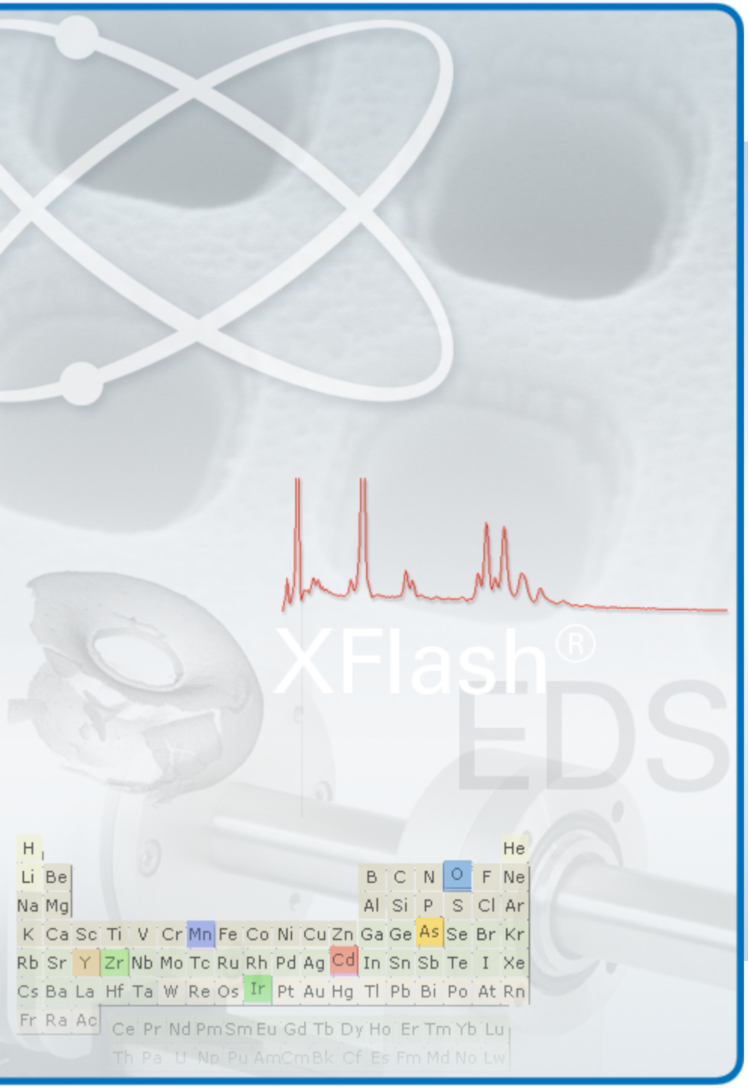


EDS User School

Principles of Electron Beam Microanalysis

Bruker Nano

Outline

1.) Beam-specimen interactions

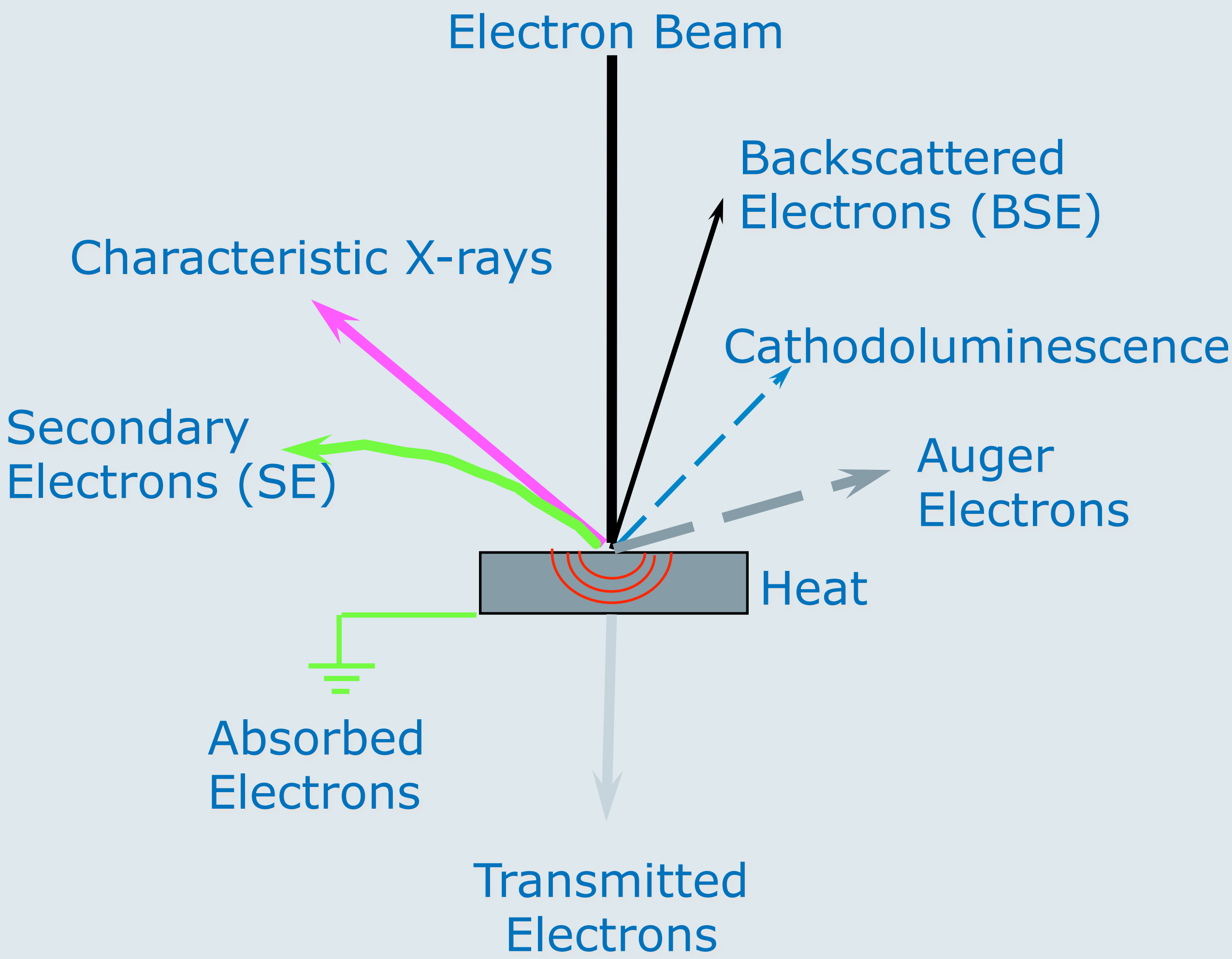
2.) EDS spectra: Origin of Bremsstrahlung and characteristic peaks

3.) Moseley's law

4.) Characteristic peaks: K-,L-, and M series

5.) Spatial resolution and excitation range in EDS analysis

1.) Beam-specimen interactions

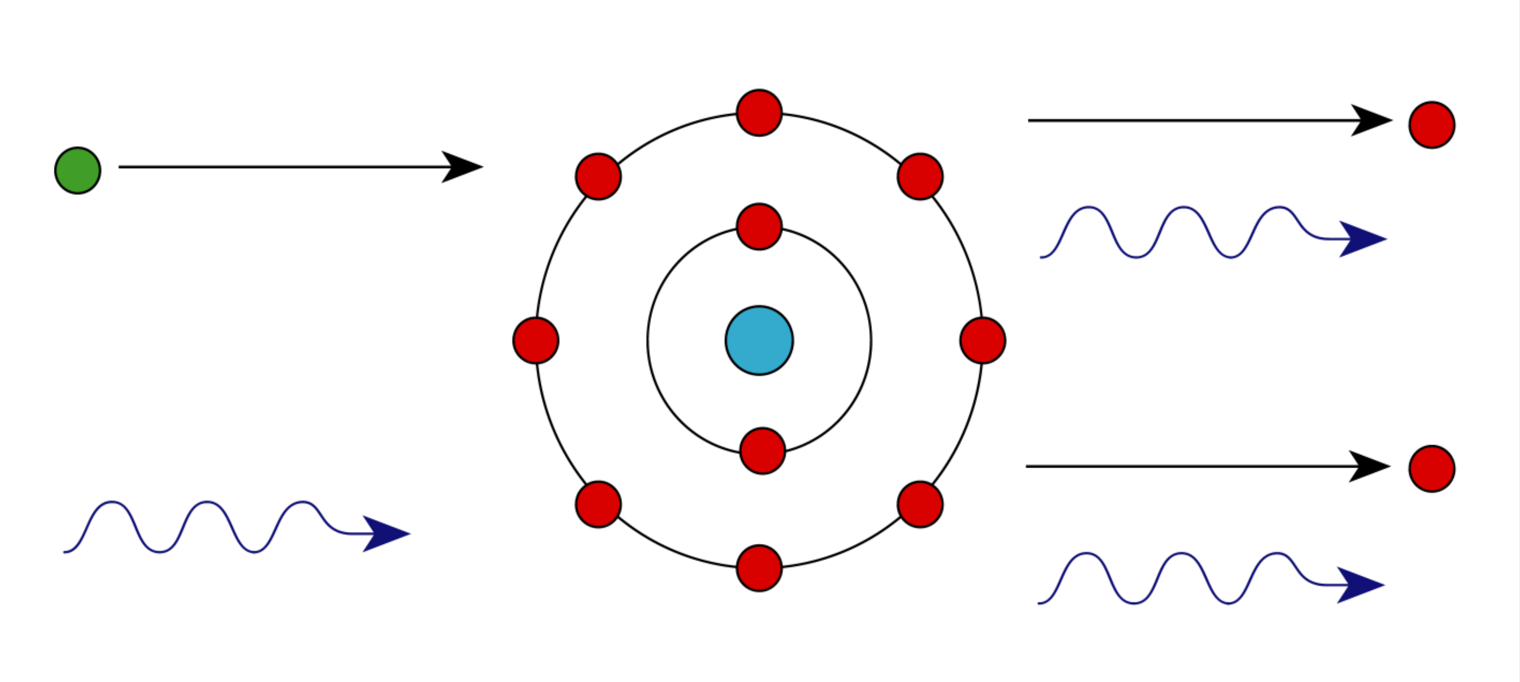


1.) Beam-specimen interactions

Accelerated from a source / Emitted from the specimen	Electrons	Ions	X-rays	Light
Electrons	**SEM, AES**		**XPS**	**UPS**
Ions		**SIMS**		
X-rays	**EDS, WDS**	**PIXE**	**XRF**	
Light	**CL**			

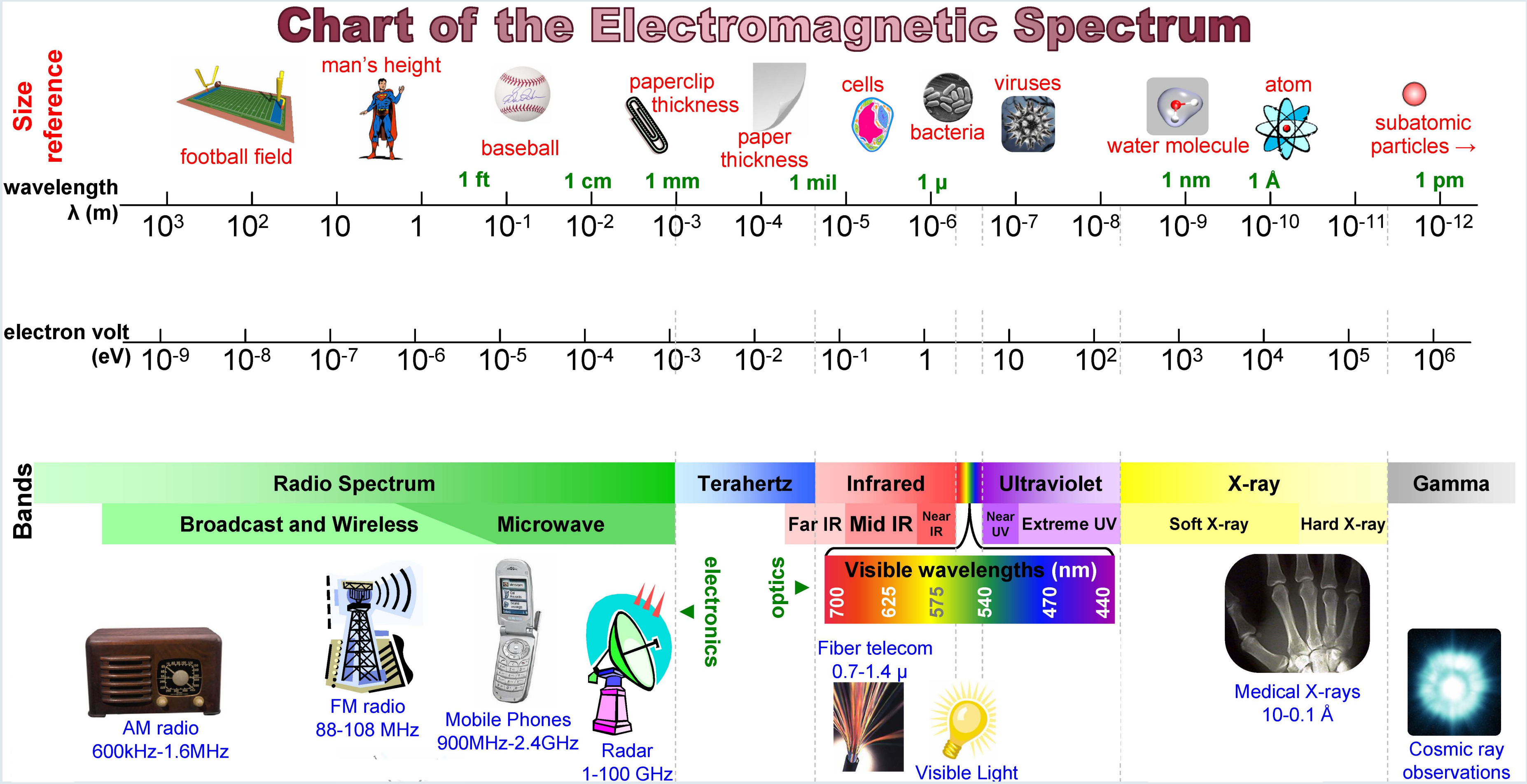
SEM - scanning electron microscopy
WDS - wavelength dispersive spectrometry
XPS - X-ray photoelectron spectroscopy
SIMS - secondary ion mass spectrometry
PIXE - proton-induced X-ray emission
EDS - energy dispersive spectrometry
AES - Auger electron spectroscopy
UPS - UV-light photoelectron spectroscopy
XRF - X-ray fluorescence spectroscopy
CL - cathodoluminescence

1.) Beam-specimen interactions



Basis: Atom model (N.Bohr)

1.) Beam-specimen interactions



$$\lambda\ (\mathrm{nm}) = 1.24\ /\ E\ (\mathrm{keV})$$

Outline

1.) Beam-specimen interactions

2.) EDS spectra: Origin of Bremsstrahlung and characteristic peaks

3.) Moseley‘s law

4.) Characteristic peaks: K-,L-, and M series

5.) Spatial resolution and excitation range in EDS analysis

Advantage of electron beam microanalysis

Chemical analysis of a very small volume of material can be done - ideal method for characterisation of a microstructure in a sample !

<u>Example:</u>

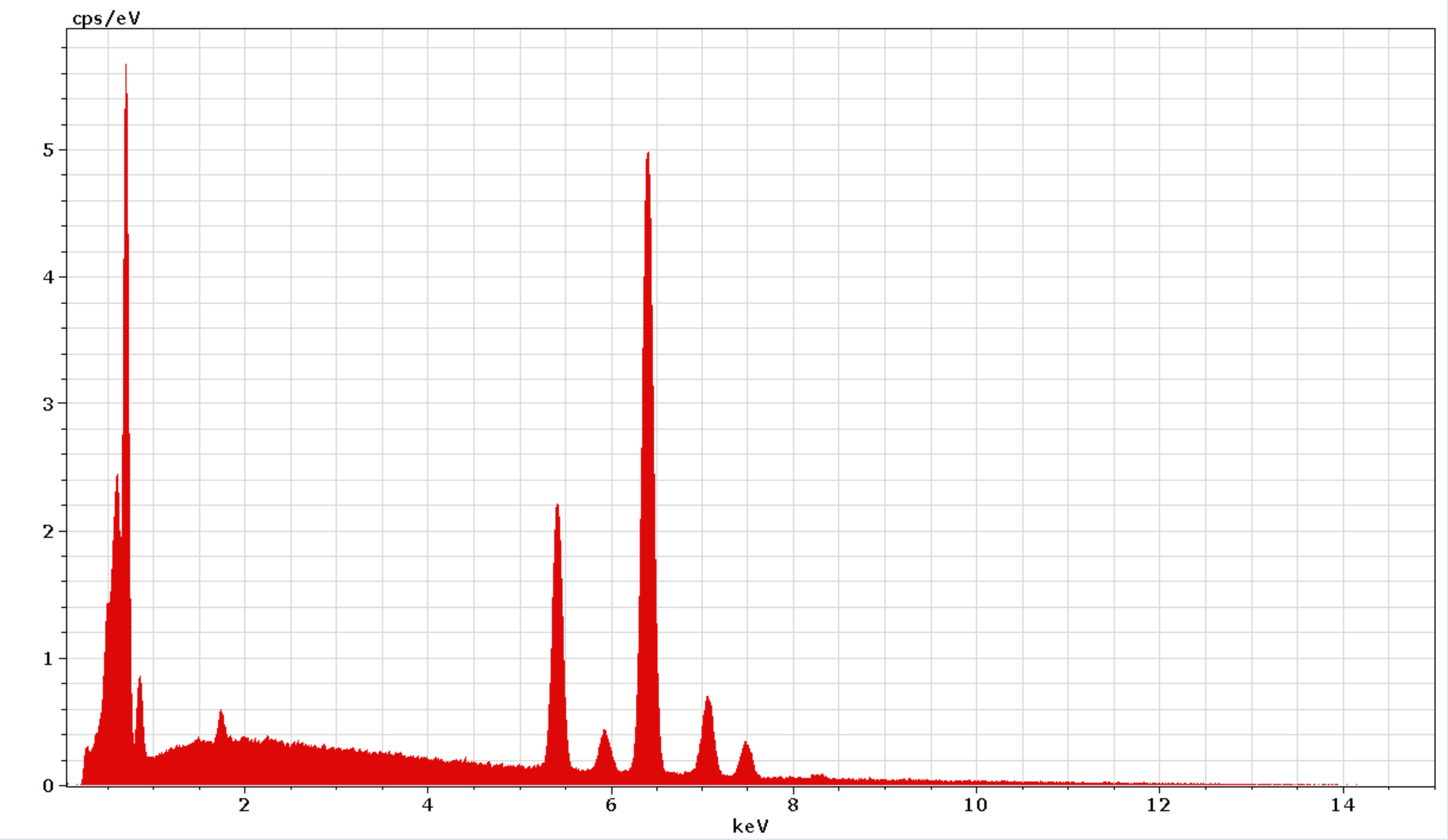
Linear dimension		Analysed volume		Assumed density		Amount of material
1µm	→	**10^{-12} cm^3**	→	**7 g/cm^3**	→	**7 x 10^{-12} g**

Detection limit: 0,1%

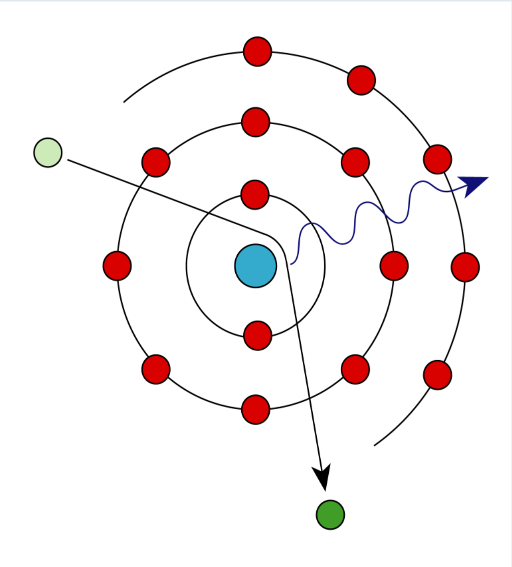
Mass detection limit: 10^{-14} g

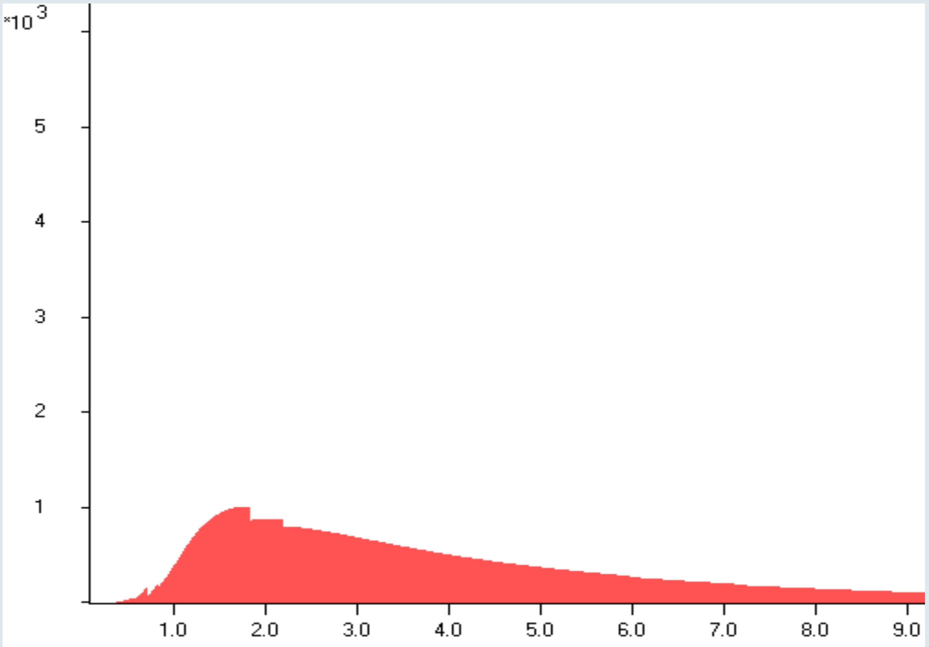
(For reference: Fe - atom weight is about 10^{-22} g)

2.) EDS spectra: Origin of Bremsstrahlung and characteristic peaks



2.) EDS spectra: Origin of Bremsstrahlung and characteristic peaks

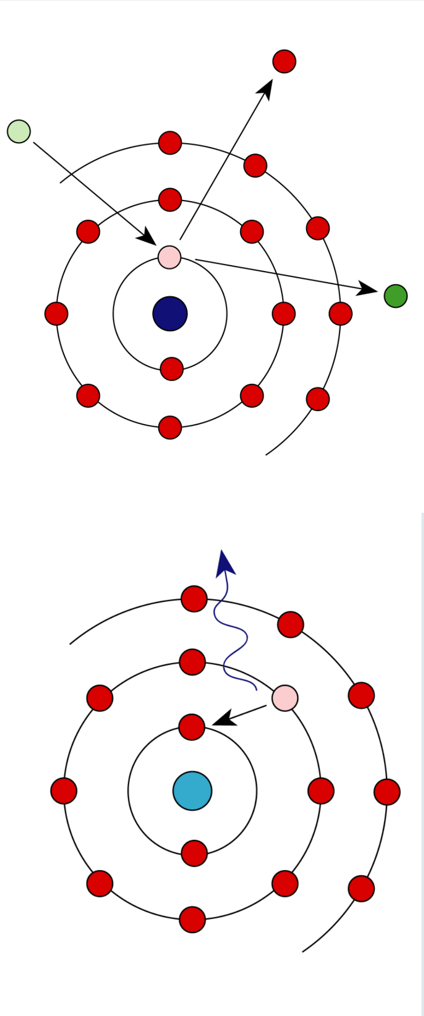




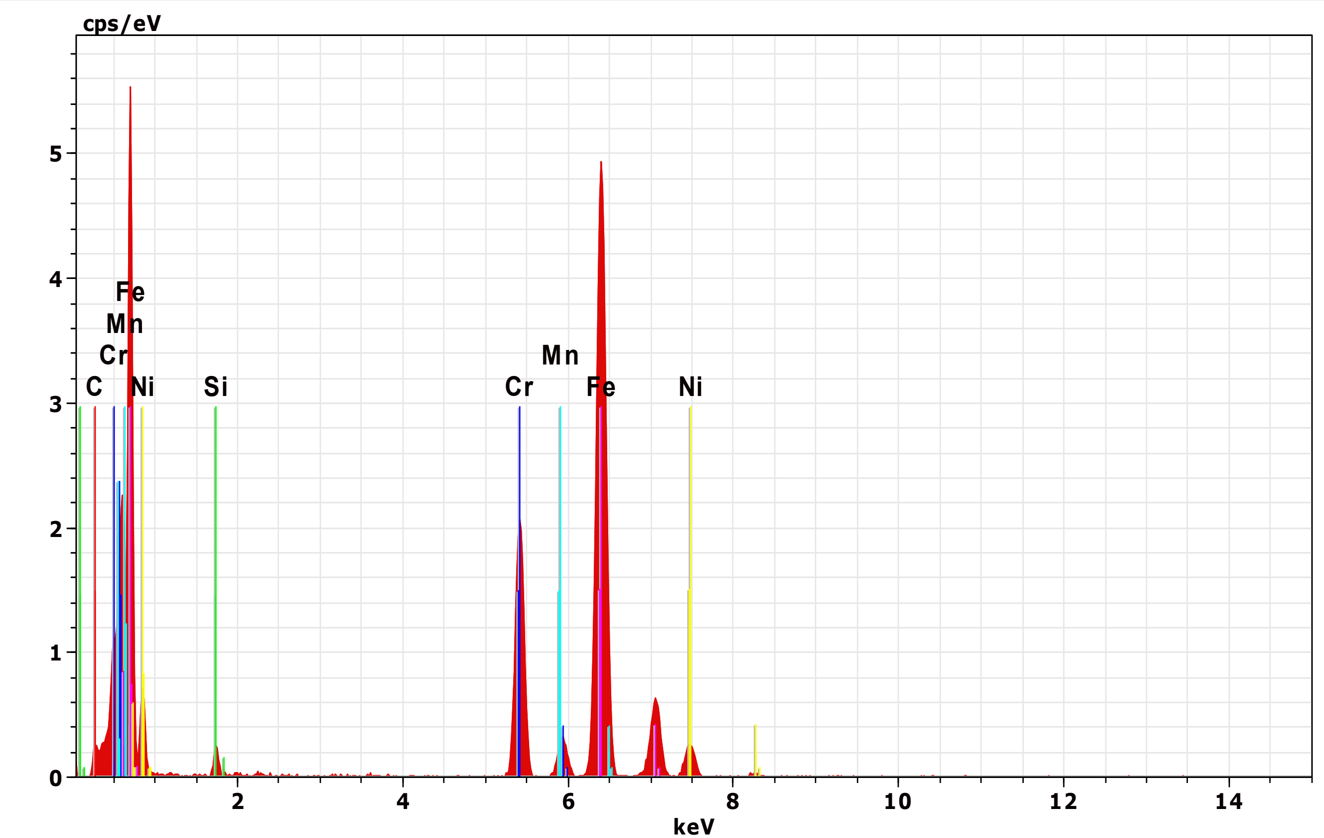
continuum or Bremsstrahlung (breaking radiation)

- results from deceleration of beam electrons in the electromagnetic field of the atom core
- combined with energy loss and creation of an X-ray with the same energy

2.) EDS spectra: Origin of Bremsstrahlung and characteristic peaks



- Characteristic X-rays are formed by excitation of inner shell electrons
- Inner shell electron is ejected and an outer shell electron replaces it
- Energy difference is released as an X-ray



2.) EDS spectra: Origin of Bremsstrahlung and characteristic peaks

If beam energy $E > E_K$ then a K-electron may be excited

Energy of emitted photon can be calculated:

$$E_{Phot} = E_1 - E_2$$

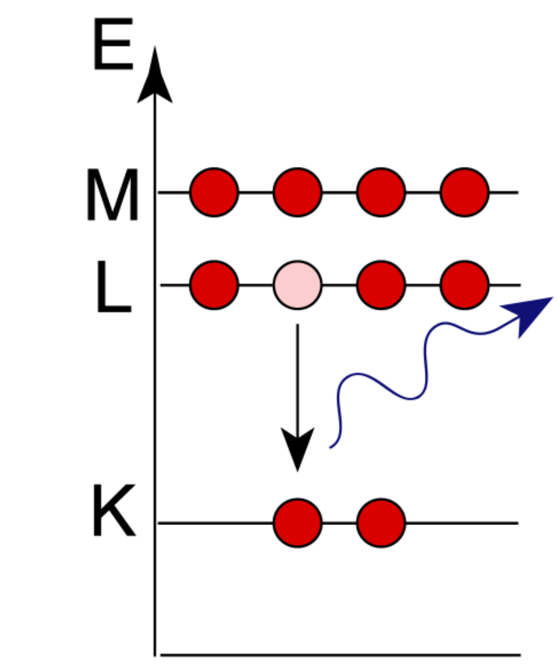
→ X-ray energy is the difference between two energy levels !

e.g.: Fe L → K

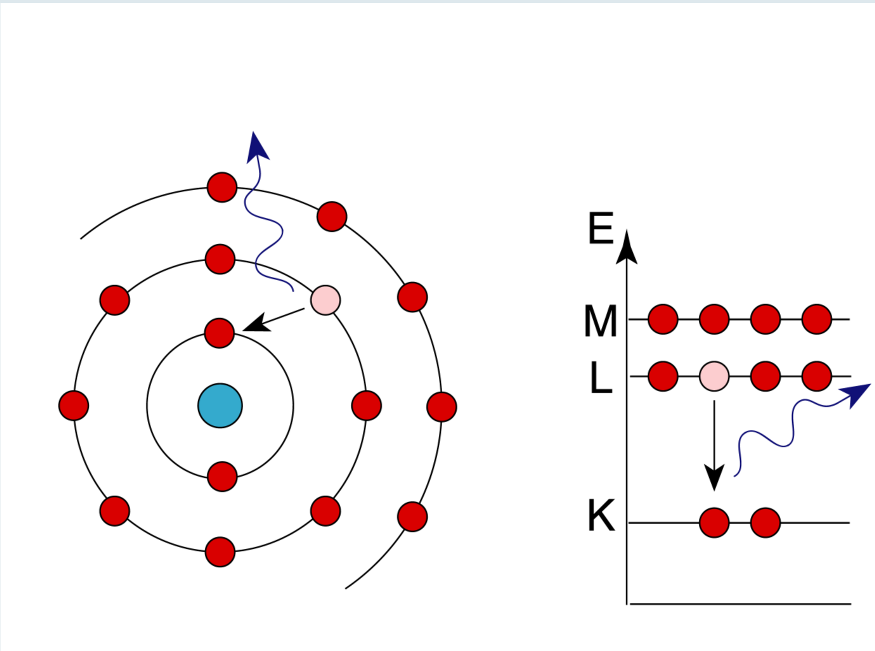
$E_1 = E_K =$ 7.11 keV

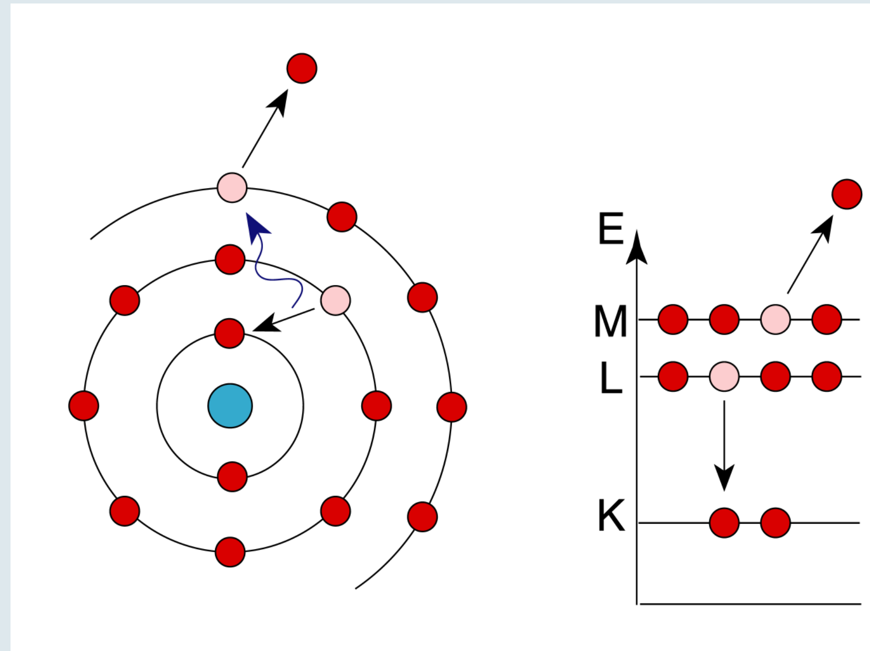
$E_2 = E_L =$ 0.71 keV

$E_{Ka} =$ 6.40 keV



X-ray and AUGER generation process





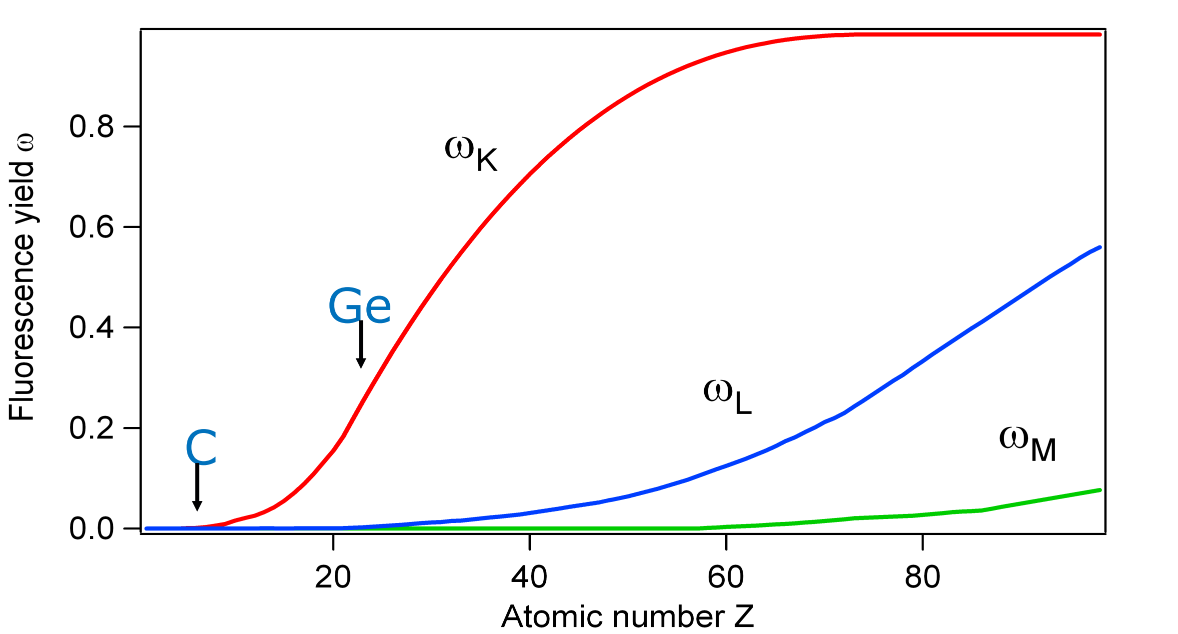
Emission of X-ray

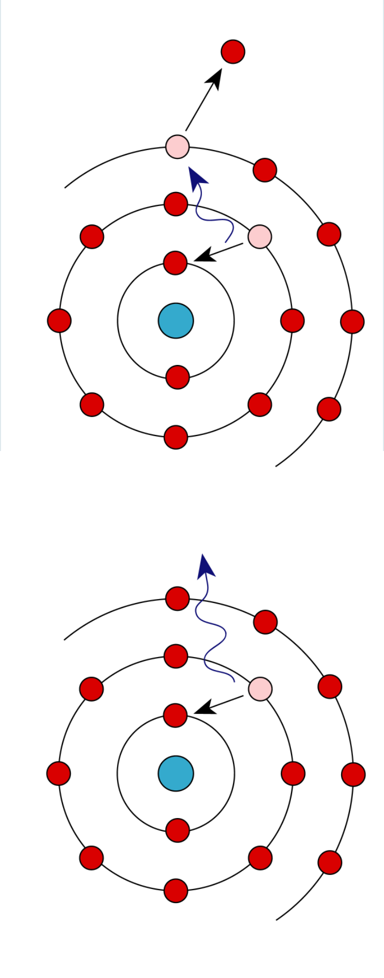
Emission of Auger electron

→ Auger and X-ray yield are competing processes

Fluorescence yield (ω)

- **ω**= fraction of ionisation events producing characteristic X-rays (rest produce Auger electrons)





- ω increases with Z
- ω for each shell: ωK ωL ωM
- Auger process is favoured for low Z,
- fluorescence dominates for high Z

$\boxed{\omega + A = 1}$

$\omega \approx 0.005$ for C K

$\omega \approx 0.5$ for Ge K

Outline

1.) Beam-specimen interactions

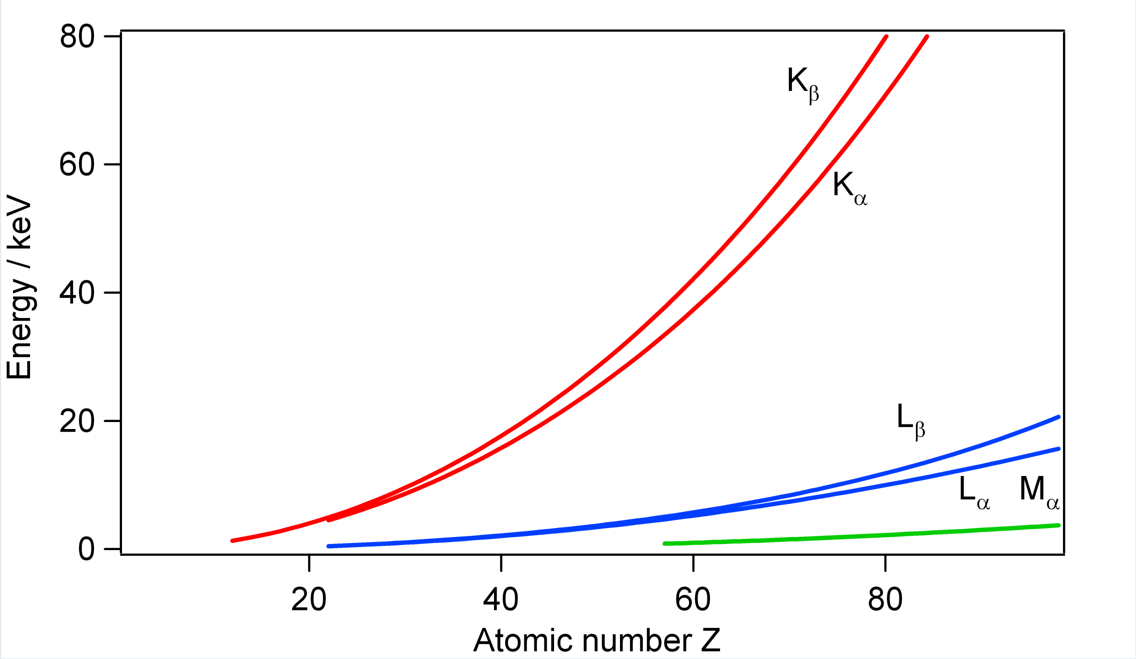
2.) EDS spectra: Origin of Bremsstrahlung and characteristic peaks

3.) Moseley‘s law

4.) Characteristic peaks: K-,L-, and M series

5.) Spatial resolution and excitation range in EDS analysis

3.) Moseley's law

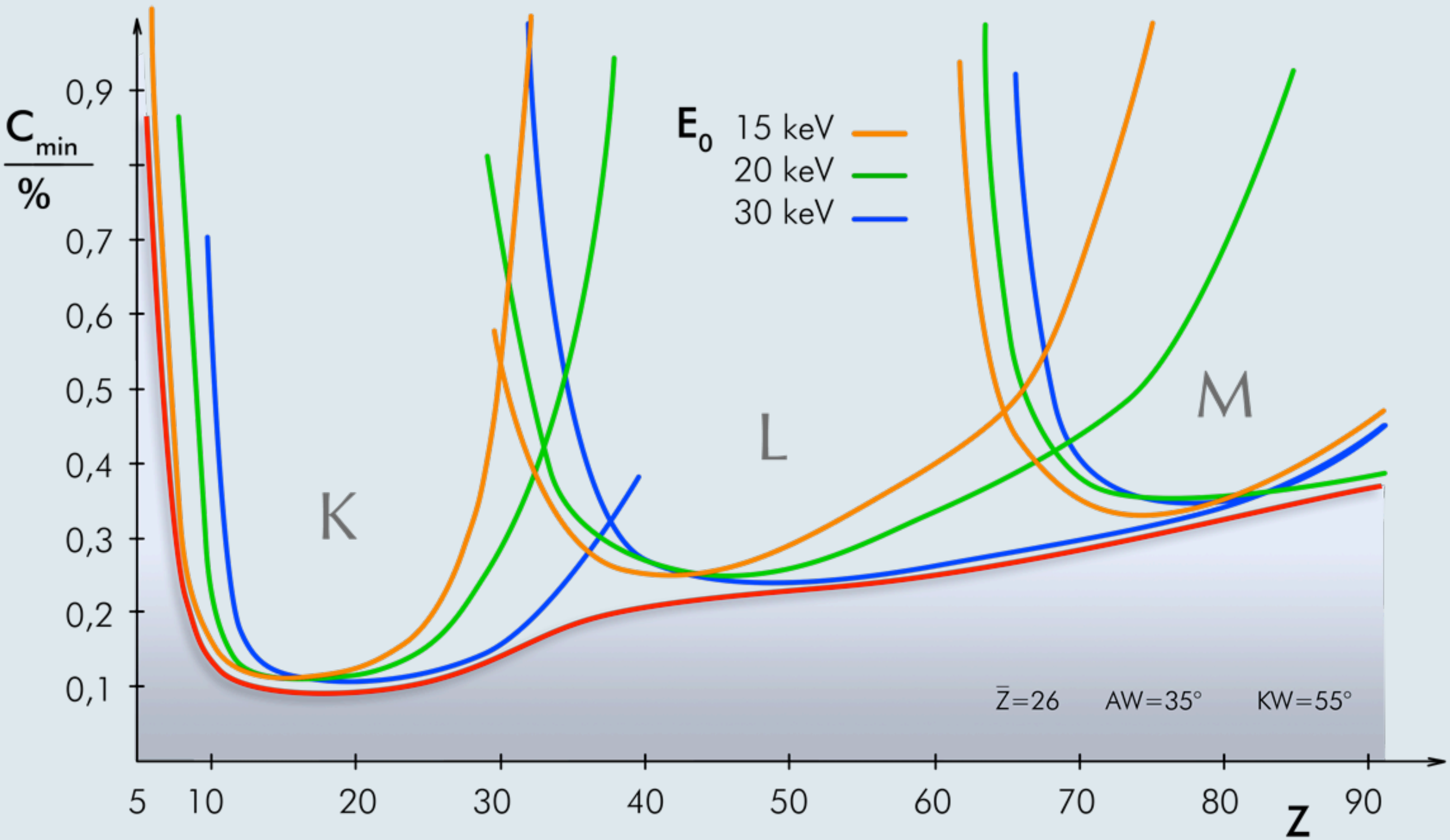


X-rays are **characteristic** because their specific energies are characteristic of the particular element which is excited.

$$E = c_1 (Z - c_2)^2$$

Moseley's law defines the relationship between the x-ray lines and the atomic number of the emitted atom.

Detection limit of EDS



Outline

1.) Beam-specimen interactions

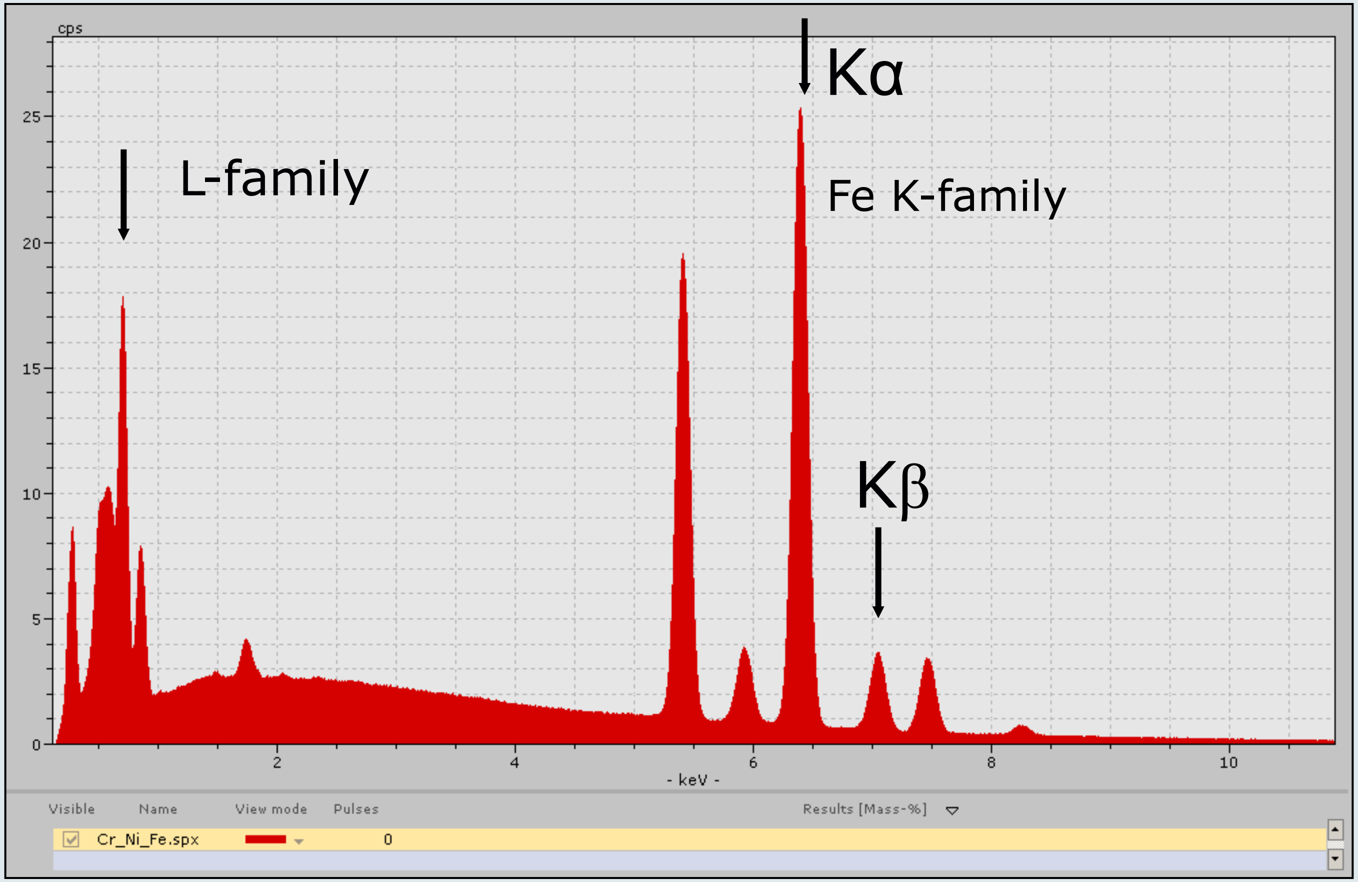
2.) EDS spectra: Origin of Bremsstrahlung and characteristic peaks

3.) Moseley's law

4.) Characteristic peaks: K-,L-, and M-series

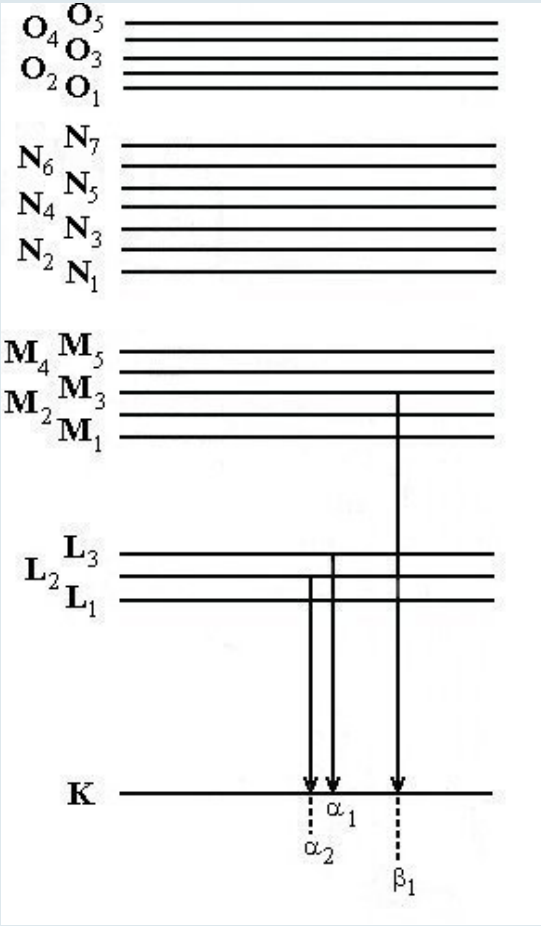
5.) Spatial resolution and excitation range in EDS analysis

4.) Characteristic peaks: K, L, M series



- Energy of characteristic peaks is defined by element
- The higher the atomic number Z the higher the peak energy

The K-family of lines (1)



K-lines: vacancy in K-level is filled

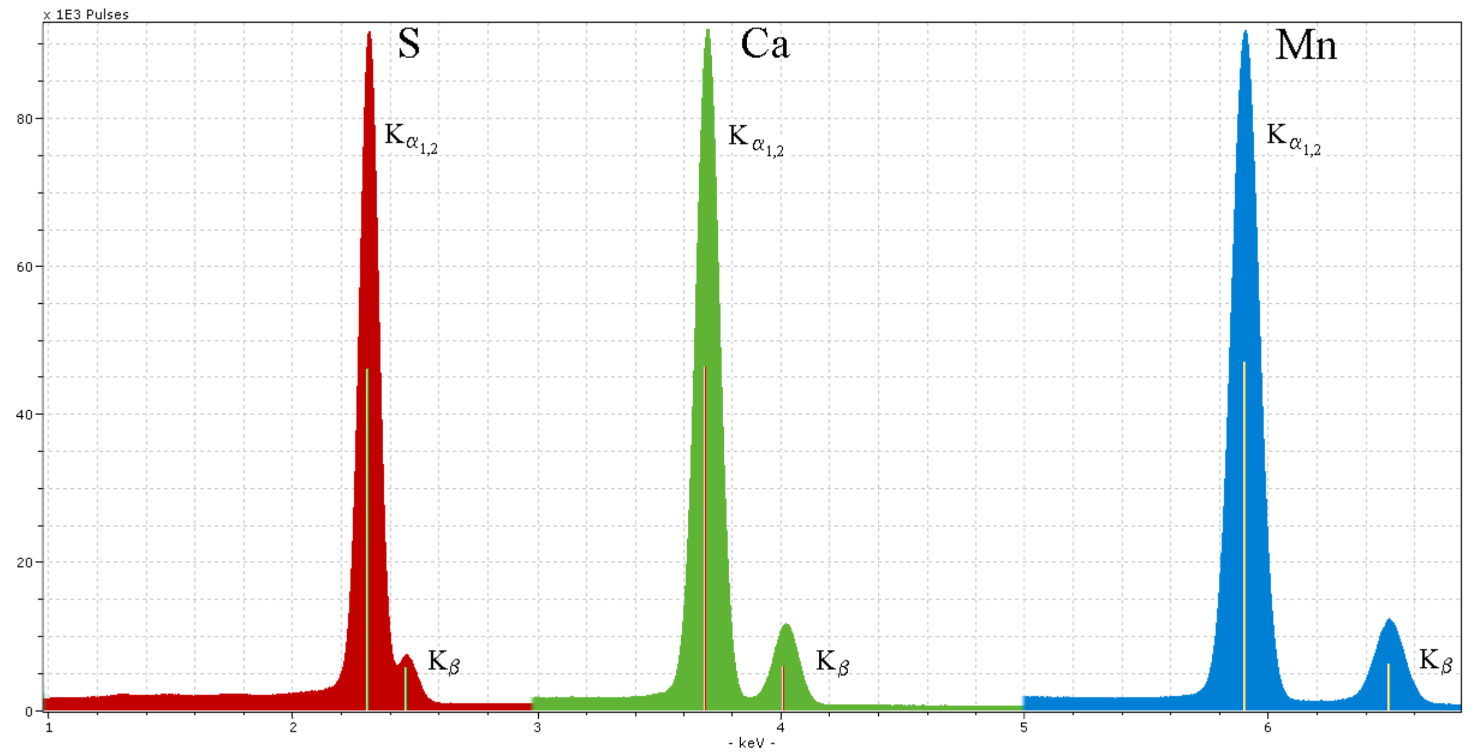
α- lines are L -K transitions

β- lines are M-K transitions

The K-family of lines (2)

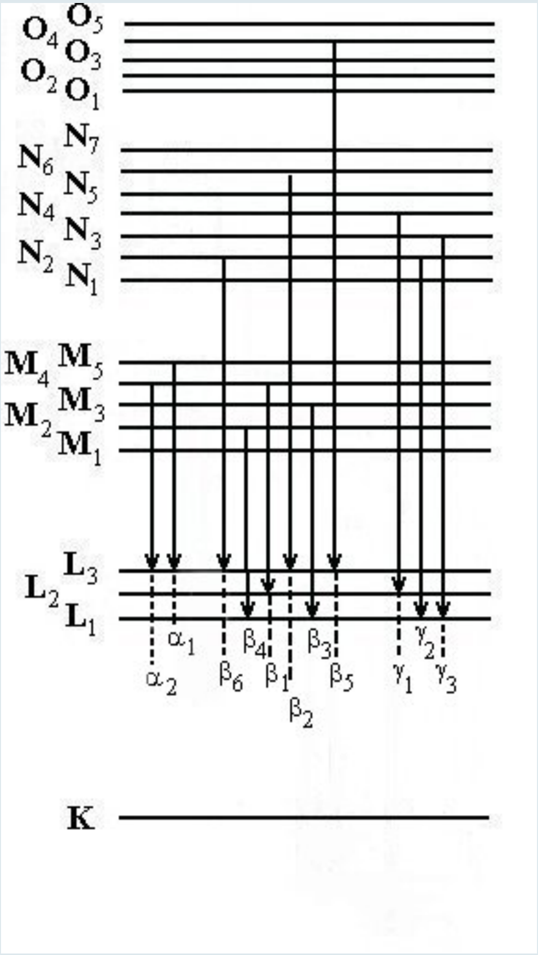
- K lines in ED spectra are either a combination of Kα + Kβ peaks or a separated pair (Kβ weight then about 1/8 ... 1/10)
- Below element S (Kα = 2308 eV) it is not possible to resolve the two peaks with EDS → a Kβ shoulder may be visible on the high-energy side of the Kα
- line energy difference (Ka-Kß) is increasing with atomic number
- for SEM (30 kV U_{max}) K lines up to atomic number 42 (Mo) can be excited

The K-family of lines (3)



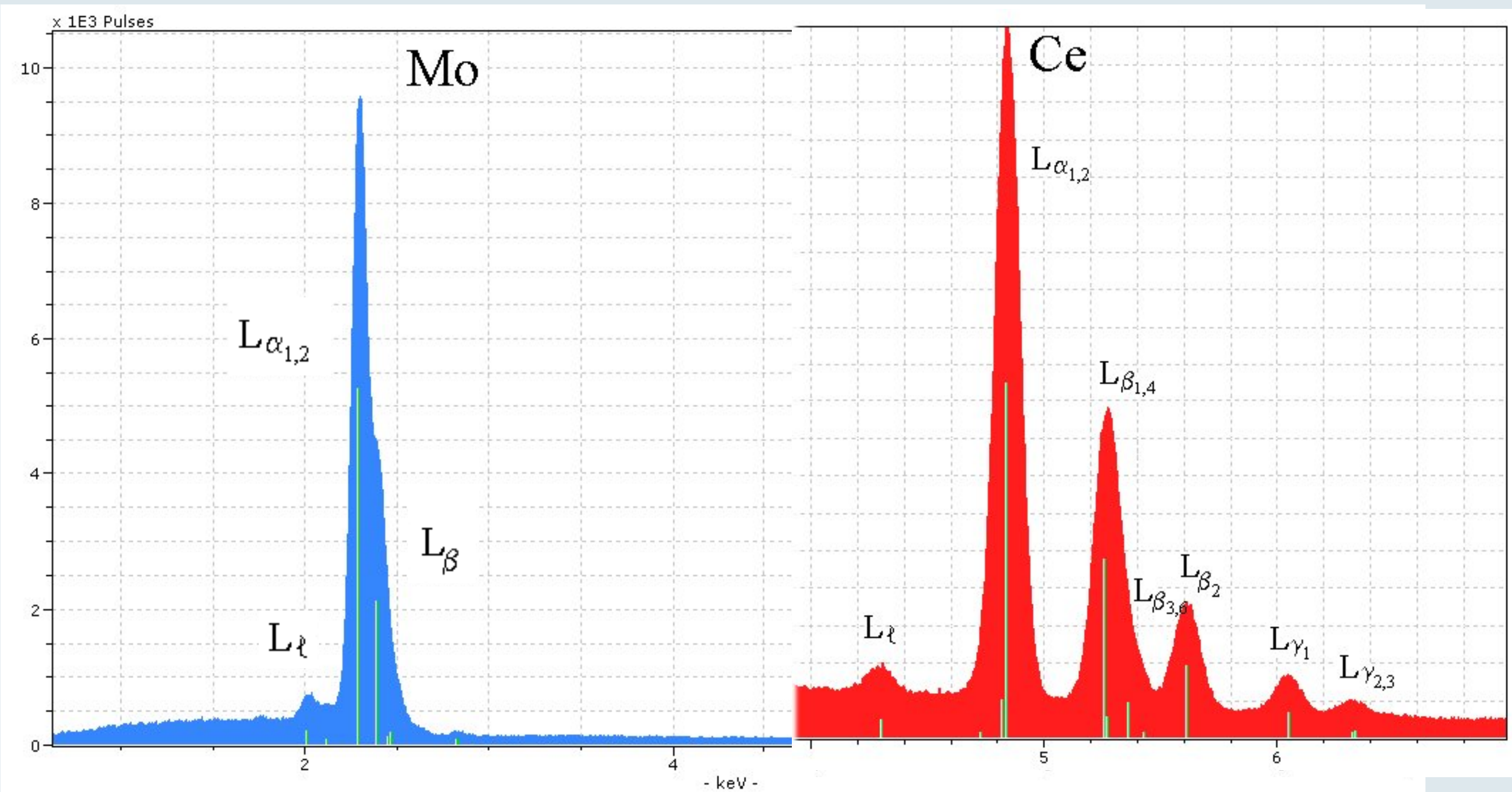
	S (16)	Ca (20)	Mn (26)
$K\alpha_{1,2}$	2308 eV	3692 eV	5900 eV
$K\beta$	2464 eV	4013 eV	6492 eV
$\Delta\ (K\beta - K\alpha_{1,2})$	156 eV	319 eV	592 eV

The L-family of lines (1)



- L-lines occur: vacancy in L-level is filled

The L-family of lines (2)



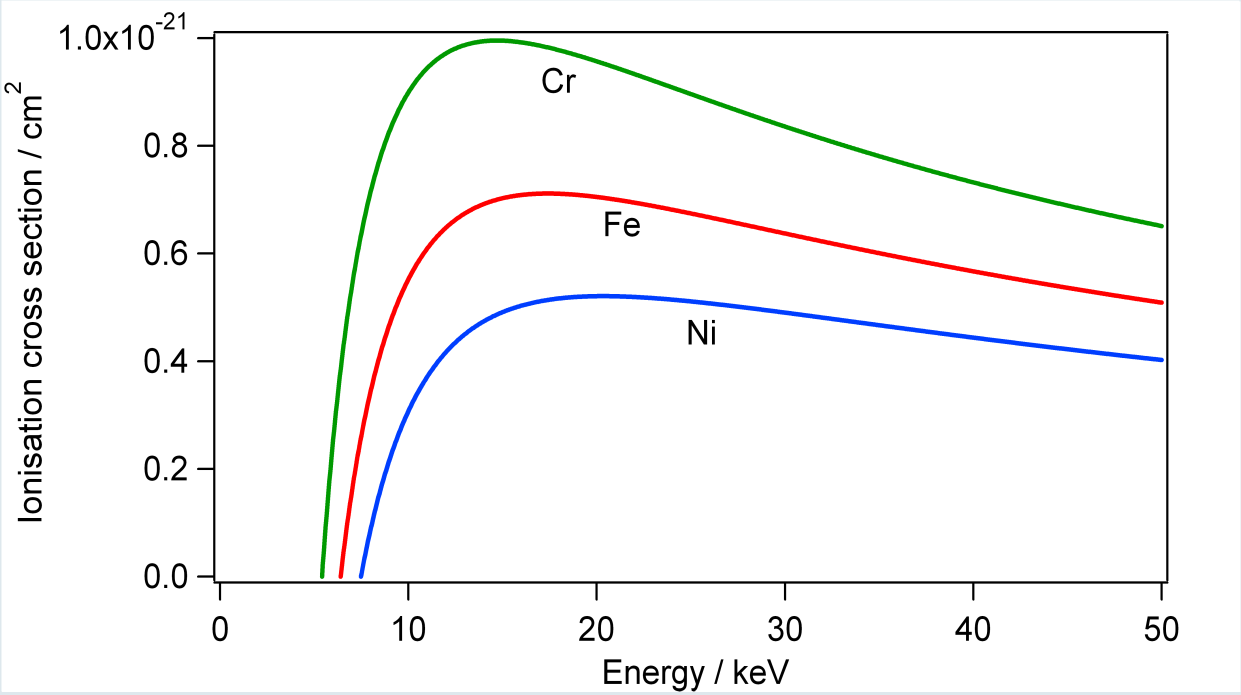
	Mo (42)		Ce (58)
$L\alpha_1$	2292 eV		4839 eV
$L\beta$	2394 eV		5262 eV
L_l	2014 eV		4287 eV

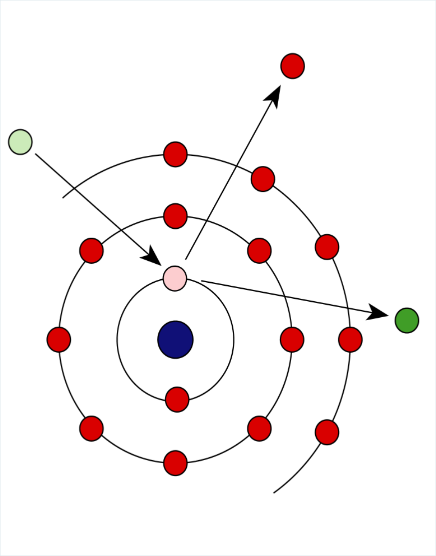
Intensity and energy of characteristic lines

- Energy of line is defined by
  - Element
  - Type of transition

- Intensity of line is defined by
  - probability of producing a hole (vacancy)
  - probability of electron transition
  - probability of x-ray emission
  - concentration

Probability of producing a hole: Ionization cross-section for electrons

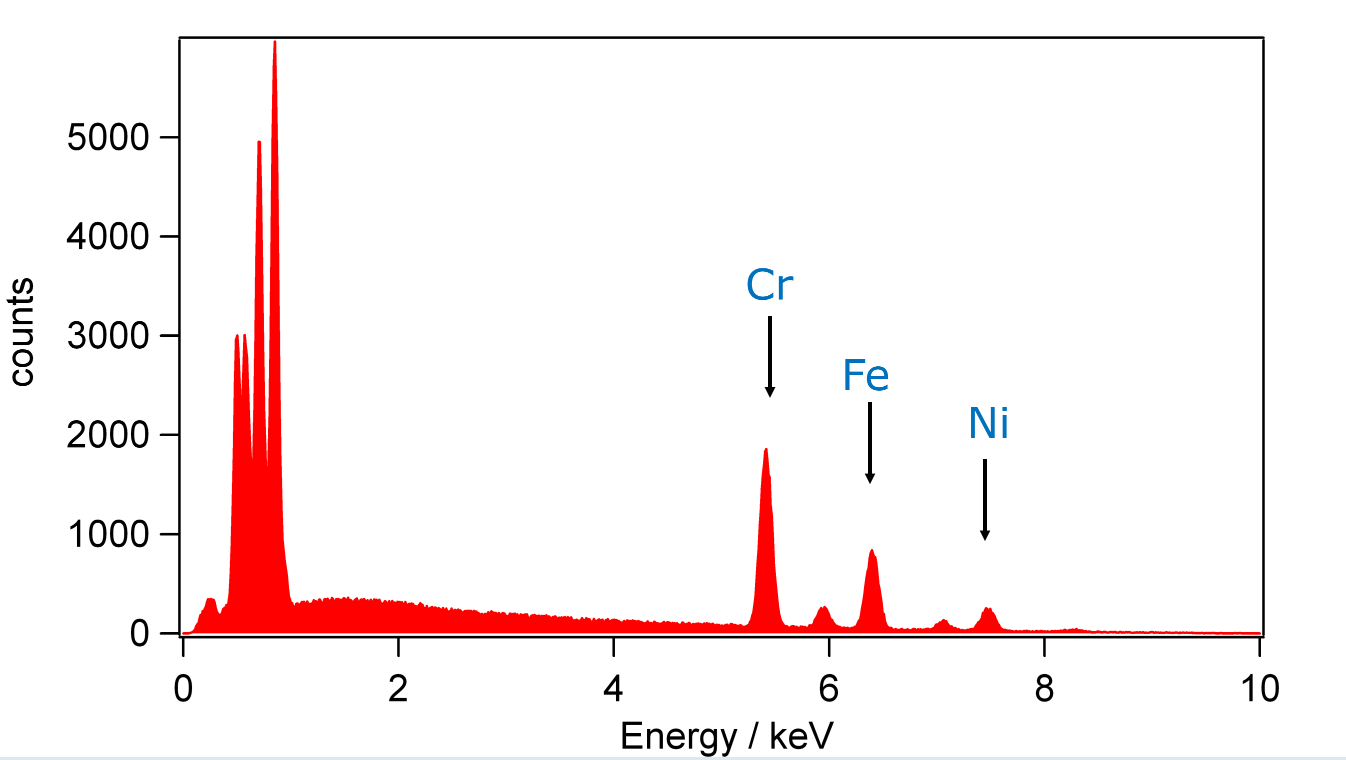




Ionisation cross section for electrons

- Ionization cross section: probability of excitation
- maximum ionization cross section: 2,5 x E_{bind}

Ionization cross section for electrons



Cr: 33%

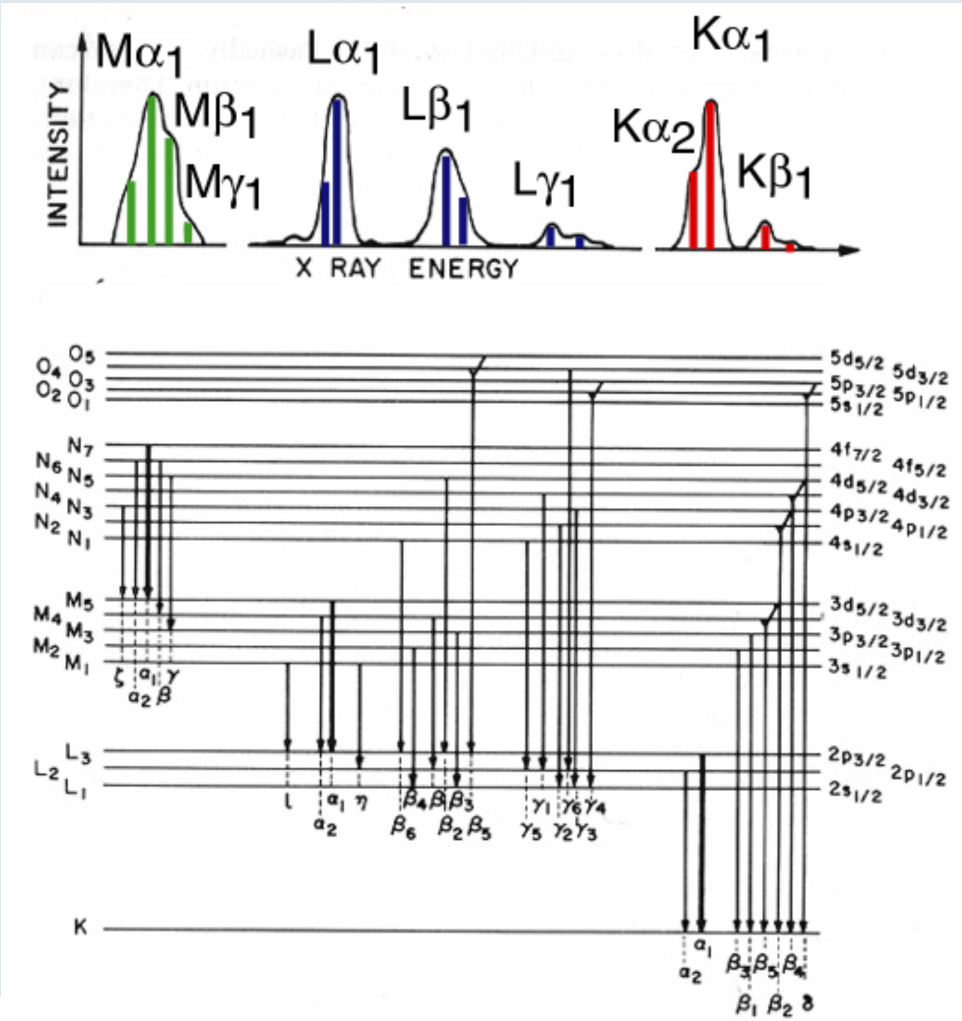
Fe: 33%

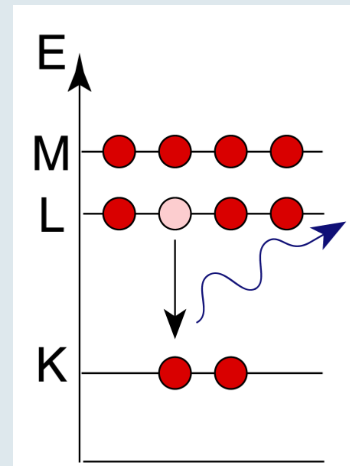
Ni: 33%

U = 10 keV

$\frac{E_{exc}}{E_{bind}}$:	Cr	Fe	Ni
	1,847	1,561	1,337

Atomic energy levels and line transition

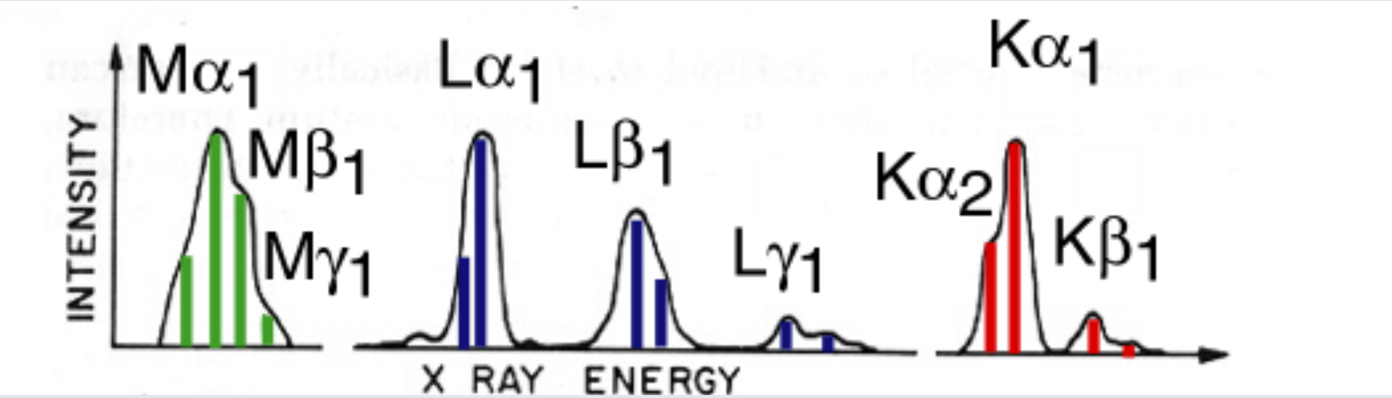




Transitions have different probabilities

Lines have different intensities

Line intensity relations



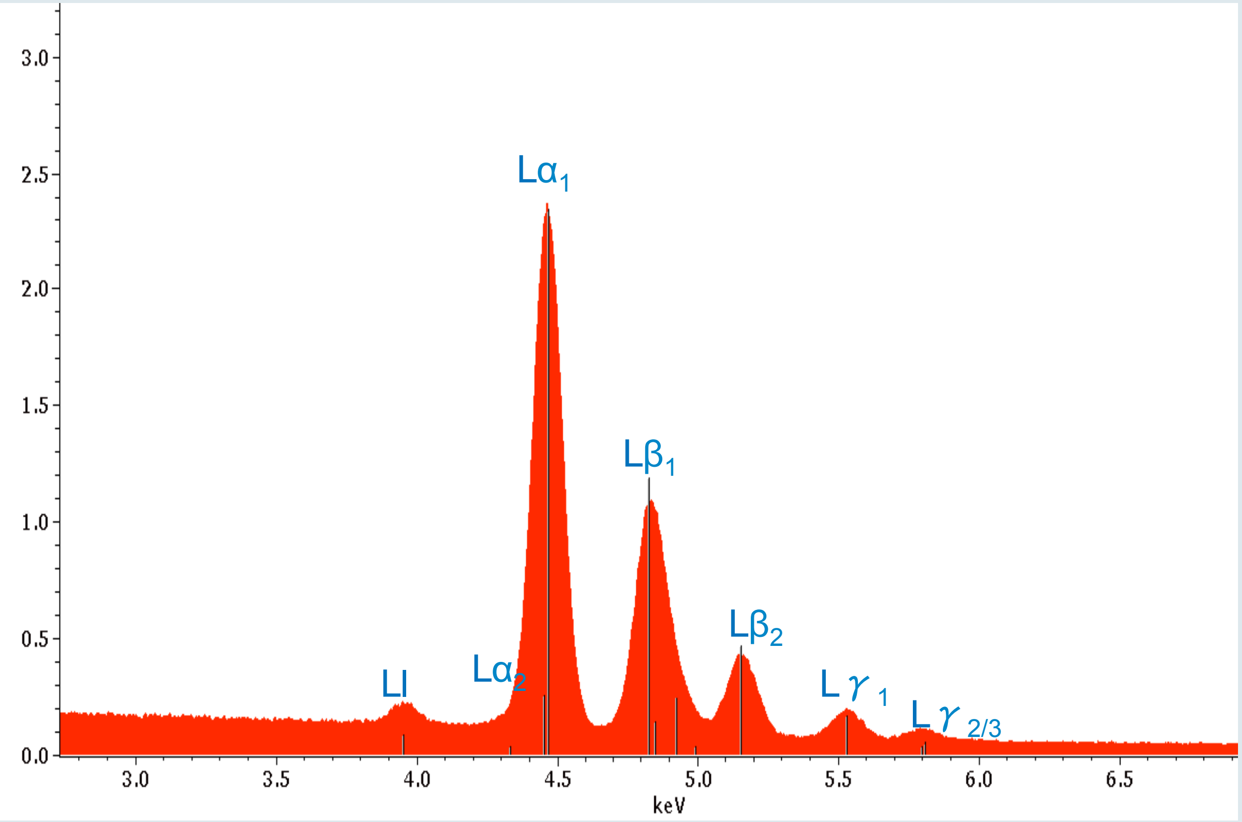
Intensity of an x-ray line is determined by the transition probability of electrons from the outer to inner shell. These values are fixed for the lines of one series.

K- series: $Z < 12 \longrightarrow \alpha_1 : \alpha_2 : \beta_1 = 100 : 50 : 15$

$13 > Z < 50 \longrightarrow \alpha_1 : \alpha_2 : \beta_1 = 100 : 53 : 18$

L- series: $15 > Z < 90 \longrightarrow \alpha_1 : \beta_1 : \gamma_1 = 100 : 52 : 10$

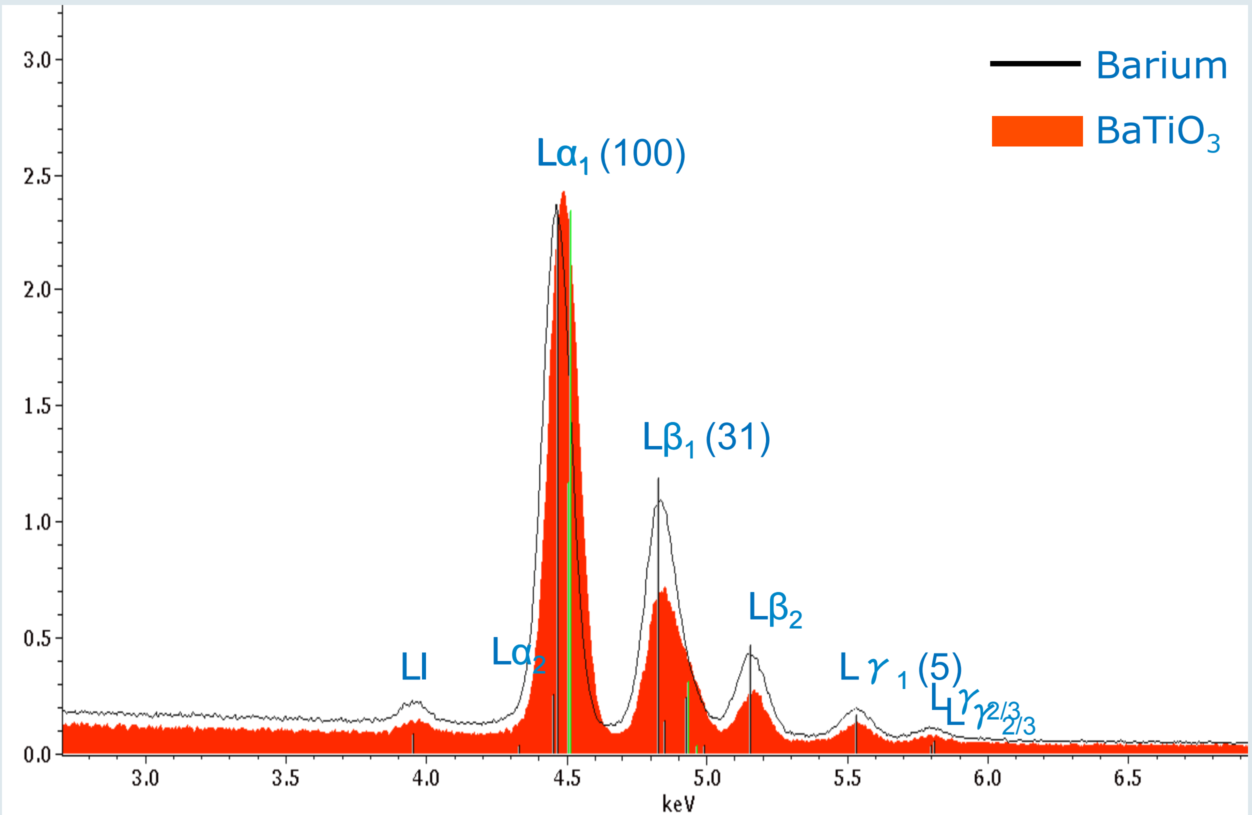
Line intensity relations (2)



Spectrum Barium L series, 15 kV

α1 : **β**1 : **γ**1 = 100 : 52 : 10

Line intensity relations (3)



~~Spectrum Barium L-series, 15 kV~~

~~**α**1 : **β**1 : **γ**1 = 100 : 52 : 10~~

Spectrum $BaTiO_3$, 15 kV

Overlapped Ba L-series and Ti K-series

Outline

1.) Beam-specimen interactions

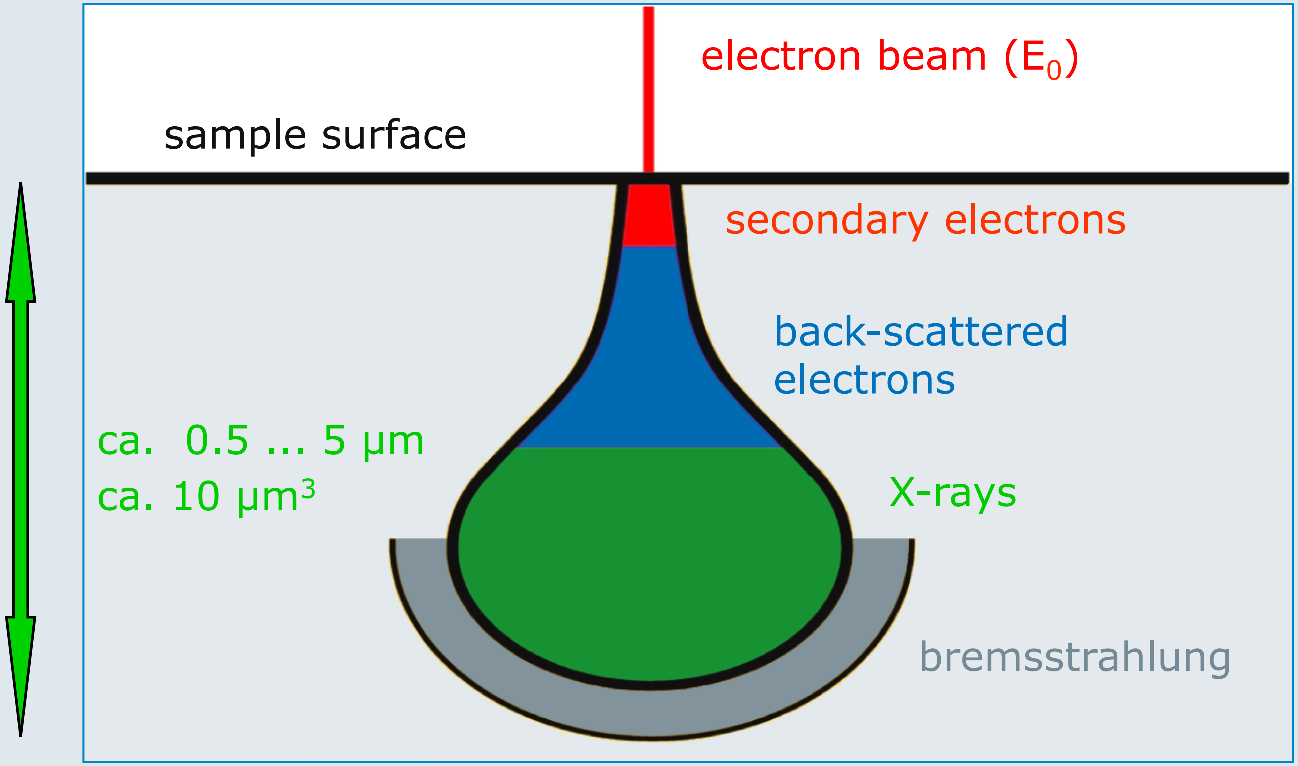
2.) EDS spectra: Origin of Bremsstrahlung and characteristic peaks

3.) Moseley‘s law

4.) Characteristic peaks: K-,L-, and M series

5.) Spatial resolution and excitation range in EDS analysis

5.) X-ray range



Different excitation ranges for:
- characteristic x-ray radiation and Bremsstrahlung,
- secondary electrons (SE)
- back-scattered electrons (BSE)

5.) X-ray range

Dependence HV - x-ray range:

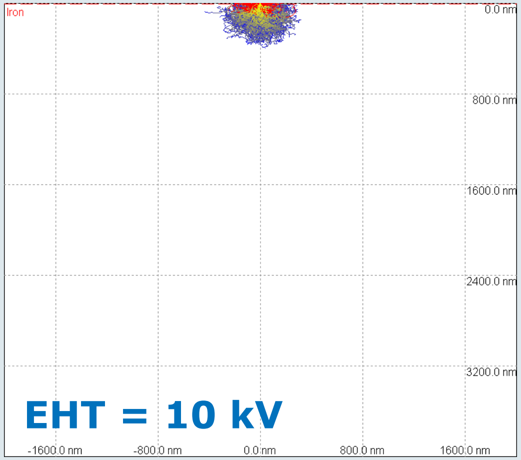
Anderson and Hasler (1966) give the depth of X-ray production range (µm) as:

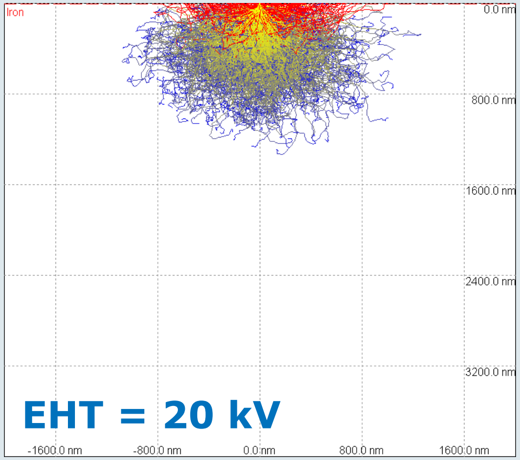
$$R_{AH}=0.064(E_0^{1.68} - E_c^{1.68}) / \rho$$

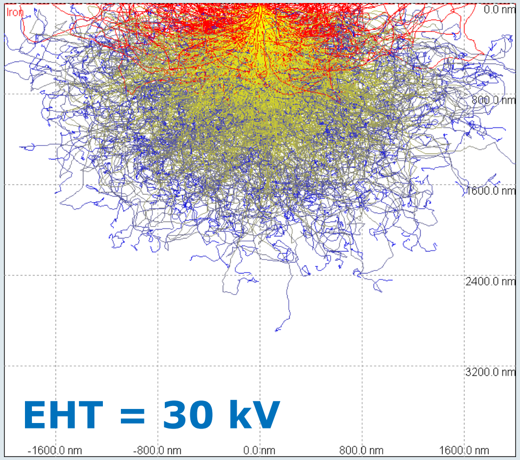
E_0: primary energy (keV),
Ec: critical energy (keV),
ρ: mean density (g/cm^3)

5.) X-ray range

- Monte Carlo electron-trajectory simulations of interaction volume in iron as function of primary beam energy





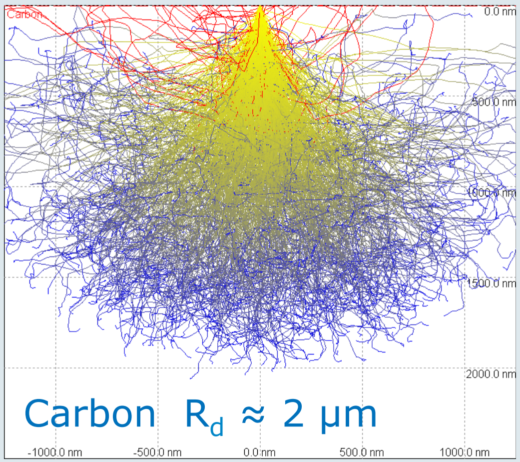


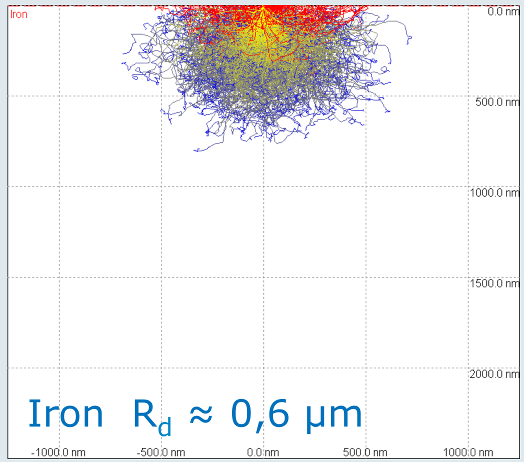
$R_d \approx 0{,}4\ \mu m$ $R_d \approx 1{,}3\ \mu m$ $R_d \approx 2{,}5\ \mu m$

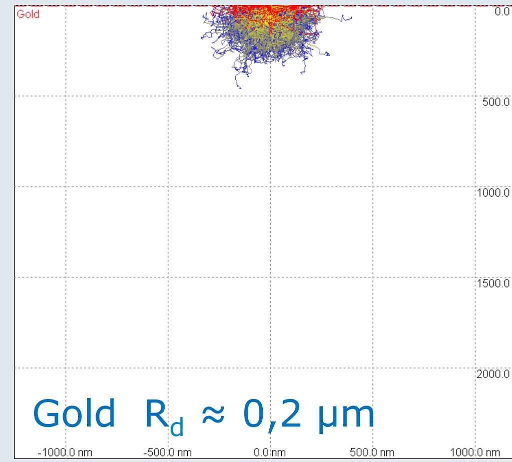
→ With higher primary electron energy penetration depth is increasing

5.) X-ray range

- Monte Carlo electron-trajectory simulations of interaction volume as function of atomic number (EHT = 15 kV)







→ With higher density penetration depth is decreasing

The kV compromise

I_{char} increases with increasing E_0/E_c

→ X-ray signal improves

R_x increases with increasing E_0/E_c

→ X-ray spatial resolution degrades

$$\boxed{U_0 = \frac{E_0}{E_C} > 2 \ldots 2{,}5}$$

www.bruker-nano.com