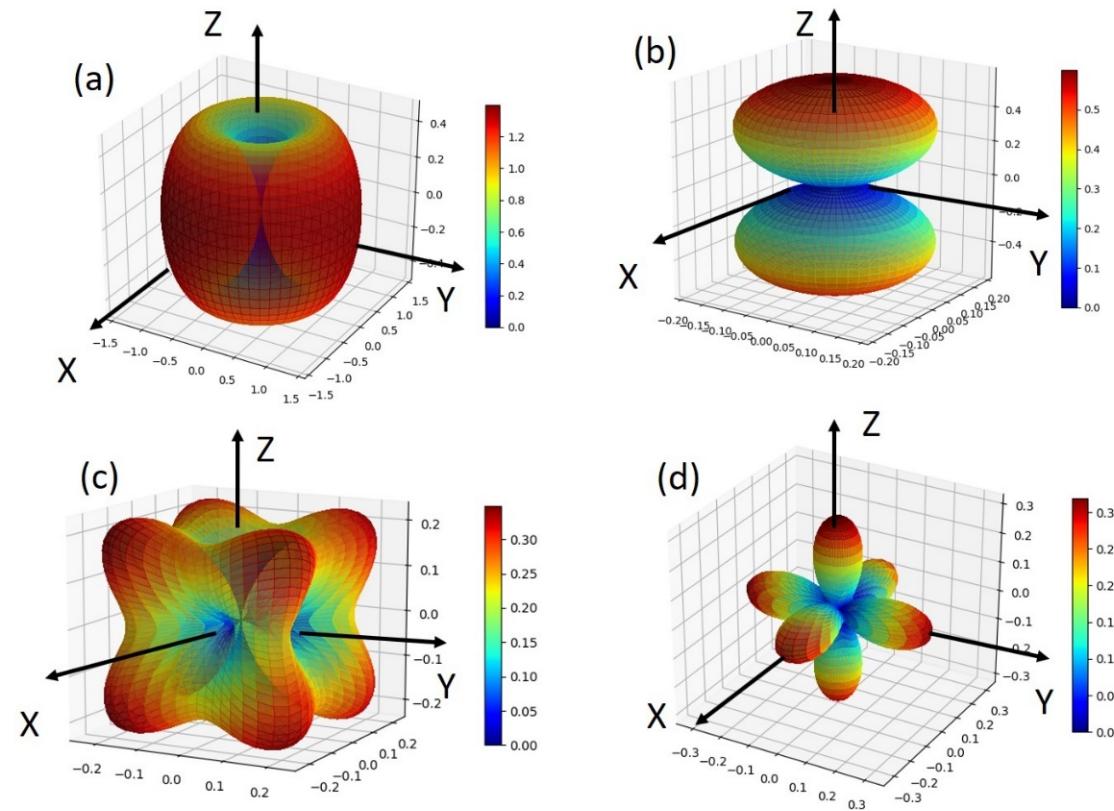


# Magnetic anisotropies

Scientific Visualization, 2020, volume 12,  
number 3, pages 26 - 37, DOI:  
[10.26583/sv.12.3.03](https://doi.org/10.26583/sv.12.3.03)



# Magnetic anisotropies

**Orientation of a single magnetic moment : isotropic, uniaxial, planar, intermediate...**

**Macroscopic magnetic state** ( long range order, spin liquid, paramagnets,...)

**Magnetic domains** (energy of the domain walls, shape of the domains, reversibility/irreversibility, ...)

**Dynamics:** ferromagnetic gap (MHz-GHz), antiferromagnetic gap (THz) .....

**Effect of a magnetic field** : dependence on its orientation...

....

**Anistotropic exchange interaction between neighboring spins**

**Macroscopic magnetic state** (long range order, spin liquid,...)

**Skyrmions** and other topological objects ...

## Measuring the magnetic anisotropy

From fundamentals to applications...

# bibliography

André HERPIN: Théorie du magnétisme 1986

Du Trémolet de Lacheisserie: Magnétisme I-Fondements / Magnetism I

Blundell: Magnetism

...

## **Quantum mechanical treatment**

RH White: Quantum magnetism

Abragam and Bleaney: Electron paramagnetic resonance of transition ions

(single ion anisotropy for 3d elements)

Werth and Bolton : Electron spin resonance , elementary theory and practical applications

recent edition : Weil and Bolton

...

**+ articles....**

# Magnetic anisotropies

- 1. Importance of magnetic anisotropy**
2. Single ion Magnetic anisotropy: phenomenological description
3. Single ion Magnetic anisotropy: microscopic origin
4. Exchange anisotropy
5. Examples with magneto-electric effects

# 1. Importance of magnetic anisotropy: domains

Example: domains in a ferromagnet magnetization curve  
 $M(H)$

reversible magnetisation

$$M = \chi H$$

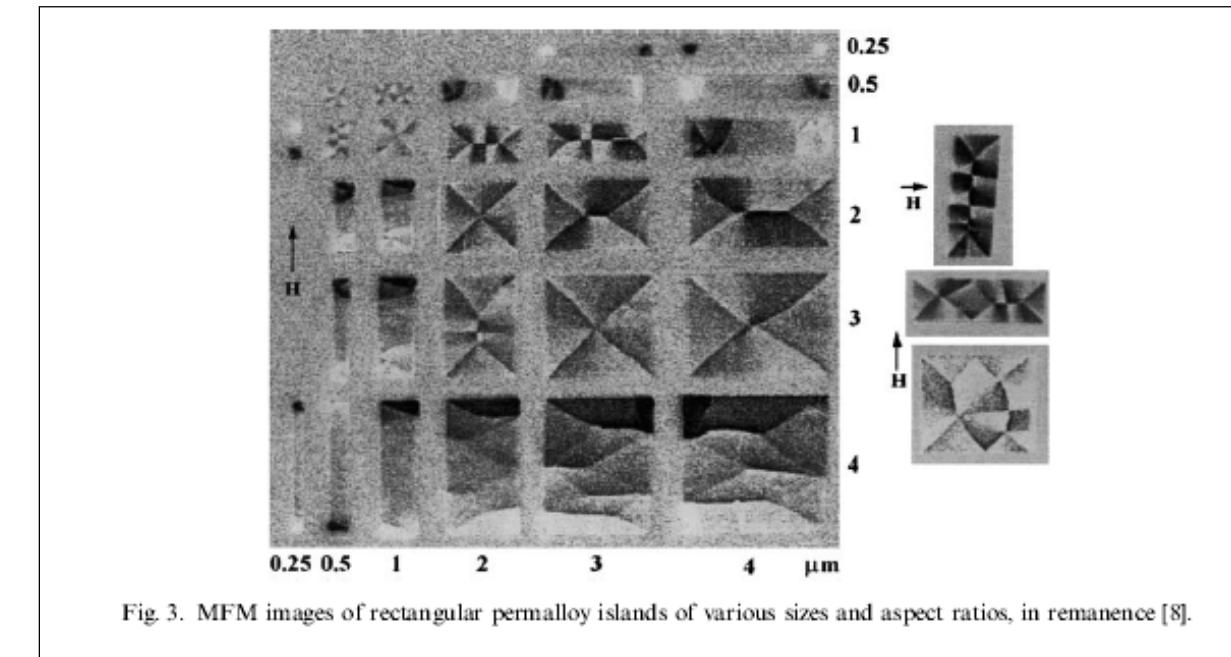
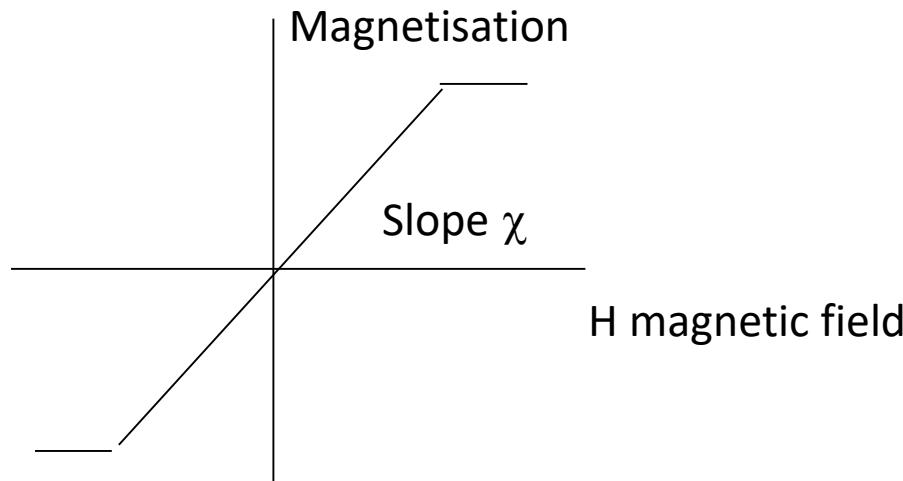
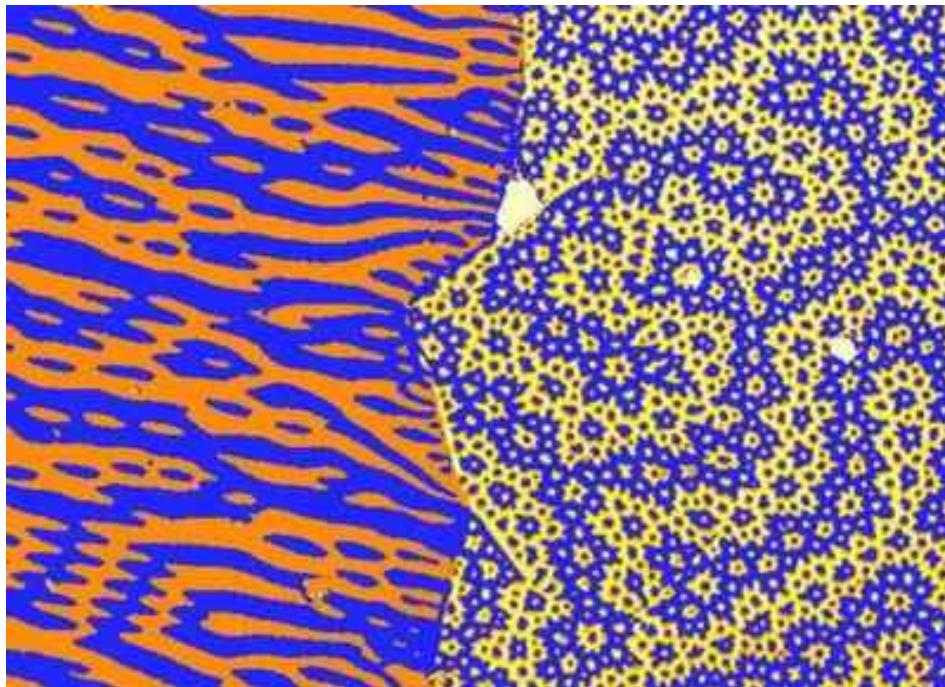


Fig. 3. MFM images of rectangular permalloy islands of various sizes and aspect ratios, in remanence [8].

# 1. Importance of magnetic anisotropy: domains

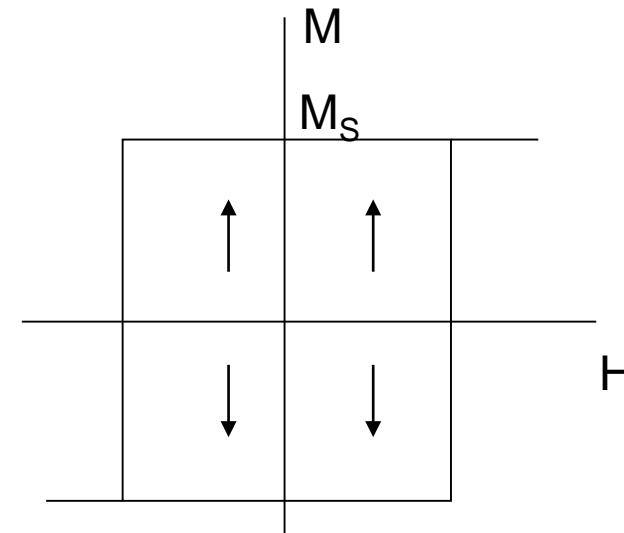
Example: domains in a ferromagnet magnetization curve

$M(H)$



NdFeB domains

Irreversible magnetisation:  
Spontaneous magnetization  
 $H = 0 \quad M = M_s \neq 0$



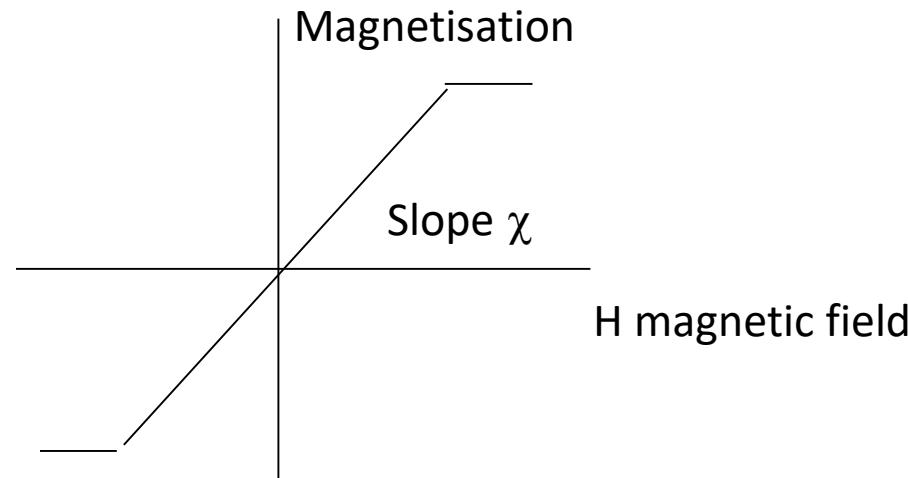
# 1. Importance of magnetic anisotropy: domains

**Example: domains in a ferromagnet magnetization curve**

**M( H )**

reversible magnetisation

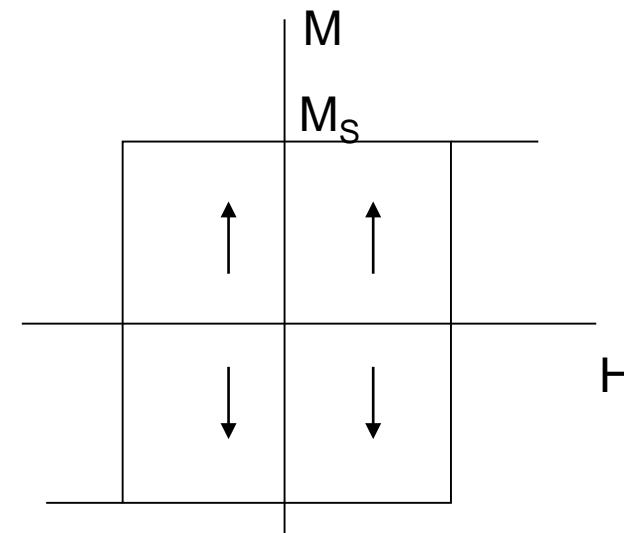
$$M = \chi H$$



Irreversible magnetisation:

Spontaneous magnetization

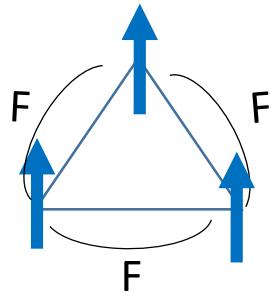
$$H = 0 \quad M = M_s \neq 0$$



# 1. Importance of magnetic anisotropy: magnetic frustration

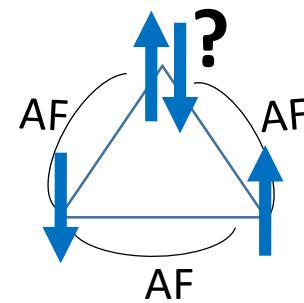
## example of spins on a triangle

F first neighbor interaction



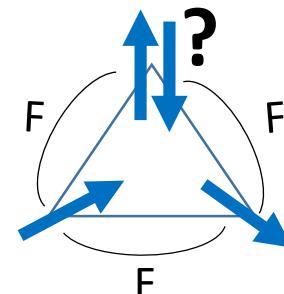
F long range magnetic order

AF first neighbor interaction



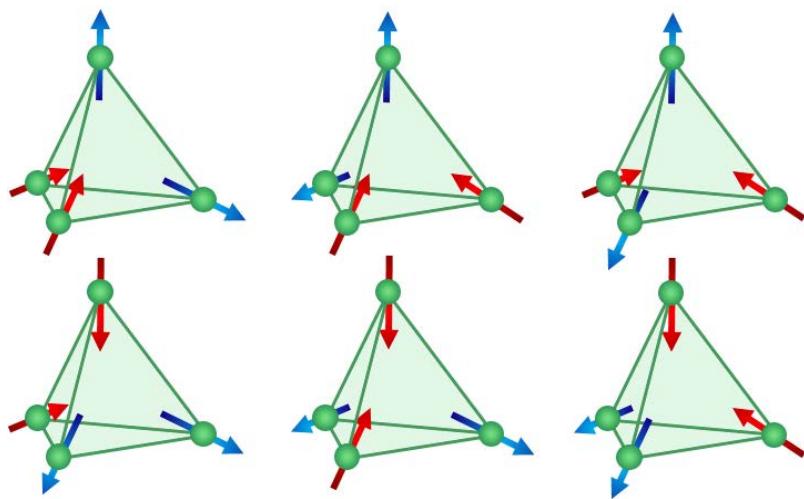
Magnetic frustration

F first neighbor interaction + multiaxial anisotropy



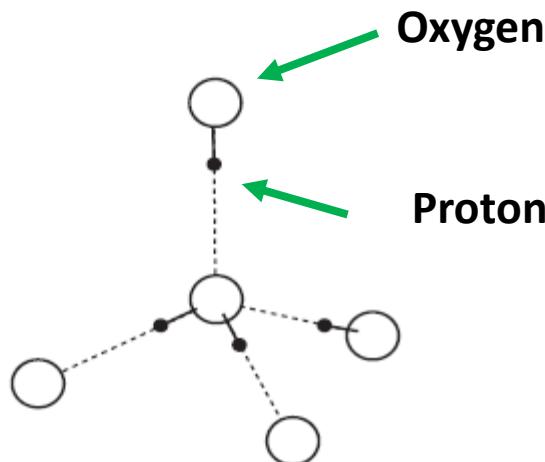
Magnetic frustration  
**SPIN ICES**

# 1. Importance of magnetic anisotropy: spin ices

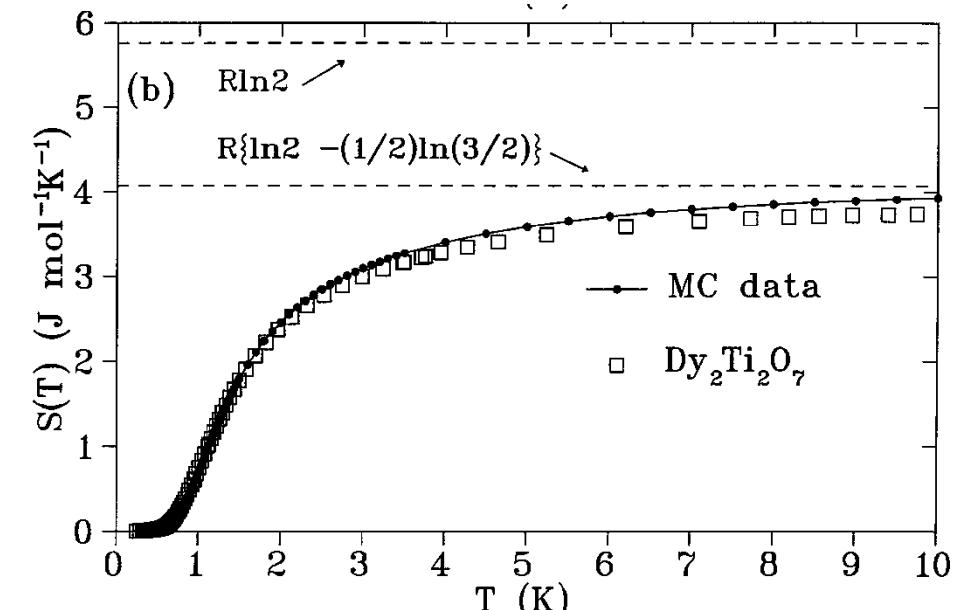


**2 in – 2 out »  
« ice rule »**

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)



From fundamentals to  
applications:

Magneto caloric effect...

# 1. Importance of magnetic anisotropy: non collinear phases

## Example: skyrmions

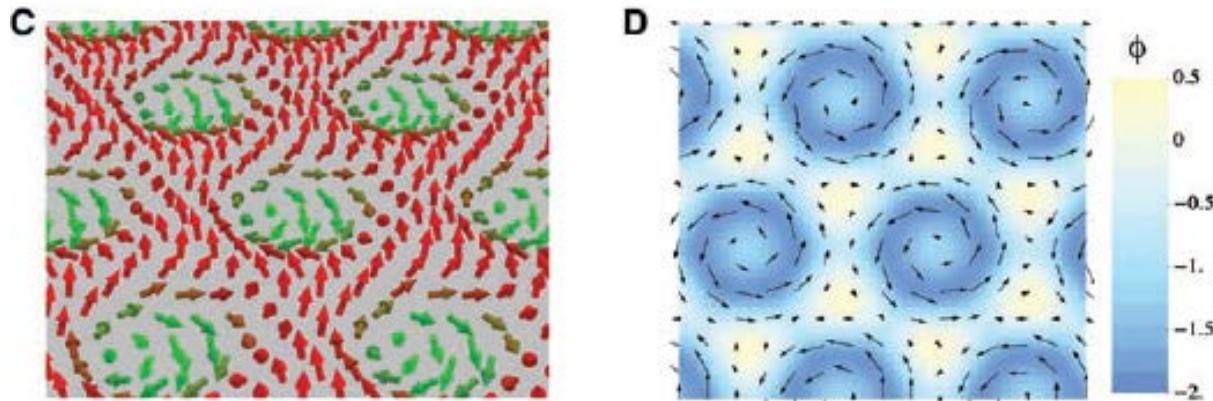
MnSi

S. Mühlbauer *et al*

Skyrmion lattice in a chiral magnet

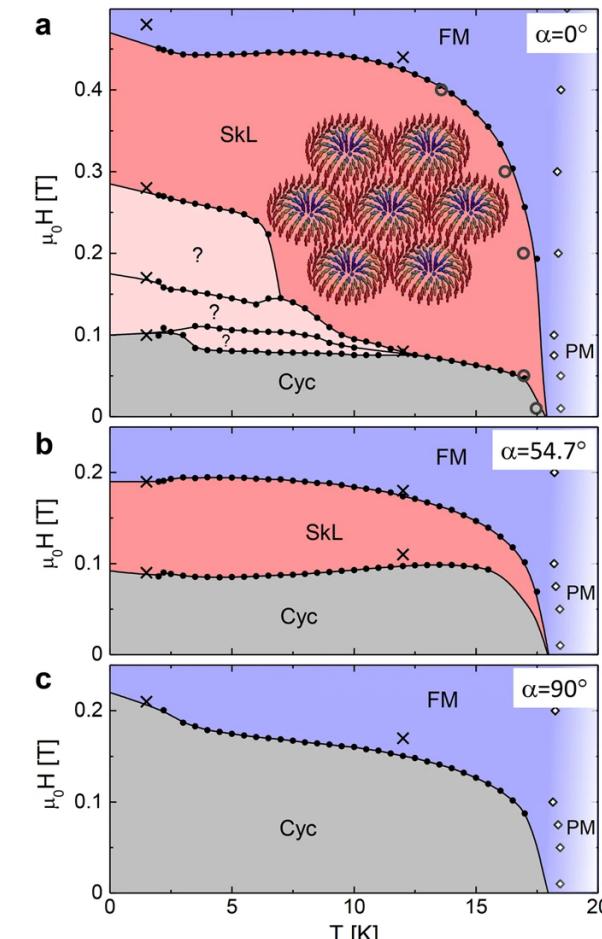
*Science* **323**, 915–919 (2009)

Neutron scattering



**GaV<sub>4</sub>Se<sub>8</sub>**

S. Bordács, *et al.* Equilibrium Skyrmion Lattice Ground State in a Polar Easy-plane Magnet. *Sci Rep* **7**, 7584 (2017). <https://doi.org/10.1038/s41598-017-07996-x>

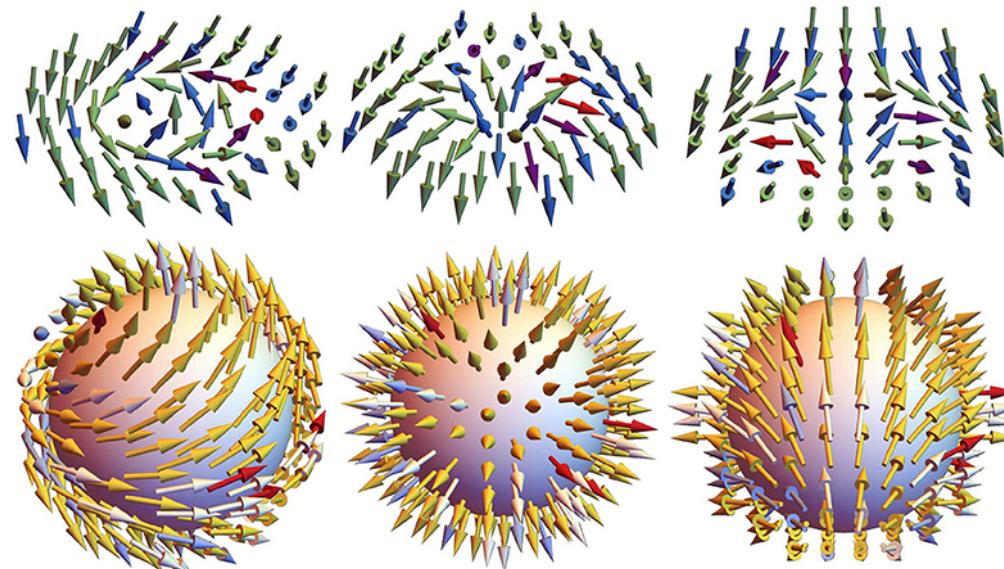


# 1. Importance of magnetic anisotropy: non collinear phases

## Example: skyrmions

Skyrmions and Antiskyrmions in Quasi-Two-Dimensional Magnets

<https://doi.org/10.3389/fphy.2018.00098>



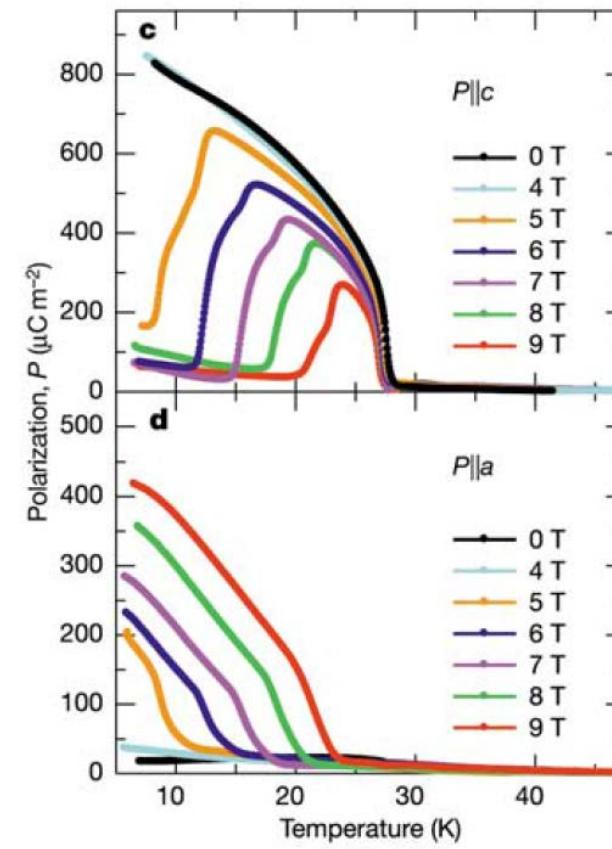
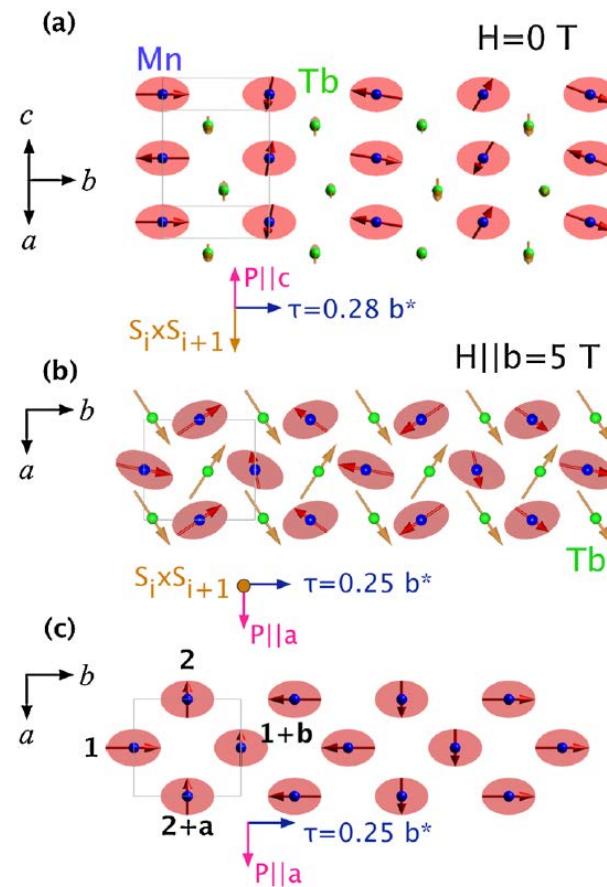
From fundamentals  
to applications:

nano electronics....

# 1. Importance of magnetic anisotropy: non collinear phases

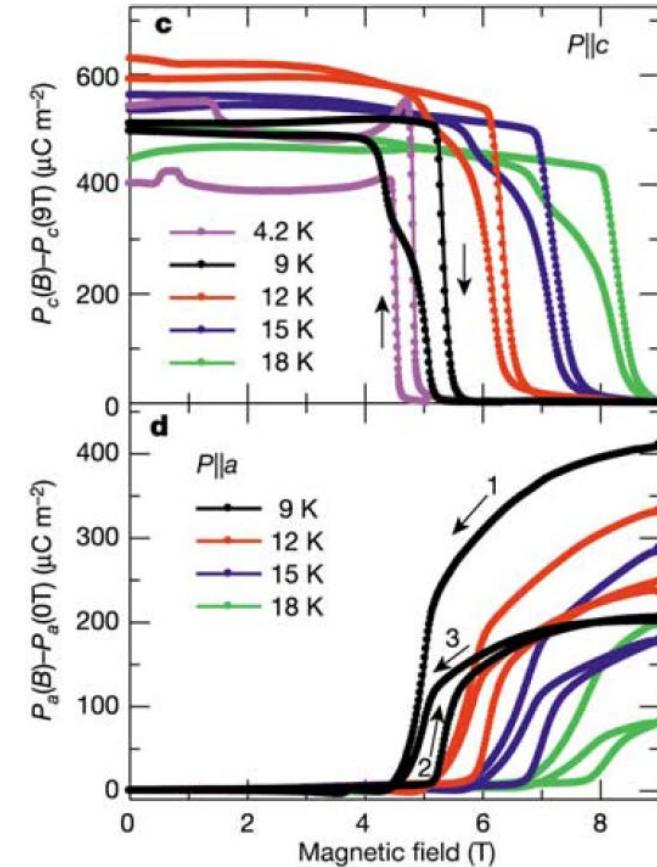
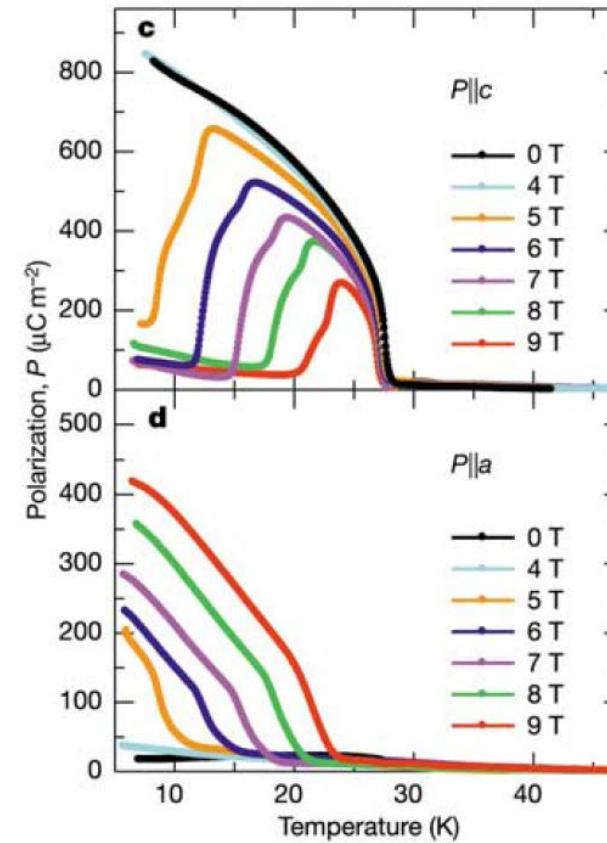
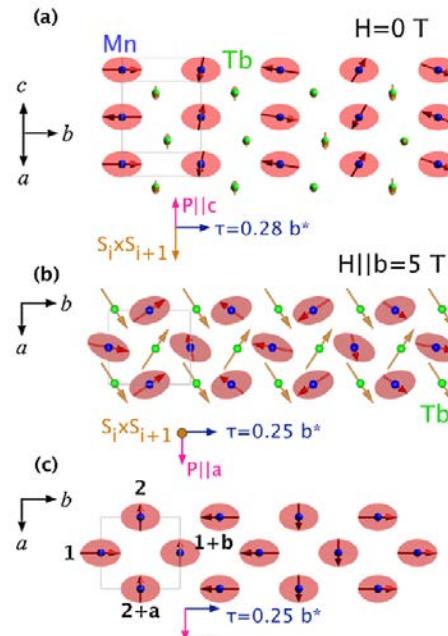
## Magnetically induced ferroelectricity

Cycloidal order and induced electric polarization in TbMnO<sub>3</sub>



# 1. Importance of magnetic anisotropy: non collinear phases

## Magnetically induced ferroelectricity



From fundamentals  
to applications:

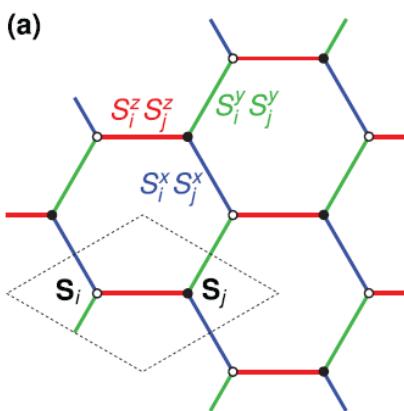
ME sensors / memory

# 1. Importance of magnetic anisotropy

## Kitaev physics

Anisotropic Exchange interactions on a honeycombe lattice  
Frustation leads to a spin liquid phase whose properties are exactly calculated  
(search for experimental realisation...)

$$H_{Kitaev} = - \sum_{i,\alpha=1,2,3} (K_x S_i^x S_\alpha^x + K_y S_i^y S_\alpha^y + K_z S_i^z S_\alpha^z)$$



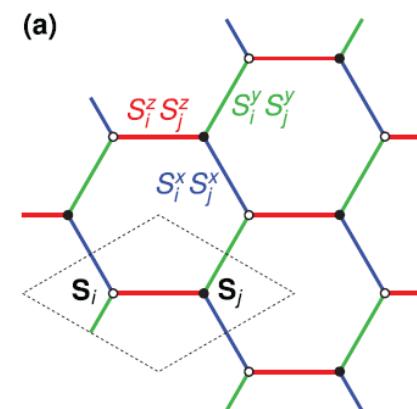
# 1. Importance of magnetic anisotropy

## Kitaev physics

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Lukas Janssen and Matthias Vojta 2019 *J. Phys.: Condens. Matter* **31** 423002



# Magnetic anisotropies

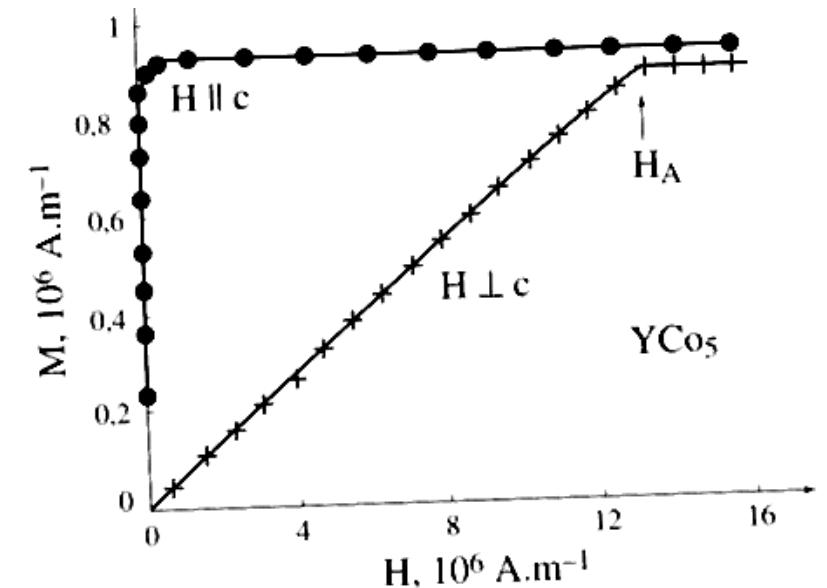
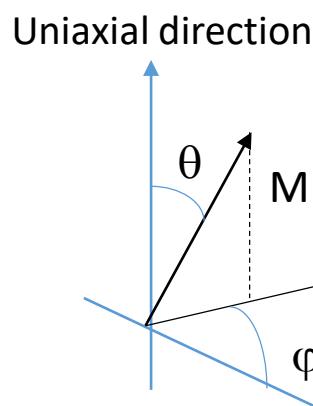
1. Importance of magnetic anisotropy
2. **Single ion Magnetic anisotropy: phenomenological description**
3. Single ion Magnetic anisotropy: microscopic origin
4. Exchange anisotropy
5. Examples with magneto-electric effects

## 2. Single ion magnetic anisotropy : phenomenological description

The magnetic moment is « pinned » to one/several directions in the periodic lattice  
thanks to its orbital momentum  
It depends also on the local crystal symmetry

Phenomenological description: Magneto crystalline energy  
Spherical coordinates  $\theta, \varphi$

Axial symmetry :  $e_{an} = K_1 \sin^2 \theta$   
 $K_1 > 0$ ,  $e_{an}$  minimum for  $\theta = 0$   
uniaxial system  
 $K_1 < 0$ ,  $e_{an}$  minimum for  $\theta = \pi/2$   
planar system

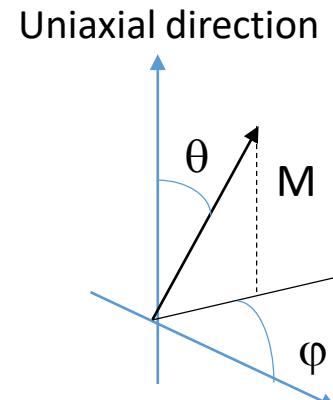


Example : magnetization curve of the  
uniaxial compound  $\text{YCo}_5$   
 $\mu_0 H_a = 2K_1 / M_s \approx 17\text{T}$

## 2. Single ion magnetic anisotropy : phenomenological description

Magneto crystalline energy in **hexagonal symmetry**

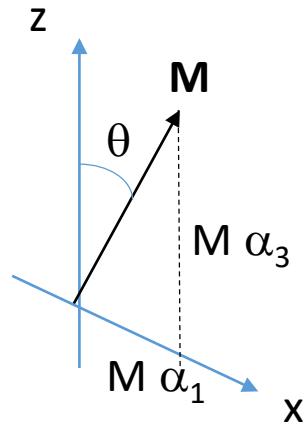
$$e_{an} = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta + K_6 \sin^6 \theta \cos 6\varphi + K_{12} \sin^{12} \theta \cos 12\varphi + \dots$$



Magneto crystalline energy in **cubic symmetry**

$$e_{an} = K_1 (\alpha_1^2 + \alpha_2^2 + \alpha_3^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2 + \dots$$

Where  $\alpha_i$  is the direction cosine in the  $i=x,y,z$  direction



**Note**



$K_i$  are temperature dependent...

## 2. Magnetic anisotropy

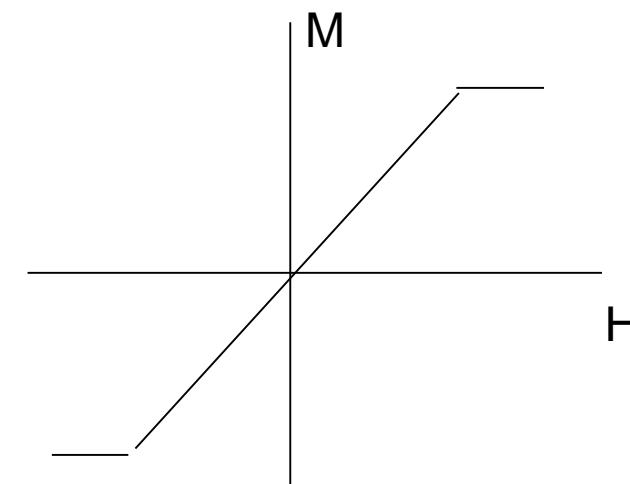
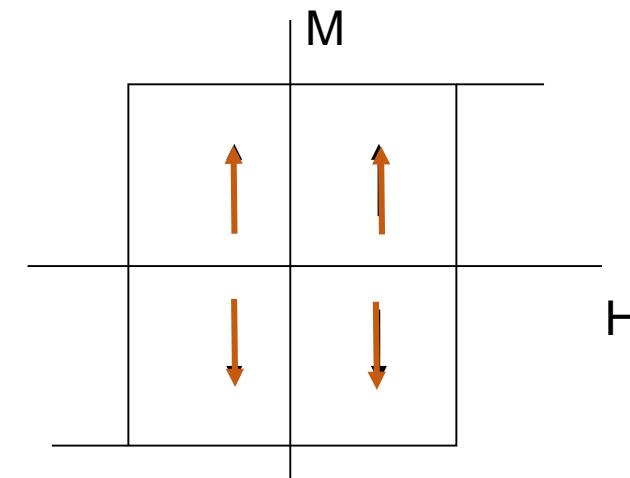
Example: single domain grain with simple uniaxial anisotropy

Large hysteresis for the magnetic field applied along the uniaxial direction, with a large magnetisation

$$H_c = H_a = \frac{2K}{\mu_0 M_S}$$

$$M = M_S$$

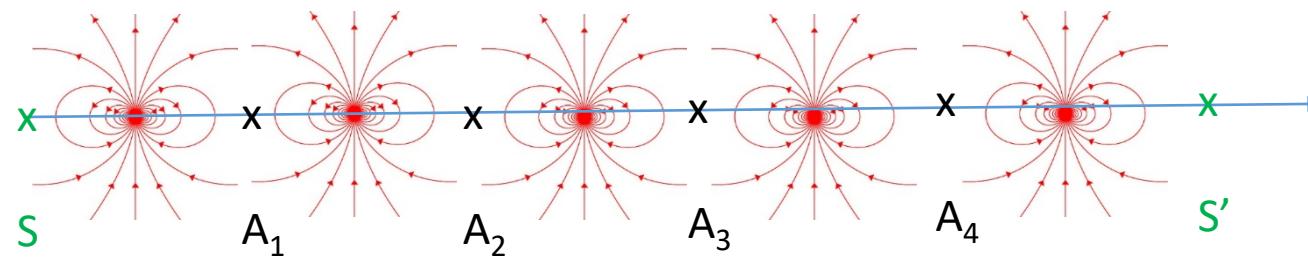
For a magnetic field perpendicular to the uniaxial direction, there is no hysteresis and a saturation occurs at  $H_a$ .



## 2. Shape anisotropy

At the surface of a macroscopic sample, there is a discontinuity in the magnetisation equivalent to magnetic ‘charges’. The associated magnetic field  $\mathbf{H}_{dem}$  is the demagnetising field that depends on the sample shape and its magnetisation

Example: A finite chain of magnetic dipoles



in  $A_i$ , the magnetic dipolar fields cancelled, not in  $S$  and  $S' \dots$

$$\mathbf{H}_{dem} = -n \mathbf{M}$$

$$e_{ms} = -\frac{1}{2}\mu_0 \mathbf{M} \cdot \mathbf{H}_{dem} = \frac{1}{2}\mu_0 n \mathbf{M}^2$$

$n$  is the demagnetising coefficient that depends on the sample shape

## 2. Shape anisotropy

At the surface of a macroscopic sample, there is a discontinuity in the magnetisation equivalent to magnetic ‘charges’. The associated magnetic field is the demagnetising field that depends on the sample shape.

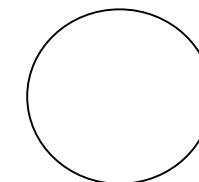
$$\mathbf{H}_{dem} = -n \mathbf{M} \quad e_{ms} = -\frac{1}{2} \mu_0 \mathbf{M} \cdot \mathbf{H}_{dem} = \frac{1}{2} \mu_0 n \mathbf{M}^2 .$$

Examples :

Spheres

All directions are equivalent: no shape anisotropy

$$\mathbf{H}_{dem} = -\frac{1}{3} \mathbf{M}$$



$$2 e_{ms} = \mu_0 \frac{\mathbf{M}^2}{3}$$

Thin film with in plane magnetisation:

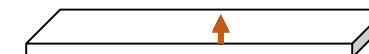
$$\mathbf{H}_{dem} = 0$$



$$e_{ms} = 0$$

Thin film with out of plane magnetisation:

$$\mathbf{H}_{dem} = -\mathbf{M}$$



$$2 e_{ms} = \mu_0 \mathbf{M}^2$$

This configuration is energetically unfavorable: in a thin film the demagnetisation field acts as to maintain the magnetisation in the plane: this is a planar **shape anisotropy**

Note



$n$  is a Tensor

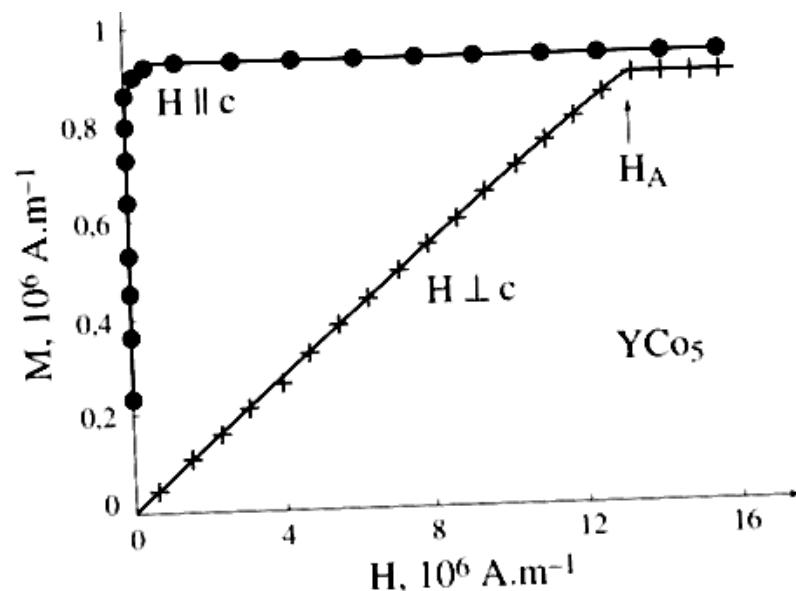
$$\mathbf{H}_{dem} = -[n] \mathbf{M}$$

$$n = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ for a thin plate, } n = \begin{bmatrix} 1/3 & 0 & 0 \\ 0 & 1/3 & 0 \\ 0 & 0 & 1/3 \end{bmatrix} \text{ for a sphere ...}$$

## 2. Shape anisotropy

Example :  $\text{YCo}_5$

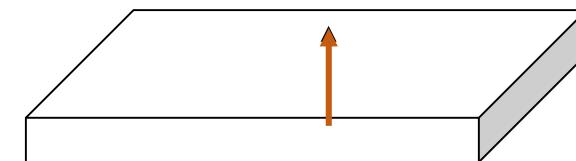
Intrinsic anisotropy



magnetization curve of the uniaxial compound  $\text{YCo}_5$

$$\mu_0 H_a = 2K_1 / M_s \approx 17 \text{ T}$$

Shape anisotropy



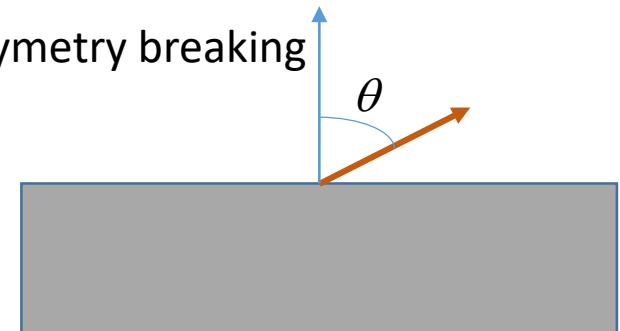
Thin film at saturated magnetization

$$\mu_0 H_{dem} = -\mu_0 M_s \approx -1.1 \text{ T}$$

## 2. Magnetic anisotropy

If the surface is large compared to the volume, you have to consider the surface symmetry breaking

$$e_{an} = K_1 \cos^2 \theta$$



+ magnetoelastic anisotropy : Induced by the strain of the substrate

Shape anistropy + Magnetocrystalline anistotropy + magneto elastic anisotropy

$$K_{eff} = K_{vol} + K_s / d$$

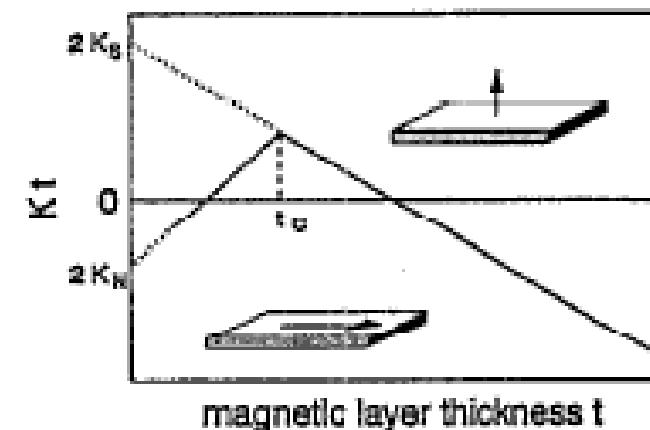


FIG. 1. Schematic dependence of  $Kt$  on layer thickness  $t$ , in the presence of negative Néel surface anisotropy  $K_N$ .

# Magnetic anisotropies

1. Importance of magnetic anisotropy
2. Single ion Magnetic anisotropy: phenomenological description
- 3. Single ion Magnetic anisotropy: microscopic origin**
4. Exchange anisotropy
5. Examples with magneto-electric effects

### 3. Single ion Magnetic anisotropy : microscopic origin

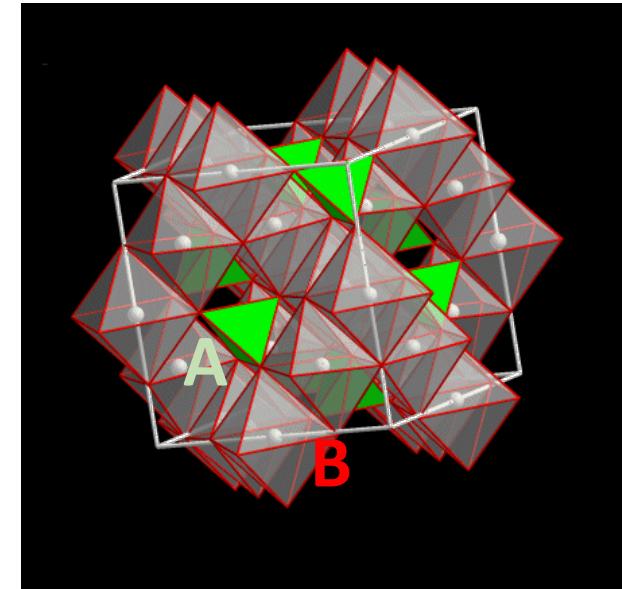
The **orbital part** of the magnetic moment is **sensitive to the electrostatic environment** (the spin part is not) created by the surroundings, **called crystal field**.

Example: spinel  $\text{AB}_2\text{O}_4$

A and B sites with a magnetic ion surrounded by  $\text{O}^{2-}$

A site: tetrahedral

B site: octahedral



How to describe this crystal field contribution?

Start with the quantum description of the single magnetic ion/element

Two main different cases: transition elements / rare earth elements

### 3. Magnetic anisotropy : microscopic origin

#### 3d elements:

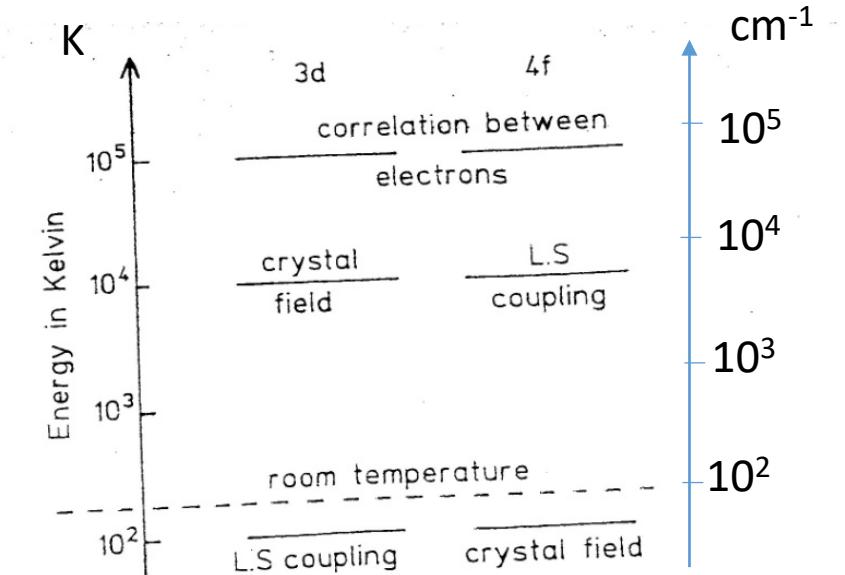
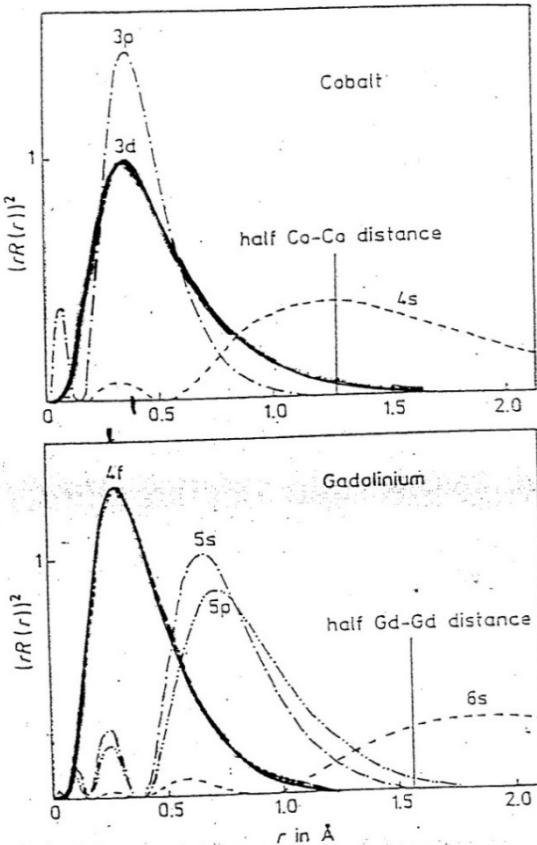
Extended electronic density

Sensitive to crystal field  
environnement

#### 4f elements:

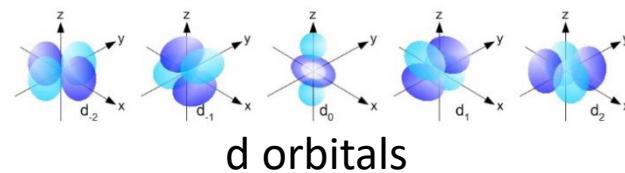
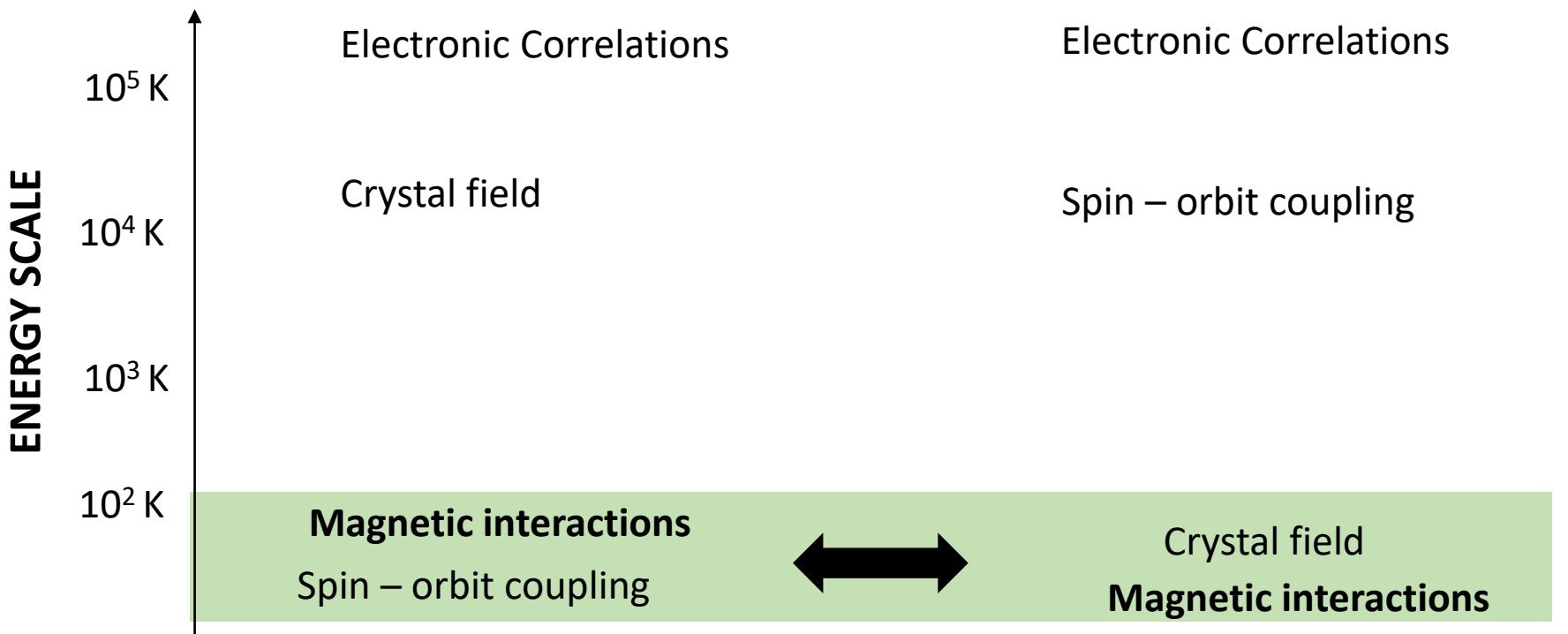
Localised electronic density

Weakly sensitive to crystal  
field environnement

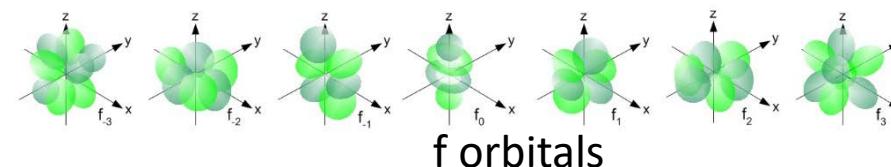


$$1 \text{ K} = 0.0862 \text{ meV} = 0.695 \text{ cm}^{-1}$$

### 3. Magnetic anisotropy : microscopic origin



**d orbitals**



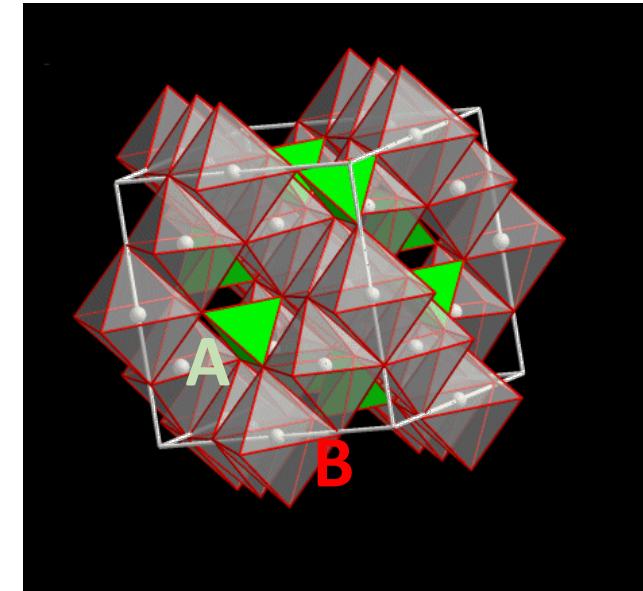
**f orbitals**

	Spin orbit ( $\text{cm}^{-1}$ )	CF ( $\text{cm}^{-1}$ )
$\text{Co}^{2+}$	-178	$\sim 1\ 000 - 10\ 000$
$\text{Tb}^{3+}$	- 1770	$\sim 10 - 100$

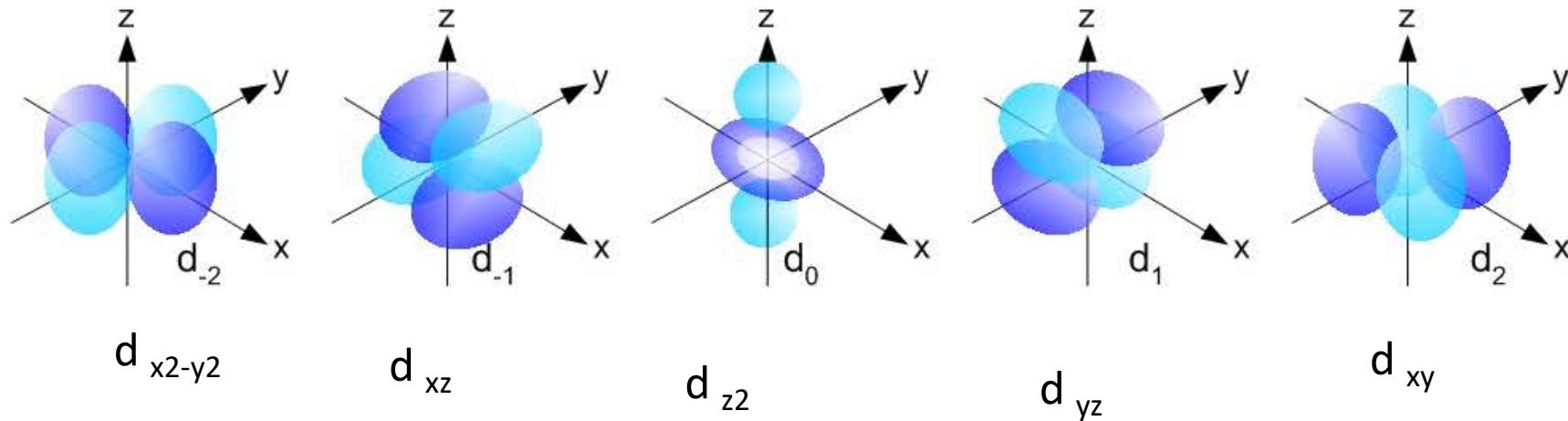
### 3. Magnetic anisotropy : microscopic origin

#### 3d elements

**Example :**  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  in octahedral environment  
for instance B site in the spinel  $\text{GeM}_2\text{O}_4$

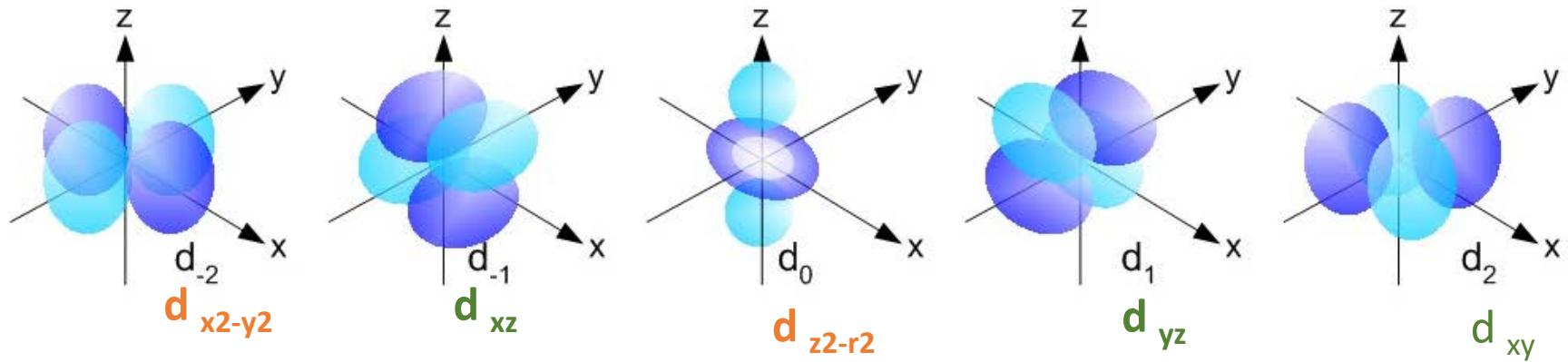


Shape of d orbitals: solutions of the Hamiltonian for electrons in the central electric potential of the positively charged nucleus



### 3. Magnetic anisotropy : microscopic origin

Shape of d orbitals



In cubic symmetry :

$O_h(m-3m)$	#	1	4	2	3	$2'$	-1	-4	m	-3	$m'$	functions
Mult.	-	1	6	3	8	6	1	6	3	8	6	.
$A_{1g}$	$\Gamma_1^+$	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
$A_{1u}$	$\Gamma_1^-$	1	1	1	1	1	-1	-1	-1	-1	-1	.
$A_{2g}$	$\Gamma_2^+$	1	-1	1	1	-1	1	-1	1	1	-1	.
$A_{2u}$	$\Gamma_2^-$	1	-1	1	1	-1	-1	1	-1	-1	1	.
$E_g$	$\Gamma_3^+$	2	0	2	-1	0	2	0	2	-1	0	$(2z^2-x^2-y^2, x^2-y^2)$
$E_u$	$\Gamma_3^-$	2	0	2	-1	0	-2	0	-2	1	0	.
$T_{2u}$	$\Gamma_5^-$	3	-1	-1	0	1	-3	1	1	0	-1	.
$T_{2g}$	$\Gamma_5^+$	3	-1	-1	0	1	3	-1	-1	0	1	$(xy, xz, yz)$
$T_{1u}$	$\Gamma_4^-$	3	1	-1	0	-1	-3	-1	1	0	1	$(x, y, z)$
$T_{1g}$	$\Gamma_4^+$	3	1	-1	0	-1	3	1	-1	0	-1	$(J_x, J_y, J_z)$

# REPRESENTATIONS OF SYMMETRY POINT GROUPS

## 1) Mulliken labels

A means *symmetric* with respect to the highest order axis  $C_n$ ;  
B - *antisymmetric*

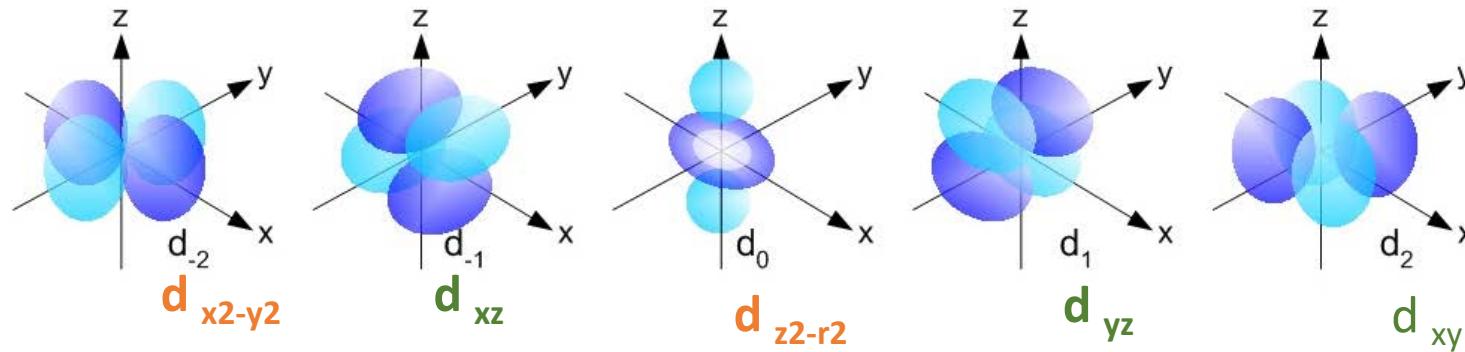
One- (A, B), two- (E), three- (T), four (G), five (H) dimensional representation

**A'** Symmetric ('') or antisymmetric ('') with respect to  $\sigma_h$   
**1g** Presence (g) or absence (u) of a center of inversion  
Symmetric (1) or antisymmetric (2) behavior with respect to a second symmetry element ( $C_2$  or  $\sigma_v$ )

$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$	
A <sub>1</sub>	1	1	1	1	z
A <sub>2</sub>	1	1	-1	-1	R <sub>z</sub>
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>
B <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>

### 3. Magnetic anisotropy : microscopic origin

Shape of d orbitals



In **cubic symmetry**,  $e_g$  and  $t^2_g$  orbitals have the same energy

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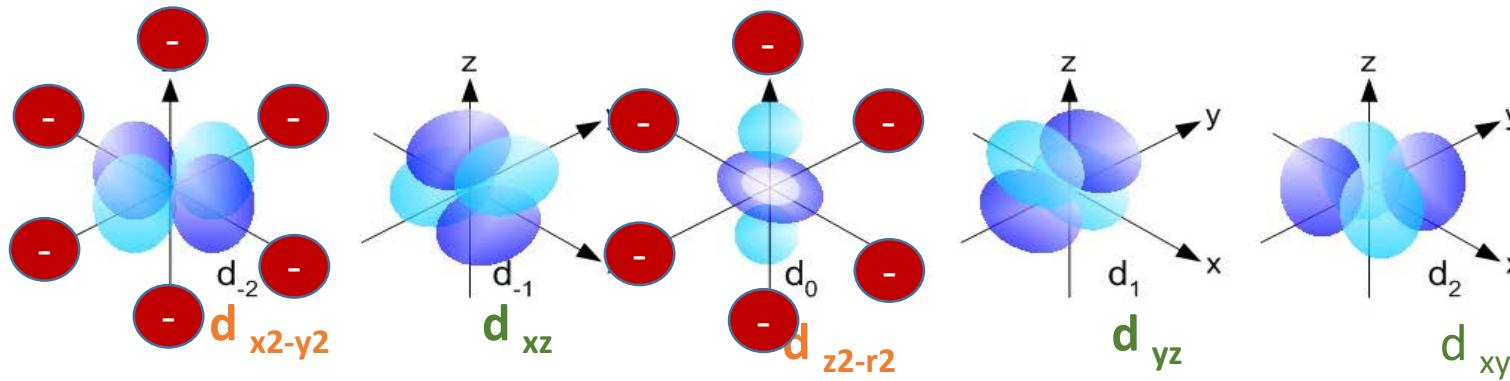
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In an **octahedral crystal field symmetry**, it is no longer the case

### 3. Magnetic anisotropy : microscopic origin

In an octahedral crystal field:

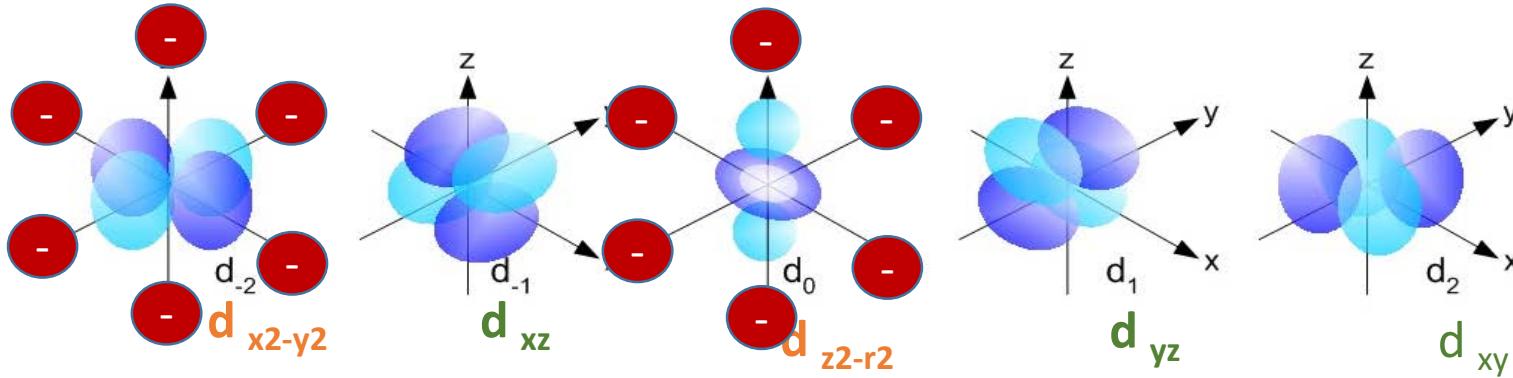


**e<sub>g</sub>** Orbitals point towards the CF electric charges :  
strong repulsion

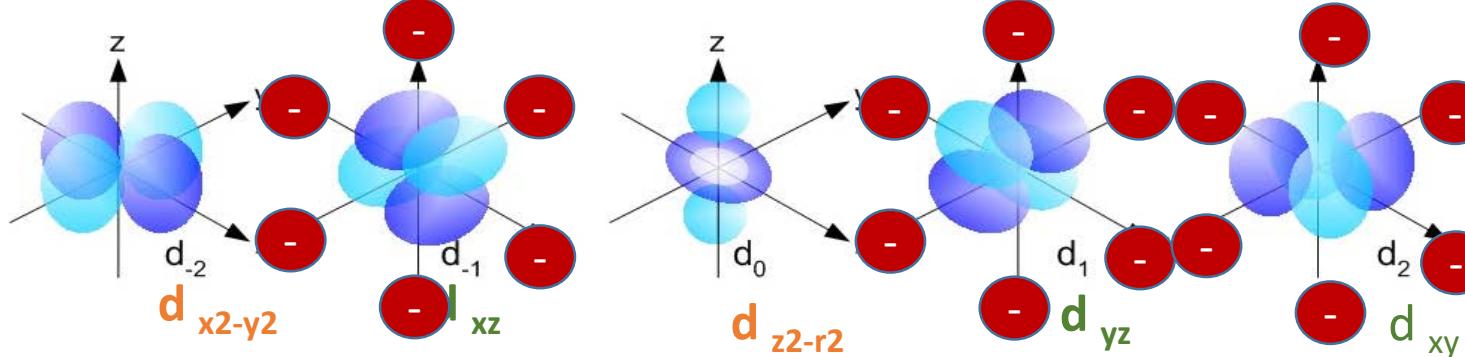
### 3. Magnetic anisotropy : microscopic origin

In an octahedral crystal field:

$e_g$  Orbitals point towards the CF electric charges : **strong repulsion**



$t_{2g}$  Orbitals point away from the CF electric charges : **weak repulsion**



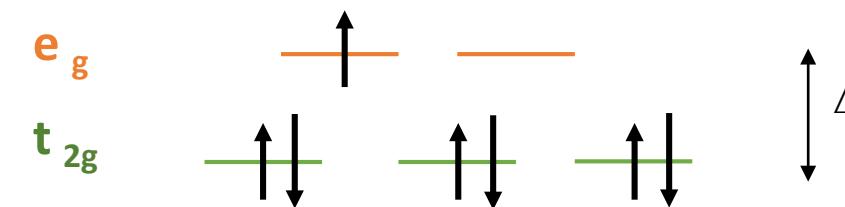
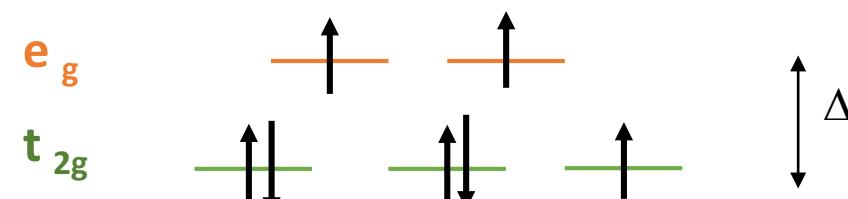
### 3. Magnetic anisotropy : microscopic origin

In an octahedral crystal field, there are two groups of orbitals:

$\text{Co}^{2+}: 3\text{d}^7$

$S = 3/2$  high spin state  
When  $\Delta \ll U$  Hund coupling

$S = 1/2$  low spin state  
When  $\Delta \gg U$  Hund coupling



What is the magnetic anisotropy for these two states? INCLUDE ORBITAL CONTRIBUTION AND SPIN ORBIT COUPLING

# Crystal field: quantum mechanical treatment

Crystal field:

For one electron  $i$  at position  $\mathbf{r}_i$  experiencing the electrostatic potential of charges  $q_j$  at position  $\mathbf{R}_j$ :

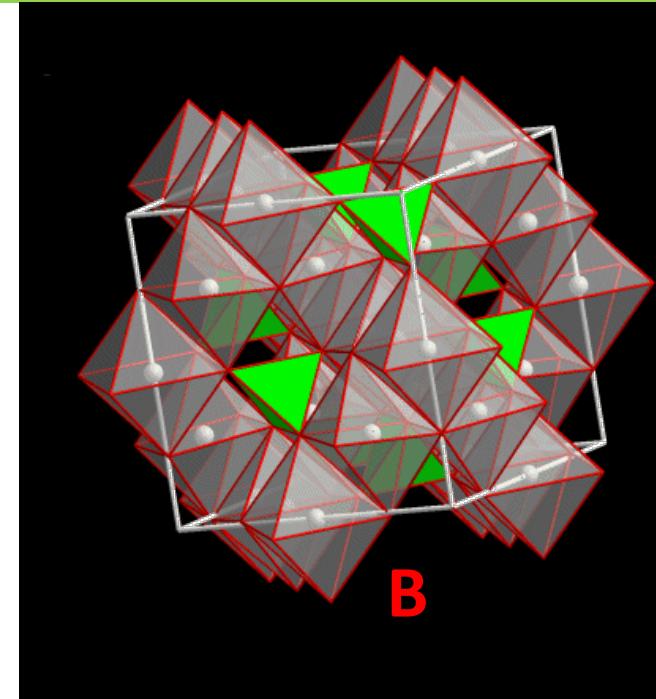
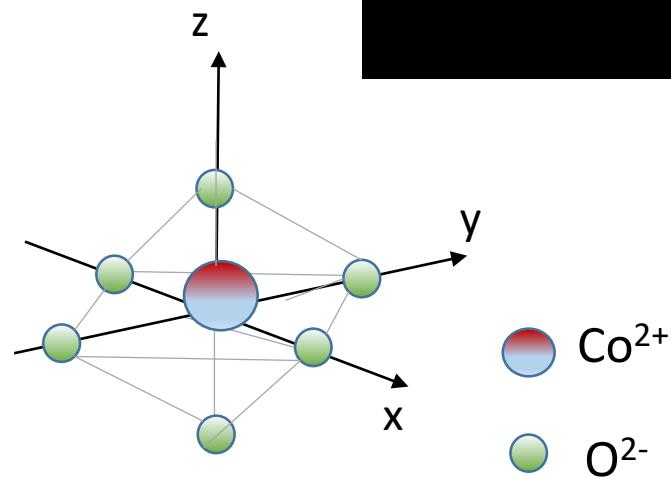
$$V_i = \frac{1}{4\pi\epsilon_0} \sum_j \frac{q_j}{|\mathbf{R}_j - \mathbf{r}_i|}$$

In a cubic coordination :

$$V_c(x, y, z) = C_4 \left[ (x^4 + y^4 + z^4) - \frac{3}{5}r^4 \right] + C_6 \left[ (x^6 + y^6 + z^6) \right] \quad (2.51)$$

$$+ \frac{15}{4} (x^2y^4 + x^2z^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4) - \frac{15}{14}r^6 \right],$$

where  $C_4 = +\frac{35}{4}qq'/d^5$  for sixfold coordination.



# Crystal field: quantum mechanical treatment

Crystal field:

For one electron  $i$  at position  $\mathbf{r}_i$ , experiencing the electrostatic potential of charges  $q_j$  at position  $\mathbf{R}_j$ :

$$V_i = \frac{1}{4\pi\epsilon_0} \sum_j \frac{q_j}{|\mathbf{R}_j - \mathbf{r}_i|}$$

Spherical coordinates

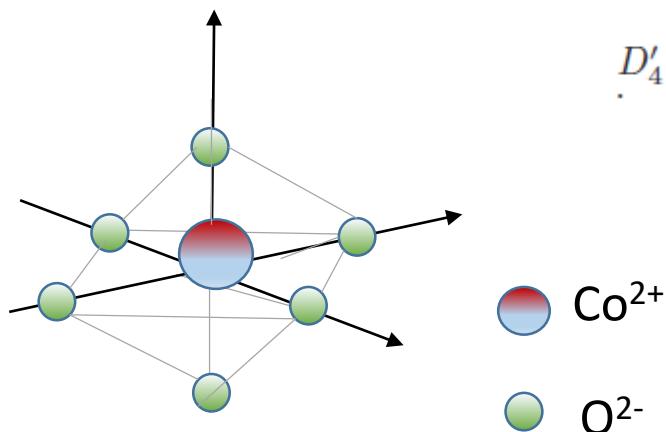
$$V(r, \theta, \varphi) = \sum_{L'} \sum_{M'} A_{L'}^{M'} r^{L'} Y_{L'}^{M'}(\theta, \varphi).$$

In a cubic coordination :

$$V_c(x, y, z) = C_4 \left[ (x^4 + y^4 + z^4) - \frac{3}{5} r^4 \right] + C_6 \left[ (x^6 + y^6 + z^6) + \frac{15}{4} (x^2 y^4 + x^2 z^4 + y^2 x^4 + y^2 z^4 + z^2 x^4 + z^2 y^4) - \frac{15}{14} r^6 \right], \quad (2.51)$$

$$V_c(r, \theta, \varphi) = D'_4 \left\{ Y_4^0(\theta, \varphi) + \sqrt{\frac{5}{14}} [Y_4^4(\theta, \varphi) + Y_4^{-4}(\theta, \varphi)] \right\} + D'_6 \left\{ Y_6^0(\theta, \varphi) - \sqrt{\frac{7}{2}} [Y_6^4(\theta, \varphi) + Y_6^{-4}(\theta, \varphi)] \right\}$$

where  $C_4 = +\frac{35}{4}qq'/d^5$  for sixfold coordination.



$D'_4 = +\frac{7}{3}\sqrt{\pi}q'r^4/d^5$  for sixfold coordination.

# Crystal field: quantum mechanical treatment

The crystal field potential can be expressed in spherical harmonics  $Y_L^M(\theta, \varphi)$  or more conveniently using angular momentum operators

Operator equivalent method: matrix elements of operators involving  $x, y$ , and  $z$  within a given  $L$  or  $J$  manifold are proportional to those of  $Lx, Ly$  and  $Lz$  or  $Jx, Jy$  and  $Jz$

$$\begin{aligned} & \sum \left( x^4 + y^4 + z^4 - \frac{3}{5} r^4 \right) \\ & \Rightarrow \frac{\beta \overline{r^4}}{8} [35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2] \\ & + \frac{\beta \overline{r^4}}{8} [(L^+)^4 + (L^-)^4] \equiv \frac{\beta \overline{r^4}}{20} O_4^0 + \frac{\beta \overline{r^4}}{4} O_4^4 = B_4^0 O_4^0 + B_4^4 O_4^4, \quad (2.52) \end{aligned}$$

where  $\overline{r^4}$  is the average value of the fourth power of the electron radius. The operators  $O_n^m$  appear frequently in the literature. The ground state  $\beta$  is a constant which depends on the term; for a  ${}^2D$  or a  ${}^5D$  term  $\beta = \frac{2}{63}$ .

Racah operators  $O_m^l$  are also used (or Wybourne....). They are linear combinations, with eventually a radial contribution and a renormalization coefficient, that are tabulated. See for instance **Point-Charge Calculations of Energy Levels of Magnetic Ions in Crystalline Electric Fields** [\\*M.T.Hutchings](#)

### 3. Magnetic anisotropy : the case of Co<sup>2+</sup>

•Co<sup>2+</sup>: 3d<sup>7</sup> S=3/2 L=3 J= 9/2  $^4F_{9/2}$

orbital degeneracy: 7 (/ 3>, /2>/1>/0>/-1>/-2>/-3> )

lifted by the crystal field

In an octahedral crystal field:

$$W(T_{1g}) = 3/5 \Delta \quad \text{triply degenerate}$$

$$W(T_{2g}) = -1/5 \Delta \quad \text{triply degenerate}$$

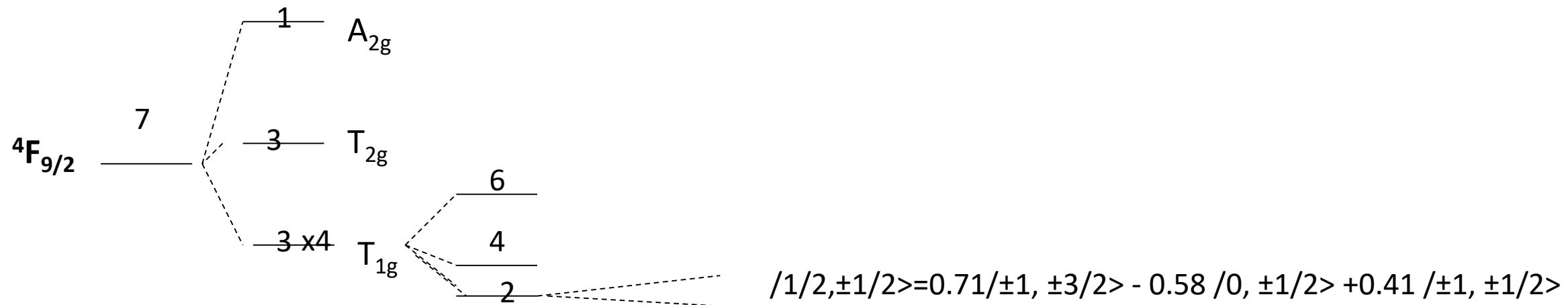
$$W(A_{2g}) = -6/5 \Delta \quad \text{non degenerate}$$

$\Delta = 30 \beta_c$  is the crystal field strength in the CF hamiltonian

Where  $\Delta$  is negative for 3 d<sup>7</sup>: the ground state is T<sub>1g</sub> and triply degenerate



### 3. Magnetic anisotropy : the case of Co<sup>2+</sup>



**high spin state Doublet:  $S_{eff} = \frac{1}{2}$**        $g = 4.33$

ex: Co<sup>2+</sup> in MgO:  $g=4.28$  **isotropic**

**Note**



In a distorted octahedra, strong g anisotropy

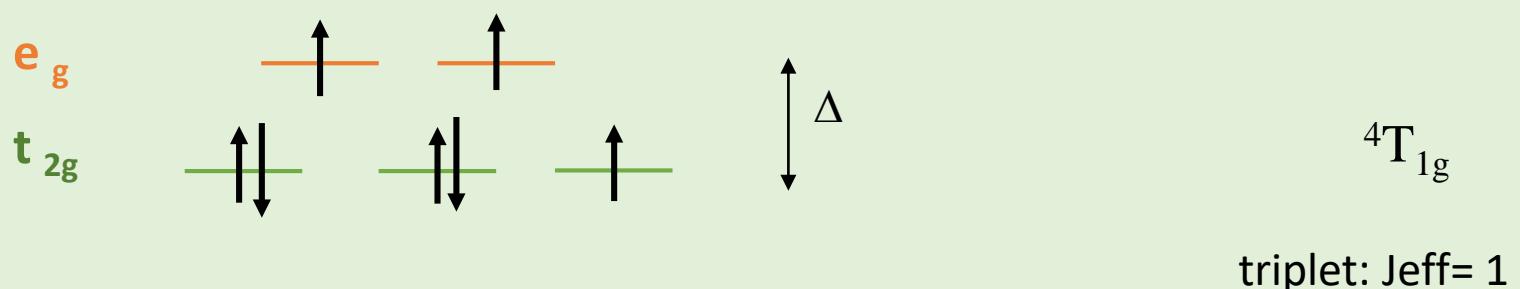
ex: Co<sup>2+</sup> in TiO<sub>2</sub>:  $g_{xx}=2.09$ ,  $g_{yy}=3.72$ ,  $g_{zz}=5.86$

### 3. Magnetic anisotropy : the case of $\text{Co}^{2+}$

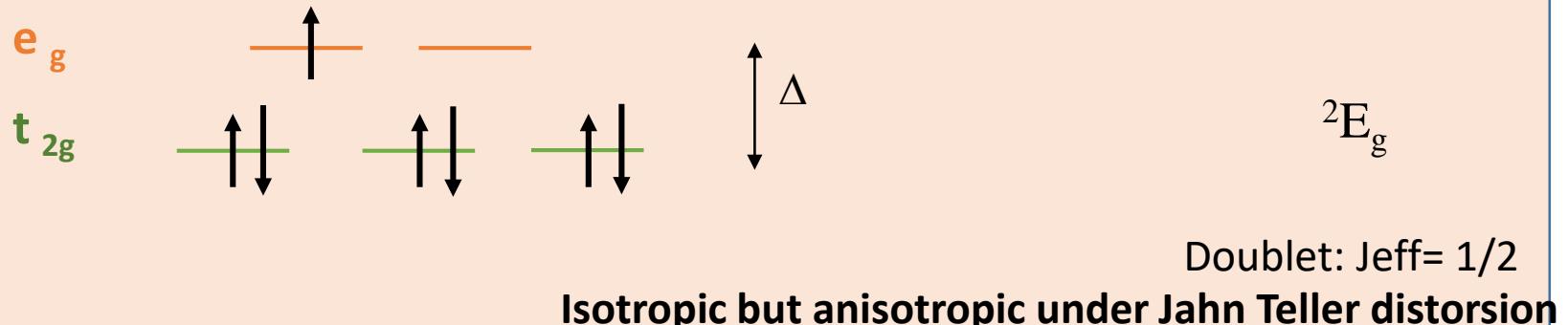
$\text{Co}^{2+}: 3d^7$

Orbital degeneracy

$S = 3/2$  high spin state  
When  $\Delta \ll U$  Hund coupling



$S = 1/2$  low spin state  
When  $\Delta \gg U$  Hund coupling

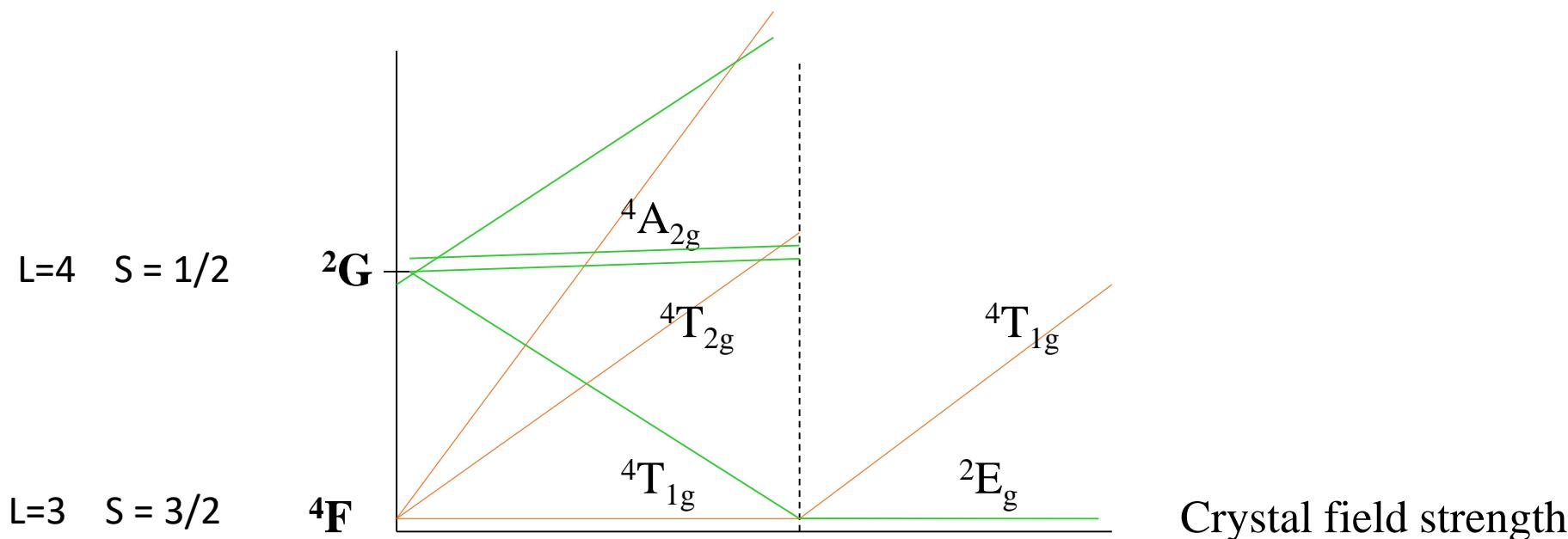


### 3. Magnetic anisotropy : the case of $\text{Co}^{2+}$

- $\text{Co}^{2+}$ :  ${}^4\text{F}_{9/2}$

octahedral crystal field

Dependence on the CF strength



**High spin state:**

Ground state  ${}^4\text{T}_{1g}$   
Triply degenerate  
( $L'=1$ )

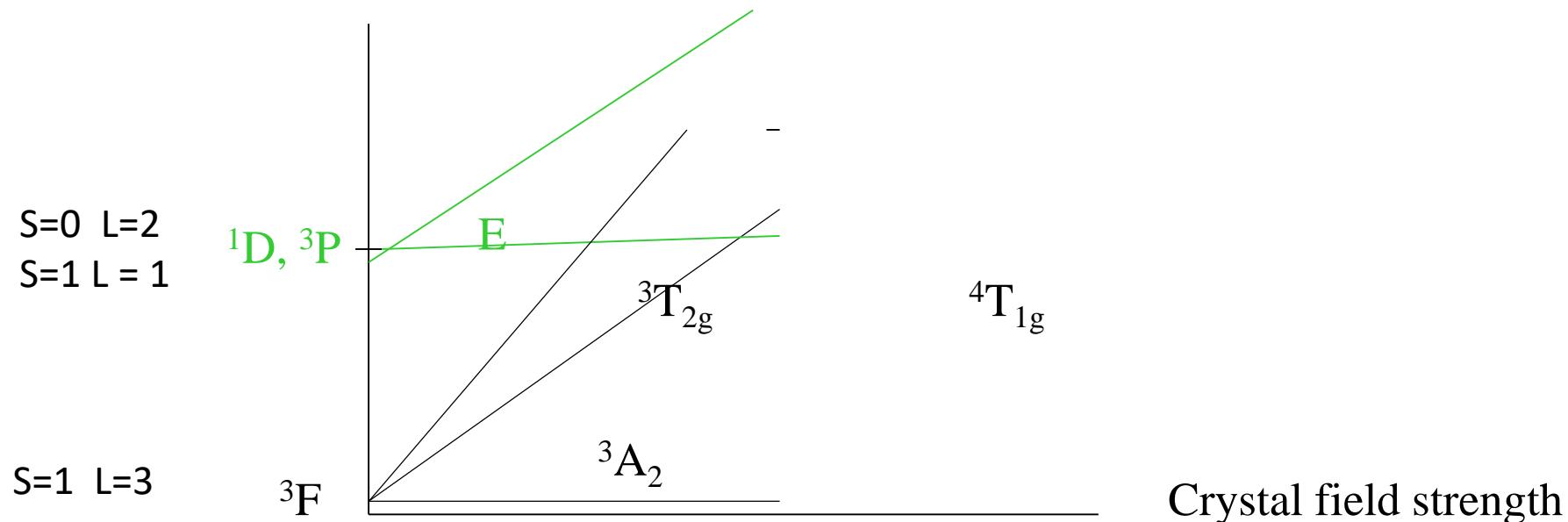
**Low spin state:**

ground state  
Doubly degenerate  ${}^2\text{E}_g$

### 3. Magnetic anisotropy : the case of $\text{Ni}^{2+}$

•  $\text{Ni}^{2+}$ :  $3d^8$   $S=1$ ,  $L=3$ ,  $J=4$   ${}^3F_4$

In octahedral crystal field:



Non degenerate ground state  ${}^3A_{2g}$

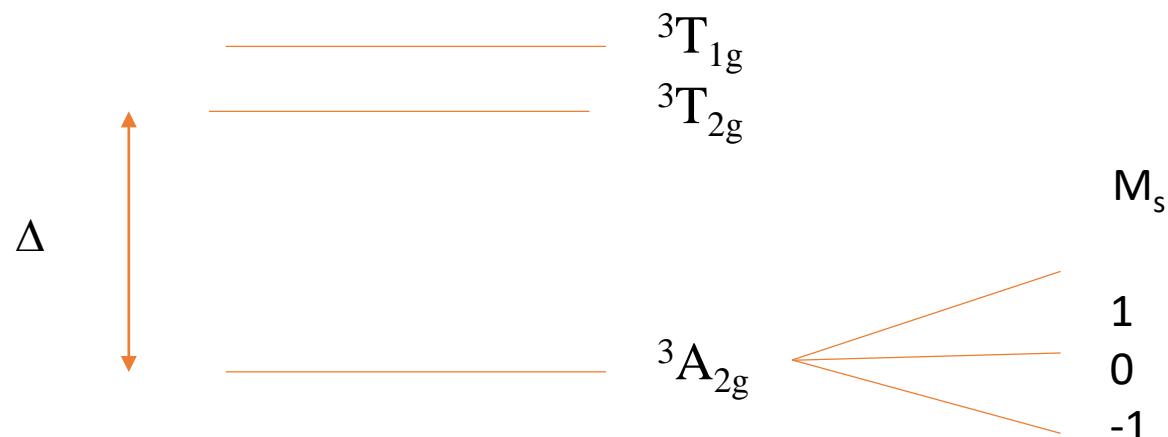
### 3. Magnetic anisotropy : the case of Ni<sup>2+</sup>

Ni<sup>2+</sup>     $^3F_4$

- in octahedral crystal field:  $^3A_{2g}$
- Spin orbit coupling with excited T2g state, S = 1

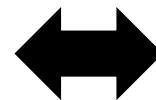
**g isotropic**   g=g<sub>e</sub>-8λ/Δ

- literature g=2.1-2.33    ( λ = -325 cm<sup>-1</sup>    Δ ≈ 12 000 cm<sup>-1</sup> )



### 3. Magnetic anisotropy : CF origin

Single ion orbitals in the CF environment created by the ion surroundings



Quantum calculations in a point charge model

Note

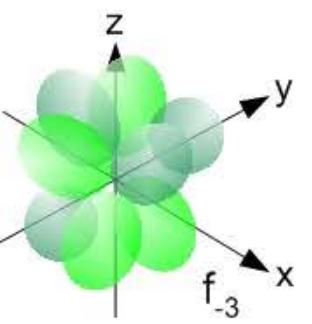
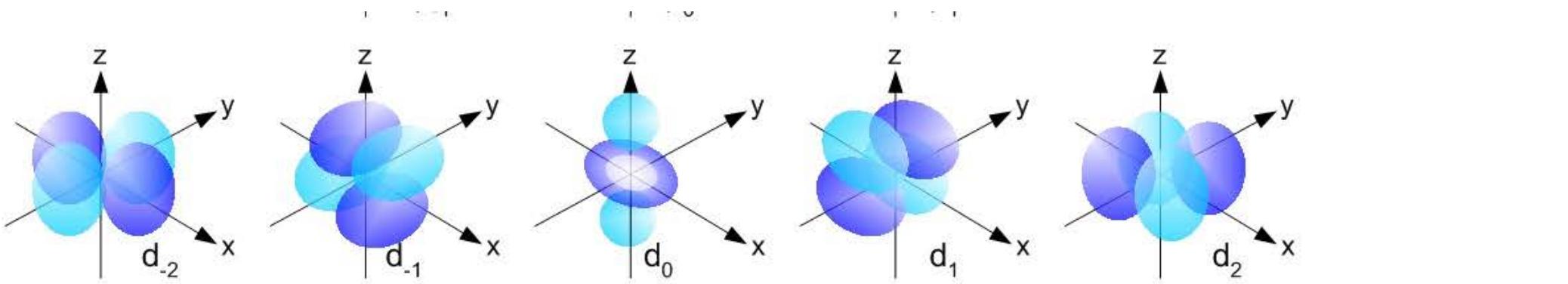


Limitation: charge screening effects from delocalized electrons : conduction electrons or covalency effects

### 3. Magnetic anisotropy : microscopic origin

Description of the single ion/element magnetic moment

3d elements



4f elements

# Crystal field: quantum mechanical treatment

Spectroscopic notation  
According to the total orbital momentum

L	0	1	2	3	4	5	6
symbol	S	P	D	F	G	H	I

$$2S+1 L_J$$

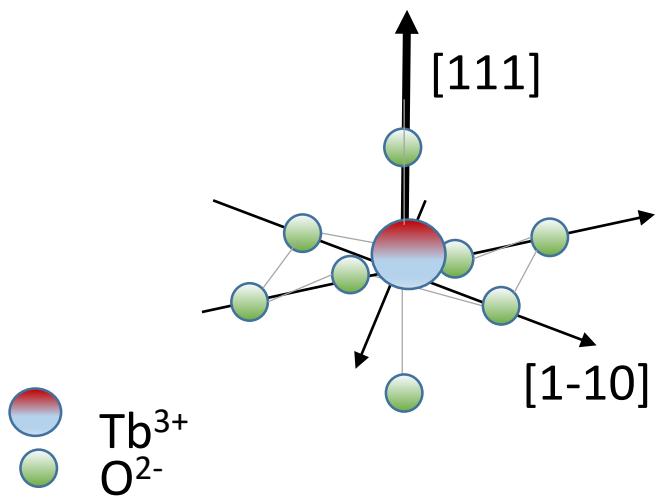
## 3d elements

No. of electrons	S Of the ground state	L	J	Orbital degeneracy	Spectroscopic symbol	examples
1	1/2	2	3/2	5	$^2D_{3/2}$	$Sc^{2+}, Ti^{3+}$
2	1	3	2	7	$^3F_2$	$Ti^{2+}, V^{3+}, Cr^{4+}$
3	3/2	3	3/2	7	$^4F_{3/2}$	$V^{2+}, Cr^{3+}, Mn^{4+}$
4	2	2	0	5	$^5D_0$	$Cr^{2+}, Mn^{3+}$
5	5/2	0	5/2	1	$^6S_{5/2}$	$Mn^{2+}, Fe^{3+}$
6	2	2	4	5	$^5D_4$	$Fe^{2+}$
7	3/2	3	9/2	7	$^4F_{9/2}$	$Co^{2+}, Ni^{3+}$
8	1	3	4	7	$^3F_4$	$Ni^{2+}, Cu^{3+}$
9	1/2	2	5/2	5	$^2D_{5/2}$	$Cu^{2+}$

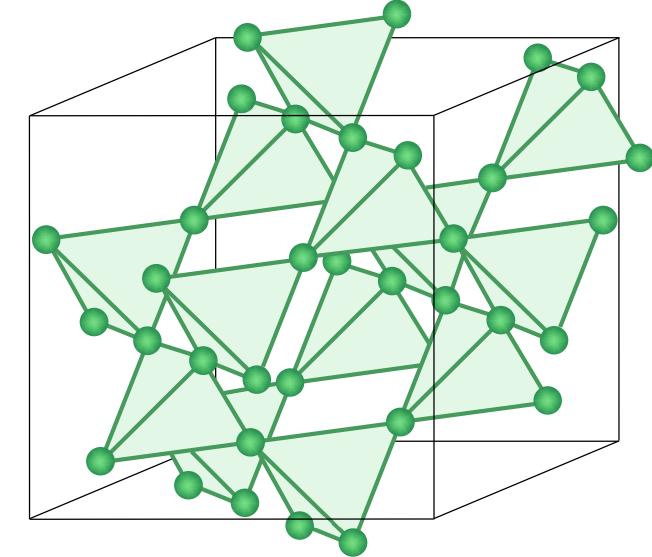
## 4f elements

No. of electrons	S Of the ground state	L	J	Orbital degeneracy	Spectroscopic symbol	examples
1	1/2	3	5/2	7	$^2F_{5/2}$	$Ce^{3+}$
2	1	5	4	11	$^3H_4$	$Pr^{3+}$
3	3/2	6	9/2	13	$^4I_{9/2}$	$Nd^{3+}$
4	2	6	4	13	$^5I_4$	$Pm^{3+}$
5	5/2	5	5/2	11	$^6H_{5/2}$	$Sm^{3+}$
6	3	3	0	7	$^7F_0$	$Eu^{2+}$
7	7/2	0	7/2	0	$^8S_{7/2}$	$Gd^{3+}$
8	3	3	6	7	$^7F_6$	$Tb^{3+}$
9	5/2	5	15/2	11	$^6H_{15/2}$	$Dy^{3+}$
10	2	6	8	13	$^5I_8$	$Ho^{3+}$
11	3/2	6	15/2	13	$^4I_{15/2}$	$Er^{3+}$
12	1	5	6	11	$^3H_6$	$Tm^{3+}$
13	1/2	3	7/2	7	$^2F_{7/2}$	$Yb^{3+}$

### 3. Magnetic anisotropy : the case of Tb<sup>3+</sup> in the pyrochlore Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>



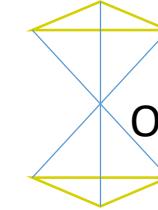
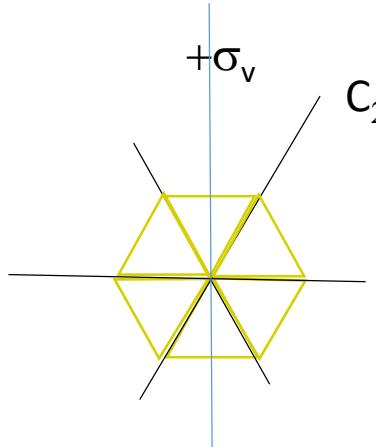
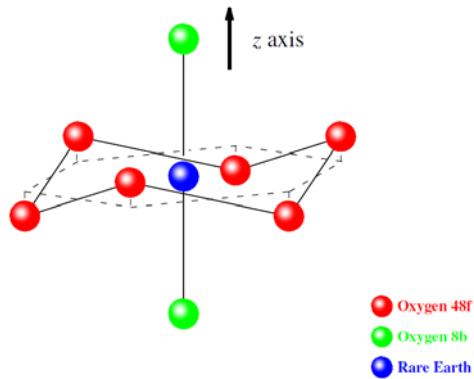
D3d symmetry



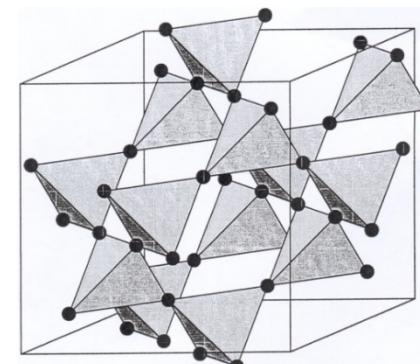
Quantum Spin ice

$$\hat{\mathcal{H}}_{\text{CF}} = B_2^0 \hat{\mathcal{O}}_2^0 + B_4^0 \hat{\mathcal{O}}_4^0 + B_4^3 \hat{\mathcal{O}}_4^3 + B_6^0 \hat{\mathcal{O}}_6^0 + B_6^3 \hat{\mathcal{O}}_6^3 + B_6^6 \hat{\mathcal{O}}_6^6,$$

### 3. Tb<sup>3+</sup> in the pyrochlore Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>



**D3d**= C3 principal axes along [111]=*z* + 3*C*<sub>2</sub> axis along [1-10]=*x* +120°+120°  
+ 3  $\sigma_v$  mirrors bisecting the angles formed by pairs of *C*<sub>2</sub> axes **centrosymmetric**  
Tb<sup>3+</sup> (16d) surrounded by 6 O<sup>2-</sup> (O1 at 48f) at 0.250 nm and 2 O<sup>2-</sup> (O2 at 8b) at 0.225 nm  
along [111] **centrosymmetric**



### 3. Tb<sup>3+</sup> in the pyrochlore Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>

$$\hat{\mathcal{H}}_{\text{CF}} = B_2^0 \hat{\mathcal{O}}_2^0 + B_4^0 \hat{\mathcal{O}}_4^0 + B_4^3 \hat{\mathcal{O}}_4^3 + B_6^0 \hat{\mathcal{O}}_6^0 + B_6^3 \hat{\mathcal{O}}_6^3 + B_6^6 \hat{\mathcal{O}}_6^6,$$

#### Stevens operators

$$\hat{X} = J(J+1)\hat{I},$$

$$\hat{\mathcal{O}}_2^0 = \hat{\mathcal{O}}_{z^2} = 3\hat{J}_z - \hat{X}$$

$$\hat{\mathcal{O}}_2^1 = \hat{\mathcal{O}}_{xz} = \frac{1}{2}(\hat{J}_z\hat{J}_x + \hat{J}_x\hat{J}_z)$$

$$\hat{\mathcal{O}}_2^{-1} = \hat{\mathcal{O}}_{yz} = \frac{1}{2}(\hat{J}_z\hat{J}_y + \hat{J}_y\hat{J}_z)$$

$$\hat{\mathcal{O}}_2^2 = 2\hat{\mathcal{O}}_{x^2-y^2} = \frac{1}{2}(\hat{J}_+^2 + \hat{J}_-^2) = \hat{J}_x^2 - \hat{J}_y^2$$

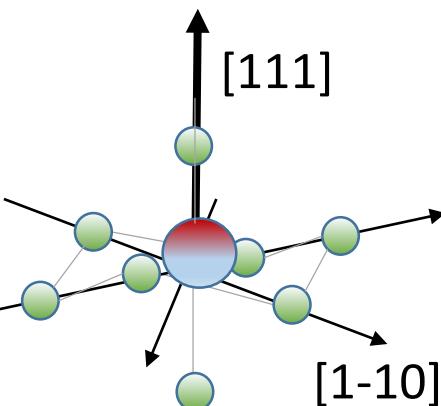
$$\hat{\mathcal{O}}_2^{-2} = 2\hat{\mathcal{O}}_{xy} = -\frac{i}{2}(\hat{J}_+^2 - \hat{J}_-^2) = \hat{J}_x\hat{J}_y + \hat{J}_y\hat{J}_x$$

$$\hat{\mathcal{O}}_4^0 = 35\hat{J}_z^4 - [30\hat{X} - 25\hat{I}]\hat{J}_z^2 + [3\hat{X}^2 - 6\hat{X}]$$

$$\hat{\mathcal{O}}_4^3 = \frac{1}{4}[\hat{J}_z(\hat{J}_+^3 + \hat{J}_-^3) + (\hat{J}_+^3 + \hat{J}_-^3)\hat{J}_z]$$

$$\hat{\mathcal{O}}_4^4 = \frac{1}{2}(\hat{J}_+^4 + \hat{J}_-^4)$$

$$\begin{aligned} \hat{\mathcal{O}}_6^0 &= 231\hat{J}_z^6 - [315\hat{X} - 735\hat{I}]\hat{J}_z^4 \\ &\quad + [105\hat{X}^2 - 525\hat{X} + 294\hat{I}]\hat{J}_z^2 \\ &\quad - [5\hat{X}^3 - 40\hat{X}^2 + 60\hat{X}] \end{aligned}$$



#### Whybourne operators operators

$$\widehat{\mathcal{O}}_n^m = (\lambda_n^m)^{-1}(\widehat{\mathcal{C}}_{-m}^n + (-1)^m \widehat{\mathcal{C}}_m^n)$$

TABLE II. Values of  $\lambda_n^m$  parameters involved in the CF Hamiltonian of the studied pyrochlore.

$\lambda_2^0$	$\lambda_4^0$	$\lambda_4^3$	$\lambda_6^0$	$\lambda_6^3$	$\lambda_6^6$
1/2	1/8	$-\sqrt{35}/2$	1/16	$-\sqrt{105}/8$	$\sqrt{231}/16$

$$\widehat{\mathcal{C}}_m^n = \sqrt{\frac{4\pi}{2n+1}} \widehat{Y}_n^m,$$

#### Other Stevens operators...

$$\widehat{\mathcal{O}}_n^m = \theta_n(J)\widehat{\mathcal{O}}_n^m,$$

TABLE III. Matrix element  $\theta_n(J)$  for Tb<sup>3+</sup> ( $J = 6$ ).

$\theta_2$	$\theta_4$	$\theta_6$
-1/99	2/16335	-1/891891

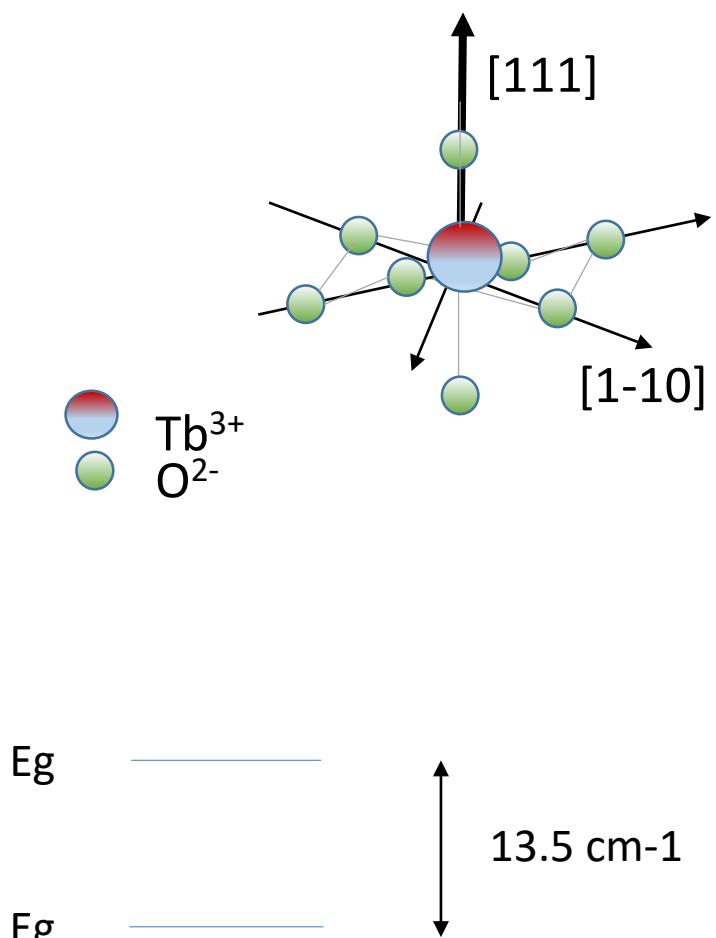
### 3. Tb<sup>3+</sup> in the pyrochlore Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>

$$\hat{\mathcal{H}}_{\text{CF}} = B_2^0 \hat{\mathcal{O}}_2^0 + B_4^0 \hat{\mathcal{O}}_4^0 + B_4^3 \hat{\mathcal{O}}_4^3 + B_6^0 \hat{\mathcal{O}}_6^0 + B_6^3 \hat{\mathcal{O}}_6^3 + B_6^6 \hat{\mathcal{O}}_6^6,$$

TABLE I. CF parameters used in the CF Hamiltonian.

$B_k^q$	meV	K
$B_2^0$	-0.26	-3.0
$B_4^0$	$4.5 \times 10^{-3}$	$5.2 \times 10^{-2}$
$B_4^3$	$-4.1 \times 10^{-2}$	$-4.8 \times 10^{-1}$
$B_6^0$	$-4.5 \times 10^{-6}$	$-5.2 \times 10^{-5}$
$B_6^3$	$-1.2 \times 10^{-4}$	$-1.4 \times 10^{-3}$
$B_6^6$	$-1.4 \times 10^{-4}$	$-1.6 \times 10^{-3}$

	$ \psi_+^0\rangle(0.0)$	$ \psi_-^0\rangle(0.0)$	$ \psi_+^1\rangle(13.5)$	$ \psi_-^1\rangle(13.5)$
$ 6\rangle$				
$ 5\rangle$	0.35		-0.89	
$ 4\rangle$		-0.91		
$ 3\rangle$				
$ 2\rangle$	0.18		-0.25	
$ 1\rangle$		-0.13		-0.14
$ 0\rangle$				
$  - 1\rangle$	-0.13		-0.11	
$  - 2\rangle$		-0.18		0.25
$  - 3\rangle$				
$  - 4\rangle$		0.91		
$  - 5\rangle$			0.35	-0.89
$  - 6\rangle$				



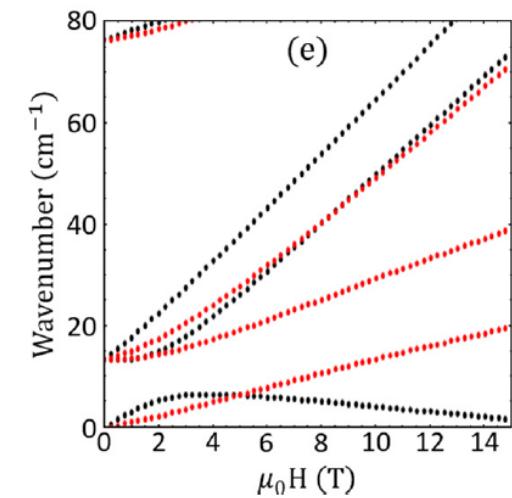
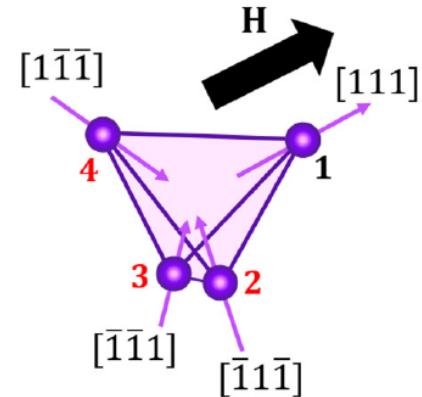
$B_k^q$  parameters have been fitted using the experimental values of the excited states energies

### 3. Tb<sup>3+</sup> in the pyrochlore Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>

$$\hat{\mathcal{H}}_{\text{CF}} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^3 \hat{O}_4^3 + B_6^0 \hat{O}_6^0 + B_6^3 \hat{O}_6^3 + B_6^6 \hat{O}_6^6,$$

TABLE I. CF parameters used in the CF Hamiltonian.

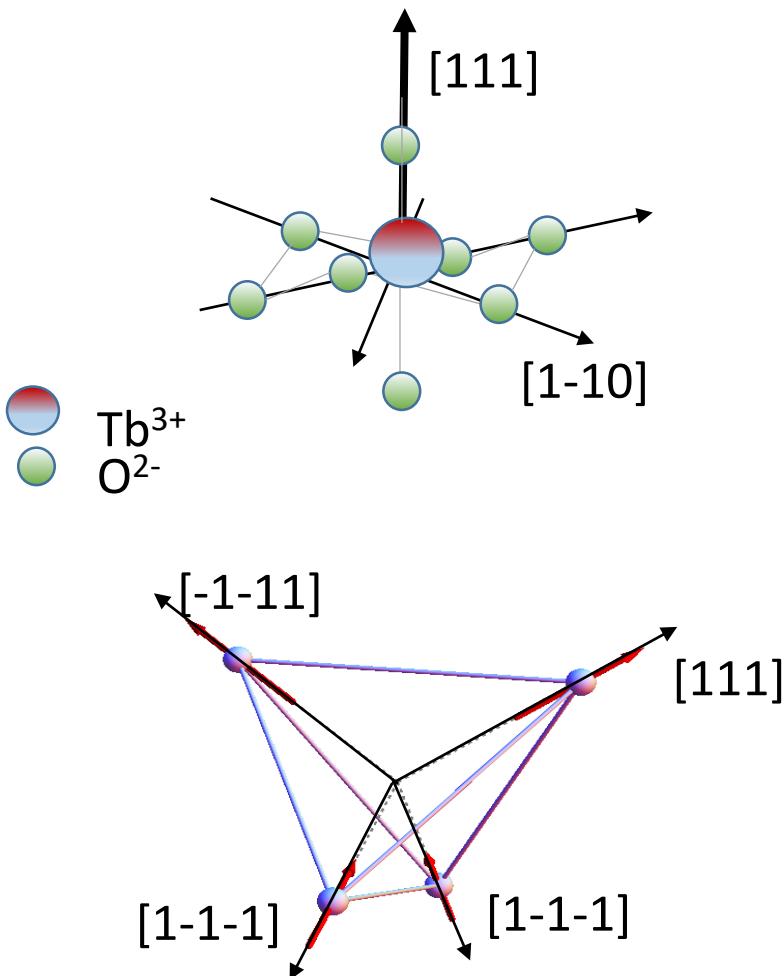
$B_k^q$	meV	K
$B_2^0$	-0.26	-3.0
$B_4^0$	$4.5 \times 10^{-3}$	$5.2 \times 10^{-2}$
$B_4^3$	$-4.1 \times 10^{-2}$	$-4.8 \times 10^{-1}$
$B_6^0$	$-4.5 \times 10^{-6}$	$-5.2 \times 10^{-5}$
$B_6^3$	$-1.2 \times 10^{-4}$	$-1.4 \times 10^{-3}$
$B_6^6$	$-1.4 \times 10^{-4}$	$-1.6 \times 10^{-3}$



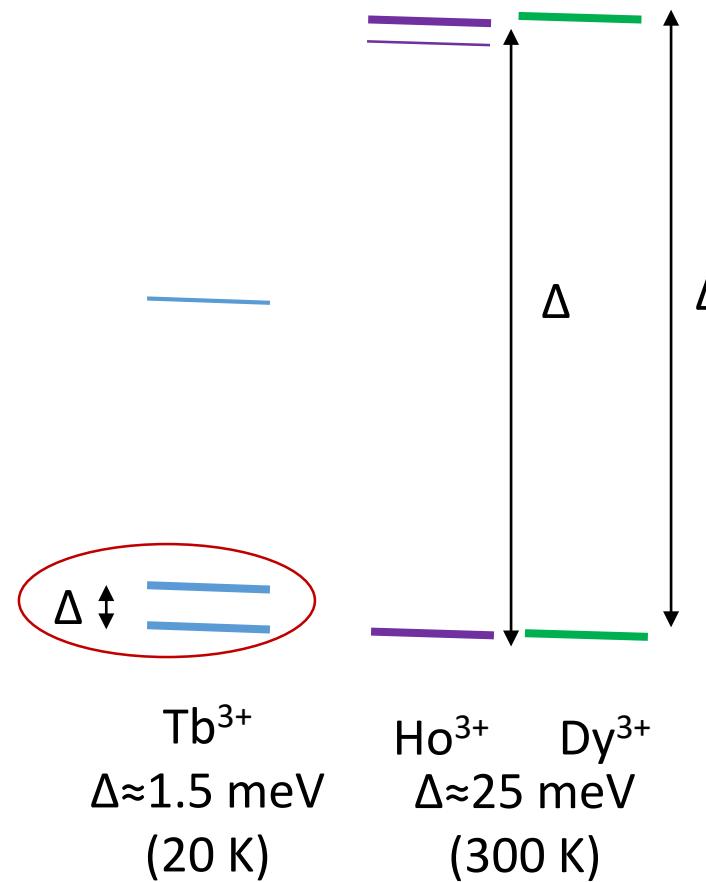
**Uniaxial Ising spins** or the ground and first excited state  
 OK spin ice BUT first excited state close in energy  $\rightarrow$  quantum spin ice

# $\text{Tb}_2\text{Ti}_2\text{O}_7$ peculiarities: Crystal Electric Field (CEF)

Local symmetry: D<sub>3d</sub>



Crystal Electric Field levels :



Weak Ising: Crystal Electric Field (CEF) level at 20 K (300 K for  $\text{Ho}_2\text{Ti}_2\text{O}_7$ )

# Magnetic anisotropies

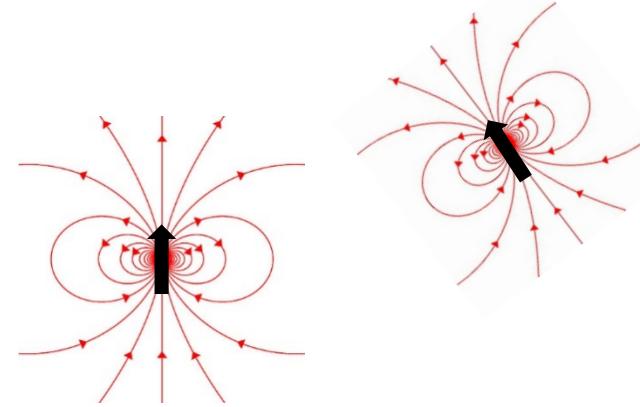
1. Importance of magnetic anisotropy
2. Single ion Magnetic anisotropy: phenomenological description
3. Single ion Magnetic anisotropy: microscopic origin
- 4. Exchange anisotropy**
5. Examples with magneto-electric effects

## 4. Exchange anisotropy

The exchange energy between two ions depends on the direction of the magnetic moment of each ion

Dipolar anisotropy between two magnetic elements of magnetic moment  $\mu_i$  and  $\mu_j$  at a distance  $r_{ij}$  from each other :

$$\mathcal{H}_{\text{dip}} = \sum_{\substack{i,j \neq j \\ i}} \frac{1}{r_{ij}^3} [\mu_i \cdot \mu_j - 3(\mu_i \cdot \hat{r}_{ij})(\mu_j \cdot \hat{r}_{ij})] \times \frac{\mu_0}{4\pi}$$



All the more large that the **TOTAL magnetic moments** are large :

$\text{Ho}^{3+}, \text{Dy}^{3+} m=10\mu_B$

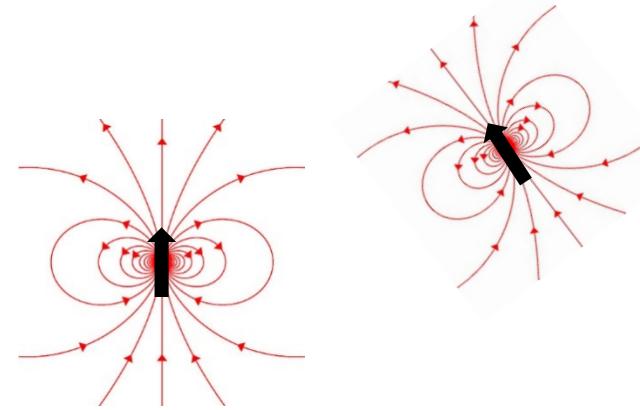
$\text{Er}^{3+}, \text{Tb}^{3+} m= 9 \mu_B$

In pyrochore  $\text{R}_2\text{Ti}_2\text{O}_7$  1-2 K

## 4. Exchange anisotropy

Dipolar anisotropy between two magnetic elements of magnetic moment  $\mu_i$  and  $\mu_j$  at a distance  $r_{ij}$  from each other :

$$\mathcal{H}_{\text{dip}} = \sum_{\substack{i,j \neq j \\ i}} \frac{1}{r_{ij}^3} [\mu_i \cdot \mu_j - 3(\mu_i \cdot \hat{r}_{ij})(\mu_j \cdot \hat{r}_{ij})] \times \frac{\mu_0}{4\pi}$$



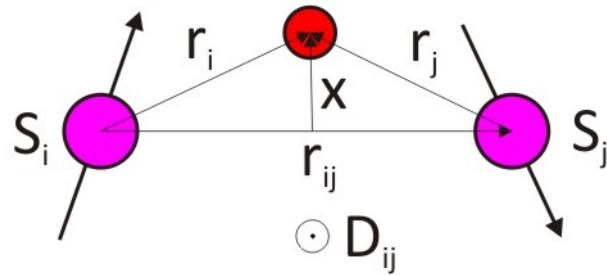
**Depends on the symmetry of the magnetic elements lattice:**

Cubic lattice (infinite) :  $\mathcal{H}_{\text{dip}} = 0$  to first order . Example: cubic  $\alpha$  Fe, even though  $\mu = 2.2 \mu_B$

## 4. Exchange anisotropy

The exchange energy between two ions depends on the direction of the magnetic moment of each ion

Dzyaloshinskii-Moriya interaction (DMI) or antisymmetric interaction



Wikipedia

$$e_{DM}^{i,j} = D_{ij} \cdot S_i \times S_j$$

Symmetry requirement for **the bond**: no inversion center  
See original paper by Moriya

Anisotropic Superexchange Interaction and Weak Ferromagnetism  
Tôru Moriya  
Phys. Rev. 120, 91 – Published 1 October 1960

## Anisotropic Superexchange Interaction and Weak Ferromagnetism

TÔRU MORIYA\*

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received May 25, 1960)

A theory of anisotropic superexchange interaction is developed by extending the Anderson theory of superexchange to include spin-orbit coupling. The antisymmetric spin coupling suggested by Dzialoshinski from purely symmetry grounds and the symmetric pseudodipolar interaction are derived. Their orders of magnitudes are estimated to be  $(\Delta g/g)$  and  $(\Delta g/g)^2$  times the isotropic superexchange energy, respectively. Higher order spin couplings are also discussed. As an example of antisymmetric spin coupling the case of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  is illustrated. In  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , a spin arrangement which is different from one accepted so far is proposed. This antisymmetric interaction is shown to be responsible for weak ferromagnetism in  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{MnCO}_3$ , and  $\text{CrF}_3$ . The paramagnetic susceptibility perpendicular to the trigonal axis is expected to increase very sharply near the Néel temperature as the temperature is lowered, as was actually observed in  $\text{CrF}_3$ .

## CRYSTAL SYMMETRY AND THE ANISOTRATIC SPIN COUPLING

In the preceding section a general theory of calculating the anisotropic superexchange interaction was developed. In an actual crystal, some components of the symmetric and antisymmetric coupling tensors vanish because of the crystal symmetry. Here we discuss the antisymmetric coupling (1.1) from the crystal symmetry point of view.

The coupling between two ions in the crystal is considered first. The two ions 1 and 2 are located at the points  $A$  and  $B$ , respectively, and the point bisecting the straight line  $AB$  is denoted by  $C$ . The following rules are obtained easily.

1. When a center of inversion is located at  $C$ ,  
 $\mathbf{D}=0$ .
2. When a mirror plane perpendicular to  $AB$  passes through  $C$ ,  
 $\mathbf{D} \parallel \text{mirror plane or } \mathbf{D} \perp AB$ .
3. When there is a mirror plane including  $A$  and  $B$ ,  
 $\mathbf{D} \perp \text{mirror plane}$ .

4. When a two-fold rotation axis perpendicular to  $AB$  passes through  $C$ ,

$$\mathbf{D} \perp \text{two-fold axis.}$$

5. When there is an  $n$ -fold axis ( $n \geq 2$ ) along  $AB$ ,

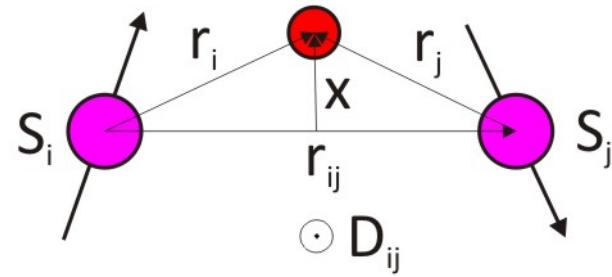
$$\mathbf{D} \parallel AB.$$

For example, for an  $\text{Fe}^{3+}-\text{Fe}^{3+}$  pair in  $\alpha\text{-Fe}_2\text{O}_3$  oriented along the three-fold axis,  $\mathbf{D}$  is parallel to the trigonal axis when the two ions are (1 or 4) and (2 or 3) in Fig. 1 and  $\mathbf{D}$  is zero for the other pairs. For the rutile type iron group difluorides,  $\mathbf{D}$  is not zero for the pairs of corner and body-center ions.  $\mathbf{D}$  for the nearest neighbor interaction is given by the following table.

	The Positions of the Ions	Direction	Magnitude
000	$\frac{1}{2}, \frac{1}{2}, \pm\frac{1}{2}$	$[1 \bar{1} 0]$	$\pm D$
000	$-\frac{1}{2}, -\frac{1}{2}, \pm\frac{1}{2}$	$[\bar{1} \bar{1} 0]$	$\pm D$
000	$-\frac{1}{2}, \frac{1}{2}, \pm\frac{1}{2}$	$[\bar{1} 1 0]$	$\pm D$
000	$\frac{1}{2}, -\frac{1}{2}, \pm\frac{1}{2}$	$[1 \bar{1} 0]$	$\pm D$

## 4. Exchange anisotropy

Dzyaloshinskii-Moriya interaction (DMI) or antisymmetric interaction



$$e_{DM}^{i,j} = D_{ij} \cdot S_i \times S_j$$

Will induce a rotation of the magnetic moment

weak ferromagnetism in antiferromagnet ( $\alpha\text{-Fe}_2\text{O}_3$ )

spiral or cycloidal phases

skyrmions

## 4. Exchange anisotropy

Anisotropic exchange :

$$H_{AE} = \mathbf{S}_i \cdot \Gamma_{i,j} \cdot \mathbf{S}_j,$$

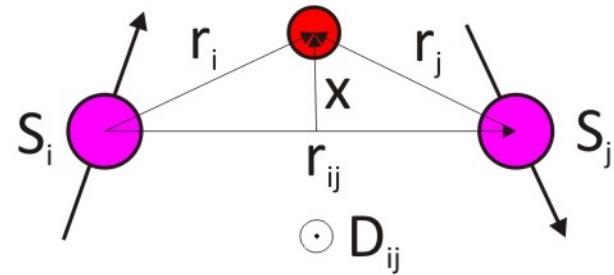
example

$$\Gamma_{1,2} = \begin{pmatrix} 0.00 & 0.00 & 0.00 \\ 0.00 & 0.05 & 0.12 \\ 0.00 & 0.12 & 0.05 \end{pmatrix}$$

That couples site 1 and 2 with their x,y,z components

## 4. Exchange anisotropy

Dzyaloshinskii-Moriya interaction (DMI) or antisymmetric interaction



$$e_{DM}^{i,j} = D_{ij} \cdot S_i \times S_j$$

Strength of DM anisotropy ( $D$ ) versus exchange anisotropy ( $\Gamma$ ) :  
a function of the anisotropy of the g factor  $\Delta g/g$

$$D \sim (\Delta g/g)J, \quad \Gamma \sim (\Delta g/g)^2 J.$$

T. Moriya PR 1960

DM: first order spin orbit effect

exchange anisotropy: second order spin orbit effect



Note

$D$  and  $\Gamma$  can be non zero even though there is no single ion anisotropy (no  $g$  anisotropy)  
It arises then from the couplings to the first excited multiplet.

## 4. Exchange anisotropy

Superexchange and beyond

Direct exchange

Double exchange

RKKY interactions in metals

through different orbitals (Goodenough Kanamori rules)

through different electronic bands



Build the appropriate , solvable Hamiltonian

Dimensionality of the spin

Form/ Strength /sign of the dominant interaction

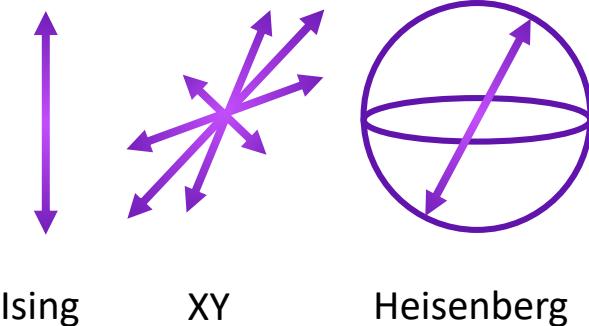
Magnetic network



Magnetic ground state

Static and dynamical properties

⋮ ⋮ ⋮



Ising

XY

Heisenberg

## 5. Measuring the magnetic anisotropy

### Static properties

Magnetization curve  
Torque  
Neutron scattering for the magnetic texture  
Magnetic imaging for nanomicroscale (AFM, ...)  
...

### Dynamical properties

Magnetic resonance  
Spin waves  
Spectroscopy  
...

Beware



When several magnetic sites or multiaxial system, the macroscopic properties do not reflect the single site properties ...

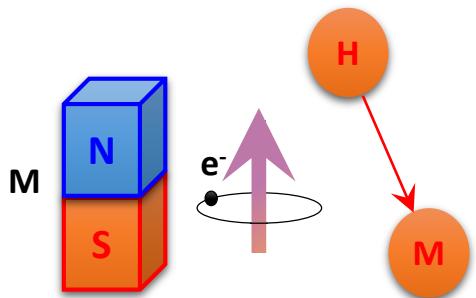
# Magnetic anisotropies

1. Importance of magnetic anisotropy
2. Single ion Magnetic anisotropy: phenomenological description
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5. Examples with magneto-electric effects

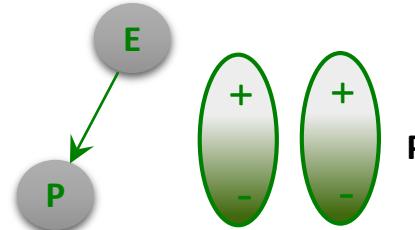
# 5. Example 1: electromagnons in multiferroics

## Static /dynamical properties

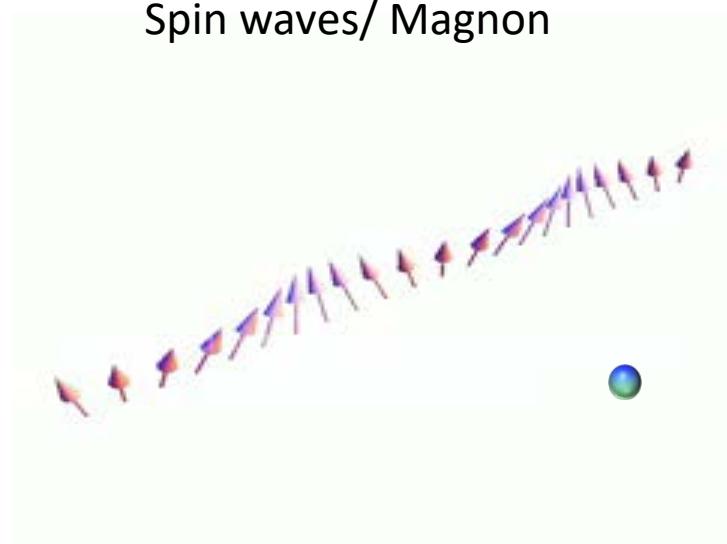
Magnetic moment / magnetic field



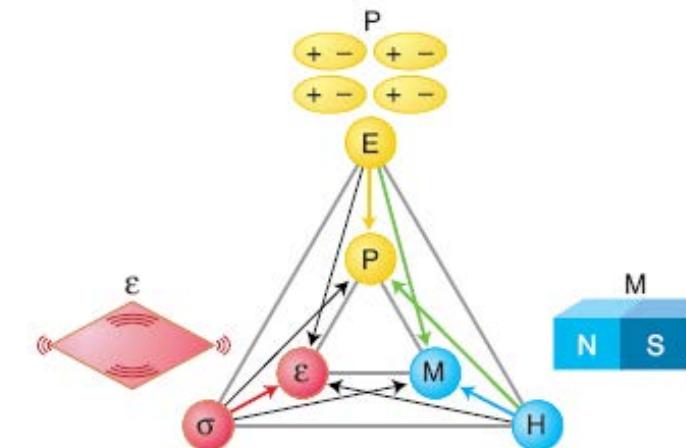
Dipolar electric moment / Electric field



Spin waves/ Magnon

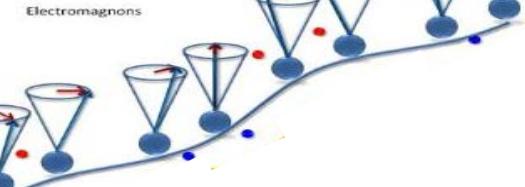


Lattice vibration / Phonon



Magneto-electric coupling

Electromagnon



A. PIMENOV et, Nature Physics 2006

# 5. Example 1: electromagnons in multiferroics

## Possible evidence for **electromagnons** in multiferroic manganites

A. PIMENOV et al, Nature Physics 2006

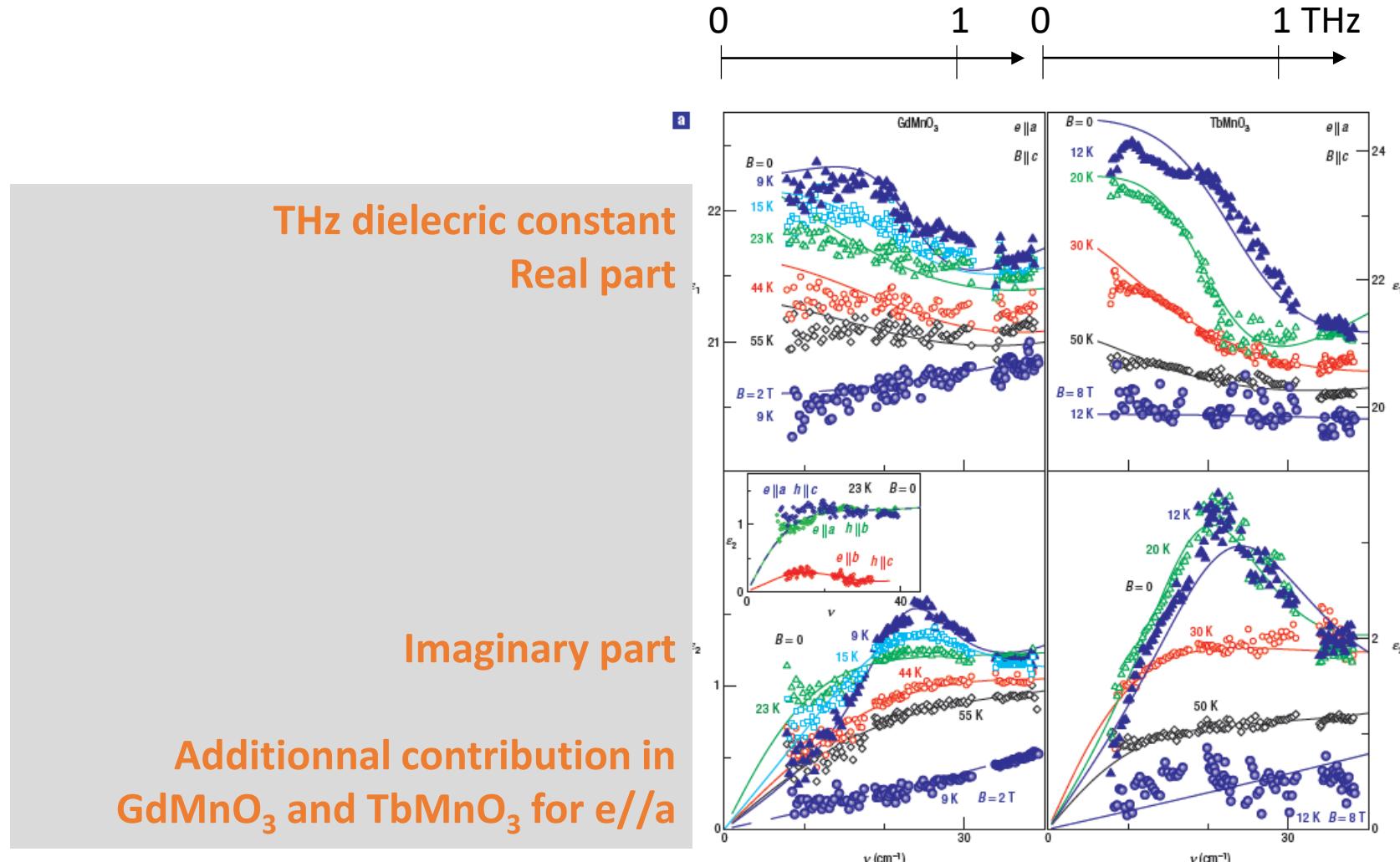
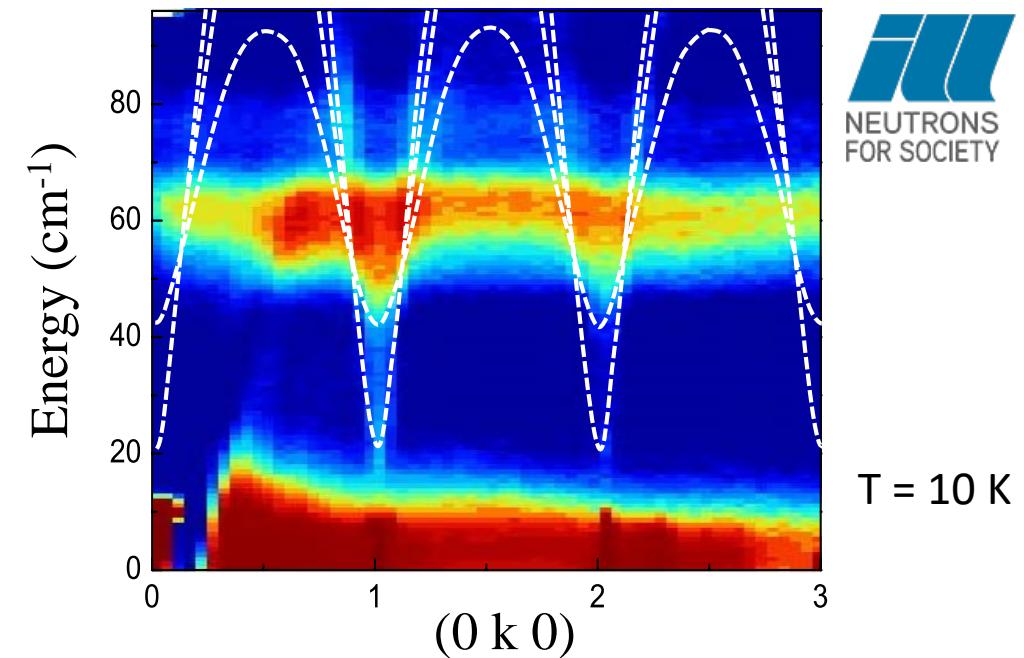


Figure 2 Spectra of electromagnons in  $\text{GdMnO}_3$  and  $\text{TbMnO}_3$ . a-d, Frequency dependence of the real (a,c) and imaginary (b,d) parts of the terahertz-dielectric function in  $\text{GdMnO}_3$  (a,b) and  $\text{TbMnO}_3$  (c,d) with  $e \parallel a$  and  $B \parallel c$ . Open symbols represent experimental data in zero external magnetic field and in the IC-AFM phase. Solid lines

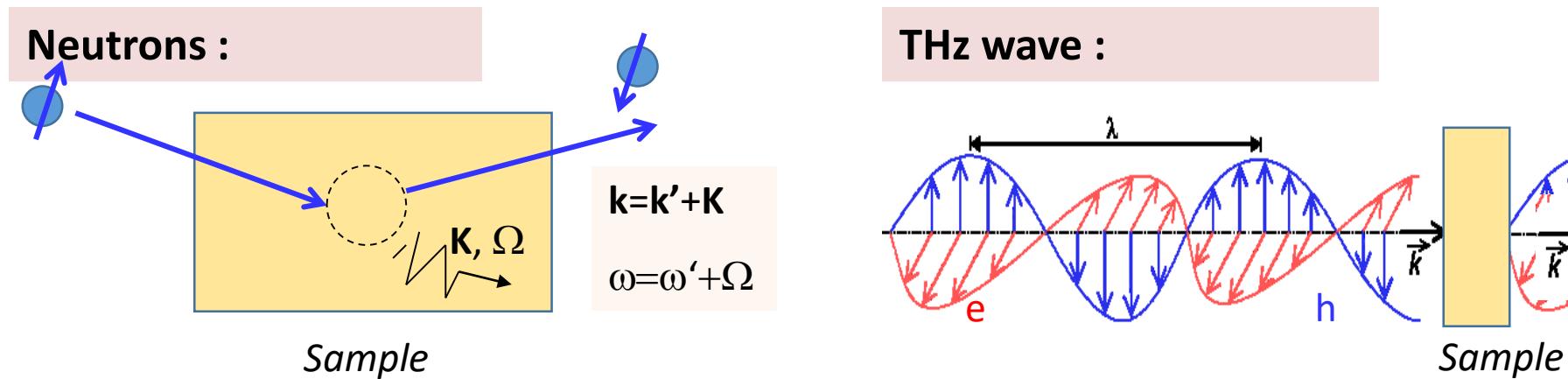
# 5. Electromagnons in the multiferroic h-ErMnO<sub>3</sub>

h-ErMnO<sub>3</sub> a type I multiferroic  
 $T_c = 800\text{K}$     $T_N(\text{Mn}) = 80\text{ K}$

Neutron inelastic scattering  
measurements



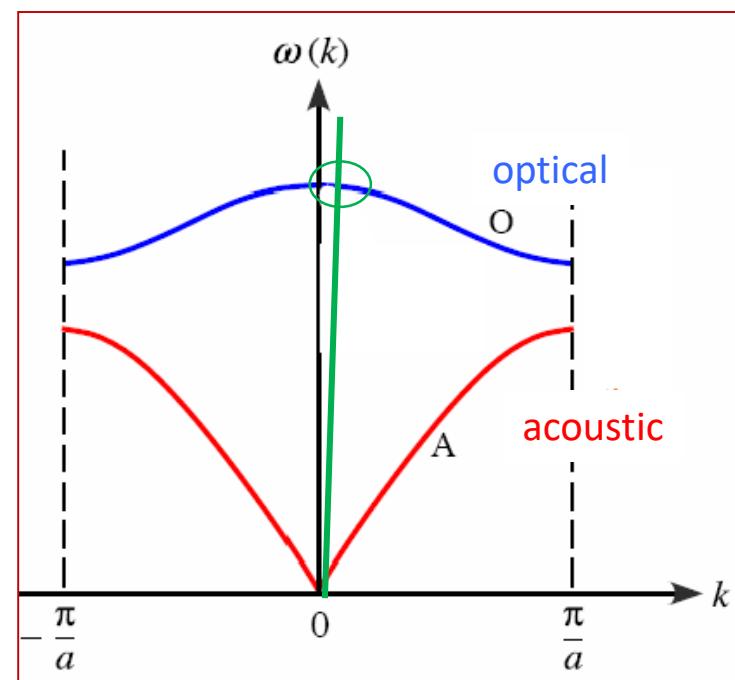
## 2. NEUTRON / THZ SPECTROSCOPY : COMPLEMENTARY TECHNIQUES



**DISPERSION CURVES**  
 $\Omega( K )$   
 $\chi_2(\Omega, K) \perp K$

**MAGNETIC AND ATOMIC PROBE**

Whole reciprocal space

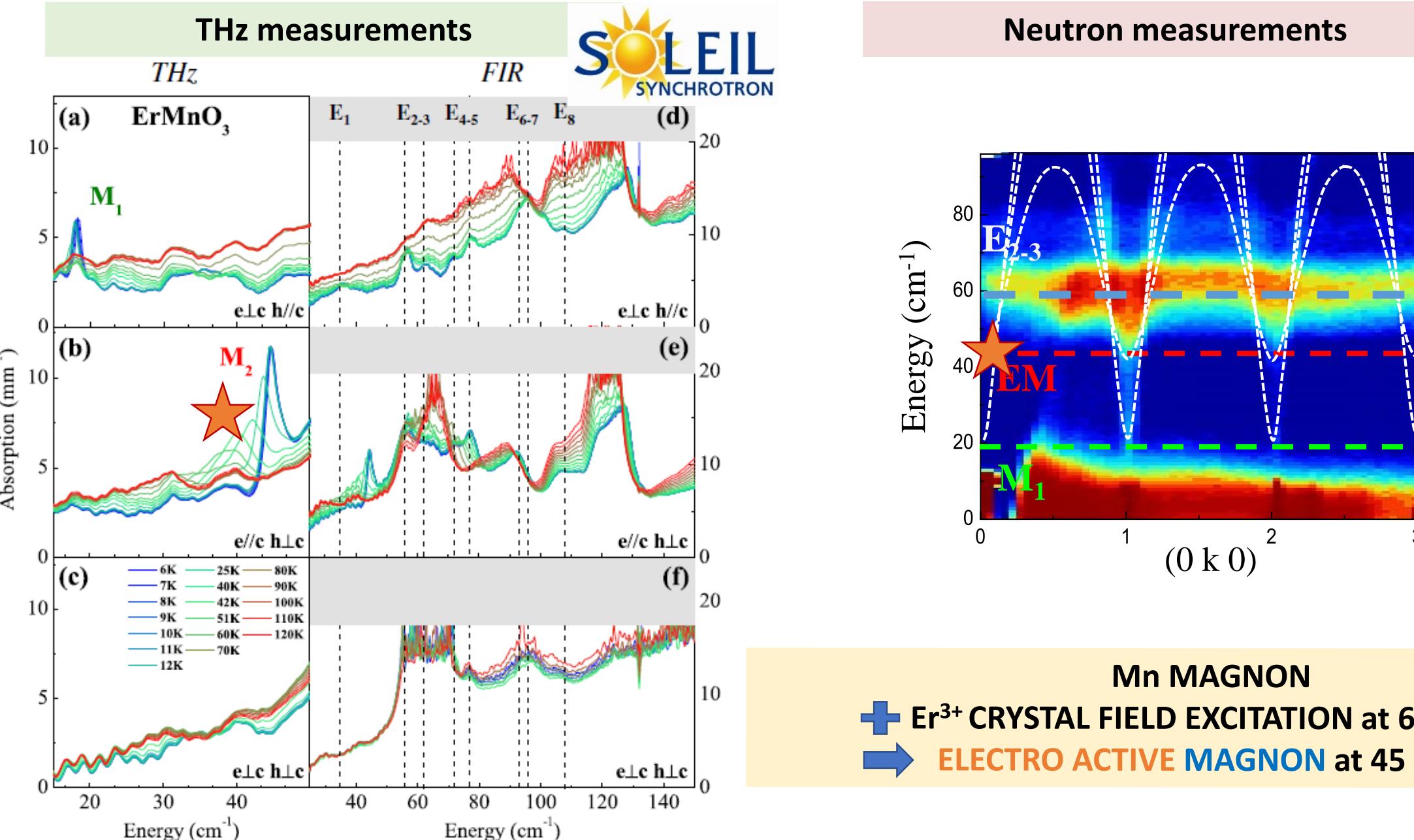


**ABSORPTION CURVES**  
 $\Omega( K \approx 0 )$   
 $\chi_2(\Omega, 0)$

**MAGNETIC AND ELECTRIC PROBE**

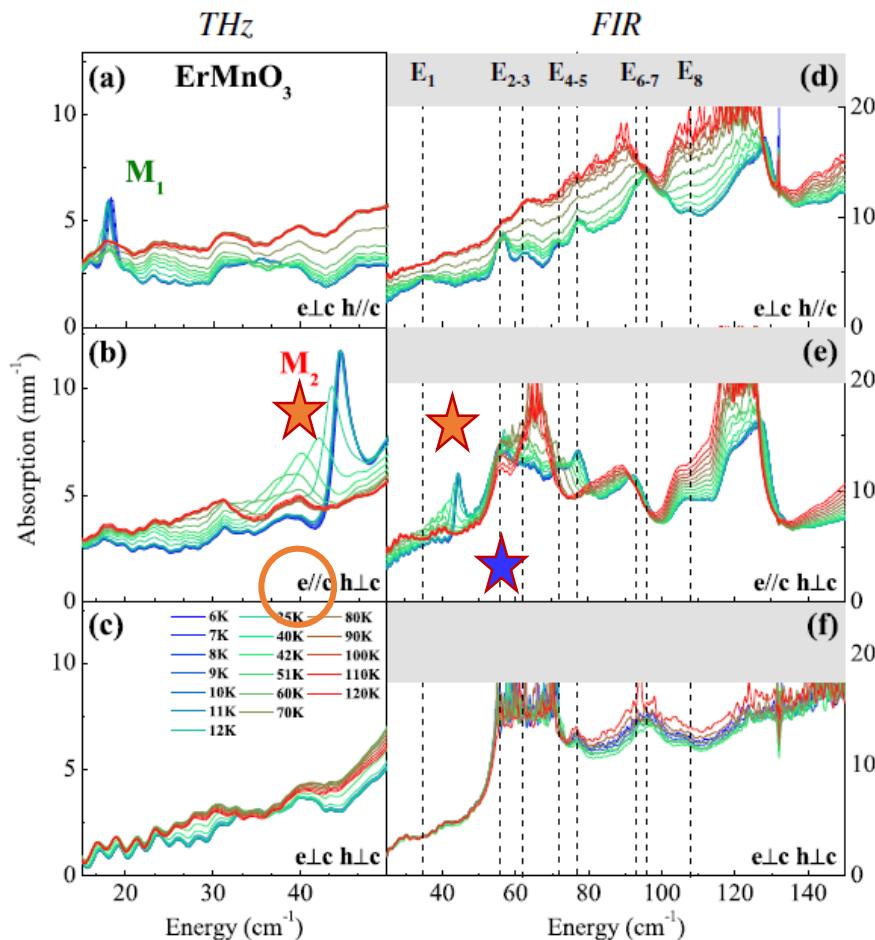
Smaller sample  
Increased energy resolution

## 2. Hexagonal manganites : $\text{ErMnO}_3$

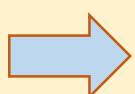
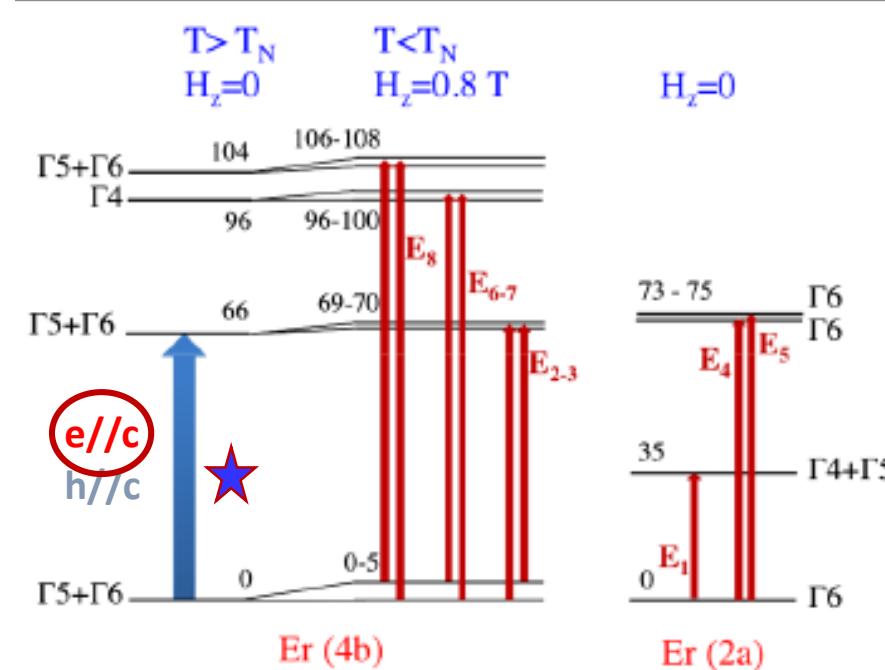


## 2. Hexagonal manganites : $\text{ErMnO}_3$

### THz measurements



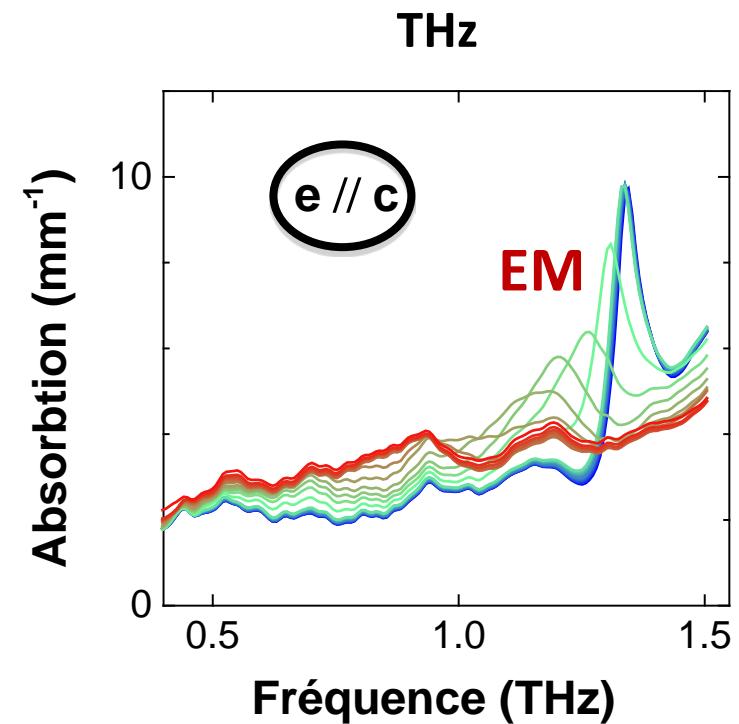
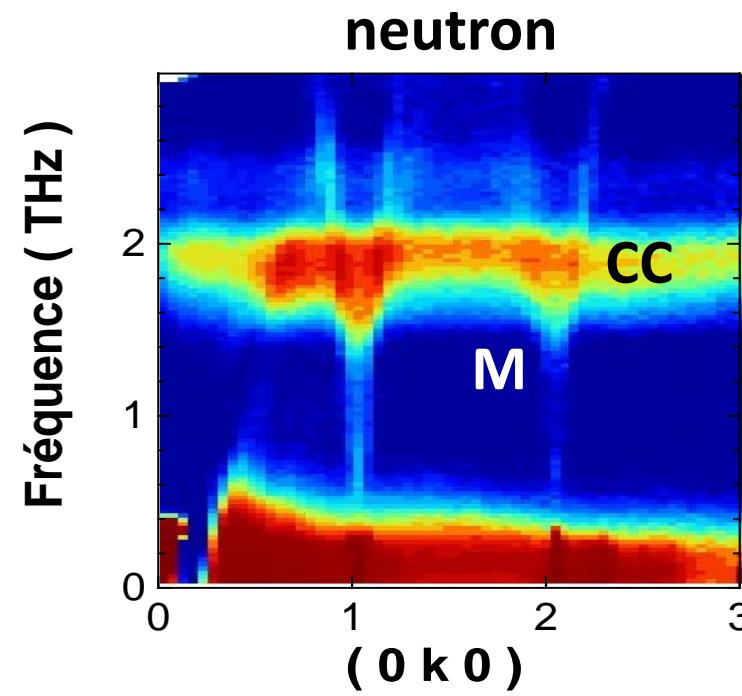
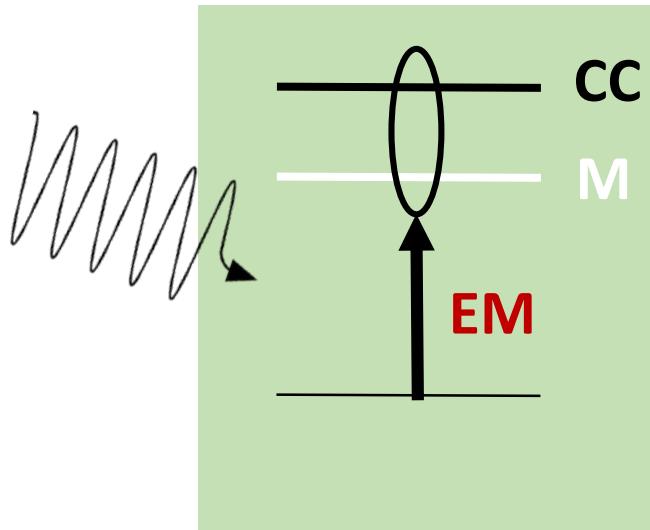
### Er Crystal field excitations



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

# EXAMPLE 1 : TRANSMUTATION OF A MAGNON into an ELECTRIC EXCITATION in the THz range

## Multiferroic h-ErMnO<sub>3</sub>

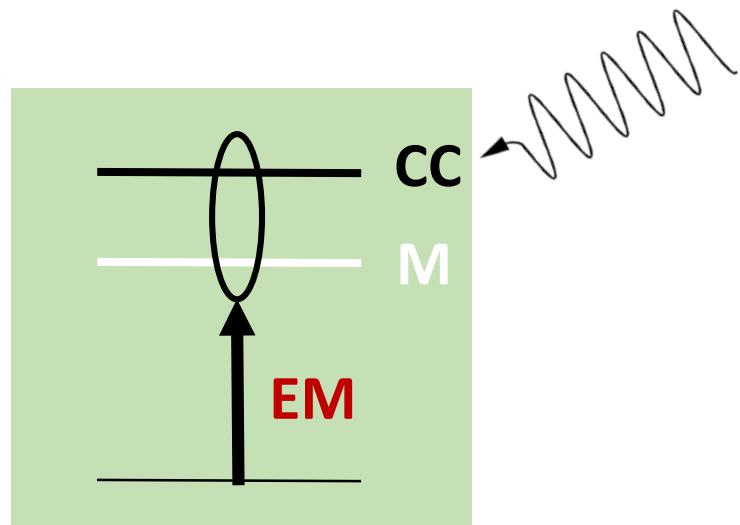


Towards manipulation of magnon through electric field...  
Check through pump probe experiment...

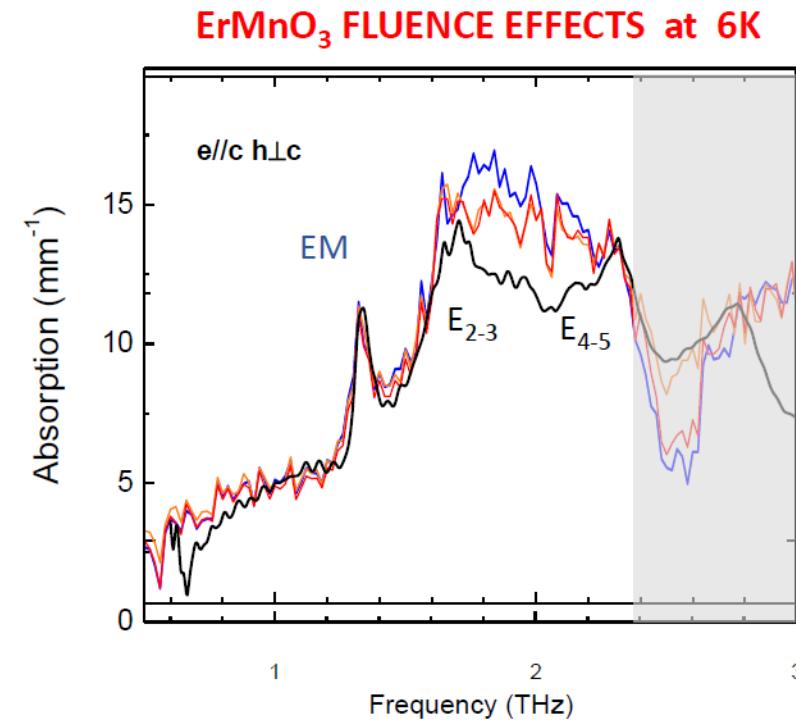
## 5. Example 2 : electro-magnetic monopoles in spin ices

THZ FEL

Pump probe experiment



TERAFERMI @ Trieste



ErMnO<sub>3</sub> THz spectrum at 6K.

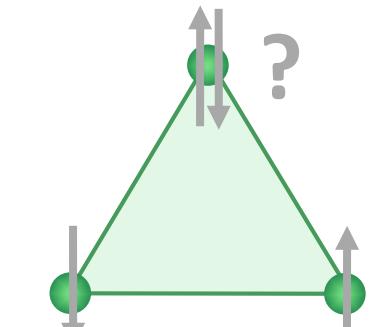
Black line: linear response from AILES@SOLEIL source. Red and blue

Red and blue lines:

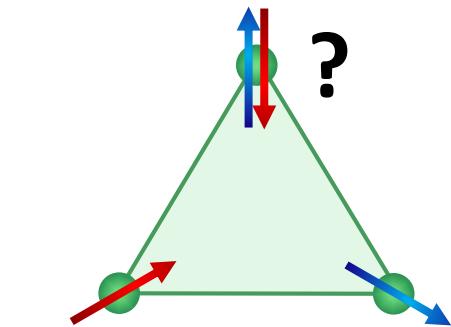
response from 0.54  $\mu\text{J}$  and 1.6  $\mu\text{J}$  pulses respectively provided by TERAFERMI.

# Magnetic frustration and spin ices

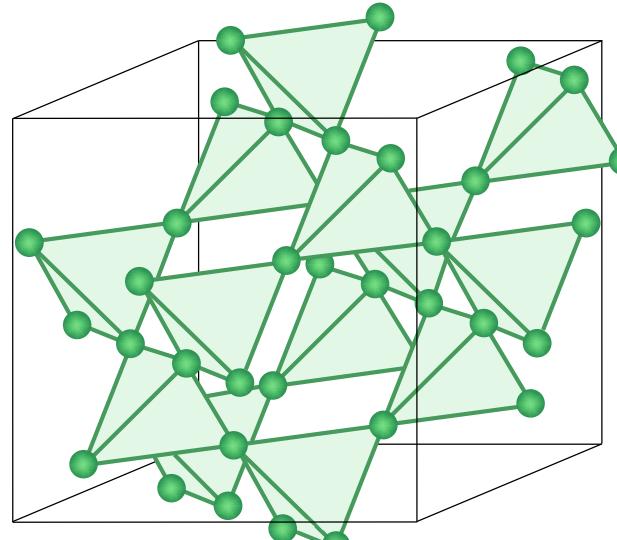
**Magnetic frustration :** One or several competing interactions can not be satisfied simultaneously



Antiferromagnetic interactions



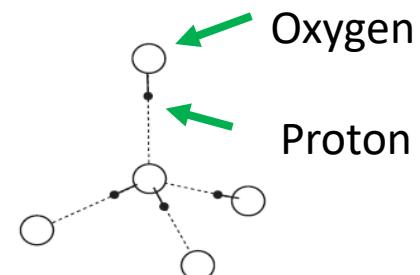
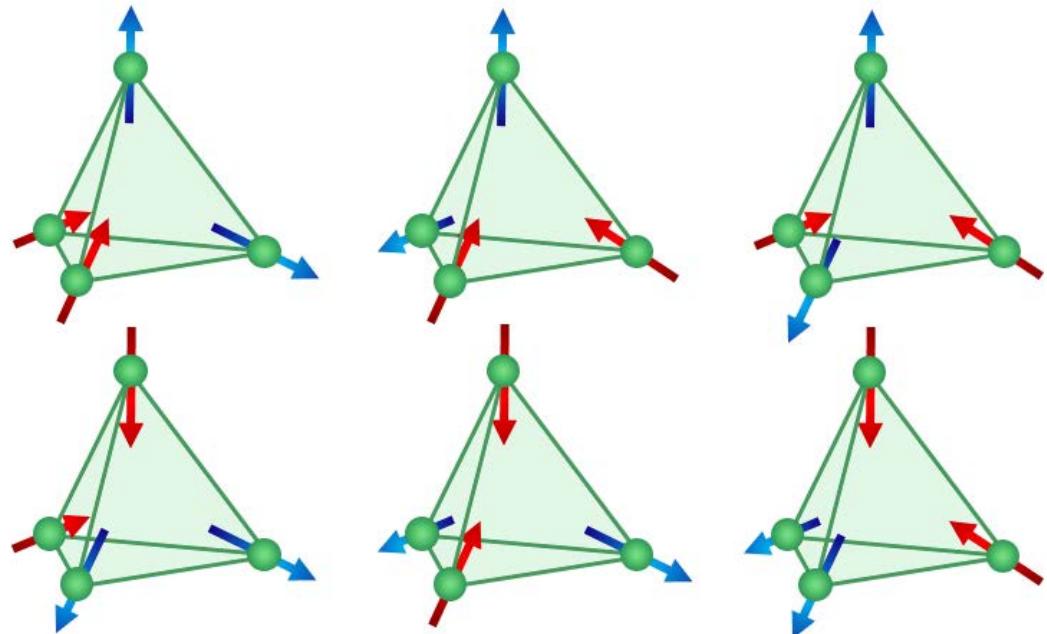
Ferromagnetic interactions +  
multiaxial anisotropy



Pyrochlore

**Spin ice :** multiaxial anisotropy + ferromagnetic interactions

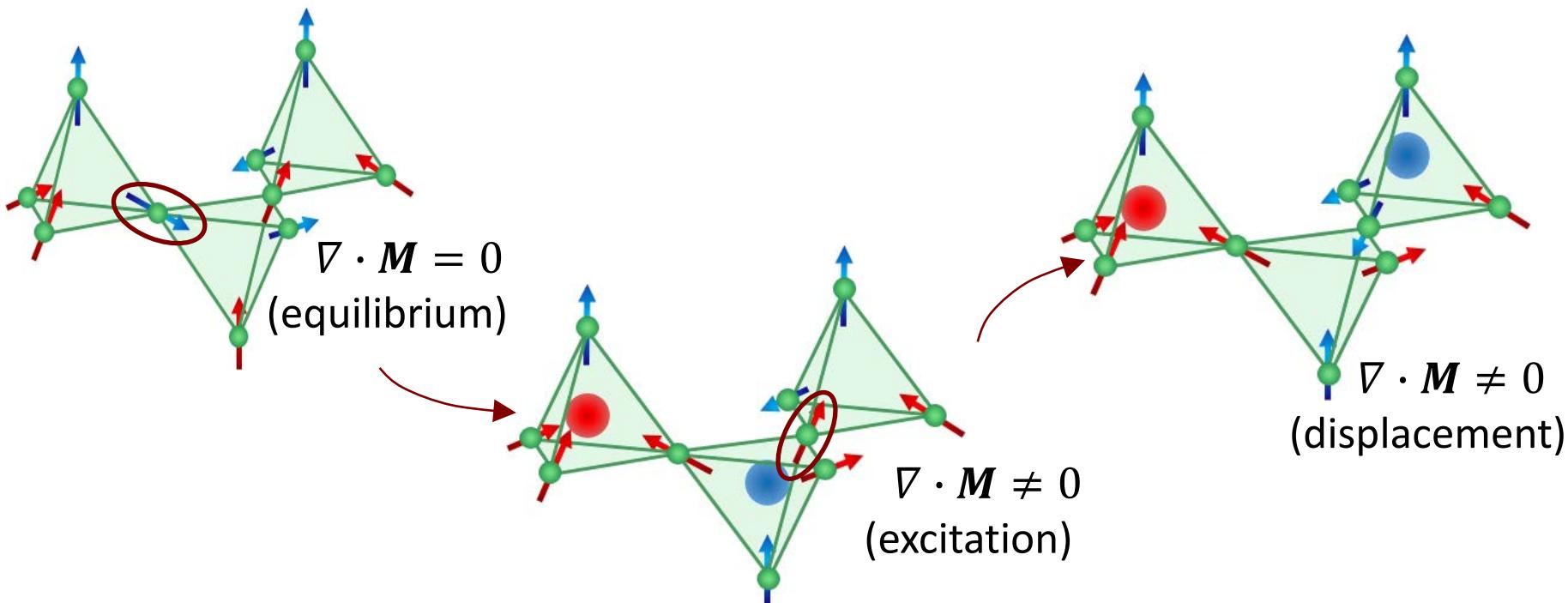
« 2 in – 2 out » degenerate state : ice rule



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

# Spin ices and magneto-electric effects

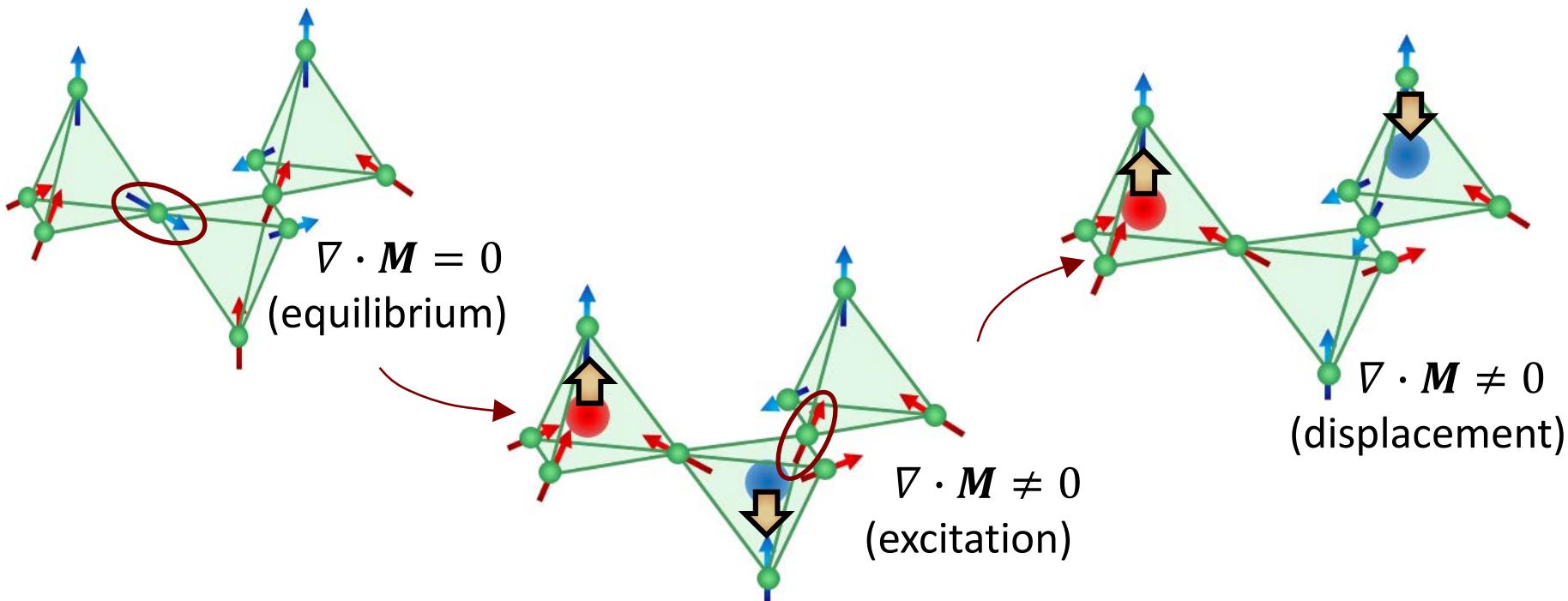
« 2 in – 2 out » spin ice



« magnetic monopoles »

# Spin ices and magneto-electric effects

« 2 in – 2 out » spin ice



« magnetic monopoles » + electric dipoles

ARTICLE

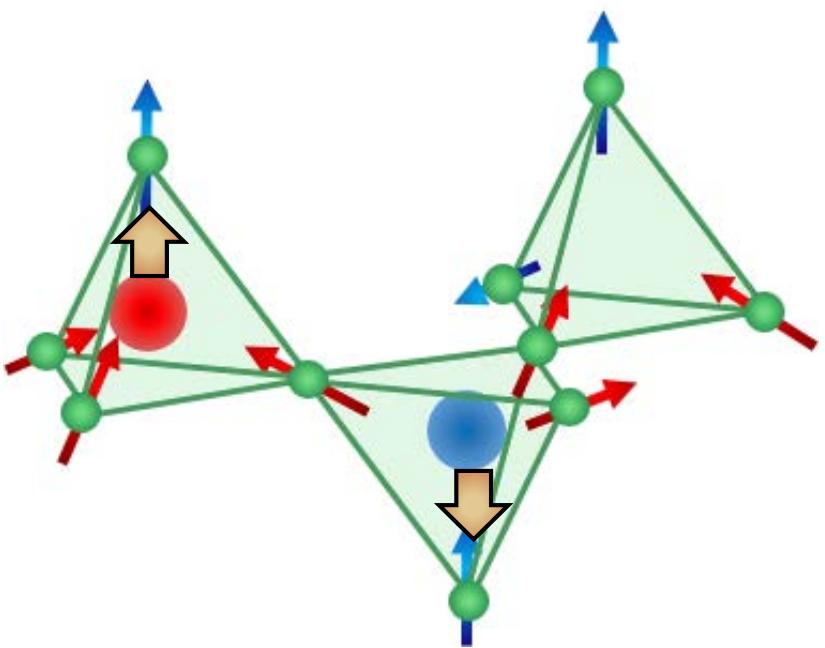
Received 23 Feb 2012 | Accepted 14 May 2012 | Published 19 Jun 2012

DOI: 10.1038/ncomms1904

Electric dipoles on magnetic monopoles in spin ice

D.I. Khomskii

# Spin ices and magneto-electric effects



## Theoretical investigations

- D. I. Khomskii, *Nat. Commun.* 3: 904 (2012)  
L. Jaubert and R. Moessner, *Phys. RevB* 91: 214422(2015)

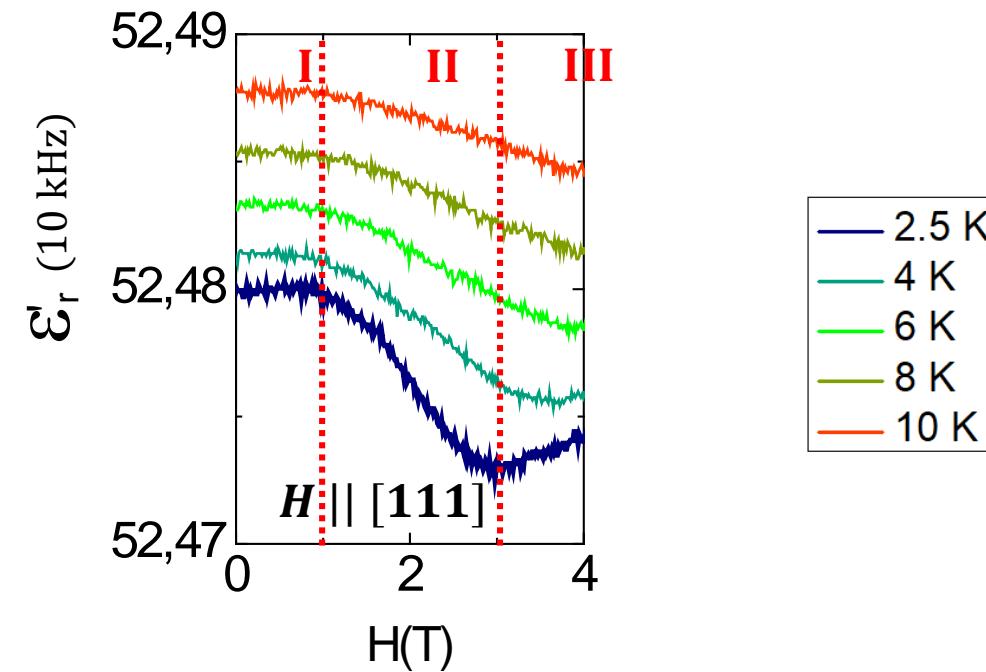
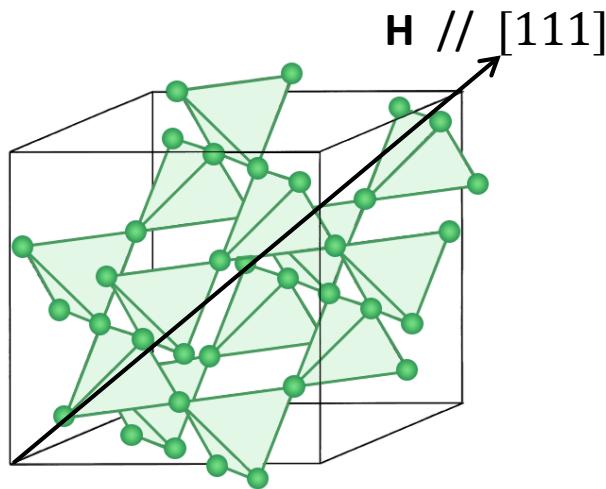
## Experimental evidences

- P. Grams et al, *Nat. Commun.* 5: 4853 (2013)  
in  $\text{Dy}_2\text{Ti}_2\text{O}_7$   
D. Liu et al , *J. Appl. Phys.* 113: 17D901 (2013)  
in  $\text{Ho}_2\text{Ti}_2\text{O}_7$   
F. Jin et al, *Phys. Rev. Lett.* 124: 087601 (2020)  
in  $\text{Tb}_2\text{Ti}_2\text{O}_7$

## Magneto-electric effects in the spin ice compound $\text{Ho}_2\text{Ti}_2\text{O}_7$

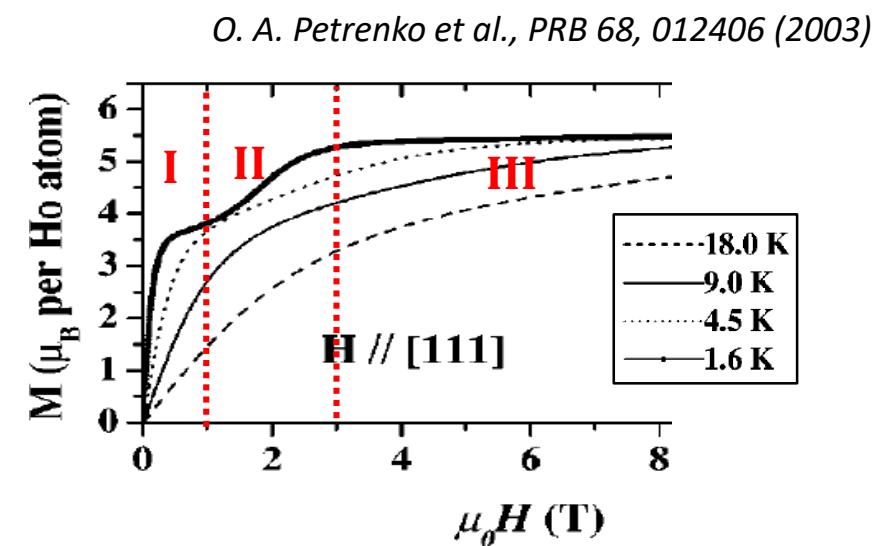
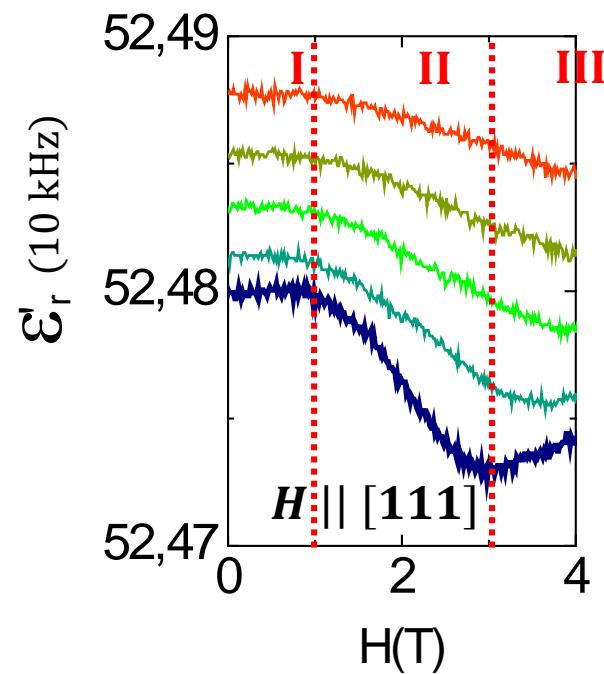
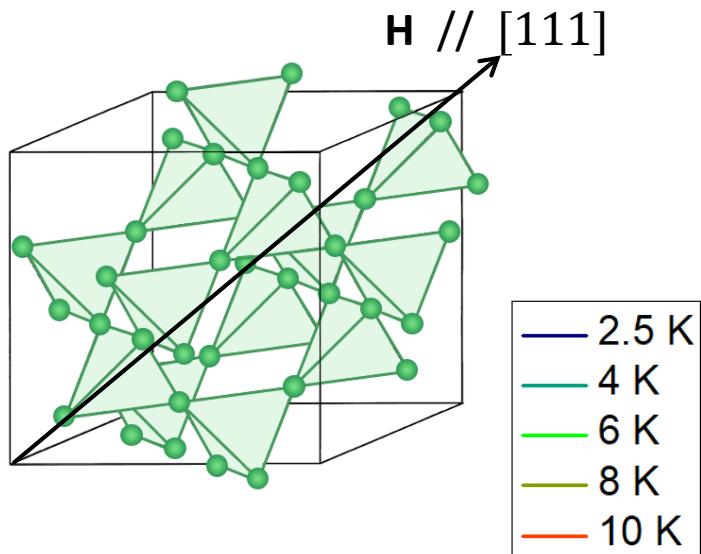
Y. Alexanian, V. Simonet, R. Ballou, J. Robert, C. Decorse, J. Debray, F. Gay, and S. de Brion

# Magneto – electric effects in $\text{Ho}_2\text{Ti}_2\text{O}_7$

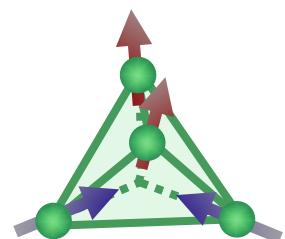


At low temperature below 4 K, 3 different regimes are observed as a function of the applied magnetic field

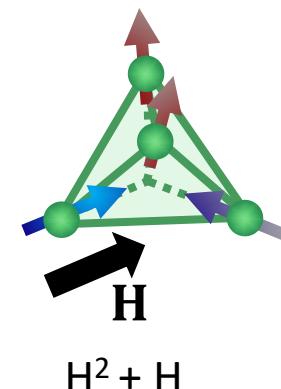
# Magneto – electric effects in $\text{Ho}_2\text{Ti}_2\text{O}_7$



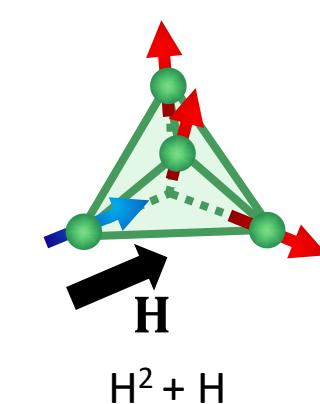
I : Spin ice  
 $\text{Fd}\bar{3}\text{m}1'$



II : Kagome ice  
 $\text{R}\bar{3}\text{m}'$



III : Monopoles ice  
 $\text{R}\bar{3}\text{m}'$

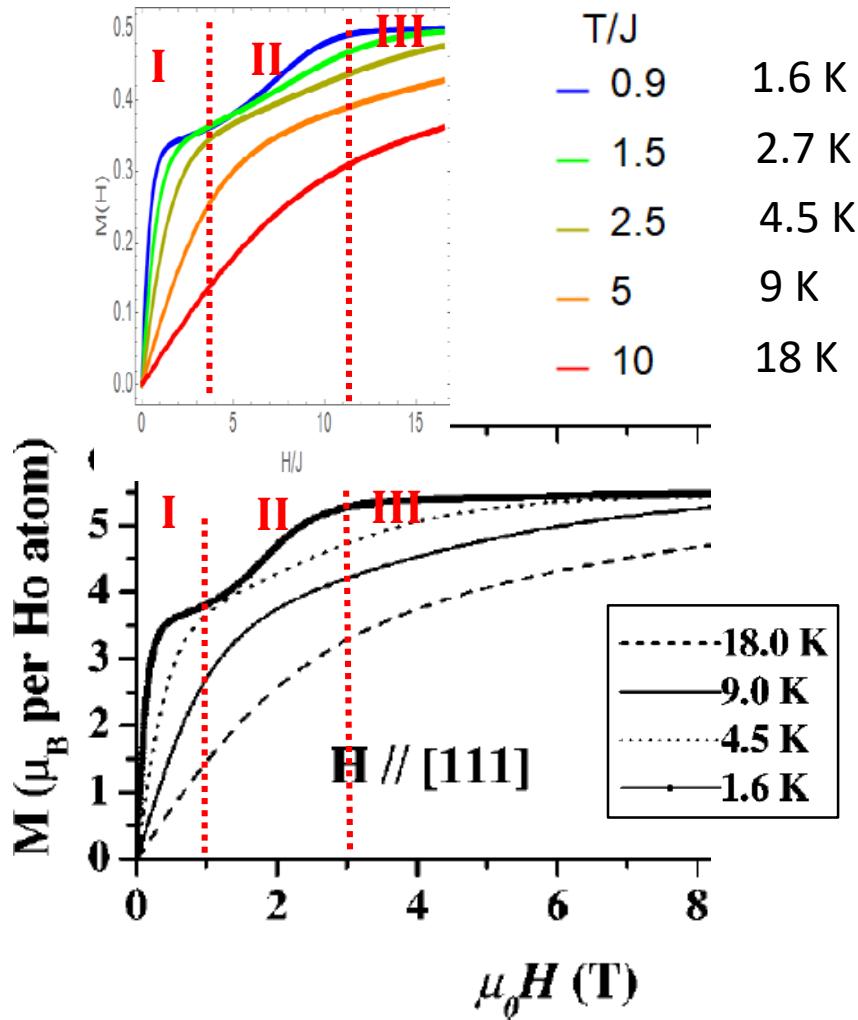


Allowed terms in  $\epsilon$  ( H ):

# Monte Carlo simulation $H // [111]$

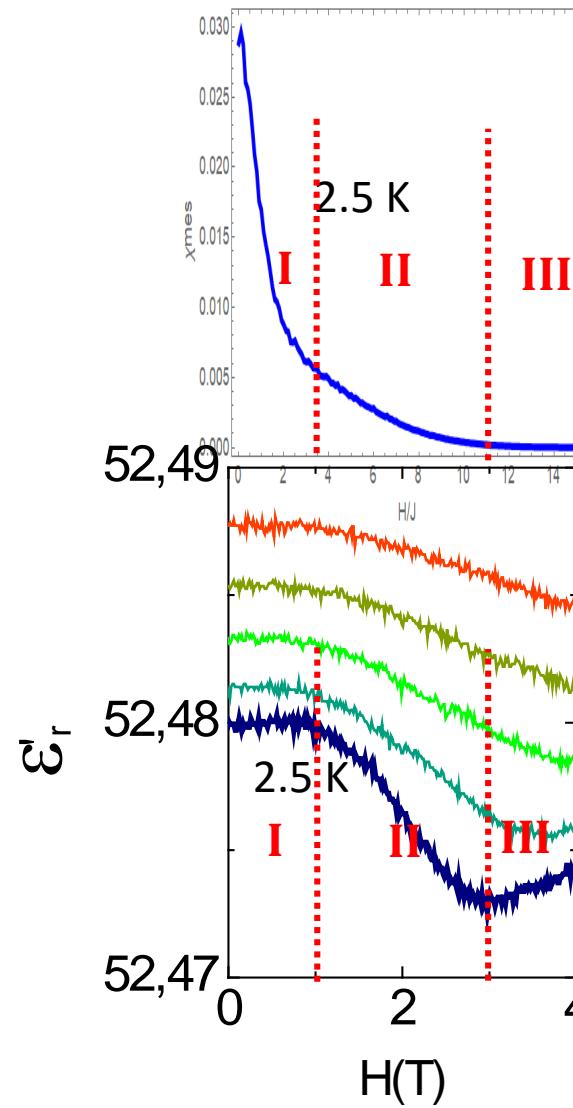
Magnetisation curves

$2 \times 2 \times 2$  units of 16 spins



MC calculations

Dielectric permittivity  
 $4 \times 4 \times 4$  units of 16 spins  
 Electric dipole oriented according to Komskii's model

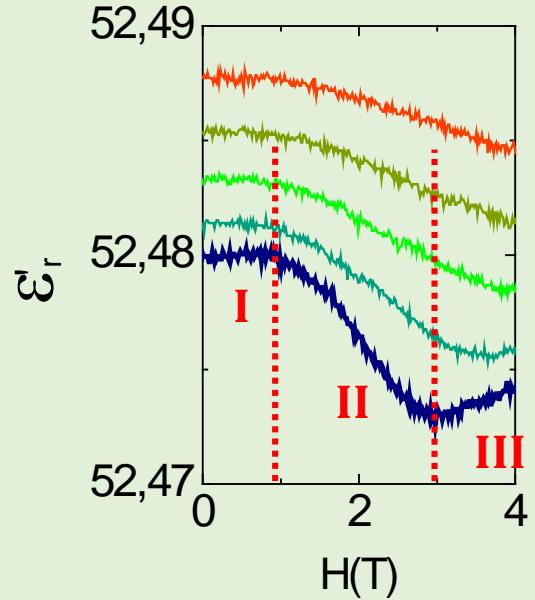


Experiments

# Conclusion : are spin ices multiferroics?

NO BUT

Magneto-electric effects are present



Signature of the different phases  
are observed but not explained  
within the Komskii's model



Y. Alexanian

END