Lecture 2
Crystal Structure

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Chapter 4
OR Solid state physics, Kittel (Wiley)

Coordination Number

- Coordination Number (CN) : The Bravais lattice points closest to a given point are the nearest neighbours.

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

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

Atomic Packing Factor

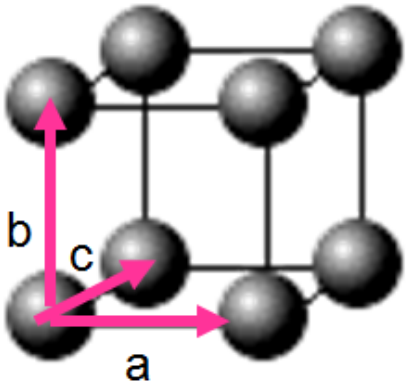
- Atomic Packing Factor (APF) is defined as the volume of atoms within the unit cell divided by the volume of the unit cell.

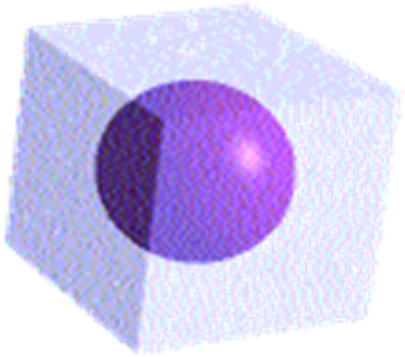
$$\text{APF} = \frac{\text{Volume of Atoms in Unit Cell}}{\text{Volume of Unit Cell}}$$

1-CUBIC CRYSTAL SYSTEM

a- Simple Cubic (SC)

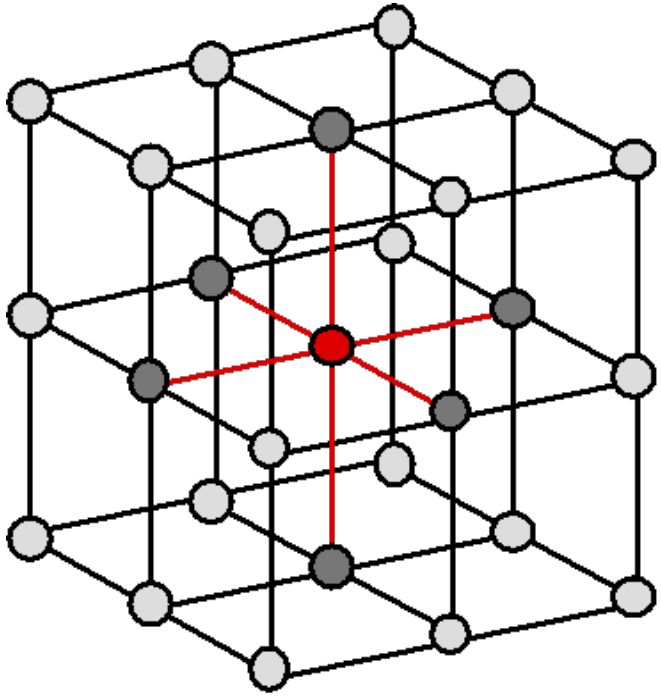
- Simple Cubic has one lattice point so its primitive cell.
- In the unit cell on the left, the atoms at the corners are cut because only a portion (in this case 1/8) belongs to that cell. The rest of the atom belongs to neighboring cells.
- Coordinatination number of simple cubic is 6.

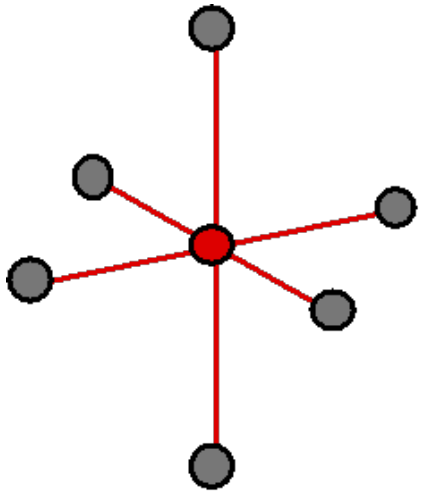




a-SIMPLE CUBIC (SC)

- **Coordination # = 6** **(# nearest neighbors)**



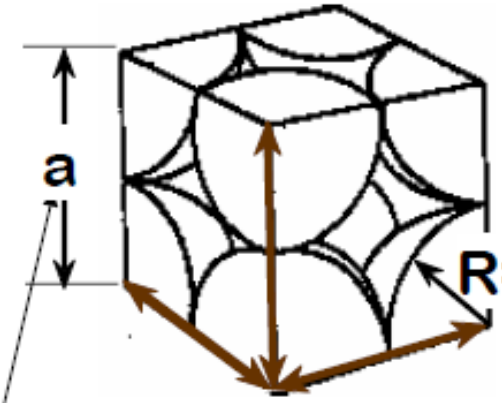


a-SIMPLE CUBIC (SC)

ATOMIC PACKING FACTOR

$$APF = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

*assume hard spheres



close-packed directions

contains 8 x 1/8 =
1 atom/unit cell

Adapted from Fig. 3.19, *Callister 6e.*

$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}}$$

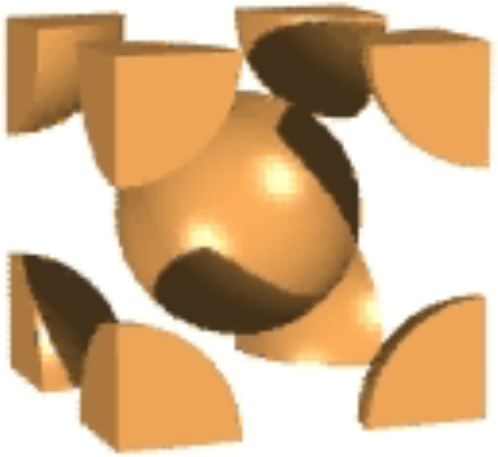
$$APF = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

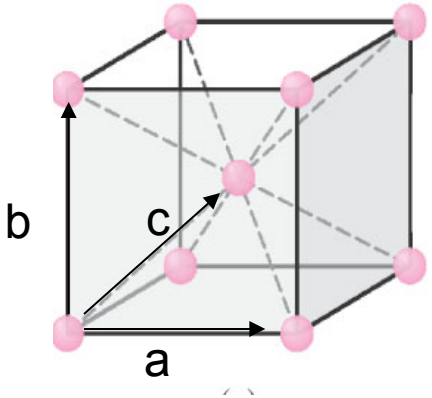
Lattice constant

- APF for a simple cubic structure = 0.52

b-Body Centred Cubic (BCC)

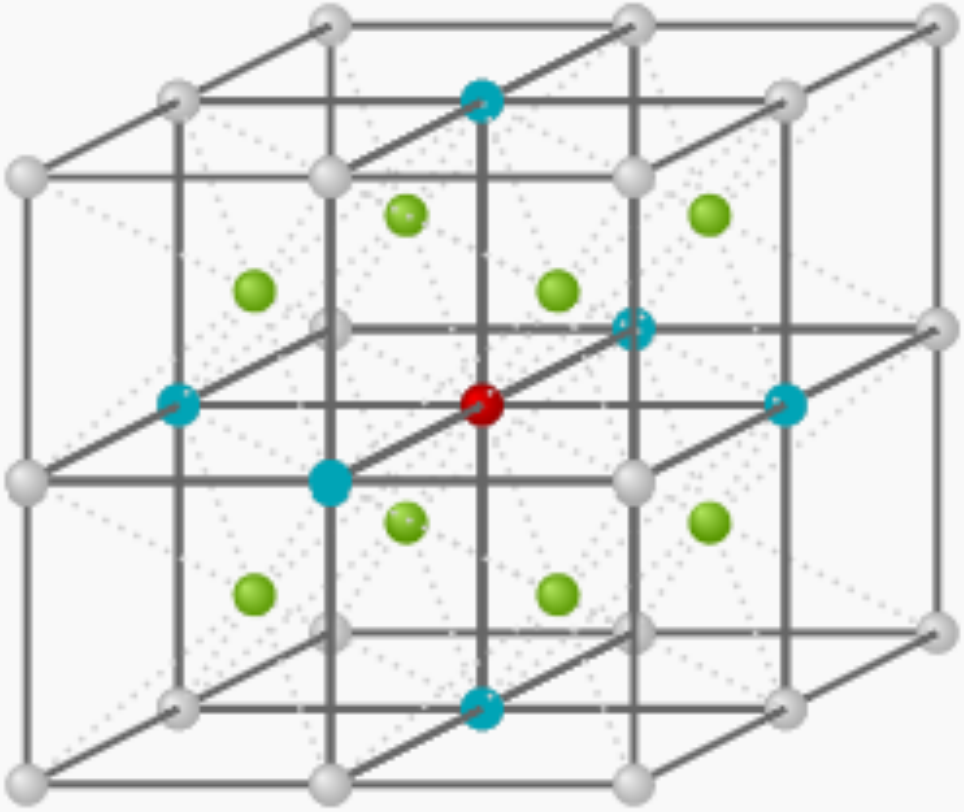
- BCC has two lattice points so BCC is a non-primitive cell.
- BCC has eight nearest neighbors. Each atom is in contact with its neighbors only along the body-diagonal directions.
- Many metals (Fe,Li,Na..etc), including the alkalis and several transition elements choose the BCC structure.





b-Body Centred Cubic (BCC)

Coordination number = 8

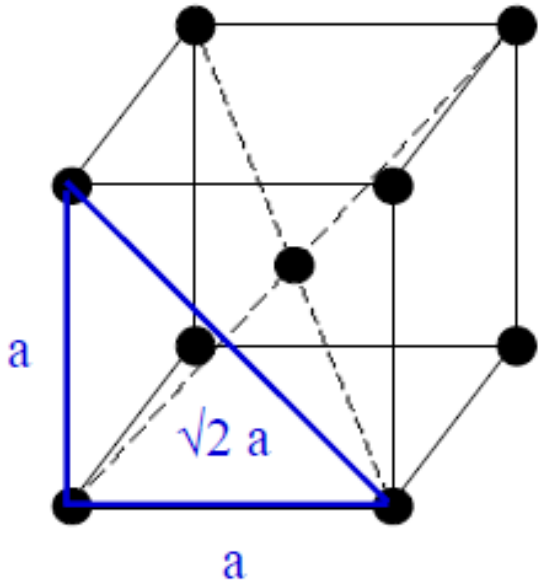


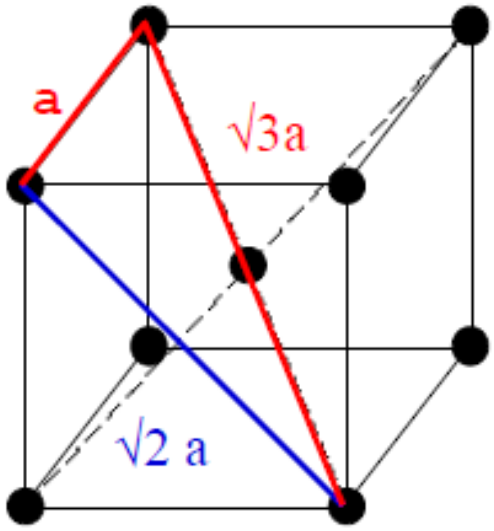
reference point

8 nearest neighbours

6 next-nearest neighbours

Cubic Packing - BCC

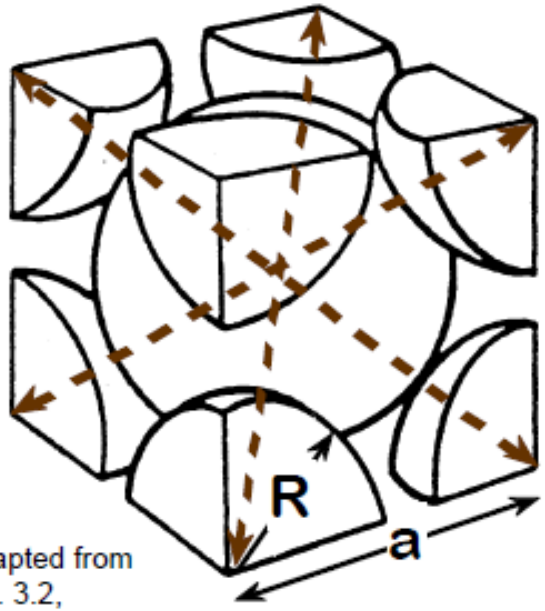




$\sqrt{3}a=4R$

$a=4R/\sqrt{3}$

ATOMIC PACKING FACTOR: BCC



Adapted from Fig. 3.2, *Callister 6e.*

Close-packed directions:

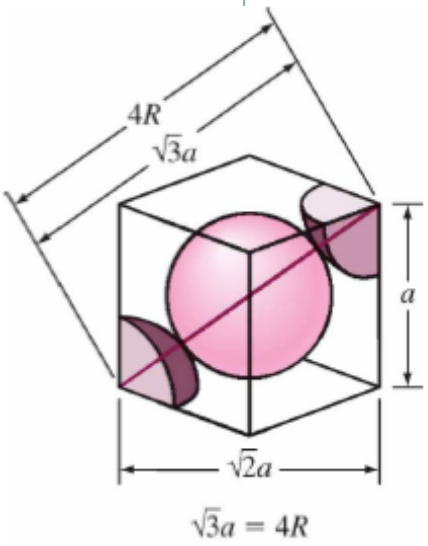
length = 4R

$= \sqrt{3}\, a$

Unit cell contains:

1 + 8 x 1/8

= 2 atoms/unit cell

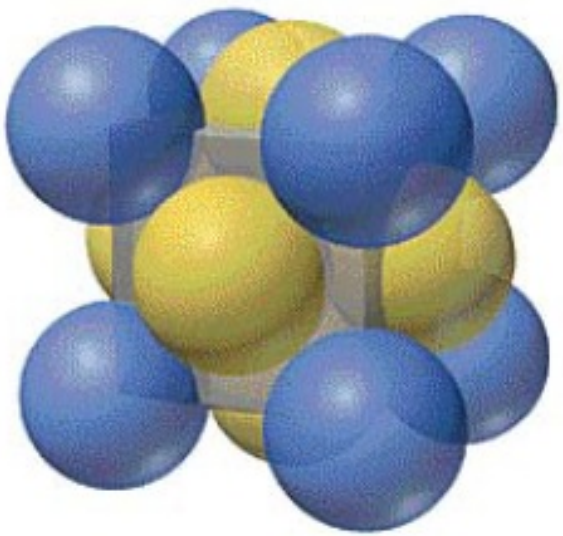


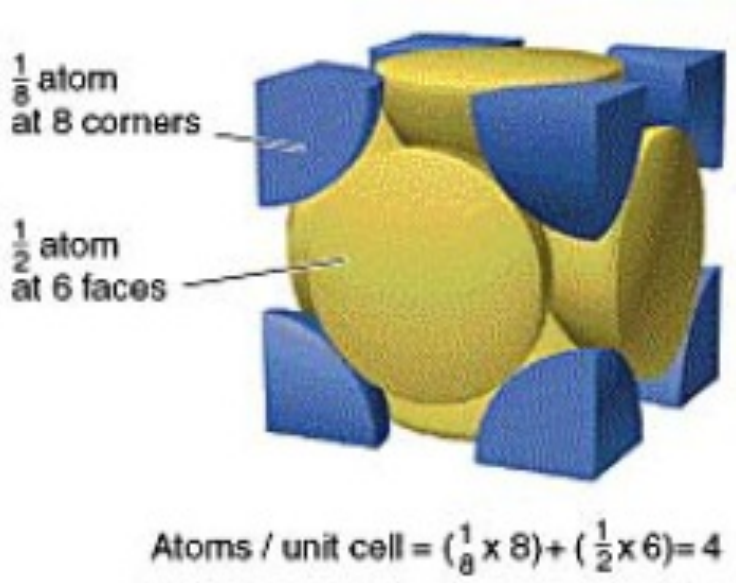
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{2 \cdot \frac{4}{3}\pi (\sqrt{3}a/4)^3}{a^3}$$

- APF for a body-centered cubic structure = $\pi\sqrt{3}/8 = 0.68$

c- Face Centred Cubic (FCC)

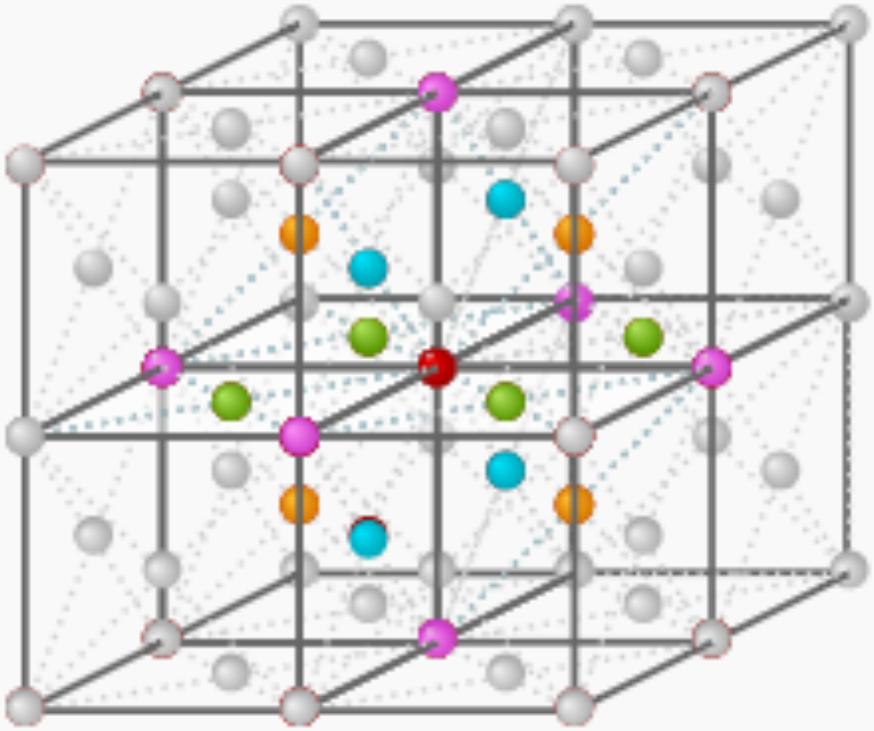
- There are atoms at the corners of the unit cell and at the centre of each face.
- Face centred cubic has 4 atoms so its non primitive cell.
- Many of common metals (Cu,Ni,Pb..etc) crystallize in FCC structure.





c- Face Centred Cubic (FCC)

Coordination number = 12

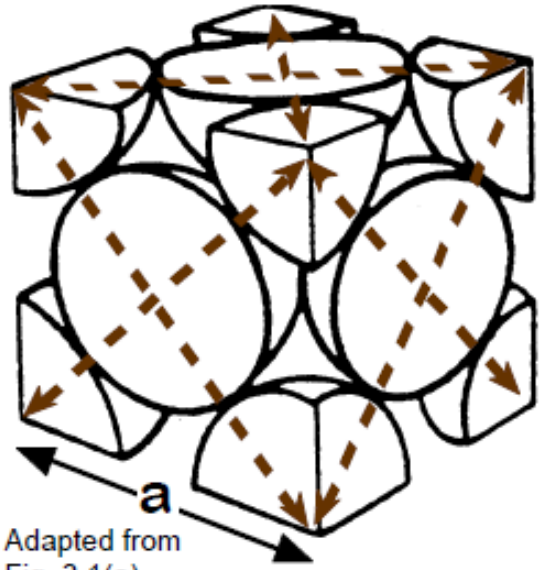


reference point

12 nearest neighbours

6 next-nearest neighbours

ATOMIC PACKING FACTOR: FCC



Adapted from Fig. 3.1(a), *Callister 6e.*

Close-packed directions:

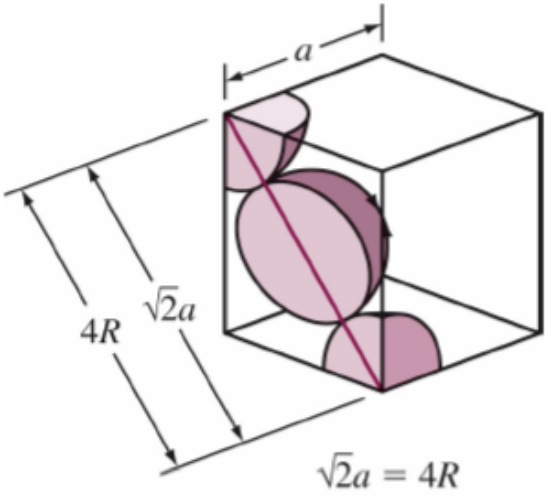
length = 4R

$= \sqrt{2}\, a$

Unit cell contains:

6 x 1/2 + 8 x 1/8

= 4 atoms/unit cell



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

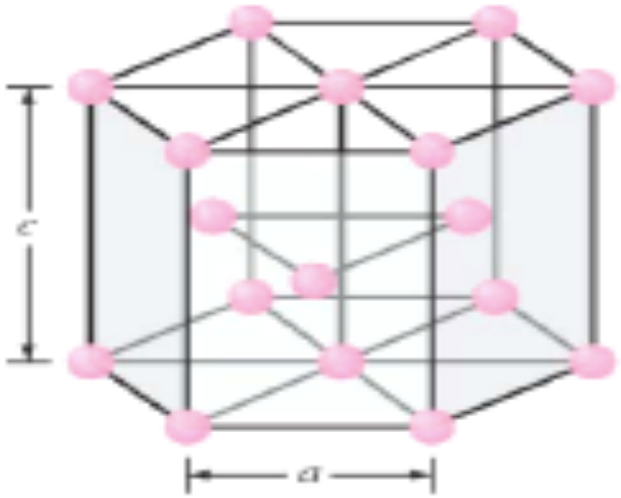
- APF for a body-centered cubic structure = $\pi/(3\sqrt{2}) = 0.74$

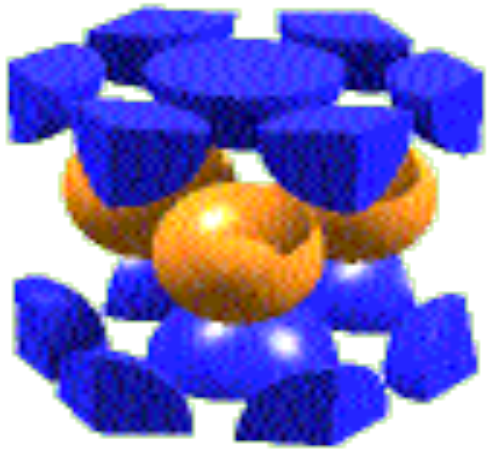
(best possible packing of identical spheres)

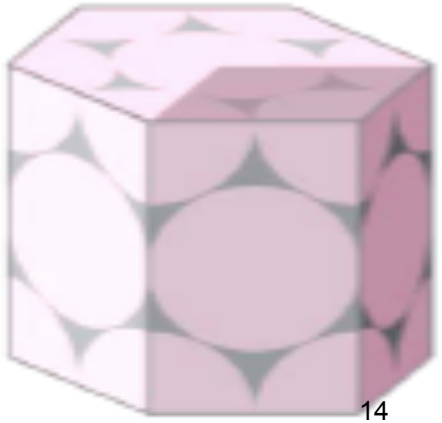
Hexagonal Close-packed Structure

Bravais Lattice : Hexagonal Lattice
He, Be, Mg, Hf, Re (Group II elements)

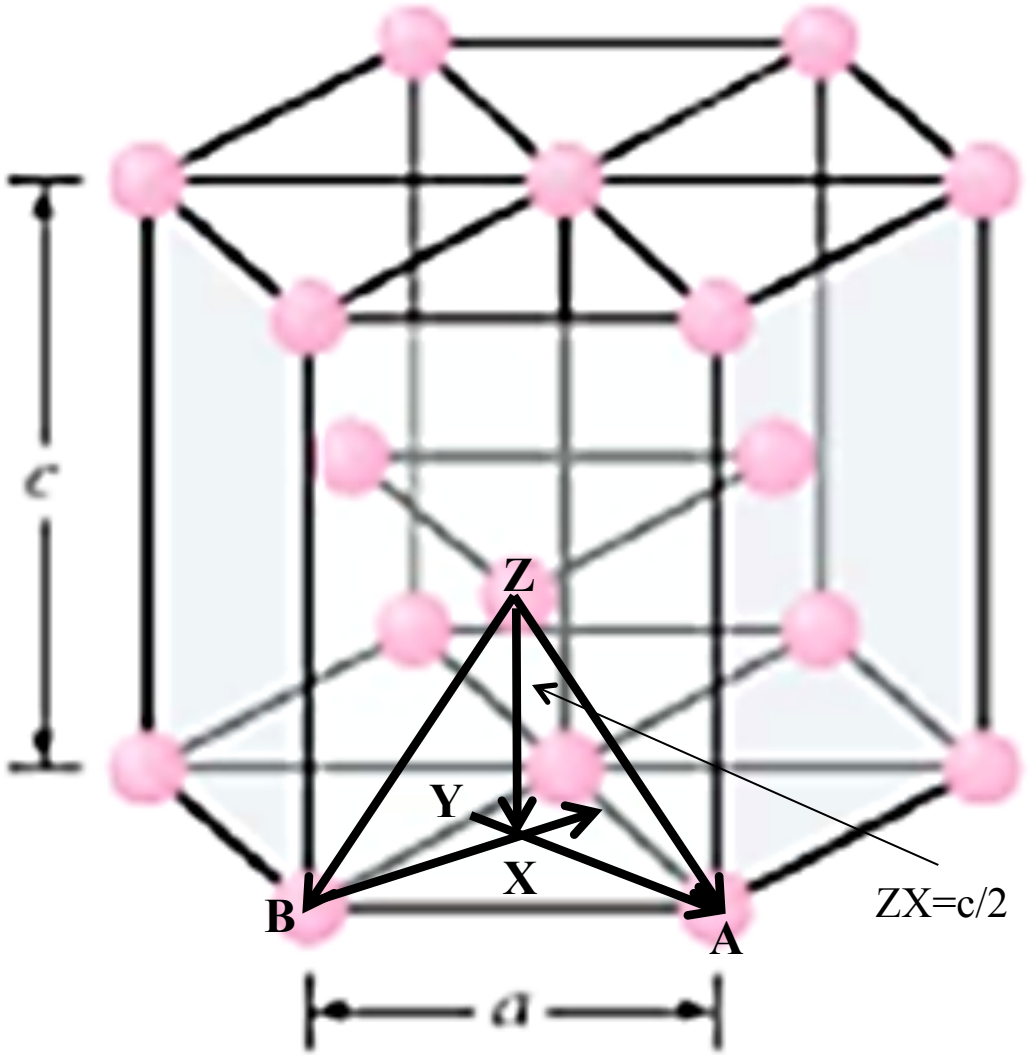
7 atoms at top and bottom layer and 3 atoms in central layer
total number of atoms in a unit cell is ***2×(1/2+6×1/6)+3=6***







~~*Imp:*~~ Calculation of c/a Ratio for an Ideal Hexagonal Close Packed Structure



In the ΔABY,

$$\cos 30^{o} = \frac{AY}{AB}$$

$$\therefore AY = a\cos 30^{o} = \frac{a\sqrt{3}}{2}$$

In the ΔAXZ

$$AX = \frac{2}{3}AY = \frac{2a}{3}\frac{\sqrt{3}}{2} = \frac{a}{\sqrt{3}}$$

$$(AZ)^2 = (AX)^2 + (ZX)^2$$

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

$$\frac{c}{a} = \left[\frac{8}{3}\right]^{1/2}$$

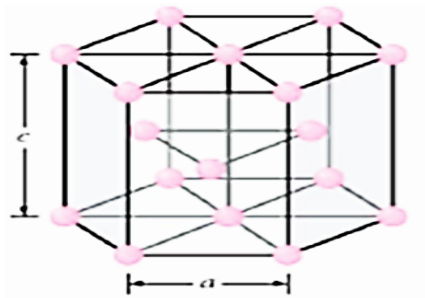
Volume of unit cell

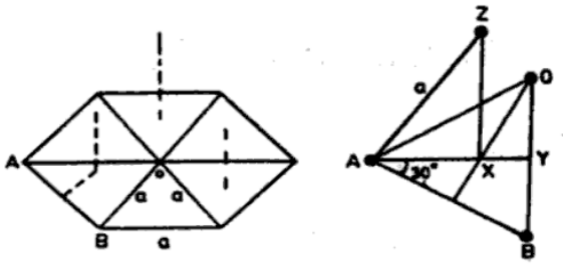
Area of the base=six times area of the ΔAOB

Area of ΔAOB = 1/2(BO)(AY)

= 1/2a×a√3/2

Thus area of the base is $3\sqrt{3}a^2/2$





VOLUME of the cell, V = $3\sqrt{3}a^2c/2$

Calculation of packing factor of hcp:

Coordination number , **N = 12**

Lattice constant , **a = 2r**

Nearest neighbor distance, **2r = a**

Number of atoms per unit cell, **n = 6**

Volume of all the atoms in a unit cell, $v = 6 \times \frac{4}{3}\pi r^3 = \pi a^3$

Volume of the unit cell $V = \frac{3}{2}\sqrt{3}a^2c$

Therefore , **APF=v/V=0.74**

Hence closely packed structure.

$$\frac{c}{a} = \left[\frac{8}{3}\right]^{1/2}$$

Packing efficiency

Describes the total volume occupied by atoms in the unit cell.

For a given atom radius, the higher the coordination, the higher the packing efficiency:

Cell Type	Coordination #	Packing Efficiency
Simple cubic	6	52%
Body-centered cubic	8	68%
Face-centered cubic	12	74%
Hexagonal	12	74%

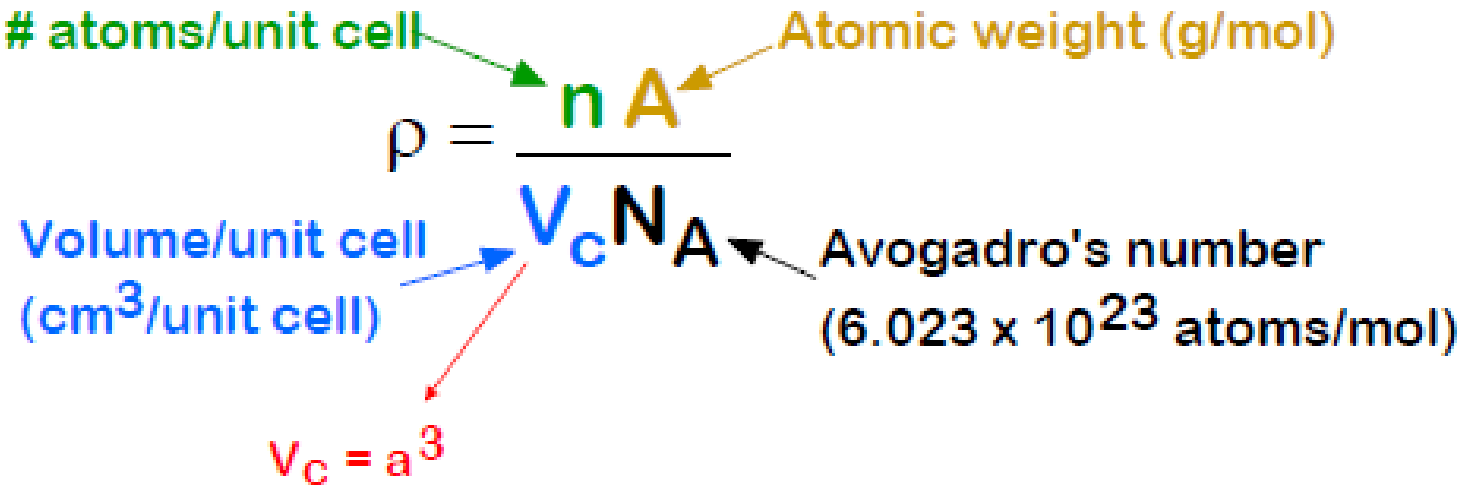
Most metallic elements pack in hexagonal closest packing lattice.
Many ionic compounds are fcc. (NaCl – two interspersed fcc lattices.)

THEORETICAL DENSITY, ρ

Density = mass/volume

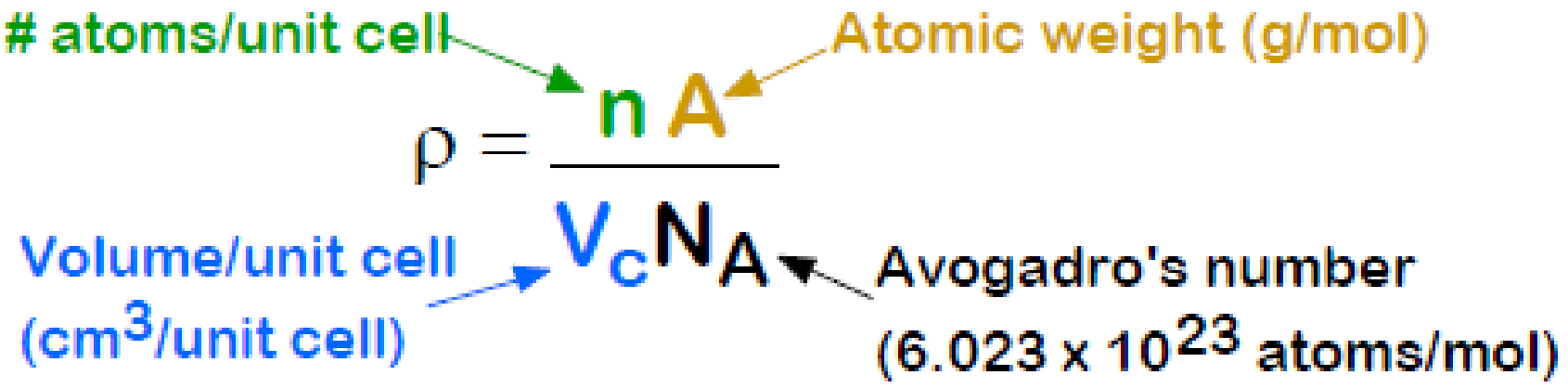
mass = number of atoms per unit cell * mass of each atom

mass of each atom = atomic weight/Avogadro's number



Atoms in the unit cell, n = 2 (BCC); 4 (FCC); 6 (HCP)
The volume of the cell, V_c = a^3 (SC, FCC and BCC)
a = 2R√2 (FCC); a = 4R/√3 (BCC),
where R is the atomic radius

THEORETICAL DENSITY, ρ

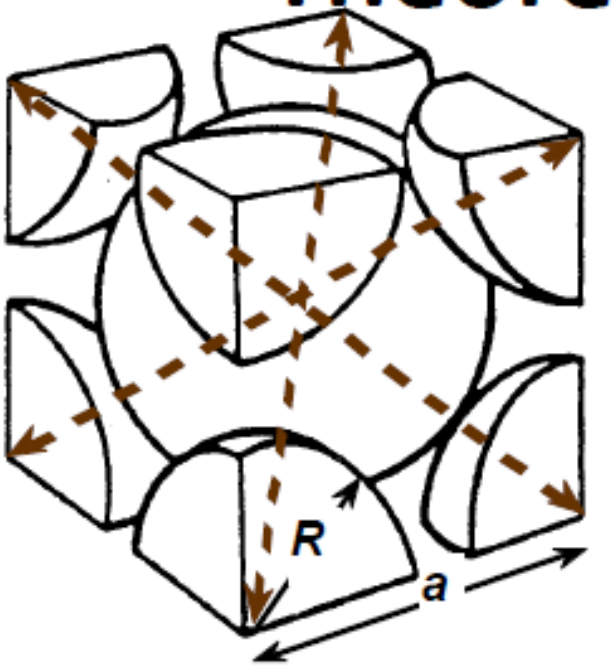


Example: Copper has a FCC structure with 4 atoms/unit cell. Its atomic weight and atomic radius R are 63.55 g/mol (1 amu = 1 g/mol) and 0.128 nm (1 nm = 10^{-7} cm) respectively. Find out the density of Copper.

Solution: $V_C = a^3$; For FCC, $a = 4R/\sqrt{2}$; $V_C = 4.75 \times 10^{-23} cm^3$

Result: theoretical $\rho_{Cu} = 8.89\ g/cm^3$

Theoretical Density, ρ



- Ex: Cr (BCC)

$A = 52.00$ g/mol

$R = 0.125$ nm

$n = 2$

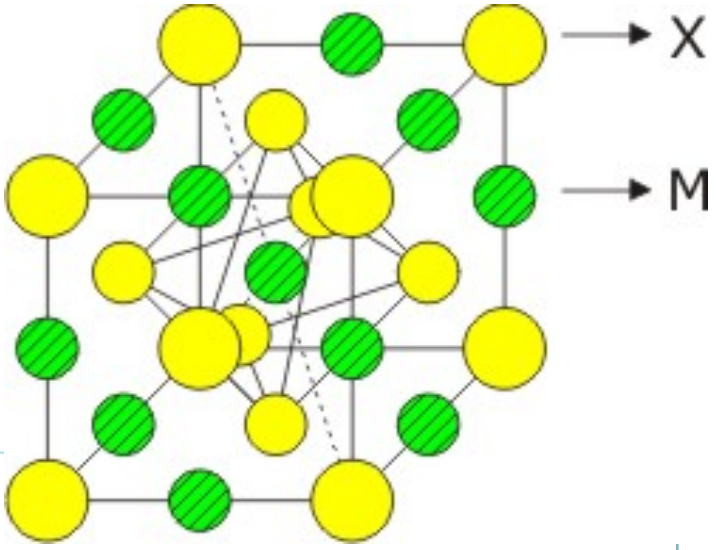
$a = 4R/\sqrt{3} = 0.2887$ nm

$$\rho = \frac{\text{atoms}}{\text{unit cell}} \times \frac{\text{g}}{\text{mol}} \times \frac{\text{volume}}{\text{unit cell}} \times \frac{\text{atoms}}{\text{mol}}$$

$$\rho = \frac{2 \times 52.00}{a^3 \times 6.023 \times 10^{23}}$$

$\rho_{theoretical}$	$= 7.18$ g/cm^3
ρ_{actual}	$= 7.19$ g/cm^3

Compounds based on FCC Packing of Ions



Rocksalt Structure

- MX Type Compounds Based on NaCl or Rocksalt Structure
- Anions (X) form the cation sub lattice with FCC structure.
- Cations (M) fill the octahedral sites.
- 100% occupancy of sites according to the stoichiometry since there will be one octahedral site per anion.
- Radius ratio, r_c/r_a is typically between 0.414 - 0.732 with some exceptions.
- Examples of ceramic materials with such structure as NaCl, MgO, NiO, FeO etc.

Numerical:

1. For NaCl: $M_A = 58.5$ $\rho = 2180 kg/m^3$
Calculate the spacing between the nearest neighboring ions

Ans: 0.282 nm

2. Zinc has hcp structure. The height of the unit cell is 0.494nm. The nearest neighbor's distance is 0.27nm. The atomic weight of the Zinc is 65.37. Calculate the volume of the unit cell and density of Zn.

Ans: $V = 9.35 \times 10^{-29} m^3$
$\rho = 6968\ kg/m^3$

3.Calculate the number of atoms /mm^2 in SC structure and FCC structure

Note: $N_A = 6.02 \times 10^{26}/kmol$
No. of molecules in a unit cell of NaCl=4