

# 결정화 응용기술-입문

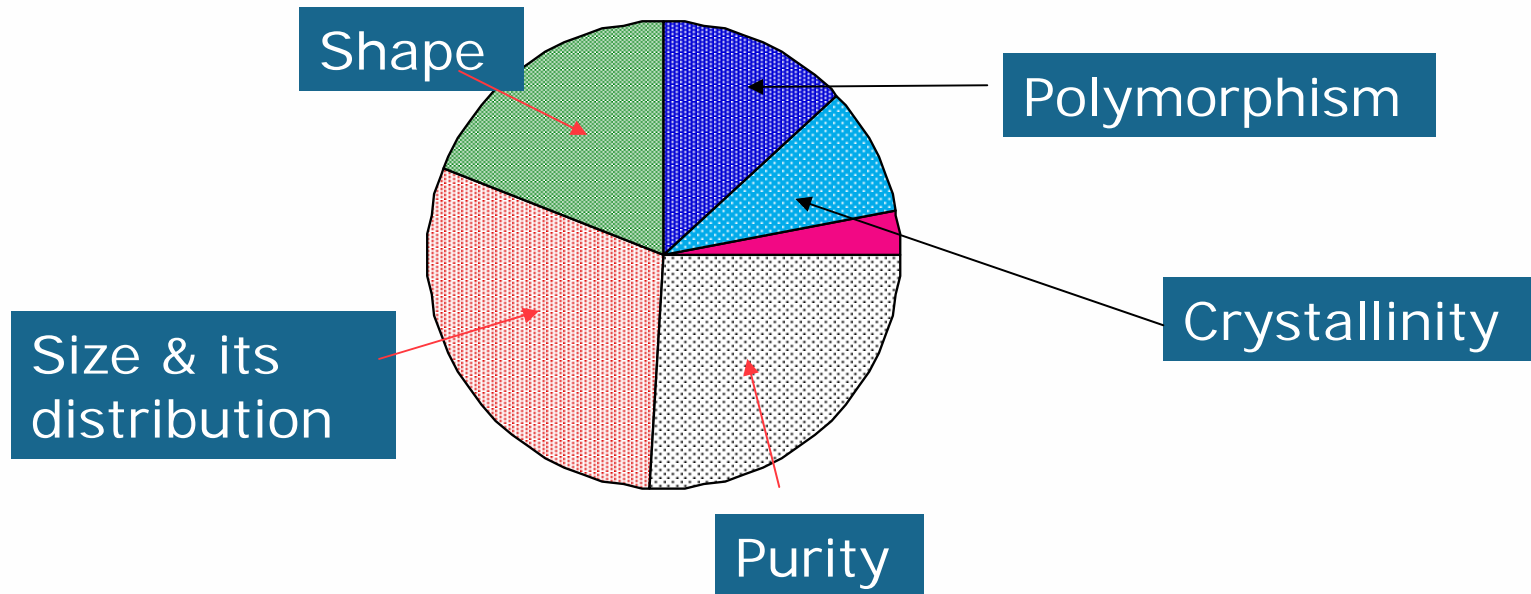


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# Troubles in crystallization process

Characteristics whose control are difficult.

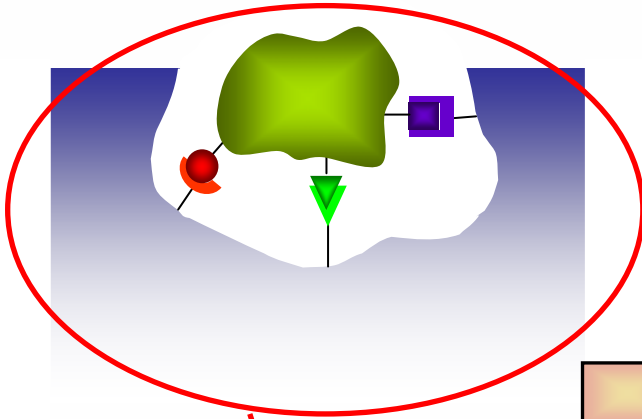


Questionnaire data (300 companies in 1998)  
[courtesy of H. Ooshima]

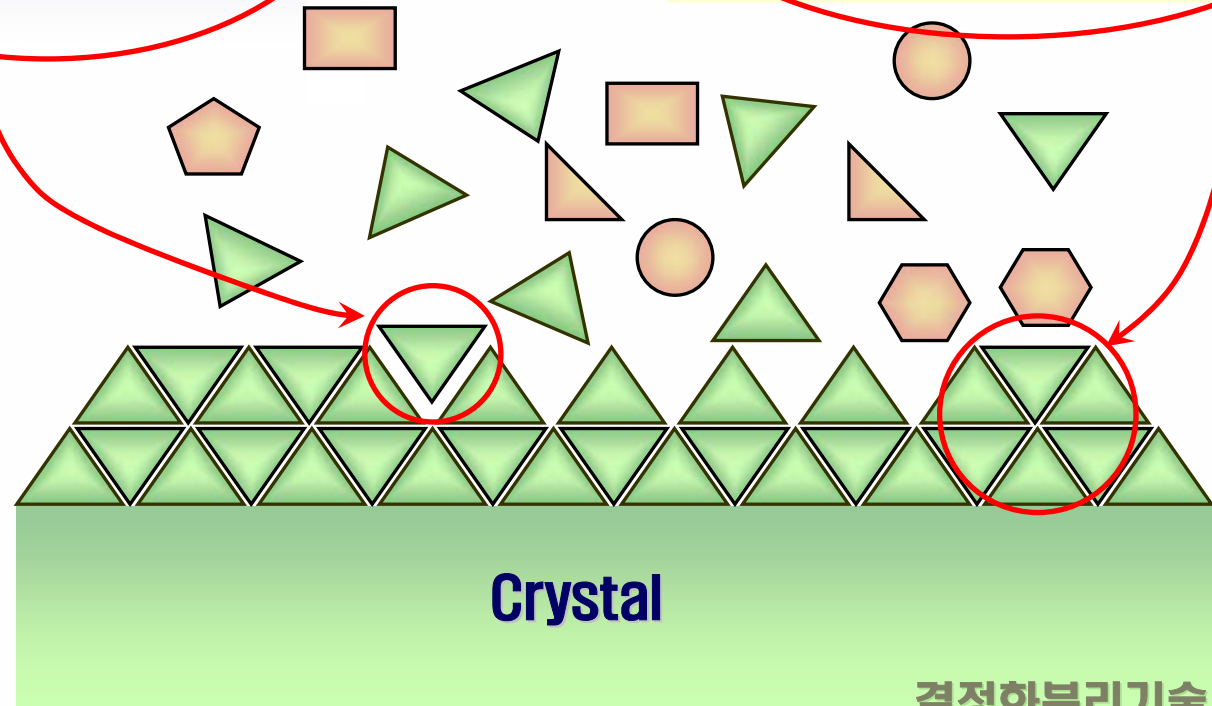
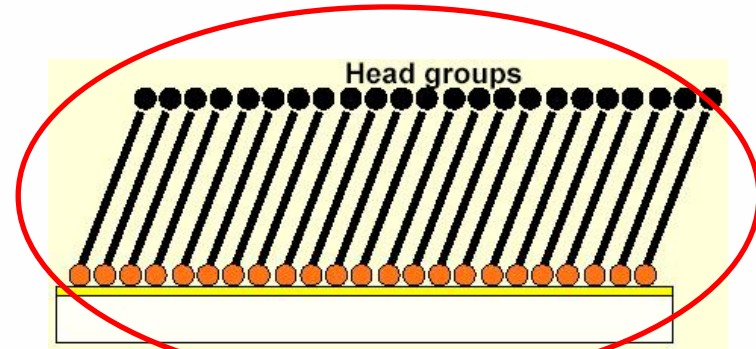


# Why crystallization?

## ➤ Molecular Recognition



## ➤ Self Assembly

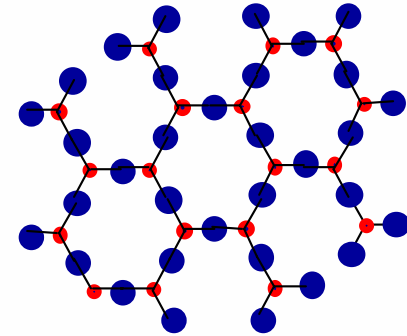


# What are crystals and how do we recognize them.

## ◆ Solid defined by way of constituent packing

### Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of:
  - metals
  - many ceramics
  - some polymers

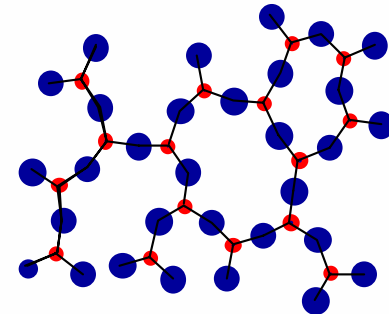


crystalline SiO<sub>2</sub>

• Si      • Oxygen

### Noncrystalline materials...

- atoms have no periodic packing
- occurs for:
  - complex structures
  - rapid cooling



noncrystalline SiO<sub>2</sub>

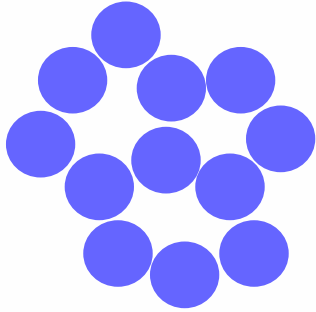
Adapted from Fig. 3.18(b),  
*Callister 6e.*

"Amorphous" = Noncrystalline

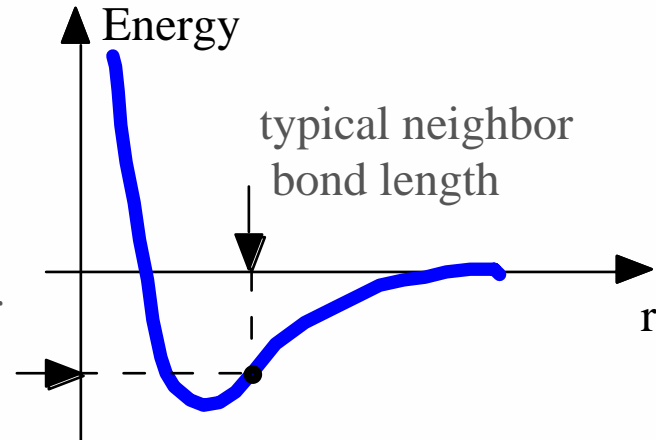


# ENERGY AND PACKING

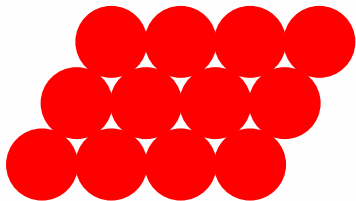
- Non dense, **random** packing



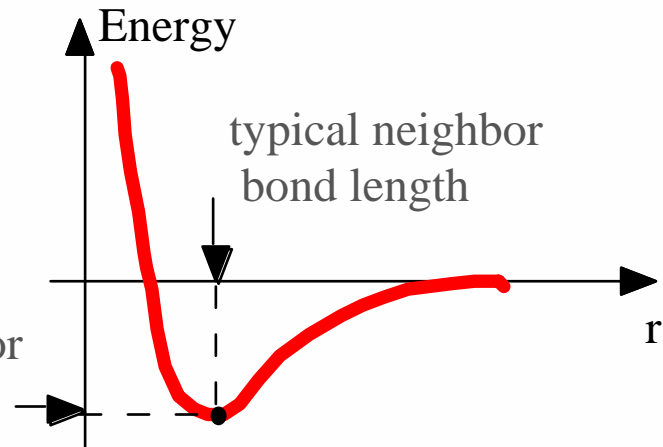
typical neighbor  
bond energy



- Dense, **regular** packing



typical neighbor  
bond energy

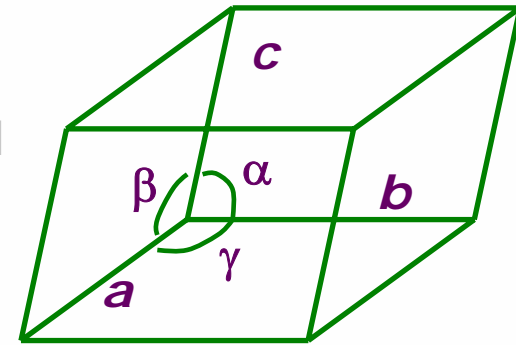


Dense, regular-packed structures tend to have lower energy.



# Crystal

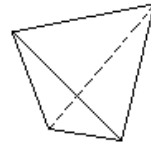
- ◆ Space group : six parameter to define three dimensional space of unit cell



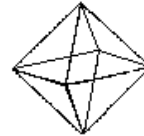
## Crystal system (7 systems)

- Cubic  $(a=b=c)$   $(\alpha=\beta=\gamma=90^\circ)$  NaCl, KCl
- Hexagonal  $(a=b \neq c)$   $(\alpha=\beta=\gamma=90^\circ)$  AgI, graphite, ice
- Tetragonal  $(a=b \neq c)$   $(\alpha=\beta=90^\circ, \gamma=120^\circ)$  Alum, diamond, rutile
- Trigonal  $(a=b=c)$   $(\alpha=\beta=\gamma \neq 90^\circ)$  Ruby, sphire,  $\text{NaNO}_3$
- Orthorhombic  $(a \neq b \neq c)$   $(\alpha=\beta=\gamma=90^\circ)$   $\text{AgNO}_3$ ,  $\alpha$ -sulphur
- Monoclinic  $(a \neq b \neq c)$   $(\alpha=\gamma=90^\circ \neq \beta)$  sucrose,  $\beta$ -sulphur
- Triclinic  $(a \neq b \neq c)$   $(\alpha=\beta=\gamma \neq 90^\circ)$  copper sulphate

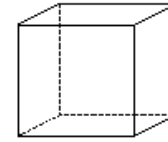




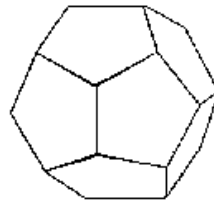
**Tetrahedron (4)**



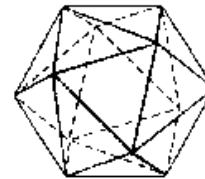
**Octahedron (6)**



**Cube (8)**

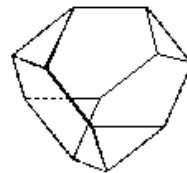


**Pentagonal Dodecahedron (20)**

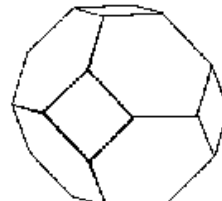


**Icosahedron (20)**

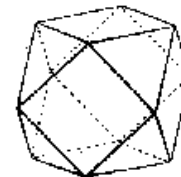
### The regular solid polyhedra



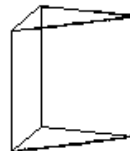
**Truncated Tetrahedron (12)**



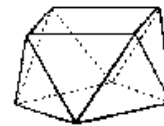
**Truncated Octahedron (24)**



**Cuboctahedron (12)**



**Trigonal prism (5)**



**Squara Antiprism (8)**

### Archimedean semi-regular solid polyhedra



## ◆ The fourteen Bravais lattices

Symmetry	lattice	crystal system
Cubic	cube	regular
	body-centered cube	
	face-centered cube	
Tetragonal	square prism	tetragonal
	body-centered square prism	
Orthorhombic	rectangular prism	orthorhombic
	body-centered rectangular prism	
	rhombic prism	
	body-centered rhombic prism	
Monoclinic	monoclinic parallelepiped	monoclinic
	clinorhombic prism	
Triclinic	triclinic parallelepiped	triclinic
Rhombohedral	rhombohedron	trigonal
Hexagonal	hexagonal prism	hexagonal

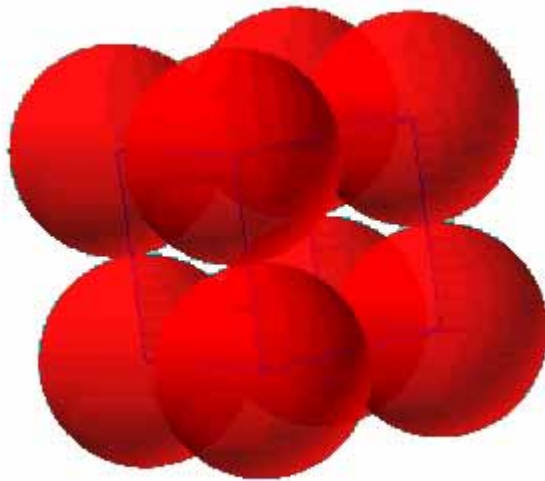
230 combinations; 32 points groups



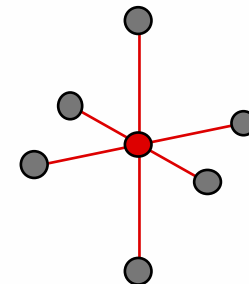
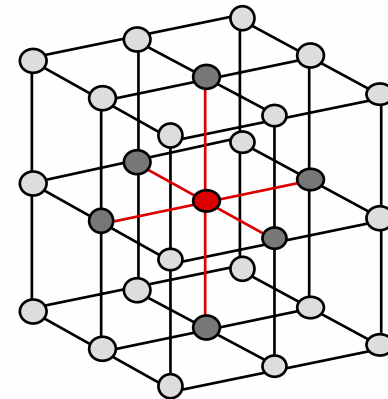


# SIMPLE CUBIC STRUCTURE (SC)

- Rare due to poor packing (only Po has this structure)
- **Close-packed directions** are cube edges.
- **Coordination # = 6**  
(# nearest neighbors)



(Courtesy P.M. Anderson)

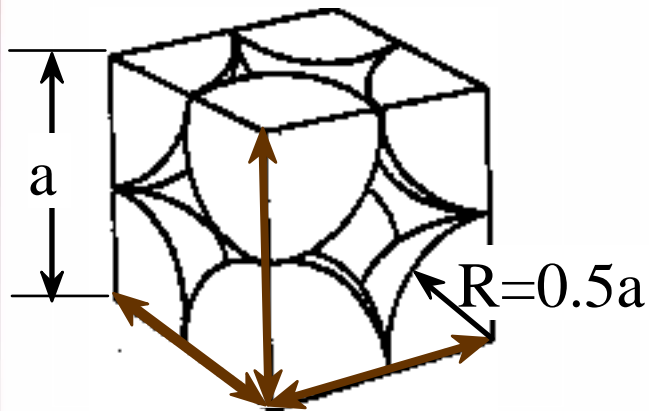


# ATOMIC PACKING FACTOR

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

\*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains  $8 \times 1/8 =$

**1 atom/unit cell**

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

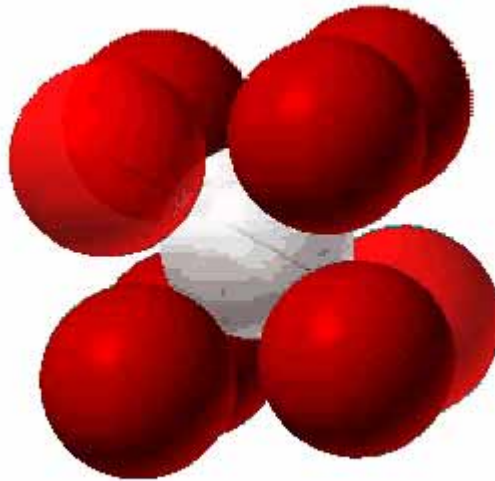
The diagram shows the calculation of the Atomic Packing Factor (APF) for a simple cubic structure. The numerator represents the total volume of atoms in the unit cell, calculated as the number of atoms per unit cell (1) multiplied by the volume of a single atom ( $\frac{4}{3} \pi (0.5a)^3$ ). The denominator represents the volume of the unit cell ( $a^3$ ). Annotations include: 'atoms unit cell' pointing to the '1', 'volume atom' pointing to the atom volume term, and 'volume unit cell' pointing to the  $a^3$  term.



Adapted from Fig. 3.19,  
Callister 6e.

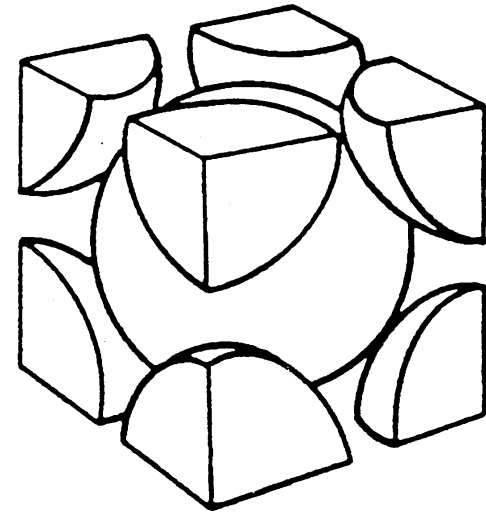
# BODY CENTERED CUBIC STRUCTURE (BCC)

- Close packed directions are cube diagonals.
  - Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.



(Courtesy P.M. Anderson)

- Coordination # = 8

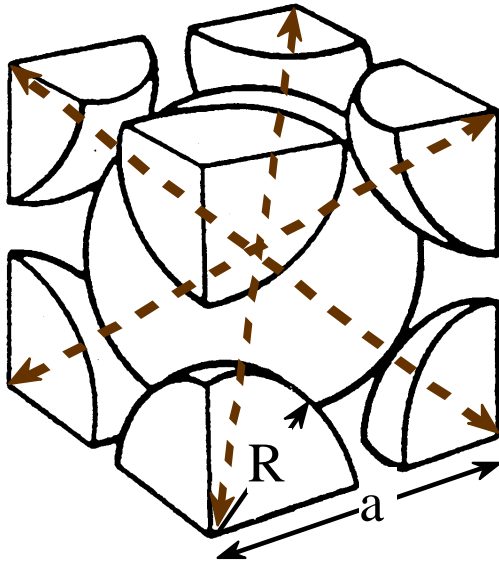


Adapted from Fig. 3.2,  
*Callister 6e.*



# ATOMIC PACKING FACTOR: BCC

- APF for a body-centered cubic structure = 0.68



Close-packed directions:

$$\begin{aligned} \text{length} &= 4R \\ &= \sqrt{3} a \end{aligned}$$

Unit cell contains:

$$\begin{aligned} &1 + 8 \times 1/8 \\ &= 2 \text{ atoms/unit cell} \end{aligned}$$

Adapted from  
Fig. 3.2,  
Callister 6e.

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

← volume atom

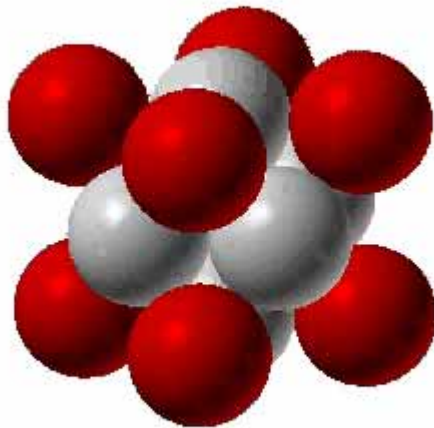
← volume unit cell



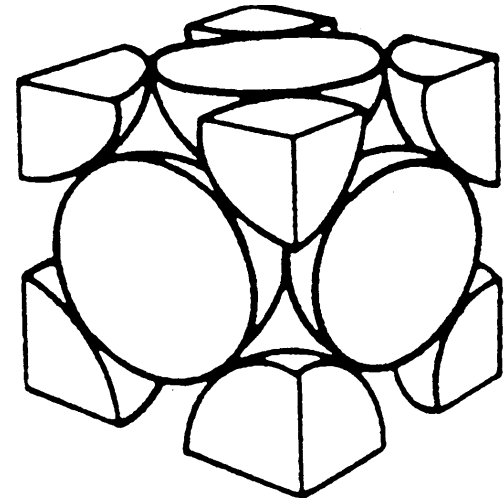
# FACE CENTERED CUBIC STRUCTURE (FCC)

- Close packed directions are face diagonals.  
-Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

- Coordination # = 12



(Courtesy P.M. Anderson)

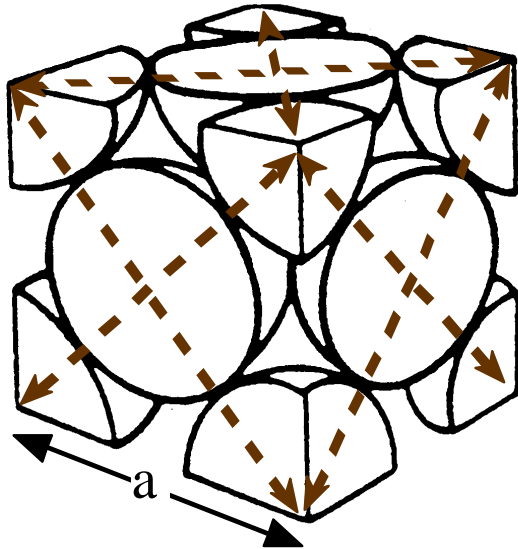


Adapted from Fig. 3.1(a),  
*Callister 6e.*



# ATOMIC PACKING FACTOR: FCC

- APF for a body-centered cubic structure = 0.74



Close-packed directions:

$$\begin{aligned} \text{length} &= 4R \\ &= \sqrt{2} a \end{aligned}$$

Unit cell contains:

$$\begin{aligned} &6 \times 1/2 + 8 \times 1/8 \\ &= 4 \text{ atoms/unit cell} \end{aligned}$$

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

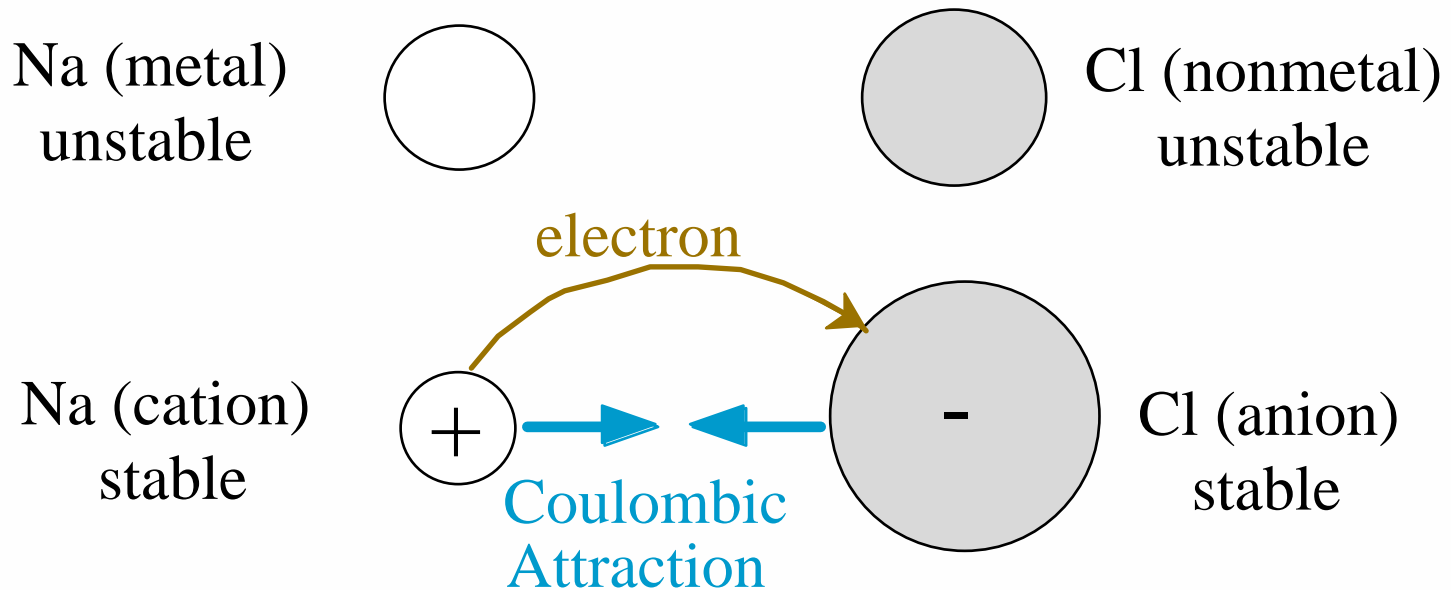
$$\text{APF} = \frac{\text{atoms/unit cell} \times \frac{4}{3} \pi \left(\frac{\sqrt{2} a}{4}\right)^3}{a^3}$$

$\frac{\text{volume}}{\text{atom}}$ 
 $\frac{\text{volume}}{\text{unit cell}}$



# IONIC BONDING

- Occurs between + and - ions.
- Requires **electron transfer**.
- Large difference in electronegativity required.
- Example: NaCl



# EXAMPLES: IONIC BONDING

IA	IIA		III A - VIII										IX A - VIIA						0
H 2.1																			He -
Li 1.0	Be 1.5																		Ne -
Na 0.9	Mg 1.2																		Ar -
K 0.8	Ca 1.0		Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.8	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr -	
Rb 0.8	Sr 1.0		Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe -	
Cs 0.7	Ba 0.9		57-71 La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn -	
Fr 0.7	Ra 0.9		80-100 Ac-No 1.1-1.7																



Give up electrons



Acquire electrons

Adapted from Fig. 2.7, Callister 6e. (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.





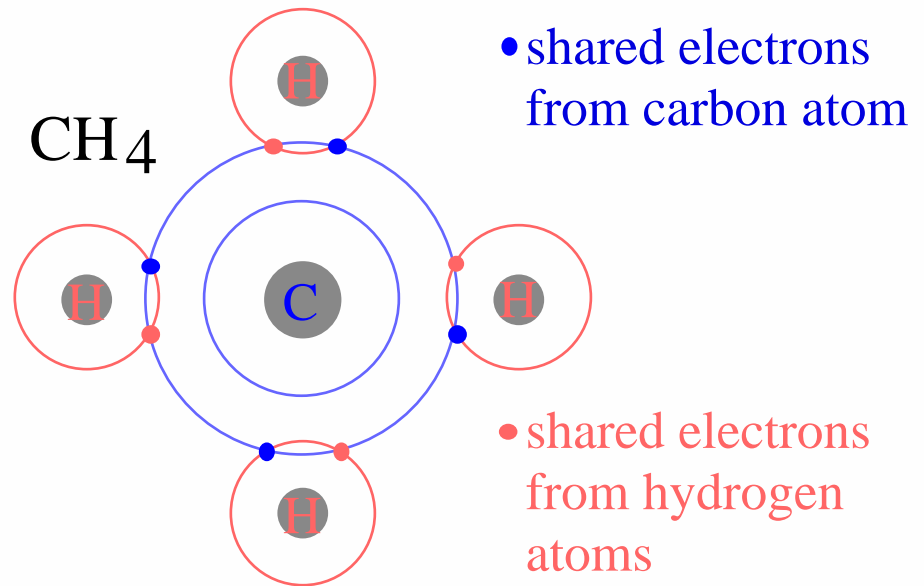
# COVALENT BONDING

- Requires **shared electrons**
- Example:  $\text{CH}_4$

**C:** has 4 valence e,  
needs 4 more

**H:** has 1 valence e,  
needs 1 more

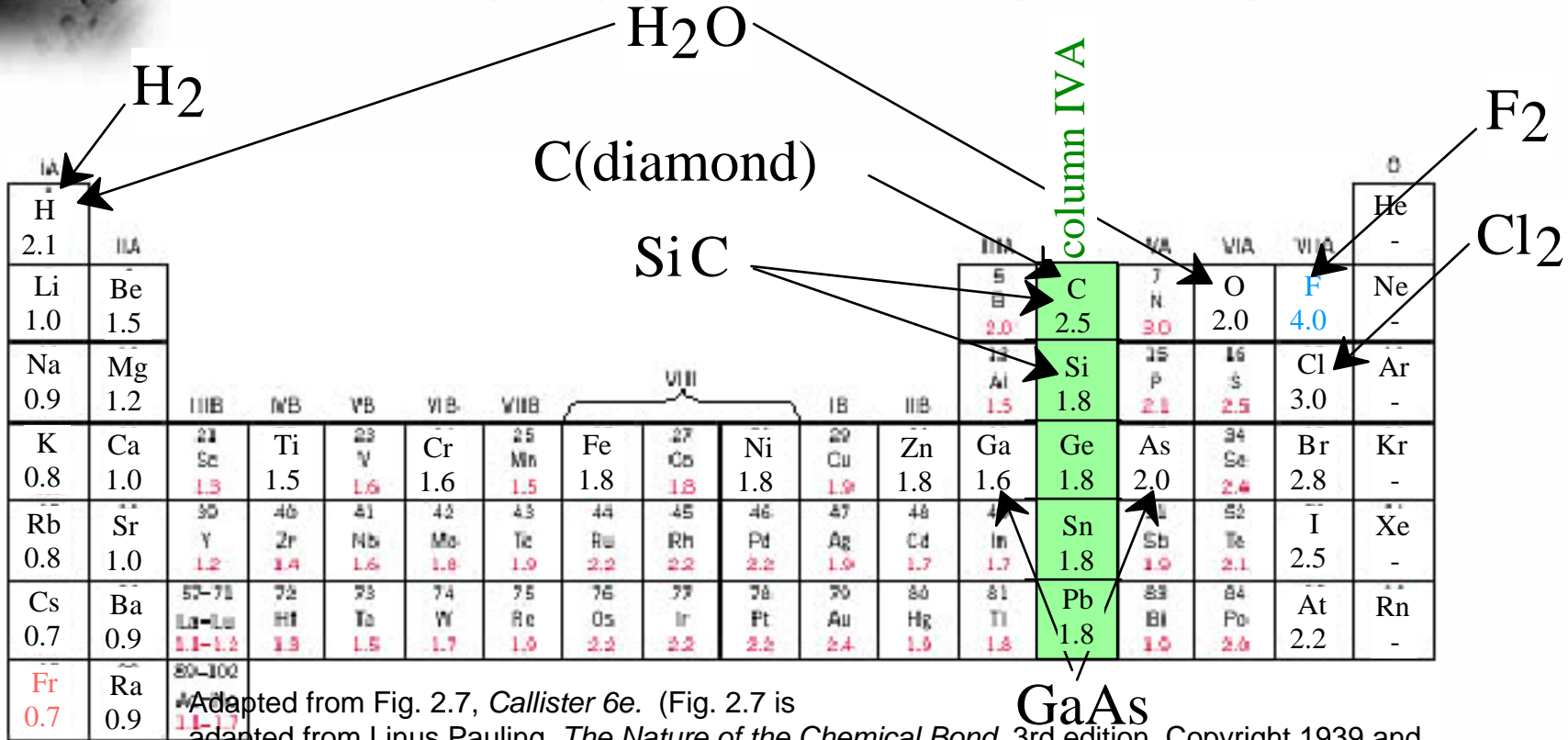
**Electronegativities  
are comparable.**



Adapted from Fig. 2.10, *Callister 6e*.



# EXAMPLES: COVALENT BONDING



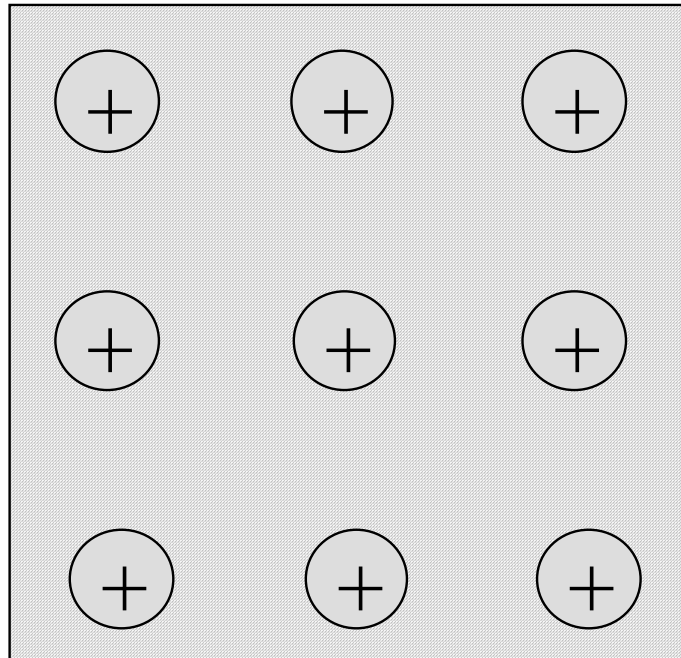
Adapted from Fig. 2.7, Callister 6e. (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.)

- Molecules with **nonmetals**
- Molecules with **metals and nonmetals**
- Elemental solids (RHS of Periodic Table)
- Compound solids (about **column IVA**)



# METALLIC BONDING

- Arises from a sea of **donated valence electrons** (1, 2, or 3 from each atom).



Adapted from Fig. 2.11  
*Callister 6e.*

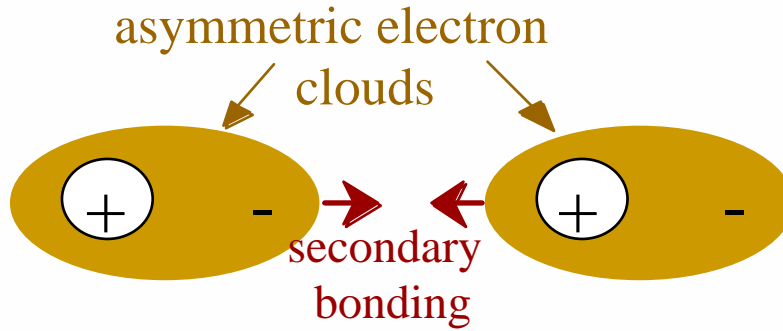
- Primary bond for **metals** and their **alloys**



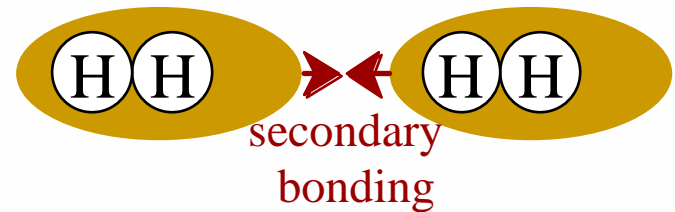
# SECONDARY BONDING

Arises from interaction between **dipoles**

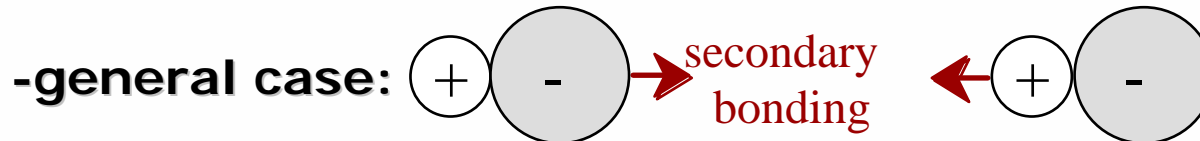
- **Fluctuating dipoles**



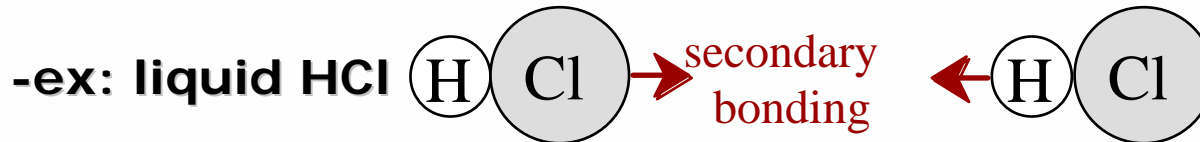
ex: liquid H<sub>2</sub>  
 H<sub>2</sub> → ← H<sub>2</sub>



- **Permanent dipoles-molecule induced**



Adapted from Fig. 2.14, Callister 6e.



Adapted from Fig. 2.14, Callister 6e.

