Fyzikální elektronika povrchů

Physical Electronics of Surfaces

(NEVF170)

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Part 1

1. Geometric & electronic structure of solids
2. Drude model, Sommerfeld model, el. bands, Fermi energy
3. Solid surfaces (model and real), electronic structure of surfaces, (electro)chemical potential
4. Work function
5. Surface electronics effects, emission of electrons, neutrals and ions
6. Conductivity of metals
7. Conductivity of semiconductors
8. Contact of solids: M-M, M-SC, SC-SC (PN junction)
9. Current conduction in contacts and PN junction

Physical Electronics of Surfaces

Introduction

Physical Electronics

- deals with phenomena occurring upon motion of charged particles in various environments
- provides theoretical grounds for development of electronic devices and diagnostic methods

- In **vacuum or very dilute gases** ($\lambda \gg d$)
  - (quasi)stationary fields ($\vec{E}$, $\vec{B}$) → **electron/ion optics**
  - HF fields → **HF electronics**

- In **gases**
  - gas ionization and recombination => electric discharges → **plasma physics**

- In **liquids**
  - often both charge and mass transfer → **electrochemistry**

- In **solids**
  - strongly interacting charged particles with high density => many-particle problem
  - typically involving mainly electrons
  - models and methods based on solid state theory

  → **optoeletronics**, **quantum electronics**, **electronics of interfaces and surfaces**

Physical Electronics of Surfaces

- deals with topics related to electronic processes occurring at the **gas-solid** or **vacuum-solid interface**

Recommended literature:

- Dekker A.J.: Fyzika pevných látek, Academia, 1966
- Kittel Ch.: Úvod do fyziky pevných látek, Academia, Praha 1985 / Introduction to Solid State Physics, 8th Ed., John Wiley & Sons, 2004.
- Eckertová L. a kol.: Fyzikální elektronika pevných látek, Univerzita Karlova, Praha 1992.
- Eckertová L.: Elektronika povrchů, SPN Praha 1983 (skripta).
- Zangwill A.: Physics at Surfaces, Cambridge University Press, Cambridge 1988.
- Davison S. G., Steslicka M.: Basic theory of Surface States, Clarendon Press, Oxford 1992.

Electronic structure of solid matter

Basics

Many-electron problem in solids $n \approx 10^{22} \div 10^{23}\ cm^{-3},\ d \approx 0.1\ nm$
+ possible external fields
=> statistical approaches only accessible, analytically treatable only with approximations

Studied phenomena:

- motion of electrons within solid → conductivity
- motion of electrons across interfaces → contact effects, PN juctions, …
- motion of electrons across surface → emissions, absorptions

Key concepts and approaches:

- most solids are crystals => symmetries & periodic boundary conditions => solutions in reciprocal space
- electronic and vibrational contributions separable: adiabatic (Born-Oppenheimer) approximation
  - Importance of each contribution strongly depends on particular phenomena (e.g. vis. light absorption – mostly els., thermal conductivity – mostly cores, el. conductivity – both)
- mostly coulombic interaction considered
- single-particle approximations

Shrödinger equation for solids (stationary)

$$\hat{H}_{sol}\psi_{sol}(\vec{R},\vec{r}) = E_{sol}\psi_{sol}(\vec{R},\vec{r})$$

$\hat{H}_{sol} = \hat{T}_{core} + \hat{T}_{el} + \hat{U}(\vec{R},\vec{r})$ — $\vec{R},\vec{r}$ … sets of coords of cores and electrons

$\hat{T}_{core} = \sum_j \frac{\vec{p}_j^{\,2}}{2M_j}$ — … total kinetic energy operator of cores

$\hat{T}_{el} = \sum_i \frac{\vec{p}_i^{\,2}}{2m_i}$ — … total kinetic energy operator of electrons

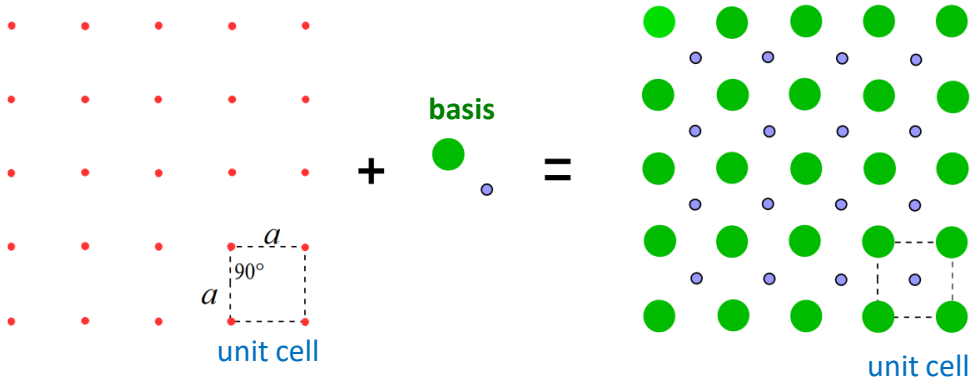
$\hat{U}(\vec{R},\vec{r}) = \hat{U}_{core-core}(\vec{R}) + \hat{U}_{core-el}\hat{U}(\vec{R},\vec{r}) + \hat{U}_{el-el}(\vec{r})$ — … total potential energy operator of solid

Geometric structure of solid state

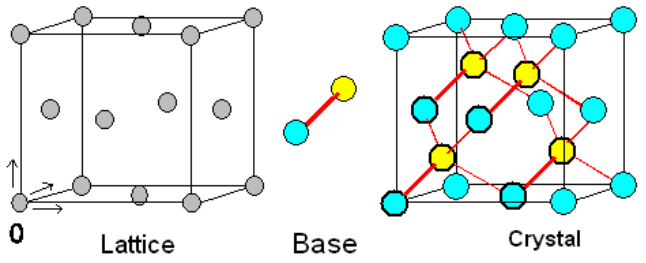
Lattices and crystals

(Bravais) lattice

– geometrical abstraction of a regular structure

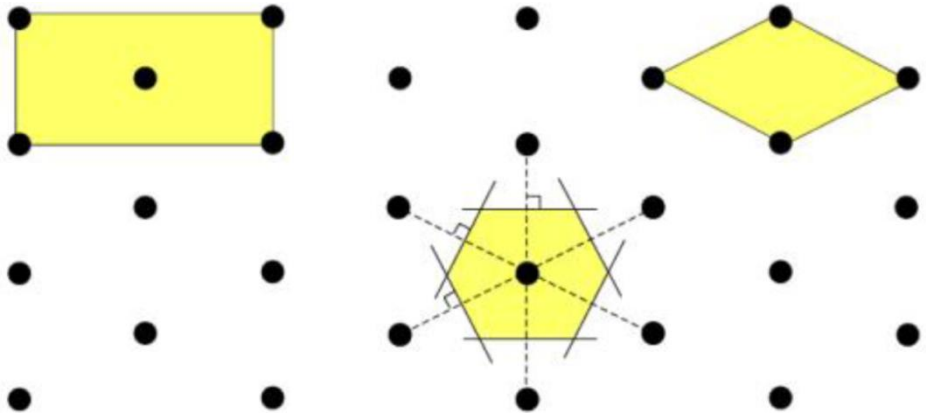


3D

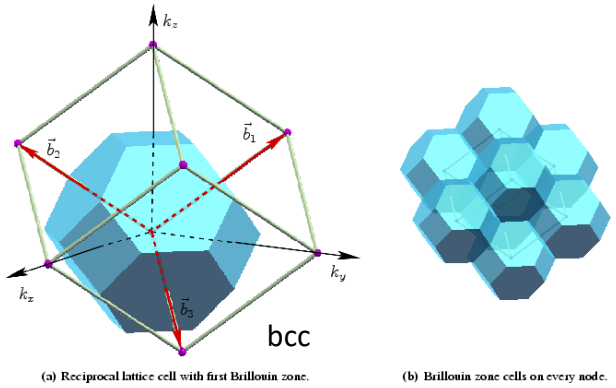


(conventional) **unit cell**

primitive unit cell



3D



Wigner–Seitz unit (elementary) **cell**

– primitive cell with the full symmetry of the Bravais lattice

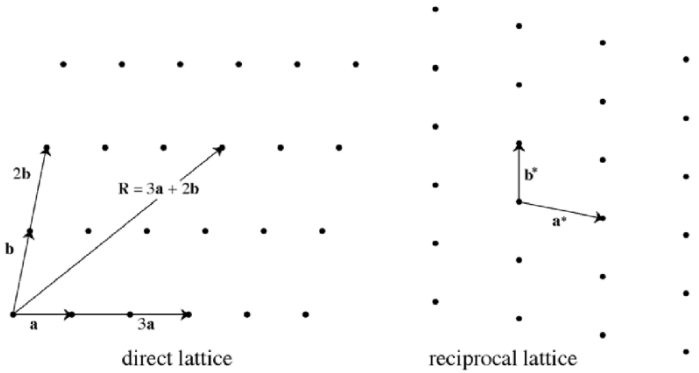
– region of space about a lattice point that is closer to that point than to any other lattice point

Geometric structure of solid state

Lattice and reciprocal lattice

Direct space **Reciprocal space**

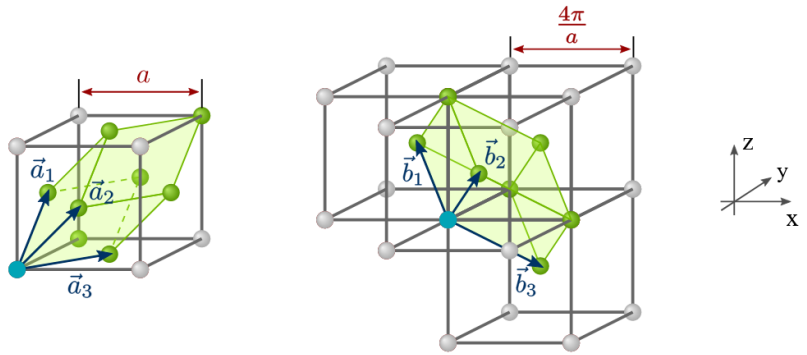
Lattice base vectors



3D

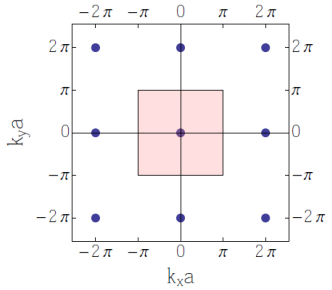
direct lattice:
fcc with edge length a

reciprocal lattice:
bcc with edge length 4π/a

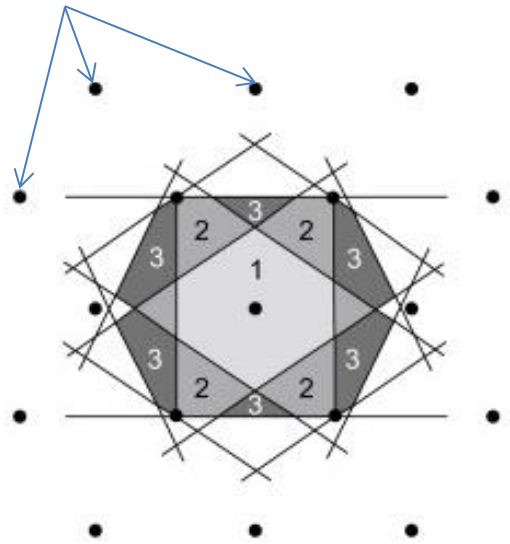


Brillouin zone

– Construction equivalent to Wigner-Seitz cell in reciprocal space



Reciprocal lattice vectors



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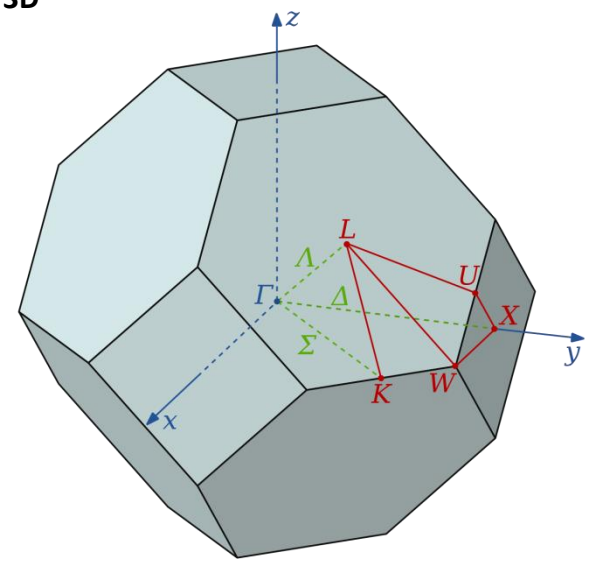


Electronic structure of solid matter

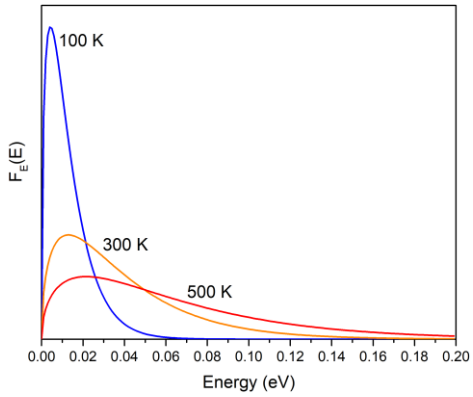
Drude model of metals

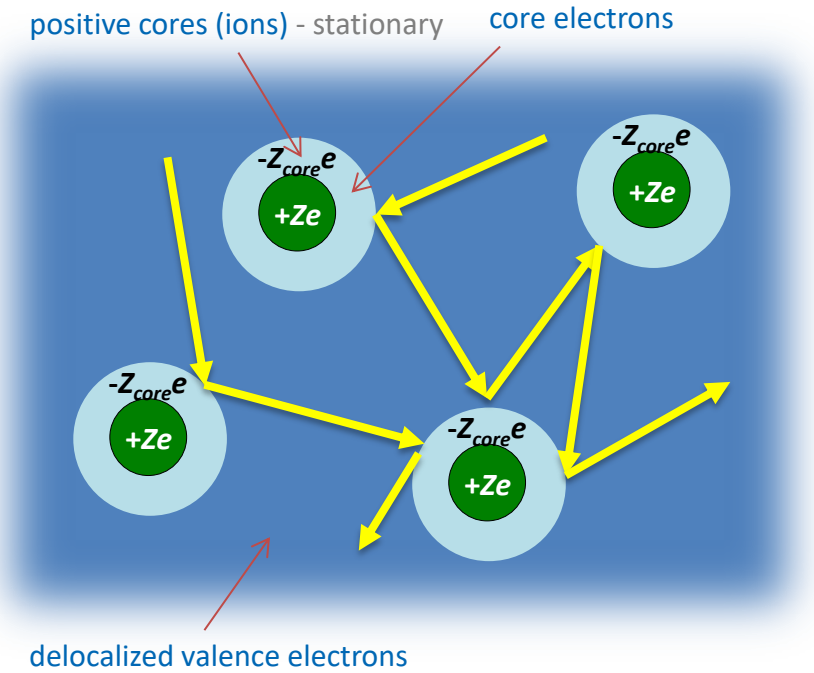
Paul Drude (1900) – microscopic model of electrical conduction, based on electron analogy of kinetic theory of ideal gases

Assumptions:

- **free electron** approximation – no acting forces between collisions
- **independent electron** approximation – electron-electron interactions neglected
- collisions of electrons are instantaneous – velocity after collision **independent** of velocity before
- electron gas in **thermodynamic equilibrium** with its surroundings (only through collisions)
  => electron velocity distribution obeys Maxwell-Boltzman (classical) statistics, randomly directed

$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}k_BT \qquad f_E(E) = 2\sqrt{\frac{E}{\pi}}\left(\frac{1}{k_BT}\right)^{3/2} e^{-\frac{E}{k_BT}}$$





Electron density $n = N_A(Z - Z_{core})\frac{\rho_m}{A}$

$n \approx 10^{22} \div 10^{23}\ \mathrm{cm}^{-3}$ $\qquad n_{surf} \approx 10^{14} \div 10^{15}\ \mathrm{cm}^{-2}$

(~1000x that of gas in normal conditions)

Average electron separation $\boldsymbol{r_s}$ (mean distance between els.) $\frac{4}{3}\pi r_s^3 = \frac{1}{n}$

Collision probability in dt $\mathrm{d}t/\tau$

τ ... relaxation time (mean free time, collision time)

Electronic structure of solid matter

Drude model of metals

Drude model provides inaccurate estimates of τ ($\tau_{Drude} << \tau_{exp}$) => only applicable to quantities independent of τ :

- DC and AC conductivity in metals (Ohm law)
- Hall effect – generation of potential across conductor transverse to current and external magnetic field (perpendicular to the current)
- Magnetoresistance in metals – change of electrical resistance in an external magnetic field

Wiedemann-Franz law (1853)

– relation between electronic contribution of **thermal** conductivity (κ) to **electrical** conductivity (σ) of a metal

$$\frac{\kappa}{\sigma} = LT$$

$L = 2.44 \times 10^{-8}\ \mathrm{W\Omega K^{-2}}$ … Lorenz number

Validity:

- Low T (near 0 K) – OK: heat and charge currents are carried by the same quasi-particles (electrons, holes)
- Medium T – deviates due to alternative carriers (phonons, magnons, …) and inelastic scattering
- High T (above Debie T) – OK: phonon contribution invariant of T

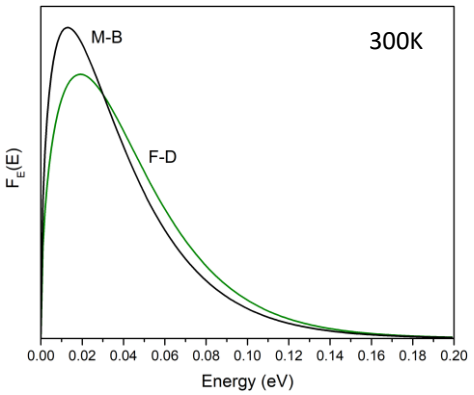
Electronic structure of solid matter

Sommerfeld model of metals

Maxwell-Boltzmann statistics is reasonable approximation in systems where distance between charge carriers >> their de-Broglie wavelength:

- low density of charge carriers (e.g. weakly doped semiconductors)
- high temperatures

=> inappropriate in most cases



Free electron (Fermi) gas

= mutually non-interacting electrons obeying **Pauli exclusion principle**

=> single-electron approximation can be made

Simplified case: metal crystal, 1D solution, stationary

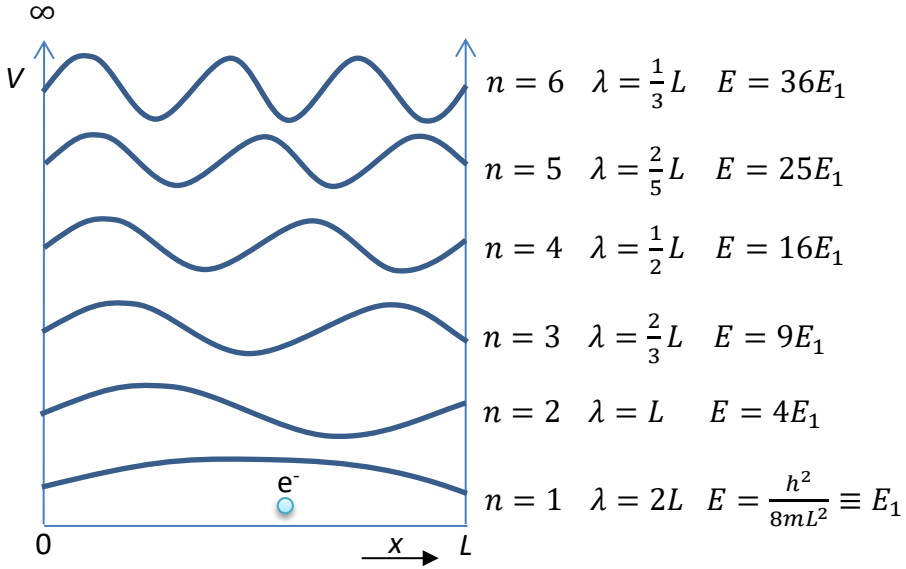
-> Schrödinger eq. of electron in potential well

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

+ boundary conditions: $\psi_n(0) = \psi_n(L) = 0$

$$\psi = \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x \qquad E_n = \frac{n^2h^2}{8mL^2}$$

n … quantum number (+/- spin for each)



N electrons: occupation of el. states according to Pauli e.p.

Fermi energy

= energy of the highest occupied state

$L = 1cm \Rightarrow \Delta E \approx 10^{-13}eV$ … quasi-continuous

Electronic structure of solid matter

Sommerfeld model of metals

Fermi-Dirac statistics

Probability of finding an electron in an one-electron state *i* of a *N*-electron system at temperature *T*:

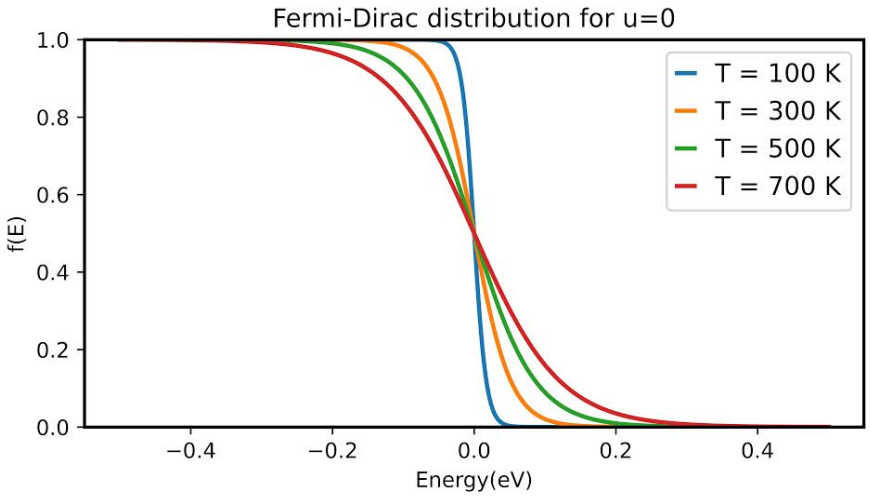
$$f_i = \frac{1}{e^{(E_i-\mu)/k_BT}+1}$$

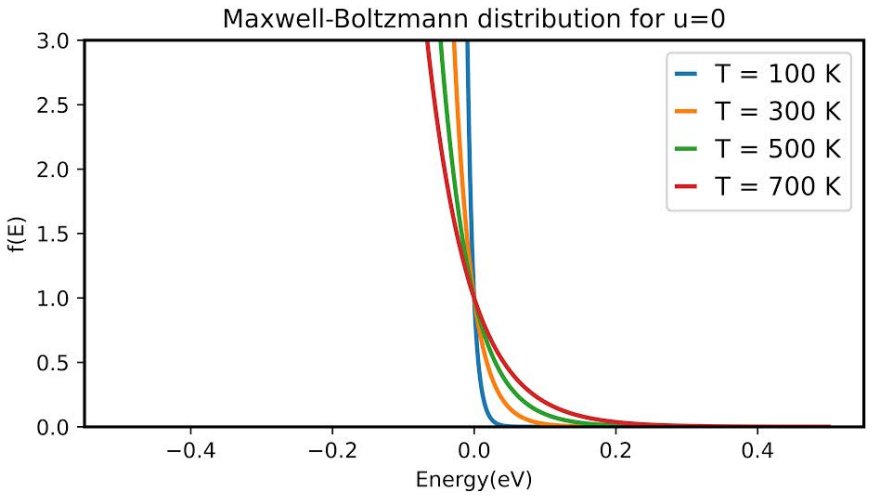
μ ... chemical potential

= E_F (at 0 K)

+ Normalization condition:

$$\sum_i f_i = N \qquad \lim_{T\to 0} \mu = \mathcal{E}_F$$



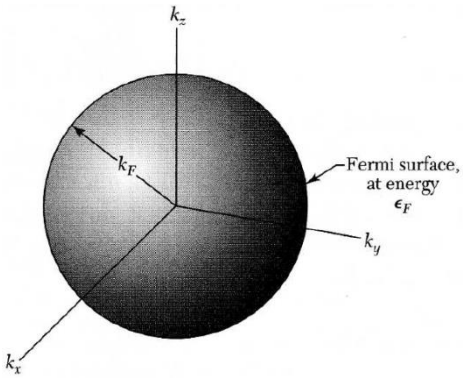


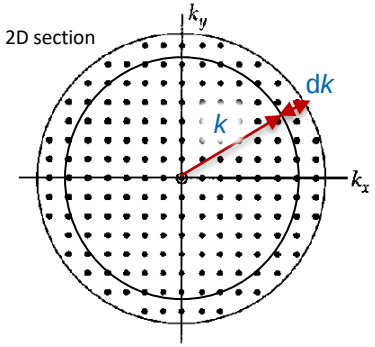
Electronic structure of solid matter

Sommerfeld model of metals

Density of electron states (DOS): How many one-electron states have the energy between *E* and *E*+d*E* per volume unit

3D box: $n^2 = ({n_x}^2 + {n_y}^2 + {n_z}^2)$ … the same n can be realized by diff. n_x, n_y, n_z





Fermi surface = Solution in k-space of $\mathcal{E}_n(\boldsymbol{k}) = \mathcal{E}_F$

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

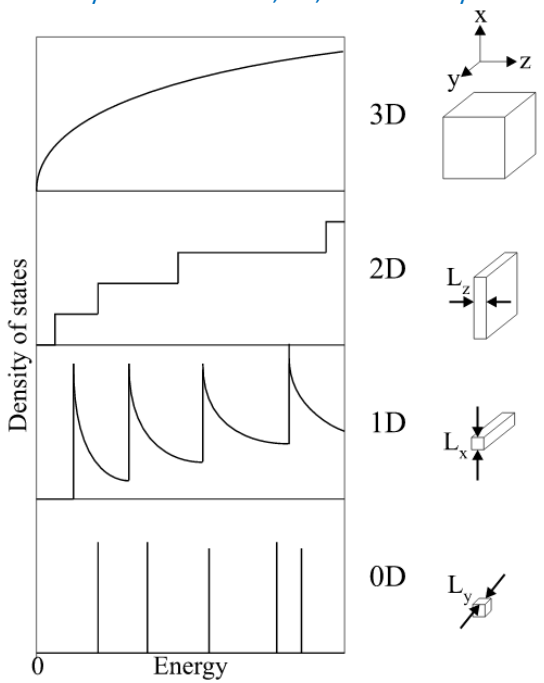
$$E_F = \frac{h^2}{2m}{k_F}^2$$

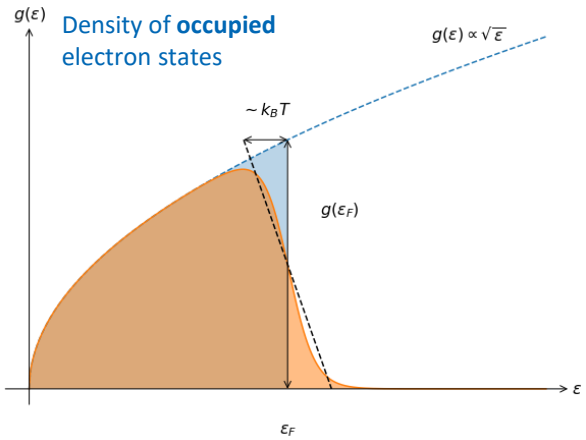
$$E_F = \frac{h^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$g(E) \equiv \frac{dN}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{h^2}\right)^{2/3}\sqrt{E}$$

DOS

Schematic representation of the energy dependence of the density of states for 3D, 2D, 1D and 0D systems.





Electronic structure of solid matter

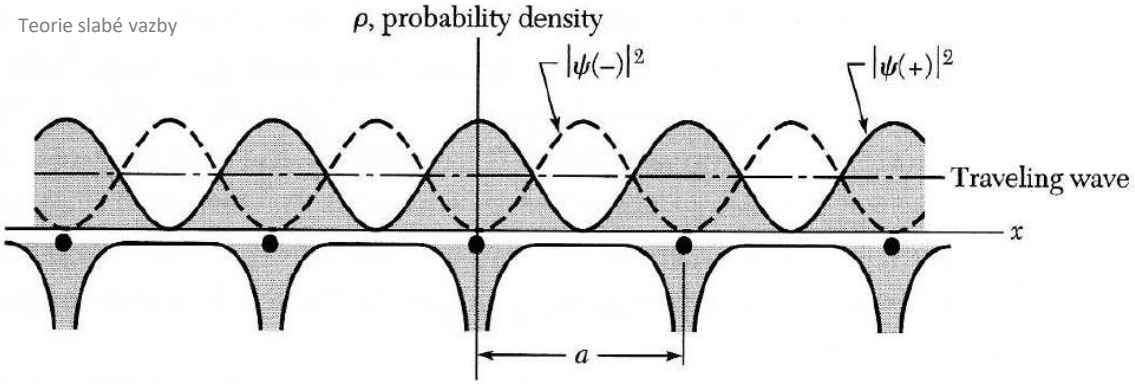
Energy bands

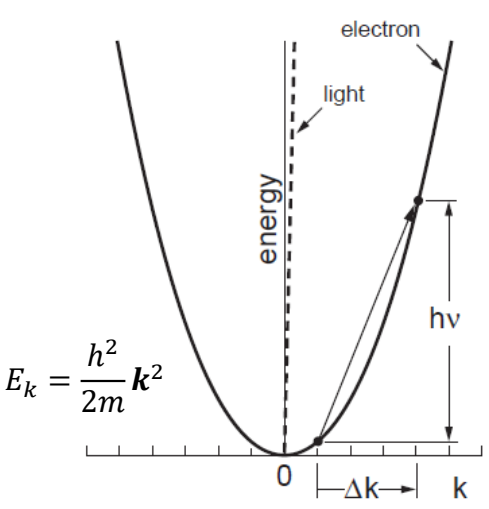
Origin of energy bands – Bragg reflection of el. wave at BZ boundaries:

- nearly-free electrons – weak periodic potential
- different solution of Sch.eq. -> standing waves
- 2 solutions with different *E*

(Sommerfeld model work relatively well only for alkali metals, not for semiconductors and insulators)

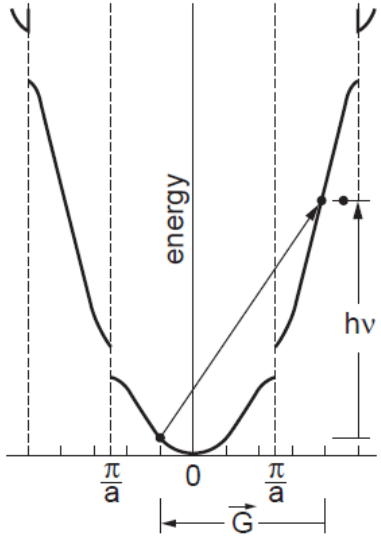
Teorie slabé vazby



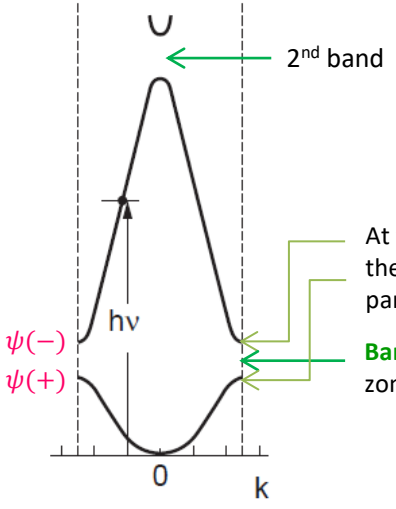


$$E_k = \frac{h^2}{2m}\boldsymbol{k}^2$$

free electron/
constant potential



extended zone
periodic potential



reduced zone
periodic potential

At the Brillouin zone boundary, the gradient of the energy is parallel to the boundary

Band gaps open at zone boundary

Electronic structure of solid matter

Energy bands – Bloch theorem

Quantitative solution: electrons in a periodic crystal field
- electrons are independent but not free: many-particle wave function is a direct product of one-particle wave functions

One-particle Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \hat{U}(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})$$

Periodic potential:

$\hat{U}(\vec{r}) = \hat{U}(\vec{r}+\vec{R})$, $\vec{R} = n_1\overrightarrow{a_1} + n_2\overrightarrow{a_2} + n_3\overrightarrow{a_3}$ $\vec{R}$... translation vector

$\hat{U}(\vec{r}) = \sum_{\vec{g}} U_{\vec{g}}(\vec{r})e^{i\vec{g}\vec{r}}$ (Fourier series) $\vec{g}$ ... reciprocal lattice vector

Bloch theorem

Solution: **Bloch wave**

plane wave function

function with periodicity of the lattice

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}u_{n,\vec{k}}(\vec{r})$$

$u_{n,\vec{k}}(\vec{r}) = \sum_{\vec{g}} u_{n,\vec{k}\vec{g}}(\vec{r})e^{i\vec{g}\vec{r}}$, $\psi_{n,\vec{k}}(\vec{r}+\vec{R}) = \psi_{n,\vec{k}}(\vec{r})e^{i\vec{k}\vec{R}}$

$E_n(\vec{k}+\vec{g}) = E_n(\vec{k})$, $\psi_{n,\vec{k}+\vec{g}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r})$

Born–von Karman boundary condition

$\vec{k}$ ... wave vector, usually from 1st Brillouin zone
n ... energy band index

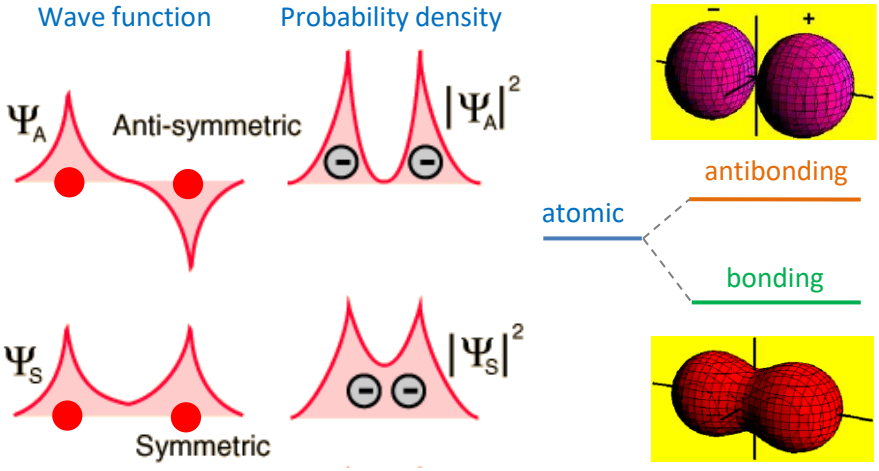
→ **repeated energy band scheme**

Electronic structure of solid matter

Energy bands - semiconductors

Metals: Nearly-free electrons => weak potential => only first 2 coefficients in the Fourier series considered
→ Solution similar as for free electron except for energy gaps

Semiconductors:
Electrons tightly bound near corresponding cores with only small overlaps between the wave functions of neighboring atoms



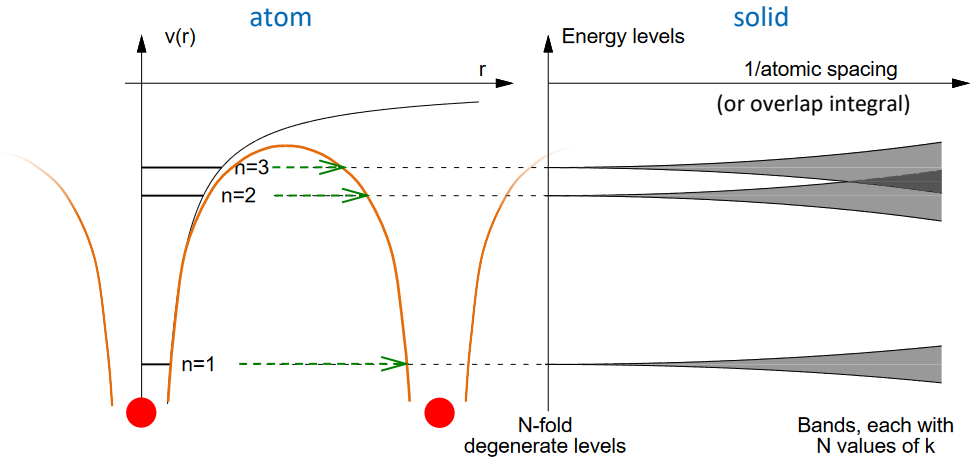
Tight-binding approximation: Teorie silné (těsné) vazby

- Electrons move between atoms by tunnelling through the potential wells created by the nuclei
- Hamiltonian based on atomic (LCAO) => solutions close to atomic:

$$\hat{H}_{at}\psi_{at} = E_{at}\psi_{at}$$

Then for solid: $\hat{H} = \hat{H}_{at} + \Delta\hat{U}(\vec{r})$

$\Delta\hat{U}(\vec{r})$ … deviation (perturbation) potential from superposition of atomic potentials
=> very small near nuclei



Wavefunctions are Bloch functions $\psi(\vec{r}) = \sum_{\vec{R}} \Phi(\vec{r} - \vec{R}) e^{i\vec{k}\vec{r}}$

where Φ is similar to ψ_{at}

Most simple case: s-state, 1D $E(k) = E_n - \beta - \gamma\cos(k)$

β … band shift from atomic level position
γ … ∝ band width (~ overlap of at. orbitals, interaction strength)

Appendix

Electronic structure of solid matter

Energy bands – solution for s-metals

Free electron: $\left[-\frac{\hbar^2}{2m}\nabla^2 + \hat{U}_0\right]\psi(\vec{r}) = E\psi(\vec{r})$ => Spherical (plane in 1D) waves $\psi(\vec{r}) = e^{i\vec{k}\vec{r}}$

Solid: $\hat{H}(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \Delta\hat{U}(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \qquad \Delta\hat{U}(\vec{r}) = \Delta\hat{U}(\vec{r}+\vec{R})$$

Periodic Bloch functions

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{R}} \psi_0(\vec{r}-\vec{R})e^{i\vec{k}\vec{R}} = e^{i\vec{k}\vec{r}}\sum_{\vec{R}} \psi_0(\vec{r}-\vec{R})e^{-i\vec{k}(\vec{r}-\vec{R})}$$

→ Solution for band constructed from single atomic orbital (s-band):

$$E(\vec{k}) = \frac{\langle\psi_{\vec{k}}{}^*(\vec{r})|\hat{H}|\psi_{\vec{k}}(\vec{r})\rangle}{\langle\psi_{\vec{k}}{}^*(\vec{r})|\psi_{\vec{k}}(\vec{r})\rangle} = E_0 + \frac{\sum_{\vec{R}}\langle\psi_0{}^*(\vec{r})|\Delta\hat{U}|\psi_0(\vec{r}-\vec{R})\rangle e^{i\vec{k}\vec{R}}}{\sum_{\vec{R}}\langle\psi_0{}^*(\vec{r})|\psi_0(\vec{r}-\vec{R})\rangle e^{i\vec{k}\vec{R}}}$$

Negligible overlap: $\langle\psi_0{}^*(\vec{r})|\psi_0(\vec{r}-\vec{R})\rangle = \delta(\vec{R})$

Transfer integral: $\langle\psi_0{}^*(\vec{r})|\Delta\hat{U}|\psi_0(\vec{r}-\vec{R})\rangle = -\gamma(\vec{R})$

Diagonal element: $\langle\psi_0{}^*(\vec{r})|\Delta\hat{U}|\psi_0(\vec{r})\rangle = -\beta$

$$E(\vec{k}) = E_0 - \beta - \sum_{\vec{R}} \gamma(\vec{R})e^{i\vec{k}\vec{R}}$$

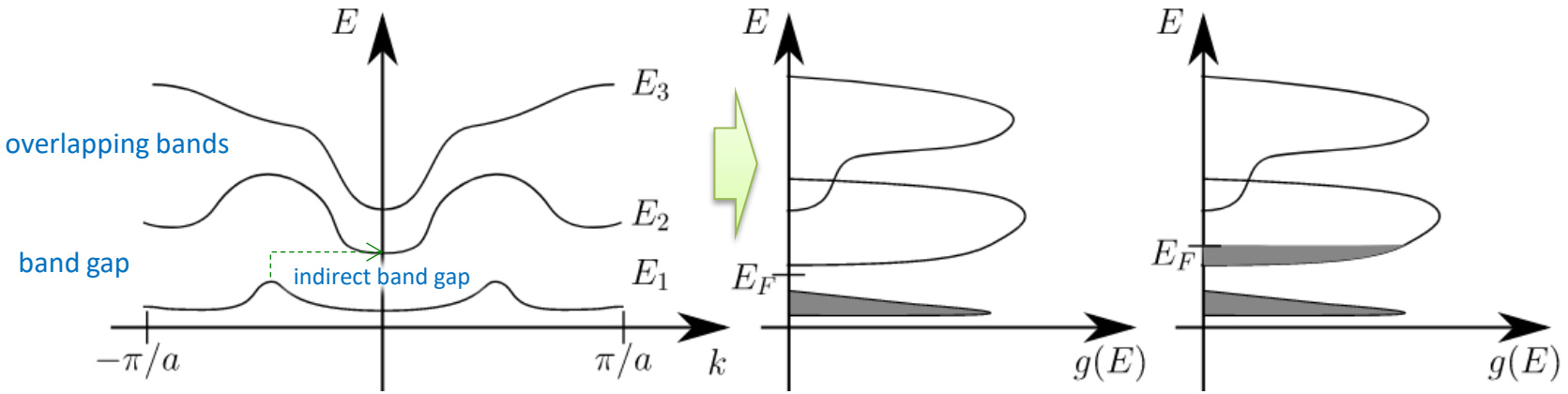
over nearest neighbors

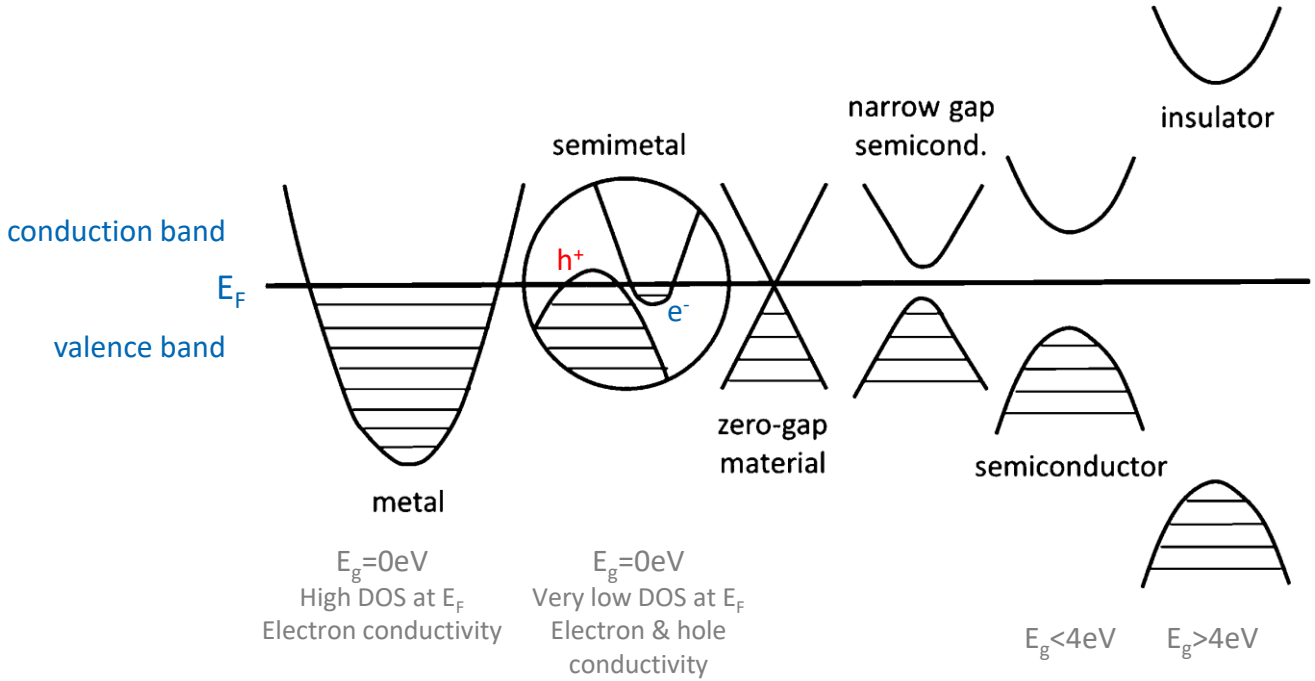
In 1D: $E(k) = E_0 - \beta - \gamma\cos(k)$

β … band shift from atomic level position
γ … ½ width of 1D s-band

Electronic structure of solid matter

Energy bands





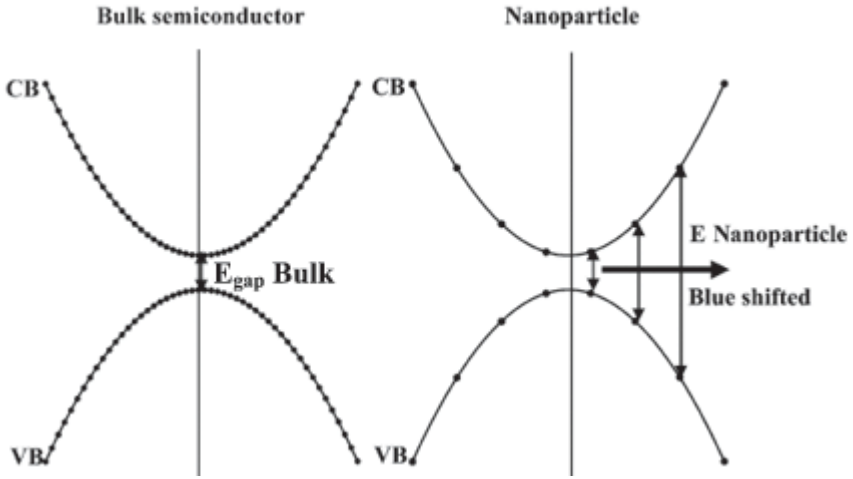
Electronic structure of solids

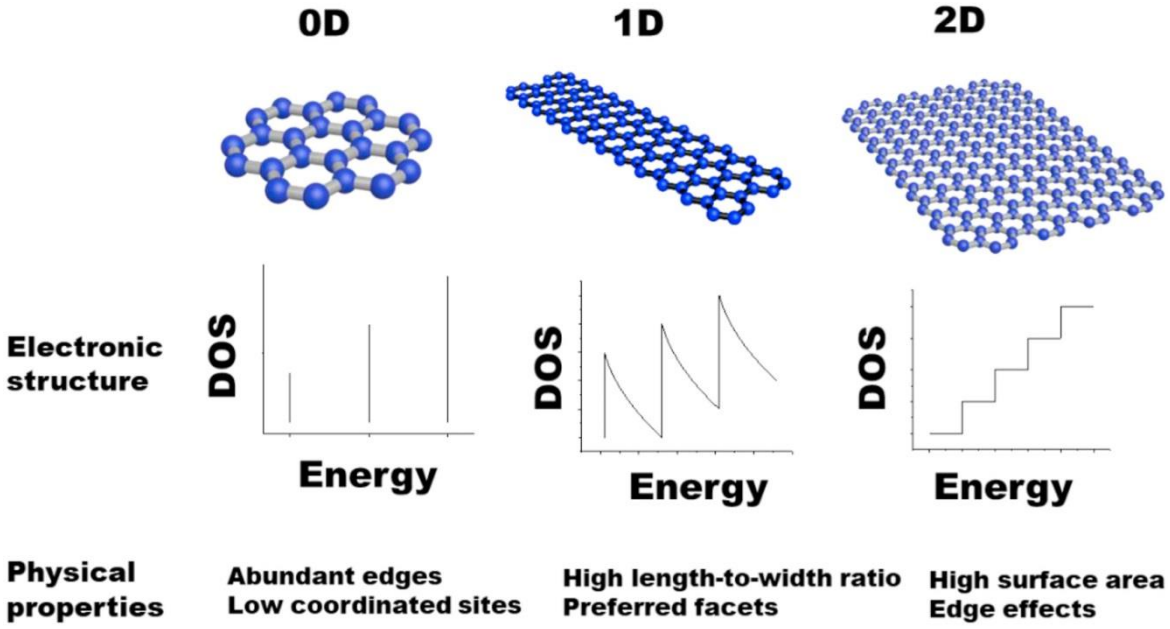
Objects with limited dimension

Very small objects – structure preserved (periodicity), but limited number of particles

$\Rightarrow$ quasi-continuous $E(\vec{k})$ changes to **discrete** in one or more dimensions (depending on actual dimensionality – NP, thin film, chain, QD)
= **quantum confinement**

Bulk-like el. structure already for $N_i \approx 10$





Electronic structure of surfaces

Jellium model

Model kladného homogenního pozadí (model želé)

Jellium (uniform electron gas) model – the most simple: ions are replaced by a uniform (delocalized) positive background charge

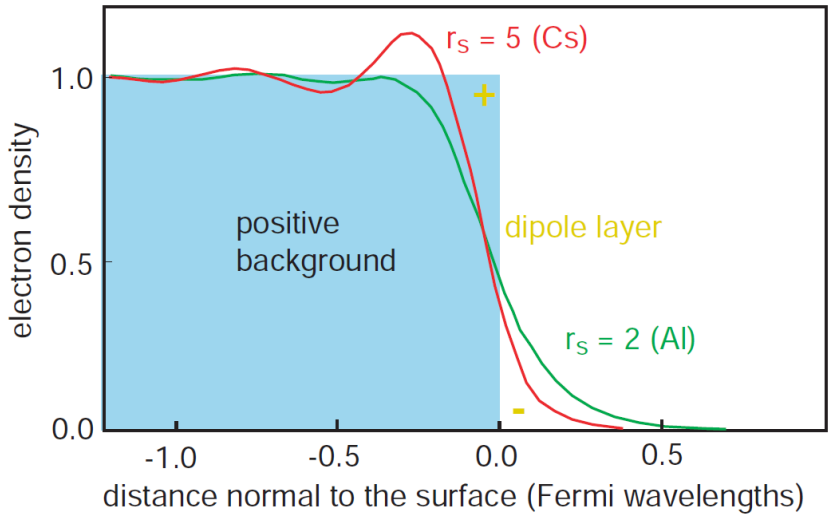
Each atom donates q electrons to the valence band => ion charge $Q_{ion} = e(Z-q)$

=> average charge $\overline{q_{ion}} = \frac{e(Z-q)}{V} = e(Z-q)/(\frac{4}{3}\pi {r_s}^3)$,

V … volume of Wigner-Seitz cell, r_s … inverse-sphere radius ($\propto$ 1/electron density)

Electron charge density does not exactly follow positive charge =>

- Negative charge spill-out to vacuum – due to lowering E_k of electrons (balanced by loss of potential energy)
- Friedel oscillations below surface – due to unability of el. gas to screen perturbation with Fourier componets $>2k_F$ (step is sharp)



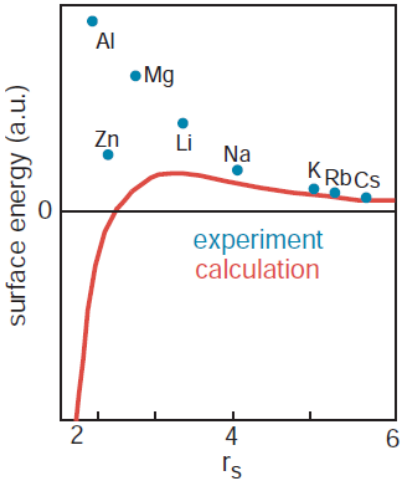
(Fermi wavelength = de Broglie wavelength of electrons present near Fermi level)

Surface charge disbalance => dipole layer
=> change of electrostatic energy of electron escaping solid

→ **Work function**

Jellium model appropriate only for higher r_s (typically univalent metals)

Other cases – lattice needs to be re-introduced



Electronic structure of surfaces

Surface electronic states

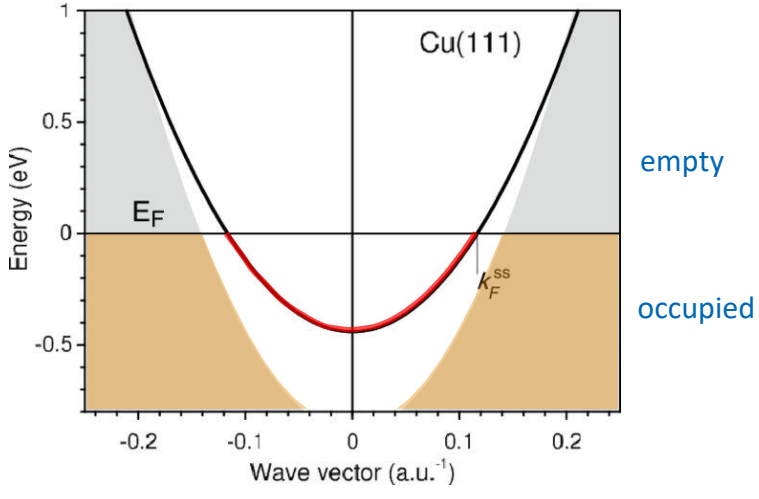
Schr.eq. solutions of terminated bulk:

- Parallel to surface – crystal symmetry obeyed
- Perpendicular to surface – symmetry broken => new solutions of Sch. eq.

→ **Surface electronic states**

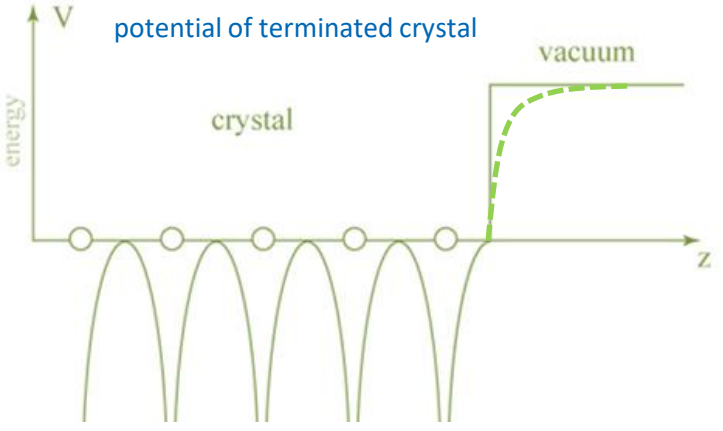
Surf. state occupation modifies local equilibrium concentration of electrons
=> shift of chemical potential position from bands

Located in
- "forbidden" band gaps of semiconductors
- local gaps of the projected band structure of metals

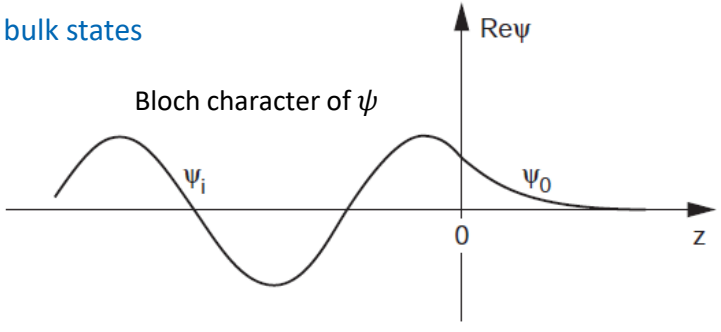


empty

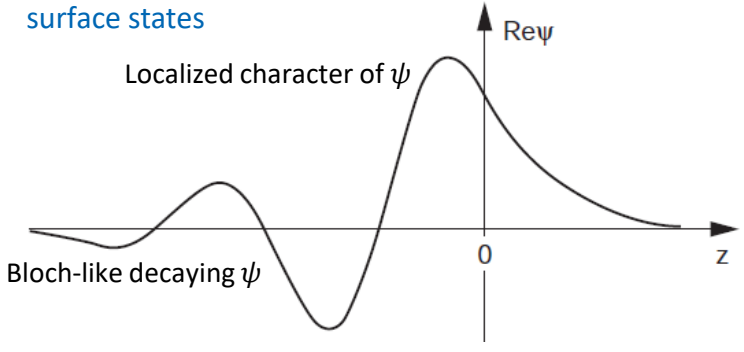
occupied



bulk states



surface states



Electronic structure of surfaces

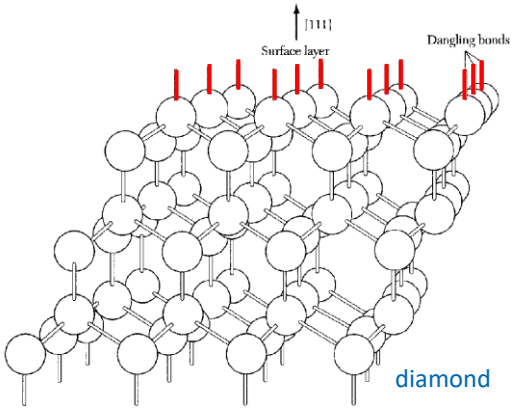
Surface electronic states

Types of surface states according to theory approach (physically equivalent):

1. **Shockley states**
   – solutions of **nearly free** electron approximation
   – associated solely with the crystal termination
   – applicable to normal (s-, p-) metals and some narrow gap semiconductors

2. **Tamm states**
   – from **tight binding** approach (perturbation of lattice potential periodicity)
   – typically a linear combination of atomic orbitals (LCAO)
   – applicable to transition (d-) metals and wide gap semiconductors

dangling bonds – reduced or no overlap
=> smaller splitting and shifting of energy levels



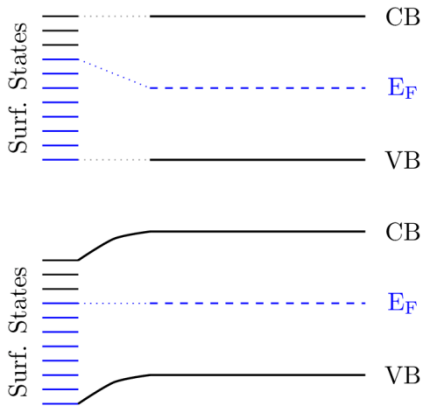
diamond

Electronic structure of surfaces

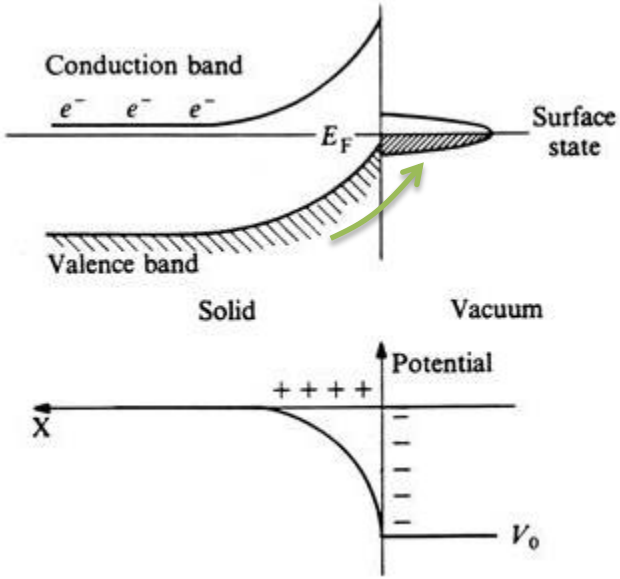
Surface electronic states – band bending

Semiconductors: **electron-donor** or **electron acceptor** surface states

– transfer of electrons between el. level near surface to/from surface states
=> electrostatic field => **band bending**



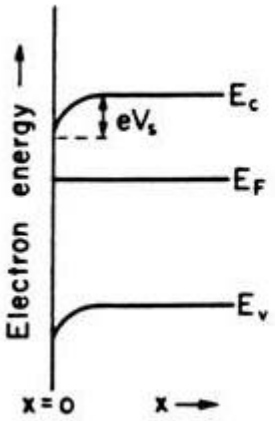
band bending due to surface state
(n-type semiconductor)



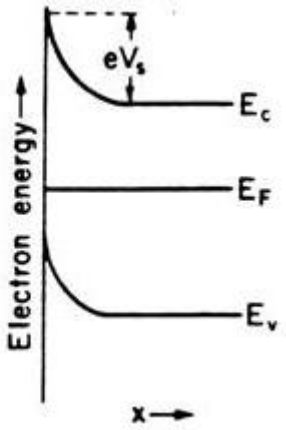
charge distribution

Intrinsic semiconductors

electron-donor



electron-acceptor



Surface of solid state

Structural phenomena

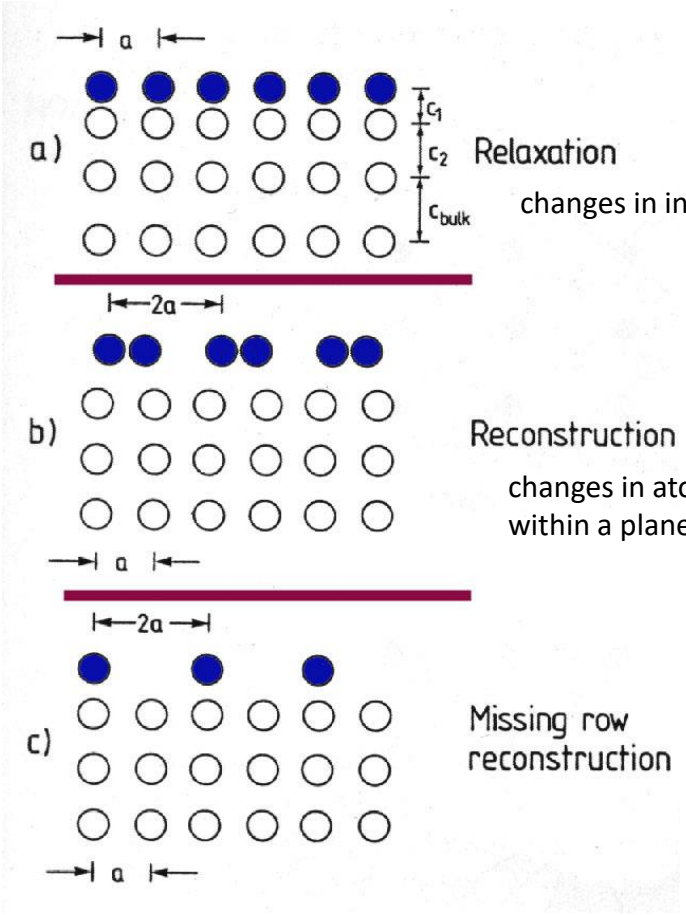
Crystal truncation => increase of system energy

Possible partial compensation via

- **relaxation**
- **reconstruction**

– Often requires activation energy
– Associated with el. structure changes

=> Surface states dependent on particular type of termination, relaxation and reconstruction



Relaxation

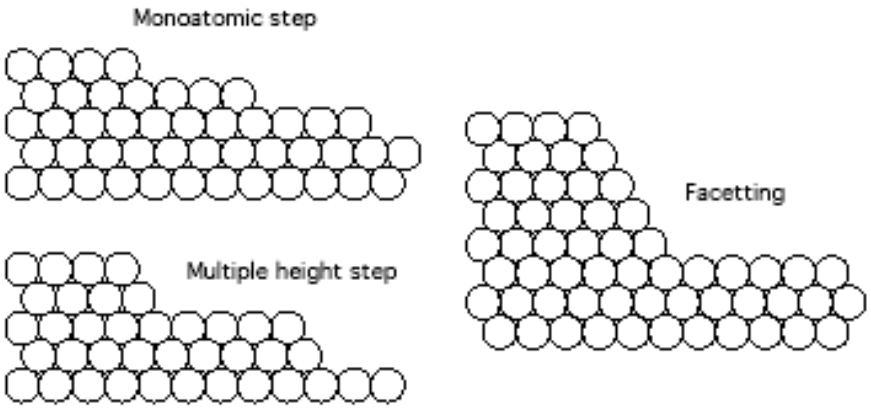
changes in interplanar distances

Reconstruction

changes in atomic positions within a plane

Missing row reconstruction

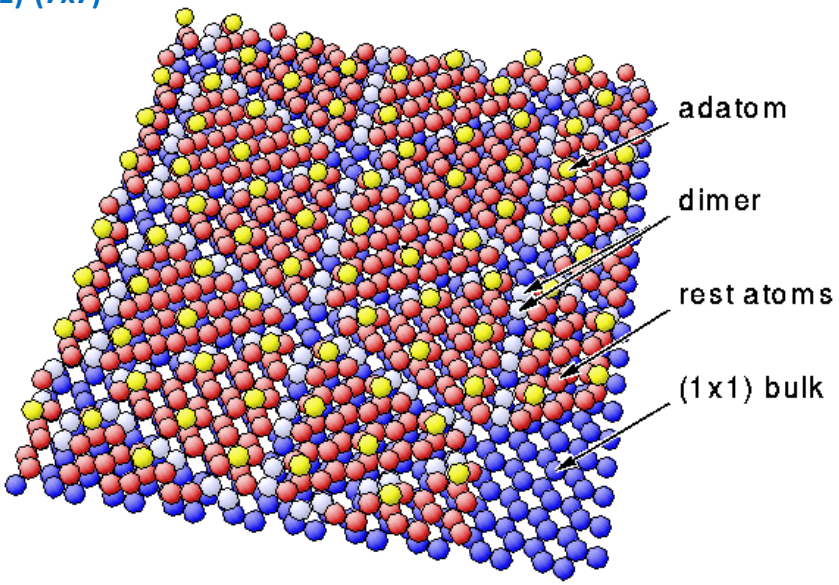
In extreme cases (adsorbate-induced or clean) may get *facetting*

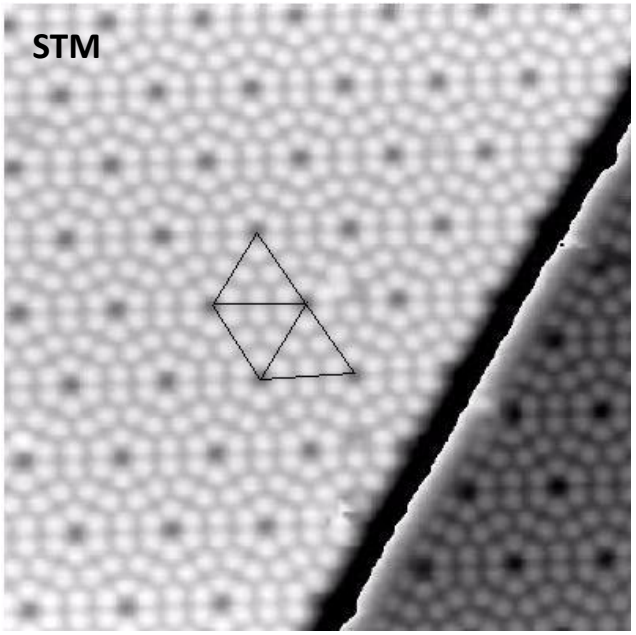


Surface of solid state

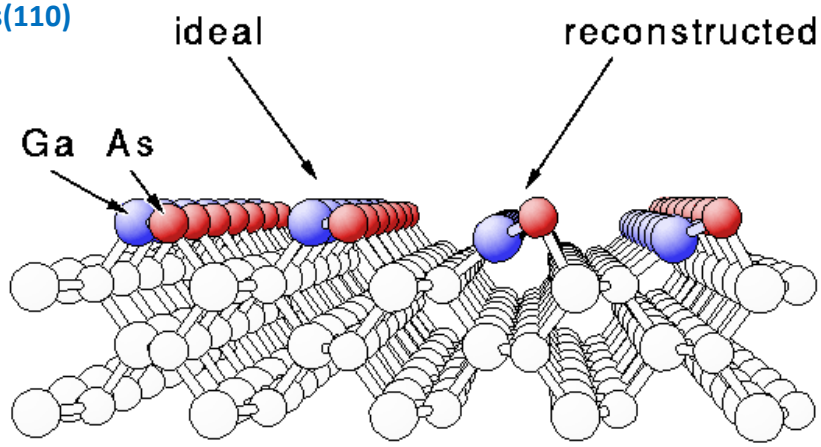
Surface reconstruction

Si(111)-(7x7)





GaAs(110)



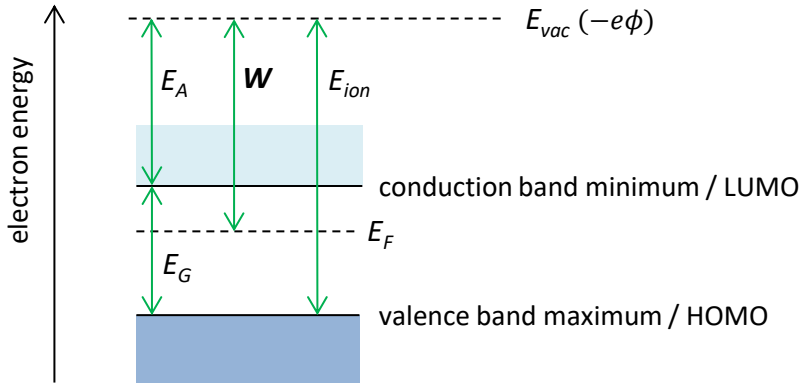
Electronic structure of surfaces

Work function

Work function = minimum thermodynamic work needed to remove an electron from a solid to vacuum

$W = -e\phi - E_F$

ϕ … electrostatic potential in the vacuum nearby the surface (sufficiently but not too far: >10nm)
E_F … Fermi level (electrochemical potential of electrons) inside the solid

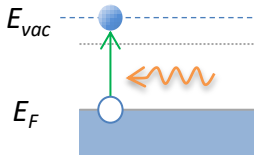


Work function is surface structure dependent

Crystal Face	Na Φ (eV)	Al Φ (eV)	W Φ (eV)	Mo Φ (eV)
(111)	2.65	4.05	4.39	4.10
(100)	2.75	4.20	4.56	4.40
(110)	3.10	3.65	4.68	5.00

Related to surface charge density and coordination of surface atoms

Metals: Work function = threshold energy for photoemission at 0 K



typical value: ~3-5.5 eV

Can be strongly modified by **adsorbate** or **deposit**
=> adsorption can be monitored by $\Delta\phi$

Surface emission

Introduction

Surface electronic effects

= electron-related phenomena at solid state – vacuum interface

– Emissions of electrons
- thermoionic emission
- field emission
- photoemission
- secondary emission

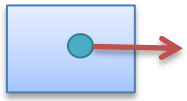
– Emissions of neutrals (sputtering)
– Emissions of ions

Thermionic Emission

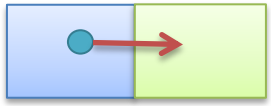
Termoemise

Basics

Thermionic Emission (or **thermal emission of electrons**)
= liberation of electrons from a matter caused by thermal energy



More general: thermally-excited charge emission process
(e.g. between 2 solid state regions)



Temperature =>
- lattice vibrations -> possible desorption or evaporation
- occupation of higher electron levels -> possible emission

-> Fermi-Dirac distribution

Conditions for emission:

1. $E \geq E_{vac}$
2. $p_x \geq p_{x0}$ (surface barrier)
3. No electron wave reflection happens

Thermionic Emission

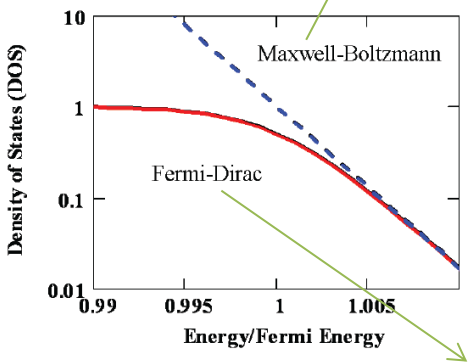
Fermi-Dirac distribution

Fermi-Dirac distribution

– obeys Pauli exclusion principle

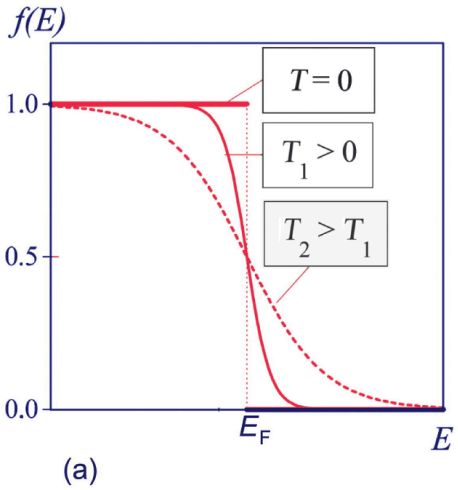
$$f_{FD}(E) = \frac{1}{1 + e^{\frac{E-E_F}{kT}}}$$

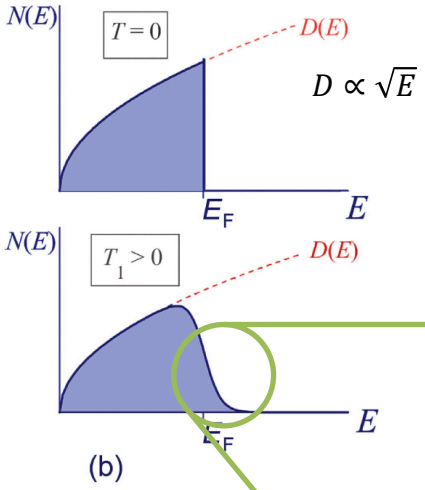
particles any number of which can share the same energy state (**bosons**)

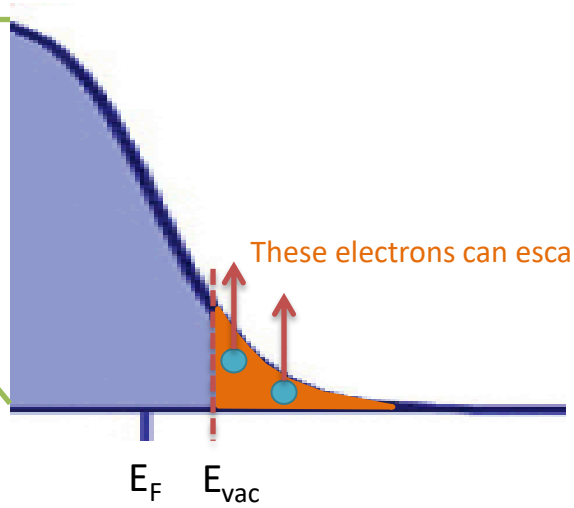


$$f_{MB}(E) = e^{-\frac{E-E_F}{kT}}$$

particles which cannot share the same energy state (**fermions**)







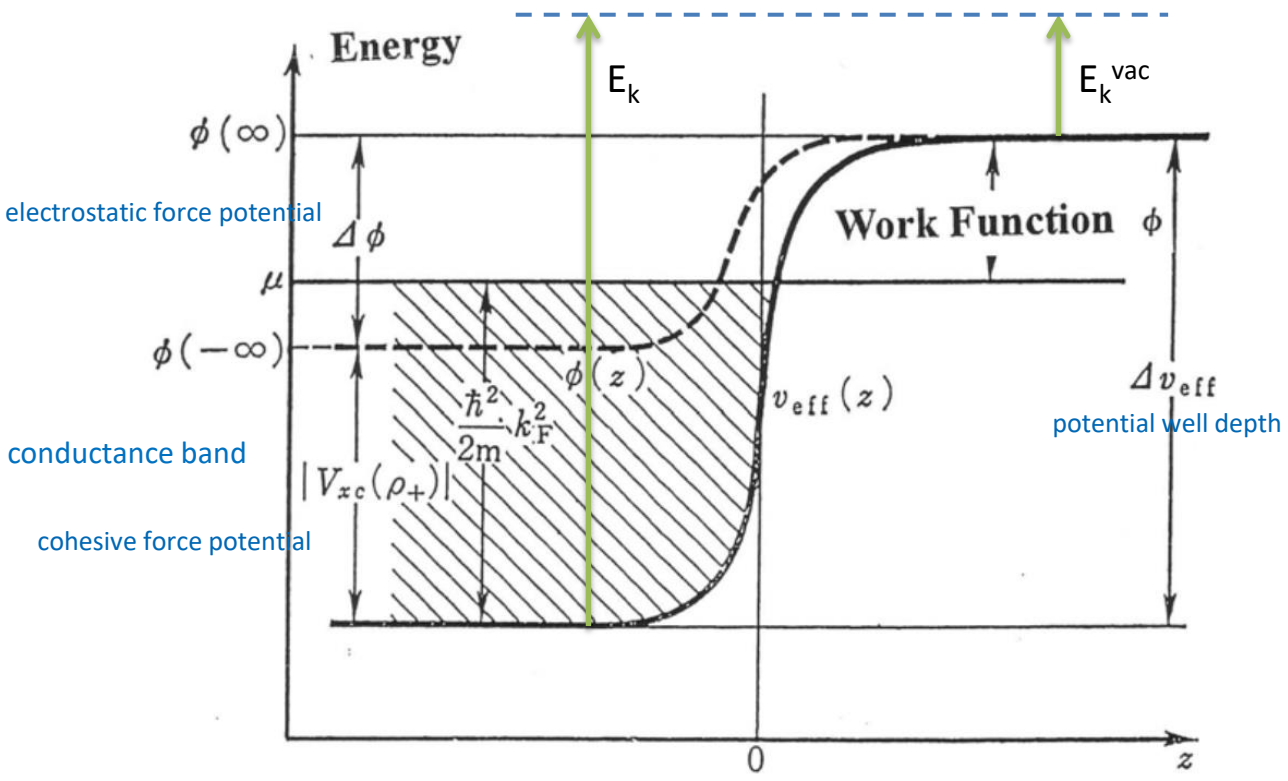
Thermionic Emission

Electron emission from metals

Metals = High electron density in conductance band

(Drude-)Sommerfeld model

– electrons in metal treated as free electron gas (with occassional scattering)
– quantum mechanics applied: F-D distribution, Heisenberg's uncertainty principle, quantized energy levels



Thermionic Emission

Thermionic current

Rate of thermionic emission – The number of thermions emitted per second from a substance

Depends on:
- Nature of the material - density of valence electrons, work function, ...
- Surface Temperature - high melting point favorable
- Surface Area - may be enhanced by surface structure

Richardson's law

$$J = A_G T^2 e^{-\frac{W}{kT}}$$

(approx. valid for metals)

J ... current density
T ... absolute temperature,
k ... Boltzmann constant,
W ... work function,
A_G ... emitter-specific constant

Work function

Thermally dependent

$$W(T) = W(T_0) + \alpha(T - T_0)$$

Richardson-Dushman law

$$A_G = \lambda_R A_0$$

λ_R ... average transmission coefficient (probability of the electrons to be transmitted through the surface potential barrier)
- Material-specific factor (~0.5)
- Depends also on surface orientation and purity

$$A_0 = \frac{4\pi q_e m k^2}{h^3} \cong 1.2 \times 10^6 \text{ Am}^{-2}\text{K}^{-2}$$

Richardson constant

$$A_G = \lambda_B (1 - r_{av}) A_0$$

r_{av} ... average el. reflection factor
- Usually small
- Weakly T dependent

λ_B ... correction factor based on particular band structure

$$J = \lambda_B (1 - r_{av}) A_0 T^2 e^{-\frac{W}{kT}}$$

Appendix

Thermionic Emission

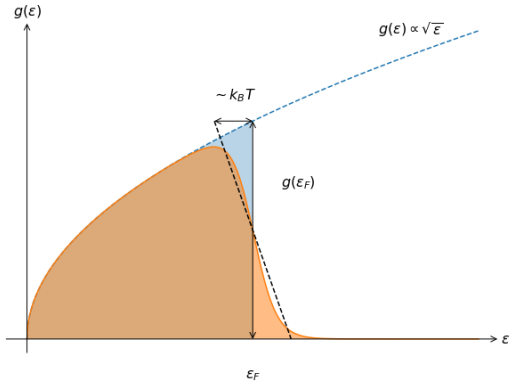
Thermionic current

$$J_z = \int qn(E)v_z(E)dE$$

Electron density in $(E; E+dE)$: $\mathrm{d}n(E) = g(E)\dfrac{1}{1+e^{\frac{E-E_F}{kT}}}\mathrm{d}E$ $\quad g(E) = \dfrac{8\pi\sqrt{2}}{h^3}m^{3/2}\sqrt{E}$ … DOS at E

$$E = \frac{1}{2}mv^2 \;\Rightarrow\; \sqrt{E}dE = \frac{1}{\sqrt{2}}m^{3/2}v^2dv$$ m … reduced electron mass

$$n(E)dE \cong \frac{8\pi}{h^3}m^3 e^{-\frac{E-E_F}{kT}}v^2dv$$ (F-D approximated by M-B distribution – OK if barrier height $\geq 3kT$)

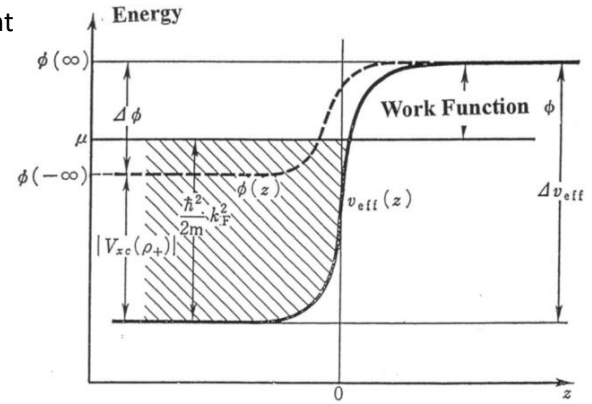


$$E = \frac{1}{2}m({v_x}^2 + {v_y}^2 + {v_z}^2)$$

$$J_z = \frac{8\pi}{h^3}qm^3 e^{\frac{E_F}{kT}} \int_{-\infty}^{\infty} e^{-\frac{m{v_x}^2}{2kT}}dv_x \int_{-\infty}^{\infty} e^{-\frac{m{v_y}^2}{2kT}}dv_y \int_{v_{z(min)}}^{\infty} v_z e^{-\frac{m{v_z}^2}{2kT}}dv_z$$

all electrons fast enough to escape to vacuum

$$\int_{-\infty}^{\infty} e^{-\alpha^2}d\alpha = \sqrt{\pi}, \qquad \int \alpha e^{-\alpha^2}d\alpha = -\frac{1}{2}e^{-\alpha^2}, \qquad E_{min} = E_F + q\Phi$$ Φ … barrier height



$$J_z = \frac{8\pi}{h^3}qm^3 e^{\frac{E_F}{kT}}\frac{kT}{m}\frac{1}{2}e^{-\frac{q\Phi}{kT}}e^{-\frac{E_F}{kT}}\sqrt{\frac{2\pi kT}{m}}\sqrt{\frac{2\pi kT}{m}} = \frac{4\pi qmk^2}{h^3}T^2 e^{-\frac{q\Phi}{kT}}$$

W for metals

A_G

Thermionic Emission

Work function measurement

Work function determination by thermoemission

- typically measured using vacuum diode with heated cathode arrangement
- electrons extracted by potential => possible W change with E (Schottky effect) => extrapolation
- yields surface averaged W

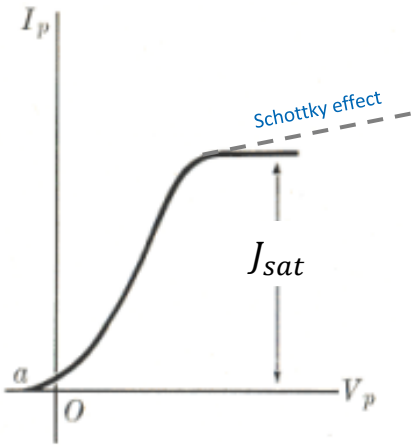
Saturation current method

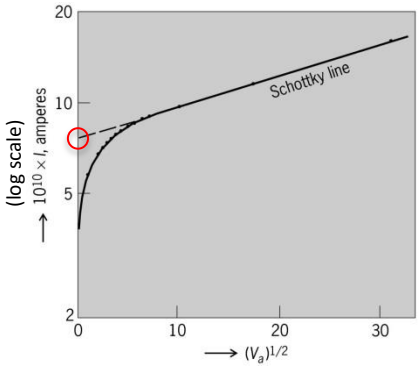
Metoda nasyceného proudu

$$J = \lambda_B (1 - r_{av}) A_0 T^2 e^{-\frac{W}{kT}}$$

If reflection neglected:

$$\Rightarrow \; W = -kT \ln \frac{\lambda_B A_0 T^2}{J_{sat}}$$





Richardson Plot method

Metoda Richardsonovy přímky

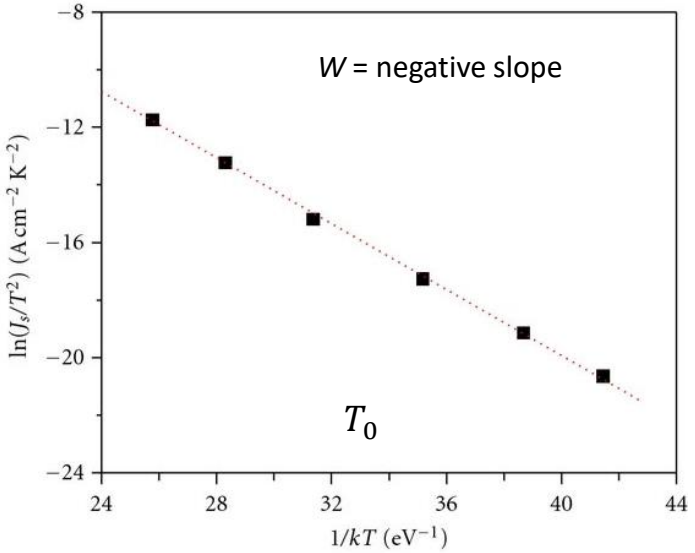
Based on determination of $J_{sat}(T)$ near T_0

$$J_{sat} = AT^2 e^{-W_R/kT}$$

→ Extrapolation to $1/T = 0$ => A
→ Slope => W_R (reduced or Richardson W) = W at 0 K

$$W_R = W(T_0) - \alpha T_0$$

for metals: $\alpha \approx 10^{-4}$ eV/K



Thermionic Emission

Electron emission from semiconductors

Semiconductor vs. metal

- E_F typically within bandgap => crucial role of surface and bulk **local states** (e.g. dopants)
- strong influence of external conditions (mainly T) on W
- emission from **N-type** much more intensive than from P-type

$$W = E_a + E_c - E_F$$

E_a... electron afinity ($E_{vac} - E_c$)
E_c ... conduction band bottom

E_a depends on crystal. structure => weakly T dependent
$E_c - E_F$ much strongly dependent on T

Richardson-Dushman law

Intrinsic semiconductor: approx. valid for $W \approx E_a + E_g/2$

Doped semiconductors → modifications:

Weakly ionized donors (acceptors) – low T or high dopings

N-type $$J = B_{N2}(1-\bar{r})T^{5/4}e^{-\frac{E_a+E_D/2}{kT}}$$

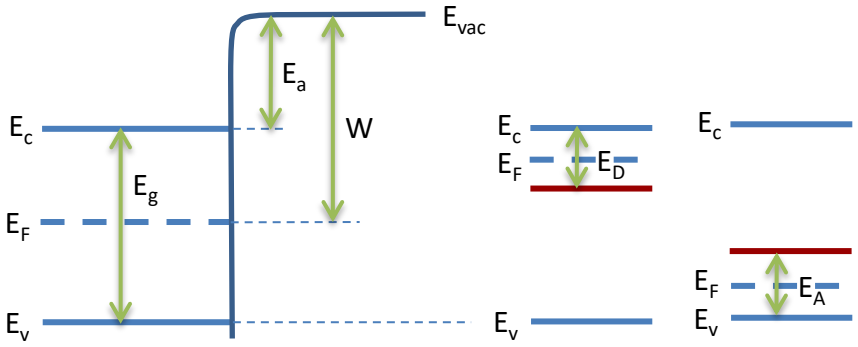
P-type $$J = B_{P2}(1-\bar{r})T^{11/4}e^{-\frac{E_a+E_g-E_A/2}{kT}}$$

Typical fully ionized donors (acceptors)

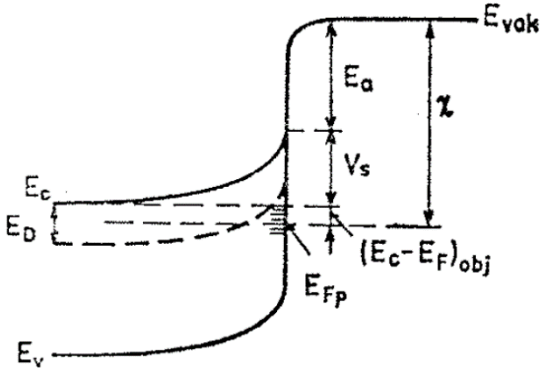
N-type $$J = B_{N3}(1-\bar{r})T^{1/2}e^{-\frac{E_a}{kT}}$$

P-type $$J = B_{P3}(1-\bar{r})T^{7/2}e^{-\frac{E_a+E_g}{kT}}$$

intrinsic **N** **P**



Role of surface states



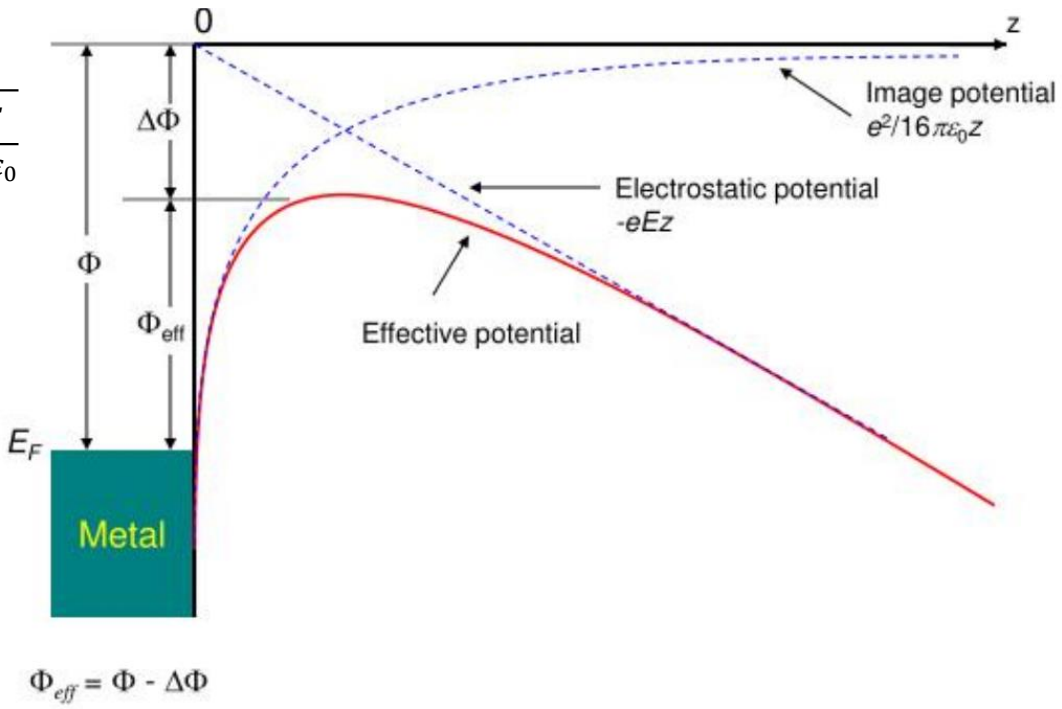
Thermionic Emission

Schottky effect

Schottky effect = field enhanced thermionic emission (thermo-field emission)

– Work function lowered by external potential

$$\Delta\Phi = \sqrt{\frac{eE}{4\pi\varepsilon_0}}$$



$$\Phi_{eff} = \Phi - \Delta\Phi$$

Schottky formula

$$J(E,T,W) = A_G T^2 e^{-\frac{W-\Delta W}{kT}}$$

$$\Delta W = e\Delta\Phi = \sqrt{\frac{e^3 E}{4\pi\varepsilon_0}}$$

E ... electric field

E = 1 kV/cm => $\Delta W \approx$ 10 meV

Thermionic Emitters

Termokatody

Materials and examples

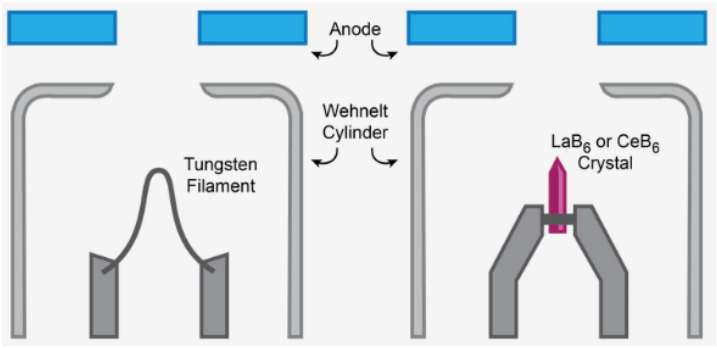
General requirements:

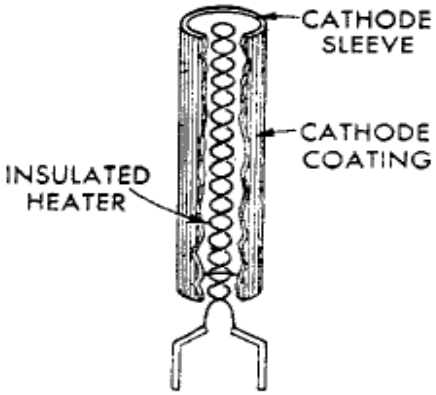
- low ratio of *W* and operating *T*
- high melting point and vapor pressure

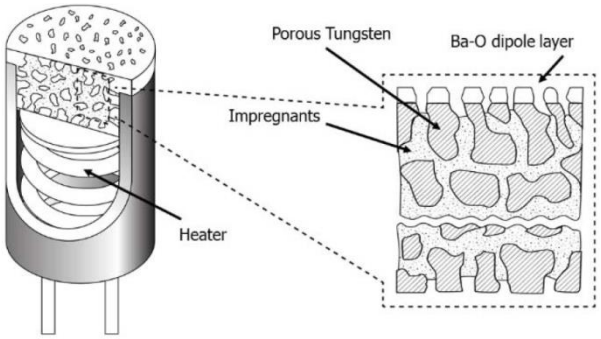
zásobníkové

Shape: Wire, coil, strip, tip, containers/pellets, ...

Material: Metal, oxide, coated metal

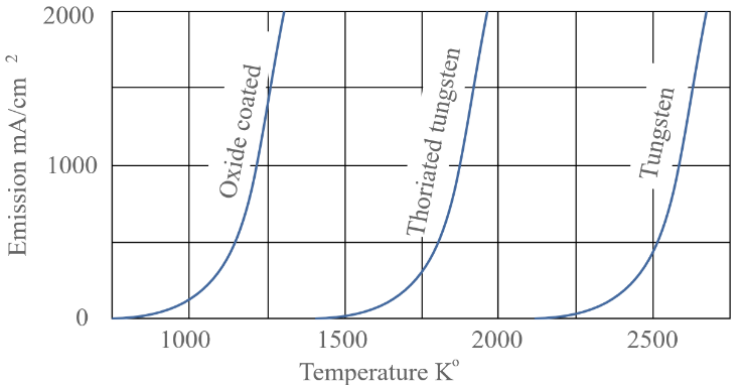






Thermionic Emitters

Materials and examples



	T (°K)	J (A/cm^2)	Relative efficiency
Tungsten	2500	0.4	1
Thoriated tungsten	1950	1.5	10
BaO (as coated cathode tube)	1050	0.2	20
BaO (filament)	1050	0.2	100

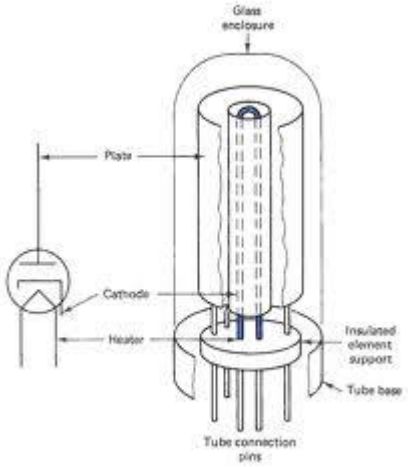
Materiál katody	χ (eV)	A (A . cm^{-2} K^{-2})	T_p (K)	j/P (mA . W^{-1})	χ/T_p (10^{-3} eV . K^{-1})
W	4,5	60—100	2500		1,8
Mo	4,2	55	2300		1,83
Ta	4,1	40—60	2100	2—10	1,95
LaB_6	2,7	30—70	1700—1800		1,55
W + Th	2,6	3	1900		1,37
W + Ba	1,6	1,5	1000	5—100	1,6
W — O — Ba	1,3	0,18	1000		1,3
Ba + Sr na Ni	1	$10^{-2} - 10^{-3}$	1100		0,9
Ba + Sr na W	1,6	$10^{-2} - 10^{-3}$	1400	100—1000	1,14
ThO na W	1—1,5		1800		0,7

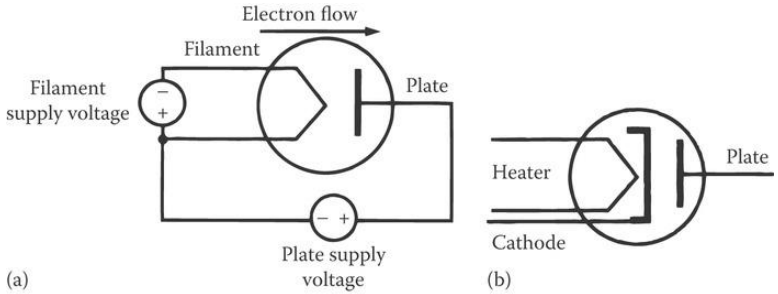
Thermionic Emission

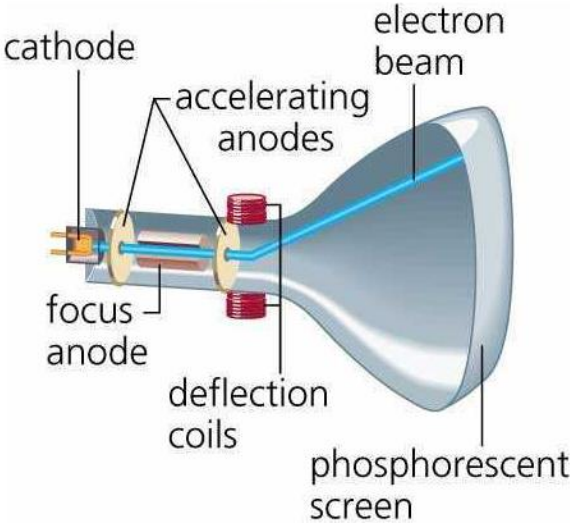
Applications

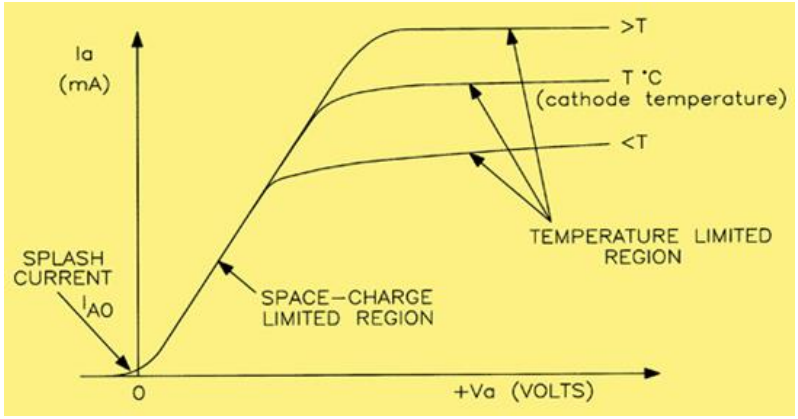
- Thermionic (vacuum) diode — vakuová dioda
- Electron (vacuum) tube — elektronky
- Electron gun — elektronové dělo (tryska)

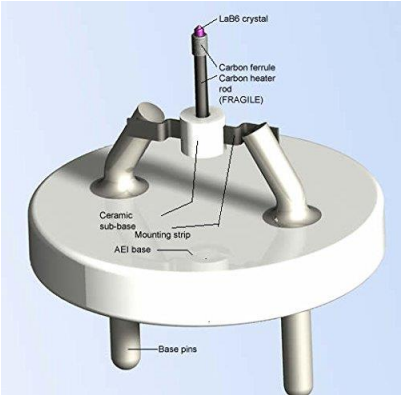
  - screens, VF generators, microscopes, spectrometers, el. litography, ...











Field Emission

Basics and theory (for metals)

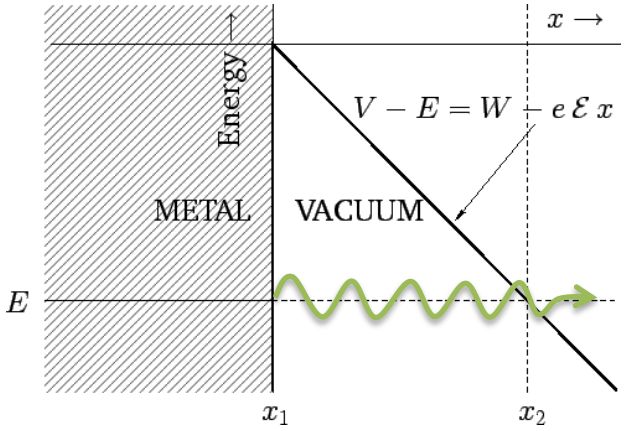
Tunelová emise
(autoemise, polní emise)

Field Emission (or **cold emission, autoemission**) of electrons
= liberation of electrons from a matter caused by strong electrostatic field

- usually from metal to vacuum

- QM phenomena: explained by quantum tunneling
- Fields $\gtrsim 10^8$–10^9 V/m required for metals
- No activation energy

Triangular potential barrier



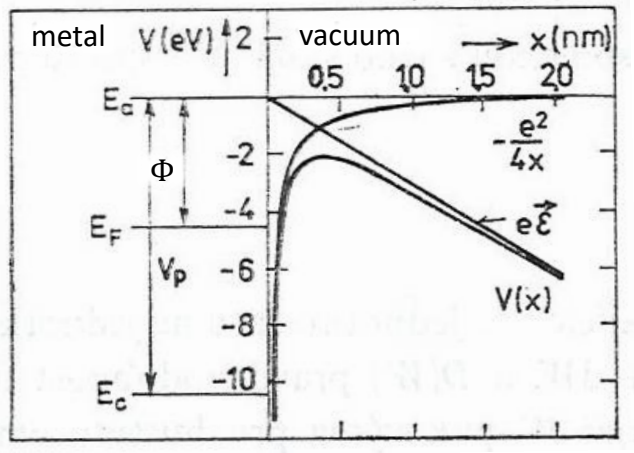
(no image charge considered)

Solution proposed for metals (perfect surface, Sommerfeld model, equilibrium)
by R.H. Fowler & L.W. Nordheim (1928)

– approximate theory (sometimes extended to other bulk crystalline solids)
– one of the verifications of the **quantum theory**

Field electron emission regime – most electron emitted via tunneling
Often multiple emission processes involved

$$V(x) = -\frac{e^2}{4\pi\varepsilon_0 2x} - e\mathcal{E}x$$



Field Emission

Theory (for metals)

Fowler–Nordheim theory of tunneling

- wave-mechanical tunneling through rounded triangular potential barrier

$$j = \int_0^\infty N(E_\perp) D(E_\perp, \mathcal{E}) \mathrm{d}E_\perp$$

$$E_\perp = \frac{{p_x}^2}{2m_e}$$ … perpendicular component of energy

Sommerfeld model:

$$N(E_\perp)\mathrm{d}E_\perp = \frac{4\pi m_e kT}{h^3} \ln\left(1 + e^{-\frac{E_\perp - e\Phi}{kT}}\right) \mathrm{d}E_\perp$$ … electron flux to surface → temper. term (F-D)

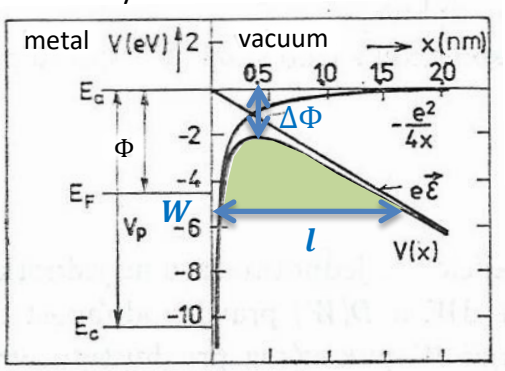
($W = e\Phi$)

$D(E_\perp, \mathcal{E}) = 1 - R(E_\perp, \mathcal{E})$ … **escape probability** (transmission coeff., "barrier transparency")

$$D(E_\perp, V(x)) = {\psi^2(l)}\Big/{\psi^2(0)}$$ … wavefunction at outer barrier edge / … wavefunction at metal-vacuum interface

$$D(E_\perp) = f(E_\perp, V) \exp\left[-2\frac{\sqrt{2m_e}}{h}\int_0^l \sqrt{V(x) - E_\perp}\,\mathrm{d}x\right]$$ ≈ … Wentzel-Kramers-Brillouin (WKB) solution

Schottky effect considered



Potential barrier (with image charge):

$$V(x) = -\frac{e^2}{4\pi\varepsilon_0 2x} - e\mathcal{E}x$$

Fowler-Nordheim formula

$$j = a\mathcal{E}^2 \exp\left(-bc\frac{W^{3/2}}{\mathcal{E}}\right)$$

a, b … material-specific factors (weakly $\mathcal{E}$ dependent)

c … barrier shape correction factor (c=1 … triangular)

$$j = \frac{1.54 \times 10^{-6}}{\Phi + t^2(y)} \mathcal{E}^2 \exp\left(-6.83 \times 10^7 f(y) \frac{W^{3/2}}{\mathcal{E}}\right)$$

$f(y)$ … Fowler-Nordheim function, $y \equiv \Delta\Phi/\Phi$

$$t(y) = f(y) - \frac{2}{3} y \left[\frac{\mathrm{d}f(y)}{\mathrm{d}y}\right]$$

Appendix

Field Emission

Theory (for metals)

QM derivation for planar surface and triangular barrier

Shrödninger eqs. in x-direction

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2}\psi_i(x) = E_\perp\psi_i(x)\,, \qquad x \le 0$$

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2}\psi_t(x) + V(x)\psi_t(x) = E_\perp\psi_t(x)\,, \qquad x \ge 0$$

$$\frac{\partial^2}{\partial x^2}\psi_t(x) = \frac{2m_e}{\hbar^2}[V(x) - E_\perp]\psi_t(x)\,, \qquad x \ge 0$$

Assuming $V(x)$ independent of x in $(x, x + \mathrm{d}x)$:

$$\psi_t(x + \mathrm{d}x) = \psi_t(x)e^{-\alpha \mathrm{d}x}, \qquad \alpha = \frac{1}{\hbar}\sqrt{2m_e[V(x) - E_\perp]}$$

For slowly varying potential
(Wigner, Kramers, Brillouin (WKB) approximation):

$$\psi_t(l) = \psi_i(0)\exp\left(-\int_0^l \frac{1}{\hbar}\sqrt{2m_e[V(x) - E_\perp]}\mathrm{d}x\right)$$

$$D(E_\perp, V(x)) = {}^{j_t}\!/_{j_i} \qquad \text{(transmitted / incident current density)}$$

$$j_{i,t} = \frac{i\hbar}{2m_e}\left(\psi_{i,t}\frac{\partial}{\partial x}{\psi_{i,t}}^* - {\psi_{i,t}}^*\frac{\partial}{\partial x}\psi_{i,t}\right)$$

$$D(E_\perp, V(x)) = {}^{\psi^2(l)}\!/_{\psi^2(0)}$$

Triangular barrier: $\quad V(x) - E_\perp = W - e\mathcal{E}x$

$$D(E_\perp, V(x)) = \exp\left(-2\frac{\sqrt{2m_e e}}{\hbar}\int_0^l \sqrt{\mathcal{E}(l - x)}\mathrm{d}x\right)$$

$$\boxed{D(E_\perp, V(x)) = \exp\left(-\frac{4}{3}\frac{\sqrt{2m_e e}}{\hbar}\frac{W^{3/2}}{\mathcal{E}}\right)}$$

$$j = e\int v_R n_e D\mathrm{d}E$$

n_e … electron density

F-D: $\mathrm{d}n_e(E) = g(E)\frac{1}{1+e^{\frac{E-E_F}{kT}}}\mathrm{d}E$

$$v_R = \sqrt{\frac{kT}{2\pi m_e}}$$

… Richardson velocity
(average velocity with which electrons approach the interface)

$$\boxed{j = a\mathcal{E}^2\exp\left(-bc\frac{W^{3/2}}{\mathcal{E}}\right)}$$

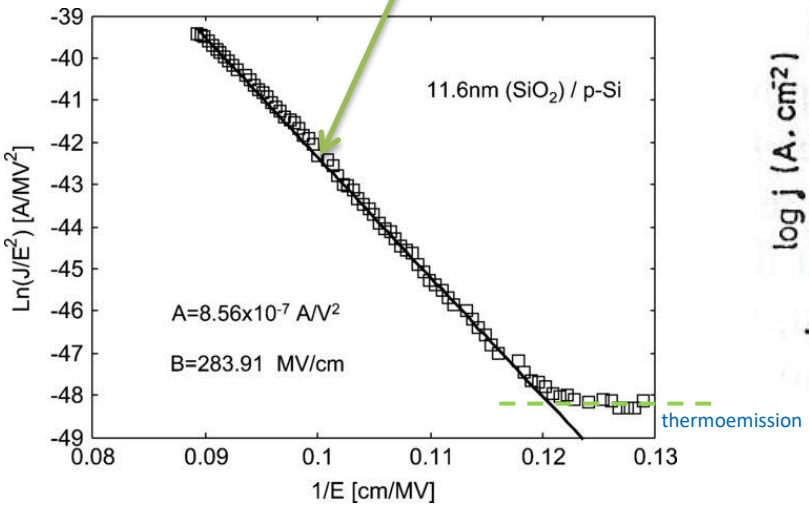
Fowler-Nordheim formula

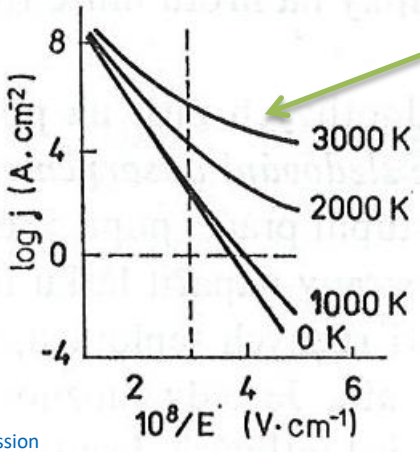
Field Emission

Theory (for metals)

VA characteristics

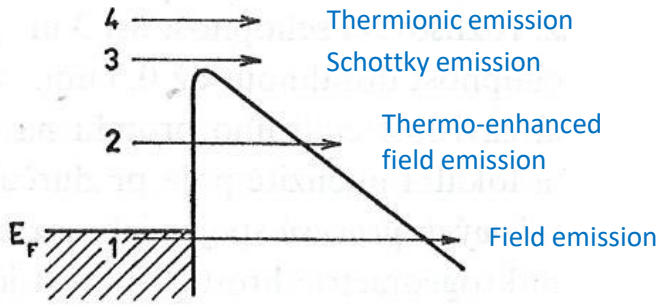
Fowler-Nordheim plot



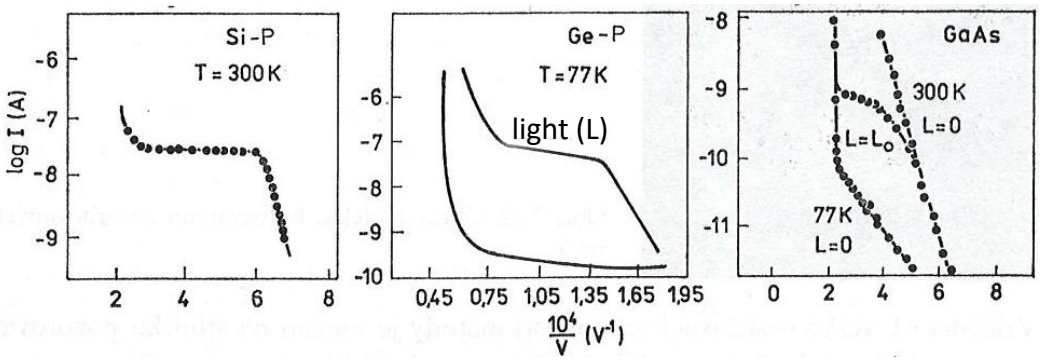


Higher temperatures
→ deviation from F-N formula

=> **Work function** determination from field emission



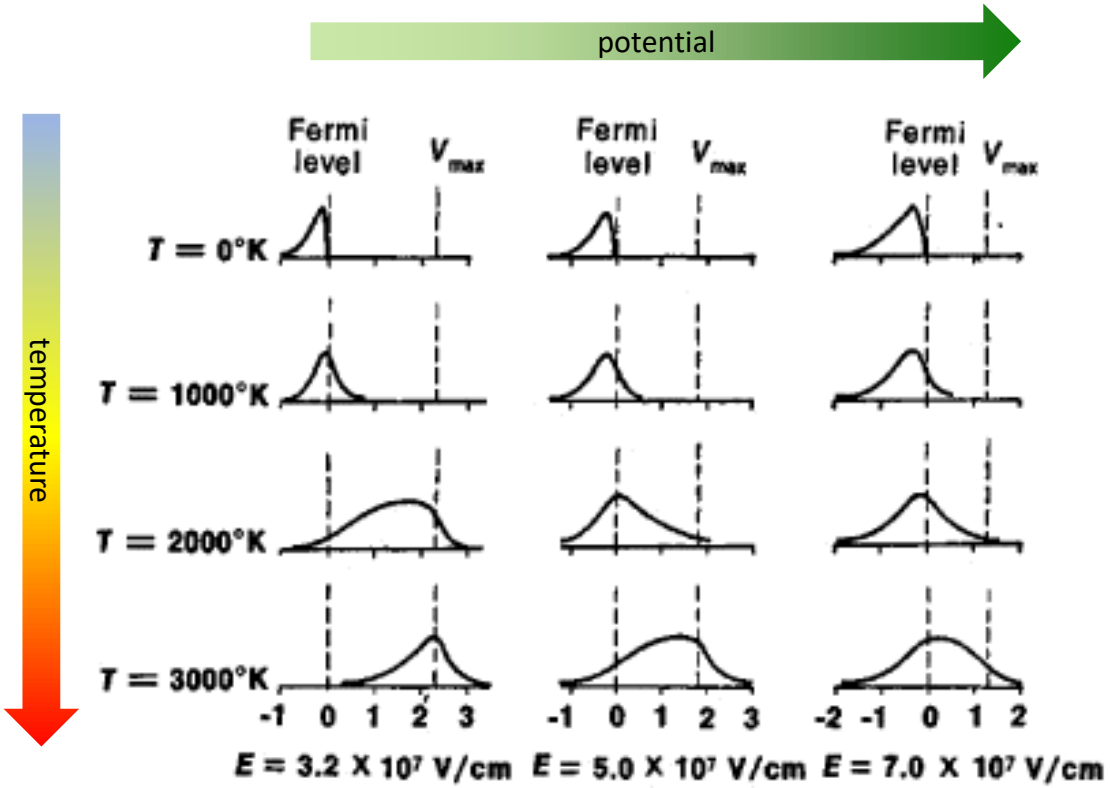
Compare: **Semiconductors** – strong **T** and **light** dependence

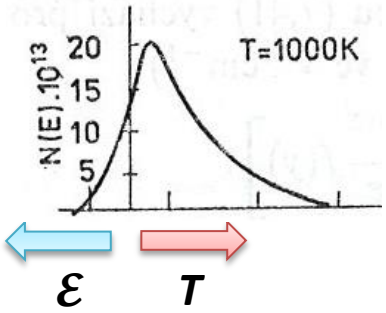


→ used as IR light detectors

Field Emission

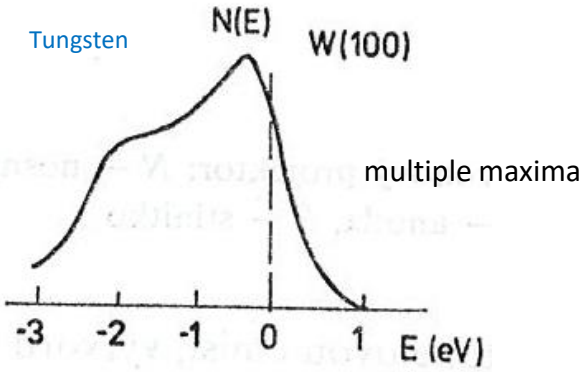
Energy distribution



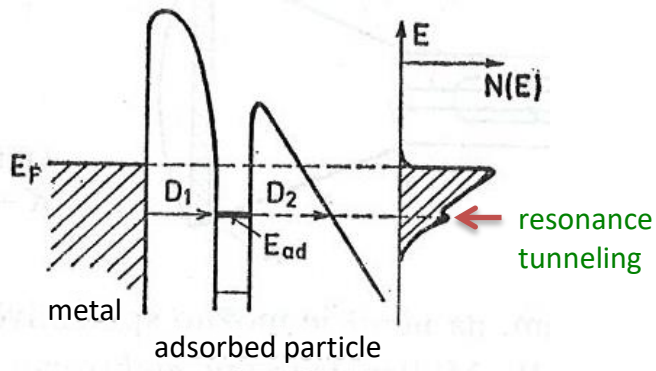


Field emission energy spectrum with DOS consideration

DOS = density of (electronic) states
(generally non-parabolic)



Surface with adsorbate in strong field



→ (Scanning) tunneling spectroscopy

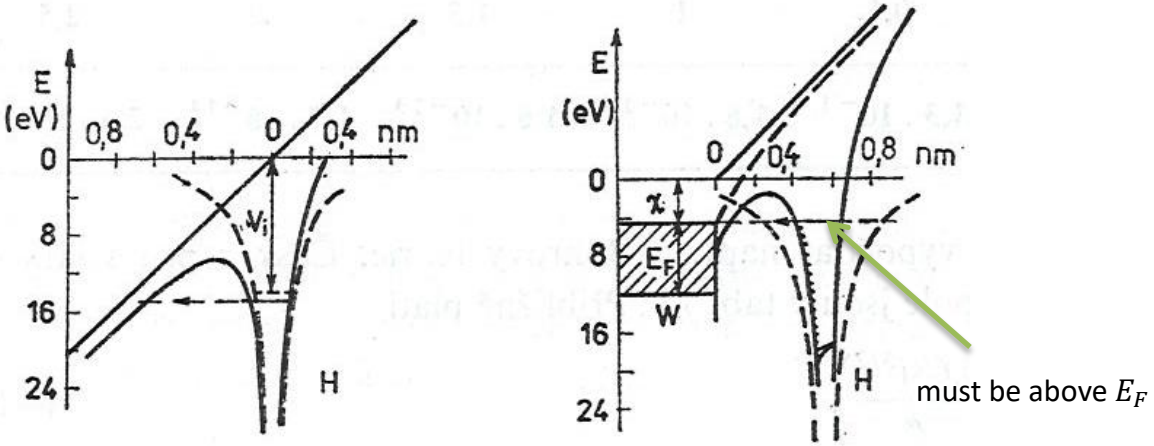
Field Emission

Other field-induced phenomena

- Field-induced ionization (gas phase)
- Field-induced desorption
- Field-induced evaporation

– Higher field required than for field electron emission (~10^{10} V/m)

Hydrogen **free** **adsorbed**



V_i … ionization energy

Applications

– surface imaging
– surface cleaning
– bulk probing (surface imaging & field evaporation)
– gas ionization

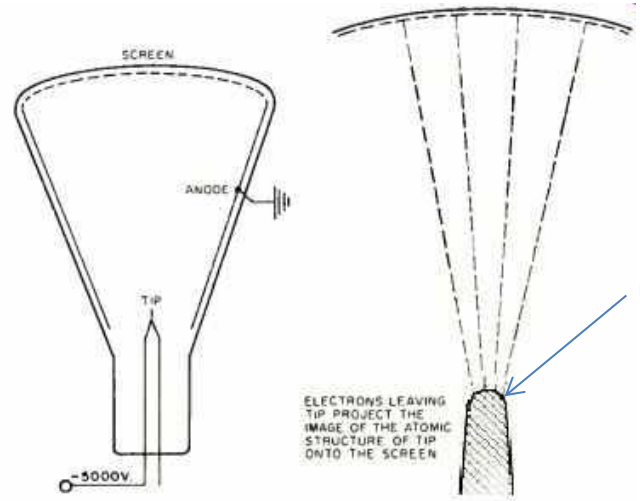
Field Emission

Applications

iontový projektor

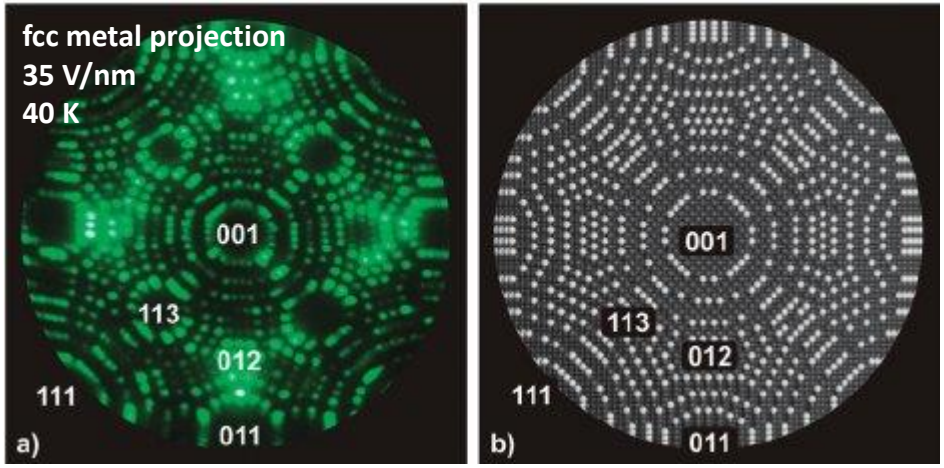
Electron projector (field electron microscope, FEM) autoemisní mikroskop

– One of the first surface-analysis instruments with near-atomic resolution
– Only strong metals (W, Pt, Mo, …) – high mechanical stress
– Magnification up to 10^6



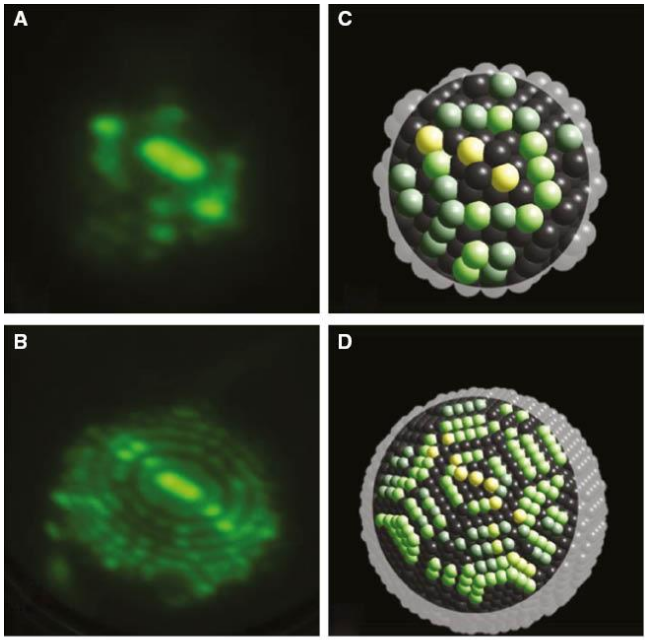
fluorescent screen
or
multichannel plate

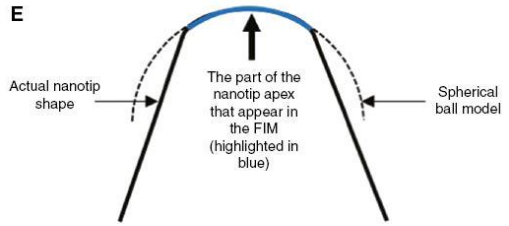
usually <50 nm



Ion projector (field ion microscope, FIM)

– Projection via imaging gas (usually inert or H) at low T and 10^{-3} – 10^{-1} Pa
– Positive tip potential – tunneling from atom to tip
– Heavier particles => better resolution
– Not too strong fields (to avoid suppression of lattice potential contrast)





Field Emission

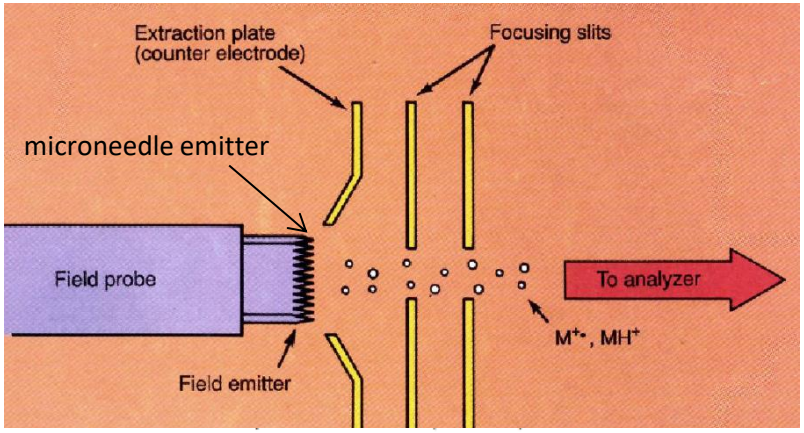
Applications

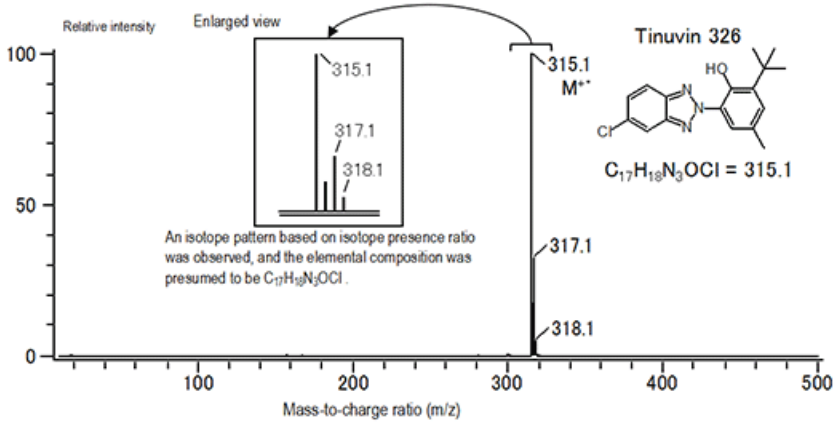
Field ionization mass spectrometry (FIMS)

– soft ionization method (weak fragmentation => molecular spectra)
– no temperature necessary (like in TPD)

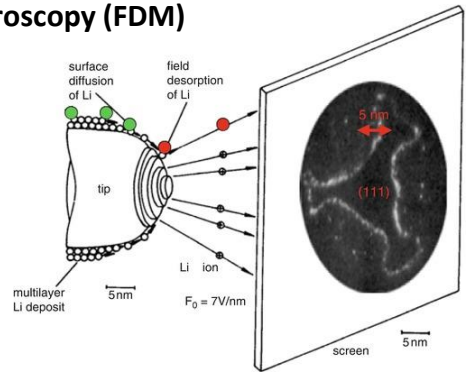
Field desorption mass spectrometry (FDMS, atom probe)

– production of ions from solid or liquid state
– alternative mechanisms: cation attachment, thermal ionization, proton abstraction



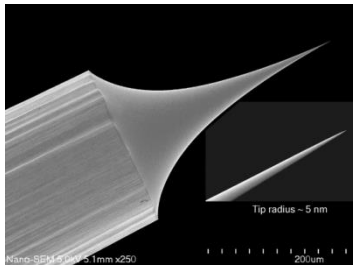


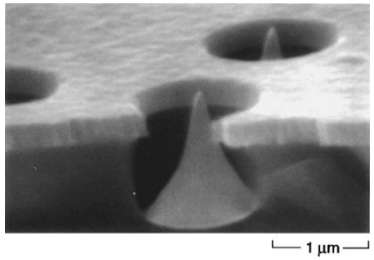
Field desorption microscopy (FDM)

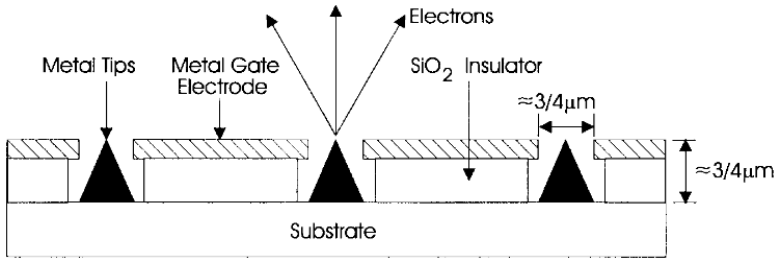


Cold cathode electron source

– tip (→ cold cathode field emission gun, CFEG) or field emission array (FEA)
– fast time modulation possible
– high currents (tips >10^9A/cm^2, arrays >2000A/cm^2)
– SEM, EELS, EDS, µvawe amps, flat displays, power switches, ...





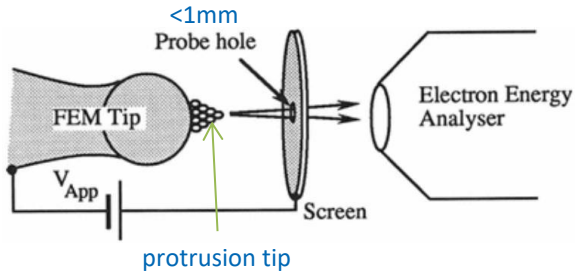


Field Emission

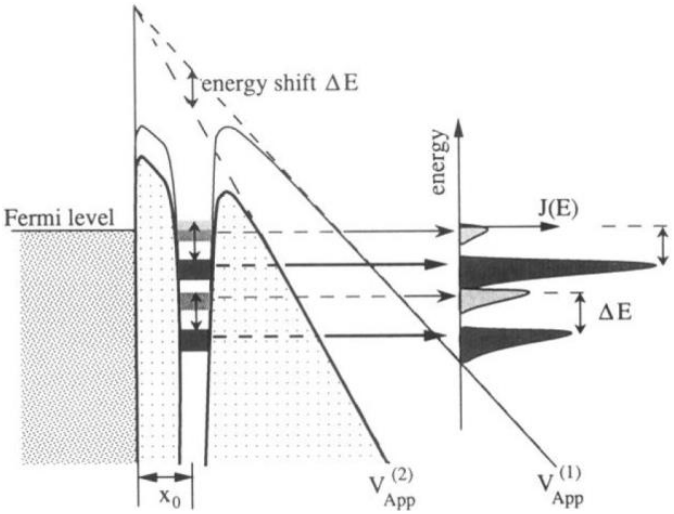
Applications

Field emission electron spectroscopy

→ Energy distribution from a small selected area
=> probing local DOS

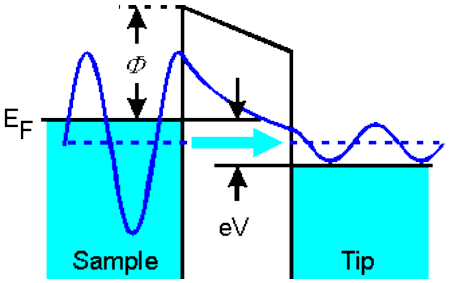


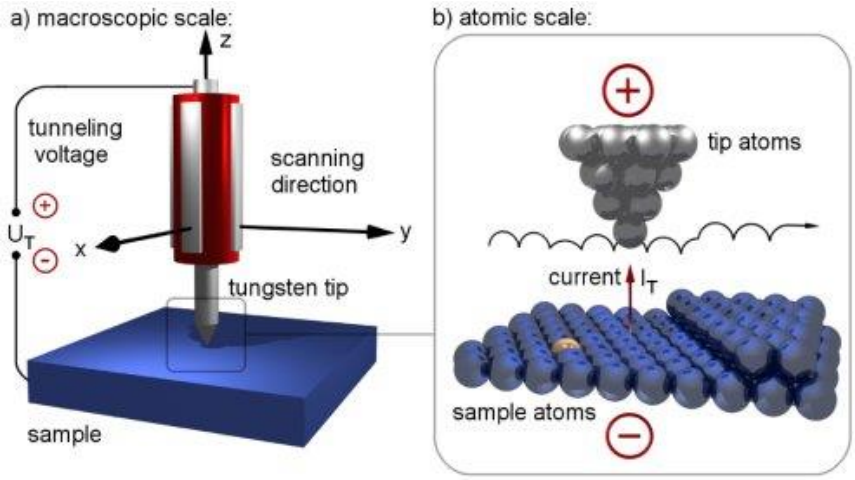
adsorbate spectra



Scanning tunneling microscopy

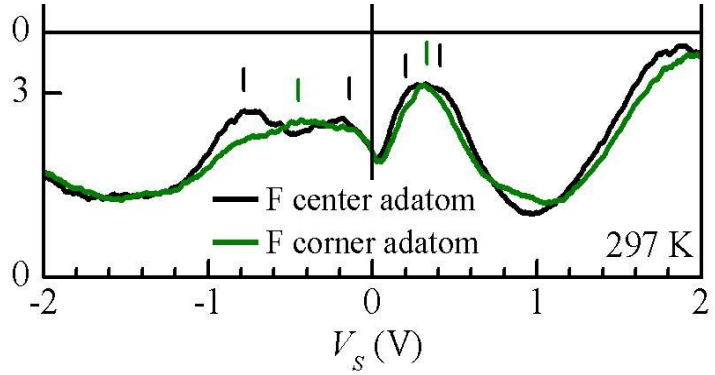
– surface-tip distance ~4-10 Å
– currents ~10pA-nA





Scanning probe spectroscopy

– probes both occupied and empty states



Photoemission

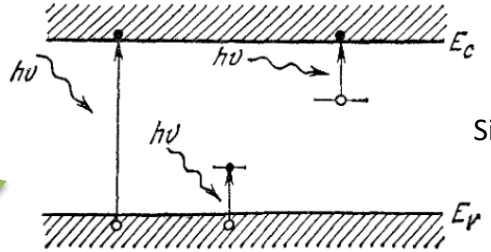
Introduction

Interaction of photons with solids:
- reflection, scattering, absorption

Photoelectric effects

Solid bulk → photoconductivity
- low $h\nu$ (IR): absorption by lattice → T increase
- high $h\nu$: electron excitation
  - – conductance el., excitation of band gap states, electron-hole pair ($h\nu \geq E_g$)
  - – more than 1 photoelectron can be created by 1 photon (quantum yield>1)

kvantový výtěžek



Silicon

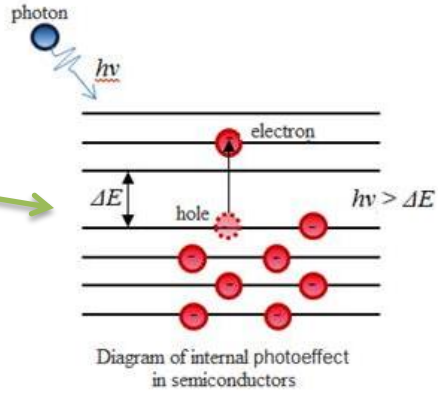
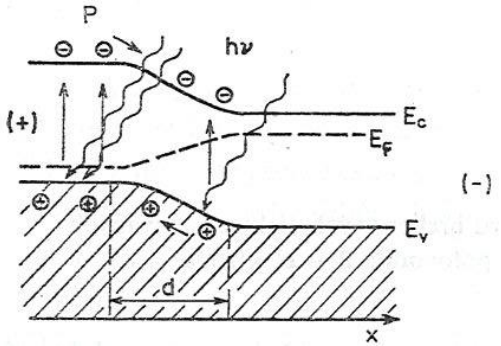


Diagram of internal photoeffect in semiconductors

Solid interface
internal → **photoelectric potential**
external → **photoemission**

Local non-homogeneity (Schottky barrier, PN junction, …)

=> light generates **local potentials** (core-hole pairs created)



Photoemission

Fundamentals

Brief history

1887: Discovery of photoelectric effect (*H. Hertz*)
1899: Discovery and identification of the electron (*J.J. Thompson*)
1900: Discovery of energy quanta (black body radiation) (*M. Planck*)
1905: Quantum theory (photoelectric eff. explanation) (*A. Einstein*)

Classical expectations

1) Force on electrons ∝ electric field of light

$$\vec{F} = -e\vec{E}$$

=> E_k of electrons should increase with $|\vec{E}|$

2) Electron should be emitted independent of light frequency ν for sufficiently large $\vec{E}$

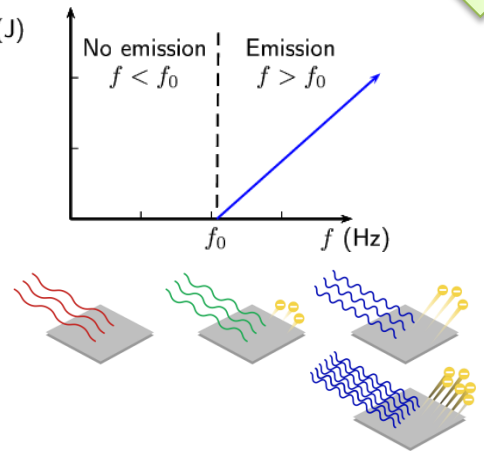
3) For very low light intensity: lag between exposure and el. emission (needed to absorb enough energy)

Actual results

1) Maximum E_k independent of intensity, but depends on ν.

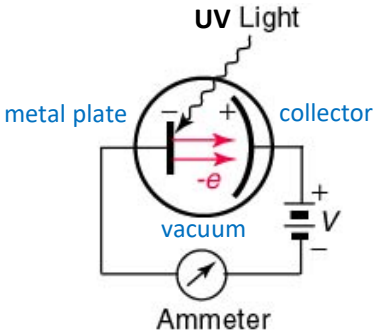
2) Minimal cut-off frequency ν_0 required for emission

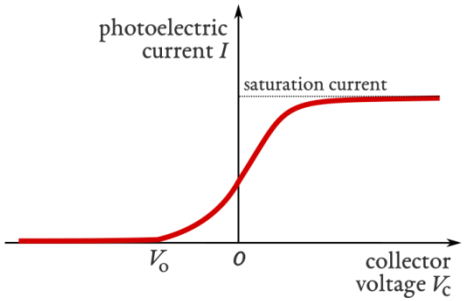
3) No time lag. Light intensity determines emission rate.



Photoelectric effect vnější fotoefekt

Experiment (discovery)





Hertz:
light → charged particles

Thompson: charged particles = electrons

Explanation (theory)

Planck, Einstein: light is emitted and absorbed in **quanta of energy**

$$E = h\nu$$

→ electron absorbs a single quantum to leave the material

dlouhovlnná mez

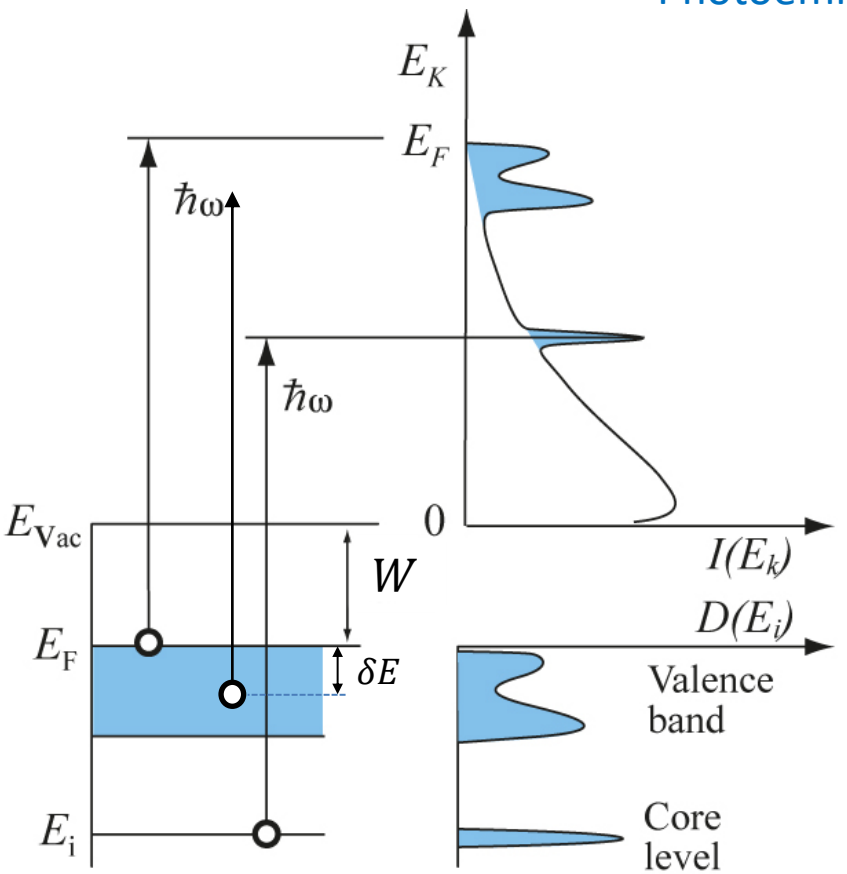
$$E_k^{max} = h(\nu - \nu_0)$$
$$E_k^{max} = h\nu - W$$

ν_0 … threshold freq.
h … Planck's constant
W … (photoelectric) work function

Millikan: further verified in subsequent experiments

Photoemission

Photoemission from metals



$$E_k = h\nu - W \pm \delta E - \Delta E$$

ΔE … energy losses

δE … can be <0 for T>0 K

No losses, emission from Fermi edge:

$$E_k = h\nu - W = h\nu - h\nu_0 = h(\nu - \nu_0)$$

$$W\ [eV] \approx \frac{1236}{\lambda_0[nm]}$$ => UV range

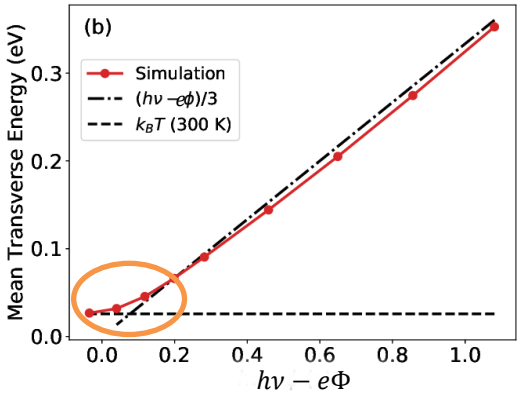
core levels => RTG range

Beyond Einsten's theory:

Optical properties
– reflection & absorption coeff. (ν dependent)
– interferences (layered materials)
Transport of excited (hot) electrons
Thermal effects

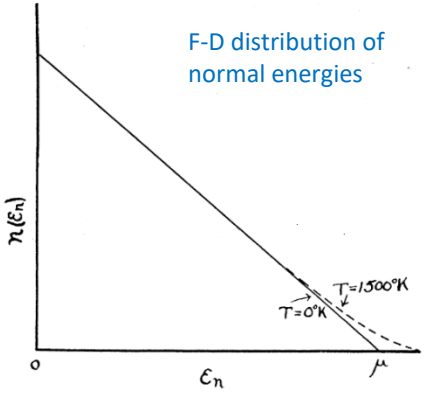
3-step model
1) Probability of absorption of photon by electron and its excitation
2) Probability of photelectron scattering on its path to surface
3) Probability of photoelectron transmission through surface

Often not well separable (the steps can interfere)
→ one-step model – more accurate



Photoemission

Photoemission from metals



Photoemission current:

$$j_f = e\int_{E_a}^{\infty} N'(E)P(E)\mathrm{d}E$$

- $P(E)$: probability of electron escape (to vacuum)
- $N'(E)$: distribution function of electron flux (supply) to surface
- E_a: electron affinity

Fowler-DuBridge theory

Assumptions:

- 1D Sommerfeld model of metal considered
  (free electron gas, F-D distribution, uniform distribution of electrons in momentum space)
- Photon absorption probability (α) independent of initial el. energy state
  => shifted distr. function: $N'(E) = N(E + h\nu)$
- Electron transport losses and reflection neglected

Valid only for metals near Fermi edge, i.e. for frequencies near ν_0
(nearly constant DOS => nearly constant excitation probability)

$$j_f = e\int_{E_a - h\nu}^{\infty} \alpha N(E_\perp)\mathrm{d}E_\perp$$

$$j_f = e\alpha\frac{4\pi m_e kT}{h^3}\int_{E_a-h\nu}^{\infty} \ln\left(1 + e^{-\frac{E_\perp - W}{kT}}\right)\mathrm{d}E_\perp$$

(see field emission theory)

Subst.: $t \equiv -\frac{E_\perp - W}{kT}$ $\quad x \equiv \frac{h(\nu-\nu_0)}{kT}$

$$j_f = \alpha\frac{4\pi e m_e k^2 T^2}{h^3}\int_{-\infty}^{x} \ln(1 + e^t)\,\mathrm{d}t$$

$$j_f = \alpha A_0 T^2 f(x)$$ $\quad A_0$ … Sommerfeld constant

$$x \le 0 : f(x) = e^x - \frac{e^{2x}}{2^2} + \frac{e^{3x}}{3^2} - \cdots$$

$$x \ge 0 : f(x) = \frac{x^2}{2} + \frac{\pi^2}{6} - e^{-x} + \frac{e^{-2x}}{2^2} + \cdots$$

Photoemission

Photoemission from metals

$$j_f = \alpha A_0 T^2 f(x) \qquad x \equiv \frac{h(\nu - \nu_0)}{kT}$$

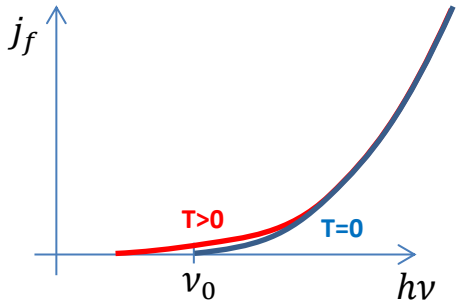
$$x \le 0 \;:\; f(x) = e^x - \frac{e^{2x}}{2^2} + \frac{e^{3x}}{3^2} - \cdots$$

$$x \ge 0 \;:\; f(x) = \frac{x^2}{2} + \frac{\pi^2}{6} - e^{-x} + \frac{e^{-2x}}{2^2} + \frac{e^{-3x}}{3^2} + \cdots$$

$T = 0$K

$\nu < \nu_0 : \; j_f = 0$ => PE threshold

$\nu > \nu_0 : \; j_f = \alpha A_0 \frac{h^2}{2k^2}(\nu - \nu_0)^2$



$T > 0$K

$$\ln\left(\frac{j_f}{T^2}\right) = \ln(\alpha A_0) + \ln f(x) = B + \Phi_F\left[\frac{h}{kT}(\nu - \nu_0)\right]$$

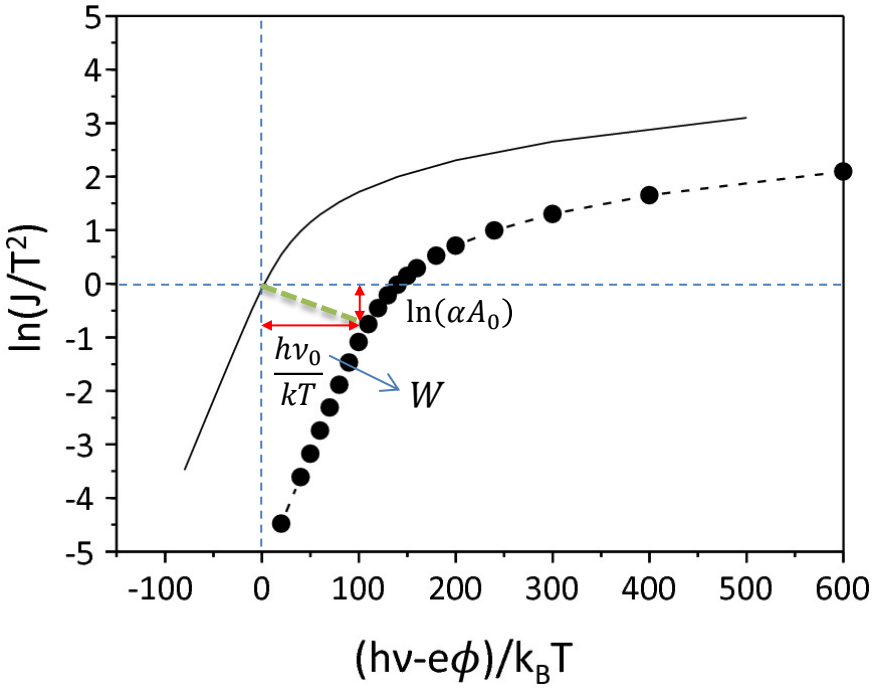
Fowler function

$\nu \approx \nu_0 : \; j_f = \alpha A_0 T^2$

$\nu < \nu_0 : \; j_f \approx \alpha A_0 T^2 e^{-\frac{h(\nu-\nu_0)}{kT}}$ = Richardson-Dushman eq.

$\nu > \nu_0 : \; j_f \approx \alpha A_0 \left[\frac{h^2(\nu-\nu_0)^2}{k^2} + \frac{\pi^2}{3}T^2\right]$

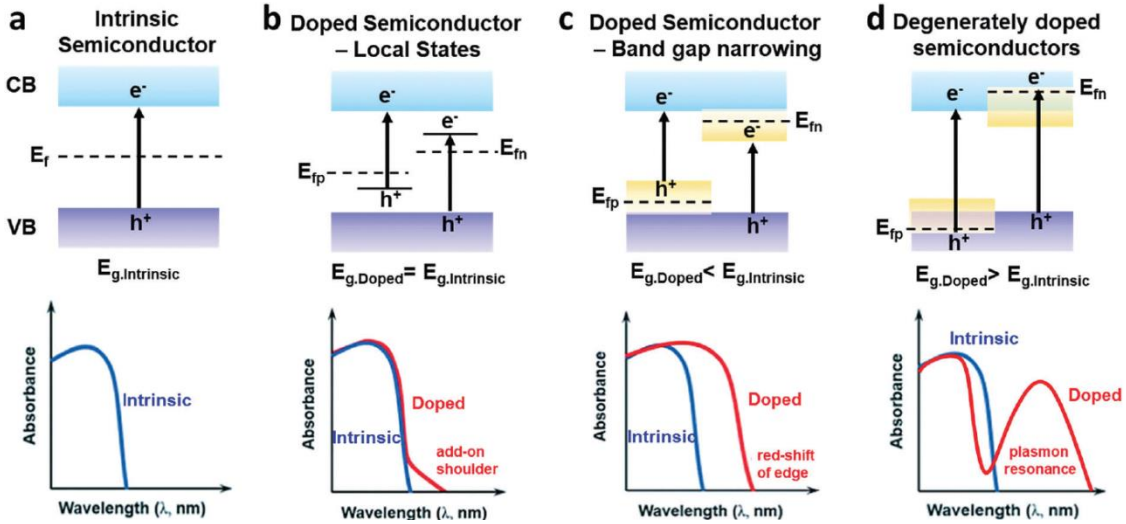
=> weak dependence on T (unless $\nu \approx \nu_0$)



Photoemission

Photoemission from semiconductors

Differences from metals:
- electronic properties
- optical properties
- external field effects
  (excitations by el. field, photoautoemission, …)

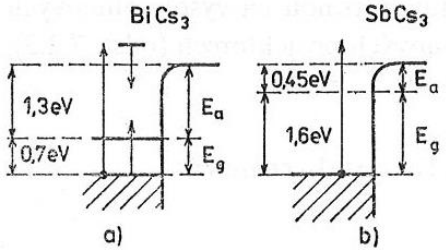


Light absorption
- intrinsic – large ($\alpha \sim 10^4$-10^5 cm^{-1}) vlastní
- doped – small (depends on N_{dop}) příměsová

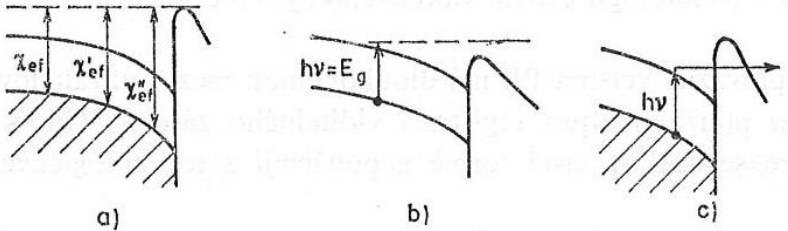
Photoexcitation
- similar to metals: depends on DOS (=> largest in valence band)

but Fowler-DuBridge theory **not** applicable: DOS near PE threshold (= VB top) strongly depends on *E*

Energy loss processes also different
- electron-hole pair creation



Escape from surface
- potential influence of band bending due to surface states
  (=> effective work function change, depth dependent)



Photoemission

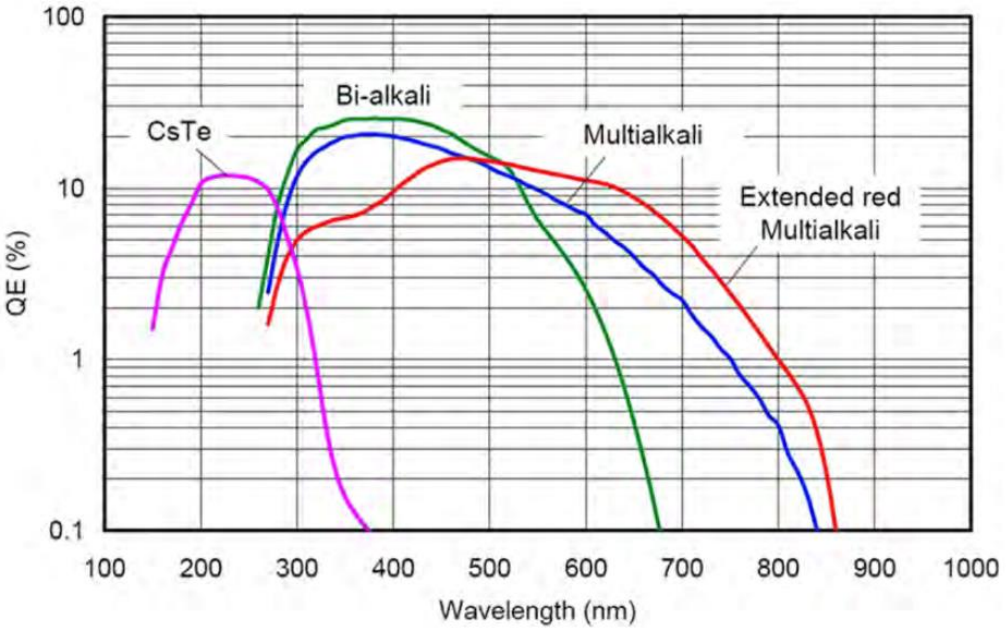
Applications

Photocathodes

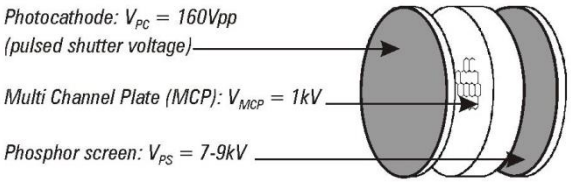
→ Total photoemission current detection and measurement

Main parameters:
- spectral characteristics / range (λ dependence) – sometimes reduced by filters
- quantum yield (q. efficiency) – electrons/photon (up to ~30%)
- integral sensitivity – total current in visible light range
- dark current – mainly due to thermionic emission (cooling needed for IR detectors)

Most **materials** in UV range
=> coatings to lower work function (e.g. Cs, Sb, …)
- Sb-Cs (cesium–antimony, Cs_3Sb)
- Bialkali materials (Sb-Rb-Cs, Sb-K-Cs, …)
- Ag-O-Cs
- Semiconductors (GaAs, InGaAs …), often activated with Cs
- Cs-I and Cs-Te
- … etc.



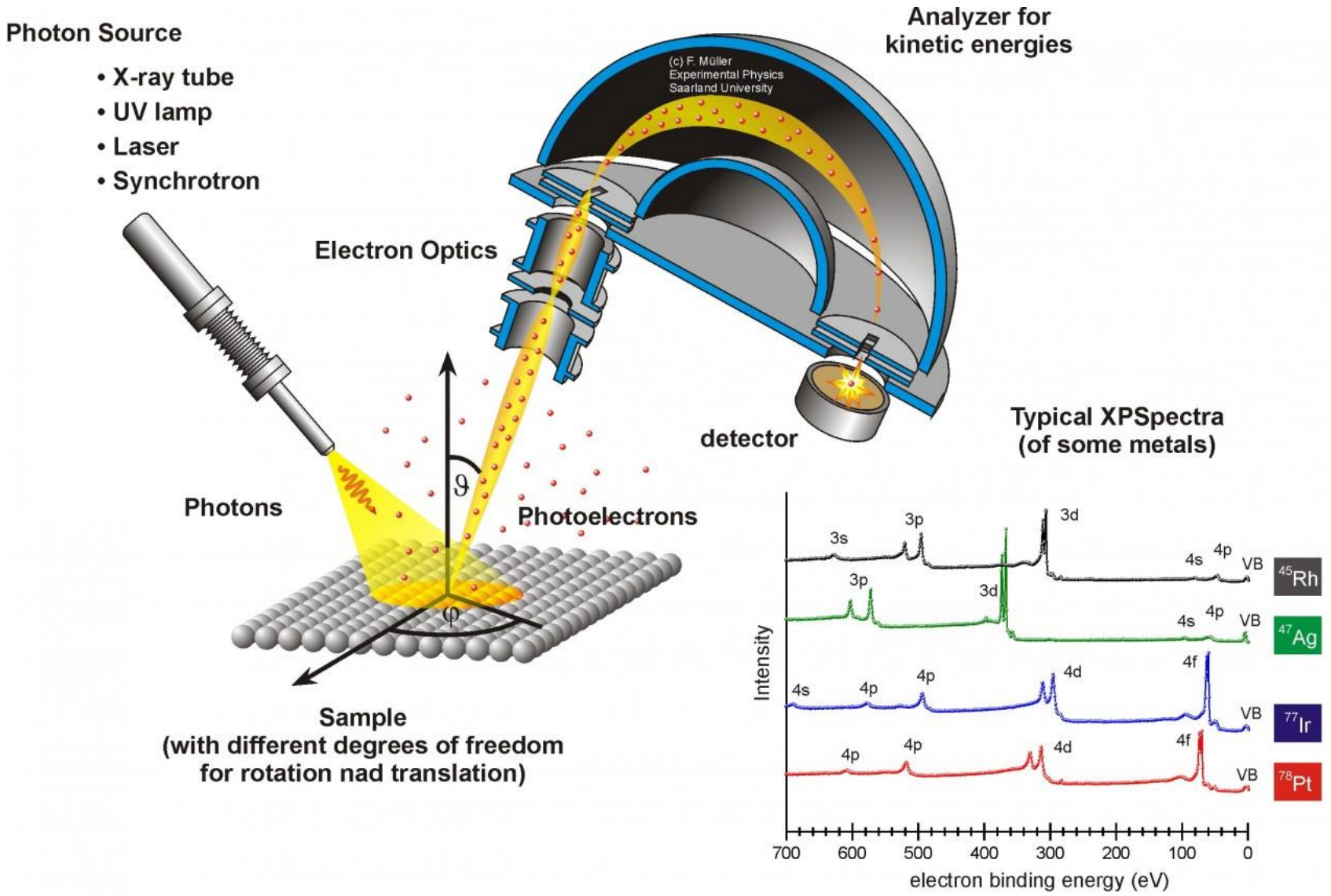
Usage
- photodetectors
- photomultipliers
- infrared viewers
- streak cameras
- image intensifiers (image amplifiers)
- image converters



Photoemission

Applications

Photoelectron spectroscopy = Energy distribution of photoelectrons



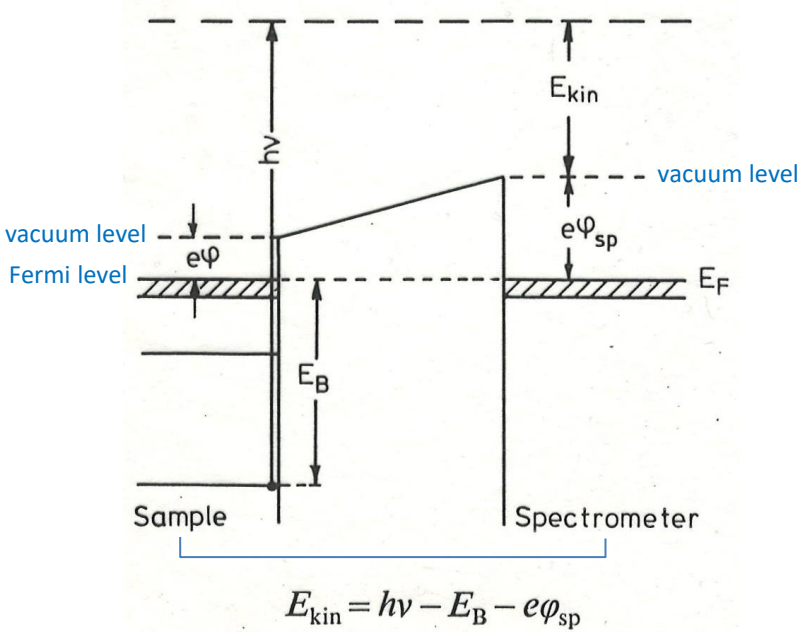
Photoemission

Applications

Photoelectron spectroscopy

- mapping of **occupied** electronic states up to Fermi level
  (empty states → Inverse photoemission spectroscopy)

Energy diagram of the photoemission process



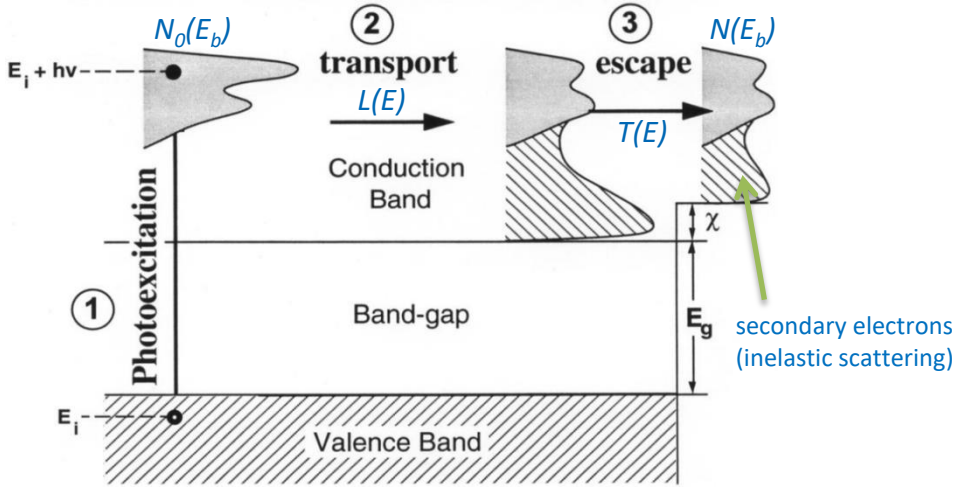
$$E_{kin} = h\nu - E_B - e\varphi_{sp}$$

- **XPS** – core level structure (X-ray)
- **UPS** – valence band structure (~0-40 eV)
- (**SR**)**PES** – synchrotron radiation (wide range, tunable)
- **H**(**A**)**XPES** – hard X-ray (up to ~8keV,)
- + **AR** (angle-resolved) variants

Three-step model

Energy distribution:

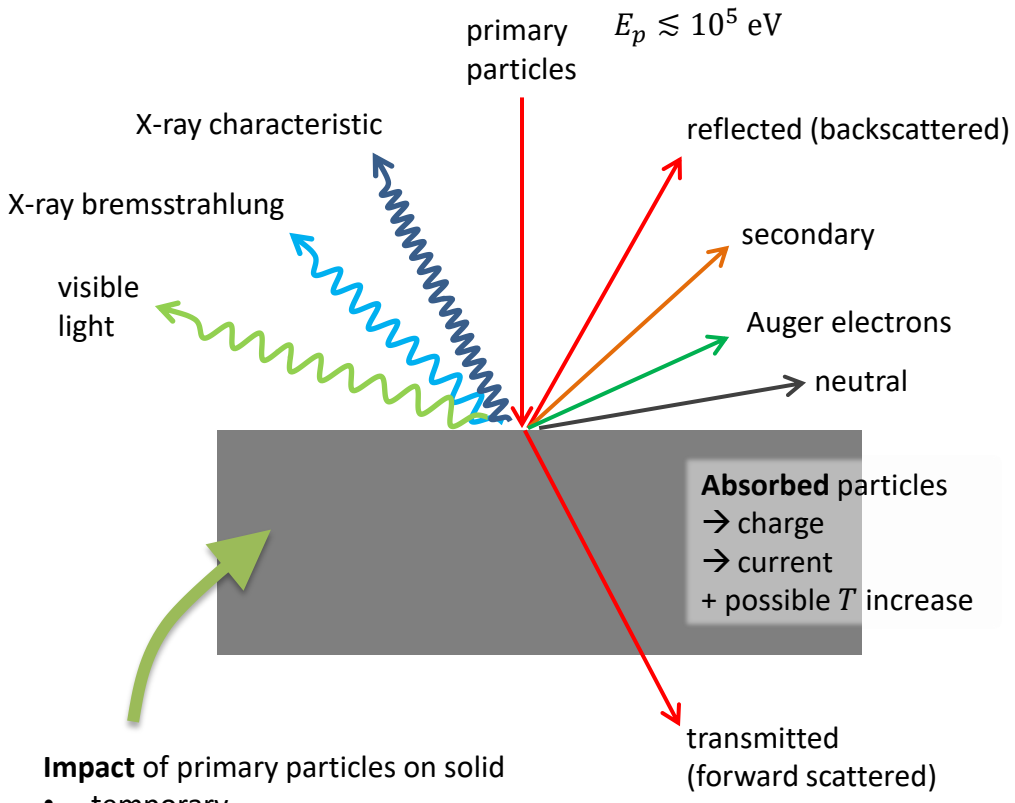
$$N(E_b) = AN_0(E_b)L(E_k)T(E_k)$$



Secondary emission

Introduction

Secondary emission = ejection of electrons from a solid upon impact of **charged particles**.



Impact of primary particles on solid
- temporary
- permanent

Ions as primaries:

→ electrons: ion detectors (ion-el. converter)
→ neutrals: ion sputtering (cleaning, deposition)
→ ions: SIMS, LEIS

Excitation mechanisms: potential, kinetic

Electrons as primaries:

→ photons: X-rays, cathodoluminescence
→ electrons

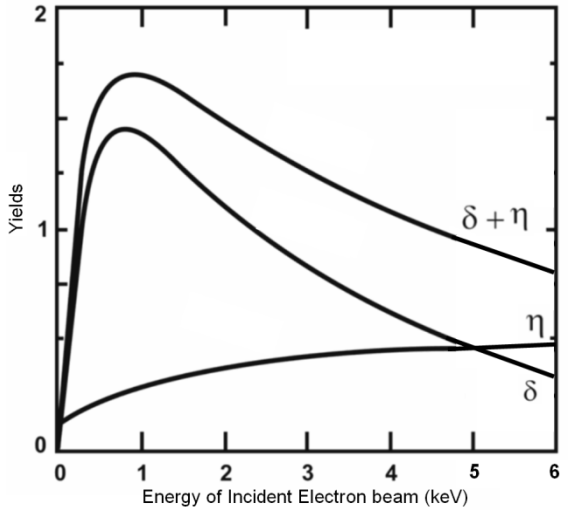
Secondary emission

Secondary electrons

Electrons leaving the surface:

1. Reflected
   – elastic
      – collisions with cores
   – inelastic (Rutherford scattering)
      – interactions with electrons

2. „True“ secondary electrons



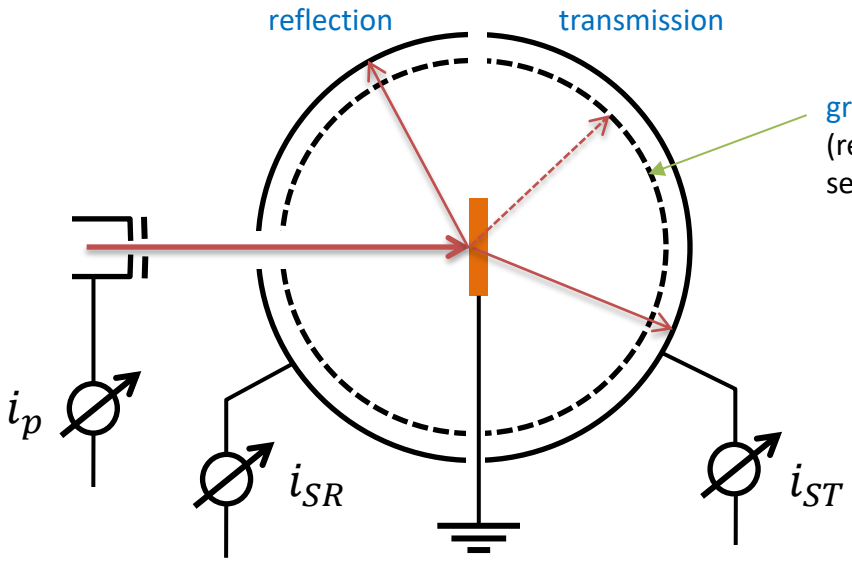
(reflection coeff.)

reflected (backscattered)

secondary

(sec. el. yield)

Measurement



grid – retarding potential (removes low energy secondary electrons)

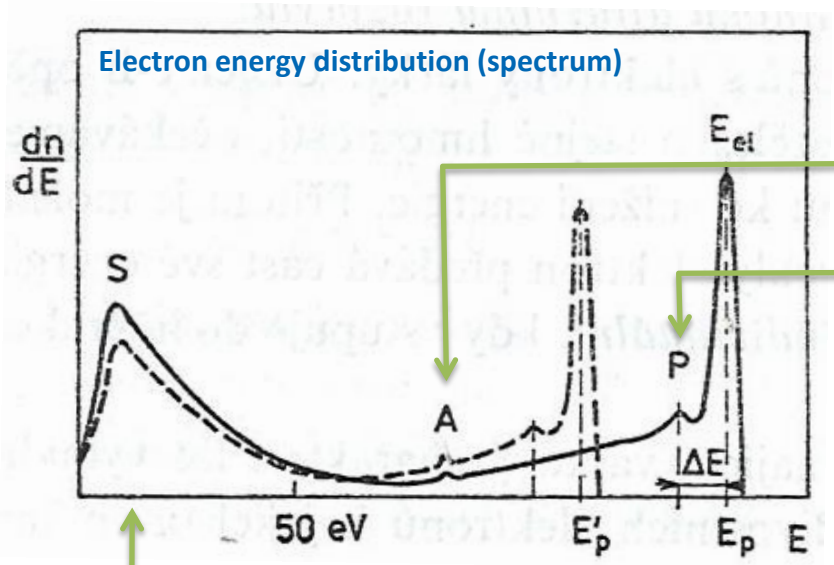
Emission yield výtežek emise

$$\sigma = \frac{i_x}{i_p}$$

$$\boldsymbol{\sigma = \eta + \delta}$$

Secondary emission

Energy distribution



Auger peak

Loss feature

$$\sigma = \delta + \eta$$

„True“ secondary electrons (almost E_p independent)

Primary energy

Secondary emission

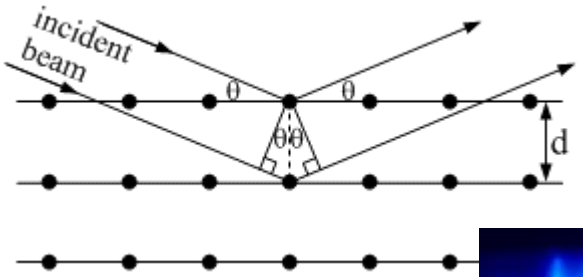
Electron reflection and scattering

Involves **primary** electrons

Elastic scattering

- no energy change (or very small)
- scattering of electron by solid without its excitation

- **Amorphous** solid – diffuse scattering
- **Monocrystal** – diffraction



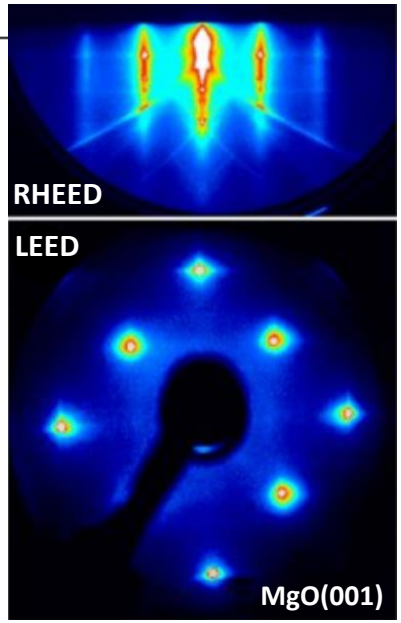
De Broglie

$$\lambda_{el} = \frac{h}{\sqrt{2m_e E \gamma_{rel}}}$$

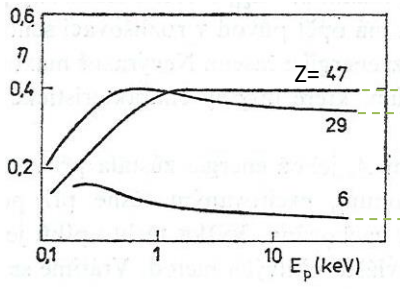
1keV ≈ 0.4Å

$$2d \sin\theta = n\lambda$$

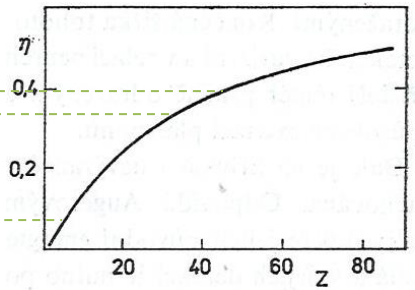
→ LEED, RHEED



Energy dependence of η

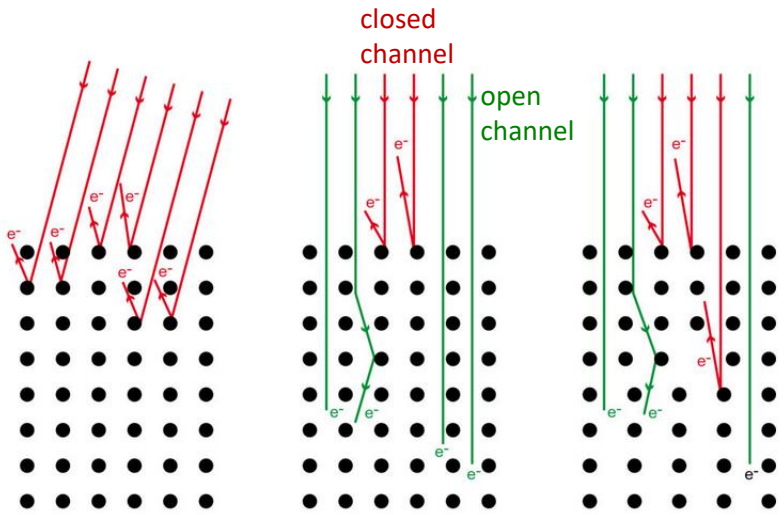


Atom. number dependence of saturated η



Electron channelling

- electron propagation along crystal planes



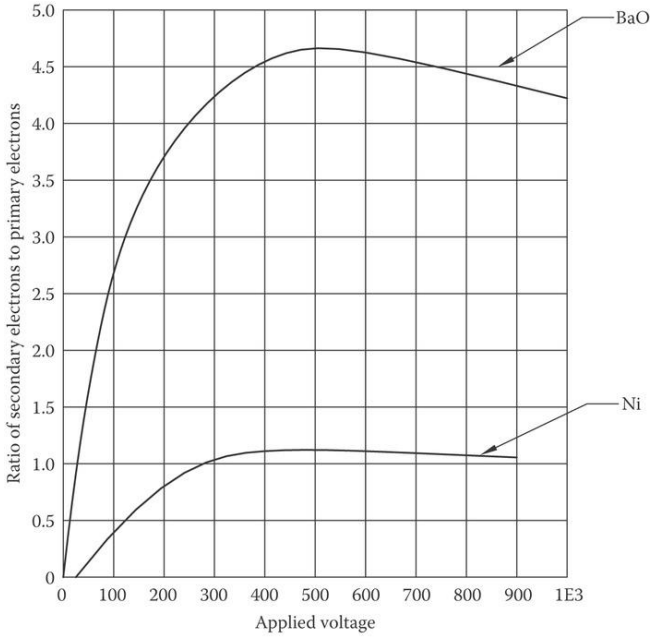
defects (dislocations, impurities, …)

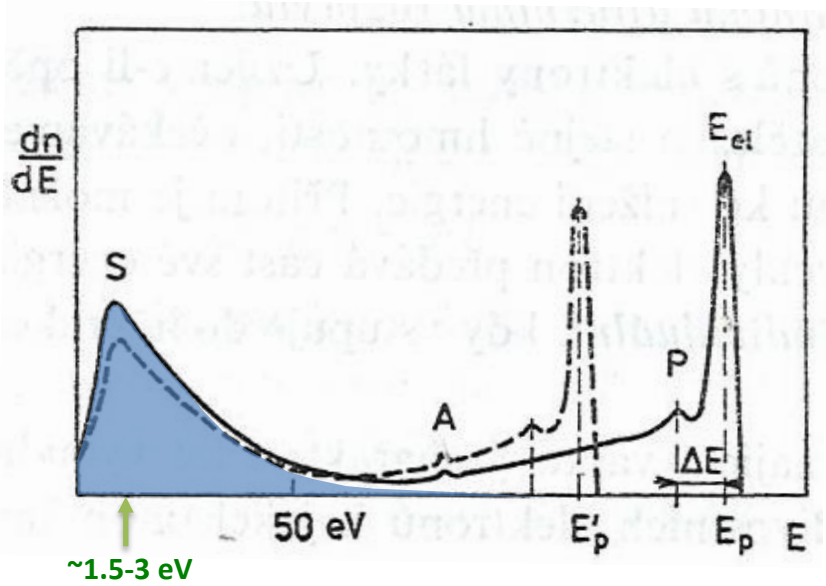
Secondary emission

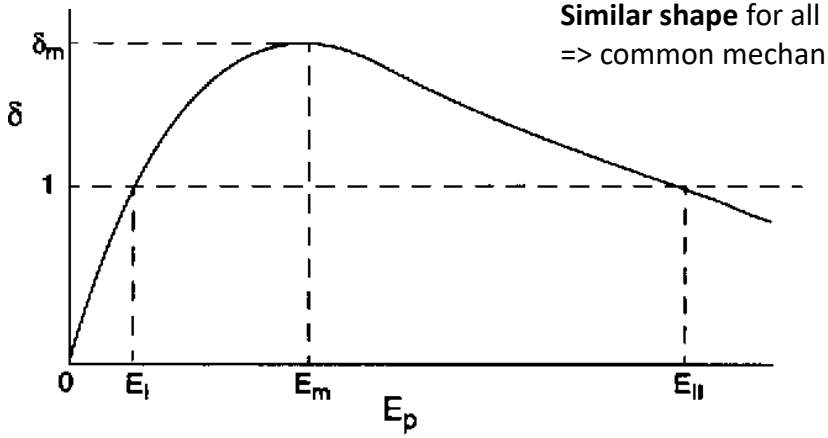
"True" secondary electrons

Liberation of **secondary** electrons

- metals $\delta \approx 1$
- semiconductors, dielectrics $\delta > 1$ (multipliers $\delta \sim 10$)







Similar shape for all materials
=> common mechanism

Temperature dependence
– weak (interaction with phonons rare and weak)

External field dependence
- metals – weak (shielding)
- dielectrics, semisconductors – may be strong

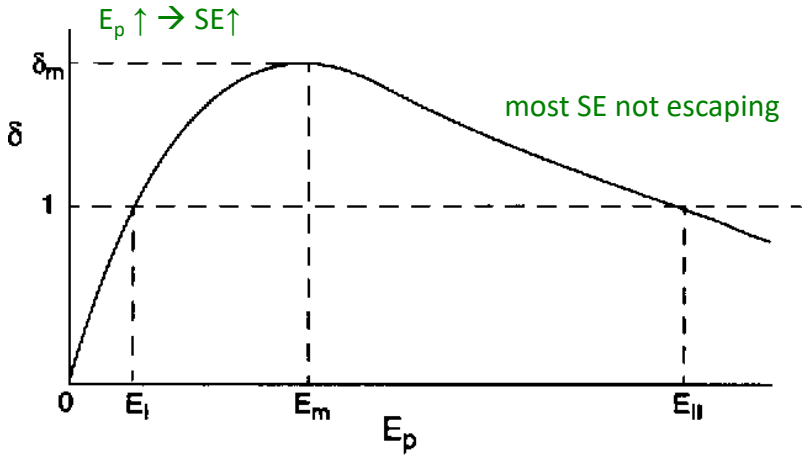
Secondary emission

Electron–electron emission mechanism

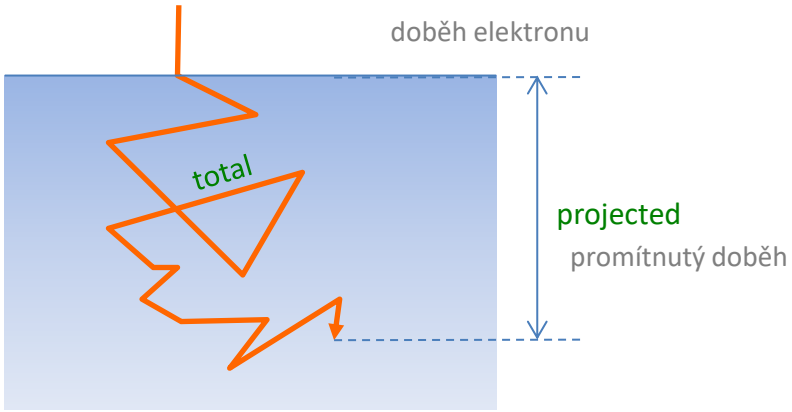
Theory of secondary el. emission

– Theoretical models complicated, especially for non-metals
– Usually treated in 2 steps:
1. excitation processes
2. transport processes

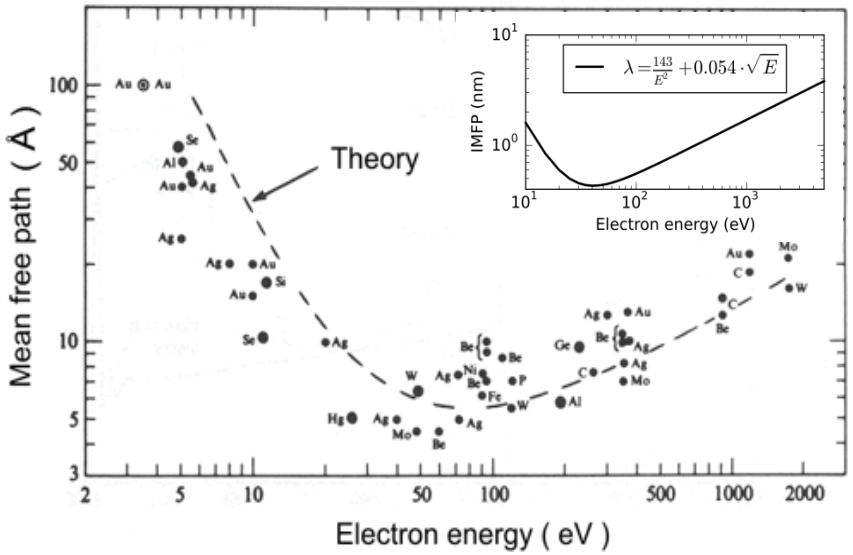
– Excitation cascades has to be considered



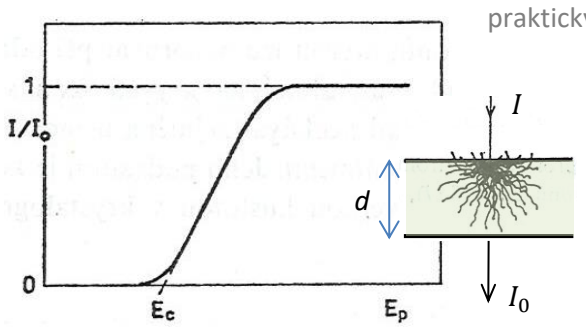
Electron attenuation length (or **TMPF** – total MFP)



Inelastic mean free path of electron in elements
"Universal IMFP curve"



effective – thin sheet, measured by current

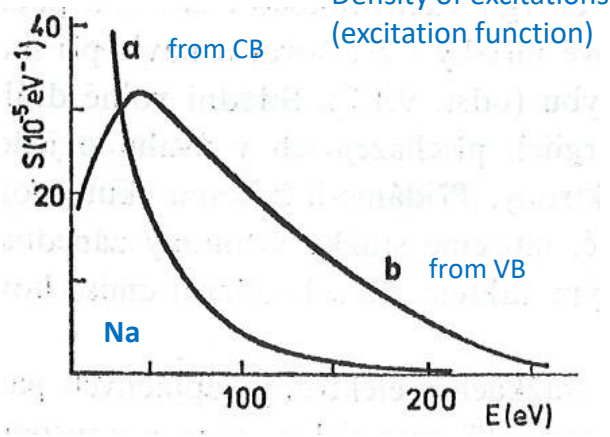


$E_c \equiv E_c(d)$

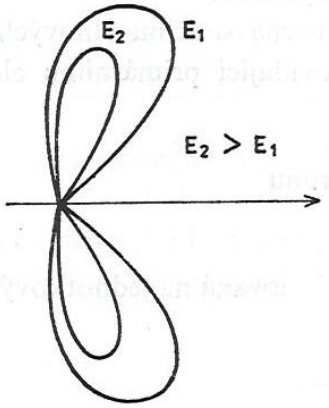
Secondary emission

Electron–electron emission mechanism

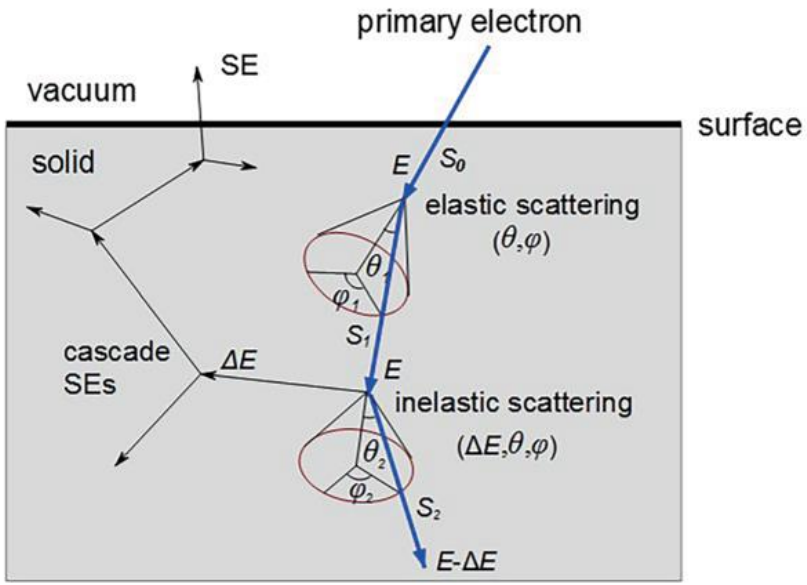
Density of excitations
(excitation function)

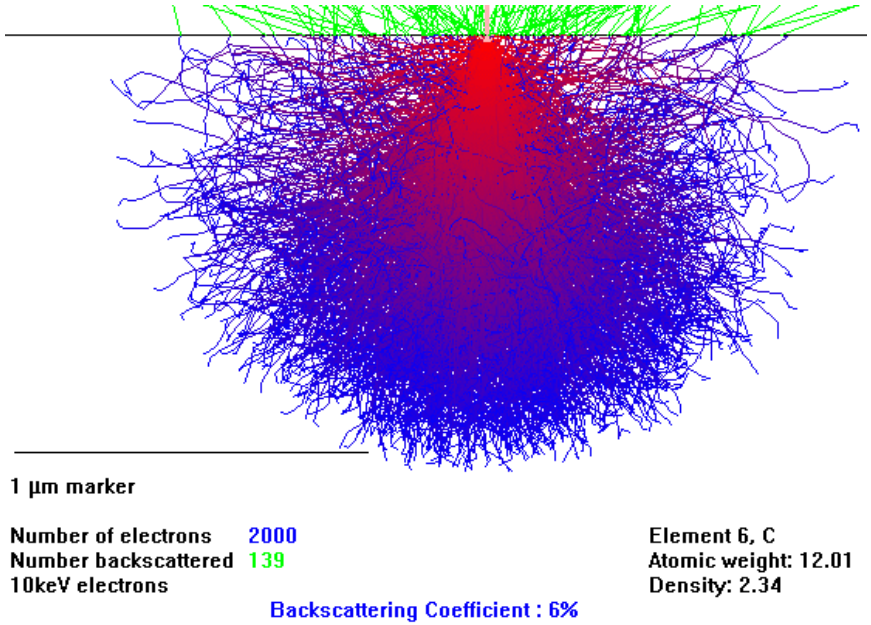


Polar distribution of
excitation probability



Electron trajectory MC simulation



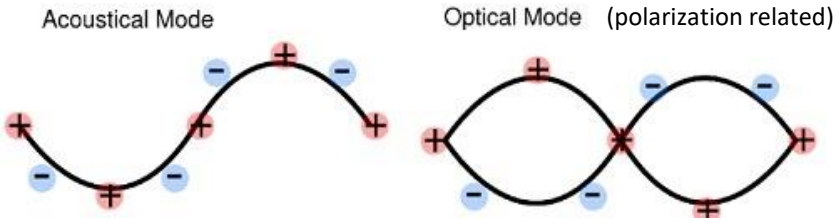


Secondary emission

Characteristic energy losses

Phonons

- collective vibrational excitations of periodic lattice
- $E_{phonon} \approx 50$ meV



Plasmons

- quantum of plasma oscillation (collective phenomena - quasiparticle)
- plasmons decay in phonons or photons
- short lifetime $\tau \approx 10^{-15}$ s
- localized to <10 nm
- typical $E_{plasmon} \approx$ 5-30 eV (UV range, $n_e \approx 10^{23}$ cm^{-3})

bulk plasmon: $\vec{k}_\perp \neq 0$

Simple case: harmonic undamped oscillations of free-electron gas within rigid lattice

$$\omega_p = \sqrt{\frac{n_e e^2}{m_e{}^* \varepsilon_0}}$$

$m_e{}^*$... effective electron weight
n_e ... density of electrons

surface plasmon: $\vec{k}_\perp = 0$

$$\omega_{p(s)} = \omega_{p(p)} \frac{1}{\sqrt{1+\varepsilon_r}}$$

ε_r ... relative permittivity

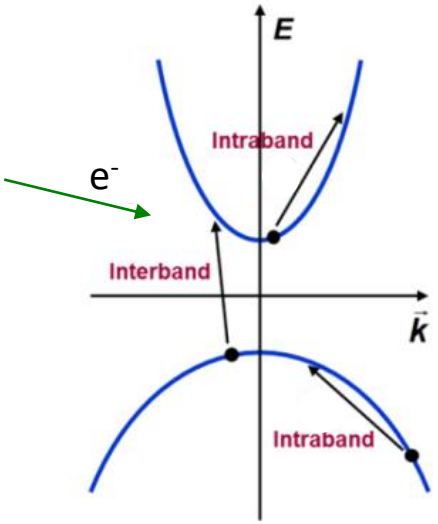
=> vacuum (no adsorbate):

$$\omega_{p(s)} = \omega_{p(p)} \frac{1}{\sqrt{2}}$$

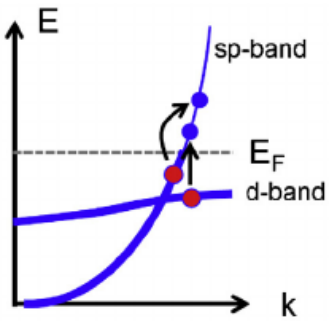
(valid for alkali metals: spher. sym. of valence el. orb.)

Interband transitions

– mainly diel. and semiconductrors



metals: bands overlap near E_F



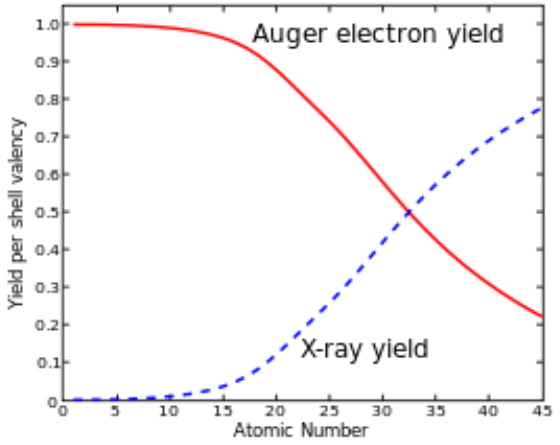
Secondary emission

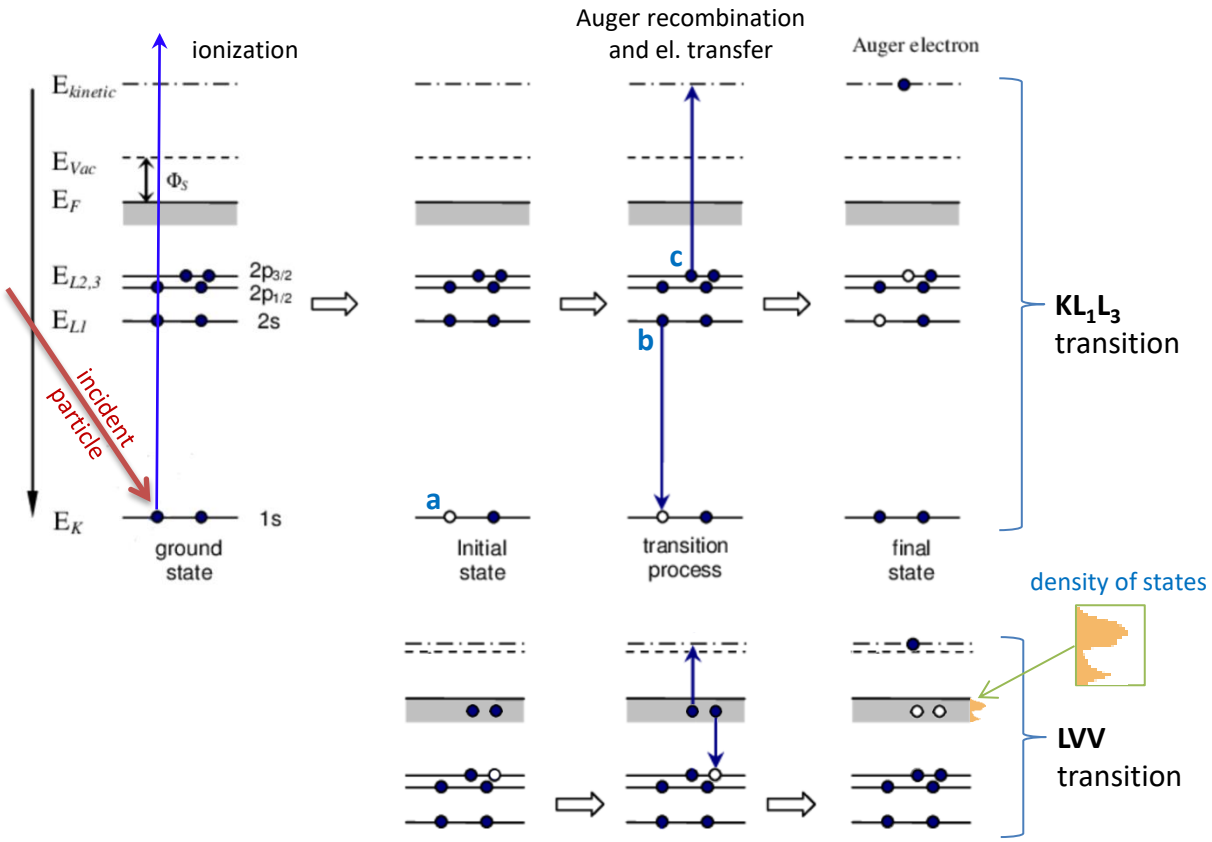
Auger electrons

Auger phenomenon

- non-irradiative electron de-excitation process
  (competitive relaxation process to irradiative fluorescence)
- occurs by Coulombic interaction:
  energy loss by emission of one or more electrons (**Auger electron**)

relative yields for K-shell



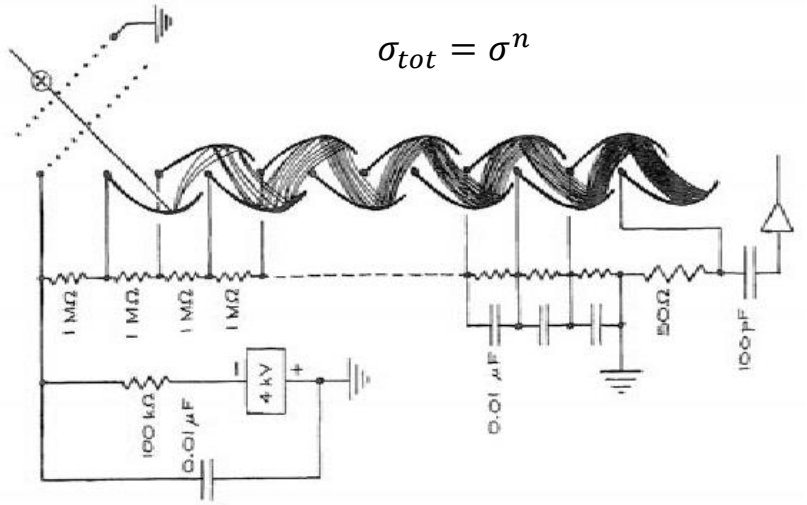


Secondary emission

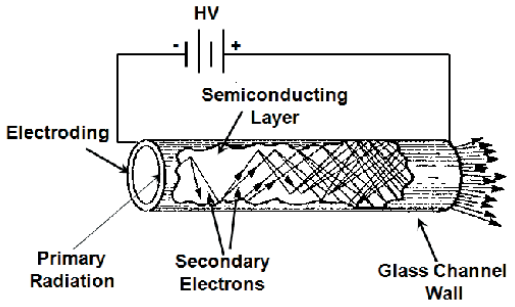
Applications

Multipliers

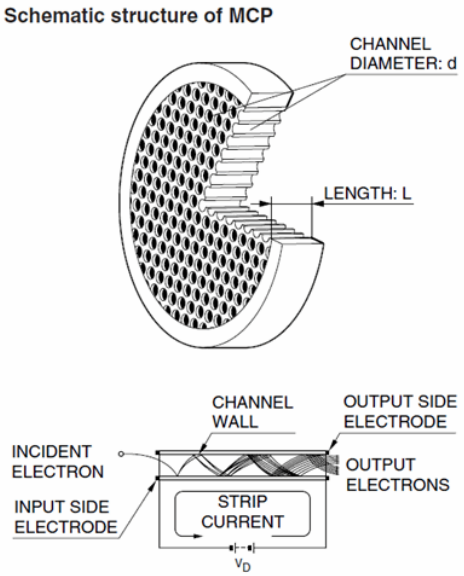
Dynode



Channeltron



Microchannel plate



Secondary emission

Applications

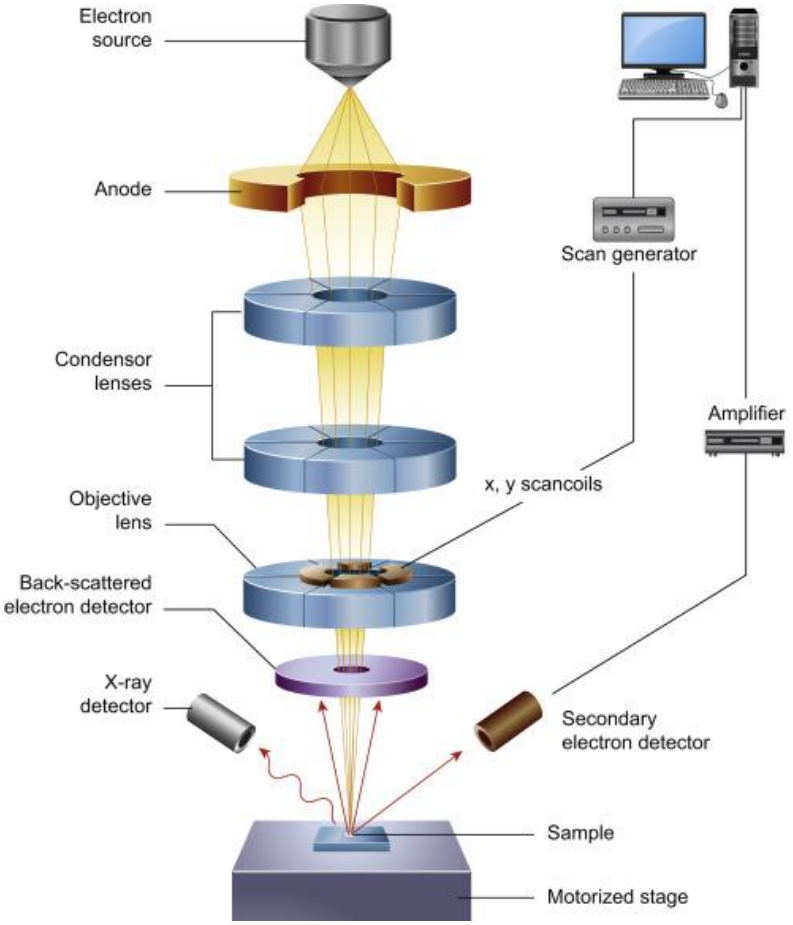
Electron microscopies

- **SEM** (scanning electron microscopy)
- **TEM** (transmission electron microscopy)

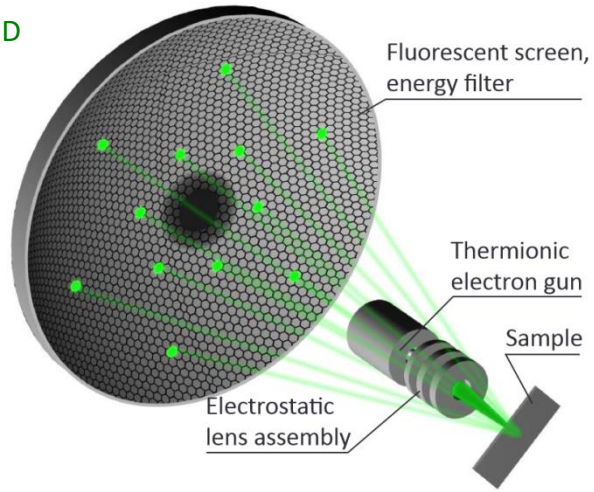
Electron diffraction methods

- **LEED** (low energy electron diffraction)
- **RHEED** (reflection high-energy electron diffraction)

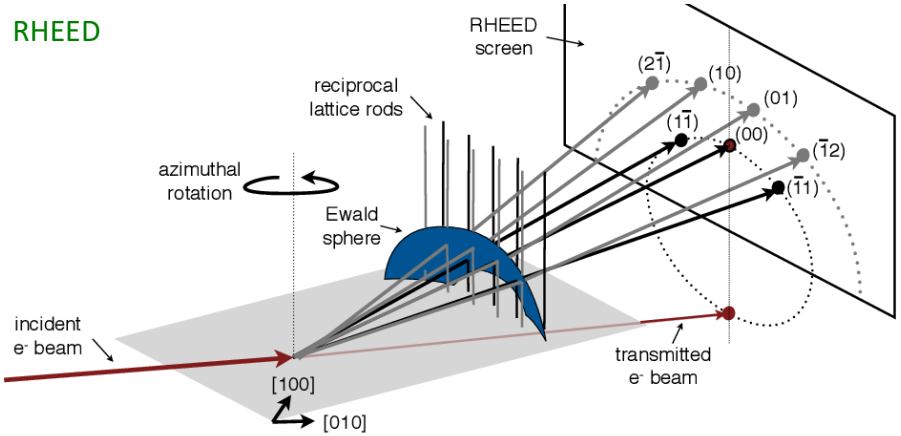
SEM



LEED



RHEED

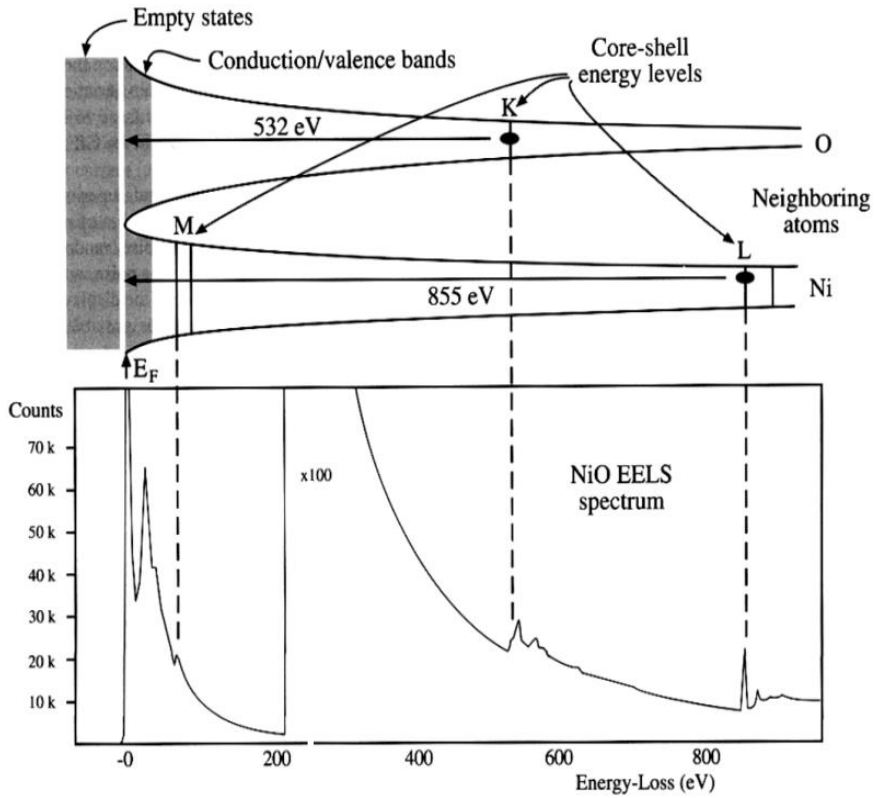


Secondary emission

Applications

Electron spectroscopies

EELS – electron energy loss spectroscopy



AES – Auger electron spectroscopy