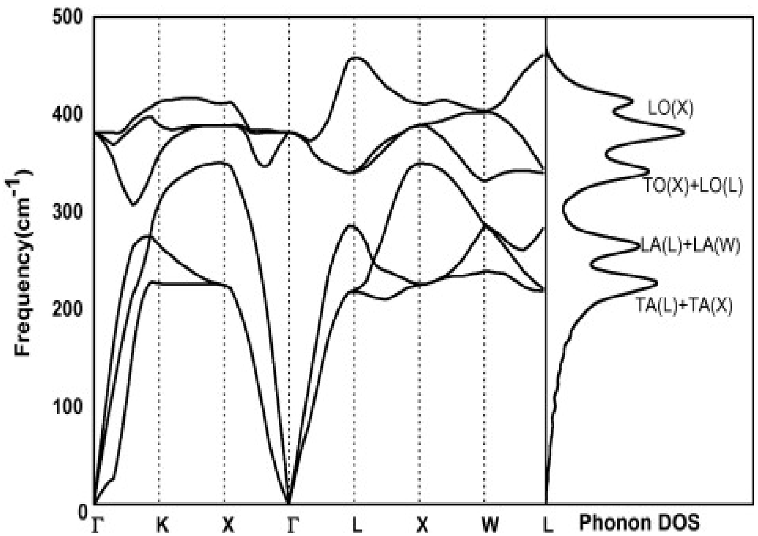
EM wave /sample interaction via
Electric field / electric charges

Atomic probe (neutron)

1. Phonons



1 THz ≈ 33 cm^{-1} ≈ 4 meV ≈ 50 K

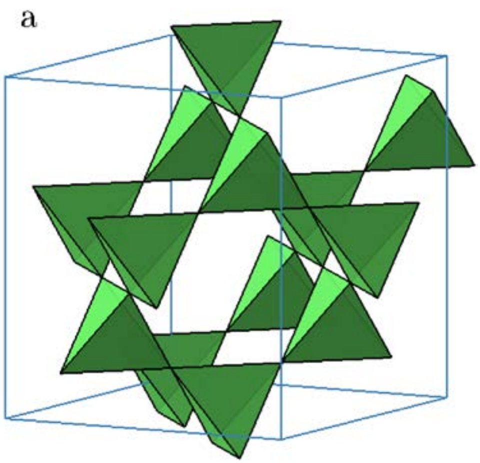


Debye Temperature

PHONONS ARE SIGNATURES OF THE ATOMIC LATTICE
OPTICAL PHONONS MAY BE PRESENT IN THE THZ range

1. example: phonons in the pyrochlore R2Ti2O7

1 THz ≈ 33 cm^{-1} ≈ 4 meV ≈ 50 K



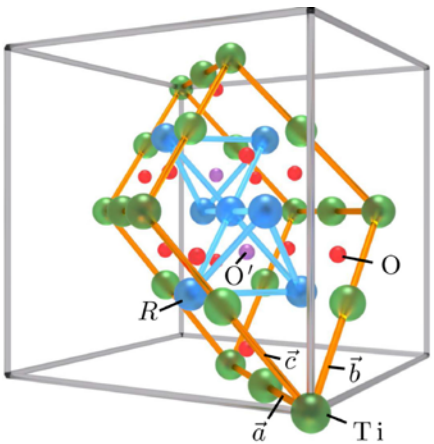


FIG. 1. The primitive cell of the pyrochlore structure, as related to the conventional cubic unit cell. The primitive cell contains 22 ions: 4 R^{3+} (blue), 4 Ti^{4+} (green), 12 O^{2-} (red), and 2 O'^{2-} (violet). The axes of the conventional cell are shown by the gray box, and the primitive cell by the orange box. The basis vectors of the primitive cell (in the conventional cell) are $\vec{a} = (1/2, 1/2, 0)$, $\vec{b} = (1/2, 0, 1/2)$, and $\vec{c} = (0, 1/2, 1/2)$. (The size of the ions is arbitrary.)

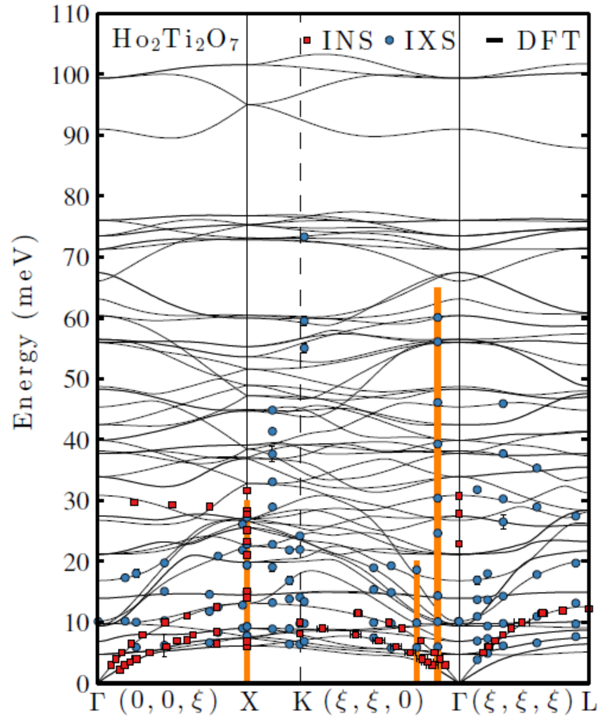


Figure 3. Phonon dispersion relations of $Ho_2Ti_2O_7$ calculated using DFT and the finite displacement method. The vibrational spectrum is presented along a path following high symmetry directions of the reciprocal lattice. The calculation is experimentally verified using inelastic neutron (INS) and x-ray (IXS) scattering. INS and IXS frequencies were obtained from fits to the measured spectra, as described in the text. The INS measurements of the acoustic phonon spectrum are presented in more detail in Fig. 6, and a comparison between simulated and measured IXS intensities along the three broad orange lines is shown in Fig. 8.

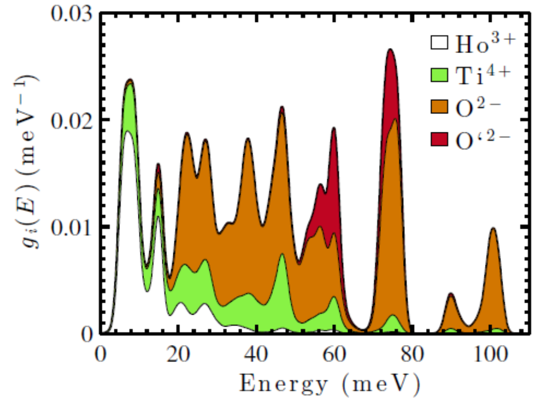


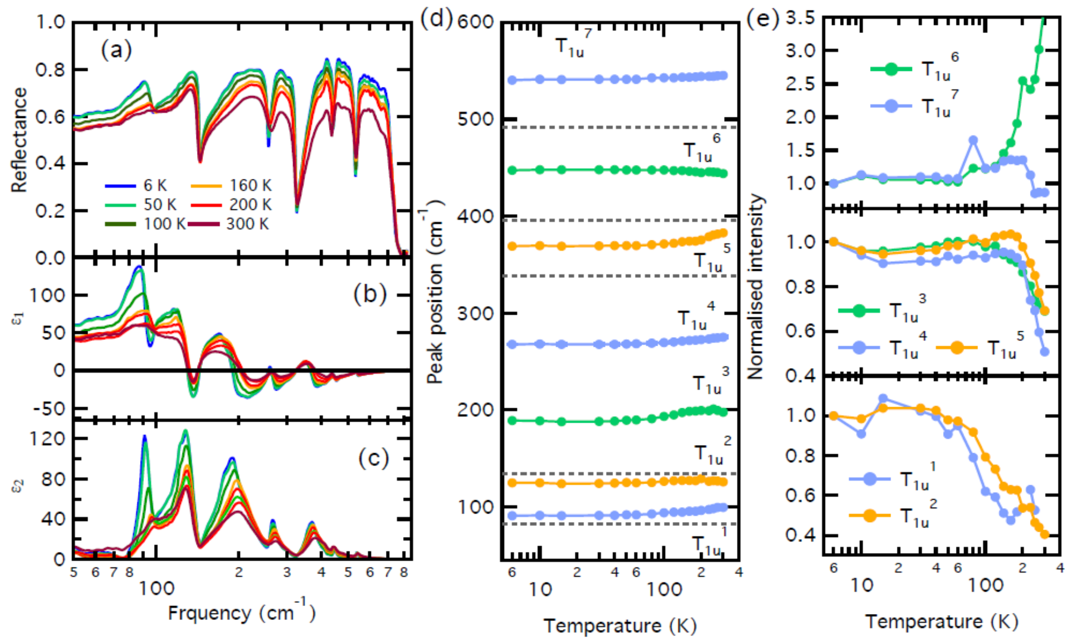
Figure 4. Normalized partial phonon densities of states $g_i(E)$ of $Ho_2Ti_2O_7$, calculated from first-principles.

Optical phonons
5-100 meV
=20 – 800 cm-1

R. Ruminy et al, Phys Rev B 2016

1. example: phonons in the pyrochlore R2Ti2O7

Reflectance and dielectric constant of a pyrochlore crystal $Tb_2Ti_2O_7$



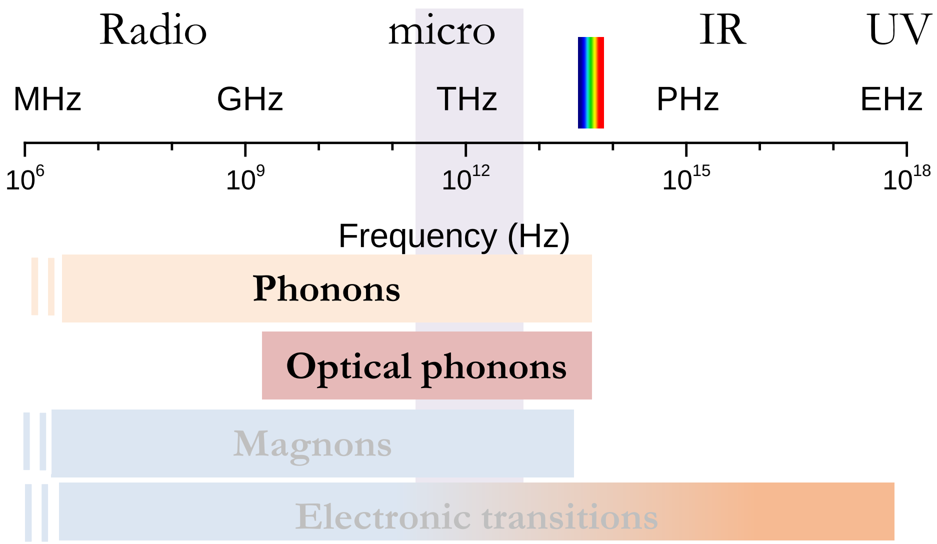
E. Constable et al, PRB (R) 2017

$$\Gamma = A_{g1} \oplus 3A_{2u} \oplus 3E_u \oplus E_g \oplus 4T_{2u} \oplus 4T_{2g} \oplus 8T_{1u} \oplus 2T_{1g} \quad .$$

No lowering of symmetry as a function of temperature
High dissipation above 80 cm-1 / low disspation below 80 cm-1

1. PHONONS

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



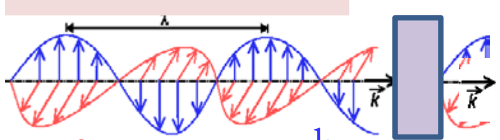
PHONONS ARE SIGNATURES OF THE ATOMIC LATTICE

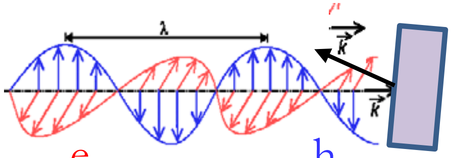
➡ **CRISTALLOGRAPHIC PHASE TRANSITIONS**

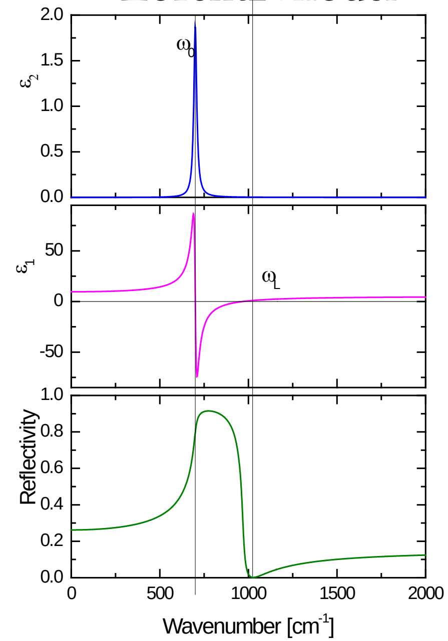
➡ **SOFT MODES**

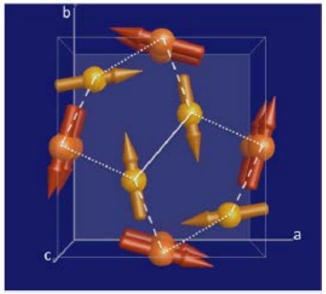
1. Phonons in the pentagonal $Bi_2Fe_4O_9$ under pressure

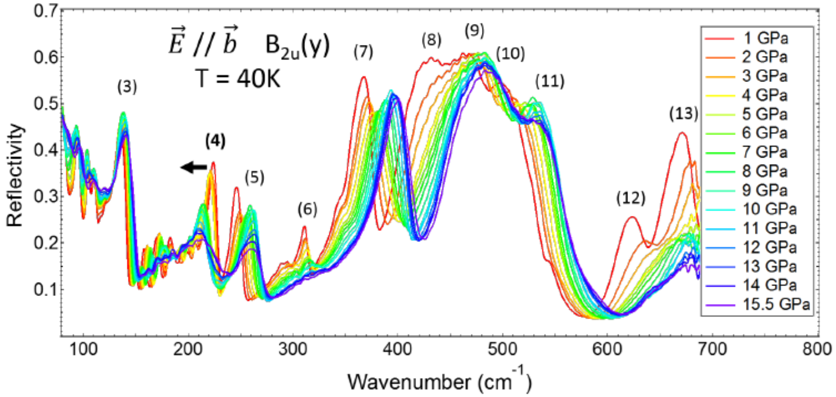
$T = I / I_0 \approx \exp(-\alpha d)$ for small α For large α, Reflectivity is used $R = 1 - T$











Magnetic order below 240 K

At ambient pressure

E. Ressouche & al PRL 2009

Pressure induced Structural transition at 6.5 Gpa :

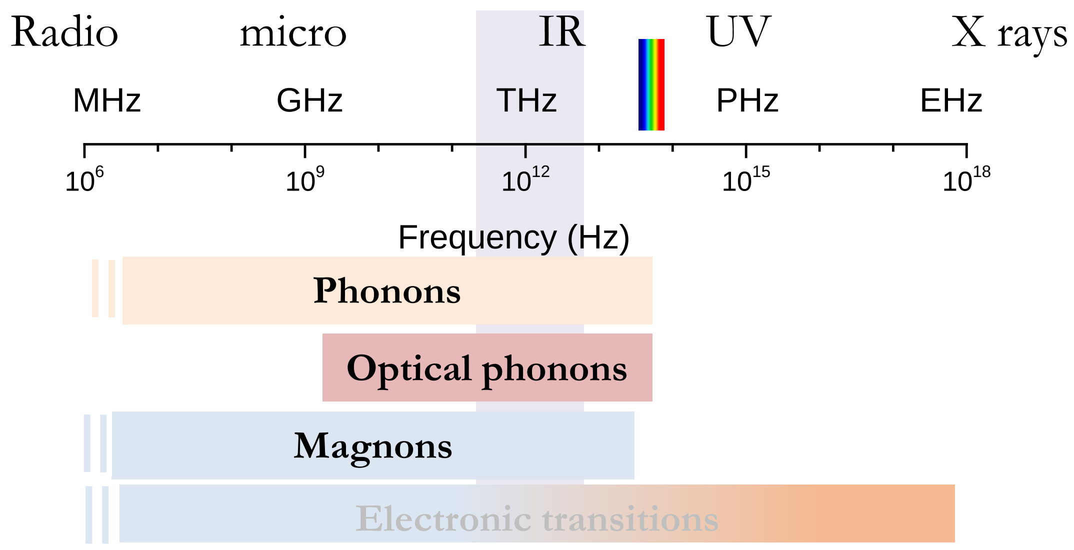
Softening of mode (4)

THz Spectroscopy under pressure at AILES @ SOLEIL

M. VERSEILS & PRB 2022

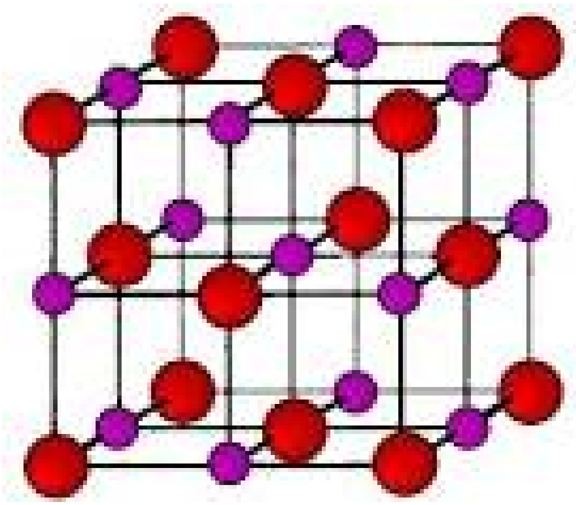
2. THz properties in oxides

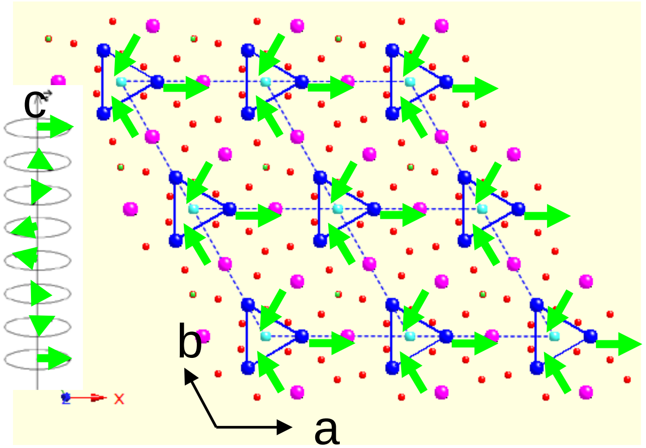
1 THz ≈ 33 cm^{-1} ≈ 300 µm ≈ 4 meV ≈ **50 K**



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

2. Periodic structures / assoicated excitations



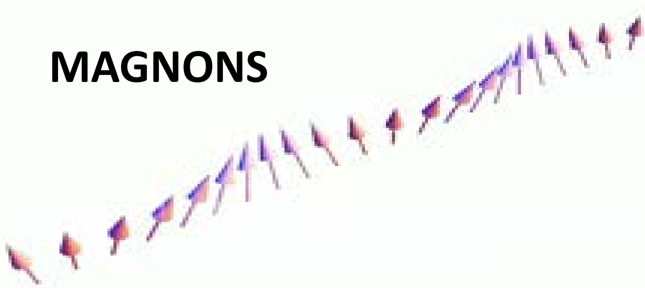


LATTICE VIBRATIONS

PHONONS

SPIN WAVES

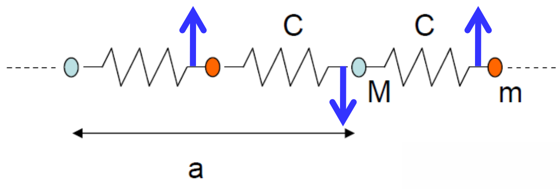
MAGNONS



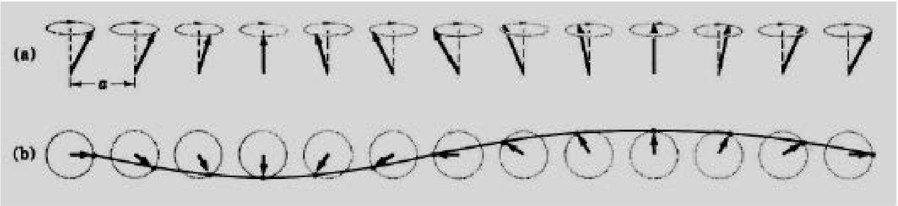
2. Periodic structures / assoicated excitations

Lattice with two different elements

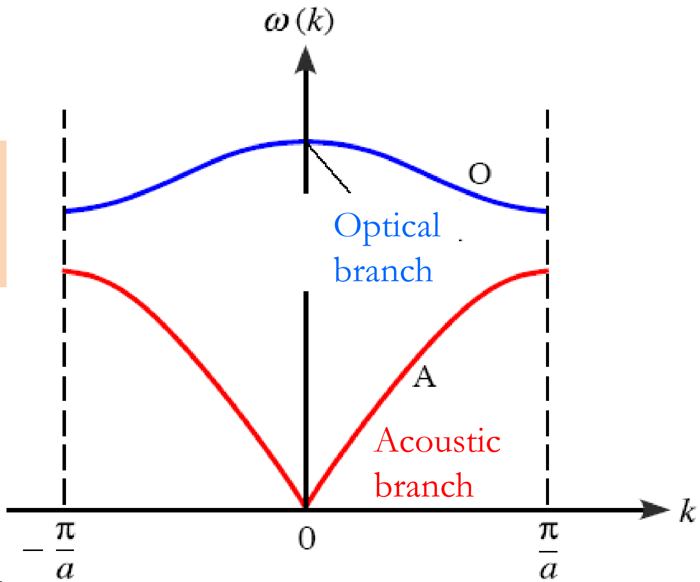
Phonon



magnon



THz



THz

The equation of motion :

Force

$$m\ddot{x} = -kx + qE$$

$$E = E_0 \exp(-i\omega t)$$

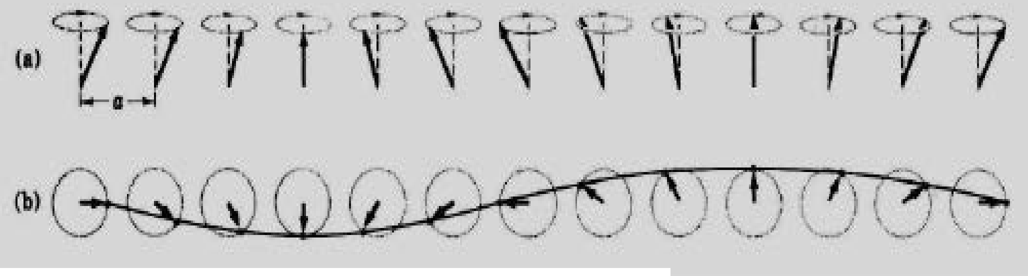
Torque

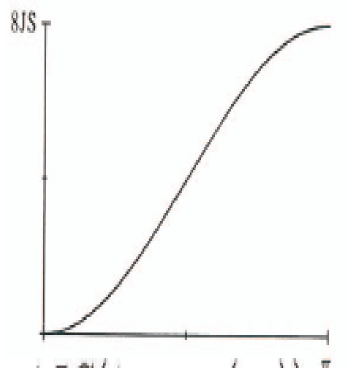
$$\frac{d\vec{L}}{dt} = \vec{M} \times \vec{H} \qquad \vec{M} = \gamma \vec{L}$$

$$\vec{H} = \vec{H}_0 \exp(-i\omega t) + \vec{H}_m$$

2. Spin waves / magons

FM spin waves



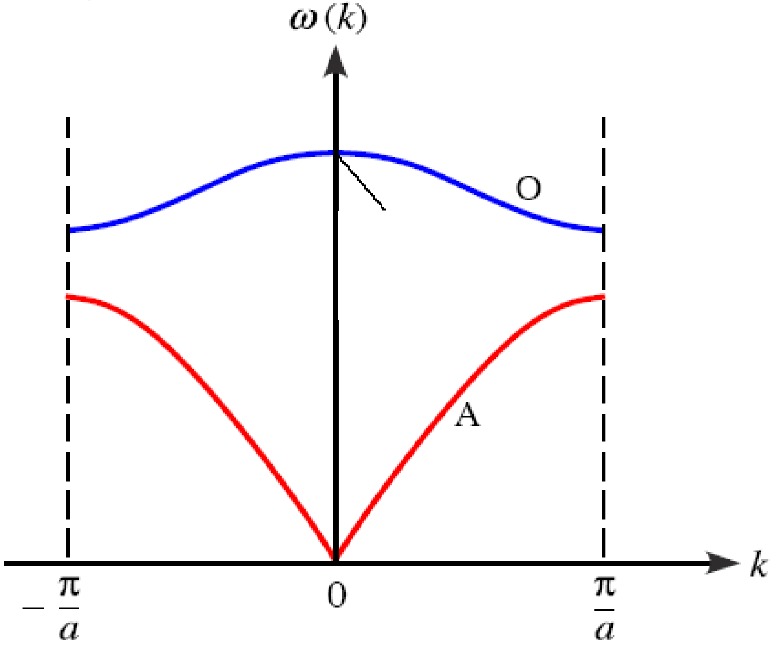


One branch

k^2 dependence at the zone center

Dispersion in the energy range $0 - \Theta_{curie\text{-}Weiss}$

AF spin waves



several branches,

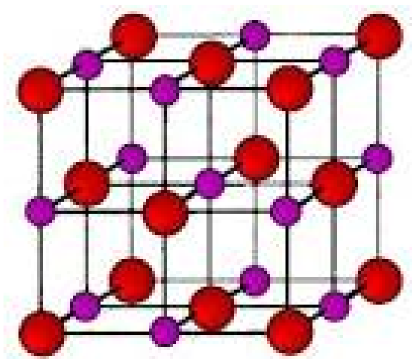
Various k dependence (Cste, k, k^2)

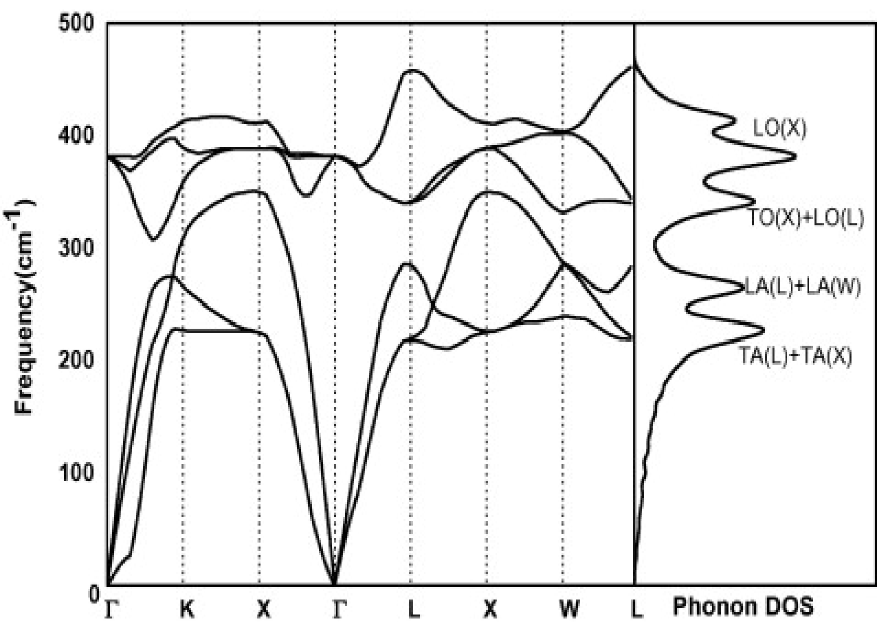
Dispersion in the energy range $0 - \Theta_{curie\text{-}Weiss}$

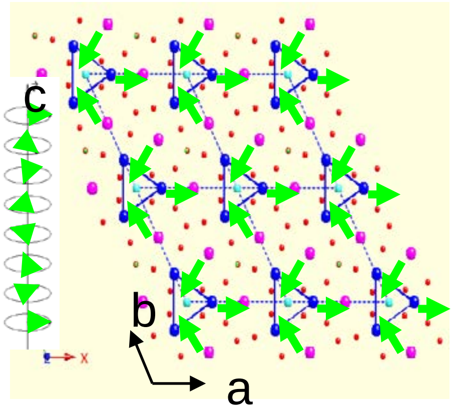
2. Periodic structures / associated excitations

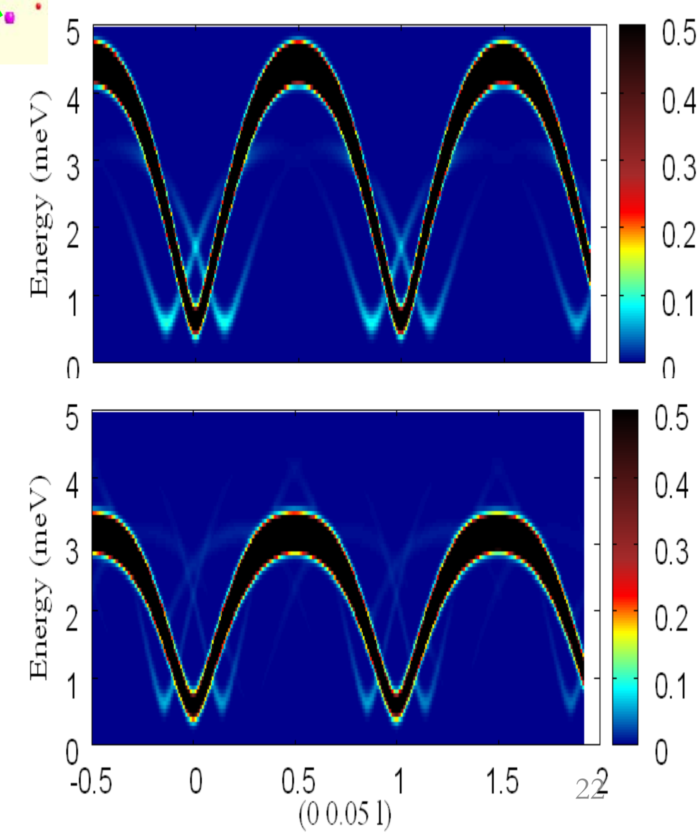
MAGNONS in Ba3TaFe3Si2O14

PHONONS in MgN

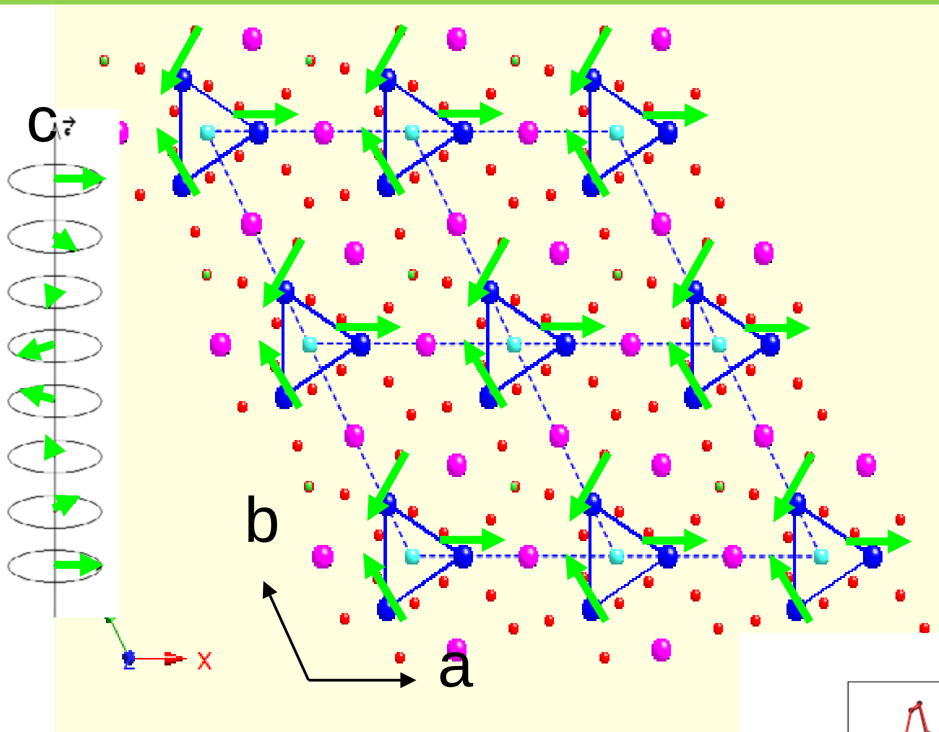


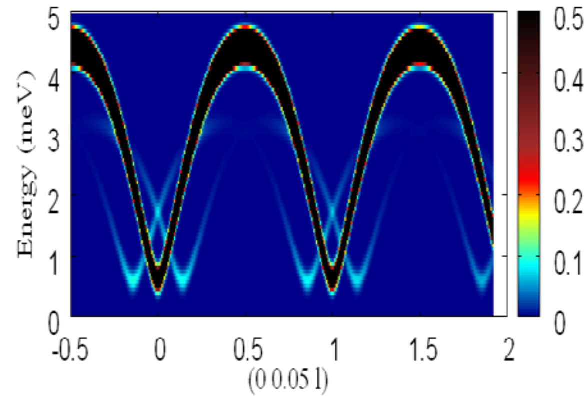




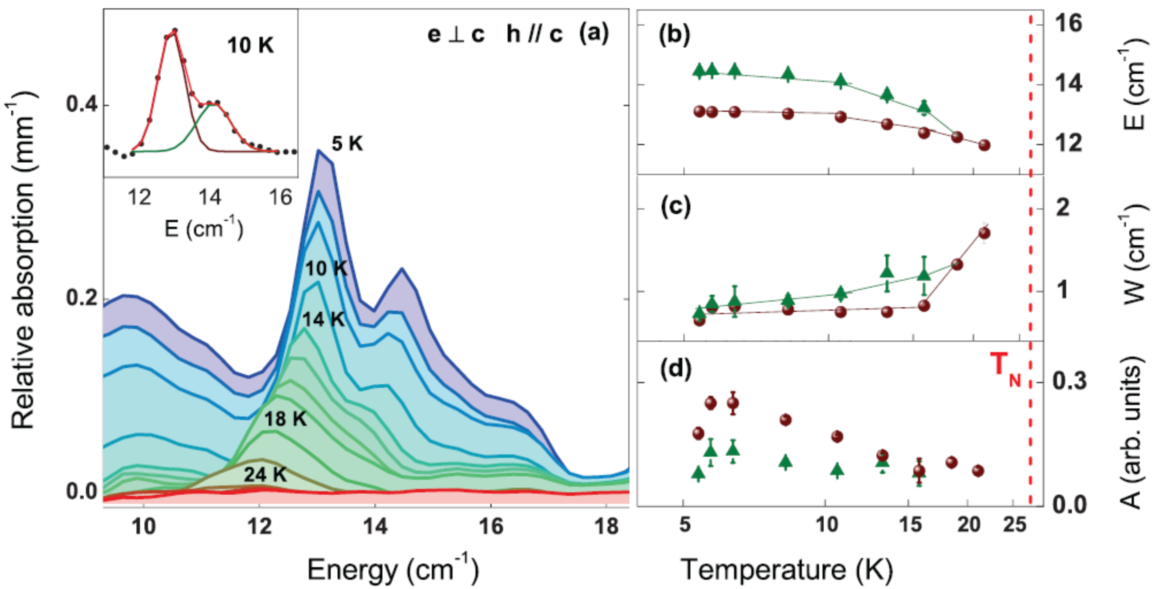


2. Magnons in Fe langassite



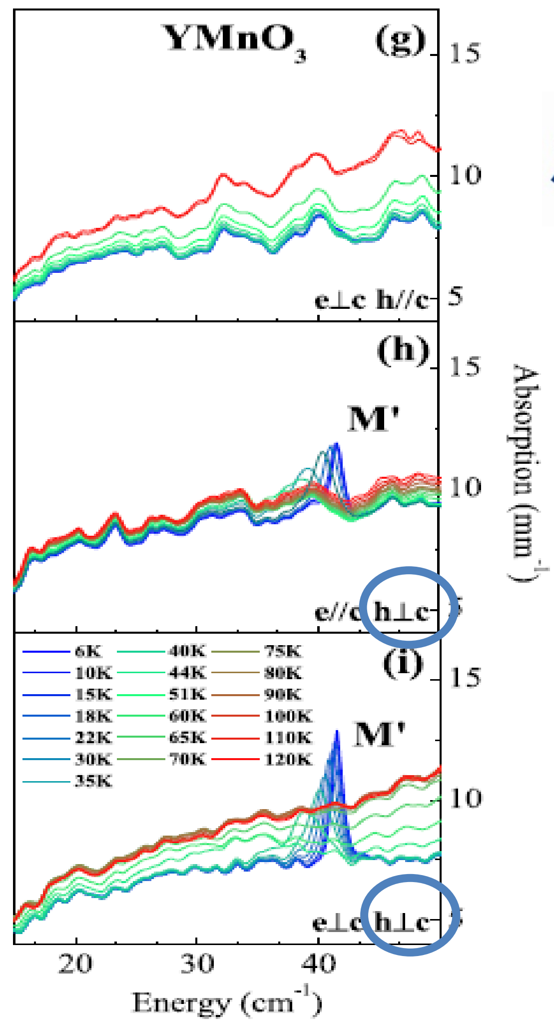


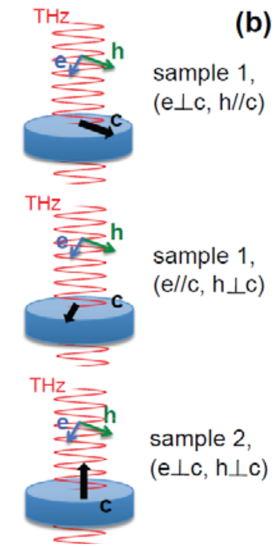
TN= 27K



2. Hexagonal manganites : $YMnO_3$

THz Spectroscopy at AILES @ SOLEIL
L. Chaix et al, PRL 2014
RAMAN
C. Toulouse et al, PRB 2014



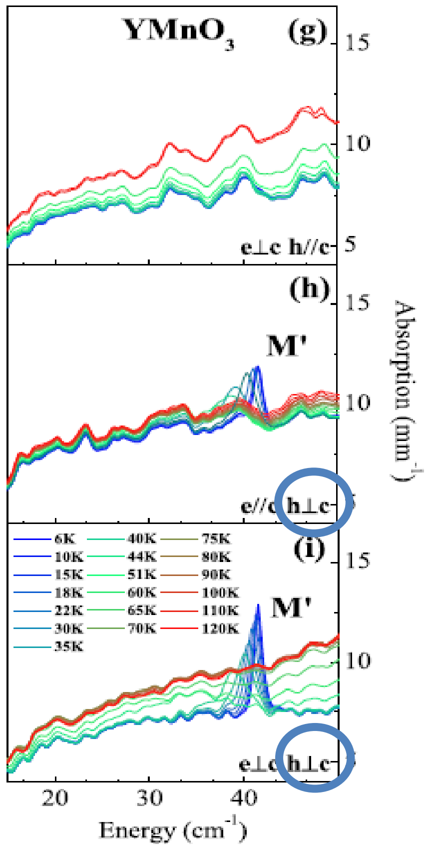


c

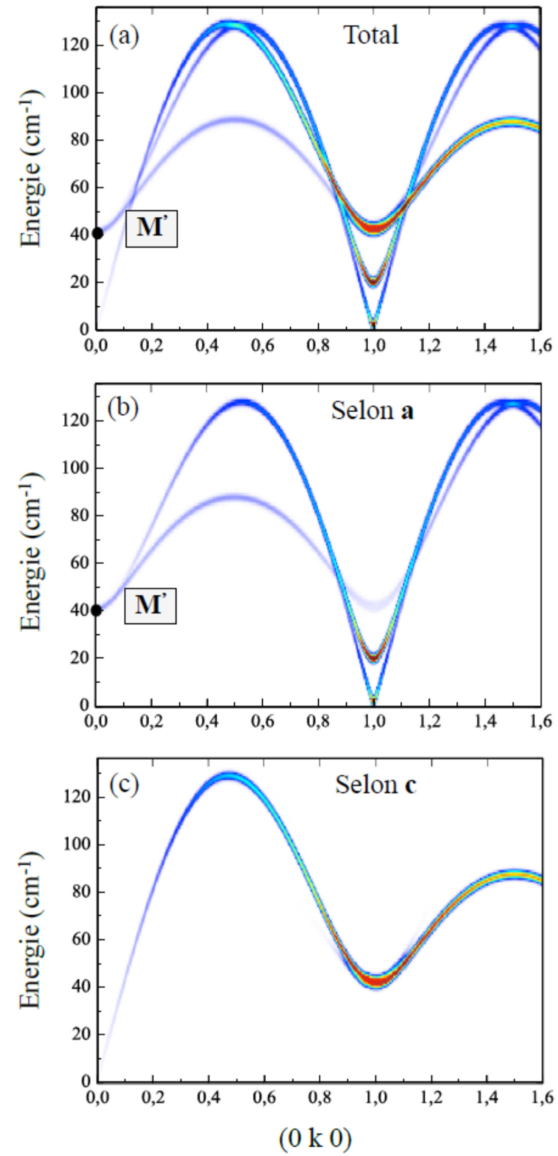
Ferroelectric order at 800 K
(Mn) Magnetic order at 80 K

2. Hexagonal manganites : $YMnO_3$

experiments



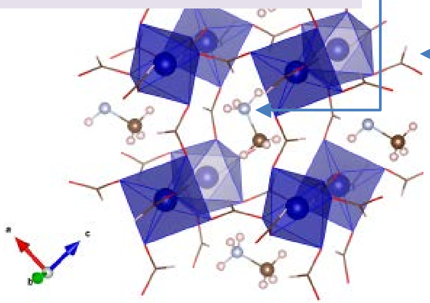
Linear spin wave calculations



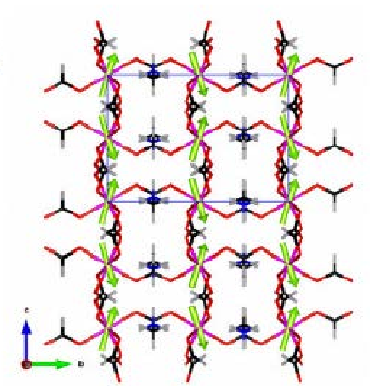
2. Phonons / magnons in MOF

L. Ding & al Phys Rev Mat 2023

$MACo(COOH)_3$ ($MA = CH_3NH_3$)



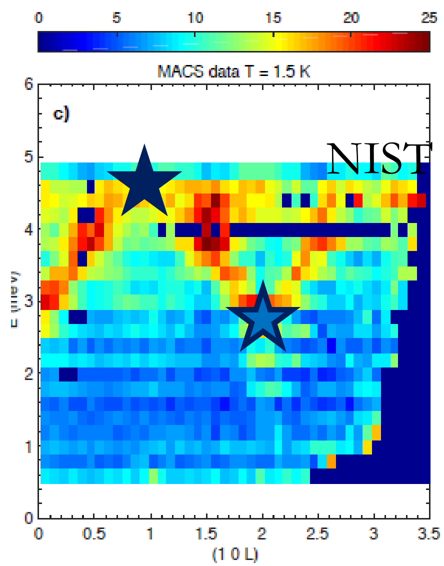
b)



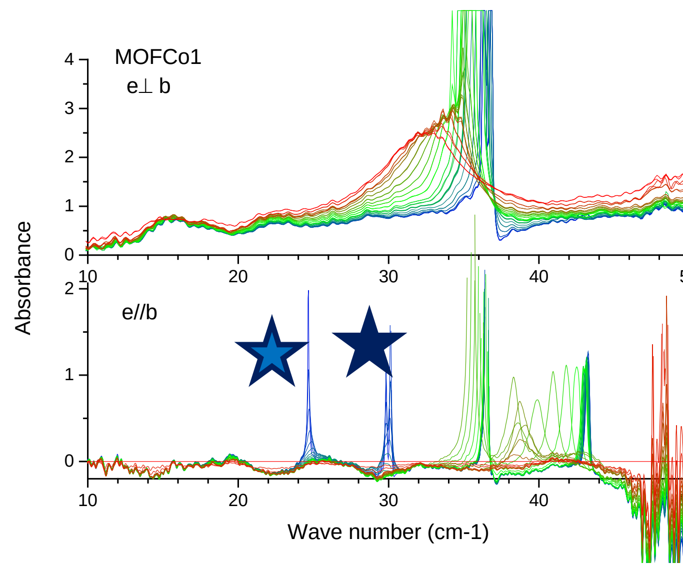
magnetic transition at 15K

L. Mazzuca et al., Chem. Sur. J. 23, 1-13 (2017)

Neutron measurements



THz measurements

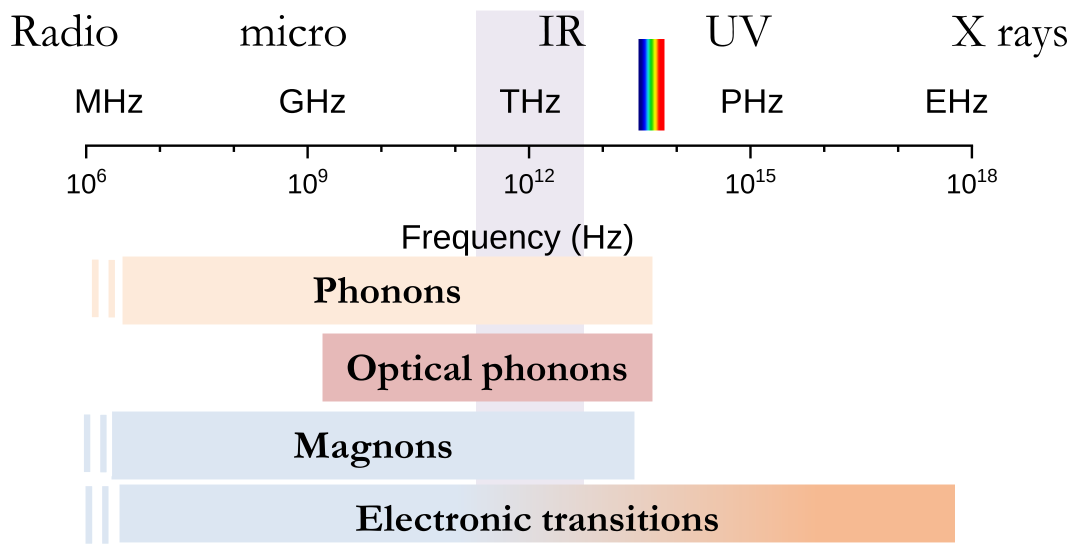


Magnons at at 24 cm^{-1} and 36 cm^{-1} associated to Co^{2+} order at 15K
+ phonons associated to Pnma/P21/n structural transition at 90 K

Magnons+ phonons as a a signature of ME effects

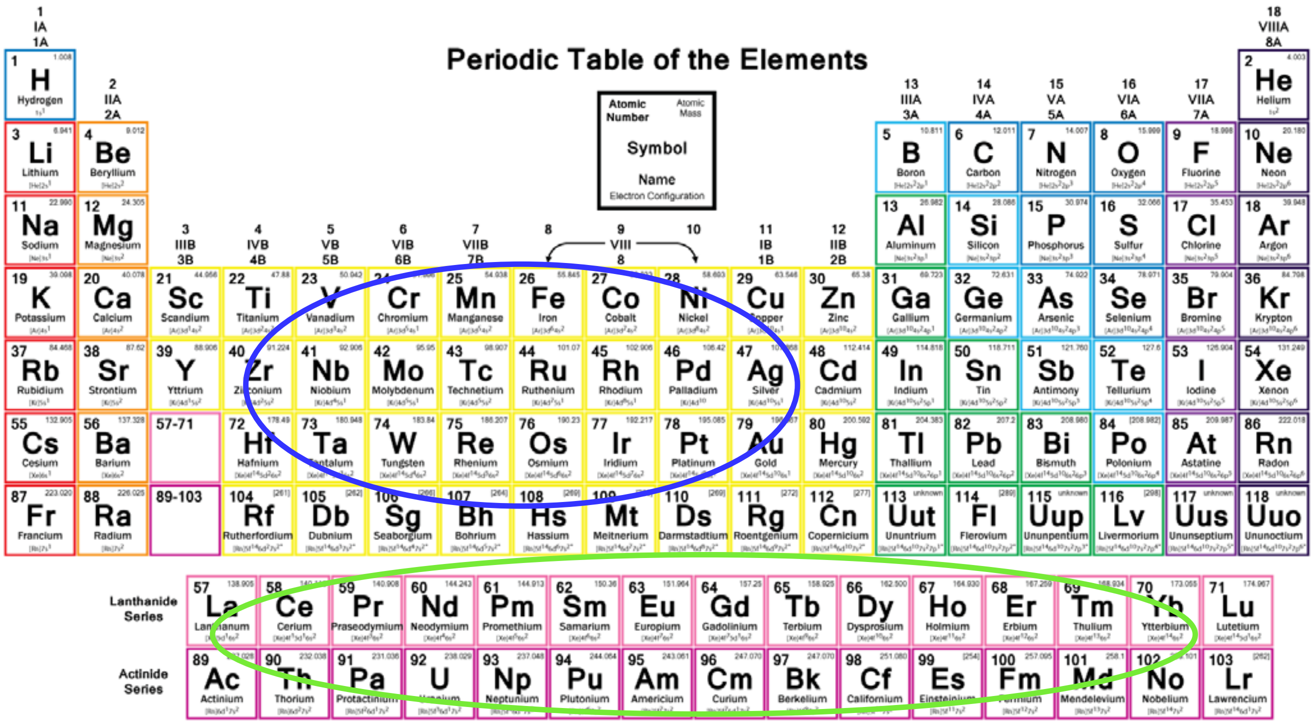
3. THz properties in oxides

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

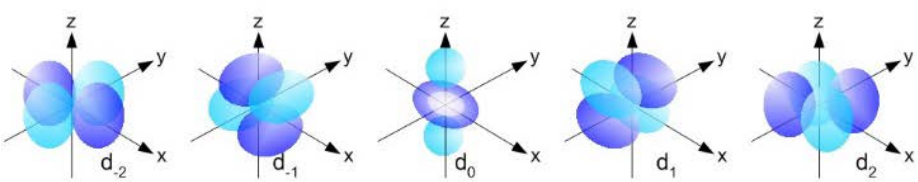


SINGLE ATOMS-IONS HAVE CHARATERICS EXCITATIONS IN THE THz RANGE

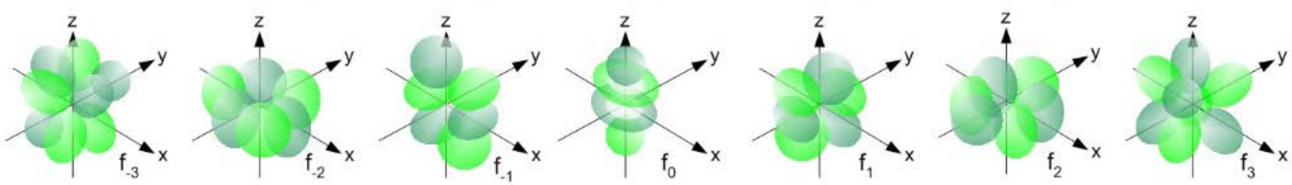
3. Electronic transitions in magnetic elements



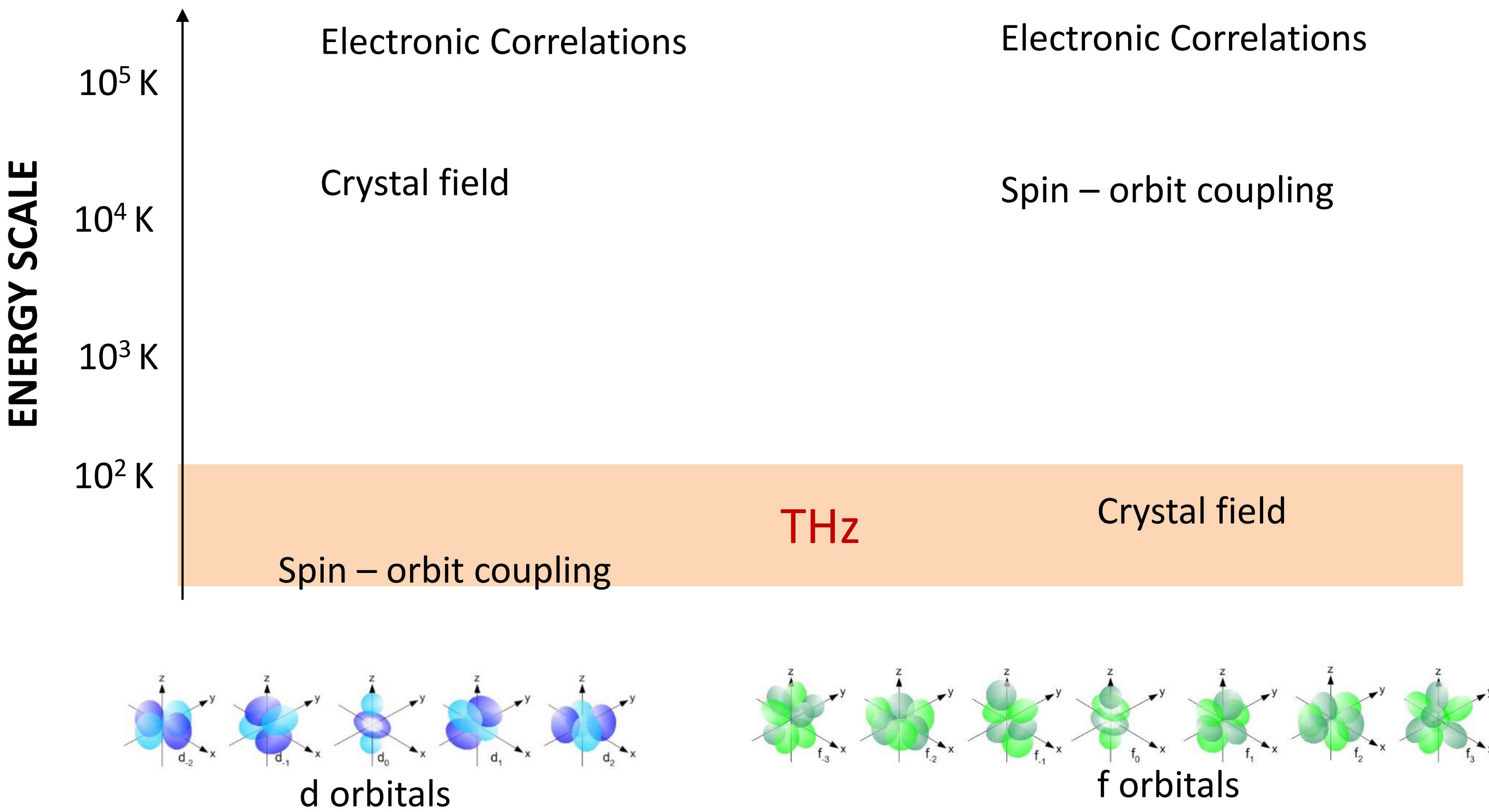
d orbitals



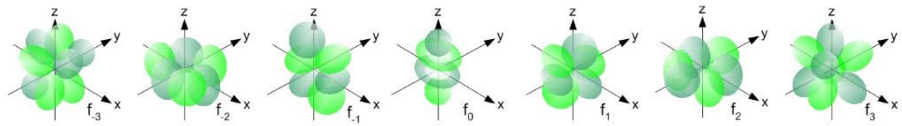
f orbitals

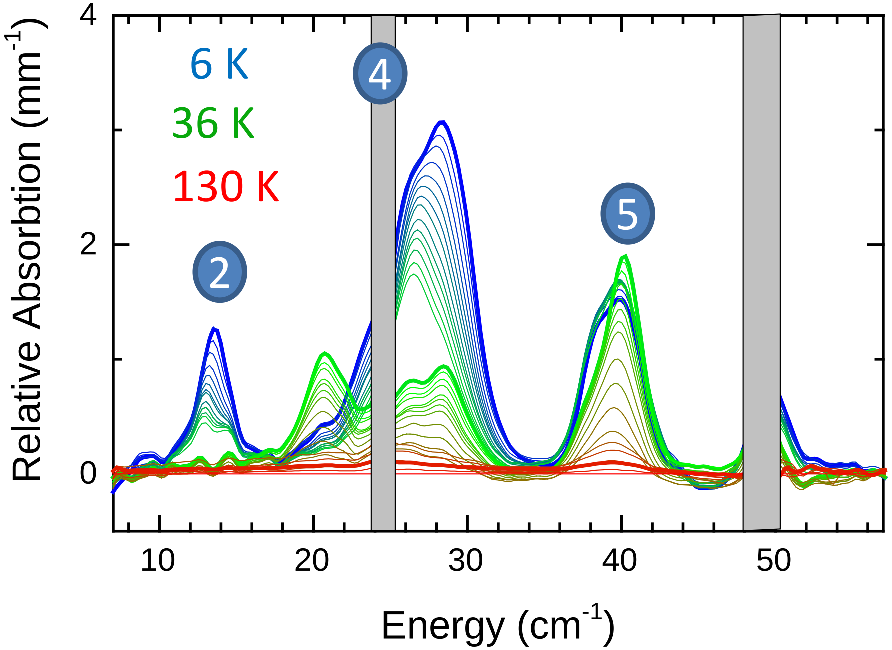


3. Electronic transitions in magnetic elements



3. Crystal field transition in rare earth elements

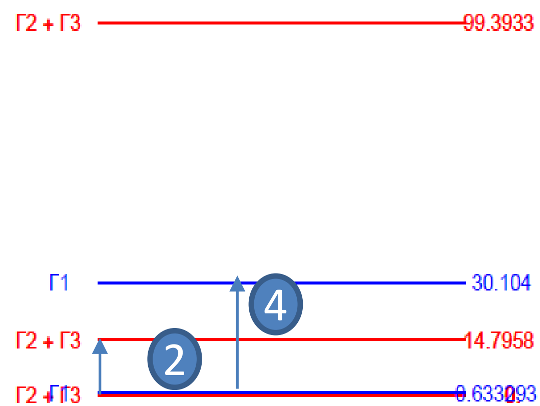




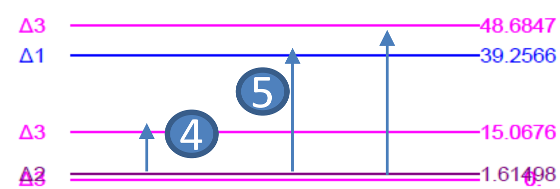
Ho^{3+} in h-$HoMnO_3$

$4f^{10}$ (S= 2 L = 6 J = 8 in the ground state)

in C3 point symmetry (site 4a)



in C3v point symmetry (site 2a)



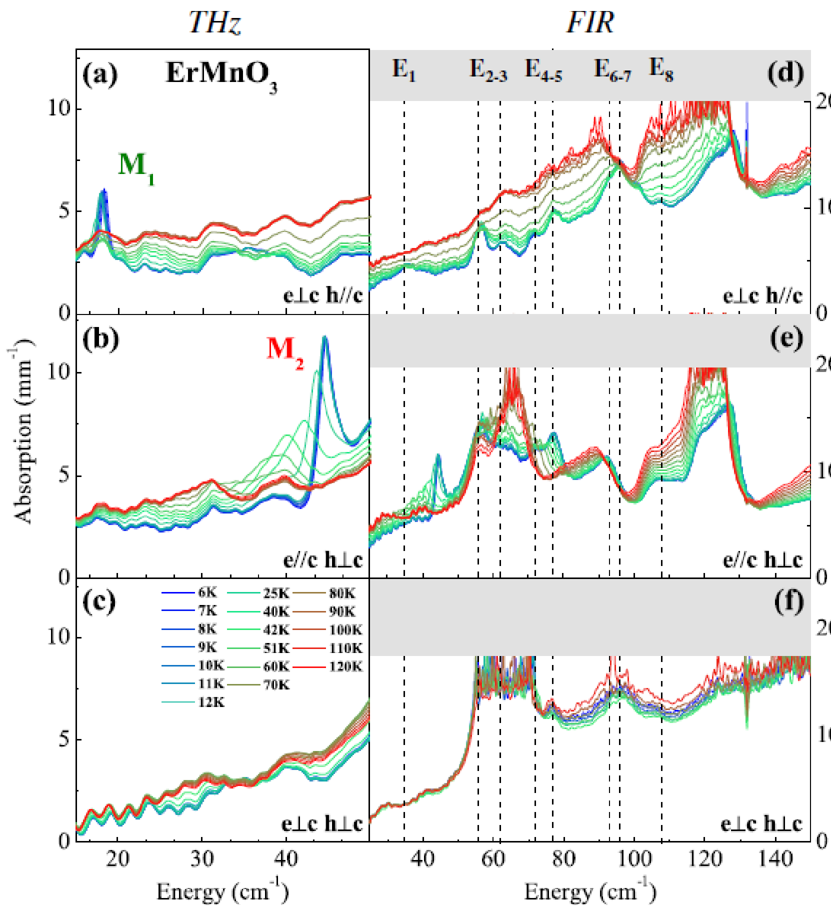
X. Fabrèges et al PRB 2019

CFE as a signature of structural/magnetic changes

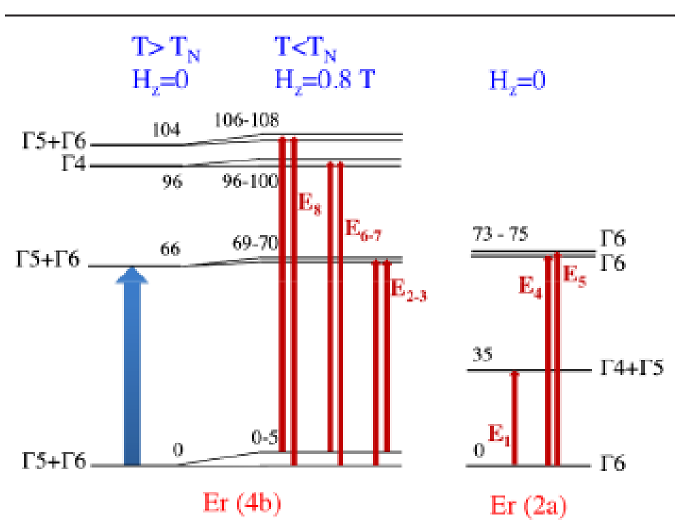
3. Crystal field transition in rare earth elements

h-$ErMnO_3$

THz measurements



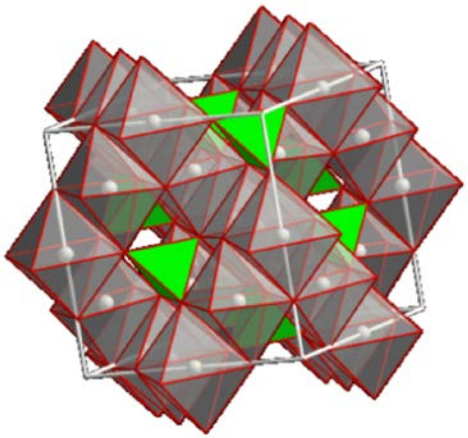
Er^{3+} Crystal field excitations



CFE / magnon coupling ….

3. Crystal field transition in 3 d elements

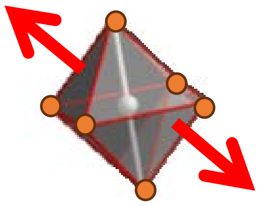
Example: Fe2+ in Spinel GeFe2O4



General spinel formula: AB_2X_4

- Octahedral A-site : Fe^{2+}
- Tetrahedral B-site: Ge^{4+}
- X anions : O^{2-}

Fe^{2+} in octahedral crystal field + trigonal distortion



3. Electronic scheme of Fe^{2+}

Free ion:

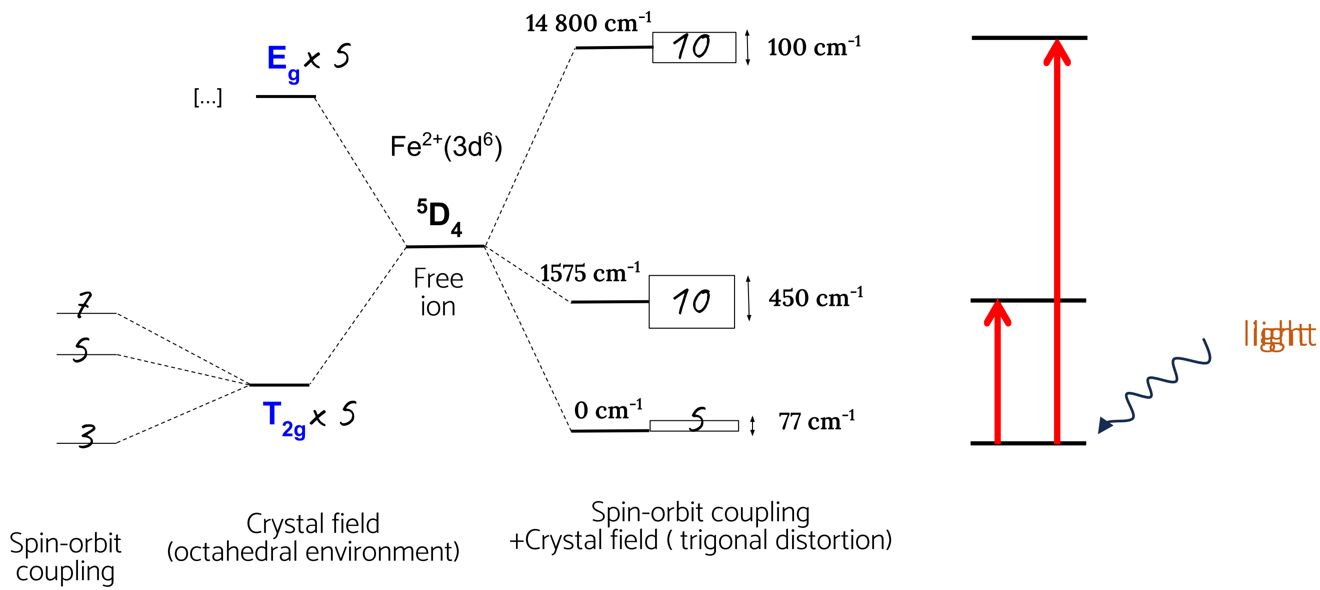
$Fe^{2+}\ (3d^6)$

$^5D_4$

S= 2
L= 2
J= 4

Fe^{2+} in octahedral crystal field

Fe^{2+} in trigonal crystalfield



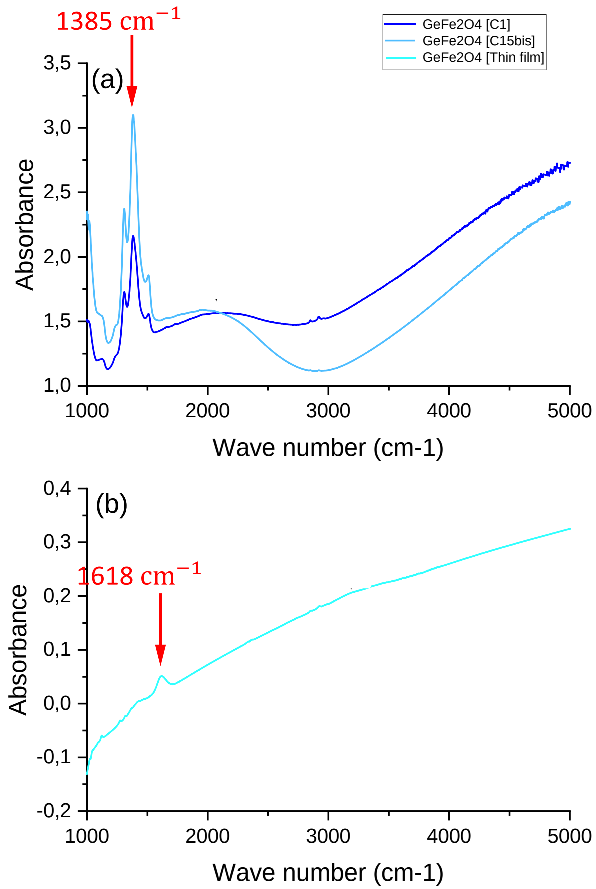
Point charge model for GeFe2O4

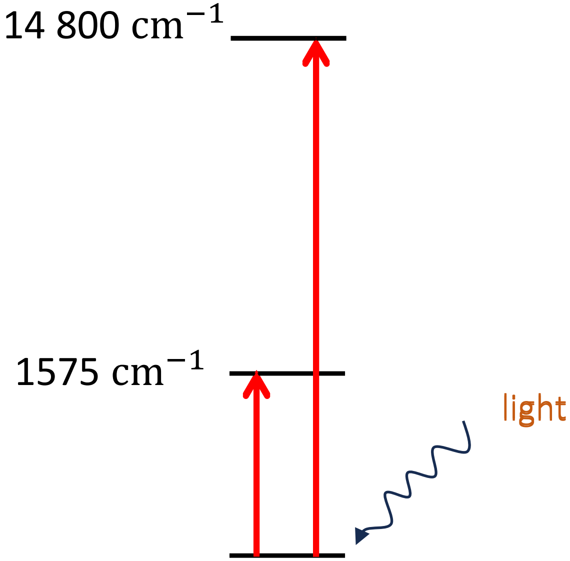
33

3. Fe 2+ Crystal field transitions in GeFe2O4

Crystals
300 µm
<1mm^2

Thin film
20 nm /MgO



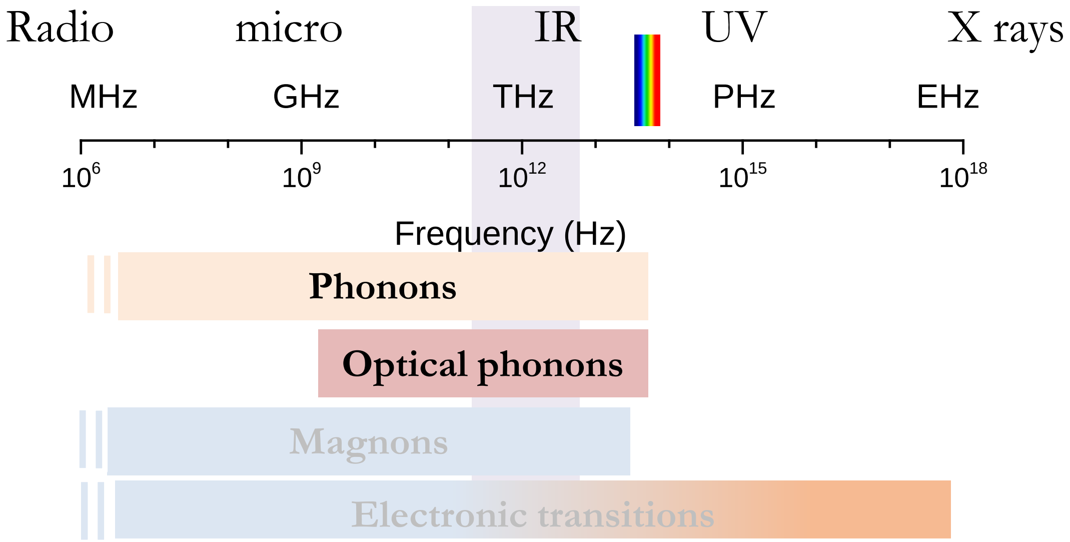


Electronic crystal field transitions calculations

34

3. THz properties in oxides

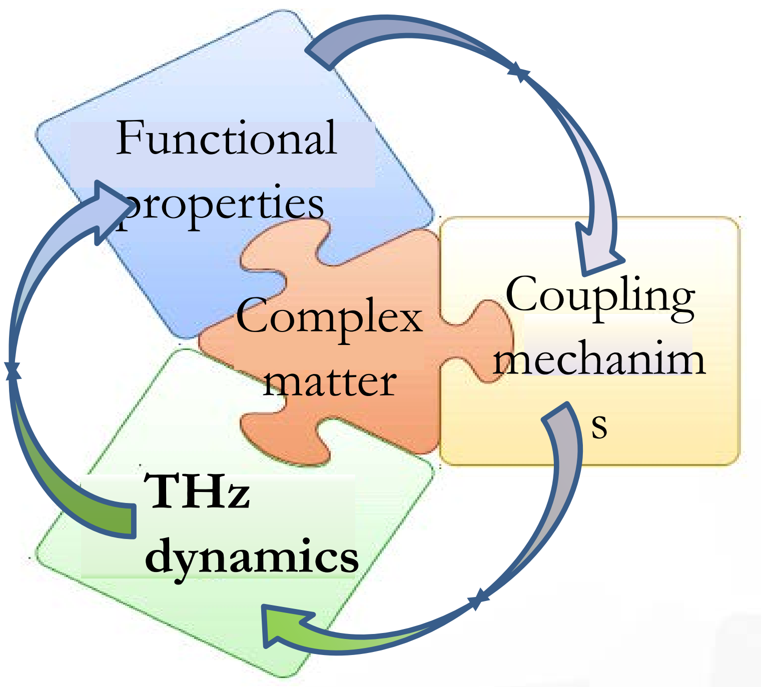
1 THz ≈ 33 cm^{-1} ≈ 300 μm ≈ 4 meV ≈ **50 K**



SINGLE ATOMS (MAGNETIC)
HAVE CHARATERICS EXCITATIONS IN THE THz RANGE

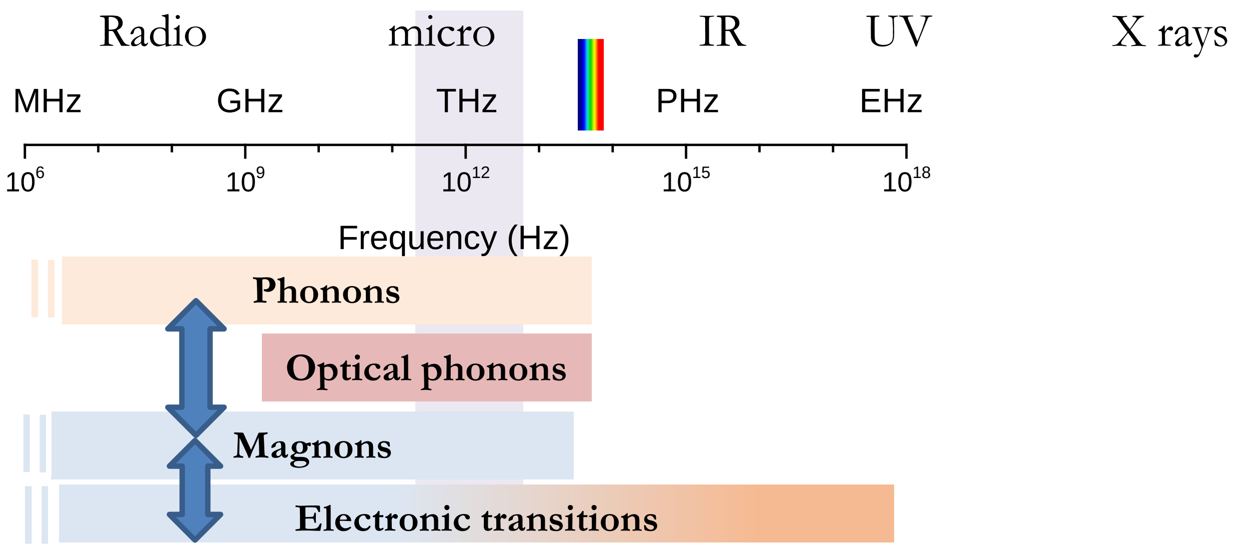
CFE as signatures of magnetic ions

4. THz PROPERTIES OF COMPLEX MAGNETIC PHASES



4. THz properties in oxides

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

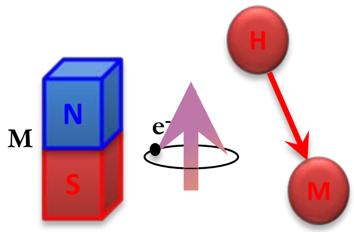


SINGLE ATOMS (MAGNETIC)
AND **ORDERED PHASES** (ATOMIC /ELECTRIC / MAGNETIC)
HAVE CHARATERICS EXCITATIONS IN THE THz RANGE

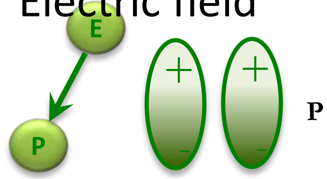
HYBRIDE EXCITATIONS : ELECTROMAGNONS

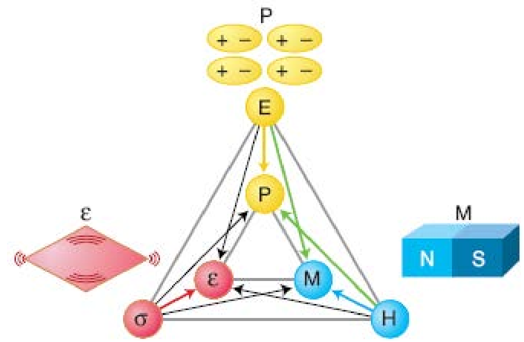
Static / dynamical properties

Magnetic moment / magnetic field

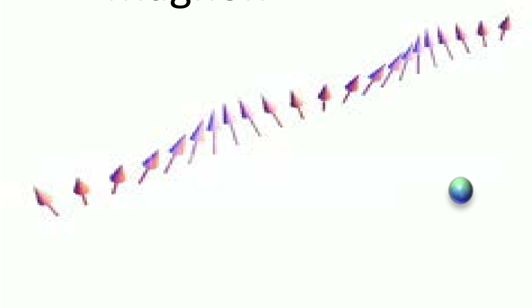


Dipolar electric moment / Electric field



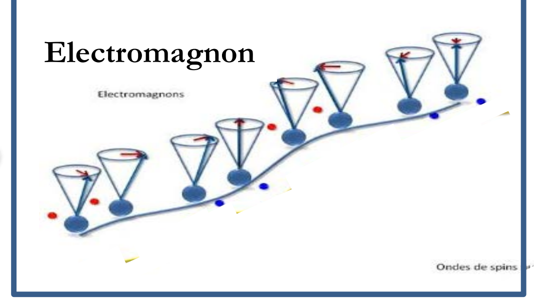


Spin waves/ Magnon



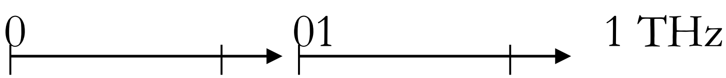
Lattice vibration / Phonon

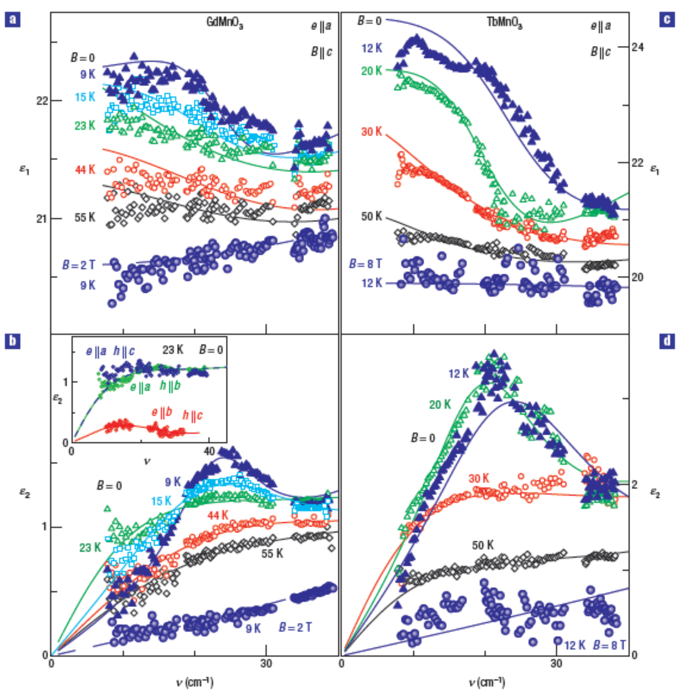
Magneto-electric coupling



4. Electro-magnons in multiferroics

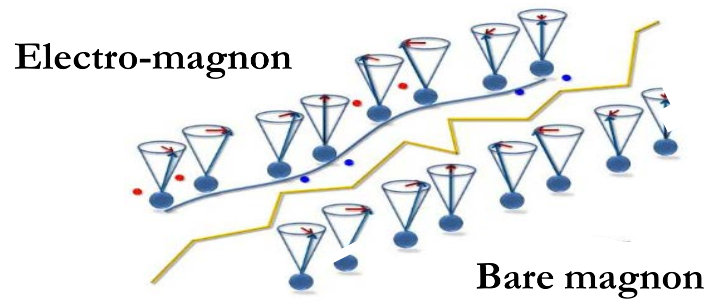
A. PIMENOV et, Nature Physics 2006
Orthorhombic $RMnO_3$





Electronic spectrometer

Magnon dressed with electric charges thanks to magneto-electric coupling



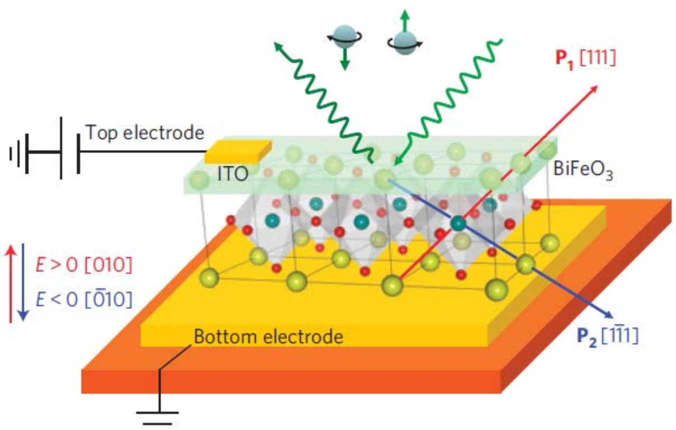
A magnon that is excited by the electric field of the THz wave

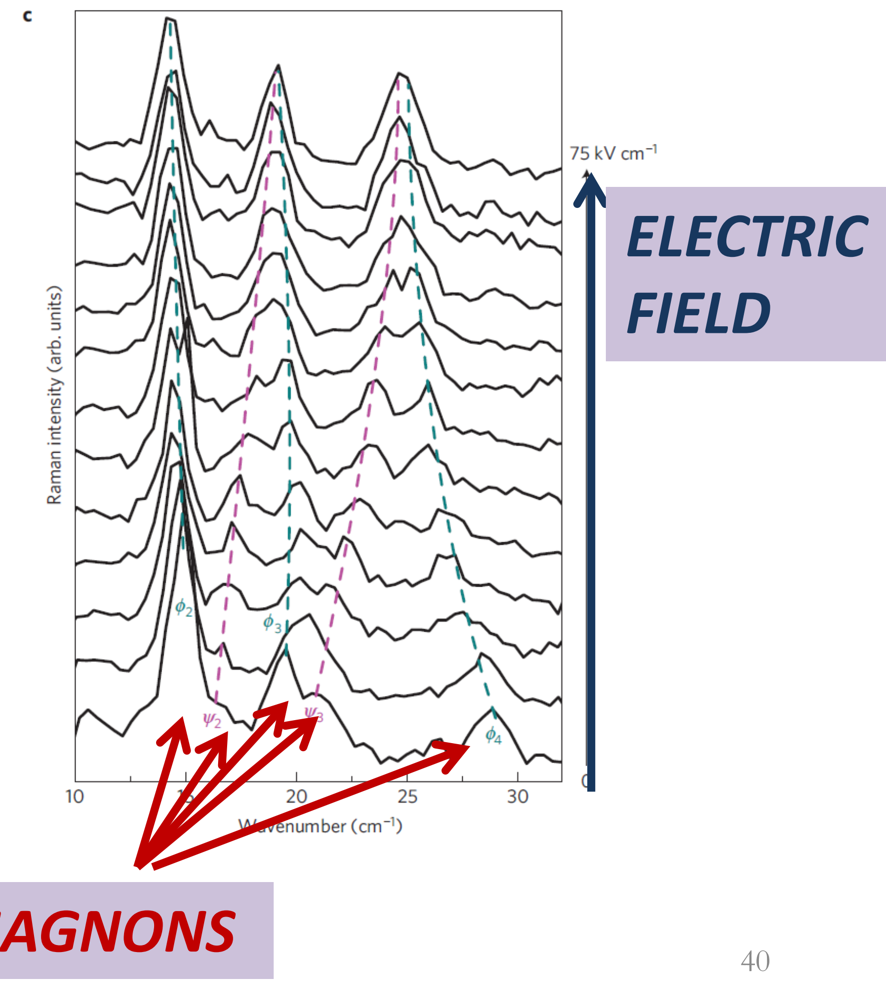
THz Applications :

- Transport and manipulation of information (MAGNONICS + …)

Electric-field control of spin waves at room temperature in multiferroic $BiFeO_3$

P. Rovillain et al, Nature Materials 2010



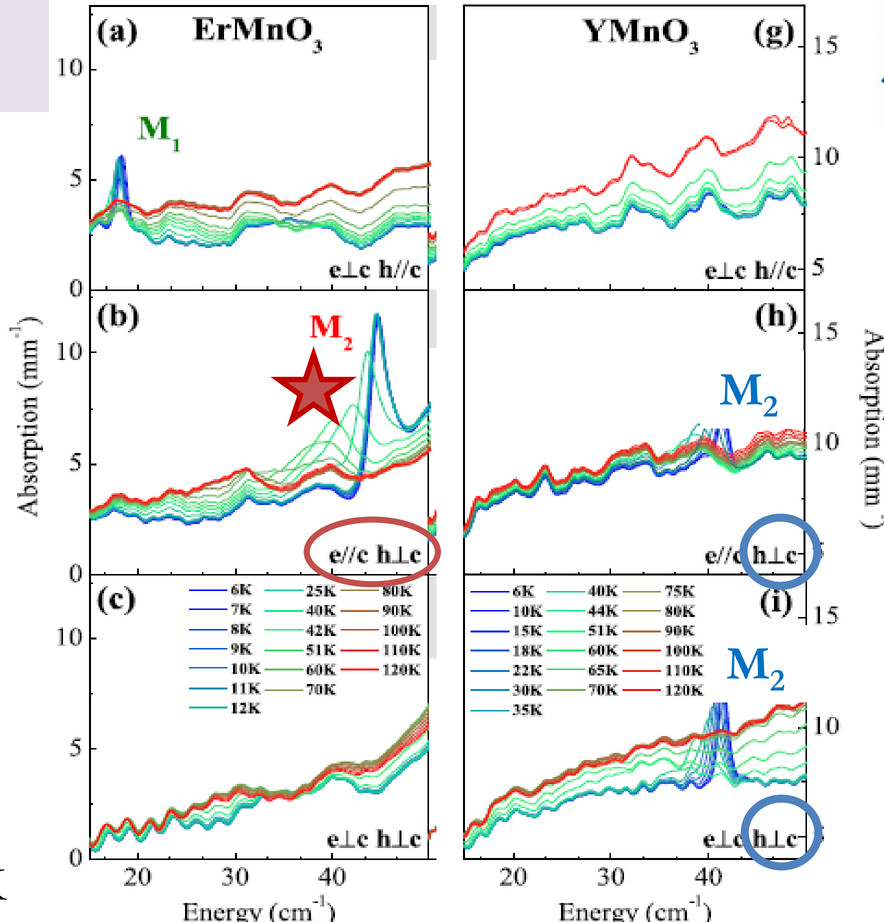


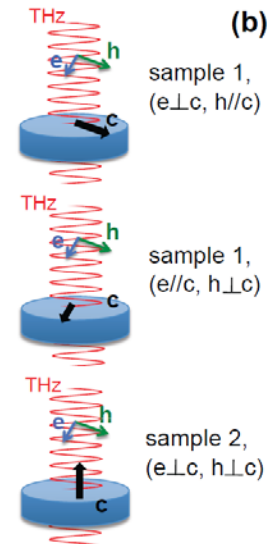
4. Electro-magnons

Other mecanisms?

4. Hexagonal manganites : $ErMnO_3$ /$YMnO_3$

THz Spectroscopy at AILES @ SOLEIL
L. Chaix et al, PRL 2014



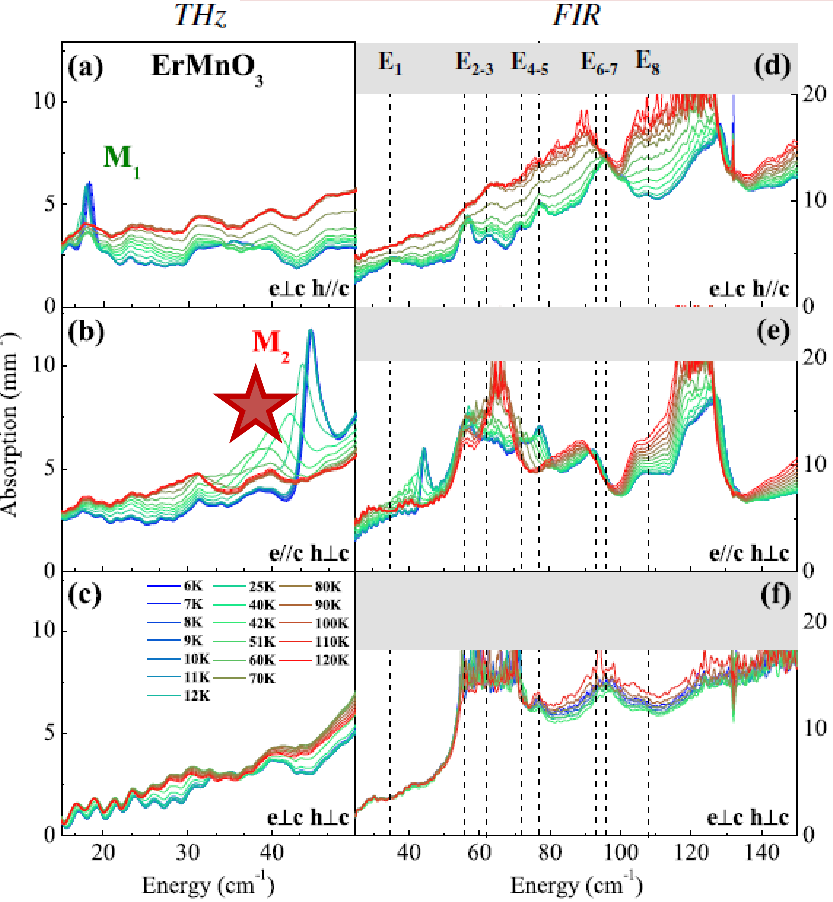


c

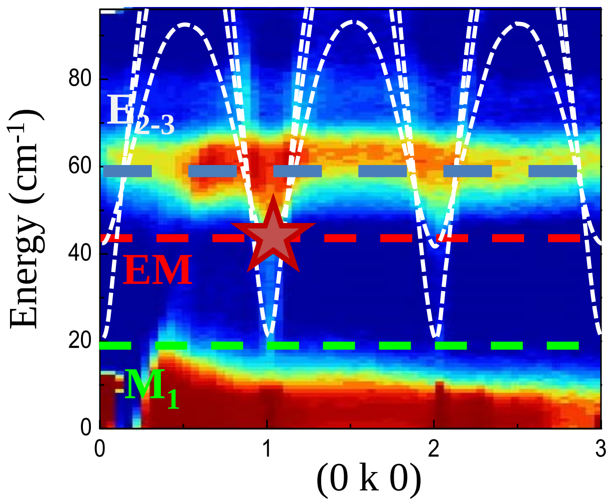
Ferroelectric order at 800 K
(Mn) Magnetic order at 80 K

4. Hexagonal manganites : $ErMnO_3$

THz measurements



Neutron measurements



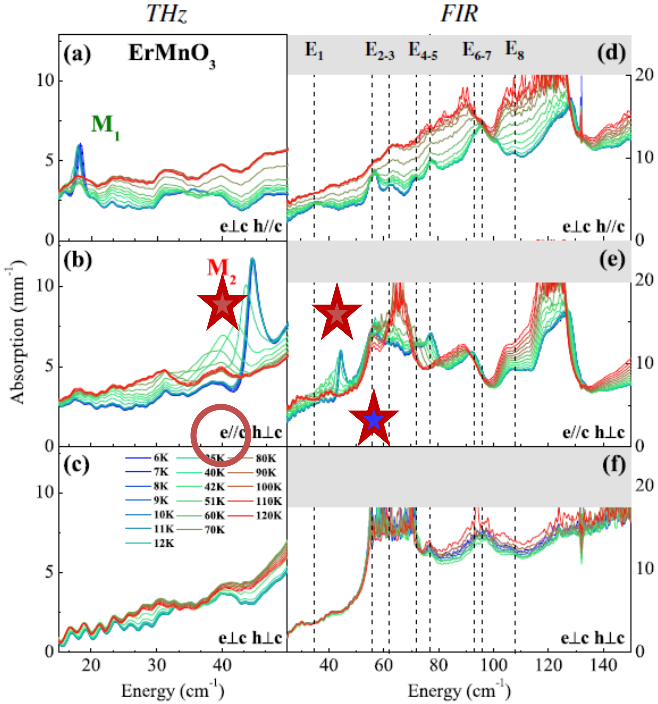
NEUTRONS FOR SOCIETY

Mn MAGNON

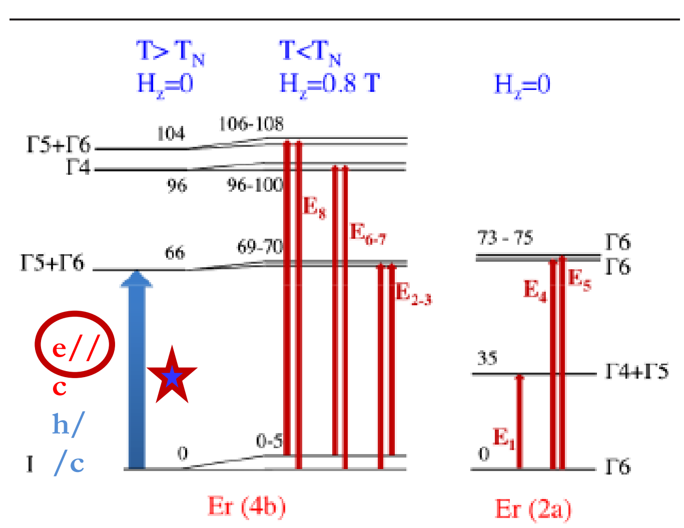
+ Er^{3+} CRYSTAL FIELD EXCITATION at 60 cm-1

4. Hexagonal manganites : $ErMnO_3$

THz measurements

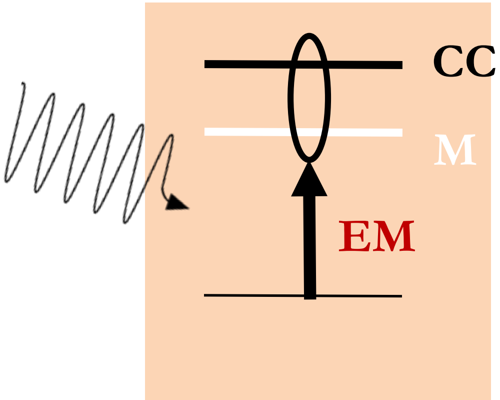


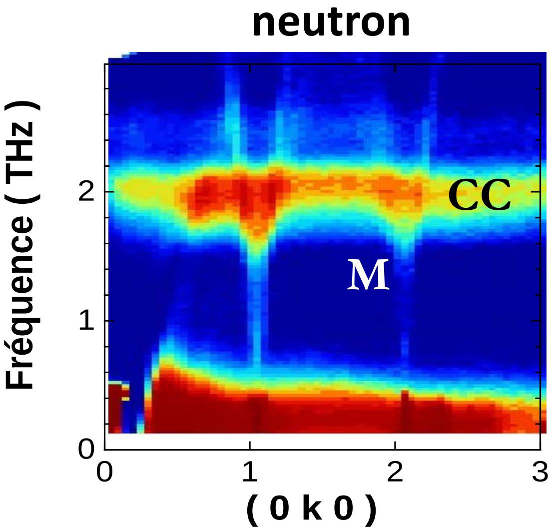
Er Crystal field excitations

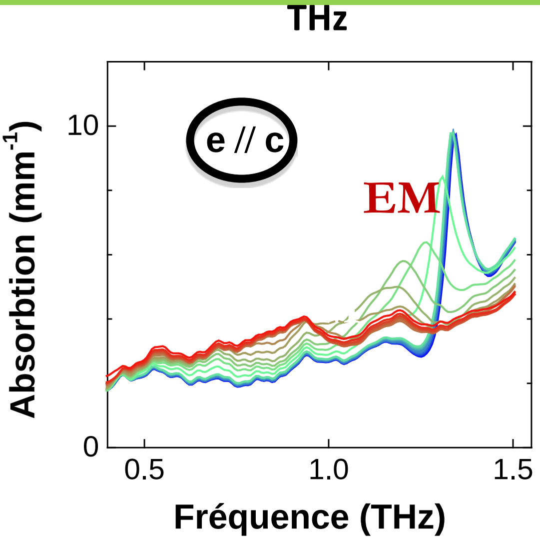


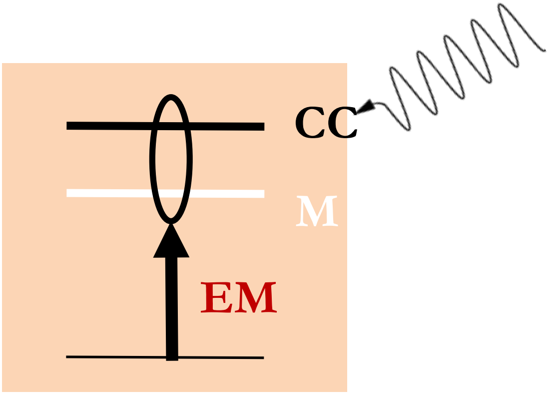
Er/Mn dynamical coupling : electroactive magnon
Mn MAGNON / Er CRYSTAL FIELD HYBRIDE EXCITATION

4. Hexagonal manganites : « electro-magnon » in $ErMnO_3$



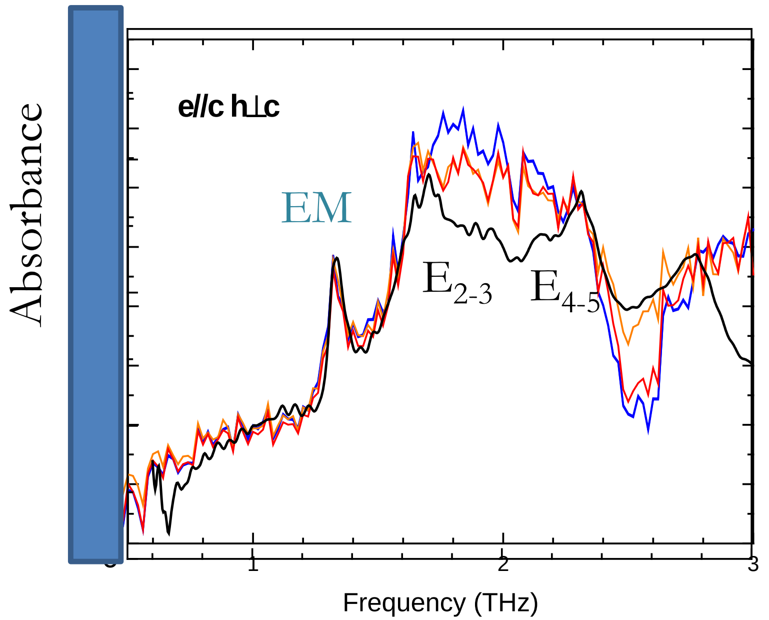




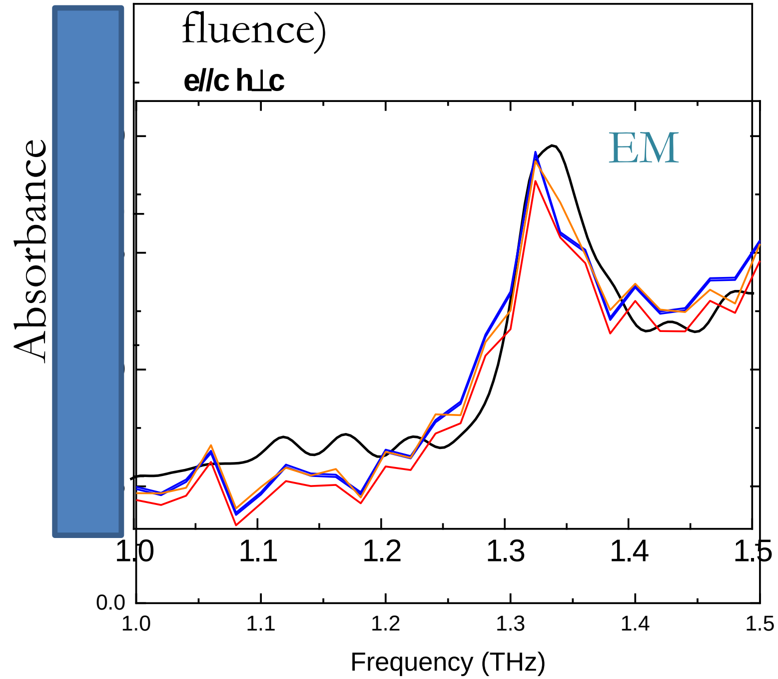


TERAFERMI @ Trieste

4. Hexagonal manganites : « electro-magnon » in $ErMnO_3$



Blue : maximum Fluence
Red : reduced Fluence
black : AILES (lowest fluence)

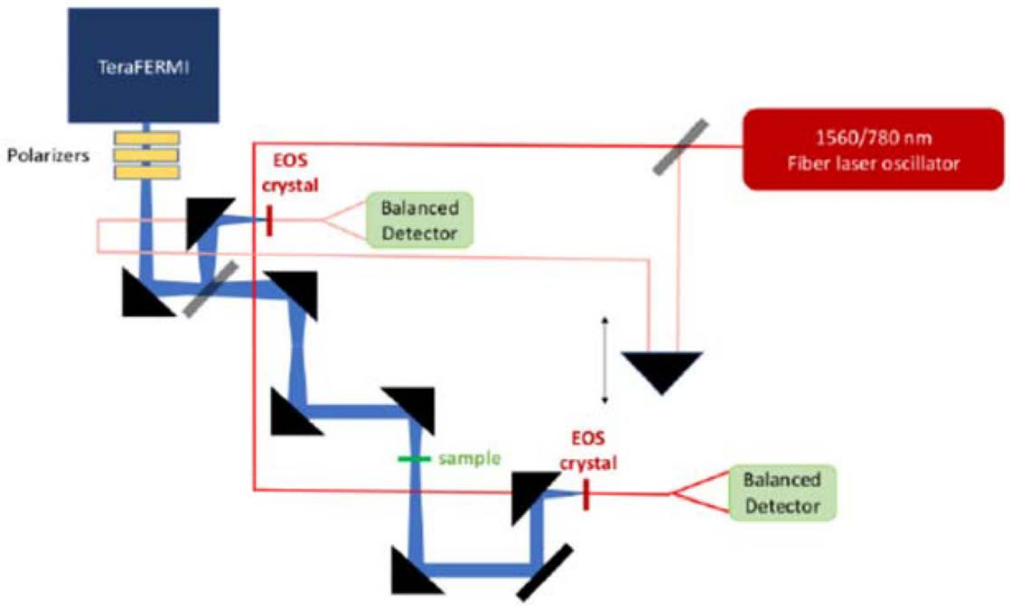


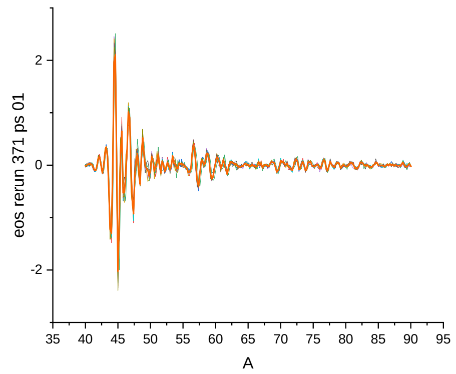
Conclusion :

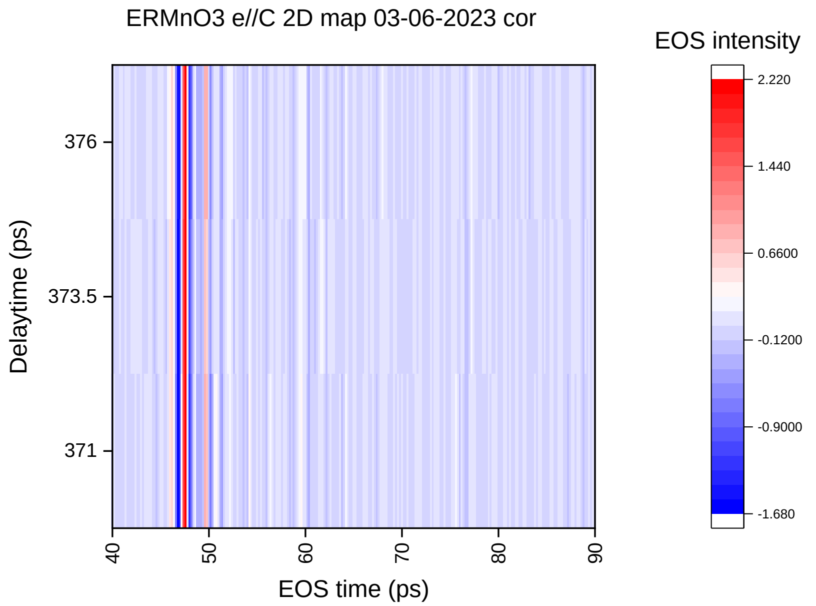
There is clearly a dependence on fluence for E_{2-3} .

For EM, it is not so clear : more acquission is required: high resolution measurements.

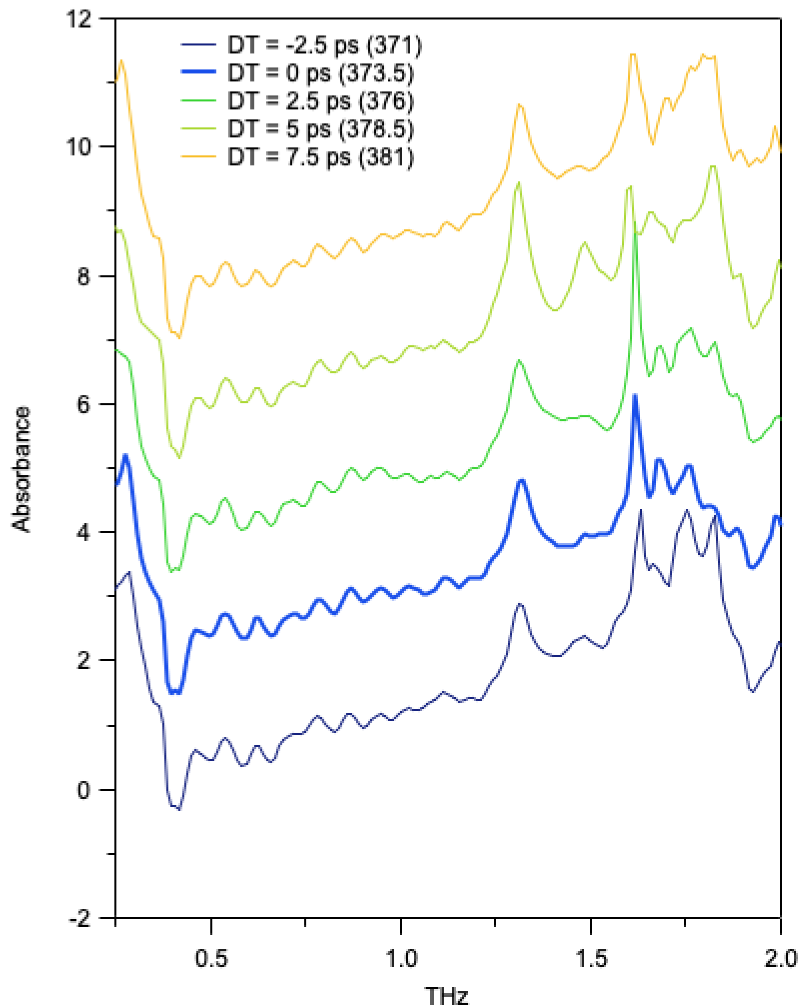
4. Time domain measureements @TERAFERMI





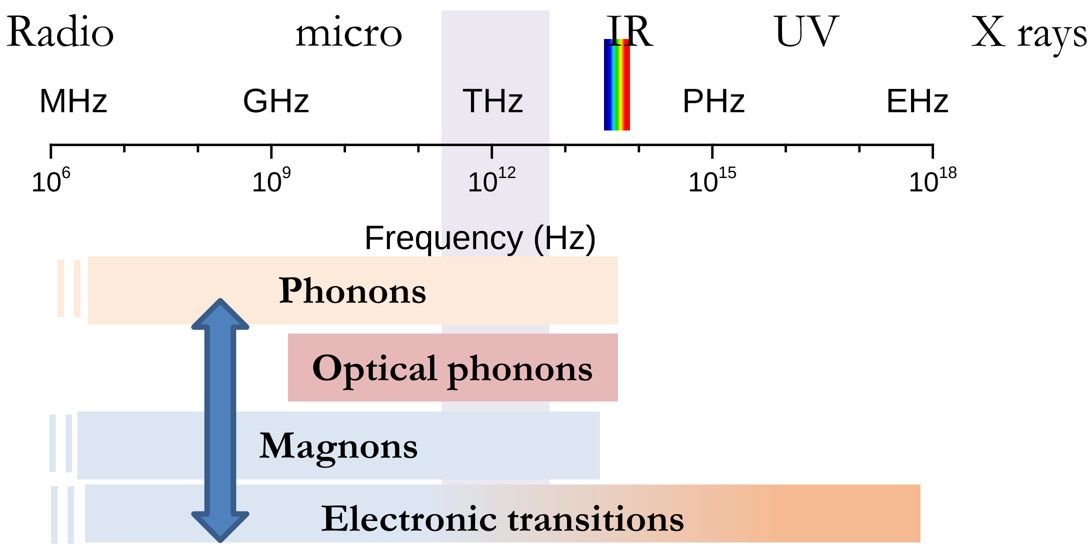


4. Hexagonal manganites : « electro-magnon » in $ErMnO_3$



4. THz properties in oxides

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

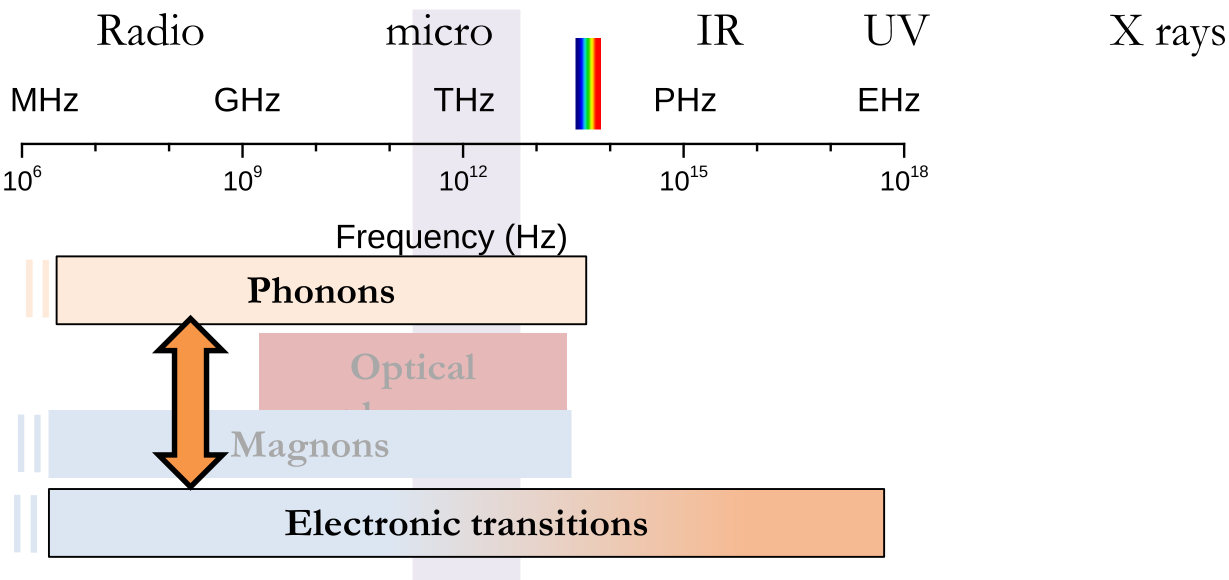


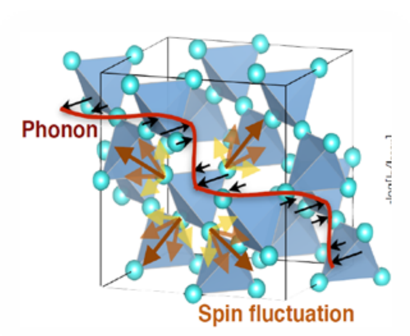
SINGLE ATOMS (MAGNETIC / ELECTRIC)
AND **ORDERED PHASES** (ATOMIC /ELECTRIC / MAGNETIC)
HAVE CHARATERICS EXCITATIONS IN THE THz RANGE

HYBRIDE EXCITATIONS : VIBRONS

4. THz properties in condensed matter probed with EM waves

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

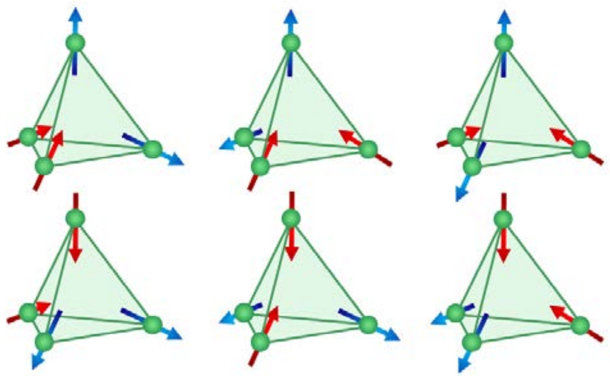




SIGNATURE OF A COMPLEX MAGNETIC PHASE :
the quantum spin ice $Tb_2Ti_2O_7$

E. Constable & al PRB (R) 2017
K. Amelin, Y. Alexanian & al PRB 2020
Y. Alexanian & al PRB 2023

4. Spin ices

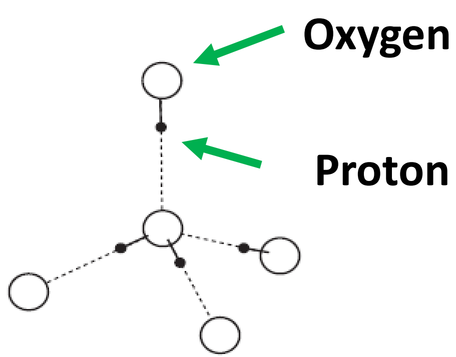


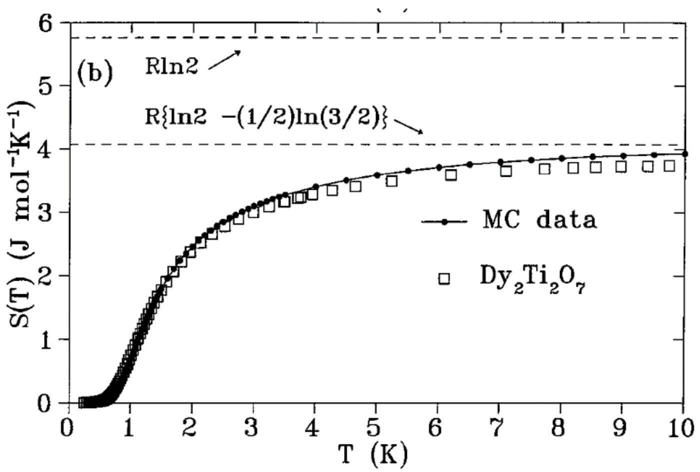
« 2 in – 2 out »

« ice rule »

Extensive degeneracy
Finite entropy

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

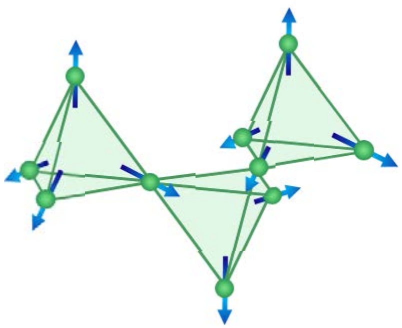




J.S.Gardner, M.J.P.Gingras, J.E.Greedan, Phys.Rev.Mod 82 (2010)

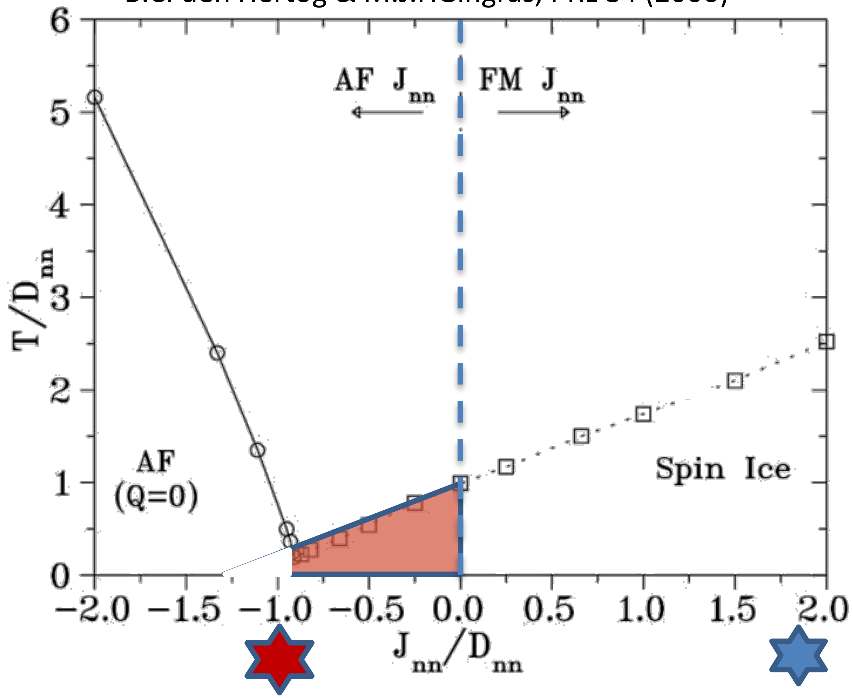
4. Ising spin Phase diagram

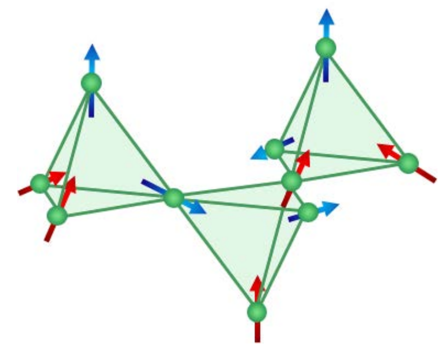
Ising spins + Jnn + Dnn



« All in – All out »
long range order

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





« 2 in – 2 out »
degenerate state

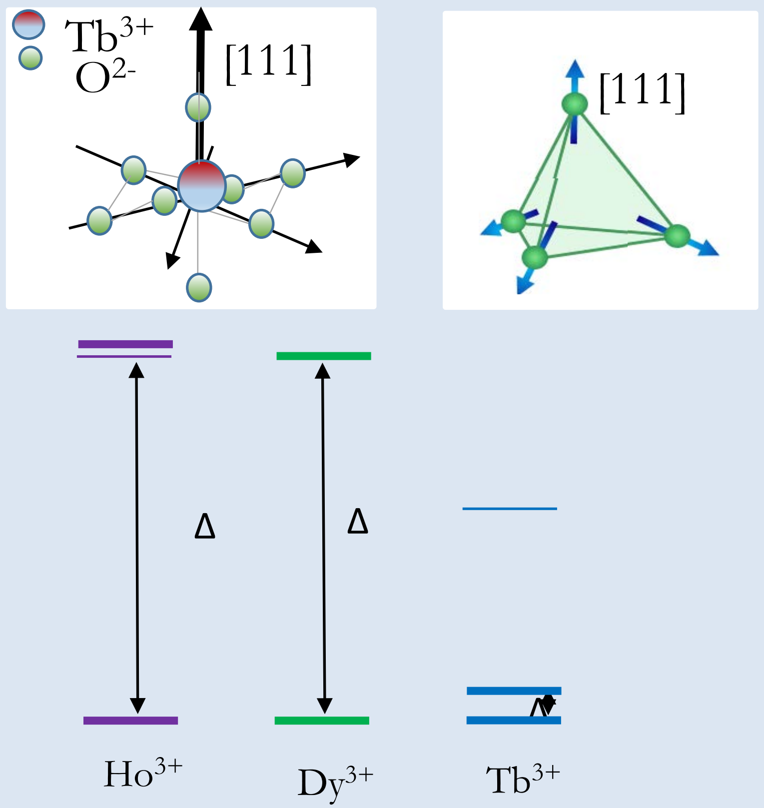
$Tb_2Ti_2O_7$

(Weak) Ising
No long range order down to 50 mK !!!

$Dy_2Ti_2O_7$	$Ho_2Ti_2O_7$
Spin ice	Spin ice

4. TTO peculiarities: Crystal Electric Field (CEF)

Crystal Field electronic levels
in local D3d symmetry



For Ho, Dy
Δ ≈ 300 K

Ising spins

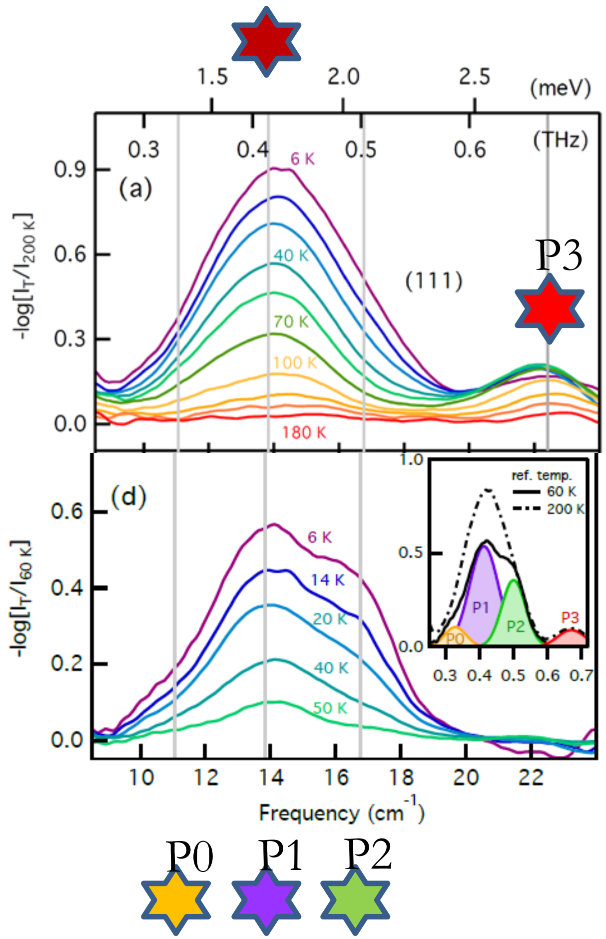
For Tb
Δ ≈ 20 K ≈ 0.4 THz

Weak Ising

⇩

THz spectroscopy

4. 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

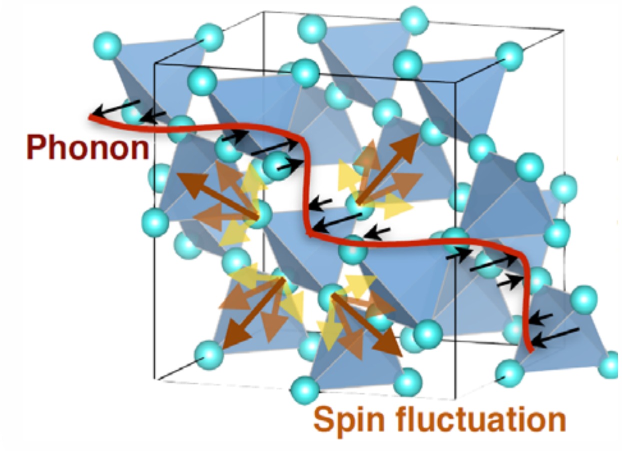
Additionnal peak below 200 K :
0.67 THz (22 cm^{-1})

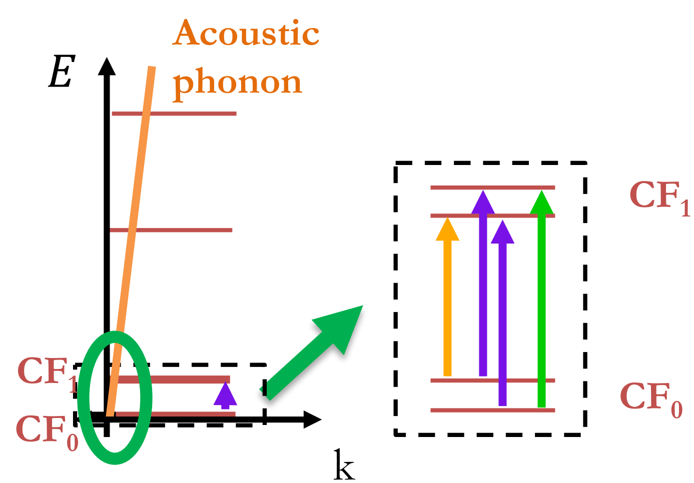
3 peaks visible below 50 K :
0.33 THz (11 cm^{-1})
0.41 THz (14 cm^{-1})
0.50 THz (17 cm^{-1})

4. MAGNETO- ELASTIC EFFECTS: VIBRONIC COUPLING IN $Tb_2Ti_2O_7$

Vibronic coupling = hybridization between crystal field excitations and phonons

P. Thalmeier and P. Fulde, Phys. Rev. Lett. **49**, 1588 (1982)





$Tb_2Ti_2O_7$:

crystal field excitations associated to Tb^{3+} in D3d symmetry
$CF_0 \rightarrow CF_1$ at 14 cm-1 = **0.4 THz** = 1.6 meV (Eg doublets)
+ acoustic phonon of the cubic Fd$\overline{3}$m structure

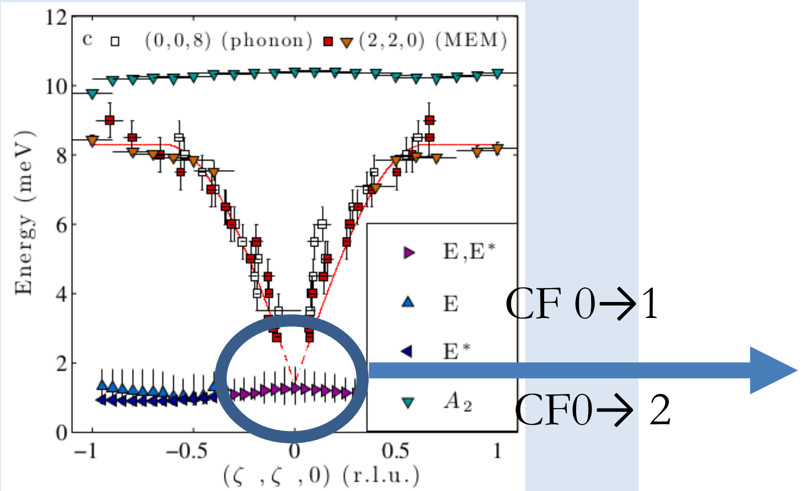
}

Splitting of the ground and first CF levels

4. TTO peculiarities: spin/lattice couplings

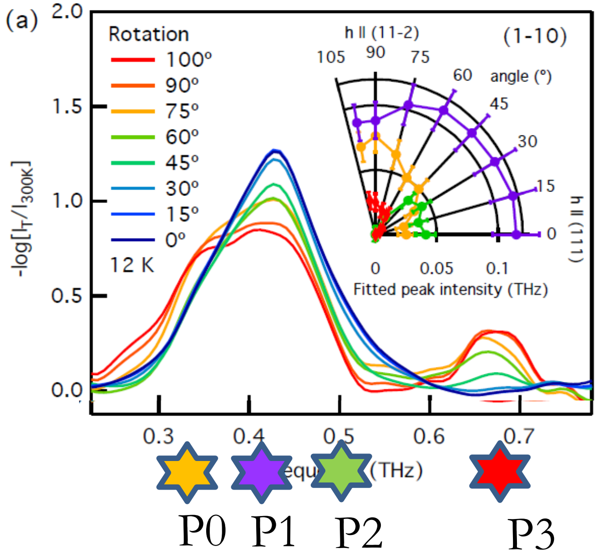
Neutron measurements

Fennell et al, PRL, 112 (2014)



Tb crystal field excitations + phonons :
Magneto-elastic mode (MEM) with the same dispersion as the transverse acoustic phonon

THz measurements



Fine structure of CF 0 → 1
4 peaks that reveal CF 0 and CF1 couplings to phonons **: Vibronic couplings**

4. MAGNETO- ELASTIC EFFECTS: VIBRONIC COUPLING IN $Tb_2Ti_2O_7$

Crystal field – phonon hybridization = vibronic coupling

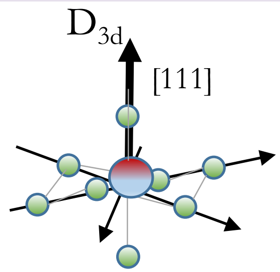
P. Thalmeier and P. Fulde, Phys. Rev. Lett. **49**, 1588 (1982)

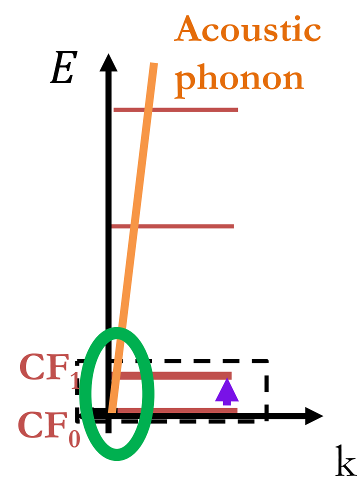
One site Hamiltonian :

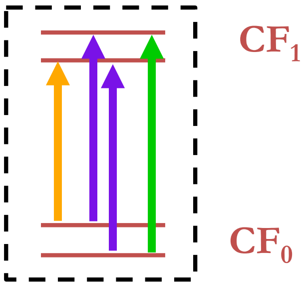
$$\hat{\mathcal{H}} = \sum_{k,q} \underbrace{B_q^k \hat{O}_q^k}_{\text{Crystal field}} + \underbrace{D_q^k \hat{O}_q^k}_{\text{Vibronic coupling}}$$

Crystal field

Vibronic coupling







Acoustic phonon: $T_{1u\downarrow D_{3d}} = A_{2u} \oplus E_2$

Coupling to E_g **CF states** through

$\hat{O}_2^k$ k = 1, 2

Quadrupolar degrees of freedom

E. Constable *et al.*, PRB (R) (2017)

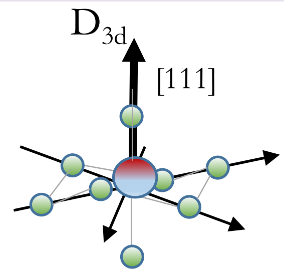
4. MAGNETO- ELASTIC EFFECTS: VIBRONIC COUPLING IN $Tb_2Ti_2O_7$

Crystal field – phonon hybridization = vibronic coupling

P. Thalmeier and P. Fulde, Phys. Rev. Lett. **49**, 1588 (1982)

One site Hamiltonian :

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

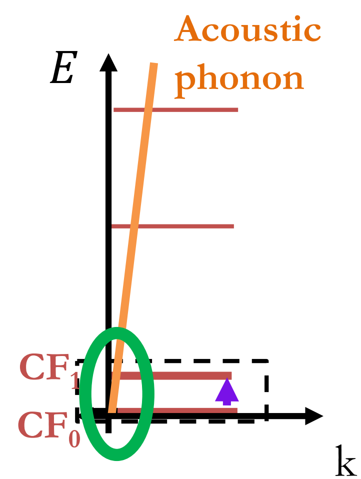


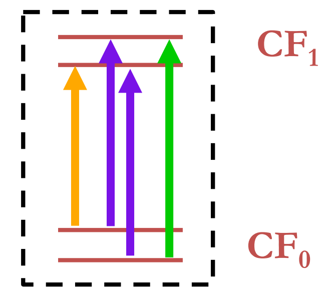
Acoustic phonon: $T_{1u\downarrow D_{3d}} = A_{2u} \oplus E_2$

Coupling to E_g **CF states** through

$\hat{O}_2^k$ k = 1, 2

Quadrupolar degrees of freedom

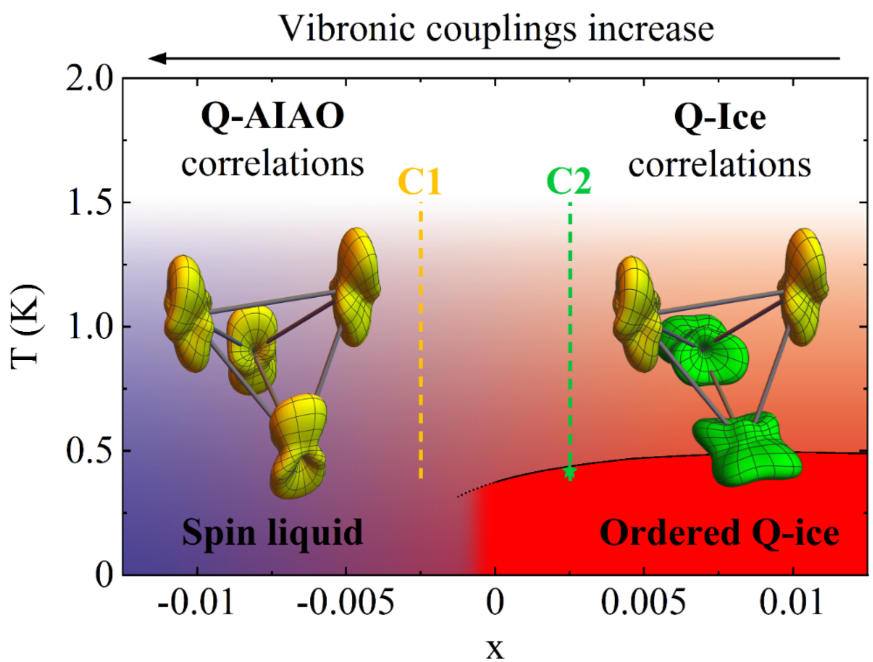




E. Constable *et al.*, PRB (R) (2017)

Quadrupolar phase diagram of $Tb_{2+x}Ti_{2-x}O_{7+y}$

Vibronic couplings favor « all-in or all out» quadrupoles correlations **(Q-AIAO)**



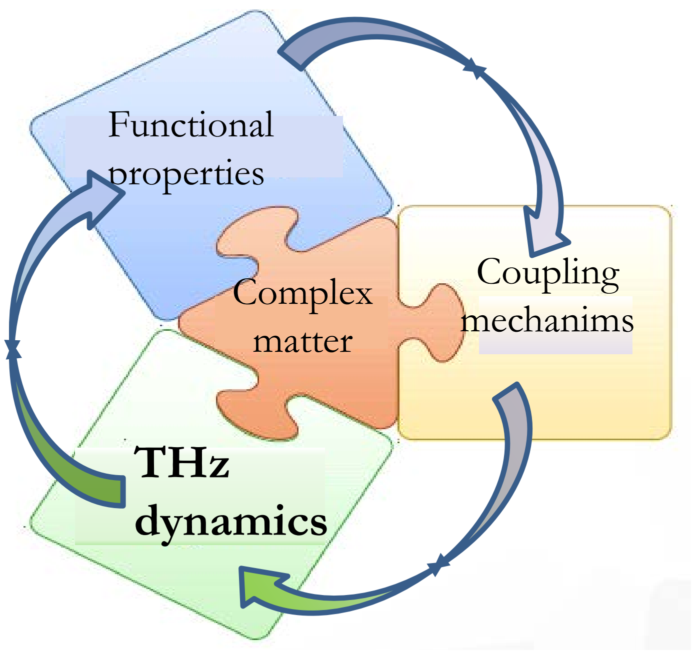
Dipolar & quadrupolar interactions favor ice « 2 in-2 out like» quadrupoles correlations **(Q-ice)**

competition between vibronic couplings and dipolar & quadrupolar interactions
If sufficiently strong, the ordered quadrupolar ice is even destroyed (crystal C1)!

Y. Alexanian *et al.* arxiv2207.10036

9

THz PROPERTIES OF COMPLEX MAGNETIC PHASES



Signatures of complex phases with several degrees of freedom (spin, charge, lattice…)

New hybride excitations

Out of equilibrium phases

"continuum" from correlated electrons/ spin liquids….