Lecture 01: Crystalline and Non-crystalline solids

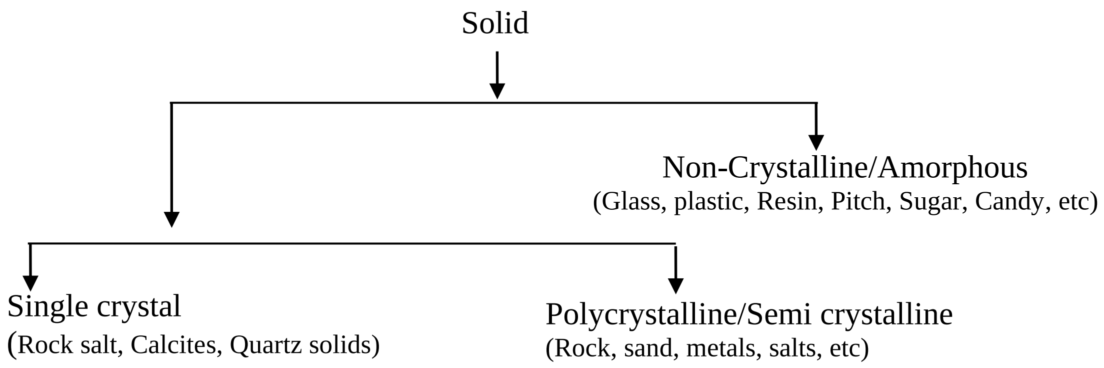
Introduction

Matter can be subdivided into two states-solid and fluid, of which the later is subdivided into liquid and gaseous state. Matter can also be subdivided into condensed stated and gaseous state where condensed state is subdivided into the solid and liquid state.

Although very little of the matter in the universe is in the solid state, solids constitute much of the physical world around us and a large part of the modern technology is based on the special characteristics of the various solid materials.

Crystalline and non-crystalline (Amorphous Solids)

Nature favors the crystalline state of the solids because the energy of the ordered atomic arrangement is lower than that of an irregular packing of atoms.



Crystalline Solids

A solid in general is said to be a crystal if the constituent particles (atoms, ions or molecules) are arranged in a three-dimensional periodic manner or simply it has a reticular structure. In crystalline solids the atoms are stacked in a regular manner, forming a 3-D pattern which may be obtained by a 3-D repetition of a certain pattern unit. It has long-range orderness and thus has definite properties such a sharp melting point. Thus, we can say, crystal is a three-dimensional periodic array of atoms. When the crystal grows under constant environment, the external geometrical shape of the crystal often remains unchanged. Thus, the shape is a consequence of the internal arrangement of constituent particles. The ideal crystal has an infinite 3D repetition of identical units, which may be atoms or molecules. All ionic solids and most covalent solids are crystalline. All solid metals, under normal circumstances, are crystalline.

Single crystal

When the periodicity in crystal pattern extends throughout a certain piece of materials, one speaks of a single crystal or unit crystal or mono-crystal. Rock salt, calcites, quartz, etc. are examples of common single crystal.

Polycrystalline solids (Polymorphism)

When the periodicity in the crystal structure is interrupted at so-called grain boundaries, the crystal is said to be polycrystalline. In this case the size of the grains or crystallites is smaller than the size of the pattern unit which forms the periodicity. The size of the grain in which the structure is periodic may vary from macroscopic dimensions to several angstroms. In general, the grains in such a solid are not related in shape to the crystal structure, the surface being random in shape rather than well defined crystal planes. Rock, sand, metals, salts, etc. are some examples of polycrystalline solids.

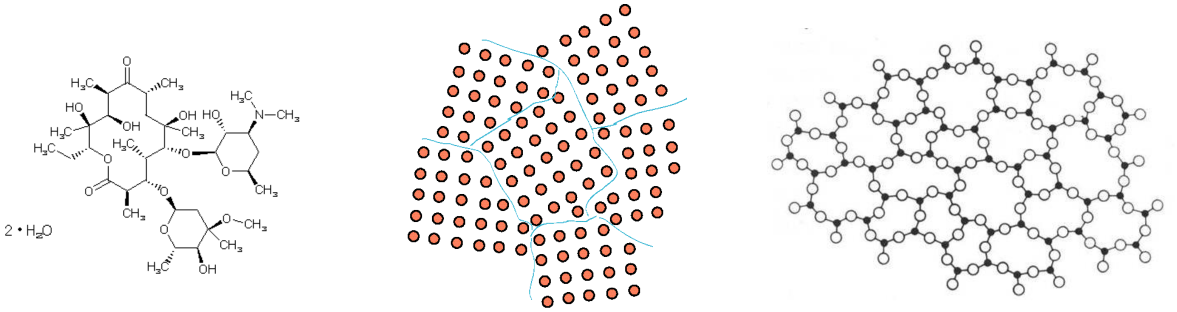
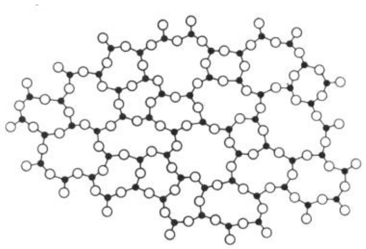


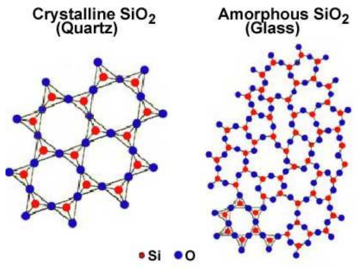
Fig. Single crystal, polycrystalline, amorphous

Noncrystalline solids

It is the opposite extreme of a single crystal. These types of solids have neither reticular nor granular structure. At most causes exhibit short range orderness in their structure. Glass and plastic are common example of this class. When the size of the grains or crystallites becomes comparable to the size of the pattern unit, we speak of amorphous substances. A typical feature of these substances is that they have no definite melting points. As their temperature is increased, they gradually become soft; their viscosity drops, and begins to behave like ordinary viscous liquids.

Amorphous solids have no long-range order. The atoms or molecules in these solids are not periodically located over large distances. An amorphous structure is shown below.





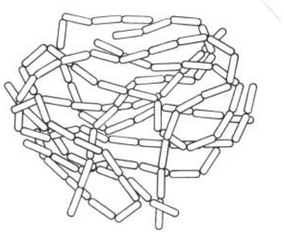
Many amorphous materials have internal structures like liquids. In fact, the only obvious distinction between amorphous materials, such as glass, and liquids is the high viscosity (resistance to flow) of the amorphous solids.

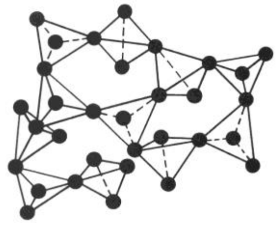
All solids tend to exist in the crystalline state rather than the amorphous state because the crystalline structure always has a larger binding energy. However, in numerous instances amorphous solids are formed when liquids are cooled below the melting temperature. This occurs for two reasons:

1) the structure of the molecules is so complex that they cannot easily rearrange themselves to form a crystalline structure, and/or
2) the solid forms so rapidly that the atoms or molecules do not have time enough to rearrange themselves in a crystalline structure.

Generally, amorphous solids have one of two distinct atomic arrangements: either a tangled mass of long-chained molecules or a 3-dimentional network of atoms with no long-range order.

Amorphous materials with long-chained molecules (e.g., polymers) have a structure like that shown below.





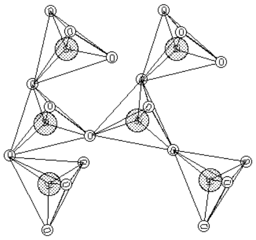
Each segment in above figure represents one of the repeating units of the polymer chain. The arrangement of the molecules is random, resulting in a loosely packed structure. Network amorphous solids are usually Oxides, the most common being Silica (SiO_2). The amorphous SiO_2 structure is also shown above. Only oxygen atoms are shown (corners of tetrahedral) in this amorphous SiO_2 structure. There is a Silicon atom at the center of each tetrahedral which is not shown here. This structure has short-range order but none of the long-range order found in crystalline Silica. Thus, in both amorphous and crystalline Silica, each Silicon atom and each

Oxygen atom have essentially the same local surroundings, even though there is no long-range periodicity in the amorphous structure.

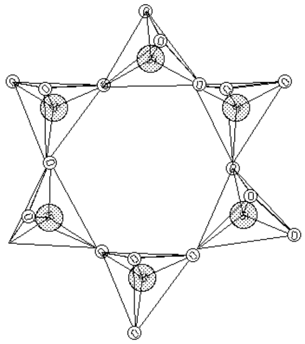
Solids that do not have long range atomic order are called amorphous solids. They often have subunits that have consistent form, but their long-range order is disturbed because the sub-units pack randomly. Amorphous solids are formed when liquids are cooled too quickly from the molten state to allow the sub-units to arrange themselves in the low energy, crystalline state.

Solids with pure ionic bonds do not form amorphous solids but all the other bond types can produce amorphous solids. Silica (SiO2) can form either covalent amorphous solids, usually called glasses or regular crystal structures (Quartz).

In glasses, the tetrahedral SiO_2 structure forms the sub-unit, and it is the flexibility of corner-to-corner links that accounts for the ability of SiO_2 to form the random structures shown below.



If the molten Silica is cooled very slowly, the sub-units fall into the regular crystal structure of Quartz, shown below.

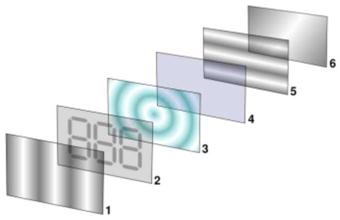


Impurities in SiO_2 hinder crystallization. Common window glass (soda lime glass) has Na_20 and CaO added. Ovenware glass (borosilicate glass) has B_20_3 added.

Liquid crystals (LCs) are a state of matter that have properties between those of a conventional liquid and those of a solid crystal. For instance, an LC may flow like a liquid, but its molecules may be oriented in a crystal-like way. There are many different types of LC phase, which can be distinguished by their different optical properties (such as birefringence). When viewed under a microscope using a polarized light source, different liquid crystal phases will appear to have distinct textures.

Examples of liquid crystals can be found both in the natural world and in technological applications. Most modern electronic displays are liquid crystal based. Lyotropic liquid-crystalline phases are abundant in living systems. For example, many proteins and cell membranes are LCs. Other well-known LC examples are solutions of soap and various related detergents, as well as tobacco mosaic virus.

Liquid crystal display



Structure of liquid crystal display:
1 – vertical polarization filter,
2,4 – glass with electrodes,
3 – liquid crystals,
5 – horizontal polarization filter,
6 – reflector

Liquid crystals find wide use in liquid crystal displays, which rely on the optical properties of certain liquid crystalline substances in the presence or absence of an electric field. In a typical device, a liquid crystal layer (typically 10 μm thick) sits between two polarizers that are crossed (oriented at 90° to one another). The liquid crystal alignment is chosen so that its relaxed phase is a twisted one (see Twisted nematic field effect). This twisted phase reorients light that has passed through the first polarizer, allowing its transmission through the second polarizer (and reflected to the observer if a reflector is provided). The device thus appears transparent. When an electric field is applied to the LC layer, the long molecular axes tend to align parallel to the electric field thus gradually untwisting in the center of the liquid crystal layer. In this state, the LC molecules do not reorient light, so the light polarized at the first polarizer is absorbed at the second polarizer, and the device loses transparency with increasing voltage. In this way, the electric field can be used to make a pixel switch between transparent or opaque on command. Color LCD systems use the same technique, with color filters used to generate red, green, and blue pixels. Similar principles can be used to make other liquid crystal based optical devices.

They are used in a wide range of applications, including computer monitors, television, instrument panels, aircraft cockpit displays, signage, etc. They are common in consumer devices such as video players, gaming devices, clocks, watches, calculators, and telephones.

Polymorphism

Polymorphism refers to the ability of a solid to exist in more than one crystalline form or structure. According to Gibbs' rules of phase equilibria, these unique crystalline phases will be dependent on such intensive variables as pressure, temperature, and volume. Polymorphism can potentially be found in many crystalline materials including polymers, minerals, and metals, and is related to allotropy, which refers to elemental solids. The complete morphology of a material is described by polymorphism and other variables such as crystal habit, amorphous fraction, or crystallographic defects. Polymorphs have different stabilities and may spontaneously convert from a metastable form (or thermodynamically unstable form) to the stable form at a particular temperature. They also exhibit different melting points, solubilities, and X-ray diffraction patterns.

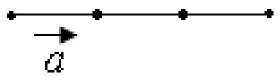
One good example of this is the quartz form of silicon dioxide, or SiO_2. Quartz is one of the several thermodynamically stable crystalline forms of silica, SiO_2. The most important forms of silica include: α-quartz, β-quartz, tridymite, cristobalite, coesite, and stishovite. In the vast majority of silicates, the Si atom shows tetrahedral coordination by 4 oxygens. All but one of the crystalline forms involve tetrahedral SiO_4 units linked together by shared vertices in different arrangements. In different minerals the tetrahedra show different degrees of networking and polymerization. For example, they occur singly, joined together in pairs, in larger finite clusters including rings, in chains, double chains, sheets, and three-dimensional frameworks. The minerals are classified into groups based on these structures. In each of its 7 thermodynamically stable crystalline forms or polymorphs of crystalline quartz, only 2 out of 4 of each the edges of the SiO_4 tetrahedra are shared with others, yielding the net chemical formula for silica: SiO_2.

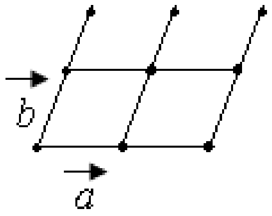
Another example is elemental tin (Sn), which is malleable near ambient temperatures but is brittle when cooled. This change in mechanical properties due to existence of its two major allotropes, α- and β-tin. The two allotropes that are encountered at normal pressure and temperature, α-tin and β-tin, are more commonly known as gray tin and white tin respectively. Two more allotropes, γ and σ, exist at temperatures above 161 °C and pressures above several GPa. White tin is metallic, and is the stable crystalline form at or above room temperature. Below 13.2 °C, tin exists in the gray form, which has a diamond cubic crystal structure, similar to diamond, silicon or germanium. Gray tin has no metallic properties at all, is a dull-gray powdery material, and has few uses, other than a few specialized semiconductor applications. Although the α-β transformation temperature of tin is nominally 13.2 °C, impurities (e.g., Al, Zn, etc.) lower the transition temperature well below 0 °C, and upon addition of Sb or Bi the transformation may not occur at al.

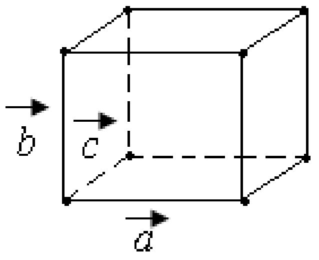
Lecture 02: Space lattice and Translation vectors

The property that distinguishes crystals from other solids is that the constituent particles in crystals are arranged in a three-dimensional periodic manner. In 1848 Bravais introduced the concept of space lattice.

Lattice: A lattice is a regular periodic array of points in space where objects are replaced by points-imaginary points. It may consider as removal of the atom, but the center remains there.







Lattice arrangement in 1-D is the line of Lattice, in 2-D is the Lattice plane, in 3-D is the space Lattice.

Thus the three dimensional lattice arrangements with translation vectors is the space lattice. Let us consider the translation of an object to a finite distance and then repeated systematically along 3-D crystallographic directions x, y, z to obtain 3-D space lattice.

Lattice is a mathematical abstraction which is defined by 3 fundamental translation vectors $\vec{a}, \vec{b}, \vec{c}$ such that the atomic arrangement looks the same in every respect when viewed from the point r as when viewed from the point

$$\bar{\boldsymbol{r}}' = \bar{r} + n_1\vec{a} + n_2\vec{b} + n_3\vec{\boldsymbol{c}} \quad \text{...} (1)$$

Where n_1, n_2, n_3 are arbitrary integers and the set of points $r^/$ defined by (1) for all n_1, n_2, n_3 defines a lattice.

Lattice point can thus be defined by 3-fundmental basis vectors called primitive translation vector in x, y, z crystallographic direction as

$$\vec{\tau} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$$

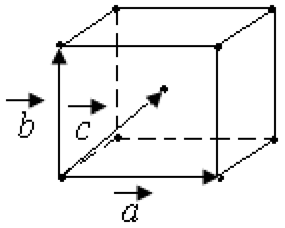
So that

$$\bar{\boldsymbol{r}}' = \bar{r} + \vec{\tau}$$

For example: If the 3-D fundamental basis vectors of a crystal are $\vec{a}=3\hat{\imath}$, $\vec{b}=3\hat{\jmath}$ and $\vec{\boldsymbol{c}}=1.5(\hat{\imath}+\hat{\jmath}+\hat{k})$, the primitive translation operation

$$\vec{\tau}= n_1(3\hat{\imath})+ n_2(3\hat{\jmath})+ n_3\times 1.5(\hat{\imath}+\hat{\jmath}+\hat{k})$$

gives the body centered cubic structure.



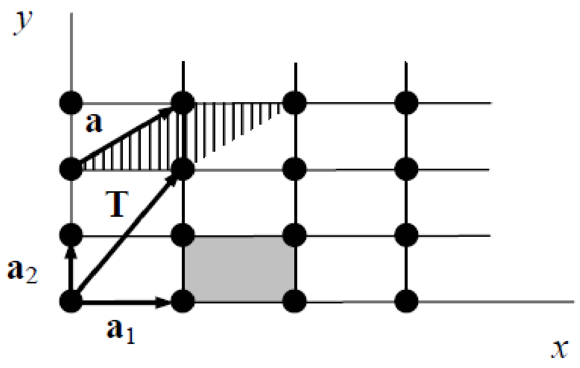
Bravais and Non-Bravais lattice

There are two classes of lattices: the *Bravais* and the *non-Bravais*. In a Bravais lattice all lattice points are equivalent and hence by necessity all atoms in the crystal are of the same kind. On the other hand, in a non-Bravais lattice, some of the lattice points are non-equivalent. Non-Bravais lattices are often referred to as a *lattice with a basis*. The basis is a set of atoms which is located near each site of a Bravais lattice.

The lattice is defined by fundamental translation vectors. For example, the position vector of any lattice site of the two-dimensional lattice in figure can be written as

$$\mathbf{T}=n_1\mathbf{a}_1+n_2\mathbf{a}_2$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the two vectors shown in figure, and n_1, n_2 is a pair of integers whose values depend on the lattice site. So, the two non-collinear vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ can be used to obtain the positions of all lattice points which are expressed by the equation. The set of all vectors **T** expressed by this equation is called the *lattice vectors*. Therefore, the lattice has a translational symmetry under displacements specified by the lattice vectors **T**. In this sense the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ can be called *the primitive translation vectors*. The choice of the primitive translations vectors is not unique. One could equally well take the vectors $\mathbf{a}_1$ and $\mathbf{a} = \mathbf{a}_1+\mathbf{a}_2$ as primitive translation vectors. This choice is usually dictated by convenience.



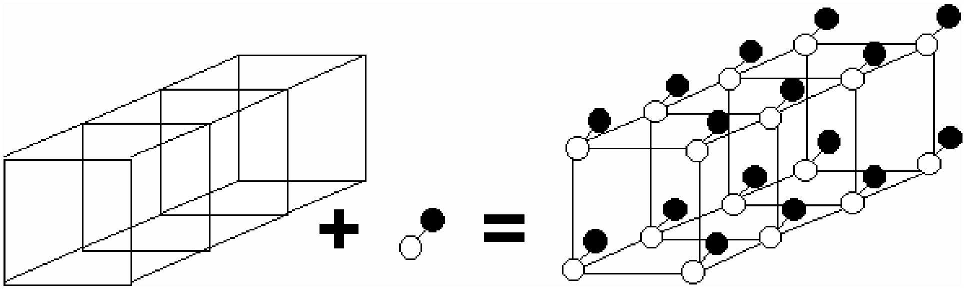
Crystal structure

A crystal structure is formed when a group of atoms or molecules are attached identically to each lattice point. This group of atoms or molecules are called basis.

Basis is identical–   in composition,

in arrangement,
in orientation .

and repeated periodically in space to form the crystal structure which can be represented by the logical formula: Lattice + Basis = crystal structure



Lattice + Basis crystal structure

2-D noncollinear translation define a plane lattice

3-D non-coplanar translation defined a space lattice

Primitive unit cell & Non-primitive unit cell

All solids are composed of discrete basic units which are the atoms. These atoms are not distributed randomly but are arranged in a highly ordered manner relative to each other. Such a group of ordered atoms is referred to as a crystal.

In 3-D, the simplest parallelepiped formed by the primitive translation operation *T* is called unit cell.

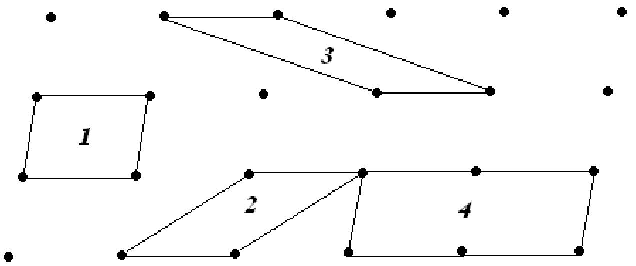
The parallelepiped defined by primitive axes a, b, c is called primitive cell. The number of atoms in a **primitive cell** or primitive basis is always the same for a given crystal structure.

It is the minimum volume cell.

It is the building block element.

It has always only one lattice point per cell.

Volume of the unit cell $V_c = \left|\bar{a}.\bar{b}\times\bar{c}\right|$ or $\left|\bar{a}\times\bar{b}.\bar{c}\right|$



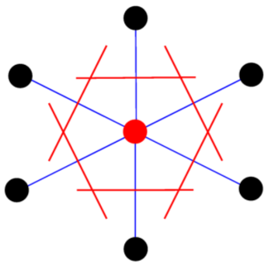
Here parallelogram 1, 2, 3 are equal in area and any one of them could be taken as the primitive cell. The parallelogram 4 has twice the area of a primitive cell and thus a compound cell. **The compound cell is also a non-primitive cell.** There is more than one lattice point and the area is constant multiple of primitive cell.

Example of primitive cell – Simple cubic; Non-primitive cell – Body centered cubic, Face centered cubic; Base centered orthorhombic, Hexagonal structure, etc.

Wigner-Seitz cell

It was first suggested by E. P Wigner and F. Seitz. A primitive cell can also be chosen as:

- Firstly, draw lines to connect a given lattice point to all nearby lattice points.
- Secondly, at the midpoint and normal to these lines draw new lines or planes.

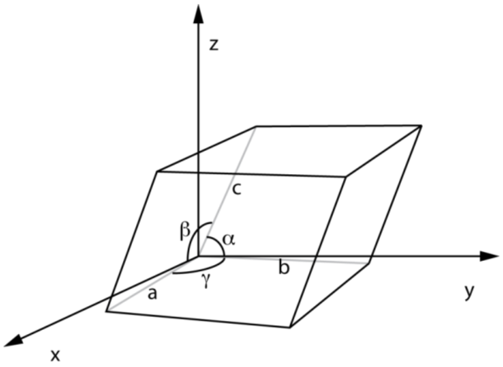


The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All the space of the crystal may be filled by these primitive cells, by translating the unit cell by the lattice vectors.

Lattice parameters and lattice constant

The lattice constant [or lattice parameter] refers to the constant distance between unit cells in a crystal lattice. Lattices in three dimensions generally have three lattice constants, referred to as *a*, *b*, and *c*. However, in the special case of cubic crystal structures, all of the constants are equal and we only refer to *a*. Similarly, in hexagonal crystal structures, the *a* and *b* constants are equal, and we only refer to the *a* and *c* constants. A group of lattice constants could be referred to as lattice parameters. However, the full set of lattice parameters consist of the three lattice constants and the three angles between them.

For example the lattice constant for a common carbon diamond is *a* = 3.57Å at 300 K. The structure is equilateral although its actual shape cannot be determined from only the lattice constant. Furthermore, in real applications, typically the average lattice constant is given. As lattice constants have the dimension of length, their SI unit is the meter. Lattice constants are typically of the order of several angstroms (i.e., tenths of a nanometer). Lattice constants can be determined using techniques such as X-ray diffraction or with an atomic force microscope (AFM).



Thus, the tree fundamental translation vectors$\bar{a}, \bar{b}, \bar{c}$ along with opposite angles α, β, γ, each of between two crystallographic axes as shown in figure are the lattice parameters and the distance between two identical atoms or molecules is the lattice constant.

Co-ordination number

The points in a Bravais lattice that are closest to a given point are called its nearest neighbors. Because of the periodic nature of a Bravais lattice, each point has the same number of nearest neighbors. This number is thus a property of the lattice and is referred to as the co-ordination number of the lattice.

In solid-state structures of crystals are defined by a simpler model in which the atoms are represented by touching spheres. In this model the coordination number of an atom is the number of other atoms which it touches. For an atom in the interior of a crystal lattice the number of atoms touching the given atom is the **bulk coordination number**; for an atom at a surface of a crystal, this is the **surface coordination number**.

A simple cubic lattice has co-ordination no. 6, Body centered cubic lattice has co-ordination no. 8 and face centered cubic lattice has co-ordination no. 12.

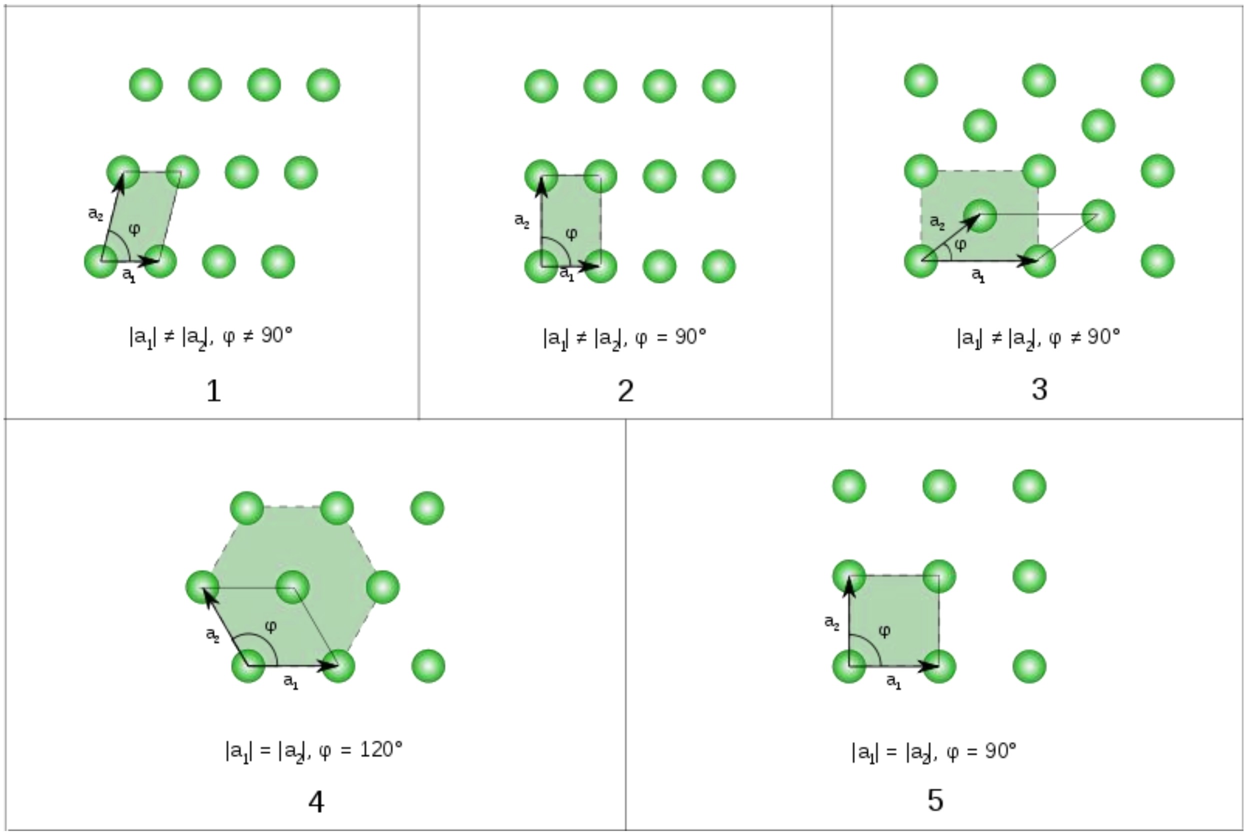
Lecture 03: Crystal Systems

Two-dimensional lattice symmetry:

There are unlimited number of possible lattices because there is no natural limitation on the lengths of the lattice translation vectors or not the angle of between them.

Bravais lattice is a common phrase for a distinct lattice type. In a Bravais lattice, all lattice points are equivalent and hence by necessity all atoms in the crystal are of the same kind.

There are five distinct types (Bravais) of lattice symmetry in two dimensions such as:
(i) Oblique (a ≠b, $\varphi \neq 90^0$) (ii) Square (a = b, $\varphi = 90^0$), (iii) Hexagonal (a = b, $\varphi = 120^0$) (iv) Rectangular (a ≠b, $\varphi = 90^0$) (v) Centered rectangular (a ≠b, $\varphi = 90^0$). Of these (i) → general, (ii) to (v) → special types.



The five fundamental two-dimensional Bravais lattices: 1 oblique, 2 rectangular, 3 centered rectangular, 4 hexagonal, and 5 square

Three-dimensional lattice symmetry:

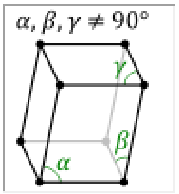
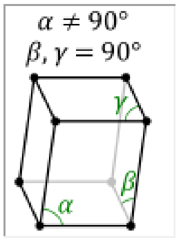
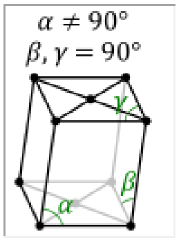
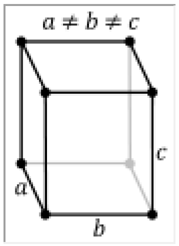
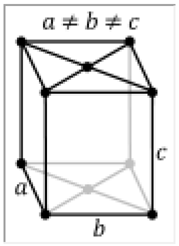
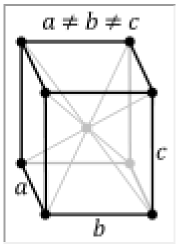
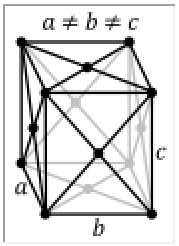
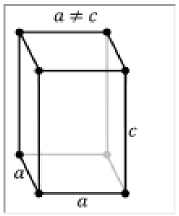
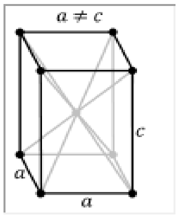
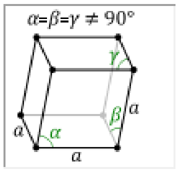
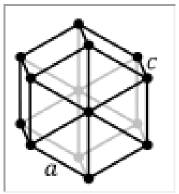
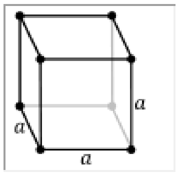
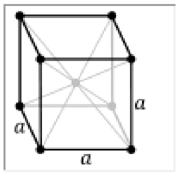
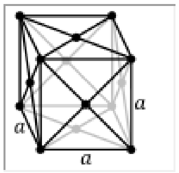
The point symmetry groups in 3-D requires the 14 different lattice types listed in Table-1. The general lattice is triclinic, and there are 13 special lattices. These are grouped for convenience into systems classified according to seven types of cells which are

1. Triclinic (General Types – $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$)
2. Monoclinic
3. Orthorhombic (Rhombic)
4. Tetragonal
5. Cubic
6. Trigonal (Rhombohedral)
7. Hexagonal

Table: 1 The seven crystal systems divided into 14 Bravais lattices.

Sl. No	**Crystal system**	**Bravais lattice (Number & symbol)**	**Unit cell characteristics (axes and angles)**	**Lattice parameters**	**Examples**
1	Triclinic	1, simple (P)	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^0$	$\left.\begin{matrix} a, b, c \\ \alpha, \beta, \gamma \end{matrix}\right\| 6$	$K_2Cr_2O_7$, $CuSO_4.5H_2O$, H_3BO_3
2	Monoclinic	2, simple (P) Base-centered (C)	$a \neq b \neq c$, $\alpha = \beta = 90^0 \neq \gamma$	$\left.\begin{matrix} a, b, c \\ \gamma \end{matrix}\right\| 4$	Monoclinic Sulpher, $Na_2SO_4.10H_2O$
3	Orthorhombic	4, simple (P) Base-centered (C) Body-centered (I) Face-centered (F)	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^0$	$a\underline{b}c\|3$	Rhombic sulphur, KNO_3 $CaCO_3$,, Ba_2SO_4
4	Tetragonal	2, simple (P) Body-centered (1)	$a = b \neq c$, $\alpha = \beta = \gamma = 90^0$	$\underline{a}c\|2$	SnO_2, White tin, TiO_2, Ca_2SO_4
5	Cubic	3, simple (P) Body-centered (I) Face-centered (F)	$a = b = c$, $\alpha = \beta = \gamma = 90^0$	$\underline{a}\|1$	Copper, KCl, NaCl, Zinc blend, Diamond
6	Trigonal	1, simple (P)	$a = b = c$, $\alpha = \beta = \gamma \neq 90^0$, $< 120^0$	$\left.\begin{matrix} a \\ \alpha \end{matrix}\right\| 2$	Ca_2CO_3 (Calcite), HgS (Cinnaber)
7.	Hexagonal	1, simple (P)	$a = b \neq c$, $\alpha = \beta = 90^0$, $\gamma = 120^0$	$\underline{a}c\|2$	Graphite, Mg, ZnO, CdS,

P → Primitive (it has atoms only at the corners of the parallelepiped)
C → Base-centered (it has extra atom at the centre of the base)
I → Body centered (From German word Innenzentriete)
F → Face-centered

triclinic	P 			
monoclinic	P 	C 		
orthorhombic	P 	C 	I 	F 
tetragonal	P 	I 		
rhombohedral	P 			
hexagonal	P 			
cubic	P (pcc) 	I (bcc) 	F (fcc) 	

The volume of the unit cell can be calculated by evaluating $\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$ where **a**, **b**, and **c** are the lattice vectors. The volumes of the Bravais lattices are given below:

Lattice system	**Volume**
Triclinic	$abc\sqrt{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma}$
Monoclinic	$abc\ \sin\alpha$
Orthorhombic	abc
Tetragonal	a^2c
rhombohedral	$a^3\sqrt{1-3\cos^2\alpha+2\cos^3\alpha}$
Hexagonal	$\frac{\sqrt{3}\ a^2c}{2}$
Cubic	a^3

Bravais lattices in 4 dimensions
In four dimensions, there are 52 Bravais lattices. Of these, 21 are primitive and 31 are centered.

Lattice points per unit cell

In primitive cell, lattice points are located only at corners, while each corners of the cell is common to eight neighboring unit cells and the contribution towards the unit cell per corner is only one-eight. Since there are eight corners, therefore the number of lattice point per unit cell is only one.

Primitive cell contains one lattice point.

Cubic cell contains one lattice point.

Body centered cubic contains 2 lattice points

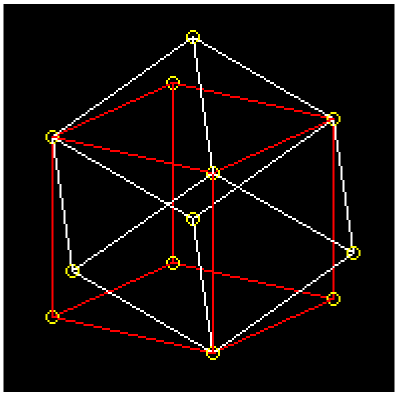
and conventional face centered cubic (fcc) cell contains four lattice points.

Characteristics of cubic lattices:

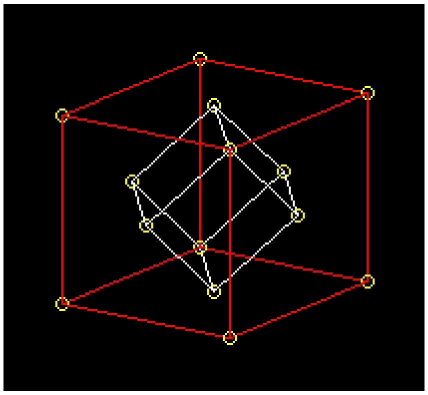
Volume, conventional cell	Simple a^3	Body-Centred a^3	Face Centred a^3
Lattice points per unit cell	1	2	4
Volume of primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Number of nearest neighbors	6	8	12
Packing fraction or efficiency	0.524 or 52%	0.680 or 68%	0.740 or 74%

Hexagonal close packed → 74%, c/a = 1.633

Primitive cell of bcc and fcc structure



Body centered cubic, showing a primitive cell which is a rhombohedron of edge $\frac{\sqrt{3}}{2}a$ and angle between adjacent edges is $109^0 28'$ and Translation vector $\vec{a}$



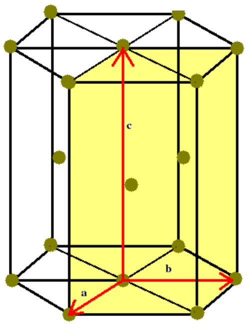
The rhombohedral primitive cell of the face centered cubic crystal with translation vectors

$$\vec{a} = \tfrac{1}{2}a(\hat{x}+\hat{y})$$

$$\vec{b} = \tfrac{1}{2}b(\hat{y}+\hat{z})$$

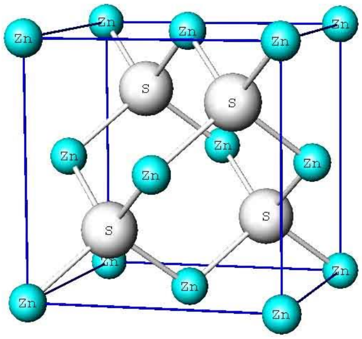
$$\vec{c} = \tfrac{1}{2}c(\hat{z}+\hat{x})$$

and the angles between the axes are 60^0



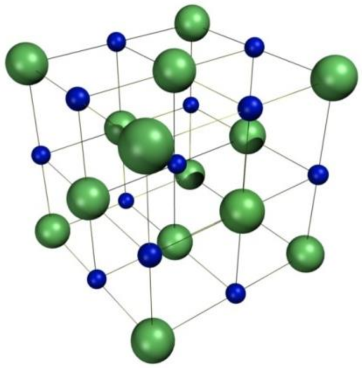
Hexagonal close packed structure (hcp)

Diamond Structure

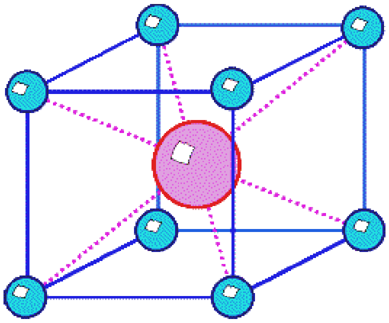


Zinc blend (ZnS) Structure

The NaCl and CsCl structure:



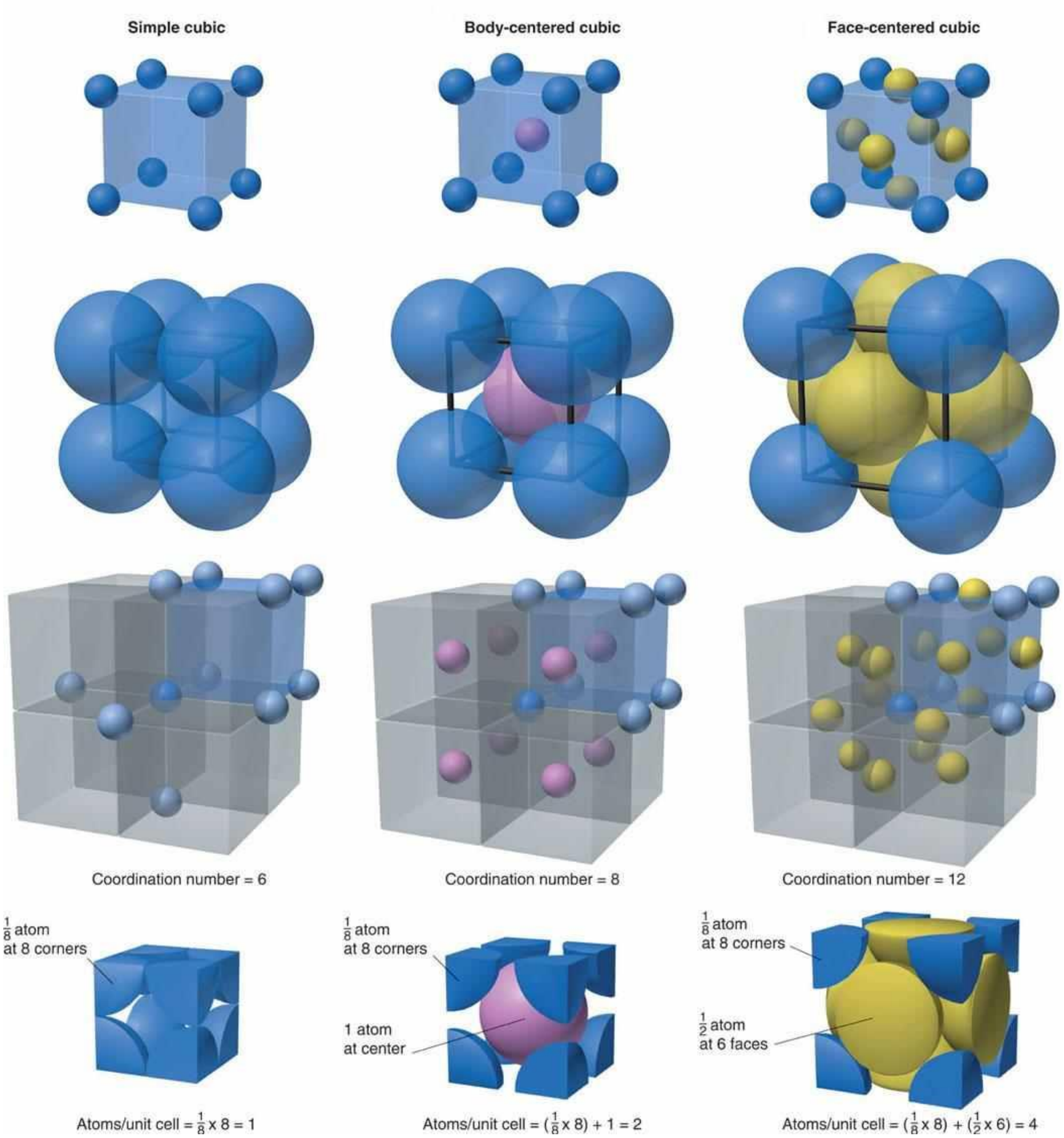
NaCl



CsCl

The sodium chloride crystal structure can be (is) construct by arranging Na^+ and Cl^- ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six (6) nearest neighbors of the opposite charge. The space lattice is *fcc* and the basis has one Cl^- ion at 000 and one Na^+ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Figure shows conventional cubic cell. Variation in ion diameters is due to clarify the spatial arrangement. Example: LiH, NaCl, KBr, KCl, PbS, NH_4I, AgBr, MgO, MnO, BaO, etc.

In the cesium chloride crystal structure, space lattice is simple cubic, and the basis has one Cs^+ ion at 000 and one Cl^- at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. There is one molecule per primitive cell, with atoms at the corners 000 and body centered positions $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ of the simple cubic space lattice. Each atom may be viewed as at the center of a cube of atoms of the opposite kind. So, the number of nearest neighbors or co-ordination number is eight (8). Example: CsCl, NH_4Cl, etc.


Simple cubic
Body-centered cubic
Face-centered cubic
Coordination number = 6
Coordination number = 8
Coordination number = 12
$\frac{1}{8}$ atom at 8 corners
$\frac{1}{8}$ atom at 8 corners
1 atom at center
$\frac{1}{8}$ atom at 8 corners
$\frac{1}{2}$ atom at 6 faces
Atoms/unit cell = $\frac{1}{8} \times 8 = 1$
Atoms/unit cell = $(\frac{1}{8} \times 8) + 1 = 2$
Atoms/unit cell = $(\frac{1}{8} \times 8) + (\frac{1}{2} \times 6) = 4$

Lecture 04: Density and Packing fraction

Density: Let us consider a cubic cell of lattice constant `$a$' contains `n' atoms per unit cell, then density of the crystal material is defined as

$$\rho = \frac{Mass of unit cell}{Volume of the unit cell} = \frac{Mn}{NV} = \frac{Mn}{Na^3}$$

Where M = atomic weight and N ≡Avogadro's number and $\frac{M}{N}$= Mass of each atom or molecule. N = 6.023×10^{23} mol^{-1} = 6.023×10^{26} kmol^{-1}.

The number of lattice points can be determined if we know the volume, density and molecular weight of the constituent atom of the cell.

Problem 1: Calculate the lattice constant for rock salt crystal of density 2180 kg/m^3 assuming that it has *fcc* lattice. Molecular weight of NaCl is 58.5.

Solution: For *fcc* lattice, n = 4 and here $V = a^3$.

Therefore, $a^3 = \frac{Mn}{\rho N} = \frac{58.5\times4}{2180\times6.023\times10^{26}} = 178.22 \times 10^{-30} m^3$

$$a = 5.63 \times 10^{-10} \rightleftarrows m = \rightleftarrows 5.63\text{Å}$$

Problem 2: Calculate the number of atoms per unit cell for an *fcc* lattice of copper (Cu) crystal. It is given that a = 3.6 Å, atomic weight of Cu = 63.6, ρ_{cu} = 8960 kg/m^3 and N = 6.023×10^{26} per kmole.

Ans: 3.959 ≈ 4

Exercise: The lattice parameter and atomic mass of a diamond crystal are 3.57Å and 12 respectively. Calculate the density of diamond.

Solution: $a^3 = (3.57 \times 10^{-10})^3, M = 12$, No of atoms $\left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right) + 1 \times 4 = 8$

$$\rho = \frac{Mn}{Na^3} = 3540 kg/m^3$$

Exercise: Aluminum has *fcc* structure. If the density of Al is 2.7×10^3 kg/m^3. Calculate the unit cell dimensions and the atomic diameter. (At wt. of Al = 26.98, Avogadro no. = 6.023×10^{26} kmole).

Solution: $V = a^3 = \frac{Mn}{\rho N} = \frac{26.98\times4}{2.7\times10^3\times6.023\times10^{26}} = 66.34 \times 10^{26} m^3$, This gives, a = 4.05 $\overset{o}{A}$

Now for fcc crystal, we know that $\sqrt{2}a$ = 4D = 2D , ∴ D = $\frac{a}{\sqrt{2}}$= 2.86 $\overset{o}{A}$

Atomic packing factor

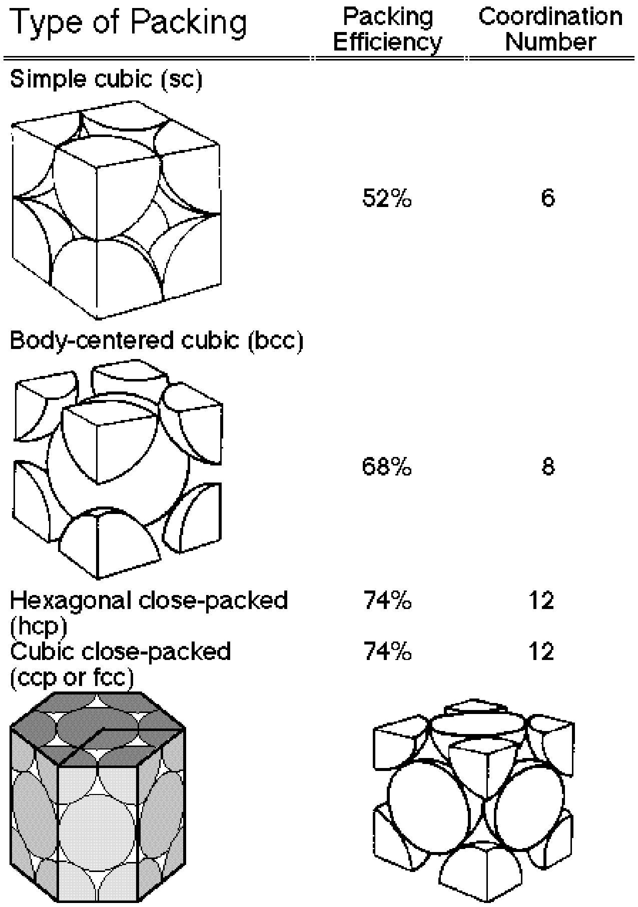
In crystallography, atomic packing factor (APF) or packing fraction is the fraction of volume in a crystal structure that is occupied by atoms. It is dimensionless and always less than unity. For practical purposes, the APF of a crystal structure is determined by assuming that atoms are rigid spheres. The radius of the spheres is taken to be the maximal value such that the atoms do not overlap. It is defined as the ratio of the actual volume occupied by the spherical atoms to the total available of the structure. It is also known as relative pacing density, efficiency or packing fraction. For one-component crystals (those that contain only one type of atom), the APF is represented mathematically by

$$APF = \frac{Volumeoccupiedbythesphereinunitcell}{Volumeoftheunitcell}$$

i.e., $APF = \frac{N_{atoms} V_{atom}}{V_{unitcell}}$

and Efficiency, $\eta = \frac{N_{atoms} V_{atom}}{V_{unitcell}} \times 100\%$

where N_{atoms} is the number of atoms in the unit cell, V_{atom} is the volume of an atom, and $V_{unit\ cell}$ is the volume occupied by the unit cell. It can be proven mathematically that for one-component structures, the most dense arrangement of atoms has an APF of about 0.74. In reality, this number can be higher due to specific intermolecular factors. For multiple-component structures, the APF can exceed 0.74.



Type of Packing	Packing Efficiency	Coordination Number
Simple cubic (sc)	52%	6
Body-centered cubic (bcc)	68%	8
Hexagonal close-packed (hcp)	74%	12
Cubic close-packed (ccp or fcc)	74%	12

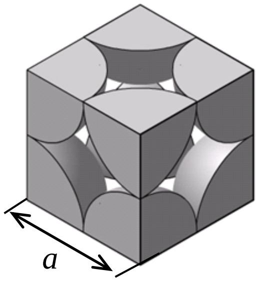
APF for simple cubic:

In this case, the side of the cube 'a' must be equal to 2R, where R is the atomic radius. i.e., $R = \frac{a}{2}$ and number of atoms in simple cubic $= \frac{1}{8} \times 8 = 1$

$\therefore$ Volume of atoms within the unit cell is $V_a = 1 \times \frac{4}{3}\pi R^3 = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}$

and volume of the unit cell, $V_c = a^3$.

Therefore, packing factor $= \frac{V_a}{V_c} \times 100\% = \frac{\pi}{6} = 0.52$

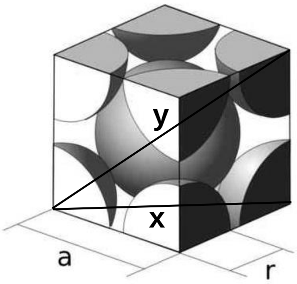


APF for body-centered cubic (bcc) structure:

In this case the diagonal of the cube y = 4R, where is the atomic radius.

From figure, we can write, $x^2 = a^2 + a^2 = 2a^2 \Rightarrow x = \sqrt{2}a$

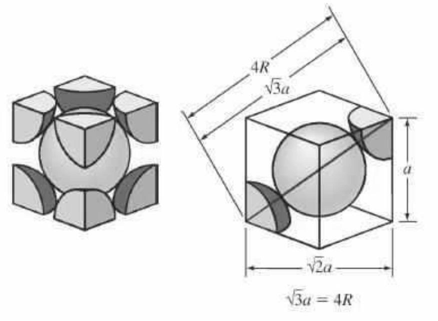
$$y^2 = x^2 + a^2 = 2a^2 + a^2 = 3a^2 \Rightarrow y = \sqrt{3}a$$



$\therefore 4R = \sqrt{3}a$ or $R = \frac{\sqrt{3}}{4}a$

Now, total number of atoms in bcc structure = $(\frac{1}{8} \times 8 + 1) = 1 + 1 = 2$

$\therefore$ The volume of atoms in the unit cell $V_a = 2 \times \frac{4}{3}\pi R^3 = \frac{8}{3}\pi(\frac{\sqrt{3}}{4}a)^3 = \frac{\sqrt{3}}{8}\pi a^3$



and volume of the unit cell, $V_c = a^3$

Therefore, efficiency, $\eta = \frac{V_a}{V_c} \times 100\% = \frac{\sqrt{3}}{8}\pi = 68\%$

The primitive unit cell for the body-centered cubic (BCC) crystal structure contains nine atoms: one on each corner of the cube and one atom in the center. Because the volume of each corner atom is shared between adjacent cells, each BCC cell contains two atoms.

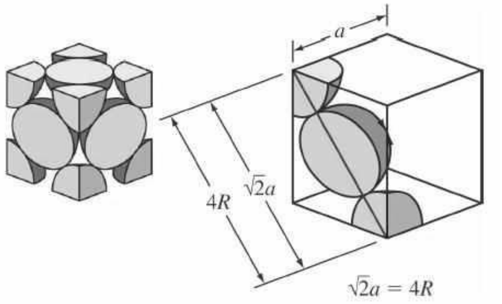
Face centered cubic lattice:

In this case the face diagonal y = 4R.

From figure we get, $y^2 = a^2 + a^2 = 2a^2$

or $y = \sqrt{2}a$

$\therefore 4R = \sqrt{2}a$ or, $R = \frac{\sqrt{2}}{4}a$



Total number of atoms in *fcc* structure is $= (\frac{1}{8} \times 8) + (\frac{1}{2} \times 6) = 1 + 3 = 4$

$\therefore$ Volume of atoms within the unit cell is $V_a = 4 \times \frac{4}{3}\pi R^3 = 4 \times \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3 = \frac{\sqrt{2}\pi a^3}{6}$

and volume of unit cell, $V_c = a^3$.

Therefore, packing density, $\eta = \frac{V_a}{V_c} \times 100\% = \frac{\rightleftarrows\sqrt{2}}{6}\pi = 74\%$

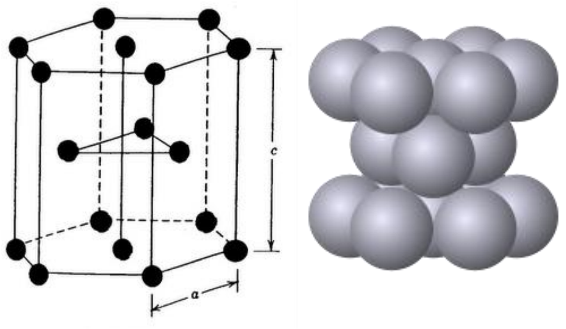
Hexagonal close-packed (hcp) structure

For the hexagonal close-packed (HCP) structure the derivation is similar. The side length of the hexagon will be denoted as a while the height of the hexagon will be denoted as c. Then:

In hexagonal close packed structure we can write $A = 2R$, where r is the atomic radius, $R = \frac{a}{2}$

Total no. of atoms in hc-p structure

$$\left(\frac{1}{6}\times 6\right)\times 2+\left(\frac{1}{2}\times 2\right)+3=2+1+3$$



Volume of the unit cell $= 3\left|\vec{c}.\left(\vec{a}\times\vec{b}\right)\right|$

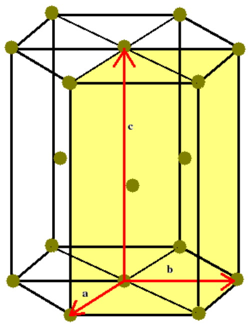
$$= 3\left|\vec{c}.(ab\,sin\,\theta)\hat{c}\right|$$

$$= 3\times c(ab\,sin\,\theta)\,cos\,0$$

$$= 3\times cab\,\sin\theta$$

$$= 3\times a^2c\,sin\,60^0[\because a=b,\theta=60^0]$$

$$= \frac{3\sqrt{3}}{2}a^2c$$



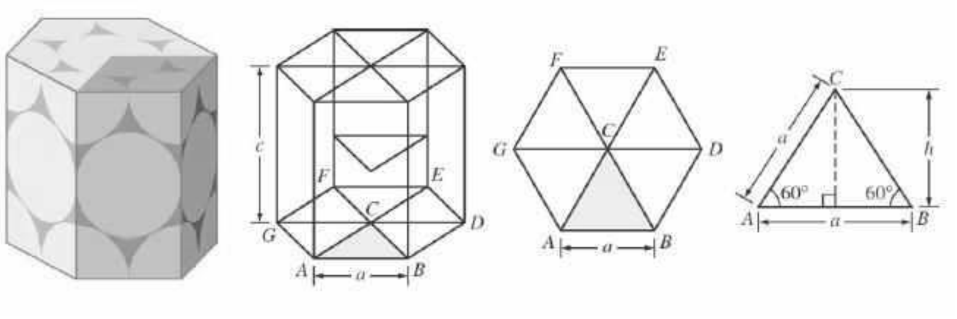
And $V_a = \frac{4}{3}\pi R^3\times 6 = 8\,\pi(a/2)^3 = \pi a^3$

$\therefore$ Packing factor for hcp structure,

$$\eta=\frac{V_a}{V_c}=\frac{\pi a^3\times 2}{3\sqrt{3}\,a^2c}=\frac{2\pi}{3\sqrt{3}}\left(\frac{a}{c}\right)=\frac{2\pi}{3\sqrt{3}\times 1.633}=74\%$$

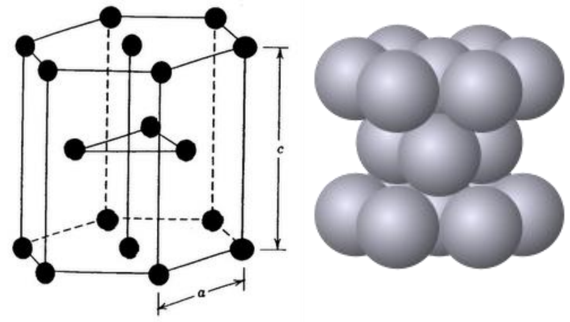
Here, $c/a = 1.633$

$$a = 2r$$
$$c = \sqrt{\frac{2}{3}}(4$$



By similar procedures, the ideal atomic packing factors of all crystal structures can be found. The common ones are collected here as reference, rounded to the nearest hundredth.

- Simple cubic: 0.52
- Body-centered cubic: 0.68
- Hexagonal close-packed: 0.74
- Face-centered cubic: 0.74
- Diamond cubic: 0.34



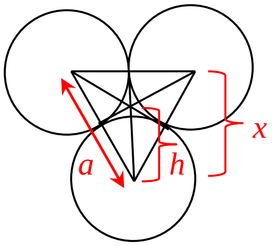
Hexagonal close-packed crystals: the axial ratio

From figure we can easily write

$$x^2 = a^2 - \left(\frac{a}{2}\right)^2 = \frac{3a^2}{4}, \qquad \therefore x = \frac{\sqrt{3}}{2}a$$

where a is the centre to centre distance of the atom.

and $$h = \frac{2}{3}x = \frac{2}{3} \times \frac{\sqrt{3}}{2}a = \frac{a}{\sqrt{3}}$$



From Δ ABC, we can write,

$(AC)^2 = (AB)^2 + (BC)^2$

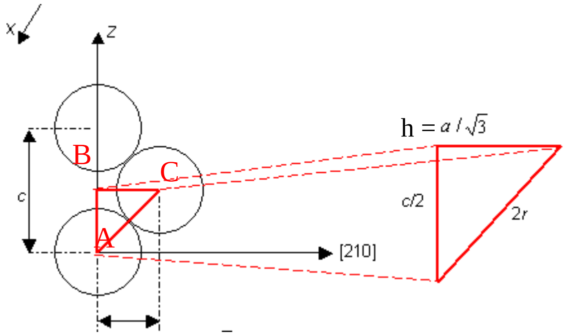
$$\Rightarrow a^2 = \left(\frac{c}{2}\right)^2 + (h)^2$$

$$\Rightarrow a^2 = \frac{c^2}{4} + \frac{a^2}{3}$$

$$\Rightarrow a^2 - \frac{a^2}{3} = \frac{c^2}{4}$$

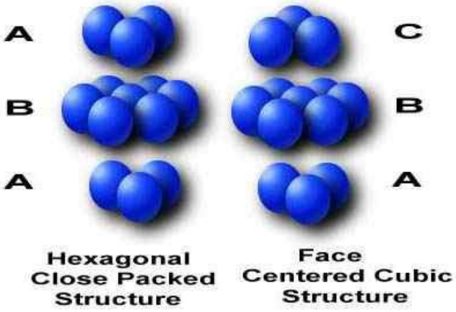
$$\Rightarrow a^2 - \frac{c^2}{3} = \frac{c^2}{4}$$

$$\Rightarrow \frac{c}{a} = \sqrt{\frac{8}{3}} == 1.633$$

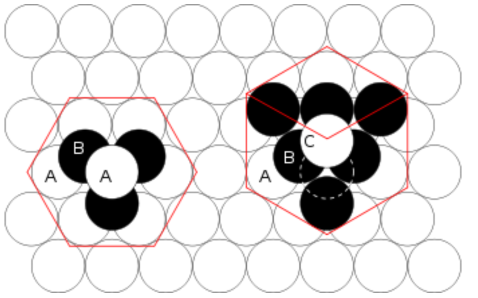


Many materials have the hexagonal P crystal system, but the axial ratio is rarely ideal. Cadmium, for example, has an axial ratio of c/a = 1.886. This non-ideal structure has implications for the behavior of the material, for example in slip.

Similarities and Difference between the FCC and HCP Structure



The face centered cubic and hexagonal close packed structures both have a packing factor of 0.74, consist of closely packed planes of atoms, and have a coordination number of 12. The difference between the fcc and hcp is the stacking sequence. The hcp layers cycle among the two equivalent shifted



HCP lattice (left) and the fcc lattice (right)

positions whereas the fcc layers cycle between three positions. As can be seen in the image, the hcp structure contains only two types of planes with an alternating ABAB arrangement. Notice how the atoms of the third plane are in exactly the same position as the atoms in the first plane. However, the fcc structure contains three types of planes with a ABCABC arrangement. Notice how the atoms in rows A and C are no longer aligned. Remember that cubic lattice structures allow slippage to occur more easily than non-cubic lattices, so hcp metals are not as ductile as the fcc metals.

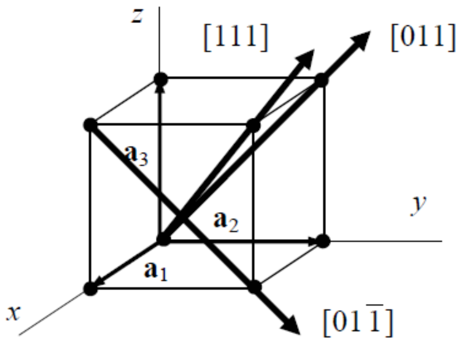
The table below shows the stable room temperature crystal structures for several elemental metals.

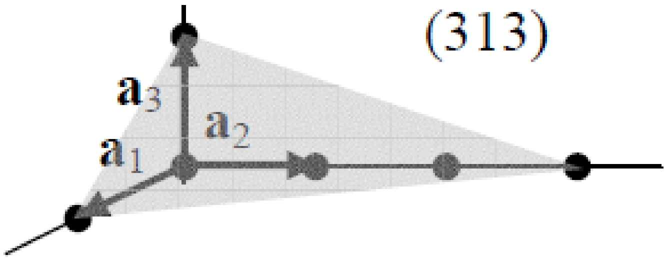
Metal	**Crystal Structure**	**Atomic Radius (nm)**
Aluminum	FCC	0.1431
Cadmium	HCP	0.1490
Chromium	BCC	0.1249
Cobalt	HCP	0.1253
Copper	FCC	0.1278
Gold	FCC	0.1442
Iron (Alpha)	BCC	0.1241
Lead	FCC	0.1750
Magnesium	HCP	0.1599
Molybdenum	BCC	0.1363
Nickel	FCC	0.1246
Platinum	FCC	0.1387
Silver	FCC	0.1445
Tantalum	BCC	0.1430
Titanium (Alpha)	HCP	0.1445
Tungsten	BCC	0.1371
Zinc	HCP	0.1332

Lecture 5: Crystal planes and Miller Indices

Index system for crystal directions and planes

Crystal directions: Any lattice vector can be written as that given by $\vec{T} = n_1\mathbf{a_1} + n_2\mathbf{a_2} + n_3\mathbf{a_3}$. The direction is then specified by the three integers $[n_1n_2n_3]$. If the numbers $n_1n_2n_3$ have a common factor, this factor is removed. For example, [111] is used rather than [222], or [100], rather than [400]. When we speak about directions, we mean a whole set of parallel lines, which are equivalent due to transnational symmetry. Opposite orientation is denoted by the negative sign over a number. For example $[01\bar{1}]$:





Crystal planes: The orientation of a plane in a lattice is specified by *Miller indices*. They are defined as follows. We find intercept of the plane with the axes along the primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. Let's these intercepts be *x*, *y*, and *z*, so that *x* is fractional multiple of a_1, *y* is a fractional multiple of a_2 and *z* is a fractional multiple of a_3. Therefore we can measure *x*, *y*, and *z* in units a_1, a_2 and a_3 respectively. We have then a triplet of integers (*x y z*). Then we invert it (1/*x* 1/*y* 1/*z*) and reduce this set to a similar one having the smallest integers multiplying by a common factor. This set is called Miller indices of the plane (*hkl*). For example, if the plane intercepts *x*, *y*, and *z* in points 1, 3, and 1, the index of this plane will be (313).

The orientation of a crystal plane is determined by three points in the plane, provided they are not collinear. If each point lay on a different crystal axis, the plane could be specified by giving the co-ordinates of the points in terms of the lattice constants *a, b, c*. **A notation conventionally used to describe lattice points (sites), directions and planes is known as Miller Indices**.

A crystal lattice may be considered as an assembly of equidistant parallel planes passing through the lattice points and are called lattice planes. In order to specify the orientation, one employs the so called Miller indices.

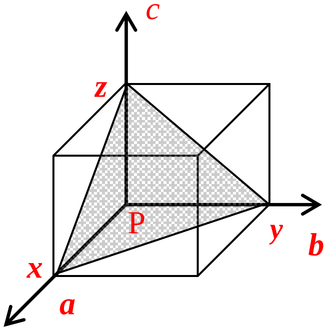
For simplicity, let us start with a two-dimensional lattice and then generalized to three-dimensional case.

The equations of plane in 2-D and 3D having the intercepts *a*, *b* and *a*, *b*, *c* respectively is

$$\frac{x}{a}+\frac{y}{b}=1 \text{ and } \quad \frac{x}{a}+\frac{y}{b}+\frac{z}{c}=1$$

Crystal direction is the direction (line) of axes or line from the origin and denoted as [111], [100], [010], etc.

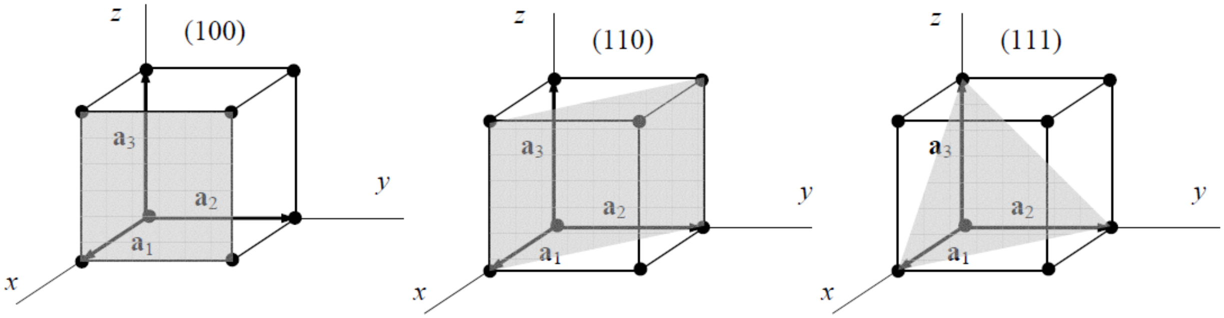
How to find Miller Indices:



To determine the indices for the plane P, in Figure 2, first we have to find the intercepts with the axes along the basis vector $\vec{a}, \vec{b}, \vec{c}$. Let these intercepts be x, y, z.

- Form the fractional triplet$\left(\frac{x}{a}, \frac{y}{b}, \frac{z}{c}\right)$.
- Take reciprocal to this set.
- Then reduce this set to a similar one having the smallest integers multiplying by common factor.
- This last set is enclosed in parentheses (h k l), is called the index of the plane or Miller Indices.

The Miller indices specify not just one plane but an infinite set of equivalent planes. Note that for cubic crystals the direction [hkl] is perpendicular to a plane (hkl) having the same indices, but this is not generally true for other crystal systems. Examples of the planes in a cubic system:



Example: Let the intercepts are x = 2a, y = (3/2)b, z = c.

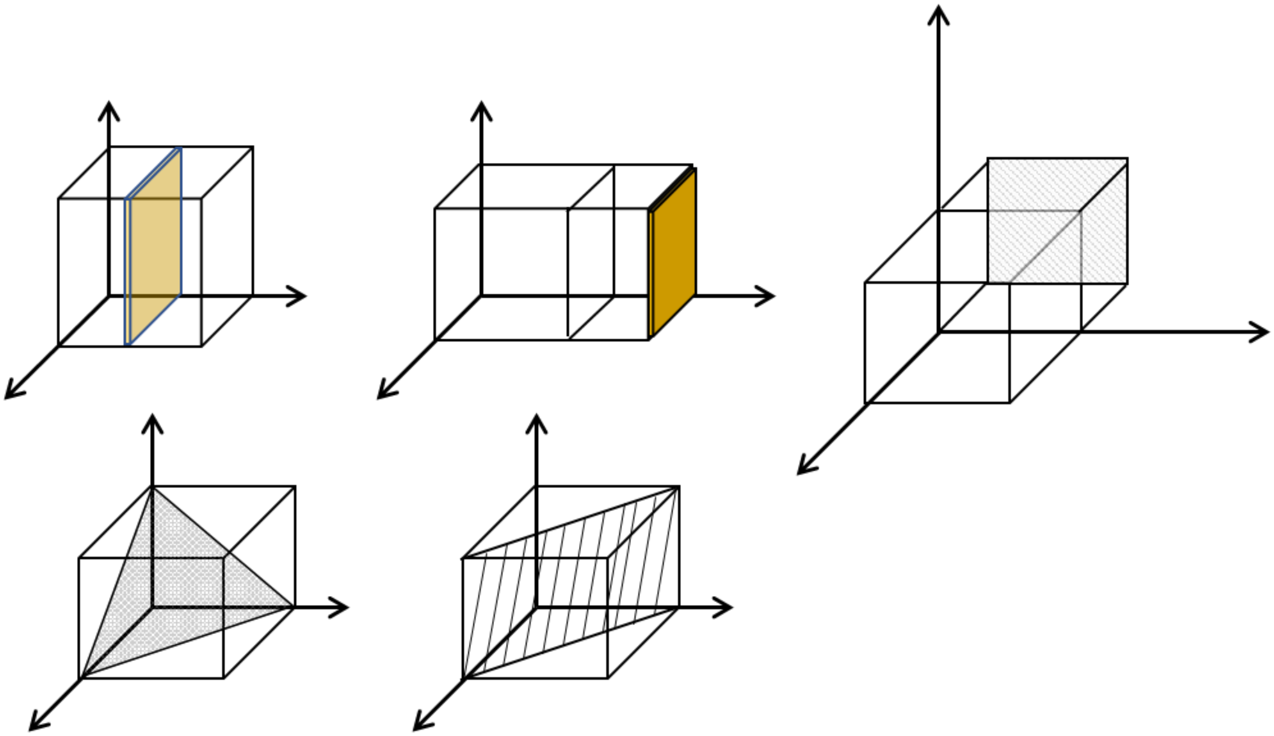
i. We first form the set $\left(\frac{x}{a}, \frac{y}{b}, \frac{z}{c}\right) = \left(2, {}^{3}\!/_{2}, 1\right)$,

ii. Then invert it $\left(\frac{1}{2}, \frac{2}{3}, 1\right)$

iii. and finally multiply by a common (factor) denominator. Which is 6, to obtain the miller indices (3 4 6).

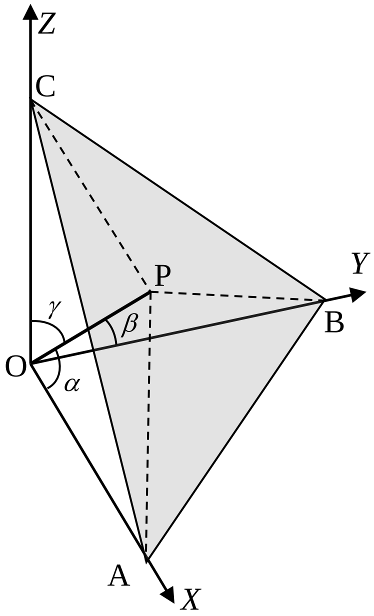
Exercise: x = 2*a*, y = 3*b*, z = 6*c* => (321).

The indices of some important planes in a cubic crystal



Relation between interplanar spacing and Miller indices:

Let us consider three mutually perpendicular coordinate axis, OX, OY, and Oz and assume that a plane (*hkl*) parallel to the plane passing through the origin makes intercepts a/h, b/k and c/l on the three axes at A. B and C respectively as shown in figure.



Let OP = d_{hkl}, the interplanar spacing be normal to the plane drawn from the origin and makes angle α, β, and γ with the three axes respectively.

Therefore, $OA = \frac{a}{h}, OB = \frac{b}{k}, OC = \frac{c}{l}$

From ΔOPA we get, $\cos\alpha = \frac{OP}{OA} = \frac{d_{hkl}}{a/h}$

Similarly, from ΔOPB we get $\cos\beta = \frac{OP}{OB} = \frac{d_{hkl}}{b/k}$

and from ΔOPC we get $\cos\gamma = \frac{OP}{OC} = \frac{d_{hkl}}{c/l}$

But, for a rectangular coordinate system, using directional cosine we have

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1 \qquad (1)$$

Substituting the values of cosα, cosβ and cosγ in Eq.1 we get,

$$d_{hkl}^2\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right) = 1$$

$$\therefore d_{hkl} = \frac{1}{\sqrt{h^2/a^2 + k^2/b^2 + l^2/c^2}} \qquad (2)$$

This is the general formula and is applicable to the primitive lattice of orthorhombic, tetragonal and cubic systems.

i) Orthorhombic system: $a \neq b \neq c$

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)}}$$

ii) Tetragonal system: $a = b \neq c$

$$\therefore \quad d_{hkl} = \frac{1}{\sqrt{\left(\frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}\right)}}$$

Example: $a = b = 2.42$Å and c = 1.74Å
Then, d_{101} = 1.41Å

ii) Cubic system: $a = b = c$

$$\therefore \quad d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

Example: a = 2Å, d_{111} = 2√3Å

Example: a = 4.21 Å, d_{321} = 1.125 Å

Example: $d_{100} = a$, $d_{110} = \frac{a}{\sqrt{2}}$ $d_{111} = \frac{a}{\sqrt{3}}$

$\therefore d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$

For *fcc* ⇒ $d_{100} = \frac{1}{2}\,(d_{100,\mathrm{sc}}) = \frac{a}{2}$

$d_{110} = (d_{110,\mathrm{sc}}) = \frac{a}{\sqrt{2}}$

$d_{111} = \frac{1}{2}\,(d_{111,\mathrm{sc}}) = \frac{a}{2\sqrt{3}}$

and $d_{100}: d_{110}: d_{111} = 1:\sqrt{2}: \frac{1}{\sqrt{3}}$

For *bcc* ⇒ $d_{100} = \frac{1}{2}\,(d_{100,\mathrm{sc}}) = \frac{a}{2}$

$d_{110} = \frac{1}{2}\,(d_{110,\mathrm{sc}}) = \frac{a}{2\sqrt{2}}$

$d_{111} = (d_{111,\mathrm{sc}}) = \frac{a}{\sqrt{3}}$

and $d_{100}: d_{110}: d_{111} = 1: \frac{1}{\sqrt{2}}: \frac{2}{\sqrt{3}}$

Ex: Determine the Miller Indices of a plane which is parallel to x-axis and cuts intercepts of 2 and $\frac{1}{2}$, respectively along y and z axes.

Solution:

i) Intercepts	∞	2b	$\frac{1}{2}c$
ii) Division by unit translation	$\frac{\infty}{a} = \infty$	$\frac{2b}{b} = 2$	$\frac{3c}{2c} = \frac{1}{2}$
iii) Reciprocals	$\frac{1}{\infty}$	$\frac{1}{2}$	2
iv) After clearing fraction	0	1	4

Therefore, the required Miller indices of the plane (014)

Ex: Determine the M. I. of a plane theat makes intercepts of 2Å, 3 Å, 4 Å on the co-ordinate axes of an orthorhombic crystal with a:b:c = 4:3:2

Solution:

Here the unit translations are a = 4, b = 3 and c = 2 following the same procedure

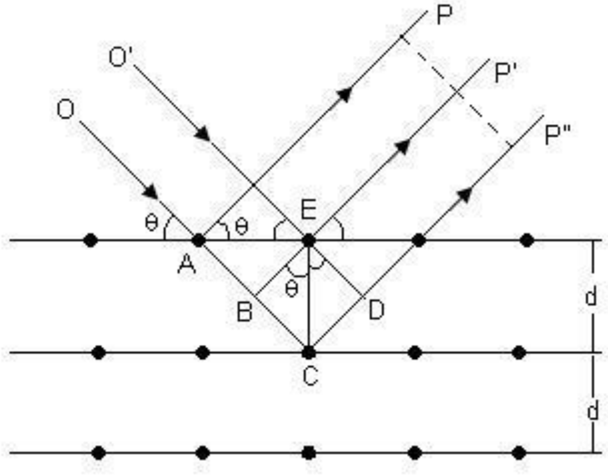
i) Intercepts	2	3	4
ii) Division by unit translation	$\frac{2}{4} = \frac{1}{2}$	$\frac{3}{3} = 1$	$\frac{4}{2} = 2$
iii) Reciprocals	2	1	$\frac{1}{2}$
iv) After clearing fraction	4	2	1

Therefore, the Miller indices of the plan is (421)

Lecture 6: X-ray diffraction and Bragg's law:

The inter-atomic spacing in crystals is of the order of 1Å. Because of the short wavelength (comparable to the inter-planer distance), X-rays are scattered by adjacent atoms in crystals which can interfere and give rise to diffraction effects. When X-rays enter into a crystal, each atom acts as a diffraction center and crystal as a whole acts like a three-dimensional diffraction grating. The diffraction pattern so produced can tell us much about the internal arrangement of atoms in crystal.

Let us consider a crystal made up of equidistant parallel planes of atoms with the inter-planer spacing d_{hkl}. Further, consider a monochromatic X-ray beam of wavelength λ having a common wave front, falls at an angle θ on the planes as shown in Figure. Each atom scatters the X-rays more or less uniformly in all directions, but because of the periodic arrangement of atoms, the scattered radiation from all atoms in a set of planes is in phase where they interfere constructively. In all other directions, there is destructive interference.



Consider two of the incoming X-ray OA and O′E inclined at an angle θ with the topmost plane of the crystal and are scattered in the directions AP and EP′, also at an angle θ with that plane. Since the path length of the rays OEP′ and O′AP are the same, they arrive at P and P′ respectively in phase with each other and again form a common wavefront. This is the condition for scattering in phase by single plane of the crystal.

Now, let us consider X-ray scattering from two adjacent planes $(hkl)_1$ and $(hkl)_2$ as shown in Figure. If EB and ED are parallel to the incident and scattered wavefront respectively, the total path OCP″ is longer than the path O′EP′ by an amount

$$\Delta = BCD = BC + BD \tag{1}$$

Now, from the right-angle triangle EBC and EDC, we have

$$BC = d\sin\theta = BD$$

So, $$\Delta = 2d\sin\theta \qquad (2)$$

If two consecutive planes scattered in phase with each other then we know that the path difference Δ must be equal to an integral multiple of wavelength, i.e., $\Delta = n\lambda$, where n = 0, 1, 2 ... gives the order of reflection. Thus, the condition for constructive interference (in-phase scattering) by a set of equidistant parallel planes in a crystal is given by

$$2d\sin\theta = n\lambda \qquad (3)$$

This is the well-known Bragg's law, which was first derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913. Thus diffraction (constructive) occurs for certain discrete values of θ for which the Bragg's condition is fulfilled.

As $(\sin\theta)_{\max} = 1$, we get, $\frac{n\lambda}{2d} \leq 1$.

That is, λ must not be greater than twice the interplanar spacing, otherwise no diffraction will occur. This observation is an example of X-ray wave interference, commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries. The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond. Although Bragg's law was used to explain the interference pattern of X-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest.

William Henry Bragg and William Lawrence Bragg were the first and (so far) the only father-son team to have jointly won the prize. Other father/son laureates include Niels and Aage Bohr, Manne and Kai Siegbahn, J. J. Thomson and George Thomson, Hans von Euler-Chelpin and Ulf von Euler, and Arthur and Roger Kornberg, who were all awarded the prize for separate contributions. W. L. Bragg was 25 years old at the time, making him the youngest Nobel laureate to date.

For certain specific wavelengths and incident angles, intense peaks of reflected radiation (known as Bragg peaks) were produced. The concept of Bragg diffraction applies equally to neutron diffraction and electron diffraction processes. When X-rays are incident on an atom, they make the electronic cloud move as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency (blurred slightly due to a variety of effects); this phenomenon is known as Rayleigh scattering (or elastic scattering). The scattered waves can themselves be scattered but this secondary scattering is assumed to be negligible. A similar process occurs upon scattering neutron waves from the nuclei or by a coherent spin interaction with an unpaired electron. These re-emitted wave fields interfere with each other either constructively or destructively (overlapping waves either add together to produce stronger peaks or subtract from each other to some degree), producing a diffraction pattern on a detector or film. The resulting wave interference pattern is the basis of diffraction analysis.

When the energetic electrons strike the target, which is a pure metal such as copper or molybdenum, and remove inner (K) shell electrons, other electrons from higher level shells drop into the vacant K-shell and in so doing emit a photon (X-ray) whose wavelength (energy) is characteristic of the metal target material. In order to remove the inner shell electron, the incoming electron must have an energy greater than the difference in energy between the inner (K) shell electron and a free electron in the conduction band of the target metal. This energy difference is referred to as the absorption edge energy.

Both KCl and KBr have *sodium chloride structure,* XRD spectra of these two are shown in the figure. In this structure the two types of atoms are arranged alternatively at the lattice sites of a simple cubic lattice. The space lattice is *fcc* with a basis of two non-equivalent atoms at 000 and ½ ½ ½.

In KCl the number of electrons of K$^+$ and Cl$^-$ ions are equal, and the charge distribution is similar. Therefore, the form factors for K$^+$ and Cl$^-$ are almost exactly equal, so that the crystal looks to X-rays as if it were a monatomic simple cubic lattice of lattice constant *a*/2. Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant *a*. In KBr the form factor of Br$^-$ is quite different than that of K$^+$, and therefore, all the reflections of the *fcc* lattice are present in the XRD pattern of KBr.

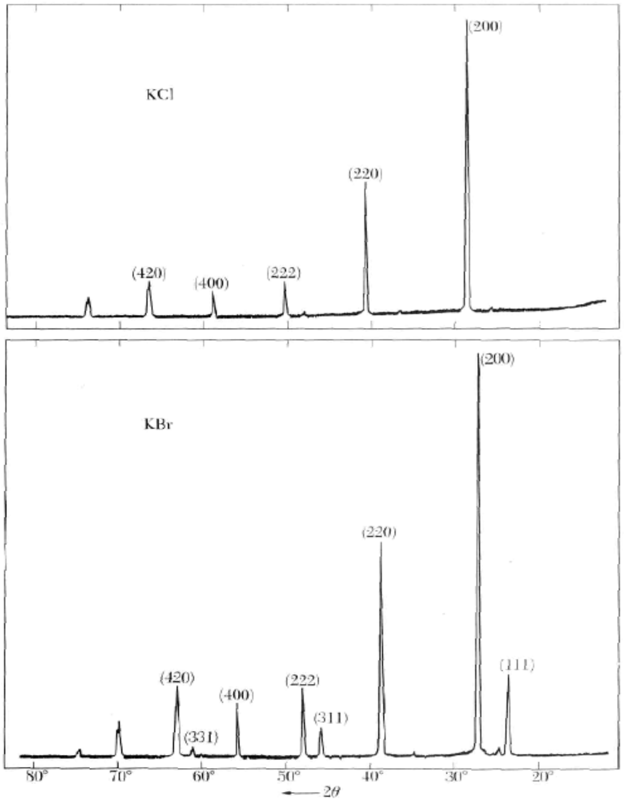


Figure: Comparison between X-ray reflections from KCl and KBr.

Exercise: Determine the angle through which an X-ray of wavelength 0.440 Å be reflected from the cube face of a rock salt crystal (d = 2.814 Å).

Solution: Given λ = 0.440 Å. d = 2.814Å $\theta = sin^{-1}\left(\frac{n\lambda}{2d}\right)$

1st order reflection, n = 1, $\theta_1 = sin^{-1}\left(\frac{1\times 0.440}{2\times 2.814}\right) = sin(\,0.0782) = 4^o 29^/$

2nd order reflection, n = 2, $\theta_2 = sin^{-1}(2\times 0.0782) = 8^o 59^/$

3rd order reflection, n = 3, $\theta_3 = sin^{-1}(3\times 0.0782) = 13^o 34^/$, etc.

Exercise: Determine the wavelength of the diffraction beam, when a beam of X-ray having wavelengths in the range 0.2 Å to 1 Å incident at an angle of 9° with the cube face of a rock salt crystal (d = 2.814 Å)

Solution: $n = 1$ $1\lambda_1 = 2(2.814)$ Sin 9° $\Rightarrow \lambda_1 = 0.8804$ Å

$n = 2$ $2\lambda_2 = 0.8804$ Å $\Rightarrow \lambda_2 = 0.4402$ Å

$n = 3$ $3\lambda_3 = 0.8804$ Å $\Rightarrow \lambda_3 = 0.2935$ Å

$n = 4$ $4\lambda_4 = 0.8804$ Å $\Rightarrow \lambda_4 = 0.2201$ Å

$n = 5$ $5\lambda_5 = 0.8804$ Å $\Rightarrow \lambda_5 = 0.1760$ Å $<$ 0.2 Å

which shows the wavelength of the X-rays are 0.8804, 0.4402, 0.2935 and 0.2201 Å.

Experimental X-ray diffraction Methods:

To satisfy Bragg's law, it is necessary to vary either the angle of inclination of the specimen to the beam or the wavelength of the radiation. The three standard methods of X-ray crystallography are-

a) **Laue Method**: A stationary single crystal is irradiated by a range of X-ray wavelengths.

b) **Rotating crystal Method**: A single crystal specimen is rotated in a beam of monochromatic X-rays.

c) **Powder Method**: A polycrystalline powder specimen is kept stationary in a beam of monochromatic radiation.

Of these techniques, Laue method is used only for known crystal orientation measurement.

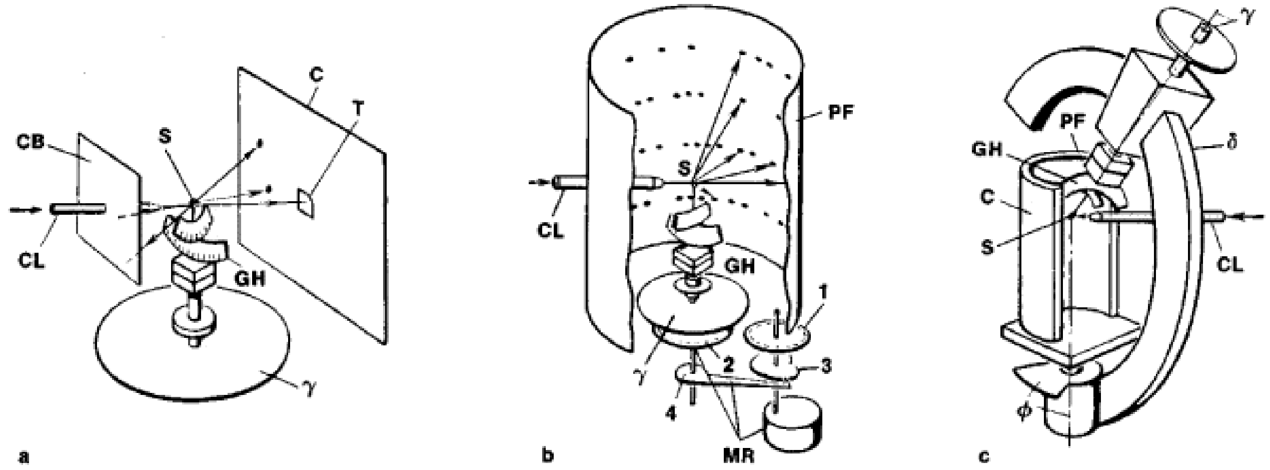


Fig. (a) Lau method, (b) Rotating crystal method, (c) Powder method.

The powder method assumes that all orientations are present in the sample, so that regardless of the angle of incidence, there will be a grain in the proper orientation for each reflection (diffraction). The patterns are very useful for identification of unknowns. There are compiled indexes of powder diffraction data for minerals, as well as inorganic compounds and organic compounds.

If the Miller indices of the diffraction peaks are known, it is possible to determine the unit cell parameters of the material from the peak positions. Cell parameters can then be used to determine composition if the cell variation with composition is known.

If more than one mineral is present in the sample, it is possible, although not easy, to determine the relative proportions of the minerals. To do this one must have a standard pattern for each pure mineral to obtain the relative intensities of the peaks form each mineral. It is then possible to use the relative intensities of non-overlapping peaks to give an estimate of the mineral proportions, called a *mode*.

Exercises:

1. Compute the lattice spacing for the (211) reflection of olivine with $a = 4.830$ Å, $b = 10.896$ Å and $c = 6.288$ Å: What is the angle for this reflection using Cu k_α radiation ($\lambda = 1.5405$ Å)

   $1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$

   $1/d^2 = (2/4.830)^2 + (1/10.896)^2 + (1/6.288)^2$

   $d = 2.2077$ Å

$n\lambda = 2d\,sin\theta$
$\theta = \sin^{-1}(\lambda/2d)$
$\theta = 20.413^{o}$
$2\theta = 40.825^{o}$

2. Compute the spacing for (131) garnet with a = 11.46 Å and Cu k_{α} radiation (λ = 1.5405 Å)

   $d = a / (h^2 + k^2 + l^2)^{1/2}$
   $d = 11.46/(11)^{1/2} = 3.455$ Å
   $n\lambda = 2d\,sin\theta$
   $\theta = \sin^{-1}(n\lambda/2d)$
   $\theta = \sin^{-1}(1.54/2(3.455))$
   $\theta = 12.876^{o}$
   $2\theta = 25.754^{o}$

3. What is the energy, in joules, of an X-ray photon of Cu k_{α} radiation (λ = 1.540 Å)?

   $E = h\,\nu$
   $\nu = c/\lambda$ h = Planck's constant = 6.6×10^{-34} J-s
   $E = hc/\lambda$ c = Speed of light = 3×10^{8} m/sec
   1 ev = 1.6019×10^{-19} J
   $E = (6.6 \times 10^{-34}$ J-s$)(3 \times 10^{8}$ m/sec$)/ 1.5405 \times 10^{-10}$ m
   $= (1.286\times10^{-15}$ J$) /(1.6019\times10^{-19}$ J/eV$)$
   = 8026 eV

4. What frequency is Mo k_{α} radiation (λ = 0.70926 Å)?

   $n = c / \lambda$
   $n = (3.0 \times 10^{8}$ m.s$^{-1}) / (0.70926 \times 10^{-10}$ m$))$
   $n = 4.2297 \times 10^{18}$ s^{-1}
   $= 4.2297\times10^{18}$ Hz (H = hertz = s^{-1})

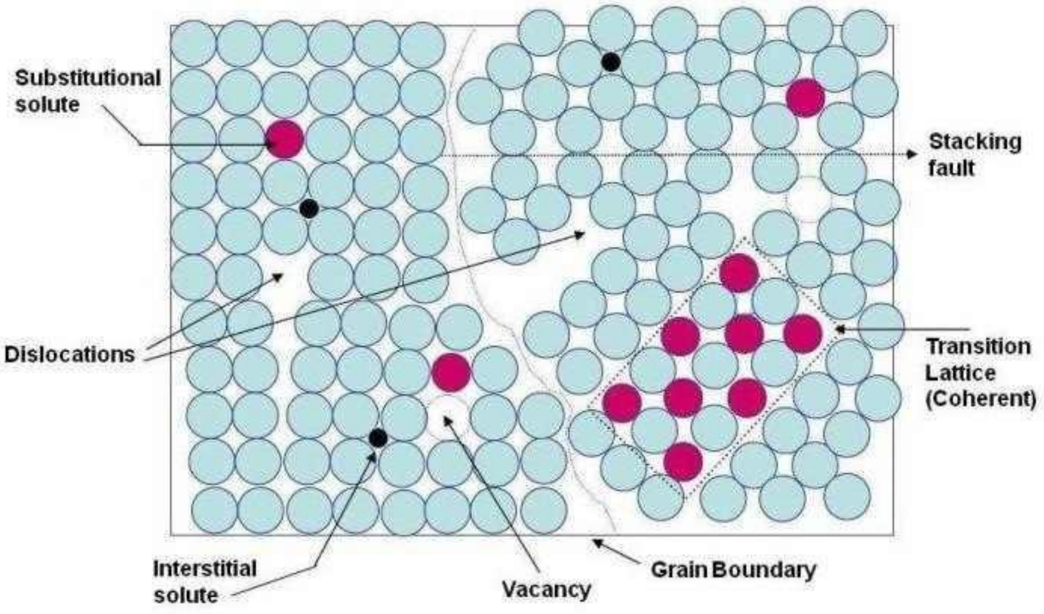
5. The absorption edge of Cu k-series radiation is 1.380 Å. What is the minimum KV setting on the X-ray generator required to produce Cu k-series radiation?

   $E = hc / \lambda = (6.6\times10^{-34}$ J.s$) (3.0\times10^{8}$ m.s$^{-1}) /(1.380 \times 10^{-10}$ m$)) / (1.6019\times10^{-19}$ J/eV$)$
   E = 8956 eV
   E = 8.956 KeV $\approx$ 8.9 KeV

Lecture 7: Defects in solids: Point defects and line defects

Imperfections or defects: Any deviation from the perfect atomic arrangement in a crystal is said to contain imperfections or defects. In fact, using the term “defect” is sort of a misnomer since these features are commonly intentionally used to manipulate the mechanical properties of a material. Adding alloying elements to a metal is one way of introducing a crystal defect. Crystal imperfections have strong influence upon many properties of crystals, such as strength, electrical conductivity and hysteresis loss of ferromagnets. Thus, some important properties of crystals are controlled by as much as by imperfections and by the nature of the host crystals.

- The conductivity of some semiconductors is due entirely to trace amount of chemical impurities.
- Color, luminescence of many crystals arise from impurities and imperfections
- Atomic diffusion may be accelerated enormously by iumpurities or imperfections
- Mechnical and plastic properties are usually controlled by imperfections



Various Crystal Defects

Imperfections in crystalline solids are normally classified according to their dimension as follows

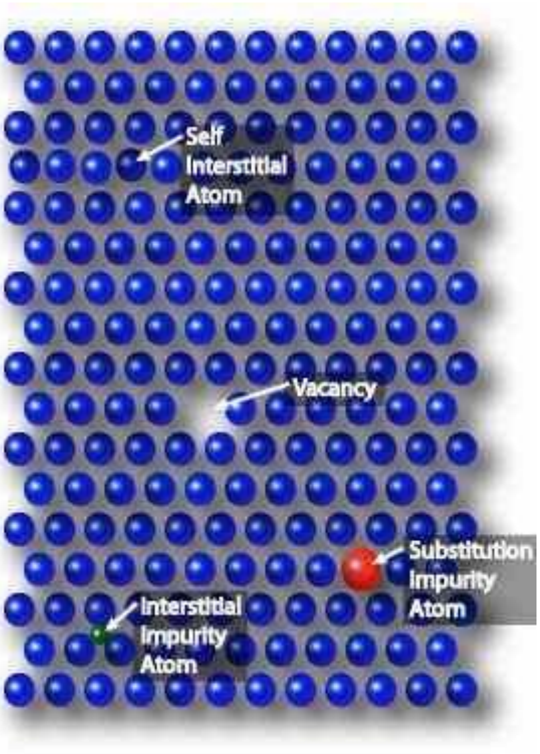
1. Point imperfections (Zero dimensional defects)
2. Line imperfections (one dimensional defects)
3. Plane or surface imperfections (Two dimensional defects)
4. Volume imperfections (three dimensional defects)

Crystal defect

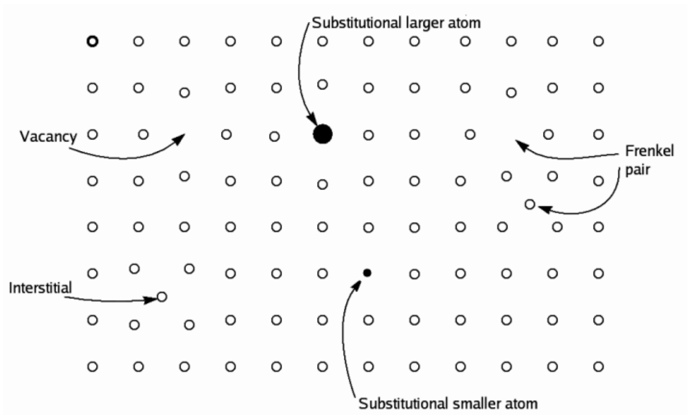
Point defects	**Line defects**	**Surface defects**	**Volume defects**
Vacancy	Edge dislocation	Grain boundaries	Inclusions
Schottky	Screw Dislocation	Tilt boundaries	Voids
Self-interstitial		Twin boundaries	
Frenkel		Stacking faults	
Substitutional			
Color centers			
Polarons			
Excitons			

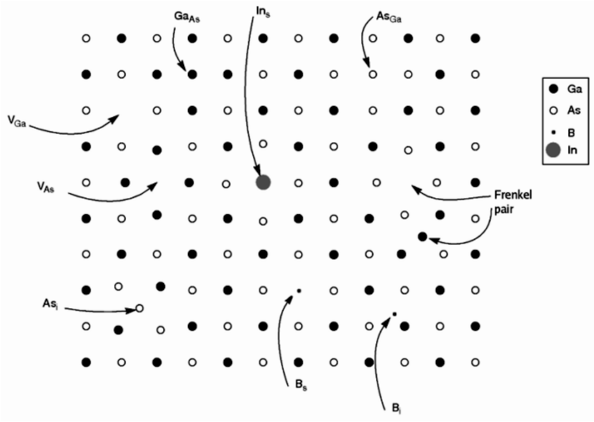
Point Defects: Point defects are where an atom is missing or is in an irregular place in the lattice structure. Point defects include self-interstitial atoms, interstitial impurity atoms, substitutional atoms and vacancies.

A **self-interstitial** atom is an extra atom that has crowded its way into an interstitial void in the crystal structure. Self-interstitial atoms occur only in low concentrations in metals because they distort and highly stress the tightly packed lattice structure. A **substitutional impurity** atom is an atom of a different type than the bulk atoms, which has replaced one of the bulk atoms in the lattice. Substitutional impurity atoms are usually close in size (within approximately 15%) to the bulk atom. An example of substitutional impurity atoms is the zinc atoms in brass. In brass, zinc atoms with a radius of 0.133 nm have replaced some of the copper atoms, which have a radius of 0.128 nm. **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.

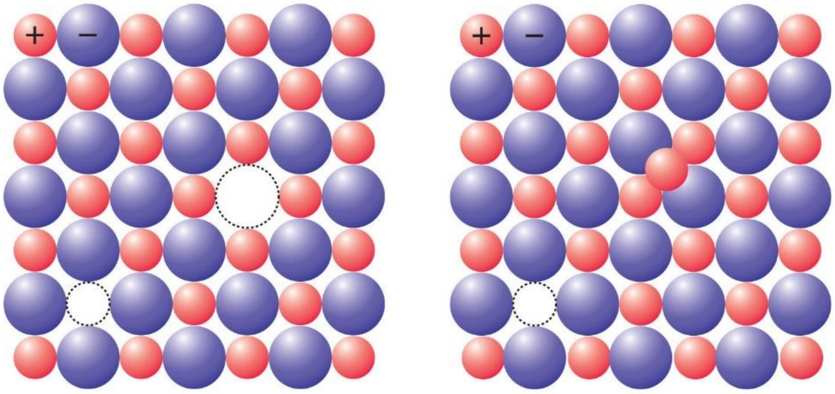


An example of interstitial impurity atoms is the carbon atoms that are added to iron to make steel. Carbon atoms, with a radius of 0.071 nm, fit nicely in the open spaces between the larger (0.124 nm) iron atoms. **Vacancies** are empty spaces where an atom should be but is missing. They are common, especially at high temperatures when atoms are frequently and randomly change their positions leaving behind empty lattice sites. In most cases diffusion (mass transport by atomic motion) can only occur because of vacancies. **Schottky imperfection** is a type of vacancy in which an atom being free from regular site, migrates through successive steps and eventually settles at the crystal surface. In a ionic crystal, however a vacancy on either a cation or anion site must be electrically balanced by some means. This may be achieved if there are an equal number of cation and anion vacancies, or if for every ionic crystal vacancy, a similar charged interstitial appears.





The combination of anion cation vacancies (in pairs) is called Schottky imperfections. The combination of a vacancy and interstitial is called a Frankel imperfection.



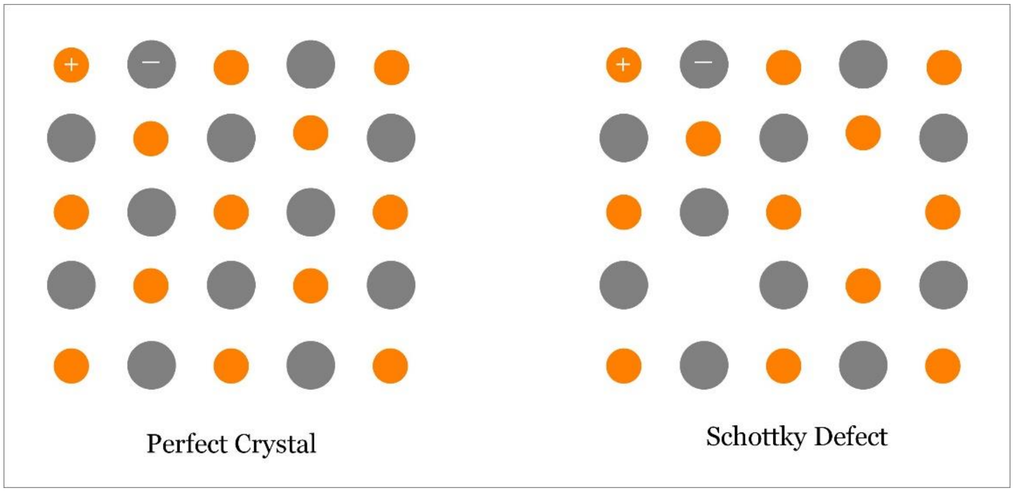
(a) Schottky defect **(b) Frenkel defect**

Schottky Defect – Point Defect in Ionic Crystal

Imperfections or defects in crystalline solid can be broadly classified into four groups, namely, point defect, line defect, surface defect and volume defect. Point defect is considered as the zero-dimensional (0-D) defect, as by mathematical definition, a point is unit-less dimensionless quantity! A point defect occurs when one or more atoms of a crystalline solid leave their original lattice site and/or foreign atoms occupy the interstitial position / lattice site of the crystal. There are several types of point defects and Schottky Defect is one of them.

What is Schottky Defect?

It is one type of Point Defect that occurs in ionic crystals. Schottky defect occurs when oppositely charged atoms (cation and anion) leave their corresponding lattice sites and create a pair of Vacancy Defects. Since both cation and anion leave the lattice sites at the same time, so overall electrical neutrality of the crystal is maintained; however, density reduces because of the vacancies.



Difference between perfect crystal and Schottky defect is shown here. In Schottky defect, one cation and one anion leave their lattice sites to create two vacancies.

Example of materials where Schottky defect can be found:

- Sodium Chloride (NaCl)
- Potassium Chloride (KCl)
- Potassium Bromide (KBr)
- Silver Bromide (AgBr)
- Cerium Dioxide (CeO_2)
- Thorium Dioxide (ThO_2)

Features of Schottky Defect:

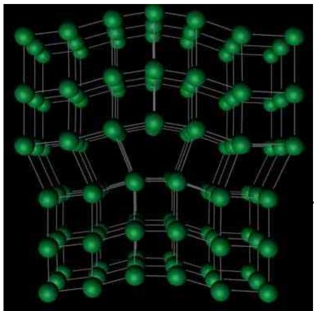
- Schottky defects occur in ionic crystals where the size of anion is almost same with the size of the cation.
- One anion and one cation leave the crystal at the same time to create Schottky defect. None of them occupies the interstitial site again.
- One Schottky defect leads to the formation of two vacancies.
- Electrical neutrality of the whole crystal is maintained.
- Density of the crystal decreases for Schottky defects as vacancies are created.

Difference with Frenkel Defect:

- Although both—Schottky and Frenkel defects occur in ionic materials, Frenkel defect occurs if size of anion is quite large as compared to that of the cation; whereas, Schottky defect occurs if the difference in size between cation and anion is small.
- In Frenkel defect, only the smaller ion (cation) leaves its original lattice site; whereas, the anion remains in corresponding lattice site. However, in Schottky defect, both cation and anion leaves the solid crystal.
- Unlike Frenkel defect where one atom shifts from original lattice site to the interstitial position, in Schottky defect two atoms leave the solid crystal. So one vacancy and one self-interstitial occur in Frenkel defect; whereas, two vacancies occur in Schottky defect.
- The number of atoms present in the crystal before and after Frenkel defect remains same. However, one Schottky defect leads to the reduction of two atoms from the crystal.
- Density of the solid crystal before and after Frenkel defect remains same as no atom leaves the solid. However, Schottky defect reduces density of the solid.

Line Imperfections:

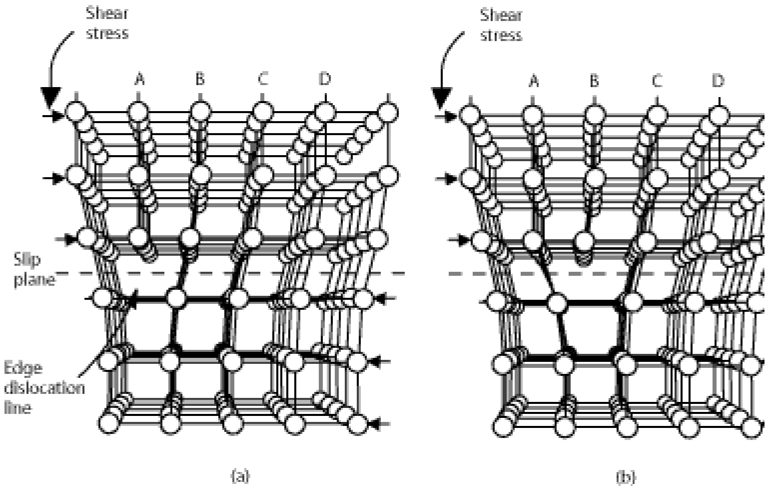
In **linear defects** groups of atoms are in irregular positions. Linear defects are commonly called dislocations. Any deviation from perfectly periodic arrangement of atoms along a line is called the line imperfection. In this case, the distortion is centered only along a line and therefore the imperfection can be considered as the boundary between two regions of a surface which are perfect themselves but are out of register with each other. The line imperfection acting as boundary between the slipped and un-slipped region, lies in the slip plane and is called a dislocation. Dislocations are generated and



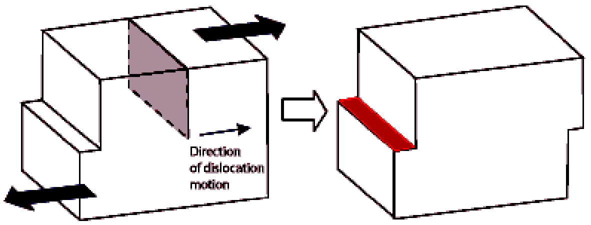
move when a stress is applied. The strength and ductility of metals are controlled by dislocations. To extreme types of dislocations are distinguish as

1. Edge dislocations and
2. Screw dislocations.

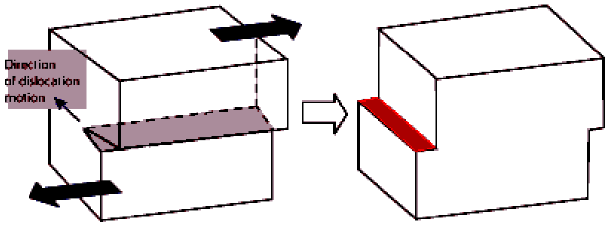
Edge Dislocations: The inter-atomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. As shown in the set of images above, the dislocation moves similarly moves a small amount at a time. The dislocation in the top half of the crystal is slipping one plane at a time as it moves to the right from its position in image (a) to its position in image (b) and finally image (c). In the process of slipping one plane at a time the dislocation propagates across the crystal. The movement of the dislocation across the plane eventually causes the top half of the crystal to move with respect to the bottom half. However, only a small fraction of the bonds are broken at any given time. Movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously.



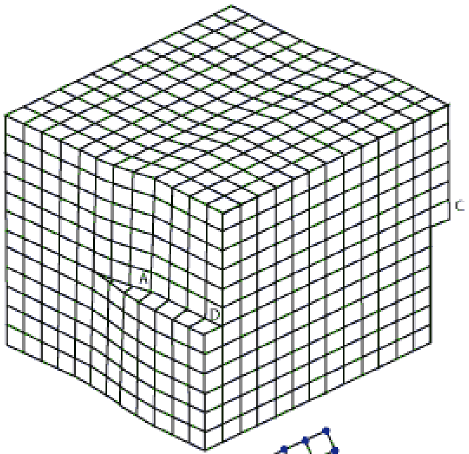
(a) (b)

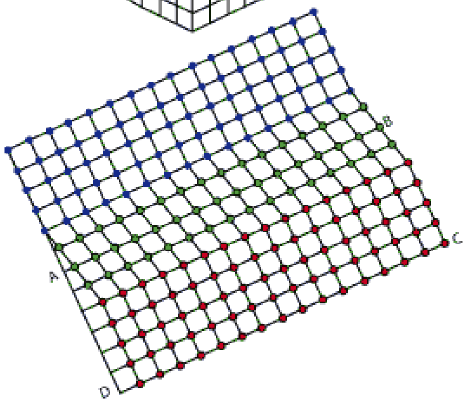


Edge Dislocation



Screw Dislocation





Screw Dislocations: The screw dislocation is slightly more difficult to visualize. The motion of a screw dislocation is also a result of shear stress, but the defect line movement is perpendicular to direction of the stress and the atom displacement, rather than parallel. To visualize a screw dislocation, imagine a block of metal with a shear stress applied across one end so that the metal begins to rip. This is shown in the upper right image. The lower right image shows the plane of atoms just above the rip. The atoms represented by the blue circles have not yet moved from their original position. The atoms represented by the red circles have moved to their new position in the lattice and have reestablished metallic bonds. The atoms represented by the green circles are in the process of moving. Only a portion of the bonds are broken at any given time. As was the case with the edge dislocation, movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously.

If the shear force is increased, the atoms will continue to slip to the right. A row of the green atoms will find their way back into a proper spot in the lattice (and become red) and a row of the blue atoms will slip out of position (and become green). In this way, the screw dislocation will move upward in the image, which is perpendicular to direction of the stress.

Planar defects, which are interfaces between homogeneous regions of the material. Planar defects include grain boundaries, stacking faults and external surfaces.

Stacking Faults and Twin Boundaries

A disruption of the long-range stacking sequence can produce two other common types of crystal defects: 1) a stacking fault and 2) a twin region. A change in the stacking sequence over a few atomic spacings produces a stacking fault whereas a change over many atomic spacings produces a twin region. A stacking fault is a one- or two-layer interruption in the stacking sequence of atom planes. Stacking faults occur in several crystal structures, but it is easiest to see how they occur in close packed structures. For example, it is known from a previous discussion that face centered cubic (*fcc*) structures differ from hexagonal close packed (hcp) structures only in their stacking order. For hcp and *fcc* structures, the first two layers arrange themselves identically, and are said to have an AB arrangement. If the third layer is placed so that its atoms are directly above those of the first (A) layer, the stacking will be ABA. This is the hcp structure, and it continues ABABABAB. However, it is possible for the third layer atoms to arrange themselves so that they are in line with the first layer to produce an ABC arrangement which is that of the *fcc* structure. So, if the hcp structure is going along as ABABAB and suddenly switches to ABABABCABAB, there is a stacking fault present.

Alternately, in the *fcc* arrangement the pattern is ABCABCABC. A stacking fault in an *fcc* structure would appear as one of the C planes missing. In other words, the pattern would become ABCABCAB_ABCABC. If a stacking fault does not correct itself immediately but continues over some number of atomic spacings, it will produce a second stacking fault that is the twin of the first one. For example, if the stacking pattern is ABABABAB but switches to ABCABCABC for a period before switching back to ABABABAB, a pair of twin stacking faults is produced. The red region in the stacking sequence that goes ABCABCACBACBABCABC is the twin plane, and the twin boundaries are the A planes on each end of the highlighted region.

Grain Boundaries in Polycrystals

Another type of planer defect is the grain boundary. Up to this point, the discussion has focused on defects of single crystals. However, solids generally consist of a number of crystallites or grains. Grains can range in size from nanometers to millimeters across and their orientations are usually rotated with respect to neighboring grains. Where one grain stops and another begins is know as a grain boundary. Grain boundaries limit the lengths and motions of dislocations. Therefore, having smaller grains (more grain boundary surface area) strengthens a material. The size of the grains can be controlled by the cooling rate when the material cast or heat treated. Generally, rapid cooling produces smaller grains whereas slow cooling result in larger grains. For more information, refer to the discussion on solidification.

Volume or Bulk Defects

Bulk defects occur on a much bigger scale than the rest of the crystal defects discussed in this section. However, for the sake of completeness and since they do affect the movement of dislocations, a few of the more common bulk defects will be mentioned. **Voids** are regions where there are a large number of atoms missing from the lattice. The image to the right is a void in a piece of metal. The

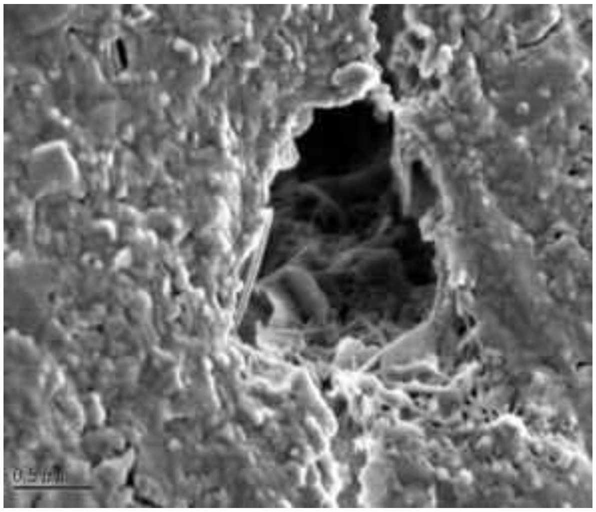
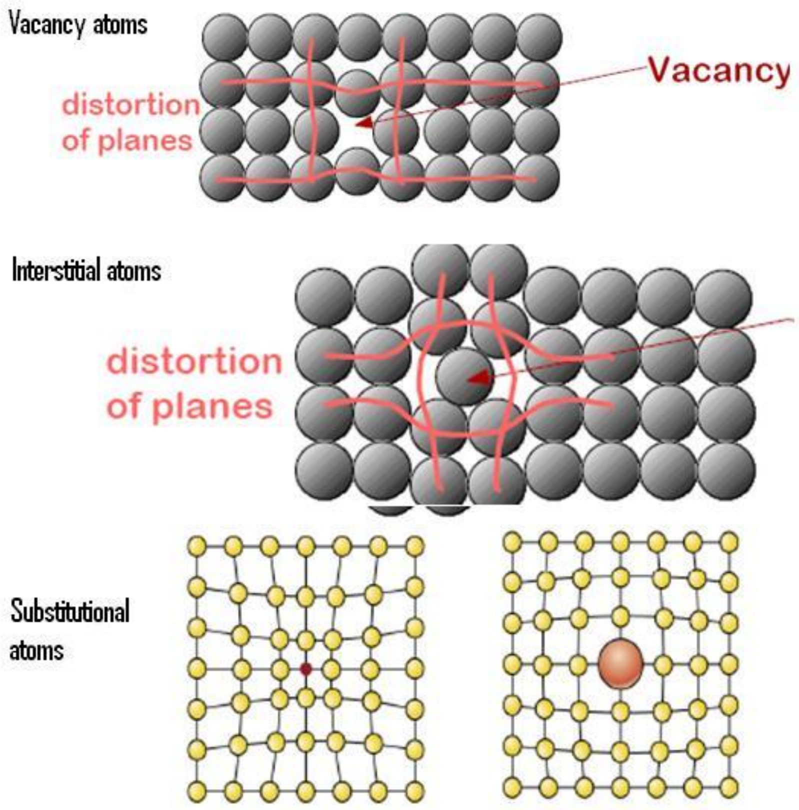


image was acquired using a Scanning Electron Microscope (SEM). Voids can occur for a number of reasons. When voids occur due to air bubbles becoming trapped when a material solidifies, it is commonly called porosity. When a void occurs due to the shrinkage of a material as it solidifies, it is called cavitation.

Another type of bulk defect occurs when impurity atoms cluster together to form small regions of a different phase. The term ‘phase’ refers to that region of space occupied by a physically homogeneous material. These regions are often called precipitates or **inclusions**.

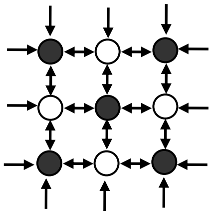
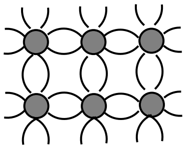
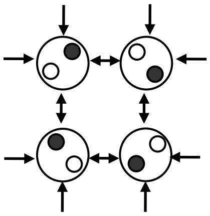
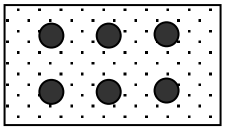
Effect of point defect:



Lecture 10: **Bonds in Solids**

A solid consists of atoms, ions, or molecules packed closely together and forces that hold them in place give rise to the distinctive properties of the various kinds of solids. The covalent bonds that can link a fixed number of atoms to forms a certain molecule can also link an unlimited number of molecules to form a solid. In addition, ionic, Van der Waals, and metallic bonds provide the cohesive forces in solids. Whose structural elements are respectively ion, molecules, and metal atoms.

Types of Crystalline solids on the basis of bonding types:

Types	**Lattice**	**Bond**	**Properties**	**Example**
Ionic		Electron attraction	• Hard • Melting point high • Soluble in polar liquids • Electrical insulators (Conductors in solution)	Alkali Halides, Alkaline oxides (Na_2O), etc.
Covalent		Shared Electrons	• Very hard • High melting points • Insoluble in nearly all liquids • Semiconductors (Except diamond)	Diamond, C, etc.
Molecular		Van der Waals forces	• Soft • Low melting and boiling points • Soluble in covalent liquids • Electrical insulators	Methane (CH_4)
Metallic		Electron gas	• Ductile • Metallic luster • High electrical and thermal conductivity	Sodium (Na)

Thus, on the basis of bonding type, we have following five categories of solids:

1. Ionic solids (NaCl, NaOH, etc.)
2. Covalent solids (Diamond, Silicon)
3. Metallic solids (various metals and alloys)
4. Van der Waals bonded solids/ molecules (O_2, H_2, Solid He, Kr, Xe)
5. Hydrogen bonded solids (Ice, Some fluorides)

- The reason of condensation is due to van der Waals bonding.
- Hydrogen bonding is a special type of van der Waals bonding containing Hydrogen atoms.

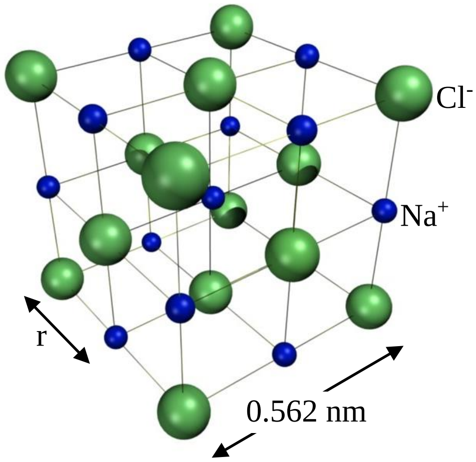
Ionic bonds come into being when atoms that have low ionization energies, and hence loss electron readily, interact with other atoms that tend to acquire excess electrons. The former atoms give up electrons to the later, and they thereupon become positive and negative ions respectively. In ionic crystals these ions assemble themselves in an equilibrium configuration in which the attractive forces between the positive and negative ions balance the repulsive forces between ions.

Electron affinity: It is the energy, released when an electron is added to an atom of a given elements; the greater the electron, the more such atoms tend to become negative ions. Sodium, with ionization energy of 5.14 eV, tends to form Na^+, and Chlorine atom with an electron affinity -3.61, tends to form Cl^- ions.

The **Madelung constant** is used in determining the electrostatic potential of a single ion in a crystal by approximating the ions by point charges. It is named after Erwin Madelung, a German physicist.

The bond energy and Madelung constant for NaCl Crystal

The cohesive energy is the work needed to remove an atom (or molecule) from the crystal and so indicates the strength of the bond holding it in place. Part of the cohesive energy is the electrical potential energy $U_{coloumb}$ of ions. Let us consider a Na^+ ion in NaCl crystal in which Na^+ has six nearest neighbors Cl^- ions, each one are in *r* distance away. The potential energy of the Na^+ ion due to these six Cl^- ions is therefore



$$U_1 = -\frac{6e^2}{4\pi\varepsilon_0 r} \qquad \ldots\ldots(1)$$

The next nearest neighbors are twelve Na^+ ions, each in the distance $\sqrt{2}r$away since the diagonal of a square of side *r* is $\sqrt{2}r$.

The potential energy of the Na^+ ion due to the Na^+ ions each

$$U_2 = +\frac{12e^2}{4\pi\varepsilon_0\sqrt{2}r} \quad \text{………………………………………………………..(2)}$$

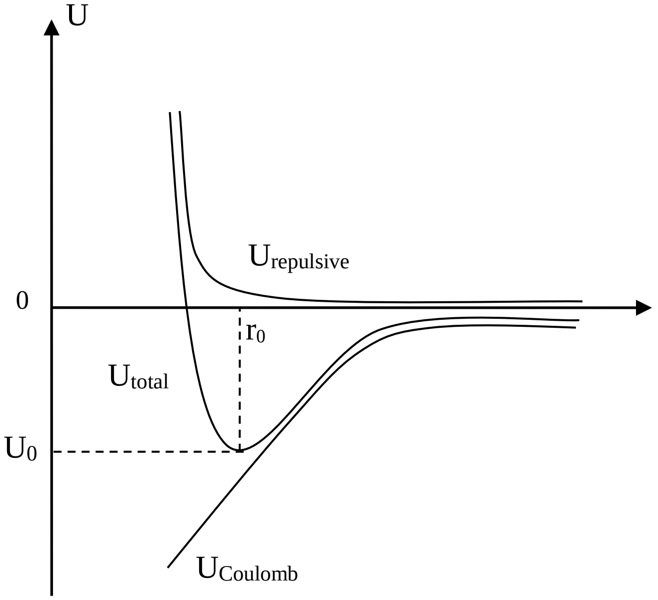
When the summation is continued over all the positive and negative ions in a crystal of infinite size, the result is

$$U_{Coulomb} = -\frac{e^2}{4\pi\varepsilon_0 r}\left(6 - \frac{12}{\sqrt{2}} + \cdots\cdots\right) = -1.748\frac{e^2}{4\pi\varepsilon_0 r}$$

In general,

$$U_{Coulomb} = -\alpha\frac{e^2}{4\pi\varepsilon_0 r} \quad \text{……………………………………………………..(3)}$$

This result holds the potential energy of a Cl^- ion as well, of course.



Here the quantity α is called the Madelung constant of the crystal, and it has the same value of the same structure. Now the potential energy contribution of the exclusion principle has approximate form

$$U_{repulsive} = \frac{B}{r^n} \quad \text{……………………………..(4)}$$

The sign of $U_{repulsive}$ is +ve, which corresponds to repulsion. The dependence on r^{-n} implies a short-range force that increases as the inter-atomic distance *r* decreases. The total potential energy of each ion due to its interactions with all the other ions is therefore,

$$U_{total} = U_{repulsive} + U_{Coulomb} = -\alpha\frac{e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n} \quad \text{…………………..……….(5)}$$

At equilibrium separation, $r = r_0$, of the ions, *U* is a minimum by definition, and so $\frac{dU}{dr} = 0$, when $r = r_0$.

Hence,

$$\left(\frac{dU}{dr}\right)_{r=r_0} = \frac{\alpha e^2}{4\pi\varepsilon_0 {r_0}^2} - \frac{nB}{r_0^{n+1}} = 0$$

$$B = \frac{\alpha e^2}{4\pi\varepsilon_0 n} {r_0}^{n-1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

The total potential energy at the equilibrium separation is therefore, (from Equations 5 and 6)

$$U_0 = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

We must add this amount of **energy per ion pair** to separate an ionic crystal into individual ions. The exponent *n* can be found from the observed compressibility of ionic crystals. The average result is $n \approx 9$. which means that the repulsive force varies sharply with *r*. Figure shows the variation of potential energy in an ionic crystal with ionic separation. The minimum value of U_{total} is U_0 occurs at an equilibrium separation of r_0. Thus

Cohesive energy = Atom separation energy = Ion separation energy + Electron transfer energy.

Problem: In an NaCl crystal, the equilibrium distance r_0 between ions is 0.281 nm. Find the cohesive energy in NaCl. Provided that ionization energy for Na is +5.14 eV and electron affinity of Cl is –3.61 eV.

Solution: Since α = 1.748 and $n \approx 9$, the potential energy per ion pair is

$$U_0 = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

$$= -\frac{(9\times10^{9} N.m^2C^{-2})(1.748)(1.6\times10^{-19}C)^2}{2.81\times10^{-10}m}\left(1 - \frac{1}{9}\right)$$

$$= 1.27 \times 10^{-18}\, J = -7.96\, eV$$

$\therefore$ The contribution to the cohesive energy per ion of the crystal = $\frac{1}{2} \times (-7.96\, eV) = -3.98\, eV$

Now, electron transfer energy = Ionization energy of Na + Electron affinity of Cl

= (+5.14 eV) + (–3.61 eV)

= 1.53 eV

Each atom therefore contributes ½(1.53) or 0.77 eV to the cohesive energy from this source. The total cohesive energy per atom is thus

E_{cohesive}= (–3.98 + 0.77) eV = –3.21 eV.

Which is not far from the experimental value of -3.28 eV.

Lecture 11: Introduction to Band Theory-Metals, Semiconductors and Insulators

There are many energy levels ($\sim 10^{23}$) in a given band. A given atom in a solid has a fixed number of nearest neighbors, but many distant neighbors as shown in Fig. 1.

If we consider just a single plane and an arbitrary atom, there may be four nearest neighbors as in Fig. 1(a). Isolated from others, this system should give rise to four split energy levels. With the widest energy separations; the interaction occurs between neighbors.

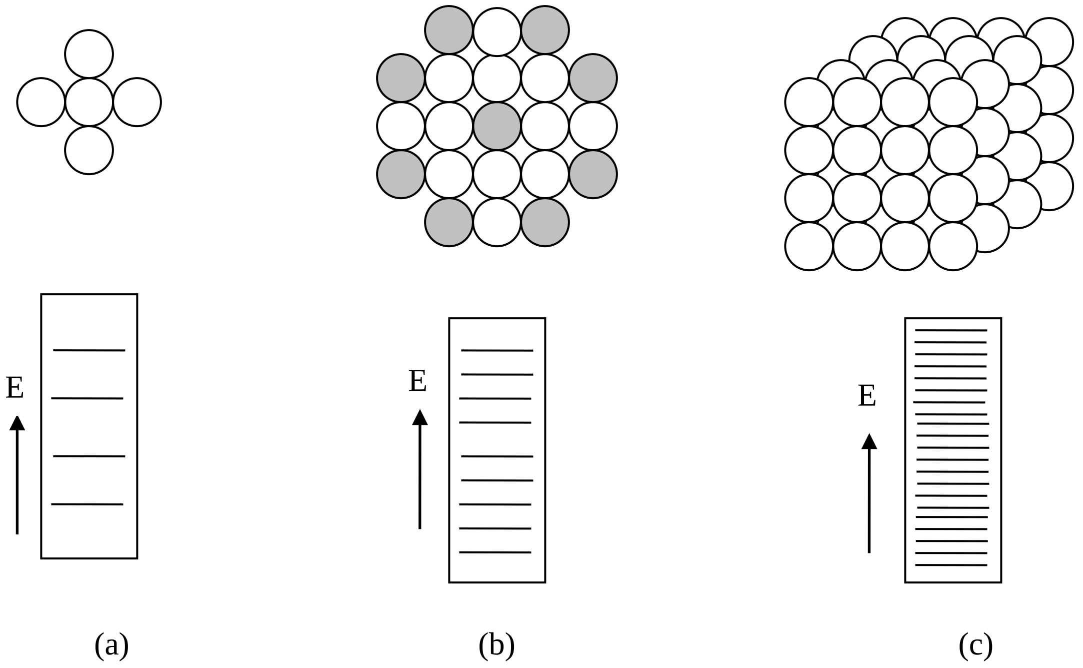
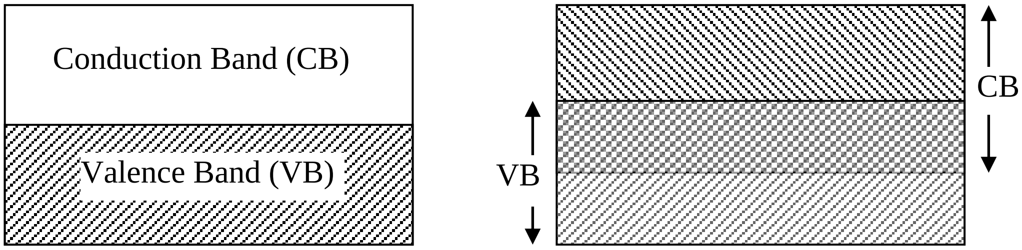


Figure 1: Splitting of valence band

As we move away from an atom, there are more and more neighbors. For example, an atom may have eight 4th neighbors in one plane as shown in Fig. 1(b). In isolation from the rest, the energy would have split into nine narrowly separated levels, since the atoms are further isolated. In a crystal, there are hundreds and thousands of distant neighbors, so the number of narrowly-split energy level will correspondingly be very large. The outermost energy band that is completely or partially filled is called the valence band in solids. The band that is above the valence band and is empty at 0 K, is called the conduction band.

According to the nature of band occupation by electrons, all solids can be classified broadly into two groups.

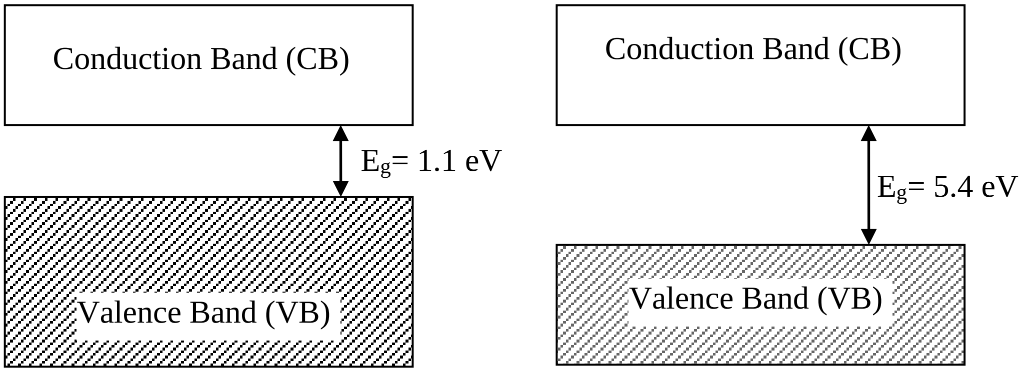
Firstly, the group in which there is partially filled band immediately above the uppermost filled valence band. This is possible in two ways. One - the balance band is only partially filled. Second- A completely filled valence band overlaps the partially filled conduction band as shown in Fig. 2.



(a) (b)

Fig. 2: Metals have partially filled or overlapping bands.

Secondly, the groups which include empty bands lying above completely filled band levels. The solids of this group conveniently subdivided into insulators (dielectrics) and semiconductors depending on the width of the forbidden band.



(a) (b)

Fig. 3: The difference between a semiconductor and an insulator in terms of energy gap.

Insulators include solids with relatively wide forbidden bands. For typical insulators the band gap, $E_g > 3$ eV. (Diamond: 5.4 eV, BN: 4.6 eV, Al_2O_3: 7 eV).

On the other hand, semiconductors include solids with relatively narrow forbidden bands. For typical semiconductors, $E_g \leq 1$ eV. (Ge: 0.7 eV, Si: 1.12 eV, InSb: 0.17 eV, GaAs: 1.43 eV)

According to Pauli's exclusion principle, each energy level must be occupied by no more than two electrons. Thus, Monovalent metals such as Cu, Ag, and Au have one electron in the outermost shell and hence the corresponding energy band is only half filled. On the other hand, the divalent metals such as Be, Mg, Ca, etc. have overlapping valence and conduction bands. The trivalent metals Al, Ga, etc. have similar band structure as monovalent metals.

The tetravalent nonmetals such as C, Si, etc. have even number of electrons in the outermost (4 electrons in each case) shell like divalent atoms. The corresponding valence band is full but unlike the divalent metals there is no overlapping of the VB with the CB in this case.

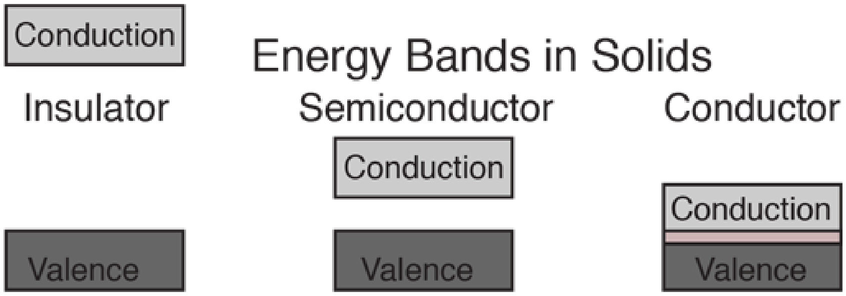
Band Theory of Solids

(*from* Hyperphyics_Department of Physics and Astronomy Georgia State University: http://hyperphysics.phy-astr.gsu.edu/hbase/Solids/band.html)

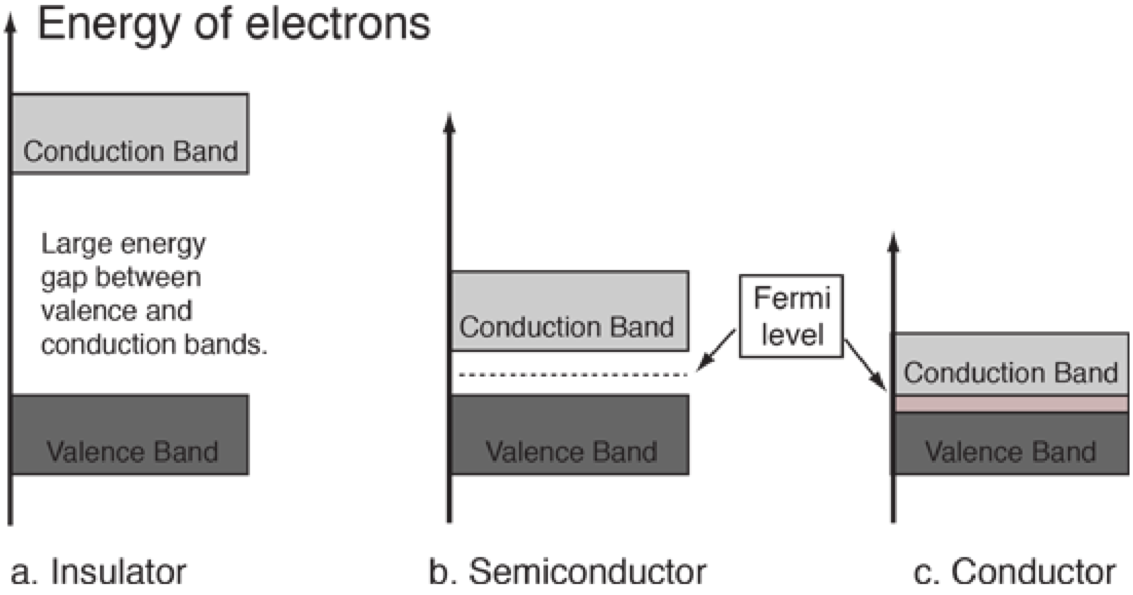
Energy Bands for Solids

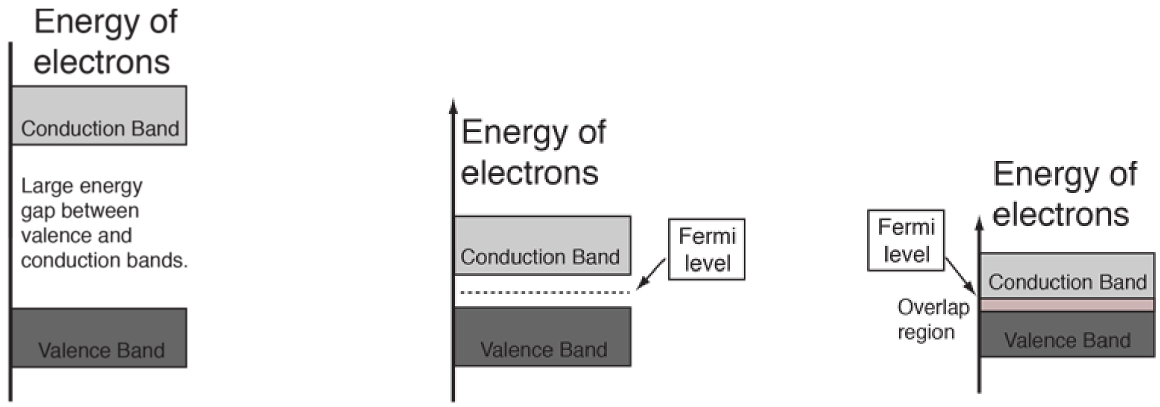
A useful way to visualize the difference between conductors, insulators and semiconductors is to plot the available energies for electrons in the materials. Instead of having discrete energies as in the case of free atoms, the available energy states form bands. Crucial to the conduction process is whether or not there are electrons in the conduction band. In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically.

An important parameter in the band theory is the Fermi level, the top of the available electron energy levels at low temperatures. The position of the Fermi level with the relation to the conduction band is a crucial factor in determining electrical properties.



Closer look at bands





a. Insulator b. Semiconductor c. Conductor

Insulator Energy Bands

Most solid substances are insulators, and in terms of the band theory of solids this implies that there is a large forbidden gap between the energies of the valence electrons and the energy at which the electrons can move freely through the material (the conduction band).

Glass is an insulating material which may be transparent to visible light for reasons closely correlated with its nature as an electrical insulator. The visible light photons do not have enough quantum energy to bridge the band gap and get the electrons up to an available energy level in the conduction band. The visible properties of glass can also give some insight into the effects of "doping" on the properties of solids. A very small percentage of impurity atoms in the glass can give it color by providing specific available energy levels which absorb certain colors of visible light. The ruby mineral (corundum) is aluminum oxide with a small amount (about 0.05%) of chromium which gives it its characteristic pink or red color by absorbing green and blue light.

While the doping of insulators can dramatically change their optical properties, it is not enough to overcome the large band gap to make them good conductors of electricity. However, the doping of semiconductors has a much more dramatic effect on their electrical conductivity and is the basis for solid state electronics.

Semiconductor Energy Bands

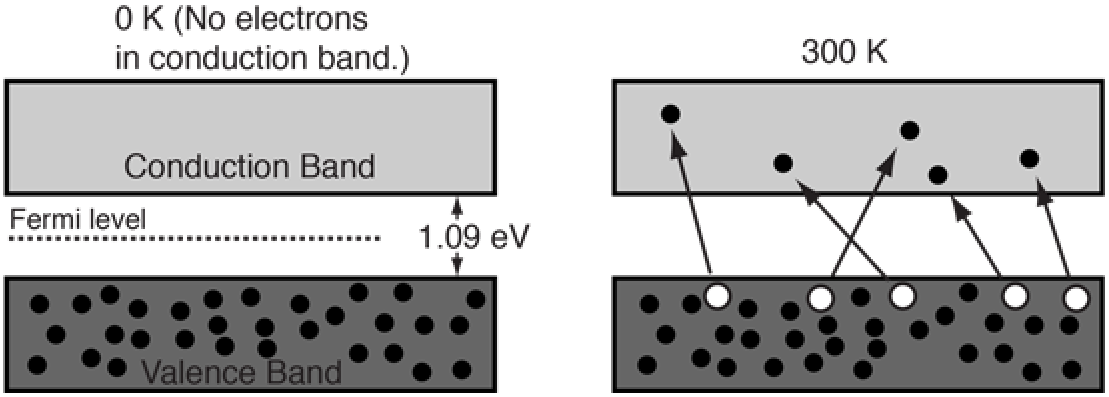
For intrinsic semiconductors like silicon and germanium, the Fermi level is essentially halfway between the valence and conduction bands. Although no conduction occurs at 0 K, at higher temperatures a finite number of electrons can reach the conduction band and provide some current. In doped semiconductors, extra energy levels are added.

The increase in conductivity with temperature can be modeled in terms of the Fermi function, which allows one to calculate the population of the conduction band.

Conductor Energy Bands

In terms of the band theory of solids, metals are unique as good conductors of electricity. This can be seen to be a result of their valence electrons being essentially free. In the band theory, this is depicted as an overlap of the valence band and the conduction band so that at least a fraction of the valence electrons can move through the material.

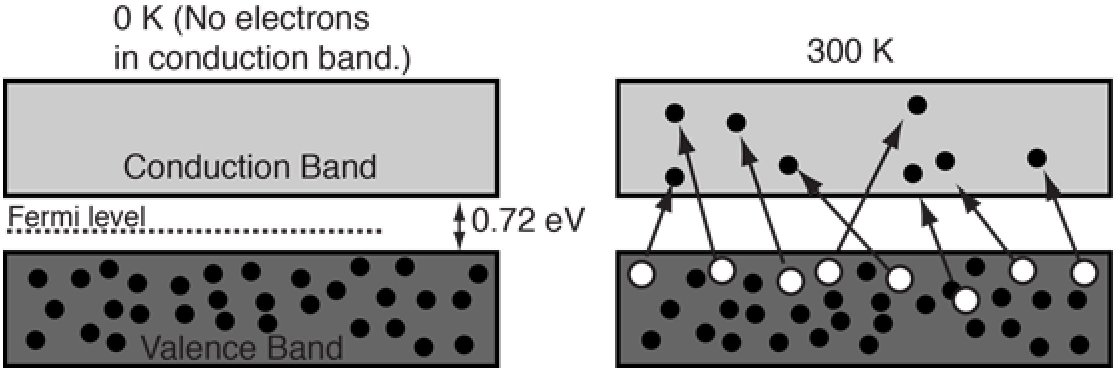
Silicon Energy Bands



At finite temperatures, the number of electrons which reach the conduction band and contribute to current can be modeled by the Fermi function. That current is small compared to that in doped semiconductors under the same conditions.

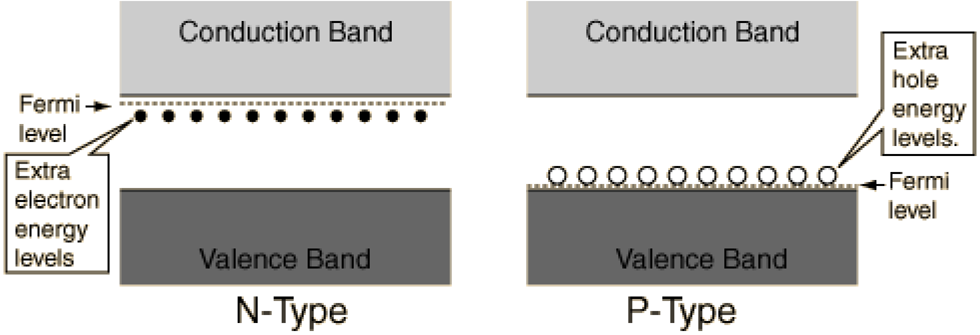
Germanium Energy Bands

At finite temperatures, the number of electrons which reach the conduction band and contribute to current can be modeled by the Fermi function. That current is small compared to that in doped semiconductors under the same conditions.



Bands for Doped Semiconductors

The application of band theory to n-type and p-type semiconductors shows that extra levels have been added by the impurities. In n-type material there are electron energy levels near the top of the band gap so that they can be easily excited into the conduction band. In p-type material, extra holes in the band gap allow excitation of valence band electrons, leaving mobile holes in the valence band.



N-Type Band Structure

The addition of donor impurities contributes electron energy levels high in the semiconductor band gap so that electrons can be easily excited into the conduction band. This shifts the effective Fermi level to a point about halfway between the donor levels and the conduction band.

Electrons can be elevated to the conduction band with the energy provided by an applied voltage and move through the material. The electrons are said to be the "majority carriers" for current flow in an n-type semiconductor.

P-Type Band Structure

The addition of acceptor impurities contributes hole levels low in the semiconductor band gap so that electrons can be easily excited from the valence band into these levels, leaving mobile holes in the valence band. This shifts the effective Fermi level to a point about halfway between the acceptor levels and the valence band.

Electrons can be elevated from the valence band to the holes in the band gap with the energy provided by an applied voltage. Since electrons can be exchanged between the holes, the holes are said to be mobile. The holes are said to be the "majority carriers" for current flow in a p-type semiconductor.