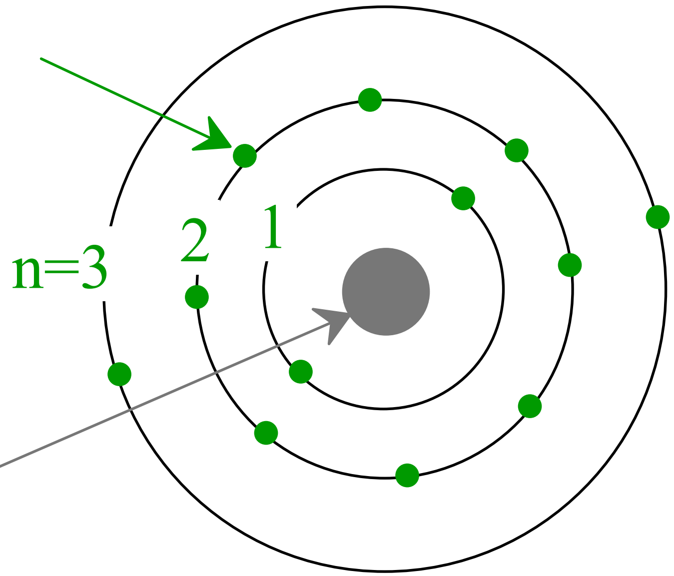
CHAPTER 2:
ATOMIC STRUCTURE, BONDING AND PROPERTIES

ISSUES TO ADDRESS...

- **Review of atomic structure**
- **What promotes bonding?**
- **What types of bonds are there?**
- **What properties are inferred from bonding?**

BOHR ATOM

orbital electrons:
n = principal
quantum number



Adapted from Fig. 2.1, *Callister 6e.*

Nucleus: Z = # protons = Atomic number(= # electrons)

= 1 for hydrogen to 94 for plutonium

N = # neutrons

Atomic mass A $\approx$ Z + N

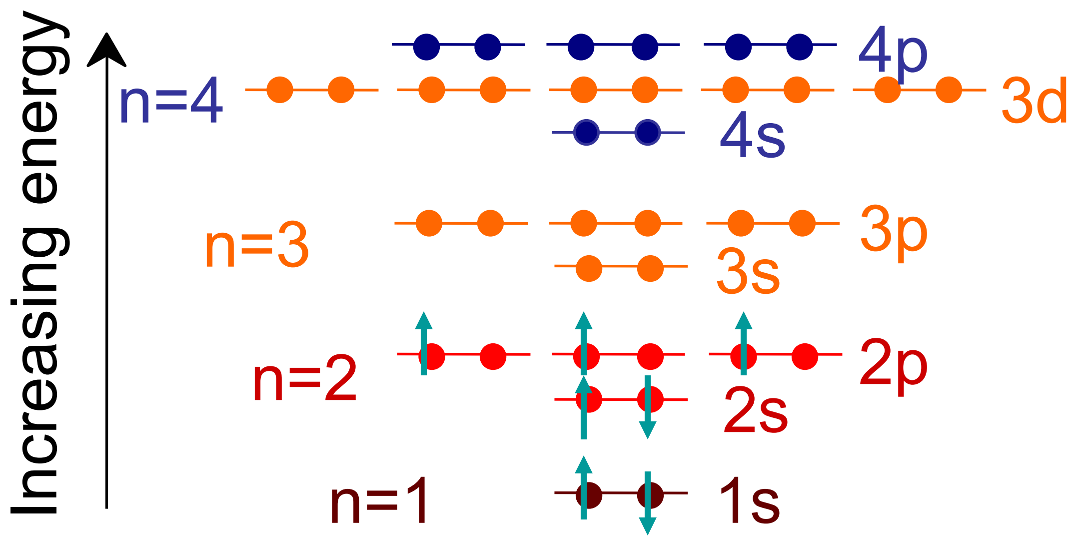
Isotopes = equal Z but different N!

1 mole = 6.023×10^{23} (Avogadro's number) atoms or molecules

ELECTRON ENERGY STATES

Electrons...

- have discrete energy states
- tend to occupy lowest available energy state.



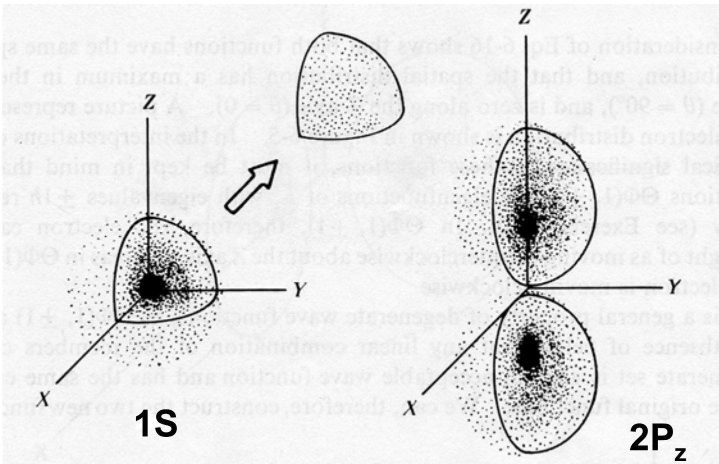
Adapted from Fig. 2.5, *Callister 6e.*

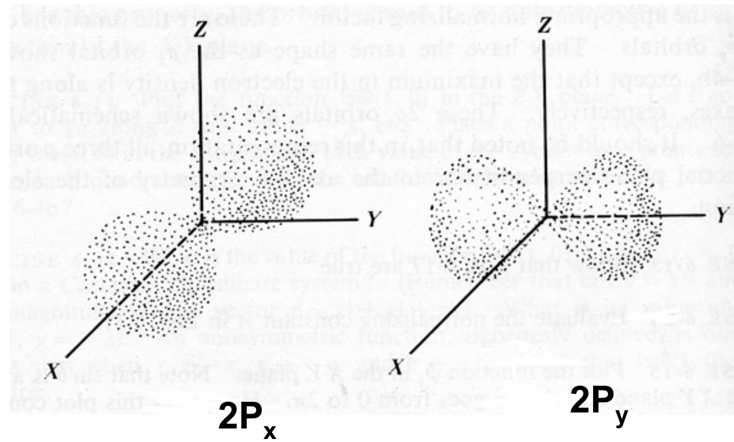
There are four quantum numbers (Problem 2-6):

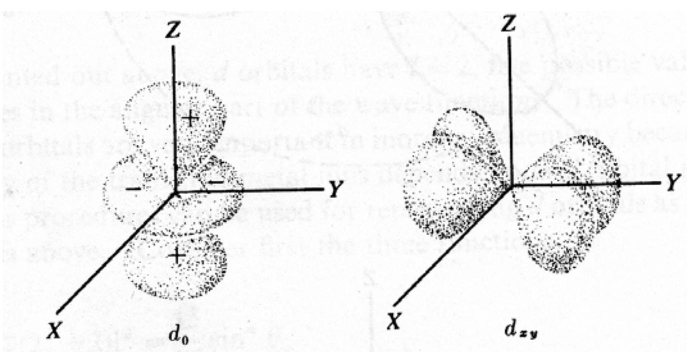
$n = 1,2,3,4,..$
$l = 0,1,2,3,..n-1$
$m_l = 0, \pm 1, \pm 2, \pm 3, \ldots \pm l$
$m_s = \pm 1/2$

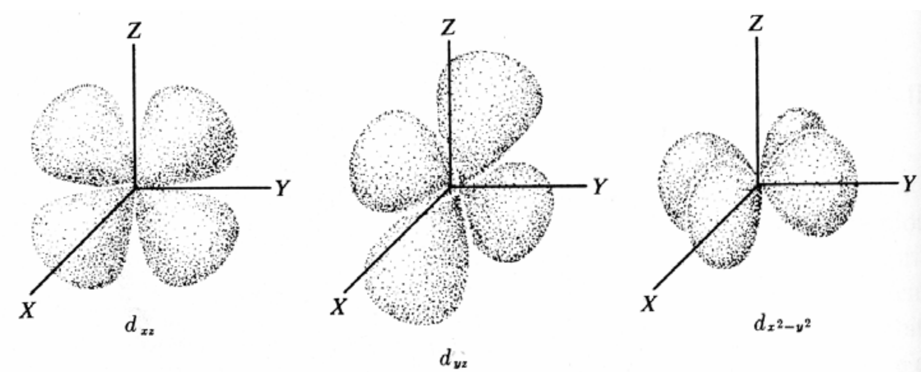
Pauli Exclusion Principle: Each energy state cannot hold more than two electrons.
Hund's Rule: For a shell with less than half full, electrons arrange themselves with all spins parallel.

Probability of Finding Electrons









Adapted from: “Quantum Mechanics in Chemistry”, M. W. Hanna, Figures 6-4 and 6-8

STABLE ELECTRON CONFIGURATIONS

Stable electron configurations...

- have complete s and p subshells
- tend to be unreactive.

Z	Element	Configuration
2	He	$1s^2$
10	Ne	$1s^2 2s^2 2p^6$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
36	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Adapted from Table 2.2, *Callister 6e.*

SURVEY OF ELEMENTS

- Most elements: Electron configuration not stable.

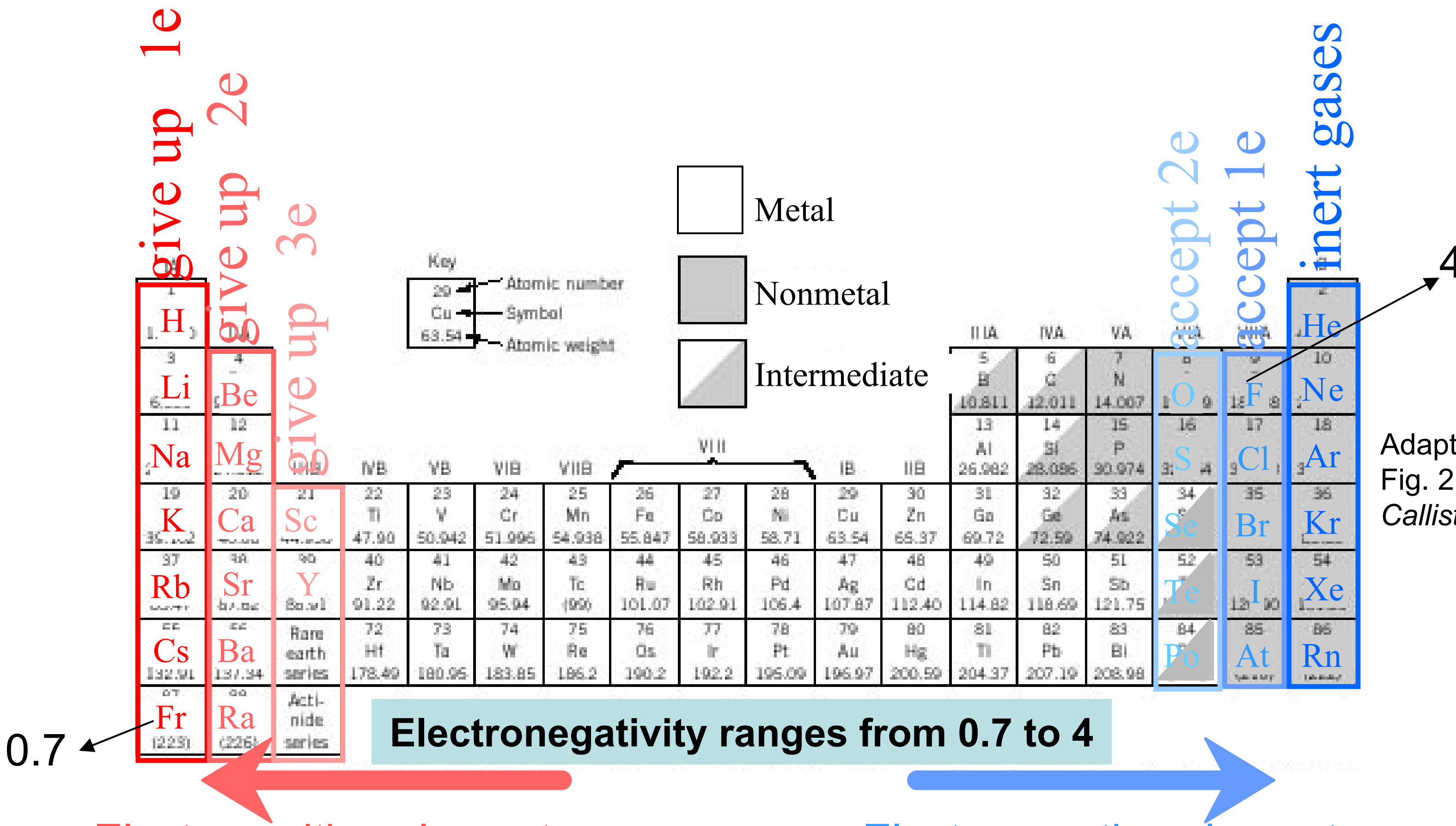
Element	Atomic #	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum	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	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4^6$	(stable)

Adapted from Table 2.2, *Callister 6e.*

- Why? Valence (outer) shell usually not filled completely.

THE PERIODIC TABLE

- Columns: Similar Valence Structure



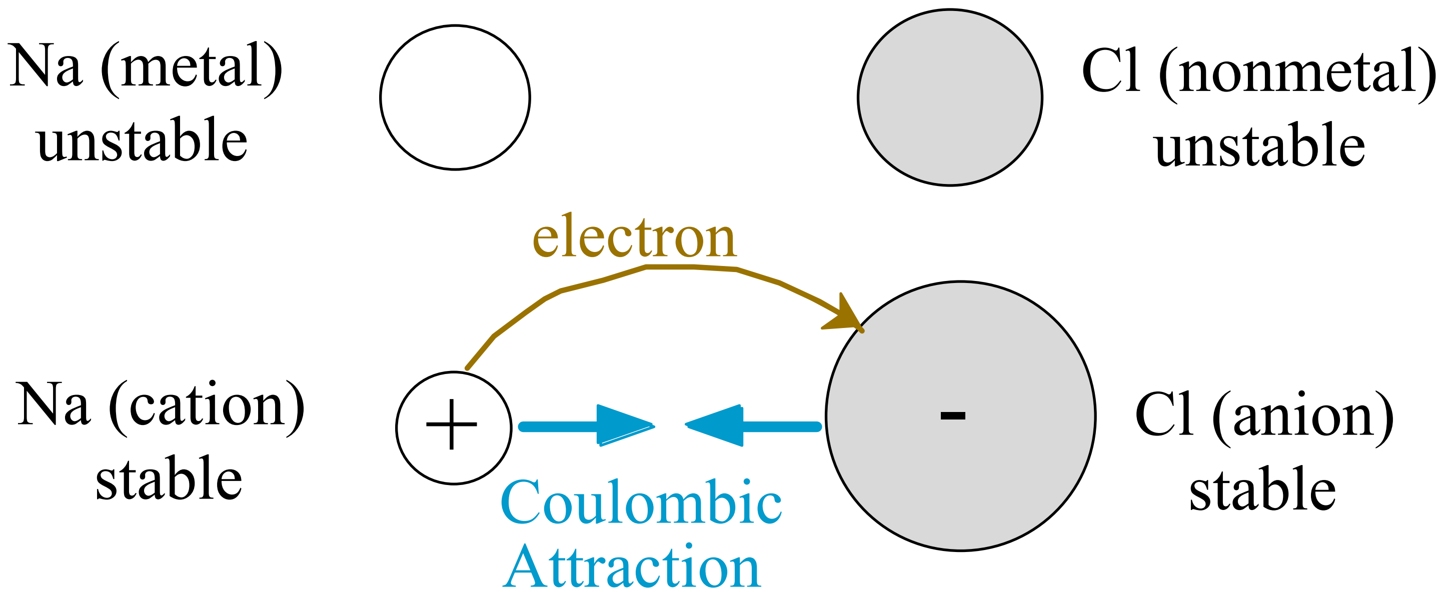
Adapted from Fig. 2.6, *Callister 6e.*

Electropositive elements:
Readily give up electrons
to become + ions.

Electronegative elements:
Readily acquire electrons
to become - ions.

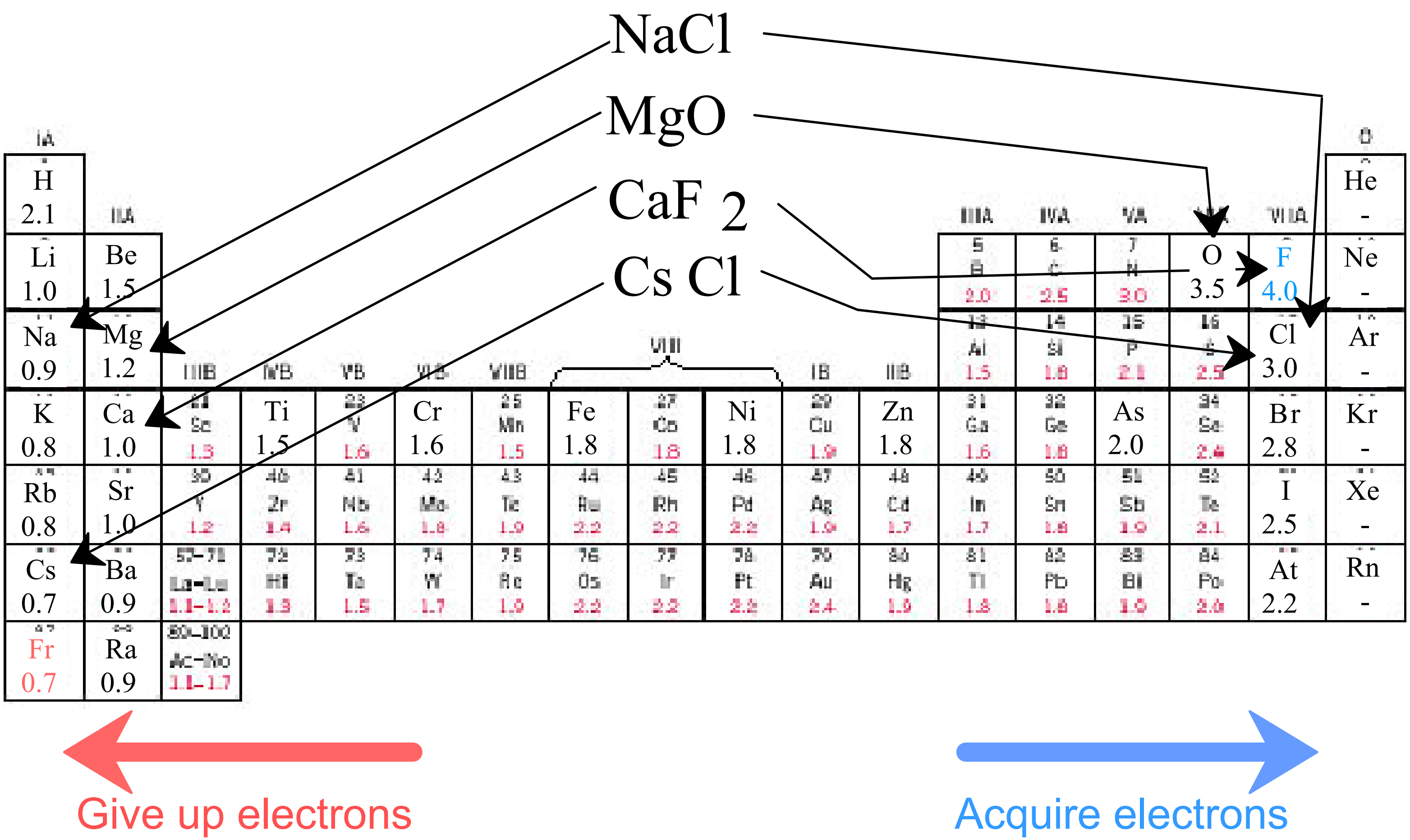
IONIC BONDING

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



EXAMPLES: IONIC BONDING

- Predominant bonding in Ceramics



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.

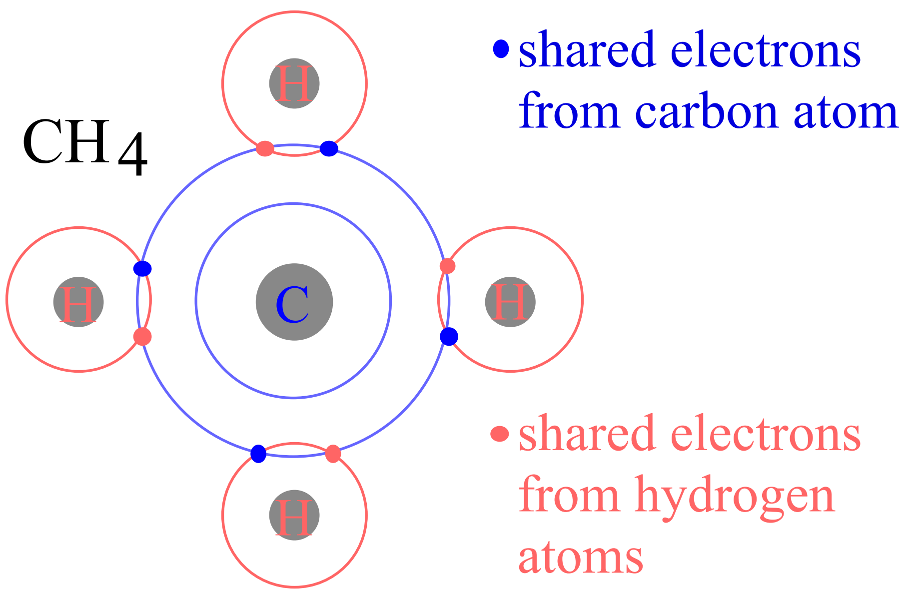
COVALENT BONDING

- Requires shared electrons
- Example: CH_4

C: has 4 valence e,
needs 4 more

H: has 1 valence e,
needs 1 more

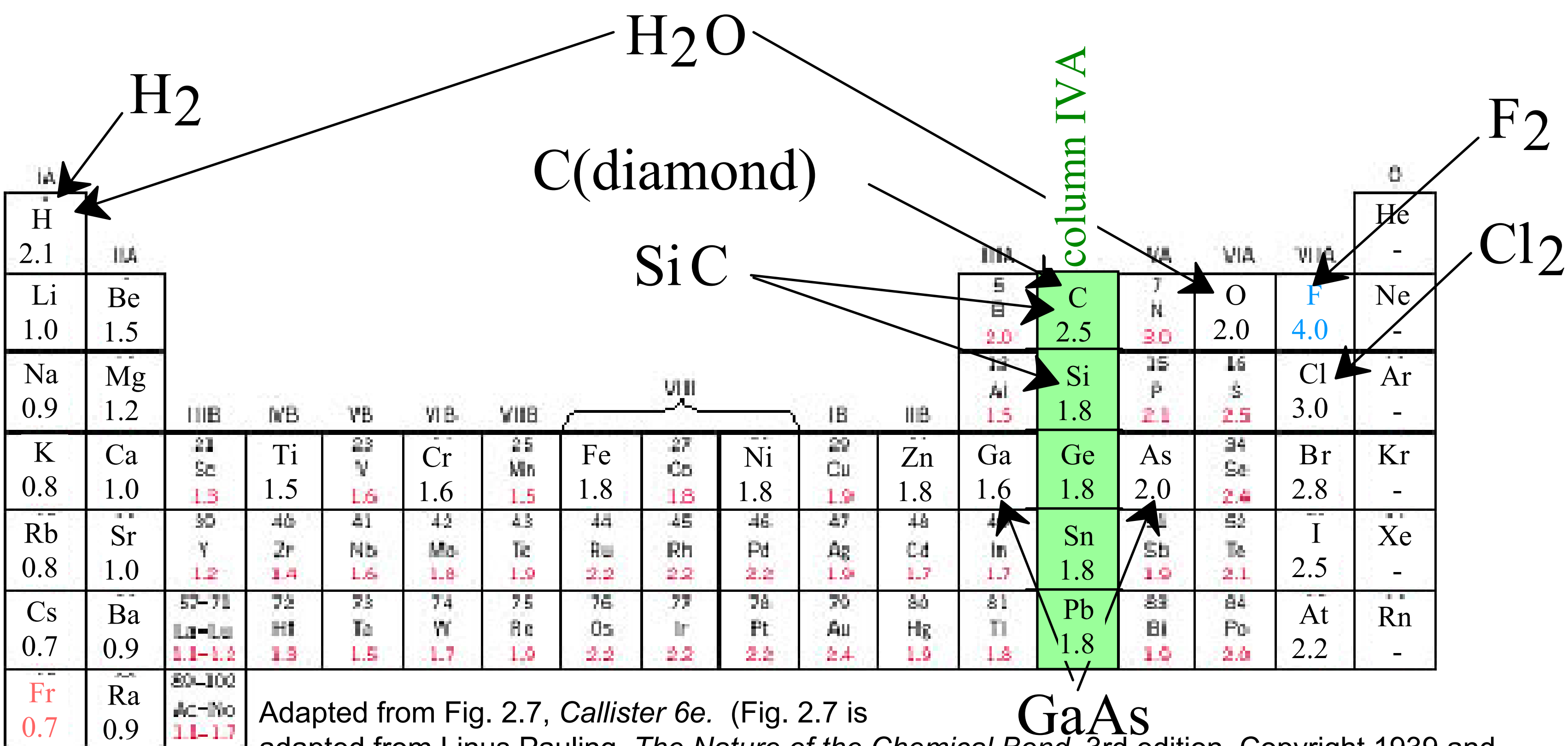
Electronegativities
are comparable.



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

% ionic character = $\{1-\exp[-(0.25)(X_A-X_B)^2]\} \times 100$
X_A and X_B are the electronegativities of the respective elements

EXAMPLES: COVALENT BONDING

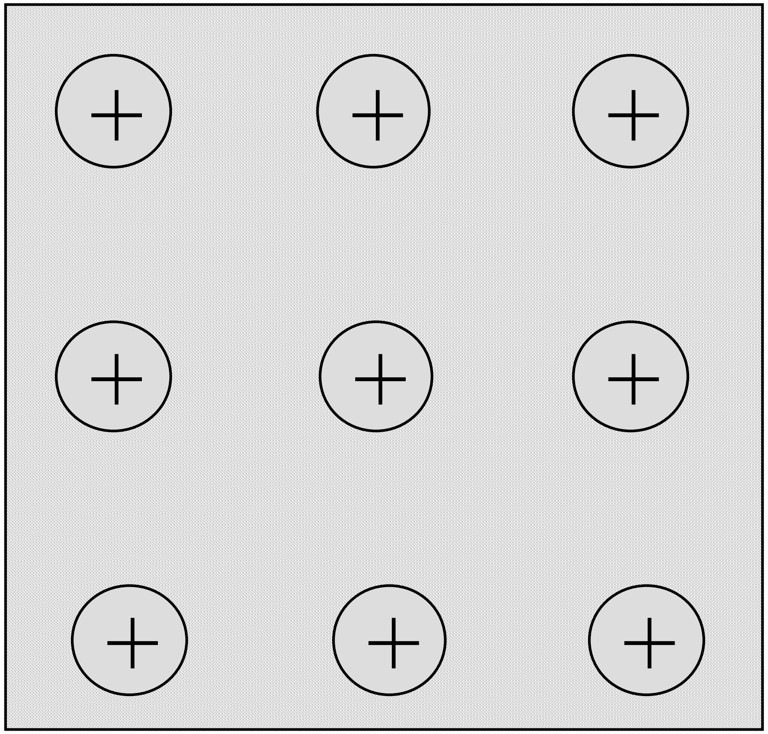


Adapted from Fig. 2.7, *Callister 6e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

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

METALLIC BONDING

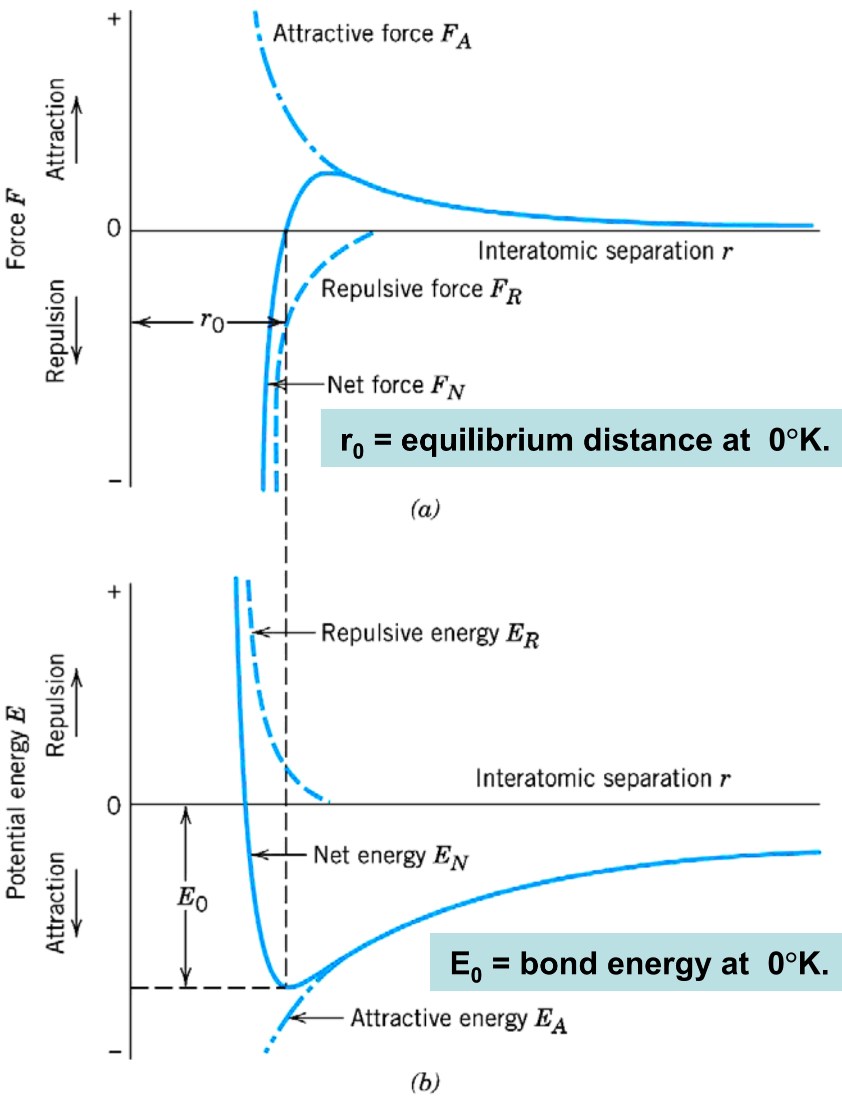
- Arises from a sea of donated valence electrons (1, 2, or 3 from each atom).



Adapted from Fig. 2.11, *Callister 6e.*

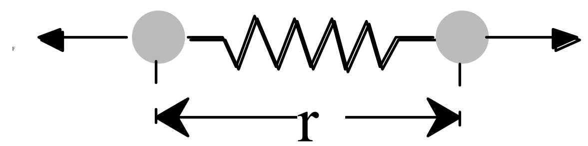
- Primary bond for metals and their alloys

BOND STRENGTH



r_0 = equilibrium distance at 0°K.

E_0 = bond energy at 0°K.



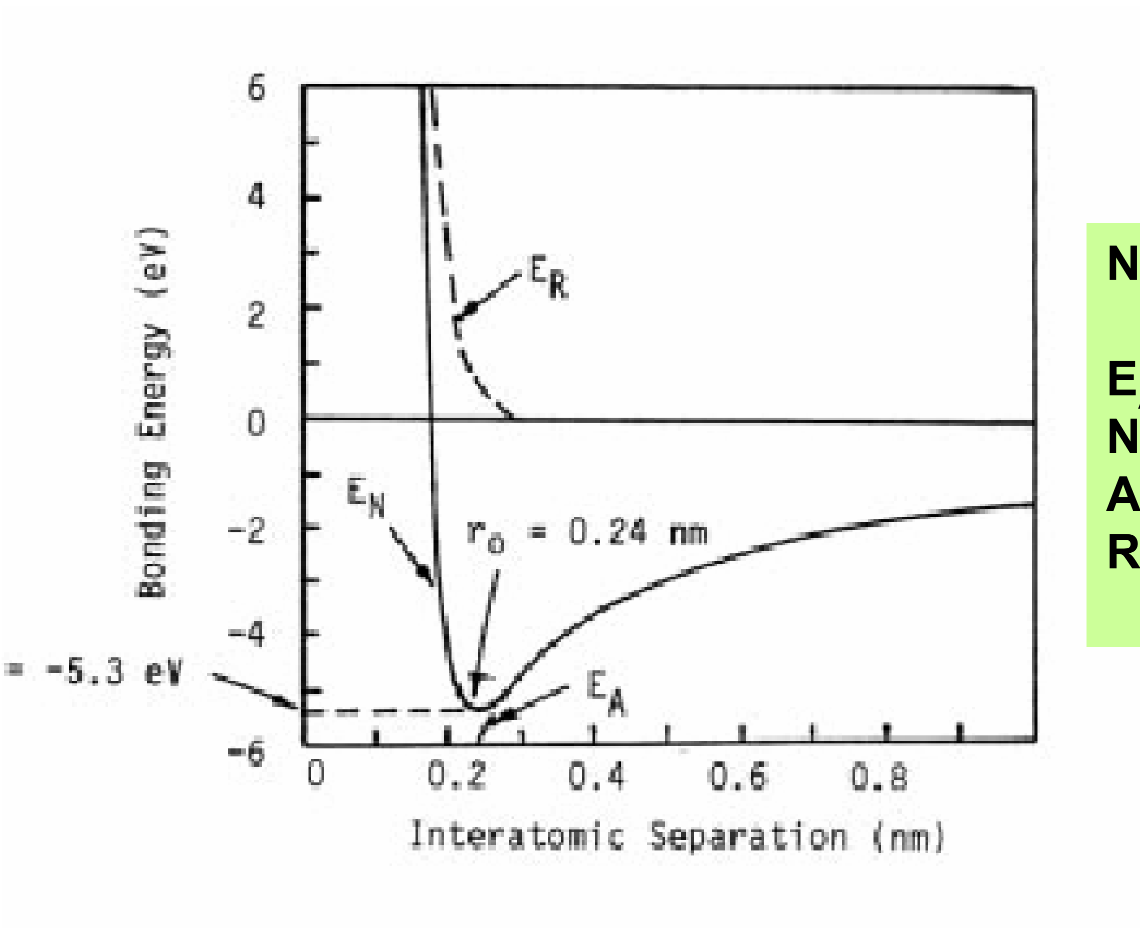
$F_A(r)$ = Attractive Force
$F_R(r)$ = Repulsive Force

$F_N(r)$ = net force = $F_A + F_R$

E = Potential Energy = $\int F.dr$
or $F(r)= dE/dr$
$E_N(r) = E_A + E_R$

Equilibrium: FA + FR = 0
or $dE_N/dr = 0$

Problem 2-14



NaCl

$E_A = -1.436/r$, $E_R = 7.32\times10^{-6}$

Note:

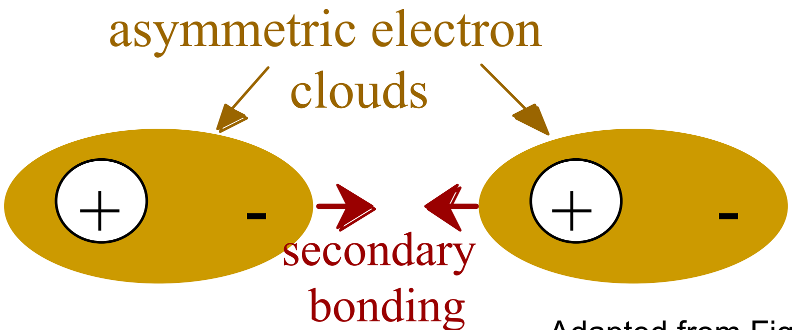
Attractive Potential energy < 0

Repulsive Potential energy > 0

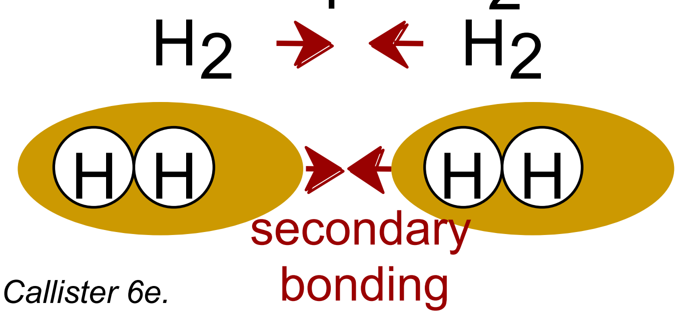
SECONDARY BONDING

Arises from interaction between dipoles

- Fluctuating dipoles



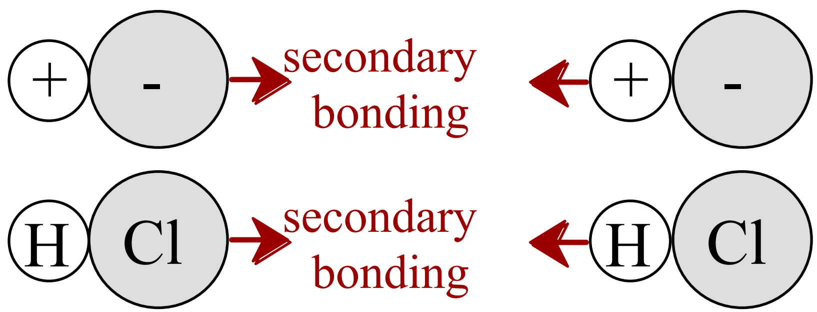
ex: liquid H_2



Adapted from Fig. 2.13, *Callister 6e.*

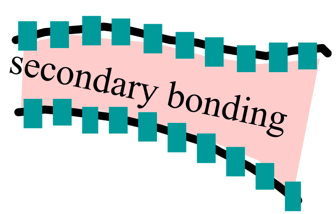
- Permanent dipoles-molecule induced

-general case:



-ex: liquid HCl

-ex: polymer



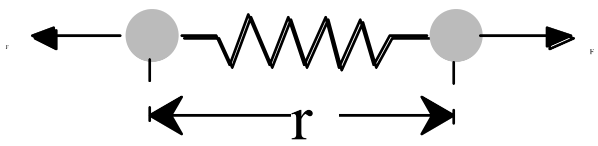
Adapted from Fig. 2.14, *Callister 6e.*

SUMMARY: BONDING

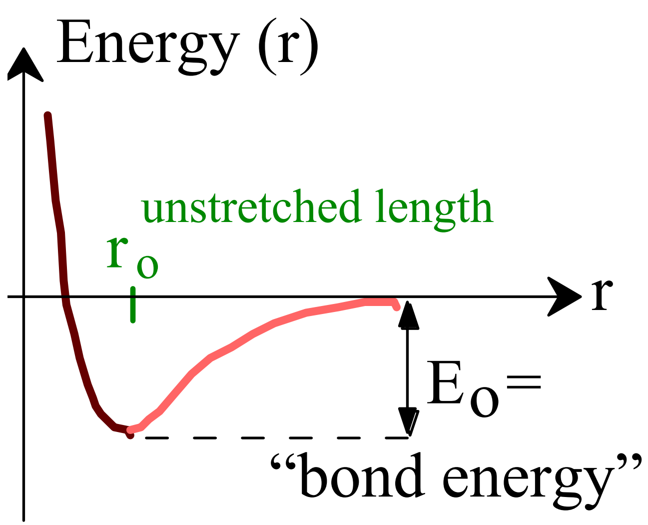
Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (**ceramics**)
Covalent	Variable large-Diamond small-Bismuth	Directional **semiconductors**, **ceramics** **polymer** chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (**metals**)
Secondary	smallest	Directional inter-chain (**polymer**) inter-molecular

PROPERTIES FROM BONDING: T_M

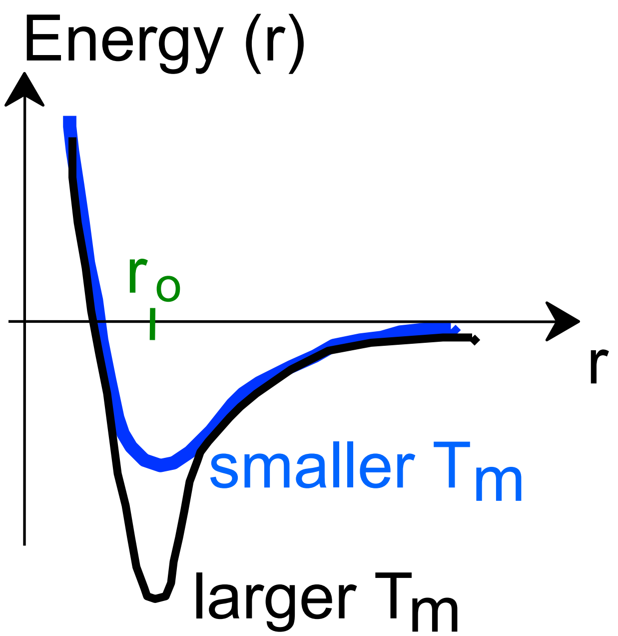
- Bond length, r



- Bond energy, E_o



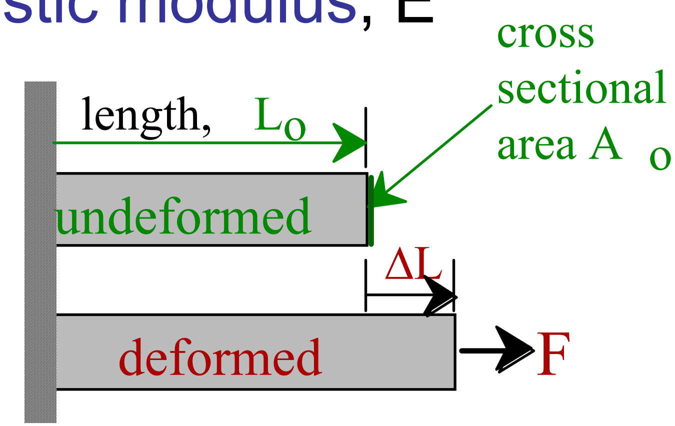
- Melting Temperature, T_m



T_m is larger if E_o is larger.

PROPERTIES FROM BONDING: E

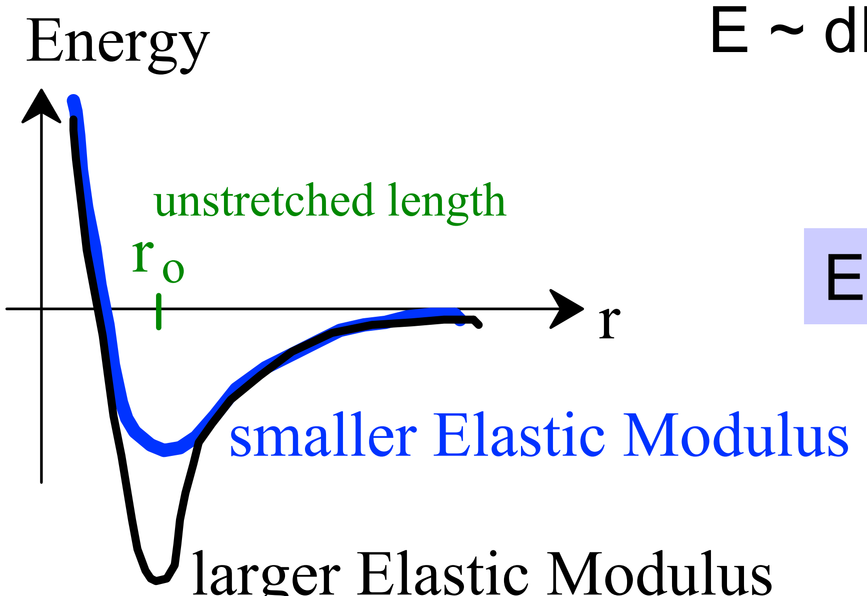
- Elastic modulus, E



Elastic modulus

$$\frac{F}{A_o} = E \frac{\Delta L}{L_o}$$

- E ~ curvature at r_o

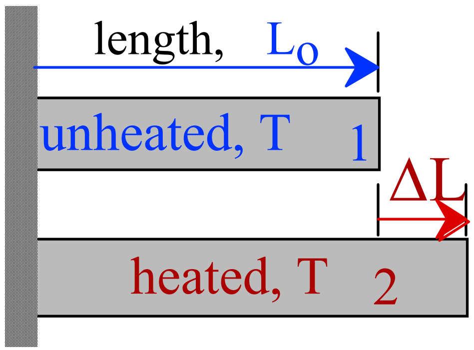


$$E \sim dF_N(r)/dr = d^2E_N(r)/d^2r$$

E is larger if E_o is larger.

PROPERTIES FROM BONDING: α

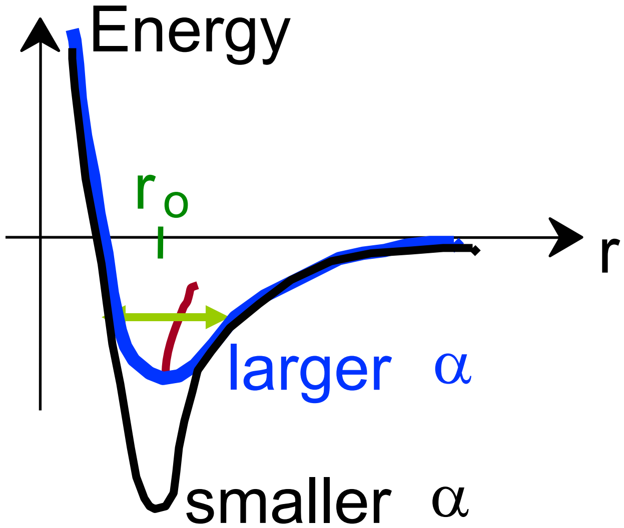
- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_o} = \alpha\,(T_2 - T_1)$$

- α ~ symmetry at r_o



α is larger if E_o is smaller.

SUMMARY: PRIMARY BONDS

Ceramics

(Ionic & covalent bonding):

Large bond energy

large T_m

large E

small α

Metals

(Metallic bonding):

Variable bond energy

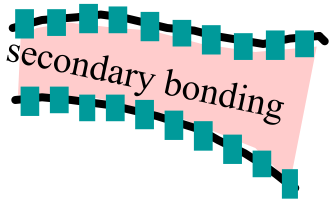
moderate T_m

moderate E

moderate α

Polymers

(Covalent & Secondary):



Directional Properties

Secondary bonding dominates

small T

small E

large α