# ELEMENTARY BAND THEORY

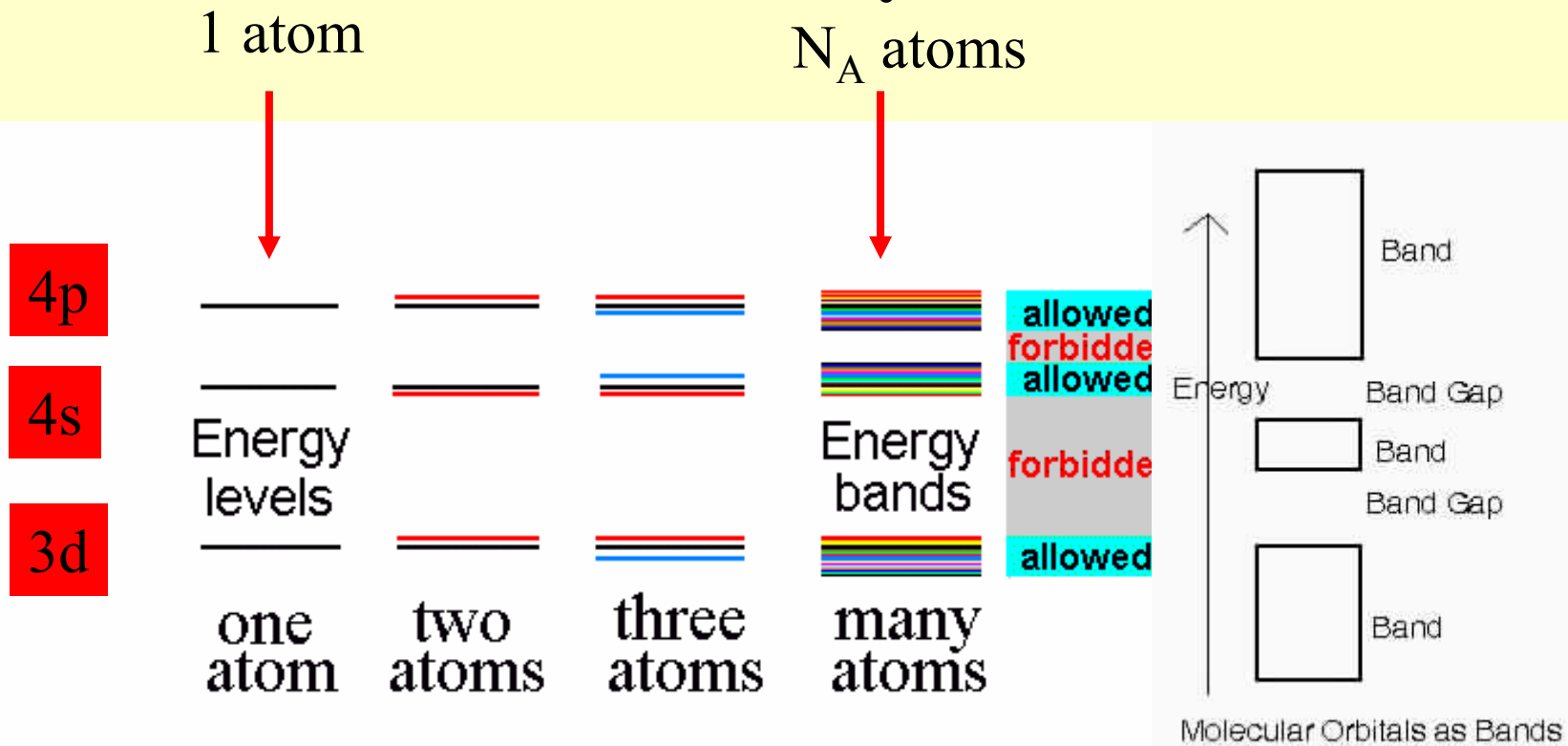| PHYSICIST | CHEMIST |
|---|---|
| Solid state band | Molecular orbital |
| Valence band, VB | HOMO |
| Conduction band, CB | LUMO |
| Fermi energy, $E_F$ | Chemical potential |
| Bloch orbital, delocalized | Molecular orbital, localized |
| n-doping | Reduction, pH scale base |
| p-doping | Oxidation, pH scale acid |
| Band gap, $E_g$ | HOMO-LUMO gap |
| Direct band gap | Dipole allowed |
| Indirect band gap | Dipole forbidden |
| Phonon or lattice vibration | Vibrational mode |
| Peierls distotion | 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)
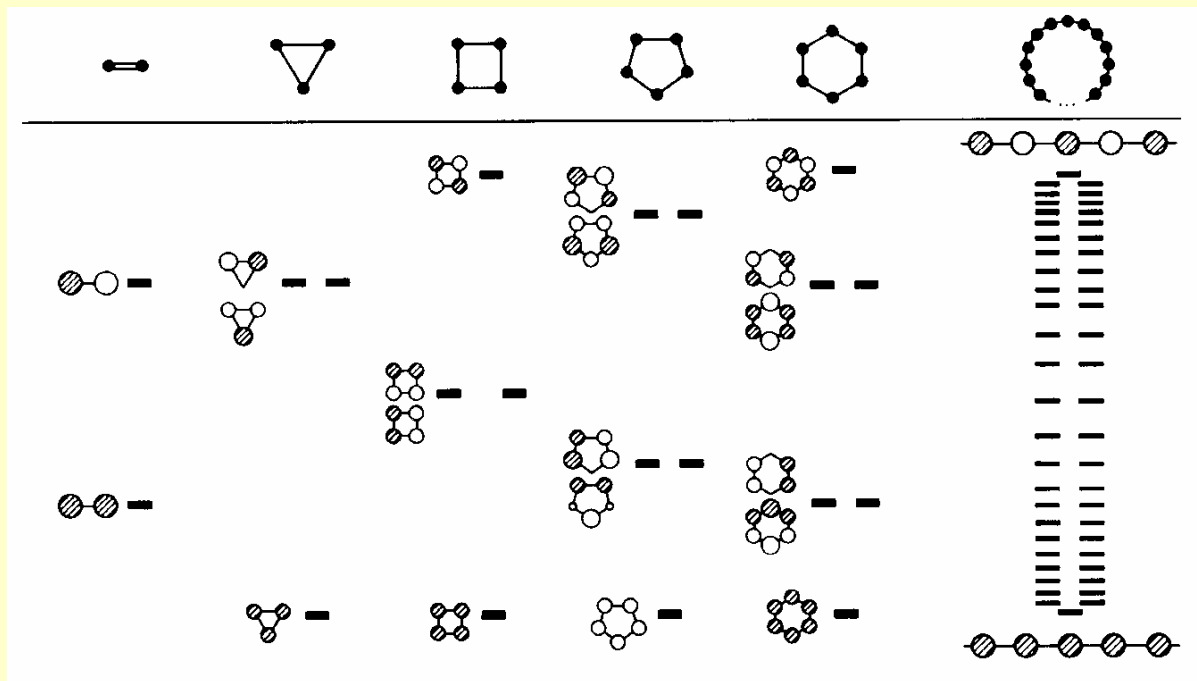
# Band Theory



1 atom          $N_A$ atoms

4p

4s

3d

Energy levels — one atom, two atoms, three atoms, many atoms — Energy bands

allowed
forbidden
allowed
forbidden
allowed

Energy — Band, Band Gap, Band, Band Gap, Band

Molecular Orbitals as Bands

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

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**Molecular orbital** ➔➔➔➔➔➔➔➔➔ **Electronic band**

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

**Large rings - cyclic boundary condition**



**A rough rule of thumb: the separation of the energy levels in the dimer corresponds to about half width of the energy band.**

# 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 anti-bonding character

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

# Band Theory

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

$n = 0 \quad 1 \quad 2 \quad 3 \quad 4 \cdots$

$\chi_0 \quad \chi_1 \quad \chi_2 \quad \chi_3 \quad \chi_4$
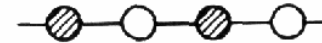
$$\psi_k = \sum_n e^{ikna} \chi_n$$

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

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

**Antibonding**

k = wavevector,
a = lattice constant,
n = orbital counter

Large number of discreet levels
= band

$$k = 0 \quad \psi_0 = \sum_n e^0 \chi_n = \sum_n \chi_n$$

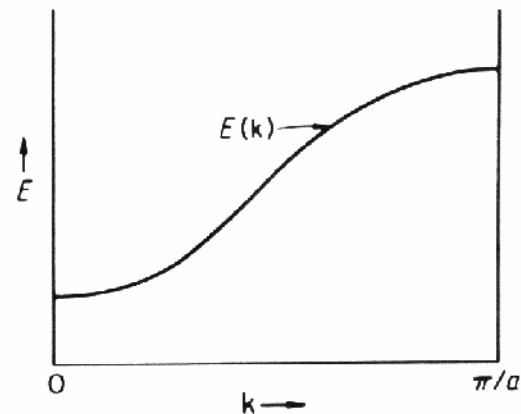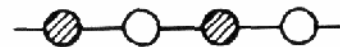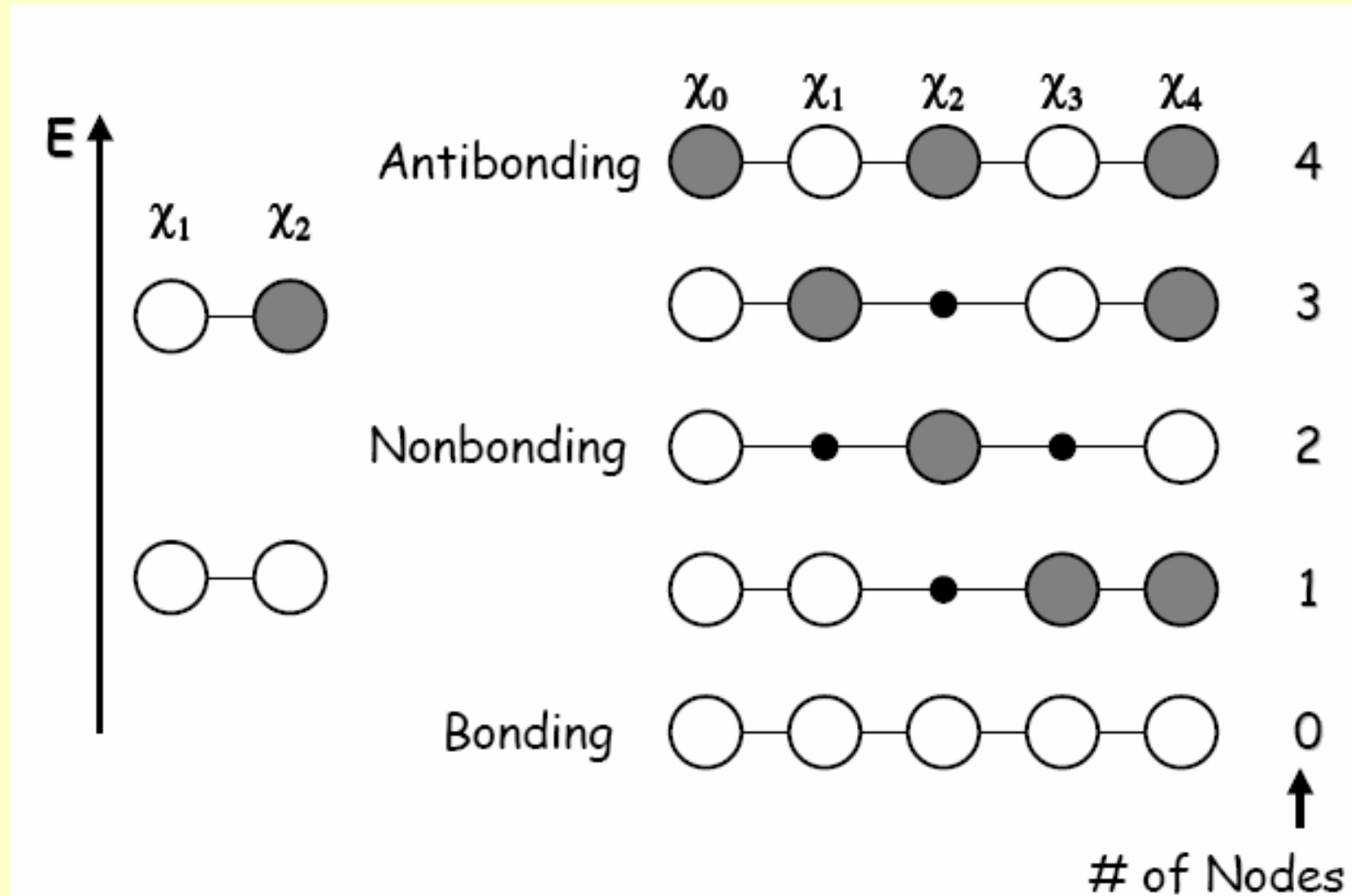$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$$

**Bonding**

# Band Theory

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

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

$$k = 0 \qquad \psi_0 = \sum_n e^0 \; \chi_n = \sum_n \chi_n$$

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

$E(k)$

$E$

$0 \qquad k \longrightarrow \qquad \pi/a$

N    2    3    14    26    44

**Bonding orbitals**

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# Crystal Orbitals in 1D

# Crystal Orbitals in 1D

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

The wavefunction for each electronic state:
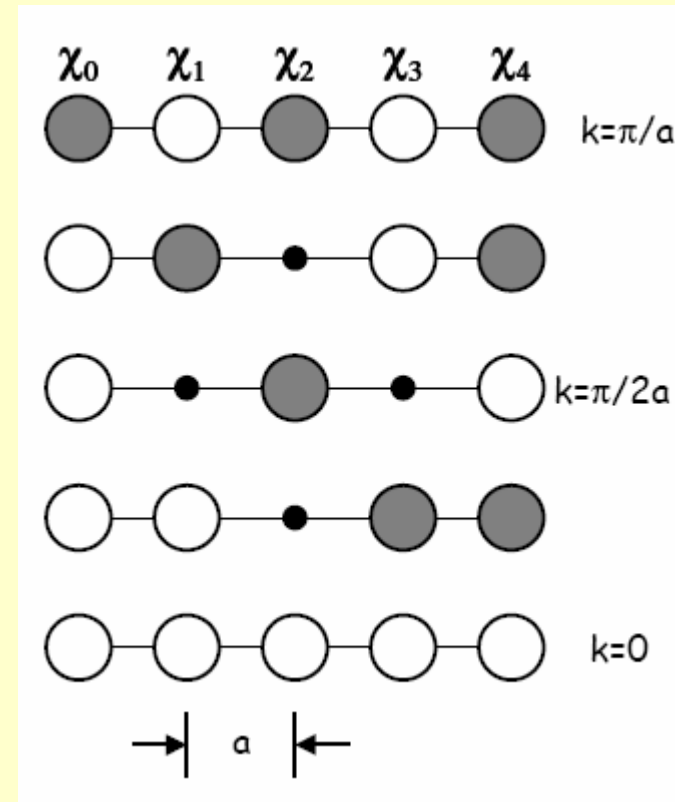
$$\Psi_k = \Sigma \; e^{ikna} \; \chi_n$$

Where:
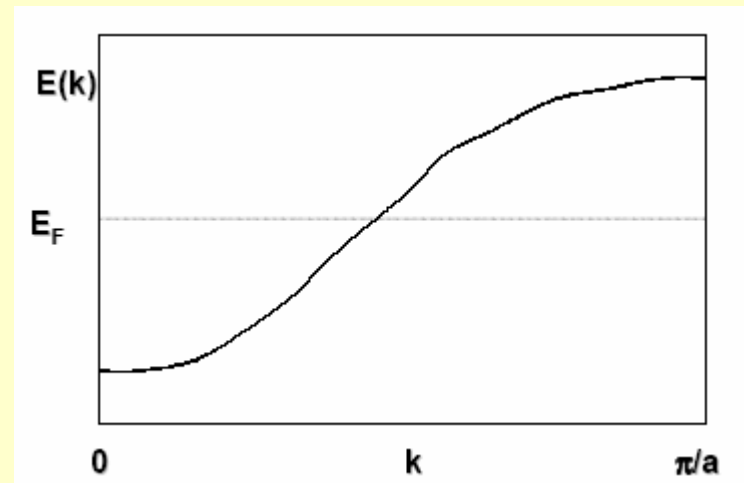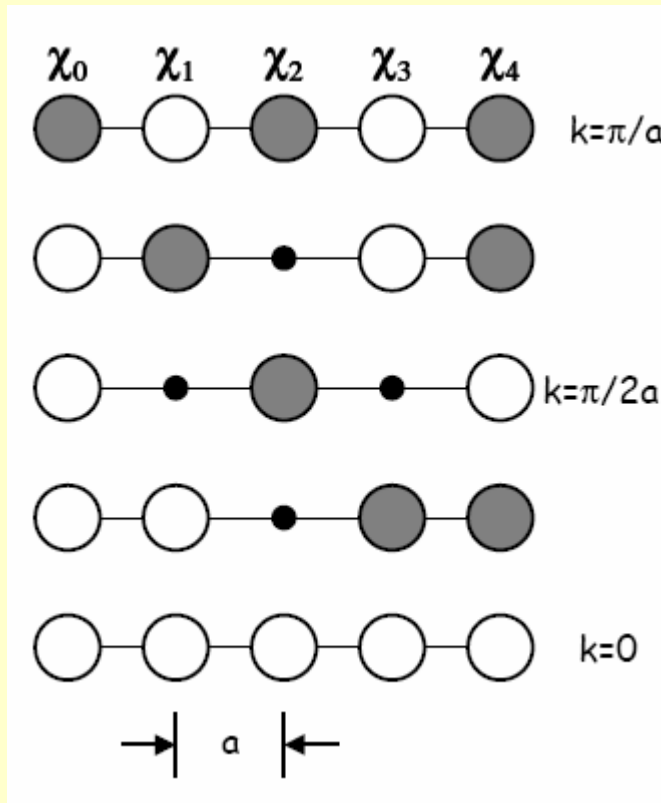**a** is the lattice constant (spacing between atoms)
**n** identifies the individual atoms within the chain
$\chi_n$ represents the atomic orbitals
**k** is a quantum number that identifies the wavefunction and the phase of the orbitals

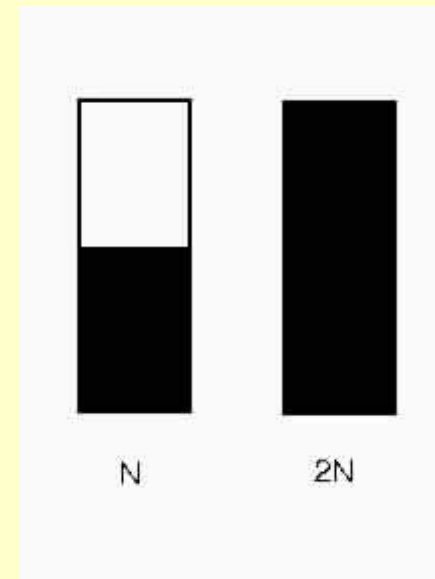# Crystal Orbitals in 1D

# Filling Bands by Electrons

N atoms, 1 electron on each

N levels in a band
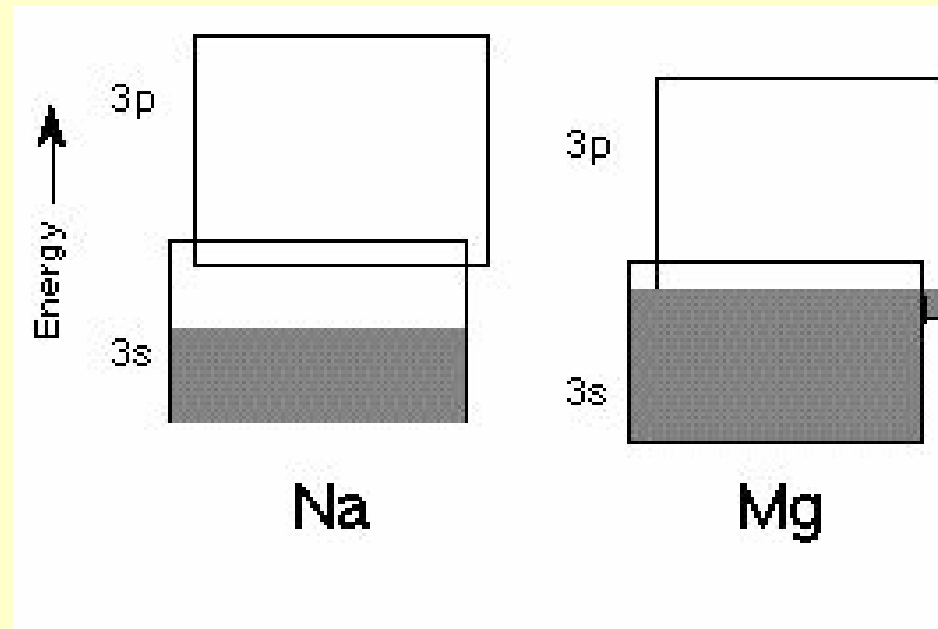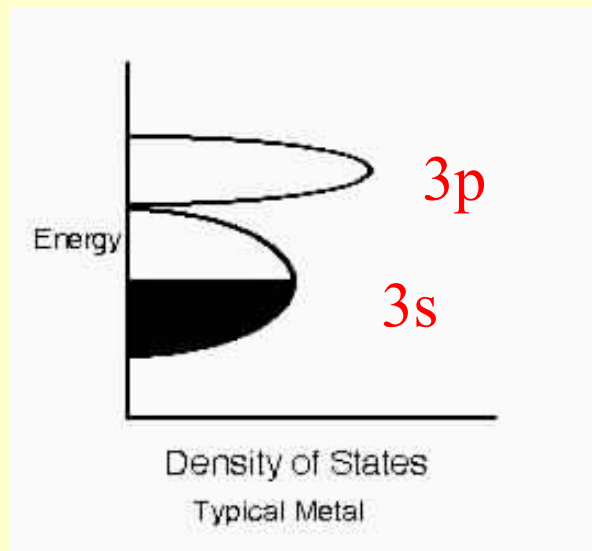
Occupied by pairs of electrons

N/2 levels filled
N/2 levels empty

# Bands in Metals



3p
3s
Energy
Density of States
Typical Metal

3p
3s
Energy
Na

3p
3s
Mg

# Bandwidth

Bandwidth or band dispersion:
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
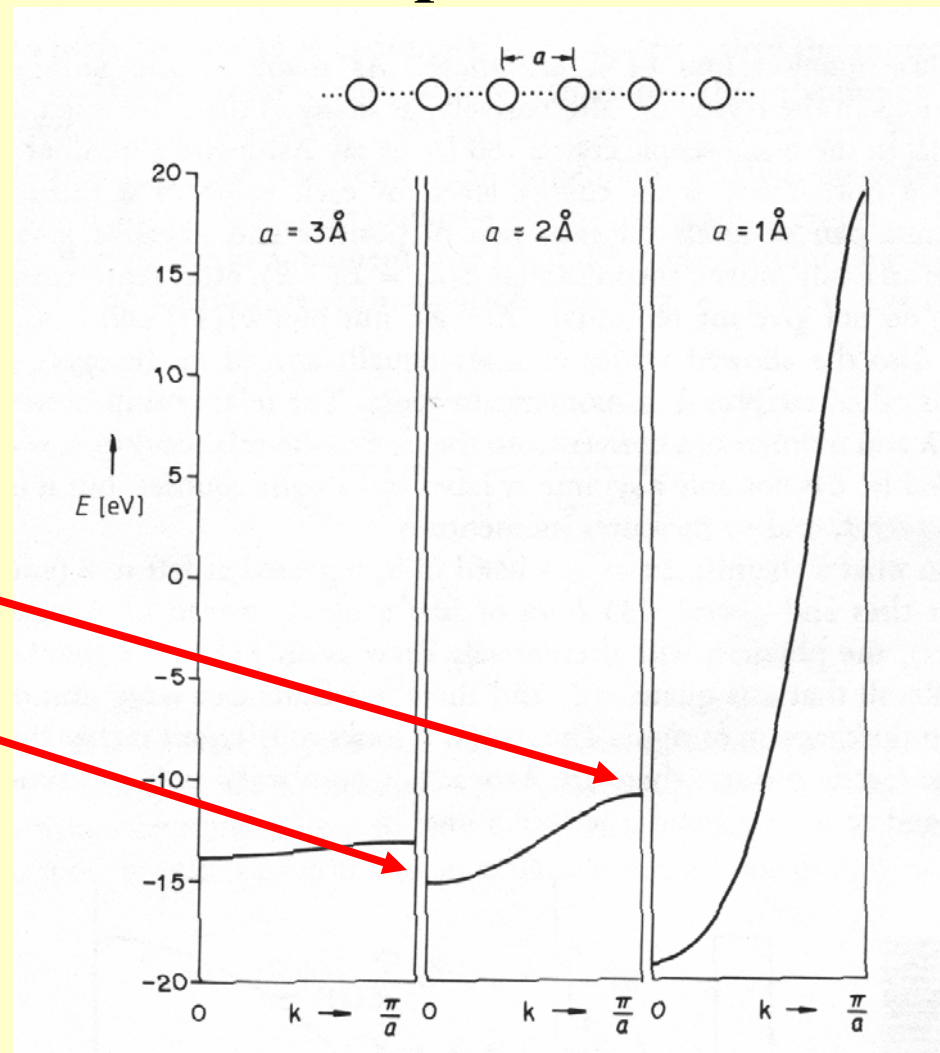Valence orbitals, s, p – wide bands (10 eV)

# Bandwidth

degree of orbital overlap between building units

Wide bands = Large intermolecular overlap = delocalized e-

Narrow bands = Weak intermolecular overlap = localized e-
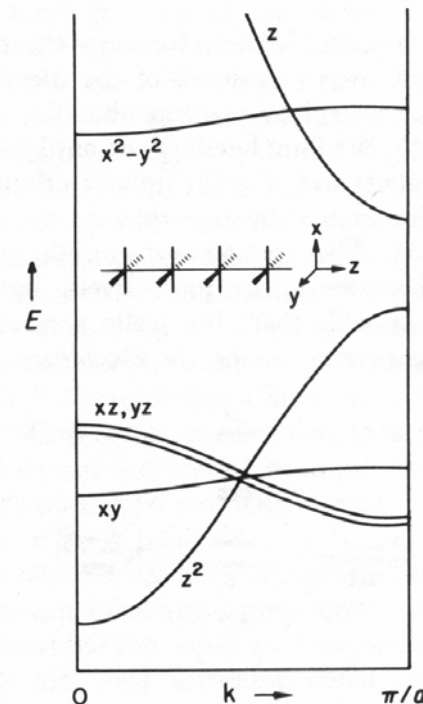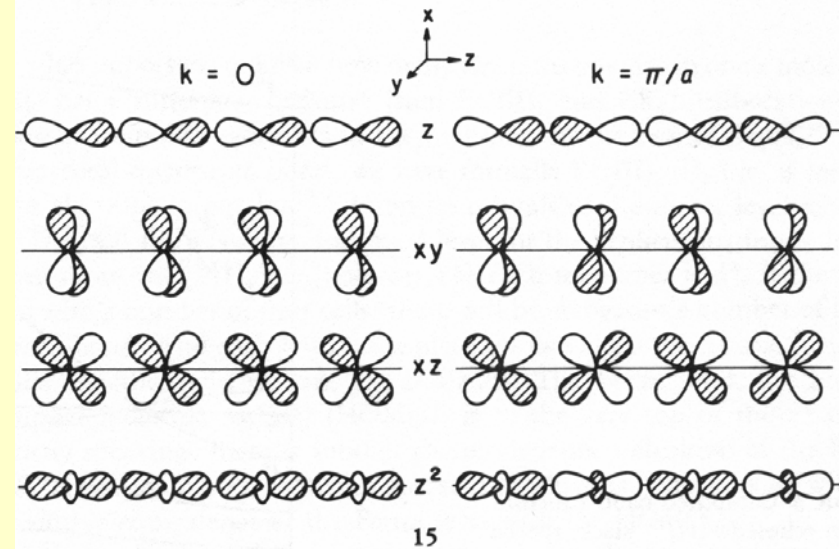
# Bandwidth or band dispersion

energy difference between the highest and lowest level



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

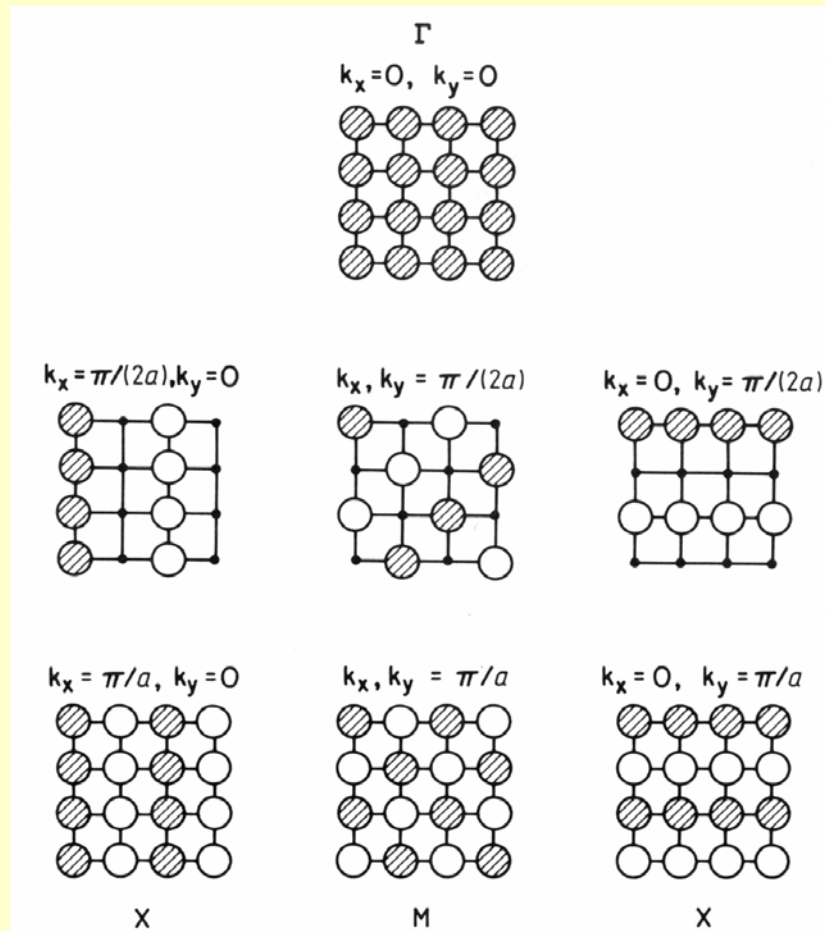distinct bands with a band gap overlaping bands

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

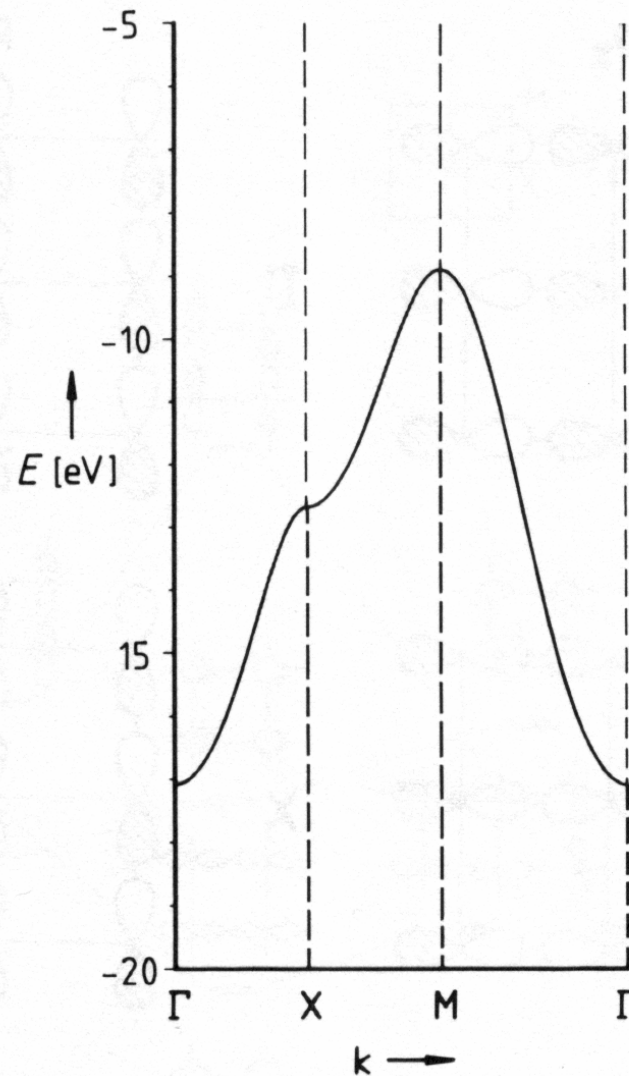Strong interaction = wide bands and a greater overlap.

# Two dimensional lattice

# Two dimensional lattice

**Band structure
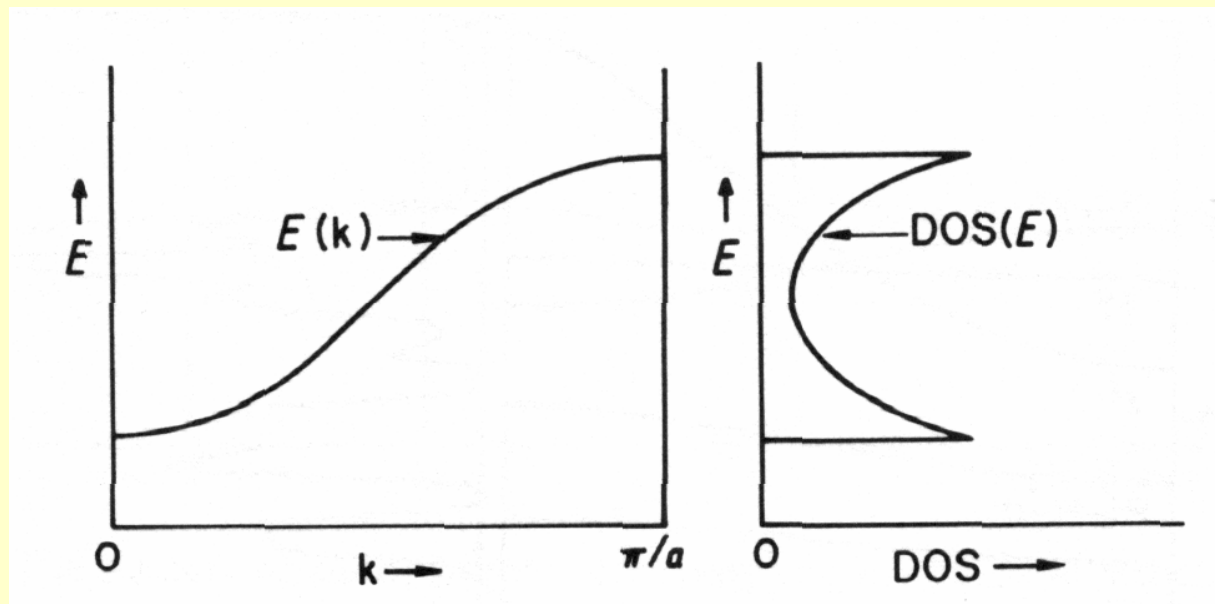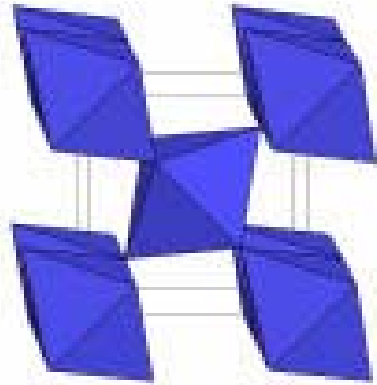of a square lattice of H atoms
($d_{HH}$ = 2.0 Å)**
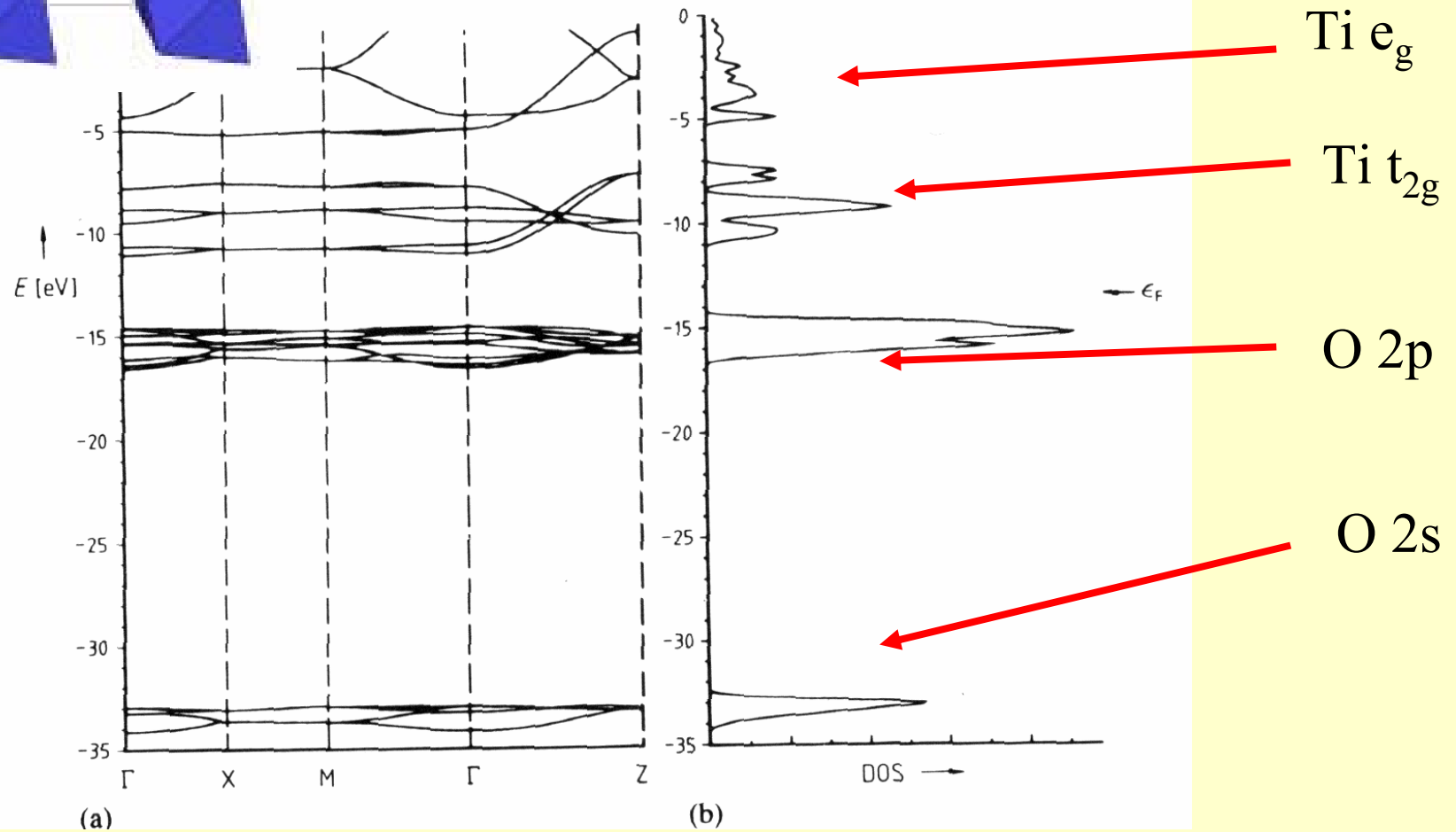
# Density of states

**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**
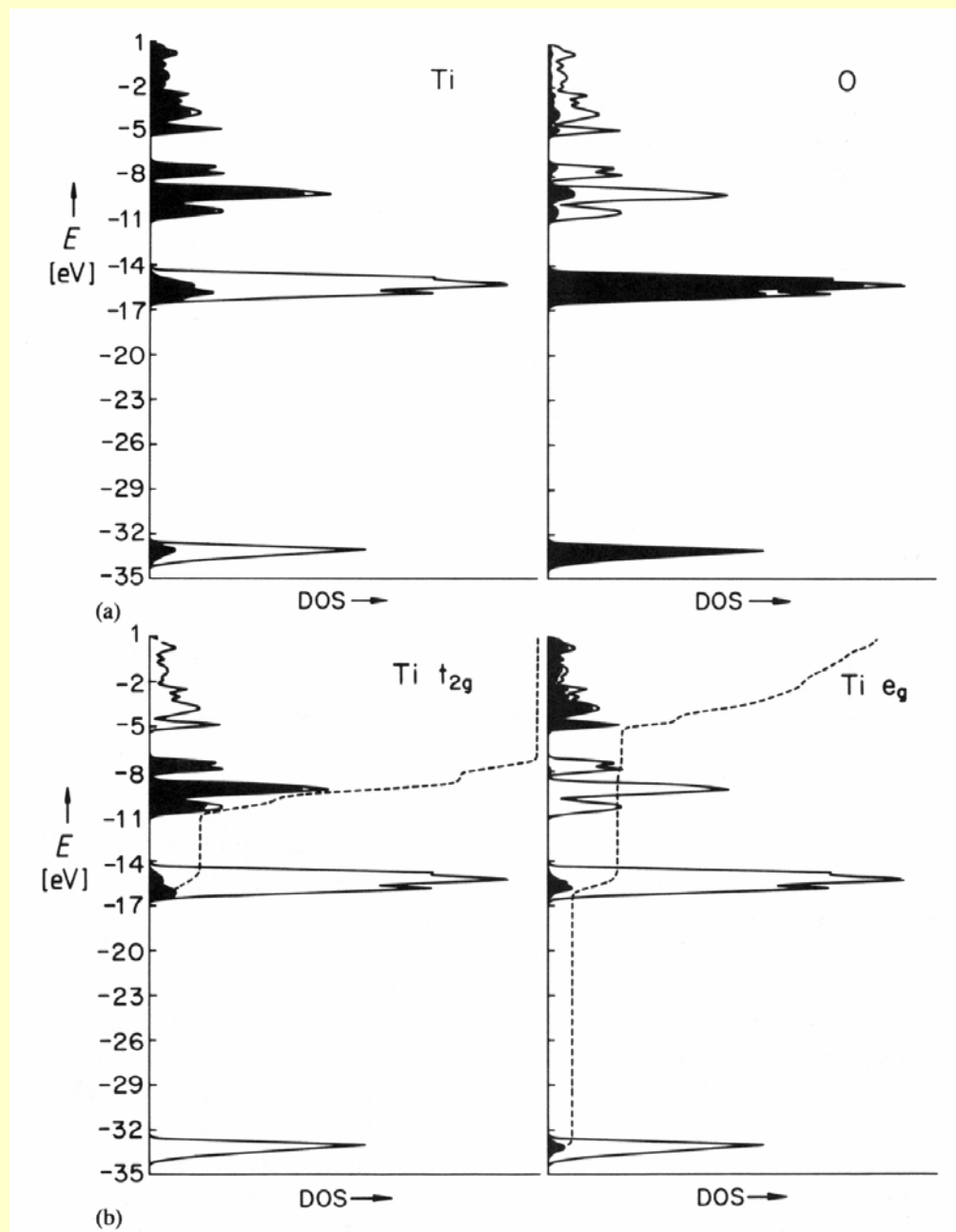
# Rutile TiO$_2$ Band Structure



band structure (a) and DOS (b)

**Contributions to
the total DOS of rutile**

**(a) Ti and O**

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



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## 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, ….**
Simple metals – 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.
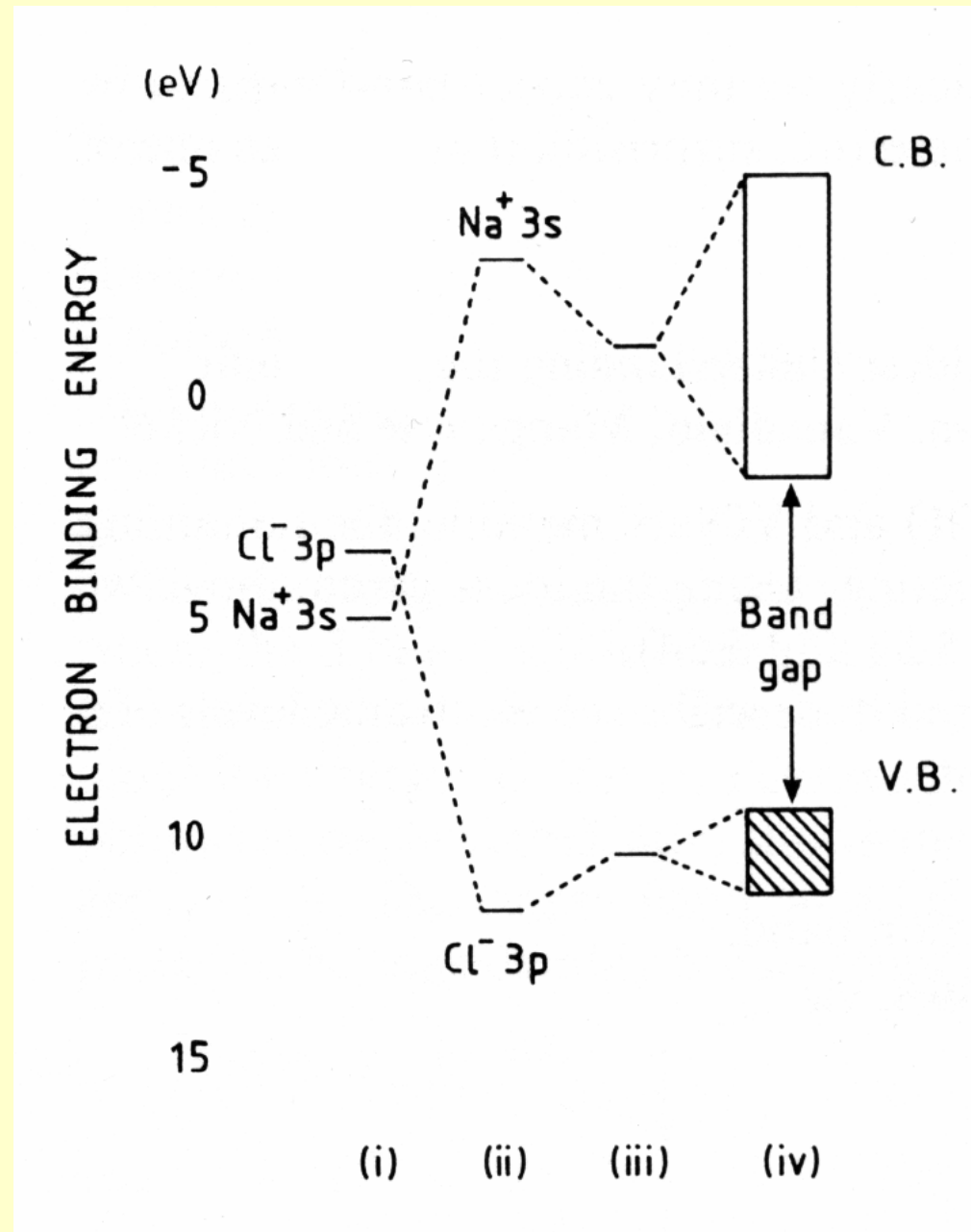
**Ionic solids**

**Example NaCl, $E_g = 9$ 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**

# 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
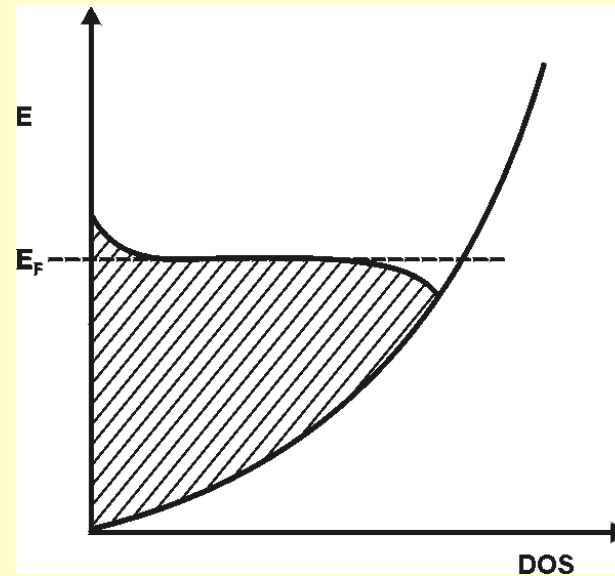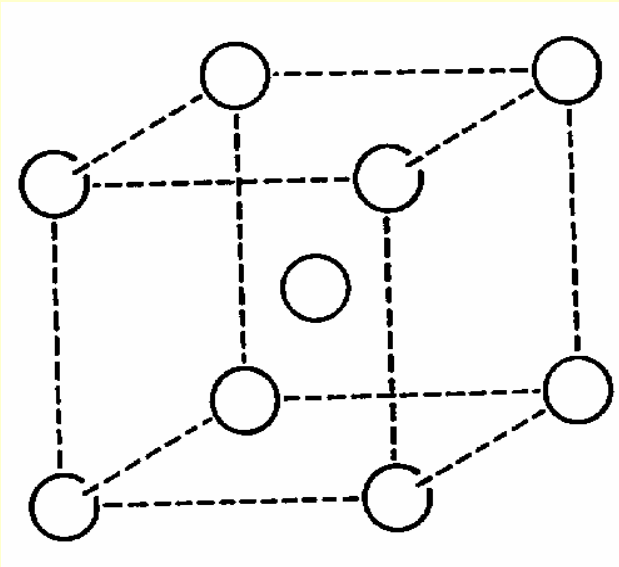
**Fermi level**

$E_F$ = the thermodynamic chemical potential for electrons in the solid

**Metals – boundary between filled and unfilled levels**

**The Fermi-Dirac distribution function:**

$f(E) = 1/[1 + \exp\{(E – E_F)/kT\}]$



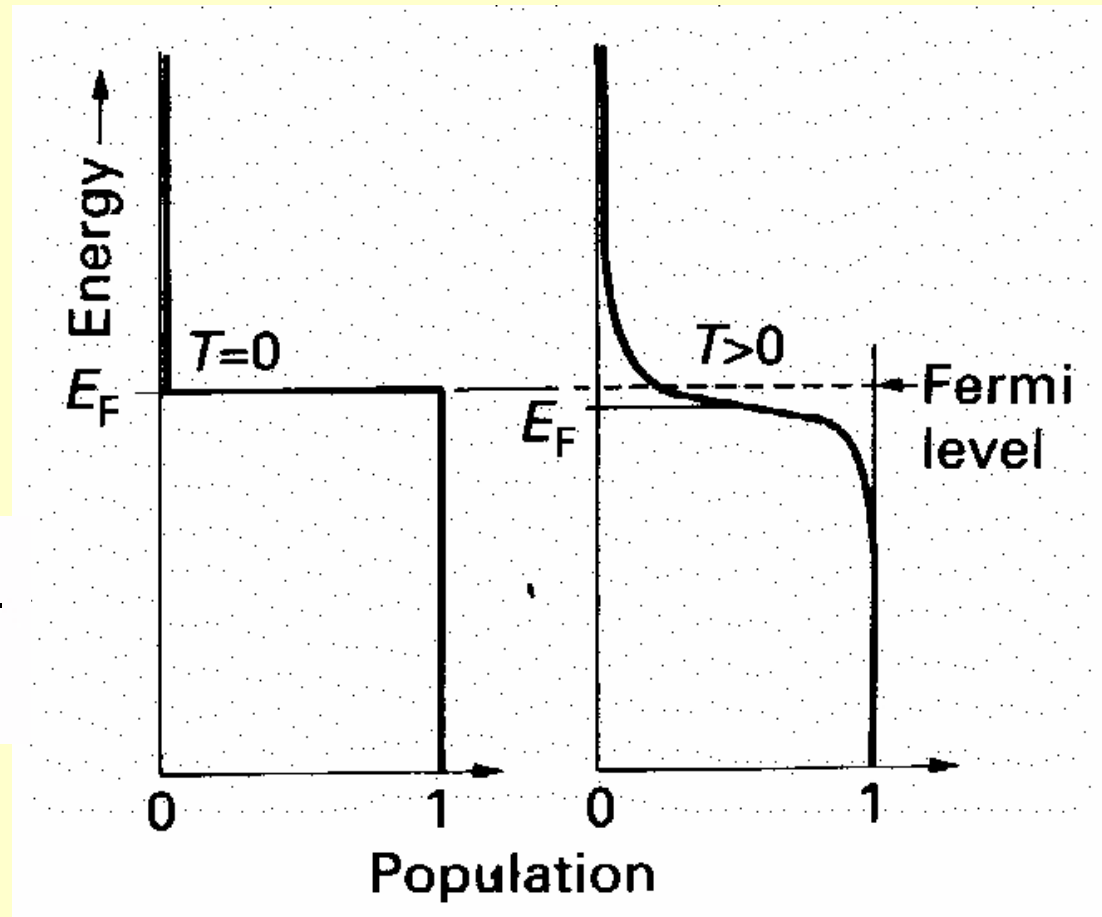The Fermi level cuts a band in a metal

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# Fermi Level

$E_f$ occupation probability ½

Levels
$E < E_f$ occupied
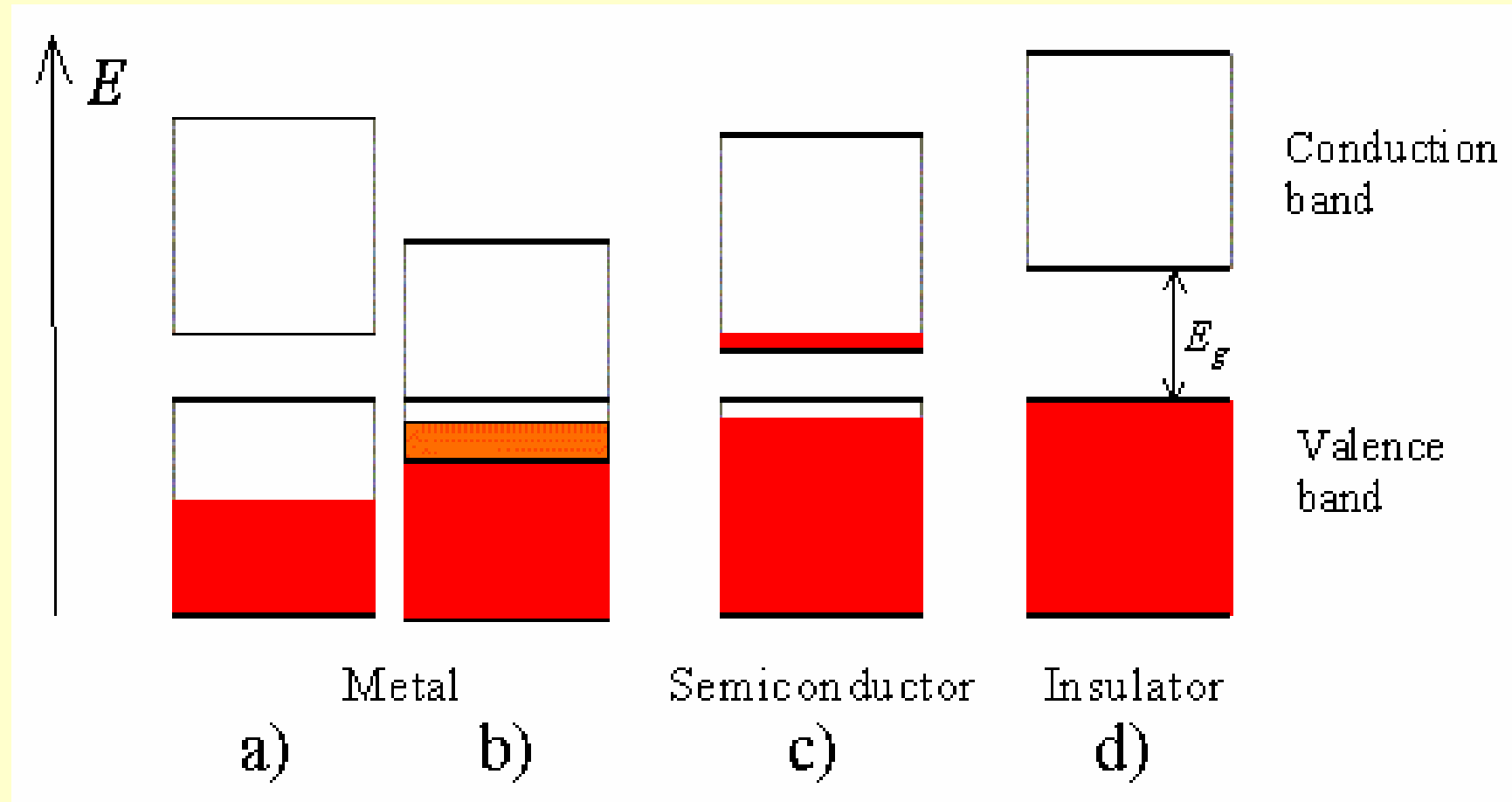$E > E_f$ empty

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

# Metallic and Non-metallic Solids

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

# Metallic and Non-metallic Solids

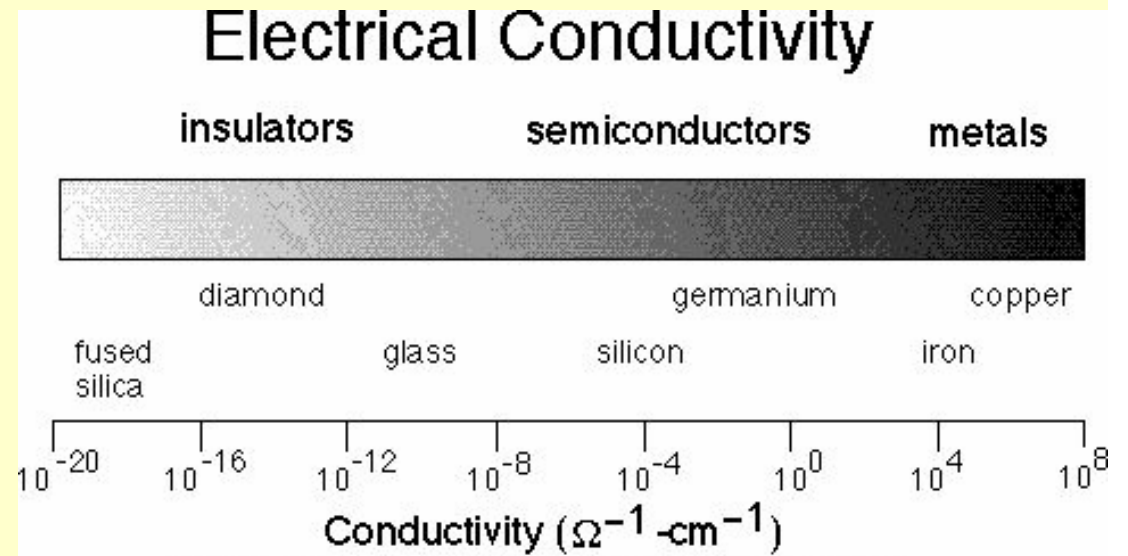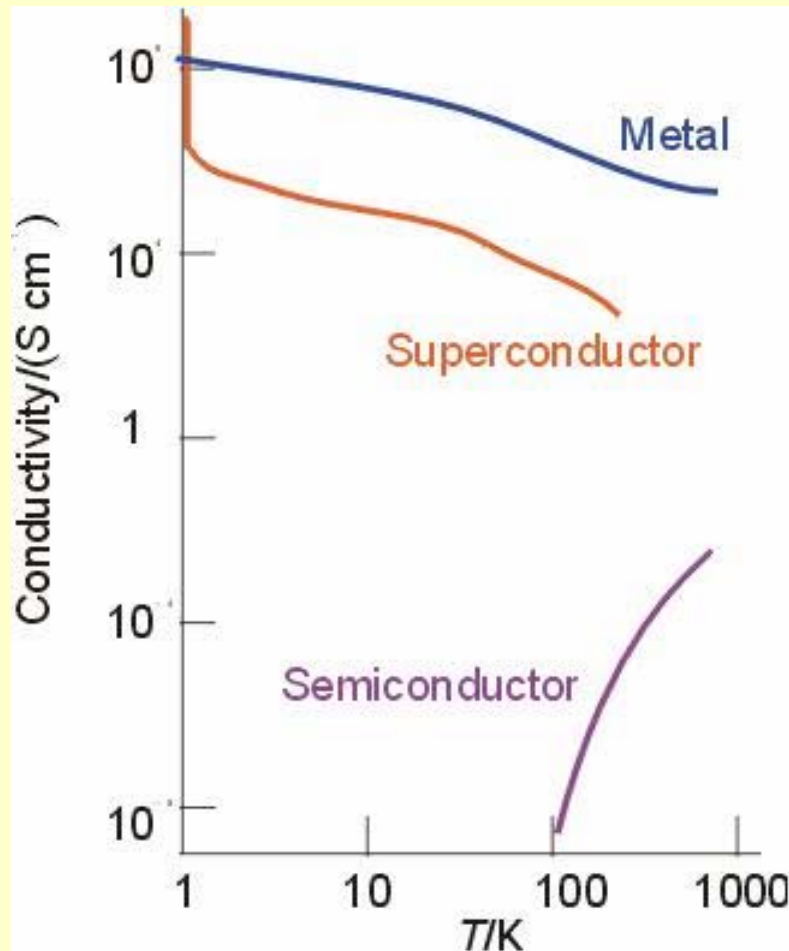The band gap size determines a semiconductor or an insulator

Band gap = the minimum photon energy required to excite an electron up to the conduction band from the valence band
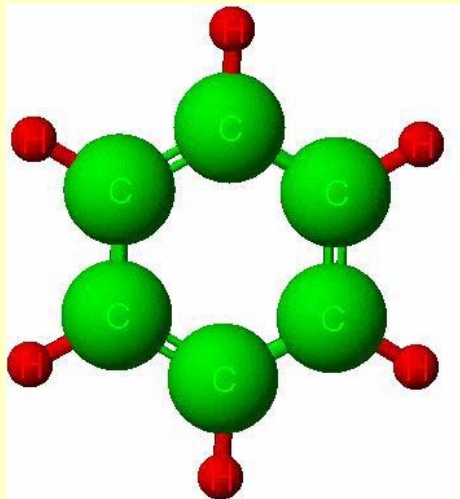
Insulators - a completely filled valence band separated from the next energy band, which is empty, by a large, forbidden gap

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

When conductivity of insulators is measured it is found to increase with temperature
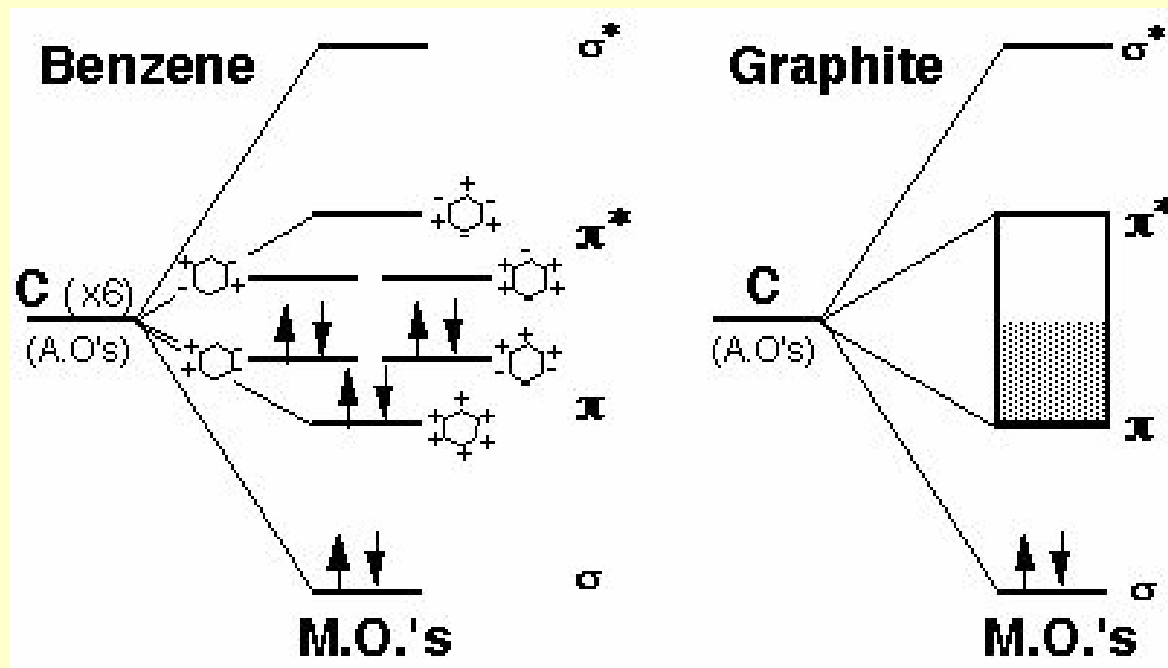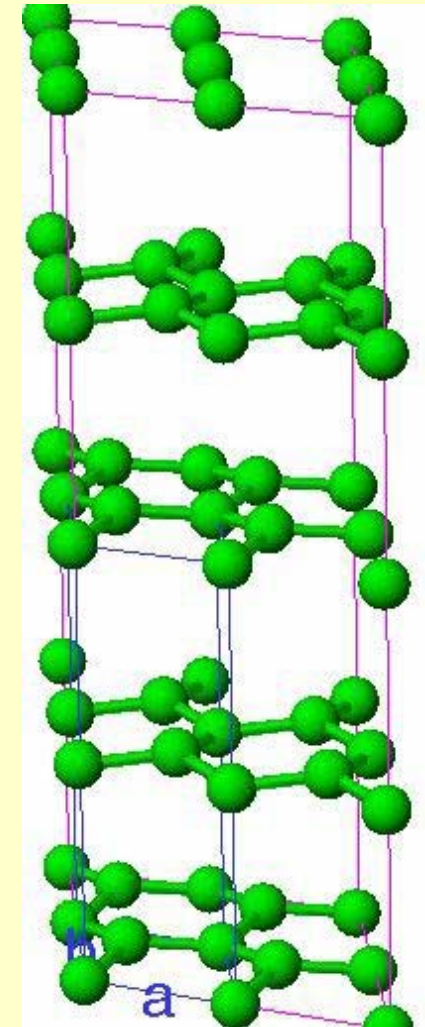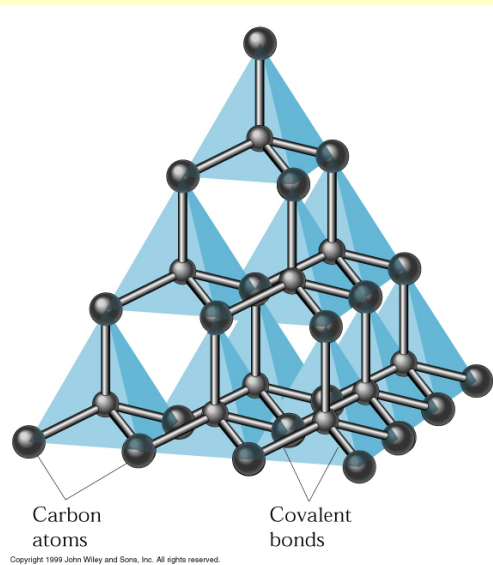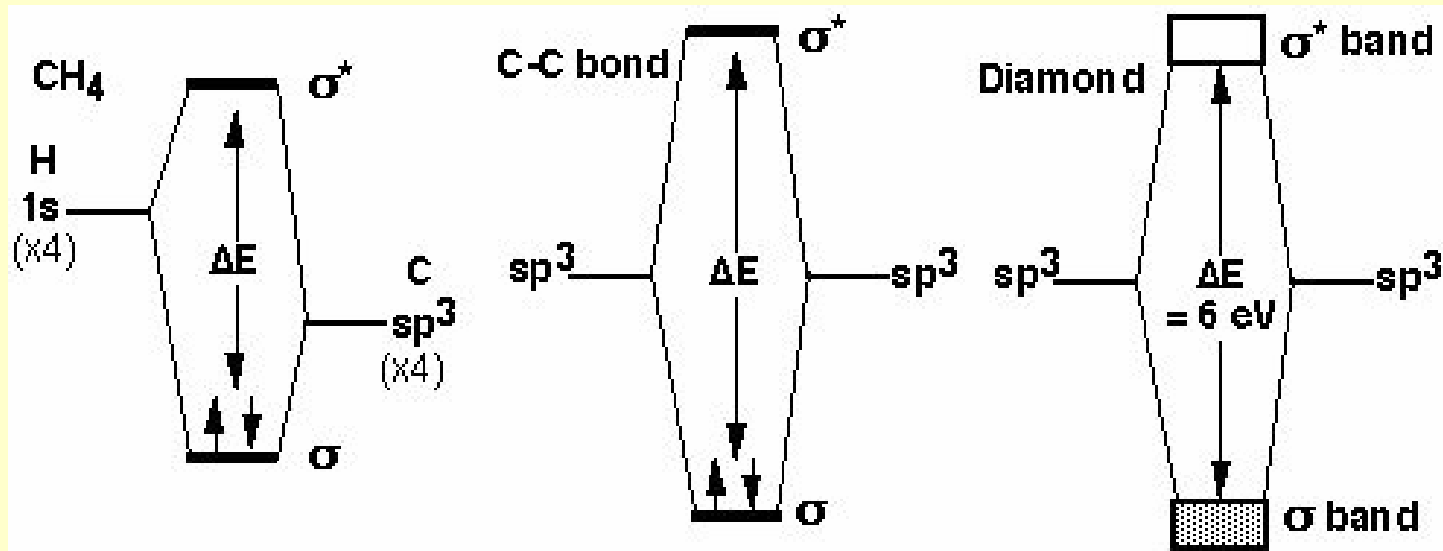
# Electrical Conductivity

# Bands in Graphite

Graphite is a conductor
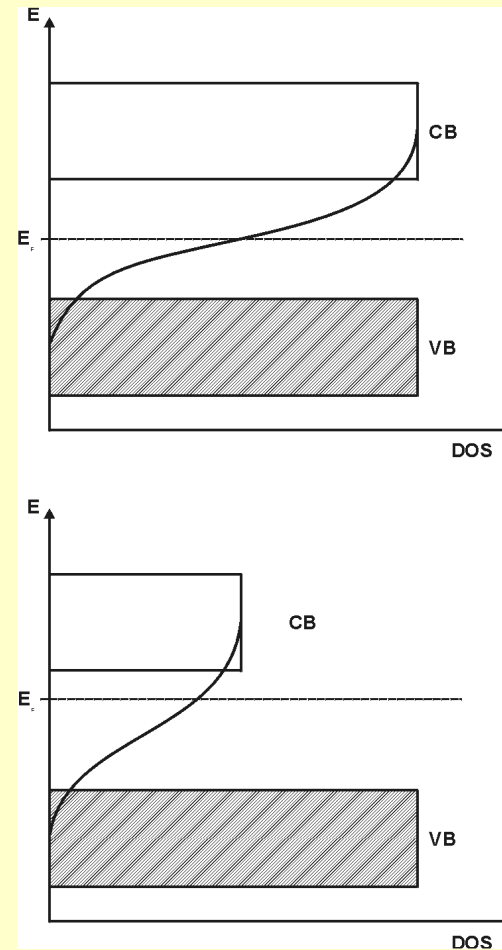
# Bands in Diamond

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# Semiconductors

Fermi level

a gap between the filled and empty states in a semiconductor/insulator

# Semiconductors

Semiconductors - a similar band structure to insulators but the band gap is not very large and 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 - new positive hole. The positive holes move in an opposite direction to the electrons.

# Semiconductors

**INTRINSIC**

Intrinsic semiconductors are pure materials with the bandstructure. 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 valenece electrons to that of the original material.

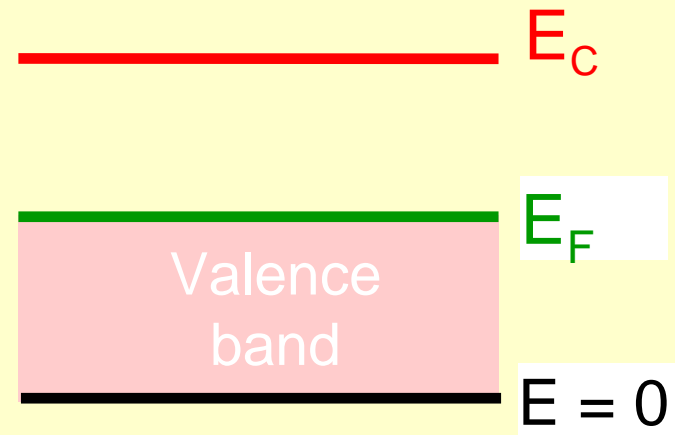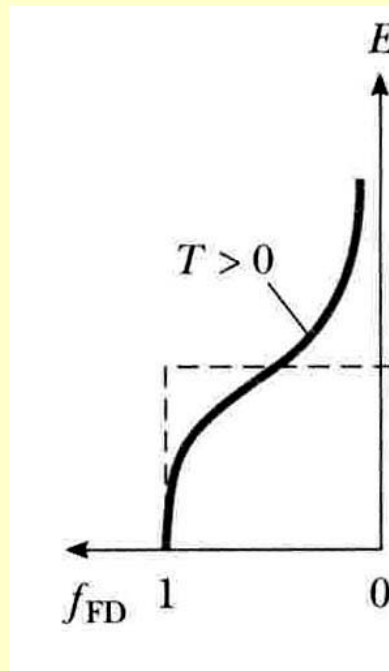Two fundamental differences between extrinsic and intrinsic semiconductors:

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.
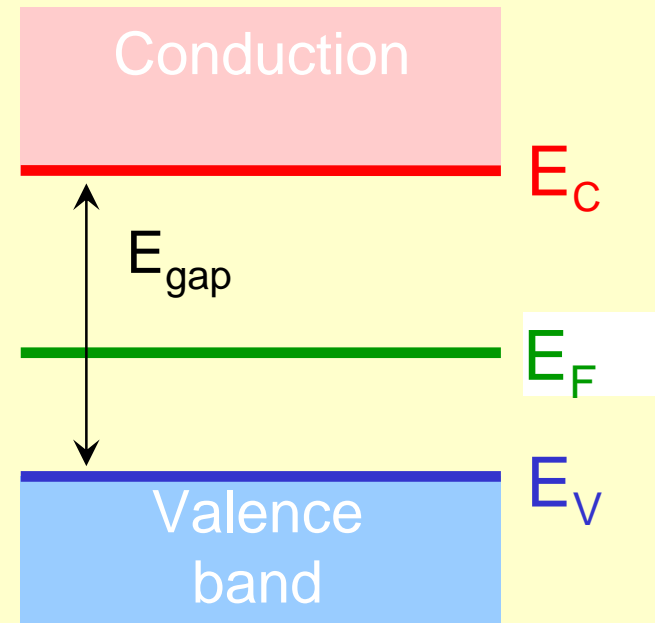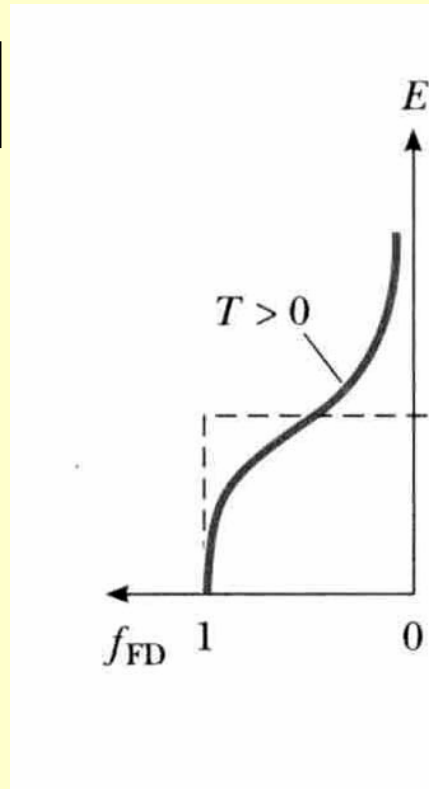
# Metals



T > 0

$E_C$

$E_F$

Valence band

E = 0

# Insulators

T > 0



Conduction

$E_C$

$E_{gap}$

$E_F$

$E_V$

Valence band

# Intrinsic Semiconductors



T > 0

Conduction

$E_C$

$E_F$

$E_V$

Valence band

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# Extrinsic Semiconductors



Semiconductors: n- and p-Type

Electrons in conduction band

Donor levels

Fermi Level

Fermi Level

Acceptor levels

Electron holes in valence band

n-type doping    p-type doping

# 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 n-type

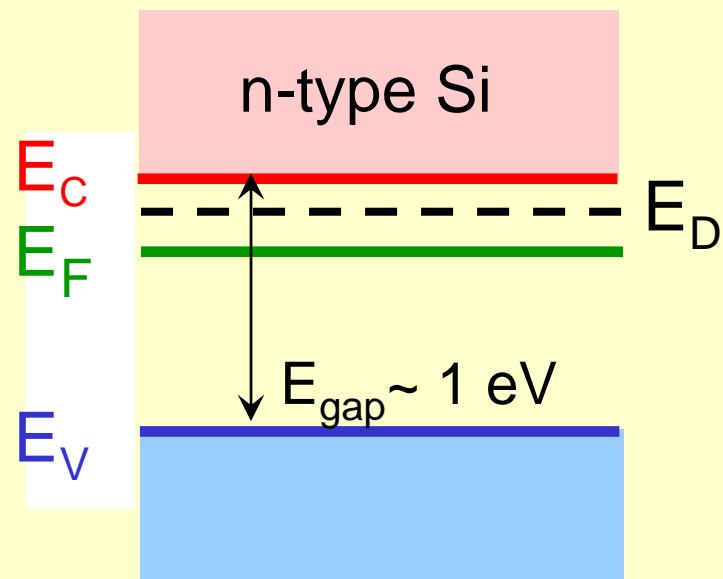# Extrinsic Semiconductors n-type

Silicon - phosphorous atoms introduce extra electrons (one extra valence electron for each dopant atom introduced as P)
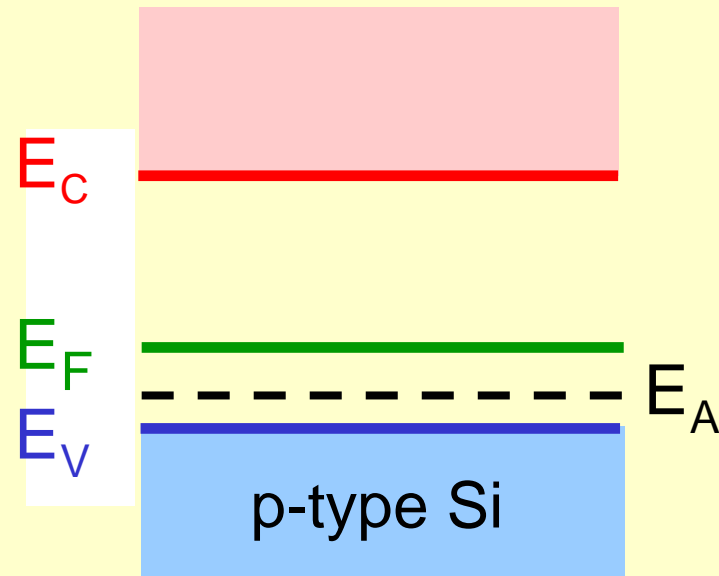
The dopant atoms form a set of energy levels that lie in the band gap between the valence and conduction bands, but close to the conduction band.

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

# Extrinsic Semiconductors p-type

Doping with an element with one less valence electron such as Ga

For every dopant atom - an electron missing,

form 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.

# Controlled Valency Semiconductors

Some transition metal compounds can be conductors due to the presence of an element in more than one oxidation state.

NiO

On oxidation - turns black and becomes a relatively good conductor

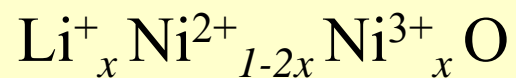Some of the $Ni^{2+}$ ions oxidized to $Ni^{3+}$ and some $Ni^{2+}$ ions diffuse out to maintain charge balance leaving cation holes. The reason for the conduction is the ability of electrons to transfer from $Ni^{2+}$ to $Ni^{3+}$ ions. This basically allows the $Ni^{3+}$ ions to move and black NiO is therefore a p-type semiconductor.

# Hopping Semiconductor

the transfer process is thermally controlled and therefore highly dependent on temperature, makes controlling the conductivity difficult.

Controlled valency semiconductors rely on control of the concentration of $Ni^{3+}$ ions by controlled addition of a dopant (such as lithium).

NiO

$Li^+_x \, Ni^{2+}_{1-2x} \, Ni^{3+}_x \, O$

the concentration of $Li^+$ ions controls the conductivity

**Delocalized Bands – Localized Bonds**
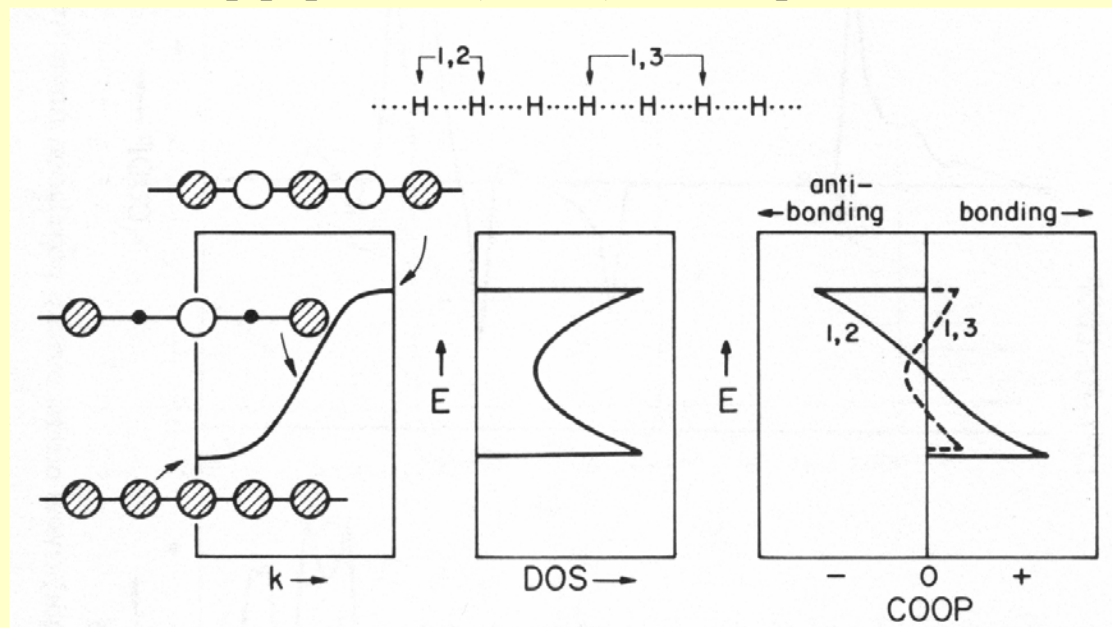
**Molecules: Mulliken overlap population**        $\Sigma\ 2\ c_1\ c_2\ S_{12}$
**$c_1$, $c_2$ same sign = bonding**
**$c_1$, $c_2$ opposite sign = antibonding**
**$S_{12}$ overlap integral**

**Solids: Overlap population-weighted density of states = crystal orbital overlap population (COOP) – for a specific bond**
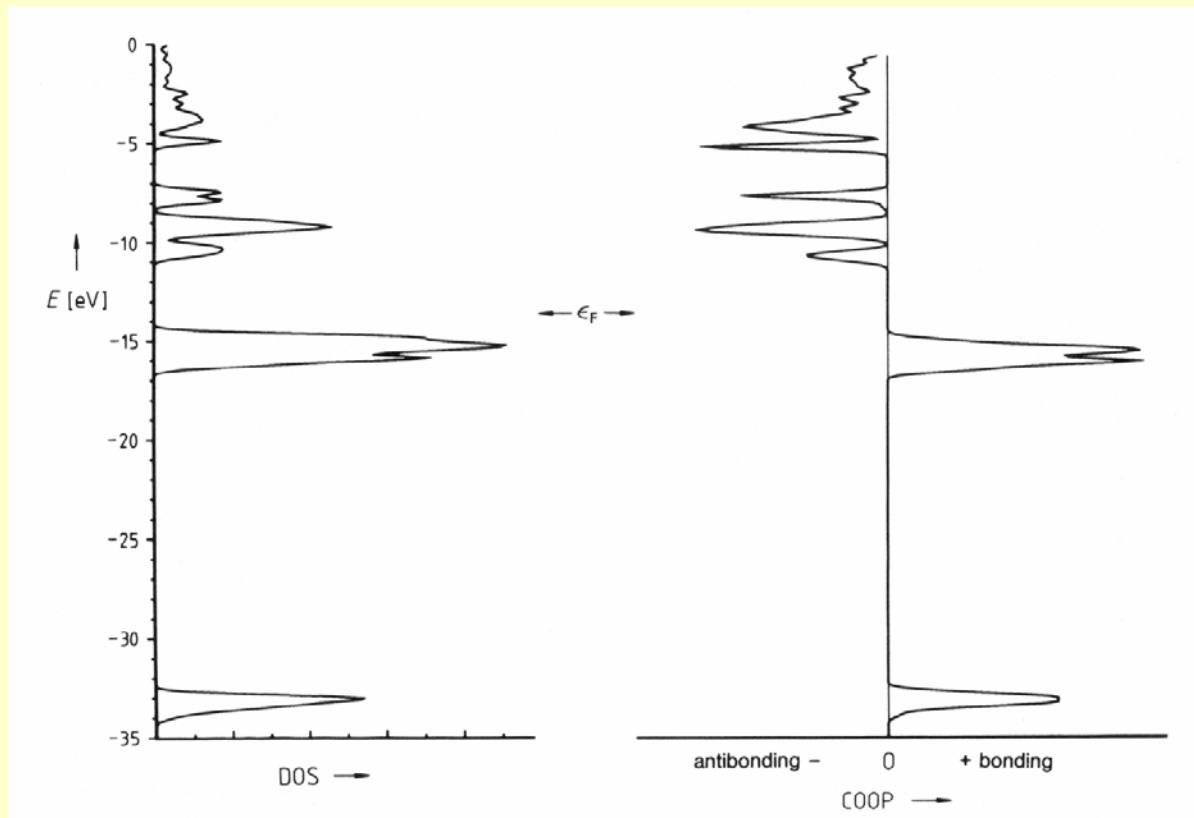


**COOP curves**
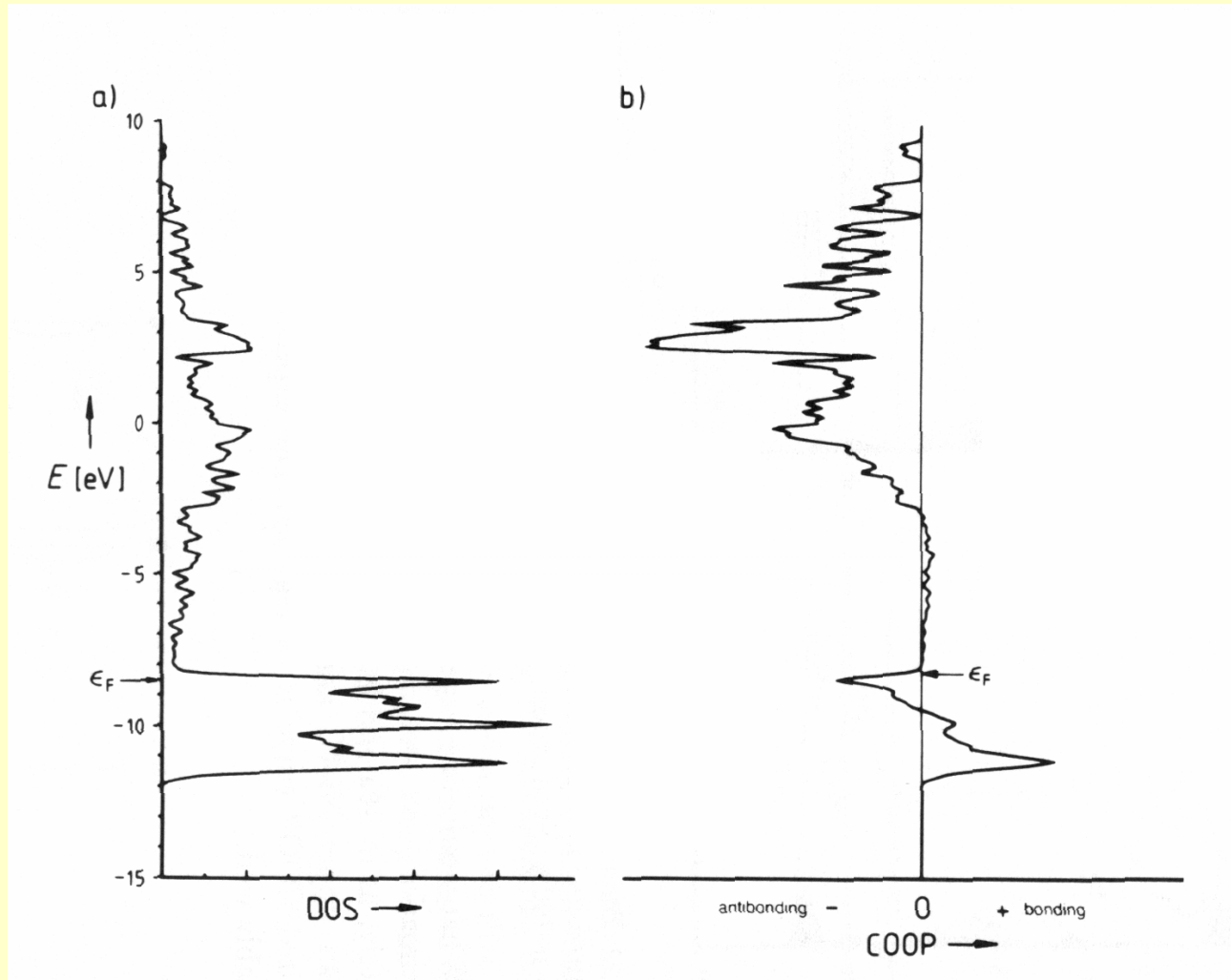**Sign – positive = bonding, negative = antibonding**
**Amplitude – depends on DOS, orbital overlap, MO coefficients**
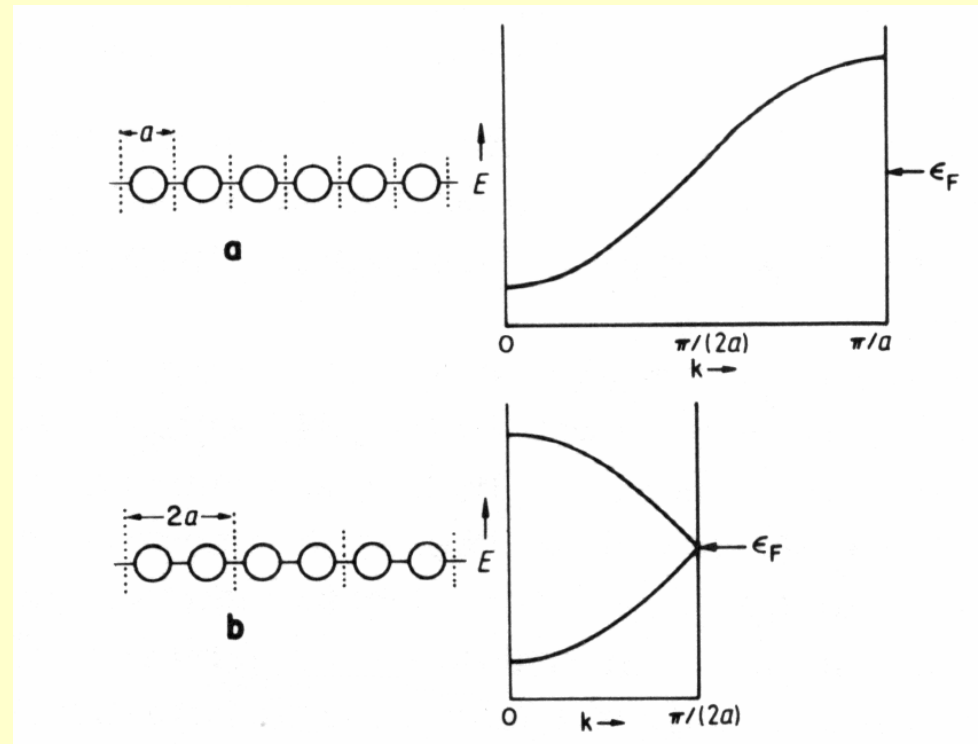
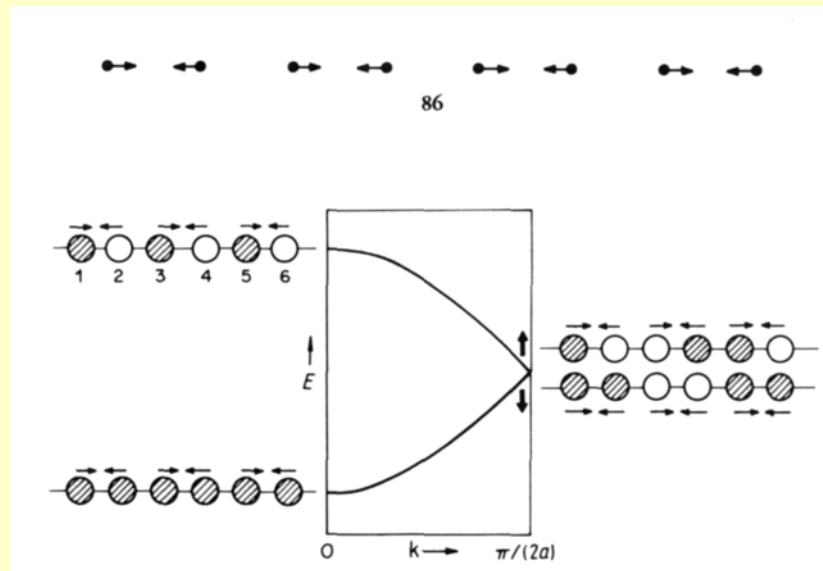**DOS and COOP for the Ti-O bonds in rutile**

**DOS and COOP for the Ni-Ni bonds in Ni metal**

**Peierls distortion**

**Peierls distortion – maximizing bonding, lowering the DOS at the Fermi level, bonding states down in energy, antibonding states up, a band gap opens at the Fermi level**



Destabilization

Stabilization

**Peierls distortion**