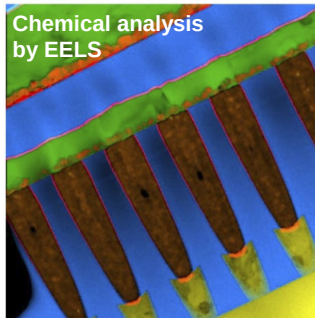
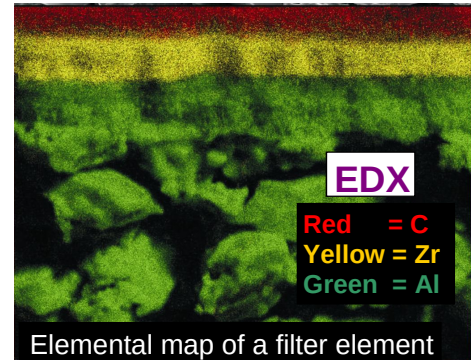
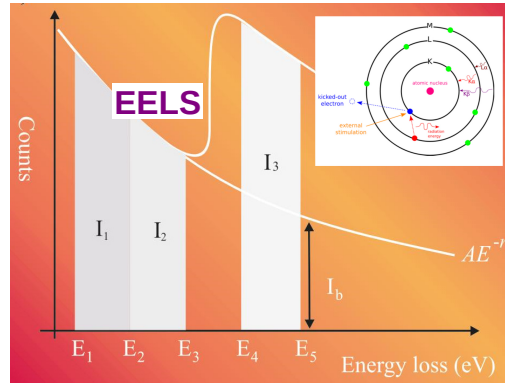


Chapter 5

Electron Based Methods



Color composite of the elemental maps of N-K, Ti-L, O-K, Al-K, and W-M of semiconductor device structure



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Electron based Methods

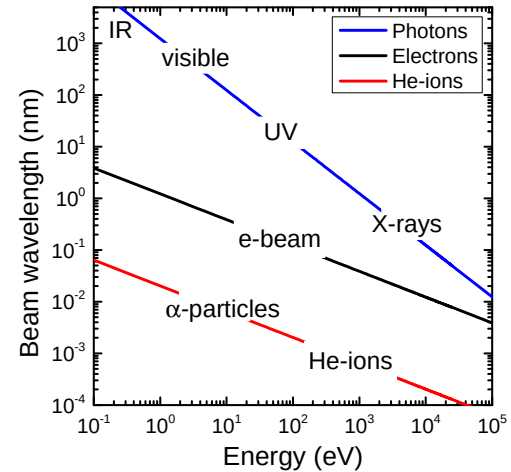
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5.1 Fundamentals

1. Particles such as **electrons have a mass** and thus a **much higher momentum** and much **smaller wavelengths** than photons:

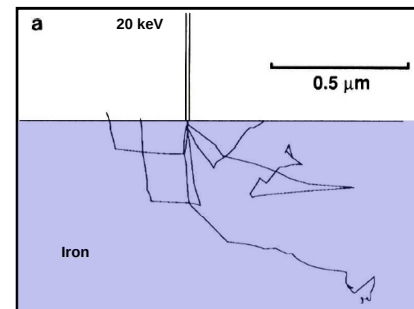
$$\lambda_e = h / p = h / \sqrt{2mE} = 1.225 \text{ nm} / \sqrt{E[\text{eV}]}$$

- ⇒ A much **higher momentum transfer** is possible in elastic and inelastic scattering processes,
- ⇒ **Diffraction** possible also with **low-energy electrons** ($\lambda \ll d_{hkl}$)
- ⇒ Much **higher spatial resolution** possible due to the smaller diffraction limit (see Chapt. 6-7)



2. **Particles are (usually) conserved**, i.e., are **not annihilated** in the interaction process - contrary to photons:

- ⇒ **any arbitrary energy** $\Delta E < E_0$ can be transferred in an inelastic scattering process, leading to an **energy loss** of the particles, which however continue their travel with reduced energy,
- ⇒ particles experience therefore many consecutive scattering events until their initial energy is absorbed, leading to complicated scattering cascades.



3. Due to their **charge**, electrons interact very strongly with solids:

- ⇒ Small penetration and escape depth, i.e., charged particles are **very surface sensitive**.

Summary of Particles versus Photon Beams

Photon beams differ strongly from particle beams (electrons or ions) due to: (1) different $E(k)$ relations, (2) different beam/sample interactions, (3) different instrumentation/optical elements

Particle Beams (Electrons/Ions/..)	Photon Beams (IR/VIS/X-rays)
1. Very small de Broglie wavelength in the sub nm range. ⇒ high spatial resolution	1. Longer wavelengths (short only for x-rays) ⇒ resolutions limited to 100 nm range
2. Strong beam/sample interactions due to charge, weak only for neutrons. ⇒ many multiple scattering events in which particle itself is conserved ⇒ high vacuum required ($<10^{-6}$ mbar) to avoid scattering (except for neutrons)	2. Weaker interactions ⇒ single step absorption ⇒ no vacuum required (except for UVU/EUV)
3. Electric and magnetic fields used for focusing elements, energy filters and spectrometers	3. Many optical elements: Lenses, mirrors, prisms, gratings, diffractive optics and diffractive spectrometers
4. Beam sources: Thermionic, field emitters, plasmas/gases (ions), radioactive substances and reactors (n , α -particles, ..)	4. Beam sources: thermal emitters, gas discharge, LEDs, coherent laser sources, plasmas,

5.2 Instrumental: Sources for Electrons

Different types of electron sources exist:

- (1) **Thermionic sources** where electrons are emitted via thermal excitation (i.e., heat),
- (2) **Field emission sources** where electron are emitted via tunneling induced by very high electric fields.
- (3) Plasma sources from which electrons are extracted via electric fields.

To describe electron emission from solid sources, the **potential $W(z, E)$ of electrons outside** of a free-electron like metal as a function of **distance z** and **applied electric field E** must be considered.

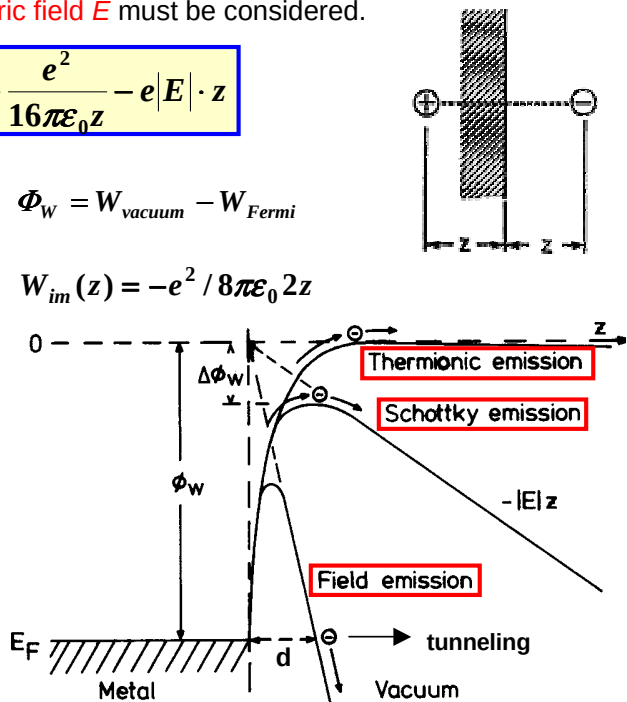
Potential:
$$W(z, E) = \Phi_w + W_{im} + W_{ES} = \Phi_w - \frac{e^2}{16\pi\epsilon_0 z} - e|E| \cdot z$$

It is made up of three contributions:

- (i) the **work function Φ_w** or W_A , i.e., the potential difference between the Fermi and vacuum level, i.e., the binding energy of the electrons,
- (ii) the **image potential W_{im}** due to the Coulomb attraction between the electron and its positive image charge inside the metal $W_{im}(z) = -e^2 / 16\pi\epsilon_0 \cdot z$
- (iii) the **electrostatic potential $W_{ES} = -e|E|z$** due to the applied negative external electric field E .

Depending on the strength of the applied electric field, three different emission mechanisms exist:

- (1) **Thermionic emission**, (2) **Schottky emission** and (3) **Field emission (tunneling)**.

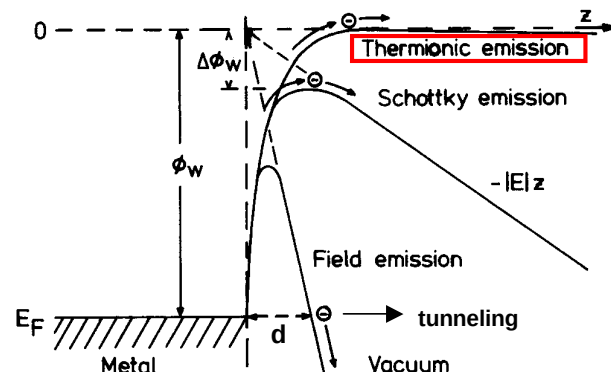


5.2.1 Thermionic Emission

Heating of a material excites electrons into higher energy states above the Fermi level. The population of these states is given by the **Fermi-Dirac distribution**.

$$f(W) = 1 / (1 + \exp(\frac{W - W_F}{k_B T}))$$

Electrons that gain energies $W > \Phi_w$ above the vacuum level can overcome the **work function Φ_w** barrier of typically a few eV and thus, can escape from the surface when a weak external electric field is applied.



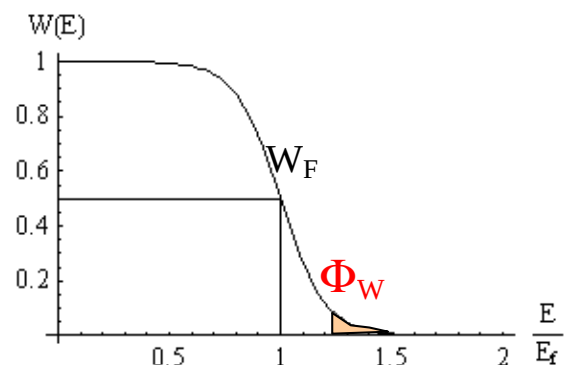
The **thermionic emission current density j_x** can be calculated by integrating of $-e \cdot v_x \cdot dn$ over all populated states with an energy W larger than the work function Φ_w

$$\text{Thus: } j_x = -e \int_{W > \Phi_A} v_x f(W) \cdot 2d^3k / (2\pi)^3$$

⇒ This yields the **Richardson law** of thermionic emission:

$$j_x = AT^2 e^{-\Phi_w / kT} \text{ (A/m}^2\text{)}$$

A := **Richardson constant** = 120 A/cm²K² for an ideal free electron gas



$$j_x = AT^2 e^{-\Phi_w/kT} \text{ (A/m}^2\text{)}$$

A := **Richardson constant** = 120 A/cm²K²
for an ideal free electron gas
 Φ_w := work function W_A

A and Φ_w are material dependent:

- The **Richardson constant** depends on the electronic band structure, density of states, effective electron mass, etc.
- The **work function** depends on the bonding and electronic structure of materials, also somewhat on the surface orientation ($\pm 5\%$)

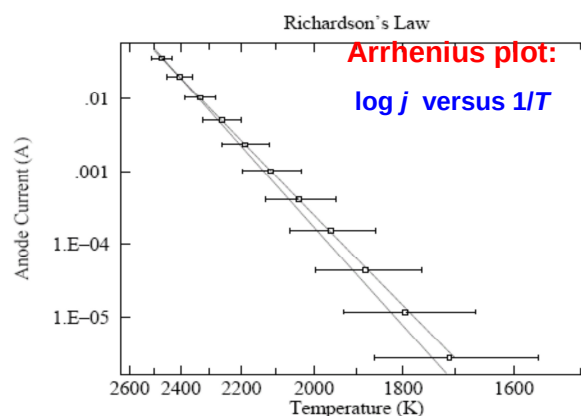
Limitation to thermionic emission:

Very high thermal energies kT of the order of $\sim 1/10$ work function of **several eV**, i.e., **very high operation temperatures** are needed to obtain a sizeable electron emission current !

Consequence: Use of materials with either:

- Very **high melting point** and **low vapor pressure** at high temperatures:
Refractory metals: W, Mo, Ta with $\Phi_w \sim 4 - 4.5$ eV .
- Low work function Φ** such as **rare earth borides** e.g., LaB_6 : $\Phi_w = 2.0 - 2.7$ eV .

Thermionic emission – Richardson Law



Work function W_A and Richardson constant A for various different materials

	W_A/eV	$A/\text{A cm}^{-2}\text{K}^{-2}$
C	4,45	35
W	4,5	60
Ta	4,09	37
Mo	4,29	107
W-Ba	2,01	100
W-Cs	1,38	3,26
W-Th	2,66	5,0
BaO	1,0...1,5	0,1

Example: Tungsten (W) electron sources

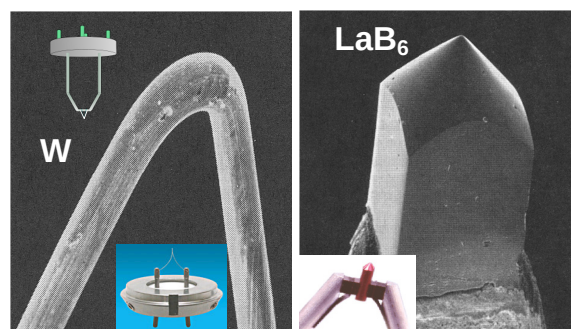
W "filaments" drawn to 0.1 mm wires, which are then bend into V-shaped **hairpins** or sharpened to a fine point by etching.

Melting point $T_m = 3410^\circ\text{C}$, operation temperature $\sim 2500^\circ\text{C}$.

2500°C: $kT = 0.24$ eV, $\exp(-\Phi_w/kT) = 7 \cdot 10^{-9}$, $A=100 \gg j \sim 4 \text{ A/cm}^2$

Other refractory metals:

Tantalum: $T_m = 2996^\circ\text{C}$, Molybdenum: $T_m = 2617^\circ\text{C}$,
→ Comparable work functions of $\Phi_w \sim 4.1\text{-}4.3$ eV.



LaB₆ electron sources (also CeB₆)

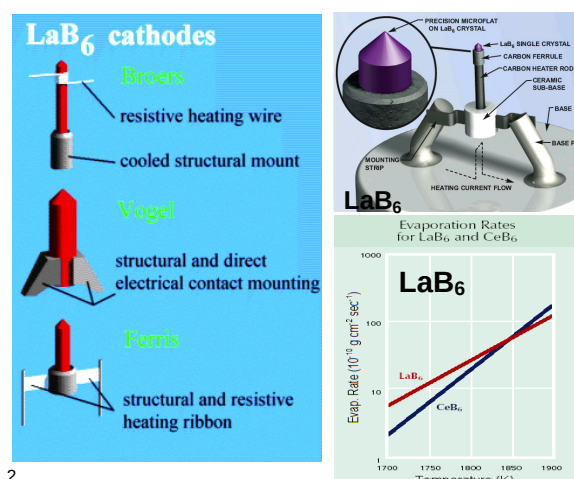
Rare earth borides exhibit low work functions and high melting points: $T_m = 2770^\circ\text{C}$ for LaB_6 .

Made from single crystals grown with $\langle 110 \rangle$ orientation, sharpened to a fine tip and heated by an external filament.

The work function is orientation and composition dependent: $\sim 2 \dots 2.5$ eV.

1800°C: $kT = 0.18$ eV $\gg j = 850 \text{ A/cm}^2$ for $\Phi_w = 2.5$ eV

Advantages: Lower operation temperature $\sim 1500^\circ\text{-}1800^\circ\text{C}$, longer operation lifetime (>1000 hours), higher electron yield, current densities up to $j \sim 50 \text{ A/cm}^2$.



Thermionic Electron Guns

To obtain a small source diameter, the electrons emitted from the filament are focused by the negatively biased **Wehnelt cylinder** and accelerated through the grounded anode aperture.

Cathode: W or LaB₆ filaments are resistively heated by an AC filament current that controls the temperature and emission current.

Wehnelt Cylinder: Negatively biased ring between filament and anode. Acts like an **electrostatic lens** to focus the beam to the cross-over point d_0 .

Emission current: With increasing **Wehnelt bias**, the total emission current decreases up to pinch-off, but the **brightness** (current density at the cross over point) increases. The Wehnelt bias therefore controls both the source size *and* the beam current. The bias is often applied through a bias resistor and thus, linked to the high voltage applied to the filament bias (=self-biasing).

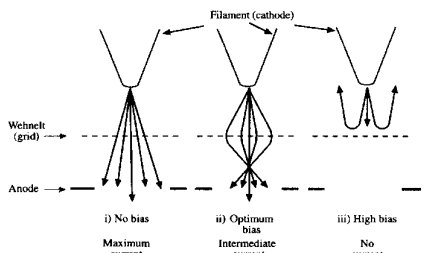
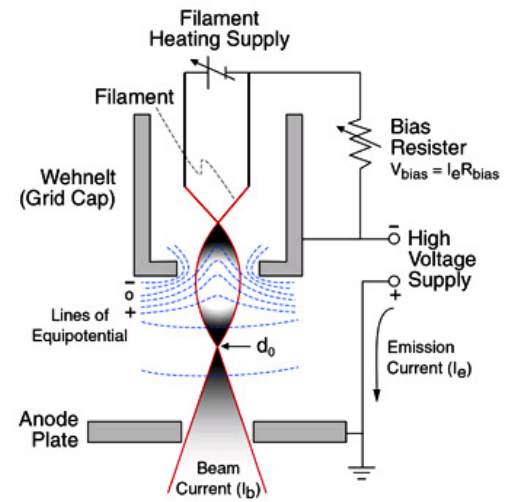
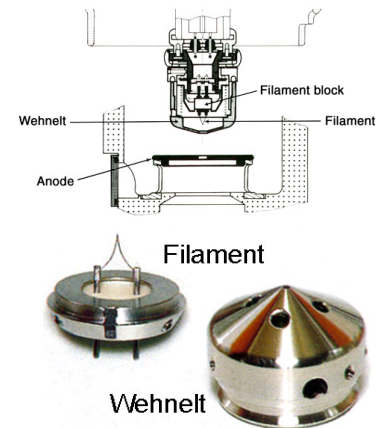
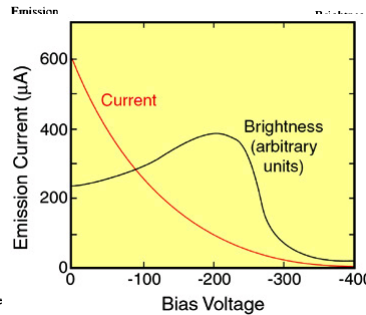


Figure 5.4. (A) The effect of increasing Wehnelt bias (i–iii) on the distribution the bias and the emission current/gun brightness. Maximum brightness is achieved [condition (ii) in A].



⇒ **Thermionic sources should be operated at or just below saturation to maximize brightness and filament lifetime.**

5.2.2 Schottky Emission

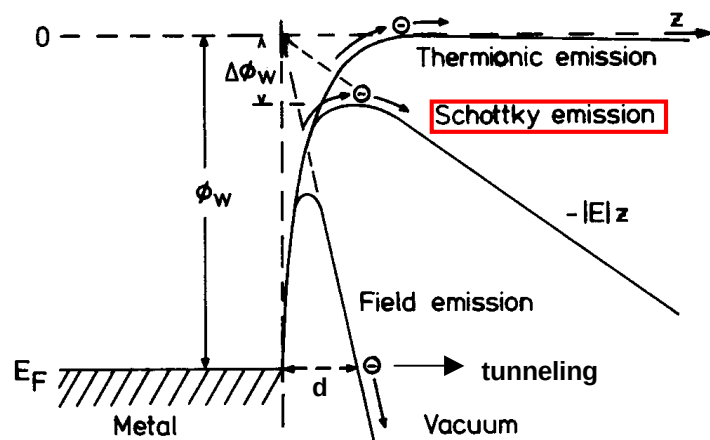
Principle:

Lowering of the work function for thermionic emission by application of a **high electric field E** to the thermionic emission source. The reduced **effective barrier height Φ_{eff}** is equal to the maximum of the electron potential $W(z, E)$.

The work function reduction is given by $\Delta\Phi_w(E) = \sqrt{e^3 E / 4\pi\epsilon_0} = 3.79 \cdot 10^{-5} \text{ eV} [E (\text{V/m})]^{1/2}$.

Result:

The emission current increases by a factor of $J/J_0 = e^{\Delta\Phi_w/kT}$ compared to thermionic emission.



Example: For electric field $E = 1 \text{ MV/cm}$: $\Delta\Phi = -190 \text{ meV}$. Thus: $J/J_0 = e^{-\Delta\Phi/kT} = 2.4$ for $T = 2200^\circ\text{C}$.

To obtain a high electric field E at the surface of the filament, a small tip radius r is required.

The corresponding electric field at the surface is given:

where r is typically of the order of $\sim 1 \mu\text{m}$ and V is the applied voltage.

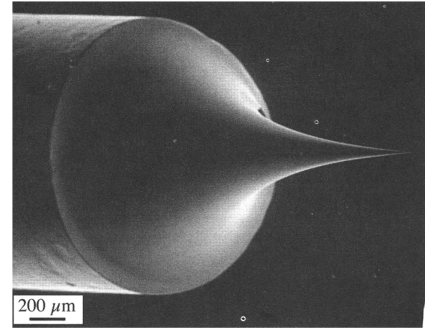
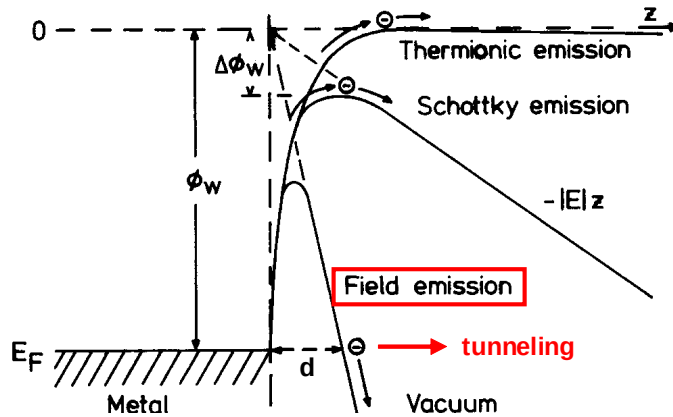
$$E = V_{\text{appl}} / r \text{ [V/m]}$$

5.2.3 Field Emission

Principle: Extraction of electrons by the **quantum mechanical tunneling effect**. Tuning is possible by bending downward strongly the potential by applying a very high **very high** electric field $E = \frac{V_0}{r} [V/m]_a$ at a metal tip with very small tip radius.

This results in a very high electric field E at the tip surface (=field of a point charge) and thus, the potential $W(z)$ is bent downward and the **emission barrier** is **reduced in height and width**.

Result: Electrons can **directly tunnel out of the metal** into the vacuum = "**Nordheim - Fowler tunneling**"



- **Very high emission currents** up to $j \sim 10^6 \text{ A/cm}^2$ can be achieved = (brightest possible electron sources).
- The field emission current is caused by the **quantum mechanical tunneling effect**. It is proportional to the **transmission probability** T of the electrons through the potential barrier $W(z)$ at the surface.

Calculation of the tunneling probability T :

Neglecting the image potential, $W(z)$ is a **triangular barrier potential**.

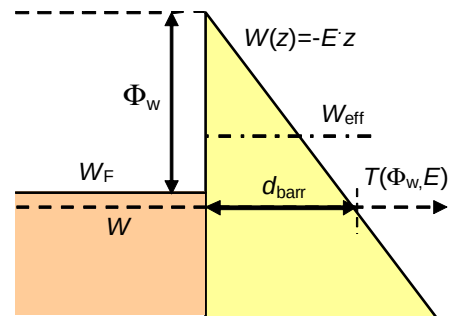
Its **width** is given by $d_{\text{barr}} = \phi_w / eE$ and its **effective height** W_{eff} .

Both rapidly decreases with increasing electric field E .

Example:

For $U_a = 1 \text{ keV}$ and $r = 100 \text{ nm}$ the barrier width is only $\sim 5 \text{ nm}$.

The corresponding **tunneling probability** $T(W_0, E, \Phi_w)$ can be calculated using the **Wentzel-Kramers-Brillouin (WKB) tunneling model**:



$$T(\Phi_w, E) \approx \exp(-2\sqrt{2m} \cdot W_{\text{eff}} / \hbar)$$

In this model, the effective barrier height is for any arbitrary potential $W(z)$ shape:

$$W_{\text{eff}} = \int_0^d (W(z) - W_0)^{1/2} dz = 2/3 W_{\text{barr}} \Phi_w^{1/2} = 2/3 \Phi_w^{3/2} / eE$$

For the simple **triangular potential** barrier one obtains the tunneling probability as:

$$T(\Phi_w, W, E) \approx \exp(-b \cdot (\Phi_w - W)^{3/2} / E)$$

$$b = 4\sqrt{2m} / 3\hbar e$$

Nach (6,97) berechnete Tunnelwahrscheinlichkeiten $T(W_0)$ in Abhängigkeit von der Stärke des angelegten Feldes E und der Energie $W_0 - W_s$

$\frac{W_0 - W_s}{\text{eV}} \rightarrow$	2 eV	3 eV	4 eV
	T	T	T
$E/10^9 \text{ Vm}^{-1} \downarrow$			
1	$4,1 \cdot 10^{-9}$	$3,8 \cdot 10^{-16}$	$1,9 \cdot 10^{-34}$
2	$6,4 \cdot 10^{-5}$	$2,0 \cdot 10^{-8}$	$1,4 \cdot 10^{-12}$
3	$1,6 \cdot 10^{-3}$	$7,3 \cdot 10^{-4}$	$1,2 \cdot 10^{-3}$
4	$8,0 \cdot 10^{-3}$	$1,4 \cdot 10^{-2}$	$1,2 \cdot 10^{-1}$

Calculation of the tunneling current j :

The **total emission tunneling current** is calculated by integrating over all occupied states up to W_F that contribute each by $dj_x = -e \cdot v_x \cdot T(W_x) \cdot dn$ to the total tunnelling current.

This gives for $T = 0$:

$$b = 4\sqrt{2m}/3\hbar e$$

$$j_{x,tunnel} \sim \int_{W_x < W_F} dk_y dk_z T(W) dW \approx (E^2 / \Phi) \cdot \exp(-b \cdot \Phi^{3/2} / E)$$

Material selection:

The easiest and most stable material for fabrication of fine tips are

electrochemically etched W tips: Radius < 100 nm; Applying 1kV yields $E > 10^7$ V/cm,

Important requirement: The emitter surface has to be **clean** and **oxide free**.

This requires UHV conditions for room temperature (cold) field emission.

Contamination of one monolayer within 1 minute @ 10^{-7} mbar, or 7 hours @ 10^{-10} mbar !

Alternative: Heating the tip up to 1000°C = **thermal field emission**. Allows to use less good vacuum conditions. In this case, the surface is often treated with ZrO_2 to improve the emission characteristics and source stability.

Field Emission Guns

The field emitter tip is the cathode with respect to 2 anodes

- **Anode 1:** Provides extraction voltage to pull electrons out of the tip
- **Anode 2:** Accelerates the electrons to 100kV

Combined fields act like an electrostatic lens and thus, control the effective source size and position of the crossover.

Contamination:

Even in UHV – tip surface contaminations build up over time.

Emission current falls and extraction voltage has to be regulated to stabilize the emission current. Cleaning can be achieved by “flashing” the tip by short application of a reverse voltage bias.

Comparison:

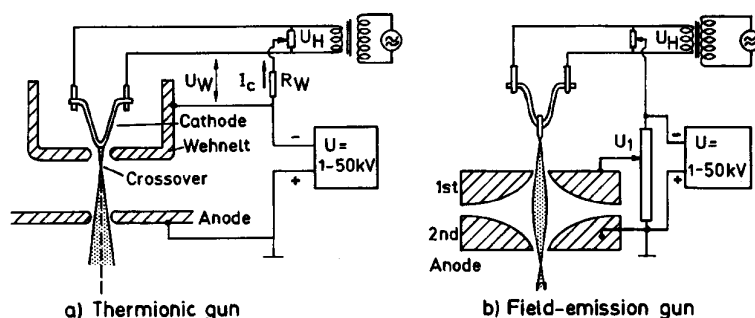
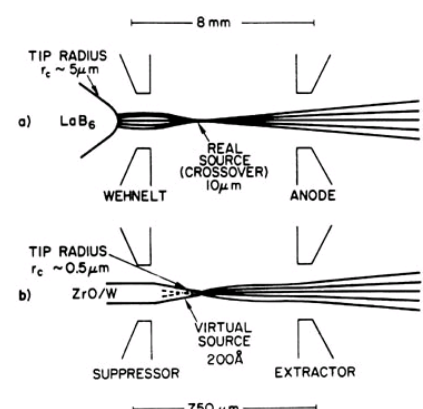
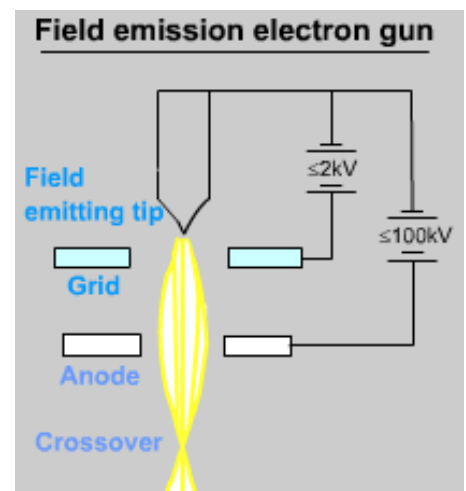


Fig. 2.2. (a) Thermionic electron gun consisting of cathode, Wehnelt cup and anode. The Wehnelt bias U_W is provided by the voltage drop of the emission current I_c across R_W . (b) Field-emission gun of the Butler type



5.2.4 Characteristics of Electron Guns

The performance of an electron source is described in terms of the following parameters:

- **brightness**, ▪ **monochromaticity (energy spread)**, ▪ **coherency**, ▪ **temporal stability**.

(i) **Brightness** β = Current density emitted per unit solid angle Ω of the source. Should be **maximized** for high performance electron microscopy. Important for spot size, signal-to-noise, recording time, visibility

...

$$\beta = \frac{I_e}{A_e \Omega} = \frac{4I_e}{\pi d_0^2 \pi \alpha_0^2} = \frac{j_e}{\pi \alpha_0^2} \quad [A/cm^2 sr]$$

$$I_e = \beta \cdot 4\pi^2 d_0^2 \alpha_0^2$$

with: 1. diameter d_0 at crossover,
2. total emission current I_e or
current density j_e at crossover
3. beam cone semi-angle α_0

- **Thermionic sources**: Beam diameter $d_0 \sim 30\text{-}100 \mu\text{m}$, $I_e \sim \text{nA}$, $\alpha_0 \sim \text{few degrees}$: $\beta \sim 10^9 \text{ A/m}^2\text{srad}$.
- **Cold FEG gun**: Beam diameter $d_0 < 5 \text{ nm}$, $I_e \sim 1\text{nA}$ @ 100kV from 1nm spot diameter: $\beta \sim 10^{13} \text{ A/m}^2\text{srad}$. Power density: 150 MW/mm². Thus, a field emission source is the brightest continuous radiation source known!
- **General features**: (a) Brightness increases with increasing electron energy E ($\beta \sim E$) and emission current I_e .
(b) The brightness β is constant along the optical axis of a microscope.

(ii) Energy Spread, Temporal and Spatial Coherency

Energy spread: Determined by emission mechanism and operating conditions.

Thermionic sources: Thermal energy spread of emitted electron sources proportional to $\sim kT$.

W hairpins: $\Delta E \sim 3 \text{ eV}$ @ $T = 2500 \text{ K}$; LaB₆ source: $\Delta E \sim 1.5 \text{ eV}$ @ $T = 1500 \text{ K}$

Field emitters: Thermal broadening of energy distribution at the Fermi edge $\Delta E \sim 25 \text{ meV}$ @ RT.

Temporal coherency: $\sim v_{el} h / \Delta E$ (determined by energy spread / monochromaticity)

Spatial coherency: $\sim \lambda / \alpha$ (determined by effective source size)

(iii) Stability and Lifetime

Electron current from the source has to be stable because the adjustment of optics depends on the beam current and because unstable currents makes microanalysis difficult. Also, source lifetime should be long.

- **Thermionic sources** are generally very stable, variations of less than 1% per hour in the current.
- **Cold field emission sources** are not as stable, electrical feedback required to get stability better than 5%. Stability improves with better UHV conditions. Due to low operation temperature, long lifetime

Summary: Characteristics of the Three Principal Sources Operating at 100 kV

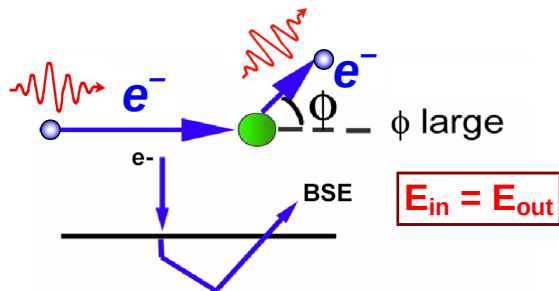
	Units	Tungsten	LaB ₆	Field Emission
Work function, Φ	eV	4.5	2.4	4.5
Richardson's constant	A/m ² K ²	6×10^5	4×10^5	
Operating temperature	K	2700	1700	300
Current density	A/m ²	5×10^4	10^6	10^{10}
Crossover size	μm	50	10	<0.01
Brightness	A/m ² sr	10^9	5×10^{10}	10^{13}
Energy spread	eV	3	1.5	0.3
Emission current stability	%/hr	<1	<1	5
Vacuum	Pa	10^{-2}	10^{-4}	10^{-8}
Lifetime	hr	100	500	>1000

Source	Advantages	Disadvantages
Tungsten:	+ cheap, robust, reliable.	- low brightness, energy spread, short life
LaB₆:	+ higher current & brightness, extended life time.	- expensive, reactive, high vacuum, sensitive
FEG:	+ very high currents & brightness, long life time.	- UHV, additional control for stable emission

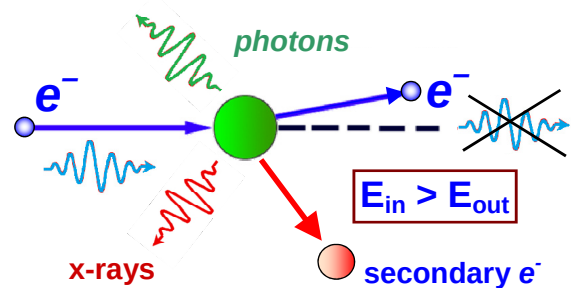
5.3 Interaction of Electrons with Solids

Charged particles strongly interact with the solid media due to the **strong Coulomb interaction**. Nevertheless, **the same excitation processes** occur as for photons, namely, lattice vibrations, generation of electron-hole pairs, secondary electron emission, ionization, core level excitations, ...

Elastic Scattering



Inelastic Scattering / Excitation



➤ Energy conserved but momentum transfer

- ❖ **Changes the direction** of photons / particles due to refraction, reflection, Rutherford or diffusive scattering, **diffraction**...

⇒ Elastic scattering is determined by atom density Z- number, atom arrangement, lattice structure as well as total number of atoms, i.e., the sample size & shape,

⇒ **Sensitive to composition and morphology,**

➤ Energy transfer to the sample but (usually) only small momentum transfer, (**small change** of trajectories)

- ❖ Excitation of vibrations, electronic transitions, core level electrons, generation of many secondary signals such as **secondary photons, electrons, ion, etc..**

⇒ Sensitive to **atomic species**, chemical composition, bonding, **electronic structure**, vibrations, magnetic structure, ...

Specific features of particle – sample interactions

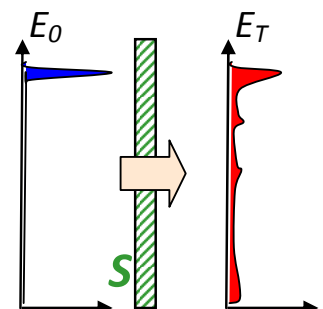
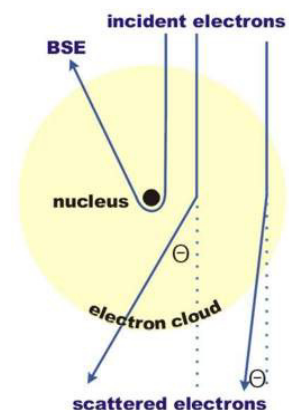
Particle-sample interaction is generally **more complex** than for photons because:

- **Particles** can transfer **any arbitrary value of their energy** as long as $\Delta E_{exc} < E_{part}$.
Thus, many different alternative excitation processes are possible, (though with different probability) whereas for photons only excitations with an energy equal to the photon energy are possible.

- Particles are intrinsically also **scattered elastically laterally** due to Coulomb interaction with the positive nuclei of the atoms. Thus, the sample excitation is “diffused” in the lateral direction.

- **Many consecutive excitation and scattering events** occur as the particles travel through the solid.
Thus, particles **quasi-continuously loose energy** along their travel path until they come to a rest and are absorbed into the solid.
Therefore, even for a mono-energetic particle beam, the transmission spectrum always consists of a continuum of energies.

- Due to the **very short wavelength**, probes can be focused to a very small spot size. Thus, particle-based methods are particularly well suited for **microprobe analysis** with high spatial resolution.



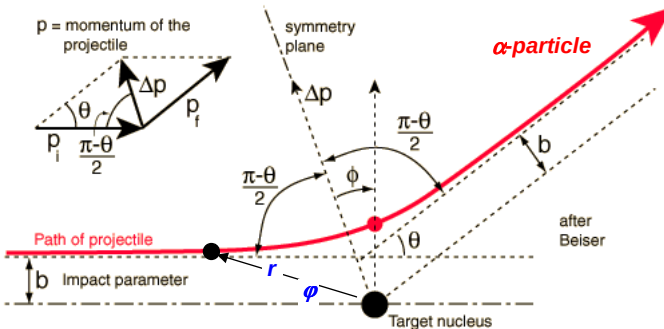
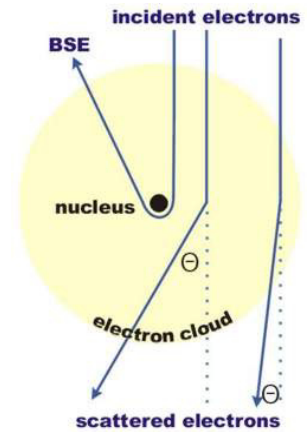
5.4 Elastic Scattering of Charged Particles

Elastic scattering is caused by the *attractive* or *repulsive Coulomb interaction* between the incident particle and the *positively charged nuclei* within the sample, which is partially screened by the electron cloud of the inner electrons. Scattering occurs over all angles from 0° to 180°.

When the nuclei are immobile (i.e., particles much lighter than the sample atoms and their kinetic energy is not too large), the particle energy is essentially conserved and they are only deflected.

Scattering angle θ = determined by the **impact parameter** b , the nucleus charge (**Z-number**), the particle charge q and energy E_0 . It can be derived by the **Rutherford scattering model** based on energy and angular momentum conservation.

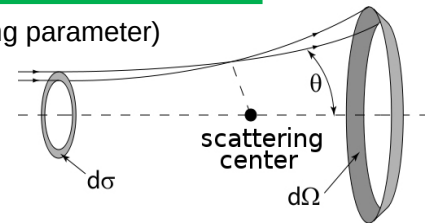
$$\cot(\theta/2) = 4\pi\epsilon_0 E_0 b / (qZe)$$



The probability that a particle is scattered in a certain angular direction is described by the **differential scattering cross section**:

$$\frac{d\sigma}{d\Omega} = \left(\frac{qZe^2}{8\pi\epsilon_0 E_0} \right)^2 \cdot \frac{1}{[\sin^2(\theta/2) + \theta_0^2/2]^2}$$

(θ_0 = screening parameter)

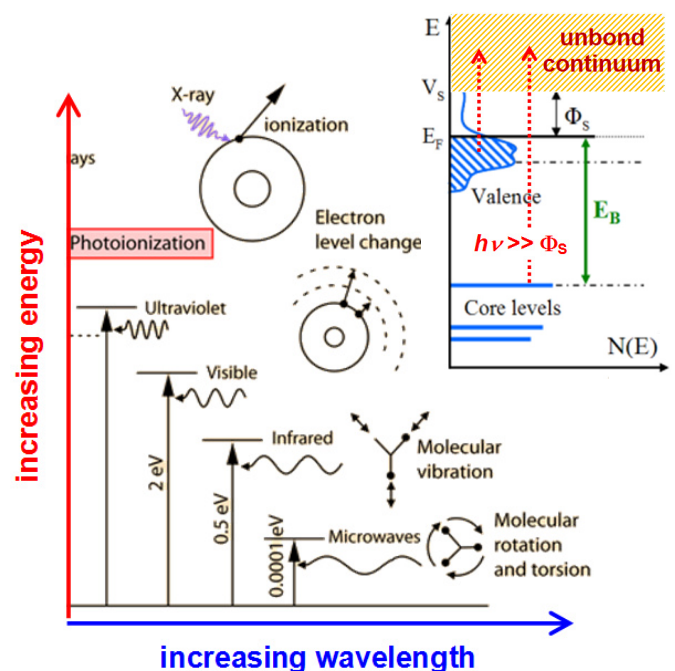


⇒ Elastic scattering strongly increases with **Z number** of the sample atoms and the particle energy E , which yields information on the composition and internal structure of the material.

5.5 Inelastic Scattering and Excitation Processes

A wide range of **energy transfers** ΔE_s to the sample (excitation) from **meV to MeV** is possible in inelastic scattering processes as discussed in the previous chapters. Additional **sample modifications** (damaging/amorphization) occur when the particle energy is large.

1-50 meV	❖ Excitation of phonons (lattice-vibrations, heat), low energy
10 - 200 meV	❖ Intra- or intersubband excitations
0.2-8eV	❖ Interband excitation, generation of electron-hole pairs,
$\Delta E_s =$	
1-10eV	❖ Excitation of plasmons (collective electron vibrations)
1-50eV	❖ Generation of secondary electrons by ionization of atoms, medium energy
>50eV	❖ Atom removal by sputtering, high energy
1-20keV	❖ Inner core-shell ionization of sample atoms, high energy
>10keV	❖ Bremsstrahlung (emission of x-rays),
>100Me	❖ Momentum transfer to nuclei by elastic knock-on scattering , amorphization, sample damaging



5.5.1 Energy Loss Rate and Penetration Depth of Electrons

A semi-quantitative approach can be used for approximation of the average amount of **energy lost by an electron per unit travel distance** without the needs to know much about the sample details except for its density and chemical composition.

This is given by the **Bethe equation**, which summarizes all inelastic scattering processes with different individual cross sections (i.e., probabilities) by an approximate **continuous energy loss rate dE/dx** :

$$\frac{dE}{dx} \cong -2\pi \frac{e^4 N_0 \rho \cdot Z}{M_A E} \ln\left(\frac{\beta \cdot E}{I}\right)$$

$$\approx -7.85 \frac{\rho \cdot Z}{M_A \cdot E} \ln\left(\frac{1.66 \cdot E}{I}\right) \left[\frac{\text{keV}}{\mu\text{m}} \right]$$

It depends on the

Beam parameters: e = electron charge, E = energy in eV

Sample parameters:

ρ = mass density (g/cm³)

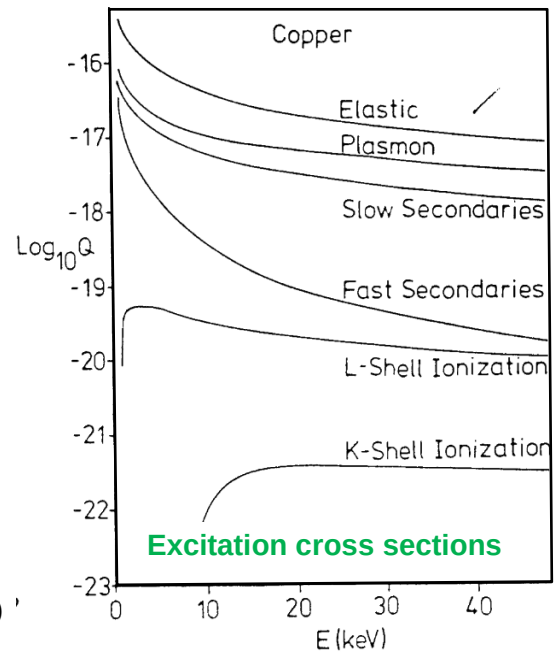
Z = average atomic number (= number of electrons per atom) ,

M_A = molar mass (g/mol)

I = mean excitation potential in eV per scattering process

N_0 = Avogadro's constant

Model parameters: $\beta = 1.166$ (quantum mechanical),
 $\beta = 1$ (classical), $\beta = 2$ (semi-classical)



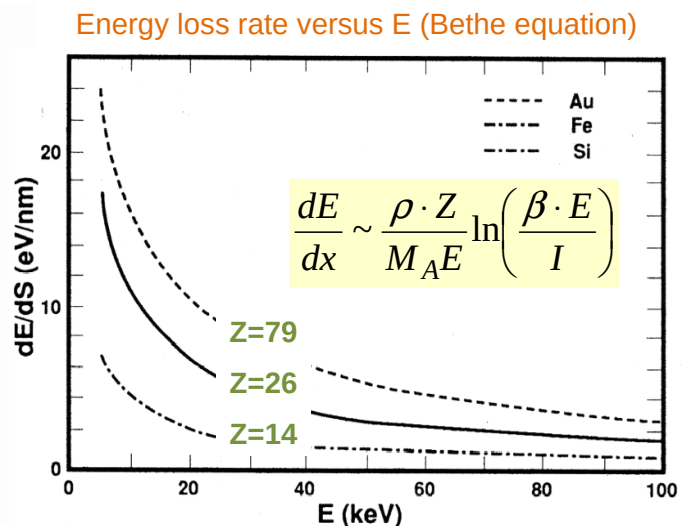
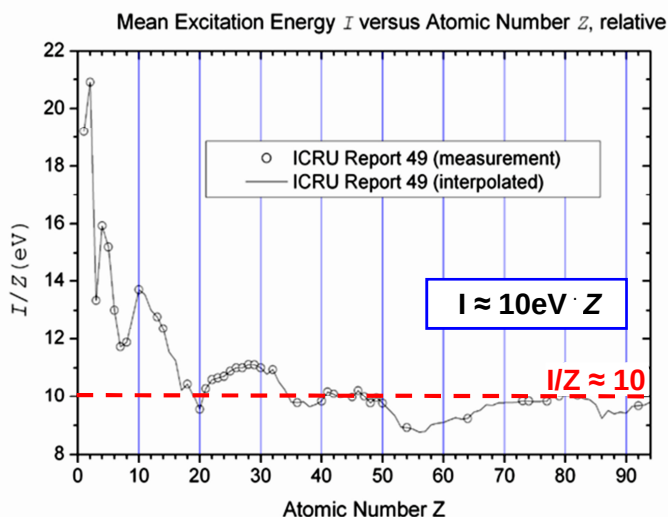
5.5.2 The Mean Excitation Potential and Energy Loss Rate

The **mean excitation potential I** represents the **average energy loss per interaction** considering all possible inelastic interaction processes. It has been approximated (Berger and Seltzer, 1964)

as: $I = (9.76 \cdot Z + 58.5 \cdot Z^{-0.19}) \text{ [eV]}$

and by Bloch as: $I = 10 \text{ eV} \cdot Z$

The figure shows experimental data on the **mean excitation potential I** of different materials. As one can see, for $Z > 16$ the mean excitation potential is roughly the same for all elements !



⇒ The average energy loss rate dE/ds per travel distance decreases as $\sim 1/E$ with electron energy and is roughly proportional to the Z number of the sample atoms

5.5.3 Mean Free Path of Inelastic Scattering

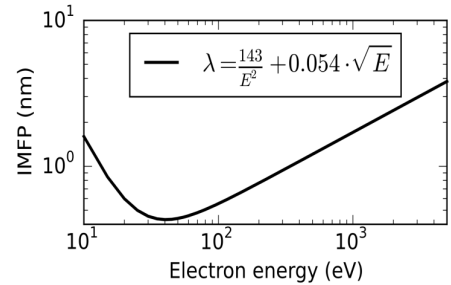
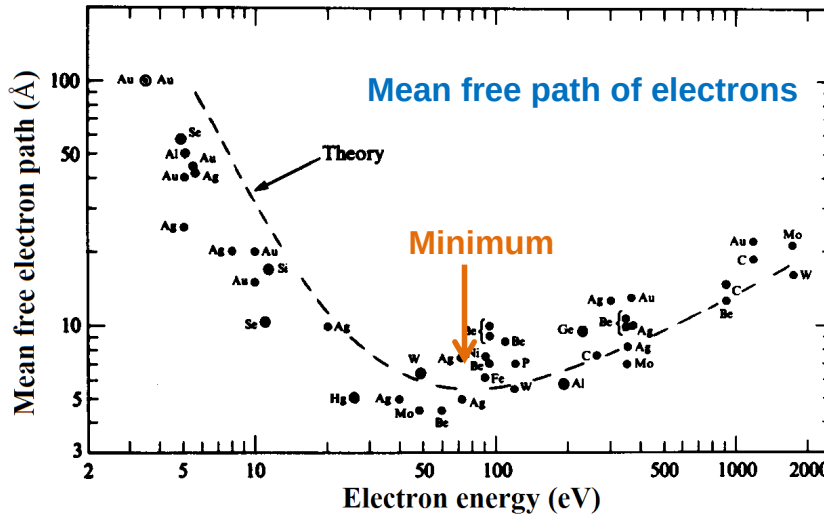
In the sequential cascade of inelastic & elastic scattering events, the average travel length of a particle between two scattering events is called **mean free path** λ_{MF} .

The **inelastic mean free path** defines how far an electron on average travels through a solid before losing energy using

$$I(d) = I_0 e^{-d/\lambda(E)}$$

Due to the very strong Coulomb interaction, the mean free path of electrons is **very small** (~few nm).

It depends on the velocity of the particle and shows a quite **universal energy dependence**, with a minimum at an energy of around 70eV, where the mean free path is less than 1 nm.



- ⇒ At **low energies**, there are only few scattering channels. Thus, the mean free path increases.
- ⇒ At **high electron energies**, the scattering cross section (probability) decreases and the path length between two scattering events increases due to the increasing particle velocity.

5.5.4 Calculation of the Electron Range

(a) **Bethe Range**: Once the **rate of energy loss rate** dE/dx as a function of E and sample material is known (Bethe equation), then the average total path length R traveled by an “average” electron until its energy is zero is given by the integral:

This is the so-called “**Bethe Range**” obtained using the Bethe equation for dE/dx .

$$R_{Bethe} = \int_{E_0}^{E=0} \left(\frac{dx}{dE} \right) dE = \int_{E_0}^{E=0} \left(\frac{dE}{dx} \right)^{-1} dE$$

(b) **Kanaya-Okayama Range**

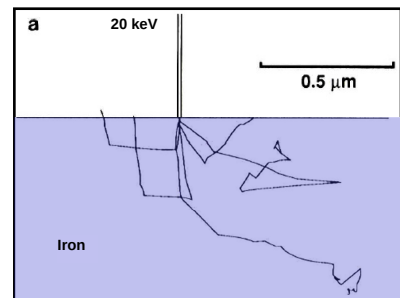
- ❖ Due to elastic scattering events, the path of particles is not along a straight line due to deflection of the particles.
- ❖ To describe more correctly the **effective electron range** (i.e., penetration depth), the total path length R_{Bethe} must be corrected to take **the path direction changes into account**.
- ❖ Kanaya and Okayama (1972) derived an expression for the **effective electron range**, which more closely describes the effective size of the interaction volume:
= “**Kanaya Okayama Range**”

where E_0 is given in keV, M_A in g/mol, ρ in g/cm³, and Z is the atomic number of the target.

This R_{KO} range is roughly the penetration depth of electron into a flat sample (not total path

traveled, which is given by R_{Bethe}). Thus, $R_{KO} < R_{Bethe}$, i.e.,

$$R_{KO} \sim 0.5 \dots 0.7 \times R_{Bethe}$$



$$R_{KO} [\mu m] = \frac{0.0276 M_A \cdot E_0^{1.67}}{\rho \cdot Z^{0.899}}$$

Electron range depends on:

- Electron Energy E_0
- Atomic Number Z
- Atomic Weight M_A
- Density ρ
- Rate of Energy Loss: dE/dx

$$R_{KO} [\mu m] = \frac{0.0276 M_A \cdot E_0^{1.67}}{\rho \cdot Z^{0.899}}$$

Trend:

$$R \sim 1/Z \text{ and } \sim E^{1.67}$$

Table 3.2. Comparison of Ranges^a

Target	Bethe range (μm)				Kanaya-Okayama range (μm)			
	Beam energy (keV)				Beam energy (keV)			
	5	10	20	30	5	10	20	30
C $Z=6$	0.61	2.1	7.5	13.0	0.52	1.7	5.3	10.4
Al $Z=13$	0.52	1.8	6.0	12.4	0.41	1.3	4.2	8.2
Cu $Z=29$	0.21	0.69	2.3	4.6	0.14	0.46	1.5	2.9
Au $Z=79$	0.19	0.54	1.6	3.2	0.085	0.27	0.86	1.7

^a Tilt angle = 0° throughout.

range in μm

Stopping Power

The travel distance of electrons inside an SEM sample can be also described in terms of a stopping power S , defined as:

$$S = -(1/\rho)dE/ds$$

which removes the density dependence of the energy loss rate.

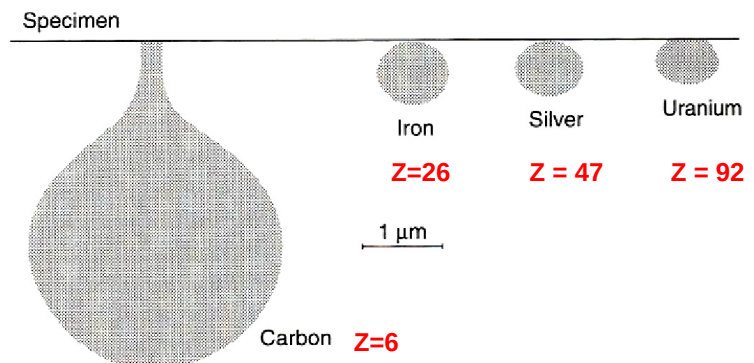


Figure 6-6 Shape and size of the specimen-beam interaction volume in specimens of different atomic number. Accelerating voltage = 20 keV.

5.5.5 Interaction Volume derived from Monte Carlo Simulations

The interaction volume can be more accurately derived by Monte Carlo simulations. In this approach, **many individual electrons trajectories** are simulated by **choosing randomly elastic scattering events**, which are weighed according to their scattering cross section.

Between two direction-changing elastic scattering events, the electrons travel along **straight lines** along which they **continuously loose energy by inelastic scattering** with the given loss rate dE/dx which is a function of E . The length of the straight lines is **equal to the elastic mean free path λ** .

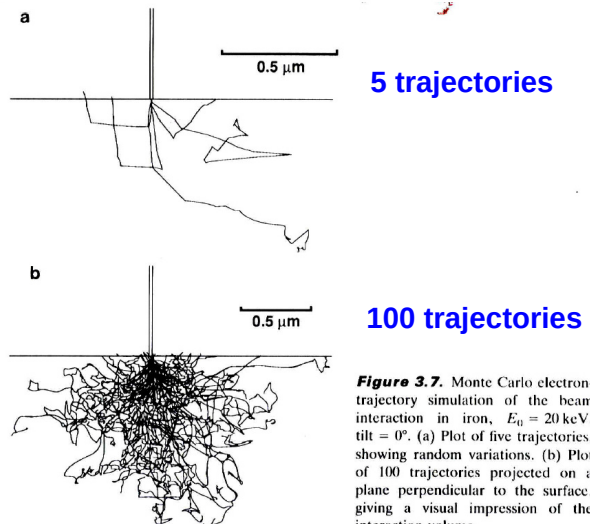
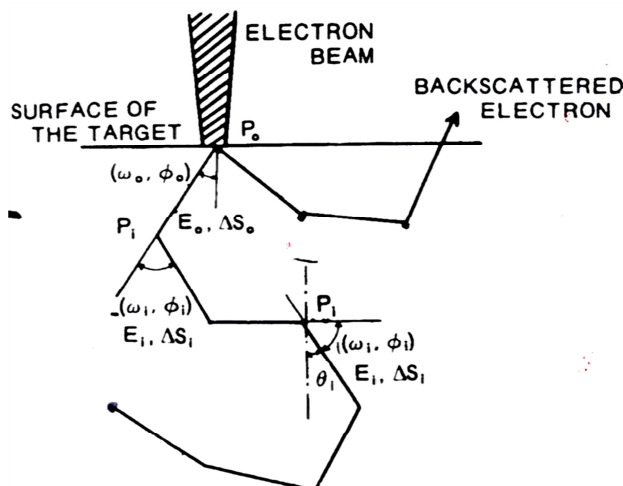
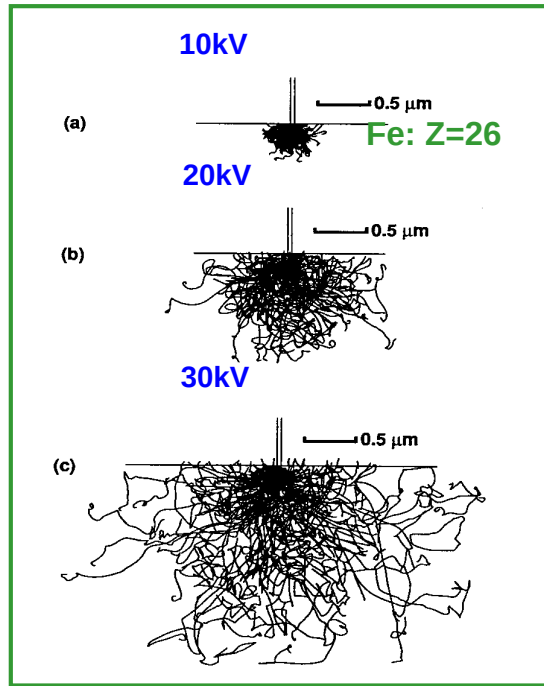


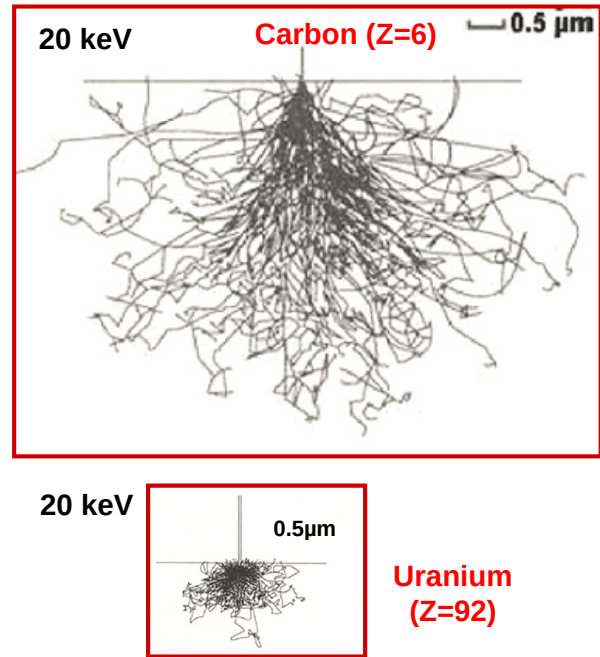
Figure 3.7. Monte Carlo electron-trajectory simulation of the beam interaction in iron, $E_0 = 20$ keV, tilt = 0° . (a) Plot of five trajectories, showing random variations. (b) Plot of 100 trajectories projected on a plane perpendicular to the surface, giving a visual impression of the interaction volume.

➤ By **averaging over many electron paths**, the **interaction volume** can be obtained.

(a) Interaction volume versus beam energy



(b) Interaction volume versus sample material.



Trends:

- Strong increase of interaction volume V_{int} with increasing electron energy.
- Very large interaction volume for low Z materials. Much smaller for large Z materials.

Comparison of Interaction Volumes

Left: Simulated trajectories of electrons as a function of energy and Z number.

Right: Calculated Bethe and Kanaya-Okamaya ranges

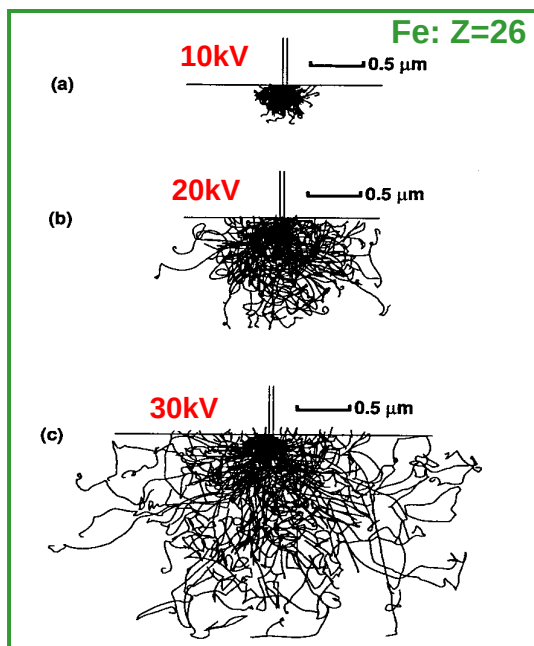


Table 3.2. Comparison of Ranges"

range in μm	Bethe range (μm)				Kanaya-Okamaya range (μm)			
	Beam energy (keV)				Beam energy (keV)			
	5	10	20	30	5	10	20	30
Target								
C Z=6	0.61	2.1	7.5	13.0	0.52	1.7	5.3	10.4
Al Z=13	0.52	1.8	6.0	12.4	0.41	1.3	4.2	8.2
Cu Z=29	0.21	0.69	2.3	4.6	0.14	0.46	1.5	2.9
Au Z=79	0.19	0.54	1.6	3.2	0.085	0.27	0.86	1.7

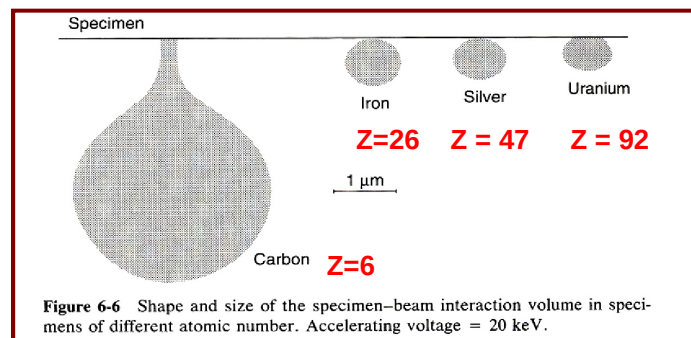


Figure 6-6 Shape and size of the specimen-beam interaction volume in specimens of different atomic number. Accelerating voltage = 20 keV.

- ⇒ Reasonable agreement between Monte Carlo and KO range.
However, lateral spreading is quantitatively obtained only by MC simulations.

5.6 Electron Energy Loss Spectroscopy (EELS)

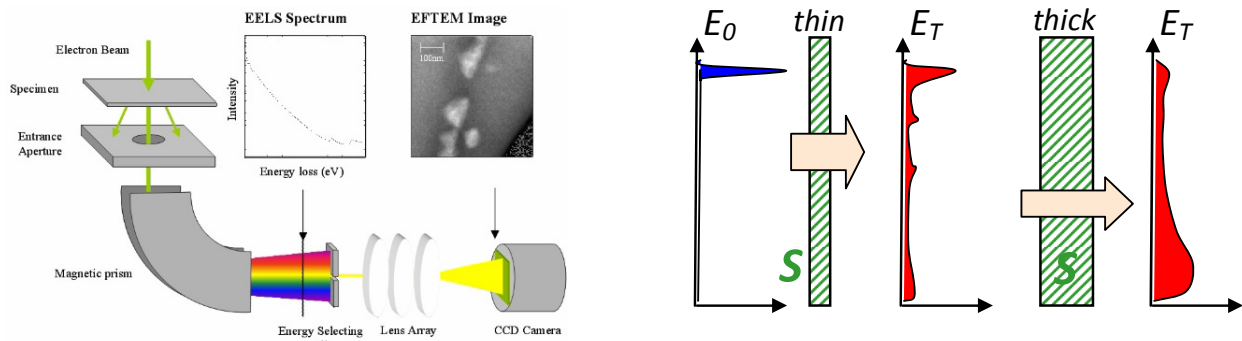
In EELS, the **energy loss spectrum** of the electrons traversing through a thin sample is measured and analyzed. In passing through the sample, the electron energy decreases.

The **energy loss** ΔE_{loss} caused by the inelastic scattering within the samples is given by:

$$\Delta E_{loss} = E_0 - E_T = \sum E_{i,exc}$$

and yields information on the sample properties.

Due to the **multiple scattering processes** that a particle experiences when it travels through a solid, the energy loss ΔE can assume a wide range of values.



- ⇒ For **thick samples** the number of experienced scattering events is large. Therefore, the energy loss per electron is rather undefined and the energy loss spectrum rather broad and fine spectral features smeared out.
- ⇒ As a result, meaningful energy loss spectra can be recorded only for **thin samples** ($d < 100\text{nm}$), where the number of multiple scattering processes per electron is small.

Typical Electron Energy Loss Spectrum (Thin Sample Specimen)

The energy spectrum contains different features in different regions:

- (a) **Zero loss peak** of electrons that were only scattered elastically
- (b) **Low loss region**, for which the transmitted electrons have induced only small energy excitations such as phonons, intraband and interband transitions, plasmons ... The information contained is similar as in VIS/IR photon absorption spectra.
- (c) **High loss region**, which consist of electrons that have either undergone **many multiple inelastic scattering processes**, or **one high energy core shell excitation**. The latter gives rise to discrete steps in the EELS spectrum, similar to the absorption edges for x-rays.

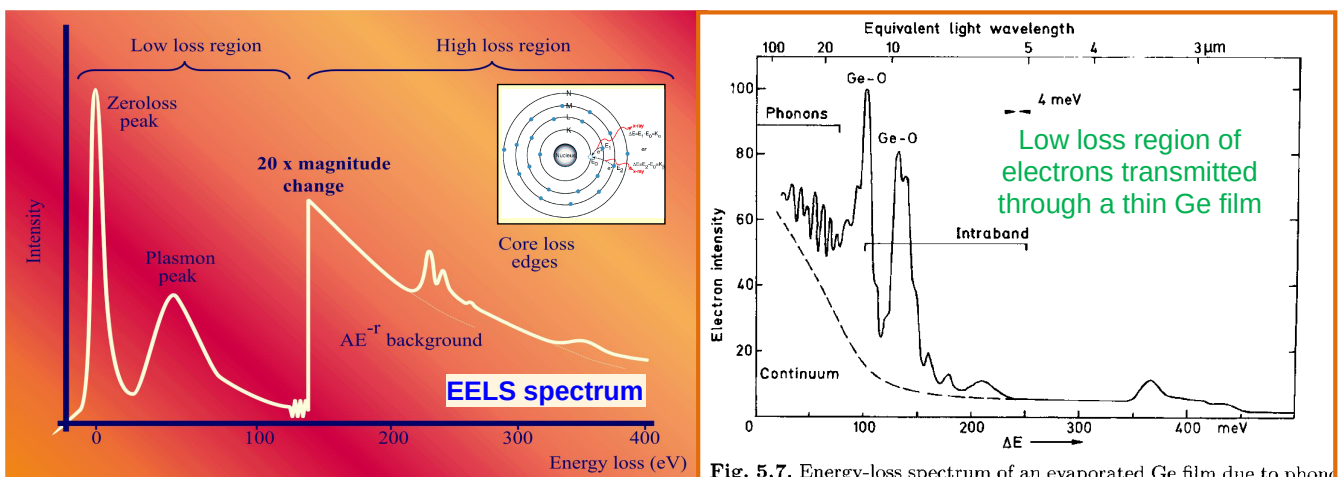


Fig. 5.7. Energy-loss spectrum of an evaporated Ge film due to phonons

Absorption edges

As for x-rays, core-level absorption sets in at a particle energies $E > E_{crit}(n)$.

This gives rise to discrete steps (**absorption edges**) in the EELS spectra.

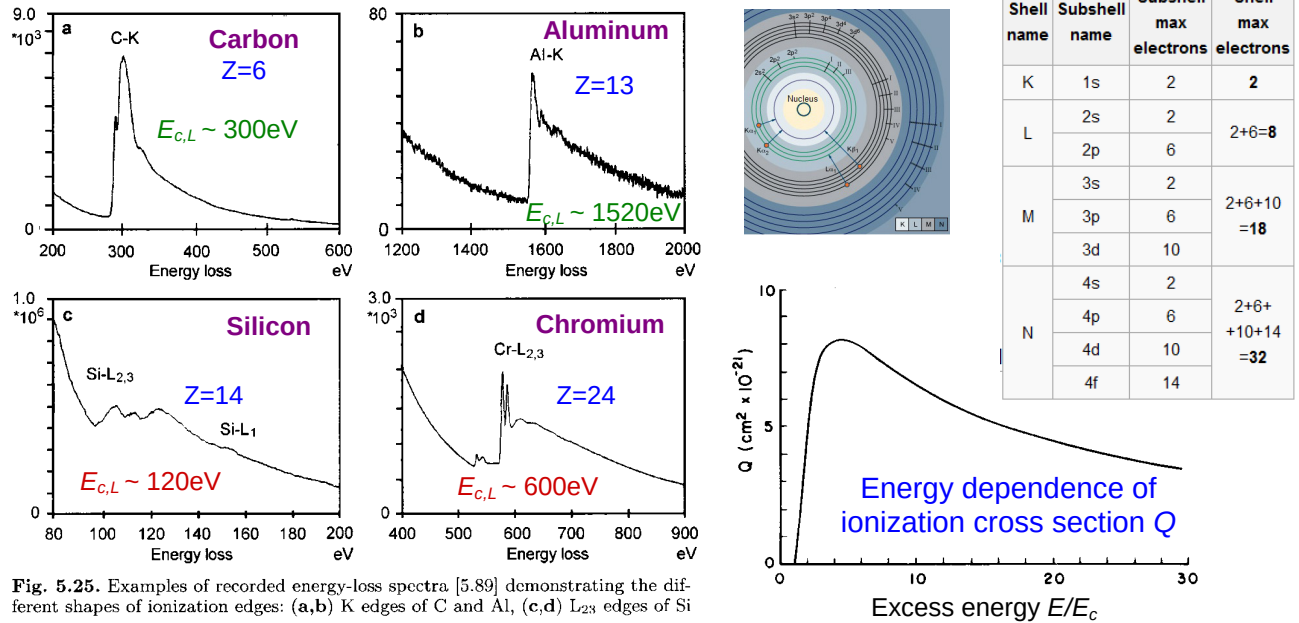


Fig. 5.25. Examples of recorded energy-loss spectra [5.89] demonstrating the different shapes of ionization edges: (a,b) K edges of C and Al, (c,d) L₂₃ edges of Si

⇒ The **position** of the edges are **element specific** and allow to identify the elements in the sample!

⇒ The **step heights** are proportional to the concentration of the elements as well as the

ionization cross section:

$$\sigma_{\text{shell}} \sim N_{\text{shell}} \cdot C_1 (E_0 - E_c)^{-1} \log(C_2 E_0/E_c)$$

N_{shell} = number of electrons per shell, C_1 and C_2 = shell constants

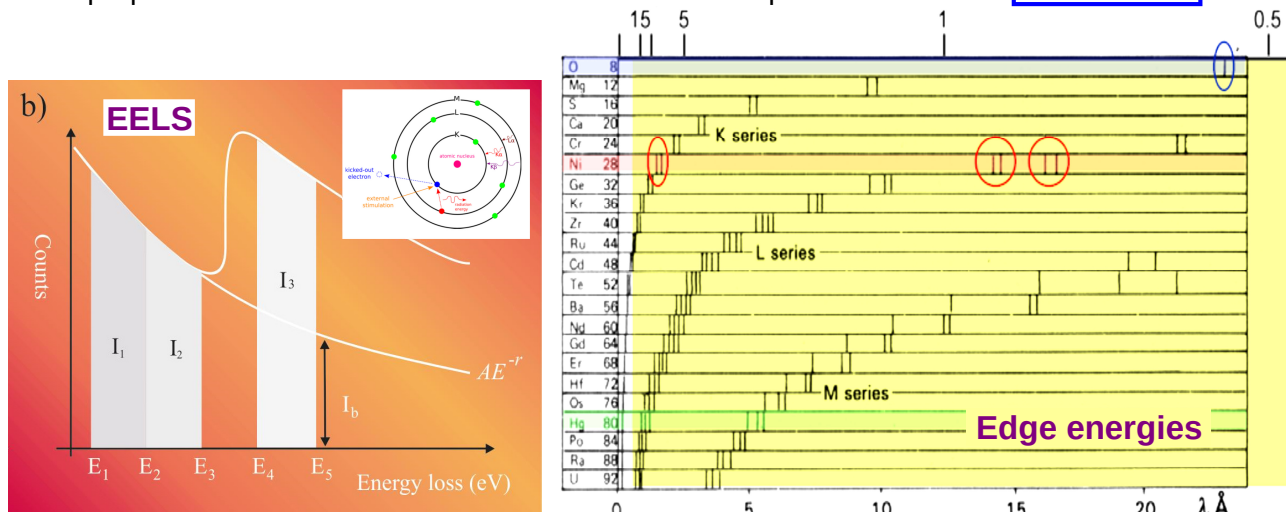
Chemical Analysis using Energy Loss Spectroscopy

The **height of the absorption steps** in the EELS spectra is proportional to the **concentration of the elements n_i** in the excited sample volume **multiplied** by the **absorption cross section σ_i** .

The step height is quantified by the **jump ratio $J_i = I_{3,i} / I_{2,i}$** , which is the post-edge signal I_3 divided by the background I_2 before the edge.

This is proportional to the content of the element in the sample.

$$\frac{n_i}{n_j} = \frac{J_i}{J_j} \frac{\sigma_i}{\sigma_j}$$

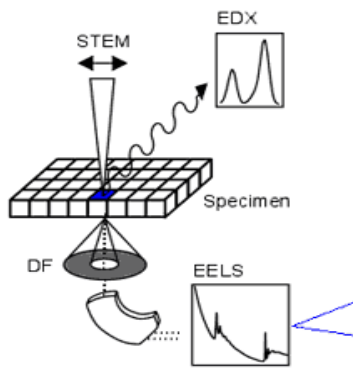


⇒ Qualitative assessment of elemental concentration by measuring the jump-ratio (I_3 / I_2)

⇒ Quantitative analysis using 'three window' method to estimate the background I_b under the post edge.

Example: Chemical Mapping using EELS combined with STEM

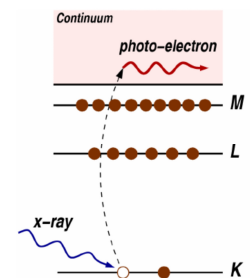
Because the electrons can be focused to a very small spot size, EELS can be recorded sequentially from very small regions of the samples while scanning the beam in a STEM.



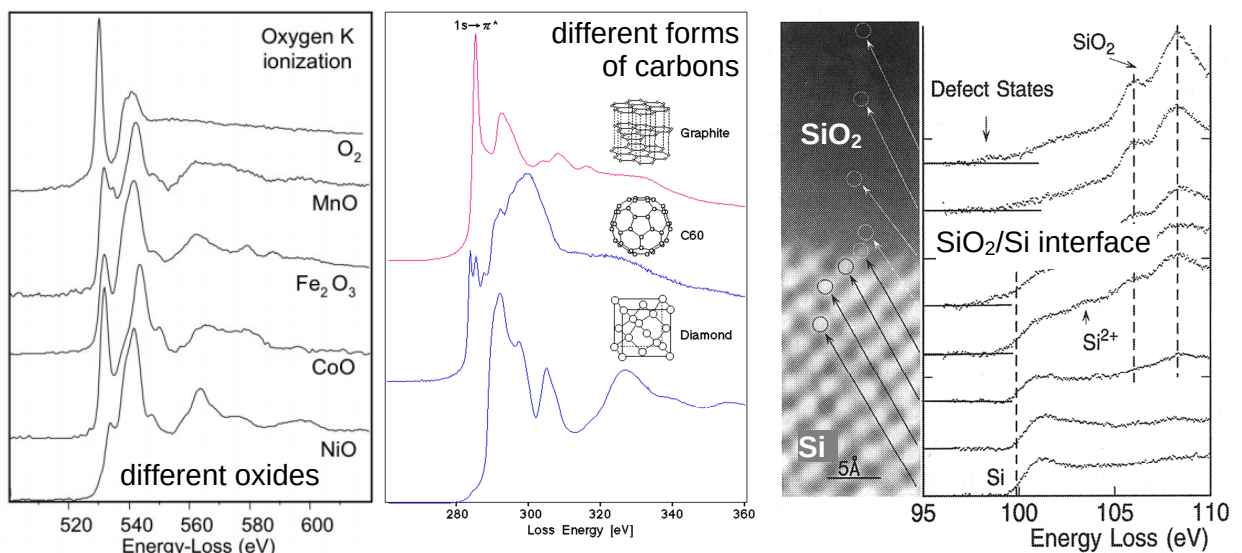
Fine Structure of the Absorption edges (ELSN)

There exist also a distinct **fine structure** of the **absorption edges** in the EELS spectra because at $E_{\text{loss}} \sim E_{\text{crit}}$ the core electrons are excited into unoccupied conduction band or antibonding molecular states, which are influenced by the chemical environment of the atoms.

⇒ This can be employed to derive not only the chemical composition, but also information on the **local bond configuration of the atoms** in the samples.



Electron Energy-Loss Near Edge Structures (ELNES)



⇒ The fine structure is a fingerprint of local environment but needs high energy resolution !

5.7 Microprobe Analysis using Secondary X-Ray Emission

When a core shell electron is knocked out by an inelastic excitation, the refilling of the hole by an outer electron leads to characteristic x-ray emission, similar to x-ray fluorescence (see Sec. 2.7.4).

The characteristic x-ray photon energy is given by: $E_{\text{photon}} = E_{2,o} - E_{1,i}$

Which can be approximated by: $E_{x\text{-ray}}(n_1 - n_2) = R_H (Z - \sigma_{n2})^2 / n_2^2 - R_H (Z - \sigma_{n1})^2 / n_1^2$

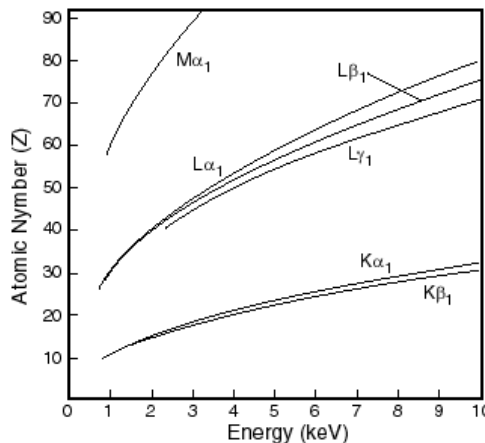
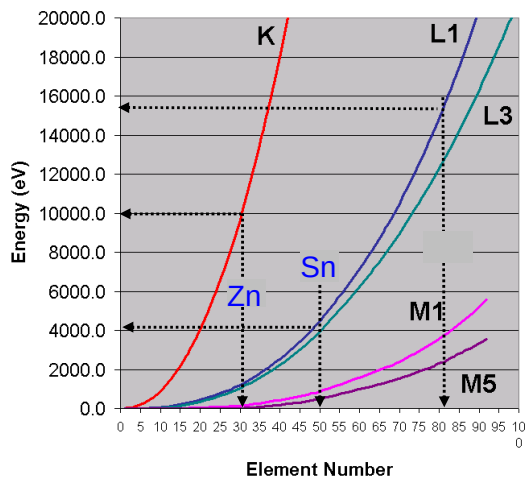
(= Moseley's law)

with $R_H = 13.6 \text{ eV}$ = Rhydberg constant and

$(Z - \sigma_n)$ = effective nucleus charge = (Z number - shell screening σ_n)

K-radiation: $\sigma_n = 1$ and $n_1 = 1$, L-radiation: $\sigma_n = 7.4$ and $n_2 = 2$

Element specific characteristic x-ray energies



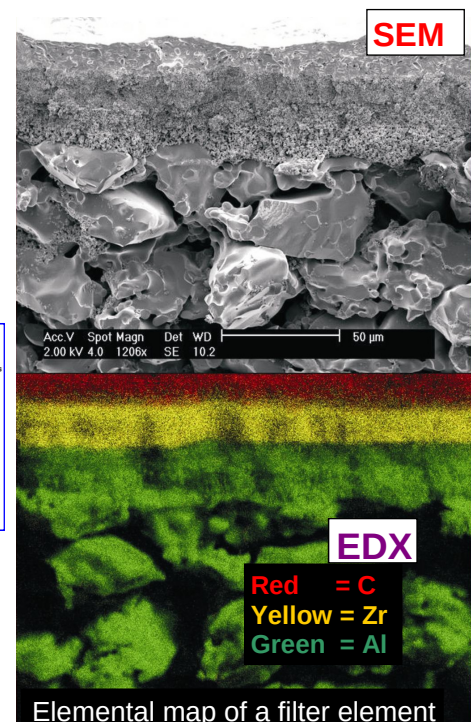
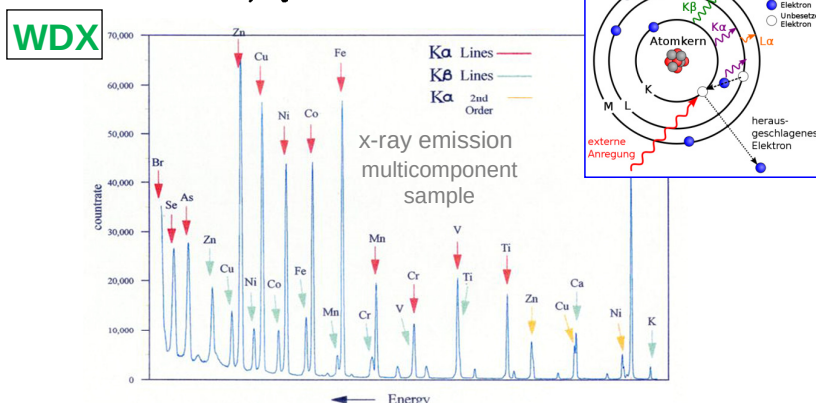
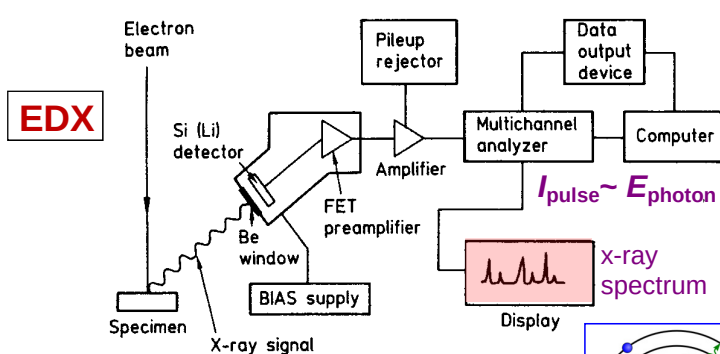
Because inner shell transitions are not much influenced by the chemical bonding, the characteristic x-ray energies do not depend much on the environment of the atoms !

Note: Chemical effects, however, are observable in the fine structure (~eV) of electronic transitions involving outer electrons.

Microprobe Analysis in Scanning Electron Microscopy (EDX / WDX)

EDX (=energy dispersive) or **WDX** (=wavelength dispersive) measurement of characteristic x-ray emission spectrum induced by high energy **electron beam irradiation**.

EDX is based on pulse height measurements of a photomultiplier, WDX uses an analyser crystal in Bragg reflection to scan the spectrum over the wavelength by rotation of the analyser crystal » higher resolution !

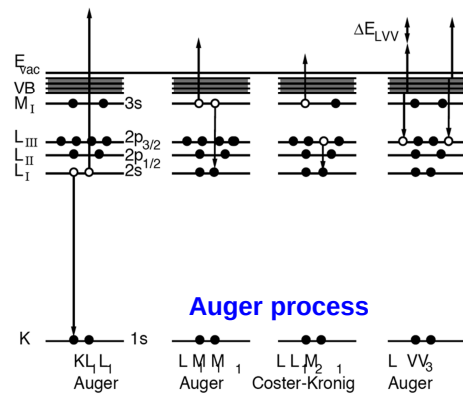
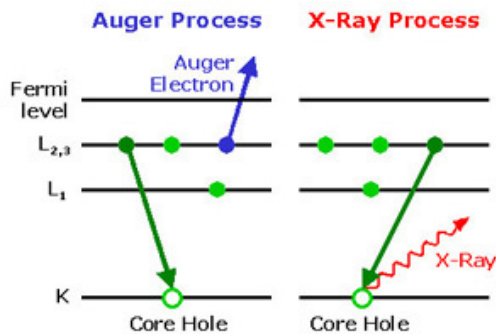


5.8 Auger Electron Emission Spectroscopy (AES)

Alternatively to characteristic x-ray emission, the **recombination of a core shell excitation** can lead to the emission of a **characteristic Auger electron**. This Auger electron is produced, when the energy ΔE_{2-1} released by recombination of an outer electron with the core hole is not emitted as x-ray photon but is transferred to another electron from the same shell ("Auger electron")

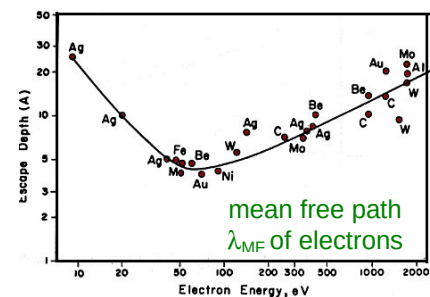
that is emitted with a characteristic energy: $E_{\text{Auger}} = \Delta E_{2-1} - E_{\text{Binding},2}$

❖ Typical Auger electron energies are ~50 to 1000 eV.

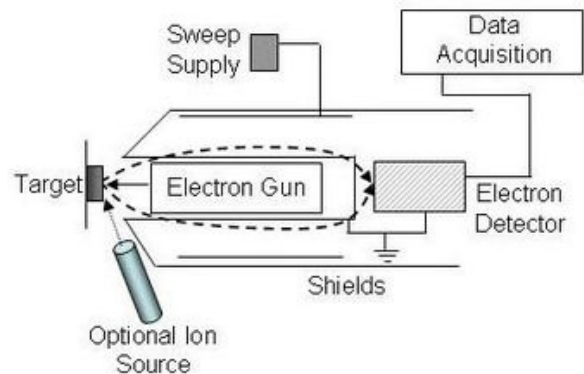
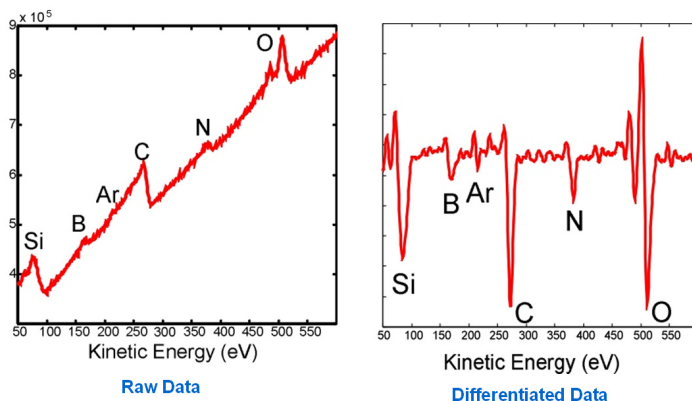


⇒ The **energy** of the emitted **Auger electrons** is **element specific**, i.e., each element yields a peak in the electron emission spectrum at a specific energy. This allows to quantify the elements contained in a sample.

⇒ The **escape depth** of Auger electrons $d \sim 5 \lambda_{\text{MF}}$ is **very small**, i.e., only a few atomic layers. Therefore, Auger electron spectroscopy is **very surface sensitive**!



Example for Auger Electron Emission Spectra



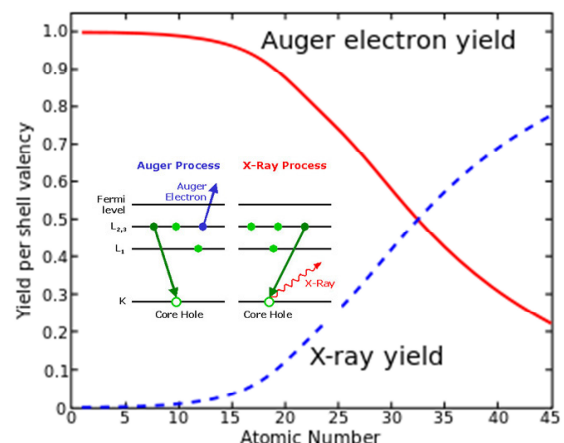
⇒ Auger peak positions: Indicates *which* elements are contained in the sample.

⇒ Relative Auger peak heights: Yields composition.

For each core recombination process, the **sum** of **Auger yield** ω_A and **x-ray yield** ω_X is **unity**.

$$\text{Thus: } \omega_A = 1 - \omega_X = 1 - \frac{W_X}{W_X + W_A}$$

⇒ As shown in the figure on the left, the Auger yield is high for light elements with small Z number, the opposite is true for characteristic x-ray emission.



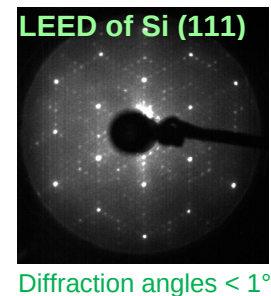
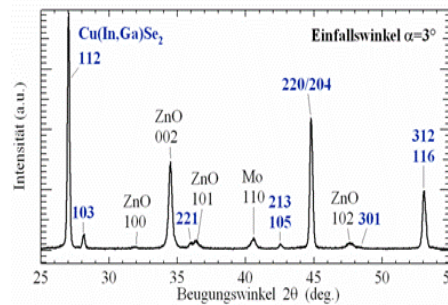
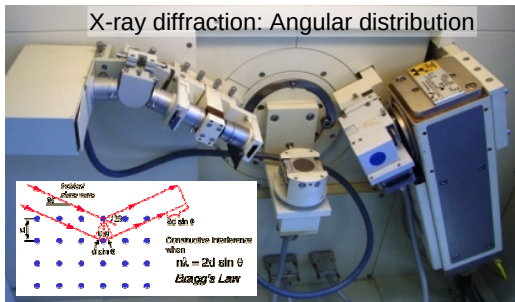
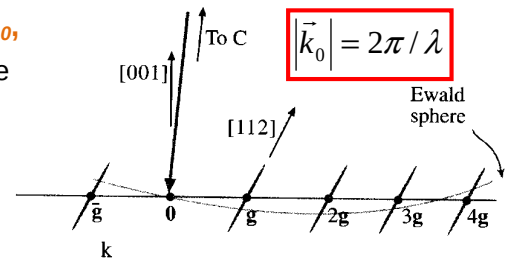
5.9 Electron Diffraction (LEED, TED)

Due to the dual particle/wave nature of electrons, elastic scattering also leads to electron diffraction, following the same principles as x-ray diffraction (Chapter 4). There are however differences:

X-Rays: » photon wavelength $\lambda \sim \text{\AA}$ is comparable to the atom distances a_0 in the sample » $k_{\text{XR}} \sim g_{hkl}$
 » Radius of Ewald sphere is $\sim n g_{hkl}$, » the Laue condition is met only at few & distinct diffraction angles.

Electrons: de Broglie wavelength $\lambda_e < 0.1 \text{\AA}$ (10keV) $\ll a_0$,

- » The radius of Ewald sphere is much larger than the distance of the reciprocal lattice points, i.e. $k_{\text{el}} \gg g_{hkl}$.
- » Thus, **many diffraction spots appear simultaneously** at small scattering angles, i.e., the diffraction pattern nearly represents a cross-section of the reciprocal lattice.



Further aspect: Particle waves induce a much stronger excitation of individual atoms than x-rays.

Thus, for electrons a much high diffraction intensity is obtained already from small sample volumes. This allows **micro-diffraction experiments**. Contrary, x-ray diffraction needs larger ensembles of nanostructures for sufficient intensity and thus, yields only averaged structure information.

Diffraction of Electrons: Atomic Form Factors

X-rays are scattered by the electron density $\rho(r)$ in the sample.

Electrons are scattered by the **atom potentials $V(r)$** and the scattering amplitudes must be calculated by quantum mechanics (Schrödinger equation).

The total scattering amplitude from a sample is then obtained by integration over all atomic potentials.

The scattering strength of the atoms is then represented by the **atomic form factor for electron diffraction**, which is given by the Mott approximation as:

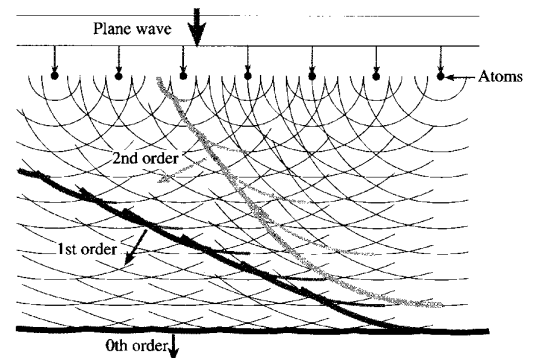
$$f^{(e)}(s) = \frac{m_0 e^2}{8\pi\epsilon_0 h^2} \frac{[Z - f^{(X)}(s)]}{s^2} = 0.023934 \frac{[Z - f^{(X)}(s)]}{s^2}$$

Where s is the scattering wave vector, Z the atomic number and $f^{(X)}$ the atomic form factor for x-ray diffraction.

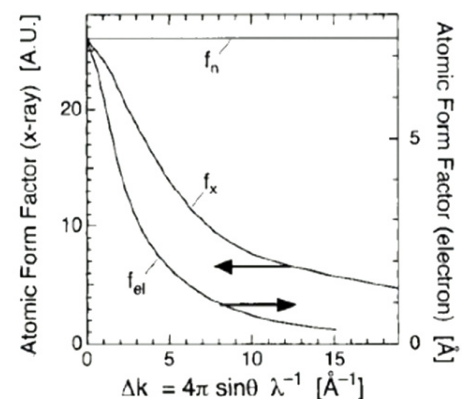
The atomic scattering strength (form factor) decays more rapidly with increasing scattering vector compared to x-rays.

Therefore, electron scattering is strongest in the forward direction.

Note: Neutrons are scattered mainly by the point-like nucleus of the atoms, i.e., there are no phase differences within the atom. Thus, the atomic form factor does not depend on scattering angle, i.e., is essentially constant.



Comparison of atomic form factors for electrons, x-rays and neutrons

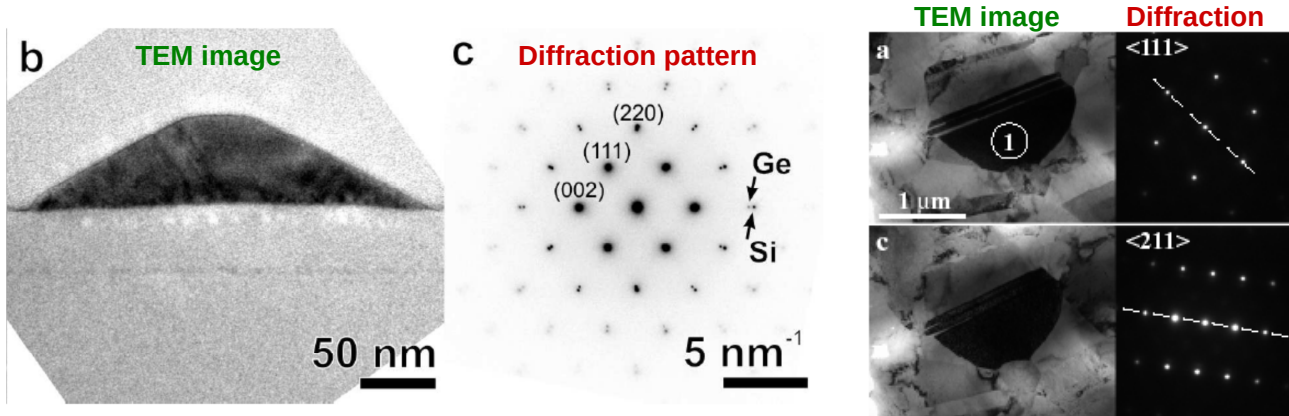


Example: Micro-Diffraction obtained with Transmission Electron Microscopy

In TEM, the electron beam can be focused to a small spot and thus, electron diffraction can be performed on very small sample areas. In this way, structure analysis can be performed on single nanostructures and thereby the *local* crystal structure and orientation obtained.

Example Left: SiGe nanoislands embedded in Si.

Right: Grain in a copper foil.



⇒ Due to the ~4% difference in the Si/Ge lattice constants, the diffraction points are slightly shifted with respect to each other

⇒ The lattice orientation of each grain differs and thus gives rise to a different diffraction pattern.

5.10 Summary

Electron based techniques have many advantages for nano-characterization due to:

(a) **High spatial resolution** due to very short electron wavelength compared to light.

De Broglie wavelength:

$$\lambda = h / m_e v = 12.25 \text{ \AA} / \sqrt{E[\text{eV}]} \quad U < 100 \text{ kV}$$

Practical limitation for resolution:

Strong aberrations of electron lenses limit the resolution (small numerical aperture NA)

$$NA = 5 \times 10^{-3} \Rightarrow \Delta x \sim 100 \lambda \text{ (Resolution)}$$

(b) **Large depth of focus** due to small collection angles.

(c) **Very strong interaction** of electrons with solids:
High surface sensitivity and sensitive to small nanostructures

(d) **Excitation of many different secondary signals:** » Sensitive to many physical properties.

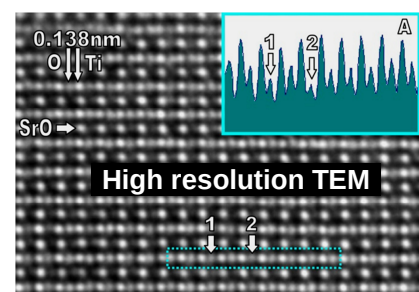
⇒ Many **different imaging modes** and **contrast mechanisms** possible,

⇒ **Microdiffraction** and with various different **quantitative chemical microanalysis techniques**.

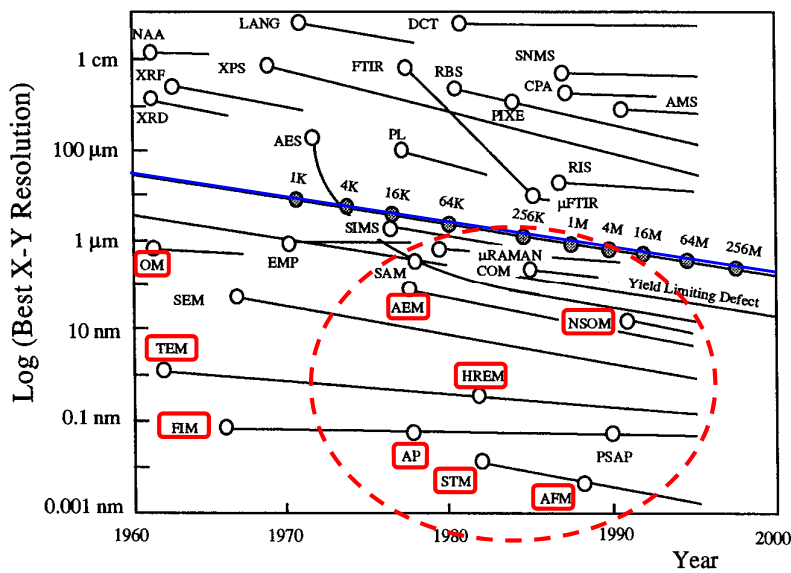
Disadvantages:

Vacuum required, limited penetration depth, complex multiple scattering processes.

ACCELERATING VOLTAGE (V)	WAVELENGTH (nm)	RESOLUTION (nm)
20,000	0.0087	0.44
40,000	0.0061	0.31
60,000	0.0050	0.25
80,000	0.0043	0.21
100,000	0.0039	0.19



Summary of Lateral Resolution of Various Characterization Techniques



Microscopy (M), Chemical Analysis & Bonds (C), Defects (D),
Structural Properties (S), Optical & Electronic Structure (OES)

AES	Auger electron spectroscopy (C)
AM	Acoustic microscopy (S)
AMS	Accelerator mass spectrometry
AP	Atom probe (M,C,S)
COM	Confocal optical microscopy (M, OES)
CPA	Charged particle activation analysis
DCT	Double crystal X-ray topography (S,C)
EMP	Electron microprobe (C)
FIM	Field ion microscope (M,S)
FTIR	Fourier transform infrared (C, OES)
HREM	High resolution electron microscopy (M,S,D)
LANG	Scanning Lang X-ray topography (S,D)
NAA	Neutron activation analysis (C)
NSOM	Near field scanning optical microscopy (M, OES)
PL	Photoluminescence spectroscopy (OES,D)
PSAP	Position sensitive atom probe (M,C,S)
RIS	Resonance ionization spectroscopy
RBS	Rutherford backscattering spectrometry (C,D)
SAM	Scanning Auger microprobe (C)
SEM	Scanning electron microscopy (M,C)
SIMS	Secondary ion mass spectrometry (C,doping)
SNMS	Sputtered neutral mass spectrometry (C,doping)
STM	Scanning tunneling microscopy (M, Spec)
TEM	Transmission electron microscopy (M,S,C)
XPS	X-ray photoelectron spectroscopy (C)
XRD	X-ray diffraction (S,C)
XRF	X-ray fluorescence (C)
μFTIR	Microspot FTIR (OES,C,S,D)
μRAMAN	Raman microprobe (C,S,D,OES)

⇒ High spatial resolution with

» Electrons, Ions, SPM !

(a) small wavelengths,
(b) small probe size and
(c) small interaction volume