Chemical Bonding

type	Energies	Forces
ionic	$E \sim 1/r$	$F \sim 1/r^2$
covalent	$E \sim 1/r^3$	$F \sim 1/r^4$
van der Waals	$E \sim 1/r^5$	$F \sim 1/r^6$

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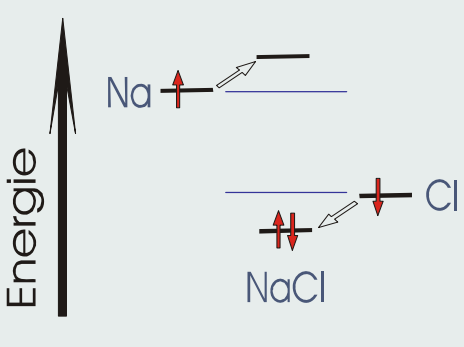
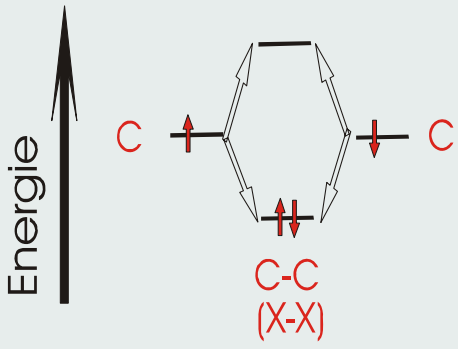
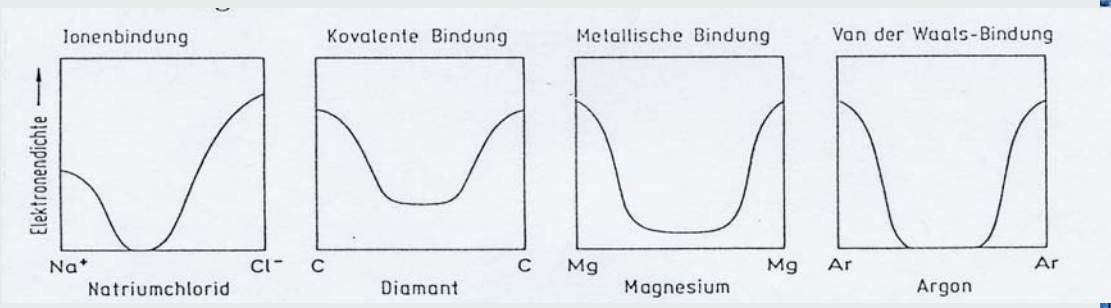
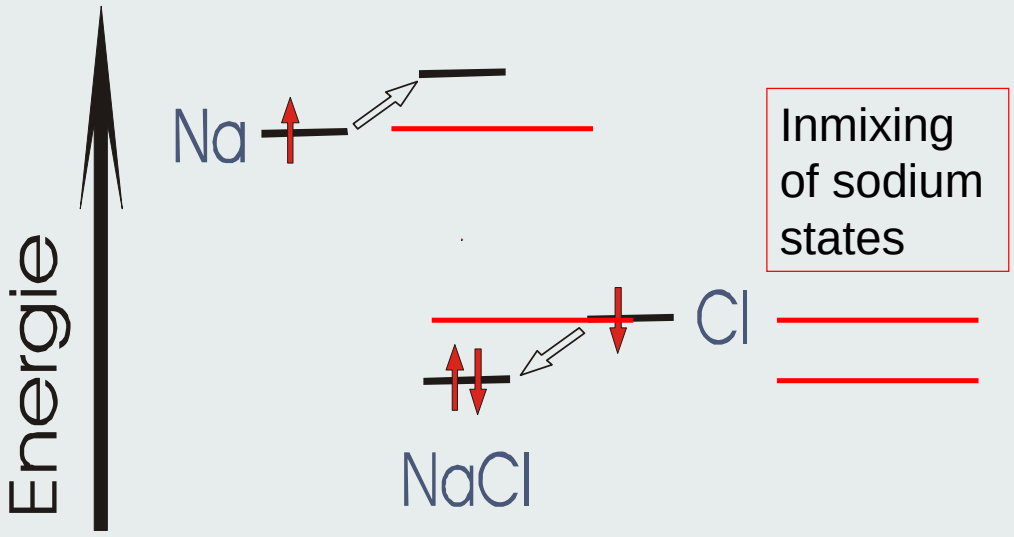
Chemical Bonding







Chemical Bonding



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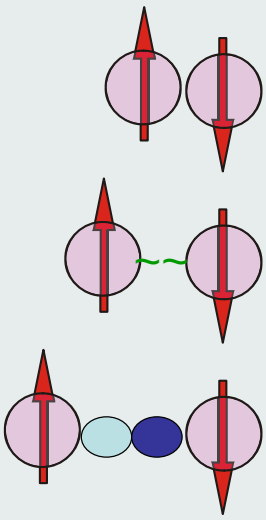
Antiparallel Couplings



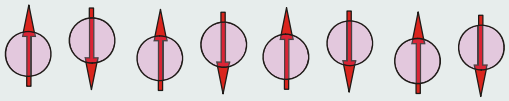
Chemical bond

Cooper pair (superconductivity)

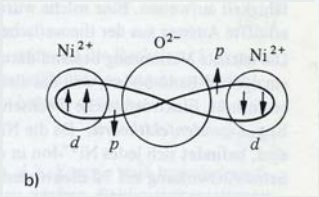
Antiferromagnetic coupling

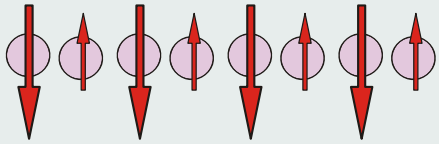
Collective Couplings

ferro

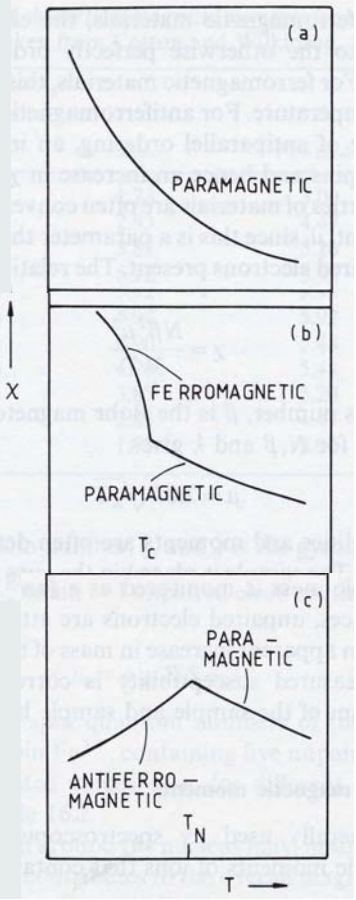


antiferro

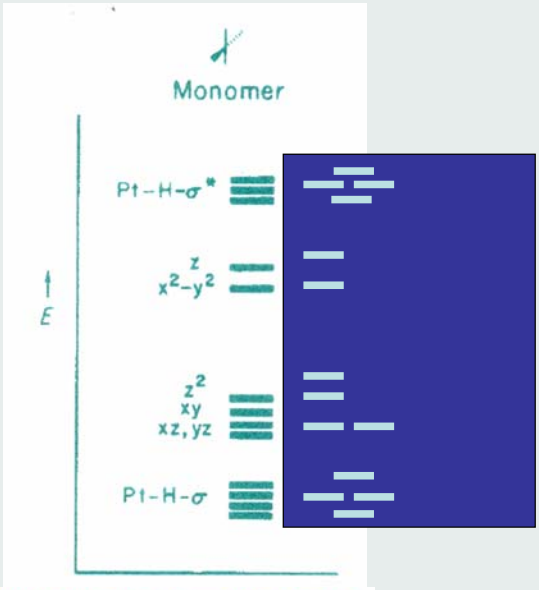




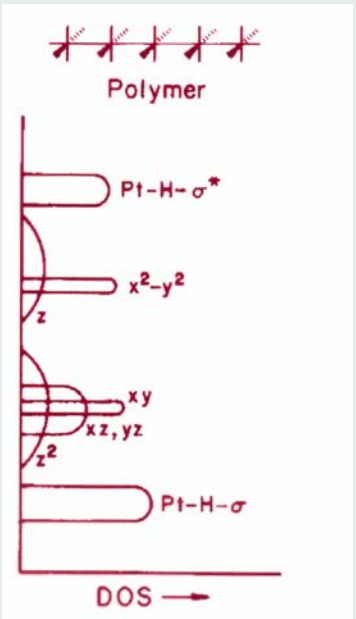
ferri



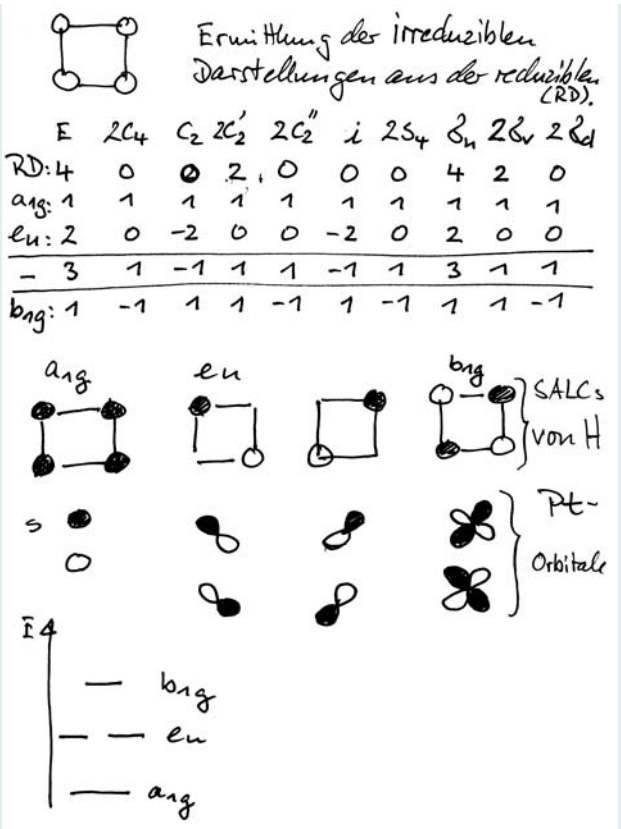
Molecules and Solids



R. Hoffmann, Solids and Surfaces, VCH, Weinheim 1988



PtH Bonds



LCAO in Polymers

LCAO approach

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

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

1

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

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

2

k controls the combination of orbitals (basis functions)
if k=0 all orbitals are unchanged
if k= every other unit cell has inversed orbital signs
a is the lattice constant (1D problem, chain)

What is k ?

k controls the combination of orbitals (basis functions)
if k=0 all orbitals are unchanged
if k= every other unit cell has inversed orbital signs
a is the lattice constant (1D problem, chain)

k is also a node counter
as k has a directionality it is always a vector (3D: k_x k_y k_z)
if there are n orbitals in the set of one kind,
there are n k vectors from k=0 to k=

π/a

What is k ?

LCAO approach

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

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

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

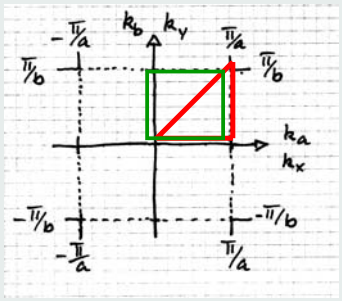
$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$

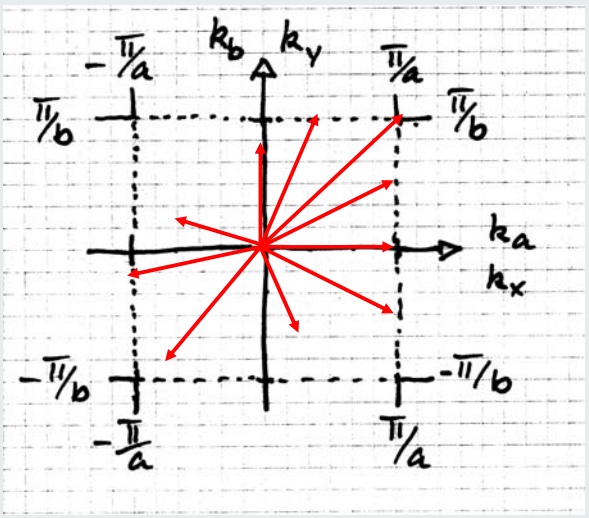
2

note that k has a reciprocal meaning

if k is small the wave of orbitals of the same sign modulation has a large length

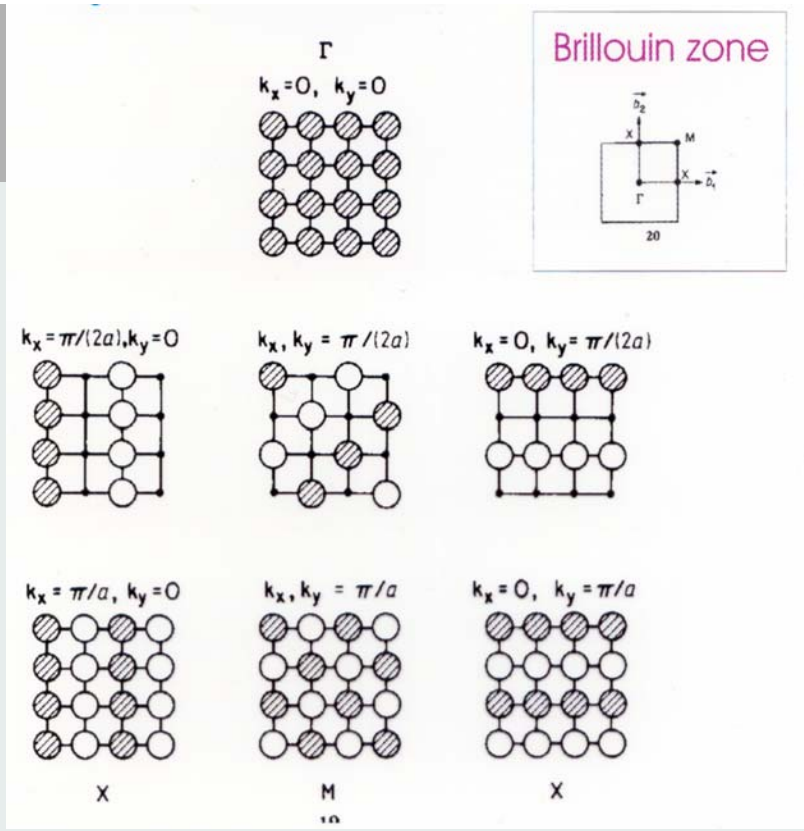
k-Vektors and Brillouin Zones



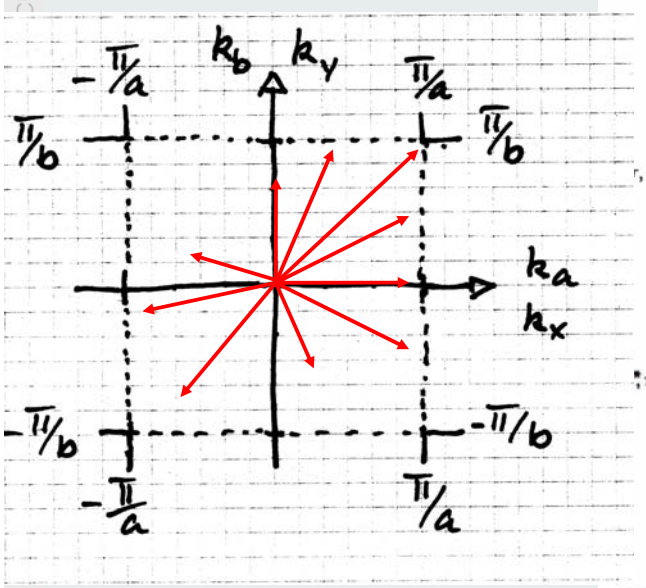


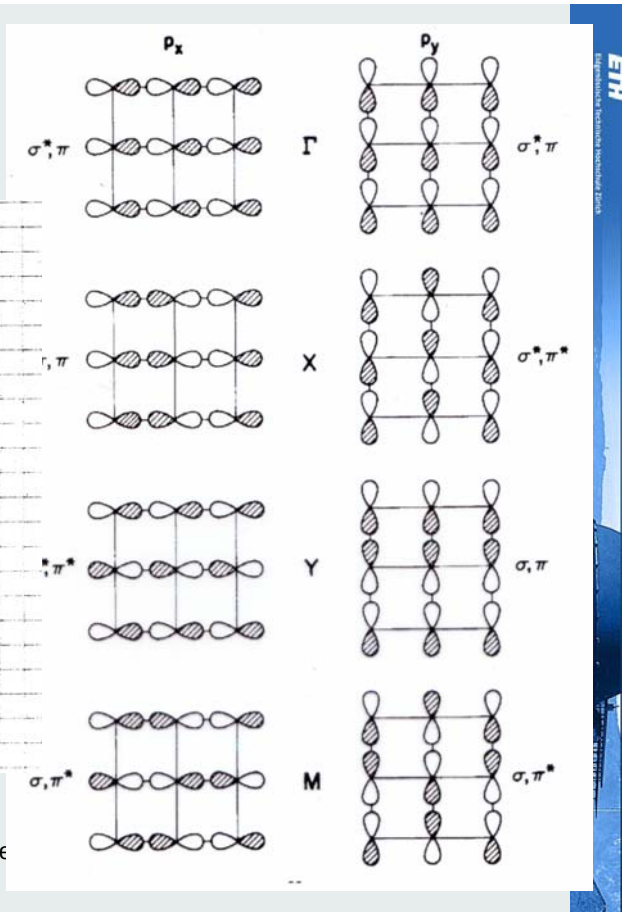
The Brillouin zone contains all the reciprocal vectors half way inbetween the first Bragg reflections

2D LCAO combinations

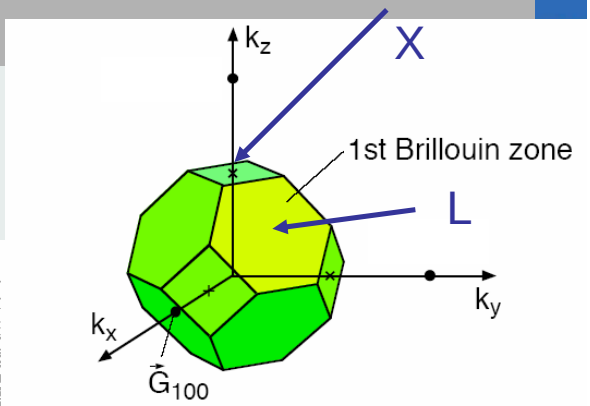


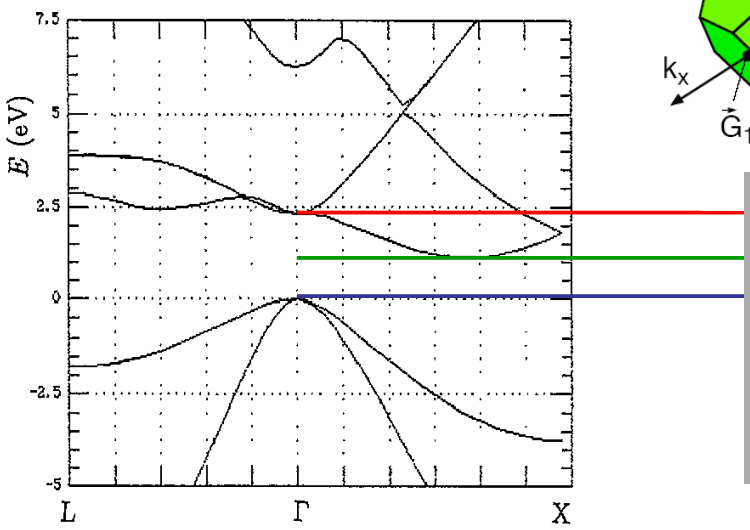
2D LCAO combinations





Bandstructure of Silicion





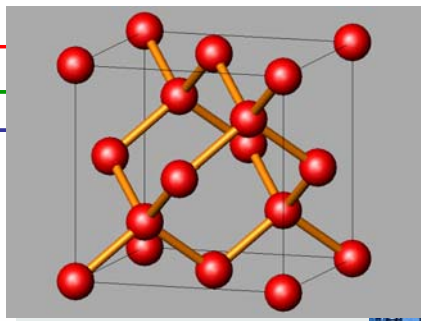


Figure 3. The band structure of silicon calculated with a (3s, 3p, 3d) basis set with complete configuration self-consistency.

Strength of Interaction and Band Width

the band width or the dispersion of the band depends on the strength of the interaction this is determined by the overlap integral and thus, is a function of the distance

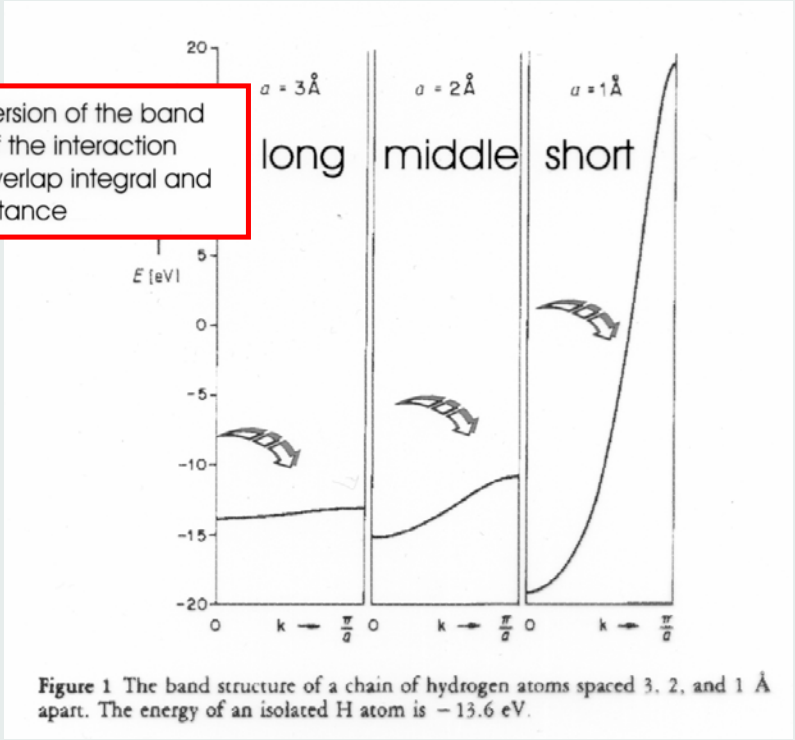
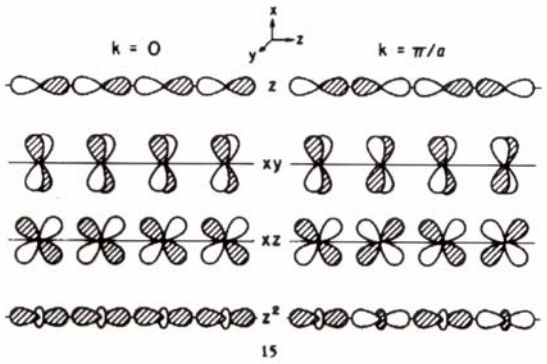


Figure 1 The band structure of a chain of hydrogen atoms spaced 3, 2, and 1 Å apart. The energy of an isolated H atom is −13.6 eV.

Strength of Interaction and Band Width



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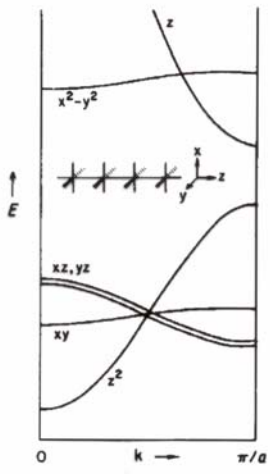
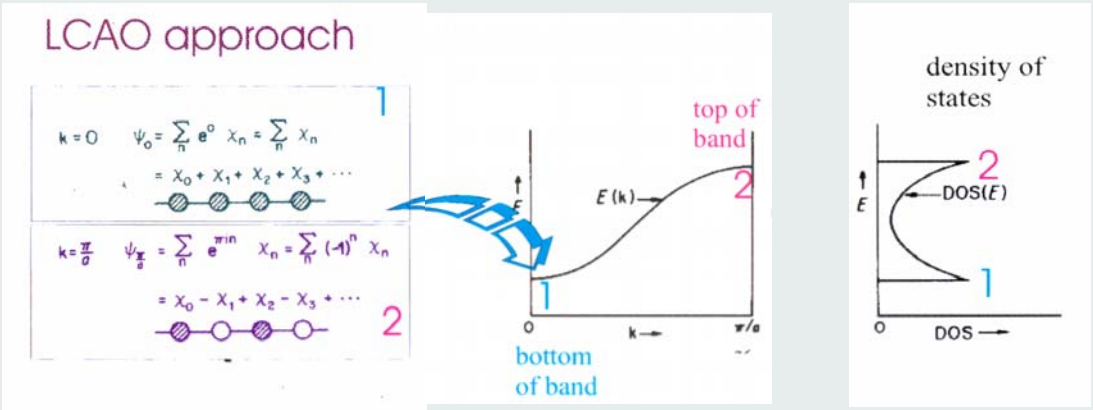
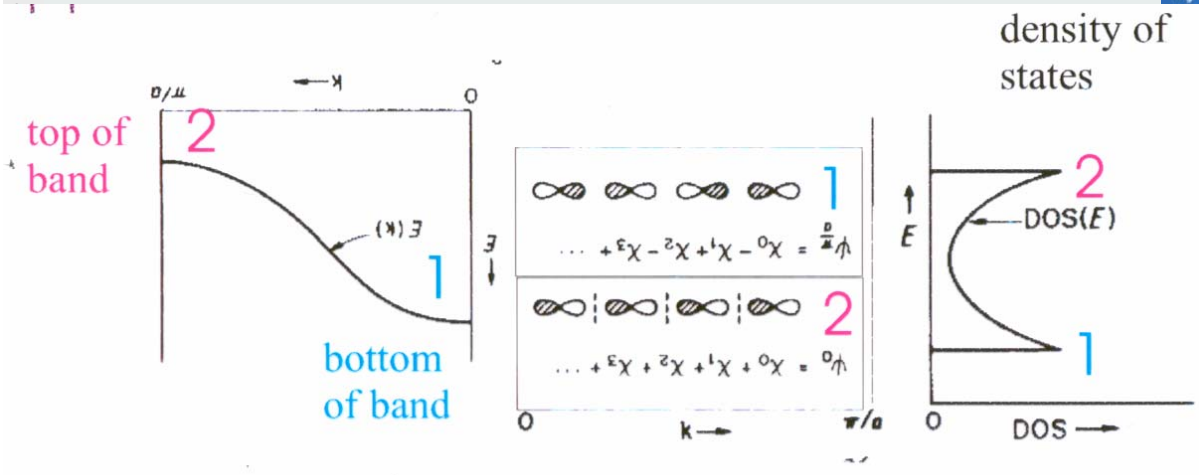


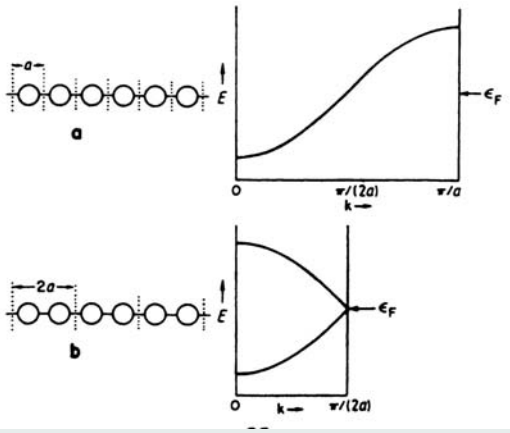
Solids

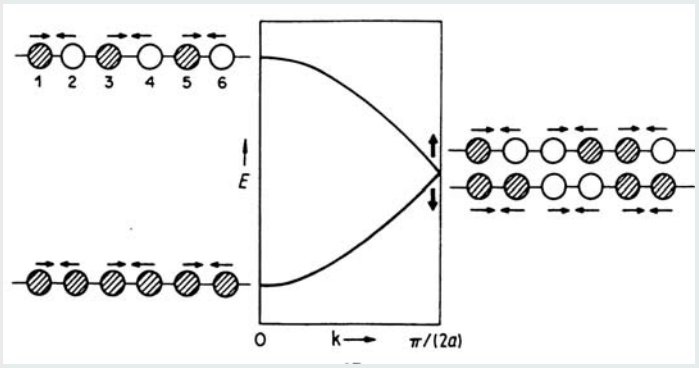


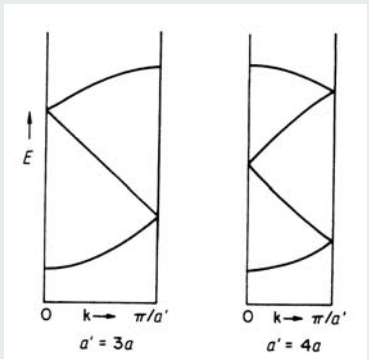
Solids



Degeneracy and Distortions



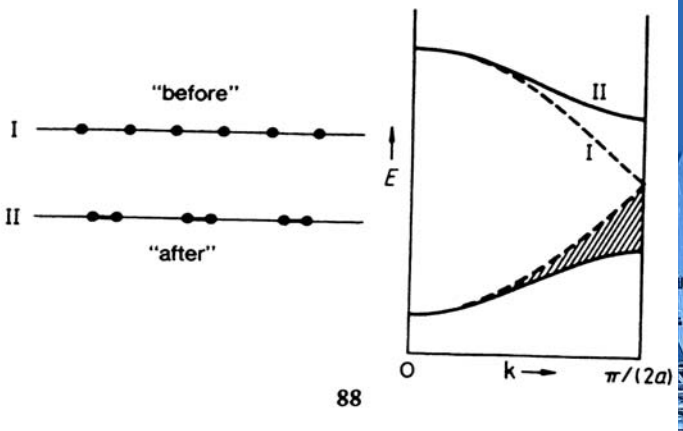




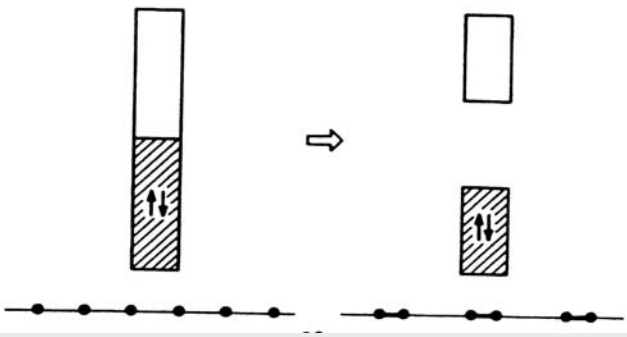
Degeneracy and Distortions

Peierls distortion in 1D systems

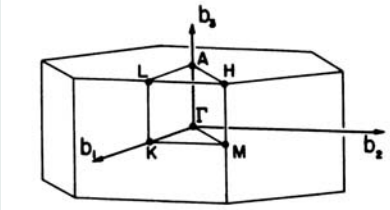
Cf. Jahn-Teller distortions

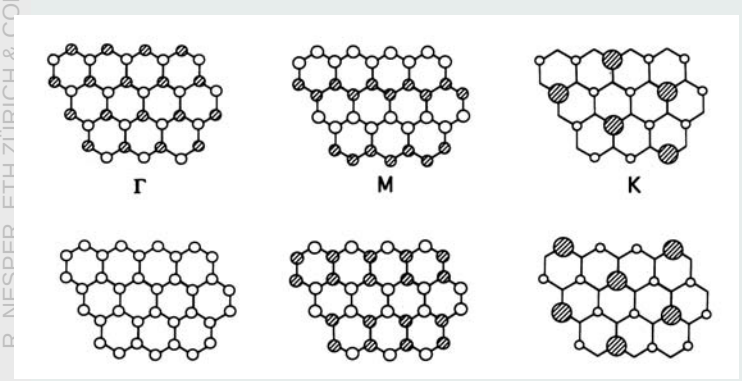


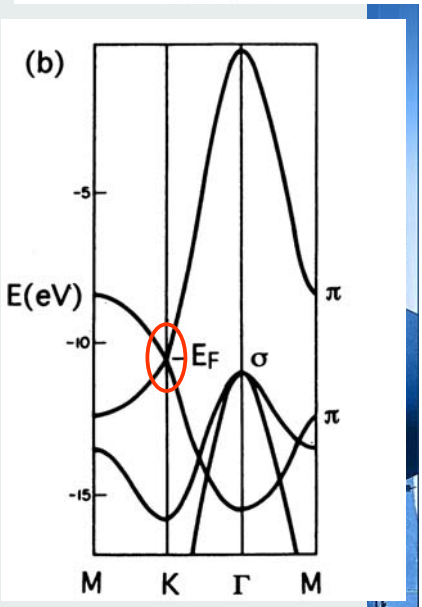
88



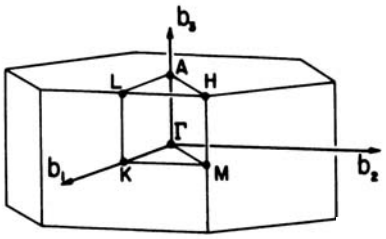
Graphite

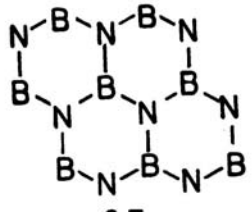


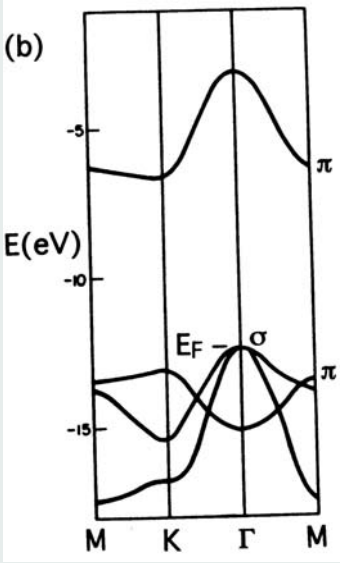


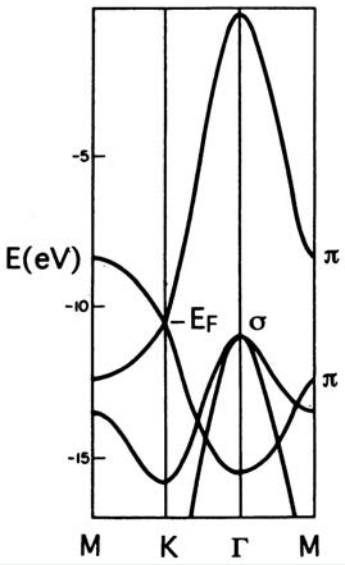


Bornitride - BN

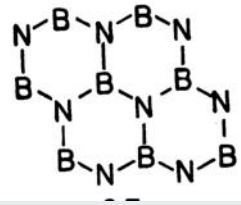


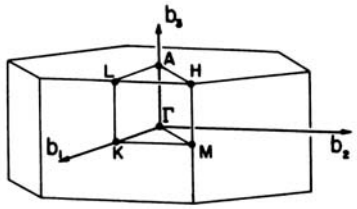


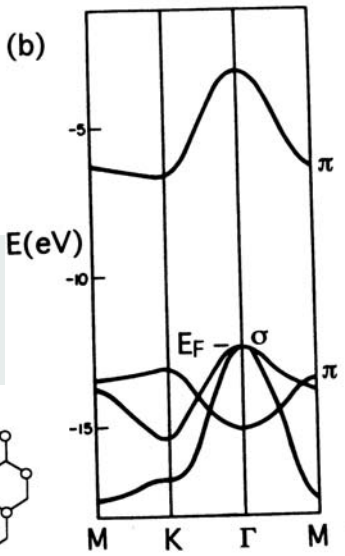


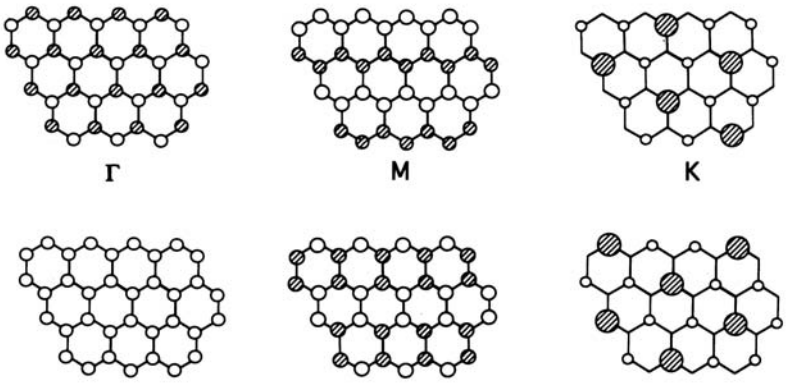


Bornitride - BN

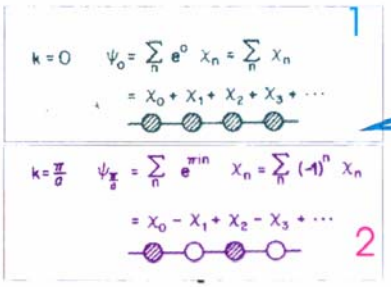




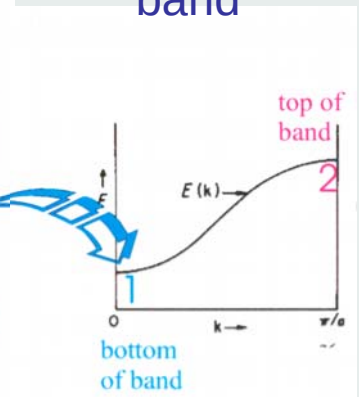




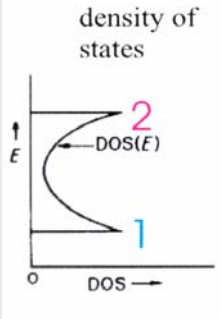
Density of States (DOS)



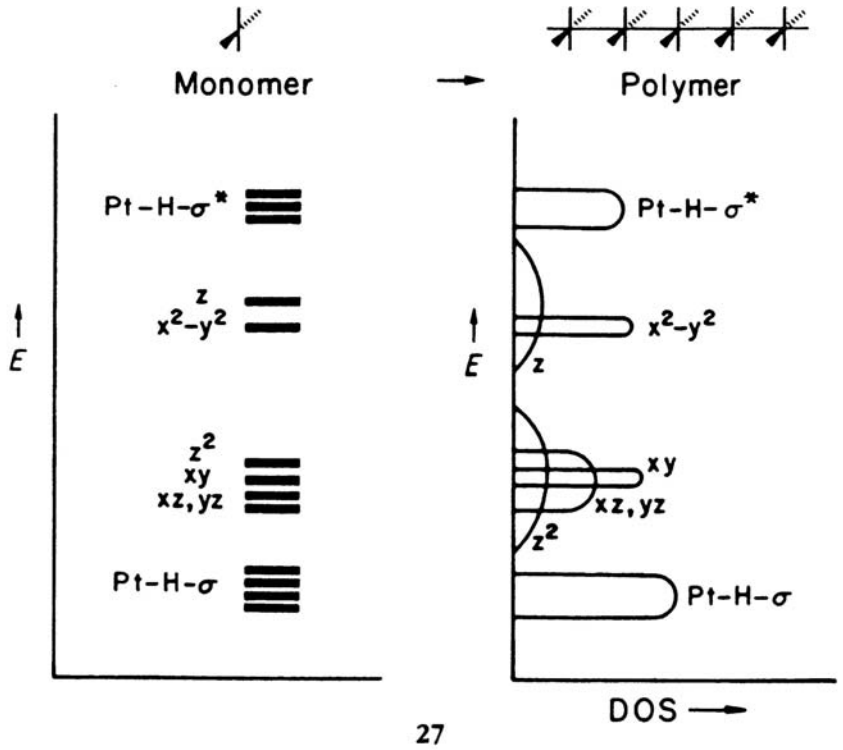
band



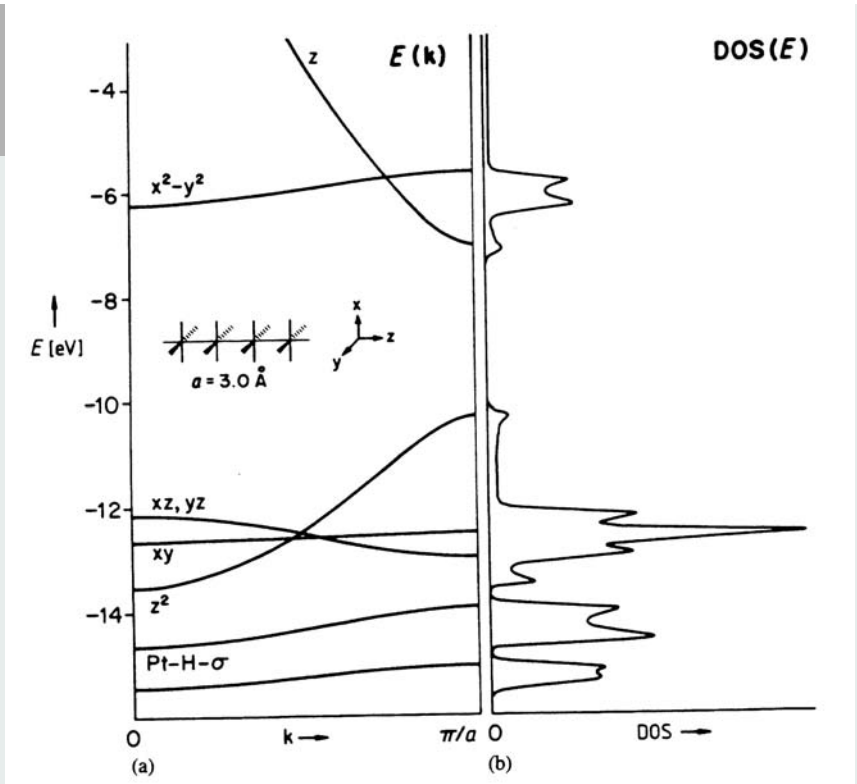
(DOS)



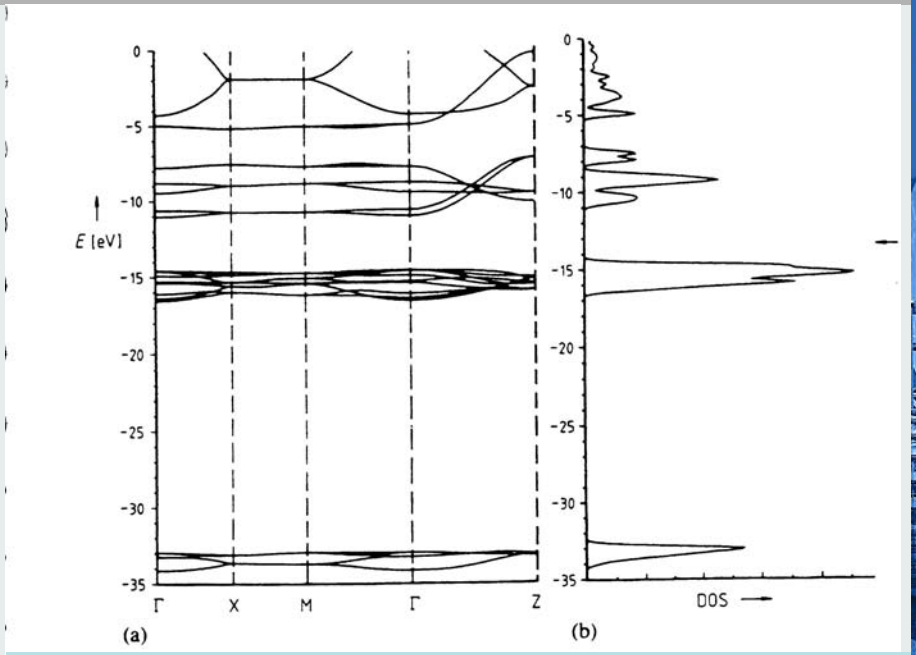
DOS –PtH_4-Polymer



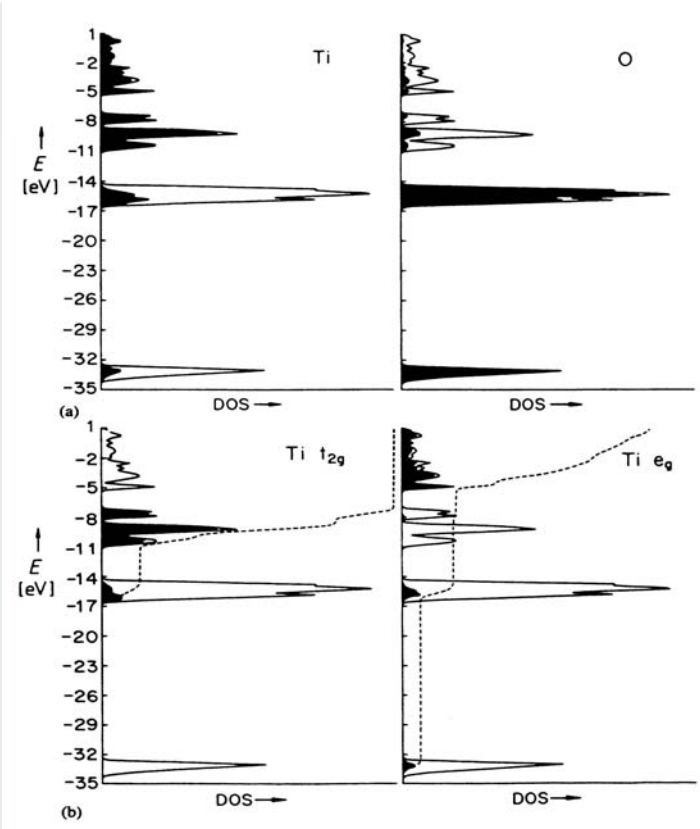
DOS of PtH_4 Chain



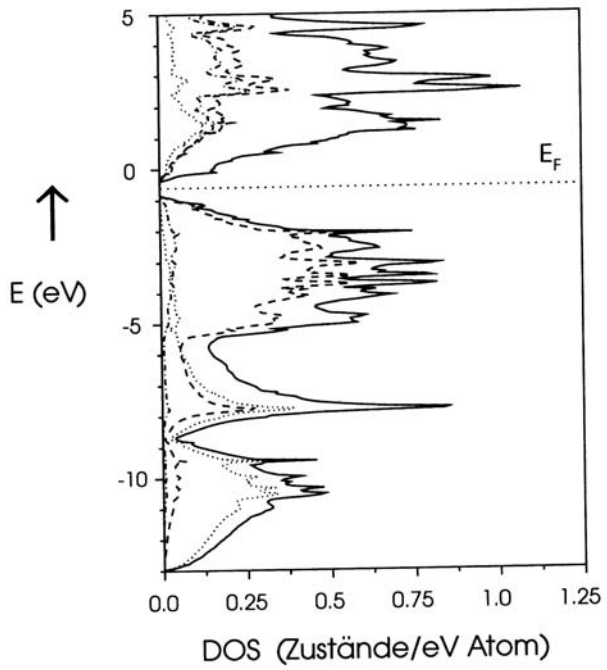
Band structure of ??

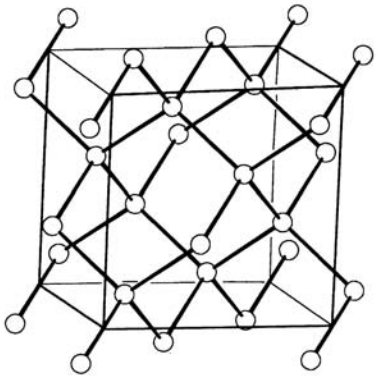


Where are the electrons of …?

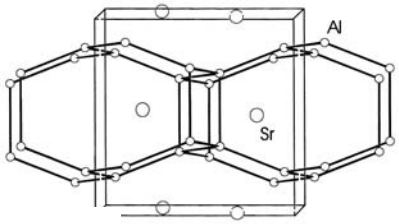


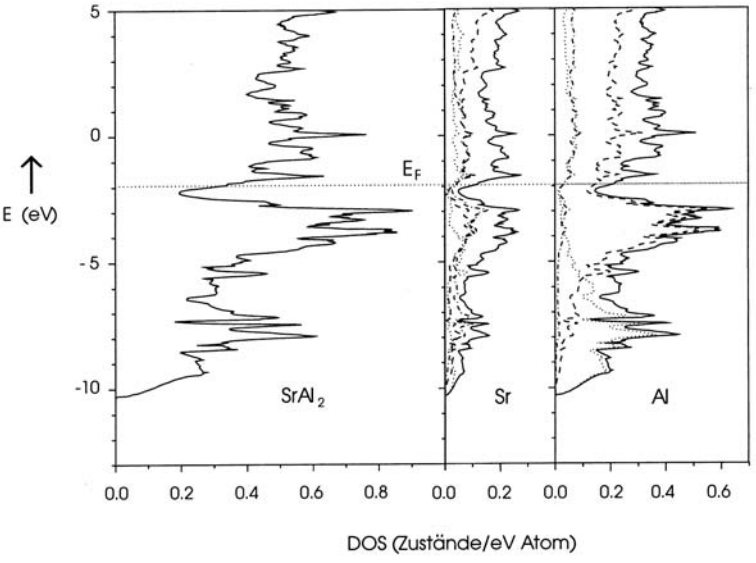
Structure and DOS



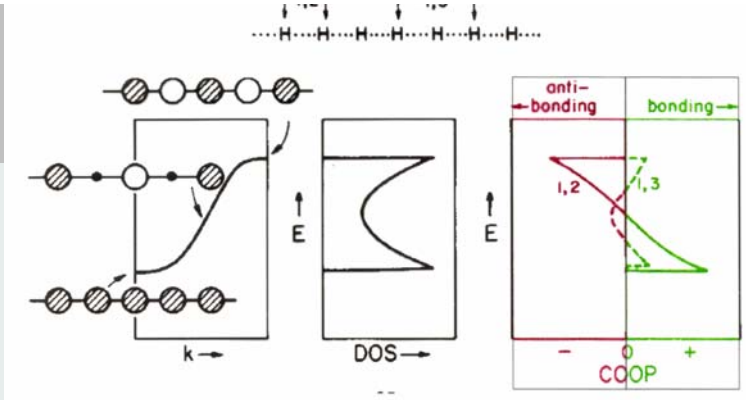


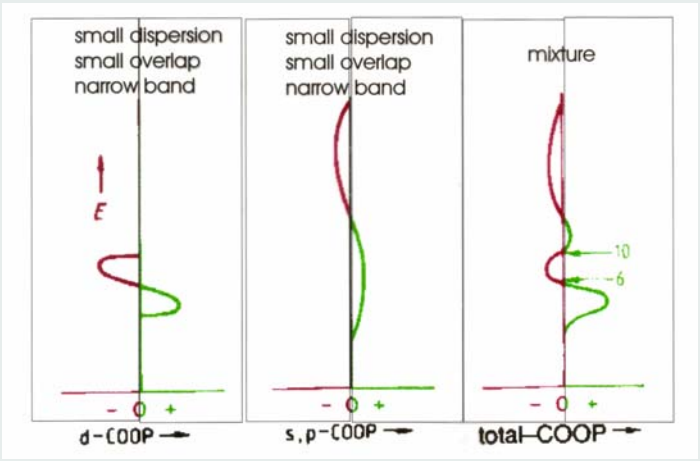
Structure and DOS





Where are the Bonds?



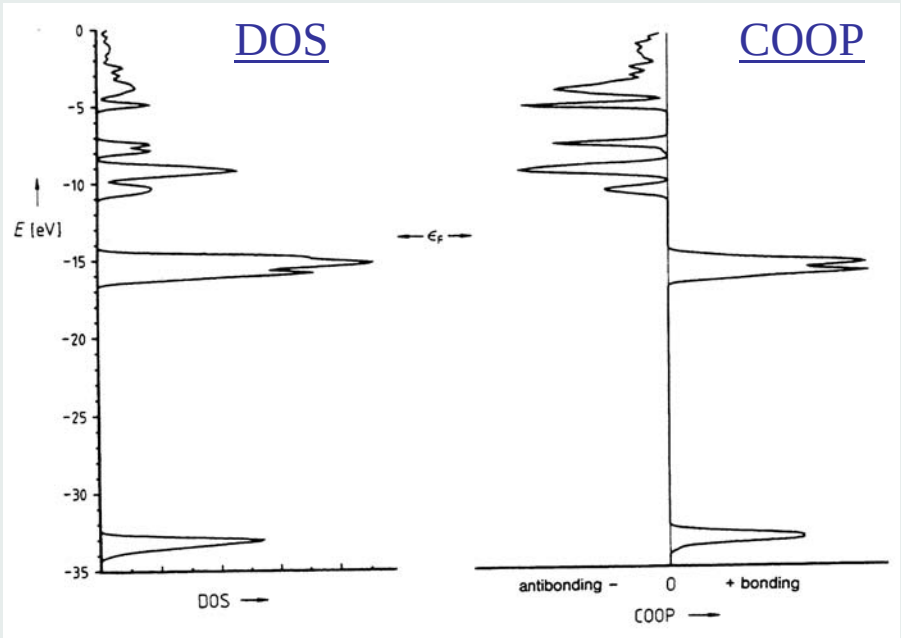


Choose a bond or a set of bonds and calculate overlap weighted DOS

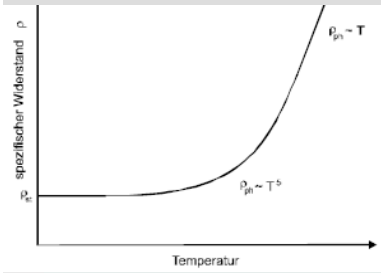
$c_i c_j S_{ij}$

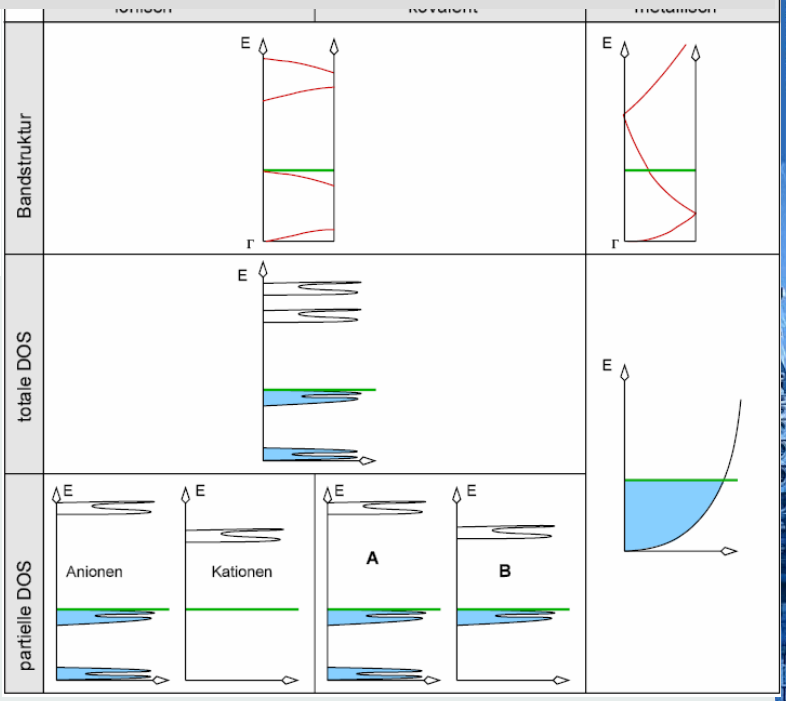
➔ $S_{ij} < 0$ antibonding
➔ $S_{ij} > 0$ bonding

From DOS to Bonds

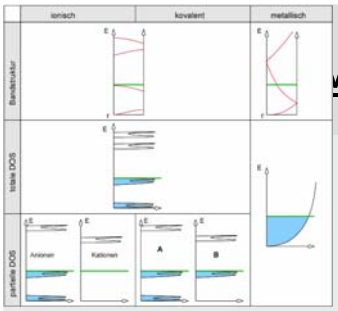


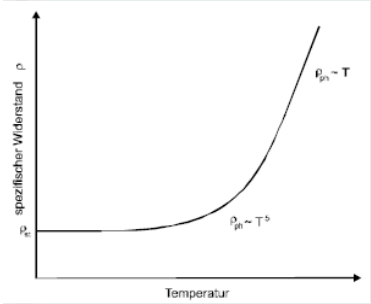
Metals, Semiconductors, Insulators





Metals, Semiconductors, Insulators



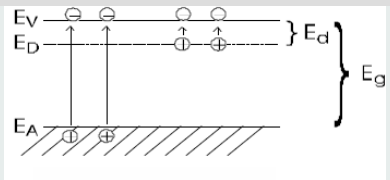


$T \ll \Theta_D$: $\rho_{Ph} \propto T^5$ (Kleinwinkelstreuung)

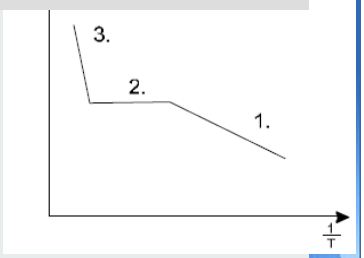
und

$T \gg \Theta_D$: $\rho_{Ph} \propto T$

wobei Θ_D die Debye-Frequenz des Festkörpers ist.



$$\sigma = n e \mu_n + p e \mu_p$$



1. *Störstellenreserve* (E_d » kT):
Die thermische Energie reicht aus, um einige der Donatoratome zu ionisieren, d.h. um Elektronen aus den Donatorniveaus ins Leitungsband anzuregen.

$$n \propto e^{\frac{-E_d}{2kT}}$$

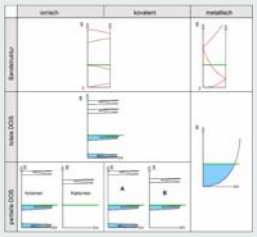
2. *Störstellenerschöpfung* (E_d « kT « E_g):
Alle Donatoratome sind ionisiert, aber die thermische Energie reicht noch nicht aus, um Elektronen über die intrinsische Bandlücke anzuregen.

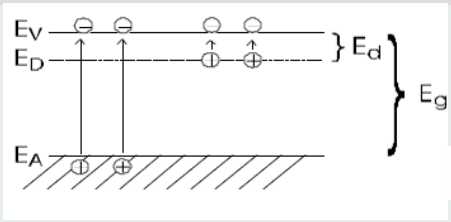
$$n = \text{const.}$$

3. *Eigenleitung* (E_g « kT):
Die thermische Energie reicht nun aus, um intrinsische Ladungsträger zu erzeugen, d.h. Elektronen über die Bandlücke anzuregen. Gleichzeitig wird die Bedeutung der dotierten Ladungsträger immer kleiner.

$$n \propto e^{\frac{-E_g}{2kT}}$$

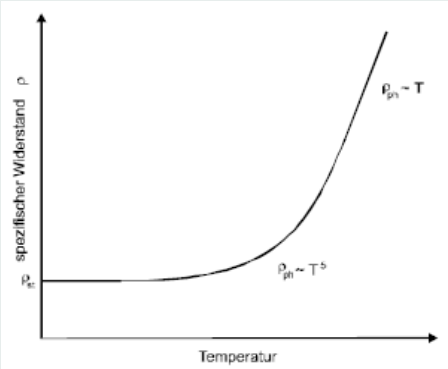
Metals, Semiconductors, Insulators





$$\sigma = n e \mu_n + p e \mu_p$$

Temperaturabhängigkeit der Leitfähigkeit setzt sich aus der der Beweglichkeit m und der Ladungsträgerkonzentration n (Elektronen) bzw. p (Löcher) zusammen



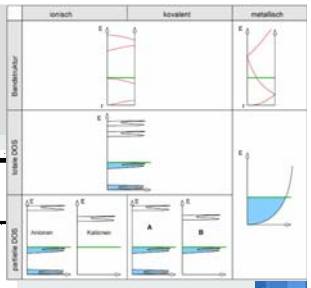
$T << \Theta_D$: $\rho_{Ph} \propto T^5$ (Kleinwinkelstreuung)

und

$T >> \Theta_D$: $\rho_{Ph} \propto T$

wobei Θ_D die Debye-Frequenz des Festkörpers ist.

Metals, Semiconductors, Insulators

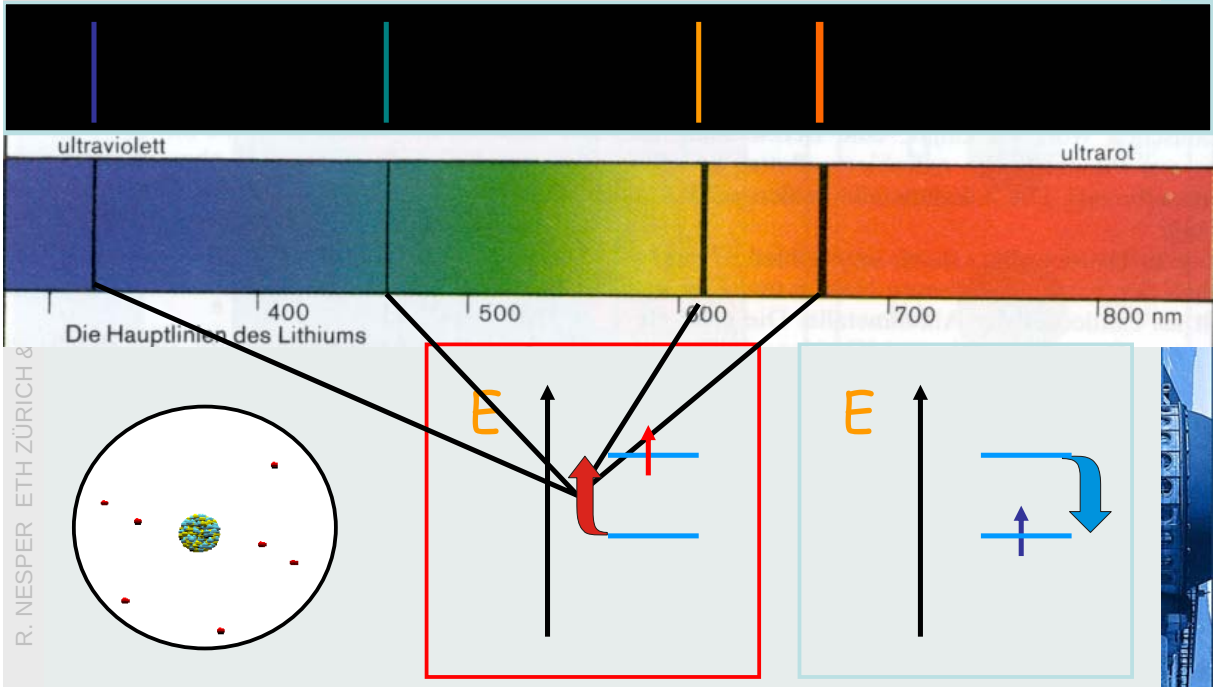


I–VII compounds		II–VI compounds		III–V compounds	
LiF	11	ZnO	3.4	AlP	3.0
LiCl	9.5	ZnS	3.8	AlAs	2.3
NaF	11.5	ZnSe	2.8	AlSb	1.5
NaCl	8.5	ZnTe	2.4	GaP	2.3
NaBr	7.5	CdO	2.3	GaAs	1.4
KF	11	CdS	2.45	GaSb	0.7
KCl	8.5	CdSe	1.8	InP	1.3
KBr	7.5	CdTe	1.45	InAs	0.3
KI	5.8	PbS	0.37	InSb	0.2
		PbSe	0.27	β-SiC	2.2
		PbTe	0.33	α-SiC	3.1

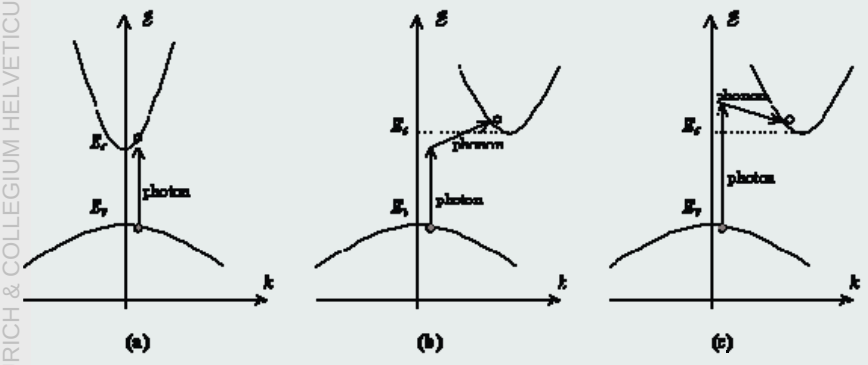
Some of these values, especially for the alkali halides, are only approximate.

Nitrides??

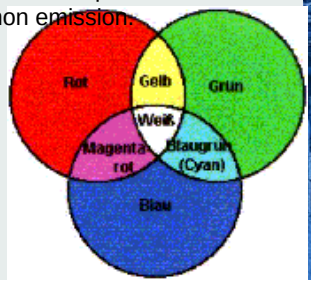
Optical Excitations and Colours



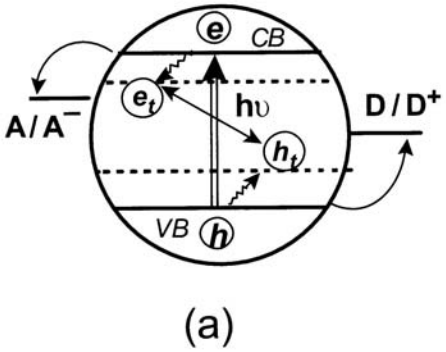
Light absorption and -emission



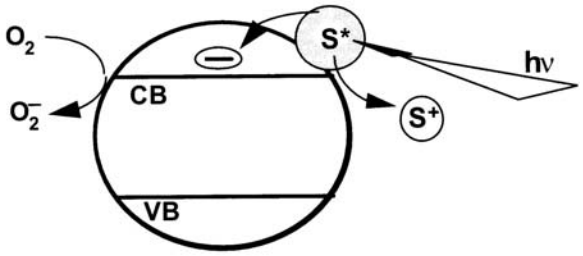
E-k diagram illustrating
(a) Photon absorption in a direct bandgap semiconductor
(b) Photon absorption in an indirect bandgap semiconductor assisted by phonon absorption
(c) Photon absorption in an indirect bandgap semiconductor assisted by phonon emission.



Excitation and Charge Separation



(a)



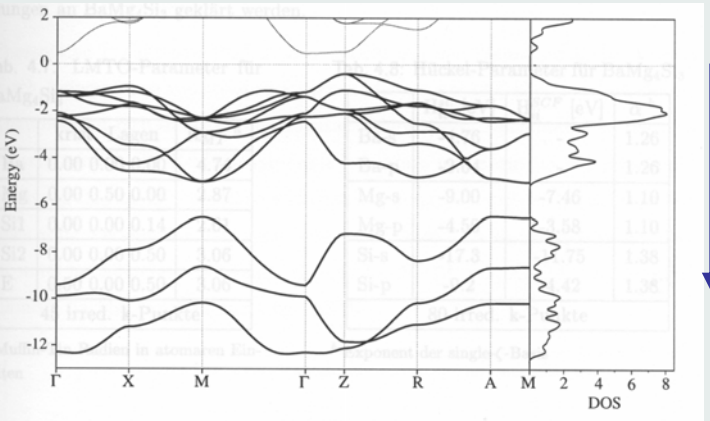
(b)

Fig. 19.1. Photoinduced charge transfer processes in semiconductor nanoclusters. (a) Under bandgap excitation and (b) sensitized charge injection by exciting adsorbed sensitizer (S). CB and VB refer to the conduction and valence bands of the semiconductor and e_t and h_t refer to trapped electrons and holes, respectively.

Electron – hole separation for avoiding quenching or recombination of charges

Photoelectron spectra (ESCA)

UPS: E_{rad} = UV radiation => valence states (bonds, etc)

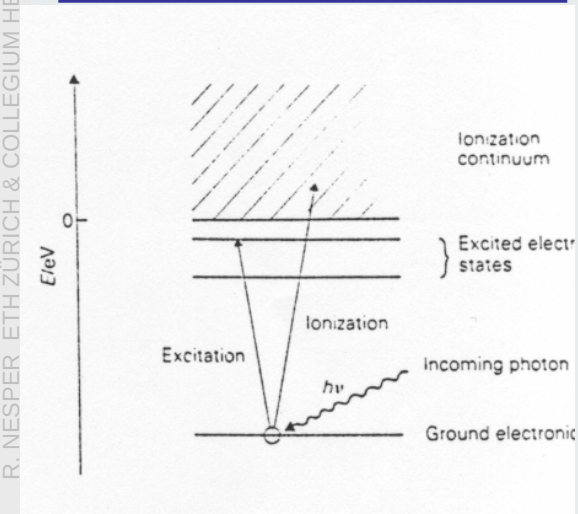


binding energy

Band structure DOS

Photoelectron spectra (ESCA)

E_{kin} (electron) = E_{rad} - E_{bind}



Surface method

2-3nm depth

Photoelectron spectra (ESCA)

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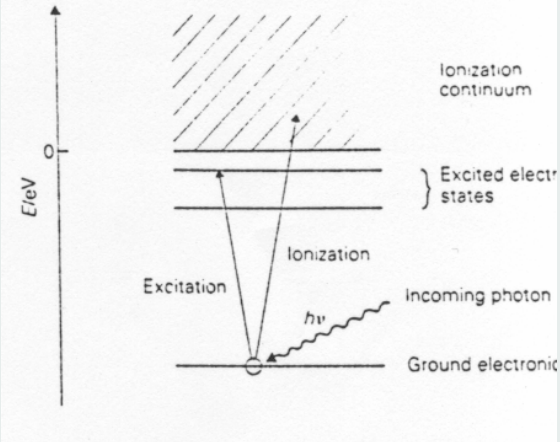
UPS: E_{rad} = UV radiation =>

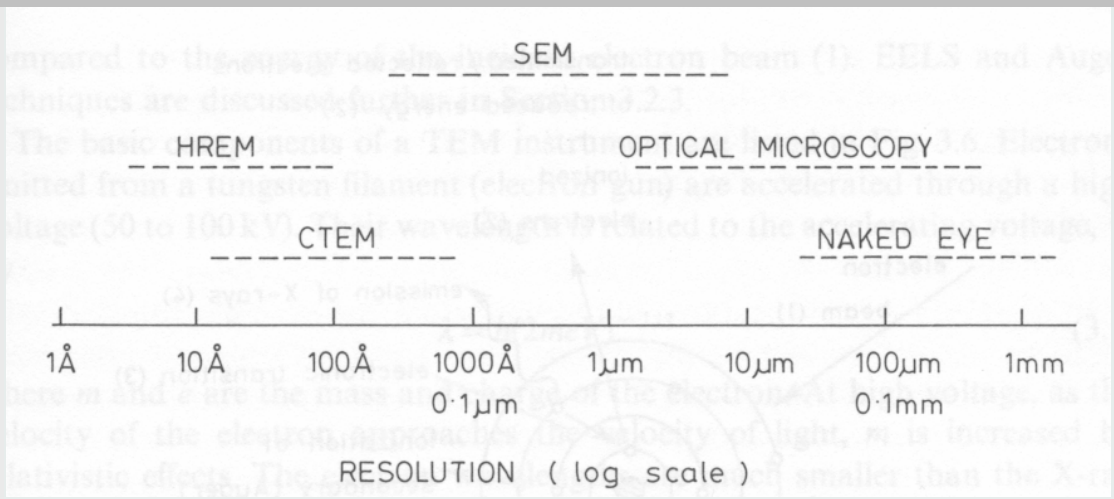
valence states (bonds, etc)

XPS: E_{rad} = X radiation =>

core states (oxidation states)

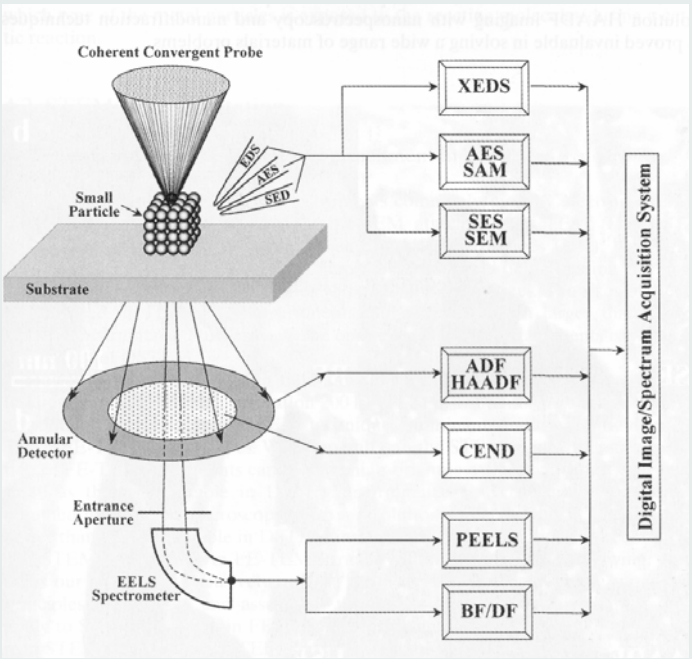


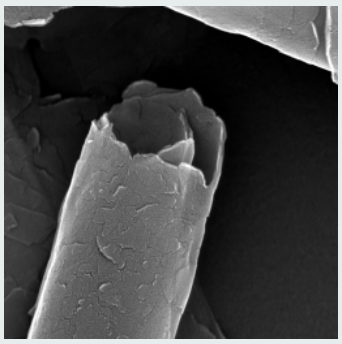
Microscopy



Scanning surface methods

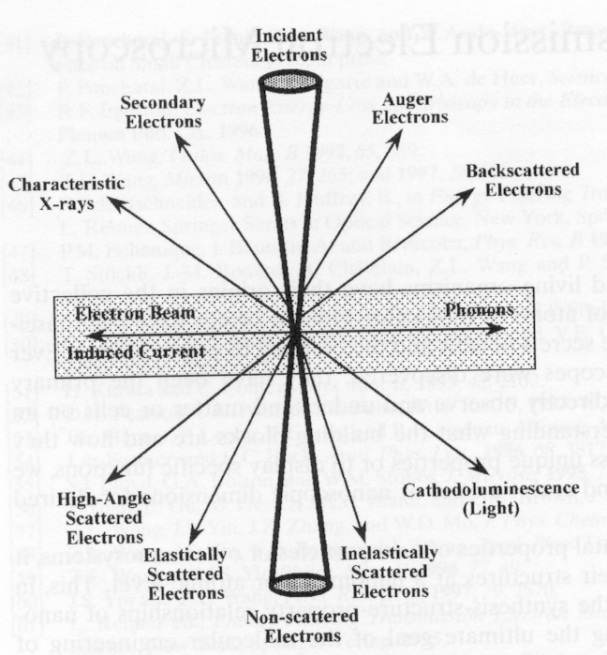
Scanning Electron Microscopy - SEM

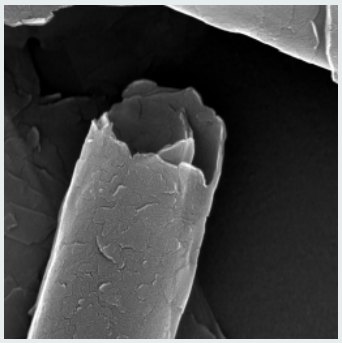




surface analysis : 1 µ m

Scanning Electron Microscopy

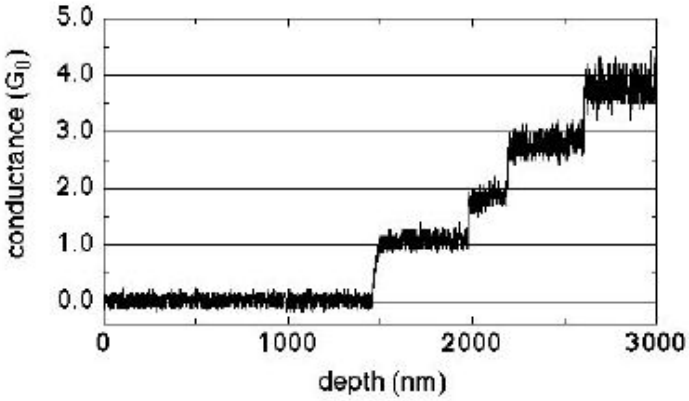




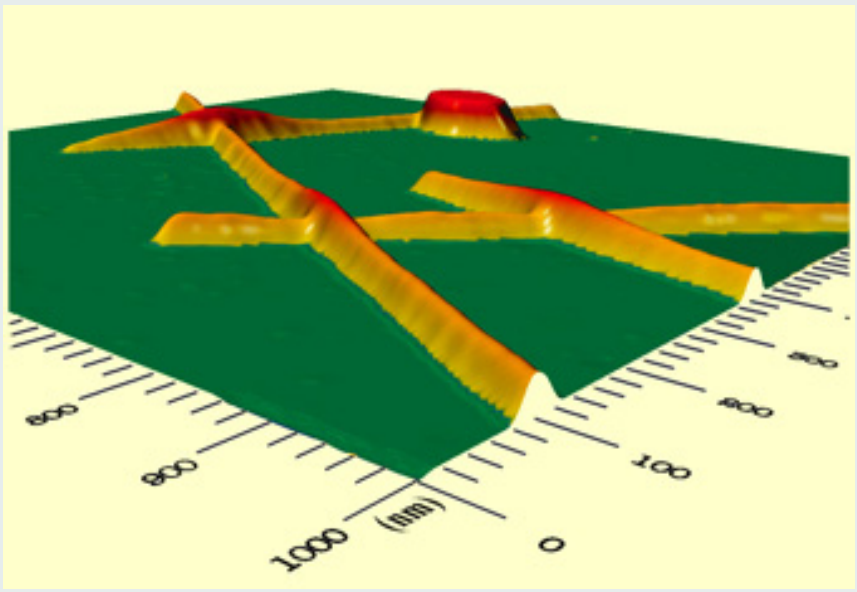
Scanning Probe Microscopies

1. Scanning tunneling Microscopy - STM
2. Atomic Force Microscopy - AFM
3. Magnetic Force Microscopy - MFM
4. Chemical Force Microscopies - CFM

Scanning Probe Microscopies



Scanning Surface Microscopies



Physical Effects and Methods

	Bond type	Electronic structure	Elemental analysis	Polycrystalline texture	Surface structure	Crystal defects	Local structure, CN, etc.	Crystal structure	Unit cell, space group	Amorphous or crystalline	Phase identification
X-ray diffraction	(√)			(√)		(√)	(√)	√	√	√	√
Electron diffraction and microscopy			√	√	√	√		√	√	√	√
Neutron diffraction						√		√	√	(√)	(√)
Optical microscopy				√	(√)	(√)				√	√
IR spectroscopy	(√)		(√)		√		√				√
UV, visual spectroscopy	√	√	(√)			(√)	√				
NMR, ESR spectroscopy	(√)	(√)	(√)			(√)	√				(√)
Electron spectroscopy—ESCA, XPS, UPS, AES, EELS	√	√	√		√	(√)	√				
X-ray spectroscopy—XRF AEFS, EXAFS	(√)	(√)	√		√	(√)	√				
Mössbauer spectroscopy	(√)		(√)				√				

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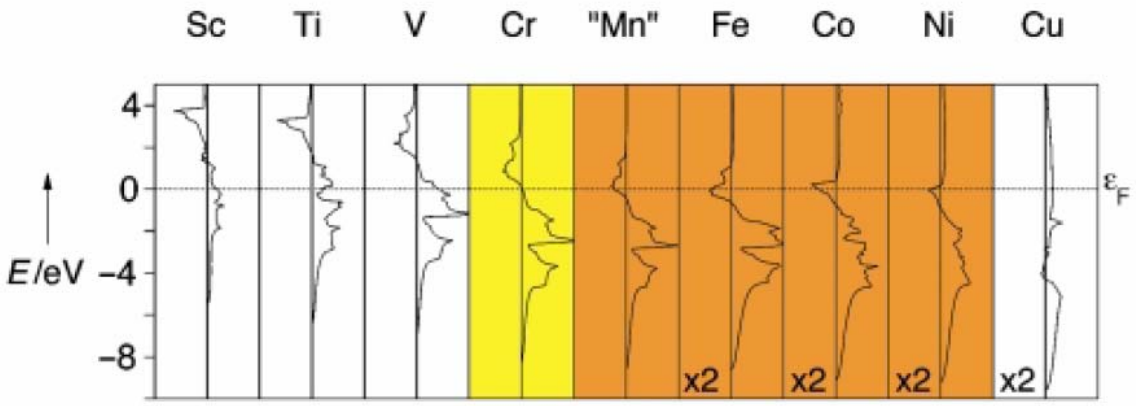
Physical Effects and Methods

EPMA	Electron Probe Micro Analysis	Analyse der charakteristischen
EMMA	Electron Microscopy with Micro Analysis	Röntgenstrahlung oder
AEM	Analytical Electron Microscopy	der Elektronenstrahlung ⇒
XRF	X-ray Fluorescence (charakteristische) Röntgenstrahlung, Moseleysches Gesetz	Elementaranalyse Analyse leichter Elemente
EDX	Energy Dispersive X-ray-Analysis	
EELS	Electron Energy Loss Spectroscopy	Analyse leichter Elemente
AES	Auger Electron Spectroscopy (Sekundärelektronen)	komplexe Spektren, bisher wenig untersucht
ESCA	Electron Spectroscopy for Chemical Analysis	$E^{\nu}_{Einfall} = E^{elektron}_{Bind} + E^{Elektron}_{Kin.}$ $E^{Elektron}_{Kin.}$ wird gemessen
XPS	X-ray Photoelectron Spectroscopy	⇒ Elektronenstruktur von
UPS	UV Photoelctron Spectroscopy	Feststoffen und Oberflächen
AEFS	Absorption Edge Fine Structure (XANES)	Oxidationszustände,
EXAFS	Extended X-ray Absorption Fine Structure	lokale Umgebung ausgewählter Atome
ESR	Electron Spin Resonance	Elektronenkonfiguration
EPR	Electron Paramagnetic Resonance	lokale Umgebung
ENDDR	Electron Nuclear Double Resonance	lokale Fehlstellen
Mößbauer	γ-Strahlen-Resonanz	Elektronenstruktur
STM	Scanning Tunnel Microscopy	magnetische Struktur
LEED	Low Energy Electron Diffraction	Oberflächenstrukturen

Magnetism

Angew. Chem. Int. Ed. **2000**, *39*, 1560 – 1585



Magnetism

Angew. Chem. Int. Ed. **2000**, *39*, 1560 – 1585

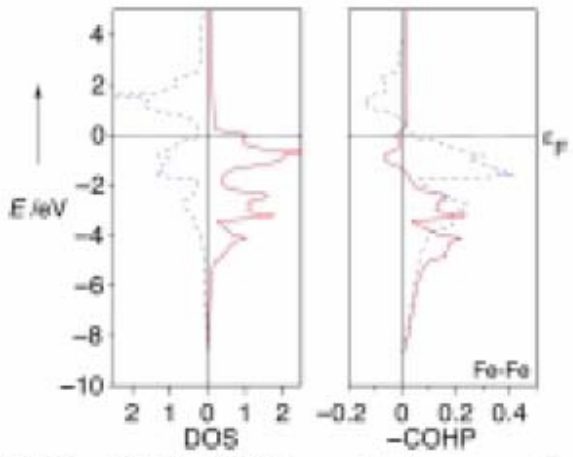


Figure 17. DOS and Fe-Fe COHP curves for ferromagnetic α-Fe. In each plot, the solid red/dashed blue line corresponds to the α/β spins. All curves have been shifted in energy so that ε_F, indicated with a horizontal dotted line, lies at 0.0 eV.