MSE-238
Structure of Materials

Week 3 – crystallography II

Spring 2025

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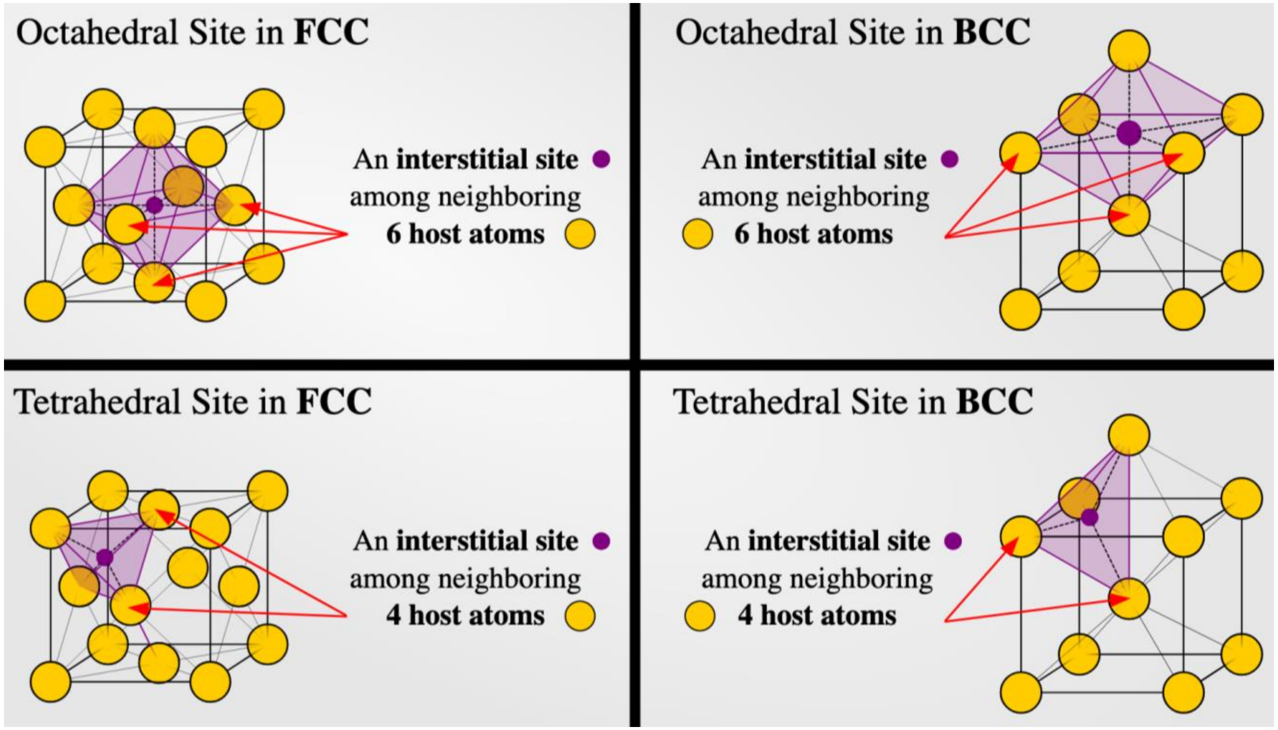
Overview

- Interstitial sites in steel
- Symmetry in 2D
  - 2D lattice
  - symmetry operations
  - plane groups
- Symmetry in 3D
  - Bravais lattice
  - point symmetry operators
  - 32 symmetry point groups
  - 230 space groups

  - →Hammond Chapter 2 - 4

Interstitial sites FCC vs. BCC



Crystal Structure	FCC	BCC
Number and Size of Octahedral Voids	4 voids, r = 0.414 R	6 voids, r = 0.155 R
Number and Size of Tetrahedral Voids	8 voids, r = 0.225 R	12 voids, r = 0.291 R

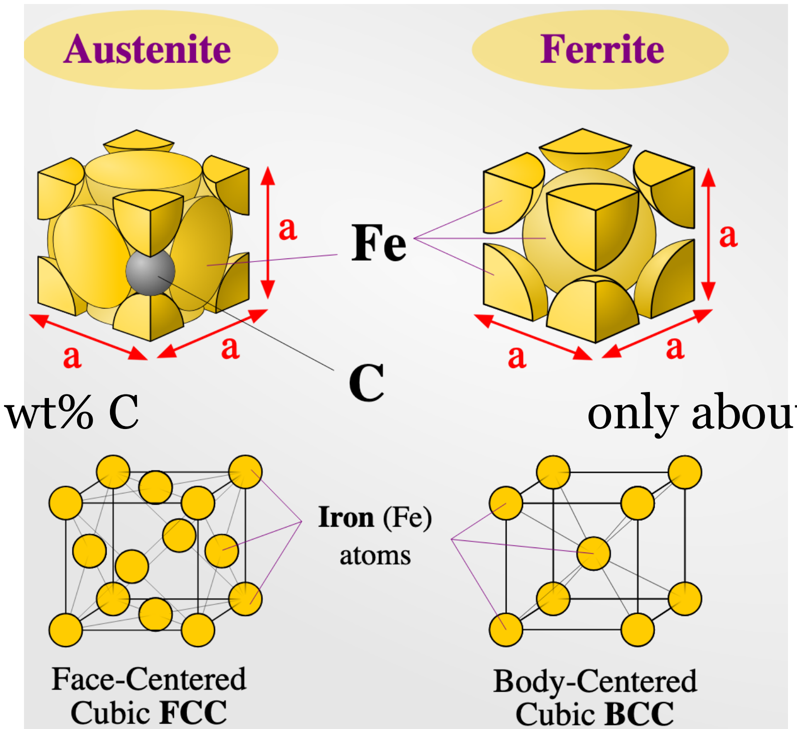
Interstitial sites FCC vs BCC → steel

- Although BCC has more total room for interstitial atoms, FCC has the largest particular interstitial site (octahedral). This can have a large impact in interstitial solubility.
- Steel: alloy of iron and carbon

does carbon fit into the crystal?

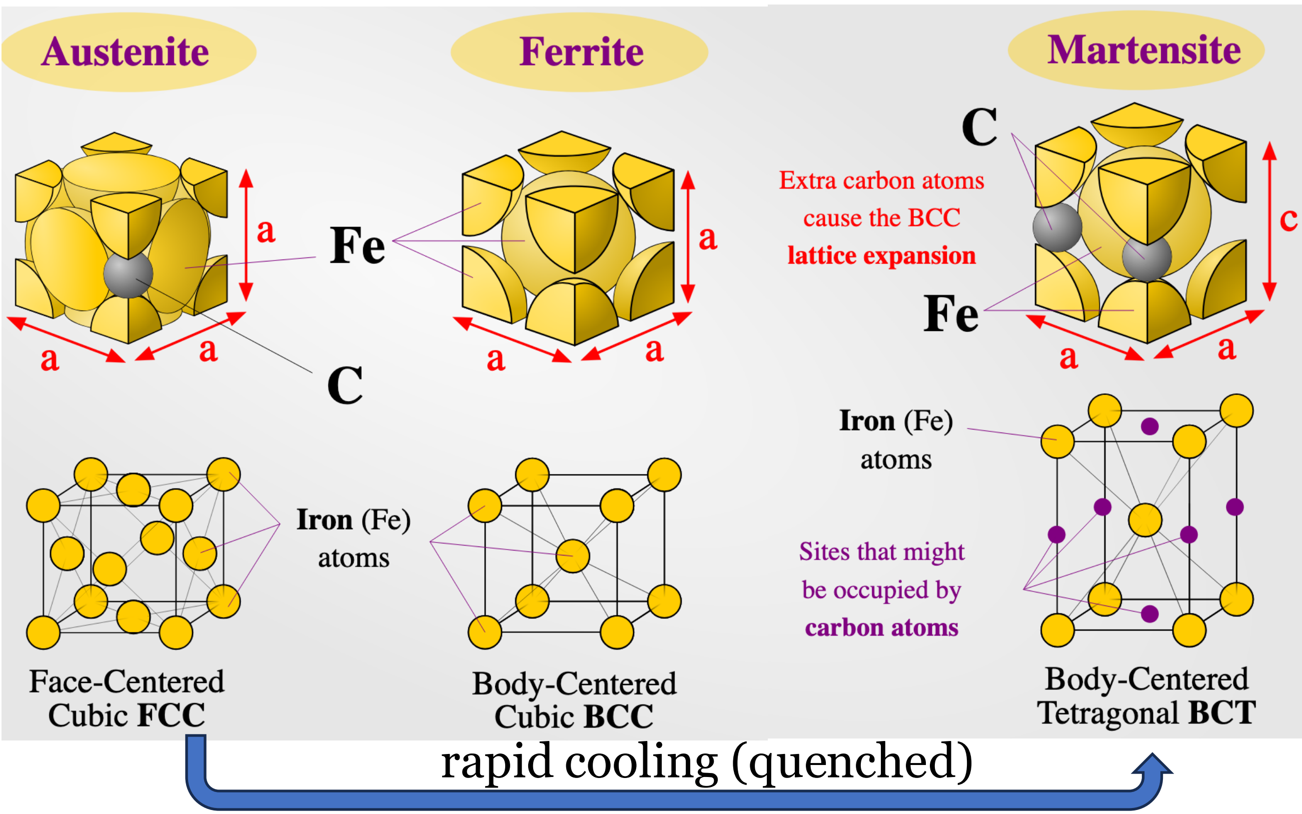
up to about 2 wt% C

only about 0.02 wt%



Interstitial sites FCC vs BCC → steel

- Heat up steel in presence of carbon (like coal or charcoal), the steel becomes FCC with more carbon dissolved. When cooled rapidly, the carbon has no time to diffuse out → end up in a body-centered tetragonal structure (Martensite)
- Steel: alloy of iron and carbon

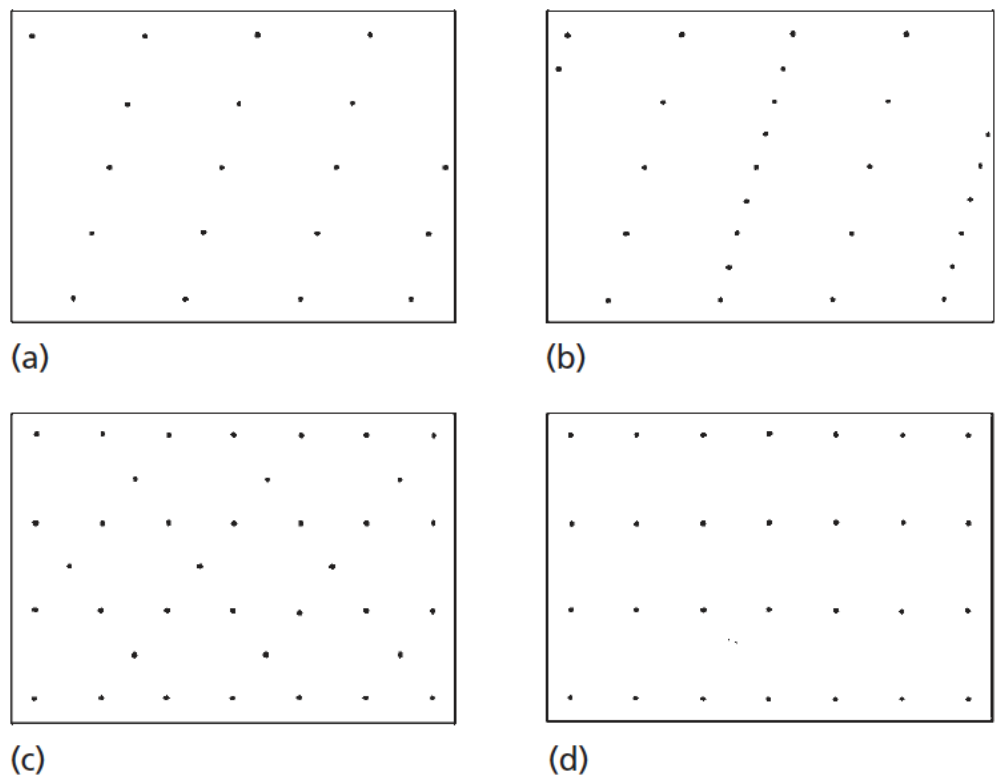


extra carbon gets trapped in the lattice and distorts the normally cubic lattice

this uniaxial distortion has a hardening effect

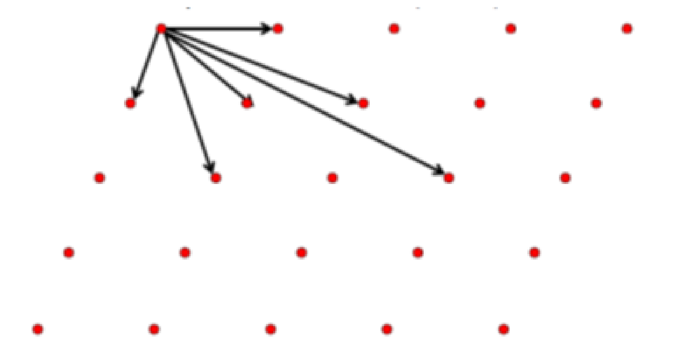
Lattice

A lattice is an array of points in space in which the environment of each point is identical



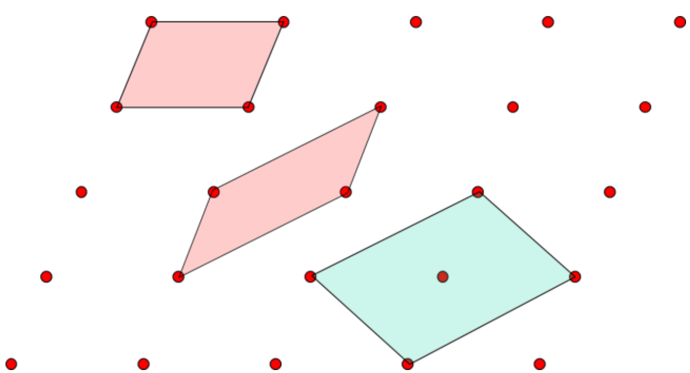
Translational periodicity and unit cell

- **Translational** periodicity is defined by the lattice



In 2D defined by two vectors
not unique!

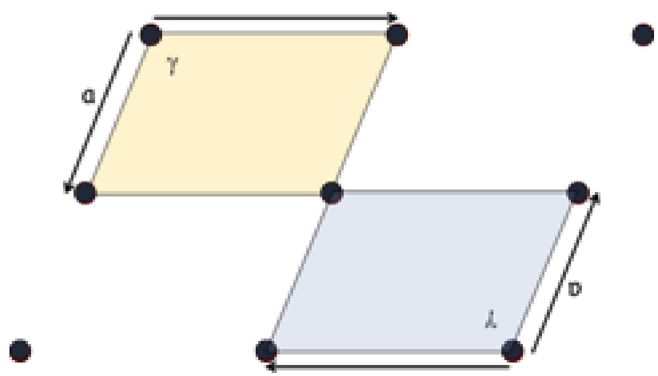
Examples of unit cells:
containing one lattice point (primitive)
containing more than one lattice point (non primitive)



Criteria used to define unit cell:
1. Short unit vectors
2. Angles between vectors closest to 90°
3. Primitive unless the cell does not reflect the major symmetry axis of the lattice → conventional unit cell

There are an infinite possibilities of lattices as the lattice parameters (vector norms and angles) can be chosen arbitrarily → classification according to symmetry

Symmetries in lattice

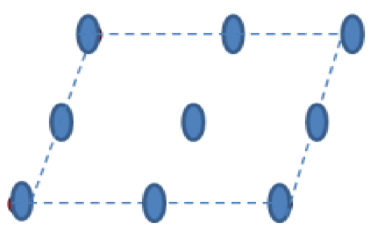


Unit cell with

- The two shortest vectors, a≠b
- Both angles are "closest" to 90°
- Primitive "P"

→ oblique lattice

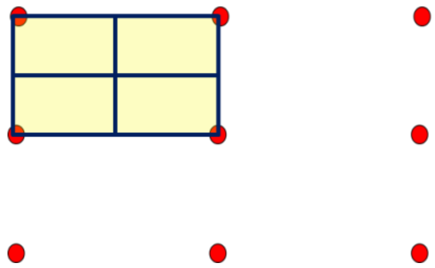
180° rotational symmetry → 2-fold axis "2"



- **A symmetry operation** is an action that leaves an object unchanged.
- **A symmetry element** is a part of the object that doesn't move during the operation: a point, a line, a plane, an entire object.

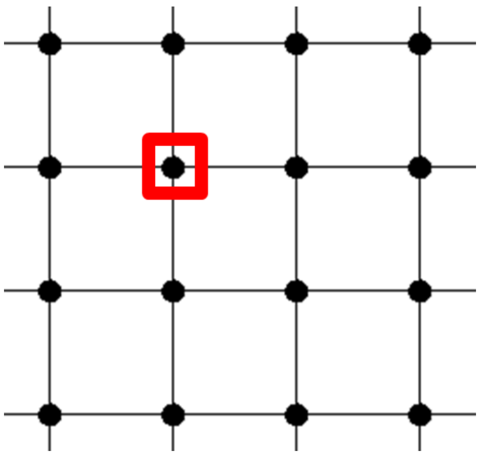
rotational symmetry is a point symmetry (at least one point remains unchanged)

Symmetries in lattice



if the 2D lattice is rectangular, there is additionally a
mirror symmetry “m”
symbol here “mm” since there are “interweaving” mirror lines
a≠b $\gamma = 90^\circ$

→ rectangular lattice



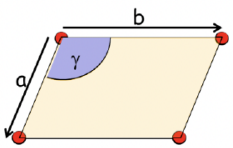
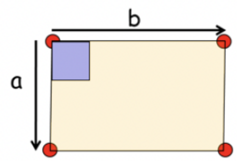
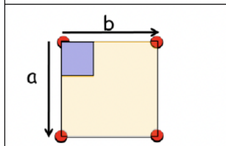
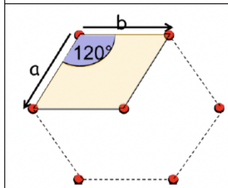
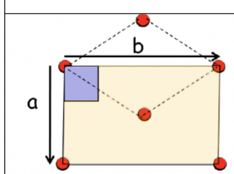
if the lattice vectors are equal there is a
four-fold rotation axis ■ “4”
a=b $\gamma = 90^\circ$

→ square lattice

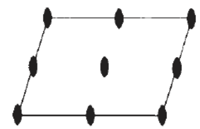
→ classified as different lattice system by level of symmetry!

5 plane lattices → classification according to symmetry

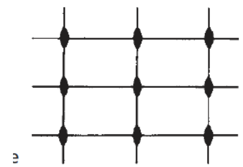
- lattice: how translation is done, classified according to symmetry in a plane

2D lattice		Maximal symmetry of 2D lattice
	***oblique P*** $a \neq b$; $\gamma \neq 90, 120°$	2-fold axis
	***rectangular P*** $a \neq b$; $\gamma = 90°$	2-fold axis with two reflection lines
	***square P*** $a = b$; $\gamma = 90°$	4-fold axis with two reflection lines
	***Hexagonal P*** $a = b$; $\gamma = 120°$	6-fold axis with three reflection lines
	***rectangular C*** $a \neq b$; $\gamma = 90°$	2-fold axis with 2 reflection lines
When a primitive lattice is taken, it is called Rhombic		

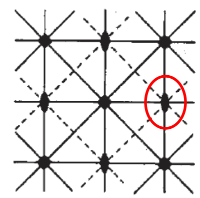
notation according to Hermann–Mauguin



p2

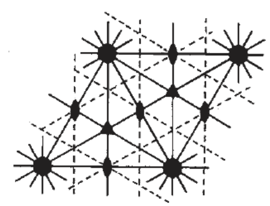


p2mm

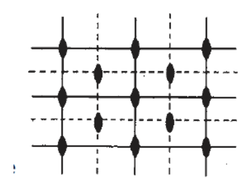


p4mm

→ additional symmetries, such as 2-fold axis, the highest symmetry is given

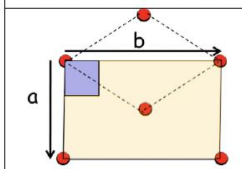


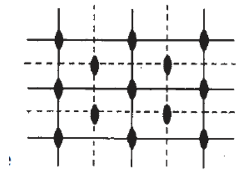
p6mm



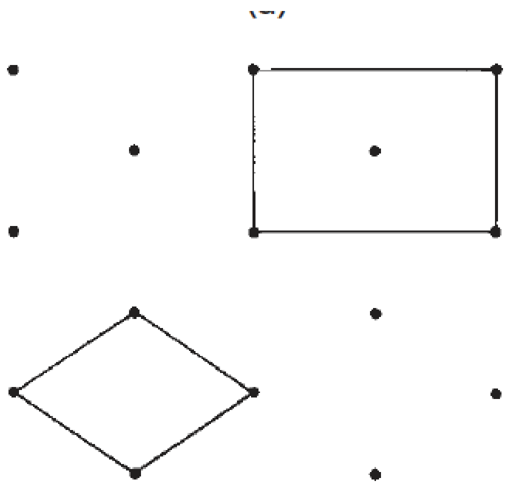
c2mm

Non primitive lattice

 ***rectangular C*** $a \neq b$; $\gamma = 90°$ When a primitive lattice is taken, it is called Rhombic	2-fold axis with 2 reflection lines



c2mm



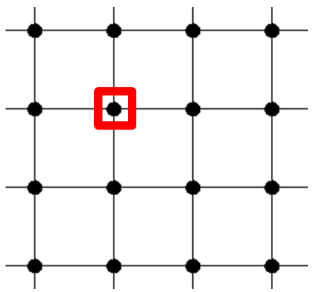
→ alternative primitive unit cell: rhombic p

→ but: 3rd convention criteria:
primitive unless the cell does not reflect the major symmetry axis of the lattice

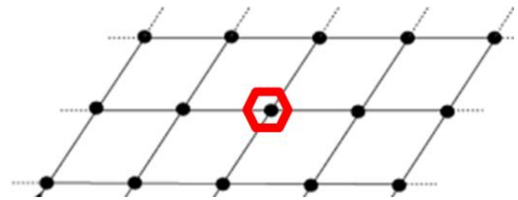
rectangular lattice vectors in conventional unit cell

Crystal symmetry

- symmetry present in the crystal is determined by
  - how the translation is done



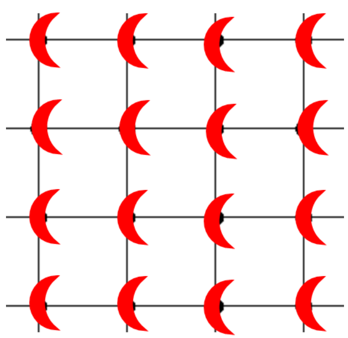
4-fold
rotation axis

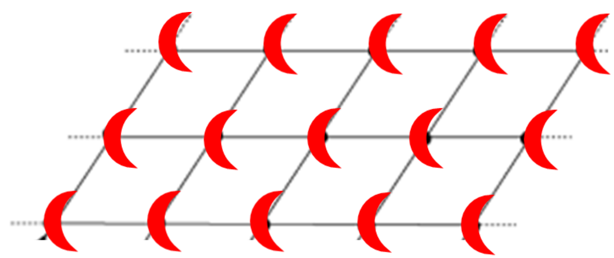


6-fold
rotation axis

A crystal with one atom per motif will have the symmetry of the lattice

  - **character of the motif**





only 1-fold symmetry left!

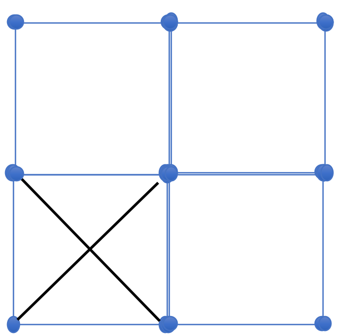
Symmetry operations in 2D

For discrete objects, rotational symmetries can only be discrete: $\frac{2\pi}{n}$

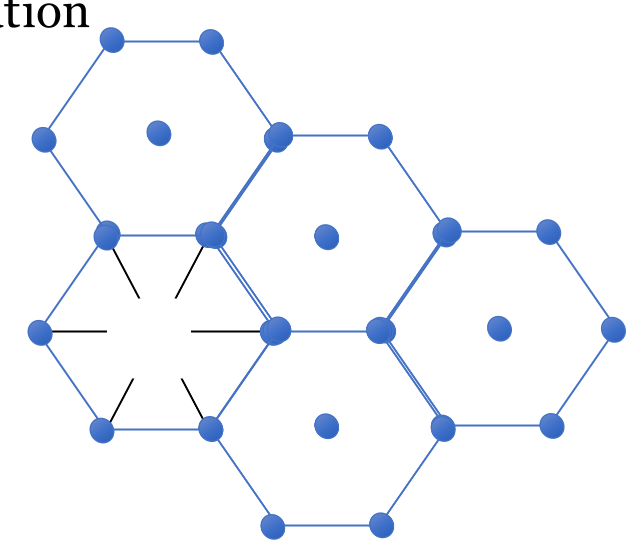
and they rotational symmetry must be compatible with a translational symmetry!

n=1 → 1-fold, no symmetry
n=2 → 2-fold, 180° rotation
n=3 → 3 fold, 120° rotation
n=4 → 4 fold, 90° rotation
n=6 → 6 fold, 60° rotation

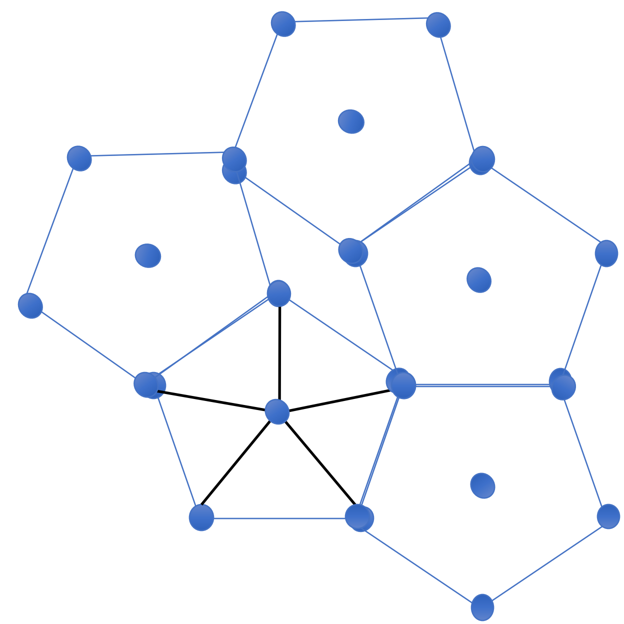
what about 5-fold?



4-fold



6-fold

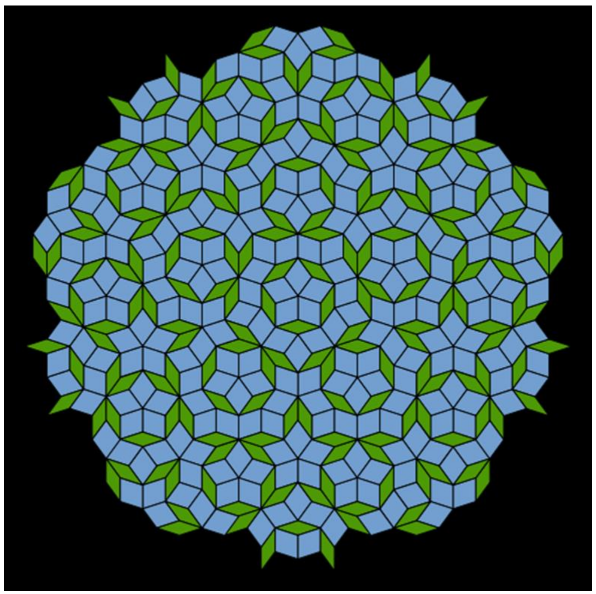


and mirror symmetry (m)

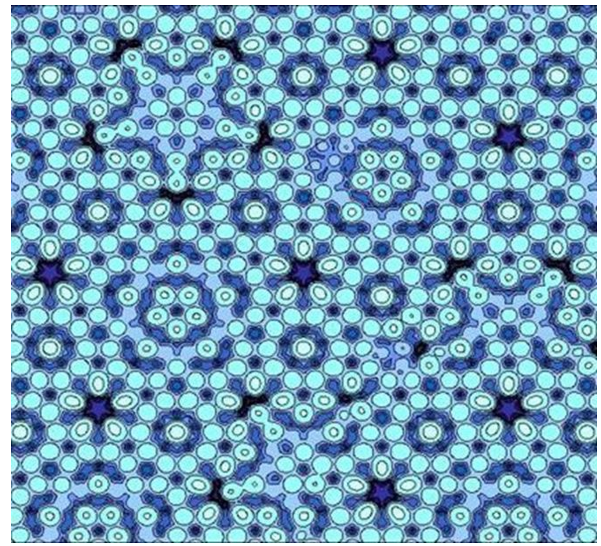
Patterns with 5-fold symmetry → Quasi-crystals

A quasiperiodic crystal (quasicrystal) is a structure that is ordered but not periodic.

A quasi-crystalline pattern can continuously fill all available space, but it lacks translational symmetry



Penrose tilling gives a quasicrystal
http://en.wikipedia.org/wiki/Penrose_tiling



Atomic model of an aluminium-palladium-manganese (Al-Pd-Mn) quasicrystal surface.

http://chemvista.org/quasicrystals1.html

Point groups

- Point groups are mathematical constructs that capture all the non-translation symmetry options that can be performed on an object: reflection, rotation, (rotoinversion in 3D)

- From mathematical group theory
  - Closure: The combination of symmetry operators is a symmetry operator in the group.
  - All symmetry operators have an inverse, some are their own inverse.
  - Identity is part of all the Point group symmetry.
  - Associativity is respected

- A Point Group describes all the symmetry operations that can be performed on a motif that result in a conformation indistinguishable from the original.
- all symmetry operations of a point group must pass through the center of the object (point symmetry)

Point groups in 2D

- From an object with no symmetry… R

bromochlorofluoroethene

1

- mirror symmetry by forming an object with R and its mirror image !

cis -difluoroethene

m

- An object with 2 mirror symmetries with perpendicular planes has a 2-fold symmetry as well.

ethene

2mm

- A motif with a 2-fold symmetry doesn’t have necessarily a mirror symmetry

trans -difluoroethene

2

- 3-fold symmetry

trifluoralkylammonia

3

10 Point groups in 2D

boric acid

3m

(4) - rotane, $C_{12}H_{16}$

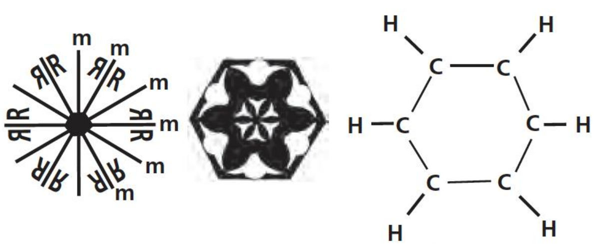
4

tungsten oxyfluoride

4mm

(6) - rotane, $C_{18}H_{24}$

6



benzene

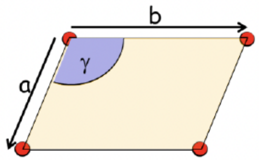
6mm

- 3-fold symmetry plus a mirror symmetry. The planes of symmetry are not orthogonal
- A motif with a 4-fold symmetry doesn't have necessarily a mirror symmetry
- A motif with a 4-fold symmetry plus mirror symmetries
- A motif with a 6-fold symmetry doesn't have necessarily a mirror symmetry
- A motif with a 6-fold symmetry plus mirror symmetries, with some planes perpendicular.

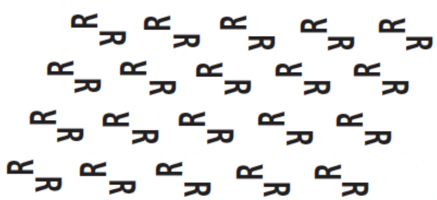
2D Plane groups

crystal = lattice + motif

combine the 10 2D point groups with the appropriate 5 lattice
→ total number of 2D pattern, the so called plane groups

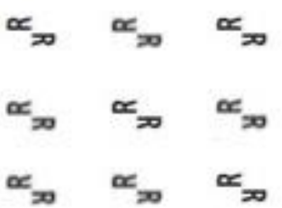
2D lattice		Maximal symmetry of 2D lattice
	***oblique P*** $a \neq b$; $\gamma \neq 90, 120°$	2-fold axis

p1 (1)



p2 (2)

For the oblique lattice, a motif with no symmetry would match.
A motif with a 2-fold symmetry also



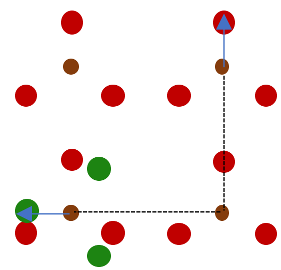
we could put the point group 2 on a square lattice

But it does not bring new symmetry, no 4-fold symmetry, but the 2-fold symmetry is maintained: so it is the same group symmetry as the oblique p2.

2D plane groups

When we want to merge the symmetry of the motif and the one of the Bravais lattice, restrictions occur and the symmetry of the crystal will result of this analysis.

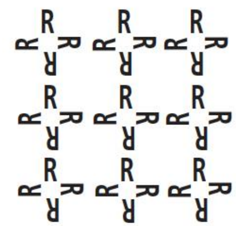
- The rotational symmetry of the motif must coincide with the one of the Lattice



4-fold symmetry is lost when combined with a 3-fold point symmetry of the motif

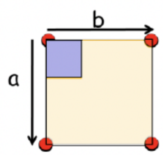
- So each point group can be associated to a certain Bravais Lattice, but all kind of new symmetries can come from merging a Motif in a Lattice.

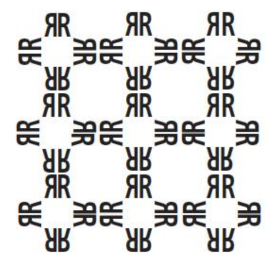
2D plane groups



p4 (10)

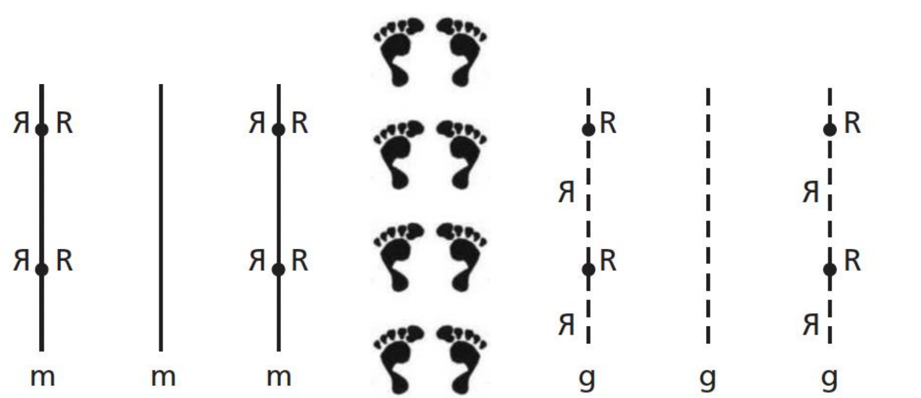
4 fold symmetry will only be associated to the square lattice.

	***square P*** a = b ; γ = 90°	4-fold axis with two reflection lines



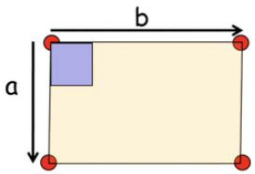
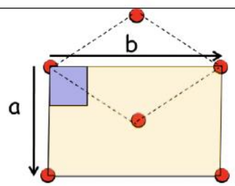
p4mm (11)

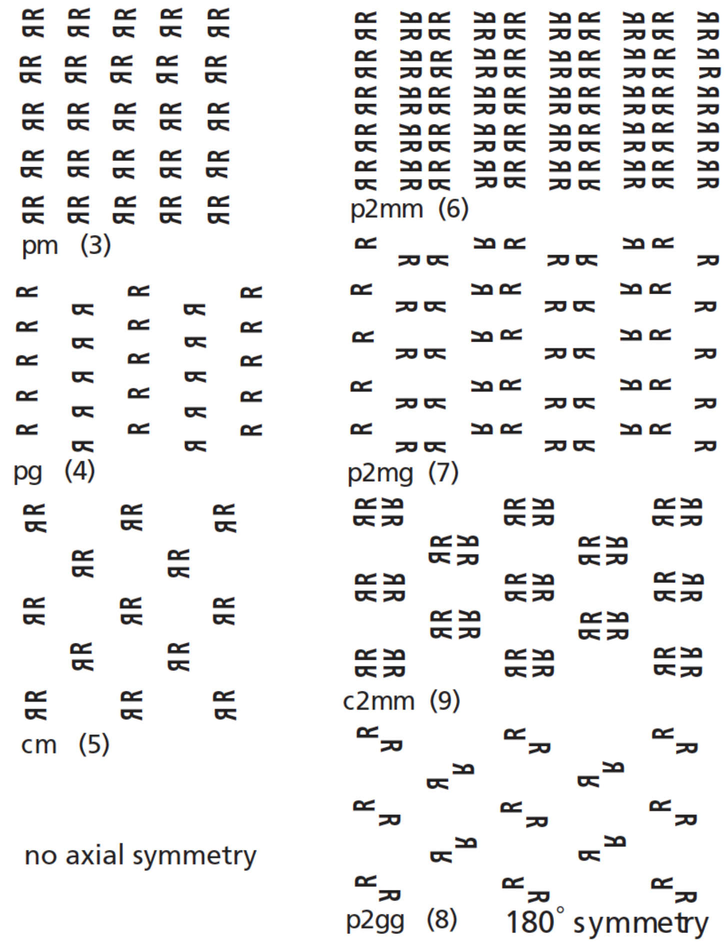
- One could think that there is only 2 plane groups associated with the 2 point groups noted 4 and 4mm.
- There is however a third one
  Associated to a glide plane symmetry noted g.
- Glide planes are added due to the translational symmetry of the crystal



2D plane groups

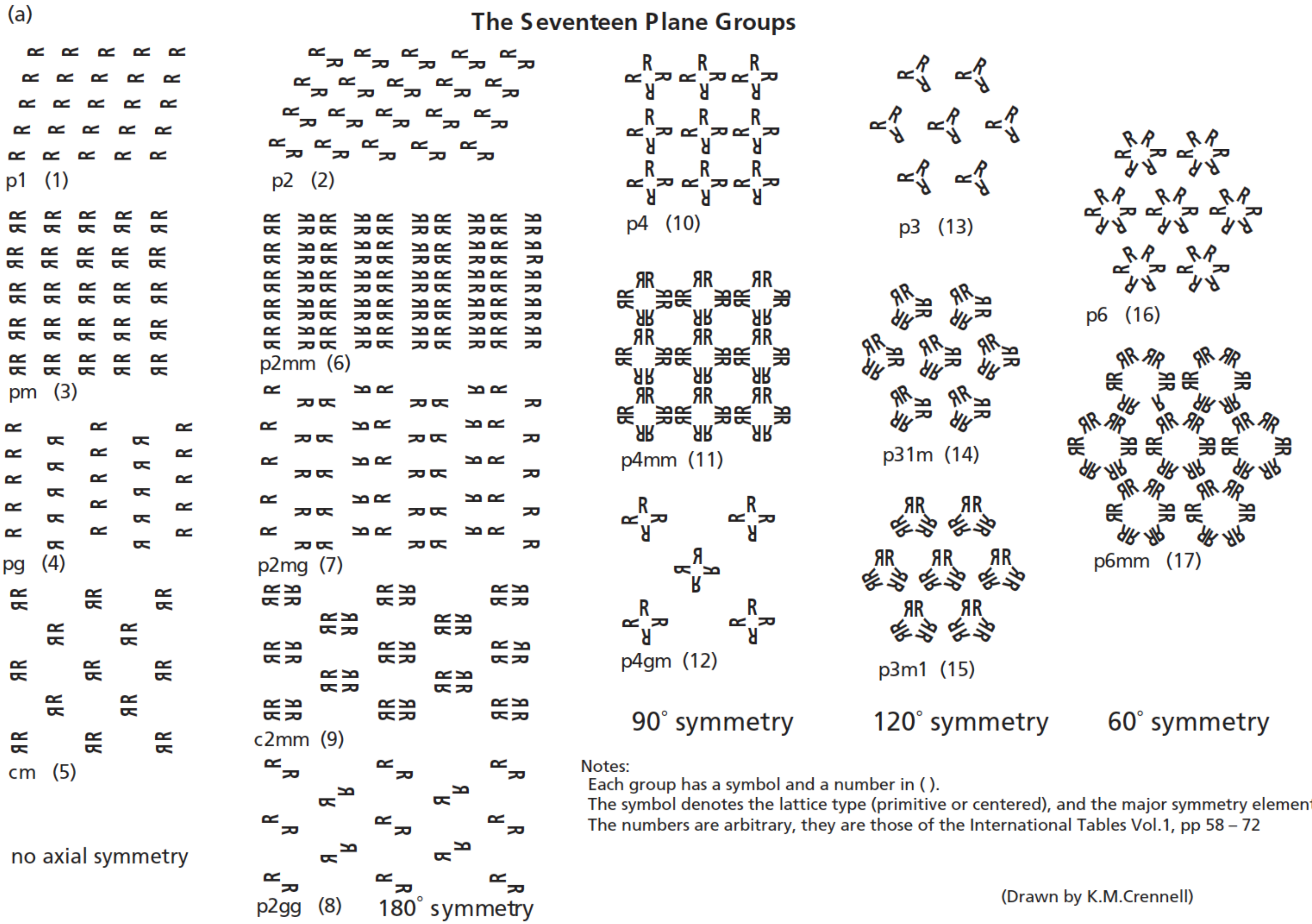
- The two rectangular lattices (p and c) gather many possible plane groups.

	***rectangular P*** $a \neq b\ ;\ \gamma = 90°$	2-fold axis with two reflection lines
 When a primitive lattice is taken, it is called Rhombic	***rectangular C*** $a \neq b\ ;\ \gamma = 90°$	2-fold axis with 2 reflection lines



- We can see mirror and glide mirror symmetries appearing. It is adding new plane groups for a given point group of the motif.

17 plane groups in 2D

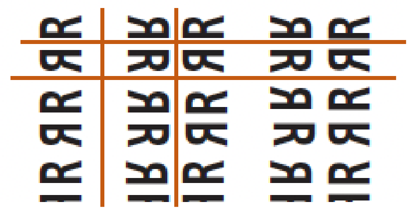


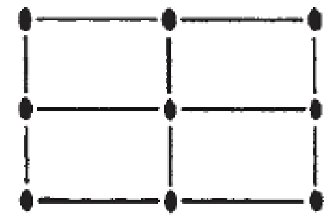
Notes:
Each group has a symbol and a number in ( ).
The symbol denotes the lattice type (primitive or centered), and the major symmetry elements
The numbers are arbitrary, they are those of the International Tables Vol.1, pp 58 – 72

(Drawn by K.M.Crennell)

Symmetry elements of the 2D plane groups

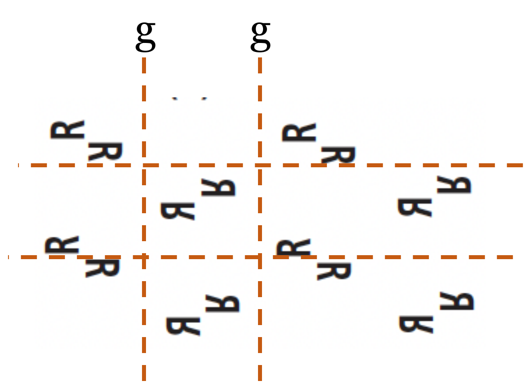
- p2mm

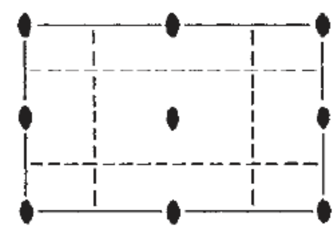




p2mm

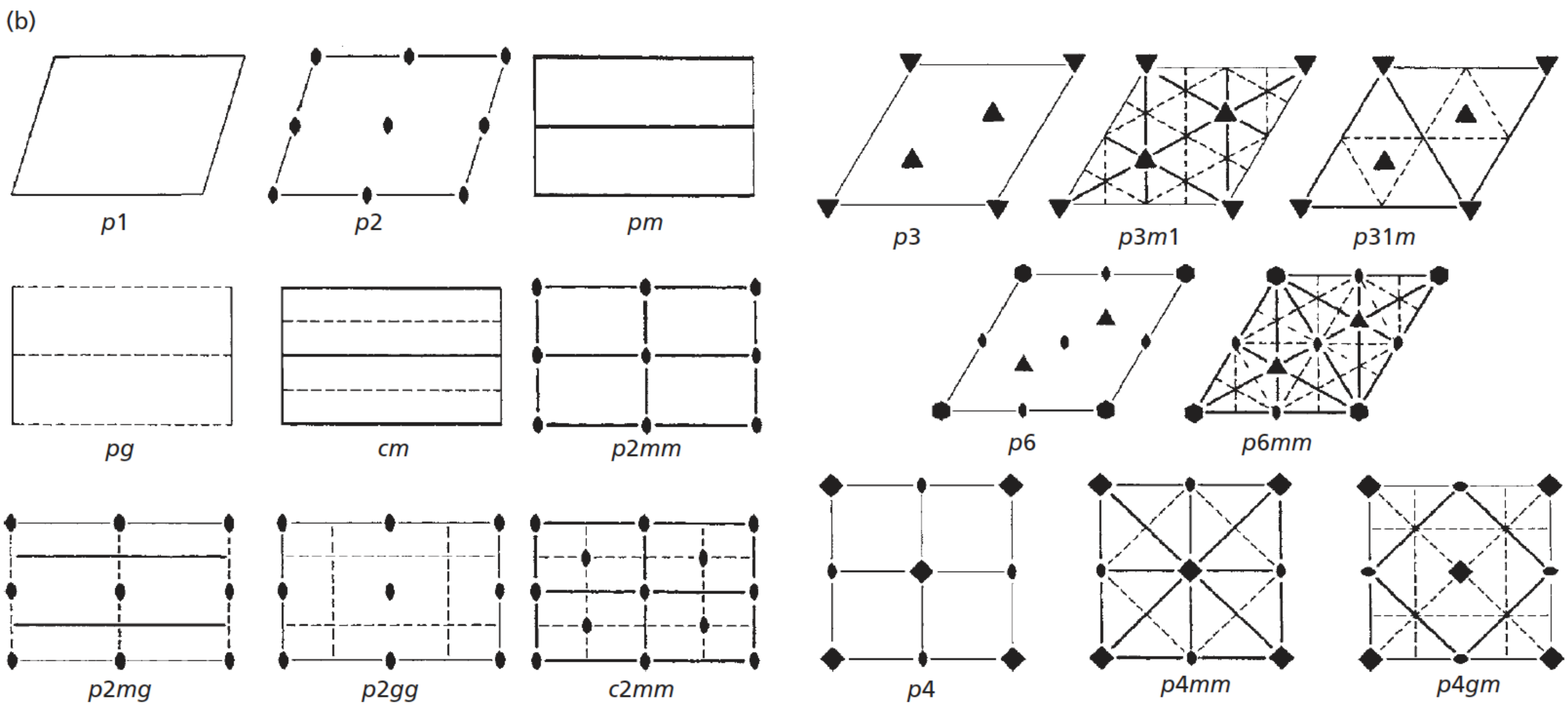
- p2gg





p2gg

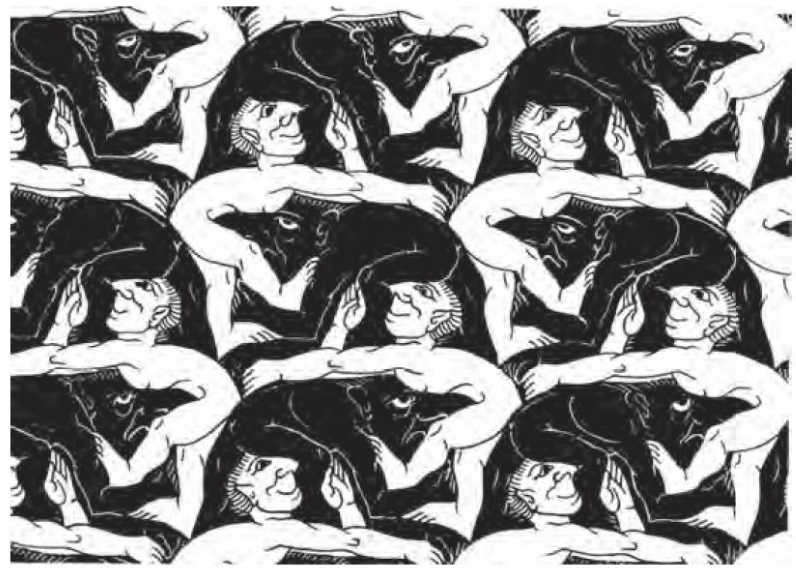
Symmetry elements of the 2D plane groups



Pattern in culture and art

- Alhambra: 11 of the plane groups are present
- M. C. Escher (1898–1971): Escher's pattern encompass all 17 plane groups!

p3m1



pg

Plane groups in 2D → space groups in 3D

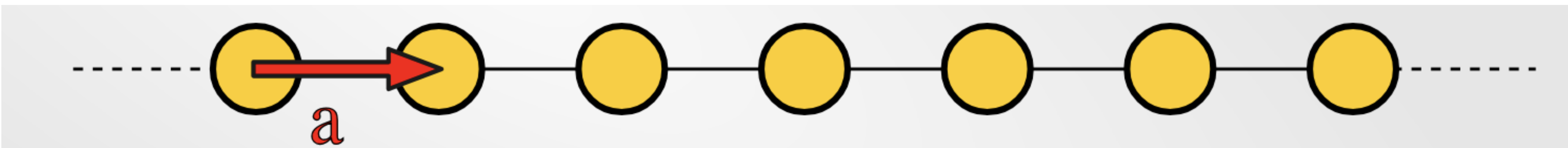
- Plane/Space groups are mathematical constructs that capture every way an object can be repeated through space, through translation (→lattice) and the symmetry operations: rotation, reflection, gliding (and screws in 3D).
- Point groups are mathematical constructs that capture all the non-translation symmetry options that can be performed on an object (reflection, rotation, rotoinversion)
- translational symmetry elements need to be added glide lines in 2D and glide planes and screw axes in 3D

in 2D
combine 5 plane lattice with 10 point groups
→ 17 plane groups

and in 3D
combine 14 Bravais lattice with 32 point groups
→ 230 space groups

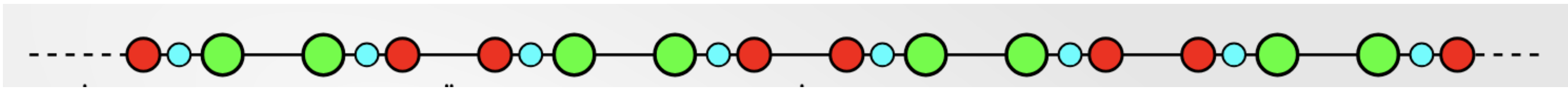
(pure combination would give more, but many combinations end up being duplicates

Linear lattice



How many 1-D lattices are there?

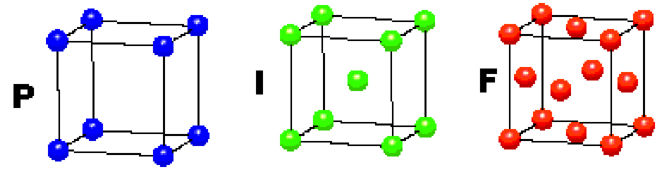
Linear lattice



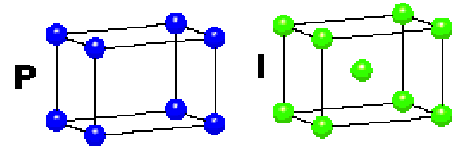
Remember, **Bravais lattices only consider translational symmetry**. If you wanted to consider other symmetrical relationships like reflection, rotation, or inversion, you'd need point groups and space groups.

7 crystal systems – 14 Bravais Lattice

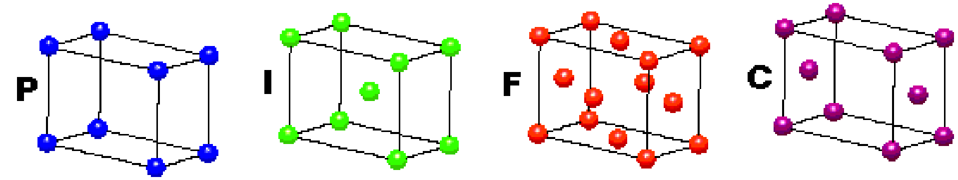
Cubic
a = b = c
a = b = g = 90°



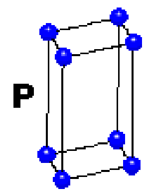
Tetragonal
a = b ≠ c
a = b = g = 90°



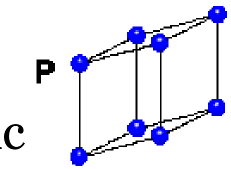
Orthorhombic
a ≠ b ≠ c
a = b = g = 90°



Hexagonal
a = b ≠ c
a = b = 90°; g = 120°

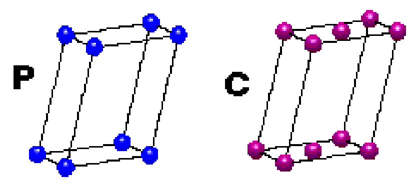


Trigonal or rhombohedric

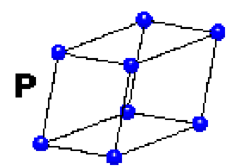


a = b = c
a = b = g ≠ 90°

Monoclinic
a ≠ b ≠ c
a = g = 90° ≠ b



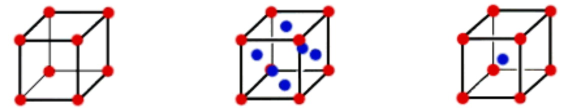
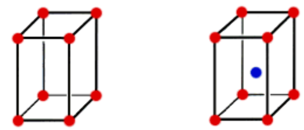
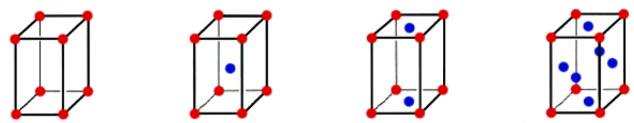
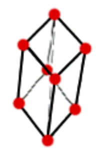
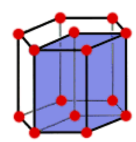
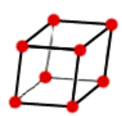
Triclinic
a ≠ b ≠ c
a ≠ b ≠ g



7 classes / 14 Bravais lattice

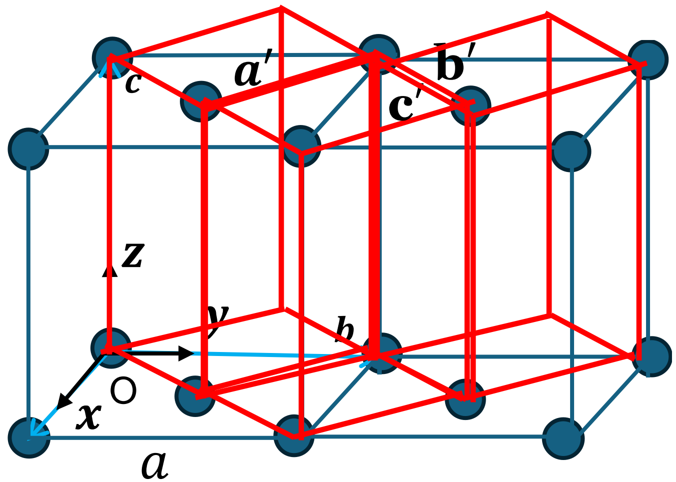
P : primitive
I : centered
F : face centered
C : base centered

http://www.chem.ox.ac.uk/icl/heyes/structure_of_solids/lecture1/Bravais.gif

crystal system		Bravais lattices	defining symmetry
Cubic	$a = b = c$ $a = b = g = 90^{o}$	 Simple cubic; Face-centered cubic; Body-centered cubic	4x 3-fold axis 3x 4-fold axis
Tetragonal	$a = b \neq c$ $a = b = g = 90^{o}$	 Simple tetragonal; Body-centered tetragonal	4-fold axis
Orthorhombic	$a \neq b \neq c$ $a = b = g = 90^{o}$	 Simple orthorhombic; Body-centered orthorhombic; Base-centered orthorhombic; Face-centered orthorhombic	3x 2-fold axis
Trigonal or rhombohedric	$a = b = c$ $a = b = g \neq$ 90^{o}	 Rhombohedral	3-fold axis
Hexagonal	$a = b \neq c$ $a = b = 90^{o};\ g = 120^{o}$	 Hexagonal	6-fold axis
Monoclinic	$a \neq b \neq c$ $a = g = 90^{o} \neq b$	 Simple Monoclinic; Base-centered monoclinic	2-fold axis
Triclinic	$a \neq b \neq c$ $a \neq b \neq g$	 Triclinic	1-fold axis

Why only 14 Bravais Lattice?

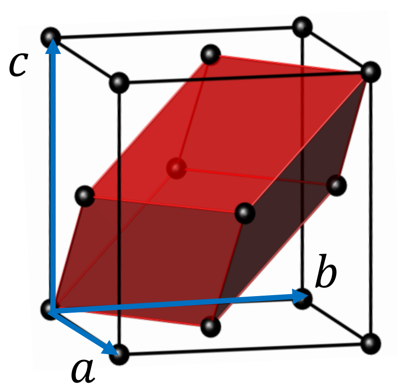
For example, why not a base-centered cubic structure ?



- It is a Primitive tetragonal !

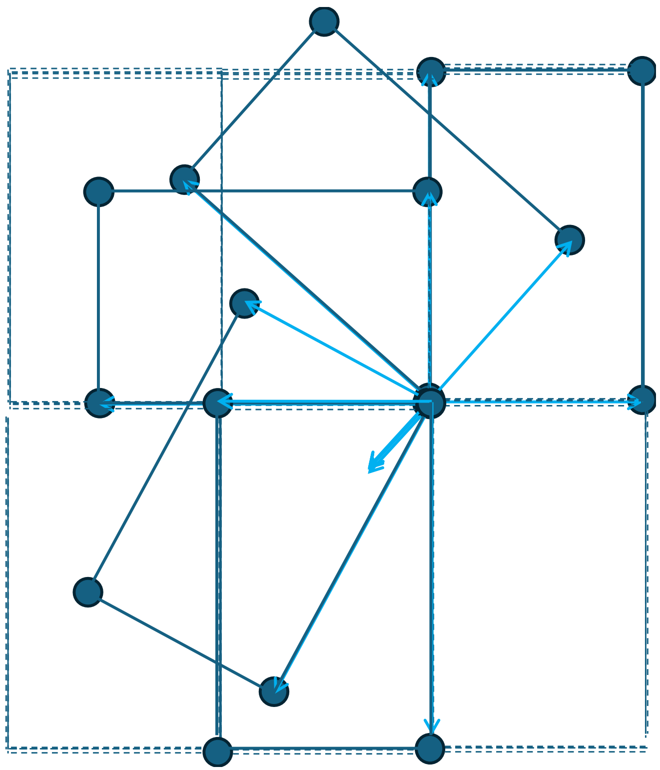
However, one can show that the FCC is also another lattice, a rhombohedric structure !

- And yet FCC is classified with its own Bravais Lattice…



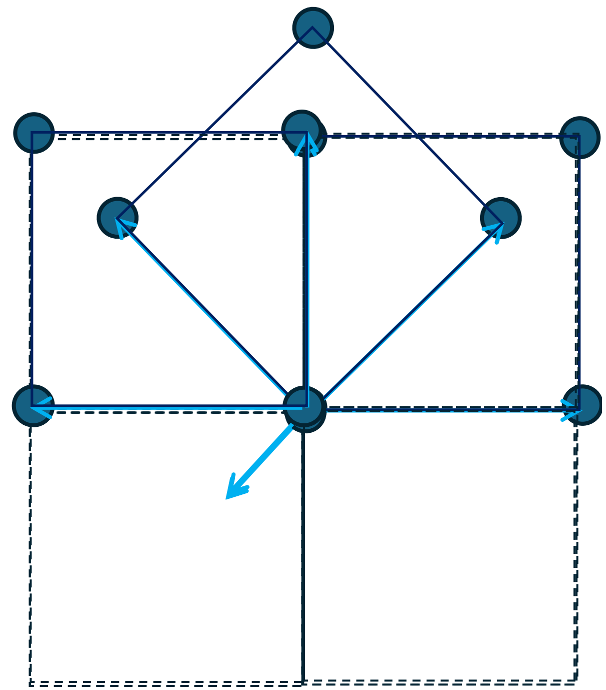
Why 14 Bravais Lattice?

- The classification is not about lattice parameter values, it classifies by level of symmetry.
  - A rhombohedric with a certain value of lattice parameters acquire novel symmetries that makes it have a specific Bravais lattice in the cubic structure system.
  - Other example: tetragonal vs cubic



Tetragonal structure: $c > a$

2-fold rotational symmetry



Cubic structure: $c = a$

4-fold rotational symmetry

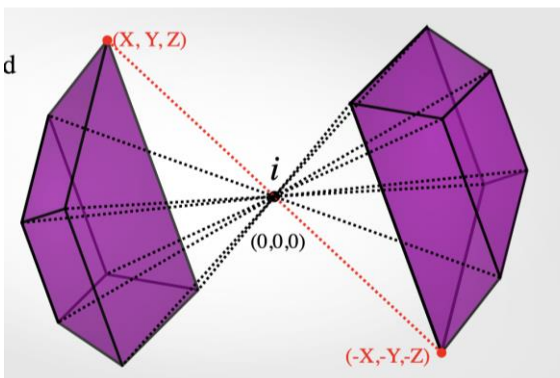
Point Symmetry operations in 3D

- **Rotation axis**
  1-fold (no symmetry)
  2-fold (180° rotation)
  3-fold (120° rotation)
  4-fold (90° rotation)
  6-fold (60° rotation)

→ in 2D rotation axis perpendicular to the plane
→ in 3D there can be several axes in idfferent directions (but always through the center of the object)

- **Reflection or mirror plane**

- **the inversion center and the roto-inversion axis**



every point pulled through center of inversion *I*

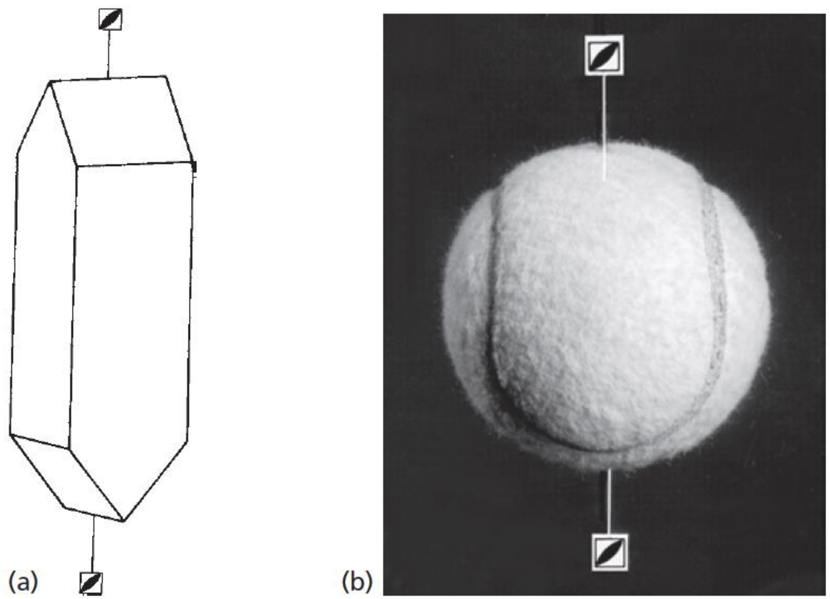
rotation and inversion combined → roto-inversion

Point symmetry operations in 3D

In 2D:

- A rotation is always around an axis perpandicular to the plane, so an inversion is a rotation by 180°.
- There is hence no roto-inversion, as they are just another rotation.

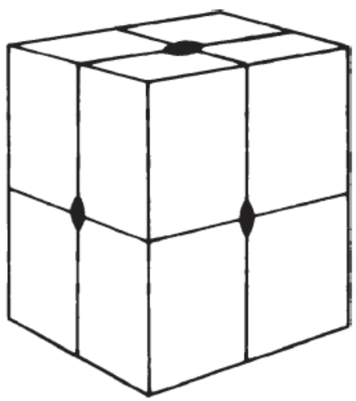
Examples of roto-inversions in 3D:



urea crystals and tennis ball have inversion four-fold axis (which is also a 2-fold rotation)

Point symmetry elements examples

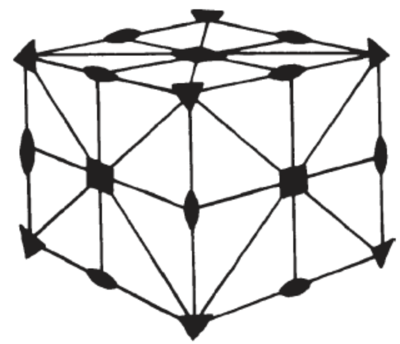
orthorhombic



→ 3 times 2-fold axis, perpendicular to the faces

→ three mirror planes parallel to faces planes

cubic

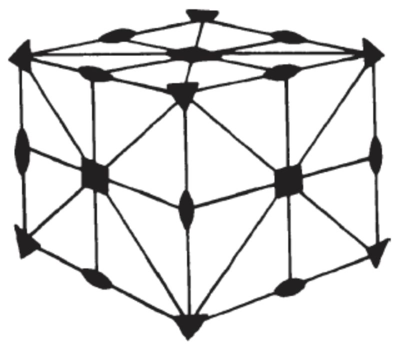


→ highest symmetry, makes it hard to see!

→ 3 times 4-fold axis perpendicular to the faces
→ 4 times 3-fold axis between opposite cube corners
→ 6 times 2-fold axis between opposite center of edges
9 mirror planes
→ 3 parallel to faces planes
→ 6 parallel to the face diagonals
plus center of inversion and rotoinversions!

Point symmetry elements examples

cubic



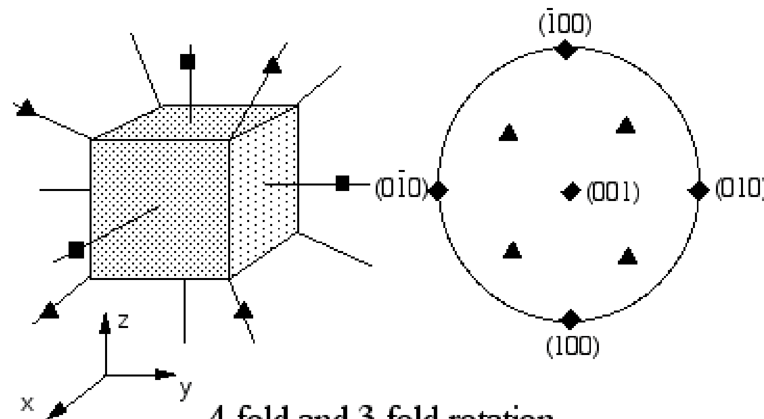
Point groups: particular number of mirror planes and axes
they must be self-consistent for example:
two 2-fold axis MUST be mutually orthogonal

→ 3 times 4-fold axis perpendicular to the faces
→ 4 times 3-fold axis between opposite cube corners
→ 6 times 2-fold axis between opposite center of edges

9 mirror planes
→ 3 parallel to faces planes
→ 6 parallel to the face diagonals

plus center of inversion and rotoinversions!

stereoprojection of symmetry elements



4-fold and 3-fold rotation axes in a cube

Point groups

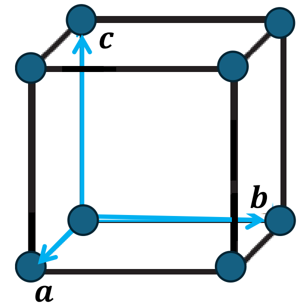
- Point groups are mathematical constructs that capture all the non-translation symmetry options that can be performed on an object: reflection, rotation, (rotoinversion in 3D)

- From mathematical group theory
  - Closure: The combination of symmetry operators is a symmetry operator in the group.
  - All symmetry operators have an inverse, some are their own inverse.
  - Identity is part of all the Point group symmetry.
  - Associativity is respected

- A Point Group describes all the symmetry operations that can be performed on a motif that result in a conformation indistinguishable from the original.
- all symmetry operations of a point group must pass through the center of the object (point symmetry)

Point groups of a cube

A cube, or a motif formed by four points at the corners, have the highest symmetry, with a point group of order 48, i.e. with 48 symmetries.
Order of a group: its cardinal, or number of elements in the group.

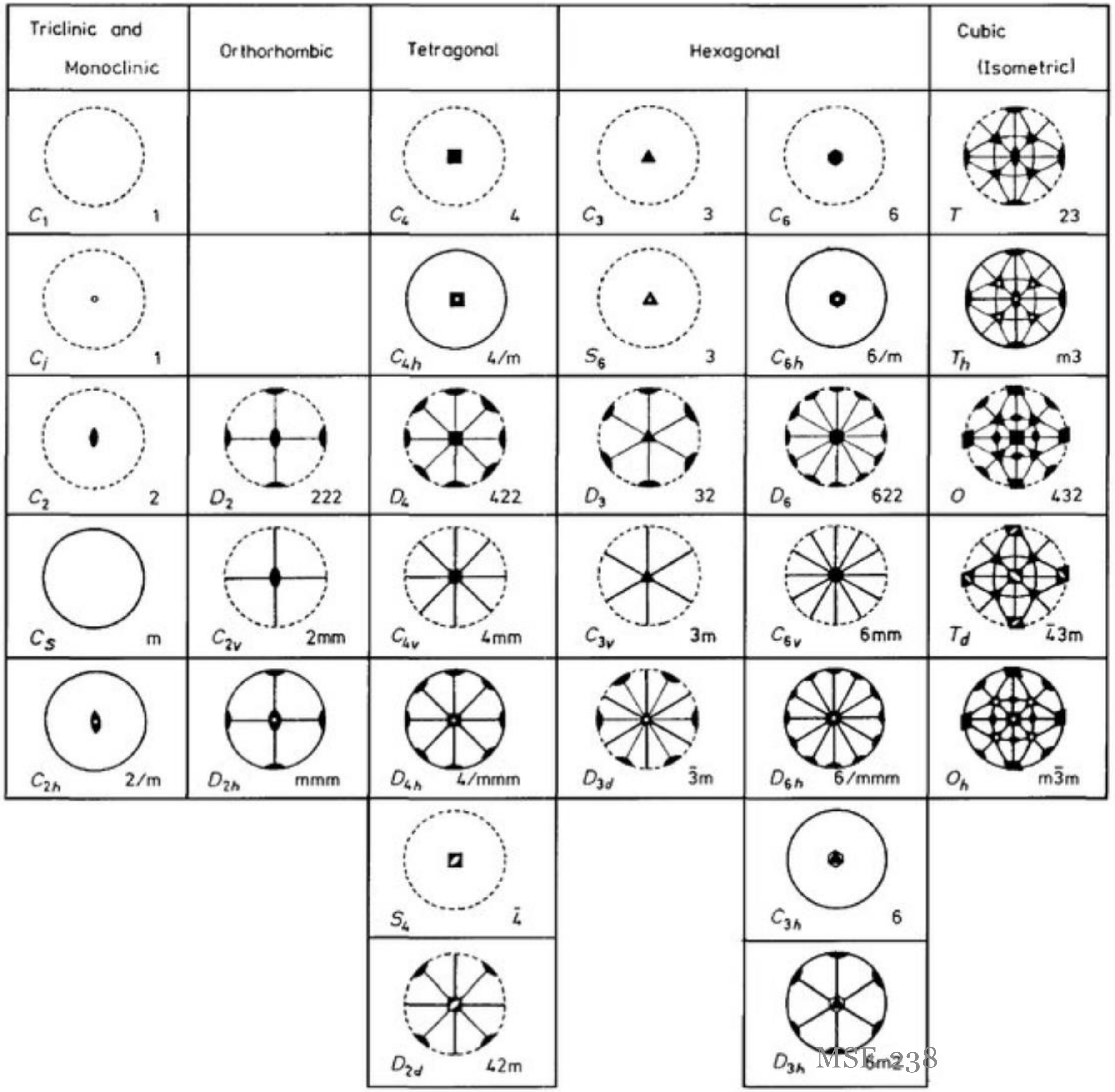


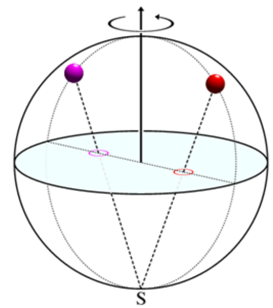
Symmetry operations

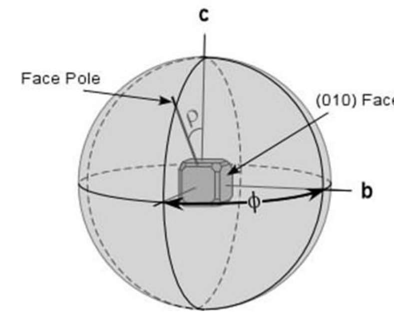
(1) 1	(2) 2 $0,0,z$	(3) 2 $0,y,0$	(4) 2 $x,0,0$
(5) 3^{+} x,x,x	(6) 3^{+} $\bar{x},x,\bar{x}$	(7) 3^{+} $x,\bar{x},\bar{x}$	(8) 3^{+} $\bar{x},\bar{x},x$
(9) 3^{-} x,x,x	(10) 3^{-} $x,\bar{x},\bar{x}$	(11) 3^{-} $\bar{x},\bar{x},x$	(12) 3^{-} $\bar{x},x,\bar{x}$
(13) 2 $x,x,0$	(14) 2 $x,\bar{x},0$	(15) 4^{-} $0,0,z$	(16) 4^{+} $0,0,z$
(17) 4^{-} $x,0,0$	(18) 2 $0,y,y$	(19) 2 $0,y,\bar{y}$	(20) 4^{+} $x,0,0$
(21) 4^{+} $0,y,0$	(22) 2 $x,0,x$	(23) 4^{-} $0,y,0$	(24) 2 $\bar{x},0,x$
(25) $\bar{1}$ $0,0,0$	(26) m $x,y,0$	(27) m $x,0,z$	(28) m $0,y,z$
(29) $\bar{3}^{+}$ x,x,x; $0,0,0$	(30) $\bar{3}^{+}$ $\bar{x},x,\bar{x}$; $0,0,0$	(31) $\bar{3}^{+}$ $x,\bar{x},\bar{x}$; $0,0,0$	(32) $\bar{3}^{+}$ $\bar{x},\bar{x},x$; $0,0,0$
(33) $\bar{3}^{-}$ x,x,x; $0,0,0$	(34) $\bar{3}^{-}$ $x,\bar{x},\bar{x}$; $0,0,0$	(35) $\bar{3}^{-}$ $\bar{x},\bar{x},x$; $0,0,0$	(36) $\bar{3}^{-}$ $\bar{x},x,\bar{x}$; $0,0,0$
(37) m $x,\bar{x},z$	(38) m x,x,z	(39) $\bar{4}^{-}$ $0,0,z$; $0,0,0$	(40) $\bar{4}^{+}$ $0,0,z$; $0,0,0$
(41) $\bar{4}^{-}$ $x,0,0$; $0,0,0$	(42) m $x,y,\bar{y}$	(43) m x,y,y	(44) $\bar{4}^{+}$ $x,0,0$; $0,0,0$
(45) $\bar{4}^{+}$ $0,y,0$; $0,0,0$	(46) m $\bar{x},y,x$	(47) $\bar{4}^{-}$ $0,y,0$; $0,0,0$	(48) m x,y,x

- The n-fold rotations have the coordinates of the rotation axis.
- The mirror symmetry (m) have the plane of symmetry indicated.
- presence of roto-inversion symmetries.
- symmetry elements which are the inverse (for example counter-clockwise 3 and 4 fold) which are there to close the group

32 Point groups in 3D







Combining point groups and lattice

Each point group must be associated to a certain Bravais Lattice (same as we looked at in 2D)
but all kind of new symmetries can come from merging a Motif in a Lattice

Crystal System	Lattice	Required symmetry	Point groups
Cubic	Cubic	3-fold axes along body diagonals	$23,\ m\bar{3},\ \bar{4}3m,\ 432,\ m\bar{3}m$
Tetragonal	Tetragonal	4-fold axis	$4,\ \bar{4},\ 4/m,\ 422,\ 4mm,\ \bar{4}m2,\ 4/mmm$
Hexagonal	Hexagonal	6-fold axis	$6,\ \bar{6},\ 6/m,\ 622,\ 6mm,\ \bar{6}m2,\ 6/mmm$
Trigonal	Hexagonal or Rhombohedral	3-fold axis	$3,\ \bar{3},\ 32,\ 3m,\ \bar{3}m$
Orthorhombic	Orthorhombic	Three mutually perpendicular 2-fold axes or mirror planes	$222,\ 2mm,\ mmm$
Monoclinic	Monoclinic	2-fold axis or mirror plane	$2,\ m,\ 2/m$
Triclinic	Triclinic	none	$1,\ \bar{1}$

Plane groups in 2D → space groups in 3D

- Plane/Space groups are mathematical constructs that capture every way an object can be repeated through space, through translation (→lattice) and the symmetry operations: rotation, reflection, gliding (and screws in 3D).
- Point groups are mathematical constructs that capture all the non-translation symmetry options that can be performed on an object (reflection, rotation, rotoinversion)
- translational symmetry elements need to be added glide lines in 2D and glide planes and screw axes in 3D

in 2D
combine 5 plane lattice with 10 point groups
→ 17 plane groups

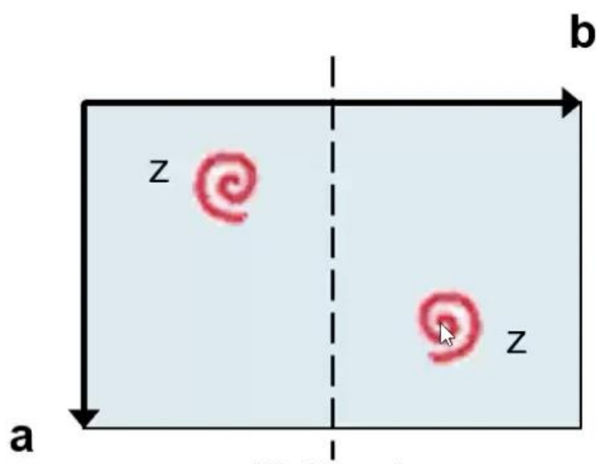
and in 3D
combine 14 Bravais lattice with 32 point groups
→ 230 space groups

(pure combination would give more, but many combinations end up being duplicates

Travel symmetry operations

Glide plane:

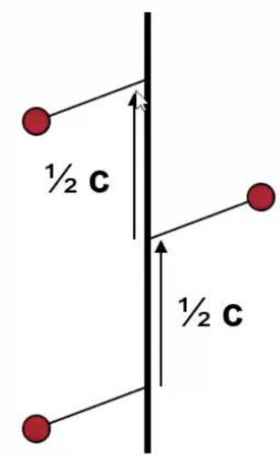
Reflect through a plane then translate parallel to it



a glide plane
translate by ½ **a**

Screw axis

Rotation by 360/N around an axis and translation along the axis



2_1 screw axis
Rotate by 180°
Translate by ½ **c**

230 space groups in 3D

- The construction of the space groups associated to the 3D 14 Bravais lattices, from the 32 3D point groups, proceed similarly than in 2D, but:
  - 3D has 32 point groups and not 10, because of extra possible symmetry operations: inversion and roto-inversion.
  - For glide planes, the glide can happens along different directions in 3D;
  - Screw axis operations also occur: n_m is a n-fold rotation followed by a translation

- The first letter is a capital letter indicating the Bravais lattice, and many different types occur: P, I, F, C

- Glides bring several new types of symmetries and notations:
  - a,b,c: glide translation along half the lattice vector of this face;
  - N,d: glide translation along half and a quarter respectively, along the face diagonal
  - e: two glides with the same glide plane and translation along two half-lattice vectors.

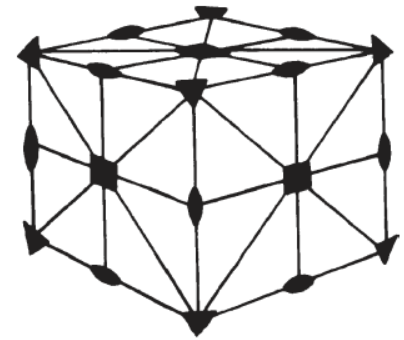
- There are 230 space groups that can be built from the 32 point group in 3D.

- A list of all the space groups can be found here: https://en.wikipedia.org/wiki/List_of_space_groups

- A more concise one: https://en.wikipedia.org/wiki/Space_group

- You can find them all here: https://onlinelibrary.wiley.com/iucr/itc/Ac/contents/

Symmetry in 3D: Space groups



Examples:

- Triclinic: no symmetry possible, only 1 and $\bar{1}$;

- Space group of the cube: $P4/m\bar{3}2/m$ (#221);
  first place in the symbol refers to the axes parallel to, or planes of
  to, the x-, y- and z-axes, the second refers to the four triads or inversion triads and the third
  to the axes parallel to, or planes of symmetry perpendicular to, the face diagonal directions.
  Hence the point group symbol for the cube is $4/\bar{3}\,2/m$, short form $m\bar{3}m$ because the
  operation of the four triads and nine mirror planes (three parallel to the cube faces and six
  parallel to the face diagonals) ‘automatically’ generates the three tetrads, six diads, and a
  centre of symmetry.

Important: for all crystals with one atom per motif, the space group corresponds to the point group of the conventional cell geometry

The **order of a space group** refers to the number of **symmetry operations** it contains.

Symmetry in 3D: Space groups

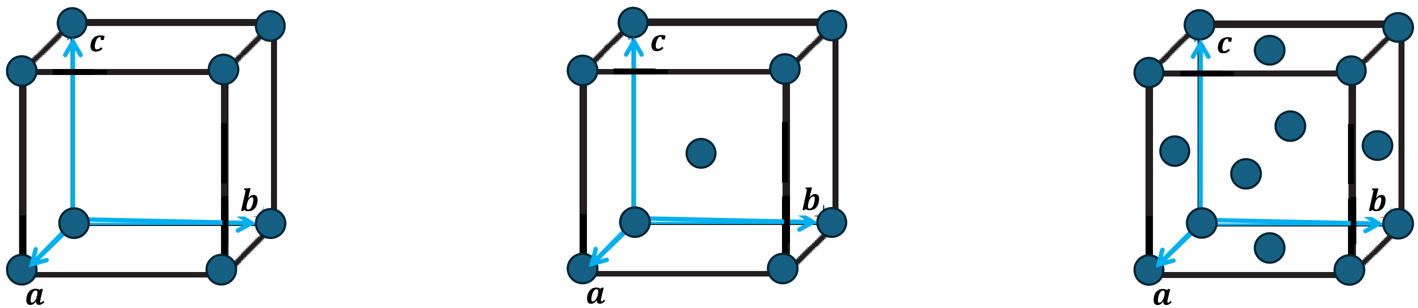
- You don't need to know:
  - All the notations;
  - All the diagrams to represent symmetries;
  - All the point groups and space groups.
  - You will not be asked to recognize the point group of a molecule or the full space group of a given structure, without explicit help on the notations and in simple cases.
  - You will not be asked to draw symmetry diagrams.

- You will be asked to:
  - Know the basics we reviewed on space groups and how they are constructed;
  - Recognize rotational, inversion, mirror or roto-inversion symmetries in a given structure;
  - after next week: Give the Miller indices of a plane symmetry or a rotational axis, or other symmetry elements.

Symmetry in 3D: Space groups

Important to understand:
For all crystals with one atom per motif, the space group corresponds to the point group of the conventional cell geometry.

- The atom being considered spherical, it conserves all other symmetries;



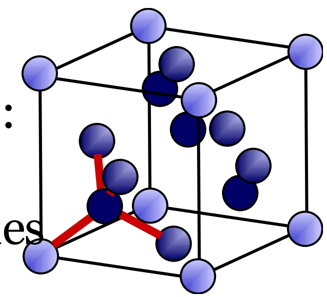
- For the cubic Bravais Lattice, the BCC and FCC structures add atoms that do not change the symmetry operations !
- Space groups are then $P4/m\bar{3}2/m$, I$4/m\bar{3}2/m$ and F$4/m\bar{3}2/m$ respectively.

Symmetry in 3D: Space groups

- For the cubic Bravais Lattice, the BCC and FCC structures add atoms that do not change the symmetry operations !
- Space groups are then $P4/m\bar{3}2/m$, I$4/m\bar{3}2/m$ and F$4/m\bar{3}2/m$ respectively.
    - Example: let's look at F$4/m\bar{3}2/m$ (#225)

for example Aluminium

- What happens when we change the motif ? Diamond structure:



  - The extra atom in this case changes the possible symmetries
  - Space group: Fd$\bar{3}m$ (#227): → a glide symmetry.
  - still highly symmetric, order of the group 48

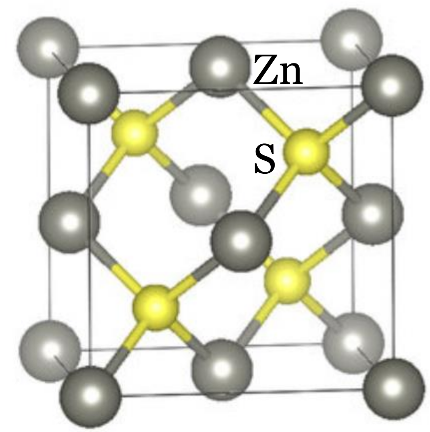
As the motif looses symmetry, the symmetry of the resulting crystal tends to be lower.

Symmetry in 3D: Space groups

What happens when we add atoms of different nature ?

- Diamond structure becomes Zincblende when considering two different atoms

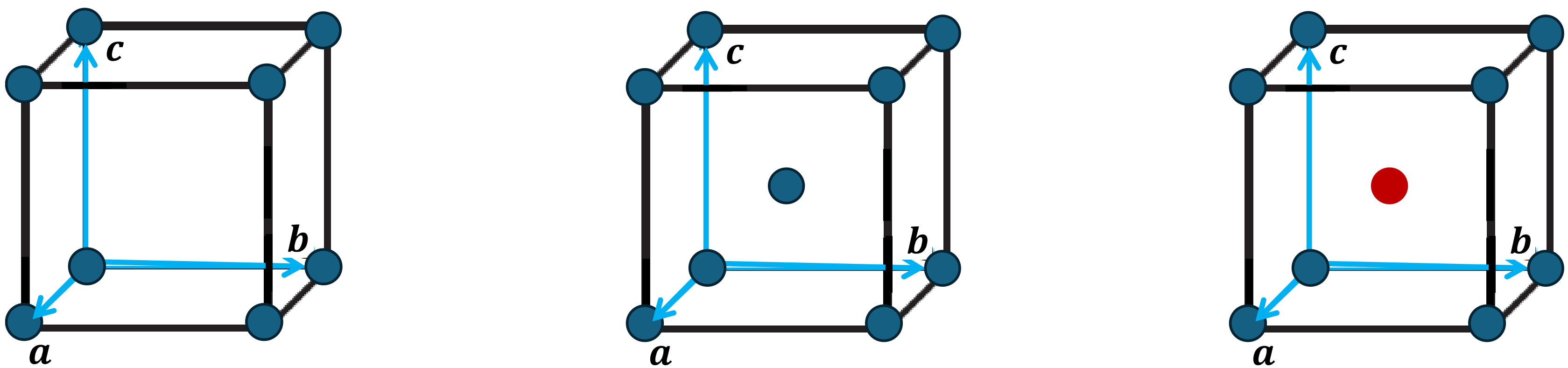
- Example: ZnS
- Space group $F\bar{4}3m$ (#216): less symmetries. Order of the group 24
- No more glide symmetry since the two atoms are of different nature



When adding atoms of different nature, the symmetry also tends to get lower.

Symmetry in 3D: Space groups

Adding a different atom to the motif



- What are the crystal structure ? Motif ?
- Do all the symmetry of the cube leave the center of the cube invariant ?
- The space group of simple cubic is $P4/m\bar{3}2/m$. What do you expect the space group of the BCC to be ?

- Different atom at the center: would you expect CsCl for example, to have the same symmetry as primitive cubic or BCC ?
- Is the space group of CsCl $P4/m\bar{3}2/m$ or $I4/m\bar{3}2/m$?

crystal symmetry and properties

- cubic crystals are isotropic towards many properties like electrical conductivity, but elastic properties are still direction dependent
- piezoelectricity, i.e. development of an electric dipole when a crystal is stressed → crystal cannot have a centro symmetry (see table slide 39) to develop opposite charges at opposite ends of a line through its center
- optical properties
    - cubic: isotropic
    - tetragonal, hexagonal, trigonal: uniaxial birefringent with the optical axis the principal symmetry axis
    - orthorhombic, monoclinic, triclinic: 3 refractive indices, bi-axial optical axis
    - rotatory polarization (chirality) in enantiomeric point groups

Summary

- looked translational symmetry and the Bravais lattice in 2D and 3D
- looked at point symmetry operations in 2D and 3D
- discussed limitations of translational symmetry on point symmetry operations and quasi crystals
- discussed how plane and space groups are built up
- discussed the point group of the cube
- examples of space groups and the effect of adding more atoms to the motif or atoms of different nature