Diffraction and neutrons

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Cristallographie et Grands Equipements

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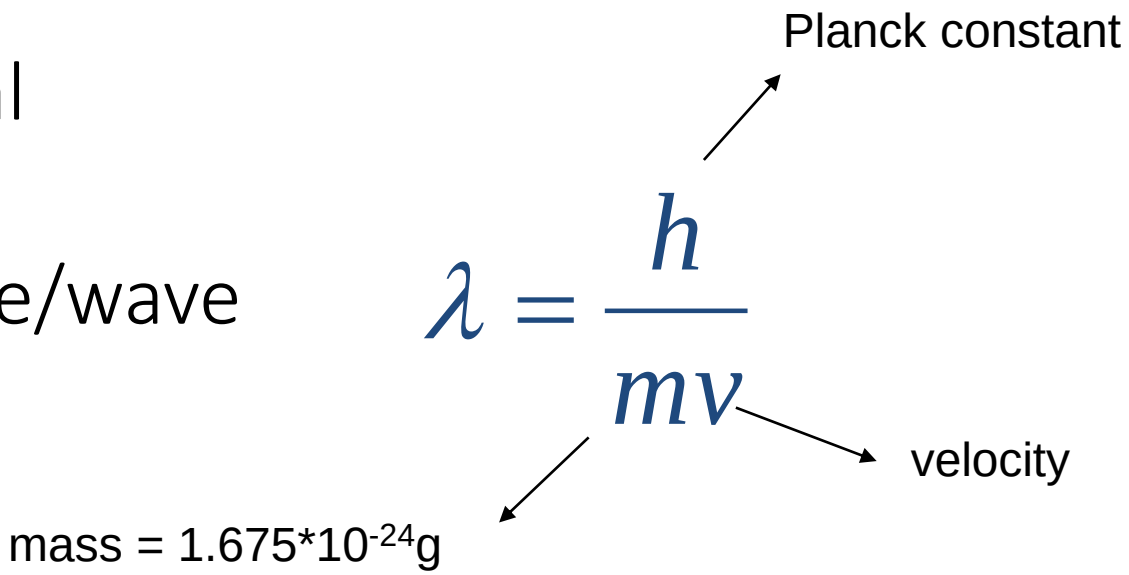
Outline

- Neutron properties
- Diffraction : generalities
  - Form and structure factors
  - Temperature factor
  - Examples
- Experimental methods (neutron diffraction)
- Magnetic diffraction
  - Magnetic structure factor
  - How to describe a magnetic order
  - Magnetic crystallography
- Neutrons/X-ray comparison

The neutron

It is a subatomic particle discovered by J. Chadwick in 1932

- neutral
- spin ½
- particle/wave



de Broglie formula

Neutron properties

Being classical particles, the kinetic energy of neutrons is given by

$$E = k_B T = \frac{1}{2} m v^2$$

But a monochromatic beam of neutrons can also be considered as plane waves with wave vector:

$$k = \frac{2\pi}{\lambda} \qquad (\lambda\text{: wavelength})$$

Because of the wave – particle duality $\lambda = \frac{h}{mv}$

hence $E = \frac{h^2}{2m\lambda^2}$ thus $\lambda(\text{Å})\sqrt{E(\text{meV})} = 9.05$ 1 Å ↔ 80 meV

X-rays $E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda(\text{Å}).E(\text{keV}) = 12.04$

1 Å ↔ 12 keV

Neutron properties

- $\boldsymbol{\lambda \sim 0.4 - 30}$ Å $\sim$ molecular sizes and interatomic distances in condensed matter

Neutrons are well adapted to be diffracted by the atoms of matter

X-rays : same

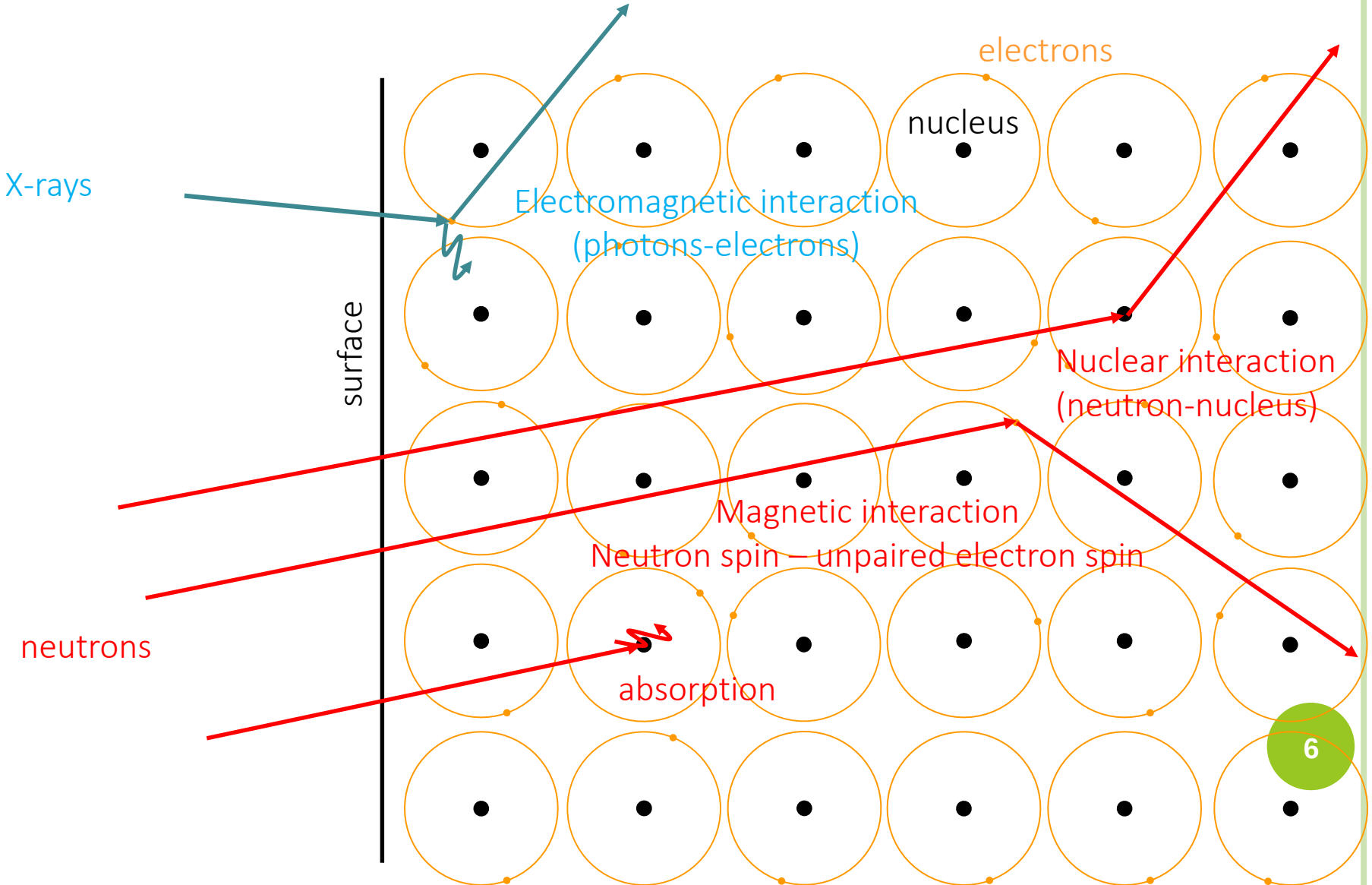
- $E \sim 0.1 - 500$ meV $\sim$ excitations (phonons, magnons, …) in condensed matter

Neutrons are well adapted for spectroscopy studies of excitations

X-rays : $E \sim 0.4 - 40$ keV $\sim$ ionization energies of the inner electronic shells

$\Rightarrow$ X-rays not so well adapted (visible & infrared light better suited)

Interactions with matter



Interactions with matter

With regards to absorption...

σ_a : [surface], given in **barn** (**1 barn = 10^{-24} cm²**)
depends on λ, Z (chemical specie) and A (isotope)

Absorption cross section

For most of the elements neutrons are weakly absorbed at the working wavelength ($\sigma_a \sim 1$ barn at $\lambda = 1.8$ Å)

$$\frac{I}{I_0} = e^{-\sigma_a N x} \qquad (\sigma_a = \frac{\mu}{N})$$

Neutrons : $\mu = 0.01 - 1$ cm^{-1} → **1 – 100 cm** of matter to attenuate the beam by *e*

X-rays : $\mu \propto Z$ (absorbed by electrons)
$\mu = 100 - 1000$ cm^{-1} → 10 – 100 µm of matter to attenuate the beam by *e*

"Pathological" elements

but a few isotopes strongly absorb neutrons: ^{3}He, ^{6}Li, ^{10}B, ^{113}Cd, ^{155}Gd and ^{157}Gd, ^{149}Sm...

Ex : substitution of natural Gd by ^{160}Gd in a neutron study of the frustrated magnet $Gd_3Ga_5O_{12}$ to avoid strong absorption

Basic principles of diffraction

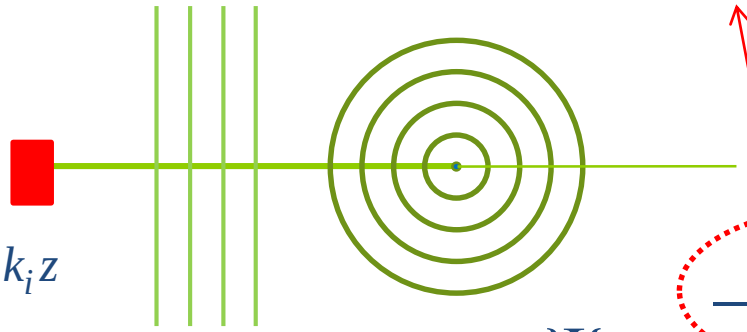
Characterizes the beam/matter interaction

Spherical wave diffused by atom O :

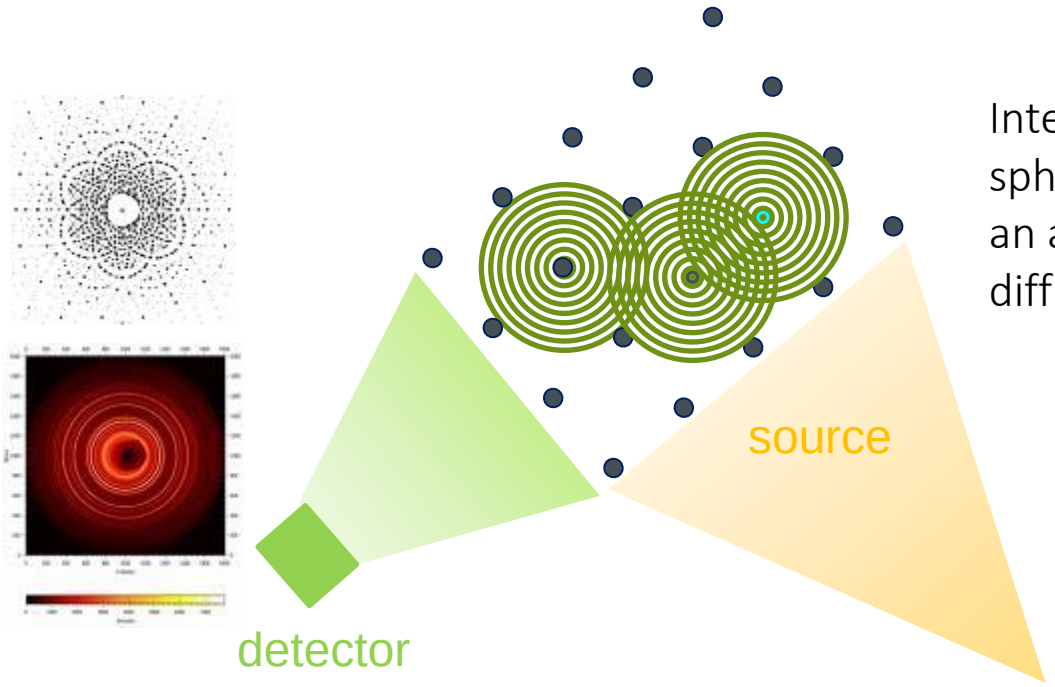
Beam source

Planar wave

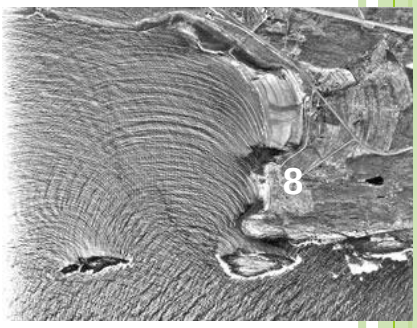
$$\Psi_i = e^{ik_i z}$$



$$\Psi_f = \frac{-f(k_i, k_f)}{r} e^{ik_f r}$$



Interferences between the spherical waves coming from an array of atoms generate a diffraction pattern



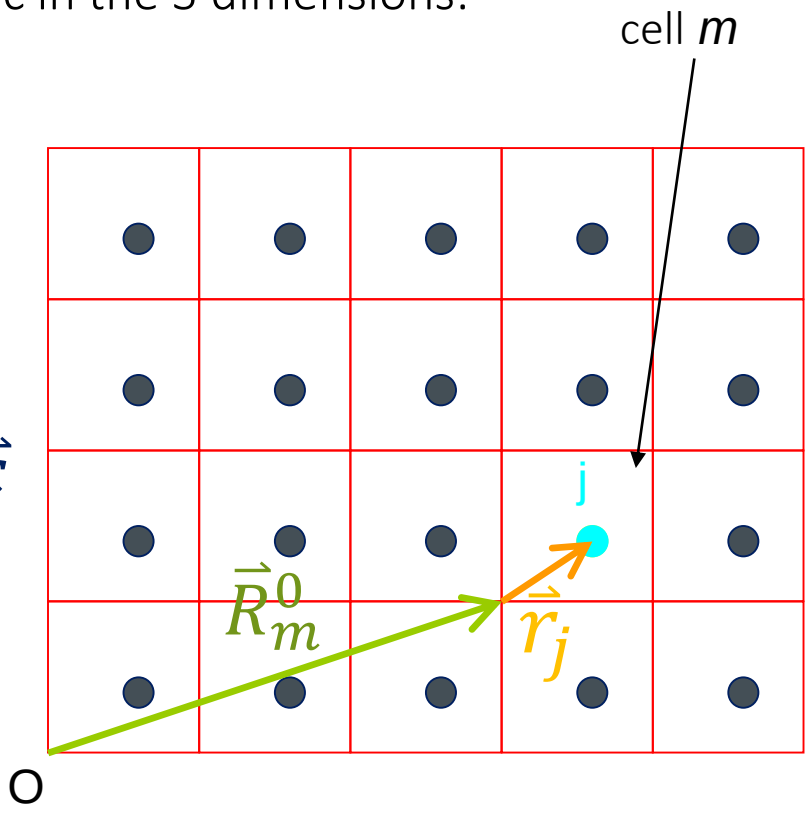
Basic principles of diffraction

If one considers a perfect crystal, periodic in the 3 dimensions:

- Position of atom j in the cell *m*:

$$\vec{R}_{mj} = \overrightarrow{R_j} = \vec{r}_j + \vec{R}_m^0$$

$$\vec{R}_j = \vec{r}_j + l_1\vec{a} + l_2\vec{b} + l_3\vec{c}$$



l_1, l_2, l_3 integers

$\vec{a}, \vec{b}, \vec{c}$ unit cell vectors

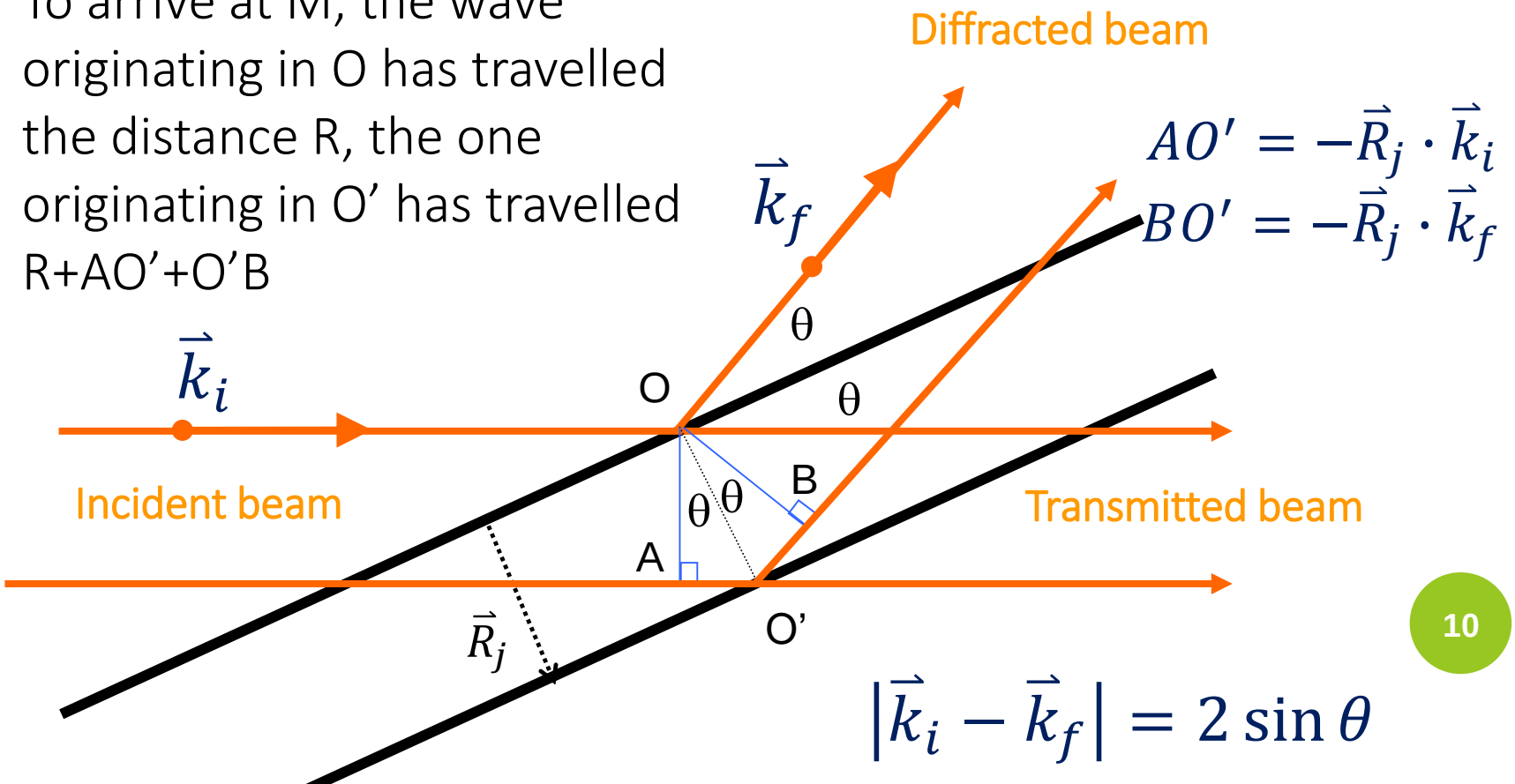
Scattering by a crystal

The detector is set at M, in the diffusion plane, at a distance R (R >> R_j) from the origin O

Incident beam, unit wave vector $\vec{k}_i$

Diffracted beam, unit wave vector $\vec{k}_f$

To arrive at M, the wave originating in O has travelled the distance R, the one originating in O' has travelled R+AO'+O'B



$$AO' = -\vec{R}_j \cdot \vec{k}_i$$

$$BO' = -\vec{R}_j \cdot \vec{k}_f$$

$$\left|\vec{k}_i - \vec{k}_f\right| = 2\sin\theta$$

Scattering by a crystal

Summing on all the crystal atomic positions, one gets the differential cross section (elastic process), which is proportional to the square of the diffracted wave modulus :

Number of neutrons scattered per second in solid angle $d\Omega$ around the direction $\vec{k}_f$ with any energy, normalized to the incident neutron flux ϕ

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)^{el} = \left|\sum_{\vec{R}_j} b_j e^{i(\vec{Q}\cdot\vec{R}_j)}\right|^2$$

with

$$\frac{2\pi}{\lambda}\left(\vec{k}_i - \vec{k}_f\right) = \vec{Q}$$

scattering vector

$$|\vec{Q}| = \frac{4\pi \sin\theta}{\lambda}$$

Scattering by a crystal

Elastic scattering differential cross section

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)^{él} = \left|\sum_j \bar{b}_j \; e^{i\vec{Q}\cdot\vec{r}_j} \, e^{-W_j}\right|^2 \left|\sum_{l_1,l_2,l_3}^{cristal} e^{i\vec{Q}\cdot(l_1\vec{a}+l_2\vec{b}+l_3\vec{c})}\right|^2$$

Sum over N atoms in the cell
Depends on the atomic positions within the unit cell

Structure factor

F(Q)

Sum over all the cells
Depends on the crystal periodicity
Non-zero when Q is a vector of the reciprocal space

Crystal form factor

C(Q)

$$\left(\frac{d\sigma}{d\Omega}\right) = |F(Q)|^2 |C(Q)|^2$$

Structure factor

The amplitude of the diffracted wave is proportionnal to

$$F(\vec{Q}) = \sum_{j=1}^{N} b_j e^{i(\vec{Q}\cdot\vec{r}_j)}$$

b_j : defines the scattering by atom j ; $\vec{r}_j$ defines its position in the unit cell ; N is the number of atoms in the cell

Point scatterer

Atom = point scatterer

In this case, the scattering amplitude does not depend on the diffusion angle : this is the case of the nuclear diffraction of neutrons

$$F(hkl) = \sum_{j=1}^{N} b_j e^{2i\pi(hx_j + ky_j + lz_j)}$$

b_j : scattering length of atom j (or fermi length, in fm (10^{-13} cm))
It describes the neutron-nucleus interaction

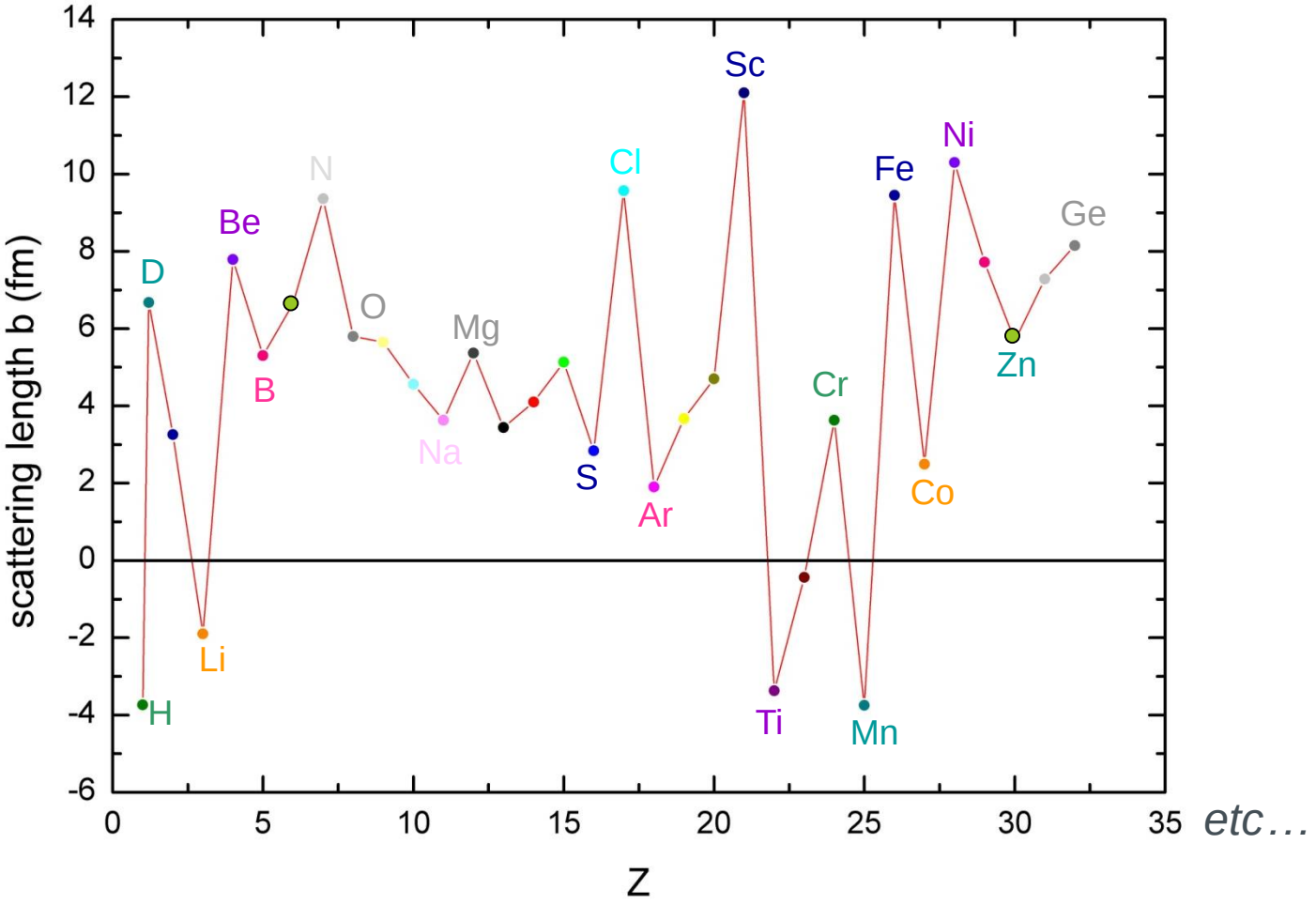
b varies in a non-monotonous way with the atomic number Z.

Isotopes can have very different b's!

→ Neutrons can distinguish atoms with similar Z numbers (≠ RX) ; can locate light atoms in a structure with heavy elements. They are also sensitive to H/D.

Neutrons are a privileged tool for the study of organic compounds

Neutron scattering lengths (Z < 35)



Atomic scatterer

Atom = scattering object, size ~ λ, group of identical point scatterers
Case of X-rays (electrons) and of neutron magnetic diffraction (unpaired electrons)

$$b_j = b_c f_j(Q)$$

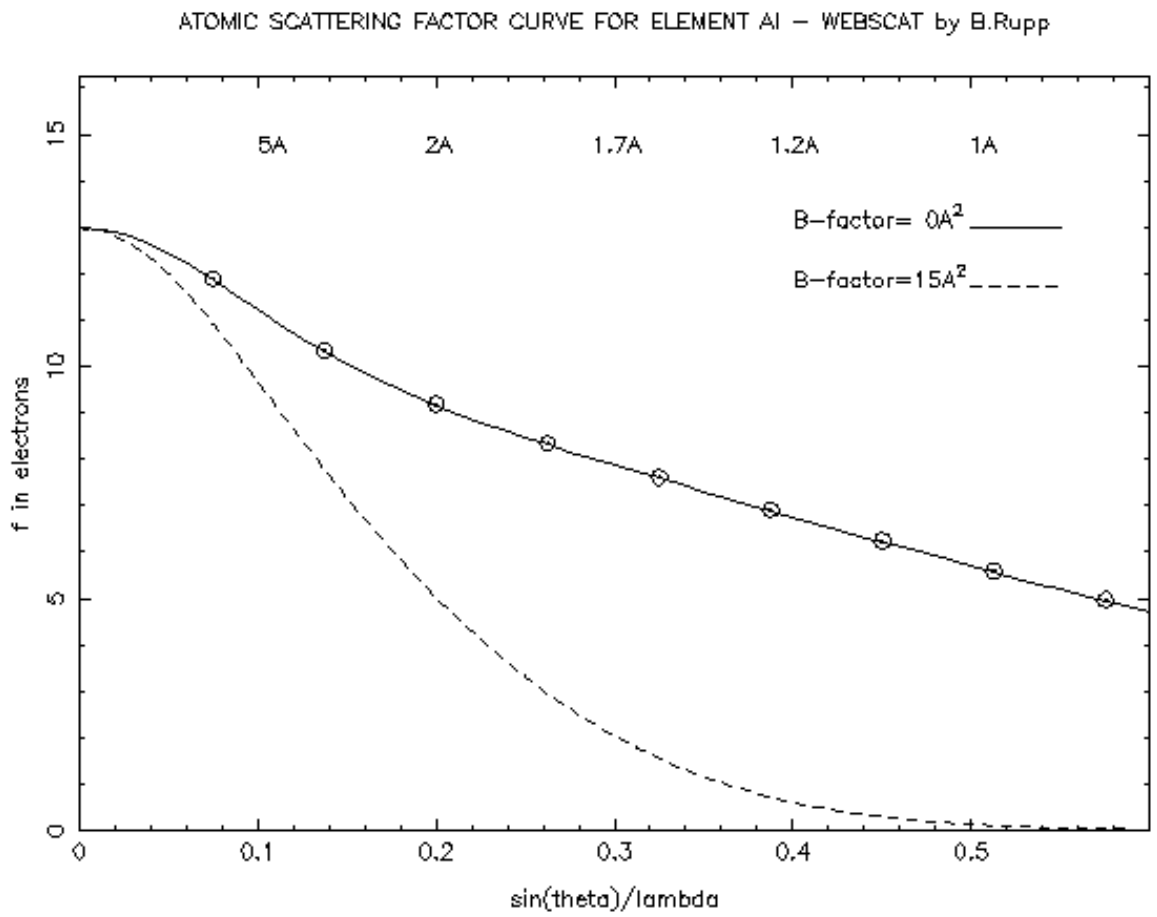
constant

depends on the diffusion θ

atomic scattering factor

X-rays :

$$f_j(Q) = f_0\left(\frac{\sin\theta}{\lambda}\right) + \text{Anomal diffusion terms}$$

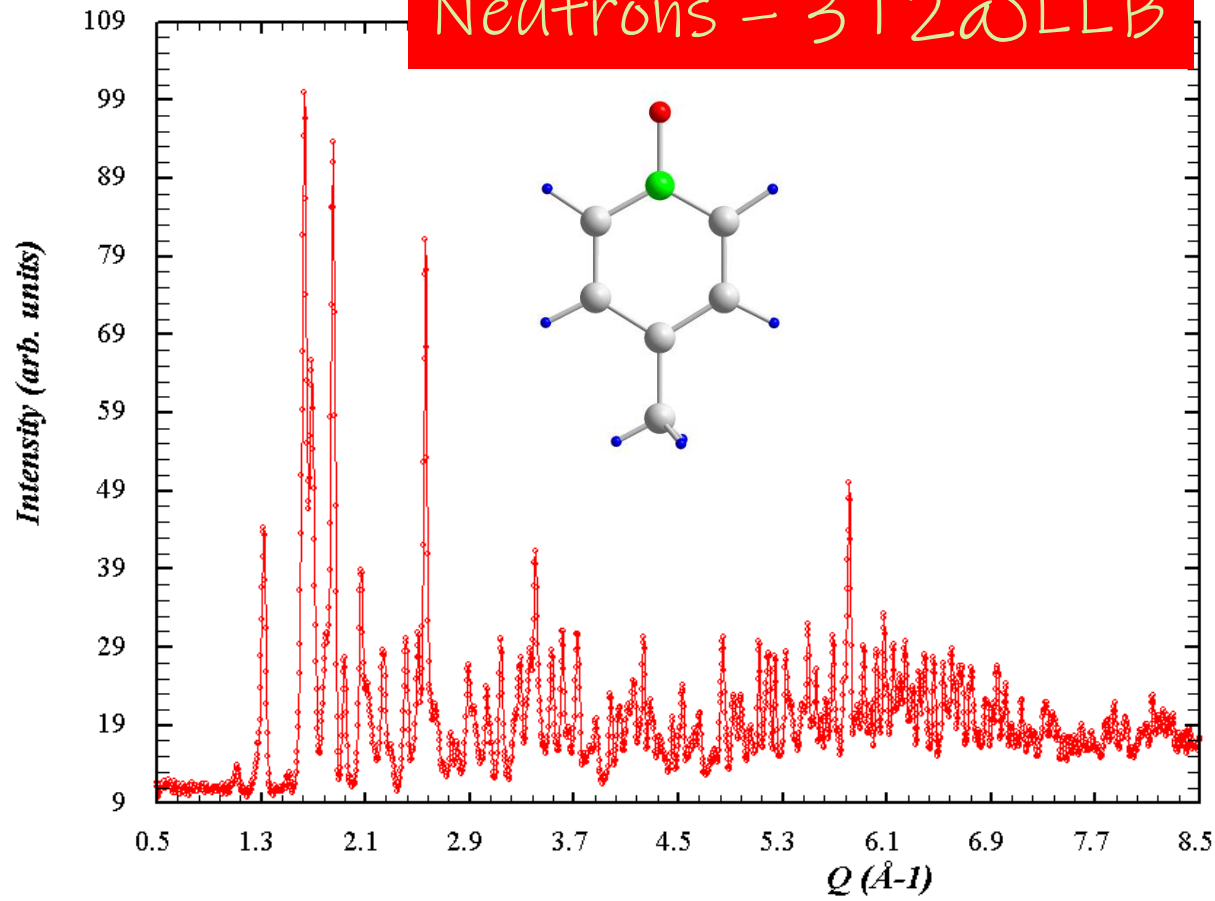


$$f_0(q=0) = Z$$
$$f_0(q \to \infty) = 0$$

The scattered intensity decreases at large angles.
≠ neutrons!! With neutrons it is possible to determine atomic positions and thermal displacement factors precisely.

Example : Méthyl-4-pyridine-1-oxyde à 10K

Neutrons – 3T2@LLB



Synchrotron – BM1@ESRF

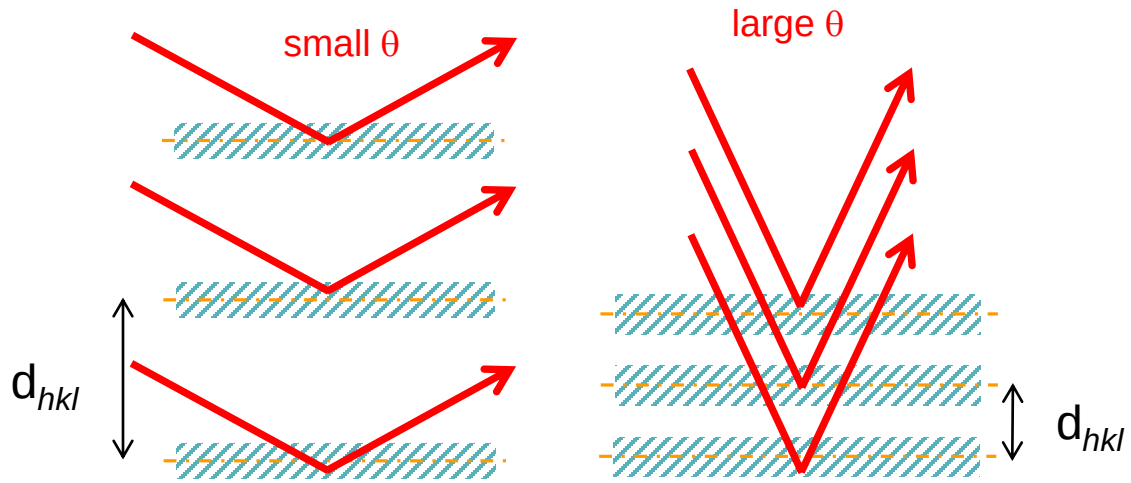
Thermal displacement parameter

Thermal displacement : oscillating motion of atoms around their equilibrium position

This displacement decreases scattering, and has a larger effect when :

- T is large
- atoms are light
- $\frac{\sin\theta}{\lambda}$ large

Displacement : atomic plane with a thickness $\sqrt{\langle u^2 \rangle}$



θ large ⟶ $\sqrt{\langle u^2 \rangle}$ becomes important compared with d_{hkl}

$\sqrt{\langle u^2 \rangle}$ inorganic compounds : ~ 0.05 Å - 0.2 Å
organic compounds : ~ 0.5 Å

Isotropic temperature factor B

$B = 8\pi^2 \langle u^2 \rangle$ inorganic compounds :~ 0.2 Å^2- 3.2 Å^2
organic compounds :~ 20 Å^2

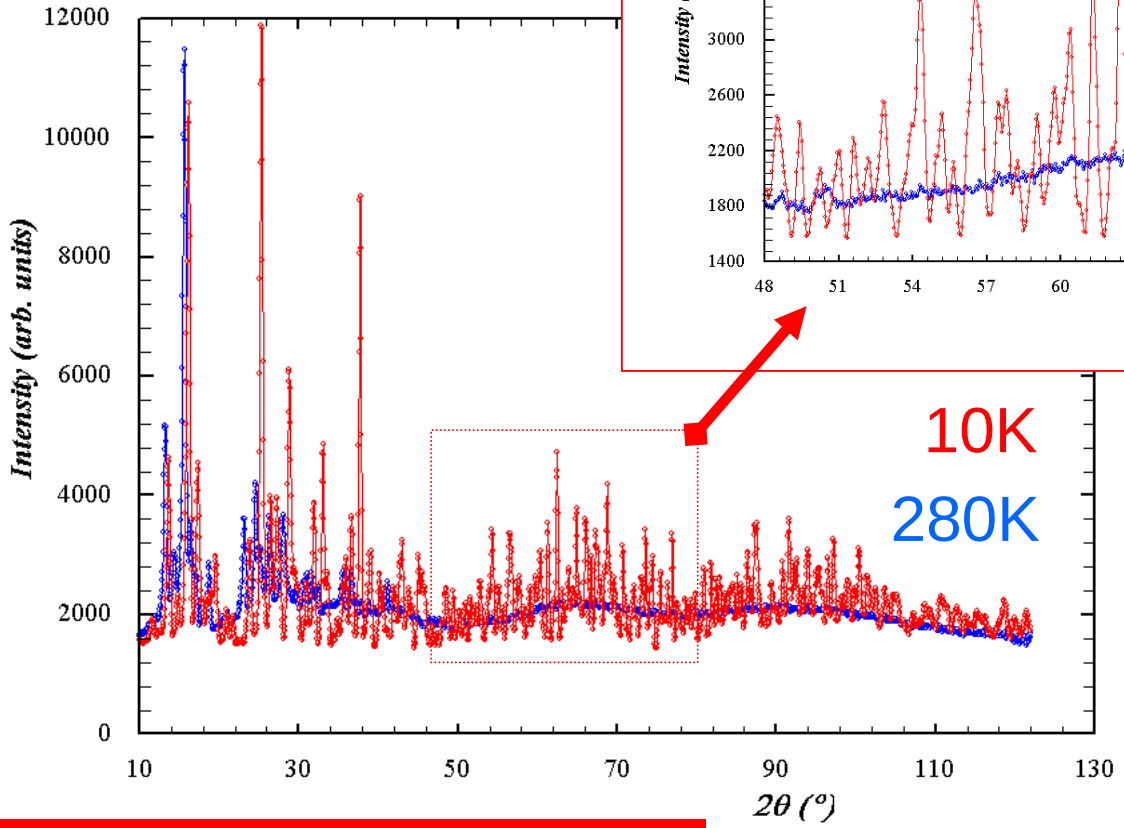
$$F_T(hkl) = F(hkl) e^{-B\frac{\sin^2\theta}{\lambda^2}}$$

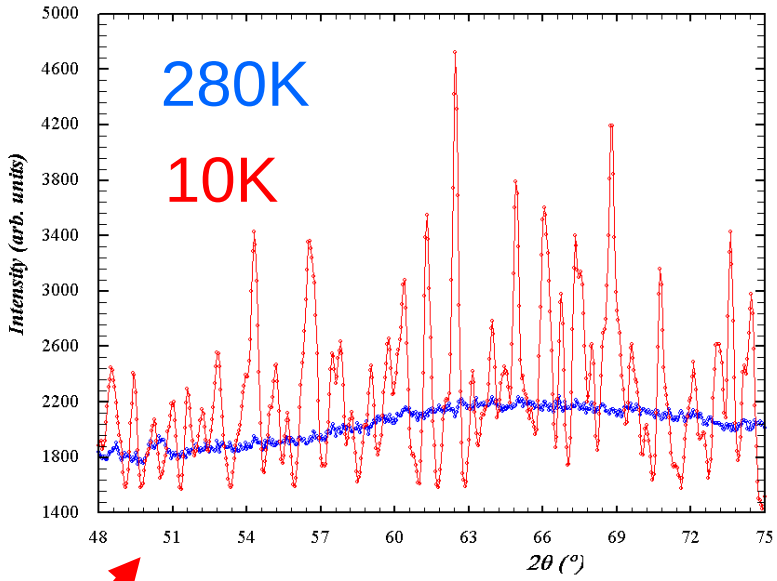
(oversimplified correction)

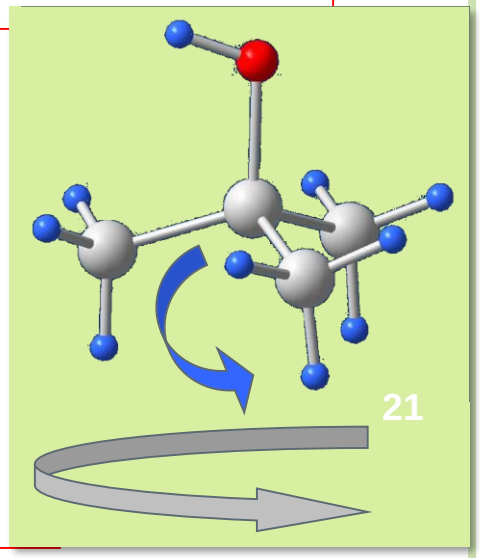
Identical effects in neutrons and X-rays
It leads to a **decrease** of the scattered intensity at large angles
(NOT to a broadening)

Anisotropic matrices can be introduced in complex cases

Example : Tert-butanol

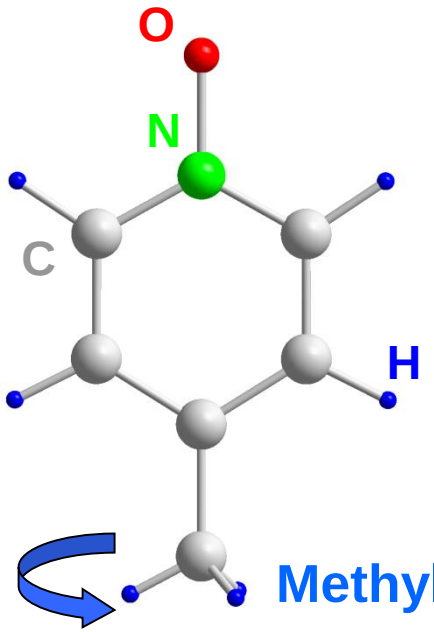






Neutrons – 3T2 (LLB)

Example of X-ray/neutrons complementarity



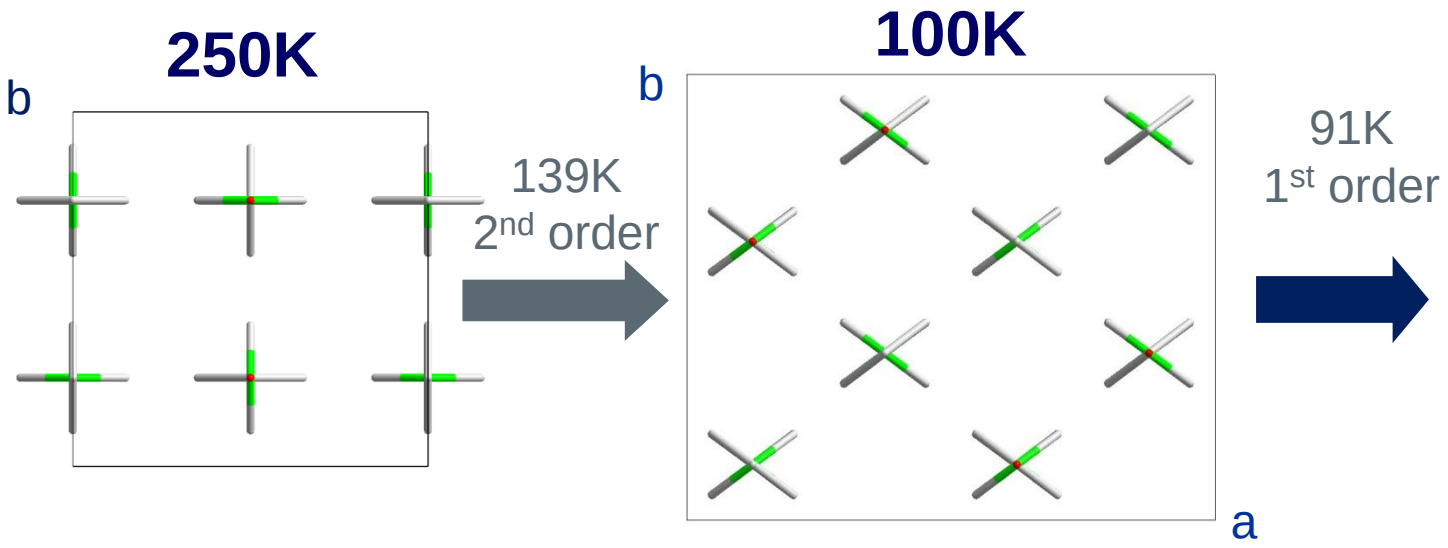
Methyl group CH_3

Phase transitions in 4MPO

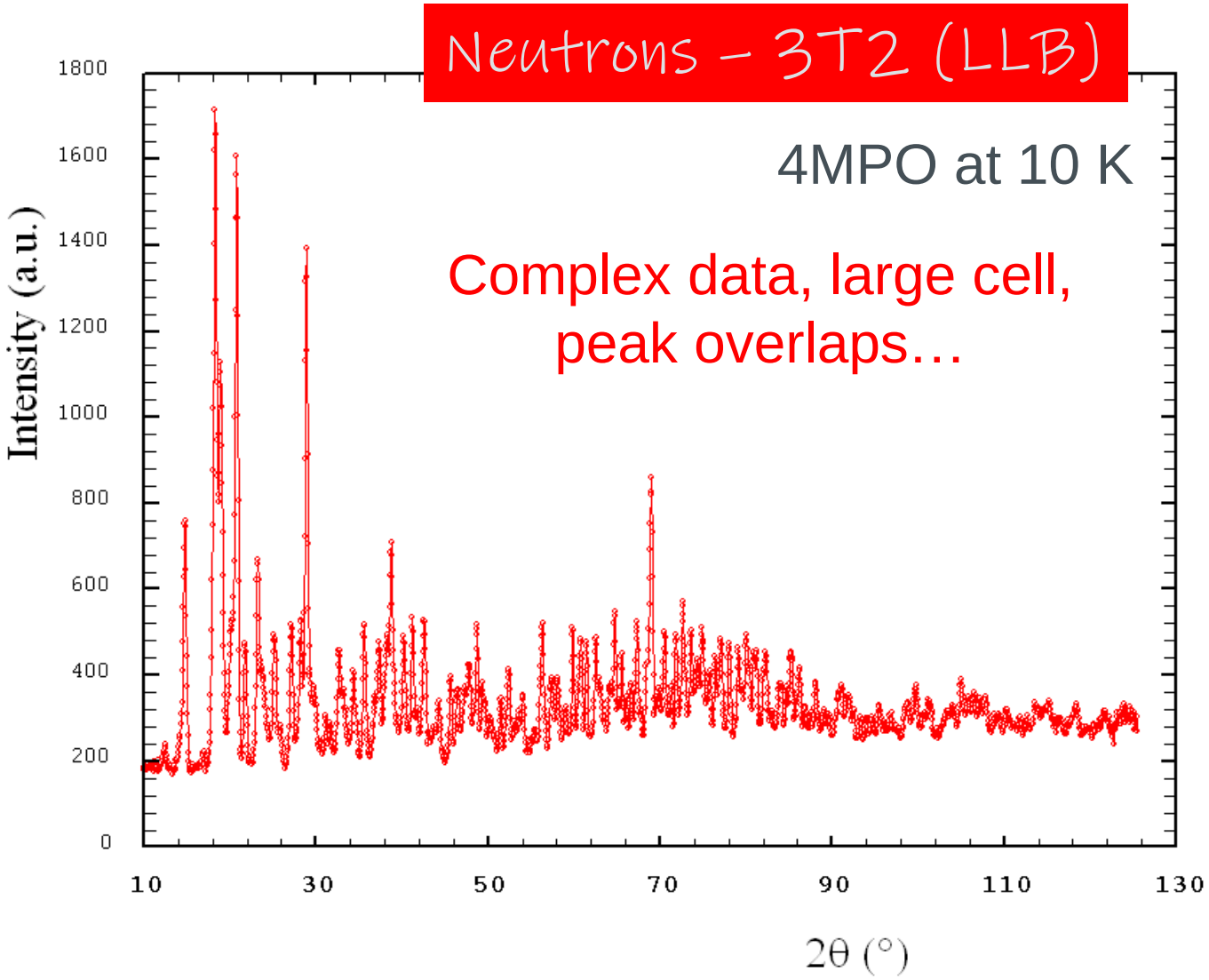
$C_5H_4NO(CH_3)$

$C_5D_4NO(CD_3)$

Planar molecule
« symmetric »

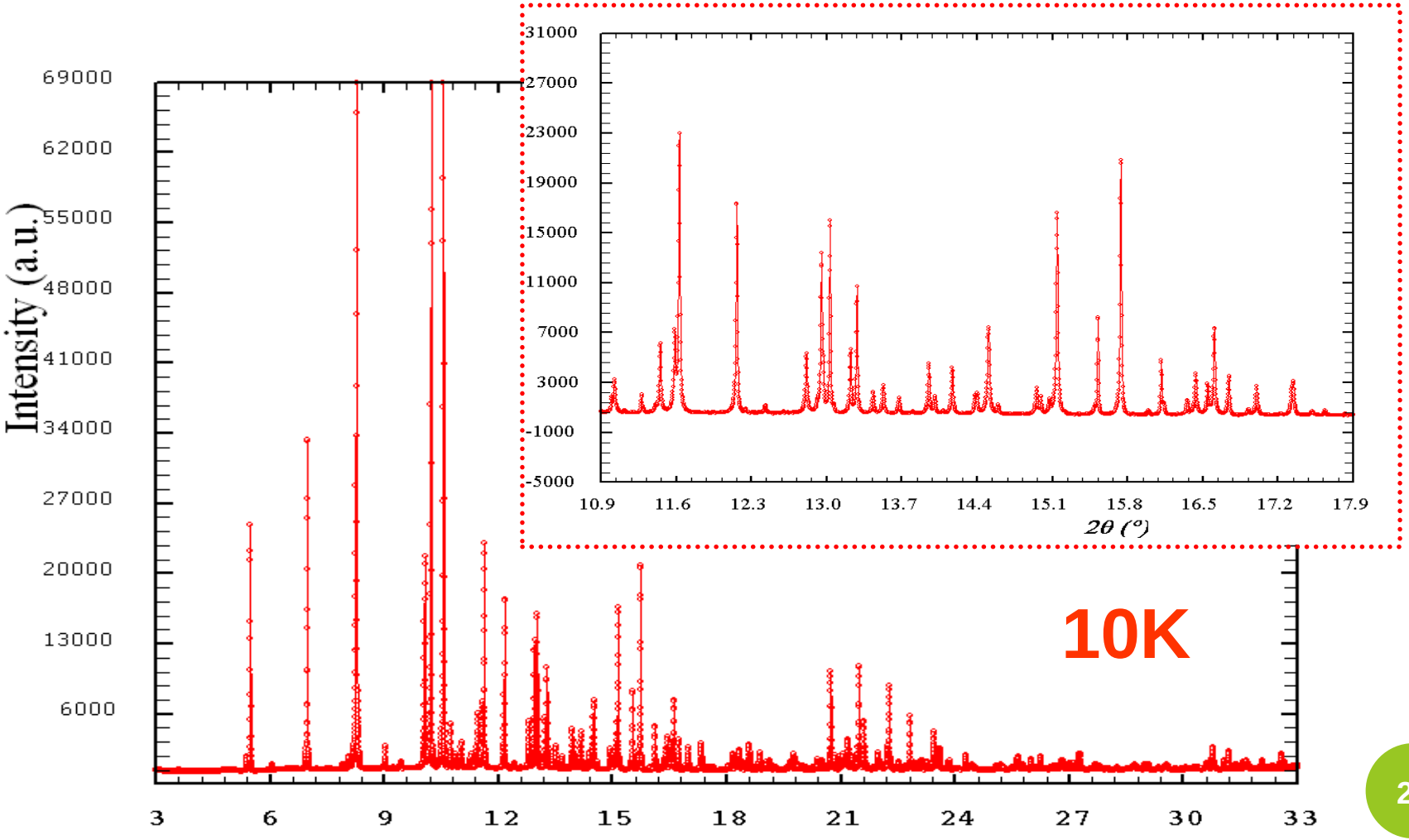


Example of X-ray/neutrons complementarity



Example of X-ray/neutrons complementarity

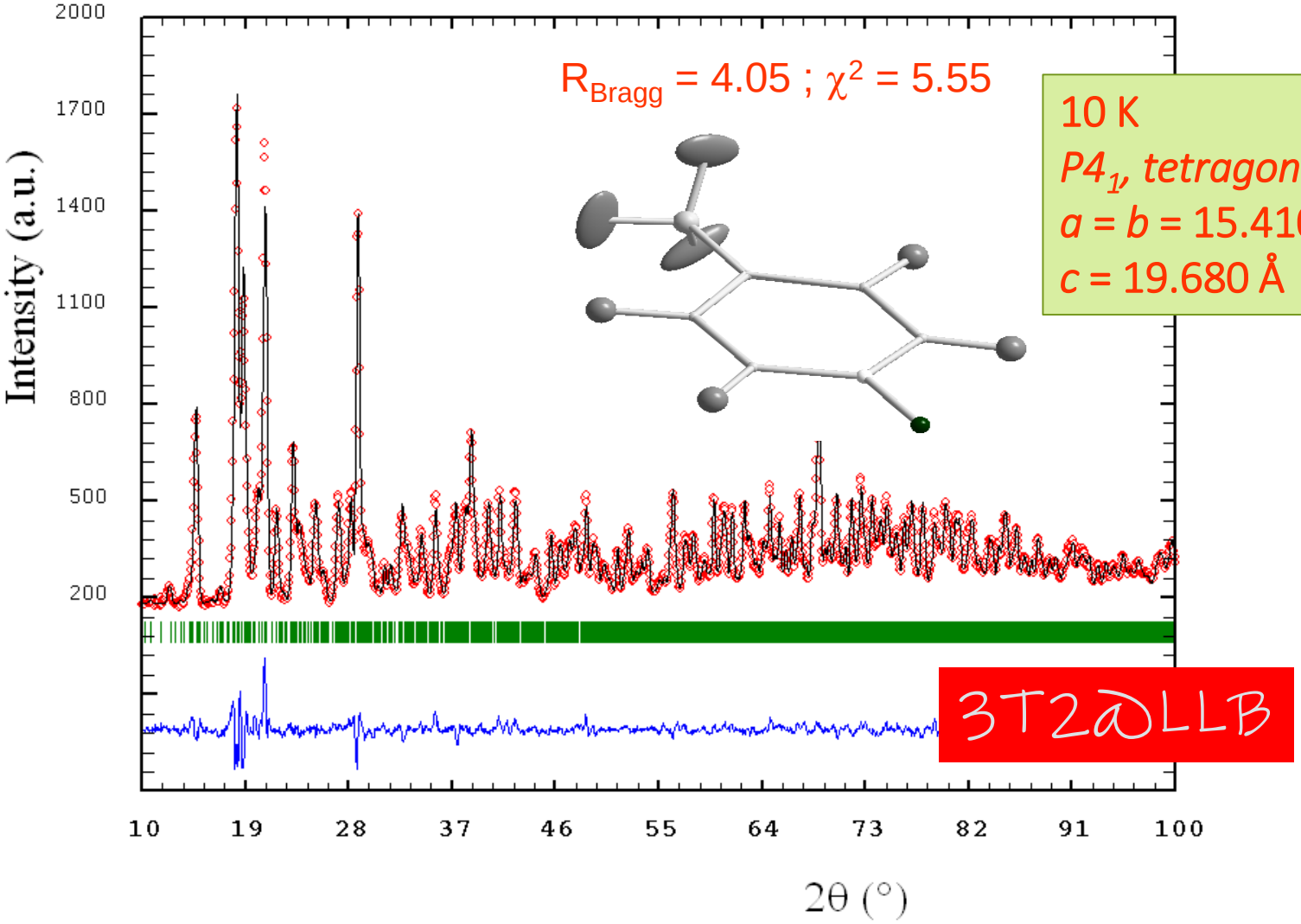
To solve the crystal structure at 10 K : synchrotron X-ray diffraction experiment at 10 K (cell parameters, space group, position of molecules (without D atoms)



BM1 – ESRF SNBL

Example of X-ray/neutrons complementarity

Neutron data analysis



Magnetic diffraction

Remember, the neutron has a spin 1/2

Web of Science: Magnetic structure(s)

Skyrmions

Superconducteurs

Magnetoresistance

Heavy fermions

Nanoparticles

Multiferroics
Magnetoelectrics

Magnetic thin films

Orbital orders

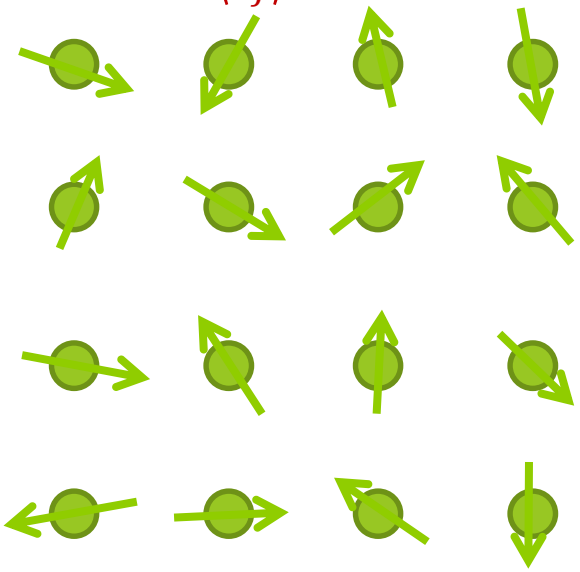
Magnetic Moment

Atoms can carry a magnetic moment, as for instance 3d elements with unpaired electrons (Mn…), but also 4d elements (Mo…), 4f (rare-earths comme Nd, Dy,…) etc…

Moments can order below an order temperature, called T_C ou T_N

Paramagnetic state

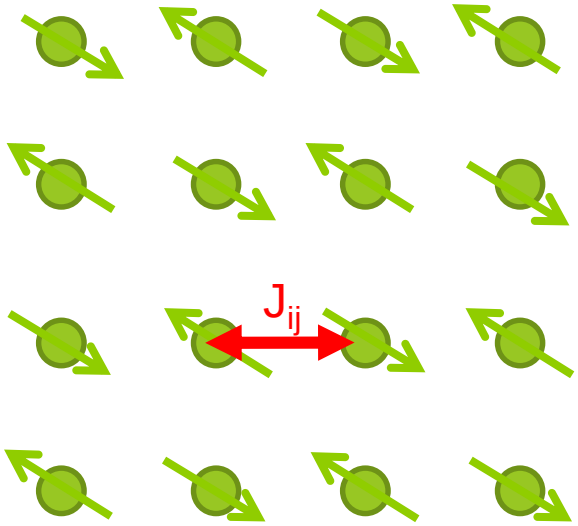
$\langle \vec{S}_j \rangle = \vec{0}$



Thermal fluctuations dominate over exchange interactions, magnetic moments are fluctuating

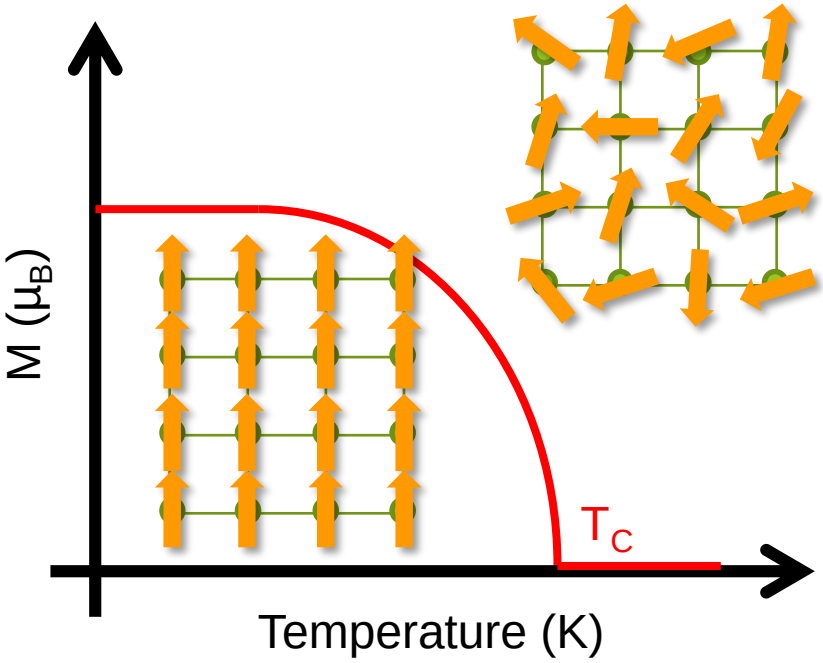
Ordered state $T<T_C,T_N$

$\langle \vec{S}_j \rangle \neq \vec{0}$

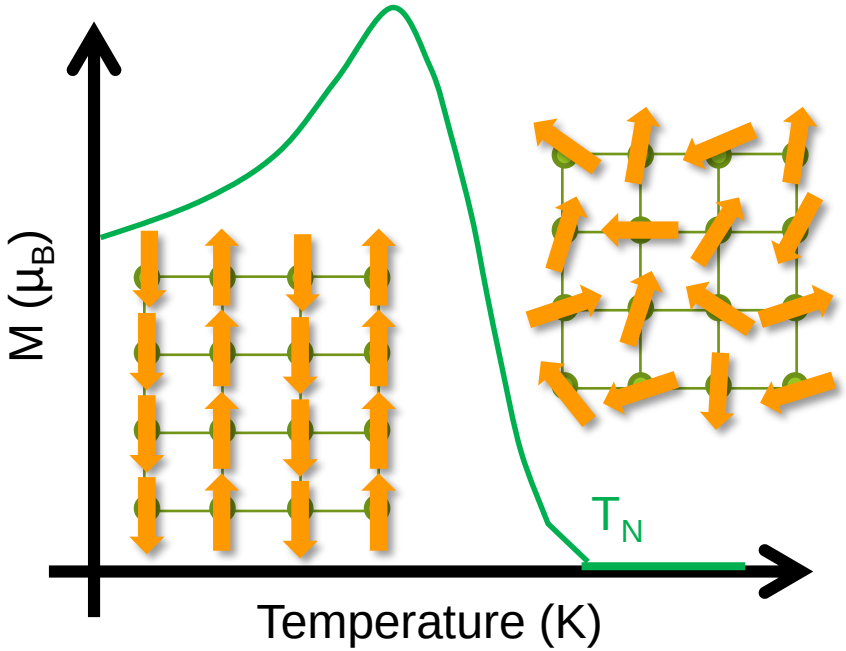


Exchange interactions dominate over thermal fluctuations, magnetic moments are ordered

Simple cases



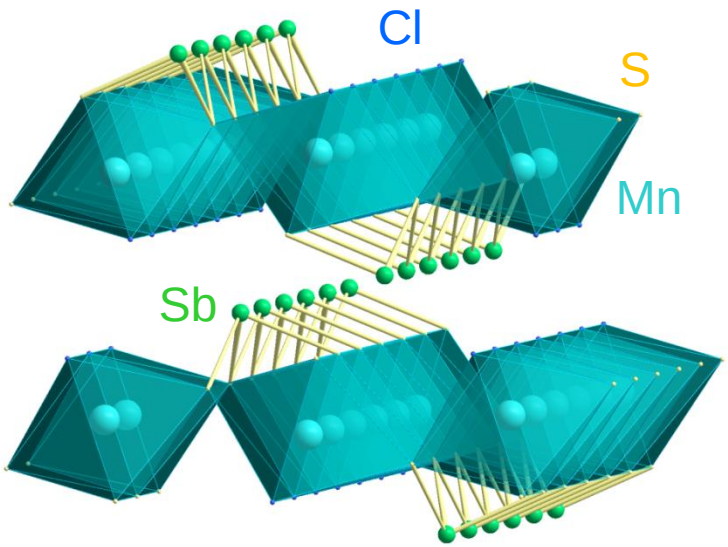
Ferromagnet

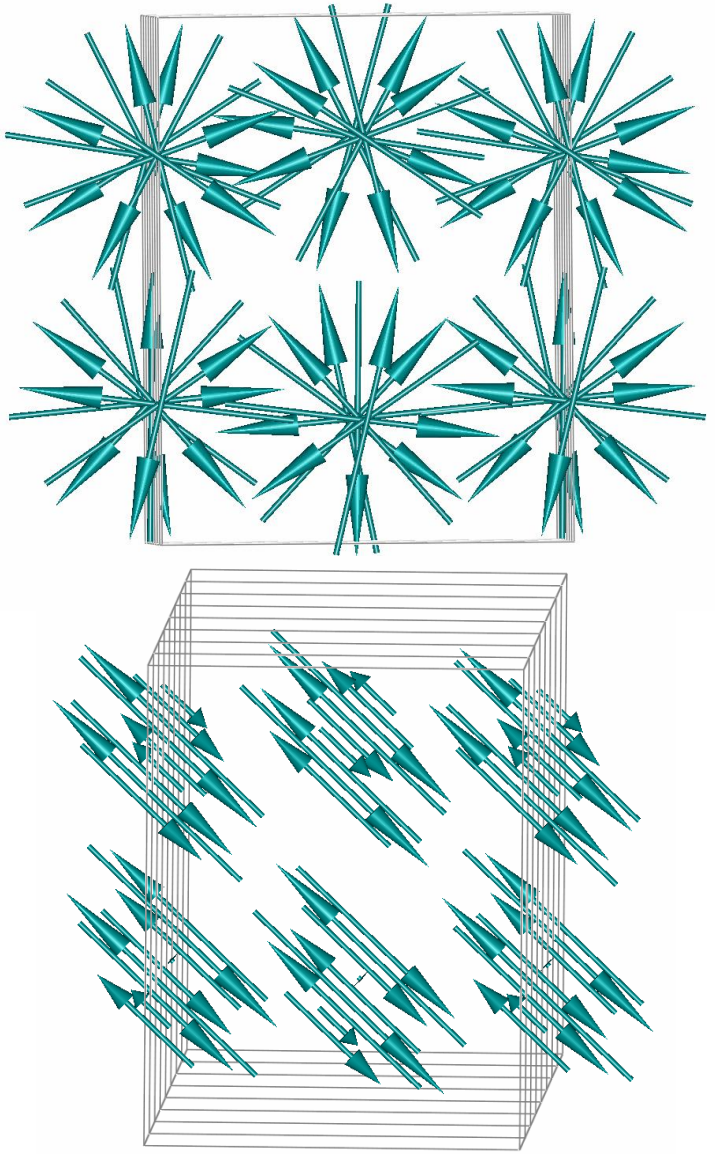


Collinear antiferromagnet

More often than not, magnetic structures can be complex, because of competing interactions, magnetic anisotropy, etc…

Example of a complex magnetic structure $MnSbS_2Cl$





Incommensurate magnetic structure, with two possible models: helicoidal or modulated sinusoidal

C. Doussier et al., J. Solid State Chem. 179 (2006), 486

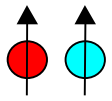
Diffraction by an ordered magnetic structure

Magnetic scattering is taken into account using the formula

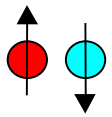
$$b_n + 2B\vec{I}\cdot\vec{S} + \frac{1}{2}\gamma r_e f_m(Q)(\overrightarrow{M_\perp}\cdot\vec{S})$$

(Isotropic) nuclear term

Interaction between neutron spin ***s*** and nucleus spin **I**



n *I*



n *I*

This depends on the spin state of the neutron and of the nuclei!

Dipolar interaction between neutron spin neutron ***s*** and atom magnetic moment

where

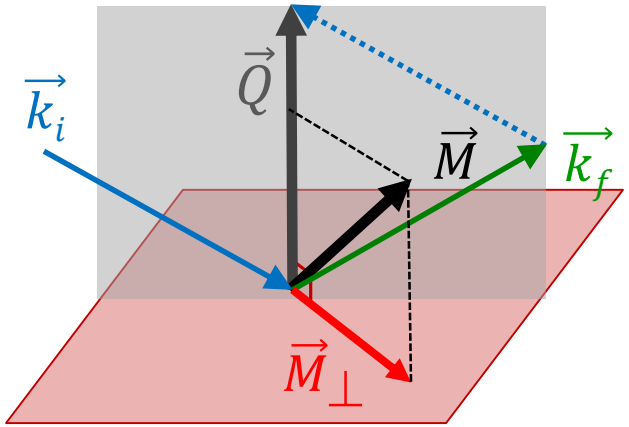
$$\frac{1}{2}\gamma r_e f_m(Q)(\overrightarrow{M_\perp}\cdot\vec{S})$$

Cst = $0.27\cdot10^{-12}$ cm

Magnetic form factor

Fourier transform of the density of the unpaired electrons of the atom

(can be pictured as the spatial extension of the electron cloud)



Projection of the magnetic moment of the atom on a plane perpendicular to the scattering vector Q

If $\vec{M} \parallel \vec{Q}$: no magnetic intensity

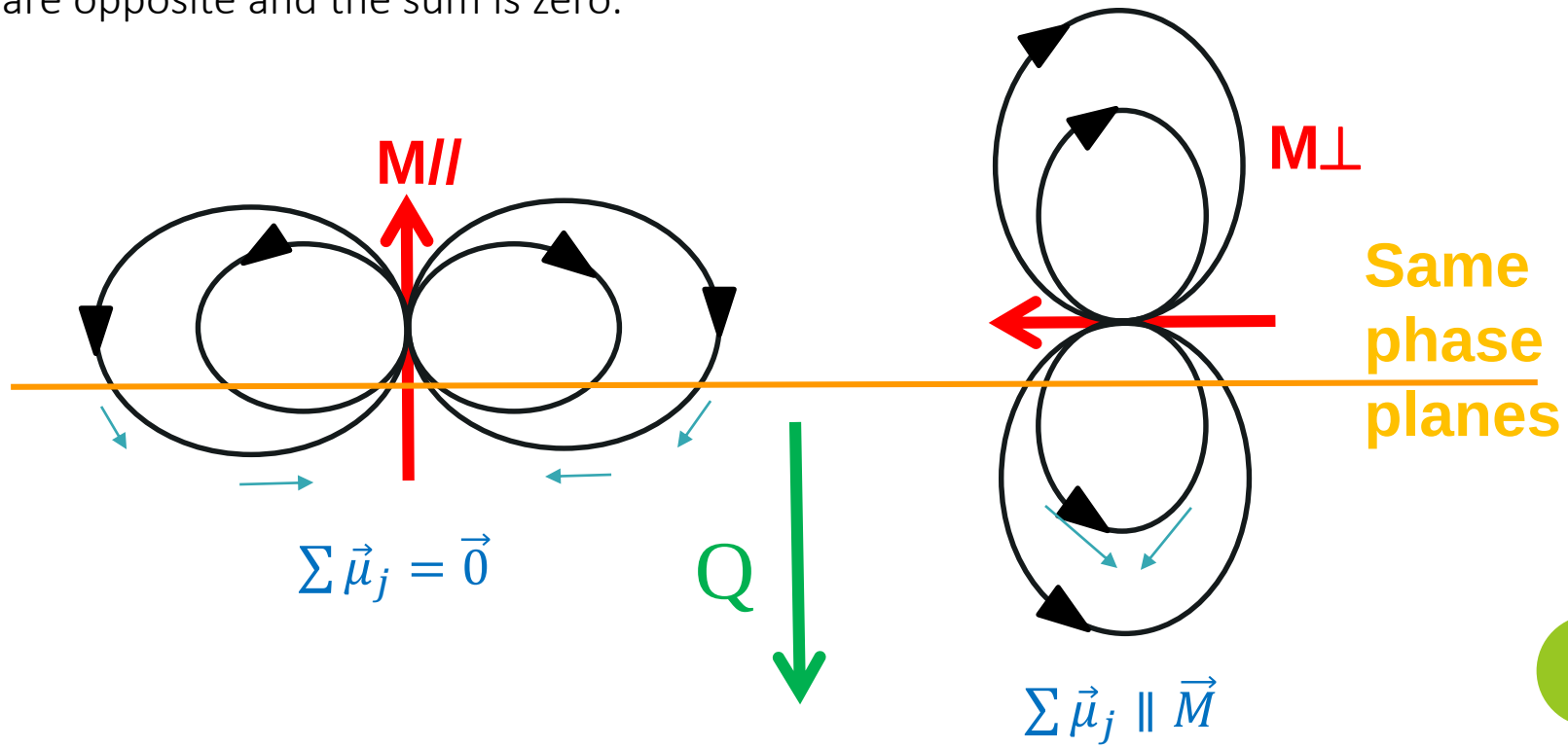
If $\vec{M} \perp \vec{Q}$: maximum magnetic intensity

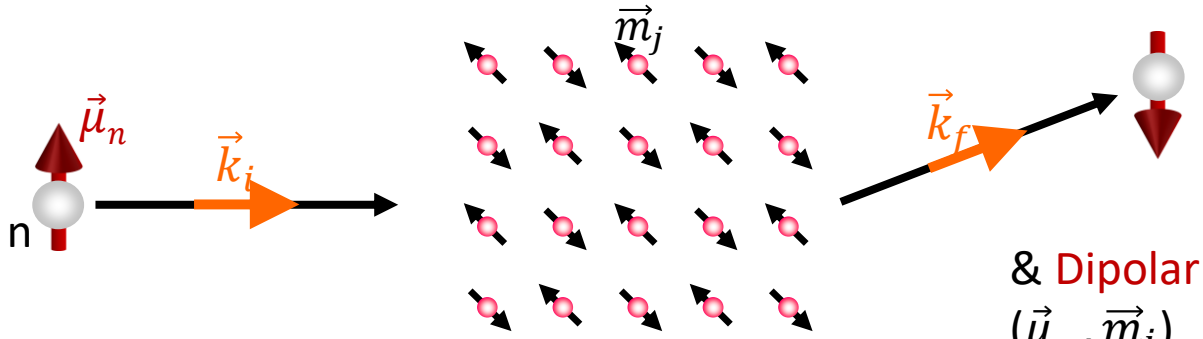
How can we understand the fact that it is $M_\perp$ which is important, and not **M**…

In a diffusion process, it is the planes which are perpendicular to Q which will contribute to the scattered amplitude, as they are in phase.

One can decompose M into two components M//Q et M⊥Q

Neutrons can feel the magnetic field created by M⊥. For M// the magnetic field are opposite and the sum is zero.





Nuclear interaction
& Dipolar interaction
$(\vec{\mu}_n\,, \vec{m}_j)$

Crystallographic structure = long-range (periodic) ordering of atoms:

- unit cell + space group + atomic positions of the asymmetric unit
- Bragg peaks at $\vec{Q} = \vec{H}$

$$F(\vec{H}) = \sum_{j=1}^{N} b_j e^{2i\pi(\vec{H}\cdot\vec{r}_j)}$$

Magnetic structure = long-range ordering of "magnetic moments"

$$F_M(\vec{H}+\vec{k}) = \frac{1}{2}\gamma r_e \sum_{j=1}^{N} f_j(\vec{H}+\vec{k}) S_{\mathbf{k}j} e^{2i\pi((\vec{H}+\vec{k})\cdot\vec{r}_j)}$$

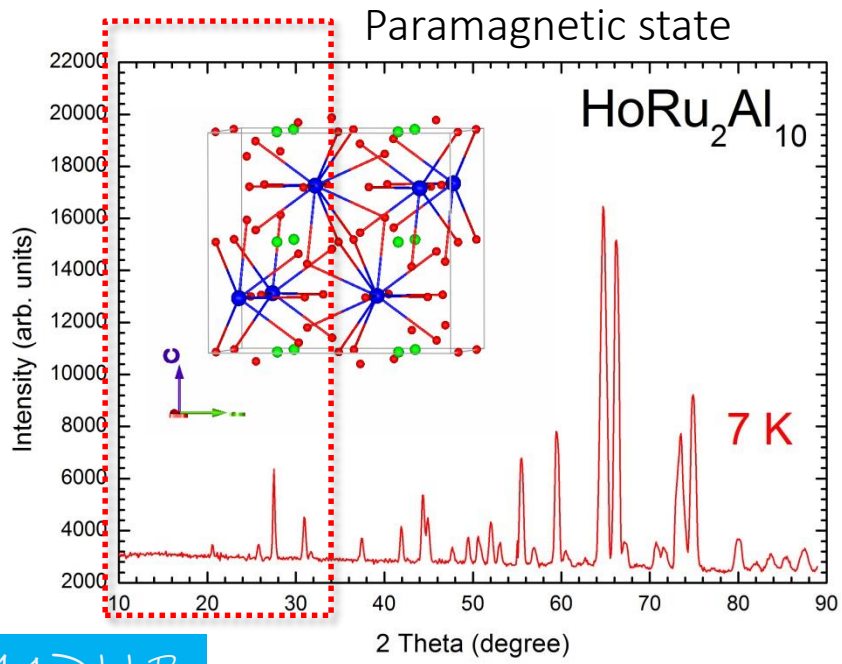
- magnetic motif (inside the crystallographic unit cell) + propagation vector $\vec{k}$
- Bragg peaks at $\vec{Q} = \vec{H} \pm \vec{k}$

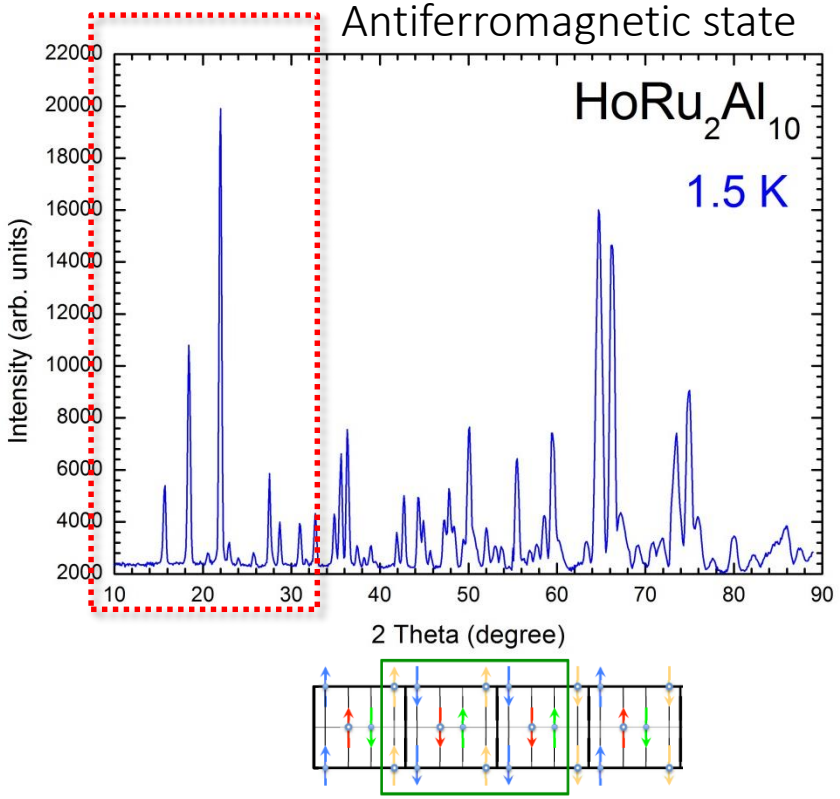
$\vec{Q} = \vec{k}_f - \vec{k}_i$: scattering vector
$\vec{H}$: vector of the reciprocal lattice

Nuclear and magnetic scattering cross sections for elastic scatterings are in general of the same order of magnitude

For a non polarised neutron beam, the total intensity will be the proportionnal to the sum of the nuclear and magnetic intensities

$$I(hkl) = I_N(hkl) + I_M(hkl)$$





G4.1@LLB

Ackowledgements J.M. Mignot, LLB

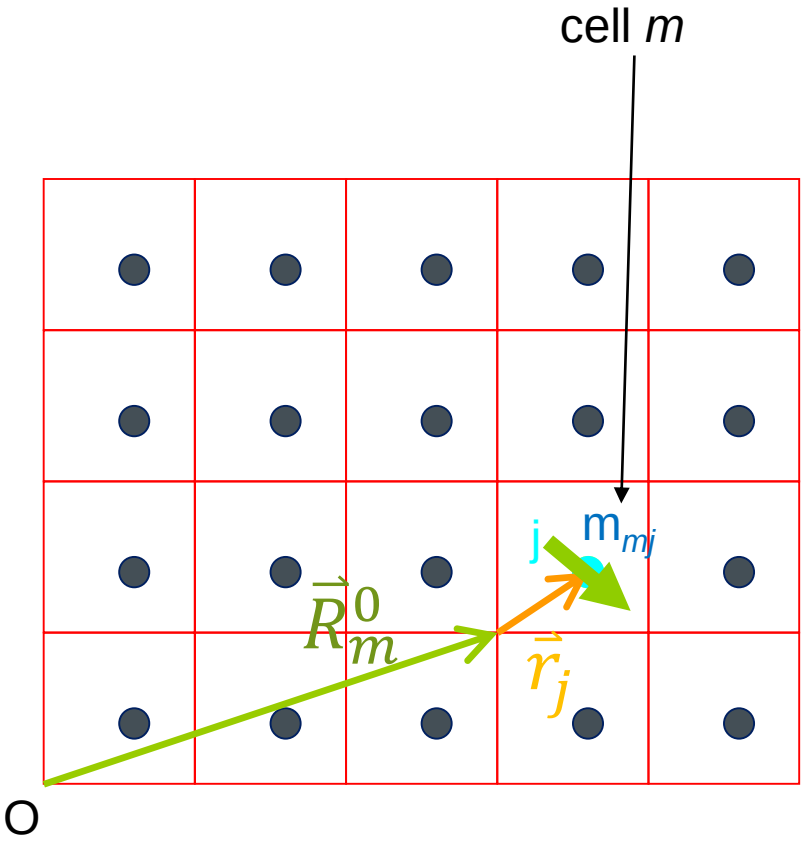
How to describe a periodic magnetic order

Similarly to what was shown previously

$$\vec{R}_{mj} = \vec{r}_j + \vec{R}^0_m$$

$$m_{mj} = \sum_{\mathbf{k}} S_{\mathbf{k}j} e^{-2\pi \mathbf{k}\cdot\vec{R}^0_m}$$

$$S_{-\mathrm{k}j} = S^*_{\mathrm{k}j}$$



k : propagation vector of the magnetic structure (vector of the reciprocal space), shows the periodicity and the direction of the propagation

S_{kj} : complex vector (Fourier component) describing the magnetic moment associated to each magnetic atom j for a given k vector

Examples

$$m_{mj} = \sum_{\mathbf{k}} S_{\mathbf{k}j} e^{-2\pi \mathbf{k}\cdot\vec{R}_m}$$

Commensurate propagation vector

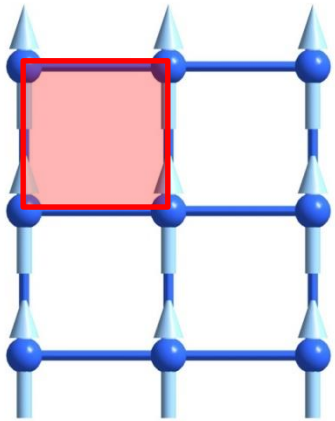
k = (0 0 0) ($\vec{k} = \vec{0}$)

Magnetic periodicty = crystal periodicity

k = (0.5 0 0)
($\vec{k} = \frac{1}{2}\vec{a^*}$)

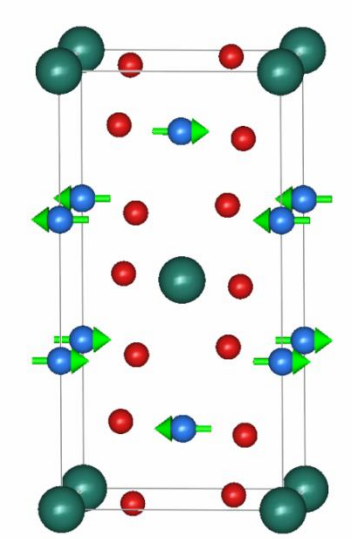
Doubling of the cell along a

Ferromagnetic

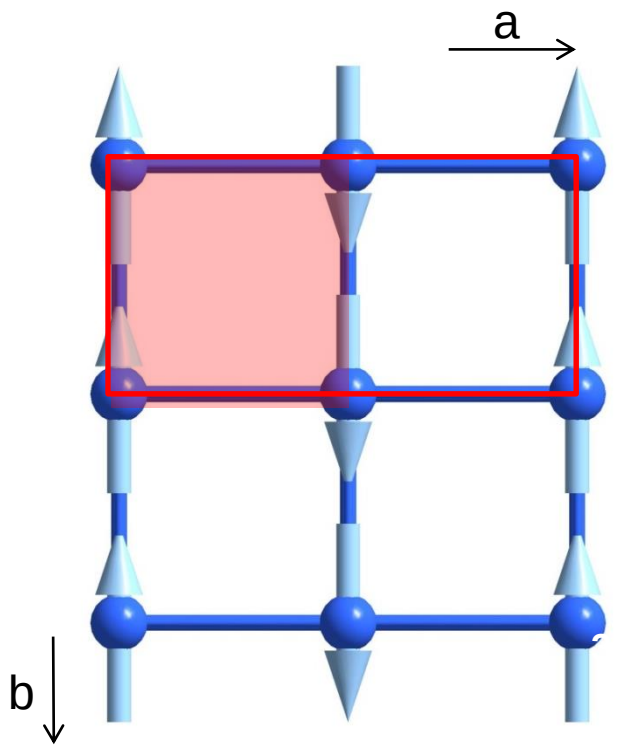


$\vec{m}_m = \vec{S}_{\vec{k}} = \vec{m}_0$

Antiferromagnetic

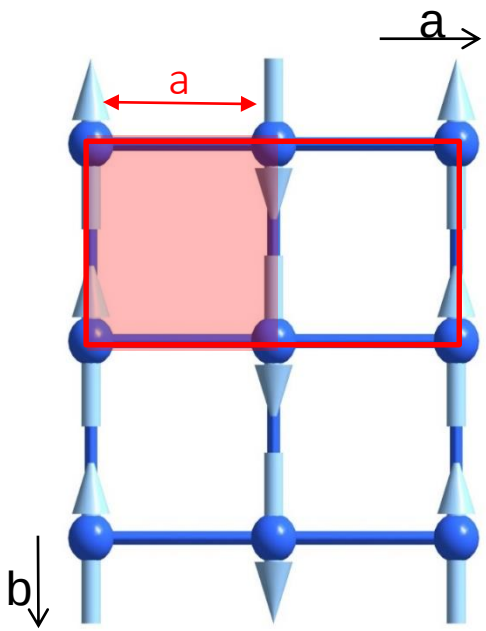


(several magnetic atoms in the unit cell)



Examples

$$m_{mj} = \sum_{\mathbf{k}} S_{\mathbf{k}j} e^{-2\pi \mathbf{k}\cdot\vec{R}_m}$$



k = (0.5 0 0)

$(\vec{k} = \frac{1}{2}\,\overrightarrow{a^*})$

Doubling of the cell along a : magnetic periodicity is twice the crystal cell periodicity

Reminder

$\vec{a}.\vec{a}^{\star} = 1$

$\vec{b}.\vec{a}^{\star} = \vec{c}.\vec{a}^{\star} = 0$

In a cell m located at $\vec{R}_l = l_a\vec{a} + l_b\vec{b} + l_c\vec{c}$

In cell $m = 0$ at $\vec{R}_0 = \vec{0}$ $\quad l_a = l_b = lc = 0 \;\Rightarrow\; \vec{m}_0 = +\vec{S}_{\vec{k}}$

In cell $m = 1$ at $\vec{R}_1 = \vec{a}$ $\quad l_a = 1, l_b = lc = 0 \;\Rightarrow\; \vec{m}_1 = -\vec{S}_{\vec{k}} = -\vec{m}_0$

In cell $m = 2$ at $\vec{R}_2 = 2\vec{a}$ $\quad l_a = 2, l_b = lc = 0 \;\Rightarrow\; \vec{m}_2 = +\vec{S}_{\vec{k}} = +\vec{m}_0$

…

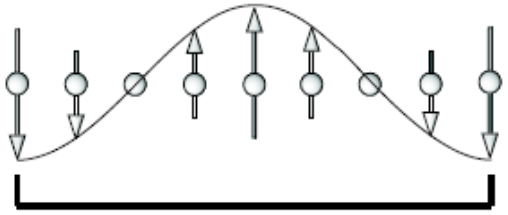
$$\vec{m}_m = \vec{S}_{\vec{k}} e^{-i\pi l_a} = (-1)^{l_a}\,\vec{S}_{\vec{k}}$$

Examples

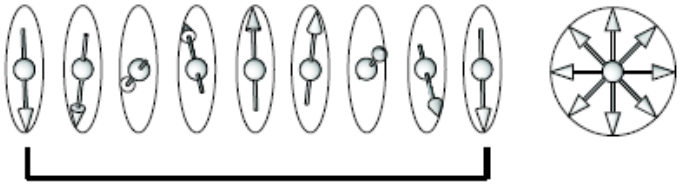
Propagation vectors can be incommensurate too!

$$m_{mj} = u_j \cos(2\pi(\mathrm{k}R_m^0 + \phi_{\mathrm{kj}}))$$

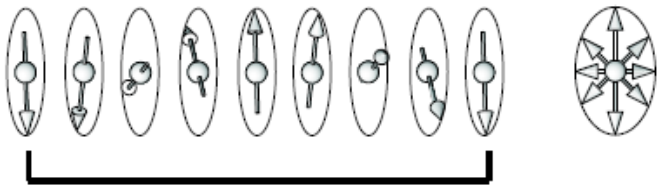
Sine wave order (amplitude modulated)



$$m_{mj} = u_j \cos(2\pi(\mathrm{k}R_m^0 + \phi_{\mathrm{kj}})) + v_j \sin(2\pi(\mathrm{k}R_m^0 + \phi_{\mathrm{kj}}))$$



Circular helix



Elliptic helix

How to determine a magnetic structure

In practice, determining a magnetic structure can be tricky :

- large number of parameters (up to 6 coefficients and one phase shift per magnetic atom and per **k**)
- few observations, especially in powders
- magnetic form factor

In fact, tools are available to make the task easier: we can simplify the analysis of systems that possess a degree of symmetry, by distinguishing the configurations that are possible given the known symmetry operations.

Possibility of using a polarized neutron beam in the most difficult cases

Description of a magnetic structure

- Based on irreducible representations and basis vectors, use of group theory, propagation vector formalism

Advantage : any magnetic structure can be described
Drawback : not very easy for beginners

- Magnetic crystallography and magnetic space groups (Shubnikov groups)

Drawback : superspace groups for incommensurate magnetic orders are still being developped
Advantage : easier for beginners

A bit of magnetic crystallography?

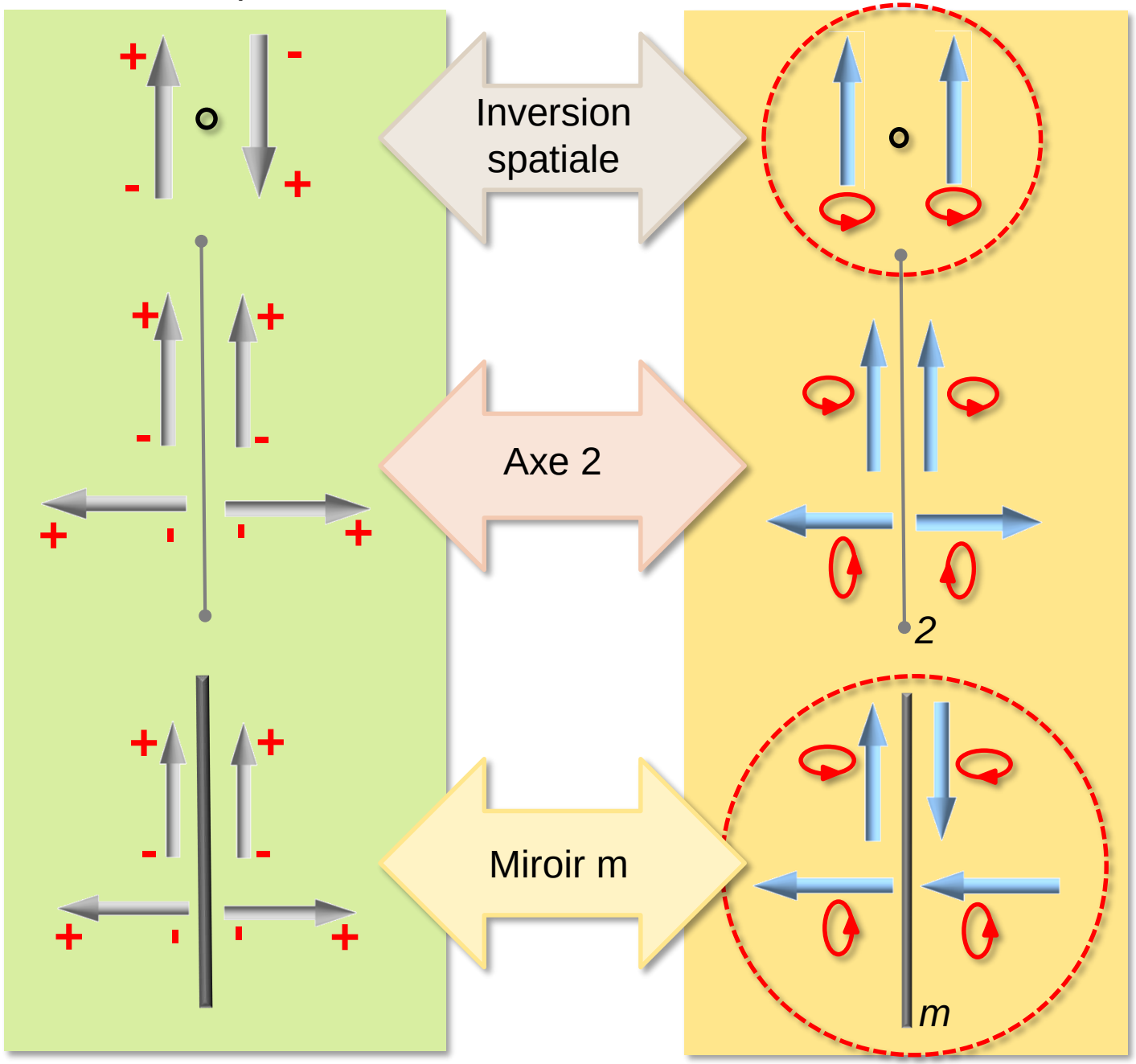
A little reminder first : the difference between a polar vector and an axial vector (= spin)

(dipôle électrique)

Vecteur polaire

(moment magnétique)

Vecteur axial



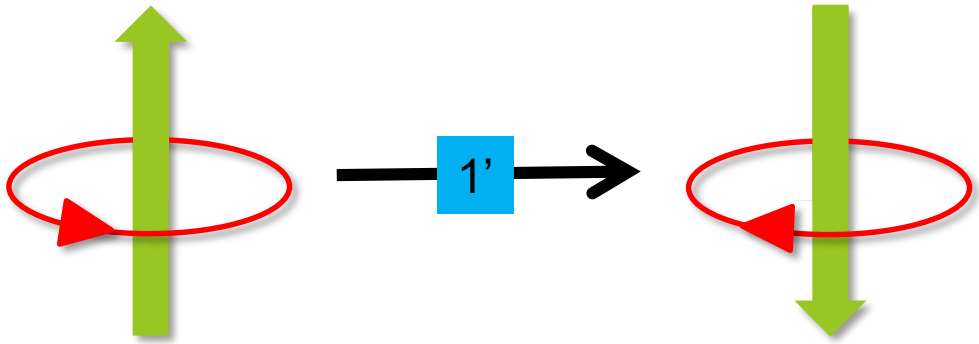
« The lost symmetry operation »

« We do not **add** but **substract** symmetry operations »

In magnetic crystallography, the lost symmetry operation, which is always present in non magnetic structures but absent in magnetically ordered ones is TIME INVERSION (or time reversal).

Time reversal

This new symmetry operator, time reversal, is written {1'|0 0 0}



(Spin : current loop)
Axial vector

Time reversal

{1'|0 0 0} does not modify atomic positions, but changes the direction (sign) of the magnetic moment

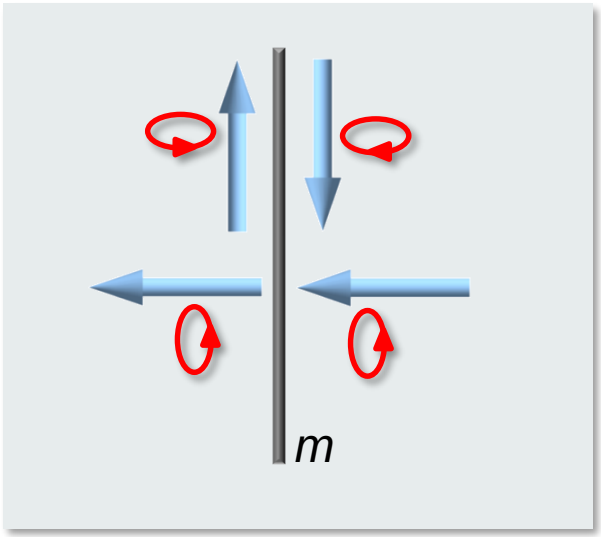
{1'|0 0 0} alone cannot be a symmetry operation in a magnetic structure

…all non magnetic structures are time reversal symmetric (but no one cares!)

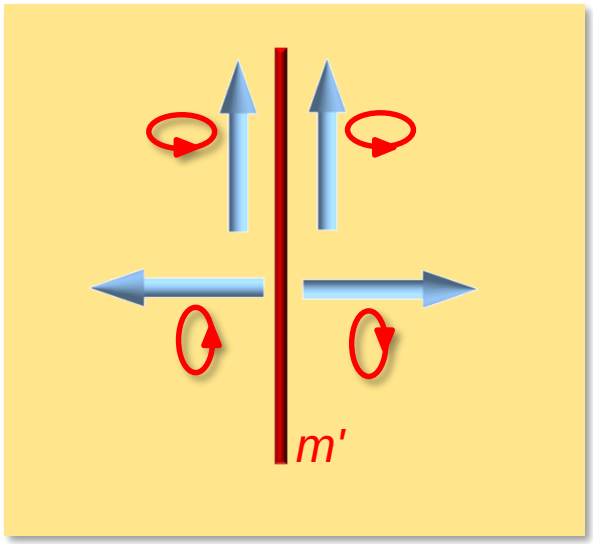
Magnetic point groups

With the addition of time reversal, one gets new symmety elements, combining a symmetry operator and 1’

Mirror m



Mirror m’



During a magnetic phase transition, some symmetry operators can become prime, or disappear alltogether

Magnetic point groups

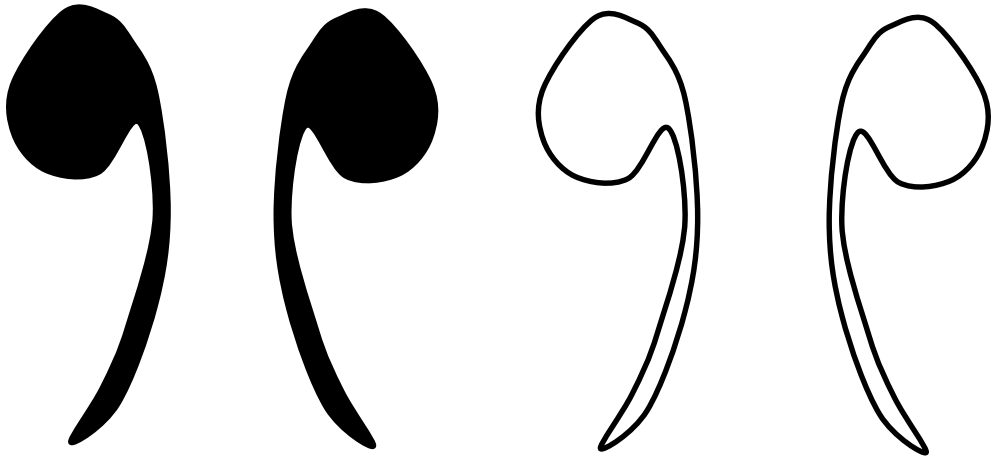
If you remember, there are 32 point groups in classical crystallography

Adding 1’ , one generates 122 magnetic point groups

32 colorless (without 1’)

32 grey (paramagnetic)

58 « black and white »



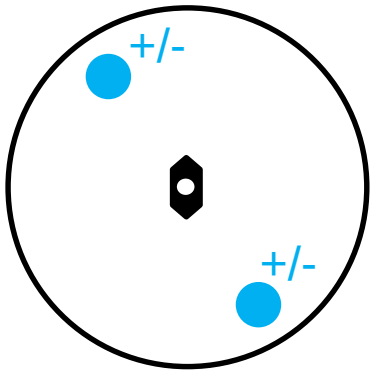
1 m 1’ m'

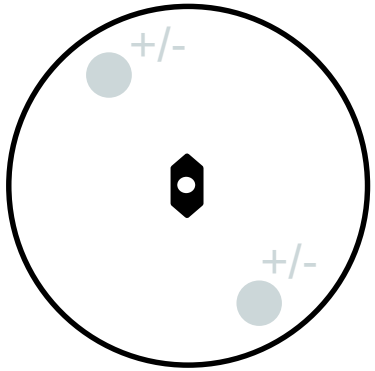
Magnetic point groups

Example with 2/*m*

2/*m*
colorless

x, y, z +1 (1)
-x, -y, z +1 (2)
x, y, -z +1 (*m*)
-x, -y, -z +1 (-1)

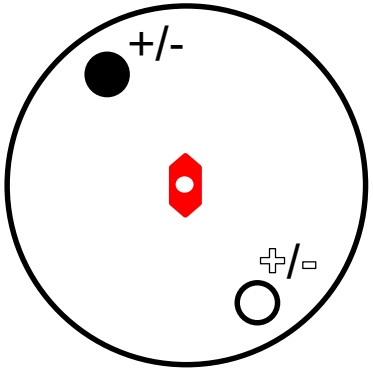




2/*m* grey

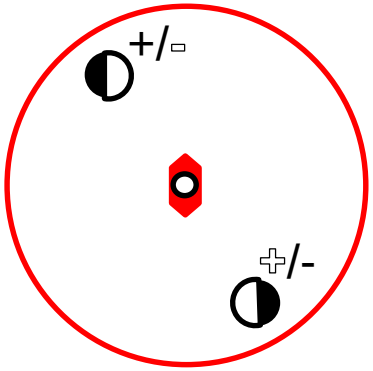
x, y, z +1 (1)
x, y, z -1 (1')
-x, -y, z +1 (2)
-x, -y, z -1 (2')
x, y, -z +1 (*m*)
x, y, -z -1 (*m*')
-x, -y, -z +1 (-1)
-x, -y, -z -1 (-1')

2'/*m*



x, y, z +1 (1)
-x, -y, z -1 (2')
x, y, -z +1 (*m*)
-x, -y, -z -1 (-1')

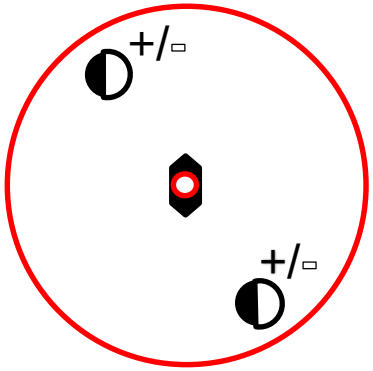
2'/*m*'



x, y, z +1 (1)
-x, -y, z -1 (2')
x, y, -z -1 (*m*')
-x, -y, -z +1 (-1)

Ferromagnetic if moments are in the mirror plane

2/*m*'



x, y, z +1 (1)
-x, -y, z +1 (2)
x, y, -z -1 (*m*')
-x, -y, -z -1 (-1')

Magnetic point groups, prediction of physical properties

Knowledge of the magnetic point group can be useful to access the tensors of various macroscopic properties, such as the linear magnetoelectric effect, electrical polarization...

Ex : ferromagnetoeletrics (ferromagnism+electric polarization)

Table 1.5.8.4. *List of the magnetic point groups of the ferromagnetoelectrics*

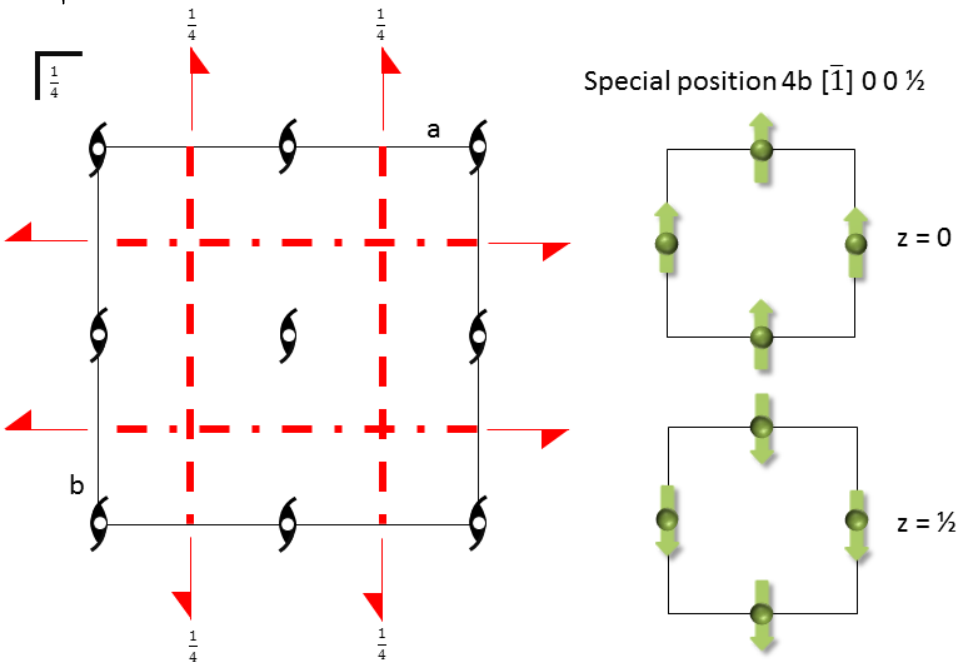
Symbol of symmetry group		Allowed direction of	
Schoenflies	Hermann–Mauguin	**P**	**M**
$\boldsymbol{C}_1$	1	Any	Any
$\boldsymbol{C}_2$	2	$\parallel 2$	$\parallel 2$
$\boldsymbol{C}_2(\boldsymbol{C}_1)$	$2'$	$\parallel 2'$	$\perp 2'$
$\boldsymbol{C}_s = \boldsymbol{C}_{1h}$	m	$\parallel m$	$\perp m$
$\boldsymbol{C}_s(\boldsymbol{C}_1)$	m'	$\parallel m'$	$\parallel m'$
$\boldsymbol{C}_{2v}(\boldsymbol{C}_2)$	$m'm'2$	$\parallel 2$	$\parallel 2$
$\boldsymbol{C}_{2v}(\boldsymbol{C}_s)$	$m'm2'$	$\parallel 2'$	$\perp m$
$\boldsymbol{C}_4$	4	$\parallel 4$	$\parallel 4$
$\boldsymbol{C}_{4v}(\boldsymbol{C}_4)$	$4m'm'$	$\parallel 4$	$\parallel 4$
$\boldsymbol{C}_3$	3	$\parallel 3$	$\parallel 3$
$\boldsymbol{C}_{3v}(\boldsymbol{C}_3)$	$3m'$	$\parallel 3$	$\parallel 3$
$\boldsymbol{C}_6$	6	$\parallel 6$	$\parallel 6$
$\boldsymbol{C}_{6v}(\boldsymbol{C}_6)$	$6m'm'$	$\parallel 6$	$\parallel 6$

International tables for crystallography (2006), Vol. D, Section 1.5.8.3, pp. 141-142

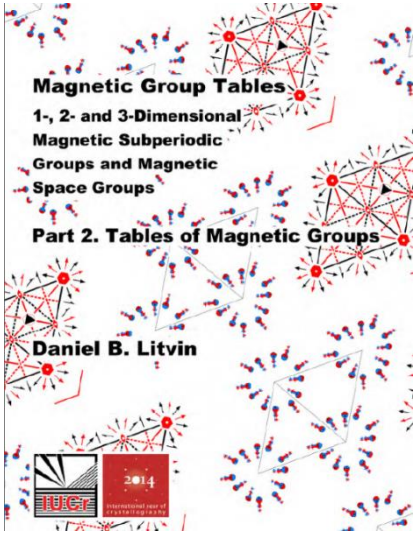
Magnetic space groups

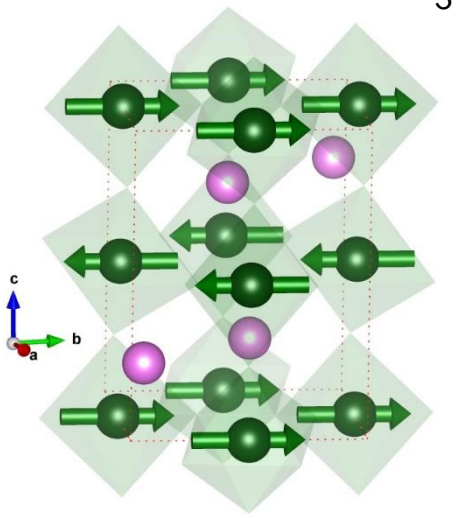
230 crystallographic space groups from *Ia-3d* to *P*1

1651 magnetic space groups (Shubnikov), 1191 of them compatible with a magnetic order



Special position 4b (1/2 0 0)
Point group symmetry 1





$LaMnO_3$
Pb'n'm

Magnetic space groups can be used in FullProf

Magnetic space groups

To take into account time reversal :

Pnma.1' = *Pnma* + {1'|0 0 0} x *Pnma*

Pnma symmetry operators are multiplied by {1'|0 0 0}

x, y, z, +1	{ 1 | 0 0 0 }
-x+1/2, -y, z+1/2, +1	{ 2_{001} | 1/2 0 1/2 }
-x, y+1/2, -z ,+1	{ 2_{010} | 0 1/2 0 }
x+1/2, -y+1/2, -z+1/2, +1	{ 2_{100} | 1/2 1/2 1/2 }
-x, -y, -z , +1	{ -1 | 0 0 0 }
x+1/2, y, -z+1/2, +1	{ m_{001} | 1/2 0 1/2 }
x, -y+1/2, z, +1	{ m_{010} | 0 1/2 0 }
-x+1/2, y+1/2, z+1/2, +1	{ m_{100} | 1/2 1/2 1/2 }

x, y, z, -1	{ 1' | 0 0 0 }
x+1/2, -y+1/2, -z+1/2, -1	{ $2'_{100}$ | 1/2 1/2 1/2 }
-x, y+1/2, -z, -1	{ $2'_{010}$ | 0 1/2 0 }
-x+1/2, -y, z+1/2, -1	{ $2'_{001}$ | 1/2 0 1/2 }
-x, -y, -z, -1	{ -1' | 0 0 0}
-x+1/2, y+1/2, z+1/2, -1	{ m'_{100} | 1/2 1/2 1/2 }
x, -y+1/2, z, -1	{ m'_{010} | 0 1/2 0 }
x+1/2, y, -z+1/2, -1	{ m'_{001} | 1/2 0 1/2 }

There are now 16 operations instead of eight

Pnma.1’ is not compatible with magnetic order as it contains the operator {1’|0 0 0} on its own
It is a grey group, which corresponds to the symmetry of the paramagnetic state

Magnetic structures only have symmetry operators where {1’|0 0 0} is combined with another operator (or is not present)

For example

A translation : {1’|t} = {1’|0 0 0}{1|t}
A mirror {m’|t} = {1’|0 0 0}{m|t}
A rotation {2’|t} = {1’|0 0 0}{2|t}
etc…

To build a space group allowing magnetic order

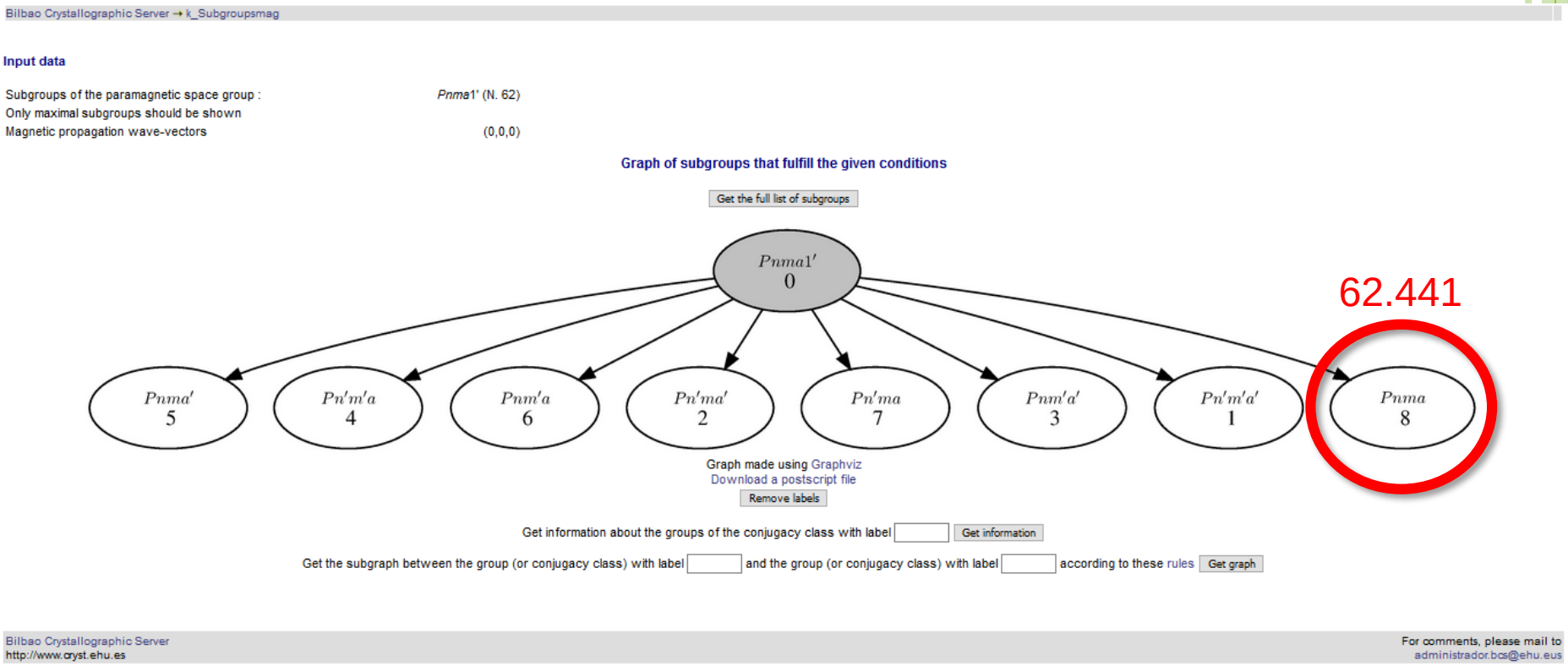
x, y, z, +1	{ 1 | 0 0 0 }
-x+1/2, -y, z+1/2, +1	{ 2_{001} | 1/2 0 1/2 }
-x, y+1/2, -z ,+1	{ 2_{010} | 0 1/2 0 }
x+1/2, -y+1/2, -z+1/2, +1	{ 2_{100} | 1/2 1/2 1/2 }
-x, -y, -z , +1	{ -1 | 0 0 0 }
x+1/2, y, -z+1/2, +1	{ m_{001} | 1/2 0 1/2 }
x, -y+1/2, z, +1	{ m_{010} | 0 1/2 0 }
-x+1/2, y+1/2, z+1/2, +1	{ m_{100} | 1/2 1/2 1/2 }

x, y, z, -1	{ 1' | 0 0 0}
x+1/2, -y+1/2, -z+1/2, -1	{ $2'_{100}$ | 1/2 1/2 1/2 }
-x, y+1/2, -z, -1	{ $2'_{010}$ | 0 1/2 0 }
-x+1/2, -y, z+1/2, -1	{ $2'_{001}$ | 1/2 0 1/2 }
-x, -y, -z, -1	{ -1' | 0 0 0}
-x+1/2, y+1/2, z+1/2, -1	{ m'_{100} | 1/2 1/2 1/2 }
x, -y+1/2, z, -1	{ m'_{010} | 0 1/2 0 }
x+1/2, y, -z+1/2, -1	{ m'_{001} | 1/2 0 1/2 }

Pnma1' → *Pn'ma'*

Sous-groupe d'index 2

Fortunately this can be computed!



Group/Subgroup relationships obtained with k-subgroupmag.

In this example, **k** = 0, maximal space groups

To visit! BCS : https://www.cryst.ehu.es/

Not to forget

To report a magnetic structure properly, use a .mcif file

STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

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Guidelines for communicating commensurate magnetic structures. A report of the International Union of Crystallography Commission on Magnetic Structures

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Keywords: IUCr Commission on Magnetic Structures; magnetic structures; magnetic space groups; representation analysis; magnetic CIF; guidelines.

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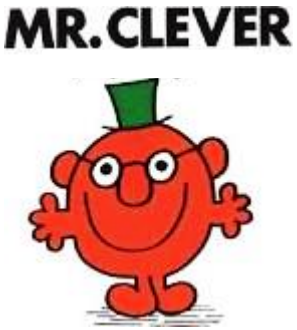
Take-home messages



With neutron diffraction you can…

… study crystal structures, locate light atoms, determine thermal parameters

…study phase transitions vs. T, P, H, …

…perform in situ, or cinetic studies

…study microstructures (stress, contraints, …)

…study magnetic ordrers, get spin density maps

…carry out quantitive analysis (H)

…

Advantages/Drawbacks

Neutrons

- bulk
- light elements
- contrast (H/D)
- magnetic structures

- low flux, bigger samples
- low resolution
- some absorption issues (Gd, B, Cd…)

RX/Synchrotron

- (very) high flux, small samples
- (very) high resolution
- surfaces

- weak scattering for light elements
- sample damage
- surfaces!

Thank you for your attention!