Formation Annuelle à la Neutronique (FAN) 2026

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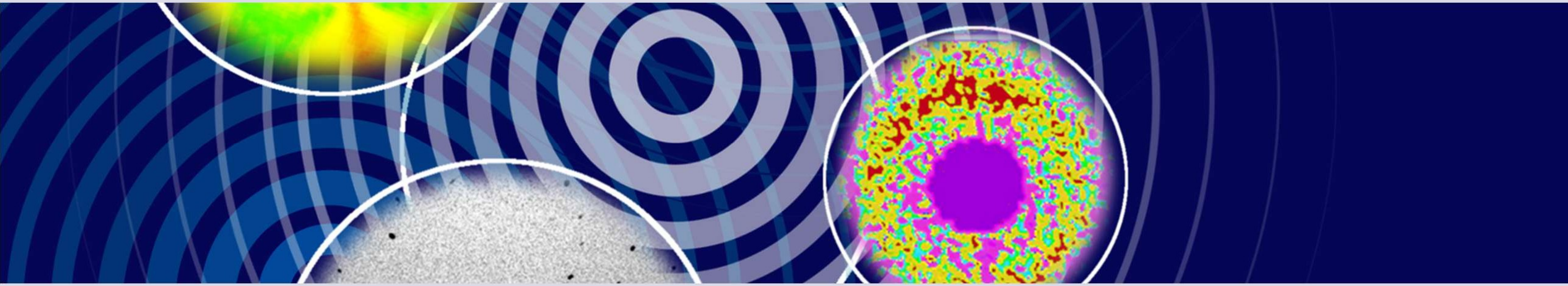


Introduction to neutron diffraction

Béatrice Grenier, UGA & CEA, Grenoble

grenier@ext.ill.fr

Outline

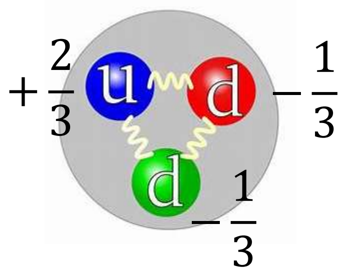
1. Neutron properties

2. Neutron interactions with matter
   - Refraction
   - Absorption
   - Scattering
     - *Nuclear scattering*
     - *Magnetic scattering*

3. Nuclear and Magnetic neutron diffraction
   - Introduction
   - Propagation vector formalism for magnetic structures
   - Nuclear/Magnetic diffracted peaks and intensities
   - Instrumentation & Examples of experimental results:
     - from powder neutron diffraction
     - from single-crystal neutron diffraction

Note: Topics marked with an asterisk (*) correspond to supplemental material included in the PDF version of the slides

Outline



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2. Neutron interactions with matter

Refraction

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Nuclear scattering

Magnetic scattering

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Propagation vector formalism for magnetic structures

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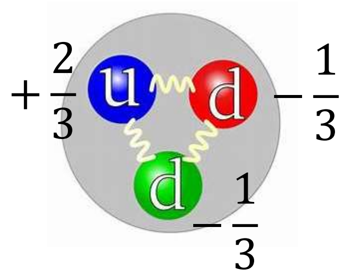
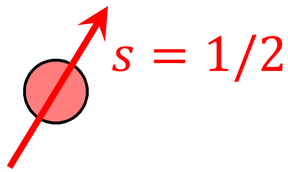
1. Neutron properties

Neutron = subatomic particle discovered in 1932 by James Chadwick
First neutron diffraction experiment in 1946 by Clifford Shull

composition 1 up quark, 2 down quarks



mass	$m = 1.675\ 10^{-27}$ kg $= 1.008665$ u
charge	0
spin	$s = 1/2$
↳ magnetic moment	$\mu_n = 9.663\ 10^{-27}$ J.T^{-1} $= 1.913\ \mu_{BN} \sim 10^{-3}\ \mu_B$



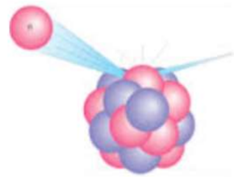
decomposition $n \rightarrow p + e^{-} + n$
life time $t = 888$ s ~ 15 min

1. Neutron properties: *wavelength and energy*

- **Neutrons** are **classical particles** of mass $m \sim 1$ u, whose kinetic energy E is given by:

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

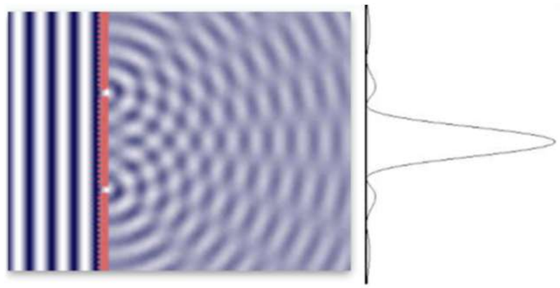
T: temperature of the moderator
v: neutron velocity



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

$$\boxed{k = \frac{2\pi}{\lambda}}$$

λ: wavelength



- **Wave – particle duality:** $\boxed{mv = \hbar k}$

$$\Rightarrow \boxed{E = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}} \Rightarrow \boxed{\lambda(\text{Å})\sqrt{E(\text{meV})} = 9.05} \qquad 1\ \text{Å} \leftrightarrow 80\ \text{meV}$$

- **X-rays** $\boxed{E = h\nu = \frac{hc}{\lambda}} \Rightarrow \boxed{\lambda(\text{Å}).E(\text{keV}) = 12.04} \qquad 1\ \text{Å} \leftrightarrow 12\ \text{keV}$

1. Neutron properties: *wavelength and energy*

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

$\Rightarrow$ **Neutrons** are well adapted to be **diffracted** by the atoms of matter

X-rays: same

$\rightarrow$ Study of structures

- $\boxed{E \sim 0.1 - 500\ \text{meV}}$ ~ excitations (phonons, magnons, ...) in condensed matter

$\Rightarrow$ **Neutrons** are well adapted for **inelastic scattering**
(change in energy = large fraction of the incident energy)

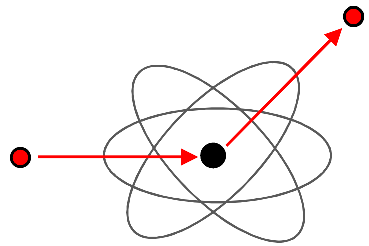
$\rightarrow$ Study of excitations

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

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

NB: X-rays are well adapted to induce electronic transitions $\rightarrow$ Selective studies at absorption edges

1. Neutron properties: *no electric charge*



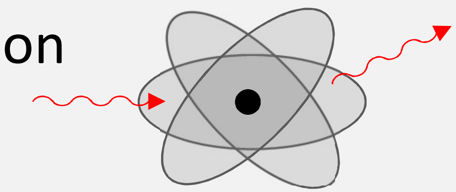
- **Neutrons have no electric charge**

$\Rightarrow$ Neutrons can penetrate deep inside the matter
and come close to the nuclei without being stopped by the Coulomb interaction

Nuclear interaction
(neutron – nucleus)

bulk studies
(neutrons are weakly absorbed)

X-rays: electromagnetic waves $(\vec{E}, \vec{B}\ ) \Rightarrow$ strong Coulomb interaction



Thomson interaction
(photons – electrons)

surface studies
(X-rays are strongly absorbed)

1. Neutron properties: *spin and magnetic moment*

- **Neutrons have a spin ½**

⇒ Possibility to **polarize a neutron beam** & **analyze its final polarization**

- using a polarizing monochromator/analyzer that diffracts only spin ↑ neutrons
- using polarized ^3He that strongly absorbs spin ↓ neutrons and not spin ↑ neutrons
- or using a polarizing multilayer device reflecting only spin ↑ neutrons

⇒ **Several experimental possibilities**

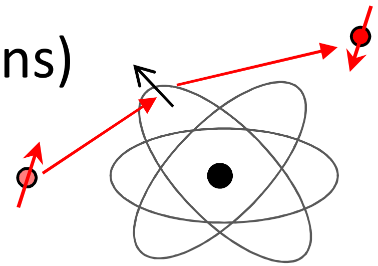
X-rays: linear or circular polarized electromagnetic wave at synchrotron

- **Neutrons have a magnetic moment** $\mu_n = 1.913\ \mu_{BN}$

⇒ μ_n is sensitive to the magnetic moments of matter (unpaired electrons)

⇒ **Magnetic interaction** with $\boxed{I_M \sim I_N}$

⇒ **Elastic and inelastic magnetic scattering**



X-rays: $\boxed{I_M \sim 10^{-6}\ I_{Thomson}}$

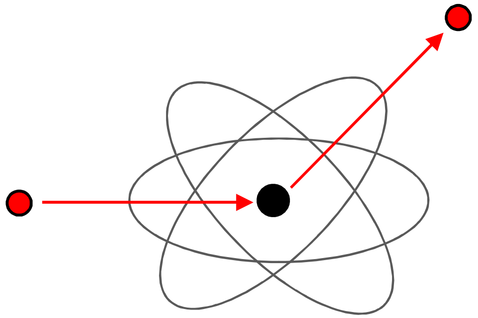
1. Neutron properties: *neutrons/X-rays comparison*

	Neutrons	**Synchrotron X-rays**
Beam flux: Beam size at sample:	$\sim 10^7 - 10^8$ neutrons.s^{-1}.cm^{-2} $\sim$ a few cm^2	$\sim 10^{13} - 10^{14}$ photons.s^{-1} in a focal spot of $\sim$ a few nm^2 – 500 mm^2 $\rightarrow$ Detection of very weak signals
Sample size:	a few mm^3 – a few cm^3	$\sim$ a few 0.1 mm^3 $\rightarrow$ Nanophysics
Wavelength: Energy:	$\lambda \sim 1$ **Å** $E \sim$ a few **meV**	$\lambda \sim 1$ **Å** $E \sim$ a few **keV**
Resolution	- **Average** in wavelength: monochromatic beam: $\frac{\Delta\lambda}{\lambda} = 10^{-2}$ - **Very good** in energy $\rightarrow$ Study of excitations	- **Very good** in wavelength: monochromatic beam: $\frac{\Delta\lambda}{\lambda} = 10^{-4}$ $\rightarrow$ Studies of peak profiles - **Poor** in energy
Absorption	**Weak**: depends on the isotope $\rightarrow$ bulk studies $\rightarrow$ sample environments easier to realize (thicker windows, many suited materials)	**Strong**: depends on λ and Z $\rightarrow$ surface studies $\rightarrow$ choice of λ according to the absorption edge of the element (EXAFS, anomalous scattering, ...)

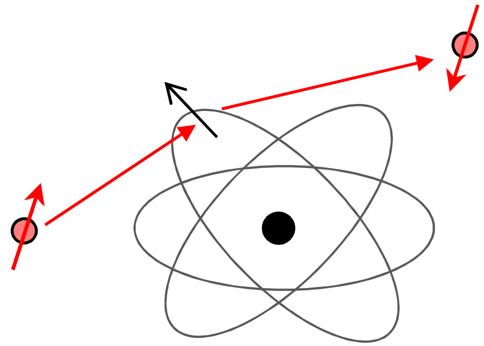
Outline

1. Neutron properties

2. Neutron interactions with matter



Refraction
Absorption
Scattering
Nuclear scattering
Magnetic scattering



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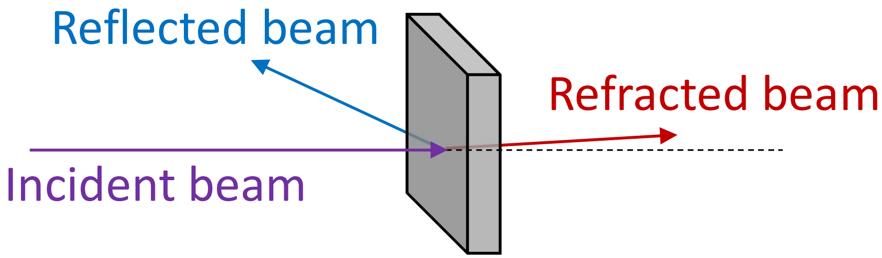
2. Neutron interactions with matter

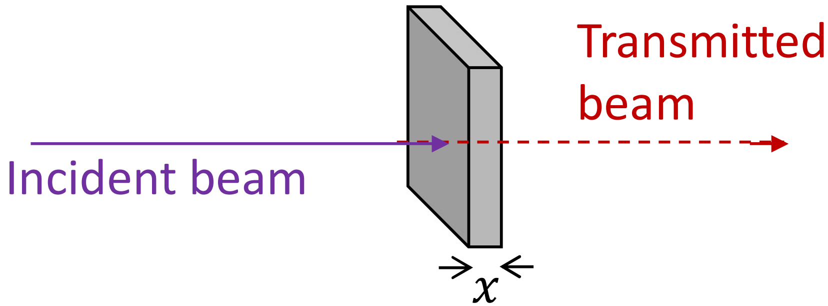
Refraction *



As for visible light…
but **tiny deviation**
($n \sim 1$ for all materials)

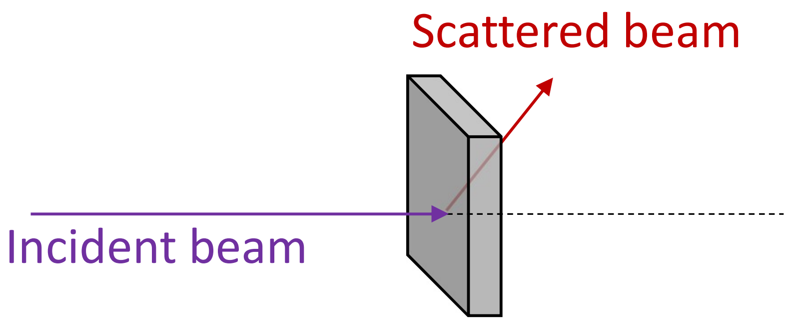
→ neutron guides and reflectivity *

Absorption *



Neutrons absorbed by the nuclei
nuclear reactions $\rightarrow$ p, α, and/or γ

Scattering
↳ diffraction



Neutrons **interact** with the nuclei and spins (unpaired electrons)
→ scattered beam
→ Bragg diffraction in crystals

- For neutrons,
  most of the materials have a **refractive index n smaller than 1** and **very close to 1**

Total reflection is possible

but with a very small critical angle θ_c

cf Snell-Descartes law (#12): $\boxed{\cos\theta_c = n}$

⇒ **APPLICATIONS**:
Instrumentation: Neutron guides & Experimental technique: reflectivity

- One can show (#12) that: $\boxed{\theta_c \propto \lambda}$

One of the most refractive materials: ^{58}Ni
$n = 0.9999985$

For $\lambda = 1$ Å: $\theta_c = 6'$
For $\lambda = 20$ Å: $\theta_c = 2°$

→ **neutron guides for thermal and cold neutrons** (larger λ)

N.B.: larger θ_c values are reached with supermirrors

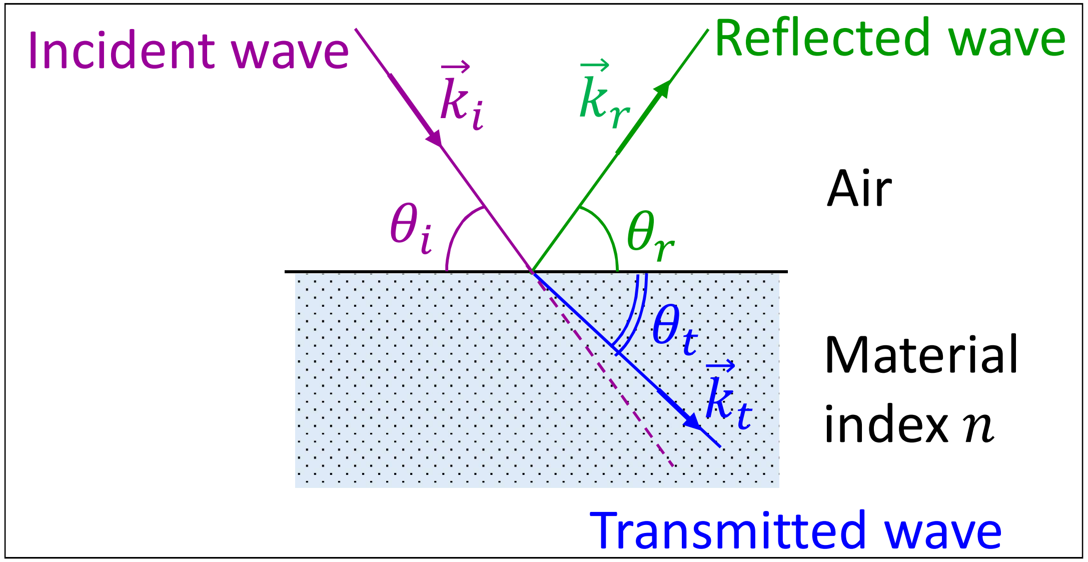
2. Neutron interactions with matter: *refraction*

- **Snell-Descartes law:**

$$\boxed{\begin{aligned}\cos\theta_i &= \cos\theta_r \\ \cos\theta_i &= n\cos\theta_t\end{aligned}} \qquad \left(n = \frac{c}{v}\right)$$

Total reflection if $\boxed{\theta_t = 0}$

$\rightarrow \theta_i \leq \theta_c$ such that $\boxed{\cos\theta_c = n}$



- **Refractive index and critical angle**

$$\boxed{n = 1 - \frac{\lambda^2}{2\pi}Nb} \qquad \text{with } b = b' + ib''$$

Imaginary part = absorption of the refracted wave

b = Fermi length (real for most of the materials)

N = number of atoms per unit volume

λ = wavelength of the neutron beam

$$\text{Thus} \quad n = \cos\theta_c \simeq 1 - \frac{\theta_c^2}{2} \quad \Rightarrow \quad \boxed{\theta_c \simeq \lambda\sqrt{\frac{Nb}{\pi}} \propto \lambda}$$

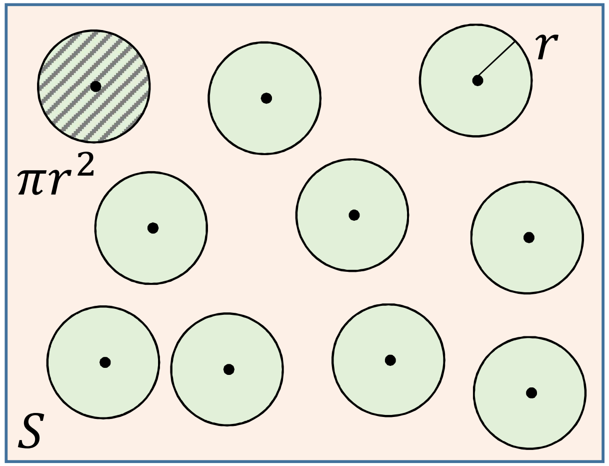
Cross section

→ quantifies the ability for a chemical element to absorb or scatter neutrons

Consider a thin sample surface S containing n atoms (assumed to be point-like)

The probability that a projectile (of negligible diameter) passes within a distance $< r$ of an atom is:

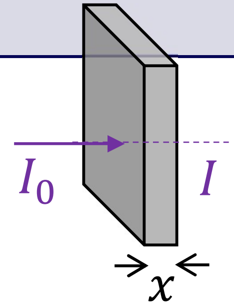
$$p = \frac{n\pi r^2}{S}$$



Cross section = fictitious area that a target atom (modeled as an impenetrable disk) would need to have in order to reproduce the observed probability of interaction between the neutron (assumed to be a point particle) and the atoms of that target.

$\boxed{\sigma_a, \sigma\text{: [surface] in barns } (1 \text{ barn} = 10^{-24}\ \text{cm}^2)}$

2. Neutron interactions with matter: *absorption*



- **Absorption cross section** $\sigma_a = \mu/N$

N: number of nuclei per unit volume
μ: linear absorption coefficient

→ quantifies the probability of neutron absorption by a nucleus

$\boldsymbol{\sigma_a}$: [surface], given in **barn** (**1 barn = 10^{-24} cm^2**)
depends on λ, Z (chemical specie) and A (isotope) *

Transmittance:

$$\frac{I}{I_0} = e^{-\sigma_a N x}$$

- **<u>For most of the elements</u>**

neutrons are weakly absorbed at the working wavelength (σ_a ~1 barn at $\lambda = 1.8$ Å)

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

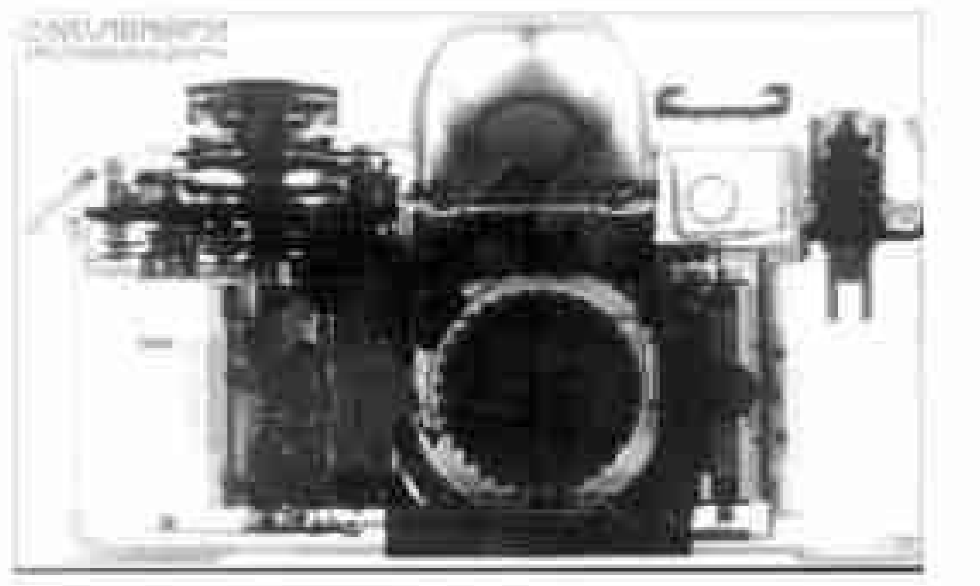
*

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

- **<u>"Pathological" elements</u>** *

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

2. Neutron interactions with matter: *absorption*



neutrons **X-rays**

Different contrast

Neutrons reveal the **hydrogen** contained in plastic materials

X-rays are more sensitive to **metallic materials** (heavy elements)

- For a given element:

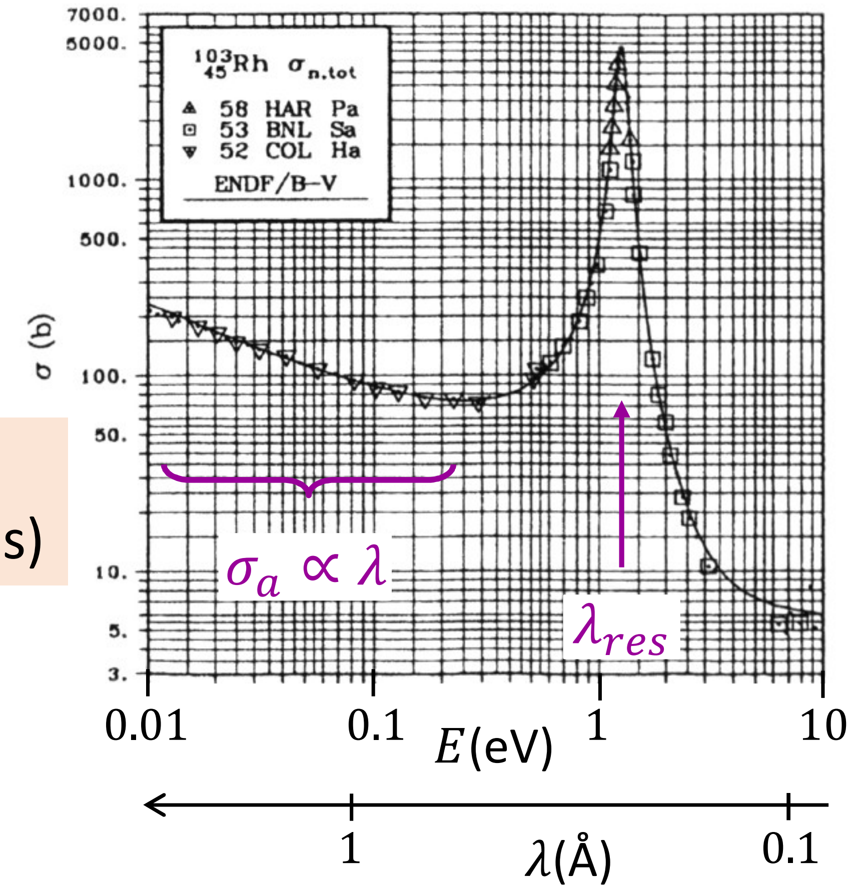
- **resonance peaks**: very strong absorption at λ_{res}
- far from λ_{res}: $\sigma_a \propto \lambda$, weak absorption

- **No particular law as a function of Z and A**:
  "random" variation of σ_a with Z and A

For most of the elements: resonance far from the working wavelengths $\rightarrow$ **weak absorption** (a few barns)

"Pathological" elements: strong absorption

Nucleus	σ_a (barn)	Nucleus	σ_a (barn)
^{3}He	5 333	^{151}Eu	9 100
^{6}Li	940	^{155}Gd	61 100
^{10}B	3 835	^{157}Gd	259 000
^{113}Cd	20 600	^{164}Dy	2 840
^{115}In	202	^{168}Yb	2 230
^{123}Te	418	^{176}Lu	2 065
^{149}Sm	42 080		



values given for thermal neutrons ($\lambda = 1.8$ Å)

2. Neutron interactions with matter: *absorption*

⇒ **Consequences/applications: use elements that…**

- weakly absorb for **sample environments** (Al, V),
  sample itself (isotopic substitution)

Al: $\sigma_a = 0.231$ barn
V: $\sigma_a = 5.08$ barn

Example:
substitution of **natural Gd** by ^{160}**Gd** in frustrated magnet $Gd_3Ga_5O_{12}$ to avoid strong absorption
Petrenko et al. PRL 1998

https://www.ncnr.nist.gov/resources/n-lengths

Neutron scattering lengths and cross sections

Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
Gd	---	6.5-13.82i	---	29.3	151.(2.)	180.(2.)	49700.(125.)
152Gd	0.2	10.(3.)	0	13.(8.)	0	13.(8.)	735.(20.)
154Gd	2.1	10.(3.)	0	13.(8.)	0	13.(8.)	85.(12.)
155Gd	14.8	6.0-17.0i	(+/-)5.(5.)-13.16i	40.8	25.(6.)	66.(6.)	61100.(400.)
156Gd	20.6	6.3	0	5	0	5	1.5(1.2)
157Gd	15.7	-1.14-71.9i	(+/-)5.(5.)-55.8i	650.(4.)	394.(7.)	1044.(8.)	259000.(700.)
158Gd	24.8	9.(2.)	0	10.(5.)	0	10.(5.)	2.2
160Gd	21.8	9.15	0	10.52	0	10.52	0.77

σ_a (barn)

- strongly absorb for **shielding** (B_4C),
  collimations and diaphragms (Cd),
  detectors (^{3}He, ^{6}Li, ^{10}B)

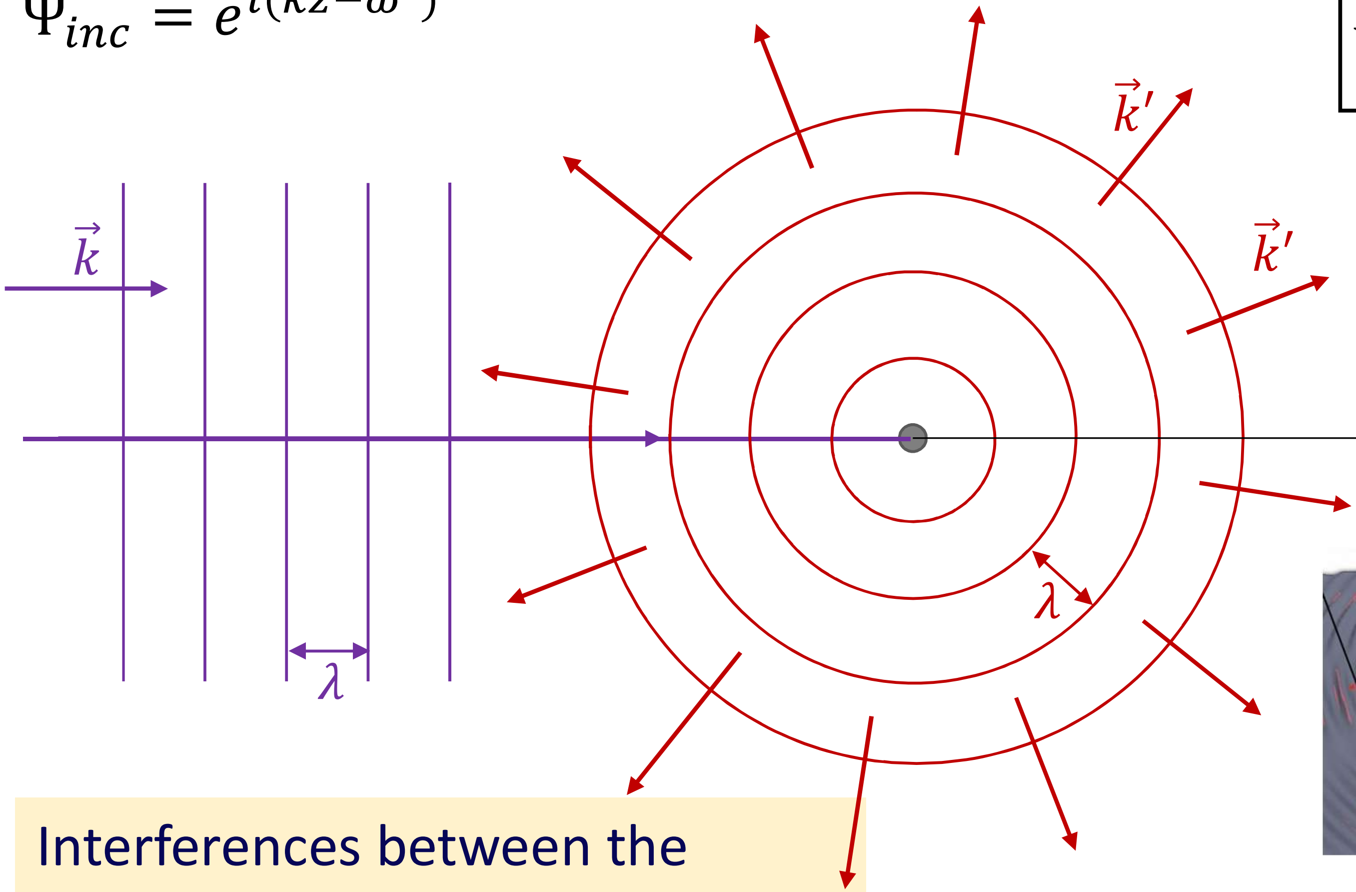
- weakly absorb at the desired wavelength and strongly absorbs elsewhere
  for **filters** (graphite, Be) → filter harmonics $\lambda/2$, $\lambda/3$, …

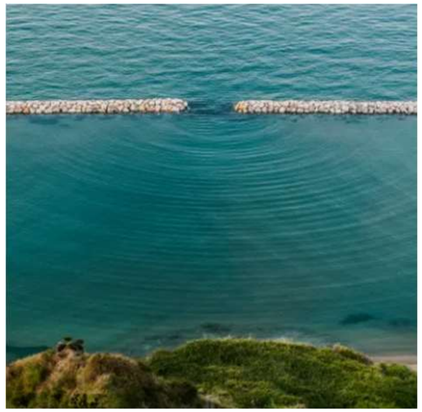
Incident beam ≡ plane wave

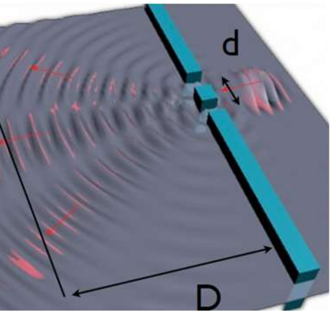
$$\Psi_{inc} = e^{i(kz-\omega\ )}$$

Scattered beam ≡ spherical wave

$$\boxed{\Psi_{dif} = -a(\vec{k},\vec{k}')\,\frac{e^{i(k' r-\omega' t)}}{r}}$$







Interferences between the spherical waves coming from an array of atoms generate a diffraction pattern (see part 3.)

$a(\vec{k},\vec{k}')$ = scattered amplitude

characterizes the beam/matter interaction (> 0 for a repulsive potential)

2. Neutron interactions with matter: *scattering*

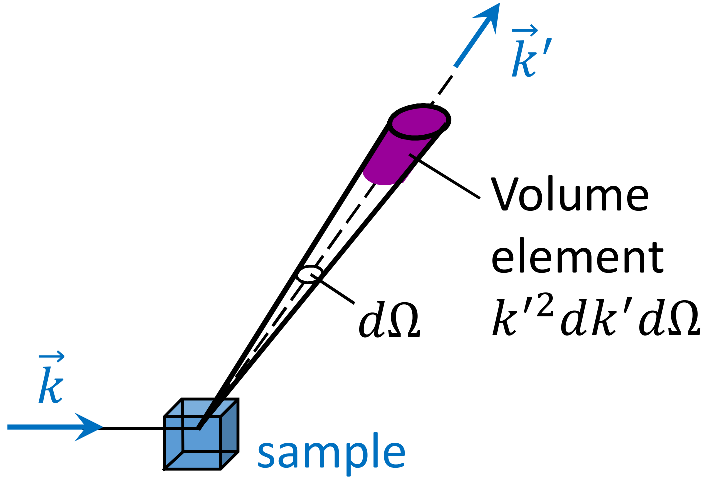
Scattered amplitude $a(\vec{k},\vec{k}')$

$$\boxed{a(\vec{k},\vec{k}') = \frac{m}{2\pi\hbar^2}\langle\vec{k}'|V(\vec{r})|\vec{k}\rangle} \Rightarrow \boxed{a(\vec{Q}) = \frac{m}{2\pi\hbar^2}\int e^{-i\vec{Q}.\vec{r}}\, V(\vec{r})\, d^3r} \qquad (\vec{Q} = \vec{k}' - \vec{k})$$

Fourier Transform (FT) of the neutron – matter interaction potential $V(\vec{r})$

Differential cross section $$\boxed{\frac{d\sigma}{d\Omega} = |a(\vec{Q})|^2}$$

= scattered intensity per solid angle dΩ around $\vec{k}'$ normalized to the incident neutron flux [m²/sr]



Total cross section σ

= total scattered intensity normalized to the incident neutron flux [m²]

$$\boxed{\sigma = \int_{\text{all directions}} \frac{d\sigma}{d\Omega} d\Omega = \int_\Omega |a(\vec{Q})|^2 d\Omega}$$

unit: barns (1 barn $= 10^{-24}$ cm²)

2. Neutron interactions with matter: *scattering*

Scattered amplitude $a(\vec{k},\vec{k}')$

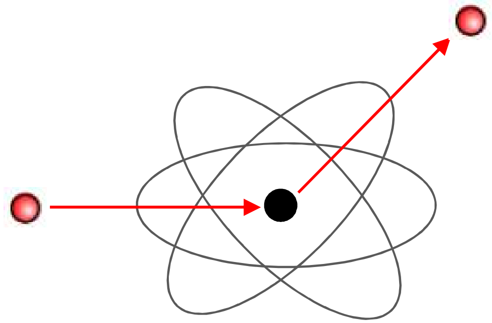
$$\boxed{a(\vec{k},\vec{k}') = \frac{m}{2\pi\hbar^2}\langle\vec{k}'|V(\vec{r})|\vec{k}\rangle} \Rightarrow \boxed{a(\vec{Q}) = \frac{m}{2\pi\hbar^2}\int e^{-i\vec{Q}.\vec{r}}\,V(\vec{r})\,d^3r} \qquad (\vec{Q} = \vec{k}' - \vec{k})$$

Fourier Transform (FT) of the neutron – matter interaction potential $V(\vec{r})$

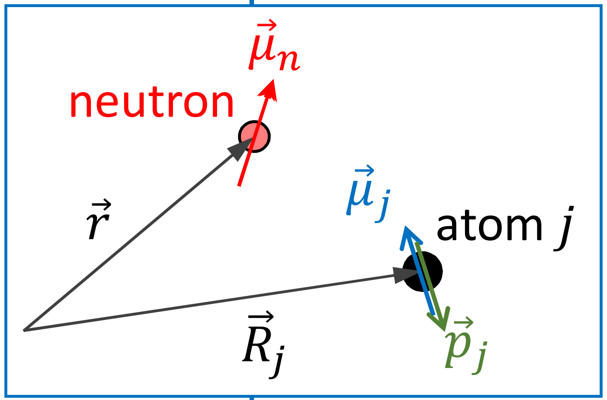
$$\left.\begin{array}{l}\text{Nuclear}\\ \text{Magnetic}\end{array}\right\} \text{interaction} \rightarrow \text{expressions of} \left\{\begin{array}{l}V_N(\vec{r})\\ V_M(\vec{r})\end{array}\right. \text{ and thus of} \left\{\begin{array}{l}a_N(\vec{Q})\\ a_M(\vec{Q})\end{array}\right. \;?$$

2. Neutron interactions with matter: *scattering*

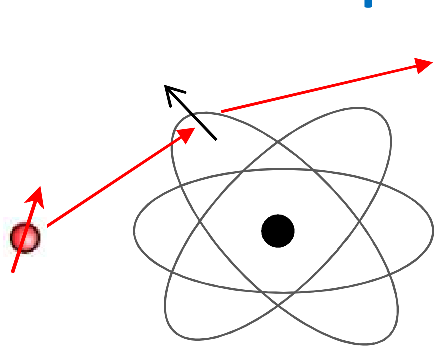
Nuclear interaction potential



$$V_{Nj}(\vec{r}) = \frac{2\pi\hbar^2}{m} b_j\, \delta(\vec{r} - \vec{R}_j)$$



Magnetic interaction potential



$$V_{Mj}(\vec{r}) = -\vec{\mu}_n . \vec{B}_j(\vec{r} - \vec{R}_j)$$

b_j: nuclear scattering length of atom j
= **Fermi length** of atom j

nucleus size $\ll \lambda$(neutrons)
→ nuclear density = $\delta(\vec{r} - \vec{R}_j)$

isotropic

$\vec{B}_j$: magnetic field arising from the unpaired electrons of atom j (spin and orbital moments)

$$\vec{B}_j = \frac{\mu_0}{4\pi}\left\{\vec{\nabla} \times \left[\frac{\vec{\mu}_j \times (\vec{r} - \vec{R}_j)}{\left|\vec{r} - \vec{R}_j\right|^3}\right] - \frac{2\vec{\mu}_n}{\hbar} \frac{\vec{p}_j \times (\vec{r} - \vec{R}_j)}{\left|\vec{r} - \vec{R}_j\right|^3}\right\}$$

dipolar interaction → *anisotropic*

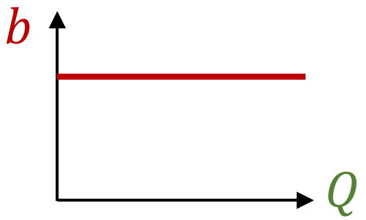
2. Neutron interactions with matter: *nuclear scattering*

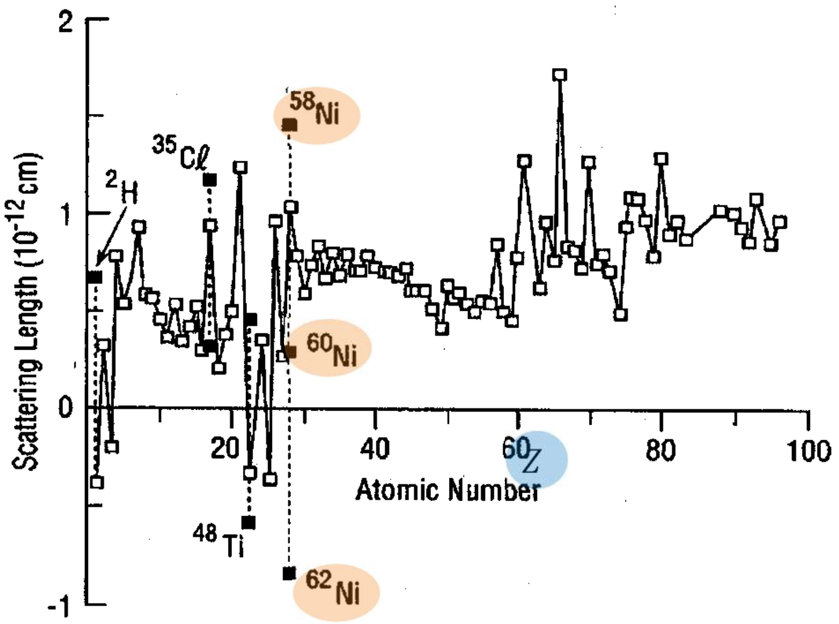
Neutrons scattered by the atomic nuclei: $\delta(r)$ in $r \overset{\text{F.T.}}{\Rightarrow}$ constant in Q-space

$$\boxed{a_N(Q) = b = C^{st}}$$

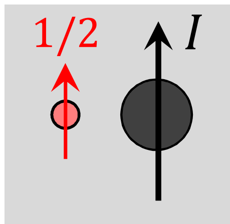
$b = (-1 \text{ to } +2)\ 10^{-12}$ cm

Nuclear scattered amplitude for neutrons
= Fourier transform (F.T.) of the nuclear density
= scattering length or **Fermi length**

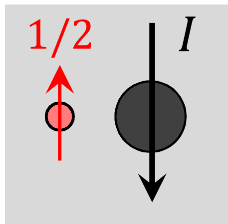




- **b does not depend on $\vec{Q} = \vec{k}' - \vec{k}$**
- **b depends on Z** (chemical specie) **and A** (isotope)
  b = superposition of slowly increasing potential scattering (due to atomic weight) and of resonance scattering → b varies ~ randomly with Z and A
- **b also depends on the neutron and nucleus spin states**



$I + \frac{1}{2} \rightarrow b_+$



$I - \frac{1}{2} \rightarrow b_-$

if $I \neq 0$:

Average ⇒ **coherent** and **incoherent** scattering lengths

$$b_{coh} = \bar{b}$$
$$b_{inc} = \sqrt{\overline{b^2} - \bar{b}^2}$$

Coherent and incoherent scattering *

Scattering total cross section: $\sigma = \int_\Omega \left|a(\vec{Q})\right|^2 d\Omega$ with $a(\vec{Q}) = b$ $\Rightarrow$ $\boxed{\sigma = 4\pi b^2}$

$$\begin{cases} b_{coh} = \bar{b} \\ b_{inc} = \sqrt{\overline{b^2} - \bar{b}^2} \end{cases}$$

Coherent scattering = Interaction between atomic pairs ($\sum_{j\,j'}$)
constructed from the **average** $\bar{b}^2$

Average potential → interferences → **pair-correlation functions**

Coherent scattering cross section: $\sigma_{coh} = 4\pi\bar{b}^2$

Incoherent scattering = Interaction of each atom with itself ($\sum_j$)
constructed from the **deviations to the average** $\overline{\Delta b^2} = \overline{b^2} - \bar{b}^2$

Random distribution of b_j → no interferences → **self-correlation functions**

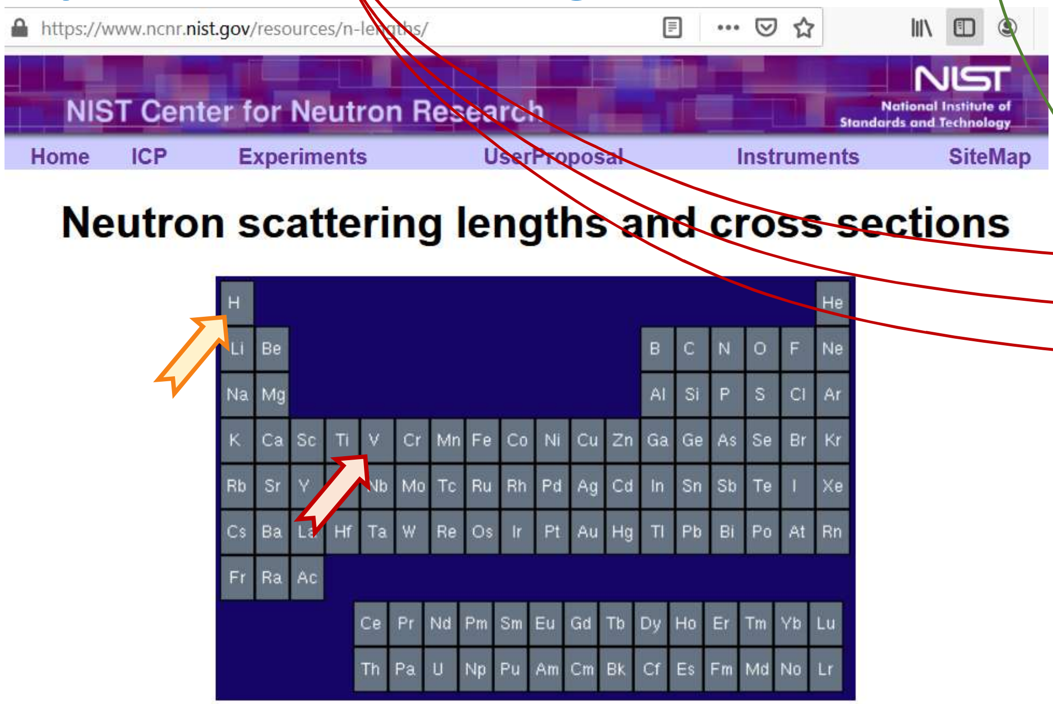
Incoherent scattering cross section: $\sigma_{inc} = 4\pi(\overline{b^2} - \bar{b}^2)$

2. Neutron interactions with matter: *nuclear scattering*

⇒ **Coherent and incoherent cross sections:** $\boxed{\sigma_{coh} = 4\pi\bar{b}^2}$ and $\boxed{\sigma_{inc} = 4\pi(\overline{b^2} - \bar{b}^2)}$

for **each isotope** and for the **natural element** (average on the various isotopes)

https://www.ncnr.nist.gov/resources/n-lengths



Hydrogen vs Deuterium:

Neutron scattering lengths and cross sections							
Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
H	---	-3.7390	---	1.7568	80.26	82.02	0.3326
1H	99.985	-3.7406	25.274	1.7583	80.27	82.03	0.3326
2H	0.015	6.671	4.04	5.592	2.05	7.64	0.000519
3H	(12.32 a)	4.792	-1.04	2.89	0.14	3.03	0

Absorption cross section

$\underbrace{b_{coh}\ b_{inc}}_{\text{Fermi lengths (fm)}}$ $\underbrace{\sigma_{coh}\ \sigma_{inc}\ \ \sigma\ \ \ \sigma_a}_{\text{Cross sections (barn)}}$

Natural abundance (%)

Fermi lengths (fm)

Cross sections (barn)

Vanadium:

Neutron scattering lengths and cross sections							
Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
V	---	-0.3824	---	0.0184	5.08	5.1	5.08
50V	0.25	7.6	---	7.3(1.1)	0.5	7.8(1.0)	60.(40.)
51V	99.75	-0.402	6.35	0.0203	5.07	5.09	4.9

Hydrogen vs Deuterium:

$$b_{coh}(^1H) = -3.74 \text{ fm}$$
$$b_{coh}(^2H) = +6.67 \text{ fm}$$

Strong isotopic effect!

Vanadium:

$$\sigma_{coh}(V) \sim 0$$
$$\sigma_{inc}(V) \sim 5 \text{ barn}$$

Purely incoherent!

Hydrogen vs Deuterium:

Hydrogen (H $= {}^1$H):
1 single proton of nuclear spin 1/2
$\Rightarrow b_+$ very different from b_-
$\Rightarrow \sigma_{inc}(\mathrm{H}) \gg \sigma_{coh}(\mathrm{H})$
(larger than for all other elements)

Deuterium (D $= {}^2$H):
Nucleus = 1 neutron and 1 proton
$\Rightarrow b_+$ not so different from b_-
$\Rightarrow \sigma_{inc}(\mathrm{D})$ strongly reduced
and $\sigma_{coh}(\mathrm{D}) > \sigma_{inc}(\mathrm{D})$

$\Rightarrow$ neutrons are a privileged tool for the study of organic compounds

Neutron scattering lengths and cross sections							
Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
H	---	-3.7390	---	1.7568	80.26	82.02	0.3326
1H	99.985	-3.7406	25.274	1.7583	$\boxed{80.27}$	82.03	0.3326
2H	0.015	6.671	4.04	$\boxed{5.592}$	2.05	7.64	0.000519
3H	(12.32 a)	4.792	-1.04	2.89	0.14	3.03	0

σ_{coh} σ_{inc}
(barns)

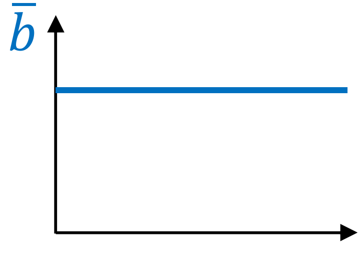
- For **coherent scattering** of organic compounds:
  use **deuterated** samples (substitution of H by D)
  Ex: crystallographic structure, phonons, …
- For **incoherent scattering** of organic compounds:
  do **partial selective deuteriation** to evidence
  a ***specific hydrogenated chemical group***
  Ex: rotation of H for CH_3 groups

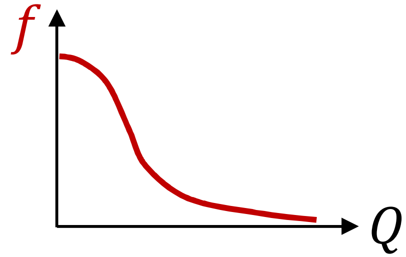
2. Neutron interactions with matter: *nuclear scattering*

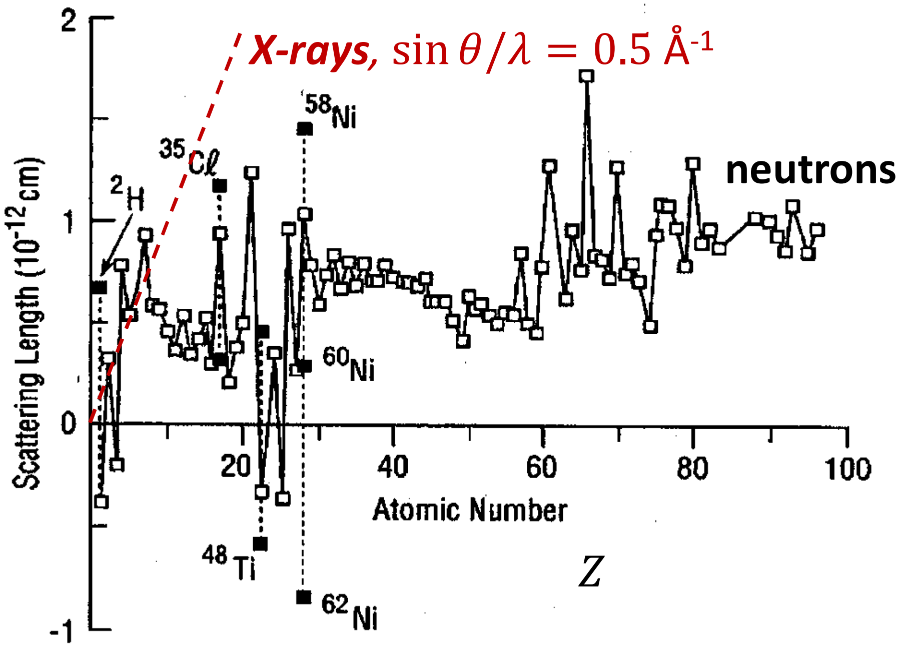
Neutron diffraction arises from coherent scattering only ($\bar{b}$ ⇒ interferences ⇒ diffraction)

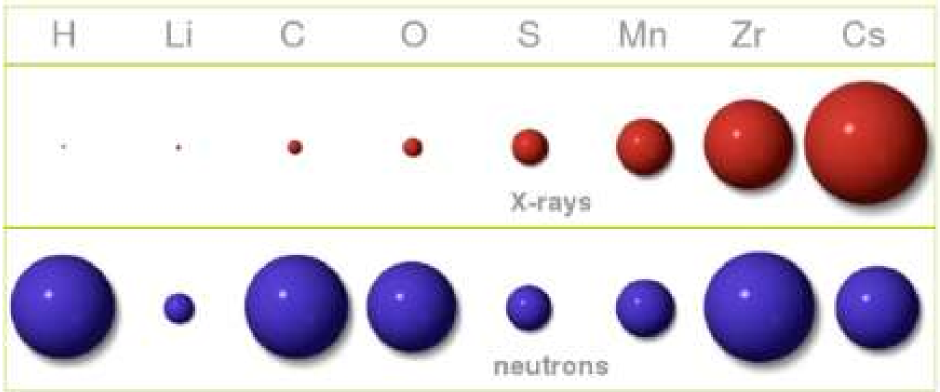
Comparison with X-rays:

Neutrons: Fermi length $\bar{b}$	X-rays: atomic form factor f
$a_N(Q) = \bar{b} = C^{st}$ $\bar{b}(Z, A)$ ~random	$a_{Thomson}(Q) = f(Q)$: f ↘ when Q↗ $f(Z) \propto Z$









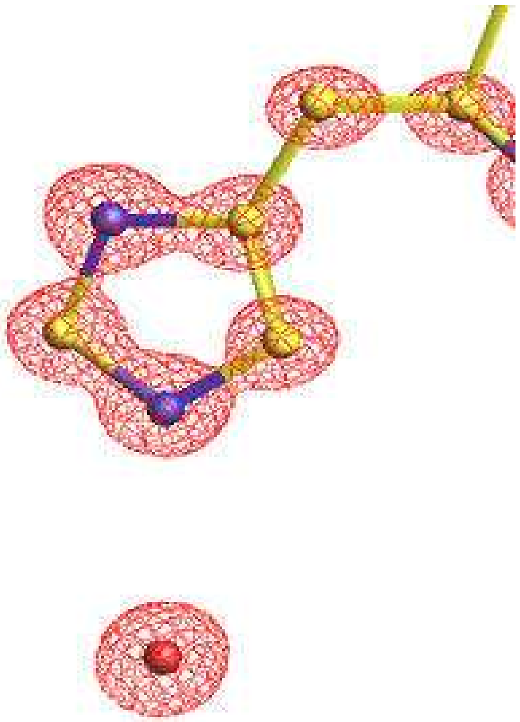
Advantages of neutrons:

- Large intensity even at large Q
- contrast between neighboring elements
- light elements can be measured easily
- isotopic effect

<u>Schematic illustration</u>: Diffraction of biological molecules

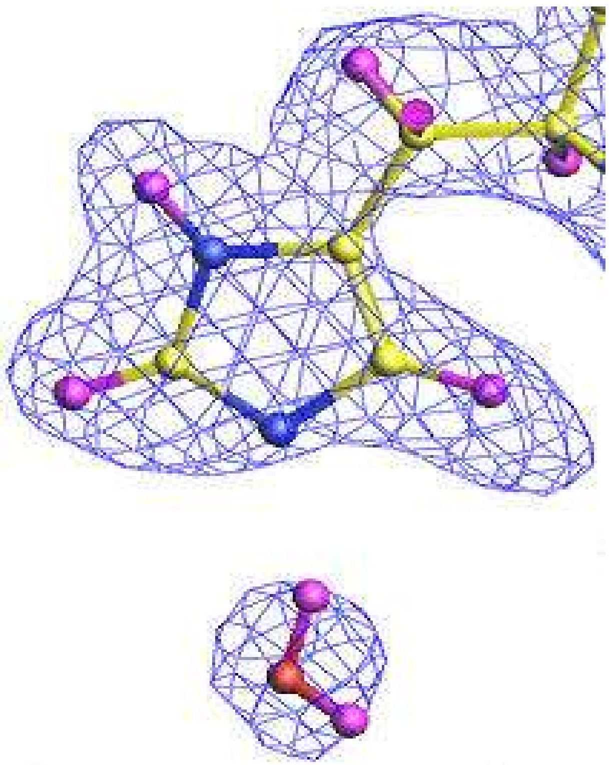
X-rays "see" the electrons

X-rays give a **very precise image** of the atomic positions inside the molecule, except for hydrogen atoms.



Neutrons "see" the nuclei

Neutrons give a less precise image but the **hydrogen atoms are clearly seen**.



⇒ **2 complementary techniques** to determine the very complex arrangement of thousands of atoms contained in a biological molecule.

2. Neutron interactions with matter: *magnetic scattering*

Neutrons scattered by the unpaired electrons: $\rho(\vec{r})$ in r-space $\overset{\text{F.T.}}{\Rightarrow}$ $f(Q)\searrow$ when $Q\nearrow$

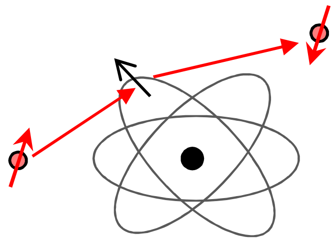
$$a_{Mj}(\vec{Q}) = p f_j(\vec{Q})\, \vec{m}_{j\perp}.\vec{\sigma}$$

Magnetic scattered amplitude for neutrons
= Fourier transform (F.T.) of the magnetic density

with

$$p = \frac{2m}{\hbar^2}\gamma\mu_N\mu_B = 0.2696 \times 10^{-12}\ \text{cm}/\mu_B$$

scattering length at $Q = 0$ for a 1 μ_B magnetic moment

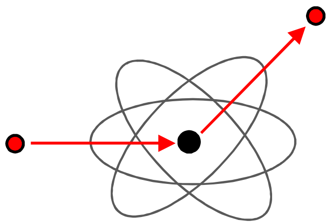


$f_j(\vec{Q})$ **magnetic form factor** of atom j $(= 1$ at $Q = 0)$
≡ F.T. of the magnetic electronic density (unpaired electrons)

$$\vec{m}_{j\perp} = \frac{1}{Q^2}\left(\vec{Q} \wedge \vec{m}_j \wedge \vec{Q}\right)$$

projection of the **magnetic moment** of atom j on the plane $\perp \vec{Q}$ (a few 0.1 μ_B to a few μ_B)

$\vec{\sigma}$ **Pauli spin matrix** for the neutron spin $s = 1/2$



Reminder: Nuclear scattering amplitude

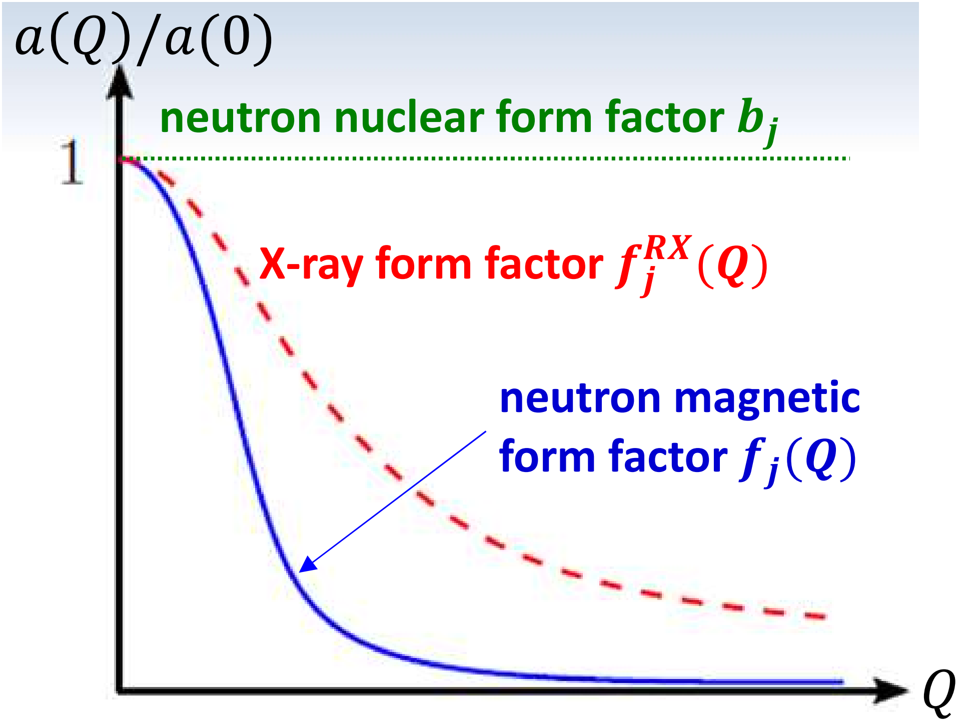
$$a_{Nj}(\vec{Q}) = b_j = (-1 \text{ to } +2)\ 10^{-12}\ \text{cm}$$

Same order of magnitude!

2. Neutron interactions with matter: *magnetic scattering*

$\boxed{f_j(\vec{Q})}$ *

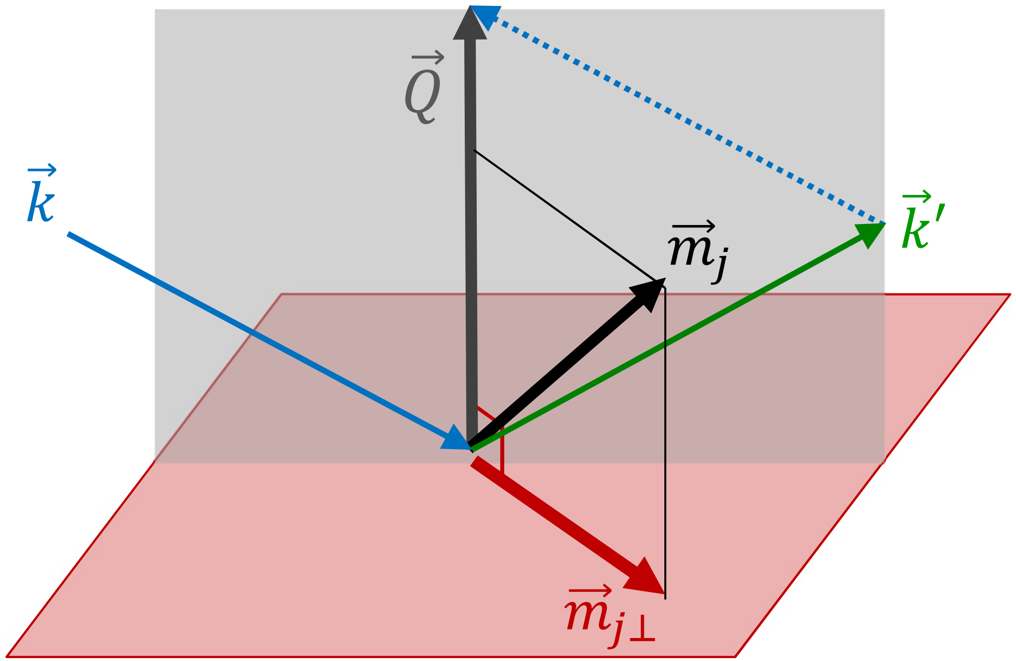
Magnetic signal should be measured at **low *Q*** (Å^{-1})



N.B.: $4f$ orbitals more localized than $3d$ orbitals
→ $f_j(Q)$ decreases slower in the first case *

$\boxed{\vec{m}_{j\perp}}$ *

Only the component of the magnetic moment **perpendicular to $\vec{Q}$** contributes to magnetic scattering *



If $\vec{m}_j \parallel \vec{Q}$: no magnetic intensity
If $\vec{m}_j \perp \vec{Q}$: maximum magnetic intensity

Magnetic form factor $f(Q)$ = F.T. of the magnetic electronic density

$$\boxed{f(\vec{Q}) = \int \rho(\vec{r}) \ \exp(i\vec{Q}.\vec{r}) \ d\vec{r} = \frac{g_S}{g} j_0(\vec{Q}) + \frac{g_L}{g} \left[j_0(\vec{Q}) + j_2(\vec{Q}) \right]}$$

in the **dipolar approximation**

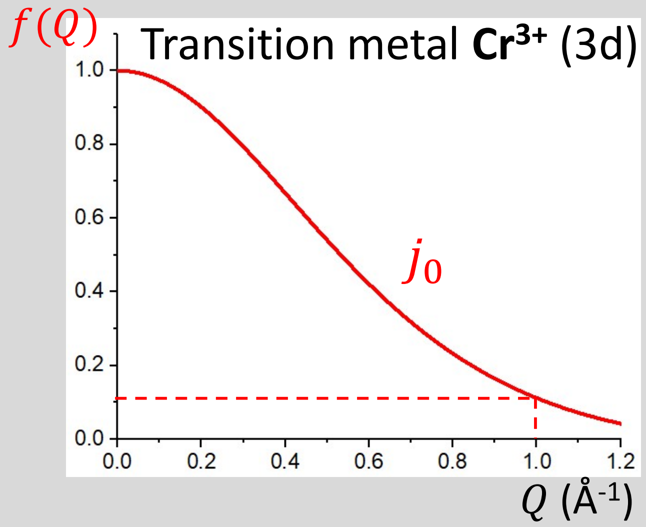
g, g_S, g_L: total, spin, and orbital g-factors
j_n: spherical Bessel functions

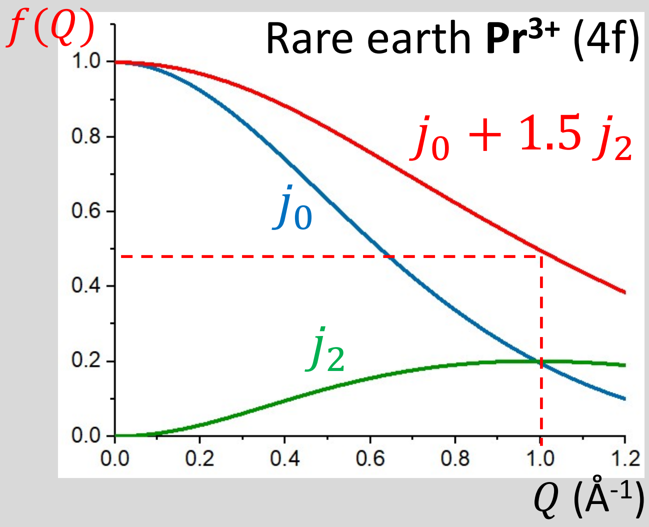
Analytical approximation:

$$j_0(s) = A\exp(-as^2) + B\exp(-bs^2) + C\exp(-cs^2) + D$$
$$j_2(s) = [\,A\exp(-as^2) + B\exp(-bs^2) + C\exp(-cs^2) + D\,]\, s^2$$

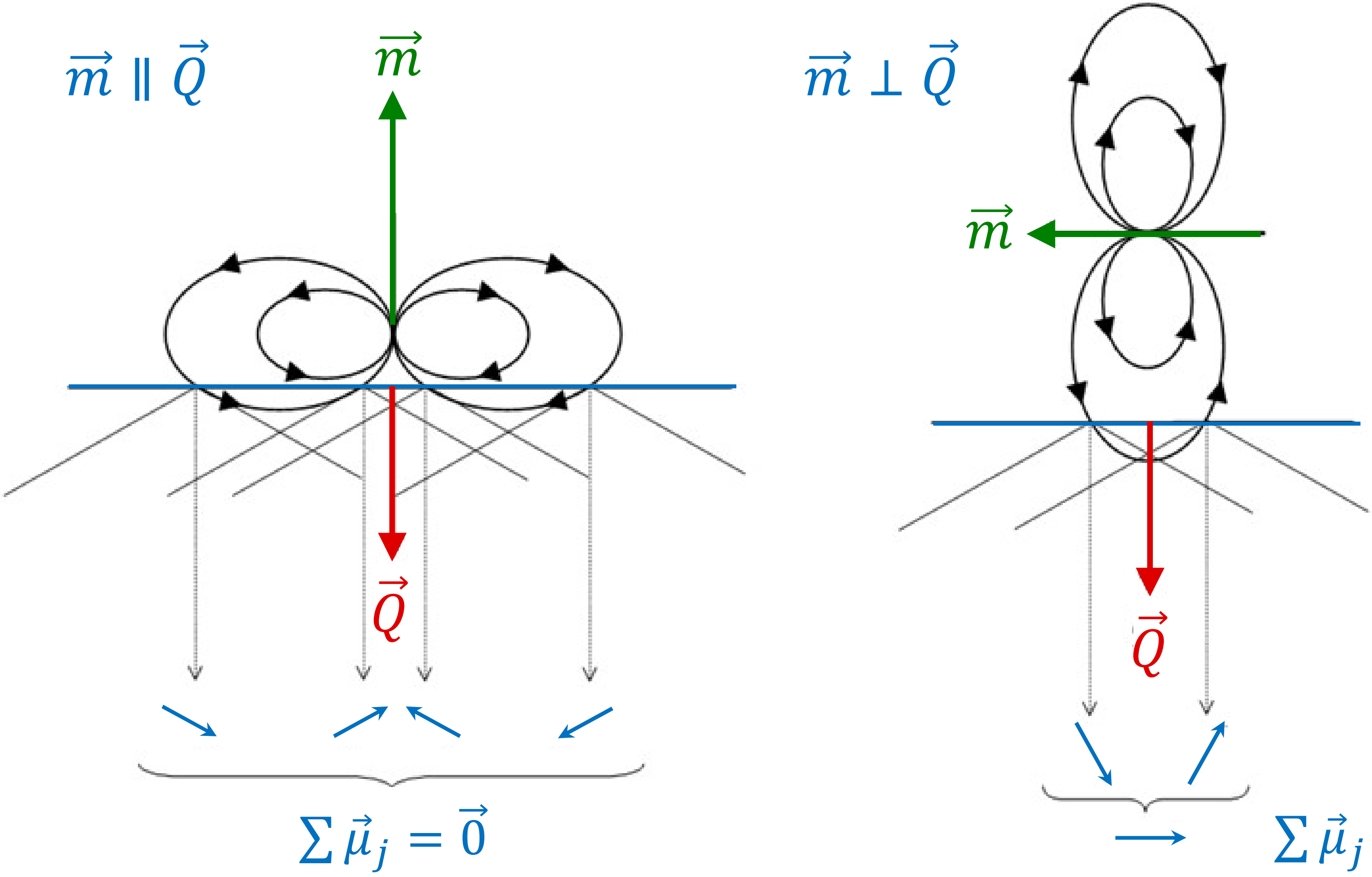
$s = \sin\theta/\lambda$ in units of Å^{-1}

A, a, B, b, C, c, D coefficients tabulated on http://www.ill.eu/sites/ccsl/ffacts





Magnetic dipole scattering

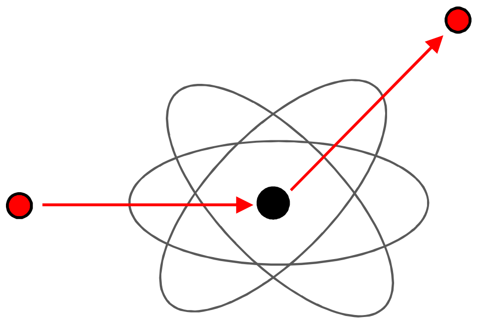


Neutrons are sensitive only to $\vec{m}_\perp$:

the component of $\vec{m}$ that is perpendicular to the scattering vector $\vec{Q} = \vec{k}' - \vec{k}$

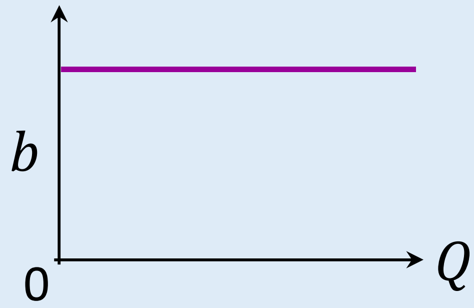
2. Neutron interactions with matter: *scattering, in summary…*

Nuclear interaction



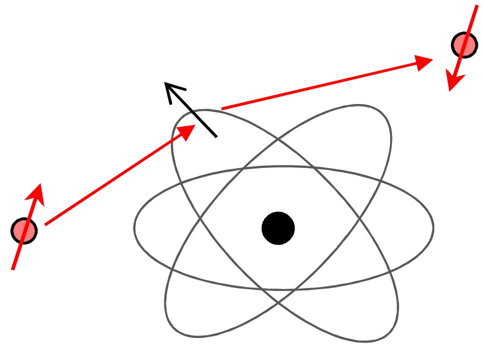
$$\boxed{a_N(Q) = \bar{b} = C^{st}}$$

- **isotropic**
- **constant in Q**



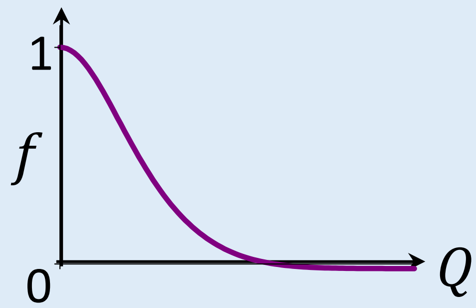
- $\boldsymbol{\bar{b} = (-1 \text{ to } 2)10^{-12}}$ **cm**

Magnetic interaction



$$\boxed{a_M(\vec{Q}) = pf(\vec{Q})\, m_\perp}$$

- **anisotropic**
- **depends on Q**



- $\boldsymbol{p = 0.2696\ 10^{-12}}$ **cm**
  $\boldsymbol{f = 1}$ **at** $\boldsymbol{Q = 0}$

$$\boxed{I_M \sim I_N}$$

$a_M(\vec{Q}) = pf(\vec{Q})\, \vec{m}_\perp . \vec{\sigma}$ for polarized neutrons

Outline

1. Neutron properties

2. Neutron interactions with matter

Refraction

Absorption

Scattering

Nuclear scattering

Magnetic scattering

3. Nuclear and Magnetic neutron diffraction

Introduction

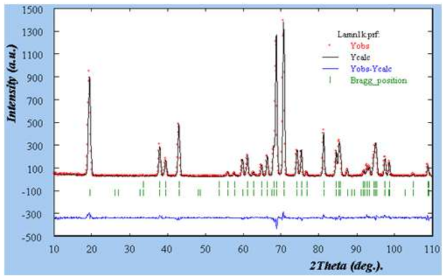
Propagation vector formalism for magnetic structures

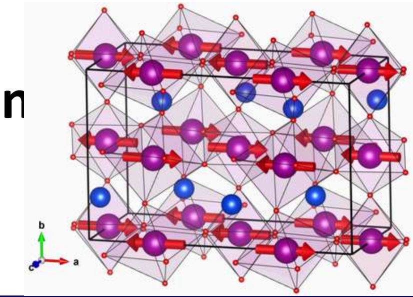
Nuclear/Magnetic diffracted peaks and intensities

Instrumentation & Examples of experimental results:

- from powder neutron diffraction

- from single-crystal neutron diffraction





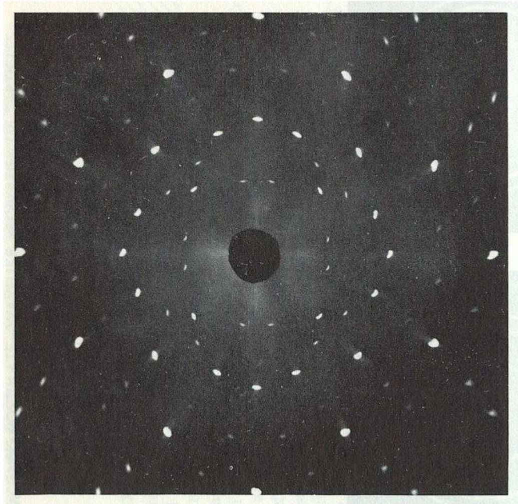
3. Neutron diffraction: *introduction – reciprocity*

Crystal space = Direct space

Diffraction space = Reciprocal space

Crystal

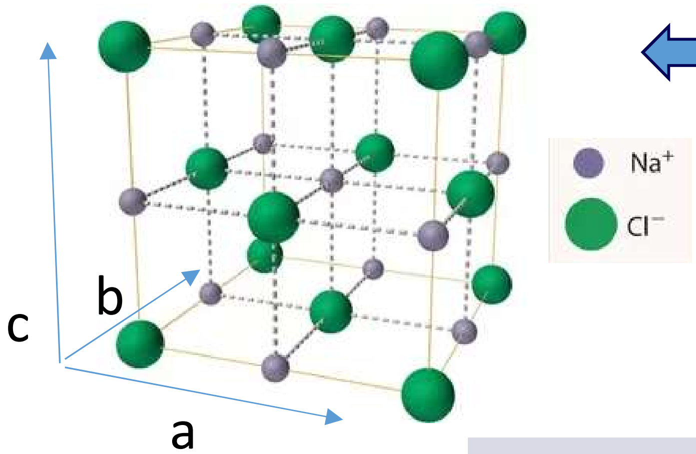
FT →

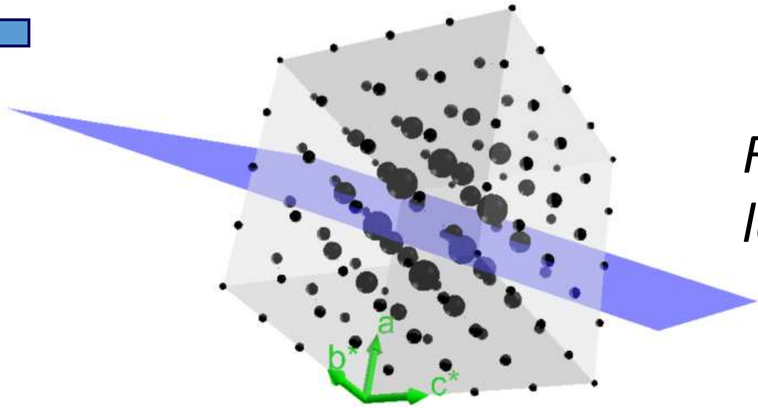


Diffraction pattern

← FT^{-1}

Crystal structure





Reciprocal lattice

Diffraction condition:

Real space description (Bragg):

$$\lambda = 2d_{hkl}\sin\theta$$

Reciprocal (Q) space description (von Laue):

$$\vec{k}' - \vec{k} = \vec{Q} = \overrightarrow{d_{hkl}^{*}}$$

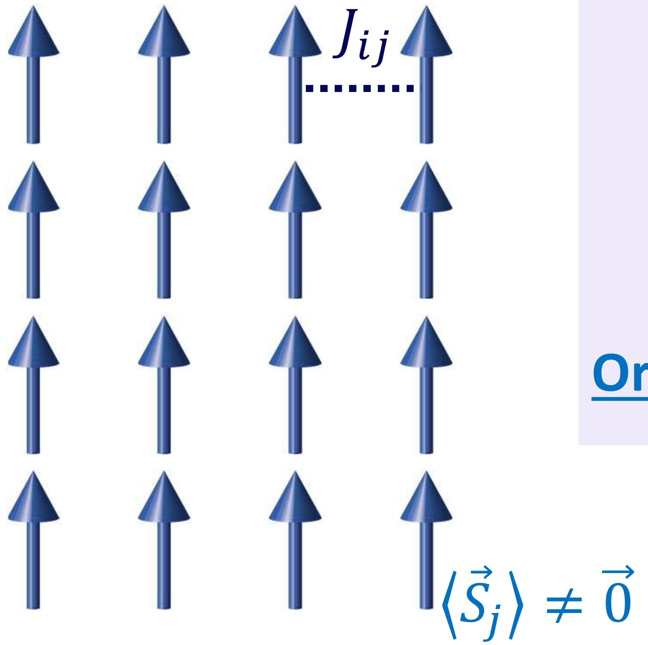
Courtesy Claire Colin

3. Magnetic neutron diffraction: *introduction*

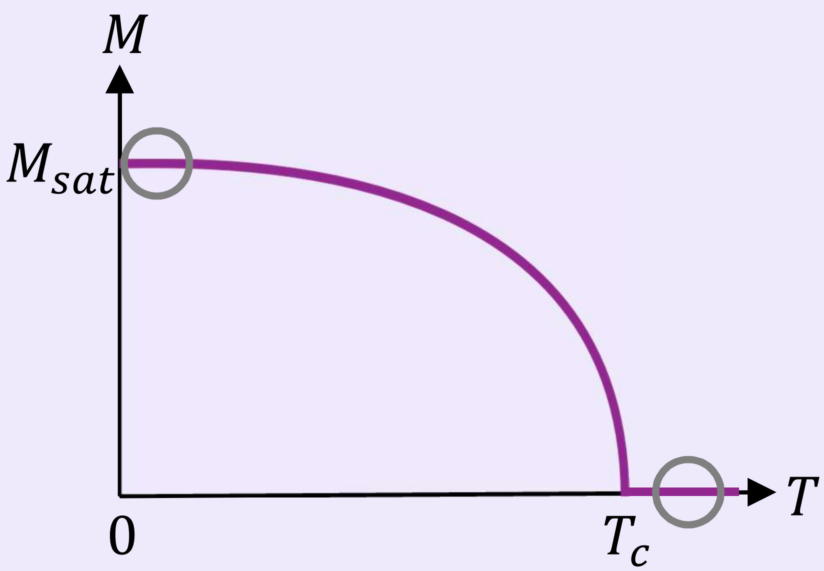
Example of magnetic phase transition:

From paramagnetic state at high T to ferromagnetic state at low T

$T \ll T_c$:
Exchange interactions dominate over thermal fluctuations



Ferromagnetic order:
Parallel magnetic moments



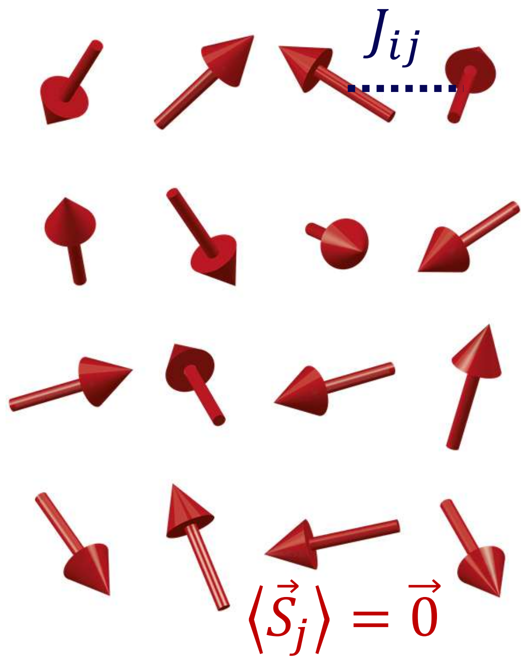
Order parameter = total magnetization

Magnetic exchange energy *

$$\boxed{E_{ij} = -J_{ij}\,\vec{S}_i.\vec{S}_j}$$

$$(J_{ij} > 0)$$

$T > T_c$:
Thermal fluctuations dominate over exchange interactions

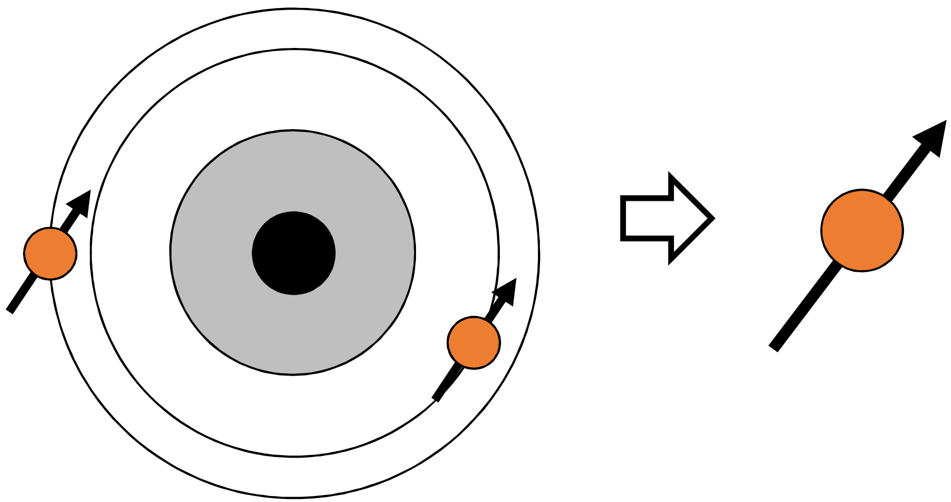


Paramagnetic disorder:
Fluctuating magnetic moments

Magnetic exchange interaction

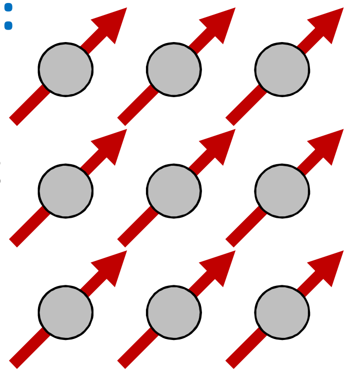
In some crystals, some of the atoms/ions have unpaired electrons (transition metals, rare earths).

Hund's rule favors a state with maximum S and J → **localized magnetic moment**

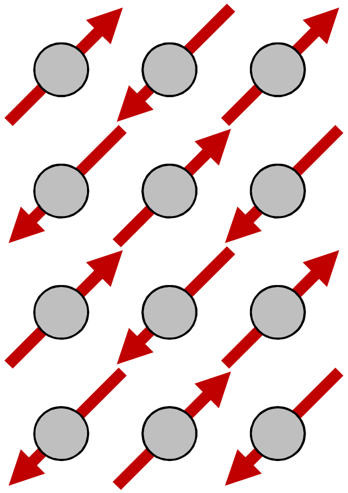


Exchange interactions J_{ij} (direct, super-exchange, double exchange, RKKY, dipolar, …) often stabilize a long-range magnetic order

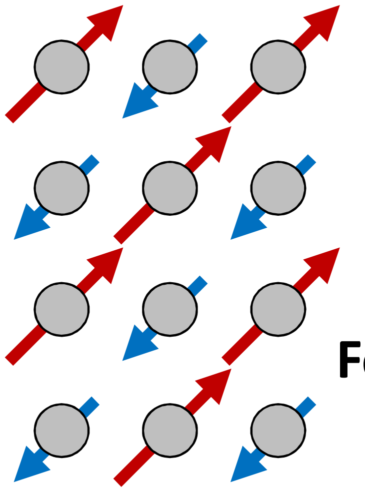
Simple magnetic structures:



Ferromagnetic

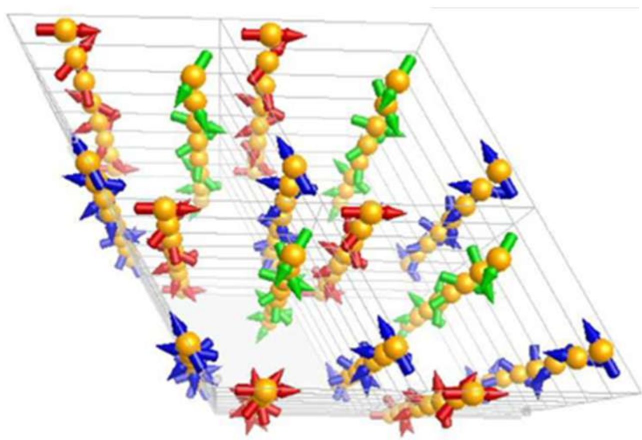


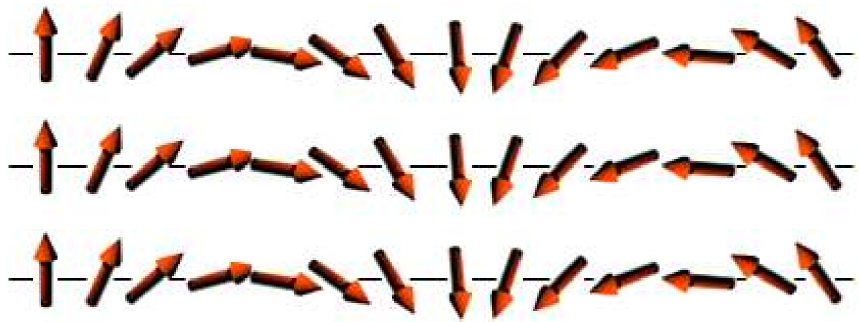
Antiferromagnetic
$(\vec{M} = \vec{0})$



Ferrimagnetic
$(\vec{M} \neq \vec{0})$

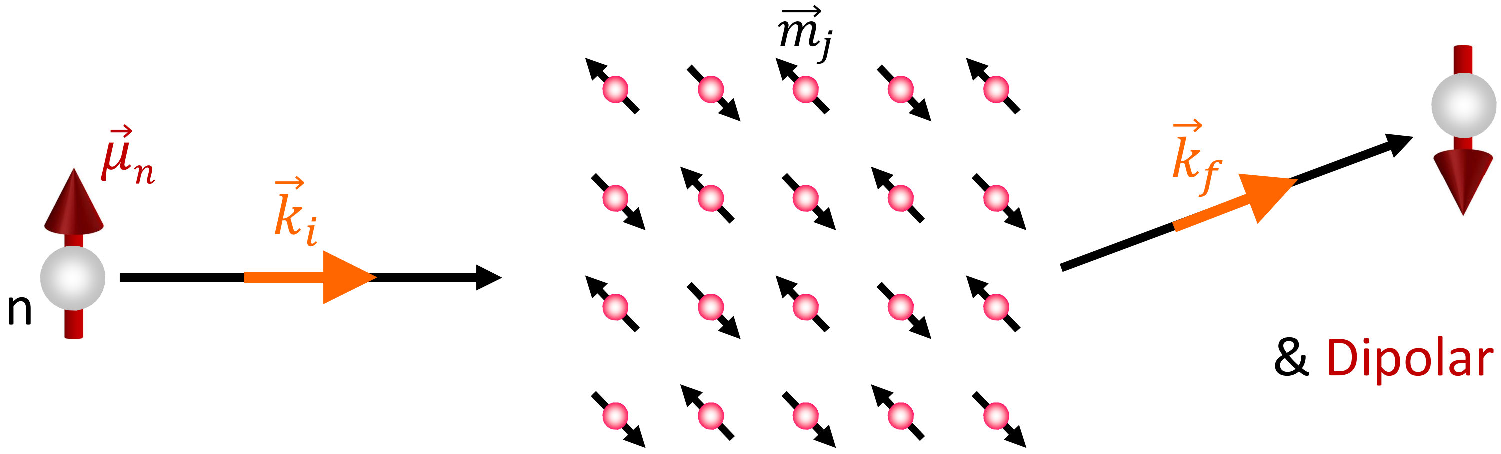
But there are also plenty of **more complex magnetic structures**, arising e.g. from frustration :
Helical,
Cycloidal,
Sinusoidal …





Knowing a magnetic structure means being able to say,
for whatever magnetic atom of whatever unit cell,
what are the direction and value of the magnetic moment

3. Nuclear and magnetic neutron diffraction : *introduction*



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 $\vec{Q} = \vec{H}$

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

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

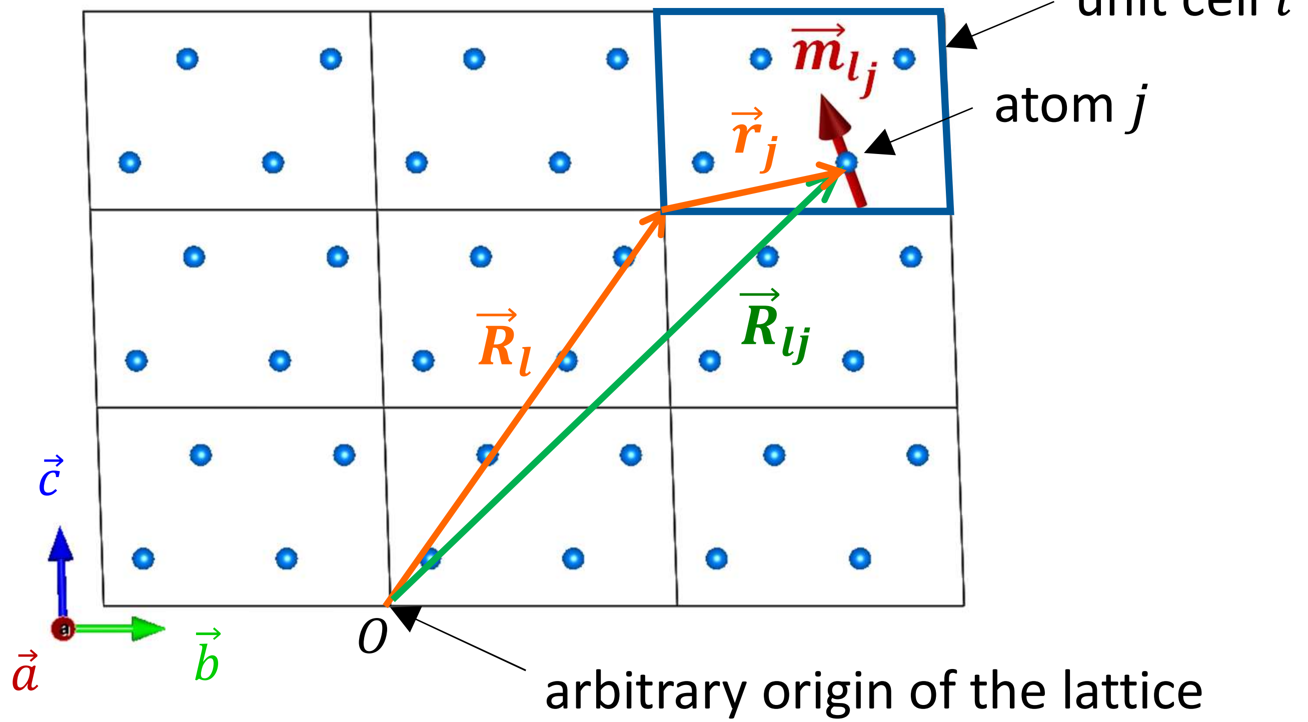
- magnetic motif (inside the crystallographic unit cell) + propagation vector $\vec{k}$
- Bragg peaks at $\vec{Q} = \vec{H} \pm \vec{k}$

Position of magnetic atom j in unit cell l: $\vec{R}_{lj} = \vec{R}_l + \vec{r}_j$

with $\vec{R}_l = l_a\,\vec{a} + l_b\,\vec{b} + l_c\,\vec{c}$ the position of cell l (= lattice translation) (l_a, l_b, l_c integers)

$\vec{r}_j = x_j\vec{a} + y_j\vec{b} + z_j\vec{c}$ the position of atom j in the unit cell (x_j, y_j, z_j reals such that $|x_j|, |y_j|, |z_j| < 1$)

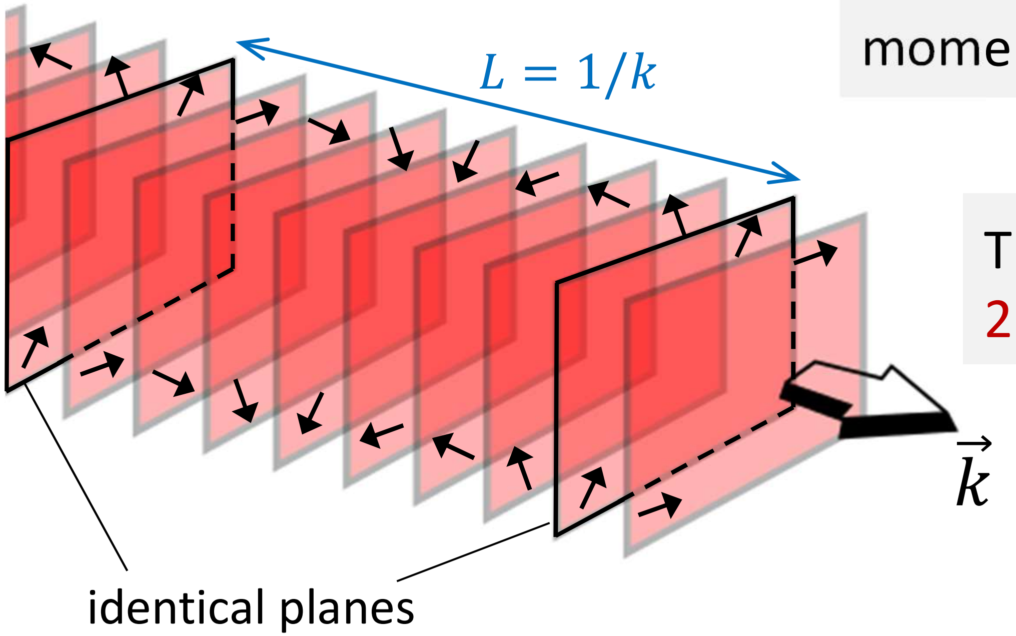
Magnetic moment of atom j in unit cell l: $\vec{m}_{lj}$



3. Magnetic neutron diffraction: *propagation vector formalism*

How to describe a magnetic structure:

- **Magnetic motif** (directions and values of all magnetic moments $\vec{m}_{0j}$ contained in the crystallographic unit cell $l = 0$)
- **Propagation vector $\vec{k}$** reflects the periodicity L of the magnetic structure ($L = 1/k$) and the direction in which it propagates (∥ $\vec{k}$)



For a magnetic atom j, the magnetic moments $\vec{m}_{lj}$ form planes of ∥ moments.

These planes are ⊥ to the direction of $\vec{k}$ and 2 planes distant by $L = 1/k$ are identical.

N.B.: When the magnetic periodicity is the same as the nuclear one: $\vec{k} = \vec{0}$

3. Magnetic neutron diffraction: *propagation vector formalism*

In the ordered state, and **whatever the nature of the magnetic ordering**, the moment distribution, which is a periodic function of space, can be **Fourier expanded** according to:

$$\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi \vec{k}.\vec{R}_l}$$

$\vec{k}$: propagation vector

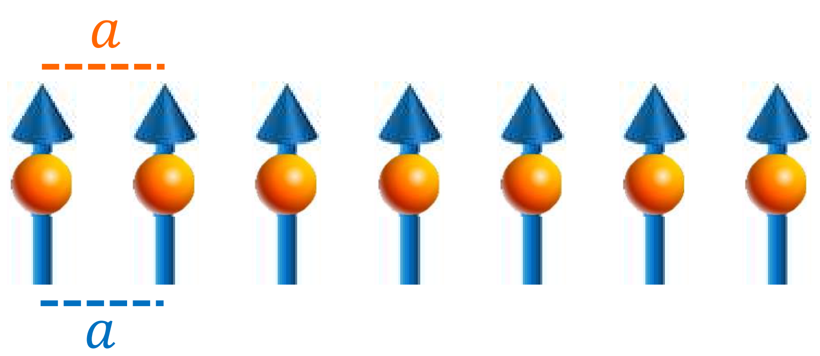
$\vec{R}_l$: position of unit cell l

Magnetic moment of atom j in unit cell l

Fourier component of $\vec{m}_{lj}$ associated to $\vec{k}$

→ *Three simple examples with <u>one single magnetic atom per unit cell</u>* (no j index needed)

<u>Example 1</u>: **ferromagnetic (FM) structure**



Magnetic periodicity = Nuclear periodicity

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

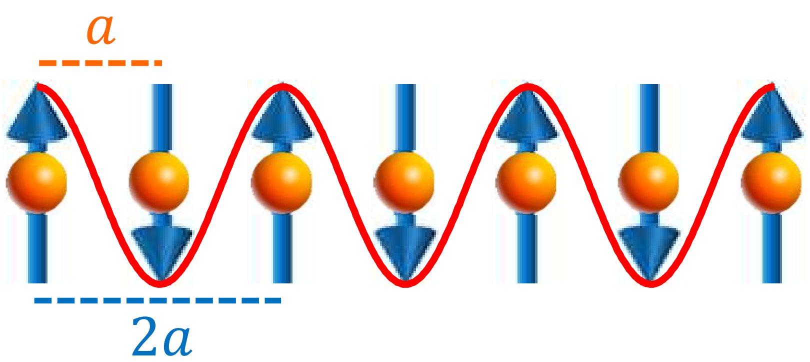
$$\forall l:\ \vec{m}_l = \vec{S}_{\vec{k}} = \vec{m}_0$$

Adapted from N. Qureshi

3. Magnetic neutron diffraction: *propagation vector formalism*

$$\boxed{\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi\vec{k}.\vec{R}_l}}$$

Example 2: **antiferromagnetic (AF) structure (with FM coupling along *b* and *c*)**



Magnetic periodicity = 2 × Nuclear periodicity (along a)

$$\vec{k} = \left(\frac{1}{2}, 0, 0\right)$$ i.e. $\vec{k} = \frac{1}{2}\,\vec{a}^\star$

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

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

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

In cell $l = 1$ at $\vec{R}_1 = \vec{a}$ $\quad l_a = 1 \;\Rightarrow\; \vec{m}_1 = -\vec{S}_{\vec{k}}$

In cell $l = 2$ at $\vec{R}_2 = 2\vec{a}$ $\quad l_a = 2 \;\Rightarrow\; \vec{m}_2 = +\vec{S}_{\vec{k}}$

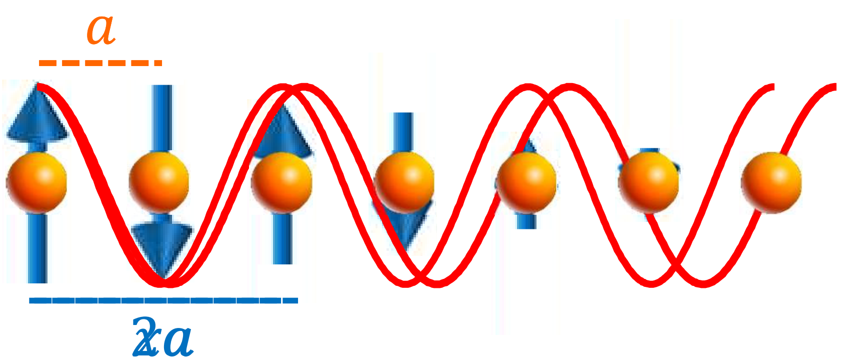
…

Reminder:
$\vec{a}.\vec{a}^\star = 1$
$\vec{b}.\vec{a}^\star = \vec{c}.\vec{a}^\star = 0$

Adapted from N. Qureshi

$$\boxed{\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi\vec{k}.\vec{R}_l}}$$

Example 3: **sine-wave modulated structure** **(with FM coupling along $\boldsymbol{b}$ and $\boldsymbol{c}$)**



Magnetic periodicity = x × Nuclear periodicity (along a)

$$\vec{k} = \left(\frac{1}{x}, 0, 0\right)$$

x irrational
→ **incommensurate AF**

in a cell l located at $\vec{R}_l = l_a\vec{a} + l_b\vec{b} + l_c\vec{c}$: $\vec{m}_l = \vec{S}_{\vec{k}} e^{-2i\pi\quad_a} + \vec{S}_{-\vec{k}} e^{+2i\pi\delta l_a}$

with:

- $\delta = 1/x$
- two Fourier components, complex conjugates (for $\vec{m}_l$ to be real):

$\vec{S}_{\vec{k}} = \frac{\vec{m}_0}{2}\, e^{-i\phi}$ and $\vec{S}_{-\vec{k}} = \frac{\vec{m}_0}{2}\, e^{+i\phi}$ associated to $\vec{k}$ and $-\vec{k}$, resp.

$$\Rightarrow \boxed{\vec{m}_l = \vec{m}_0 \cos(2\pi\delta l_a + \phi)}$$

Adapted from N. Qureshi

3. Magnetic neutron diffraction: *magnetic structures description*

All magnetic structures:

- **Magnetic motif**
(directions and values of all magnetic moments contained in a crystallographic unit cell)

$+$

- **Propagation vector $\vec{k}$**
(how the magnetic motif propagates from one cell to the next one)

→ Group representation theory, **with the help of Irreducible Representations (Ireps), allows to predict all magnetic structures compatible with the crystallographic space group (and position occupied by the magnetic atoms) & the propagation vector of the magnetic structure**

Simple magnetic structures: those with $\vec{k} = \vec{H}$ or $\vec{k} = \frac{1}{2}\vec{H}$

→ **Magnetic symmetry approach can be used:**
symmetry invariance of magnetic configurations,
involving space group symmetries + time reversal $1'$ ($\vec{m} \to -\vec{m}$)
→ Magnetic Space Groups, also called Shubnikov groups

Complex magnetic structures: those with $\vec{k} \neq \frac{n}{2}\vec{H}$ (incommensurate, …)
→ Magnetic Super Space Groups

3. Nuclear neutron diffraction: *diffracted peaks and intensities*

Nuclear diffracted intensity:

$$\boxed{I_N(\vec{Q}) \propto \sum_{\vec{H}} |F_N(Q)|^2\ \delta(\vec{Q}-\vec{H})}$$

motif (atomic nature + positions)
→ **amplitudes of diffraction**

crystal lattice (lattice parameters)
→ **directions of diffraction**

with F_N the nuclear structure factor (FT of the nuclear density in the unit cell)

(b_j: Fermi length of atom j)

$$\boxed{F_N(\vec{Q}) = \sum_{j=1}^{N} b_j\ e^{2i\pi\,\vec{\ }.\vec{r}_j}\ e^{-W_j}}$$

Diffraction peaks: hkl
h, k, l integers

with $\begin{cases} \vec{Q} = h\vec{a}^\star + k\vec{b}^\star + l\vec{c}^\star \\ \vec{r}_j = x_j\vec{a} + y_j\vec{b} + z_j\vec{c} \end{cases}$ $\Rightarrow$ $\vec{Q}.\vec{r}_j = hx_j + ky_j + lz_j$

and $e^{-W_j} = e^{-B_j\frac{\sin^2\theta}{\lambda^2}}$ Debye-Waller factor in which $B_j = \langle u_j{}^2\rangle$ reflects the amplitude of thermal vibration

same as for X-rays, with b_j instead of $f_j(\mathrm{Q})$

3. Magnetic neutron diffraction: *diffracted peaks and intensities*

Magnetic diffracted intensity:

$$I_M(\vec{Q}) \propto \sum_{\vec{H}} \sum_{\vec{k}} \left|\vec{F}_{M\perp}(Q)\right|^2 \delta(\vec{Q}-\vec{H}-\vec{k})$$

magnetic motif (amplitude + direction of the magnetic moments: all $\vec{m}_{0j}$)
→ **amplitudes of diffraction**

magnetic lattice (periodicity of the magnetic structure: $\vec{k}$ propagation vectors)
→ **directions of diffraction**

$\vec{F}_{M\perp}$: projection of $\vec{F}_M$ in the plane $\perp \vec{Q}$

with $\vec{F}_M$ the magnetic structure factor (FT of the magnetic moments in the unit cell)

$$\vec{F}_M(\vec{Q}) = p \sum_{j=1}^{N} f_j(\vec{Q})\, \vec{S}_{\vec{k}j}\, e^{2i\pi\vec{Q}.\vec{r}_j}\, e^{-W_j}$$

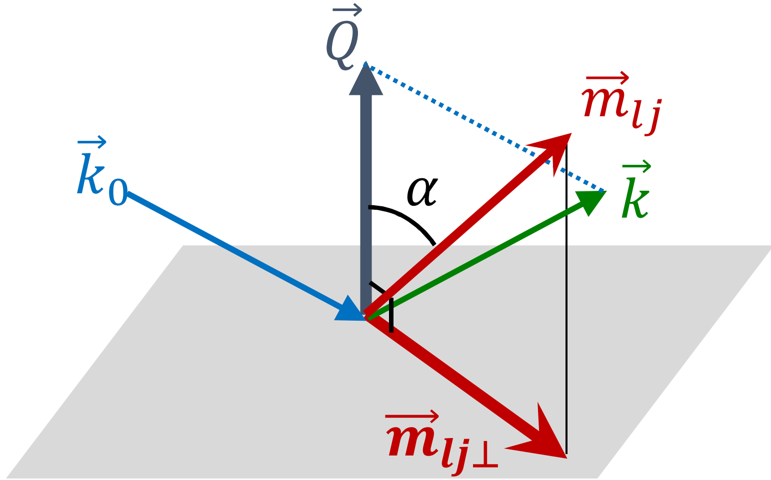
with $p = 0.2696\ 10^{-12}$ cm/μ_B,
$f_j(Q)$: magnetic form factor of atom j
$\vec{S}_{\vec{k}j}$: Fourier component of magnetic moments $\vec{m}_{lj}$, associated to the propagation vector $\vec{k}$ (Reminder: $\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi\vec{k}.\vec{R}_l}$)

Diffraction peaks: hkl
h, k, l often non integers!

3. Magnetic neutron diffraction: *diffracted intensity – reminder*

(see slide 29)

Magnetic diffracted intensity – consequences:



- One measures $\left|\vec{F}_{M\perp}\right|^2$ and not $\left|\vec{F}_M\right|^2$:

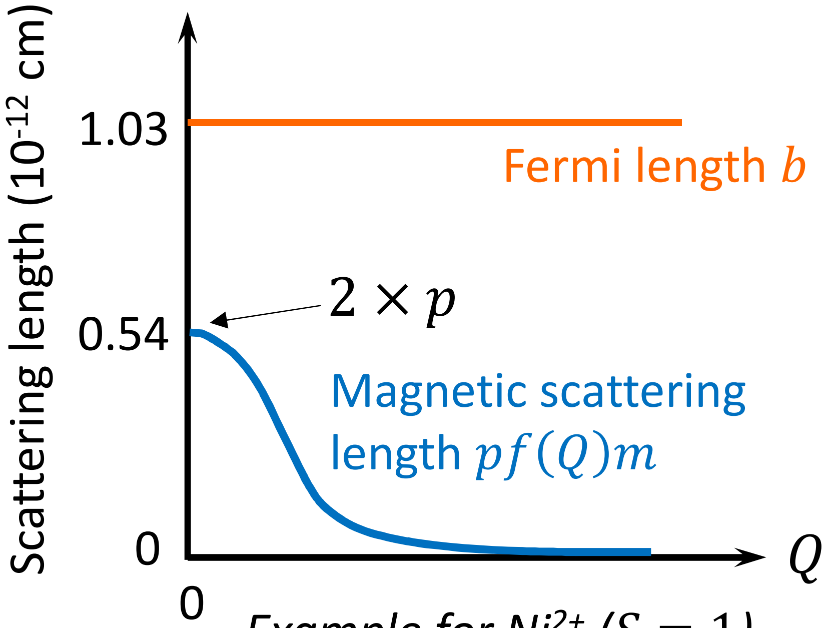
  if $\vec{m}_{lj} \perp \vec{Q}$: $\quad \vec{F}_{M\perp} = \vec{F}_M \quad$ → maximum of intensity
  if $\vec{m}_{lj} \parallel \vec{Q}$: $\quad \vec{F}_{M\perp} = \vec{0} \quad$ → no intensity!

  if $\widehat{(\vec{m}_{lj}, \vec{Q})} = \alpha$: $\quad \left\|\vec{F}_{M\perp}\right\| = F_M \sin\alpha$

- The intensity depends on $f_j(Q)$

  $f_j(Q)$: magnetic form factor
  (FT transform of the unpaired electrons)

  → measure at low Q (i.e., small h, k, l)
  → low angle (or large wavelength)



Example for Ni^{2+} ($S = 1$)

3. Nuclear and magnetic neutron diffraction: *diffracted intensity*

Total (nuclear + magnetic) diffracted intensity:

- **With non polarized neutrons**, the total diffracted intensity is:

$$\boxed{I = |F_N|^2 + |F_{M\perp}|^2}$$

If $\vec{k} = \vec{0}$: both signals superimpose

→ measure above and below the magnetic transition to extract $I_M(Q)$

(difference between both measurements,
assuming the crystallographic structure has not changed)

If $\vec{k} \neq \vec{0}$: nuclear and magnetic peaks appear at different positions

- **With polarized neutrons…** crossed NM terms (beyond the scope of this lecture)

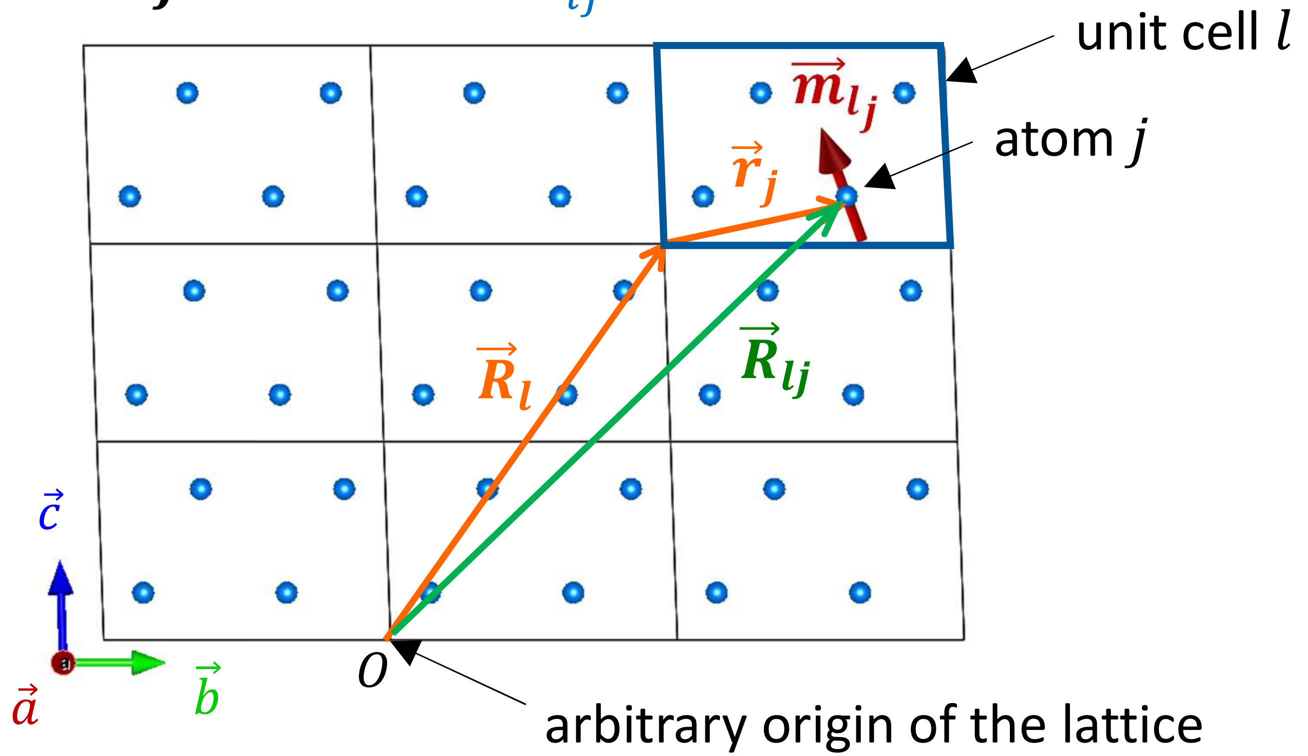
3. Nuclear and magnetic neutron diffraction: *notations – reminder*

Position of magnetic atom j in unit cell l: $\vec{R}_{lj} = \vec{R}_l + \vec{r}_j$

with $\vec{R}_l = l_a\,\vec{a} + l_b\,\vec{b} + l_c\,\vec{c}$ the position of cell l (= lattice translation) (l_a, l_b, l_c integers)

$\vec{r}_j = x_j\vec{a} + y_j\vec{b} + z_j\vec{c}$ the position of atom j in the unit cell (x_j, y_j, z_j reals such that $|x_j|, |y_j|, |z_j| < 1$)

Magnetic moment of atom j in unit cell l: $\vec{m}_{lj}$



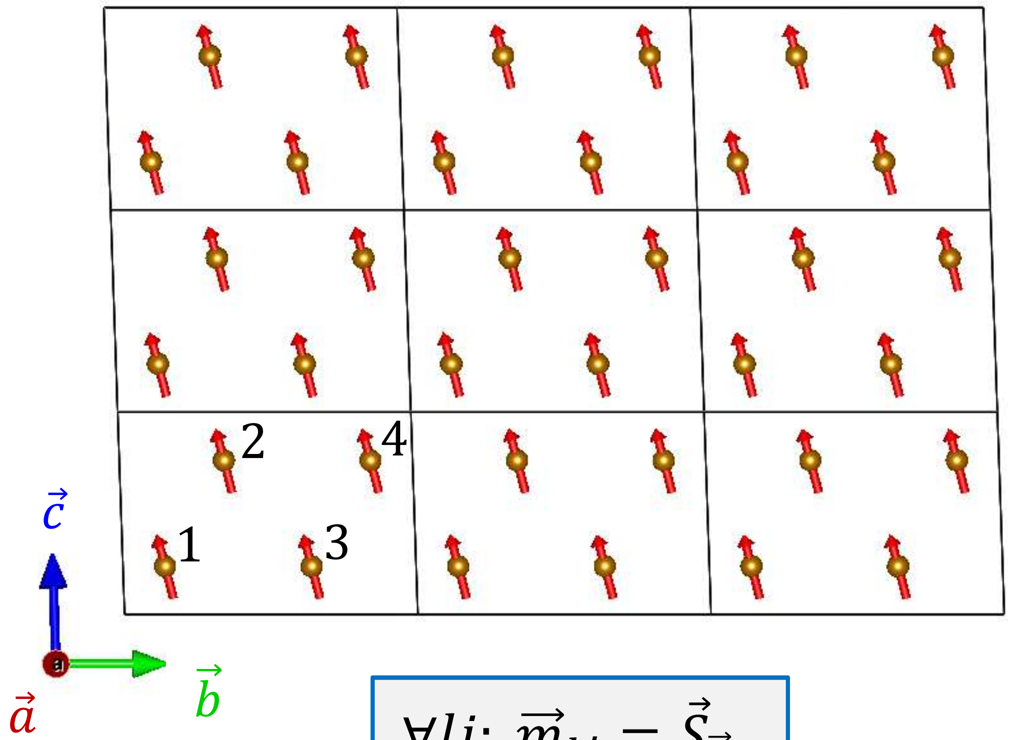
3. Magnetic neutron diffraction: *diffracted peaks and intensities*

- **Commensurate: $\vec{k} = \vec{0}$**

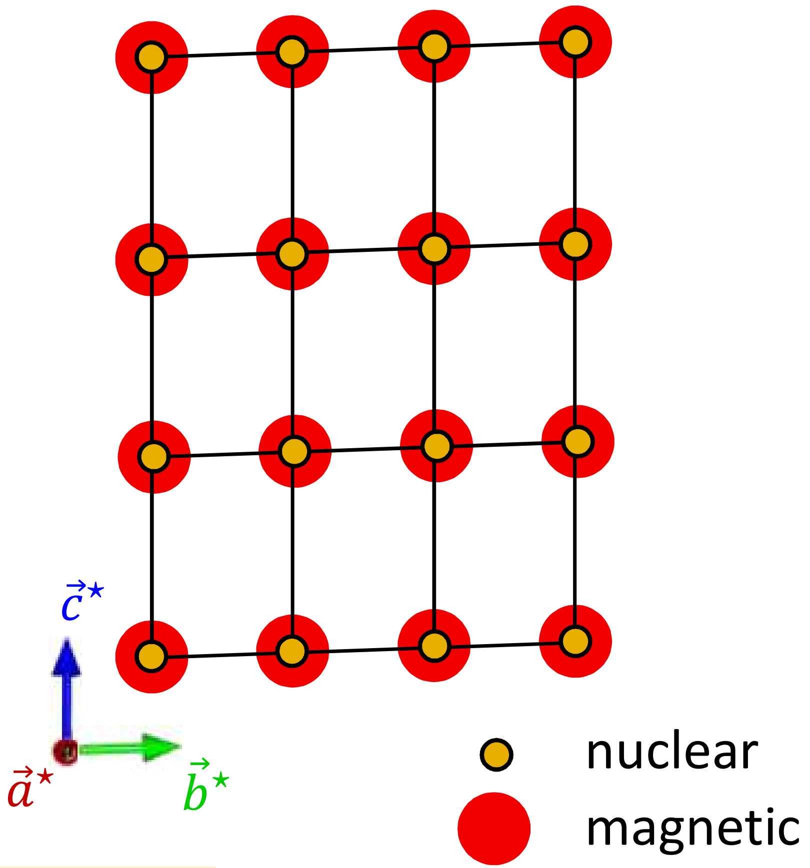
$$\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi\vec{k}.\vec{R}_l}$$

1/ All ferromagnetic (FM) structures

Example: *Direct space:* *Reciprocal space:*



$$\forall lj:\ \vec{m}_{lj} = \vec{S}_{\vec{k}j}$$



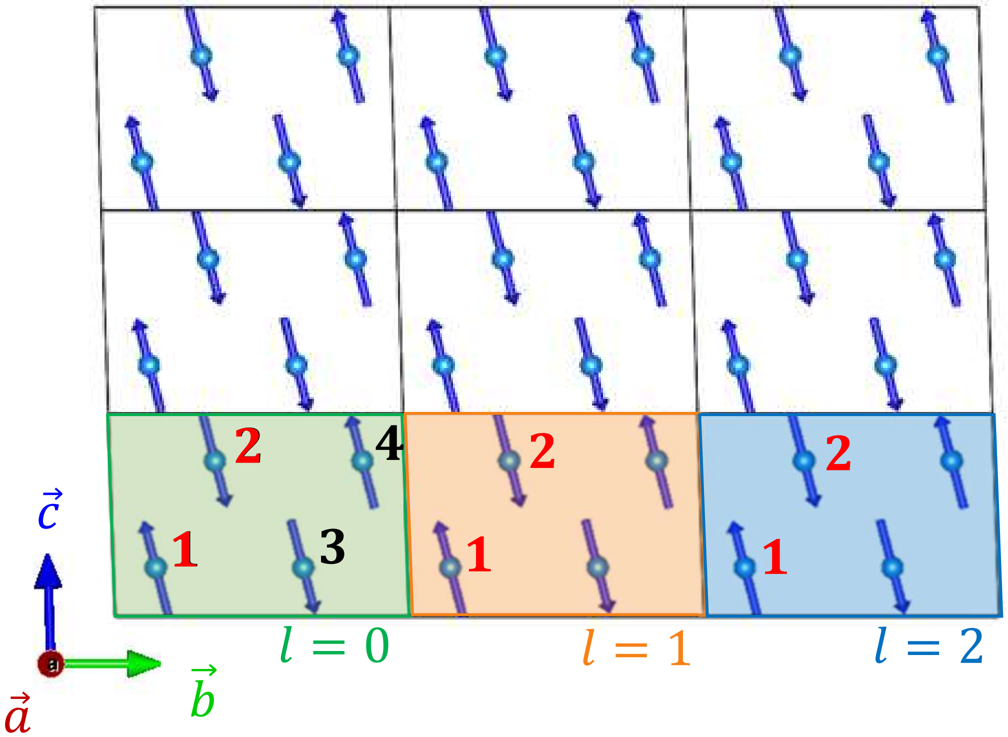
All FM structures have $\vec{k} = \vec{0}$, but the reserve is not true!

- **Commensurate: $\vec{k} = \vec{0}$**

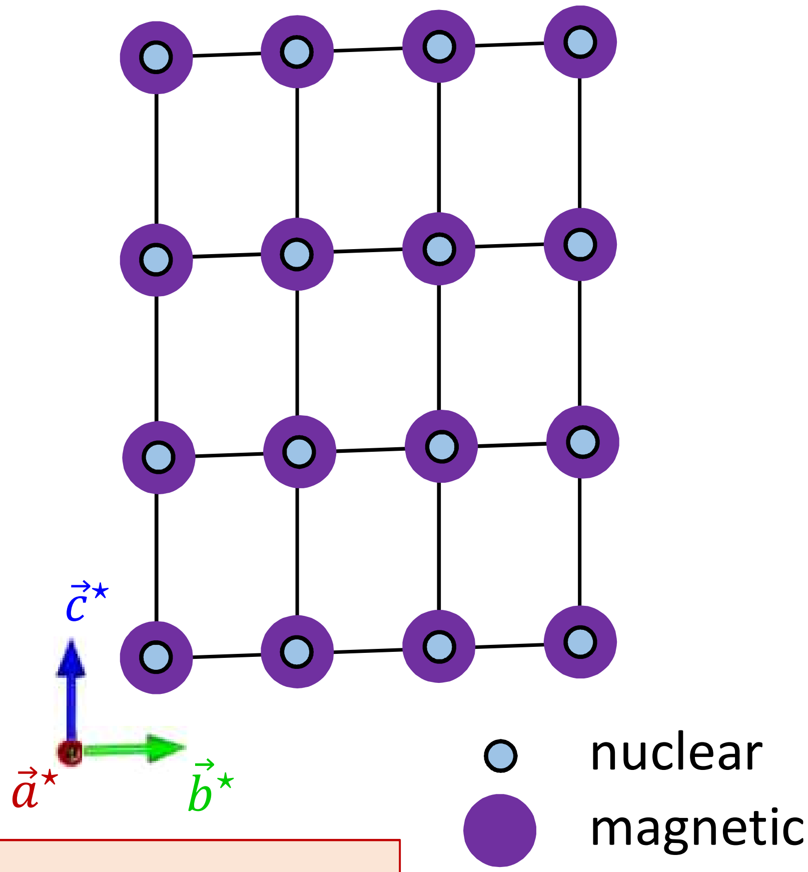
$$\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi\vec{k}.\vec{R}_l}$$

2/ Some antiferromagnetic (AF) structures

<u>Example</u>: *Direct space:* *Reciprocal space:*



$$\forall l: \vec{m}_{lj} = \vec{S}_{\vec{k}j}$$



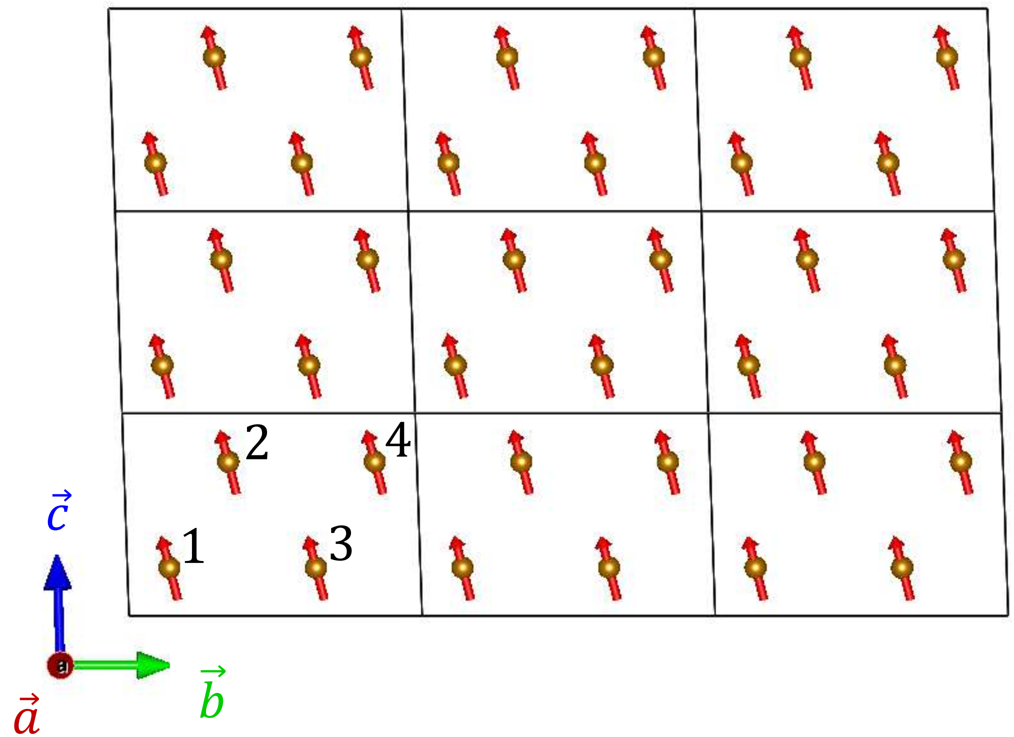
Bragg peaks:
same positions but ≠ intensities

3. Magnetic neutron diffraction: *diffracted peaks and intensities*

- **Commensurate: $\vec{k} = \vec{0}$**

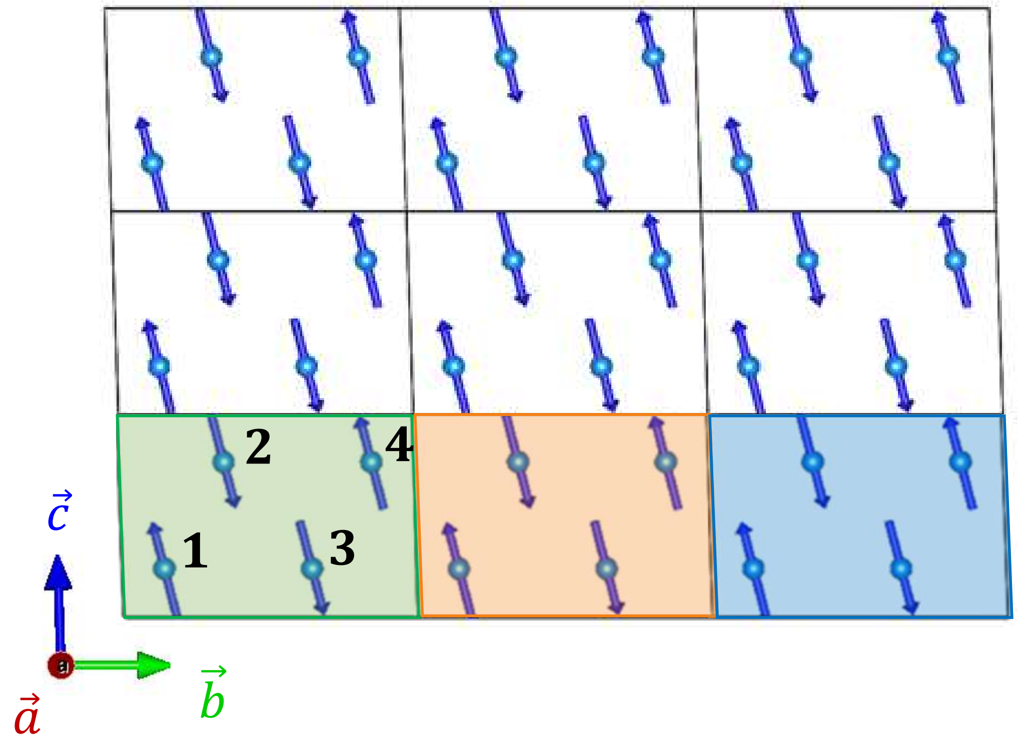
$$I \propto |F_{M\perp}|^2 \text{ with } \vec{F}_M(\vec{Q}) = p \sum_{j=1}^{N} f_j(\vec{Q})\, \vec{S}_{\vec{k}j}\, e^{2i\pi\vec{Q}.\vec{r}_j}\, e^{-W_j}$$

1/ FM structure



$$\vec{F}_M(\vec{Q}) = pf(\vec{Q})e^{-W}\,\vec{m}_0$$
$$\times\,(e^{2i\pi\vec{Q}.\vec{r}_1} + e^{2i\pi\vec{Q}.\vec{r}_2} + e^{2i\pi\vec{Q}.\vec{r}_3} + e^{2i\pi\vec{Q}.\vec{r}_4})$$

2/ AF structure



$$\vec{F}_M(\vec{Q}) = pf(\vec{Q})e^{-W}\,\vec{m}_0$$
$$\times\,(e^{2i\pi\vec{Q}.\vec{r}_1} - e^{2i\pi\vec{Q}.\vec{r}_2} - e^{2i\pi\vec{Q}.\vec{r}_3} + e^{2i\pi\vec{Q}.\vec{r}_4})$$

- **Commensurate: $\vec{k} = \frac{1}{2}\vec{H}$**

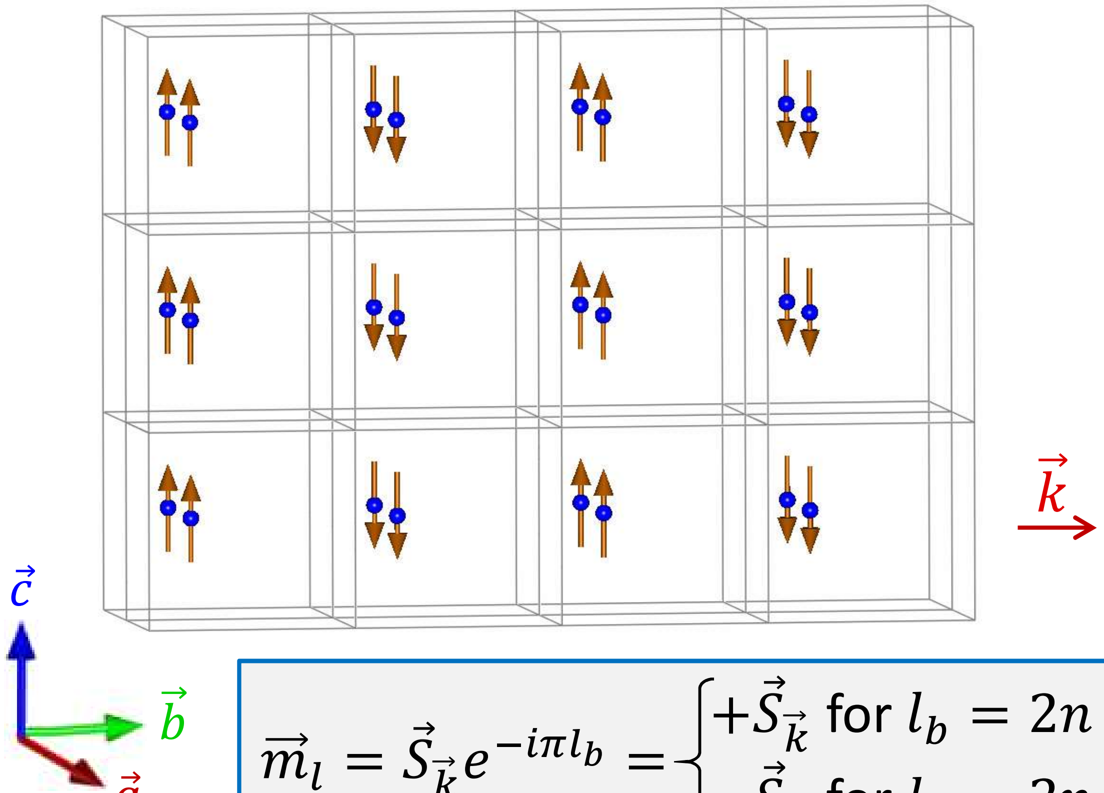
$$\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi\vec{k}.\vec{R}_l}$$

Some other antiferromagnetic structures

Example:

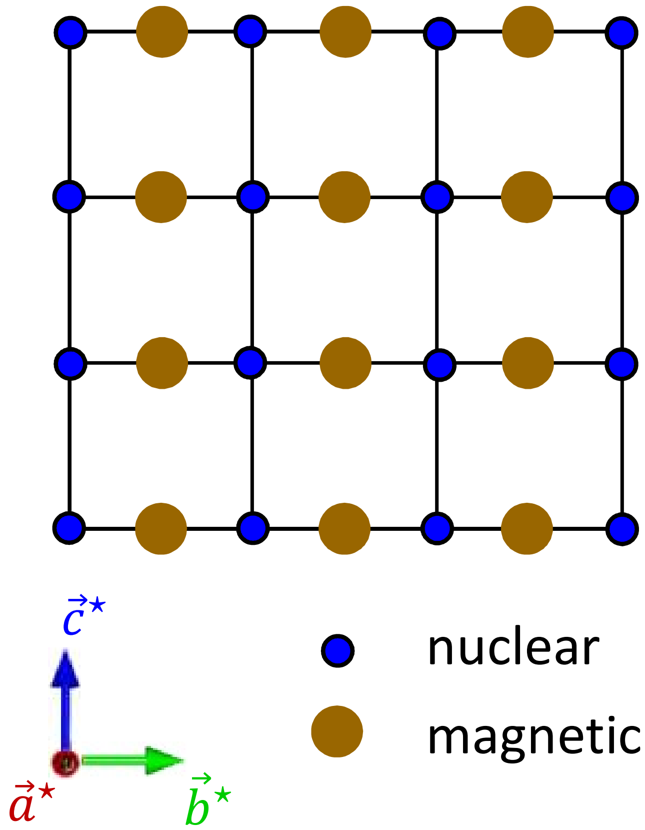
$$\vec{k} = \left(0, \frac{1}{2}, 0\right)$$

Direct space:



$$\vec{m}_l = \vec{S}_{\vec{k}} e^{-i\pi l_b} = \begin{cases} +\vec{S}_{\vec{k}} \text{ for } l_b = 2n \\ -\vec{S}_{\vec{k}} \text{ for } l_b = 2n+1 \end{cases}$$

Reciprocal space:

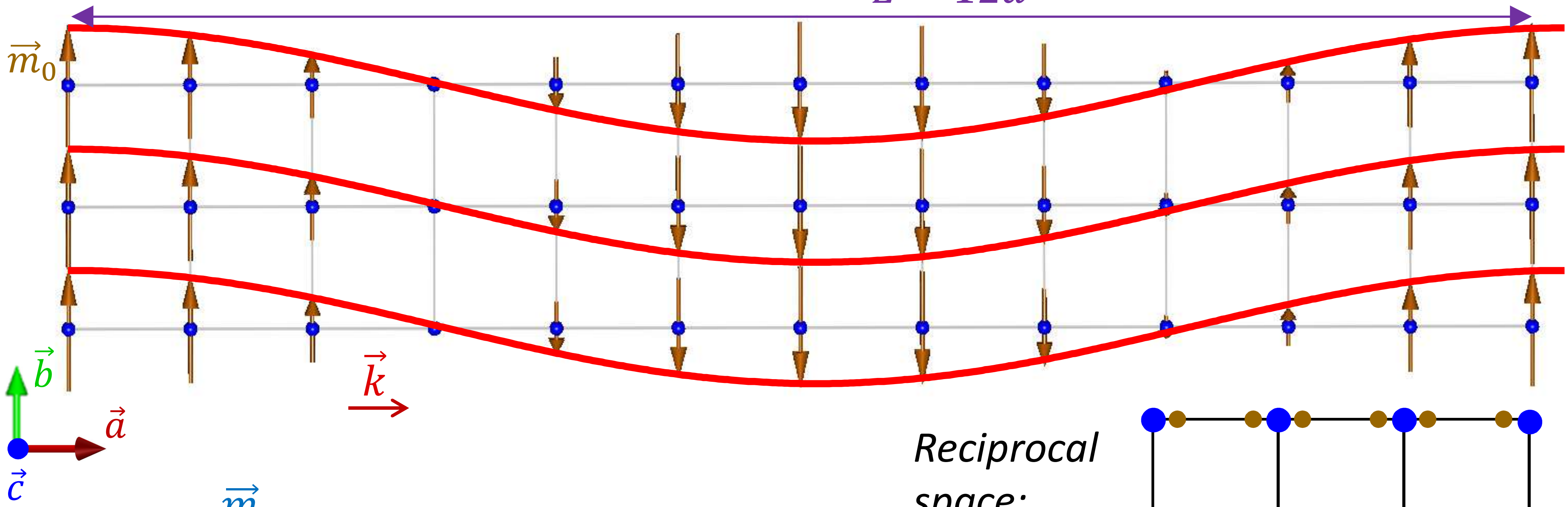


- **Sinusoidal (or sine-wave modulated) magnetic structures**

$$\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi\vec{k}.\vec{R}_l}$$

Example: $\vec{k} = (\delta, 0, 0)$

1/ transverse: $\boxed{\vec{m}_{lj} \perp \vec{k}}$

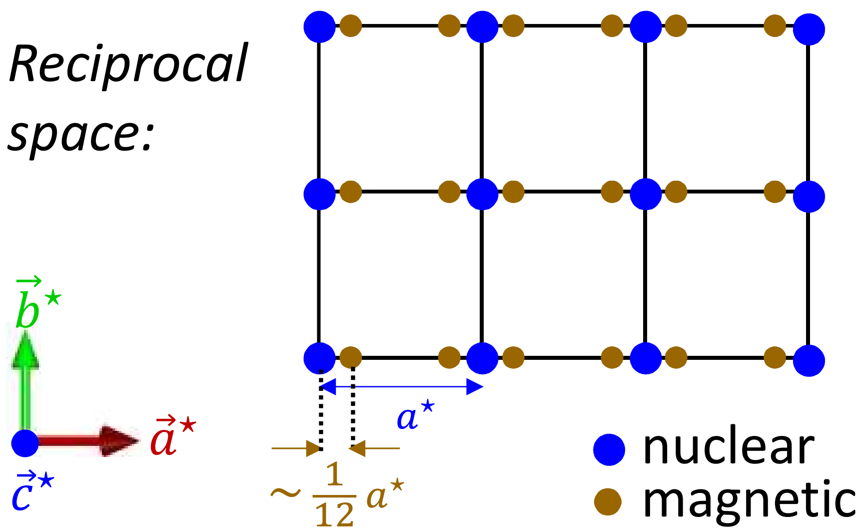


$$\vec{S}_{\pm\vec{k}} = \frac{\vec{m}_0}{2}\, e^{\pm i\phi}$$

$$\boxed{\Rightarrow \quad \vec{m}_l = \vec{m}_0 \cos(2\pi\delta l_a + \phi)}$$

with $\delta \sim \frac{1}{12}$ and $\vec{\boldsymbol{m}}_{\mathbf{0}} \parallel \vec{\boldsymbol{b}}$

Reciprocal space:



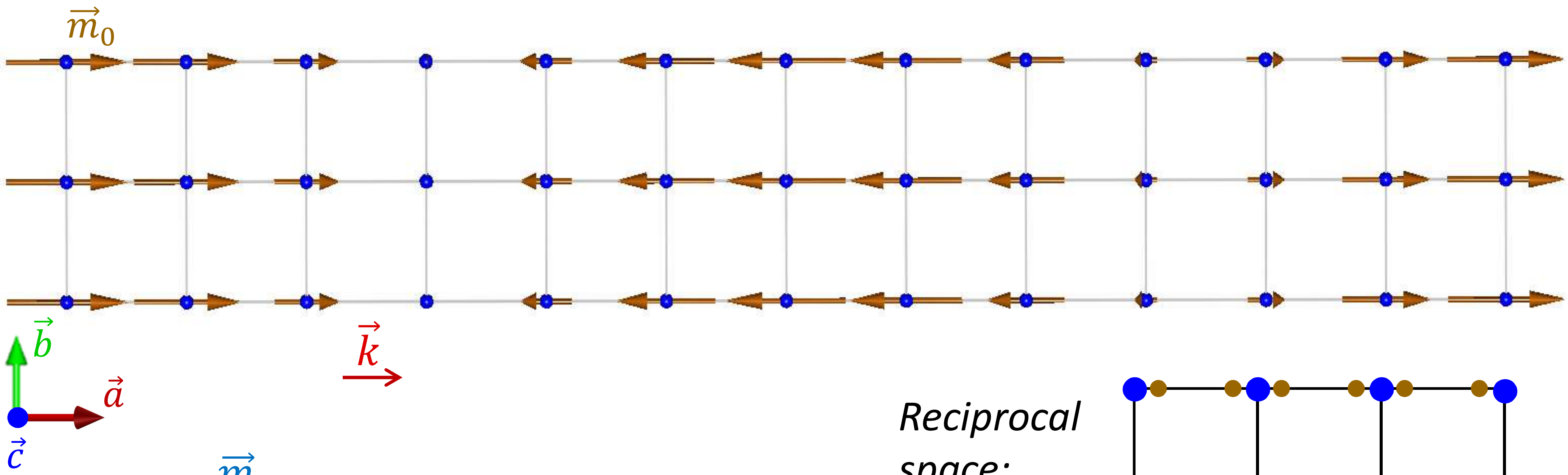
3. Magnetic neutron diffraction: *diffracted peaks and intensities*

- **Sinusoidal (or sine-wave modulated) magnetic structures**

$$\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi\vec{k}.\vec{R}_l}$$

Example: $\vec{k} = (\delta, 0, 0)$

2/ longitudinal: $\boxed{\vec{m}_{lj} \parallel \vec{k}}$



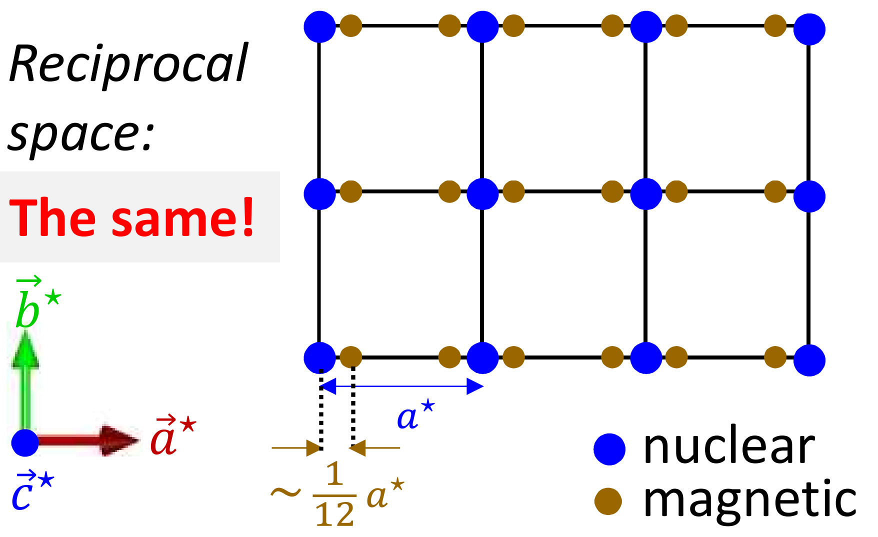
$$\vec{S}_{\pm\vec{k}} = \frac{\vec{m}_0}{2}\, e^{\pm i\phi}$$

$$\boxed{\Rightarrow \quad \vec{m}_l = \vec{m}_0 \cos(2\pi\delta l_a + \phi)}$$

with $\delta \sim \frac{1}{12}$ and $\vec{m}_0 \parallel \vec{a}$

Reciprocal space:

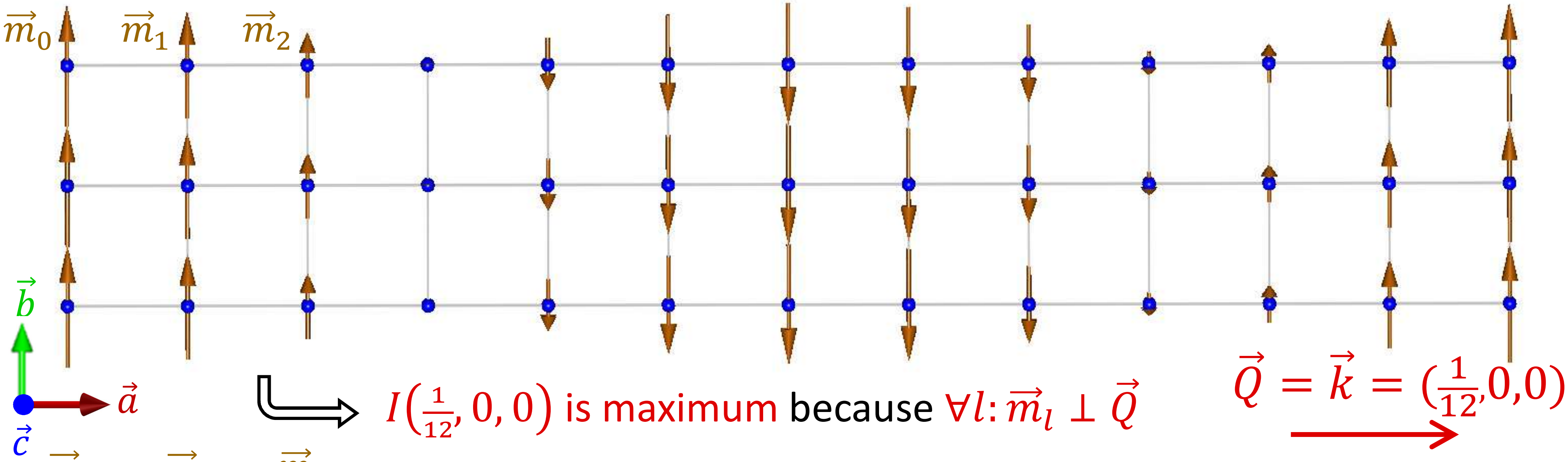
The same!



3. Magnetic neutron diffraction: *diffracted peaks and intensities*

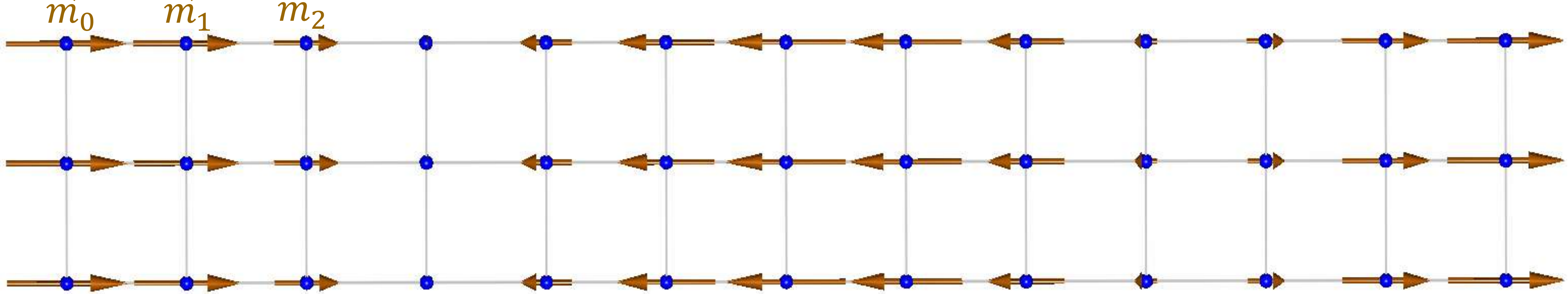
How to distinguish between both structures then?

→ Thanks to the **intensities** $\propto |\boldsymbol{F}_{M\perp}|^2$



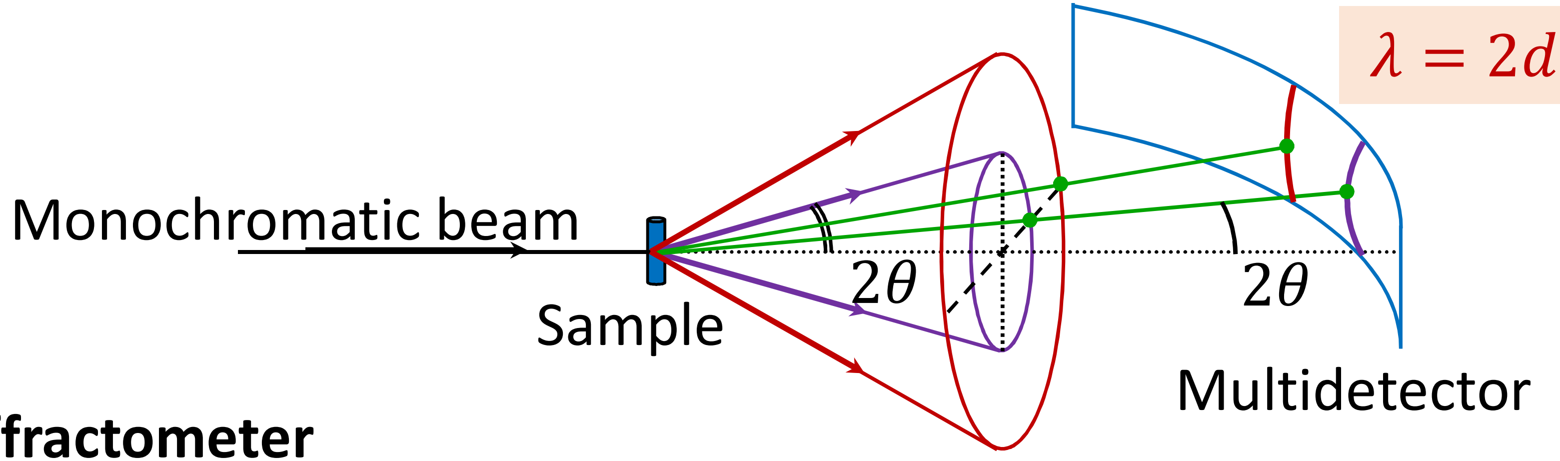
$\vec{Q} = \vec{k} = (\frac{1}{12}, 0, 0)$

⮡ $I\left(\frac{1}{12}, 0, 0\right)$ is maximum because $\forall l: \vec{m}_l \perp \vec{Q}$

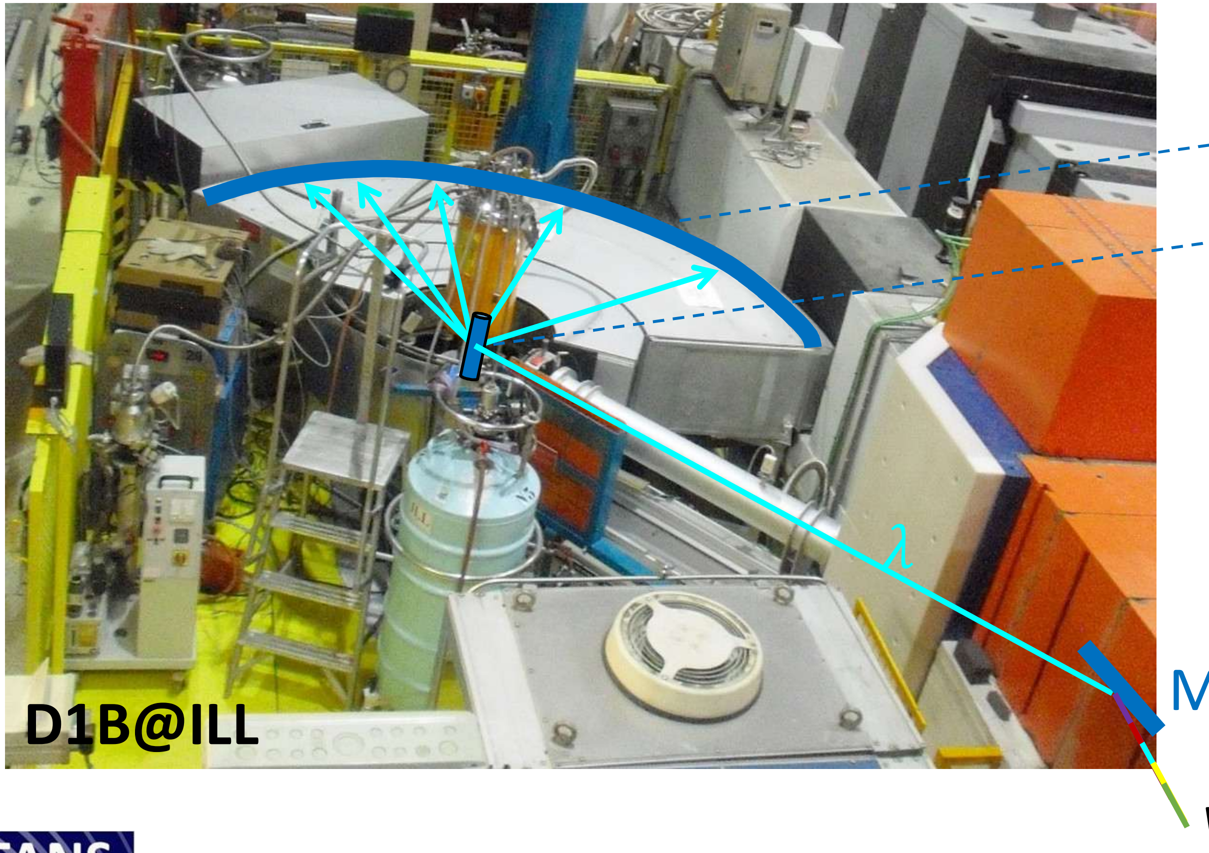


⮡ $I\left(\frac{1}{12}, 0, 0\right) = 0$ because $\forall l$: $\vec{m}_l \parallel \vec{Q}$

$$\lambda = 2d_{hkl}\sin\theta$$



Powder diffractometer



Multidetector (1280 cells)

Powder sample

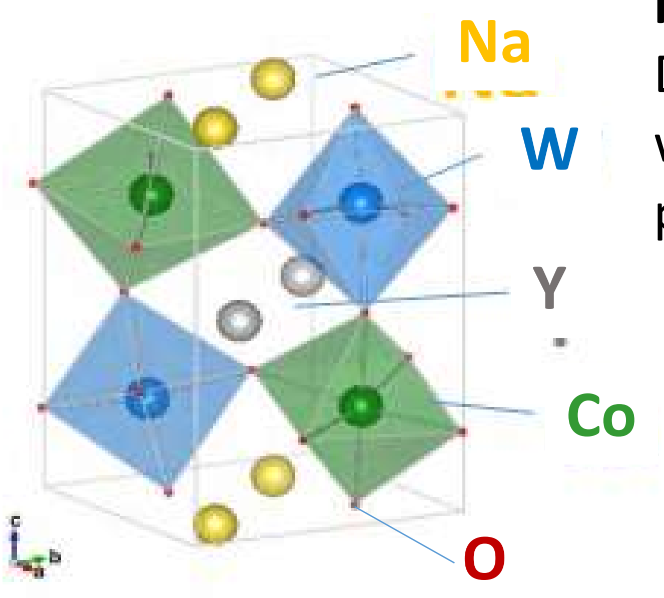
Monochromator

various λ_i

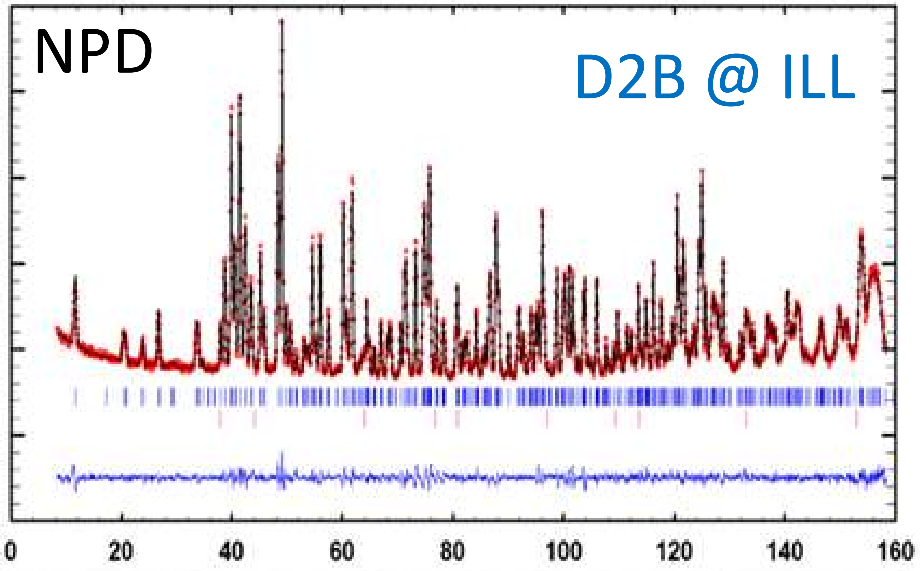
Nuclear and magnetic Bragg peaks

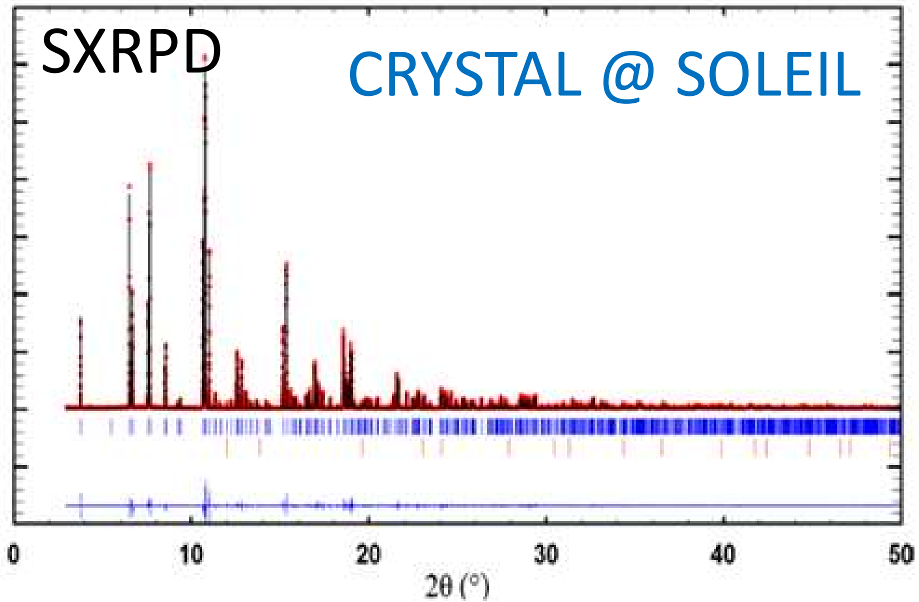
3. Nuclear PND: *example 1 – $NaYCoWO_6$*

X-ray & neutron joint crystallographic structure refinement from powder diffraction



$NaYCoWO_6$
Doubly ordered perovskite with polar structure $P2_1$ pseudo-tetragonal





Joint refinement to combine the best of:

X-ray: high resolution

→ indexation, lattice parameters

<u>Neutron</u>: sensitive to light elements

→ oxygen positions and octahedral distortion

P. Zuo *et al.*, Inorg. Chem **56**, 8478-8489 (2017)

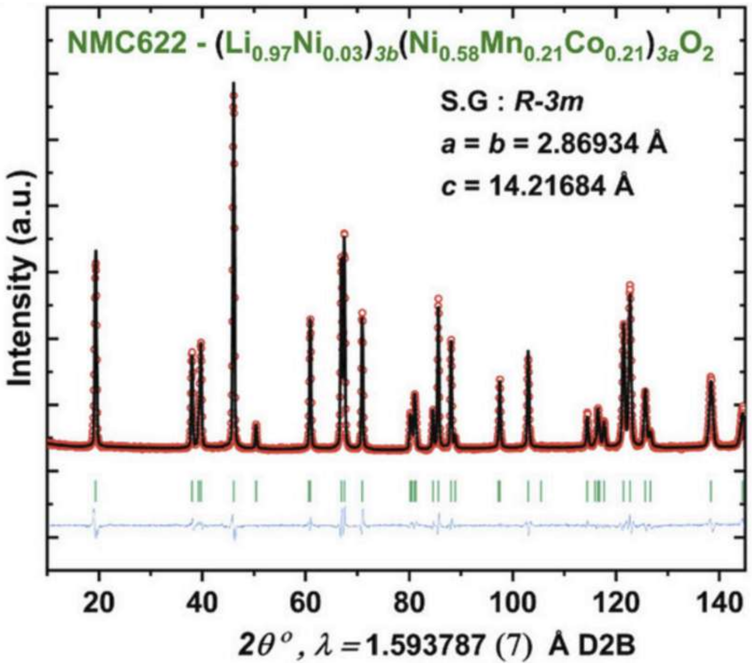
3. Nuclear PND: *example 2 – Solid state battery*

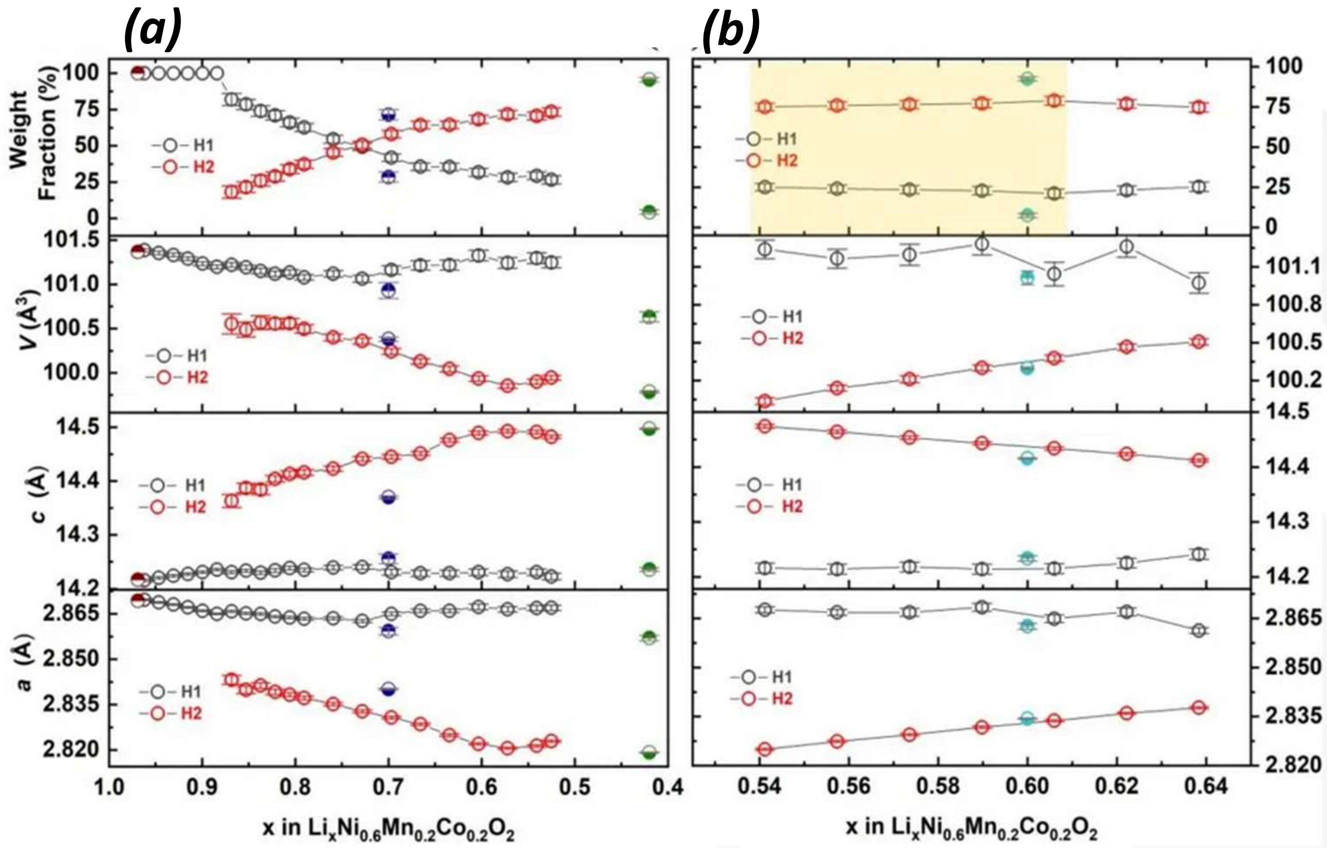
Probing Mechanism of Lithium Extraction within a Solid-State Battery in Real Time using operando powder neutron diffraction

*Evolution of structural parameters and phase fractions of H1 and H2-NMC622 during the **(a)** first charge at C/60 and **(b)** first discharge at room temperature*

Upon delithiation: H1 → H2 phase

Rietvield refinement of H1-NMC622



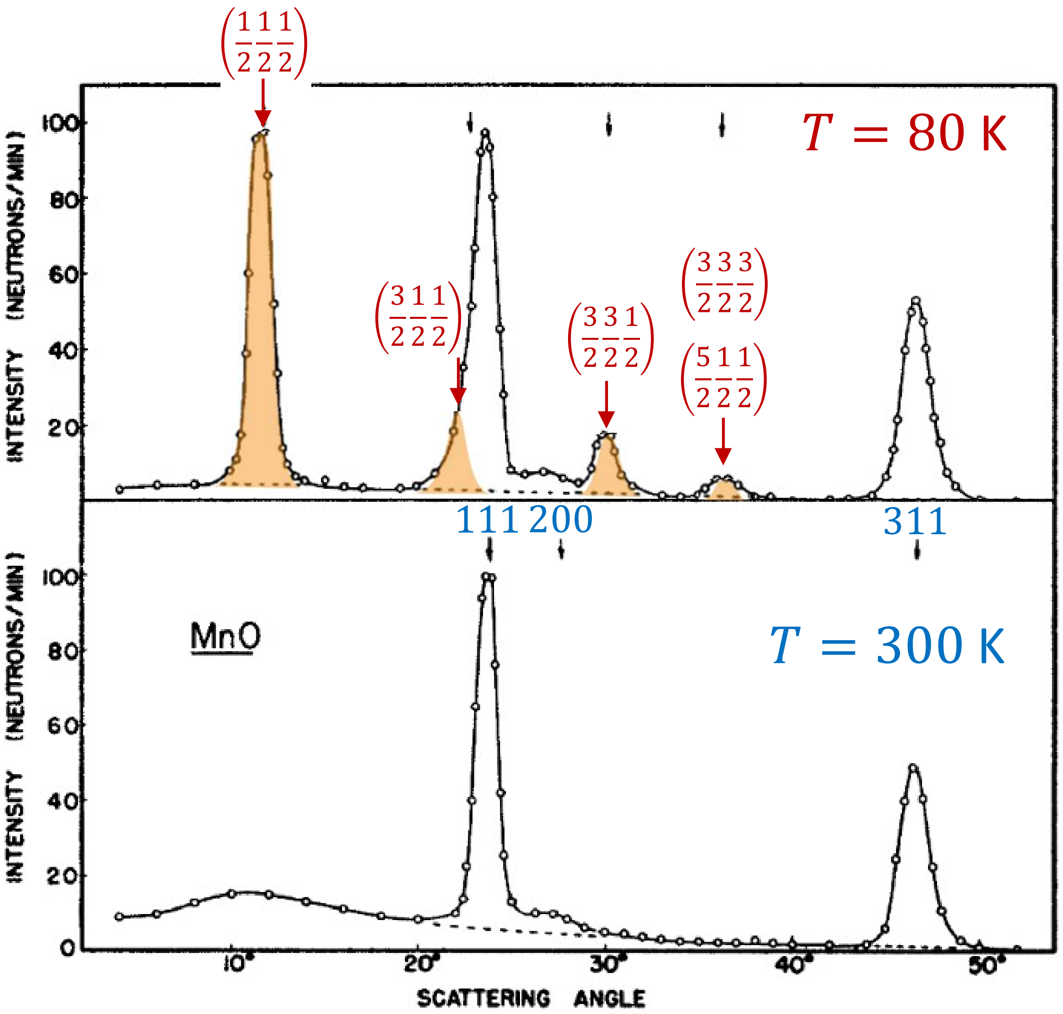


S. A. Kumar et al., *Advanced Energy Materials* **16**, e06600 (2026)

3. Nuclear and magnetic PND: *example 3 – MnO*

A historical example: Néel ordering determined by powder diffraction (1949)

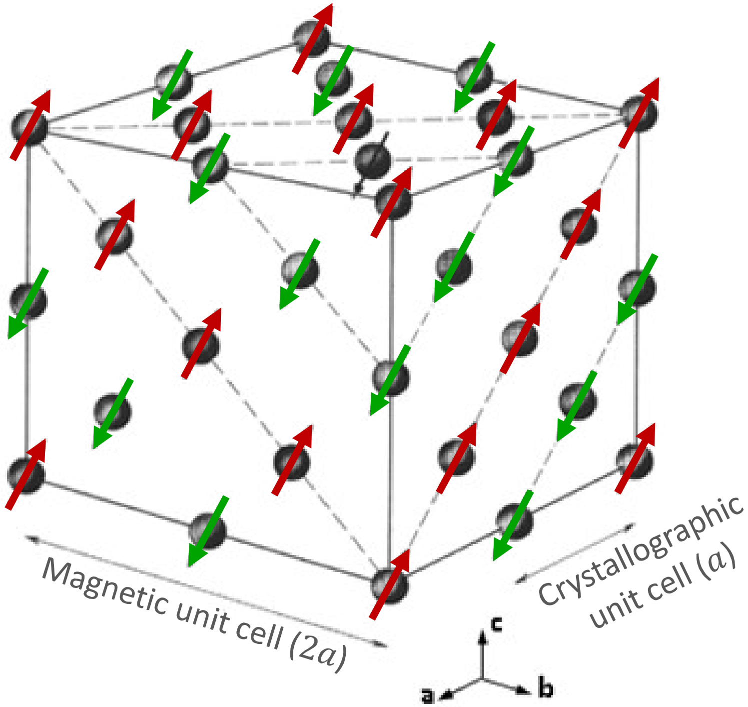
Propagation vector:
$\vec{k} = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$



Clifford G. Shull

Crystallographic unit cell: a, b, c

Magnetic unit cell: $2a, 2b, 2c$

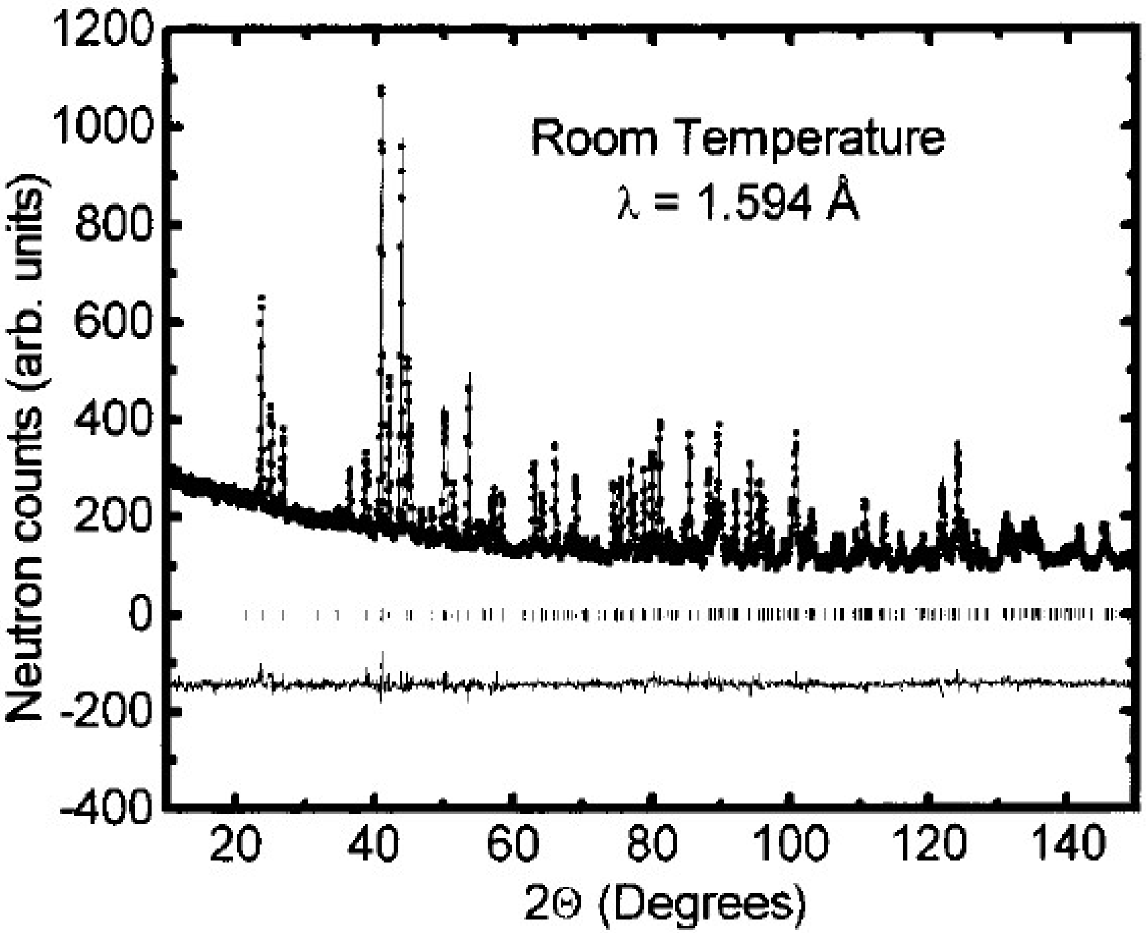


C. G. Shull and J. S. Smart., Phys. Rev. **76**, 1256 (1949)

Nuclear and magnetic structure refinement from powder diffraction

- **Acquisition at room temperature** on D2B at $\lambda = 1.6$ Å

→ refinement of the nuclear structure at room temperature



$Pnma$ space group

$a = 5.83536(6)$ $b = 7.36060(8)$ $c = 5.25722(5)$ Å

atom	x	y	z	B (Å^2)
Ho 4c	0.0839(2)	0.25	0.9825(3)	0.25(3)
Mn 4b	0	0	0.5	0.39(6)
O1 4c	0.4622(4)	0.25	0.1113(4)	0.38(4)
O2 8d	0.3281(3)	0.0534(2)	0.7013(3)	0.45(3)

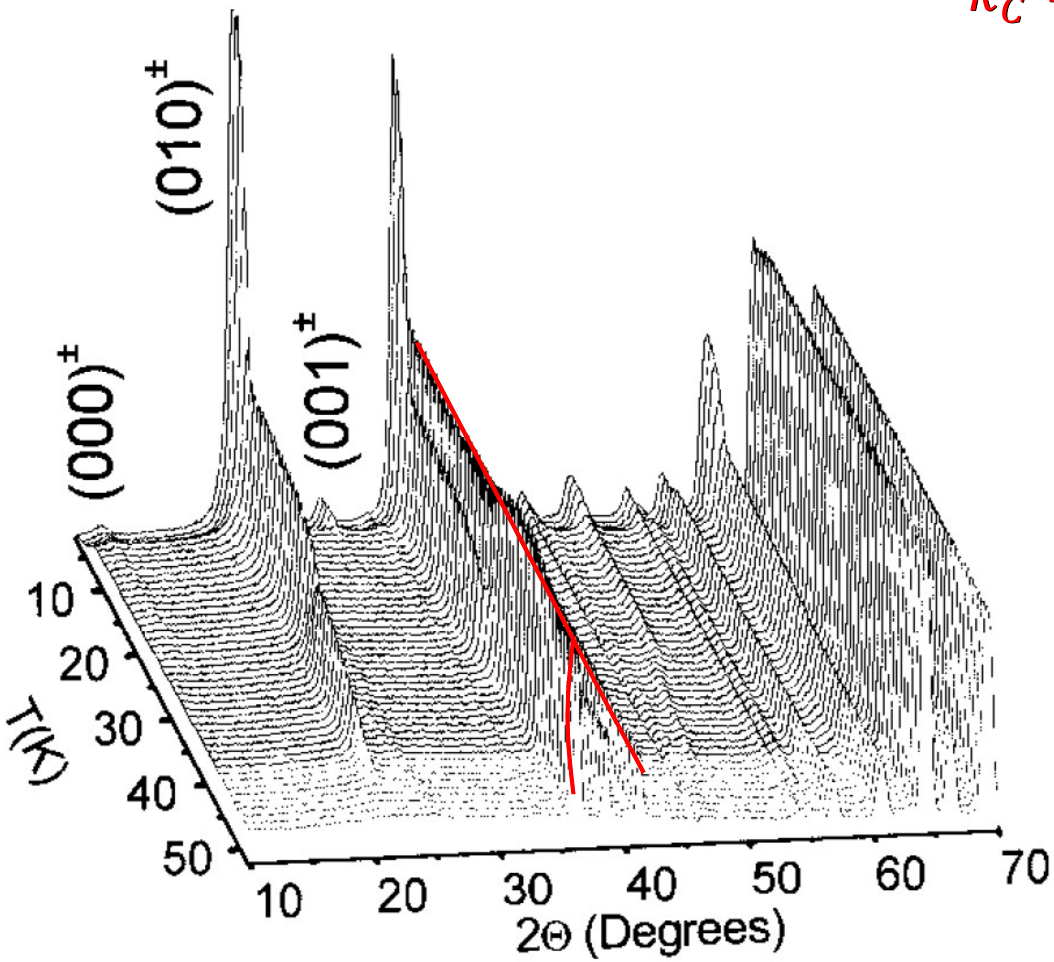
Rf-factor = 3.6%, $\chi^2 = 1.5$

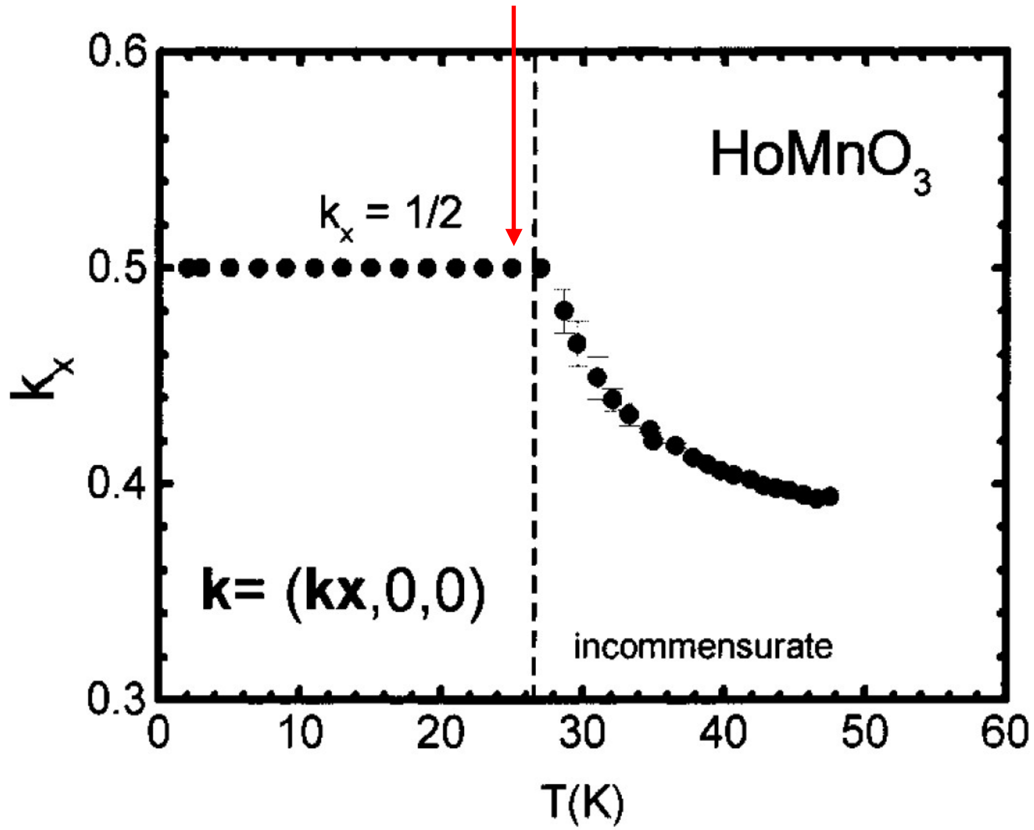
A. Munoz *et al.*, Inorg. Chem. **40**, 1020 (2001)

Nuclear and magnetic structure refinement from powder diffraction

- **Temperature dependance** on D20 at $\lambda = 2.4$ Å

→ propagation vector: $\vec{k}_{IC} = (k_x, 0,0)$ below $T_N \sim 48$ K
$\vec{k}_C = (1/2,0,0)$ below 27 K



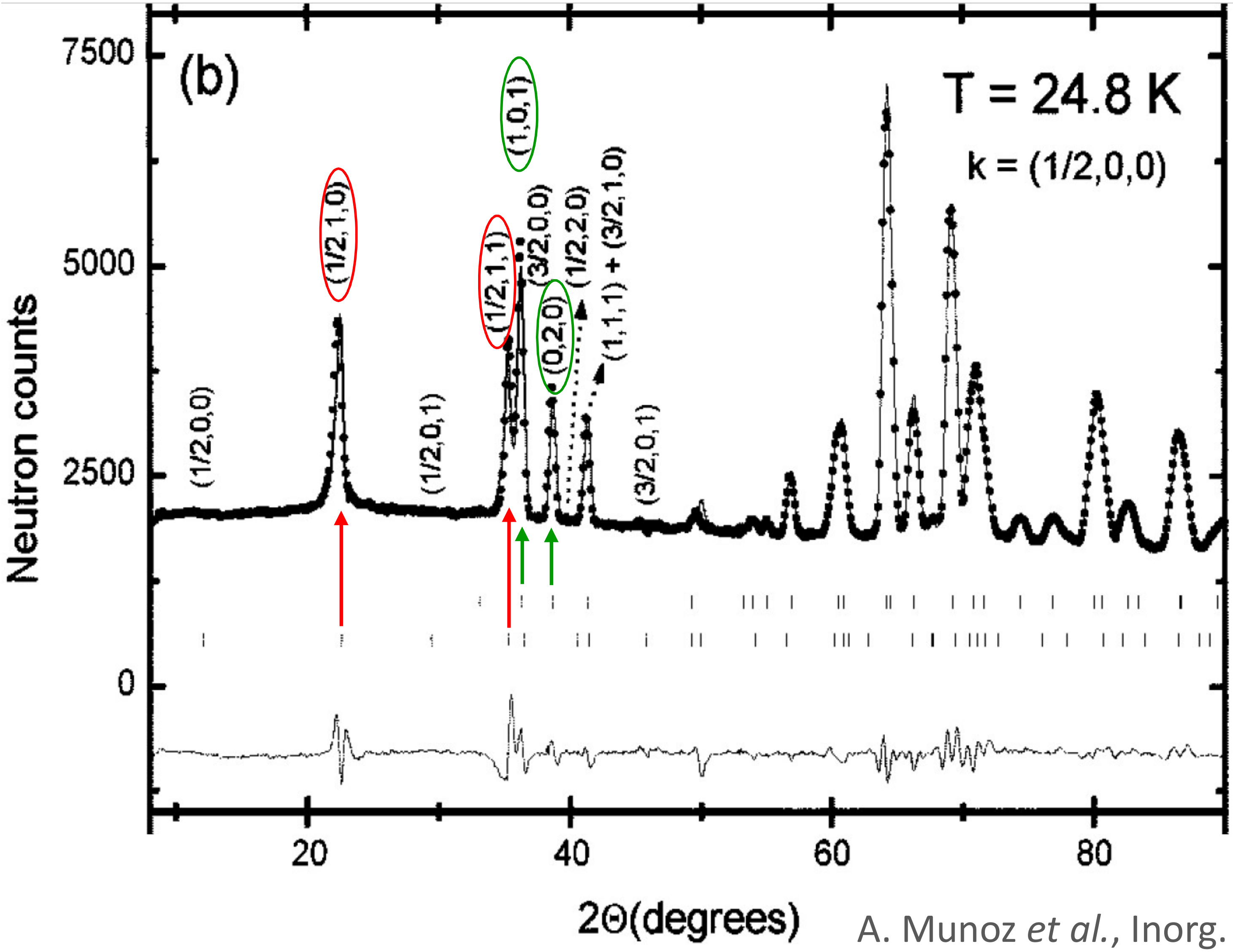


A. Munoz *et al.*, Inorg. Chem. **40**, 1020 (2001)

3. Nuclear and magnetic PND: *example 4 – $HoMnO_3$*

Nuclear and magnetic structure refinement from powder diffraction

- **Acquisition at $T \sim 25$ K** on D2B at $\lambda = 1.6$ Å



A. Munoz *et al.*, Inorg. Chem. **40**, 1020 (2001)

3. Nuclear and magnetic PND: *example 4 – $HoMnO_3$*

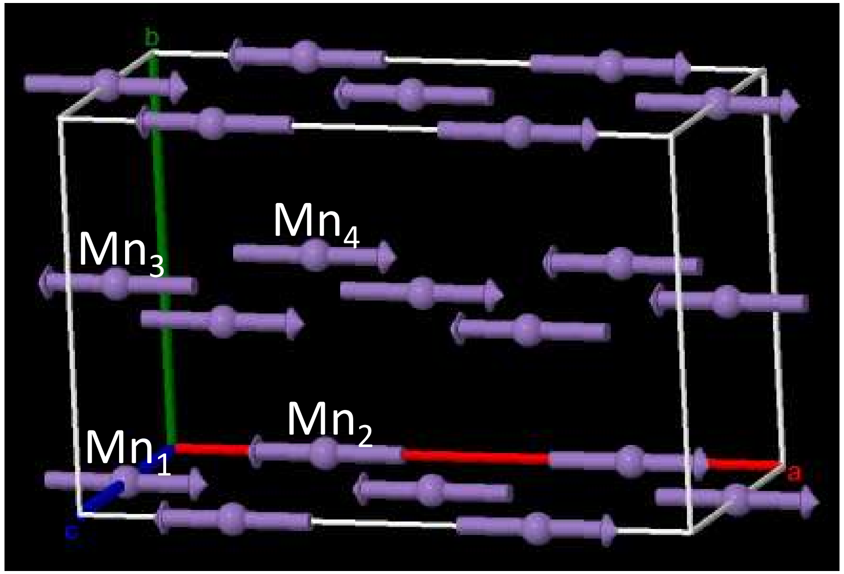
→ Symmetry analysis (***BasIreps*** *from the FP_Suite* or ***Sarah***):

crystallographic space group + propagation vector + atomic coordinates of Mn^{3+} and Ho^{3+}

2 irreducible representations (Ireps) Γ_j of dimension 2 for Mn^{3+} : $\Gamma = 3\Gamma_1 \oplus 3\Gamma_2$

Idem for Ho^{3+}: $\Gamma' = 3\Gamma'_1 \oplus 3\Gamma'_2$

	Γ_1	Γ_2
$Mn_1\left(0,0,\frac{1}{2}\right)$	$u, \quad v, \quad w$	$u, \; 0, \; 0$
$Mn_2\left(\frac{1}{2},0,0\right)$	$u', \quad v', \quad w'$	$-u, \; 0, \; 0$
$Mn_3\left(0,\frac{1}{2},\frac{1}{2}\right)$	$u, \; -v, \; w$	$-u, \; 0, \; 0$
$Mn_4\left(\frac{1}{2},\frac{1}{2},0\right)$	$u', -v', w'$	$u, \; 0, \; 0$



→ Magnetic structure refinement: test of the 2 Ireps for both magnetic atoms (with all structural and profile parameters fixed, from the nuclear structure refinement)

For Mn^{3+}: Γ_2 with $u' = -u, \; v' = v = 0, \; w' = w = 0$; $\boldsymbol{m_x = 3.87(4)\mu_B}$

For Ho^{3+}: $\vec{\boldsymbol{m}}' = \vec{\boldsymbol{0}}$ $\qquad \chi^2 = 1.9$

A. Munoz *et al.*, Inorg. Chem. **40**, 1020 (2001)

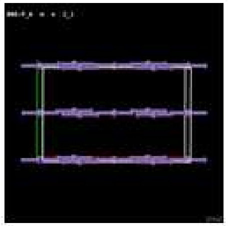
3. Nuclear and magnetic PND: *example 4 – $HoMnO_3$*

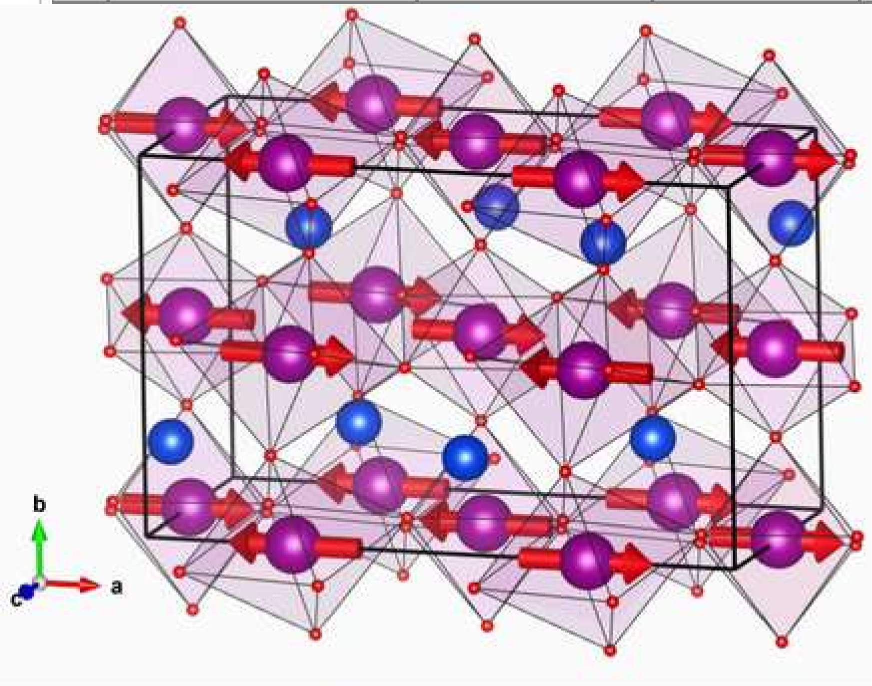
bilbao crystallographic server

View Full Database

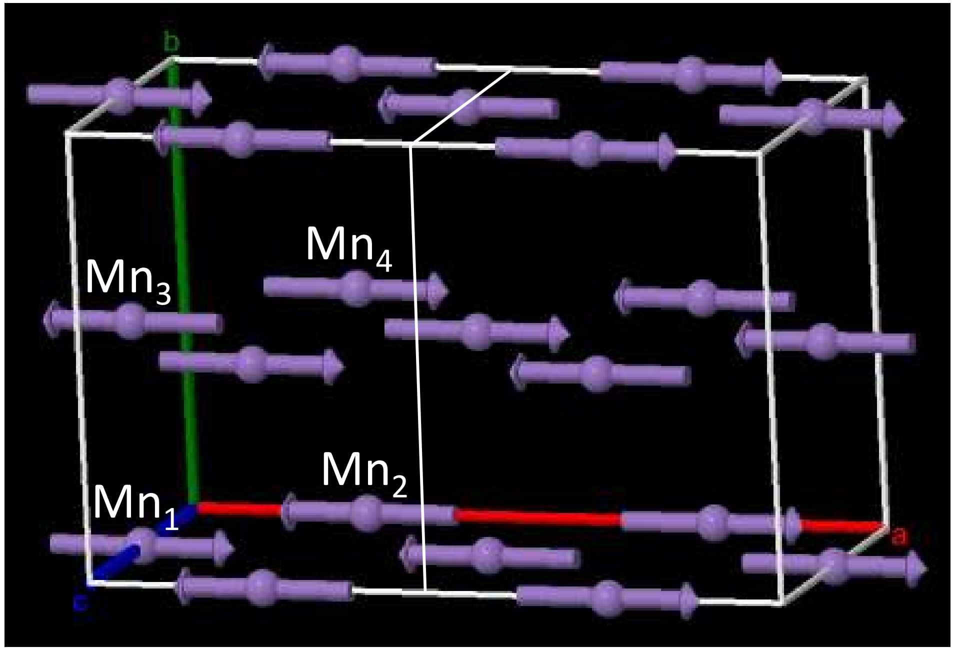
Element search (separate with space or comma): Ho Mn O AND OR Search

MAGNDATA A collection of magnetic structures with transportable cif-type files

N	Entry	Structure	Propagation vector(s)	Parent space group	Transformation from parent	Magnetic (super)space group	Magnetic point group
13	1.20 $HoMnO_3$		1/2,0,0	Pnma (62) (standard)	(2**a**,**b**,**c**;0,0,0)	P_bmn2_1 (31.129) (-**b**,**a**,**c**;1/8,1/4,0)	mm2.1' (7.2.21)



Magnetic structure with all atoms



3. Single-crystal Neutron diffraction: *instrumentation*

Diffraction condition:

put a reciprocal lattice vector $\vec{H}$ in coincidence with the scattering vector $\vec{Q} = \vec{k}_f - \vec{k}_i$

- Either we work with various λ and we keep the crystal fixed

Laue technique

$\rightarrow$ **Laue* & TOF* diffractometers**
❶ ❷

- Or we work at fixed λ and we make the sample rotate

Rotating crystal technique

$\rightarrow$ **4-circles*** or **2-axes lifting arm* diffractometers**
❸ ❹

$\Rightarrow$ **Measurement of $\dfrac{d\sigma}{d\Omega}$**

Possibility to analyze the final energy $(E' = E)$

$\rightarrow$ **2-axis with an analyzer added**

or **3-axis spectrometer at $\hbar\omega = 0$**

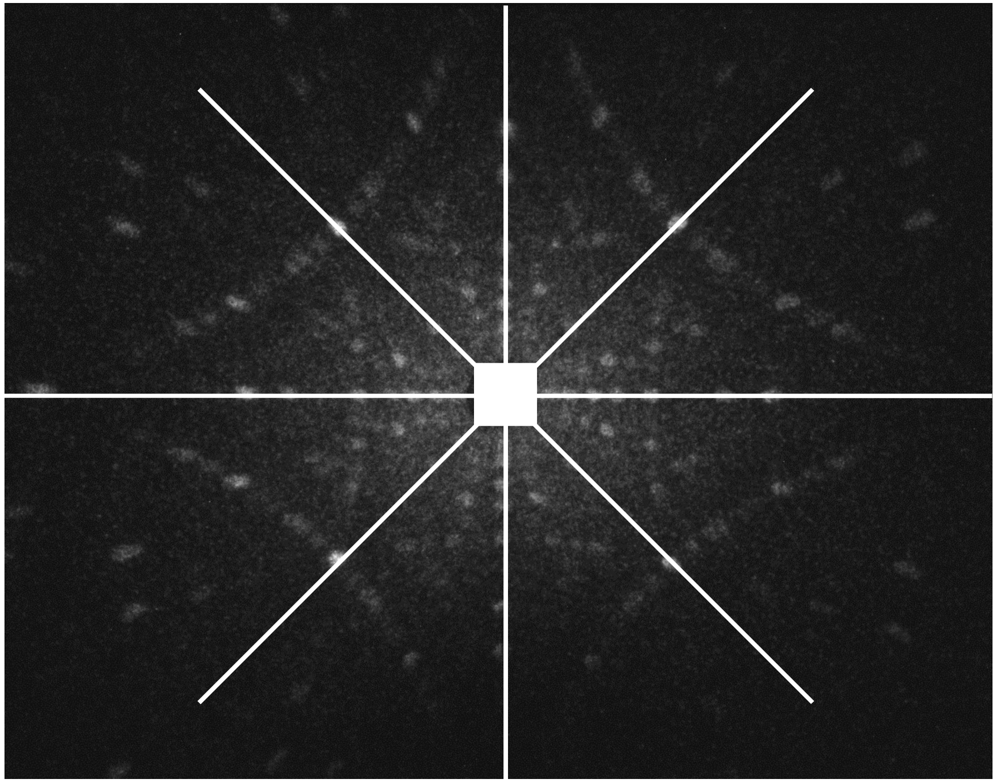
$\Rightarrow$ **Measurement of $\left(\dfrac{d^2\sigma}{d\Omega dE'}\right)_{E'=E}$**

Laue diffraction (polychromatic beam, fixed crystal)

OrientExpress @ ILL

Diffraction pattern = Laue diagram showing a wide part of the reciprocal space

- Evidence the symmetry planes and axes
  → Determine the **Laue class**, **align a crystal**, …
- Observe **superlattice peaks**, **diffuse scattering**, …

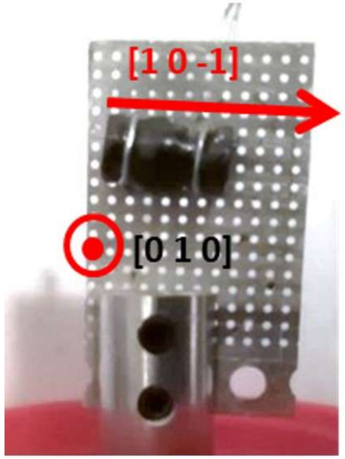


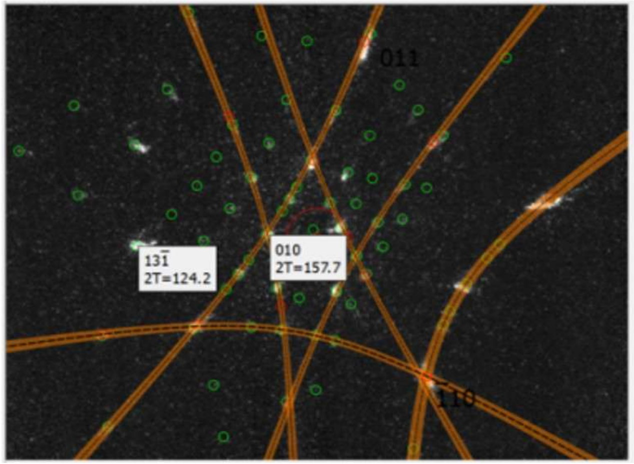
$BaCo_2V_2O_8$
Laue pattern showing the symmetries

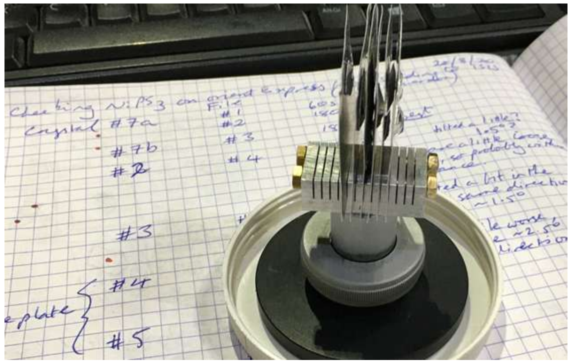
Laue diffraction: crystal alignment

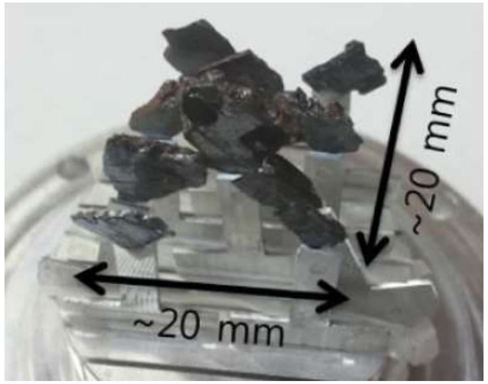
Orient Express widely used to **align a crystal**
prior to a diffraction or INS experiment:

Examples



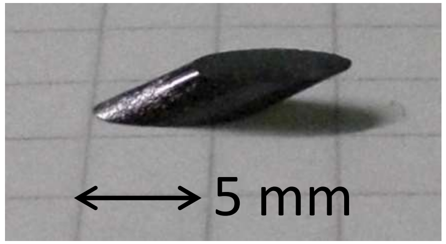


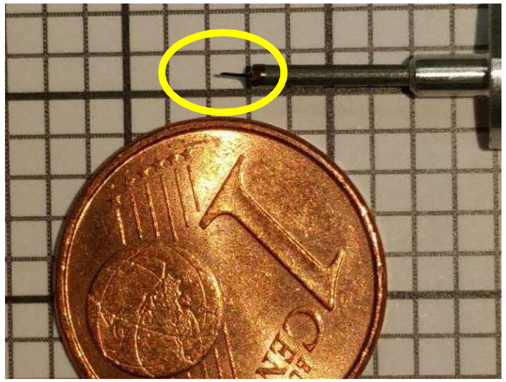




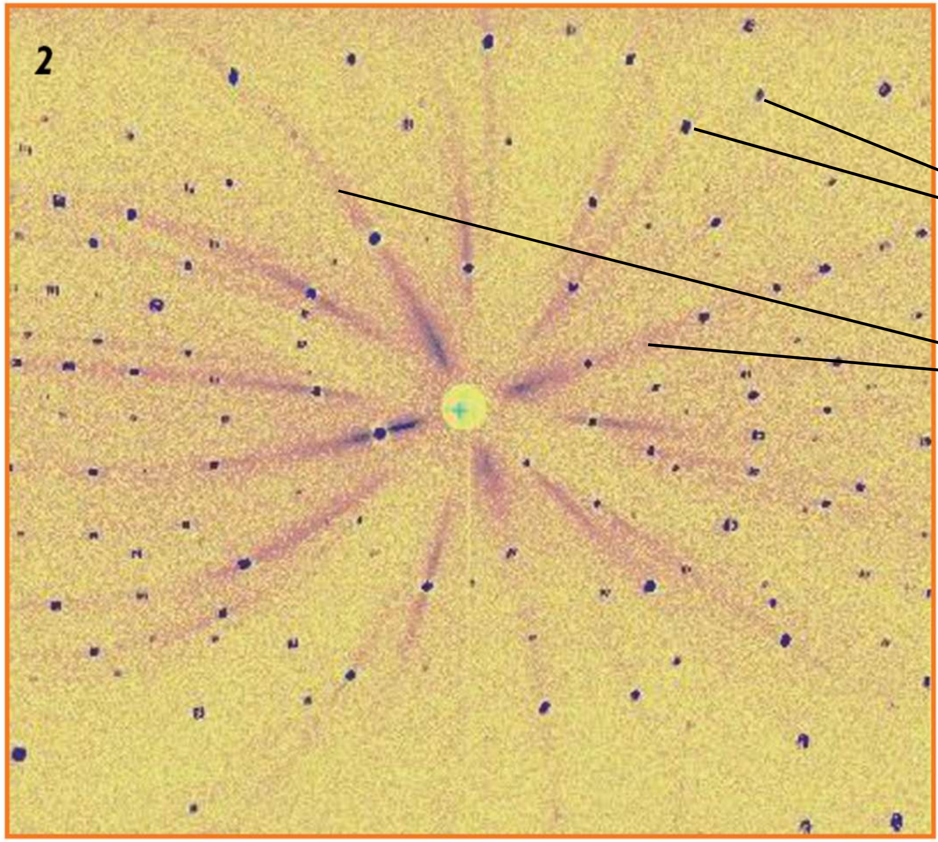
For inelastic neutron scattering (INS) exp.

For diffraction experiments





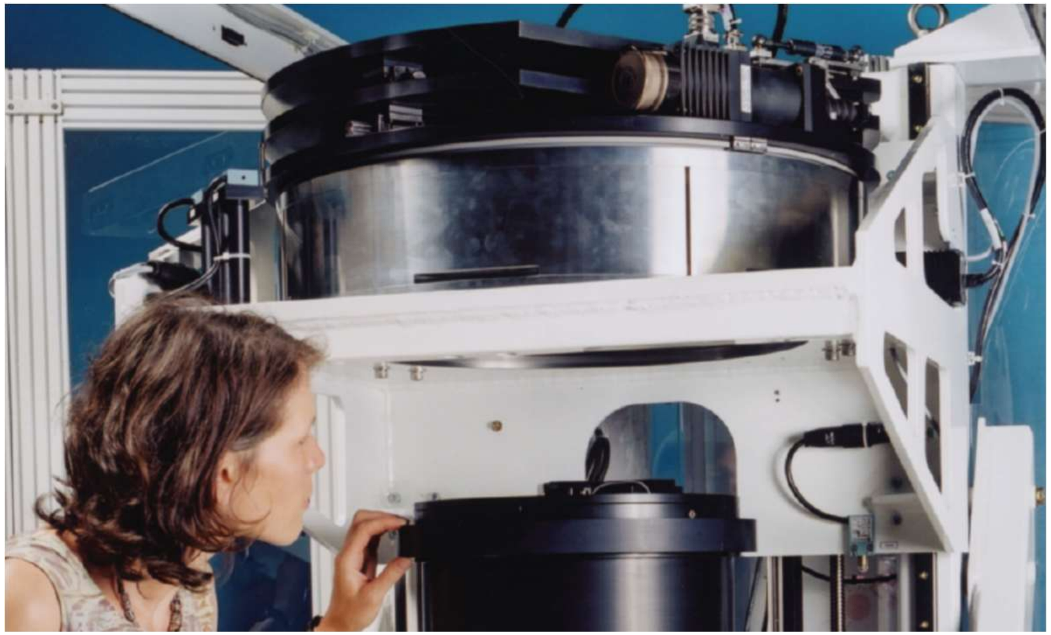
Laue diffraction: 2D ordering



$FeTaO_6$
Neutron Laue pattern at $T < T_N$

Bragg peaks: crystallographic structure

Diffuse scattering: 2D magnetic ordering

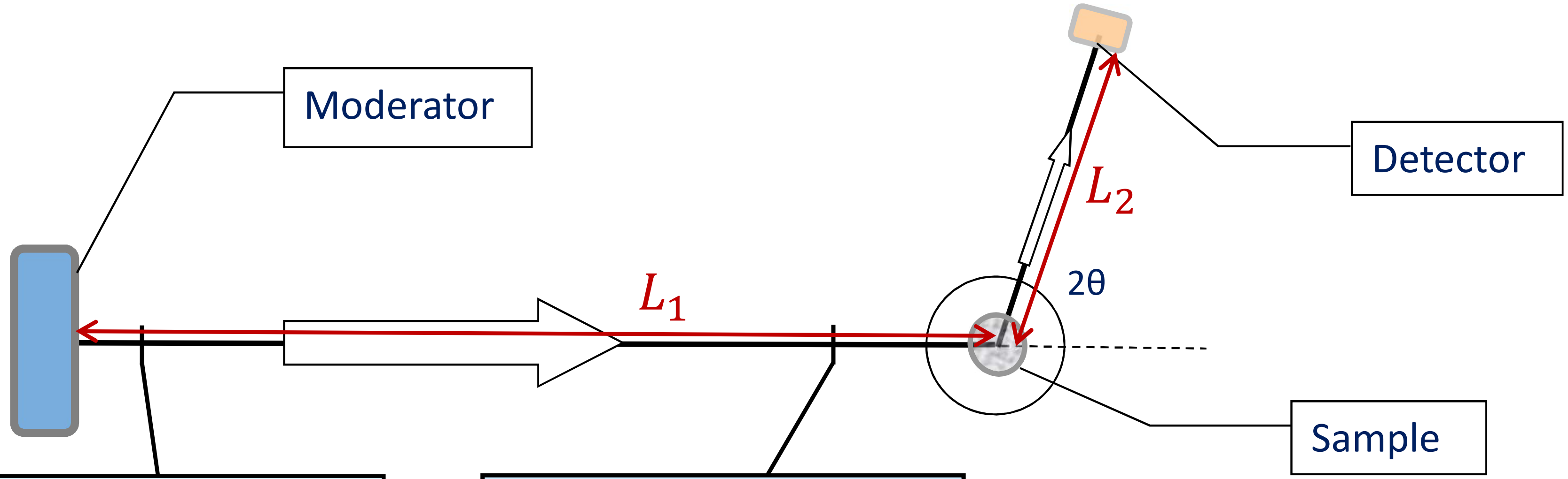


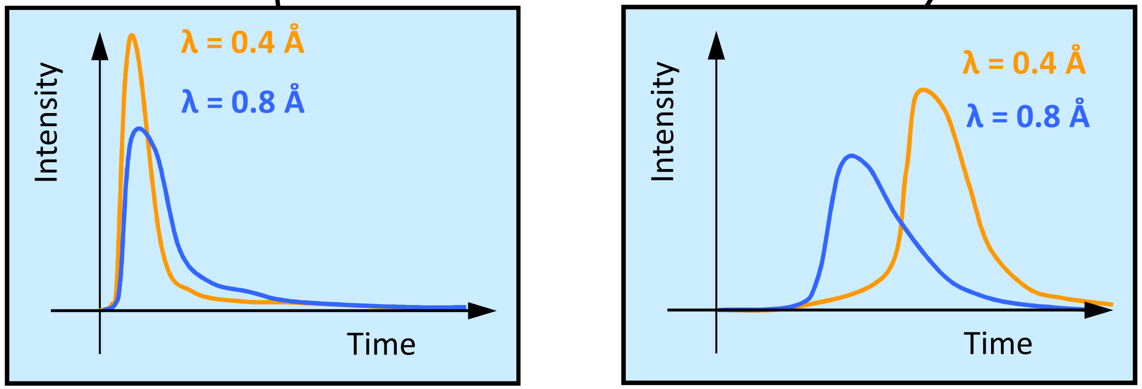
VIVALDI @ ILL
Very-Intense Vertical-Axis Laue Diffractometer

3. Single-crystal Neutron diffraction: *instrumentation* ❷*

Time of Flight (TOF) diffractometer (on a pulsed source)

→ Laue diffraction + determination of the wavelength





The initial pulse from the moderator contains all neutron wavelengths

As they travel down the instrument the faster shorter wavelength neutrons arrive first

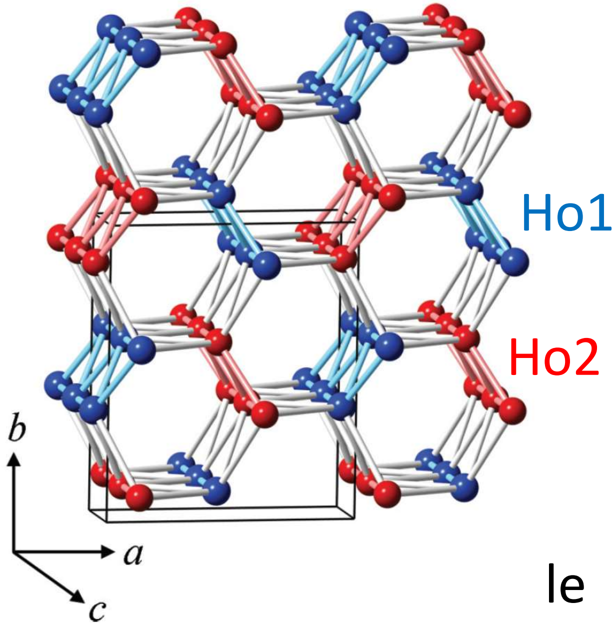
- **The neutrons are sorted by time at the sample and the diffraction done as a function of time *t***
- **A full diffraction pattern is collected at a fixed angle**

$$\boxed{v = \frac{L_1 + L_2}{t} \rightarrow \lambda = \frac{h}{mv}}$$

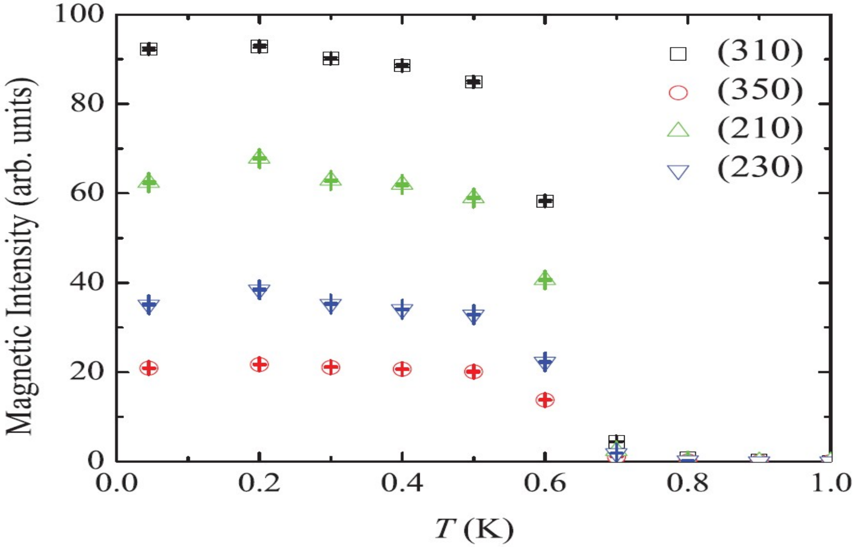
Adapted from P. Manuel

TOF diffractomer: Short range order below 700 mK in $SrHo_2O_4$

Magnetic sublattice

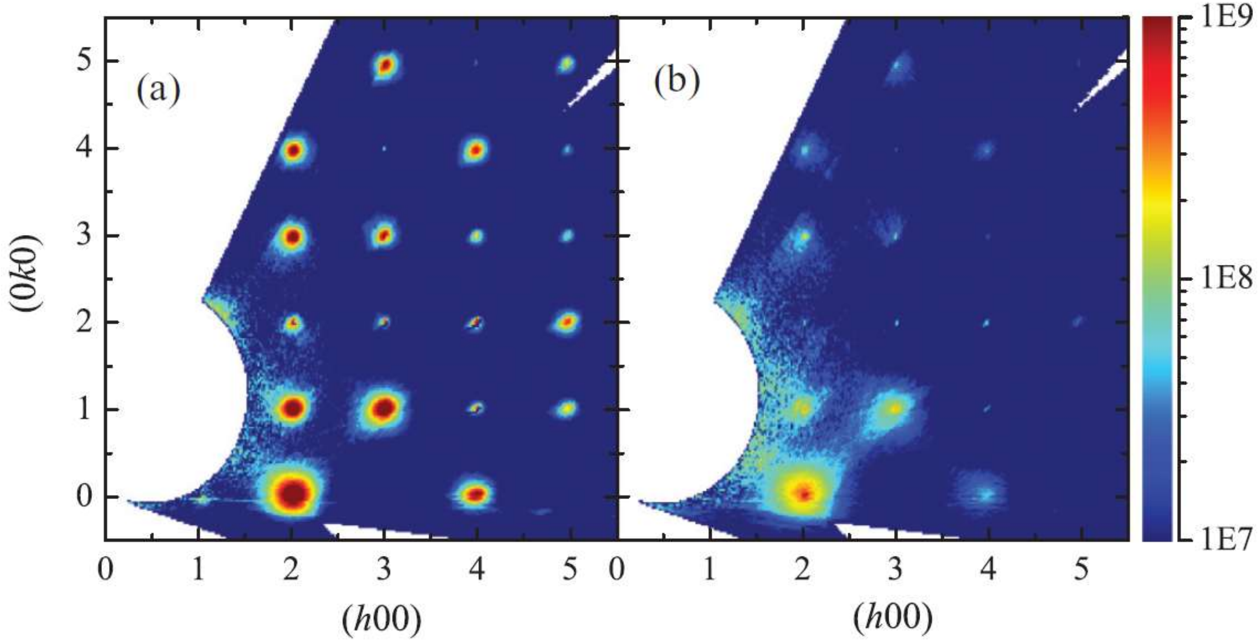


le



Magnetic contribution measured on WISH @ ISIS (after subtracting the 1 K data):

$T = 55$ mK $\quad$ $T = 700$ mK



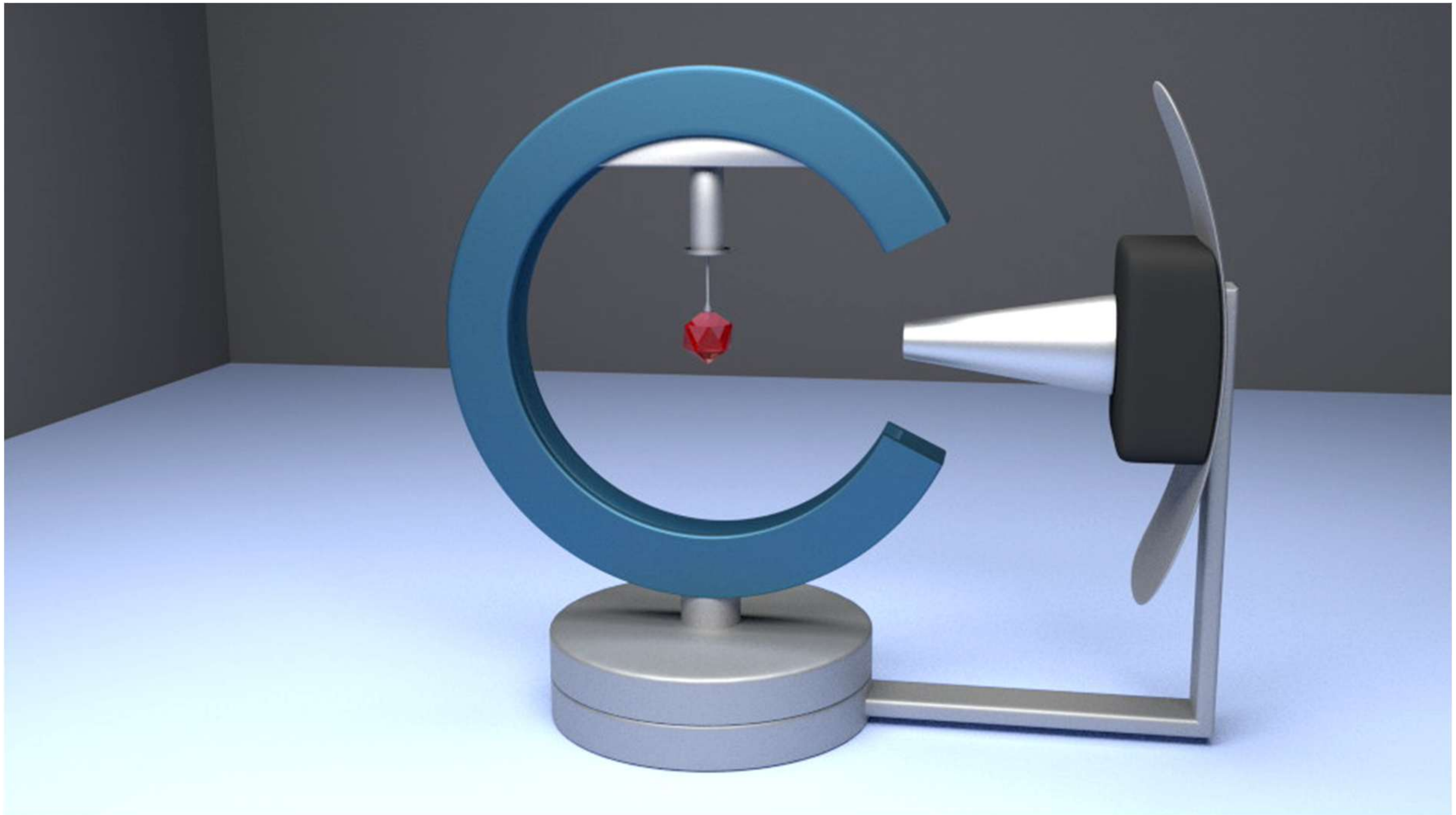
⇒ **Diffuse scattering peaks** appear below 700 mK at $h\ k\ 0$ positions → $\vec{k} = \vec{0}$

O. Young *et al.*, Phys. Rev. B **88**, 024411 (2013)

3. Single-crystal Neutron diffraction: *instrumentation*

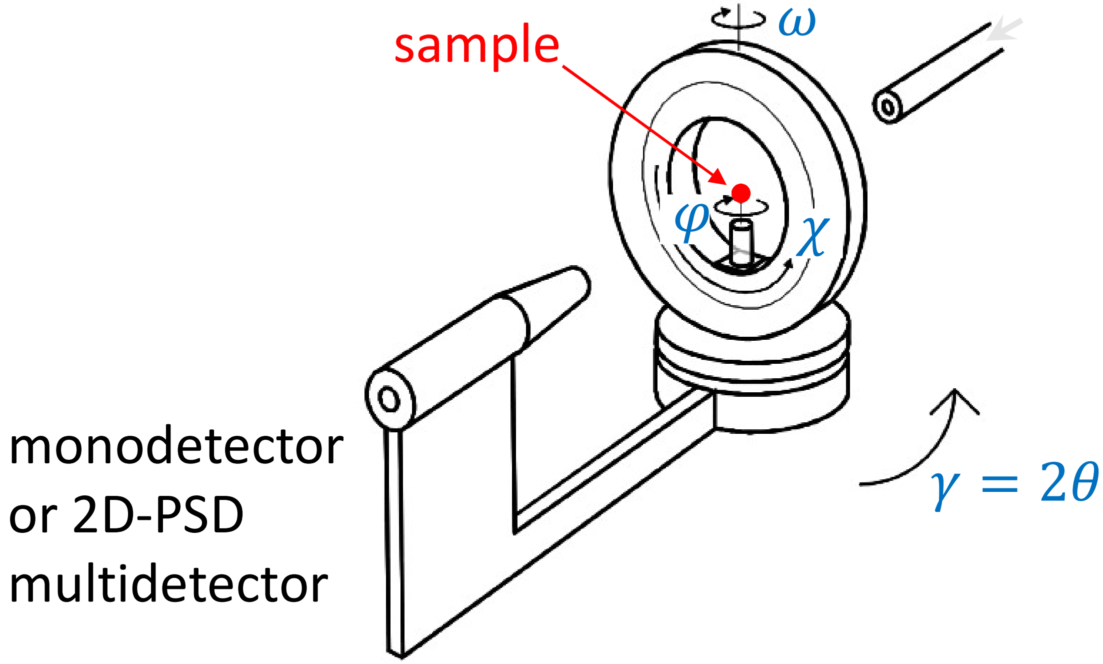
Rotate the crystal to align $\vec{Q}$ with the diffraction condition
$\vec{Q} \perp$ diffracting lattice planes (hkl) and satisfies Bragg's law $n\lambda = 2d_{hkl} \sin\theta$

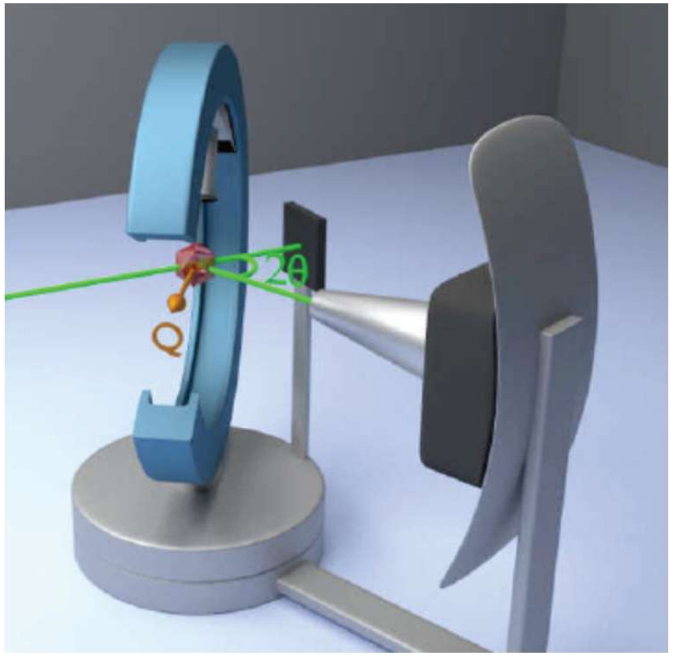
4-circle diffractometer (monochromatic beam, rotating crystal)



Courtesy N. Qureshi

4-circle diffractometer

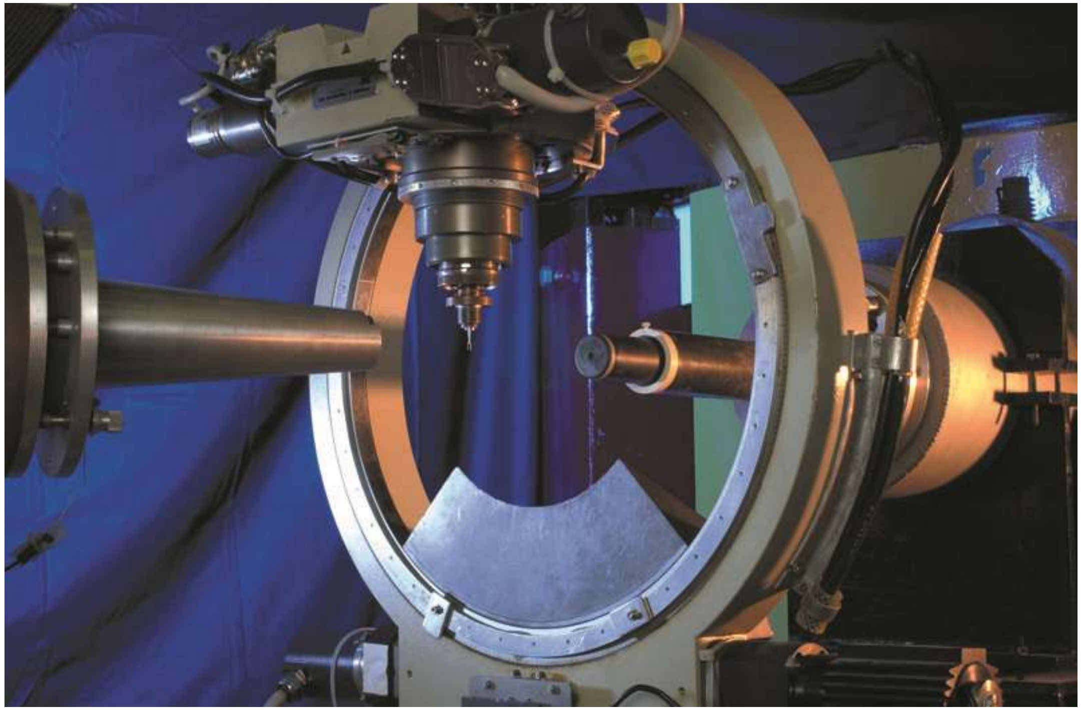




The single-crystalline sample can rotation in all directions (3-circles)
$\rightarrow \vec{Q}$ can be put in any direction

Limitation on the sample environments

4-circle diffractometer



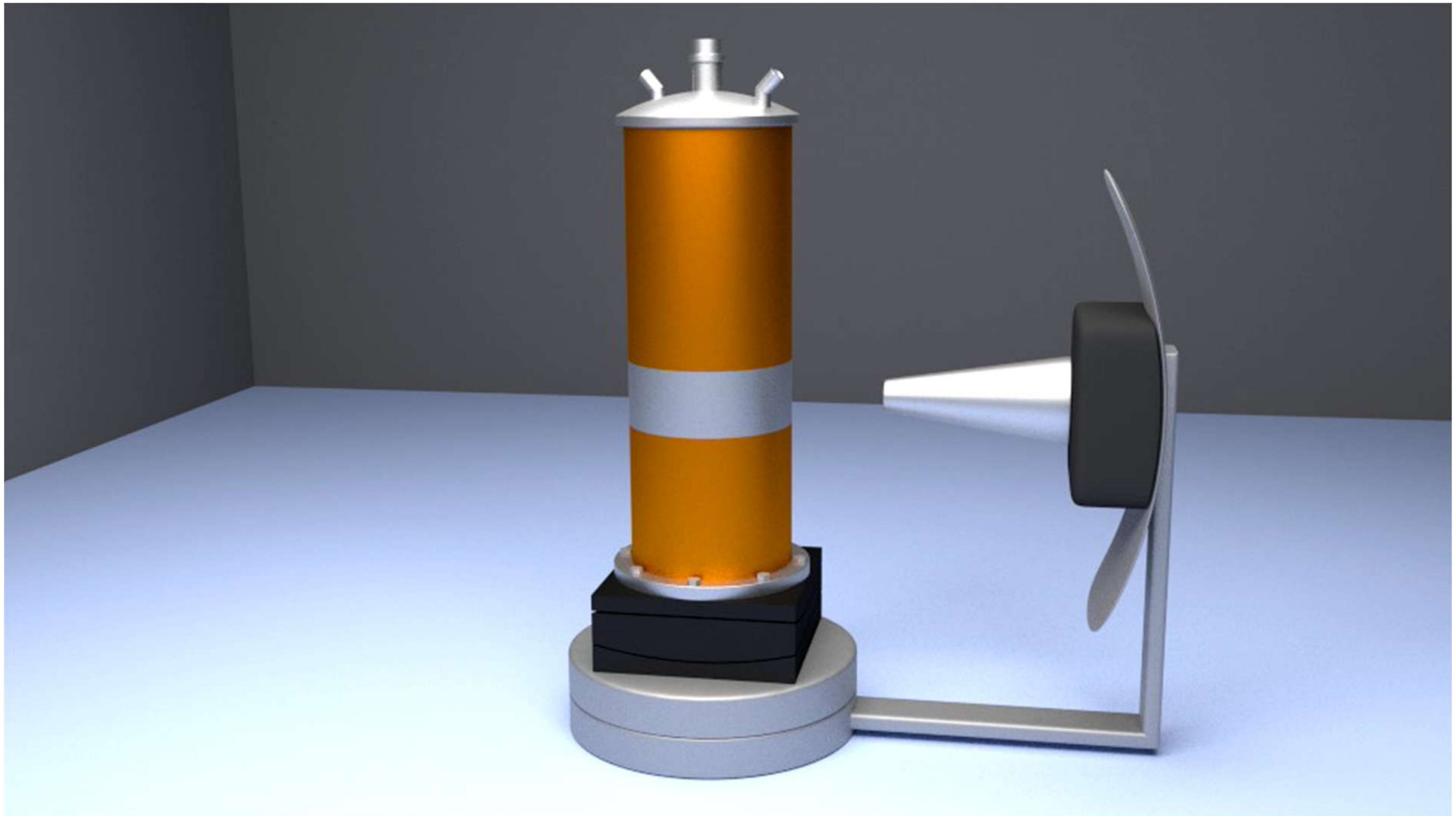
4-circle goniometer on **D9 @ ILL**

Hot neutron 4-circle diffractometer
D9 @ ILL

3. Single-crystal Neutron diffraction: *instrumentation* ❹

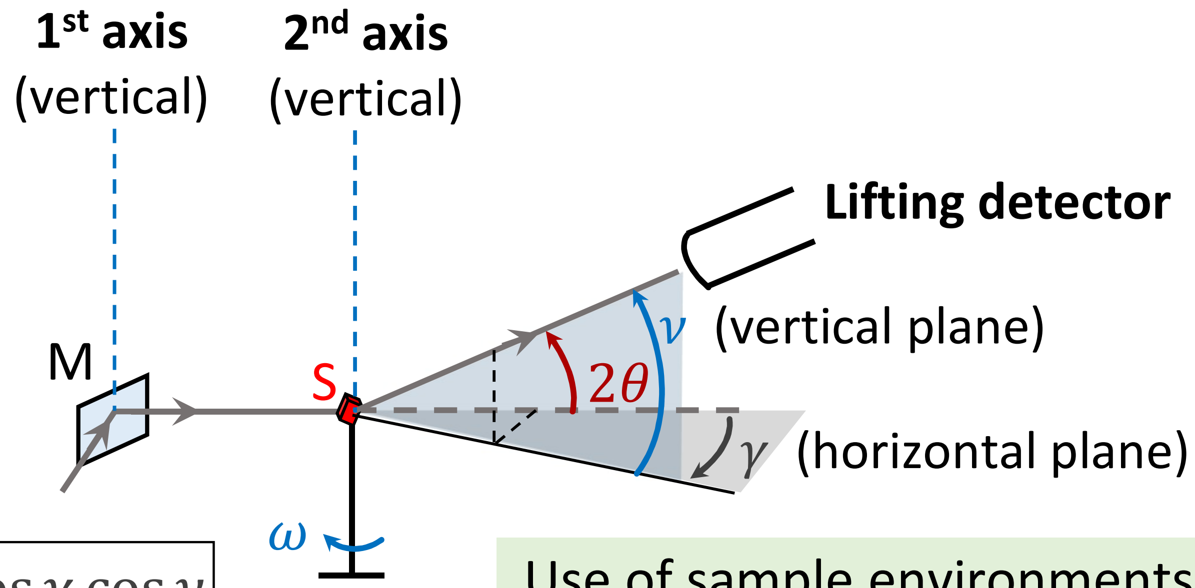
Rotate the crystal to align $\vec{Q}$ with the diffraction condition
$\vec{Q} \perp$ diffracting lattice planes (hkl) and satisfies Bragg's law $n\lambda = 2d_{hkl}\sin\theta$

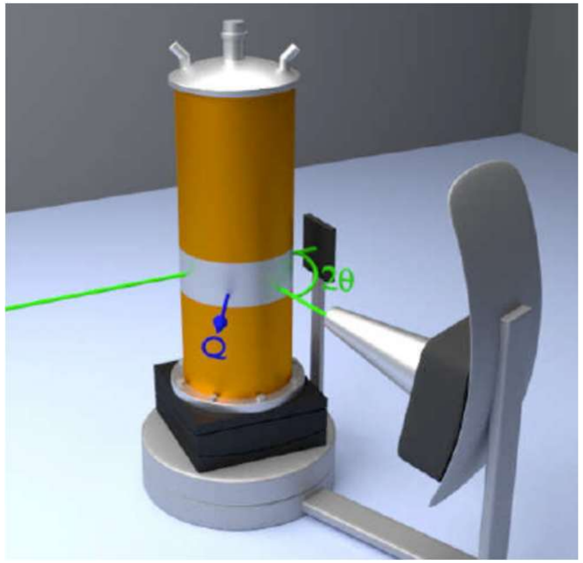
2-axis diffractometer with a lifting arm detector (monoλ beam, rotating crystal)



Courtesy N. Qureshi

2-axis diffractometer with a lifting arm detector





$$\cos 2\theta = \cos\gamma \cos\nu$$

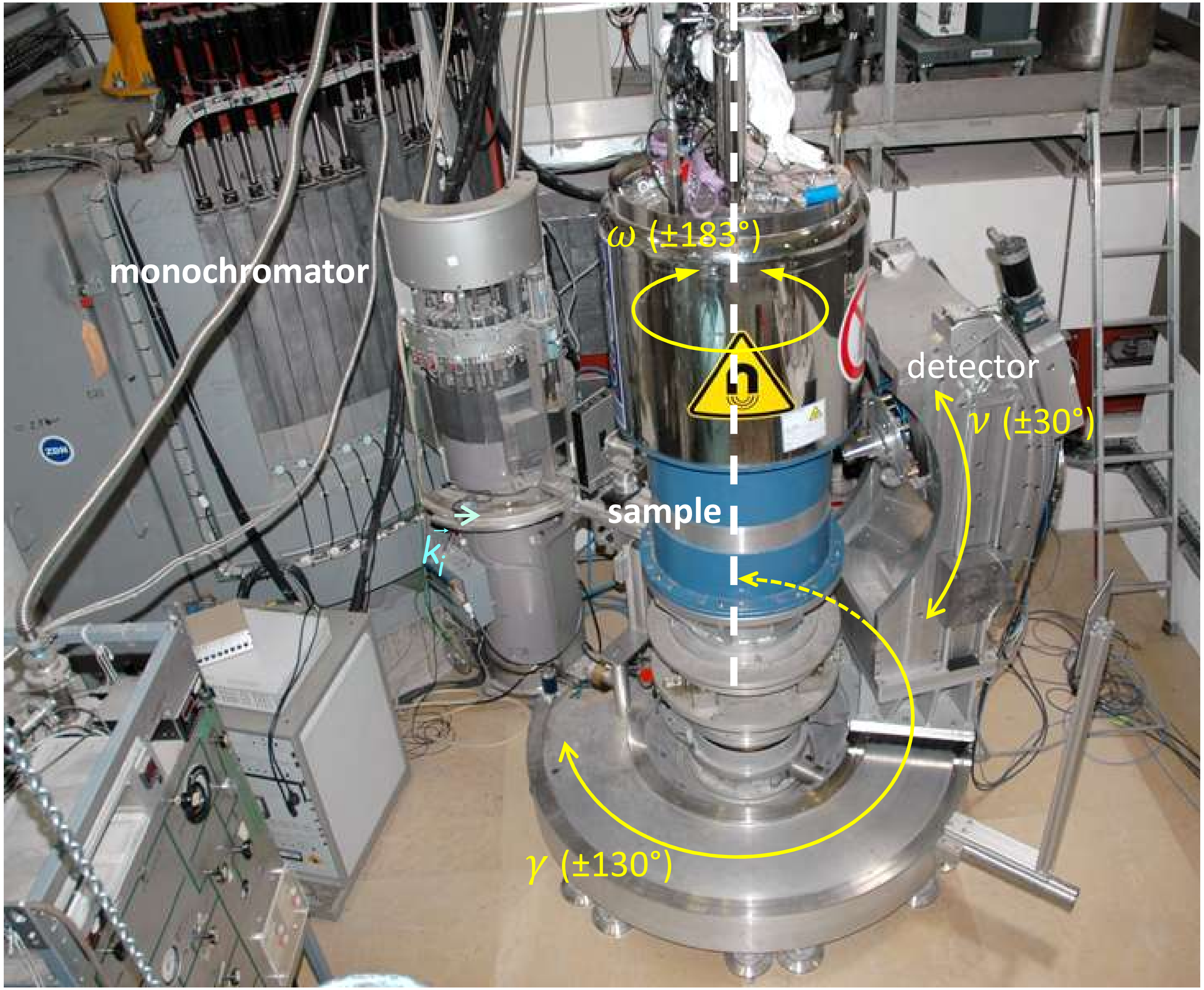
Use of sample environments for **extreme conditions**:
Magnets (→ 15 T steady, 40 T pulsed)
Dilution (→ 30 mK), Furnaces (→ 800 K)
Pressure cells, …

The single-crystalline sample rotates only around the vertical direction
→ **limitation on $\vec{Q}$ in the vertical direction**

2-axis diffractometer with a lifting arm detector

Thermal neutron
2-axis diffractometer
with a lifting arm detector
D23 @ ILL

(= normal beam geometry)



Possibility to install
a 4-circle goniometer

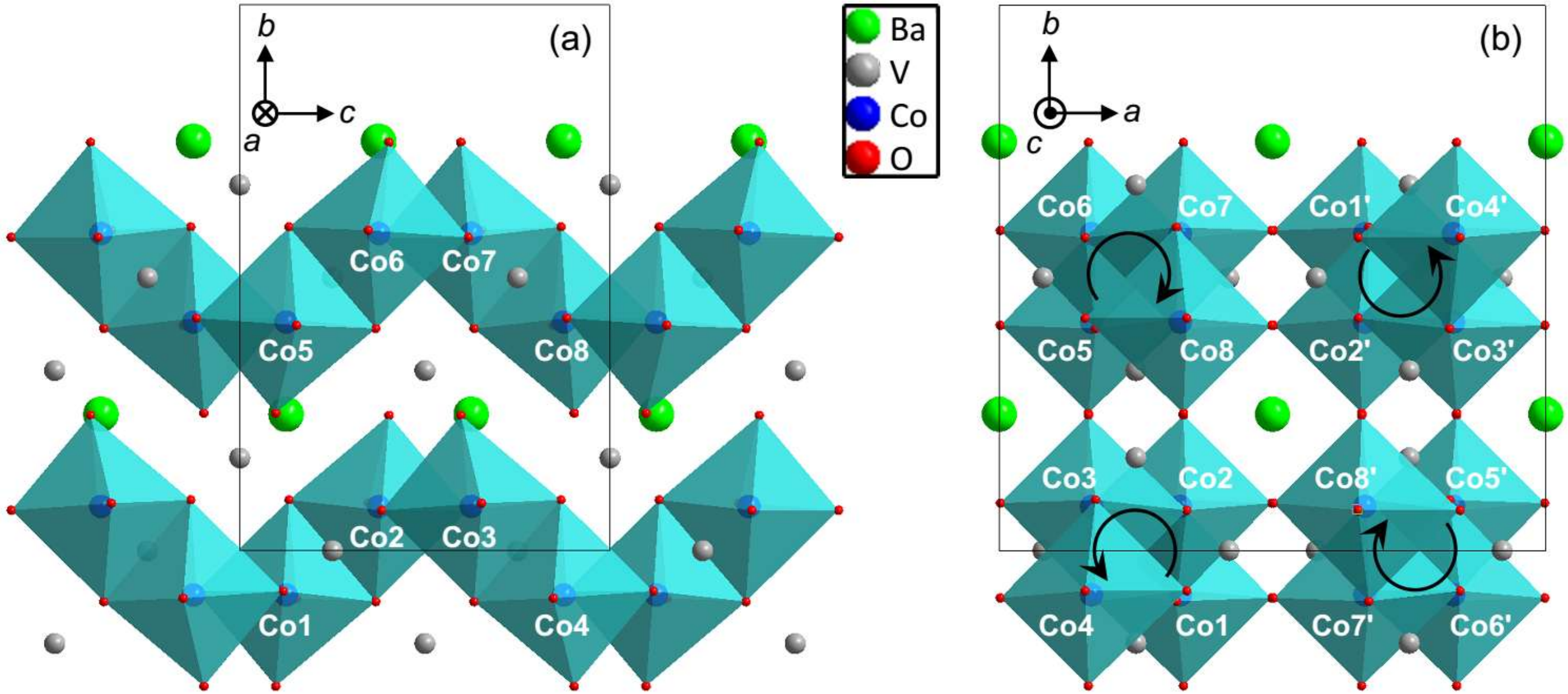
Field-induced magnetic behavior in quasi-1D Ising-like antiferromagnet $BaCo_2V_2O_8$

Screw chains of effective spin 1/2 along the c-axis

space group: $I4_1/acd$

$a = 12.44$ Å
$c = 8.42$ Å

AF ordering below $T_N \sim 5.6$ K



Refinement of the nuclear structure at 1.8 K
(~620 nuclear reflections collected on D23)

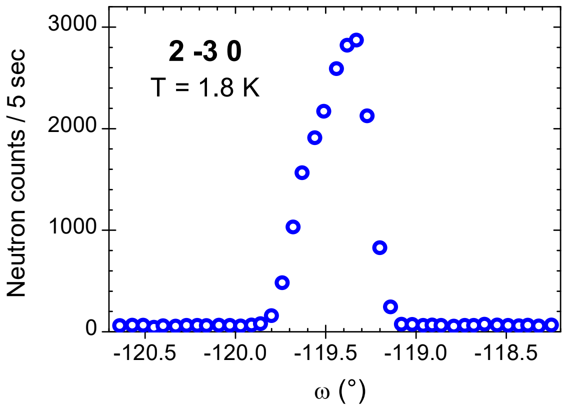
Atom	Wyckoff site	x	y	z	B_{iso} (Å^2)
Ba	8 a	0	0.25	0.375	0.041(21)
V	16 e	0.080 00	0	0.25	0.200
Co	16 f	0.168 97(5)	0.418 97(5)	0.125	0.398(28)
O1	32 g	0.158 68(3)	0.075 01(3)	0.381 71(14)	0.301(10)
O2	32 g	0.498 45(2)	0.087 29(3)	0.348 72(12)	0.247(11)

E. Canévet *et al.*, PRB **87**, 054408 (2013)

Refinement of the magnetic structure at 1.8 K

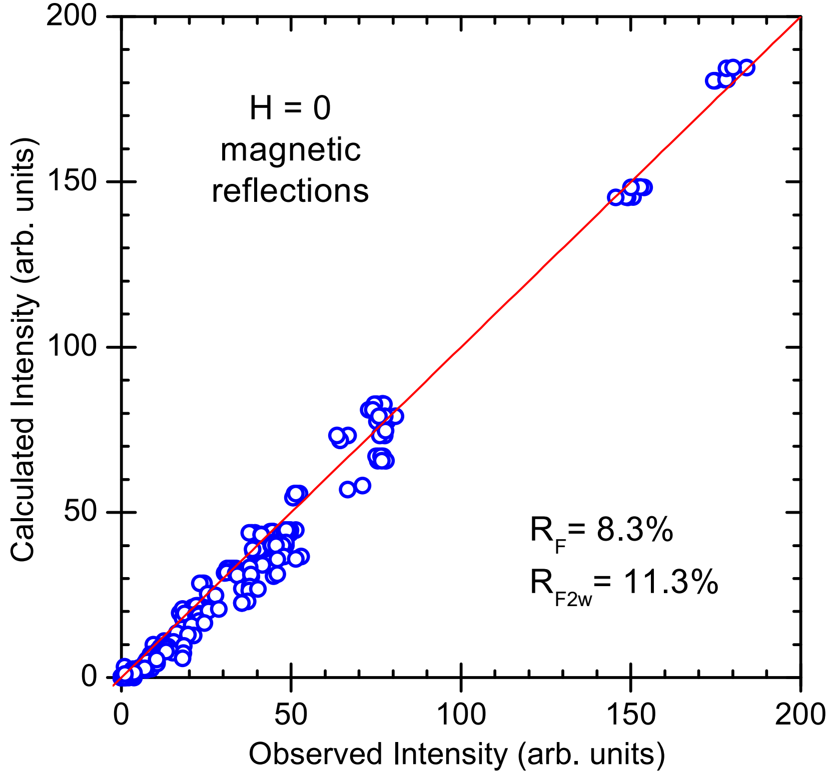
(~300 magnetic reflections collected on D23)

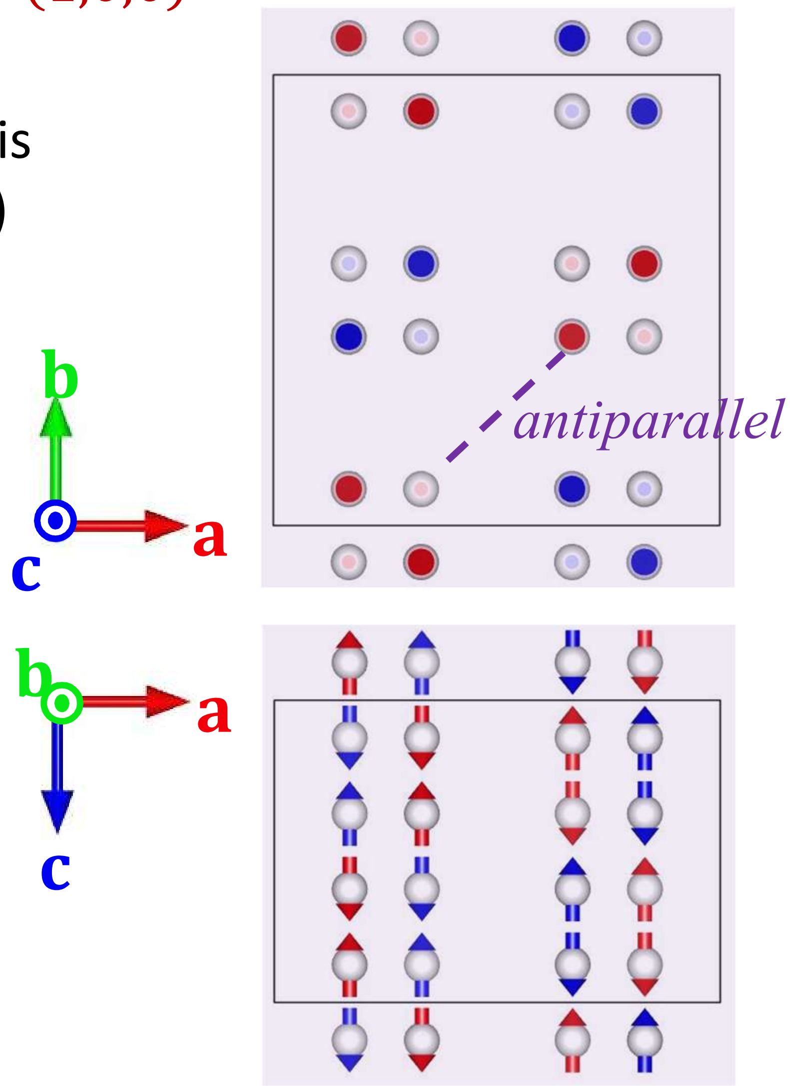
$\vec{k}_{AF} = (1,0,0)$



AF phase with $\vec{m}$ ∥ Ising c axis stabilized by J' (diagonal: AF)

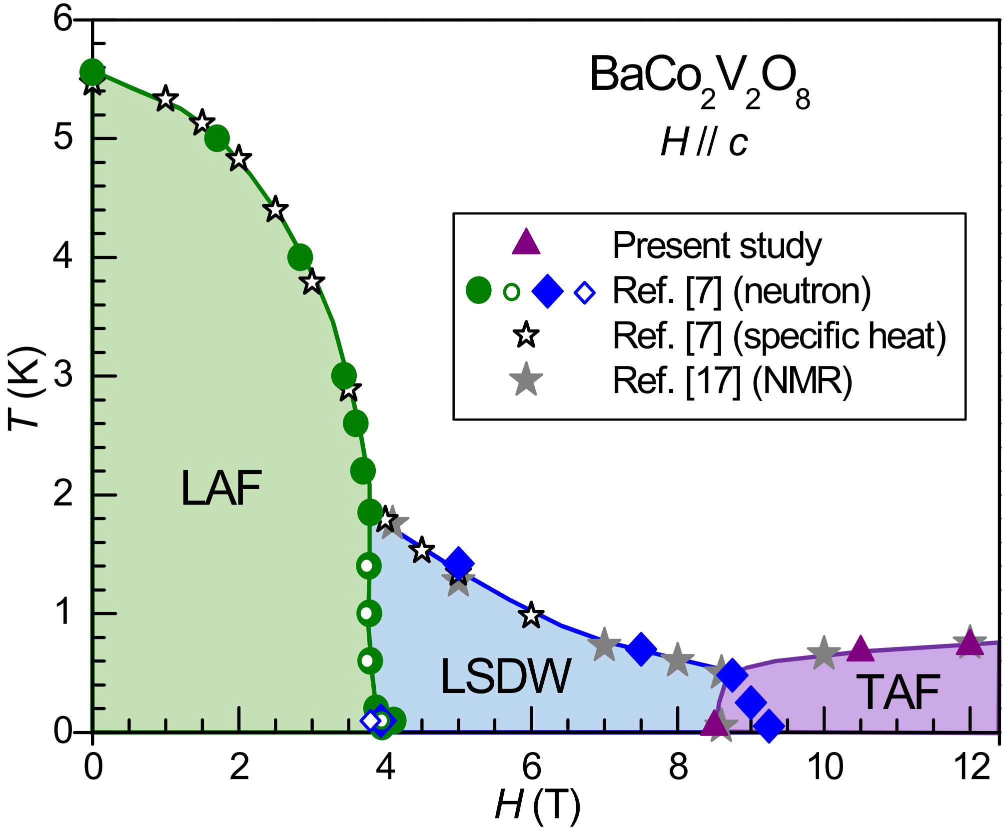
$m_c^{AF} = 2.267(3)\ \mu_B/\mathrm{Co}^{2+}$

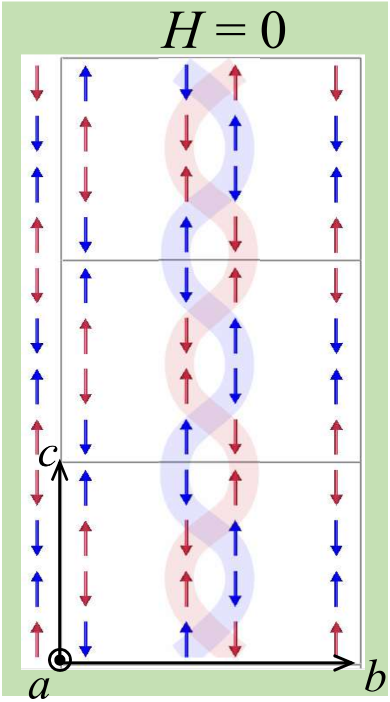




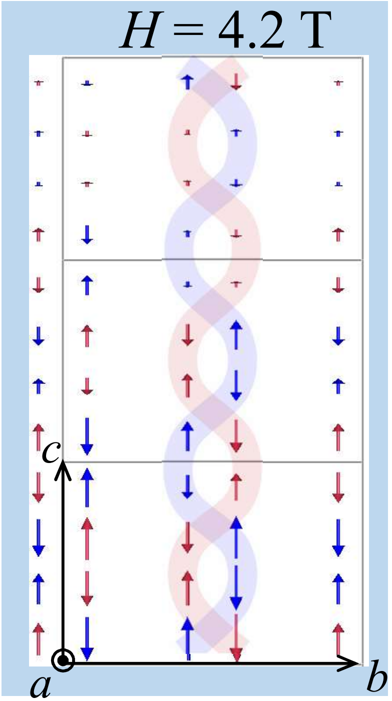
E. Canévet *et al.*, PRB **87**, 054408 (2013)

Refinement of the various magnetic structures upon *H*

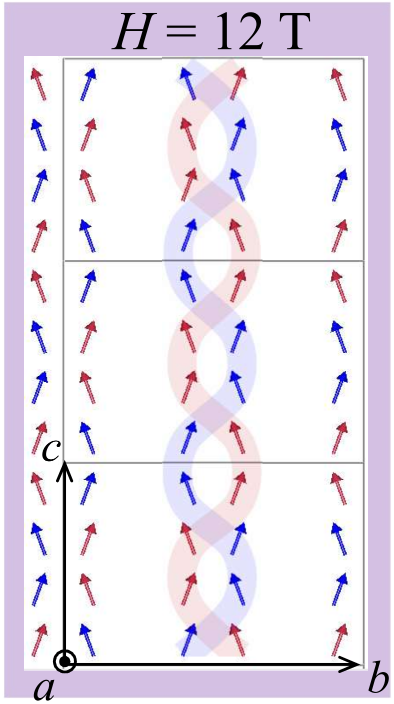




$\vec{k}_{AF} = (1,0,0)$



$\vec{k}_{LSDW} = (1,0,\delta)$



$\vec{k}_{AF} = (1,0,0)$
$\vec{k}_{FM} = (0,0,0)$

LAF: Longitudinal AF ($\vec{m}_{AF} \parallel \vec{c}$)

LSDW: Longitudinal Spin Density Wave ($\vec{m}_{IC} \parallel \vec{c}$)

TAF: Transverse AF ($\vec{m}_{AF} \parallel \vec{a}$)

E. Canévet *et al.*, PRB **87**, 054408 (2013)
B. Grenier *et al.*, PRB **92**, 134416 (2015)

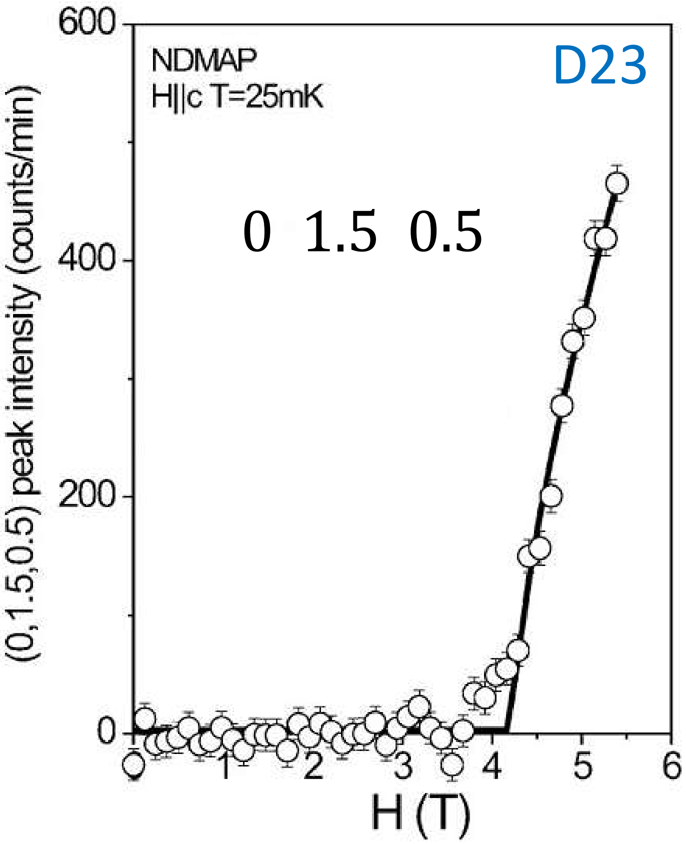
Neutron magnetic structure refinement from single-crystal diffraction:

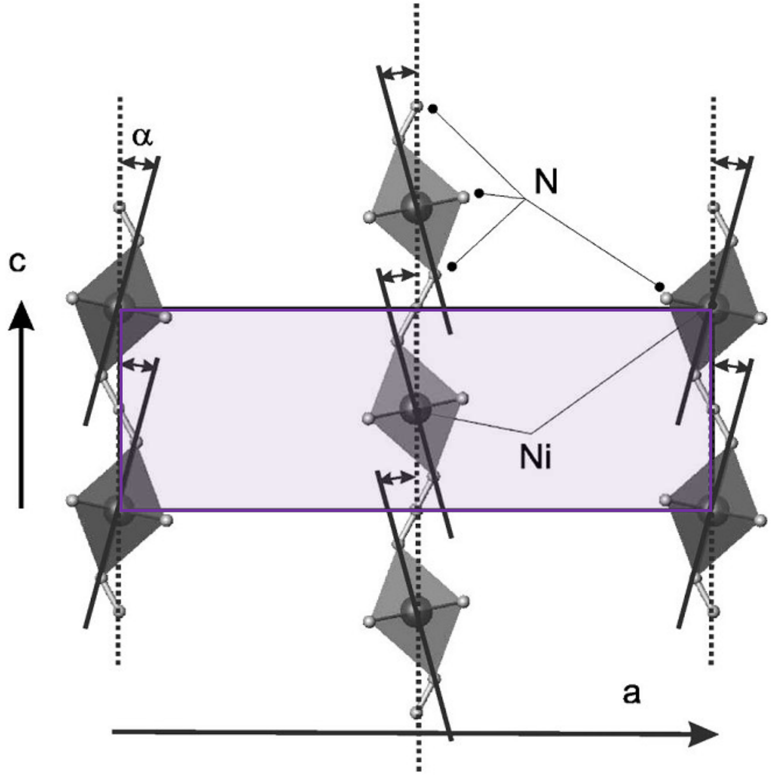
deuterated NDMAP $Ni(C_5D_{14}N_2)_2N_3(PF_6)$

space group $Pnmn$

Ni^{2+}: $S = 1$ chains ∥ c

2 Ni atoms / unit cell at $(0,0,0)$ and $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$





Field-induced AF ordering at $T < 800$ mK

Magnetic structure in the AF phase ?

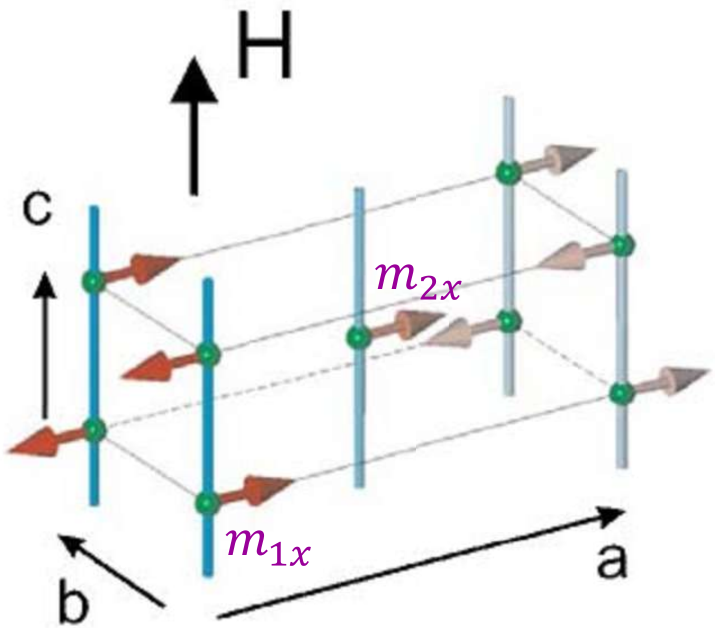
A. Zheludev *et al.*, PRB **69**, 054414 (2004)

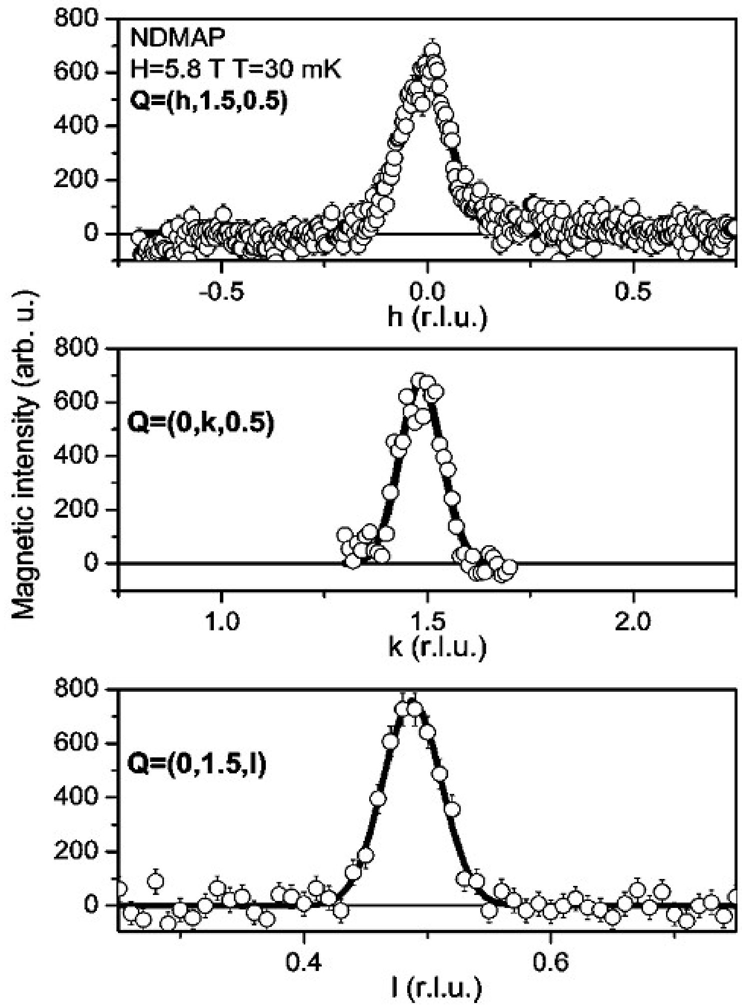
0 1.5 0.5 = magnetic reflection

- $\vec{k} = \left(0, \frac{1}{2}, \frac{1}{2}\right)$

Macroscopic measurements: $\vec{m} \parallel \vec{a}$

- Magnetic moments on the corners ?
- Magnetic moment on the center ?





Q-scans along h, k, and l

→ width: resolution limited

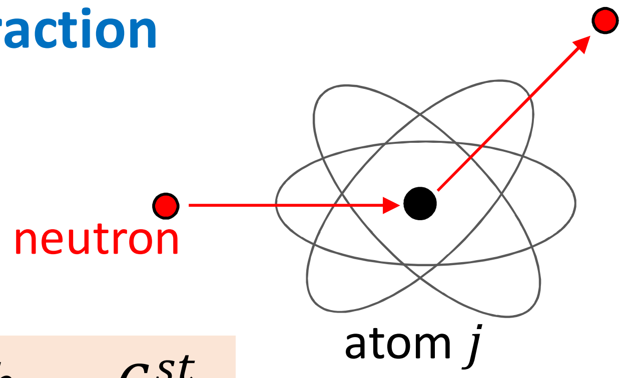
→ **true 3D LRO**

Refinement: $m_{1x} = m_{2x} = 0.9\ \mu_B/\text{Ni}^{2+}$

A. Zheludev *et al.*, PRB **69**, 054414 (2004)

To go further… Polarized neutrons – *Nuclear vs Magnetic scattering*

Nuclear interaction



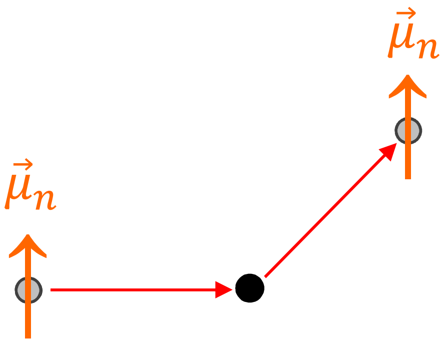
$$a_{Nj}(Q) = b_j = C^{st}$$

Nuclear scattering process:

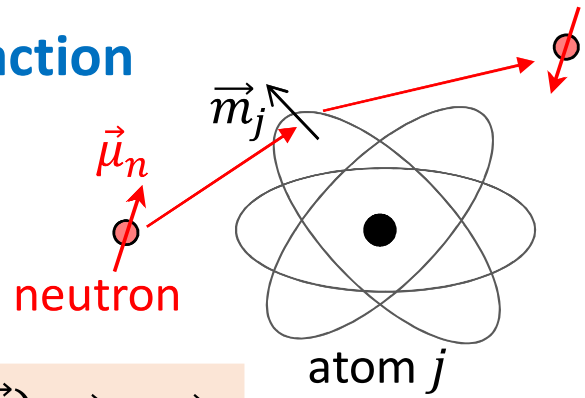
- isotropic

- non spin flip

NSF



Magnetic interaction



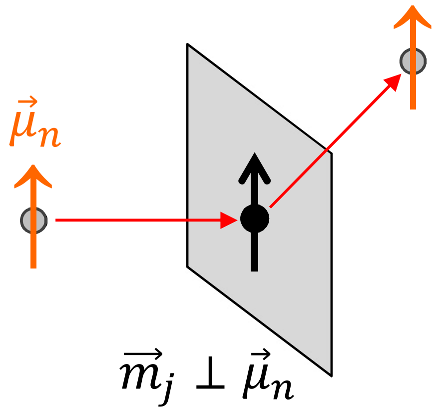
$$a_{Mj}(\vec{Q}) = p f_j(\vec{Q})\, \vec{m}_{j\perp}.\vec{\sigma}$$

Magnetic scattering process:

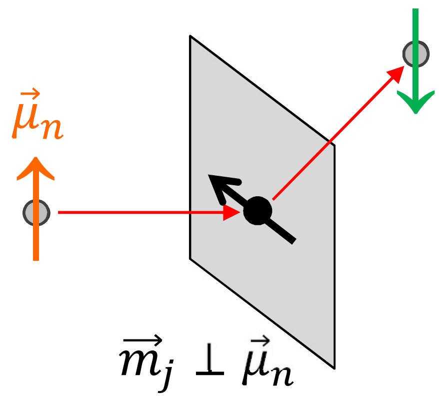
- anisotropic → neutrons see only $\vec{m}_{j\perp}$
  = projection of $\vec{m}_j$ on the plane ⊥ $\vec{Q}$

- non spin flip if $\vec{\mu}_n \parallel \vec{m}_j$; spin flip if $\vec{\mu}_n \perp \vec{m}_j$

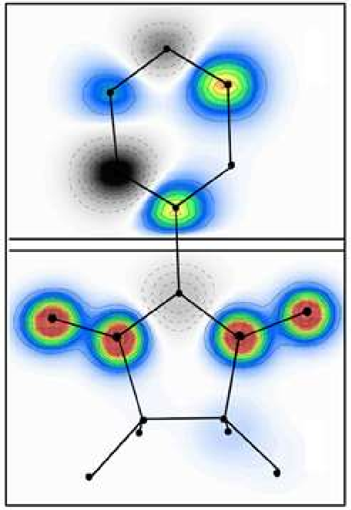
NSF



SF

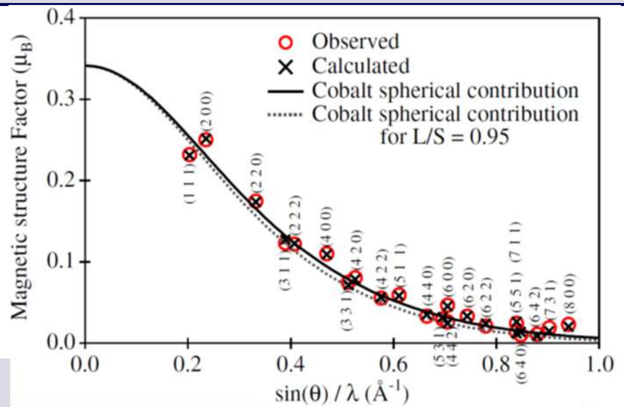


To go further… Polarized neutrons: *What for?*



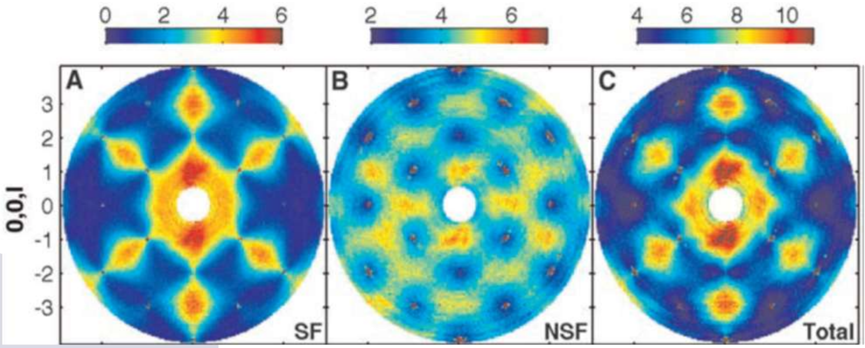
A. Zheludev *et al.*, J. Magn. Magn. Mater. **140**, 1441 (1995)

- Determine magnetization distributions
- Measure magnetic form factors



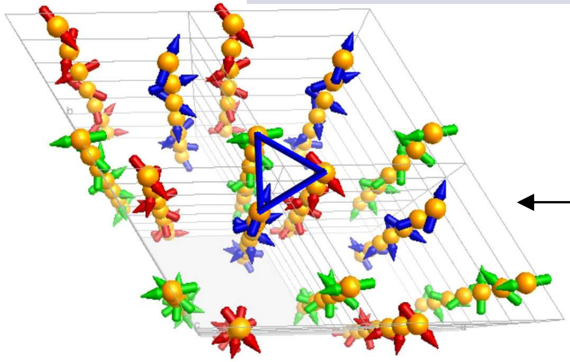
N. Kernavanois *et al.*, J. Phys.: Condens. Matter **15**, 3433 (2003)

- Separate magnetic from nuclear contributions
- Separate coherent from incoherent nuclear contributions
- Separate magnetic components along y and z (in the plane $\perp \vec{Q}$)
- Evidence nuclear-magnetic interference terms



T. Fennell *et al.*, Science **326**, 415 (2009)

- Determine complex magnetic structures
- Measure very small magnetic signals



K. Marty *et al.*, Phys. Rev. Lett. **101**, 247201 (2008)

- Probe magnetic domains
- Probe chirality in magnetic structures
- …

Merci et bon TP !

APPENDIX

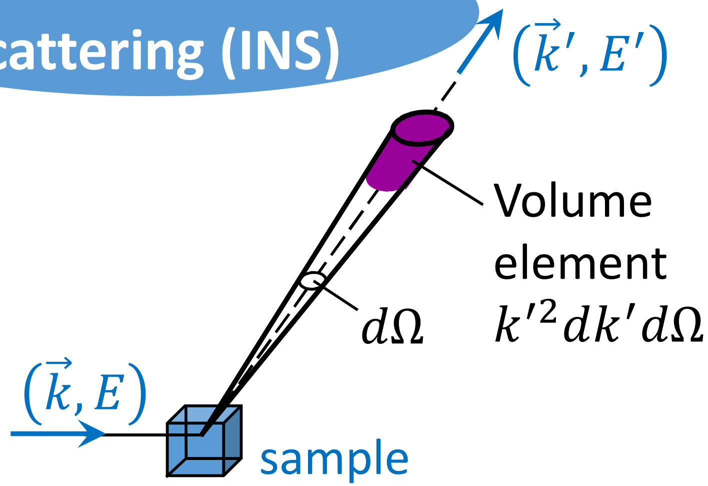
2. Neutron interactions with matter: *scattering*

Inelastic neutron scattering (INS)

- **Partial differential cross section:**

Number of neutrons scattered per second in solid angle $d\Omega$ around the direction $\vec{k}'$ with an energy comprised between E' and dE', normalized to the incident neutron flux ϕ

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{1}{\phi}\,\frac{\text{number of neutrons scattered in } d\Omega \text{ and } dE' \text{ per second}}{d\Omega dE'}$$



→ see lecture by Sylvain Petit

- If the final energy E' is not analyzed → **Differential cross section:**

Diffraction

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

$$\frac{d\sigma}{d\Omega} = \int_0^{+\infty} \frac{d^2\sigma}{d\Omega dE'} dE' = \frac{1}{\phi}\,\frac{\text{number of neutrons scattered in } d\Omega \text{ per second}}{d\Omega}$$

2. Neutron interactions with matter: *scattering*

** Supplemental for slide 19*

In practice…

In standard diffraction experiments: $\frac{d\sigma}{d\Omega}$ is measured instead of $\frac{d^2\sigma}{d\Omega dE'}$ with $E' = E$,

since elastic intensity $\gg$ inelastic intensity
(neutrons scattered with $E' \neq E$ are also detected $\rightarrow$ background)

- If, in addition, neutrons are detected in all directions $\rightarrow$ **Total cross section:**

$$\sigma = \int_{\text{al directions}} \frac{d\sigma}{d\Omega} d\Omega = \frac{\text{total number of scattered neutrons per second}}{\phi}$$

σ: [surface] in barns (1 barn $= 10^{-24}$ cm^2)

Let's come back to the **Partial differential cross section**…

Fermi golden rule:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\lambda s\to\lambda' s'} = \frac{k'}{k}\left(\frac{m}{2\pi\hbar^2}\right)^2 \left|\langle\lambda'\vec{k}'s'|V(\vec{r})|\lambda\vec{k}s\rangle\right|^2 \delta(E_{\lambda'}+E'-E_\lambda-E)$$

	initial	final
state of matter:	λ	λ'
neutron wave vector:	$\vec{k}$	$\vec{k}'$
neutron spin:	s	s'

→ *to be considered for polarized neutrons only*

Neutron – matter interaction potential

Energy conservation

The scattered amplitude a is defined by:

$$\frac{m}{2\pi\hbar^2}\langle\vec{k}'s'|V(\vec{r})|\vec{k}s\rangle = \langle s'|a(\vec{Q})|s\rangle$$

Fourier Transform (F.T.) of $V(\vec{r})$

where $\vec{Q}=\vec{k}-\vec{k}'$ is the scattering vector

2. Neutron interactions with matter: *scattering*

** Supplemental for slide 19*

$$\Rightarrow \frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k}\frac{1}{2\pi\hbar}\sum_{jj'} a_j a_{j'}^{\star} \int_{-\infty}^{+\infty} \left\langle e^{-i\vec{Q}.\vec{R}_j(0)} e^{i\vec{Q}.\vec{R}_{j'}(t)} \right\rangle e^{-i\omega t}\, dt$$

= **Double Fourier Transform** on space and time of the **correlation function** between nuclei/spins at $(\vec{0}, 0)$ and $(\vec{r}, t)$

Measured quantity

as a function of $\begin{cases} \vec{Q} = \vec{k} - \vec{k}' & \text{the scattering vector} \\ \hbar\omega = E - E' & \text{the energy transfer} \end{cases}$

with $\langle\quad\rangle$: statistical average on the initial sample states λ associated to probabilities p_λ

⚠ For elastic scattering (=diffraction) experiments:

- $\vec{Q} = \vec{k}' - \vec{k}$
- $t \rightarrow +\infty$ and thus $\hbar\omega = 0$

$\left.\begin{matrix}\text{Nuclear}\\ \text{Magnetic}\end{matrix}\right\}$ interaction → expressions of $\begin{cases} V_N(\vec{r}) \\ V_M(\vec{r}) \end{cases}$ and thus of $\begin{cases} a_N(\vec{Q}) \\ a_M(\vec{Q}) \end{cases}$?

** Supplemental for slide 23*

Coherent and incoherent scattering

Coherent scattering = Interaction between atomic pairs ($\sum_{jj'}$) constructed from the **average** $\bar{b}^2$

Average potential → interferences → **pair-correlation functions**

Incoherent scattering = Interaction of each atom with itself ($\sum_{j}$) constructed from the **deviations to the average** $\overline{\Delta b^2} = \overline{b^2} - \bar{b}^2$

Random distribution of b_j → no interferences → **self-correlation functions**

The fly correloscope (by R. Scherm)
"What can neutrons learn about flies in a box?"

1 fly in the box: Where is the fly after a time t?
→ **self-correlation** function

several flies in the box: Where is any fly relative to another after a time t?
→ **pair-correlation** function