

CEMA-CC-4-9-TH

SEM 4

Dr. Sudeshna Sawoo

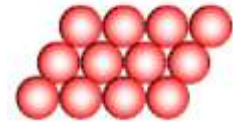
Solid State

In Solids constituent particles held closely by strong intermolecular forces. They are highly incompressible and rigid and has definite shape, volume, etc.

Types of solid: Two types (based upon atomic arrangement, binding energy, physical & chemical properties):

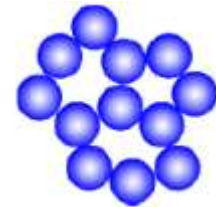
1. **Crystalline:** High bond energy, closely packed ordered structure of atoms or ions with definite geometry extended in all special dimensions. Possesses sharp melting point. Give x-ray diffraction bands.

Examples: NaCl, CsCl, quartz etc.



2. **Amorphous:** Random arrangement of atoms or ions, less bond energy. No sharp m.p. No Do not give x-ray diffraction bands. do not form defined patterns or lattice structures. Amorphous materials may have order only within a few atomic or molecular dimensions.

Examples: wood, rubber, plastics, glass etc.



Types of Crystal depend on nature of bonding present:

Ionic crystals: Mainly salts, with ionic bond (between a metal and a non-metal atom), strong electrostatic force of attraction between cations and anions are present. Lattice points are occupied by positive and negative ions E. g. NaCl, CsCl, CuSO₄, etc.

Covalent crystals: Covalent bonding (between non-metal atoms) present in a continuous network extending throughout the material. Lattice points are occupied by neutral atoms. E. g. Graphite, diamond, quartz, mica, BN etc.

Molecular crystals: Molecules held together by the van der Waals forces or by Hydrogen bonding. Lattice points are occupied by neutral molecules. E. g. Fullerene, sugar, ice, iodine etc.

Metallic crystals: Possess metallic bonds, may be described as the sharing of free electrons among positively charged metal ions presents at lattice points. E.g. Na, Al, Ga, Au, Cu, Ag, W etc.



Copper sulfate



Table salt



Graphite



Quartz



Sugar



Ice



Gallium

Crystal Structure

To describe ordered structure of a crystalline solid we use concept of a **lattice**.

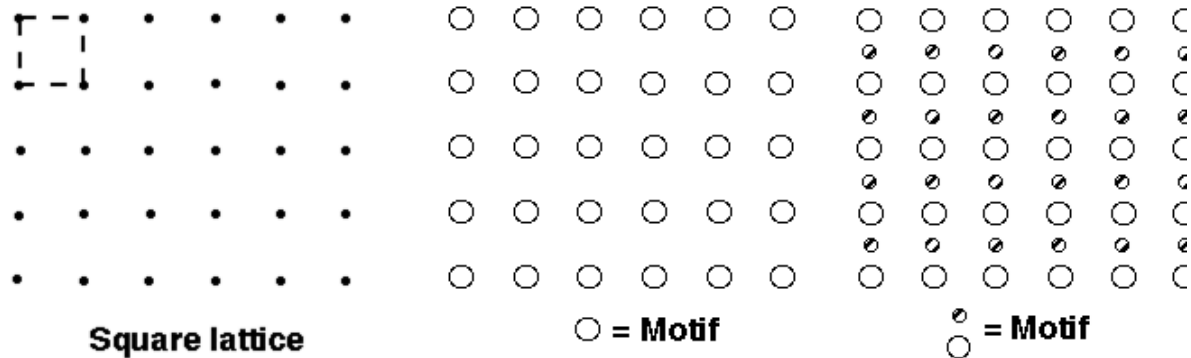
A lattice is "an infinite 1, 2, or 3-D regular arrangement of points, each of which has **identical surroundings**".

The **lattice points** can be obtained by replacing atoms, group of atoms, or ions in the **unit cells** of the crystals.

To recover original pattern we add the **structural motif** to each lattice point.

Structural motifs are atoms, group of atoms or molecules in case of crystals.

2-D Lattice:



3-D Space Lattice:

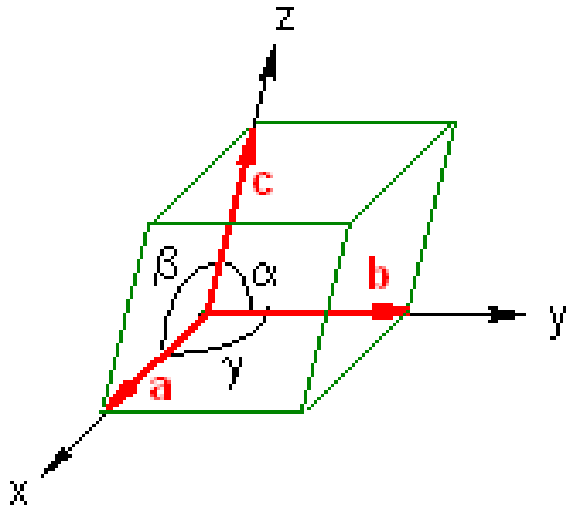
Lattice arranged in 3 dimensions. The motif can be single atoms or groups of atoms. Again we assign lattice points (every point has identical surrounding) to the atomic structure and produce a Space Lattice, .

Space lattice + motif (basis) = Crystal Structure

Unit Cell

The smallest component of the crystal with maximum number of symmetry, its pure translational repetition in all three dimensions will produce the whole crystal.

The unit cells must be adjacent to each other, no gap is allowed between unit cells.



We define the size of the unit cell using **lattice parameters** (sometimes called lattice constants, or cell parameters). These are 3 vectors, a, b, c. The angles between these vectors are given by α (angle between b and c), β (angle between a and c), and γ (angle between a and b).

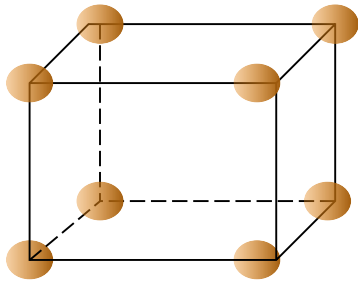
Unit Cell Shapes (Crystal Classes)

Based on the lattice parameters we can have 7 popular crystal systems shown in the table

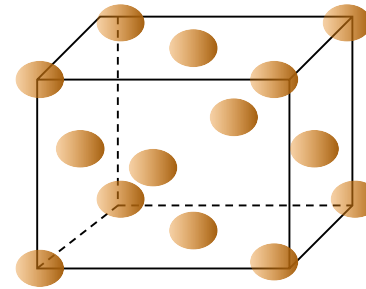
Crystal System	Unit Cell Dimensions	Required Symmetry Element
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Four 3-fold axes Three 4-fold axes Six 2-fold axes
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Any combination of three mutually \perp 2-fold axes or mirror (glide) planes
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	One 4-fold axis
Rhombohedral Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$ $a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	One 3-fold axis
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	Either a mirror (glide) plane or a 2-fold axis
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	None
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ \gamma = 120^\circ$	One 6-fold axis

Unit Cell Types in Space lattice

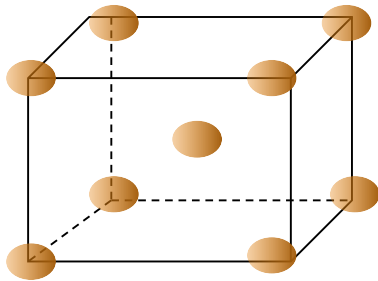
- **Primitive (P)** unit cells contain only a *single lattice point*.
- **Body /Internal (I)** unit cell contains an atom in the *body center*.
- **Face (F)** unit cell contains atoms in the *all faces of the planes* composing the cell.
- **Side Centered (C)** unit cell contains atoms *centered on the sides* of the unit cell.



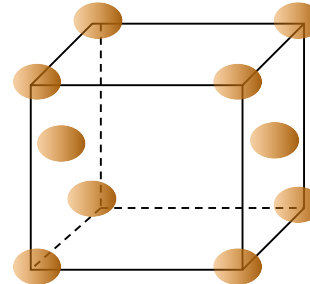
Primitive (P)



Face-Centered (F)




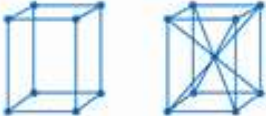





Body-Centered (I)



End-Centered (C)

Bravais Lattices:

Combining **7 Crystal Classes** (cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic, trigonal) **with 4 unit cell types (P, I, F, C) symmetry** allows for only **14 types of 3-D lattice known as Bravais Lattices**. In 1850, M. A. Bravais showed that identical points can be arranged spatially to produce only 14 types of regular pattern. These 14 space lattices are known as 'Bravais lattices'.

 <p>Cubic P Cubic I Cubic F</p>	<p>Three axes at right angles; all equal: $a = b = c; \alpha = \beta = \gamma = 90^\circ$</p>
 <p>Tetragonal P Tetragonal I</p>	<p>Three axes at right angles; two equal: $a = b \neq c; \alpha = \beta = \gamma = 90^\circ$</p>
 <p>P C I F Orthorhombic</p>	<p>Three axes at right angles; all unequal: $a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$</p>
 <p>Monoclinic P Monoclinic C</p>	<p>Three axes, one pair not at right angles, all unequal: $a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta$</p>
 <p>Triclinic P</p>	<p>Three axes not at right angles; all unequal: $a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90^\circ$</p>
 <p>Rhombohedral</p>	<p>Three axes equally inclined, not at right angles; all equal: $a = b = c; \alpha = \beta = \gamma \neq 90^\circ$</p>
 <p>Hexagonal</p>	<p>Three axes coplanar at 120°, fourth axis at right angles to these: $a_1 = a_2 = a_3 \neq c$; $\alpha = \beta = 90^\circ, \gamma = 120^\circ$</p>

How many lattice points and/or atoms "belong" to a unit cell ?

Corners: The points at the corner of the cell are shared by the surrounding unit cells, therefore each one is shared by 8 in total and is only "worth" $1/8$ to each cell.

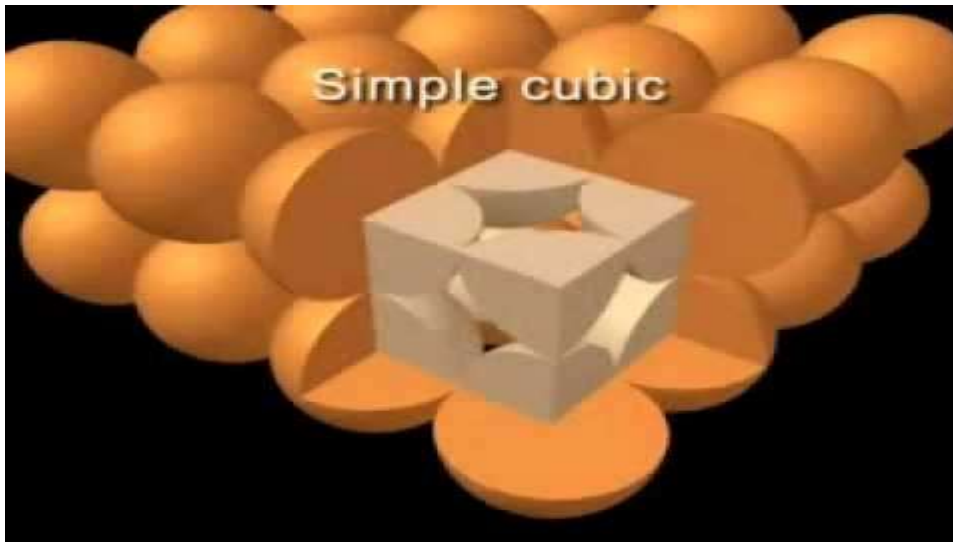
Faces : - these lattice points are shared by 2 cells, each one is "worth" $1/2$ to each cell.

Body : - this is the sole possession of that cell, worth 1.

Total number lattice points for cubic unit cells:

primitive cubic or simple cubic = $8(1/8) = 1$; FCC = $6 \times 1/2 + 8(1/8) = 4$; BCC = $8(1/8) + 1 = 2$.

Lookout !! <https://www.youtube.com/watch?v=KNgRBqj9FS8>

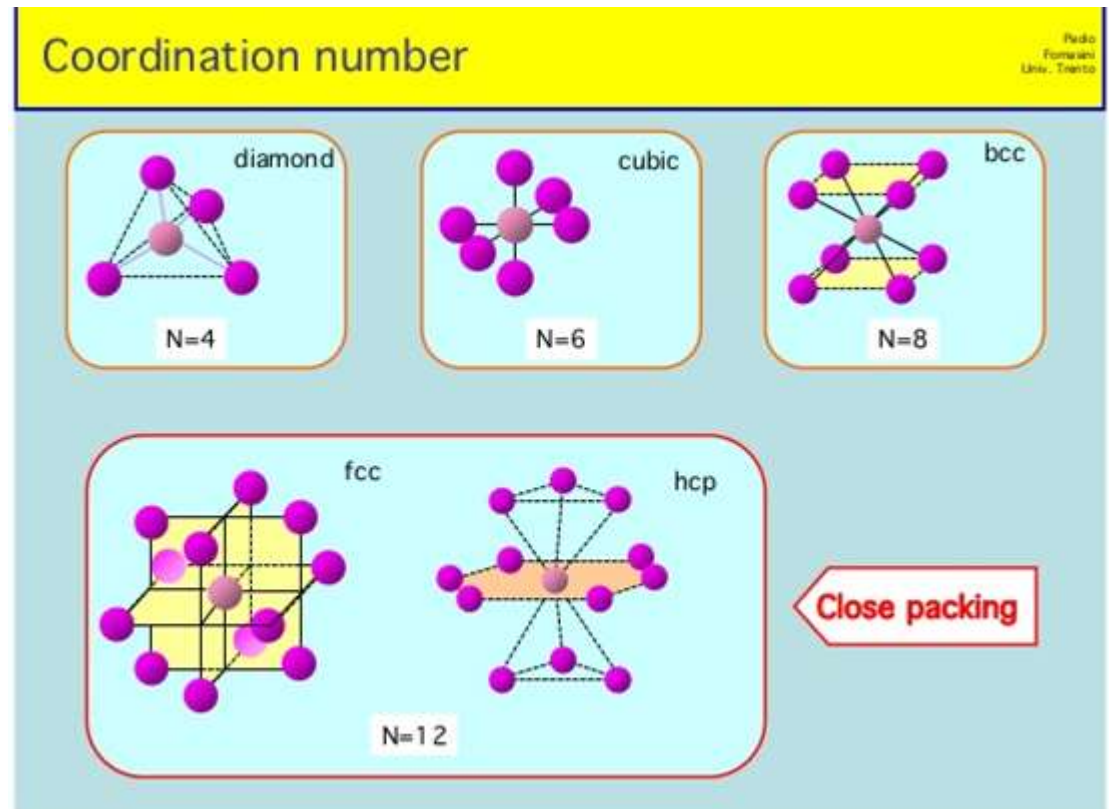


Coordination Number

Coordination Number (CN) : The number of Bravais lattice points closest to a given point.

Because the Bravais lattice is periodic, all points have the same number of nearest neighbours or coordination number.

A simple cubic has coordination number 6; a body-centered cubic lattice, 8; and for a face-centered cubic lattice 12.



Assuming the atoms are the hard spheres and identical, mathematical calculation shows Packing density for primitive cubic $pc < bcc < fcc$

Crystal structure of some metals:

- ❖ **PC type:** Rare due to low packing density, *52% of the space is occupied by the atoms*
E. g. only Po – Polonium -- has this structure.
- ❖ **BCC type:** Atoms touch each other along cube diagonals within a unit cell. *68% of the space is occupied by the atoms.* E.g. Cr, W, Fe (α), Tantalum, Molybdenum etc.
- ❖ **FCC type:** Atoms touch each other along face diagonals. *74% of the space is occupied by the atoms.* E.g. Al, Cu, Au, Pb, Ni, Pt, Ag etc.
- ❖ **HCC type:** One six fold axis of symmetry present. *74% of the space is occupied by the atoms.* E.g. Co, Cd, Zn etc.

THEORETICAL DENSITY Calculation

Density = ρ = Mass of atoms in unit cell/Volume of unit cell

$$\text{Therefore, } \rho = n A / V_C N_A$$

where n = number of atoms/unit cell A = atomic weight V_C = Volume of unit cell = a^3 for cubic, N_A = Avogadro's number = 6.023×10^{23} atoms/mol

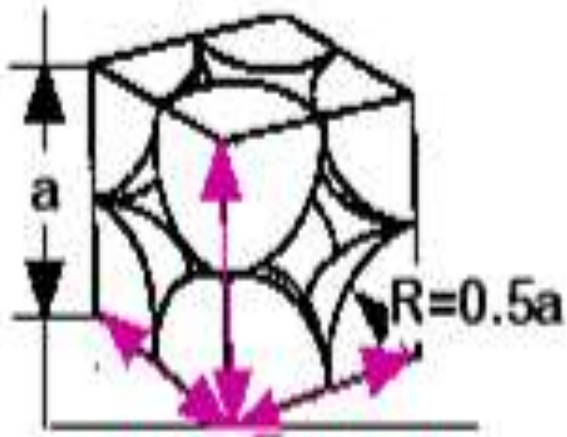
NOTE: The theoretical density is always larger than the measured density. WHY? Because the theoretical density assumes perfect crystals, whereas experimentally measured densities always use imperfect, or defective, materials. The other point is that the agreement should come as no surprise since the values for the atomic radii are actually determined from the measured densities and calculated using the hard sphere model!

Atomic Packing Factor

Atomic Packing Factor (APF) is defined as the volume of atoms within the unit cell divided by the volume of the unit cell.

$$\text{APF} = \frac{\text{Volume of Atoms in Unit Cell}}{\text{Volume of Unit Cell}}$$

Atomic Packing Factor of SC



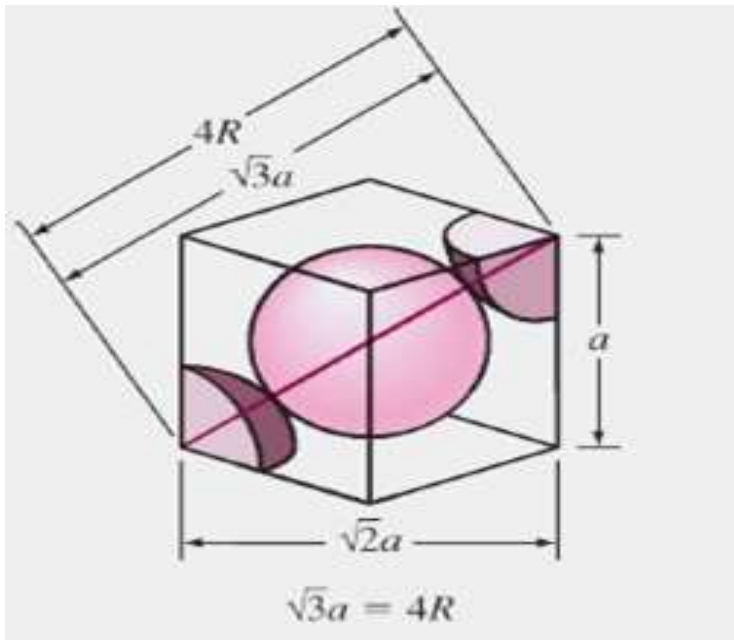
contains $8 \times 1/8 =$
1 atom/unit cell

APF = 0.52 for simple cubic

$$\text{APF} = \frac{\text{atom}}{\text{unit cell}} \frac{4}{3} \pi (0.5a)^3}{\text{volume}} \frac{\text{atom}}{\text{unit cell}}}{a^3}$$

The diagram illustrates the calculation of the Atomic Packing Factor (APF) for a simple cubic unit cell. The APF is defined as the ratio of the volume of atoms in the unit cell to the volume of the unit cell. The numerator is the volume of one atom, $\frac{4}{3} \pi (0.5a)^3$, multiplied by the number of atoms per unit cell, 1. The denominator is the volume of the unit cell, a^3 . The final result is $\text{APF} = 0.52$.

Atomic Packing Factor of BCC

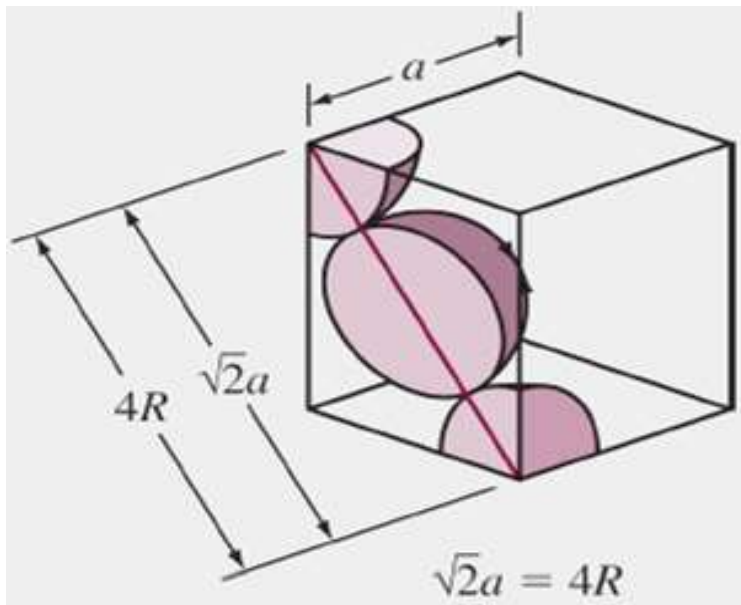


$$APF_{BCC} = \frac{V_{atoms}}{V_{unit\ cell}} = 0.68$$

$$APF = \frac{\text{atom unit cell} \cdot 2 \cdot \frac{4}{3} \pi (0.433a)^3}{\text{volume unit cell} \cdot a^3}$$

The diagram shows the calculation of the Atomic Packing Factor (APF) for a BCC unit cell. The numerator represents the total volume of atoms in the unit cell, calculated as 2 atoms per unit cell multiplied by the volume of a single atom, $\frac{4}{3} \pi (0.433a)^3$. The denominator represents the volume of the unit cell, a^3 . Arrows point from the labels "atom unit cell", "volume atom", and "volume unit cell" to their respective parts in the equation.

Atomic Packing Factor of FCC



$$APF_{\text{FCC}} = \frac{V_{\text{atoms}}}{V_{\text{unit cell}}} = \mathbf{0.74}$$

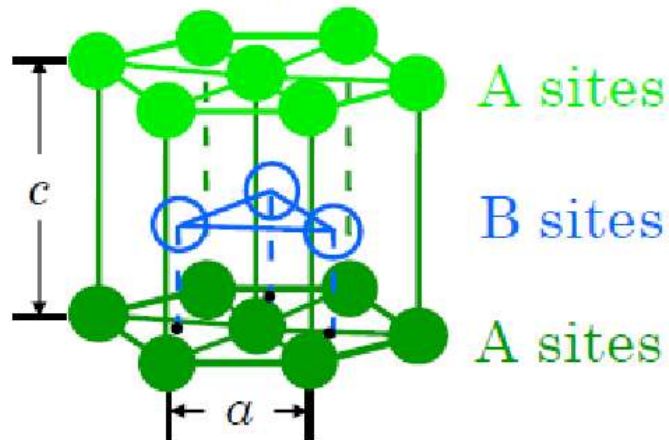
$$APF = \frac{\text{atom unit cell} \left(4 \frac{4}{3} \pi (0.35a)^3 \right)}{\text{volume unit cell} \left(a^3 \right)}$$

The diagram shows the calculation of the Atomic Packing Factor (APF) for FCC. The numerator is labeled "atom unit cell" and the denominator is labeled "volume unit cell". The volume of an atom is given as $\frac{4}{3} \pi (0.35a)^3$, and the volume of the unit cell is a^3 .

4. HEXAGONAL CLOSE-PACKED STRUCTURE (HCP)

ex: Cd, Mg, Ti, Zn

- ABAB... Stacking Sequence
- 3D Projection



- Coordination # = 12

- 2D Projection

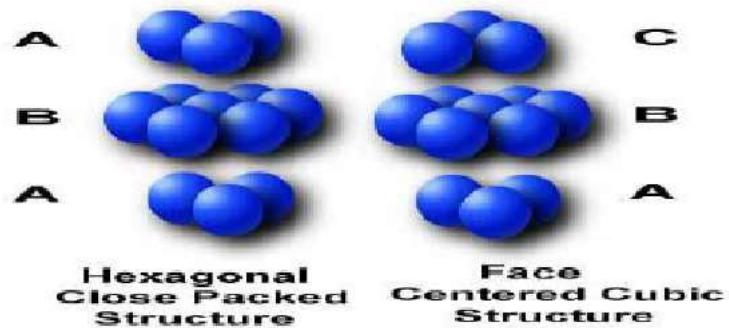
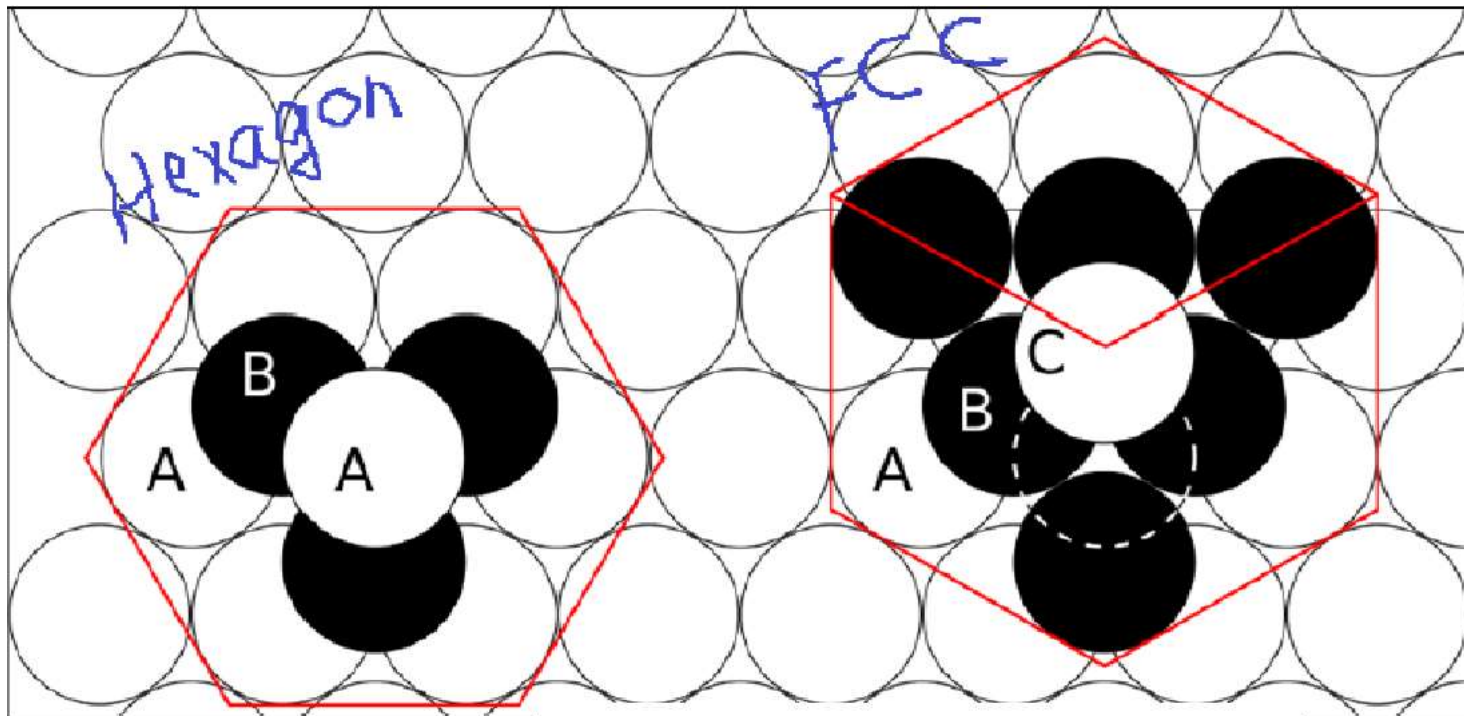


6 atoms/unit cell

- APF = 0.74



[Ref: Kapoor, 4th Ed. Vol.1 page 176-177]



Both FCC and HCC has $APF=0.74$, but the stacking sequence for FCC is ABCABCABC..... and for HCC is ABABAB.....



Structures of some important ionic compounds

Crystal structure depend upon **radius ratio** of cations to anions and coordination number of atoms or ions present. Larger the radius ratio, larger will be the coordination number.

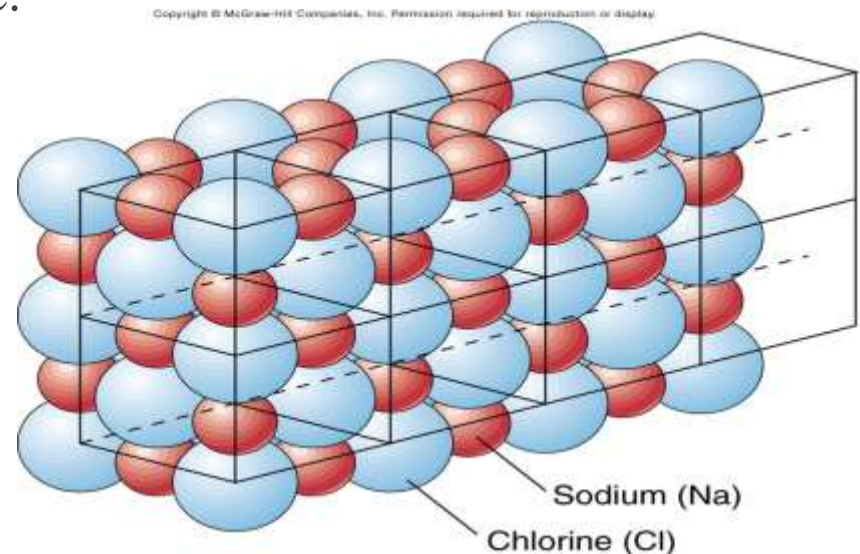
1. AB type: NaCl (rock salt), fcc type.

ZnS , fcc type

CsCl, bcc type

2. AB₂ type: CaF₂ (fluorite), fcc
TiO₂ (rutile), tetragonal
SiO₂ , hexagonal

3. A₂B type: K₂O (antifluorite), fcc



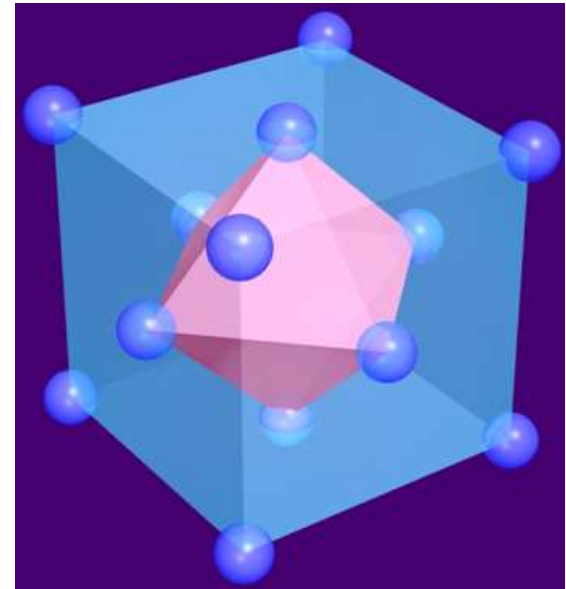
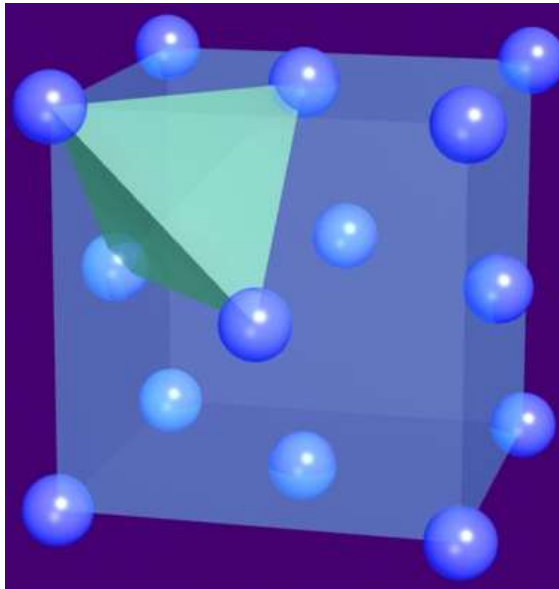
Structural analysis by radius ratio rule

$$\text{Radius Ratio} = \frac{\text{Radius of cation } (r^+)}{\text{Radius of anion } (r^-)}$$

S.NO.	RADIUS RATIO	CO-ORDINATION NUMBER	SHAPE	EXAMPLE
1.	0.0 – 0.155	2	Linear	HF ⁻
2.	0.155–0.225	3	Triangular planar	B ₂ O ₃ , BN
3.	0.225– 0.414	4	Tetrahedral	ZnS, SiO ₄ ⁻⁴
4.	0.414– 0.732	6	Octahedral	NaCl
5.	0.732 – 1.0	8	Body-centered cubic	CsCl

Interatomic Voids*

- ❑ In the hard sphere model of atoms, atoms are visualized as spheres. We have already seen that as spheres cannot fill entire space. This implies that the packing fraction (PF) < 1 (for all crystals).
- ❑ In the 'BCC crystal' the voids do NOT have the shape of the regular tetrahedron or the regular octahedron (*in fact the octahedral void is a 'linear void'!!*)
- ❑ In the close packed crystals (FCC, HCP) there are two types of voids → **tetrahedral** and **octahedral** voids (*identical in both the structures as the voids are formed between two layers of atoms*)



HW: Calculate limiting radius ratios?

Problems:

A crystalline metal **A** of crystal type FCC has the length of the unit cell 3.65 \AA and metal **B** of BCC type has the length of its unit cell is 2.90 \AA . What will be ratio of their densities?

Potassium has BCC type crystal structure, its density is 0.856 g/cc . Calculate the length of the unit cell and the distance between (110) planes.

Li has a density 0.53 g/cm^3 . The distance between (100) planes is 350 pm . Determine whether it is FCC type or BCC type.