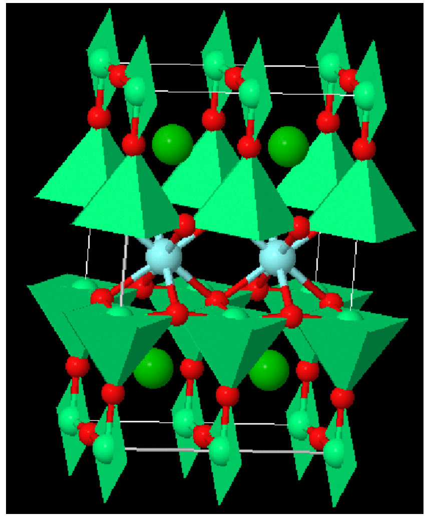
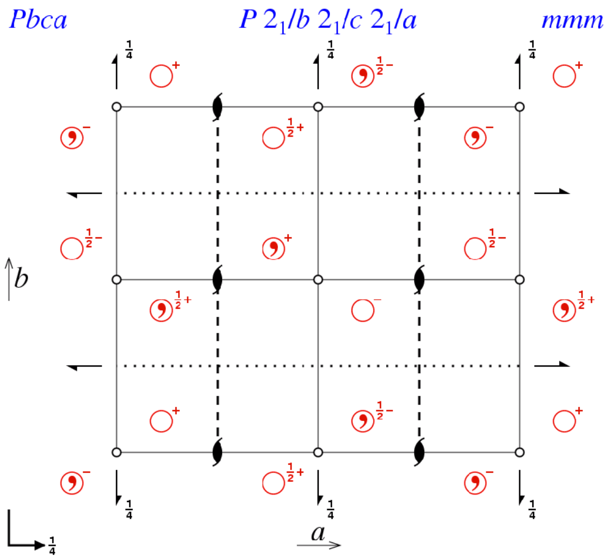
Ecole du GDR MICO
(Matériaux et Interactions en COmpétition)

Mai 2014



Cristallographie et techniques expérimentales associées



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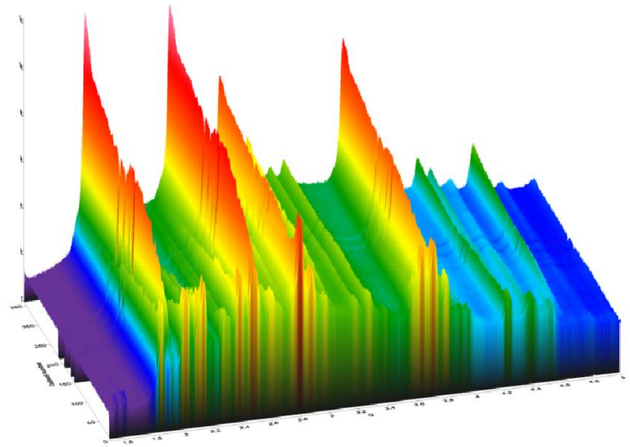

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NEUTRONS FOR SCIENCE

Outline

part I: CRYSTALLOGRAPHY IN DIRECT SPACE

Outline

part II: DIFFRACTION - CRYSTALLOGRAPHY IN RECIPROCAL SPACE

II.1. The reciprocal space

Definition
Examples
First Brillouin zone
Properties

II.2. X-ray and neutron diffraction by a crystal

Diffraction condition
Diffraction by an atom: scattered amplitude
Diffraction by a crystal: structure factor
Symmetry and extinction rules
Beyond basic crystallography: aperiodic crystals and magnetic structures

II.4. Experiments

How to solve a structure
Technique 1: powder diffraction
Technique 2: single-crystal Laue diffraction
Technique 3: single-crystal (four circle / normal beam) diffraction

I.4. Beyond basic crystallography: *Aperiodic crystals*

Incommensurate modulated structures

Ex: displacive modulation along one direction: $\vec{r}(\vec{n},j) = \vec{n} + \vec{r}_j + \vec{U}_j \sin\left[2\pi\vec{q}.(\vec{n}+\vec{r}_j)+\varphi_j\right]$

Average structure → 3D lattice
Deviations from the lattice-periodic structure → modulation waves

⇒ **(3+*d*)-dimensional superspace group**

Same approach based on higher-dimension crystallography for:

Incommensurate composite structures

Subsystems with different incommensurate lattices

Quasicrystals

No translation symmetry
Presence of non-crystallographic symmetry elements: 5, 8 or 12-fold axes

I.4. Beyond basic crystallography: *Aperiodic crystals*

- The six (3+1)-dimensional superspace groups derived from Pnma (ITC, Volume C)

9. BASIC STRUCTURAL FEATURES

Table 9.8.3.5. (3 + 1)-*Dimensional superspace groups (cont.)*

No.	Basic space group	Point group K_s	Bravais class No.	Group symbol
62.1	*Pnma*	$(mmm, 11\bar{1})$	9	$Pnma(00\gamma)$
62.2			9	$Pnma(00\gamma)0s0$
62.3			9	$Pbnm(00\gamma)$
62.4			9	$Pbnm(00\gamma)s00$
62.5			9	$Pmcn(00\gamma)$
62.6			9	$Pmcn(00\gamma)s00$

- The two icosahedral point groups (quasicrystals):

$$\begin{cases} 235 & \text{(order 60)} \\ \frac{2}{m}\bar{3}\bar{5} & \text{(order 120)} \end{cases}$$

II.2. Diffraction: *Beyond basic crystallography*

Diffraction by an aperiodic crystal

$$\vec{H} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* + m_1\vec{q}_1 + m_2\vec{q}_2 ... + m_d\vec{q}_d$$

Average structure → main reflections: $\forall i,\ m_i = 0$

Modulation → satellite reflections of weaker intensity (intensity ↓ when m_i↑): $\forall i,\ m_i \neq 0$

Reflection conditions for the six (3+1)-dimensional superspace groups derived from *Pnma* *(ITC, Volume C)*

9. BASIC STRUCTURAL FEATURES

Table 9.8.3.5. (3 + 1)-*Dimensional superspace groups (cont.)*

No.	Basic space group	Point group K_s	Bravais class No.	Group symbol	Special reflection conditions
62.1	*Pnma*	$(mmm, 11\bar{1})$	9	$Pnma(00\gamma)$	$0klm$: $k+l=2n$; $hk00$: $h=2n$
62.2			9	$Pnma(00\gamma)0s0$	$0klm$: $k+l=2n$; $h0lm$: $m=2n$; $hk00$: $h=2n$
62.3			9	$Pbnm(00\gamma)$	$0klm$: $k=2n$; $h0lm$: $h+l=2n$
62.4			9	$Pbnm(00\gamma)s00$	$0klm$: $k+m=2n$; $h0lm$: $h+l=2n$
62.5			9	$Pmcn(00\gamma)$	$h0lm$: $l=2n$; $hk00$: $h+k=2n$
62.6			9	$Pmcn(00\gamma)s00$	$0klm$: $m=2n$; $h0lm$: $l=2n$; $hk00$: $h+k=2n$

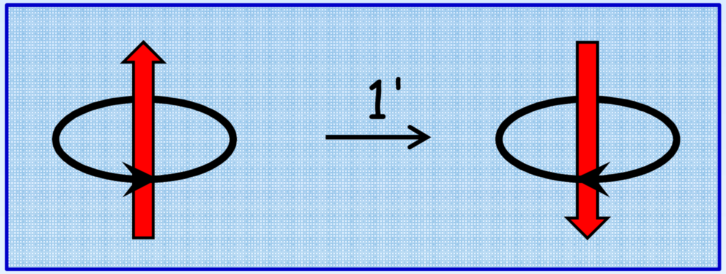
I.4. Beyond basic crystallography: *Magnetic structures*

Invariance properties of magnetic structures

Consider the spin, in addition to the atomic position

Spin = axial vector (magnetic dipole), supposed to be generated by an electrical current

- Additional symmetry operation:
time reversal = spin reversal = 1'



⇓

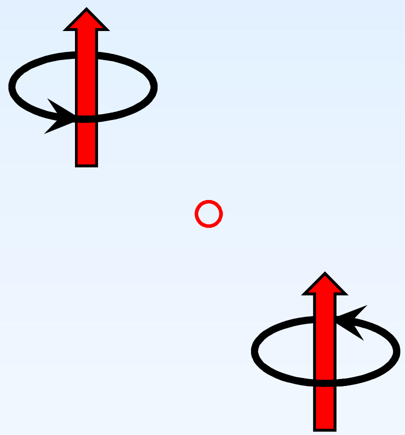
Primed operators
(= anti-symmetry operators):
operator n or $\bar{n}$ combined with 1'

e.g.: $m' = m \times 1'$
$4' = 4 \times 1'$

- Rotation: same effect as for polar vector (electrical dipole)

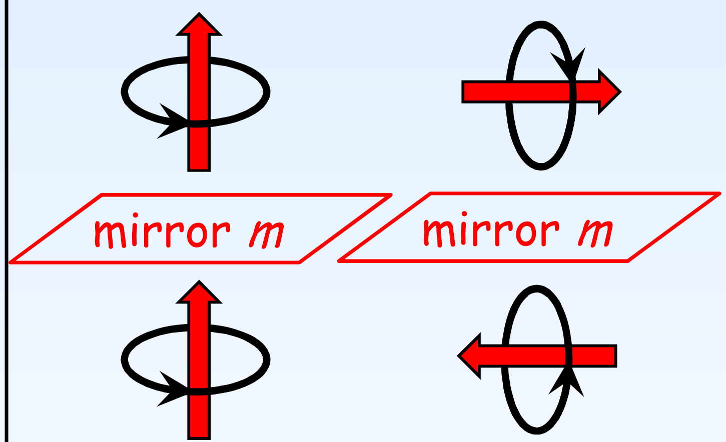
But opposite effect for rotoinversion

Inversion $\bar{1}$



$\bar{1}$: $\vec{M} \rightarrow \vec{M}$

Mirror m



$\vec{M} \perp m$ plane: $\vec{M} \rightarrow \vec{M}$

$\vec{M} // m$ plane: $\vec{M} \rightarrow -\vec{M}$

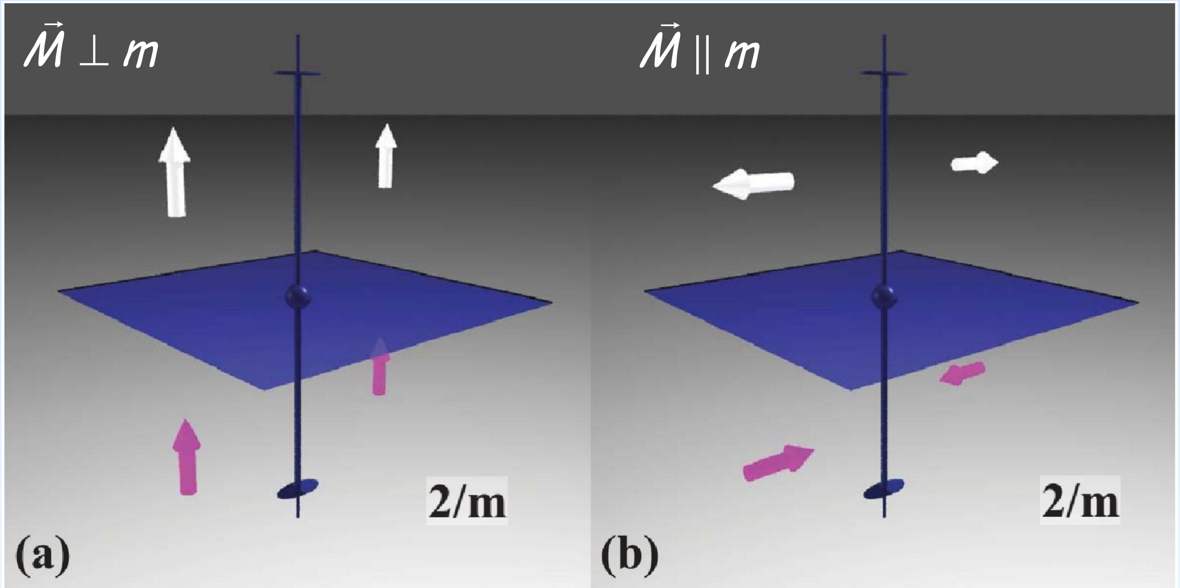
I.4. Beyond basic crystallography: *Magnetic point groups*

Ex: Magnetic point groups M derived from crystallographic point group G = **2/*m***

1- **Colorless magnetic** (trivial) **PG**:

$M = G$

$2/m$



⇓

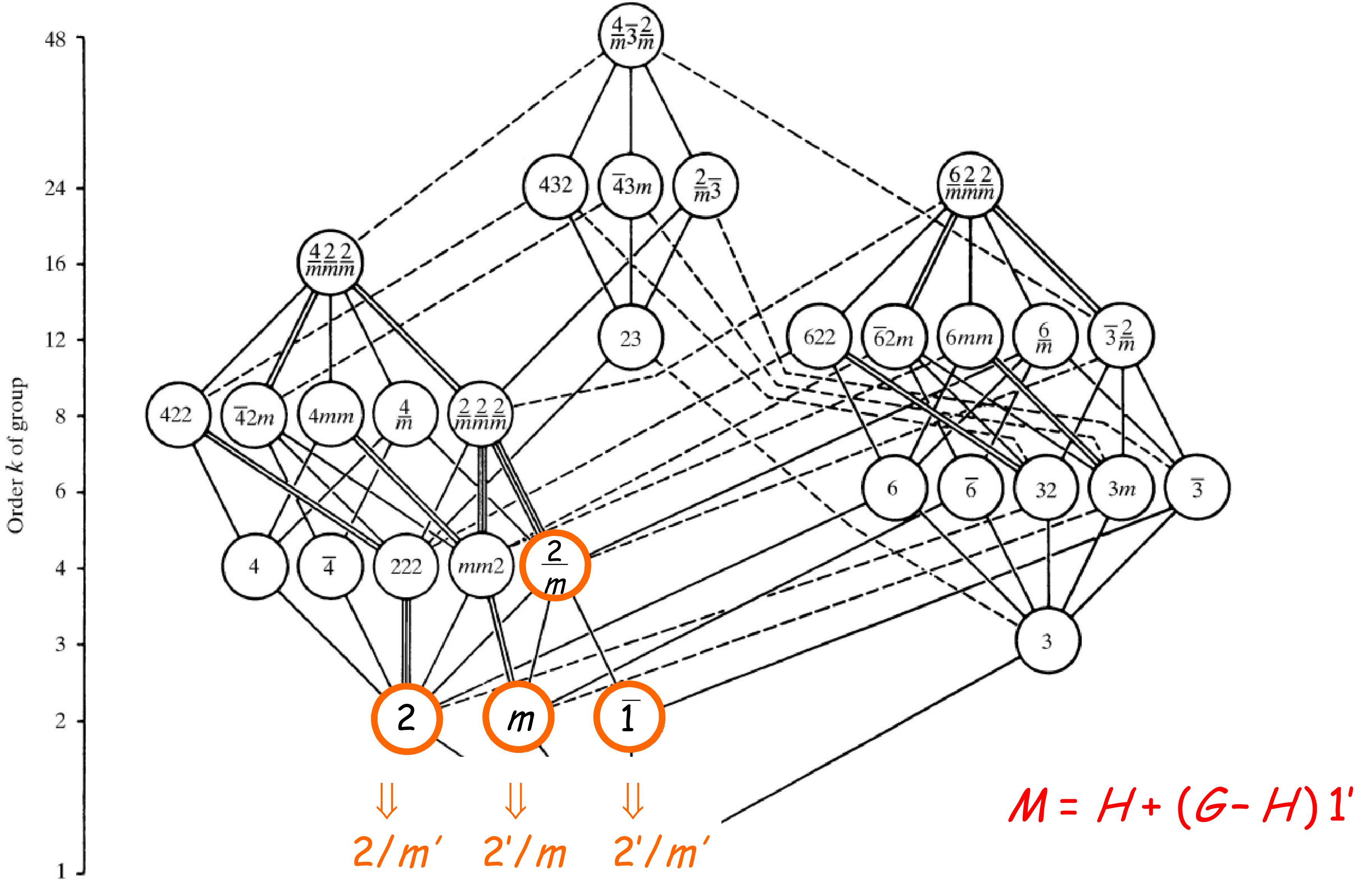
$2/m$ = admissible magnetic point group
with admissible spin direction // 2-axis

→ conserves a spin located at the origin
→ FM state possible

2- **Black-white PG**:

$M = H + (G - H)1'$

I.4. Beyond basic crystallography: *Magnetic point groups*



$M = H + (G - H)1'$

Fig. 10.1.3.2. Maximal subgroups and minimal supergroups of the three-dimensional crystallographic point groups. Solid lines indicate maximal normal subgroups; double or triple solid lines mean that there are two or three maximal normal subgroups with the same symbol. Dashed lines refer to sets of maximal conjugate subgroups. The group orders are given on the left. Full Hermann–Mauguin symbols are used.

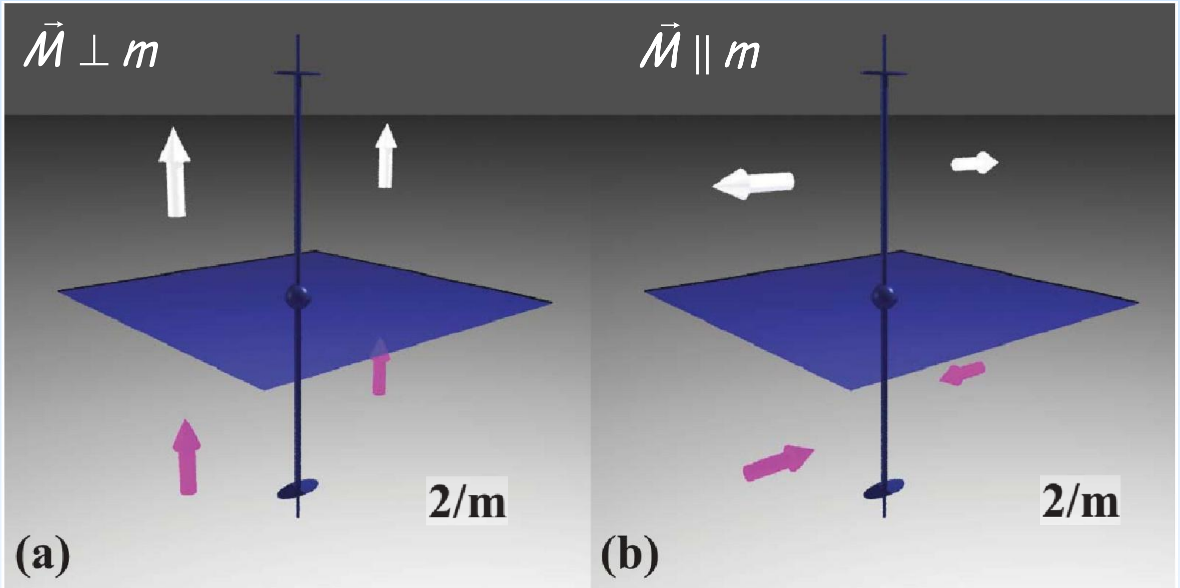
I.4. Beyond basic crystallography: *Magnetic point groups*

Ex: Magnetic point groups M derived from crystallographic point group G = **2/m**

1- **Colorless magnetic** (trivial) **PG**:

$M = G$

$2/m$



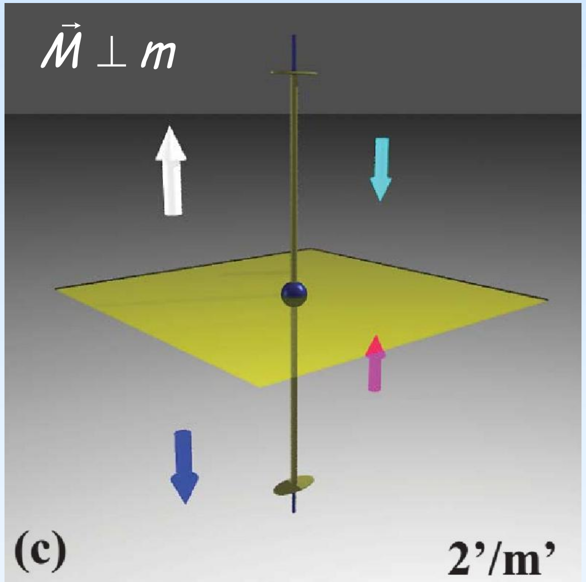
⇓

$2/m$ = admissible magnetic point group
with admissible spin direction // 2-axis

→ conserves a spin located at the origin
→ FM state possible

2- **Black-white PG**:

$M = H + (G - H)\,1'$



...

$2/m'$
$2'/m$
$2'/m'$

$2'/m'$ = admissible magnetic PG
with admissible spin direction ⊥ 2-axis

3- **Gray** (paramagnetic) **PG**: $2/m1'$

$M = G + G1'$

I.4. Beyond basic crystallography: *Magnetic point groups*

The 122 magnetic point groups

32 colorless magnetic point groups (among which 13 admissible)
58 black-white magnetic point groups (among which 18 admissible)
32 gray point groups (among which 0 admissible)

The 31 admissible magnetic point groups

Admissible magnetic point groups					Admissible spin (magnetic moment) direction
1	$\bar{1}$				Any direction
$2'$	$2'/m'$	$m'm2'$			Perpendicular to the 2-fold axis (& to m for $m'm2'$)
m'					Any direction within the plane
m					Perpendicular to the plane
$m'm'm$					Perpendicular to the unprimed plane
$2'2'2$					Along the unprimed axis
2	$2/m$	$m'm'2$			Along the 2-fold axis
4	$\bar{4}$	$4/m$	$42'2'$		Along the four-fold axis
$4m'm'$	$\bar{4}2m'$		$4/mm'm'$		Along the four-fold axis
3	$\bar{3}$	$32'$	$3m'$	$\bar{3}m'$	Along the three-fold axis
6	$\bar{6}$	$6/m$	$62'2'$		Along the six-fold axis
$6m'm'$	$\bar{6}m'2'$		$6/mm'm'$		Along the six-fold axis

I.4. Beyond basic crystallography: *Magnetic space groups*

The 1651 Shubnikov magnetic space groups

230 **colorless** trivial magnetic SG of the form $M = G$

1191 **black-white** magnetic SG of the form $M = H + (G - H)\,1'$

- 674 in which the subgroup H has the same translation as G (**first kind: BW1**)
- 517 in which the subgroup H contains anti-translations (**second kind: BW2**)

230 **gray** magnetic space groups of the form $M = G + G1'$

Example:

bilbao crystallographic server

[The crystallographic site at the Condensed Matter Physics Dept. of the University of the Basque Countr

[Space Groups] [Layer Groups] [Rod Groups] [Frieze Groups] [Wyckoff Sets]

http://www.cryst.ehu.es

The magnetic space groups derived from the Fedorov space group: Ima2 (#46)

Listed with respect to the BNS setting: Belov-Neronova-Smirnova

- #46.241 Ima2 [OG: Ima2 #46.1.338] *Type I (Fedorov)*
- #46.242 Ima21' [OG: Ima21' #46.2.339] *Type II (grey group)*
- #46.243 Im'a2' [OG: Im'a2' #46.3.340] *Type III (translationgleiche)*
- #46.244 Ima'2' [OG: Ima'2' #46.4.341] *Type III (translationgleiche)*
- #46.245 Im'a'2 [OG: Im'a'2 #46.5.342] *Type III (translationgleiche)*
- #46.246 $I_c$ma2 [OG: C_Im'm2' #35.12.247] *Type IV (klassengleiche)*
- #46.247 $I_a$ma2 [OG: A_Im'm'2 #38.13.277] *Type IV (klassengleiche)*
- #46.248 $I_b$ma2 [OG: $A_I$bm2 #39.8.285] *Type IV (klassengleiche)*

Listed with respect to the OG setting: Opechowski-Guccione

- #46.1.338 Ima2 [BNS: Ima2 #46.241] *Type I (Fedorov)*
- #46.2.339 Ima21' [BNS: Ima21' #46.242] *Type II (grey group)*
- #46.3.340 Im'a2' [BNS: Im'a2' #46.243] *Type III (translationgleiche)*
- #46.4.341 Ima'2' [BNS: Ima'2' #46.244] *Type III (translationgleiche)*
- #46.5.342 Im'a'2 [BNS: Im'a'2 #46.245] *Type III (translationgleiche)*
- #46.6.343 $I_P$ma2 [BNS: $P_I$ma2 #28.98] *Type IV (klassengleiche)*
- #46.7.344 I_Pm'a2' [BNS: $P_I$na2_1 #33.155] *Type IV (klassengleiche)*
- #46.8.345 $I_P$ma'2' [BNS: $P_I$mc2_1 #26.77] *Type IV (klassengleiche)*
- #46.9.346 I_Pm'a'2 [BNS: $P_I$nc2 #30.122] *Type IV (klassengleiche)*

Nuclear neutron diffraction

Diffracted intensity

$$I_M(\vec{Q}) \propto \left| \vec{F}_N(\vec{Q}) \right|^2 \delta(\vec{Q} - \vec{\tau})$$

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

II.2. Diffraction: *Beyond basic crystallography*

Magnetic neutron diffraction

Diffracted intensity

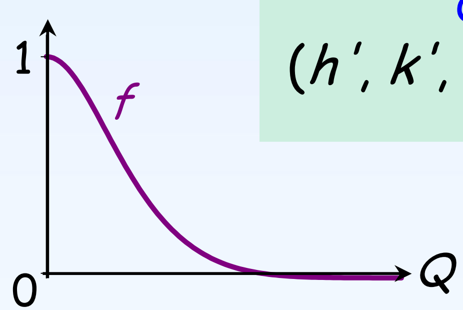
$$I_M(\vec{Q}) \propto \left| \vec{F}_{M\perp}(\vec{Q}) \right|^2 \delta(\vec{Q} - \vec{\tau} - \vec{k})$$

Magnetic structure factor $\vec{F}_M(\vec{Q})$
related to the magnetic motif
(arrangement and values of the
magnetic moments in the unit cell)
⇒ governs the amplitudes of diffraction

Dirac function $\delta(\vec{Q}-\vec{\tau}-\vec{k})$
related to the magnetic lattice
(periodicity of the magnetic structure)
⇒ governs the directions of diffraction

$$\vec{F}_M(\vec{Q}) = \sum_{j=1}^{N_{mag}} \underbrace{p f_j(\vec{Q})\, \vec{M}_j^k}_{\equiv\, b_j} e^{2i\pi \vec{Q}.\vec{r}_j}$$

diffraction peaks $h'k'l'$
(h', k', l' are not necessarily integers)



$f_j(\vec{Q})$ = Magnetic form factor

$\vec{M}_j^k$ = Fourier component of the magnetic moment

II.2. Diffraction: *Beyond basic crystallography*

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

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

$(\vec{F}_M // \vec{M})$

$\Rightarrow$ the neutrons are sensitive to the projection of the magnetic moment in the plane $\perp$ to the scattering vector

if $\vec{M} // \vec{Q}$ $\Rightarrow$ $F_{M\perp} = 0$

if $\vec{M} \perp \vec{Q}$ $\Rightarrow$ $F_{M\perp} = F_M$ (*i.e.* maximum)

Propagation vector $\vec{k}$

(analogous to the wave vector of a plane wave)

It reflects:

1- the periodicity L of the magnetic structure ($k = 0$ if it is the same as the nuclear one, $k = 2\pi/L$ otherwise),

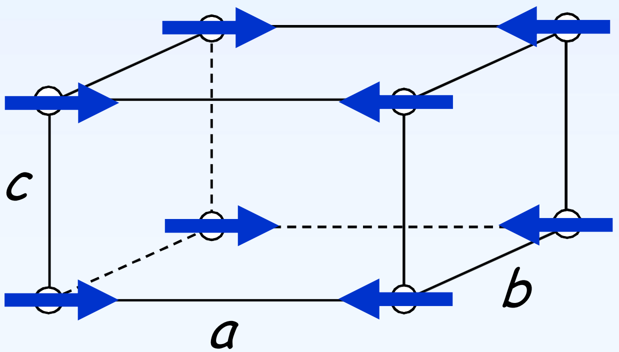
2- its direction of propagation.

Examples:

- All ferromagnets, some antiferromagnets:

  $\vec{k} = \vec{0}$ $\rightarrow$ Magnetic peaks at $\vec{Q} = \vec{\tau} = (h,k,l)$

- AF with periodicity doubled along 1, 2 or 3D:



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

$\rightarrow$ Magnetic peaks at

$\vec{Q} = \vec{\tau} + \vec{k} = \left(h+\frac{1}{2}, k, l\right)$

- Sine wave modulated structure along c (periodicity L):

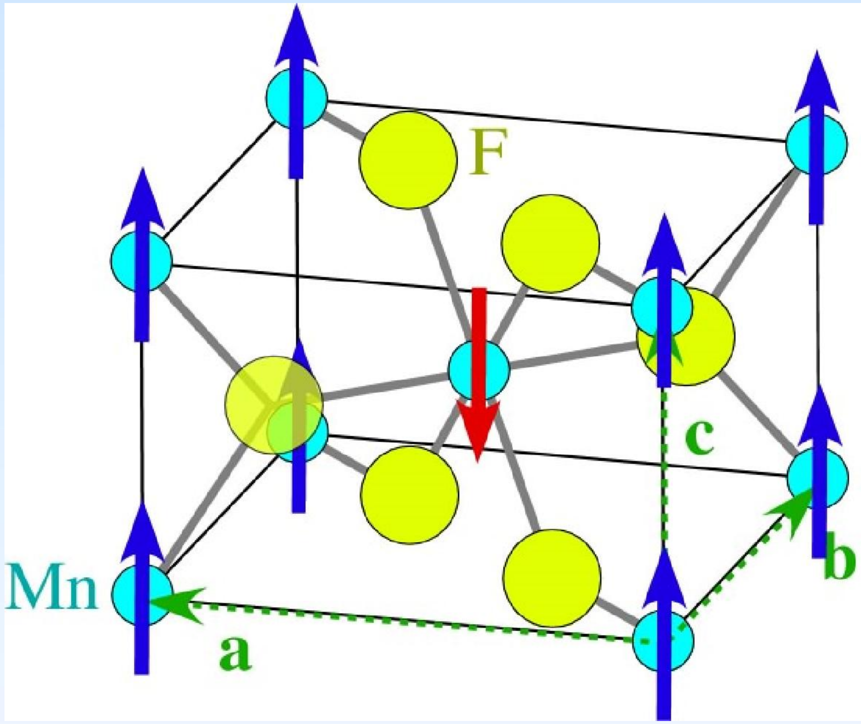
$\vec{k} = (0\ 0\ \frac{1}{L})$

$\rightarrow$ Magnetic peaks at

$\vec{Q} = \vec{\tau} \pm \vec{k} = \left(h, k, l \pm \frac{1}{L}\right)$

MnF_2: space group $P4_2/mnm$

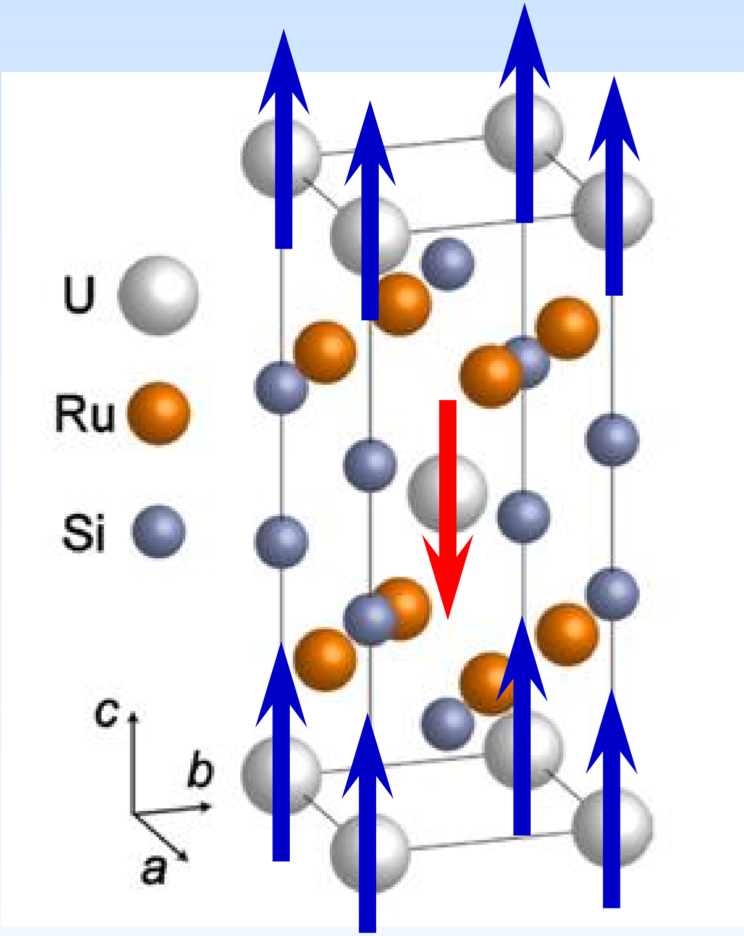
No extinction on *hkl*



Antiferromagnet with **k** = (0, 0, 0)

URu_2Si_2: space group $I4/mmm$

Reflection condition *hkl*: $h+k+l = 2n$



Antiferromagnet with **k** = (0, 0, 1)

$$\vec{F}_M\left(\vec{Q}\right) = pf_0(\vec{Q})\vec{M}_0\left[1 - e^{i\pi(h+k+l)}\right] \neq 0 \quad \text{if} \quad h+k+l = 2n+1$$