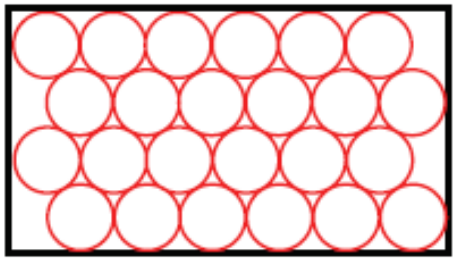
M. MORALES

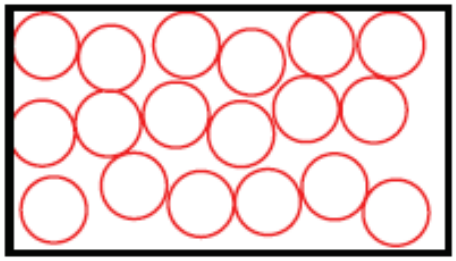
Introduction to Crystallography

magali.morales@ensicaen.fr

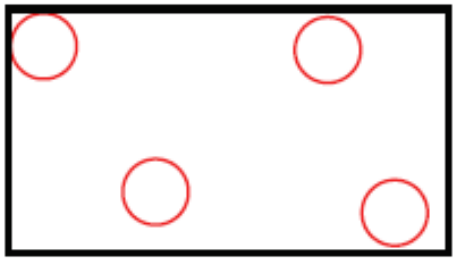
Classification of the matter in 3 states :



Crystallised solid



liquid or amorphous solid



gaz

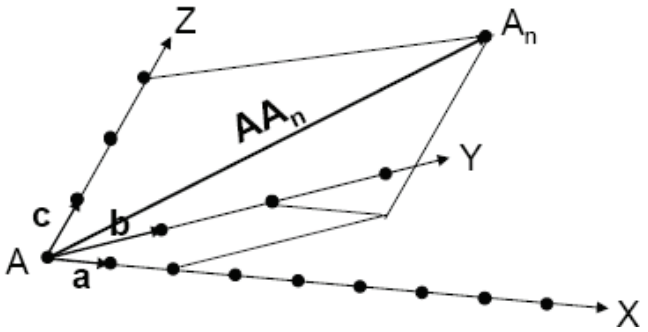
Crystallised solid :

unique arrangement of atoms + long-range order and symmetry

⬇

3D periodic array of atoms (translational periodicity) :

A_n can be deduced from A (arbitrary origin) by:



$$\overrightarrow{AA_n} = u\vec{a} + v\vec{b} + w\vec{c} = \vec{r}_{uvw}$$

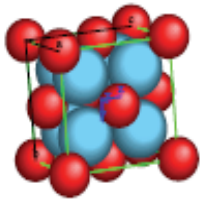
$\vec{a}, \vec{b}, \vec{c}$: direct lattice basis vectors

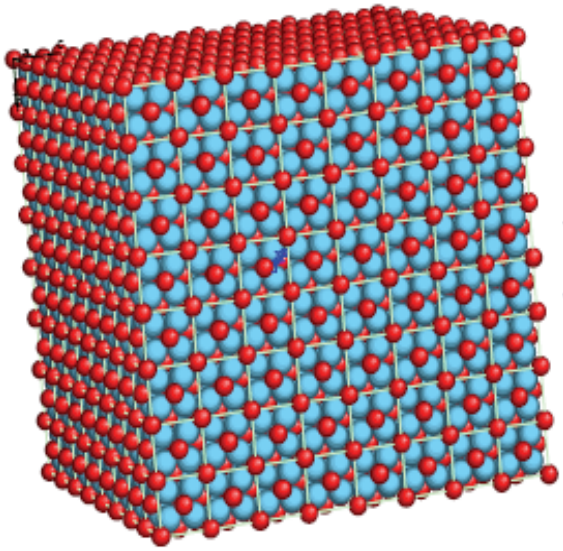
u, v, w integers

A_n is called "node"

↳ From the unit cell to the crystal :

CaF_2





Ca^{2+}

F^-

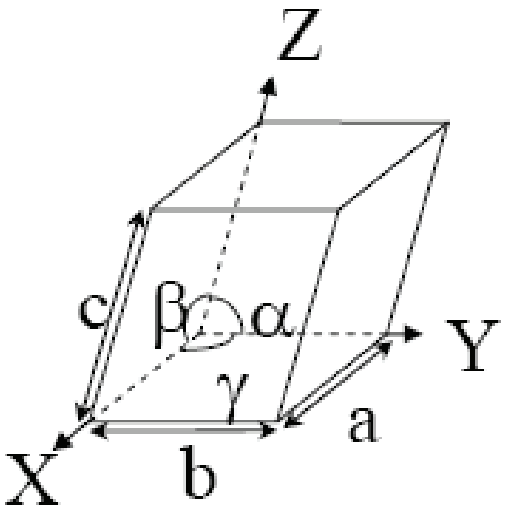
Unit cell : The smallest set of atoms arranged in a particular way.

periodically repeated in three dimensions

Macroscopic crystal

↳ The unit cell is the parallelepiped built on the crystallographic basis vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ of the direct lattice (or direct space DS).

In 3D, the unit cell is determined by 6 parameters: the a, b and c cell lengths and the α, β and γ angles.



- Unit cell volume V:

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

- Arbitrary choice of DS basis vectors ➔ unit cell multiplicity:

➥ primitive cell contains only one lattice point (1 node).

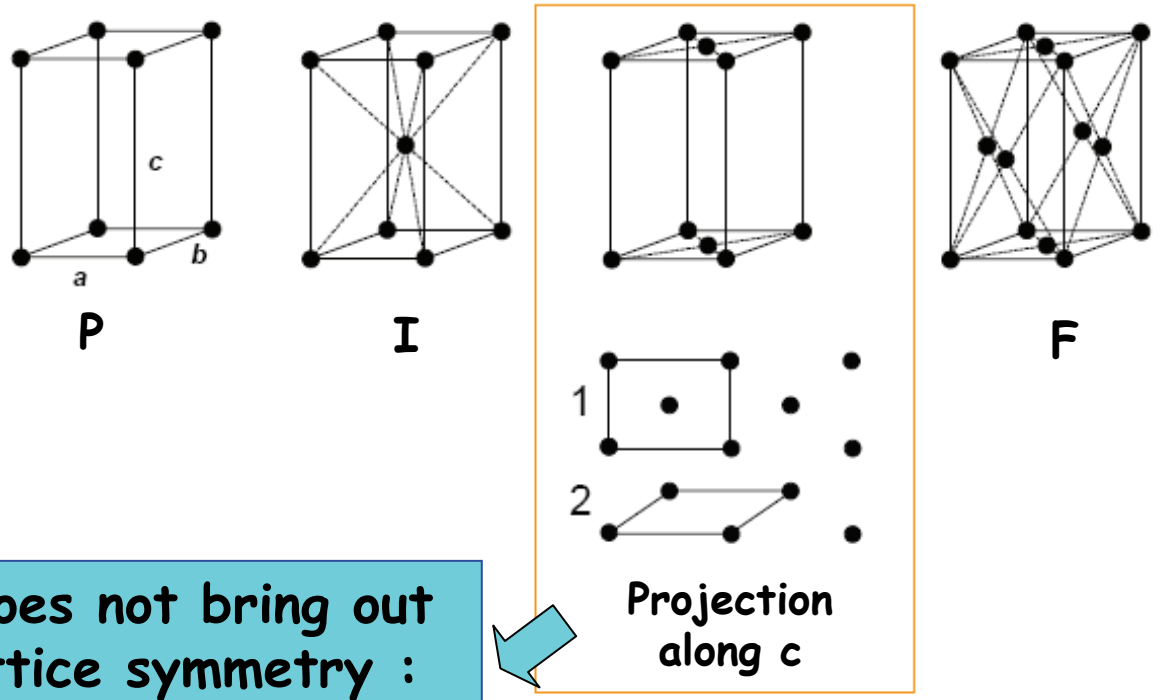
➥ Non-primitive cell (multiple cell) contains more than one node.

Multiplicity of the cell = ratio of its volume to the volume of primitive cell.

Which choice for the unit cell?

When several unit cells are possible, the choice corresponds to the smallest unit cell exhibiting all the direct lattice symmetry.

Example: Orthorombic system ($a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$):
Primitive, body centered (I), a,b or faced (F) centered unit cell

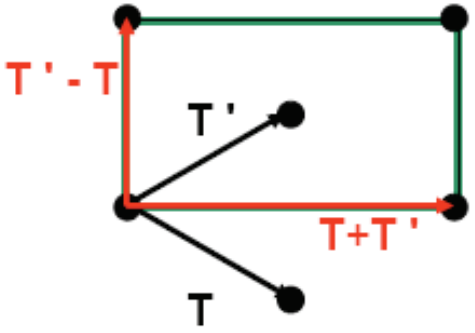


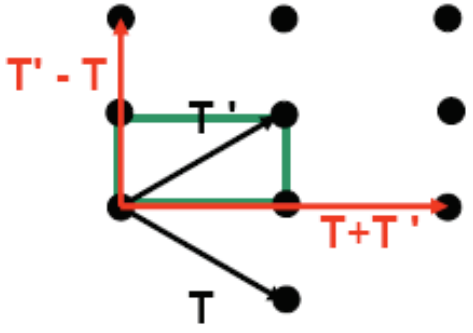
The unit cell 2 does not bring out all the direct lattice symmetry :

Conventionnal unit cell = unit cell 1

Unit cell choice:

T and T' : 2 simple translations





T+T' and T-T' are simple translations

Unit cell kept is rectangular and centered (in green)

T+T' and T-T' are not simple translations

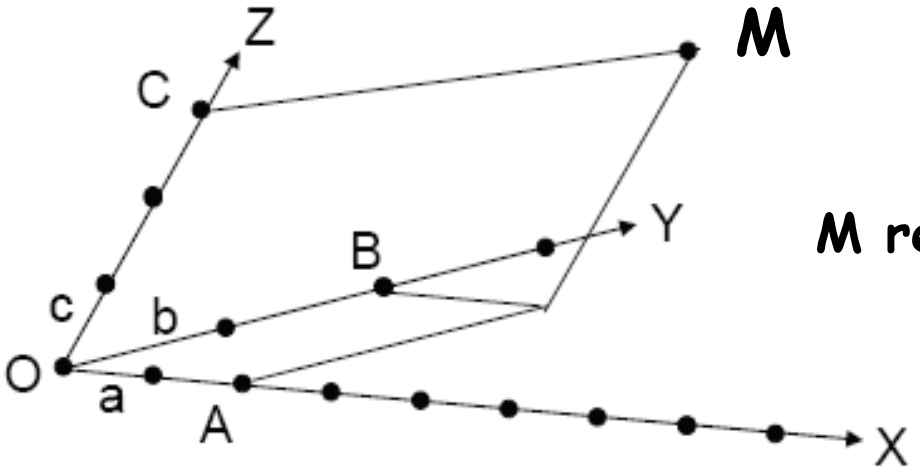
Unit cell kept is simple rectangular (in green)

Reduced coordinates x, y, z

- OA, OB and OC : coordinates corresponding respectively to the 3 crystallographic axes X, Y and Z (dimension of a length)

- x, y and z : reduced coordinates (without any dimension)

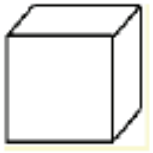
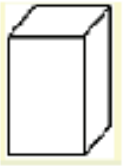
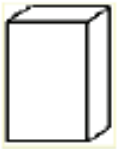
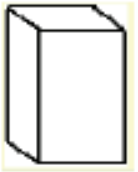
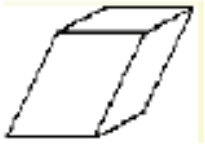
$$x = \frac{OA}{a} \qquad y = \frac{OB}{b} \qquad z = \frac{OC}{c}$$



M reduced coordinates : $\begin{pmatrix} 2 \\ 2 \\ 3 \end{pmatrix}$ OA = 2a, OB = 2b, OC = 3c

$$\overrightarrow{OM} = u\vec{a} + v\vec{b} + w\vec{c} = \vec{r}_0$$

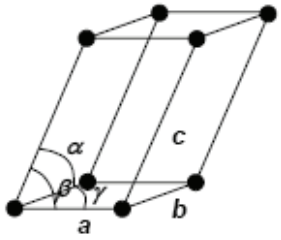
Cristalline structures classification (function of their symmetry) ➔ 3D Bravais lattice systems (7)

cubic		$a = b = c$ $\alpha = \beta = \gamma = 90°$
tetragonal		$a = b \neq c$ $\alpha = \beta = \gamma = 90°$
orthorhombic		$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$
hexagonal		$a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$
monoclinic		$a \neq b \neq c$ $\alpha = \gamma = 90°$ $\beta \neq 90°$
rhombohedric		$a = b = c$ $\alpha = \beta = \gamma \neq 90°$
triclinic		$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$

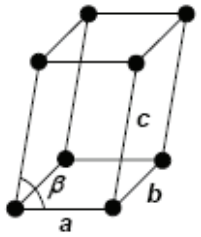
Different node positions for a given symmetry : different types of lattices (A, B, C, P, I, F, R) ➔ 14 Bravais lattices

Bravais system	type	symbol	Unit cell multiplicity
Cubic	Primitive Body centered Faced centered	P I F	1 2 4
Tetragonal	Primitive Body centered	P I	1 2
Orthorhombic	Primitive Body centered Faced centered Base centered	P I F A, B or C	1 2 4 2
Hexagonal	Primitive	P	1
Monoclinic	Primitive Base centered	P B	1 2
Rhombohedric	Primitive	R	1 (with rhombohedric axes)
Triclinic	Primitive	P	1

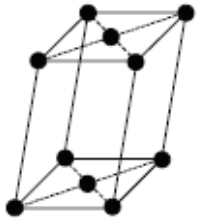
14 Bravais lattices Λ(r)



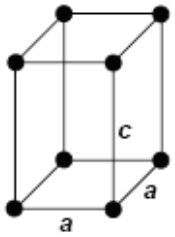
Triclinic P



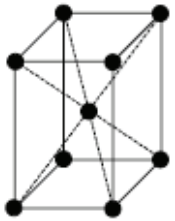
Monoclinic P



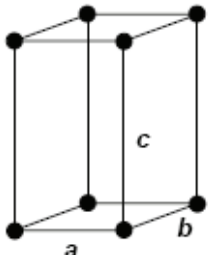
Monoclinic C



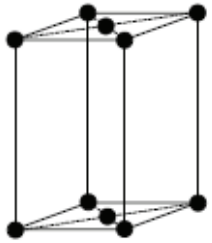
Tetragonal P



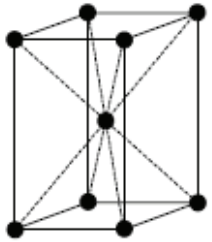
Tetragonal I



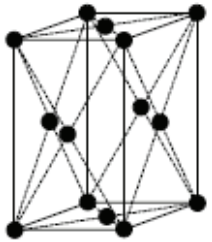
Orthorhombic P



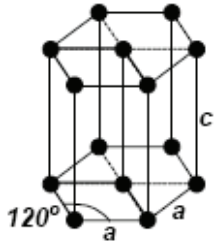
Orthorhombic C



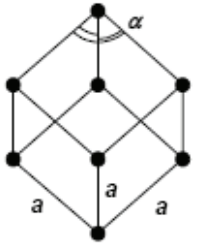
Orthorhombic I



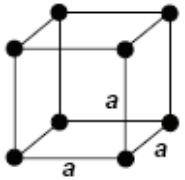
Orthorhombic F



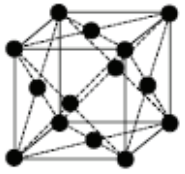
Hexagonal P



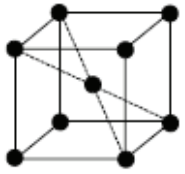
Rhombohedric P



Cubic P



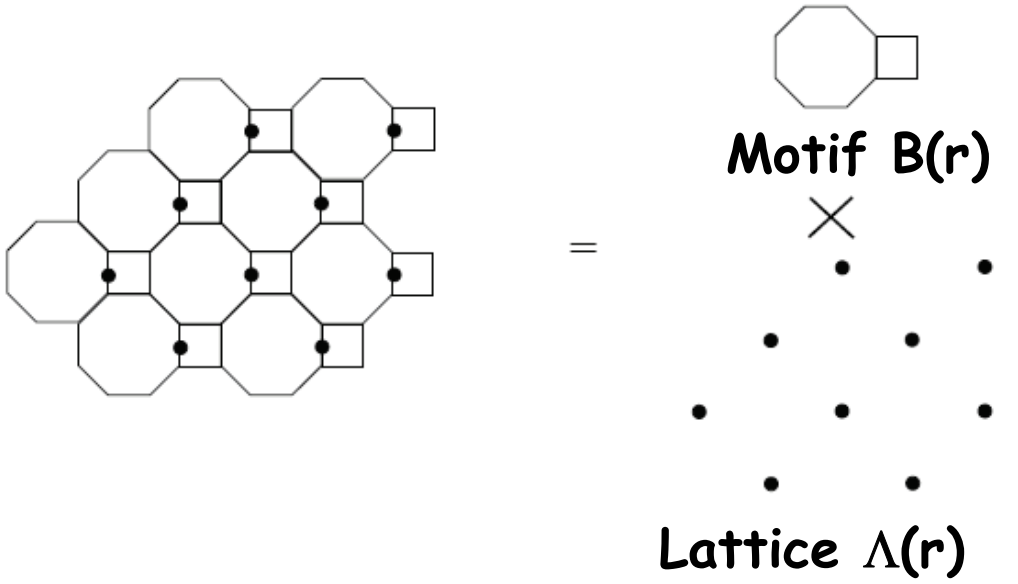
Cubic F



Cubic I

Motif and crystal lattice:

↳ The crystal structure C(r) can be considered to arise from the convolution of a basis domain B(r) also called the motif with the Bravais lattice $\Lambda(r)$: $C(r) = B(r) \times \Lambda(r)$.



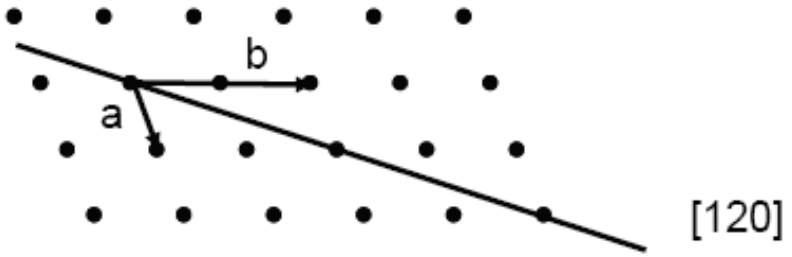
The motif B(r) = smallest possible unit of atoms which by application of all translational symmetry generates the whole crystal

↳ The lattice $\Lambda(r)$ can be viewed as a set of periodically spaced Dirac distributions, i.e. a Dirac $\delta(\vec{r}-\vec{r}_0)$ distribution located on each node of the lattice: $\Lambda(\vec{r}) = \sum_{u=-\infty}^{+\infty} \sum_{v=-\infty}^{+\infty} \sum_{w=-\infty}^{+\infty} \partial(\vec{r} - u\vec{a} - v\vec{b} - w\vec{c})$

Lattice rows

- set of nodes that lie on a straight line that passes through the origin

- labelled by three integers inserted into square brackets ([. . .]) without commas, corresponding to the first node next to the origin on the row: i.e. if $\vec{R}_{uvw} = u\vec{a} + v\vec{b} + w\vec{c}$ is the first node next to the origin on the straight line, the lattice row is labelled [u v w]
  ➔ u, v and w have no common integer divisor different from one.

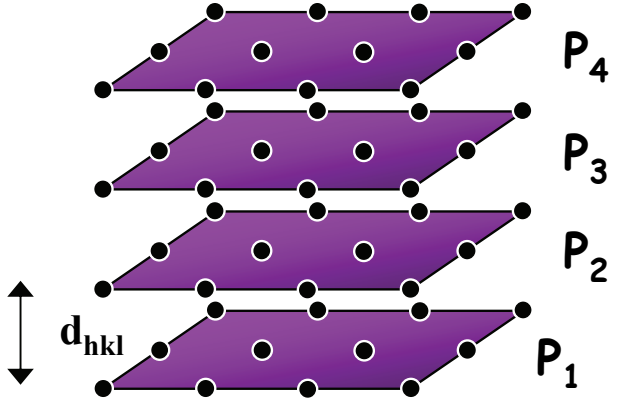


Following nodes : nu nv nw with n Є Z

Families of lattice planes:

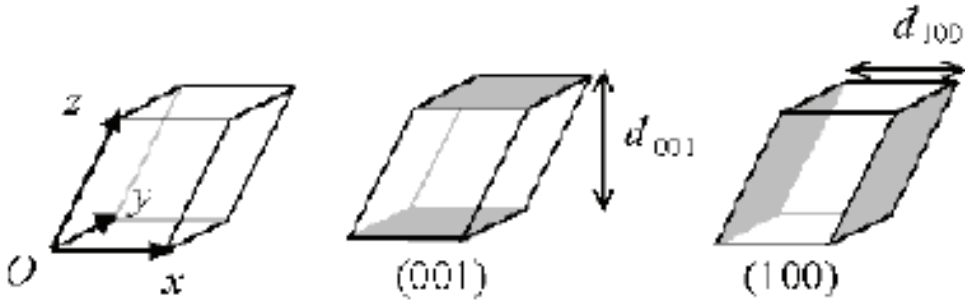
(001)

↳ Lattice plane (h k l) = plane which passes through lattice nodes that do not all lie on the same straight line and labelled by three prime integer numbers h, k, l named Miller indices.



↳ Family of lattice planes = set of parallel lattice planes P_i.

Distance between two neighbouring lattice planes = spacing d_{hkl}.

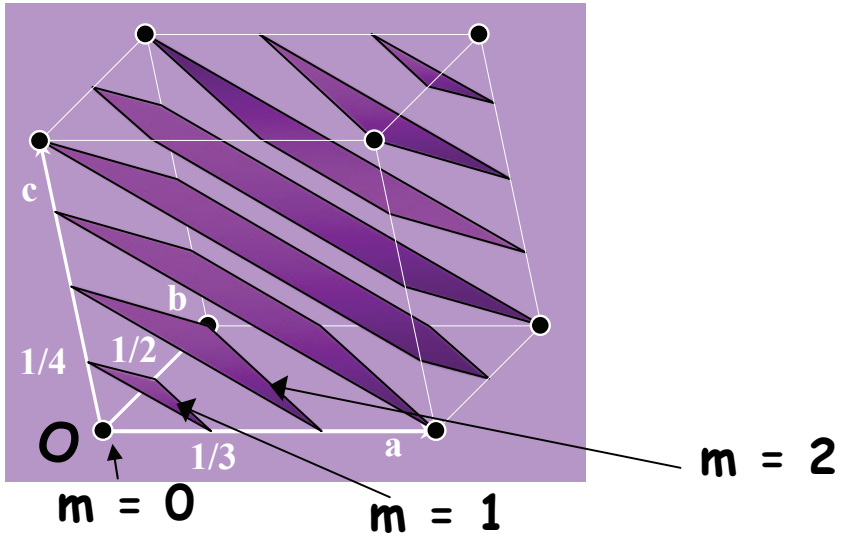


Families of lattice planes:

↳ Family lattice plane (hkl) equation: $hx + ky + lz = m$ with m integer

- m = 0 the plane passes from the origin O
- m = 1 or -1 : first neighbour planes of the origin.

(3,2,4)



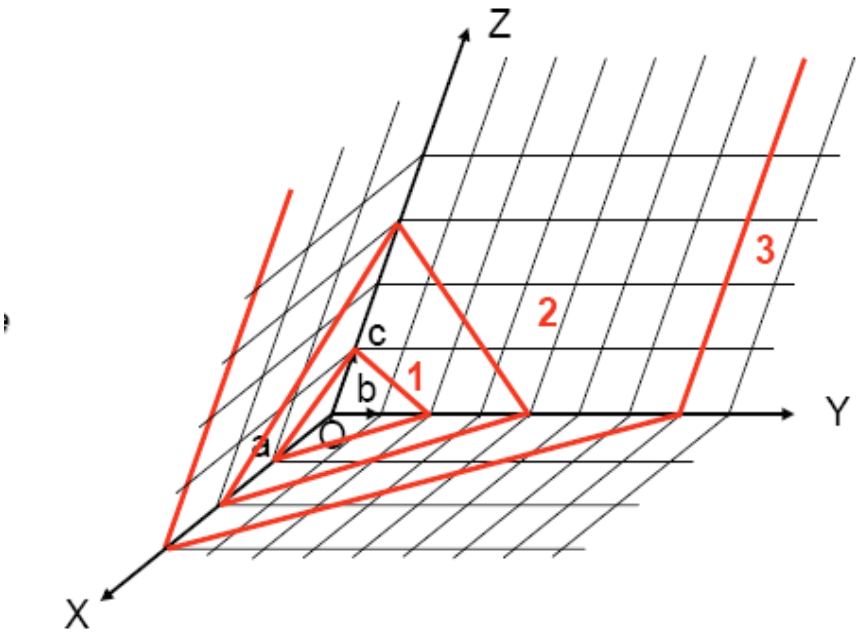
↳ The plane with m = 1, P_1, cuts the [1 0 0], [0 1 0] and [0 0 1] directions at integer fractions of the basis vectors: a/h, b/k, c/l.

For m = n, P_n plane cuts at na/h, nb/k, nc/l.

↳ If the plane P_1 is parallel to one of the basis vectors, the corresponding index is set to zero.

Example: Miller indices

Plane	Reduced coordinates			Inverse values			A'	Miller indices		
	x	y	z	1/x	1/y	1/z		h=A'/x	k=A'/y	l=A'/z
1	1	2	1	1/1	1/2	1	× 2	2	1	2
2	2	4	3	1/2	1/4	1/3	× 12	6	3	4
3	3	7	∞	1/3	1/7	0	× 21	7	3	0



Reciprocal space
RS

Reciprocal space (RS): Geometric definition

Introduced by Bravais and used again by Ewald (1917) : an essential concept for the study of crystal lattices and their diffraction properties.

- Basic vector definitions:

$$\vec{a}^* = \frac{\vec{b} \wedge \vec{c}}{V}, \quad \vec{b}^* = \frac{\vec{c} \wedge \vec{a}}{V}, \quad \vec{c}^* = \frac{\vec{a} \wedge \vec{b}}{V}$$

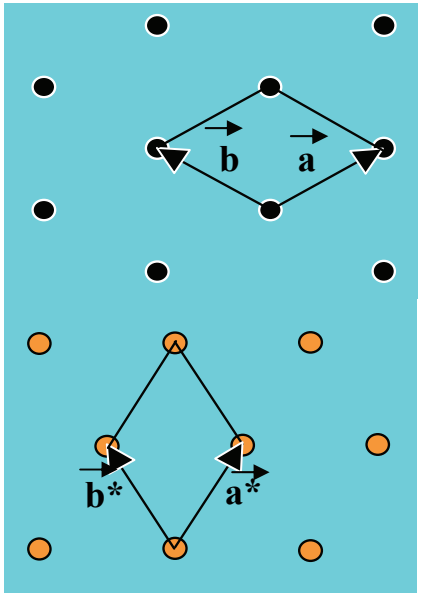
with $V=(a,b,c)$ direct cell volume
and $V^*=(a^*,b^*,c^*)=1/V$ reciprocal cell volume

- Equivalent definitions (2D, 3D...)

$$\begin{array}{lll} \vec{a}^*.\vec{a}=1 & \vec{b}^*.\vec{a}=0 & \vec{c}^*.\vec{a}=0 \\ \vec{a}^*.\vec{b}=0 & \vec{b}^*.\vec{b}=1 & \vec{c}^*.\vec{b}=0 \\ \vec{a}^*.\vec{c}=0 & \vec{b}^*.\vec{c}=0 & \vec{c}^*.\vec{c}=1 \end{array}$$

direct space
DS

RS

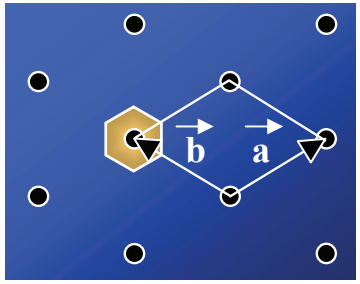


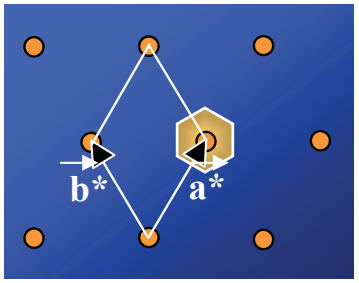
- Reciprocal lattice point coordinates: $\overrightarrow{Q_{hkl}} = n(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*)$ with h,k,l and n integers

RS Properties

- **Symmetry** :

RS has the same symmetry as the direct space DS :

DS 



RS

Duality :

The reciprocal space of RS is the direct space DS

Indeed, RS of RS is constituted by nodes verifying $\forall \vec{Q}_{hkl}, \quad \vec{Q}_{hkl}.\vec{R} = m$

- If $R=R_{uvw}$ the equation is verified (i. e. R is a node of DS)
- reciprocally if $R=x'a+y'b+z'c$ and verify $x'u + y'v + z'w = m$, x', y' and z' must be integers

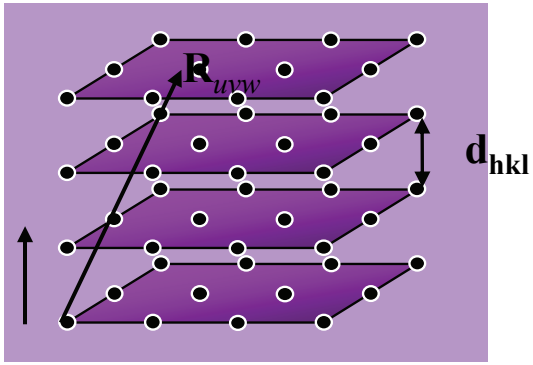
Relation between lattice planes and RS

↳ To every lattice planes family (h k l) in the DS corresponds a lattice row [h k l]* of the same indices in the RS.

↳ The reciprocal lattice row [h k l]* is perpendicular to the direct lattice planes (h k l) and its spacing $|r^*_{hkl}|$ is the inverse of the direct lattice plane spacing d_{hkl}.

$$[h\ k\ l]^* \perp (h\ k\ l) \text{ and } |r^*_{hkl}| = 1/d_{hkl}$$

Since a family of direct lattice planes (h k l) defines a reciprocal lattice row [h k l]*, the nodes on this reciprocal lattice row are: nh nk nl with n integer.



➔ So $Q_{nh\ nk\ nl}$ belonging to the RS

is perpendicular to a direct family plane

and verify : $Q = \frac{1}{d} n$

➔ The smallest lattice row vector modulus : $q_{hkl} = 1/d_{hkl}$ and $Q_{nh\ nk\ nl} = n\ q_{hkl}$

d_{hkl} spacings

- d_{hkl} spacing: $d_{hkl} = \frac{1}{q_{hkl}}$ with q_{hkl} smallest vector of the lattice row

- **General case**:

$$d_{hkl} = \frac{1}{\sqrt{h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hka^*b^*\cos\gamma^* + 2klb^*c^*\cos\alpha^* + 2lha^*c^*\cos\beta^*}}$$

- Hexagonal system :

$$a^* = b^* = \frac{2}{\sqrt{3}a}, \quad c^* = \frac{1}{c}, \quad \gamma^* = 60°$$

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

- Cubic system :

$$a^* = b^* = c^* = \frac{1}{a}, \quad \alpha^* = \beta^* = \gamma^* = 90°$$

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

Case of multiple cells

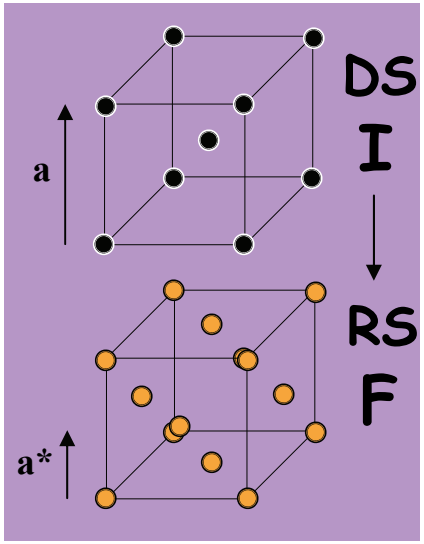
Body centered cubic unit cell

$$\vec{R}_{uvw} = u\vec{a} + v\vec{b} + w\vec{c}$$
$$\vec{R}_{uvw} = (u+0.5)\vec{a} + (v+0.5)\vec{b} + (w+0.5)\vec{c}$$

The condition $\forall \vec{R}_{uvw} \quad \vec{Q}_{hkl}.\vec{R}_{uvw} = n$ implies

1) h, k ,l integers
2) $h+k+l=2n$

➔ RR of RD : face centered cubic cell

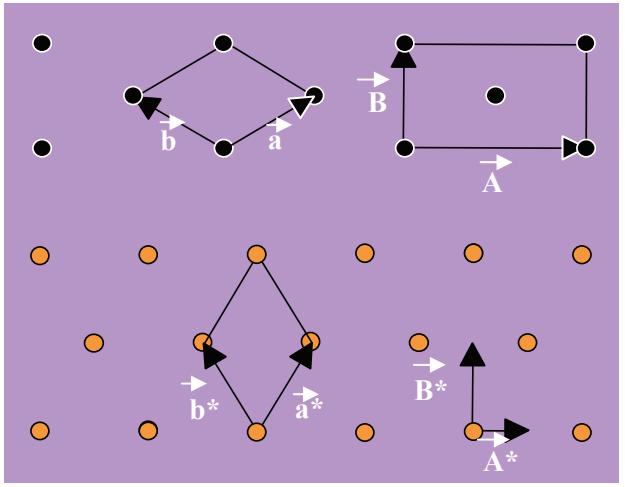


Hexagonal unit cell

$\vec{A} = \vec{a}-\vec{b}$; $\vec{B}=\vec{a}+\vec{b}$; $\vec{C}=\vec{c}$

$$h+k=2n$$

$$\vec{A}^* = \frac{\vec{B}\wedge\vec{C}}{2V} = \frac{(\vec{a}+\vec{b})\wedge\vec{c}}{2V} = \frac{1}{2}(\vec{a}^*-\vec{b}^*)$$
$$\vec{B}^* = \frac{\vec{C}\wedge\vec{A}}{2V} = \frac{\vec{c}\wedge(\vec{a}-\vec{b})}{2V} = \frac{1}{2}(\vec{b}^*+\vec{a}^*)$$



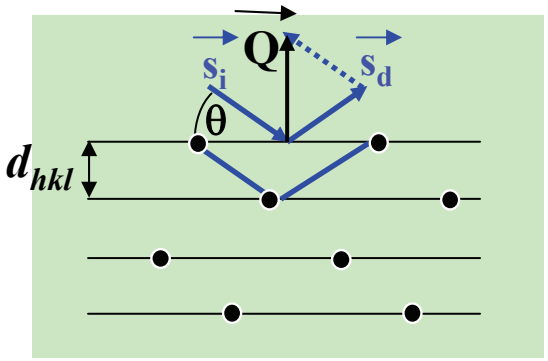
DS	Existence conditions	RS
P	no conditions	P
I	h + k + l = 2n	F
F	h, k ,l same parity	I
A	k + l = 2n	A

RS and diffraction

* Bragg law

Family lattice plane diffraction with d_{hkl} spacing

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



* Diffusion vector

$$\vec{Q} = \frac{\vec{s}_d - \vec{s}_i}{\lambda}$$

$\vec{s}_i$ and $\vec{s}_d$: unitary incident and diffused vectors

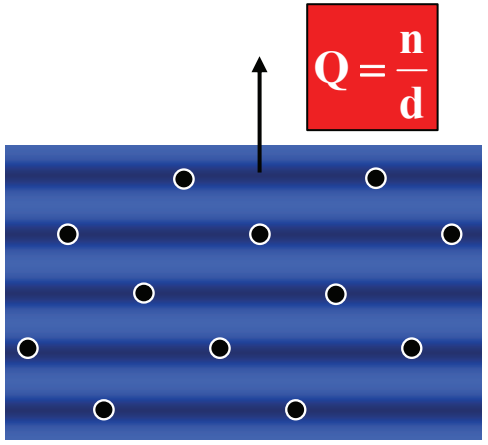
- $\vec{Q}$ is perpendicular to the diffracting planes

$$\|Q\| = \frac{2}{\lambda}\sin\theta = \frac{m}{d}$$

* The reciprocal lattice can therefore be viewed as being a representation of all those scattering vectors Q that can give rise to diffraction.

* To each scattering vector Q corresponds a reciprocal lattice node.

Diffraction ⇔ $\vec{Q}$ is a RS vector (in a reciprocal lattice row ⊥ to the diffracting planes)



DS Fourier transform

- **Définition**
  - Function or $S(\mathbf{r})$ distribution

$$TF(S(\mathbf{r})) = F(\mathbf{q}) = \int S(\mathbf{r}) e^{-i\mathbf{q}.\mathbf{r}} d^3\mathbf{r}$$

$$TF^{-1}(F(\mathbf{q})) = S(\mathbf{r}) = \int F(\mathbf{q}) e^{i\mathbf{q}.\mathbf{r}} d^3\mathbf{q}$$

$$\frac{1}{T}\sum_u e^{-i\frac{q}{T}u} = \sum_h \delta(q - hT)$$

- Direct lattice is described by the « node density » distribution :

$$TF(S(\mathbf{r})) = F(\mathbf{q}) = \int \sum_{uvw} \delta(\mathbf{r} - \mathbf{R}_{uvw}) e^{-i\mathbf{q}.\mathbf{r}} d^3\mathbf{r}$$

$$= \sum_{uvw} e^{-i\mathbf{q}.\mathbf{R}_{uvw}} = \sum_u e^{-iq_x u} \sum_v e^{-iq_y v} \sum_w e^{-iq_z w}$$

$$= \sum_h \delta(q_x - h) \sum_k \delta(q_y - k) \sum_l \delta(q_z - l)$$

$$\mathbf{q} = q_x\mathbf{a}^* + q_y\mathbf{b}^* + q_z\mathbf{c}^*$$

$$F(\mathbf{q}) = v^* \sum_{hkl} \delta(\mathbf{q} - \mathbf{Q}_{hkl})$$

« node density » of RS $(V^*=(a^*,b^*,c^*)=(1/V)$

RS = TF (DS)

TF properties

- **RS and DS duality**

$$TF^{-1}\left(\sum_{hkl}\delta(q-Q_{hkl})\right)=V\sum_{uvw}\delta(r-R_{uvw})$$

- **Direct and reciprocal space symmetry**
  - If O is a symmetry operator in direct space

$$F(O(q))=\int S(r)e^{-iO(q).r}d^{3}r=\int S(r)e^{-iq.O^{-1}(r)}d^{3}r$$
$$=\int S(O(r'))e^{-iq.r'}d^{3}r'=\int S(r')e^{-iq.r'}d^{3}r'=F(q)$$

…O is a symmetry operator in reciprocal space

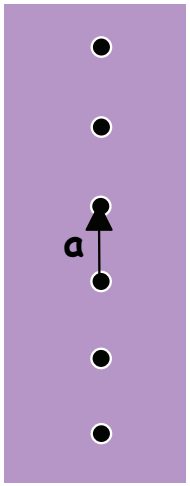
- **Convolution product** :

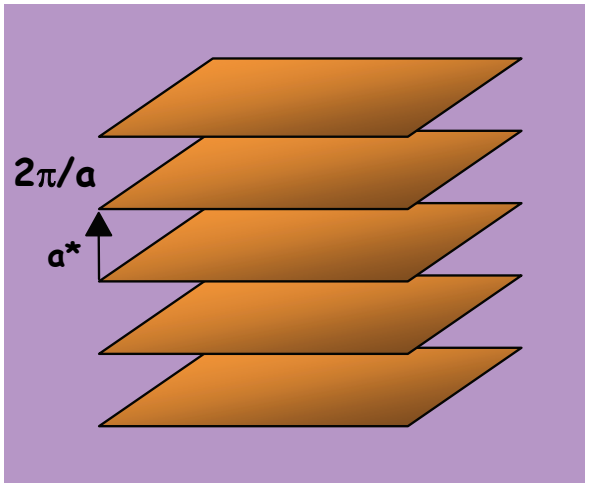
Convolution product of f and g is $f*g$

$$(f*g)(r)=\int f(u)g(r-u)d^{3}u$$

$$TF(f*g)=TF(f)TF(g)$$
$$TF(fg)=TF(f)*TF(g)$$

Application to low dimensional objects





• 1D : chain

$$S(r) = \sum_u \delta(r_{//} - ua)\,\delta(r_\perp)$$

$$q = q_x a^*$$

$$F(q) = \sum_h \delta(q_x - h)$$

= set of parallel plane

• 2D : plane

$$q = q_x a^* + q_y b^*$$

$$S(r) = \sum_{uvw} \delta(r_{//} - ua + vb)\,\delta(r_\perp)$$

$$F(q) = \sum_{hk} \delta(q_x - h)\delta(q_y - k)$$

= Rod lattice