AMSC5720

Advanced Materials Synthesis

(先進材料合成)

Basic Concepts of Structure and Properties of Materials

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Topic Overview

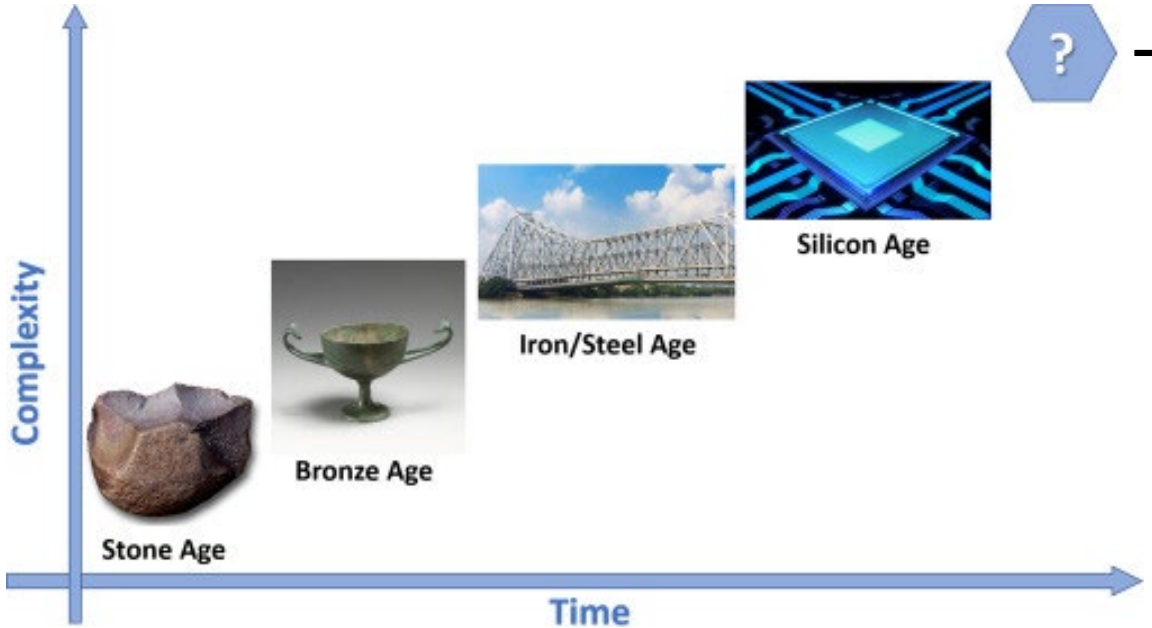
- **Classification of Materials**
- **Building Blocks of Materials**
- **Structure of Crystalline Solids**
- **Imperfections in Solids**
- **Failure**

- Major textbook for this topic:

Materials Science and Engineering: An Introduction, by William D. Callister, David G. Rethwisch, 9th ed. 2014.

Why Materials Are Important

- Materials drive advancements in our society
  - Stone Age → Bronze Age → Iron Age



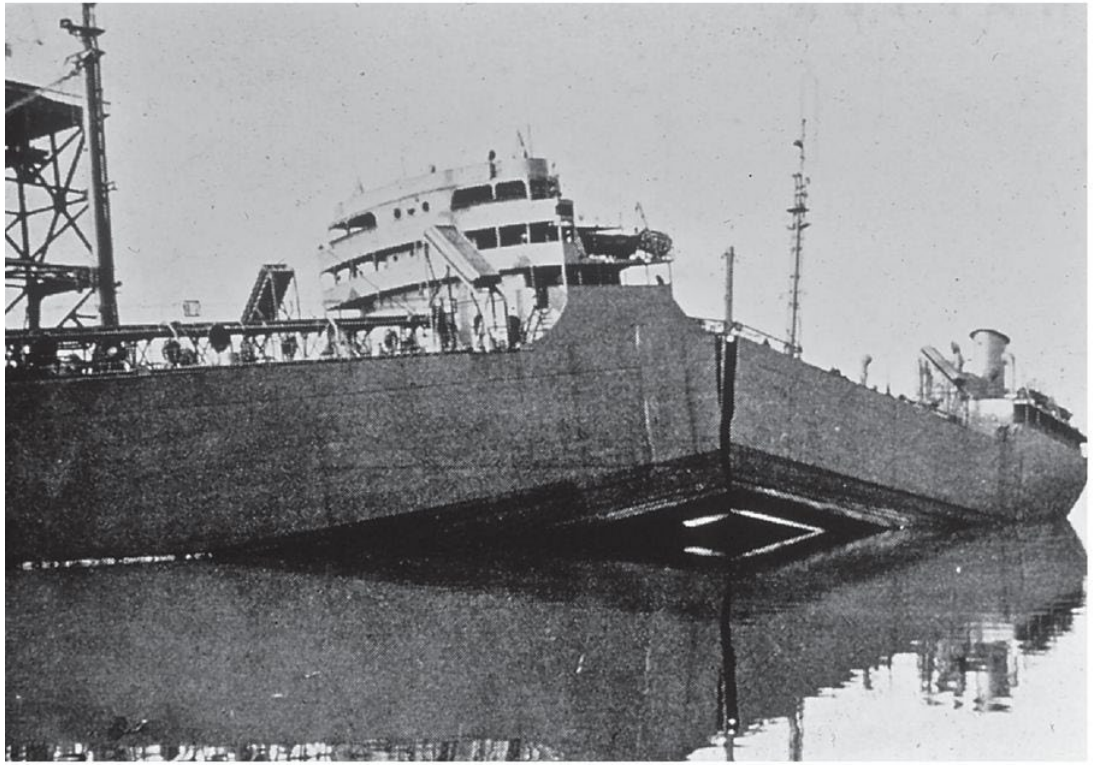
→ What is today's material age?

- Silicon Age (Electronic Materials)?
- Nanomaterials Age?
- Polymer Age?

https://doi.org/10.1016/B978-0-12-818475-2.00019-2

Why Materials Science Is Important

- The Liberty Ship Failure



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Metal can be very ductile

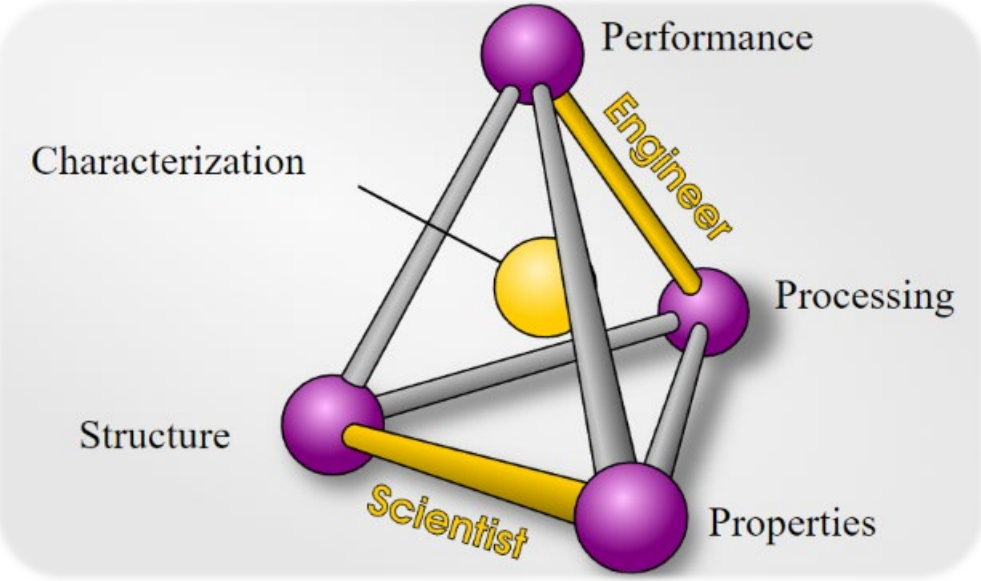
https://www.youtube.com/watch?v=bhL8WlDHKaY

or very brittle

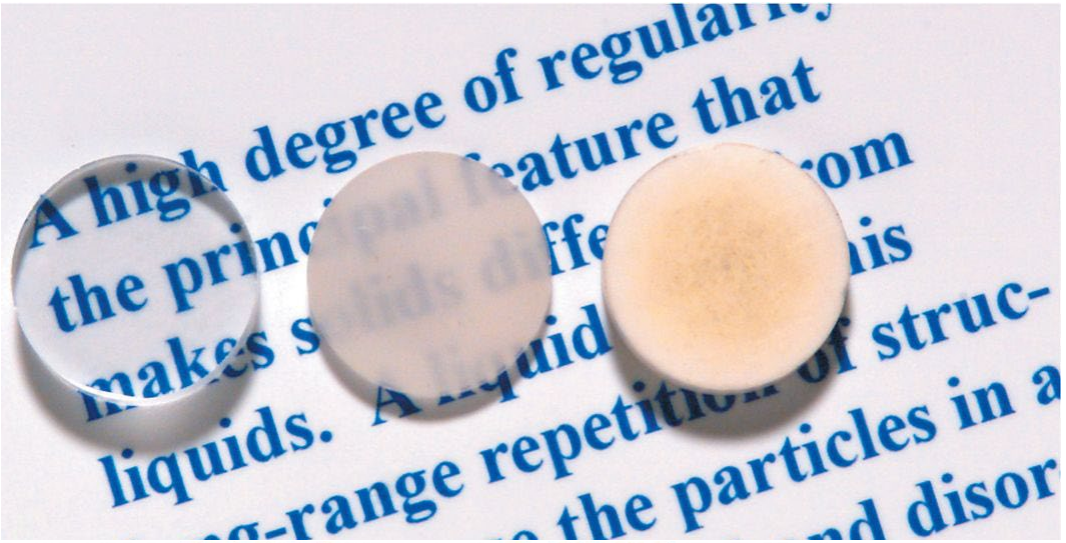
https://www.youtube.com/watch?v=OSt11SA16KU

What is Materials Science

- **Materials science** investigates the *relationships* that *exist* between the *structures* and *properties* of materials.
- In other words: why materials have their properties.



"Materials tetrahedron"



William D. Callister Jr./ Specimen preparation, P.A. Lessing

Aluminum oxide with different structures show different light-transmittance characteristics.

What is Structure

- **Structure** can be a nebulous term
- It relates to the arrangement of a material's internal components
- Structural elements may be classified based on *size*:
  - Subatomic structure (electrons within atoms, their energies and interactions with nuclei)
  - Atomic structure (organization of atoms to form molecules/crystals)
  - Nanostructure (aggregates of atoms to form nanoscale particles) < around 100 *nm*
  - Microstructure (can be directly observed using optical microscopes) 100 *nm* to several *mm*
  - Macrostructure (may be viewed by naked eyes) Several *mm* to *m*

What is Property

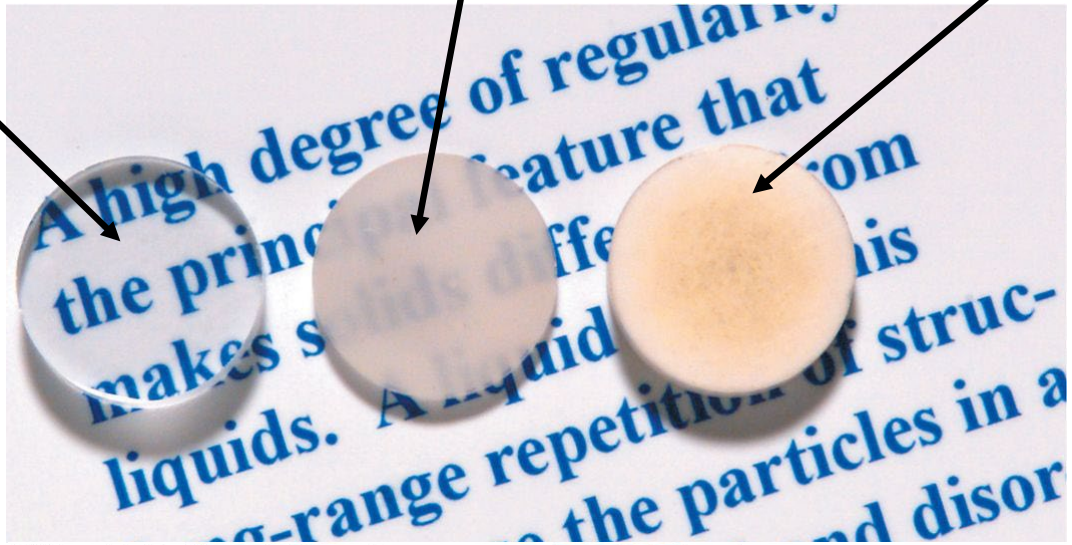
- **Property** describes the kind and magnitude of response of a material to a specific imposed stimulus
- All important properties of materials may be grouped into:
  - Mechanical properties (deformations to an applied load)
  - Electrical properties (stimulated by applied electric field)
  - Magnetic properties (response to an applied magnetic field)
  - Thermal properties (*e.g.* changes in temperature or temperature gradients)
  - Optical properties (stimulated by electromagnetic or light radiation)
  - Deteriorative properties (relate to chemical reactivity)
  - and so on…

Example: optical property

Aluminum oxide single crystal (high degree of perfection)—is optically transparent

Aluminum oxide polycrystalline material (having many small grains)—is optically translucent

Aluminum oxide polycrystalline material having some porosity—is optically opaque



William D. Callister Jr./ Specimen preparation, P.A. Lessing

Classification of Materials

- **Metals** (no or small amounts of nonmetal elements)
  - Strong, ductile
  - High thermal & electrical conductivities
  - Opaque, reflective

© William D. Callister, Jr.

- **Polymers/plastics** (often compounds of non-metal elements)
  - Soft, ductile, low strengths, low densities
  - Low thermal & electrical conductivities
  - Opaque, translucent or transparent

© William D. Callister, Jr.

- **Ceramics** (often compounds of metal & non-metal elements)
  - Hard, Brittle
  - Low thermal & electrical conductivities
  - Opaque, translucent, or transparent

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Classification of Materials

- **Composites** (more than one individual material)
  - Combination of properties that is not displayed by any single material

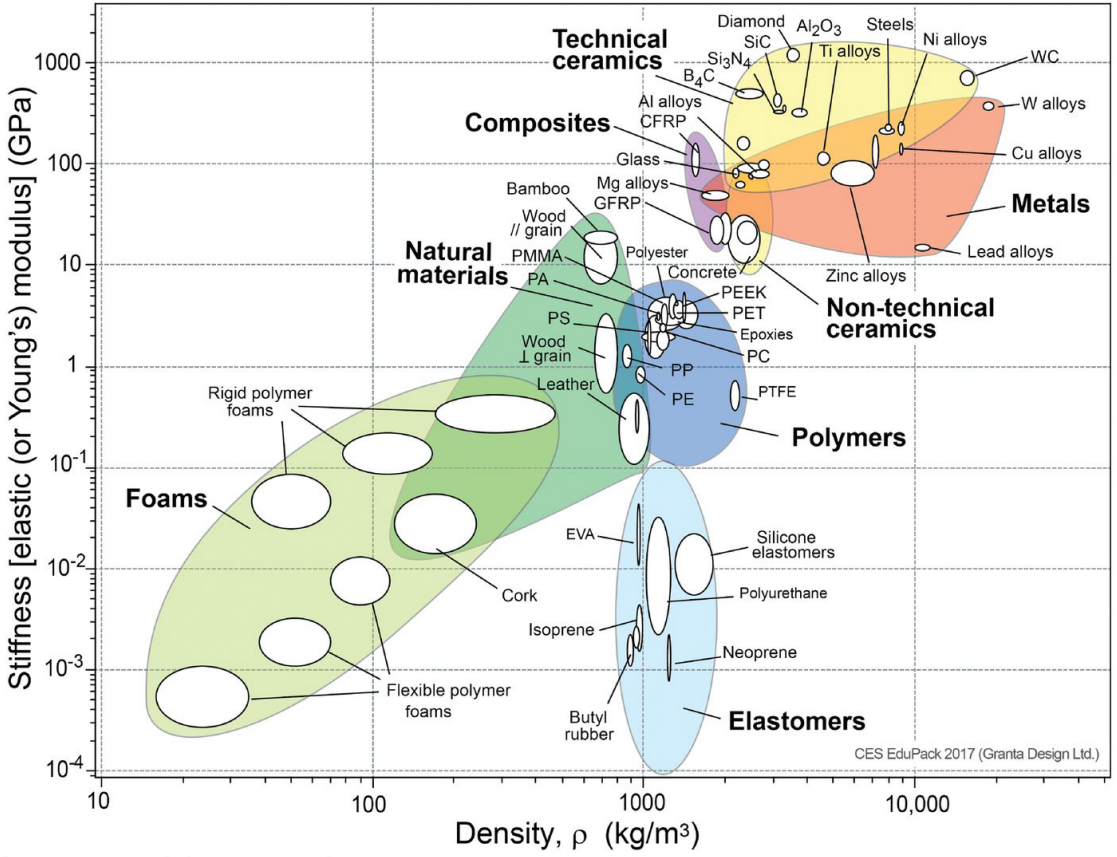
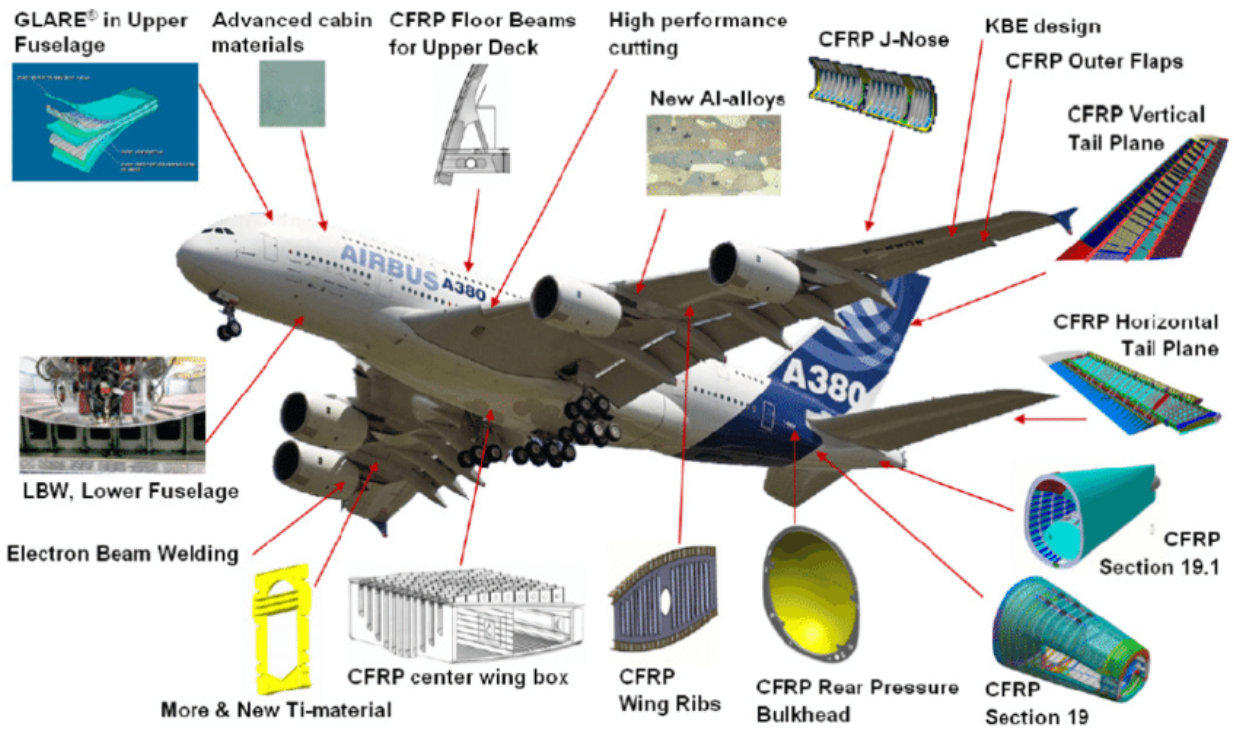
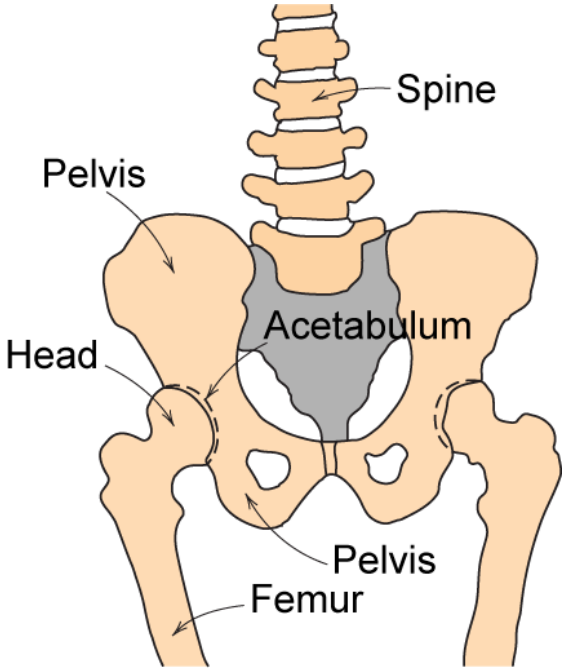


Chart created using CES EduPack 2017, Granta Design Ltd.



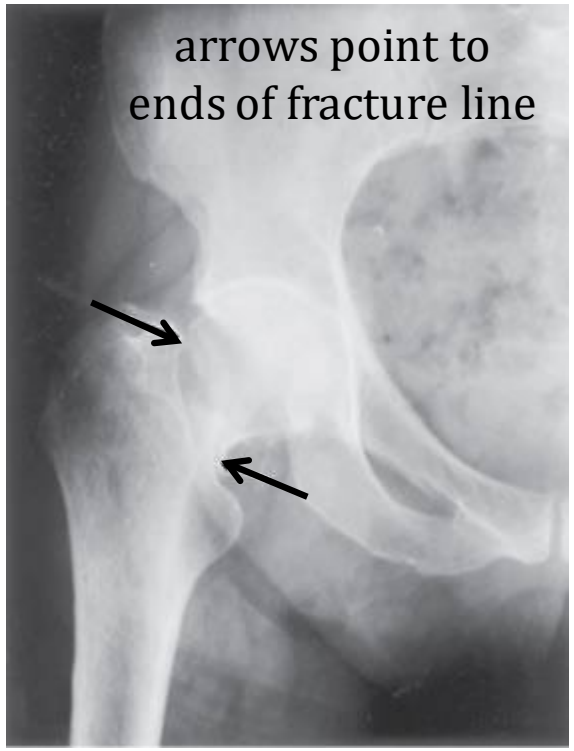
The AIRBUS A380 aircraft composite applications [www.airbus.com]

Example: Materials For Artificial Hip



Anatomy of a human hip joint and adjacent skeletal features

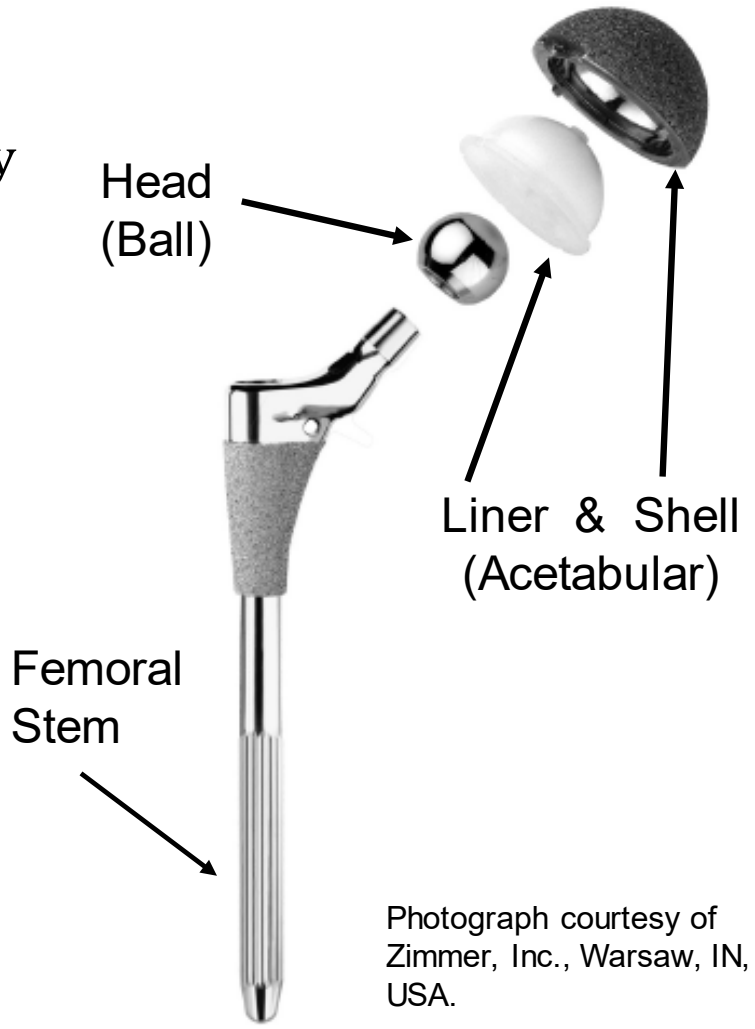
X-ray of normal hip joint



X-ray of fractured hip joint

Example: Materials For Artificial Hip

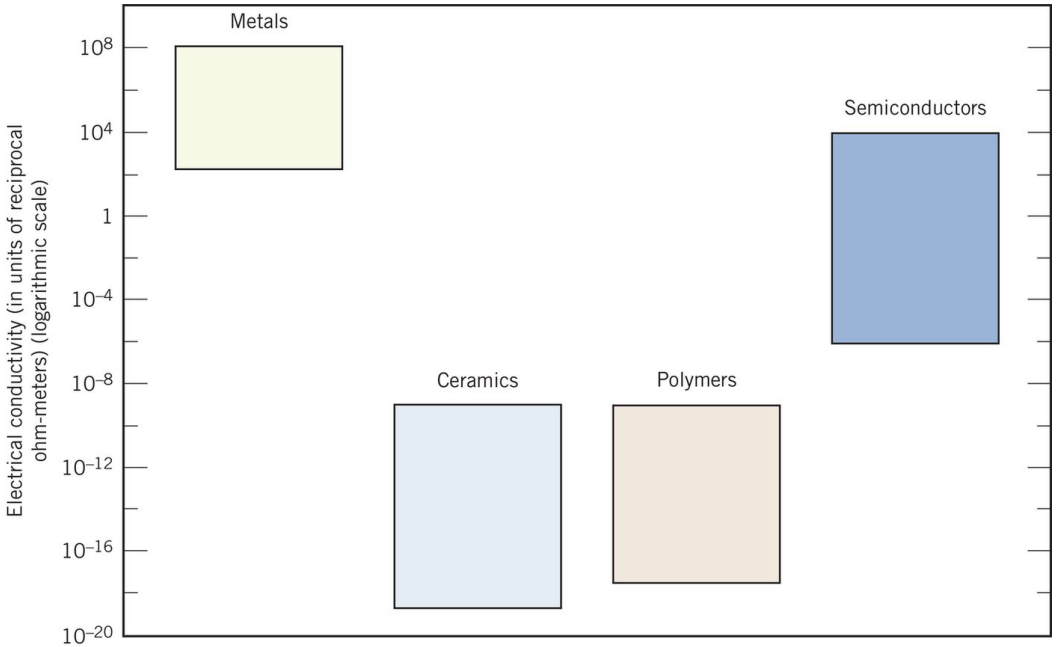
- Materials requirements for artificial joints
  - Biocompatible – minimum rejection by surrounding body tissues
  - Chemically inert to body fluids
  - Mechanical strength to support forces generated
  - Good lubricity and high wear resistance between articulating surfaces
- Materials used
  - Femoral stem — titanium or CoCrMo alloy (metal)
  - Head (Ball) — CoCrMo alloy or Al_2O_3 (ceramic)
  - Shell — titanium alloy (metal)
  - Liner — polyethylene (polymer) or Al_2O_3 (ceramic)



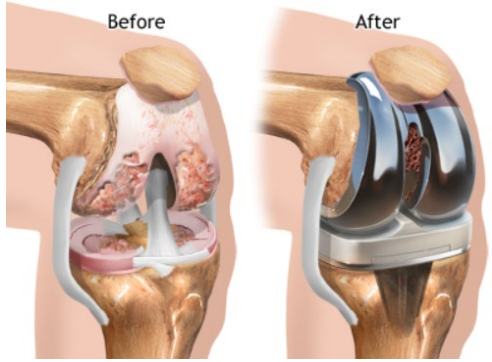
Photograph courtesy of Zimmer, Inc., Warsaw, IN, USA.

Advanced Materials

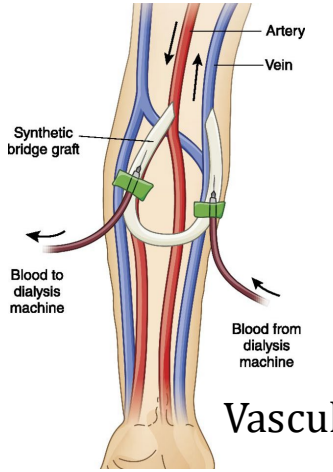
- **Semiconductors**
  - Electrical properties are intermediate between conductors (metals and metal alloys) and insulators (ceramics and polymers)



- **Biomaterials**
  - Biocompatible: compatible with body tissues and fluids
  - Can be metals, ceramics, polymers, and composites



Artificial knee

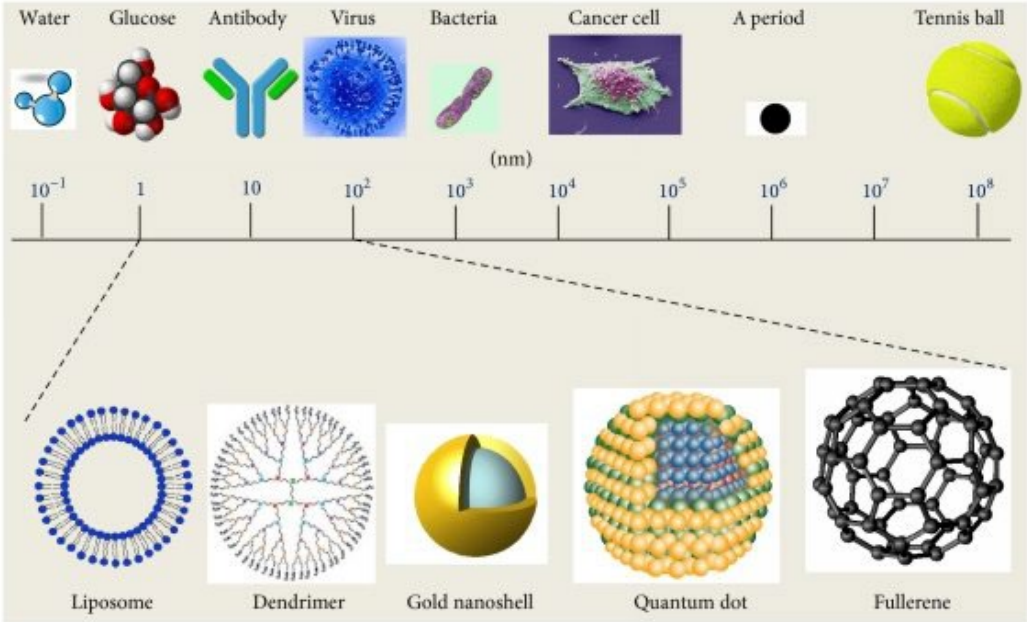


Vascular graft

Advanced Materials

- **Smart Materials**
  - Smart implies the ability to sense changes in environment and respond in predetermined manners
  - e.g. shape-memory alloys, piezoelectric ceramics

- **Nanomaterials**
  - Dimensions are on the order of 10^{-9} m
  - Physical and chemical characteristics may experience dramatic changes
  - Can be metals, ceramics, polymers, and composites



Examples: Different packaging materials for coke

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Atomic Structure and Interatomic Bonding

- Understanding of interatomic interaction helps to explain a material's property:

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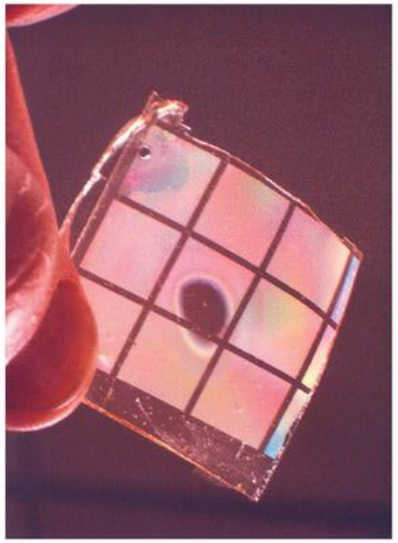
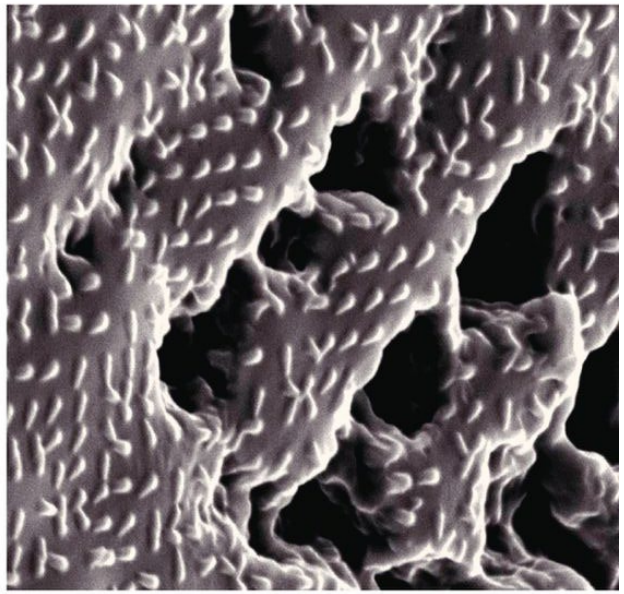
Courtesy Jeffrey Karp, Robert Langer and Alex Galakatos



Courtesy Jeffrey Karp, Robert Langer and Alex Galakatos



Gecko's very sticky feet —*Mechanism of adhesion*→ *Synthetic adhesive*

https://www.youtube.com/watch?v=YeSuQm7KfaE

Atomic Structure

Let's recap some fundamental concepts

- Atom
  - Electron: 9.11×10^{-31} kg
  - Proton: 1.67×10^{-27} kg
  - Neutron: 1.67×10^{-27} kg
- **Atomic number**, Z = no. of protons in nucleus = no. of electrons in neutral species
- **Atomic mass unit,** *amu*, is 1/12 mass of ^{12}C
- **Atomic weight,** A, is weight of N_A (6.022×10^{23}) molecules or atoms
- $A \approx Z + N$, where N is no. of neutrons
- 1 amu/atom = 1 g/mol

Electronic Structure

- Some of the chemical, electrical, thermal, & optical properties are determined by an atom's electronic structure
- Electrons have *wave-like* and *particle-like* characteristics
- Two wave-like characteristics are:
  - Electron position in terms of probability density
  - Shape, size, spatial orientation of probability density are determined by quantum numbers

Electronic Structure

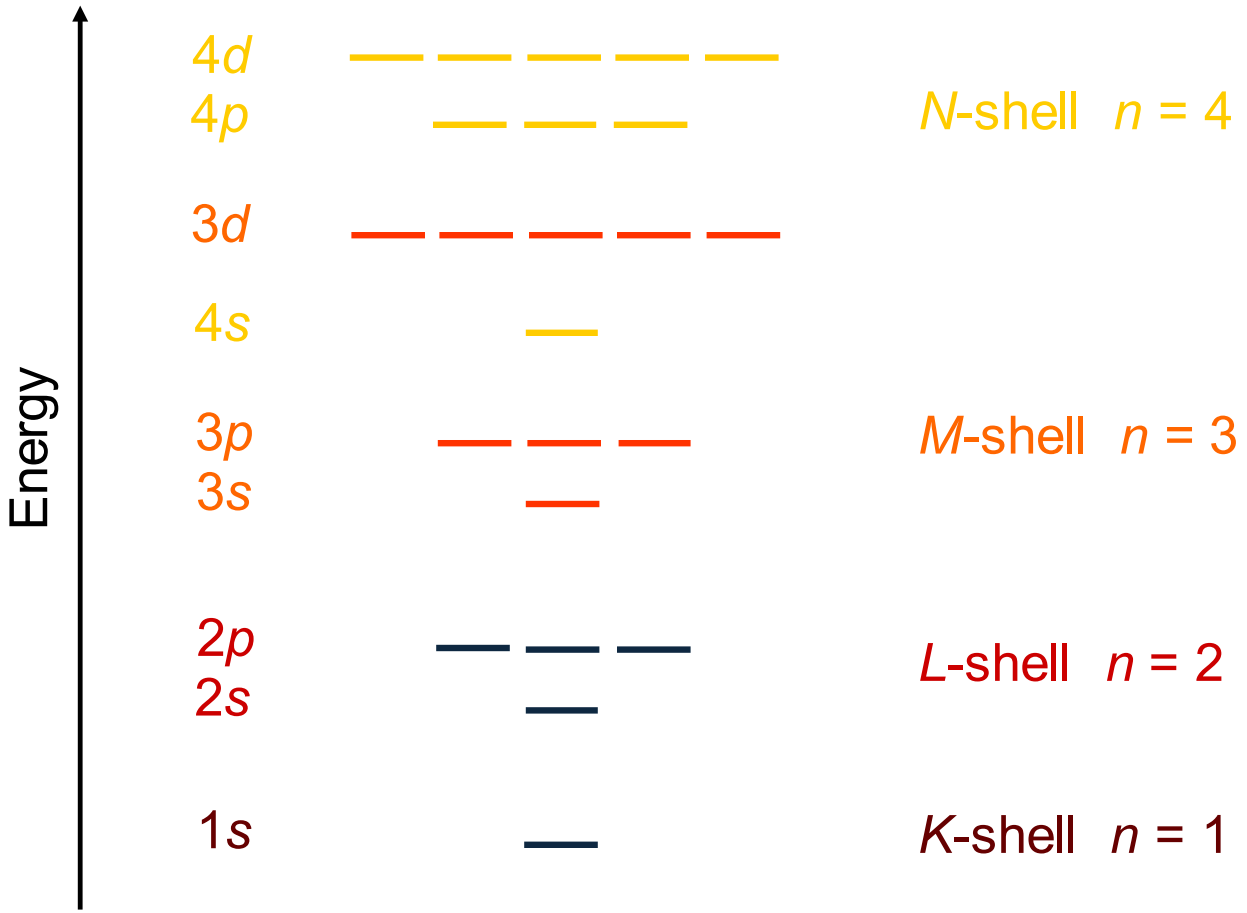
TABLE 6.2 Relationship among Values of n, l, and m_l through $n = 4$

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	
	1	2p	1, 0, −1	3	4
3	0	3s	0	1	
	1	3p	1, 0, −1	3	
	2	3d	2, 1, 0, −1, −2	5	9
4	0	4s	0	1	
	1	4p	1, 0, −1	3	
	2	4d	2, 1, 0, −1, −2	5	
	3	4f	3, 2, 1, 0, −1, −2, −3	7	16

(Chapter 6, Brown *et al.)*

Electron Energy States

- Electrons have discrete energy values
- Electrons tend to occupy lowest available energy states



Survey of Elements

- In most elements, electron configurations are not stable

Element	Atomic No.	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	
...		...	
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	(stable)
...	...	...	
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	(stable)

Why not stable?

- Valence (outer) shell usually not completely filled.

Electronic Configurations

- **Valence electrons** – electrons in outer unfilled shells
- Filled shells are more stable – require more energy to gain or lose electrons
- Valence electrons are available for bonding and tend to determine an atom's chemical properties
  - example: C (atomic number = 6)

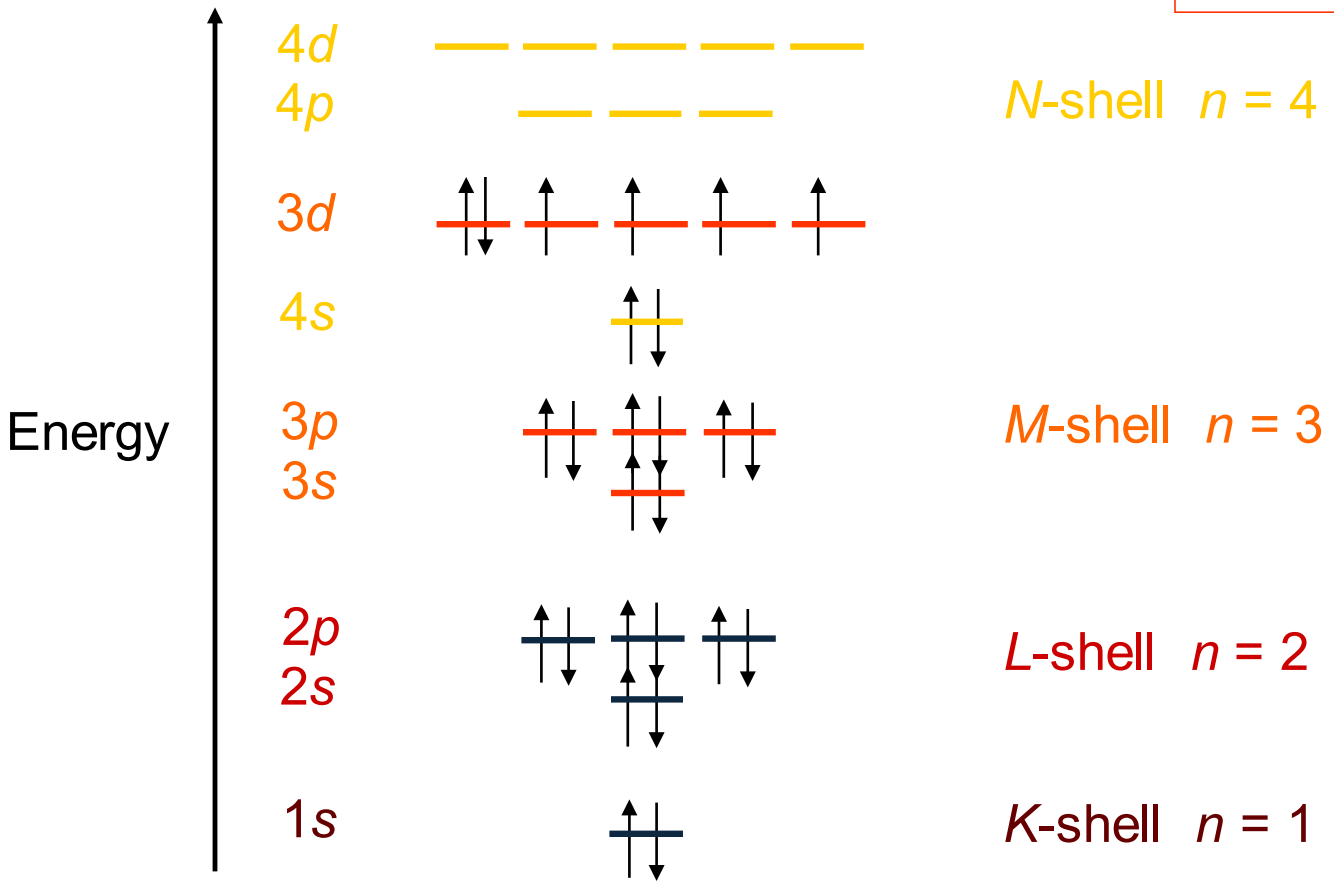
$$1s^2 \; \boxed{2s^2 \; 2p^2}$$

valence electrons

Electronic Configurations

- Example: Fe (atomic number = 26)

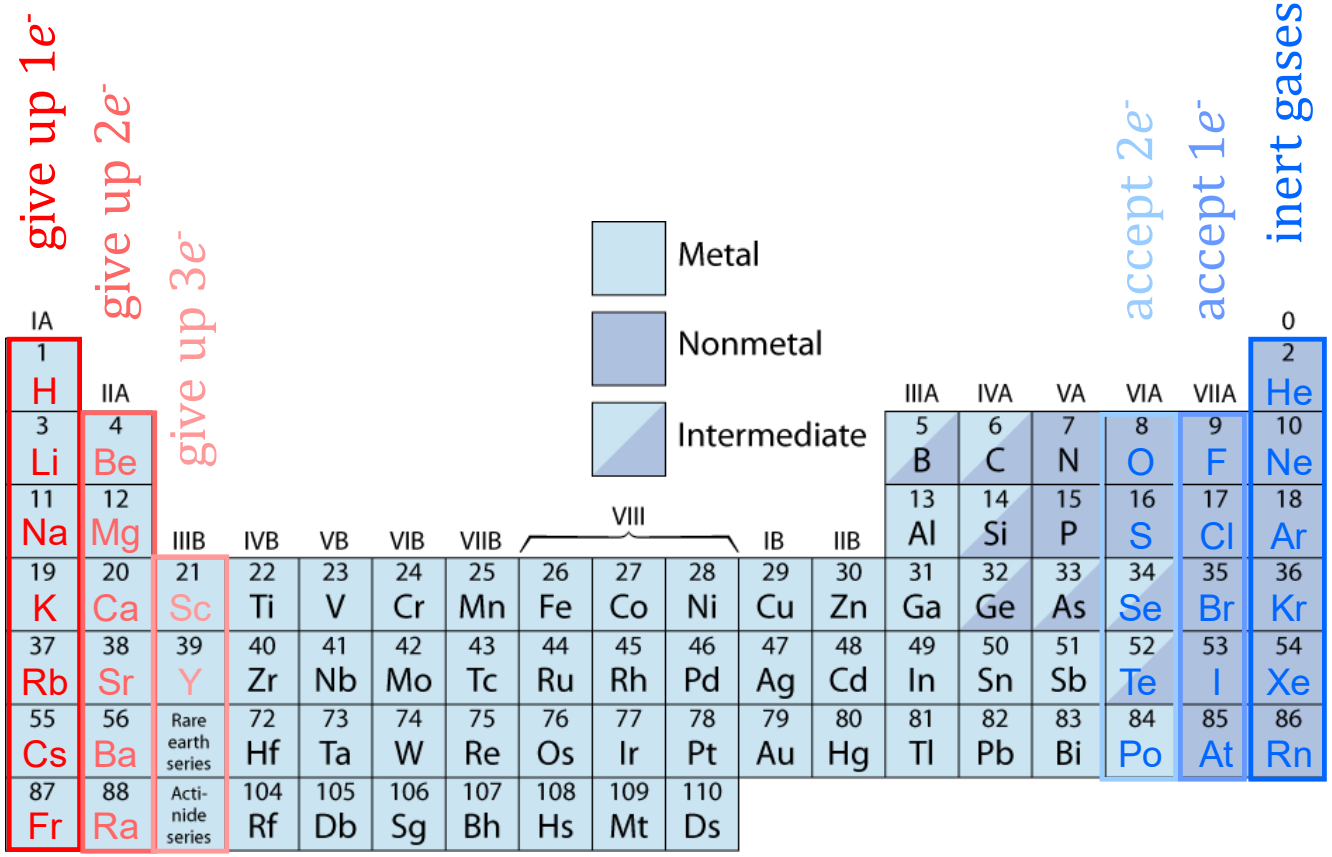
Electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \boxed{4s^2\ 3d^6}$ valence electrons



✓ Transition metals can use the electrons in their d subshells as valence electrons.

Trends in Periodic Table

- Elements in each group has similar valence electron structure

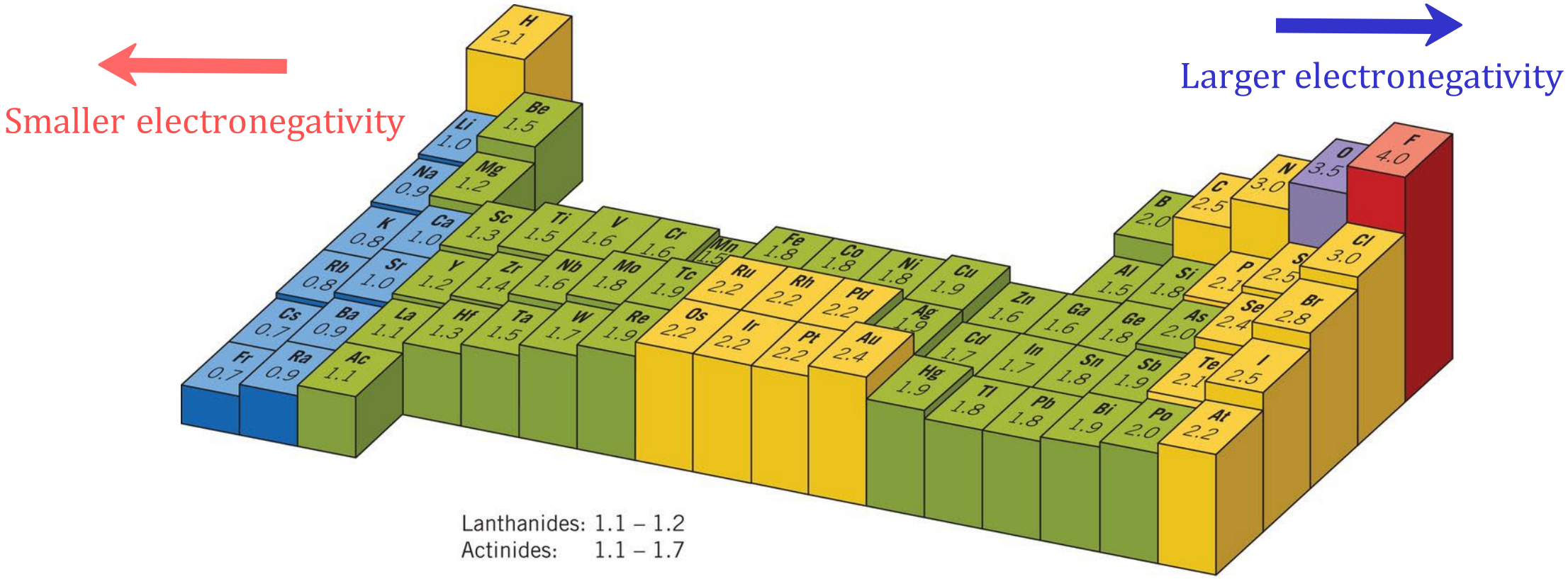


Electropositive elements: Readily give up electrons to become cations.

Electronegative elements: Readily acquire electrons to become anions.

Electronegativity

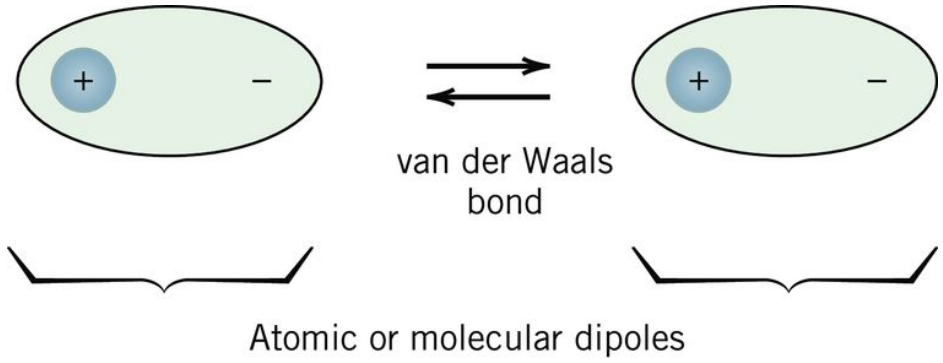
- Ability of atoms to *attract* electrons, ranges from 0.7 to 4.0
- Larger electronegativity → higher tendency to acquire electrons



From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition, 2004. This material is reproduced with permission of John Wiley & Sons, Inc.

Atomic Bonding in Solids

- **Primary** Interatomic Bonds
  - Ionic bonding
  - Covalent bonding
  - Metallic bonding
- **Secondary** Bonding or **van der Waals** Bonding (arisen from atomic or molecular dipoles)
  - Permanent dipole bonds
    - Hydrogen bonding
  - Fluctuating induced dipole bonds
  - Polar molecule-induced dipole bonds



Ionization Process

- Main text

metal atom + nonmetal atom

↑ donates electrons

↑ accepts electrons

Dissimilar electronegativities:

example: MgO

Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$

[Ne] $3s^2$

O $1s^2\ 2s^2\ 2p^4$

Mg^{2+} $1s^2\ 2s^2\ 2p^6$

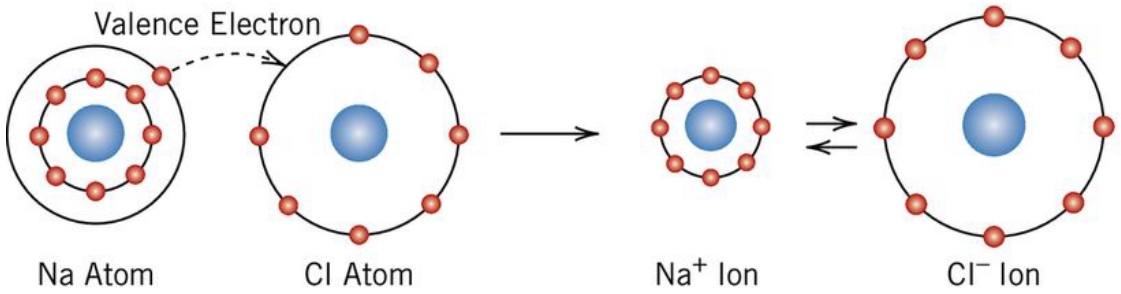
[Ne]

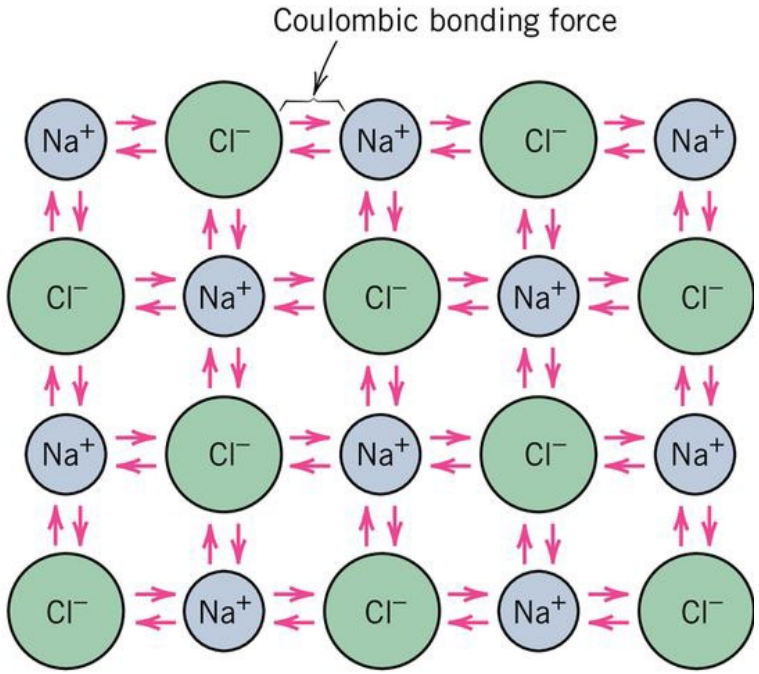
O^{2-} $1s^2\ 2s^2\ 2p^6$

[Ne]

Ionic Bonding

- Occurs between positive and negative ions (often metal + nonmetal)
- Requires electron transfer → often achieves inert gas configurations
- Requires large difference in electronegativity
  - Example: NaCl





Ionic Bonding

- Predominant bonding in Ceramics

Examples:

NaCl

MgO

CaF_2

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	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 1.6	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	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	Ac–No 1.1–1.7															

Give up electrons

Acquire electrons

Ionic Bonding

- Net energy (E_N) = sum of attractive and repulsive energies
- Equilibrium separation when net energy is at minimum (E_0)
- **Bonding energy**: minimum energy to separate two atoms to an infinite distance

$$E_N = E_A + E_R$$

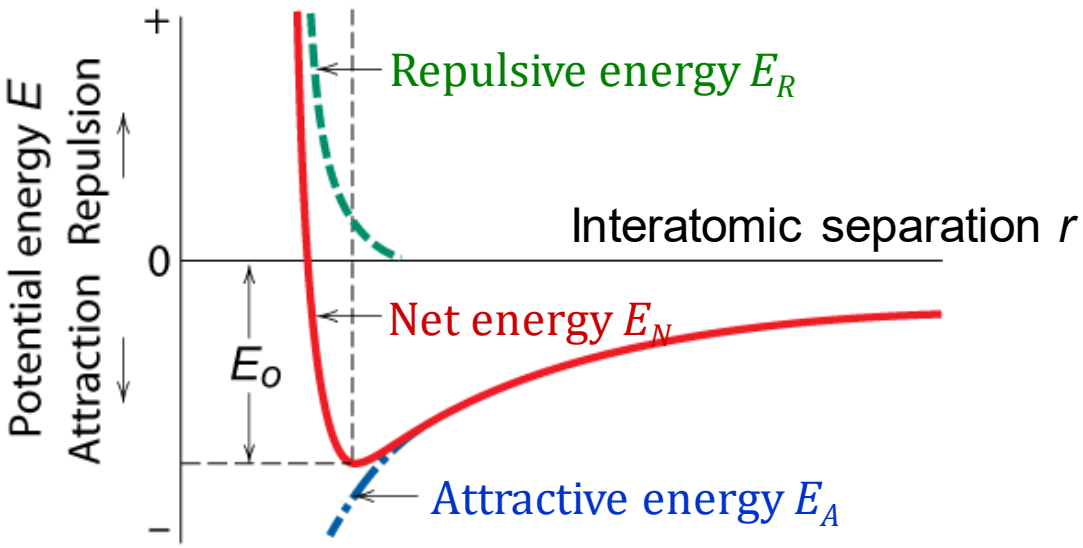
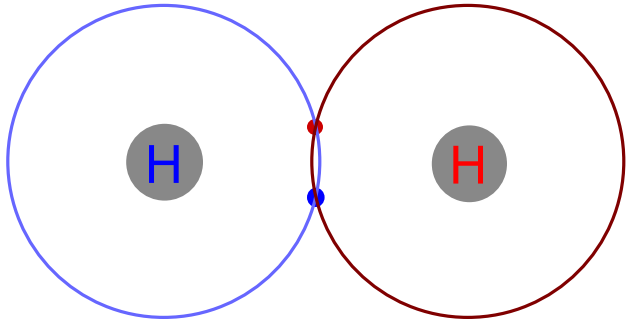


Fig. 2.10(b), *Callister & Rethwisch 10e.*

Covalent Bonding

- Atoms have small differences in electronegativity
- Stable electron configurations are assumed by *sharing* of valence e^-
- Normally s and p orbitals are involved
  - Example:

H_2



- ✓ Each H has 1 valence e^-, needs 1 more
- ✓ Electronegativities are the same

- shared 1*s* electron from 1st hydrogen atom
- shared 1*s* electron from 2nd hydrogen atom

Fig. 2.12, *Calliser & Rethwisch 10e.*

Bond Hybridization in Covalent Bonding

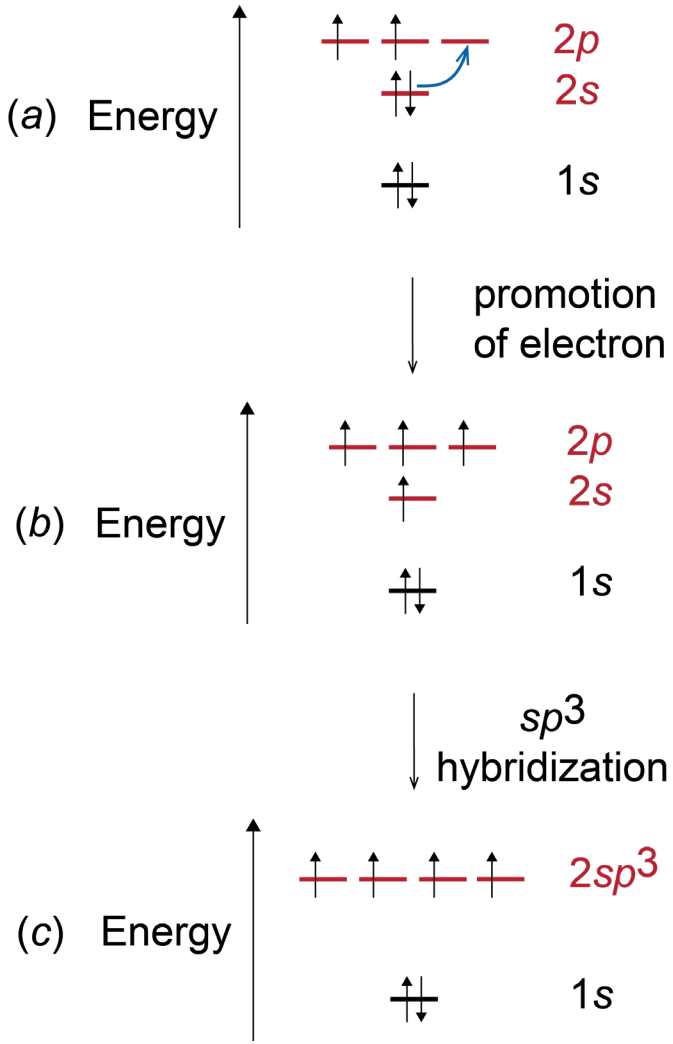


Fig. 2.13, *Callister & Rethwisch 10e.*

- Example : carbon can form sp^3 hybrid orbitals

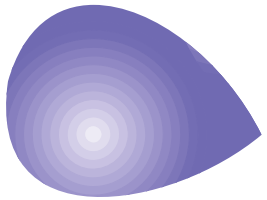


Fig. 2.14, *Callister & Rethwisch 10e.*
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

Bond Hybridization in Covalent Bonding

Hybrid sp^3 bonding involving carbon

Example: CH_4

- ✓ Each C has 4 valence e^-, needs 4 more
- ✓ Each H has 1 valence e^-, needs 1 more

Electrons are shared in sp^3 hybrid covalent bonds.

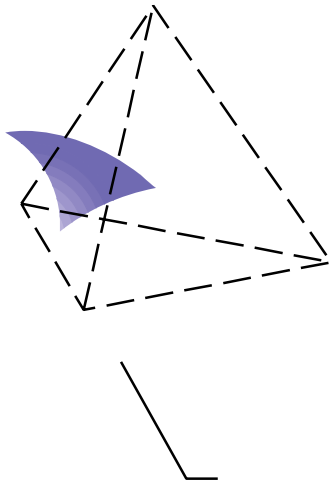


Fig. 2.15, *Callister & Rethwisch 10e.*
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Metallic Bonding

- Seen in metals and their alloys
- Electrons delocalized to form an "electron cloud" or "sea of electrons"
- Free electrons act as "glue" to hold ion cores together

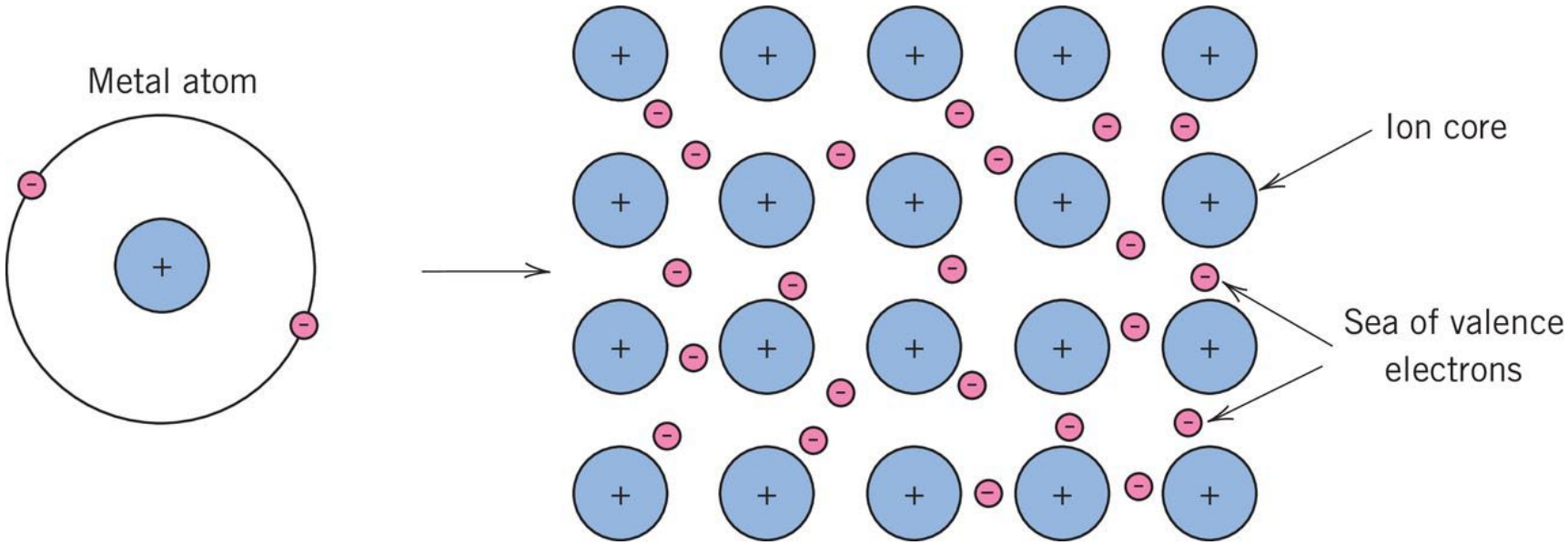
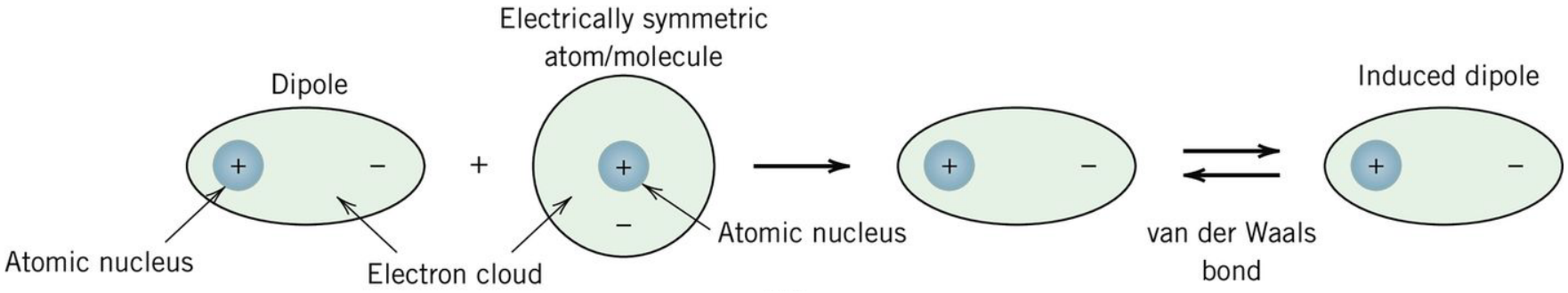


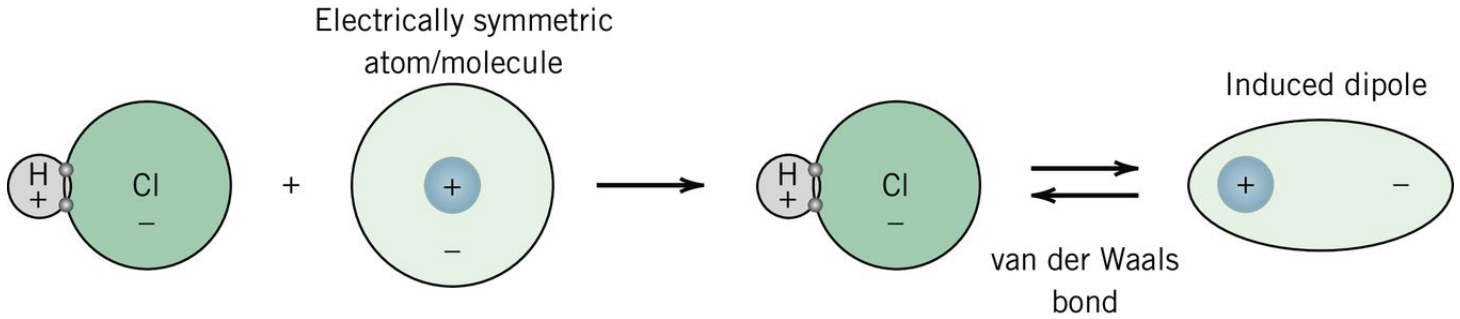
Fig. 2.19, *Callister & Rethwisch 10e.*

Secondary Bonding

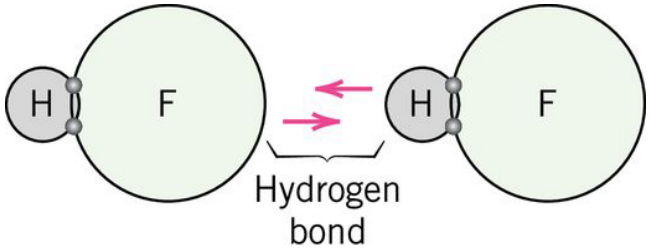
- Arises from attractive forces between dipoles
  - Fluctuating dipoles



  - Polar molecule-induced dipole bonds

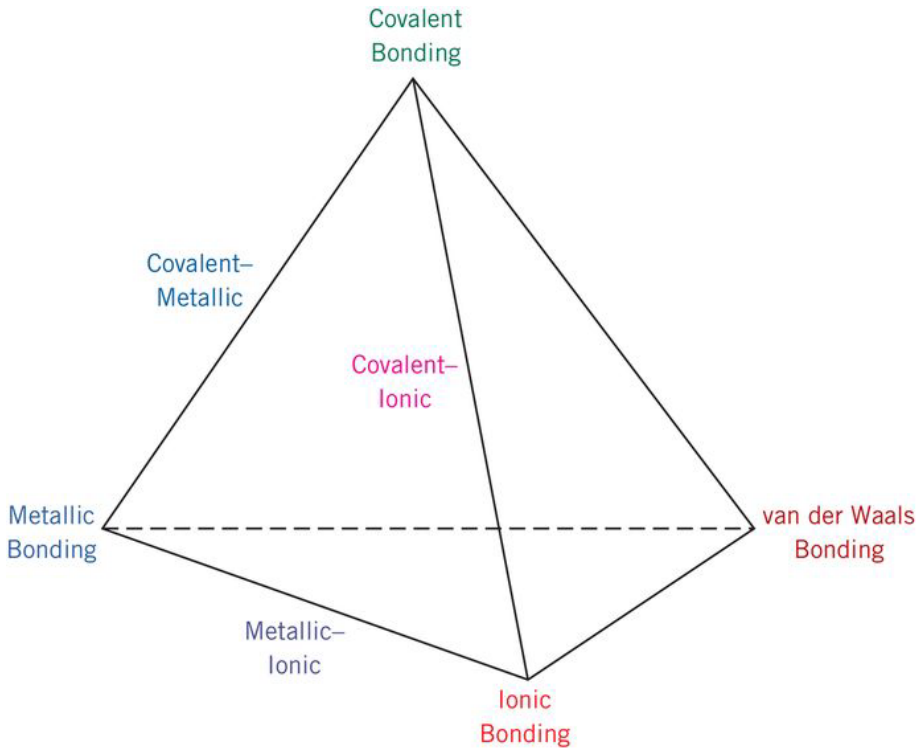


  - Permanent dipoles
    - Example: Hydrogen bond

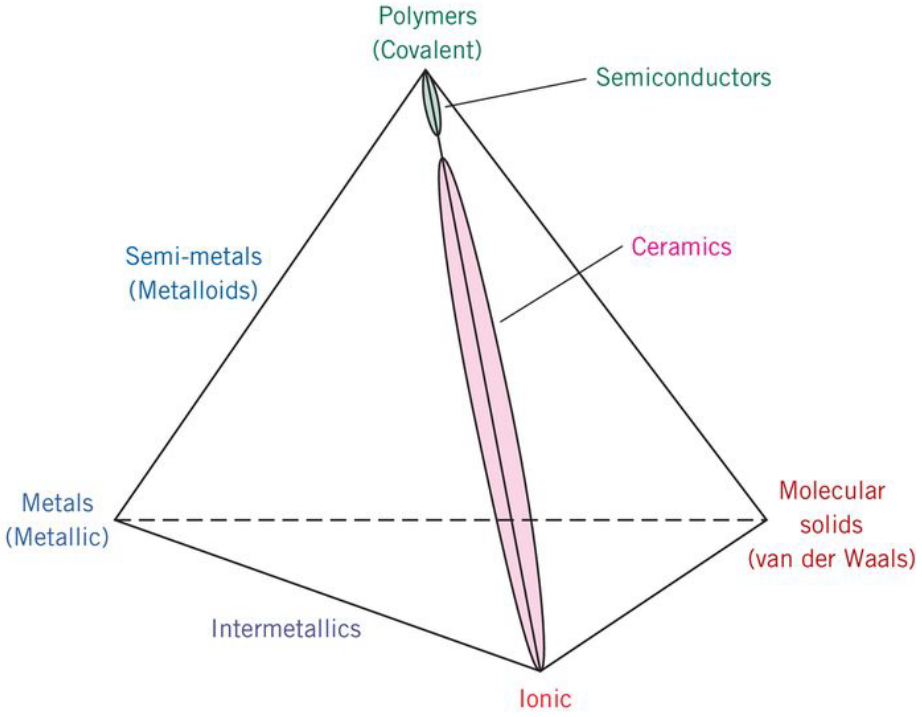


Mixed Bonding

- In real materials, the bonds are sometimes *mixtures* of several bond types
- We can use a bonding tetrahedron to illustrate



"Bonding tetrahedron"



"Material-type tetrahedron"

Mixed Bonding

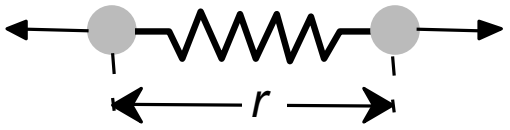
- Most common mixed bonding is mixed covalent-ionic bonds
- Percent ionic character (%IC) of a bond between elements A and B (A being the most electronegative) may be approximated by:

- X_A and X_B being the electronegativities of the respective elements
- *Example*: compute the percent ionic character (IC%) of the interatomic bond that forms between C and H, given X_C is 2.5 and X_H is 2.1:

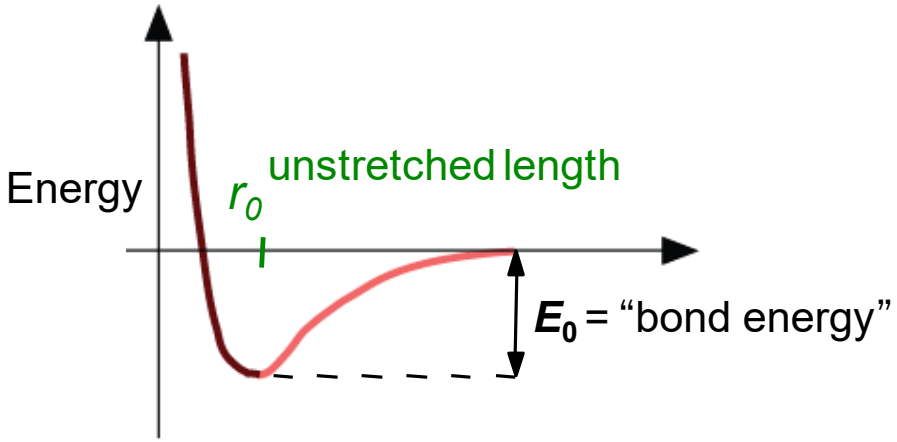
- Thus the C–H bond is primarily covalent (96.1%)

Properties Related to Bonding

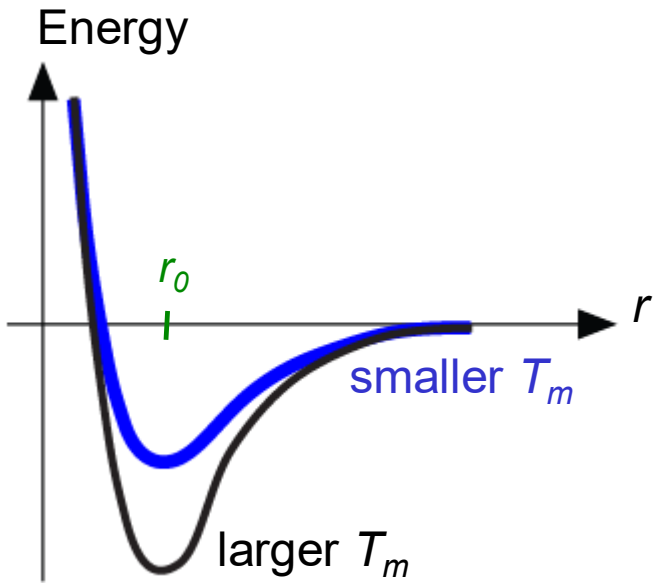
- Many physical and chemical properties of materials are closely related to the information from ***E–r curve***
  - Bond length, **r**



  - Bond energy, $\mathbf{E_0}$



  - Melting temperature (T_m): higher E_0 → higher T_m



Bonding Energy & T_m

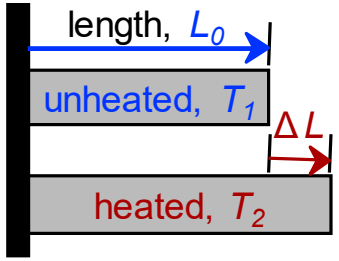
Table 2.3
Bonding Energies and Melting Temperatures for Various Substances

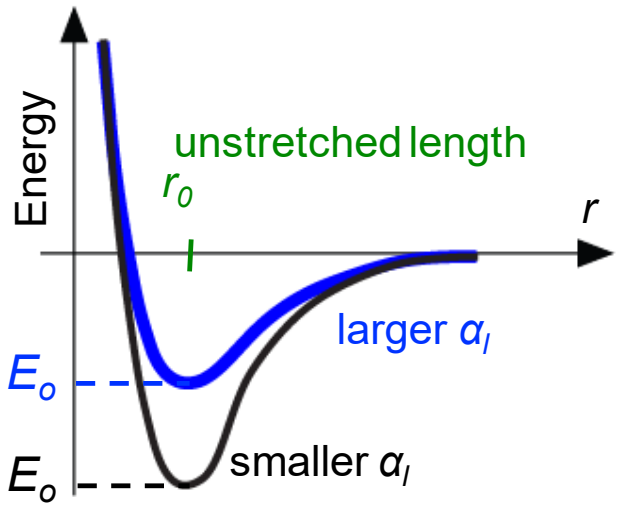
Substance	*Bonding Energy (kJ/mol)*	*Melting Temperature (°C)*
	Ionic	
NaCl	640	801
LiF	850	848
MgO	1000	2800
CaF_2	1548	1418
	Covalent	
Cl_2	121	−102
Si	450	1410
InSb	523	942
C (diamond)	713	>3550
SiC	1230	2830
	Metallic	
Hg	62	−39
Al	330	660
Ag	285	962
W	850	3414
	van der Waals[a]	
Ar	7.7	−189 (@ 69 kPa)
Kr	11.7	−158 (@ 73.2 kPa)
CH_4	18	−182
Cl_2	31	−101

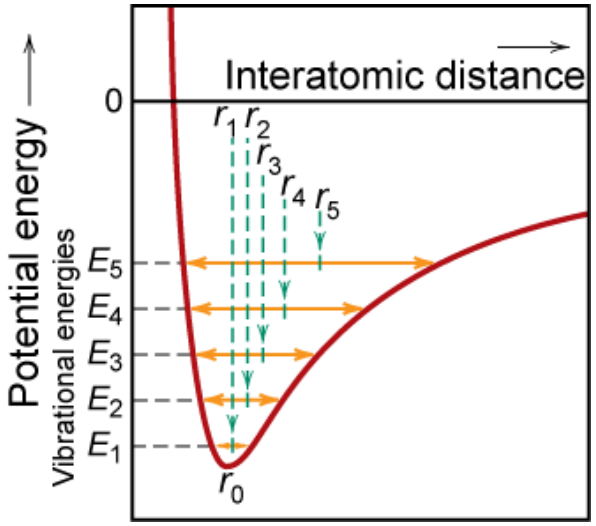
Properties Related to Bonding

- Linear coefficient of thermal expansion (α_l): deeper/narrower shape of the curve (typically means larger E_0) → lower α_l (smaller dimensional alterations upon T change)

$$\frac{\Delta L}{L_0} = \alpha_l \, (T_2 - T_1)$$







- Increase in bond length is due to asymmetry of the ***E–r curve***. This results in an increase in α_l.
- As E_0 increases this asymmetry decreases.

Properties Related to Bonding

Ceramics	Ionic & covalent bonding	Large bond energy ➢ high T_m ➢ small α_l
Metals	Metallic bonding	Variable bond energy ➢ moderate T_m ➢ moderate α_l
Polymers	Covalent & Secondary 	Weak bond energy (between chains) Secondary bonding responsible for most physical properties • low T_m • large α_l

Brief Summary

- A material's chemical, electrical, thermal, and optical properties are determined by electronic configuration.
- Valence electrons occupy the outermost unfilled electron shell.
- Primary bonding types include covalent, ionic, and metallic bonding.
- Secondary or van der Waals bonds are weaker than the primary bonding types.
- In real materials, bonding type can be mixed, an estimated percent ionic character may be calculated
- Some physicochemical properties can be deduced from E–r curve

The Structure of Crystalline Solids

Let's step into the next level of the structure of materials: arrangement of atoms in solid state

- Fundamental concepts to cover in this topic:

- Crystallinity *vs.* noncrystallinity
- Crystal structure
  - Crystallographic points
  - Directions
  - Planes
- Single crystal *vs.* polycrystalline materials
- Some important crystal structures

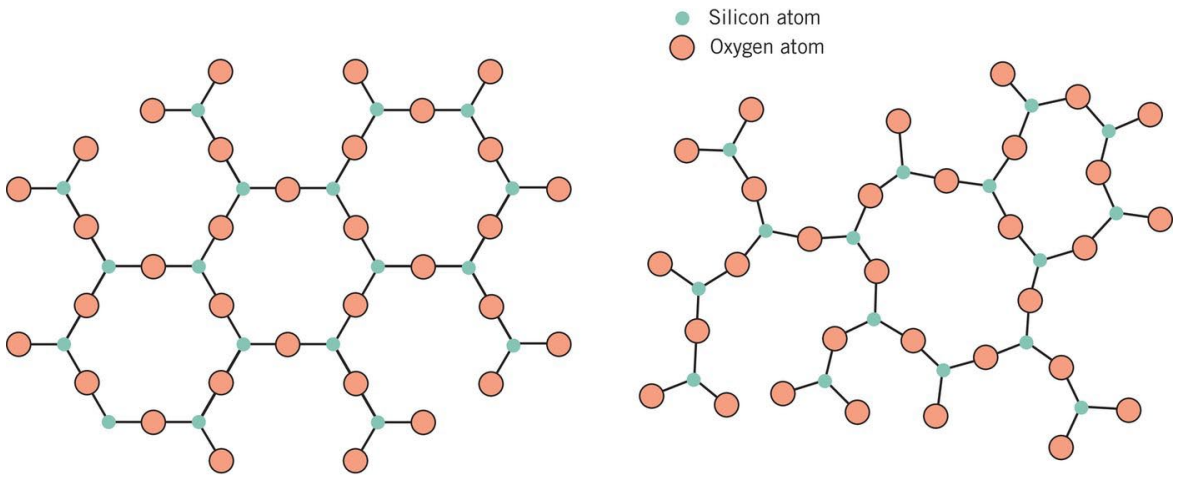
Crystalline vs. Noncrystalline

- A **crystalline** material is one in which the atoms are situated in a *repeating* or *periodic* array over large atomic distances
- That is, long-range order exists, such that upon solidification, atoms will position themselves in a repetitive three-dimensional pattern
- All metals, many ceramics, and certain polymers are crystalline under normal solidification conditions
- A **noncrystalline** (or **amorphous**) material do not crystalline, that is, long-range atomic order is absent

Crystalline vs. Noncrystalline

- Some substances have both crystalline or noncrystalline forms

Quartz
(crystalline SiO_2)

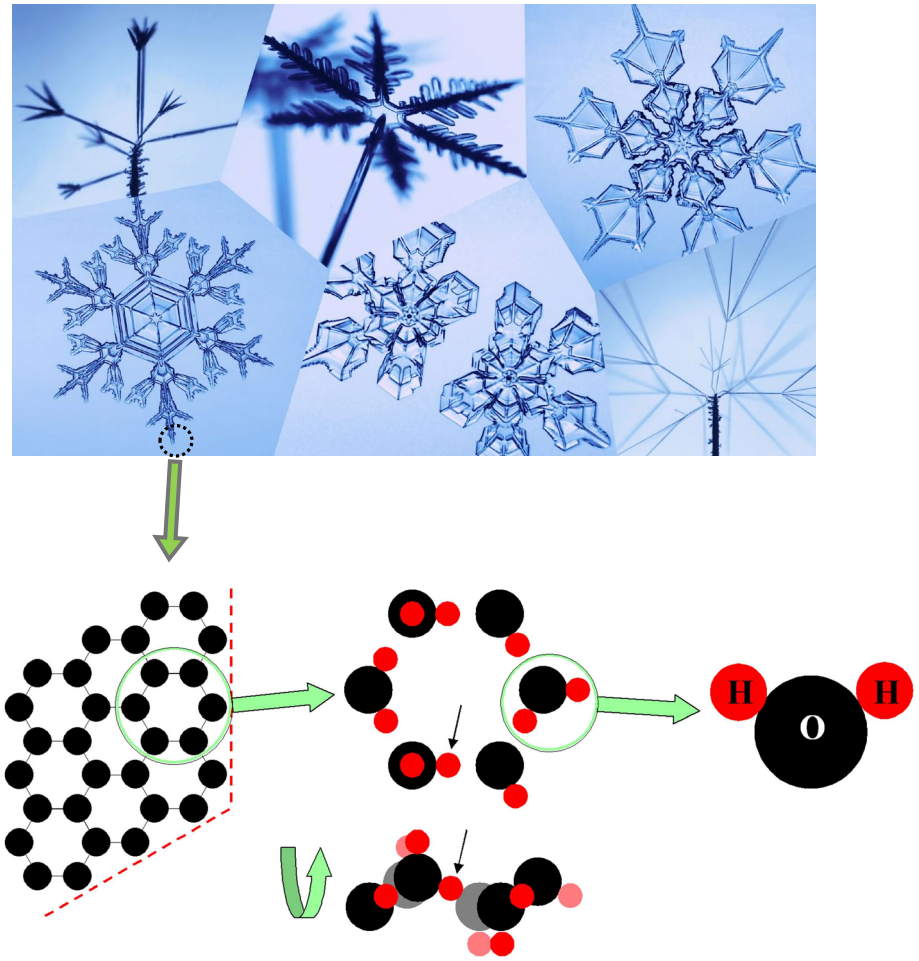


Glass
(noncrystalline SiO_2)

- Many properties of solid materials depends on their crystallinity and/or crystal structure

Crystal Structure

- **Crystal structure** is the manner in which atoms, ions, or molecules are spatially arranged
- Crystal structures of different materials can be relative simple or extremely complex
- To better describe crystal structure, atoms or ions are often thought of as solid spheres
- In **atomic hard-sphere model**, hard spheres representing nearest-neighboring atoms touch one another



Crystal Structures in Metals

- Metallic solids adopt metallic bonds
  - Non-directional
  - Electrons are highly delocalized

→ minimal restriction of number and position of nearest-neighbor atoms

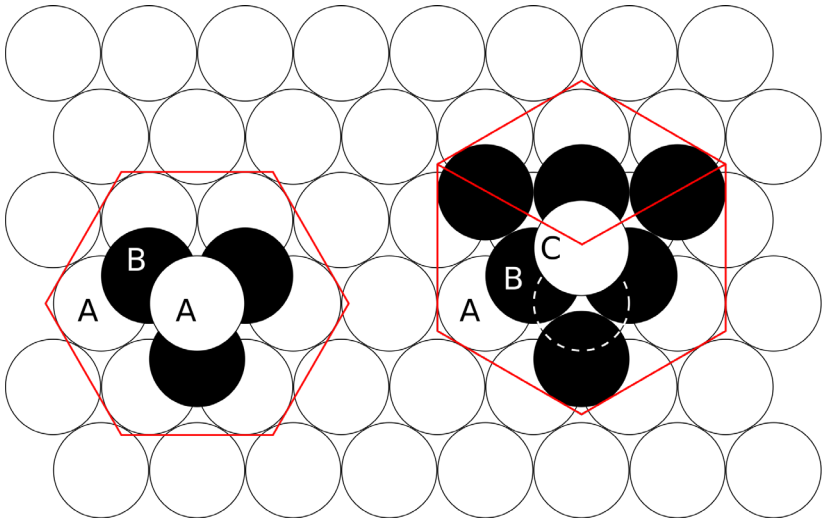
- Most metallic crystal structure adopt **dense (close) atomic packings**
  - **Face-centered cubic (FCC)** crystal structure
  - **Hexagonal close-packed (HCP)** crystal structure
- Some metals adopt non-close-packed structures
  - **Body-centered cubic (BCC)** crystal structure
  - **Simple cubic (SC)** structure

Packing and Close Packing in Metals

- In *two* dimensions, close packing refers to the hexagonal close-packed arrangement of spheres
- In *three* dimensions, close-packing structure can be achieved by stacking the two-dimensional close-packing layers
- **Lattice**: three-dimensional array of points coinciding with atom positions
- **Unit cell**: the smallest repeating unit of the structure which carries *all* the information necessary to construct unambiguously an infinite lattice
- **Coordination number** (for metals): number of nearest-neighbor atoms

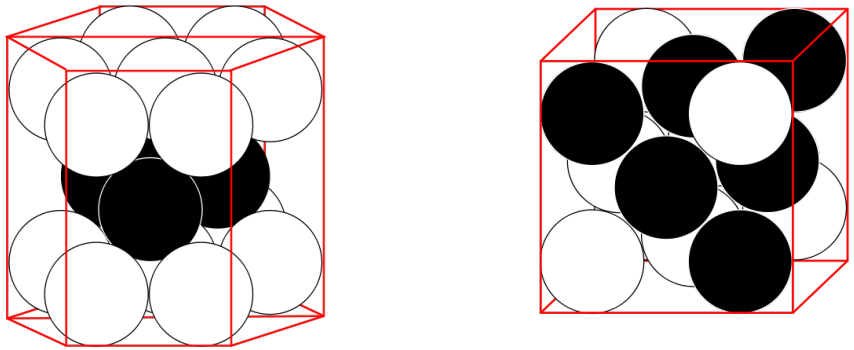
Unit Cells of HCP and FCC Structures

Top view:



HCP FCC (CCP)

3D view:

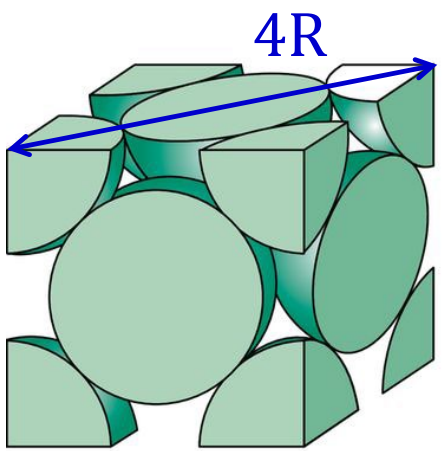


HCP FCC (CCP)

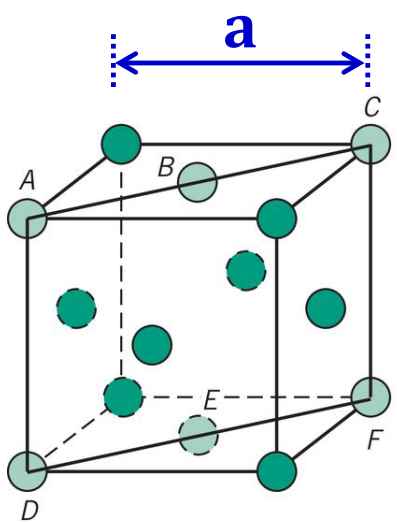
- FCC structure is also called cubic-close-packed (CCP) structure

Unit Cell Representations of FCC Crystal Structure

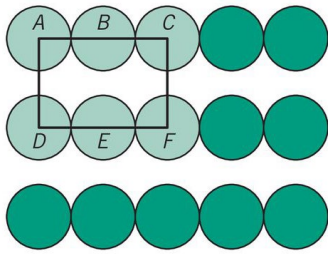
- Examples: Cu, Al, Ag, Au, Pt
- $a = 2\sqrt{2}R$
- Coordination number: 12

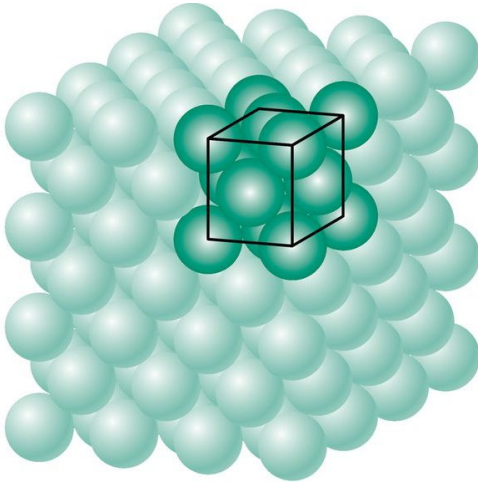


Hard-sphere unit cell



Reduced-sphere unit cell

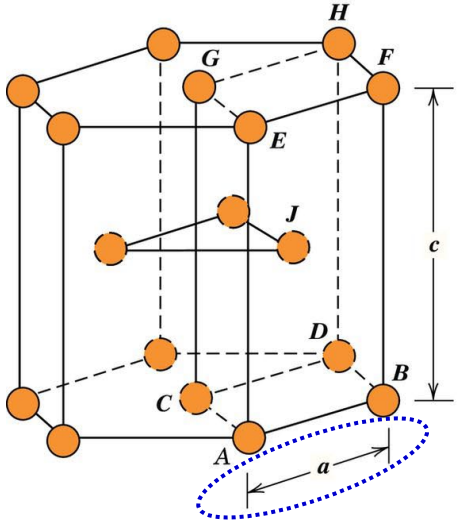




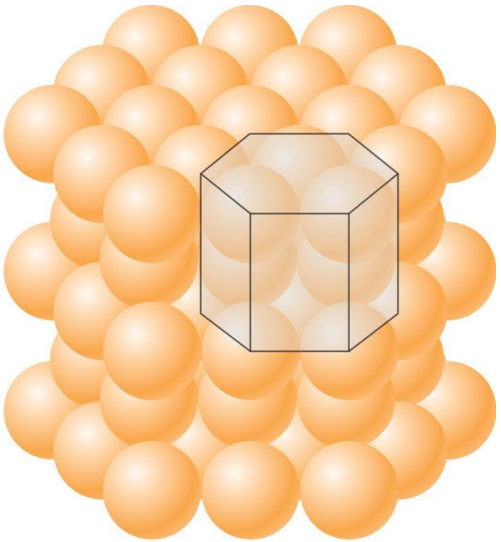
An aggregate of many atoms

Unit Cell Representations of HCP Crystal Structure

- Examples: Co, Ti, Mg, Ru
- a = 2R
- Coordination number: 12



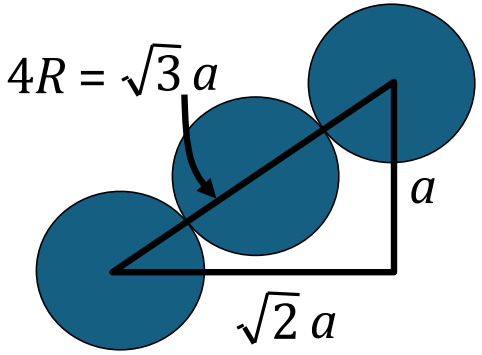
Reduced-sphere unit cell

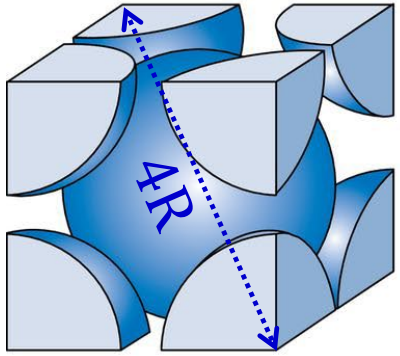


An aggregate of many atoms

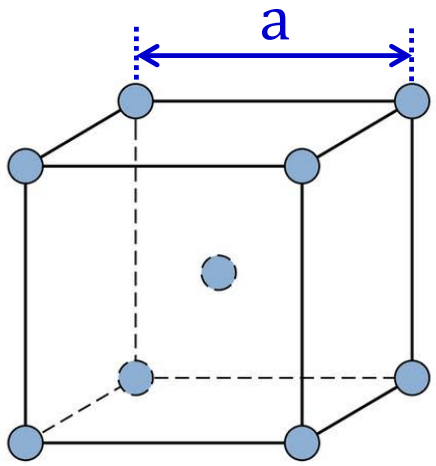
Unit Cell Representations of BCC Crystal Structure

- Examples: Fe, Cr, W, Mo
- $a = \frac{4R}{\sqrt{3}}$
- Coordination number: 8

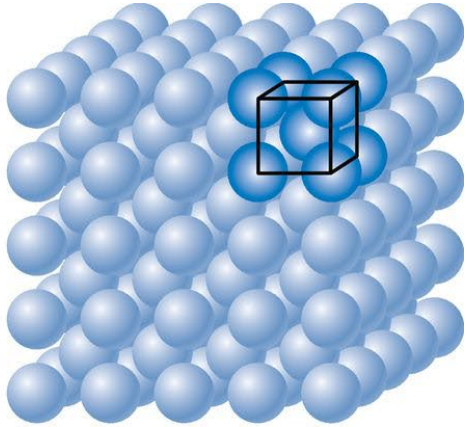




Hard-sphere unit cell



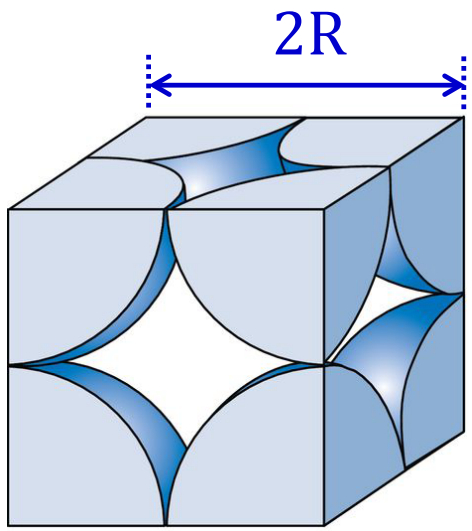
Reduced-sphere unit cell



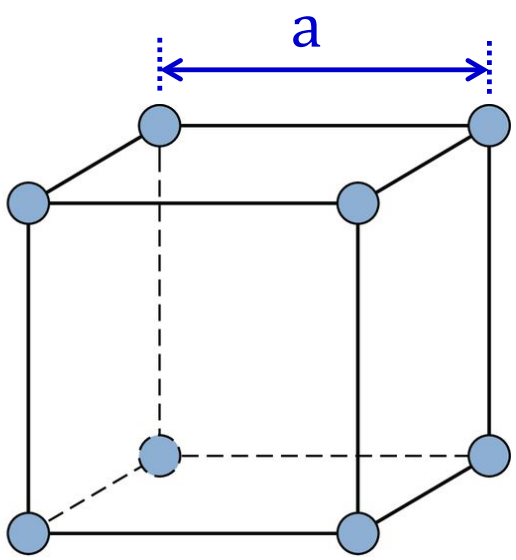
An aggregate of many atoms

Unit Cell Representations of SC Crystal Structure

- Examples: Po
- a = $2R$
- Coordination number: 6



Hard-sphere unit cell



Reduced-sphere unit cell

Atomic Packing Factor (APF)

- **Atomic Packing Factor (APF)**: sum of the sphere volumes of all atoms within a unit cell, assuming the atomic hard-sphere model, divided by the unit cell volume

$$\textbf{APF} = \frac{\text{volume of atoms actually inside the unit cell}}{\text{total volume of unit cell}}$$

- To calculate APF, we need to first find out number of atoms inside one unit cell, then calculate the total volume
- Recall the volume of each sphere is $\frac{4\pi R^3}{3}$

Exercise

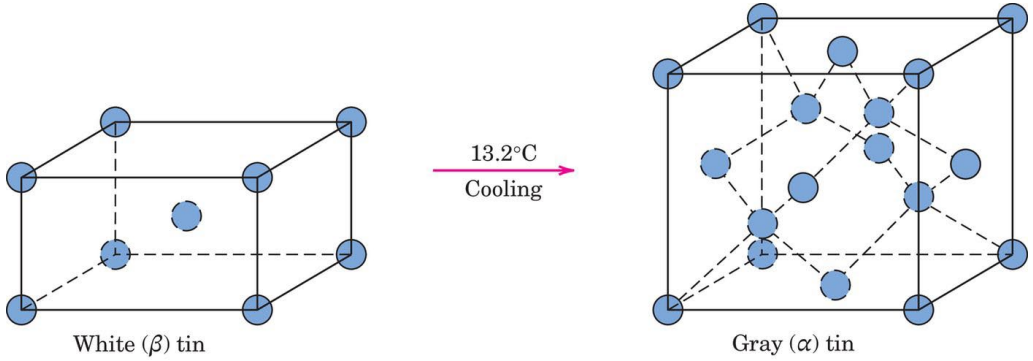
Show that in an FCC structure, the APF is approximately 0.74.

Exercise

Copper has an atomic radius of 0.128 nm, an FCC crystal structure, an atomic weight of 63.5 g/mol, and a measured density of 8.94 g/cm^3. Compute its theoretical density in g/cm^3.

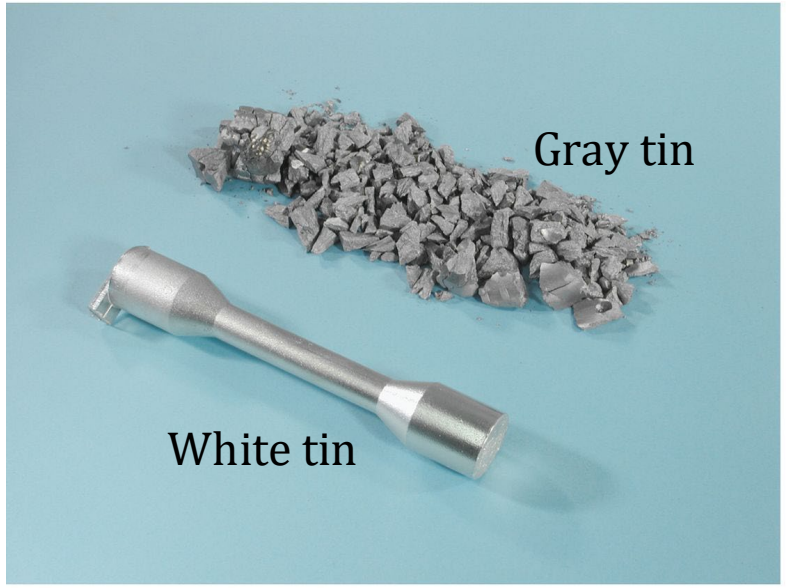
Polymorphism and Allotropy

- Some metals and non-metals have *more than one* crystal structure
- This is **polymorphism** or **allotropy**
- The prevailing crystal structure of a metal depends on *temperature* and *pressure*
- Example: Sn



Body-centered tetragonal crystal structure

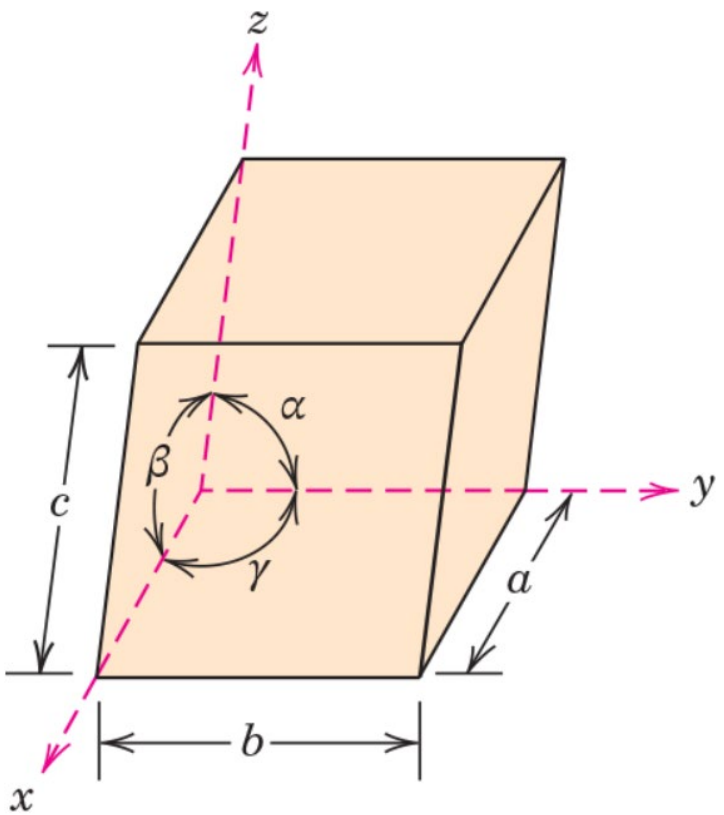
Diamond cubic crystal structure



Photograph courtesy of Professor Bill Plumbridge, Department of Materials Engineering, The Open University, Milton Keynes, England.

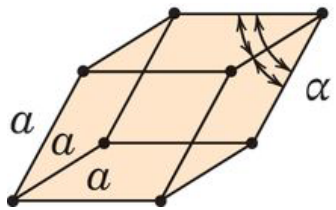
Crystal Systems

- There are many different possible crystal structures
- We can group all crystal structures based on unit cell geometry
- The geometry of a unit cell can be *completely* defined in terms of 6 parameters:
  - 3 edge lengths a, b, and c
  - 3 interaxial angles α, β, and γ

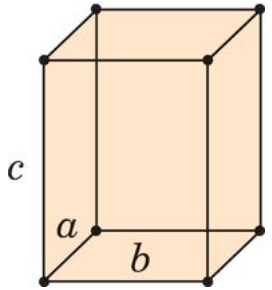


Seven Crystal Systems

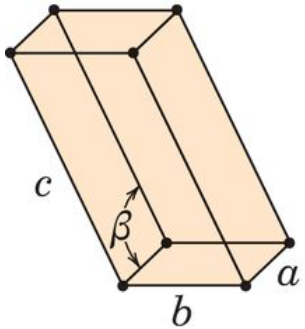
Crystal system	Axial relationships	Interaxial angles
Cubic	a = b = c	α = β = γ = 90°
Hexagonal	a = b ≠ c	α = β = 90°, γ = 120°
Tetragonal	a = b ≠ c	α = β = γ = 90°
Rhombohedral (trigonal)	a = b = c	α = β = γ ≠ 90°
Orthorhombic	a ≠ b ≠ c	α = β = γ = 90°
Monoclinic	a ≠ b ≠ c	α = β = 90° ≠ γ
Triclinic	a ≠ b ≠ c	α ≠ β ≠ γ ≠ 90°



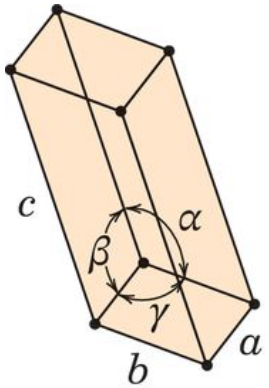
Rhombohedral



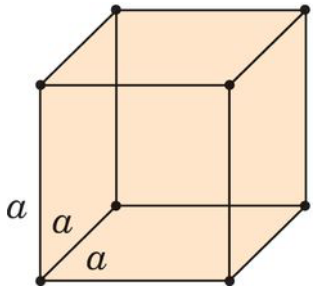
Orthorhombic



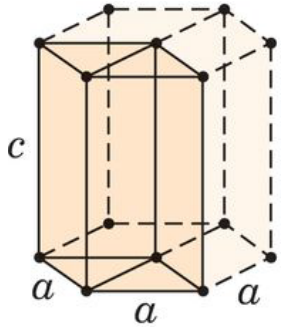
Monoclinic



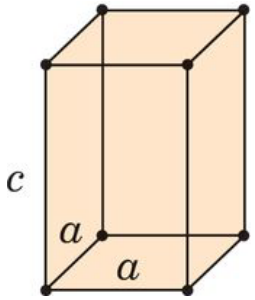
Triclinic



Cubic



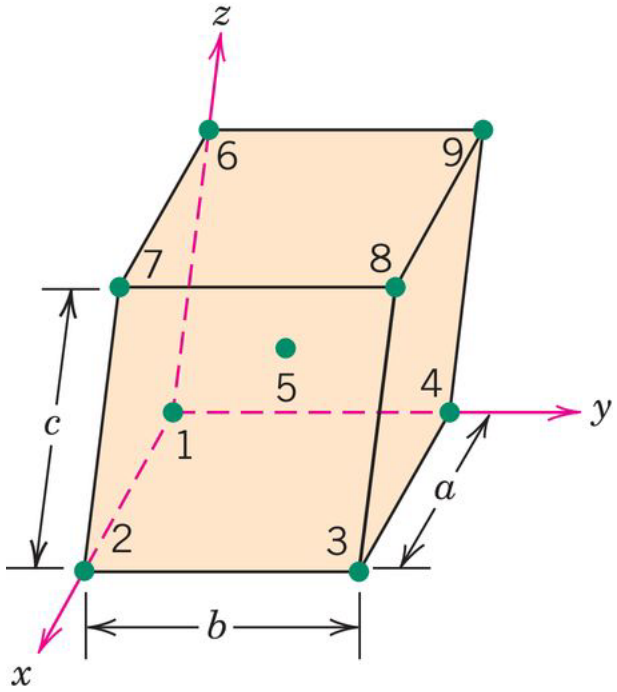
Hexagonal



Tetragonal

Crystallographic Points

- To specify a position within a unit cell, **lattice position coordinates** are used, specifically 3 **point indices**: ***q***, ***r***, ***s***
- They are *fractional multiples* of unit cell lengths
  - For example, in terms of crystallographic points, the positions of atoms in a body-centered unit cell can be expressed as:



Point number	*q*	*r*	*s*
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	½	½	½
6	0	0	1
7	1	0	1
8	1	1	1
9	0	1	1

Crystallographic Directions

- To describe a **crystallographic direction**, a *vector containing three dimensional indices* is used.
- Steps to determine the three directional indices:

1. Place a unit cell at the corner of a right-handed x-y-z coordinate system
2. Find the coordinates of two points lying on the direction:
   - *e.g.* Point 1 (x_1, y_1, z_1) as vector tail, Point 2 (x_2, y_2, z_2) as vector head
3. Tail point coordinates are subtracted from head point coordinates
   - we get (x_2-x_1, y_2-y_1, z_2-z_1)

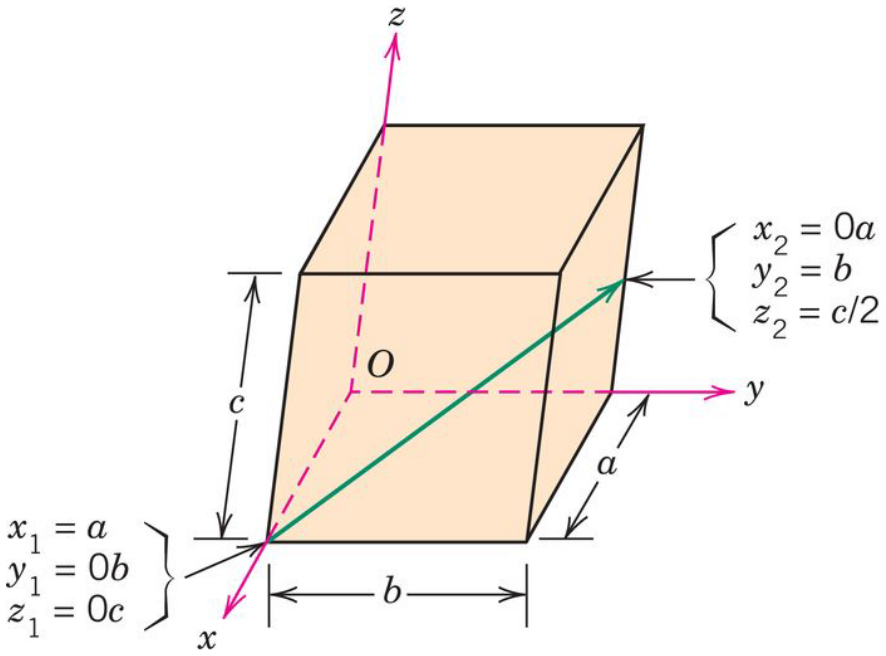
Crystallographic Directions

- Steps to determine the three directional indices (continued):

4. The coordinate differences are normalized in terms of (*i.e.* divided by) their respective a, b, and c lattice parameters
   - we get $\left(\frac{x_2-x_1}{a}, \frac{y_2-y_1}{b}, \frac{z_2-z_1}{c}\right)$
5. For convenience, the three numbers are often multiplied/divided by a common factor (n) to change to smallest integer values
6. The final indices, not separated by commas, are enclosed in square brackets: **[*uvw*]**
   - $\boldsymbol{u} = n\left(\frac{x_2-x_1}{a}\right)$, $\boldsymbol{v} = n\left(\frac{y_2-y_1}{b}\right)$, $\boldsymbol{w} = n\left(\frac{z_2-z_1}{c}\right)$

Crystallographic Directions

Example: procedure to determine the following directional indices

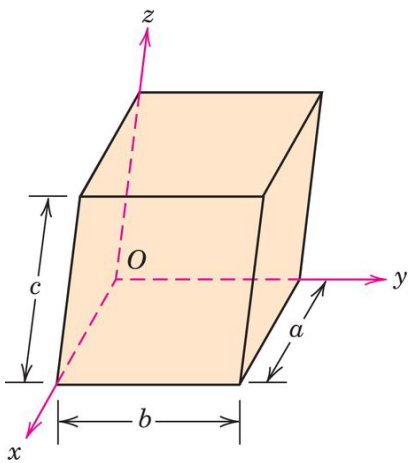


	x	***y***	***z***
Head coordinates (x_2, y_2, z_2)	0	b	c/2
Tail coordinates (x_1, y_1, z_1)	a	0	0
Coordinate differences	−a	b	c/2
Calculated values of u, v, w	$u = -2$	$v = 2$	$w = 1$
Final expression		$[\bar{2}21]$	

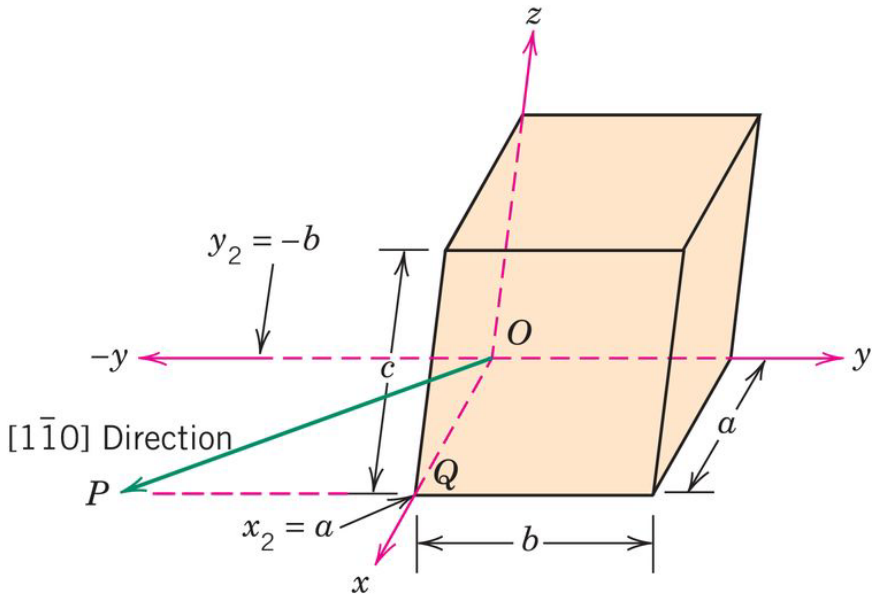
Crystallographic Directions

Example: construct a *specified* crystallographic direction

- Within the following unit cell, draw a $[1\bar{1}0]$ direction with its tail located at the origin of the coordinate system, Point O
- This problem can be solved by reversing the aforementioned procedure



	x	y	z
Head coordinates (x_2, y_2, z_2)	a	−b	0
Tail coordinates (x_1, y_1, z_1)	0	0	0
Coordinate differences	a	−b	0
Calculated values of u, v, w	$u = 1$	$v = -1$	$w = 0$
Final expression		$[1\bar{1}0]$	



Equivalent Crystallographic Directions

- For some crystal structures, several nonparallel directions with different indices are crystallographically equivalent
  - *e.g.*, in cubic crystals, all the directions represented by the following indices are equivalent: $[100]$, $[\bar{1}00]$, $[010]$, $[0\bar{1}0]$, $[001]$, $[00\bar{1}]$
- As a convenience, equivalent directions are grouped together into a **family**, which is enclosed in angle brackets, thus ***<uvw>*** (*e.g. <100>*)
- In cubic system, directions having the same indices *without* regard to order or sign, are equivalent
  - *e.g.* in cubic crystals, $[123]$ and $[\bar{2}1\bar{3}]$ are equivalent
- In other crystal systems, this is not always true
  - *e.g.* for tetragonal symmetry, $[100]$ and $[010]$ are equivalent, but $[100]$ and $[001]$ are *not* equivalent

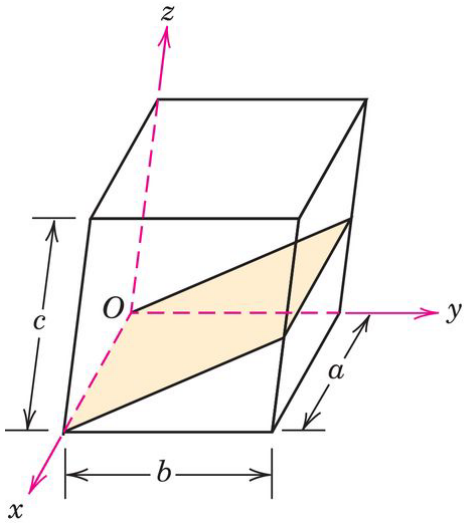
Crystallographic Planes

- Similar to directions, crystallographic planes are also represented by three indices, known as **Miller indices**
- Steps to determine the three Miller indices:

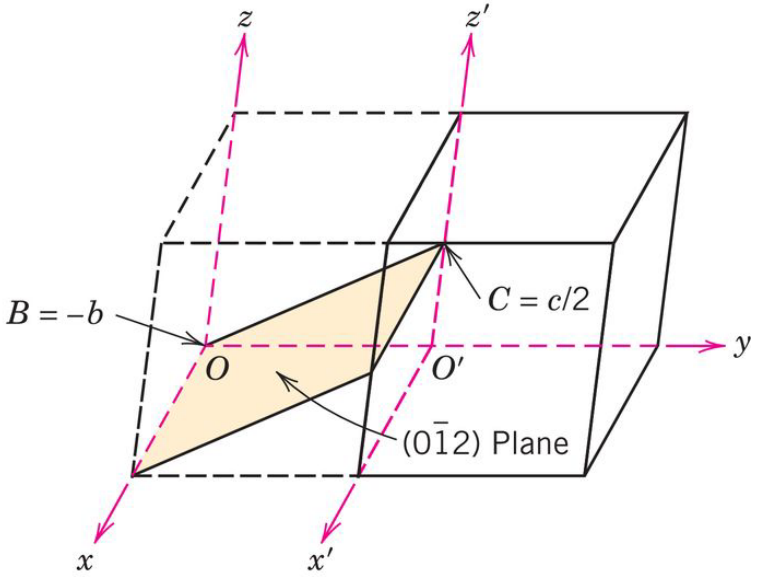
1. If the plane passes through the origin, establish a new origin in another unit cell
2. Read values of intercepts of plane (A, B, C) with x, y, and z axes in terms of a, b, c
3. Take reciprocals of intercepts (1/A, 1/B, 1/C)
4. Normalize them by multiplying by lattice parameters a, b, and c (a/A, b/B, c/C)
5. Reduce to smallest integer values (na/A, nb/B, nc/C)
6. Enclose resulting Miller Indices in round brackets, no commas: **(*hkl*)**

Crystallographic Planes

Example: determine the Miller indices for the plane shown on the right

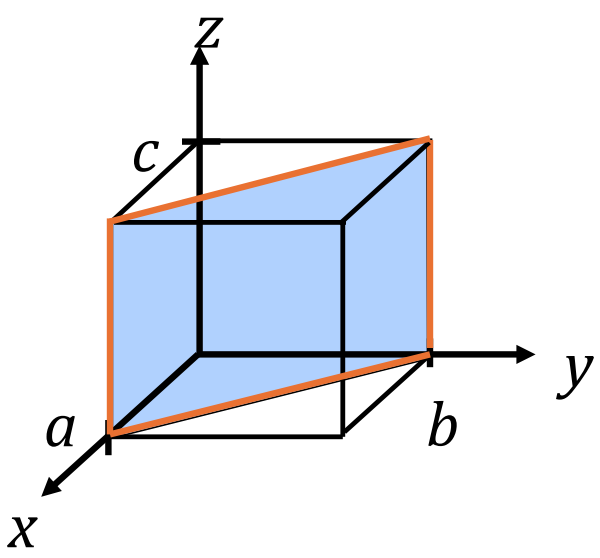


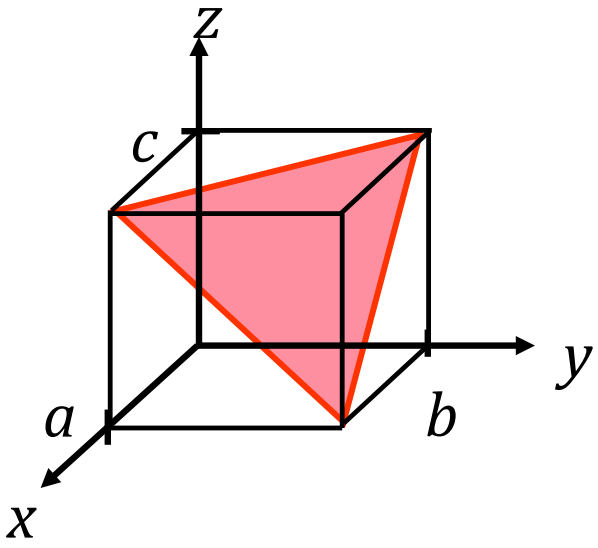
1. The plane passes through origin O, we choose a new origin O' in adjacent unit cell
2. Intercepts (A, B, C) of plane:
3. Take reciprocals of intercepts:
4. Normalize them by multiplying by lattice parameters *a*, *b*, and *c:*
5. Reduce to smallest integer values:
6. Enclosure of Miller Indices:



Exercise

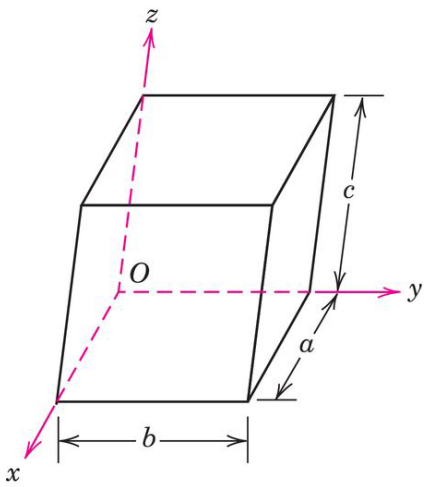
Quick test: what are the Miller indices for the planes shown below:

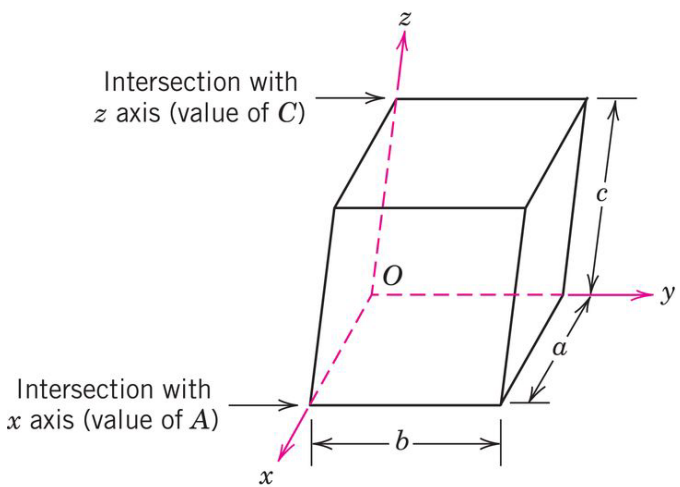


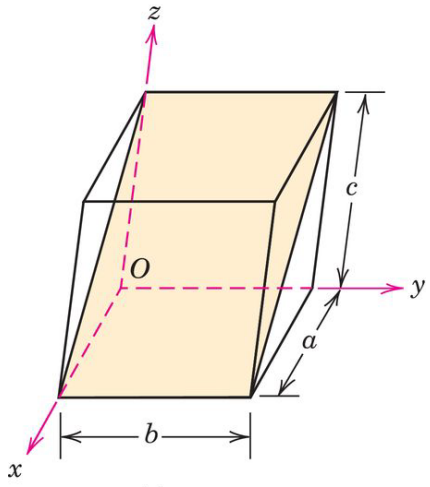


Crystallographic Planes

Example: construct a (101) plane within the following unit cell







$$h = \frac{\mathrm{na}}{\mathrm{A}} = 1$$

$$k = \frac{\mathrm{nb}}{\mathrm{B}} = 0$$

$$l = \frac{\mathrm{nc}}{\mathrm{C}} = 1$$

already are the smallest integer so n = 1

$A = \mathrm{a}$

$B = \infty$

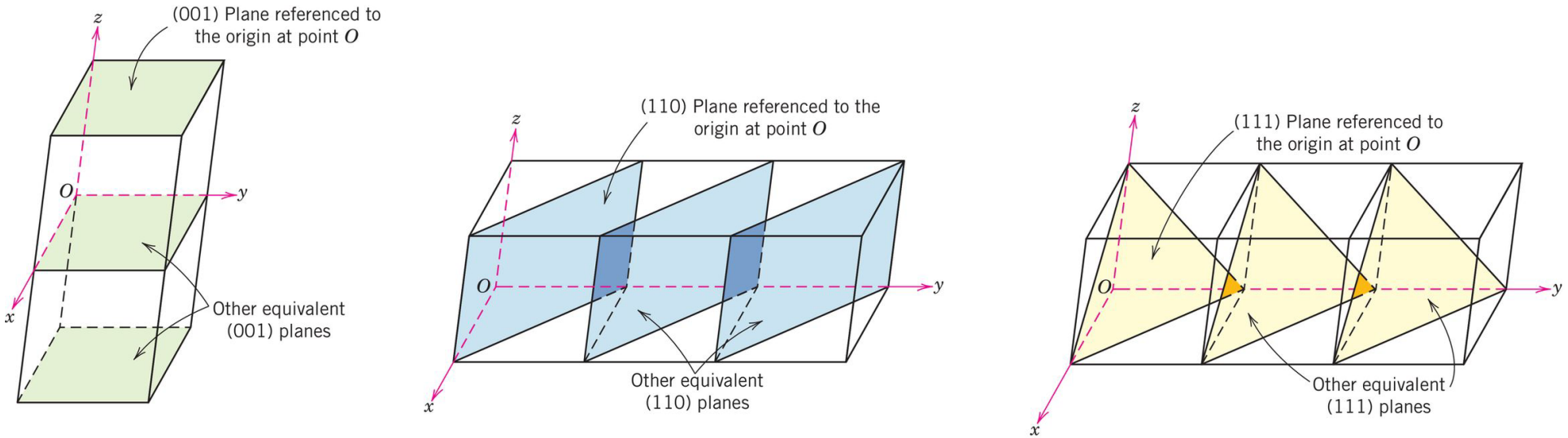
$C = \mathrm{c}$

Therefore, (101) plane

- Intersects the x axis at a
- Parallel to y axis
- Intersects the z axis at c

Equivalent Crystallographic Planes

- Any two planes parallel to each other are equivalent and have identical indices



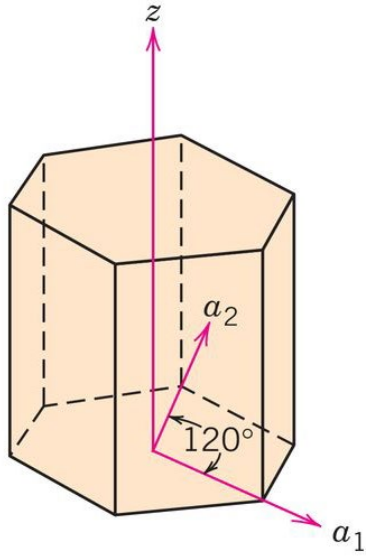
- A family of crystallographically equivalent planes is denoted in curly brackets, ***{hkl}***
  - *e.g.*, in cubic crystals, (111), ($\bar{1}$11), (1$\bar{1}$1), (11$\bar{1}$), (1$\bar{1}\bar{1}$), ($\bar{1}$1$\bar{1}$), ($\bar{1}\bar{1}$1), and ($\bar{1}\bar{1}\bar{1}$) planes all belong to the {111} family

Directions and Planes in Hexagonal Crystals

- There are two ways to express directions and planes in hexagonal unit cell

- **Three-index** system: [UVW]

- **Four-index** system (Miller-Bravais coordinate system): [uvtw]



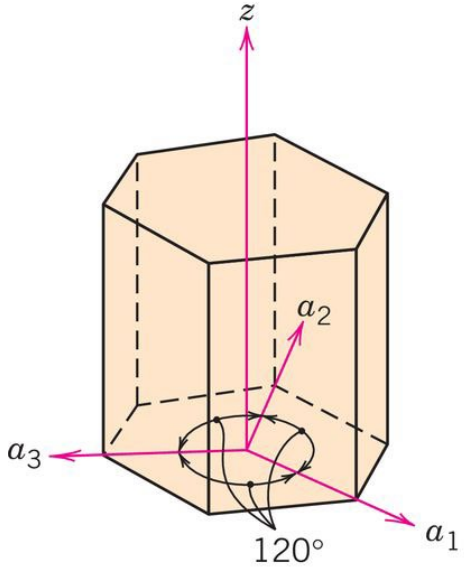
Conversion formula:

$$u = \frac{1}{3}(2U - V)$$

$$v = \frac{1}{3}(2V - U)$$

$$t = -(u + v)$$

$$w = W$$

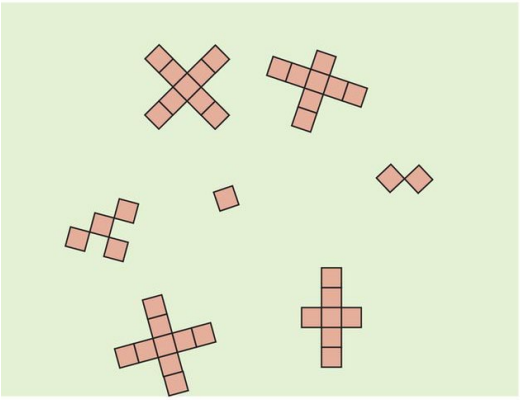


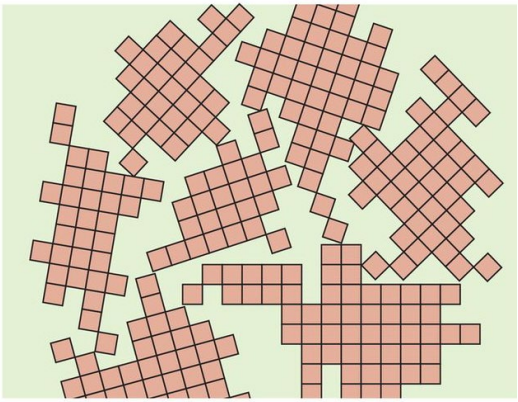
Single Crystal and Polycrystalline Materials

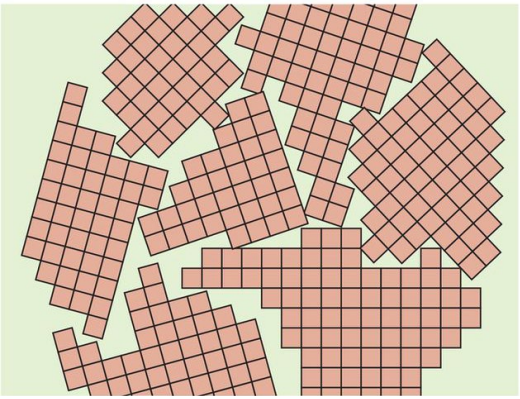
- If the unit cell can repeat itself in a crystalline solid without interruption, the result is a **single crystal**
- A single crystal usually assumes a regular geometric shape with flat faces; the shape is indicative of the crystal structure
- Most crystalline solids are composed of many small single crystals, or grains; they are **polycrystalline**

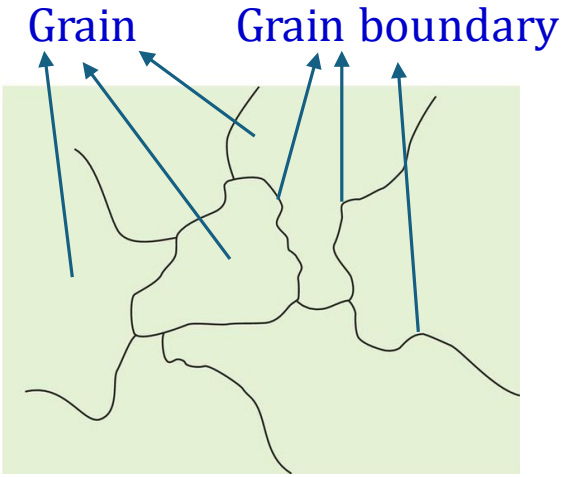
Iron pyrite (FeS_2) single crystal

© William D. Callister, Jr.





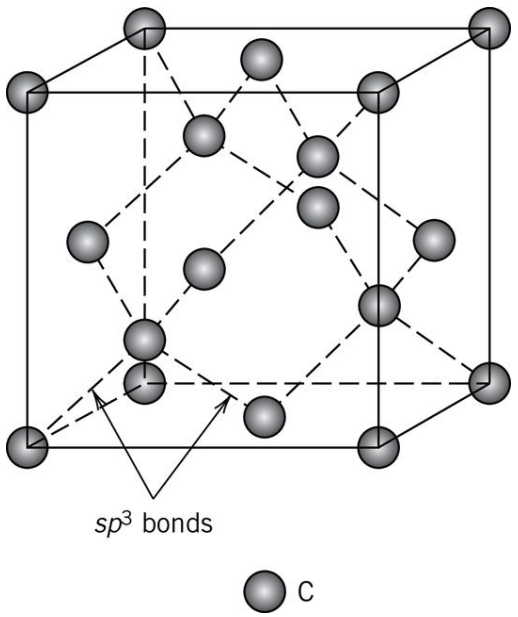




Stages of solidification of a polycrystalline material

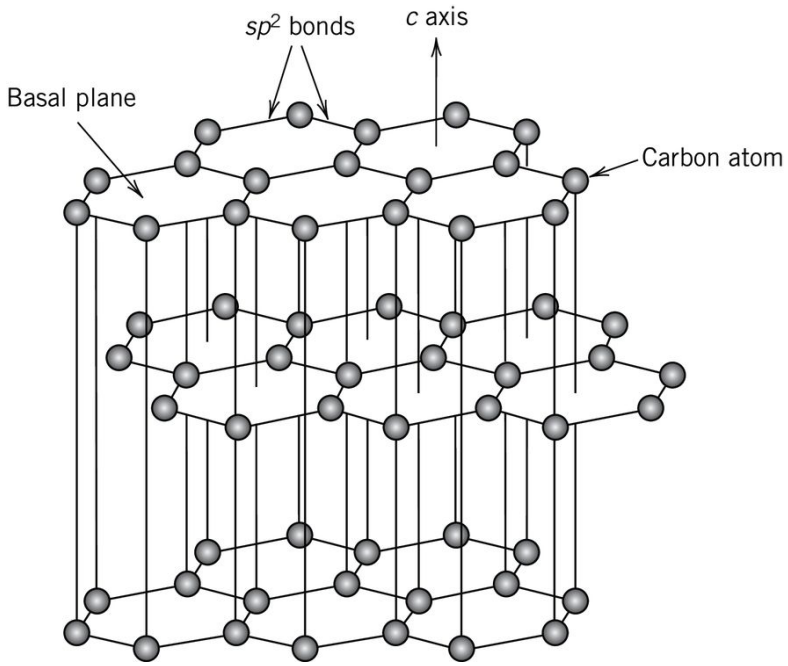
Some Important Structure Types

- **Carbon**
  - ***Diamond***



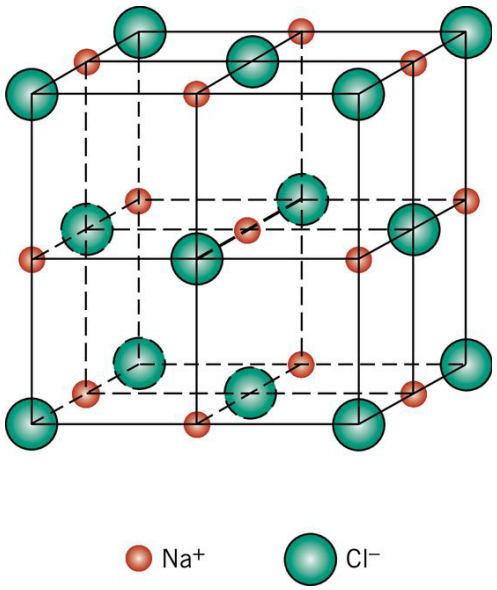
e.g. C, Si, Ge

  - ***Graphite***



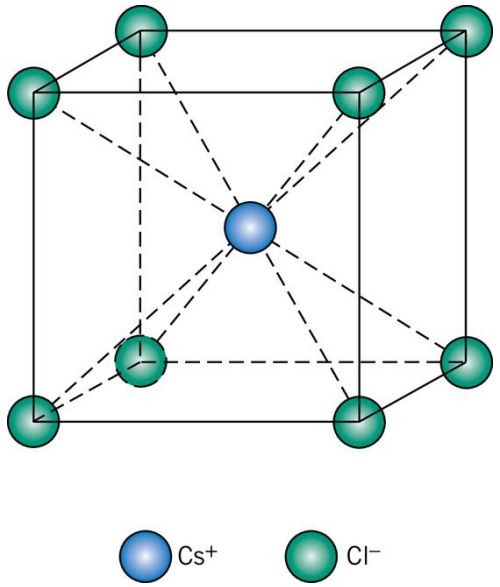
Some Important Structure Types

- **AX-Type** Crystal Structures
  - ***Rock Salt Structure***



e.g. NaCl, MgO, FeO

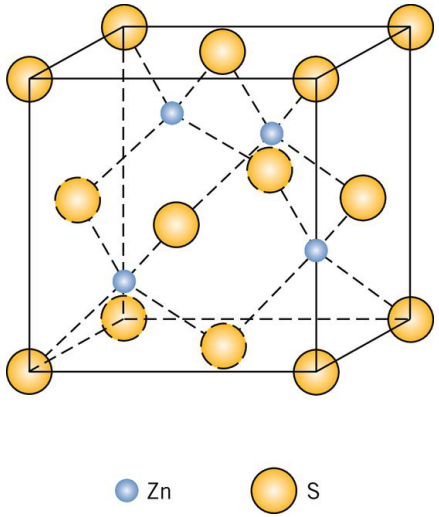
  - ***Cesium Chloride Structure***



e.g. CsCl, CsBr

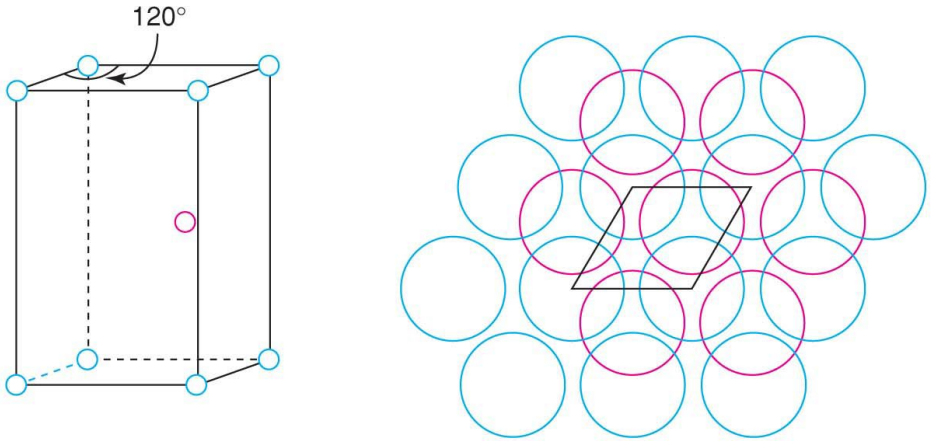
Some Important Structure Types

- **AX-Type** Crystal Structures
  - ***Zinc Blende*** *(sphaleirite)*



e.g. ZnS, SiC, GaAs

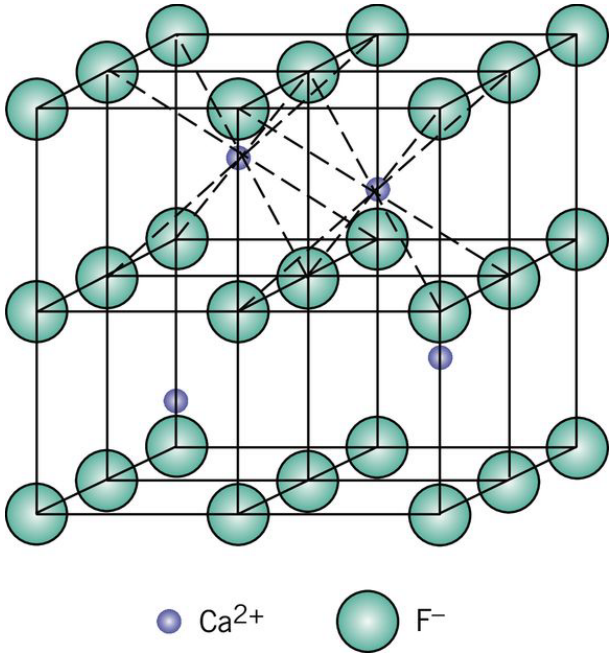
  - ***Wurtzite***



e.g. ZnS, ZnO, CdS, CdSe

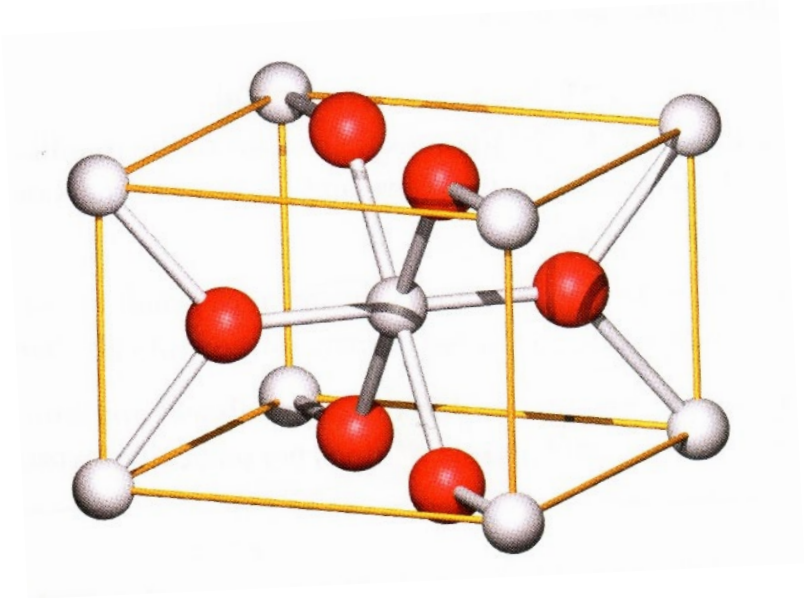
Some Important Structure Types

- **AX_2**-Types Crystal Structures
  - ***Fluorite***



e.g. CaF_2, UO_2, ThO_2,

  - ***Rutile***

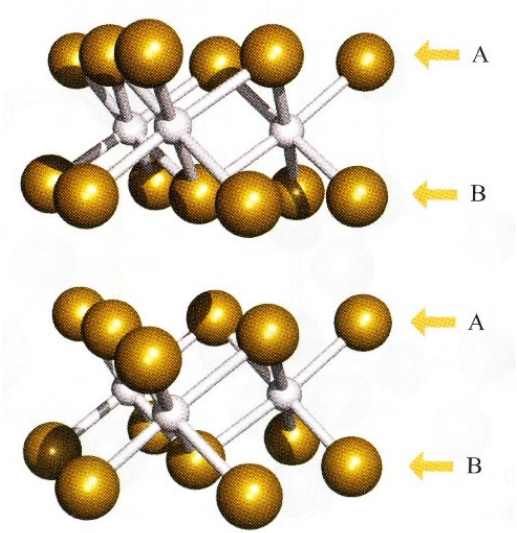


e.g. TiO_2, RuO_2, IrO_2

Inorganic Chemistry, Housecroft C. E. and Sharpe A. G.

Some Important Structure Types

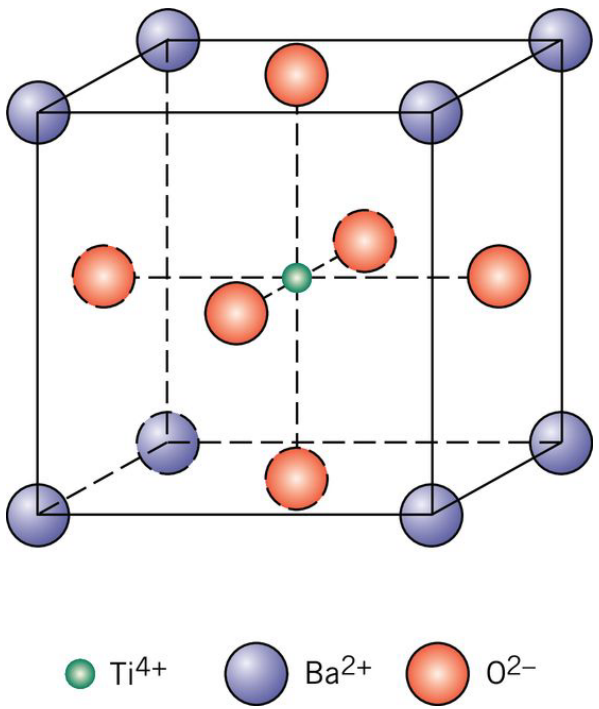
- **AX_2**-Types Crystal Structures
  - ***CdI_2 Structure*** (one kind of layer structures)



e.g. CdI_2, $FeBr_2$, $Mg(OH)_2$, $Co(OH)_2$

Some Important Structure Types

- **ABX_3**-Type Crystal Structures
  - ***Perovskite***



e.g. $BaTiO_3$, $SrZrO_3$, $SrSnO_3$