



Lec.3 Atomics Bonding, Crystal lattice and Arrangement of Atoms

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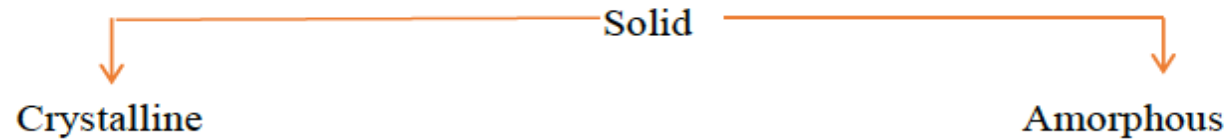
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Atomics Bonding

Crystal structure is one of the most important aspects of materials science and engineering as many properties of materials depend on their crystal structures.



Crystalline – periodic arrangement of atoms: definite repetitive pattern

Non-crystalline or Amorphous – random arrangement of atoms.

The periodicity of atoms in crystalline solids can be described by a network of points in space called lattice.

At a high level of classification, materials can be divided into two classes: natural and synthetic. At a more fundamental level, materials can be separated into different general categories based on their molecular structure and the type of bonding between their atoms. Since the latter plays a primary role in determining the properties of a biomaterial, it is important to first gain an understanding of the different types of bonds.

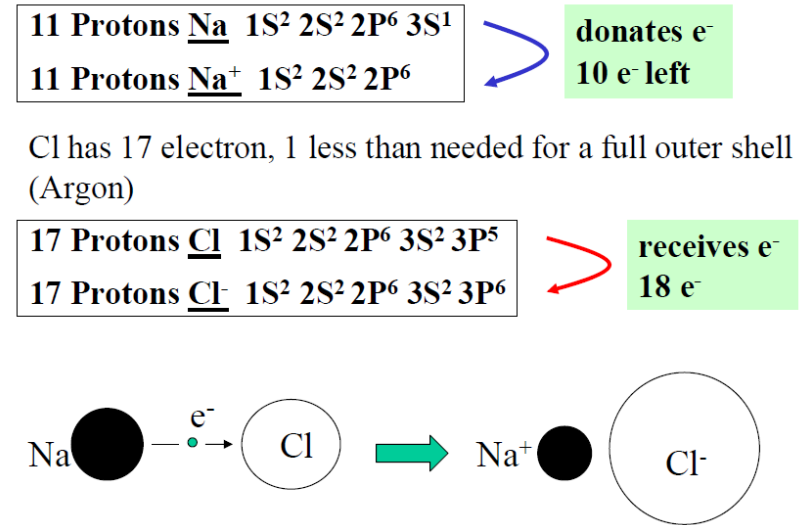
Types of atomic bonds

primary (or chemical) bonds and secondary (van der Waals or physical) bonds.

- A- Primary bonds are: **Ionic, covalent, and metallic.**

Ionic Bonding

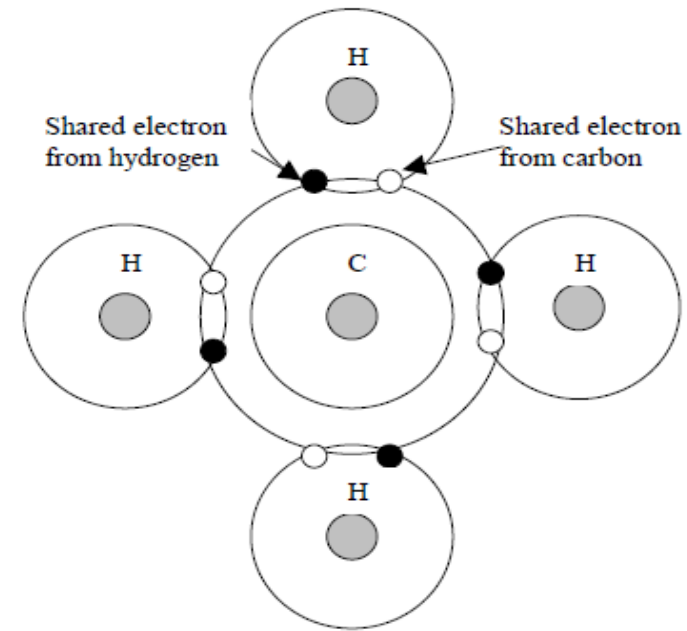
- In Ionic Bonding, one atom **gives out one valence electron** and **another accepts that electron.**
- The ones that loose electrons become **Cations** and the ones that gain them **become Anions.**
- The elements that have tendency to become Cations are called “**electropositive**” and those who have tendency to become Anions are called “**electronegative**”.
- The best example of such bonding in materials is NaCl (Sodium Chloride or rock salt). See sketch for NaCl.
- Factors that determine ionic bond strength: **electronegativity difference, charge of ions, ionic radius**
- Examples of ionic compounds (sodium chloride, magnesium oxide)
- Properties of ionic compounds (**high melting/boiling points, brittleness, poor conductivity**)



sketch for NaCl

Types of atomic bonds

- **Covalent Bonding**
- In Covalent Bonding none of the atoms involved loose or gain atoms per say but rather they get close to one another such that they **can share the valence electrons**.
- See the CH₄ example below whereby one Carbon atom shares its 4 valence electrons with 4 Hydrogen atoms located symmetrically around it.
- The sharing is done **to achieve a stable electronic structure by filling the outermost atomic shell**.
- Similarly, **diamond is simply made of carbon atoms** each sharing 4 electrons with 4 neighboring atoms.
- Factors that determine covalent bond strength: **electronegativity, bond length, bond angle**
- Examples of covalent compounds (water, methane, carbon dioxide)
- Properties of covalent compounds (**lower melting/boiling points, poor conductivity**)



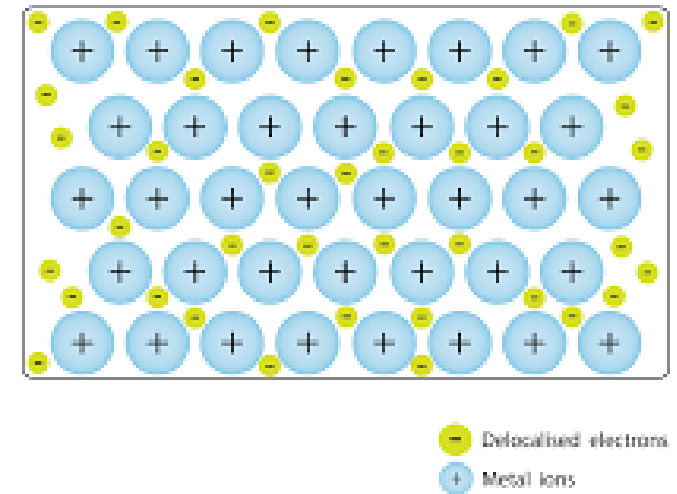
sketch for CH₄

Types of atomic bonds

- **Metallic Bonding**

- In many metals (e.g. Al, Cu, Ag, Pd, etc.), the atoms share their valence electrons but not only or necessarily with neighboring atoms but rather with *all the atoms in the matter*.
- This is facilitated by *the electrons forming a sea or cloud that* engulfs the rest of the atom (i.e. the positively charged nucleus with its remaining non-valence electrons).
- Factors that determine metallic bond strength: *number of valence electrons, atomic radius*
- Examples of metallic substances (copper, aluminum, iron)
- Properties of metals (*high conductivity, ductility, malleability*)

Metallic bonding



Secondary bonds

- Secondary = van der Waals = physical (as opposite to chemical bonding that involves e- transfer)
bonding results from interaction of atomic or molecular dipoles and is weak,



Permanent dipole moments exist in some molecules (called **polar molecules**) due to the asymmetrical arrangement of positively and negatively regions (HCl, H₂O).

Bonds between adjacent polar molecules – **permanent dipole bonds** – are the strongest among secondary bonds .

Polar molecules can induce dipoles in adjacent non-polar molecules and bond is formed due to the attraction between the permanent and induced dipoles.

Even in electrically symmetric molecules/atoms an electric dipole can be created by fluctuations of electron density distribution.

Polar molecules are molecules that have a difference in electronegativity between their atoms.

The greater the difference in electronegativity between the atoms that make up a molecule, the more likely the molecule is to be polar.

Secondary bonds

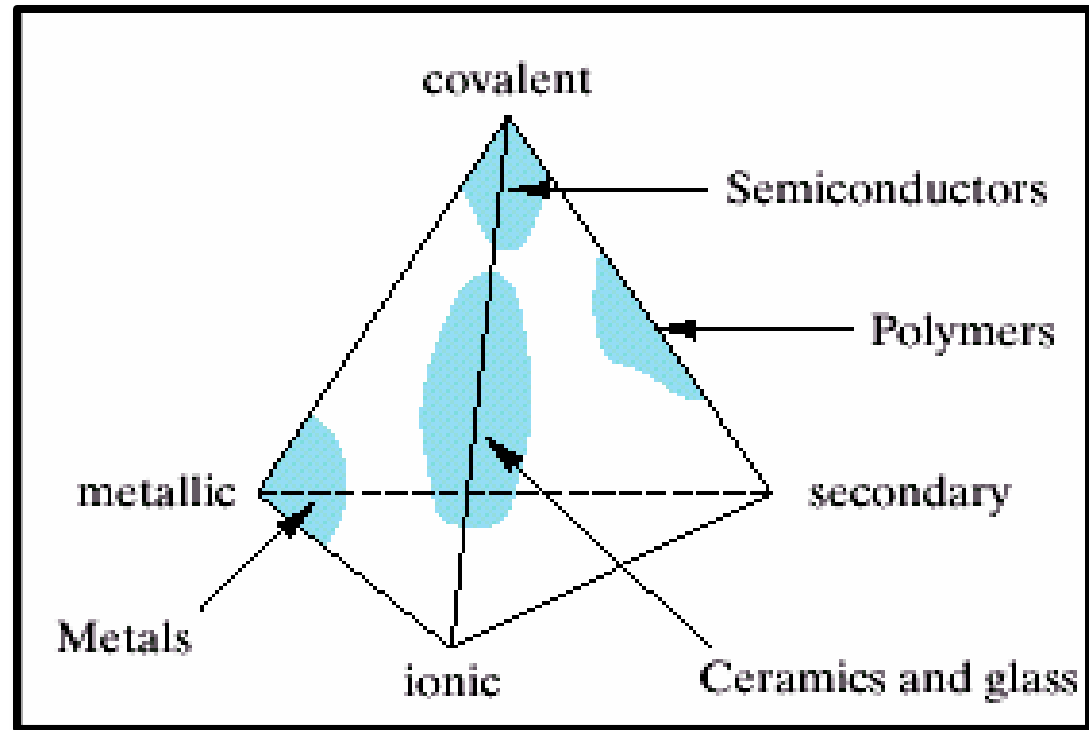
- **Van der Waal's Forces**
- Secondary bonds are bonds of a different kind to the primary ones. They are weaker in nature and are broadly classified as **Van der Waal's forces and hydrogen bonds**. These bonds are due to **atomic or molecular dipoles, temporary**.
- Van der Waal's bond is formed due to **temporary dipoles**.
- A temporary dipole is formed in a **symmetric molecule** but which **has fluctuations of charges giving rise to partial dipole moments for only a few moments**.
- This can also be seen in atoms of **inert gases**.
- For instance, **a molecule of methane has one carbon atom and four hydrogen atoms joined together by single covalent bonds between the carbon and the hydrogen atoms**.
- Methane is a **symmetric molecule** but when it is **solidified**, the bonds between the molecules **are of weak Van der Waal's forces** and thus such a solid cannot exist for a long time without tremendously cared for laboratory conditions.

Secondary bonds

- **Hydrogen Bonds**
- Hydrogen bonds are relatively stronger than Van der Waal's forces but compared to primary bonds they are weak.
- Bonds between hydrogen atom and atoms of the most electronegative elements (N, O, F) are called hydrogen bonds.
- It is based on the fact that hydrogen being the smallest atom provides very little repulsion when interacting with highly electronegative atoms in other molecules and thus succeeds in forming partial bonds with them.
- This makes hydrogen bonds strong but weaker compared to primary bonds since the interactions here are permanent dipole interactions.

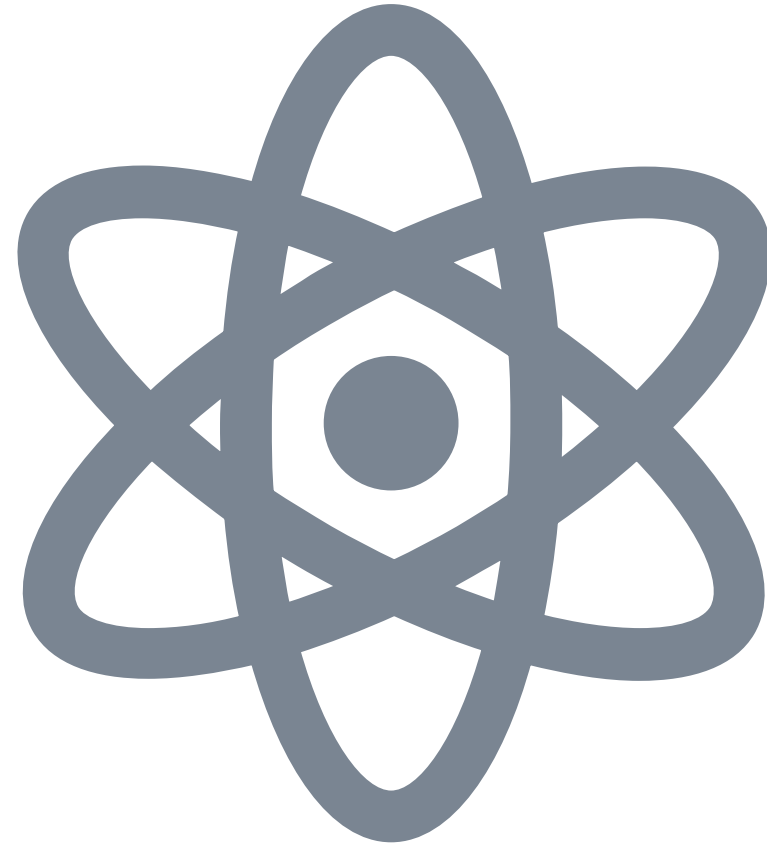
Bonding in real materials

- In many materials more than one type of bonding is involved (ionic and covalent in ceramics, covalent and secondary in polymers, covalent and metallic in semiconductors)
- **Examples of bonding in Materials:**
 - Metals: Metallic
 - Ceramics: Ionic / Covalent
 - Polymers: Covalent and Secondary

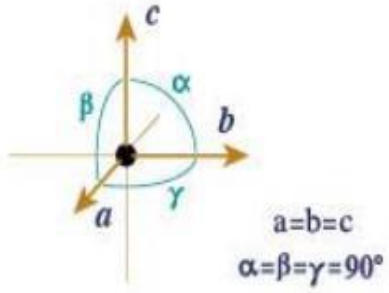


Crystal System

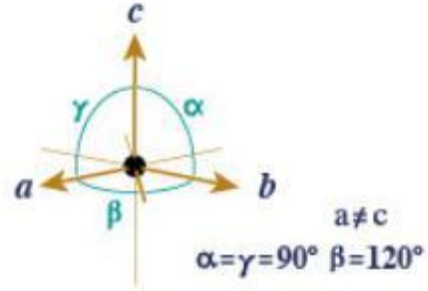
- The crystal system is a **grouping of crystal structures** that are categorized according **to the axial system** used to describe their "lattice".
- **A crystal's lattice** is a **three dimensional network** of atoms that are arranged in a symmetrical pattern.
- Each crystal system consists of a set of three axes in a particular geometrical arrangement.
- The seven unique crystal systems, listed in order of decreasing symmetry, are: 1. Isometric System, 2. Hexagonal System, 3. Tetragonal System, 4. Rhombohedral (Trigonal) System, 5. Orthorhombic System, 6. Monoclinic System, 7. Triclinic System.



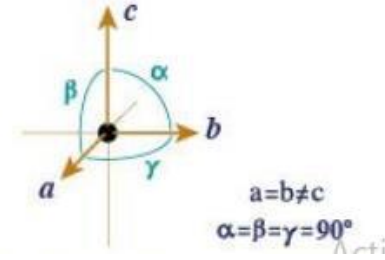
Crystal System



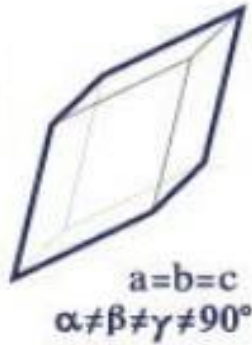
1. Cubic



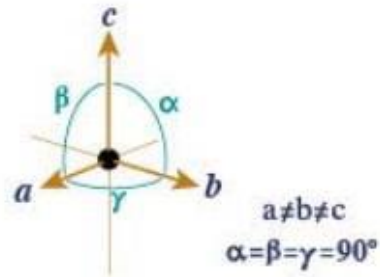
2-Hexagonal



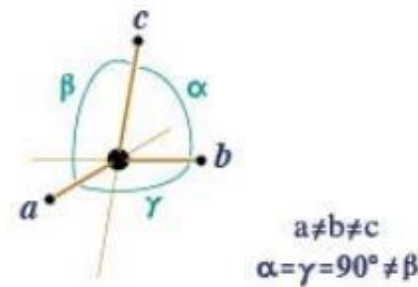
3. Tetragonal



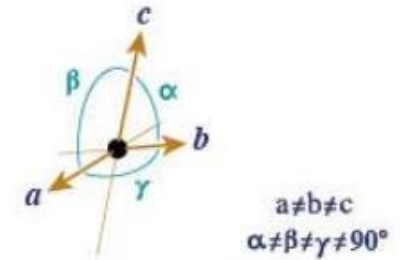
4. Rhombohedral



5. Orthorhombic



6. Monoclinic



7. Triclinic

Unit Cell:

- The unit cell is a structural unit or building block that can describe the Crystal structure.
- Repetition of the unit cell generates the entire crystal.

The most common types of unit cells are:

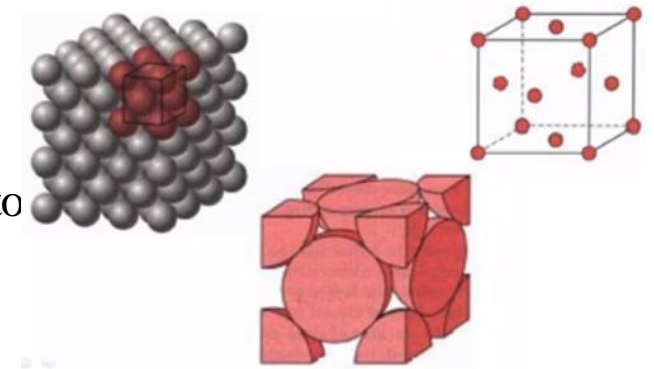
- Face-centered cubic (FCC)
- Body-centered cubic (BCC)
- Hexagonal close-packed (HCP).

For each crystal structure mentioned above we will determine:

1. Position of atoms
2. Examples
3. The relation between the length (a) of cell and the radius of the atom R .
4. The coordination number CN.
5. Number of atoms / unit cell.
6. Atomic packing factor APF.

1- Face Centered Cubic Structure (FCC) (Cubic System)

- - Atoms are located at the corners and on the centers of all the faces of cubic unit cell.
- - Cu, Al, Ag, Au have this crystal structure.
- The relation between the length (a) and the radius of the atom R ($a = 2\sqrt{2}R$)
- - The coordination number CN = The number of closest neighbors to which an atom is bonded. CN (FCC)= 12
- - Number of atoms per unit cell = $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$ atom/ unit cell.



Atomic packing factor (APF) = or packing efficiency indicates how closely atoms are packed in a unit cell and is given by the ratio of volume of atoms in the unit cell and volume of the unit cell

$$APF = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}}$$

$$= 0.74 \text{ (maximum possible)}$$

Atomic packing factor

$$\text{APF} = (\text{Sum of atomic volumes})/(\text{Volume of unit cell})$$

$$\text{Volume of 4 hard spheres in the unit cell: } 4 \times \frac{4}{3} \pi R^3$$

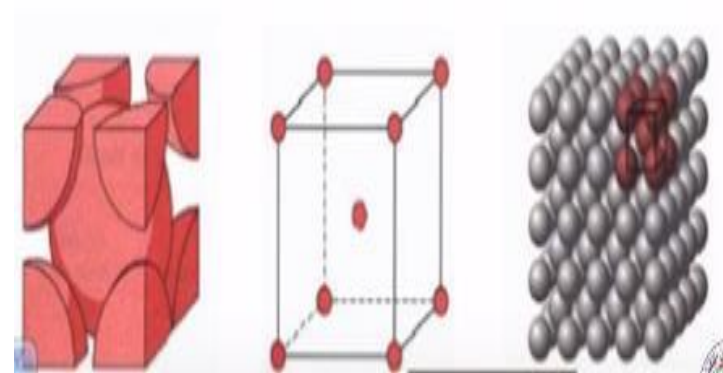
$$\text{Volume of the unit cell: } a^3 = 16R^3 \sqrt{2}$$

$$APF = \frac{16}{3} \pi R^3 / 16R^3 \sqrt{2} = \pi / 3\sqrt{2} = 0.74$$

maximum possible packing of hard spheres

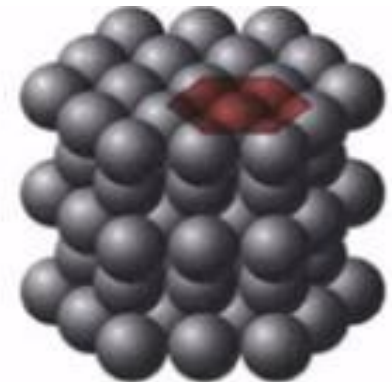
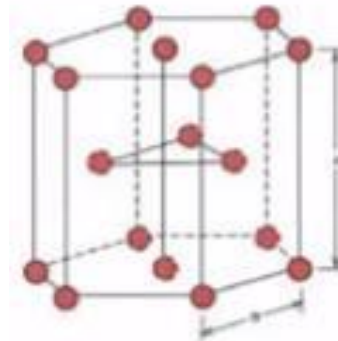
2- Body Centered Cubic Structure (BCC) (Cubic System)

- Atom at each corner and at center of cubic cell.
- Cr, Na, Fe have this crystal structure.
- Number of atoms per unit cell $n = 8 \times \frac{1}{8} + 1 = 2$ atom/ unit cell.
- - Relation between a and R is $a = \frac{4R}{\sqrt{3}}$
- - The coordination number $CN = 8$
- - Atomic packing factor $APF = 0.68$



2- Hexagonal close packed (HCP)

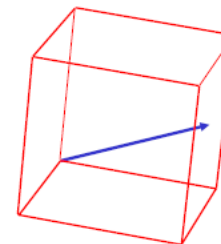
- HCP is one more common structure of metallic crystals
- Six atoms form regular hexagon, surrounding one atom in center. Another plane is situated halfway up unit cell (c-axis), with 3 additional atoms situated at interstices of hexagonal (close-packed) planes
- Zn, Cd, Mg, etc. Hexagonal closest packed structures in all crystal systems.
- Number of atoms per unit cell $n = 1/2 + 3 = 6$ atom/ unit cell.
- - The coordination number $CN = 12$



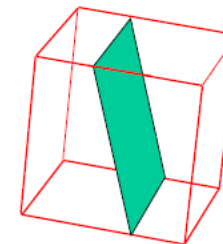
Crystallographic Directions, and Planes

we need a way to identify directions and planes of atoms. Why?

- Deformation under loading (*slip*) occurs on certain crystalline planes and in certain crystallographic directions.
- Before we can predict how materials fail, we need to know what modes of failure are more likely to occur.
- It is often necessary to be able to specify certain directions and planes in crystals.
- Many material properties and processes vary with direction in the crystal.
- Directions and planes are described using three integers -**Miller Indices**



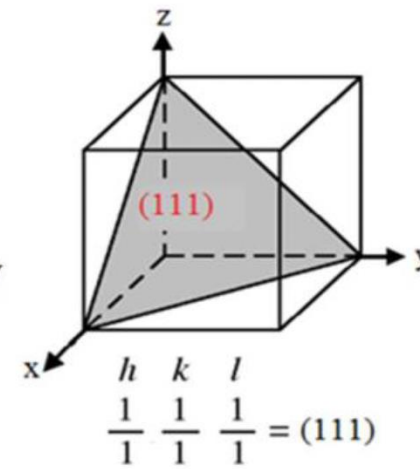
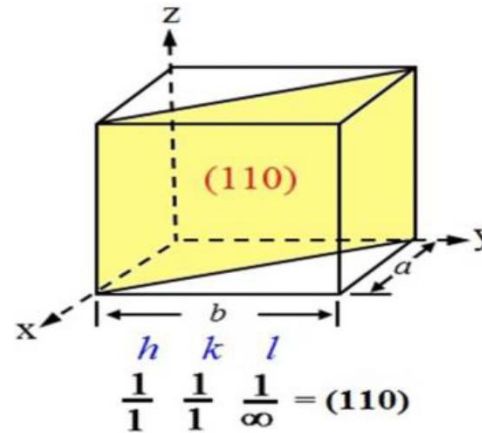
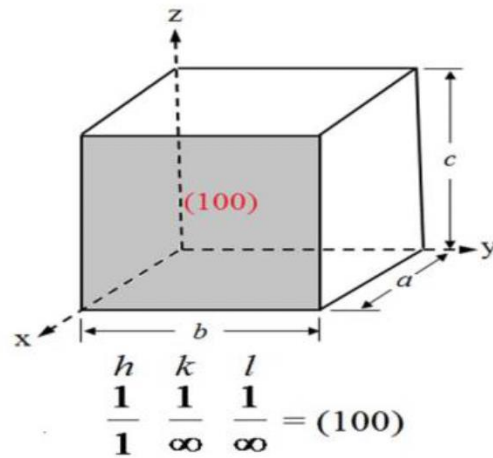
direction



plane

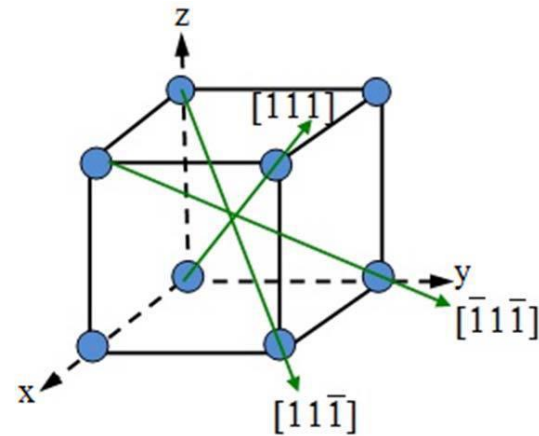
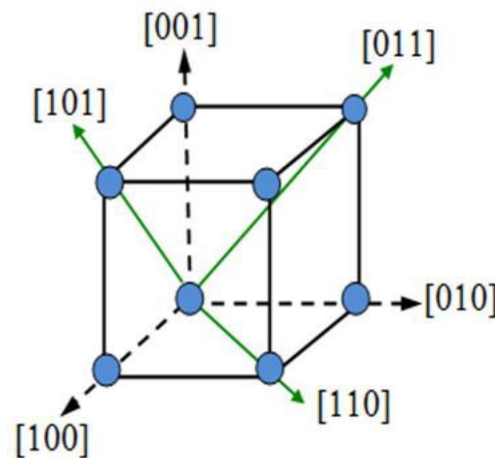
Crystal Planes

- **Miller Indices**
- Planes in a crystal are described by notations called Miller indices
- Miller indices of a plane, indicated by $h\ k\ l$, are given by the reciprocal of the intercepts of the plane on the three axes.
- Miller indices of some other planes in the cubic system are shown in the figures



Crystal Planes

- **Crystal Directions**
- The directions in a crystal are given by specifying the coordinates (u, v, w) of a point on a vector (ruvw) passing through the origin. $ruvw = ua + vb + wc$. It is indicated as [uvw].
- For example, the direction [110] lies on a vector r110 whose projection lengths on x and y axes are one unit (in terms of unit vectors a and b).
- Directions of a form or family like [110], [101], [011] are written as $\langle 110 \rangle$.



H.W// find the miller indices with direction for following

- 1- $[101]$
- 2- $[002]$
- 3- $[301]$
- 4- $[011]$
- 5- $[222]$
- 6- $[210]$

Linear and Planar density

- **Linear Density:**
 - Number of atoms per length whose centers lie on the direction vector for a specific crystallographic direction

ex. calculate linear atomic density ρ_l in $[110]$ direction in Cu crystal lattice in atoms/mm. (Cu is FCC and lattice constant $a = 0.361$ nm)

solution:

$$\text{no. of atoms} = \frac{1}{2} + 1 + \frac{1}{2} = 2 \text{ atoms}$$

$$\text{length} = \sqrt{2} a = \sqrt{2} (3.61 \times 10^{-7})$$

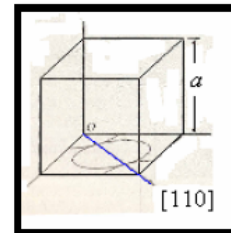
$$= 5.104 \times 10^{-7} \text{ mm}$$

$$LD = \frac{\text{\# of atoms centered on a direction vector}}{\text{length of direction vector}}$$

$$2 \text{ atoms}$$

$$\rho_l = \frac{\text{2 atoms}}{5.104 \times 10^{-7} \text{ mm}} = 3.92 \times 10^6 \text{ atoms/mm}$$

$$5.104 \times 10^{-7} \text{ mm}$$



Linear and Planar density

- **Planar Density**
 - Number of atoms per unit area that are centered on a particular crystallographic plane.

ex. calculate planar atomic density ρ_p on (110) plane of the α -Fe in BCC lattice in atoms/mm². (lattice constant $a = 0.287$ nm)

solution:

1 atom (center) + $\frac{1}{4}$ atom (corner) $\times 4 = 2$ atoms

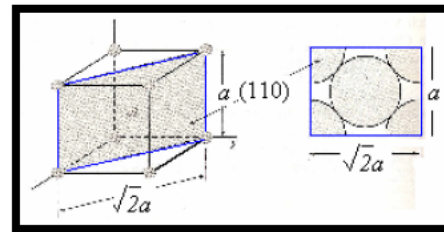
area = $a \times \sqrt{2} a = \sqrt{2} a^2 = \sqrt{2} (2.87 \times 10^{-7})^2$

= 1.164×10^{-13} mm²

2 atoms

$$\rho_p = \frac{2 \text{ atoms}}{1.164 \times 10^{-13} \text{ mm}^2} = 1.72 \times 10^{13} \text{ atoms/mm}^2$$

$$PD = \frac{\text{\# of atoms centered on a plane}}{\text{area of plane}}$$



Crystalline Defects

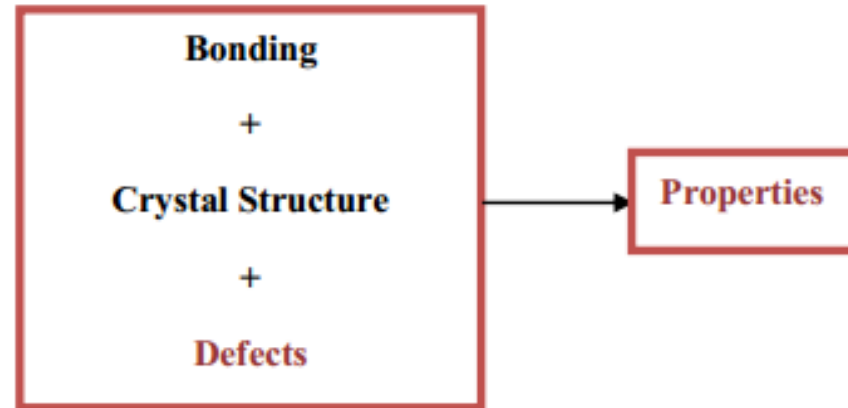
The properties of some materials are profoundly influenced by the presence of defects. •

:For example •

The mechanical properties of pure metals experience significant alterations when alloyed. (i.e, when impurity atoms are added)- for example, brass (70% copper – 30% zinc) is much harder and stronger than pure copper. •

Crystals are like people, it is the defects in them which tend to make them Interesting “Colin Humphreys •

Why are defects important?



Types of Crystalline Defects

- Point Defects - Vacancies, Interstitial, and Substitutional

A. Vacancy Defects

- A vacancy defect is formed when an atom is missing from a normal atomic site in a crystalline structure.
- The number of vacancies present in a material increases exponentially as the temperature increases
- **How many vacancies are there?**
- Statistical thermodynamics predicts that the number of vacancies N_v , have very strong dependence on temperature, T , and can be estimated using the Boltzmann distribution:

$$N_v = N \exp\left(\frac{-Q_v}{K_B T}\right)$$

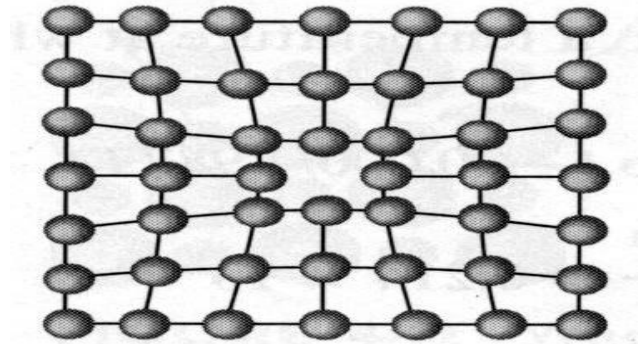
Where

N :- is the total number of regular lattice sites , (total number of atomic sites).

Q_v :- is the energy required to form a vacant lattice site in a perfect crystal.

K_B :- is the Boltzmann's constant , $= 1.38 * 10^{-23}$ J/ atom .K

T :- is the temperature in Kelvin (K).



Types of Crystalline Defects

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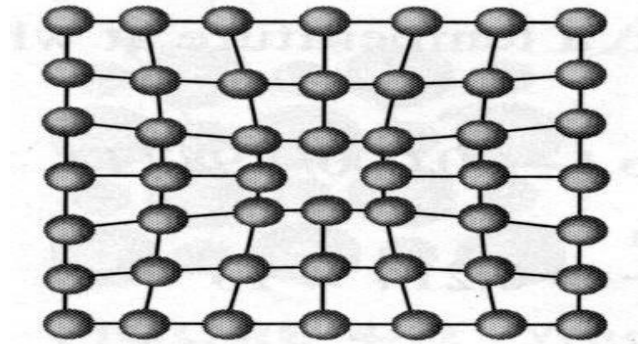
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Vacancy Defects

Number of Vacancies Computation at a Specified Temperature

Calculate the equilibrium number of vacancies per cubic meter for copper at 1000°C. The energy for vacancy formation is 0.9 eV/atom; the atomic weight and density (at 1000°C) for copper are 63.5 g/mol and 8.4 g/cm³, respectively.

Solution

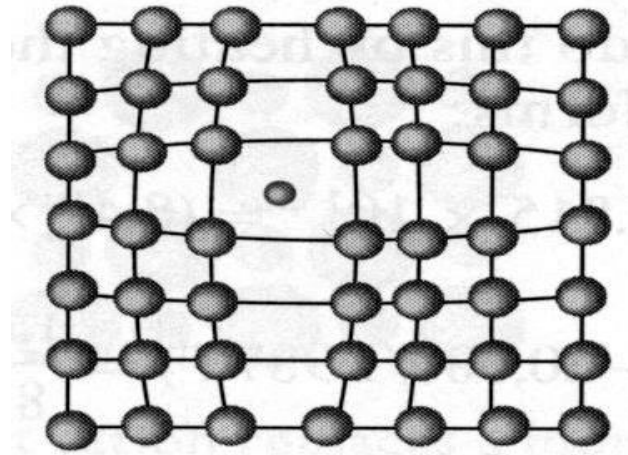
$$\begin{aligned} N &= \frac{N_A \rho}{A_{\text{Cu}}} \\ &= \frac{(6.023 \times 10^{23} \text{ atoms/mol})(8.4 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{63.5 \text{ g/mol}} \\ &= 8.0 \times 10^{28} \text{ atoms/m}^3 \end{aligned}$$

Thus, the number of vacancies at 1000°C (1273 K) is equal to

$$\begin{aligned} N_v &= N \exp\left(-\frac{Q_v}{kT}\right) \\ &= (8.0 \times 10^{28} \text{ atoms/m}^3) \exp\left[-\frac{(0.9 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV/K})(1273 \text{ K})}\right] \\ &= 2.2 \times 10^{25} \text{ vacancies/m}^3 \end{aligned}$$

- **B- Interstitial Defects**

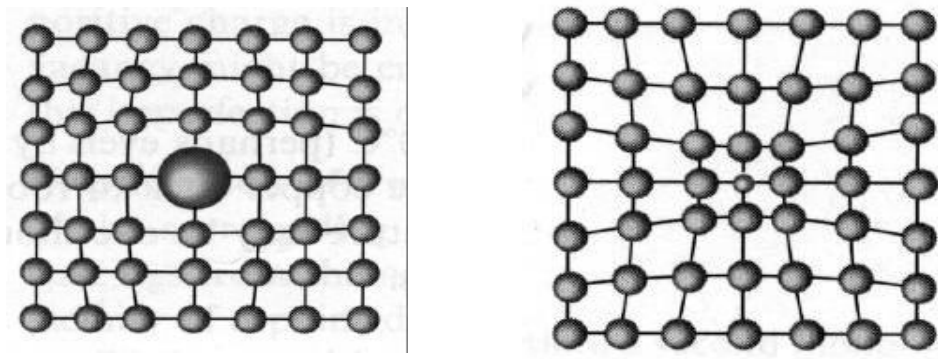
- An Interstitial defect is formed when an extra atom occupies a normally unoccupied site (interstitial site).
- Since the interstitial atoms are larger than the interstitial sites the surrounding lattice is in compression.



- **C- Substitutional Defects**

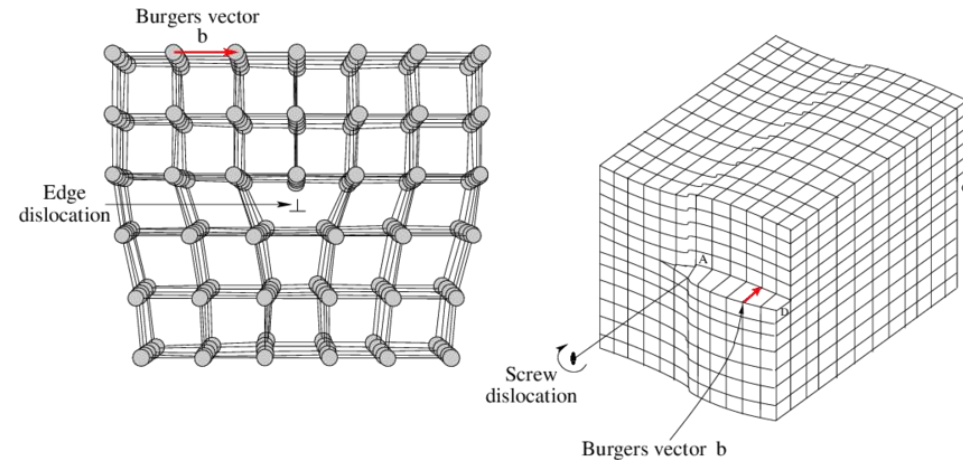
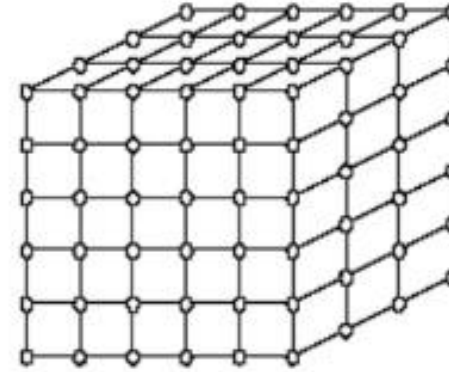
Substitutional defects are produced when one atom is replaced by a different type of atom.

- If the substitutional atom is smaller than the original atom then the Lattice is in tension.
- If the substitutional atom is larger than the original atom then the lattice is in compression.



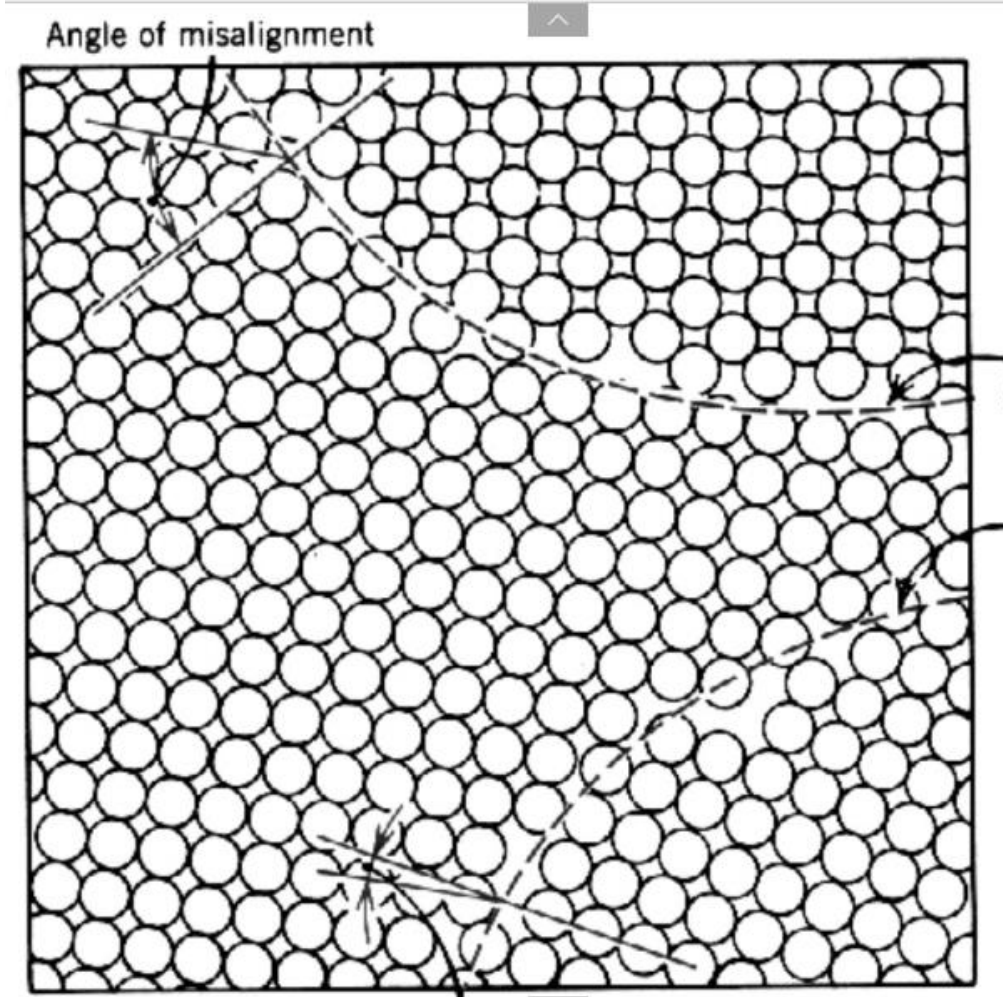
2- Line defect

- There are two type
1. **Edge dislocation:** is a type of line defect in crystal lattices in which the defect occurs either due to the presence of **an extra plane of atoms** or due to **the loss of a half of a plane of atoms** in the middle of the lattice. This defect causes the nearby planes of atoms to bend towards the dislocation. Therefore, the adjacent planes of atoms are not straight. The region in which the defect occurs is the **dislocation core or area**. **When we apply stress on a crystal having this defect, the dislocation area moves parallel to the direction of stress.**
 2. **Screw dislocation:** is another type of line defect in which the defect occurs when **the planes of atoms in the crystal lattice trace a helical path around the dislocation line**. **Visualizing this type of defects in crystals is difficult.** **Unlike** in edge dislocation, when we apply stress on a crystal having this defect, **the dislocation area moves perpendicular to the direction of stress**



3- Surface defect

- These defects are named because they arise from a combination of many linear defects consisting of a surface of defects.
- Grain boundary
- Some solid materials **do not consist of crystalline structure of one crystalline** but of many small crystals, which are called **grain** and that each grain within the structure of the solid matter vary in **direction, size, shape** and **distance from neighbor**. And therefore have to be separated from each other delineated boundary called the **grain boundaries**

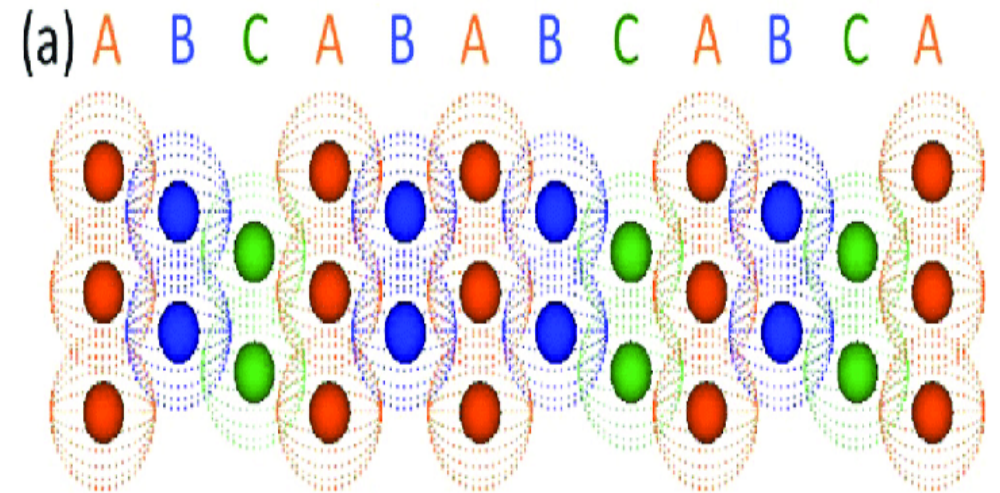


3- Surface defect

Stacking fault

These occur in FCC metals and represent an error in the stacking sequence of close-packed planes. Normally, a stacking sequence of *ABCABCABC* is produced in a perfect FCC lattice. But, suppose the sequence *ABCABABCABC* occurs. In the portion *ABAB*, a type A plane is shown where a type C plane should be located.

This small region, which has a HCP stacking sequence instead of the FCC stacking sequence, represents a stacking fault. Stacking faults interfere with the slip process.

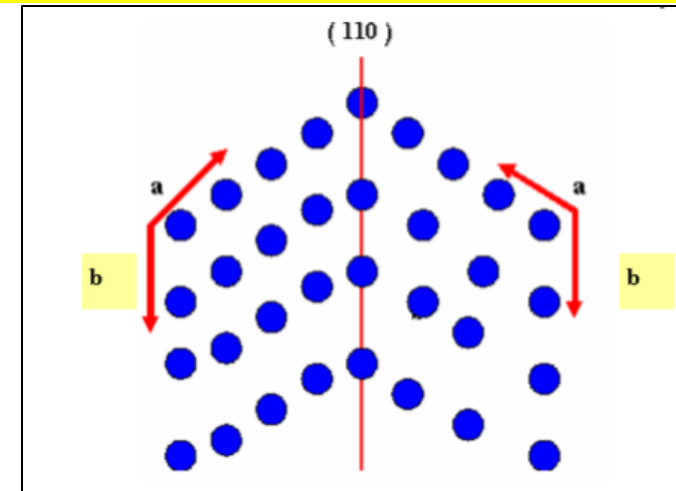


3- Surface defect

Twin Boundaries

- A **twin boundary** is a plane across which there is a special mirror image misorientation of the lattice structure as shown:
- Twins can be produced **when a shear force, acting along the twin boundary, causes the atoms to shift out of position**. Twinning occurs during **deformation or heat treatment** of certain metals. The twin boundaries interfere with the slip process and increase the strength of a metal. Movement of twin boundaries can also cause a metal to deform. The following figure shows that the formation of a twin has changed the shape of the metal.

when two identical regions of a crystal grow in a mirror-image way.





Thank you for your
Kind Attention