02 Crystal II

Symmetries

Translation

- Already dealt with translational symmetries
  - This comes from Bravais Lattices
  - Shape of Lattice
    - Cubis, tetragonal, hexagonal, etc.....
  - Type of Lattice
    - Primitive, face centered, body centered, base centered

Point Group Symmetries

- Keep at least one point fixed (not translations)
- Seven of them:
  - Identity
  - Rotation
  - Reflection
  - Inversion
  - Improper rotation
  - Glide plane
  - Screw axis
- First five keep at least one point fixed
  - Called **point operations**

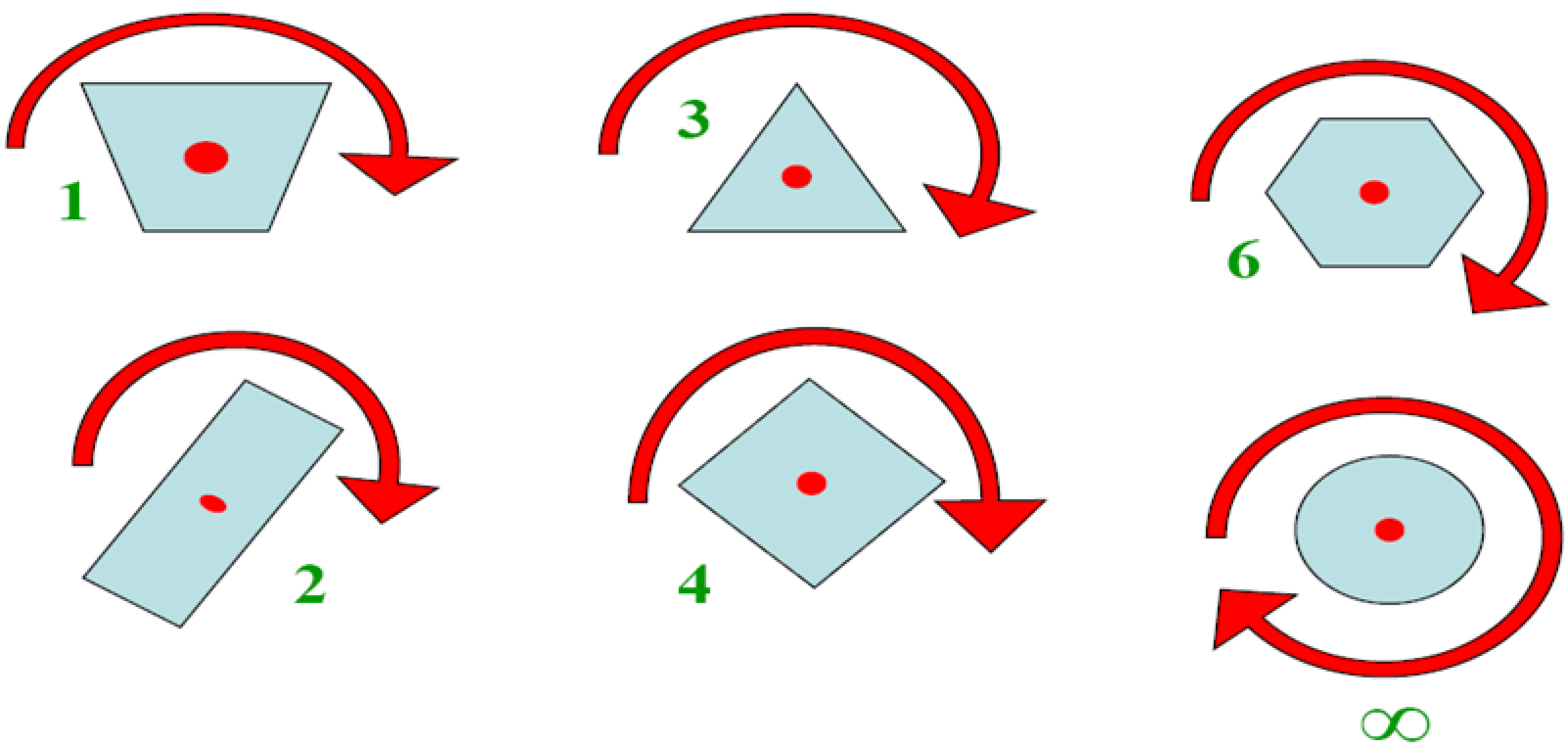
Identity

- Changes nothing
- Trivial
- Don't need to discuss further

Rotation

- N-fold rotation equates to a 360/N° about an axis
- Only some N's possible for crystals (1, 2, 3, 4, 6)

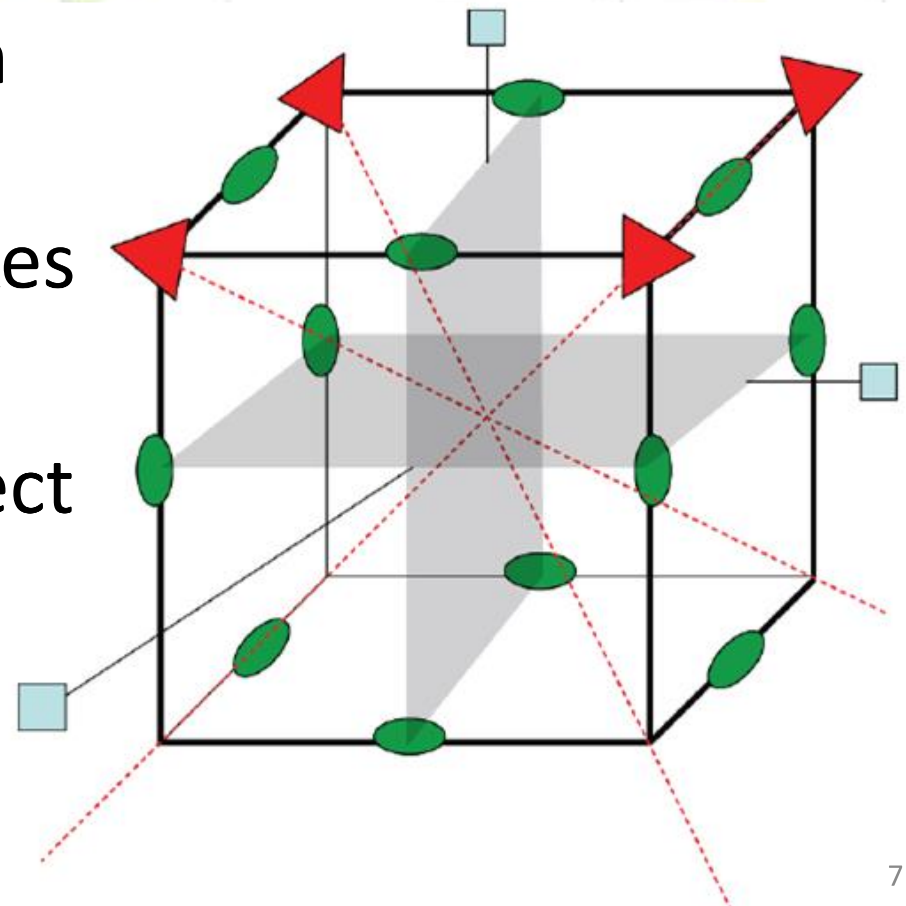
N	Hermann-Mauguin	Schoenflies
1	1	C_1
2	2	C_2
3	3	C_3
4	4	C_4
6	6	C_6


1
3
6
2
4
∞

Rotations in Cubes

- Four 3-fold rotation axes
- Three 4-fold rotation axes
- Six 2-fold rotation axes

- Note, they all intersect at centre of cell (in general true)



Reflection Plane - Mirror

- Reflection through a mirror plane
- Hermann-Mauguin symbol – m
- Schoenflies symbol – C_s

Inversion – Centre of Symmetry

- Reflection through a point
- Hermann-Mauguin symbol – $\bar{1}$
- Schoenflies symbol – C_1

Improper Rotation - RotoInversion

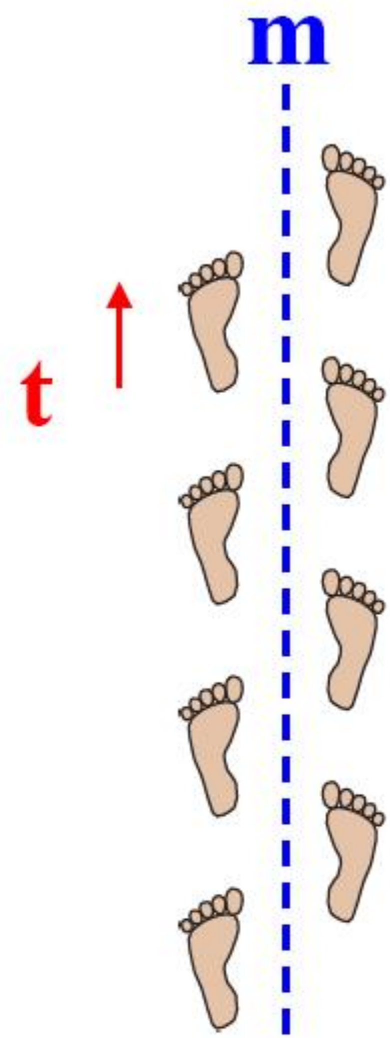
- Composite operation of two symmetries in succession
  - N-fold rotation followed by inversion through a point

N	Hermann-Mauguin	Schoenflies
1	$\bar{1}$	C_i
2	$\bar{2}$ (m)	C_s
3	$\bar{3}$	S_6
4	$\bar{4}$	S_4
6	$\bar{6}$	S_3

- A bit different in Schoenflies
  - Rotation followed by reflection in plane ⊥ to rotation axis

Glide Reflection

A two-step operation: reflection followed by translation (*g*)



Glide Reflection (Glide Plane)

- Reflection followed by translation
- Translation is parallel to mirror plane
- Unlike the footsteps example, in 3D several choices of translation vector parallel to mirror plane
- Unique symbol for each glide plane

Glide Reflection (Glide Plane)

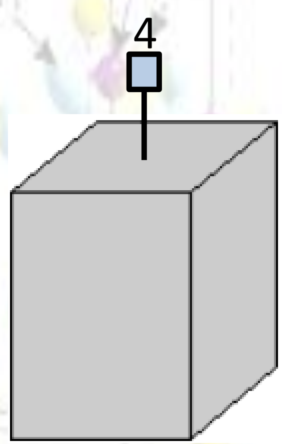
Hermann-Mauguin	Axis ⊥ to Glide Plane	Displacement vector
a	b or c	a/2
b	a or c	b/2
c	a or b	c/2
n	a b c	b/2+c/2 a/2+c/2 a/2+b/2
d	a b C	b/4+c/4 a/4+c/4 a/4+b/4

Screw Rotation

- Rotation followed by translation parallel to rotation axis
- Example: rotate by 120° and translate by ⅓ of axis length. Denoted by 3_1
- Total possibilities are:
  - 2_1, 3_1, 4_1, 4_2, 6_1, 6_2, 6_3, 3_2, 4_3, 6_4, and 6_5

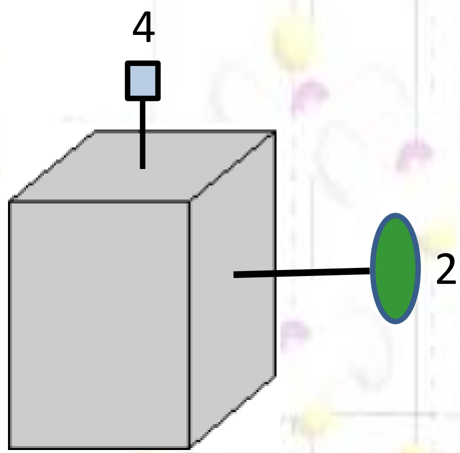
Symmetries Go Together

- Some symmetries will imply others
- For example, look at shape below
  - Square top face with rectangular sides (orthorhombic)
  - Square top face implies 4-fold axis of rotation (shown)

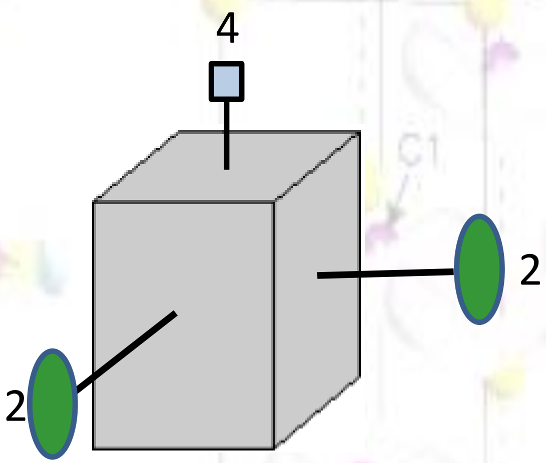


Symmetries Go Together

– Rectangular face on right must have a 2-fold axis. Goes right through the cell



– The 4-fold axis on the top face necessitates that the 2-fold axis is repeated on the front-to-back faces



The Minimum Symmetries to describe each Crystal System

These can be used, rather than the lattice parameters and angles (i.e. instead of the unit cells) to define the 7 systems.

Crystal System	Point Groups that define* them
Triclinic	Only inversion
Monoclinic	One 2-fold axis of rotation or one mirror plane
Orthorhombic	Three 2-fold axes of rot, or one 2-fold axis plus 2 mirror planes
Tetragonal	One 4-fold axis of rotation
Rhombohedral	One 3-fold axis of rotation
Hexagonal	One 6-fold axis of rotation
Cubic	Four 3-fold axes of rotation (4 triads)

**These are the symmetries that each system MUST have, by definition; there can be others.*

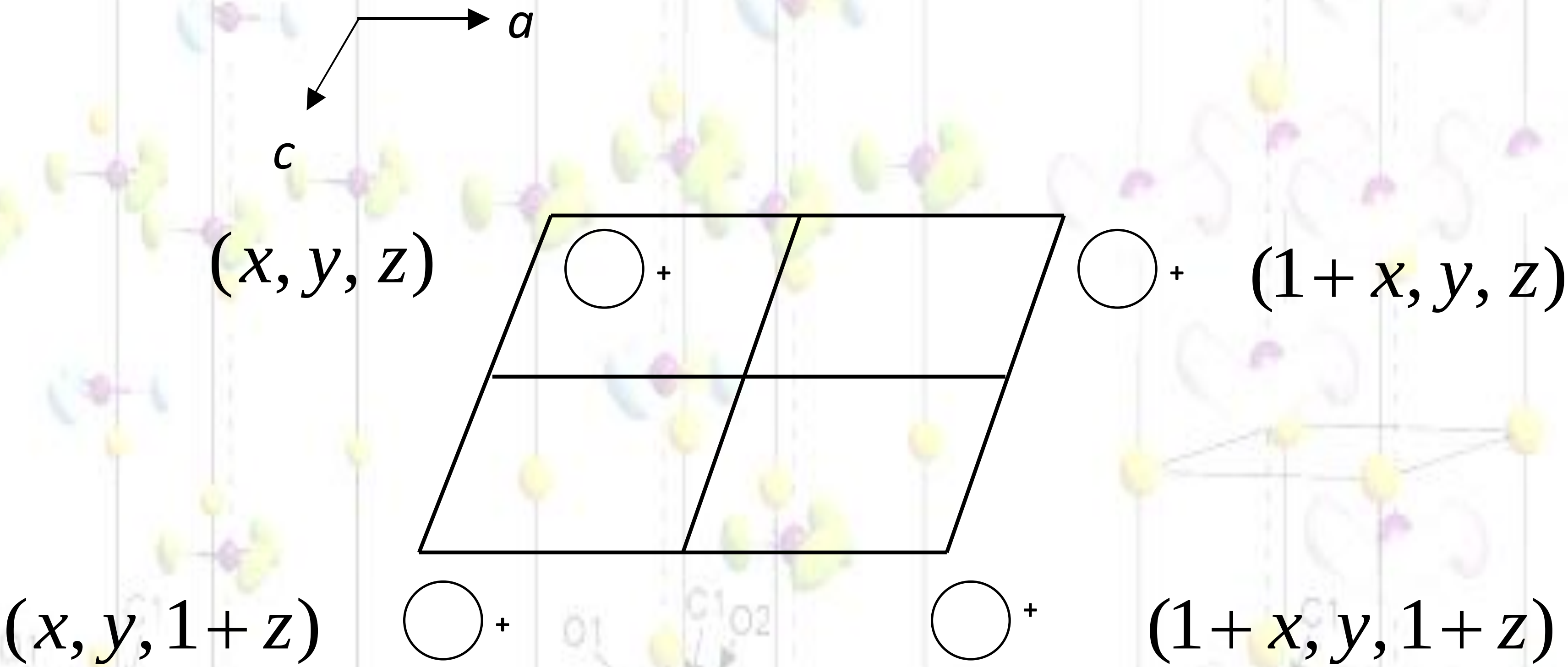
The Minimum Symmetries to describe each Crystal System

- Cubic – The secondary symmetry symbol will always be either 3 or –3 (i.e. Ia3, Pm3m, Fd3m)
- Tetragonal – The primary symmetry symbol will always be either 4, (-4), 4_1, 4_2 or 4_3 (i.e. $P4_12_12$, I4/m, P4/mcc)
- Hexagonal – The primary symmetry symbol will always be a 6, (-6), 6_1, 6_2, 6_3, 6_4 or 6_5 (i.e. P6mm, $P6_3/mcm$)
- Rhombohedral – The primary symmetry symbol will always be a 3, (-3) 3_1 or 3_2 (i.e P31m, R3, R3c, P312)
- Orthorhombic – All three symbols following the lattice descriptor will be either mirror planes, glide planes, 2-fold rotation or screw axes (i.e. Pnma, $Cmc2_1$, Pnc2)
- Monoclinic – The lattice descriptor will be followed by either a single mirror plane, glide plane, 2-fold rotation or screw axis or an axis/plane symbol (i.e. Cc, P2, $P2_1/n$)
- Triclinic – The lattice descriptor will be followed by either a 1 or a (-1).

Space Groups

- 230 of these
- Start from low symmetry
  - First two are triclinic
    - No 1 = P1 has no symmetry beyond the triclinic shape
    - No 2 = $P\bar{1}$ has a centre of inversion
  - Nos 3-15 are monoclinic with various combinations of a 2-fold axis, a mirror plane, and base centred
  - Nos 16-74 are orthorhombic
  - Nos 75-142 are tetragonal
  - Nos 143-167 are rhombohedral
  - Nos 168-194 are hexagonal
  - Rest are cubic

No 1 – P1

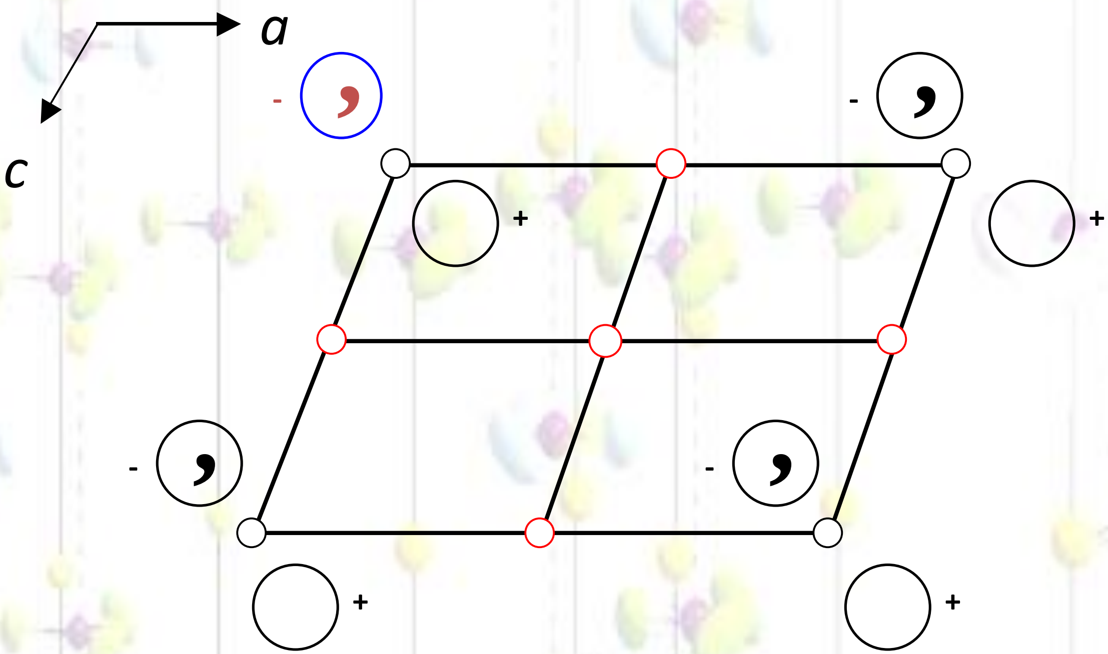


Z=1; (x, y, z)

No 1 – P1

- This space group can contain molecules of one chirality only
  - Enantiomorphous
- It doesn't have a centre of symmetry
  - Non-centrosymmetric
- It contains one molecule per unit cell
  - Z=1

No 2 – P$\bar{1}$

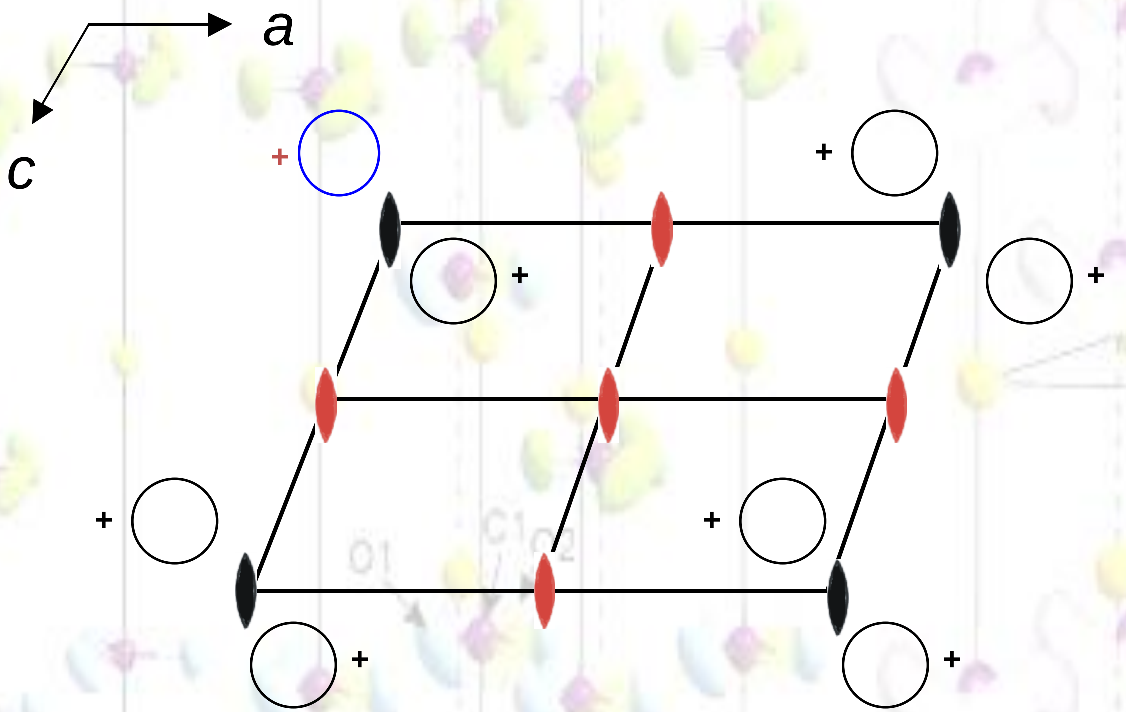


- The red circles represent the centres of symmetry
- The commas in the circles represent molecules of opposite chirality
- The centres of symmetry correspond to points of reduced multiplicity

No 2 – $P\bar{1}$

- $P\bar{1}$ is centrosymmetric
- It is non-enantiomorphous
- Z=2
- It contains positions of reduced multiplicity
  - These always correspond to position on point symmetries

No 3 – P2
A Monoclinic Space Group



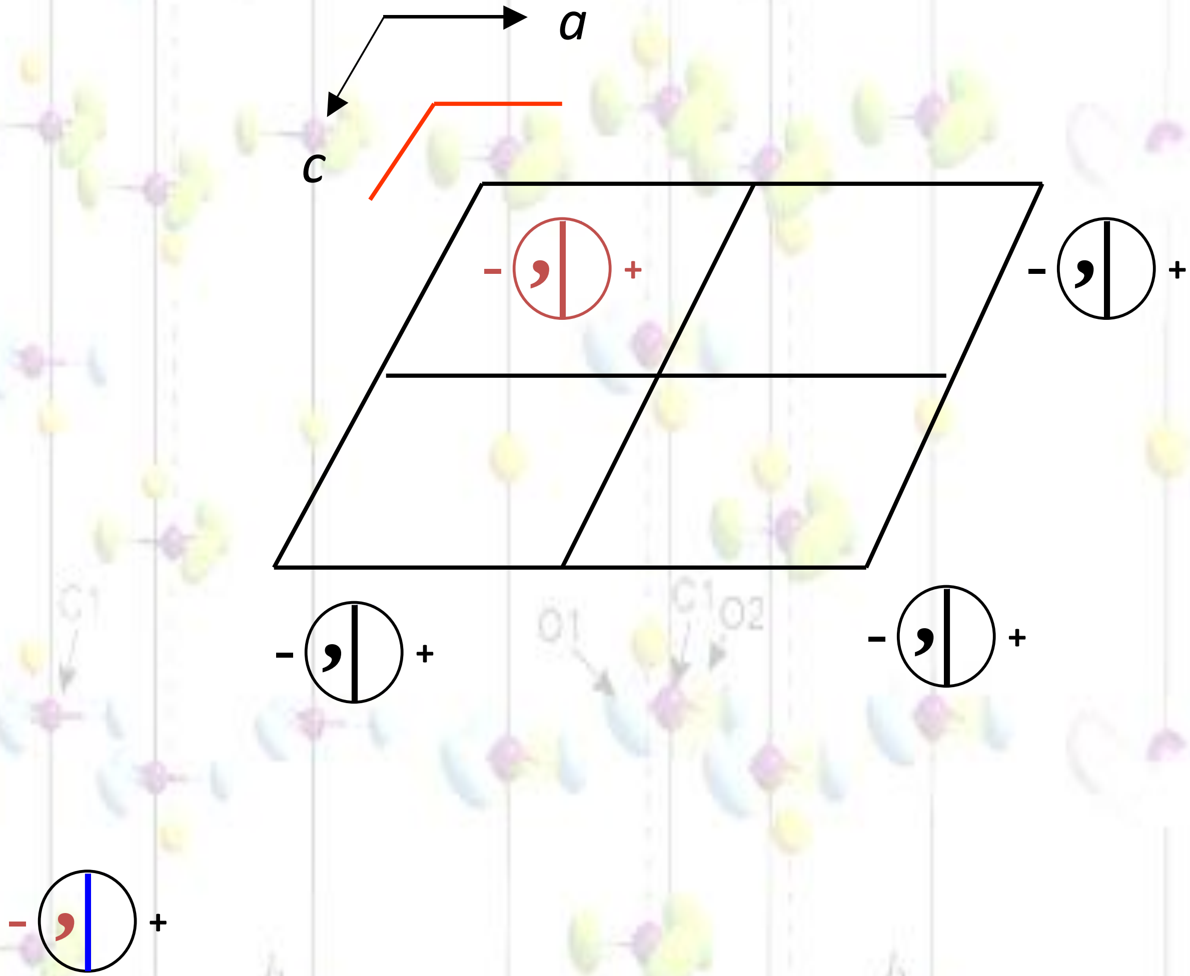
No 3 – P2

- P2 is non-centrosymmetric
- It is enantiomorphous
- Z=2
- Note the  stand for 2-fold rotation axes

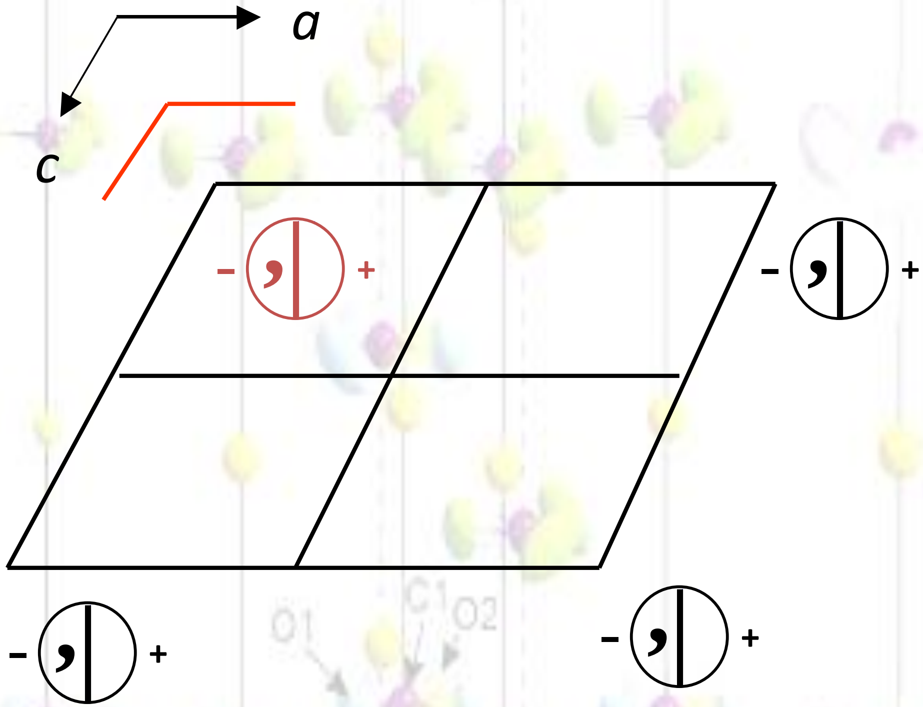
Enantiomorphism and Centrosymmetric

- If a group is centrosymmetric is must be non-non-enantiomorphous
- If it is non-centrosymmetric it can be either enantiomorphous or non-enantiomorphous

No 6 – Pm



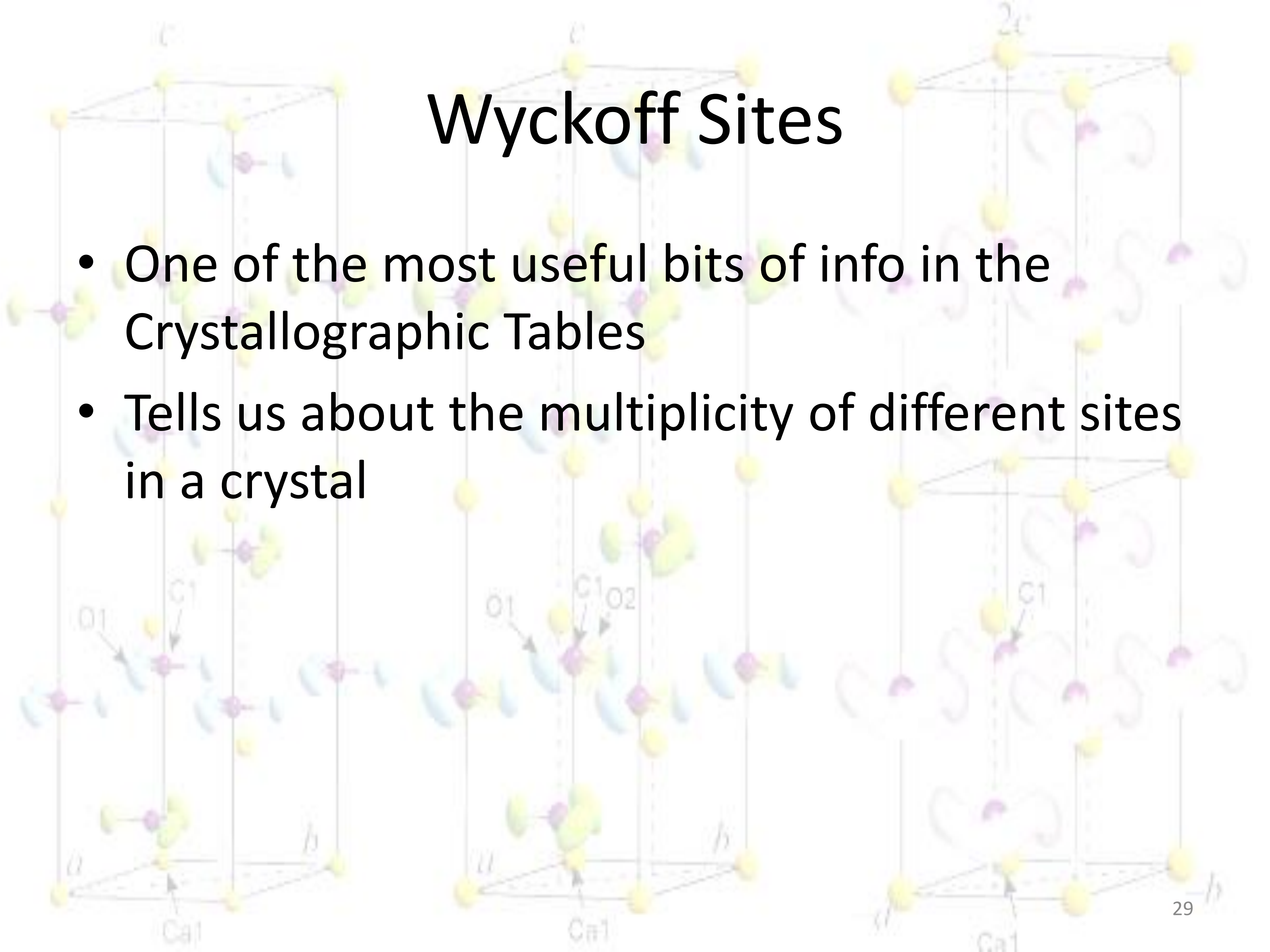
No 6 – Pm



This notation means there is a molecule of opposite chirality underneath the first

Wyckoff Sites

- One of the most useful bits of info in the Crystallographic Tables
- Tells us about the multiplicity of different sites in a crystal



Wyckoff Sites

- Take the Pm monoclinic space group above
  - Pm has only two symmetry elements
    - Mirror plane at y=0
    - Mirror plane at y = ½
  - A general position in the unit cell will create two molecules
    - (x, y, z)
    - (x, -y, z)
  - But a position on either mirror plane won’t generate a second molecule

Wyckoff Sites

- International table of space groups include Wyckoff sites
- Gives three for Pm

Multiplicity	Wyckoff Letter	Symmetry	Coordinates
2	c	1	(1)x,y,z (2)x, -y, z
1	b	m	x, ½ , z
1	a	m	x, 0, z

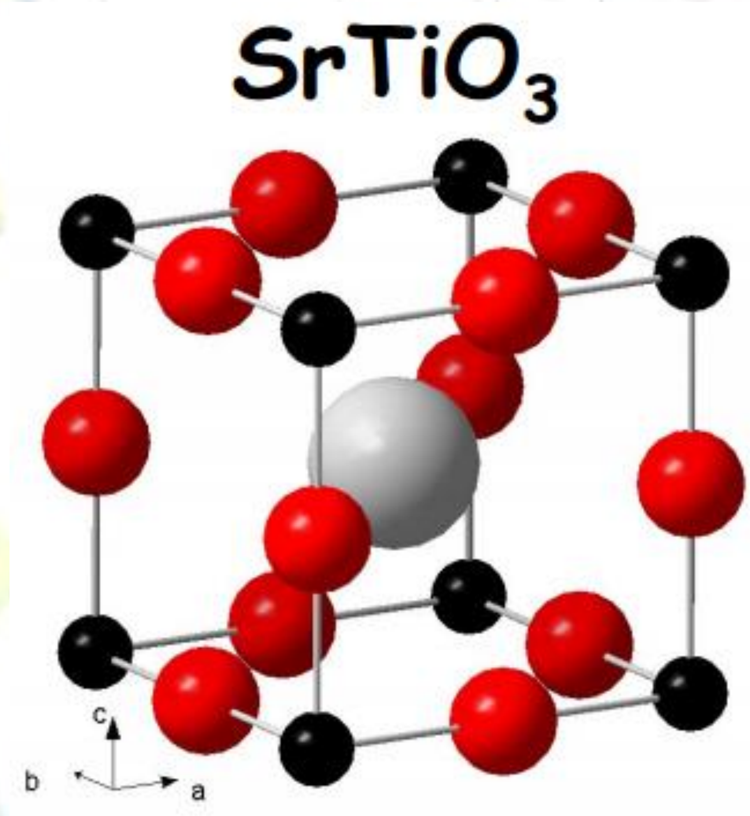
Wyckoff Sites - $SrTiO_3$

- From x-ray diffraction get space group Pm3m
- Lattice parameter 0.590nm
- Density 5100kg/m^3
- Means Z=1
- For Pm3m there are lots of Wyckoff sites, but most have high multiplicity (up to 48). Can ignore these
- Possibilities for multiplicity ≤ 3 are given below

Multiplicity	Wyckoff Letter	Symmetry	Coordinates
3	d	4/mm	(1)½, 0, 0 (2) 0, ½, 0 (3) 0, 0, ½
3	c	4/mm	(1) 0, ½, ½ (2) ½, 0, ½ (3) ½, ½, 0
1	b	$m\bar{3}m$	½ , ½, ½
1	a	$m\bar{3}m$	0, 0, 0

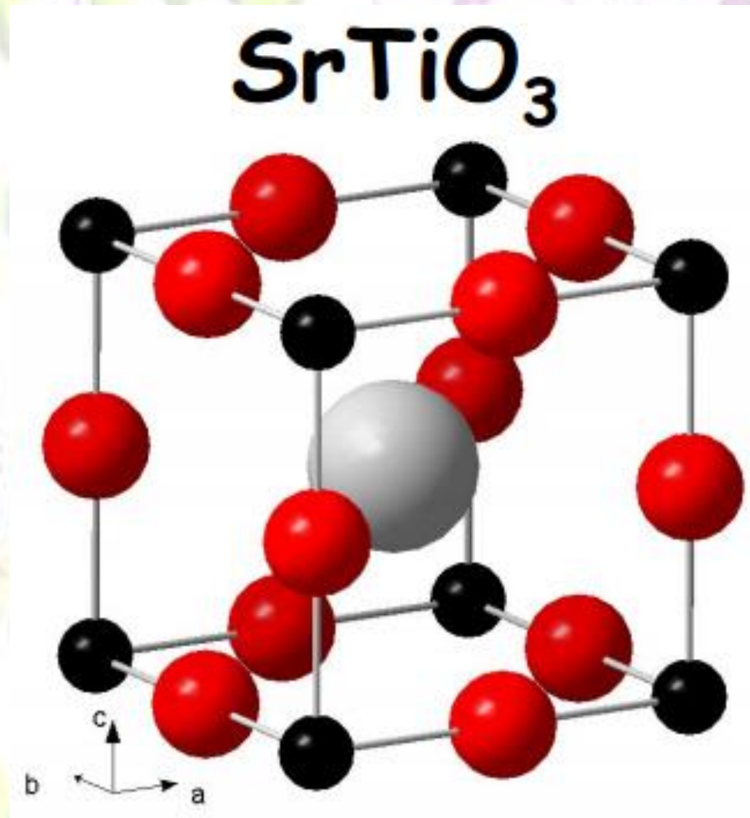
Wyckoff Sites - $SrTiO_3$

- Put Ti in site a (at the corners)
- Put Sr in site b (very centre)
- From bond lengths, obvious that O must be in site d
-



Example – $SrTiO_3$

- Space group Pm3m
- a=0.390nm



Example – CaF_2

- Space group Im3m
- a=0.546nm