CRYSTALLOGRAPHIC and MAGNETIC STRUCTURES from NEUTRON DIFFRACTION: the POWER of SYMMETRIES (Lecture I)

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Global outline *(Lectures I, II, and III)*

I- Crystallographic structures

Point Group Symmetry: *from the elementary point symmetries to the 32 point groups*

Translation Symmetry: *lattice, motif, unit cell, directions and net planes, twins*

Space group symmetry: *glide planes and screw axes, the 230 space groups, the ITC*

II- Magnetic structures

Description in terms of propagation vector: *the various orderings, examples*

Description in terms of symmetry:

  - Magnetic point groups: *time reversal, the 122 magnetic point groups*
  - Magnetic lattices: *translations and anti-translations, the 36 magnetic lattices*
  - Magnetic space groups = Shubnikov groups

III- Determination of nucl. and mag. structures from neutron diffraction

Nuclear and magnetic neutron diffraction: *structure factors, extinction rules*

Examples in powder neutron diffraction

Examples in single-crystal neutron diffraction
Crystallography: *introduction*

The word *crystal* comes from Greek (*krustallas*) and means “solidified by the cold”.

*Crystallography = science of crystals*
→ external shape, internal structure, crystal growth, and physical properties.

**Objective:** determine the *atomic positions in the unit cell.*

**Mean:** *diffraction techniques* (X-rays, neutrons, electrons)

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**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

**Examples:** existence or not of ferroelectricity
relations between the various components of the stress tensor...

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[Image]
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)*
  - *Electric conductivity, optical, mechanical, magnetic, .... properties*

To describe crystals: geometrical aspects, symmetries, atomic positions, ...
**Direct space**

To determine the crystal structure: diffraction
**Reciprocal space**
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*

At the macroscopic & atomic (to within a translation) scales, \( \exists \) point symmetries, named point symmetries, that keep at least one point fixed, the origin.

**Inversion (through a point)**

\[ \rightarrow \text{centrosymmetric crystal} \]

\[ \alpha(1) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{Det} = -1 \]

**Rotation (around an axis)**

*Rotation of order* \( n \) = rotation by \( \frac{2\pi}{n} \)

\[ \alpha(n) = \begin{pmatrix} \cos \phi & -\sin \phi & 0 \\ \sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{Det} = +1 \]
1. Point Group Symmetry: *Elementary point symmetries*

**Rotoinversion**
(around an axis and through a point)

\[ \alpha(n) = \begin{pmatrix} -\cos \phi & \sin \phi & 0 \\ -\sin \phi & -\cos \phi & 0 \\ 0 & 0 & -1 \end{pmatrix} \text{ Det } = -1 \]

\[ \alpha(n) = \begin{pmatrix} -\cos \phi & \sin \phi & 0 \\ -\sin \phi & -\cos \phi & 0 \\ 0 & 0 & -1 \end{pmatrix} \text{ Det } = -1 \]

**Reflection**
(through a mirror plane)

\[ \alpha(m) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \text{ Det } = -1 \]

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

→ 10 elementary operations: point groups 1, 2, 3, 4, 6, \(1, 2 = m, 3, 4, 6\)

Proper (Det = 1)  Improper (Det = -1)
A group \((G, \times)\) of order \(n\) is a set of distinct 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 the four axioms:

**Closure:** \[ g_i \times g_j \in G \]

**Identity:** \[ \exists! e \text{ such that } g \times e = e \times g = g \]

**Invertibility:** each element \(g\) has a unique inverse \(g^{-1}\) such that: \[ g \times g^{-1} = g^{-1} \times g = e \]

**Associativity:** \[ (g_i \times g_j) \times g_k = g_i \times (g_j \times g_k) \]

For point symmetry operations:
\[ \times \leftrightarrow \text{ apply successively 2 symmetry operations} \]
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
⇒ 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)

Examples:

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

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 normal to mirror $m$ along same direction
(i.e. plane of the mirror ⊥ to axis $n$)

There exists another notation: *Schoenflies symbol* → widely used in spectroscopy
1. Point Group Symmetry: *Elementary point symmetries*

**SF₆ molecule**

- Octahedral site: $m\bar{3}m$ symmetry
- Point group: $\frac{4}{m} \bar{3} \frac{2}{m}$ ($= m\bar{3}m$)

**CH₄ molecule**

- Tetrahedral site: $\bar{4}3m$ symmetry
- Point group: $\bar{4}3m$

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Crystallographic and Magnetic Structures / Neutron Diffraction, Béatrice GRENIER & Gwenaëlle ROUSSE
## 1. Point Group Symmetry: *Elementary point symmetries*

<table>
<thead>
<tr>
<th>Order of the point symmetry primary direction</th>
<th>Secondary direction</th>
<th>Tertiary direction</th>
<th>Point groups (short symbols) and Laue classes</th>
</tr>
</thead>
<tbody>
<tr>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1, 1</td>
</tr>
<tr>
<td>2</td>
<td>—</td>
<td>—</td>
<td>2, m, 2/m</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2 222, 2mm, mmm</td>
</tr>
<tr>
<td>3</td>
<td>—</td>
<td>—</td>
<td>3, 3</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>—</td>
<td>32, 3m, 3m</td>
</tr>
<tr>
<td>4</td>
<td>—</td>
<td>—</td>
<td>4, 4, 4/m</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>2</td>
<td>4 222, 4mm, 4m2, 4/mmm</td>
</tr>
<tr>
<td>6</td>
<td>—</td>
<td>—</td>
<td>6, 6, 6/m</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>2</td>
<td>6 222, 6mm, 6m2, 6/mmm</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>—</td>
<td>23, m3</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>2</td>
<td>4 32, 43m, m3m</td>
</tr>
</tbody>
</table>
1. Point Group Symmetry: *Elementary point symmetries*

- **Example**: *dielectric properties*
  They can only be found for particular crystal symmetries

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

**Ferroelectricity** and **pyroelectricity**
→ piezoelectric point groups (i.e. non centrosymmetric)
  with a unique polar axis ($\vec{p} \parallel n$-axis and contained in the plane of the mirror):

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

**polar groups**

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**NH$_3$**

Point group: 3$m$
→ $\exists$ 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.

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

(positive or negative)

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

$\mathbf{Crystal} = \mathbf{Lattice} + \mathbf{Motif}$

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

N.B. : $\vec{r} = x\hat{a} + y\hat{b} + z\hat{c} \ (|x|, |y|, |z| < 1)$
2. Translation Symmetry: *Lattice and motif*

**Example 1**: terracotta floor tiles (2D)

- **Lattice**
  - $\vec{b}$
  - $O$
  - $\tilde{a}$

- **Motif**
2. Translation Symmetry: *Lattice and motif*

**Example 2**: CsCl single-crystal (3D)

**Unit cell:**
- cubic primitive

**Motif:**
- Cs\(^+\) on the corner
- Cl\(^-\) at the center
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
2. Translation Symmetry: **Unit cell**

**Lattice parameters:**
- 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 \( n = \) 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: \( V_m = m V \)
  → used only when more symmetrical than any primitive cell of the lattice

**Volume of the unit cell:**
\[
V = (\vec{a}, \vec{b}, \vec{c}) = (\vec{a} \wedge \vec{b}).\vec{c}
\]

**Lengths**
- \( a \)
- \( b \)
- \( c \)

**Angles**
- \( \alpha = (\vec{b}, \vec{c}) \)
- \( \beta = (\vec{c}, \vec{a}) \)
- \( \gamma = (\vec{a}, \vec{b}) \)
2. Translation Symmetry: *Unit cell*

**Primitive unit cells**

- **Primitive cells:** 4 lattice nodes (on corners) ∈ 4 cells → \( m = 4 \times 1/4 = 1 \)

- **Doubly primitive cell:** 4 nodes (on corners) ∈ 4 cells → \( 4 \times 1/4 = 1 \)

  + 2 nodes (on edges) ∈ 2 cells → \( 2 \times 1/2 = 1 \)

\[ m = 2 \]

**Best choice?**

- **Primitive unit cell** reflects the lattice symmetry

**doubly primitive cell**

**motif**
2. Translation Symmetry: *Unit cell*

N.B.: For a primitive cell, the translation vectors $\vec{T}$ are defined by:

$$\vec{T} = u\hat{a} + v\hat{b} + w\hat{c}$$

with $u, v, w$ integers.

For a non-primitive cell of multiplicity $m$, one must add $(m - 1)$ translation vectors such as:

$$\vec{T} = u'\hat{a} + v'\hat{b} + w'\hat{c}$$

with $u', v', w'$ integers or fractionals.

Ex.: For unit cell $\odot$ ($m = 2$):

$$\begin{align*}
\vec{T}_1 &= u\hat{a}' + v\hat{b}' \\
\vec{T}_2 &= \vec{T}_1 + \frac{1}{2}(\hat{a}' + \hat{b}') = \left(u + \frac{1}{2}\right)\hat{a}' + \left(v + \frac{1}{2}\right)\hat{b}'
\end{align*}$$

Cell ❶ is primitive but does not reflect the $\perp^{ty}$ motif

Best choice: ❷

Conventional unit cell
(basis vectors $\parallel$ directions of symmetry of the lattice)
2. Translation Symmetry: The 6 conventional cells and 7 crystal systems

Translation and orientation (point) symmetries:

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, by increasing degree of symmetry:

<table>
<thead>
<tr>
<th>Cell</th>
<th>Description</th>
<th>Parameters</th>
<th>Number of parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>triclinic</td>
<td>$a \neq b \neq c$</td>
<td>6</td>
</tr>
<tr>
<td>m</td>
<td>monoclinic</td>
<td>$a \neq b \neq c$</td>
<td>4</td>
</tr>
<tr>
<td>o</td>
<td>orthorhombic</td>
<td>$a \neq b \neq c$</td>
<td>3</td>
</tr>
<tr>
<td>t</td>
<td>tetragonal or quadratic</td>
<td>$a = b \neq c$</td>
<td>2</td>
</tr>
<tr>
<td>h</td>
<td>hexagonal **</td>
<td>$a = b \neq c$</td>
<td>2</td>
</tr>
<tr>
<td>c</td>
<td>cubic</td>
<td>$a = b = c$</td>
<td>1</td>
</tr>
</tbody>
</table>

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

** 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*

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Point groups and Laue classes</th>
<th>Primary direction</th>
<th>Secondary direction</th>
<th>Tertiary direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>triclinic</td>
<td>1, 1</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>monoclinic</td>
<td>2, m, 2/m</td>
<td>( \vec{b} ) (ou ( \vec{c} ))</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>orthorhombic</td>
<td>222, 2(mm), (mmm)</td>
<td>( \vec{a} )</td>
<td>( \vec{b} )</td>
<td>( \vec{c} )</td>
</tr>
</tbody>
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## 2. Translation Symmetry: *Crystal system vs point group*

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</thead>
<tbody>
<tr>
<td>triclinic</td>
<td>$1, \overline{1}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>monoclinic</td>
<td>$2, m, 2/m$</td>
<td>$\vec{b}$ (ou $\vec{c}$)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>orthorhombic</td>
<td>$222, 2mm, mmm$</td>
<td>$\vec{a}$</td>
<td>$\vec{b}$</td>
<td>$\vec{c}$</td>
</tr>
<tr>
<td>trigonal</td>
<td>$3, \overline{3}$&lt;sup&gt;2&lt;/sup&gt;</td>
<td>$\vec{c}$</td>
<td>$\vec{a}, \vec{b}, -\vec{a} - \vec{b}$</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>$32, 3m, \overline{3}m$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetragonal or quadratic</td>
<td>$4, \overline{4}, 4/m$</td>
<td>$\vec{c}$</td>
<td>$\vec{a}, \vec{b}$</td>
<td>$\vec{a} + \vec{b}, \vec{a} - \vec{b}$</td>
</tr>
<tr>
<td></td>
<td>$422, 4mm, \overline{4}2m, 4/mmm$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hexagonal</td>
<td>$6, \overline{6}, 6/m$</td>
<td>$\vec{c}$</td>
<td>$\vec{a}, \vec{b}, -\vec{a} - \vec{b}$</td>
<td>$2\vec{a} + \vec{b}, ...$</td>
</tr>
<tr>
<td></td>
<td>$622, 6mm, \overline{6}2m, 6/mmm$</td>
<td></td>
<td></td>
<td></td>
</tr>
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## 2. Translation Symmetry: *Crystal system vs point group*

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<tbody>
<tr>
<td>triclinic</td>
<td>1,1</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>monoclinic</td>
<td>2, m, 2/m</td>
<td>$\vec{b}$ (ou $\vec{c}$)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>orthorhombic</td>
<td>222, 2mm, mmm</td>
<td>$\vec{a}$</td>
<td>$\vec{b}$</td>
<td>$\vec{c}$</td>
</tr>
<tr>
<td>trigonal</td>
<td>3, 3</td>
<td>$\vec{c}$</td>
<td>$\vec{a}$, $\vec{b}$, $-\vec{a} - \vec{b}$</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>32, 3m, 3m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetragonal or quadratic</td>
<td>4, 4, 4/m</td>
<td>$\vec{c}$</td>
<td>$\vec{a}$, $\vec{b}$</td>
<td>$\vec{a} + \vec{b}$, $\vec{a} - \vec{b}$</td>
</tr>
<tr>
<td></td>
<td>422, 4mm, 42m, 4/mmm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hexagonal</td>
<td>6, 6, 6/m</td>
<td>$\vec{c}$</td>
<td>$\vec{a}$, $\vec{b}$, $-\vec{a} - \vec{b}$</td>
<td>$2\vec{a} + \vec{b}$, ...</td>
</tr>
<tr>
<td></td>
<td>622, 6mm, 62m, 6/mmm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cubic</td>
<td>23, m$\bar{3}$</td>
<td>$\vec{a}$, $\vec{b}$, $\vec{c}$</td>
<td>$\vec{a} + \vec{b} + \vec{c}$, ...</td>
<td>$\vec{a} + \vec{b}$, ...</td>
</tr>
<tr>
<td></td>
<td>432, 4$\bar{3}$m, m$\bar{3}$m</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2. Translation Symmetry: The 14 Bravais lattices

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

<table>
<thead>
<tr>
<th>Symbole</th>
<th>Lattice mode</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>primitive</td>
<td>1</td>
</tr>
<tr>
<td>$I$</td>
<td>body centered</td>
<td>2</td>
</tr>
<tr>
<td>$F$</td>
<td>all face centered</td>
<td>4</td>
</tr>
<tr>
<td>$A, B, C$</td>
<td>$A$-, $B$-, $C$-face centered:</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>$(\vec{b}, \vec{c}), (\vec{a}, \vec{c}), (\vec{a}, \vec{b})$ respectively</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>rhombohedral centered: additional lattice nodes at 1/3 and 2/3 of the long diagonal of the $h$ cell ($\to$ trigonal system)</td>
<td>3</td>
</tr>
</tbody>
</table>

N.B.: the primitive cell of the $hR$ cell is a rhombohedral cell
($a = b = c, \alpha = \beta = \gamma \neq 90^\circ$)
## 2. Translation Symmetry: The 14 Bravais lattices

<table>
<thead>
<tr>
<th>Conventional cell</th>
<th>Lattice mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P$</td>
</tr>
<tr>
<td>triclinic</td>
<td><img src="image" alt="triclinic" /></td>
</tr>
<tr>
<td>monoclinic</td>
<td><img src="image" alt="monoclinic" /></td>
</tr>
<tr>
<td>orthorhombic</td>
<td><img src="image" alt="orthorhombic" /></td>
</tr>
<tr>
<td>tetragonal</td>
<td><img src="image" alt="tetragonal" /></td>
</tr>
<tr>
<td>hexagonal</td>
<td><img src="image" alt="hexagonal" /></td>
</tr>
<tr>
<td>cubic</td>
<td><img src="image" alt="cubic" /></td>
</tr>
</tbody>
</table>

**Reminder:**
For centered cells, there exist additional lattice translations.

**Example:** $I$ lattice

\[
\begin{align*}
\mathbf{T} &= u\mathbf{a} + v\mathbf{b} + w\mathbf{c} \\
\mathbf{T}' &= \mathbf{T} + \frac{1}{2}(\mathbf{a} + \mathbf{b} + \mathbf{c})
\end{align*}
\]

with $u, v, w$ integers.
2. Translation Symmetry: *Example – the diamond structure*

Silicon (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 ($m = 4$) $\to$ lattice translations:

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

$\to 4 \times 2 = 8$ 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
2. Translation Symmetry: **Lattice directions** $[\mathbf{uvw}]$

- **Family of lattices directions**

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

$n_{\mathbf{uvw}}$ (length of the direction vector): direction parameter $u, v, w$ (coprime integers): direction indices

A family of lattice directions contains all lattice points.

- **Examples:**

  ![Diagram](image)

  - [111]
  - [10\bar{1}]
  - [001]
  - [010]
  - [100]

  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: \(hx + ky + lz = m\) 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: \(
  \rightarrow \text{planes symmetrically equivalent are labeled } \{110\}\)
**Twinned crystal**: association of identical single-crystals with different orientations, connected through a point group symmetry: reflection, rotation, or inversion.

**Formation of twinned crystals**
- **Growth twins**: occurs during the crystal growth;
- **Annealing or Transformation twins**: upon cooling (phase transition)
- **Deformation or gliding twins**: result of stress after the crystal has formed
Symmetry relations between crystals: *phase transitions*

Example: $\text{BaTiO}_3$

- **Tetragonal ($4mm$)**
  - $a = 4.000 \, \text Å$
  - $c = 4.017 \, \text Å$

- **Cubic ($m\bar{3}m$)**
  - $c = 4.007 \, \text Å$

At $120°C$,

- Ferroelectric
- Paraelectric

With no external stress (pressure, electric field, ...):

- **3 different twins** with 2 domains at $180°$ each
2\textsuperscript{nd} order phase transition:  
There exist a group / subgroup relation between the 2 phases  

Example: cooling down → \textbf{symmetry lowers} (change of point group)
3. Space group symmetry

Crystal = lattice + motif

\[ \text{translations } \vec{T} \]

\[ + \]

\[ \exists \text{ symmetries acting inside the motif (symmetry planes and axes)} \]

\[ \downarrow \]

230 SPACE GROUPS

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

14 Bravais lattices

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

- 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

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)
- Symmetry database
-Retrieve scattering factors for electron diffraction
-Plot scattering factors for electron diffraction
-Retrieve scattering lengths for neutron diffraction
-Resources for Volume D (Tenyar and GI*KBo-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

https://it.iucr.org/resources/
3. Space group symmetry

Crystallographic Space Group Diagrams and Tables

Contact us | About us | Publications | How to
--- | --- | --- | ---
GENPOS | Generators and General Positions of Space Groups | Wyckpos | Wyckoff Positions of Space Groups
HKLCND | 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 symmetry operations | IDENTIFY GROUP | Identification of a Space Group from a set of generators in an arbitrary setting
3. Space group symmetry: symmetry planes

- Glide plane
  Combination of a reflection (through a plane) and a fractional translation $\vec{t} \parallel$ plane acting inside the unit cell

Example: glide plane $\vec{a} \perp \vec{c}$ at $z = \frac{1}{4}$

$a \times a \rightarrow$ lattice translation

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

Seitz notation: $\{\alpha|\vec{t}_{\alpha}\} = \{m_z|\frac{1}{2}, 0, \frac{1}{2}\}$

$4 \times 4$ matrix:

$$
\begin{pmatrix}
1 & 0 & 0 & 1/2 \\
0 & 1 & 0 & 0 \\
0 & 0 & -1 & 1/2 \\
0 & 0 & 0 & 1
\end{pmatrix}
$$

$\alpha$: point symmetry

$\vec{t}_{\alpha}$: translation embedding the glide translation + the position of $\alpha$
# 3. Space group symmetry: symmetry planes

The various symmetry planes and their Hermann-Mauguin symbol

<table>
<thead>
<tr>
<th>Printed symbol</th>
<th>Symmetry plane</th>
<th>Graphic symbol</th>
<th>Nature of the gliding (fractional translation $\hat{t}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m$</td>
<td>mirror</td>
<td>![Mirror Symbol]</td>
<td>none</td>
</tr>
<tr>
<td>$a, b, c$</td>
<td>Axial glide plane</td>
<td>$\hat{t} \parallel \text{proj. plane}$</td>
<td>$a/2, b/2, \text{or } c/2$ respectively</td>
</tr>
<tr>
<td>$e$</td>
<td>Double glide plane</td>
<td>![Double Glide Plane Symbol]</td>
<td>$a/2$ 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</td>
</tr>
<tr>
<td>$n$</td>
<td>Diagonal glide plane</td>
<td>![Diagonal Glide Plane Symbol]</td>
<td>$(a+b)/2, (b+c)/2 \text{ or } (c+a)/2$ ; OR $(a+b+c)/2$ in some cases for $t$ and $c$ systems</td>
</tr>
<tr>
<td>$d$</td>
<td>Diamond glide plane</td>
<td>![Diamond Glide Plane Symbol]</td>
<td>$(a+b)/4, (b+c)/4 \text{ or } (c+a)/4$ ; OR $(a+b+c)/4$ in some cases for $t$ and $c$ systems</td>
</tr>
</tbody>
</table>
3. Space group symmetry: symmetry axes

- **Screw axes**

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

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

$$n_p \times \cdots \times n_p \rightarrow \text{lattice translation}$$

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

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

with $\left\{\begin{array}{l} n = 1, 2, 3, 4, \text{ or } 6 \\ p \text{ integer } < n \end{array}\right.$

$$\Rightarrow \vec{t} = \frac{p}{n} \vec{c}$$

with $p = 0, 1, \ldots, n - 1$
3. Space group symmetry: *symmetry axes*

Example: screw axes $4_p \parallel \vec{c}$

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

$z = 0$

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

$z = \frac{1}{2}$

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

$z = \frac{3}{4}$

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

$z = \frac{9}{4} \equiv \frac{1}{4}$
### 3. Space group symmetry: symmetry axes

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

<table>
<thead>
<tr>
<th>Printed symbol</th>
<th>Symmetry axis</th>
<th>Graphic symbol</th>
<th>Gliding $\mathbf{t}$</th>
<th>Printed symbol</th>
<th>Symmetry axis</th>
<th>Graphic symbol</th>
<th>Gliding $\mathbf{t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Identity</td>
<td>none</td>
<td>none</td>
<td>4</td>
<td>4-fold rotat°</td>
<td>⬤</td>
<td>none</td>
</tr>
<tr>
<td>$\bar{1}$</td>
<td>Inversion</td>
<td>o</td>
<td>none</td>
<td>$4_1$</td>
<td>4-fold screw axes</td>
<td>⬤</td>
<td>$c/4$</td>
</tr>
<tr>
<td>2</td>
<td>2-fold rotation axis</td>
<td>(\perp) plan proj. (\parallel) plan proj.</td>
<td>none</td>
<td>$4_2$</td>
<td>4-fold screw axes</td>
<td>⬤</td>
<td>$2c/4$</td>
</tr>
<tr>
<td>$2_1$</td>
<td>2-fold screw axis</td>
<td>(\perp) plan proj. (\parallel) plan proj.</td>
<td>$c/2$</td>
<td>$4_3$</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>3</td>
<td>3-fold rotation axis</td>
<td>$\perp) plan proj.</td>
<td>none</td>
<td>$6_1$</td>
<td>6-fold rotat°</td>
<td>⬤</td>
<td>$c/6$</td>
</tr>
<tr>
<td>$3_1$</td>
<td>2-fold screw axes</td>
<td>$c/3$</td>
<td>none</td>
<td>$6_2$</td>
<td>6-fold screw axes</td>
<td>⬤</td>
<td>$2c/6$</td>
</tr>
<tr>
<td>$3_2$</td>
<td>2-fold screw axes</td>
<td>$2c/3$</td>
<td>none</td>
<td>$6_3$</td>
<td>6-fold screw axes</td>
<td>⬤</td>
<td>$3c/6$</td>
</tr>
<tr>
<td>$\bar{3}$</td>
<td>3-fold rotoinversion</td>
<td>$\perp) plan proj.</td>
<td>none</td>
<td>$6_4$</td>
<td>4c/6</td>
<td>⬤</td>
<td>none</td>
</tr>
<tr>
<td>$\bar{3}$</td>
<td>3-fold rotoinversion</td>
<td>$\perp) plan proj.</td>
<td>none</td>
<td>$6_5$</td>
<td>5c/6</td>
<td>⬤</td>
<td>none</td>
</tr>
</tbody>
</table>
### 3. Space group symmetry: the 230 space groups

#### International notation (Hermann-Mauguin symbol)

**1st letter:** capital letter designating the lattice 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)

<table>
<thead>
<tr>
<th>Conventional cell</th>
<th>Primary direction</th>
<th>Secondary direction</th>
<th>Tertiary direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>triclinic</td>
<td>A single symbol (1 or $\bar{1}$), thus no direction of symmetry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>monoclinic</td>
<td>A single direction of symmetry: $b$ or $c$ (order 2, unique axis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>orthorhombic</td>
<td>$a$ (order 2)</td>
<td>$b$ (order 2)</td>
<td>$c$ (order 2)</td>
</tr>
<tr>
<td>tetragonal</td>
<td>$[001]$ (order 4)</td>
<td>$&lt;100&gt;$, i.e. $a$ and $b$ (order 2)</td>
<td>$&lt;110&gt;$, i.e. $a \pm b$ (order 2)</td>
</tr>
<tr>
<td>hexagonal</td>
<td>$c$ (order 6 or 3)</td>
<td>$&lt;100&gt;$, i.e. $a$, $b$, $[1\bar{1}0]$ (order 2)</td>
<td>$&lt;210&gt;$, i.e. $[210]$, $[\bar{1}20]$, $[1\bar{1}0]$ (order 2)</td>
</tr>
<tr>
<td>cubic</td>
<td>$&lt;100&gt;$ (order 4 or 2)</td>
<td>$&lt;111&gt;$ (order 3)</td>
<td>$&lt;110&gt;$ (order 2)</td>
</tr>
</tbody>
</table>

Ex. $P4_2/mmc$
3. Space group symmetry: the 230 space groups

6 conventional cells
14 Bravais lattices (translation symmetry)

32 point groups
Symmetry at the macroscopic scale

230 space groups
Symmetry at the microscopic scale
3. Space group symmetry: space group $Pnma$ – ITC

Non symmorphic SG
($\exists$ glide translations)

Diagrams of symmetry operations

$\exists$ different settings (permutations of $a$, $b$, $c$)

Diagrams of equivalent positions

Location of the origin

Symmetry operations:
(number), nature, location

Smallest volume of the unit cell containing all structural information

Page 1/2 of $Pnma$ taken from the ITC, volume A
3. Space group symmetry: space group \( Pnma \) – ITC

**Point group:** \( \frac{2}{m} \frac{2}{m} \frac{2}{m} \)

\((n, m, a \rightarrow m \text{ and } 2_1 \rightarrow 2)\)

**Bravais lattice**

- **Screw axis** \( 2_1 \parallel \hat{a} \)
- **Glide plane** \( n \perp \hat{a} \)

- **Screw axis** \( 2_1 \parallel \hat{b} \)
- **Mirror plane** \( m \perp \hat{b} \)

"Representation" of the symmetry operations

<table>
<thead>
<tr>
<th>Symmetry operations</th>
<th>2-fold rotation</th>
<th>Glide plane ( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ( 1 ) ( 1 ) ( 0,0,0 )</td>
<td>( 2(0,0,1) ) ( \frac{1}{4},0,z )</td>
<td>( 2(0,\frac{1}{2},0) ) ( 0,y,0 )</td>
</tr>
<tr>
<td>(5) ( 1 ) ( 0,0,0 )</td>
<td>( a ) ( x,y,\frac{1}{4} )</td>
<td>( m ) ( x,\frac{1}{4},z )</td>
</tr>
<tr>
<td>(6) ( 0,0,0 )</td>
<td>( \frac{1}{4},0,z )</td>
<td>( \frac{1}{2},0,1 )</td>
</tr>
<tr>
<td>(7) ( m ) ( x,\frac{1}{4},z )</td>
<td>( x = \frac{1}{4} ) ( \text{et} \ y = 0 )</td>
<td>( x = \frac{1}{4} ) ( \text{plane} \ (x,y) ), i.e. ( \perp \hat{a} )</td>
</tr>
<tr>
<td>(8) ( n(0,\frac{1}{4},1) )</td>
<td>( \frac{1}{4},y,z )</td>
<td>( \frac{1}{2},0,1 )</td>
</tr>
</tbody>
</table>
**3. Space group symmetry: space group \(Pnma\) – ITC**

**Generators selected**

1. \(r(1,0,0); \(r(0,1,0); \(r(0,0,1))\)
2. \((2); (3); (5)\)

**Positions**

- Identity
- Elementary translations + some of the symmetry axes and planes

**Symmetry of special projections**

- Along \([001]\), \(p_{2GM}\)
  - \(a' = a\)
  - \(b' = b\)
  - Origin at \(0,0,0\)

- Along \([100]\), \(c_{2mm}\)
  - \(a' = b\)
  - \(b' = c\)
  - Origin at \(x,1/2,1/2\)

**Maximal non-isomorphic subgroups**

- I
  - \(P 2_1 2_1 2_1\)
  - \(P 1 1 2_1/a(P 2_1/c)\)
  - \(P 2 1 2_1/m1(P 2_1/m)\)
  - \(P 2_1/n 1 1(P 2_1/c)\)
  - \(P nm 2_1(P m n 2_1)\)
  - \(P n 2_1 a(P n a 2_1)\)
  - \(P 2_1 m a(P m c 2_1)\)

- II
  - none

- III
  - none

**Maximal isomorphic subgroups of lowest index**

- \(P n m a(a' = 3a)\)
- \(P n m a(b' = 3b)\)
- \(P n m a(c' = 3c)\)

**Minimal non-isomorphic supergroups**

- I
  - none

- II
  - \(Am ma(Cm cm)\)
  - \(B nn m(Cm cm)\)
  - \(C c m b(Cm c a)\)
  - \(I m ma\)
  - \(P nm m(2a' = a)(P m n m)\)
  - \(P cm a(2b' = b)(P b a m)\)
  - \(P b m a(2c' = c)(P b c m)\)

**Reference conditions**

- General:
  - \(0k l : k + l = 2n\)
  - \(h00 : h = 2n\)
  - \(h00 : h = 2n\)
  - \(0k0 : k = 2n\)
  - \(00l : l = 2n\)

- Special: as above, plus no extra conditions
  - \(hk l : h + l, k = 2n\)
  - \(hk l : h + l, k = 2n\)

See Lecture III

Subgroups / supergroups, for crystallogr. transitions to a lower / higher symmetry phase

See also [www.cryst.ehu.es](http://www.cryst.ehu.es)

---

*Page 2/2 of \(Pnma\) taken from the ITC, volume A*
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)

<table>
<thead>
<tr>
<th>Site name</th>
<th>Multiplicity</th>
<th>Wyckoff letter</th>
<th>Symmetry of the site</th>
<th>Coordinates of all equivalent positions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8 d 1</td>
<td></td>
<td></td>
<td>(1) $x, y, z$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2) $x + \frac{1}{4}, y, z + \frac{1}{4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(3) $x, y + \frac{1}{4}, z$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(4) $x + \frac{1}{4}, y + \frac{1}{4}, z + \frac{1}{4}$</td>
</tr>
<tr>
<td></td>
<td>4 c m</td>
<td></td>
<td></td>
<td>(5) $x, y, z$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(6) $x + \frac{1}{4}, y, z + \frac{1}{4}$</td>
</tr>
<tr>
<td></td>
<td>4 b \bar{1}</td>
<td></td>
<td></td>
<td>(7) $x, y + \frac{1}{4}, z$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(8) $x + \frac{1}{4}, y + \frac{1}{4}, z + \frac{1}{4}$</td>
</tr>
<tr>
<td>4 a \bar{1}</td>
<td>0,0,0</td>
<td></td>
<td></td>
<td>$\frac{1}{4}, 0, 0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$0, \frac{1}{4}, 0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\frac{1}{4}, \frac{1}{4}, 0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\frac{1}{4}, 0, \frac{1}{4}$</td>
</tr>
</tbody>
</table>

3. Space group symmetry: space group *Pnma – ITC*
### 3. Space group symmetry: *space group Pnma – ITC*

**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)

<table>
<thead>
<tr>
<th>Positions</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>8 d 1</strong></td>
<td>(1) $x, y, z$</td>
</tr>
<tr>
<td>(5) $x, y, z$</td>
<td>(6) $x + \frac{1}{2}, y, z + \frac{1}{2}$</td>
</tr>
</tbody>
</table>

### Symmetry operations

| (1) 1 | (2) $2(0,0,\frac{1}{2}) \quad \frac{1}{2}, 0, z$ | (3) $2(0,\frac{1}{2},0) \quad 0, y, 0$ | (4) $2(\frac{1}{2}, 0, 0) \quad x, \frac{1}{2}, \frac{1}{2}$ |
| (5) $1 \quad 0, 0, 0$ | (6) $a \quad x, y, \frac{1}{2}$ | (7) $m \quad x, \frac{1}{2}, z$ | (8) $n(0, \frac{1}{2}, \frac{1}{2}) \quad \frac{1}{2}, y, z$ |
3. Space group symmetry: *space group* *Pnma* – *ITC*

**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)

<table>
<thead>
<tr>
<th>Positions</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiplicity, Wyckoff letter, Site symmetry</td>
<td></td>
</tr>
</tbody>
</table>
| 8 d 1 | (1) \(x, y, z\)  
(2) \(x + \frac{1}{2}, y, z + \frac{1}{2}\)  
(3) \(x, y + \frac{1}{2}, z\)  
(4) \(x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}\)  
(5) \(x, y, z\)  
(6) \(x + \frac{1}{2}, y, z + \frac{1}{2}\)  
(7) \(x, y + \frac{1}{2}, z\)  
(8) \(x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}\) |
| 4 c .m. | \(x, \frac{1}{4}, z\)  
\(x + \frac{1}{4}, \frac{1}{4}, z + \frac{1}{4}\)  
\(x, \frac{1}{4}, z\)  
\(x + \frac{1}{4}, \frac{1}{4}, z + \frac{1}{4}\) |
| 4 b \(\bar{1}\) | 0,0,\(\frac{1}{4}\)  
\(\frac{1}{4}, 0, 0\)  
0,\(\frac{1}{4}, \frac{1}{4}\)  
\(\frac{1}{4}, \frac{1}{4}, 0\) |
| 4 a \(\bar{1}\) | 0,0,0  
\(\frac{1}{4}, 0, \frac{1}{4}\)  
0,\(\frac{1}{4}, 0\)  
\(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\) |

**Origin at \(\bar{1}\) on 12, 1**
3. Space group symmetry: *space group Pnma*

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

![Space group diagram](http://img.chem.ucl.ac.uk/sgp/)  

**Symmetry Operators**

1. \( x, y, z \)
2. \( \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z \)
3. \( x, \frac{1}{2} - y, z \)
4. \( \frac{1}{2} + x, y, \frac{1}{2} - z \)
5. \( x, \bar{y}, \bar{z} \)
6. \( \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z \)
7. \( \bar{x}, \frac{1}{2} + y, \bar{z} \)
8. \( \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z \)

---

**Careful: different order as compared to the ITC!**
3. Space group symmetry: *space group* \( \text{Pnma} \)

### Wyckoff Positions of Group 62 (\( \text{Pnma} \))

<table>
<thead>
<tr>
<th>Multiplicity</th>
<th>Wyckoff letter</th>
<th>Site symmetry</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>d</td>
<td>1</td>
<td>((x,y,z) (-x+1/2,-y,z+1/2) (-x,y+1/2,-z) (x+1/2,-y+1/2,-z+1/2) (-x,-y,-z) (x+1/2,y,z+1/2) (x,-y+1/2,z) (-x+1/2,y+1/2,z+1/2))</td>
</tr>
<tr>
<td>4</td>
<td>c</td>
<td>.m.</td>
<td>((x,1/4,z) (-x+1/2,3/4,z+1/2) (-x,3/4,-z) (x+1/2,1/4,-z+1/2))</td>
</tr>
<tr>
<td>4</td>
<td>b</td>
<td>-1</td>
<td>((0,0,1/2) (1/2,0,0) (0,1/2,1/2) (1/2,1/2,0))</td>
</tr>
<tr>
<td>4</td>
<td>a</td>
<td>-1</td>
<td>((0,0,0) (1/2,0,1/2) (0,1/2,0) (1/2,1/2,1/2))</td>
</tr>
</tbody>
</table>

**Wyckoff position and site symmetry group of a specific point**

Specify the point by its relative coordinates (in fractions or decimals)

Variable parameters \((x,y,z)\) are also accepted

\[
x = \underline{\text{_____}} \quad y = \underline{\text{_____}} \quad z = \underline{\text{_____}}
\]

If you want to see the Wyckoff position in other setting, click here

http://www.cryst.ehu.es/
### 3. Space group symmetry: space group Pnma

#### ITC

<table>
<thead>
<tr>
<th>8</th>
<th>d</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>x, y, z</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>x + 1/2, y, z + 1</td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>x, y + 1/2, z</td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td>x + 1/2, y + 1/2, z + 1</td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td>x, y, z</td>
<td></td>
</tr>
<tr>
<td>(6)</td>
<td>x + 1/2, y, z + 1</td>
<td></td>
</tr>
<tr>
<td>(7)</td>
<td>x, y + 1/2, z</td>
<td></td>
</tr>
<tr>
<td>(8)</td>
<td>x + 1/2, y + 1/2, z + 1</td>
<td></td>
</tr>
</tbody>
</table>

#### Symmetry operations

<table>
<thead>
<tr>
<th>No.</th>
<th>(1)</th>
<th>2(0,0,1/2)</th>
<th>(3)</th>
<th>2(0,1/2,0)</th>
<th>(4)</th>
<th>2(1/2,0,0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>1</td>
<td>1, 0, z</td>
<td>(3)</td>
<td>0, y, 0</td>
<td>(4)</td>
<td>x, 1/2, 1/2</td>
</tr>
<tr>
<td>(5)</td>
<td>1</td>
<td>0, 0, 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6)</td>
<td>a</td>
<td>x, y, 1/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7)</td>
<td>m</td>
<td>x, 1/2, z</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8)</td>
<td>n</td>
<td>1/2, y, z</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

Click here to get the general positions in text format

<table>
<thead>
<tr>
<th>No.</th>
<th>(x,y,z) form</th>
<th>Matrix form</th>
<th>Symmetry operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>x,y,z</td>
<td>(\begin{pmatrix} 1 &amp; 0 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 &amp; 0 \end{pmatrix})</td>
<td>1 {1</td>
</tr>
<tr>
<td>2</td>
<td>-x+1/2,-y,z-1/2</td>
<td>(\begin{pmatrix} -1 &amp; 0 &amp; 0 &amp; 1/2 \ 0 &amp; -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 &amp; 1/2 \end{pmatrix})</td>
<td>2 {(0,0,1/2) 1/4,0,z} {2</td>
</tr>
</tbody>
</table>

### Same order
3. Space group symmetry: *space group Pnma* – \( \text{LaMnO}_3 \)

Example: \( \text{LaMnO}_3 \) (space group *Pnma*)

<table>
<thead>
<tr>
<th></th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.518</td>
<td>0.25</td>
<td>0.007</td>
</tr>
<tr>
<td>Mn</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( O_1 )</td>
<td>-0.005</td>
<td>0.25</td>
<td>0.075</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>0.288</td>
<td>0.096</td>
<td>0.226</td>
</tr>
</tbody>
</table>

\( \rightarrow 4c \) \( \rightarrow 4a \) \( \rightarrow 4c \) \( \rightarrow 8d \)

\( \rightarrow \) Motif = \( \text{La}_4\text{Mn}_4\text{O}_{12} \)

\( \equiv \text{Pbnm if } \vec{a} \rightarrow \vec{b} \rightarrow \vec{c} \rightarrow \vec{a} \)

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

**Positions**

- **Multiplicity**, **Wyckoff letter**, **Site symmetry**

<table>
<thead>
<tr>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O_2 )</td>
<td>8</td>
<td>( d )</td>
</tr>
</tbody>
</table>

(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) \( x+\frac{1}{2}, \bar{y}+\frac{1}{2}, \bar{z}+\frac{1}{2} \)

<table>
<thead>
<tr>
<th>( x ), ( \frac{1}{2}, z )</th>
<th>( x+\frac{1}{2}, \frac{1}{2}, z+\frac{1}{2} )</th>
<th>( \bar{x}, \frac{1}{2}, \bar{z} )</th>
<th>( x+\frac{1}{2}, \frac{1}{2}, \bar{z}+\frac{1}{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0,0,\frac{1}{2} )</td>
<td>( \frac{1}{2},0,0 )</td>
<td>( 0,\frac{1}{2},\frac{1}{2} )</td>
<td>( \frac{1}{2},\frac{1}{2},0 )</td>
</tr>
<tr>
<td>( 0,0,0 )</td>
<td>( \frac{1}{2},0,\frac{1}{2} )</td>
<td>( 0,\frac{1}{2},0 )</td>
<td>( \frac{1}{2},\frac{1}{2},\frac{1}{2} )</td>
</tr>
</tbody>
</table>
3. Space group symmetry: space group \textit{Pnma} – \textit{LaMnO}_3
3. Space group symmetry: space group Pnma – LaMnO₃

...
## 3. Space group symmetry: space group Pnma – LaMnO₃

![ICSD Database Screenshot](http://icsd.ill.eu/icsd/index.php)

<table>
<thead>
<tr>
<th>Year</th>
<th>Authors</th>
<th>Title</th>
<th>Struct. Formula</th>
<th>sgr</th>
<th>Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004</td>
<td>Hansteen, O.H.; Breard, Y.; Fjellvag, H.; Hauback, B.C.;</td>
<td>Divalent manganese in reduced La Mn O₃-d - effect of oxygen nonstoichiometry on structural and magnetic properties</td>
<td>La (Mn O₂.78)</td>
<td>PNMA</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>Cherepanov, V.A.; Filonova, E.A.; Voronin, V.I.; Berger, I.F.;</td>
<td>Phase equilibria in the (La Co O₃) - (La Mn O₃) - (Ba Co O₂) (Ba Mn O₃) system</td>
<td>La Mn O₃</td>
<td>PNMA</td>
<td></td>
</tr>
<tr>
<td>1999</td>
<td>Taguchi, H.; Matsuura, S.-I.; Nagan, M.; Kido, H.;</td>
<td>Electrical properties of perovskite-type La (Cr₁-x Mnₓ) O₃+d</td>
<td>La0.951 Mn0.951 O₃</td>
<td>R3-CR</td>
<td></td>
</tr>
<tr>
<td>1997</td>
<td>Ferris, Y.; Goglio, G.; Brohan, L.; Joubert, C.; Molinie, P.;</td>
<td>Transport properties and magnetic behavior in the polycrystalline lanthanum-deficient manganese perovskite (La(1-x) Mn O₃)</td>
<td>La0.91 (Mn0.99 O₃)</td>
<td>R3CR</td>
<td></td>
</tr>
<tr>
<td>1997</td>
<td>Alonso, J.A.; Martinez-Lopez, M.J.; Casais, M.T.; MacManus-Driscoll, J.L.; de Silva, P.S.I.P.N.; Cohen, I.F.; Fernandez-Diaz, M.T.;</td>
<td>Non-stoichiometry, structural defects and properties of La Mn O₃+d with high d values (0.11)</td>
<td>La0.969 Mn0.93 O₃</td>
<td>R3-CR</td>
<td></td>
</tr>
<tr>
<td>1996</td>
<td>Shimura, T.; Hayashi, T.; Inaguma, Y.; Itoh, M.;</td>
<td>Magnetic and electrical properties of Lay Ax Mnw O₃ (A = Na, K, Rb and Sr) with perovskite-type structure</td>
<td>La0.953 Mn0.935 O₃</td>
<td>R3-CR</td>
<td></td>
</tr>
<tr>
<td>1996</td>
<td>Hauback, B.C.; Fjellvag, H.; Sakai, N.;</td>
<td>Effect of nonstoichiometry on properties of La1-t Mn O₃+d. III. Magnetic order studied by neutron powder diffraction</td>
<td>La0.92 Mn O₂.88</td>
<td>PNMA</td>
<td></td>
</tr>
<tr>
<td>1996</td>
<td>Hauback, B.C.; Fjellvag, H.; Sakai, N.;</td>
<td>Effect of nonstoichiometry on properties of La1-x Mn O₃+delta III. Magnetic order studied by powder neutron diffraction</td>
<td>La0.88 Mn O₂.82</td>
<td>PNMA</td>
<td></td>
</tr>
</tbody>
</table>
3. Space group symmetry: *space group Pnma* – LaMnO$_3$
3. Space group symmetry: space group $Pnma$ – $LaMnO_3$
3. Space group symmetry: \textit{space group} \textit{Pnma} – \textit{LaMnO}_3

**ICSD for WWW**

Details of the selected entries

- **Title**: Phase equilibria in the (La Co O3) - (La Mn O3) - (Ba Co O2) (Ba Mn O3) system.
- **Authors**: Cherepanov, V.A.; Filonova, E.A.; Voronin, V.I.; Berger, I.F.
- **Compound**: La1 Mn1 O3 - Lanthanum manganese trioxide [\textit{ABX3}] [\textit{dP20}] [\textit{d c2 a}].
- **Cell**: 5.4820(9), 7.778(2), 5.5253(9), 90., 90., 90.
- **PNMA (62)** \(V = 235.59\).
- **Remarks**: RVP XDP.
  At least one temperature factor missing in the paper.
  The coordinates are those given in the paper but the atomic distances do not agree with those calculated during testing. The coordinates are probably correct.
  No R value given in the paper.

<table>
<thead>
<tr>
<th>Atom (site)</th>
<th>Oxid.</th>
<th>x, y, z, B, Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>La1</td>
<td>(4c)</td>
<td>0.5184(4) 0.25 0.007(2) 0 1</td>
</tr>
<tr>
<td>Mn1</td>
<td>(4a)</td>
<td>0 0 0 0 1</td>
</tr>
<tr>
<td>O1</td>
<td>(4c)</td>
<td>-0.005(7) 0.25 0.075(1) 0 1</td>
</tr>
<tr>
<td>O2</td>
<td>(8d)</td>
<td>0.288(9) 0.096(9) 0.23(2) 0 1</td>
</tr>
</tbody>
</table>

Please switch to our new ICSD Web service \textit{http://icsd.fiz-karlsruhe.de}

Current PHP version: 4.3.8 - Current MySQL version: 4.0.21

\textit{Demo database} (The Full database will be used if available after the first query is entered)

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3. Space group symmetry: space group I4mm

Symmorphic SG

Bravais lattice: body centered (I) tetragonal
Axis 4 $\parallel \vec{c}$; mirrors $m \perp <100>$; mirrors $m \perp <110>$
3. Space group symmetry: *space group I4mm*

### Symmetry operations

**For (0,0,0)+ set**

| (1) | l          |
| (2) | m x,0,z    |
| (3) | 4⁺ 0,0,z   |
| (4) | 4⁻ 0,0,z   |
| (5) | m x,0,z    |
| (6) | m 0,y,z    |

**For (¹/₂,¹/₂,¹/₂)+ set**

| (1)  | t(¹/₂,¹/₂) |
| (2)  | n(⁰⁄₄,¹/₂) |
| (3)  | 4⁺(₀,₀,½)  |
| (4)  | 4⁻(₀,₀,½)  |
| (5)  | n(¹/₂,¹/₂) |
| (6)  | n(⁰⁄₄,¹/₂) |
| (7)  | c x⁺₁,½,𝑧 |
| (8)  | n(½,½,½)  |

**Generators selected**

1. \( t(1,0,0); t(0,1,0); t(0,0,1); t(¹/₂,¹/₂) \)

**Positions**

- Multiplicity, Wyckoff letter, Site symmetry
- Coordinates

<table>
<thead>
<tr>
<th>Numbers</th>
<th>Wyckoff letter, Site symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>e</td>
</tr>
</tbody>
</table>

\[ (0,0,0)^+ \quad (¹/₂,¹/₂,¹/₂)^+ \]

**Add** \((0,0,0)\) and \((¹/₂ \ ¹/₂ \ ¹/₂)\) **to these coordinates**

\[ \rightarrow 8 \times 2 \text{ atomic coordinates} \]
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 III

Structure completely described by:
Space group + lattice parameters + asymmetric unit
Then use Wyckoff positions to calculate the coordinates of the other atoms of the motif, and last the lattice translations

The same approach can be done for magnetic structures → see lecture II
Point group: to go further ...

From crystallographic point groups ...

2mm

3m

4mm

6mm

... to Curie point groups

∞m

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

Thank you ...

et bonne dégustation