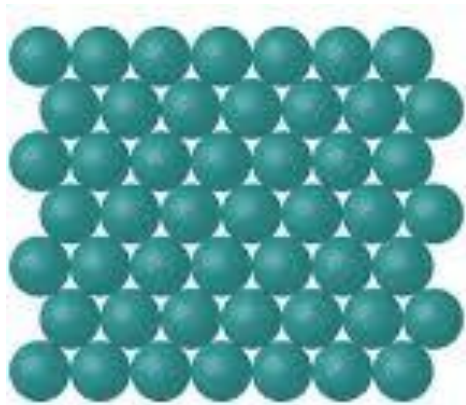
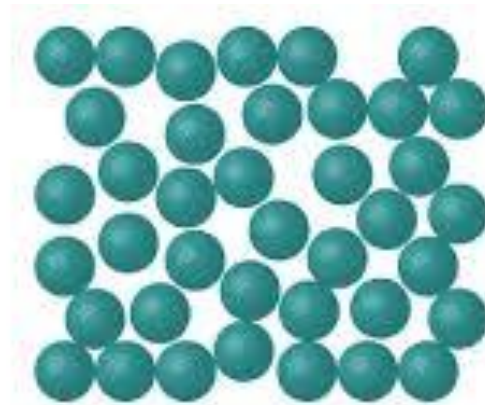


X ray Diffraction (XRD)

Concepts in Crystallography



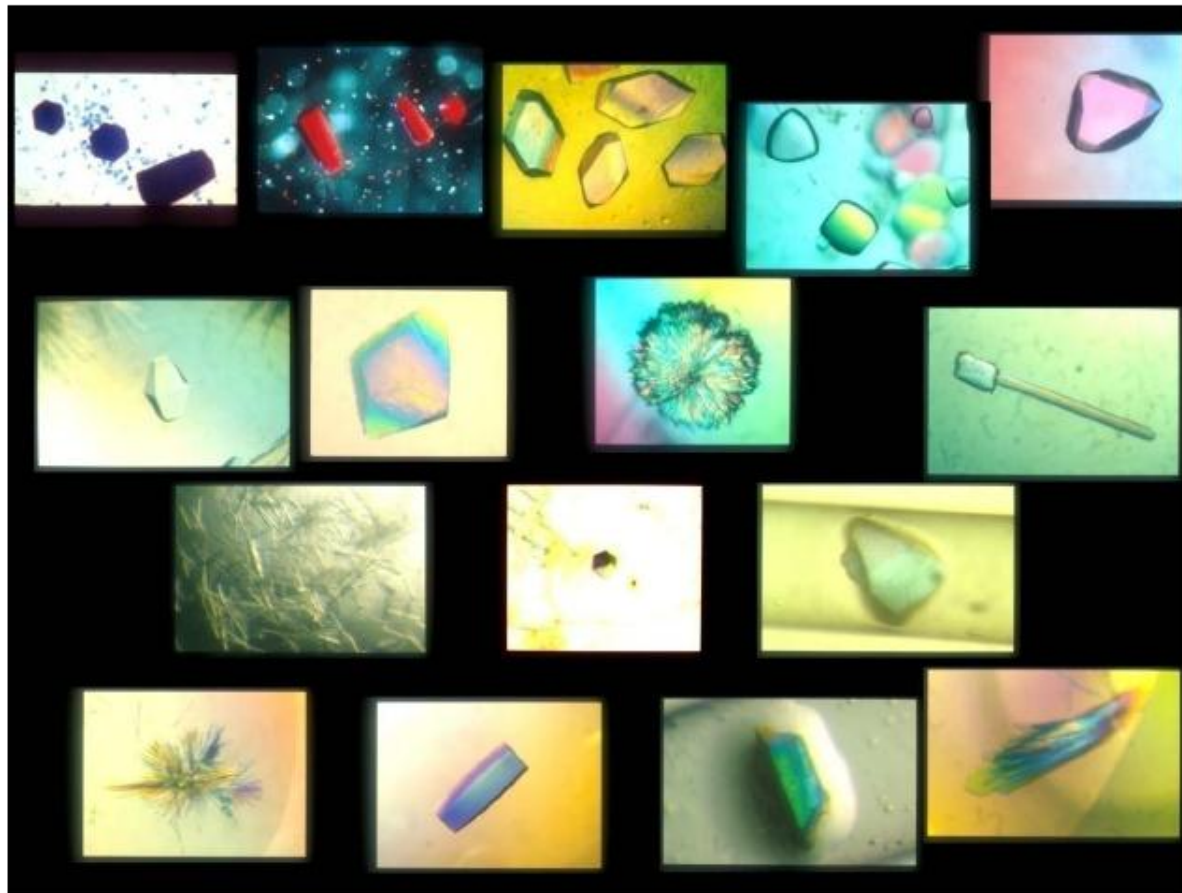
Crystalline



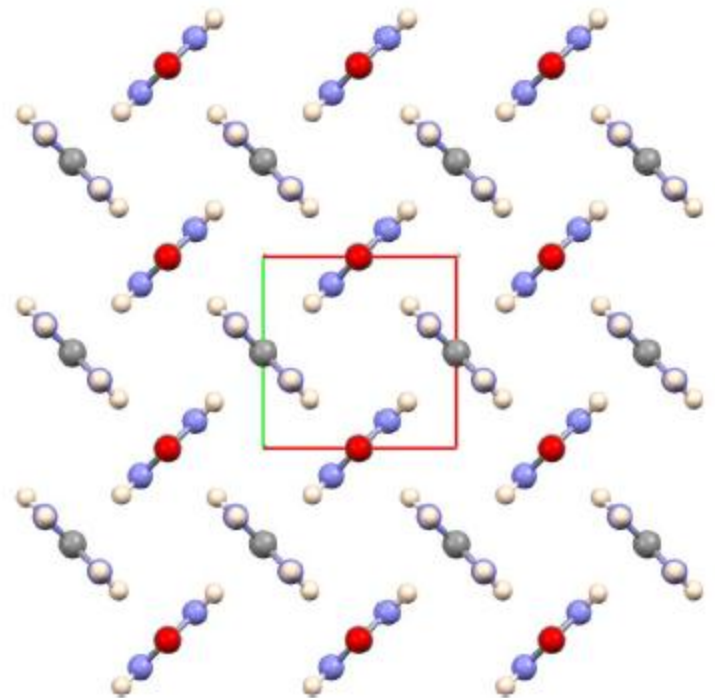
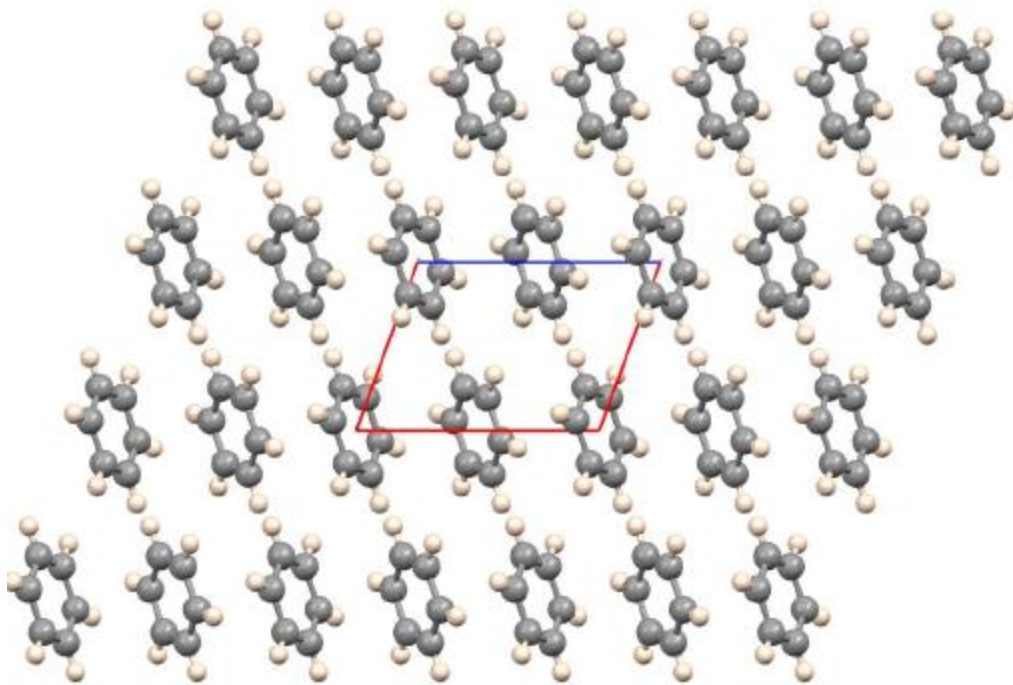
Amorphous

Crystallography deals with crystals

° A crystal is a solid with an orderly, repeating arrangement of atoms



Repeating Arrangements of Atoms or Molecules



Crystalline solids

- Particles are highly ordered & in repeating patterns
- Long Range Order
- Sharp Melting Point
- Well developed symmetry
- Ex: snow, sodium chloride, sugar



The atoms or ions arrange in a pattern that repeats itself in three dimensions to form a solid which has long-range order.

Amorphous solids

- Rigid and appear solid
- Short-Range order
- Don't have a specific pattern
- Referred to as supercooled liquids
- When heated particles get softer and softer before they melt
- Ex: glass, rubber, plastics



Difference between crytsalline and amorphous solids

1) Characteristic geometry

A crystalline solid has a **definite and regular geometry** due to definite and orderly arrangement of molecules or atoms or ions in 3 dimensional space.

Amorphous solid does **not any pattern of arrangement** of molecules or atoms and therefore does not have any definite geometrical shape. Even if some orderly arrangement of molecules or atoms exists in a few amorphous solids, it does not extend more than a few Angstrom units. Thus unlike crystalline solids, amorphous solids do not have a long range order

Melting point: With increase in temperature the molecular vibrations increase and ultimately become so great that molecules break away from their fixed positions. They now begin to move more freely and have rotational motion as well. The solid now changes into liquid state. The temperature at which this occurs is known as the melting point.

2) Melting point

Crystalline substance has a **sharp melting point** i.e. it changes abruptly into liquid state

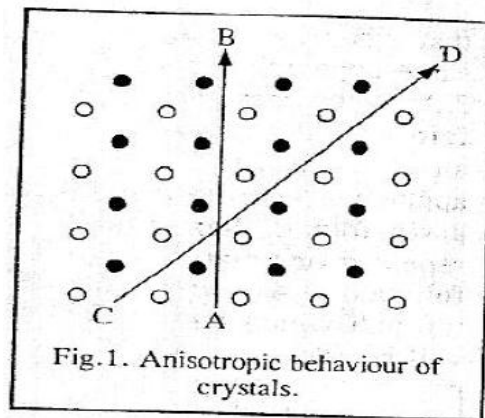
Amorphous solid does **not have sharp melting point**. E.g. if glass is heated gradually, it softens and starts to flow without undergoing a definite and abrupt change.

3) Isotropy and anisotropy

Crystalline solids are **anisotropic**, i.e. their physical properties are different in different directions. E.g. velocity of light passing through a crystal varies with the direction in which it is measured. Thus ray of light entering such a crystal may split up into two components each following a different velocity. This phenomenon is known as double refraction.

Fig.

Properties such as electrical conductivity, thermal conductivity, mechanical strength and refractive index are the same in all directions. Amorphous solids are therefore said to be **isotropic**. Liquids and gases are also isotropic.



4) Size and shape crystals

Several naturally occurring solids have **definite crystalline** shapes which can be recognized easily. There are many other solid materials which occur as powders or agglomerates of the particles and appear to be amorphous. But when an individual particle examined under a microscope, it is also seen to have a definite crystalline shape. Such solids, in which the crystals are so small that they can be recognized only under a powerful microscope, are said to be **microcrystalline**. The size of a crystal depends on the rate at which it is formed : **the slower the rate, the bigger the crystal**. This is because time is needed by the atoms or ions or molecules to find their proper positions in the crystal structure. Thus large transparent crystals of sodium chloride, silver nitrate, lithium chloride etc. can be prepared by melting these salts and allowing them to cool very slowly at a uniform rate. It is for this reason that crystals of most of the **minerals formed by geological processes in nature are often very large**.

5) Interfacial angle:

Crystals are **bound by plane faces** . The **angle between any two faces** is called an interfacial angle. **Although the size of the faces or even shapes of the crystals of one and the same substance may vary widely with conditions of formation, etc. yet the interfacial angles between any two corresponding faces of the crystal remain invariably the same throughout.** Although the external shape is different yet the interfacial angles are the same. The measurement of interfacial angles in crystals is , therefore, important in the study of crystals. The subject is known as crystallography. Fig.

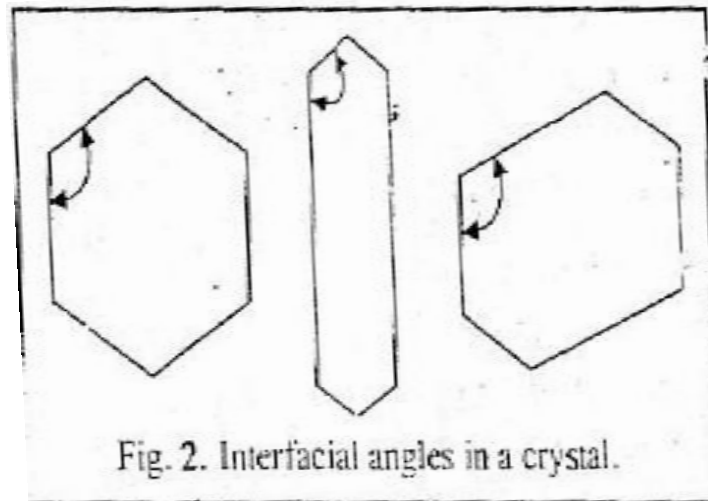
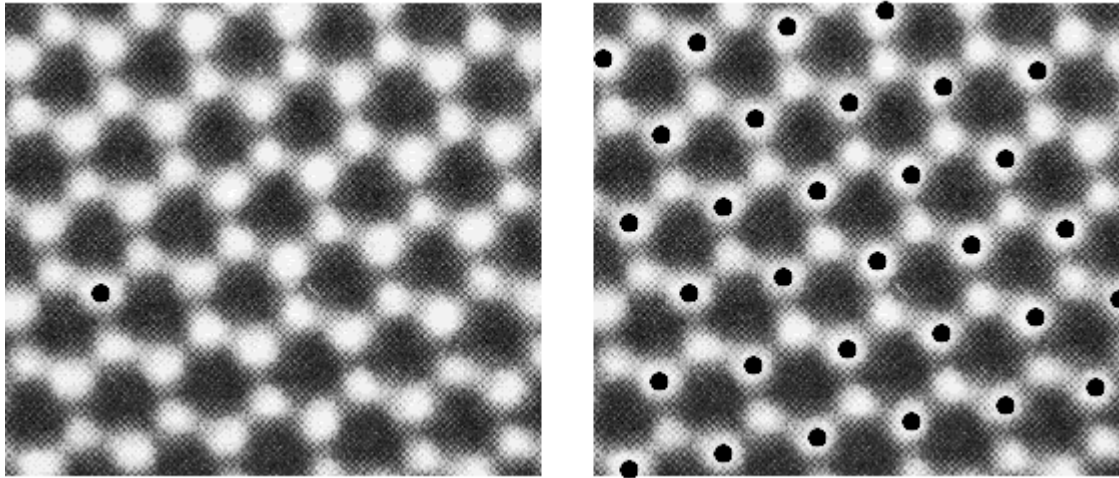


Fig. 2. Interfacial angles in a crystal.

Lattice

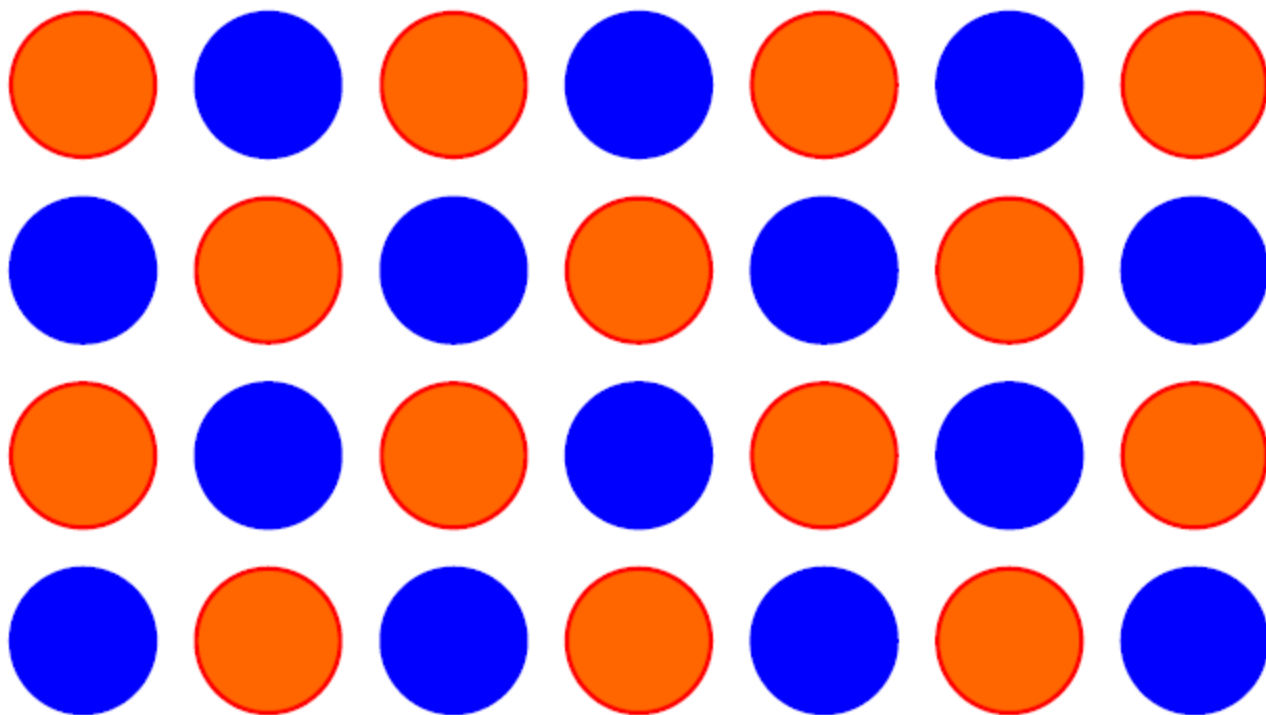
Crystalline structures are characterised by a repeating pattern in three dimensions. The periodic nature of the structure can be represented using a lattice.

To generate the lattice from any repeating pattern, we choose an arbitrary reference point and examine its environment. We then simply mark in all the points in the pattern that are identical to the chosen reference point. The set of identical points is the lattice, and each point within it is a **lattice point**.



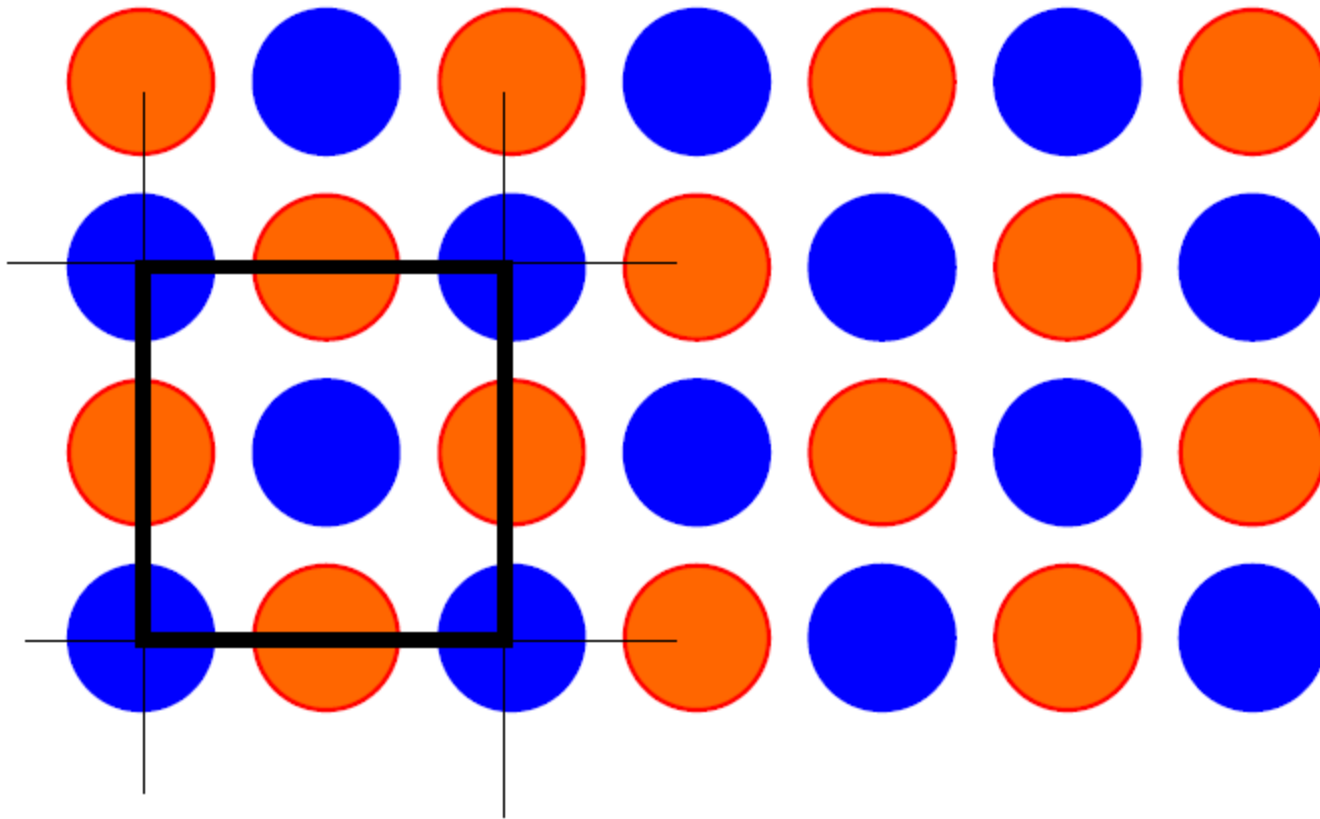
Note that not all white discs within this pattern are exactly equivalent, and therefore they are not all lattice points. The discs marked with a black spot have different arrangements around them than those that are unmarked (each is surrounded by 3 others in a triangle, but the orientation of the triangles is different).

2D example - rocksalt (sodium chloride, NaCl)

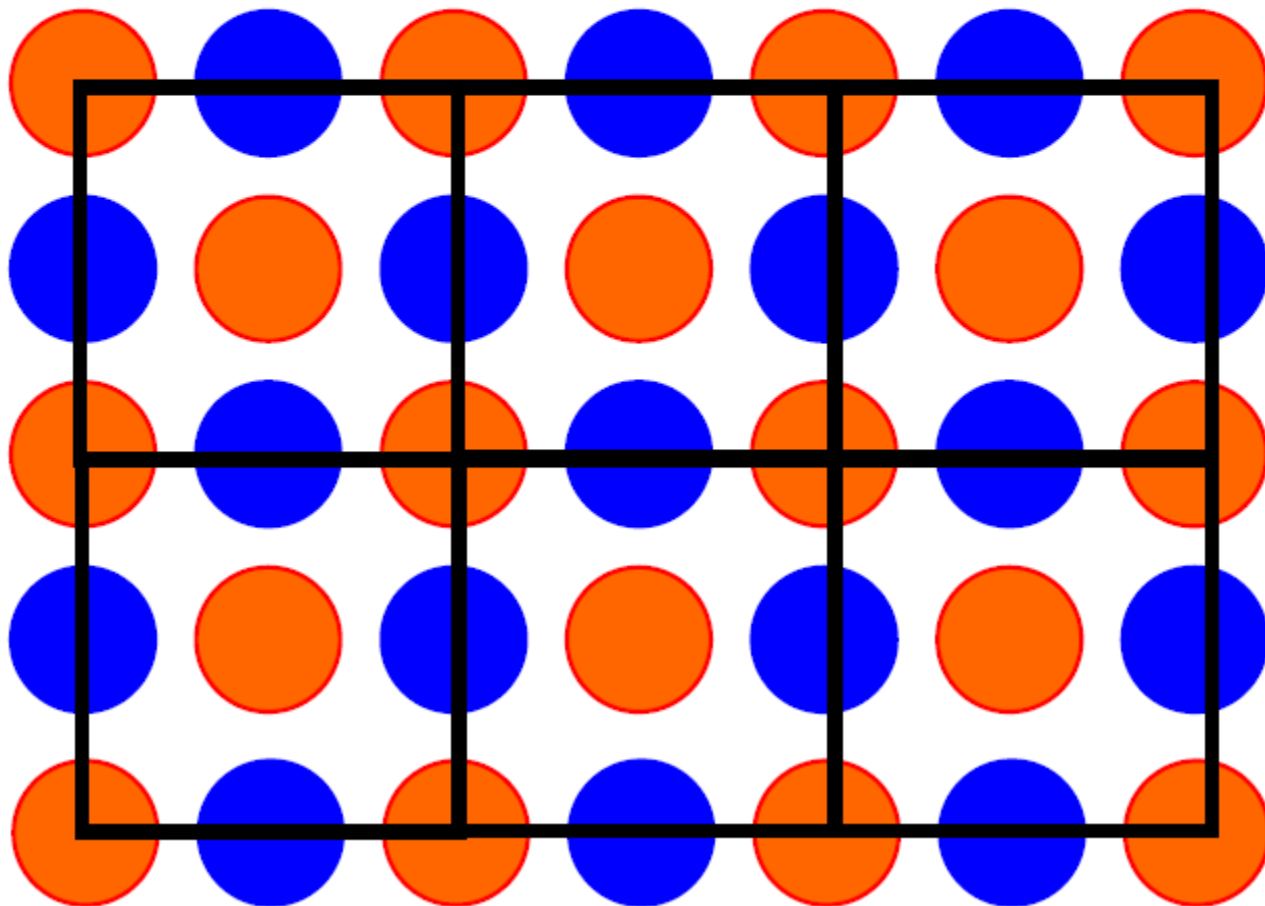


We define **lattice points** ; these are points with *identical environments*

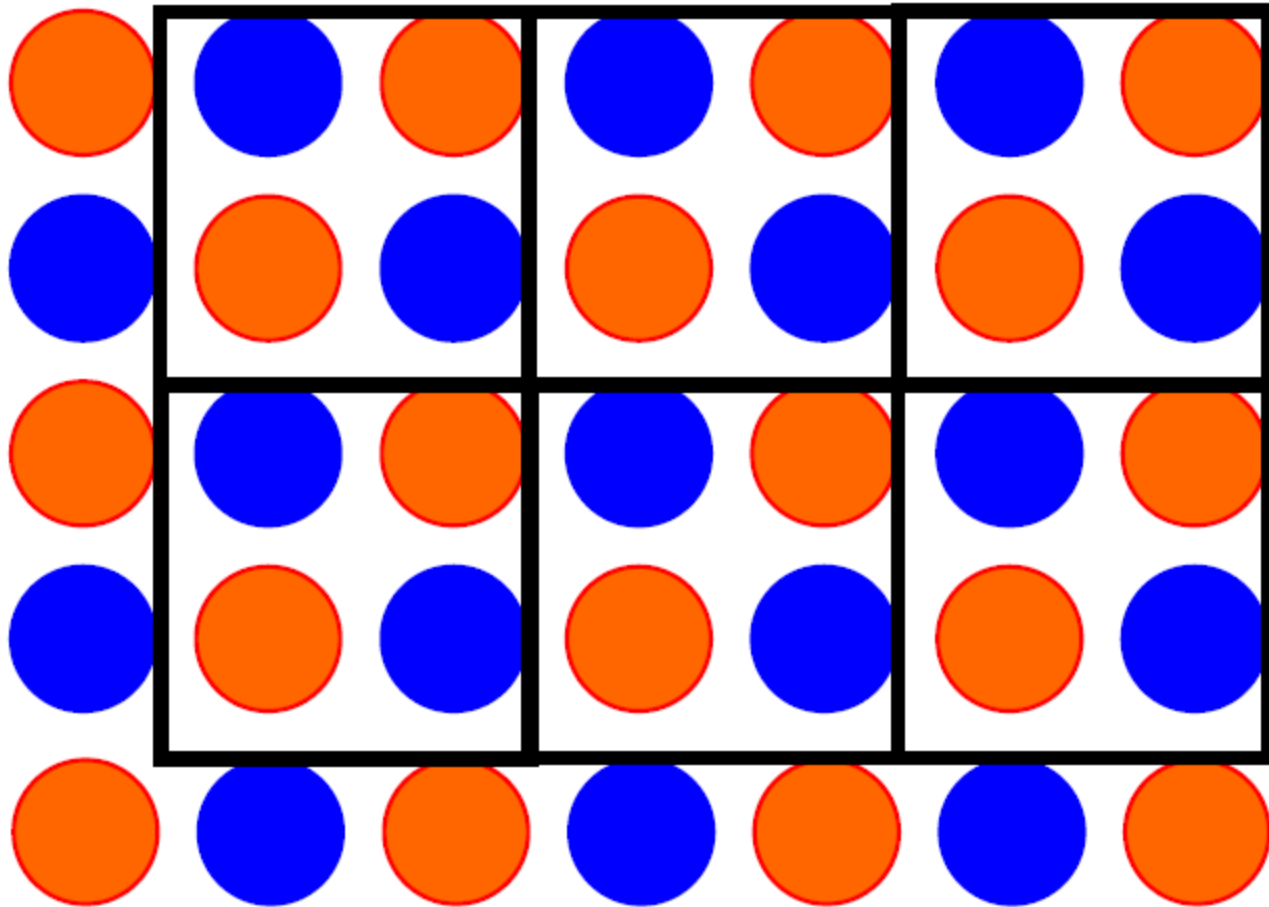
Choice of origin is arbitrary - lattice points need not be atoms - **but** unit cell size should always be the same.



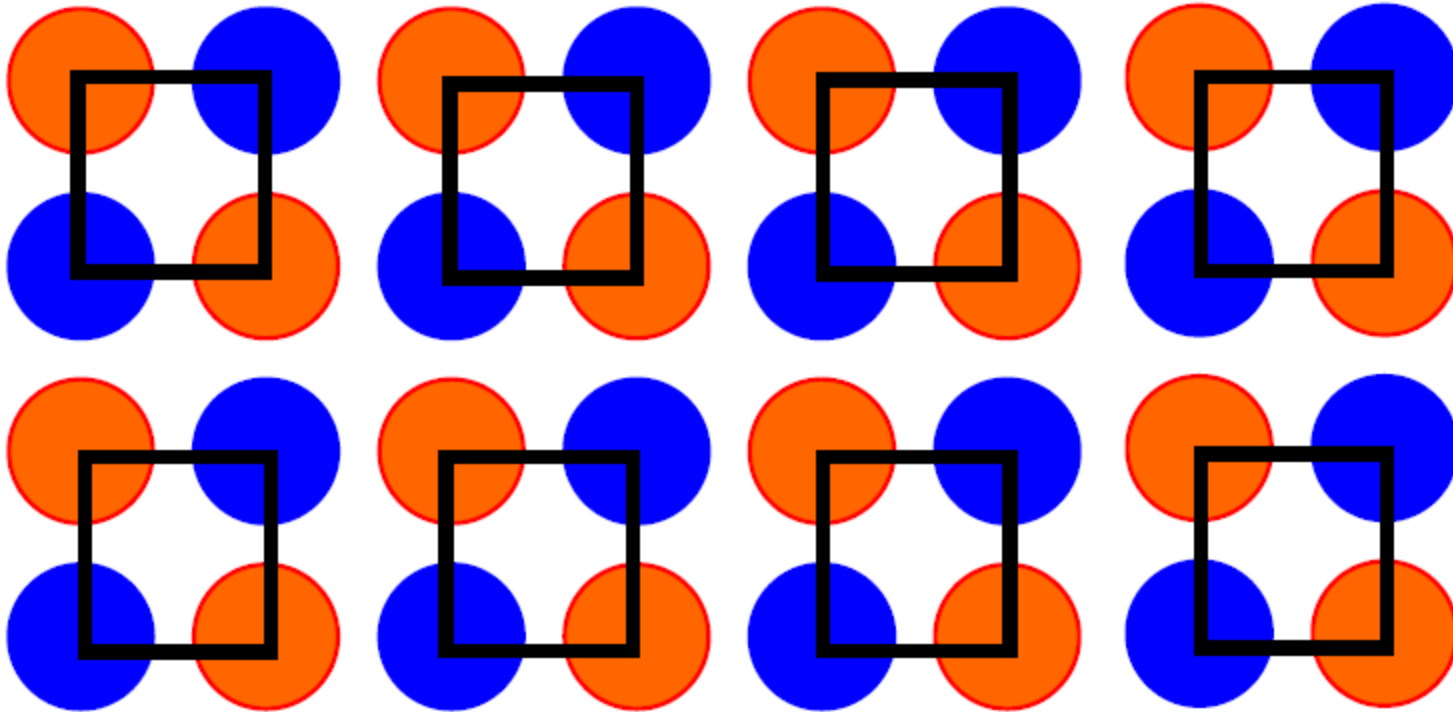
This is also a unit cell -
it doesn't matter if you start from Na or Cl



- or if you don't start from an atom



This is NOT a unit cell even though they are all the same -
empty space is not allowed!



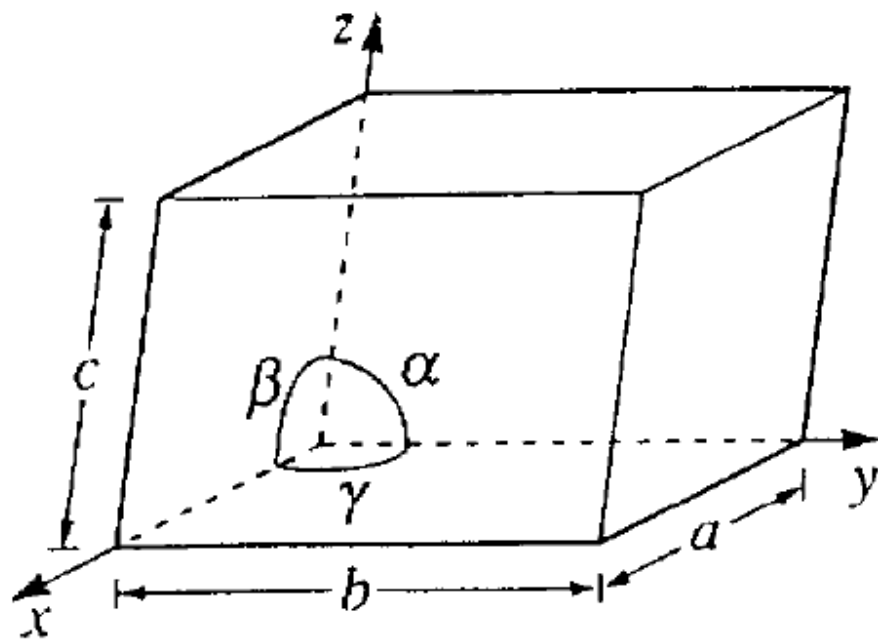
Definitions

The unit cell

“The smallest repeat unit of a crystal structure, in 3D, which shows the full symmetry of the structure”

The unit cell is a box with:

- 3 sides - a , b , c
- 3 angles - α , β , γ



right-handed system

How to select a “correct unit cell for a crystal”

- **Selection rules:**
 - 1. three non-coplanar vectors
 - 2. highest symmetry
 - 3. smallest volume

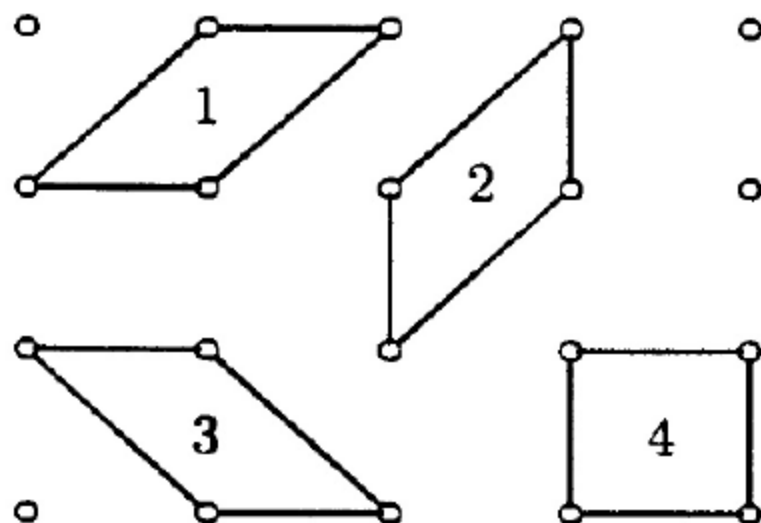


Fig. 2.5. Various choices of primitive unit cells in a lattice.

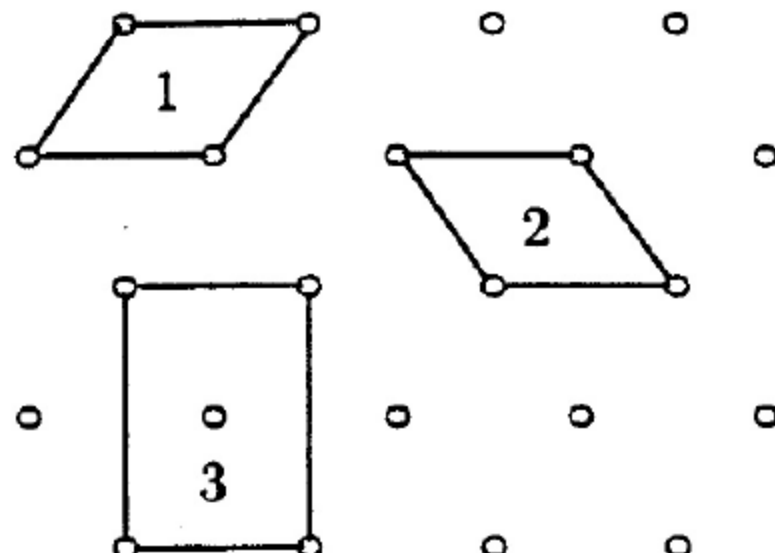
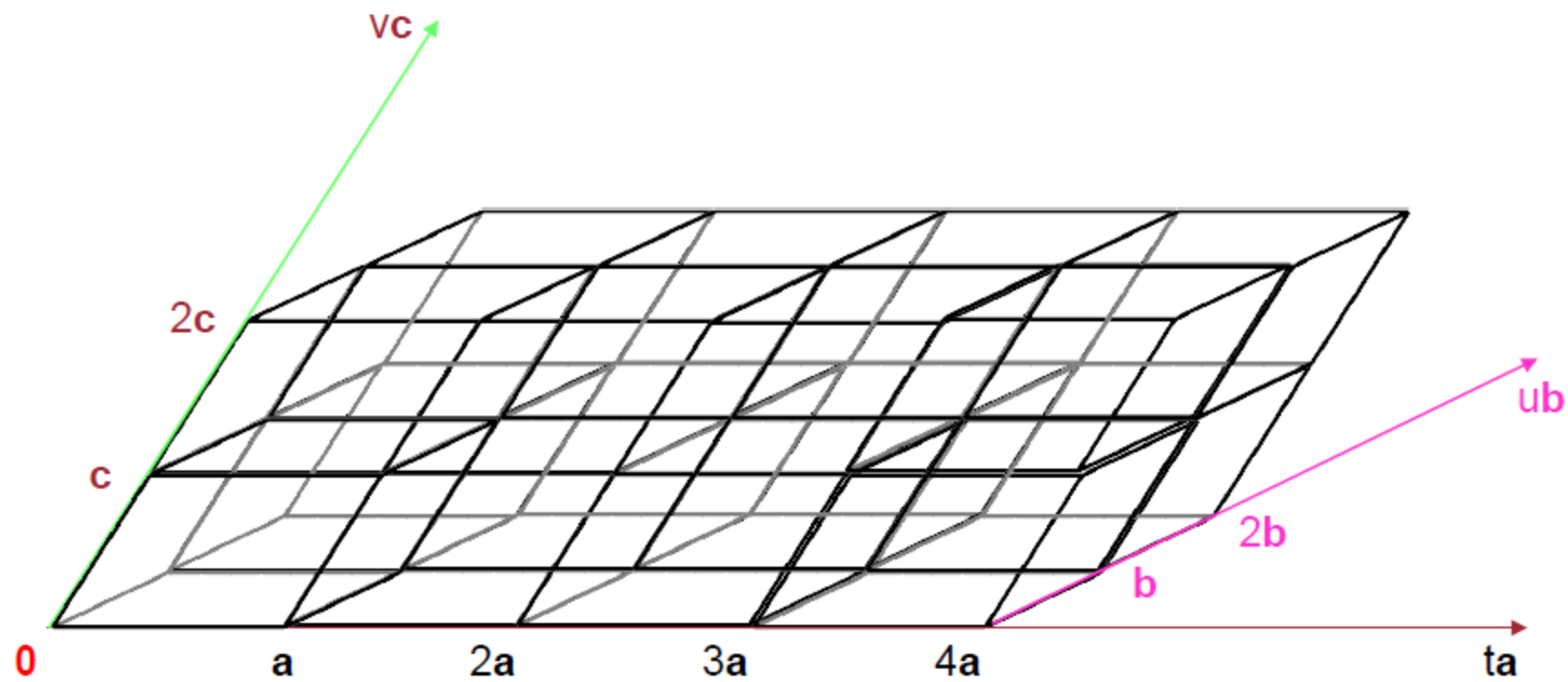
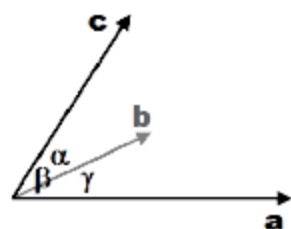


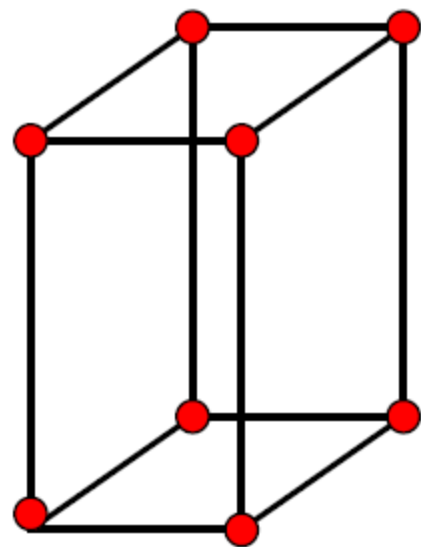
Fig. 2.6. The choice of cell 3 illustrates a centred lattice.

Building a crystal

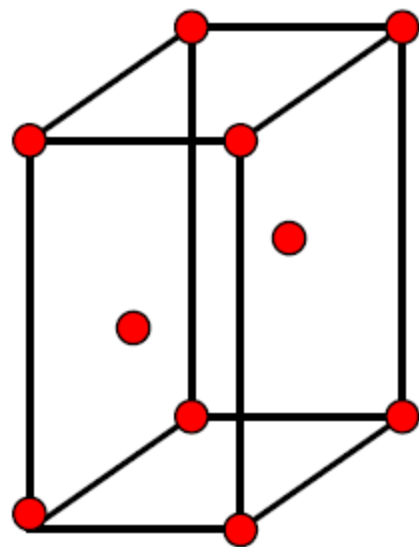


Non-primitive unit cell.

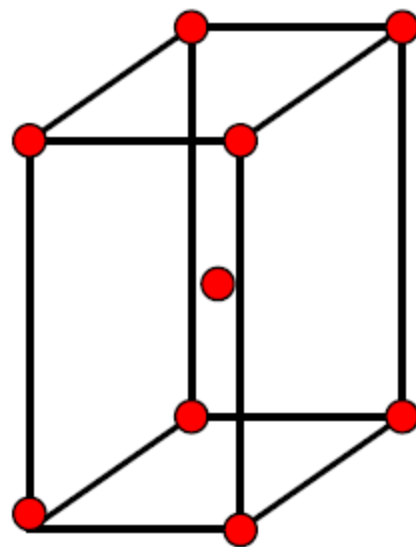
- Four classes:
 - Primitive unit cell (P).
 - Plane centred unit cell (A, B or C).
 - Body centred unit cell (I).
 - Face centred unit cell (F).



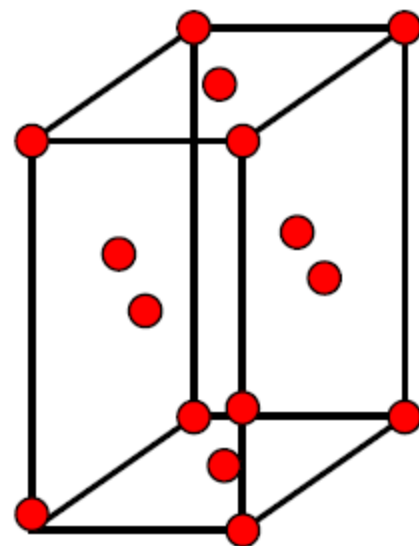
P



C



I



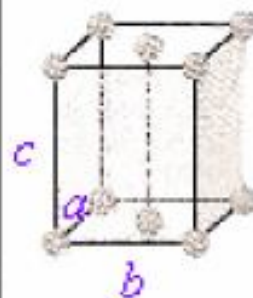
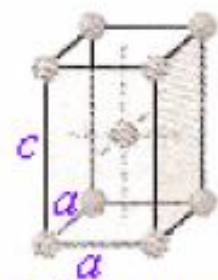
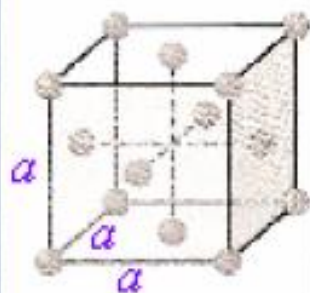
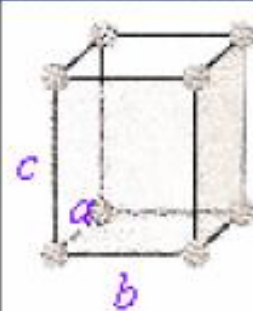
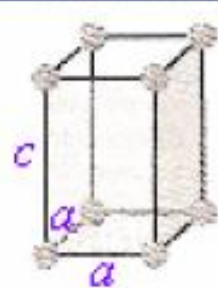
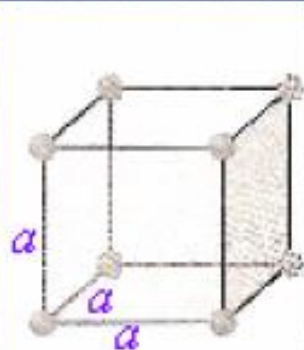
F

- In combination with previous 7 primitive cells leads to 14 Bravais lattices.

⇒ Seven unit cell shapes

• Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
• Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
• <u>Orthorhombic</u>	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
• <u>Tetragonal</u>	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
• Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
• <u>Hexagonal</u>	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
• <u>Cubic</u>	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$

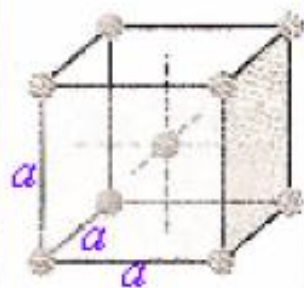
crystal system	axial lengths & interaxial angles	space lattice
cubic	$a = b = c$	simple cubic
	$\alpha = \beta = \gamma = 90^\circ$	body-centered cubic
		face-centered cubic
tetragonal	$a = b \neq c$	simple tetragonal
	$\alpha = \beta = \gamma = 90^\circ$	body-centered tetragonal
orthorhombic	$a \neq b \neq c$	simple orthorhombic
	$\alpha = \beta = \gamma = 90^\circ$	body-centered orthorhombic
		base-centered orthorhombic
		face-centered orthorhombic
rhombohedral	$a = b = c$	simple rhombohedral
	$\alpha = \beta = \gamma \neq 90^\circ$	
hexagonal	$a = b \neq c$	simple hexagonal
	$\alpha = \beta = 90^\circ$	
	$\gamma = 120^\circ$	
monoclinic	$a \neq b \neq c$	simple monoclinic
	$\alpha = \gamma = 90^\circ \neq \beta$	base-centered monoclinic
triclinic	$a \neq b \neq c$	simple triclinic
	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	



Tetragonal

Rhombohedral

Monoclinic



Cubic

Hexagonal

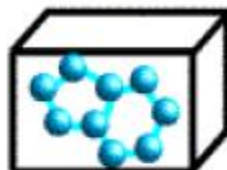
Orthorhombic

Triclinic

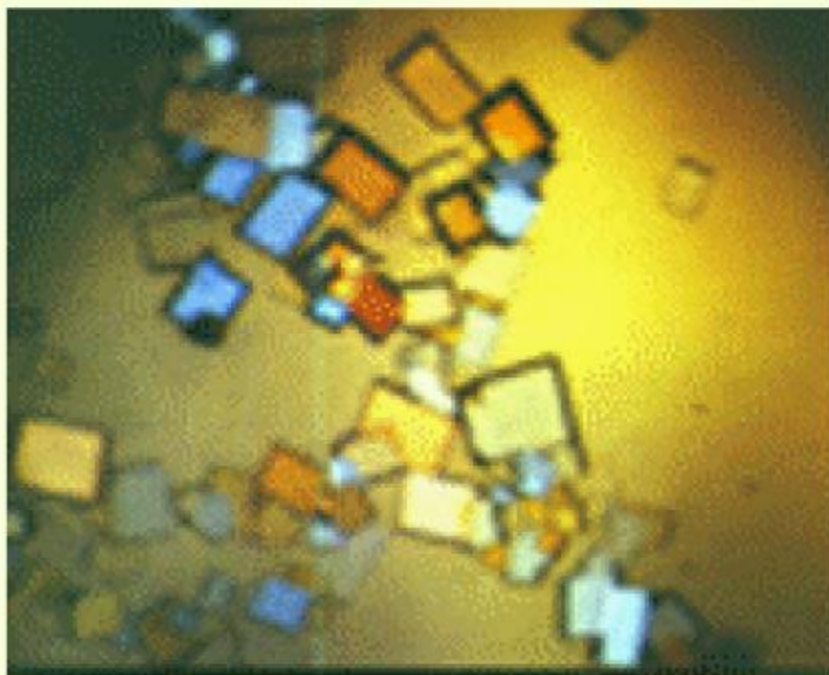
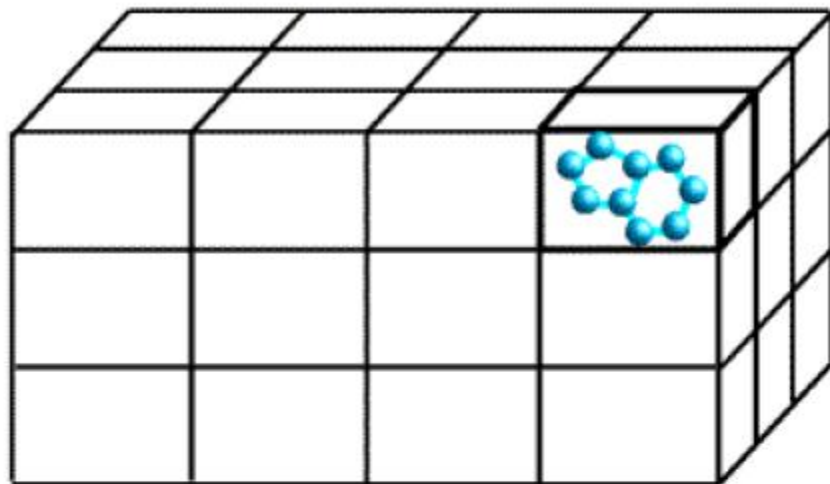
molecule



unit cell



crystal



single crystal
size < 0.5 mm

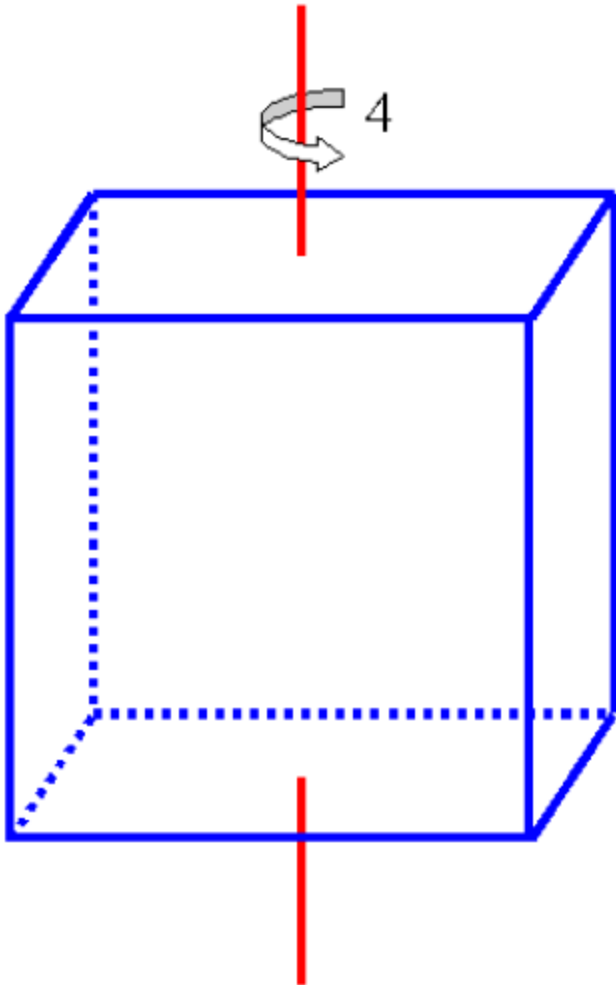
Plane of symmetry:

When an imaginary plane can divide a crystal into two parts such that one is the exact mirror image of the other, the crystal is said to have plane of symmetry.

Rectangular plane of symmetry -3

Diagonal plane of symmetry. - 6

Unit cell symmetries - cubic

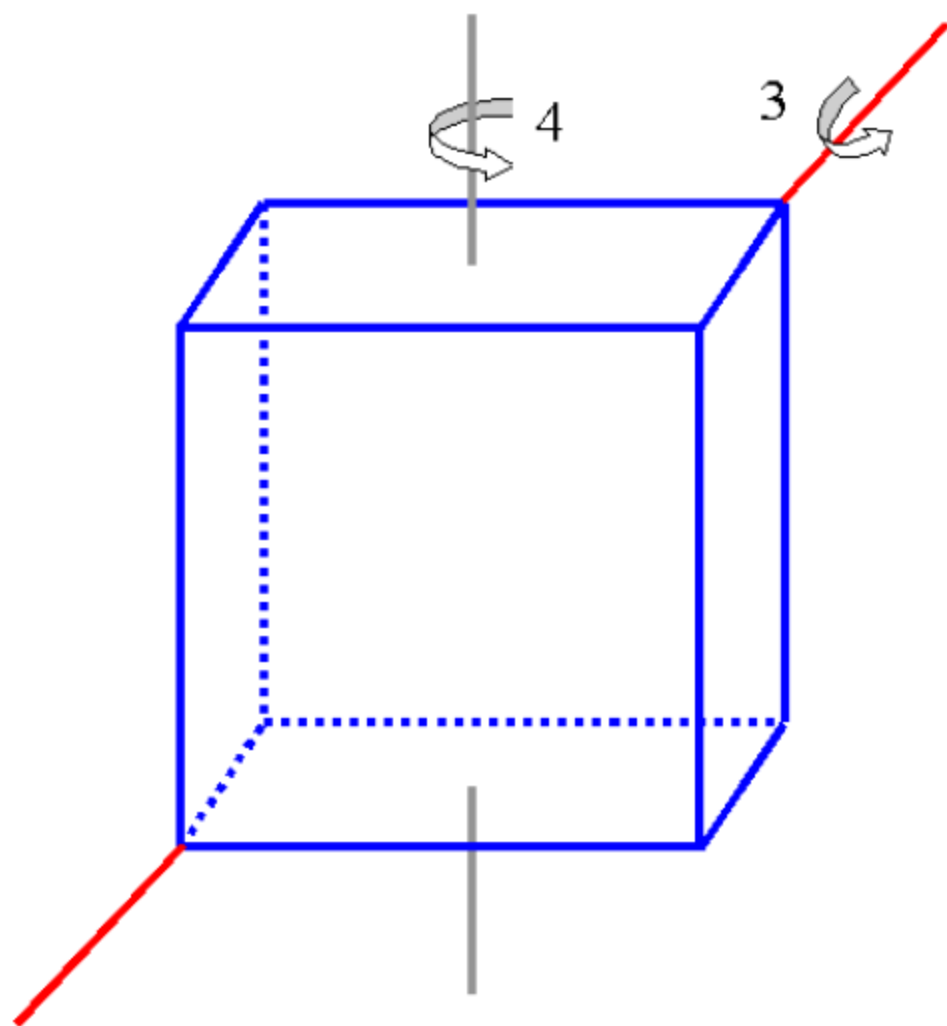


- **4 fold rotation axes**
(passing through pairs of opposite face centres, parallel to cell axes)

TOTAL = 3

Axis of symmetry: it is a line about which the crystal may be rotated such that it presents the same or similar appearance more than once during the complete revolution.

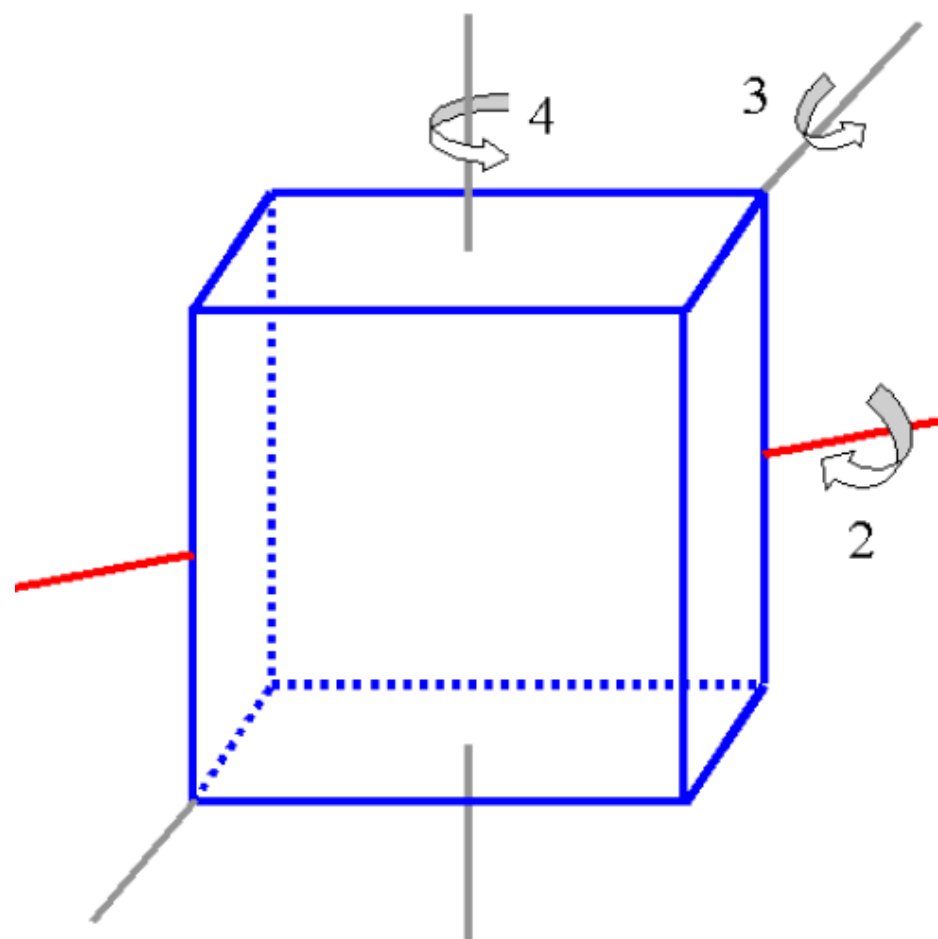
Unit cell symmetries - cubic



• 4 fold rotation axes
TOTAL = 3

3-fold rotation axes
(passing through cube
body diagonals)
TOTAL = 4

Unit cell symmetries - cubic



- 4 fold rotation axes
TOTAL = 3

3-fold rotation axes
TOTAL = 4

2-fold rotation axes
(passing through
diagonal edge centres)
TOTAL = 6

Total 13 axis of symmetry

Centre of symmetry:

It is such a point that any line drawn through it intersects the surface of the crystal at equal distances in both directions.

A crystal may have any number of planes or axes of symmetry but it has only one centre of symmetry.

Cubic crystal has 23 elements of symmetry:

Rectangular planes = 3

Diagonal planes = 6

4 fold axis of symmetry = 3

Three fold axis of symmetry = 4

Two fold axis of symmetry = 6

Centre of symmetry = 1

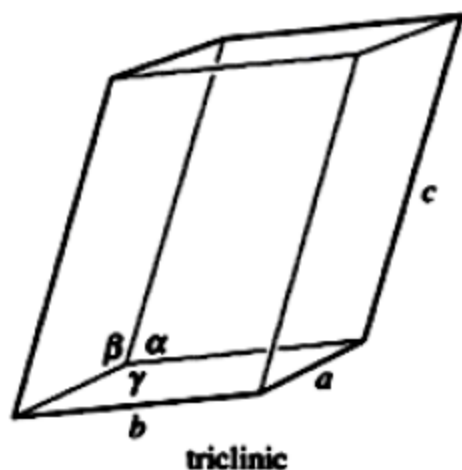
Primitive crystal systems

- Have 2, 3, 4 & 6 fold rotational symmetry possible.
- At least two axes must be equal for 3, 4 or 6 fold rotational symmetry
 - These ideas underly the division into seven primitive unit-cells.
 - Based on the lattice symmetry, there are seven different crystal systems

Triclinic:

contains **no extra symmetry**.

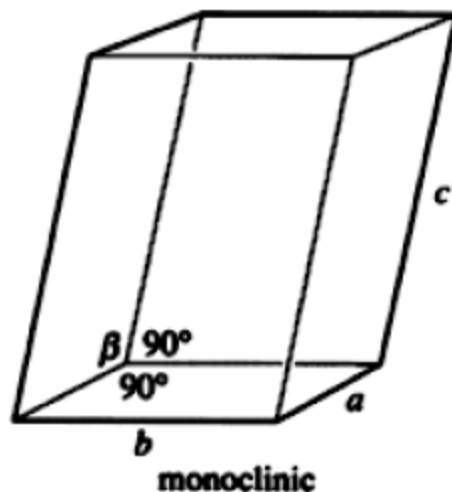
$$a \neq b \neq c \text{ \& } \alpha \neq \beta \neq \gamma \neq 90^\circ$$



Monoclinic:

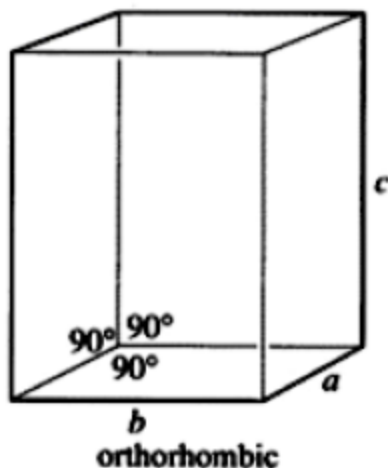
contains **one 2-fold** rotation.

$$a \neq b \neq c \text{ \& } \alpha, \gamma = 90^\circ$$



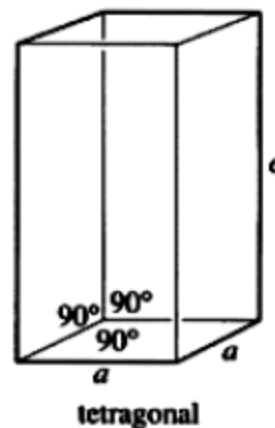
Orthorhombic:

$a \neq b \neq c$ & $\alpha = \beta = \gamma = 90^\circ$
has **three 2-fold axes**.



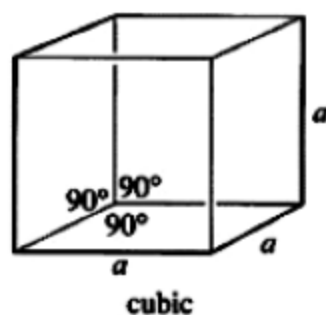
Tetragonal:

$a = b \neq c$ & $\alpha = \beta = \gamma = 90^\circ$
has **a 4-fold axes**.



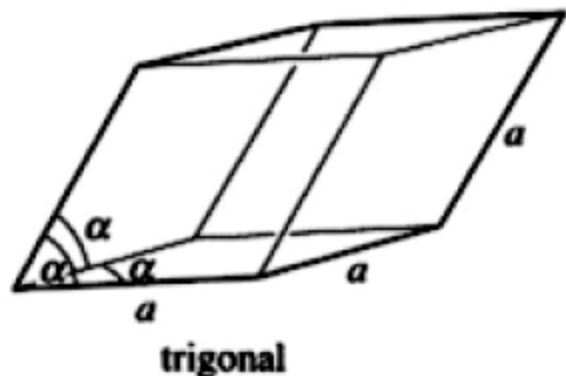
Cubic:

$a = b = c$ & $\alpha = \beta = \gamma = 90^\circ$
has **four 3-fold axes**.



Rhombohedral:

$a = b = c$ & $\alpha = \beta = \gamma \neq 90^\circ$
has a 3-fold axis.

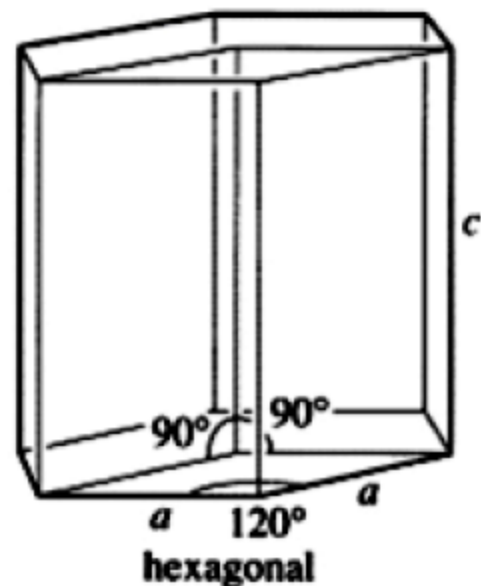


Trigonal:

The combination of both
Rhombohedral &
Hexagonal with **only 3-
fold** rather than 6-fold
symmetry.

Hexagonal:

$a = b \neq c$ & $\alpha = \beta = 90^\circ$ & $\gamma = 120^\circ$
has a **6-fold axis**.



Reduction in symmetry

Cubic

Three 4-axes

Four 3-axes

Six 2-axes

Nine mirrors

Tetragonal

One 4-axis

Two 2-axes

No 3-axes

Two 2-axes

Five mirrors

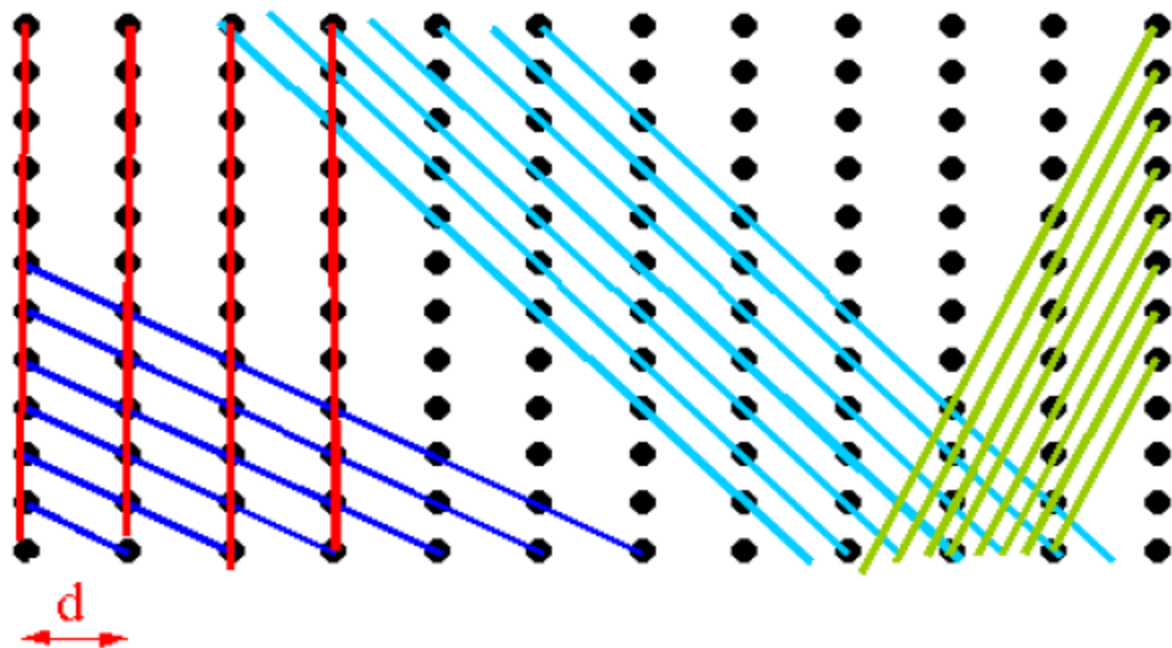
Essential Symmetry

Essential symmetry is that which defines the crystal system (i.e. is unique to that shape).

<i>System</i>	<i>Essential Symmetry</i>	<i>Symmetry axes</i>
Cubic	4 3-fold axes	along the body diagonals
Tetragonal	1 4-fold axis	parallel to c, in the centre of ab
Orthorhombic	3 mirrors or 3 2-fold axes	perpendicular to each other
Hexagonal	1 6-fold axis	down c
Trigonal (R)	1 3-fold axis	down the long diagonal
Monoclinic	1 2-fold axis	down the “unique” axis
Triclinic	no symmetry	

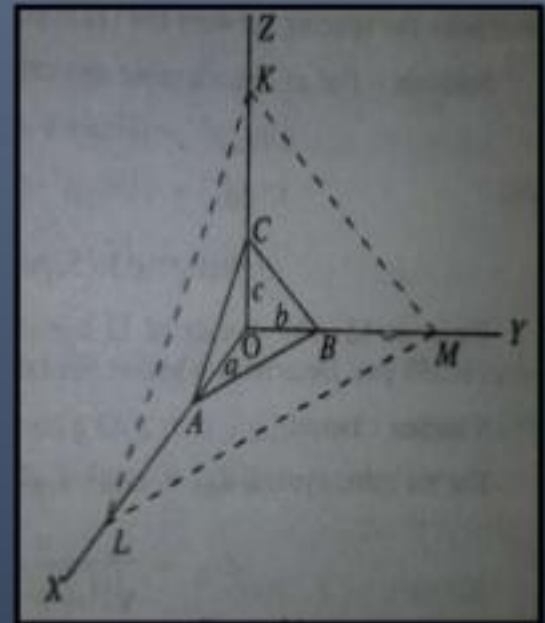
Lattice Planes

Imagine representing a crystal structure on a grid (lattice) which is a 3D array of points (lattice points). Can imagine dividing the grid into sets of “planes” in different orientations



Law of Rational indices

This law states that the ratio of intercepts of different faces of a crystal with the three axes are constant and can be expressed by rational numbers that the intercepts of any face of a crystal along the crystallographic axes are either equal to unit intercepts (i.e., intercepts made by unit cell) a , b , c or some simple whole number multiples of them ,e.g., na , $n'b$, $n''c$ etc. are simple whole numbers .



Miller Indices. Miller indices are a set of integers (h, k, l) which are used to describe a given plane in a crystal. The miller indices of a face of a crystal are inversely proportional to the intercepts of that face on the various axes. The procedure for determining the Miller indices for a plane is as follows :

1. Prepare a three-column table with the unit cell axes at the tops of the columns.
2. Enter in each column the intercept (expressed as a multiple of a, b or c) of the plane with these axes.
3. Invert all numbers.
4. Clear fractions to obtain h, k and l .

Example 11. Calculate the Miller indices of crystal planes which cut through the crystal axes at (i) $(2a, 3b, c)$ (ii) (a, b, c) (iii) $(6a, 3b, 3c)$ and (iv) $(2a, -3b, -3c)$.

Solution : Following the procedure given above, we prepare the table as follows :

(i)	a	b	c	
	2	3	1	intercepts
	$1/2$	$1/3$	1	reciprocals
	3	2	6	clear fractions

Hence, the Miller Indices are (326) .

(iii)	a	b	c	
	6	3	3	intercepts
	$1/6$	$1/3$	$1/3$	reciprocals
	1	2	2	clear fractions

Hence, the Miller indices are (122) .

(ii)	a	b	c	
	1	1	1	intercepts
	1	1	1	reciprocals
	1	1	1	clear fractions

Hence, the Miller indices are (111) .

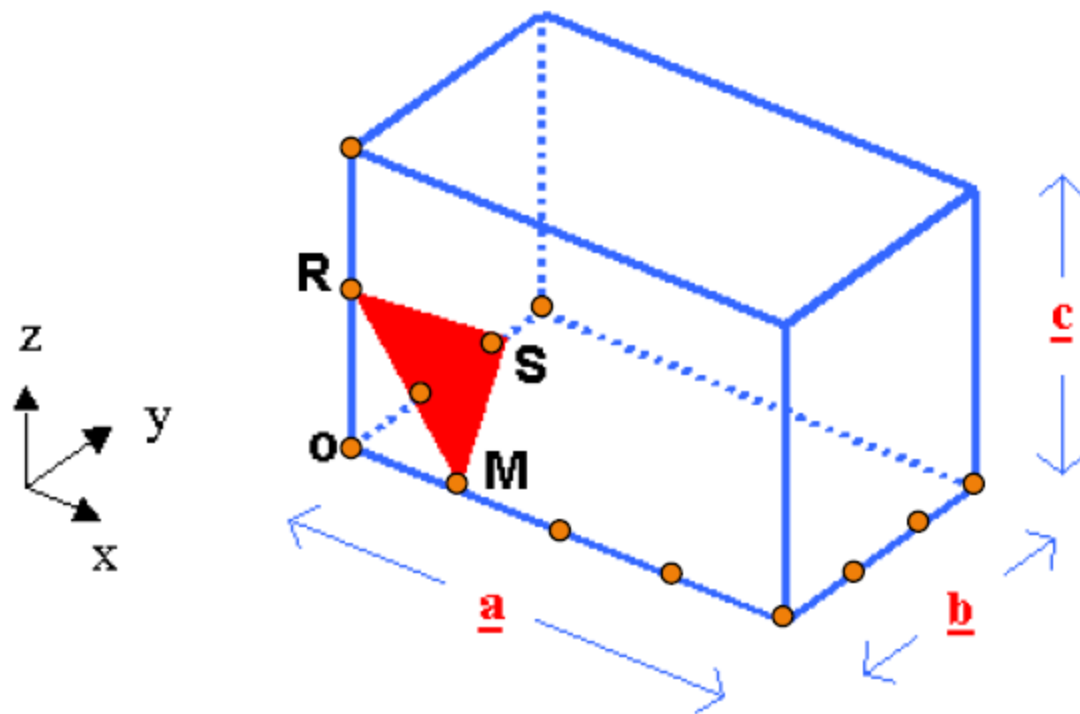
(iv)	a	b	c	
	2	-3	-3	intercepts
	$1/2$	$-1/3$	$-1/3$	reciprocals
	3	-2	-2	clear fractions

Hence, the Miller indices are $(3\bar{2}\bar{2})$

Note. The negative sign in the Miller indices is indicated by placing a bar on the integer. The Miller indices are enclosed within parentheses.

- All planes in a set are identical
- The planes are “imaginary”
- The perpendicular distance between pairs of adjacent planes is the d-spacing

Need to label planes to be able to identify them



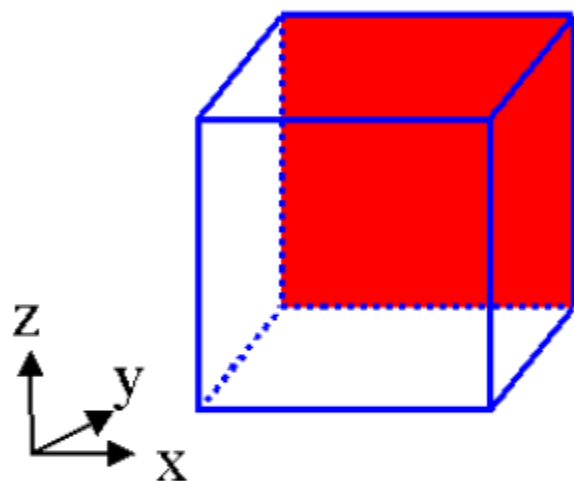
Find intercepts on
a,b,c: $1/4, 2/3, 1/2$

Take reciprocals $4, 3/2, 2$

Multiply up to
integers: **(8 3 4)**
[if necessary]

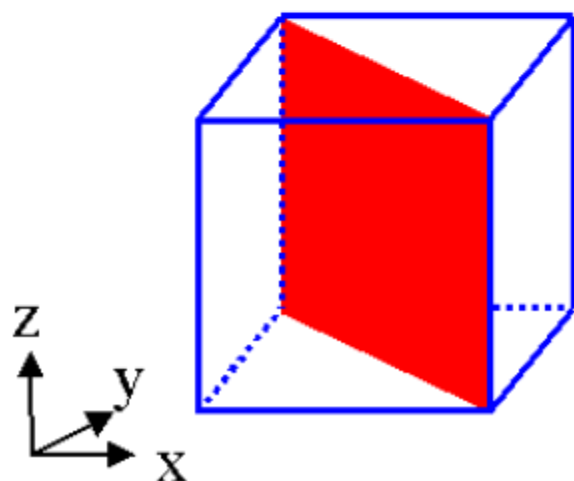
General label is $(h\ k\ l)$ which intersects at \mathbf{a}/h , \mathbf{b}/k , \mathbf{c}/l

(hkl) is the **MILLER INDEX** of that plane (round brackets, no commas).



Plane perpendicular to y
cuts at $\infty, 1, \infty$

→ **$(0\ 1\ 0)$ plane**

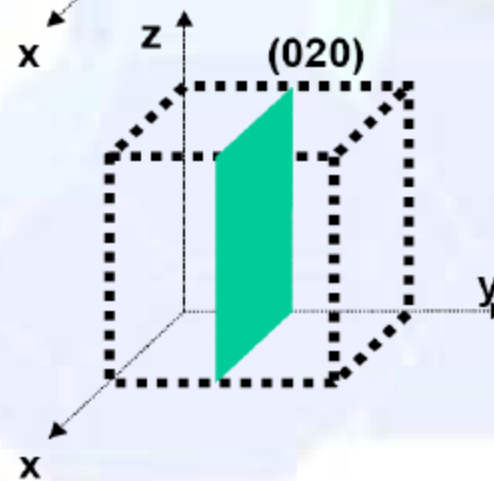
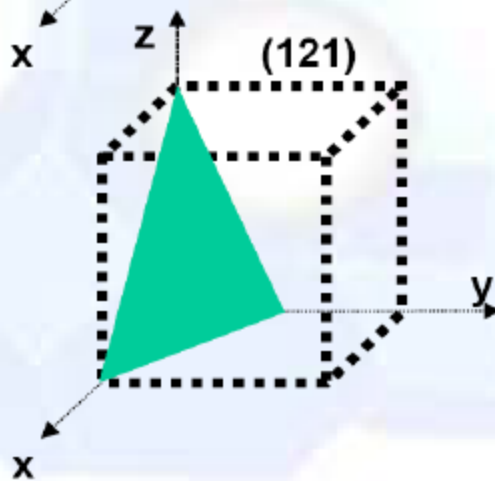
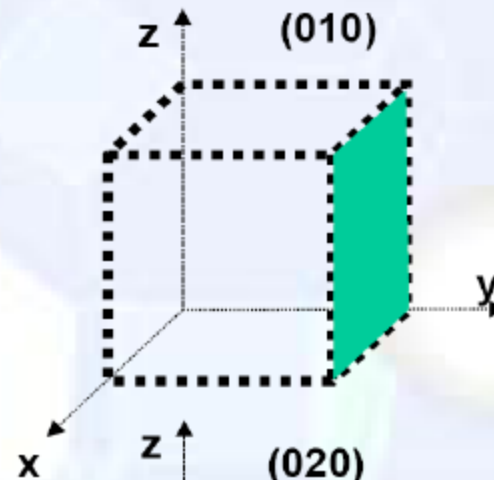
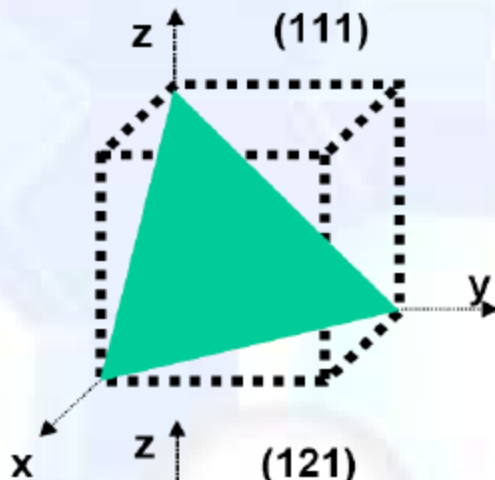


This diagonal cuts at $1, 1, \infty$

→ **$(1\ 1\ 0)$ plane**

NB an index 0 means that the plane is parallel to that axis

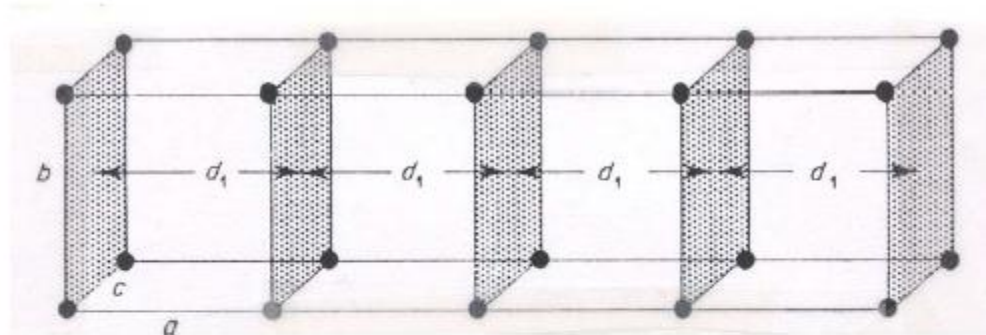
Crystallographic Planes: Miller Indices (hkl)



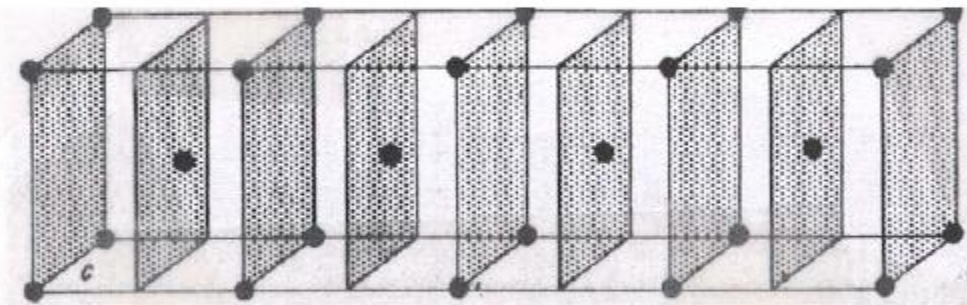
Planes - conclusions 1

- Miller indices define the orientation of the plane within the unit cell
- The Miller Index defines a *set of planes* parallel to one another (remember the unit cell is a subset of the “infinite” crystal)
- (002) planes are parallel to (001) planes, and so on

Crystal Planes



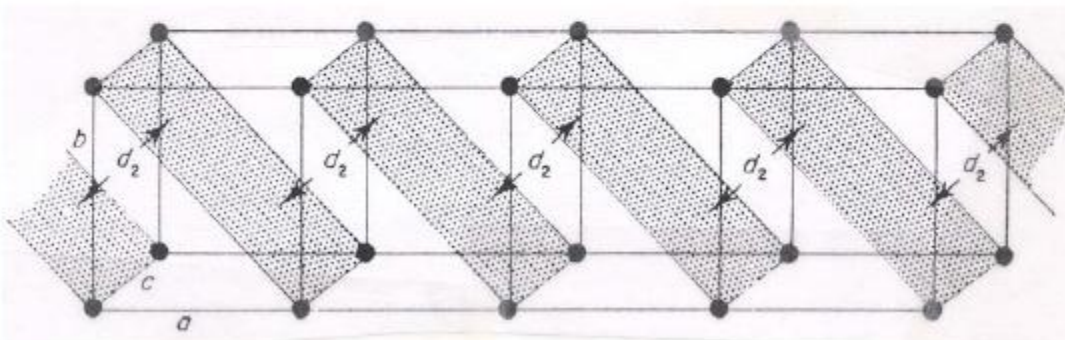
(100)



(200)

$$d_{100} = a$$

$$d_{200} = \frac{1}{2}a$$



(110)

$$d_{n00} = \left(\frac{1}{n}\right)a$$

$$d_{nn0} = \left(\frac{1}{n}\right)d_{110}$$

d-spacing formula

For orthogonal crystal systems
 $a \neq b \neq c$ & $\alpha = \beta = \gamma = 90^\circ$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

For cubic crystals (special case of orthogonal) ;

$$a = b = c \text{ \& } \alpha = \beta = \gamma = 90^\circ$$

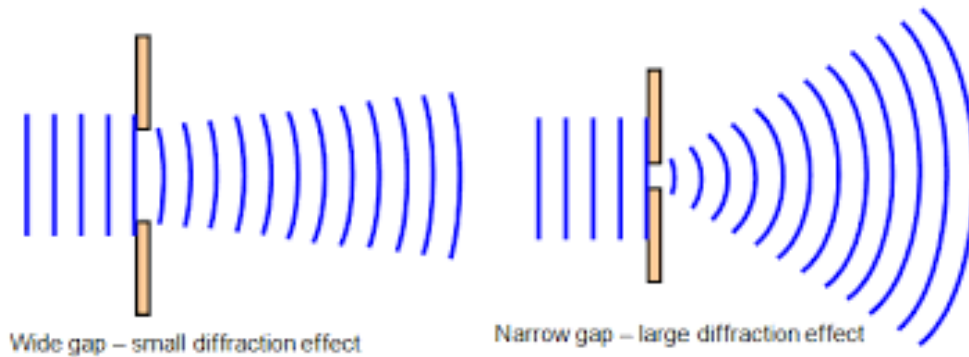
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal:
$$\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2}$$

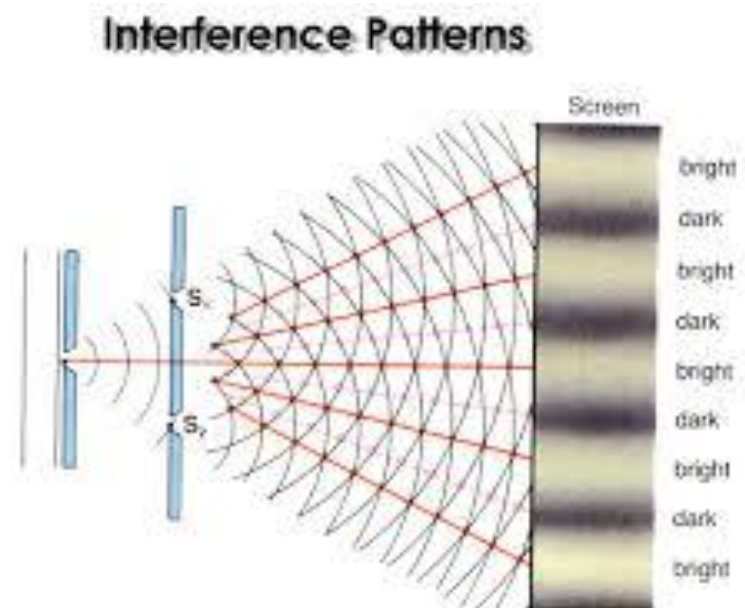
$$a = b \neq c \text{ \& } \alpha = \beta = \gamma = 90^\circ$$

e.g. for (1 0 0) $d = a$
(2 0 0) $d = a/2$
(1 1 0) $d = a/\sqrt{2}$ etc.

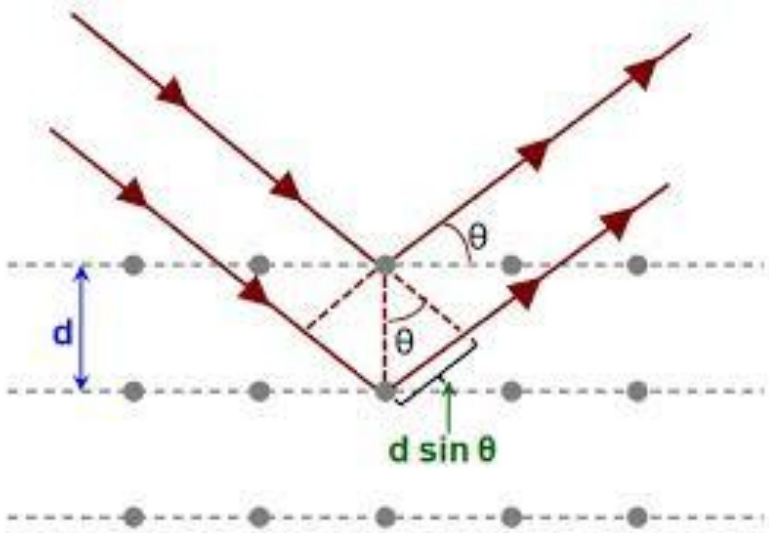
What is diffraction?



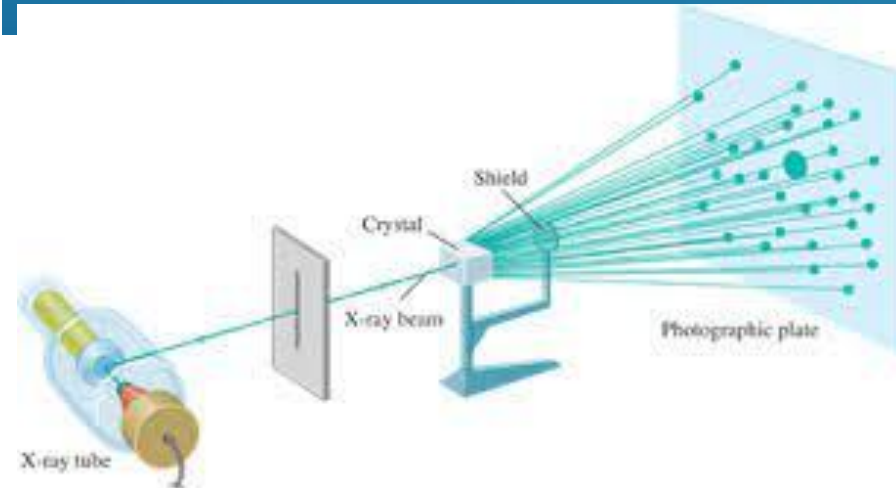
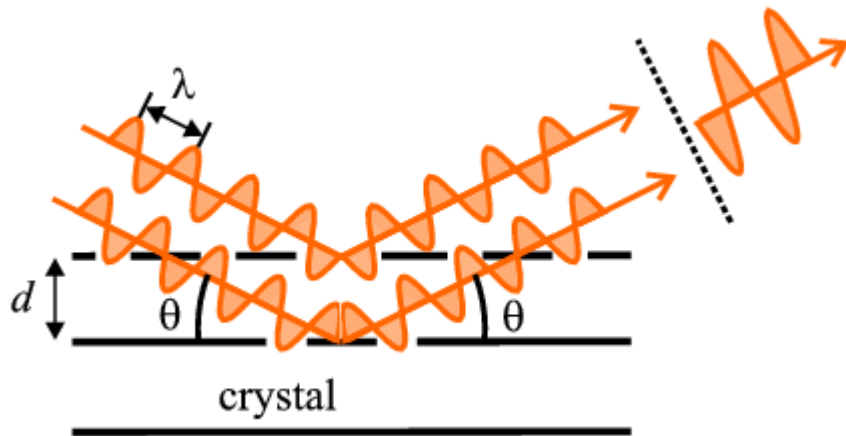
- Diffraction is **the spreading out** of waves as they pass through an aperture or around objects.
- It occurs when the size of the aperture or obstacle is of the **same order of magnitude** as the wavelength of the incident wave.



Diffraction of x-rays by crystals :



X-ray crystallography is a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.



X-rays are used to produce the **diffraction** pattern because their wavelength λ is typically the same order of magnitude (1–100 angstroms) as the spacing d between planes in the **crystal**. ... However, visible light has too long a wavelength (typically, 5500 angstroms) to observe **diffraction** from **crystals**.

Simple derivation of Bragg's Law

Bragg's Law can be derived using simple geometry by considering the distances traveled by two parallel X-rays reflecting from adjacent planes. The X-ray hitting the lower plane must travel the extra distance AB and BC. To remain in phase with the first X-ray, this distance must be a multiple of the wavelength thus:

$$n\lambda = AB + BC = 2AB$$

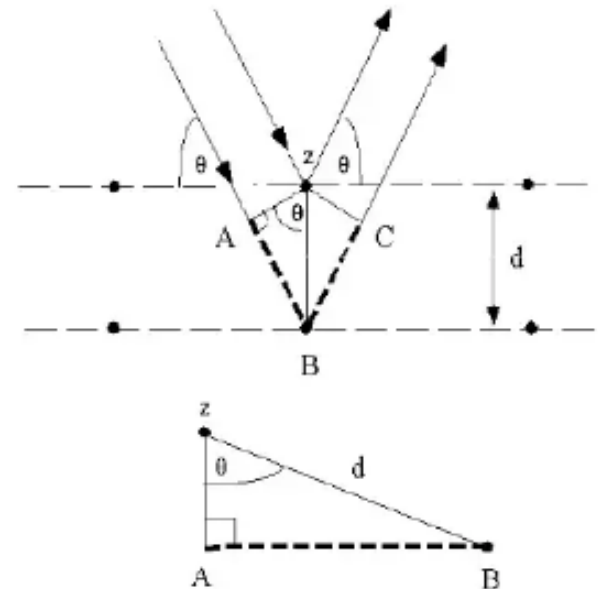
(since the two triangles are identical)

The distance AB can be expressed in terms of the interplanar spacing (d) and incident angle (θ) because d is the hypotenuse of right triangle zAB shown at right. *Remember $\sin = \text{opposite}/\text{hypotenuse}$*

$$\sin(\theta) = AB/d \quad \text{thus } AB = d \sin(\theta)$$

Therefore:

$$n\lambda = 2 d \sin(\theta)$$

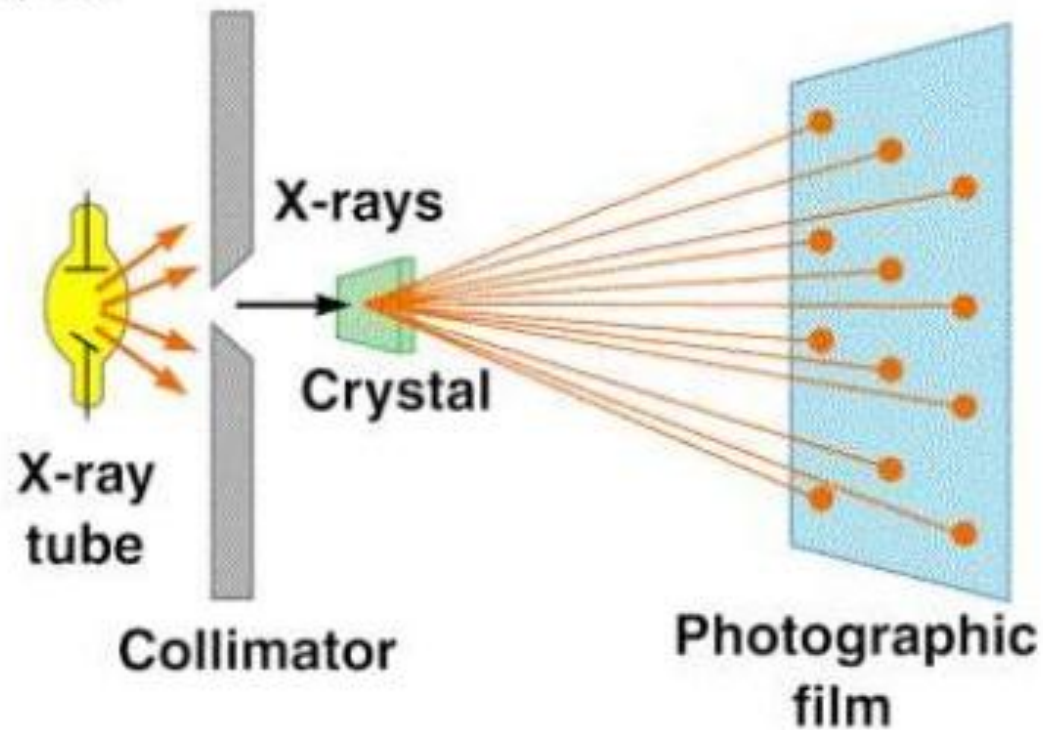


Note: d and $\sin(\theta)$ are inversely proportional (reciprocal). This means that smaller values of d diffract at higher angles – this is the importance of “high angle” data!

DIFFRACTION :

X-RAY USED ON CRYSTAL

Serway, College Physics, 5/e
Text Figure 27.14



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