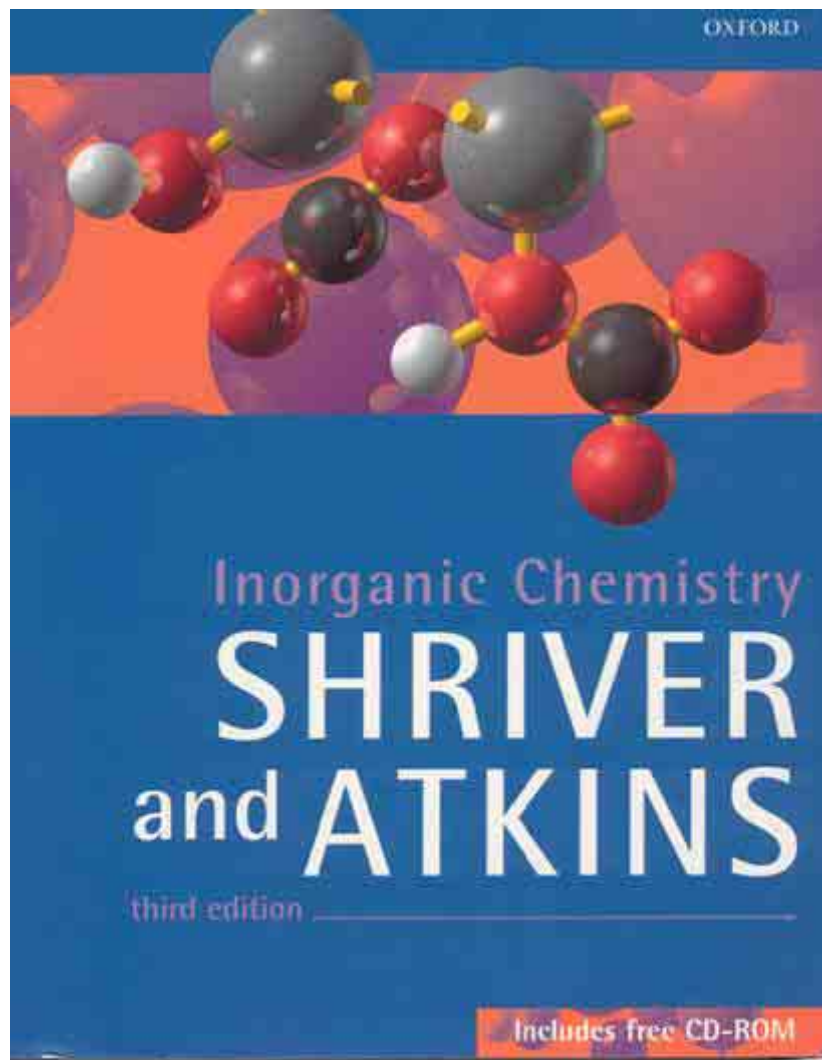


Lecture: Solid State Chemistry
(Festkörperchemie)

Part 1

H.J. Deiseroth, SS 2006

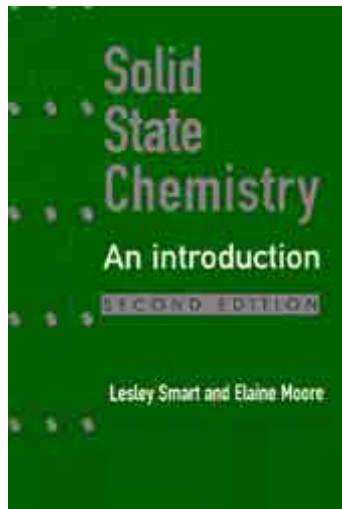
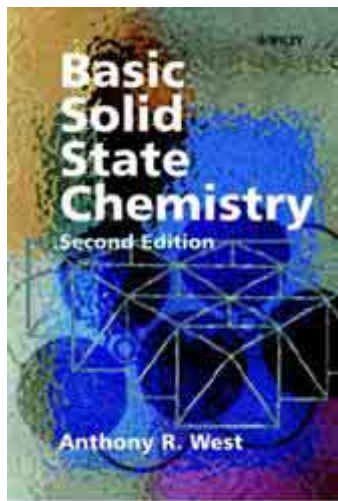
Resources



Resources

Textbooks: Shriver, Atkins, *Inorganic Chemistry* (3rd ed, 1999)
W.H. Freeman and Company (Chapter 2, 18 ...)

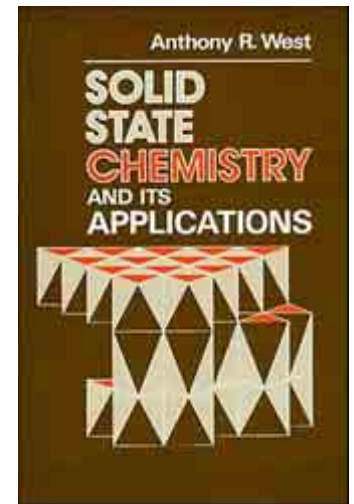
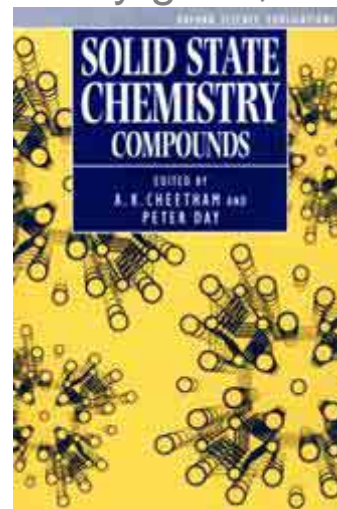
recommendation



german



very good, but not basic level

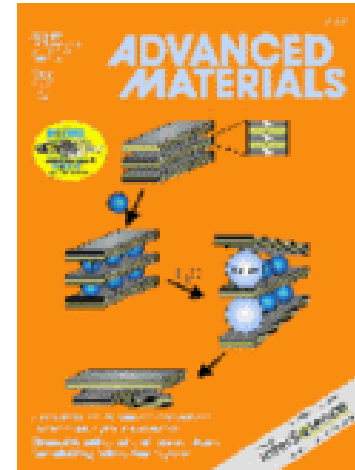
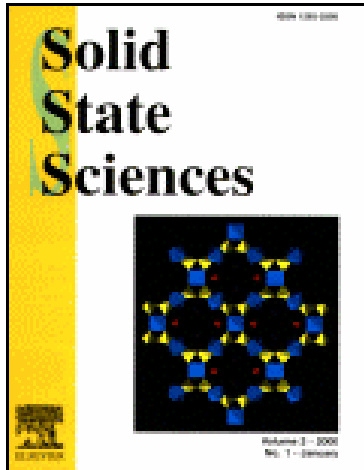
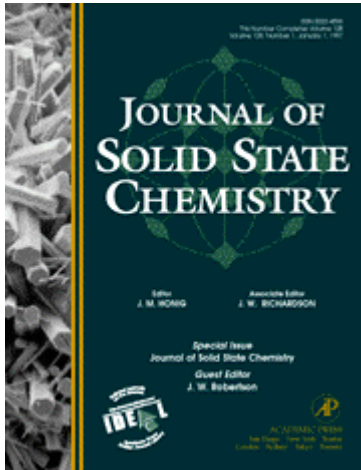


Internet resources

- <http://ruby.chemie.uni-freiburg.de/Vorlesung/> (german)
- <http://www.chemistry.ohio-state.edu/~woodward/ch754...> (pdf-downloads)
- IUCR-teaching resources (International Union for Crystallography, advanced level)

Resources

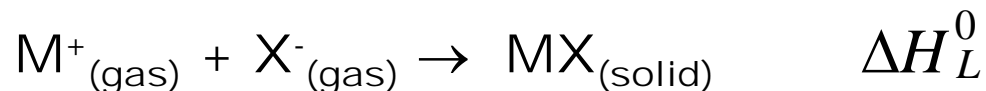
Journals



Lattice Energy and Chemical Bonding in Solids

Lattice enthalpy

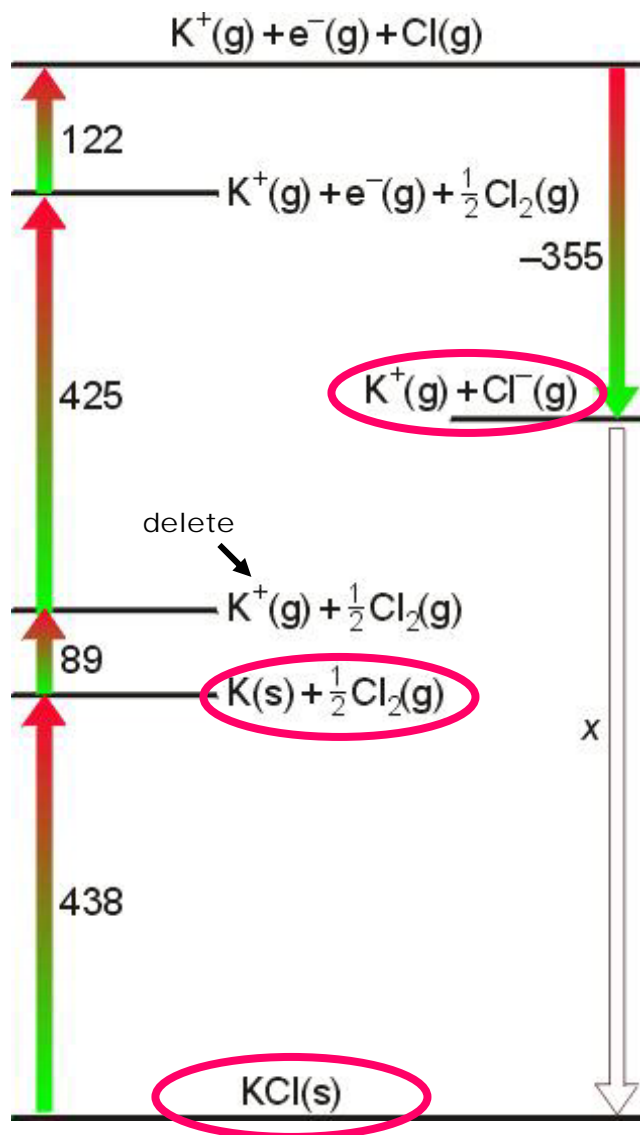
The lattice enthalpy change ΔH_L^0 is the standard molar enthalpy change for the following process:



Because the formation of a solid from a „gas of ions“ is always exothermic lattice enthalpies (defined in this way !!) are usually negative numbers.

If entropy considerations are neglected the most stable crystal structure of a given compound is the one with the highest lattice enthalpy.

Lattice enthalpies can be determined by a thermodynamic cycle → Born-Haber cycle



A Born-Haber cycle for KCl

(all enthalpies: kJ mol⁻¹ for normal conditions → standard enthalpies)

standard enthalpies of

- sublimation: +89 (K)
- ionization: + 425 (K)
- atomization: +244 (Cl₂)
- electron affinity: -355 (Cl)
- lattice enthalpy: x

Calculation of lattice enthalpies

$$\Delta H_L^0 = V_{AB} + V_{Born}$$

V_{AB} = Coulomb (electrostatic) interaction between all cations and anions treated as point charges (Madelung part of lattice enthalpy („MAPLE“))

V_{Born} = Repulsion due to overlap of electron clouds (Born repulsion)

Calculation of lattice enthalpies

1. MAPLE (V_{AB})

(Coulombic contributions to lattice enthalpies, MADELUNG part of lattice enthalpy, atoms treated as point charges)

$$V_{AB} = -A \left(\frac{z_+ z_- e^2}{4\pi\epsilon_0 r_{AB}} \right) N$$

← Coulomb potential of an ion pair

V_{AB} : Coulomb potential (electrostatic potential)

A: Madelung constant (depends on structure type)

N: Avogadro constant

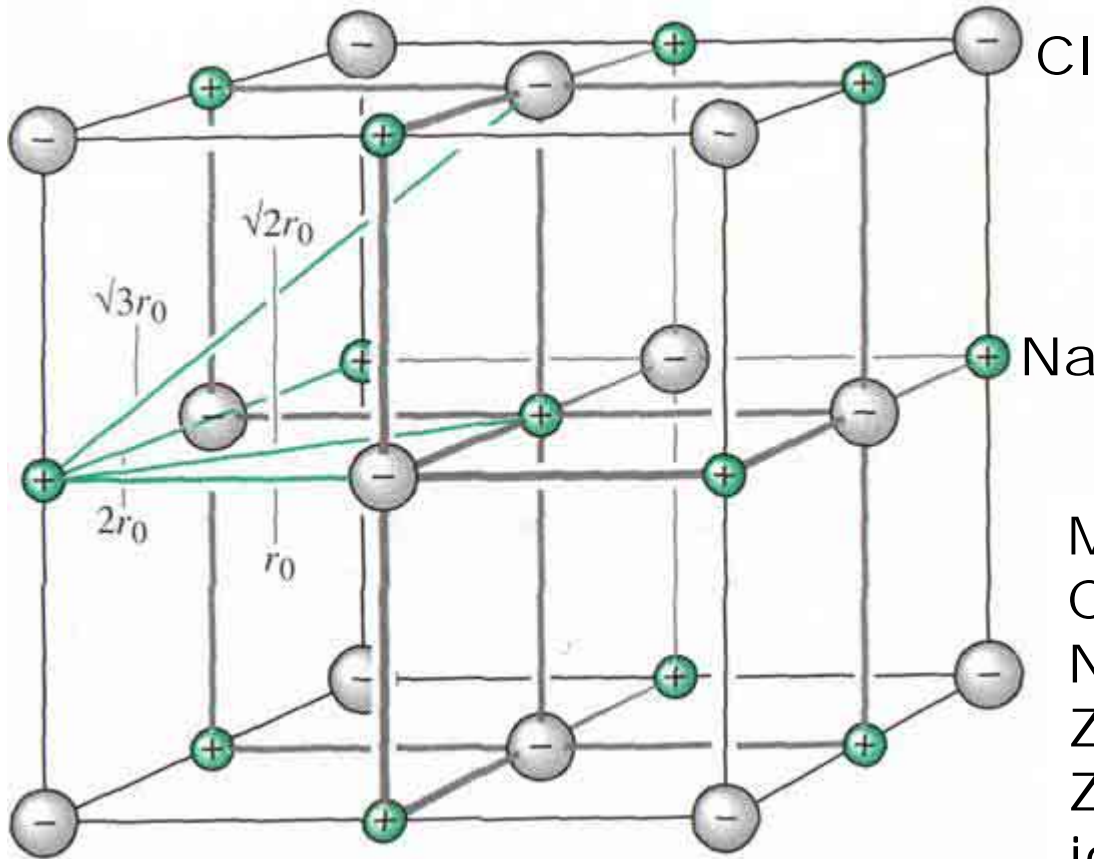
z: charge number

e: elementary charge

ϵ_0 : dielectric constant (vacuum permittivity)

r_{AB} : shortest distance between cation and anion

Calculation of the Madelung constant



typical for 3D ionic solids:
Coulomb attraction and repulsion

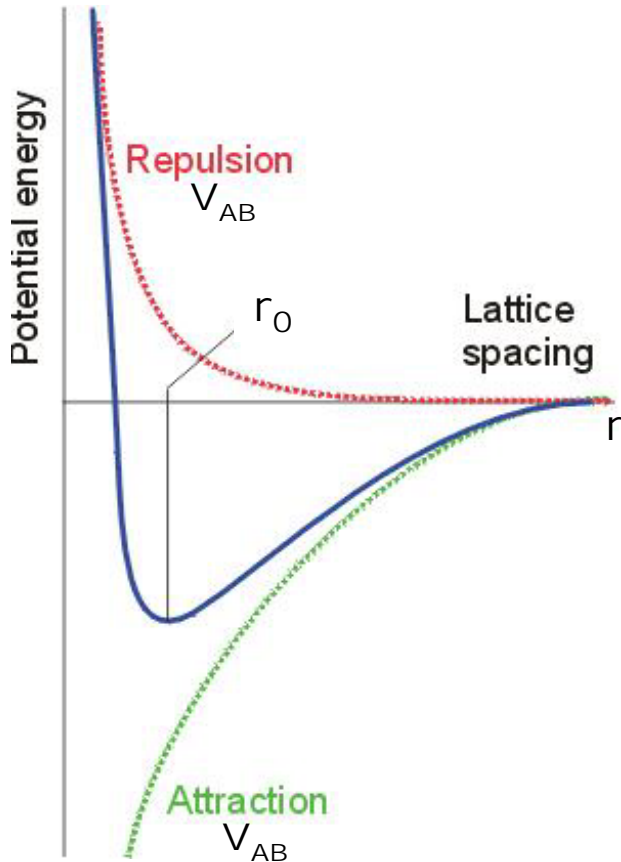
Madelung constants:
CsCl: 1.763
NaCl: 1.748
ZnS: 1.641 (wurtzite)
ZnS: 1.638 (sphalerite)
ion pair: 1.0000 (!)

$$A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} \dots = 1.748\dots \text{ (NaCl)}$$

(infinite summation)

2. Born repulsion (V_{Born})

(Repulsion arising from overlap of electron clouds, atoms do not behave as point charges)



Because the electron density of atoms decreases exponentially towards zero at large distances from the nucleus the Born repulsion shows the same behaviour

approximation:

$$V_{\text{Born}} = \frac{B}{r^n}$$

B and n are constants for a given atom type; n can be derived from compressibility measurements (~8)

Total lattice enthalpy from Coulomb interaction and Born repulsion

$$\Delta H_L^0 = \text{Min.}(V_{AB} + V_{Born})$$

(set first derivative of the sum to zero)

$$\Delta H_L^0 = -A \frac{z_+ z_- e^2}{4\pi\epsilon_0 r_0} N \left(1 - \frac{1}{n}\right)$$

Calculated lattice enthalpies (kJ mol⁻¹):

NaCl (-772), CsCl (-653)

From Born Haber cycle:

NaCl (-757), CsCl (-623)

(based on the known enthalpy of formation !!)

Applications of lattice enthalpy calculations:

- lattice enthalpies and stabilities of „non existent“ compounds and calculations of electron affinity data (see next transparencies)
- Solubility of salts in water (see Shriver-Atkins)

Calculation of the lattice enthalpy for NaCl

$$\Delta H_L^0 = -A \frac{z_+ z_- e^2}{4\pi\epsilon_0 r_0} N \left(1 - \frac{1}{n}\right)$$

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ As/Vm}; e = 1.6 \times 10^{-19} \text{ As (=C)}; N = 6.023 \times 10^{23} \text{ mol}^{-1}$$

$$A = 1.746; r = 2.8 \times 10^{-10} \text{ m}; \quad n = 8 \text{ (Born exponent)}$$

$$1/4\pi\epsilon_0 = 8.992 \times 10^9 \quad e^2 N = 1.542 \times 10^{-14} \text{ (only for univalent ions !)}$$

$$\Delta H_L = -1.387 \times 10^{-5} \times A/r_0 \times (1-1/n) \quad \text{(only for univalent ions !)}$$

$$\text{Dimensions: } \frac{\text{Vm A}^2\text{s}^2}{\text{As m mol}^{-1}} = \frac{\text{VAs}}{\text{mol}} = \text{J/mol}$$

$$\text{NaCl: } \Delta H_L' = -865 \text{ kJ mol}^{-1} \text{ (only MAPLE)}$$

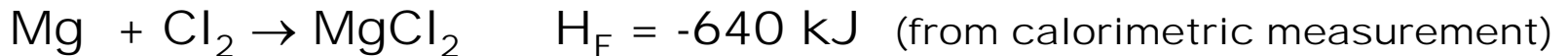
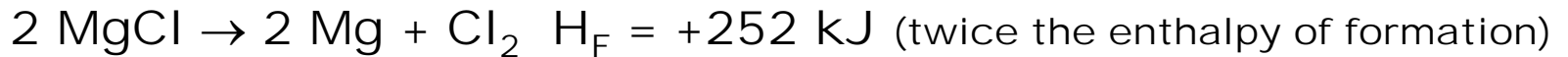
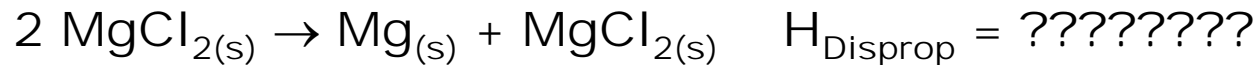
$$\Delta H_L = -756 \text{ kJ mol}^{-1} \text{ (including Born repulsion)}$$

Can MgCl (Mg⁺Cl⁻) crystallizing in the rocksalt structure be a stable solid ?

$H_{\text{Formation}} \sim -126 \text{ kJ mol}^{-1}$ (calculated from Born Haber cycle based on similar r_{AB} as for NaCl !!)

MgCl should be a stable compound !!!!!

However: Chemical intuition should warn you that there is a risk of disproportionation:



(Disproportionation reaction is favored)

Calculation of the electron affinity for Cl from the Born-Haber cycle for CsCl

Standard enthalpy of formation	- 433.0 kJ/mol
sublimation	70.3
$\frac{1}{2}$ atomization	121.3
ionization	373.6
Lattice enthalpy	- 640.6

$$H_{\text{Formation}} = H_{\text{subl}} + \frac{1}{2} H_{\text{Diss}} + H_{\text{Ion}} + H_{\text{EA}} + H_{\text{Lattice}}$$

$$H_{\text{EA}} = H_{\text{F}} - (H_{\text{S}} + \frac{1}{2} H_{\text{D}} + H_{\text{I}} + H_{\text{L}})$$

$$H_{\text{EA}} = - 433 - (70.3 + 121.3 + 373.6 - 640.6) = \underline{\underline{-357.6}}$$

Chemical bonding in solids

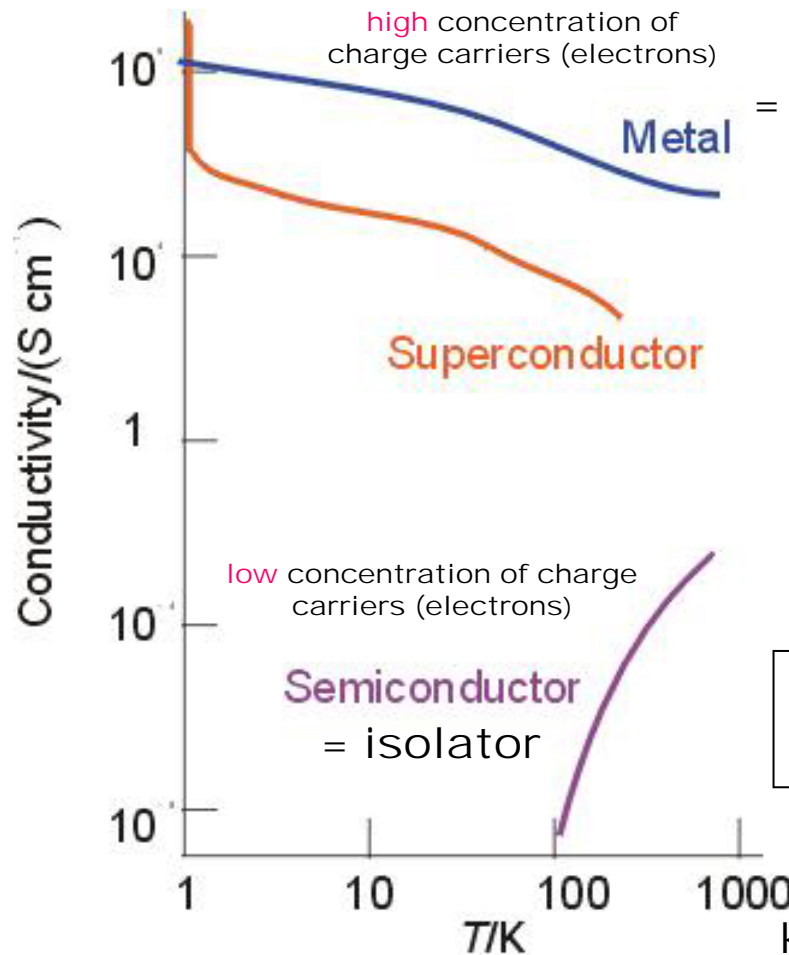
→ bonding theory of solids must account for their basic properties as:

- mechanism and temperature dependence of the electrical conductivity of isolators, semiconductors, metals and alloys

(further important properties: luster of metals, thermal conductivity and color of solids, ductility and malleability of metals)

...

Temperature dependence of the electrical conductivity (σ) and resistivity (R) of metals, semiconductors, isolators, superconductors



= alloy

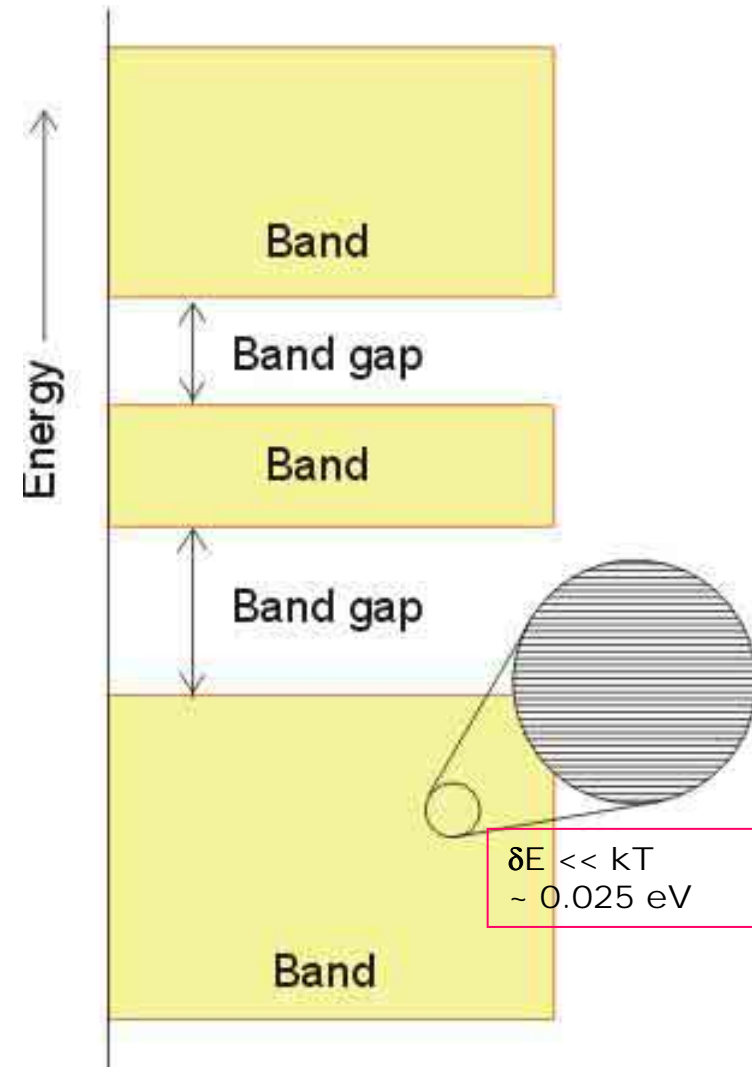
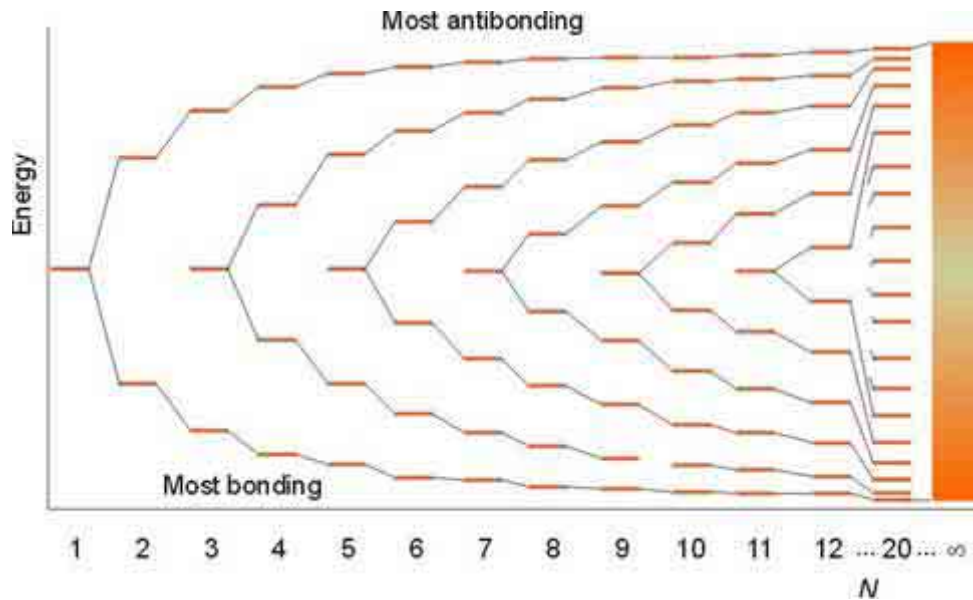
→ increasing resistivity with temperature
(due to increased „scattering“ of charge carriers)

→ resistivity below T_c is zero !!
(special mechanism of conductivity)

→ decreasing resistivity with temperature
(due to increasing thermal excitation of electrons)

key to understanding: „band model“

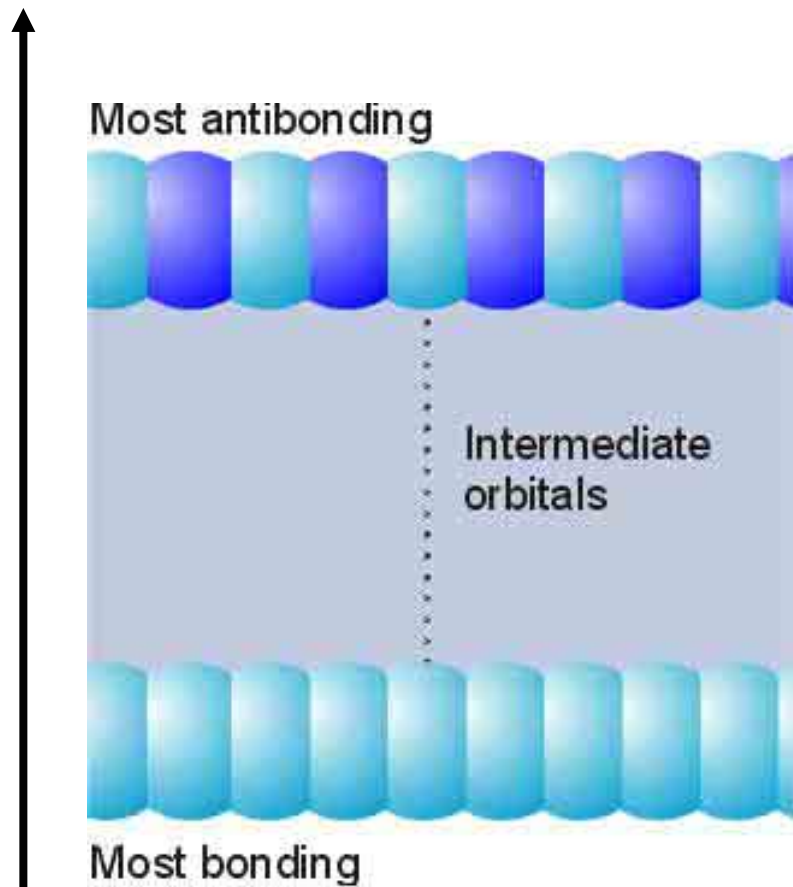
The origin of the simple band model for solids:
Band formation by orbital overlap
(in principle a continuation of the Molecular Orbital model)



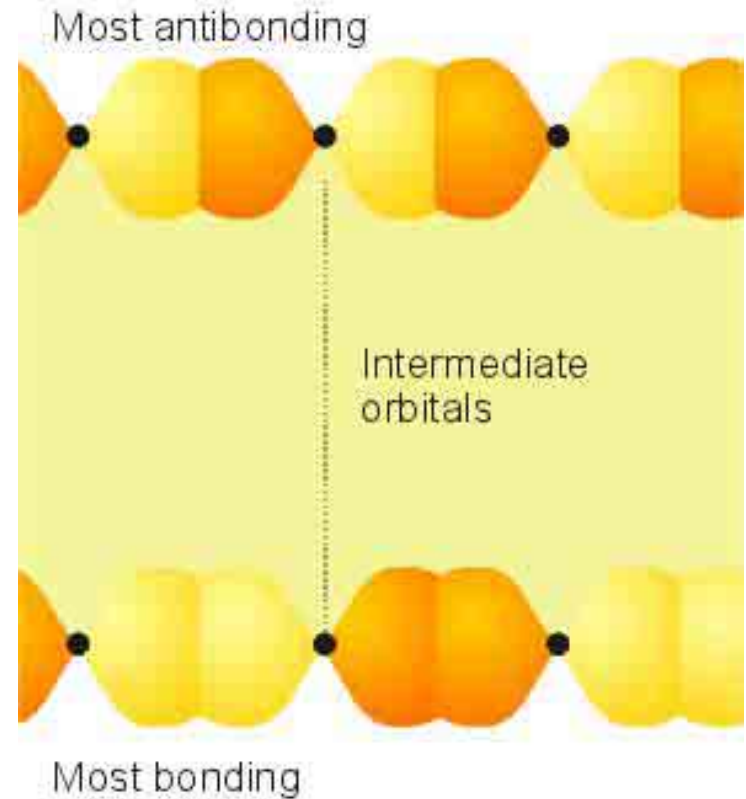
the overlap of atomic orbitals in a solid gives rise to the formation of bands separated by gaps (the band width is a rough measure of interaction between neighbouring atoms)

s- and p-bands in a one-dimensional solid

Energy

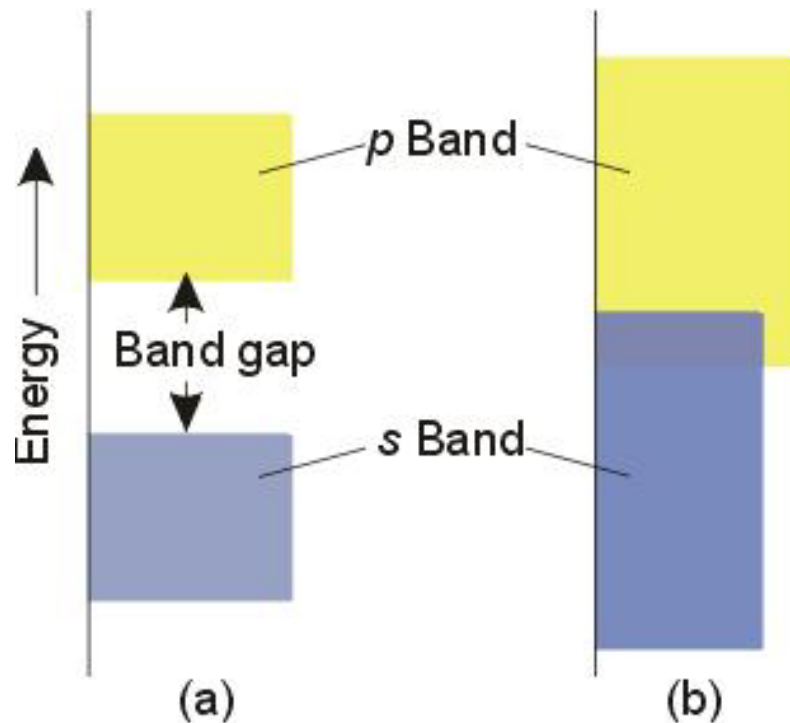


s-band

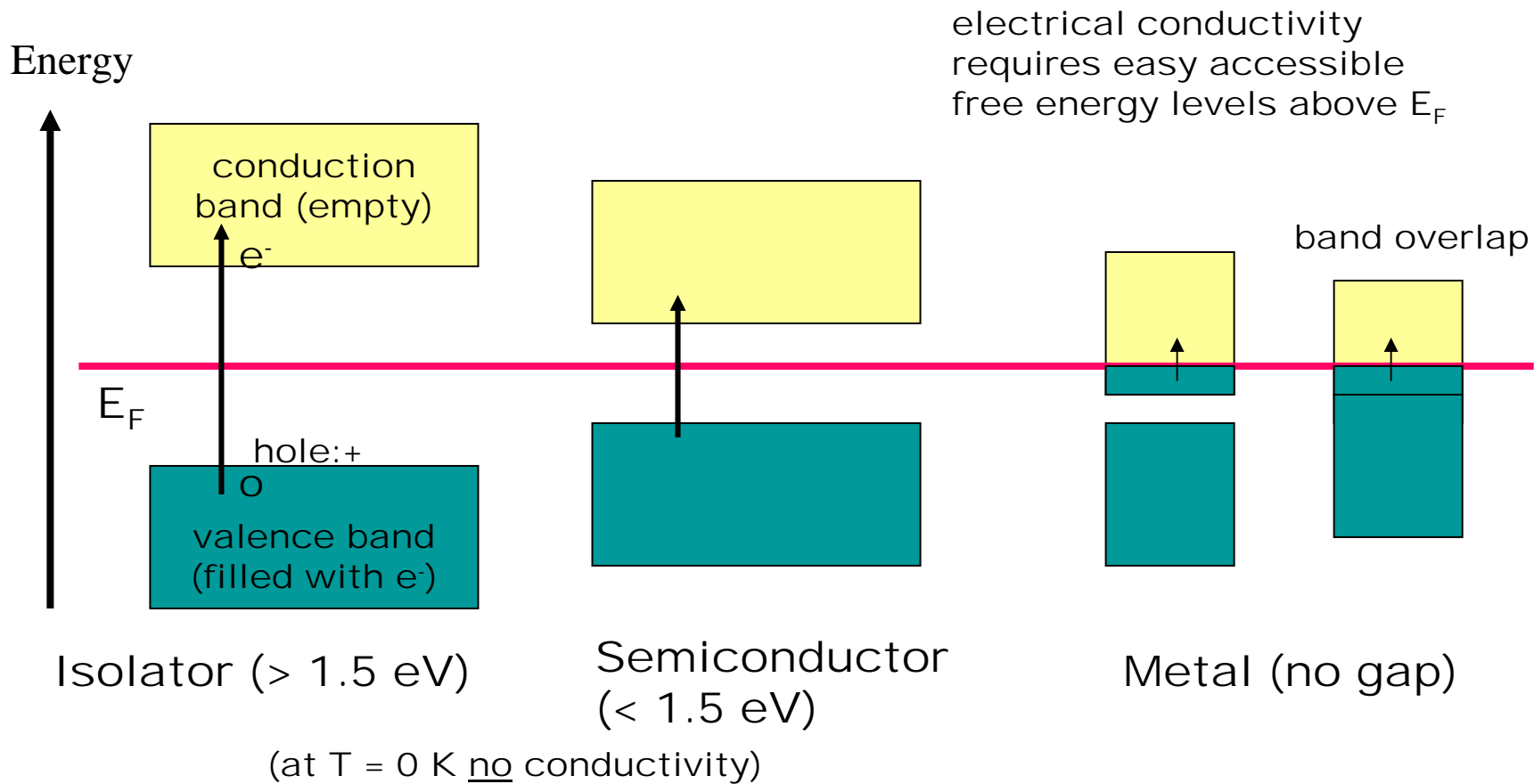


p-band

- Whether there is in fact a gap between bands (e.g. s and p) depends on the energetic separation of the respective orbitals of the atoms and the strength of interaction between them.
- If the interaction is strong, the bands are wide and may overlap.

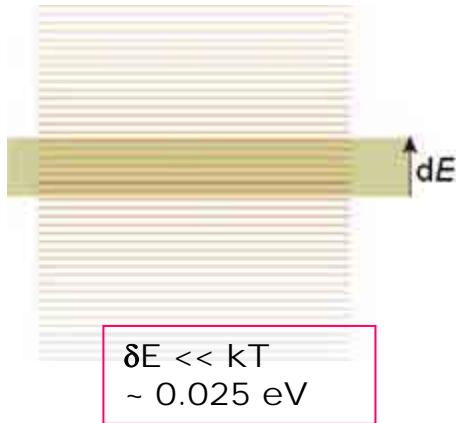


Isolator, Semiconductor, Metal ($T = 0 \text{ K}$)

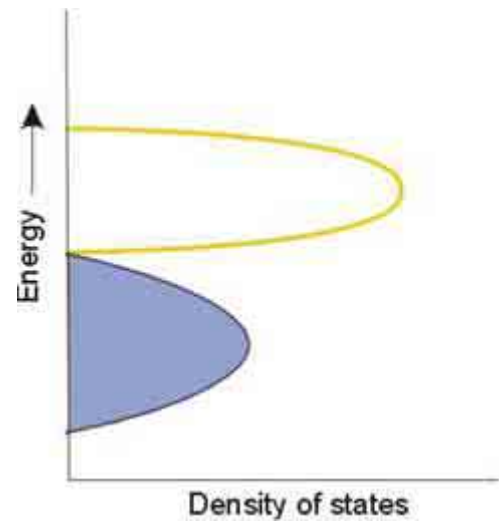
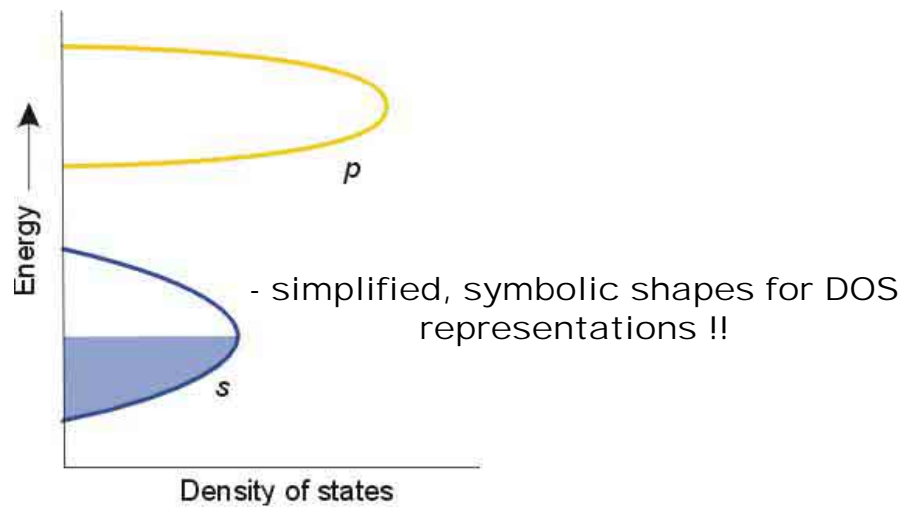


E_F = Fermi-level (energy of highest occupied electronic state, states above E_F are empty at 0 K)

A more detailed view not only for metals: (DOS = Densities of states)



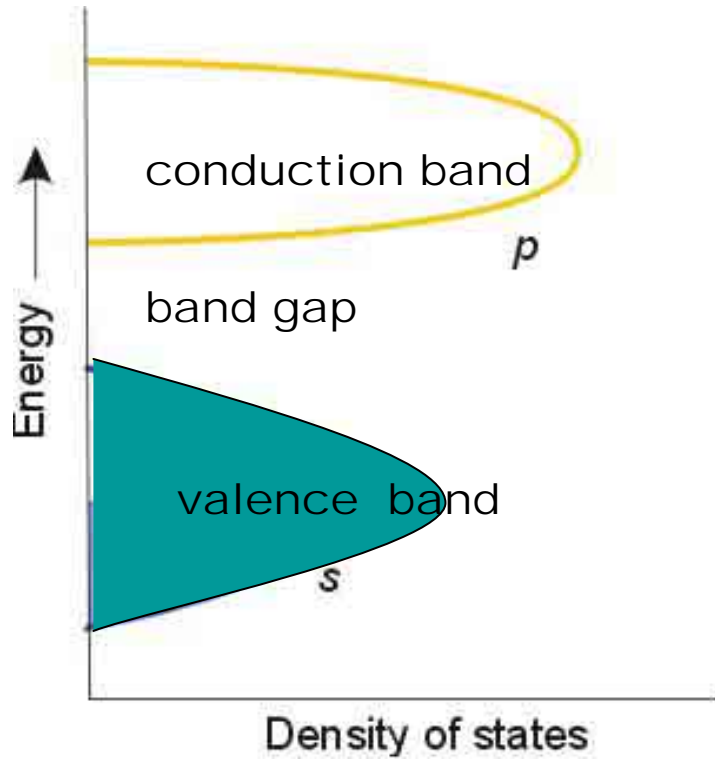
The number of electronic states in a range divided by the width of the range is called the density of states (DOS).



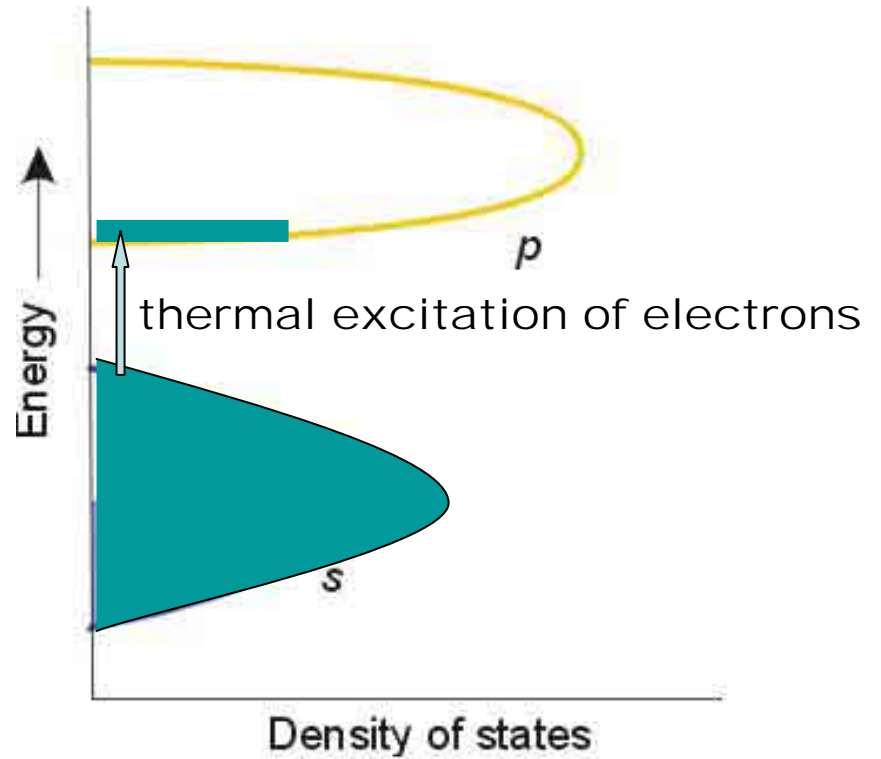
Typical DOS representation for a metal

Typical DOS representation for a semimetal

Semiconductors

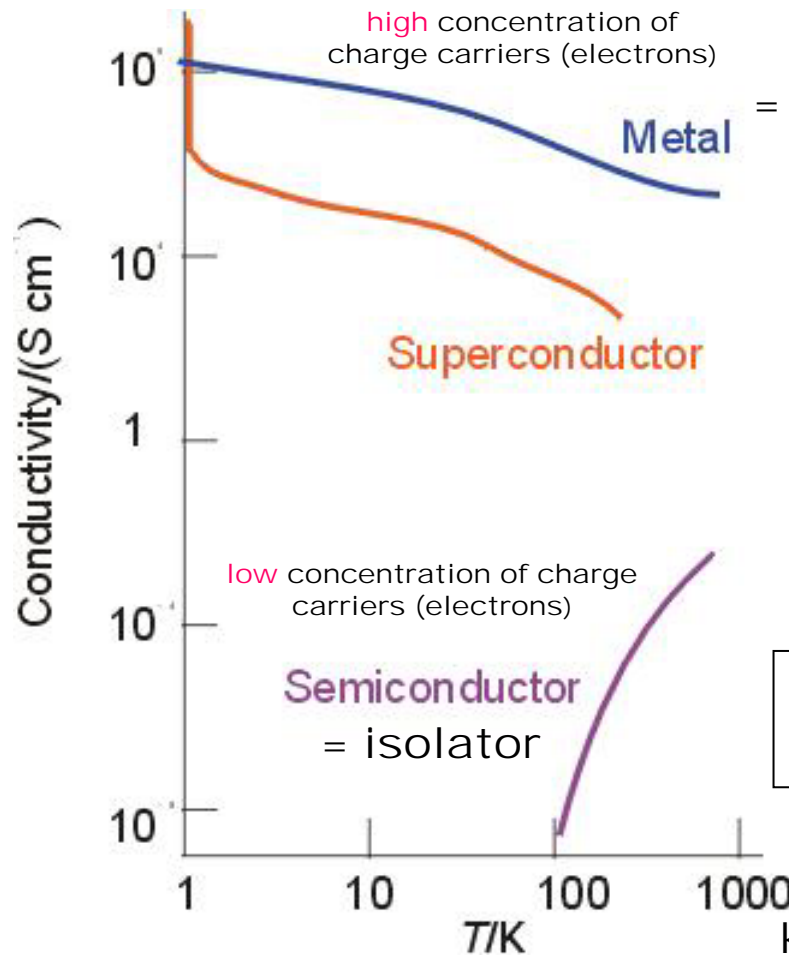


$T = 0 \text{ K}$



$T > 0 \text{ K}$

Temperature dependence of the electrical conductivity (σ) and resistivity (R) of metals, semiconductors, isolators, superconductors



= alloy

→ increasing resistivity with temperature
(due to increased „scattering“ of charge carriers)

→ resistivity below T_c is zero !!
(special mechanism of conductivity)

→ decreasing resistivity with temperature
(due to increasing thermal excitation of electrons)

key to understanding: „band model“

Semiconductors (more in detail)

The electrical conductivity σ of a semiconductor:

$$\sigma \sim qcu \quad [\Omega^{-1}\text{cm}^{-1}]$$

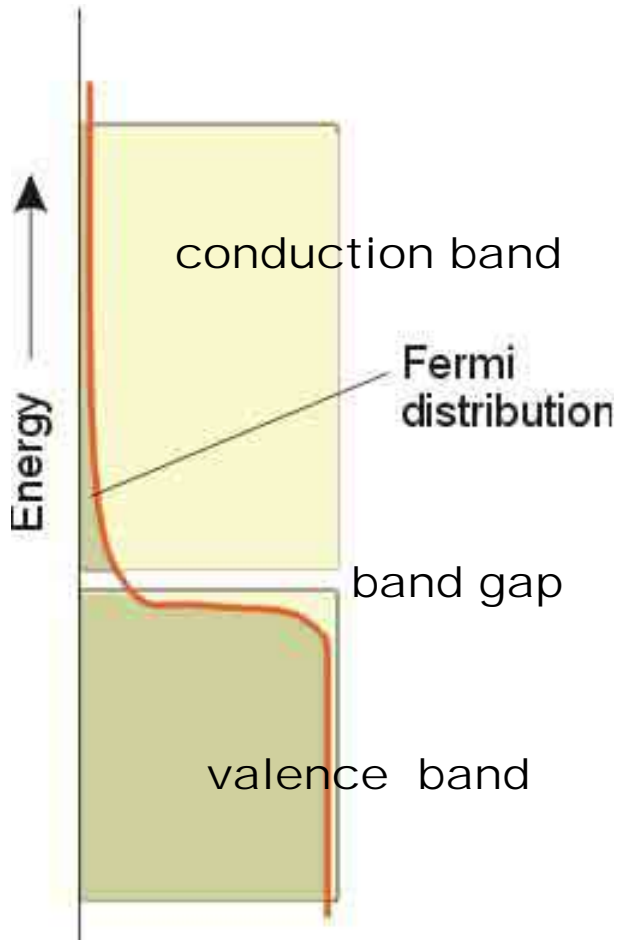
q: elementary charge

c: concentration of charge carriers

u: electrical mobility of charge carriers [cm^2/Vsec]

- charge carriers can be electrons or holes (!)

Semiconductors



Temperature dependence of the electrical conductivity (σ [$\Omega^{-1}\text{cm}^{-1}$]) (Arrhenius type behaviour):

$$\sigma = \sigma_0 \cdot e^{\frac{-E_a}{kT}}$$

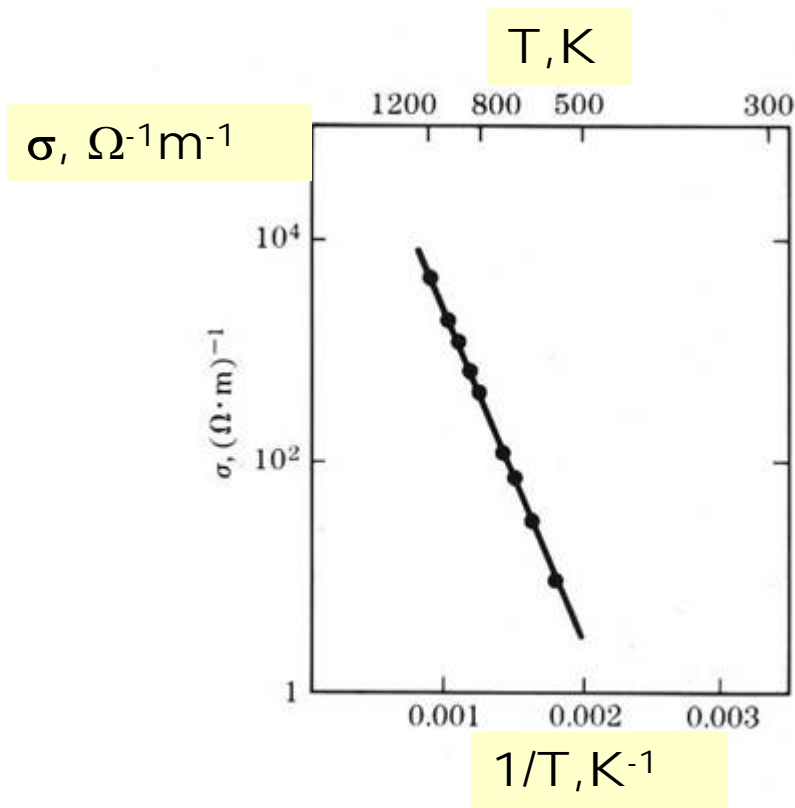
$$\ln \sigma = -\frac{E_a}{kT} + \ln \sigma_0$$

→ $\ln \sigma = f(1/T)$ → linear

Typical band gaps (eV): C(diamond) 5.47, Si 1.12, GaAs 1.42

Semiconductors

Electrical conductivity σ as a function of the reciprocal absolute temperature for intrinsic silicon.

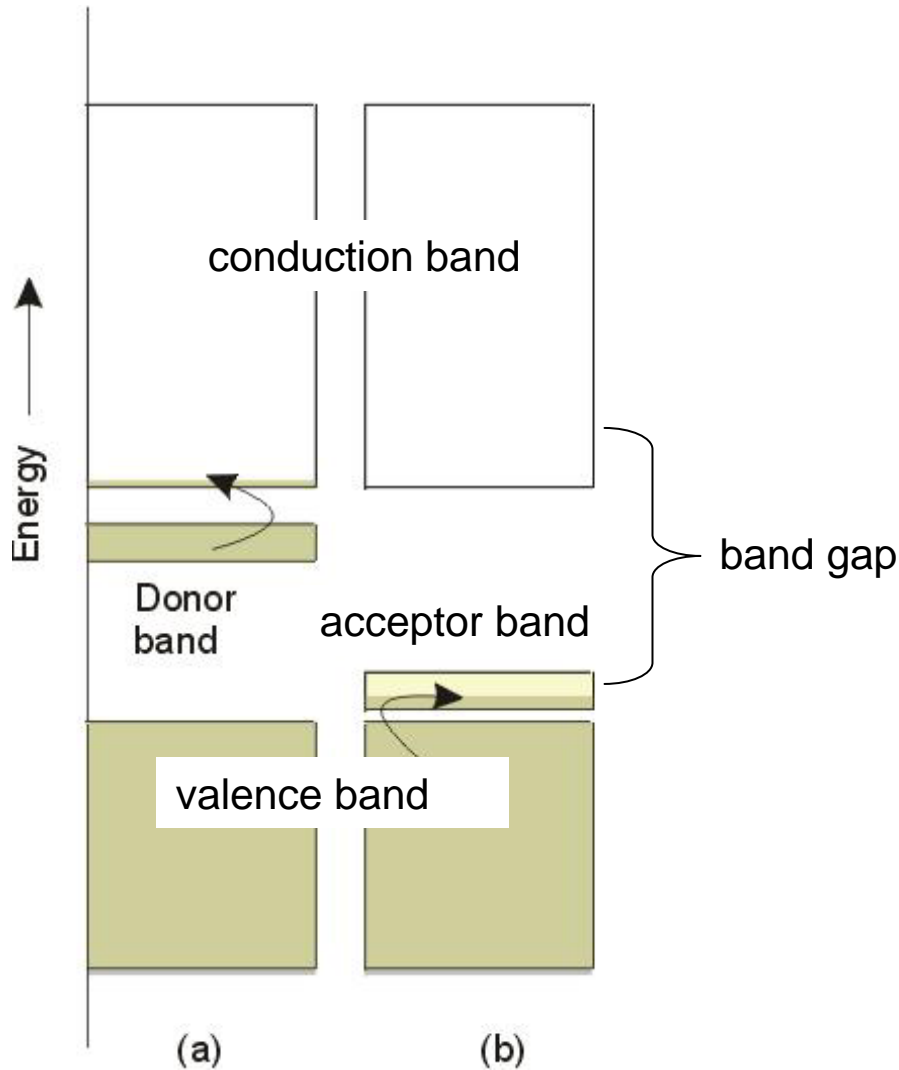


A semiconductor at room temperature usually has a much lower conductivity than a metallic conductor because only few electrons and/or holes can act as charge carriers

$$\ln \sigma = -\frac{E_a}{kT} + \ln \sigma_0$$

→ slope gives E_a

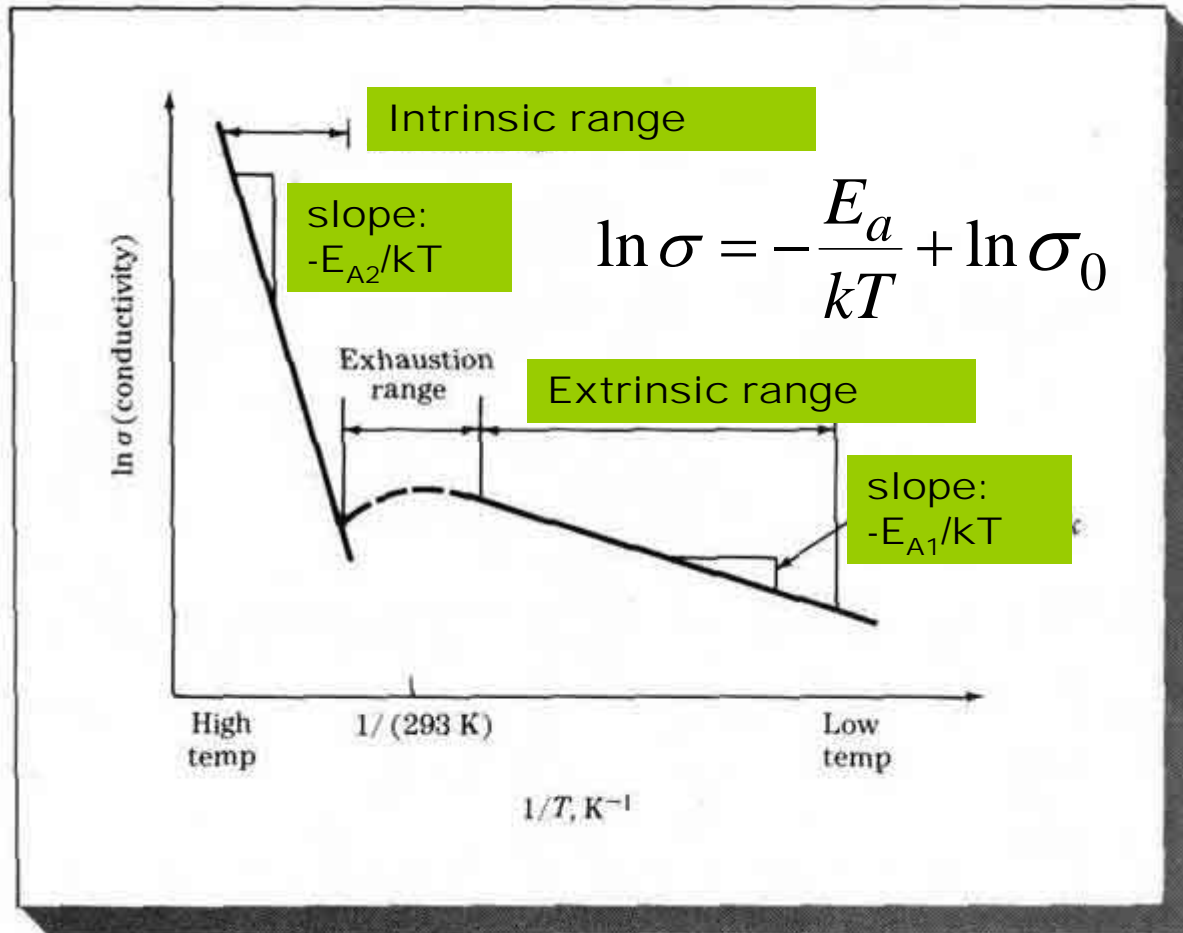
An even more detailed view of semiconductors: Intrinsic and extrinsic Semiconduction



Intrinsic semiconduction corresponds to the mechanism just described: charge carriers are based on electrons excited from the valence into the conduction band (e.g. very pure silicon).

Extrinsic semiconduction appears if the semiconductor is not a pure element but „doped“ by atoms of an element with either more or less electrons (e.g. Si doped by traces of phosphorous [n-type doping] or traces of boron [p-type doping]).

Intrinsic and extrinsic Semiconduction



Semiconductors: Comparison of conductivity to metals and insulators

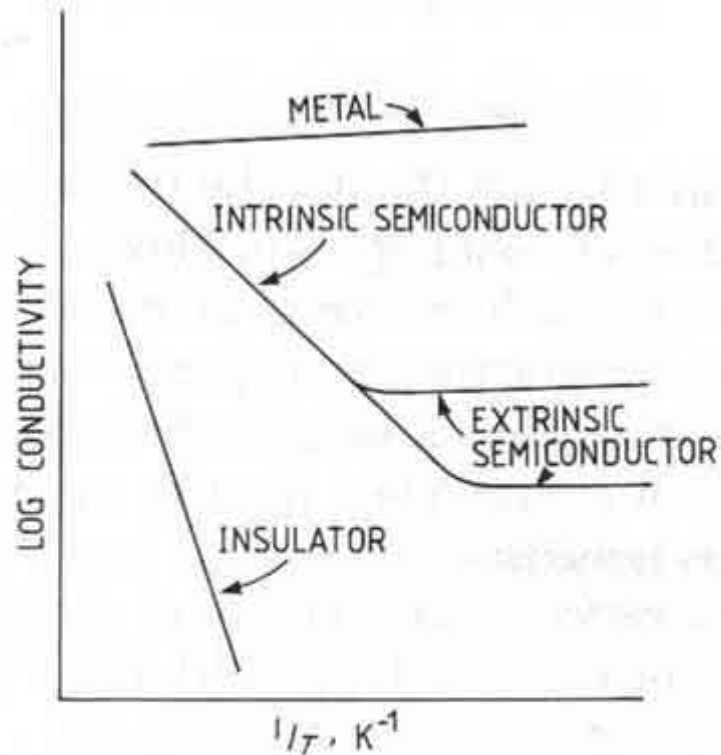
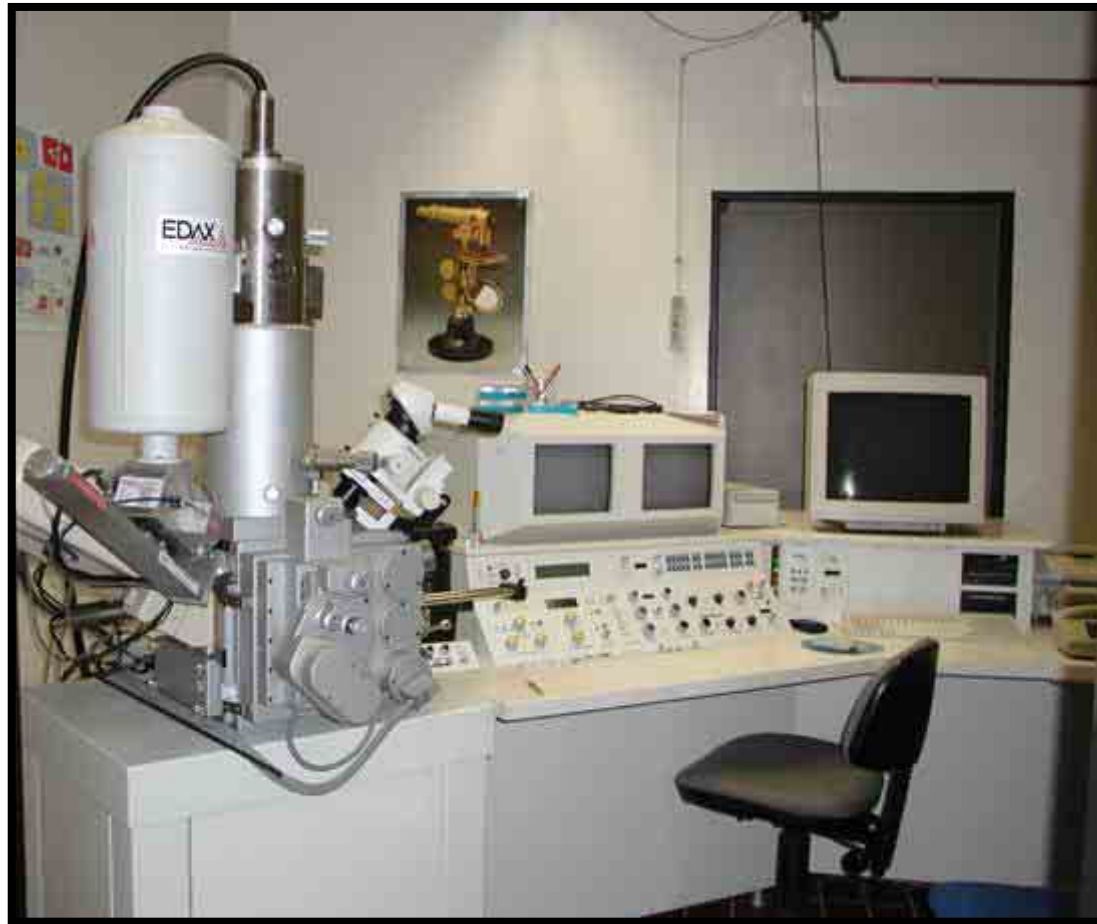
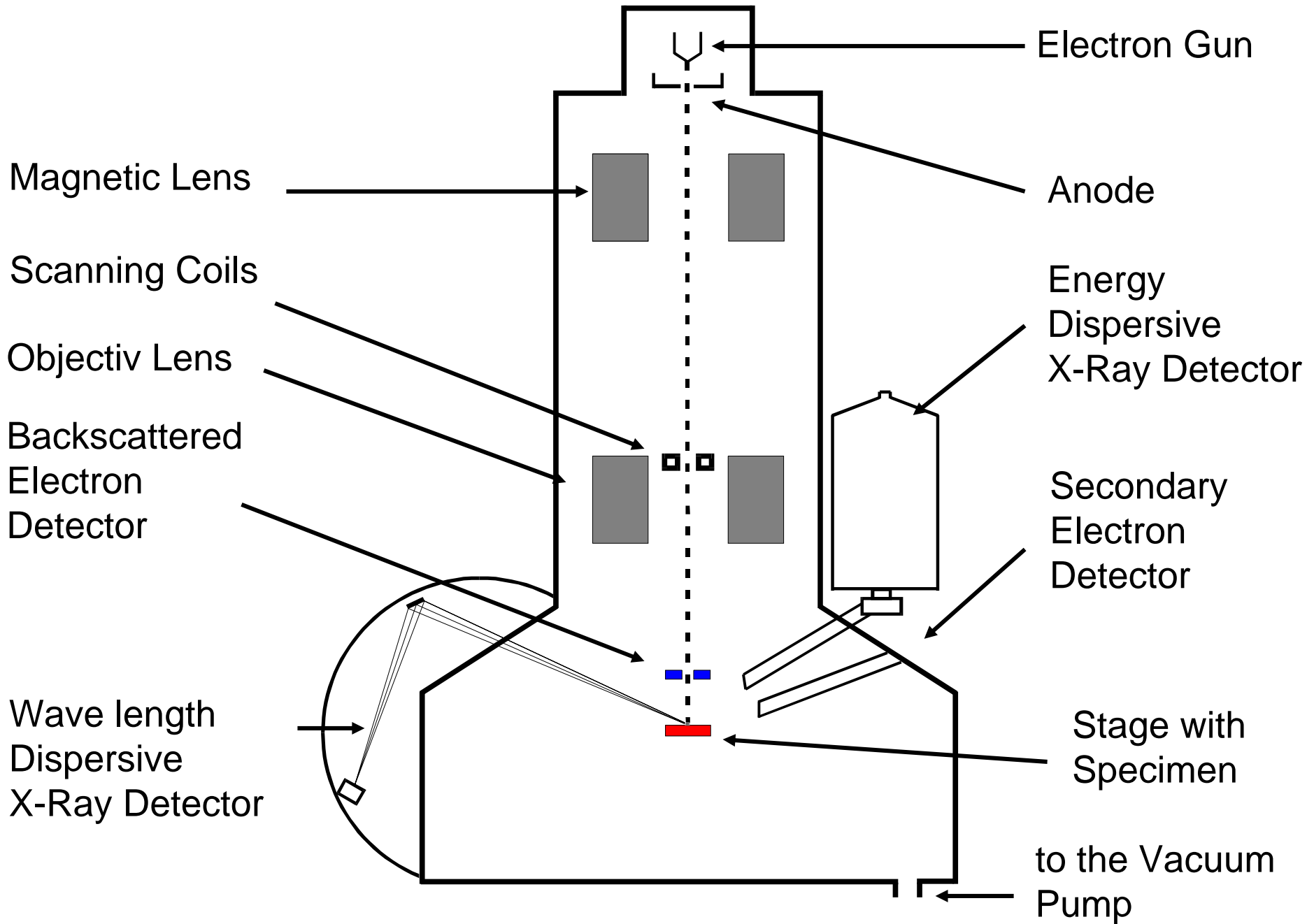


Fig. 7.9 Conductivity characteristics of metals, semiconductors and insulators

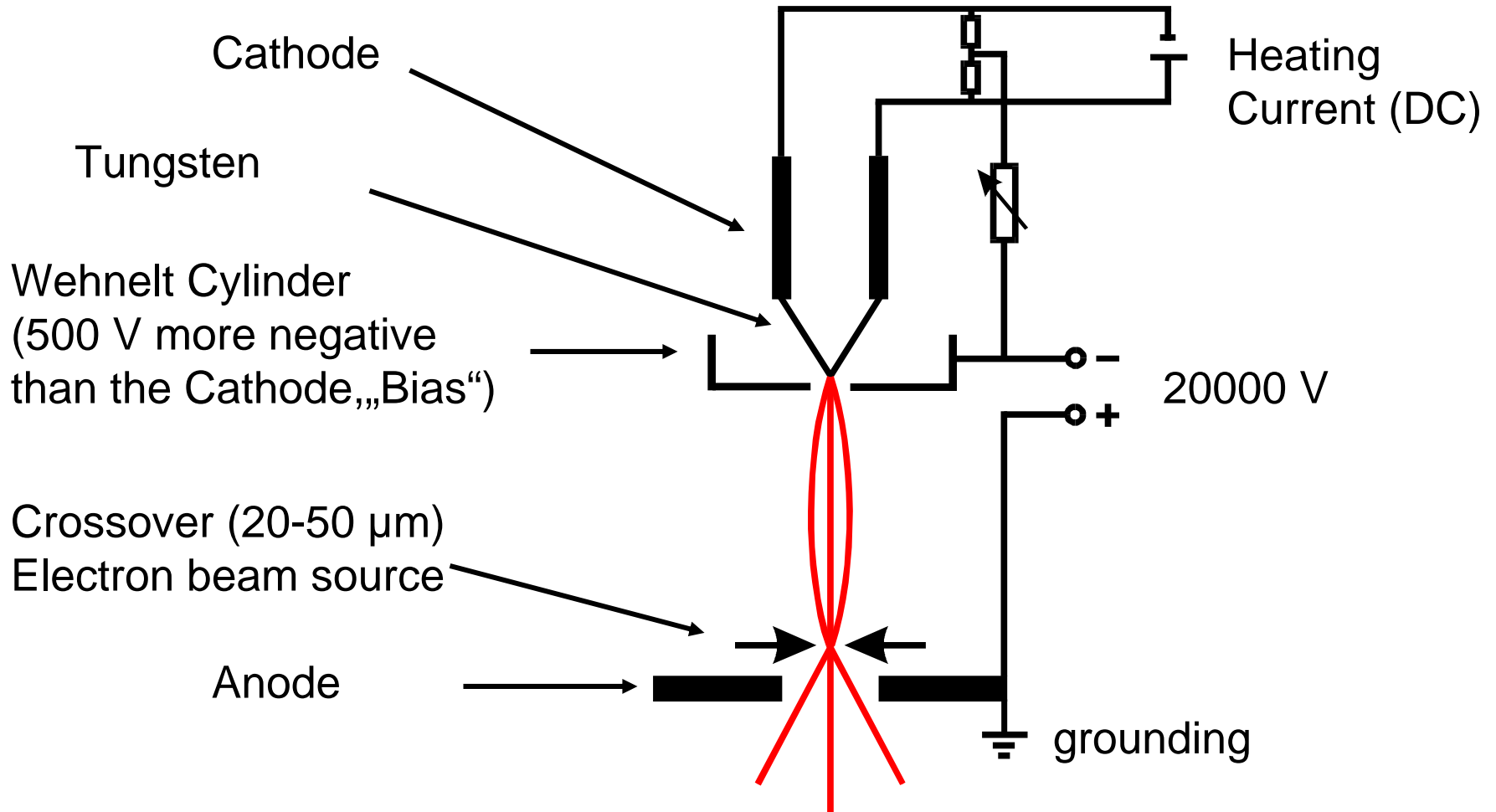
Analytical Scanning Electron Microscope



CamScan 44

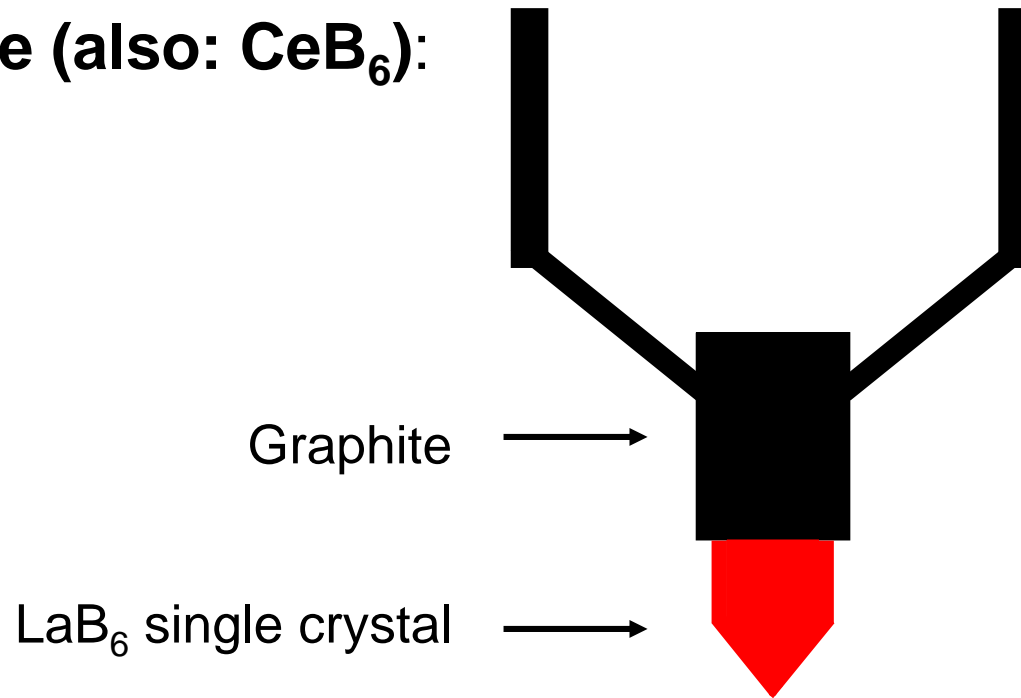


Electron Gun (W-Cathode)



The crossover is belittlet projected on the sample by the electronic-optical system (minimal diameter of the beam: ca. 5 nm)

LaB₆-Cathode (also: CeB₆):



- indirect heating (because of the low conductivity of LaB₆)
- lower work function than the W-cathode (→ higher brightness)
- damageable by ionic shooting (→ high vacuum necessary)
- expensive!

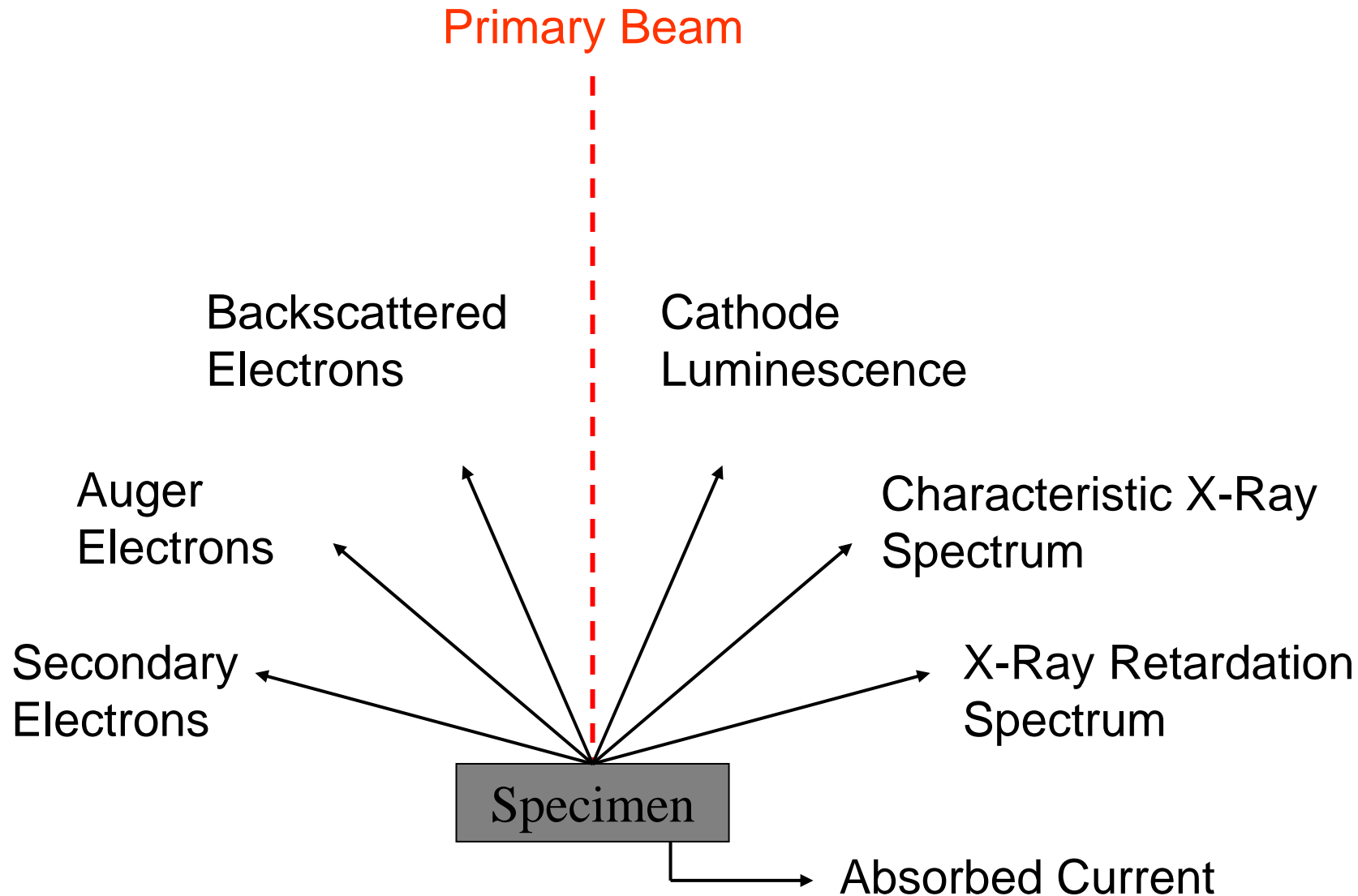
Field Emission-Cathode

- W – cathode with a fine apex
- two anodes:
 1. one to bring up the work function
 2. one for the acceleration
- high brightness
- high vacuum necessary

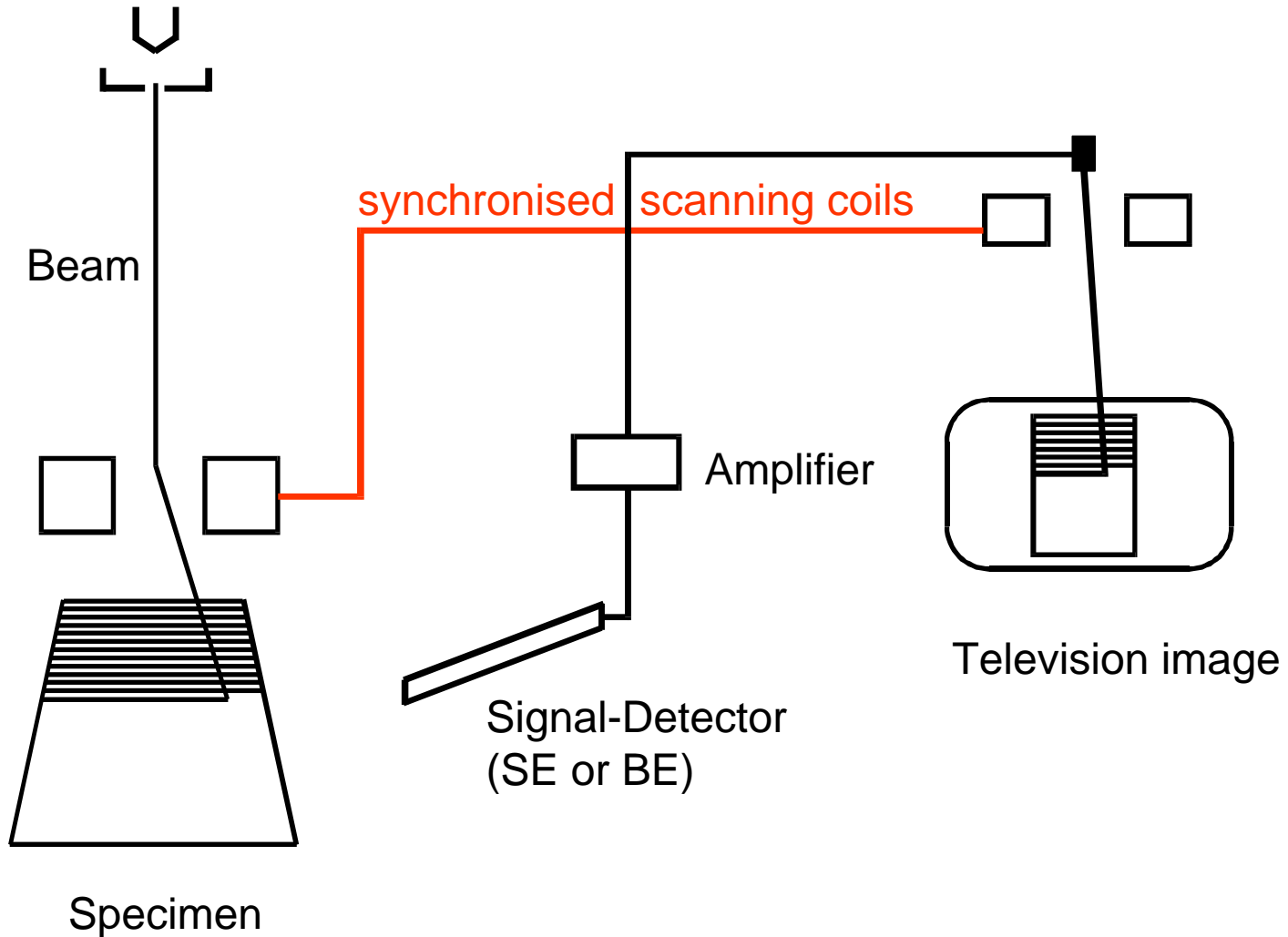
Comparison of W-, LaB₆-, and Field emission-cathods

	W	LaB ₆	FE
work function /eV	4,5	2,7	4,5
crossover / μm (important for high resolution images)	20-50	10-20	3-10
T _{cathod} /K	2700	<2000	300
emission current density /A/cm ²)	1-3	25	10 ⁵
gun Brightness /A/cm ² sr	10 ⁵ -10 ⁶	10 ⁷	10 ⁹
vacuum /mbar	10 ⁻⁵	10 ⁻⁷	10 ⁻⁹
service life /h	40-100	1000	>2000

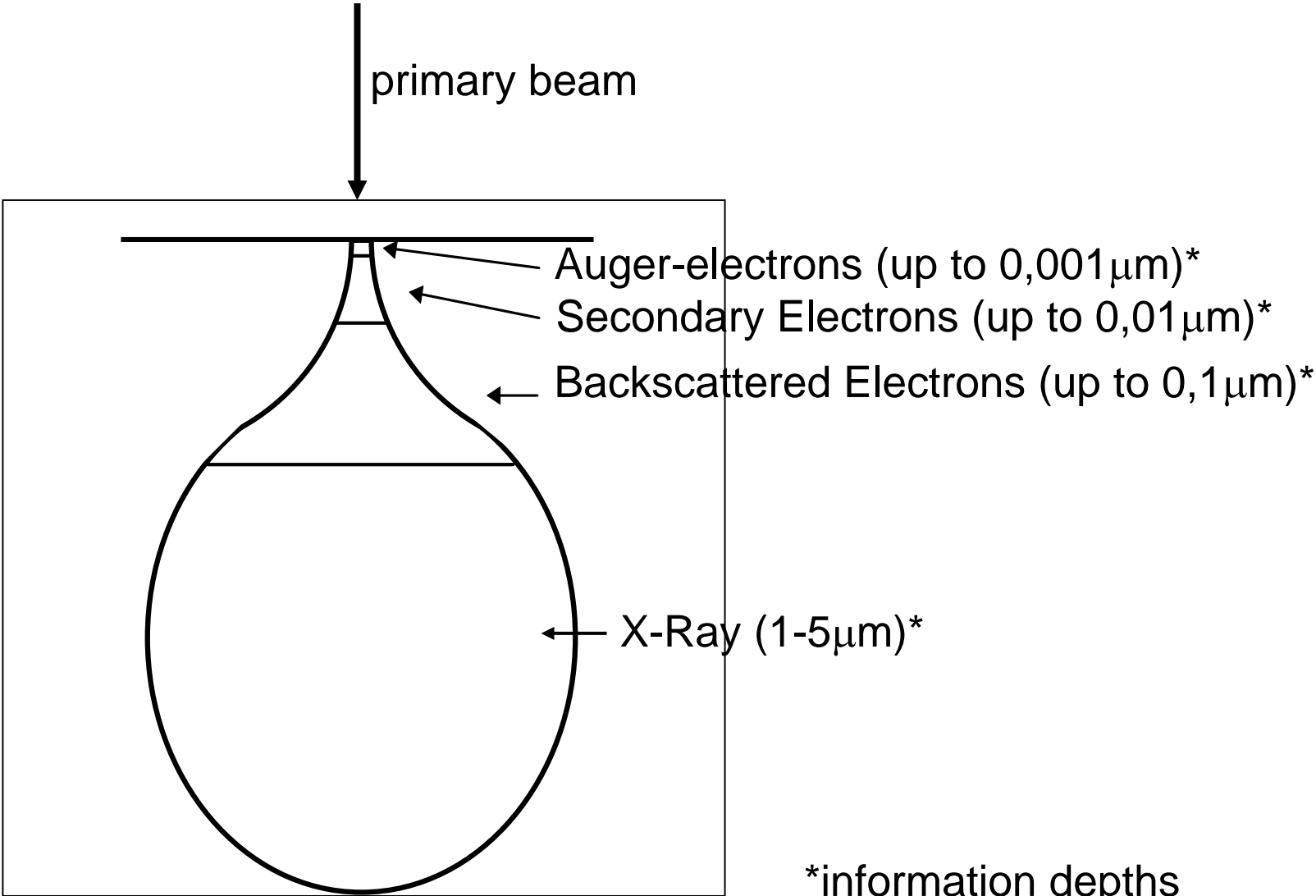
Interaction of a high energy electron beam with material



Principle of the image formation




Interaction volume of the electron beam (pear-like)




Dependence of the interaction volume on the acceleration voltage and material (simulations)




Fe (10 kV)




Au (20 kV)



Fe (20 kV)



Al (20 kV)



Fe (30 kV)

1 μm

Secondary Electrons:

- inelastic scattered PE (Primary Electrons)
- energy loss by interaction with orbital electrons or with the atomic nucleus
- energy: **< 50 eV**
- maximal emission depth: **5-50 nm**

→ high resolution images

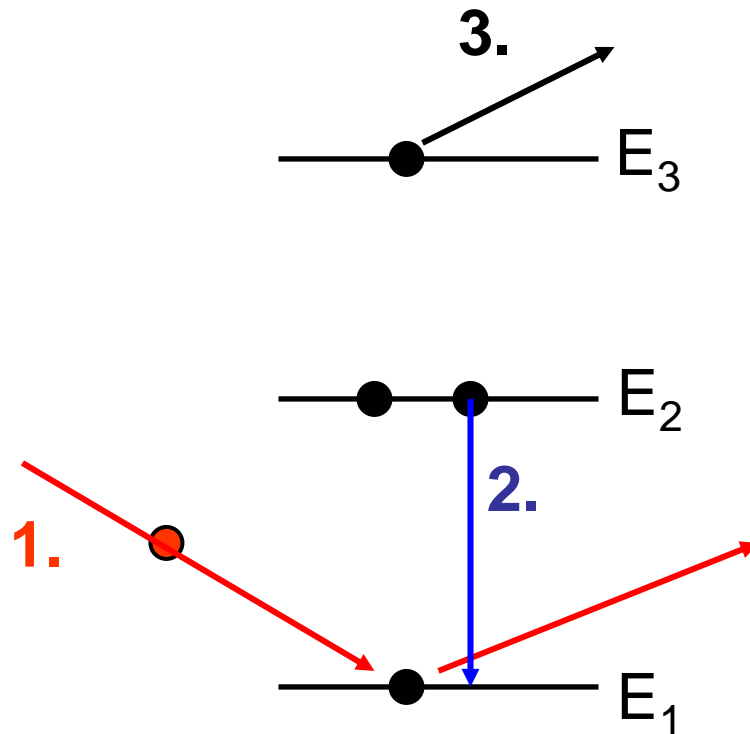
Backscattered Electrons:

- elastic and inelastic scattered PE
- energy: **50 eV – energy of the PE** (e.g. 20 keV)
- maximal emission depth: **0.1 - 6 μ m** (dependent on the specimen)

- intensity depends on the average atomic number of the material → **material contrast images**
- high interaction volume → **low resolution images**

Auger Electrons:

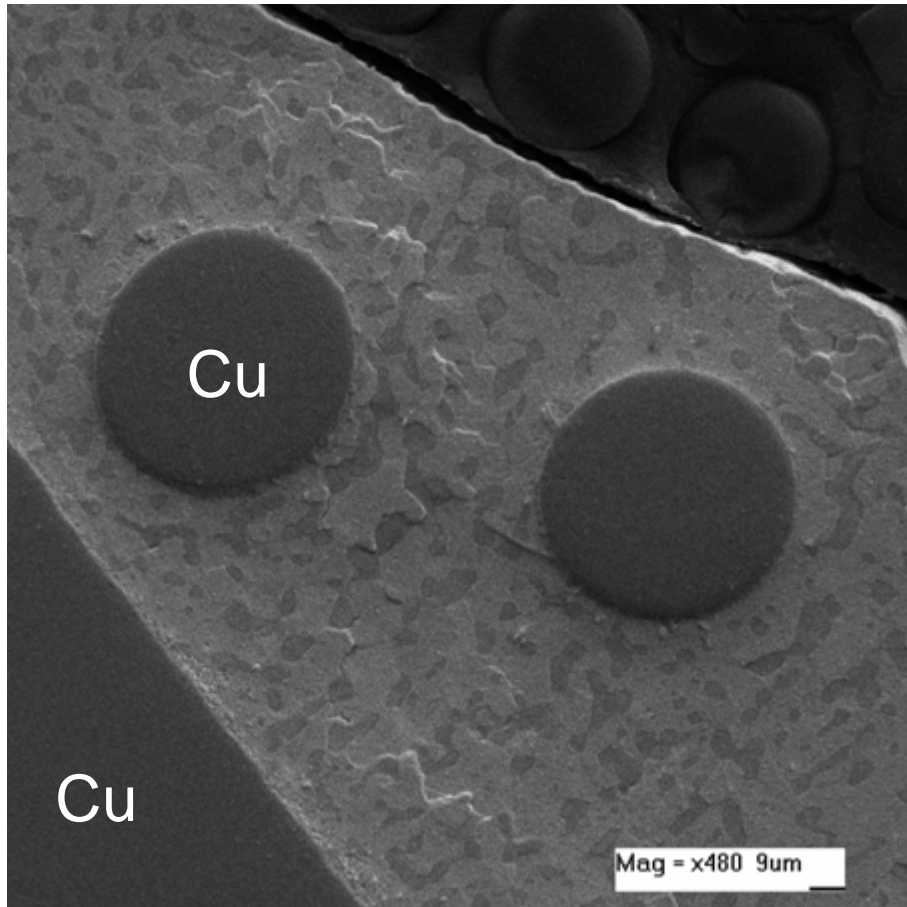
- energy characteristic for the element
→ Auger Electron Spectroscopy (AES)



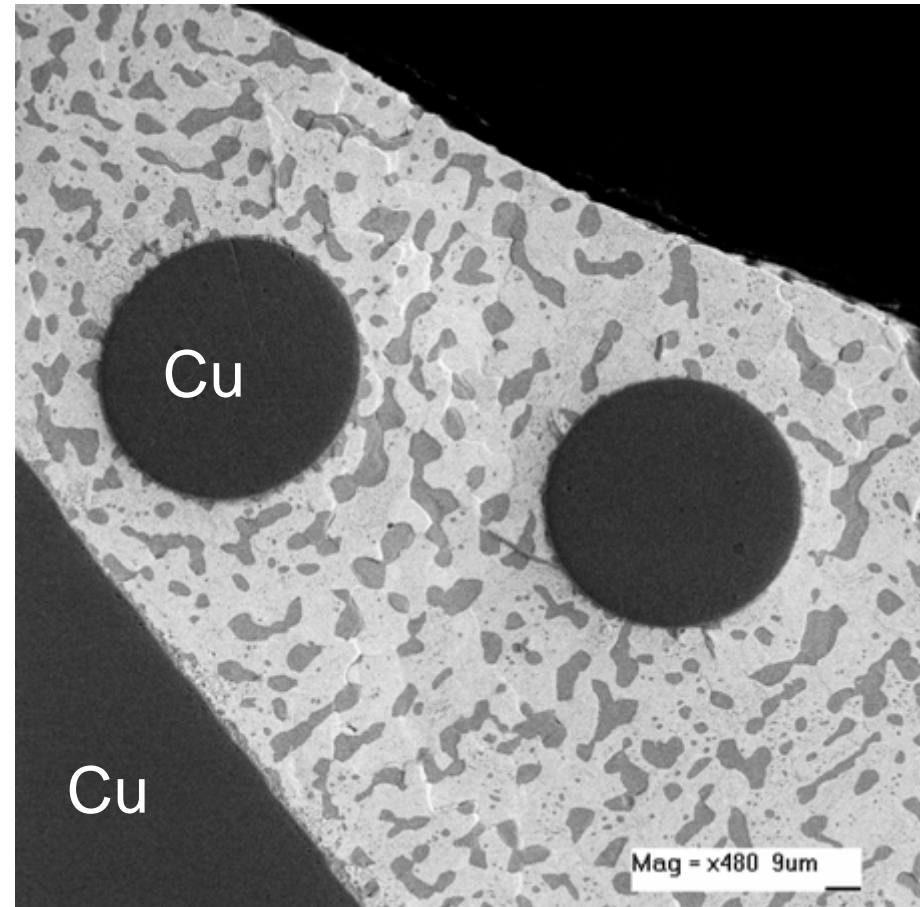
$$E_{\text{Auger-Electron}} = E_1 - E_2 - E_3$$

Cu-wire imbedded in solder

SE-image
(high resolution)

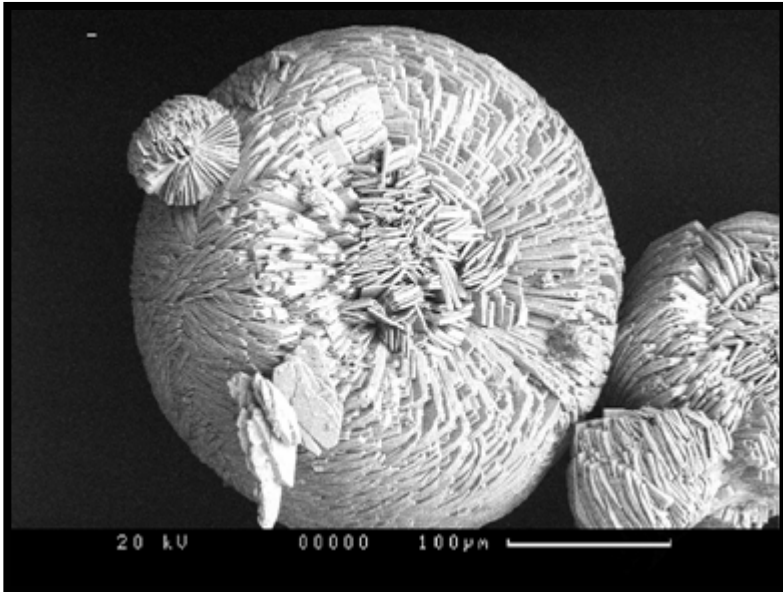


BE-image
(high Z-contrast)

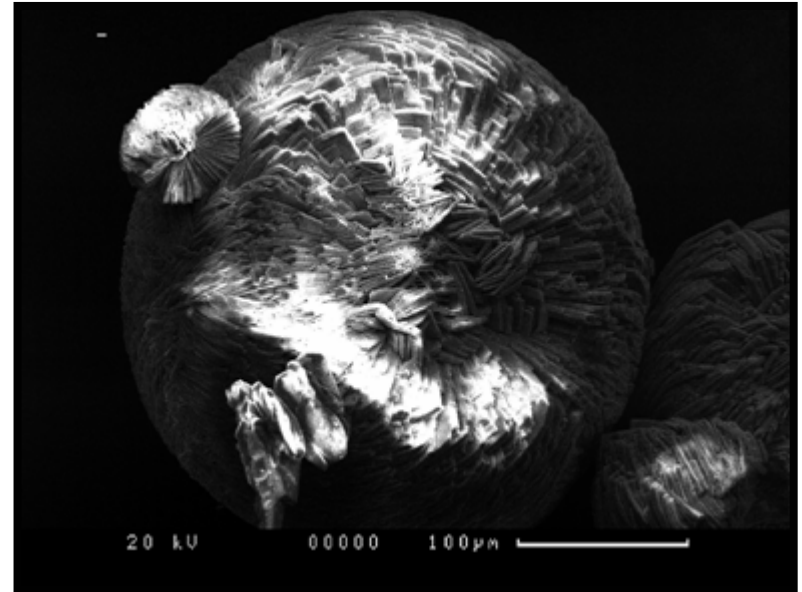


$$Z_{\text{Pb}} > Z_{\text{Sn}} > Z_{\text{Cu}}$$

Backscattered electron images are less sensitive on charging:



BE-image



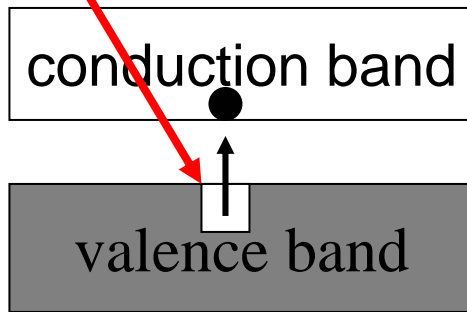
SE-image

cause: the average energy of the backscattered electrons is higher

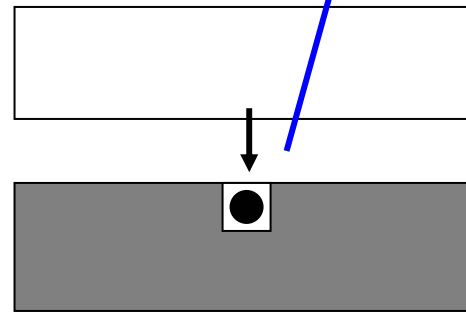
Cathode luminescence

- visible and UV radiation
- special detectors necessary
- not for metals

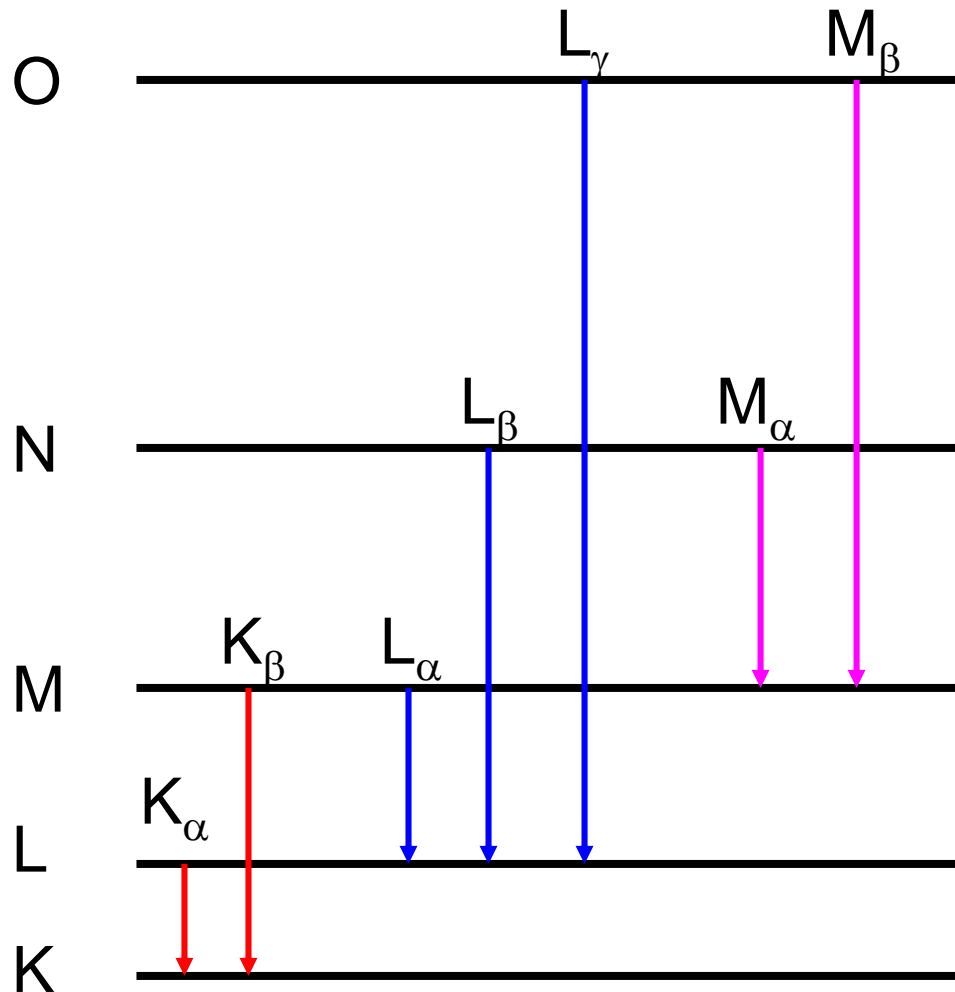
PE



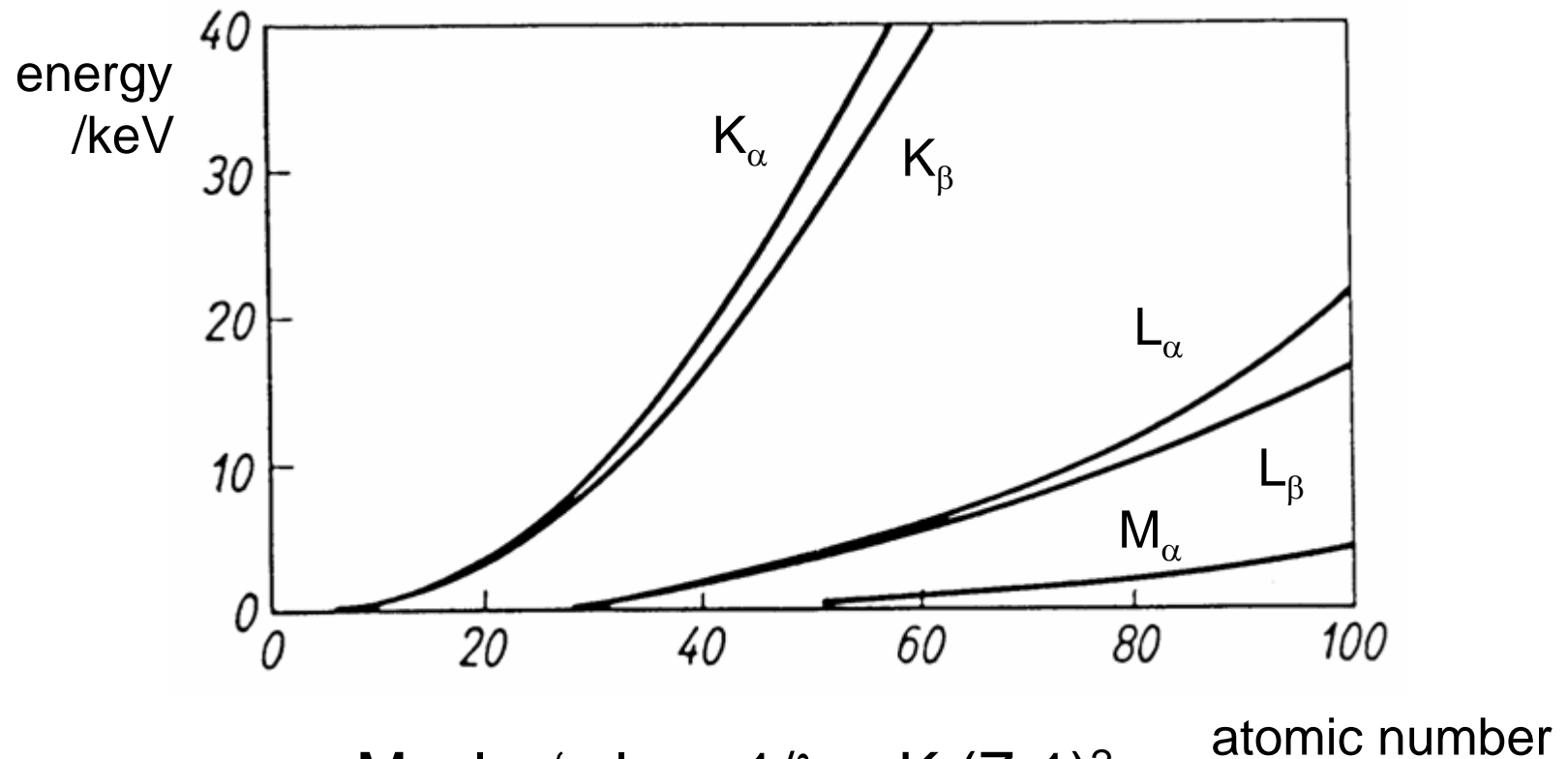
$h\nu$



Characteristic X-Ray spectrum (without fine structure)



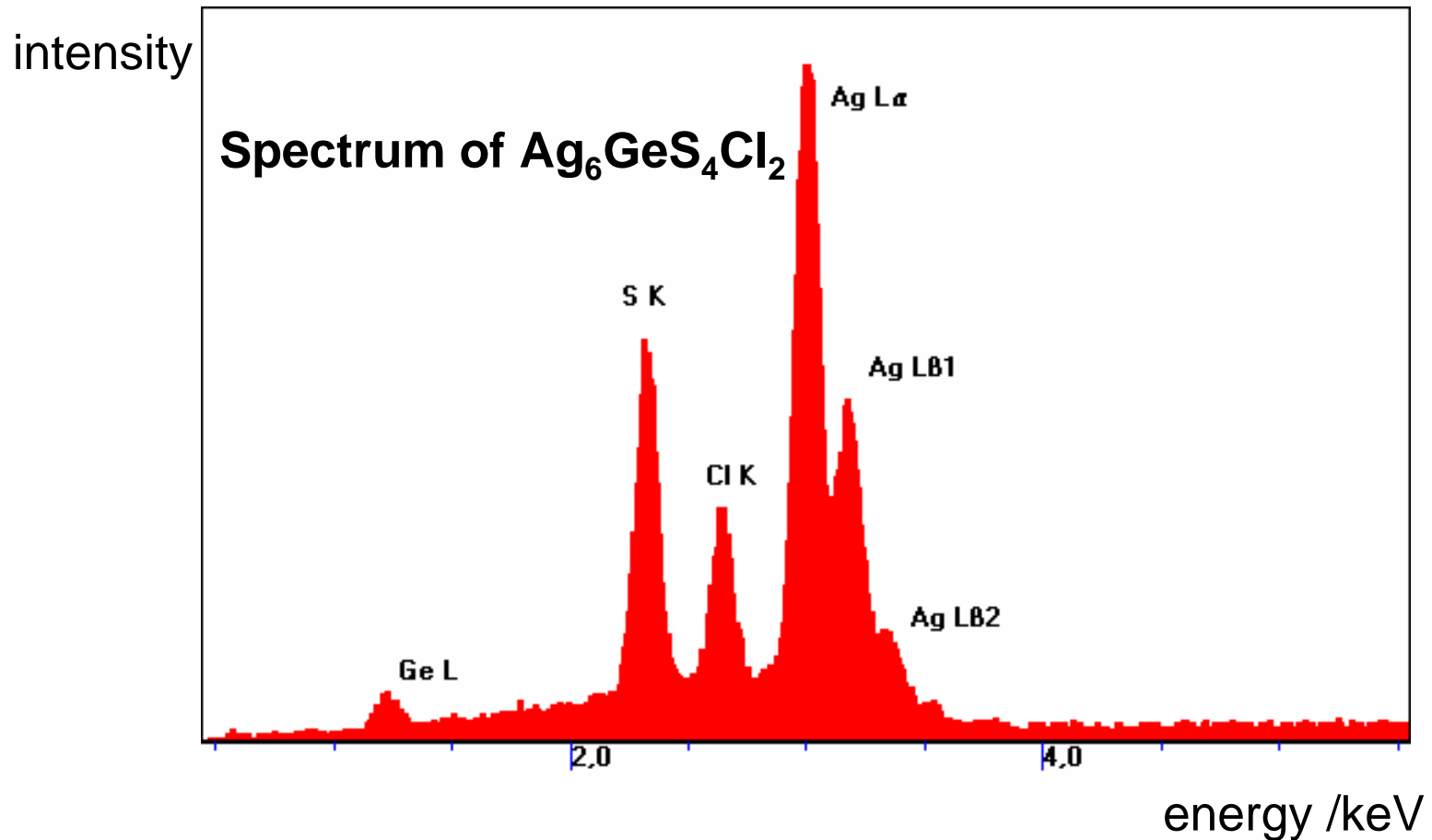
Energy range of the main series as a function of the atomic number:



Mosley's law: $1/\lambda = K (Z-1)^2$

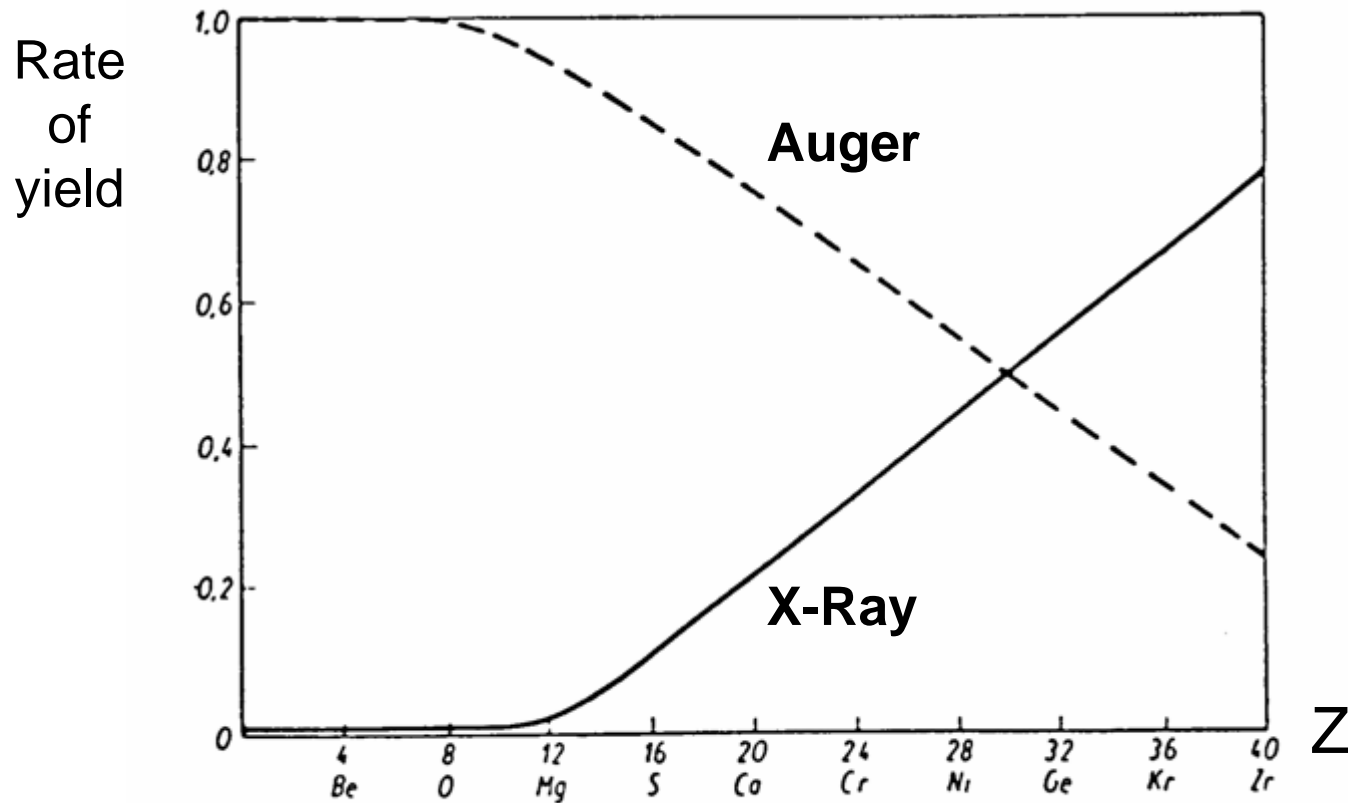
(K: constant, Z = atomic number)

Typical (characteristic) X-Ray spectrum (EDX)



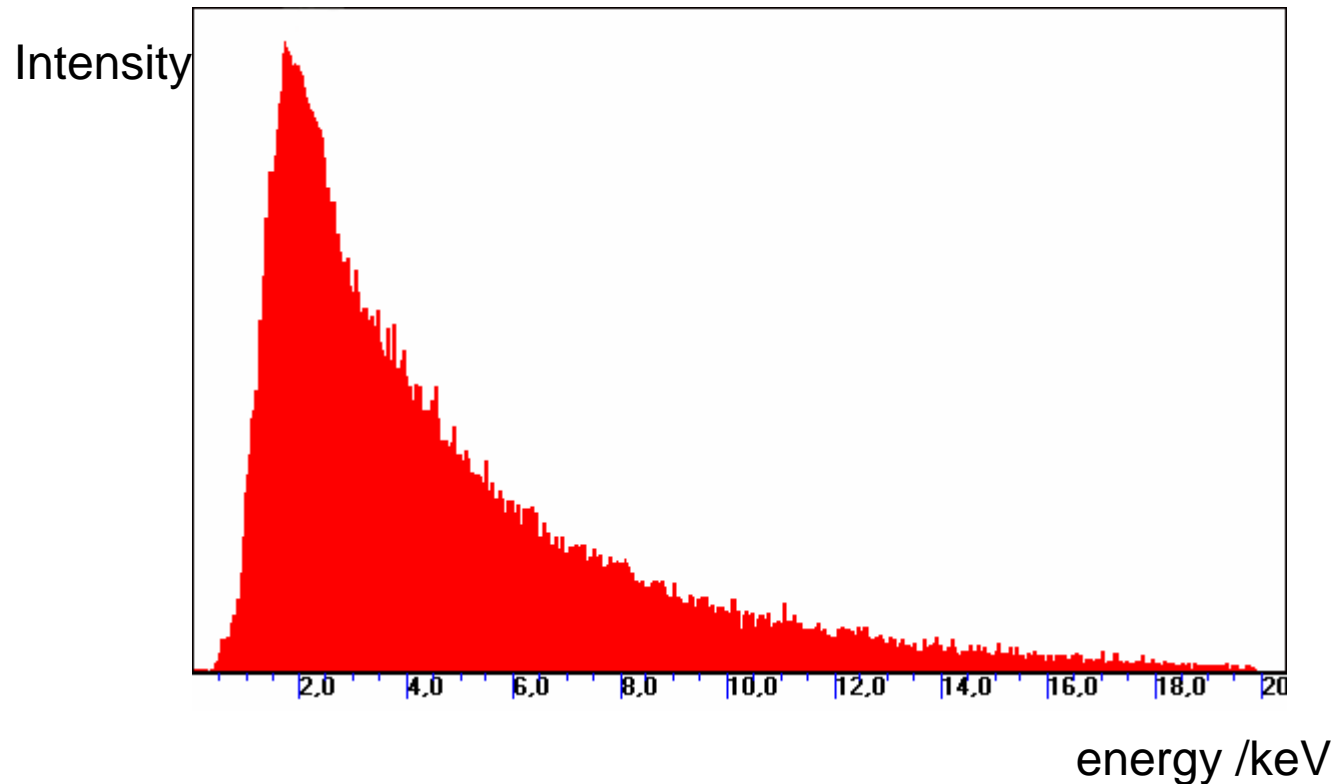
- sulfur ($Z = 16$) and chlorine ($Z = 17$) easily distinguishable (in contrast to X-Ray diffraction)

Competition Auger / X-Ray



→ small X-Ray yield for light elements (B, C, N, O, F)

X-Ray Retardation Spectrum

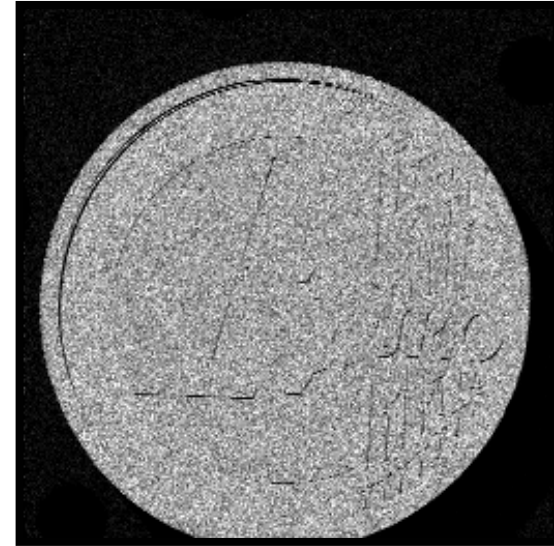


- primary electrons are retarded by the electron clouds of the atoms
- E_{\max} of the X-Ray's: $e \times U_{\text{accelerating voltage}}$

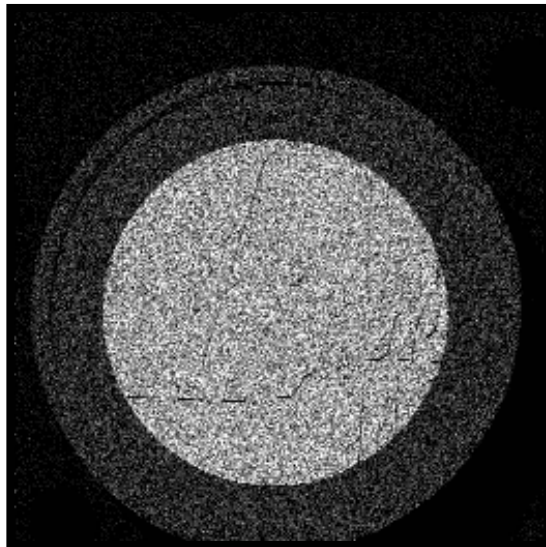
Large area mapping (X-Ray-images)



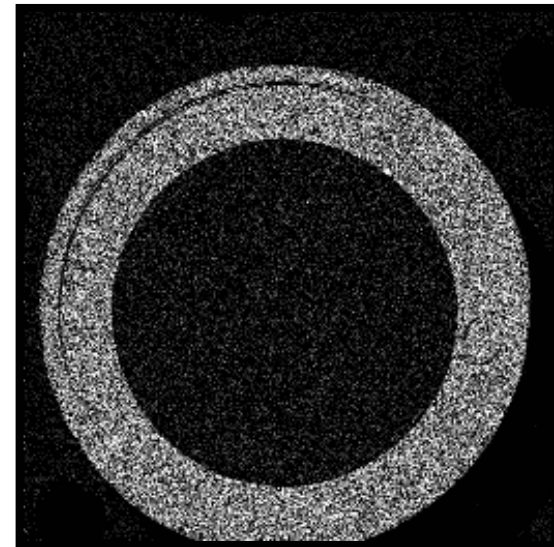
SE-Image



Cu-K α -
mapping



Ni-K α -
mapping



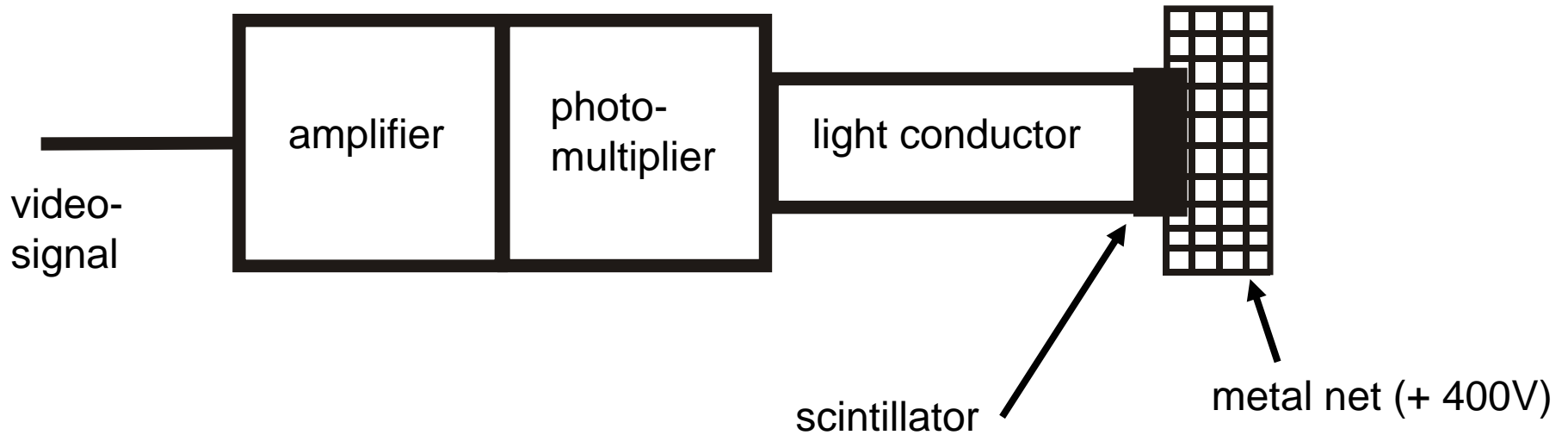
Zn-K α -
mapping

256x256 pixel, moving of the specimen holder

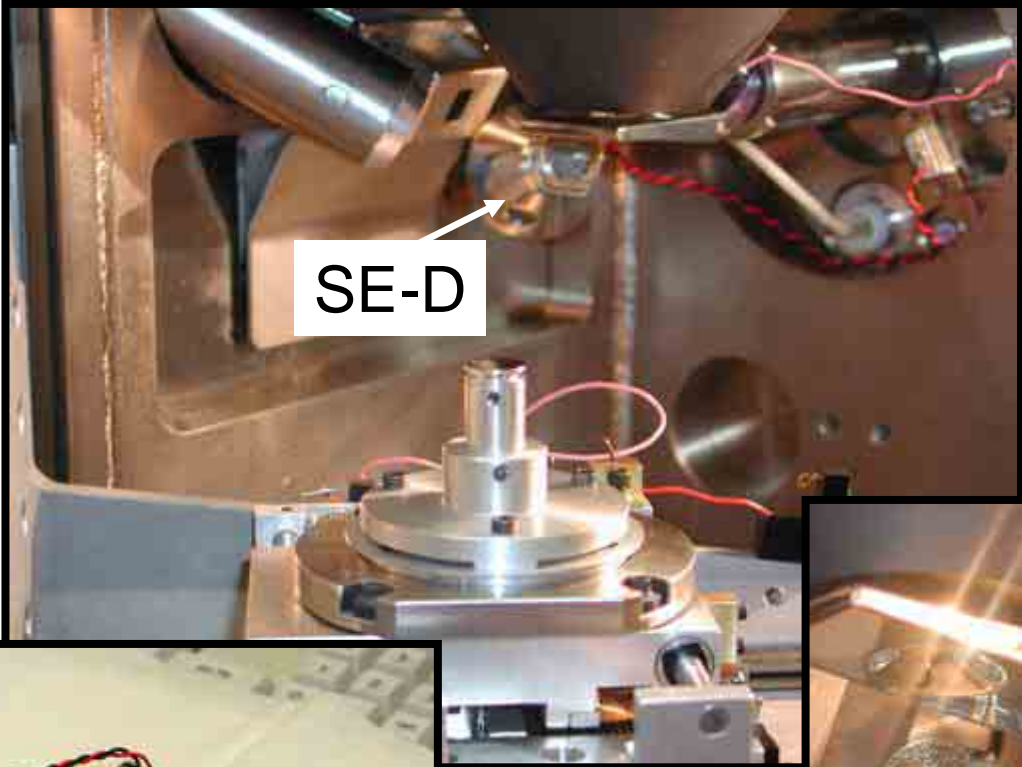
Electron Detectors

1. Secondary Electron (**SE-**) Detector

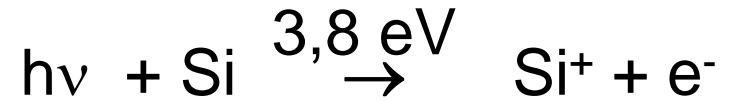
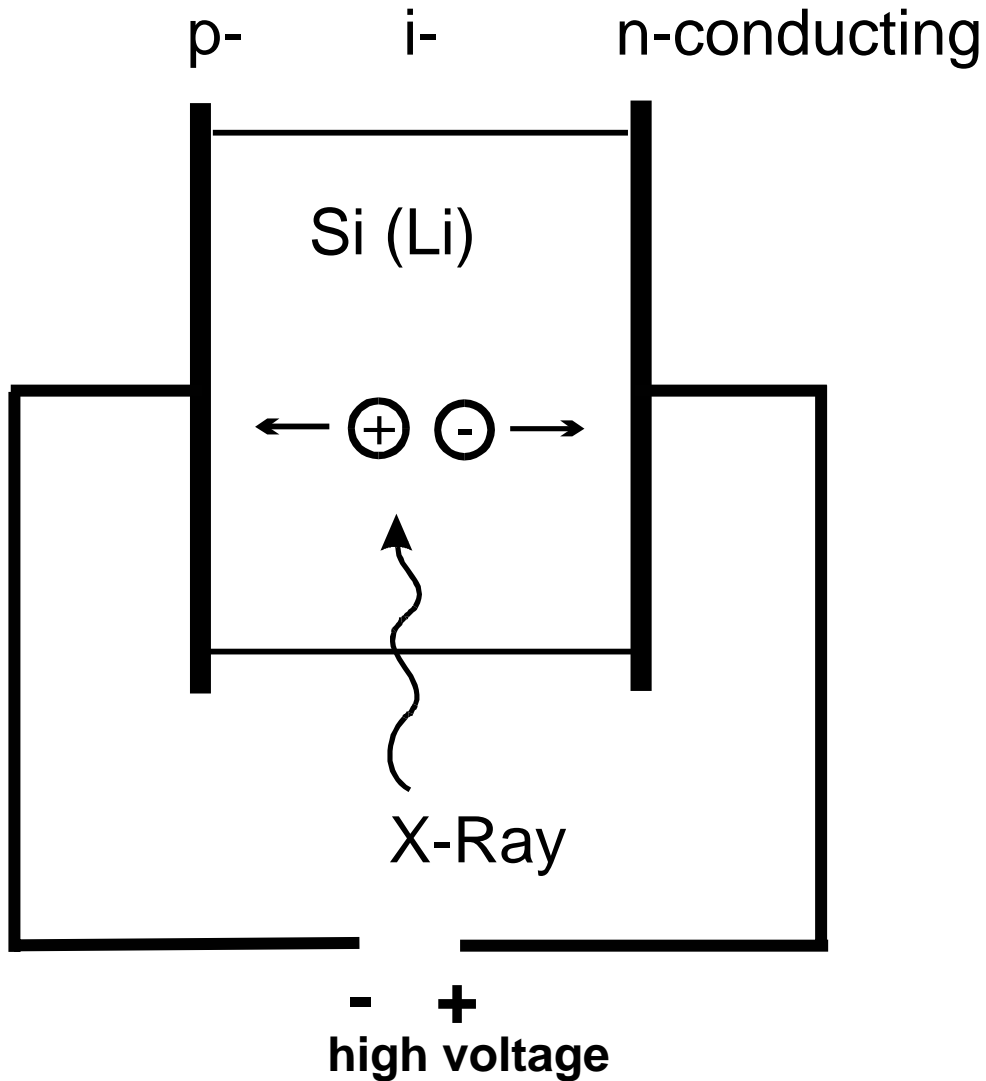
Szintillator-Photomultiplier-Detector
(Everhart-Thornley-Detector)



SE-detektor:



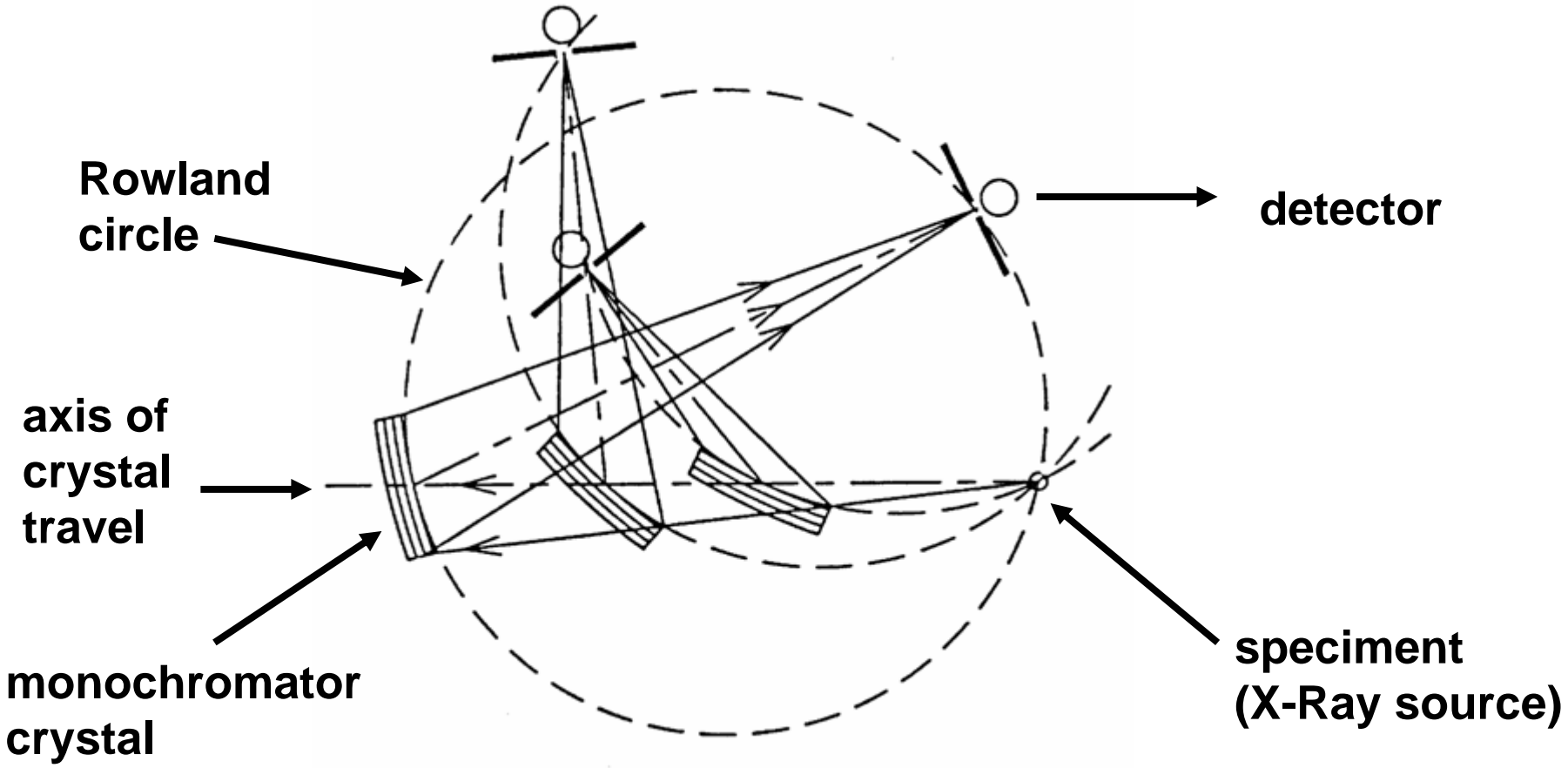
Principle of an EDX-detector



e.g. Mn K_{α} : 5894 eV

$5894/3.8 = 1550$
electron hole pairs

WDX-Spectrometer: Scanning of a λ -range with *one* monochromator crystal



Detector's for WDX:

two proportional counter switched in series

1. FPC, Flow proportional counter (for low energy X-Ray's)

the counting gas (Ar / CH₄) flows through the counter (very thin polypropylen window, not leak-free for the counting gas)

2. SPC, Sealed proportional counter (for high energy X-Ray's)

counting gas: Xenon / CO₂

WDX detector



4 monochromator
crystals

proportional
counter

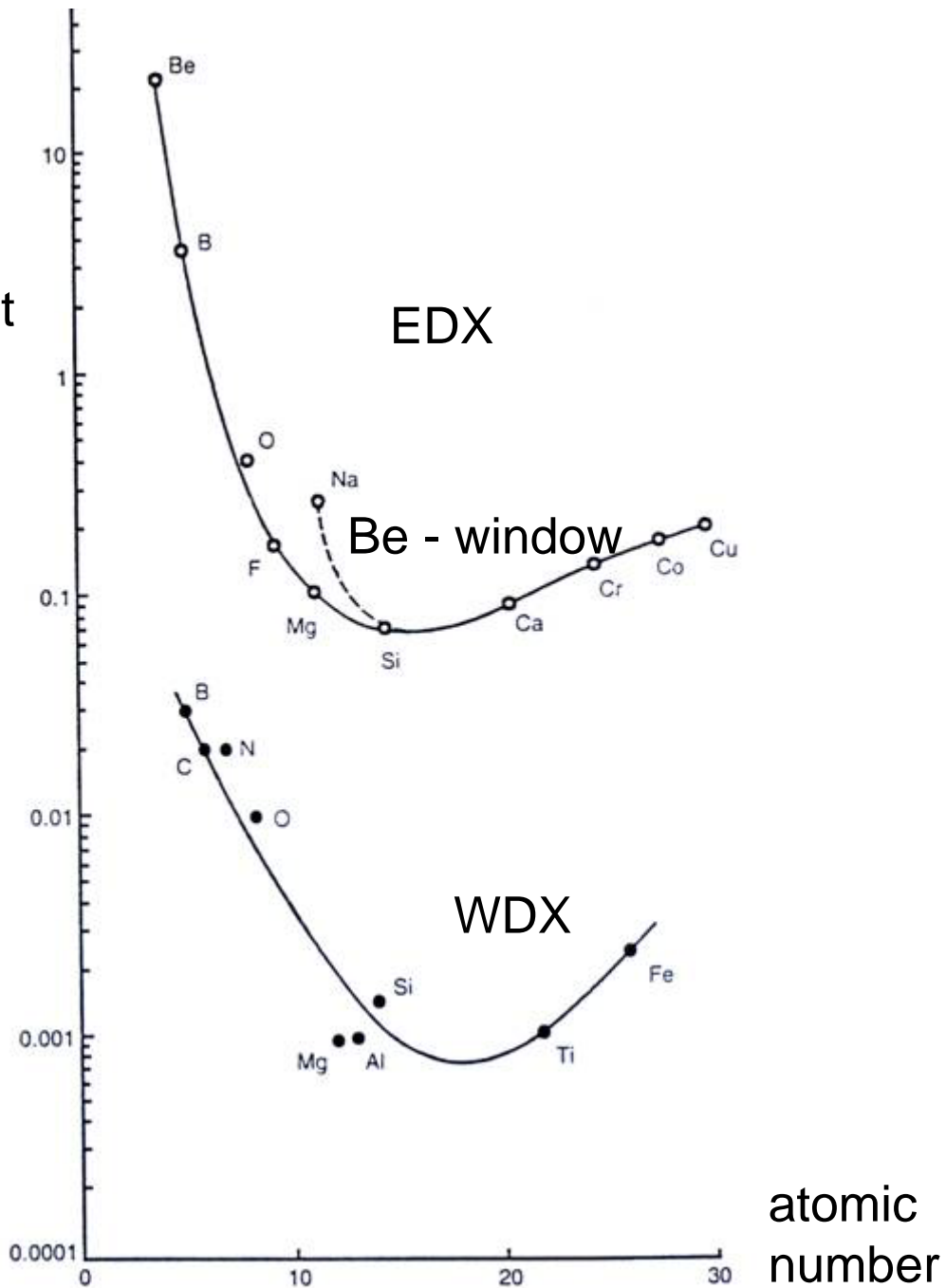


Comparison of EDX and WDX

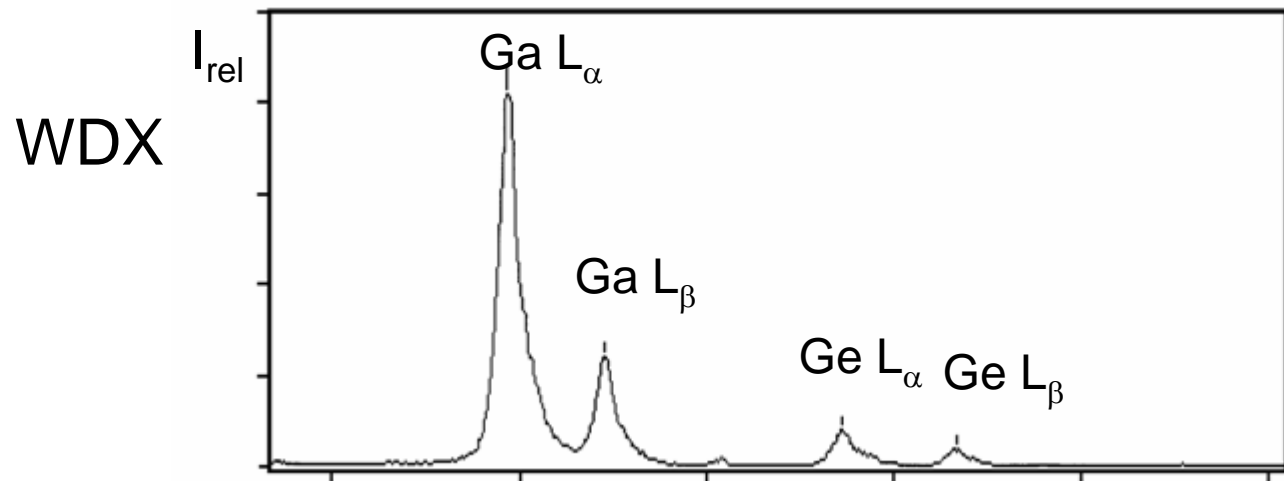
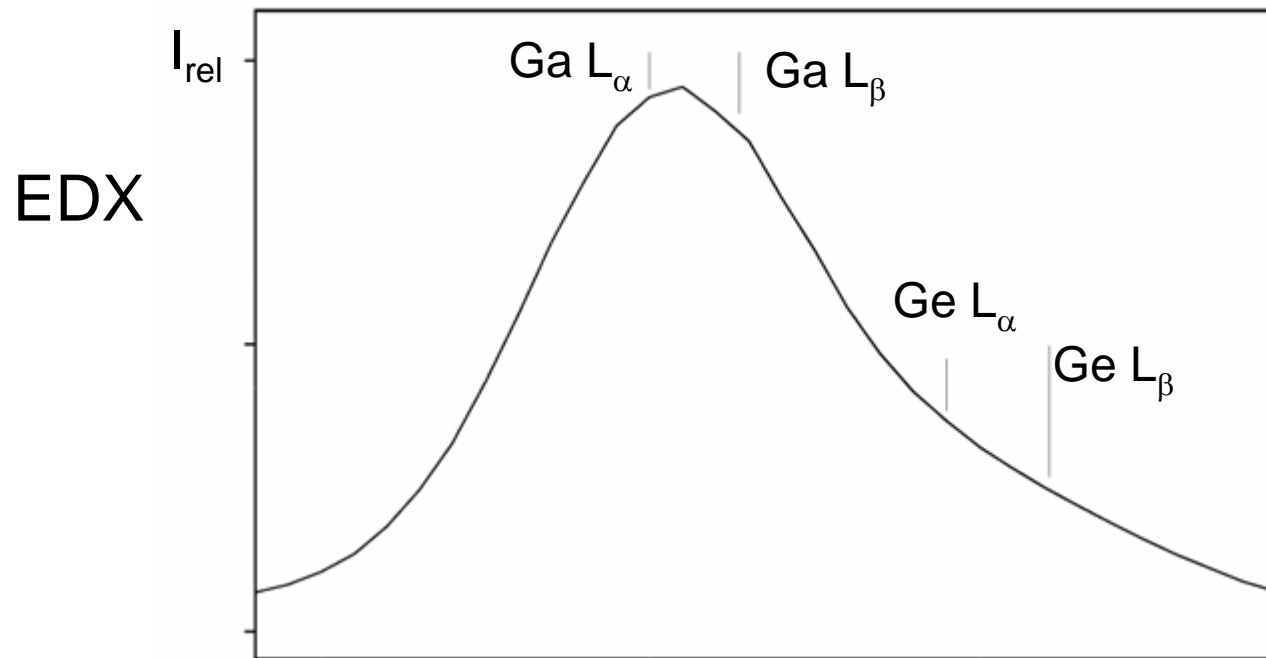
	EDX	WDX
spectral resolution	110-140 eV	10 eV
specimen current	10^{-10} A	10^{-7} A
analysis time	1-2 min	30-100 min
spectrum develops	simultaneous	sequential

Sensitivity of EDX and WDX

atomic percent



Comparison EDX - WDX



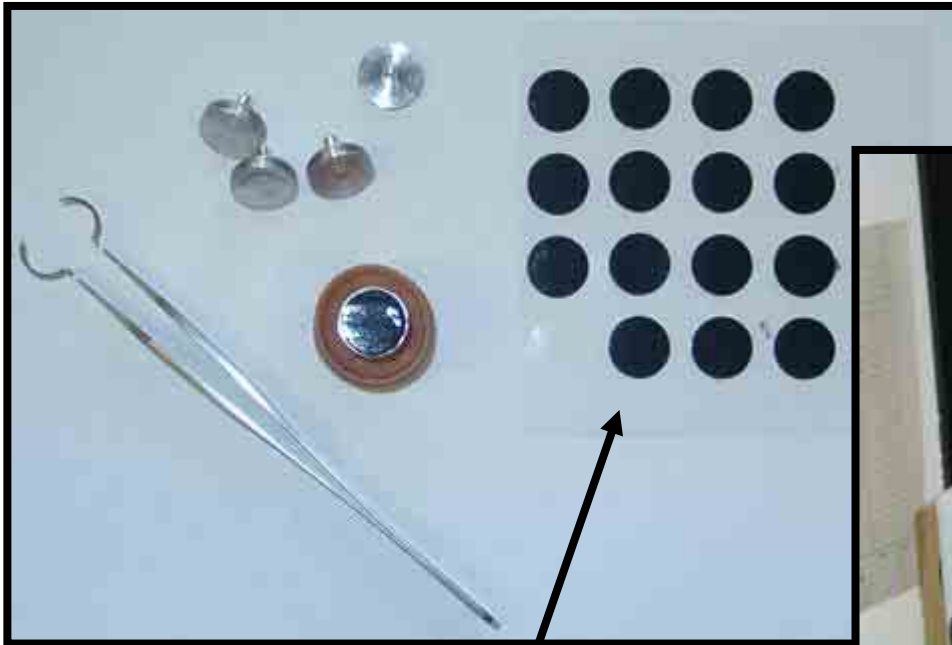
(compound: GeGa_4S_4)

1.1

1.2

energy /keV

typical sample holder equipment



conducting tabs
(adhesive plastic with graphite)

typical preparation of
small crystals



Special preparation for insulating material:

- metallisation with gold (sputtering process)

 - high resolution images

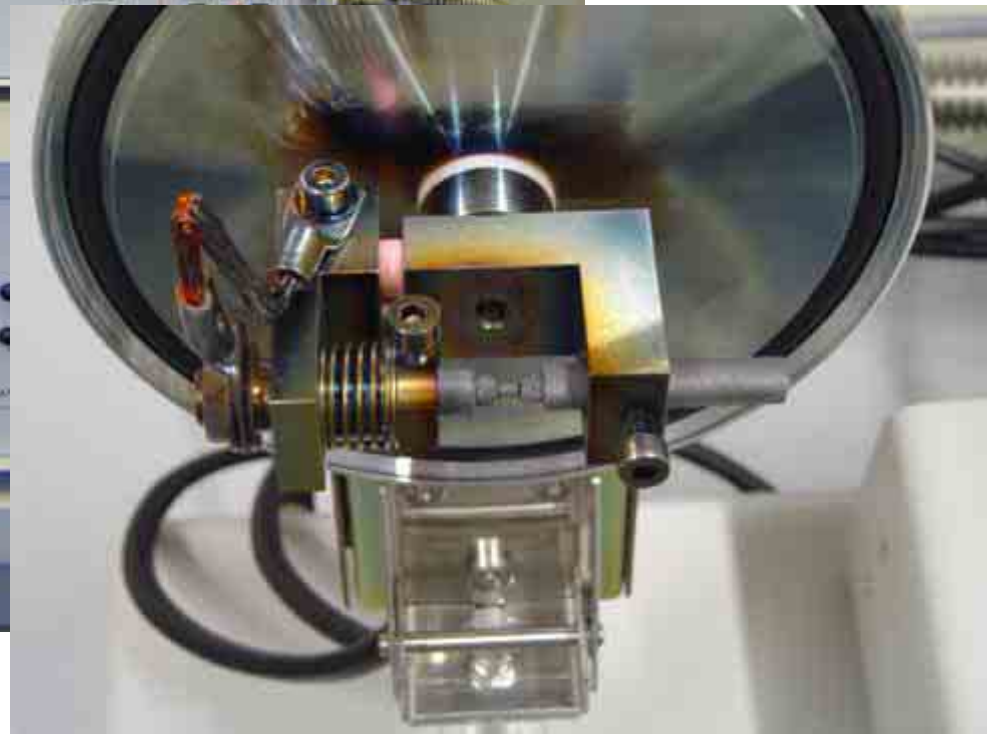
- carbon deposition (evaporation process)

 - quantitative analysis

Sputter coater



Carbon coater

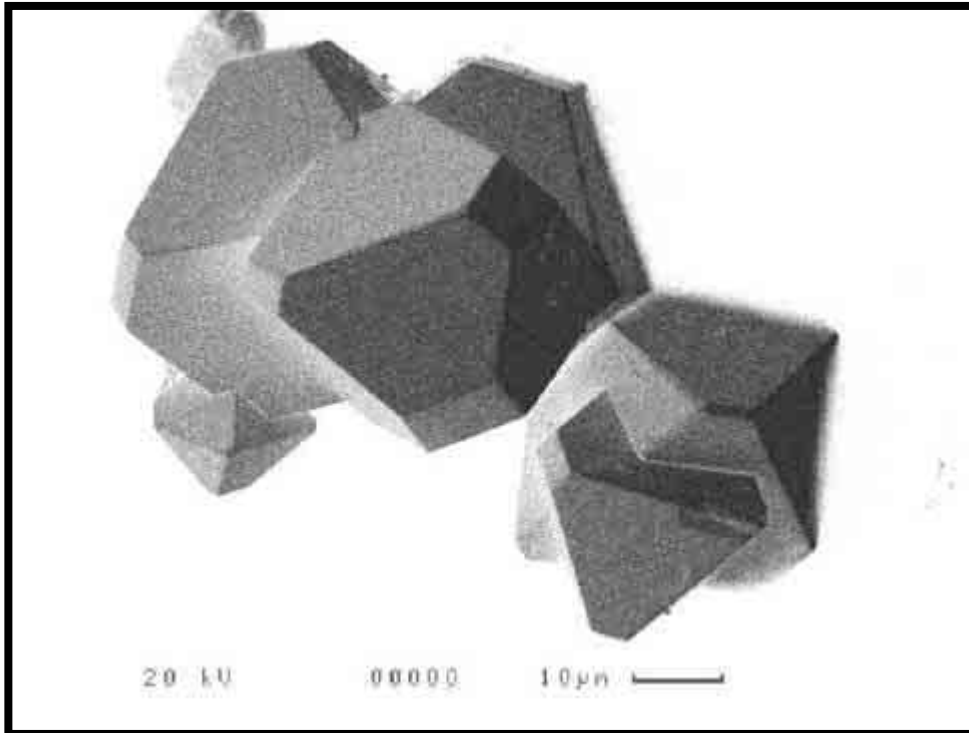


Applications:

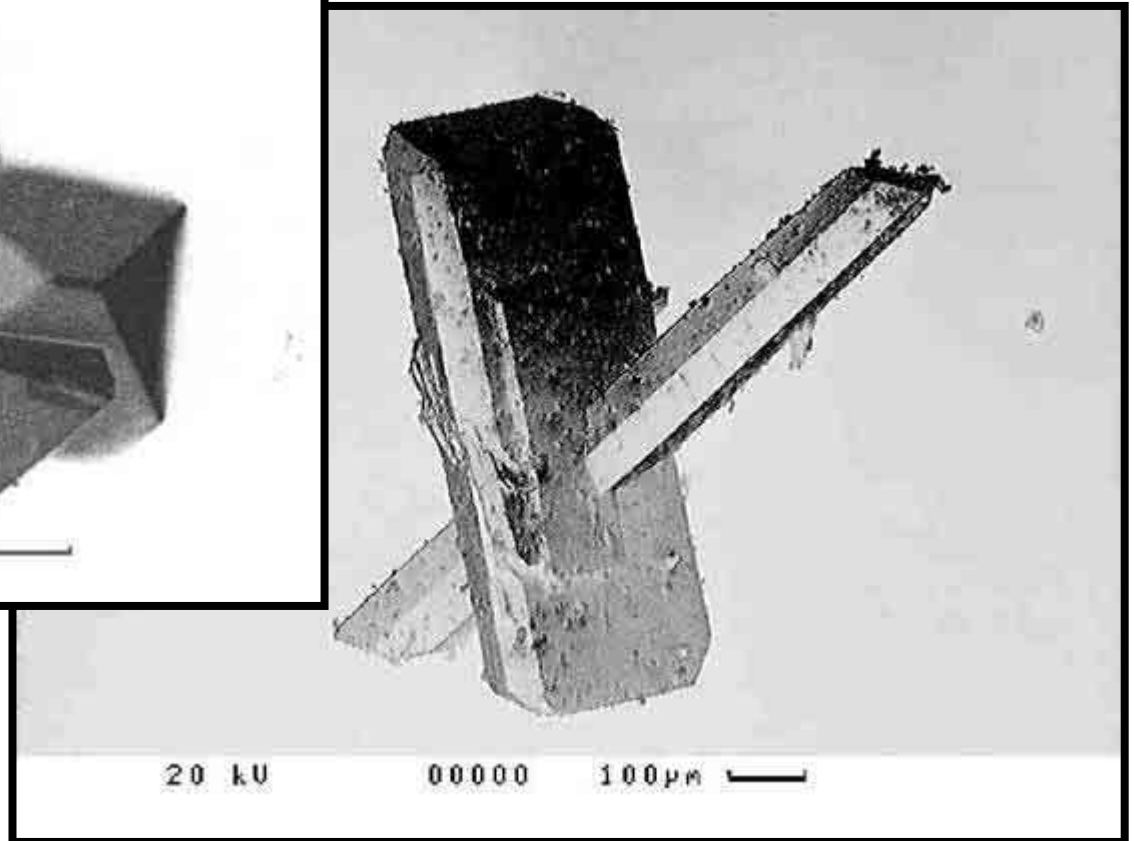
I) High resolution Images

II) Qualitative and quantitative analysis

Twinning of Crystals

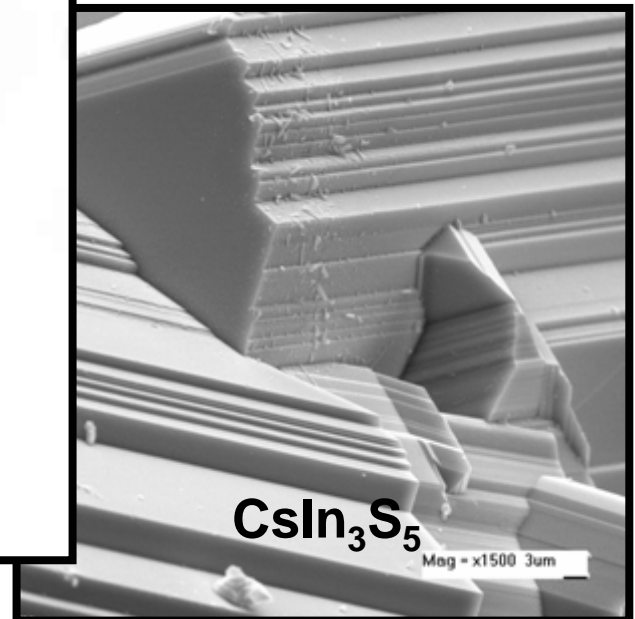
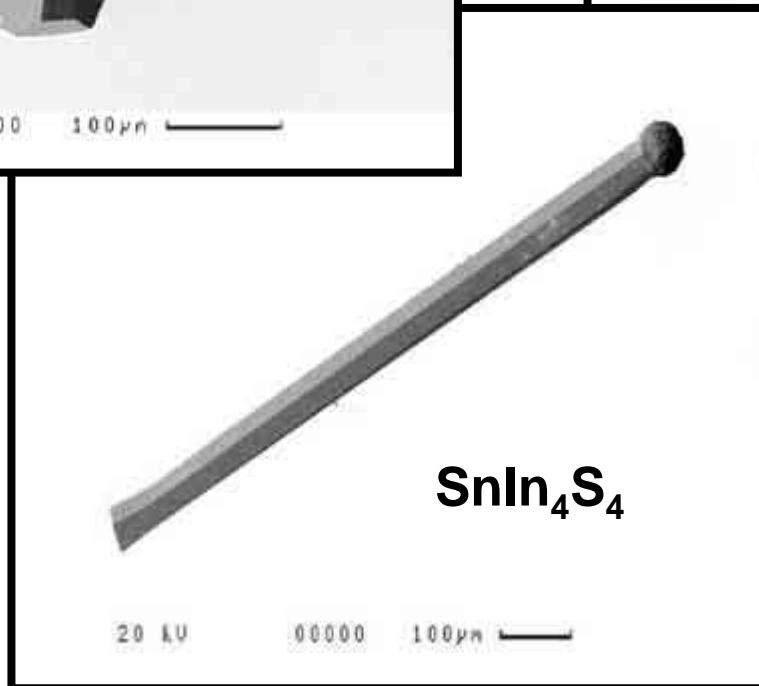
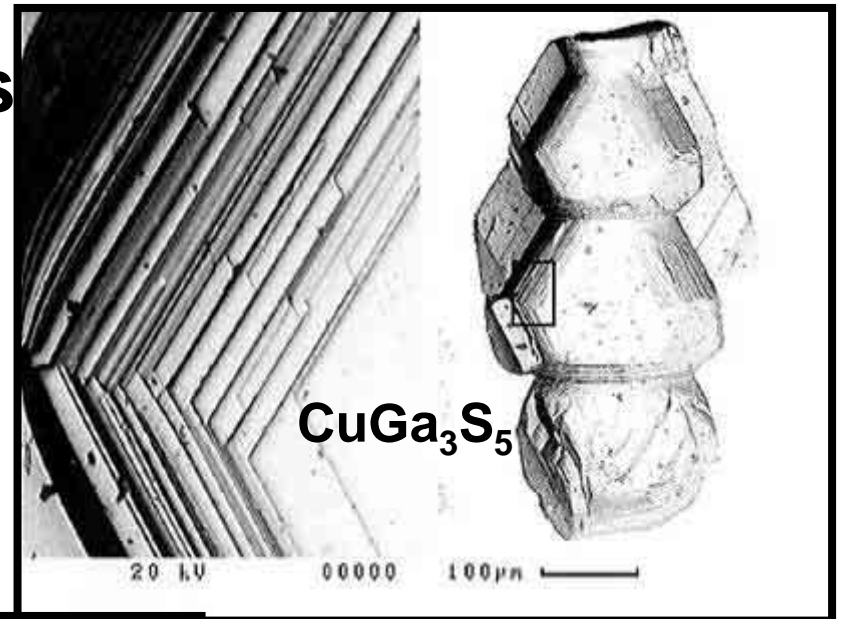
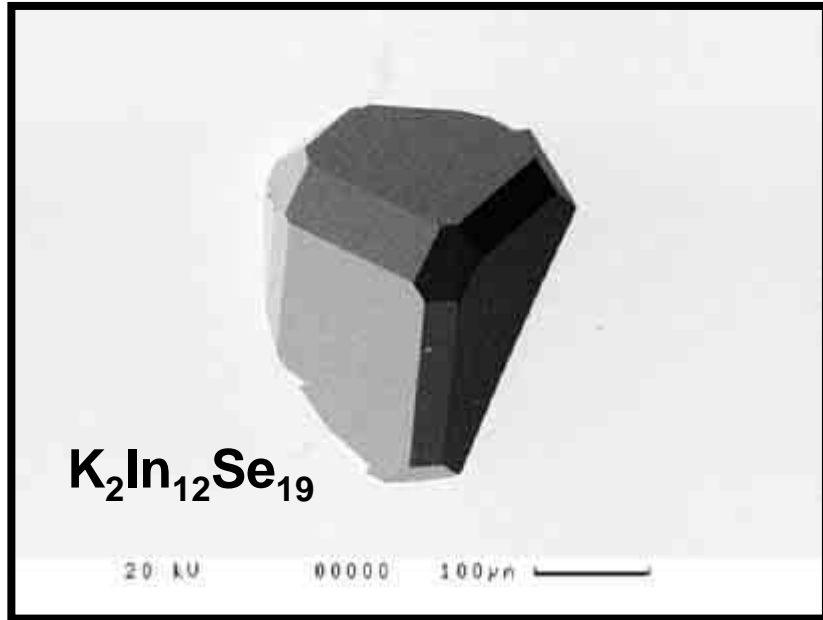


PbS

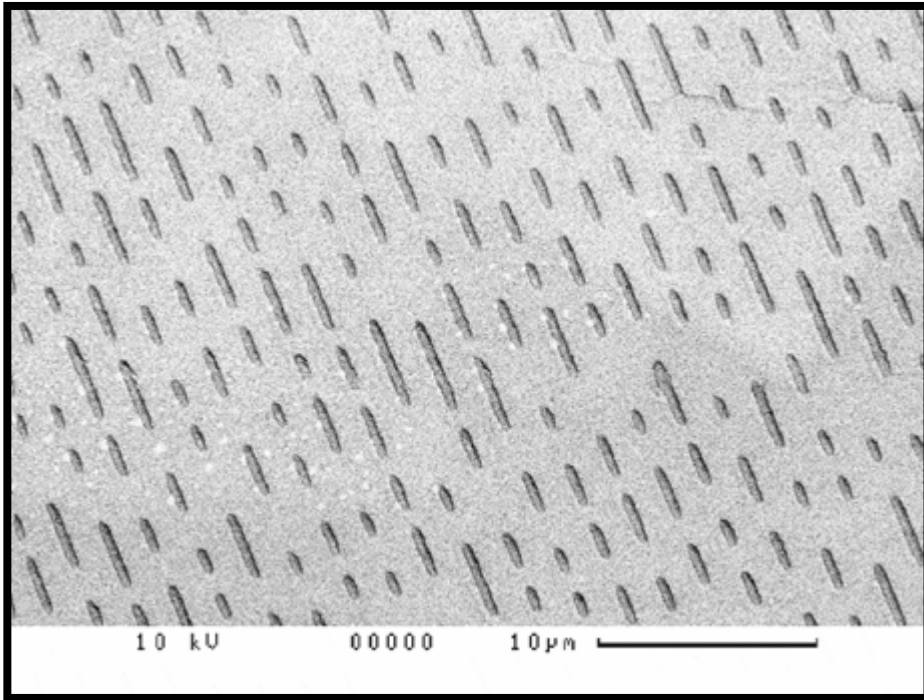


$\text{Na}_2\text{Zn}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$

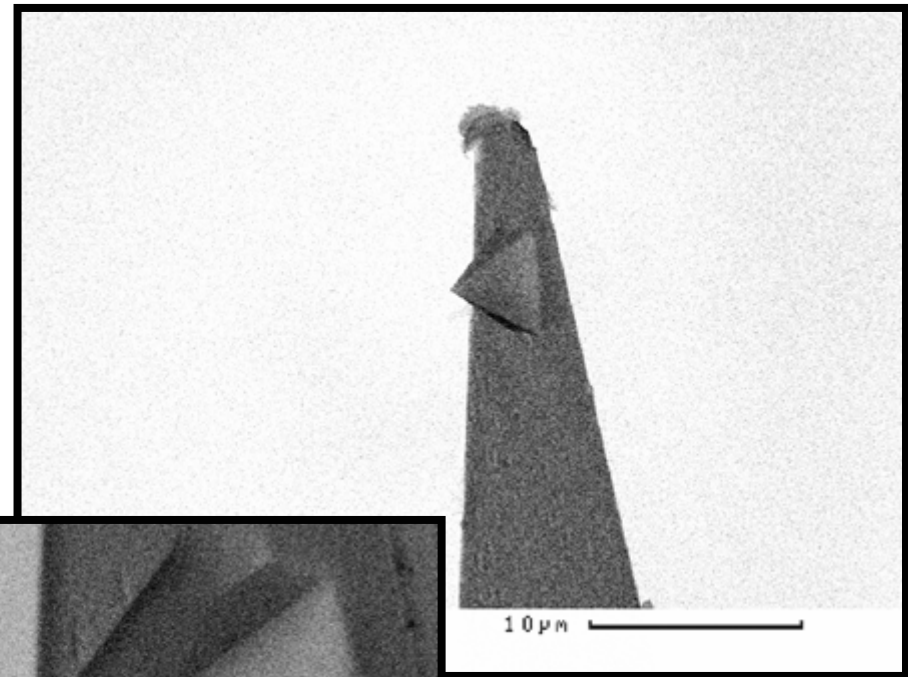
Morphology of crystals



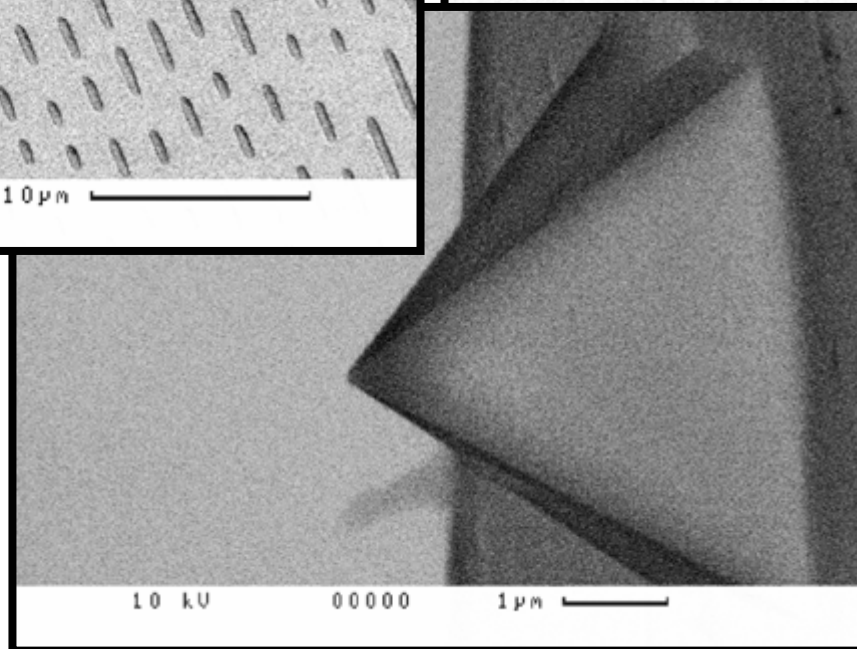
Quality control of small technical objects

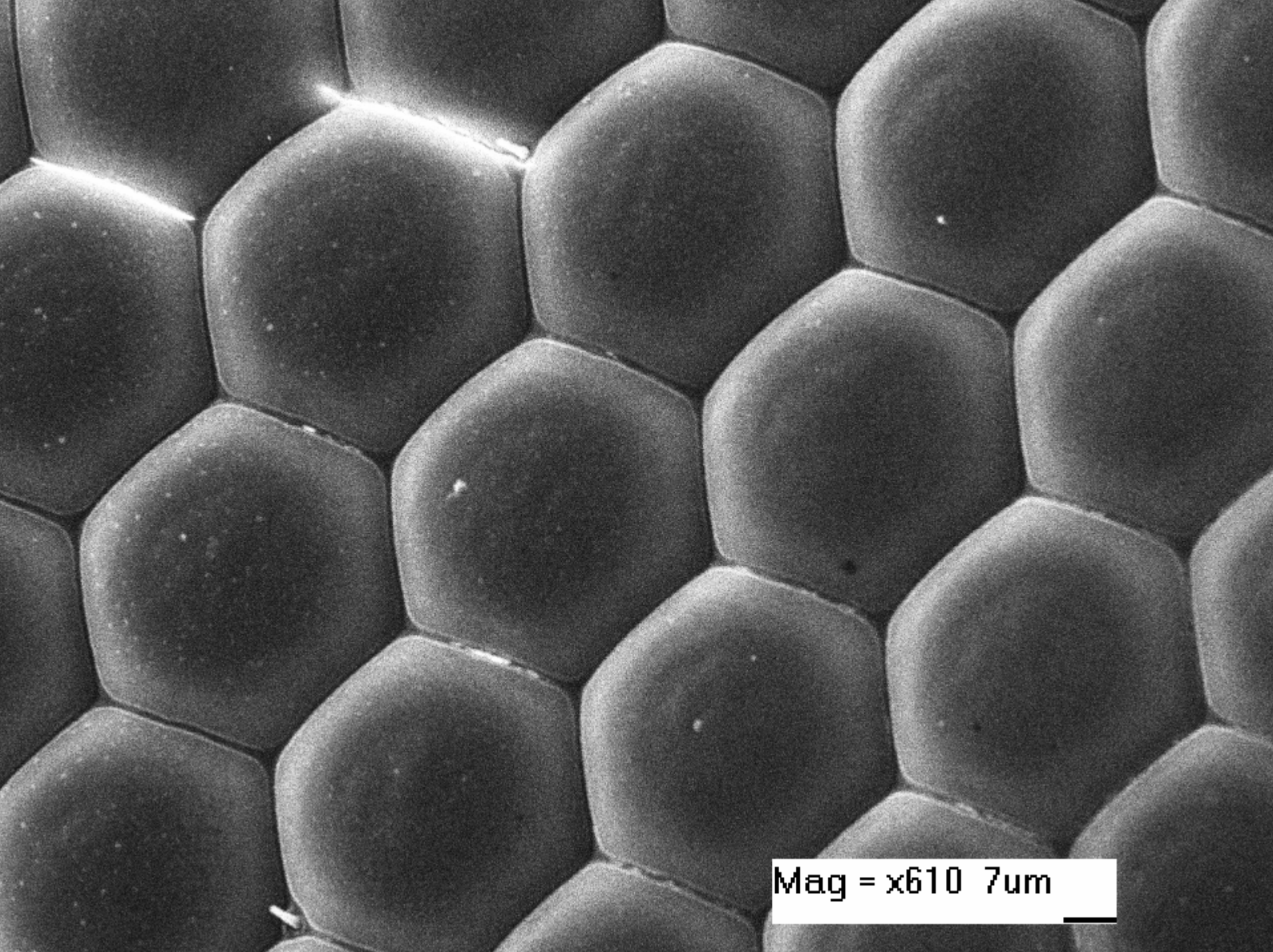


Compact disc

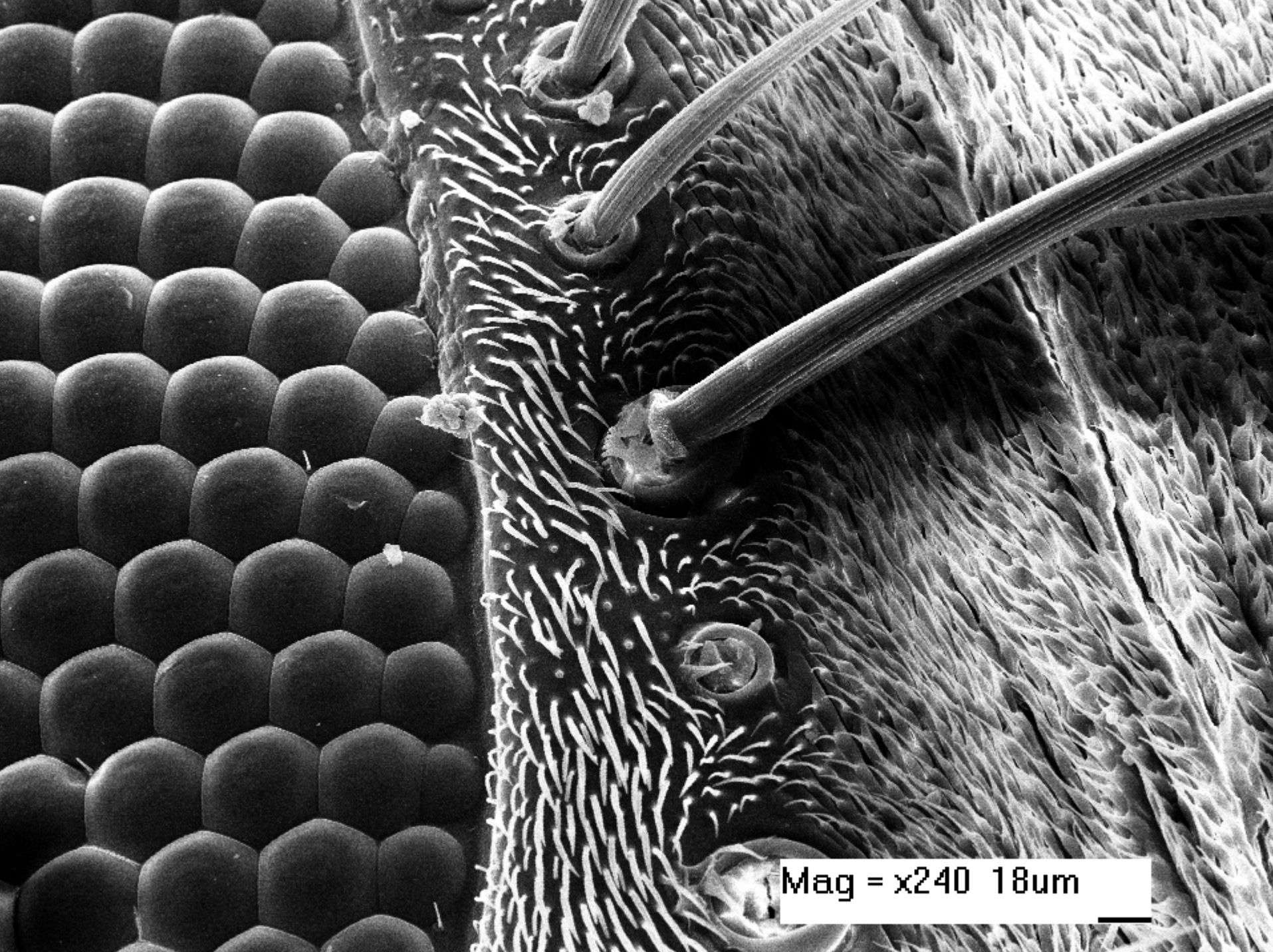


**Cantilever
of an AFM**

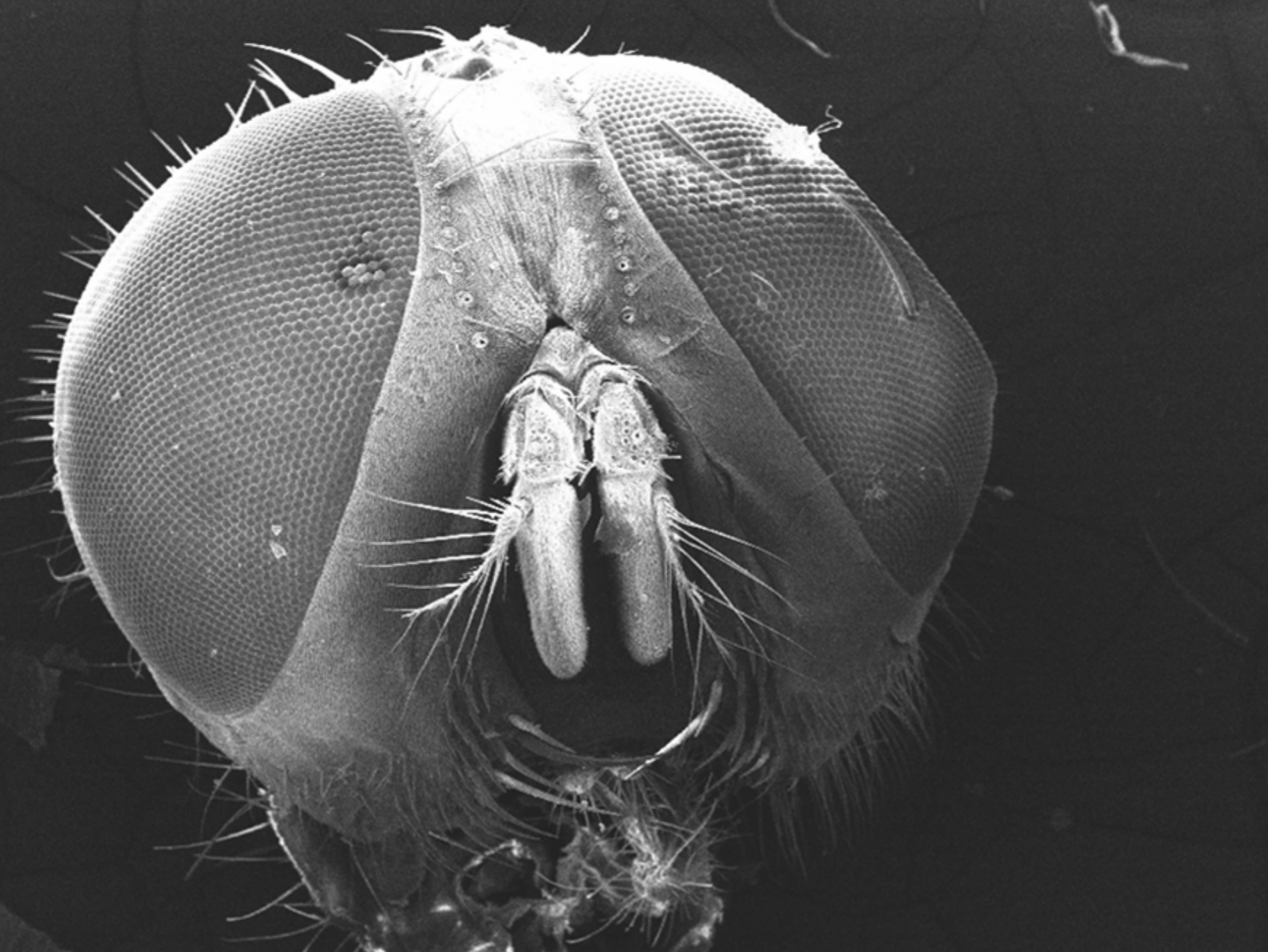




Mag = x610 7um



Mag = x240 18um



Quantitative analysis:

The X-ray intensity of a characteristic element-line in the sample is compared with the intensity of this element-line in a standard

standard: element or compound with known composition

first approximation: $I_{\text{sample}}/I_{\text{standard}} = C_i$

but: corrections are necessary!!

Corrections:

- 1) Atomic number correction (**Z-correction**)
 - a) „stopping power“ of the material
 - b) „back-scatter power“ of the material

- 2) Absorption correction (**A-correction**)

Different absorption of X-rays in different material

- 3) Fluorescence correction (**F-correction**)

X-rays with high energy generate secondary radiation with lower energy

$$I_{\text{sample}}/I_{\text{standard}} = k_i = c_i \times K_Z \times K_A \times K_F$$

Further requirements for a quantitative measurement:

- constant beam current during the measurement
- defined take-off angle
- plane surface
- surface orientated perpendicular to the beam
- conductive surface