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Crystal Symmetry

Lecture 3

Symmetry Elements

Point Groups

Lecture 4

Periodic Translation

Unit Cells

Bravais Lattices

Crystal Symmetry Elements

Lecture 5

Space Groups

Ionic Crystals

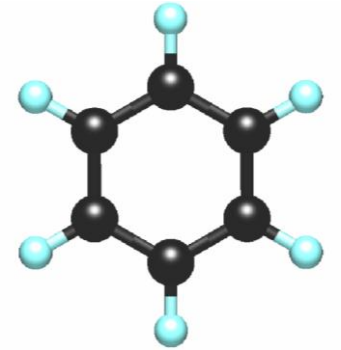
Symmetry Operations

E	Identity operation ('do nothing')
C_n	Rotation (by 360°/n about an axis)
σ	Reflection (through mirror plane; can have σ_v and σ_h)
i	Inversion (through single point – the centre of inversion)
S_n	Improper rotation (rotation by 360°/n and σ_h ($\perp$) reflection)
$\bar{n}$	Inversion axis (rotation by 360°/n and inversion)

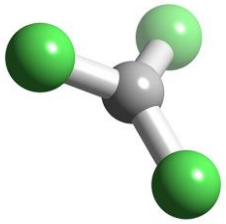
Dihedral Point Groups

D_{nh} : As for C_{nv} but with an additional mirror plane perpendicular to the principal C_n axis

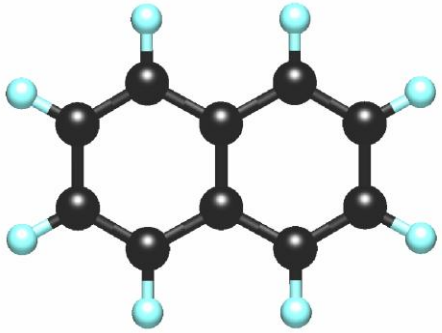
D_{nd} : As for C_{nv} but with n additional C_2 axes perpendicular to the principal C_n axis



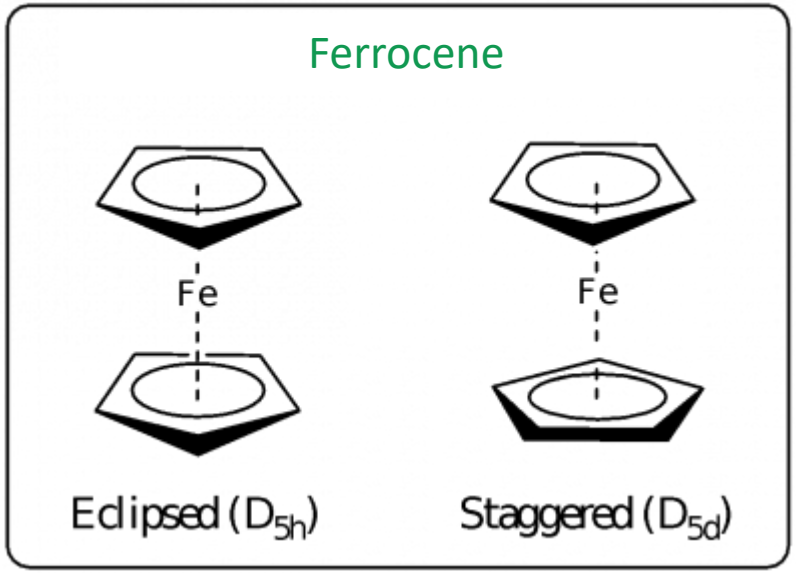
Benzene (D_{6h})



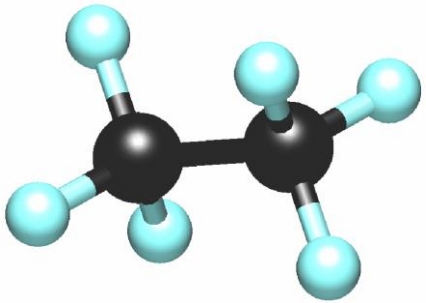
BF_3 (D_{3h})



Naphthalene (D_{2h})

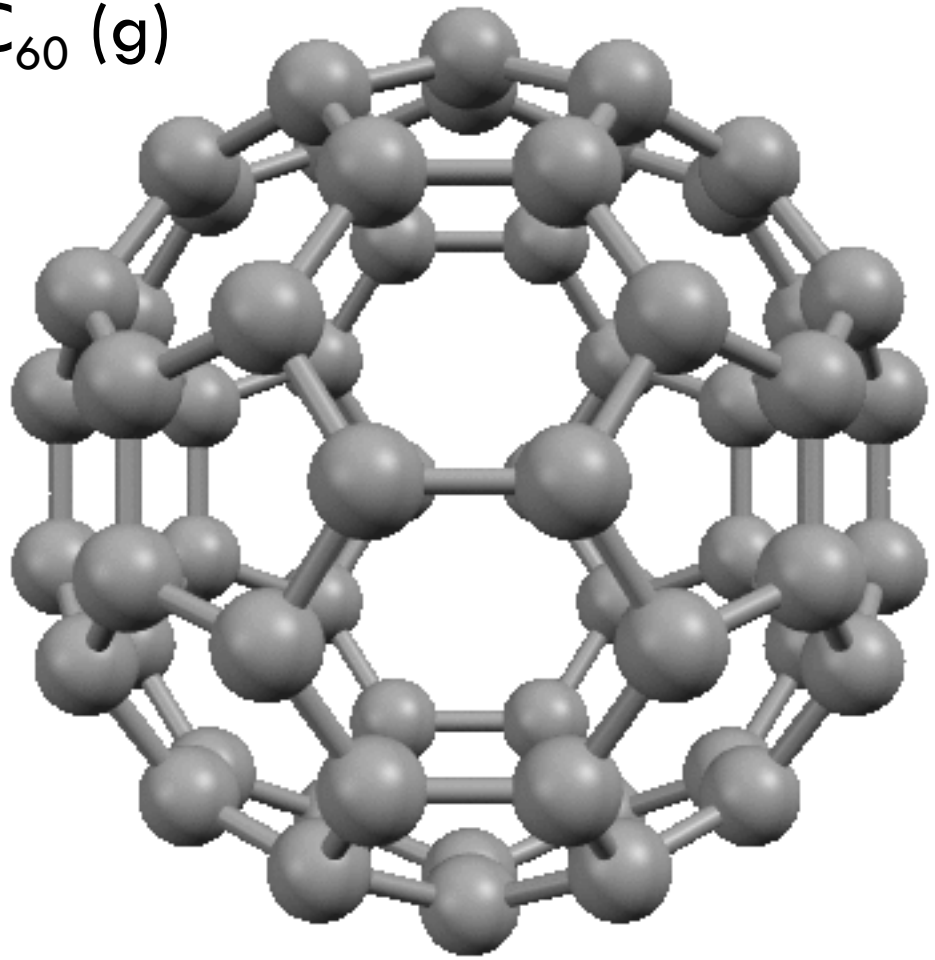


Staggered Ethane (D_{3d})

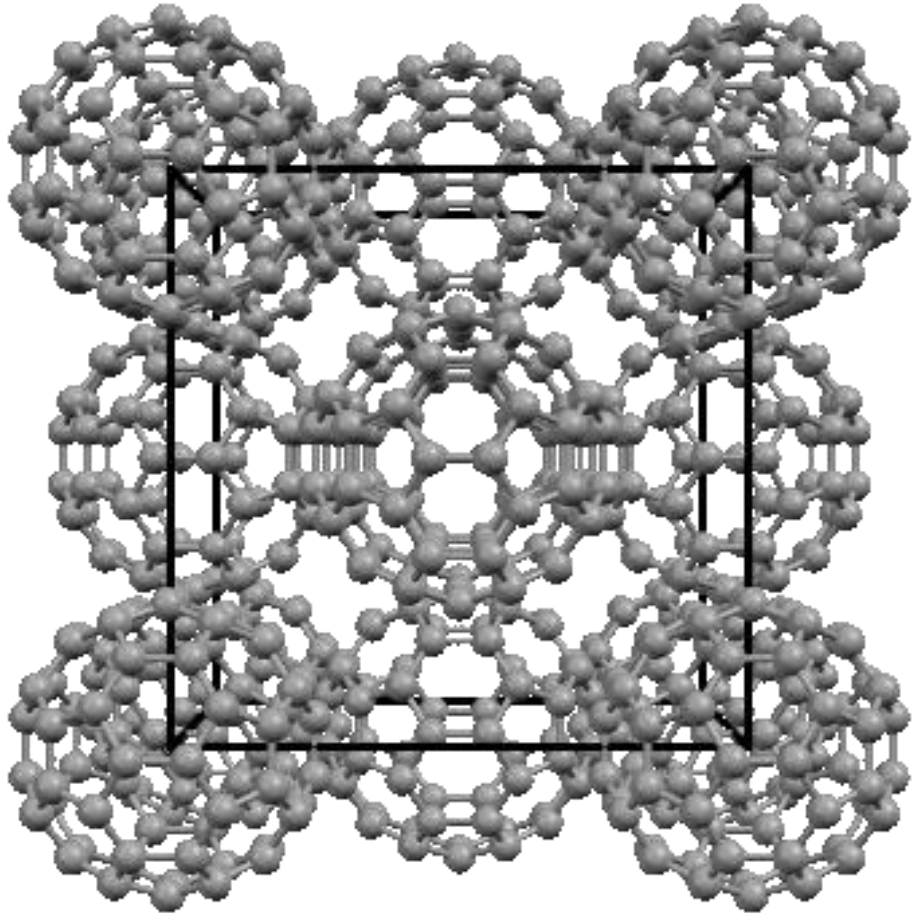


What tools do we need to describe, understand and determine the structure of molecules and materials?

C_{60} (g)



C_{60} (s)

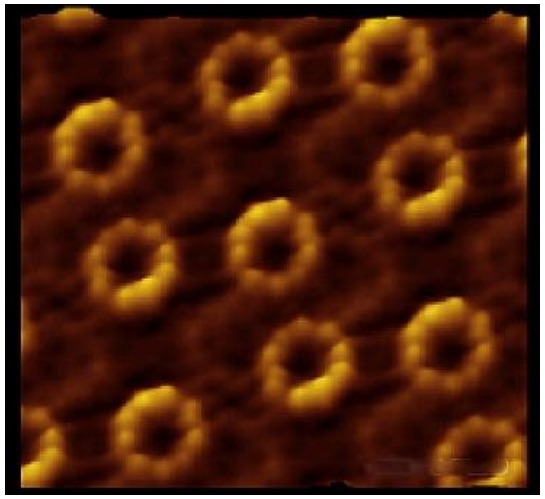


Symmetry Elements

- Rotational symmetry
- Reflection (mirror) symmetry
- Inversion symmetry
- Translational symmetry
- Symmetry combinations











Symmetry Elements

- Point symmetry – at least one point will not be changed



- Translational symmetry – everything moves



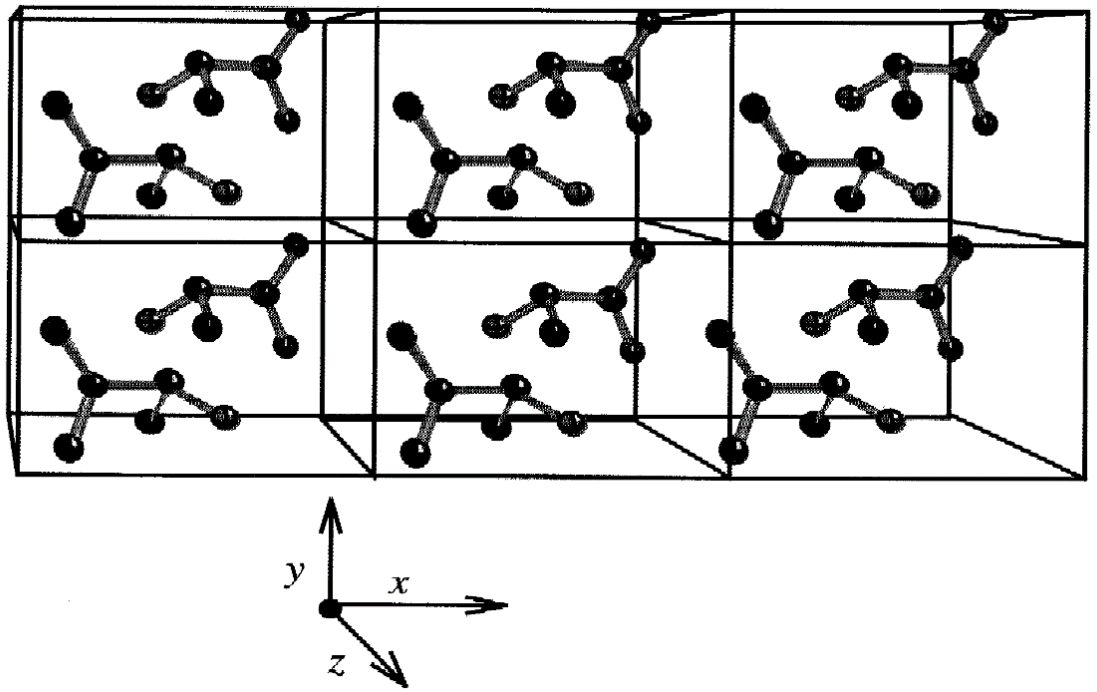
Symmetry Elements

Translational symmetry

The distinguishing feature of a lattice is its translational symmetry.

A translation of the entire crystal structure by a step of one unit cell edge length leaves the structure looking the same.

The presence of an atom at coordinates (x, y, z) implies the presence of one at (1+x, y, z), and (x, 3+y, z) etc.



Each box represents a unit cell.

What tools do we need to describe, understand and determine the structure of materials?

1) The size and shape of the 3D repeating unit – the 'unit cell'.

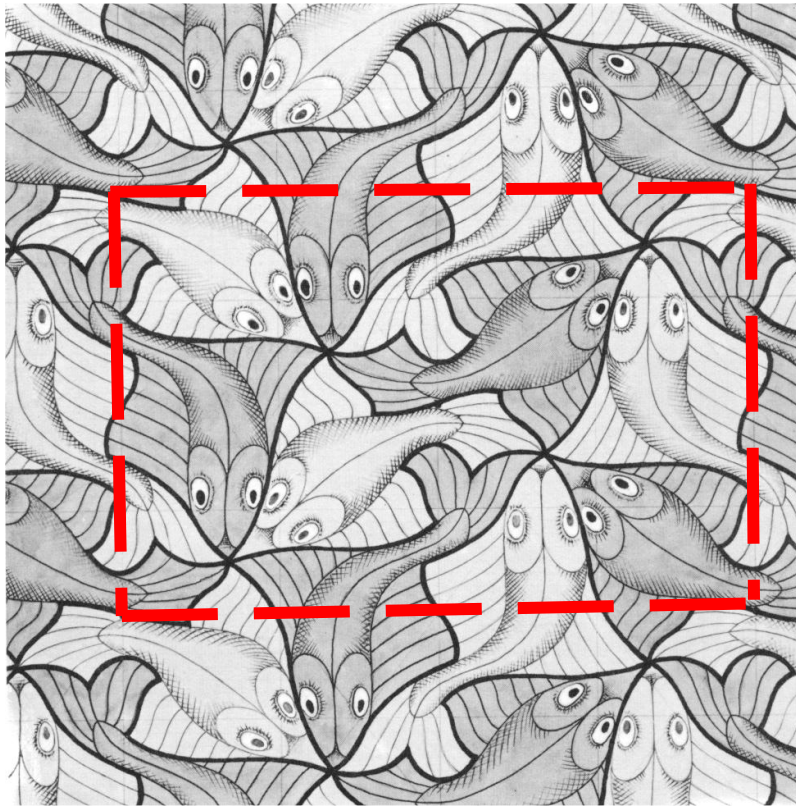
2) What symmetry elements exist within the unit cell.

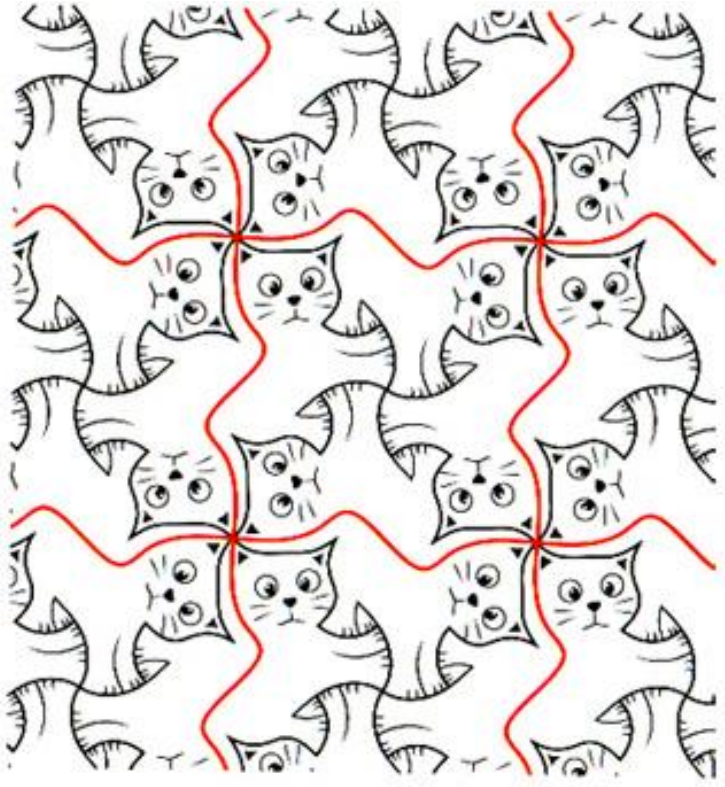
3) Where the atoms sit within the unit cell.

Q: How is all of this determined experimentally?

A: By diffraction (most commonly with X-rays, but also with neutrons and electrons – see Lecture 6).

The Unit Cell: An example in 2D



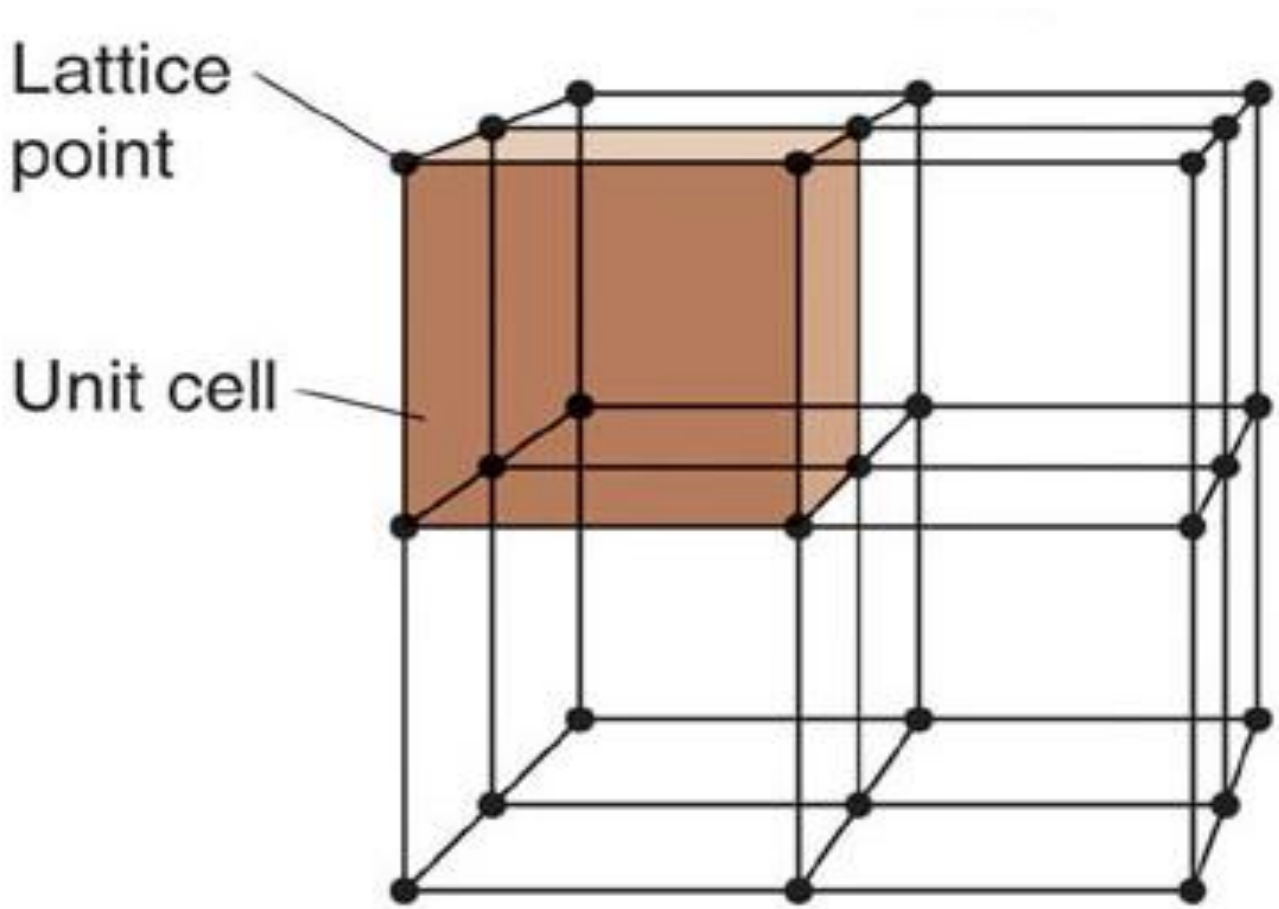


Unit cell is the smallest part of the drawing which, if repeated in all directions will generate the pattern.

Can find many examples of such a repeat unit (note that all are the **same** size).

The Unit Cell in Three Dimensions

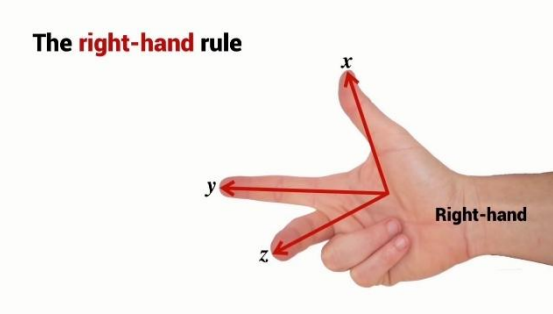
- Lattice points can be shared between multiple unit cells.

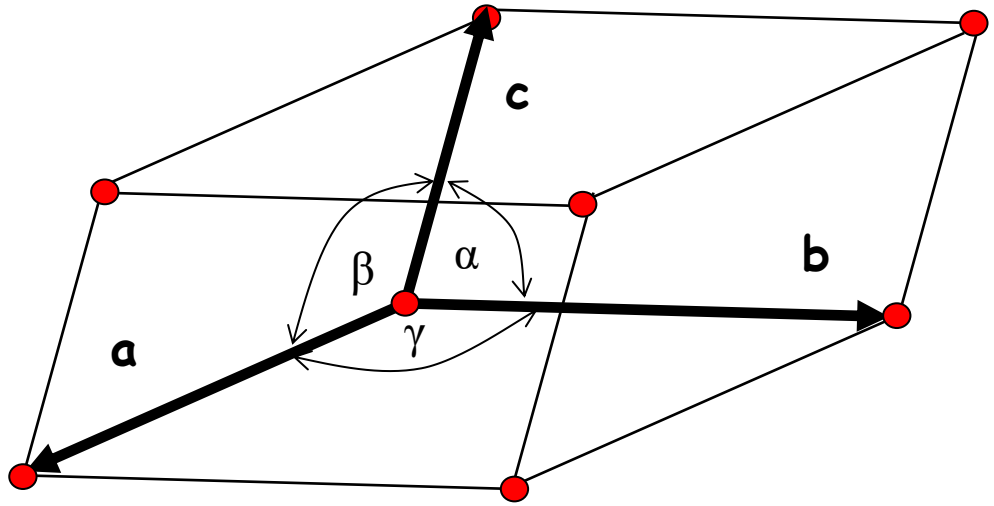


Unit Cell

A **unit cell** is the smallest unit which if repeated along the unit cell vectors produces the whole crystal.

- **a**, **b** & **c** are called unit cell vectors.
- Unit cell vector lengths are $a = |\mathbf{a}|$, $b = |\mathbf{b}|$, $c = |\mathbf{c}|$.
- α, β & γ describe the angles *between* unit cell vectors.





- Use a right-handed coordinate system.
- *Any* position within the unit cell can be described by a vector

$$\mathbf{r} = x \cdot \mathbf{a} + y \cdot \mathbf{b} + z \cdot \mathbf{c}$$

- *x*, *y*, *z* are so called *fractional coordinates* ($0 \leq x, y, z \leq 1$).

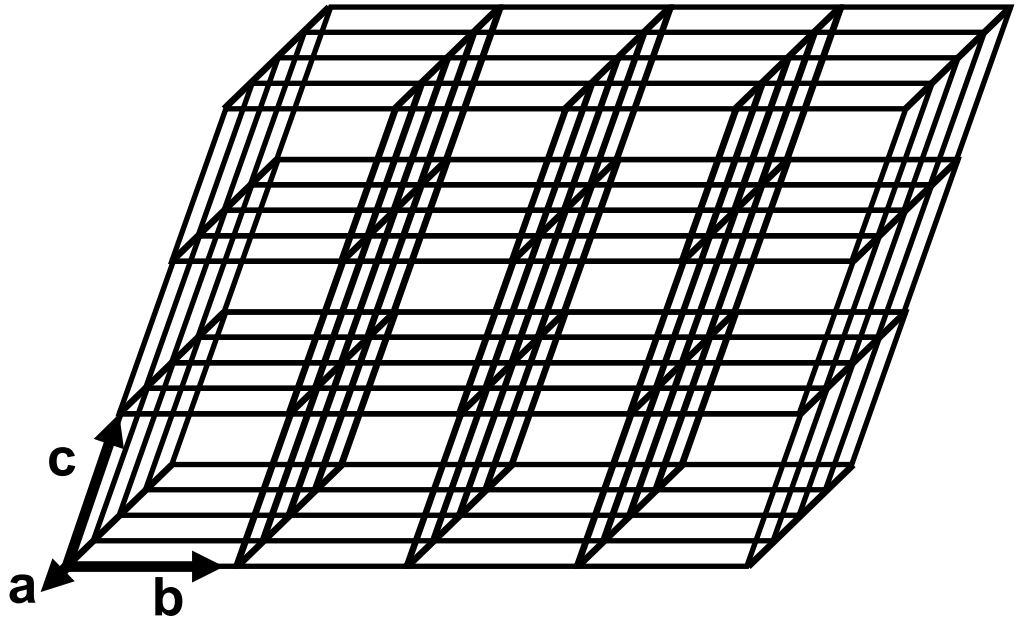
Translational Symmetry

By definition, a crystal has translational symmetry.

Any position within the crystal can be described by

$$\mathbf{r} = (u + x)\cdot \mathbf{a} + (v + y)\cdot \mathbf{b} + (w + z)\cdot \mathbf{c}$$

- x, y, z are *fractional coordinates* and u, v, w are *integers*.



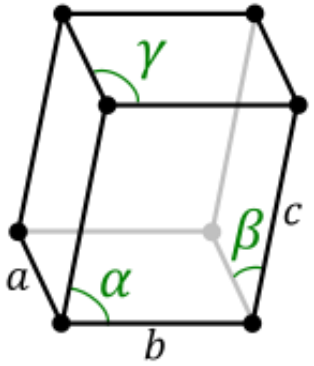
7 Crystal Systems

- There are seven possible shapes of unit cells:

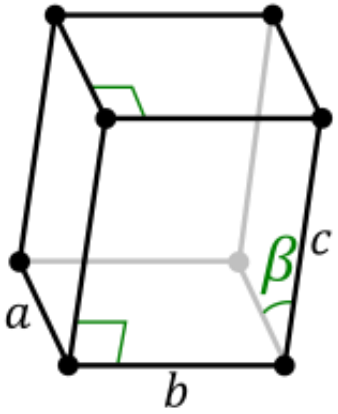
System	Relationships	Unit Cell defined by	Essential Symmetries
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	$a\ b\ c\ \alpha\ \beta\ \gamma$	None
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90°\ \beta \neq 90°$	$a\ b\ c\ \beta$	One twofold rotation axis and/or a mirror plane
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	$a\ b\ c$	Three perpendicular twofold axes and/or mirror planes
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	$a\ c$	One fourfold rotation axis
Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	a	One threefold rotation axis
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°\ \ \gamma = 120°$	$a\ c$	One sixfold rotation axis
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	a	Four threefold rotation axes tetrahedrally arranged

7 Crystal Systems

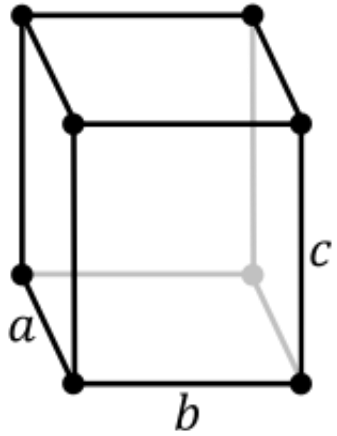
Triclinic



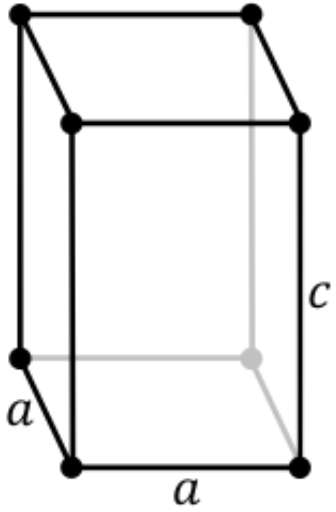
Monoclinic



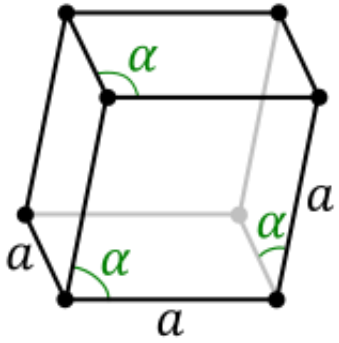
Orthorhombic



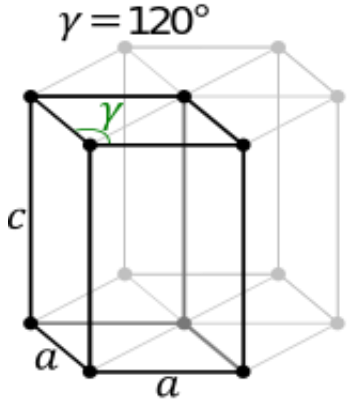
Tetragonal



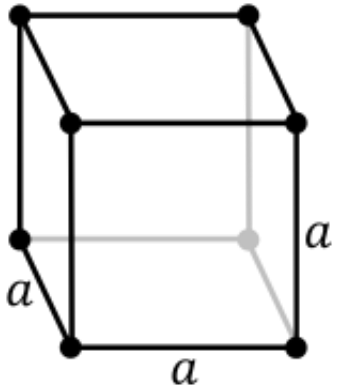
Trigonal



Hexagonal



Cubic

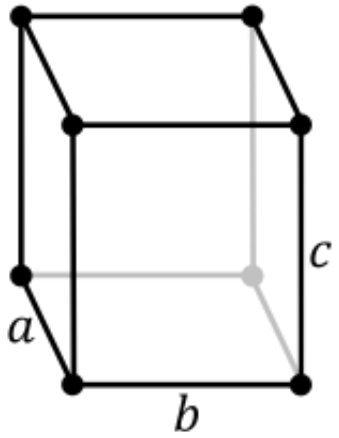


https://en.wikipedia.org/wiki/Crystal_system

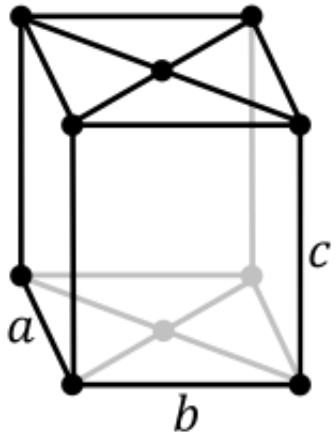
14 Crystal (Bravais) Lattices

- Each crystal system can be *Primitive*, *Base-Centred*, *Body-Centred* or *Face-Centred*.
- Not all combinations are unique.
- E.g., for orthorhombic

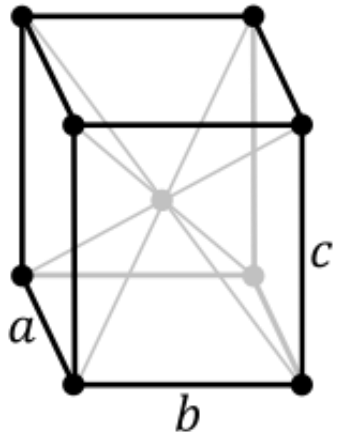
Primitive



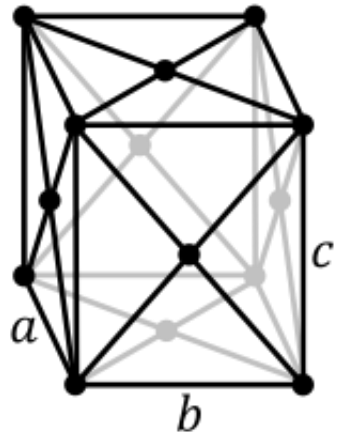
Base-Centred



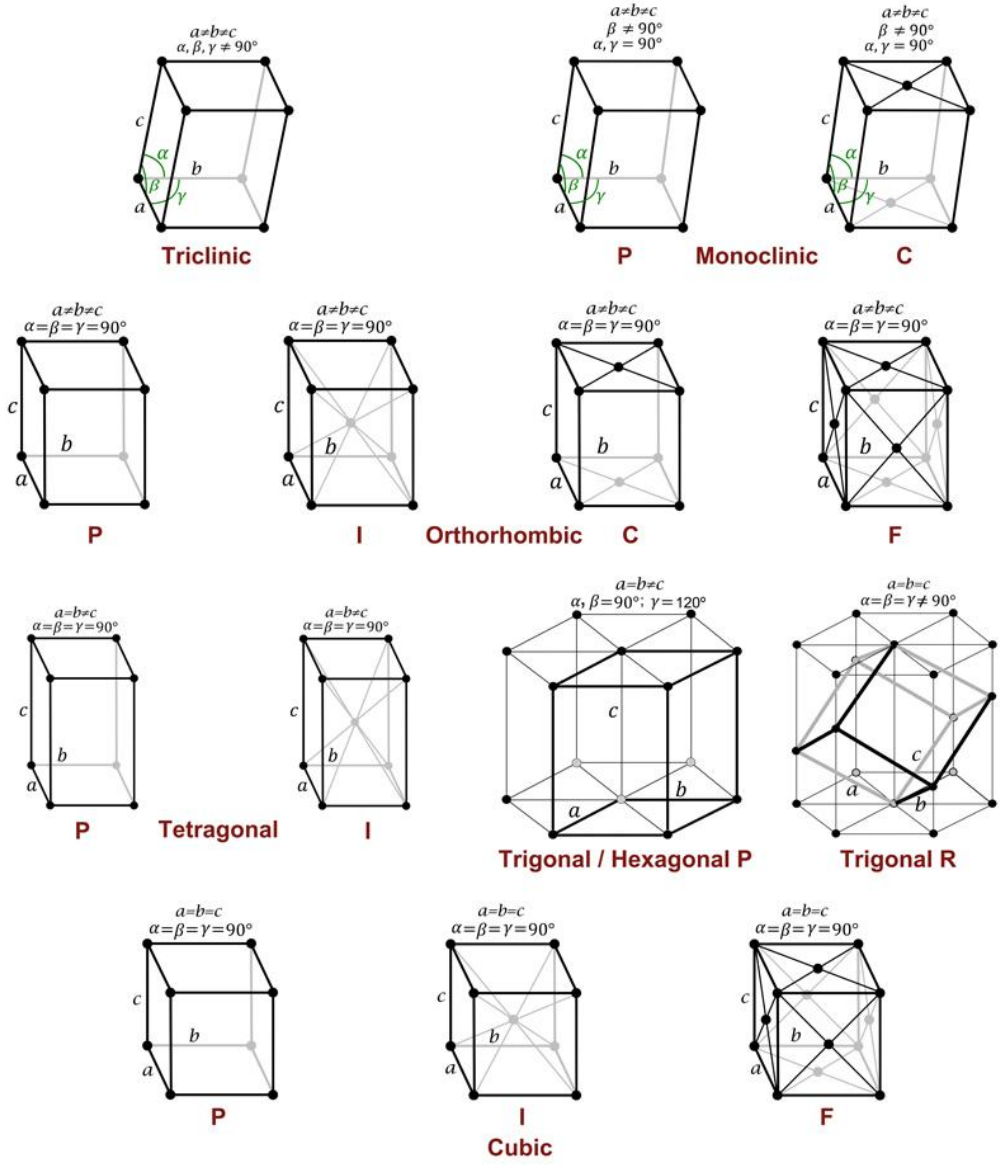
Body-Centred



Face-Centred



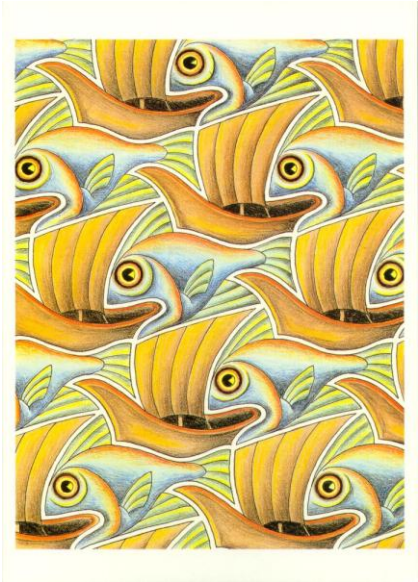
14 Crystal (Bravais) Lattices



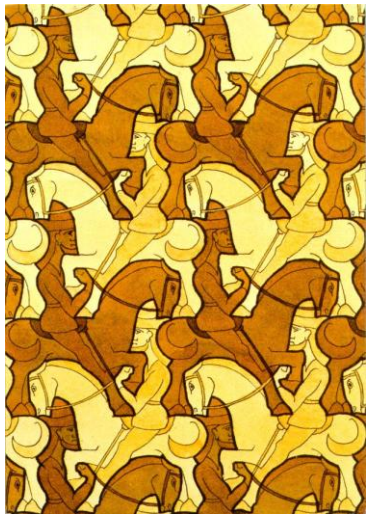
Other Crystallographic Symmetry

In addition to translational symmetry, atoms are often subject to other symmetry within the crystal lattice:

- Rotational symmetry
- Mirror planes
- Inversion
- Combinations of rotation or mirror planes plus translation



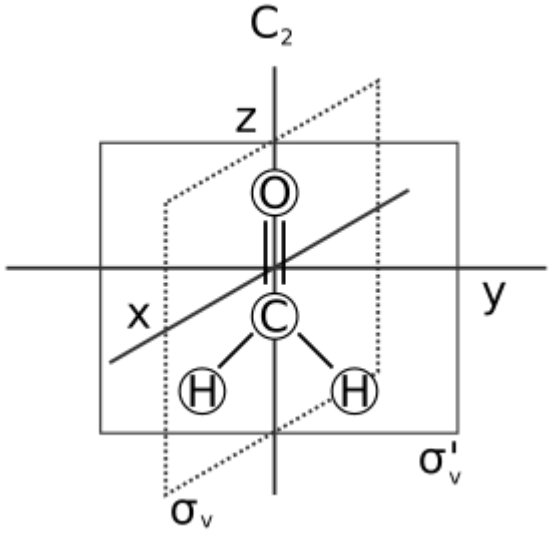




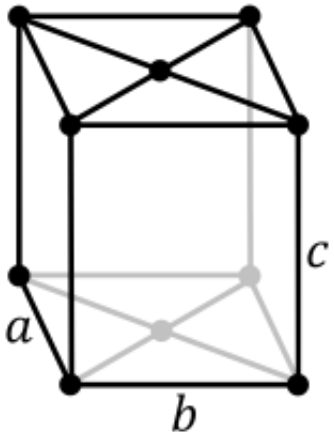
The Grand Idea:

Point Groups + Translational Symmetry ⇒ Space Groups

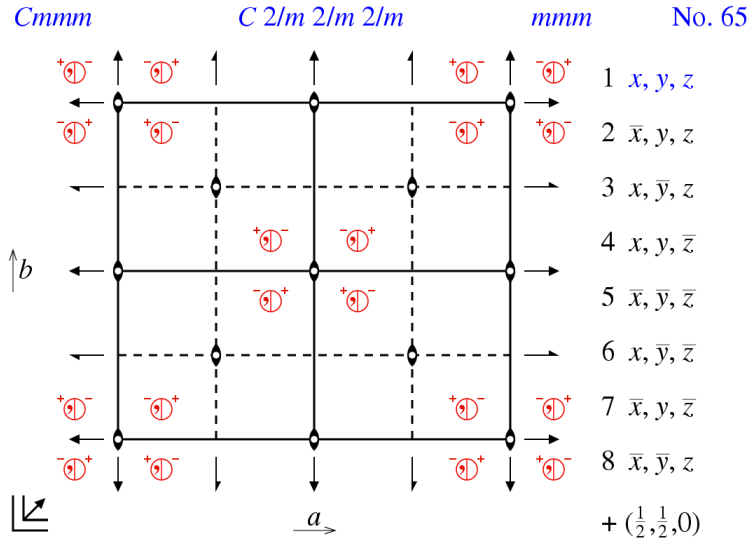
To understand the symmetry of crystals, the grand idea is that we will combine point group symmetry elements with translational symmetry to generate a range of periodic symmetries called **Space Groups** ('space' because we're now occupying space with a symmetric object rather than just growing an object around a 'point').



+



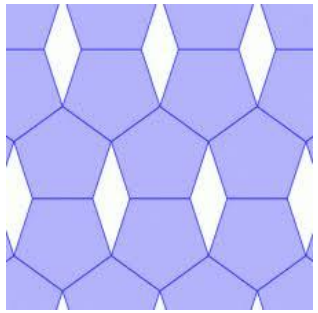
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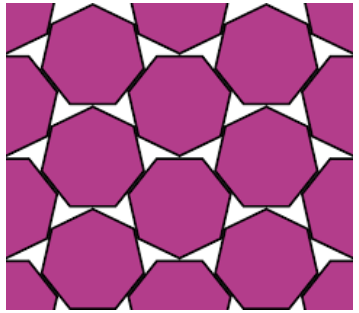


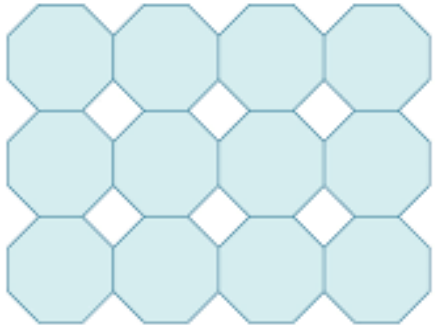
The Grand Idea:

Point Groups + Translational Symmetry ⇒ Space Groups

For reasons we won't dwell on, it turns out that not all point group symmetries are compatible with each Bravais lattice: e.g., triclinic cells can't have rotational axes or mirror planes (and can only have inversion centres); it's not possible to have 5-fold, 7-fold, 8-fold, etc., rotational symmetry in a periodic crystal.







Crystal system	Hermann-Mauguin (full)	Hermann-Mauguin (short)	Shubnikov[1]	Schoenflies	Orbifold	Coxeter	Order
Triclinic	1	1	1	C_1	11	$[\,]^+$	1
	$\bar{1}$	$\bar{1}$	$\bar{2}$	$C_i = S_2$	×	$[2^+,2^+]$	2
Monoclinic	2	2	2	C_2	22	$[2]^+$	2
	m	m	m	$C_s = C_{1h}$	*	$[\,]$	2
	$\frac{2}{m}$	2/m	$2:m$	C_{2h}	2*	$[2,2^+]$	4
Orthorhombic	222	222	$2:2$	$D_2 = V$	222	$[2,2]^+$	4
	mm2	mm2	$2\cdot m$	C_{2v}	*22	$[2]$	4
	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	mmm	$m\cdot 2:m$	$D_{2h} = V_h$	*222	$[2,2]$	8
Tetragonal	4	4	4	C_4	44	$[4]^+$	4
	$\bar{4}$	$\bar{4}$	$\bar{4}$	S_4	2×	$[2^+,4^+]$	4
	$\frac{4}{m}$	4/m	$4:m$	C_{4h}	4*	$[2,4^+]$	8
	422	422	$4:2$	D_4	422	$[4,2]^+$	8
	4mm	4mm	$4\cdot m$	C_{4v}	*44	$[4]$	8
	$\bar{4}$2m	$\bar{4}$2m	$\bar{4}\cdot m$	$D_{2d} = V_d$	2*2	$[2^+,4]$	8
	$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	4/mmm	$m\cdot 4:m$	D_{4h}	*422	$[4,2]$	16
Trigonal	3	3	3	C_3	33	$[3]^+$	3
	$\bar{3}$	$\bar{3}$	$\bar{6}$	$C_{3i} = S_6$	3×	$[2^+,6^+]$	6
	32	32	$3:2$	D_3	322	$[3,2]^+$	6
	3m	3m	$3\cdot m$	C_{3v}	*33	$[3]$	6
	$\bar{3}\frac{2}{m}$	$\bar{3}$m	$\bar{6}\cdot m$	D_{3d}	2*3	$[2^+,6]$	12
Hexagonal	6	6	6	C_6	66	$[6]^+$	6
	$\bar{6}$	$\bar{6}$	$3:m$	C_{3h}	3*	$[2,3^+]$	6
	$\frac{6}{m}$	6/m	$6:m$	C_{6h}	6*	$[2,6^+]$	12
	622	622	$6:2$	D_6	622	$[6,2]^+$	12
	6mm	6mm	$6\cdot m$	C_{6v}	*66	$[6]$	12
	$\bar{6}$m2	$\bar{6}$m2	$m\cdot 3:m$	D_{3h}	*322	$[3,2]$	12
	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	6/mmm	$m\cdot 6:m$	D_{6h}	*622	$[6,2]$	24
Cubic	23	23	$3/2$	T	332	$[3,3]^+$	12
	$\frac{2}{m}\bar{3}$	m$\bar{3}$	$\bar{6}/2$	T_h	3*2	$[3^+,4]$	24
	432	432	$3/4$	O	432	$[4,3]^+$	24
	$\bar{4}$3m	$\bar{4}$3m	$3/\bar{4}$	T_d	*332	$[3,3]$	24
	$\frac{4}{m}\bar{3}\frac{2}{m}$	m$\bar{3}$m	$\bar{6}/4$	O_h	*432	$[4,3]$	48

Crystal Molecular

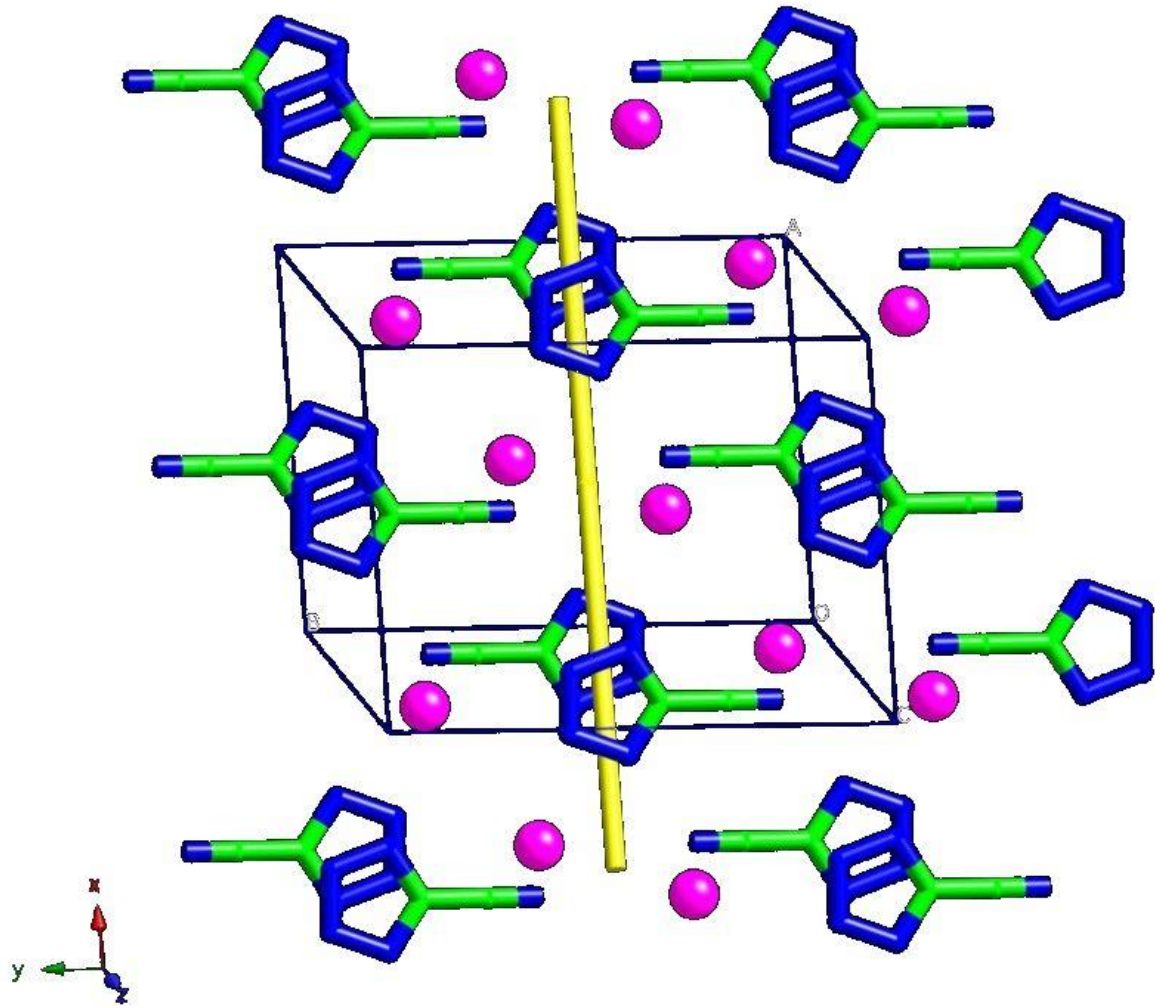
32 Point Groups + 14 Bravais Lattices ⇒ 230 Space Groups

https://en.wikipedia.org/wiki/Crystallographic_point_group

Rotational Symmetry in Crystals

Symbol: n (*cf.* C_n)

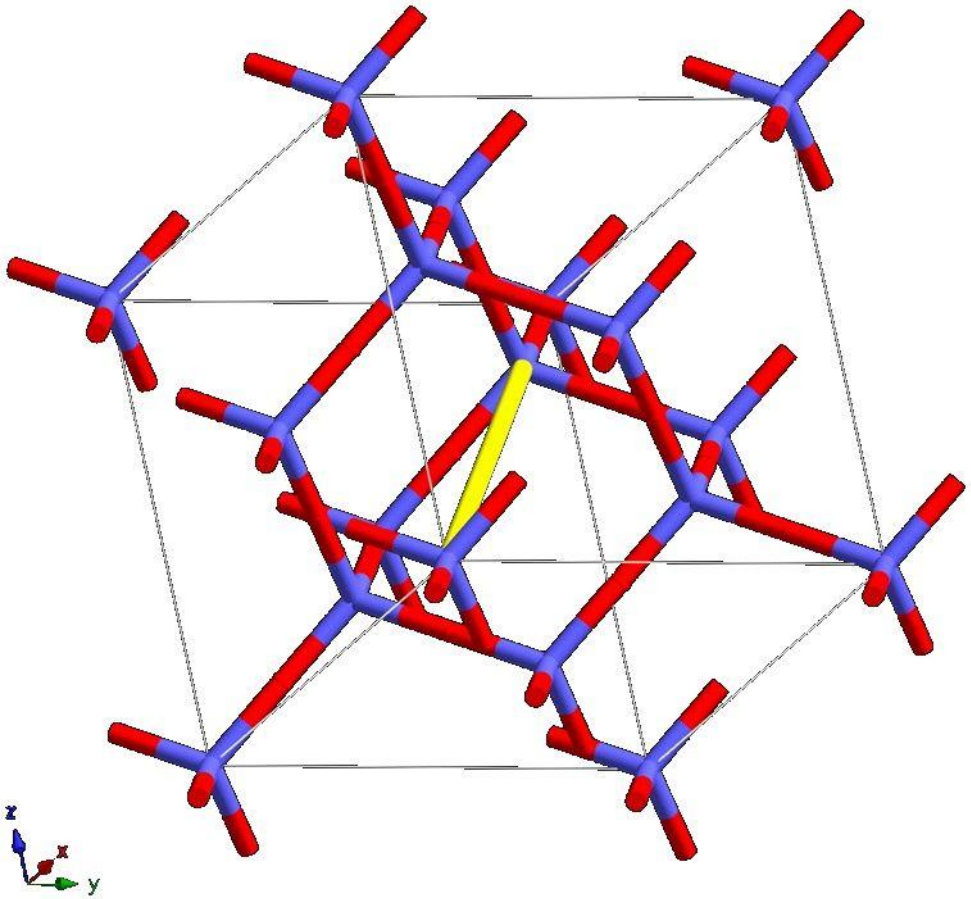
A twofold rotation axis (yellow) in the structure of CsC_2N_5.
Symbol: 2 (*cf.* C_2)



Rotational Symmetry in Crystals

Symbol: n (*cf.* C_n)

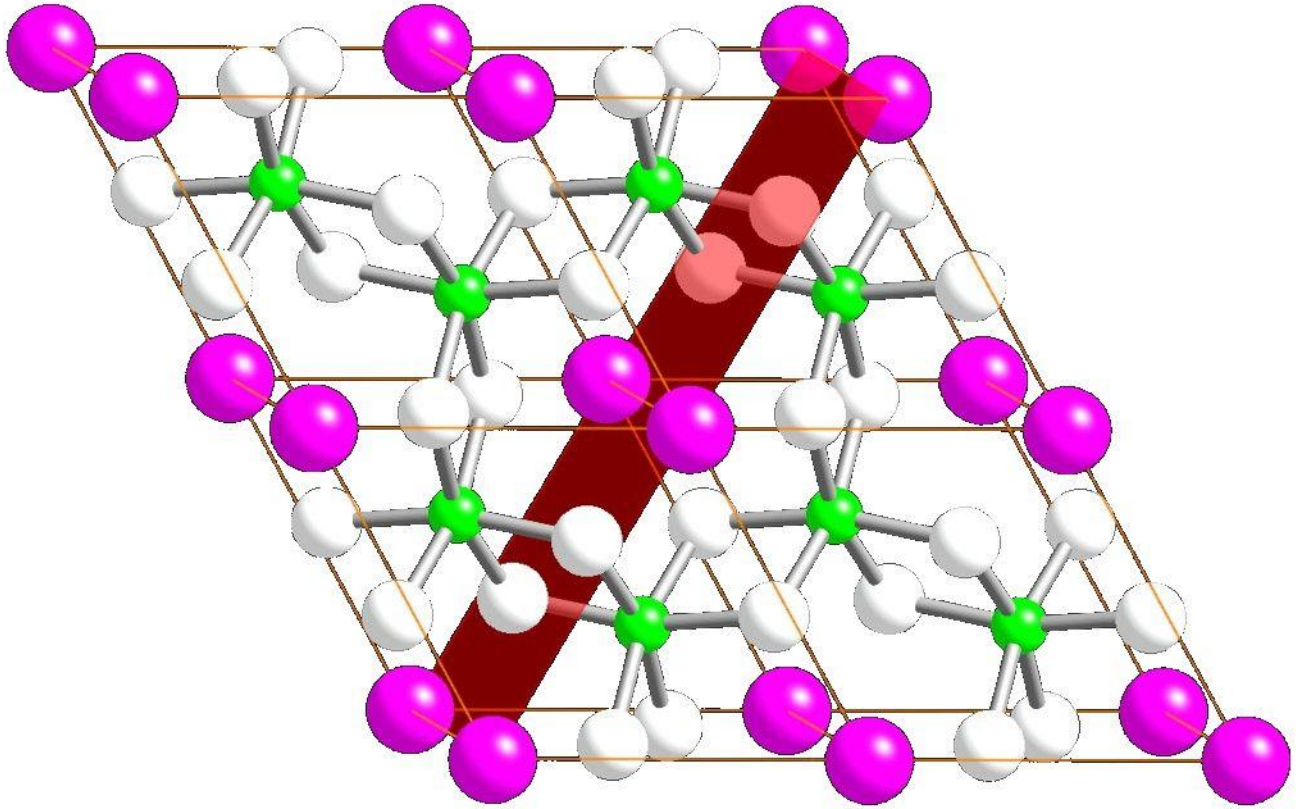
A threefold rotation axis (yellow) in the structure of cristobalite (SiO_2).
Symbol: 3 (*cf.* C_3)



Mirror Symmetry in Crystals

Symbol: m (*cf.* σ)

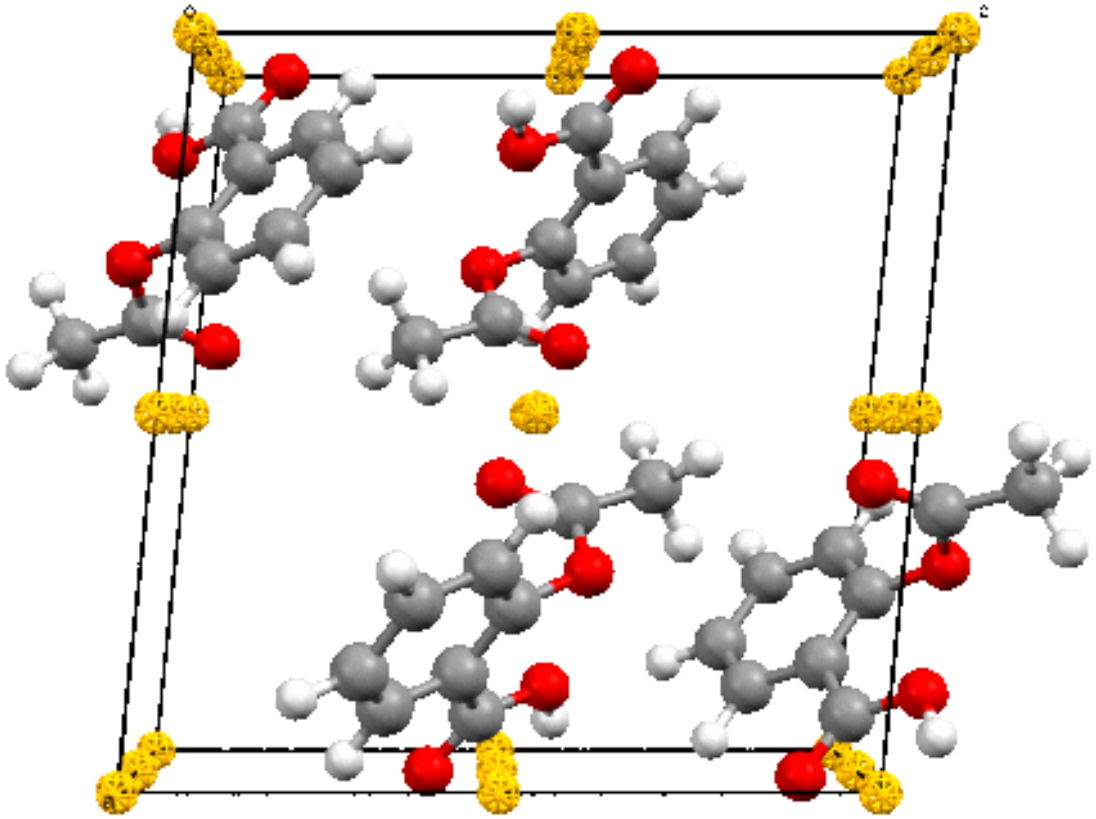
A mirror plane (red) in the structure of $BaSb_2O_6$.



Inversion Symmetry in Crystals

Symbol: $\bar{1}$ (*cf.* i)

Inversion centres (orange) in the structure of aspirin.

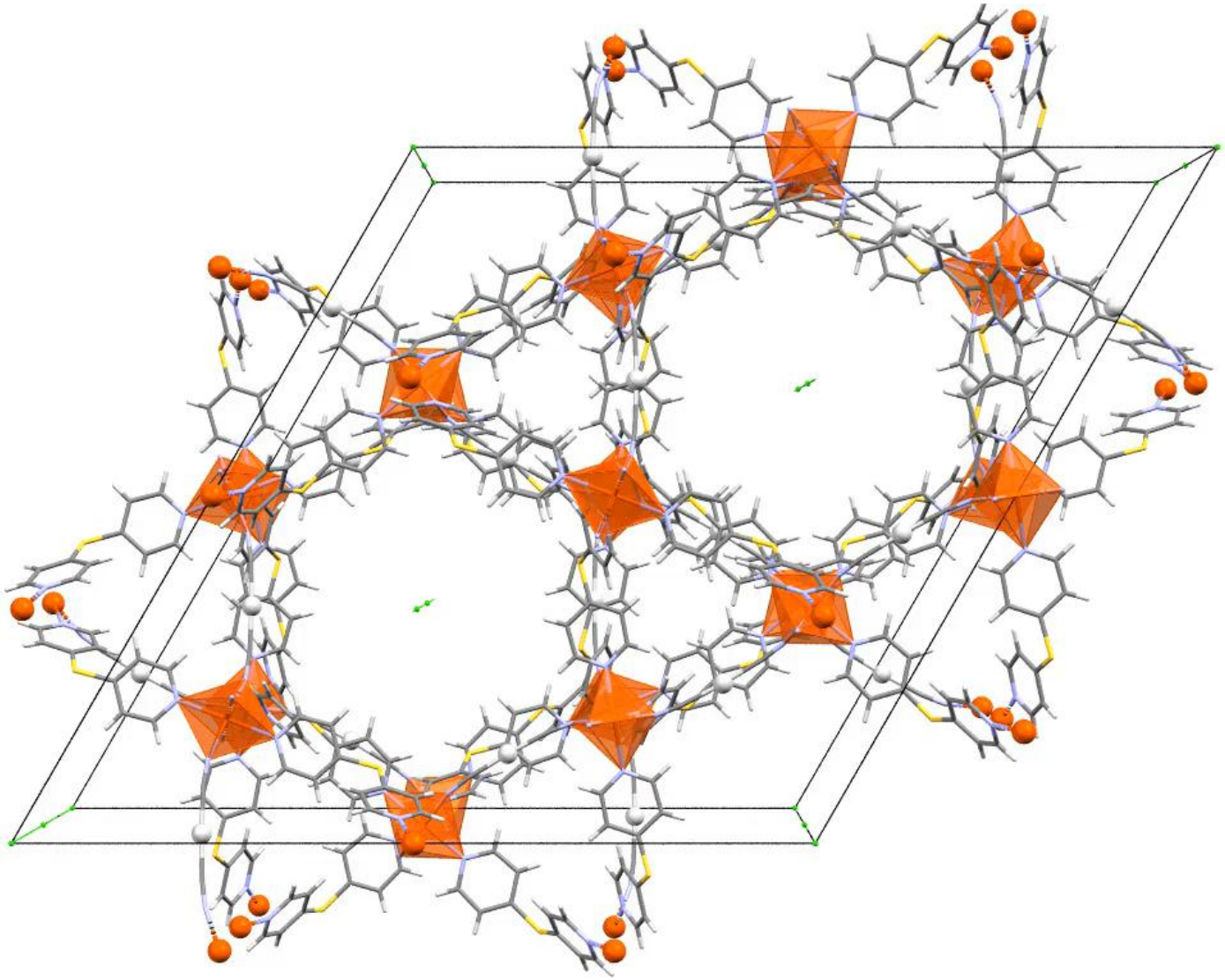


(*For reference after Lecture 5*: the space group is $P2_1/c$, which is primitive monoclinic and contains inversion centres, 2_1 screw axes and c-glide planes)

Inversion Axes ($\bar{n}$) in Crystals

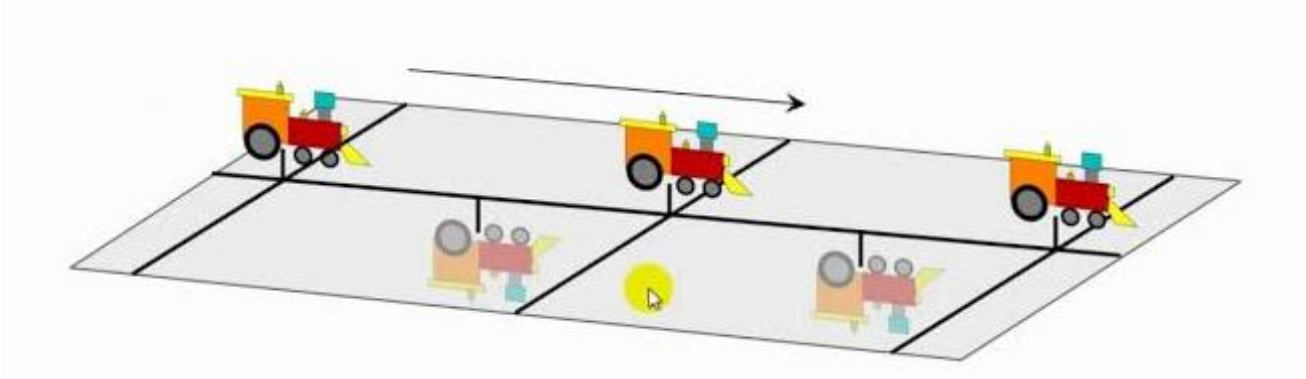
Symbol: $\bar{n}$

$\bar{3}$ rotary inversion (rotation then inversion) axes (green) in a Metal-Organic Framework (materials of this type will be covered in lectures 37-39 in week 13).



Glide Planes

Additional symmetry elements are possible which involve **translations** *within* the crystal lattice.



- A *glide plane* is a translation followed by a reflection in a plane whose normal is parallel to a rotational symmetry element.

  a is a glide translation of ½ along *a*.

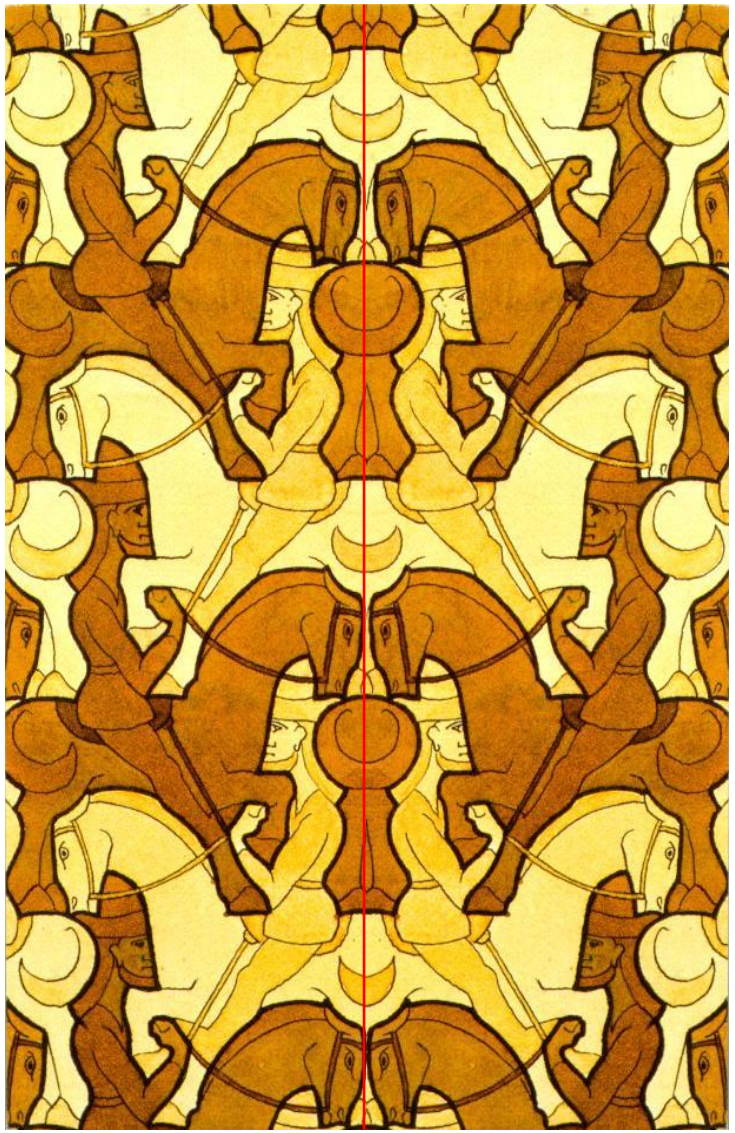
  b is a glide translation of ½ along *b*.

  c is a glide translation of ½ along c.

  Also have diagonal glide planes *n* (½ along diagonal) and *d* (¼ along face or diagonal)

crystalsymmetry.wordpress.com/chapter-4/

Glide Planes: 2D Example (disregard the colours)



Glide plane

Reflection

Translate

Now it is the same as before!

Worksheet: Combining point symmetry and translation

- Can you identify any symmetry that is not a point group element or a simple translation?





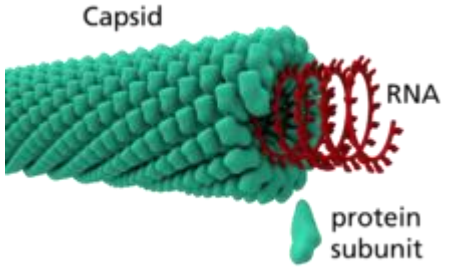


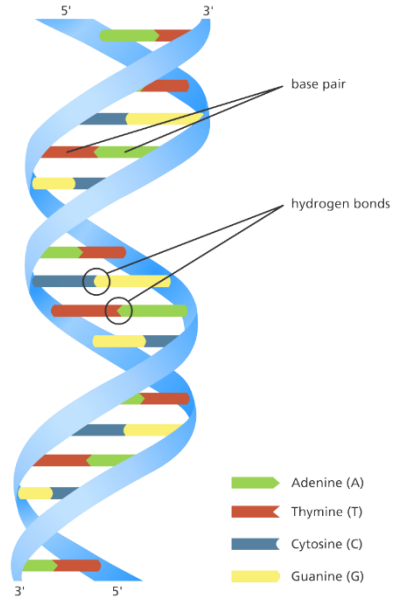




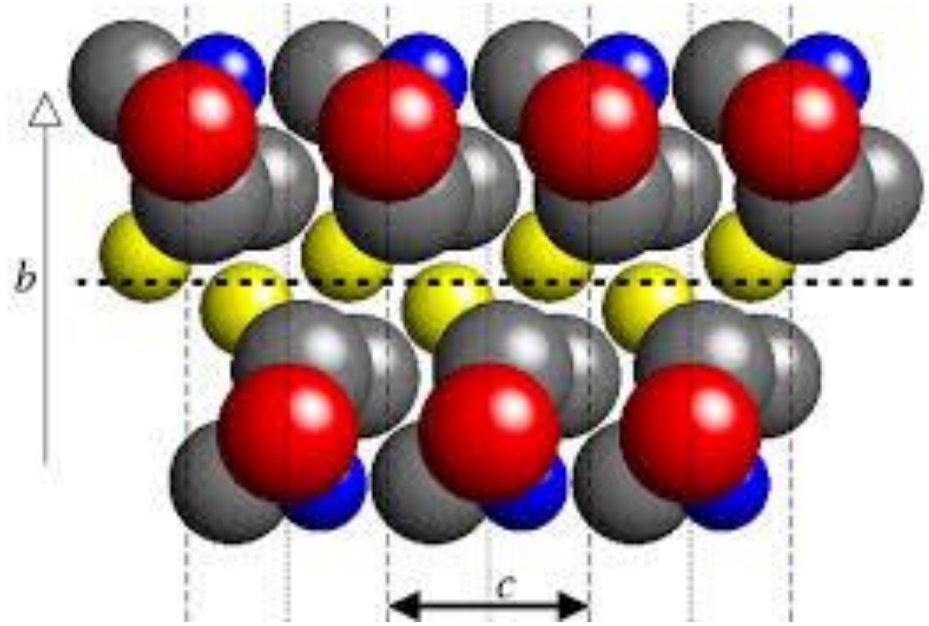








Glide Planes in Crystals



Combination of a mirror plane and a translation.

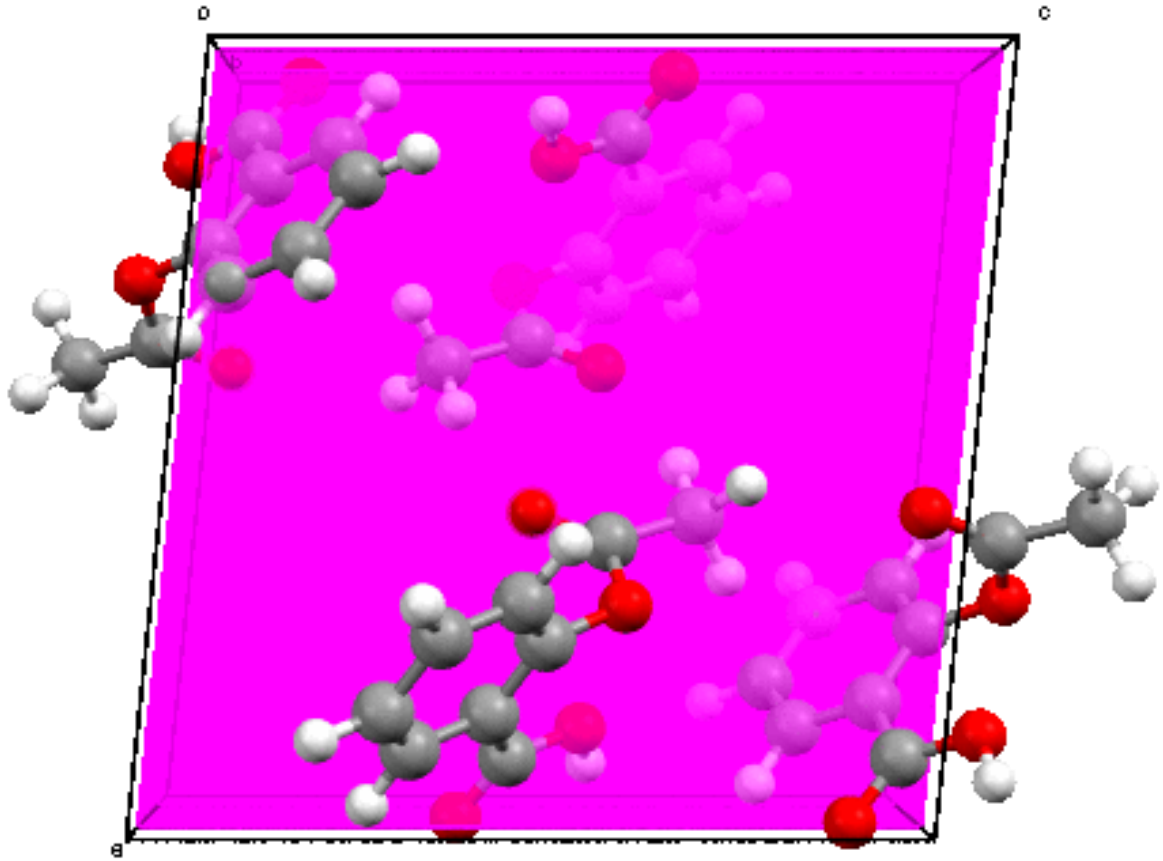
Translation is usually half the unit cell edge or diagonal involved.

Here we have reflection ⊥ to *b* with translation of c/2.

Note: Glide planes change the handedness since they contain a reflection operation.

Glide Planes in Crystals

Glide planes (pink) in the structure of aspirin.



(*For reference after Lecture 5*: the space group is $P2_1/c$, which is primitive monoclinic and contains inversion centres, 2_1 screw axes and glide planes)

Screw Axes

A *screw axis* describes helical symmetry. It is a translation by a fraction of the unit cell followed by a rotation, where m_n means translate n/m of the unit cell and then rotate around the axis by 360°/m.

Symbols:

2_1 3_1 4_2 6_3

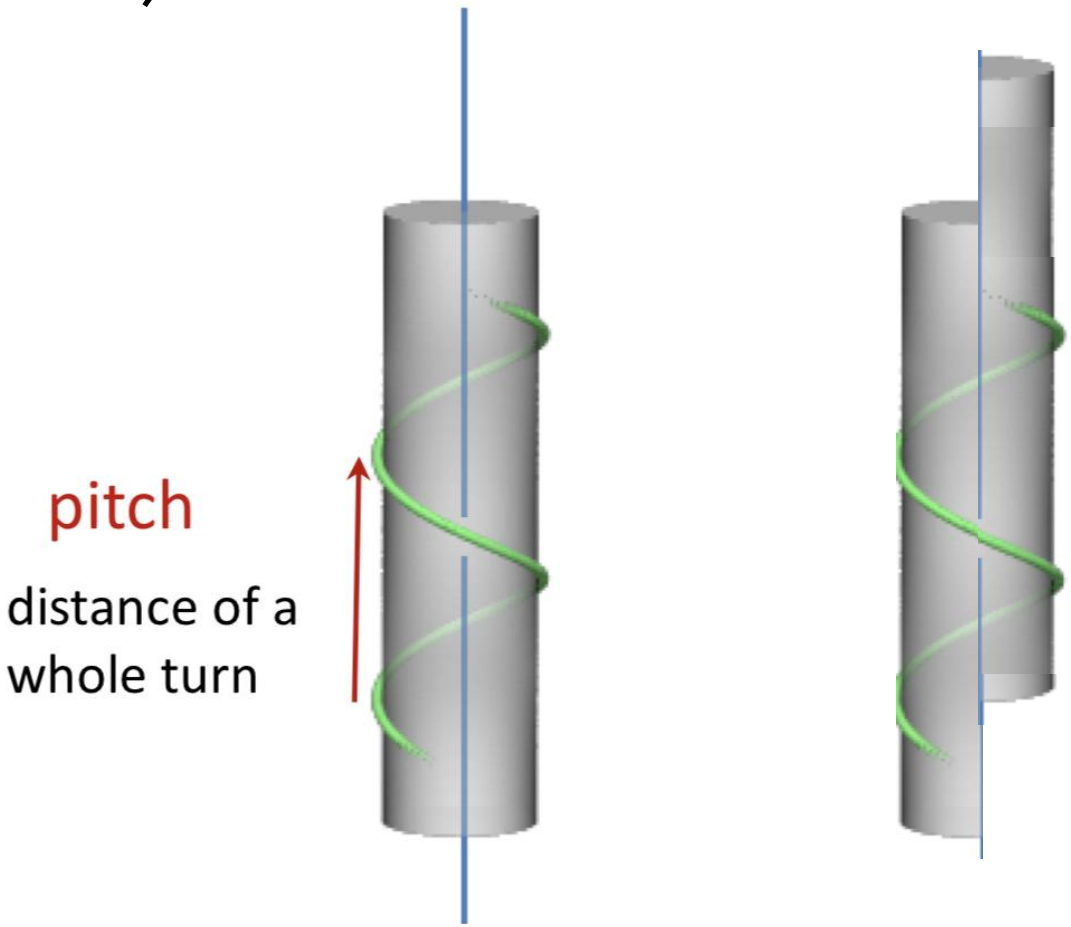


- 2_1 means translate 1/2 of the unit cell & rotate 180°.
- 3_1 means translate 1/3 of the unit cell & rotate 120°.
- 4_2 means translate 2/4 of the unit cell & rotate 90°.
- 6_3 means translate 3/6 of the unit cell & rotate 60°.

Screw Axes

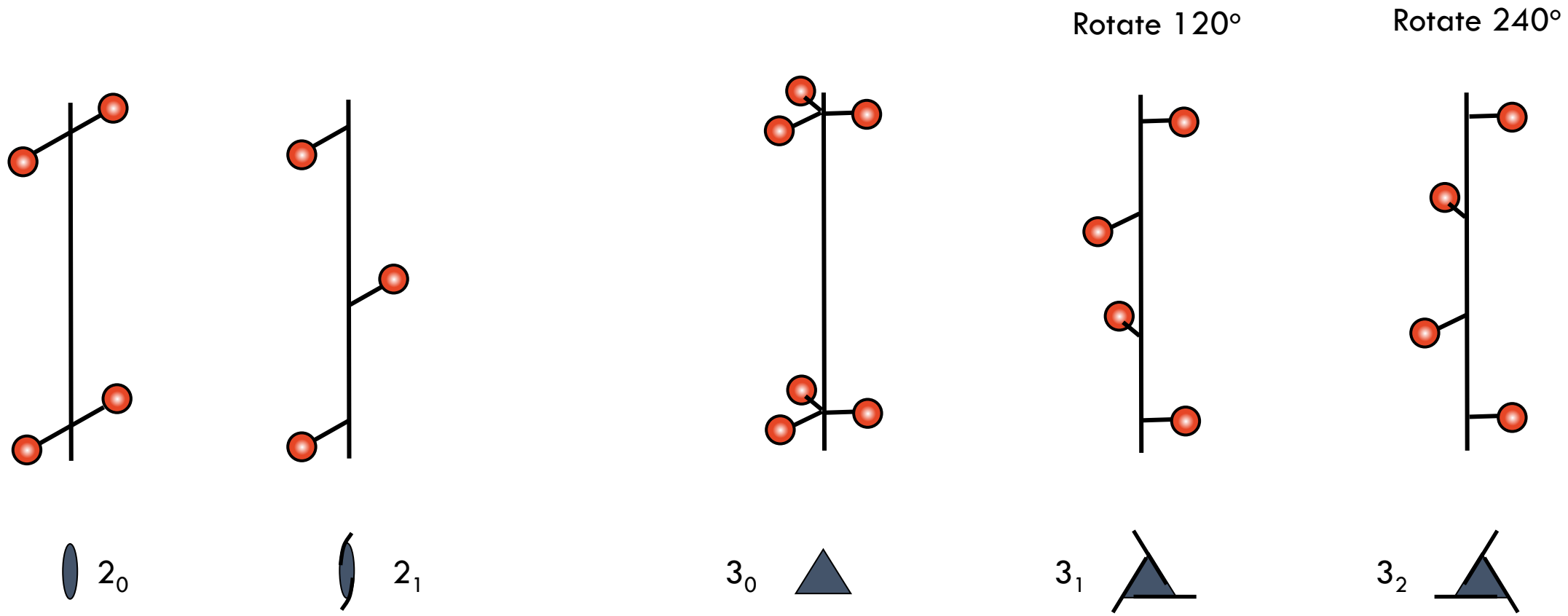


2_1 screw/helix axis



https://commons.wikimedia.org/wiki/File:Helix_diagram-de.png

Two-Fold and Three-Fold Screw Axes

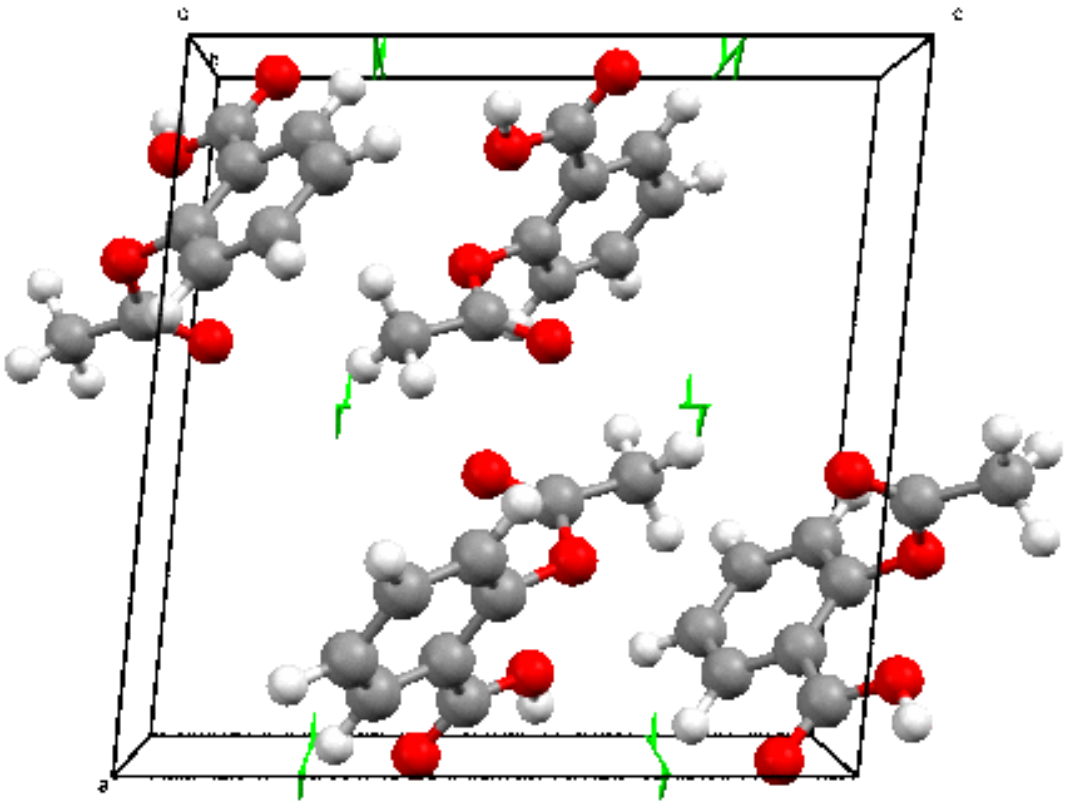


Note: The crystallographic convention is that rotations are clockwise with respect to translation in the 'away direction'.
I.e., Use the right-hand rule where your thumb is the direction of translation and your fingers are the direction of rotation.
This only matters for helical screw axes (e.g., 3_1 & 3_2), which are chiral (have handedness).

Screw Axes in Crystals

2_1 screw axes (green) in the structure of aspirin.

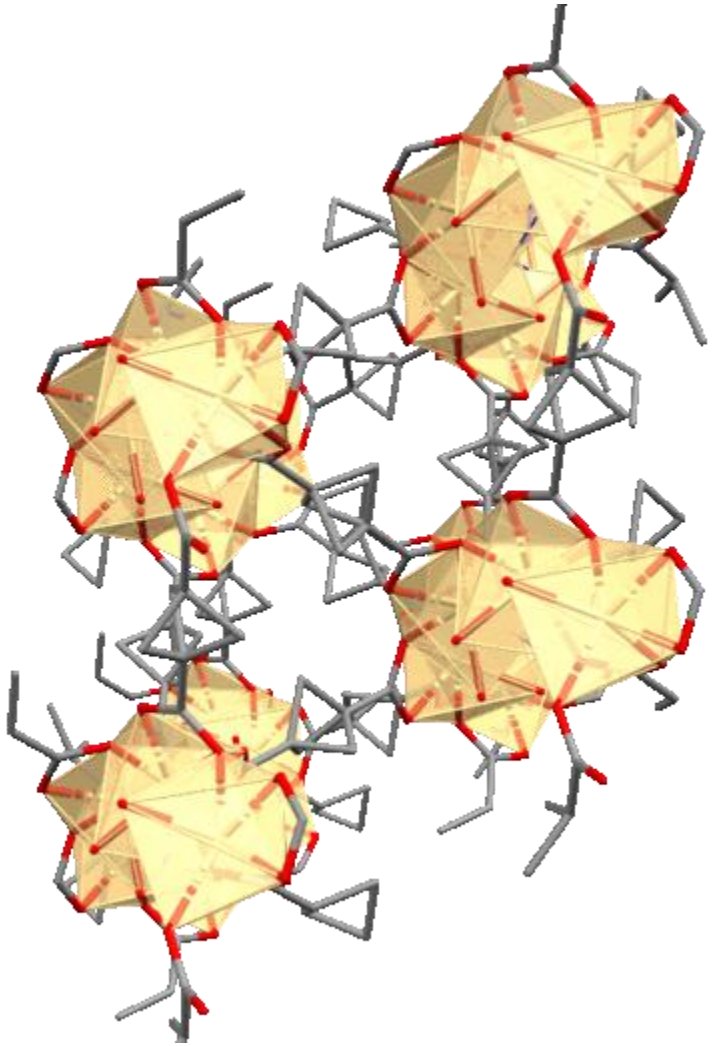
- i.e., rotate by 180 degrees and translate ½ of unit cell



(*For reference after lecture 5*: the space group is $P2_1/c$, which is primitive monoclinic and contains inversion centres, 2_1 screw axes and c-glide planes)

Screw Axes in Crystals

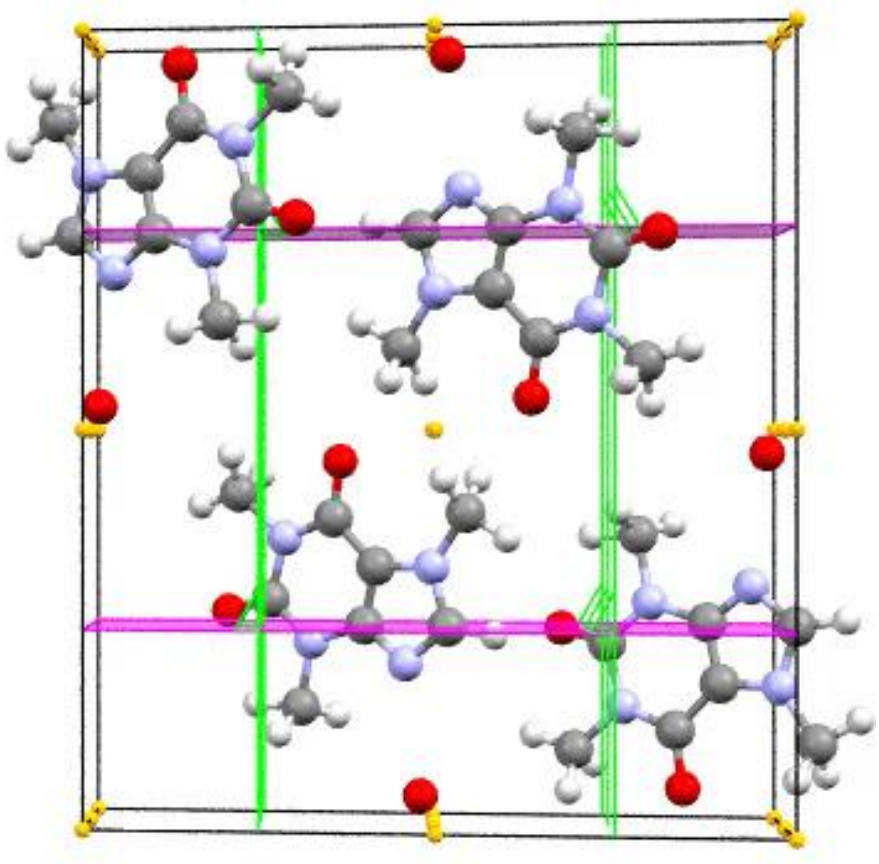
6_5 screw axes (blue) in a Metal-Organic Framework (materials of this type will be covered in lectures 37-39 in week 13).



NOTE: screw axes don't change the handedness since they contain a rotation operation.

Showing All Symmetry in Crystals

Inversion centres (orange), **2_1 screw axes** (green) and **glide planes** (pink) in the structure of caffeine hydrate.



(*For reference after lecture 5*: the space group is $P2_1/a$, which is primitive monoclinic and contains inversion centres, 2_1 screw axes and glide planes)

Space Groups

To fully describe a crystal packing we need to know:

- Length of unit cell axes, *a*, *b* & *c*
- Unit cell angles, α, β & γ
- Bravais lattice: Primitive, base-centred, body-centred, or face-centred
- Additional symmetry: rotation, screw axes, mirror, inversion & glide symmetries
- Unit cell contents

➢ There are 14 Bravais lattices

➢ There are 230 **Space Groups**.

Learning Outcomes

After this lecture and pre-lecture video you should be able to

- Understand what is meant by translational symmetry, and how this applies to crystals.
- Know the 7 Crystal Systems.
- Identify rotation axes, mirror planes, inversion centres, inversion axes, glide planes and screw axes.
- Understand how a crystal can be uniquely characterised by its unit cell, the combination of its point and translational symmetry elements (its *space group* – see next lecture for examples), and unit cell contents.
- Complete the lecture worksheet, Q3 of Tutorial 1 (week 2; possibly retrospectively but that's OK) and Q1 of Tutorial 2 (week 4).

Further reading: Weller, Overton, Rourke & Armstrong, Inorganic Chemistry 6th Ed. OUP, 2014, Chapter 3.1–3.5.

For interest/future reference/completeness (i.e., beyond scope of this course)

Crystal System	*Minimum required symmetry for each Crystal System*
Triclinic	No rotations (as no 90°); P then 1 or -1.
Monoclinic	One 2-fold rotation (as some 90°); P or C then one entry with <3 rotation (and mirror, glide…after).
Orthorhombic	Three mutually perpendicular 2-fold rotations and/or mirrors as all angles 90°; P, C, I, F followed by three entries.
Rhombohedral	One 3-fold rotation; P or R and first entry 3, -3, 3_n.
Tetragonal	One 4-fold rotation; P or I and first entry 4, -4, 4_n (although some cubic can have 4; but if only one entry then tetragonal) – first entry refers to c-axis, second is *a* and *b*, third entry is diagonally across.
Hexagonal	One 6-fold rotation; 6, -6, 6_n; P only – could have one or three entries.
Cubic	Four independent 3-fold rotations equally inclined at 109.47°; P, F, I – different numbers of entries fine, but must be more than one (two or three). First entry has many options (rot, m, glide). The second entry is the most important, it is always a 3 or -3; first is the *a*,*b*,*c* direction; second is body diagonal which is why it's a 3; third is at 45° to the unit cell axes.

For interest/future reference/completeness (i.e., beyond scope of this course)

Crystallographic symbols for different symmetry elements within space groups

