Level 2
Solid State Lectures

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Physics Building 01.020

Open door policy, available by email and Teams.
Reply within 1 working day.

Office hours from 9 am – 4.30 pm.

Please submit your attendance at:

https://go.qub.ac.uk/mpattendance

Or Scan the QR code below with a mobile device by:
Open the camera app on your device
Point the camera towards the QR code
Login with your QUB credentials

If attending On Campus, please specify a location and room number

Course structure:

1. Crystallography, weeks 1-3 (Miryam Arredondo):
Periodicity and symmetry, basic crystallographic definitions, packing of atomic planes, crystal structures, the reciprocal lattice, diffraction from crystals, Bragg condition and Ewald sphere.

2. Phase transitions, weeks 4-6 (Marty Gregg):
Concepts related to phase transitions in materials such as: free energy, enthalpy, entropy, order parameter, classification of phase transitions, Landau theory.

3. Thermal properties, weeks 7-9 (Marty Gregg):
Lattice waves and dispersion relations, phonons, Brillouin zones, heat capacity, density of vibrational states, Einstein and Debye models of heat capacity, thermal conductivity and anharmonicity.

4. Electrical properties, weeks 10-12 (Ray McQuaid):
Metals, insulators and semiconductors, Fermi energy and density of electron states, energy bands, intrinsic and extrinsic semiconductors, donors and acceptors, carrier transport properties, p-n junction

Crystallography breakdown

1-3 Crystal structure definitions, common crystal structures and structure plans

4-5 Symmetry, point groups

6-8 Diffraction and reciprocal space +TEQs

- Assignment 1 : topics 1 + 2, deadline: **Feb 18th**.

- Your assignment scores contribute 10% of the module's final mark

Sources

Core Books:

1. “Introduction to Mineral Sciences” – A. Putnis, Cambridge University Press
2. “Physical Properties of Crystals” – J. F. Nye
3. “Essentials of Crystallography” – McKie & McKie, Blackwell Scientific
4. “Crystallography and Crystal Defects” – A. Kelly and K. M. Knowles. 2nd Edition. Wiley.

Links of interest:

- University of Cambridge DoItPoMS
- The Royal Institution
- MIT lectures: Symmetry, Structure, & Tensor Properties of Materials by Prof. B. Wuensch)
- Chemistry LibreTexts: Lattice Structures in Crystalline Solids

Also from the library:

- “Space groups for solid state scientists” – M. Glazer & G. Burns [electronic resource]

Review lectures

- Jan 28th 1 - 2 pm

- Feb 4th, 1 – 2 pm

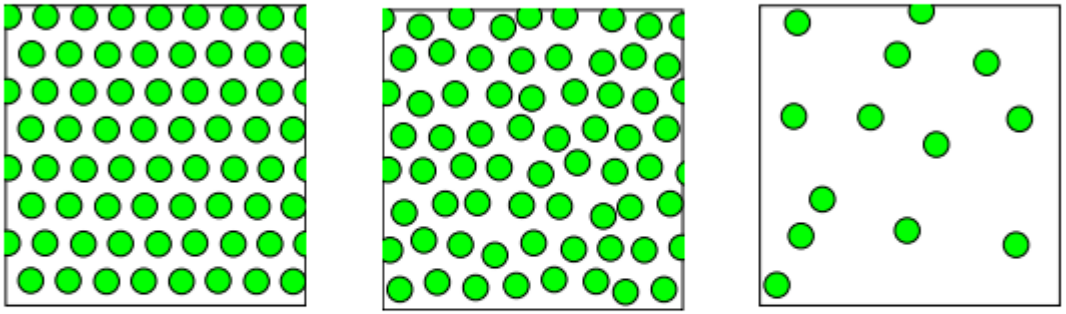
* Not compulsory

Introduction

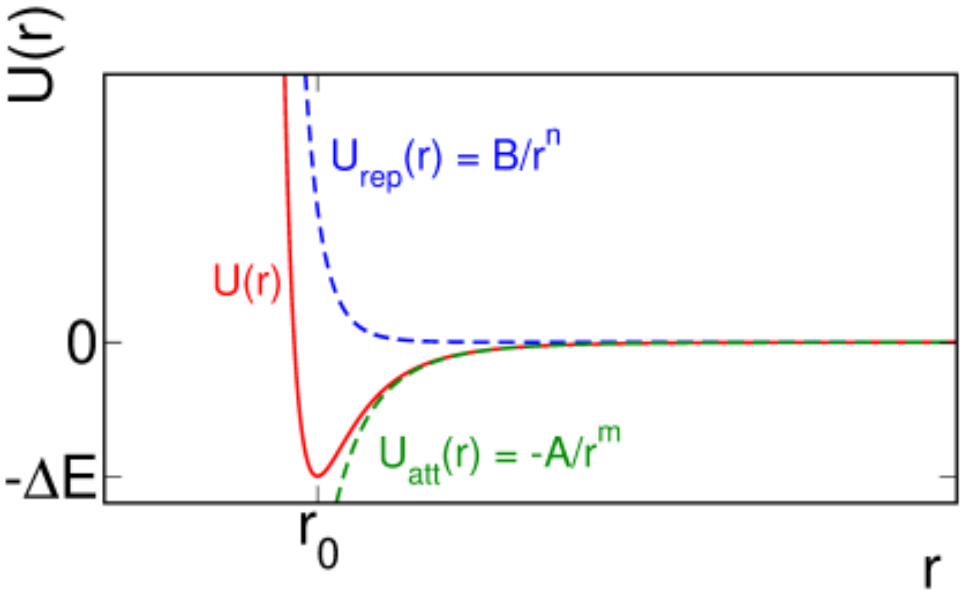
PHY1001
Solid state physics
lecture Notes

What are the characteristics of a **solid**?

Low T ⟶ High T

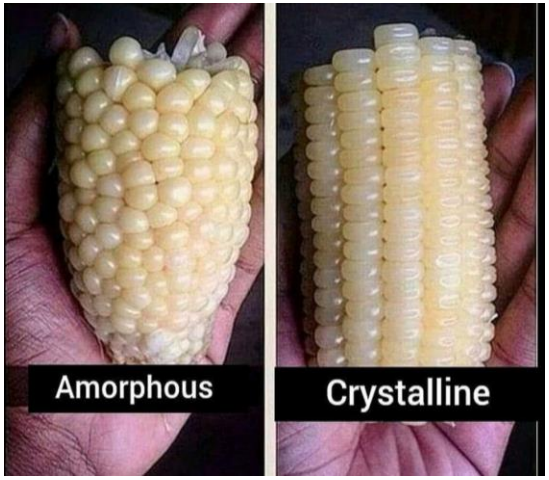


Solid	Liquid	Gas
Order	Some disorder	Disorder
$A \simeq U$	$A = U - TS$	$A \simeq -TS$
Energy		Entropy

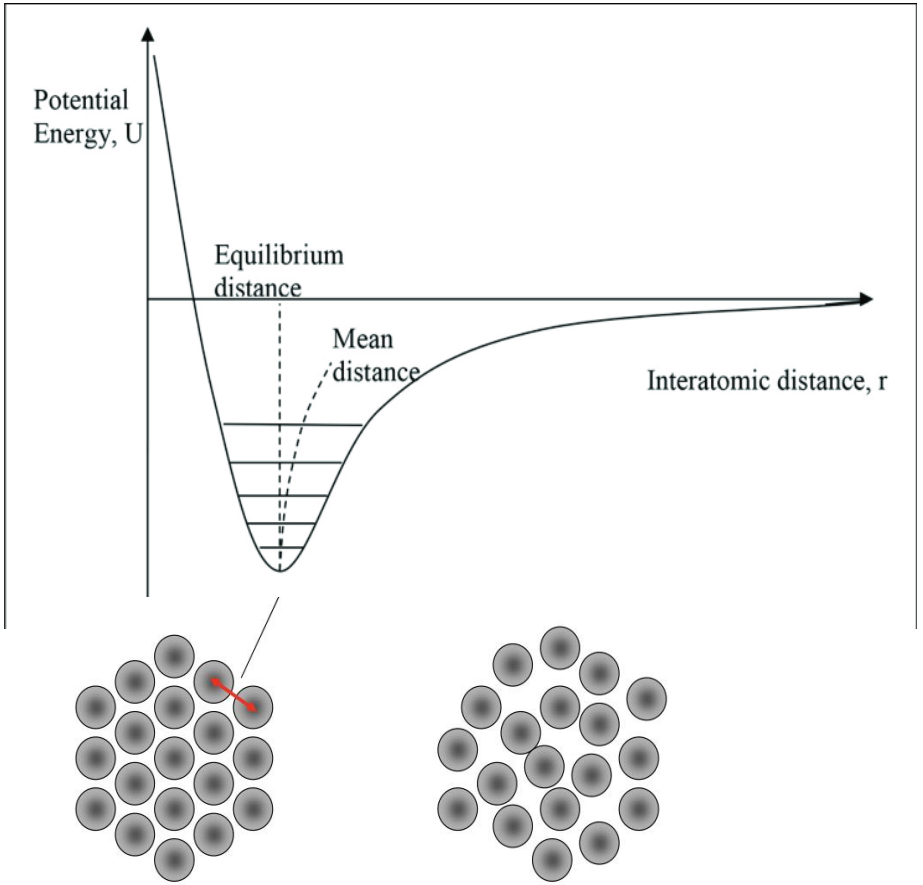


- Interatomic Potential energy
- Bonding

Introduction



A *solid* is a *regular* arrangement of atoms or molecules in a *3D array:*
Crystal



Energy of the Crystal< Energy of the amorphous solid

Learning Objectives:

- To understand how crystals are defined, the symmetry elements present and how to represent a crystal.

- To recognize the importance and relationship between crystals and *diffraction*.

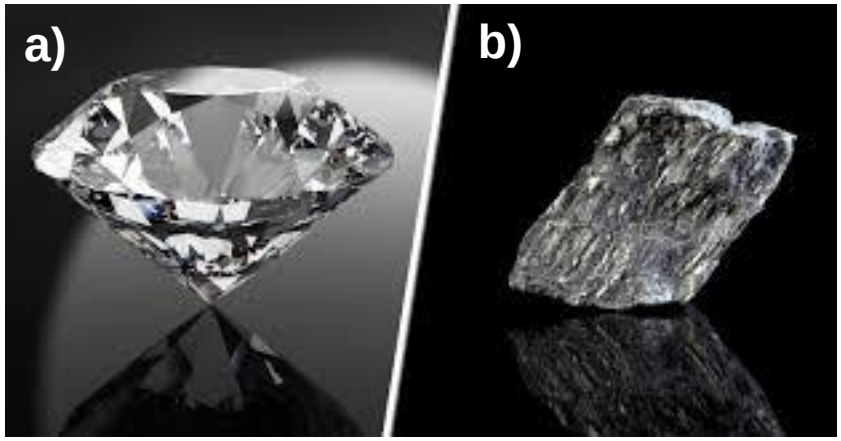
- **Crystallography:** A branch of science that studies the shapes and structures of crystalline solids (crystals).
- **Crystalline solid:** a solid with a regular, repeating internal structure of atoms, ions and/or molecules.

*"**Crystallography** has dramatically advanced our ability to understand the fine detail of materials and plays a key role in finding new, cleaner energy solutions, and even ways to combat the growing problem of environmental pollution and climate change"*

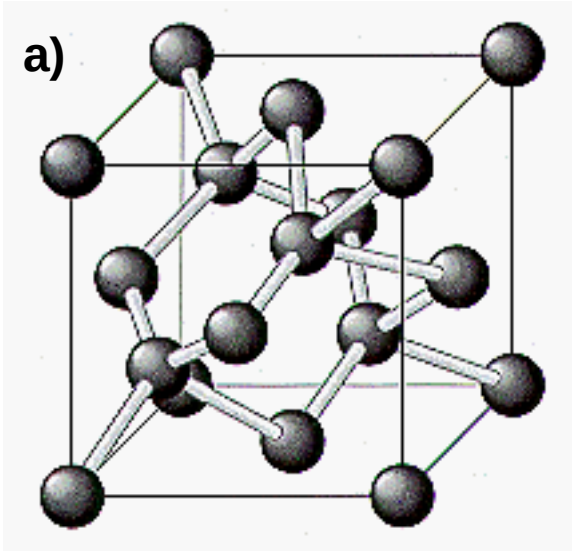
The properties are a consequence of the crystal structure

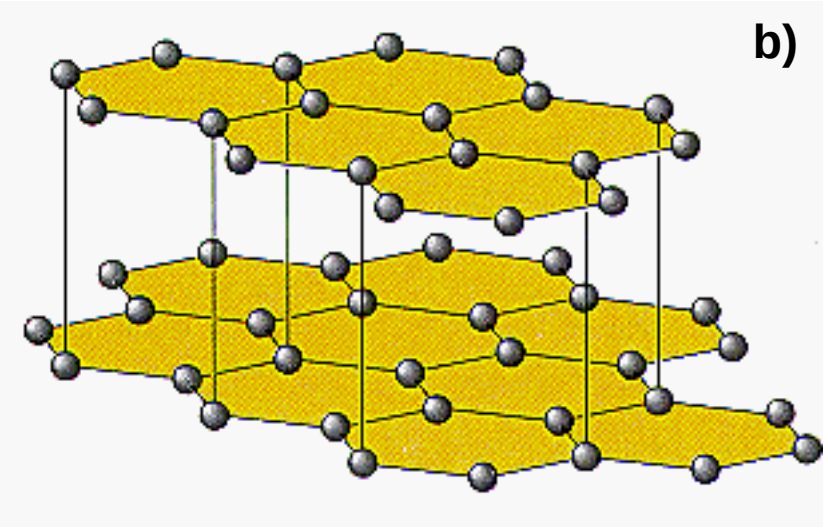
Differences?

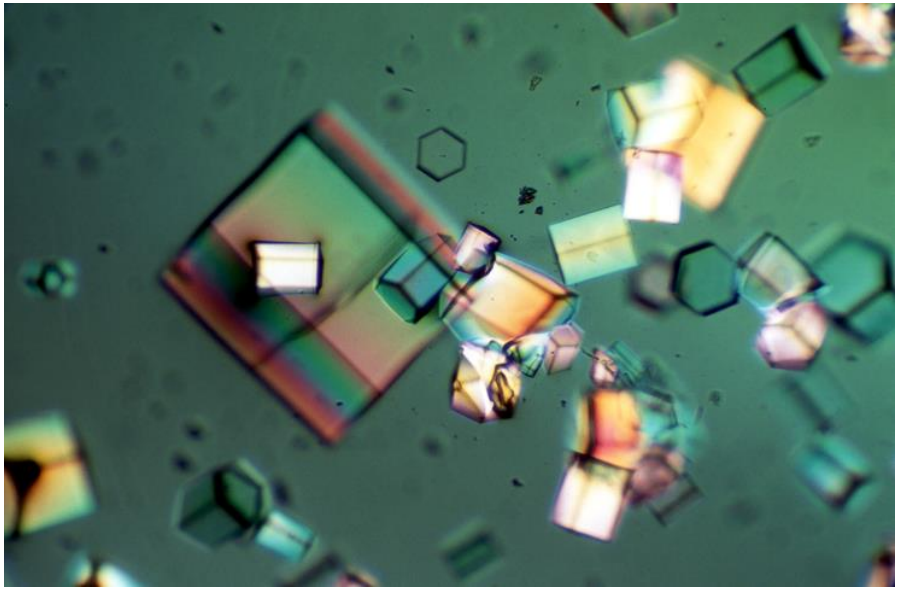
Properties?



Diamond vs Graphite







Why is Crystallography important?

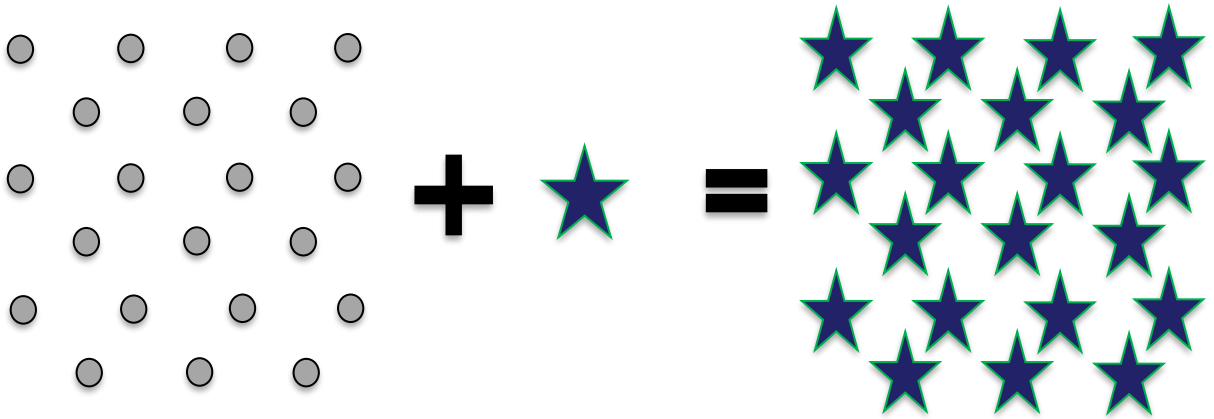
1. Establishes a f**ramework to understand much of solid state physics**: thermal physics, phonons, electronic structure & semiconductors.

2. Furthers the **understanding and prediction of properties**: **Neumann's Principle**: *Any* physical property displayed by a crystal adheres to the symmetry of that crystal.

3. **Determine crystal structure**: Diffraction by a crystal can be used to determine structure of complex molecules if formed into crystalline array: DNA, nucleic acids, etc.

Formal Definitions

CRYSTAL: It is an arrangement of matter (atoms, ions or molecules), that repeat periodically in three dimensions. These constituents are held together by interatomic forces (bonds). *It is a convolution of lattice with motif:*

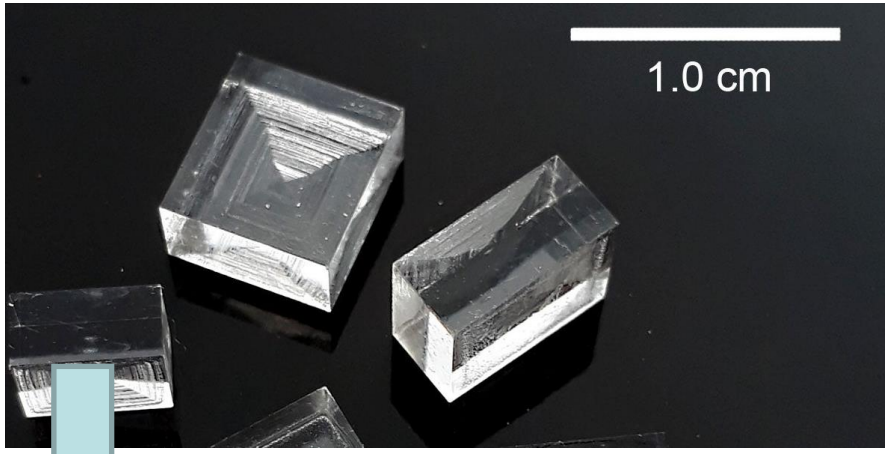


Lattice **Motif** **Crystal Structure**

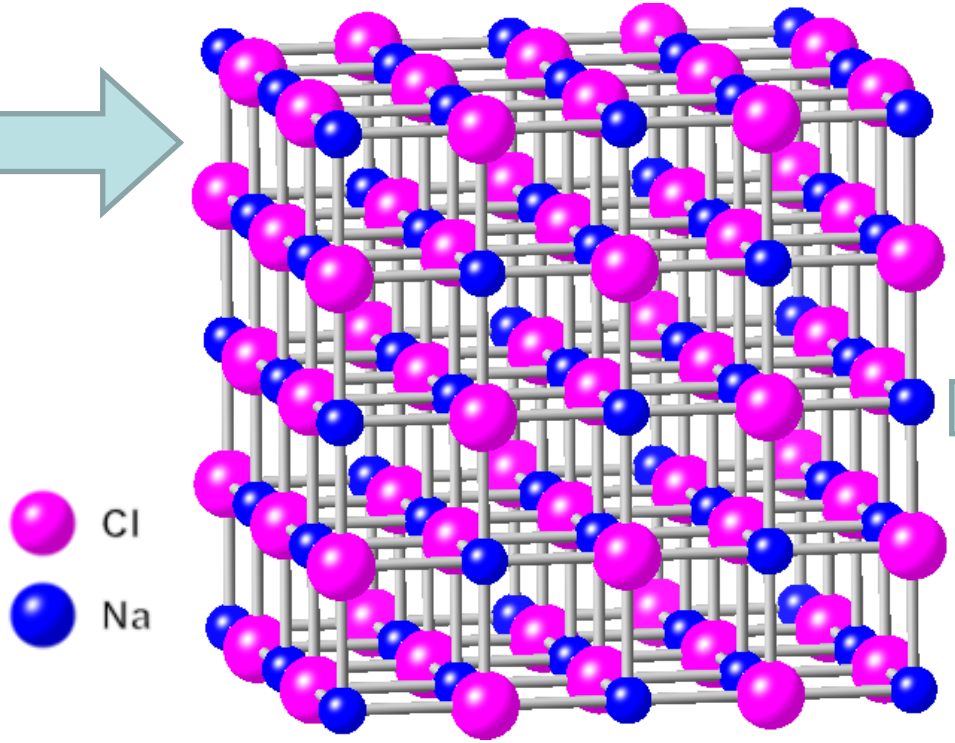
- **Lattice**: An infinite array of points (*lattice points*) repeated periodically throughout space. The environment of each lattice point is identical to and indistinguishable from all others. These points may coincide with atom positions.

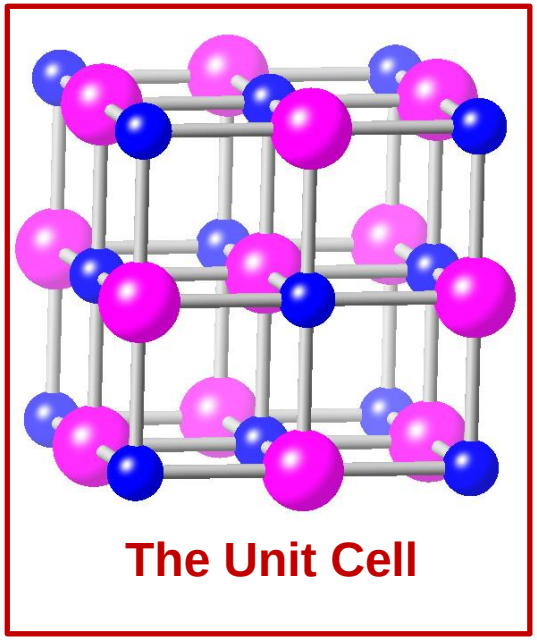
- **Motif:** Element of structure (i.e. atoms, ions) associated with each lattice point such that the complete crystal structure is produced by adding the motif to each lattice point.

Formal Definitions



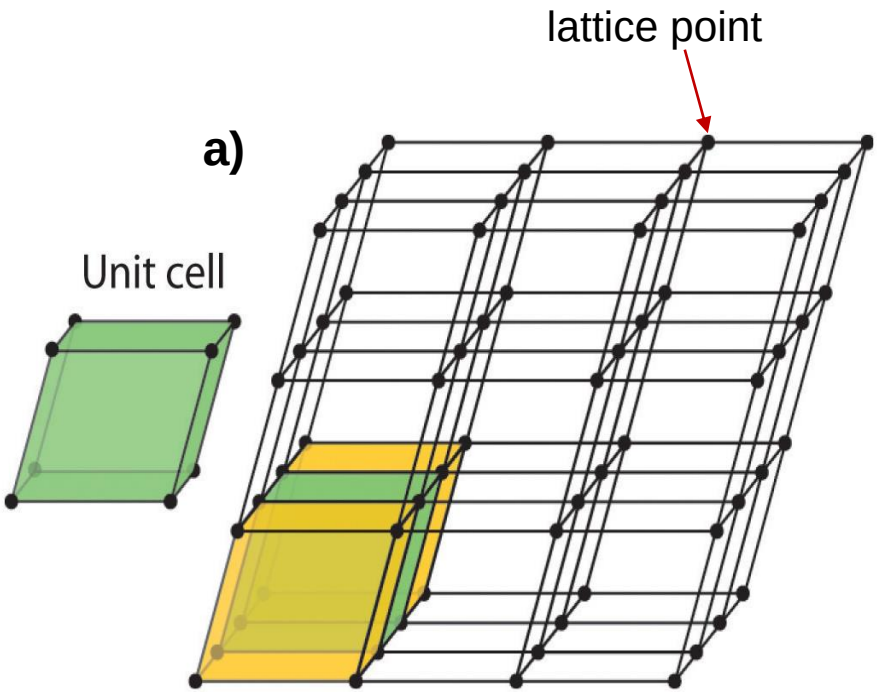
Crystal: A solid with a highly regular, repeating internal structure of atoms, ions & molecules.



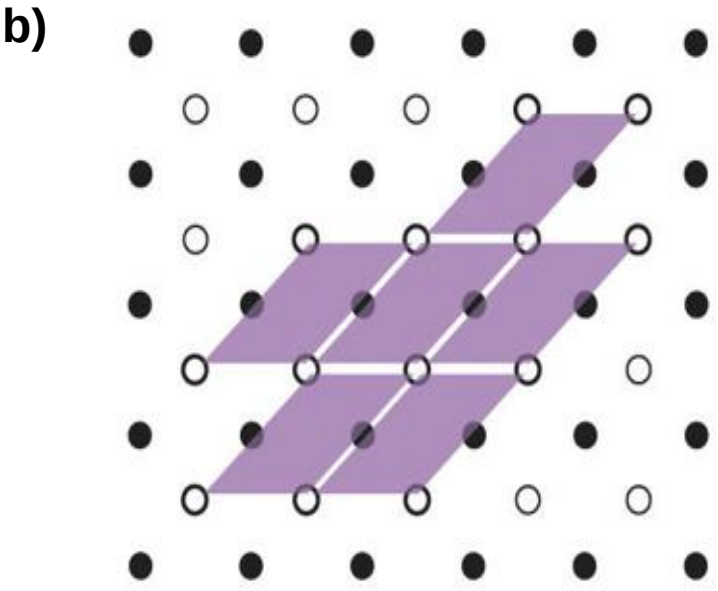


The Unit Cell

The structure of a *perfect* crystal can be seen as **a repetition of *identical units* across all space.** Thus, to study the crystal structure as a whole it is useful to consider the building block: **the *unit cell.***



3D - parallepiped shapes



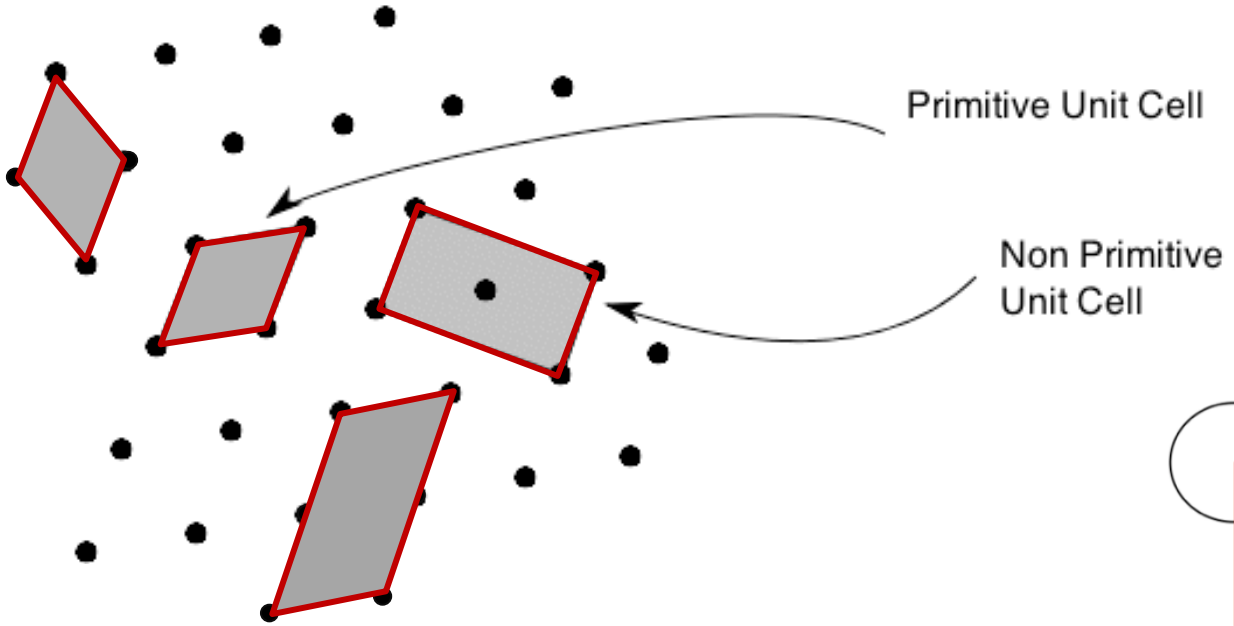
2D - parallelogram

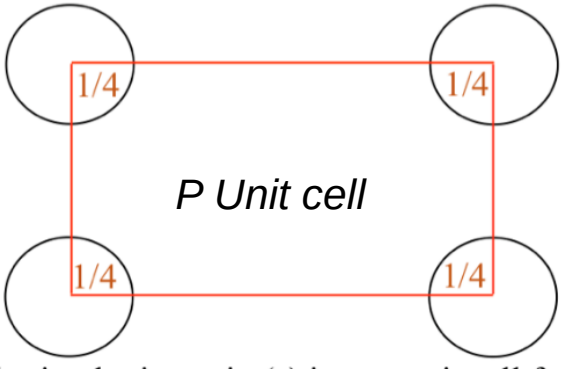
Types of unit cell

The **unit cell** is the most basic (smallest) unit that defines the full crystal structure and also reflects its symmetry. There are two types of unit cell:

a) ***Primitive*:** Contains only one lattice point per unit cell, and are labelled P.

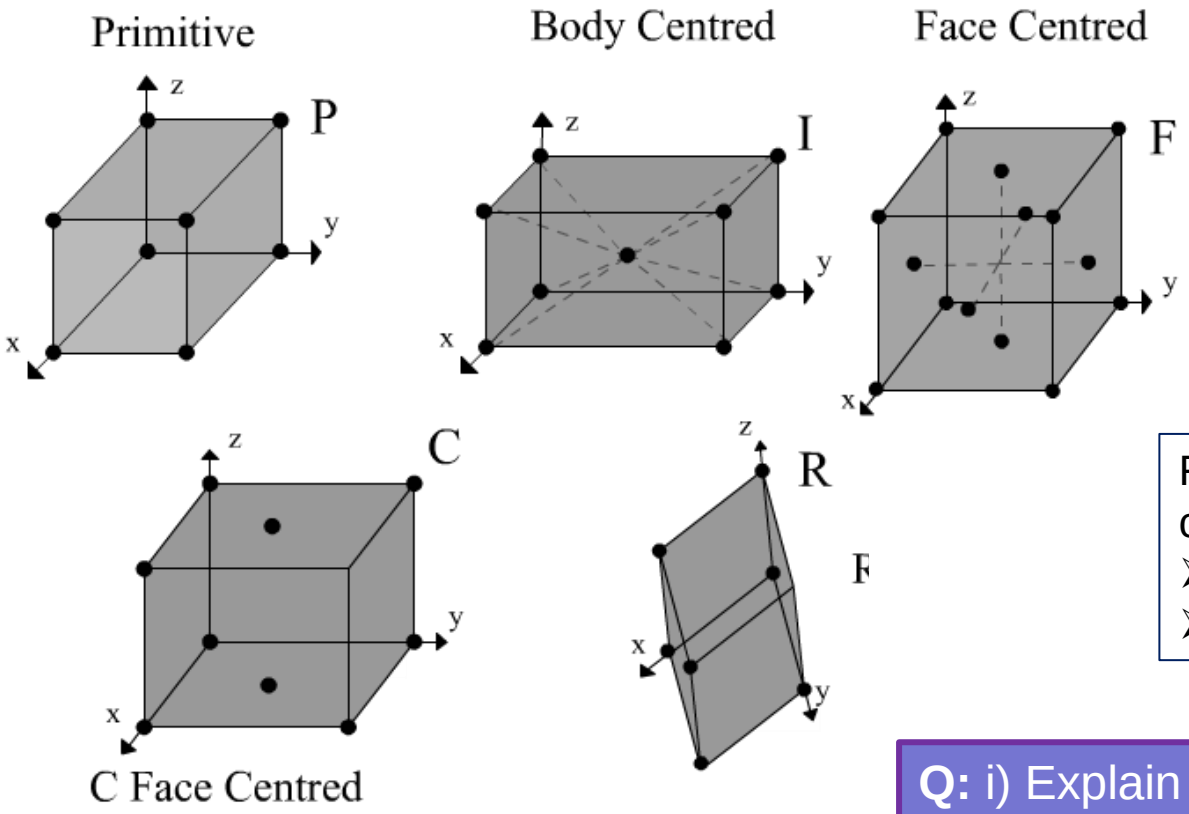
b) ***Non-primitive*:** Contains more than one lattice points per unit cell.





Non-primitive unit cells

- **Face centred (F):** A lattice point at the centre of each face of the cell
- **Centred (A, B, or C):** A lattice point at the centre of opposite faces of the cell**.**
- **Body centred (I): A** lattice point at each centroid of the cell

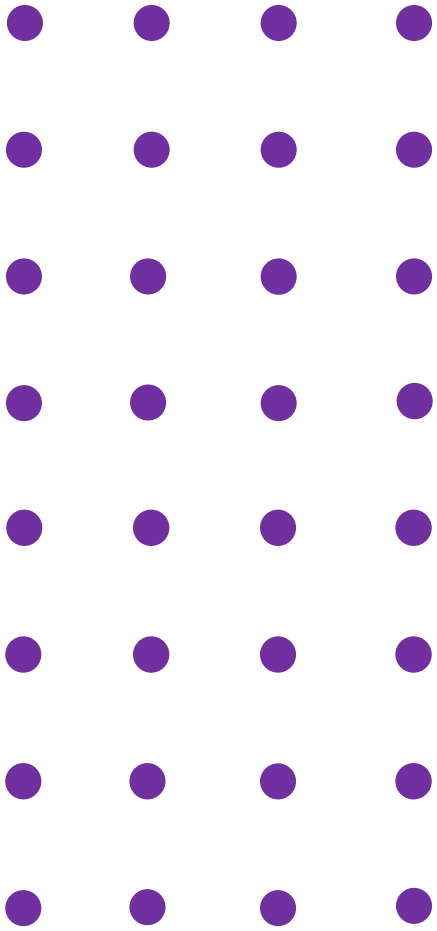


For cubic unit cells, these are called:

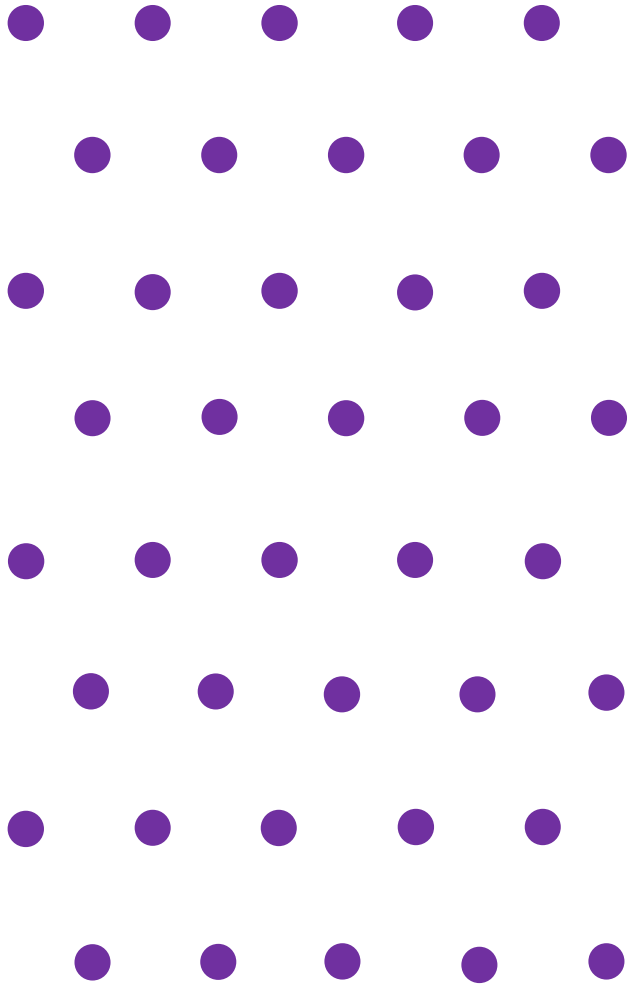
- **BCC** – body centred cubic
- **FCC –** Face centred cubic

Q: i) Explain the difference between a primitive and a non-primitive unit cell, and ii) clearly prove that a triangle is not suitable as a unit cell in a crystal lattice.

Unit Cell in 2D examples

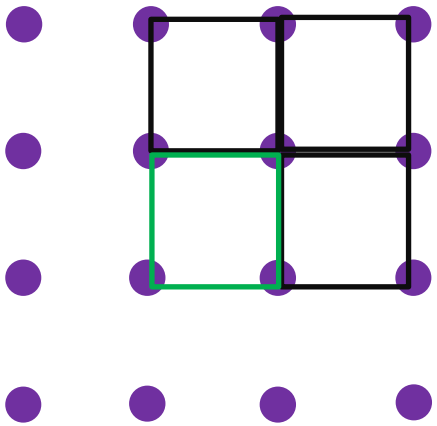


Lattice type 1



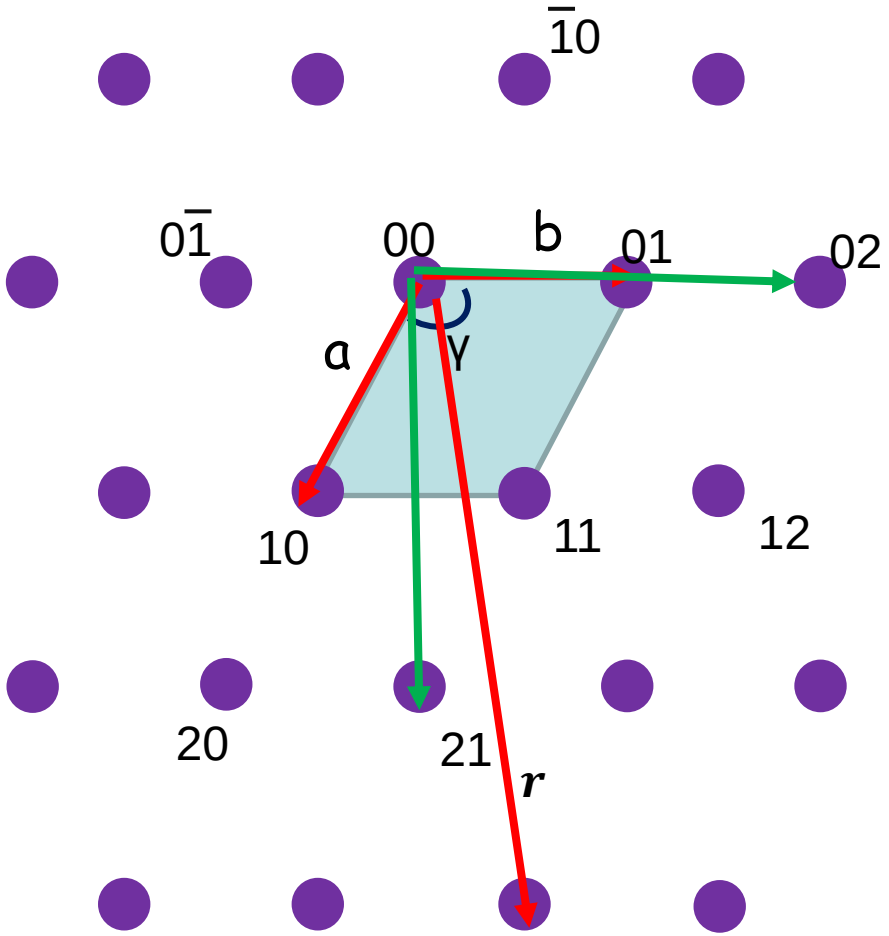
Lattice type 2

The Unit Cell : Why not a triangle?



The unit cell should be the smallest unit that reflects the *symmetry* of the full structure.

Lattice points in a 2D Lattice



- In 2D, lattice points can be identified by *indices: P(u, v)*.

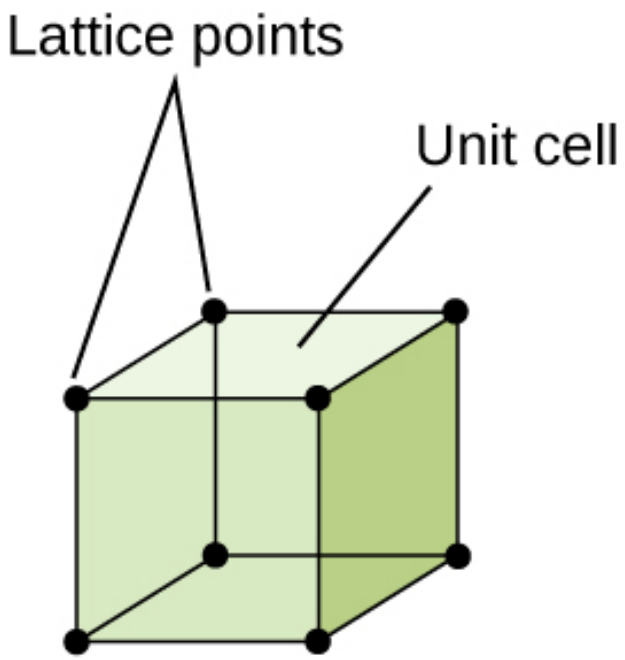
- All lattice points can be reached by a primitive translation lattice vector:

$$\boldsymbol{t}_n = n_1\boldsymbol{a} + n_2\,\boldsymbol{b}$$

- A direction in a crystal is given by:

$$\boldsymbol{r} = u\boldsymbol{a} + v\boldsymbol{b}$$

Lattice points in 3D



Every lattice point is uniquely defined with respect to the origin of the lattice.

$$P(u,v,w) = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$$

a, **b**, and **c** are the basis vectors and **u, v** and **w** are positive or negative integers or rational numbers.

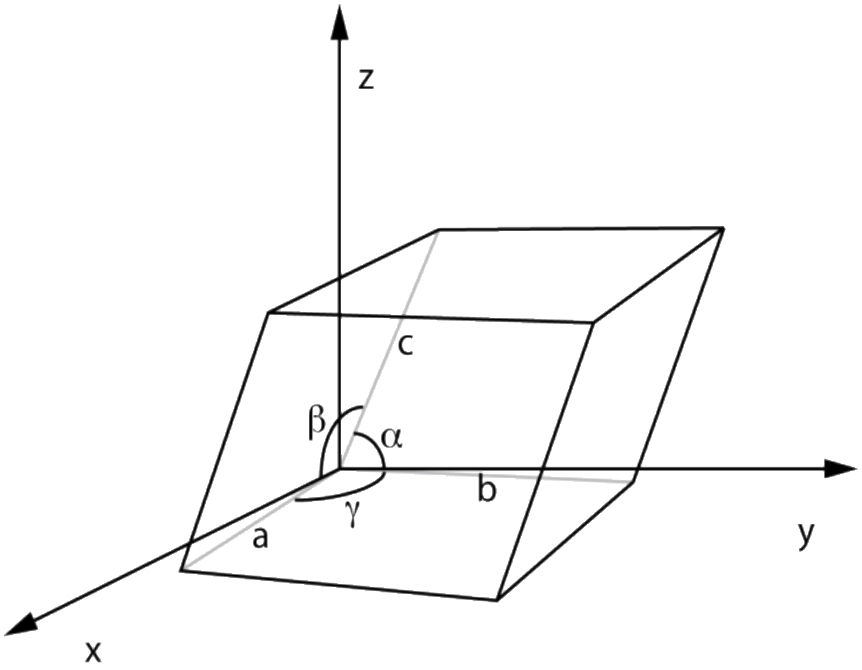
Negative directions are denoted with a bar on top on the number. For example: $\bar{1}$.

Primitive translation lattice vector:

$$t_n = n_1 a + n_2 b + n_3 c$$

https://opentextbc.ca/chemistry/chapter/10-6-lattice-structures-in-crystalline-solids/

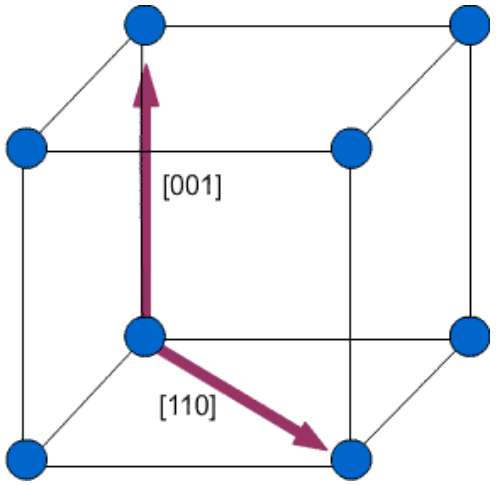
Unit Cells Parameters



Length of lattice vectors	Lattice angles
$\lvert\vec{a}\rvert = a_0$	$\vec{a} \wedge \vec{b} = \gamma$
$\lvert\vec{b}\rvert = b_0$	$\vec{a} \wedge \vec{c} = \beta$
$\lvert\vec{c}\rvert = c_0$	$\vec{b} \wedge \vec{c} = \alpha$

- The edges of the *unit cell* are bound by the lattice vectors of the crystal, given as *a, b, and c*.
- The angles between lattice vectors are given as *α, β and γ*.
- These vectors and angles are known as the ***lattice parameters.***
- The *translation* of these vectors will produce the entire lattice.

Lattice planes and directions (Miller Indices)



- ***Direction [uvw].*** *V*ectors (**r**) that connect 2 lattice points, can be written as:

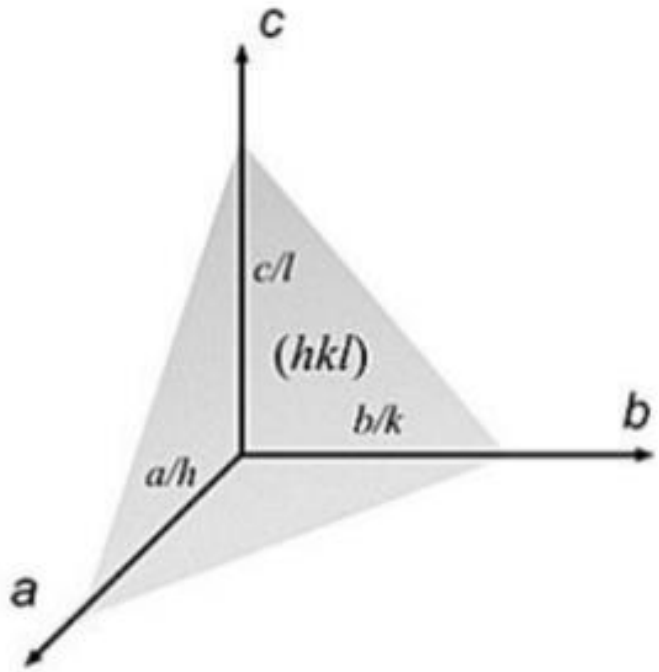
$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

In most cubic materials [001], [010] and [100] are equivalent vectors, related by symmetry. These 3 vectors may then be written as <100> (a family of directions).

Example

- **Planes (hkl).** Planes intersect the lattice vectors at: a/h, b/k and c/l.
  e.g. in most cubic materials (001), (010), (100), $(00\bar{1})$, $(0\bar{1}0)$ and $(\bar{1}\,00)$ are equivalent planes all related by symmetry. These three planes may then be written as {100} (a family of planes).

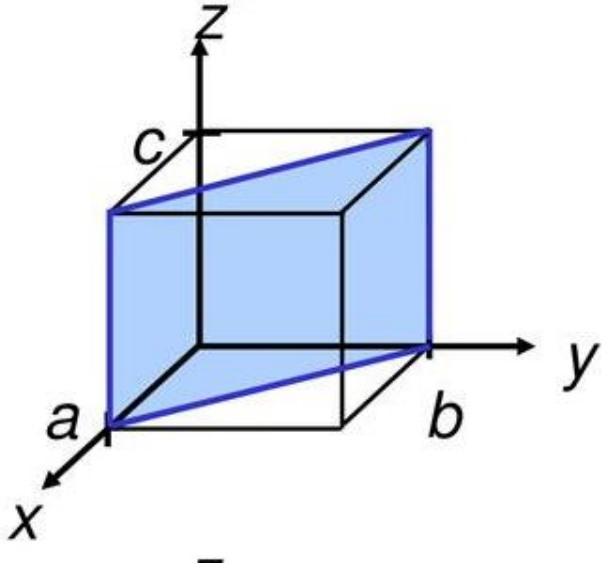
The number of different planes contained within a group is called *multiplicity*. For example, the multiplicity of {100} in most cubic systems is 6, and 8 for {111}.



Q: Using a conventional cubic crystal, with designated general axes and lattice vectors, sketch the following planes and directions: (hkl), {hkl}, [uvw] or <uvw>

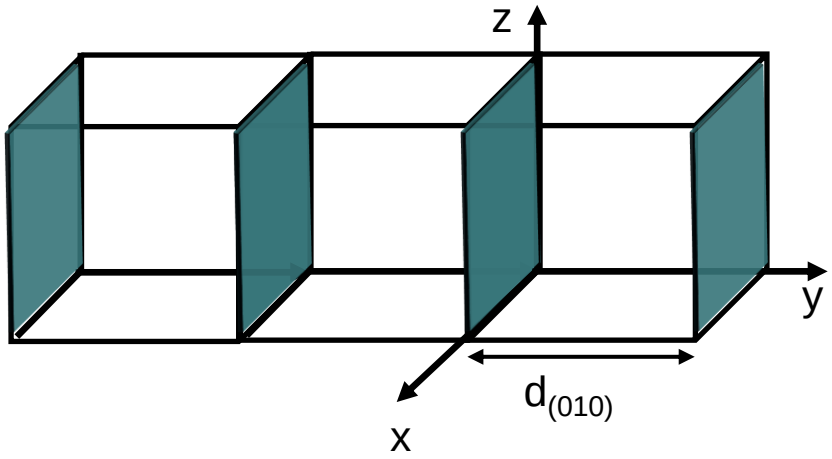
Crystallographic Planes

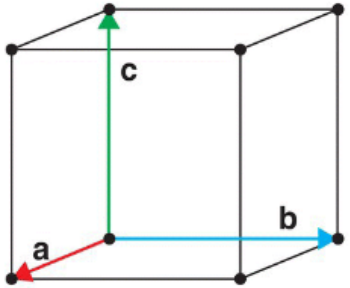
example		*a*	*b*	*c*
1.	Intercepts	1	1	∞
2.	Reciprocals	1/1	1/1	1/∞
		1	1	0
3.	Reduction	1	1	0
4.	Miller Indices	(110)		



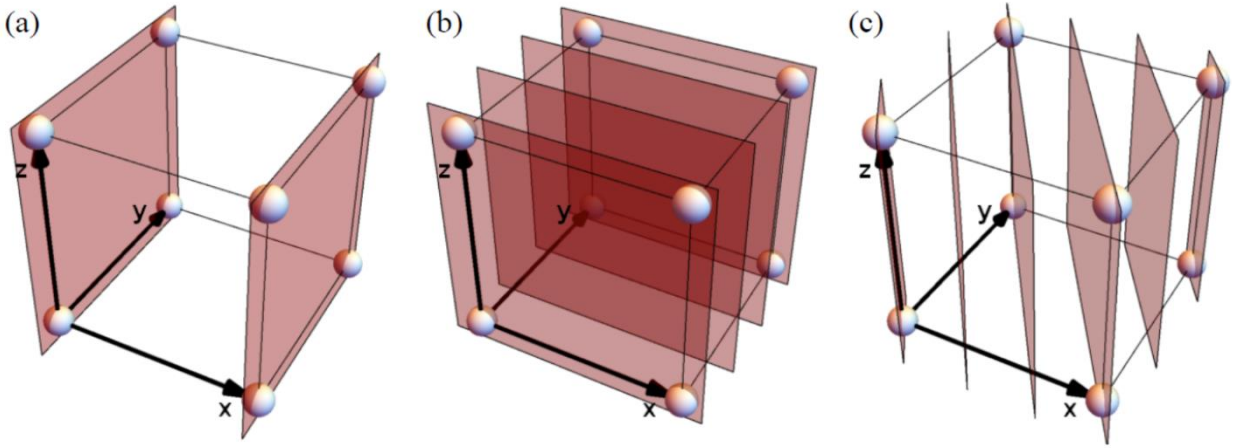
Examples: Identification of crystallographic directions and planes

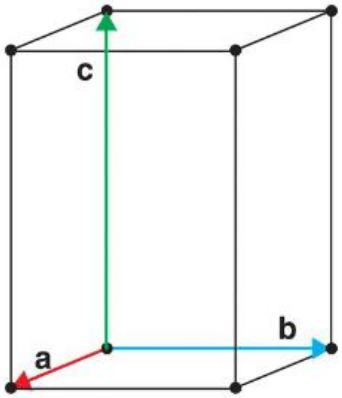
Interplanar spacing (d_{hkl})





$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

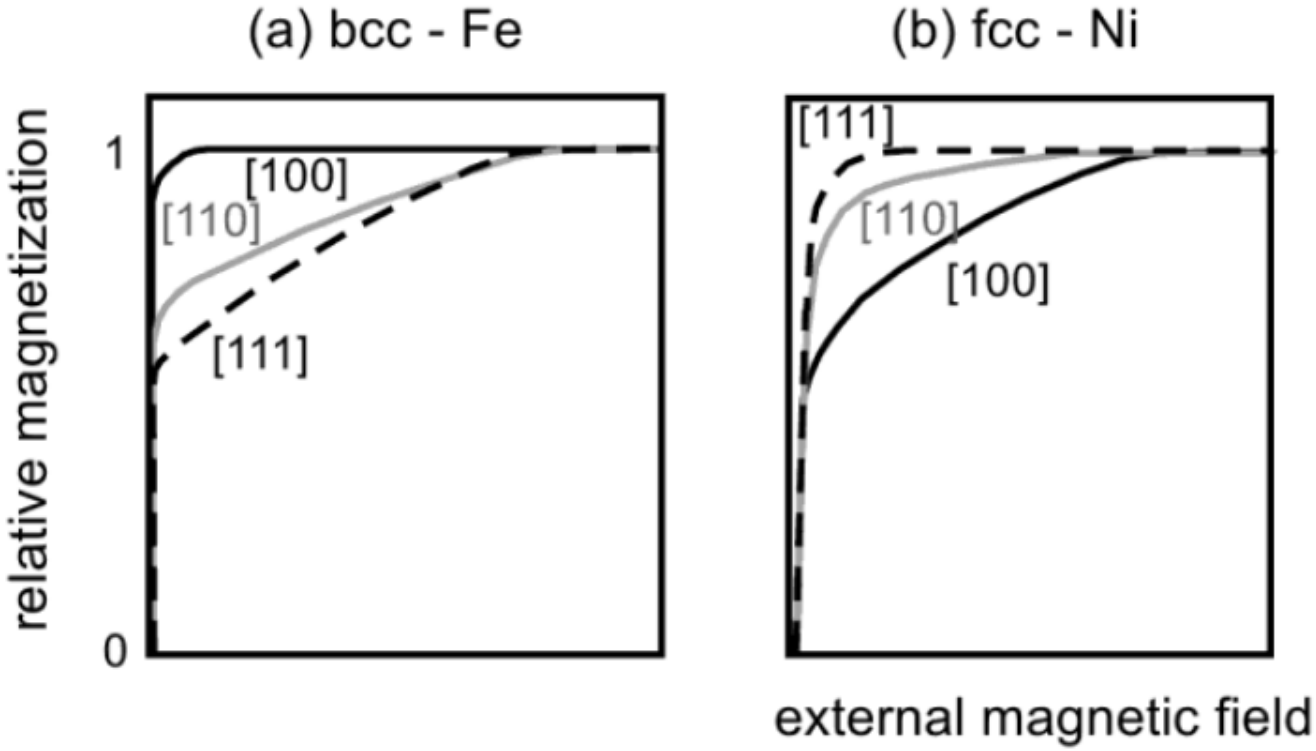




$$d = \frac{a}{\sqrt{h^2+k^2}} + \frac{c}{\sqrt{l^2}}$$

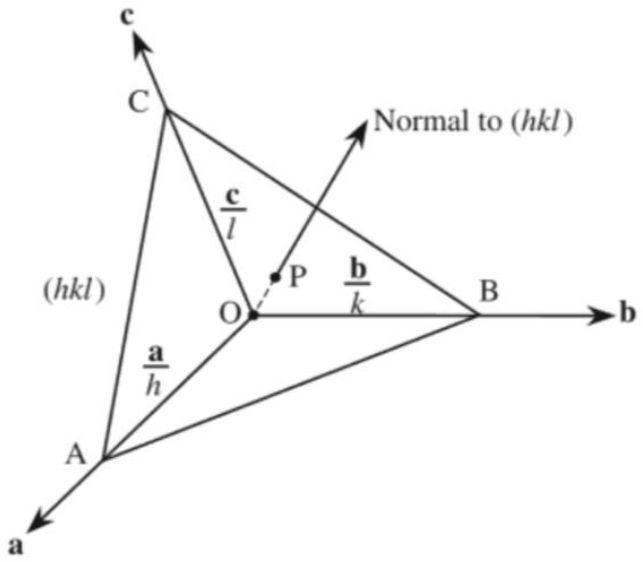
The properties are a consequence of the crystal structure

Magnetocrystalline anisotropy



Crystal Structure Quiz

Weiss Zone Law (Zone Axis)



Consider the plane hkl: A general vector, r, lying in (hkl) can be expressed as a linear combination of any two vectors lying in this plane $\overrightarrow{AB}$ & $\overrightarrow{AC}$:

$$r = \lambda\overrightarrow{AB} + \mu\overrightarrow{AC}$$

Expressed in terms of the primary lattice vectors a, b and c:

$$r = \lambda\left(\frac{b}{k} - \frac{a}{h}\right) + \mu\left(\frac{c}{l} - \frac{a}{h}\right) = -\frac{(\lambda+\mu)}{h}a + \frac{\lambda}{k}b + \frac{\mu}{l}c$$

Expressing this as r [uvw]:

$$u = -\frac{(\lambda+\mu)}{h} \qquad v = \frac{\lambda}{k} \qquad w = \frac{\mu}{l}$$

So the condition for a vector [uvw] to lie in the plane (hkl) is: **hu + kv + lw = 0.**

*This can only be true if each set of *scalar prefactors* equate.

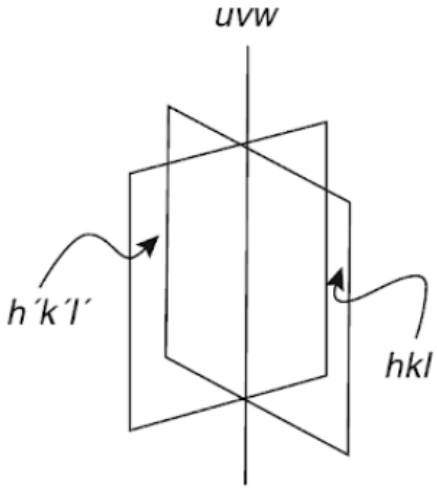
• In a cubic system this is exactly analogous to taking the scalar product of the vector and the plane normal, so that if they are perpendicular, the angle between them, θ, is 90°, then cosθ = 0, and the direction lies in the plane.

• The Weiss Zone Law is general and valid for **all** crystal systems.

Weiss Zone Law (Zone Axis)

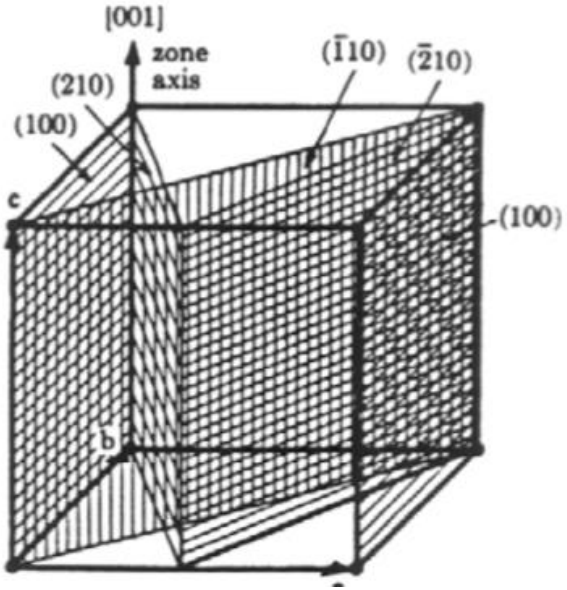
Any two non-parallel planes within a crystal can intersect in a line that lies in both planes. This line, is said to be the zone axis of the zone in which the two planes are situated.

Let the miller indices of two planes be: (h_1, k_1, l_1) and (h_2, k_2, l_2), then the indices [uvw] of the zone axis are defined by solving:



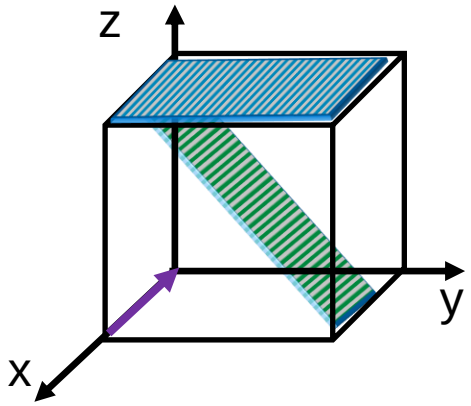
$$u = \begin{vmatrix} k_1 & l_1 \\ k_2 & l_2 \end{vmatrix} \qquad v = \begin{vmatrix} l_1 & h_1 \\ l_2 & h_2 \end{vmatrix} \qquad w = \begin{vmatrix} h_1 & k_1 \\ h_2 & k_2 \end{vmatrix}$$

For example, in this cubic structure, the shaded planes are planes of the [001] zone axis (shared direction).



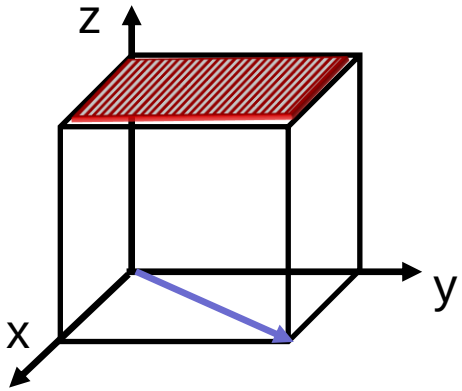
Weiss Zone Law examples

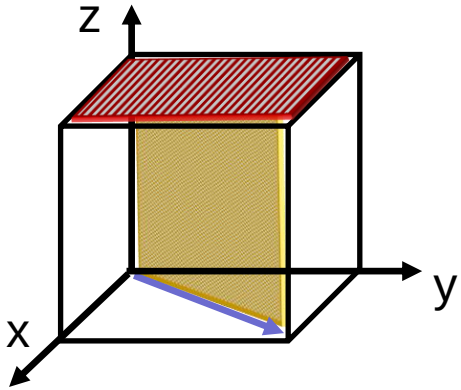
1. Calculate the zone axis for (001) and (011)



$[\bar{1}00]$

2. A zone axis is [110], and one of the planes is (001). Identify the other plane(s) that shares this zone axis.

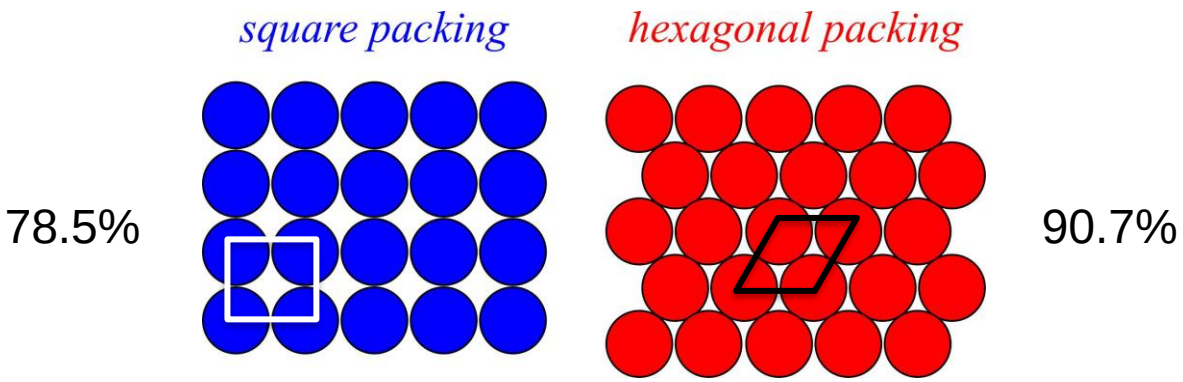




$(1\bar{1}0)$

Crystal Structures: Packing in 2D

Consider two ways of packing *identical* atoms:



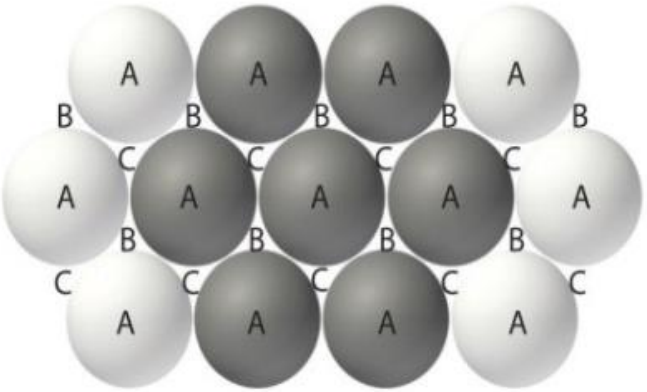
The Packing Efficiency: $\frac{\text{Area of circles in unit cell}}{\text{Area of unit cell}} \times 100\%$

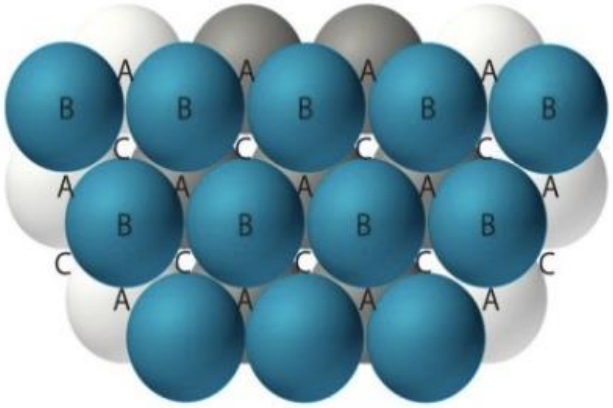
Close packed structure are often energetically favoured, and many crystals are based on this structure.

Crystal Structures: Packing in 3D

Packing of Close-Packed Planes in 3D

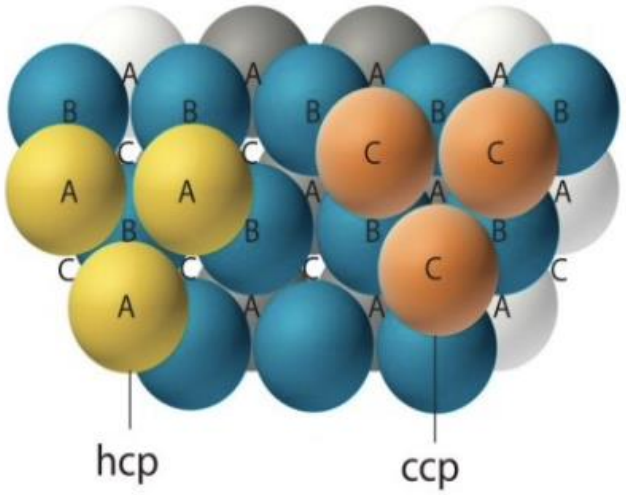
- A close-packed layer is shown, with atoms on ‘A’- sites.



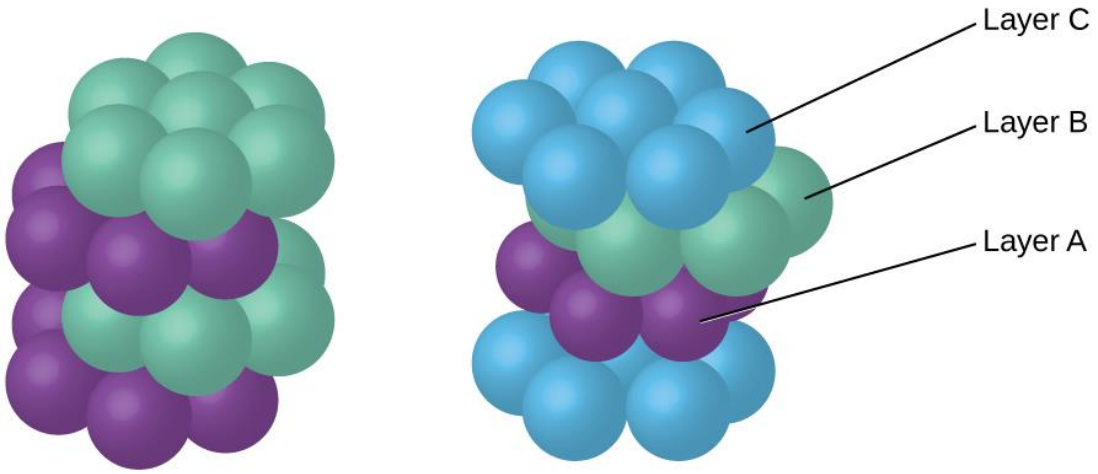


- When a second layer is placed on top, the atoms may sit in either the B or C sites.

- If a third layer is then placed onto the structure, again there is a choice of two positions: A or C.



Packing of Close-Packed Planes in 3D



Hexagonal closest packed

HCP

Cubic closest packed

FCC

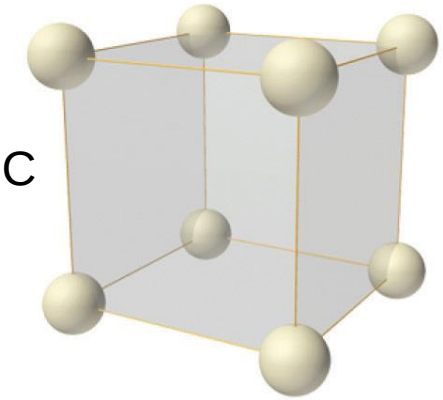
Different stacking patterns may therefore occur:

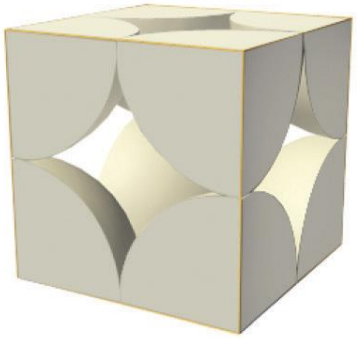
- ABAB… stacking gives hexagonally close packed structure (HCP): 32 of the elements crystallise with HCP structure – *e.g. Mg, Co, Ti...*

- ABCABC… stacking gives cubic close packed (CCP). The unit cell of this structure is a cube. 30 elements crystallise as face centred cubic (FCC) structures – *e.g. Au, Al, Cu*..

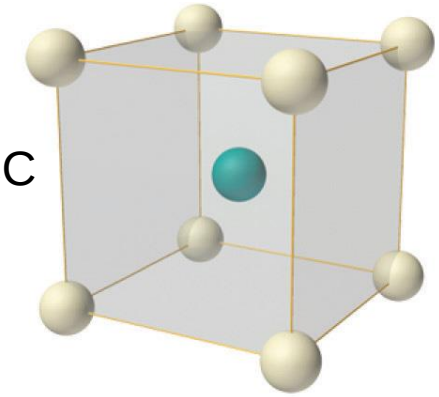
Crystal Structures: Packing in 3D

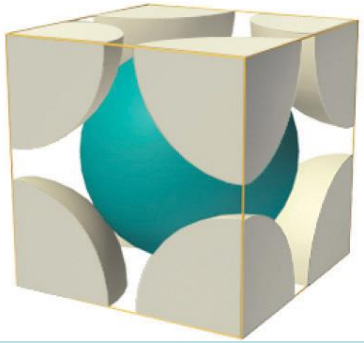
SC



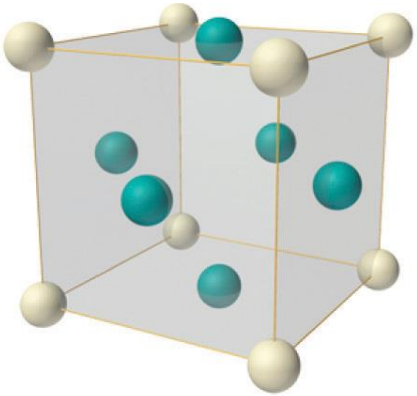


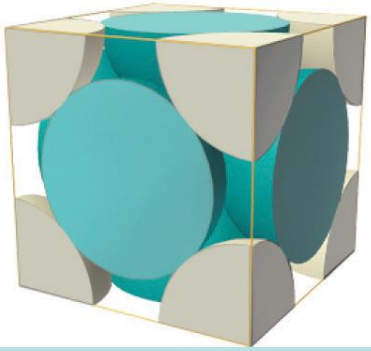
BCC





FCC



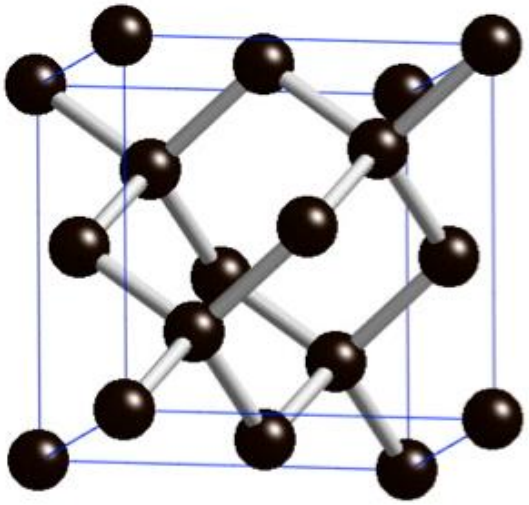


1 atom per unit cell	2 atoms per unit cell	4 atoms per unit cell
52.4%	68%	74%

$$\text{Packing efficiency} = \frac{Volume\ occupied\ by\ all\ atoms\ in\ the\ unit\ cell}{Volume\ of Unit\ cell} = \frac{{}^{4}/_{3}\pi r^{3} * number\ of\ atoms}{a^{3}}$$

Visualising crystals 2D: Structure Plan

The diagrammatic representation of crystalline solids is usually displayed as a *structure plan* (2D), viewed down a particular crystallographic direction, or onto a crystallographic plane.



Information needed:

1. Lattice type
2. Fractional Coordinates of the atoms which constitute the motif of the crystal
3. Projection: Viewing direction or plane

Notes:

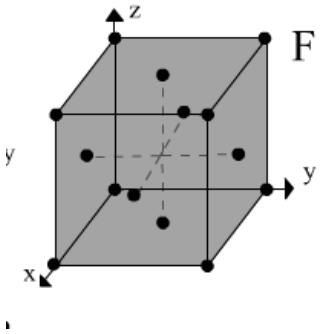
- The fractional coordinates of the atoms in a crystal are simply the vector position in the terms of *a*, *b* and *c*.
- If the fractional coordinates of the motif are specified, then this motif must be represented at every lattice point.

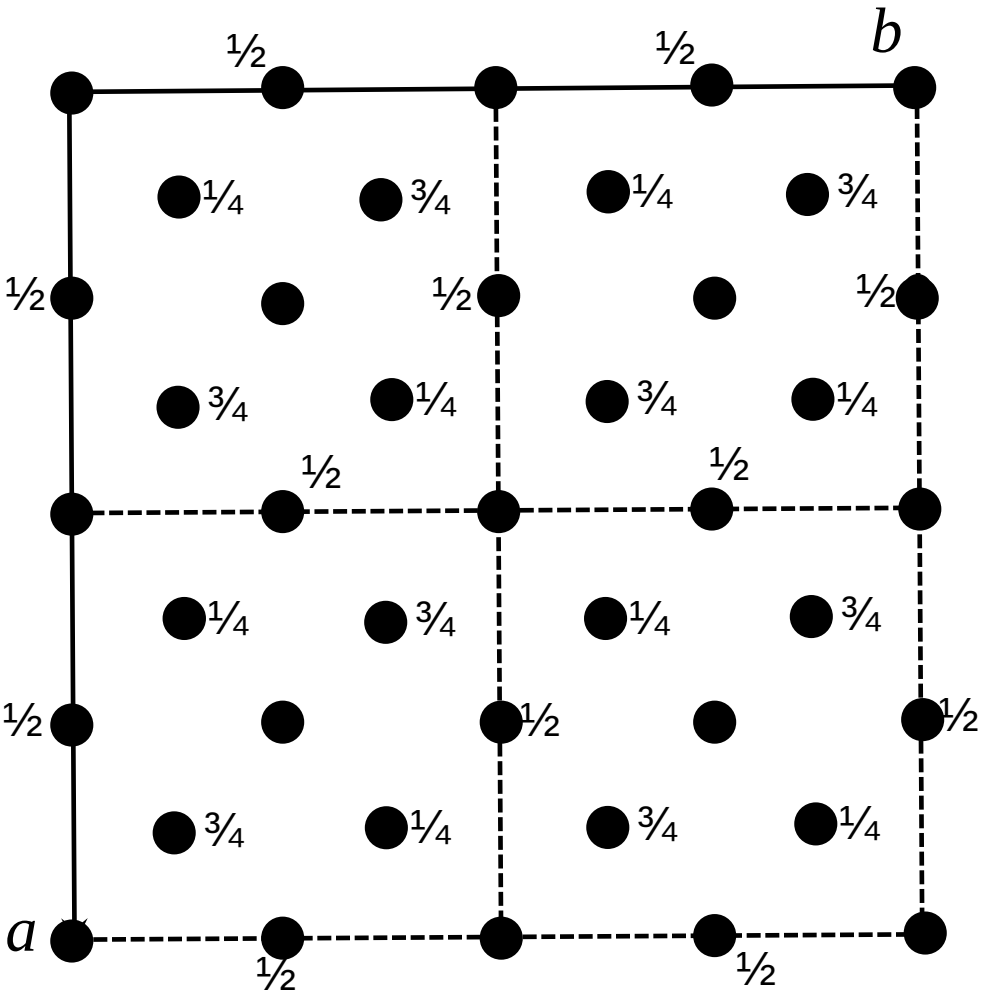
Drawing out a Structure Plan

Example 1: Diamond Structure

Lattice Type: Cubic F
Motif: C at 0,0,0 and ¼, ¼, ¼
View down [001]
2x2 lattice

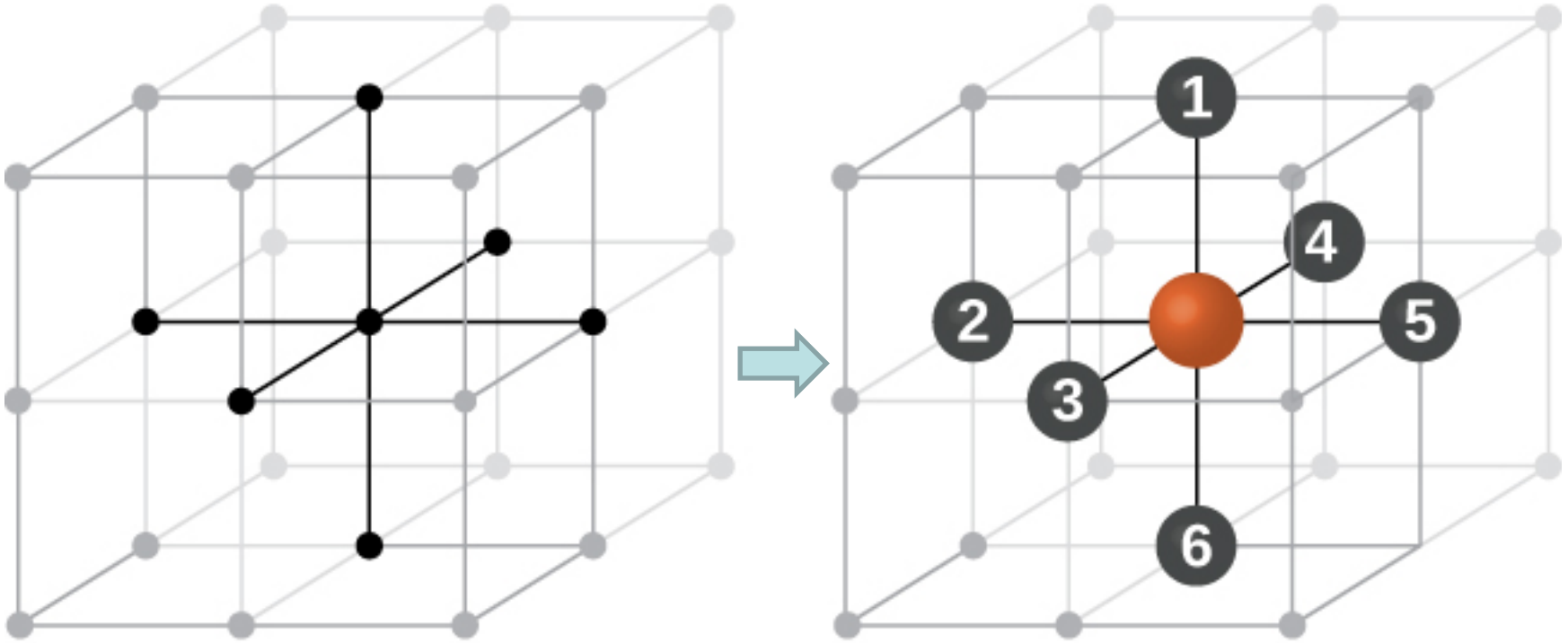
Face Centred





Lattice points ○
Motif ●

Coordination number: More ways to describe the crystal structure



Simple cubic structure (SC): Each atom in the lattice has 6 nearest neighbors. Thus, this is an *octahedral* arrangement or coordination.

https://opentextbc.ca/chemistry/chapter/10-6-lattice-structures-in-crystalline-solids/

Visualization of Crystal Structures: Coordination Geometry

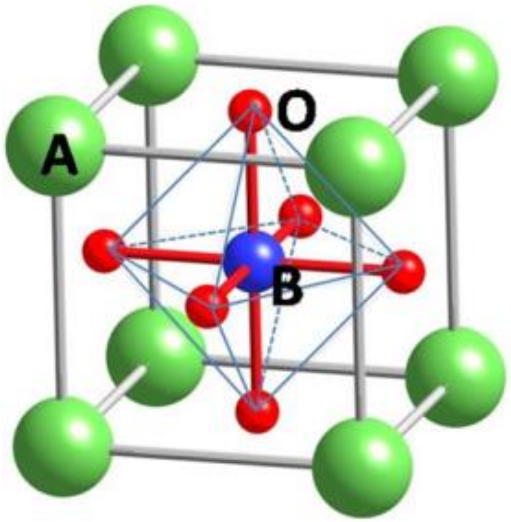
Structure plans are easy and accurate but give a poor feel for the 3D structure.

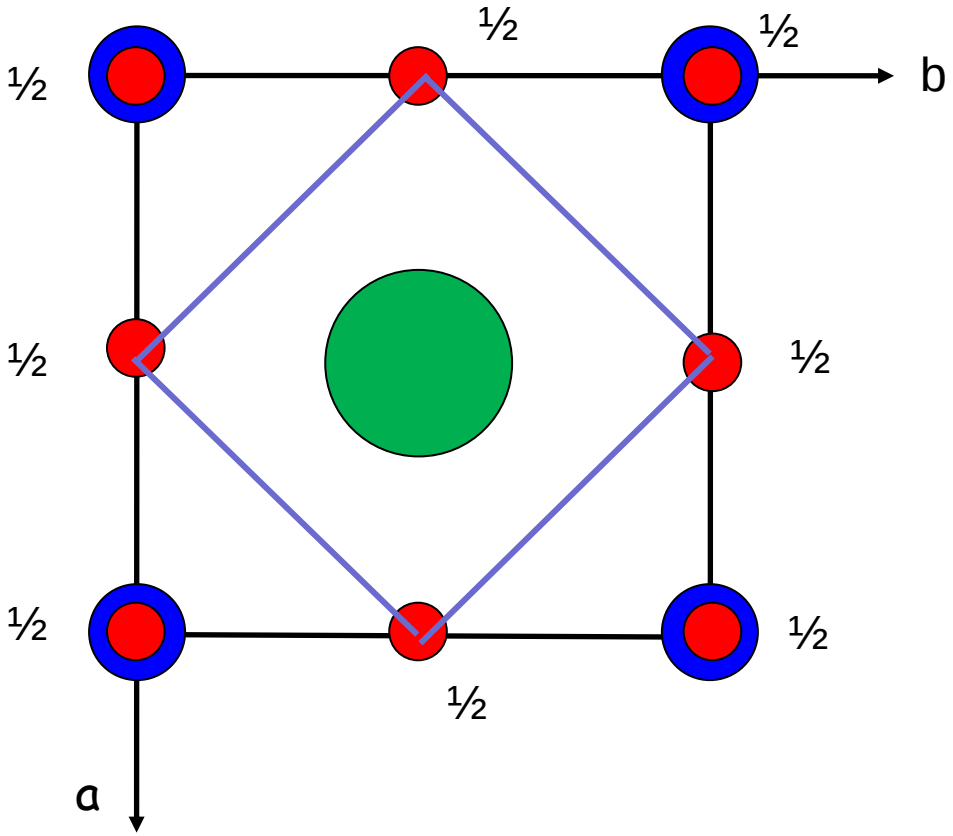
It is often useful to think of distinct bonded units as polyhedra, and the crystal structure as a series of linked polyhedra, sharing corners, edges or faces.

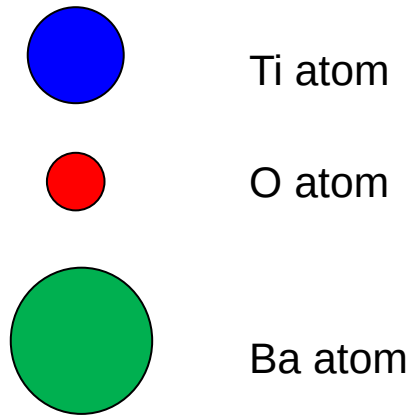
For example, *the perovskite structure*

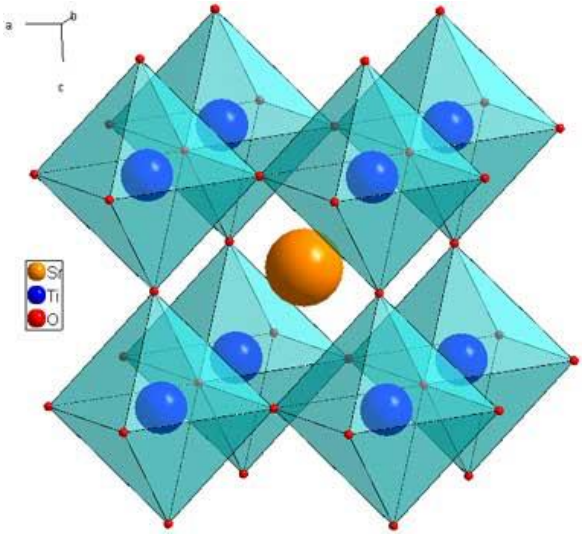
P*erovskites* are a group of materials with the general formula ABO_3. Examples are $BaTiO_3$, $SrTiO_3$, $CaTiO_3$, etc.

Lattice type:	Cubic P
Motif:	Ba ½ ½ 0
	Ti 0 0 ½
	O ½ 0 ½
	0 0 0
	0 ½ ½
Viewed down:	[001]









If the TiO_6 units in the above structure are represented by octahedra then polyhedra forming cages in which large Ba atoms sit. the structure may be easily visualised as corner TiO_6

Symmetry

- The crystal structure alone is not sufficient to describe the full nature of a crystal.
- The essence of crystallography lies on the study and understanding of crystal symmetry.

Neumann's Principle:

"Any property of a crystal must obey at least the symmetry of that crystal"

'***Symmetry*** *is that property possessed by an object that, when transformed in some way (e.g., by rotation, inversion, repetition etc.), looks the same after as before the transformation. In other words, symmetry is a demonstration of the invariance of an object to some sort of transformation*' (M. Glazer & G. Burns)

Symmetry Elements:

1. Translation
2. Rotation
3. Mirror
4. Inversion
5. Mixed

Q: Briefly describe the terms *point group* and the *symmetry* operation *rotoinversion*.

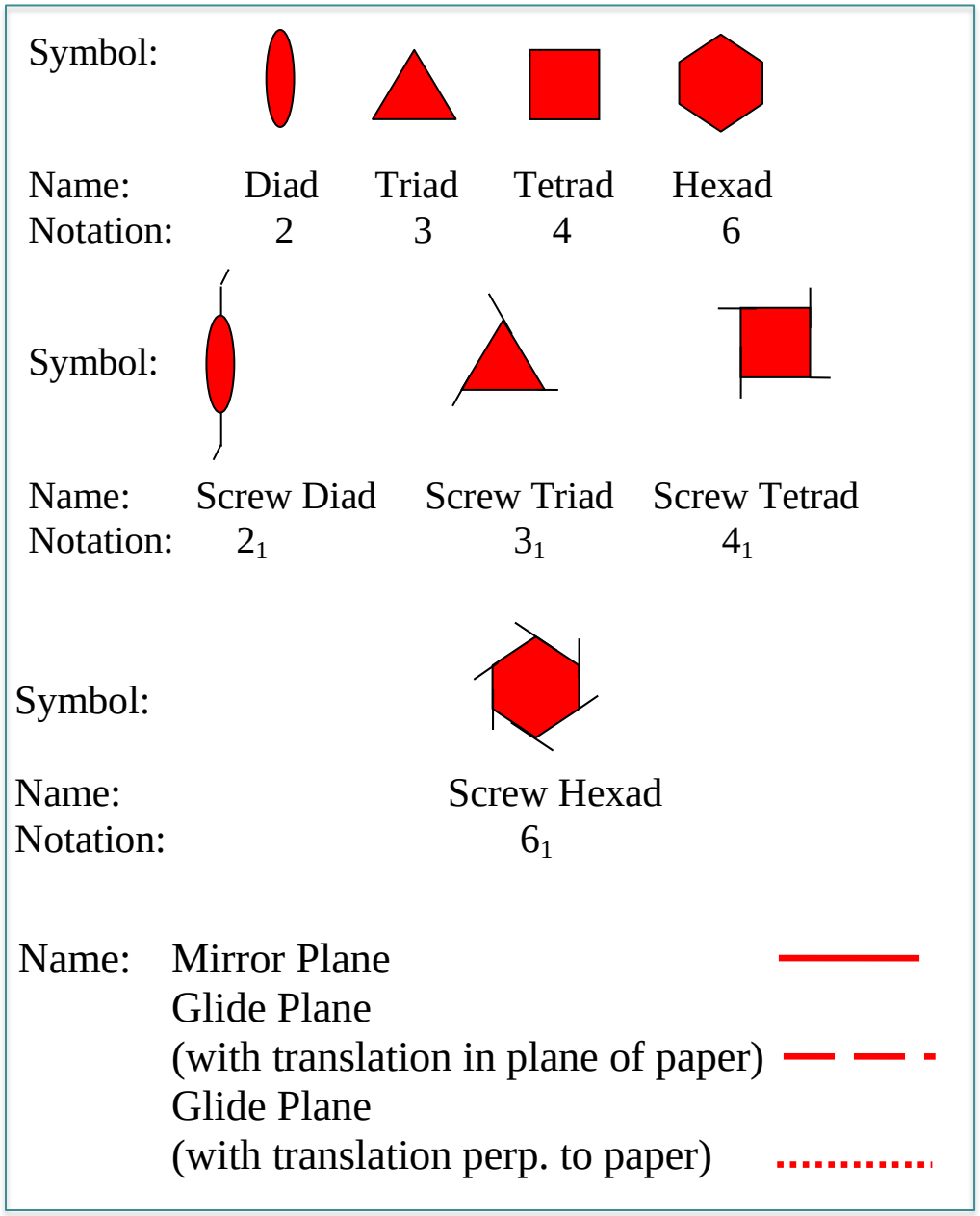
Symmetry Notation

In crystallography, the symmetry elements are represented by the Schoenflies and **Herman-Mauguiny** symbols:

Symmetry operation	Description of the operation	Schoenflies symbol	Hermann-Mauguin symbol
Identity	Doing nothing or rotation by 360°	E (sometimes I) or C_1	1
***n*-fold rotation (n = 2,3,4,(5),6)**	(Proper) rotation by 360°/n about rotation axis	C_n	n
Mirror plane	reflection	σ_v, σ_h *or* σ_d [1)]	m
Inversion	point reflection through a centre of symmetry	i	$\bar{1}$
Improper rotation [2)] (Sch.)	Rotation by 360°/n followed by reflection in a plane perpendicular to the n-fold axis.	S_n	-
Rotary inversion [2)] (H.-M.)	Rotation by 360°/n followed by inversion	-	$\bar{n}$

Remarks: 1) σ_v – vertical mirror plane, σ_h – horizontal mirror plane, σ_d – diagonal/dihedral mirror plane
2) Improper rotation and rotary inversion actually describe the same.

Representation of Symmetry Elements



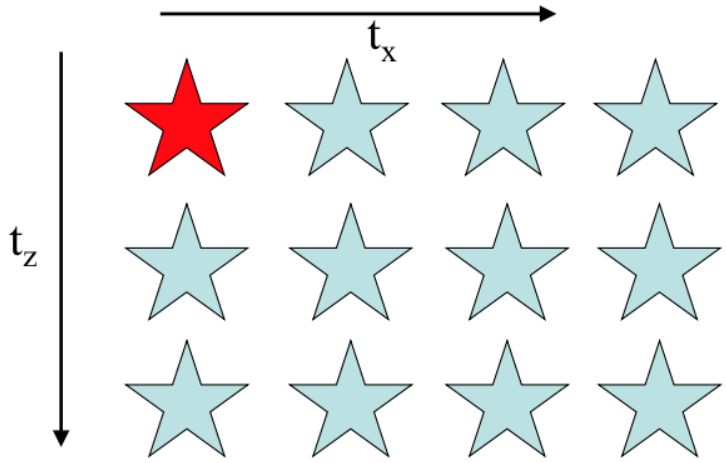
- The numerals 1, 2, 3, 4, and 6 indicate an axis of rotation.
- The numerals with a bar-over indicate an axis of inversion.
- m, indicates a mirror plane
- A slash, /, means "perpendicular to“
- Two symbols in succession means "parallel to".
- The subscripts denote the translation along the axis of rotation associated with each operation of the symmetry.
- e.g. N_m expresses an anticlockwise rotation of $2\pi/N$ followed by a translation of $(m/N)\mathbf{t}$ where t is the lattice vector parallel to the screw axis.

More @ Appendix 6 M. Glazer & G. Burns

Translation

The lattice itself generates translational symmetry (the motif is repeated on every lattice point): the unmoved crystal is indistinguishable from that moved by the translational lattice vector.

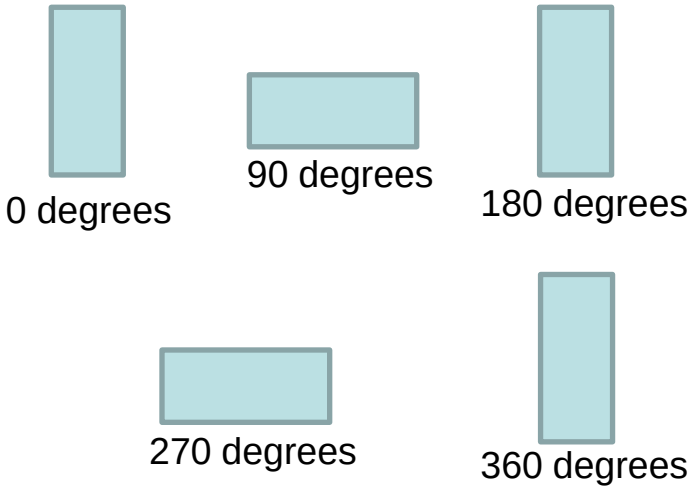
The result of this lattice translation is indistinguishable from the unmoved lattice.



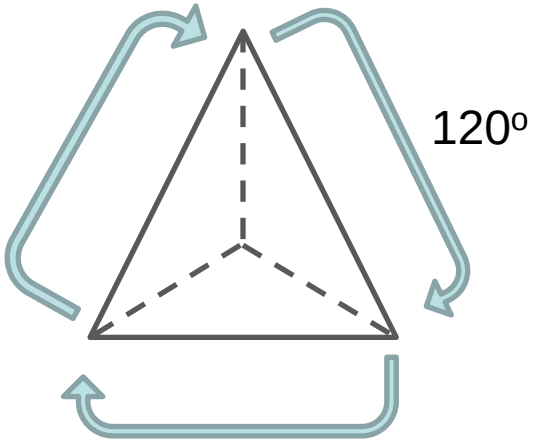
In a 3D space, translations can be labelled x, y and z.

Rotation *(n)*

Rotational symmetry causes an object to come into coincidence with itself after rotation of 360°/*n*, where *n* is an integer, the order of the axis.



Rotational symmetry = 2-fold (n =2)



Rotational symmetry = 3-fold (n = 3)

n = 1 ⇨ Identity (E or 1)

Rotation *(n)*

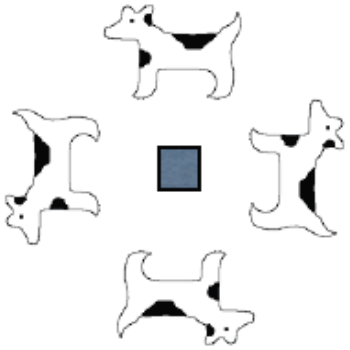
Rotational symmetry causes an object to come into coincidence with itself after rotation of 360°/*n*, where *n* is an integer.

2 fold
'Diad'

(180°)

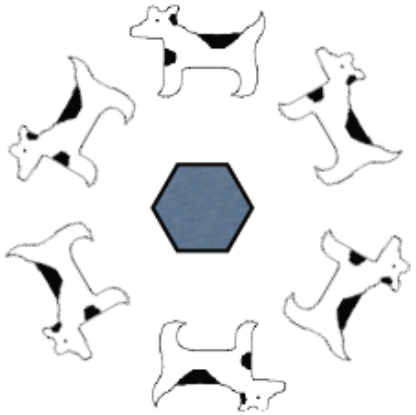
3 fold
'Triad'

(120°)



4 fold
'Tetrad'

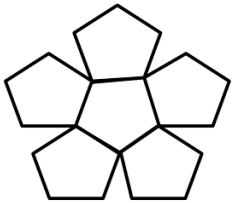
(90°)



6 fold
'Hexad'

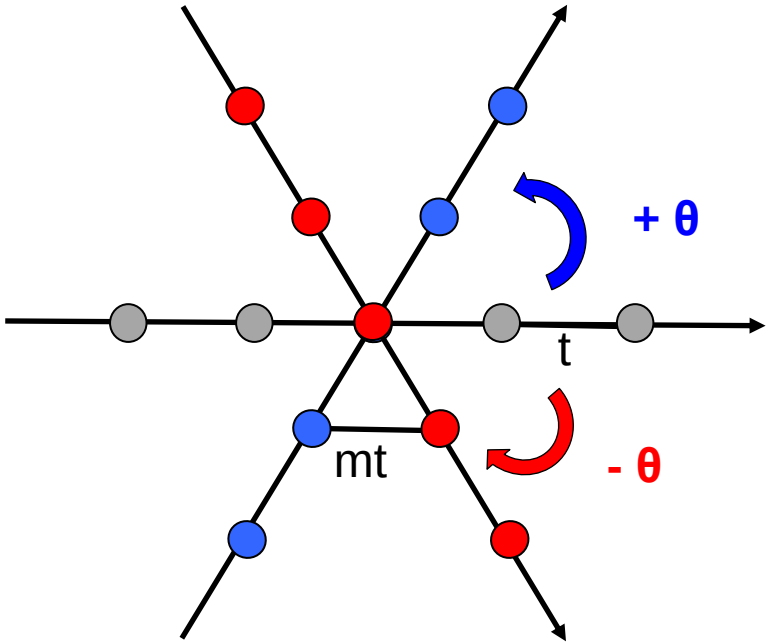
(60°)

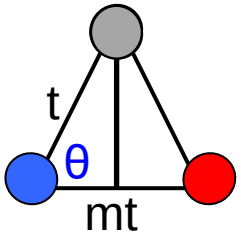
Q: Why not a 5-fold rotation axis?



Consider a grid line with lattice points separated by a translation vector *t:*

If the lattice is rotated by an angle: +θ and -θ, then the blue and red circles correspond to new lattice point positions. Thus, any distance between blue and red lattice points must be equal to an integral multiple (m), an integer to keep rotational symmetry consistent with the lattice, of the lattice translation (t).





$$cos\theta = \left(\frac{mt}{2}\right)\left(\frac{1}{t}\right) = \frac{m}{2}$$

$$m = 2cos\theta$$

m	-2	-1	0	1	2
cos θ	-1	½	0	½	1
θ	180	120	90	60	0/360
n	2	3	4	6	1

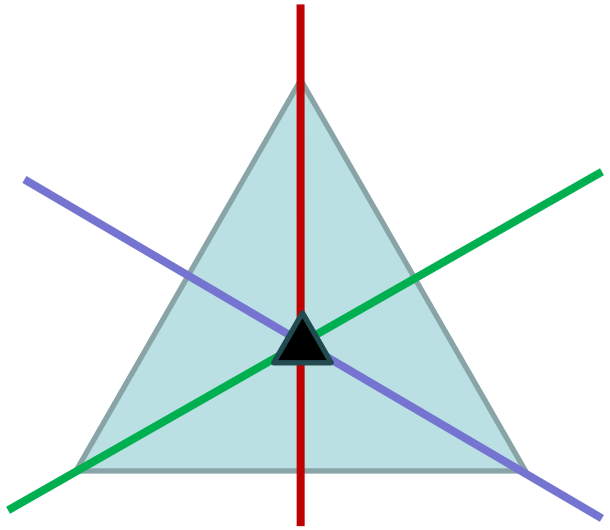
There's no pentad (n = 5, θ = 72º). Solutions are only valid for θ = 180º, 60º, 90º, 120º, 360º.

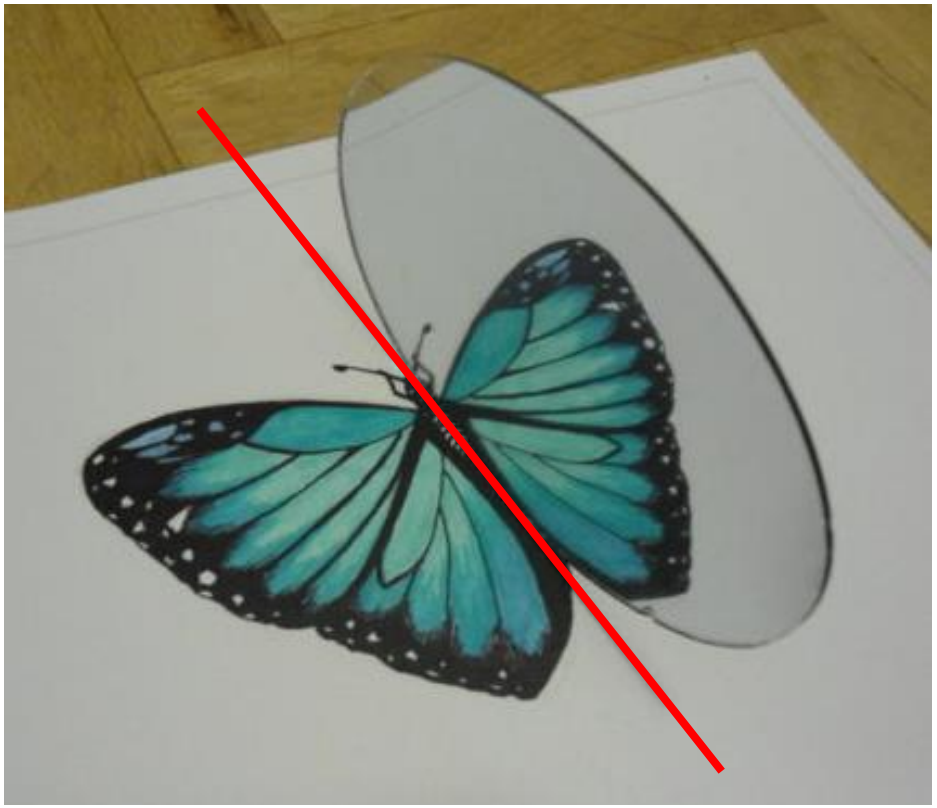
A 5-fold of rotation symmetry would leave either voids or an overlap of the pentagons.

More @ Appendix A, Putnis

Mirror or Reflection Symmetry *(m)*

An object has mirror symmetry if reflection of the object in a **plane** brings it into coincidence with itself:

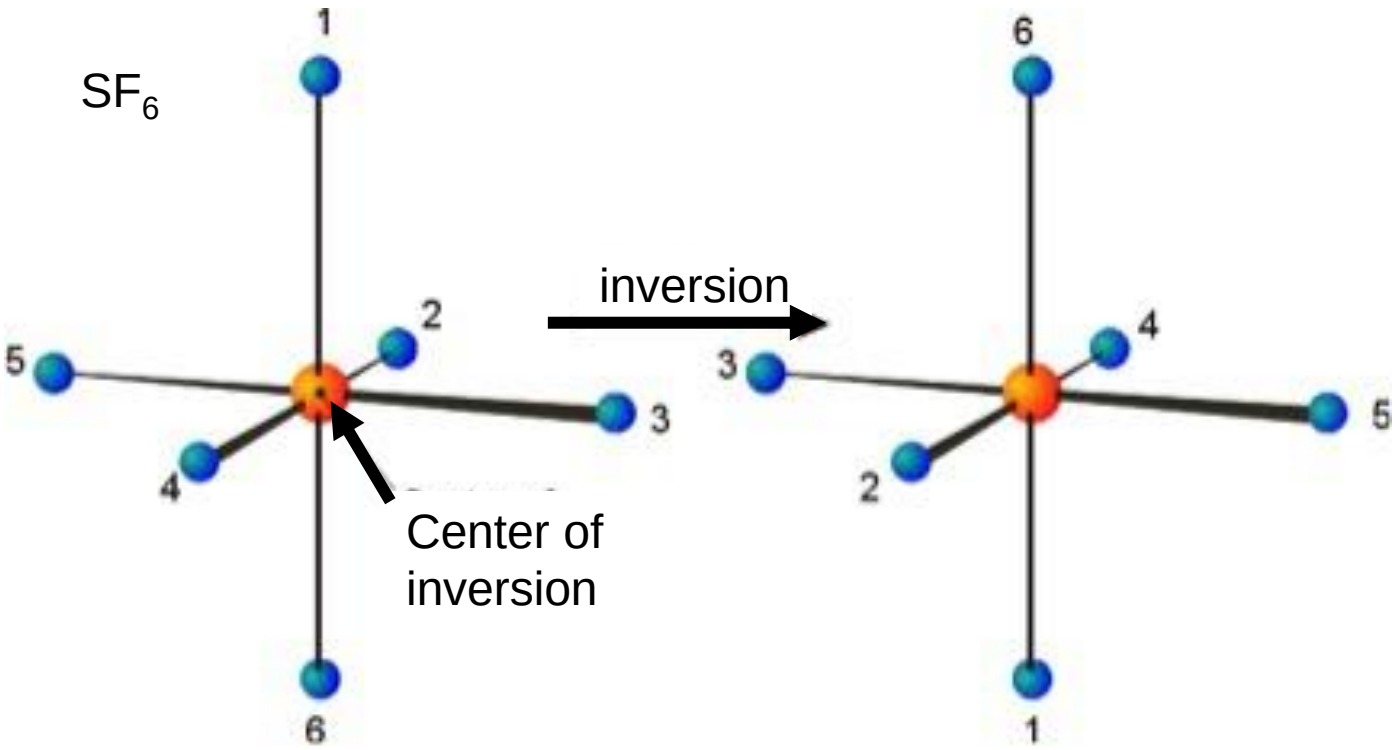




m

Inversion Symmetry $\bar{n}$ *(n)*

It exists when for any point on the object x, y, z, an exactly similar point is found at –x, -y, -z. The origin is called centre of symmetry, and the object is said to be centrosymmetryc.

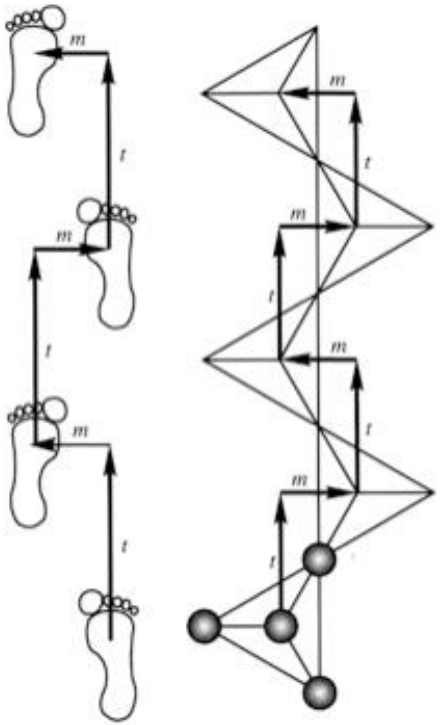


Mixed Symmetry

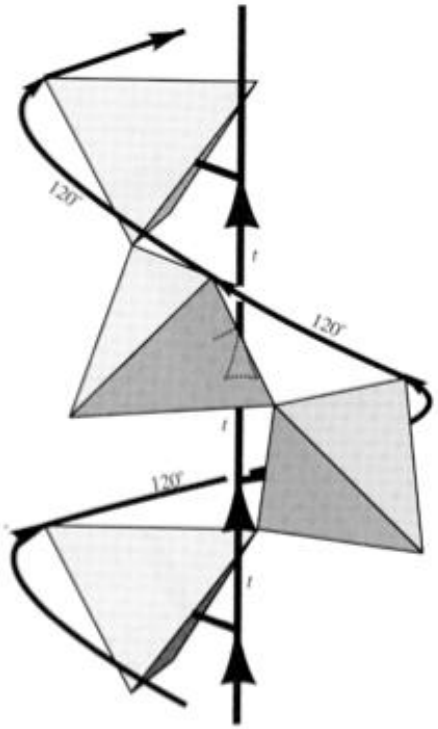
A combination of two symmetry elements:

1. ***Glide Plane (c):*** Mirror planes reflect the point x, y, z, and then translate parallel to the plane of the mirror.

2. ***Screw axes (N_m):*** Rotation axis combined with a translation along the symmetry axes.



Glide: Translation + mirror
Single chain silicates - pyroxenes

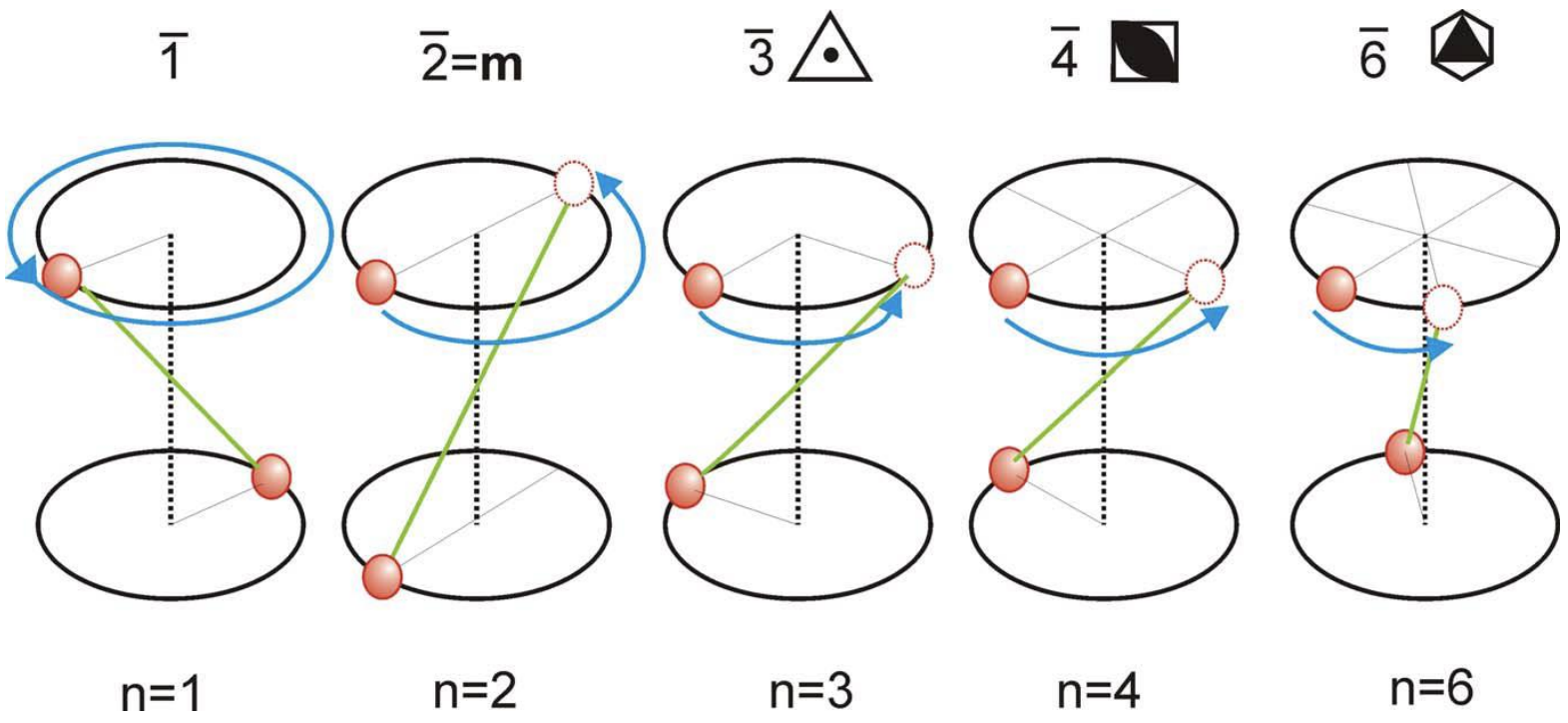


3_1

Screw: Translation + rotation
3D network silicates - quartz

Mixed Symmetry

3. Rotoinversion (Rotation + Inversion)***:*** A rotation axis is combined with a centre of symmetry (inversion). For a rotation of 360°/n, the rotation axis is given by n, and the corresponding rotoinversion axis is given by $\bar{n}$



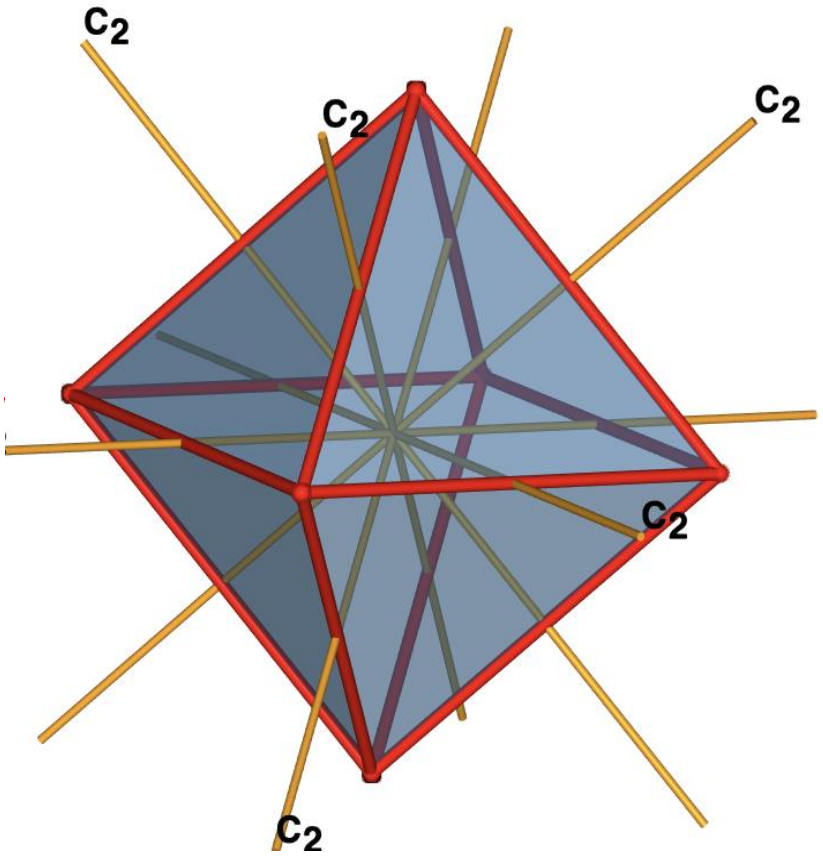
- This is also called improper rotation axes.
- To differentiate between normal rotation and rotoinversion we add a bar (−) above the rotation symbol

Q: What Symmetry elements can you recognize in this drawing?

Q: What Symmetry elements can you identify in this octahedron?

Some symmetry elements are:

- Three 2-fold axes (180 degrees) pass through opposite pairs of apices: 6 apices, 3 axes.
- Six 2-fold axes pass through mid points of opposite edges.
- 4-fold axes (90 degrees) pass through opposite pairs of apices: 6 apices, 3 axes.



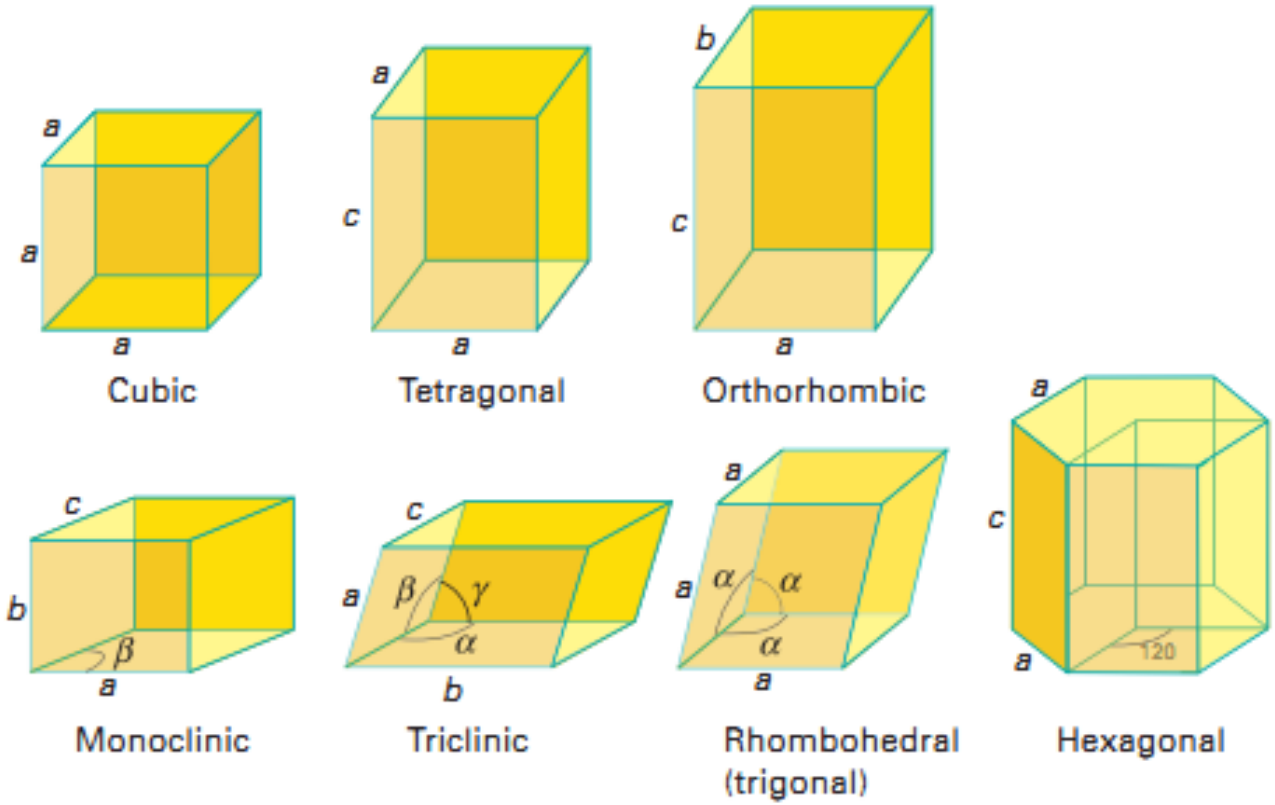
http://symmetry.otterbein.edu/gallery/index.html

The Seven Crystal Systems

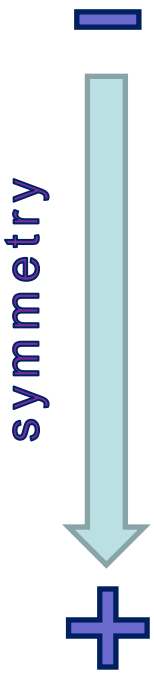
When a group of symmetry elements operates on the unit cell of a crystal, it restricts various aspects of the unit cell geometry.

e.g. when a tetrad operates along one of the crystallographic directions, the unit cell vectors perpendicular to the tetrad must be equal in magnitude and at 90° to each other.

These constrains lead to the existence of only **7** distinct unit cells geometries, or ***crystal systems***:



Crystal Systems' Symmetry



System	Defining Symmetry	Unit Cell Geometry
Triclinic	Only translational	$a \neq b \neq c; \alpha \neq \beta \neq \gamma$
Monoclinic	Diad parallel to b or/and one mirror plane perp. to b.	$a \neq b \neq c; \alpha = \gamma = 90^o; \beta \geq 90^o$
Orthorhombic	Diads parallel to a,b,c, and/or perpendicular mirror planes	$a \neq b \neq c; \alpha = \beta = \gamma = 90^o$
Trigonal	One triad parallel to c.	$a = b \neq c; \alpha = \beta = 90^o; \gamma = 120^o$
(Rhombohedral)	(One triad parallel to [111])	$a = b = c; \alpha = \beta = \gamma = 60^o$
Hexagonal	One hexad parallel to c.	$a = b \neq c; \alpha = \beta = 90^o; \gamma = 120^o$
Tetragonal	One tetrad parallel to c.	$a = b \neq c; \alpha = \beta = \gamma = 90^o$
Cubic	Four triads parallel to <111>	$a = b = c; \alpha = \beta = \gamma = 90^o$

NB. The inequality sign means that the lattice parameters are not required to be equal by symmetry. They may coincidentally be equal.

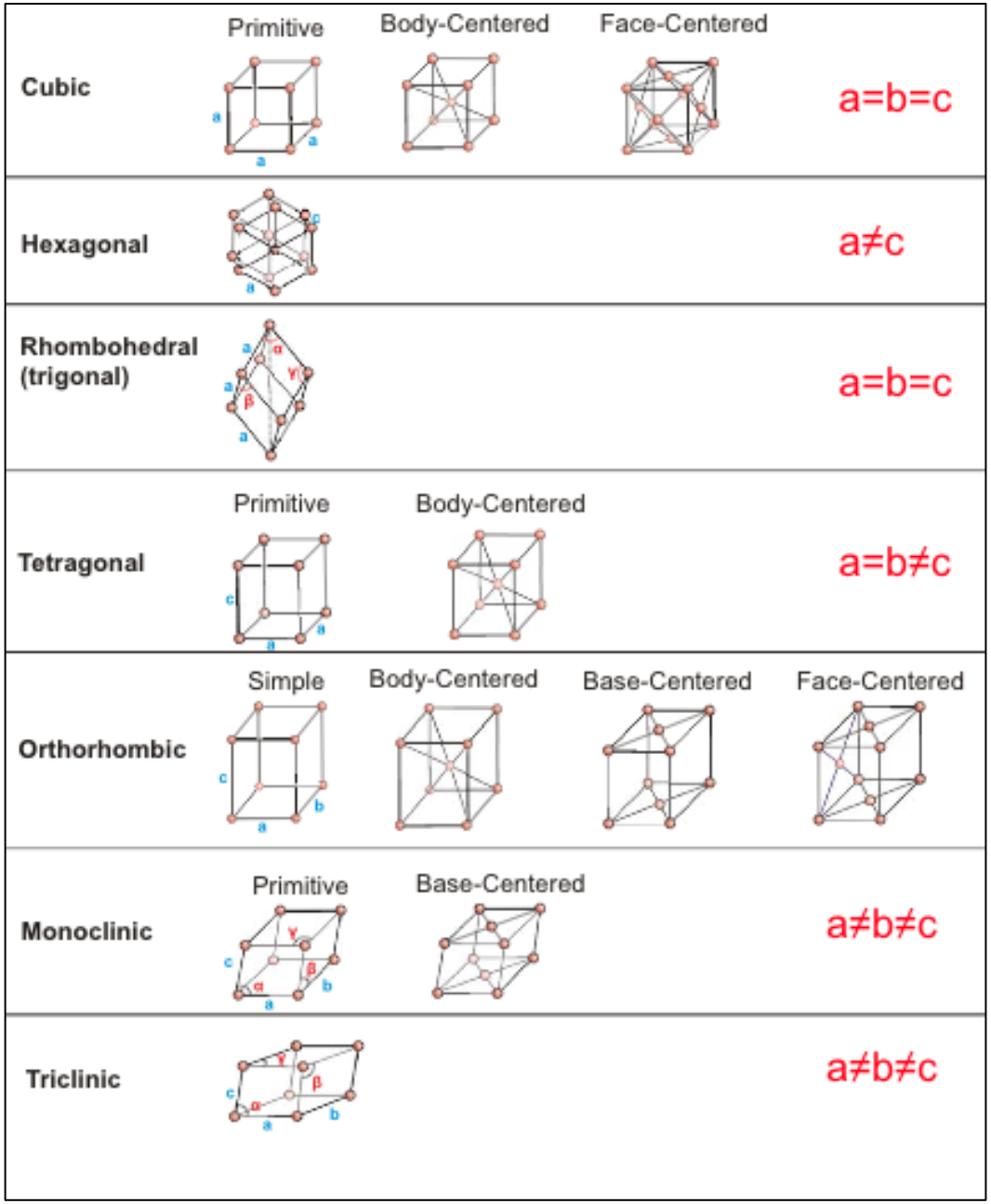
The 14 Bravais Lattices

We have already seen that lattices may be of the type P, F, I or C. Within each crystal system these 4 types of lattice exist.

P	Primitive
I	Body-centred
F	Face-centred
C	Base-Centred

The combination of these lattice types and the 7 crystal systems leads to 14 distinct lattices known as Bravais Lattices.

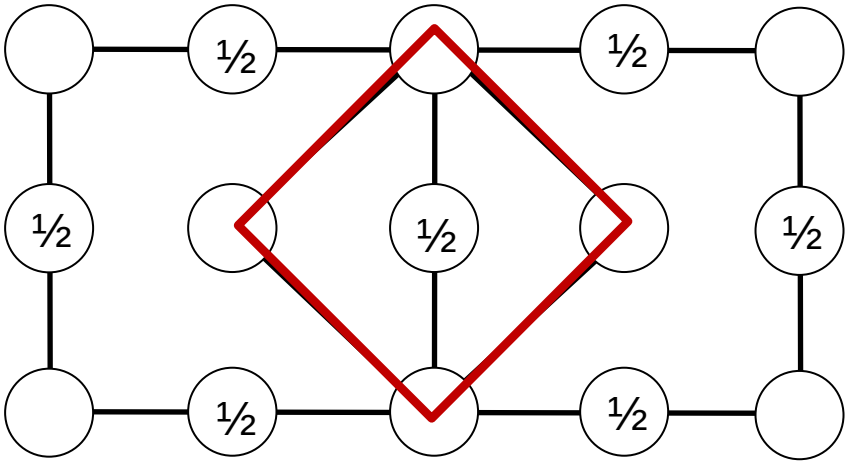
(Putnis pg 10)



Song @ www.haverford.edu/physics/songs/bravais.htm
More @ http://users.aber.ac.uk/ruw/teach/334/bravais.php

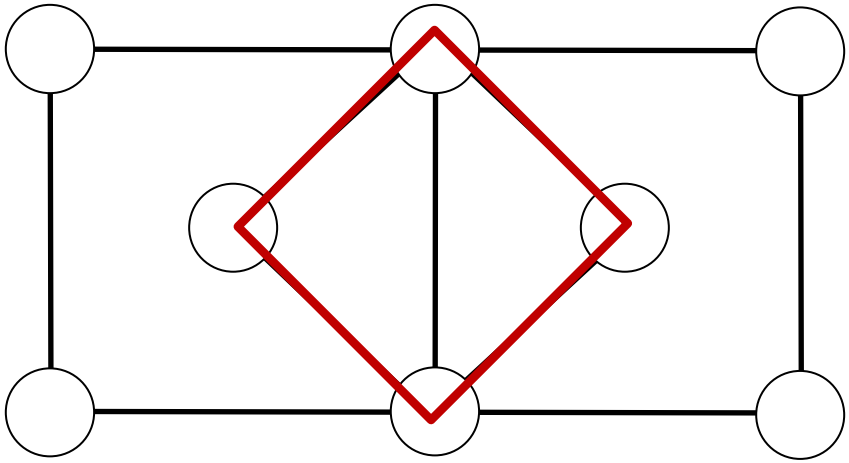
Why are there not 7x4=28 Bravais Lattices?

Tetragonal FC

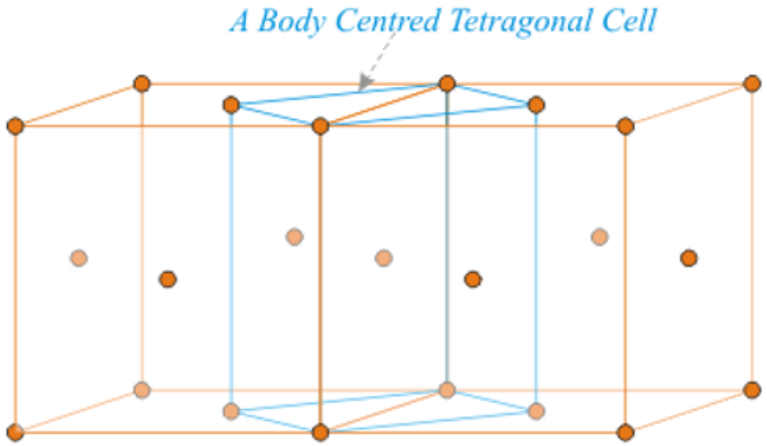


Tetragonal FC may be represented by a different *tetragonal I* cell.
Thus, Tetragonal FC is not a distinct Bravais Lattice..

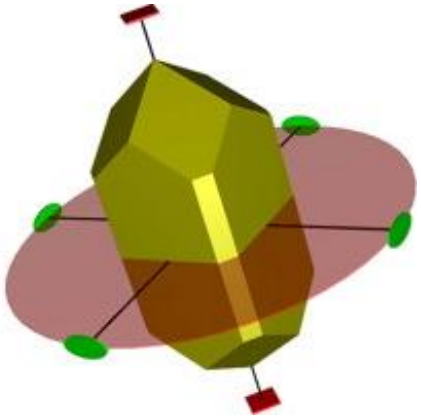
Tetragonal BC



Tetragonal BC may be represented by a different *tetragonal P cell* (with smaller cross-section). Thus, Tetragonal BC is not a distinct Bravais Lattice.



Point Groups



After considering the simple symmetry operators, it is necessary to consider that only the combination of all symmetry operations present in a crystal, will enable us to describe the full symmetry of a crystal.

- The collection of symmetry operations is referred as **point groups**

- There are only 32 possible combinations of symmetry elements, known as the 32 crystallographic point groups.

- The word ‘point’ means that *all the symmetry operations act about one point of origin in common (translation is not considered).*

Crystallographic point groups can be described by:
- The Hermann-Mauguin (or Shoenflies) notation
- Stereographic projections
- Matrices of their symmetry operations

The Hermann-Mauguin (H-M) notation is the international notation used to describe all 32 points groups.

The order of the H-M symbols in point groups

To determine a point group of an object, it is only necessary to write down a list of all the symmetry elements that it possesses and order these following certain rules.

Consider that a point group symbol has the general form ***ijk***. This represents the symmetry elements in primary (i), secondary (j) and tertiary (k) *directions*.

The rules are:

- The primary position (i) is given to the most important (or defining) symmetry element, which is often a symmetry rotation axis.
- The secondary position (j) is usually for secondary axes of rotation and/or mirror planes.
- The third position (k) is for the remaining symmetry.

Notes:

- Symmetry axes are taken as parallel to the direction described.
- Mirror planes are taken to run normal to the direction described.
- If a symmetry axis and the normal to a symmetry plane are parallel, the two symmetry characters are separated by a slash (/).

The order of the H-M symbols in point groups

Crystal System	Primary	Secondary	Tertiary	H-M symbols
Triclinic	-	-	-	1 and $\bar{1}$
Monoclinic	[010]	-	-	2, m and 2/m
Orthorhombic	[100]	[010]	[001]	222, 2mm and 2/m 2/m 2/m
Tetragonal	[001]	[100], [010]	$[1\bar{1}0]$, [110]	4, $\bar{4}$, 4/m, 422, 4mm, $\bar{4}$2m and 4/m 2/m 2/m
Trigonal	[111] Rhombohedral	[111]	$[1\bar{1}0]$, $[01\bar{1}]$, $[\bar{1}01]$	3, $\bar{3}$, 32, 3m and $\bar{3}m$
Hexagonal	[001]	[100], [010]. $[\bar{1}\bar{1}0]$	$[1\bar{1}0]$, [120], $[\bar{2}\bar{1}0]$	$\bar{6}$ (3/m), 6, 6/m, $\bar{6}m2$ (3/mm), 6mm, 622 and 6/m 2/m 2/m
Cubic	[100], [010], [001]	[111], $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, $[\bar{1}\bar{1}1]$	$[1\bar{1}0]$, [110], $[01\bar{1}]$, [011], $[\bar{1}01]$, [101]	23, 2/m$\bar{3}$ (m$\bar{3}$), 432, $\bar{4}3m$, and 4/m $\bar{3}$ 2/m (m$\bar{3}$m)

- Example for cubic point group 23

Space groups

The space group fully describes the crystal structure of any material and takes into account *translational* symmetry.

No. of space group	Schoenflies symbol	Short symbol	Full symbol	No. of space group	Schoenflies symbol	Short symbol	Full symbol
195	T^1	$P23$		213	O^7	$P4_132$	
196	T^2	$F23$		214	O^8	$I4_132$	
197	T^3	$I23$		215	T_d^1	$P\bar{4}3m$	
198	T^4	$P2_13$		216	T_d^2	$F\bar{4}3m$	
199	T^5	$I2_13$		217	T_d^3	$I\bar{4}3m$	
200	T_h^1	$Pm\bar{3}$	$P\frac{2}{m}\bar{3}$	218	T_d^4	$P\bar{4}3n$	
201	T_h^2	$Pn\bar{3}$	$P\frac{2}{n}\bar{3}$	219	T_d^5	$F\bar{4}3c$	
202	T_h^3	$Fm\bar{3}$	$F\frac{2}{m}\bar{3}$	220	T_d^6	$I\bar{4}3d$	

Cubic System space groups

Q: Gallium nitride (GaN), has a space group P6$_3$mc (hexagonal crystal system), and lattice parameters ...

(i) Explain what the element 'P' means and what symmetry element does '6$_3$' describe?

Q: The space group 221 is $Pm\bar{3}m$. State which type of lattice P represents in this space group, and describe the symmetry operation referred as *m*.

The 32 Point Groups Summary and remarks

- There are only **32** distinct ways that symmetry elements can act through a single point in space in a self-consistent manner: **point groups**

- Point groups **do not contain any symmetry elements that involve *translation*** – cannot account for all symmetry within crystal at the lattice level – therefore point groups tend to *describe macroscopic symmetry and behaviour*.

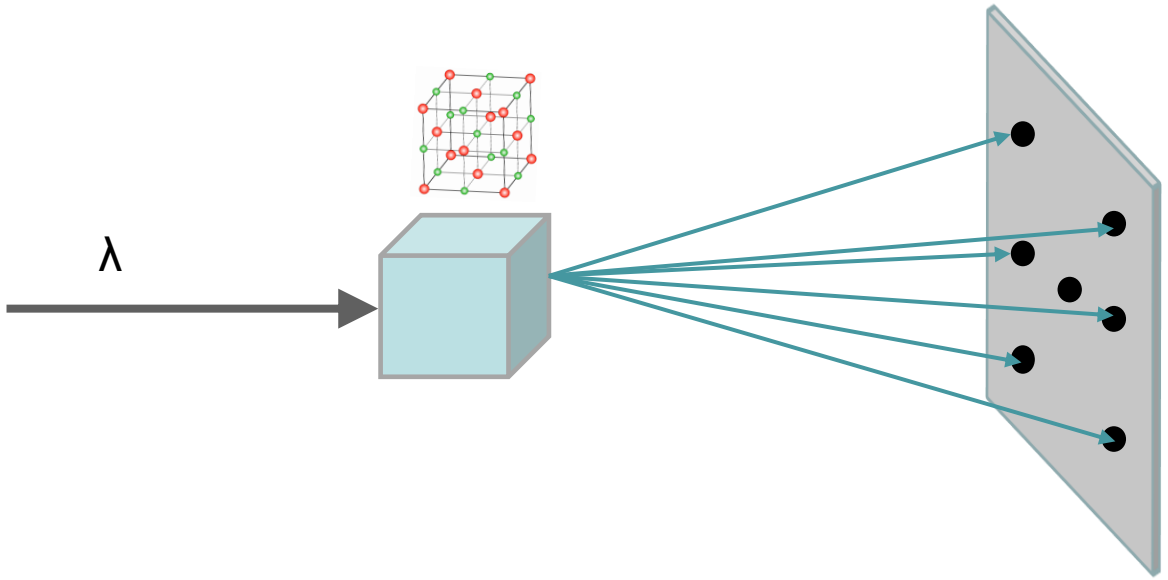
- Combining the 14 Bravais lattices with the 32 point groups results in **230 distinct space groups.** Every crystalline material has one of these 230 structures. All 230 space groups are listed in the:

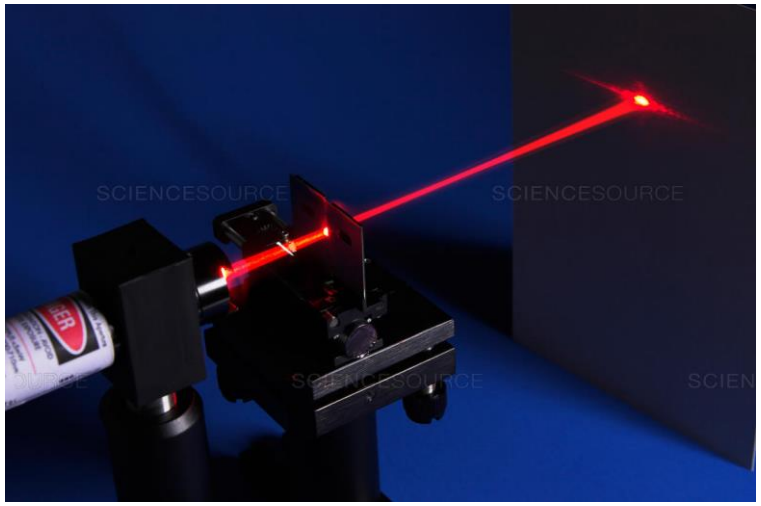
International Tables from the International Union of Crystallography.
(***International Tables for Crystallography*** **(2006). Vol. A, Section 10.1.2, pp. 763–795**)

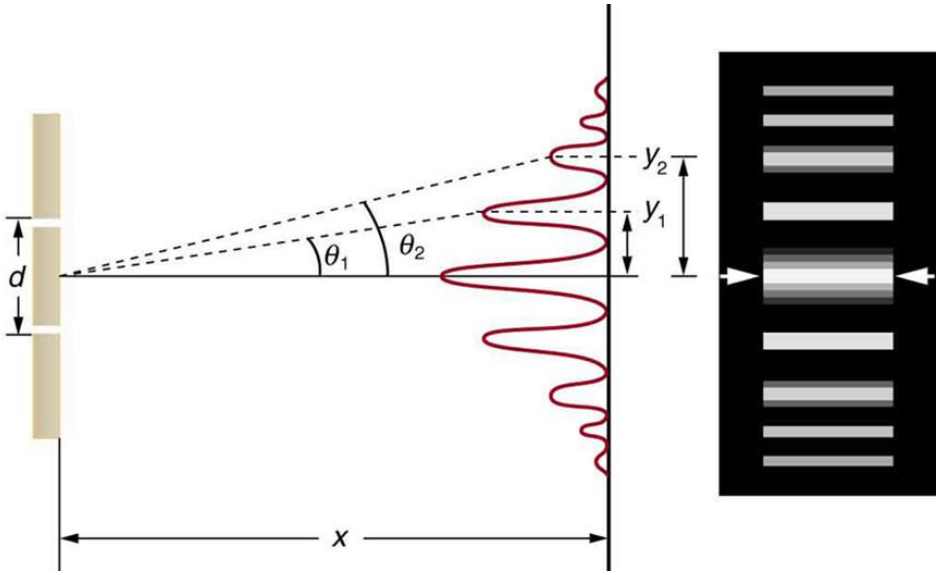
- **Symmetry Dictates Function: Neumann's Principle.**

More @ Appendix 4 & 5 - M. Glazer & G. Burns

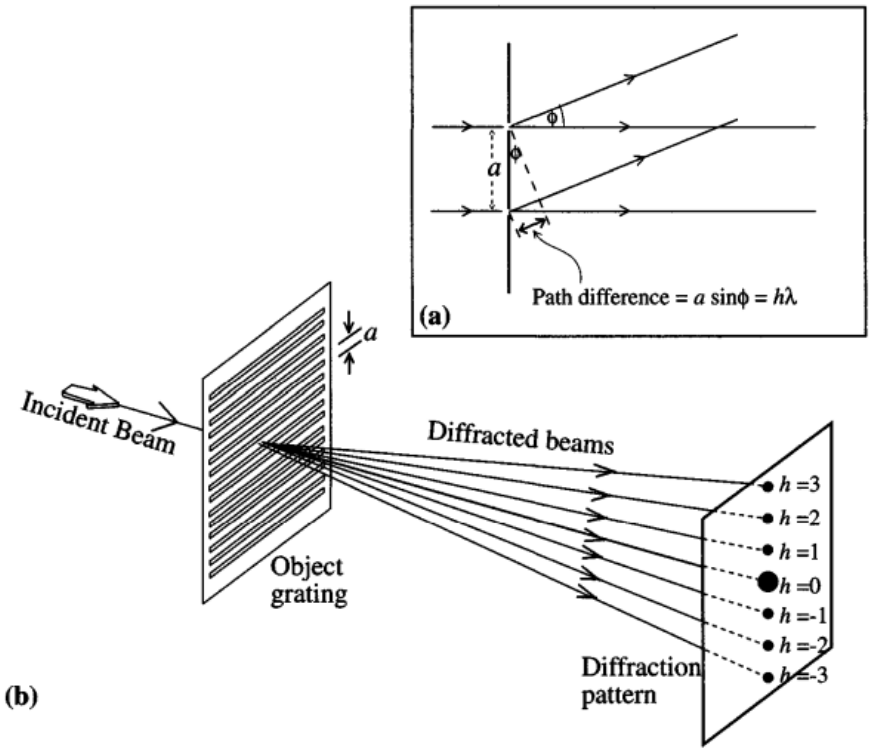
Diffraction and Crystallography

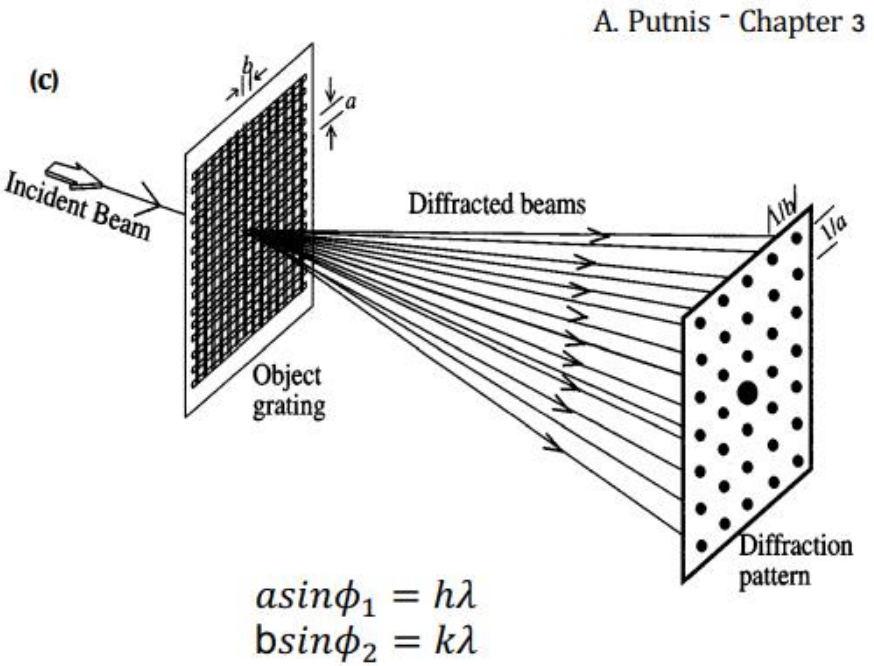






An overview of Optical Diffraction

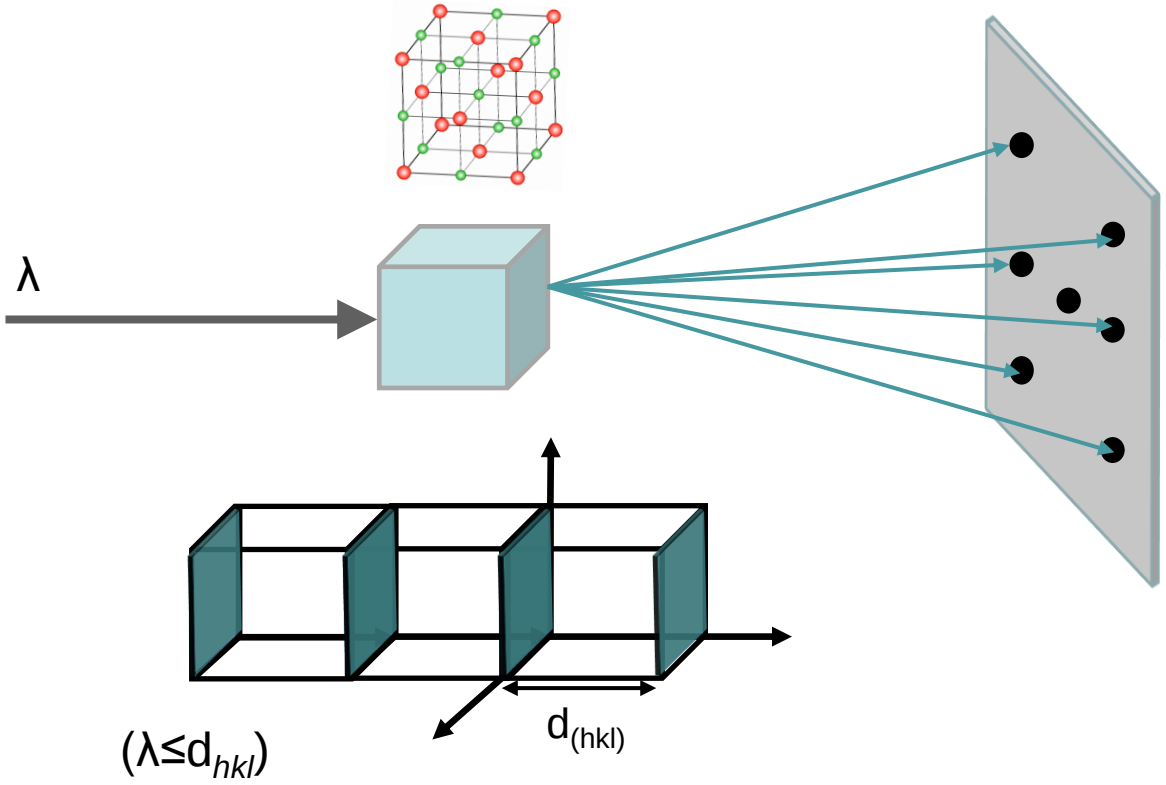




Conclusions:

1. For a diffraction pattern to be formed, the distance between the slits (a) can't be smaller than λ. Otherwise, that would lead to the sin of the angle > 1. Thus $a \sim \lambda$.
2. The spacing in the diffraction spots is reciprocally related to the slit spacing in the grating.
3. The direction of the row of spots in the diffraction pattern is normal to the lines of the grating.

Crystal Diffraction



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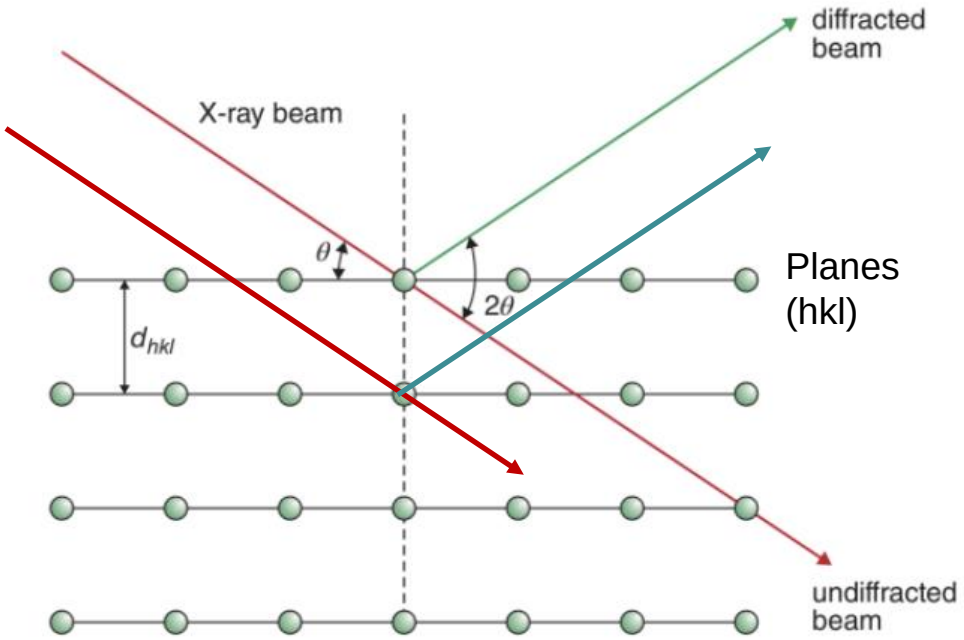
Diffraction and Crystallography: Bragg's Equation

- Consider the diffraction of X-rays from atomic planes, shown below. Where *d* is the interplanar spacing. For constructive interference, the path difference between the two rays has to be an integer multiple of the wavelength, nλ. From trigonometry, the **path difference** between the incident and diffracted beam is: **$2d_{hkl}\sin\theta$.**



X-rays: 10^{-8} m ≤ λ ≤ 10^{-10} m

- Bragg's Law represents the inverse relationship between the angle of diffraction (**θ)** and the interplanar spacing (distance between repeating lattice points in real space) and thus, *defines* the orientation conditions for the crystal to undergo coherent scattering.

Real space and reciprocal space

Conclusions:

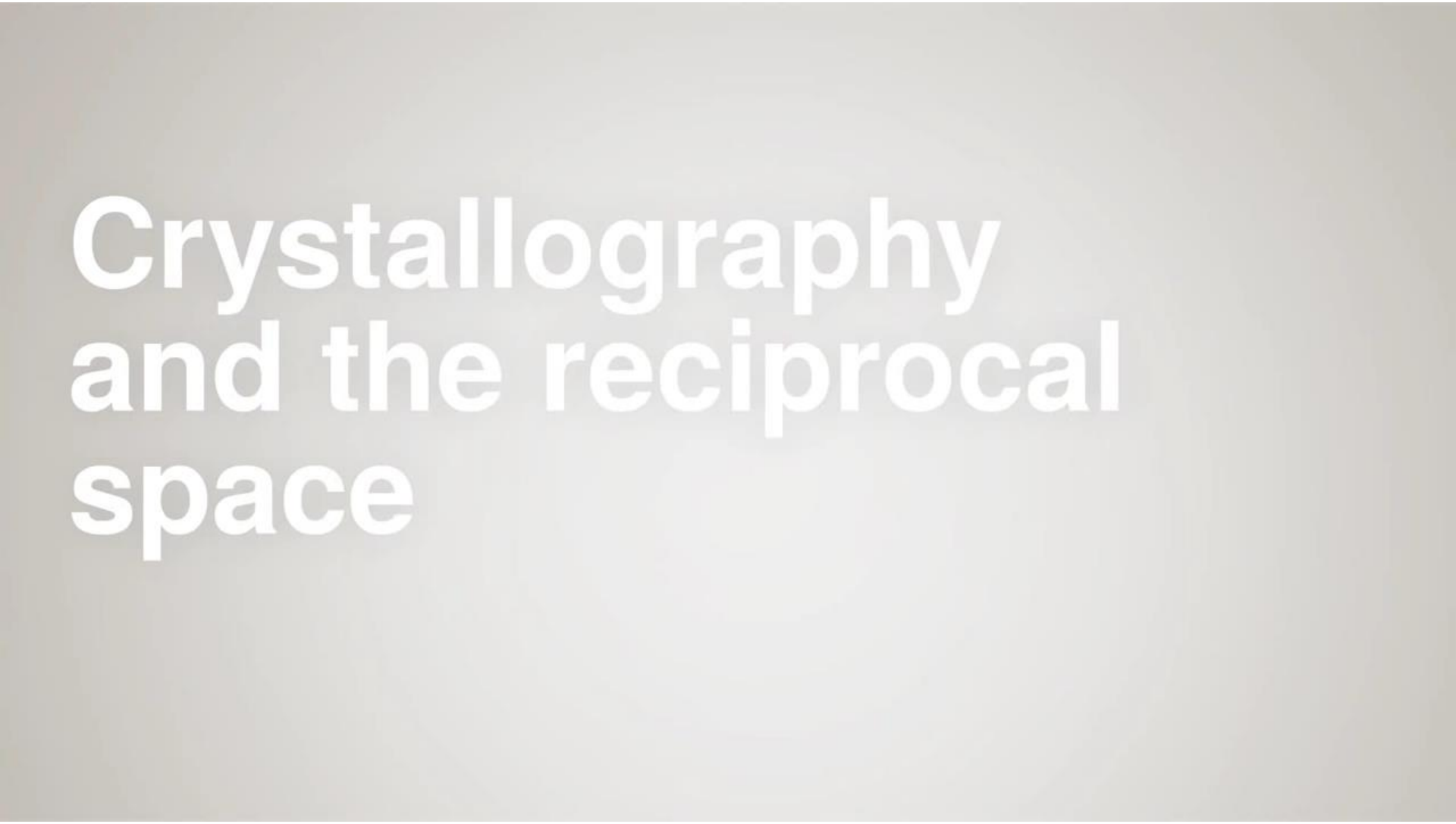
1. For a diffraction pattern to be formed, the distance between the slits (a) can't be smaller than λ. Otherwise that would lead to the sin of the angle > 1. Thus $a \sim \lambda$.

2. **The spacing in the diffraction spots is reciprocally related to the slit spacing in the grating.**

3. **The direction of the row of spots in the diffraction pattern is normal to the lines of the grating.**

https://www.youtube.com/watch?v=DFFU39A3fPY

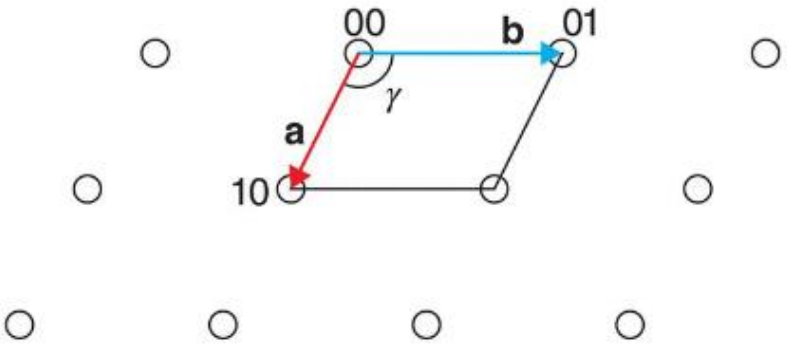
Real space and reciprocal space



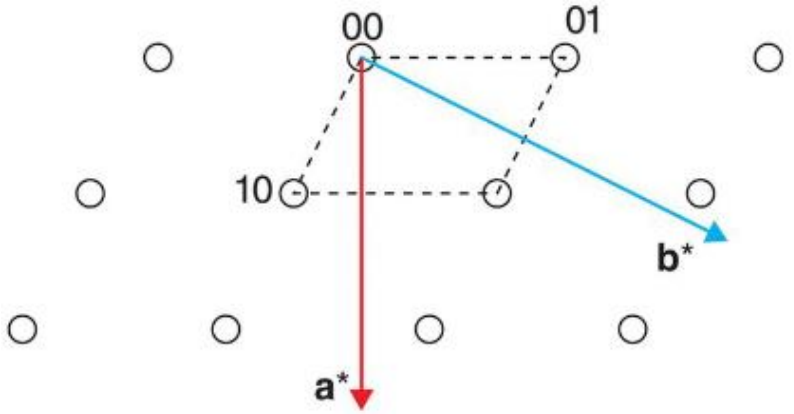
https://www.youtube.com/watch?v=DFFU39A3fPY

Reciprocal space construction in 2D

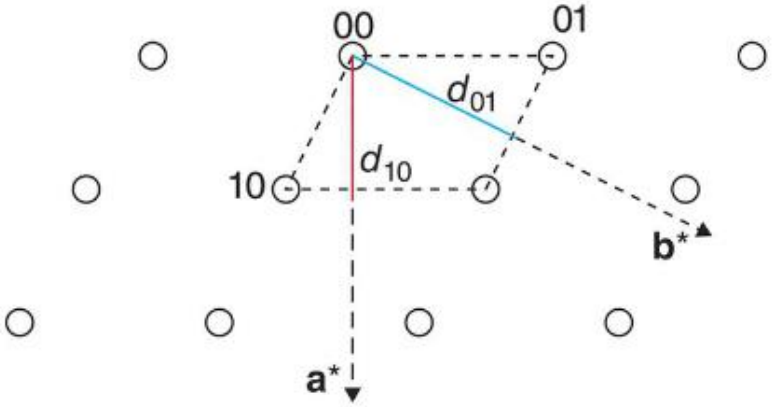
1. Draw the lattice and mark the unit cell.



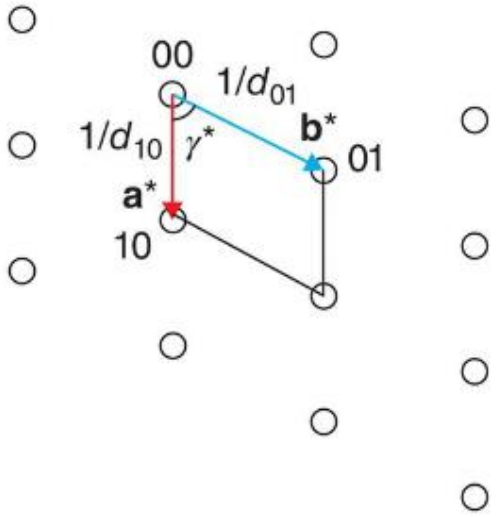
2. Draw lines perpendicular to the sides of the unit cell:



3. Determine the perpendicular distances from the origin of the real lattice to the end faces of the unit cell, d:

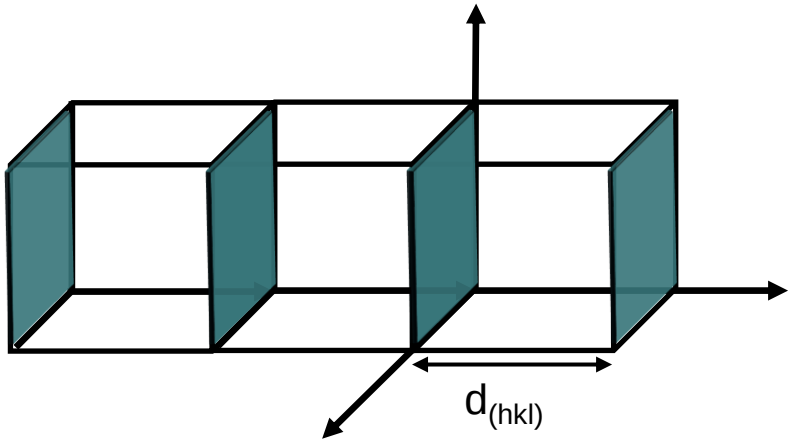


4. The reciprocal lattice axial lengths, a* and b* mark the reciprocal unit cell:



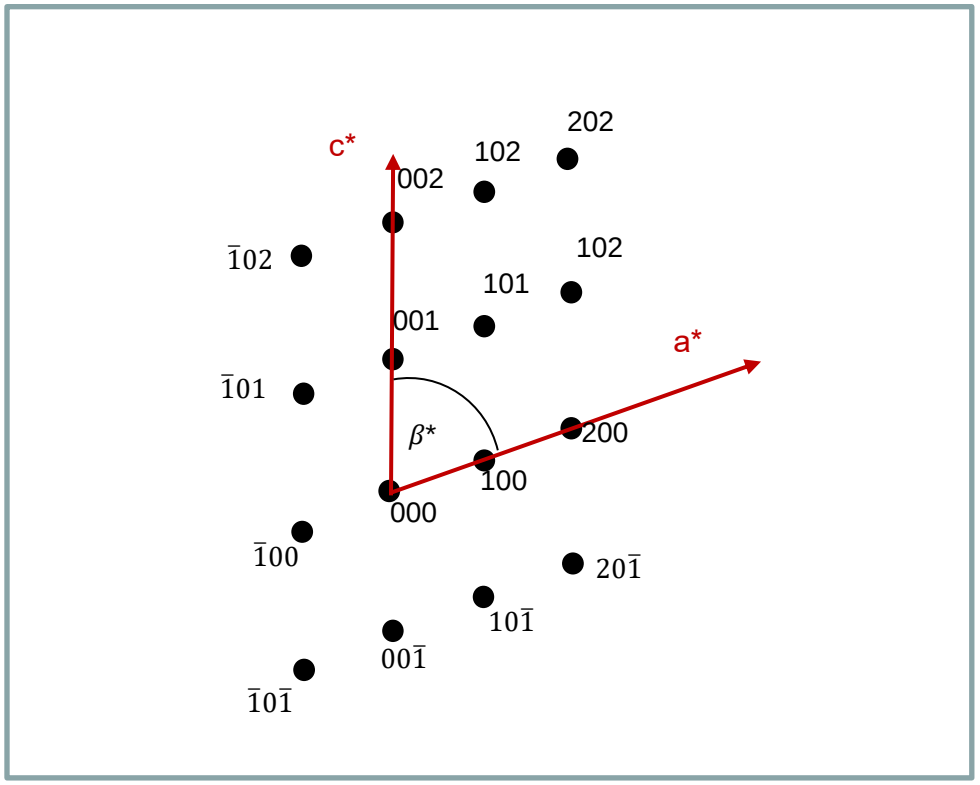
Real space and reciprocal space

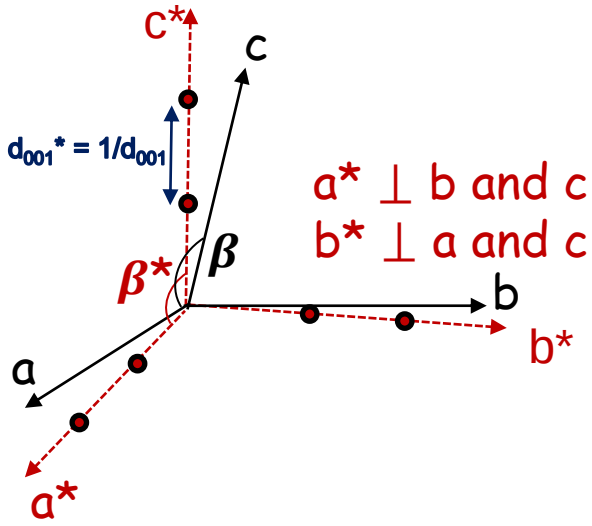
Due to the linear relationship between planes, a periodic lattice can be generated: The reciprocal vector from the origin to each spot is *perpendicular to the atomic plane (hkl) producing a diffraction spot (or reflection)*, and the magnitude vector is <u>*reciprocally*</u> related to the inter-planar spacing (d_{hkl}) of those atomic planes.



$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \Rightarrow \quad \frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{4\,sin^2\theta}{\lambda^2}$$

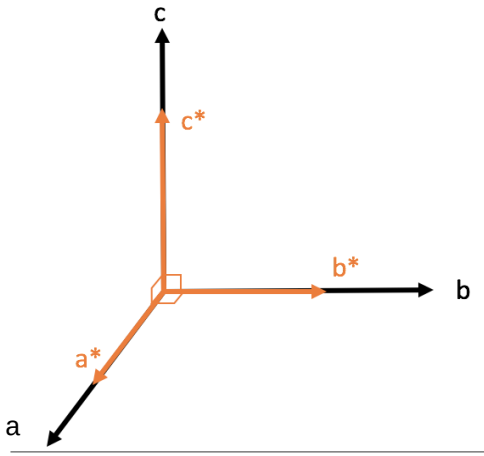
Constructing the Reciprocal Lattice





- All atomic planes can potentially contribute to the diffraction pattern and so every plane is associated with a reciprocal lattice spot.
- However, the reciprocal lattice itself is defined by PRIMARY RECIPROCAL LATTICE VECTORS which boil down to being the reflections expected from the planes of the unit cell of the crystal: (100), (010), (001).
- **RULES of RECIPROCAL LATTICE CONSTRUCTION:** Each reciprocal lattice vector **is perpendicular to the plane** with which it is associated AND of magnitude reciprocal to the interplanar separation ($\boldsymbol{d^*_{hkl}} = \frac{\mathbf{1}}{\boldsymbol{d_{hkl}}}$) of successive parallel planes with which it is associated.

Real space and reciprocal space



In *real space*, a lattice vector is: $\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$

A reciprocal lattice vector can be defined in the same way:

$$\mathbf{r^*} = h\mathbf{a^*} + k\mathbf{b^*} + l\mathbf{c^*} = \boldsymbol{d}^*_{hkl}$$

(sometimes called vector *g*)

where *h, k and l* are the Miller indices of the crystal plane *(hkl)* & a*, b* and c* define the reciprocal space vectors - similar to the real space crystal with lattice vectors a, b, c.

The relation between the real and reciprocal space lattice vectors is:

$$a^* = \frac{bxc}{a\cdot(bxc)} = \frac{bxc}{V} \qquad b^* = \frac{cxa}{b\cdot(cxa)} \qquad c^* = \frac{axb}{c\cdot(axb)}$$

From these definitions it is apparent that a* is normal to the plane containing b and c, and its magnitude is equal to the reciprocal of the spacing of the (100) planes in real space. Such that:

$$a^* = \frac{1}{a} \quad \text{and} \quad \boldsymbol{d}^*_{\boldsymbol{hkl}} = \frac{1}{d}$$

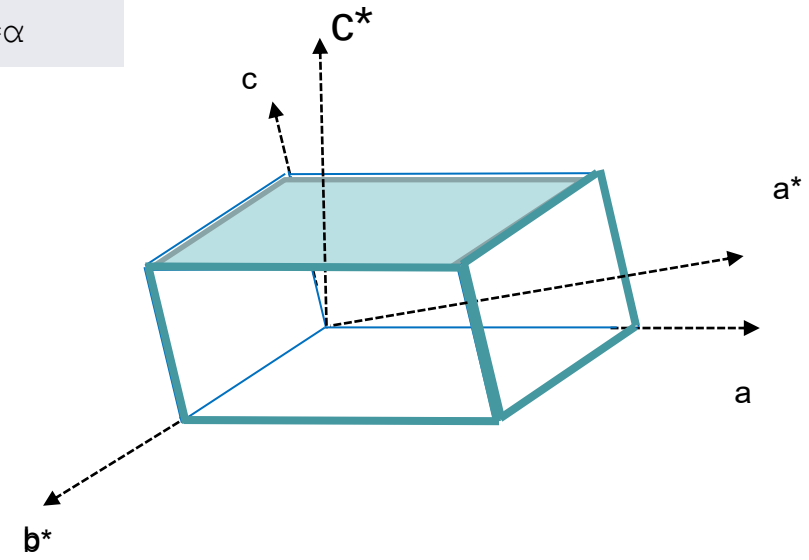
In crystals with orthogonal axes the reciprocal lattice vectors are parallel to the real space ones. Hence the following relationships:

a* · b = 0	b* · c = 0	a* · a = 1
a* · c = 0	c* · b = 0	b* · b = 1
b* · a = 0	c* · a = 0	c* · c = 1

Example 1

Monoclinic system: a ≠ b ≠ c;
α = **γ** = 90∘ ; **β** ≥ 90∘

Lattice angles
aΛb=γ
aΛc=β
bΛc=α



Lengths:

$$a^* = \frac{1}{d_{100}} = \frac{1}{a\ sin\beta}$$

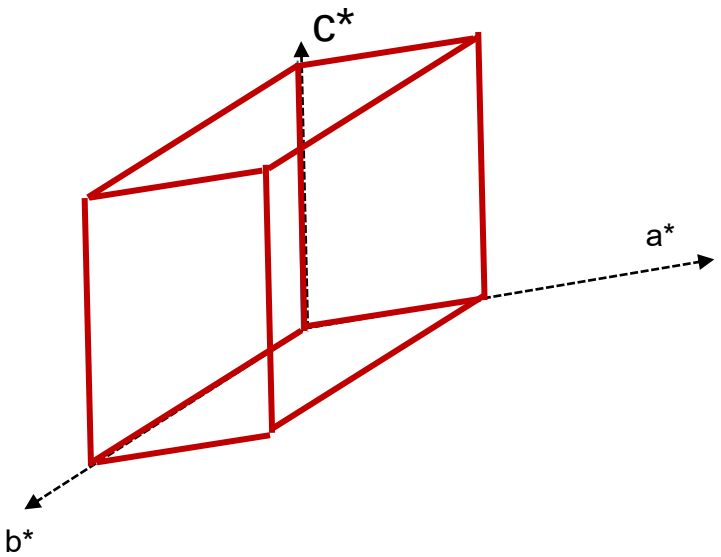
$$b^* = \frac{1}{d_{010}}$$

$$c^* = \frac{1}{d_{001}} = \frac{1}{a\ sin\beta}$$

a* is not parallel to a

b* is parallel to b

c* is not parallel to c



Q: Draw the reciprocal space unit cell for an tetragonal crystal system with the following lattice parameters…

EXAMPLE 2

SiO_2 - quartz - trigonal (a=b, $\gamma=120^o$)

a=4.913Å

c=5.405Å

Calculate the separation between (110) planes in quartz:

EXAMPLE 3

Rutile (TiO_2) has a tetragonal structure ($P4_2/mnm$) with the lattice parameters:

a = 4.59 Å

c = 2.96 Å

i. Draw the reciprocal lattice a^* - c*.

ii. Draw the reciprocal lattice section perpendicular to the [110] real space direction

Summary: Reciprocal space and diffraction

- Families of crystallographic real space planes {hkl} can be represented simply by their normal vectors which form the reciprocal lattice. The reciprocal lattice can be used to define a diffraction pattern, where each point represents a set of parallel planes. Reciprocal space is diffraction!

- All planes of atoms can *potentially* contribute to the final diffraction pattern.

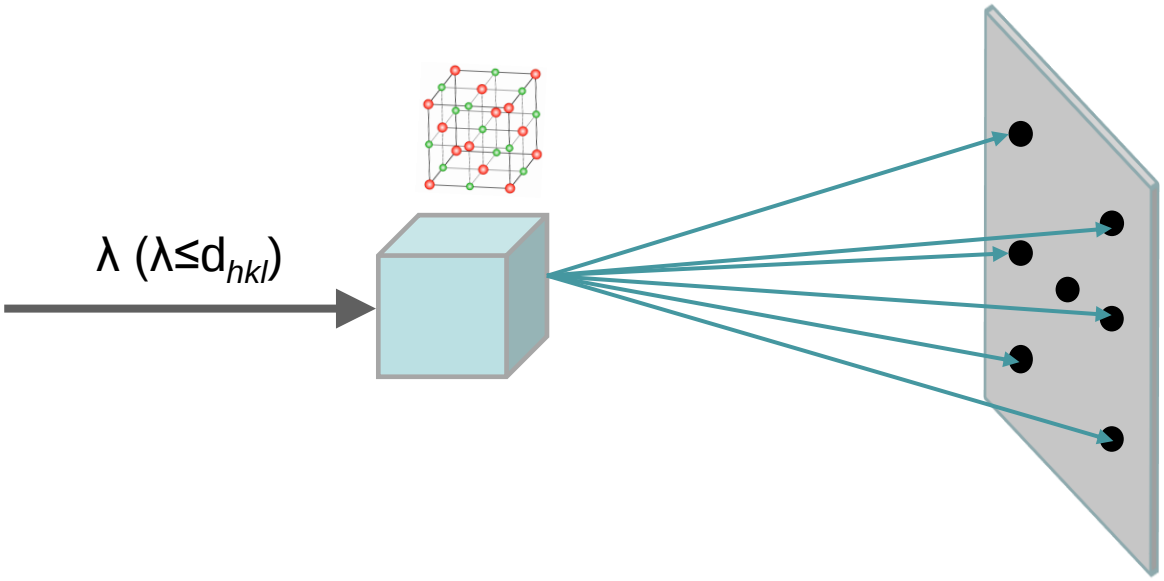
- A diffraction pattern (an array of spots) results from sets of parallel planes (hkl) which are represented by a single diffraction spot.

- Mathematically, diffraction corresponds to a Fourier Transform of the geometry in real space.

Reciprocal Lattice remarks

- The most used technique to determine a crystal structure is some form of diffraction; methods include x-ray, electron and neutron diffraction. The patterns resulting from crystal diffraction are more easily represented & analysed using the concept of *reciprocal lattice*.
- *Reciprocal lattice and the Ewald sphere* provide a simple geometrical basis for understanding the geometry of diffraction patterns & the behaviour of electrons in crystals.

Ewald Sphere



For a particular set of planes (hkl) to undergo diffraction, a distinct geometrical relationship must exist between, as detailed by Braggs' equation:

- the wavelength (λ),
- the spacing between successive planes (d_{hkl})
- the angle of incidence (θ).

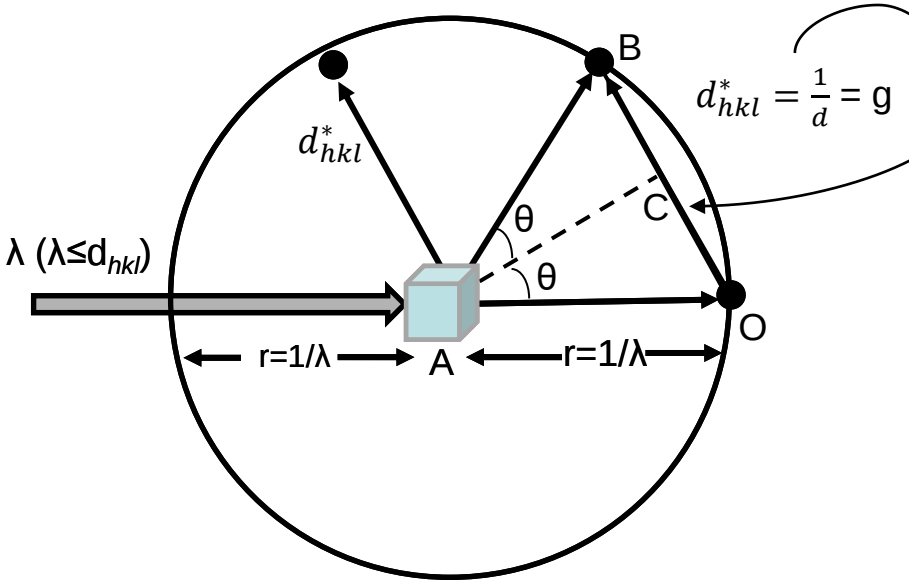
Ewald Sphere

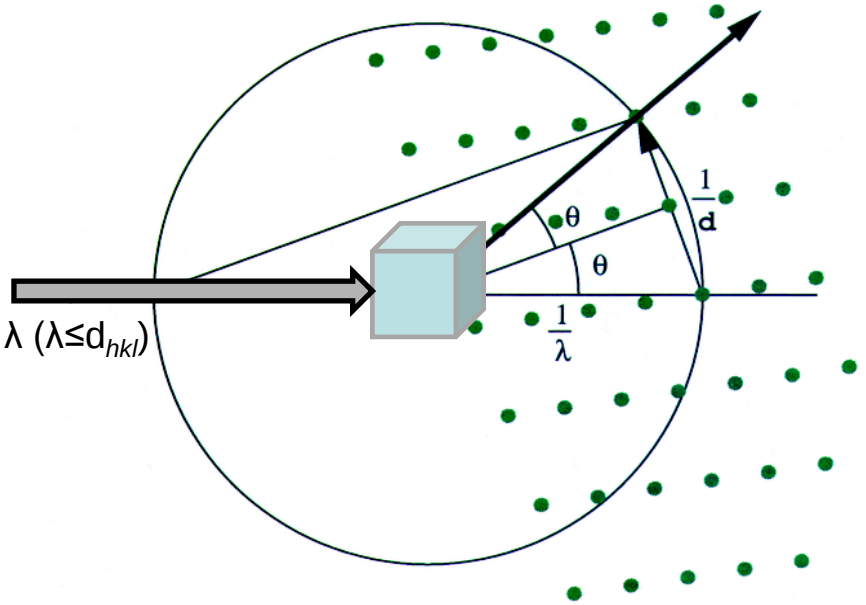
- Only the reciprocal lattice points that intersect the Ewald sphere represent the points for which the Bragg condition is satisfied.

- g_{hkl} is the reciprocal vector that represents the solutions to the Bragg equation: $g_{hkl} = d_{hkl}^* = 1/d_{hkl}$

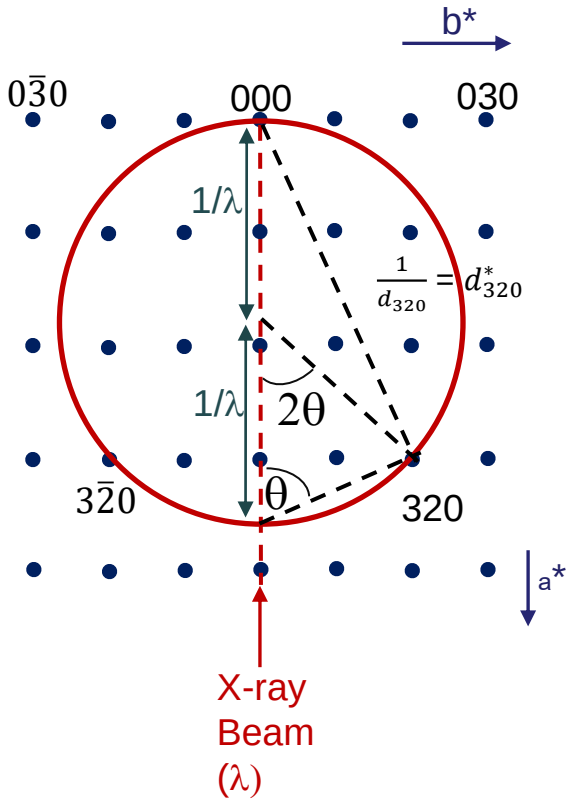
- All g vectors must lie at a radial distance 1/λ from the point of diffraction. Hence all the solutions to Bragg's equation lie on a sphere with r =1/λ: The **Ewald Sphere**.

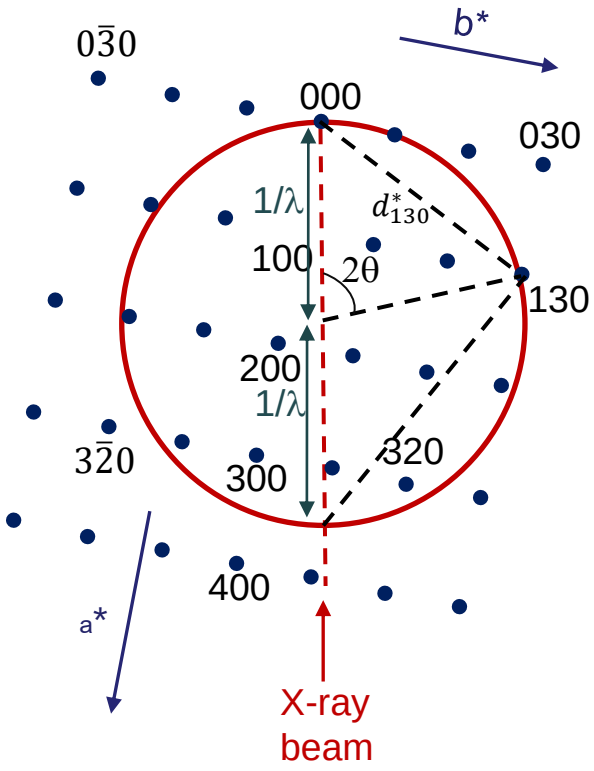
  - The observed diffraction pattern is the *intersection* of the reciprocal space lattice & the Ewald Sphere.
  - Each point in the reciprocal lattice represents a set of planes
  - Translational symmetry in the real space lattice results in the *systematic absence* of certain classes of reflections in the reciprocal lattice – destructive interference (forbidden reflections).





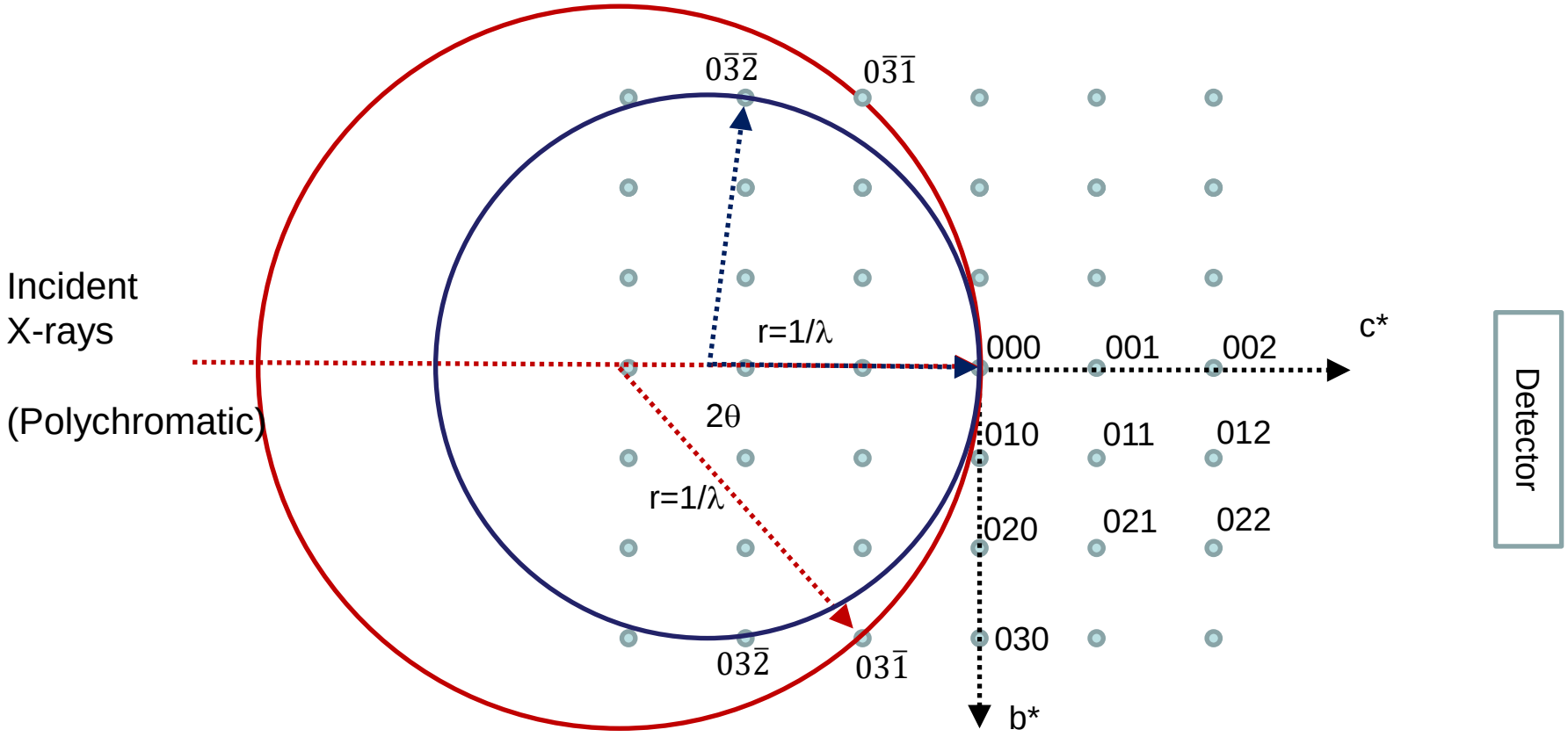
Ewald sphere and Crystal rotation





- The orientation of the reciprocal lattice is coupled to the orientation of the crystal.
- Rotation of the crystal about the centre of the Ewald sphere results in an equivalent rotation of the reciprocal lattice about the reciprocal-lattice origin
- To observe the diffraction from a number of reflections, the reciprocal-lattice points have to be moved to the surface of the Ewald sphere, or the sphere radius has to be changed so that different reflections will lie on its surface.

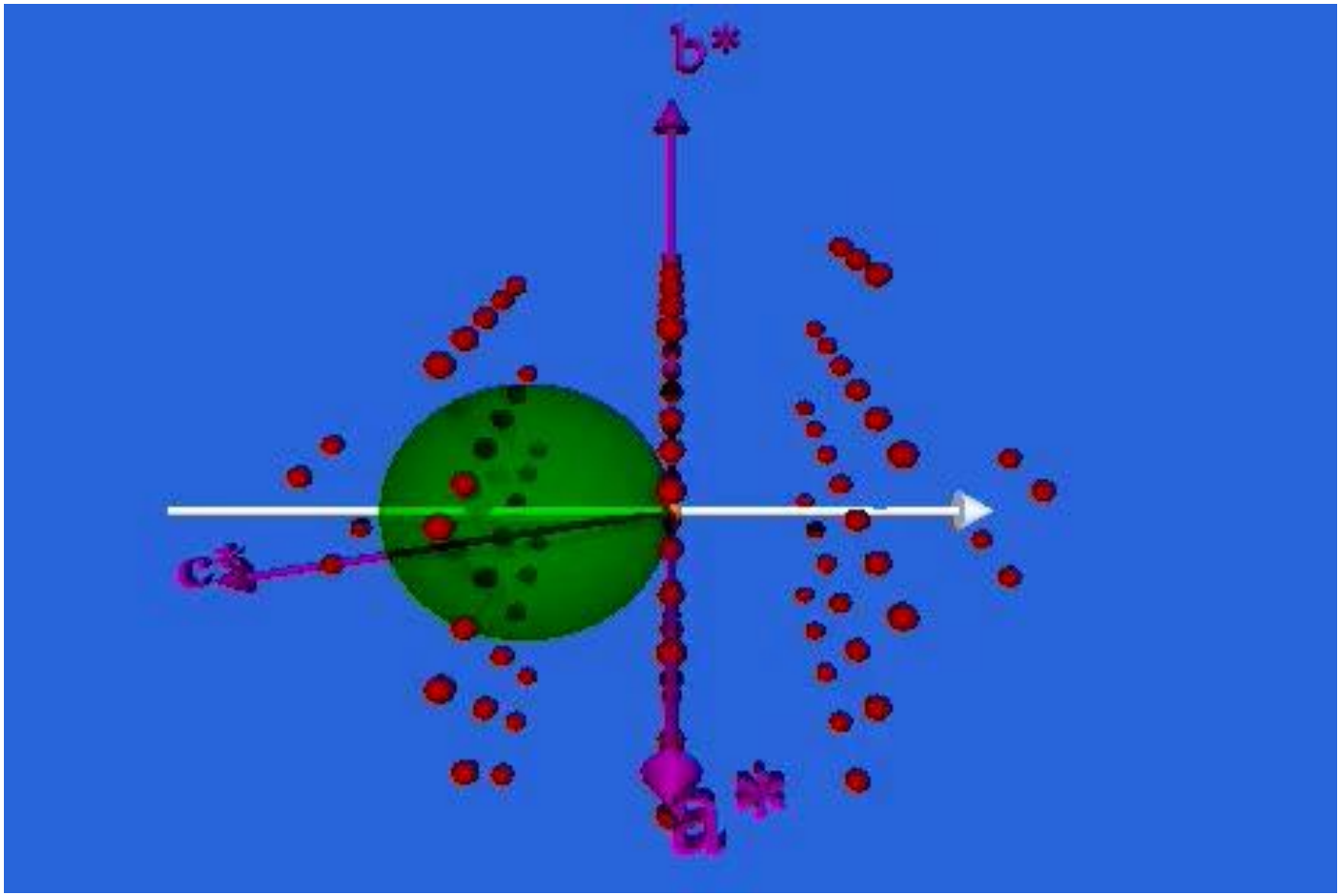
Ewald Sphere and various wavelengths.



- All geometrical considerations of diffraction can be rationalized using the concept of the Ewald sphere: Bragg's law of diffraction in three dimensions.
- The radiation (λ) is represented by a sphere of radius 1/λ.
- The crystal is represented by the reciprocal lattice, with its origin at the point on the Ewald sphere where the direct beam leaves it
- If the reciprocal lattice point lies on the surface of the Ewald sphere, Bragg's law is satisfied: when a reciprocal-lattice point with indices (*hkl*) lies at the surface of the Ewald sphere, the interference condition for that particular reflection is fulfilled and it gives rise to a diffracted beam directed along the line joining the sphere centre with the reciprocal-lattice point at the surface.

Q: Explain what the Ewald sphere is and how can it be used to determine the crystal orientations in an observed diffraction pattern.

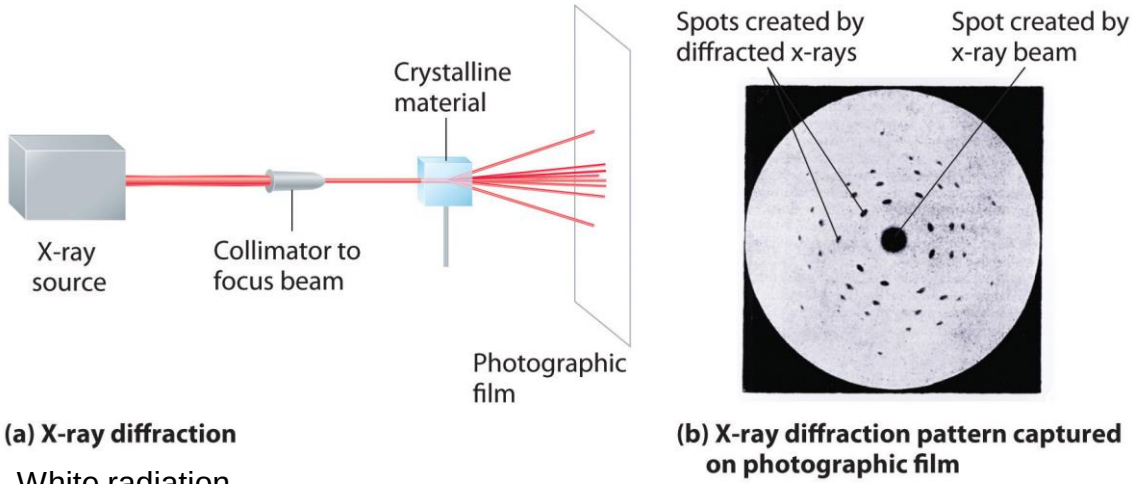
DoITPoMS - Ewald Sphere animation



https://www.epfl.ch/schools/sb/research/iphys/teaching/crystallography/ewald-sphere-animation/

Laue Diffraction (transmission)

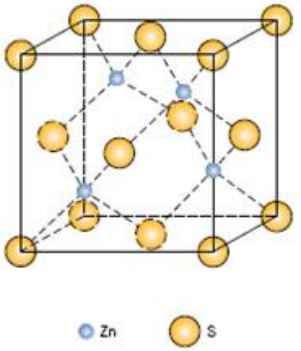
To ensure that Bragg's law is satisfied for must of the planes in a fixed single crystal, a range of wavelengths in the beam is then necessary (white radiation).



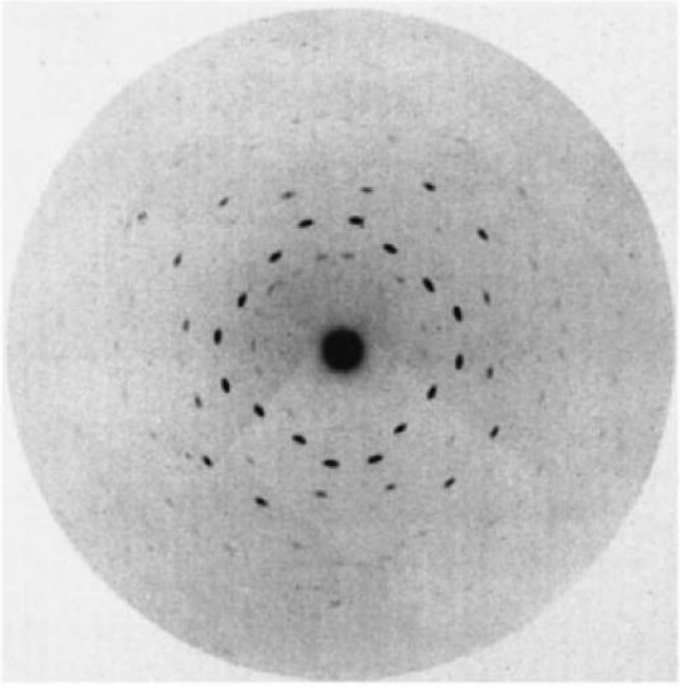
White radiation

- For Laue diffraction, either a transmission photograph or a back-reflection photograph may be taken.
- The pattern of spots which are produced lie on "ellipses" in the transmission case.
- All spots on any ellipse are reflections from planes of a single axis and, consequently, *the Laue pattern is able to indicate the symmetry of the crystal.*

Examples of Laue Photographs of ZnS

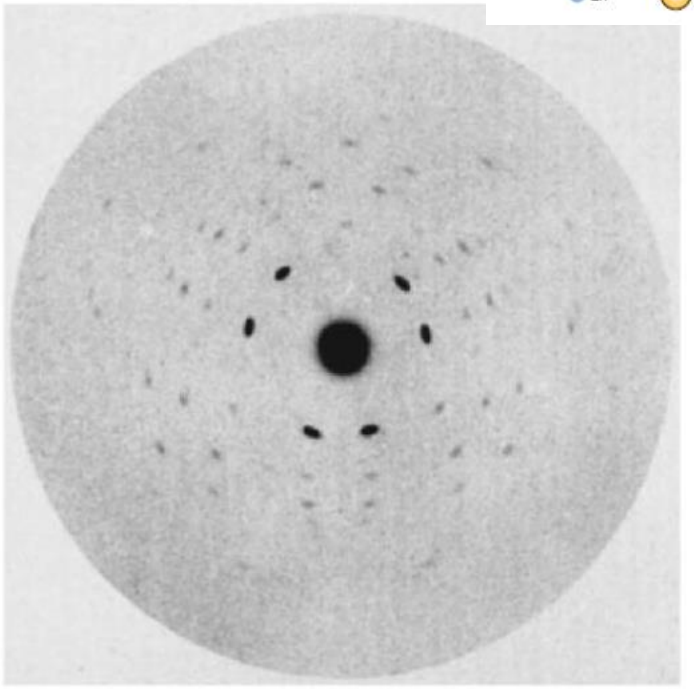


$\bar{4}3m$



Primary beam normal to (001)

4-fold axis

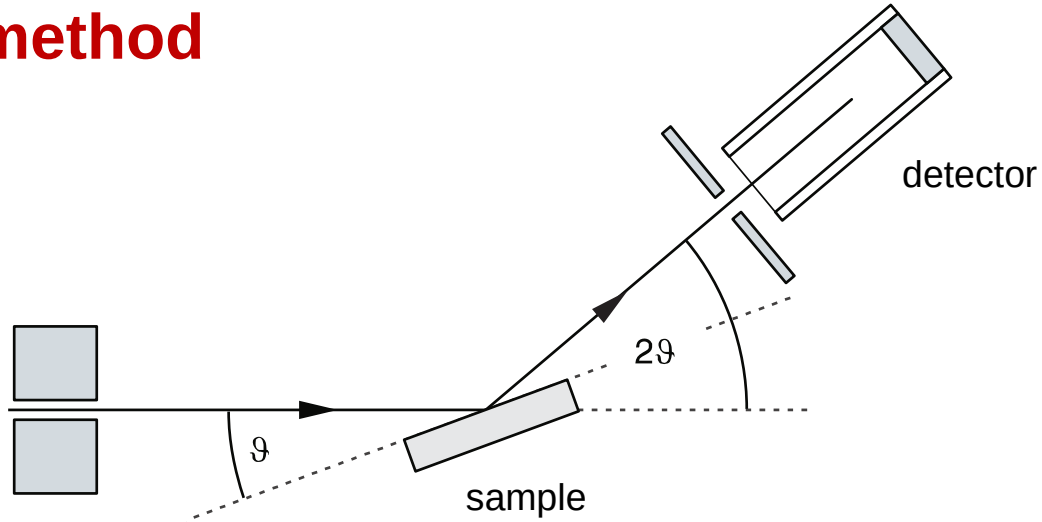


Primary beam normal to (111)

3-fold axis

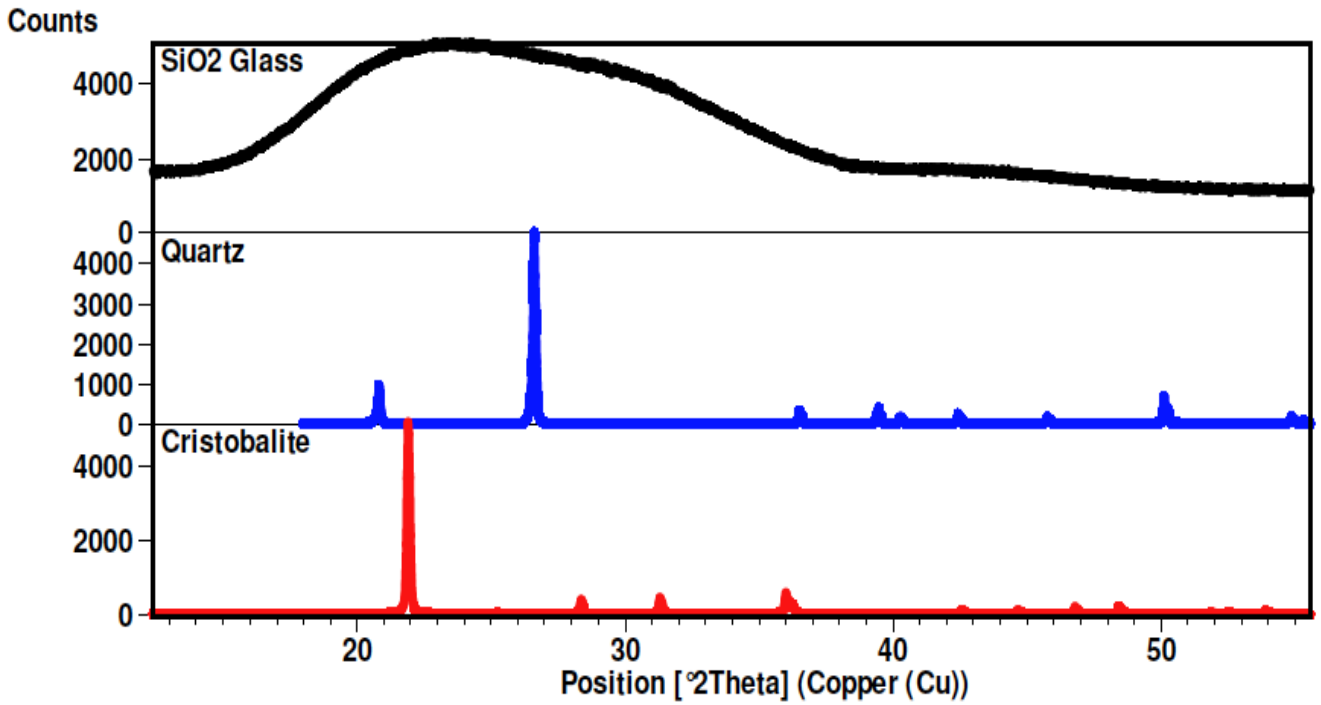
Rotating crystal method

Q: Explain the difference between a transmission Laue photograph and a Bragg-Brentano (single crystal) Scan.



- This condition is known as Bragg-Brentanno geometry, and uses a monochromatic X-ray beam from a source that is fixed, and the incident angle θ is variable by rotating the crystal orientation.
- In this reflection geometry, the incident angle (between the x-ray source and sample) is always half of the diffraction angle (between the detector and the incident beam. Thus, the diffraction angle is always 2θ.
- Mainly used in Powder diffraction, as one of the most important material characterization methods.
- In X-ray diffraction of powered materials all possible reflections present in reciprocal space can be sample up to a certain limit of *hkl* size. For single crystal work, only specific sections of reciprocal space will be sampled.

XRD patterns: Diffractogram



- Every x-ray reflection is characteristic of a unique (hkl).
- Each (hkl) can be associated to an intensity, equivalent to the intensity of the diffracted beam from the equivalent (hkl) planes.
- The intensity of the peaks depends on the atomic structure of the material: the position of atoms in the unit cell.