

Introduction to Band Theory

PHYSICS

Solid state band

Valence band, VB

Conduction band, CB

Band gap, E_g

Fermi energy, E_F

n-doping

p-doping

Direct band gap

Indirect band gap

Phonon or lattice vibration

Peierls distortion

CHEMISTRY

Molecular orbital

HOMO

LUMO

HOMO-LUMO gap

Chemical potential

Reduction, pH scale base

Oxidation, pH scale acid

Dipole allowed

Dipole forbidden

Vibrational mode

Jahn-Teller effect

Electronic Structure of Solids

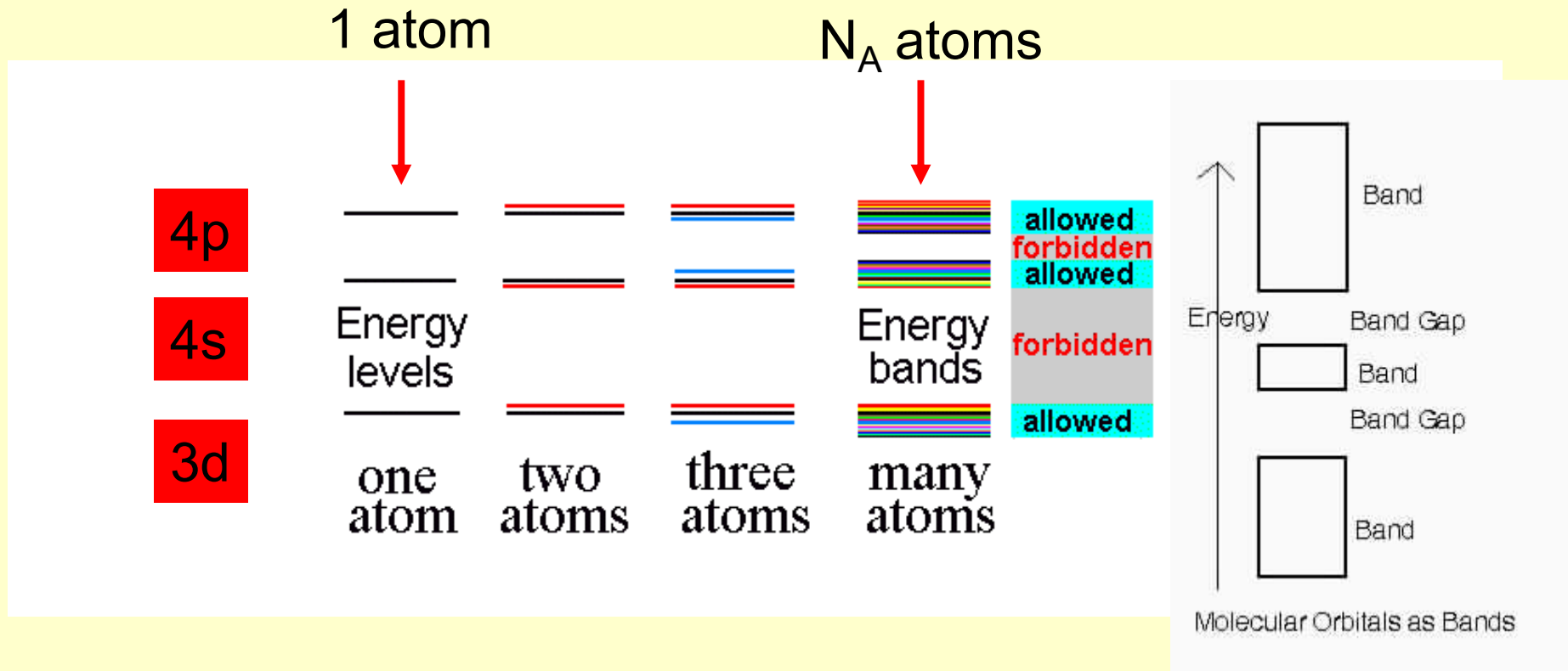
Valence **electrons** from the atoms **spread** throughout the entire structure

Molecular **orbitals** are **extended** over all the constituent atoms

A large number of overlapping atomic orbitals lead to molecular orbitals with very similar energies = continuous **band**

The bands are separated by **band gaps** (energy values where there are no available levels)

Formation of Bands

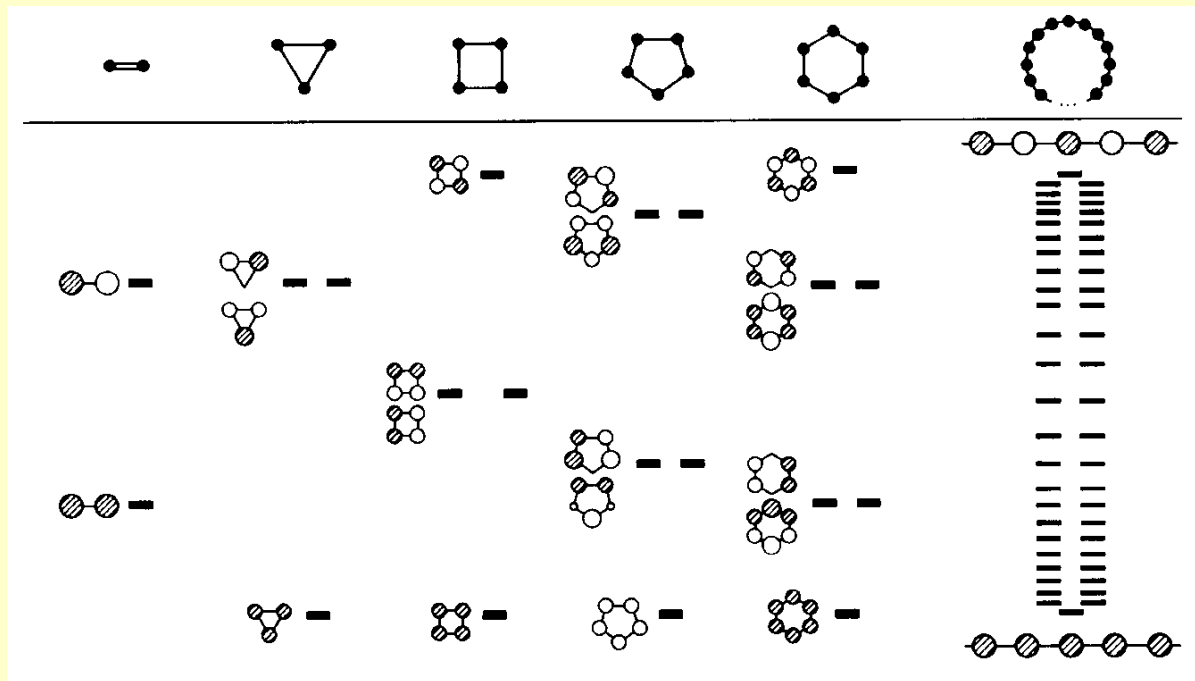


Energies of electrons are **quantized** = can possess only allowed energies, can occupy only allowed levels, cannot enter forbidden band gaps

Formation of Electronic Bands

Molecular orbitals

Electronic bands

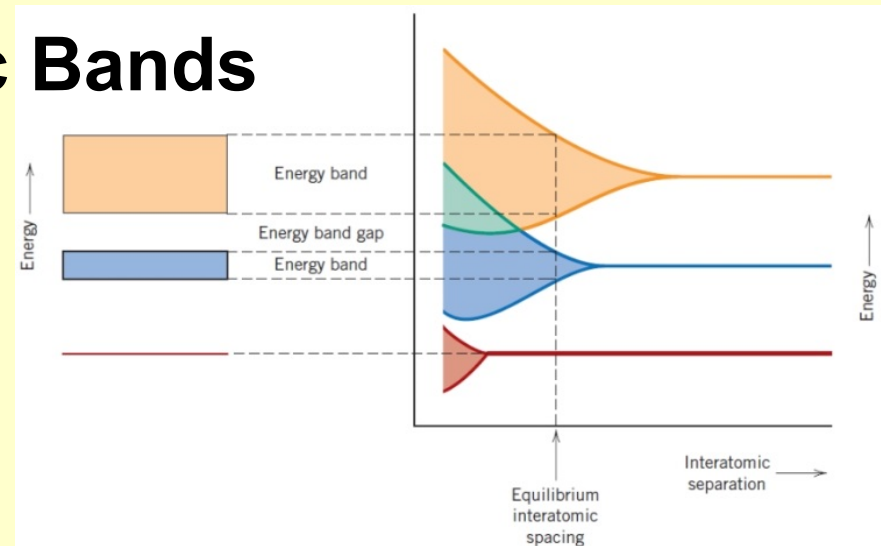


N atomic orbitals combine to form bonding and antibonding molecular orbitals = **N energy levels**

Electronic Bands

As atoms get closer:

- Bands widen
- Bonding/Antibonding orbitals get lower/higher in energy

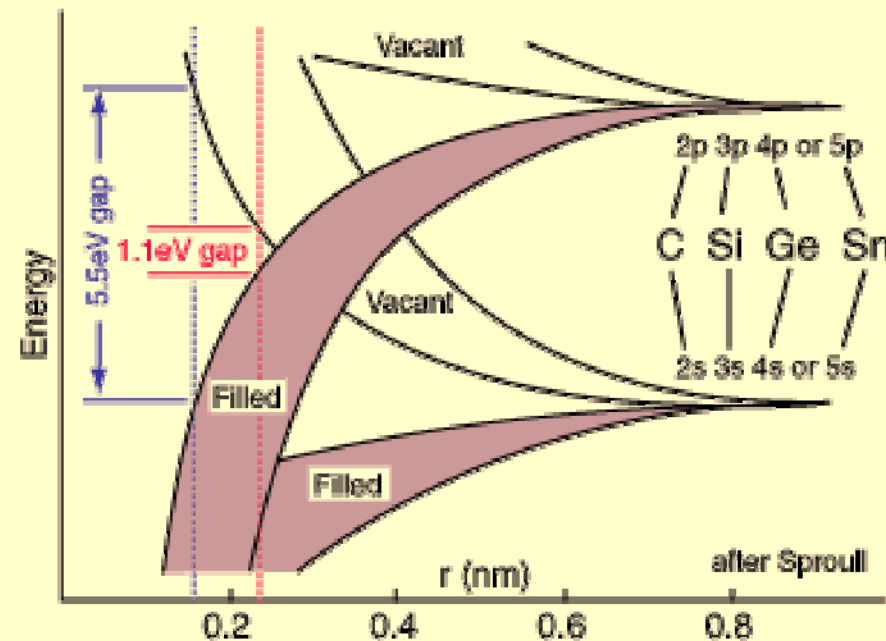


Insulator
Carbon
(diamond)
 $r_0 = 0.17 \text{ nm}$

Semiconductor
Silicon
 $r_0 = 0.24 \text{ nm}$

Periodic table environment of semiconductors

B	C $2p^2$	N
Al	Si $3p^2$	P
Ga	Ge $4p^2$	As
In	Sn $5p^2$	Sb
Tl	Pb $6p^2$	Bi



← p - orbital

← s - orbital

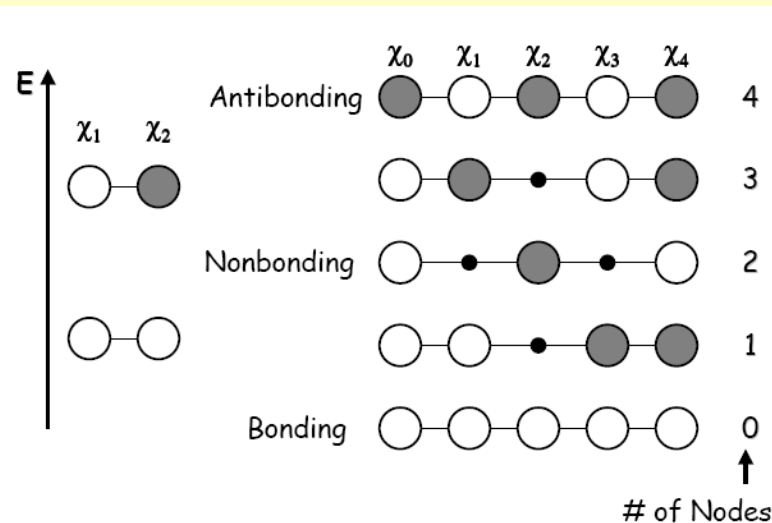
Electronic Structure of Solids

Bands arise from many MO's of slightly different energies - different degree of bonding

The **bottom** of the band – the lowest energy MO, all **bonding** character

The **top** – the highest energy MO with all **antibonding** character

The rest of the band is formed from all the MO's with intermediate bonding character between the two extremes



Crystal Orbitals

N atoms in the chain = N energy levels and N electronic states (MO)

The wavefunction for each electronic state:

$$\Psi_k = \sum e^{ikna} \chi_n$$

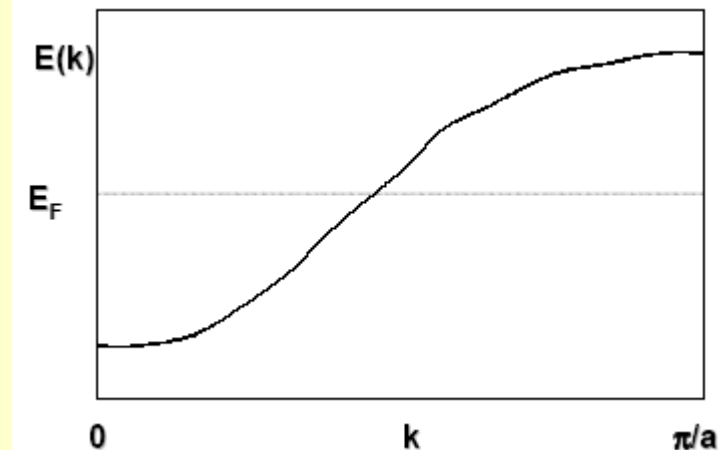
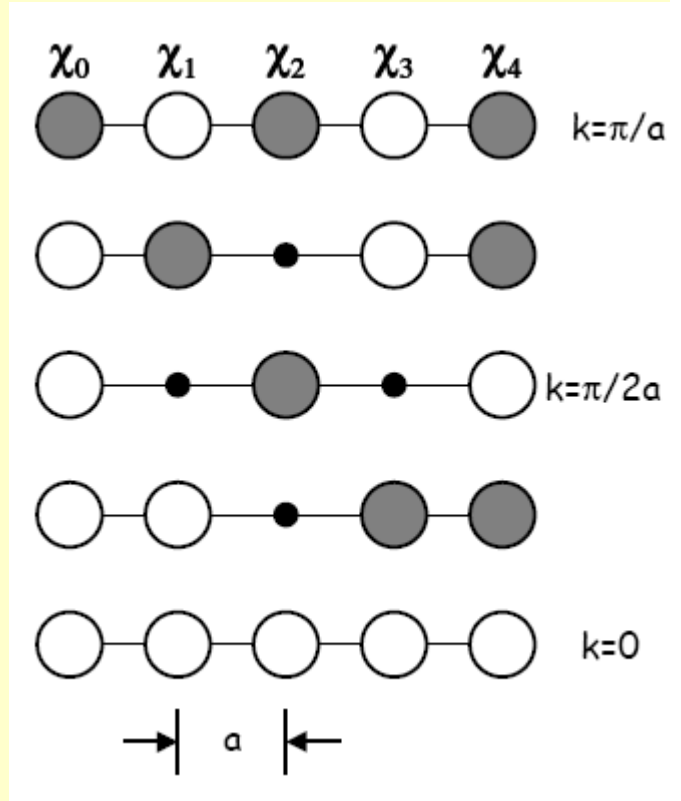
Where:

a = the lattice constant (spacing between atoms)

n identifies the individual atoms within the chain

χ_n represents the atomic orbitals

k = a quantum number that identifies the wavefunction and the phase of the orbitals

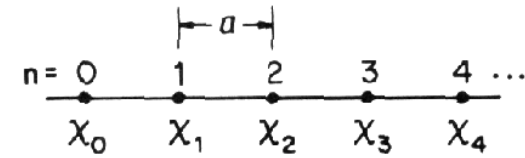


Band Theory

Bloch functions, crystal orbitals
 simple example:
 infinite one-dimensional array of
 s-orbitals

k = wavevector gives the phase
 of the AOs as well as the
 wavelength of the electron
 wavefunction (crystal momentum)
a = lattice constant
n = orbital counter

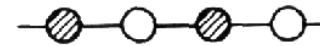
Large number of discrete levels =
band



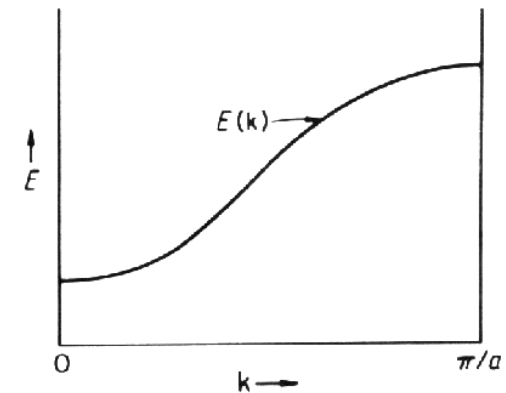
$$\psi_k = \sum_n e^{ikna} \chi_n$$

$$k = \frac{\pi}{a} \quad \psi_{\frac{\pi}{a}} = \sum_n e^{i\pi n} \chi_n = \sum_n (-1)^n \chi_n$$

$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$



Antibonding



Bonding

$$k = 0 \quad \psi_0 = \sum_n e^{i0} \chi_n = \sum_n \chi_n$$

$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$

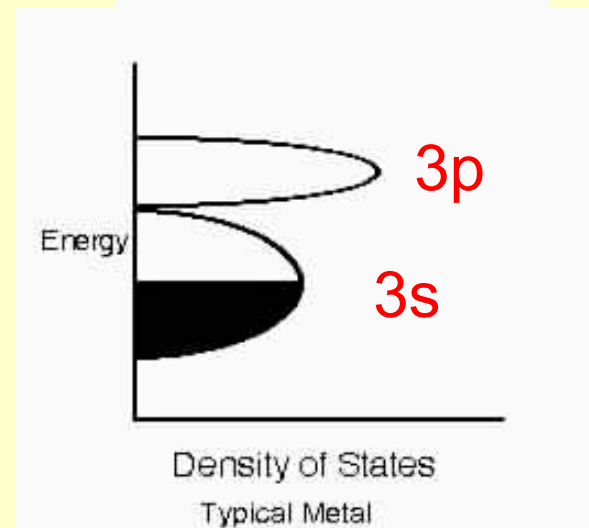
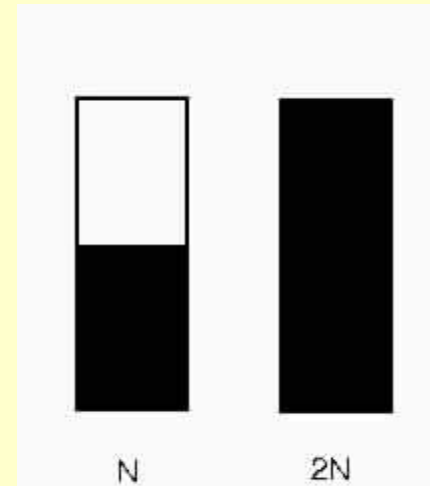
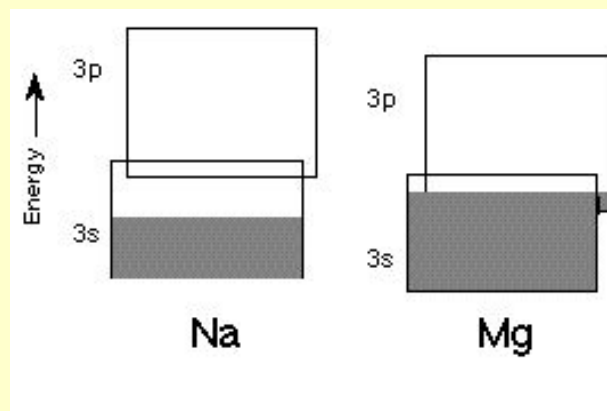


Filling Bands by Electrons

N atoms - 1 electron on each
N levels in a band

Occupied by **pairs** of electrons

N/2 levels filled
N/2 levels empty



Bandwidth or Band Dispersion

Bandwidth = energy difference between the highest and lowest level

Bandwidth **increases** with better orbital overlap

- shorter interatomic distance
- closer energy match
- topology
- density, oxides more diffuse than halides, wider bands
- localization of electrons = narrow bands

Bandwidth arising from **sigma > pi > delta** overlap

Core orbitals – narrow bands (0.1 eV), 4f in lanthanides

Valence orbitals, s, p – wide bands (10 eV)

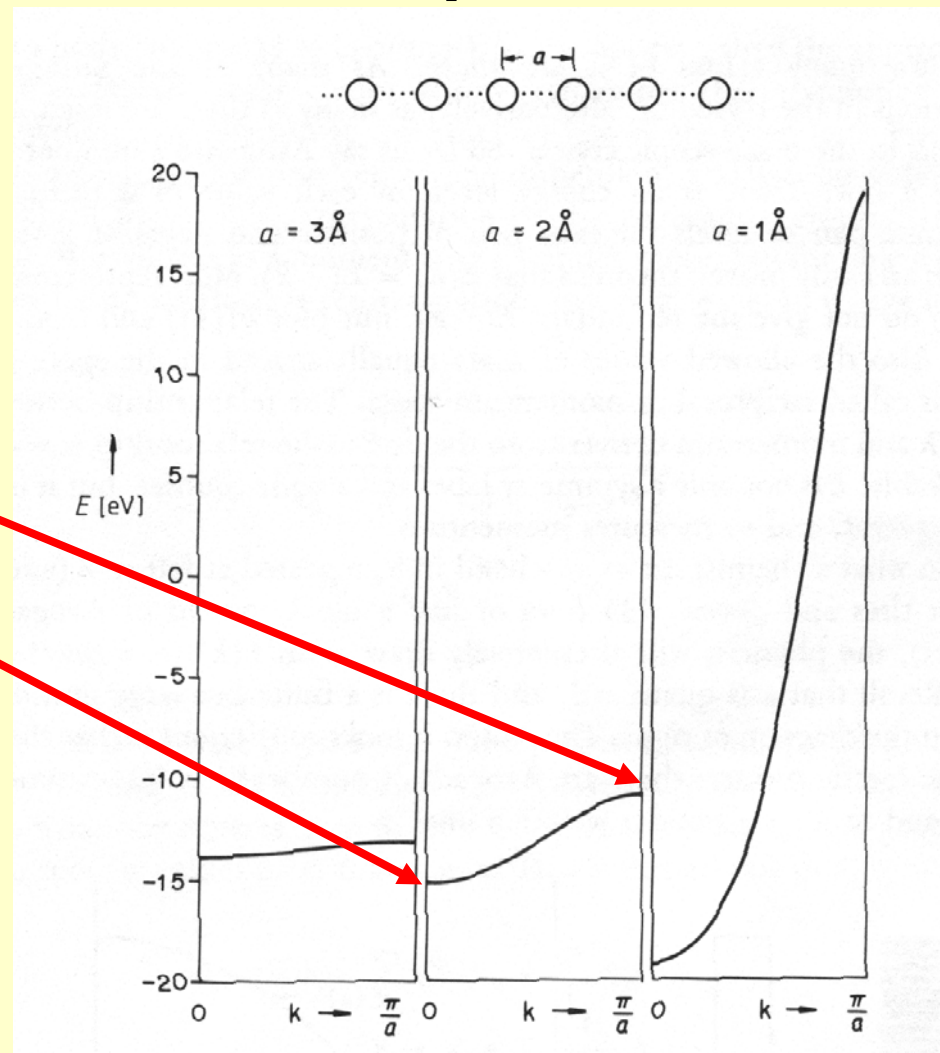
Wide bands = Large intermolecular overlap = delocalized e⁻

Narrow bands = Weak intermolecular overlap = localized e⁻

Bandwidth or Band Dispersion

Bandwidth = energy difference between the highest and lowest level

Bandwidth **increases** with better orbital overlap = shorter interatomic distance



Bands

Different types of orbitals (symmetry)
form separate bands
s, p, d bands

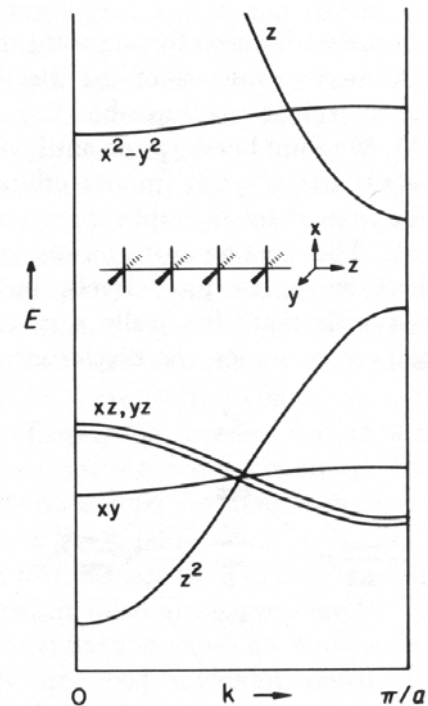
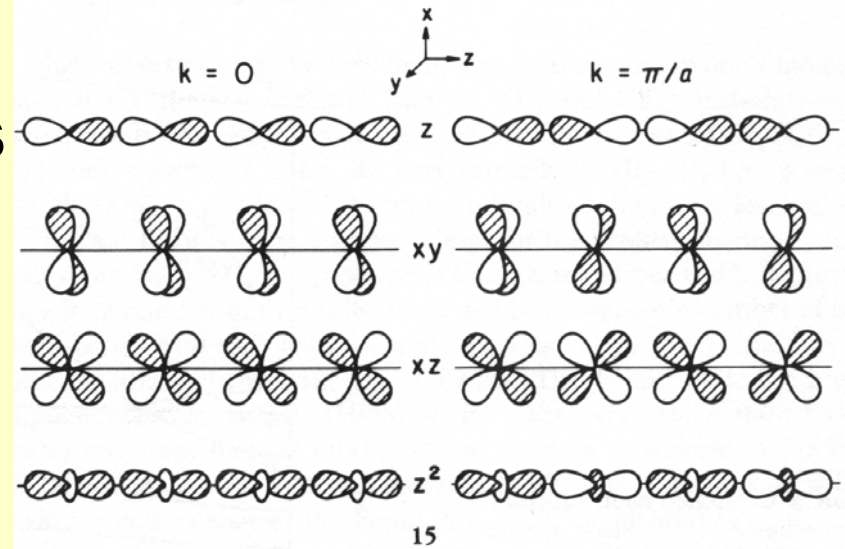
Sigma, pi, delta

Distinct bands with a band gap

Overlapping bands

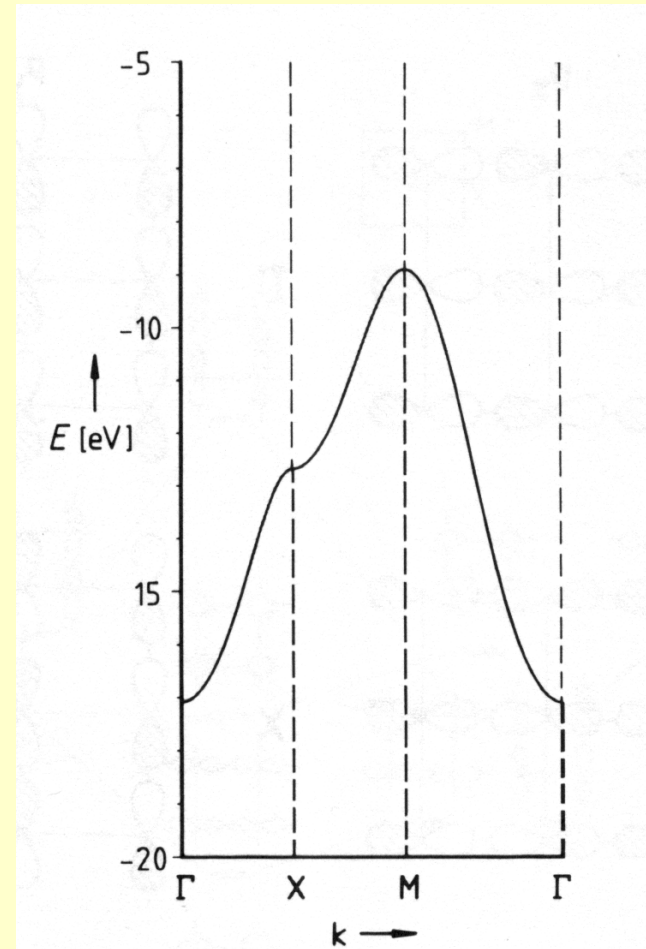
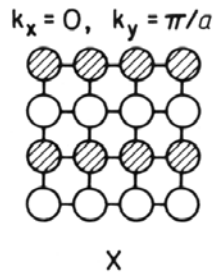
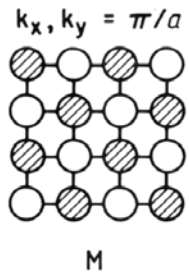
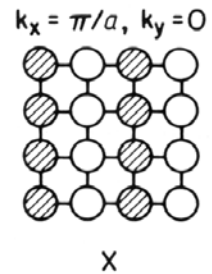
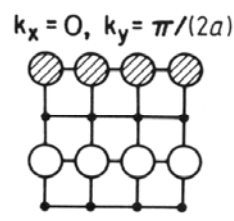
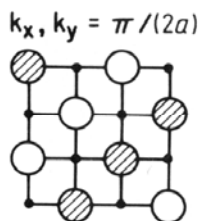
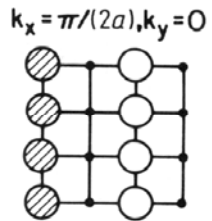
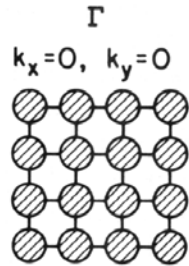
Depends on the separation of the
orbitals and strength of the interaction
between the atoms

Strong interaction = **wide** bands and a
greater overlap



Two Dimensional Lattice

**Band structure
of a square lattice
of H atoms
($d_{HH} = 2.0 \text{ \AA}$)**



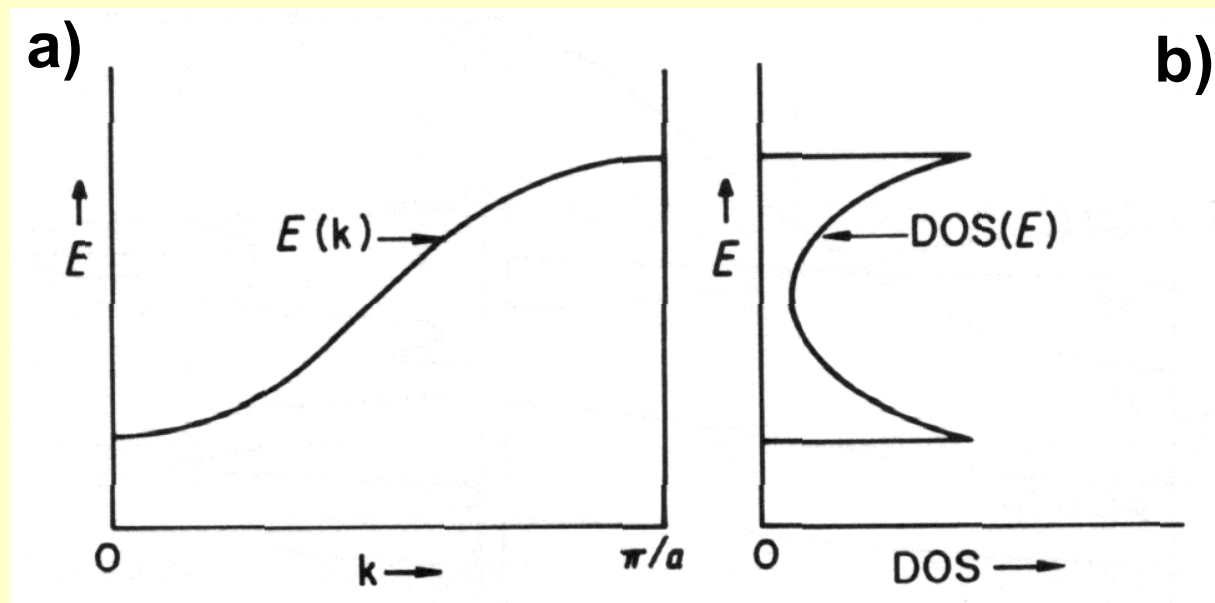
Density of States -DOS

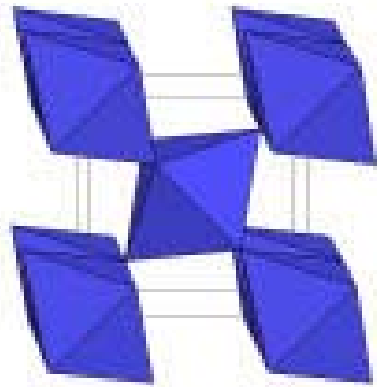
a) MO diagram with translational symmetry

b) Density of states (DOS, $N(E) dE$)

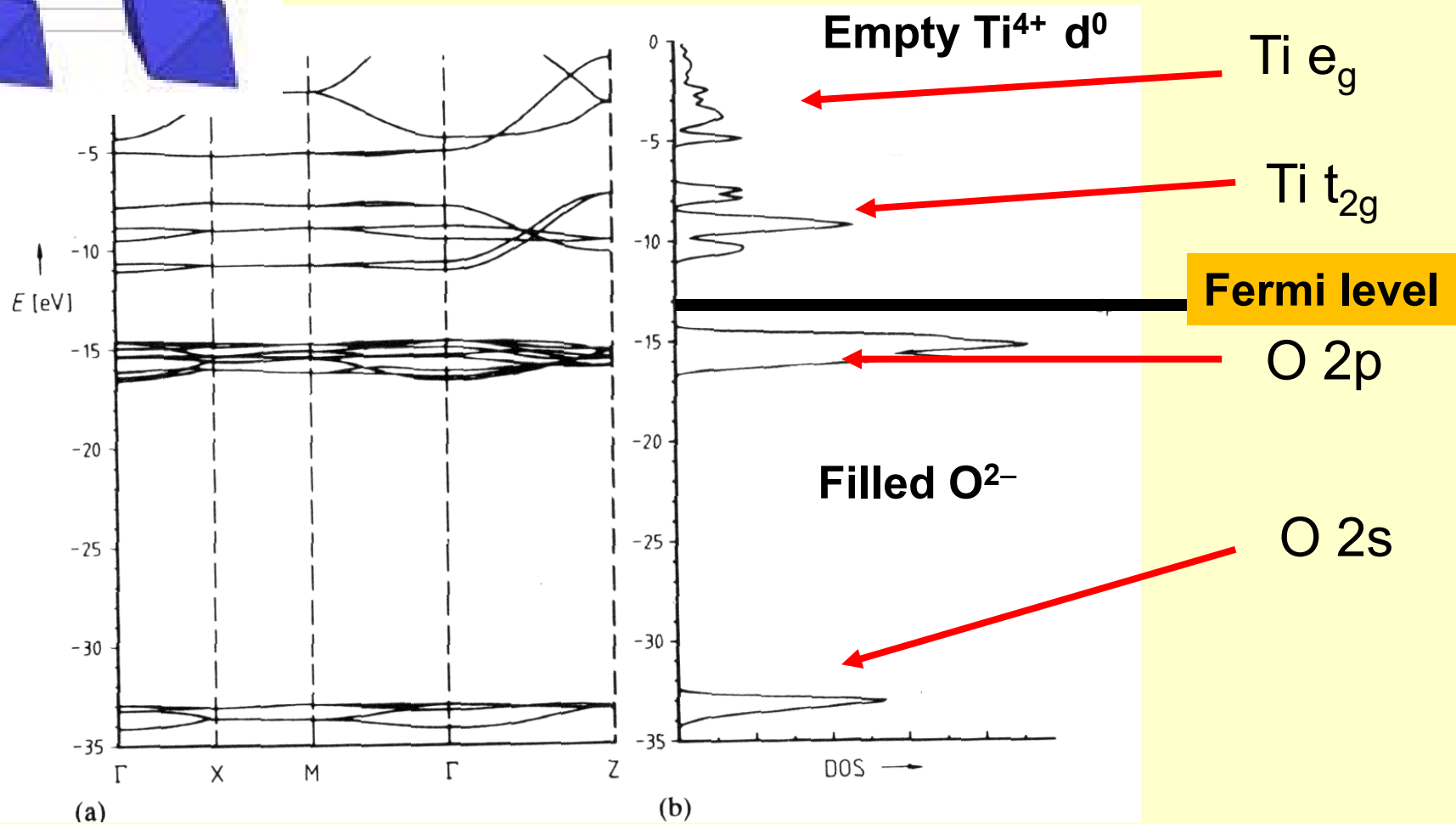
Number of levels available for electrons at different energies per unit volume of the solid

DOS is zero in the band gap





Rutile TiO₂ Band Structure



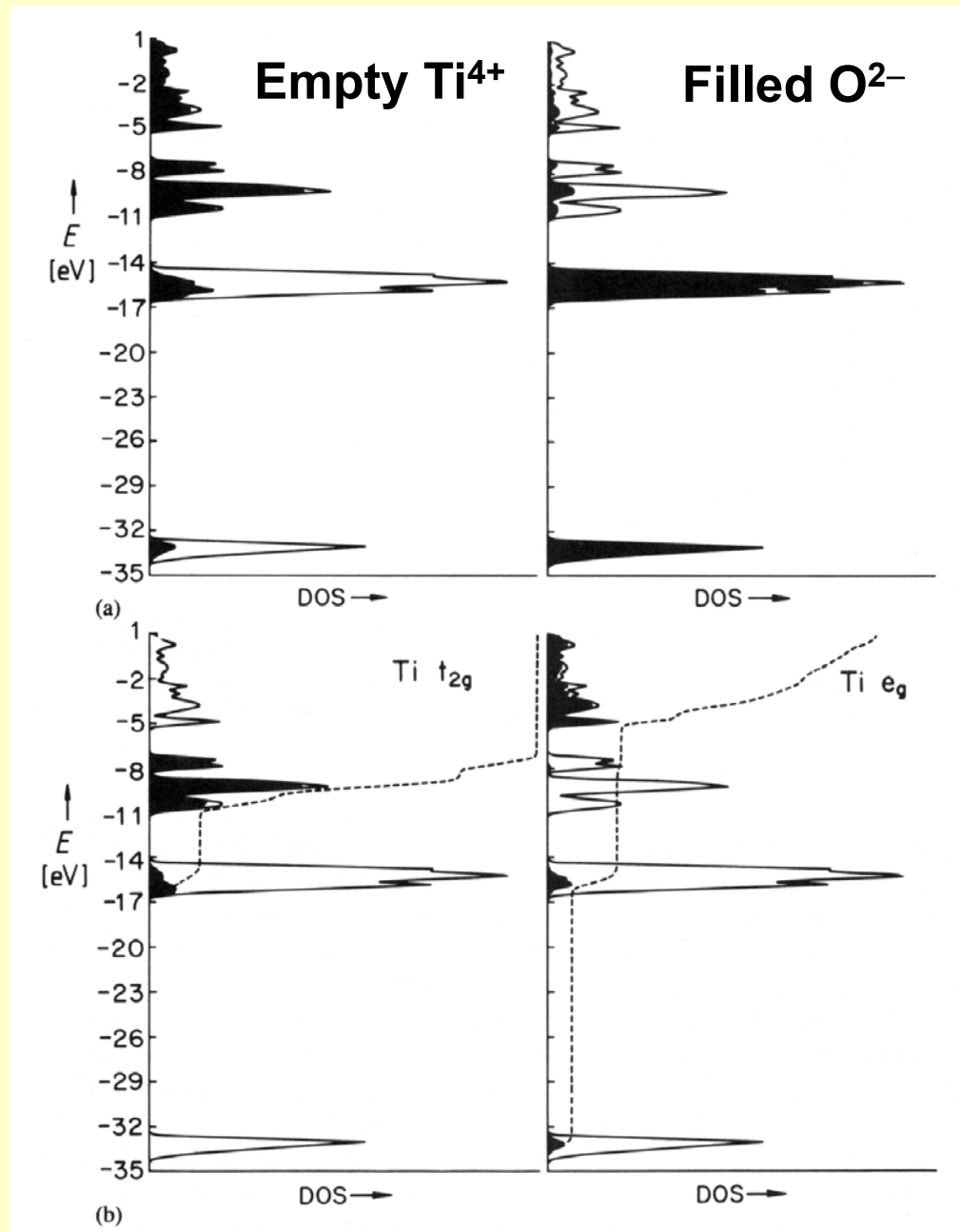
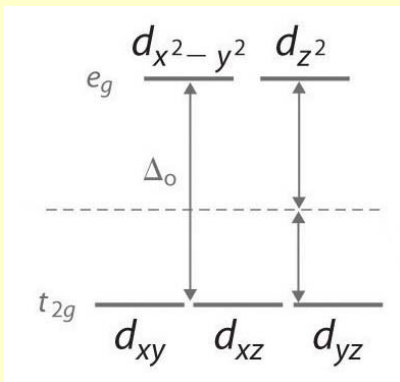
Band structure – spaghetti (a) and DOS (b)

Rutile TiO₂ Band Structure

Contributions to the total DOS of rutile

(a) Ti and O

(b) Ti d-orbitals, t_{2g} and e_g



Classification of Solids

Molecular solids – N_2 , C_6H_6 , I_2 , ...

Van der Waals forces, little change from the gas phase, electronic bands correspond to empty and filled MOs of the individual molecules

Ionic solids – NaCl , CaF_2 , NiO , ...

Charge transfer from cations to anions, energy bands made up from the atomic orbitals of cations and anions

NaCl : 3p of Cl is the top filled band, 3s of Na is the lowest empty band

Covalent solids – diamond, Si,

Overlap of orbitals and electron sharing between adjacent atoms, filled bands are made up from bonding MOs, empty bands are made up from antibonding MOs

Metallic solids – Cu, Mg, W, TiO,

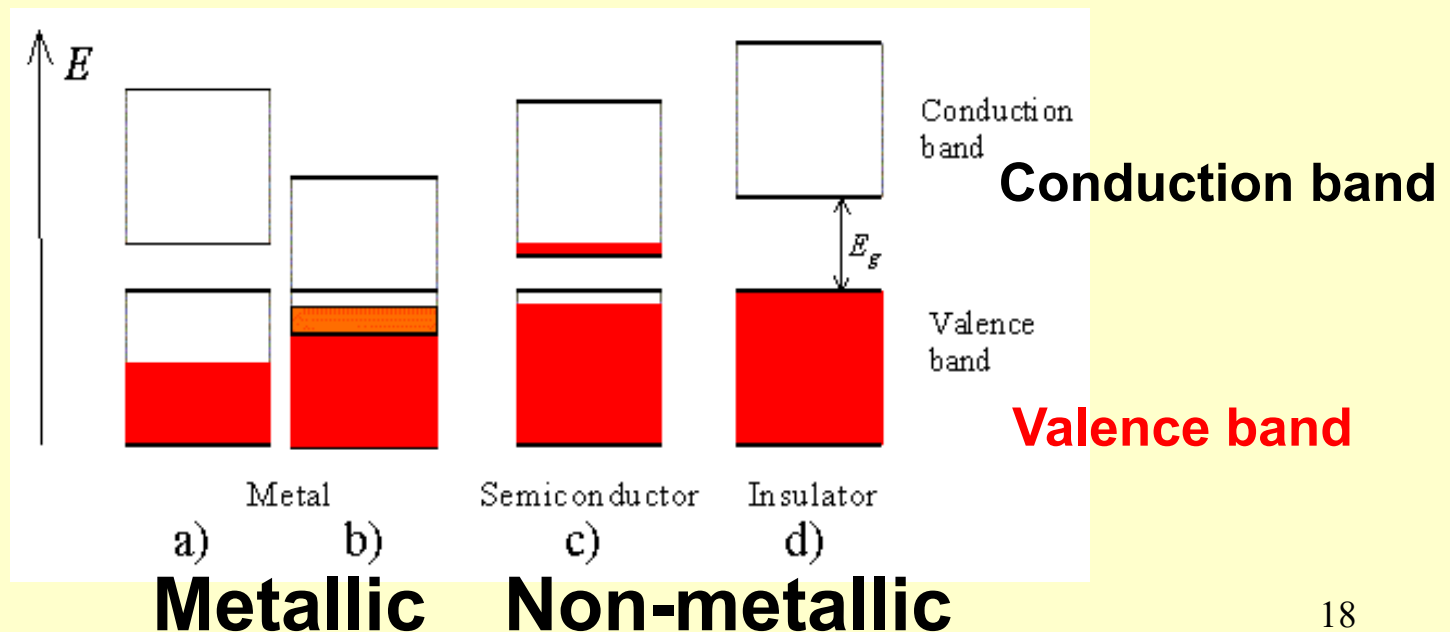
Na - very strong overlap of atomic orbitals on adjacent atoms, arising bands are very broad, 3s, 3p, and 3d merge into a single wide band, electrons move freely, little attraction to the atomic cores

Metallic and Non-metallic Solids

The distinction between metallic and non-metallic solids - the orbitals filling

Metallic behavior – a partially filled band, no gap between the top filled level (Fermi level) and the lowest empty one

Non-metallic behavior – a completely filled level (the valence band) and an empty one (the conduction band) separated by a band gap



Ionic Solids

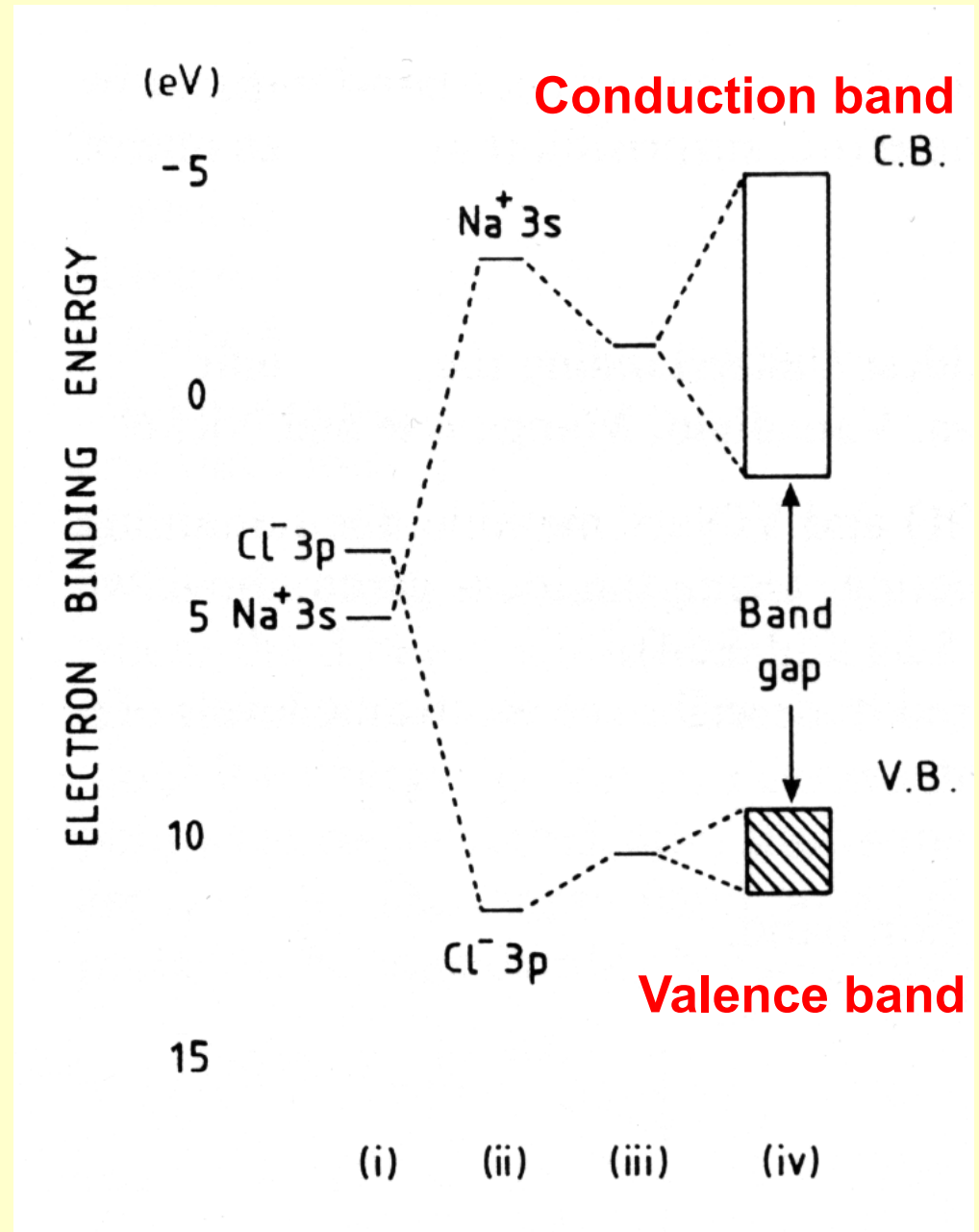
Example NaCl, $E_g = 9 \text{ eV}$

i = ions in the gas phase

ii = ions in the lattice,
Madelung potential,
filled levels stabilized by
positive potential of cations,
empty levels destabilized

iii = polarization energy

iv = electronic bands



Fermi Level

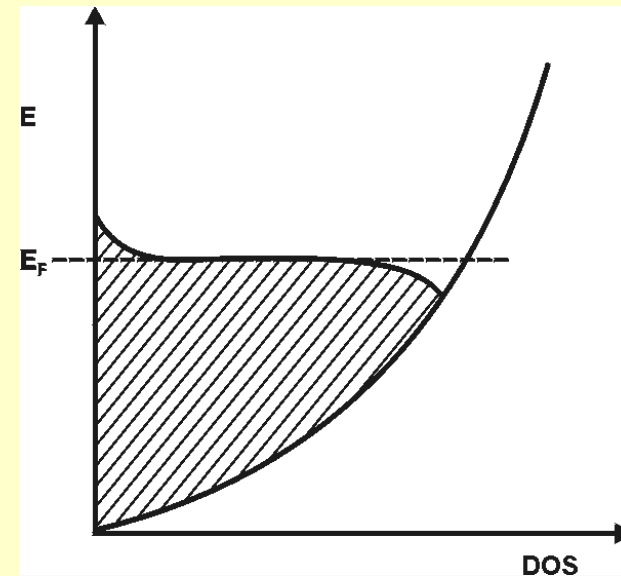
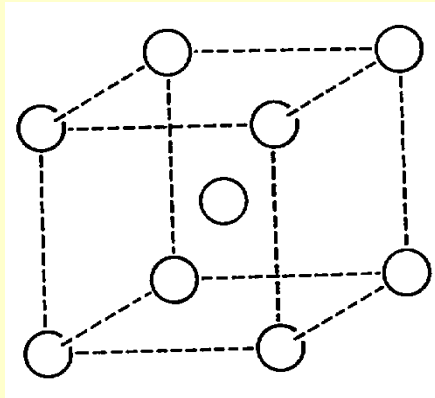
E_F = the thermodynamic chemical potential for electrons in the solid

Metals – boundary between filled and unfilled levels

Nonmetals – situated in the band gap

The Fermi-Dirac distribution function:

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



The Fermi level cuts a band in a metal

Fermi Level

E_F occupation probability $\frac{1}{2}$

Levels at $T = 0$ K

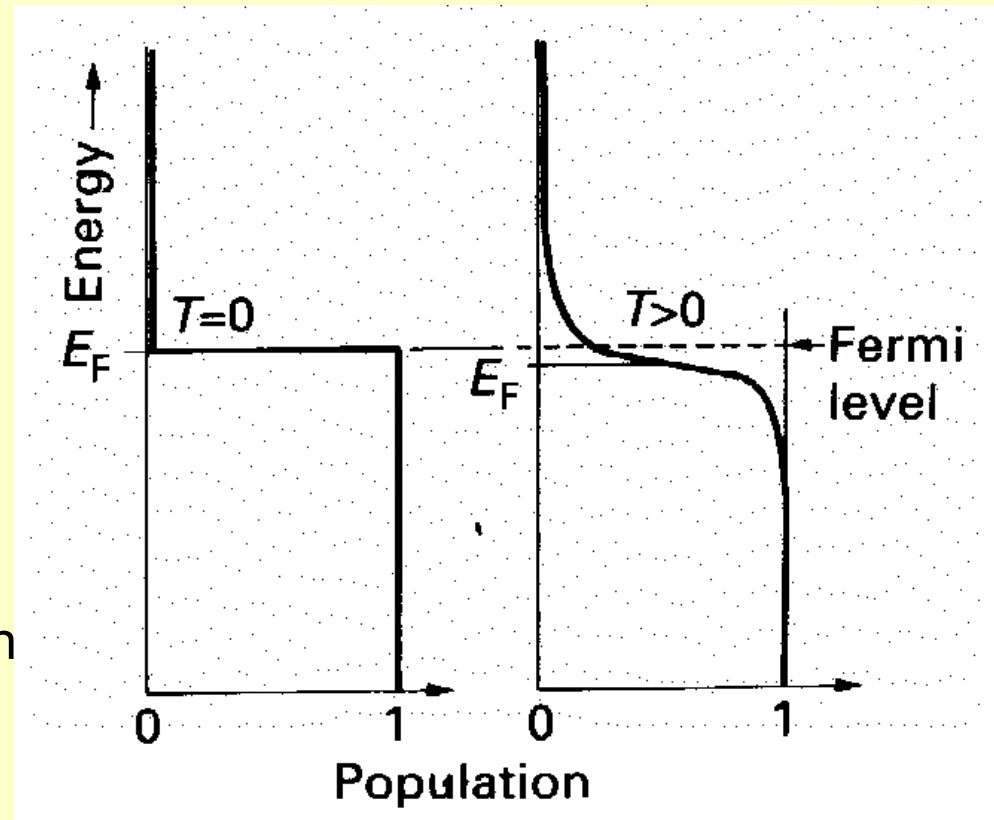
$E < E_F$ occupied - probability = 1

$E > E_F$ empty - probability = 0

$E = E_F$ probability = $\frac{1}{2}$

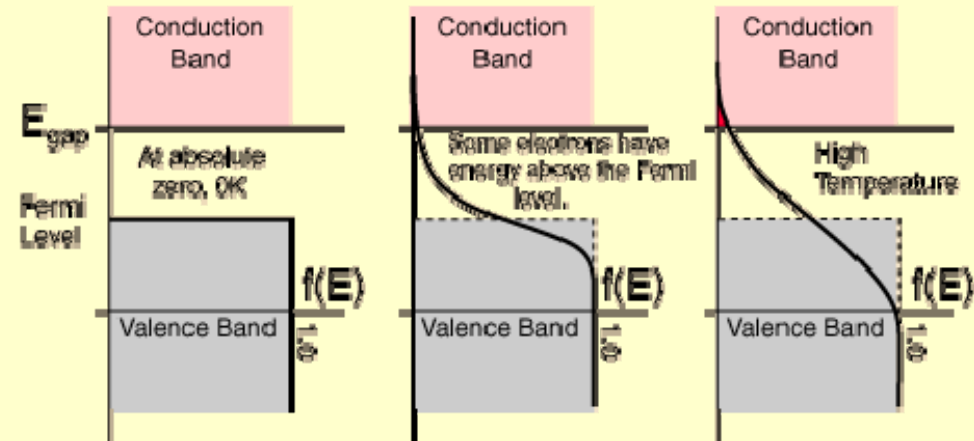
The Fermi-Dirac distribution function

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



Fermi Level and Conduction

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



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.

In the **filled band** every electron is matched by another
- no overall net motion of electric charge

For conduction to occur electrons have to be excited up to the conduction band by overcoming an activation energy and hence, the conduction of these compounds increases with temperature

Semiconductors and Insulators

Band gap = the minimum photon energy required to excite an electron up to the conduction band from the valence band
The band gap size determines a semiconductor or an insulator

Insulators - a completely filled valence band separated from the next empty energy band by a large, forbidden gap

Diamond = insulator, a very large band gap of ~ 6 eV
very few electrons have sufficient energy to be promoted and the conductivity is negligibly small

Conductivity of nonmetallic solids increases with temperature

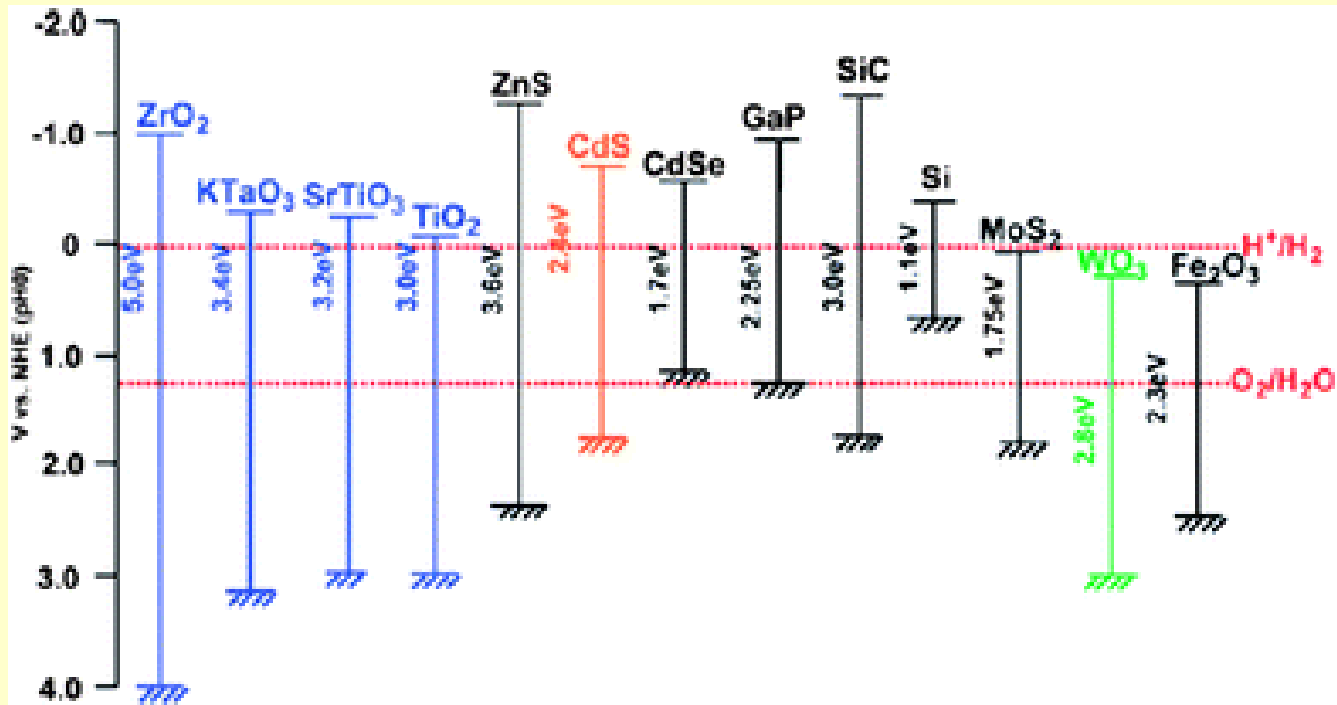
Band Gap Energies, kJ mol⁻¹

NaCl	840
Diamond	480
ZnO	315
CdO	210
B	170
Si	125
Ge	85
Te, InAs	40
PbTe, InSb	20
α -Sn (grey)	8
Mg, Al, Cu, β -Sn (white).....	0

$$1 \text{ eV} = 1.60210 \times 10^{-19} \text{ J}$$

$$1 \text{ eV (molecule)}^{-1} = 1 \text{ eV} \times N_A = 96 \text{ 485 J mol}^{-1}$$

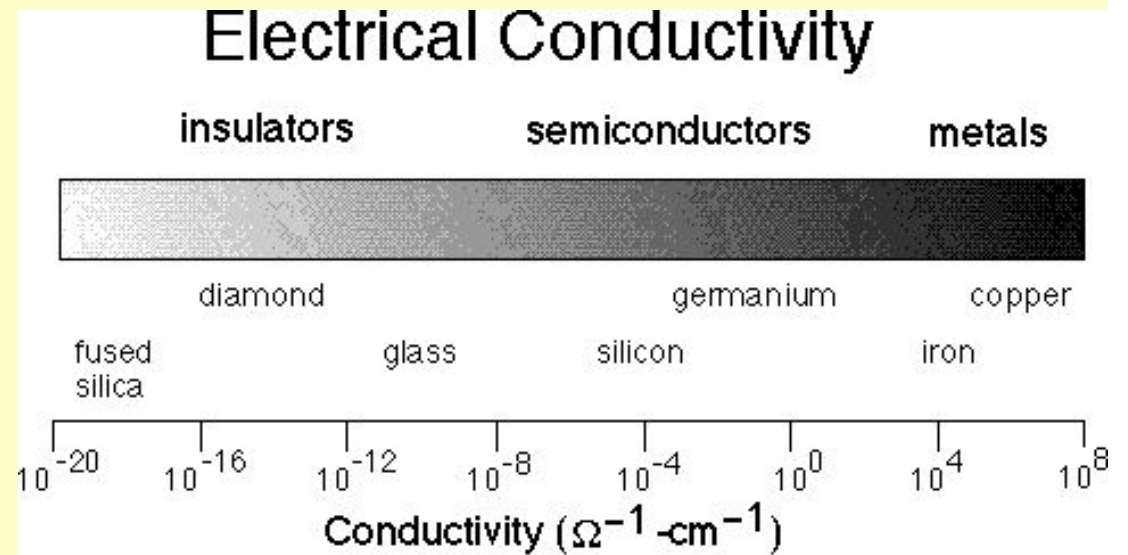
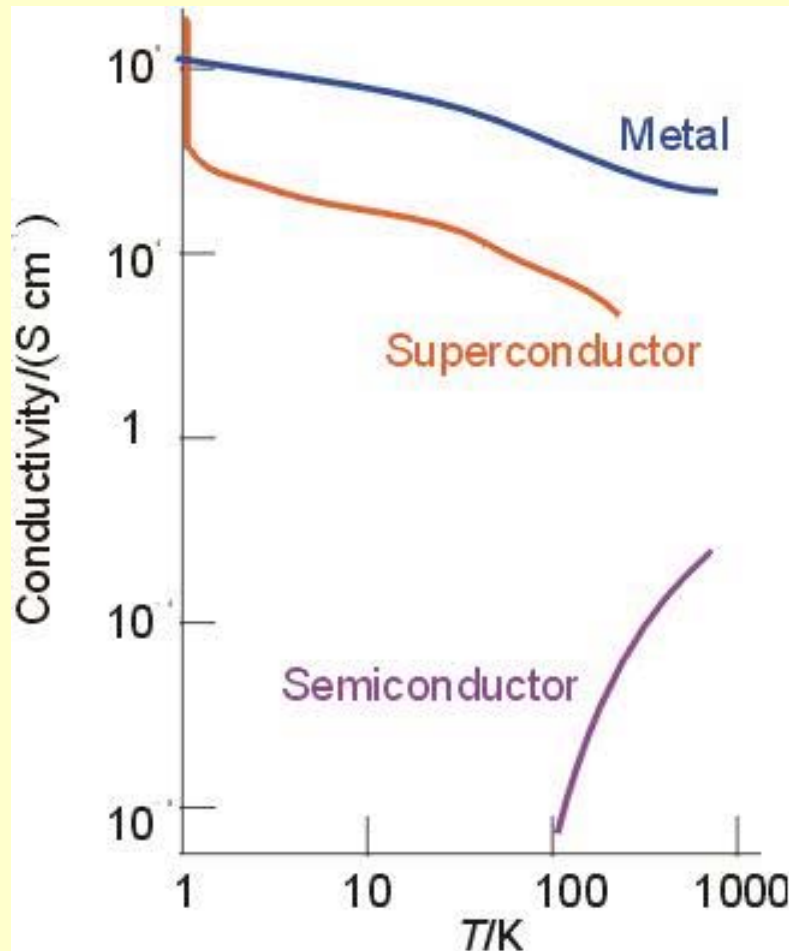
Band Gap Energies



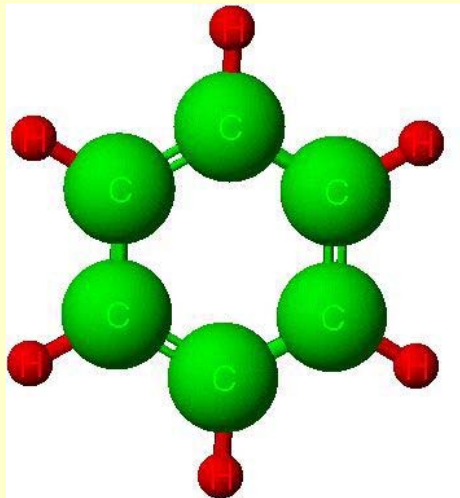
$$1 \text{ eV} = 1.60210 \times 10^{-19} \text{ J}$$

$$1 \text{ eV (molecule)}^{-1} = 1 \text{ eV} \times N_A = 96\,485 \text{ J mol}^{-1}$$

Electrical Conductivity

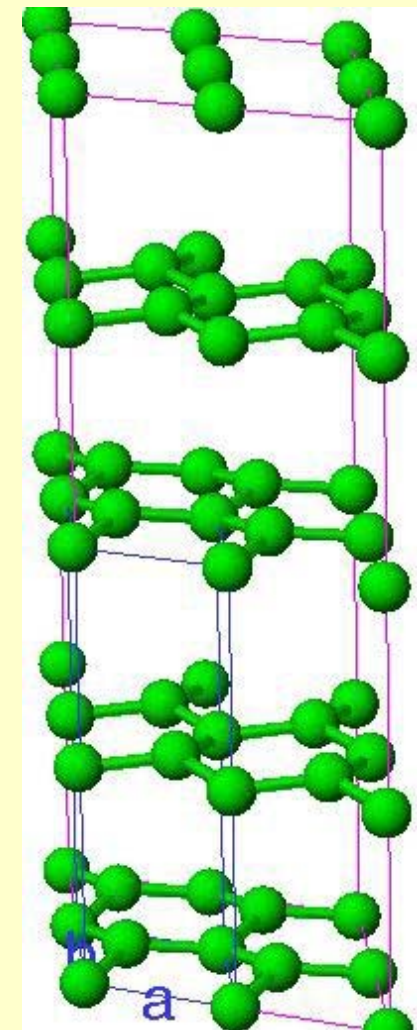
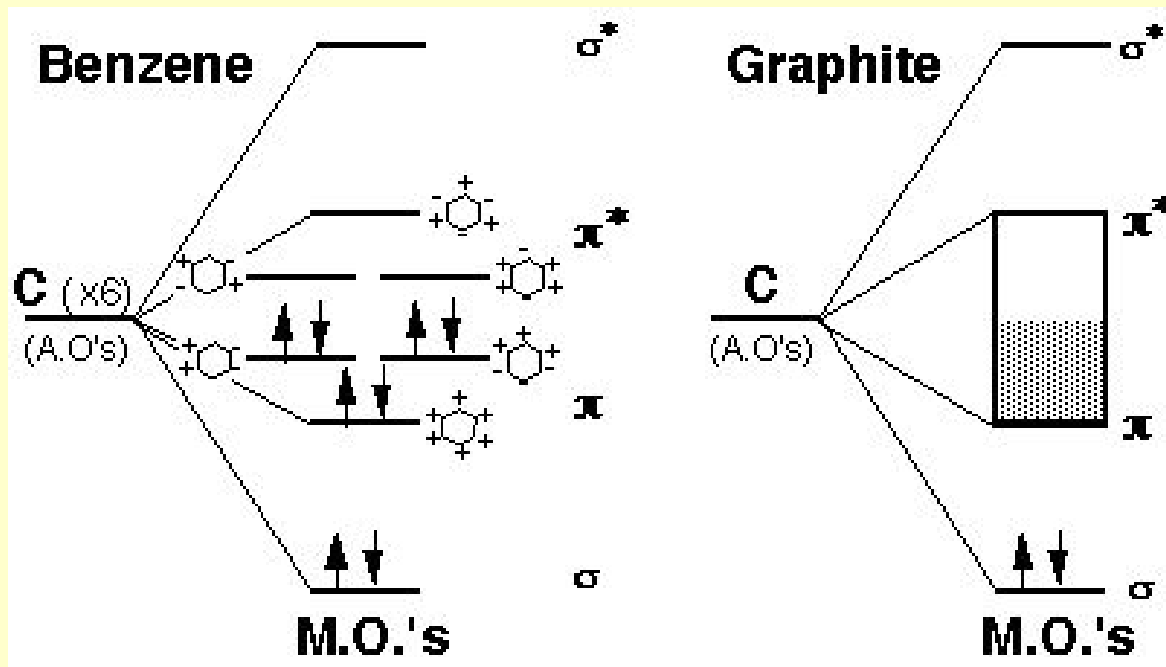


Conductivity of insulators and semiconductors increases with temperature

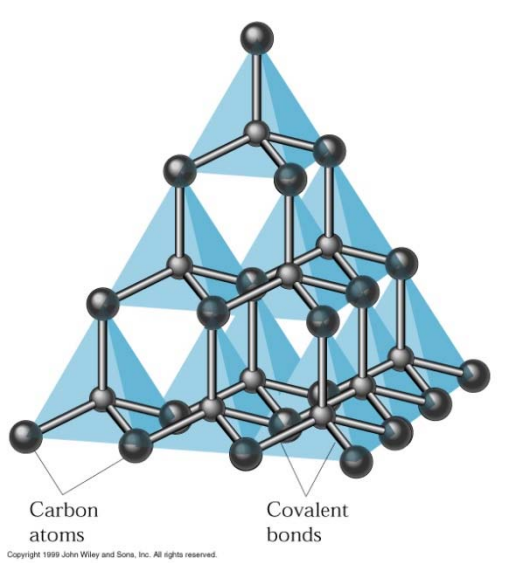
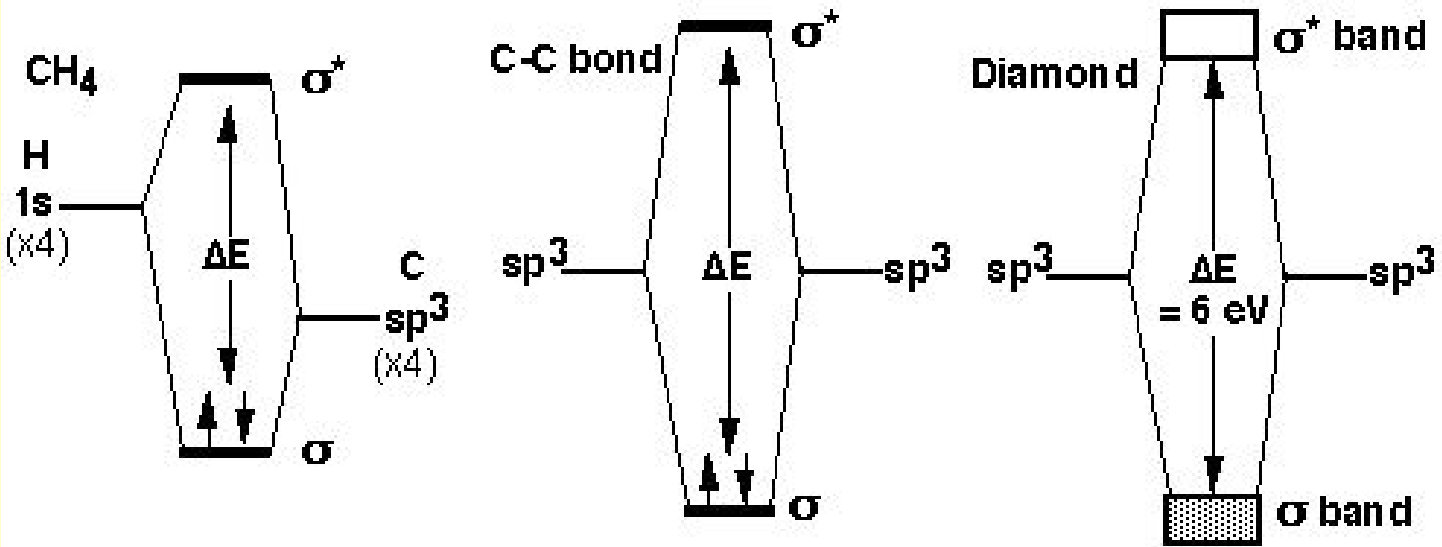


Bands in Graphite

Graphite is a conductor



Bands in Diamond



Semiconductors

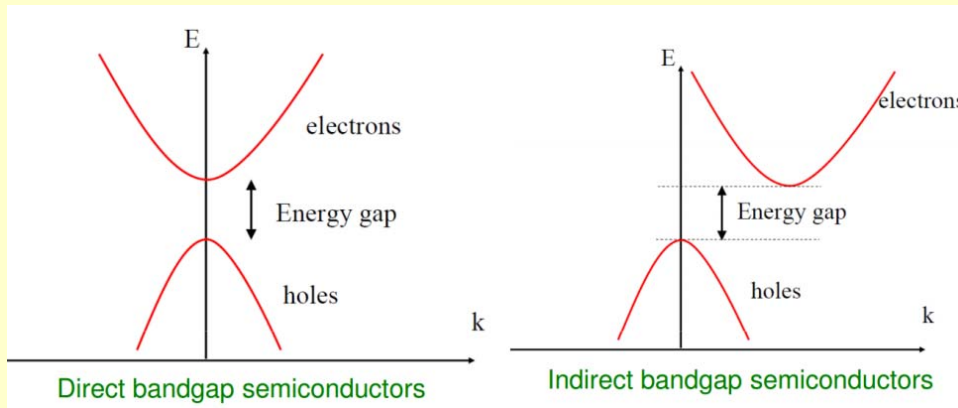
Semiconductors - a similar band structure to insulators but the band gap is small, some electrons have sufficient thermal energy to be promoted up to the empty **conduction** band

Two types of conduction mechanism in semiconductors:

- **Electrons** promoted into the conduction band = **negative charge carriers**, move towards a positive electrode under an applied potential

- **The holes** these electrons leave behind = **positive holes**
Holes move when an electron enters them - a new positive hole is created, the positive holes move in an opposite direction to the electrons

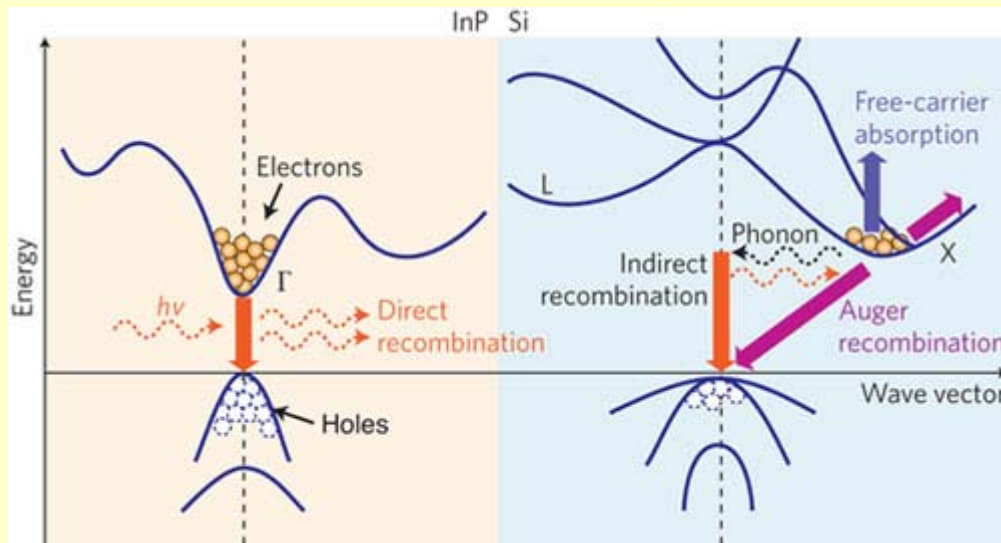
Semiconductors



A direct band gap

(InP, InAs, GaAs)

the band edges aligned in k , so that an electron can transit from the valence band to the conduction band, with the emission of a photon, without changing considerably the momentum



An indirect band gap

(Si, Ge, AlSb)

the band edges are not aligned so the electron does not transit directly to the conduction band, in this process both a photon and a phonon are involved

Semiconductors

INTRINSIC

Intrinsic semiconductors are **pure materials** with the band structure, the number of electrons in the conduction band is determined only by the size of the band gap and the temperature (more electrons with small band gap and high temperature)

EXTRINSIC

Extrinsic semiconductors are materials where the conductivity is controlled by adding **dopants** with different numbers of valence electrons to that of the original material

Semiconductors

Two fundamental differences between extrinsic and intrinsic semiconductors:

1) At standard temperatures **extrinsic** semiconductors tend to have significantly **greater conductivities** than comparable **intrinsic** ones

2) The **conductivity** of an **extrinsic** semiconductor can easily and accurately be **controlled** by controlling the amount of dopant

Materials can be manufactured to exact specifications of conductivity

Extrinsic Semiconductors

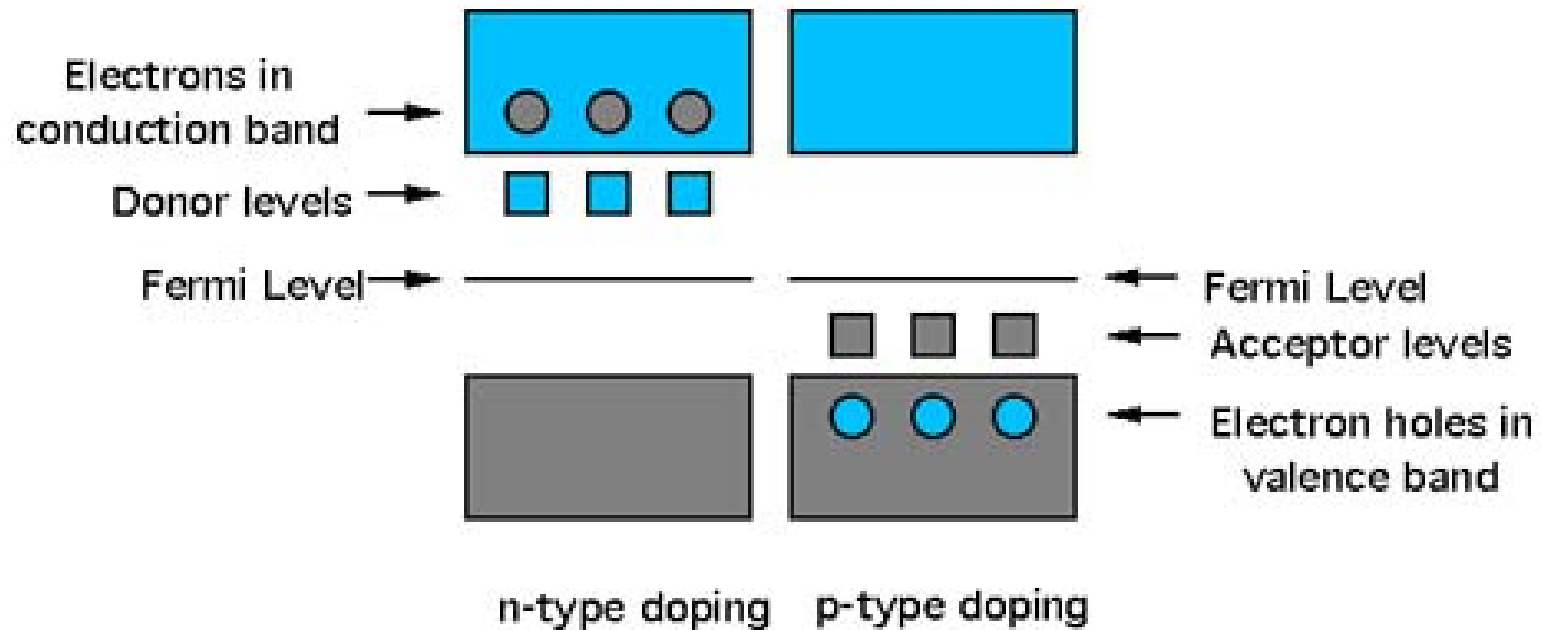
Doping of semiconductors - introducing atoms with **more or less electrons** than the parent element

Doping is substitutional, the dopant atoms directly replace the original atoms

Very low levels of dopant are required, only 1 atom in 10^9 of the parent atoms

Extrinsic Semiconductors

Semiconductors: n- and p-Type



Extrinsic Semiconductors n-type

Silicon - phosphorous atoms introduce extra electrons (one extra valence electron for each dopant atom introduced as P)

The dopant atoms form a set of energy levels that lie in the band gap between the valence and conduction bands, but close to the conduction band

The electrons in the dopant levels cannot move directly - there is not enough of them to form a continuous band

The levels act as **donor levels** because the electrons have enough thermal energy to get up into the conduction band where they can move freely

n-type semiconductors = the negative charge carriers or electrons

Extrinsic Semiconductors p-type

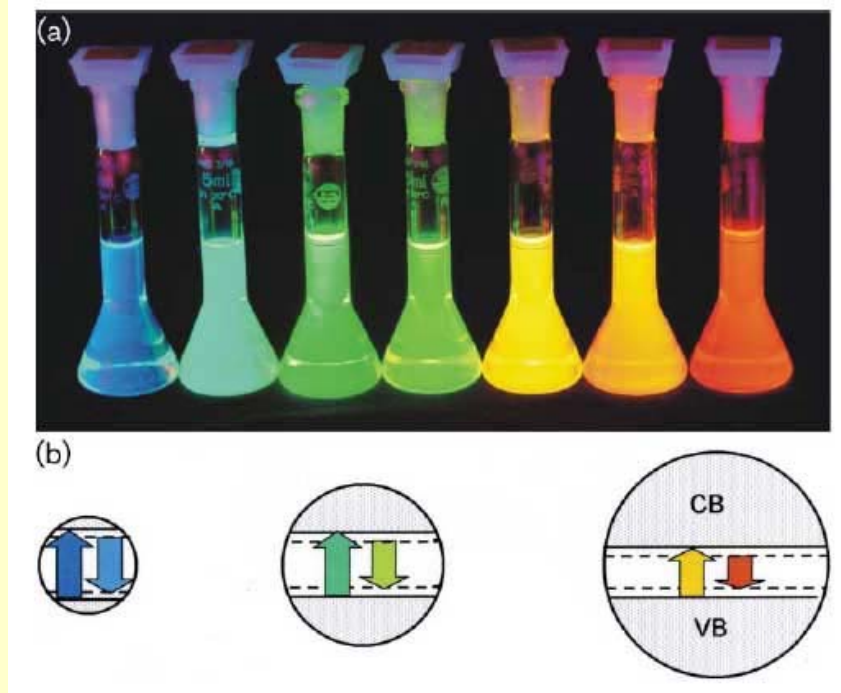
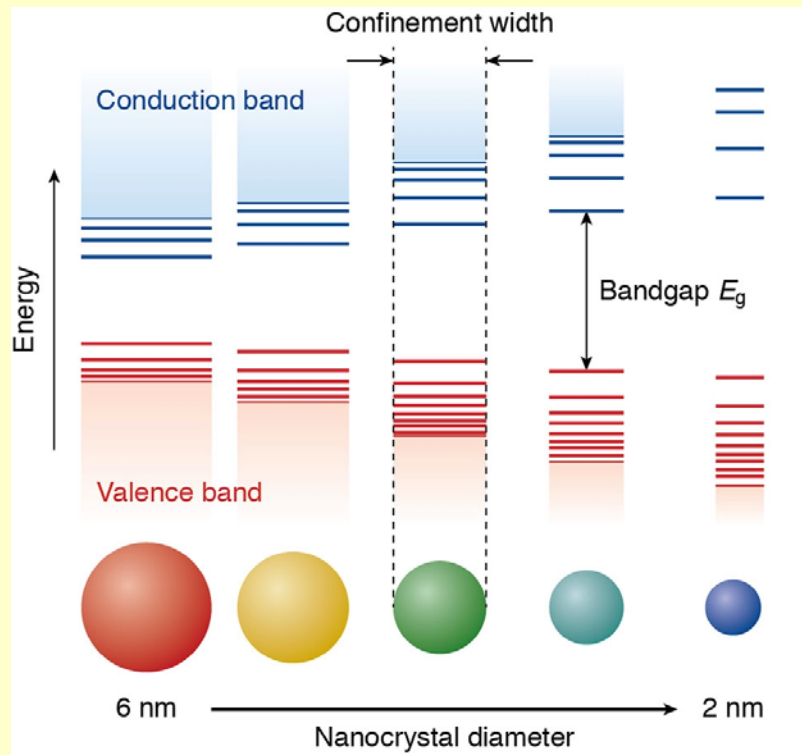
Silicon doping with an element with one less valence electron, such as Ga, for every dopant atom - an electron missing

Ga forms a narrow, empty band consisting of **acceptor levels** which lie just above the valence band, discrete levels if the concentration of gallium atoms is small

Electrons from the valence band have enough thermal energy to be promoted into the acceptor levels, electrons in the acceptor levels cannot contribute to the conductivity of the material

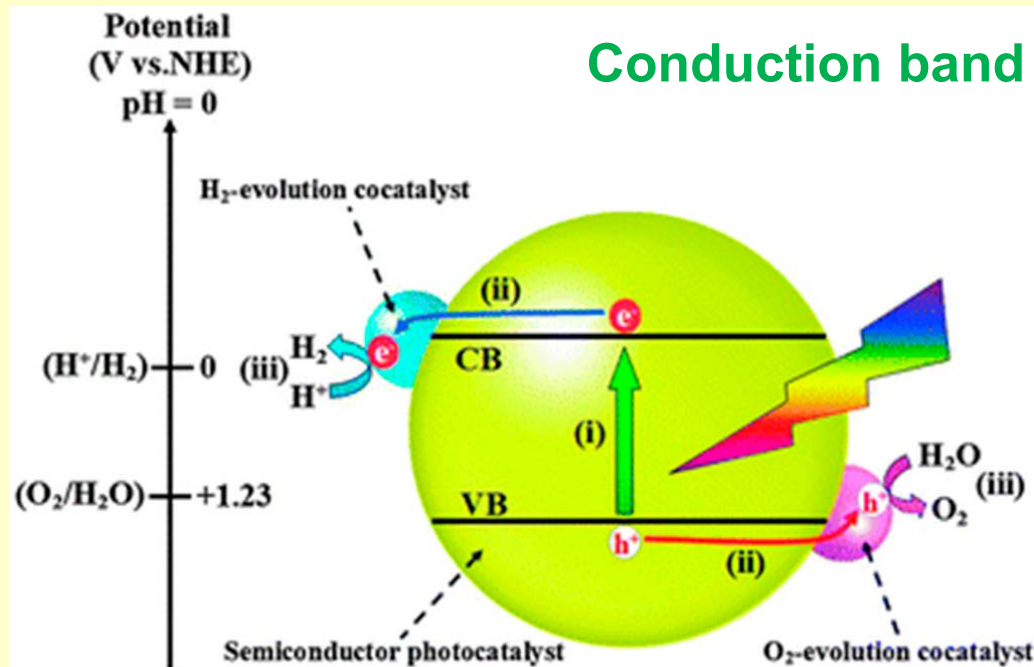
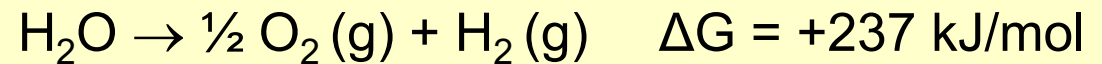
The positive holes in the valence band left behind by the promoted electrons are able to move - **p-type semiconductors**, the positive holes

Electronic Bands in Nanoparticles



Photocatalysis

1972 Fujishima and Honda Photochemical splitting of water



- A photon-driven reaction
- TiO_2 adsorbs photons with an energy higher than or equal to its bandgap (E_g)
- Electrons in the filled VB are excited to the vacant CB, leaving holes in the VB
- The generation of the electron-hole pair
- Electron-hole pair separation
- The separated electrons or holes migrate to the surface
- Redox reactions at the surface

TiO_2 band gaps: 3.0 eV Rutile
3.15 eV Anatase