Physics of Materials:

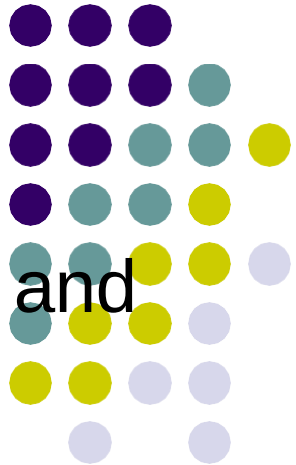
Bonding and Material Properties

On The basis of Geometry and Bonding (Intermolecular forces)

Dr. Anurag Srivastava

Atal Bihari Vajpayee

Indian Institute of Information Technology and Manegement, Gwalior



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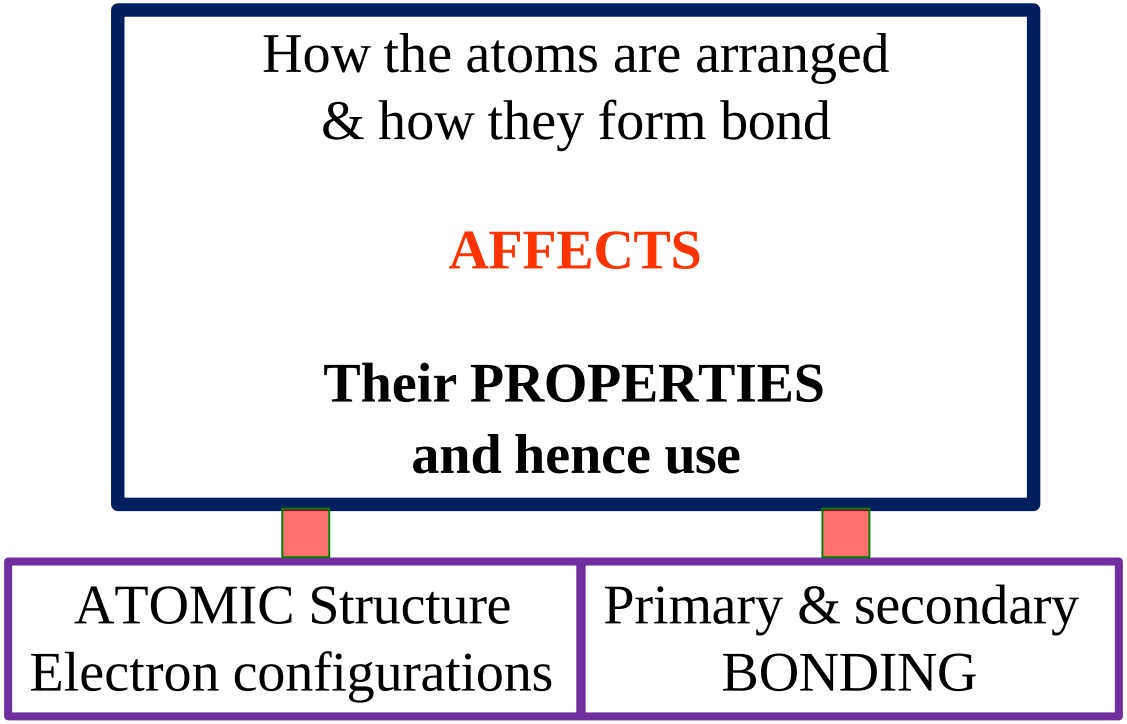


Atomic Structure (Freshman Chem.)

- atom – electrons – 9.11×10^{-31} kg $(.000911 \times 10^{-27}$ kg)
  protons, neutrons } 1.67×10^{-27} kg
- atomic number = # of protons in nucleus of atom
  = # of electrons of *neutral* species
- A [=] atomic mass unit = amu = 1/12 mass of ^{12}C

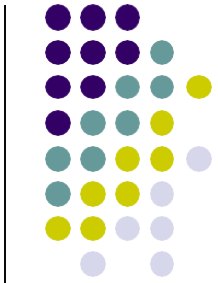
  Atomic wt = wt of 6.023×10^{23} molecules or atoms

  1 amu/atom = 1g/mol

  C 12.011
  H 1.008 etc.

  Atomic Weight is rarely a whole number – it is a weighted average of all of the natural isotopes of an "Element"

Structure of Matter – an Element

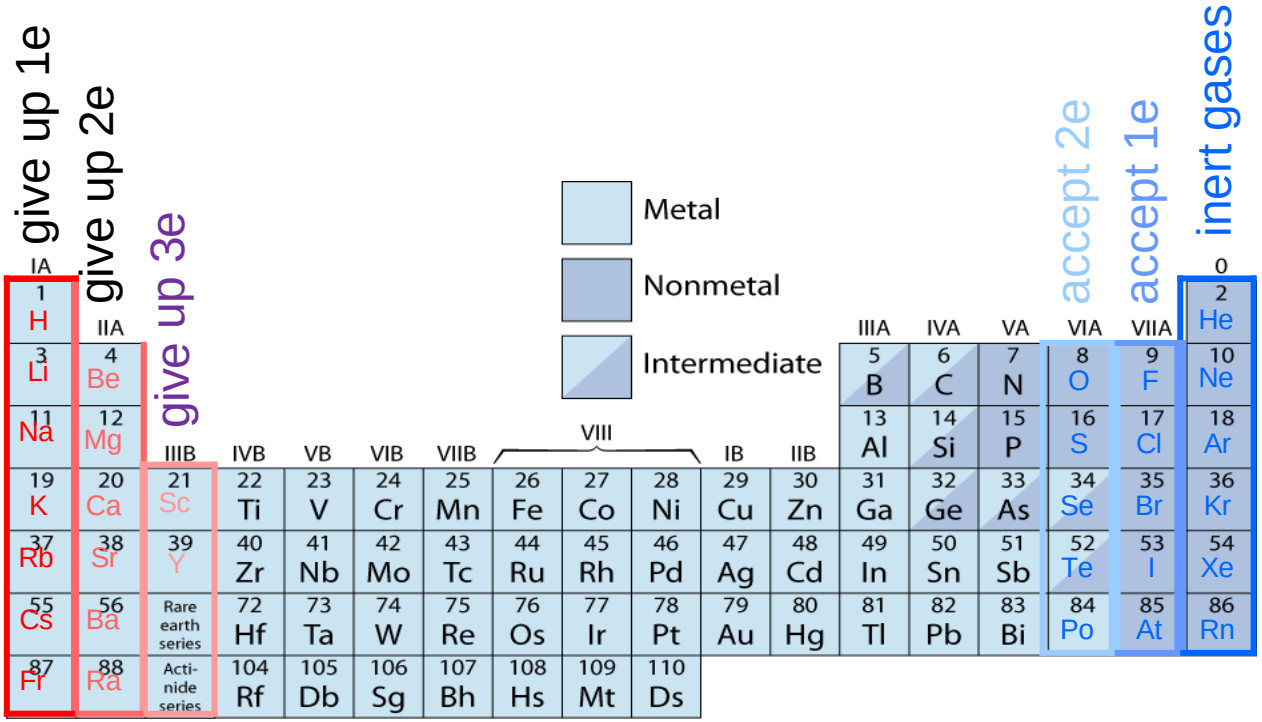


- ✓ Any material that is composed of only one type of atom is called a chemical element, a basic element, or just an element.
- ✓ Every element has a unique atomic structure.
- ✓ Scientists know of only about 118 basic elements at this time. (This number has a habit of changing!)
- ✓ All matter is composed of combinations of one or more of these elements.
- ✓ Ninety-one of these basic elements occur naturally on or in the Earth (Hydrogen to Uraninum).
- ✓ These elements are pictured in the "Periodic Table"

Structure of Matter

- These outermost or Valence electrons determine all of the following properties concerning an element:
  1) Chemical
  2) Electrical
  3) Thermal
  4) Optical

Matter (or elements) Bond as a result of their Valance states



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

Electronegative elements:
Readily acquire electrons to become - ions.

Molecular/Elemental Bonding

- Bonding is the result of the balance of the force of attraction and the force of repulsion of the electric nature of atoms (ions)
- Net Force between atoms: $F_N = F_A + F_R$ and at some equilibrium (stable) bond location of separation, $F_N = 0$ or $F_A = F_R$
- From Physics we like to talk about bonding energy where:

$$E = \int F dr = \int_{\infty}^{r} F dr$$

Bonding

Primary bonding:

Ionic (transfer of valence electrons)
Covalent (sharing of valence electrons, directional)
Metallic (delocalization of valence electrons)

Secondary or van der Waals Bonding:

(Common, but weaker than primary bonding)

Dipole-dipole
H-bonds
Polar molecule-induced dipole
Fluctuating dipole (weakest)

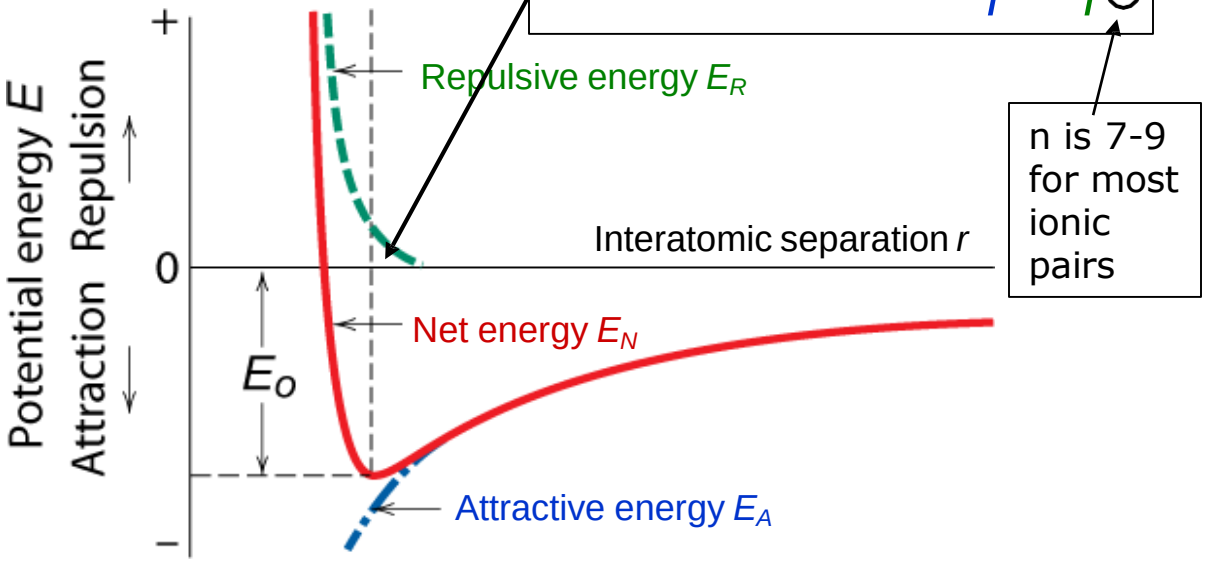
Bonding Energy

- Energy – minimum energy most stable
  - Energy balance of attractive and repulsive terms

Equilibrium separation (r_0) is about .3 nm for many atoms

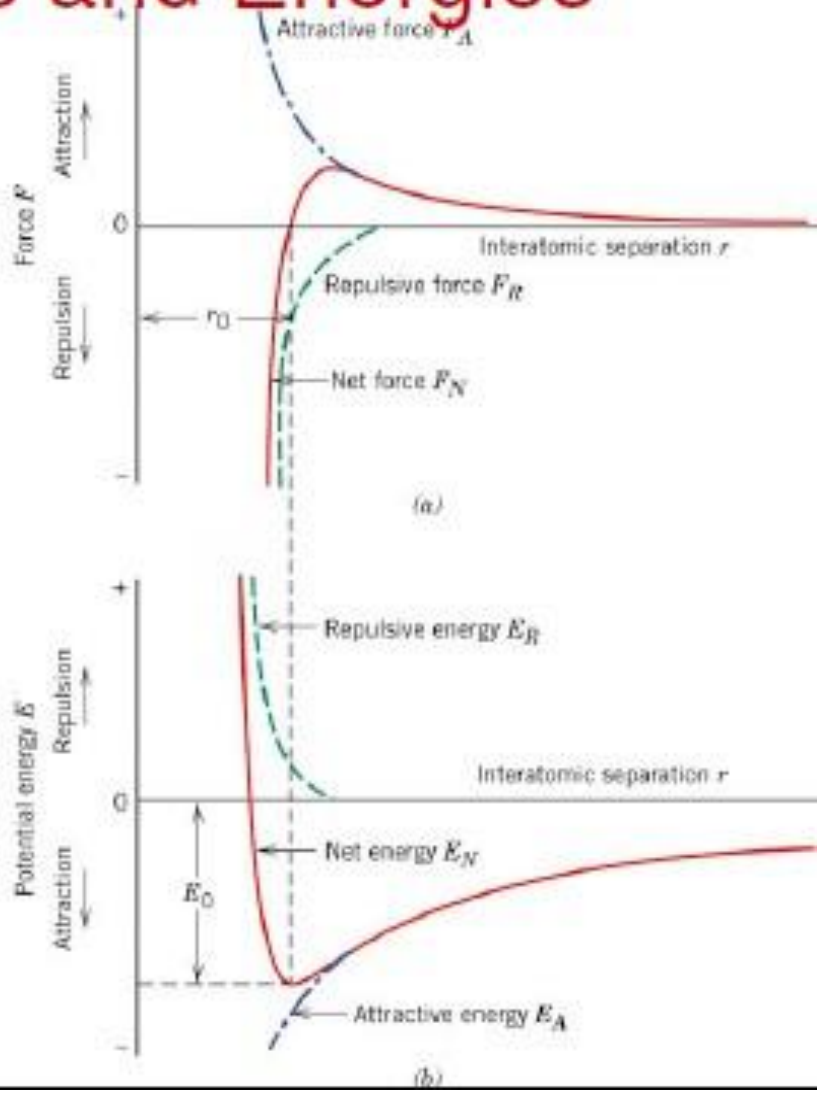
$$E_N = E_A + E_R = -\frac{A}{r} - \frac{B}{r^n}$$

n is 7-9 for most ionic pairs



Bonding Forces and Energies

- Considering the interaction between two isolated atoms as they are brought into close proximity from an infinite separation.
- At larger distances, the interactions are negligible.
- As the atoms approach, each exerts forces on the other.
  - Attractive
  - Repulsive
- Ultimately, the outer electron shells of the two atoms begin to overlap, and a strong repulsive force comes into play.



Bonding Energy, the Curve Shape, and Bonding Type

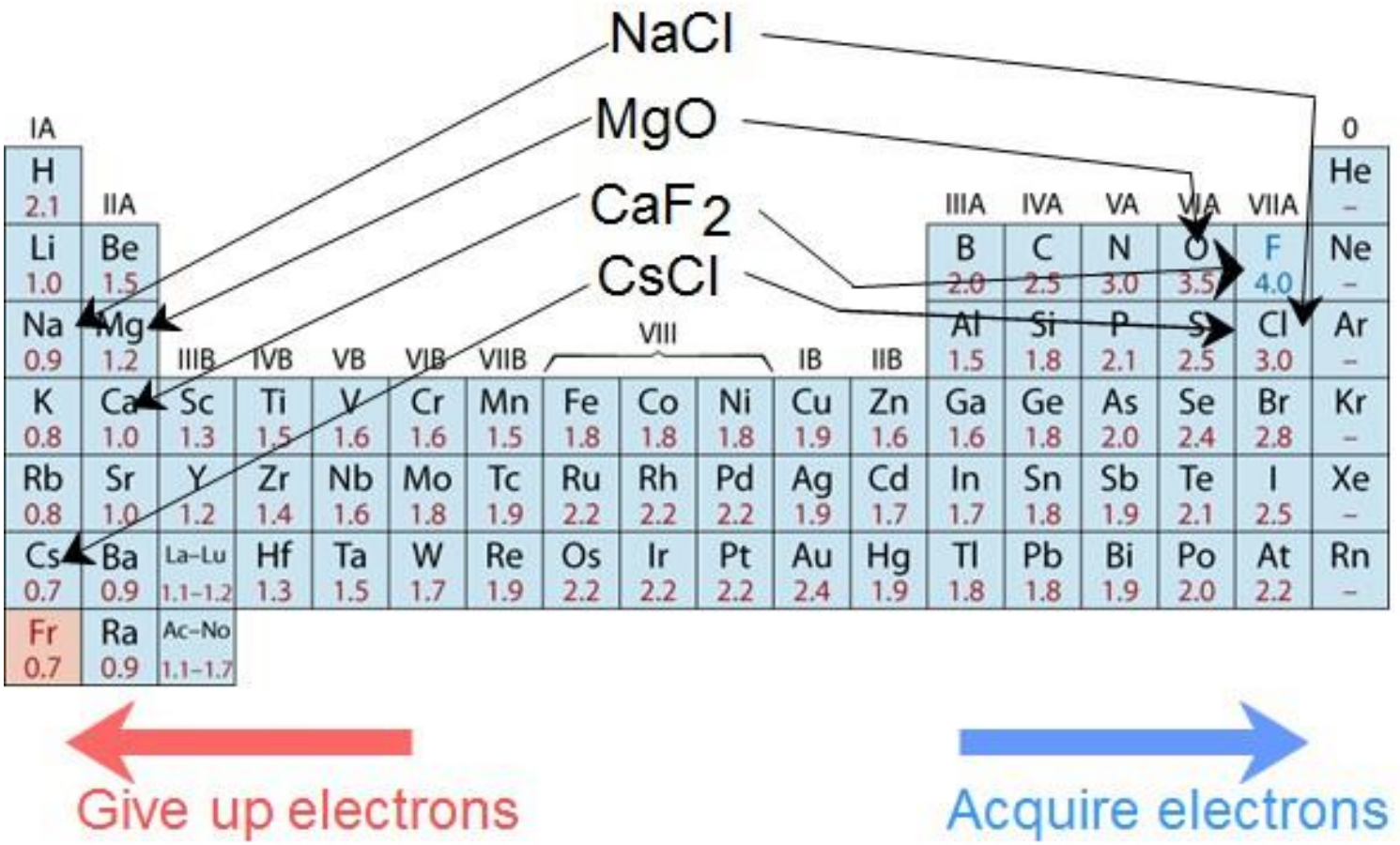
- Properties depend on shape, bonding type and values of curves: they vary for different materials.
- Bonding energy (minimum on curve) **is the energy that would be required to separate the two atoms to an infinite separation.**
- Modulus of elasticity depends on energy (force) versus distance curve: the slope at $r = r_0$ position on the curve will be quite steep for very stiff materials, slopes are shallower for more flexible materials.
- Coefficient of thermal expansion depends on E_0 versus r_0 curve: a deep and narrow trough correlates with a low coefficient of thermal expansion

Bonding Types of Interest:

- **Ionic Bonding**: Based on donation and acceptance of valance electrons between elements to create strong "ions" – CatIONs and AnIONs due to large electro-negativity differences
- **Covalent Bonding**: Based on the 'sharing' of valance electrons due to small electro negativity differences
- **Metallic Bonding**: All free electrons act as a moving 'cloud' or 'sea' to keep charged ion cores from flying apart in their 'stable' structure
- **secondary bonding**: van der wahl's attractive forces between molecules (with + to – 'ends')
  - This system of attraction takes place without valance electron participation in the whole
  - Valence Electrons participate in the bonding to build the molecules not in 'gluing' the molecules together

Ionic Bonding

- Predominant bonding in Ceramics



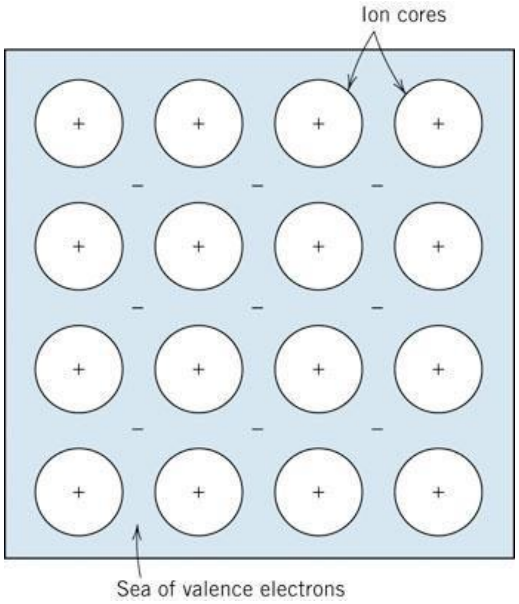
“Electro-negativity” Values for determining Ionic vs. Covalent Bond Character

IA							VIII					IIIA	IVA	VA	VIA	VIIA	0
H 2.1	IIA																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	IIIB	IVB	VB	VIB	VIIB				IB	IIB	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

Metallic Bonding:

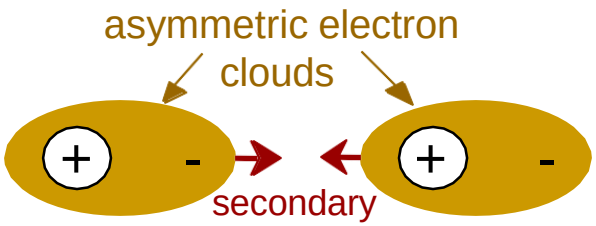


In a metallic bonded material, the valence electrons are "shared" among all of the ionic cores in the structure not just with nearest neighbors!

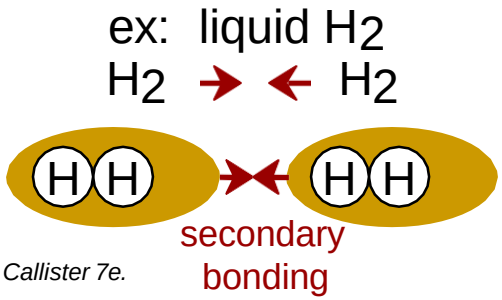
SECONDARY BONDING

Arises from interaction between “electric” dipoles

- Fluctuating dipoles

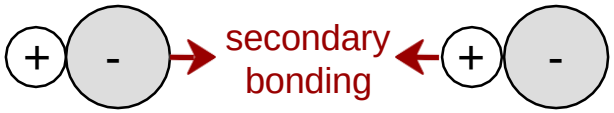


Adapted from Fig. 2.13, *Callister 7e.*



- Permanent dipoles-molecule induced

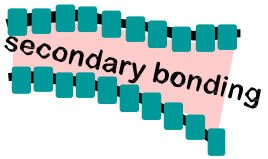
-general case:



Adapted from Fig. 2.14, *Callister 7e.*

-ex: liquid HCl

-ex: polymer



secondary bonding

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

Bonding and materials properties

- Materials with large bonding energies usually have high melting temperatures.
- There is a correlation between the magnitude of the bonding energy and the state of materials
  - Solids have large bonding energies
  - Liquids tend to have relatively lower energies
- The expansion/contraction during heating/cooling of materials is related to the shape of its *E*(r) curve.
- A deep and narrow 'trough,' which typically occurs for materials having large bonding energies, usually imply a low coefficient of thermal expansion.

Effect of Bonding on properties: a broad flavour

- ✓ Two important contributing factors to the properties of materials is the nature of bonding and the atomic structure.
- ✓ Both of these are a result of electron interactions and resulting distribution in the material.
- ✓ Bonding is an *'easily accessible term'* for the electromagnetic structure of an assemblage of atoms/molecules/ions. The interaction between atoms/molecules/ions may lead to a lowering of the energy of the system→ *the bonded state*.

Bond	Melting point	Hardness (Ductility)	Electrical Conductivity	Examples
Covalent	High	Hard (poor)	Usually Low	Diamond, Graphite, Ge, Si
Ionic	High	Hard (poor)	Low	NaCl, ZnS, CsCl
Metallic	Varies	Varies	High	Fe, Cu, Ag
Van der Waals	Low	Soft (poor)	Low	Ne, Ar, Kr
Hydrogen	Low	Soft (poor)	Usually Low	Ice

Understanding Potential energy Curve

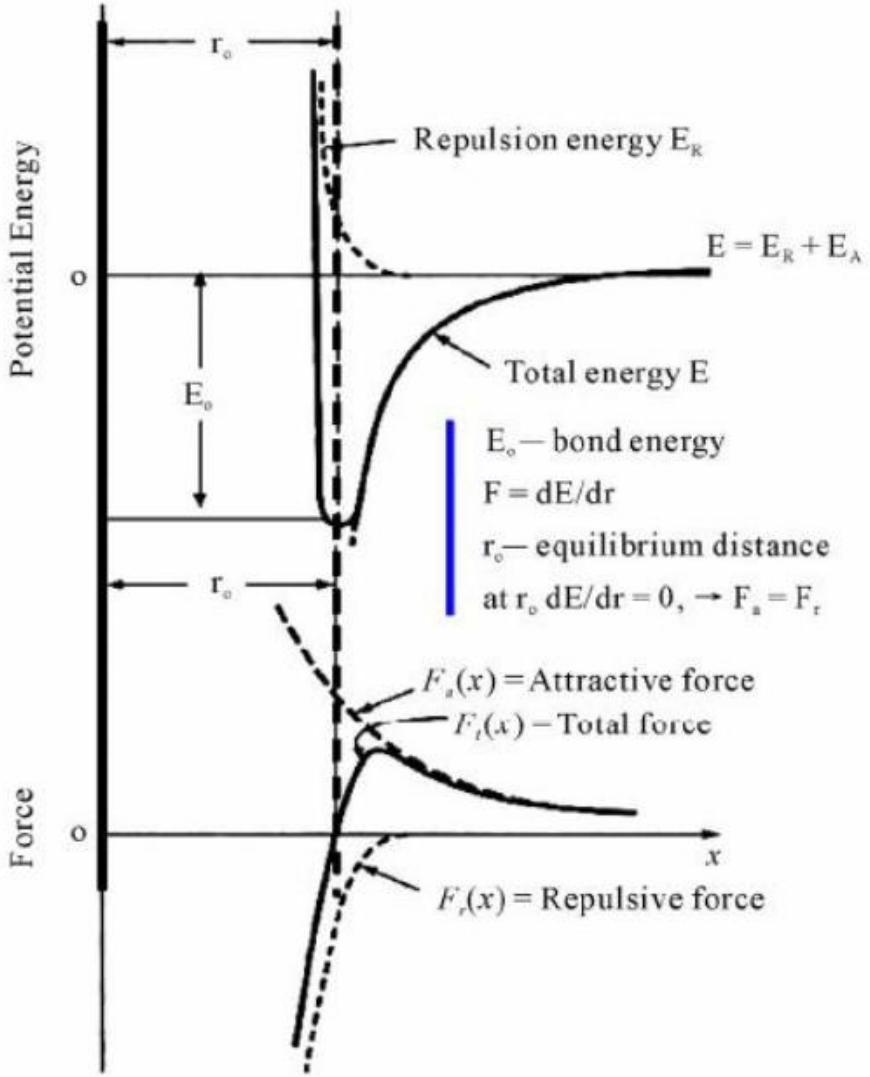


Figure 1. A typical potential well indicating bonding energies E_o and forces for two interacting atoms.

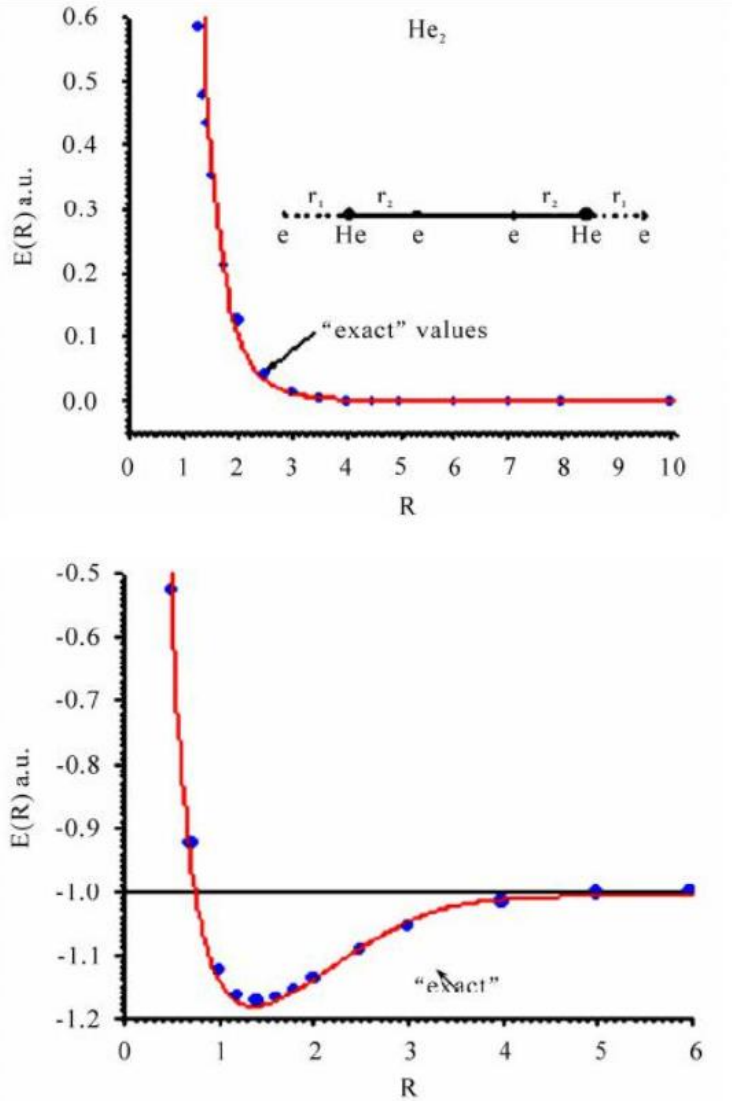


Figure 2. Calculated quantum mechanical potential energy curves of He_2 and H_2.

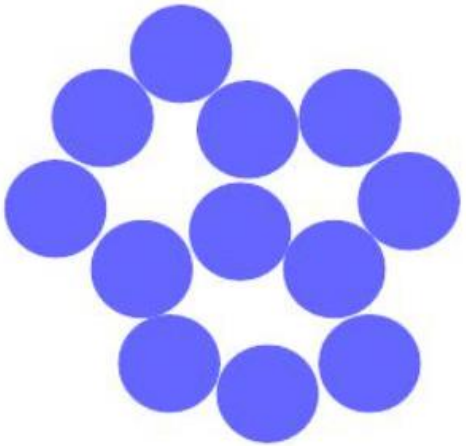
Packing of Crystal Structures and Their Influence on Bonding Energies

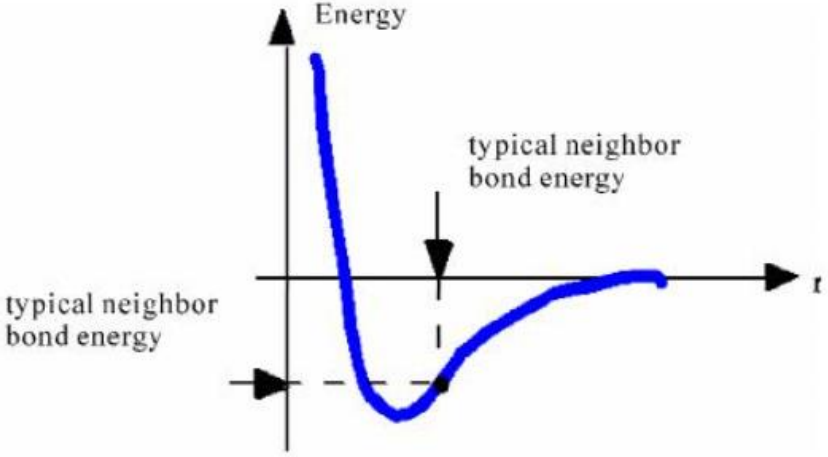
Table 1. Bonding energies and melting temperatures for various substances.

Bonding Type	Substance	Bonding Energy (kcal/mol)	Melting Temperature (°C)
Ionic	NaCl	153	801
	MgO	239	1000
Covalent	Si	108	1410
	C	170	> 3550
Metallic	Hg	16	–39
	Al	77	660
	Fe	97	1538
	W	203	3410
vander Waals	Ar	1.8	–189
	Cl_2	7.4	–101

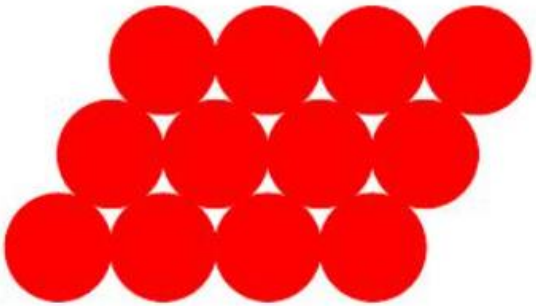
- Different atoms based on their nature, arrange them- selves in different crystalline forms. The order in which atoms associate with neighbors, determine the bonding energy, the shape and depth of the potential well
- And hence materials with high ordered packing have good density and hence good strength
- Different ordered packing results in different crystal- line patterns. Pure Mg hexagonal closely packed crystal is more brittle than Al a face centered cubic crystal due to less number of slip planes and hence undergoes fracture at lower degrees of deformation

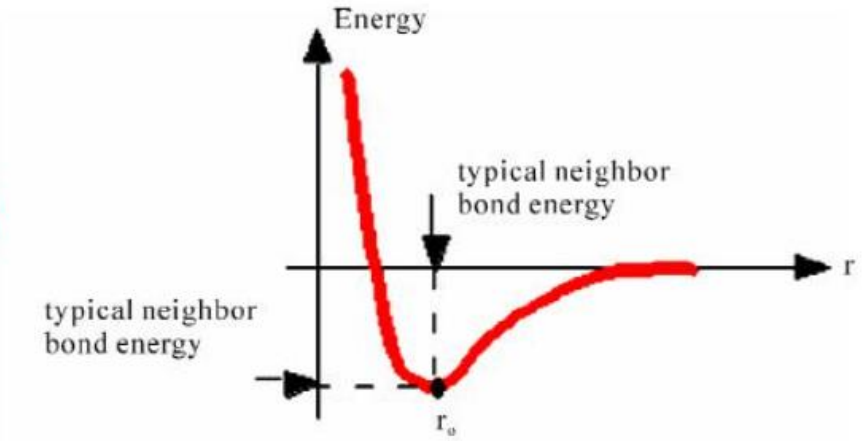
Packing of Crystal Structures and Their Influence on Bonding Energies





(a)



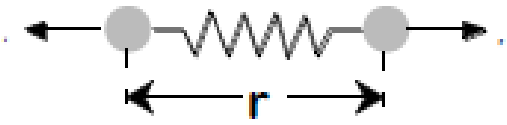


(b)

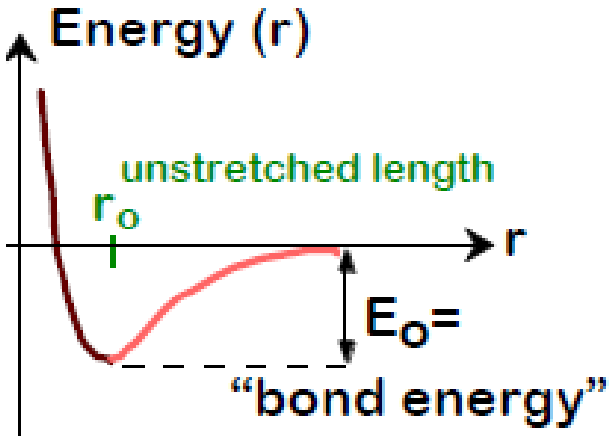
Figure 4. (a) Random packing of atoms and the corresponding potential energy curve; (b) Dense ordered packing of atoms and the corresponding potential energy curve.

PROPERTIES FROM BONDING: T_M

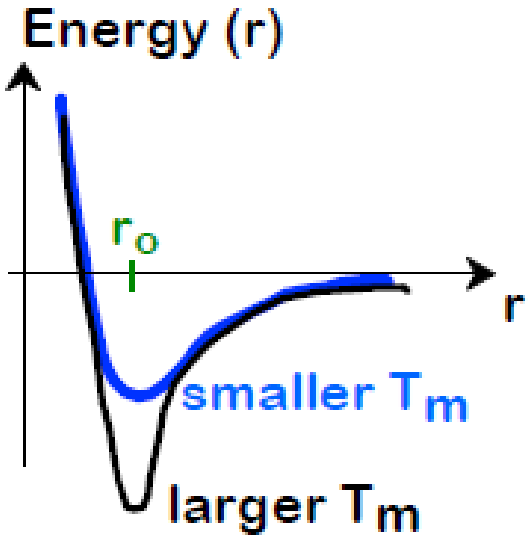
- Bond length, r



- Bond energy, E_o



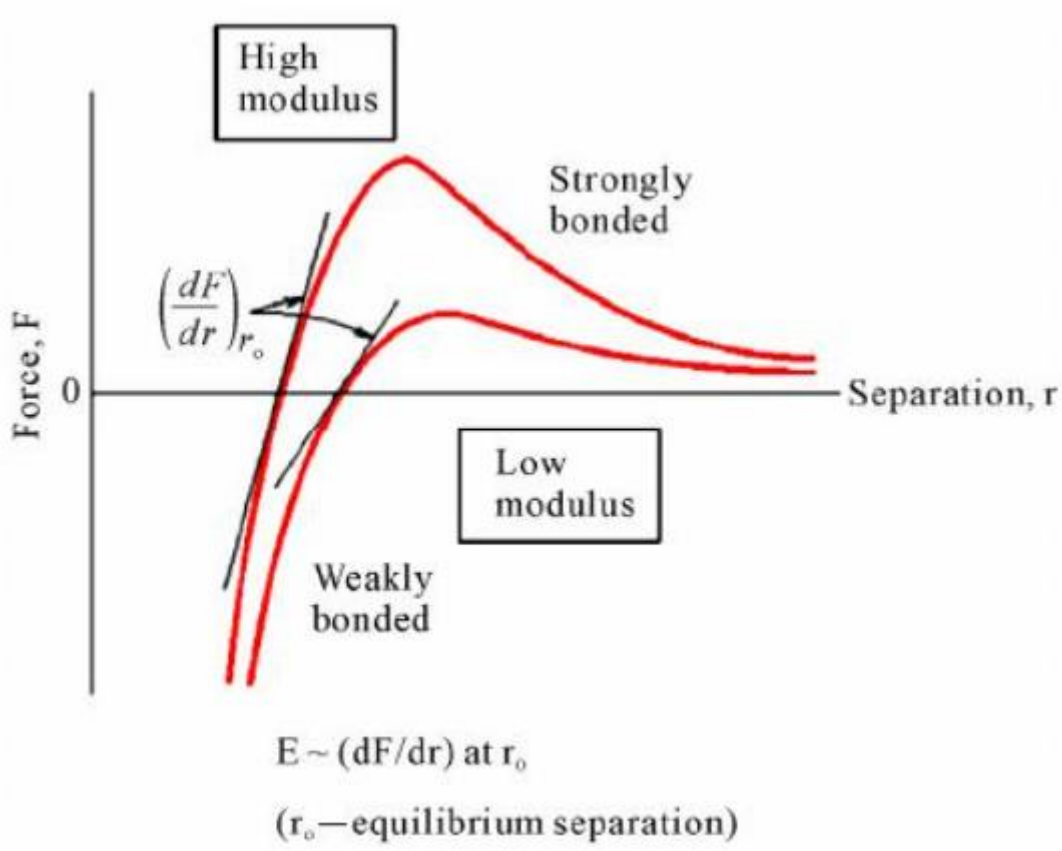
- Melting Temperature, T_m



T_m is larger if E_o is larger.

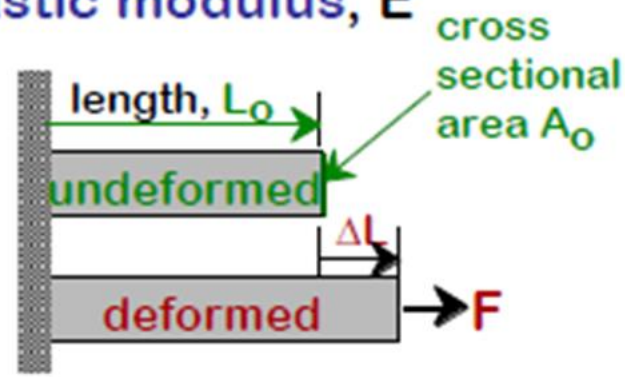
From Callister 6e resource CD.

Mechanical Properties



Mechanical Properties

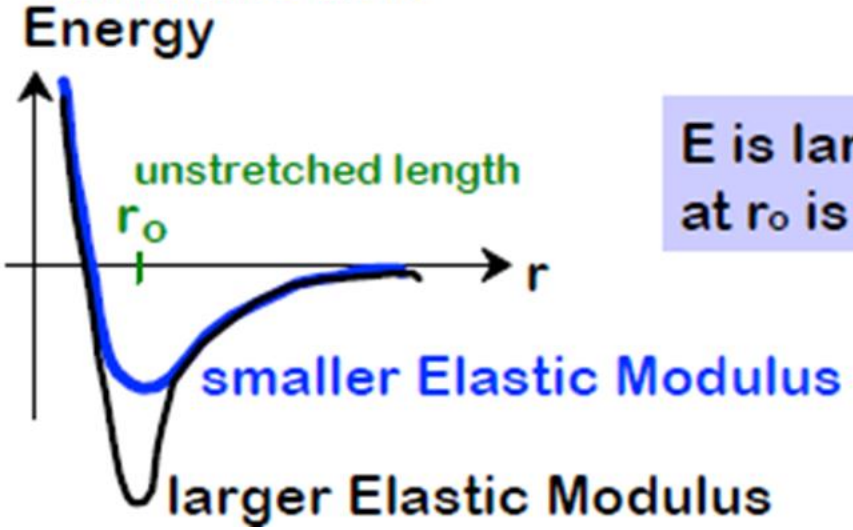
- Elastic modulus, E



Elastic modulus

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

- E ~ curvature at r_o



E is larger if curvature at r_o is larger.

From Callister 6e resource CD.

Thermal Properties

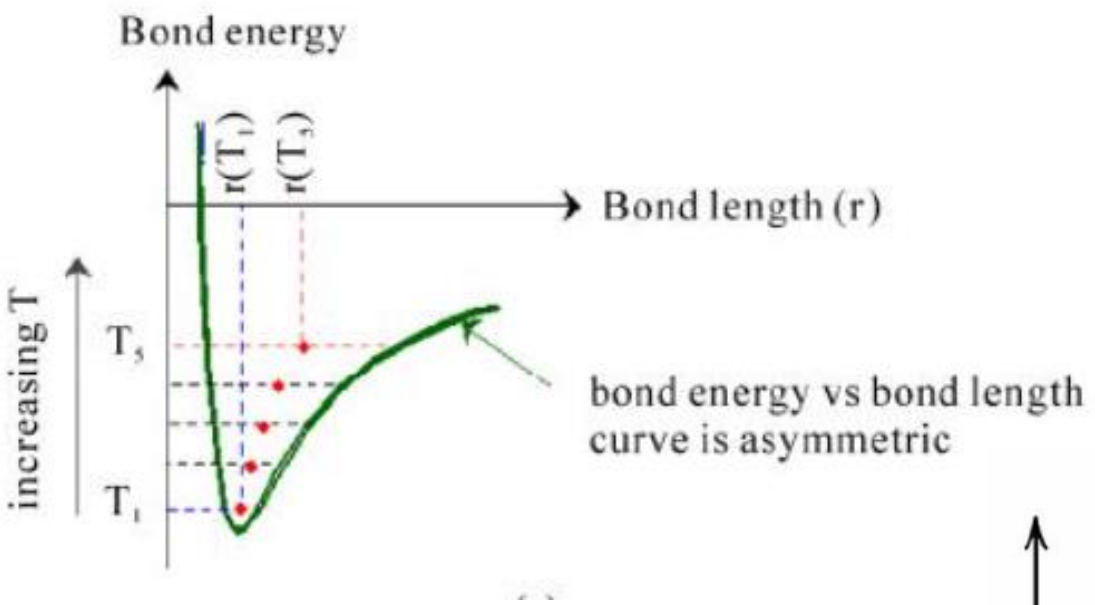
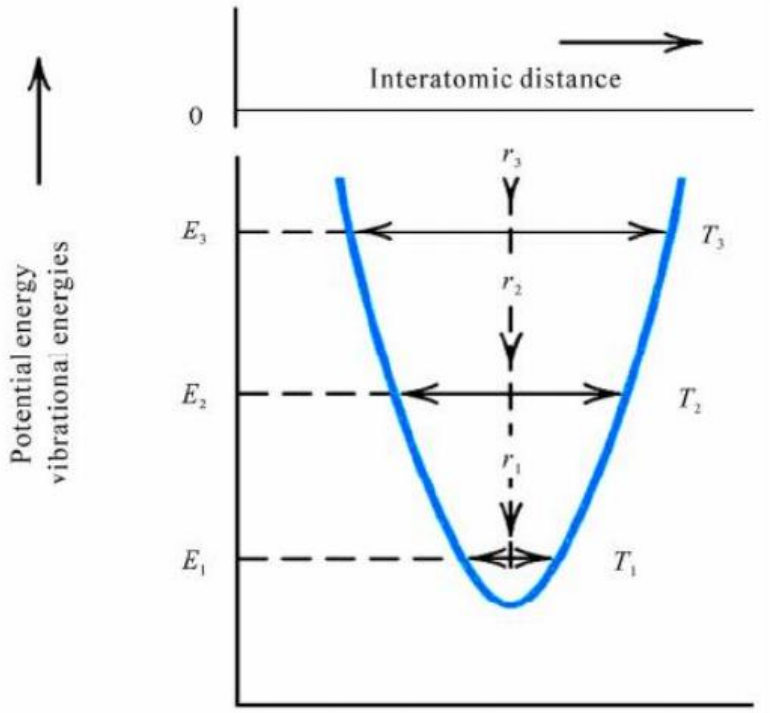
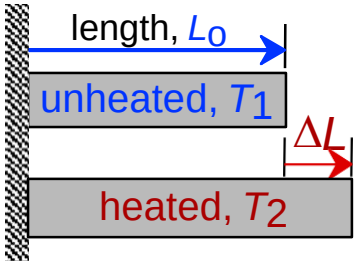


Figure 8. (a) Variation of asymmetric potential energy curve with Temperature T; (b) Variation of symmetric potential energy curve with Temperature T.



Properties From Bonding : α

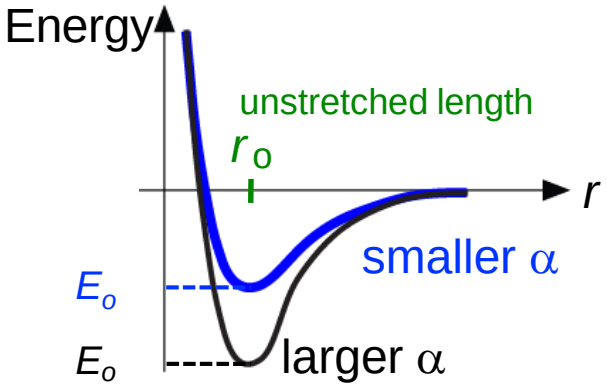
- Coefficient of thermal expansion, α



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.

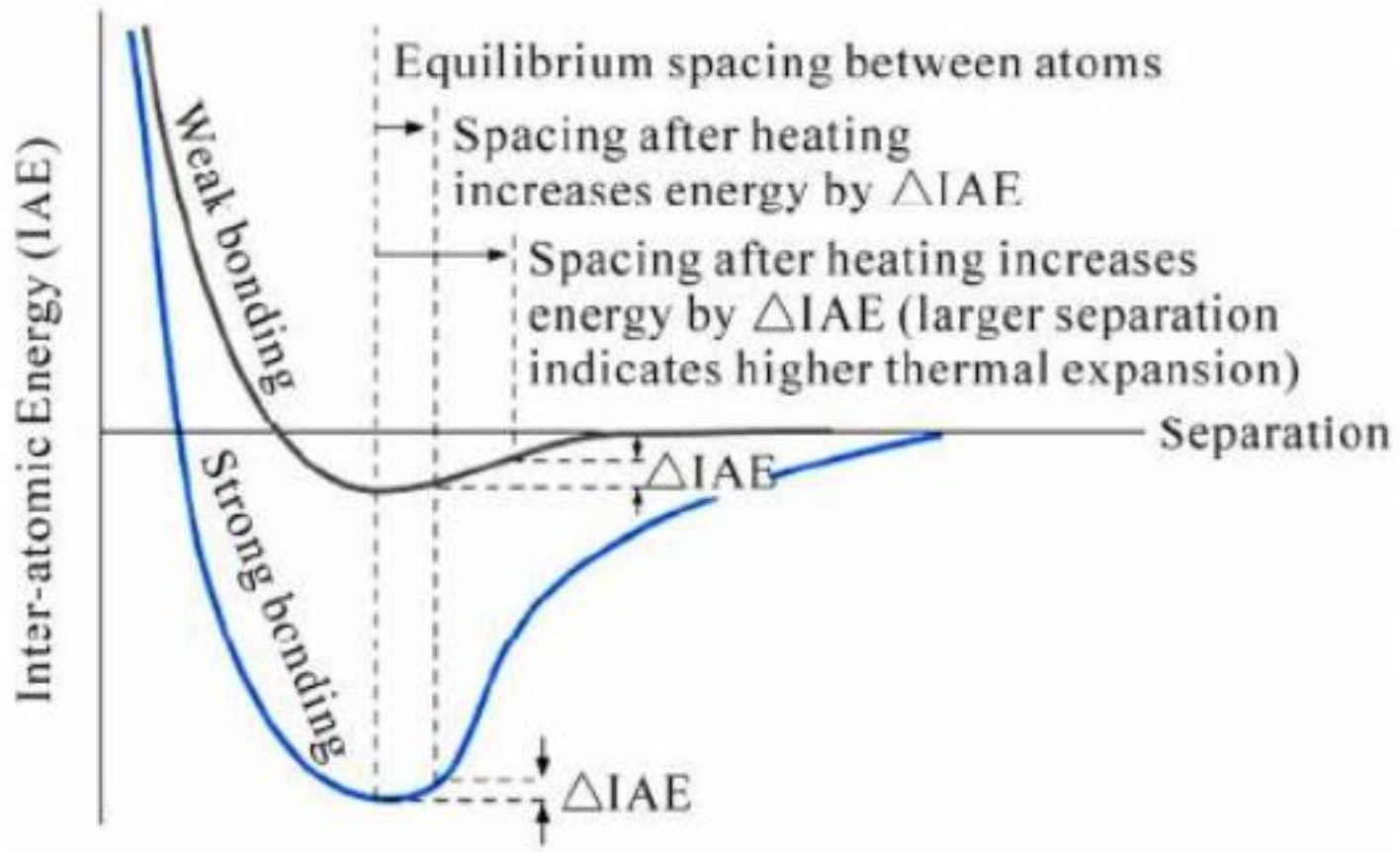


Figure 9. The inter-atomic energy separation curve for two atoms. Materials that display a steep curve with a deep trough have low linear coefficients of thermal expansion.

Electrical Properties

Solid materials exhibit a very wide range of electrical conductivity. Electrical conductivity and resistivity are the materials parameter and geometry independent.

The magnitude of electrical conductivity strongly dependent on the number of electrons, available to participate in the conduction process

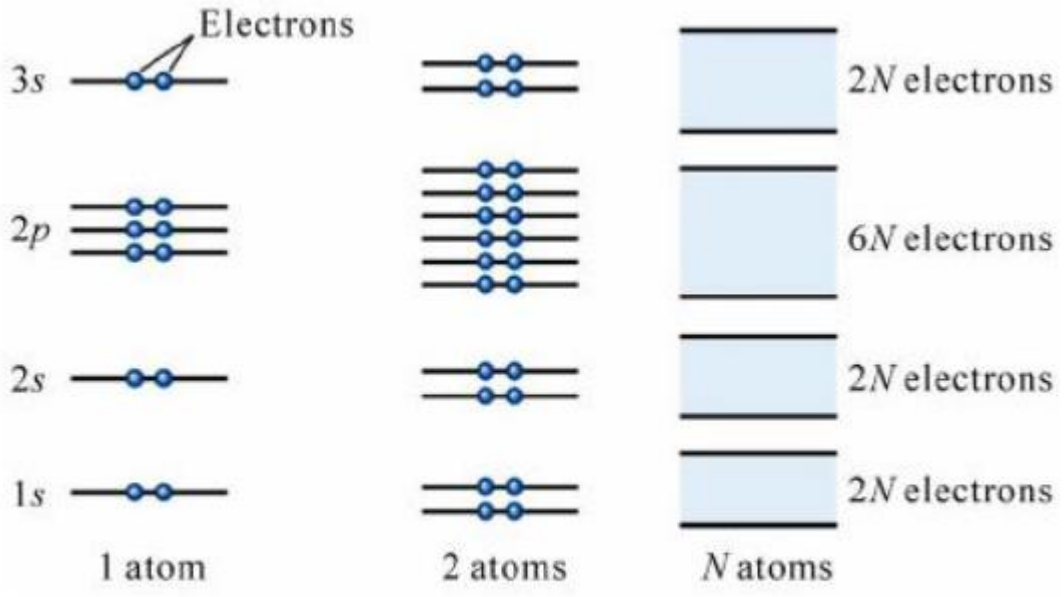
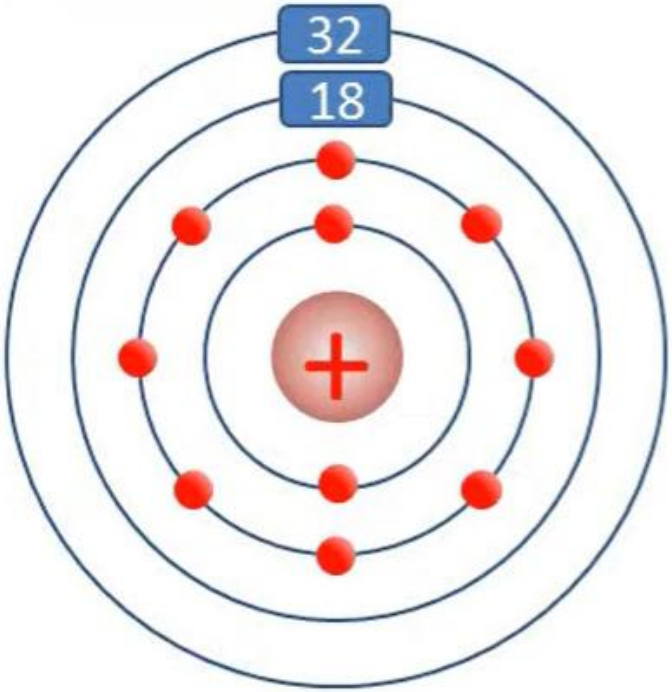
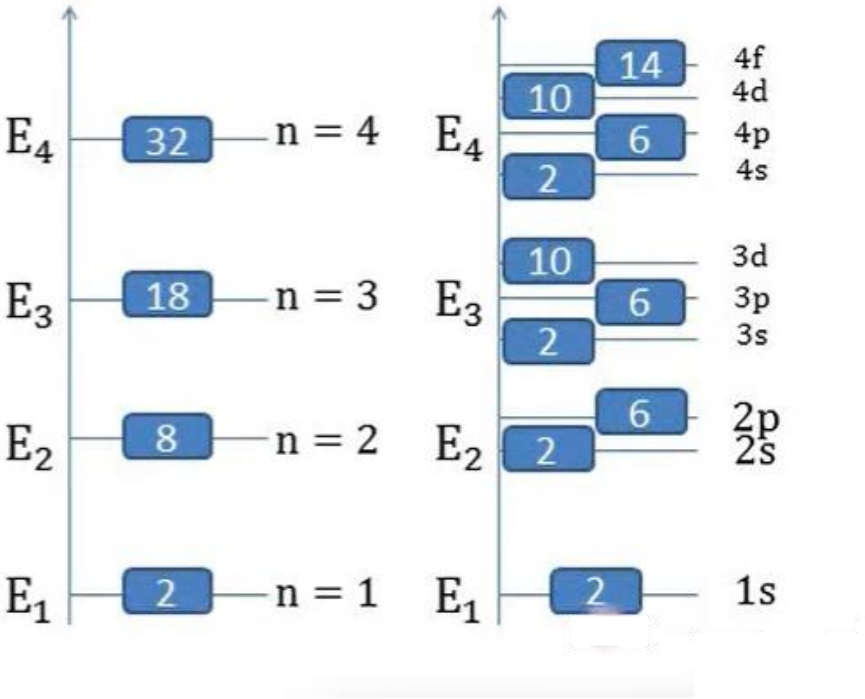


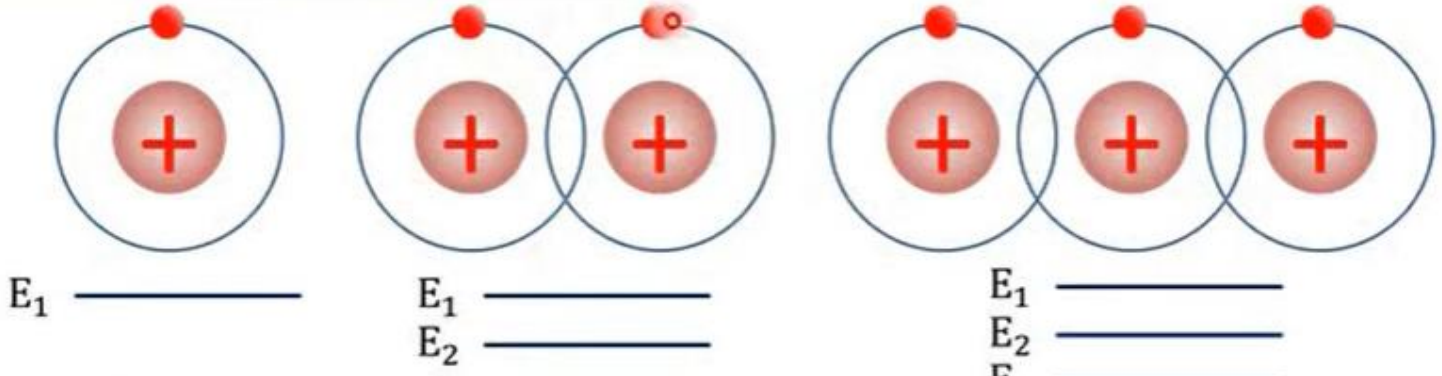
Figure 10. The energy levels broaden into bands as the number of electrons grouped together increases.

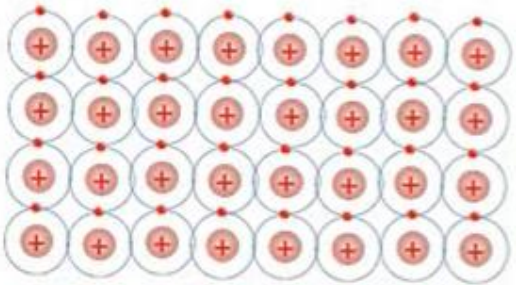
Energy Levels



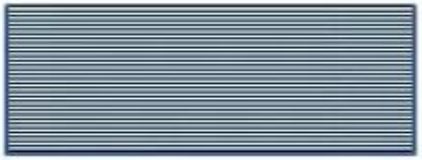


Formation of Energy Bands





N-atoms



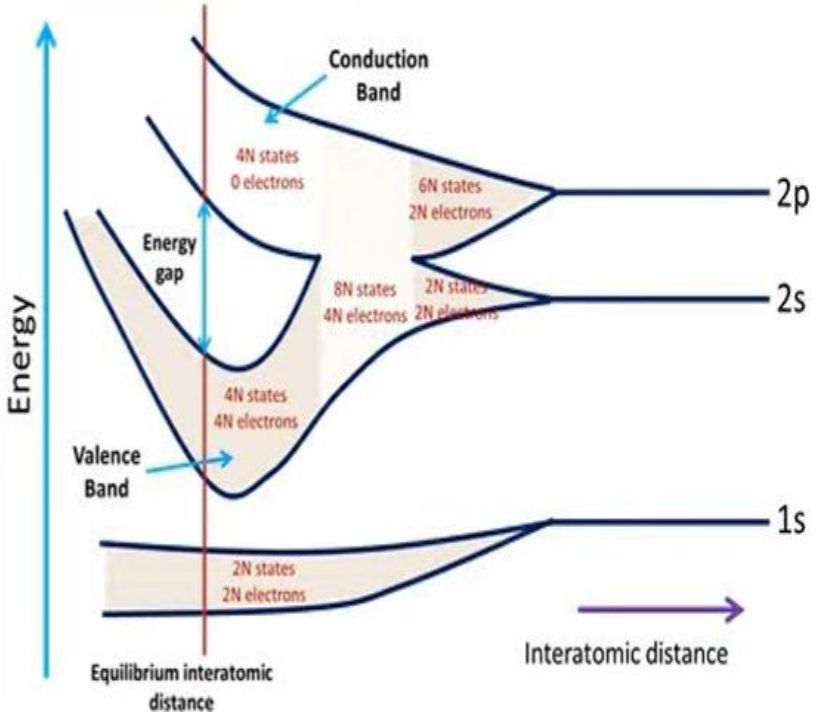
N-levels

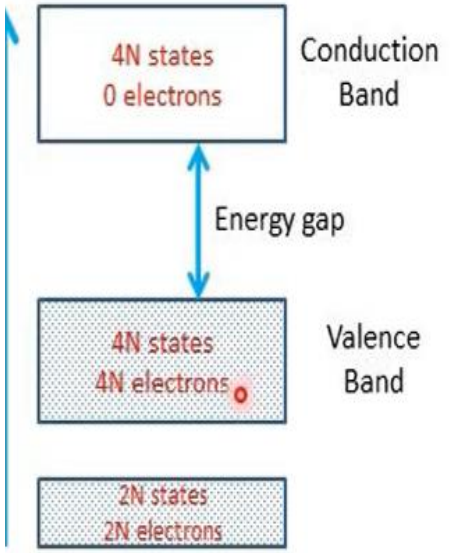
Pauli's Exclusion Principle

No two electrons in a given interacting system can have same quantum state and hence same energy.

Formation of Energy Bands in Diamond

- Electronic structure individual carbon atom: $1s^2\ 2s^2\ 2p^2$
- Each atom has two 1s states, two 2s states, six 2p states and the higher states.
- Hence for N atoms, there will be 2N, 2N and 6N available states of type 1s, 2s, and 2p respectively.





SUMMARY: BONDING and Materials' properties

Ceramics
(Ionic & covalent bonding):

Large bond energy
large T_m
large E
small α

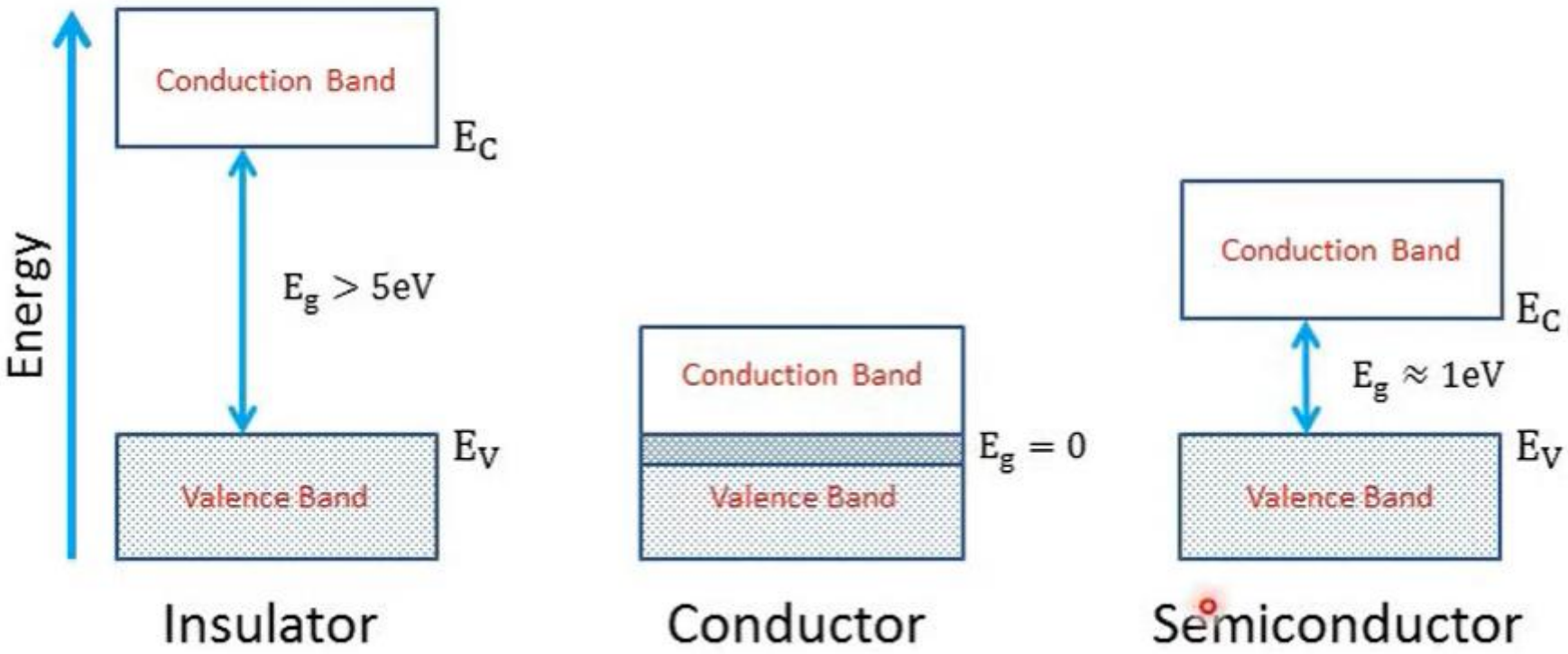
Metals
(Metallic bonding):

Variable bond energy
moderate T_m
moderate E
moderate α

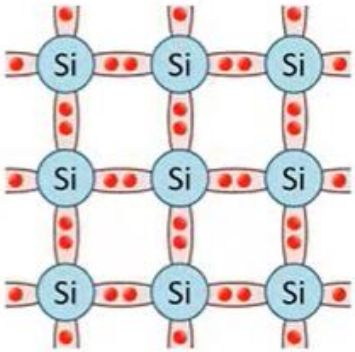
Polymers
(Covalent & Secondary):

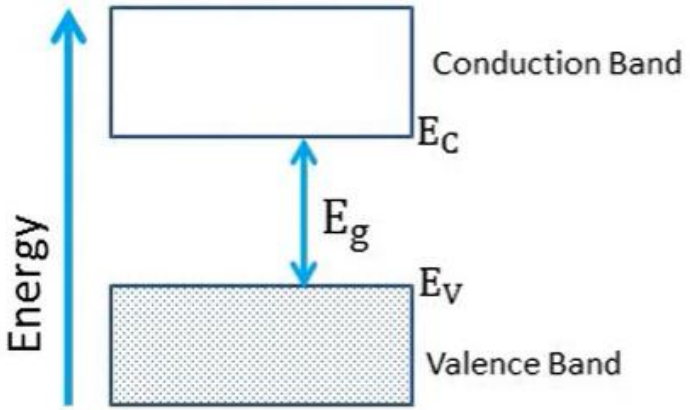
Directional Properties
Secondary bonding dominates
small T
small E
large α

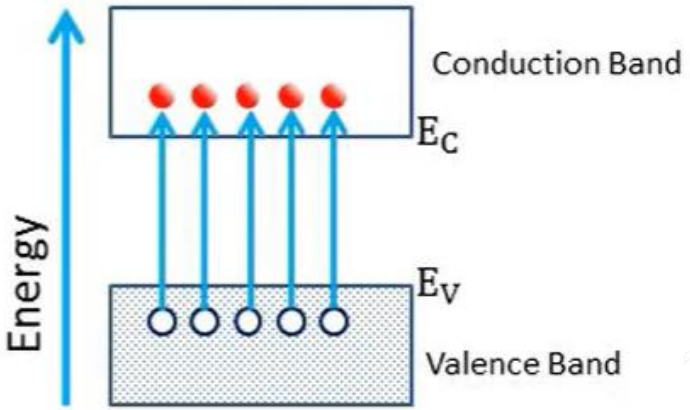
Classification of solids on the basis of band theory



Intrinsic Semiconductors





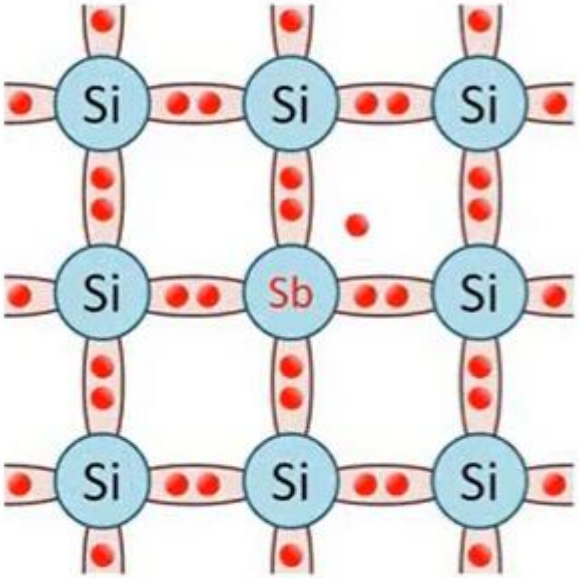


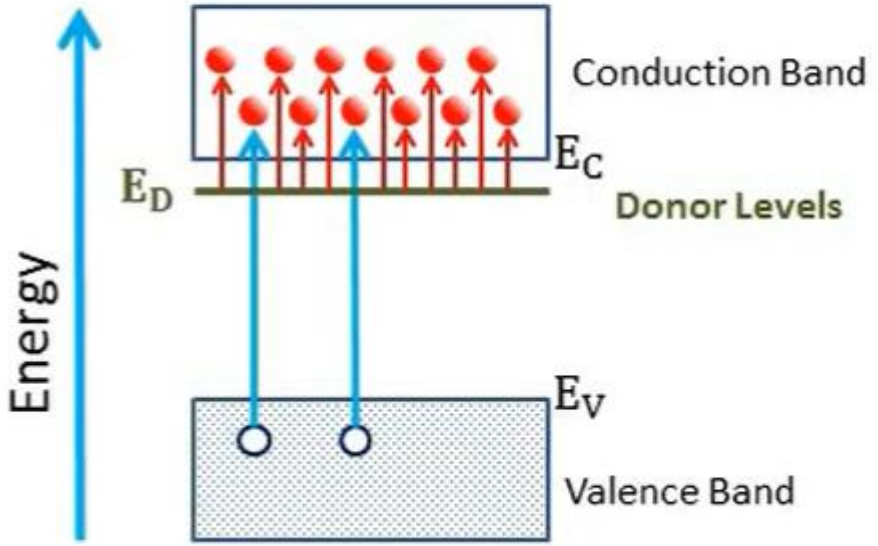
Why Silicon is preferred over Germanium?

- Silicon and Germanium are two most widely used semiconductors.
- Silicon is preferred over Germanium because of its superior thermal properties.
- The maximum operational temperature for Ge-devices is 80^0C while Si-devices may be used at up to 160^0C.
- Also, at room temperature, silicon crystal has almost no free electrons compared with Germanium crystal

Extrinsic Semiconductors (Doped Semiconductors)

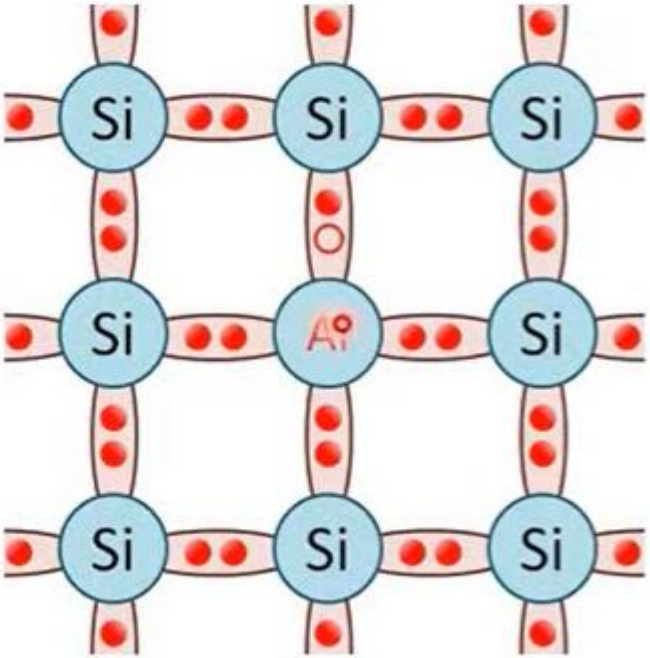
n-type semiconductor

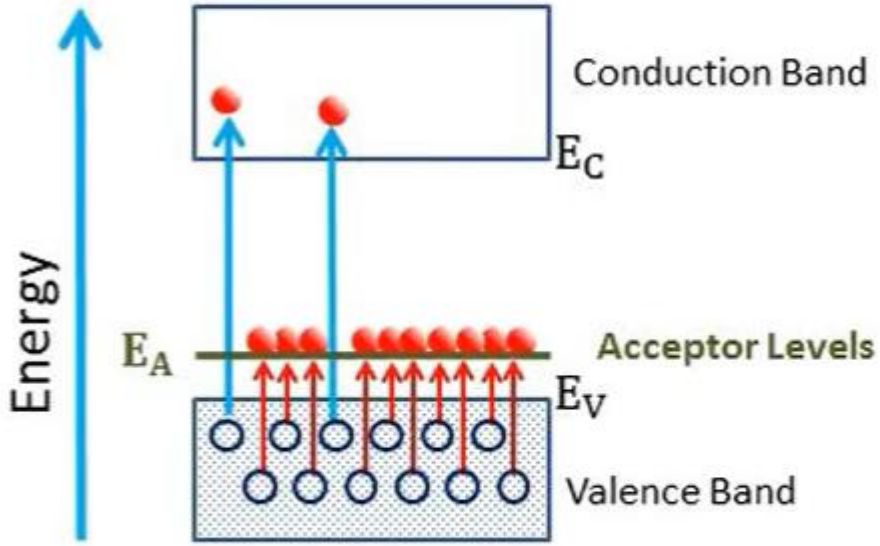




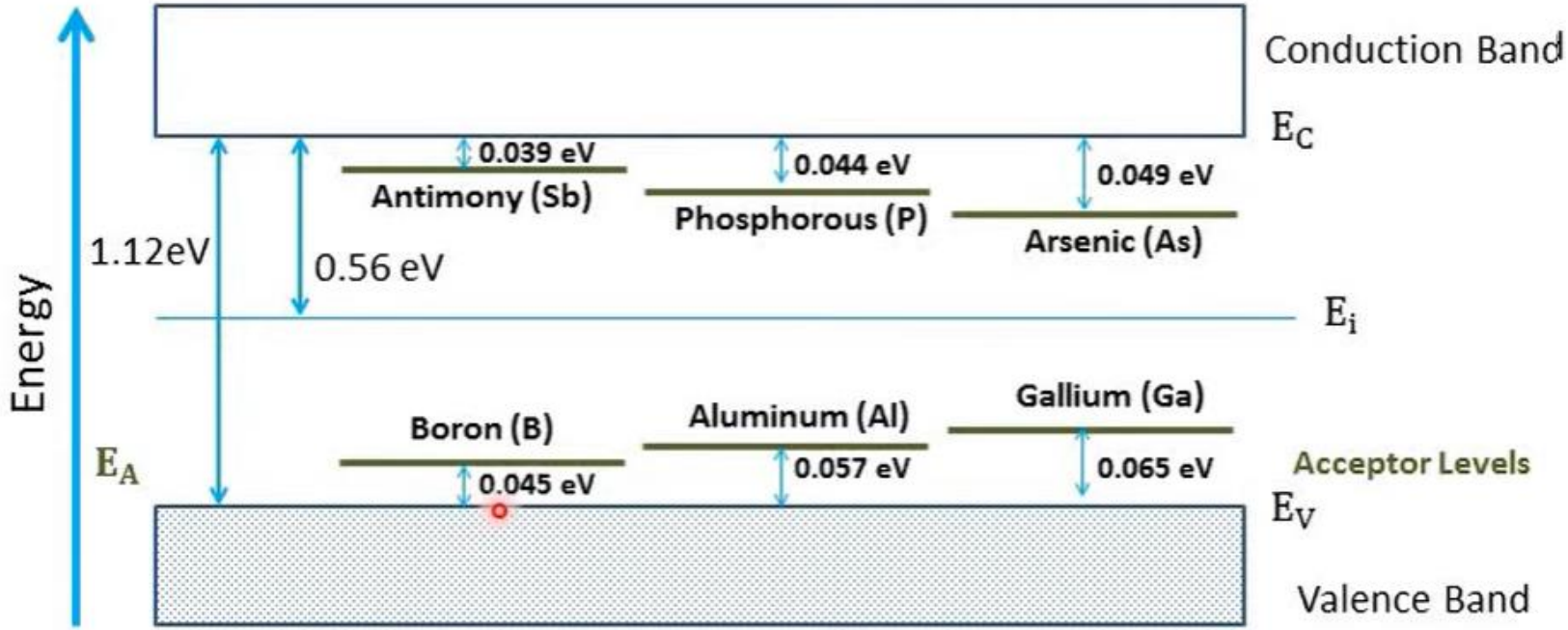
Extrinsic Semiconductors (Doped Semiconductors)

p-type semiconductor





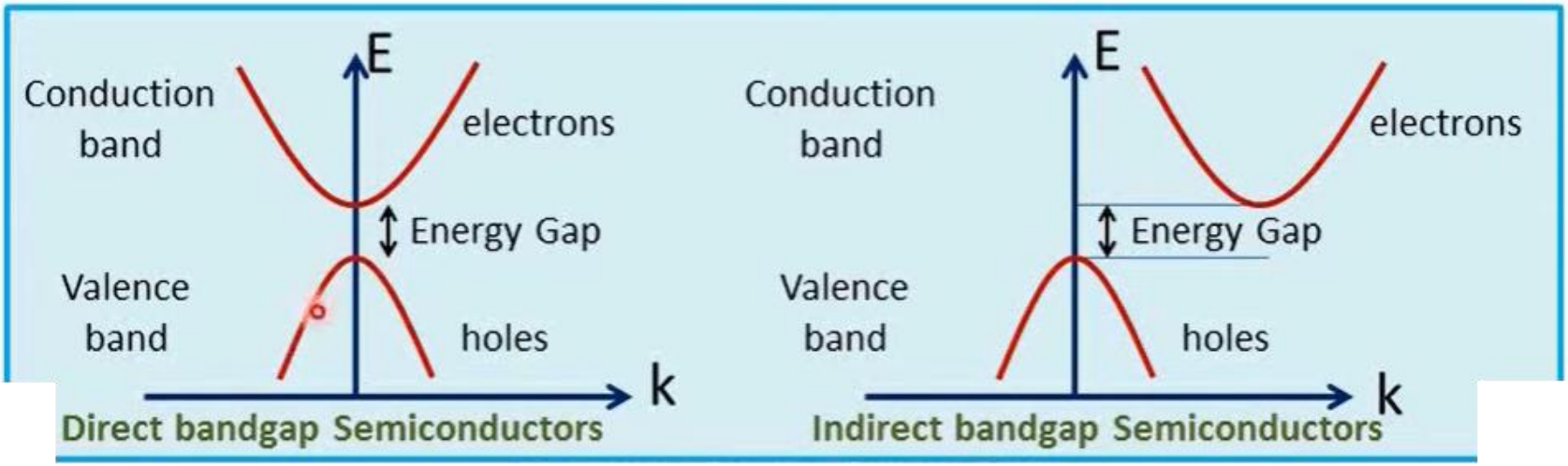
Extrinsic Semiconductors (Doped Semiconductors)

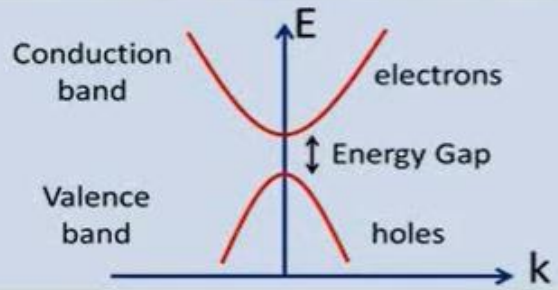
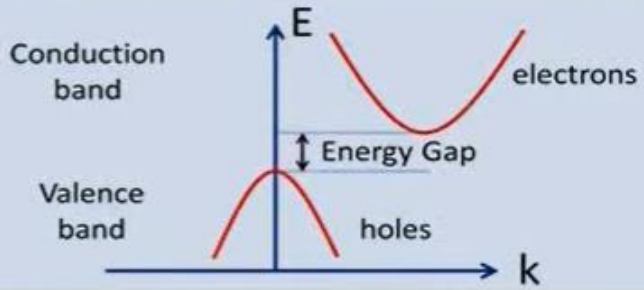


Direct Gap and Indirect Gap Semiconductors

The energy of an electron is given by $E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$ where p is momentum, m is mass of an electron, $\hbar$ is Planck's constant and k is propagation constant

Thus $E \propto k^2$ which is an equation of parabola. The graph of E vs k is shown below -



Direct bandgap Semiconductors	Indirect bandgap Semiconductors
	
Maximum of valence band and minimum of conduction band occur at same momentum values	Maximum of valence band and minimum of conduction band occur at two different momentum values.
Electron making a transition from valence band to conduction band need not undergo any change in its momentum.	In order to make a transition from maximum point in valence band to minimum point in conduction band, the electron requires energy for the change in momentum in addition to the energy gap E_g
The compound semiconductors such as GaAs, are direct gap semiconductors	All elemental semiconductors such as Si, Ge, are indirect gap semiconductors
These direct gap semiconductors are used in LED and Semiconductor Lasers.	Not useful for LEDs and Semiconductor Lasers