Symmetry Operations and Space Groups

Crystal Symmetry

32 point groups of crystals compatible with 7 crystal systems
crystallographers use Hermann-Mauguin symmetry symbols

Carl Hermann  
German  
1898 - 1961

Charles-Victor Mauguin  
French  
1878 - 1958

Symmetry Elements

there are 5 types in point symmetry
1. center of symmetry (or inversion): point \( \overline{1} \)
2. rotation (or proper) axis : line \( n \)
3. mirror : plane \( m \)
4. rotation–inversion axis : line \( \overline{n} \)
5. identity : no element \( \text{I} \)

Center of Symmetry: \( \overline{1} \)
a point in the molecule through which if another point on the molecule is taken, will meet an identical point on the molecule an equal distance away

Center of Symmetry: \( \overline{1} \)
all points \((x, y, z)\) \(\rightarrow (-x, -y, -z)\) if \(\overline{1}\) is placed at the origin

Rotation Axis: \( n \)

\( n \) is an integer which gives the degrees of rotation: \( \frac{2\pi}{n} \) or \( \frac{360^\circ}{n} \)
\( n \) is the number of times molecule is rotated, each time stopping at an identical appearance, before returning to the starting point

\( n \) is the foldness of the rotation axis
only 2, 3, 4, and 6-fold axes allowed in crystal symmetry
Rotation Axis: 4

\[ \frac{360^\circ}{4} = 90^\circ \]

Mirror: \( m \)
plane within the molecule that, when acting as a mirror, reflects the molecule into itself

Rotation-Inversion \( \bar{n} \)

rotation followed by inversion

this is a different definition than Schoenflies system

Arthur Moritz Schönflies – German 1891
rotation followed by reflection

Representation of Symmetry

point symmetry often represented symbolically in the form of points on a circle (projection of a sphere)

- a point above plane is a filled circle: ●
- a point below plane is an open circle: ○
- two points directly on top of each other: ⮞

starting with one point, find other points generated by symmetry

32 point groups compatible with 7 crystal systems

Triclinic

1 \((C_1)\) 1 \((C_1)\)

highest symmetry in each crystal system is called: Laue Group

(Schoenflies symbol) have center of symmetry

Monoclinic

2 \((C_2)\) 2 \((C_2)\) 2/m \((C_{2h})\)

monoclinic convention: symmetry located wrt b axis

2: 2-fold axis along b
m: mirror perpendicular to b
2/m: 2-fold axis along b, perpendicular to a mirror
Monoclinic

Orthorhombic

xyz

3 symbols refer to:

axes along a, b, or c

mirrors perpendicular to a, b, or c

Rhombohedral (Trigonal)

Tetragonal

Hexagonal
**Hexagonal**

- $6$
- $6/m$
- $6mm$
- $6m2$
- $622$
- $6/mmm$

**Cubic**

- $23$ ($T$)
- $m3$ ($T_d$)
- $43m$ ($T_d$)
- $432$ ($O$)
- $m3m$ ($O_h$)

**Lattices**

14 Bravais lattices have Laue symmetry

**14 Bravais Lattices**

- **Triclinic**
  - $rI$
- **Monoclinic**
  - $P2_1/n$ or $C2/m$
- **Orthorhombic**
  - $Pmnm$, $Cmcm$, $Immm$
- **Rhombohedral**
  - $R3m$
- **Tetragonal**
  - $P4/nmm$, $P4/n2m$, $I4/mmm$
- **Cubic**
  - $P6/mmm$, $Pn3m$, $Ia3m$, $Fd3m$

**Translational Symmetry**

in repeating lattices, two additional symmetry elements

- **Translation**
- **Rotation**
- **Screw Axis**
- **Glide Plane**

1. **Screw Axis** rotation and translation: $n$, rotation by $360^\circ/n$; followed by translation of $r/n$ along the axis ($a$, $b$, or $c$)
2. **2-fold Screw Axis** most common: $2_1$
3. **Glide Plane** reflection and translation: $a$, $b$, $c$, $n$, or $d$ reflection across plane; followed by translation of $1/2$ (usually) unit cell parallel to plane along $a$, $b$, or $c$ (face diagonal ($n$)), or body diagonal ($d$)
**Screw Axis - \(2_1\)**

\[\begin{array}{c}
\text{a} \\
\text{b} \\
\text{c}
\end{array}\]

**Glide Plane - \(a\)**

\[\begin{array}{c}
\text{a} \\
\text{b} \\
\text{c}
\end{array}\]


**Space Groups**

translational elements + point symmetry \(\Rightarrow\) space groups

in 2-D, referred to as plane groups

there are 17 distinct ways of packing repeating object in 2-D

wallpaper patterns

**Plane Groups**

- \(p1\)
- \(p2\)
- \(pm\)
- \(pg\)
- \(p2mm\)

**Plane Groups**

- \(p2mg\)
- \(p2gg\)
- \(cm\)
- \(c2mm\)
Plane Groups

Plane Groups

Space Groups

translational elements + 32 crystal point groups;

230 space groups

230 distinct ways of packing repeating object in 3-D
tetragonal

Space Groups

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<tr>
<th></th>
<th>4</th>
<th>P4</th>
<th>P4₁</th>
<th>P4₂</th>
<th>P4₃</th>
<th>I4</th>
<th>I₄₁</th>
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<td>P4/m</td>
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<td>P4₂/2</td>
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<td>P4₂/m</td>
<td>P4₂/m</td>
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<td>14/acd</td>
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dihexagonal

Space Groups

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<th>P3₂</th>
<th>R3</th>
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<td>R3</td>
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<td>P312</td>
<td>P312</td>
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<td>P3m1</td>
<td>P3m1</td>
<td>P3m1</td>
<td>R3m</td>
</tr>
<tr>
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<td>P3m1</td>
<td>P3m1</td>
<td>P3m1</td>
<td>P3m1</td>
<td>R3m</td>
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<td>P6/m</td>
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all compounds crystallize in one or more of these space groups
usually possible to find P1, but always try to find the
highest possible symmetry.

structures observed in all 230 space groups

~95% of all structures: monoclinic, triclinic, orthorhombic
~83% of all structures: P₂₁/c, P₁, P₂₁/2₁, C₂₁/c, P₂₁, Phca

7 crystal systems: point symmetry of external lattice
14 Bravais lattices: translational symmetry of lattice points
32 point groups: point symmetry of external crystal
230 space groups: translational symmetry inside crystal molecules

Cambridge Structural Database (CSD)

http://www.ccdc.cam.ac.uk/

592938 structures
Space Group Frequency

Space Group Nomenclature
space group name comes from Bravais lattice symbol, modified for translational symmetry
easy to understand the components of many names, especially monoclinic and orthorhombic:
P2₁/c  (P 2-1 on c)
- primitive unit cell (1 lattice point)
- 2-fold screw axis along b (unique axis)
- c glide (translation along c axis) in ac plane (⊥ to b)
Pbca  primitive unit cell (1 lattice point)
- b glide (translation along b axis) in bc plane (⊥ to a)
- c glide (translation along c axis) in ac plane (⊥ to b)
- a glide (translation along a axis) in ab plane (⊥ to c)

Standard and Non-standard Settings
sometimes a space group that is not on the list of 230 is given in a publication
some space groups can be derived which are identical with another space group ⇒ choice depends on convention
P2₁/a  identical with P2₁/c  switching a and c label in monoclinic
does not change the symmetry
P2₁/n  alternate setting of P2₁/c
β closer to 90° preferred
Pnam  same as Pnma
   switch b and c label

Equivalent Positions
space groups used to locate symmetry related atoms in unit cell
for example, if a benzene ring is located on a mirror:
locate 3 C and 3 H, others at symmetry equivalent positions
asymmetric unit is the smallest part that generates the rest of the unit cell contents by all symmetry operations of space group

Equivalent Positions, Asymmetric Unit and Z
equivalent positions are divided into:
general positions
special positions
asymmetric unit along with general and special positions allows an interpretation of Z (number of molecules in unit cell), and possible molecular symmetry

Equivalent Positions of Symmetry Elements

<table>
<thead>
<tr>
<th>axis</th>
<th></th>
<th></th>
<th>(to) axis</th>
<th>plane</th>
<th>(⊥ to) plane</th>
<th>to position</th>
<th>plane</th>
<th>(⊥ to) plane</th>
<th>to position</th>
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<tbody>
<tr>
<td>2</td>
<td>a</td>
<td>x, y, z</td>
<td>a</td>
<td>c</td>
<td>x + ½, y, z</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>b</td>
<td>x, y, z</td>
<td>b</td>
<td>a</td>
<td>x, y + ½, z</td>
<td></td>
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<td></td>
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<tr>
<td>2</td>
<td>c</td>
<td>x, y, z</td>
<td>b</td>
<td>c</td>
<td>x, y + ½, z</td>
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<tr>
<td>2</td>
<td>a</td>
<td>x + ½, y, z</td>
<td>c</td>
<td>a</td>
<td>x, y, z + ½</td>
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<td></td>
<td></td>
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<tr>
<td>2</td>
<td>b</td>
<td>x, y + ½, z</td>
<td>c</td>
<td>b</td>
<td>x, y, z + ½</td>
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<td>a</td>
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<tr>
<td>2</td>
<td>l</td>
<td>x, y, z</td>
<td>m</td>
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<td>x + ½, y + ½, z</td>
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<tr>
<td>2</td>
<td>a</td>
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<td>d</td>
<td>c</td>
<td>x + ½, y + ½, z</td>
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<td></td>
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</tr>
</tbody>
</table>
Equivalent Positions from Centering

for centered groups, add the following to each P general position:

A \( x, y + \frac{1}{2}, z + \frac{1}{2} \)
C \( x + \frac{1}{2}, y + \frac{1}{2}, z \)
F \( x + \frac{1}{2}, y + \frac{1}{2}, z \)
\( x, y + \frac{1}{2}, z + \frac{1}{2} \)
I \( x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2} \)
R \( x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2} \)

Transforming Coordinates

\( x - \frac{1}{4} = -(x + \frac{1}{4}) = -(x - \frac{1}{4} + \frac{1}{2}) = -(x + \frac{1}{2}) = x + \frac{1}{2} \) (by adding \( \frac{1}{3} \))
\( y + \frac{1}{4} = y - \frac{1}{4} + \frac{1}{2} = y + \frac{1}{2} \)
\( x + \frac{1}{4} = (x - \frac{1}{2}) + \frac{1}{2} = x + \frac{1}{2} + \frac{1}{2} = x \) (by subtracting \( \frac{1}{3} \))

Special Positions

if an object is located at \( x, y, z = 0, 0, 0 \);
only one unique point generated by symmetry is at \( 0, \frac{1}{2}, \frac{1}{2} \)
also true for: \( 0, 0, \frac{1}{2} \)
Special Positions

0, 0, 0 0, ½, ½
0, ½, 0 0, ½, 0
½, 0, ½ ½, ½, 0
½, ½, 0 ½, ½, ½

Note: an object (molecule) at a special position has to have the same symmetry as the special position in P2₁/c; a center of symmetry

Z = 4 for an object on a general position in P2₁/c
Z = 2 for an object on a special position in P2₁/c

Asymmetric unit is ½ of the molecule

Special Positions

An atom on a special position has at least one fixed coordinate; part of the atom generates the rest:

One fixed position (axis ⊥ to plane) for an atom on a mirror
Two fixed positions (other axes) for an atom on a rotation axis
Three fixed positions for an atom on an inversion center

\[(x, 0, z) \text{ or } (x, ½, z)\]
General Positions for Other Space Groups

http://www.cryst.ehu.es/cryst/get_gen.html
http://it.iucr.org/A/

$P2_1/c: Z = 4$

$P2_1/c: Z = 4$

$P2_1/c: Z = 2$

atom on special position
no atom on special position