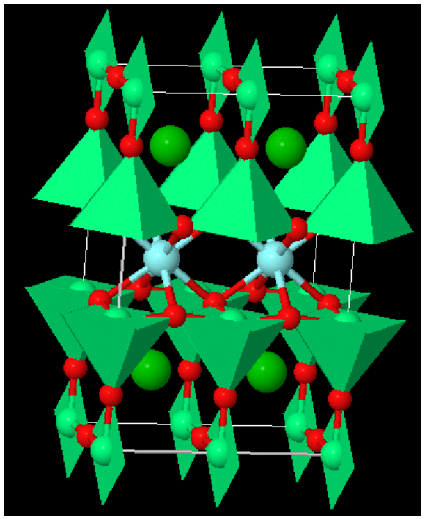
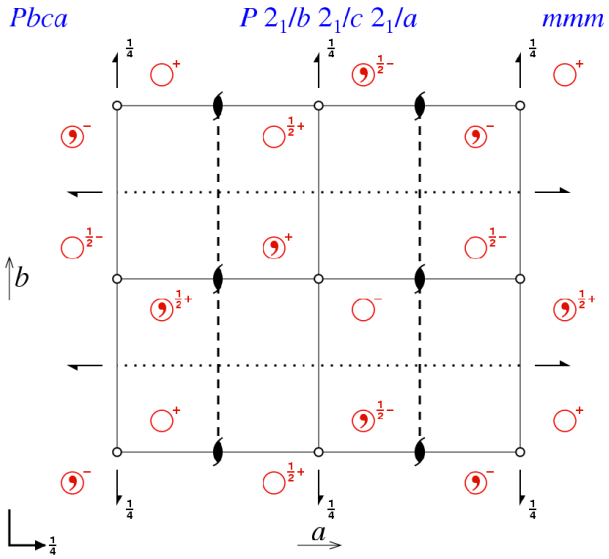
Ecole du GDR MICO

(Matériaux et Interactions en COmpétition)

Mai 2014



Cristallographie et techniques expérimentales associées



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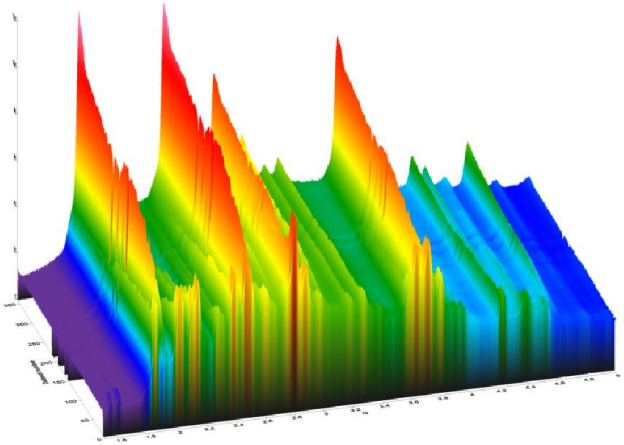


Introduction: *Crystallography*

Crystallography = science of crystals

External shape + internal structure + growth + physical properties of crystals

Crystallography = study the matter which is crystallized

→ determine the positions of the atoms inside
→ X-ray or neutron (or electronic) diffraction techniques

Polycrystal or Single crystal ?
(or powder)

An assembly of crystals with different orientations and separated by grain boundaries:
grain size ≈ 0.5 μm to 100 μm

Only one crystal

Each grain of a polycrystal is thus a single crystal

Introduction : *The two types of symmetries in crystals*

Symmetry group: set of symmetry operations that leave the atomic positions unchanged

1- Translation symmetry

Periodicity of the physical properties of crystals: **solid state physics**

- *Phonons, magnons, ...*
- *Diffraction*

2- Orientation symmetry: point symmetry

Anisotropy of the physical properties of crystals: **macroscopic physics**

→ reflects the point symmetry of the crystal.

- *External shape of crystals (natural faces)*
- *Electric conductivity, optics, mechanical and magnetic properties, ...*

To describe the crystals: geometry, symmetry, atomic coordinates, ... **direct space**	To determine the crystal structure: diffraction **reciprocal space**

Outline

part I: CRYSTALLOGRAPHY IN DIRECT SPACE

I.1. Orientation symmetry

Elementary point symmetries
How to obtain and name all crystallographic point groups?
Examples of point groups
The 32 point groups and 11 Laue classes

I.2. Translation symmetry

Lattice and motif, Unit cell
The orientation symmetries of lattices:
the 6 conventional cells, 7 crystal systems and 14 Bravais lattices
Rows and net planes

I.3. Space group symmetry

Glide planes and screw axes
The 230 space groups
The International Tables for Crystallography

I.4. Beyond basic crystallography

Aperiodic crystals: superspace groups
Magnetic structures: magnetic point groups and space groups

Voir fichier Compléments

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 ➡ *Voir fichier Compléments*

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.1. Orientation Symmetry: *Elementary point symmetries*

At microscopic (to within a translation in some cases) & macroscopic scale:

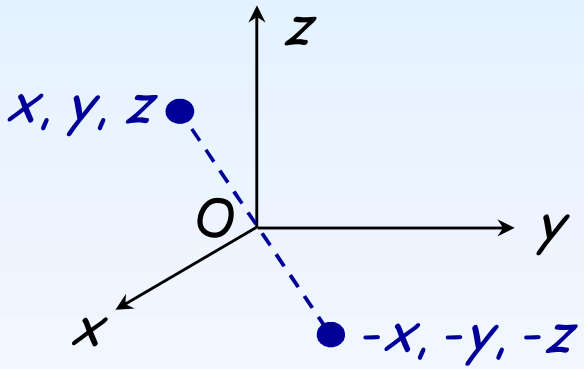
∃ orientation symmetries called point symmetries.

These operations are isometries that <u>leave at least one point fixed</u>.

Inversion (through a point)

→ *centrosymmetric crystal*

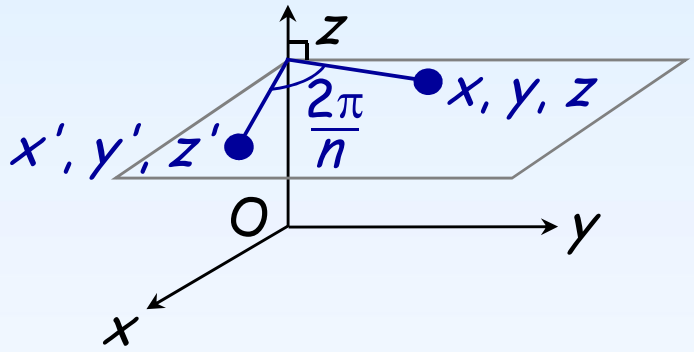
$\bar{1}$



Rotation (around an axis)

Rotation of order n ≡ *rotation by* $\phi = \frac{2\pi}{n}$

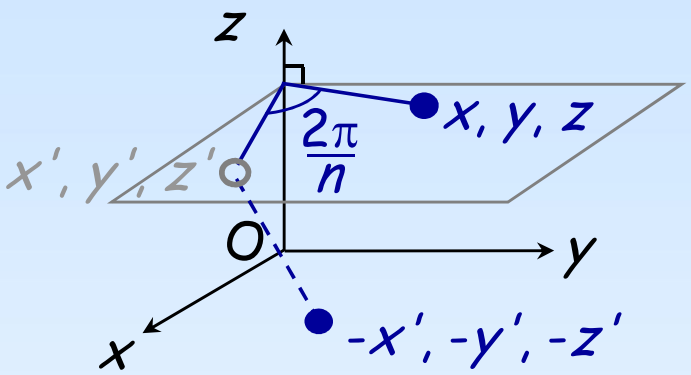
n



I.1. Orientation Symmetry: *Elementary point symmetries*

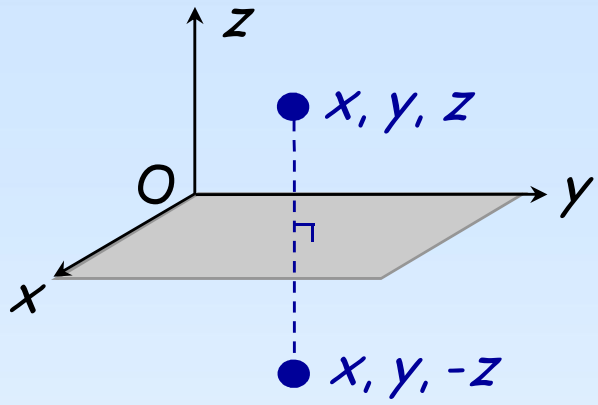
Roto-inversion
(around an axis and through a point)

$\bar{n}$



Reflection (through a mirror plane)

m



Note that: $m = \bar{2}$ *!*

Rotations compatible with the translation symmetry = those of orders 1, 2, 3, 4, 6

→ 10 elementary operations: point groups $\underbrace{1, 2, 3, 4, 6}_{\text{Proper}}, \underbrace{\bar{1}, \bar{2} = m, \bar{3}, \bar{4}, \bar{6}}_{\text{Improper}}$

I.1. Orientation Symmetry: *How to obtain and name all point groups ?*

Group structure

Operation: × (apply successively 2 sym. op.); Closure; associativity;
Neutral element: 1 (do nothing); Inverse: $n \rightarrow -n$ (rotate in the other way)

How to obtain all various crystallographic point groups (= crystal classes) ?

Combine these 10 elementary symmetry operations, with the following constraints:

- all symmetry elements go through a common point,
- point group compatible with translation symmetry

→ constraints between the orientations of the various symmetry operations

Notation of the point groups: 1- International (Hermann-Mauguin) symbols

Symmetry elements along 1, 2 or 3 non equivalent directions (primary, secondary, tertiary), ordered with decreasing or equal degree of symmetry *(except for 2 cubic point groups)*

The direction of a rotation is given by its axis
The direction of a mirror is given by its normal
'n/m' = axis n and mirror along the same direction
(*i.e.* mirror plane ⊥ to axis n)

→ used for crystallography

Examples: $4/m$

$\frac{4}{m}\frac{2}{m}\frac{2}{m} \rightarrow 4/mmm$

I.1. Orientation Symmetry: *How to obtain and name all point groups ?*

Notation of the point groups: 2- Schoenflies symbols

C_n	**Cyclic**	n-fold rotation axis (n = 1, 2, 3, 4, 6)
D_n	**Dihedral**, or two-sided	n-fold rotation axis plus n twofold axes $\perp$ to that axis

subscript h : addition of a mirror plane $\perp$ to the n-fold axis (C_{nh}, D_{nh})
subscript v : addition of a mirror plane // to the n-fold axis (C_{nv}, D_{nv})
subscript d : addition of a mirror plane // to the n-fold axis and bisecting the angle between the axes 2 $\perp$ to the n-fold axis (D_{nd})

S_{2n}	**Spiegel = Mirror**	$2n$-fold rotoinversion axis ($2n$ = 2, 4, 6)
T	**Tetrahedral**	symmetry of a tetrahedron with (T_d) or without (T) improper rotations, T_h = T with the addition of an inversion
O	**Octahedral**	symmetry of an octahedron (or **cube**) with (O_h) or without (O) improper operations

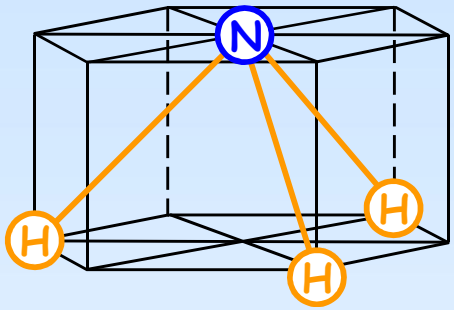
Other notations: $S_2 = C_i$; $S_6 = C_{3i}$; $C_{1h} = C_s$

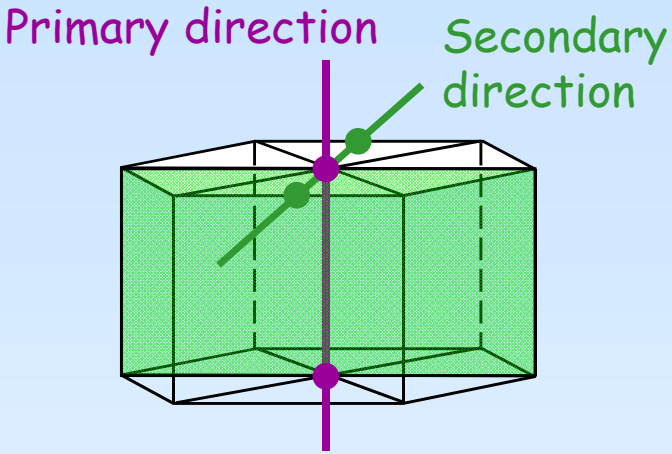
→ used for spectroscopy

I.1. Orientation Symmetry: *Examples of point groups*

Examples: point groups of molecules

NH_3



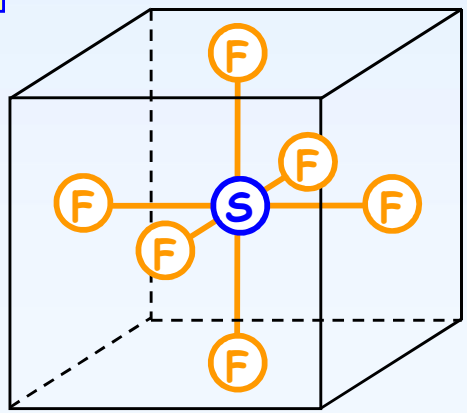


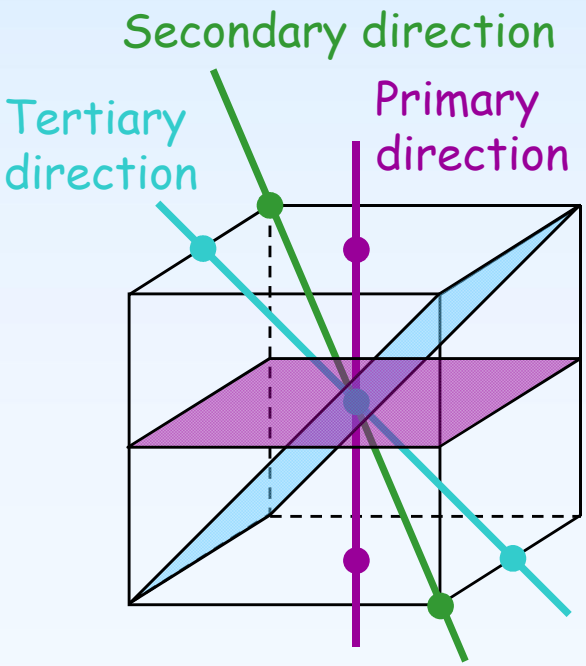
Axis 3
3 equivalent mirrors

⇓

Point group: $3m$

SF_6





axis 4 and mirrors
axis $\bar{3}$
axis 2 and mirror

⇓

Point group: $\frac{4}{m}\bar{3}\frac{2}{m}$

⟶ $m\bar{3}m$

I.1. Orientation Symmetry: *The 32 point groups and 11 Laue classes*

Order of the point symmetry along the: primary direct°	secondary direct°	tertiary direct°	Point groups and Laue groups
-	-	-	$1, \bar{1}$
2	-	-	$2, m, 2/m$
2	2	2	$222, 2mm, \frac{2}{m}\frac{2}{m}\frac{2}{m}$ (mmm)
3	-	-	$3, \bar{3}$
3	2	-	$32, 3m, \bar{3}\frac{2}{m}$ $(\bar{3}m)$
4	-	-	$4, \bar{4}, 4/m$
4	2	2	$422, 4mm, \bar{4}2m, \frac{4}{m}\frac{2}{m}\frac{2}{m}$ $(4/mmm)$
6	-	-	$6, \bar{6}, 6/m$
6	2	2	$622, 6mm, \bar{6}2m, \frac{6}{m}\frac{2}{m}\frac{2}{m}$ $(6/mmm)$
2	3	-	$23, \frac{2}{m}\bar{3}$ $(m\bar{3})$
4	3	2	$432, \bar{4}3m, \frac{4}{m}\bar{3}\frac{2}{m}$ $(m\bar{3}m)$

International vs Schoenflies symbols

(table 10.1.2.4. from the International Tables for Crystallography, Volume A)

System used in this volume	Point group: International symbol, Short	Point group: International symbol, Full	Schoenflies symbol
Triclinic	1	1	C_1
	$\bar{1}$	$\bar{1}$	$C_i(S_2)$
Monoclinic	2	2	C_2
	m	m	$C_s(C_{1h})$
	$2/m$	$\frac{2}{m}$	C_{2h}
Orthorhombic	222	222	$D_2(V)$
	$mm2$	$mm2$	C_{2v}
	mmm	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	$D_{2h}(V_h)$
Tetragonal	4	4	C_4
	$\bar{4}$	$\bar{4}$	S_4
	$4/m$	$\frac{4}{m}$	C_{4h}
	422	422	D_4
	$4mm$	$4mm$	C_{4v}
	$\bar{4}2m$	$\bar{4}2m$	$D_{2d}(V_d)$
	$4/mmm$	$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	D_{4h}
Trigonal	3	3	C_3
	$\bar{3}$	$\bar{3}$	$C_{3i}(S_6)$
	32	32	D_3
	$3m$	$3m$	C_{3v}
	$\bar{3}m$	$\bar{3}\frac{2}{m}$	D_{3d}
Hexagonal	6	6	C_6
	$\bar{6}$	$\bar{6}$	C_{3h}
	$6/m$	$\frac{6}{m}$	C_{6h}
	622	622	D_6
	$6mm$	$6mm$	C_{6v}
	$\bar{6}2m$	$\bar{6}2m$	D_{3h}
	$6/mmm$	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	D_{6h}
Cubic	23	23	T
	$m\bar{3}$	$\frac{2}{m}\bar{3}$	T_h
	432	432	O
	$\bar{4}3m$	$\bar{4}3m$	T_d
	$m\bar{3}m$	$\frac{4}{m}\bar{3}\frac{2}{m}$	O_h

I.2. Translation Symmetry: *Lattice and motif*

At the atomic scale, ∃ translation vectors $\vec{T}$ that put the crystallographic structure in coincidence with itself.

$$\vec{T} = u\,\vec{a} + v\,\vec{b} + w\,\vec{c} \quad \text{with } u, v, w \text{ integers}$$

$\vec{a}, \vec{b}$ and $\vec{c}$ are called the basis vectors and the volume they define is called the unit cell

Crystal = Lattice + Motif

The set of extremities of the $\vec{T}$ vectors define an abstract network of points (= nodes): the **lattice**.

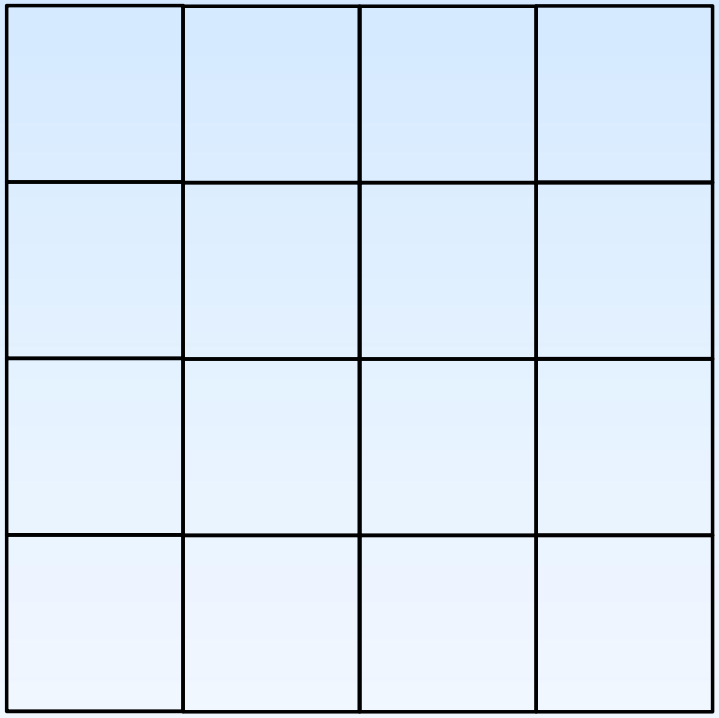
At each lattice node, one associates a group of atoms: the **motif**.

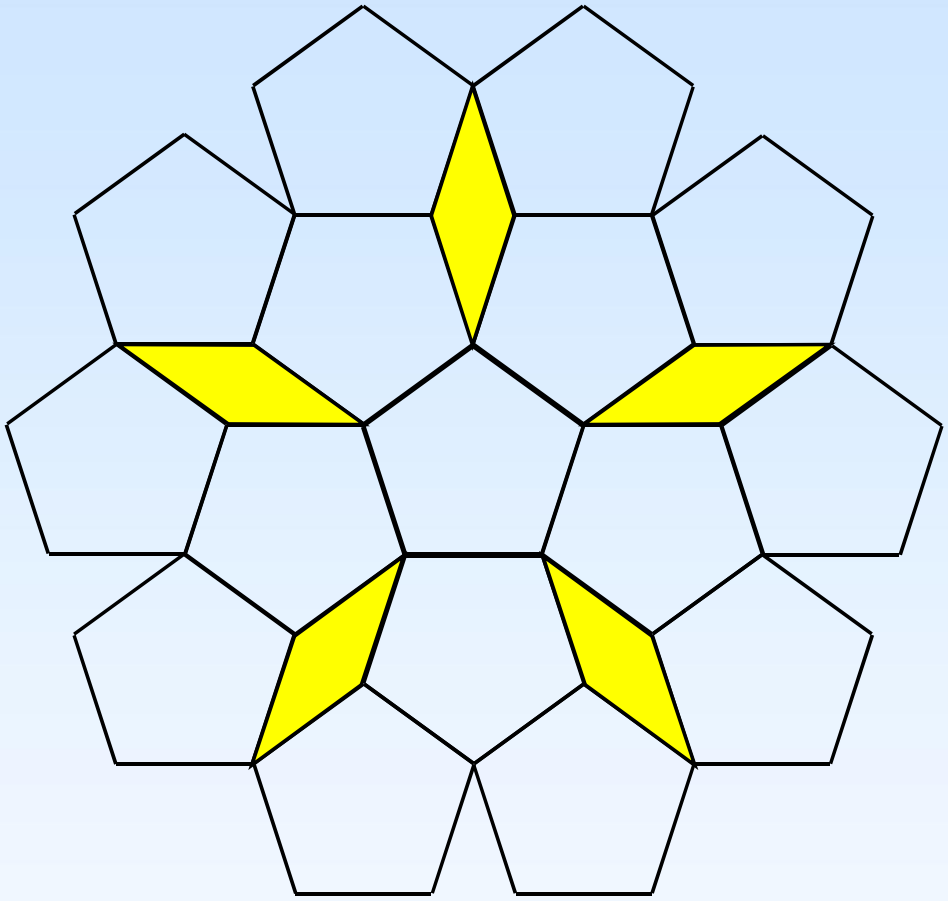
The knowledge of the lattice (basis vectors $\vec{a}, \vec{b}, \vec{c}$) and of the motif (nature and positions x, y, z of the atoms in the cell) completely characterizes the crystalline structure.

I.2. Translation Symmetry: *Unit cell*

The **unit cell** allows to pave the space with no empty space nor overlap, by applying the lattice translations.

Examples at 2D:

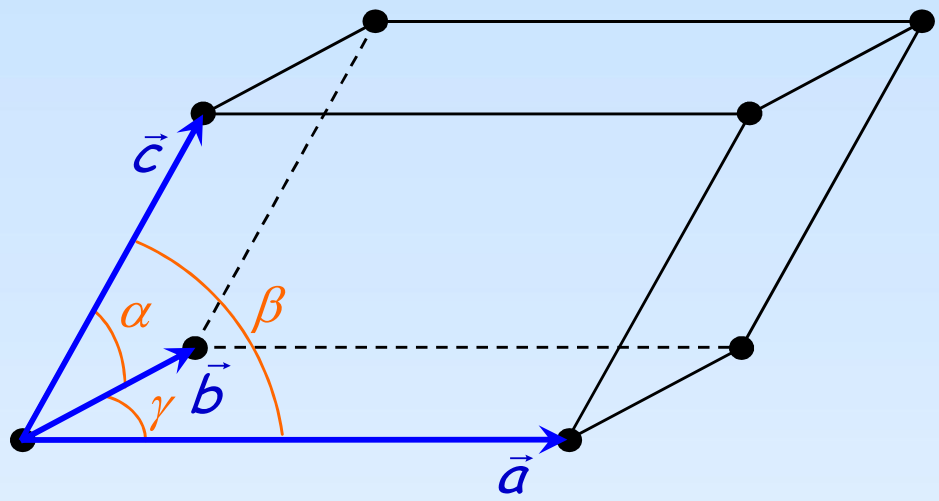




Rotation of order 4:
Compatible with the translation symmetry

Rotation of order 5:
not compatible with translation symmetry
→ **quasicrystals**

I.2. Translation Symmetry: *Unit cell*



Lattice parameters

lengths of the unit translations:

a

b

c

angles between them:

$\alpha = (\widehat{\vec{b}, \vec{c}})$

$\beta = (\widehat{\vec{c}, \vec{a}})$

$\gamma = (\widehat{\vec{a}, \vec{b}})$

- Multiplicity m of a unit cell = Number of lattice nodes (and thus of motifs) per unit cell

  How to count the number of lattice nodes per unit cell?
  → each lattice node counts for $1/n$, with n the number of unit cells to which it belongs.

- Primitive unit cell: $m = 1$

  For a given lattice, all primitive unit cells have the same volume: $V_p = (\vec{a}, \vec{b}, \vec{c}) = (\vec{a} \wedge \vec{b}).\vec{c}$

- Centered unit cell: $m = 2, 3, \ldots$ (doubly, triply, … primitive)

  Volume: $V_m = m\, V_p$

  These cells are used only when more symmetrical than any primitive cell of the lattice.

I.2. Translation Symmetry: *6 conventional cells and 7 crystal systems*

Translation symmetry & Orientation symmetry

The crystals can be classified into 6 conventional cells and 7 crystal systems each of them having a characteristic orientation symmetry.

The **6 conventional cells** are, from the lowest to the highest symmetric one:

a	triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
m	monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta > 90°$
o	orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
t	tetragonal or quadratic	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
h	hexagonal *	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$
c	cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$

* *The hexagonal cell splits in two crystal systems: trigonal (axis 3) and hexagonal (axis 6); the others are the same.*

I.2. Translation Symmetry: *Crystal system vs point group*

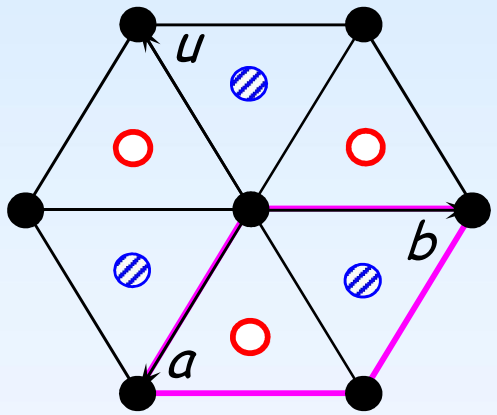
Crystal system	Point groups and Laue classes	primary direction	secondary direction	tertiary direction
monoclinic	$1, \bar{1}$	-	-	-
triclinic	$2, m, 2/m$	b	-	-
orthorhombic	$222, 2mm, mmm$	a	b	c
trigonal	$3, \bar{3}$ $32, 3m, \bar{3}m$	c	$a, b, -a-b$	-
Tetragonal or quadratic	$4, \bar{4}, 4/m$ $422, 4mm, \bar{4}2m, 4/mmm$	c	a, b	$a+b, a-b$
hexagonal	$6, \bar{6}, 6/m$ $622, 6mm, \bar{6}2m, 6/mmm$	c	$a, b, a+b$ ...	$2a+b, \ldots$
cubic	$23, m\bar{3}$ $432, \bar{4}3m, m\bar{3}m$	a, b, c	$a+b+c, \ldots$	$a+b, \ldots$

I.2. Translation Symmetry: *The 14 Bravais lattices*

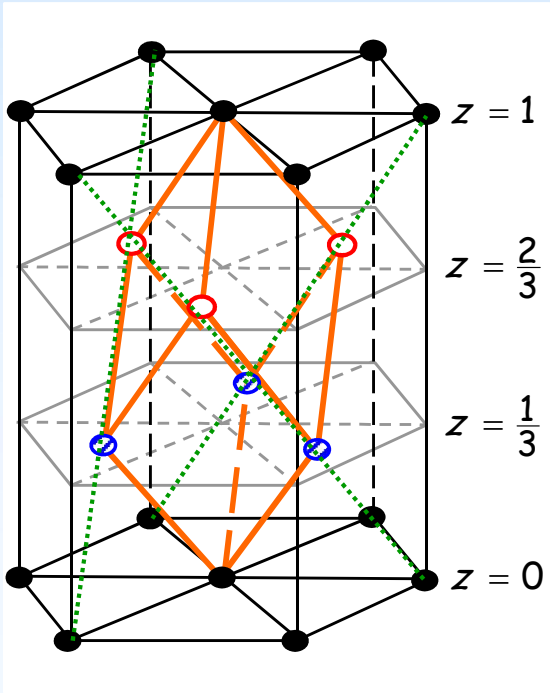
Classification in 14 Bravais lattices (Bravais, 1848):
- 6 primitive lattices, built from the 6 conventional cells,
- 8 non primitive (centered) lattices, by adding some nodes in the former cells, provided no symmetry element is lost and there exists no primitive cell having the same symmetry.

Symbol	lattice type	multiplicity
P	primitive	1
I	body centered	2
F	all-face centered	4
A, B, C	one-face centered: $(\vec{b},\vec{c}), (\vec{a},\vec{c}), (\vec{a},\vec{b})$ respectively	2
R	rhombohedrally centered: additional nodes at 1/3 and 2/3 of the diagonal of the hexagonal cell (trigonal system)	3

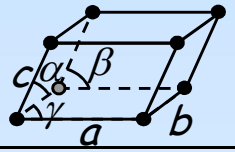
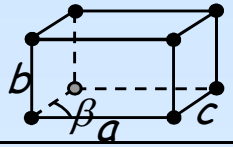
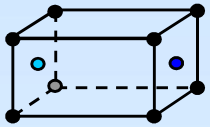
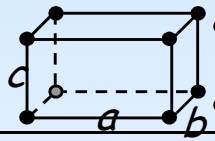
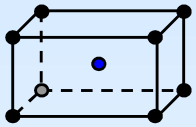
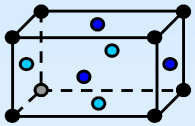
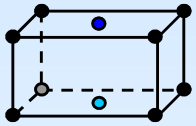
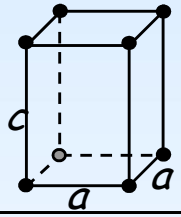
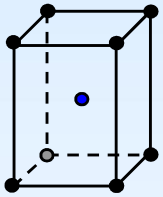
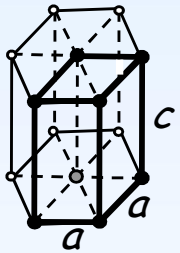
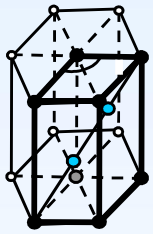
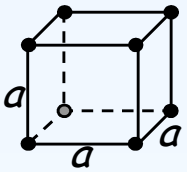
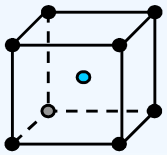
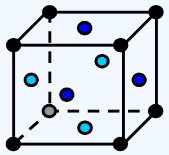
NB: the primitive cell of the hR cell is a rhombohedral cell ($a = b = c$, $\alpha = \beta = \gamma \neq 90°$).

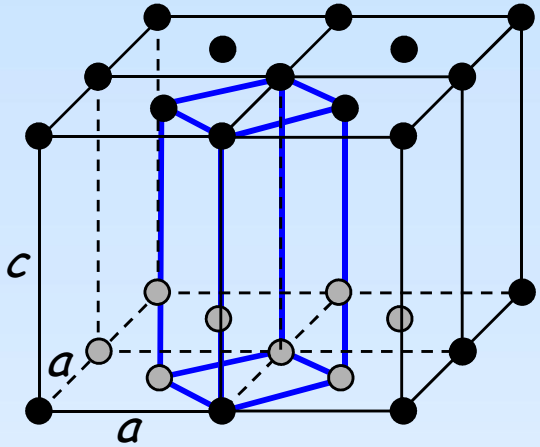


nodes in planes 0 et 1
nodes in plane 1/3
nodes in plane 2/3



I.2. Translation Symmetry: *The 14 Bravais lattices*

conventional cell	Lattice types				
	P	*I*	*F*	*C*	*R*
triclinic					
monoclinic					
orthorhombic					
tetragonal				×	
hexagonal					
cubic				×	



NB: for centered lattices,
∃ additional lattice translations

<u>Example</u>: *I* lattice

$$\begin{cases} \vec{T} = u\,\vec{a} + v\,\vec{b} + w\,\vec{c} \\ \vec{T}' = \vec{T} + \frac{1}{2}(\vec{a} + \vec{b} + \vec{c}) \end{cases}$$

with u, v, w integers

I.2. Translation symmetry: *Rows and net planes*

• Family of [*uvw*] rows

One can group all lattice nodes into parallel equidistant rows noted [*uvw*]

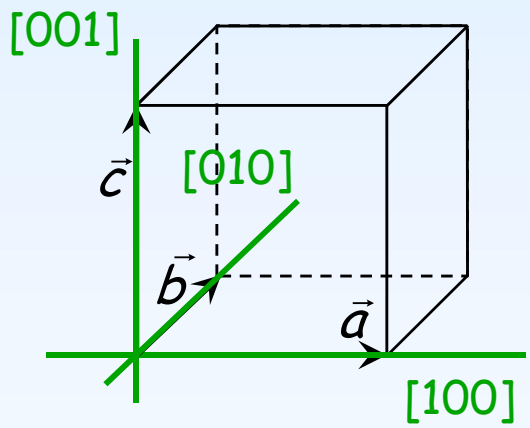
along $\vec{n}_{uvw} = u\vec{a} + v\vec{b} + w\vec{c}$

n_{uvw} : **row parameter**

u, v, w : coprime integers
indices of the row

Examples:

cubic cell:



symmetrically equivalent rows: <100>

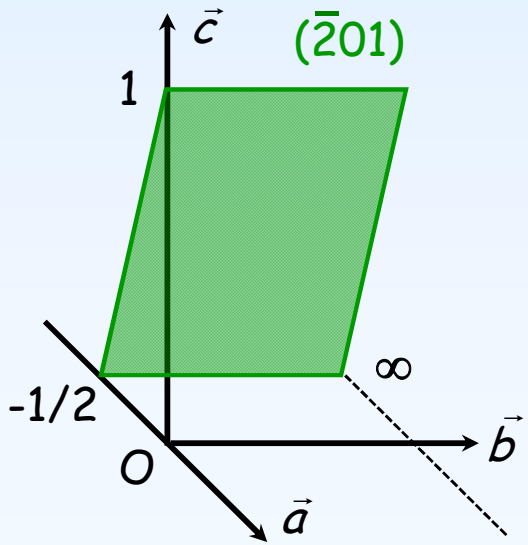
• Family of (*hkl*) net planes

One can group all lattice nodes into parallel equidistant net planes noted (*hkl*) spaced by d_{hkl}, such as $hx + ky + lz = m$

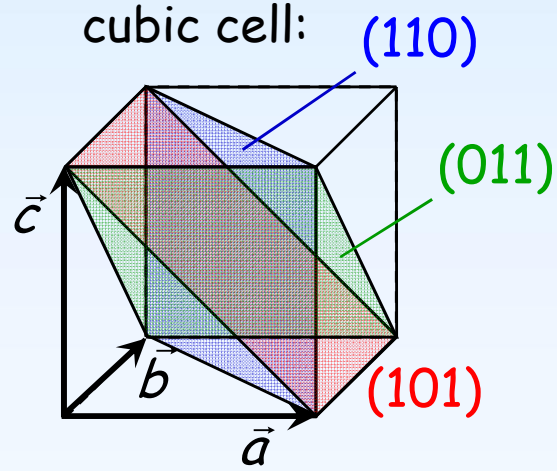
d_{hkl} : **d-spacing**

h, k, l : coprime integers for a *P* lattice
Miller indices

Examples:



cubic cell:



sym. equivalent planes: {110}

I.3. Space group symmetry

Description of the entire crystal = lattice + motif

translations of the lattice $\vec{T}$ — 14 Bravais lattices

+

symmetries acting inside the motif (point symmetries combined possibly with fractional translations) — 32 point groups with or without additional glide translations

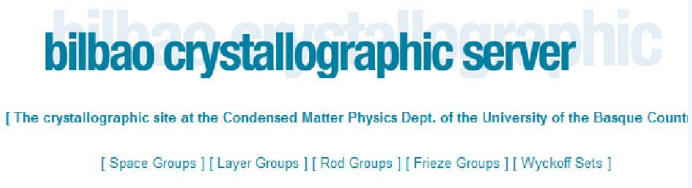
⇩

230 SPACE GROUPS

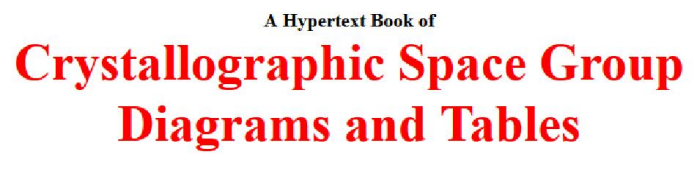
→ they describe the symmetry of the microscopic structure of crystals
= "identity card" of a crystal

The 230 space groups allow to classify all crystals.

http://it.iucr.org



http://www.cryst.ehu.es

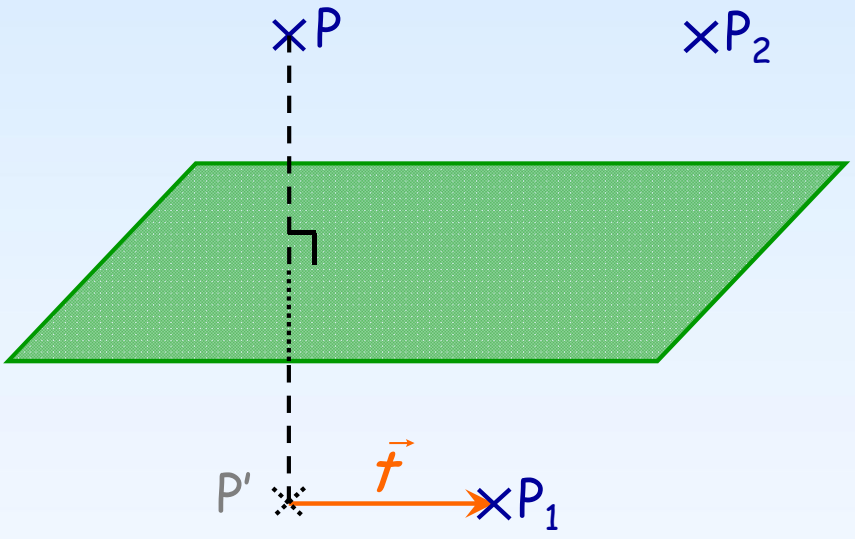


http://img.chem.ucl.ac.uk/sgp/mainmenu.htm

I.3. Space group symmetry: *Glide planes*

- **Glide planes**

Combination of a reflection (through a plane) and a fractional translation $\vec{t} \parallel$ plane



Example: glide plane $c \perp \vec{a}$

when applying twice the glide plane operation, one must recover a translation vector of the lattice:

$$\overrightarrow{PP_2} = 2\vec{t} = p\vec{c} \quad \text{with } p < 2 \Rightarrow p = 1$$

$$\rightarrow \boxed{\vec{t} = \frac{\vec{c}}{2}}$$

I.3. Space group symmetry: *Glide planes*

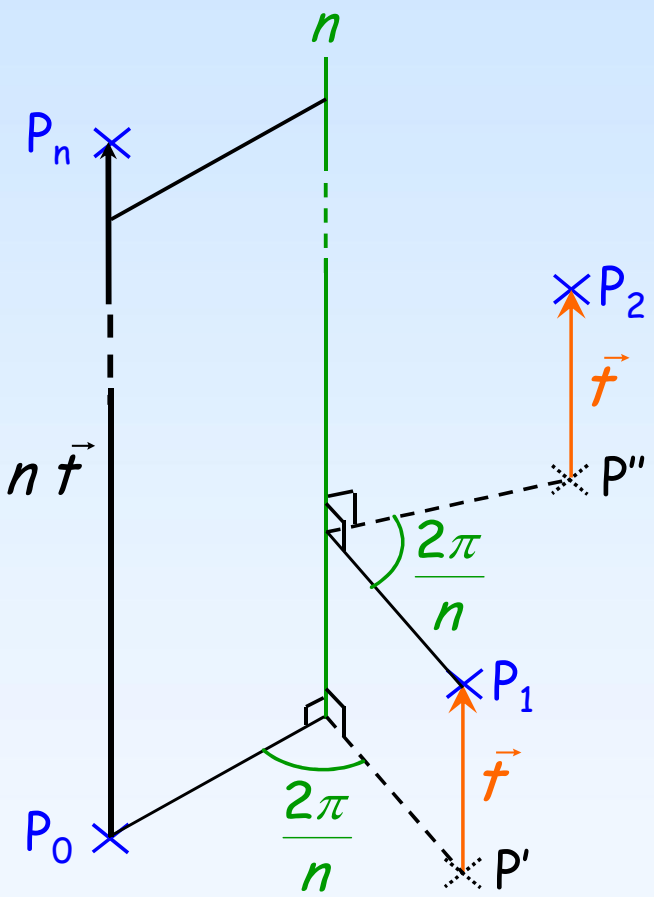
The various symmetry planes and their symbol

printed symbol	symmetry plane	graphical symbol		nature of glide translation
		normal to projection plane	parallel to projection plane	
m	reflection plane (mirror)			none
a, *b*, *c*	axial glide plane	$\vec{t}$ ∥ proj. plane $\vec{t}$ ⊥ proj. plane		*a*/2, *b*/2, or *c*/2 respectively
e	double glide plane			*a*/2 and *b*/2, *b*/2 and *c*/2 or *a*/2 and *c*/2; OR (*a*±*b*)/2 and *c*/2 etc … for *t* and *c* systems
n	diagonal glide plane (*net*)			(*a*+*b*)/2, (*b*+*c*)/2 or (*c*+*a*)/2; OR (*a*+*b*+*c*)/2 for *t* and *c* systems
d	"diamond" glide plane		$\frac{1}{8}$ $\frac{3}{8}$	(*a*±*b*)/4, (*b*±*c*)/4 or (*c*±*a*)/4; OR (*a*±*b*±*c*)/4 for *t* and *c* systems

I.3. Space group symmetry: *Screw axes*

- **Screw axes**

Combination of a rotation (around an axis n) and a fractional translation $\vec{t} \parallel$ axis



Example: screw axis $n_p \parallel \vec{c}$

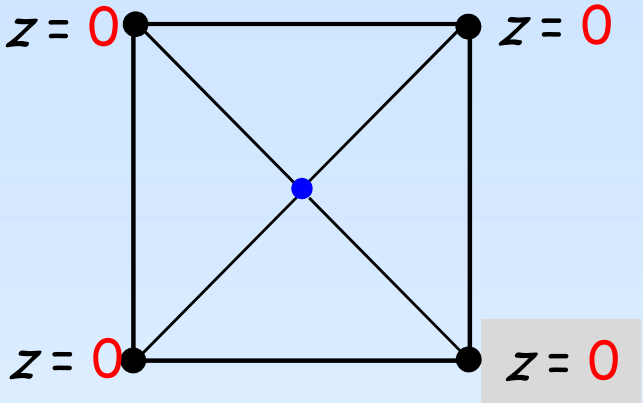
when applying n times the screw axis operation, one must recover a translation vector of the lattice:

$$\overrightarrow{PP_n} = n\vec{t} = p\vec{c} \quad \text{with} \quad p < n$$

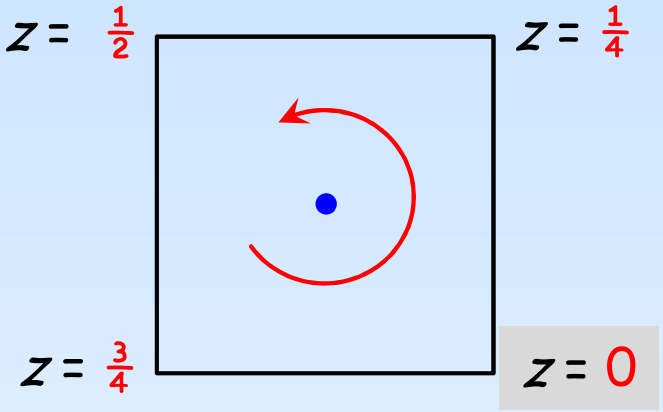
$$\rightarrow \boxed{\vec{t} = \frac{p}{n}\vec{c}} \qquad \boxed{p = 0, 1, \ldots, n\text{-}1}$$

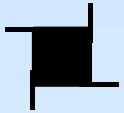
I.3. Space group symmetry: *Screw axes 4_p*

4 axis: $\vec{t} = \vec{0}$

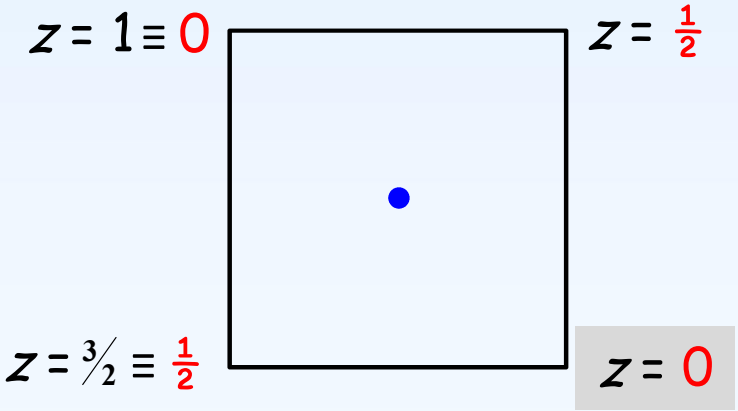


4_1 axis: $\vec{t} = \frac{1}{4}\vec{c}$

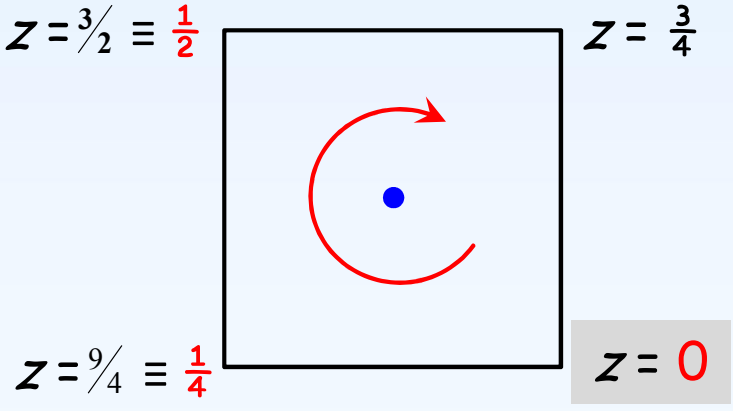


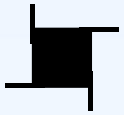


4_2 axis: $\vec{t} = \frac{1}{2}\vec{c}$



4_3 axis: $\vec{t} = \frac{3}{4}\vec{c}$





The various rotation and screw axes and their symbol

printed symbol	symmetry axis	graphic symbol	nature of the screw translation
1	Identity	none	none
$\bar{1}$	Inversion	○	none
2	Rotation diad or twofold rotation axis	(⊥ paper) (‖ paper)	none
2_1	Screw diad or twofold screw axis	(⊥ paper) (‖ paper)	*c*/2 *a*/2 or *b*/2
3	Rotation triad	⊥ paper	none
3_1 3_2	Screw triad		*c*/3 2*c*/3
$\bar{3}$	Inverse triad		none

printed symbol	symmetry axis	graphic symbol	nature of the screw translation
4	Rotation tetrad		none
4_1 4_2 4_3	Screw tetrads		*c*/4 2*c*/4 3*c*/4
$\bar{4}$	Inverse tetrad		none
6	Rotation hexad		none
6_1 6_2 6_3 6_4 6_5	Screw hexads		*c*/6 2*c*/6 3*c*/6 4*c*/6 5*c*/6
$\bar{6}$	Inverse hexad		none

I.3. Space group symmetry: *The 230 space groups*

- **International (Hermann-Mauguin) symbol of a space group** (Ex. $P4_2/mmc$)

1st letter: capital letter designing the lattice type *P, I, F, A* (*B* or *C*), *R*

following letters: nature of the symmetry elements

Space group symmetries: symmetry axes (largest *n*, smallest *p*) and symmetry planes ($m > e > a > b > c > n > d$)

Along the primary, secondary and tertiary directions: 3 non equivalent directions of symmetry of the cell (same as for point groups)

Conventional cell	Primary direction	Secondary direction	Tertiary direction
triclinic	only one symbol which denotes all directions of the crystal		
monoclinic	primary direction only: *b* (1st setting) or *c* (2nd setting) (order 2)		
orthorhombic	*a* (order 2)	*b* (order 2)	*c* (order 2)
tetragonal	*c* (order 4)	*a* and *b* (order 2)	[110] and [1$\bar{1}$0] (order 2)
hexagonal	*c* (order 6 or 3)	*a*, *b* and [$\bar{1}\bar{1}$0] (order 2)	[210], [$\bar{1}$20] and [1$\bar{1}$0] (order 2)
cubic	‹100› (order 4 or 2)	‹111› (order 3)	‹110› (order 2)

I.3. Space group symmetry: *The 230 space groups*

Cryst. system	Point group	Space group No	Space group symbol
a	1	1	$P1$
	$\bar{1}$	2	$P\bar{1}$
m	2	3	$P2$
		4	$P2_1$
		5	$C2$
	m	6	Pm
		7	Pc
		8	Cm
		9	Cc
	2/*m*	10	$P2/m$
		11	$P2_1/m$
		12	$C2/m$
		13	$P2/c$
		14	$P2_1/c$
		15	$C2/c$
o	222	16	$P222$
		17	$P222_1$
		18	$P2_12_12$
		19	$P2_12_12_1$
		20	$C222_1$
		21	$C222$
		22	$F222$
		23	$I222$
		24	$I2_12_12_1$
	*mm*2	25	$Pmm2$
		26	$Pmc2_1$
		27	$Pcc2$
		28	$Pma2$
		29	$Pca2_1$
		30	$Pnc2$
		31	$Pmn2_1$
		32	$Pba2_1$
		33	$Pna2_1$
		34	$Pnn2$
		35	$Cmm2$
		36	$Cmc2_1$
		37	$Ccc2$
		38	$Amm2$
		39	$Aem2$
		40	$Ama2$
		41	$Aea2$
		42	$Fmm2$
		43	$Fdd2$
		44	$Imm2$
		45	$Iba2$
		46	$Ima2$

Cryst. system	Point group	Space group No	Space group system
	mmm	47	$Pmmm$
		48	$Pnnn$
		49	$Pccm$
		50	$Pban$
		51	$Pmma$
		52	$Pnna$
		53	$Pmna$
		54	$Pcca$
		55	$Pbam$
		56	$Pccn$
		57	$Pbcm$
		58	$Pnnm$
		59	$Pmmn$
		60	$Pbcn$
		61	$Pbca$
		62	$Pnma$
		63	$Cmcm$
		64	$Cmce$
		65	$Cmmm$
		66	$Cccm$
		67	$Cmme$
		68	$Ccce$
		69	$Fmmm$
		70	$Fddd$
		71	$Immm$
		72	$Ibam$
		73	$Ibca$
		74	$Imma$
t	4	75	$P4$
		76	$P4_1$
		77	$P4_2$
		78	$P4_3$
		79	$I4$
		80	$I4_1$
	$\bar{4}$	81	$P\bar{4}$
		82	$I\bar{4}$
	4/*m*	83	$P4/m$
		84	$P4_2/m$
		85	$P4/n$
		86	$P4_2/n$
		87	$I4/m$
		88	$I4_1/a$
	422	89	$P422$
		90	$P42_12$
		91	$P4_122$
		92	$P4_12_12$

Cryst. system	Point group	Space group No	Space group system
		93	$P4_222$
		94	$P4_22_12$
		95	$P4_322$
		96	$P4_32_12$
		97	$I422$
		98	$I4_122$
	4*mm*	99	$P4mm$
		100	$P4bm$
		101	$P4_2cm$
		102	$P4_2nm$
		103	$P4cc$
		104	$P4nc$
		105	$P4_2mc$
		106	$P4_2bc$
		107	$I4mm$
		108	$I4cm$
		190	$I4_1md$
		110	$I4_1cd$
	$\bar{4}2m$	111	$P\bar{4}2m$
		112	$P\bar{4}2c$
		113	$P\bar{4}2_1m$
		114	$P\bar{4}2_1c$
		115	$P\bar{4}m2$
		116	$P\bar{4}c2$
		117	$P\bar{4}b2$
		118	$P\bar{4}n2$
		119	$I\bar{4}m2$
		120	$I\bar{4}c2$
		121	$I\bar{4}2m$
		122	$I\bar{4}2d$
	4/*mmm*	123	$P4/mmm$
		124	$P4/mcc$
		125	$P4/nbm$
		126	$P4/nnc$
		127	$P4/mbm$
		128	$P4/mnc$
		129	$P4/nmm$
		130	$P4/nnc$
		131	$P4_2/mmc$
		132	$P4_2/mcm$
		133	$P4_2/nbc$
		134	$P4_2/nnm$
		135	$P4_2/mbc$
		136	$P4_2/mnm$
		137	$P4_2/nmc$
		138	$P4_2/ncm$

Cryst. system	Point group	Space group No	Space group system
		139	$I4/mmm$
		140	$I4/mcm$
		141	$I4_1/amd$
		142	$I4_1/acd$
h	3	143	$P3$
		144	$P3_1$
		145	$P3_2$
		146	$R3$
	$\bar{3}$	147	$P\bar{3}$
		148	$R\bar{3}$
	32	149	$P312$
		150	$P321$
		151	$P3_112$
		152	$P3_121$
		153	$P3_212$
		154	$P3_221$
		155	$R32$
	3*m*	156	$P3m1$
		157	$P31m$
		158	$P3c1$
		159	$P31c$
		160	$R3m$
		161	$R3c$
	$\bar{3}m$	162	$P\bar{3}1m$
		163	$P\bar{3}1c$
		164	$P\bar{3}m1$
		165	$P\bar{3}c1$
		166	$R\bar{3}m$
		167	$R\bar{3}c$
h	6	168	$P6$
		169	$P6_1$
		170	$P6_5$
		171	$P6_2$
		172	$P6_4$
		173	$P6_3$
	$\bar{6}$	174	$P\bar{6}$
	6/*m*	175	$P6/m$
		176	$P6_3/m$
	622	177	$P622$
		178	$P6_122$
		179	$P6_522$
		180	$P6_222$
		181	$P6_422$
		182	$P6_322$
	6*mm*	183	$P6mm$
		184	$P6cc$

Cryst. system	Point group	Space group No	Space group system
		185	$P6_3cm$
		186	$P6_3mc$
	$\bar{6}m2$	187	$P\bar{6}m2$
		188	$P\bar{6}c2$
		189	$P\bar{6}2m$
		190	$P\bar{6}2c$
	6/*mmm*	191	$P6/mmm$
		192	$P6/mcc$
		193	$P6/mcm$
		194	$P6/mmc$
c	23	195	$P23$
		196	$F23$
		197	$I23$
		198	$P2_13$
		199	$I2_13$
	*m*3	200	$Pm\bar{3}$
		201	$Pn\bar{3}$
		202	$Fm\bar{3}$
		203	$Fd\bar{3}$
		204	$Im\bar{3}$
		205	$Pa\bar{3}$
		206	$Ia\bar{3}$
	432	207	$P432$
		208	$P4_232$
		209	$F432$
		210	$F4_132$
		211	$I432$
		212	$P4_332$
		213	$P4_132$
		214	$I4_132$
	$\bar{4}3m$	215	$P\bar{4}3m$
		216	$F\bar{4}3m$
		217	$I\bar{4}3m$
		218	$P\bar{4}3n$
		219	$F\bar{4}3c$
		220	$I\bar{4}3d$
	$m\bar{3}m$	221	$Pm\bar{3}m$
		222	$Pn\bar{3}n$
		223	$Pm\bar{3}n$
		224	$Pn\bar{3}m$
		225	$Fm\bar{3}m$
		226	$Fm\bar{3}c$
		227	$Fd\bar{3}m$
		228	$Fd\bar{3}c$
		229	$Im\bar{3}m$
		230	$Ia\bar{3}d$

I.3. Space group symmetry: *The International Tables for Crystallography*

Example: *Pnma*

non symmorphic SG

⚠ ∃ different settings
(permutations of *a*, *b*, *c*)

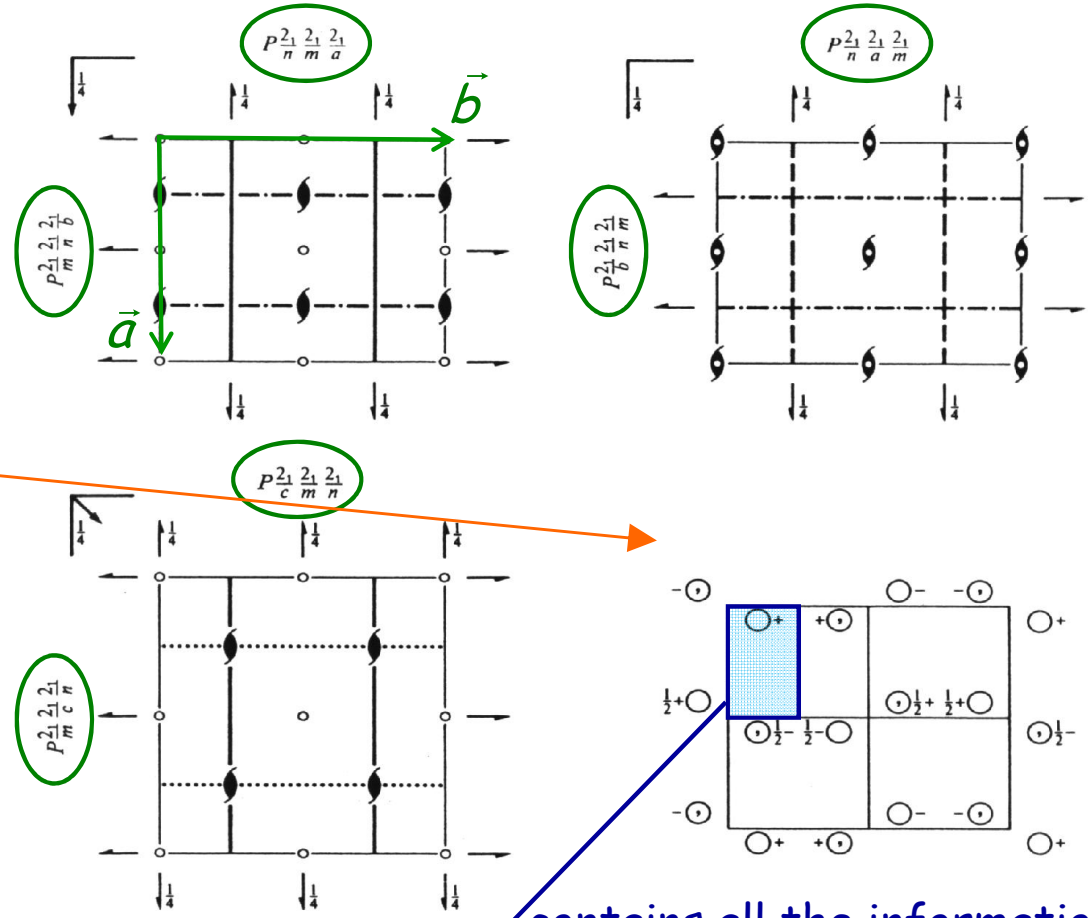
8 equivalent
atomic positions

8 symmetry operations

First page of Pnma space group taken from the International Tables for Crystallography

$Pnma$ **D_{2h}^{16}** mmm Orthorhombic

No. 62 $P\,2_1/n\,2_1/m\,2_1/a$ Patterson symmetry $Pmmm$



Origin at $\bar{1}$ on $1\,2_1\,1$

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{4}$; $0 \le z \le 1$

Symmetry operations

(1) 1	(2) $2(0,0,\frac{1}{2})$ $\frac{1}{4},0,z$	(3) $2(0,\frac{1}{2},0)$ $0,y,0$	(4) $2(\frac{1}{2},0,0)$ $x,\frac{1}{4},\frac{1}{4}$
(5) $\bar{1}$ $0,0,0$	(6) a $x,y,\frac{1}{4}$	(7) m $x,\frac{1}{4},z$	(8) $n(0,\frac{1}{2},\frac{1}{2})$ $\frac{1}{4},y,z$

contains all the information necessary for the complete description of the crystal structure

I.3. Space group symmetry: *The International Tables for Crystallography*

Orthorhombic $P2_1/n2_1/m2_1/a$

Bravais lattice

screw axis $2_1 \parallel \vec{a}$
glide plane $n \perp \vec{a}$

screw axis $2_1 \parallel \vec{b}$
mirror plane $m \perp \vec{b}$

screw axis $2_1 \parallel \vec{c}$
glide plane $a \perp \vec{c}$

Symmetry operations

(1) 1	(2) $2(0,0,\frac{1}{2})$ $\frac{1}{4},0,z$	(3) $2(0,\frac{1}{2},0)$ $0,y,0$	(4) $2(\frac{1}{2},0,0)$ $x,\frac{1}{4},\frac{1}{4}$
(5) $\bar{1}$ $0,0,0$	(6) a $x,y,\frac{1}{4}$	(7) m $x,\frac{1}{4},z$	(8) $n(0,\frac{1}{2},\frac{1}{2})$ $\frac{1}{4},y,z$

rotation of order 2
followed by $\vec{t} = \frac{1}{2}\vec{c}$

axis $\parallel \vec{c}$ at
$x = \frac{1}{4}$ and $y = 0$

glide plane n
with $\vec{t} = \frac{1}{2}\vec{b} + \frac{1}{2}\vec{c}$

plane $\parallel (\vec{b},\vec{c})$
at $x = \frac{1}{4}$

I.3. Space group symmetry: *The International Tables for Crystallography*

Arbitrary choice of generators

Identity
Lattice translations
+ Others
(axes and/or planes)

CONTINUED **No. 62** ***P n m a***

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
8	d	1	(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$	(3) $\bar{x},y+\frac{1}{2},\bar{z}$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$
			(5) $\bar{x},\bar{y},\bar{z}$	(6) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$	(7) $x,\bar{y}+\frac{1}{2},z$	(8) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$
4	c	$.m.$	$x,\frac{1}{4},z$	$\bar{x}+\frac{1}{2},\frac{3}{4},z+\frac{1}{2}$	$\bar{x},\frac{3}{4},\bar{z}$	$x+\frac{1}{2},\frac{1}{4},\bar{z}+\frac{1}{2}$
4	b	$\bar{1}$	$0,0,\frac{1}{2}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$
4	a	$\bar{1}$	$0,0,0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$

Reflection conditions

General:
$0kl$: $k+l=2n$
$hk0$: $h=2n$
$h00$: $h=2n$
$0k0$: $k=2n$
$00l$: $l=2n$

Special: as above, plus

no extra conditions

hkl : $h+l, k=2n$

hkl : $h+l, k=2n$

Symmetry of special projections

Along [001] $p\,2g\,m$
$\mathbf{a}'=\frac{1}{2}\mathbf{a}$ $\mathbf{b}'=\mathbf{b}$
Origin at $0,0,z$

Along [100] $c\,2m\,m$
$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}$
Origin at $x,\frac{1}{4},\frac{1}{4}$

Along [010] $p\,2g\,g$
$\mathbf{a}'=\mathbf{c}$ $\mathbf{b}'=\mathbf{a}$
Origin at $0,y,0$

See Part II

Maximal non-isomorphic subgroups

I	$[2]P\,2_1\,2_1\,2_1$	1; 2; 3; 4
	$[2]P\,1\,1\,2_1/a\,(P\,2_1/c)$	1; 2; 5; 6
	$[2]P\,1\,2_1/m\,1\,(P\,2_1/m)$	1; 3; 5; 7
	$[2]P\,2_1/n\,1\,1\,(P\,2_1/c)$	1; 4; 5; 8
	$[2]P\,n\,m\,2_1\,(P\,m\,n\,2_1)$	1; 2; 7; 8
	$[2]P\,n\,2_1\,a\,(P\,n\,a\,2_1)$	1; 3; 6; 8
	$[2]P\,2_1\,m\,a\,(P\,m\,c\,2_1)$	1; 4; 6; 7
IIa	none	
IIb	none	

Maximal isomorphic subgroups of lowest index

IIc $[3]P\,n\,m\,a\,(\mathbf{a}'=3\mathbf{a})$; $[3]P\,n\,m\,a\,(\mathbf{b}'=3\mathbf{b})$; $[3]P\,n\,m\,a\,(\mathbf{c}'=3\mathbf{c})$

subgroups /supergroups

see also *www.cryst.ehu.es*

Minimal non-isomorphic supergroups

I none

II $[2]A\,m\,m\,a(C\,m\,c\,m)$; $[2]B\,b\,m\,m(C\,m\,c\,m)$; $[2]C\,c\,m\,b(C\,m\,c\,a)$; $[2]I\,m\,m\,a$; $[2]P\,n\,m\,m\,(2\mathbf{a}'=\mathbf{a})(P\,m\,m\,n)$; $[2]P\,c\,m\,a\,(2\mathbf{b}'=\mathbf{b})(P\,b\,a\,m)$; $[2]P\,b\,m\,a\,(2\mathbf{c}'=\mathbf{c})(P\,b\,c\,m)$

Second page of Pnma space group taken from the International Tables for Crystallography

I.3. Space group symmetry: *The International Tables for Crystallography*

Wyckoff sites: List of the different sites from the most general (*i.e.* less symmetrical) to the less general (*i.e.* most symmetrical: special position)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
8	*d*	1	(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$	(3) $\bar{x},y+\frac{1}{2},\bar{z}$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$
			(5) $\bar{x},\bar{y},\bar{z}$	(6) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$	(7) $x,\bar{y}+\frac{1}{2},z$	(8) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$
4	*c*	$.m.$	$x,\frac{1}{4},z$	$\bar{x}+\frac{1}{2},\frac{3}{4},z+\frac{1}{2}$	$\bar{x},\frac{3}{4},\bar{z}$	$x+\frac{1}{2},\frac{1}{4},\bar{z}+\frac{1}{2}$
4	*b*	$\bar{1}$	$0,0,\frac{1}{2}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$
4	*a*	$\bar{1}$	$0,0,0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$

site name

Multiplicity of the site

Wyckoff letter

Site symmetry

Coordinates of all equivalent positions

I.3. Space group symmetry: *The International Tables for Crystallography*

Example: $LaMnO_3$ (space group *Pnma*)

→ **Bravais lattice** = primitive orthorhombic

	x	*y*	*z*	
La	0.518	0.25	0.007	→ 4*c*
Mn	0	0	0	→ 4*a*
O_1	-0.005	0.25	0.075	→ 4*c*
O_2	0.288	0.096	0.226	→ 8*d*

→ **Motif** = $La_4Mn_4O_{12}$

7 coordinates to determine for (4+4+12)x3 = **60** in total!

Positions

	Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
O_2	8 *d*	1		(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$	(3) $\bar{x},y+\frac{1}{2},\bar{z}$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$
				(5) $\bar{x},\bar{y},\bar{z}$	(6) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$	(7) $x,\bar{y}+\frac{1}{2},z$	(8) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$
La, O_1	4 *c*	.*m*.		$x,\frac{1}{4},z$	$\bar{x}+\frac{1}{2},\frac{3}{4},z+\frac{1}{2}$	$\bar{x},\frac{3}{4},\bar{z}$	$x+\frac{1}{2},\frac{1}{4},\bar{z}+\frac{1}{2}$
	4 *b*	$\bar{1}$		$0,0,\frac{1}{2}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$
Mn	4 *a*	$\bar{1}$		$0,0,0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$

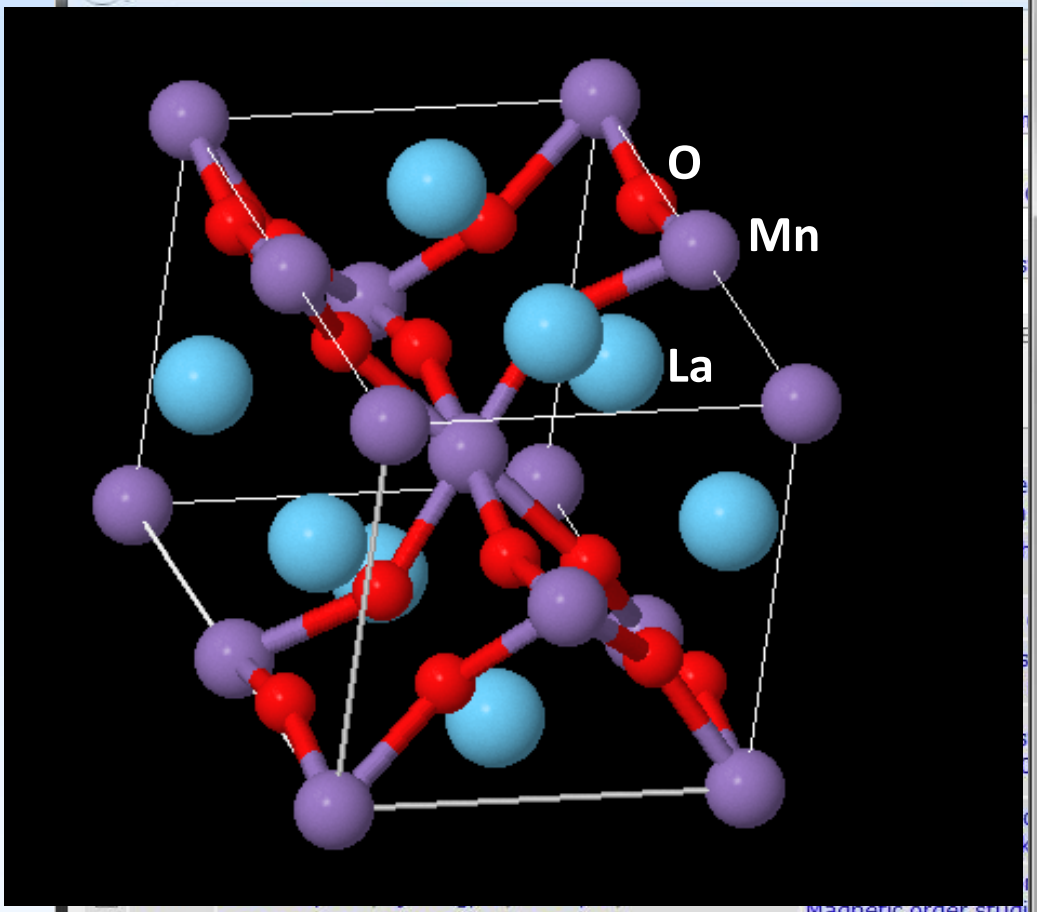
I.3. Space group symmetry: *The International Tables for Crystallography*

ICSD for WWW - Mozilla Firefox

Fichier Édition Affichage Historique Marque-pages Outils ?

ICSD for WWW

icsd.ill.eu/icsd/index.php?action=Search&page=1&nb_rows=10&order_by=yearDesc&au



1996	Hauback, B.C.; Fjellvag, H.; Sakai, N.;	Effect of nonstoichio Magnetic order studi

Page : [1](8 results) 10 results per page.

http://icsd.ill.eu/icsd/index.php

ICSD for WWW : Details - Mozilla Firefox

icsd.ill.eu/icsd/details.php?id[]=424625

ICSD for WWW

Details of the selected entries

Print 1 entry selected.

CC=Collection Code: [AB2X4]=ANX Form: [cF56]=Pearson: [e d a]=Wyckoff Symbol: [Al2MgO4]=Structure Type:

Click the ANX, Pearson or Wyckoff Symbol to find structures with that symbol.

CC=168694 Help CIF Export Bonds Pattern Structure Jmol

Title	Rapid synthesis of room temperature ferromagnetic Ag-doped La Mn O3 perovskite phases by the solution combustion method.
Authors	Bellakki, M.B.;Shivakumara, C.;Vasanthacharya, N.Y.;Prakash, A.S.
Reference	Materials Research Bulletin (2010) **45**, 1685-1691 **Link XRef SCOPUS SCIRUS Google**
Compound	**La1 Mn1 O3** - Lanthanum trioxomanganate **[ABX3] [oP20] [d c2 b] [GdFeO3]**
Cell	5.477(6), 5.524(4), 7.805(6), 90., 90., 90. **PBNM (62)** V=236.14
Remarks	R=0.046000 : RVP XDP TYP =GdFeO3 : TEM =293 : At least one temperature factor missing in the paper.

Atom (site)		Oxid.	x, y, z, B, Occupancy				
La1	(4c)	3	0.005(12)	0.0120(5)	0.25	0	1
Mn1	(4b)	3	0.5	0.	0.	0	1
O1	(4c)	-2	0.0109(7)	0.4869(6)	0.25	0	1
O2	(8d)	-2	0.7500(8)	0.2803(6)	0.0675(3)	0	1

- part II -

DIFFRACTION
CRYSTALLOGRAPHY IN RECIPROCAL SPACE

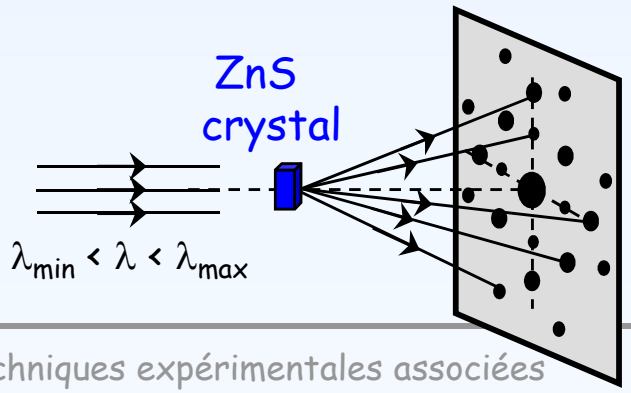
An incident beam of X-rays or neutrons can be considered as a plane wave.

For an incident beam to be diffracted by a crystal, its wavelength must be of the same order of magnitude than the inter-atomic distances (a few angströms).

Medecine (X-ray): 0.2 Å $\leq \lambda \leq$ 0.5 Å
Crystallography (X-ray & neutrons): 0.5 Å $\leq \lambda \leq$ 10 Å

→ *visible light cannot be scattered by a single crystal (4000 Å < λ < 8000 Å)*

First X-ray experiment:
Laue experiment (1912)



II.1. The reciprocal space: *Definition*

The **reciprocal lattice** is defined as a network of points in the Fourier space (*Q*-space) which are the extremities of vectors: $\vec{\tau} = h\ \vec{a}^* + k\ \vec{b}^* + l\ \vec{c}^*$

with $\vec{a}^*$, $\vec{b}^*$, and $\vec{c}^*$ the unit vectors of the reciprocal lattice, and *h*, *k*, *l* integers.

$$\vec{a}^* = C\frac{\vec{b}\wedge\vec{c}}{V} \quad \rightarrow \quad \vec{a}^* \perp \vec{b} \text{ and } \vec{c}$$

$$\vec{b}^* = C\frac{\vec{c}\wedge\vec{a}}{V} \quad \rightarrow \quad \vec{b}^* \perp \vec{c} \text{ and } \vec{a}$$

$$\vec{c}^* = C\frac{\vec{a}\wedge\vec{b}}{V} \quad \rightarrow \quad \vec{c}^* \perp \vec{a} \text{ and } \vec{b}$$

In solid state physics, $C = 2\pi$
In crystallography, $C = 1$

for $C = 1$

$$\vec{a}^*.\vec{a} = \vec{b}^*.\vec{b} = \vec{c}^*.\vec{c} = 1$$

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

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

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

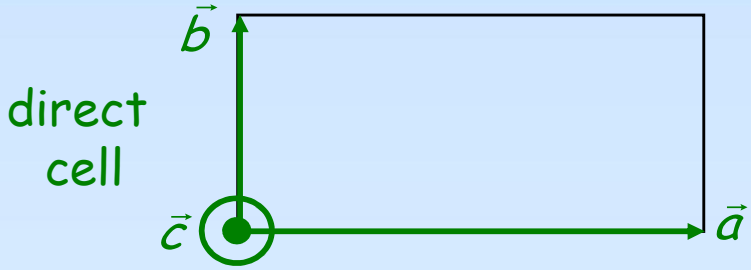
where *C* is a constant
and V is the volume of the unit cell
in the direct space:

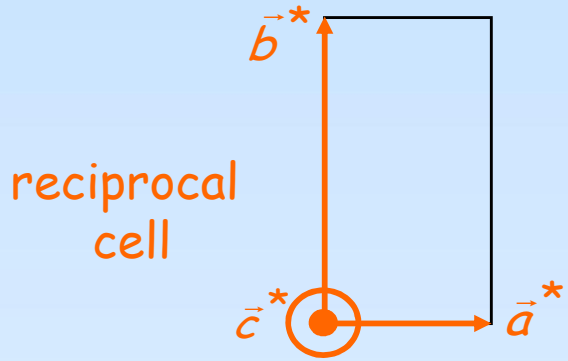
$$V = (\vec{a}, \vec{b}, \vec{c}) = (\vec{a}\wedge\vec{b}).\vec{c} = \vec{a}.(\vec{b}\wedge\vec{c})$$

II.1. The reciprocal space: *Examples*

- Orthorhombic ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$)

$$\vec{a}^* \parallel \vec{a} \quad \text{and} \quad a^* = \frac{1}{a}$$
$$\vec{b}^* \parallel \vec{b} \quad \text{and} \quad b^* = \frac{1}{b}$$
$$\vec{c}^* \parallel \vec{c} \quad \text{and} \quad c^* = \frac{1}{c}$$



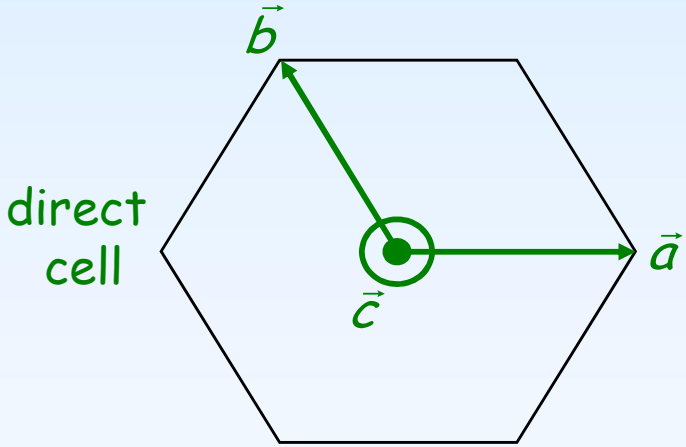


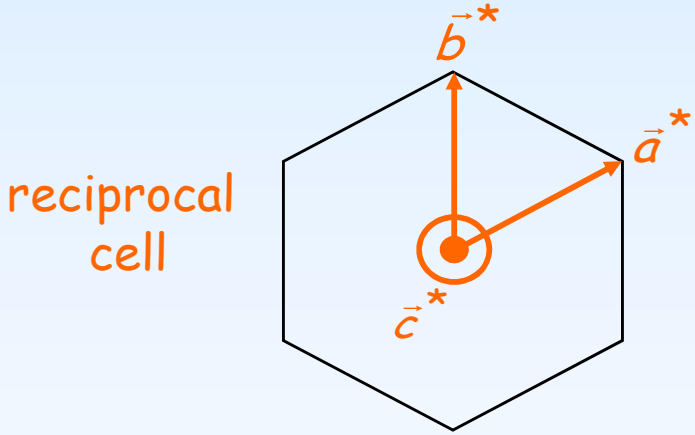
- Hexagonal ($a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$)

$$\left.\begin{array}{l} \vec{a}^* \perp \vec{b}, \vec{c} \\ \vec{b}^* \perp \vec{a}, \vec{c} \end{array}\right\} \quad \gamma^* = 60°$$
$$\vec{c}^* \parallel \vec{c} \qquad \alpha^* = \beta^* = 90°$$

$$a^* = \frac{bc \sin\alpha}{V} = \frac{2}{a\sqrt{3}}$$
$$b^* = \frac{ac \sin\beta}{V} = \frac{2}{a\sqrt{3}}$$
$$c^* = \frac{ab \sin\gamma}{V} = \frac{1}{c}$$

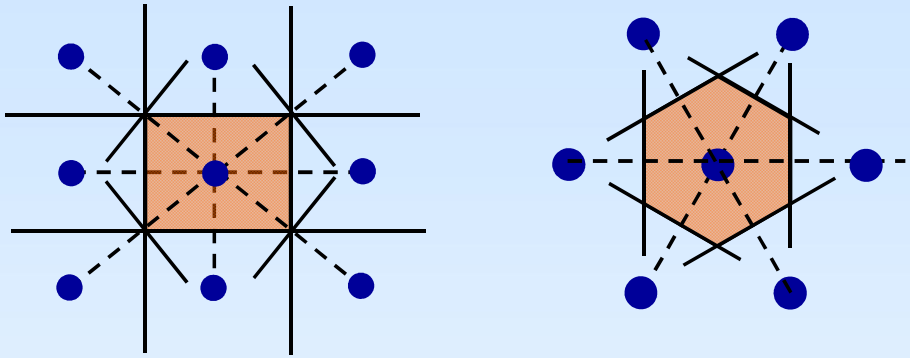
$$\left(V = abc \sin\gamma = \frac{\sqrt{3}}{2} a^2 c \right)$$





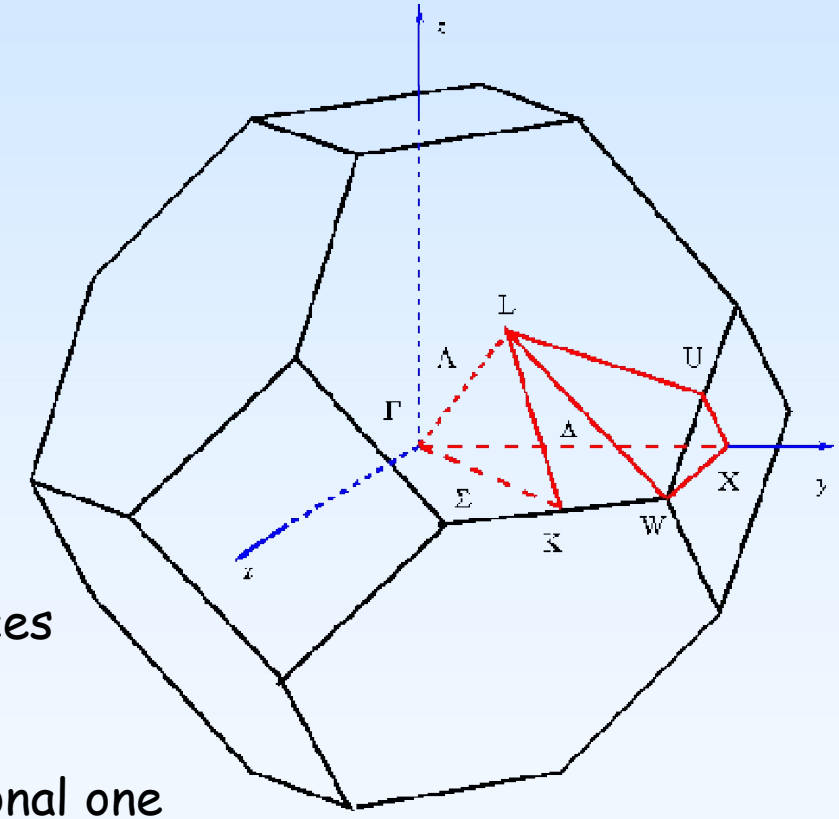
II.1. The reciprocal space: *First Brillouin zone*

First Brillouin zone (BZ) = the smallest polyhedron enclosed by the perpendicular bisectors of the nearest neighbors to a given point of the reciprocal space.



Special points: Points of high symmetry

Symbole	Description
Γ	center of Brillouin zone
K	middle of an egde between 2 hexagonal faces
L	center of an hexagonal face
U	middle of an edge between a square face and an hexagonal one
X	center of a square face
W	corner



First Brillouin zone of a *F* cubic lattice

II.1. The reciprocal space: *Properties*

- Direct space (DS) used to describe the atomic positions in the crystal (lengths in Å)
  Reciprocal space (RS) used to describe the positions of the diffracted peaks, phonons, magnons, … (lengths in $Å^{-1}$)

- Each family of rows [*hkl*]* in RS is ⊥ to the family of net planes (*hkl*) in the DR:
  $\vec{n}^*_{hkl} // \vec{d}_{hkl}$ and $n^*_{hkl}.d_{hkl} = 1$
  each family of net planes (*uvw*)* in RS is ⊥ to the family of rows [*uvw*] in DS:
  $\vec{d}^*_{uvw} // \vec{n}_{uvw}$ and $d^*_{uvw}.n_{uvw} = 1$

- The reciprocal cell of a primitive direct cell is primitive,
  The reciprocal cell of a non primitive direct cell is non primitive.

Examples:

cubic *P* ⟶ cubic *P*
cubic *I* ⟶ cubic *F*
cubic *F* ⟶ cubic *I*

II.1. The reciprocal space: *Properties*

- The *d*-spacing d_{hkl} for the net planes (*hkl*) is equal to the inverse of the length of the reciprocal lattice vector $\vec{n}^*_{hkl} = \vec{\tau} = h\ \vec{a}^* + k\ \vec{b}^* + l\ \vec{c}^*$

$$d_{hkl} = \frac{1}{|\vec{\tau}|} \quad \Rightarrow \quad d_{hkl} = \frac{1}{\sqrt{\left(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*\right).\left(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*\right)}}$$

<u>*Examples:*</u>

Orthorhombic cell:

$$d_{hkl} = \frac{1}{\sqrt{h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2}}} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

Cubic cell:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

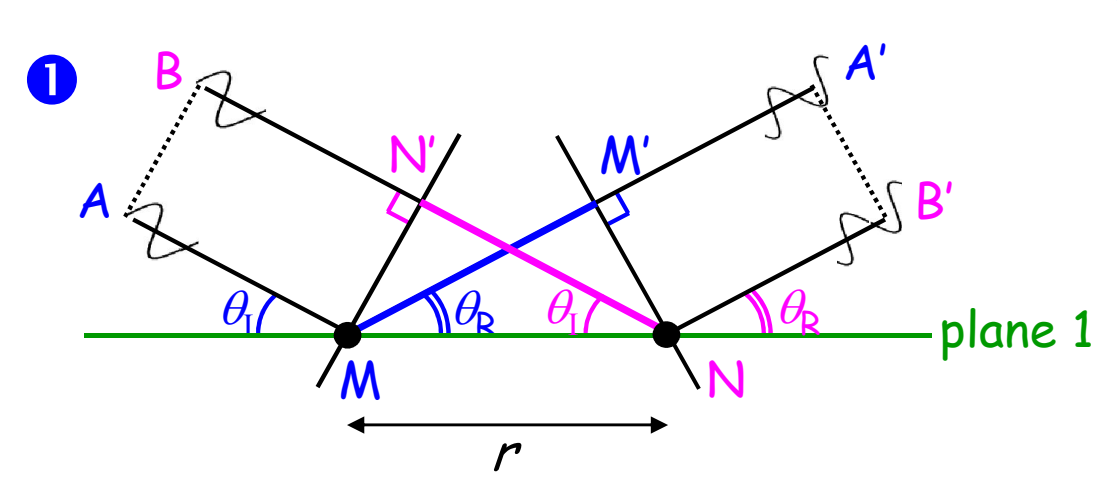
Hexagonal cell:

$$d_{hkl} = \frac{1}{\sqrt{h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hk\cos 60^\circ\ a^{*2}}}$$

$$= \frac{1}{\sqrt{\frac{4}{3a^2}\left(h^2 + k^2 + h\,k\right) + \frac{l^2}{c^2}}}$$

a- Bragg's law

The beams scattered by any lattice nodes must be in phase in order to get constructive interferences → difference in path δ has to be a multiple of the wavelength λ



$\forall$ M, N: δ = MM' – NN' = $n\,\lambda$ (n integer)

$\rightarrow$ $\forall$ r: $r\,(\cos\theta_R - \cos\theta_I) = n\,\lambda$

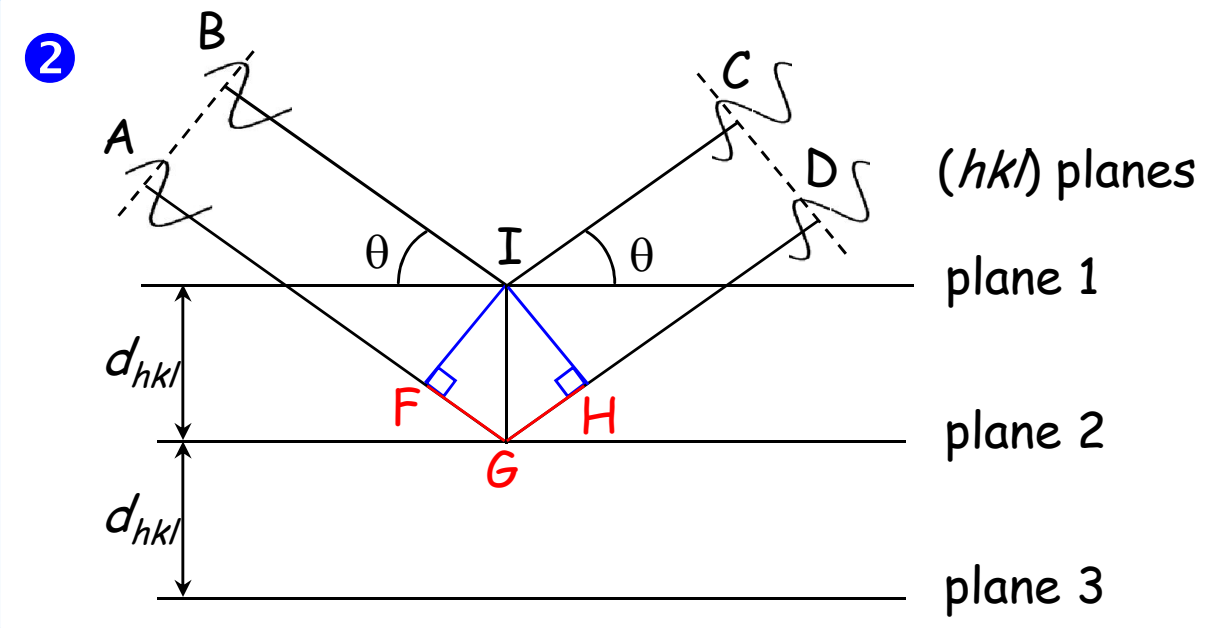
⇩

Descartes' law, as for optics:

$\theta_I = \theta_R$ (n = 0)

Diffraction by a 2D lattice of nodes ⇔ reflection on the net plane containing the nodes

II.2. Diffraction: *Diffraction condition*



$\delta = FG + GH = n\lambda$ (n integer)

with $FG = GH = \sin\theta \,.\, d_{hkl}$

$$\boxed{n\lambda = 2\, d_{hkl} \sin\theta}$$

Bragg's law

A family of (hkl) net planes of the crystal diffracts with different orders n only for discrete angle values given by the Bragg's law → Bragg peaks hkl

- $n\lambda \leq 2d_{hkl} \Rightarrow \lambda$ **musn't be too large**
- $n\lambda = 2d_{hkl}\sin\theta$

  for a P lattice:

  h, k, l = coprime integers

  $\Leftrightarrow$

  $\lambda = 2d_{h'k'l'}\sin\theta$ with $d_{h'k'l'} = \dfrac{d_{hkl}}{n}$

  $\Rightarrow h' = nh,\ k' = nk,\ l' = nl$

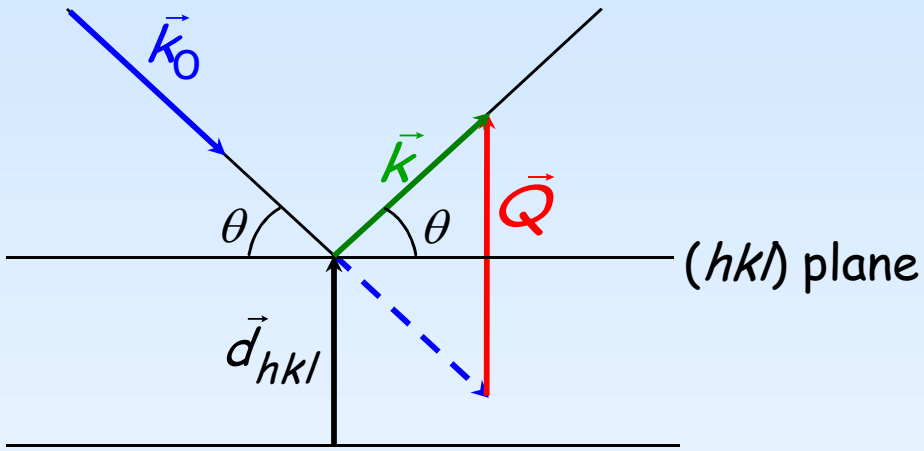
  h', k', l' are now any integers

II.2. Diffraction: *Diffraction condition*

❸ $\vec{k}_0$ = incident wave vector
$\vec{k}$ = diffracted wave vector

scattering vector $\vec{Q} = \vec{k} - \vec{k}_0$

$$|\vec{k}_0| = |\vec{k}| = \frac{1}{\lambda}$$



By construction (Descartes law and $k = k_0 = \frac{1}{\lambda}$):

we see that $\boxed{\vec{Q} \parallel \vec{d}_{hkl}}$ and $Q = \frac{2\sin\theta}{\lambda}$

The Bragg's law $n\lambda = 2d_{hkl}\sin\theta$

can thus be rewritten: $\boxed{Q = \frac{n}{d_{hkl}}}$

⇒ the diffraction condition can be reformulated as follows:

The scattering vector must be a vector of the reciprocal lattice

Its extremity must be a point from a row [*hkl*]* passing through the origin of the RS ⊥ to the family of (*hkl*) net planes in DS: $\vec{Q} = n\left(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*\right) = h'\vec{a}^* + k'\vec{b}^* + l'\vec{c}^*$

b- Ewald's construction

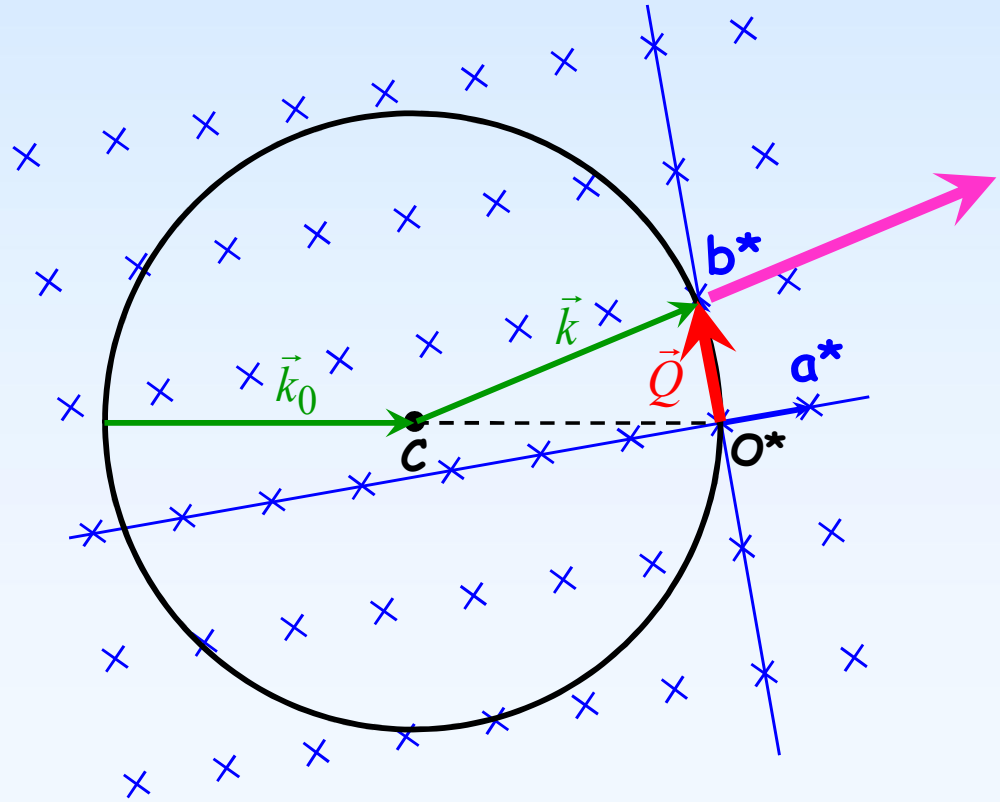
This construction allows to predict all directions of diffraction, which, for a given wavelength, only depend on the lattice parameters of the studied crystal.

Let us consider a monochromatic incident beam of X-rays or neutrons

Diffraction occurs if $\vec{Q}$ is a vector of the reciprocal lattice

⇕

Diffraction occurs each time a lattice node intersects the Ewald sphere

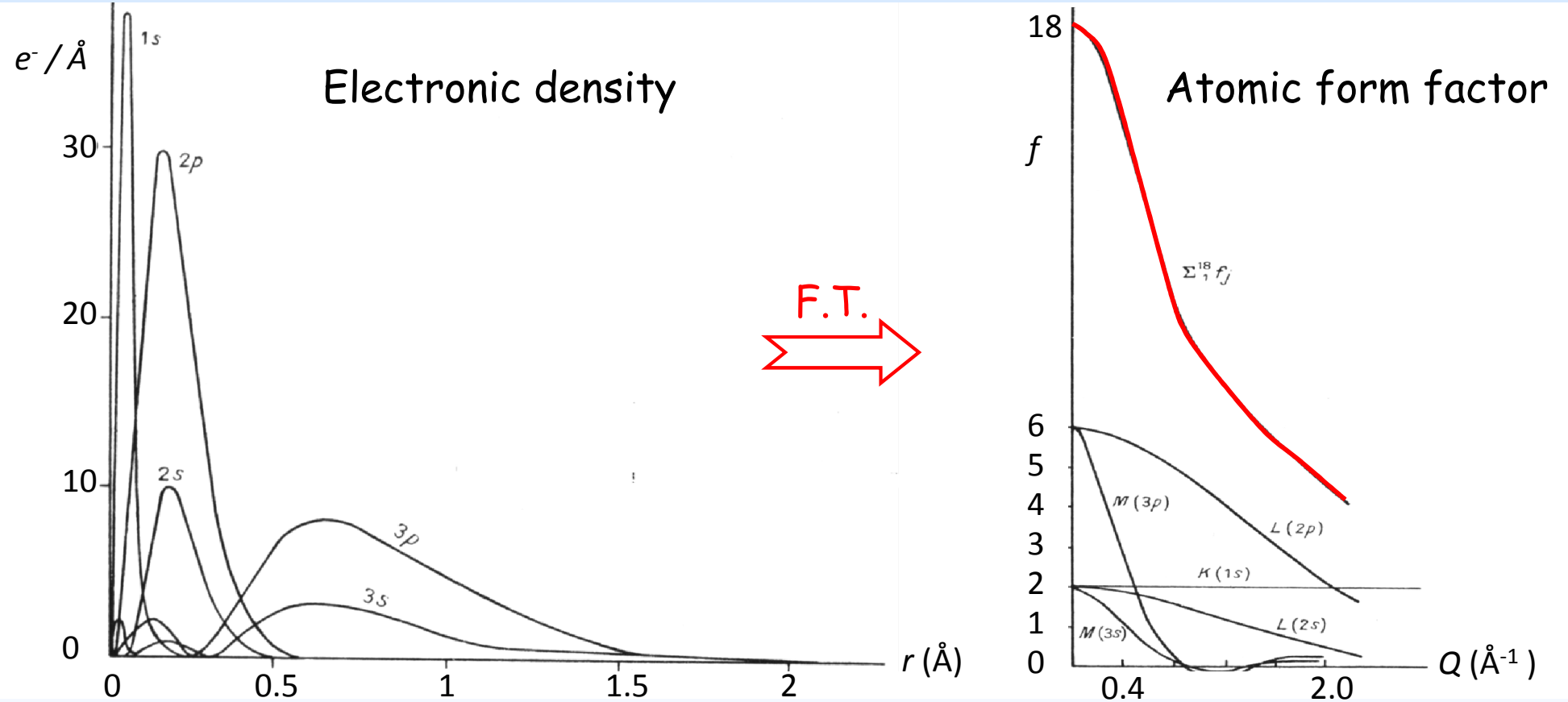


II.2. Diffraction by an atom: *Scattered amplitude*

a- <u>X-rays</u> Photons scattered by the electronic cloud of atoms: electronic interaction
Size of electronic cloud ≈ a few Å ≈ λ (X-rays)
→ destructive interferences (more and more as Q increases)

$$f(\vec{Q}) = \int_V \rho(\vec{r})\, e^{2i\pi\, \vec{Q}.\vec{r}}\, dV$$

Scattered amplitude for X-rays
= Fourier transform of the electronic density
= atomic scattering factor or atomic form factor



II.2. Diffraction by an atom: *Scattered amplitude*

b- <u>Neutrons</u> Neutrons scattered by the nucleus of atoms: nuclear interaction*
Size of nucleus << λ (neutrons) $\rightarrow$ nuclear density $\rho(r) = \delta(r)$

Dirac function $\delta(r)$ in r-space $\Rightarrow$ constant in Q-space

$b(Q) = b = Cst$

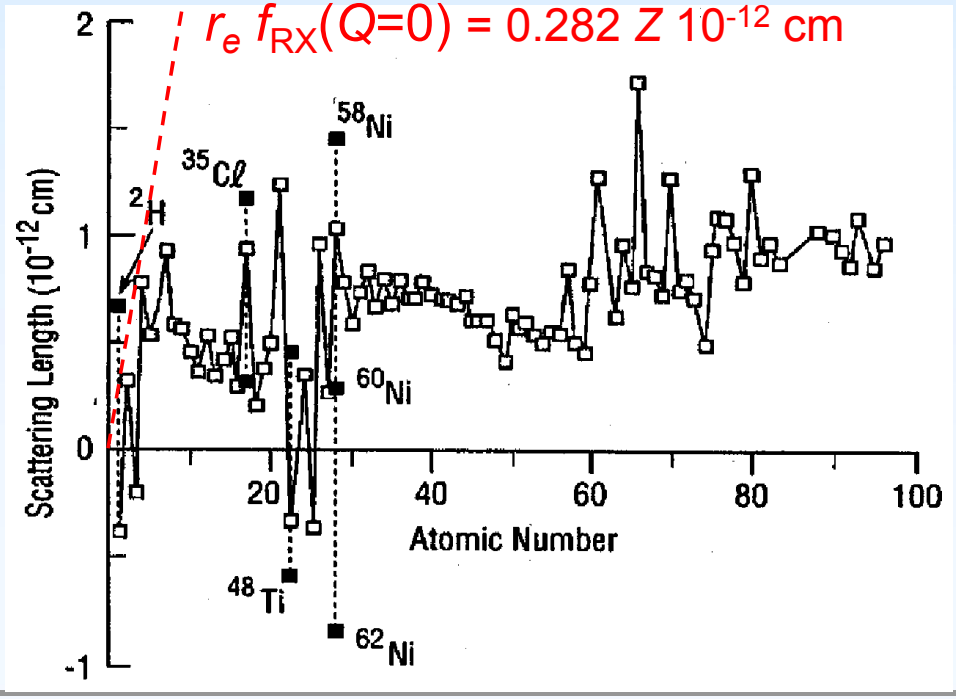
Scattered amplitude for neutrons
= Fourier transform of the nuclear density
= scattering length or Fermi length

**Neutrons are also scattered by unpaired electrons (spins): magnetic interaction*

c- <u>Comparison X-rays / Neutrons</u>

X-rays:
- $f \searrow$ when $\theta \nearrow$
- $f \propto Z$

Neutrons:
- $b(\theta) = Cte$
- b varies erratically with Z and A (chemical nature and isotope)



II.2. Diffraction by a crystal: *Structure factor*

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

Scattered amplitude by a unit cell
= Fourier transform of the atomic density of the cell
= structure factor

with $\begin{cases} a_j = f_j(Q) \text{ or } b_j \\ \vec{Q} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \\ \vec{r}_j = x_j\vec{a} + y_j\vec{b} + z_j\vec{c} \end{cases}$

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

Diffracted intensity

$$I(\vec{Q}) \propto \left| \sum_{j=1}^{N} a_j \, e^{2i\pi(hx_j + ky_j + lz_j)} e^{-W_j} \right|^2 \delta(\vec{Q} - \vec{\tau})$$

Structure factor $F(Q)$
related to the motif
(nature and positions of the atoms)
⇒ governs the amplitudes of diffraction

Dirac function
related to the direct lattice
(periodicity of the structure)
⇒ governs the directions of diffraction

We find again the two concepts that characterize a crystal

II.2. Diffraction by a crystal: *Structure factor*

The phase problem

In the most general case, the structure factor is a complex number and can be written as follows: $F\left(\vec{Q}\right) = \left|F\left(\vec{Q}\right)\right| e^{i\phi}$

The structure factor is the quantity which we are interested in: it contains the atomic positions x_j, y_j, z_j.

We measure: $I\left(\vec{Q}\right) = F^*\left(\vec{Q}\right).F\left(\vec{Q}\right) = \left|F\left(\vec{Q}\right)\right|^2$

$\Rightarrow$ we do not access to the scattered amplitude but only to the intensity: the information concerning the phase is lost.

II.2. Diffraction: *Symmetry and Extinction rules*

Effect in the RS of a symmetry operation from the DS:

- **Symmetry** of the reciprocal space given by the **Laue class** (inversion always there) * +

- **Systematic extinctions** given by the **space group**

→ they lead to a systematic absence of intensity of Bragg reflections concerned by this extinction rule, and this, independently from the atomic positions in the cell.

Lattice type (if not *P*)
→ "artificial" extinction (due to the fact that a centered cell was chosen)

Symmetry operations containing a glide translation*
= non symmorphic operations

- **Particular extinctions** given by the **motif** *

they concern atoms* occupying some special Wyckoff sites
→ the atoms occupying such special positions give a null contribution to the intensity of Bragg reflections concerned by this extinction rule.

* *provided the nucleus (neutrons) or electronic cloud (X-rays) of the atoms is spherical*
\+ *provided the Fermi length (neutrons) or atomic form factor (X-rays) is real*

II.2. Diffraction: *Symmetry and Extinction rules*

Example of a glide plane $a \perp [001]$ at $z = 1/4$

→ Reflection trough a plane ⊥ [001] with the glide translation $\frac{\vec{a}}{2}$

→ equivalent positions: $\left(x_j \; y_j \; z_j\right)$ and $\left(x_j + \frac{1}{2} \quad y_j \quad \bar{z}_j + \frac{1}{2}\right)$

The structure factor $F(hkl) = \sum_{j=1}^{N} a_j e^{2i\pi\left(hx_j + ky_j + lz_j\right)}$ can thus be split in two parts:

→ $F(hkl) = \sum_{j=1}^{N/2} a_j \left\{ e^{2i\pi\left(hx_j + ky_j + lz_j\right)} + e^{2i\pi\left[h\left(x_j + \frac{1}{2}\right) + ky_j + l\left(\frac{1}{2} - z_j\right)\right]} \right\}$

→ $F(hkl)$ cannot be completely factorized except for $l = 0$

→ $F(hk0) = \left[1 + e^{i\pi h}\right] \sum_{j=1}^{N/2} a_j \, e^{2i\pi\left(hx_j + ky_j\right)}$

Extinction

$$\Rightarrow \begin{cases} F(hk0) = 0 & \text{if} \quad h = 2n+1 \\ F(hk0) \neq 0 & \text{if} \quad h = 2n \end{cases}$$

Reflection condition

II.2. Diffraction: *Symmetry and Extinction rules*

Systematic extinctions due to the lattice type

Primitive lattice: no extinction

Centered lattice: direct cell m times too large $\rightarrow$ reciprocal cell m times too small

$\rightarrow$ systematic absence of intensity on some hkl spots

Ex. I lattice $\rightarrow$ additional lattice translation $\frac{1}{2}\left(\vec{a}+\vec{b}+\vec{c}\right)$ in DS $\rightarrow 2\left(\vec{a}^{*}+\vec{b}^{*}+\vec{c}^{*}\right)$ in RS

$\rightarrow$ reflection condition for hkl : $h+k+l=2n$

Systematic extinctions due to non symmorphic symmetry operations

Ex. plane $a \perp \vec{c}$ $\rightarrow$ extinction concerning Bragg peaks $hk0$ (plane $\perp \vec{c}^{*}$ through O*)

& glide translation $\vec{t}=\frac{1}{2}\vec{a}$ in DS $\rightarrow$ $\vec{t}^{*}=2\vec{a}^{*}$ in RS

$\rightarrow$ reflection condition for $hk0$: $h=2n$

Ex. axis $2_1 // \vec{b}$ $\rightarrow$ extinction concerning Bragg peaks $0k0$ (row$//\vec{b}^{*}$ through O*)

& glide translation $\vec{t}=\frac{1}{2}\vec{b}$ in DS $\rightarrow$ $\vec{t}^{*}=2\vec{b}^{*}$ in RS

$\rightarrow$ reflection condition for $0k0$: $k=2n$

II.2. Diffraction: *Symmetry and Extinction rules*

<u>Example</u>: Space group Cc (glide plane $c \perp \vec{b}$)

- *Symmetry* :

Laue class: $2/m$ → same intensity for: hkl, $\underbrace{h\bar{k}l}_{\text{mirror } m\perp\vec{b}}$, $\underbrace{\overbrace{\bar{h}\bar{k}\bar{l}}^{\text{inversion}}, \text{ and } \overbrace{\bar{h}k\bar{l}}^{\text{axis } 2\|\vec{b}}}_{\text{2 previous Bragg peaks} \times \bar{1}}$

- *Reflection conditions* :

C-centering → reflection condition: hkl with $h+k=2n$

c glide plane → reflection condition: $h0l$ with $l=2n$

The International Tables for Crystallography

- **Example: *Pnma***

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
8	d	1	(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$	(3) $\bar{x},y+\frac{1}{2},\bar{z}$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$	$0kl$: $k+l=2n$
			(5) $\bar{x},\bar{y},\bar{z}$	(6) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$	(7) $x,\bar{y}+\frac{1}{2},z$	(8) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$	$hk0$: $h=2n$
							$h00$: $h=2n$
							$0k0$: $k=2n$
							$00l$: $l=2n$
							Special: as above, plus
4	c	$.m.$	$x,\frac{1}{4},z$	$\bar{x}+\frac{1}{2},\frac{3}{4},z+\frac{1}{2}$	$\bar{x},\frac{3}{4},\bar{z}$	$x+\frac{1}{2},\frac{1}{4},\bar{z}+\frac{1}{2}$	no extra conditions
4	b	$\bar{1}$	$0,0,\frac{1}{2}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	hkl : $h+l$, $k=2n$
4	a	$\bar{1}$	$0,0,0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	hkl : $h+l$, $k=2n$

- glide plane $n \perp a$-axis
- glide plane $a \perp c$-axis
- diad axis 2_1 // a-axis
- diad axis 2_1 // b-axis
- diad axis 2_1 // c-axis

Reflection conditions

General

If the reflection condition is not fulfilled, the diffracted intensity is null

Special

The contribution to the diffracted intensity of atoms located on special positions is null if the condition is not fulfilled

II.3. Experiments: *How to solve a crystallographic structure*

❶ Symmetry of the diffraction pattern → Laue class

❷ Positions of Bragg reflections → Lattice parameters

Direction of the diffracted beams (2θ) ⇒ Better precision at large angle

$\lambda = 2\, d_{hkl} \sin\theta$ ⇒ *long wavelength and/or large Miller indices (small d_{hkl})*

❸ Extinction rules → Possible space group(s)

❹ Intensities of the Bragg peaks → Structure determination

There are as many F(hkl) as measured hkl Bragg peaks (h, k, l any integers)
⇒ measure up to large Q

$\lambda = 2\, d_{hkl} \sin\theta \;\Rightarrow\; Q \leq \frac{2}{\lambda}$ ⇒ short wavelength (in particular for large unit cells)

⚠ Phase problem: *Patterson function, direct methods, …*

II.3. Experiments: *How to solve a crystallographic structure*

❶ Symmetry of the diffraction pattern → Laue class

→ Laue diffraction

❷ Positions of Bragg reflections → Lattice parameters

→ Powder or single-crystal diffraction

❸ Extinction rules → Possible space group(s)

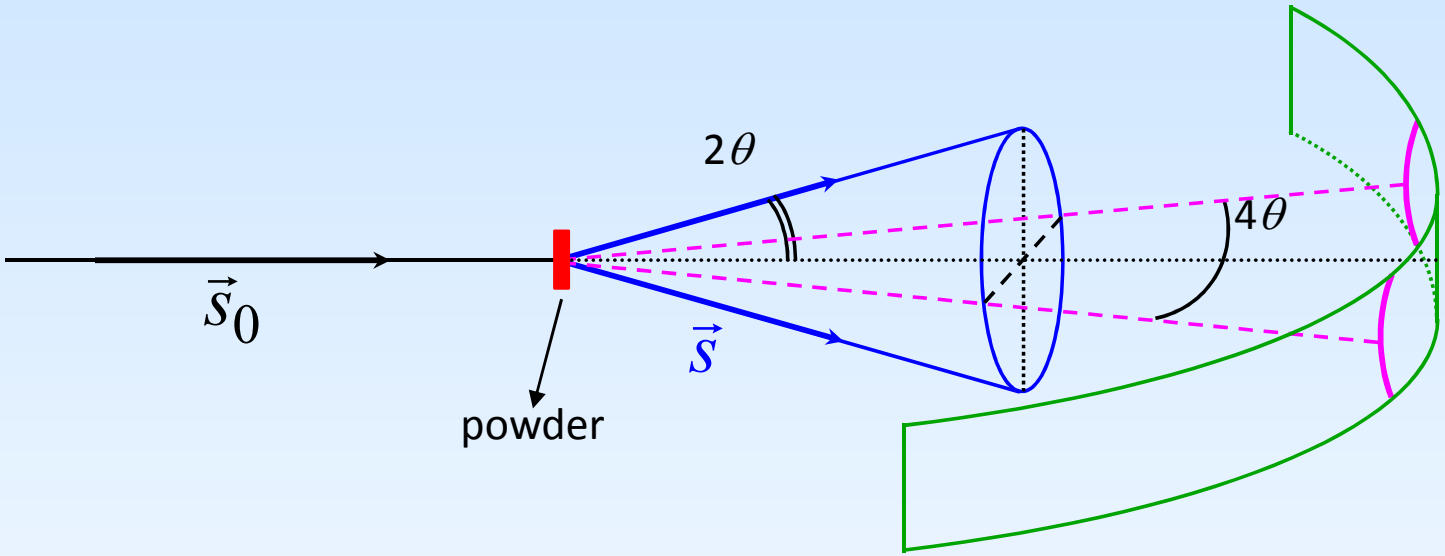
→ single-crystal diffraction

❹ Intensities of the Bragg peaks → Structure determination

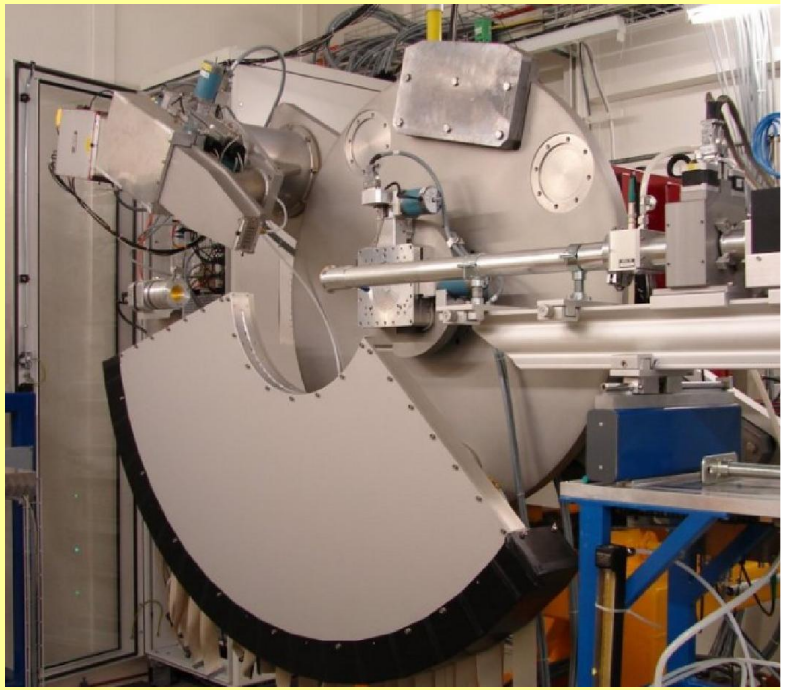
→ Laue, powder or single-crystal diffraction

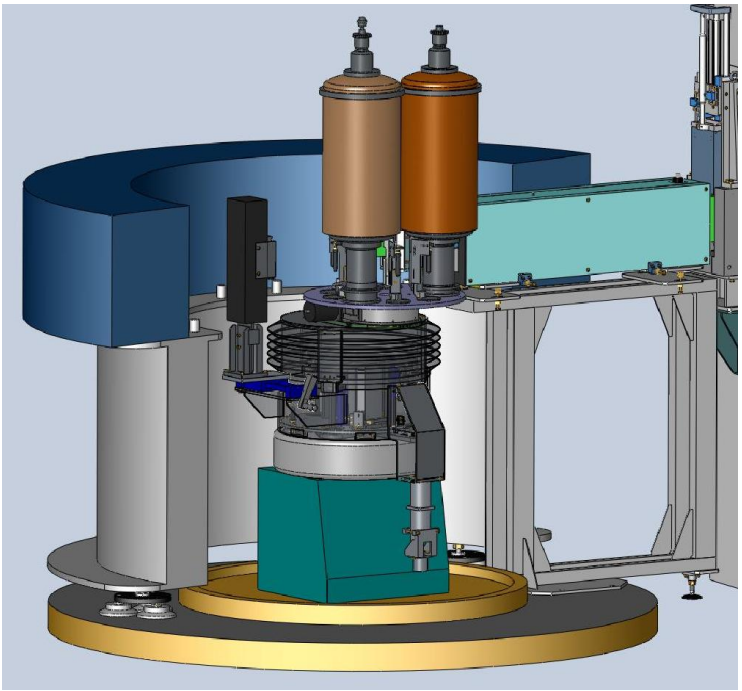
⚠ Phase problem: *Patterson function, direct methods, …*

II.3. Experiments: *Technique 1 – powder diffraction*

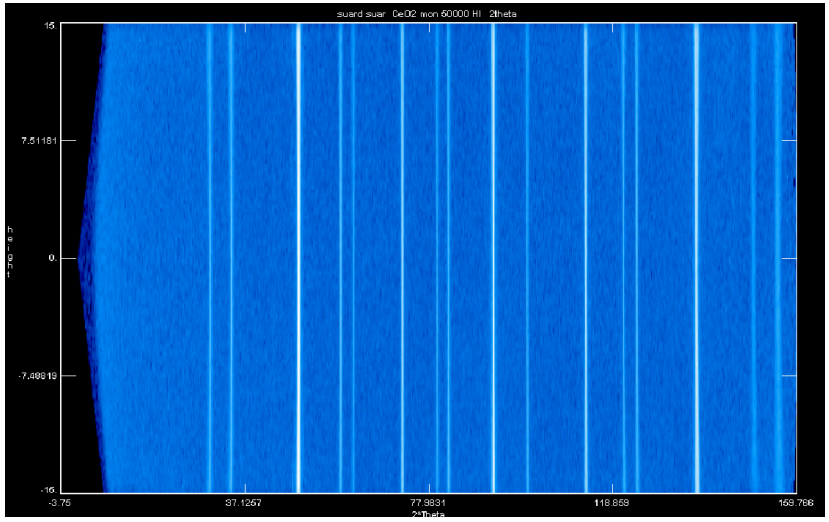


II.3. Experiments: *Technique 1 – powder diffraction*

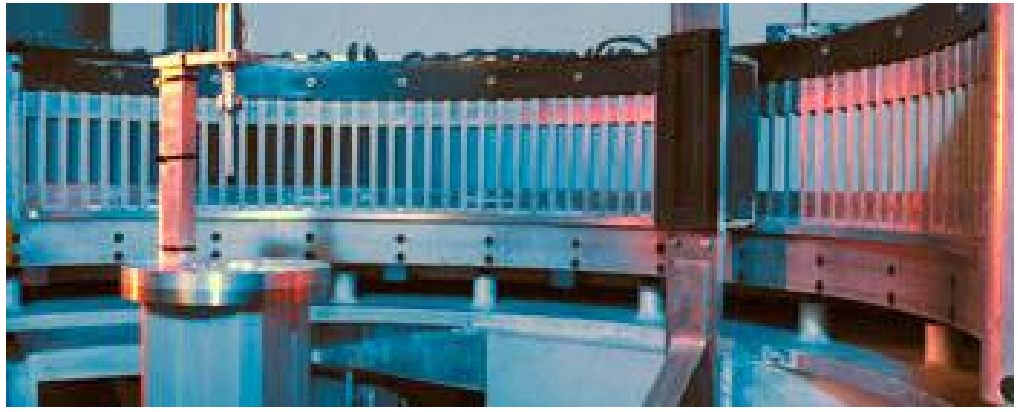




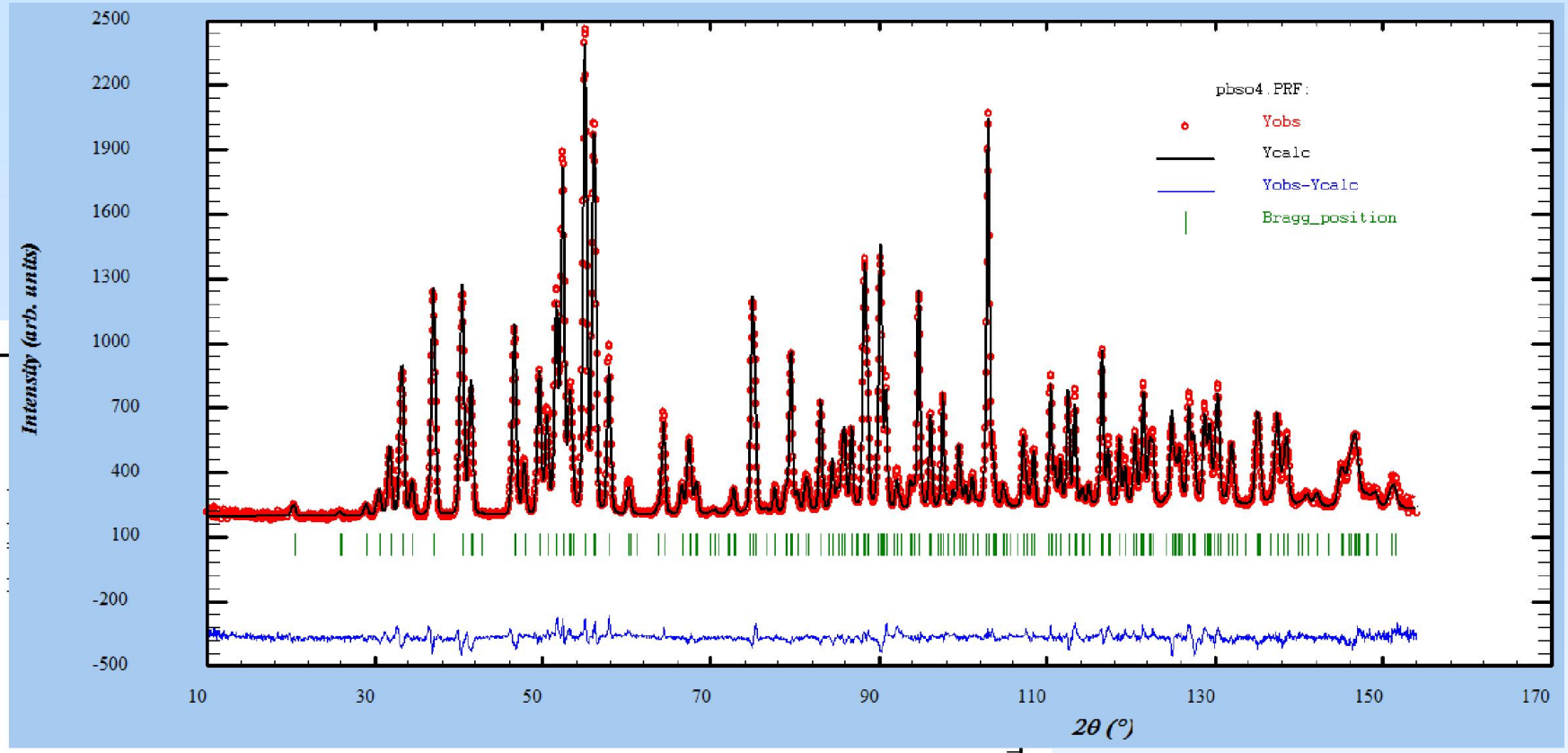
X-ray powder diffractometer @ SLS

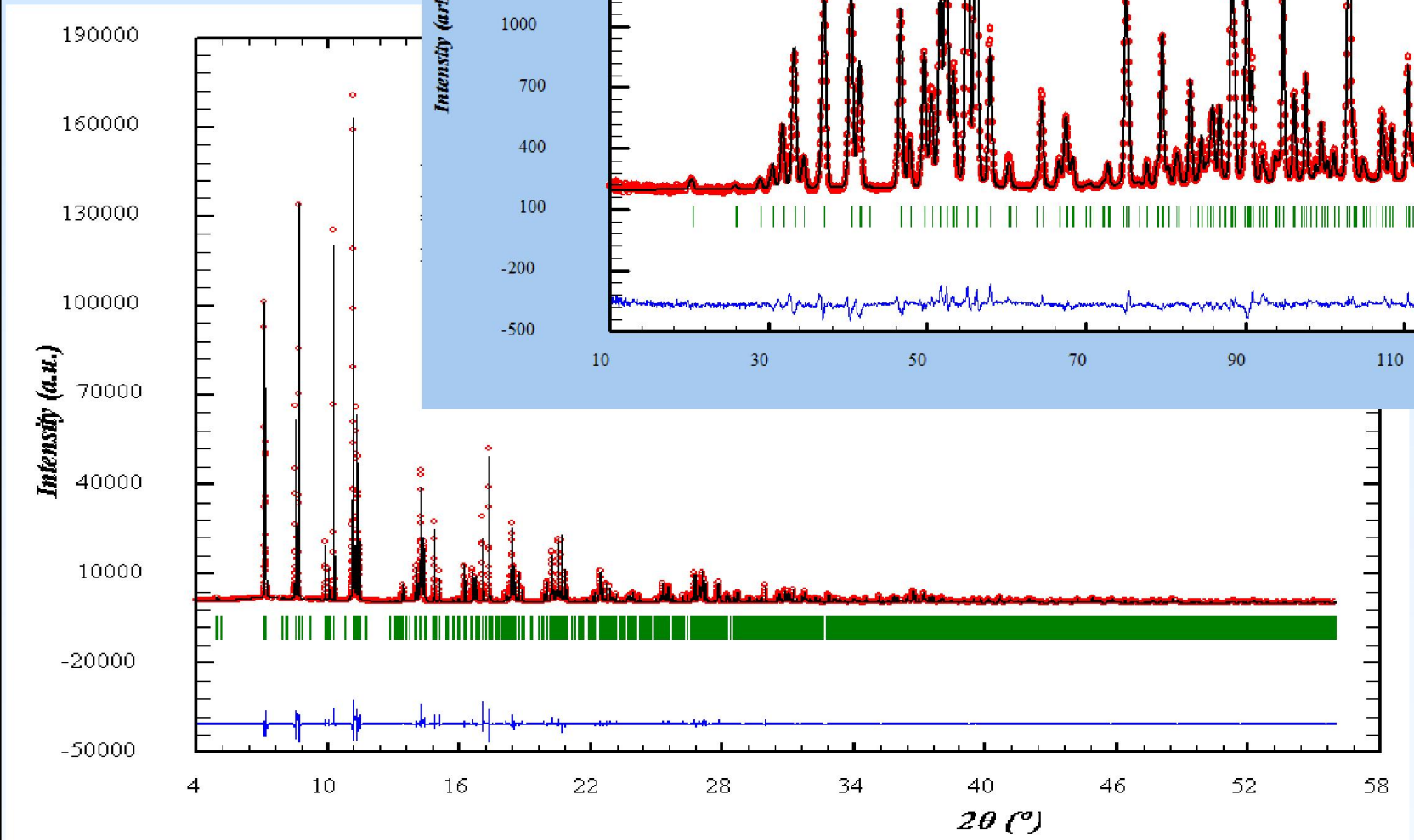


Neutron powder diffractometer @ ILL

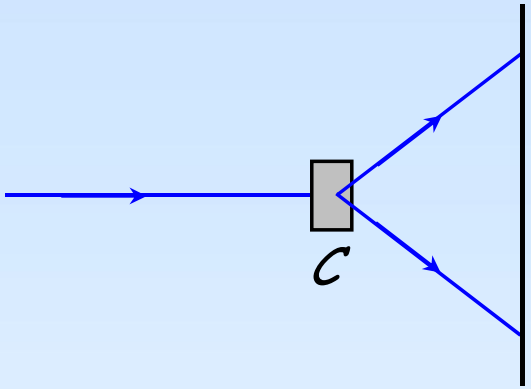


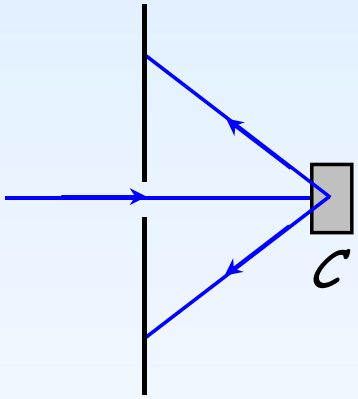
II.3. Experiments: *Technique 1 – powder diffraction*

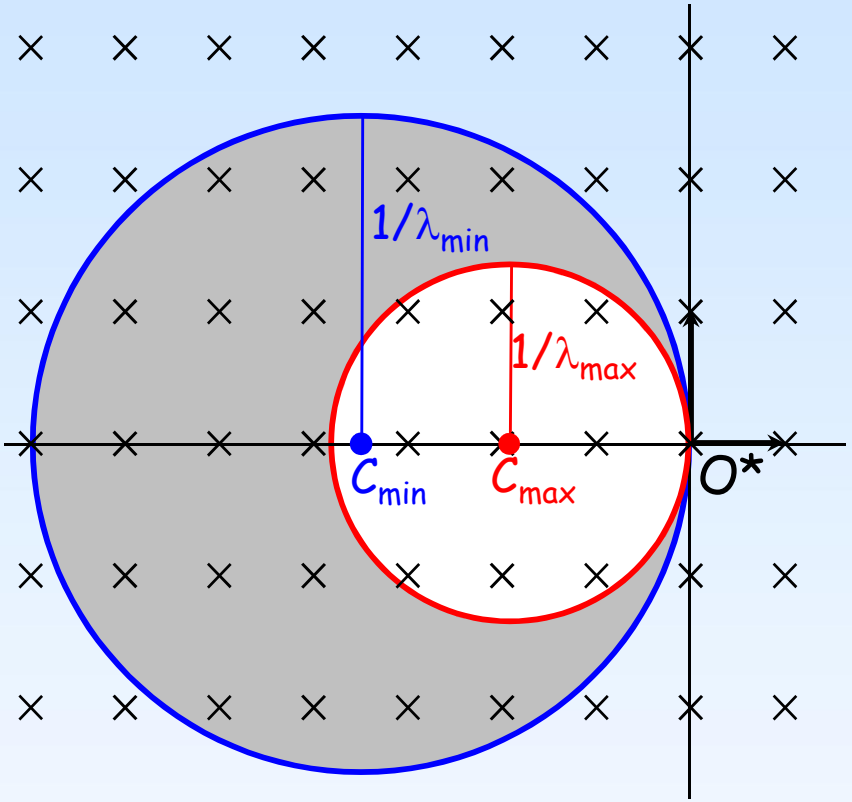




II.3. Experiments: *Technique 2 – single-crystal Laue diffraction*





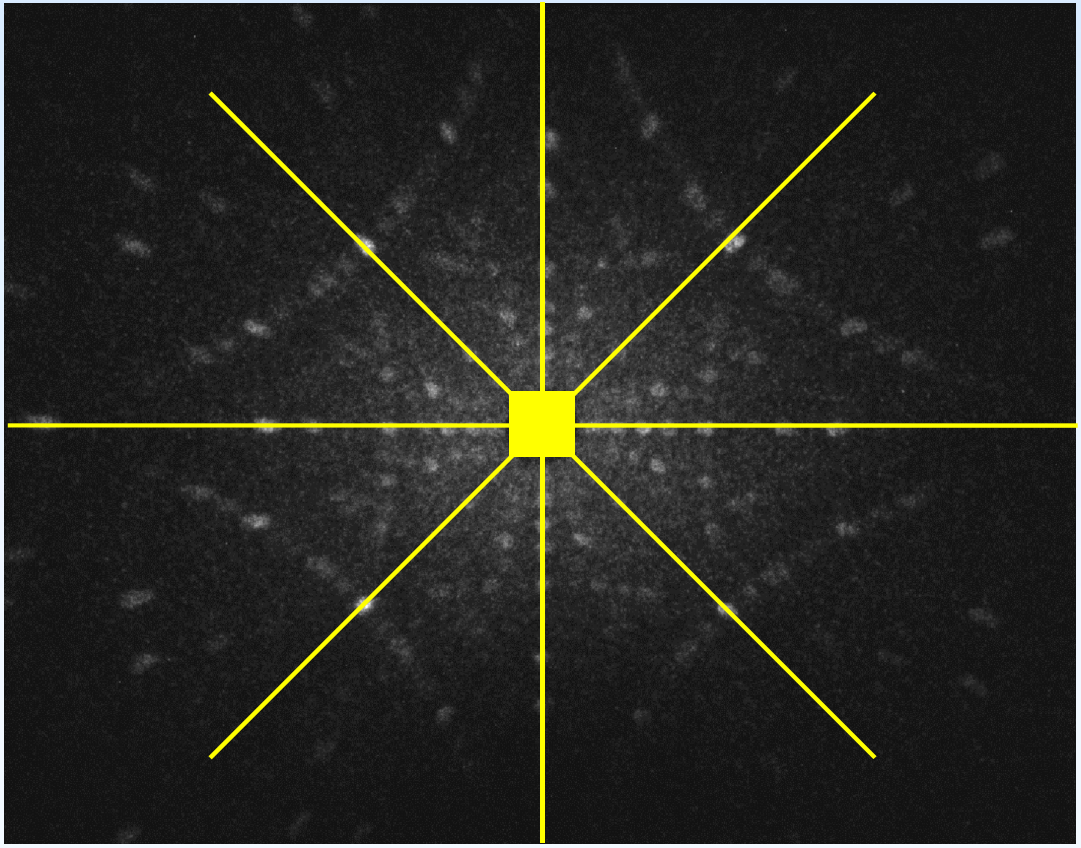


II.3. Experiments: *Technique 2 – single-crystal Laue diffraction*

OrientExpress @ ILL

→ diffraction pattern = Laue diagram evidencing the symmetry planes and axes in reciprocal space

→ Determine the Laue class, align a crystal, …

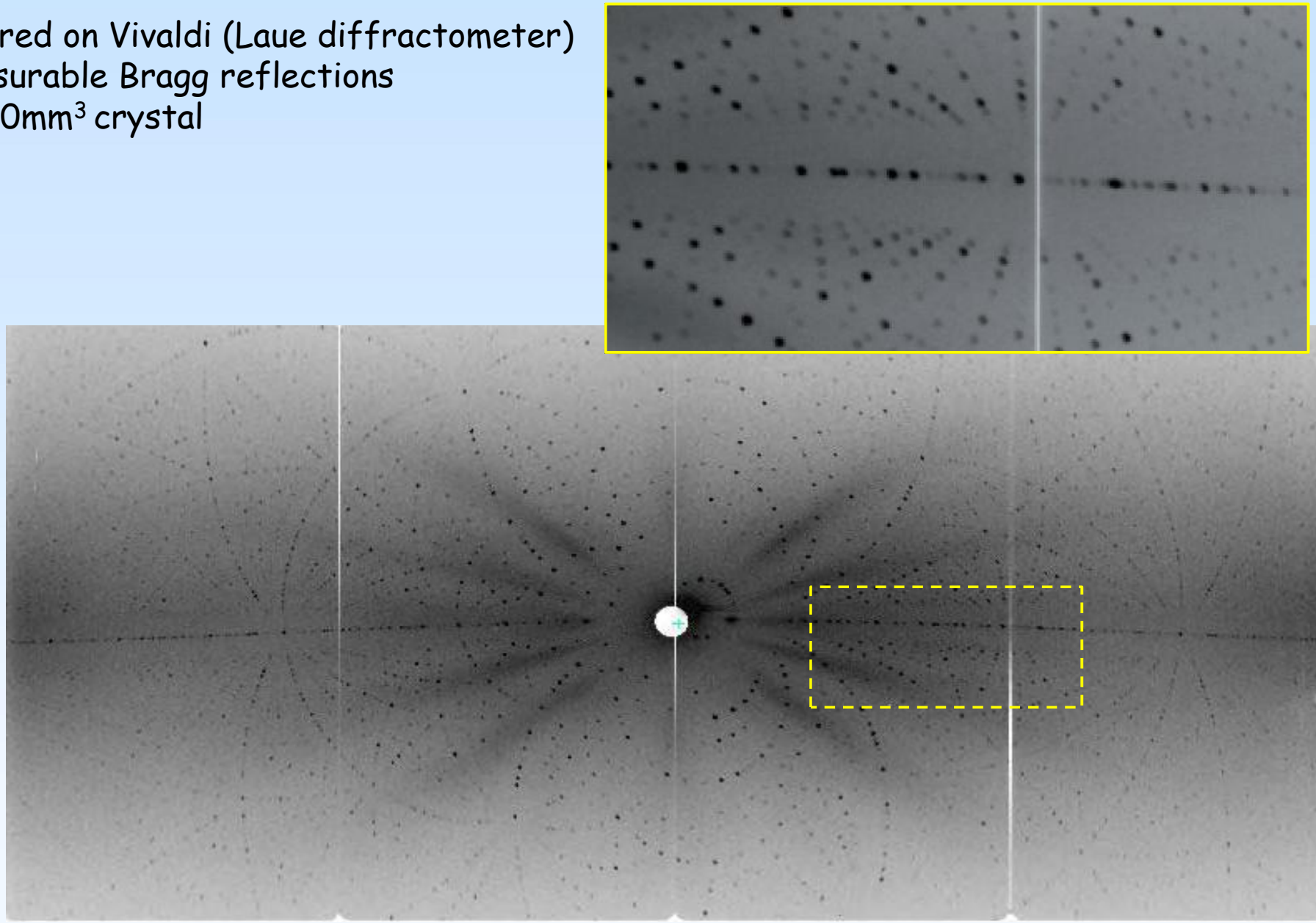


$BaCo_2V_2O_8$
Laue pattern showing the symmetries

II.3. Experiments: *Technique 2 – single-crystal Laue diffraction*

Vitamin B12 measured on Vivaldi (Laue diffractometer)
Nearly 10000 measurable Bragg reflections
8-hour exposure, 10mm^3 crystal

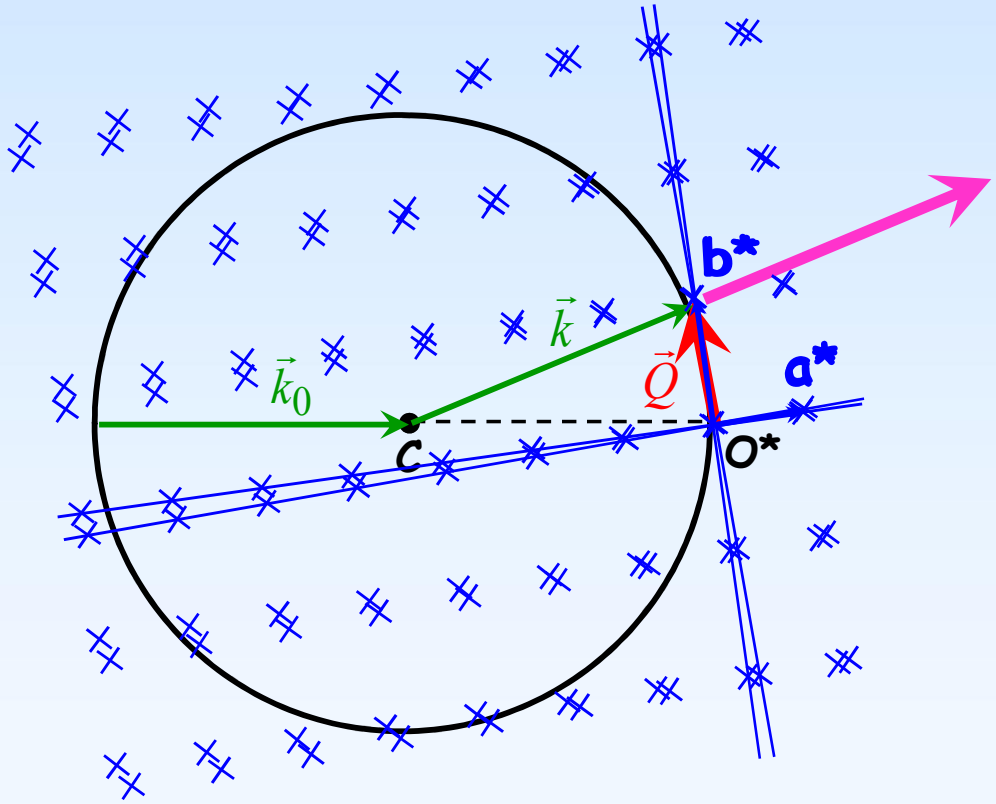
VIVALDI @ ILL



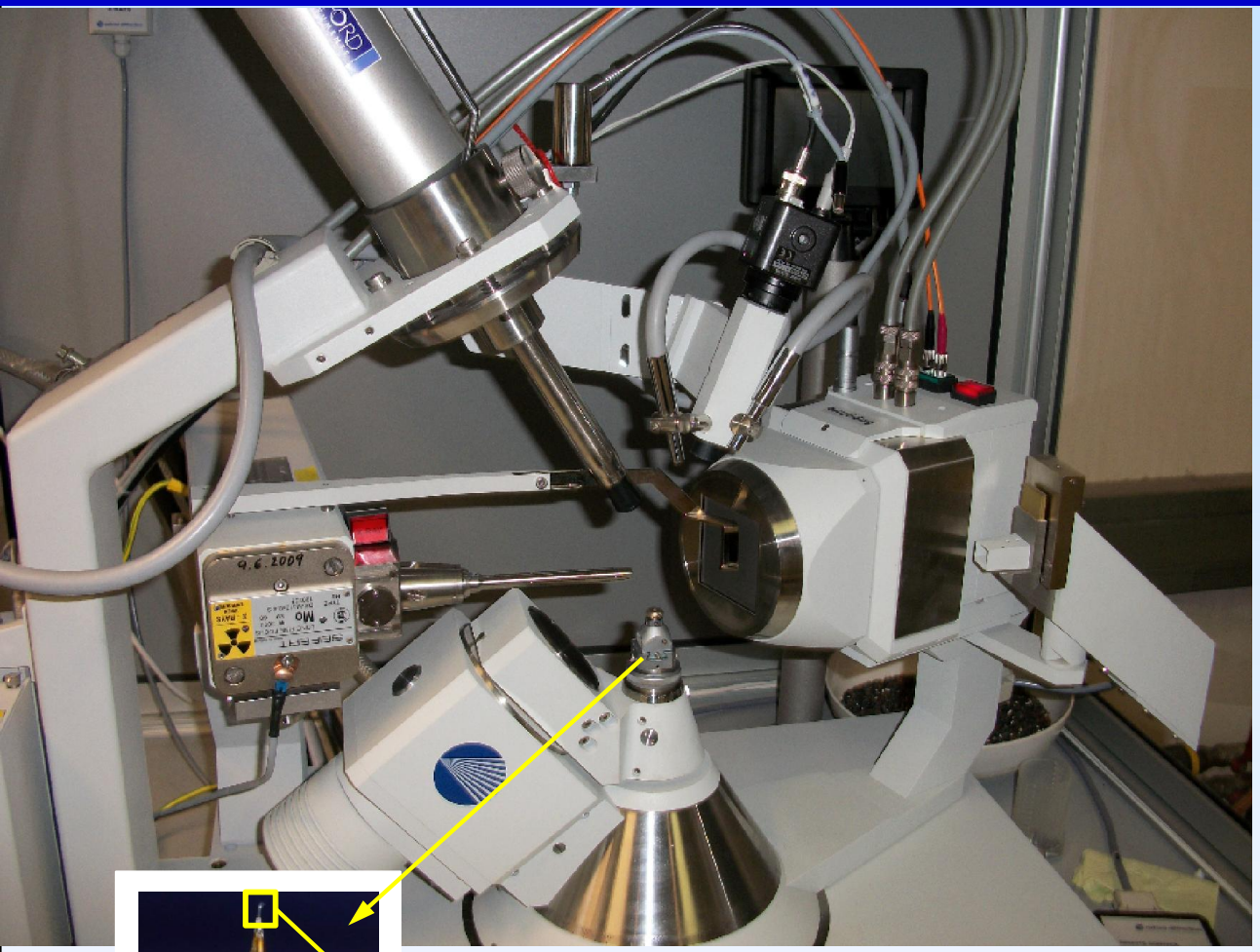
Wagner, Luger, Mason, McIntyre (2002) – ILL

II.3. Experiments: *Technique 3 – single-crystal diffraction*

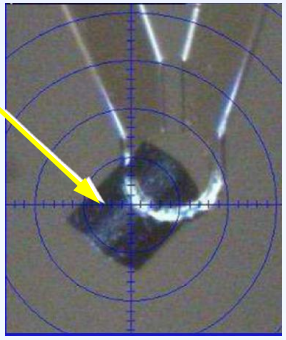
four circle / normal beam



II.3. Experiments: *Technique 3 – single-crystal diffraction (4-circle)*

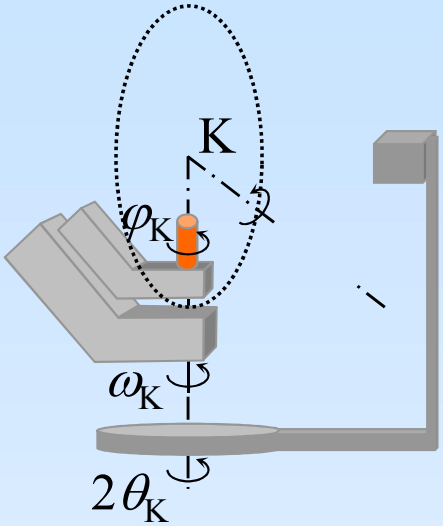


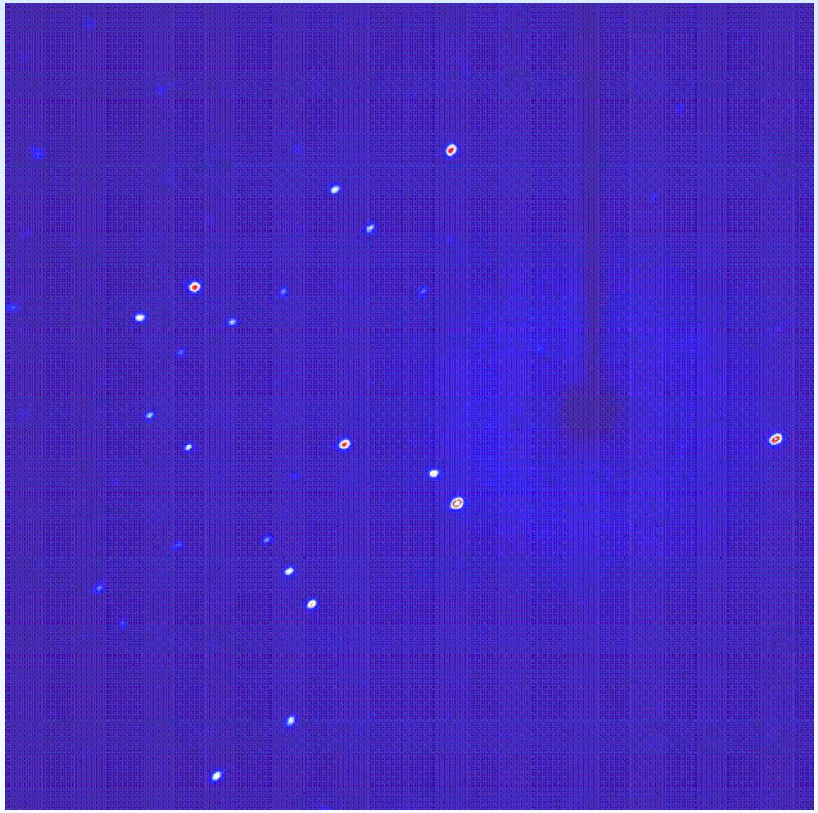
X-ray 4-circle @ CEA



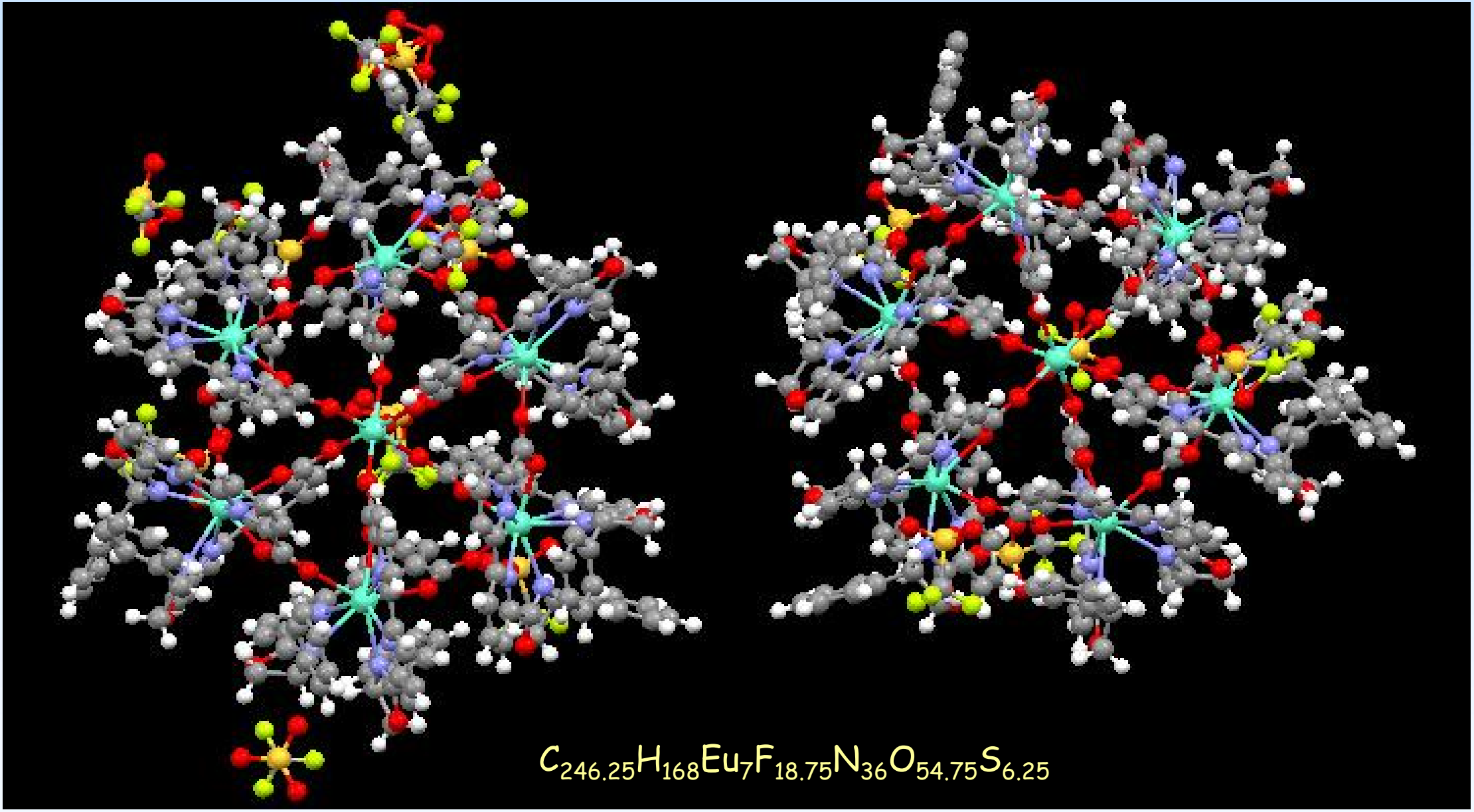
max. size ~ 150 μm

« kappa » geometry





II.3. Experiments: *Technique 3 – single-crystal diffraction (4-circle)*

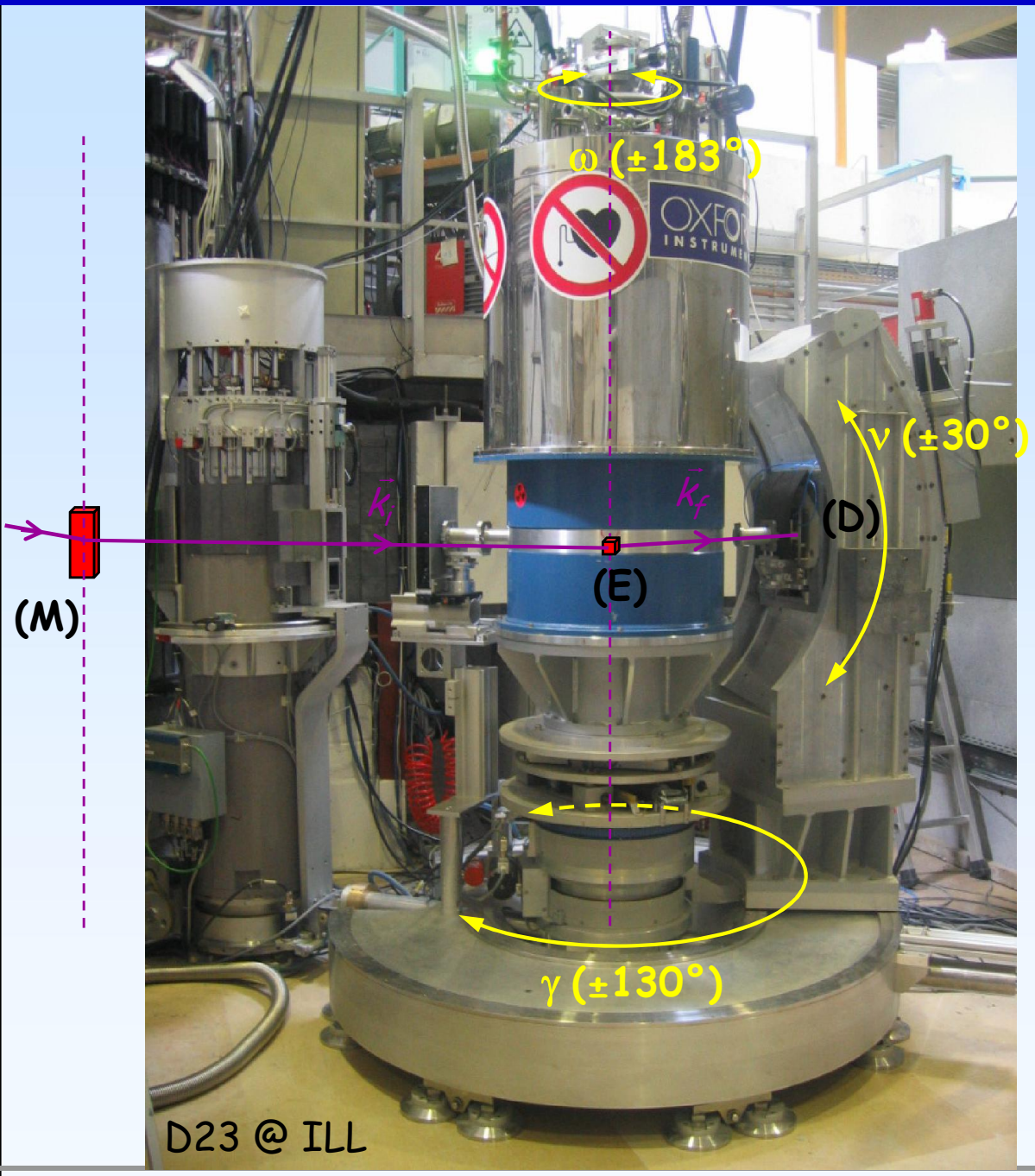


Chiral Heptanuclear Europium Wheels

Bozoklu et al. (2010) – ESRF

Space group $C2$, a = 45.7446 Å, b = 31.0966 Å, c = 45.7325 Å, β = 92.945°, Z = 8

II.3. Experiments: *Technique 3 – single-crystal diffraction (normal beam)*



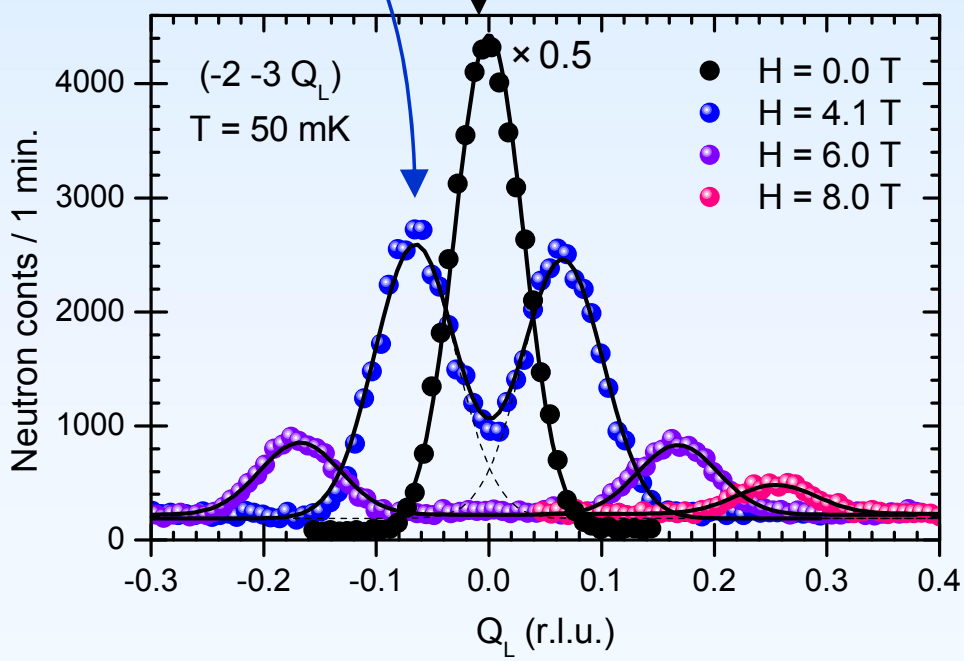
$BaCo_2V_2O_8$ (body-centered tetragonal)

$H = 0$:
Antiferromagnetic ordering

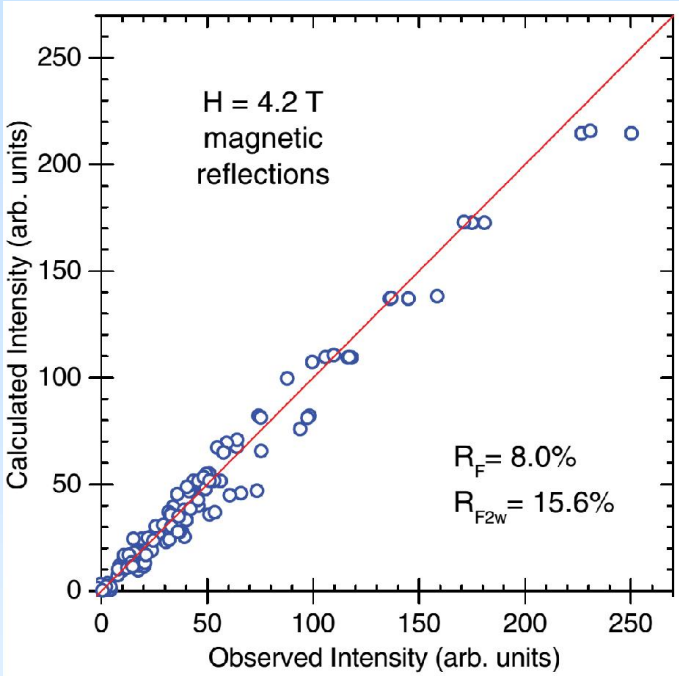
$\vec{k} = (1,0,0)$

$H > 4$ T:
Incommensurate magnetic structure

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

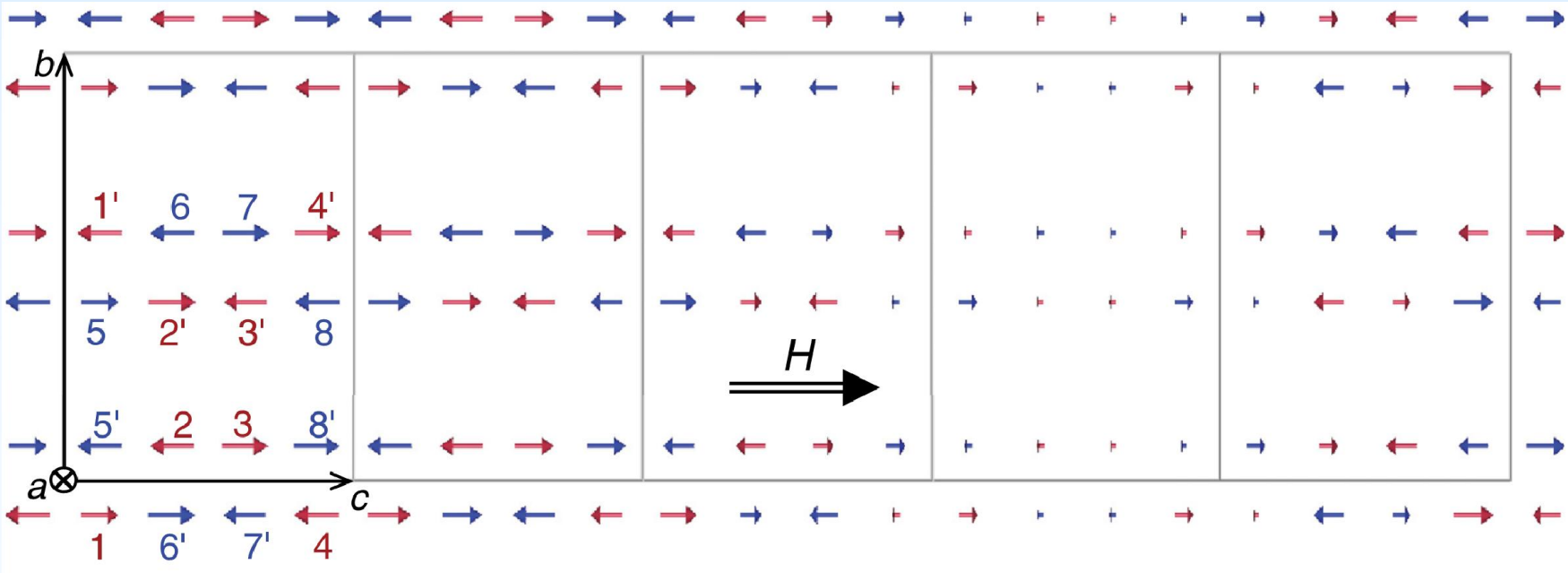


II.3. Experiments: *Technique 4 – single-crystal diffraction (normal beam)*



Collect of magnetic Bragg peaks (rocking curves)

Refinement of the magnetic structure using *e.g.* Fullprof



Thank you!

Any questions?