Structure of crystalline solids

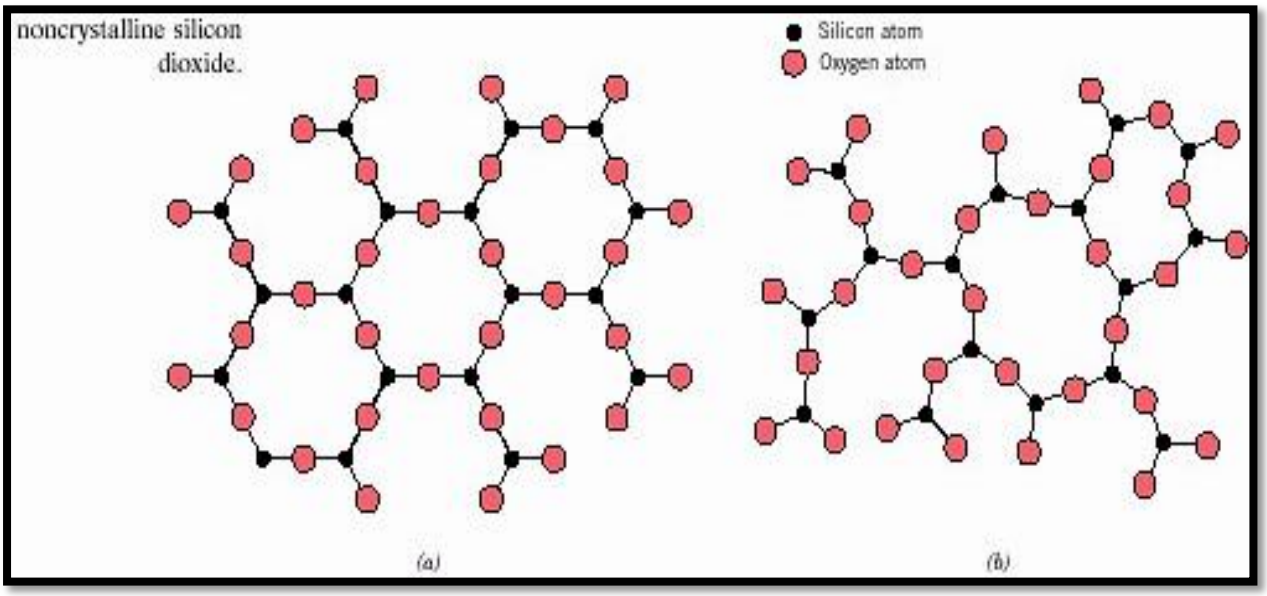
Types of Solids:

Crystalline material: atoms self-organize in a periodic array.

Single crystal: atoms are in a repeating or periodic array over the entire extent of the material.

Polycrystalline material: comprised of many small crystals or **grains**

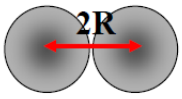
Amorphous: disordered – lack of a systematic atomic arrangement



Crystal structure

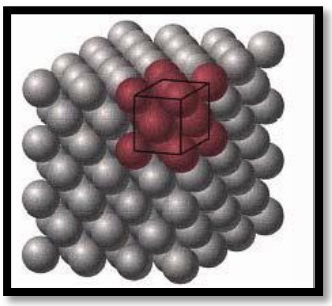
To discuss crystalline structures it is useful to consider atoms as being hard spheres with well-defined radii.

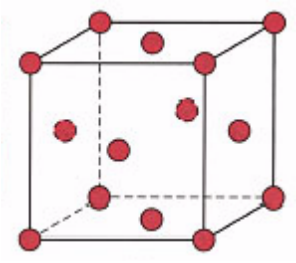
In this hard-sphere model, the shortest distance between two like atoms is one diameter of the hard sphere.



- hard-sphere model

We can also consider crystalline structure as a lattice of points at atom/sphere centers.





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:

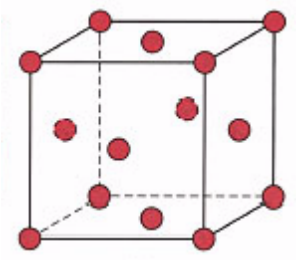
• faced-centered cubic (FCC)

• body-centered cubic (BCC)

• hexagonal close-packed (HCP).

1.Face-Centered Cubic (FCC) Crystal Structure

- Atoms are located at each of the corners and on the centers of all the faces of cubic unit cell
- Cu, Al, Ag, Au have this crystal structure



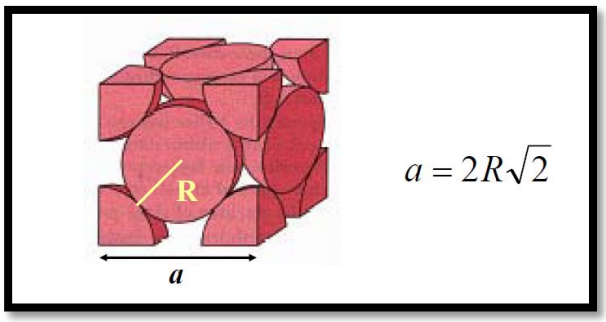
- The hard spheres touch one another across a face diagonal ⇒ the cube edge length, **a= 2R√2**
- **The coordination number, CN** = the number of closest neighbors to which an atom is bonded = number of touching atoms, **CN = 12**
- **Number of atoms per unit cell, n = 4**. (For an atom that is shared with m adjacent unit cells, we only count a fraction of the atom, 1/m). In FCC unit cell we have:

6 face atoms shared by two cells: 6 × 1/2 = 3

8 corner atoms shared by eight cells: 8 × 1/8 = 1

- **Atomic packing factor**, APF = fraction of volume occupied by hard spheres = (Sum of atomic volumes)/(Volume of cell) = 0.74 (maximum possible)

❖ Let's calculate the atomic packing factor for FCC crystal



APF = (Sum of atomic volumes)/(Volume of unit cell)

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

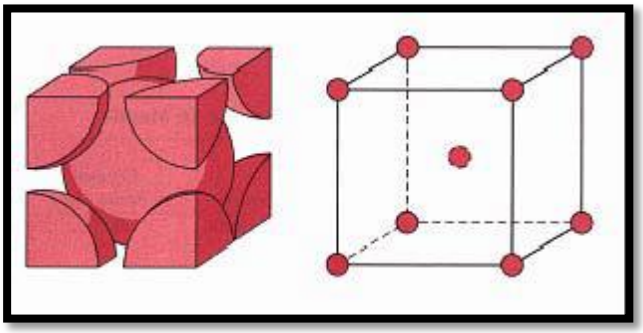
Volume of the unit cell: $a^3 = 16R^3\sqrt{2}$

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

maximum possible packing of hard spheres

2.Body-Centered Cubic (BCC) Crystal Structure

Atom at each corner and at center of cubic unit cell Cr, α-Fe, Mo have this crystal structure.



- The hard spheres touch one another along cube diagonal ⇒ the cube edge length, **a= 4R/√3**
- **The coordination number, CN = 8**
- **Number of atoms per unit cell, n = 2**

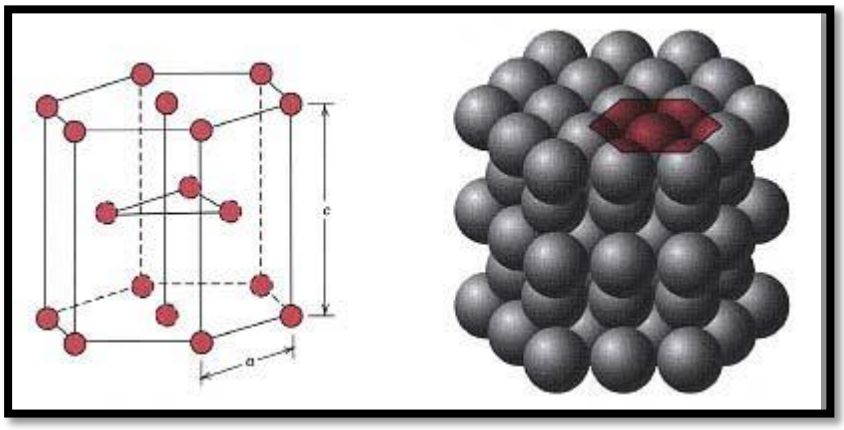
Center atom (1) shared by no other cells: 1 x 1 = 1

8 corner atoms shared by eight cells: 8 x 1/8 = 1

- **Atomic packing factor, APF = 0.68**
- Corner and center atoms are equivalent

3.Hexagonal Close-Packed Crystal Structure

- 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
- Cd, Mg, Zn, Ti have this crystal structure



- Unit cell has two lattice parameters a and c. Ideal ratio c/a = 1.633
- **The coordination number, CN = 12 (same as in FCC)**
- **Number of atoms per unit cell, n = 6**:

3 mid-plane atoms shared by no other cells: 3 x 1 = 3

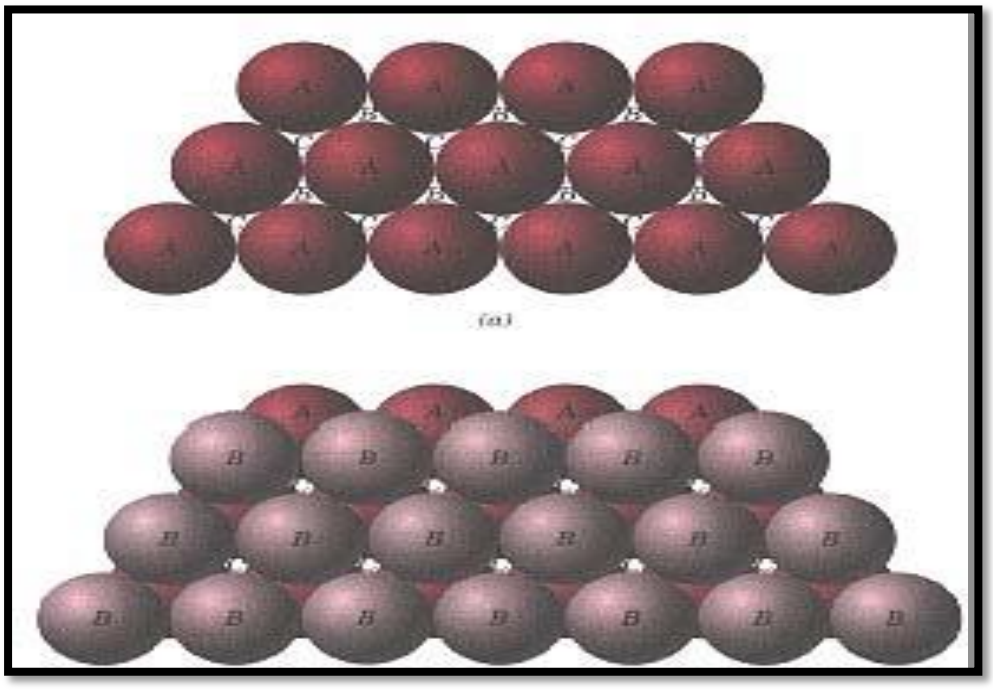
12 hexagonal corner atoms shared by 6 cells: 12 x 1/6 = 2

2 top/bottom plane center atoms shared by 2 cells: 2 x 1/2 = 1

- **Atomic packing factor, APF = 0.74 (same as in FCC)**
- All atoms are equivalent

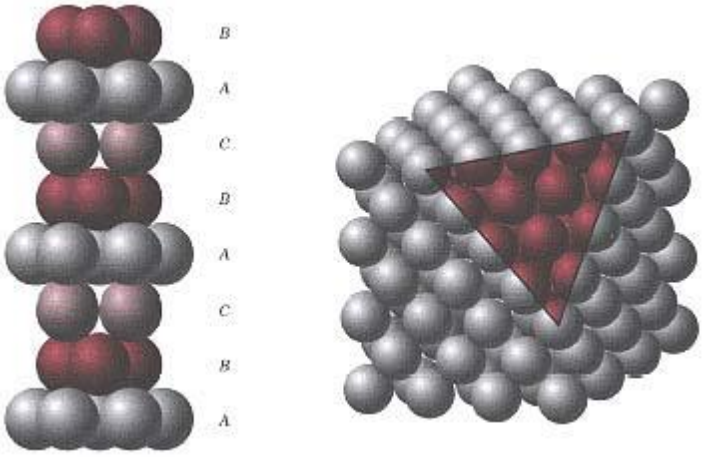
Close-packed Structures (FCC and HCP)

- Both FCC and HCP crystal structures have atomic packing factors of 0.74 (maximum possible value)
- Both FCC and HCP crystal structures may be generated by the stacking of close-packed planes.
- **The difference between the two structures is in the stacking sequence**

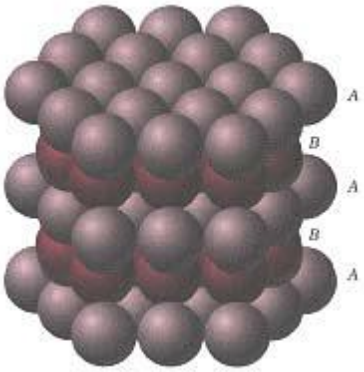


HCP: ABABAB... **FCC: ABCABCABC…**

FCC: Stacking Sequence ABCABCABC...



HCP: Stacking Sequence ABABAB...



Density Computations

Since the entire crystal can be generated by the repetition of the unit cell, the density of a crystalline material,

ρ **= the density of the unit cell = (atoms in the unit cell, n)** $\times$ **(mass of an atom, M) / (the volume of the cell, Vc)**

- Atoms in the unit cell, n = 2 (BCC); 4 (FCC); 6 (HCP)
- Mass of an atom, M = Atomic weight, A, in amu (or g/mol) is given in the periodic table.
- To translate mass from amu to grams we have to divide the atomic weight in amu by the **Avogadro number NA = 6.023 × 1023 atoms/mol**
- The volume of the cell, Vc = a3 (FCC and BCC) a = 2R√2 (FCC); a = 4R/√3 (BCC) ,where R is the atomic radius

Thus, the formula for the density is:

$$\rho = \frac{nA}{V_c N_A}$$

ex. Cu has FCC structure, atomic radius of 0.1278 nm, atomic mass of 63.54 g/mol calculate the density of Cu in Mg/m3.

FCC structure $\sqrt{2}\, a = 4\, R$

$a = 2\sqrt{2}\, R = 2\sqrt{2}\,(1.278 \times 10\text{-}10) = 3.61 \times 10\text{-}10\text{m}$

V = (3.61 × 10-10 m)3 = 4.70 × 10-29 m3 4 Cu per unit cell

$m = 4 \times 63.54 \times 1.66 \times 10\text{-}30\ \text{Mg} = 4.22 \times 10\text{-}28\ \text{Mg}$

$\rho_v = 4.22 \times 10\text{-}28\ \text{Mg} / 4.70 \times 10\text{-}29\ \text{m3}$

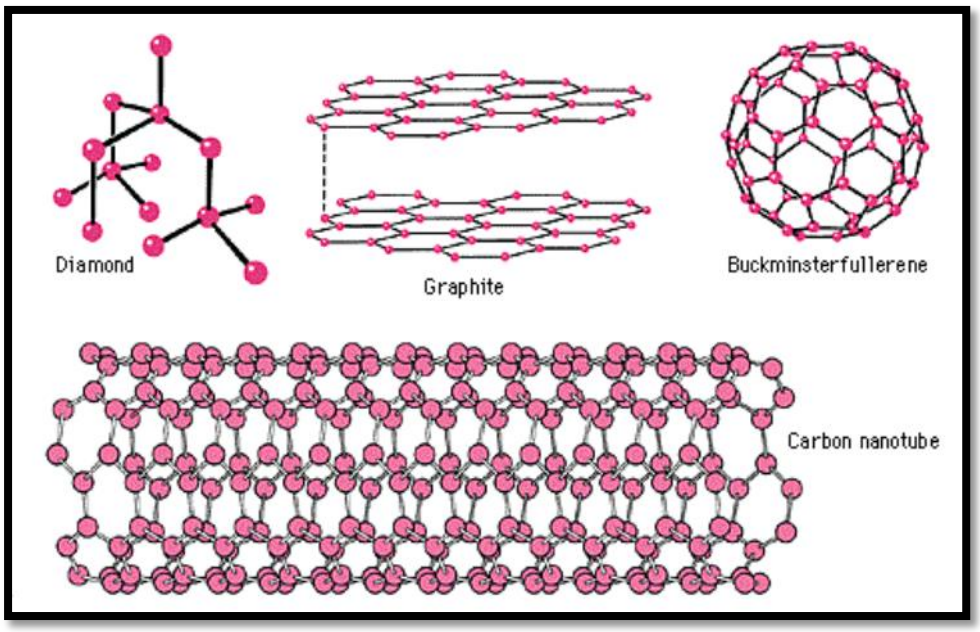
= 8.98 Mg/m3 (exp. = 8.96 Mg/m3)

Polymorphism and Allotropy

Some materials may exist in more than one crystal structure, this is called **polymorphism**.

If the material is an elemental solid, it is called **allotropy.**

An example of allotropy is carbon, which can exist as diamond, graphite, and amorphous carbon.



- Pure, solid carbon occurs in three crystalline forms – diamond, graphite; and large, hollow fullerenes.
- Two kinds of fullerenes are shown here: buckminsterfullerene (buckyball) and carbon nanotube.