UNIT - I

Material Technology:

Materials technology is a relatively comprehensive discipline that begins with the production of goods from raw materials to processing of materials into the shapes and forms needed for specific applications.

Materials - metals, plastics and ceramics - typically have completely different properties, which means that the technologies involved in their production are fundamentally different. Materials technology is a constantly evolving discipline, and new materials with interesting properties lead to new applications. For example, the combination of different materials into composites gives rise to entirely new material properties.

Material Science:

Materials Science is closely related to materials technology. Materials Science is a multidisciplinary field that connects material properties to the material's chemical composition, micro-structure and crystal structure. Crystal structure is a description of the ordered arrangement of atoms, ions or molecules in a crystalline material. The crystalline lattice, is a periodic array of the atoms. When the solid is not crystalline, it is called amorphous. Examples of crystalline solids are metals, diamond and other precious stones, ice, graphite. Examples of amorphous solids are glass, amorphous carbon (a-C), amorphous Si, most plastics

Polymorphism and Allotropy:

Some materials may exist in more than one crystal structure, this is called **polymorphism**. If the material is an elemental solid, it is called **allotropy**. An example of allotropy is carbon, which can exist as diamond, graphite, and amorphous carbon.

Anisotropy:

Different directions in the crystal have a different packing. For instance, atoms along the edge FCC crystals are more separated than along the face diagonal. This causes *anisotropy* in the properties of crystals; for instance, the deformation depends on the direction in which a stress is applied.

Crystal Structure:

It is the manner in which atoms, ions, or molecules are spatially arranged.

Lattice:

It is a 3D collection of points that divide space into smaller equally sized units.

Basis:

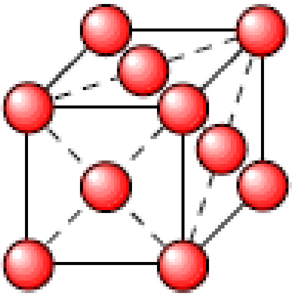
It is a group of atoms associated with a lattice point. This may be one single atom or a group of atoms.

Atomic Radius:

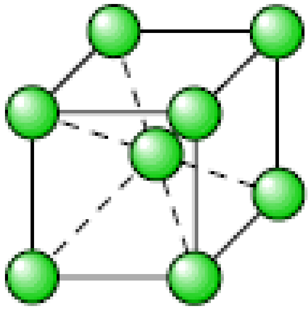
Atomic radius is the apparent radius of an atom, typically calculated from the dimensions of the unit cell, using close-packed directions

Unit Cells:

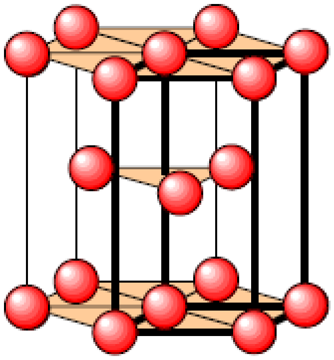
It is the basic building block of the crystal structure. It defines the entire crystal structure with the atom positions within. The unit cell is the smallest structure that repeats itself by translation through the crystal. The most common types of unit cells are the faced-centered cubic (FCC), the body-centered cubic (BCC) and the hexagonal close-packed (HCP).



FCC



BCC



HCP

The properties of the unit cells are

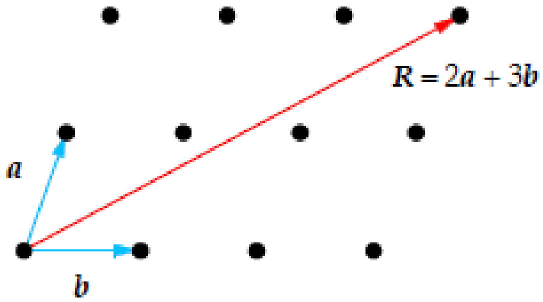
- The type of atoms and their radii *R*.
- cell dimensions (side *a* in cubic cells, side of base *a* and height *c* in HCP) in terms of *R*.
- *n*, number of atoms per unit cell. For an atom that is shared with *m* adjacent unit cells, we only count a fraction of the atom, 1/*m*.
- *CN*, the coordination number, which is the number of closest neighbors to which an atom is bonded.

Space lattice:

A space lattice is a set of points such that a translation from any point *P* in the lattice by a vector.

$\boldsymbol{R}_{lmn} = l\boldsymbol{a} + m\boldsymbol{b} + n\boldsymbol{c}$ (l, m, n integers)

locates an exactly *equivalent* point, *i.e.* a point with the same environment as *P*. This is **translational symmetry**. The vectors ***a***, ***b***, ***c*** are known as **lattice vectors**



Coordination number:

The number of nearest neighbor atoms or ions surrounding an atom or ion.

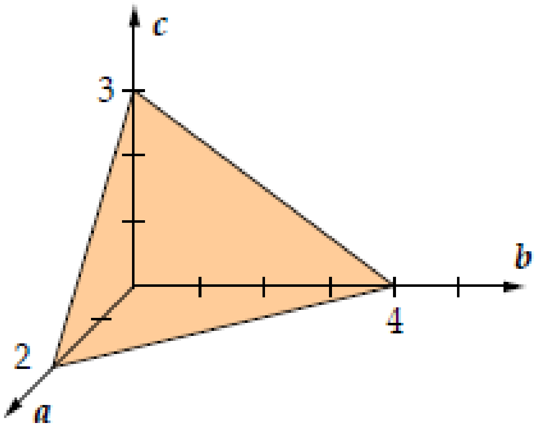
The Atomic Packing Factor (APF):

APF is the fraction of the volume of the cell actually occupied by the hard spheres.
APF = Sum of atomic volumes/Volume of cell.

Miller indices:

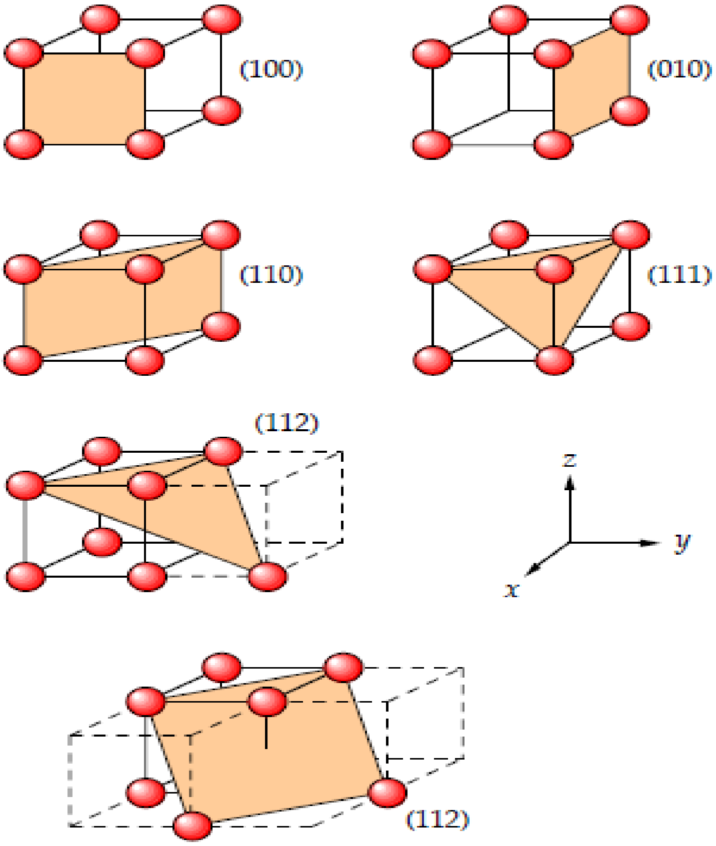
The plane of atoms in a crystal are defined using mathematical notation known as **Miller indices**.

Procedure for finding millers indices:
(*i*) Find the intercepts of the plane with the 3 crystal directions or axes in terms of primitive vectors ***a*** , ***b*** , ***c***
(*ii*) Take the reciprocals
(*iii*) Multiply the resulting 3 numbers by the smallest number that makes the result equal to 3 integers h, k, l. The plane is then defined by the notation (h k l).



Thus, in the above example :

intercepts = 2 , 4 , 3
reciprocals = 1/2 , 1/4 , 1/3
x 12 = 6 , 3 , 4 and so the plane is (6 3 4).



In a crystal with true cubic symmetry the choice of which of the three axes to label the .*x*-axis., and which the .*y*. and the .*z*., is entirely arbitrary. Thus the (100) plane is physically *equivalent* to the mathematically distinct (010) and (001) planes. This leads to the grouping of various numbers of planes into sets, or families

_ _ _
(001) (010) (100) (100) (010) (100) 3 x 2 = 6
(110) (011) .... 3 x 2 x 2 = 12
(111) .... 2 x 2 x 2 = 8
(210) .... 6 x 2 x 2 = 24
(321) .... 6 x 2 x 2 x 2 = 48
The sets of planes are denoted { h k l }.
For directions in a crystal, take components (or projections) on axes ***a*** , ***b*** and ***c*** . For example, the direction whose components are 2*a*, 3*b*, 2*c* is denoted [2 3 2]. Directions also occur in sets, and are denoted < h k l >.
For a **cubic** lattice, the direction [h k l] is perpendicular to the plane (h k l).

Body Centred Cubic:

In BCC atoms are arranged at the corners of the cube with another atom at the cube center. The BCC structure is commonly found for the elements at the lighter end of all the rows of the periodic table, from the alkali metals (Li, Na, K, Rb, Cs) through to the start of the transition metals (V, Cr, Fe, Nb, Mo, Ba, Ta, W).

Face Centred Cubic:

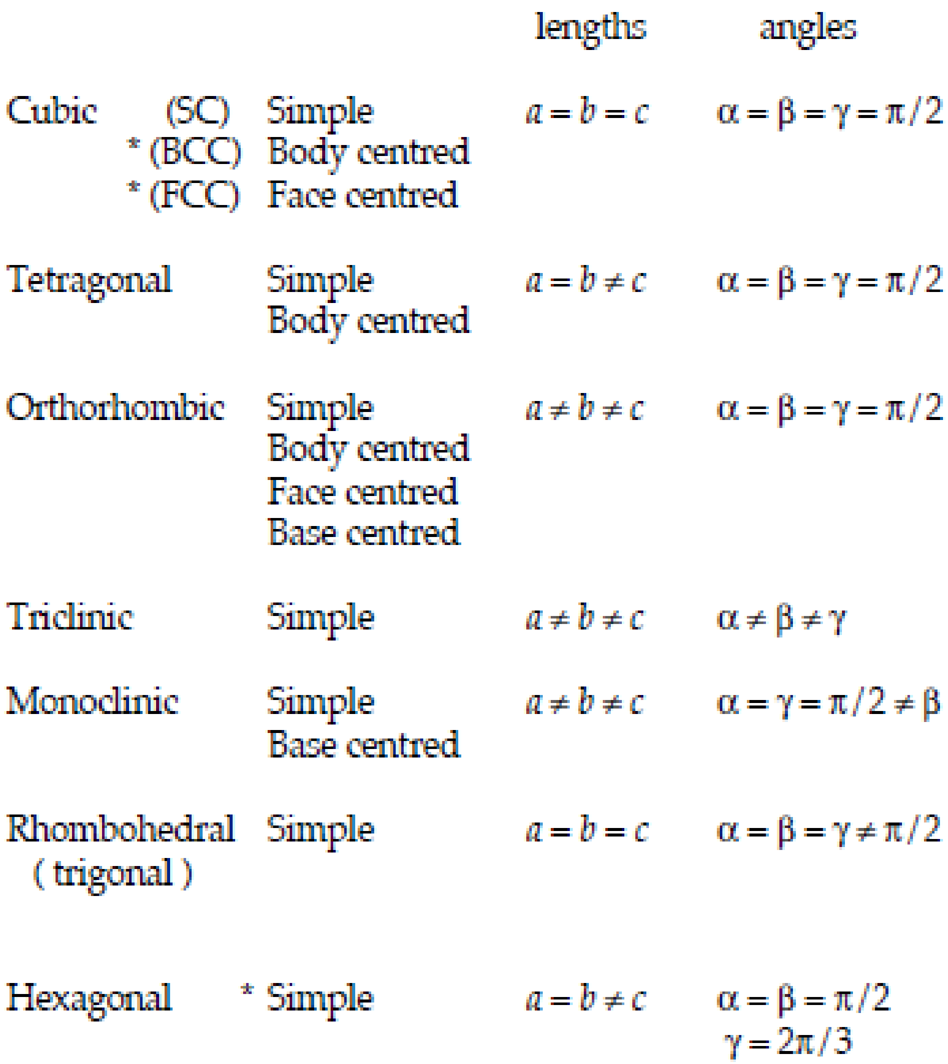
Atoms are arranged at the corners and center of each cube face of the cell. The FCC structure is adopted by a large number (~ 20) of metals, including the heavier end of the transition metals (Ni, Rh, Pd, Ir, Pt), the noble metals (Cu, Ag, Au), and some of the rare gases (Ne, Ar, Kr, Xe). In addition, many compounds and alloys are based on the cubic structure. Two examples of general interest are NaCl and CsCl, and these compounds have given their names to these generic types of structure.

Hexagonal Close-Packed:

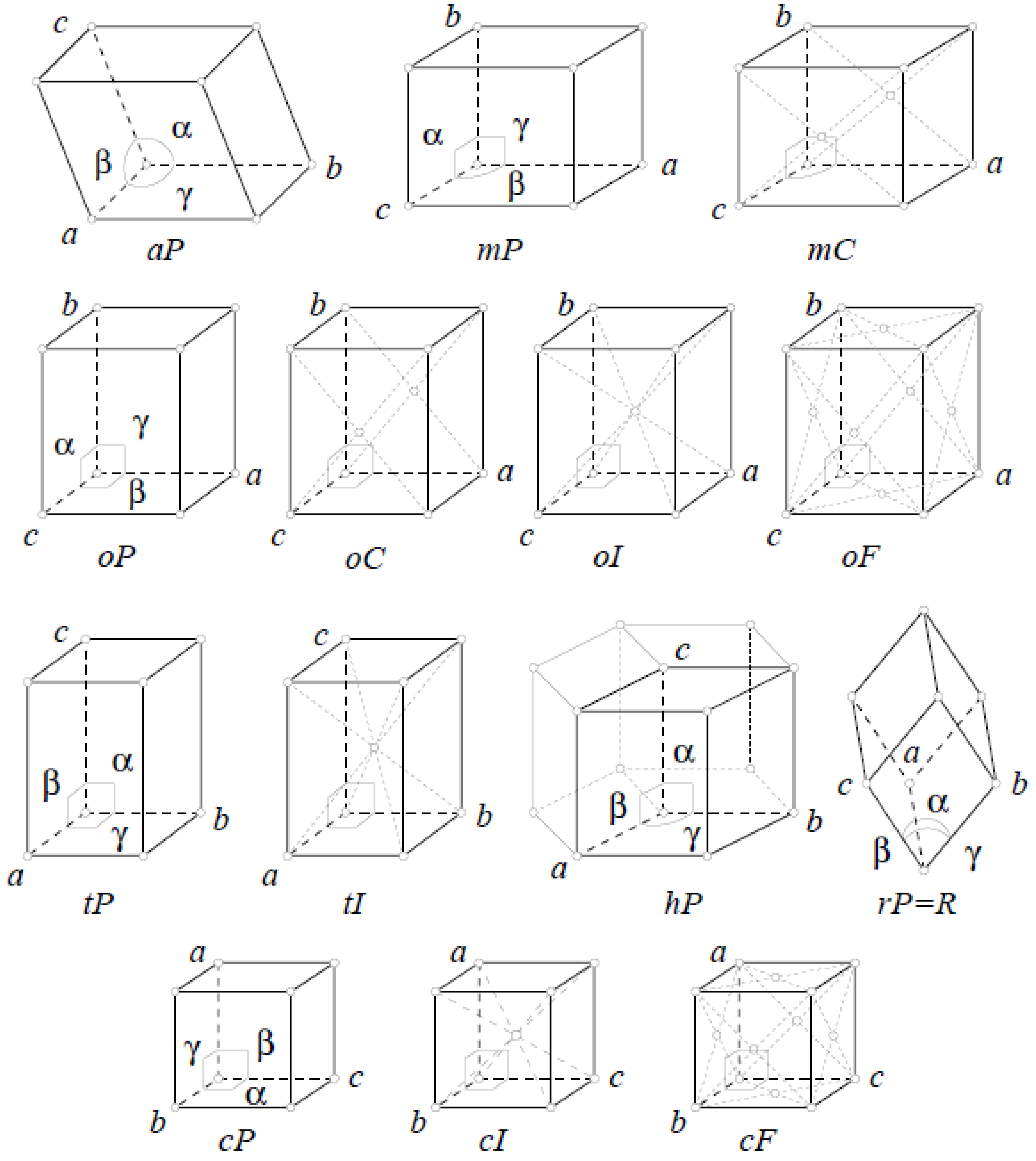
The HCP structure is based on the simple hexagonal lattice and has a two-atom basis. The second atom of the basis is positioned half way up the cell and so forms another
hexagonal layer of close-packed atoms half-way between the top and bottom layers of the unit cell.

The Bravais Lattice:

Crystals possess a regular, repetitive internal structure. The concept of symmetry describes the repetition of structural features. Symmetries are most frequently used to classify the different crystal structures. In general one can generate 14 basic crystal structures through symmetries. These are called Bravais lattices. Any crystal structures can be reduced to one of these 14 Bravias lattices. A Bravais Lattice is a three dimensional lattice. A Bravis Lattice tiles space without any gaps or holes. There are 14 ways in which this can be accomplished. Lattices are characterized by translation symmetry.



			lengths	angles
Cubic	(SC)	Simple	$a=b=c$	$\alpha=\beta=\gamma=\pi/2$
	* (BCC)	Body centred		
	* (FCC)	Face centred		
Tetragonal		Simple	$a=b\neq c$	$\alpha=\beta=\gamma=\pi/2$
		Body centred		
Orthorhombic		Simple	$a\neq b\neq c$	$\alpha=\beta=\gamma=\pi/2$
		Body centred		
		Face centred		
		Base centred		
Triclinic		Simple	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma$
Monoclinic		Simple	$a\neq b\neq c$	$\alpha=\gamma=\pi/2\neq\beta$
		Base centred		
Rhombohedral (trigonal)		Simple	$a=b=c$	$\alpha=\beta=\gamma\neq\pi/2$
Hexagonal	*	Simple	$a=b\neq c$	$\alpha=\beta=\pi/2$ $\gamma=2\pi/3$



Key: a = triclinic (anorthic), m = monoclinc, o = orthorhombic, t = tetragonal, h = hexagonal (trigonal), r = rhombohedral, c = cubic, P = primitive, C = base centered, I = body centered, F = face centered.

Crystal Structure Determination:

The determination of an unknown structure proceeds in three major steps: 1. The shape and size of the unit cell are deduced from the angular positions of the diffraction lines. 2. The number of atoms per unit cell is then computed from the shape and size of the unit cell, the chemical composition of the specimen, and its measured density. 3. Finally, the position of the atoms within the unit cell are deduced from the relative intensities of the diffraction lines. The third step is generally the most difficult and there are many structures which are known only incompletely, in the sense that this final step has not yet been made. Size and Shape of the Unit Cell

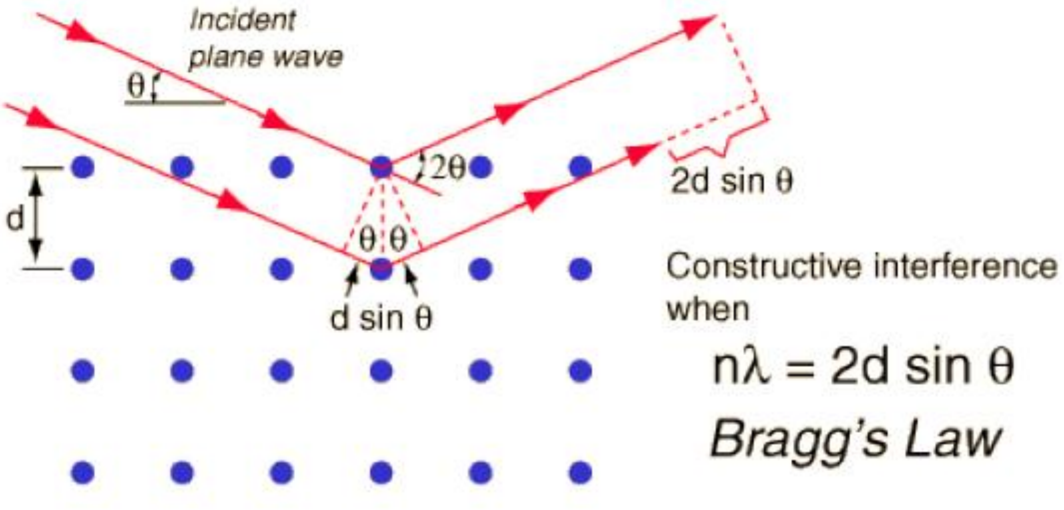
Bragg's Law:

When x-rays are scattered from a crystal lattice, peaks of scattered intensity are observed which correspond to the following conditions:

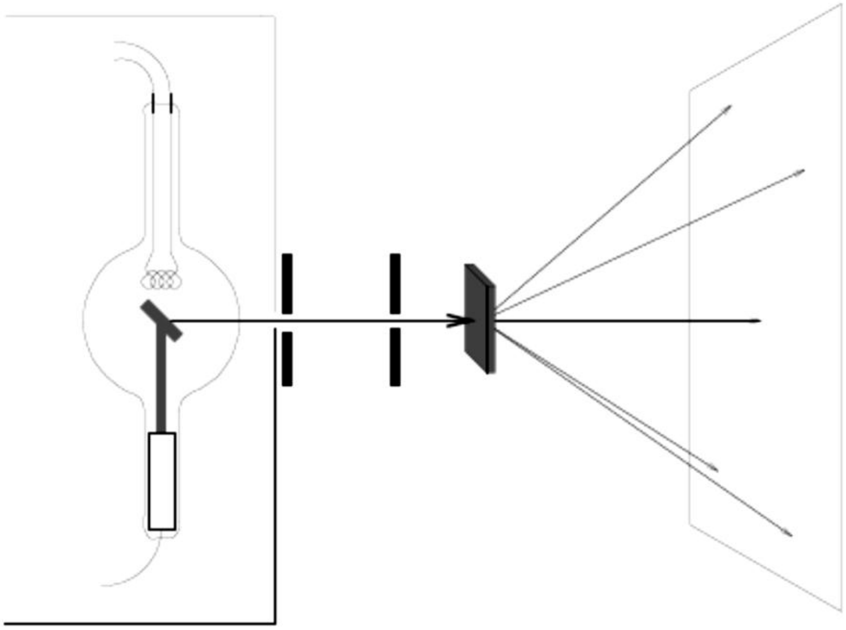
1. The angle of incidence = angle of scattering.

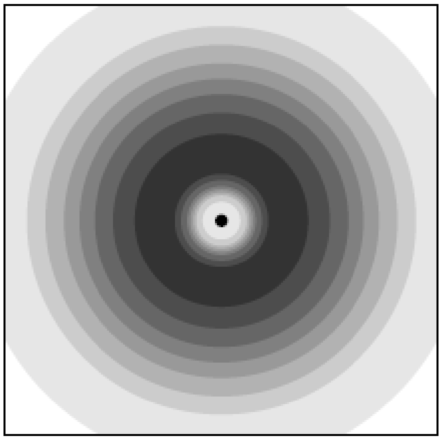
2. The path length difference is equal to an integer number of wavelengths.

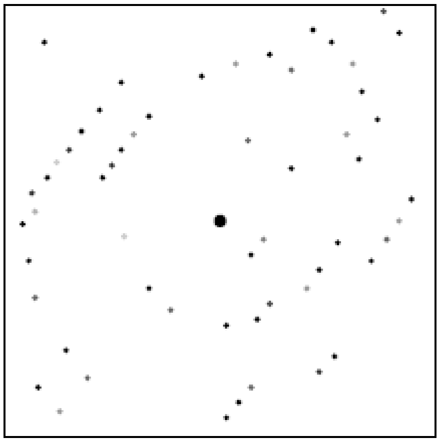
The condition for maximum intensity contained in Bragg's law above allow us to calculate details about the crystal structure, or if the crystal structure is known, to determine the wavelength of the x-rays incident upon the crystal.



X-ray diffraction:




amorphous material

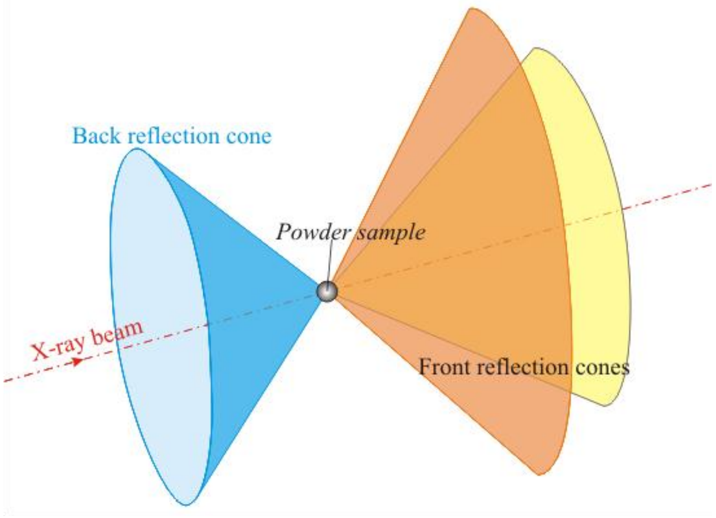

single crystal

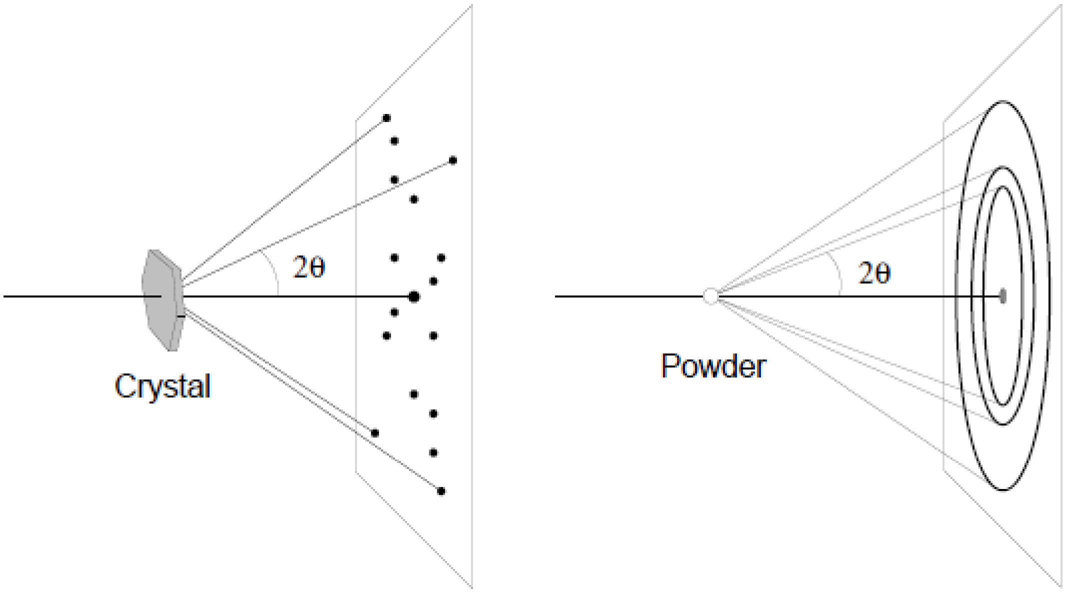
Powder diffraction method:

A crystalline powder consist of small grains; each grain is a single crystal. In general the orientation of the grains in a powder sample is random. Grains with anisotropic shapes tend to show some ordering. The diffraction pattern consists of discrete cones, with top angle 4θ, dictated by Bragg's law. When projected on a plane perpendicular to the incident beam, a series of concentric circles is obtained. The diffraction pattern of a single crystal will change when the sample is rotated. The diffraction pattern of a powder will keep the same appearance when the sample is rotated, although other powder grains will contribute to the pattern.

In a powder diffraction pattern large numbers of reflections will overlap, causing problems with indexing (determination of the unit cell) and intensity measurement. Powder diffraction can be used to identify materials without solving the structure.

- In the powder sample there are crystallites in different 'random' orientations (a polycrystalline sample too has grains in different orientations)
- The coherent x-ray beam is diffracted by these crystallites at various angles to the incident direction
- All the diffracted beams (called 'reflections') from a single plane, but from different crystallites lie on a cone.
- Depending on the angle there are forward and back reflection cones.
- A diffractometer can record the angle of these reflections along with the intensities of the reflection
- The X-ray source and diffractometer move in arcs of a circle- maintaining the Bragg 'reflection' geometry as in the figure (right)





Diffusion:

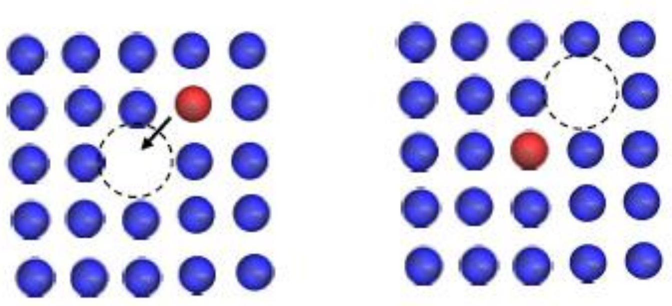
Diffusion is a process of mass transport by atomic movement under the influence of thermal energy and a concentration gradient. Atoms move from higher to lower concentration region. If this movement is from one element to another e.g. Cu to Ni, then it is termed *inter-diffusion*. If the movement is within similar atoms as in pure metals, it is termed *self-diffusion*.

Diffusion Mechanism:

Diffusion of atoms involves movement in steps from one lattice site to the another. An empty adjacent site and breaking of bonds with the neighbor atoms are the two necessary conditions for this.

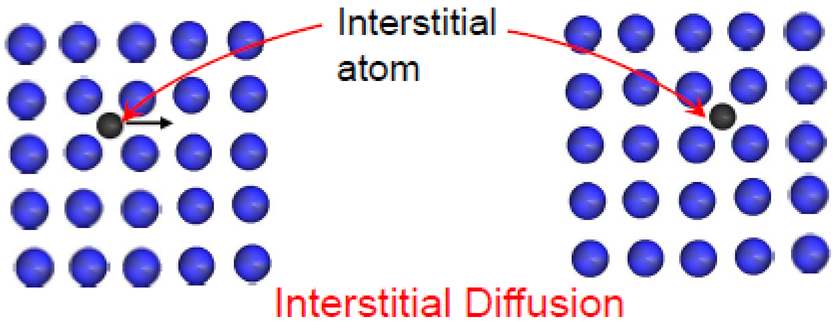
1.**Vacancy Diffusion:**

This mechanism involves movement of atoms from a regular lattice site to an adjacent vacancy. Since vacancy and atoms exchange position, the vacancy flux is in the opposite direction.



2. Interstitial Diffusion:

This mechanism involves migration of atoms from one interstitial site to a neighbouring empty interstitial site. This mechanism is more prevalent for impurity atoms such as hydrogen, carbon, nitrogen, oxygen which are small enough to fit in to an interstitial position. For substitutional diffusion atoms exchange their places directly or along a ring (ring diffusion mechanism).



3. Inter Diffusion or Impurities Diffusion:

Interdiffusion (or impurity diffusion) occurs in response to a concentration gradient.

Factors that influence diffusion:

1. **Diffusing species**
2. **Host solid**
3. **Temperature**
4. **Microstructure**

The Phase Rule:

The *Phase Rule* expresses the relation between phases, phase compositions, and intensive variables (temperature and pressure) in a system of a given composition at equilibrium.

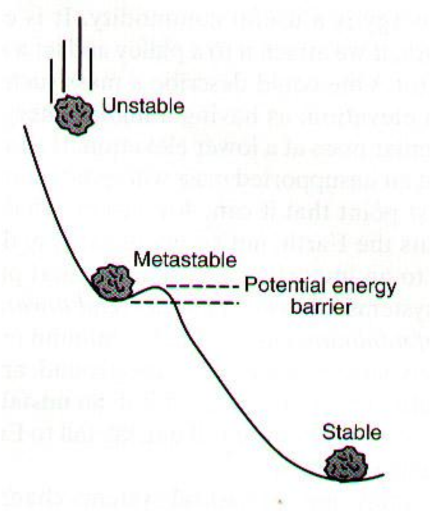
Gibbs Phase Rule: The Gibbs phase rule describes the degrees of freedom available to describe a particular system with various phases and substances.

System: An assemblage of materials that is isolated in some manner from rest of the universe.

- ***isolated system:*** one that does not exchange matter or energy with its surroundings.
- ***closed system:*** one that exchanges only energy with its surroundings.
- ***open system:*** one that exchanges both matter and energy with its surroundings.
- ***adiabatic system:*** a system with changes in energy caused only by a change in volume as pressure changes.

Equilibrium: The lowest energy state of a system in which there is no tendency for a spontaneous change.

Metastable Equilibrium: state of a system which is not in its lowest energy state at the imposed conditions, but cannot spontaneously change due to high activation energy for change.



Phase Rule:

$$\mathbf{F = C - \phi + 2}$$

ϕ (# of phases): a phase is any portion of a system that is chemically and physically homogenous and can be mechanically isolated from any other portion of the system.

C (# of components): minimum number of chemically distinct constituents necessary to describe the composition of each phase in the system.

"2" stands for temperature and pressure. Temperature (T) and pressure (P) are *intensive* parameters of a system. Intensive parameters do not depend on amount or mass. *Extensive* parameters (e.g., volume, number of moles) depend on mass.

F (degrees of freedom; variance):

- number of attributes of a system (T, P, phase composition) that can be changed independently without creating or destroying a phase, or ...
- number of parameters (T, P, system composition) that need to be described to completely define the composition and identity of each phase.

$F = 3$: trivariant

$F = 2$: divariant

$F = 1$: univariant

$F = 0$: invariant

if $F < 0$ then there must be disequilibrium.

The meaning of "C" - minimum number of components necessary to describe each phase in a system:

One-component system (unary):

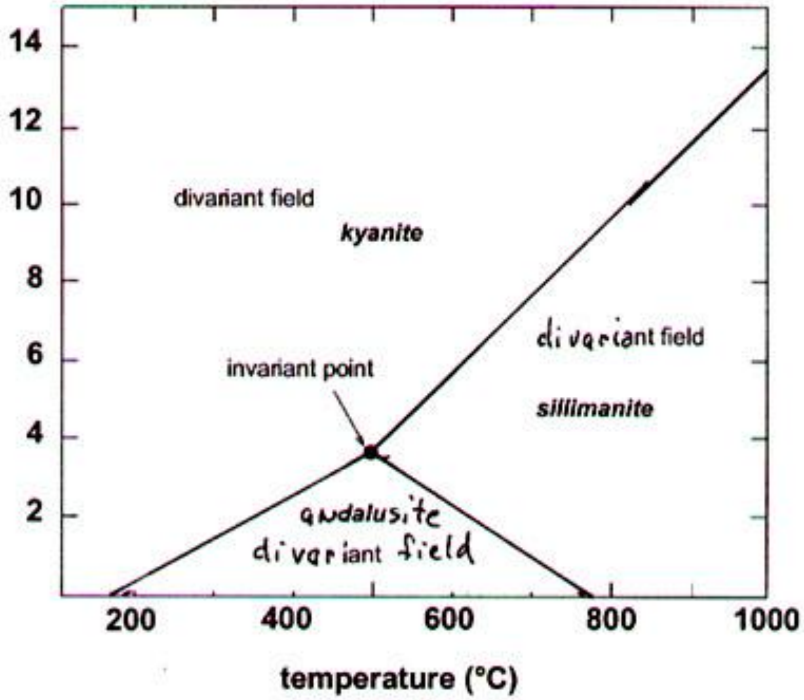
Consider the minerals andalusite, kyanite, and sillimanite. The formula of each is Al_2SiO_5. The chemical constituents we could choose to describe all three minerals could be:

Al, Si, O … 3 components

Al_2O_3, SiO_3 … 2 components

Al_2SiO_5 … 1 component

Thus we can describe all the phases in the system in terms of *one* component.



To calculate the variance or F at a given position in the P-T diagram, we have

$F = 1 - \phi + 2$

- In any one-phase field, F = 2. To be able to state which phase is present, we need to specify two parameters. Also, within a divariant field both P and T can change without loosing or gaining a minerals.

- Along any reaction curve, two phases are present. Thus, F = 1. To be able the state which minerals are present, we need to define only either *P* or *T*. Or, if we know that two of the minerals are present, if we know *P*, we can deduce *T*, or vice-versa. Or, if *T* is changed, to keep the two phases coexisting, *P* has to change accordingly to keep the system along the univariant line.
- At the intersection of the three reaction curves, three phases are present. Thus, F = 0. This means, that if all three phases are present, both *T* and *P* are fixed. If either of the intensive parameters is changed, at least one phase will be lost.

Two-component system:

Consider the minerals muscovite and orthoclase. We could describe them in terms of the following components:

K, Al, Si, O, H	... 5 components
K_2O, Al_2O_3, SiO_2, H_2O	... 4 components
$KAlSi_3O_8$, Al_2O_3, H_2O	... 3 components
$KAlSi_3O_8$, $KAl_3Si_3O_{10}(OH)_2$	... 2 components

So the phase rule would work properly, we would choose the two-component option.

Three-component system:

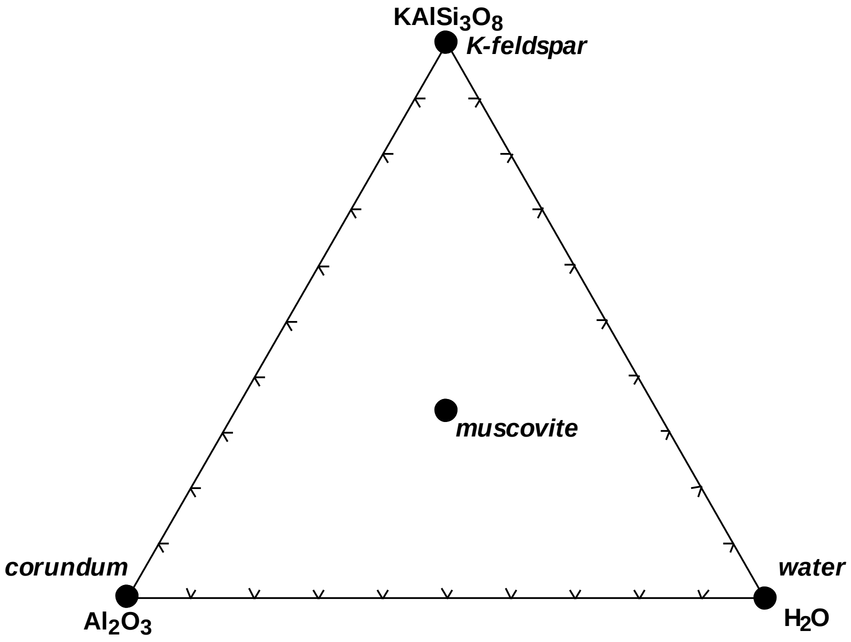
Let us add corundum and water to the above system. We can describe all the phases in this system in terms of the following components:

K, Al, Si, O, H	... 5 components
K_2O, Al_2O_3, SiO_2, H_2O	... 4 components
$KAlSi_3O_8$, Al_2O_3, H_2O	... 3 components

corundum consists of 0 $KAlSi_3O_8$, 1 Al_2O_3, 0 H_2O

water consists of 0 $KAlSi_3O_8$, 0 Al_2O_3, 1 H_2O

So the phase rule would work properly, we would choose the three-component option.



Two-component system with a solution:
Consider the melting reaction

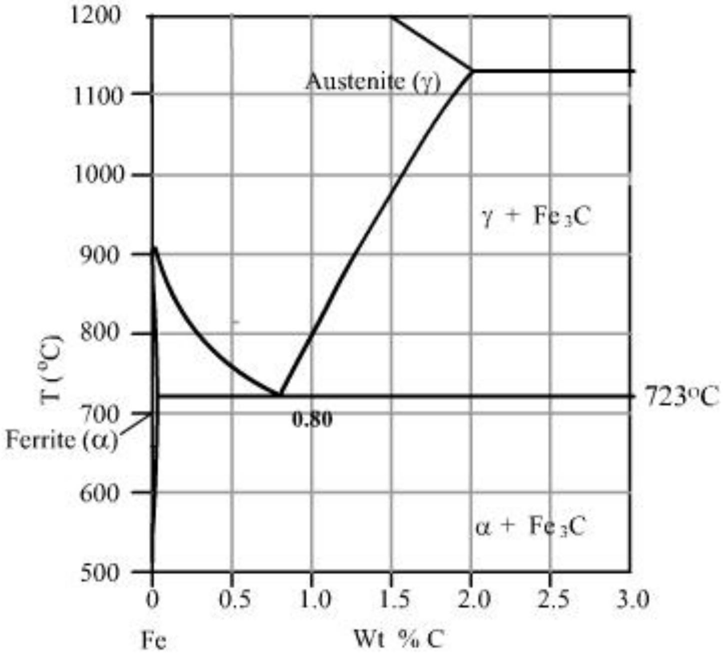
0.5 quartz + 0.5 K-feldspar → 1 melt .

Quartz is made-up of the SiO_2 component, K-feldspar of the $KAlSi_3O_8$ component. The fraction of SiO_2 in the melt is 0.5 and the fraction of $KAlSi_3O_8$ in the melt is also 0.5. Thus, all three phases can be described by some combination of the two components SiO_2 and $KAlSi_3O_8$.

The eutectoid reaction:

The **eutectoid reaction** describes the phase transformation of one solid into two different solids. In the Fe-C system, there is a eutectoid point at approximately 0.8wt% C, 723°C. The phase just above the eutectoid temperature for plain carbon steels is known as austenite or gamma. We now consider what happens as this phase is cooled through the eutectoid temperature (723°C).

The phase diagram which we will be considering throughout this section is shown below:



Definitions

Component: pure metal or compound (e.g., Cu, Zn in Cu-Zn alloy, sugar, water, in a syrup.)

Solvent: host or major component in solution.

Solute: dissolved, minor component in solution.

System: set of possible alloys from same component (e.g., iron-carbon system.)

Solubility Limit: Maximum solute concentration that can be dissolved at a given temperature.

Phase: part with homogeneous physical and chemical characteristics

Solubility Limit:

Effect of temperature on solubility limit. Maximum content: saturation. Exceeding maximum content (like when cooling) leads to precipitation.

Phases:

> One-phase systems are homogeneous. Systems with two or more phases are heterogeneous, or mixtures. This is the case of most metallic alloys, but also happens in ceramics and polymers.
>
> A two-component alloy is called binary. One with three components, ternary.

Microstructure

The properties of an alloy do not depend only on concentration of the phases but how they are arranged structurally at the microscopy level. Thus, the microstructure is specified by the number of phases, their proportions, and their arrangement in space.

A binary alloy may be

a. a single solid solution
b. two separated, essentially pure components.
c. two separated solid solutions.
d. a chemical compound, together with a solid solution.

The way to tell is to cut the material, polish it to a mirror finish, etch it a weak acid (components etch at a different rate) and observe the surface under a microscope.

Phase Equilibrium:

Equilibrium is the state of minimum energy. It is achieved given sufficient time. But the time to achieve equilibrium may be so long (the *kinetics* is so slow) that a state that is not at an energy minimum may have a long life and appear to be stable. This is called a *metastable state.*

A less strict, operational, definition of equilibrium is that of a system that does not change with time during observation.

Equilibrium Phase Diagrams

Give the relationship of composition of a solution as a function of temperatures and the quantities of phases in equilibrium. These diagrams do not indicate the dynamics when one phase transforms into another. Sometimes diagrams are given with pressure as one of the variables. In the phase diagrams we will discuss, pressure is assumed to be constant at one atmosphere.

Binary Isomorphous Systems

This very simple case is one complete liquid and solid solubility, an *isomorphous* system. The example is the Cu-Ni alloy of Fig. 9.2a. The complete solubility occurs because both Cu and Ni have the same crystal structure (FCC), near the same radii, electronegativity and valence.

The *liquidus line* separates the liquid phase from solid or solid + liquid phases. That is, the solution is liquid above the liquidus line.

The *solidus line* is that below which the solution is completely solid (does not contain a liquid phase.)

Interpretation of phase diagrams

Concentrations: Tie-line method

a. locate composition and temperature in diagram
b. In two phase region draw tie line or isotherm
c. note intersection with phase boundaries. Read compositions.

Fractions: lever rule

a. construct tie line (isotherm)
b. obtain ratios of line segments lengths.

Note: the fractions are inversely proportional to the length to the boundary for the particular phase. If the point in the diagram is close to the phase line, the fraction of that phase is large.

Development of microstructure in isomorphous alloys

a) Equilibrium cooling

Solidification in the solid + liquid phase occurs gradually upon cooling from the liquidus line. The composition of the solid and the liquid change gradually during cooling (as can be determined by the tie-line method.) Nuclei of the solid phase form and they grow to consume all the liquid at the solidus line.

b) Non-equilibrium cooling

Solidification in the solid + liquid phase also occurs gradually. The composition of the liquid phase evolves by diffusion, following the equilibrium values that can be derived from the tie-line method. However, diffusion in the solid state is very slow. Hence, the new layers that solidify on top of the grains have the equilibrium composition at that temperature but once they are solid their composition does not change. This lead to the formation of layered (cored) grains (Fig. 9.14) and to the invalidity of the tie-line method to determine the composition of the solid phase (it still works for the liquid phase, where diffusion is fast.)

Eutectic or invariant point. Liquid and two solid phases exist in equilibrium at the *eutectic composition* and the *eutectic temperature.*

Alloys which are to the left of the eutectic concentration (*hipoeutectic*) or to the right (*hypereutectic*) form a *proeutectic* phase before reaching the eutectic temperature, while in the solid + liquid region. The eutectic structure then adds when the remaining liquid is solidified when cooling further. The eutectic microstructure is lamellar (layered) due to the reduced diffusion distances in the solid state.

A *terminal phase* or *terminal solution* is one that exists in the extremes of concentration (0 and 100%) of the phase diagram. One that exists in the middle, separated from the extremes, is called an *intermediate phase* or solid solution.

An important phase is the *intermetallic compound*, that has a precise chemical compositions. When using the lever rules, intermetallic compounds are treated like any other phase, except they appear not as a wide region but as a vertical line.

The *eutectoid* (eutectic-like) reaction is similar to the eutectic reaction but occurs from one solid phase to two *new* solid phases. It also shows as V on top of a horizontal line in the phase diagram. There are associated eutectoid temperature (or temperature), eutectoid phase, eutectoid and proeutectoid microstructures.

Solid Phase 1 à Solid Phase 2 + Solid Phase 3

The *peritectic* reaction also involves three solid in equilibrium, the transition is from a solid + liquid phase to a *different* solid phase when cooling. The inverse reaction occurs when heating.

Solid Phase 1 + liquid à Solid Phase 2

Congruent transformation is one where there is no change in composition, like allotropic transformations (e.g., a-Fe to g-Fe) or melting transitions in pure solids.

Ternary phase diagrams are three-dimensional. Example: Ceramic phase diagrams