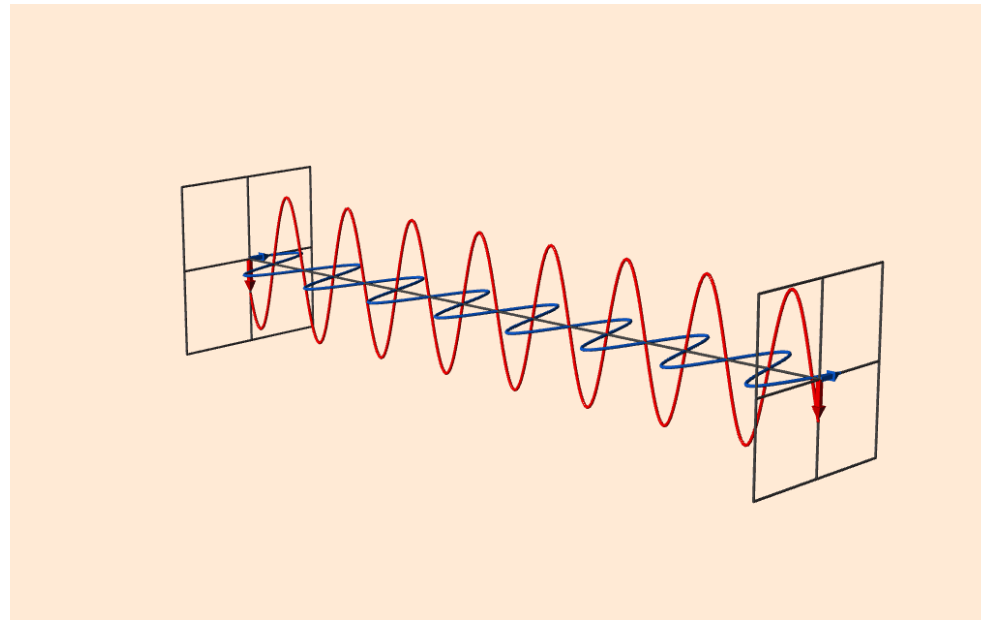


THZ DYNAMICS IN OXIDES

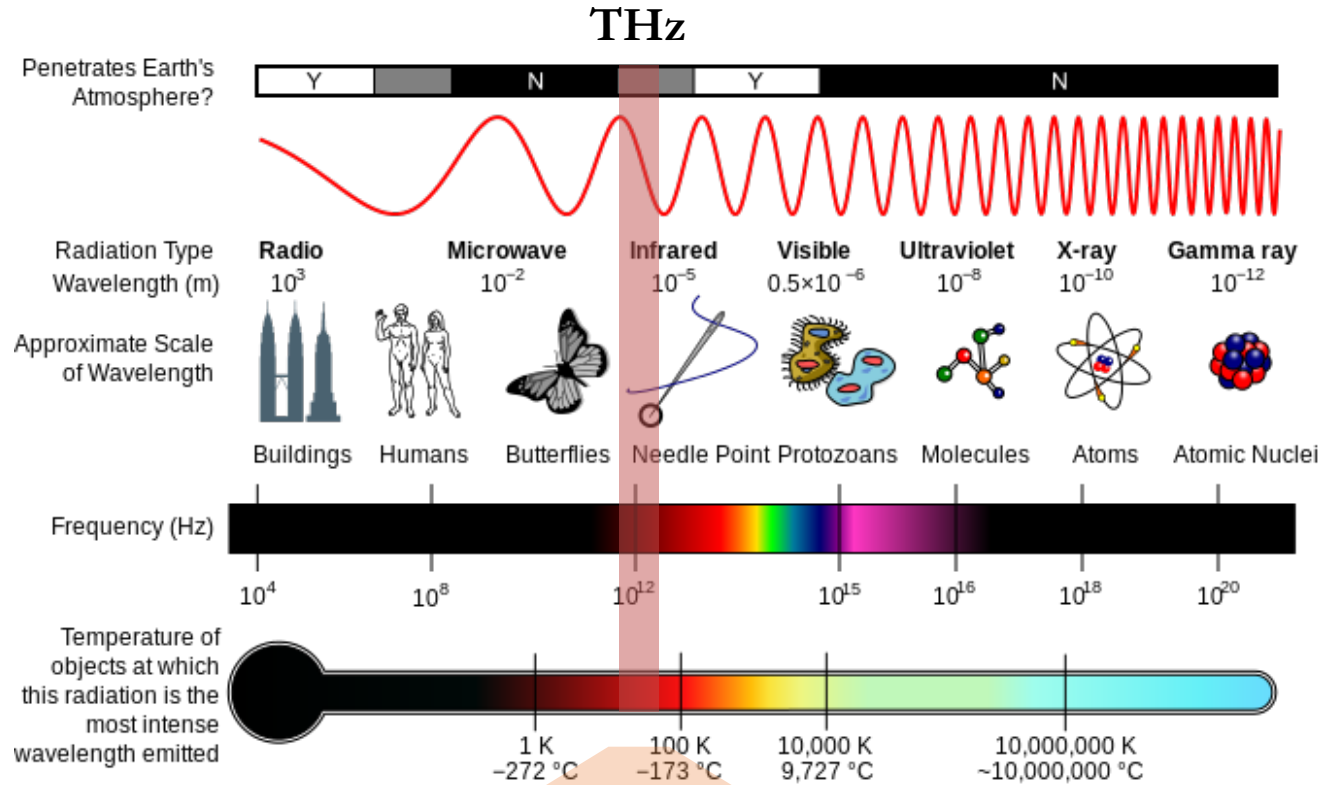
with Electro-magnetic waves



EMANIM

Electric and **magnetic** fields

The THz range in the electromagnetic spectrum



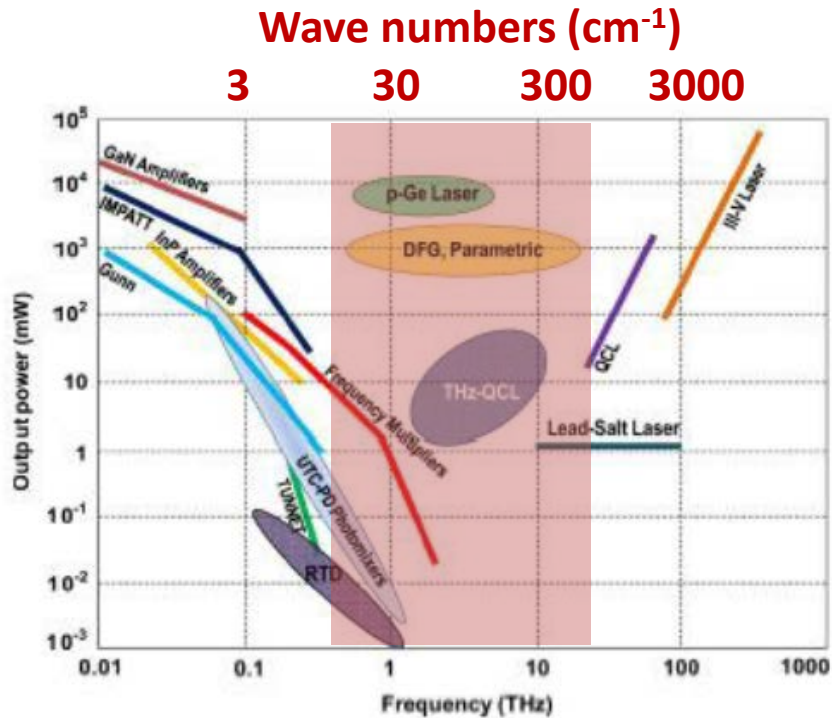
wikipedia

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

The THz gap

2011

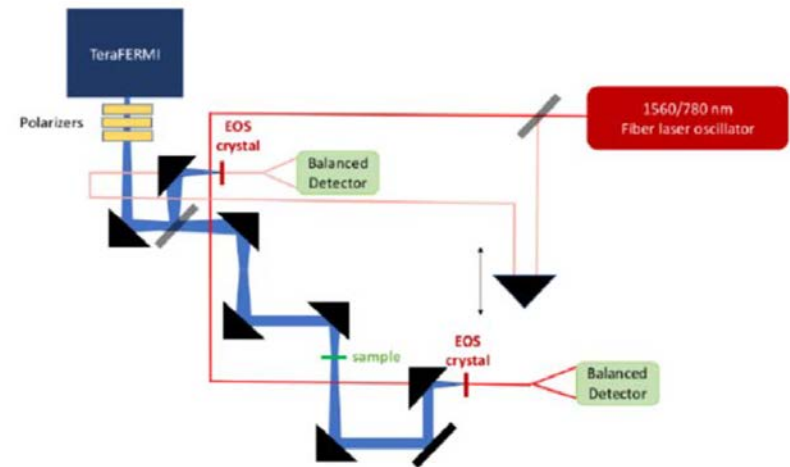
2023



Electronics

Photonics

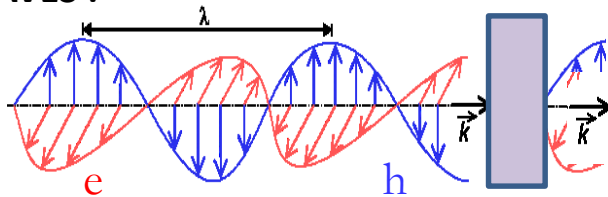
Time domain spectrometers
Synchrotron base THz emission
 FEL strong THz pulses



Time domain spectrometer at TeraFERMI

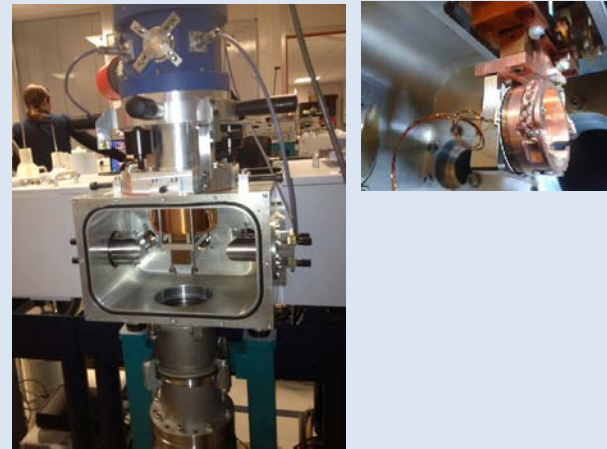
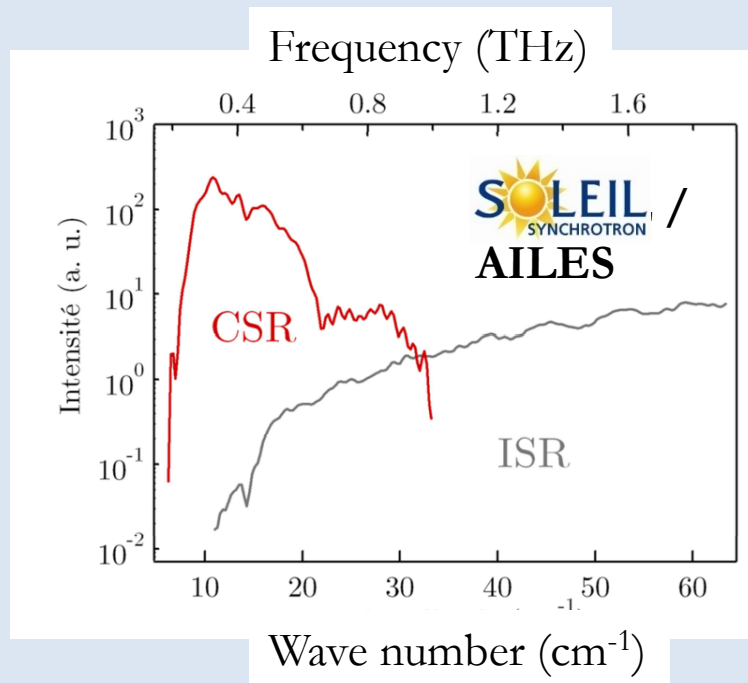
THz spectroscopy at SOLEIL@AILES

THz WAVES :



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

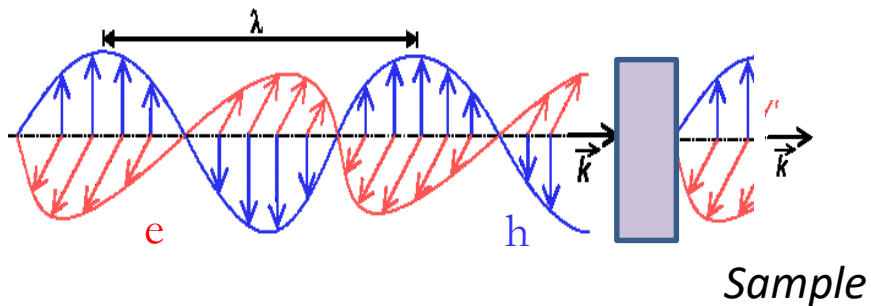
SYNCHROTRON BASED SPECTROSCOPY:



An intense, stable broadband THz source in a cryogenic environment

THz spectroscopy

THz wave :



Fourier transform spectroscopy

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

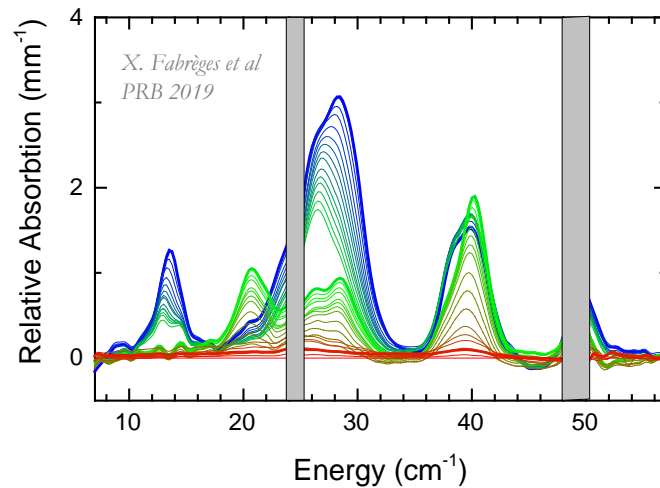
Absorbance : $\text{Abs} = -\text{Log}(T) \approx \alpha d$

Absorption $\alpha(\omega)$



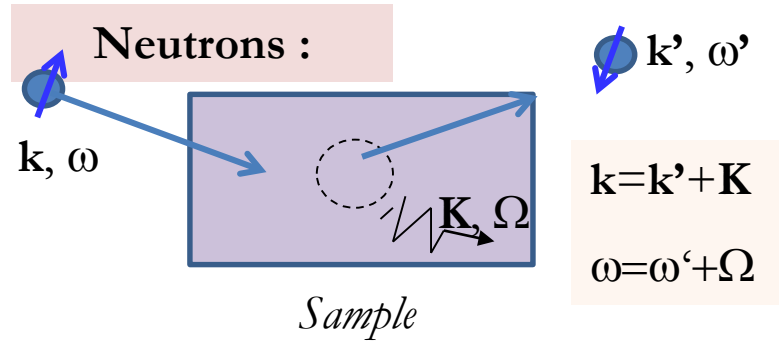
dissipative part of the susceptibility

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



CF excitations in h- HoMnO_3

Inelastic neutron scattering



DISPERSION CURVES :

Position in energy $\Omega(\mathbf{K})$

Intensity map $I = \text{form factor} \times \text{dissipative part of the susceptibility}$

$$\chi_2(\Omega, \mathbf{K}) \perp \mathbf{K}$$

MAGNETIC AND ATOMIC PROBE :

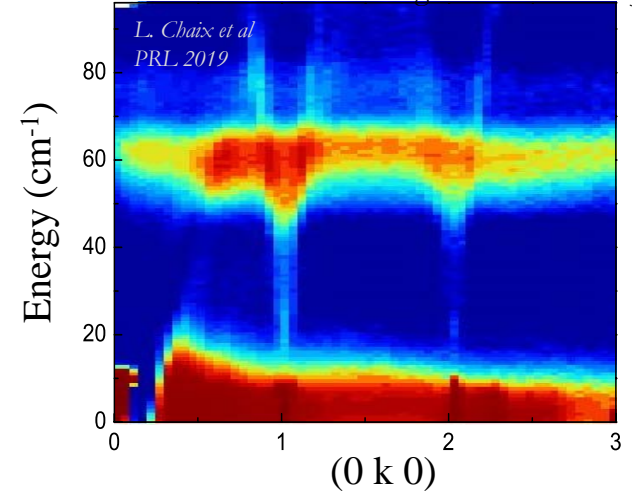
Low $\mathbf{K} \rightarrow$ magnetic contribution

large $\mathbf{K} \rightarrow$ atomic contribution

Polarised neutron \rightarrow magnetic /atomic contribution

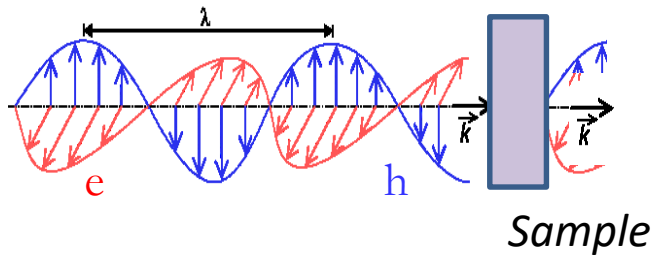


CEF excitations and magnons in ErMnO_3

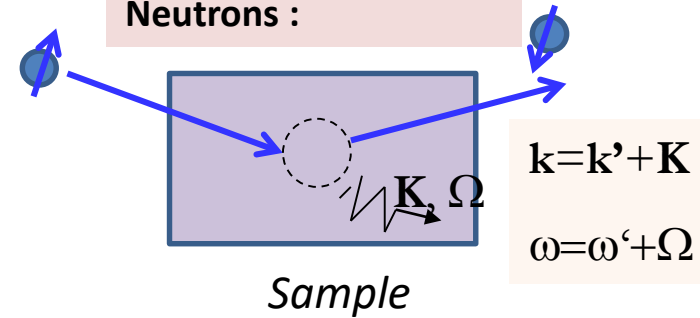


Electromagnetic waves versus Neutrons

THz wave :



Neutrons :



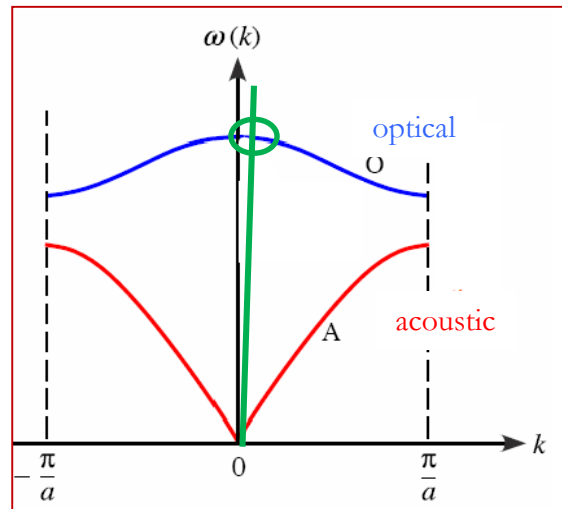
ABSORPTION CURVES

$$\Omega (K \approx 0)$$

$$\chi_2 (\Omega, \approx 0)$$

MAGNETIC AND ELECTRIC PROBE

Smaller sample
Increased energy
resolution



DISPERSION CURVES

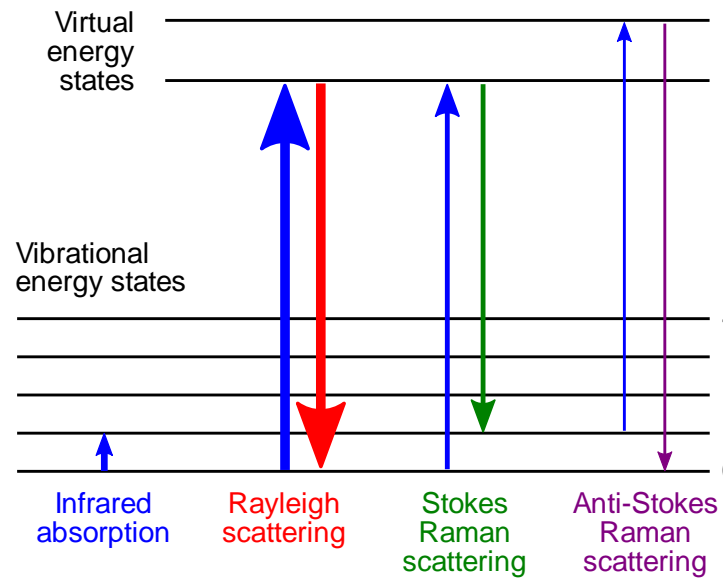
$$\Omega(K)$$

$$\chi_2 (\Omega, K) \perp K$$

MAGNETIC AND ATOMIC PROBE

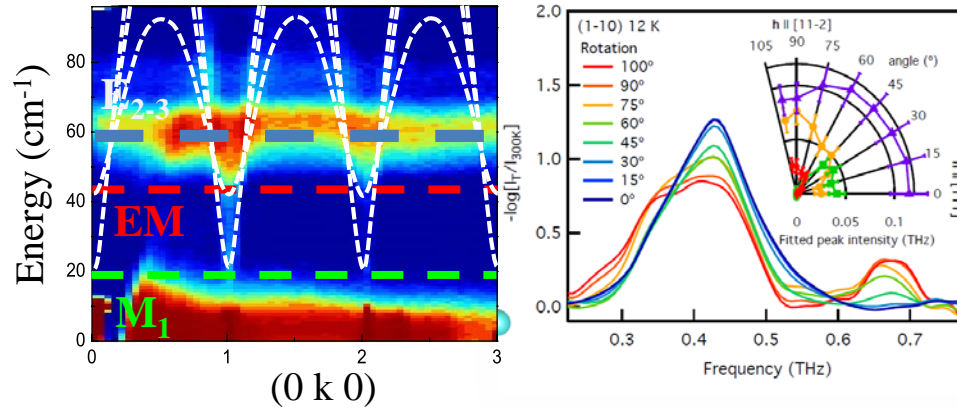
Whole reciprocal space

RAMAN spectroscopy



Indirect probe:
High energy excitation
Indirect process
Different selection rules (phonons, etc...)
THz: close to Rayleigh scattering

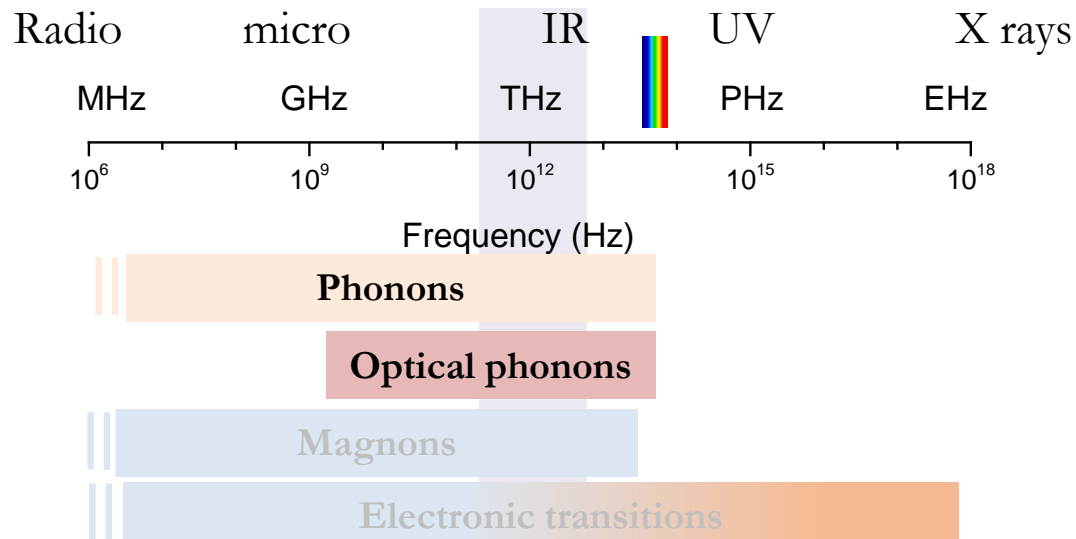
THZ DYNAMICS IN OXIDES



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

1. THz properties in oxides

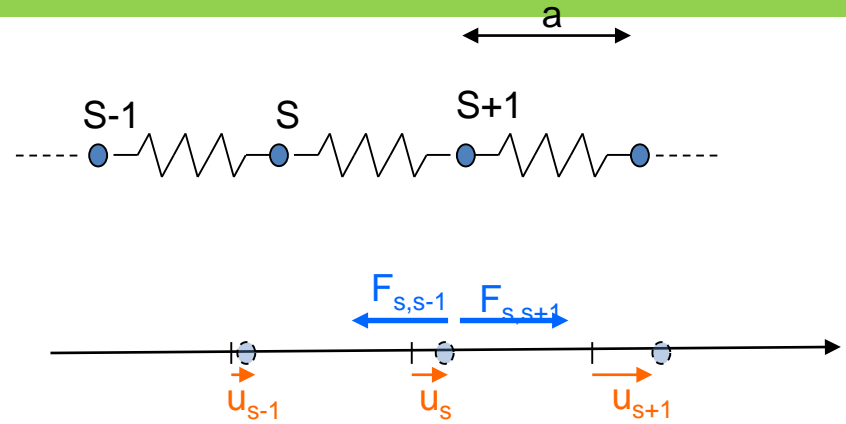
$$1 \text{ THz} \approx 33 \text{ cm}^{-1} \approx 300 \text{ } \mu\text{m} \approx 4 \text{ meV} \approx 50 \text{ K}$$



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

1. Phonons

Mono atomic chain :



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

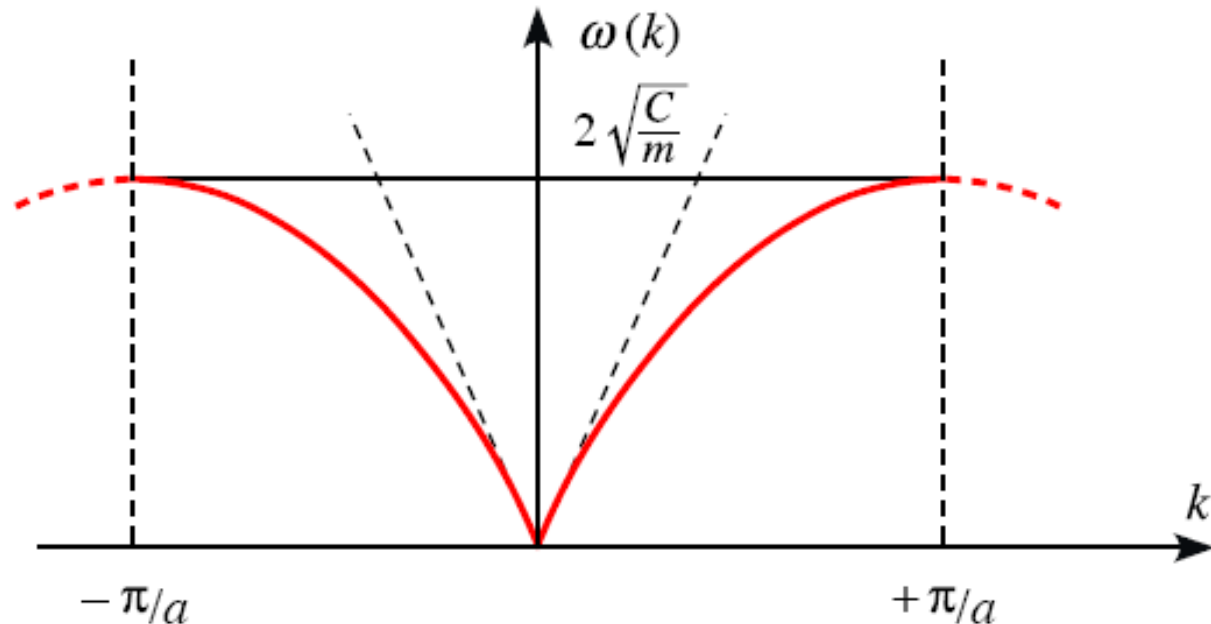
- Small k, large wave length (zone center):

Atoms vibrate in phase.

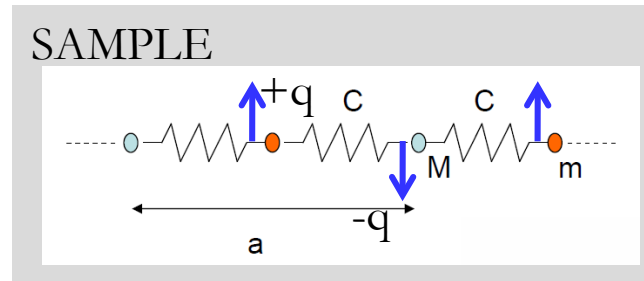
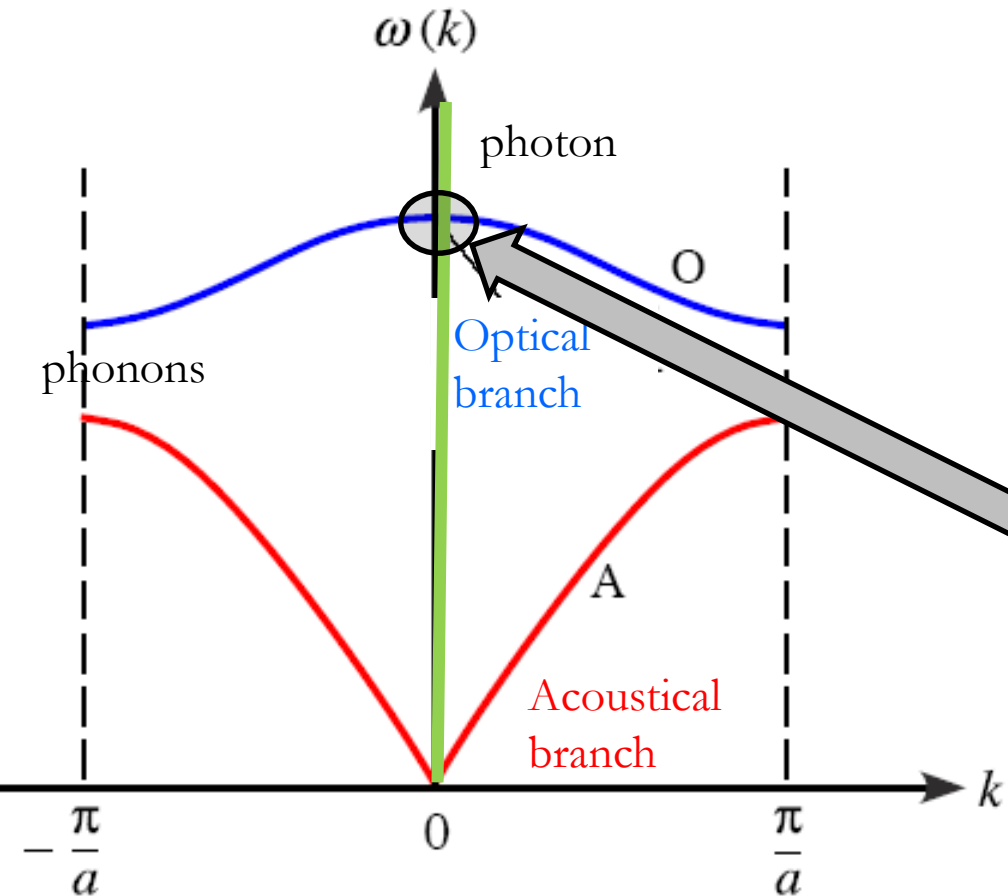
$$\omega = v_s k v_s = a \sqrt{\frac{C}{M}}$$

- Brillouin zone boundary : atoms vibrate out of phase.

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



1. PHONONS

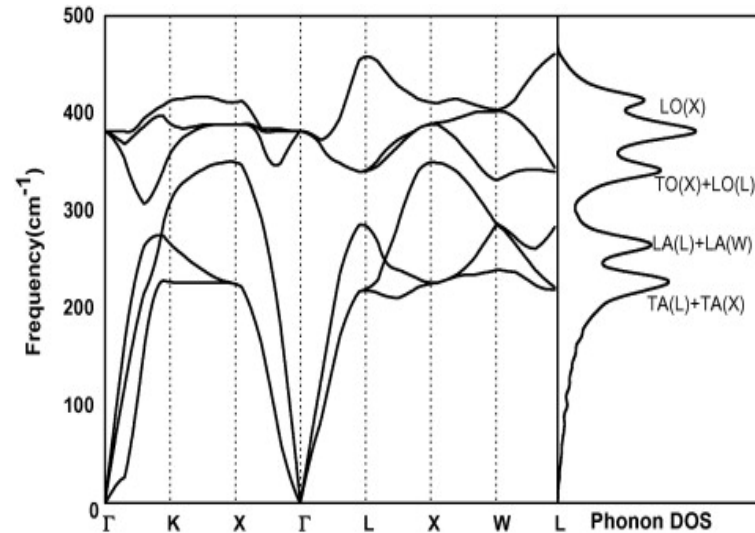
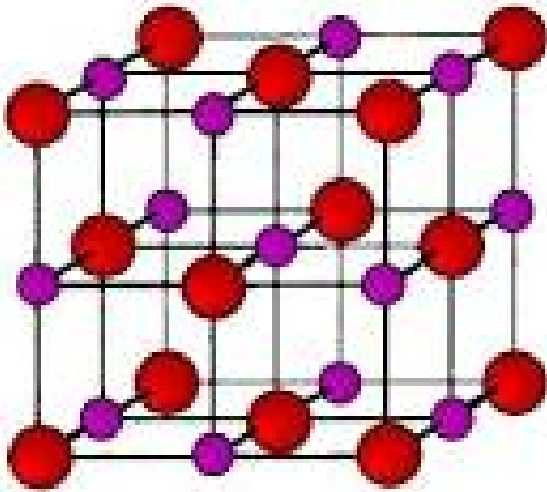


Several branches
 Dispersion in the energy range $0 - \Theta_{\text{Debye}}$

EM wave /sample interaction via
 Electric field / electric charges
 Atomic probe (neutron)

1. Phonons

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



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

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

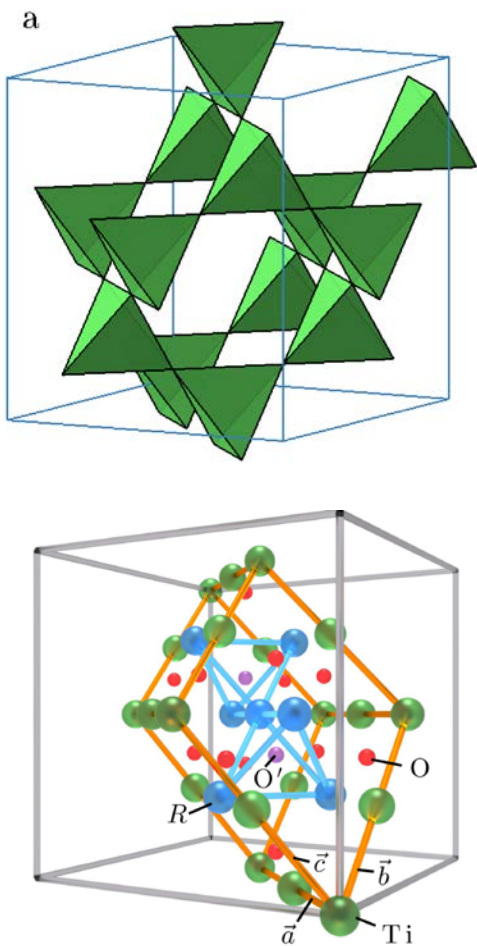


FIG. 1. The primitive cell of the pyrochlore structure, as related to the conventional cubic unit cell. The primitive cell contains 22 ions: 4 R^{3+} (blue), 4 Ti^{4+} (green), 12 O^{2-} (red), and 2 O'^{2-} (violet). The axes of the conventional cell are shown by the gray box, and the primitive cell 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.)

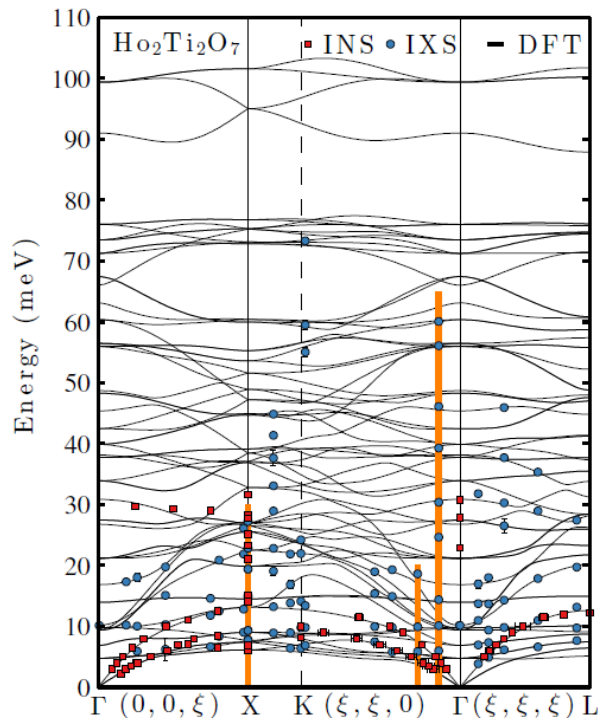


Figure 3. Phonon dispersion relations of $Ho_2Ti_2O_7$ calculated using DFT and the finite displacement method. The vibrational spectrum is presented along a path following high symmetry directions of the reciprocal lattice. The calculation is experimentally verified using inelastic neutron (INS) and 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.

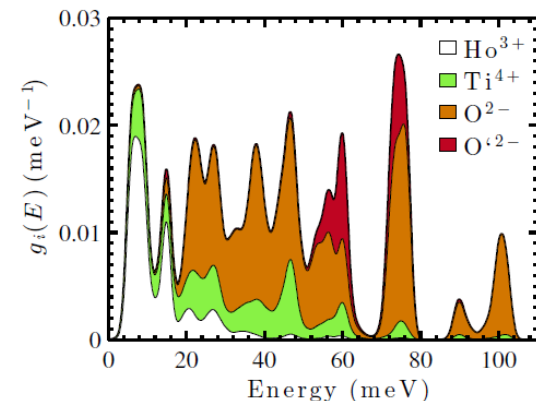
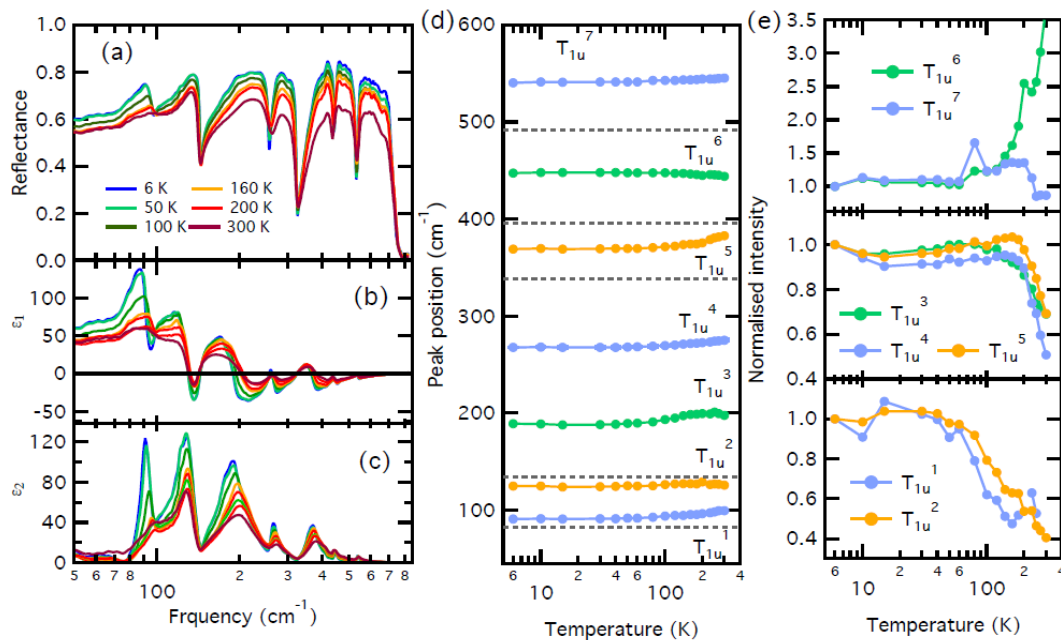


Figure 4. Normalized partial phonon densities of states $g_i(E)$ of $Ho_2Ti_2O_7$, calculated from first-principles.

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

1. example: phonons in the pyrochlore R₂Ti₂O₇

Reflectance and dielectric constant of a pyrochlore crystal Tb₂Ti₂O₇



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

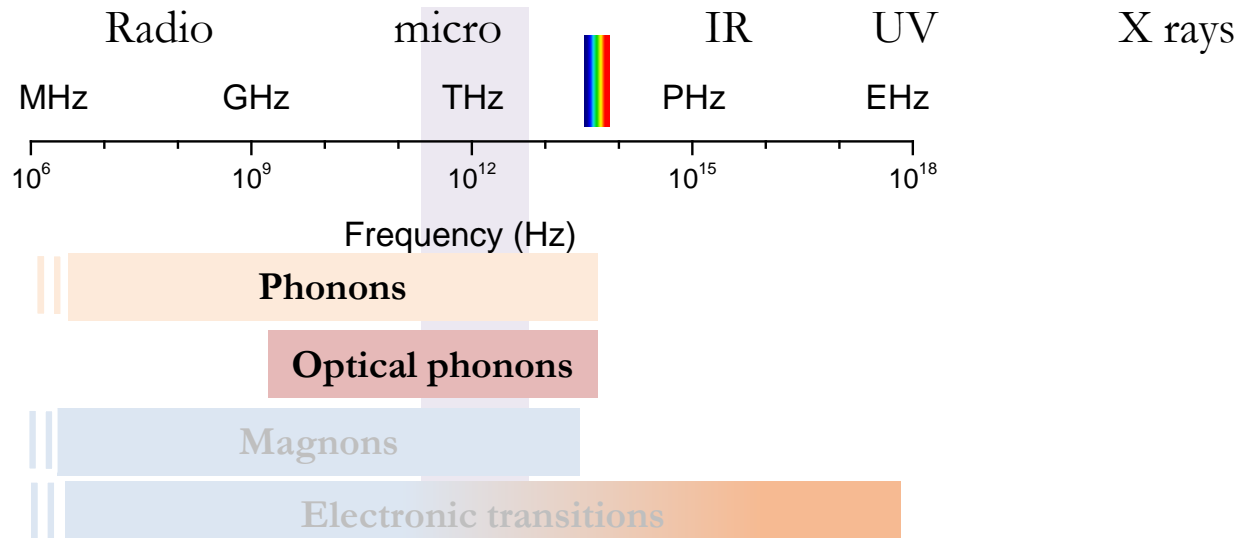
$$\Gamma = A_{g1} \oplus 3A_{2u} \oplus 3E_u \oplus E_g \oplus 4T_{2u} \oplus 4T_{2g} \oplus 8T_{1u} \oplus 2T_{1g} \quad .$$

No lowering of symmetry as a function of temperature

High dissipation above 80 cm⁻¹ / low dissipation below 80 cm⁻¹

1. PHONONS

$$1 \text{ THz} \approx 33 \text{ cm}^{-1} \approx 300 \text{ } \mu\text{m} \approx 4 \text{ meV} \approx 50 \text{ K}$$



PHONONS ARE SIGNATURES OF THE ATOMIC LATTICE



CRISTALLOGRAPHIC PHASE TRANSITIONS



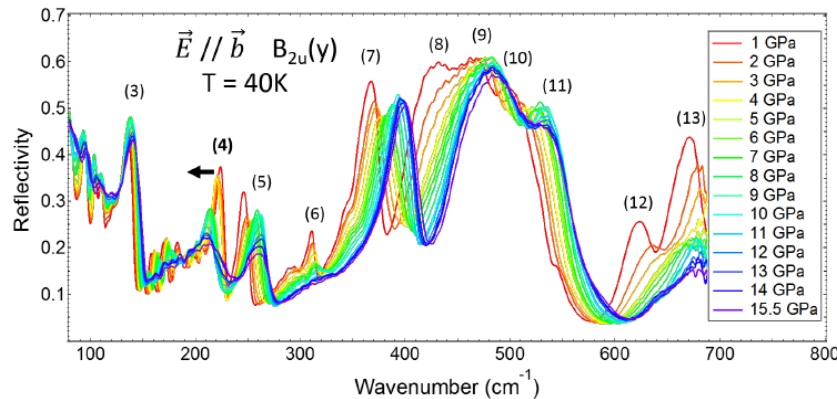
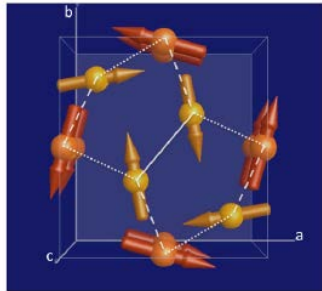
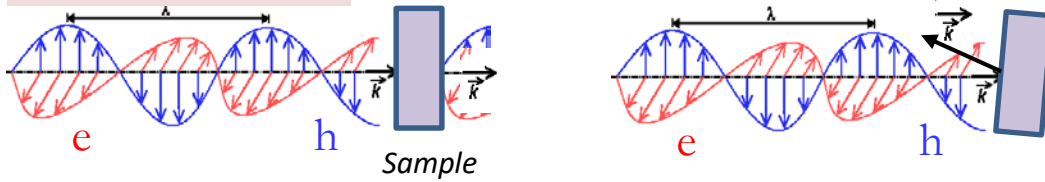
SOFT MODES

1. Phonons in the pentagonal $\text{Bi}_2\text{Fe}_4\text{O}_9$ under pressure

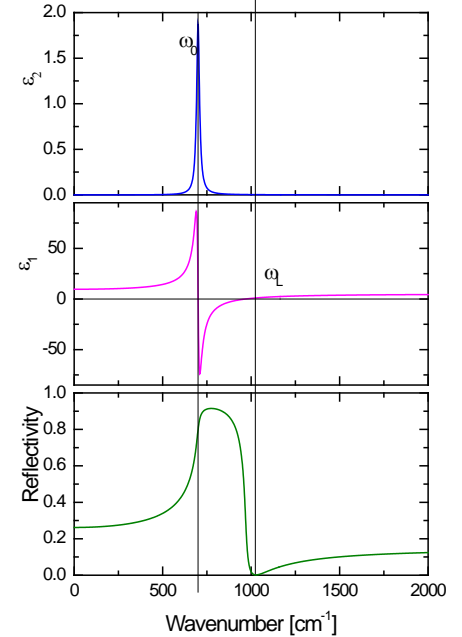
$T = I / I_0 \approx \exp(-\alpha d)$ for small α

For large α , Reflectivity is used $R = 1 - T$

THz wave :



Lorentz model



Magnetic order below
240 K

At ambient pressure

E. Ressouche et al PRL 2009

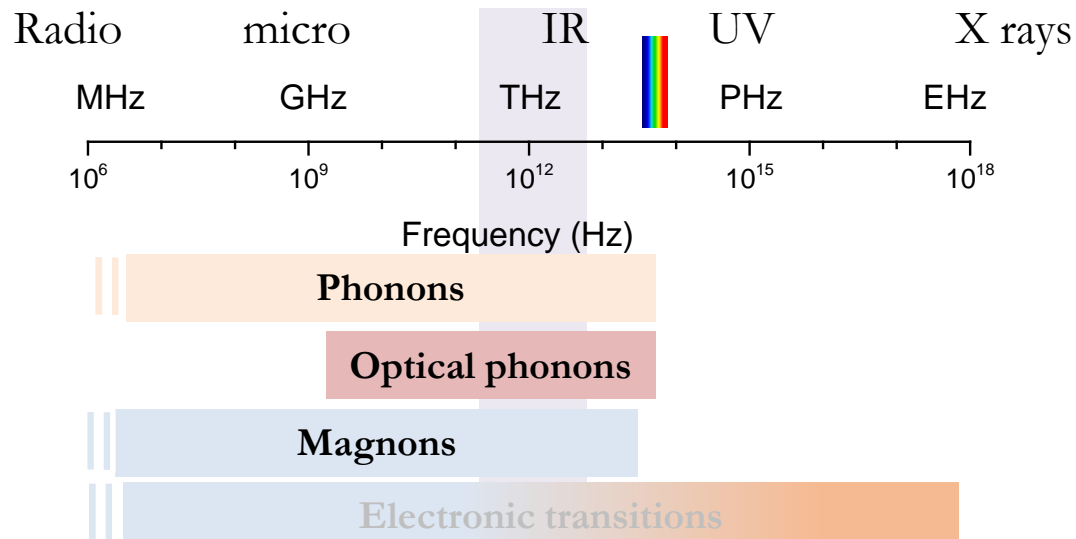
Pressure induced Structural transition at
6.5 GPa :
Softening of mode (4)

THz Spectroscopy under
pressure at AILES @
SOLEIL

M. VERSEILS & PRB 2022

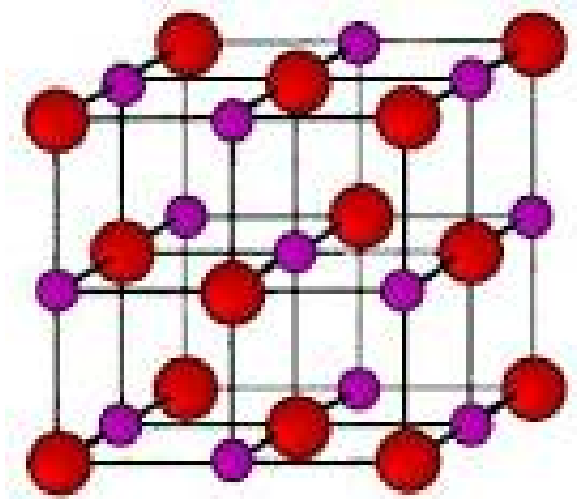
2. THz properties in oxides

1 THz \approx 33 cm⁻¹ \approx 300 μ m \approx 4 meV \approx 50 K



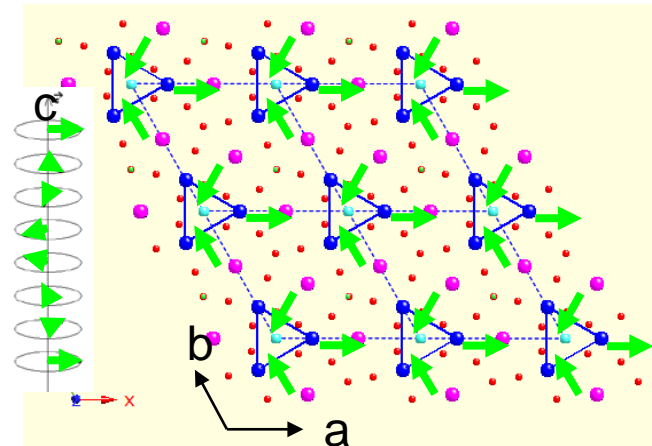
**ORDERED PHASES (ATOMIC /ELECTRIC /
MAGNETIC)
HAVE CHARACTERISTIC EXCITATIONS IN THE THz
RANGE**

2. Periodic structures / associated excitations



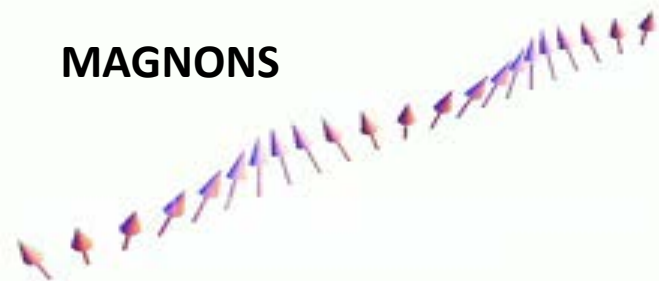
LATTICE VIBRATIONS

PHONONS



SPIN WAVES

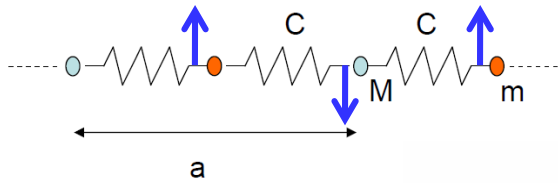
MAGNONS



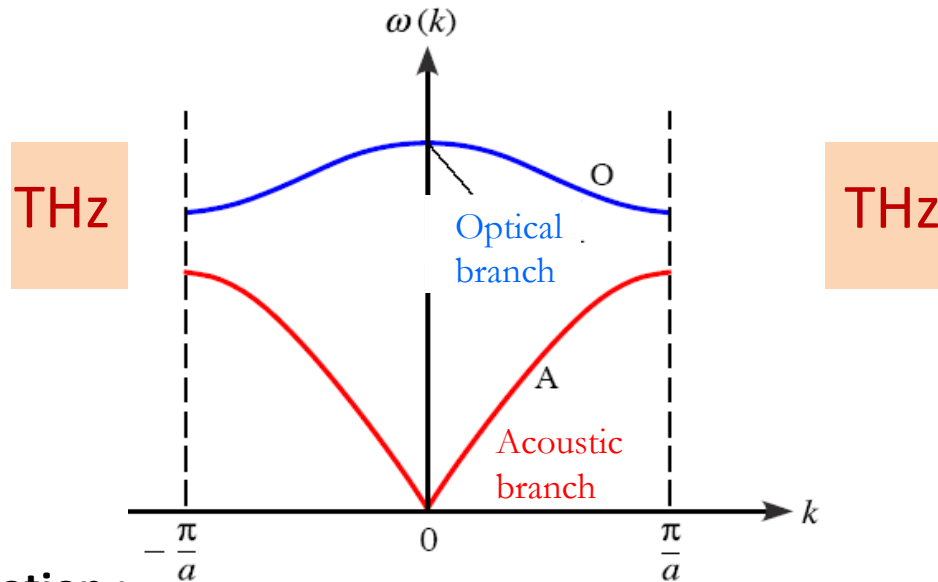
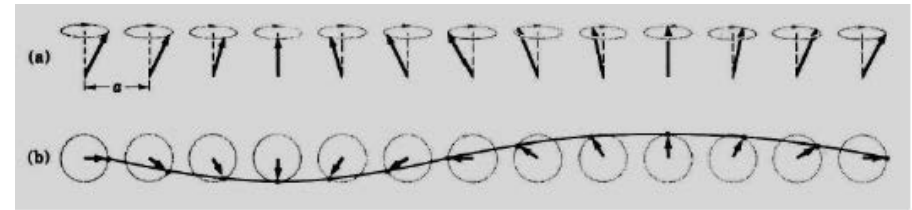
2. Periodic structures / associated excitations

Lattice with two different elements

Phonon



magnon



The equation of motion :

Force

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

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

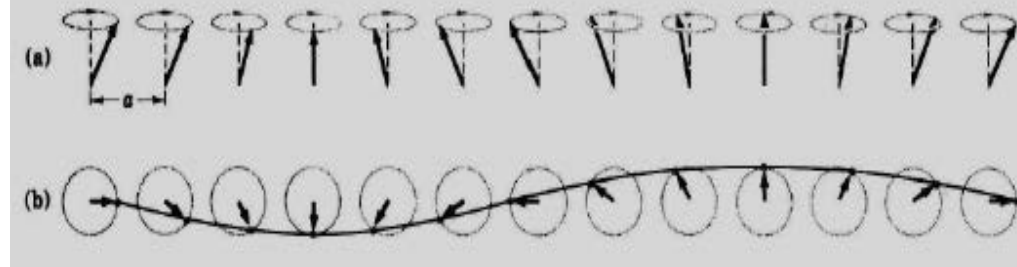
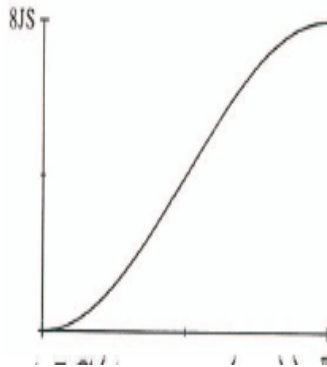
Torque

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

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

2. Spin waves / magons

FM spin waves

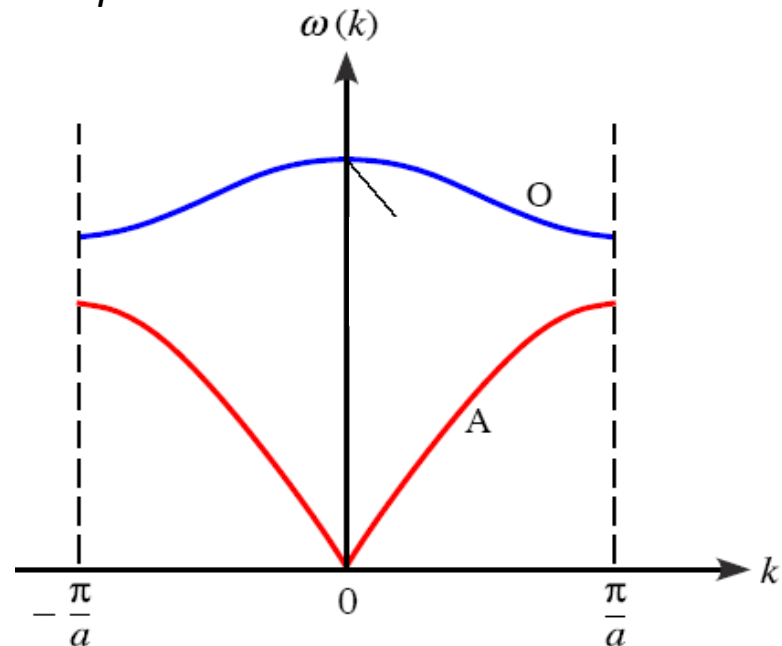


One branch

k^2 dependence at the zone center

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

AF spin waves



several branches,

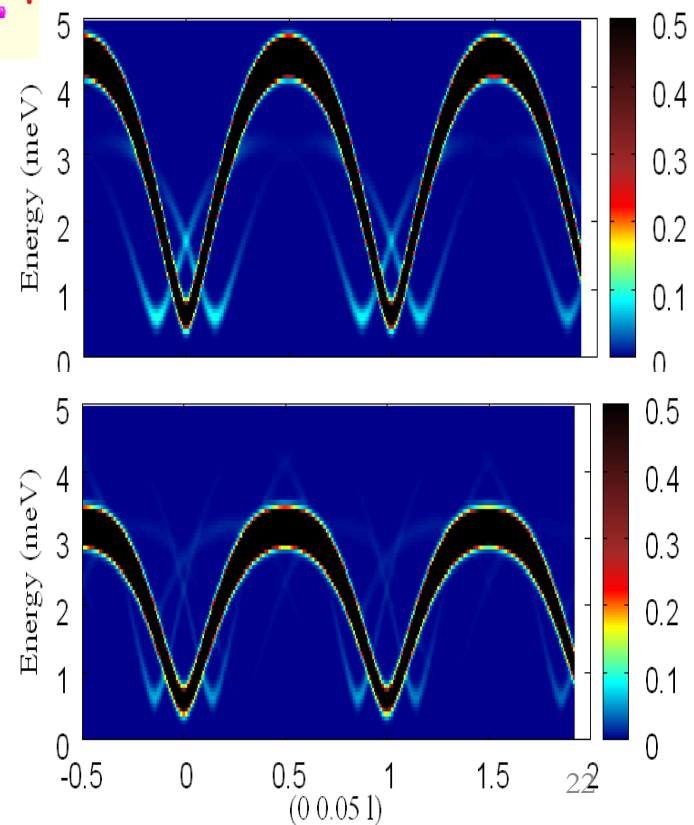
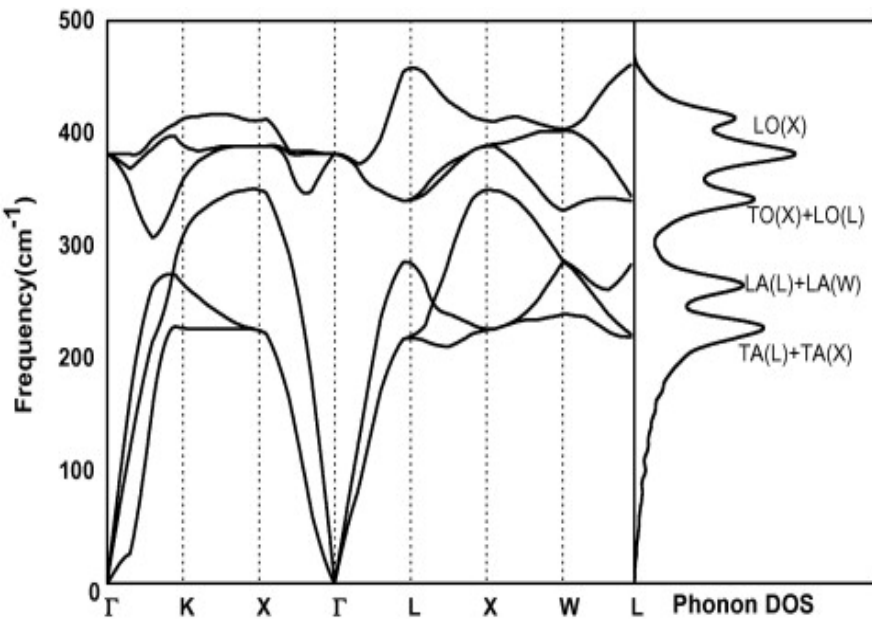
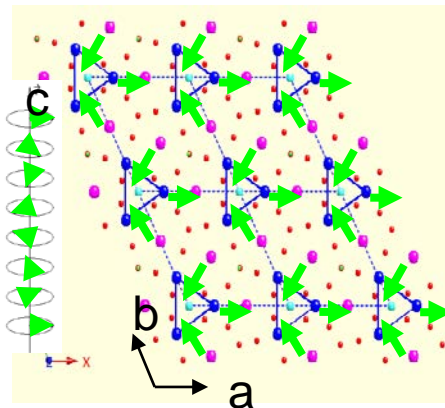
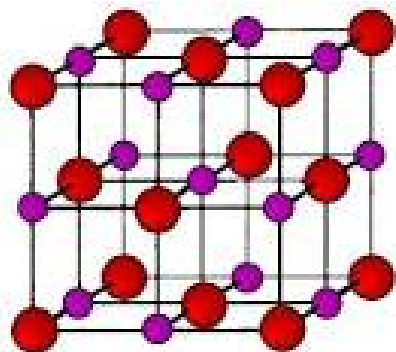
Various k dependence (Cste, k , k^2)

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

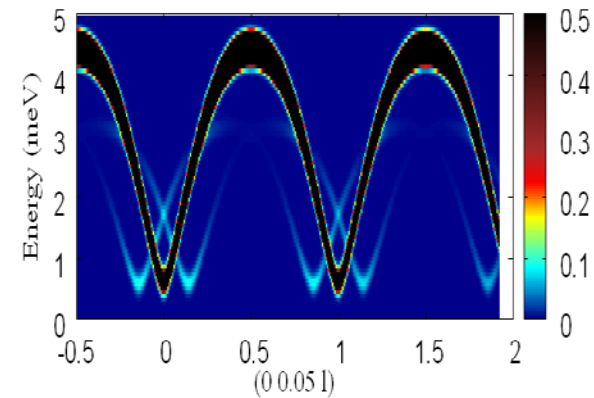
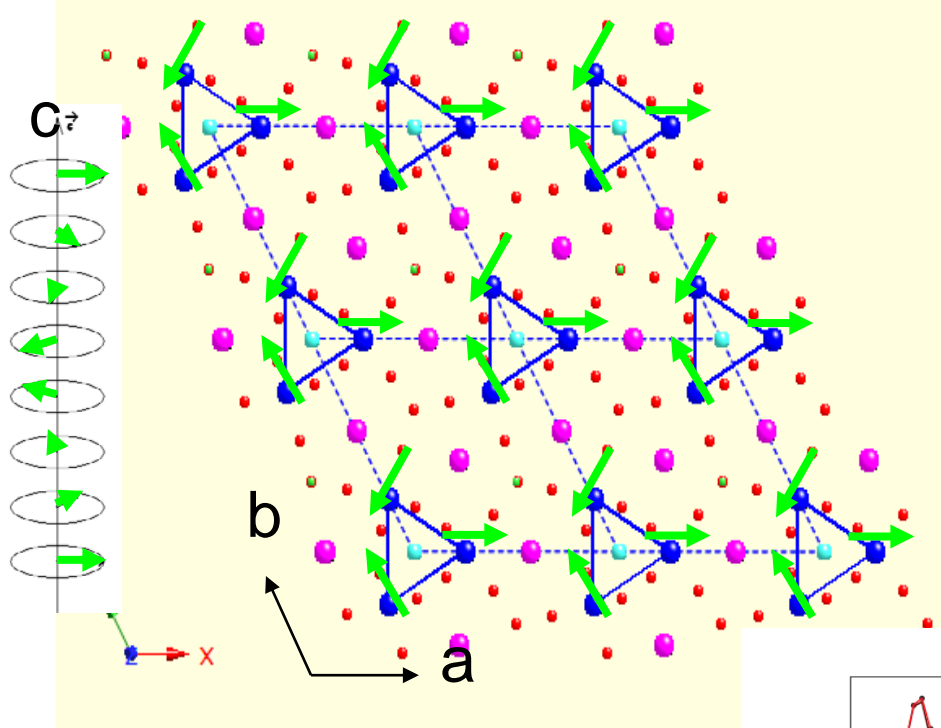
2. Periodic structures / associated excitations

MAGNONS in Ba₃TaFe₃Si₂O₁₄

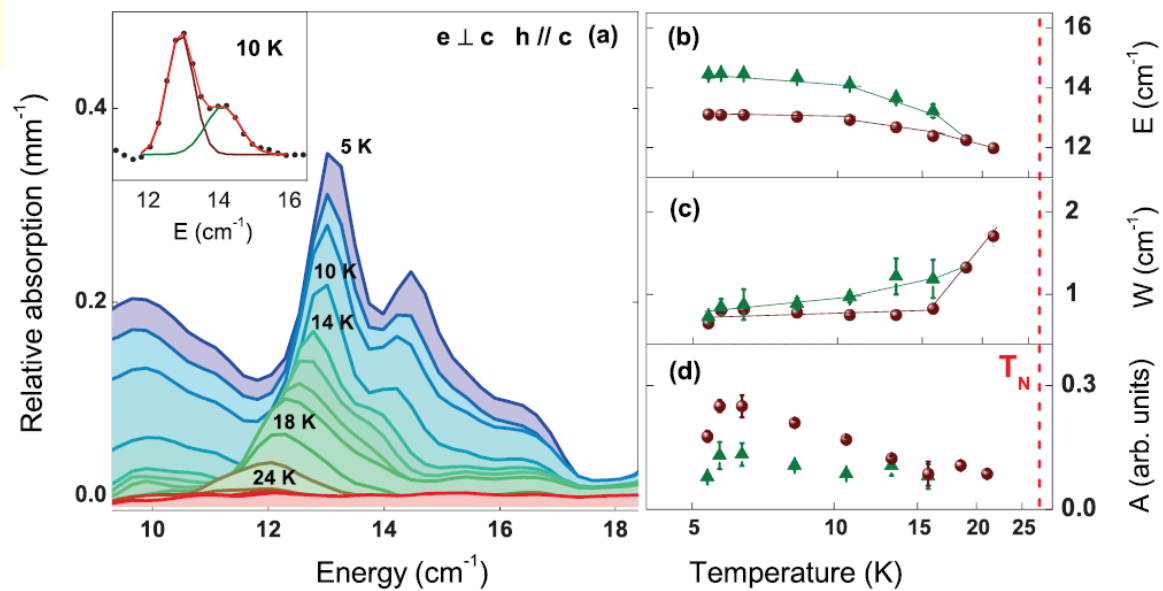
PHONONS in MgN



2. Magnons in Fe langassite



$T_N = 27\text{K}$



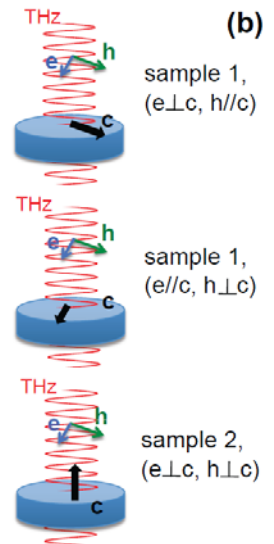
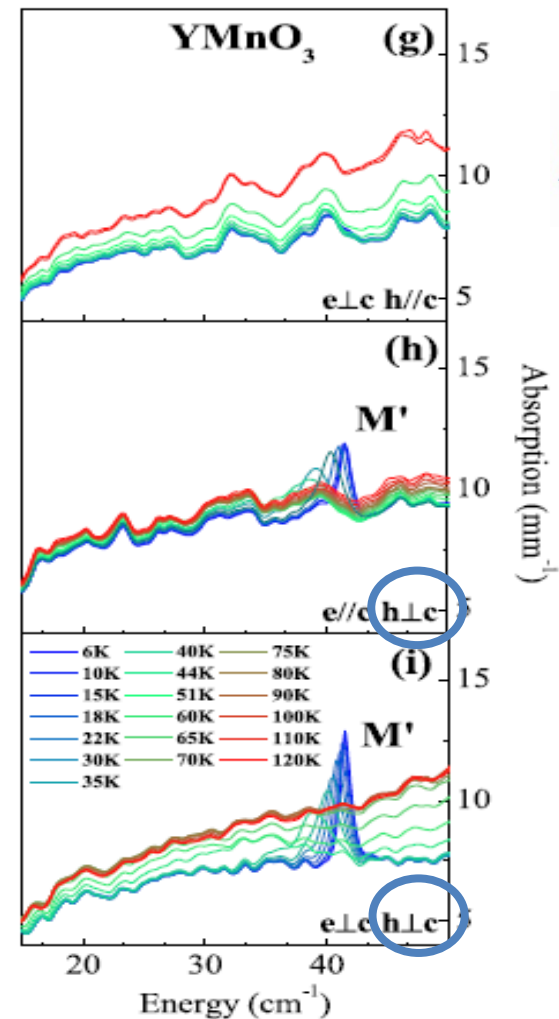
2. Hexagonal manganites : YMnO_3

THz Spectroscopy at AILES @ SOLEIL

L. Chaix et al, PRL 2014

RAMAN

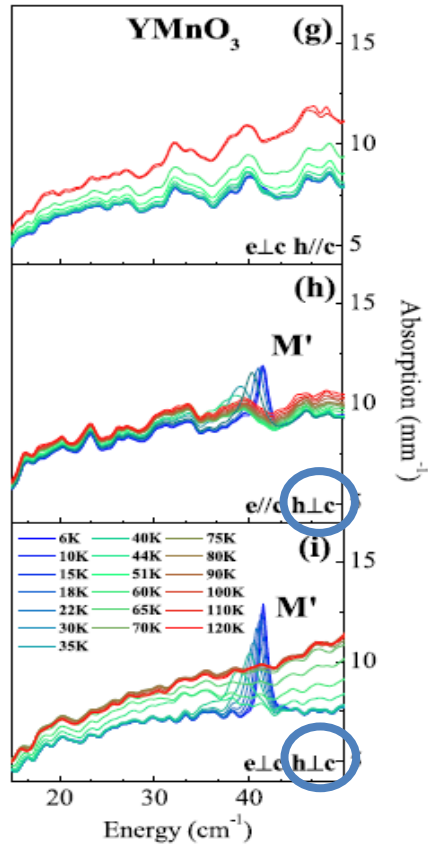
C. Toulouse et al, PRB 2014



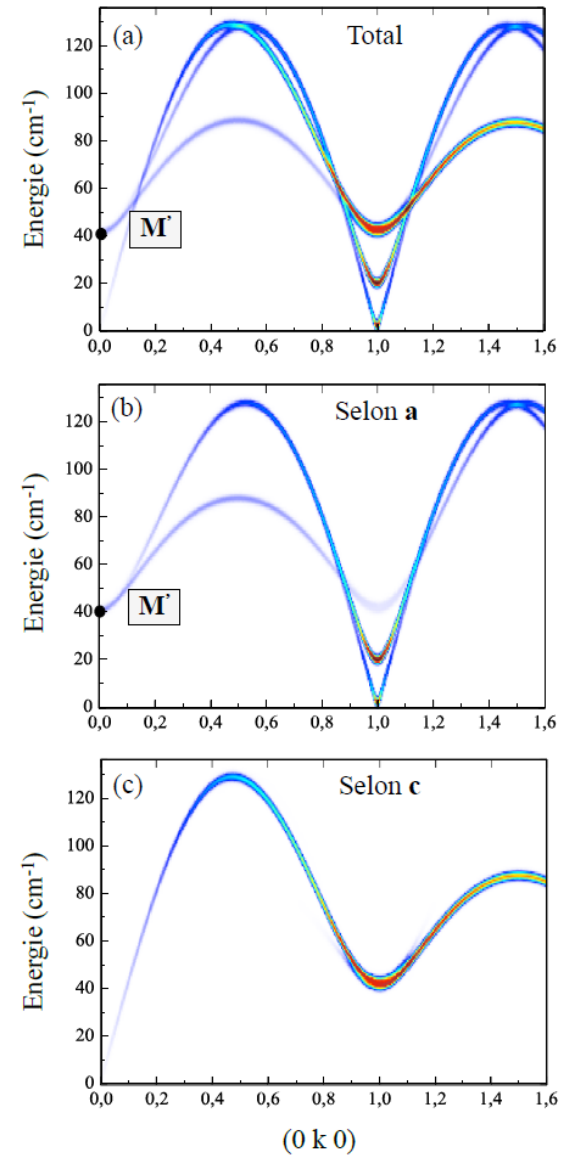
Ferroelectric order at 800 K
(Mn) Magnetic order at 80 K

2. Hexagonal manganites : YMnO_3

experiments



Linear spin wave calculations

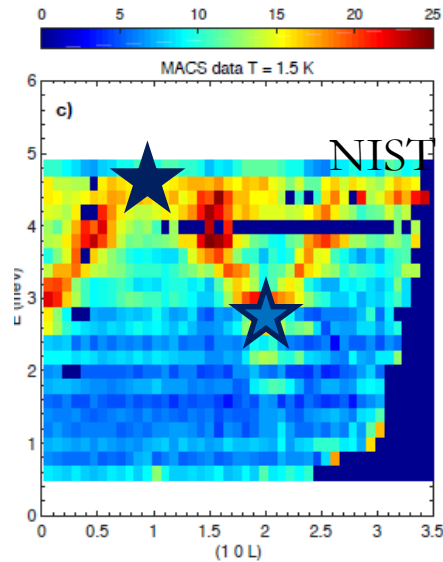


2. Phonons / magnons in MOF

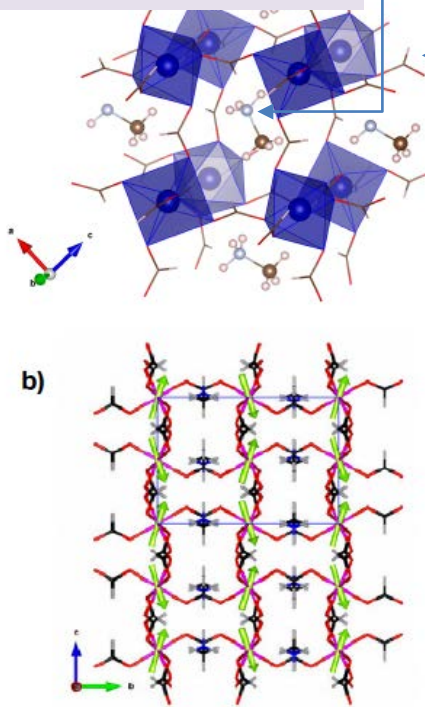
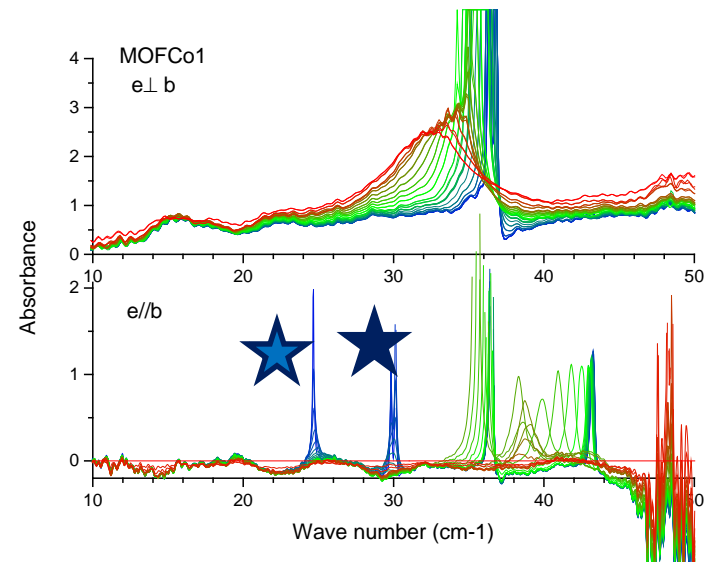
L. Ding & al Phys
Rev Mat 2023

$\text{MAGCo}(\text{COOH})_3$ (MA = CH_3NH_3)

Neutron measurements



THz measurements



magnetic transition

at 15K

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

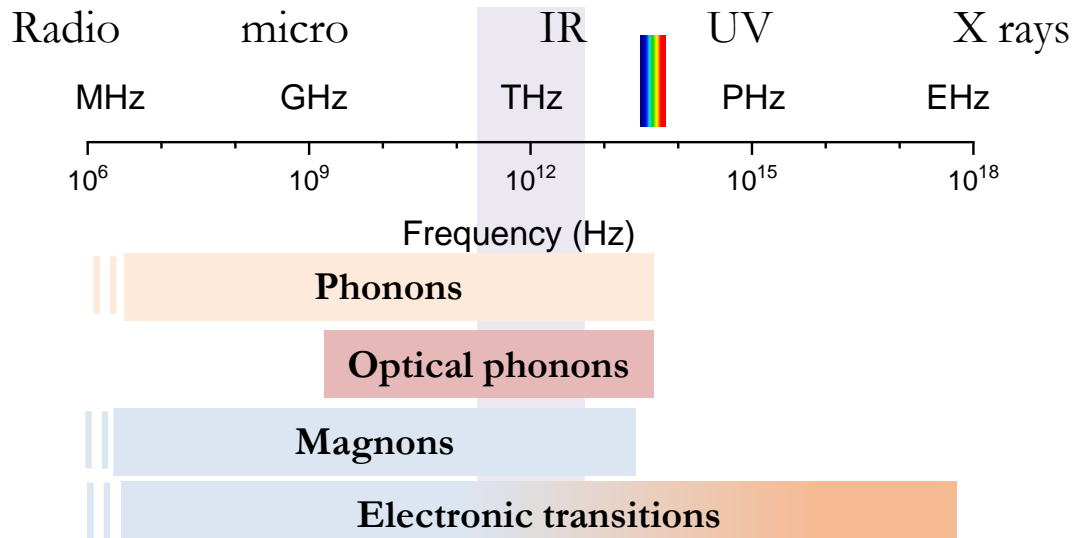
Magnons at at 24 cm^{-1} and 36 cm^{-1} associated to Co^{2+}
order at 15K

+ phonons associated to Pnma/P21/n structural
transition at 90 K

Magnons+ phonons as a signature of ME effects

3. THz properties in oxides

$$1 \text{ THz} \approx 33 \text{ cm}^{-1} \approx 300 \text{ } \mu\text{m} \approx 4 \text{ meV} \approx 50 \text{ K}$$



SINGLE ATOMS-IONS HAVE CHARACTERISTIC EXCITATIONS IN THE THz RANGE

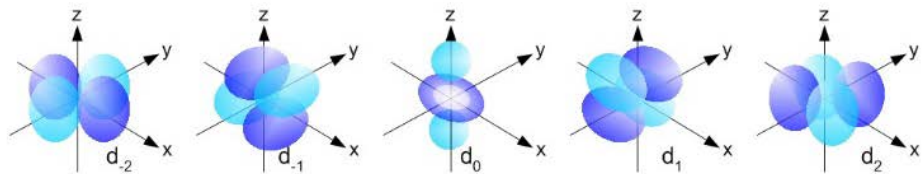
3. Electronic transitions in magnetic elements

Periodic Table of the Elements

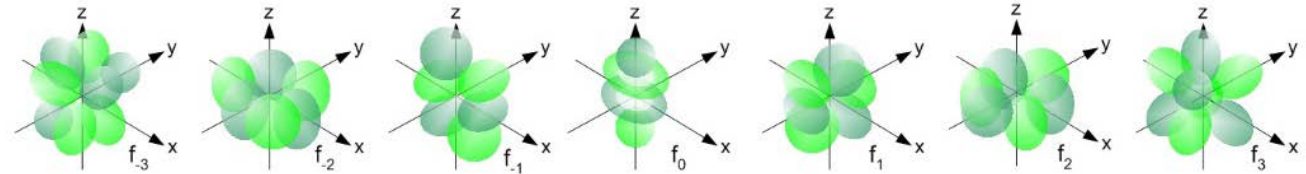
1 IA 1A 1 H Hydrogen 1.008	2 IIA 2A 4 Be Beryllium 9.012											13 IIIA 3A 5 B Boron 10.811	14 IVA 4A 6 C Carbon 12.011	15 VA 5A 7 N Nitrogen 14.007	16 VIA 6A 8 O Oxygen 15.999	17 VIIA 7A 9 F Fluorine 18.998	18 VIIIA 8A 10 Ne Neon 20.180
3 Li Lithium 6.941	4 Be Beryllium 9.012	3 IIIB 3B 21 Sc Scandium 44.956	4 IVB 4B 22 Ti Titanium 47.88	5 VB 5B 23 V Vanadium 50.942	6 VIB 6B 24 Cr Chromium 51.996	7 VIIB 7B 25 Mn Manganese 54.938	8 VIII 8 26 Fe Iron 55.845	9 VIII 8 27 Co Cobalt 58.933	10 VIII 8 28 Ni Nickel 58.693	11 IB 1B 29 Cu Copper 63.546	12 IIB 2B 30 Zn Zinc 65.38	13 IIIB 3A 31 Al Aluminum 26.982	14 IIIA 4A 32 Si Silicon 28.086	15 IIIA 5A 33 P Phosphorus 30.974	16 IIIA 6A 34 S Sulfur 32.06	17 IIIA 7A 35 Cl Chlorine 35.453	18 IIIA 8A 36 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.738
37 Rb Rubidium 84.464	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.905	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.222	78 Pt Platinum 195.084	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.384	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium 209	85 At Astatine 210	86 Rn Radon 222
87 Fr Francium 223	88 Ra Radium 226	89-103 Actinide Series	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 263	107 Bh Bohrium 264	108 Hs Hassium 265	109 Mt Meitnerium 266	110 Ds Darmstadtium 269	111 Rg Roentgenium 272	112 Cn Copernicium 285	113 Nh Nihonium 284	114 Fl Flerovium 289	115 Uup Ununpentium 288	116 Lv Livermorium 293	117 Uus Ununseptium 289	118 Uuo Ununoctium 294

Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.12	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium 252.083	100 Fm Fermium 257.095	101 Md Mendelevium 258.10	102 No Nobelium 259.10	103 Lr Lawrencium 262

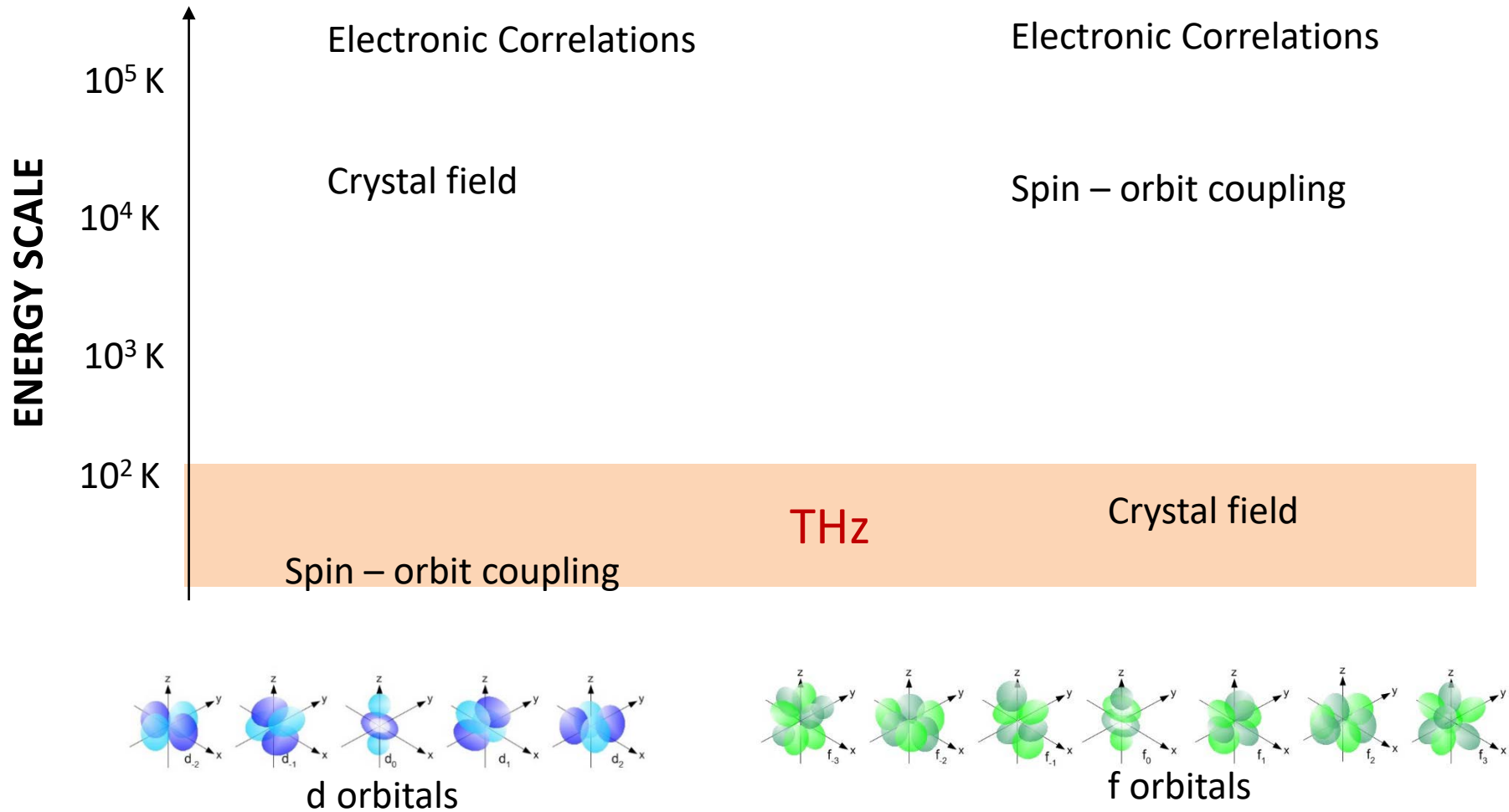
d orbitals



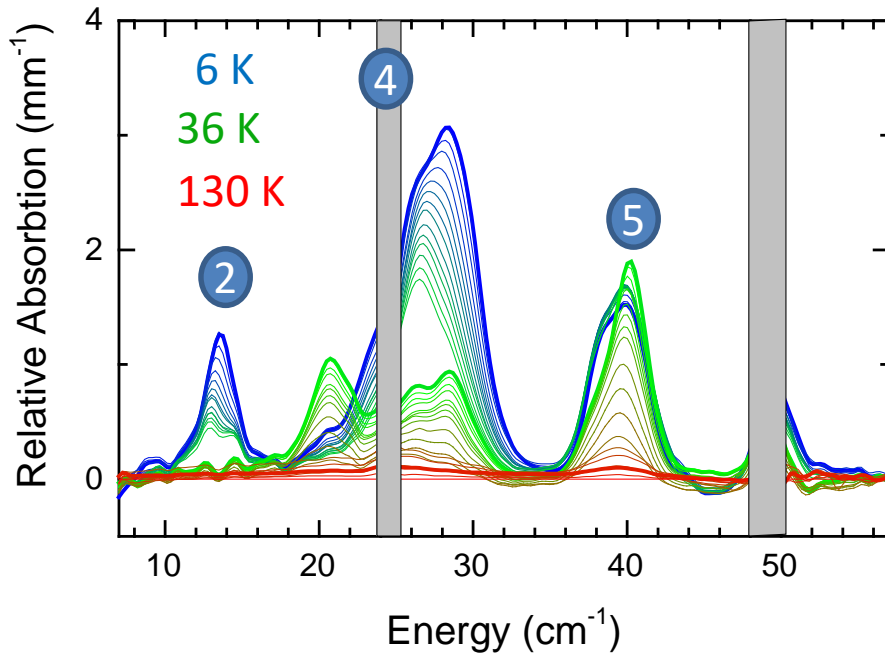
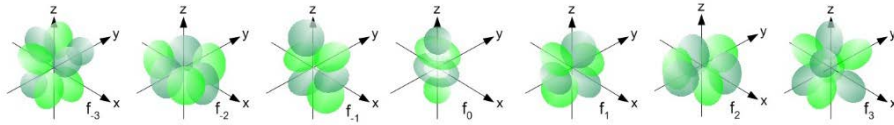
f orbitals



3. Electronic transitions in magnetic elements

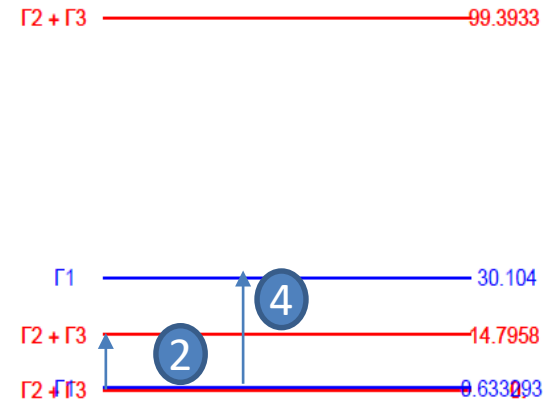


3. Crystal field transition in rare earth elements

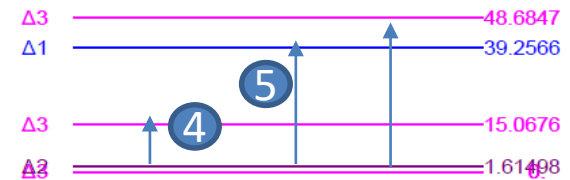


Ho³⁺ in h-HoMnO₃

4f¹⁰ (S = 2 L = 6 J = 8 in the ground state) in C₃ point symmetry (site 4a)



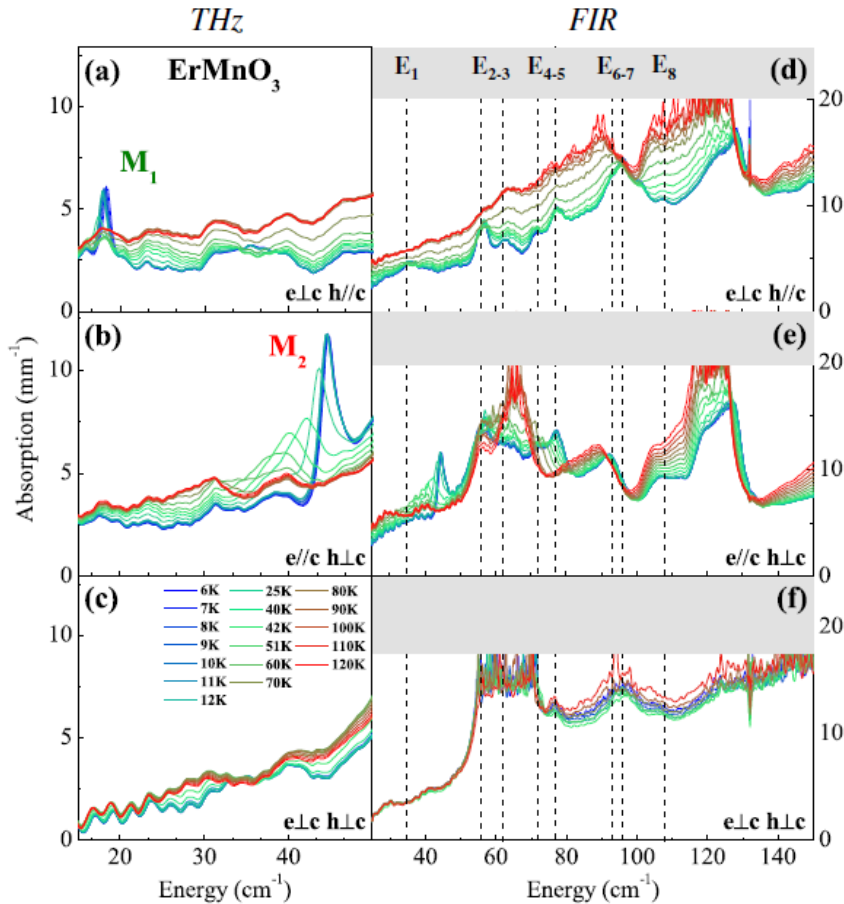
in C_{3v} point symmetry (site 2a)



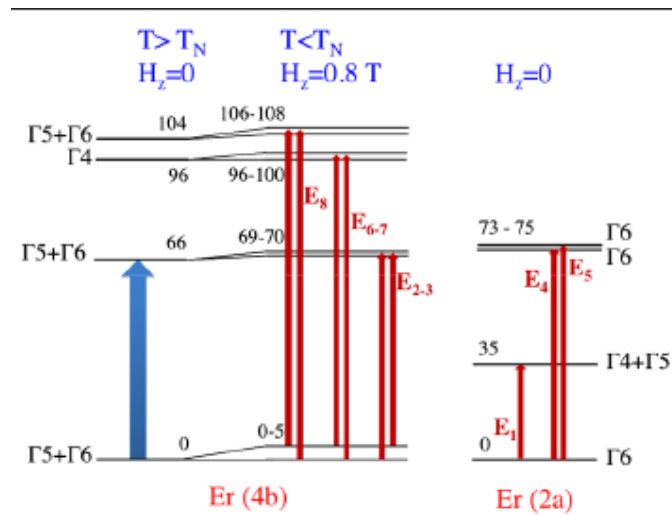
3. Crystal field transition in rare earth elements

h-ErMnO₃

THz measurements



Er³⁺ Crystal field excitations



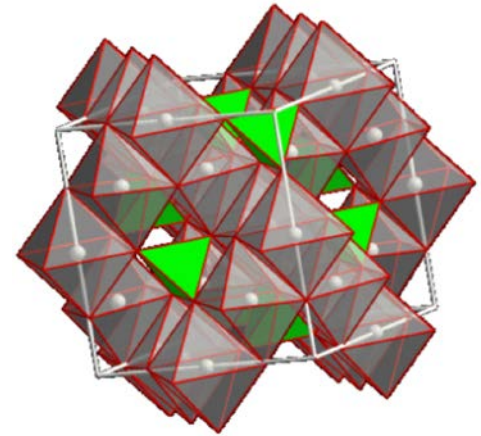
CFE / magnon coupling

3. Crystal field transition in 3 d elements

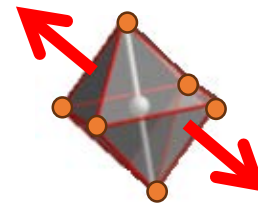
Example: Fe^{2+} in Spinel $GeFe_2O_4$

General spinel formula: AB_2X_4

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

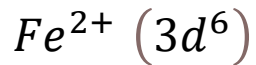


Fe^{2+} in octahedral crystal field + trigonal distortion



3. Electronic scheme of Fe²⁺

Free ion:



⁵D₄

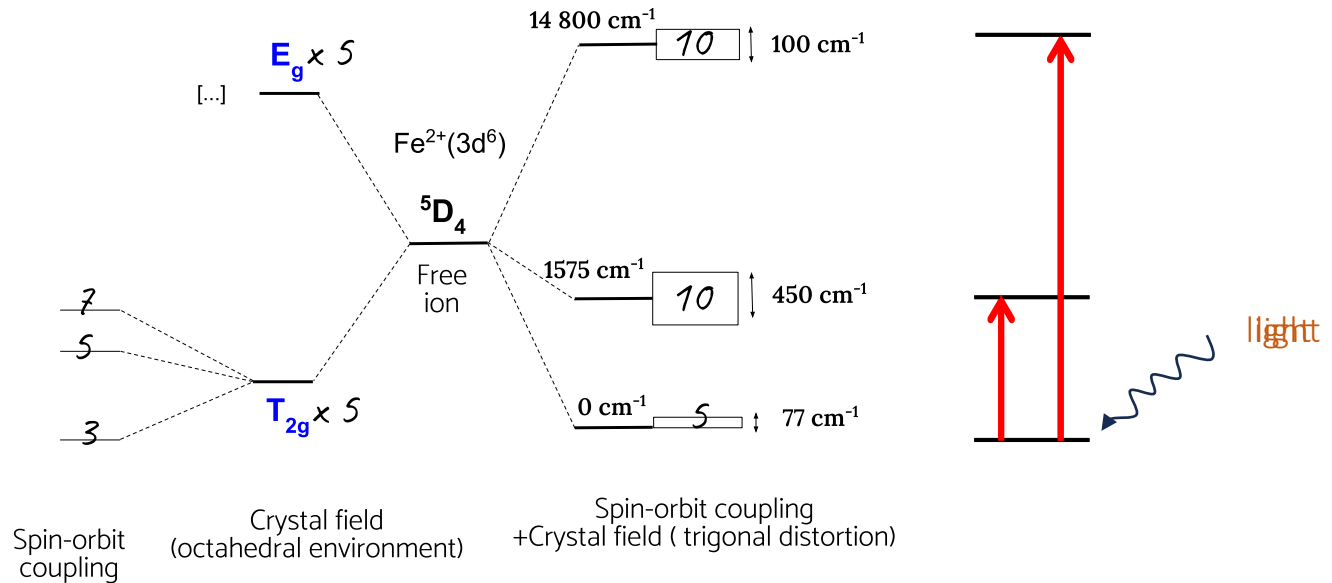
S= 2

L= 2

J= 4

Fe²⁺ in octahedral crystal field

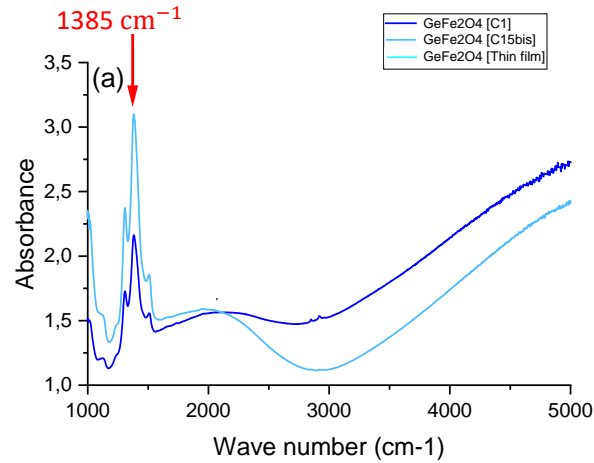
Fe²⁺ in trigonal crystalfield



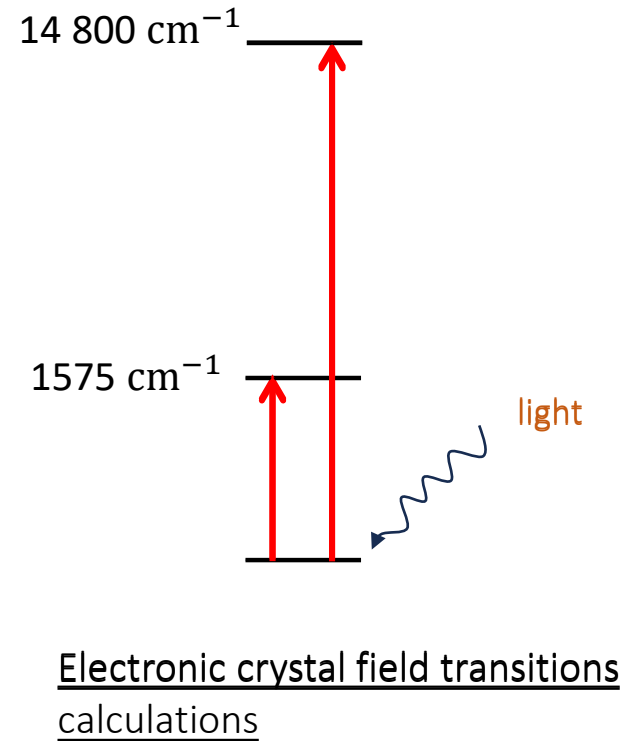
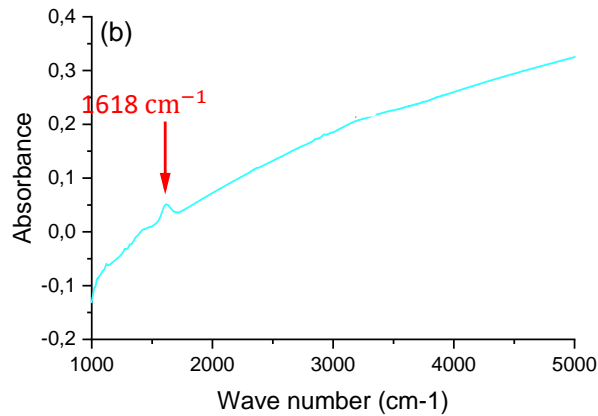
Point charge model for GeFe₂O₄

3. Fe 2+ Crystal field transitions in GeFe2O4

Crystals
300 μm
<1mm²

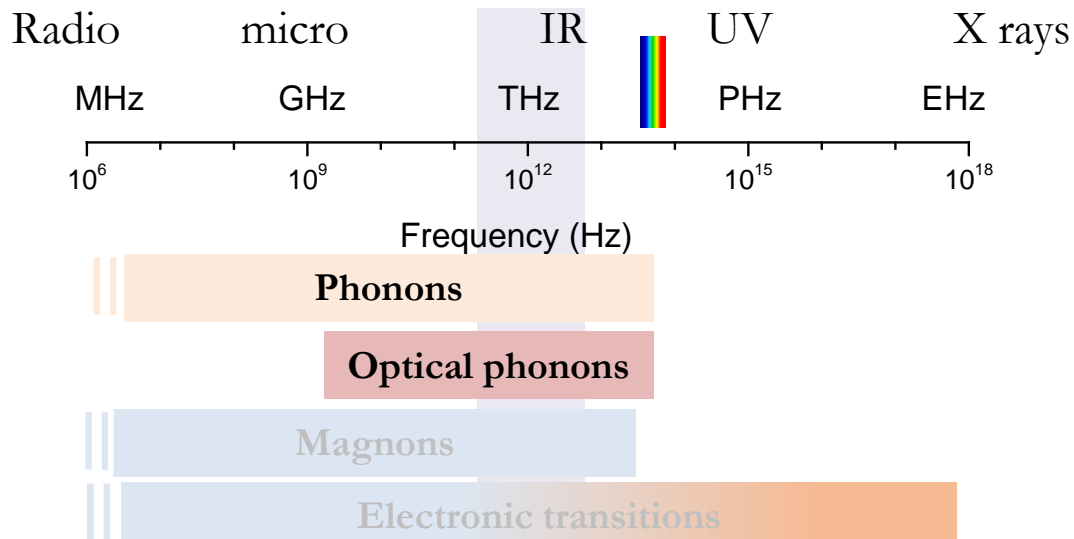


Thin film
20 nm /MgO



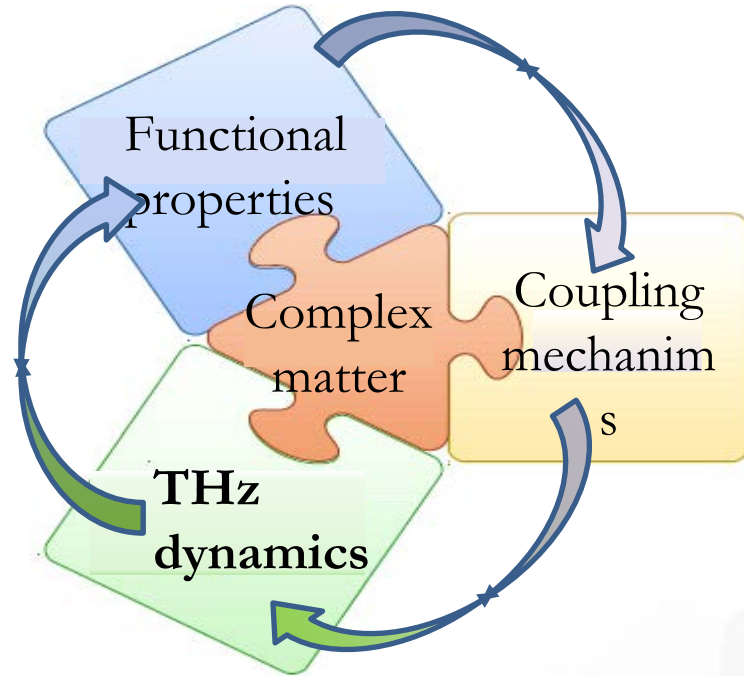
3. THz properties in oxides

$$1 \text{ THz} \approx 33 \text{ cm}^{-1} \approx 300 \text{ } \mu\text{m} \approx 4 \text{ meV} \approx 50 \text{ K}$$



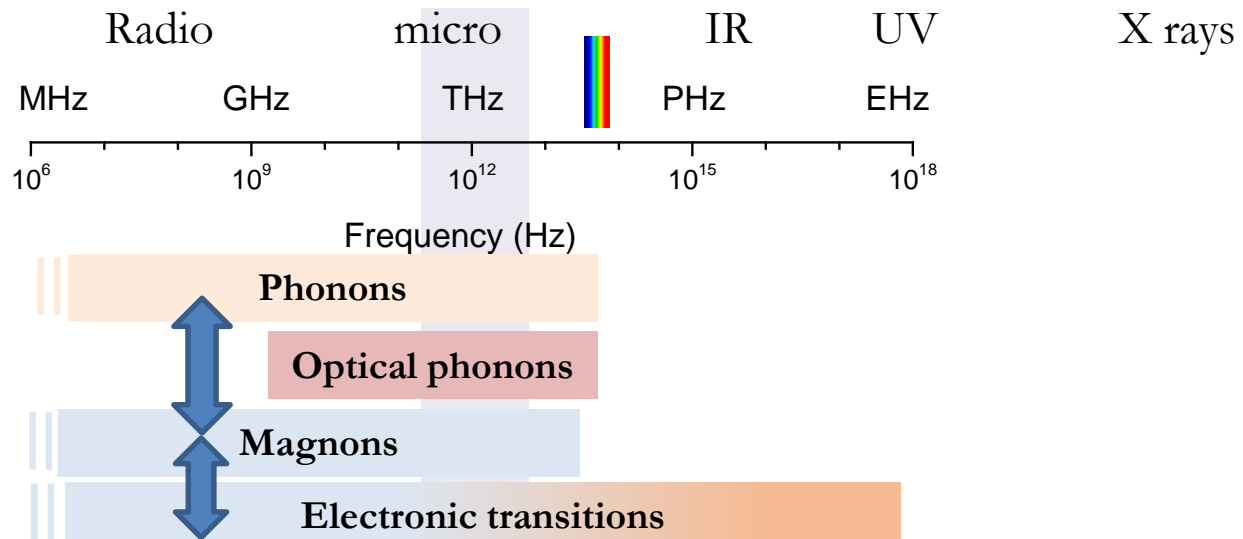
SINGLE ATOMS (MAGNETIC)
HAVE CHARACTERISTIC EXCITATIONS IN THE THz RANGE

4. THz PROPERTIES OF COMPLEX MAGNETIC PHASES



4. THz properties in oxides

$$1 \text{ THz} \approx 33 \text{ cm}^{-1} \approx 300 \mu\text{m} \approx 4 \text{ meV} \approx 50 \text{ K}$$



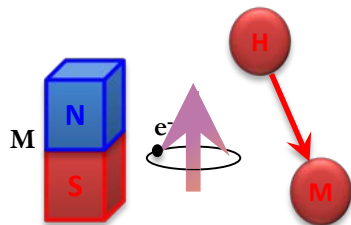
SINGLE ATOMS (MAGNETIC)
AND ORDERED PHASES (ATOMIC /ELECTRIC /
MAGNETIC)
HAVE CHARACTERISTIC EXCITATIONS IN THE THz
RANGE

HYBRID EXCITATIONS : ELECTROMAGNONS

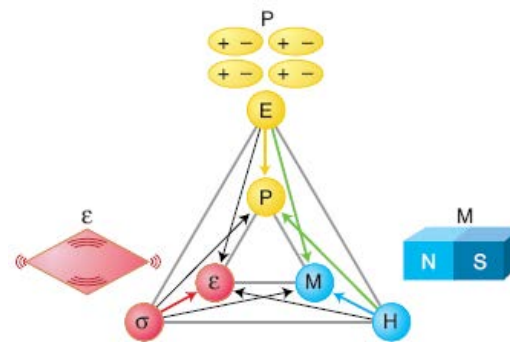
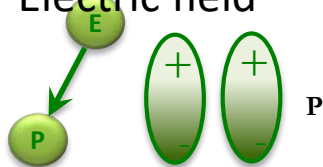
4. Example : Multiferroics

Static / dynamical properties

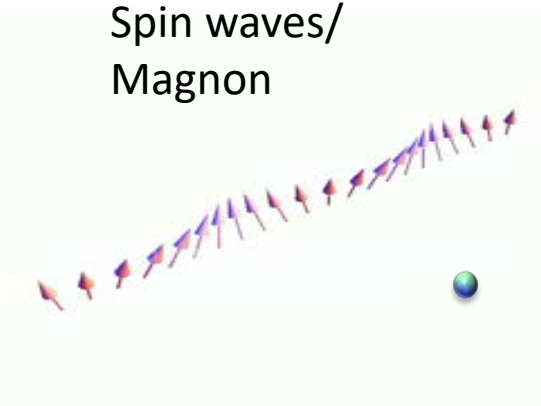
Magnetic moment /
magnetic field



Dipolar electric moment /
Electric field



Spin waves/
Magnon



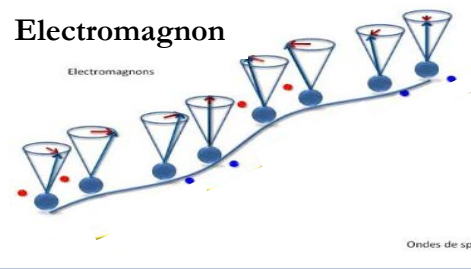
Lattice vibration /
Phonon



Magneto-electric
coupling

Electromagnon

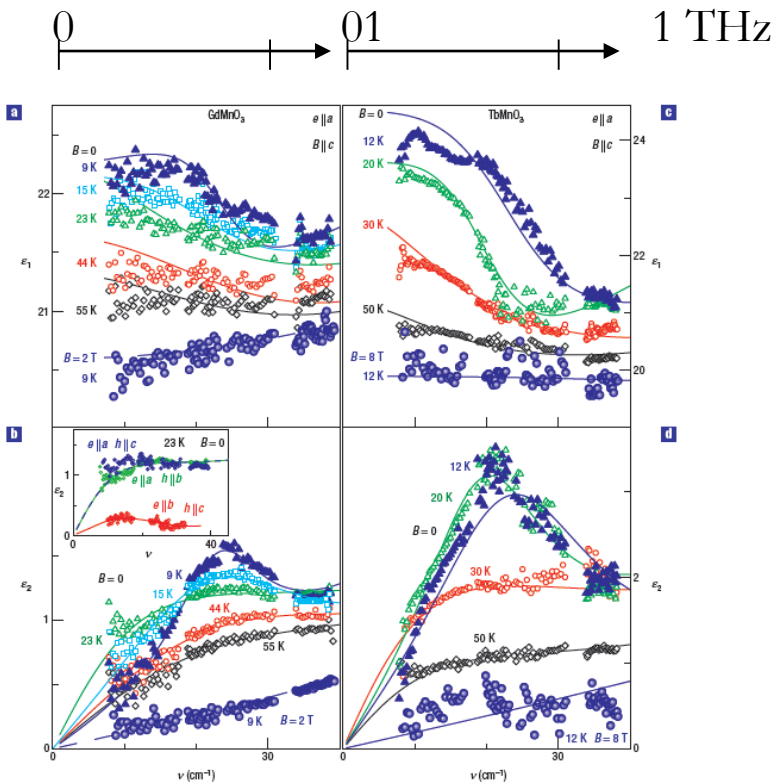
Electromagnons



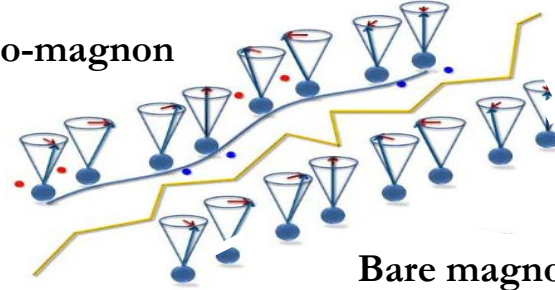
4. Electro-magnons in multiferroics

A. PIMENOV et, Nature Physics 2006
Orthorhombic RMnO_3

Magnon dressed with electric charges thanks to magneto-electric coupling



Electro-magnon



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

Electronic spectrometer

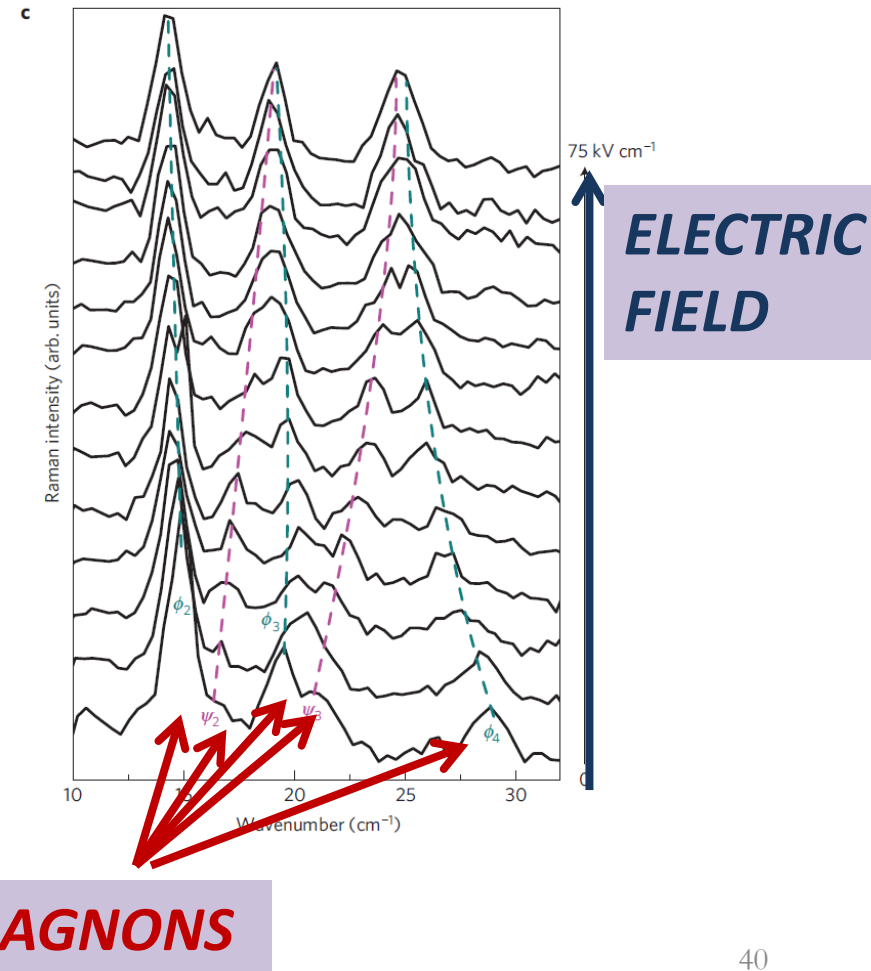
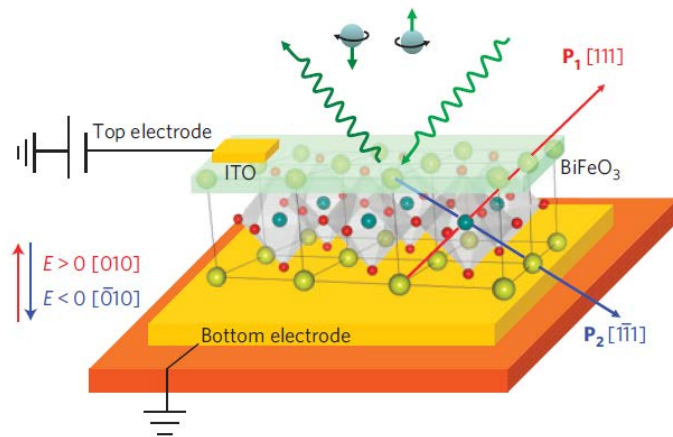
4. Electro-magnons in multiferroics

THz Applications :

- Transport and manipulation of information (MAGNONICS + ...)

Electric-field control of spin waves at room temperature in multiferroic BiFeO₃

P. Rovillain et al, Nature Materials 2010

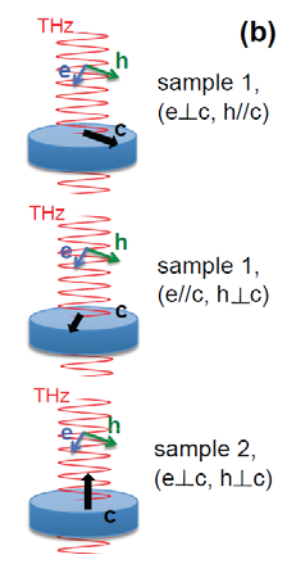
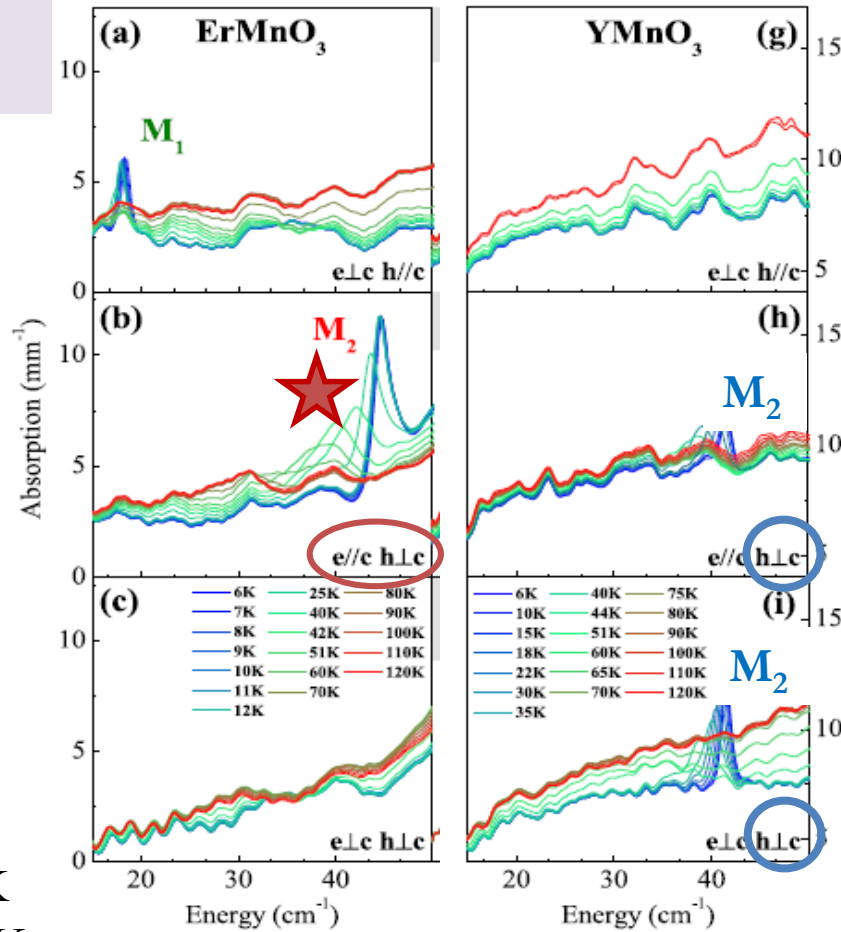


4. Electro-magnons

Other mechanisms?

4. Hexagonal manganites : ErMnO_3 / YMnO_3

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

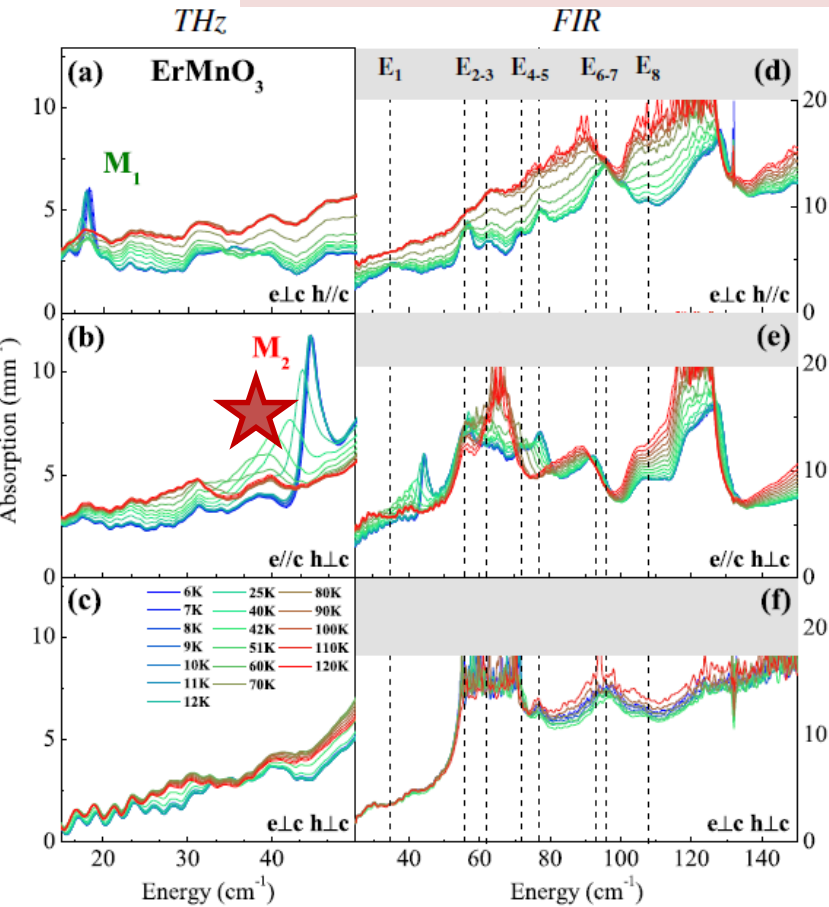


↑
c

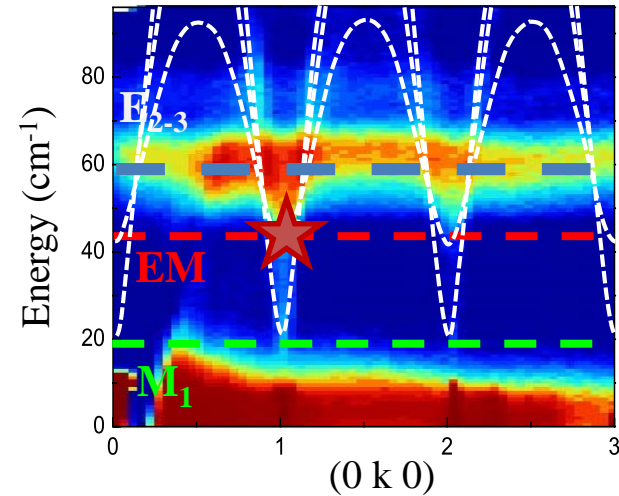
Ferroelectric order at 800 K
 (Mn) Magnetic order at 80 K

4. Hexagonal manganites : ErMnO_3

THz measurements



Neutron measurements

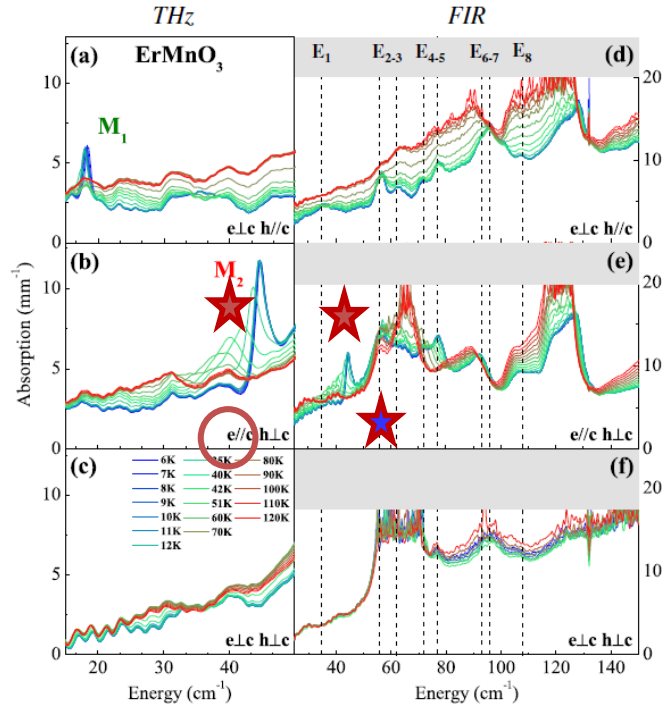


Mn MAGNON

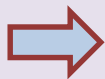
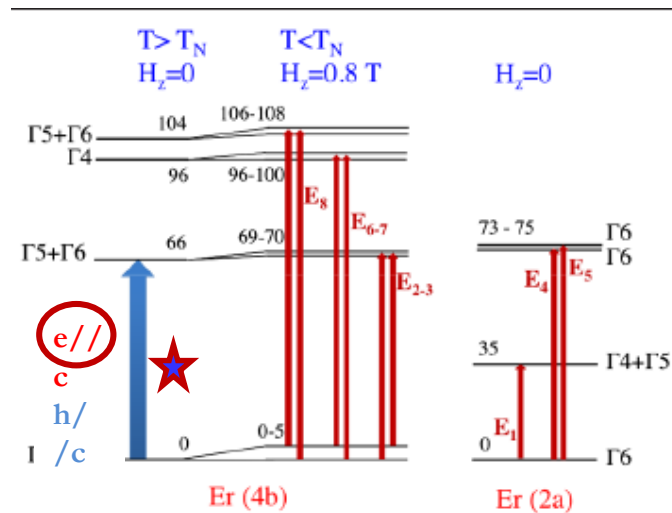
+ Er^{3+} CRYSTAL FIELD EXCITATION at 60 cm⁻¹

4. Hexagonal manganites : ErMnO_3

THz measurements

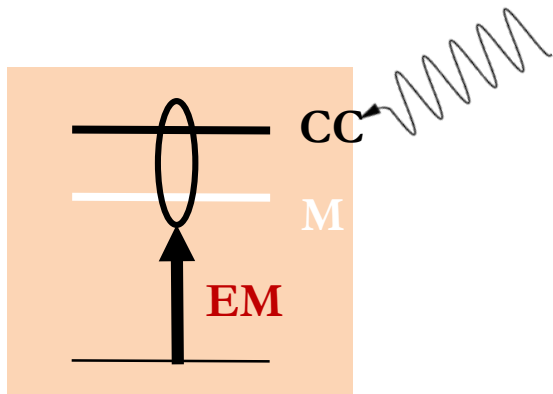
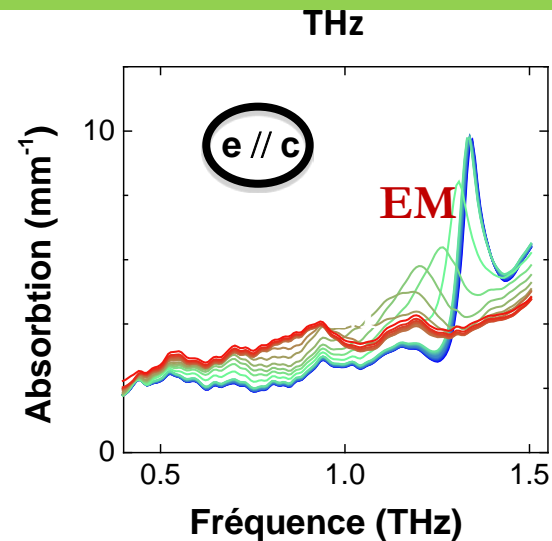
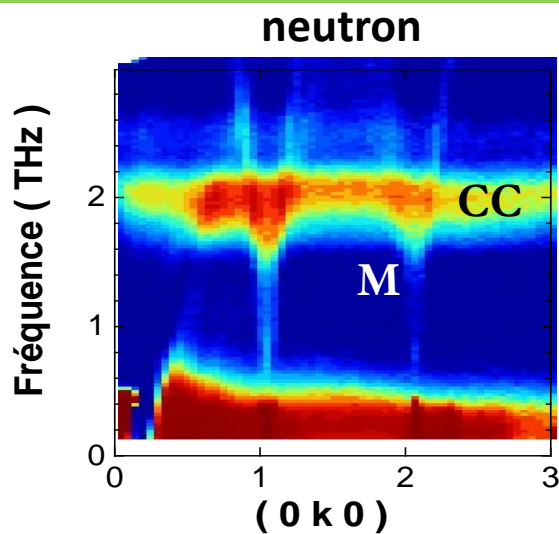
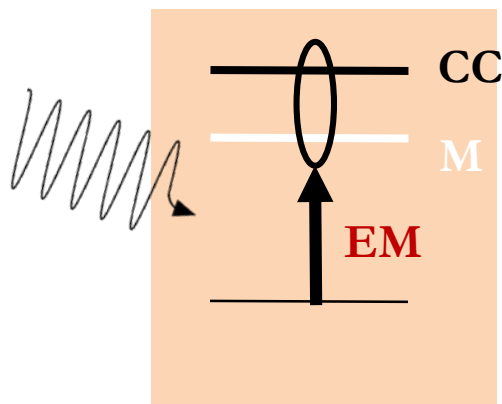


Er Crystal field excitations



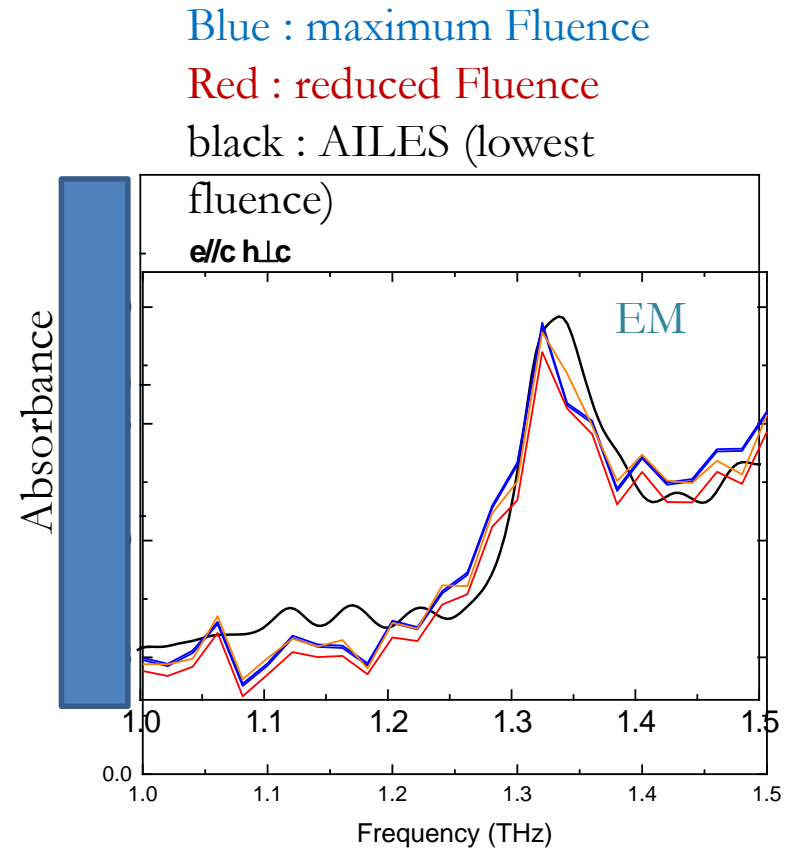
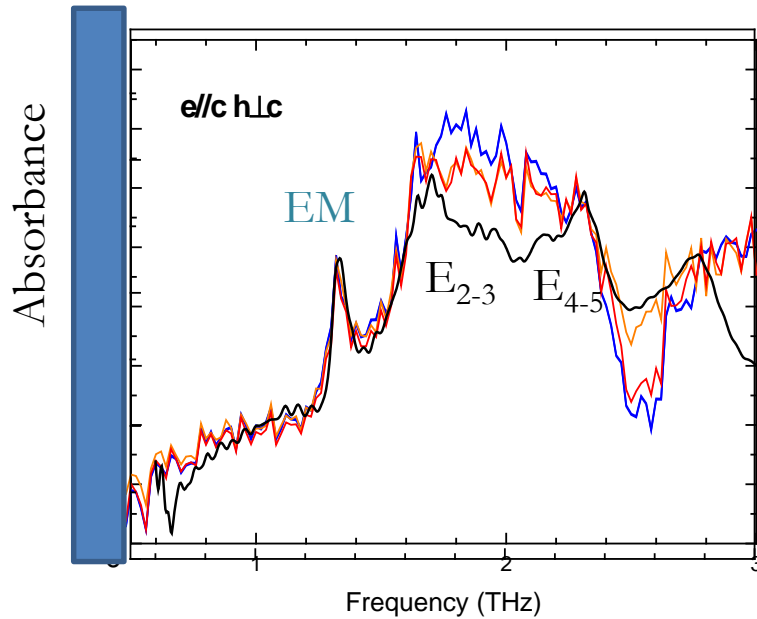
**Er/Mn dynamical coupling : electroactive magnon
Mn MAGNON / Er CRYSTAL FIELD HYBRIDE EXCITATION**

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



TERAFERMI @ Trieste

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

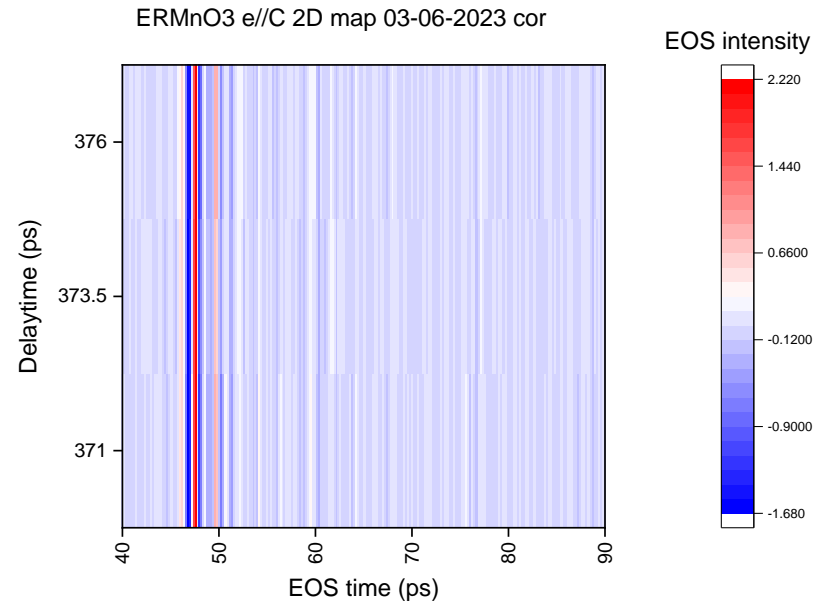
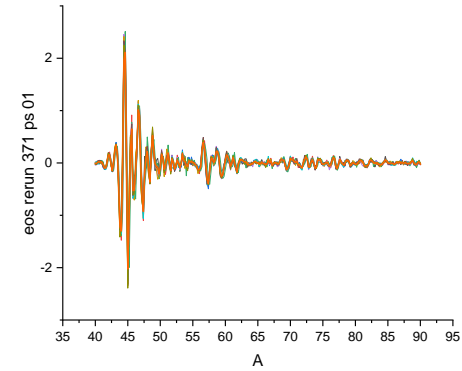
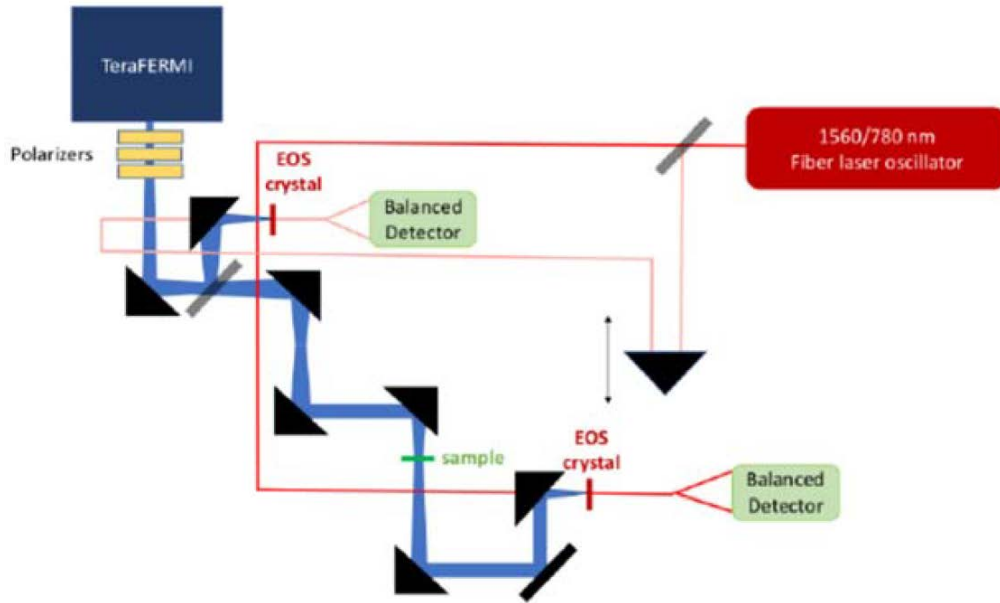


Conclusion :

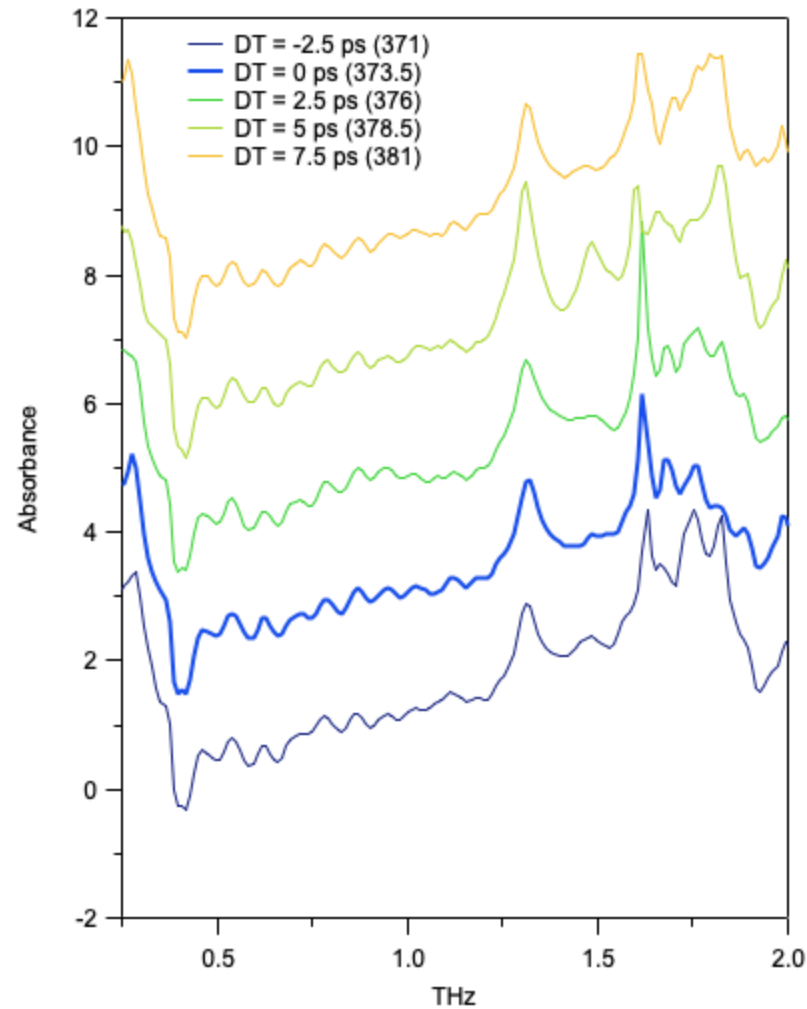
There is clearly a dependence on fluence for E_{2-3} .

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

4. Time domain measurements @TeraFERMI

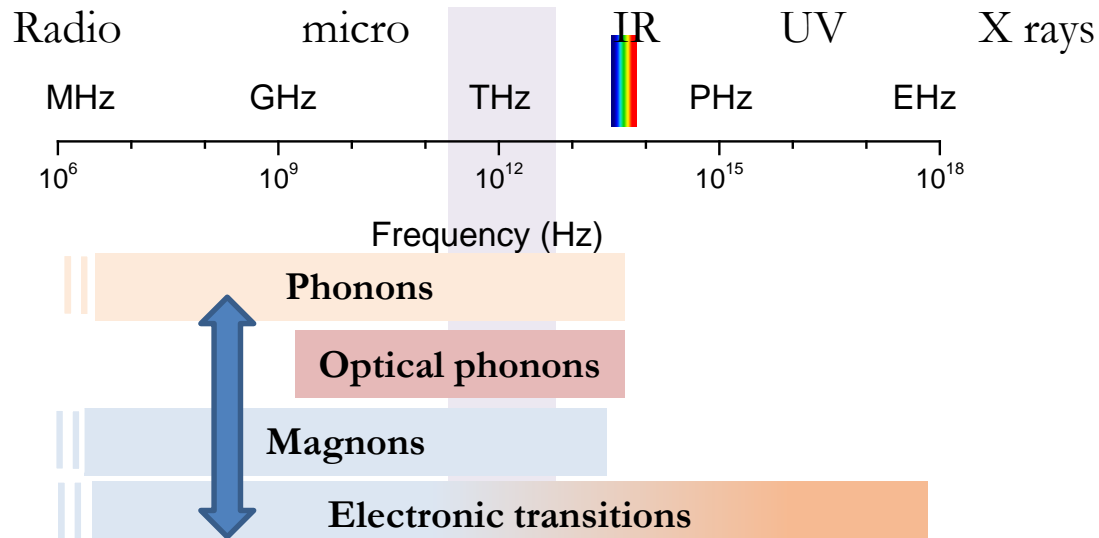


4. Hexagonal manganites : « electro-magnon » in ErMnO_3



4. THz properties in oxides

$$1 \text{ THz} \approx 33 \text{ cm}^{-1} \approx 300 \text{ } \mu\text{m} \approx 4 \text{ meV} \approx 50 \text{ K}$$

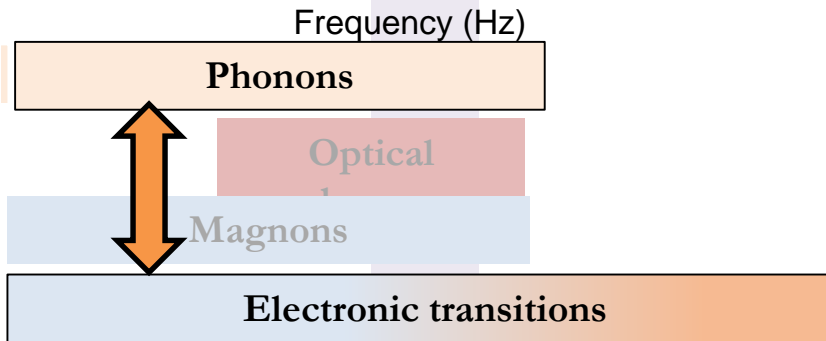
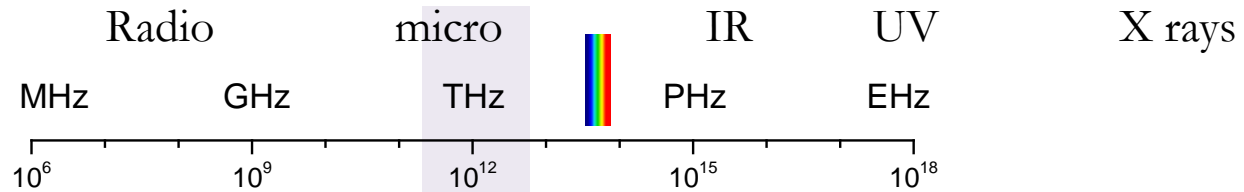


SINGLE ATOMS (MAGNETIC / ELECTRIC)
AND ORDERED PHASES (ATOMIC / ELECTRIC /
MAGNETIC)
HAVE CHARACTERISTIC EXCITATIONS IN THE THz
RANGE

HYBRID EXCITATIONS : VIBRONS

4. THz properties in condensed matter probed with EM waves

$$1 \text{ THz} \approx 33 \text{ cm}^{-1} \approx 300 \mu\text{m} \approx 4 \text{ meV} \approx 50 \text{ K}$$



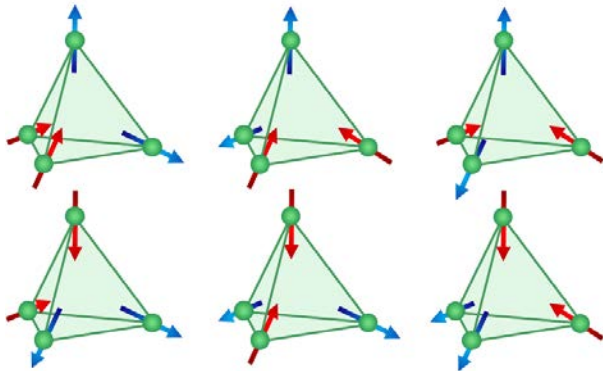
**SIGNATURE OF A COMPLEX MAGNETIC PHASE :
the quantum spin ice $\text{Tb}_2\text{Ti}_2\text{O}_7$**

E. Constable & al PRB (R) 2017

K. Amelin, Y. Alexanian & al PRB 2020

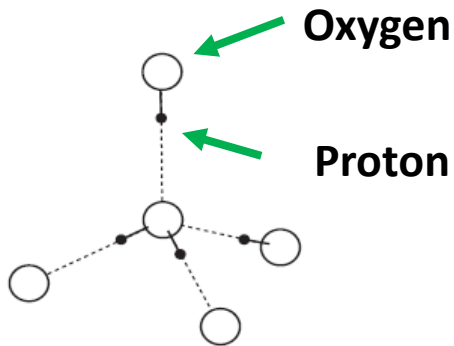
Y. Alexanian & al PRB 2023

4. Spin ices

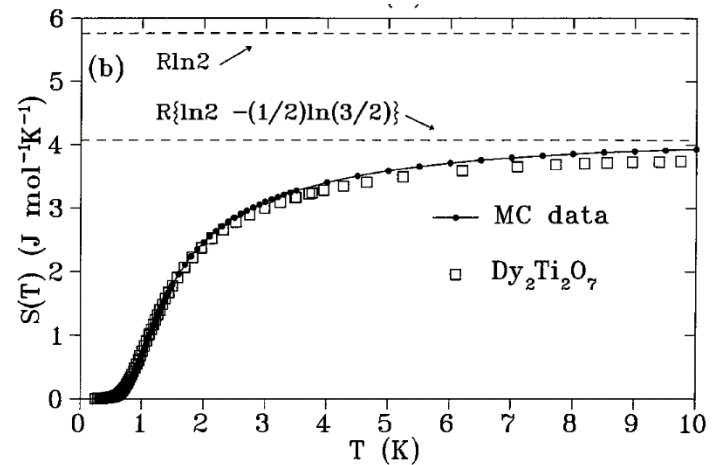


« 2 in – 2 out »
« ice rule »

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



Extensive degeneracy
Finite entropy

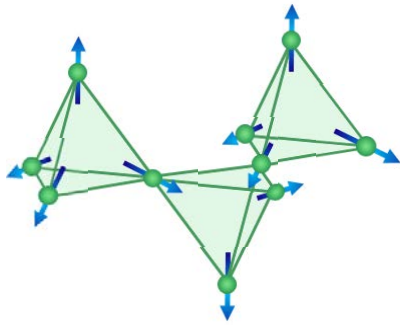
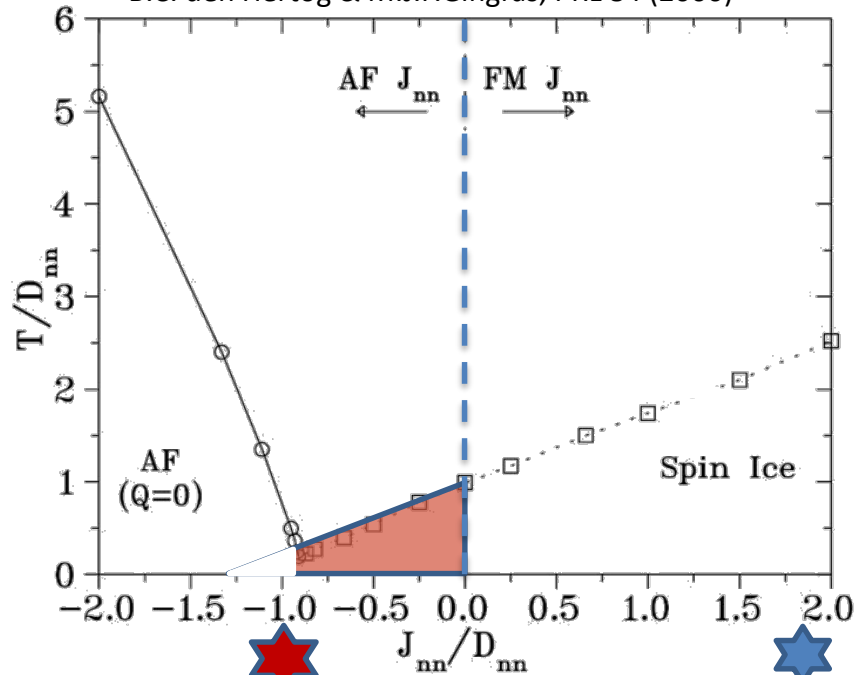


J.S.Gardner, M.J.P.Gingras, J.E.Greedan, Phys.Rev.Mod 82 (2010)

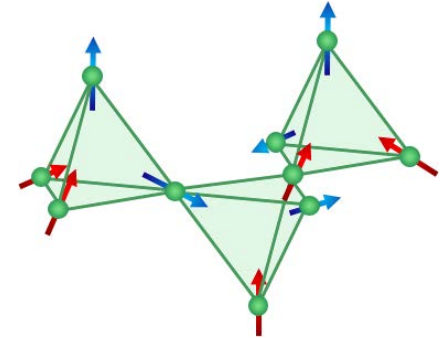
4. Ising spin Phase diagram

Ising spins + J_{nn} + D_{nn}

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



« All in – All out »
long range order



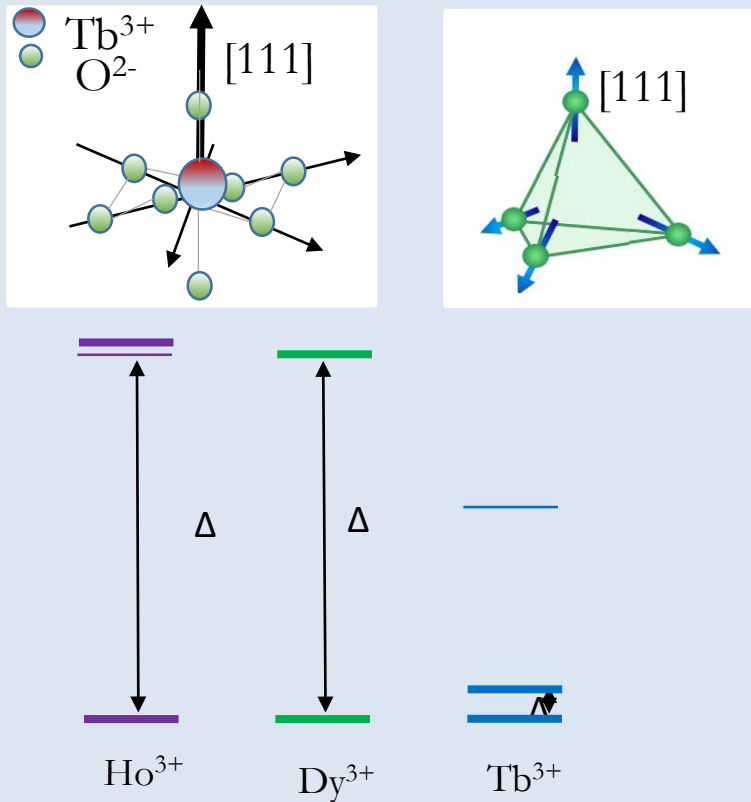
« 2 in – 2 out »
degenerate state

$Tb_2Ti_2O_7$
(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 D_{3d} symmetry



For Ho, Dy
 $\Delta \approx 300 \text{ K}$

Ising spins

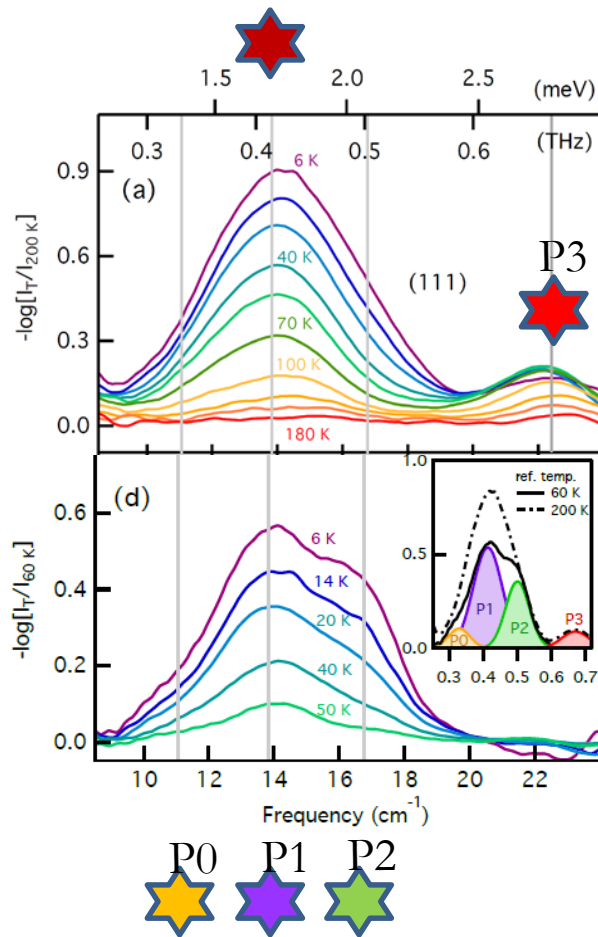
For Tb
 $\Delta \approx 20 \text{ K} \approx 0.4 \text{ THz}$

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

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

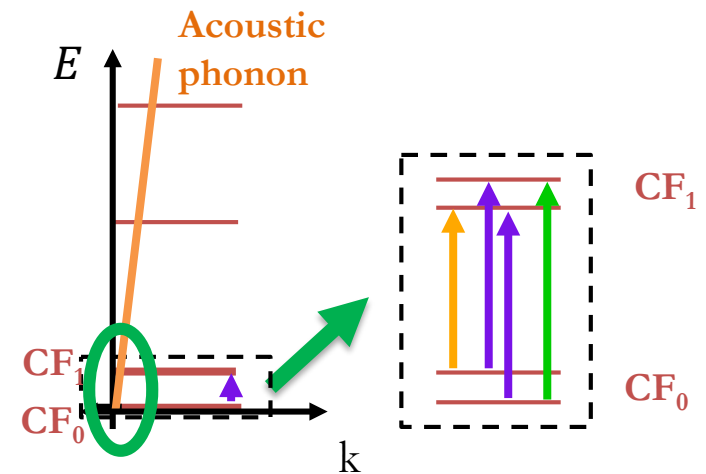
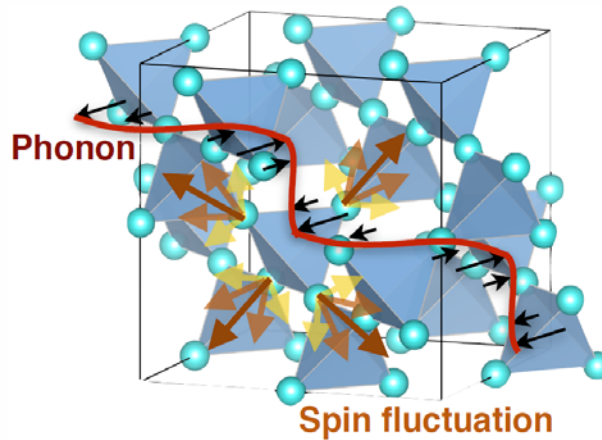
3 peaks visible below 50 K :
0.33 THz (11 cm^{-1})
0.41 THz (14 cm^{-1})
0.50 THz (17 cm^{-1})

4. MAGNETO- ELASTIC EFFECTS: VIBRONIC COUPLING IN



Vibronic coupling = hybridization between **crystal field excitations** and **phonons**

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



Tb₂Ti₂O₇ :

crystal field excitations associated to Tb³⁺ in D_{3d} symmetry
 $CF_0 \rightarrow CF_1$ at $14 \text{ cm}^{-1} = 0.4 \text{ THz} = 1.6 \text{ meV}$ (E_g doublets)
+ acoustic phonon of the cubic Fd $\bar{3}$ m structure

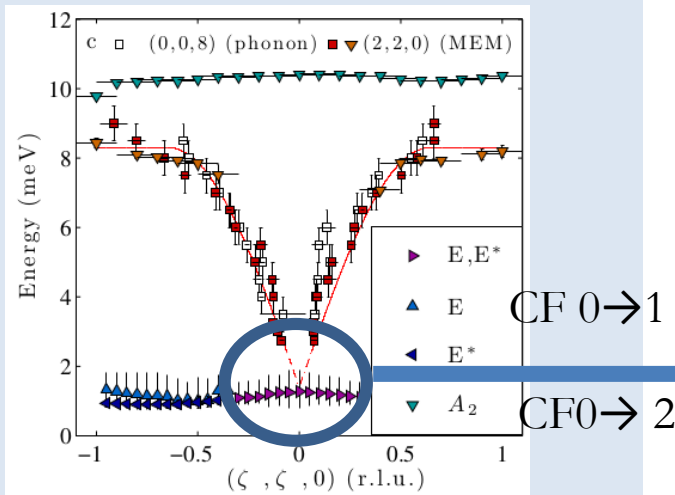
}

Splitting of the
ground and first
CF levels

4. TTO peculiarities: spin/lattice couplings

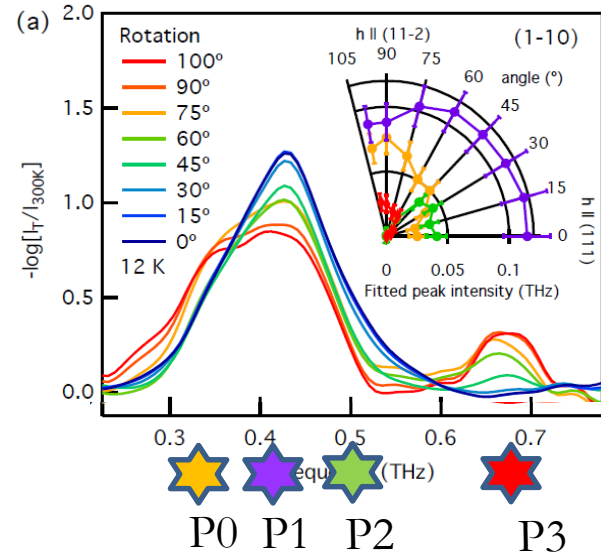
Neutron measurements

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 \rightarrow 1
 4 peaks that reveal CF 0 and CF1 couplings to phonons : **Vibronic couplings**

4. MAGNETO- ELASTIC EFFECTS: VIBRONIC COUPLING IN



Crystal field – phonon hybridization = vibronic coupling

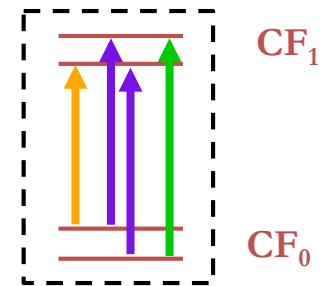
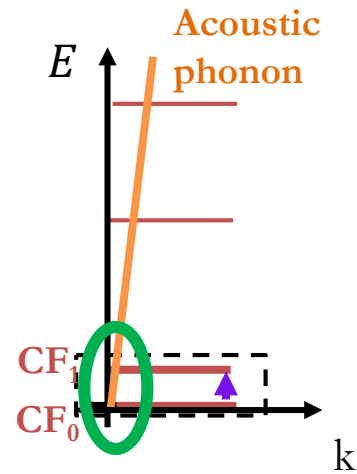
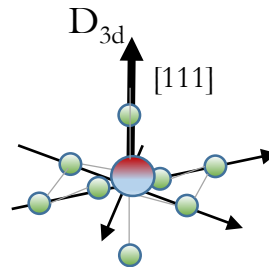
P. Thalmeier and P. Fulde, Phys. Rev. Lett. **49**, 1588 (1982)

One site Hamiltonian :

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

Crystal field

Vibronic coupling



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

Coupling to E_g CF states through

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

Quadrupolar degrees of freedom

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

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Crystal field – phonon hybridization = vibronic coupling

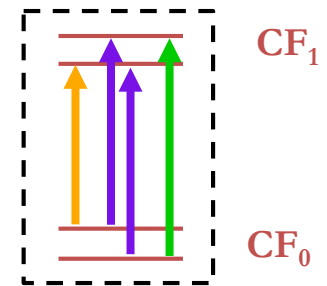
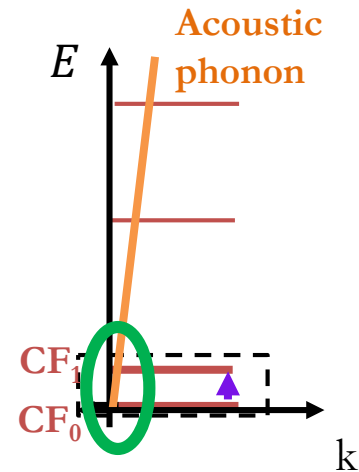
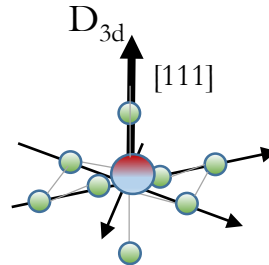
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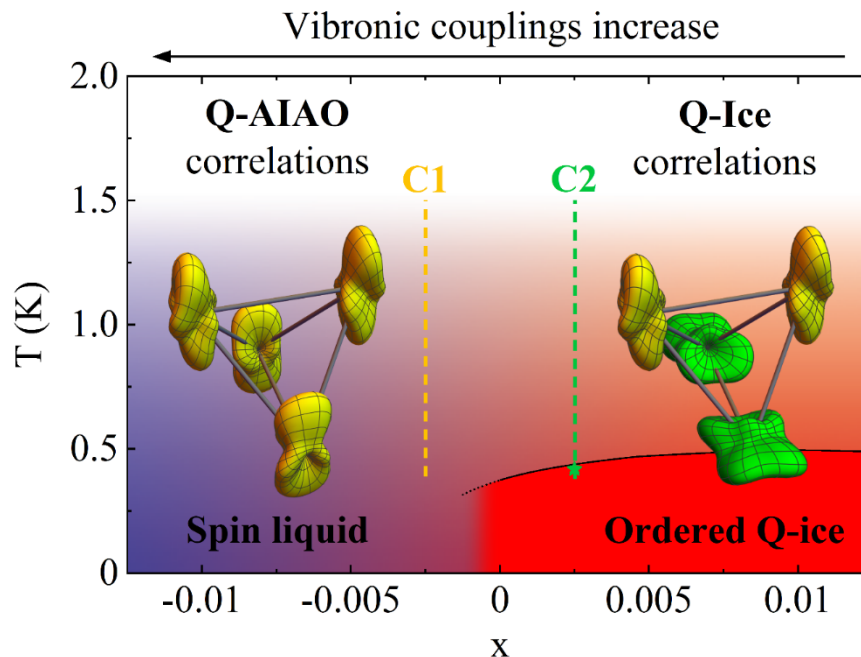
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Quadrupolar degrees of freedom

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

Quadrupolar phase diagram of $\text{Tb}_{2+x}\text{Ti}_{2-x}\text{O}_{7+y}$

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

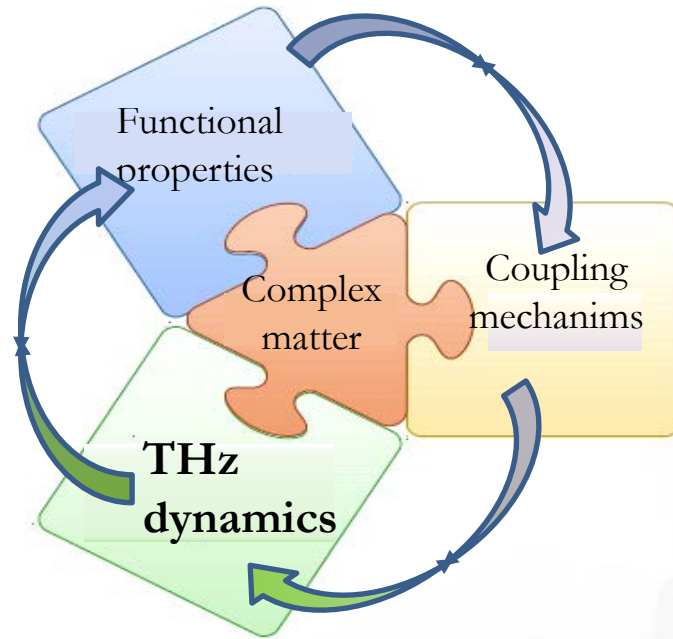


Dipolar & quadrupolar interactions favor ice « 2 in-2 out like » quadrupoles correlations (Q-ice)

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

THz PROPERTIES OF COMPLEX MAGNETIC PHASES



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

New hybrid excitations

Out of equilibrium phases

“continuum” from correlated electrons/ spin liquids....