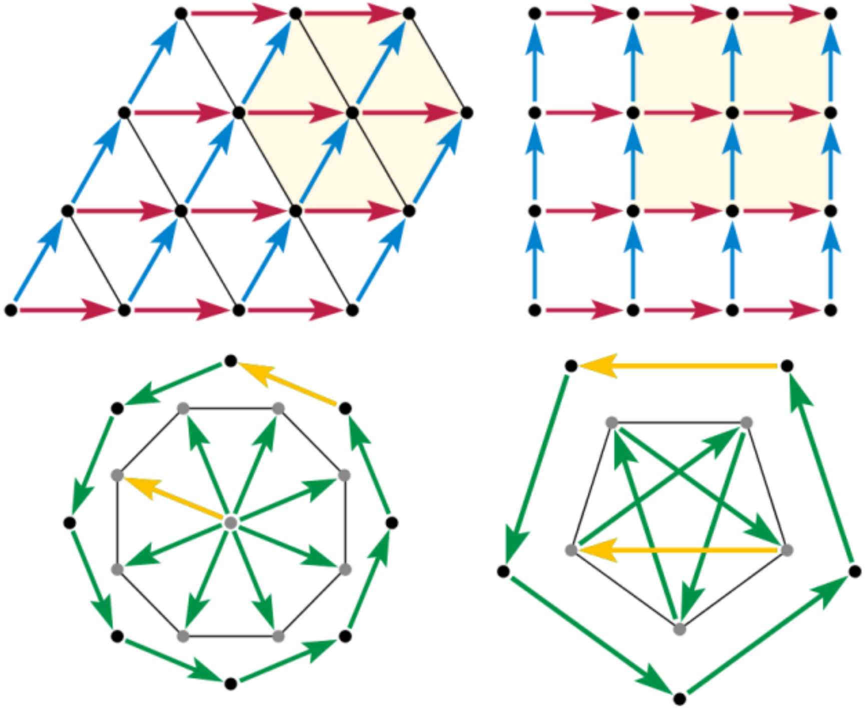
Crystal structure

Introduction

- Solids composed of discrete basic units – atoms
- Atoms arranged in a highly ordered manner.
- Such group of ordered arrangement of atoms – Crystal
- Atoms which appear randomly arranged in a solid is called : non-crystalline or amorphous solids

- Position of atoms are exactly periodic in a crystal
- The distance between nearest neighbours are constant
- Distance need not be orthogaonal.
- Atoms at A, B, C etc are equivalent.
- To an observer they all looks the same.
- It is called translational symmertry.
- Crystal remains invariant under such translations
- Perfect crystalline material is impossible.
- All materials have imperfections or defects.



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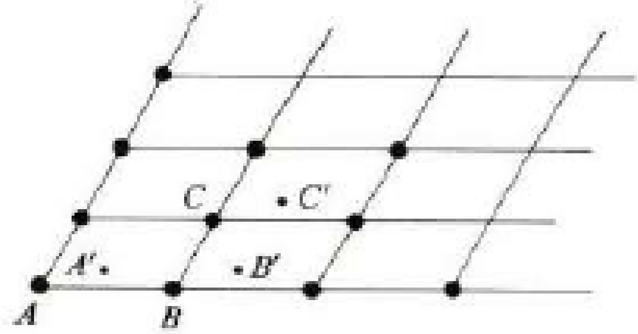
Crystal Lattice

Crystal Lattice / lattice: Geometrical pattern where atomic sites are replaced by lattice sites.

Lattice + Basis = Crystal Structure

Bravais lattice: All lattice points are equivalent

Non-Bravais lattice: Some lattice points are non equivalent. Non-bravais lattice can be considered as a combination of two or more interpenetrating Bravais lattices.



Non-Bravais lattice

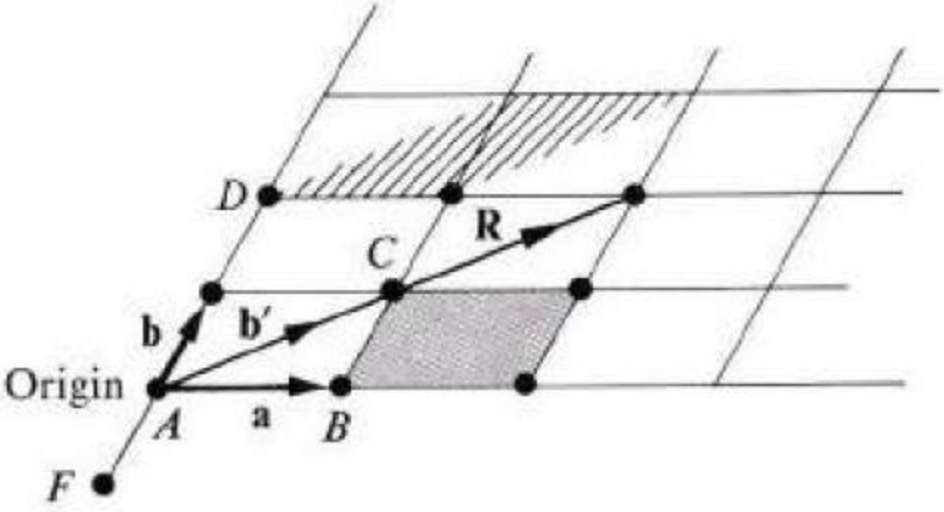
Basis Vector:

Position vector of any lattice point

$$R_n = n_1 \mathbf{a} + n_2 \mathbf{b}$$

n_1 and n_2 are integers.

Vectors **a** and **b** are non-collinear vectors
The set of vectors expressed by this equation is called lattice vectors

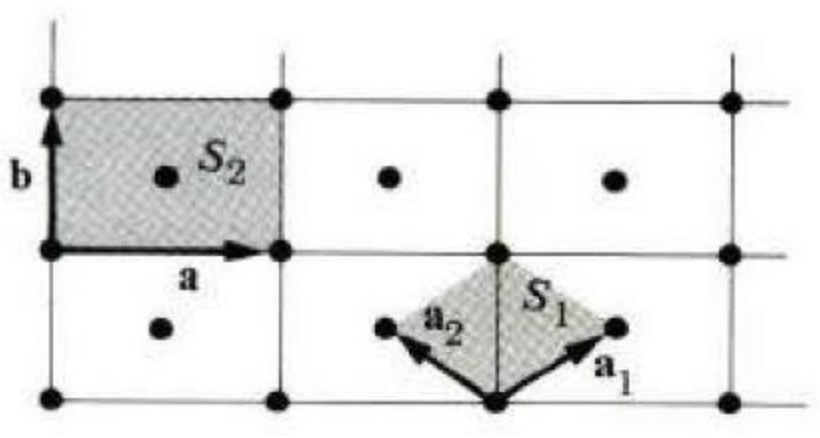


Unit Cell

Smallest repeating unit
a and **b** forms the sides of the unit cell.

Primitive vs nonprimitive unitcell

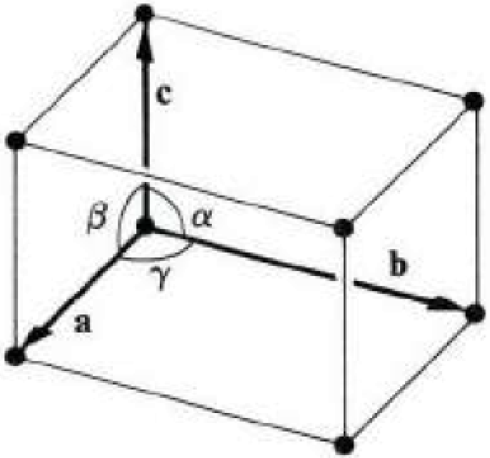
Unit cell with smallest are/volume : Primitive cell
Sometimes larger unit cells which exhibit the symmetry of lattice is considered: nonprimitive



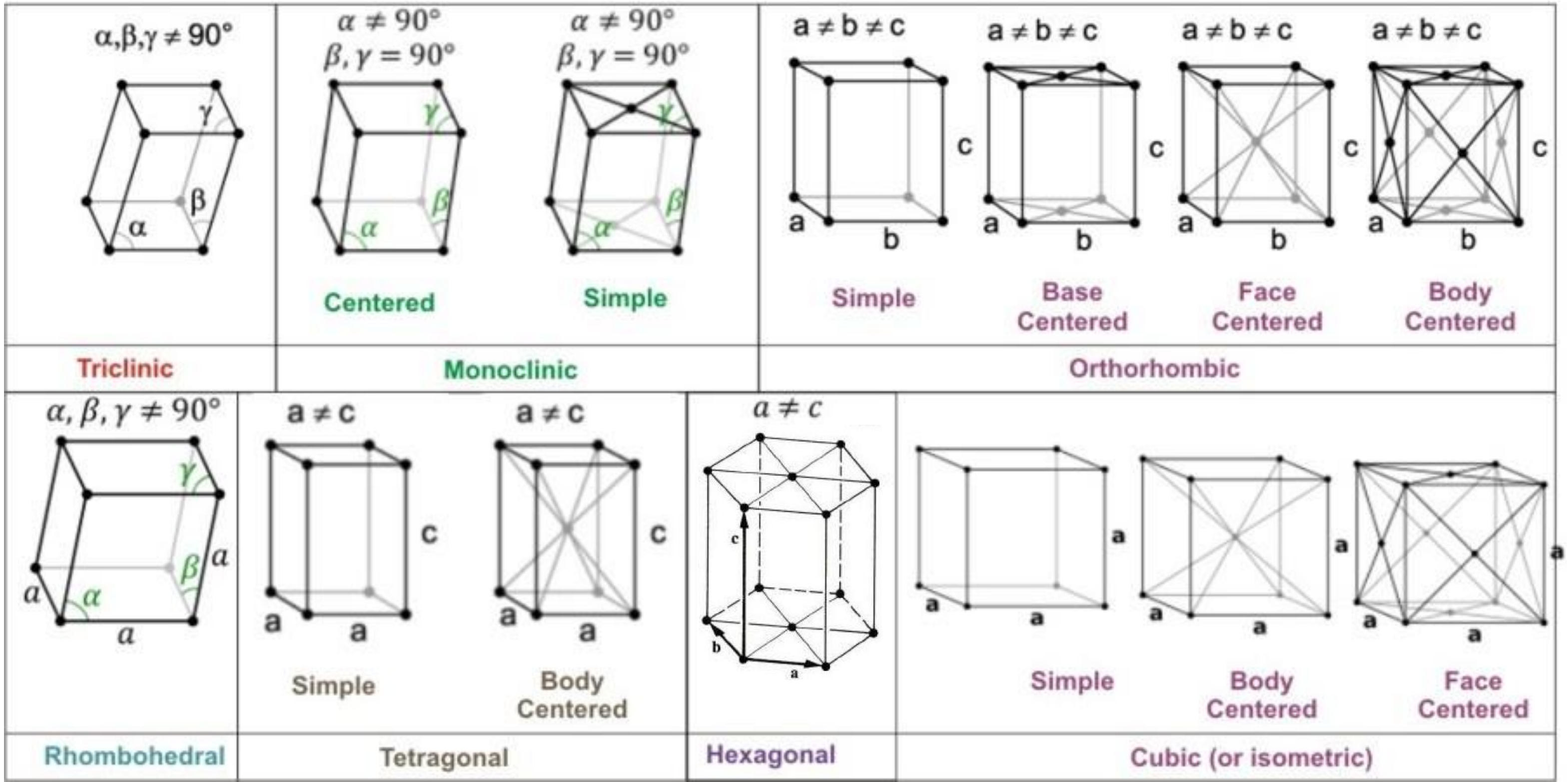
S1- Primitive
S2- Nonprimitive

For 3 dimensional case : $\mathbf{R_n} = n_1\,\mathbf{a} + n_2\,\mathbf{b} + n_3\mathbf{c}$

7 Crystal system & 14 Bravais Lattices



Sr. No.	Crystal System	Axial length of Unit Cell	Inter axial angles	Number of Lattice in the system
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^0$	3
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$	2
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^0$	4
4	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^0 \neq \gamma$	2
5	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^0$	1
6	Trigonal	$a = b = c$	$\alpha = \beta = \gamma < 120^0, \neq 90^0$	1
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^0$, and $\gamma = 120^0$	1



Elements of Symmetry

Inversion Centre: A cell has an inversion center if there is a point at which the cll remains invariant when the mathematical transformation **r** --> **-r** is performed on it.
$\mathbf{R_n} = n_1\,\mathbf{a} + n_2\,\mathbf{b} + n_3\mathbf{c}$ and $\mathbf{R_n} = -n_1\,\mathbf{a} - n_2\,\mathbf{b} - n_3\mathbf{c}$ are lattice vector.

Reflection Plane: A plane in a cell such that when mirror reflection in that plane is performed, the cell remains invariant.

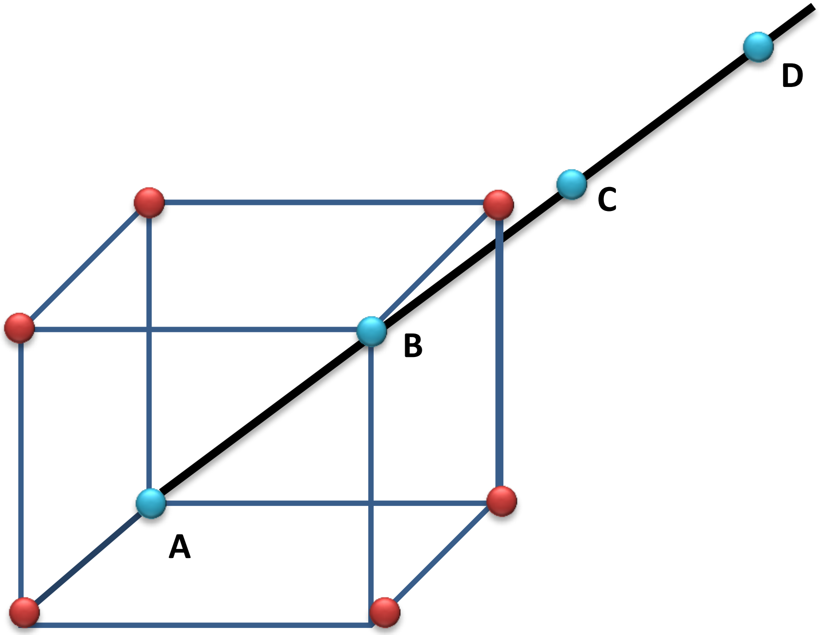
Rotation axis: IF the cell is rotated around it through some angle, the cell remains invariant. The axis is called 'n' fold rotation if the angle of rotation is 2π/n

Point-group symmetry: All possible rotations (Including inversion and reflection) which leave the basis invariant. For all these operations one point must be fixed. **Only 32 point-groups exists.** Lattice cannot take any random shape only fixed shape can be taken.

Space-group symmetry: Rotation symmetry of the pointgroup with translational symmetry results in space-group symmetry. **72 space-groups.**

Apart from these other symmetry elements such as ***screw axis, glide plane etc. exists.*** *When added altogether 230 different space-groups are existing.*

Crystal Directions



Consider a straight line passing through the lattice points A, B & C. This vector is
$\mathbf{R_n} = n_1\,\mathbf{a} + n_2\,\mathbf{b} + n_3\mathbf{c}$.

The direction is specified by the integral triplet **[n_1 n_2 n_3].**
Remove common factor and find the smallest integers of the same relative ratio. Here it is **[1 1 1]**.

When the direction of a straight line is specified, it mean whole set of parallel straight lines which are completely equivalent by virtue of translational symmetry, not just a single line.

<n1 n2 n3> represents all directions equivalent to [n1 n2 n3].

For a cubic crystal $[100], [010], [001], [\bar{1}00], [0\bar{1}0], [00\bar{1}]$ are equivalent directions. Hence **<1 1 1>** represents all these directions.

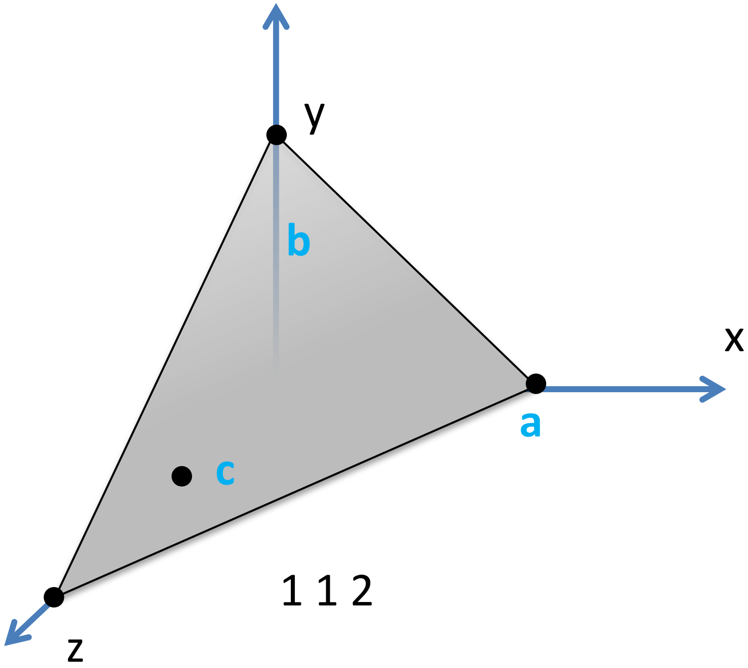
Crystal planes and *Miller Indices*

The orientation of a plane in a lattice is specified by ***Miller Indices.***

Steps:

1. Findintercepts with the axis along the basis vectors **a, b** and **c**. Let it be x, y &z.
2. Find fractional multiples on each direction.

   Ie. $\left(\frac{x}{a}\frac{y}{b}\frac{z}{c}\right)$
3. Invert the values ie. $\left(\frac{a}{x}\frac{b}{y}\frac{c}{z}\right)$
4. Reduce this set to smaller integers by multiplying by a common factor. This last set is called ***Miller Indices (h k l).***



1 1 2

(1/a 1/a 2/a) since a=b=c

(a a a/2)

(2 2 1) - Miller Indices

Sometimes due to symmetry several non parallel planes may be equivalent.

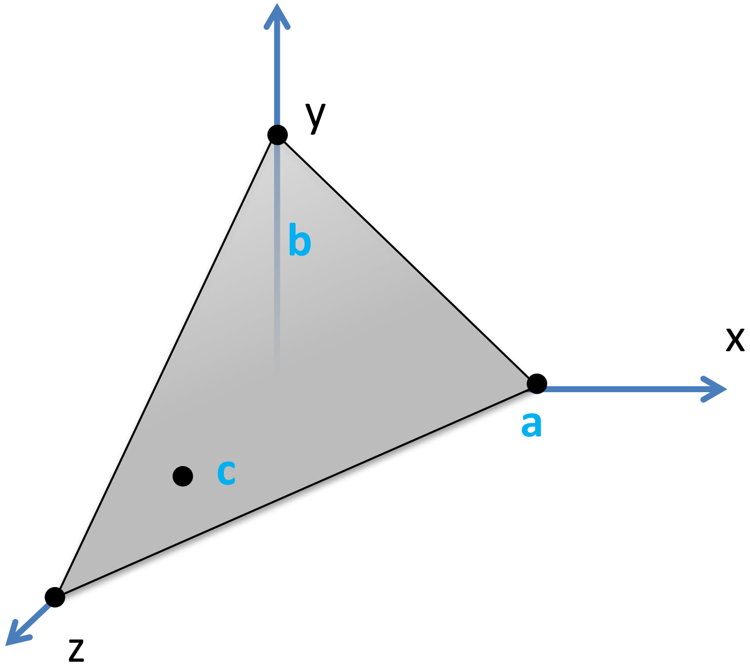
To group these planes we use **{ }**

Hence {h k l} represents all set of planes equivalent to (h k l) through rotational symmetry. Or family of planes.

For cubic system {1 0 0} represents the planes

$(100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$

Spacing between planes



Spacing between two adjacent (hkl) parallel planes can be considered as the distance from the plane and another parallel plane passing through the centre.

The perpendicular distance from (hkl) plane to the origin is
$d_{hkl} = x\cos\alpha = y\cos\beta = z\cos\gamma$

We also have a relation $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$

On substituting, we get $d_{hkl} = \dfrac{1}{\left(\frac{1}{x^2}+\frac{1}{y^2}+\frac{1}{z^2}\right)^{1/2}}$

We have h = n $\frac{a}{x}$ k = n $\frac{b}{y}$ l = n $\frac{c}{z}$

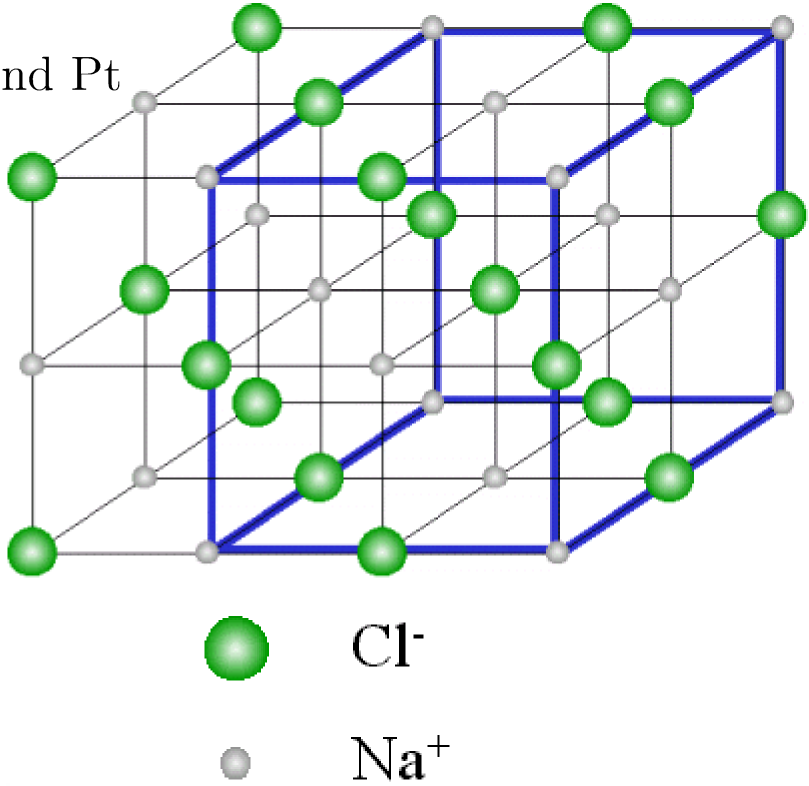
Hence $d_{hkl} = \dfrac{n}{\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)^{1/2}}$

Examples of simple crystal structures

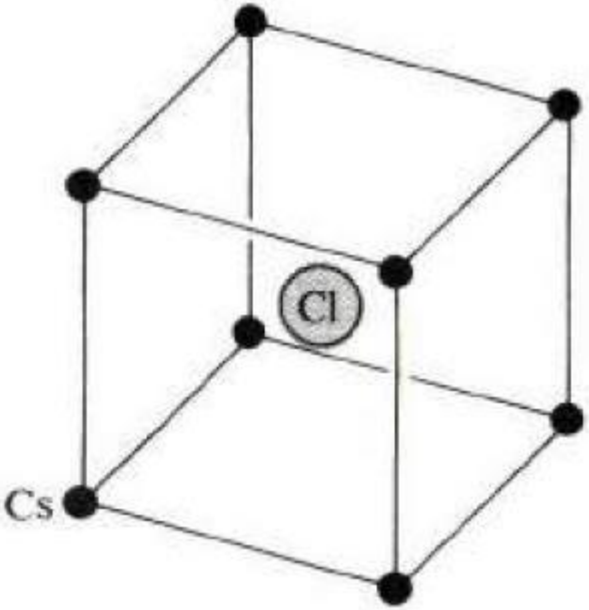
FCC: Metals Ag, Al, Au Cu, Co(β), Fe(γ), Ni(β), Pb and Pt

BCC: Li, Na, K, Rb, Cs

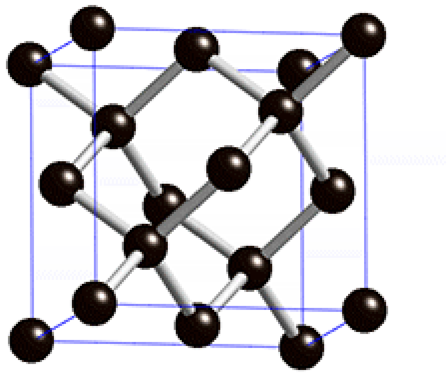
NaCl:



CsCl

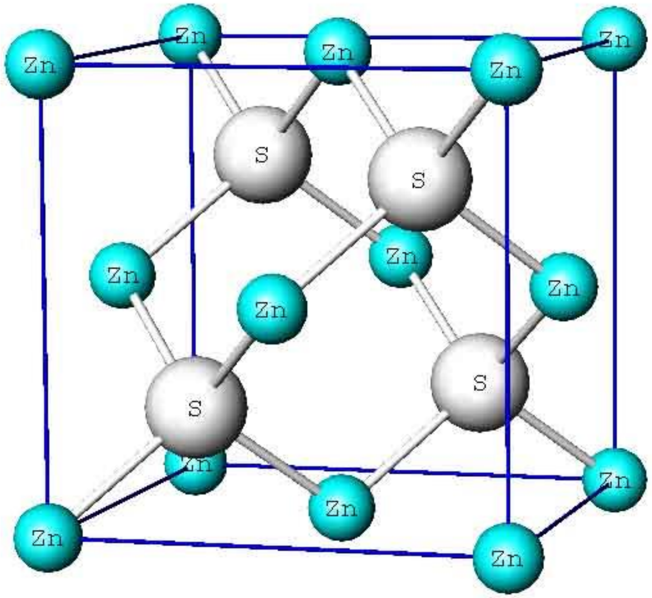


Diamond



Each atom finds bond with four nearby atoms. : Tetrahedral bond

ZnS



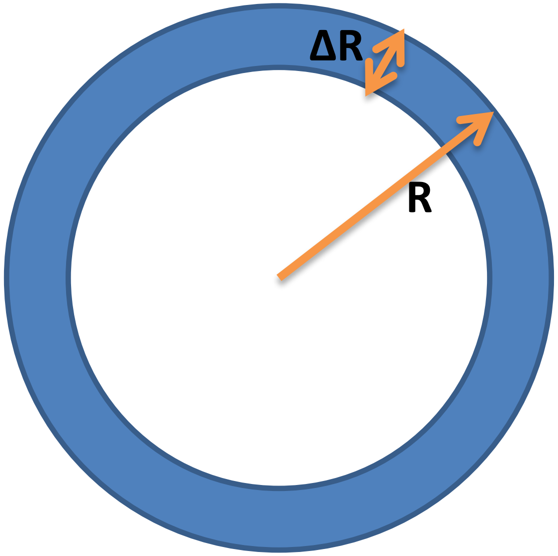
Hexagonal Close Packing (hcp): Be, Mg, Ca, Zn and Hg

Amorphous solids and liquids

- No crystal structure
- No order (random order)
- With time atoms shifts or drift from point to point without altering randomness.

Eg: Glass (super cooled liquid), mercury in room temperature…..

- ➢ Even liquids has some order.
- ➢ For a system the number of neighbours and its nearest neighbour and next-nearest neighbours are concerned.
- ➢ The numbers are average numbers.
- ➢ Inter atomic forces make them hold their positions.
- ➢ Thus liquid has **only short range order** and ***no long range order***.
- ➢ A crystal has both long range and short range order.

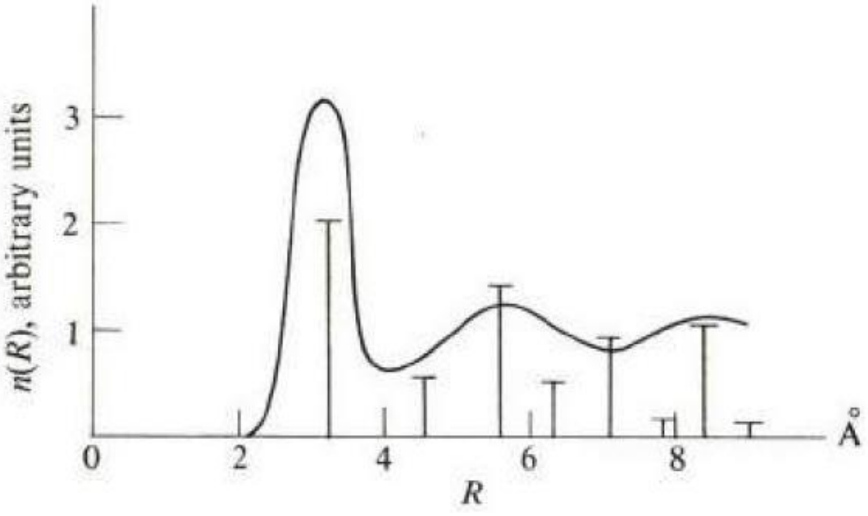


Sphere

$$\Delta N(R) = n(R) 4\pi R^2 \, \Delta R$$

- $n(R)$ is concentration of the liquid
- Once n(R) and its variation with radial distance is known, structure of the liquid is known

- Peak value at 3 A^{o}
- Concentration vanishes for R< 2.2 A^{o}
- n(R) nearly zero upto diameter of the particles.
- For smaller R values strong repulsive forces dominates
- Reason for major peak is due to interatomic force.
- Except at very short distance, atoms attracts together, which tends to pull other atoms to the centre resulting in increased density



Concentration vs R in liquid mercury as revealed by x-ray diffraction

Correlation between atoms by calculating

Pair distribution function, $g(R) = \frac{n(R)}{n_0}$

g(R) -→1 as R → infinity which corresponds to absence of correlation between atoms

Interatomic Forces

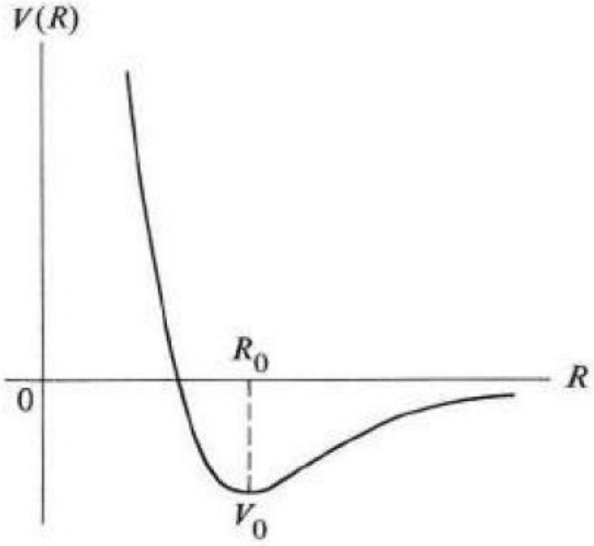
Solids are stable structures

NaCl is more stable than free Na and Cl atoms Similarly Ge crystal more stable than free Ge atom

Due to attractive interatomic force.

Energy of crystal is lower than free atoms by an amount of energy required to pull crystal apart into a set of free atoms, called ***Binding energy.(Cohesive energy)***

Potential energy representing the interaction between two atoms varies greately with distance as in figure.



The atom pair system, tend to possess the lowest possible energy state the equilibrium position.

At equilibrium position the distance is R_0. which is few angstroms for most cases.

The interatomic force F(R) can be derived as

$$F(R) = -\frac{\partial V(R)}{\partial R}$$

Force is negative to that of potential.

ie for $R>R_0$ the force is negative or attractive

For $R<R_0$ the force is positive and repulsive it tend the atoms to repel apart.

Interatomic forces consists of attractive and repulsive forces

Types of bonds

(i) Ionic Bond

- Observed in Ionic crystals like NaCl
- Attractive electrostatic coulomb force between oppositely charged particles.
- In very close distance electrons in these ions start to repel each other.
- Ionic bod is strong compared with other bonds.

(ii) Covalent Bond

- Found in Diamond, H_2 molecule, IV column elements like Si, Ge, Sn etc.
- Bond composed of two electron known as *double-electron bond.*
- Covalent bond is sharing of electrons to get stable shell structure.
- Covalent crystals hard and brittle, incapable of bending.
- There is also material with partial sharing of electrons.

(iii) Metallic Bond

- Metals: High electrical conductivity, high mechanical strength and highly ductile.
- Eg: Na,
- Each atom has a free electron(Valence or conduction electron) which is loosely bound to the atom.
- Conduction electron(Valance) is different from covalent electron.
- Positive ions immersed in gas of free electron.
- Since electron cloud shields ions from each other nearby ions may not repel.
- In Quantum Mechanics if particle motion is restricted to a small volume, it will have large Kinetic Energy. (For gases)
- For metals since atoms are placed at crystal lattice, electron can roam around crystal lattice, resulting in reduction of kinetic energy.
- Thus total energy decreases and results in metallic bonding.
- Weaker bond than ionic or covalent.
- High density due to close packing of atoms.
- High ductility is due to nondirectional metallic bonding.
- High electrical and thermal conductivity due to mobile electrons.

(iv) Secondary Bonds

- Explains fine structure phenomenon
- Oxygen bond with hydrogen atom of another molecule in water.
- Oxygen attracts electrons more tightly towards them resulting in net –ve charge near Oxygen and +ve charge in Hydrogen, creating electric dipole.
- -ve oxygen atom in one water molecule is attracted towards that corner in another water molecule which contains a positive hydrogen atom. This bond is hydrogen bond.
- Van der Waals bond:
- Inert gases possess weak interaction between themselves and other atoms.
- Which also explains their low melting point.
- Electron cloud generally screens nucleus by symmetrically covering it.
- If it is not covering, dipole may be created. Which gives attractive force between atoms, which is why gas can be solidified.
- Van der Waals force (London force) is weak due to
    - ☐ Fluctuating atomic dipoles are small
    - ☐ Dipoles on different atoms are not synchronized with each other, resulting in cancellation of net moment.