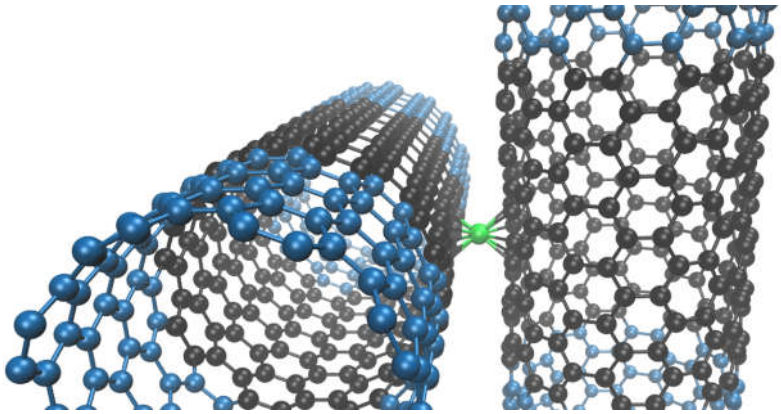
CRYSTAL STRUCTURES



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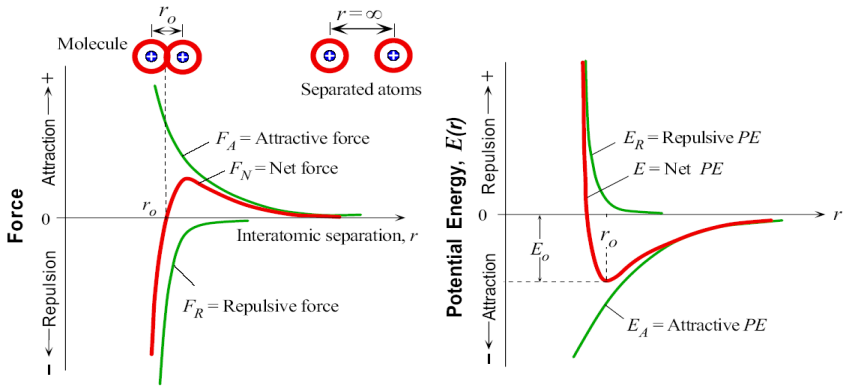
General Bonding Principle

- Net force, $F_N = F_A + F_R$, at equilibrium: $F_N = FA + FR = 0$.
- Potential Energy E(r) is related as $F_N = \frac{dE(r)}{dr}$



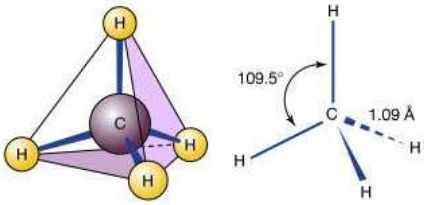
(a) Force vs r

(b) Potential energy vs r

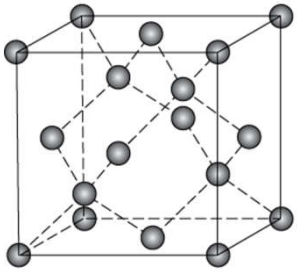
Covalently Bonded Solid: Diamond

- Due to the strong Coulombic attraction between the shared electrons and the positive nuclei, the covalent bond energy is usually the highest for all bond types, leading to very high melting temperatures and very hard solids: diamond is one of the hardest known materials.

C-H bond: Methane



C-C bond: Diamond



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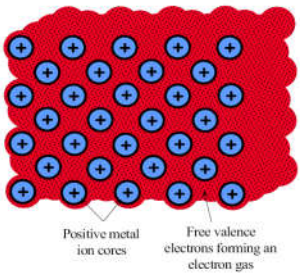
Metallic Bonding



The free electrons inside a metal can drift under the action of the applied field and give rise to a current. These free electrons in the metallic bond are called **conduction electrons**.

- **Metals are good electrical conductors**
- **Metals are also good thermal conductors**

Silver
© McGraw-Hill Education/Mark Dierker (mhhe022468.jpg)

Copper
© McGraw-Hill Education/Stephen Frisch (MHHE005312.JPG)

Aluminum (98.5%)
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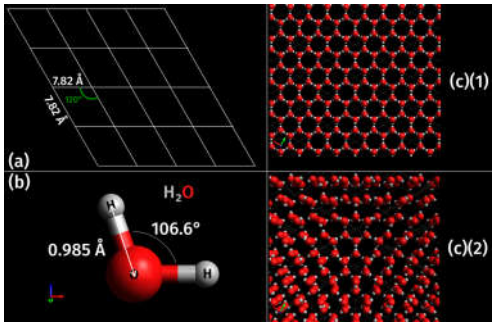
Crystalline Solids

- A crystalline solid is a solid object in which atoms bond with each other in a regular pattern to form a periodic collection or array of atoms.
- Most important property of a crystal is periodicity leading to long-range order (location of each atom is well-known by virtue of periodicity).
- Examples of periodic array/crystalline solids: nearly all metals, many ceramics, semiconductors, various polymers.



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Crystalline Solids

- **Crystal = Lattice + Basis**
- **Lattice** → an infinite periodic array of geometric points in space (without atoms)
- **Basis** → an identical group of atoms
- By putting the basis at each lattice point, we obtain the actual crystal.
- Thus the crystal becomes essentially a periodic repetition of a small volume, called the **unit cell**.
- The length of the cubic unit cell is called **lattice constant**.
- The repetition of the unit cell in 3D will generation the whole crystal.

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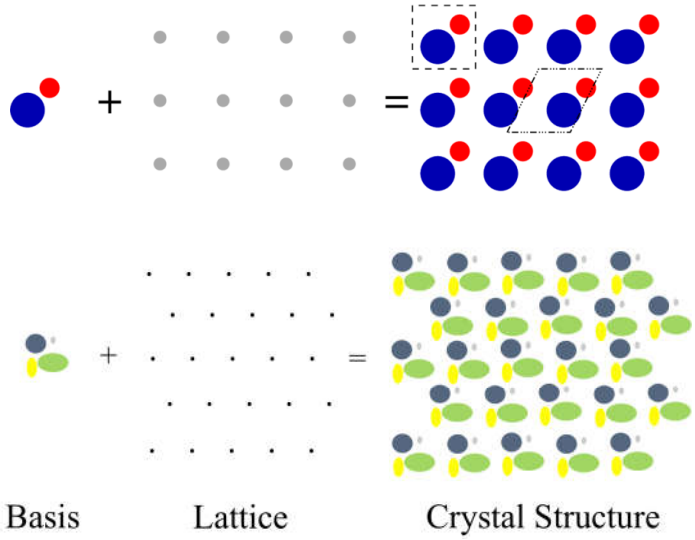
Lattice and Basis



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Packing of Solids

- Crystals can be
  - Face centered cubic, FCC
  - Body centered cubic, BCC
  - Hexagonal close packed, HCP

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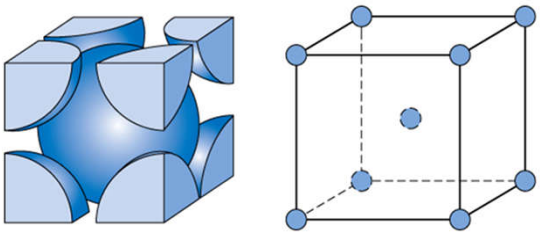
BCC



- Atom in the corner and one atom at the center
- In one BCC unit cell, there is one atom in the center, $1/8^{th}$ atom in 8 corners $\rightarrow$ Total of 2 atoms in BCC unit cell
- Coordination number: 8
- Example: Fe, Cr, Mo, W
- Close packed structure with a packing density of 68%

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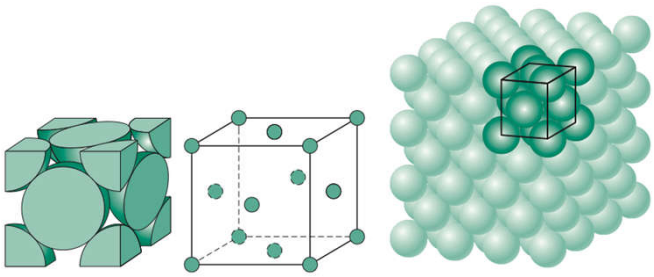
FCC



- Atoms in the corners and in the centers of the faces
- In one FCC unit cell, $1/8^{th}$ atom in 8 corners and ½ atom in each of 6-planes $\rightarrow$ Total of 4 atoms in FCC unit cell
- Coordination number: 12
- Examples: Ag, Au, Cu, Pt
- Close packed structure with a packing density of 74%.

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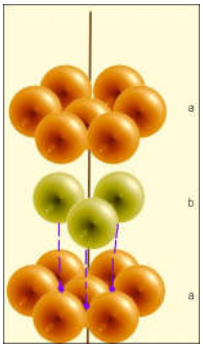
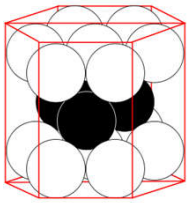
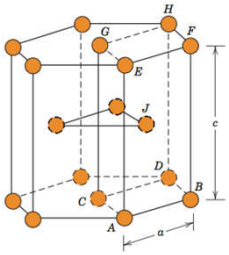
HCP







- On top of layer a, we can place an identical layer b, with the spheres taking up the voids on layer a. The third layer can be placed on top of b and lined up with layer a.
- The stacking sequence is abab …
- Number of atoms per unit cell: 6, 2
- Coordination number: 12
- Examples: Many metals → Co, Mg, Ti, Zn

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Atomic Packing Factor

- **Atomic packing factor** (APF), **packing efficiency** or **packing fraction** is the fraction of volume in a crystal that is occupied by constituent particles → a dimensionless quantity and always less than unity.
- APF is determined by assuming that atoms are rigid spheres. Radius of spheres is taken to be the maximum (atoms do not overlap). For crystals with only one type of particle, the APF is

$$\text{APF} = \frac{N_{\text{particle}} V_{\text{particle}}}{V_{\text{unit cell}}}$$

N_{particle} : number of particles in the unit cell; V_{particle} : volume of each particle; and $V_{\text{unit cell}}$: volume occupied by the unit cell.

- For one-component structures, the maximum APF is about 0.74 → close-packed structures. For multiple-component structures, the APF can exceed 0.74.
- APF explains many properties of materials. Metals with a high APF will have a higher "workability" (malleability or ductility).

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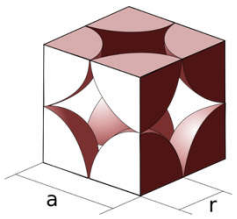
APF of BCC

$$\text{APF} = \frac{N_{\text{particle}} V_{\text{particle}}}{V_{\text{unit cell}}}$$

- **Simple cubic:**

$$a = 2r$$

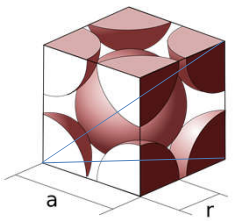
$$\text{APF} = \frac{1 \cdot \frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6} \approx 0.5236$$



- **Body centered cubic:**

$$a = \frac{4r}{\sqrt{3}}$$

$$\text{APF} = \frac{2 \cdot \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{\pi\sqrt{3}}{8} \approx 0.6802$$



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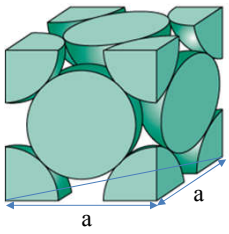
APF of FCC

$$\text{APF} = \frac{N_{\text{particle}} V_{\text{particle}}}{V_{\text{unit cell}}}$$

$$a = 2\sqrt{2}r$$

$$\text{APF} = \frac{4 \cdot \frac{4}{3}\pi r^3}{\left(2\sqrt{2}r\right)^3} = \frac{\pi}{\sqrt{18}} \approx 0.7405$$



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APF of HCP

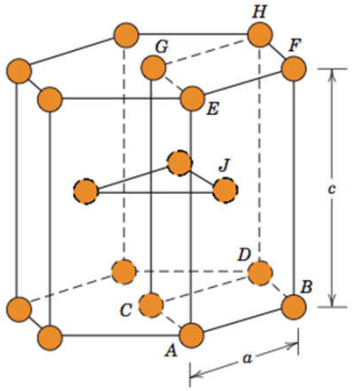
$$\text{APF} = \frac{N_{\text{particle}} V_{\text{particle}}}{V_{\text{unit cell}}} = ?$$

$V_{\text{unit cell}} = ?$

$V_{\text{unit cell}} = \frac{3\sqrt{3}}{2} a^2 c$

$a = ?$
c $= ?$

$a = 2r$



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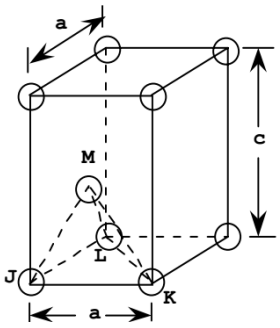
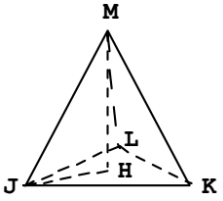
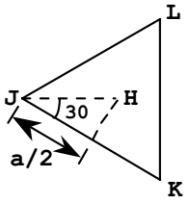
APF of HCP

c =?







$\overline{MH} = c/2.$ $\overline{JM} = \overline{JK} = 2R = a$

$(\overline{JM})^2 = (\overline{JH})^2 + (\overline{MH})^2$ $a^2 = (\overline{JH})^2 + \left(\frac{c}{2}\right)^2$

$\cos 30° = \frac{a/2}{JH} = \frac{\sqrt{3}}{2}$ $\overline{JH} = \frac{a}{\sqrt{3}}$

$a^2 = \left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{c}{2}\right)^2 = \frac{a^2}{3} + \frac{c^2}{4}$

$\frac{c}{a} = \sqrt{\frac{8}{3}}$

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APF of HCP

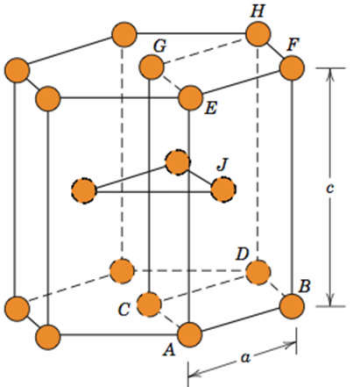
$$\text{APF} = \frac{N_{\text{particle}} V_{\text{particle}}}{V_{\text{unit cell}}}$$

$V_{\text{unit cell}} = ?$

$$V_{\text{unit cell}} = \frac{3\sqrt{3}}{2} a^2 c$$

$$a = 2r$$

$$c = \sqrt{\frac{2}{3}} \cdot 4r$$



$$\text{APF} = \frac{6 \cdot \frac{4}{3}\pi r^3}{\frac{3\sqrt{3}}{2} a^2 c} = \frac{6 \cdot \frac{4}{3}\pi r^3}{\frac{3\sqrt{3}}{2} (2r)^2 \sqrt{\frac{2}{3}} \cdot 4r}$$

$$= \frac{\pi}{\sqrt{18}} \approx 0.7405$$

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