

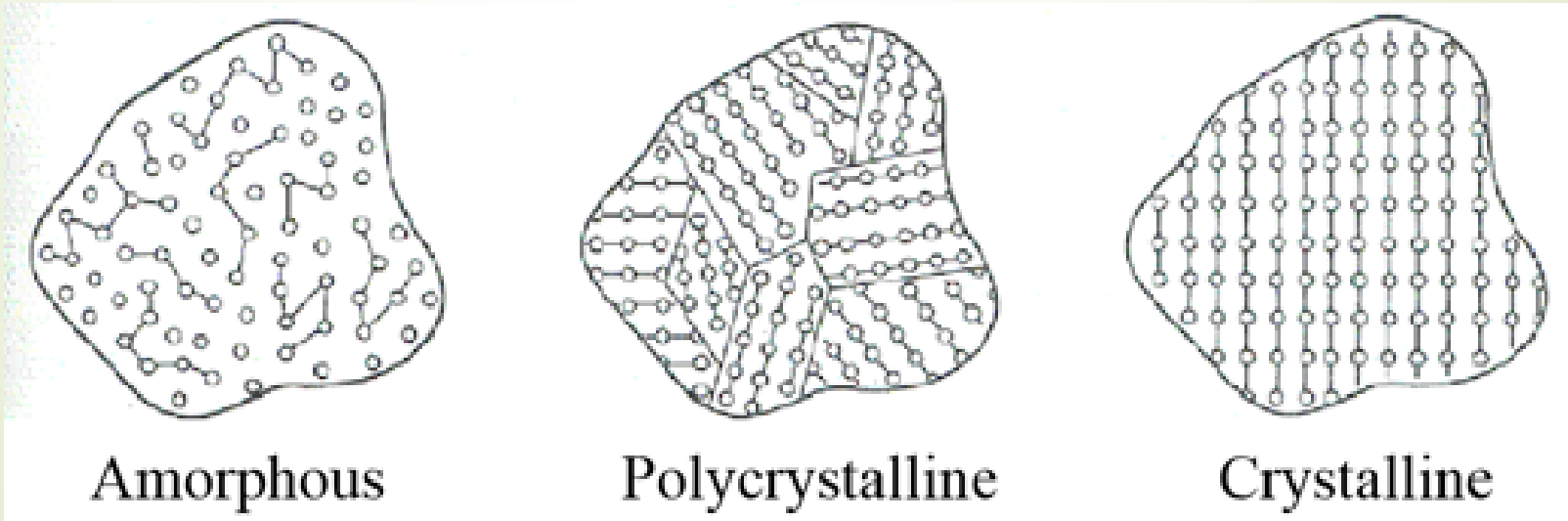
# Crystal

## Crystal Structure



# Crystal

- In general, solids can be classified into:
  - I. **Amorphous**-particles are randomly oriented.
  - II. **Polycrystalline**-Completely ordered in segments
  - III. **Crystalline**-particles are orderly arranged (long range order).



## Single Crystal or mono crystalline or crystalline solid

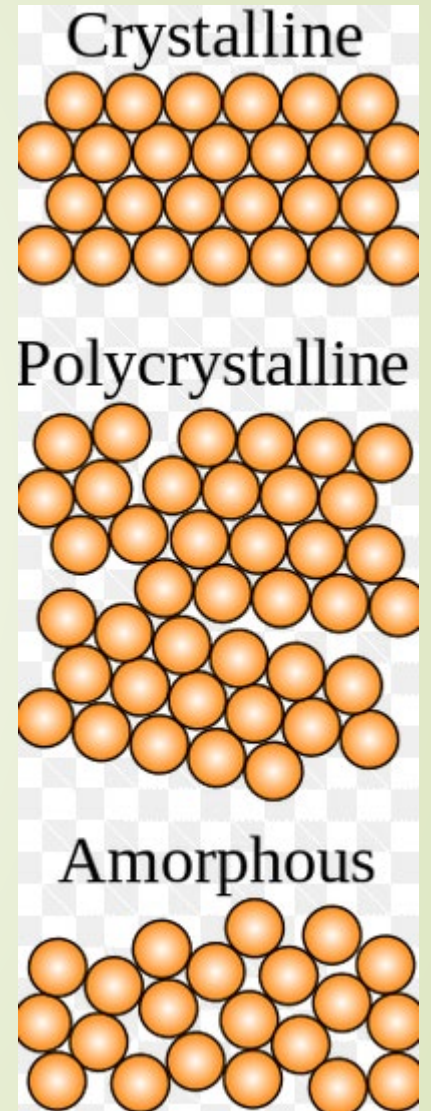
- The whole solid is one crystal.
- The crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries.
- Have unique properties, particularly mechanical, optical and electrical.
- Ex: quartz, salt, diamond, and topaz are some of natural single crystals.

## Polycrystalline Materials

- A solid composed of many crystalline grains(crystallites) of varying size and orientation.
- The grains not aligned with each other.
- Where the grains meet is called a **grain boundary**.
- Ex. Inorganic solids, Most of the Metal, ceramic.
- Sulfur can be found as single crystal as well as in poly crystalline form.

## Non-Crystalline / Amorphous Solid

- no long-range order, in many cases there may exist some form of short-range order
- Ex: Rubber, plastic, glass

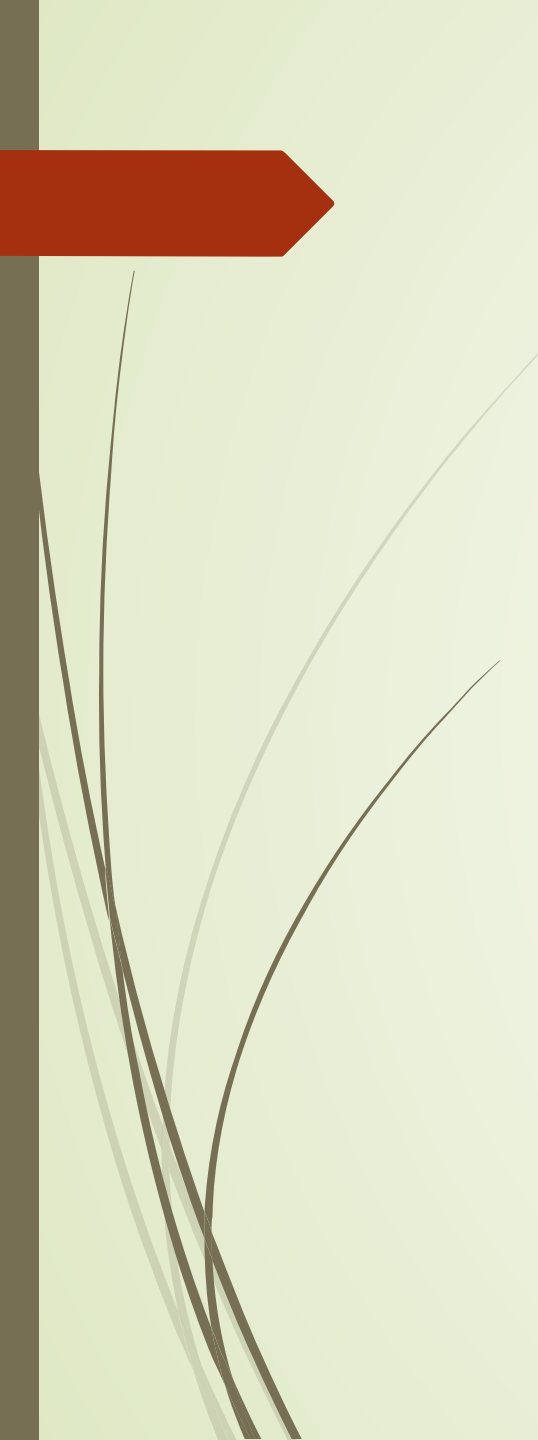


## Polymorphism and Allotropy

- Some materials may exist in more than one crystal structure, this is called polymorphism. Ex: Silica, Glycine.
- ✓ Special case of polymorphism called **allotropy** when the material **is an elemental solid**.
- ✓ For other **compounds** it is **Polymorphism**.
- ✓ In Allotropes the atoms of the element are bonded together in a different manner.
- ✓ Ex: carbon, which can exist as diamond, graphite, and amorphous carbon.

### Interesting example of Polymorphism, shown by Silica ( $\text{SiO}_2$ ).

- ❑ Silicon dioxide ( $\text{SiO}_2$ ), also known as silica is the major constituent of sand and most commonly found in nature as quartz. Silica is the primary ingredient in the production of most glass.
- ❑ Quartz, formed by 99% silica is **Crystalline silica** whereas Glass is formed by 80% of silica is an **Amorphous solid**.



**Liquid crystals** are a state of matter which has properties between those of conventional liquids and those of solid crystals.


A liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way.

Liquid crystals have mobile molecules, but a type of long range order can exist; the molecules have a permanent dipole. Applying an electric field rotates the dipole and establishes order within the collection of molecules.





## ➡ Crystal

- ➡ Is a small piece of a substance that has many sides and is formed when the substance turns into a solid.
  - ➡ is made up of atoms of the same element or atoms of different elements
  - ➡ it may take around one year to form about one atomic layer; thus growing a two centimeter crystal can take over a period of ten million years
- 

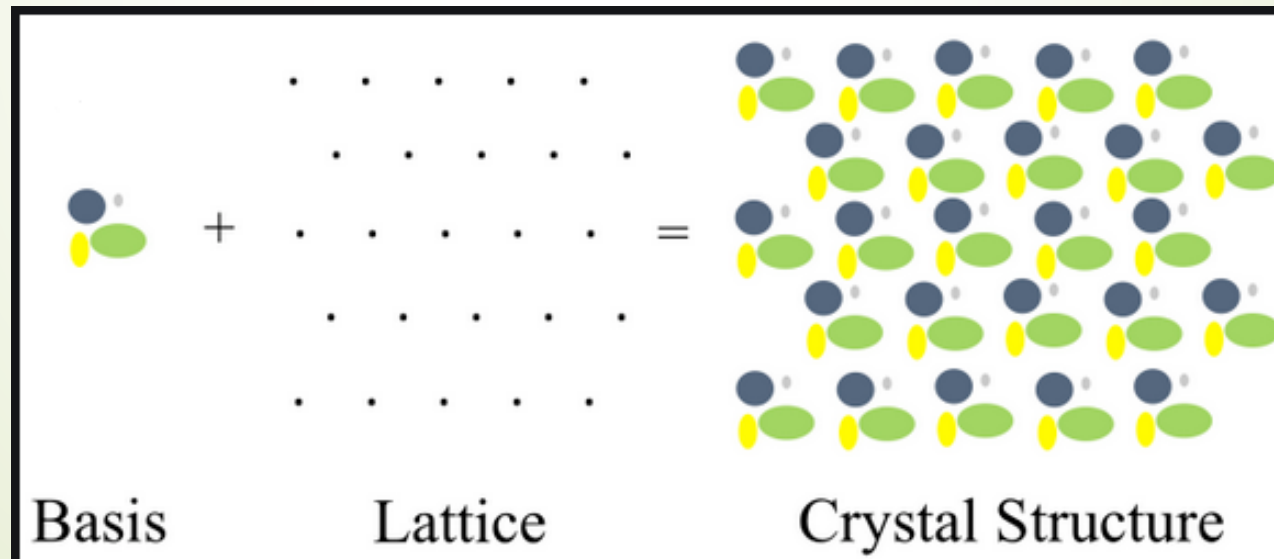


# Crystal

- A **crystal** or crystalline solid is a solid material whose constituents (such as atoms, molecules or ions) are arranged in a highly ordered microscopic structure, forming a **crystal** lattice that extends in all directions.
- Long range order
- Symmetry
- Periodicity (main property)

# Crystal Structure

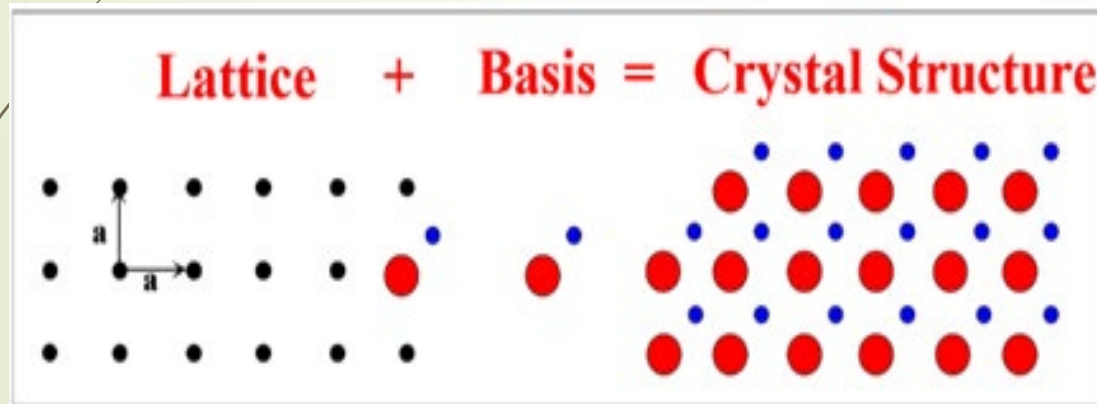
- A **crystal structure** is a unique arrangement of atoms in a **crystal**.
- A crystal structure is composed of a **unit cell**, a set or group of atoms arranged in a particular way; which is periodically repeated in three dimensions on a lattice.





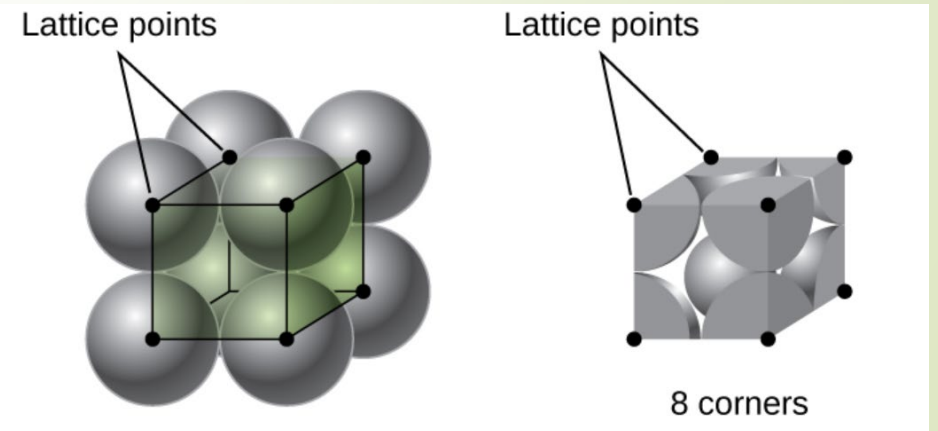
# Crystal Structure

- ❑ **Lattice** : A lattice is an infinite three dimensional array of points in which every point has surroundings identical with that of every other point. These are called lattice points.
- ❑ **Basis**: A basis is a specific arrangement of atoms which belong to a lattice point. The group of atoms or molecules is called a basis.



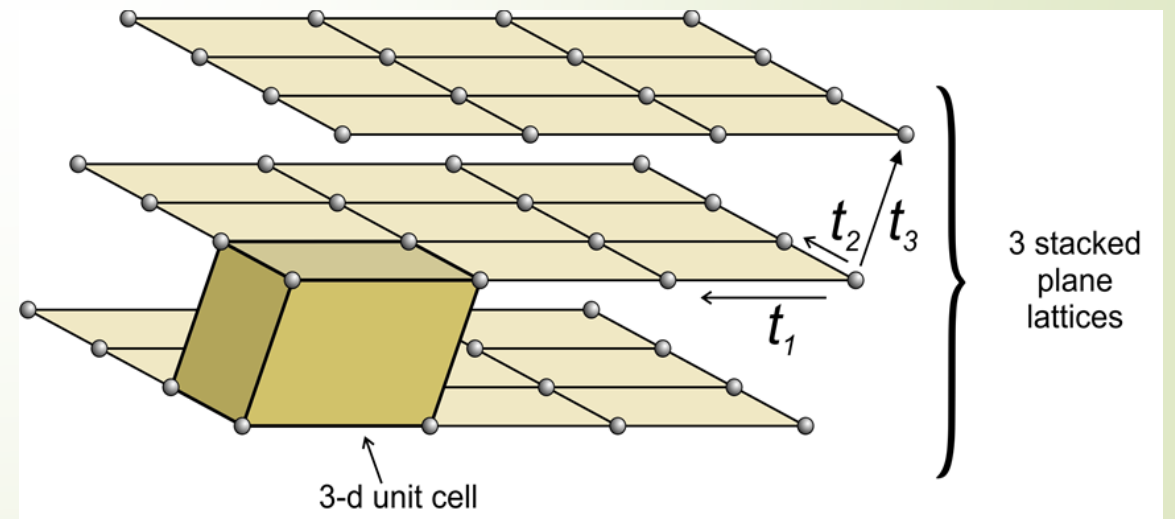
- ❑ **Unit cell**: A unit cell is the smallest repeating unit of the space lattice which can be used to reproduce the entire cell.

**Lattice + Basis = crystal structure**



## Translation, plane and space lattice

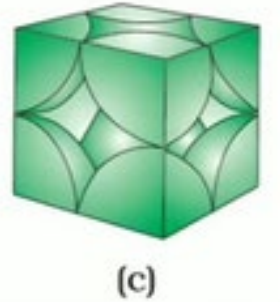
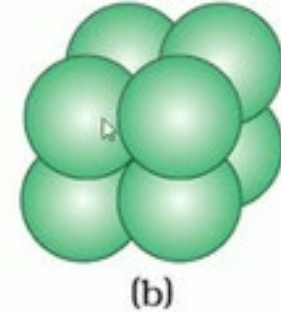
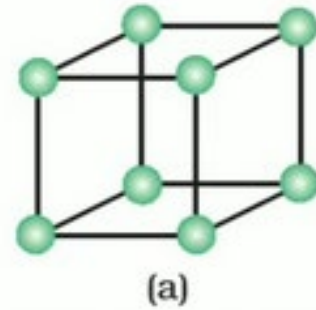
- Line joining any two points = translation in lattice.
- Two non-collinear translation = a plane
- three non coplanar translation = a space lattice.



## Types Of Unit Cell

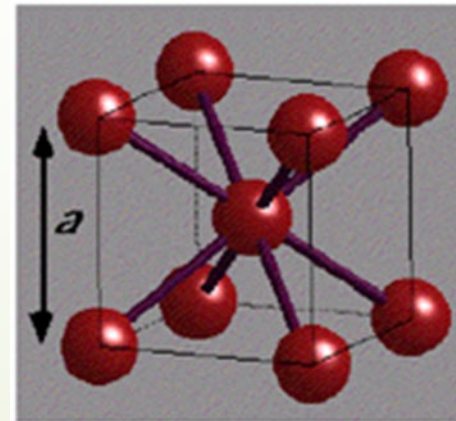
### 1. Simple cubic (SC) or Primitive Cell:

- has only 1 lattice points per cell.
- One atom at each corner i.e; total 8 atoms at 8 corners of unit cell but per unit cell atom no. is 1.
- Inefficient structure; Ex: Polonium, Po crystallizes in SC structure.

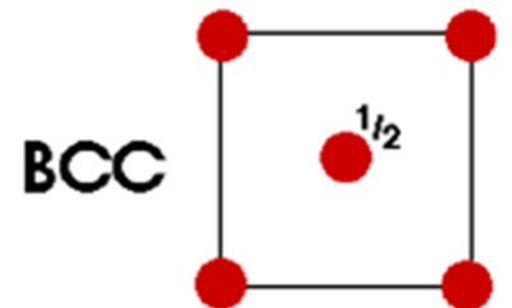


### 2. Body centered cubic (BCC)

- has only 2 lattice point per unit cell.
- One atom at each corner i.e; total 8 atoms at 8 corners of unit cell and one atom at center make total no. atom per unit cell = 2.



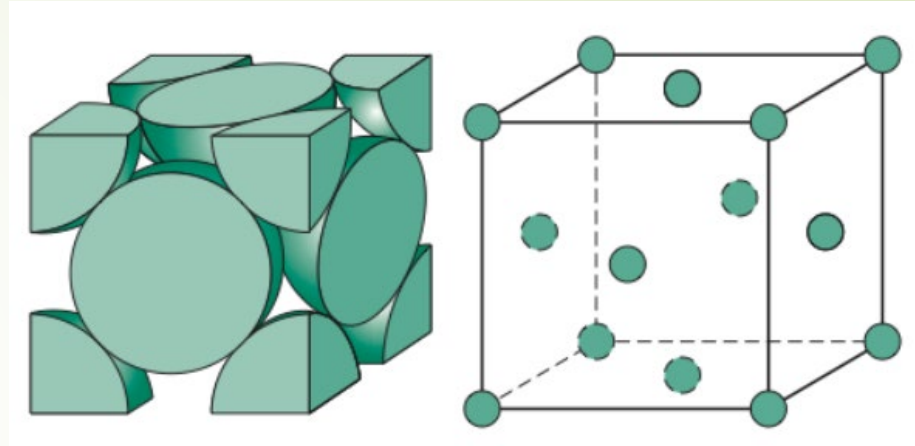
### Body-Centred Cubic



## Types Of Unit Cell (Cont.)

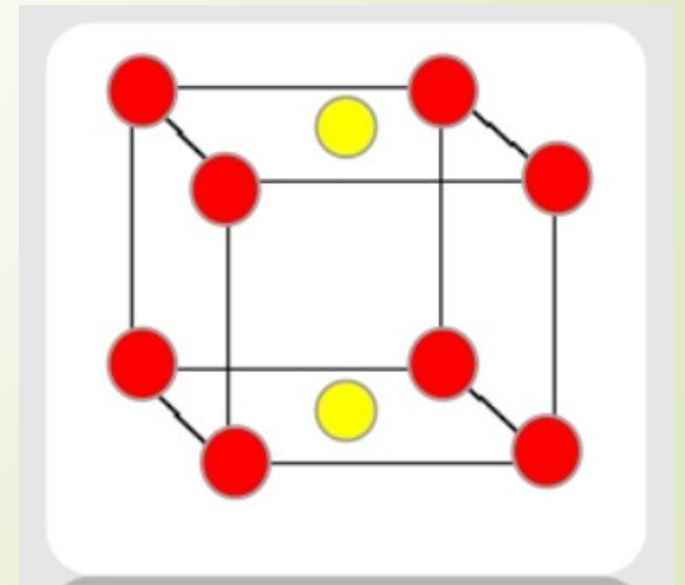
### 3. Face centered cubic (FCC)

- has 4 lattice point per unit cell.
- 1 atom at each of 8 corners of unit cell and 1 atom at each of 6 faces make total no. atom per unit cell = 4.



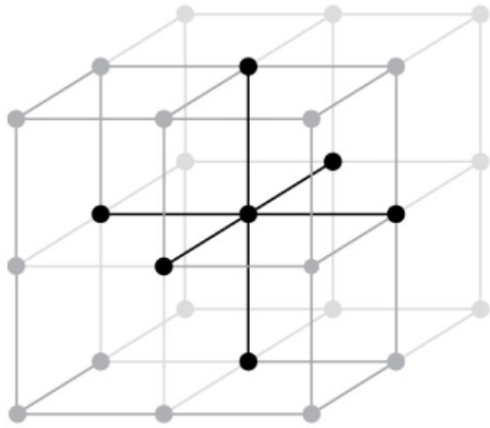
### 4. End centered cubic (ECC)

- Atoms present at each corner and at center of any two faces which are opposite to each other.
- has 2 lattice point per unit cell.
- 1 atom at each of 8 corners of unit cell and 1 atom at each of any 2 opposite faces make total no. atom per unit cell = 2.





**Coordination number** (the number of **nearest neighboring** atoms surrounding an atom) and the **no. of atoms present in varieties of cubic unit cell**



Simple Cubic:

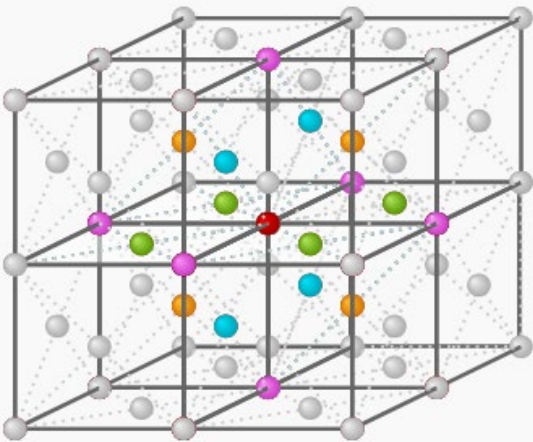
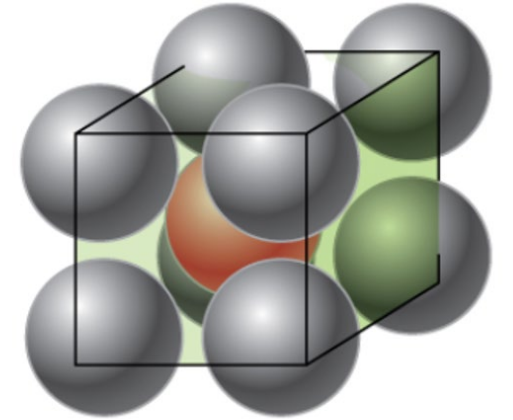
C.N. : 6

No. Atoms:  $(1/8 \times 8) = 1$

Body Centered Cubic:

C.N. : 8 (for both center and corner atoms)

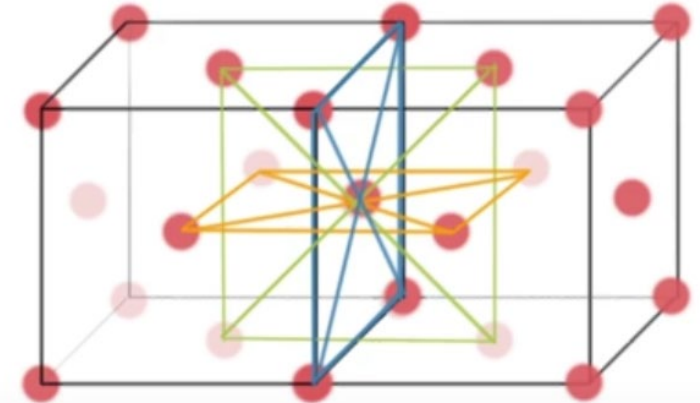
No. Atoms:  $(1/8 \times 8) + 1 = 2$



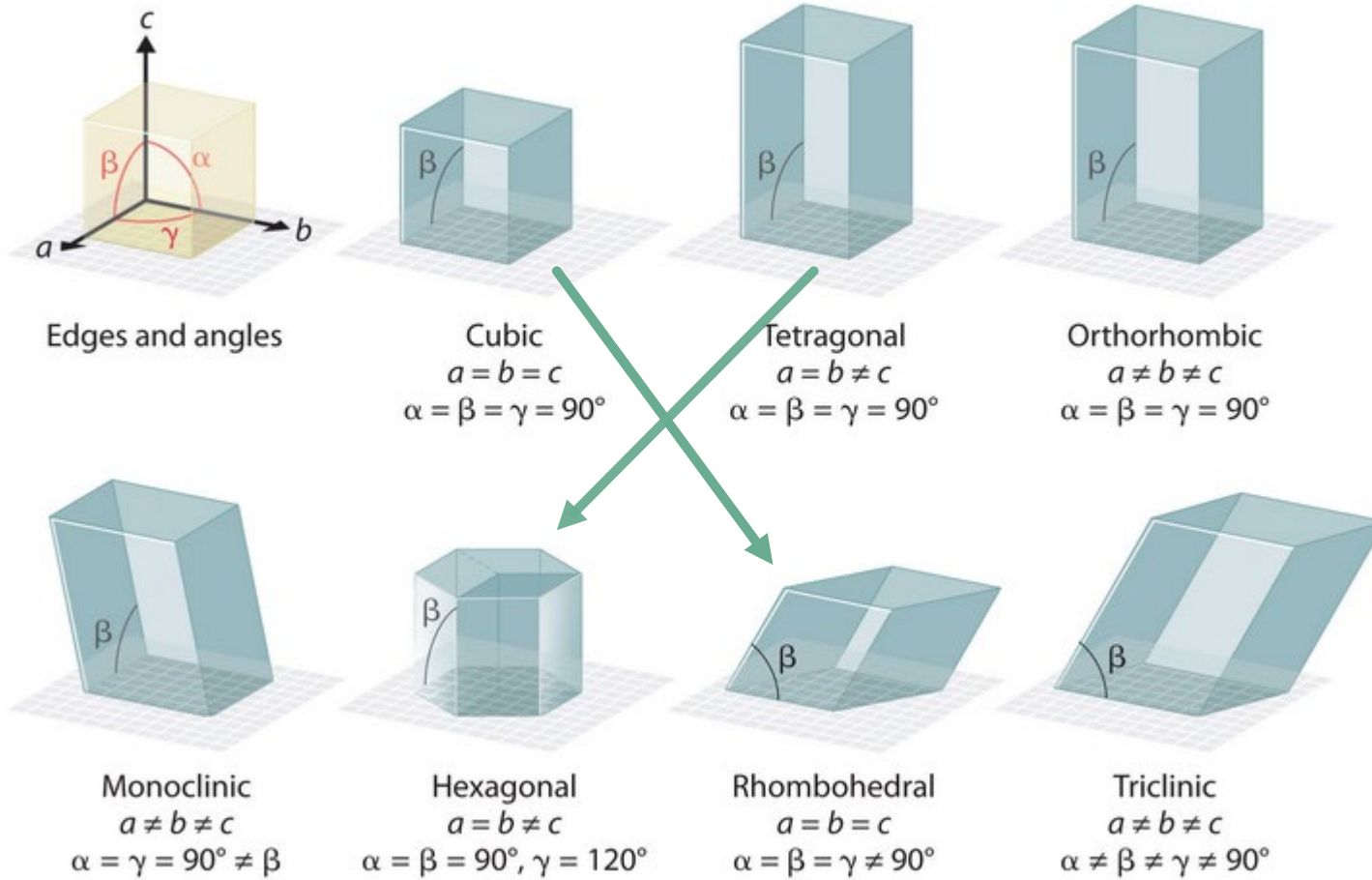
Face Centered Cubic:

C.N. : 12 (for both face centered and corner atoms)

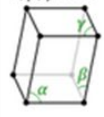
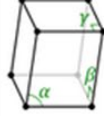
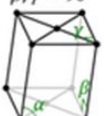
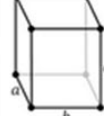
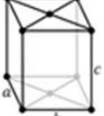
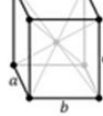

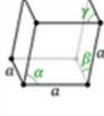
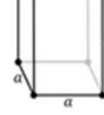
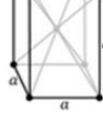
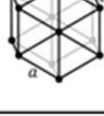
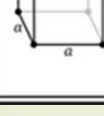
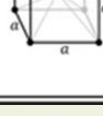
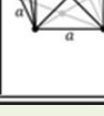
No. Atoms:  $(1/8 \times 8) + (1/2 \times 6) = 4$



# 7 Crystal Systems





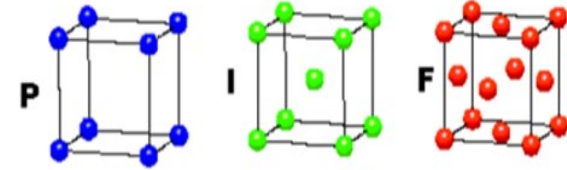
No:	Lattice Systems	Simple	Base-centered	Body-centered	Face-centered	Example
1	triclinic(none)	$\alpha, \beta, \gamma \neq 90^\circ$ 				$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , $\text{K}_2\text{Cr}_2\text{O}_7$
2	monoclinic(1 diad)	$\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$ 	$\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$ 			$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , $\text{FeSO}_4$ , $\text{Na}_2\text{SO}_4$
3	orthorhombic(3 perpendicular diads)	$a \neq b \neq c$ 	$a \neq b \neq c$ 	$a \neq b \neq c$ 	$a \neq b \neq c$ 	$\text{KNO}_3$ , $\text{BaSO}_4$
4	rhombohedral(1 triad)	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$ 				As, Sb, Bi
5	tetragonal(1 tetrad)	$a \neq c$ $a = a$ 		$a \neq c$ $a = a$ 		$\text{TiO}_2$ , $\text{SnO}_2$ , $\text{NiSO}_4$
6	hexagonal(1 hexad)					$\text{SiO}_2$ , Zn, Mg, Cd
7	cubic(4 triads)	$a = a = a$ 		$a = a = a$ 	$a = a = a$ 	Au, Cu, NaCl

# 14 Bravais Space Lattices in 3-D

## CUBIC

$$a = b = c$$

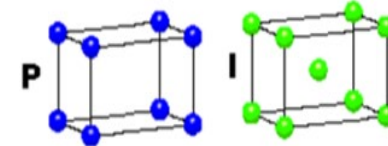
$$\alpha = \beta = \gamma = 90^\circ$$



## TETRAGONAL

$$a = b \neq c$$

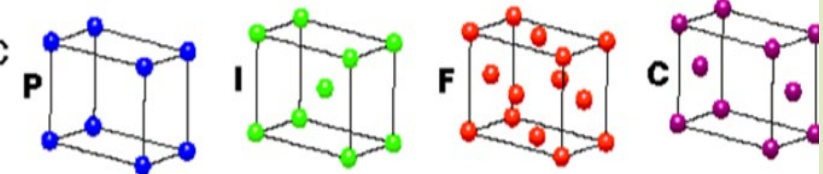
$$\alpha = \beta = \gamma = 90^\circ$$



## ORTHORHOMBIC

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

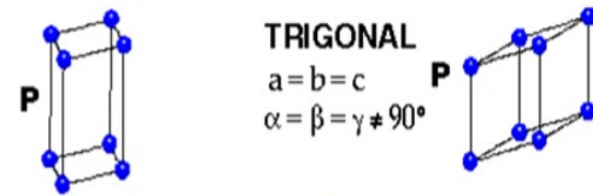


## HEXAGONAL

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ$$

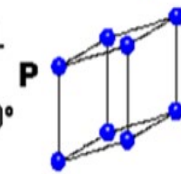
$$\gamma = 120^\circ$$



## TRIGONAL

$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

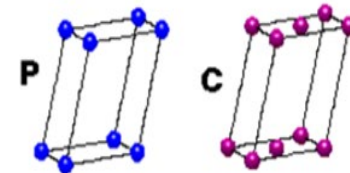


## MONOCLINIC

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ$$

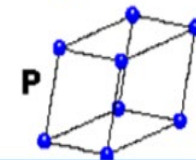
$$\beta \neq 120^\circ$$



## TRICLINIC

$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



### 4 Types of Unit Cell

P = Primitive

I = Body-Centred

F = Face-Centred

C = Side-Centred

+

7 Crystal Classes

→ 14 Bravais Lattices

# Miller Indices

Miller indices are used to specify directions and planes.

➤ **Orientation of plane not exactly the position of the plane**

- The number of indices will match with the dimension of the lattice or the crystal. Ex. in 1D there will be 1 index and 2D there will be two indices etc.

## Why are planes in a lattice important:

☐ Determining crystal structure

Diffraction methods measure the distance between parallel lattice planes of atoms and also the angles between lattice planes.

☐ Transport Properties

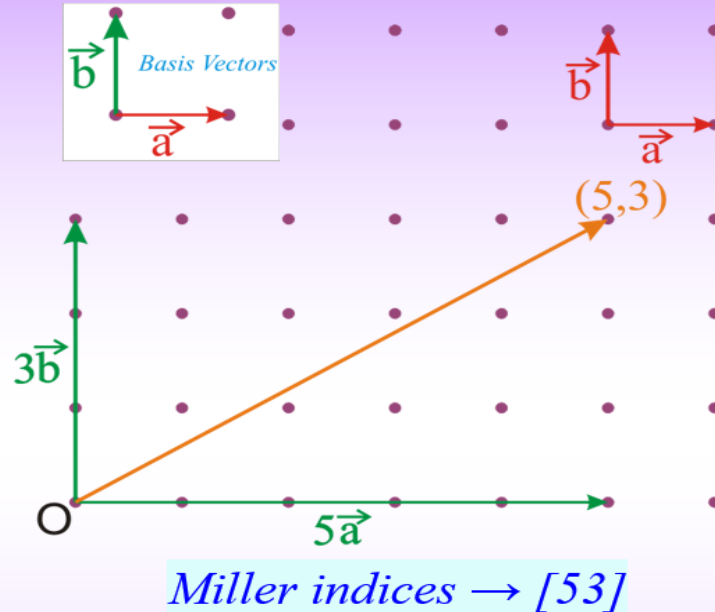
In certain materials, atomic structure in some planes causes the transport of electrons and/or heat to be particularly rapid in that plane.

## Notation Summary

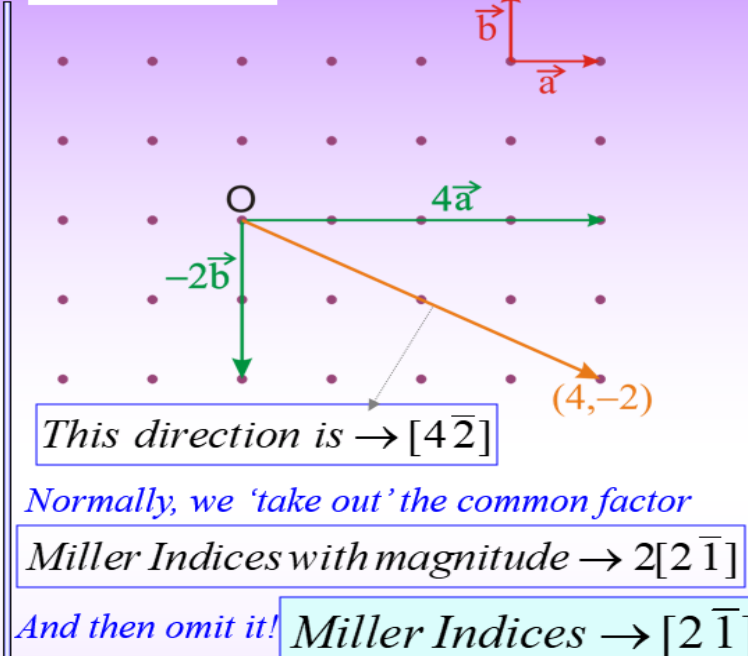
- $(h,k,l)$  represents a point – note the exclusive use of commas
- Negative numbers/directions are denoted with a bar on top of the number
- $[hkl]$  represents a direction
- $\langle hkl \rangle$  represents a family of directions
- $(hkl)$  represents a plane
- $\{hkl\}$  represents a family of planes

# Miller indices for directions

## Miller Indices for directions in 2D



## Another 2D example

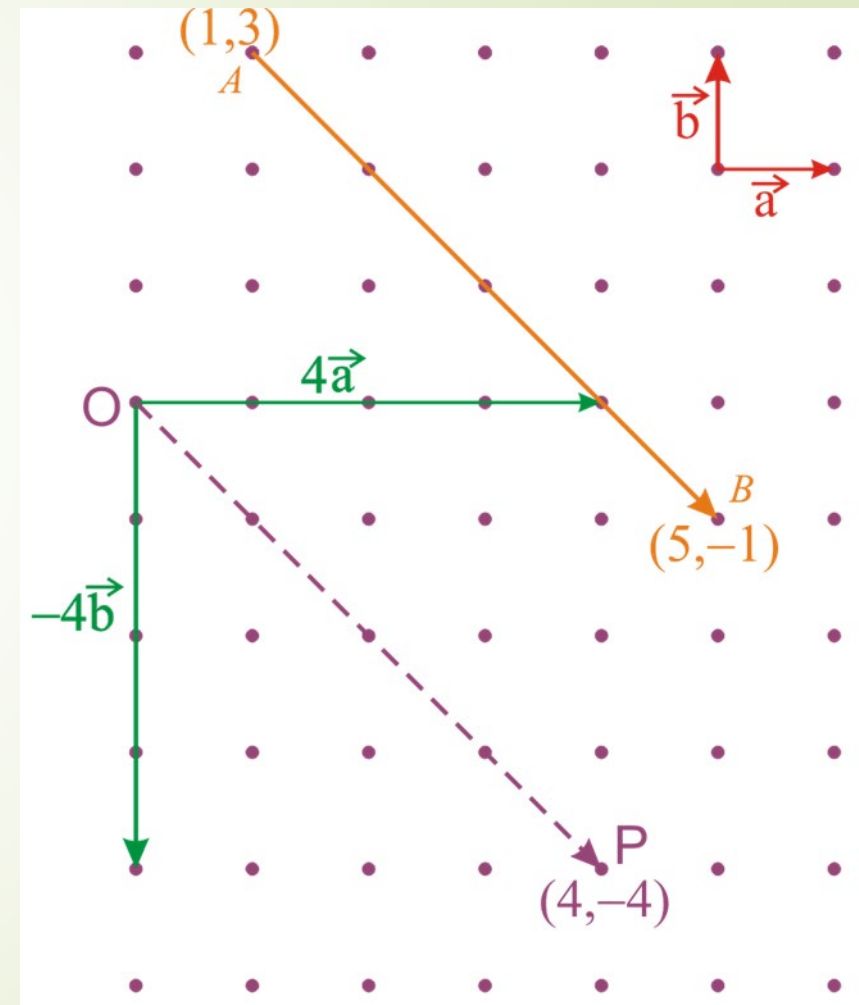


## STEPS in the determination of Miller indices for directions

- Position of the vector, such that start (S:  $(x_1, y_1)$ ) and end points (E:  $(x_2, y_2)$ ) are lattice points and note the value of the coordinates. Subtract to obtain:  $((x_2 - x_1), (y_2 - y_1))$ .
- Write these number in square brackets, without the 'comma':  $[* *]$ .
- 'Remove' the common factors

## For an arbitrary direction not including origin as one of the two lattice points

- ✓ Subtract the coordinates of the end point from the starting point of the vector denoting the direction
- ✓ If the starting point is A(1,3) and the final point is B(5,- 1)
- ✓ the difference (B-A) would be (4, -4).
- ✓ Enclose in square brackets, remove comma and write negative numbers with a bar, like :  $[4 \bar{4}]$
- ✓ Factor out the common factor :  $4[1 \bar{1}]$
- ✓ Miller indices:  $[1 \bar{1}]$





# Miller indices of any plane

## Steps to perform to obtain Miller indices of any plane

### 1. Select the origin

- Nearest corner to the plane with max no. of intercepts
- Origin should never coincide with the plane
- Planes can be shifted parallel without changing its orientation to obtain a proper origin.

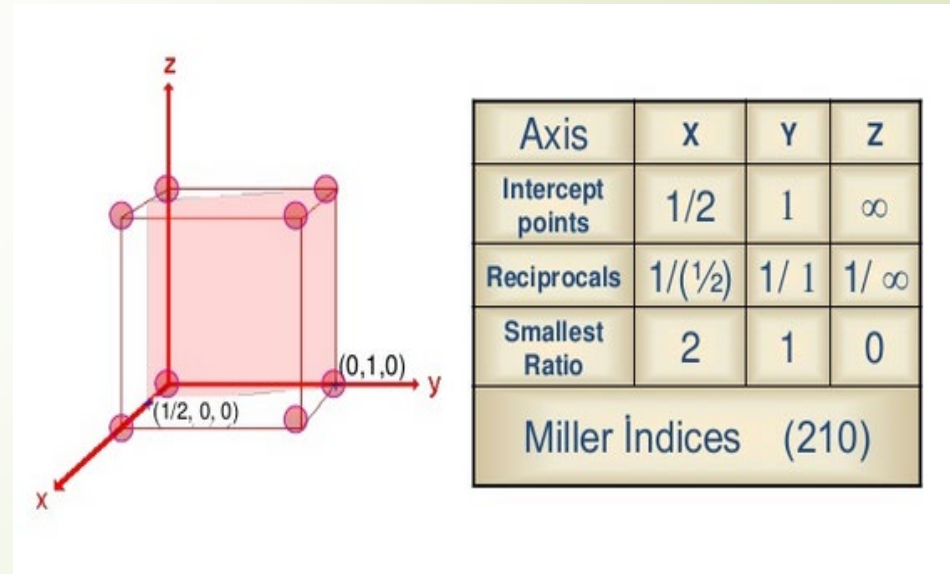
### 2. Find the intercepts of the plane along the axes (x,y,z).

### 3. Take the reciprocal of the intercepts.

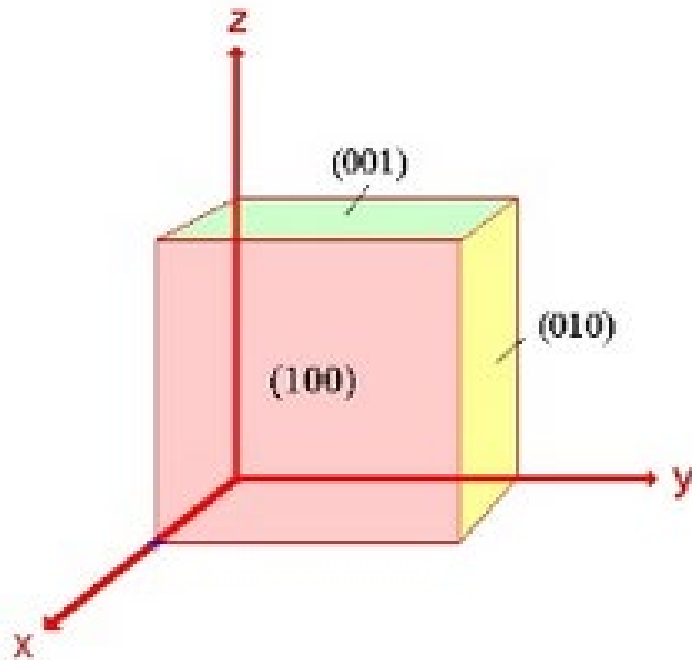
### 4. Using appropriate multiplier convert the reciprocals, to smallest set of whole numbers.

### 5. Enclose these numbers without 'comma' in () to identify a plane.

### 6. Use a bar at the top of the index number that have a negative sign.

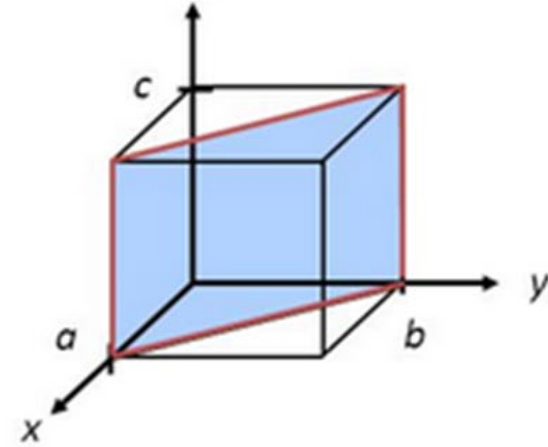






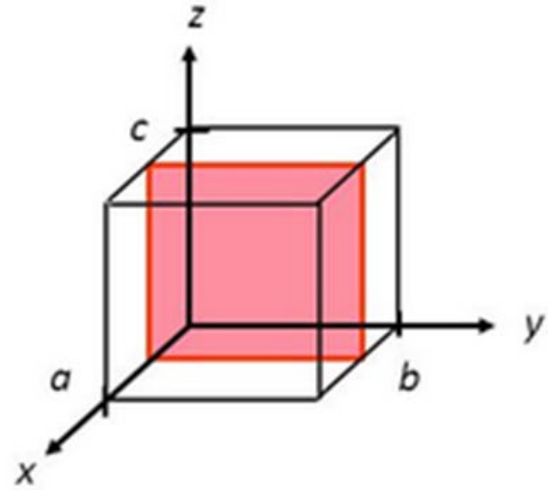
example

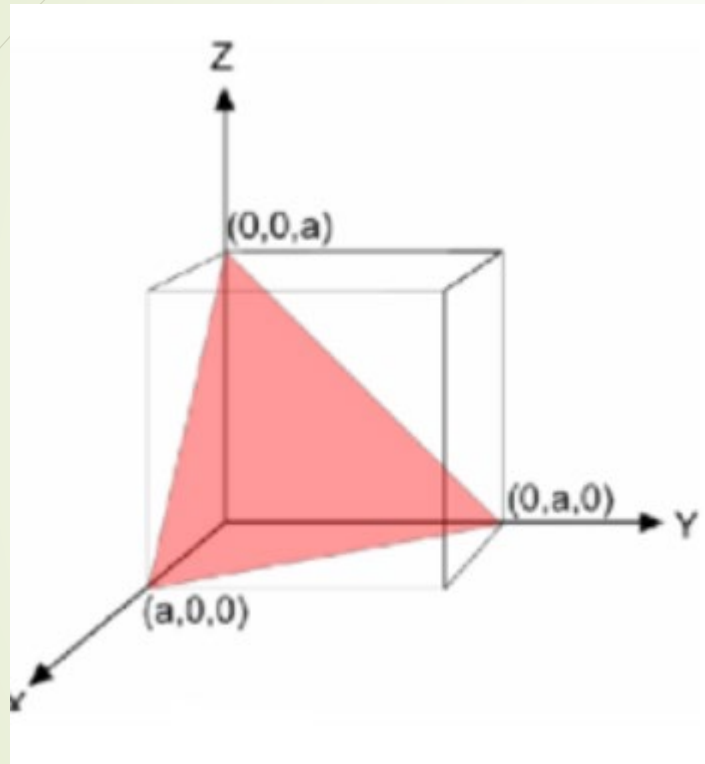
	$a$	$b$	$c$
1. Intercepts	1	1	$\infty$
2. Reciprocals	$1/1$	$1/1$	$1/\infty$
	1	1	0
3. Reduction	1	1	0
4. Miller Indices	(110)		



example

	$a$	$b$	$c$
1. Intercepts	$1/2$	$\infty$	$\infty$
2. Reciprocals	$1/1/2$	$1/\infty$	$1/\infty$
	2	0	0
3. Reduction	2	0	0
4. Miller Indices	(200)		



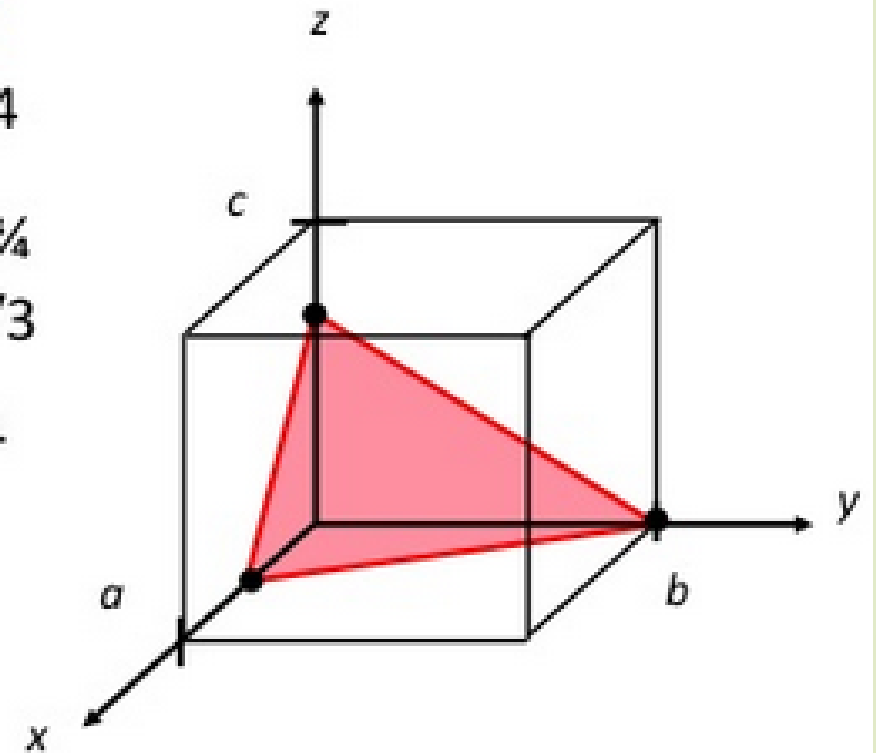


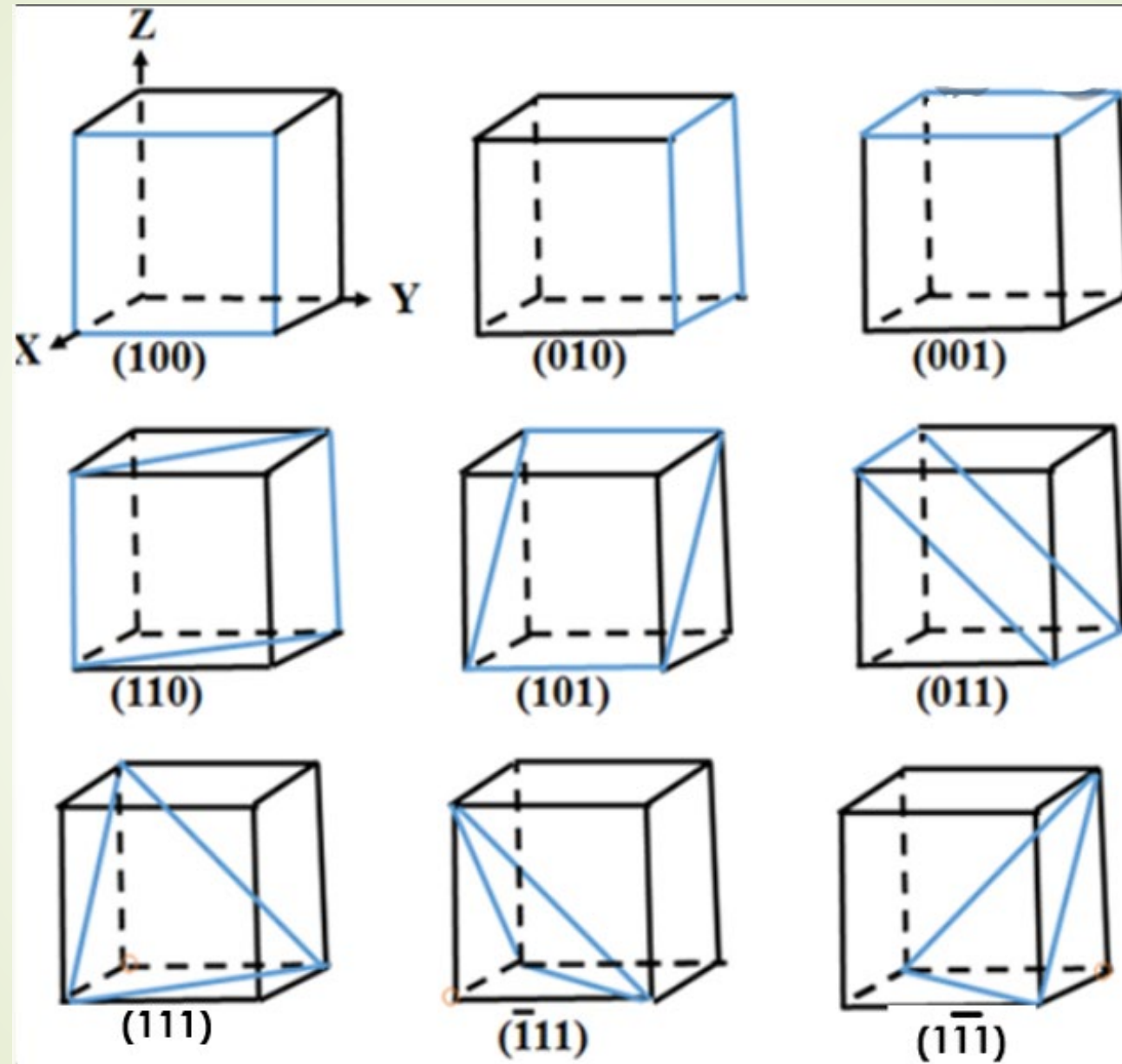
	$h$	$k$	$l$
Intercept length	1	1	1
Take reciprocal	$1/1$	$1/1$	$1/1$
Cleared fraction	1	1	1

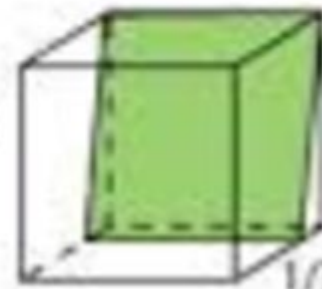
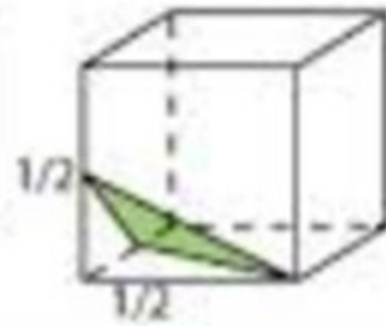
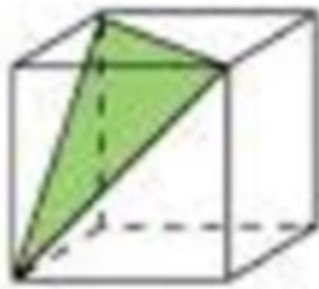
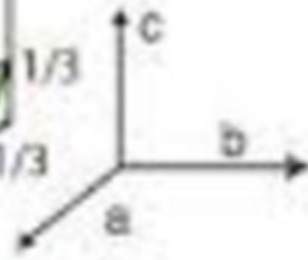
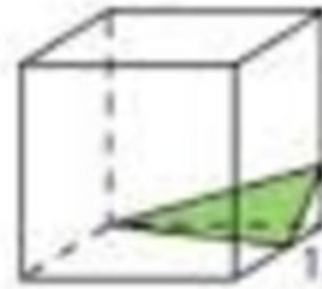
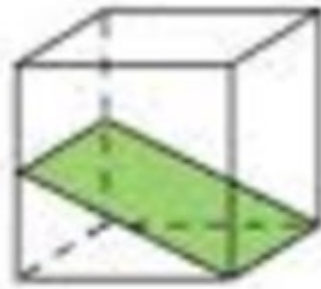
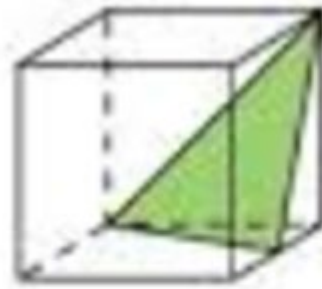
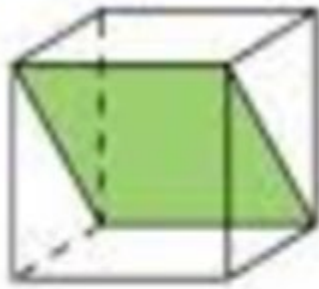
Miller Indices:  $(111)$

example

	<i>a</i>	<i>b</i>	<i>c</i>
1. Intercepts	$1/2$	$1$	$3/4$
2. Reciprocals	$1/(1/2)$ $2$	$1/1$ $1$	$1/(3/4)$ $4/3$
3. Reduction	$6$	$3$	$4$
4. Miller Indices	$(634)$		












# ➡ Crystal Defects

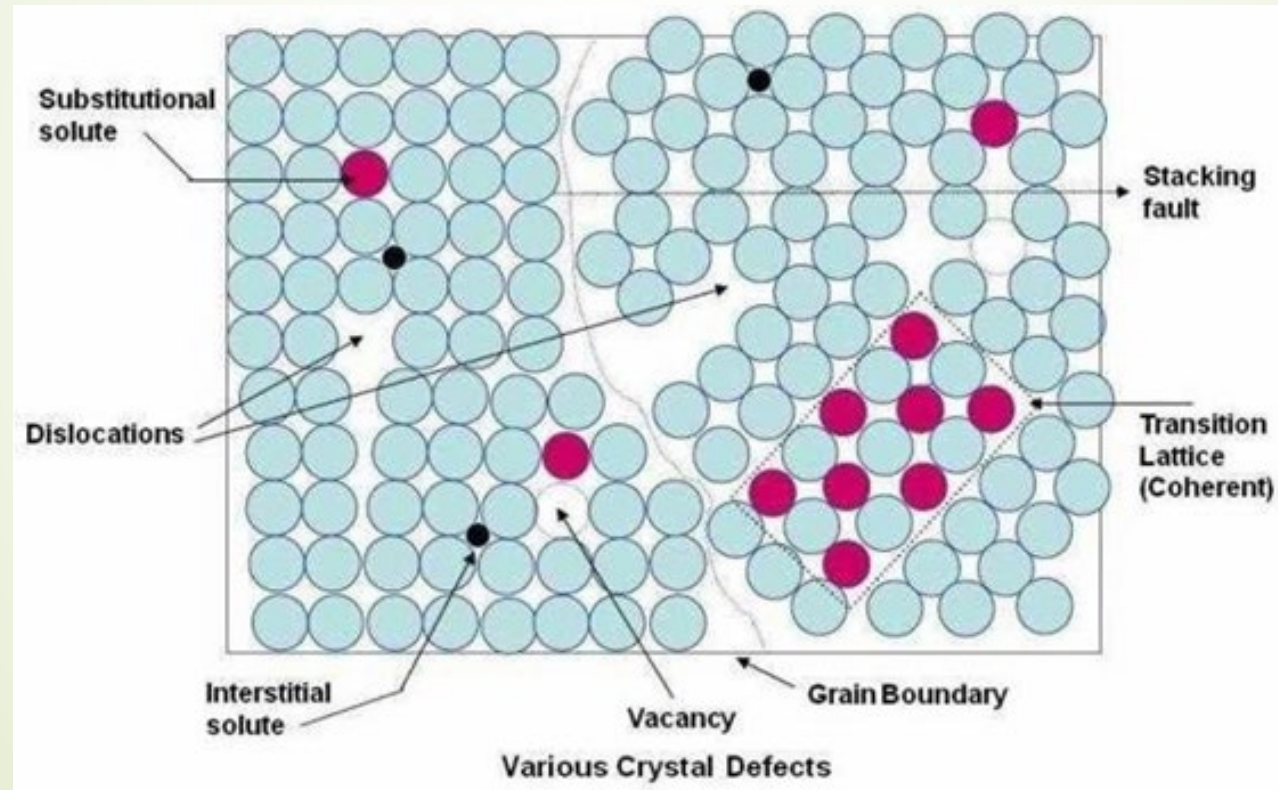


**Any deviation from the perfect atomic arrangement in a crystal is said to contain imperfections or defects.**

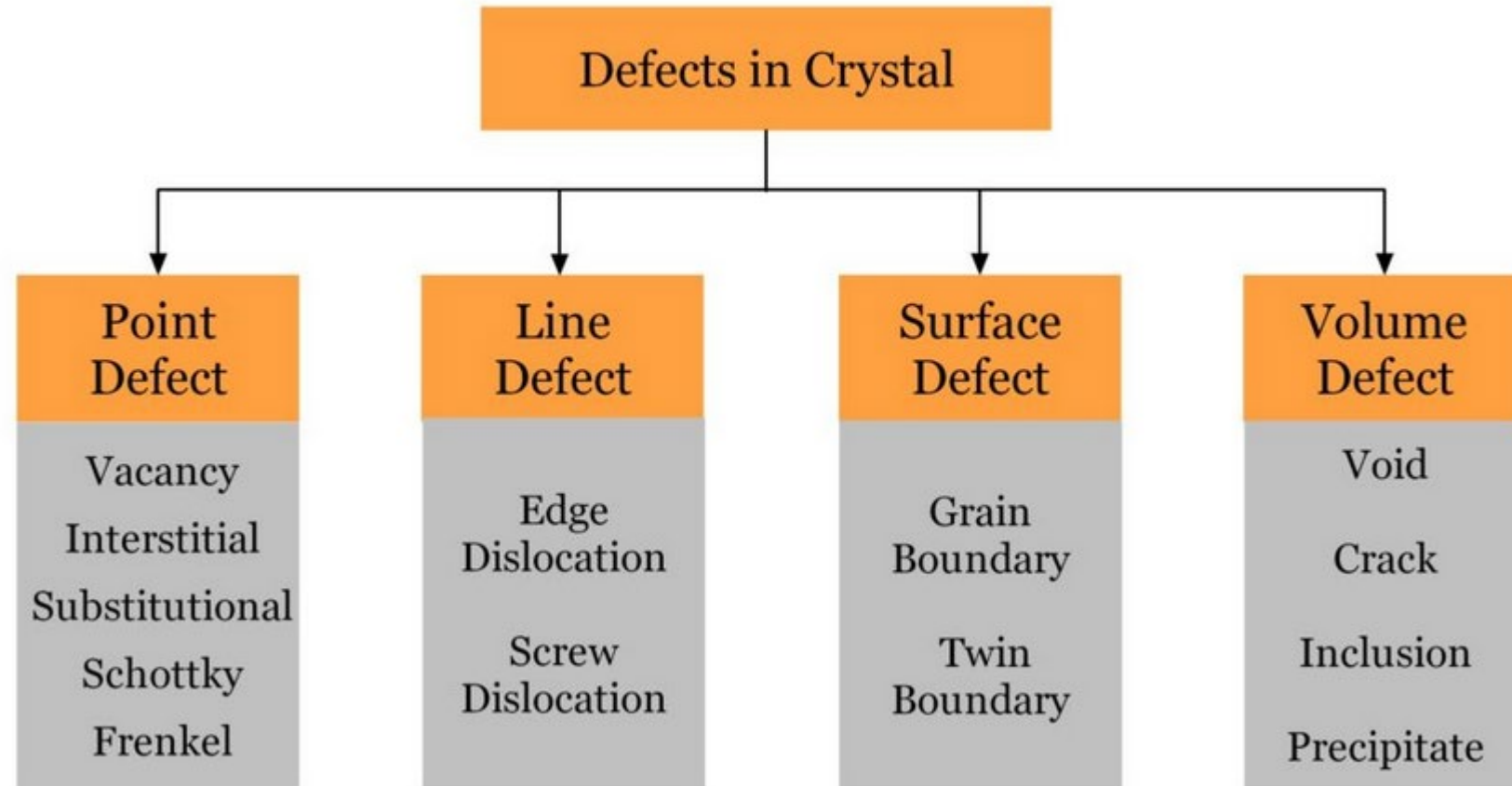
- Adding alloying elements to a metal is one way of introducing a crystal defect.
- Crystal imperfections have strong influence upon many properties of crystals.  
Ex. strength, electrical conductivity and hysteresis loss of Ferro magnets.
- Presence of impurities causes:
  - ✓ Color, luminescence of many crystals
  - ✓ Mechanical properties are usually controlled by imperfections

Imperfections in crystalline solids are normally classified according to their dimension

1. Point imperfections (Zero dimensional defects)
2. Line imperfections (one dimensional defects)
3. Plane or surface imperfections (Two dimensional defects)
4. Volume imperfections (three dimensional defects)



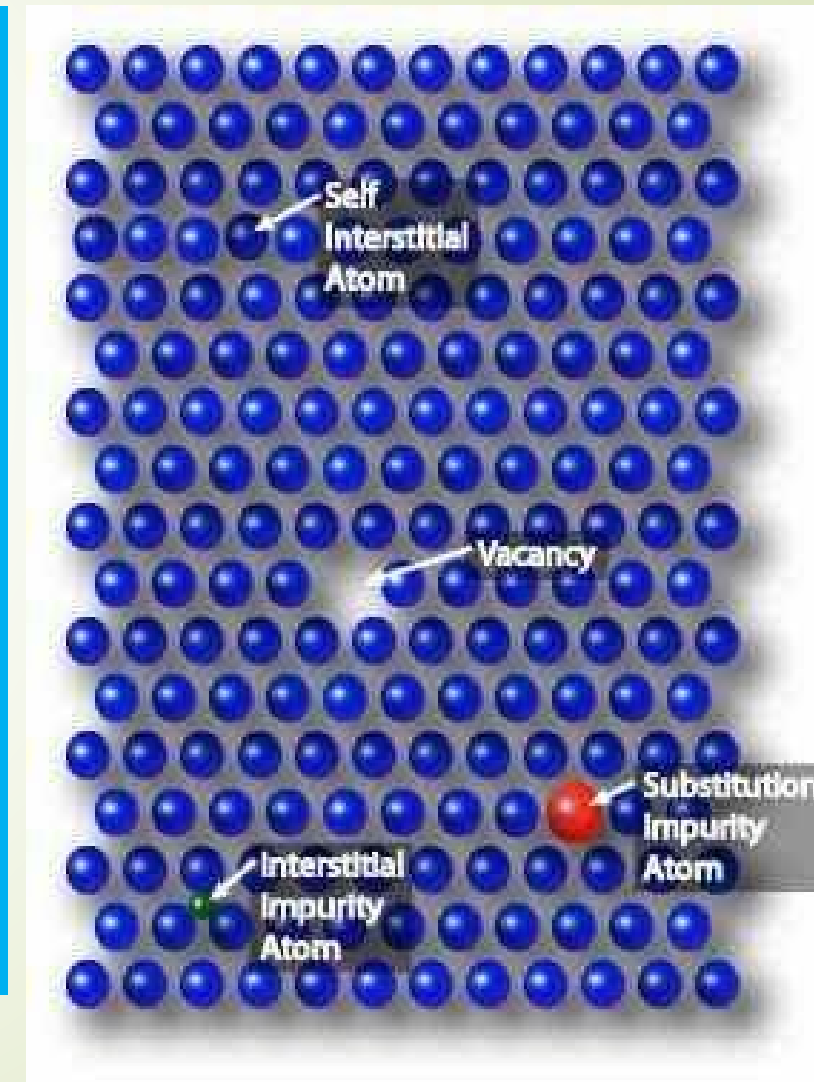
# CLASSIFICATION OF DEFECTS IN CRYSTALLINE SOLID



## Point Defect

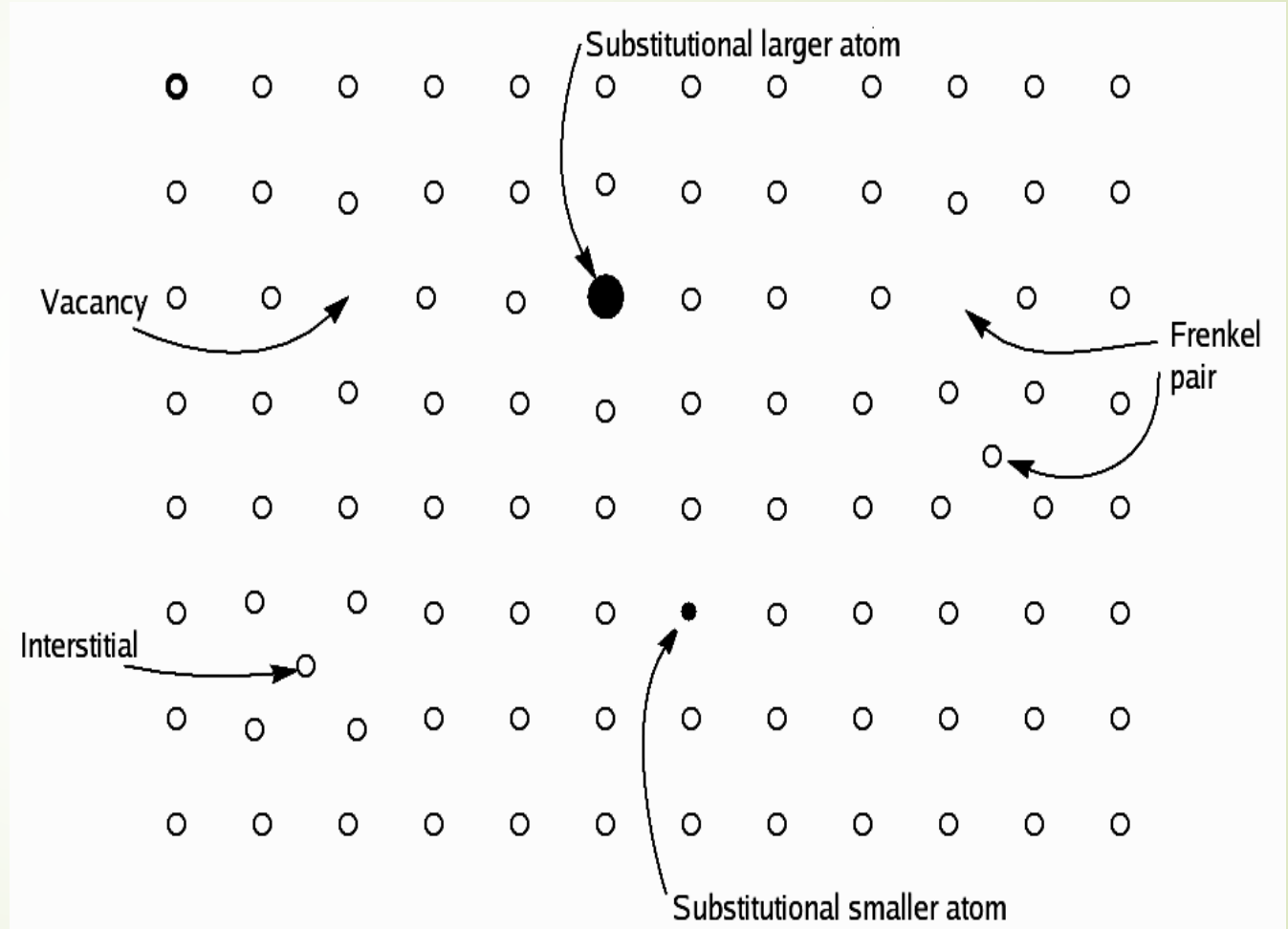
An atom is missing or is in an irregular place in the lattice structure.

- I. **Self interstitial atoms:** an extra atom that has crowded its way into an interstitial void in the crystal structure.
- II. **Interstitial impurity:** atoms are much smaller than the atoms in the bulk matrix. Interstitial impurity atoms fit into the open space between the bulk atoms of the lattice structure.
- III. **Substitutional impurity:** an atom of a different type than the bulk atoms, which has replaced one of the bulk atoms in the lattice. They are usually close in size to the bulk atom (substitutional large) or sometimes could be smaller in size (substitutional small).



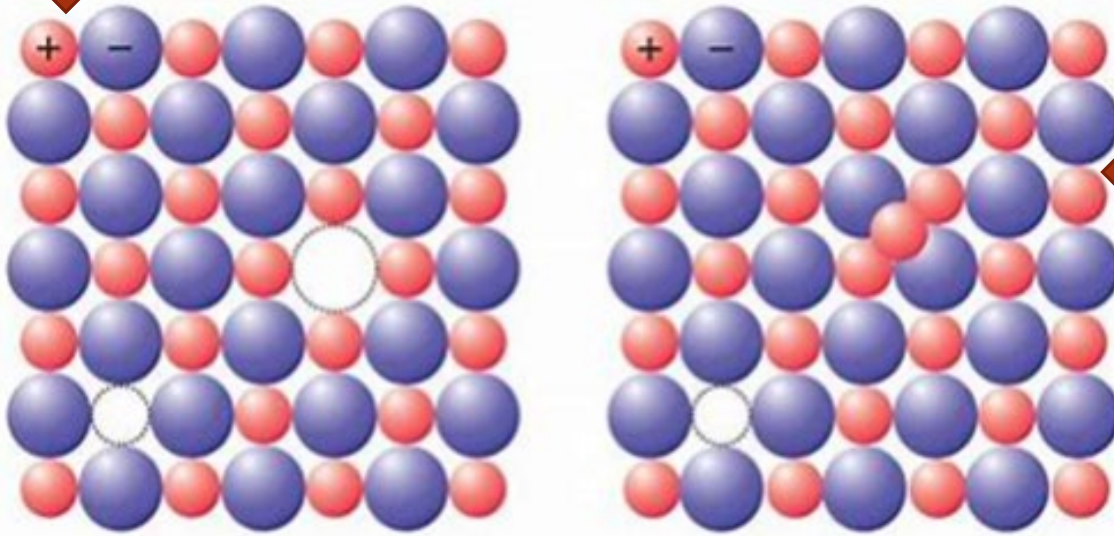


**IV. Vacancies** are empty spaces where an atom should be, but is missing. They are common, especially at high temperatures when atoms frequently and randomly change their positions leaving behind empty lattice sites.



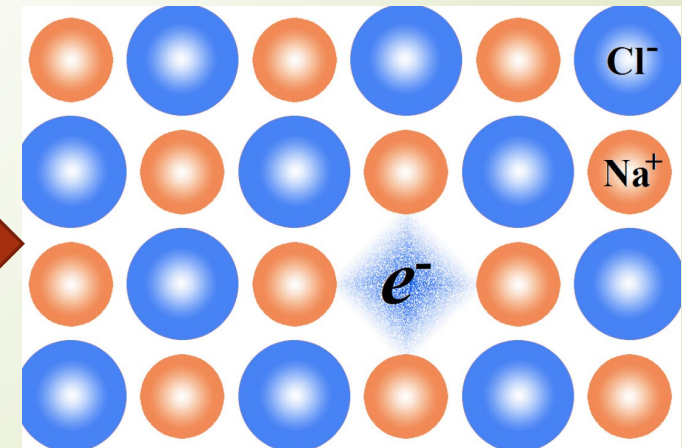


- v. In ionic crystals, **Schottky imperfection** forms when oppositely charged ions leave their lattice sites, creating vacancies. These vacancies are formed in stoichiometric units, to maintain an overall neutral charge in the ionic solid.

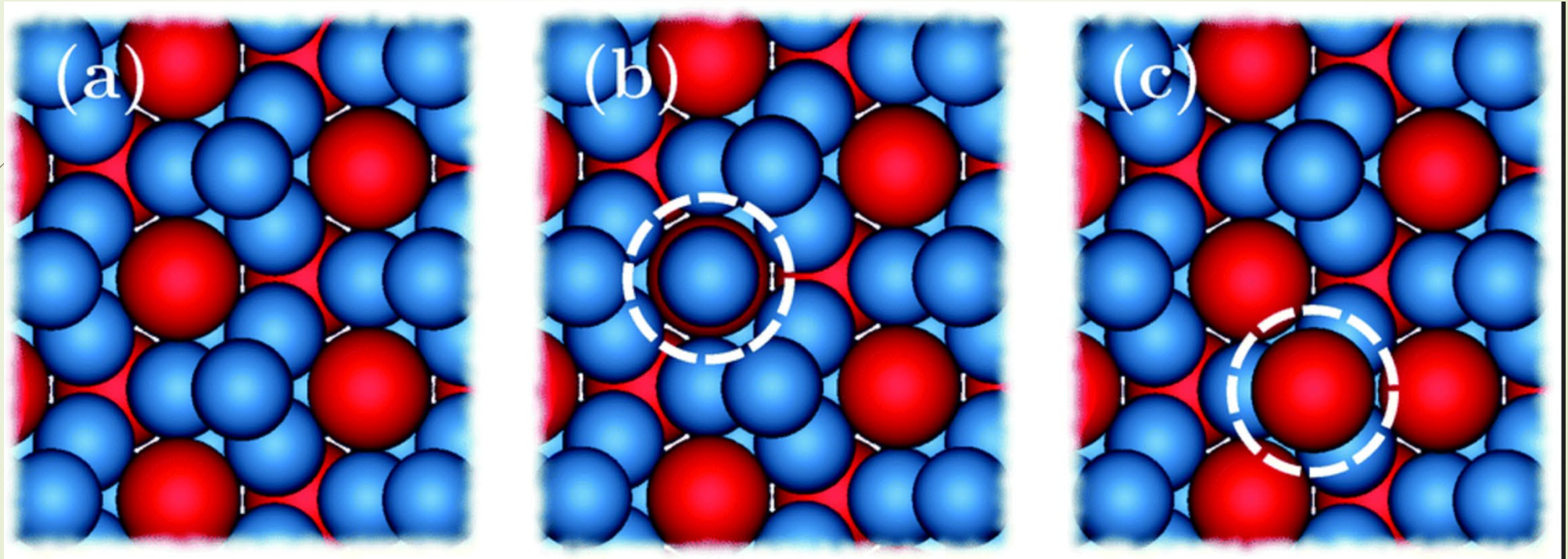


- vi. **Frenkel defect** is a type of defect in crystalline solids wherein an atom is displaced from its lattice position to an interstitial site, creating a vacancy at the original site and an interstitial defect at the new location.

- vii. **F-center** or **color center** is a type of crystallographic defect in which an anionic vacancy in a crystal is filled by one or more electrons.



**viii. Antisite defects** occur in an ordered alloy or compound when atoms of different type exchange positions.



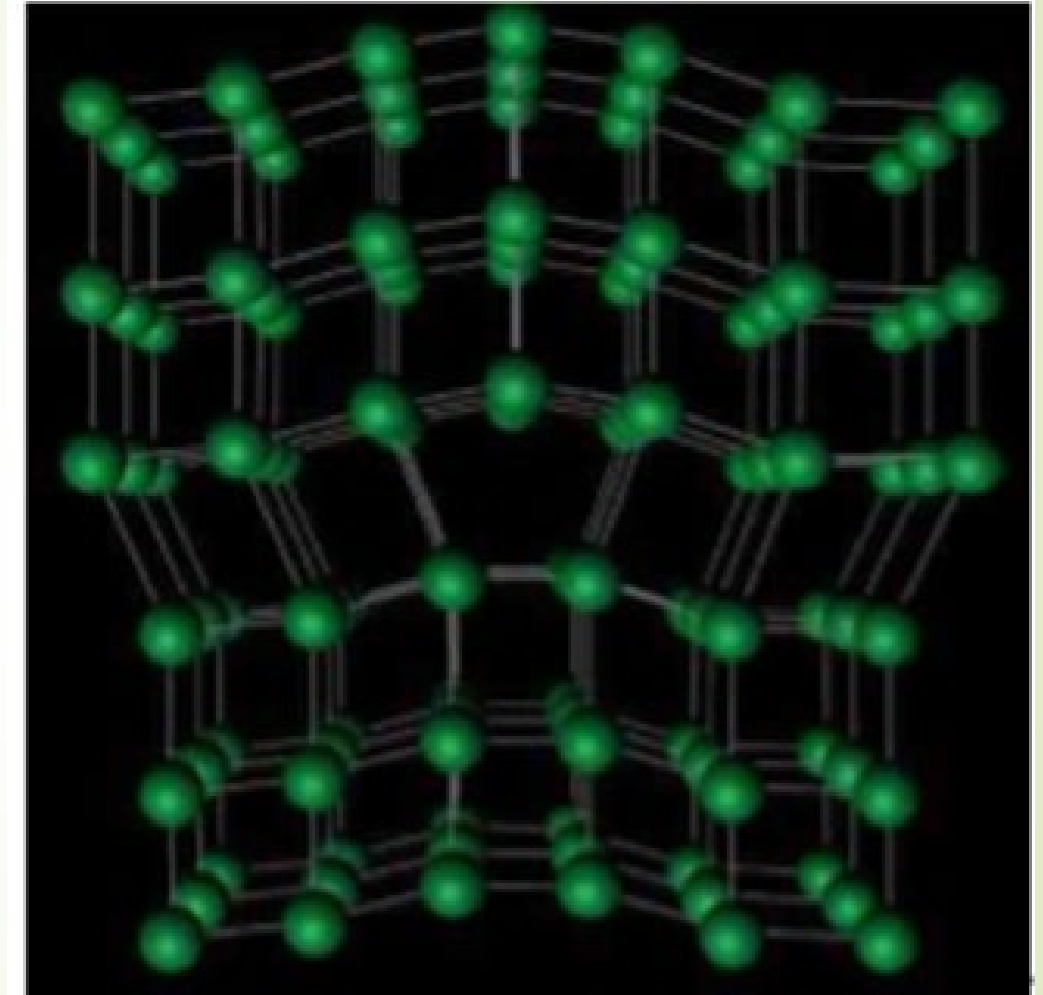


## Line Imperfections

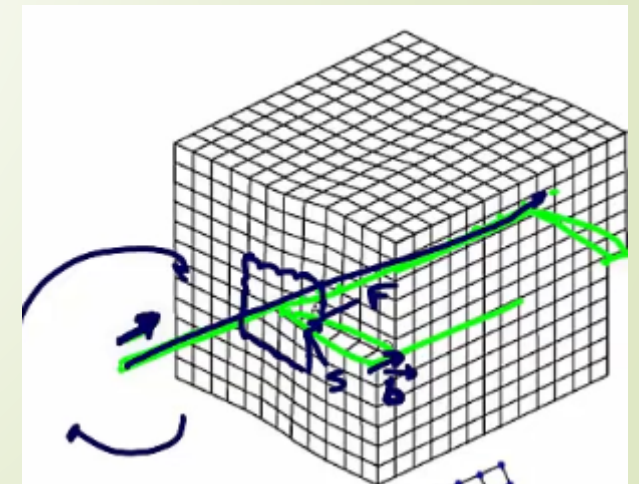
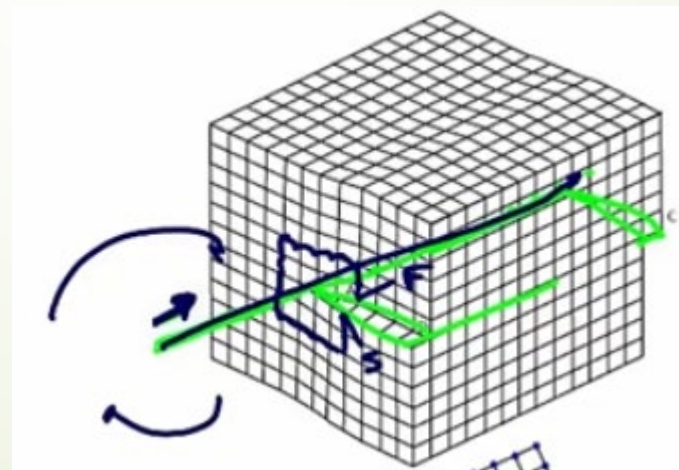
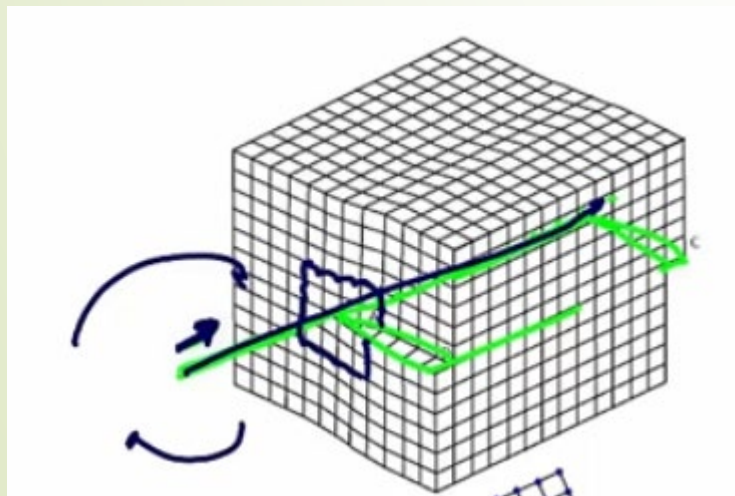
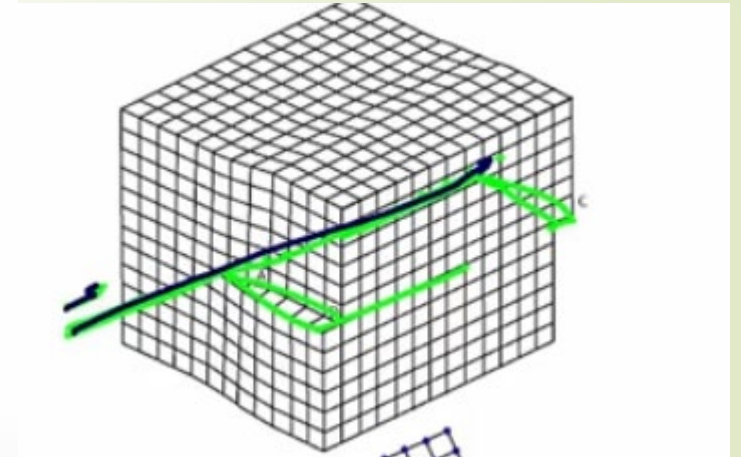
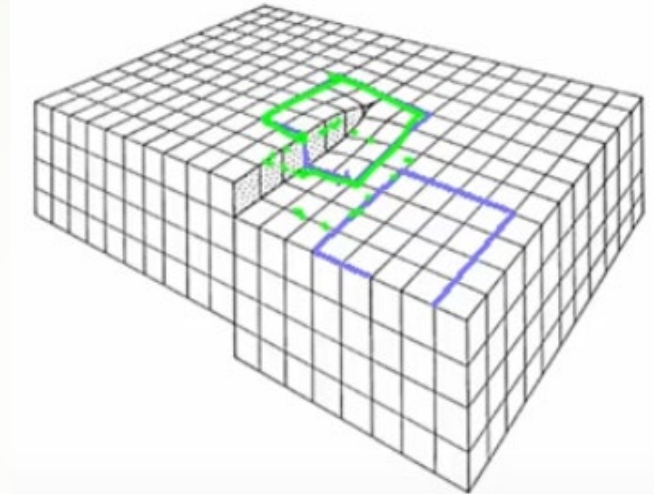
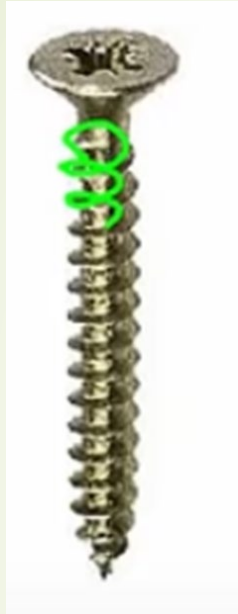
Groups of atoms are in irregular positions.

- commonly called **dislocations**.
- Any deviation from perfectly periodic arrangement of atoms along a line is called the line imperfection.

- I. **Edge dislocations** are caused by the termination of a plane of atoms in the middle of a crystal. In such a case, the adjacent planes are not straight, instead bend around the edge of the terminating plane so that the crystal structure is perfectly ordered on either side.



## II. **Screw dislocation** is a result of shear stress

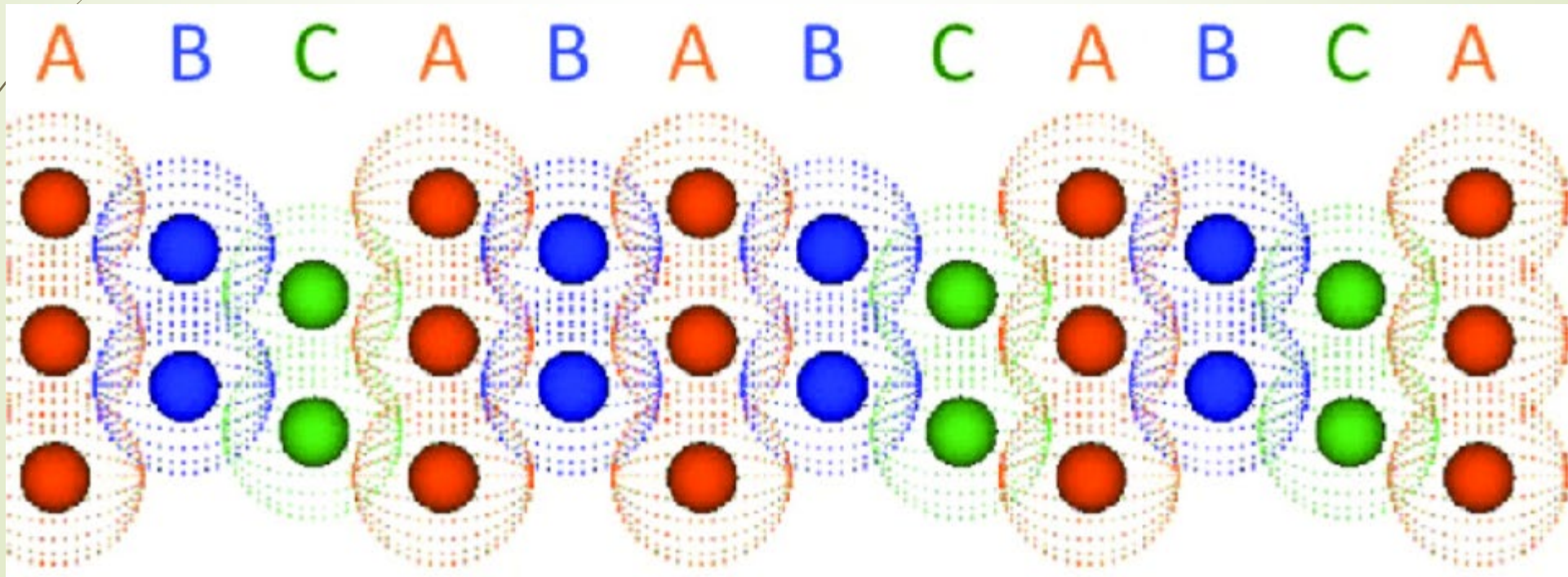




## Planar defects

- ❑ **Stacking faults:** Different stacking sequences of close-packed crystals
  - A change in the stacking sequence over a few atomic spacings produces a stacking fault
- ❑ **Twin region:** a change over many atomic spacings.

Stacking faults are common example is in close-packed structures.



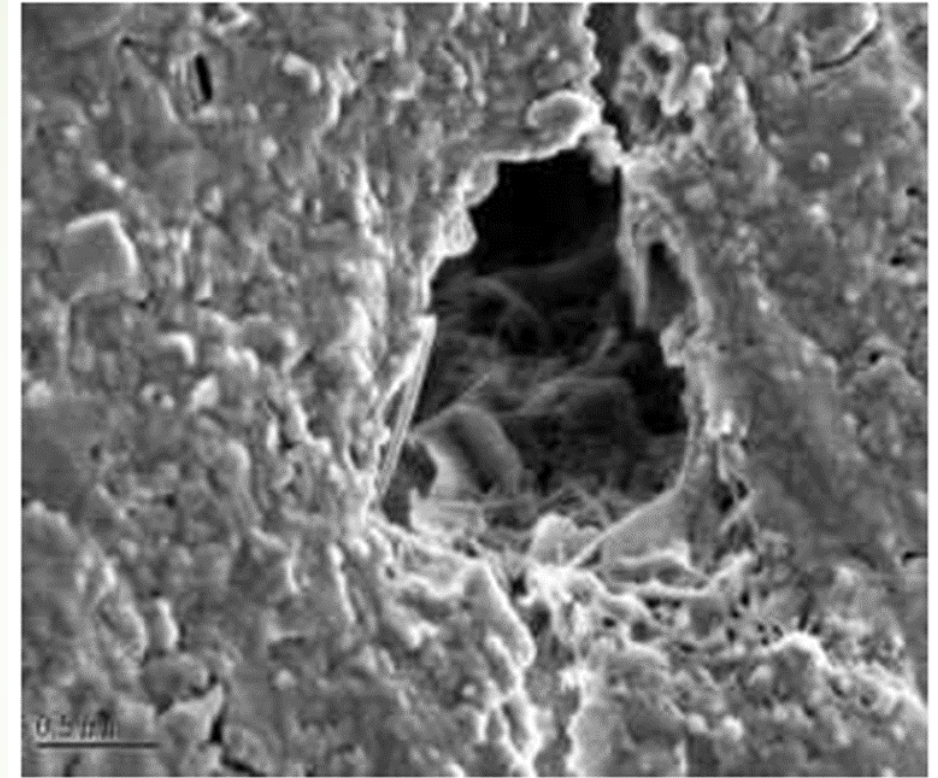


## Volume or Bulk Defects

Voids are regions where there are a large number of atoms missing from the lattice.

- occur on a much bigger scale than the rest of the crystal defects.
- Voids can occur for a number of reasons.

- a) Porosity** : occurs due to air bubbles becoming trapped when a material solidifies.
- b) Cavitation** : occurs due to the shrinkage of a material as it solidifies.
- c) Inclusions**: when impurity atoms cluster together to form small regions of a different phase. These regions are often called precipitates or inclusions.



The image is a void in a piece of metal. The image was acquired using a Scanning Electron Microscope (SEM).