# ISOE2019

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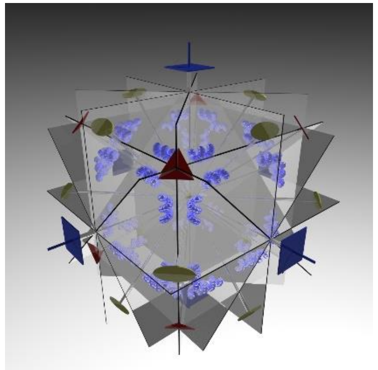

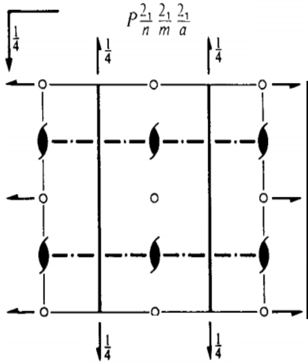


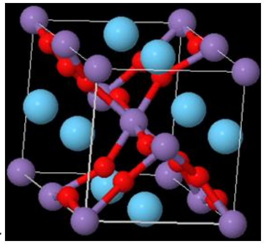

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Cargèse

# CRYSTAL SYMMETRY


**Béatrice GRENIER**
Univ. Grenoble Alpes & CEA-IRIG-MEM
Grenoble, France

# Introduction

**Crystallography → Link between structure and physical properties**

## 1- Translation symmetry

**Periodicity** of the physical properties: **Solid state physics**

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

## 2- Point (group) symmetry

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

→ reflects the point symmetry of crystals

- *External shape of crystals (natural faces)*
- *Optical, mechanical, magnetic, …. properties; Electric conductivity, …*

**Curie's principle: The symmetry of a cause is always preserved in its effects**

⇩

Existence or not of some phenomena, symmetries of the possible ones

Ex.: existence or not of ferroelectricity, relations between the various components of the stress tensor, …

# Outline

## 1. Point group symmetry

Elementary point symmetry operations
Crystallographic point groups: definition, international notation
Examples of point groups
The 32 crystallographic point groups and 11 Laue classes

## 2. Translation symmetry

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

## 3. Space group symmetry

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

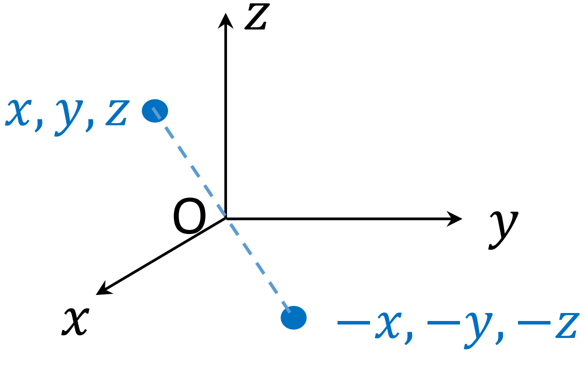
# 1. Point Group Symmetry: *Elementary point symmetries*

**Point symmetries** exist at the macroscopic & atomic scales. They **keep at least one point fixed**: the origin

**Inversion** (through a point)

→ *centrosymmetric crystal*

$\boxed{\bar{1}}$

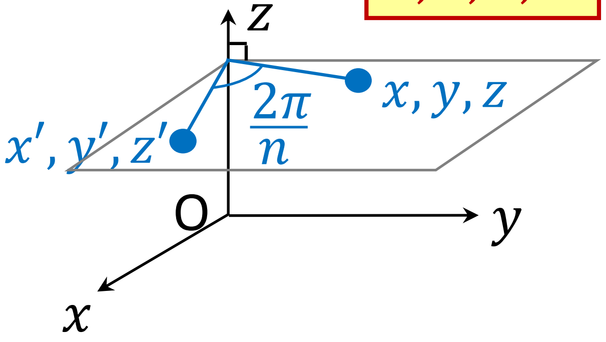



**Rotation** (around an axis)

*Rotation of order* $n$

*= rotation by* $\frac{2\pi}{n}$

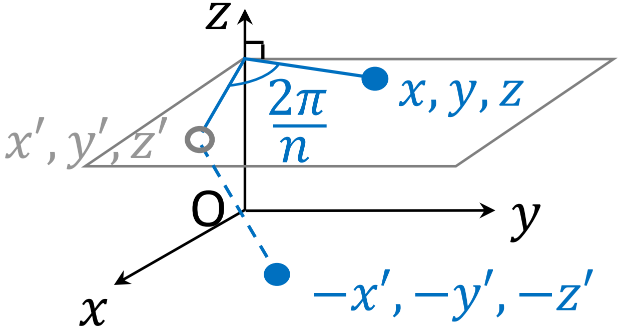
$\boxed{1, 2, 3, \ldots}$




**Rotoinversion**

→ combination of $n$ and $\bar{1}$

$\boxed{\bar{1}, \bar{2}, \bar{3}, \ldots}$

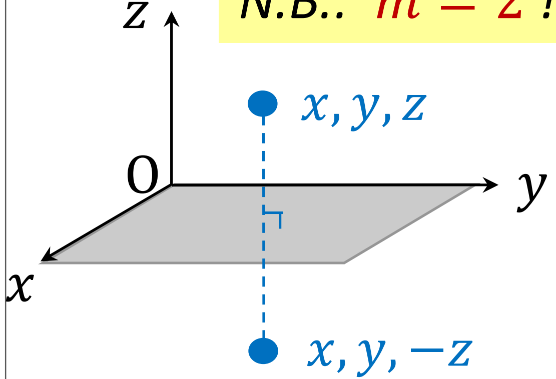



**Reflection**

(through a mirror plane)

$\boxed{m}$

*N.B.:* $m = \bar{2}$ *!*



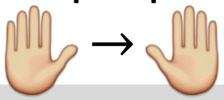

Rotations compatible with the translation symmetry = those of orders 1, 2, 3, 4, 6

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

*see demonstration in appendix*

Proper

Improper



*see appendix for matrix representation*

# 1. Point Group Symmetry: *Definition of a group*

**The point symmetry operations form a group**

A **group** $(G,\times)$ of order $n$ is a set of $n$ elements $g_1, g_2, \ldots, g_n$ equipped with an operation (**group multiplication** $\times$) that combines any two elements to form a third element and that satisfies four conditions called the group axioms, namely:

Closure: $g_i \times g_j \in G$

Identity: $\exists!\, e$ such that $g_i \times e = e \times g_i = g_i$ → 1 (does nothing)

Invertibility: each element $g_i$ has a unique inverse $g_i^{-1}$ such that: $g_i \times g_i^{-1} = g_i^{-1} \times g_i = e$

inverse of $n$: $-n$ (rotate in the other way)
Inverse of $m$: $m$

Associativity: $(g_i \times g_j) \times g_k = g_i \times (g_j \times g_k)$

**For point symmetry operations:**

$\times \leftrightarrow$ apply successively 2 symmetry operations

# 1. Point Group Symmetry: *How to obtain and name all point groups?*

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

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

- all symmetry elements go through a common point,
- compatibility with the translation symmetry

$\Rightarrow$ constraints between the orientations of the various symmetry axes / planes

**Notation of the point groups – *International (Hermann-Mauguin) symbol***

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

N.B.: the direction of a mirror is given by its normal

'$n/m$' = axis $n$ and normal to mirror $m$ along same direction

(*i.e.* plane of the mirror $\perp$ to axis $n$)

*Examples* :

$4/m$

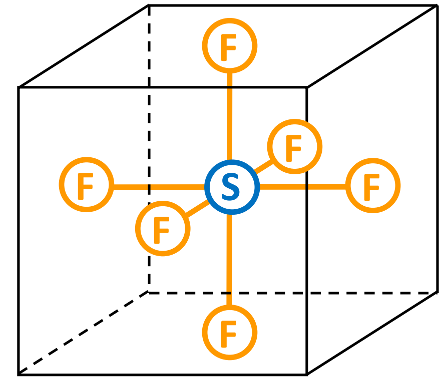
$\frac{4}{m}\frac{2}{m}\frac{2}{m}$ (= $4/mmm$)

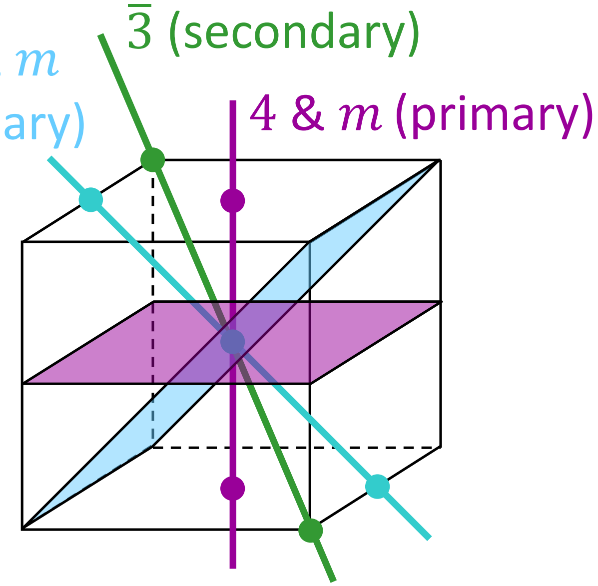
There exists another notation: ***Schoenflies symbol*** → widely used in spectroscopy *(see appendix)*

Convenient way to represent and visualize the point groups: ***stereographic projections*** *(see appendix)*

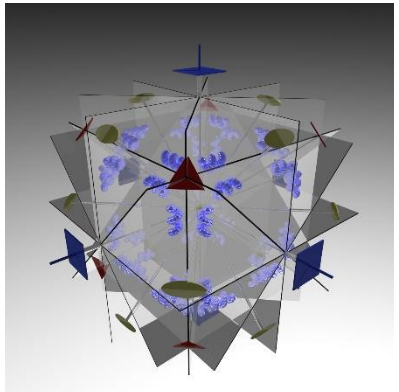
# 1. Point Group Symmetry: *Points groups of molecules*

**$SF_6$ molecule**

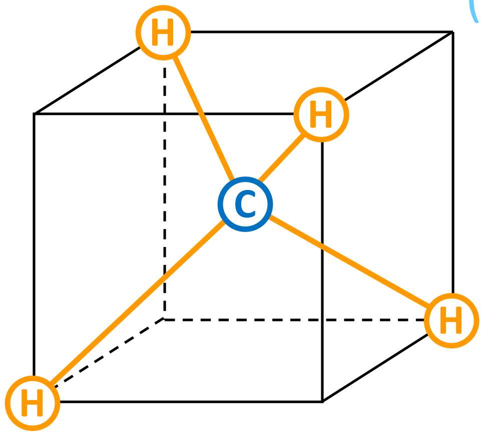


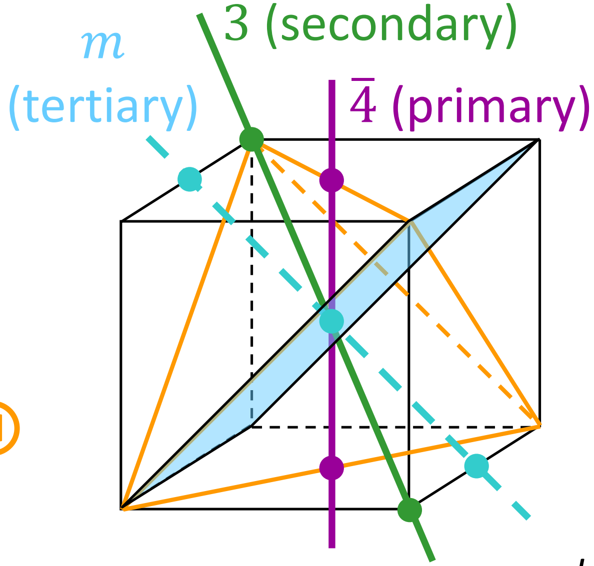




→ Point group: $\boxed{\dfrac{4}{m}\bar{3}\dfrac{2}{m}}$ (= $m\bar{3}m$)

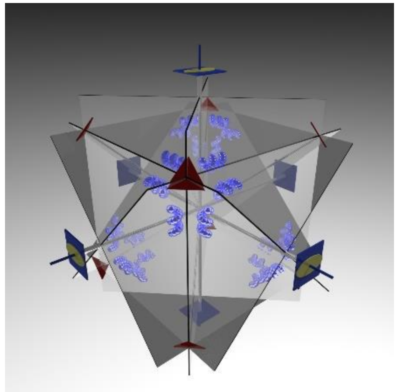


**$CH_4$ molecule**

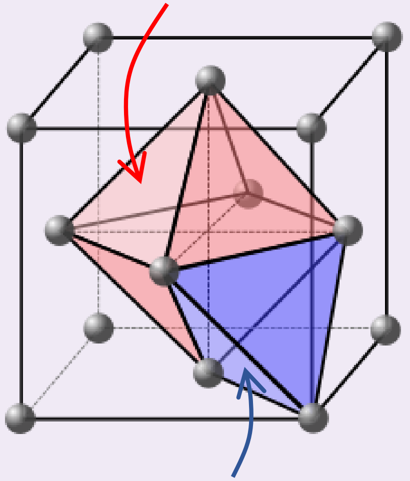



→ Point group: $\boxed{\bar{4}3m}$



**Octahedral site :** $m\bar{3}m$ symmetry



**Tetrahedral site :** $\bar{4}3m$ symmetry

*http://materials.cmu.edu/degraef/pg/*

# 1. Point Group Symmetry: *Classification – The 32 point groups*

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

*(see appendix for their stereographic projection)*

• <u>Example</u>: **dielectric properties**

They can only be found for particular crystal symmetries

**Piezoelectricity** → point groups that do not possess inversion

**Ferroelectricity** and **pyroelectricity**

→ - piezolectric point groups, i.e. non centrosymmetric

- with a unique polar axis: $\vec{p} \parallel n$-axis and contained in the plane of the mirror(s)

$1, 2, m, 2mm, 3, 3m, 4, 4mm, 6, 6mm$

**polar groups**

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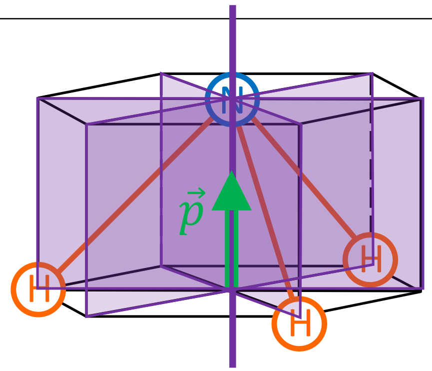
$NH_3$




Point group: $3m$

→ ∃ dipolar moment ($p = 1.46$ Debye)

# 2. Translation Symmetry: *Lattice and motif*

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

$\boxed{\vec{T} = u\vec{a} + v\vec{b} + w\vec{c} \text{ with } u, v, w \text{ integers}}$ (positive or negative)

$\vec{a}, \vec{b}, \vec{c}$ are called basis vectors (non-coplanar elementary translation vectors defining a right-handed system). The volume they define is called the unit cell.

Crystal = Lattice + Motif

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

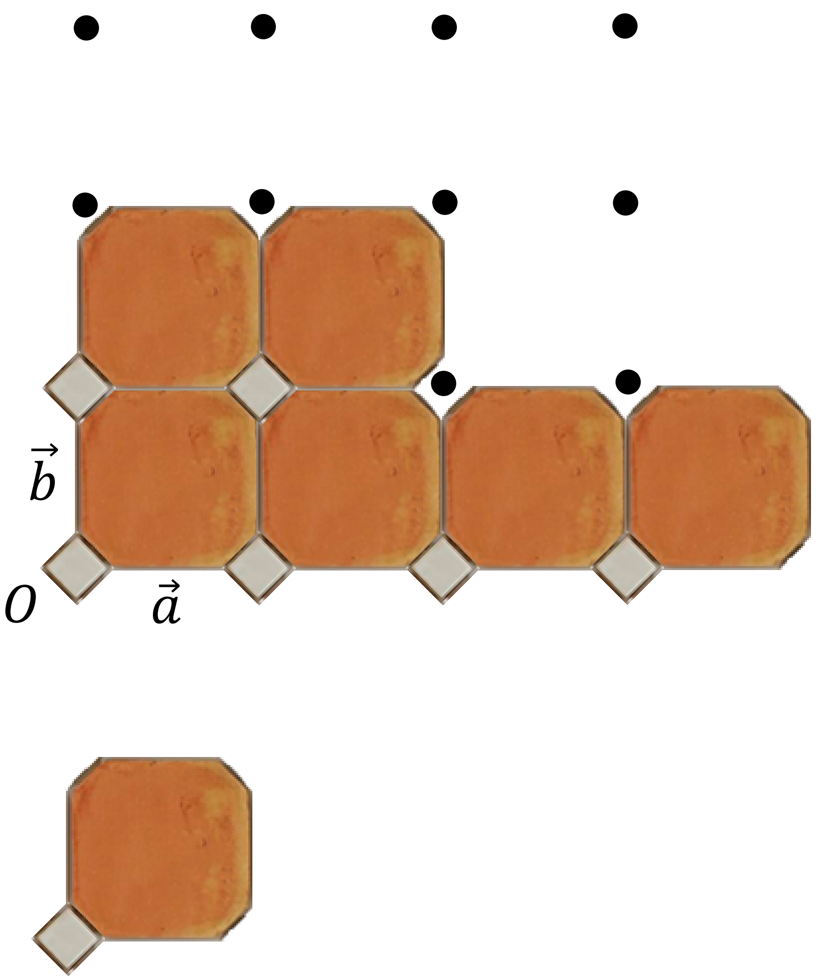
At each lattice node, one associates a group of atoms: the **motif**.

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.

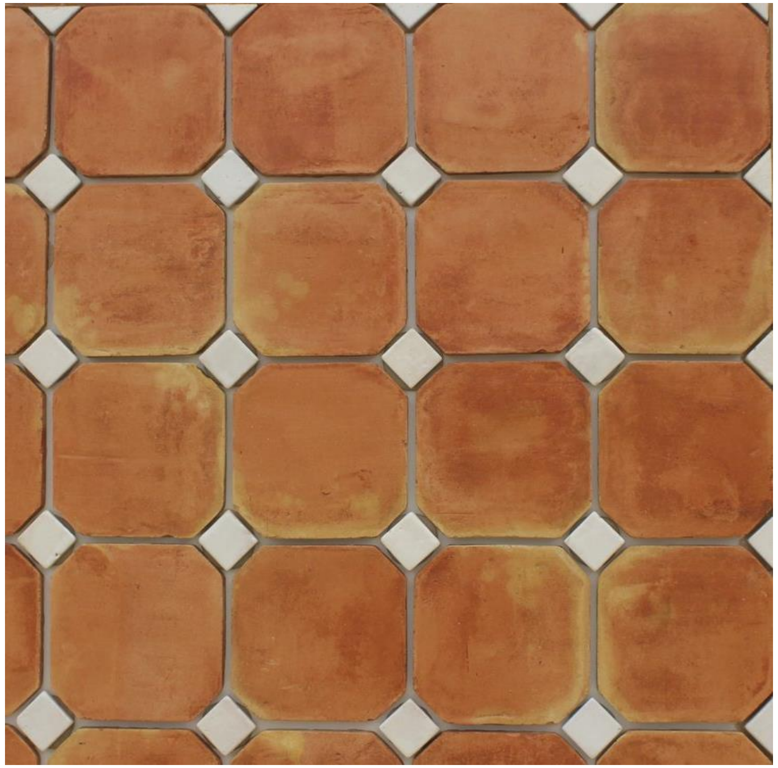
N.B. : $\vec{r} = x\vec{a} + y\vec{b} + z\vec{c} \quad (|x|, |y|, |z| < 1)$

Example 1: terracotta floor tiles (2D)

Lattice



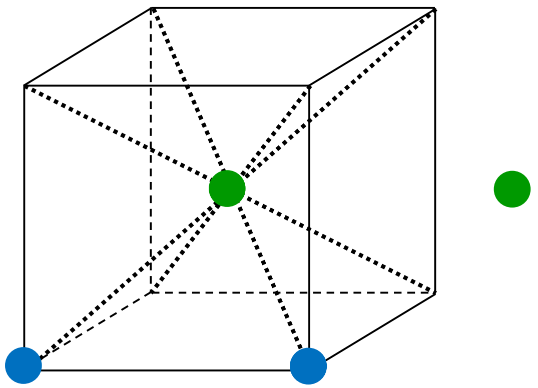

Motif



Example 2: CsCl single-crystal (3D)

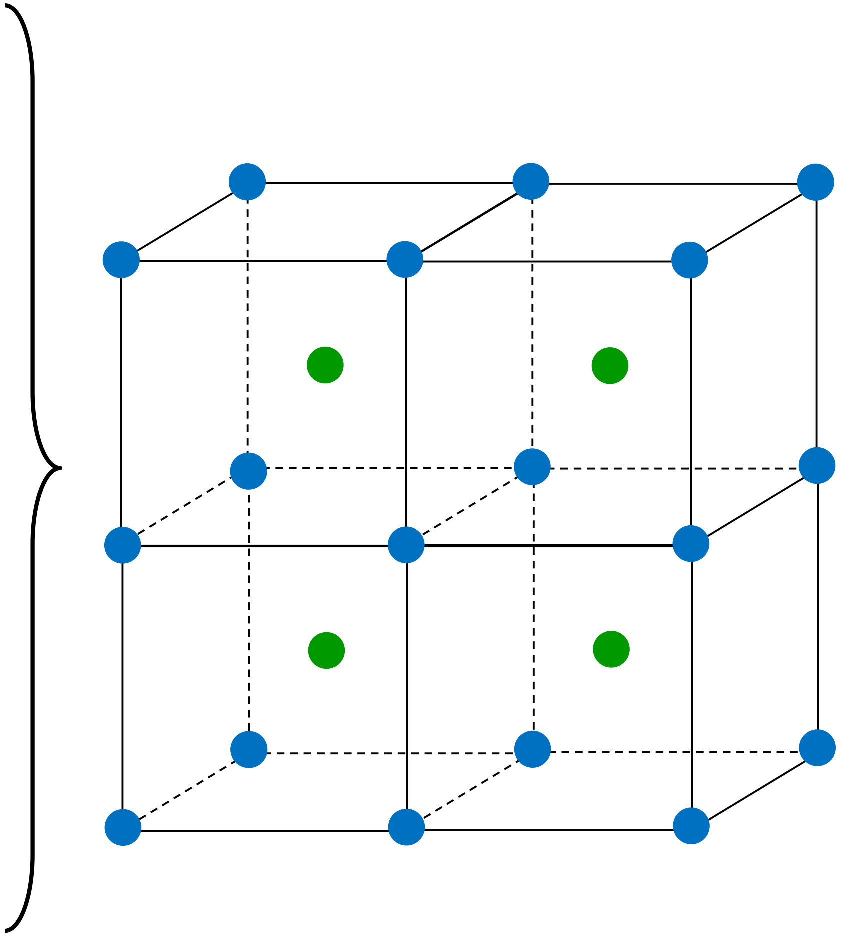
Unit cell:

cubic
primitive



Motif:

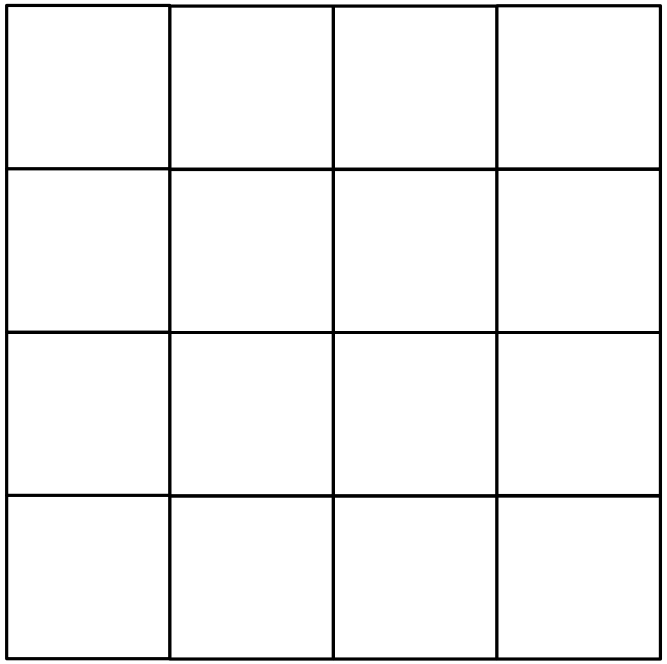
$Cs^+$ on the corner
$Cl^-$ at the center

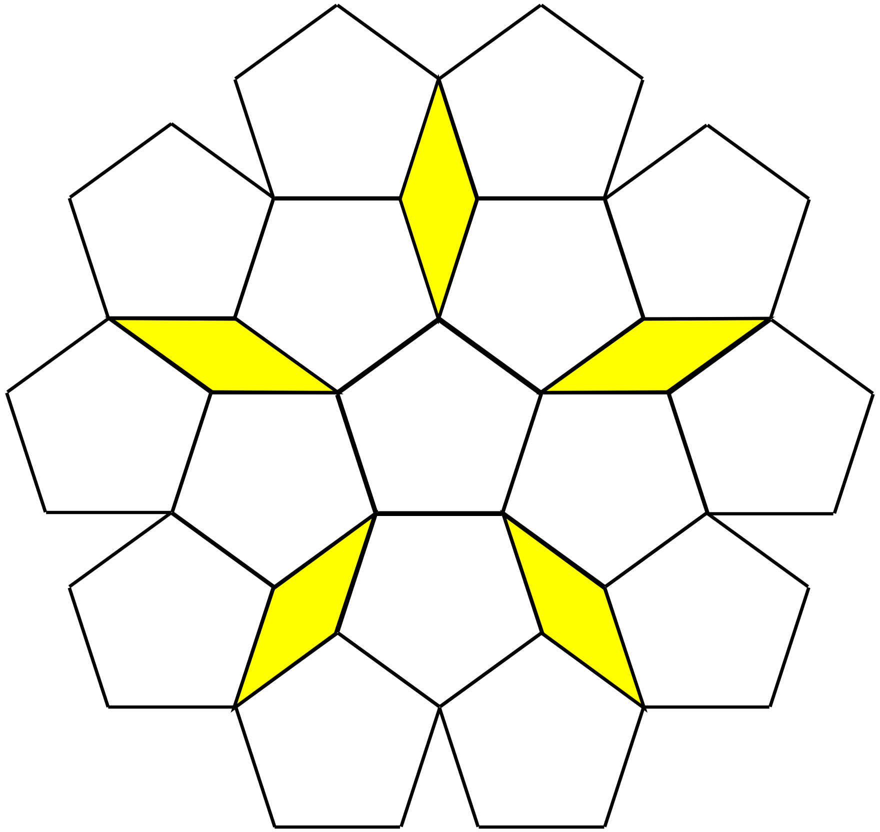



# 2. Translation Symmetry: *The unit cell*

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

Examples at 2D:



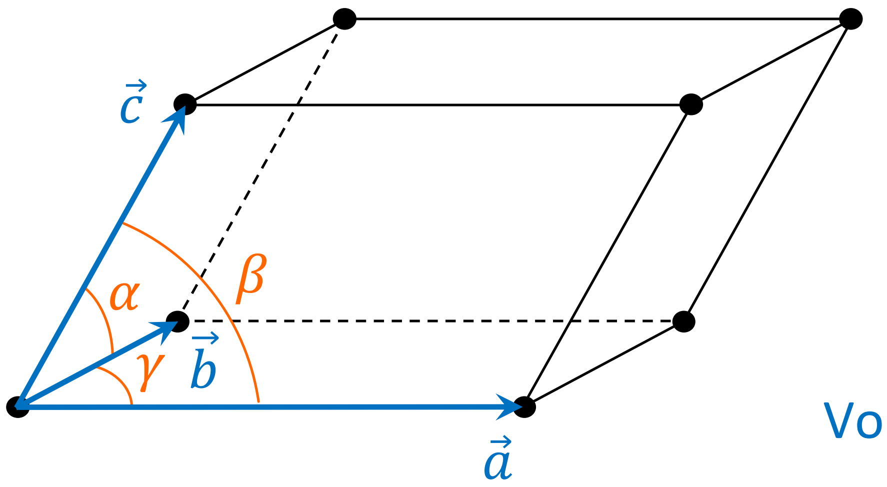


Rotation of **order 4**: compatible with translation symmetry.

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

*(see appendix for the mathematical demonstration)*

# 2. Translation Symmetry: *Lattice and motif*




Lattice parameters:

| Lengths | Angles |
|---|---|
| $a$ | $\alpha = (\widehat{\vec{b},\vec{c}})$ |
| $b$ | $\beta = (\widehat{\vec{c},\vec{a}})$ |
| $c$ | $\gamma = (\widehat{\vec{a},\vec{b}})$ |

Volume of the unit cell: $\boxed{V = \left(\vec{a},\vec{b},\vec{c}\right) = \left(\vec{a} \wedge \vec{b}\right).\vec{c}}$

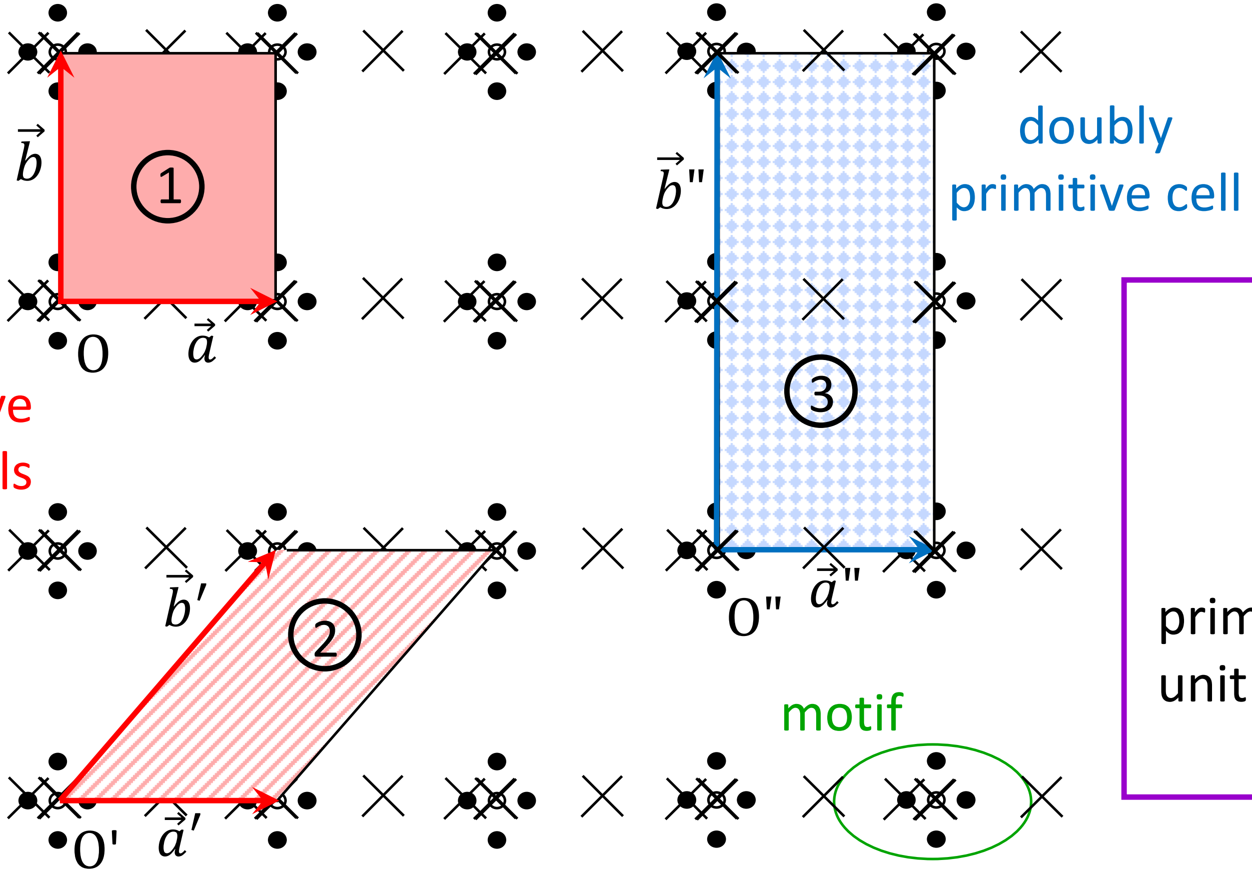
- Multiplicity $m$ of a unit cell: Number of lattice nodes (and thus of motifs) per unit cell

How to count the number of lattice nodes per unit cell?
$\rightarrow$ each lattice node counts for $1/n$, with $n$ = 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 $V$

- Centered unit cell: $m = 2, 3$ or $4$ (doubly, triply … primitive) → Volume: $V_m = m\,V$
  $\rightarrow$ **used only when more symmetrical than any primitive cell of the lattice**

# 2. Translation Symmetry: *Unit cell – Example in a 2D lattice*




**Best choice?**

1

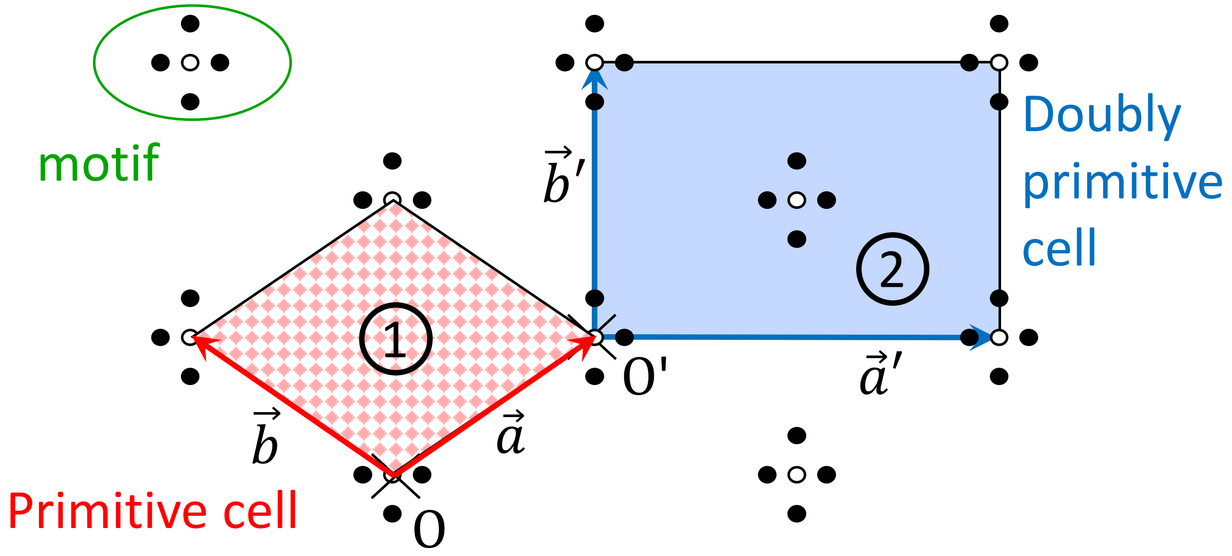
primitive unit cell

reflects the lattice symmetry

Primitive cells: 4 lattice nodes (on corners) $\in$ 4 cells $\rightarrow m = 4 \times 1/4 = 1$

Doubly primitive cell: 4 nodes (on corners) $\in$ 4 cells $\rightarrow 4 \times 1/4 = 1$
+ 2 nodes (on edges) $\in$ 2 cells $\rightarrow 2 \times 1/2 = 1$
$\Big\}\ m = 2$

# 2. Translation Symmetry: *Unit cell – Example in a 2D lattice*




Cell 1 is primitive but does not reflect the perpendicularity
⇨ **Best choice**: 2

**Conventional unit cell**
(basis vectors ∥ directions of symmetry of the lattice)

N.B.: For a primitive cell, the translation vectors $\vec{T}$ are defined by: $\vec{T} = u\vec{a} + v\vec{b} + w\vec{c}$ with $u, v, w$ integers.

For a non primitive cell of multiplicity $m$, one must add $(m-1)$ translation vectors such as:
$\vec{T} = u'\vec{a} + v'\vec{b} + w'\vec{c}$ with $u', v', w'$ integers or fractionnals

*half integers*

Ex.: For unit cell 2 $(m = 2)$: $\begin{cases} \vec{T}_1 = u\vec{a}' + v\vec{b}' \\ \vec{T}_2 = \vec{T}_1 + \frac{1}{2}(\vec{a}' + \vec{b}') = \left(u + \frac{1}{2}\right)\vec{a}' + \left(v + \frac{1}{2}\right)\vec{b}' \end{cases}$

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

Translation and point group symmetries:

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

The 6 conventional cells are, by increasing degree of symmetry:

| | | | | Number of parameters |
|---|---|---|---|---|
| $a$ | triclinic | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma$ | 6 |
| $m$ | monoclinic | $a \neq b \neq c$ | $\alpha = \gamma = 90°,\ \beta > 90°$ | 4 |
| $o$ | orthorhombic | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90°$ | 3 |
| $t$ | tetragonal or quadratic | $a = b \neq c$ | $\alpha = \beta = \gamma = 90°$ | 2 |
| $h$ | hexagonal ** | $a = b \neq c$ | $\alpha = \beta = 90°,\ \gamma = 120°$ * | 2 |
| $c$ | cubic | $a = b = c$ | $\alpha = \beta = \gamma = 90°$ | 1 |

* $\gamma = 120°$ *and not 60° (for the hexagonal reciprocal lattice:* $\gamma^* = 60°$*)*

** *The hexagonal conventional cell splits in two crystal systems:*
*trigonal (axis 3) and hexagonal (axis 6); the 5 other ones are the same.*

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

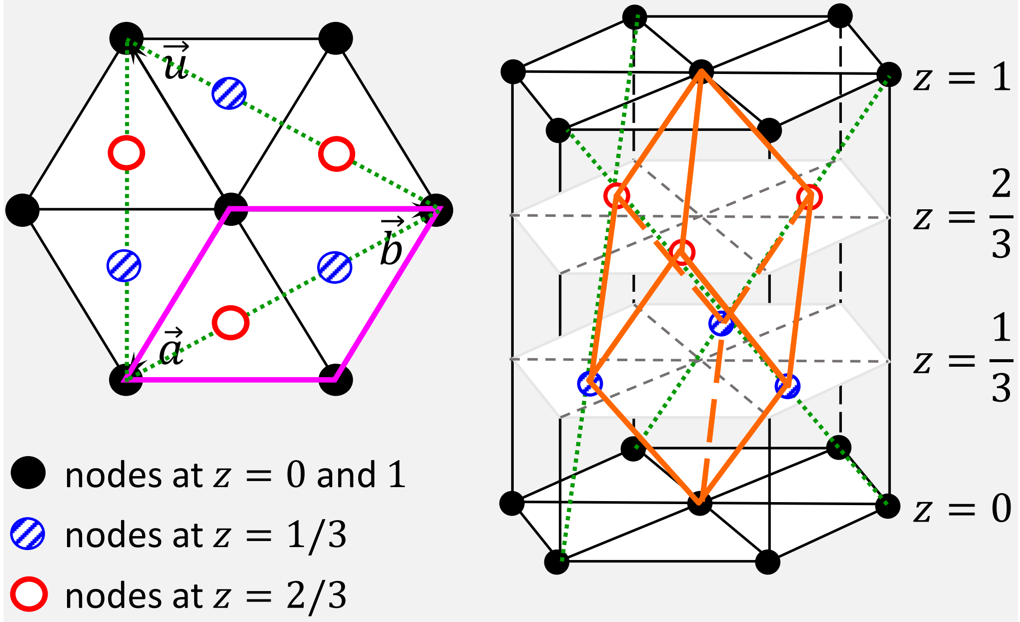
| Crystal system | Point groups and Laue classes | Primary direction | Secondary direction | Tertiary direction |
|---|---|---|---|---|
| triclinic | $1, \bar{1}$ | – | – | – |
| monoclinic | $2, m, 2/m$ | $\vec{b}$ (ou $\vec{c}$) | – | – |
| orthorhombic | $222, 2mm, mmm$ | $\vec{a}$ | $\vec{b}$ | $\vec{c}$ |
| trigonal | $3, \bar{3}$<br>$32, 3m, \bar{3}m$ | $\vec{c}$ | $\vec{a}, \vec{b}$, -$\vec{a}$-$\vec{b}$ | – |
| tetragonal or quadratic | $4, \bar{4}, 4/m$<br>$422, 4mm, \bar{4}2m, 4/mmm$ | $\vec{c}$ | $\vec{a}, \vec{b}$ | $\vec{a} \pm \vec{b}$ |
| hexagonal | $6, \bar{6}, 6/m$<br>$622, 6mm, \bar{6}2m, 6/mmm$ | $\vec{c}$ | $\vec{a}, \vec{b}$, -$\vec{a}$-$\vec{b}$ | $2\vec{a}$+$\vec{b}$, … |
| cubic | $23, m\bar{3}$<br>$432, \bar{4}3m, m\bar{3}m$ | $\vec{a}, \vec{b}, \vec{c}$ | $\vec{a} \pm \vec{b} \pm \vec{c}$ | $\vec{a} \pm \vec{b}$, … |

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

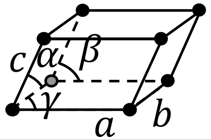
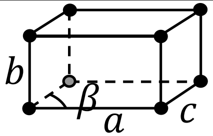
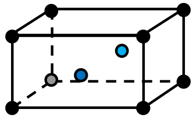
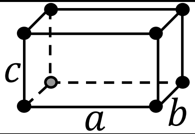
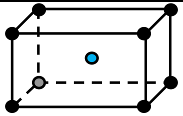
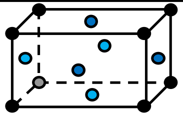
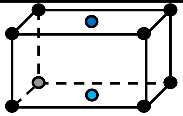
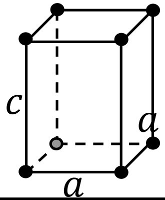
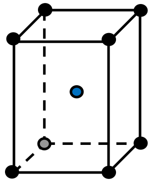
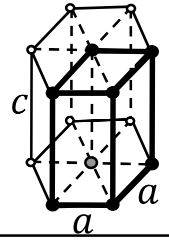
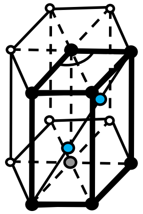
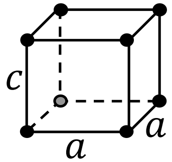
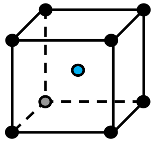
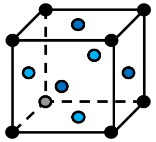
- 6 primitive lattices (one for each of the 6 conventional cells),
- 8 non primitive (= centered) ones, by adding nodes in the former cells, provided no symmetry element is lost & the centered cell is more symmetric than any primitive unit cell.

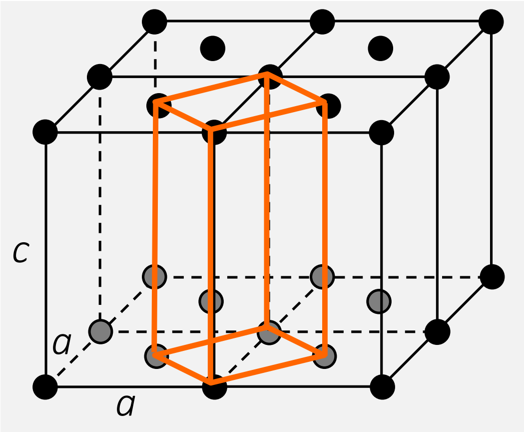
| Symbol | Centering mode | $m$ |
|---|---|---|
| $P$ | primitive | 1 |
| $I$ | body centered | 2 |
| $F$ | all face centered | 4 |
| $A, B, C$ | $A$-, $B$-, $C$-face centered: $(\vec{b}, \vec{c}), (\vec{a}, \vec{c}), (\vec{a}, \vec{b})$ respectively | 2 |
| $R$ | rhombohedrally centered: additional lattice nodes at 1/3 and 2/3 of the long diagonal of the $h$ conventional cell (→ trigonal system) | 3 |

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



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

| Conventional cell | Centering mode | | | | |
|---|---|---|---|---|---|
| | $P$ | $I$ | $F$ | $C$ | $R$ |
| triclinic |  | | | | |
| monoclinic |  | | |  | |
| orthorhombic |  |  |  |  | |
| tetragonal |  |  | | | |
| hexagonal |  | | | |  |
| cubic |  |  |  | | |




**Reminder**:
For centered cells,
∃ 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

# 2. Translation Symmetry: *Example – The diamond structure*

Si (diamond structure): cubic $F$ lattice, motif = atoms at $(0,0,0)$ and $\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$

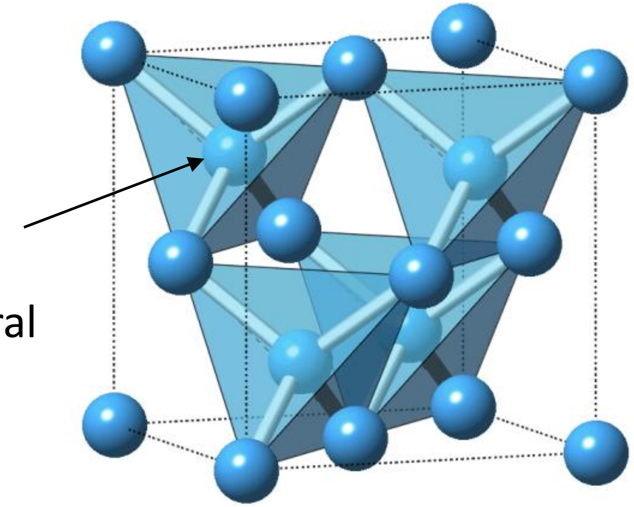
$F$ lattice $(m = 4) \rightarrow$ lattice translations:

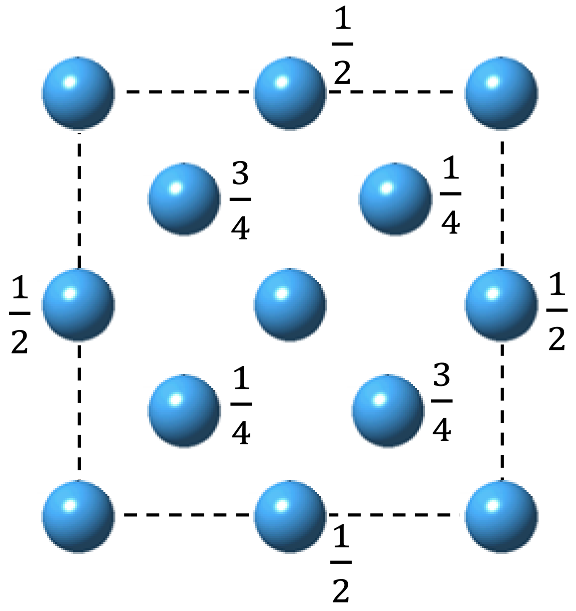
$\vec{T}_1 = u\vec{a} + v\vec{b} + w\vec{c}, \vec{T}_2 = \vec{T}_1 + \frac{1}{2}(\vec{a} + \vec{b}), \vec{T}_3 = \vec{T}_1 + \frac{1}{2}(\vec{b} + \vec{c}), \vec{T}_4 = \vec{T}_1 + \frac{1}{2}(\vec{a} + \vec{c})$

$\rightarrow 4 \times 2 = 8$ Si atoms per unit cell with coordinates:

$(0,0,0), \left(\frac{1}{2},\frac{1}{2},0\right), \left(0,\frac{1}{2},\frac{1}{2}\right), \left(\frac{1}{2},0,\frac{1}{2}\right)$, and $\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right), \left(\frac{3}{4},\frac{3}{4},\frac{1}{4}\right), \left(\frac{1}{4},\frac{3}{4},\frac{3}{4}\right), \left(\frac{3}{4},\frac{1}{4},\frac{3}{4}\right)$

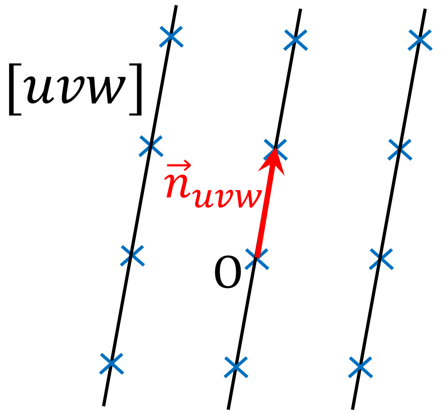
Si on a tetrahedral site





- Family of **lattices directions**

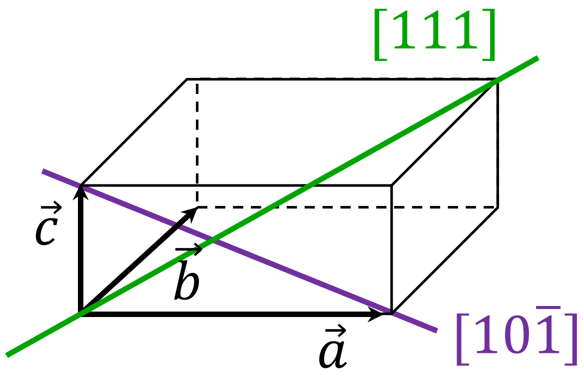
One can group all lattice nodes into parallel equidistant directions labelled $[uvw]$ along the direction vector $\boxed{\vec{n}_{uvw} = u\vec{a} + v\vec{b} + w\vec{c}}$

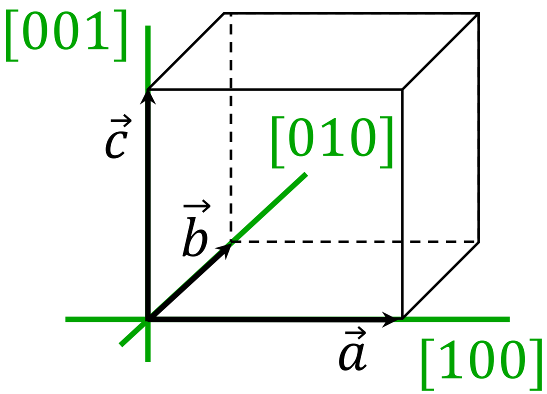



$n_{uvw}$: direction parameter
$u, v, w$: direction indices (coprime integers)

A family of lattice directions contains all lattice points.

- Examples:




Cubic unit cell:
→ directions symmetrically equivalent are labeled $\langle 100 \rangle$

# 2. Translation Symmetry: *Net planes* $(hkl)$

- Family of **net planes**

One can group all lattice nodes into parallel equidistant net planes labelled $(hkl)$ of equation: $\boxed{hx + ky + lz = m}$ with $m$ integer ($> 0$ or $< 0$)

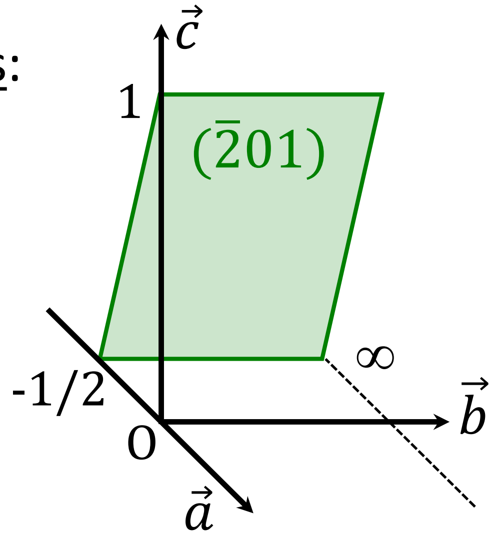
The plane the closest to the origin ($m = 1$) intercepts the $\vec{a}$ axis at $1/h$, the $\vec{b}$ axis at $1/k$, and the $\vec{c}$ axis at $1/l$.

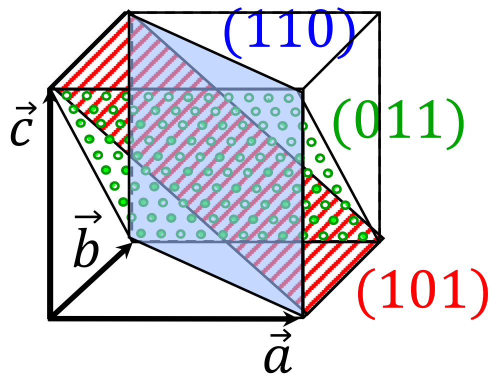
$h, k, l$ (integers, which are coprime for a $P$ lattice): Miller indices

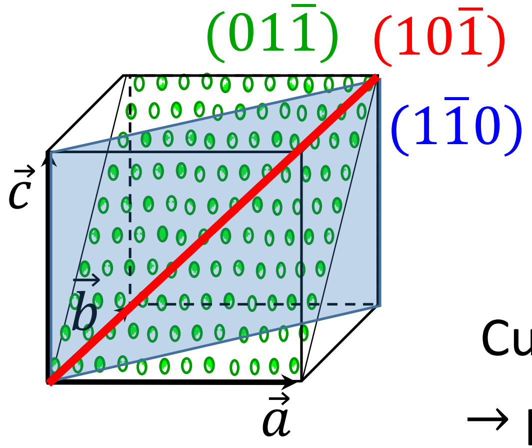
$d_{hkl}$ (distance between 2 consecutive planes): $d$-spacing

A family of net planes contains all lattice points.

- Examples:




Cubic unit cell:

→ planes symmetrically equivalent are labeled $\{110\}$

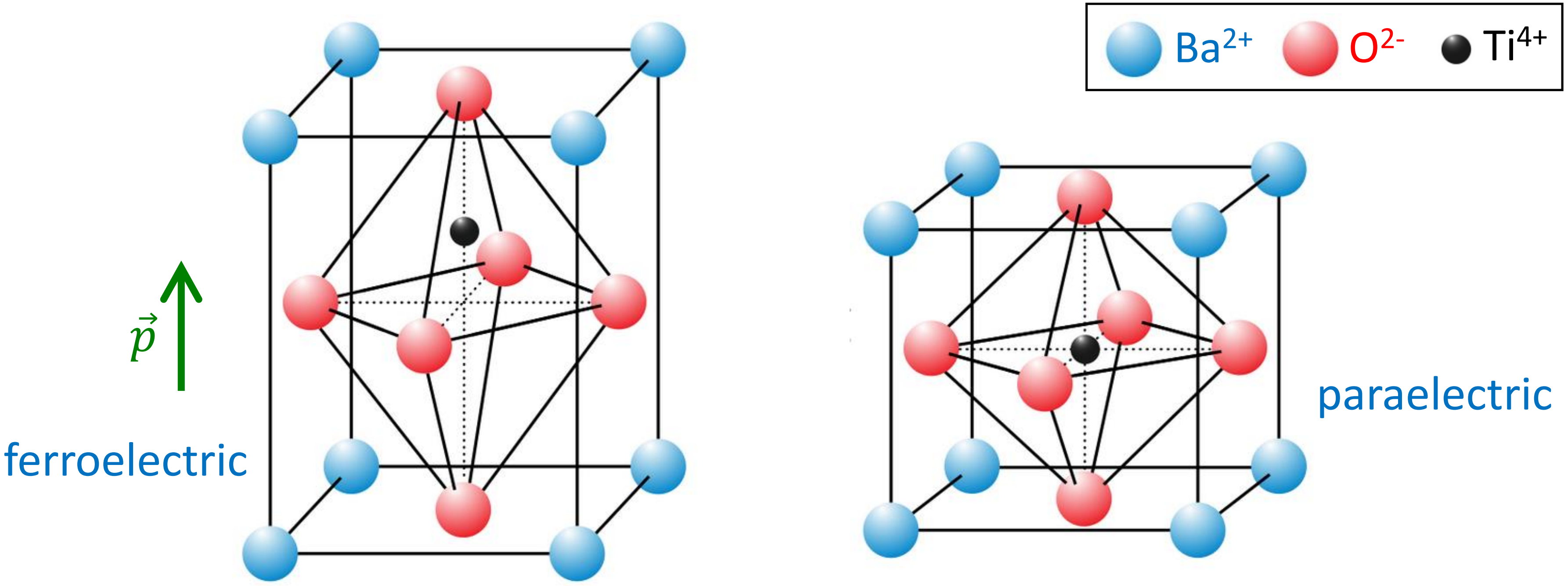
# Phase transitions and symmetry relations

**Example : $BaTiO_3$**

$$\xrightarrow[\qquad\qquad 120°C \qquad\qquad]{} T$$

Tetragonal ($4mm$)
$a = 4.000$ Å
$c = 4.017$ Å

Cubic ($m\bar{3}m$)
$c = 4.007$ Å



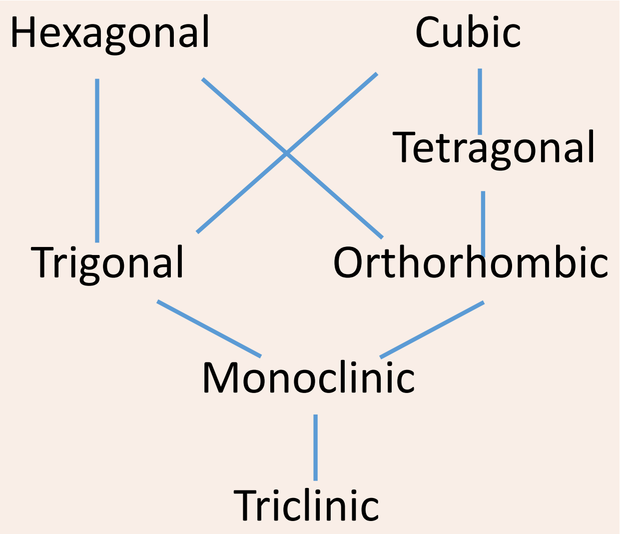

N.B.: With no external stress (pressure, electric field, …): 3 different twins with 2 domains at 180° each

# Phase transitions and symmetry relations

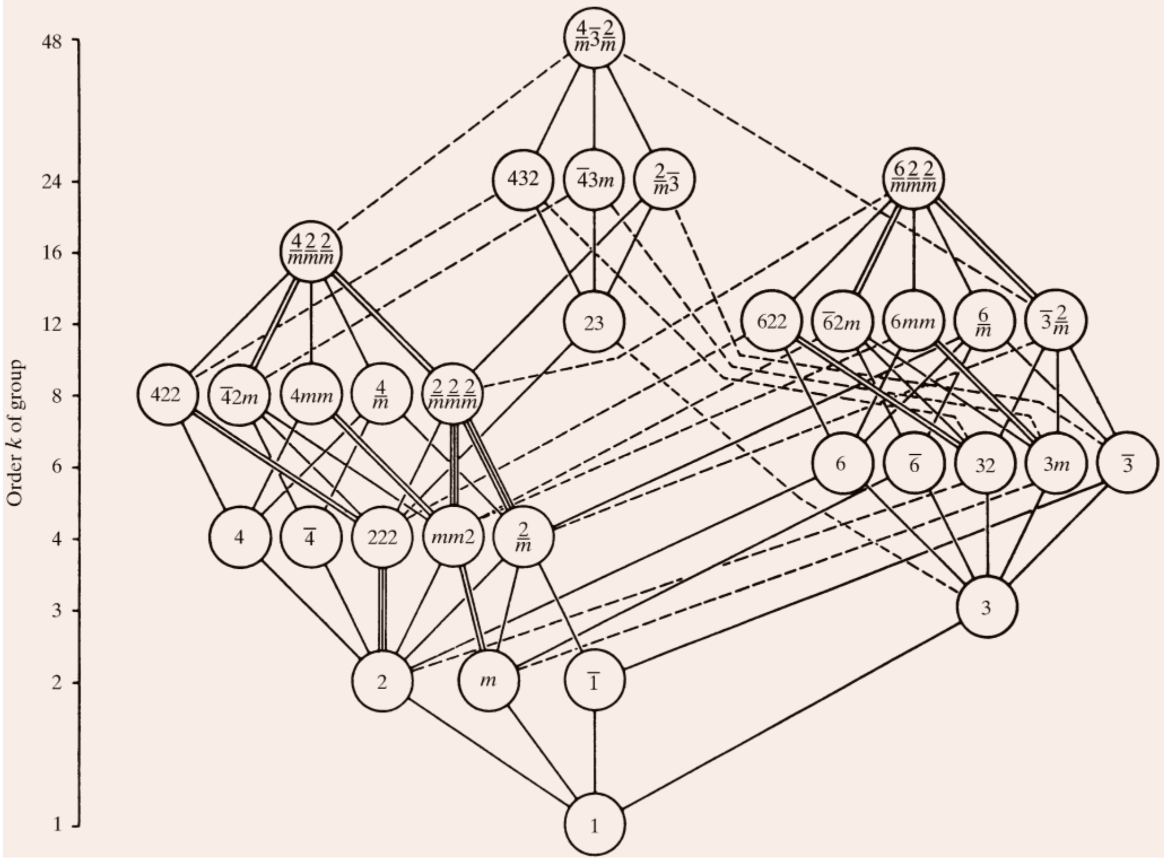
**2nd order phase transition:**

There exist a group / subgroup relation between the 2 phases

<u>Example</u>: cooling down → **symmetry lowers** (change of point group)




*Relation between the 7 crystal systems*




*Group / subgroup relations between the 32 point groups*
*Source: ITC, volume A, page 796*

# 3. Space group symmetry

Crystal = lattice + motif

**translations $\vec{T}$**

14 Bravais lattices

+

**∃ symmetries acting inside the motif**
(symmetry planes and axes)

Point symmetries (32 point groups)
combined or not with a fractional translation

⇓

230 SPACE GROUPS

- Describe the symmetry of the internal structure of crystals
- Allow to classify all the crystals

- International Tables for Crystallography (ITC) (**https://it.iucr.org**)
- Bilbao Crystallographic Server (**http://www.cryst.ehu.es**)
- A Hypertext Book of Crystallographic Space Group Diagrams and Tables (**http://img.chem.ucl.ac.uk/sgp/mainmenu.htm**)

# 3. Space group symmetry

INTERNATIONAL TABLES for CRYSTALLOGRAPHY


https://it.iucr.org/resources/

| home | resources | purchase | contact us | help |

INTERNATIONAL TABLES Resources

| A | A1 | B | C | D | E | F | G |

Home > Resources

## International Tables for Crystallography Resources

The following resources are available as part of **International Tables Online**:

- Search for a crystallographic symmetry group

**Go to** space group **No.** 1 (P 1) Go

- Symmetry database
- Retrieve scattering factors for electron diffraction
- Plot scattering factors for electron diffraction
- Retrieve scattering lengths for neutron diffraction
- Resources for Volume D (*Tenχar* and *GI*KoBo-1*)
- Superspace Group Finder
- CIF dictionaries
  - Core CIF Dictionary
  - Electron Density CIF Dictionary
  - Image CIF Dictionary
  - Macromolecular CIF Dictionary
  - Modulated Structures CIF Dictionary
  - Powder CIF Dictionary
  - Symmetry CIF Dictionary

www.cryst.ehu.es

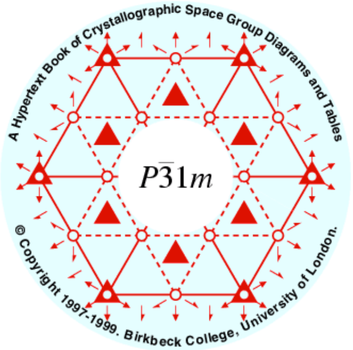
**bilbao crystallographic server**

Contact us About us Publications

**Space-group symmetry**

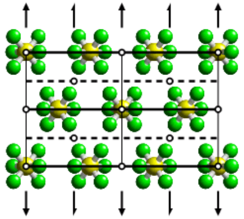
| | |
|---|---|
| GENPOS | Generators and General Positions of Space Groups |
| WYCKPOS | Wyckoff Positions of Space Groups |
| HKLCOND | Reflection conditions of Space Groups |
| MAXSUB | Maximal Subgroups of Space Groups |
| SERIES | Series of Maximal Isomorphic Subgroups of Space Groups |
| WYCKSETS | Equivalent Sets of Wyckoff Positions |
| NORMALIZER | Normalizers of Space Groups |
| KVEC | The k-vector types and Brillouin zones of Space Groups |
| SYMMETRY OPERATIONS | Geometric interpretation of matrix column representations of |
| IDENTIFY GROUP | Identification of a Space Group from a set of generators in ar |

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




A Hypertext Book of

**Crystallographic Space Group Diagrams and Tables**



CD-ROM Cover Picture

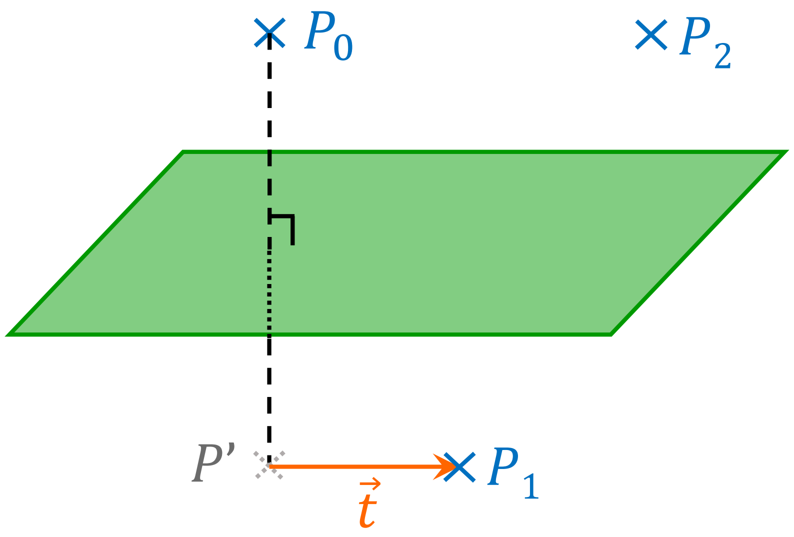
High-Resolution Space Group Diagrams and Tables (1280 × 1024 pixel screens)

Medium-Resolution Space Group Diagrams and Tables (1024 × 768 pixel screens)

- Glide plane

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

*acting inside the unit cell*




Example: **glide plane** $a \perp \vec{c}$ $(\vec{t} \parallel \vec{a})$

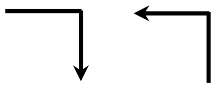
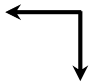
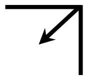
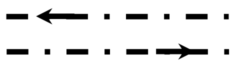
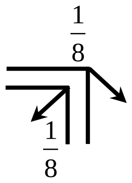
$a \times a \rightarrow$ lattice translation

$$P_0P_2 = \vec{a} \rightarrow \boxed{\vec{t} = \frac{\vec{a}}{2}}$$

*(see appendix for the Seitz notation and the $4 \times 4$ matrix representation)*

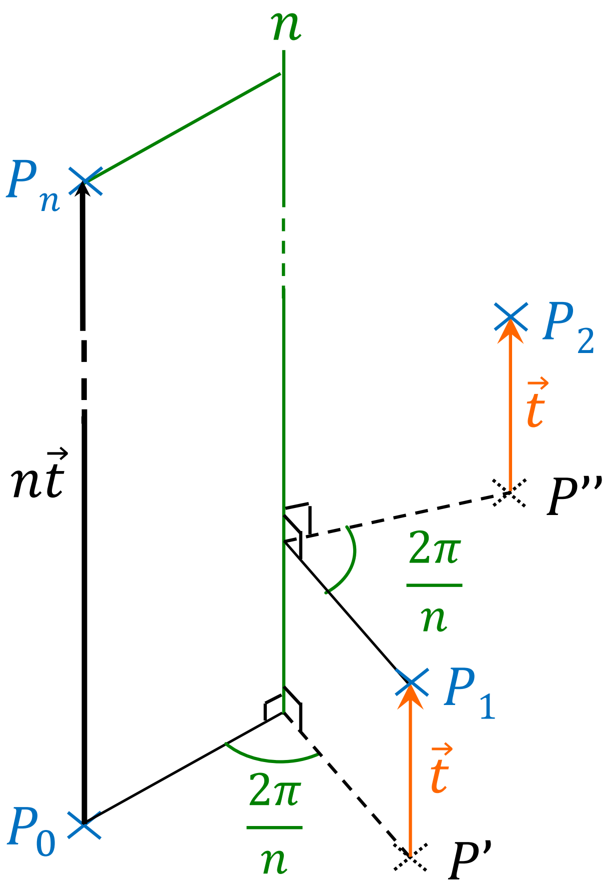
# 3. Space group symmetry: *Symmetry planes*

## The various symmetry planes and their Hermann-Mauguin symbol

| Printed symbol | Symmetry plane | Graphic symbol: ⊥ projection plane | Graphic symbol: ∥ projection plane | Nature of the gliding (fractional translation $\vec{t}$) |
|---|---|---|---|---|
| $m$ | 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 $a/2$ et $c/2$ ; OR $(a \pm b)/2$ and $c/2$, etc … for $t$ and $c$ systems |
| $n$ | Diagonal glide plane |  |  | $(a+b)/2, (b+c)/2$ or $(c+a)/2$ ; OR $(a+b+c)/2$ in some cases for $t$ and $c$ systems |
| $d$ | Diamond glide plane |  |  | $(a+b)/4, (b+c)/4$ or $(c+a)/4$ ; OR $(a+b+c)/4$ in some cases for $t$ and $c$ systems |

- Screw axes

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




Example: **screw axis** $n_p$ ‖ $\vec{c}$

$$\underbrace{n_p \times \cdots \times n_p}_{n \text{ times}} \rightarrow \text{lattice translation}$$

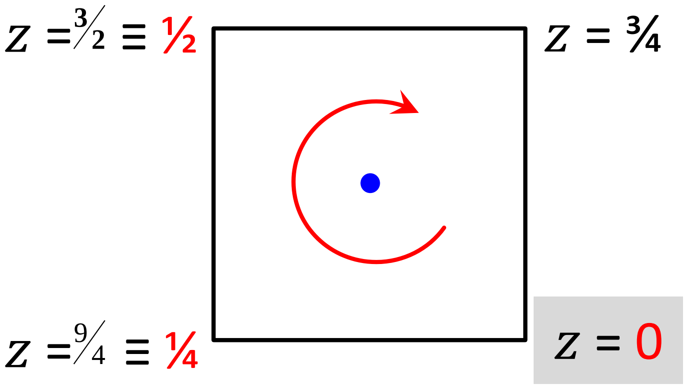
$$\overrightarrow{P_0P_n} = n\vec{t} = p\vec{c}$$

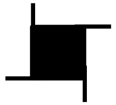
$$\text{with} \begin{cases} n = 1,2,3,4, \text{or } 6 \\ p \text{ integer} < n \end{cases}$$

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

Example: $4_3$ ‖ $\vec{c}$

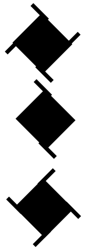
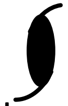
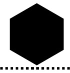
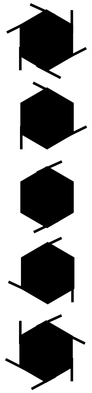
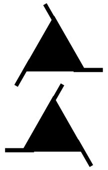
Axis $4_3$: $\vec{t} = \frac{3}{4}\vec{c}$



# 3. Space group symmetry: *Symmetry axes*

The various symmetry axes and their Hermann-Mauguin symbol *(projection plane ⊥ $\vec{c}$)*

| Printed symbol | Symmetry axis | Graphic symbol | Gliding $\vec{t}$ | Printed symbol | Symmetry axis | Graphic symbol | Gliding $\vec{t}$ |
|---|---|---|---|---|---|---|---|
| $1$ | Identity | none | none | $4$ | 4-fold rotat° |  | none |
| $\bar{1}$ | Inversion | ○ | none | $4_1$<br>$4_2$<br>$4_3$ | 4-fold screw axes |  | $c/4$<br>$2c/4$<br>$3c/4$ |
| $2$ | 2-fold rotation axis |  (⊥ plan proj.)<br> (∥ plan proj.) | none | $\bar{4}$ | 4-fold rotoinversion |  | none |
| $2_1$ | 2-fold screw axis |  (⊥ plan proj.)<br> (∥ plan proj.) | $c/2$<br>$a/2$ ou $b/2$ | $6$ | 6-fold rotat° |  | none |
| $3$ | 3-fold rotation axis | ⊥ plan proj.<br> | none | $6_1$<br>$6_2$<br>$6_3$<br>$6_4$<br>$6_5$ | 6-fold screw axes |  | $c/6$<br>$2c/6$<br>$3c/6$<br>$4c/6$<br>$5c/6$ |
| $3_1$<br>$3_2$ | 2-fold screw axes |  | $c/3$<br>$2c/3$ | | | | |
| $\bar{3}$ | 3-fold rotoinversion |  | none | $\bar{6}$ | 6-fold rotoinversion |  | none |

# 3. Space group symmetry: *How to name all space groups?*

Ex. $P4_2/mmc$

- International notation (Hermann-Mauguin symbol)

1st letter : capital letter designing the centering mode $P, I, F, A$ ($B$ or $C$ ), $R$

Following letters: nature of the symmetry elements

Symmetry axes (with $n$ max and $p$ min) and planes ($m > e > a > b > c > n > d$)

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

| Conventional cell | Primary direction | Secondary direction | Tertiary direction |
|---|---|---|---|
| triclinic | A single symbol (1 or $\bar{1}$), thus no direction of symmetry | | |
| monoclinic | A single direction of symmetry: $b$ or $c$ (order 2, unique axis) | | |
| orthorhombic | $a$ (order 2) | $b$ (order 2) | $c$ (order 2) |
| tetragonal | $[001]$ (order 4) | $\langle 100 \rangle$, i.e. $a$ and $b$ (order 2) | $\langle 110 \rangle$, i.e. $a \pm b$ (order 2) |
| hexagonal | $c$ (order 6 or 3) | $\langle 100 \rangle$, i.e. $a$, $b$, $[1\bar{1}0]$ (order 2) | $\langle 210 \rangle$, i.e. $[210]$, $[\bar{1}20]$, $[1\bar{1}0]$ (order 2) |
| cubic | $\langle 100 \rangle$ (order 4 or 2) | $\langle 111 \rangle$ (order 3) | $\langle 110 \rangle$ (order 2) |

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

*(see appendix for short vs full symbols)*

6 conventional cells

14 Bravais lattices (translation symmetry)

32 point groups

*Symmetry at the **macroscopic** scale*

230 space groups

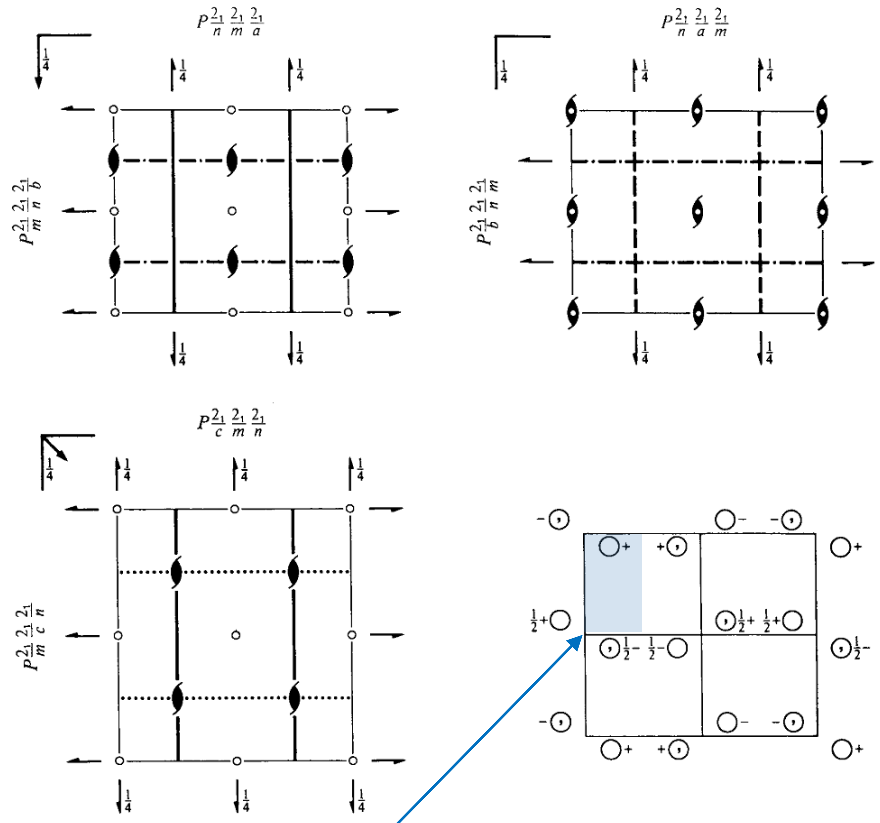
*Symmetry at the **microscopic** scale*

| cryst. syst. | 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 | $Ima2$ |
| | *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 | $P4_12_12$ |
| | | 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 | $P4_2/ncm$ |
| | | 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 | $P6cc$ |
| | | 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 | $I2_13$ |
| | $m\bar{3}$ | 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 | $Ia\bar{3}d$ |

# 3. Space group symmetry: *Space group Pnma – ITC, volume A*

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

No. 62 $P\ 2_1/n\ 2_1/m\ 2_1/a$ Full symbol Patterson symmetry *Pmmm*



**Origin** at $\bar{1}$ on $12_11$

**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) $n(0,\frac{1}{2},\frac{1}{2})$ $\frac{1}{4},y,z$ |

Symmetry operations

CONTINUED No. 62 *Pnma*

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

**Positions** Wyckoff sites

| Multiplicity, Wyckoff letter, Site symmetry | | | Coordinates | | | | Reflection conditions |
|---|---|---|---|---|---|---|---|
| | | | | | | | General: |
| 8 | *d* | 1 | (1) $x,y,z$ (5) $\bar{x},\bar{y},\bar{z}$ | (2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$ (6) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$ | (3) $\bar{x},y+\frac{1}{2},\bar{z}$ (7) $x,\bar{y}+\frac{1}{2},z$ | (4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$ (8) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$ | $0kl$ : $k+l=2n$; $hk0$ : $h=2n$; $h00$ : $h=2n$; $0k0$ : $k=2n$; $00l$ : $l=2n$ |
| | | | | | | | 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* | $\bar{1}$ | $0,0,0$ | $\frac{1}{2},0,\frac{1}{2}$ | $0,\frac{1}{2},0$ | $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ | $hkl$ : $h+l,k=2n$ |

**Symmetry of special projections**

Along [001] $p2gm$
$\mathbf{a}'=\frac{1}{2}\mathbf{a}$ $\mathbf{b}'=\mathbf{b}$
Origin at $0,0,z$

Along [100] $c2mm$
$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}$
Origin at $x,\frac{1}{4},\frac{1}{4}$

Along [010] $p2gg$
$\mathbf{a}'=\mathbf{c}$ $\mathbf{b}'=\mathbf{a}$
Origin at $0,y,0$

**Maximal non-isomorphic subgroups**

| | | |
|---|---|---|
| **I** | [2] $Pn2_1a$ ($Pna2_1$, 33) | 1; 3; 6; 8 |
| | [2] $Pnm2_1$ ($Pmn2_1$, 31) | 1; 2; 7; 8 |
| | [2] $P2_1ma$ ($Pmc2_1$, 26) | 1; 4; 6; 7 |
| | [2] $P2_12_12_1$ (19) | 1; 2; 3; 4 |
| | [2] $P112_1/a$ ($P2_1/c$, 14) | 1; 2; 5; 6 |
| | [2] $P2_1/n11$ ($P2_1/c$, 14) | 1; 4; 5; 8 |
| | [2] $P12_1/m1$ ($P2_1/m$, 11) | 1; 3; 5; 7 |
| **IIa** | none | |
| **IIb** | none | |

**Maximal isomorphic subgroups of lowest index**

**IIc** [3] *Pnma* ($\mathbf{a}'=3\mathbf{a}$) (62); [3] *Pnma* ($\mathbf{b}'=3\mathbf{b}$) (62); [3] *Pnma* ($\mathbf{c}'=3\mathbf{c}$) (62)

**Minimal non-isomorphic supergroups**

**I** none

**II** [2] *Amma* (*Cmcm*, 63); [2] *Bbmm* (*Cmcm*, 63); [2] *Ccme* (*Cmce*, 64); [2] *Imma* (74); [2] *Pcma* ($\mathbf{b}'=\frac{1}{2}\mathbf{b}$) (*Pbam*, 55); [2] *Pbma* ($\mathbf{c}'=\frac{1}{2}\mathbf{c}$) (*Pbcm*, 57); [2] *Pnmm* ($\mathbf{a}'=\frac{1}{2}\mathbf{a}$) (*Pmmn*, 59)

*See appendix for more explanations*

# 3. Space group symmetry: *Space group $Pnma$ – ITC, volume A*

Orthorhombic $\quad P\,2_1/n\,2_1/m\,2_1/a$

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 $a \perp \vec{c}$

Point group: $\frac{2}{m}\frac{2}{m}\frac{2}{m}$

$(n, m, a \rightarrow m$ and $2_1 \rightarrow 2)$

**Symmetry operations**

(1) $1$ $\qquad$ (2) $2(0,0,\frac{1}{2})\ \ \frac{1}{4},0,z$ $\qquad$ (3) $2(0,\frac{1}{2},0)\ \ 0,y,0$ $\qquad$ (4) $2(\frac{1}{2},0,0)\ \ x,\frac{1}{4},\frac{1}{4}$

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

2-fold rotation followed by $\vec{t} = \frac{1}{2}\vec{c}$
i.e. axis $2_1 \parallel \vec{c}$

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

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

plane $\perp \vec{a}$ located at $x = \frac{1}{4}$

Wyckoff sites: List of the different sites from the most general (*i.e.* less symmetrical) to the less general position (*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 | $a$ | $\bar{1}$ | $0,0,0$ | $\frac{1}{2},0,\frac{1}{2}$ | $0,\frac{1}{2},0$ | $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ |

**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) $n(0,\frac{1}{2},\frac{1}{2})$ $\frac{1}{4},y,z$ |

Site name

Multiplicity of the site

Wyckoff letter

Site symmetry

Coordinates of all equivalent positions

# 3. Space group symmetry: *Space group Pnma – Univ. London website*

<u>http://img.chem.ucl.ac.uk/sgp/</u>


High-Resolution
## Space Group Diagrams and Tables

Return link to the main menu

⋮

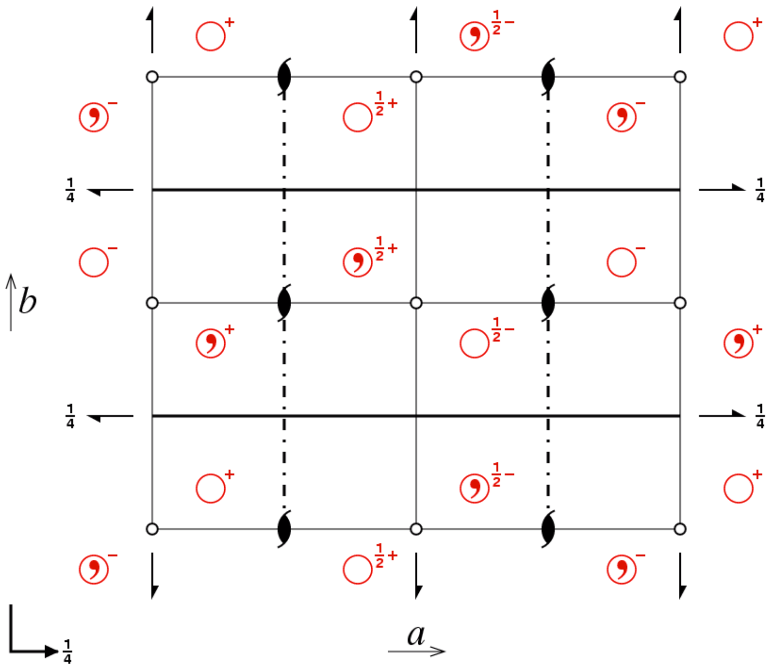
**Orthorhombic**

(For a fuller list with alternative axes and origins click here)

⋮

| | | | | |
|---|---|---|---|---|
| 61. *P b c a* | 62. *P n m a* | 63. *C m c m* | 64. *C m c a* | 65. *C m m m* |
| 66. *C c c m* | 67. *C m m a* | 68. *C c c a* | 69. *F m m m* | 70. *F d d d* |
| 71. *I m m m* | 72. *I b a m* | 73. *I b c a* | 74. *I m m a* | |

*Pnma* $P\,2_1/n\,2_1/m\,2_1/a$ *mmm* No. 62

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### Symmetry Operators

| | | | |
|---|---|---|---|
| 1 | $x, y, z$ | $1$ | |
| 2 | $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$ | $n$ | $(\frac{1}{4}, y, z)\ [0, \frac{1}{2}, \frac{1}{2}]$ |
| 3 | $x, \frac{1}{2}-y, z$ | $m$ | $(x, \frac{1}{4}, z)$ |
| 4 | $\frac{1}{2}+x, y, \frac{1}{2}-z$ | $a$ | $(x, y, \frac{1}{4})\ [\frac{1}{2}, 0, 0]$ |
| 5 | $\bar{x}, \bar{y}, \bar{z}$ | $\bar{1}$ | $(0, 0, 0)$ |
| 6 | $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$ | $2_1$ | $(x, \frac{1}{4}, \frac{1}{4})\ [\frac{1}{2}, 0, 0]$ |
| 7 | $\bar{x}, \frac{1}{2}+y, \bar{z}$ | $2_1$ | $(0, y, 0)\ [0, \frac{1}{2}, 0]$ |
| 8 | $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$ | $2_1$ | $(\frac{1}{4}, 0, z)\ [0, 0, \frac{1}{2}]$ |

***Careful: different order as compared to the ITC!***

# 3. Space group symmetry: *Space group Pnma – Bilbao Cryst. Server*

**bilbao crystallographic server**

**Space-group symmetry**

**http://www.cryst.ehu.es**

**WYCKPOS**

### Wyckoff Positions of Group 62 (*Pnma*)

| Multiplicity | Wyckoff letter | Site symmetry | Coordinates |
|---|---|---|---|
| 8 | d | 1 | (x,y,z) (-x+1/2,-y,z+1/2) (-x,y+1/2,-z) (x+1/2,-y+1/2,-z+1/2)<br>(-x,-y,-z) (x+1/2,y,-z+1/2) (x,-y+1/2,z) (-x+1/2,y+1/2,z+1/2) |
| 4 | c | .m. | (x,1/4,z) (-x+1/2,3/4,z+1/2) (-x,3/4,-z) (x+1/2,1/4,-z+1/2) |
| 4 | b | -1 | (0,0,1/2) (1/2,0,0) (0,1/2,1/2) (1/2,1/2,0) |
| 4 | a | -1 | (0,0,0) (1/2,0,1/2) (0,1/2,0) (1/2,1/2,1/2) |

**GENPOS**

### General Positions of the Group 62 (*Pnma*)

| No. | (x,y,z) form | Matrix form | Symmetry operation ITA | Symmetry operation Seitz |
|---|---|---|---|---|
| 1 | x,y,z | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ | 1 | { 1 \| 0 } |
| 2 | -x+1/2,-y,z+1/2 | $\begin{pmatrix} -1 & 0 & 0 & 1/2 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}$ | 2 (0,0,1/2) 1/4,0,z | { $2_{001}$ \| 1/2 0 1/2 } |

*Same order as in the ITC*

Atomic coordinates

Symmetry operation

# 3. Space group symmetry: *Space group $Pnma$ – LaMnO$_3$*

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

($\equiv Pbnm$ if $\vec{a} \to \vec{b} \to \vec{c} \to \vec{a}$)

| | $x$ | $y$ | $z$ | |
|---|---|---|---|---|
| La | 0.518 | 0.25 | 0.007 | $\to 4c$ |
| Mn | 0 | 0 | 0 | $\to 4a$ |
| $O_1$ | -0.005 | 0.25 | 0.075 | $\to 4c$ |
| $O_2$ | 0.288 | 0.096 | 0.226 | $\to 8d$ |

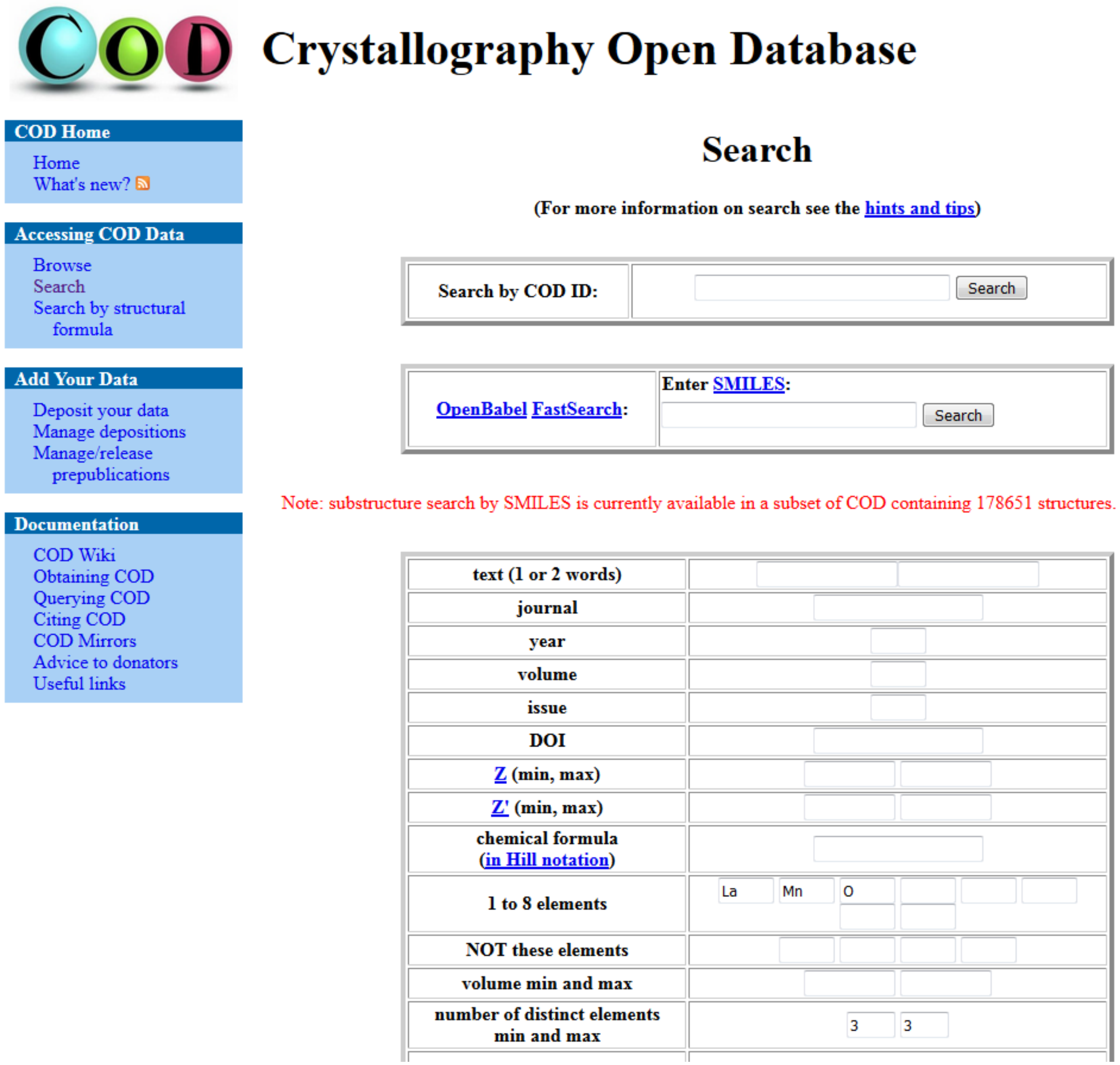
→ Motif = $La_4Mn_4O_{12}$

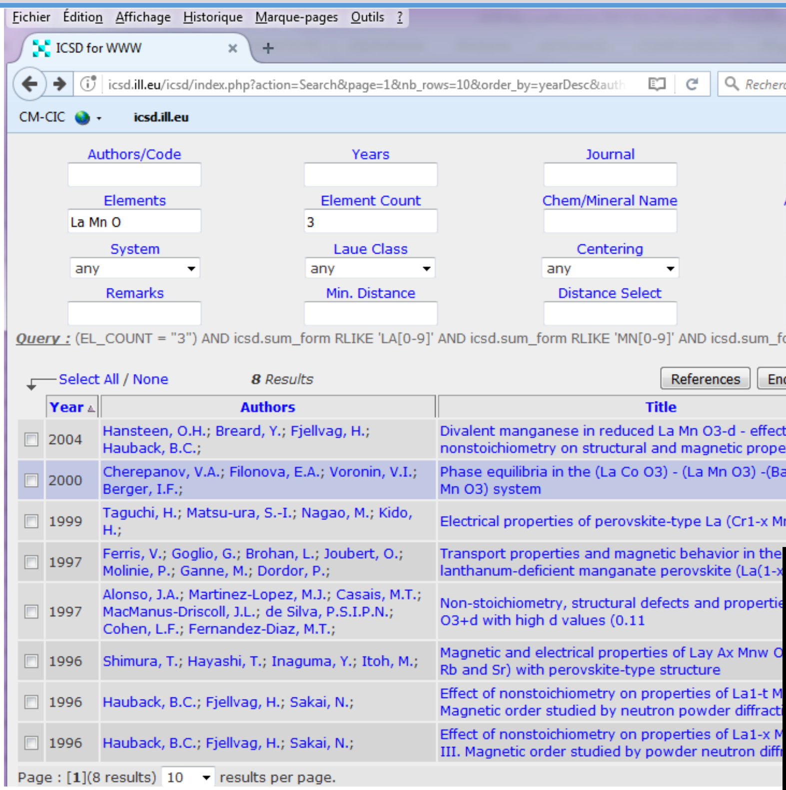
7 coordinates to determine out of (4+4+12)×3 = 60 !!!

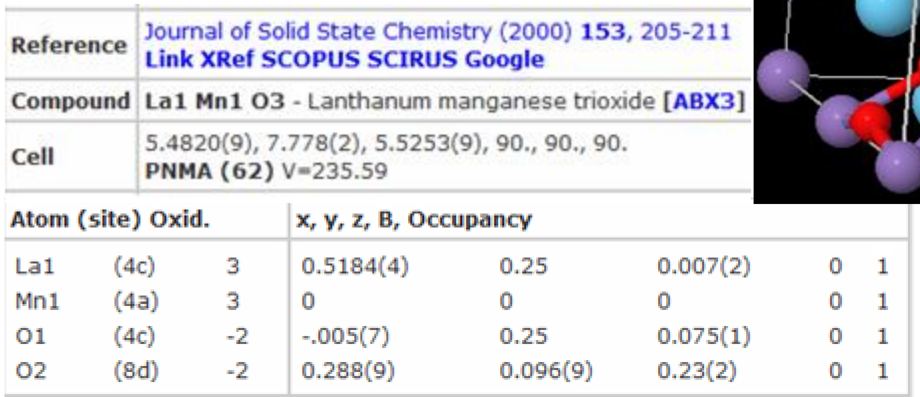
**Positions**

| | Multiplicity, Wyckoff letter, Site symmetry | | | Coordinates | | | |
|---|---|---|---|---|---|---|---|
| $O_2$ | 8 | $d$ | 1 | (1) $x,y,z$<br>(5) $\bar{x},\bar{y},\bar{z}$ | (2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$<br>(6) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$ | (3) $\bar{x},y+\frac{1}{2},\bar{z}$<br>(7) $x,\bar{y}+\frac{1}{2},z$ | (4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$<br>(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 | $a$ | $\bar{1}$ | $0,0,0$ | $\frac{1}{2},0,\frac{1}{2}$ | $0,\frac{1}{2},0$ | $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ |

# 3. Space group symmetry: *Websites for structures*

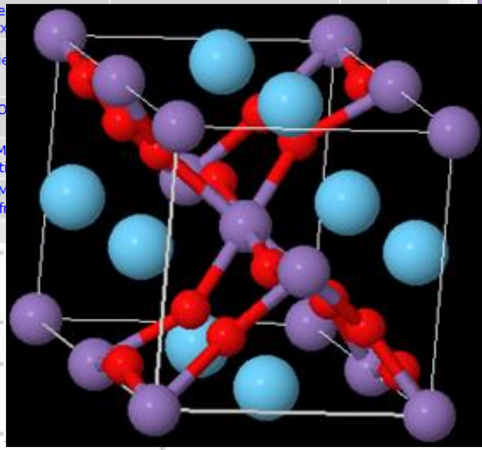


| | |
|---|---|
| Reference | Journal of Solid State Chemistry (2000) **153**, 205-211<br>**Link XRef SCOPUS SCIRUS Google** |
| Compound | **La1 Mn1 O3** - Lanthanum manganese trioxide **[ABX3]** |
| Cell | 5.4820(9), 7.778(2), 5.5253(9), 90., 90., 90.<br>**PNMA (62)** V=235.59 |

| Atom (site) | | Oxid. | x, y, z, B, Occupancy | | | | |
|---|---|---|---|---|---|---|---|
| La1 | (4c) | 3 | 0.5184(4) | 0.25 | 0.007(2) | 0 | 1 |
| Mn1 | (4a) | 3 | 0 | 0 | 0 | 0 | 1 |
| O1 | (4c) | -2 | -.005(7) | 0.25 | 0.075(1) | 0 | 1 |
| O2 | (8d) | -2 | 0.288(9) | 0.096(9) | 0.23(2) | 0 | 1 |



http://www.crystallography.net/cod/search.html → **.cif** files

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

# Crystal symmetry: *Summary*

**Point group symmetry:**

Allows to predict the existence or not of some macroscopic physical properties
And in the case they do exist, the direction of the vectorial quantity or form of the tensor, …

**Translation symmetry:**

Responsible for diffraction → see lecture II

**Structure completely described by:**

Space group + lattice parameters + asymmetric unit
Starting from the asymmetric unit, use the Wyckoff positions to calculate the coordinates of the other atoms of the motif, then apply the lattice translations

**Thank you …**


REFERENCES:

- Transcript of a similar lecture:
*"**Crystallography: Symmetry groups and group representations**", B. Grenier and R. Ballou,*
*Chapter 6 in "Contribution of symmetries in condensed matter", EPJ Web of Conferences Vol. 22, EDP Science (2012).*
- Slides and video of a similar lecture:
*website: http://gdr-meeticc.cnrs.fr/ecole-du-gdr-meeticc-school_v3/*