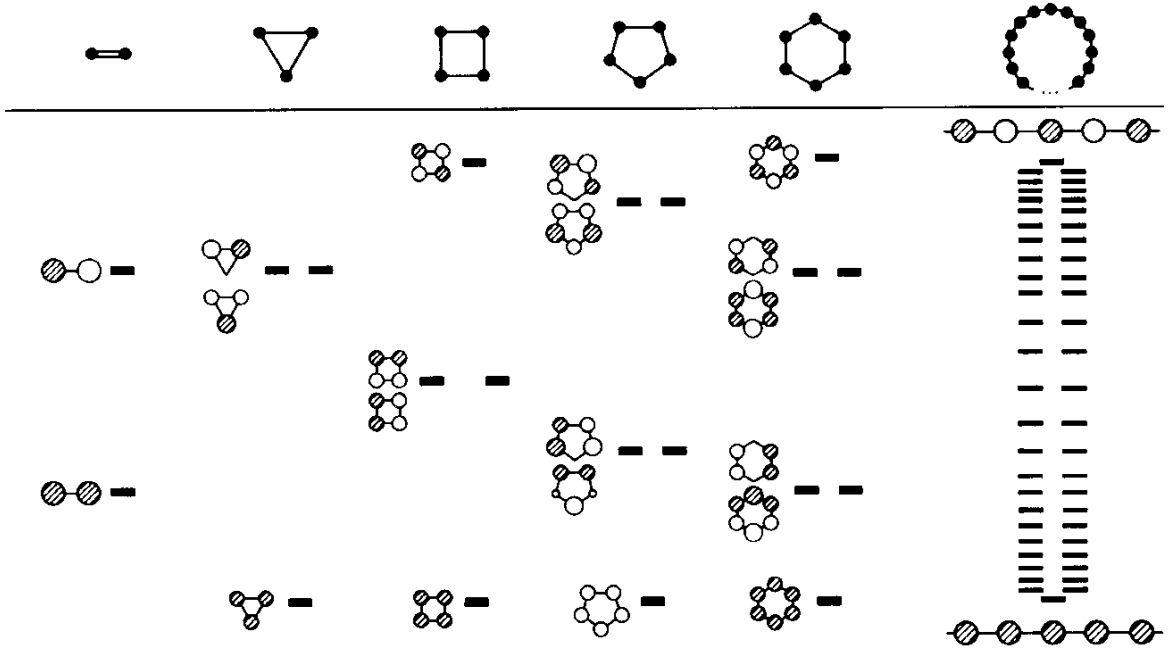
ELEMENTARY BAND THEORY

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

Molecular orbital →→→→→→→→→→ Electronic band

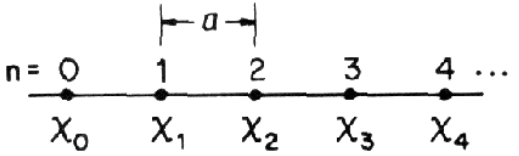
N atomic orbitals combine to form bonding and antibonding molecular orbitals, N energy levels.

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.

Bloch functions, crystal orbitals



simple example:
infinite one-dimensional array of s-orbitals

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

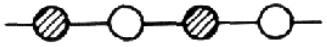
k = wavevector,
a = lattice constant,
n = orbital counter

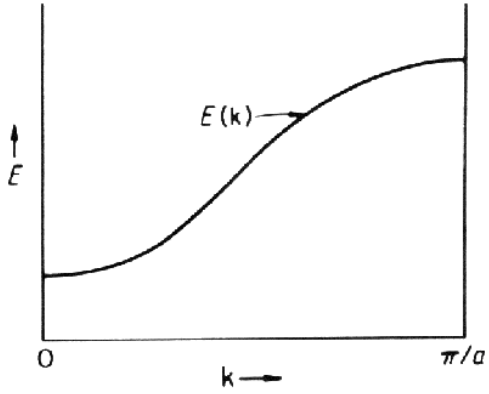
$$k=\frac{\pi}{a} \qquad \psi_{\frac{\pi}{a}} = \sum_n e^{\pi i n}\ \chi_n = \sum_n (-1)^n\ \chi_n$$

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

Large number of discreet levels = band

Antibonding

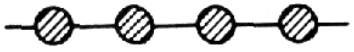




$$k = 0 \qquad \psi_0 = \sum_n e^0\ \chi_n = \sum_n \chi_n$$

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

Bonding



Bandwidth or band dispersion:
energy difference between the highest and lowest level

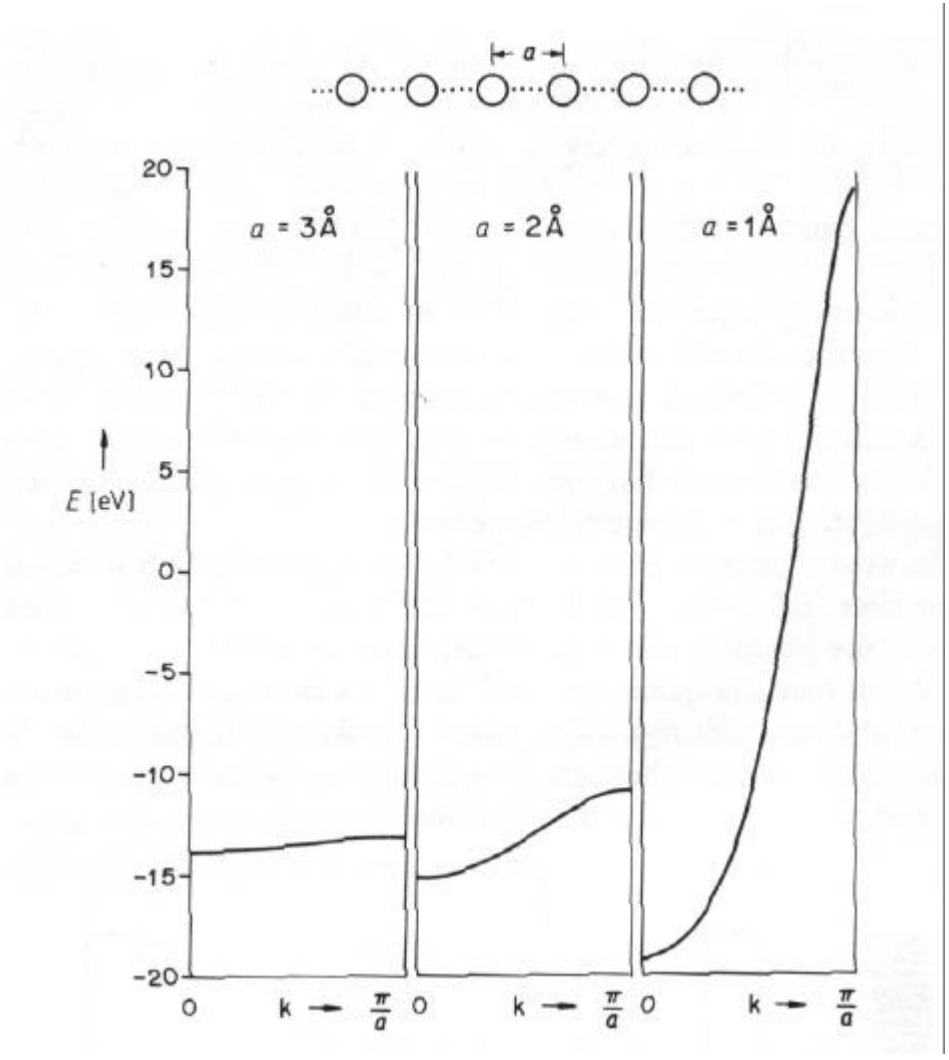
Bandwidth increases with better orbital overlap

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

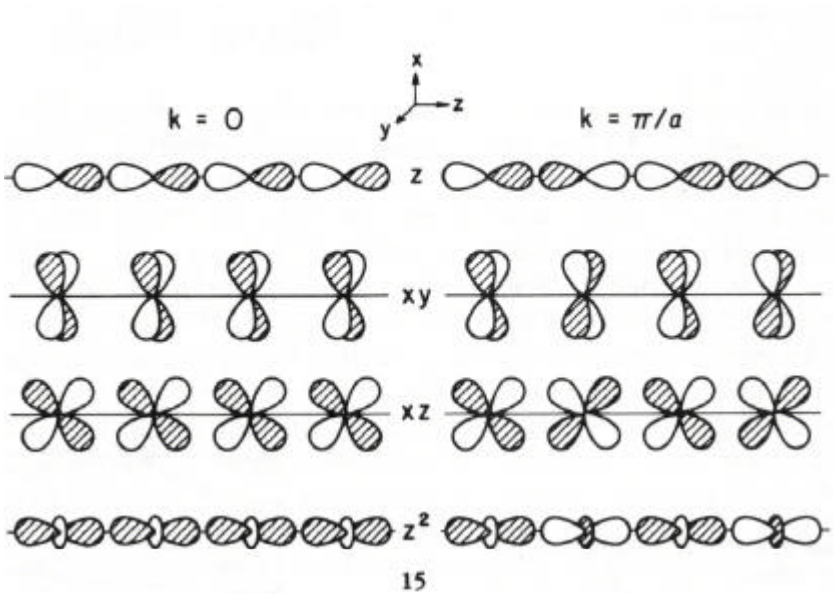
Bandwidth arising from sigma > pi > delta overlap

Core orbitals – narrow bands (0.1 eV), 4f in lanthanides
Valence orbitals, s, p – wide bands (10 eV)

Bandwidth or band dispersion:
energy difference between the highest and lowest level



p, d-orbital interactions



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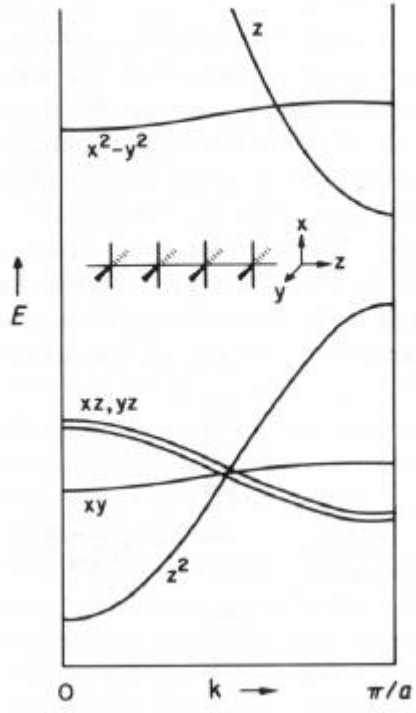
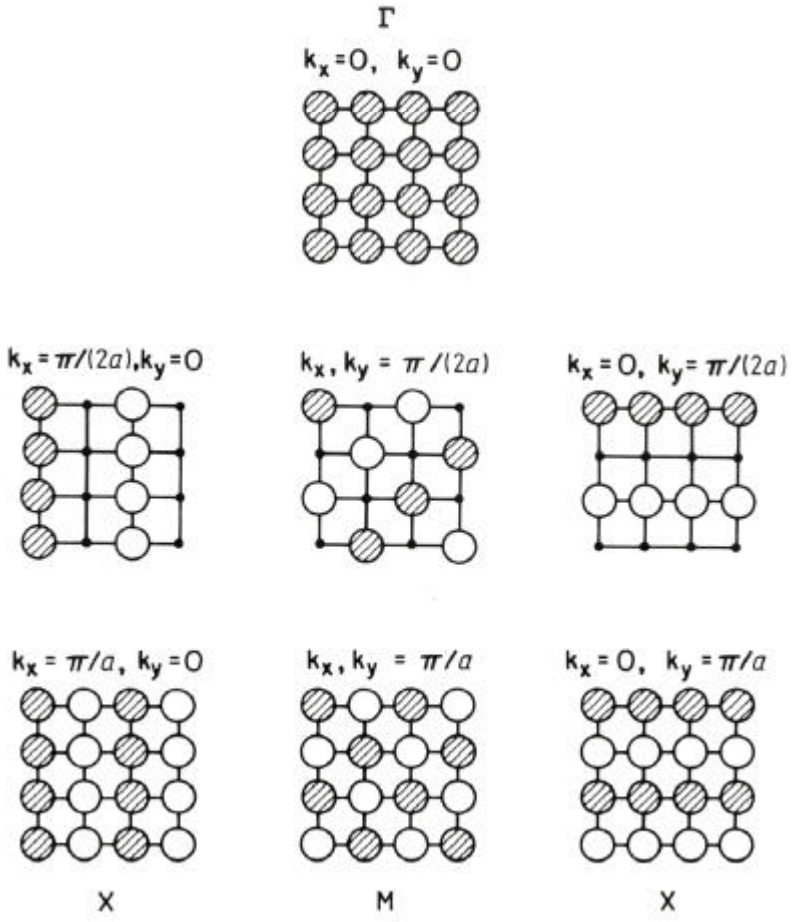
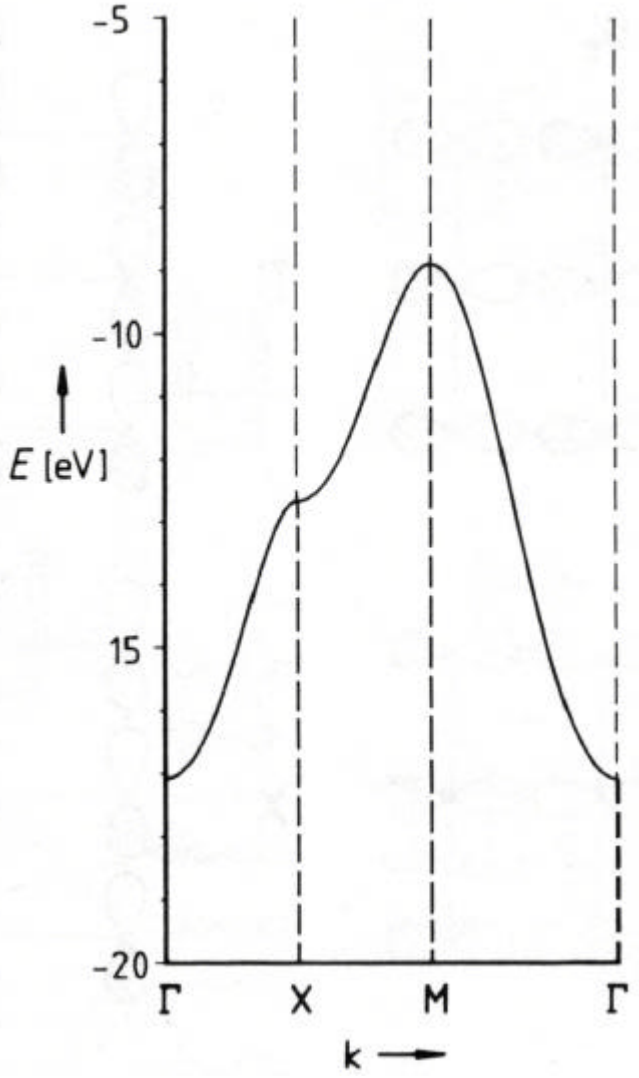


Two dimensional lattice



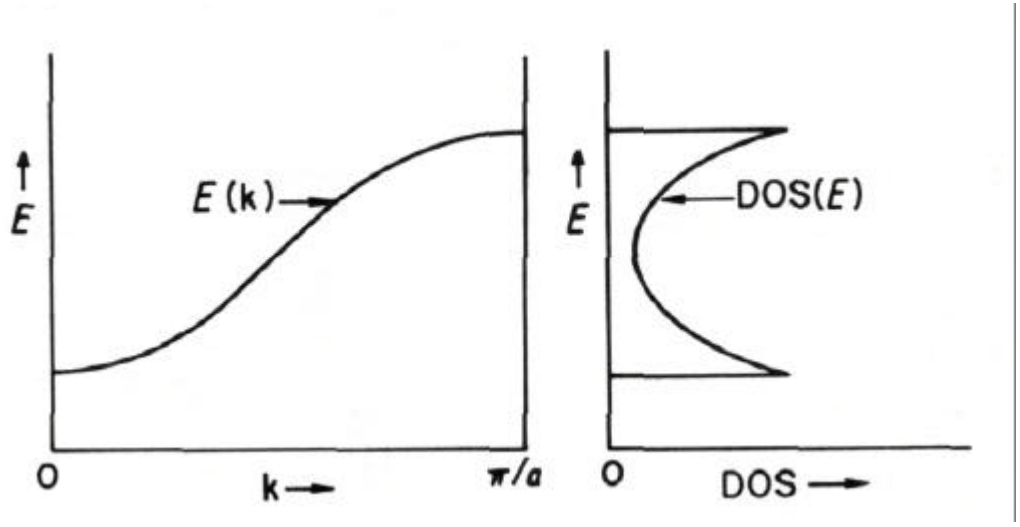
Two dimensional lattice

Band structure of a square lattice of H atoms (d_{HH} = 2.0 Å)

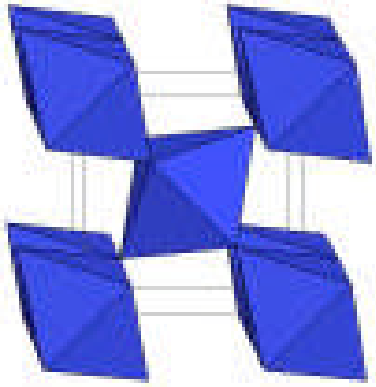


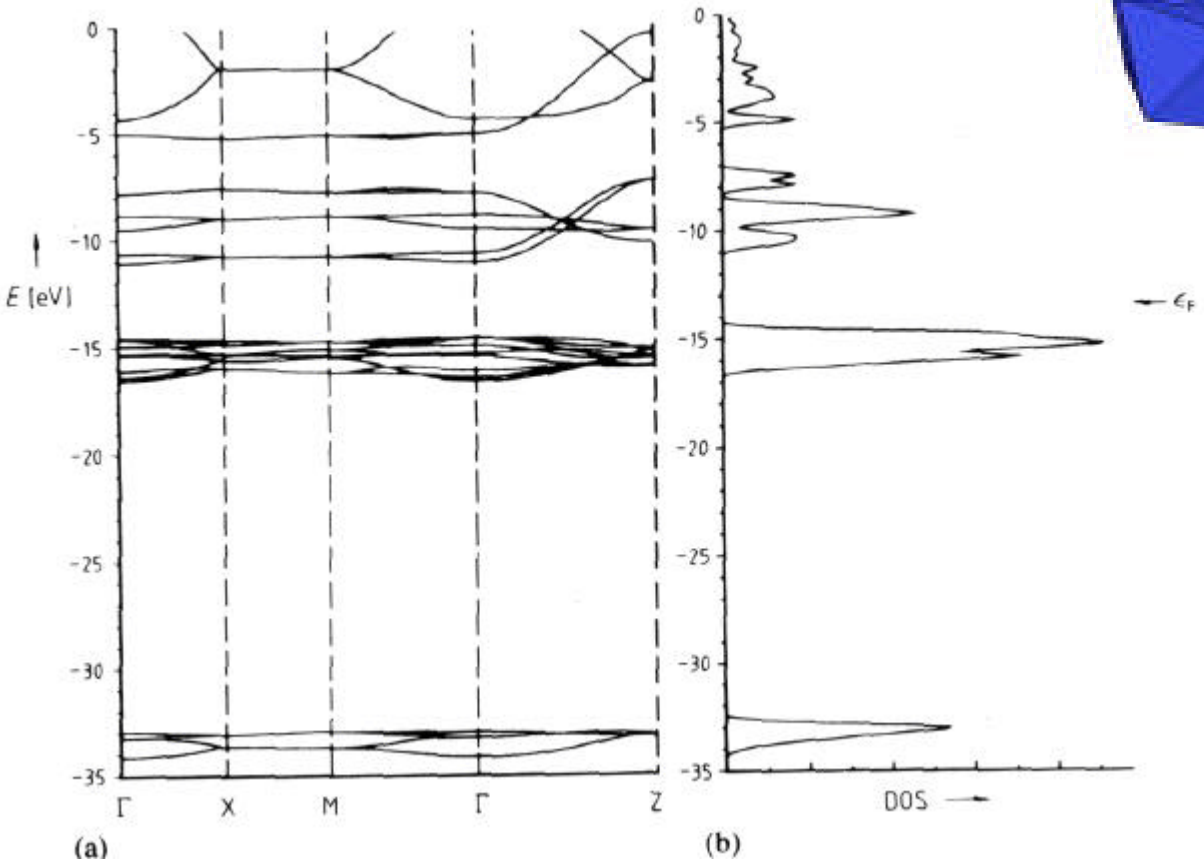
Density of states (DOS, N(E) dE)
Number of levels available for electrons at different energies per unit volume of the solid.

DOS is zero in the band gap



Rutile TiO_2
band structure (a) and DOS (b)

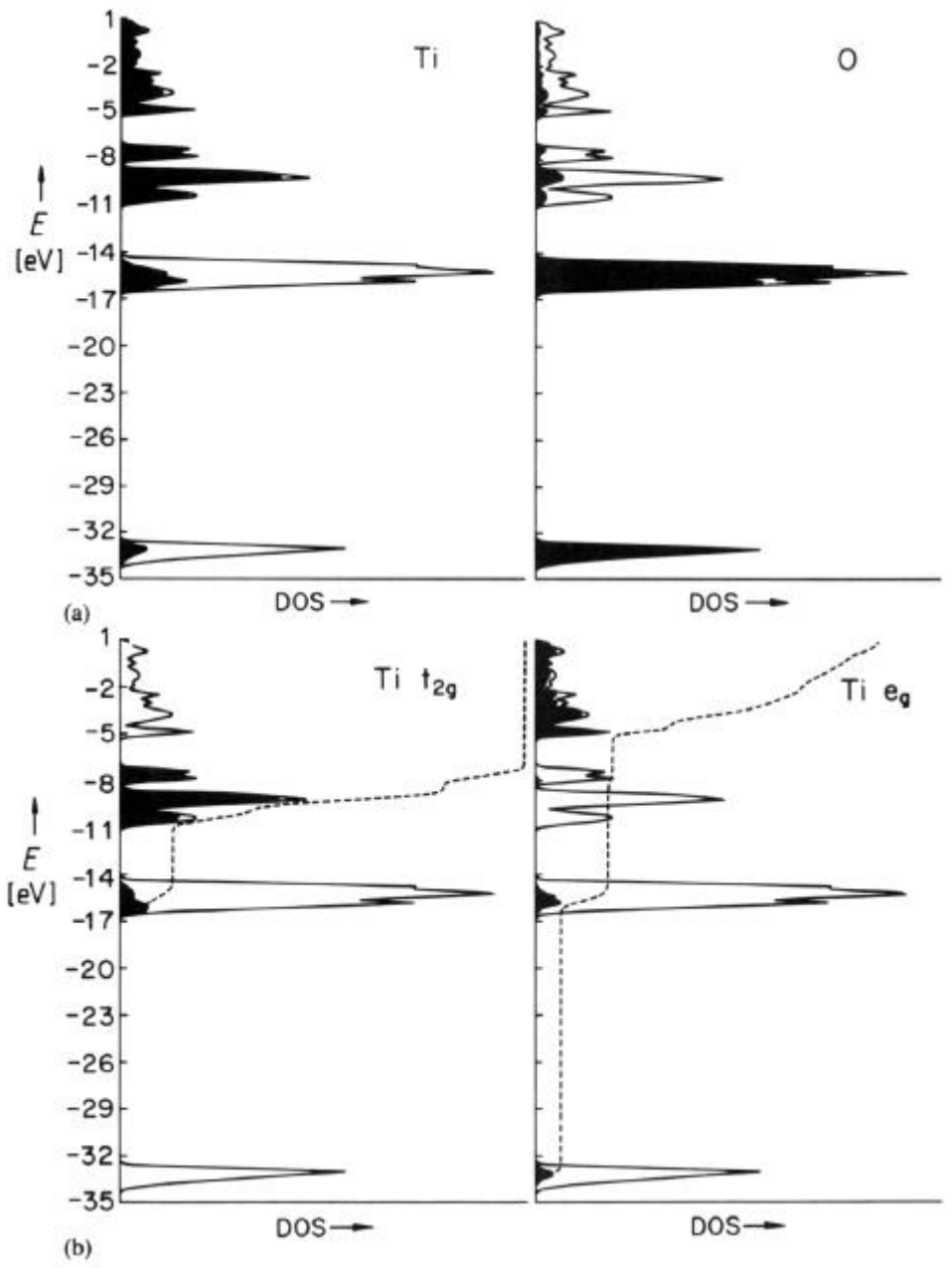




Contributions to the total DOS of rutile

(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.

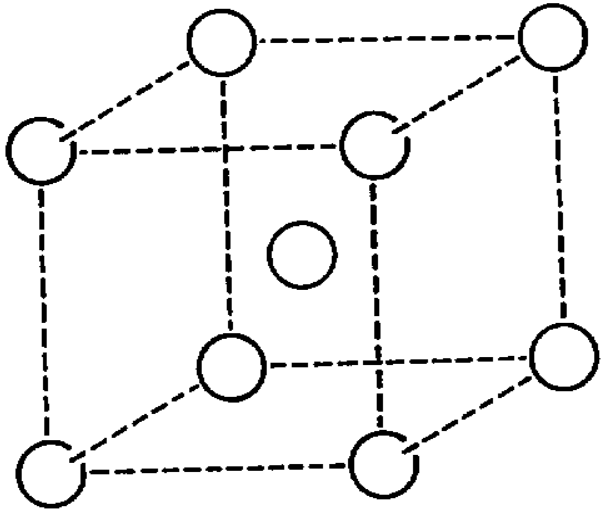
Metallic solids – Cu, Mg, W, TiO, ….
Simple metals – Na
Very strong overlap of atomic orbitals on adjacent atoms, arising bands are very broad, 3s, 3p, and 3d merge into a single wide band, electrons move freely, little attraction to the atomic cores.

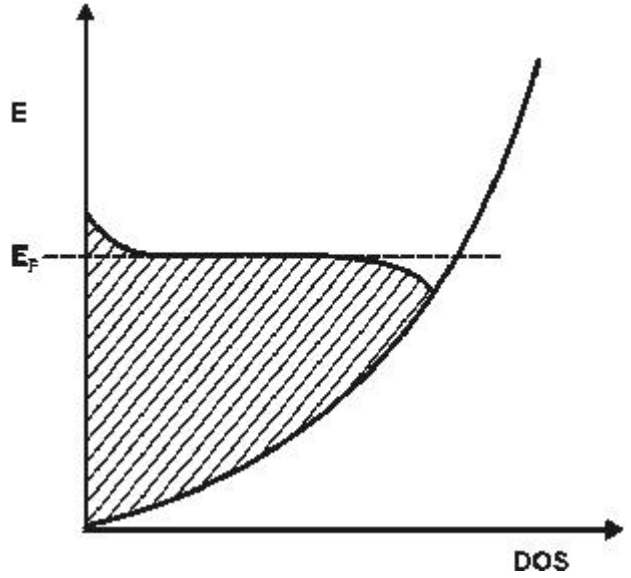
Fermi level
E_F = the thermodynamic chemical potential for electrons in the solid

Metals – boundary between filled and unfilled levels

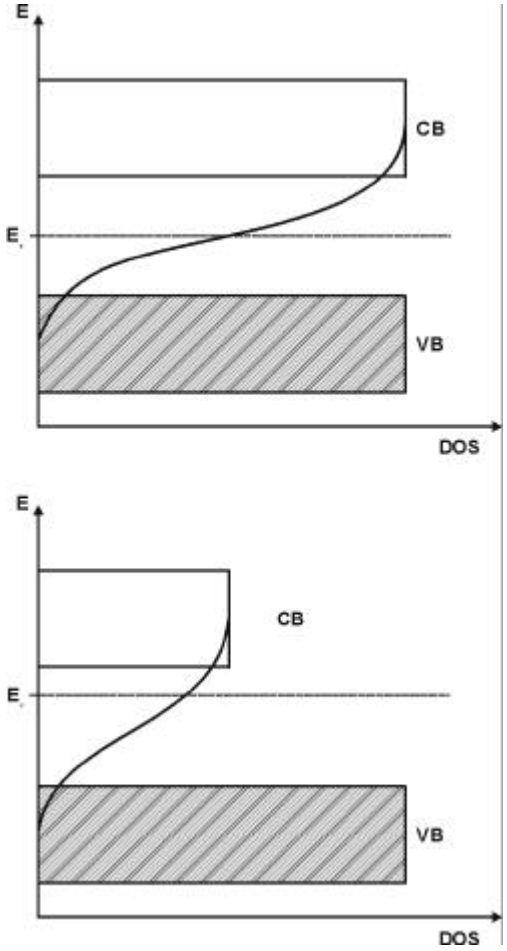
The Fermi-Dirac distribution function:

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



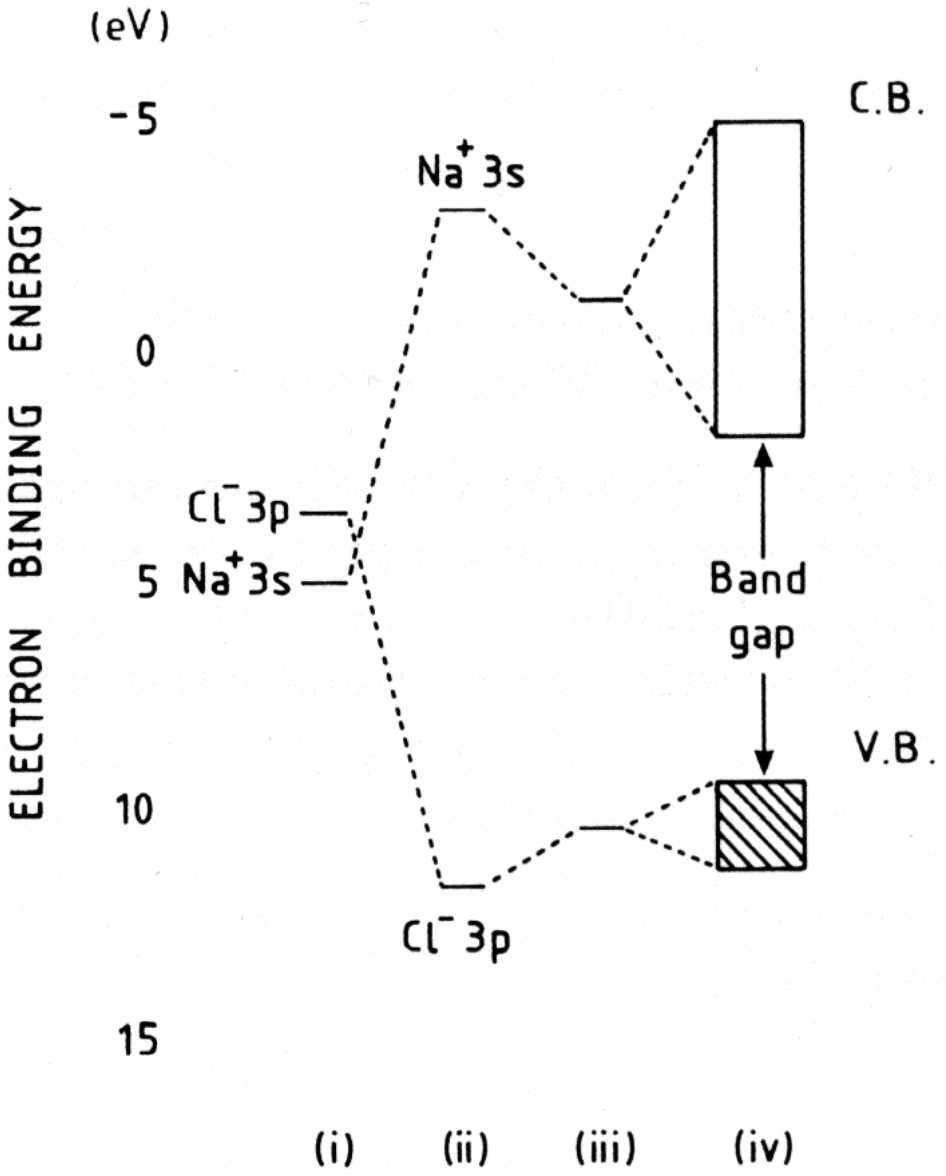


Semiconductors



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

Delocalized Bands – Localized Bonds

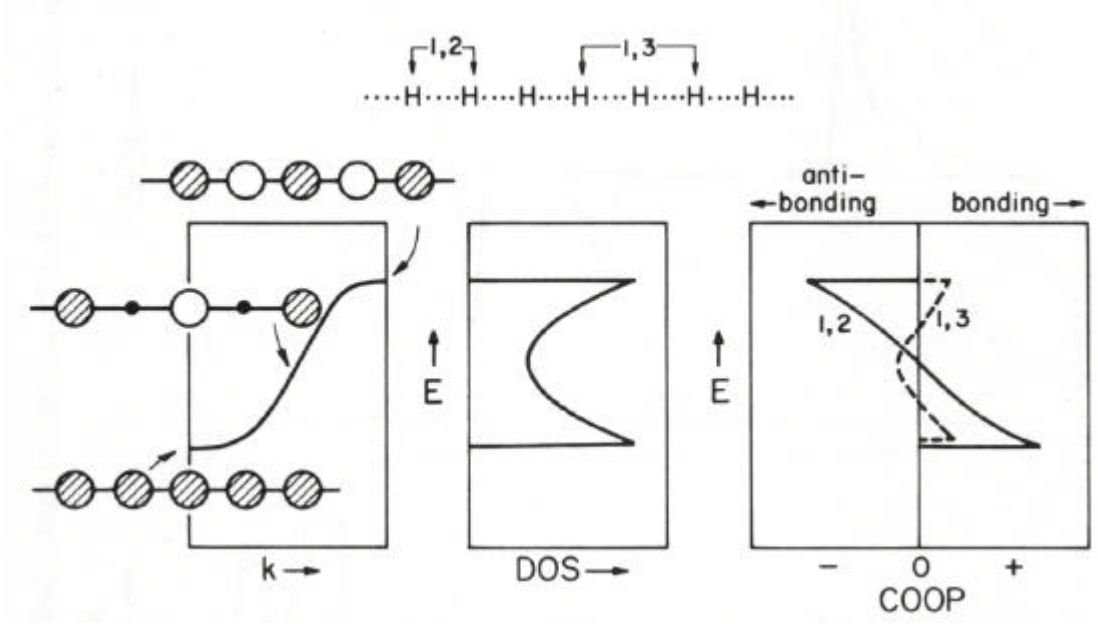
Molecules: Mulliken overlap population $S\ 2\ c_1\ c_2\ S_{12}$

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

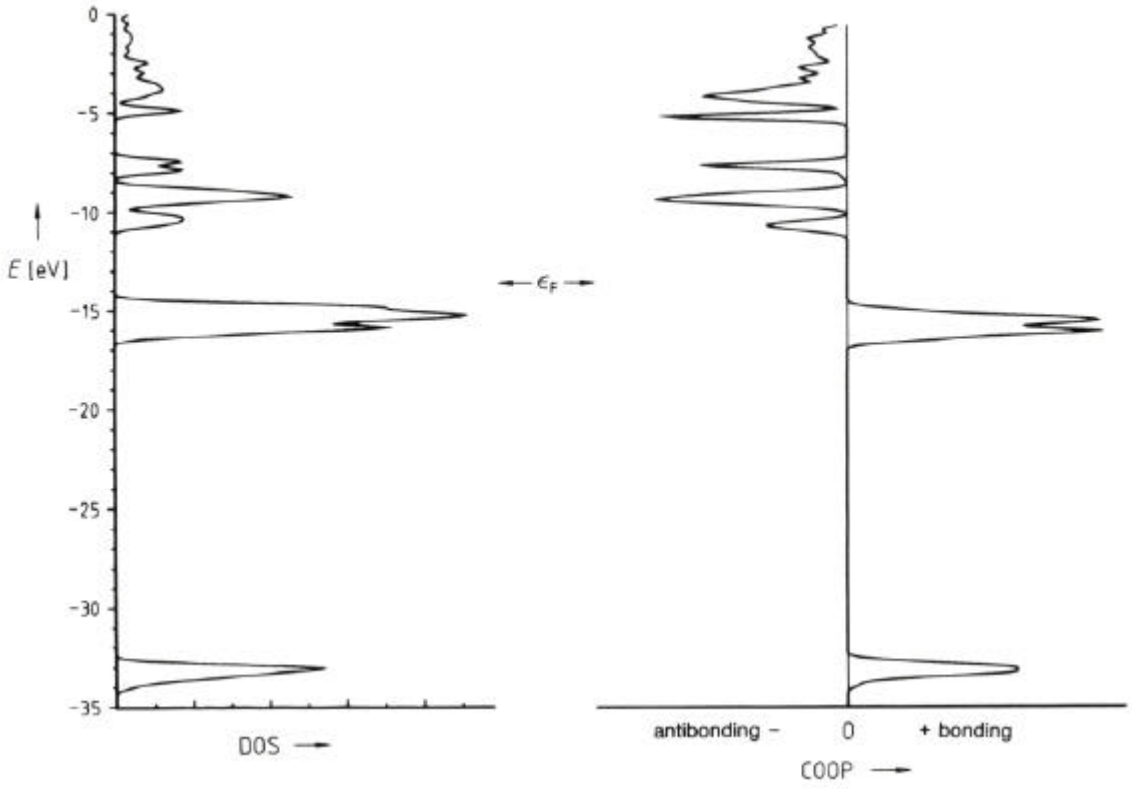


COOP curves

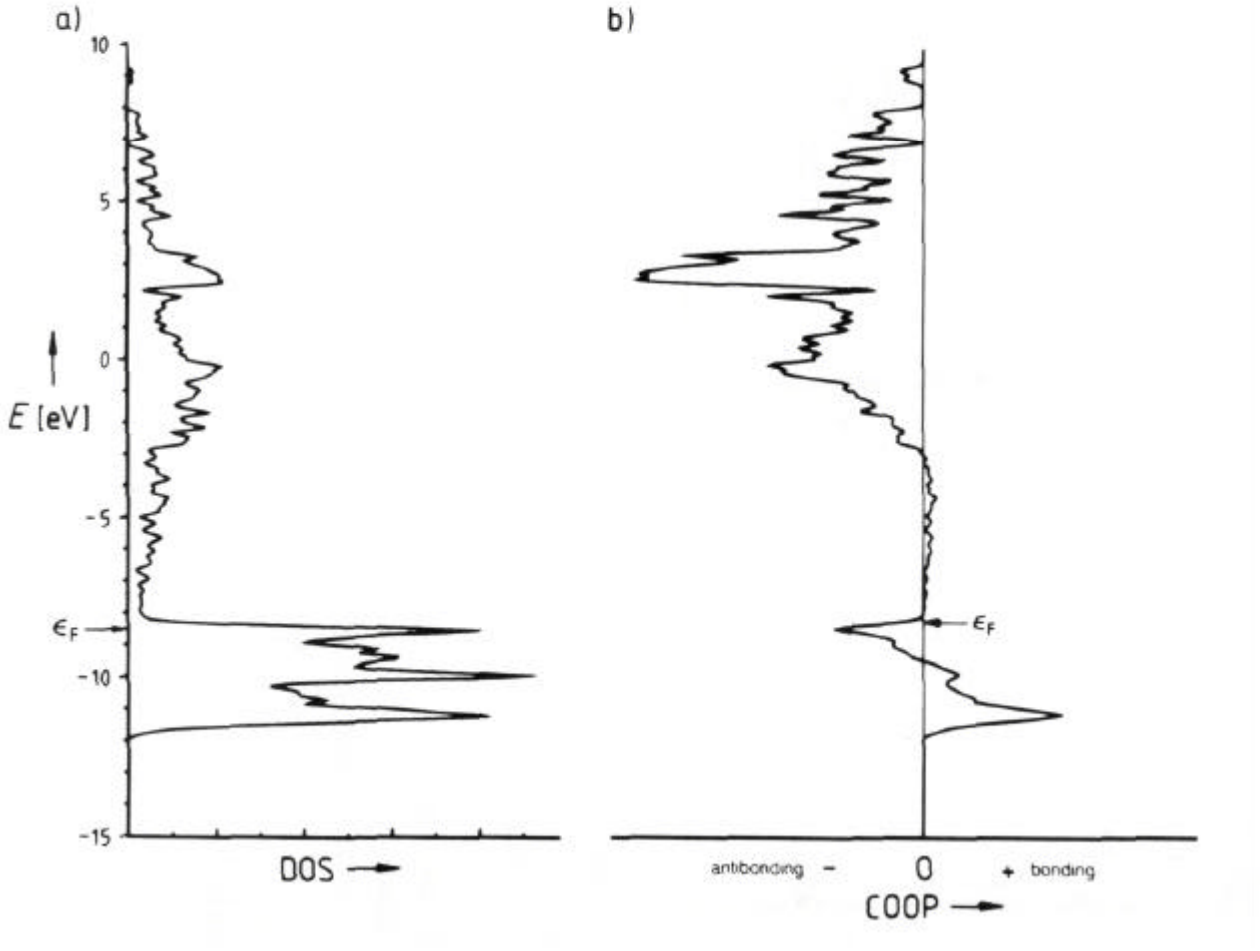
Sign – positive = bonding, negative = antibonding

Amplitude – depends on DOS, orbital overlap, MO coefficients

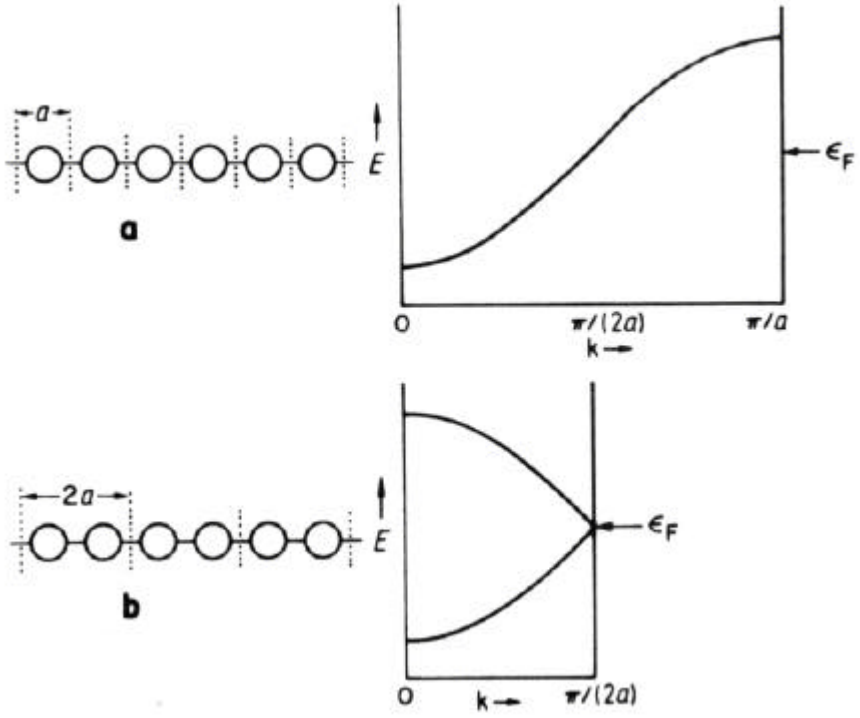
DOS and COOP for the Ti-O bonds in rutile



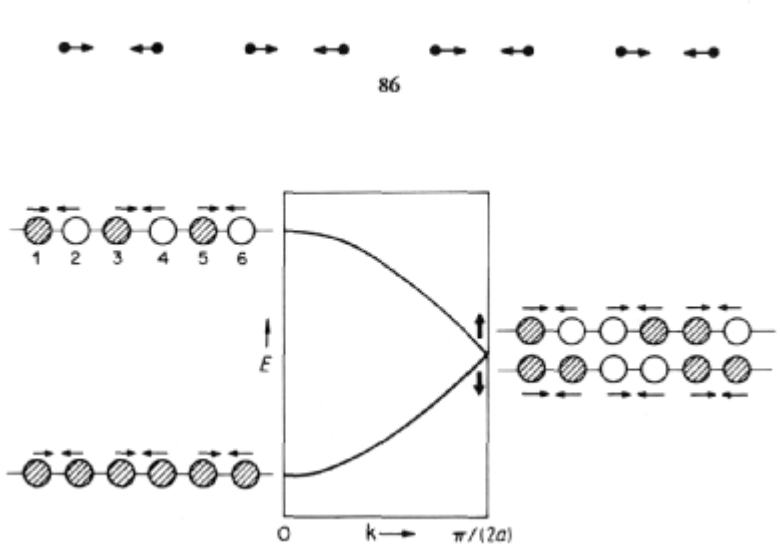
DOS and COOP for the Ni-Ni bonds in Ni metal



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