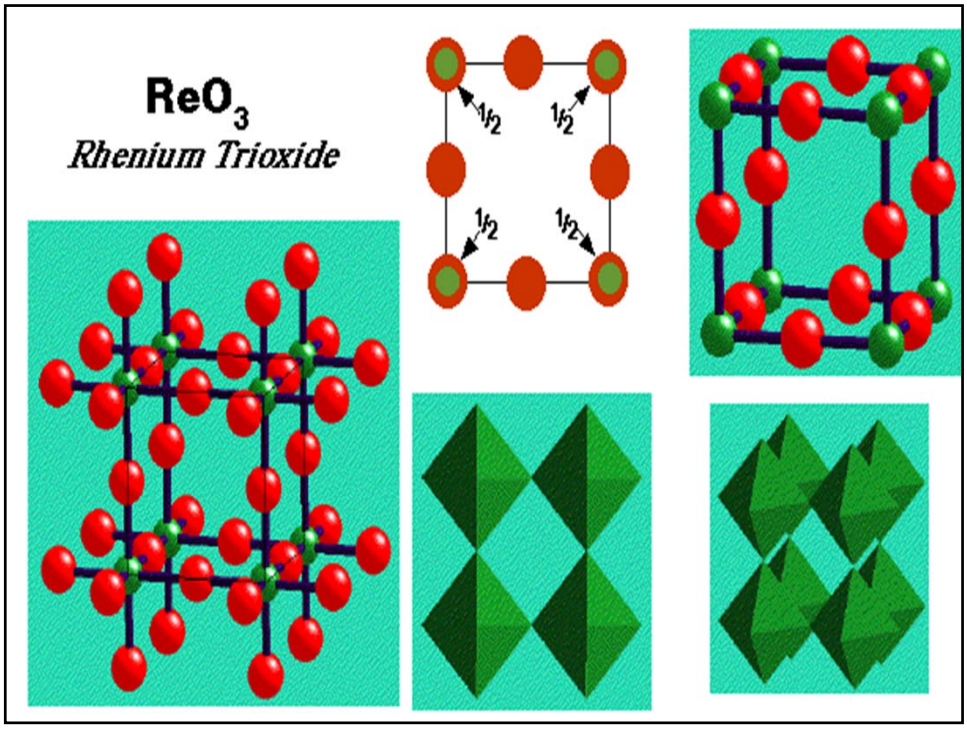
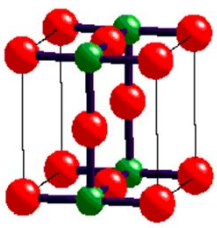
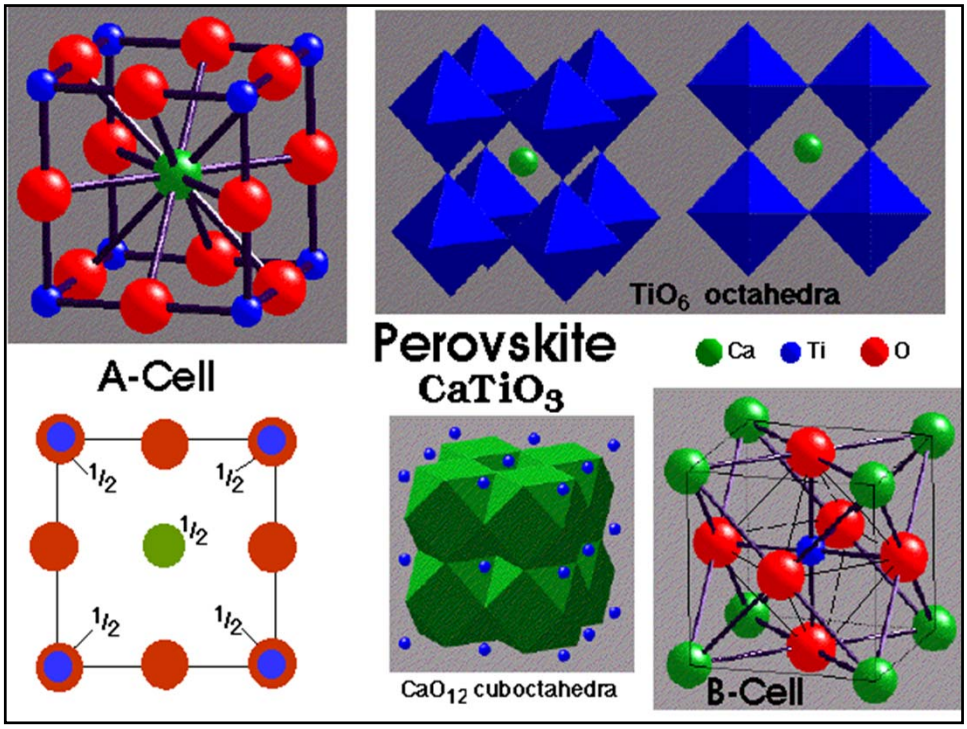


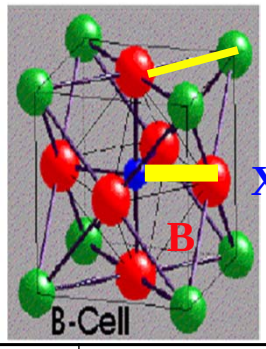
•*Lattice*: **Primitive** Cubic
•1ReO_3 per unit cell
•*Motif*: Re at (0, 0, 0); 3O at ($^1/_2$, 0, 0), (0, $^1/_2$, 0), (0, 0, $^1/_2$)
•Re: 6 (**octahedral** coordination)
•O: 2 (**linear coordination**)
•ReO_6 octahedra share only **vertices**
•May be regarded as ccp oxide with $^1/_4$ of ccp sites vacant
(*at center of the cell*)



Examples:
•WO_3 , AlF_3 , ScF_3 , FeF_3 , CoF_3 ,
•$Sc(OH)_3$ (*distorted*)



- ***Lattice*: Primitive Cubic (idealised structure)**
- **1$CaTiO_3$ per unit cell**
- ***A-Cell Motif*: Ti at (0, 0, 0); Ca at ($^1/_2$, $^1/_2$, $^1/_2$); 3O at ($^1/_2$, 0, 0), (0, $^1/_2$, 0), (0, 0, $^1/_2$)**
- **Ca 12-coordinate by O (cuboctahedral)**
- **Ti 6-coordinate by O (octahedral)**
- **O distorted octahedral (4xCa + 2xTi)**
- **TiO_6 octahedra share only vertices**
- **CaO_{12} cuboctahedra share faces**
- **Ca fills the vacant ccp site in ReO_3, ⇒ a CaO_3 ccp arrangement with $^1/_4$ of octahedral holes (those defined by 6xO) filled by Ti**
- ***Examples*: $NaNbO_3$, $BaTiO_3$, $CaZrO_3$, $YAlO_3$, $KMgF_3$**
- **Many undergo small distortions: e.g. $BaTiO_3$ is *ferroelectric***



Perovskite Structure: ABO_3

Tolerance factor:

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$$

t	Effect	Possible structure
>1	A cation too large to fit in interstices	Hexagonal perovskite
0.9-1.0	ideal	Cubic perovskite
0.71-0.9	A cation too small	Orthorhombic perovskite
<0.71	A cation same size as B cation	Possible close packed lattice

Perovskite: most widely studied oxide structure

Wide range of chemistries possible
- thousands of examples known

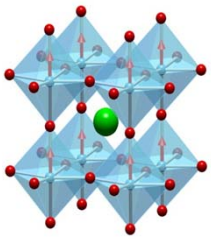
Unique properties of perovskites:

- high T_c cuprate superconductors
- Colossal Magneto-Resistance ($La,SrMnO_3$)
- fast ion conduction (Li^+, O^{2-}), batteries, fuel cells
- mixed electronic/ionic conduction, fuel cells
- oxidation/reduction catalysts
- ferroelectric / piezoelectric ceramics ($BaTiO_3$, $Pb(ZrTi)O_3$)
- important mineral structure in lower mantle ($MgSiO_3$)
- frequency filters for wireless communications : $Ba(Zn_{1/3}Ta_{2/3})O_3$

Ferroelectrics

$BaTiO_3$: Ba^{2+} r=1.56 Å
Ti^{4+} r=0.75 Å
O^{2-} r=1.26 Å

t=0.992



$KNbO_3$ K^+ 1.65 Å
Nb^{5+} 0.78 Å

t=1.01

$LiNbO_3$ Li^+ 1.06 Å
Nb^{5+} 0.78 Å

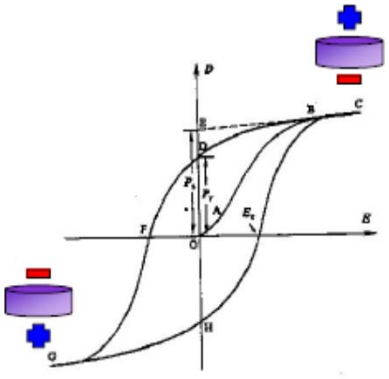
t=0.81

Rhombhedral distortion

What is a Ferroelectric

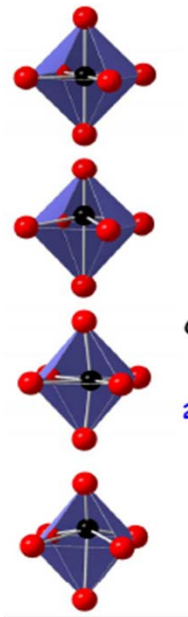
A ferroelectric material develops a spontaneous polarization (builds up a charge) in response to an external electric field.

- The polarization does not go away when the external field is removed.
- The direction of the polarization is reversible.



Applications of Ferroelectric Materials

- Multilayer capacitors
- Non-volatile FRAM (Ferroelectric Random Access Memory)



Cubic (Pm3m)
T > 393 K
Ti-O Distances (Å)
6x2.00

Tetragonal (P4mm)
273 K < T < 393 K
Ti-O Distances (Å)
1.83, 4x2.00, 2.21
Toward a corner

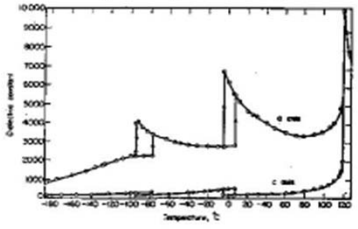
Orthorhombic (Amm2)
183 K < T < 273 K
Ti-O Distances (Å)
2x1.87, 2x2.00, 2x2.17
Toward an edge

Rhombohedral (R3m)
183 K < T < 273 K
Ti-O Distances (Å)
3x1.88, 3x2.13
Toward a face

$BaTiO_3$ Phase Transitions

In the cubic structure $BaTiO_3$ is paraelectric. That is to say that the orientations of the ionic displacements are not ordered and dynamic.

Below 393 K $BaTiO_3$ becomes ferroelectric and the displacement of the Ti^{4+} ions progressively displace upon cooling.



See Kwei *et al. J. Phys. Chem.* **97**, 2368 (1993).

Magnetoresistive materials:

$LaMnO_3$: 1.30 Å ; 0.72 Å t=0.91

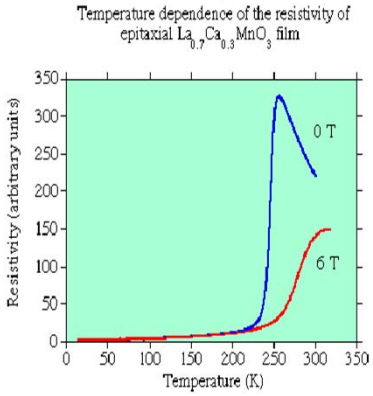
$La_{0.5}Sr_{0.5}MnO_3$: 1.28 Å, 0.695 Å t=0.92

Mn^{3+}, d^4:

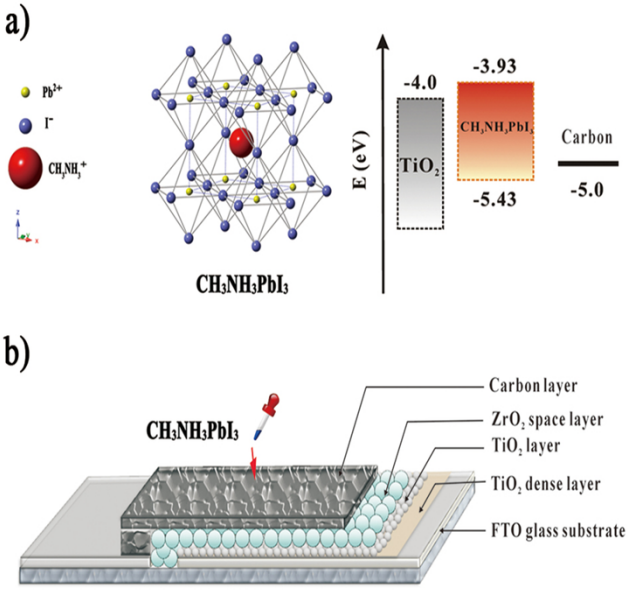
large Jahn-Teller effect, tetragonal distortion

Colossal Magnetoresistance

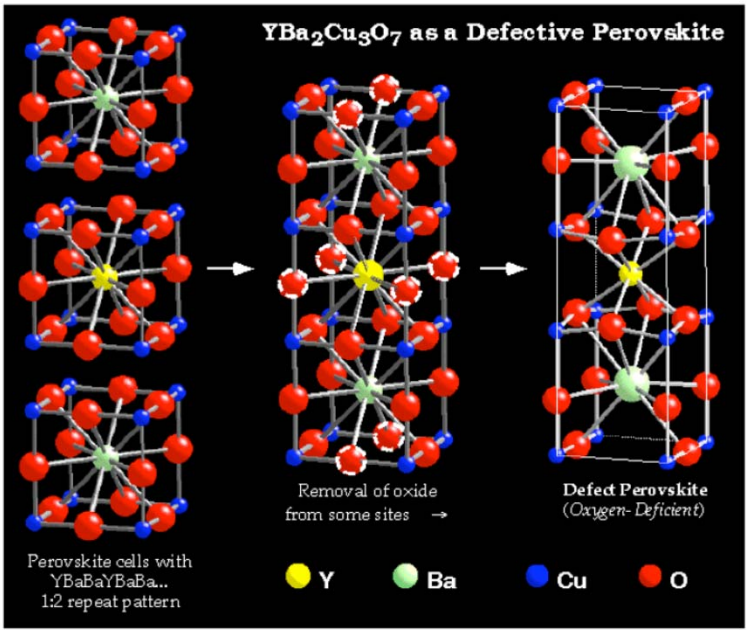
Temperature Dependence



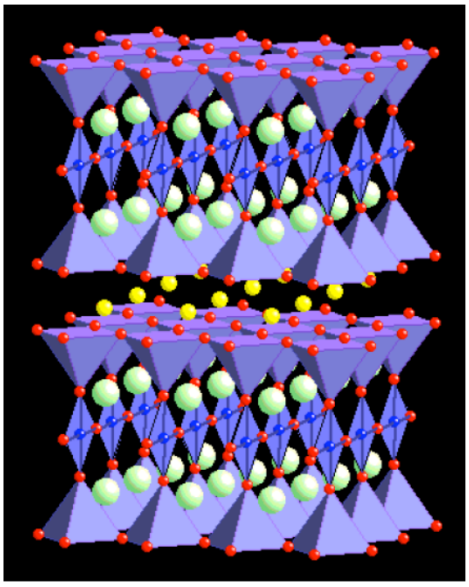
As the temperature is increased through the ferromagnetic Curie temperature T_c, the electrical resistance rises sharply, and becomes strongly dependent on applied magnetic field.



Superconductor Structure ($YBa_2Cu_3O_{7-x}$)



Superconductor Structure ($YBa_2Cu_3O_{7-x}$) -Polyhedral Representation



Electronic Structure of Solids

Band Theory

Reading:

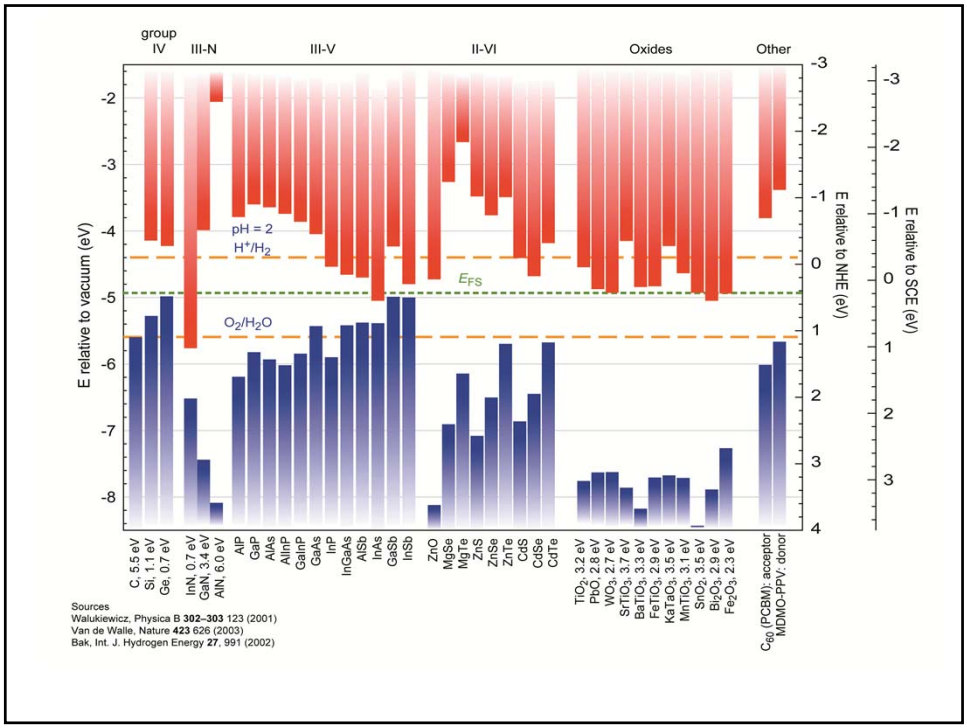
MT 7, DG 7

Resistivities of Real Materials

Compound	Resistivity (Ω-cm)	Compound	Resistivity (Ω-cm)
Ca	3.9×10^{-6}	Si	~ 0.1
Ti	42×10^{-6}	Ge	~ 0.05
Mn	185×10^{-6}	ReO_3	36×10^{-6}
Zn	5.9×10^{-6}	Fe_3O_4	52×10^{-6}
Cu	1.7×10^{-6}	TiO_2	9×10^{4}
Ag	1.6×10^{-6}	ZrO_2	1×10^{9}
Pb	21×10^{-6}	Al_2O_3	1×10^{19}

Most semiconductors in their pure form are not good conductors, they need to be doped to become conducting.

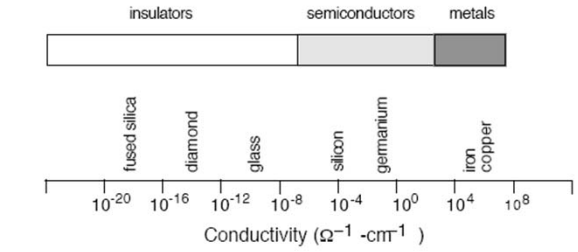
Not all so called "ionic" materials like oxides are insulators.



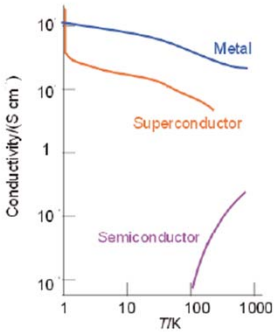
Properties of Semiconductors

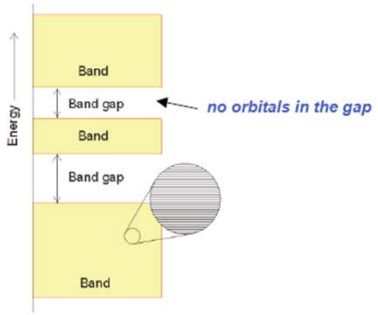
Compound	Structure	Bandgap (eV)	e^- mobility ($cm^2/V\text{-}s$)	h^+ mobility ($cm^2/V\text{-}s$)
Si	Diamond	1.11 (I)	1,350	480
Ge	Diamond	0.67 (I)	3,900	1,900
AlP	Sphalerite	2.43 (I)	80	---
GaAs	Sphalerite	1.43 (D)	8,500	400
InSb	Sphalerite	0.18 (D)	100,000	1,700
AlAs	Sphalerite	2.16 (I)	1,000	180
GaN	Wurtzite	3.4 (D)	300	---

Conductors, Semiconductors and Insulators

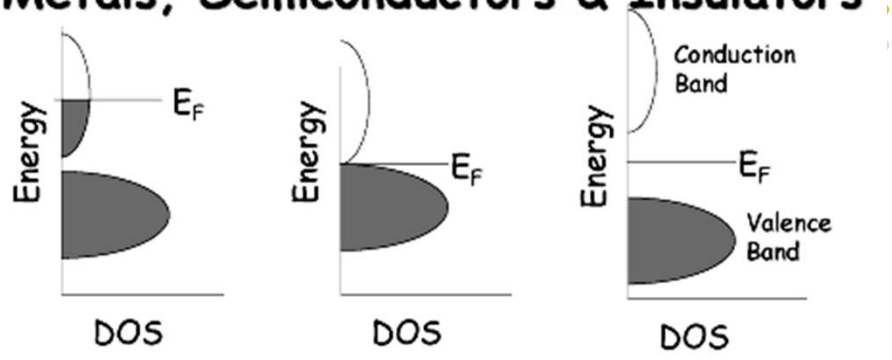


The entire range of conductivities of solids spans roughly 30 orders of magnitude.



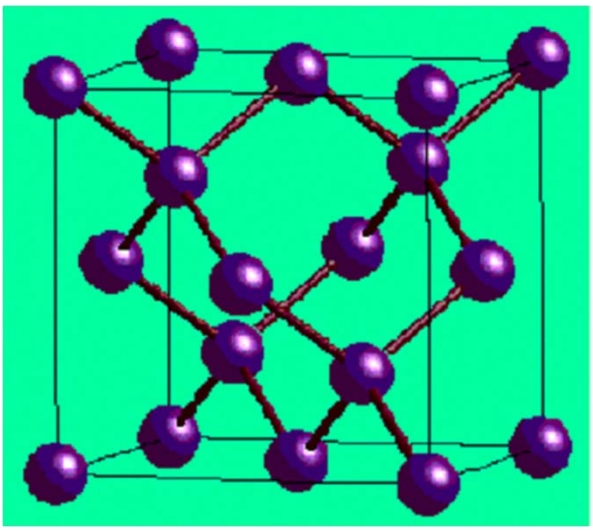


Metals, Semiconductors & Insulators



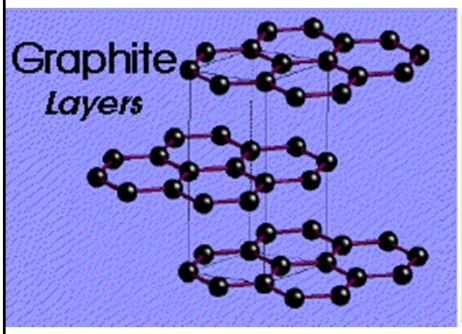
In a metal the Fermi level cuts through a band to produce a partially filled band. In a semiconductor/insulator there is an energy gap between the filled bands and the empty bands. The distinction between a semiconductor and an insulator is artificial, but as the gap becomes large the material usually becomes a poor conductor of electricity. A semimetal results when the band gap goes to zero.

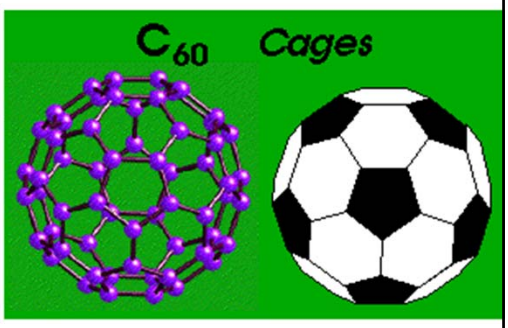
Silicon vs. *Diamond*



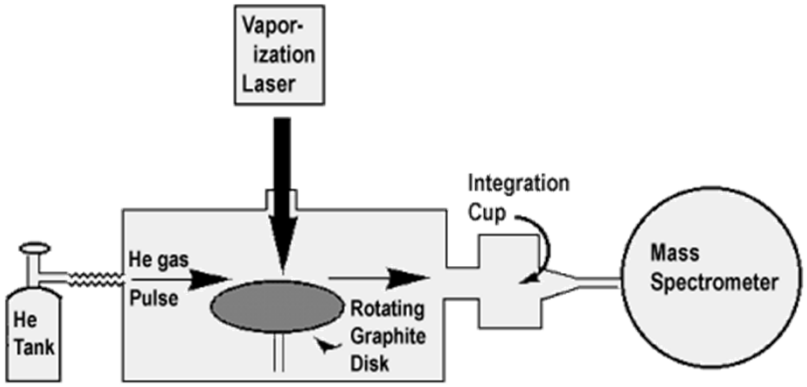
CARBON Allotropes

Carbon shows both Layer and Cage Networks

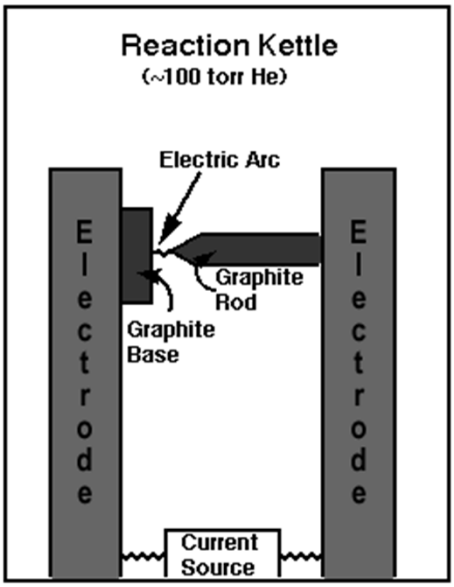


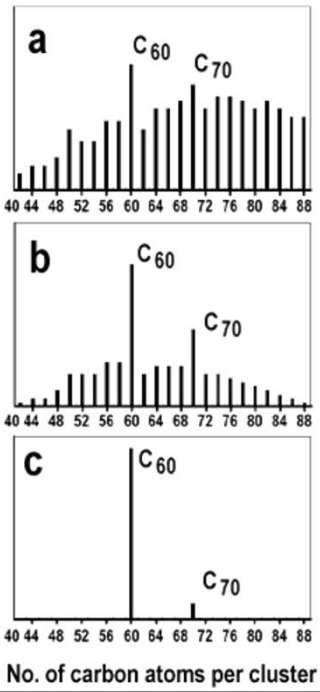


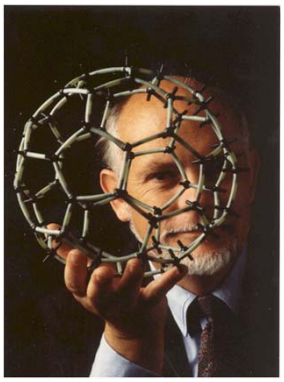
Synthesis of C_{60}: Laser Ablation



Arc-discharge

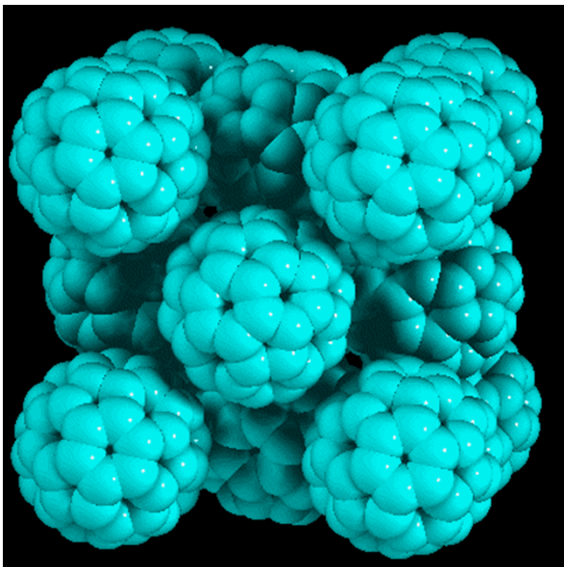


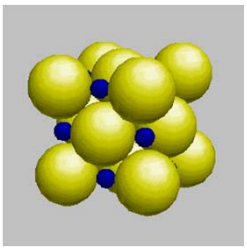


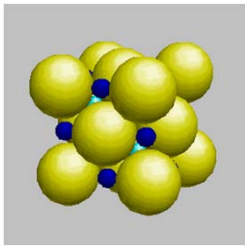


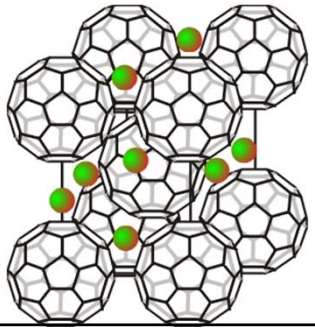
Smalley, Kroto, Curl
1996, Nobel prize

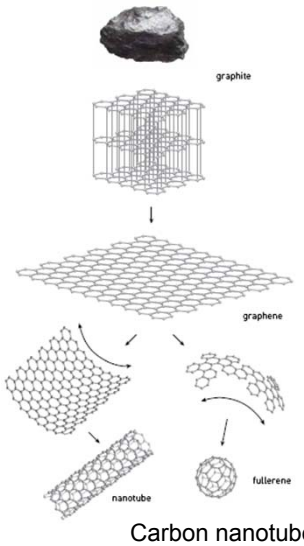
Chem 104A, UC, Berkeley

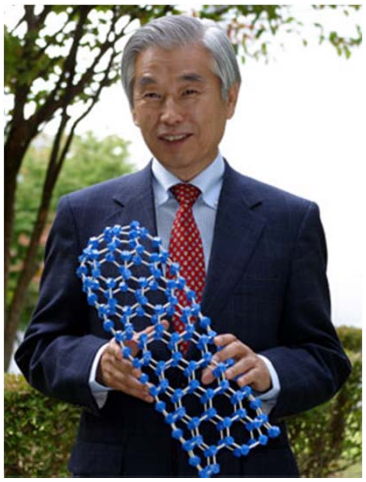












Carbon nanotube, 1991, NEC's Fundamental Research Laboratories

Discovery of Graphene

Andre Geim and Konstantin Novoselov
Nobel prize in Physics, 2010

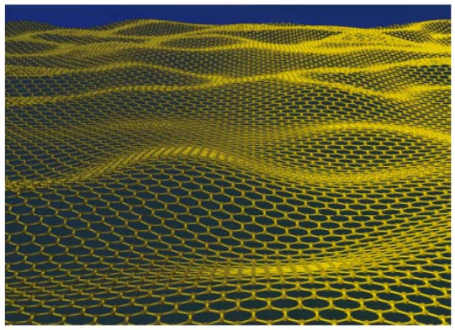
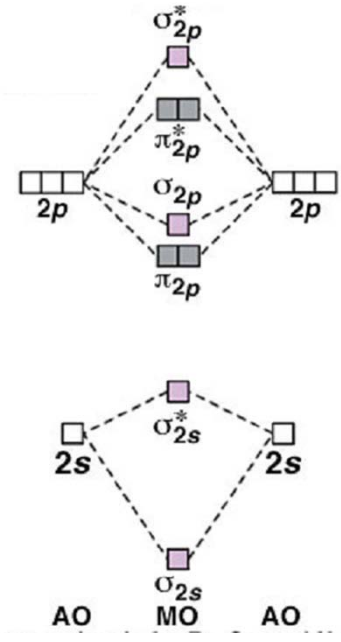


Figure 1. Graphene. The almost perfect web is only one atom thick. It consists of carbon atoms joined together in a hexagonal pattern similar to chicken wire.



$2\sigma_u$ Antibonding

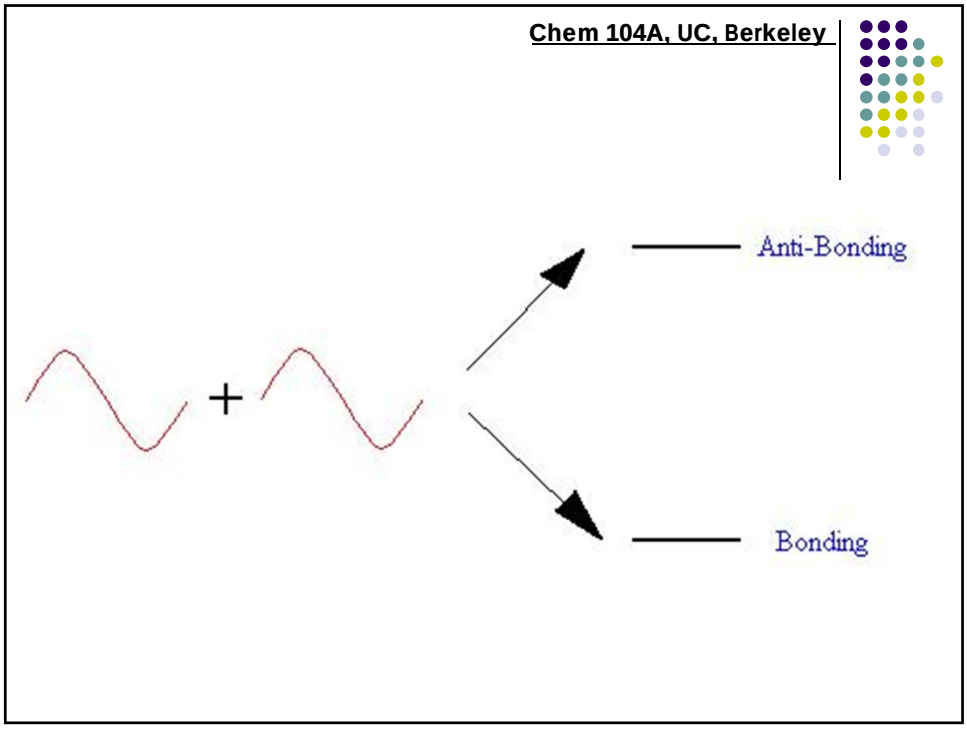
$1\pi_g$ Node π^*_{2p}MO (antibonding)

$2\sigma_g$ **Relative non-bonding**
Slightly bonding

$1\pi_u$ π_{2p}MO (bonding)

$1\sigma_u$ **Relative non-bonding**
Slightly antibonding

$1\sigma_g$ bonding



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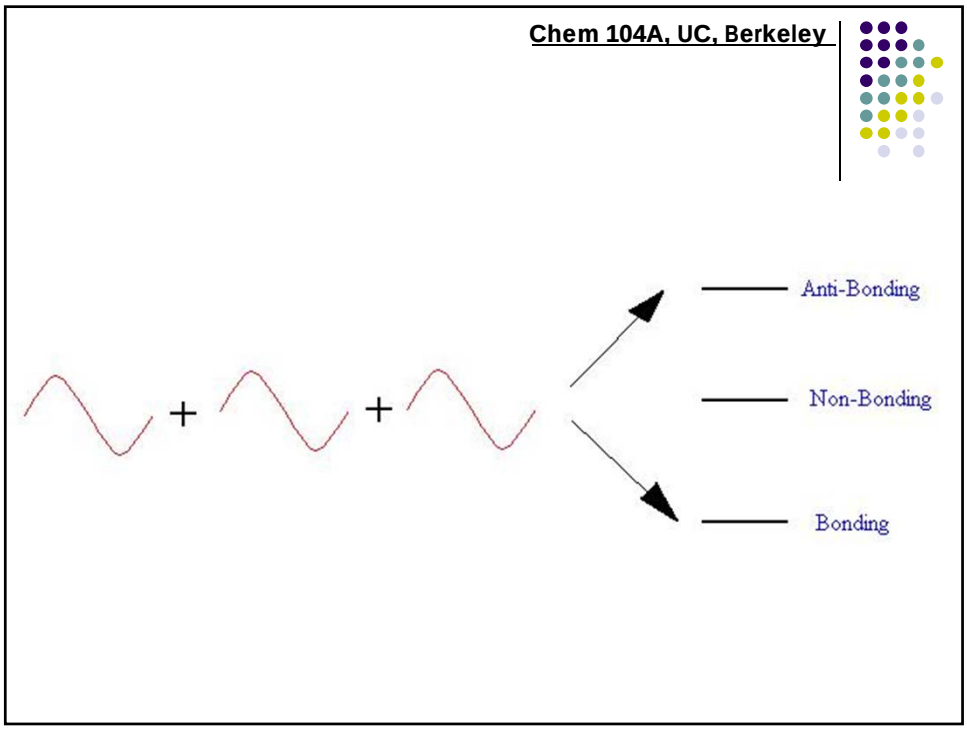
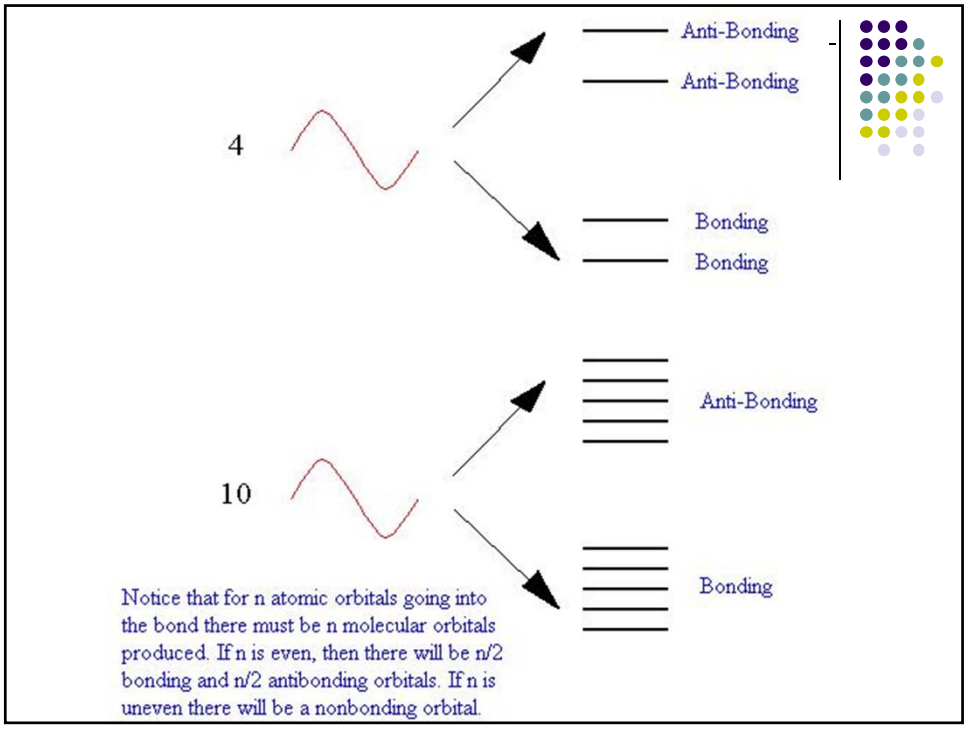
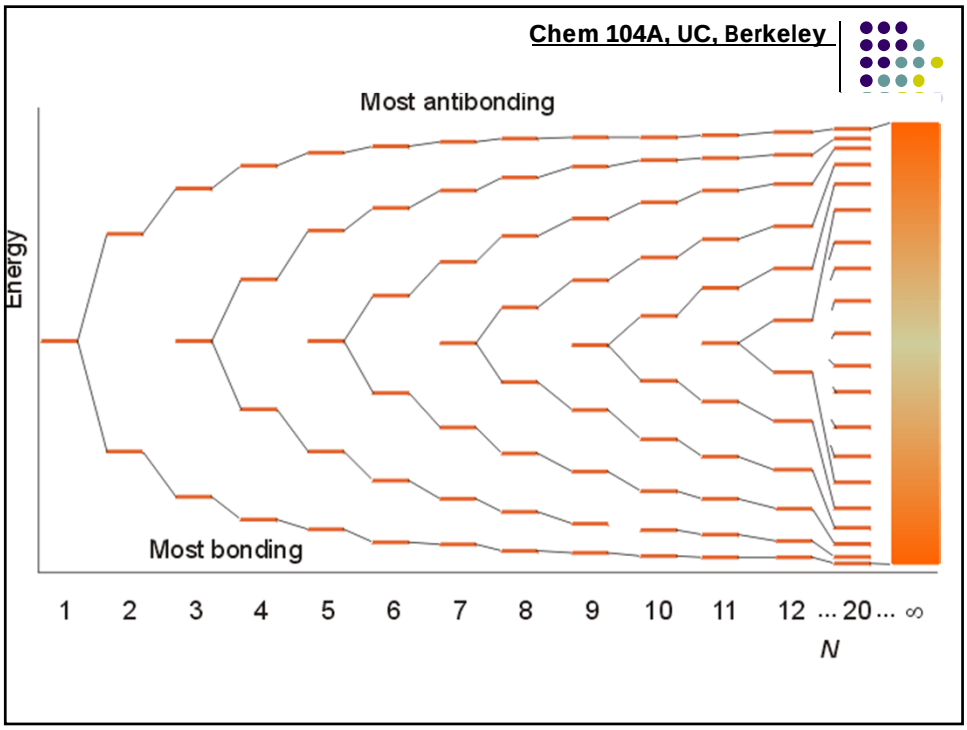
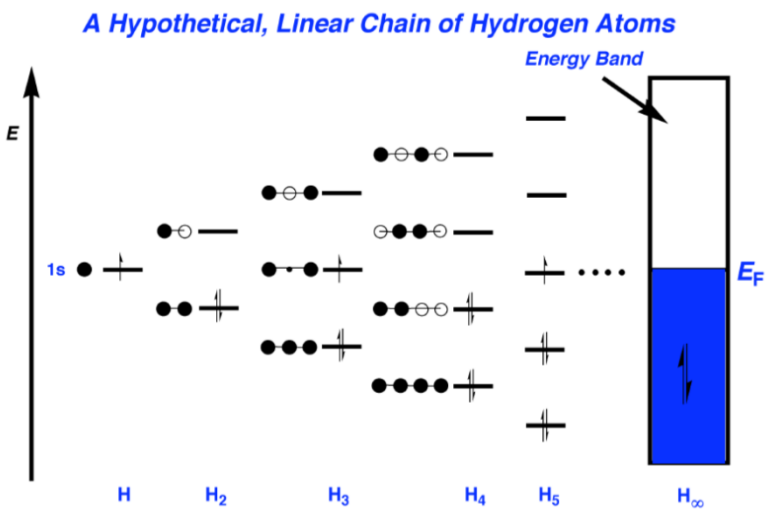
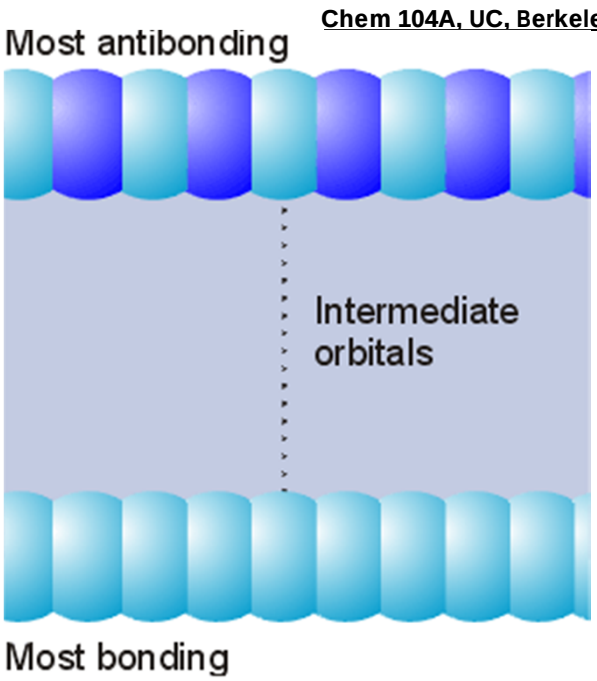



Anti-Bonding
Anti-Bonding
4
Bonding
Bonding
Anti-Bonding
10
Bonding
Notice that for n atomic orbitals going into the bond there must be n molecular orbitals produced. If n is even, then there will be n/2 bonding and n/2 antibonding orbitals. If n is uneven there will be a nonbonding orbital.


Chem 104A, UC, Berkeley
Most antibonding
Energy
Most bonding
1 2 3 4 5 6 7 8 9 10 11 12 ... 20 ... ∞
N



Chem 104A, UC, Berkeley



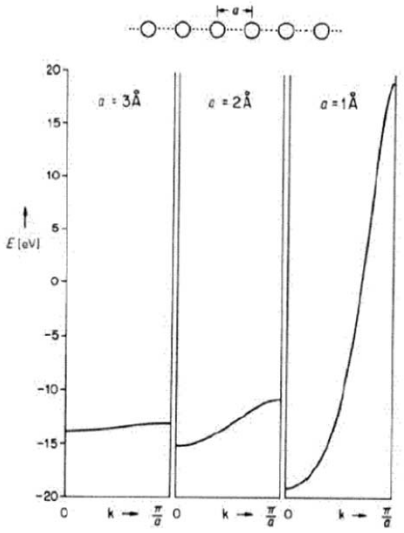
Elementary Band Theory for Extended Solids

Bandwidth (dispersion)

The difference between highest and lowest level of one band.

The bandwidth is determined by the **overlap** between the interacting orbitals.

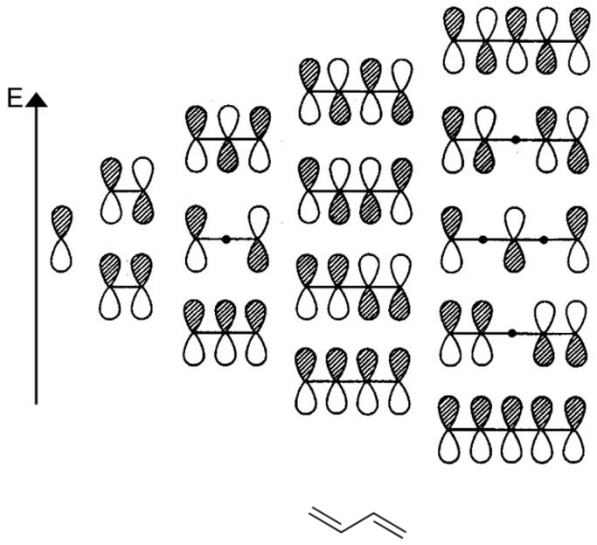
The smaller the distance between the atoms, the larger the bandwidth.



Infinite chain of H atoms

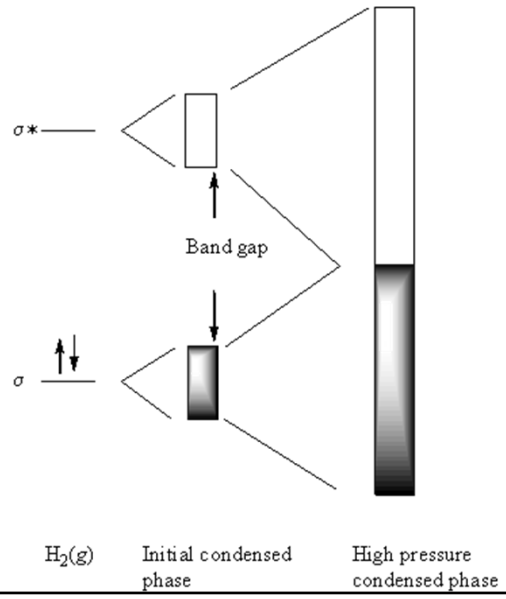
General scheme for 'linear' polyenes

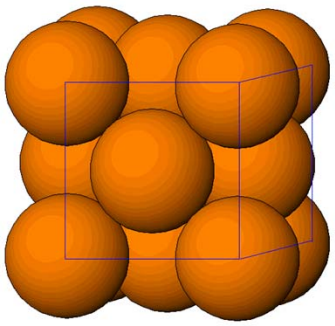
C_nH_{n+2}

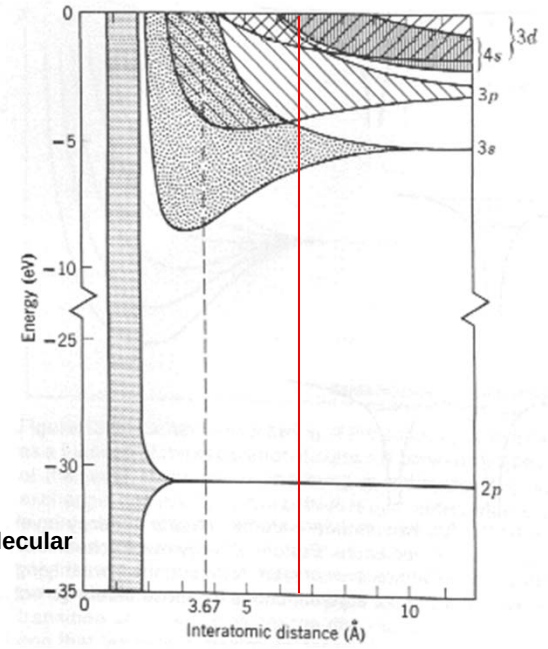


Metal

Metallic Hydrogen

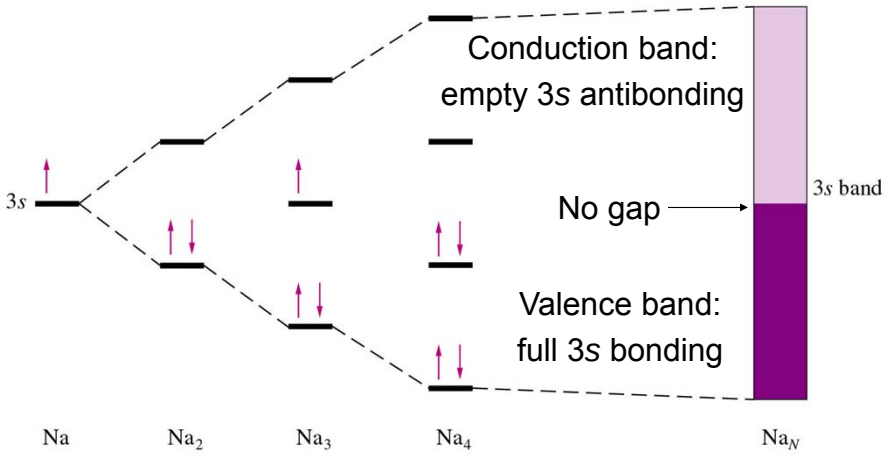






In extended solid, each atomic/molecular orbtial will develop into one band!

Sodium According to Band Theory



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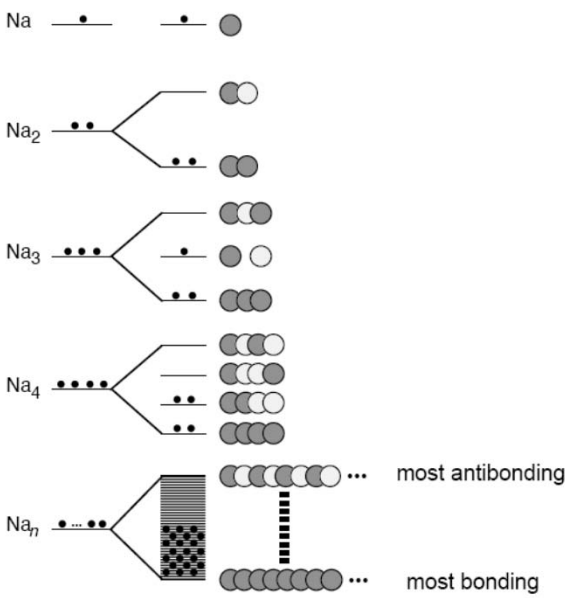
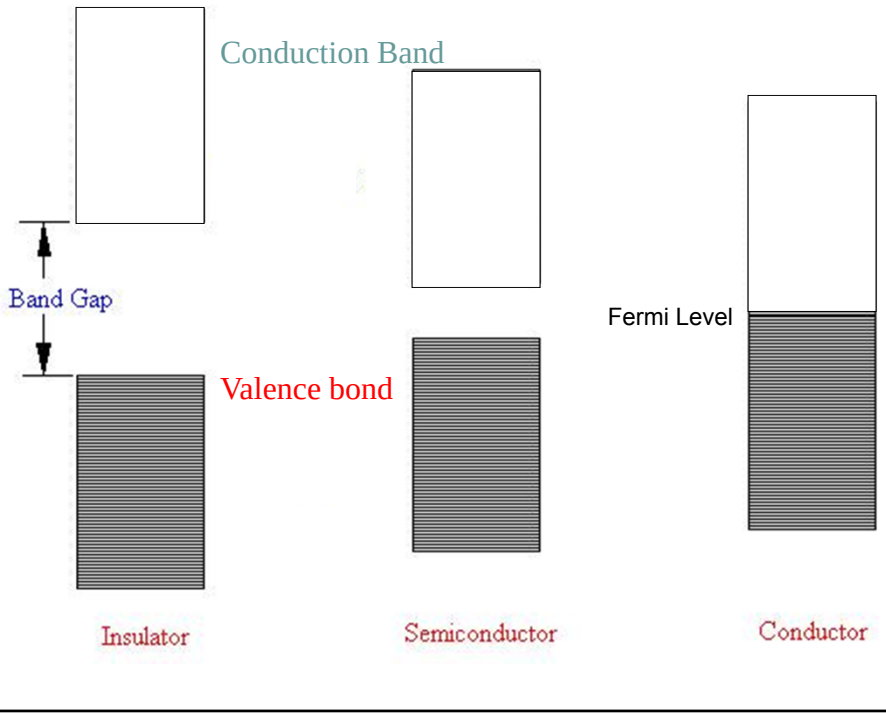
Combinations of 3s Orbitals of Sodium Atoms





Bonding in Metals

- The **electron-sea model** is a simple depiction of a metal as an array of positive ions surrounded by delocalized valence electrons.
  - Metals are good conductors of electricity because of the mobility of these delocalized valence electrons.
  - A metal also conducts heat well because the mobile electrons can carry additional kinetic energy.

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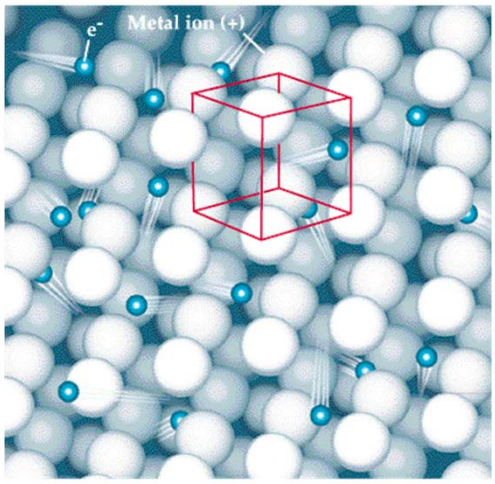
Bonding in Metals



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Bonding in Metals

- Molecular orbital theory gives a more detailed picture of the bonding in metals.
  - According to band theory, the electrons in a crystal **become free to move when they are excited to the unoccupied orbitals of a band**.
  - In a metal, **this requires little energy** since the unoccupied orbitals lie just above the occupied orbitals of highest energy.

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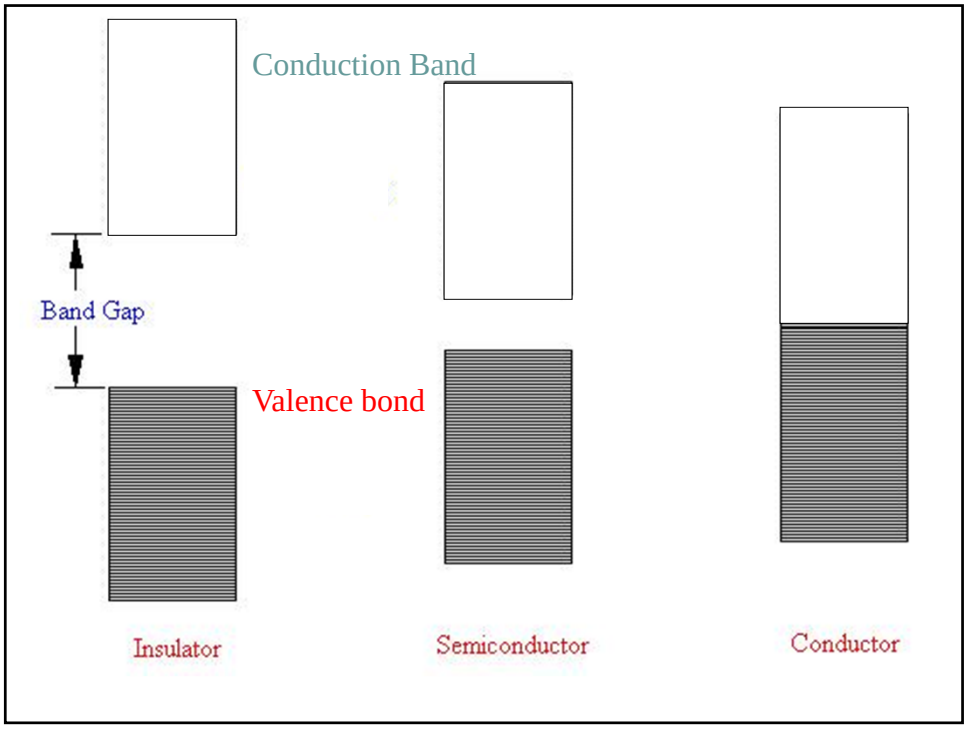
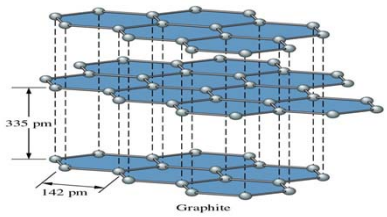
Semiconductor



Graphite

- **Graphite** has a layered structure, in which the carbon atoms in each layer bond to three other carbons with sp^2 orbitals.
  - Of the covalent network solids, only graphite conducts electricity.
  - This is due to the delocalization of the resonant π electrons in graphite's sp^2 hybridization.



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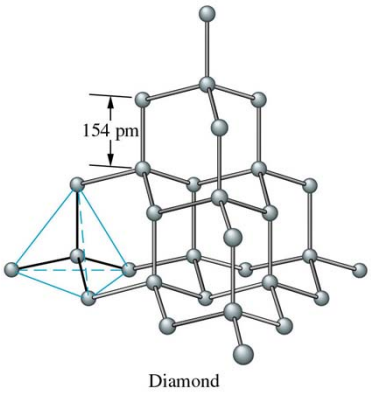
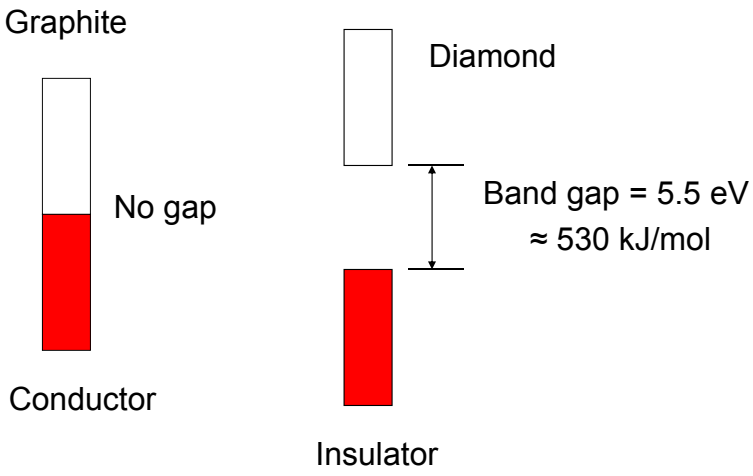
Structure of Diamond



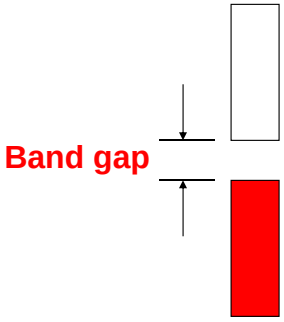
Solids: Conductors, Insulators and Semiconductors



Solids: Conductors, Insulators and Semiconductors

Band Gap for Semiconductors

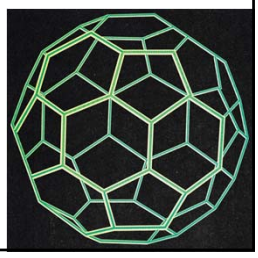
Diamond	5.5 eV
Si	1.1 eV
Ge	0.67 eV

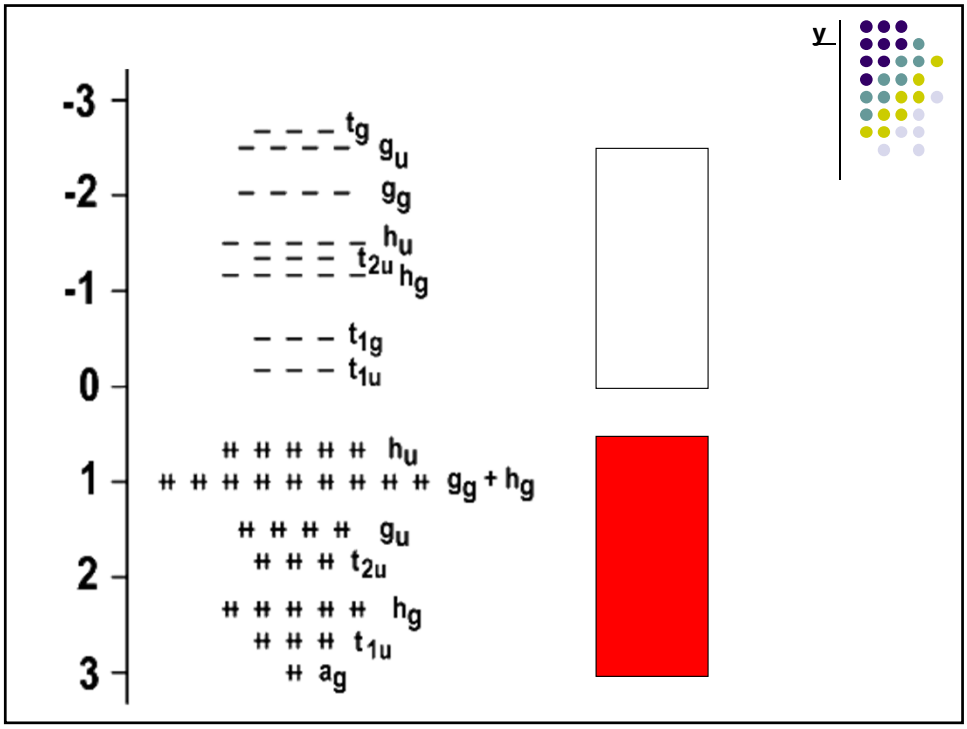


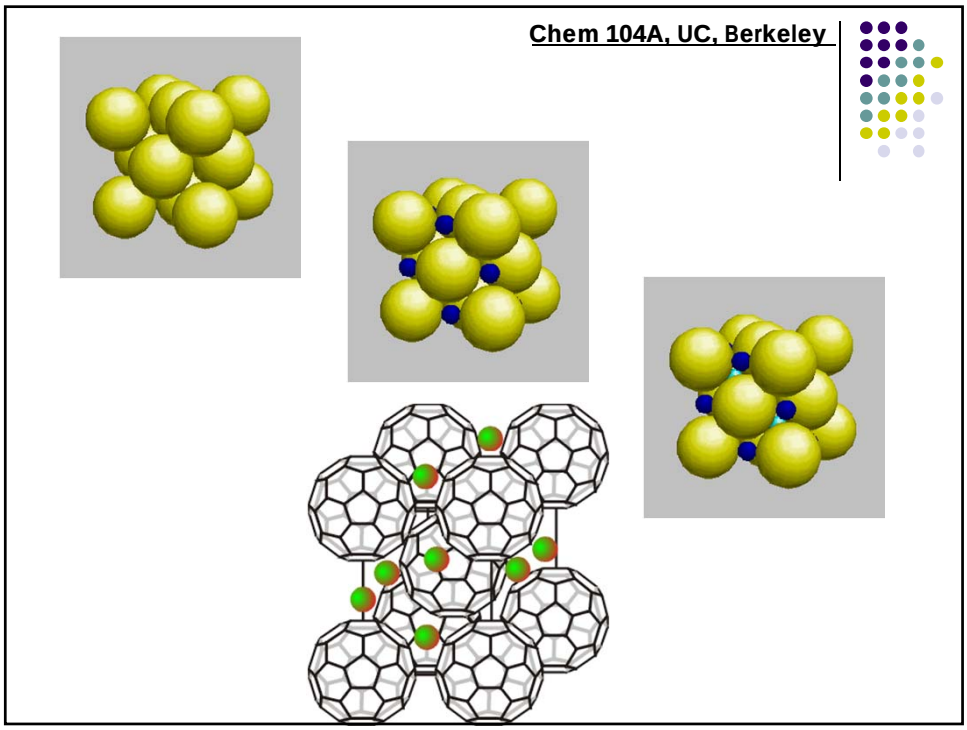
Semiconductor

Fullerenes

- The **fullerenes** are a family of molecules with a closed cage of carbon atoms arranged in pentagons and hexagons. Each carbon is sp^2 hybridized.
  - The most symmetrical member is buckminsterfullerene, C_{60}.
  - Buckminsterfullerenes show potential for applications in superconductivity and catalytic activity.




y
-3
-2
-1
0
1
2
3
t_g g_u
g_g
h_u
t_{2u} h_g
t_{1g}
t_{1u}
h_u
$g_g + h_g$
g_u
t_{2u}
h_g
t_{1u}
a_g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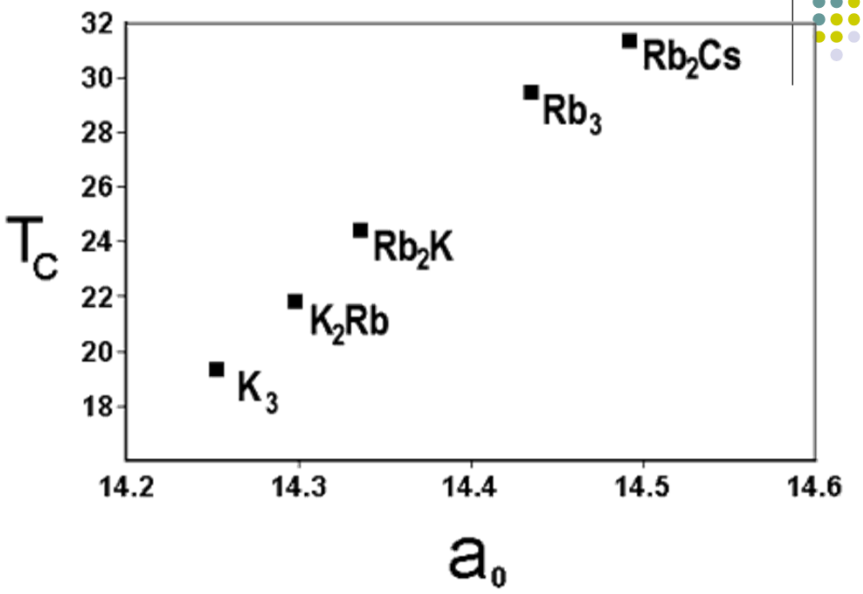
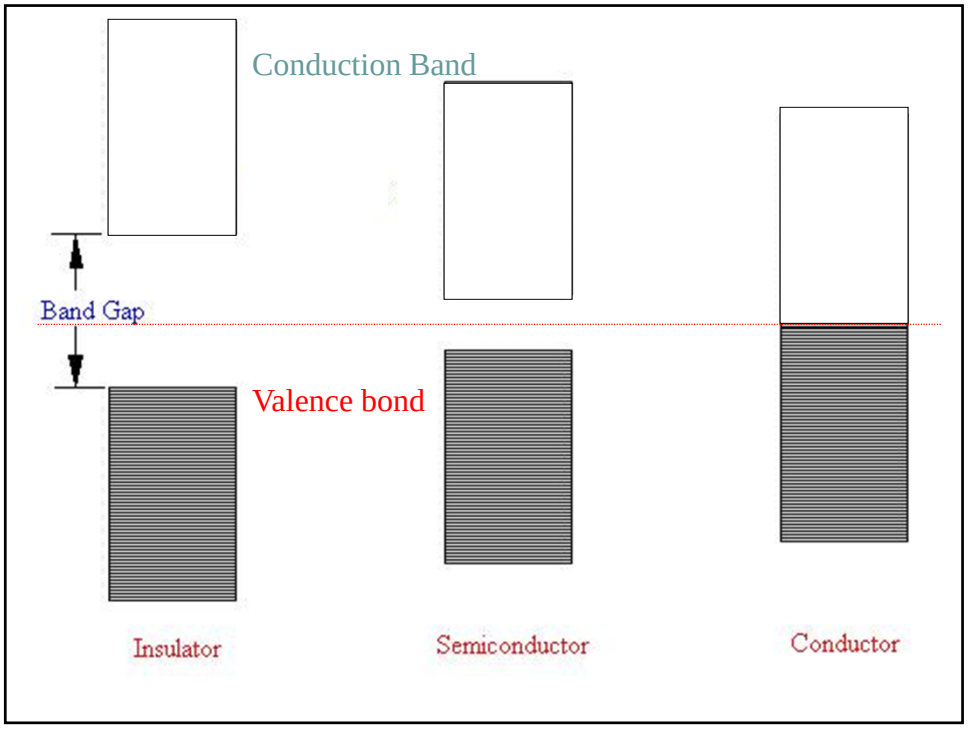


Fermi Level E_F
corresponds to the highest occupied energy at T=0
(HOMO energy)

Fermi-Dirac distribution

$$P = \frac{1}{e^{(E-E_F)/kT} + 1}$$

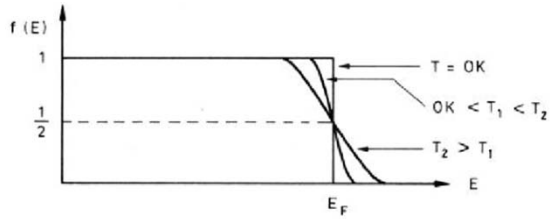
population P of the valence band orbitals.



Fermi-Dirac distribution:

$$f(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1}$$

Energy distribution of electrons



Fermi-Dirac Function

The Fermi-Dirac function gives the fraction of allowed states, f(E), at an energy level E, that are populated at a given temperature.

$$f(E) = 1/[1 + \exp\{(E-E_F)/kT\}]$$

where the Fermi Energy, E_F, is defined as the energy where f(E) = 1/2. That is to say one half of the available states are occupied. T is the temperature (in K) and k is the Boltzman constant ($k = 8.62 \times 10^{-5}$ eV/K)

As an example consider f(E) for T = 300 K and a state 0.1 eV above E_F:

$$f(E) = 1/[1 + \exp\{(0.1\ eV)/((300K)(8.62 \times 10^{-5}\ eV/K)\}]$$
$$f(E) = 0.02 = 2\%$$

Consider a band gap of 1 eV.

$$f(1\ eV) = 1.6 \times 10^{-17}$$

See that for even a moderate band gap (Silicon has a band gap of 1.1 eV) the intrinsic concentration of electrons that can be thermally excited to move about the crystal is tiny. Thus pure Silicon (if you could make it) would be quite insulating.

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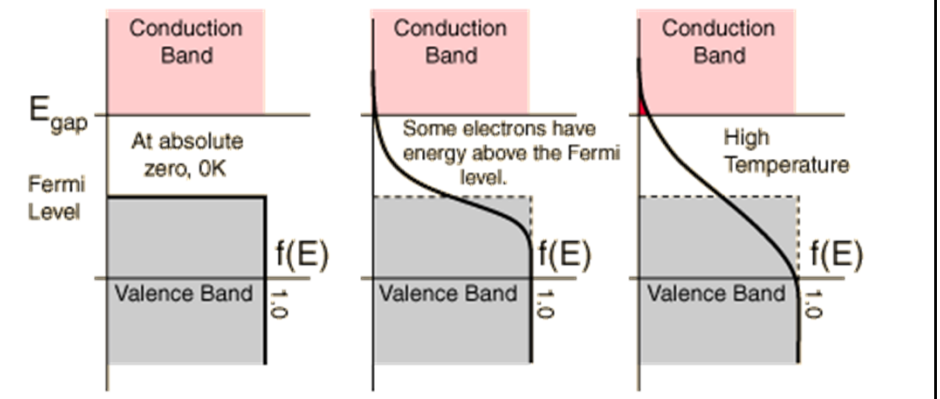


No electrons can be above the valence band at 0K, since none have energy above the Fermi level and there are no available energy states in the band gap.

At high temperatures, some electrons can reach the conduction band and contribute to electric current.

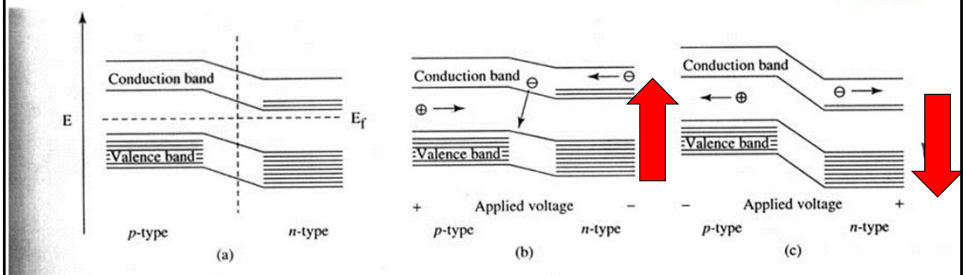
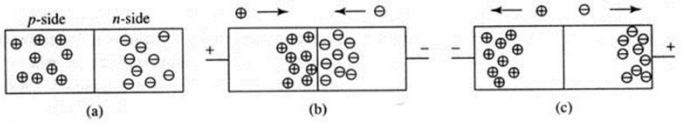


FIGURE 7-15 Band-energy Diagram of a *p-n* Junction. (a) At equilibrium, the two Fermi levels are at the same energy, changing from the pure *n*- or *p*-type Fermi levels because a few electrons can move across the boundary (vertical dashed line). (b) With forward bias. Current flows readily. (c) With reverse bias. Very little current flows.

FIGURE 7-16 Diode Behavior. (a) With no applied voltage; charges are neutralized near the junction by transfer of electrons. (b) Forward bias; current flows readily, with holes and electrons combining at the junction. (c) Reverse bias; very little current can flow because the holes and electrons move away from each other.



Semiconductors

- **Semiconducting elements** form the basis of solid state electronic devices.
  - When silicon is doped with phosphorus, it becomes an **n-type semiconductor**, in which electric current is carried by electrons.

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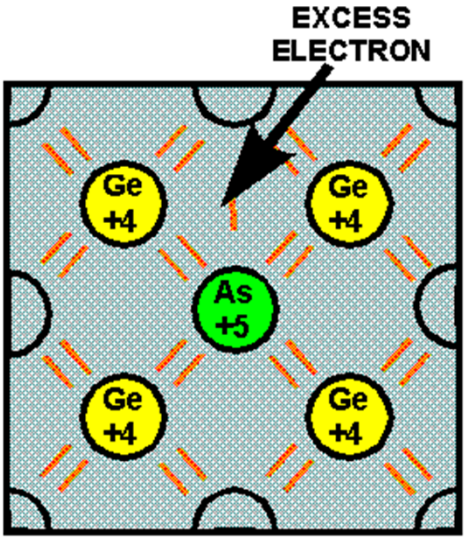
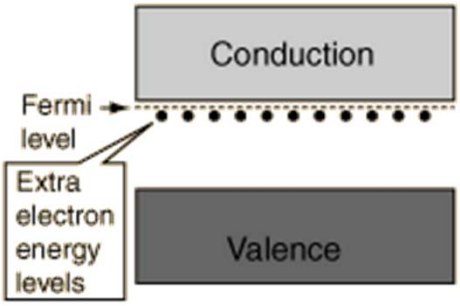
Doping in semiconductor: n-type



"Carrier type: electron"

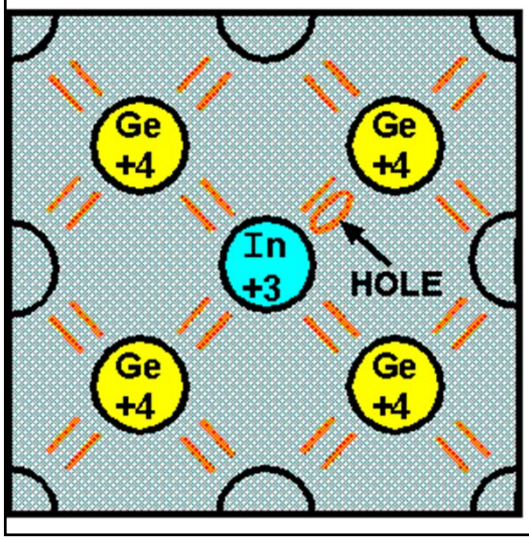


Semiconductors

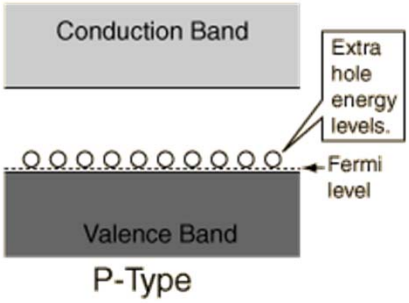
- **Semiconducting elements** form the basis of solid state electronic devices.
  - When silicon is doped with boron, it becomes a **p-type semiconductor**, in which an electrical current is carried by positively charged holes

201

Doping in semiconductor: p-type



"Carrier type: Hole"



Semiconductors

- **Semiconducting elements** form the basis of solid state electronic devices.
  - Joining a p-type semiconductor to an n-type semiconductor produces a **p-n junction**, which can function as a rectifier.
  - A **rectifier** is a device that allows current to flow in one direction, but not the other.

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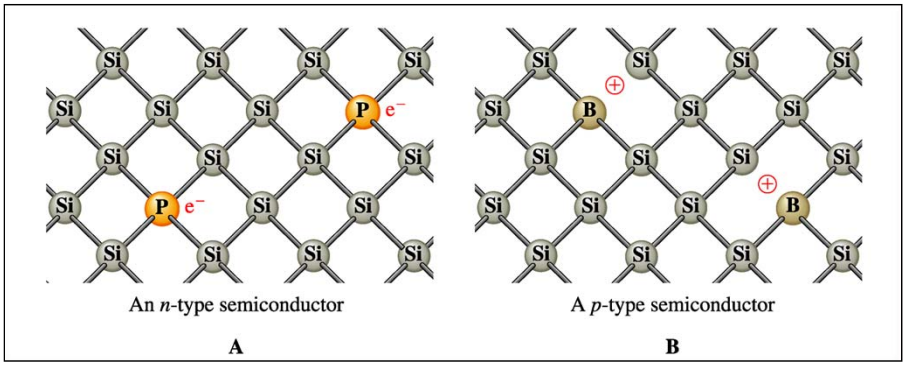
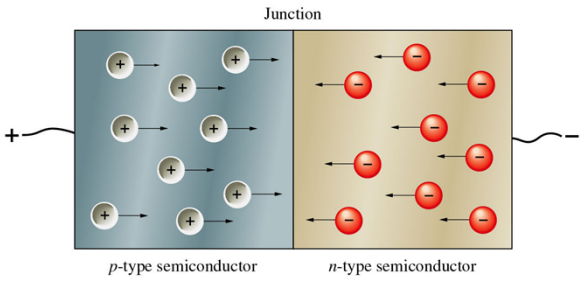
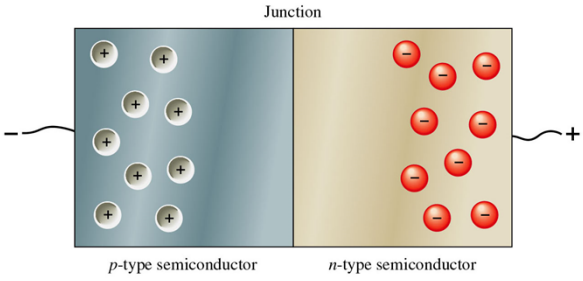
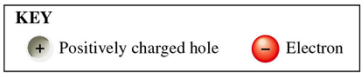

Si
P
e⁻
B
An n-type semiconductor
A
A p-type semiconductor
B

204


Junction
+
−
p-type semiconductor
n-type semiconductor


Junction
−
+
p-type semiconductor
n-type semiconductor


KEY
Positively charged hole
Electron

205

Light Emitting Diodes

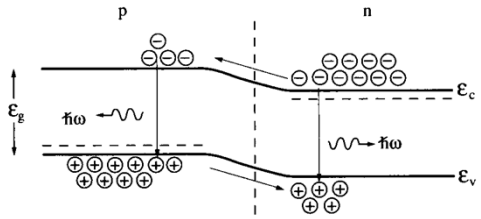
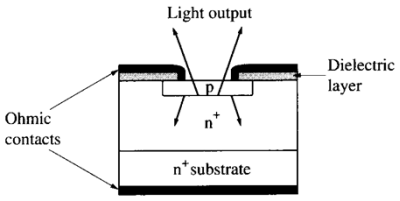


Figure 5.1 Injection of minority carriers in a forward-biased p-n junction leading to spontaneous emission of photons.

Forward bias at a p-n junction forces minority carriers across the junction. This causes electrons to fall into vacant holes radiatively, giving off light. Dopants are important sites for localizing carriers, thus transitions are often CB → acceptor, or donor → VB



Common LED materials

- **GaAs (E_g=1.43 eV) → Near IR**
- **GaP:N (E_g = 2.25 eV) → Yellow**
- **GaP:Zn,O (E_g = 2.25 eV) → Red**
- **GaN, SiC, ZnO, AlN → Blue, UV**

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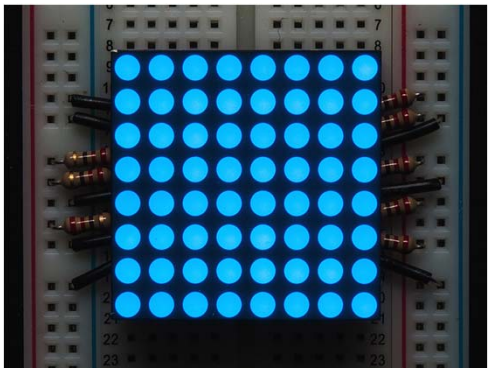
2014 Nobel Prize in physics



Common LED materials

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