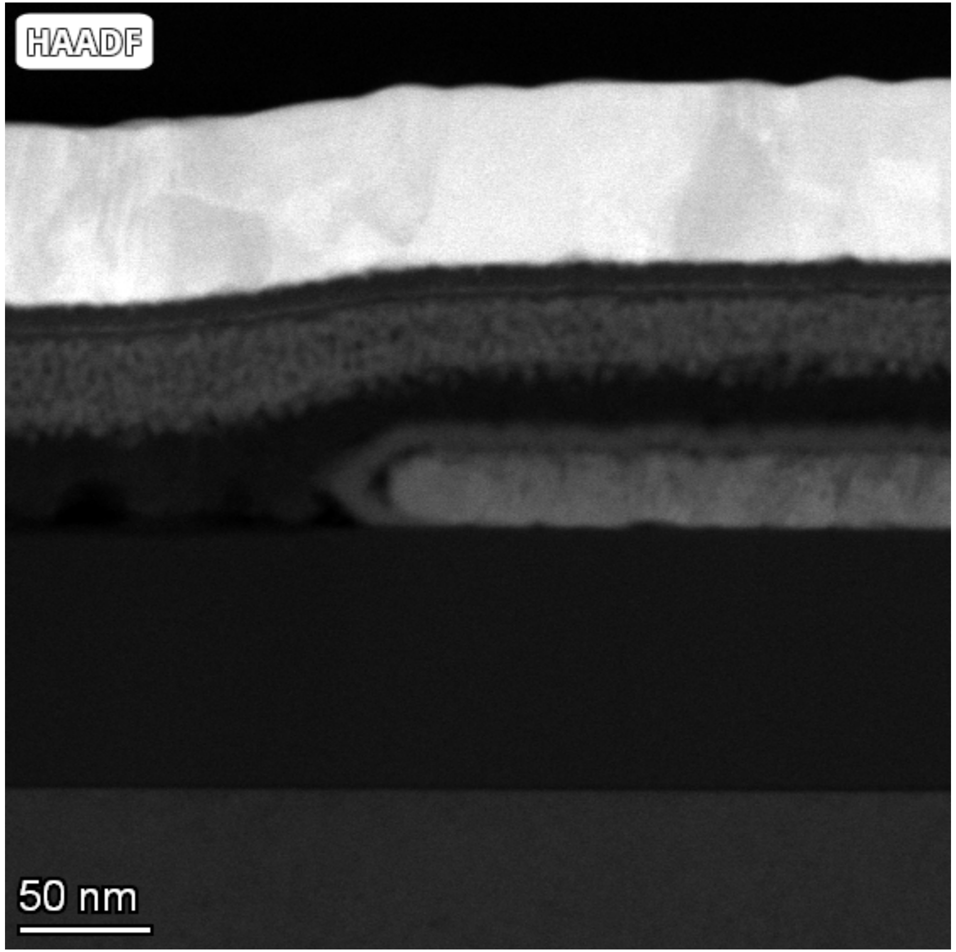
Analytical TEM part I

Duncan Alexander
EPFL-IPHYS-LSME

Adding colour to microscopy!

- Multilayer from first STEM lecture

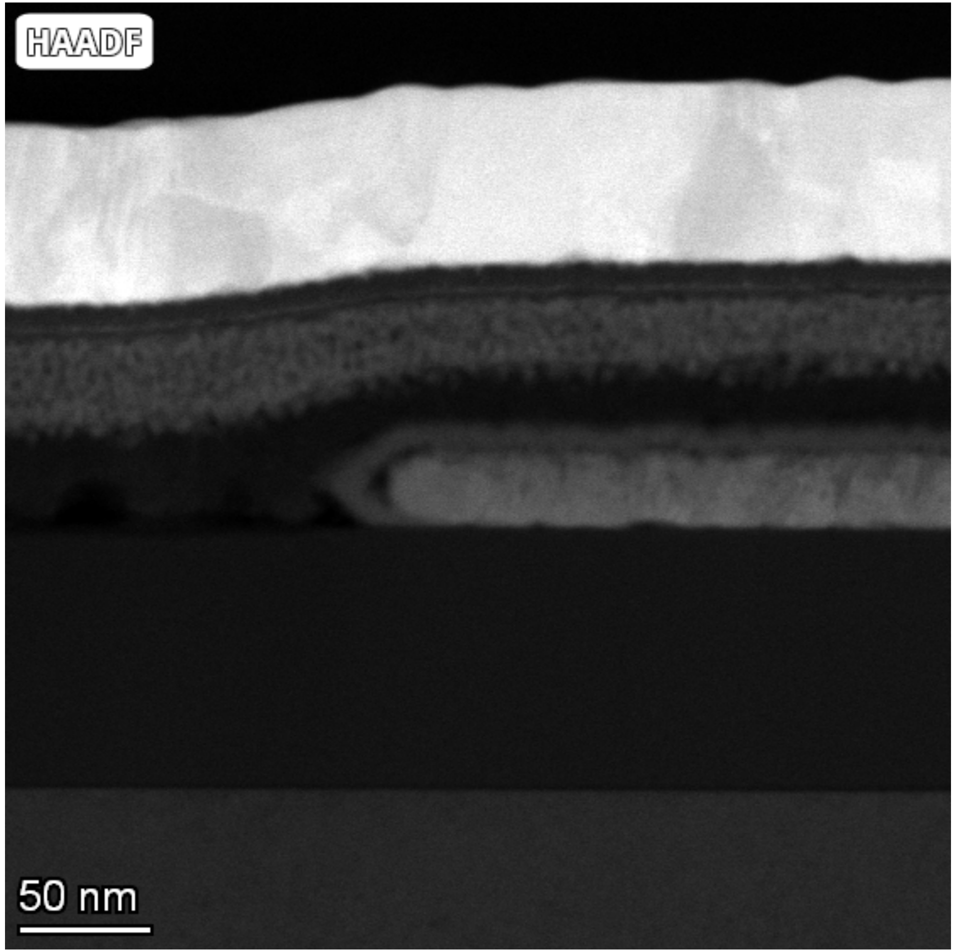


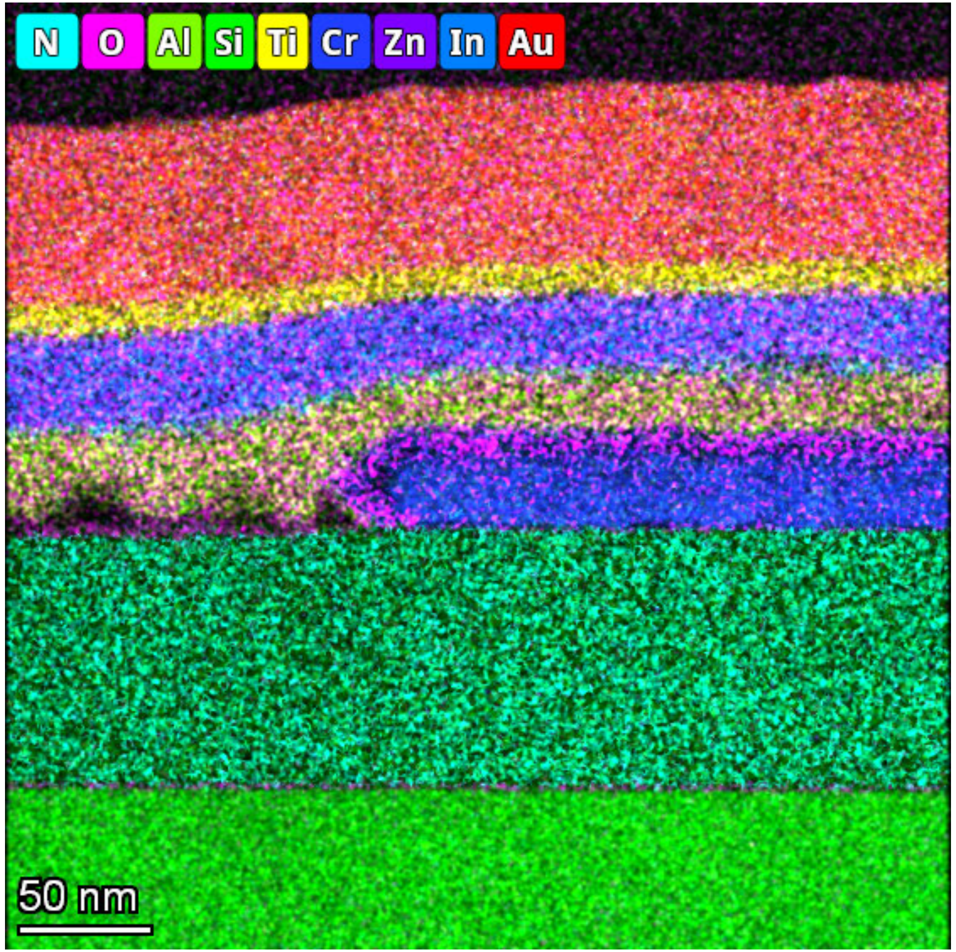
$I \propto Z^{1.6-1.9}$

Adding colour to microscopy!

EDX spectroscopy

- Multilayer from first STEM lecture





Contents

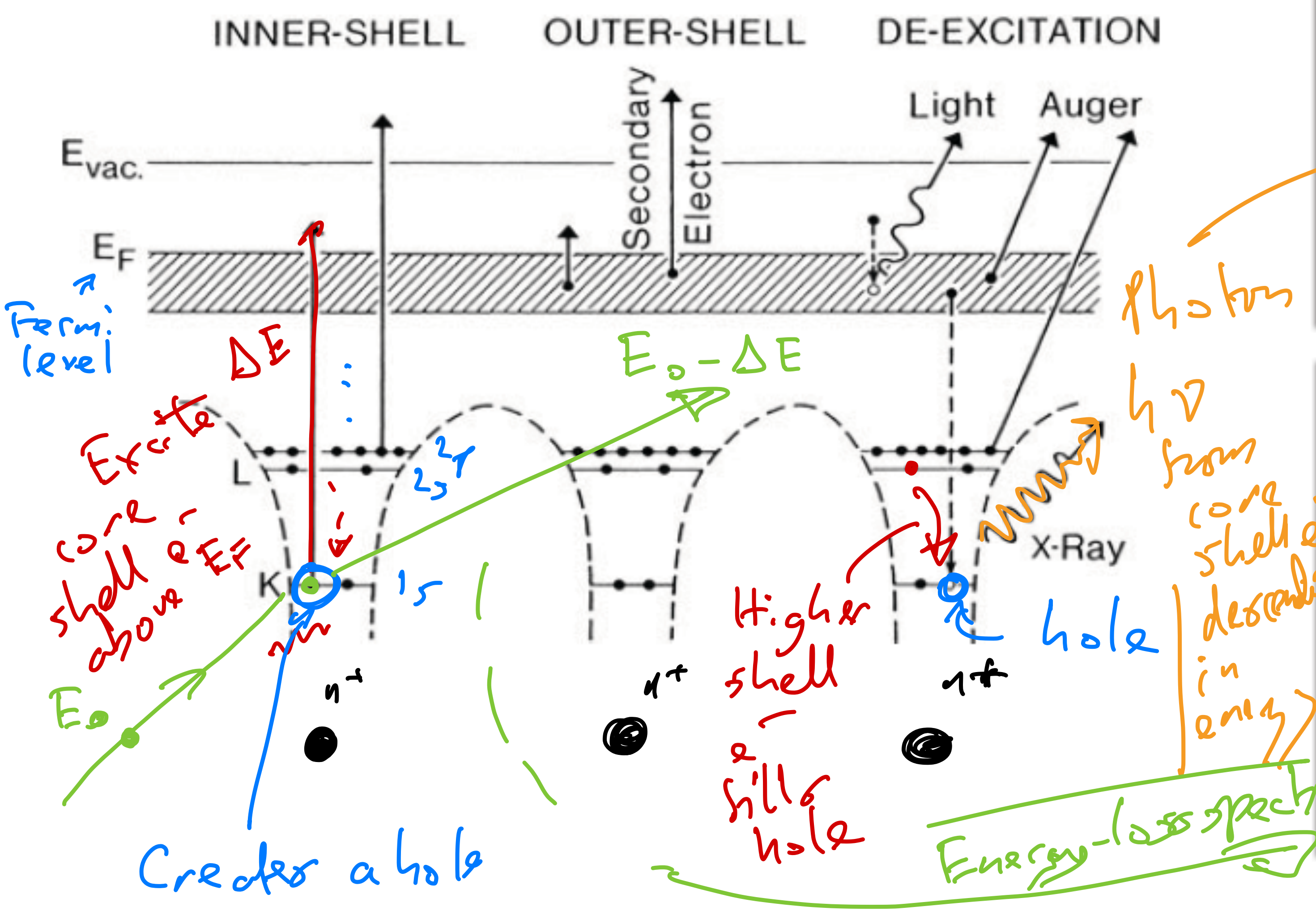
- Introduction to EDX spectroscopy and EELS
- Energy dispersive X-ray (EDX) spectroscopy
  - X-ray generation
  - EDX spectrum
  - Detector setup
  - Applications

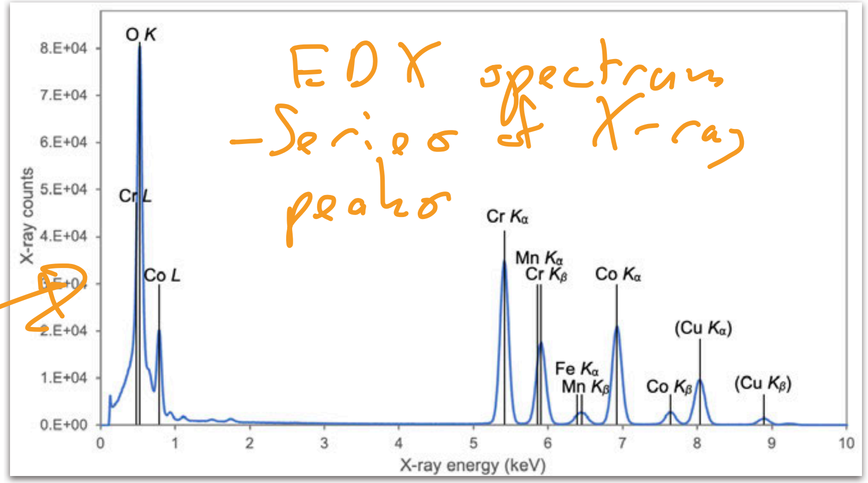
A way to probe chemistry

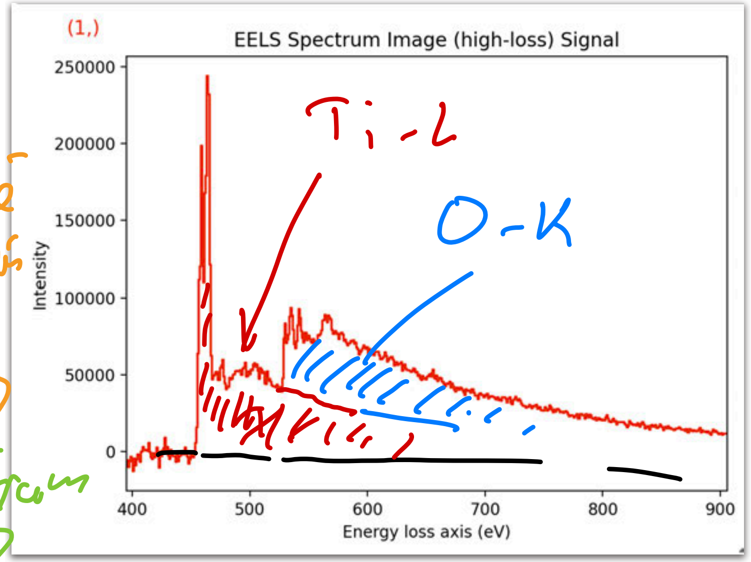
[IONIZE ATOM]

Incident e⁻ energy E_0

E_0 : 80–300 keV (from high tension)

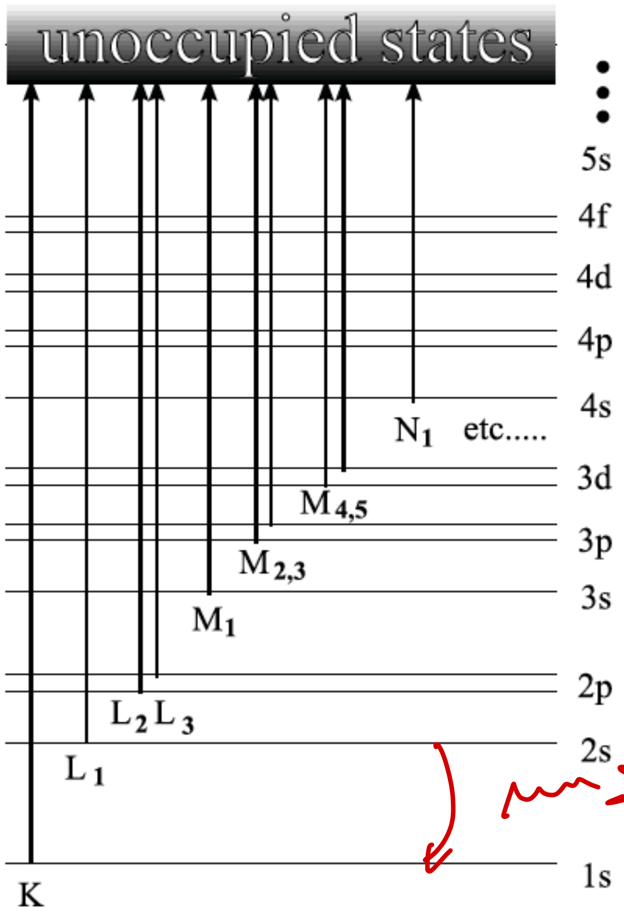






Edges and peaks nomenclature

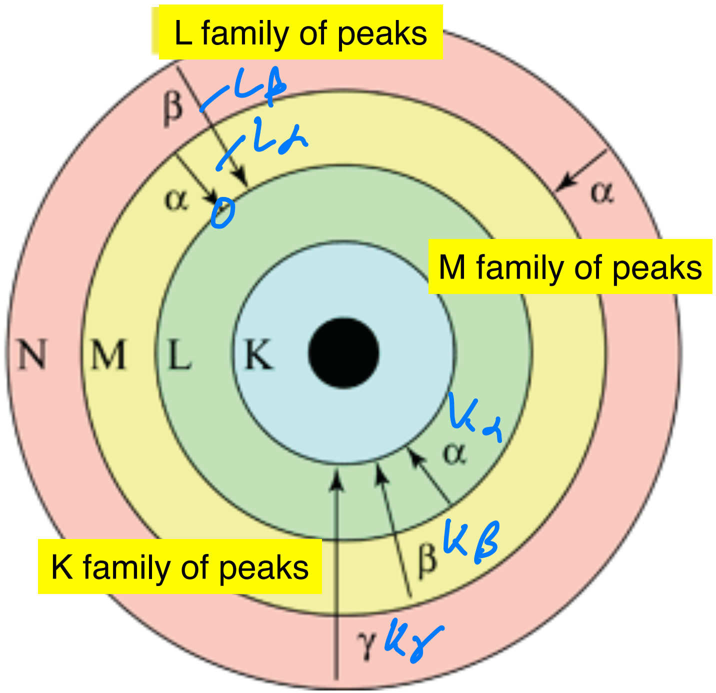
EELS



ΔE

→ hν X-ray

EDXS – X-ray transition



Kα, Kβ
Lα, Lβ
M.....

Quiz

EDX, EDS, XEDS

- EDXS: energy dispersive X-ray spectroscopy
  $\Longrightarrow$ intensity spectrum of X-ray peaks separated by energy
- EELS: electron energy-loss spectroscopy
  $\Longrightarrow$ intensity spectrum of energy lost by transmitting e^- (ΔE)
- We look at a sample containing Oxygen. We detect the Oxygen K-edge both in EELS and in EDXS. We find the transition at E_{EELS} in EELS and E_{EDXS} in EDXS
- Do we have:
  - 1) $E_{EELS} > E_{EDXS}$
  - 2) $E_{EELS} = E_{EDXS}$
  - 3) $E_{EELS} < E_{EDXS}$

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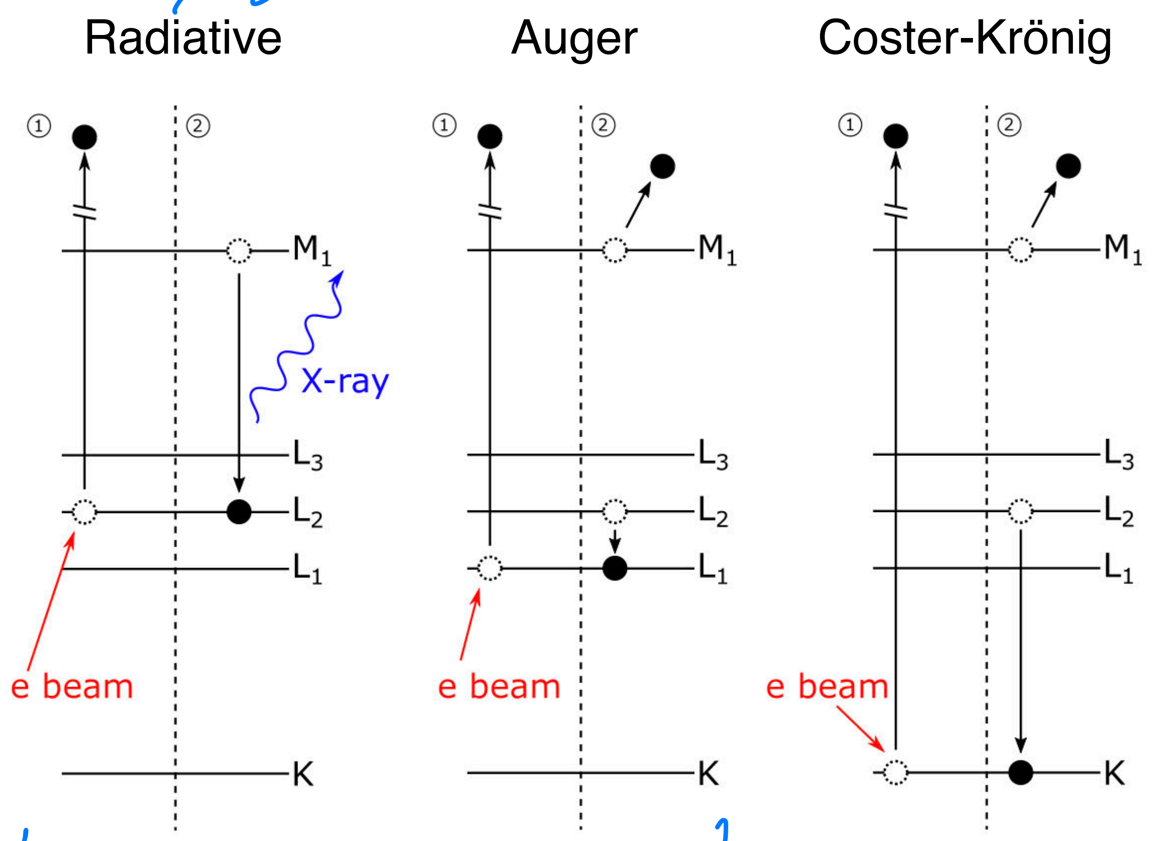
X-ray generation

X-ray generation

- 3 basic de-excitation process:
  - Radiative X-ray emission
  - Auger transitions/emission
  - Coster-Krönig transitions
- Complex "cascade" effects possible

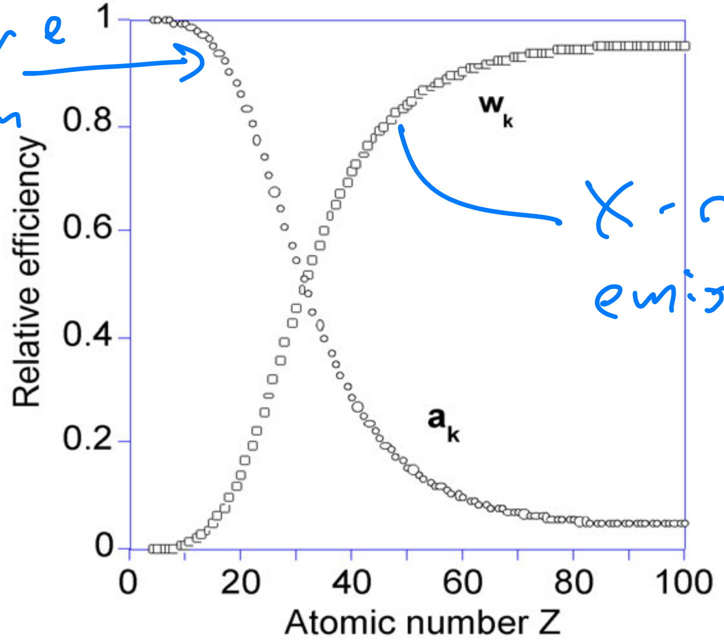


Excitation probabilities can be calculated

2 transitions "in competition"

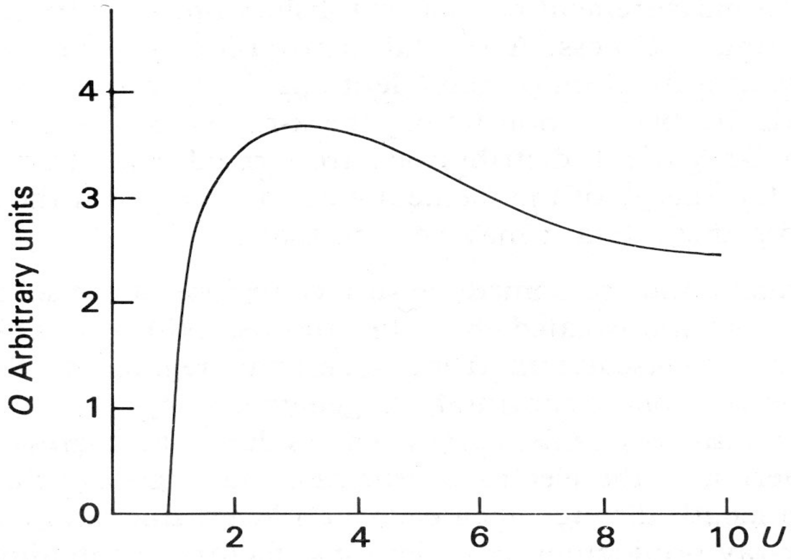
X-ray generation

Relative efficiency of X-ray and Auger emission vs. atomic number for K lines



Light element atoms return to fundamental state mainly by Auger emission. For that reason, their K-lines are weak. In addition their low energy makes them easily absorbed.

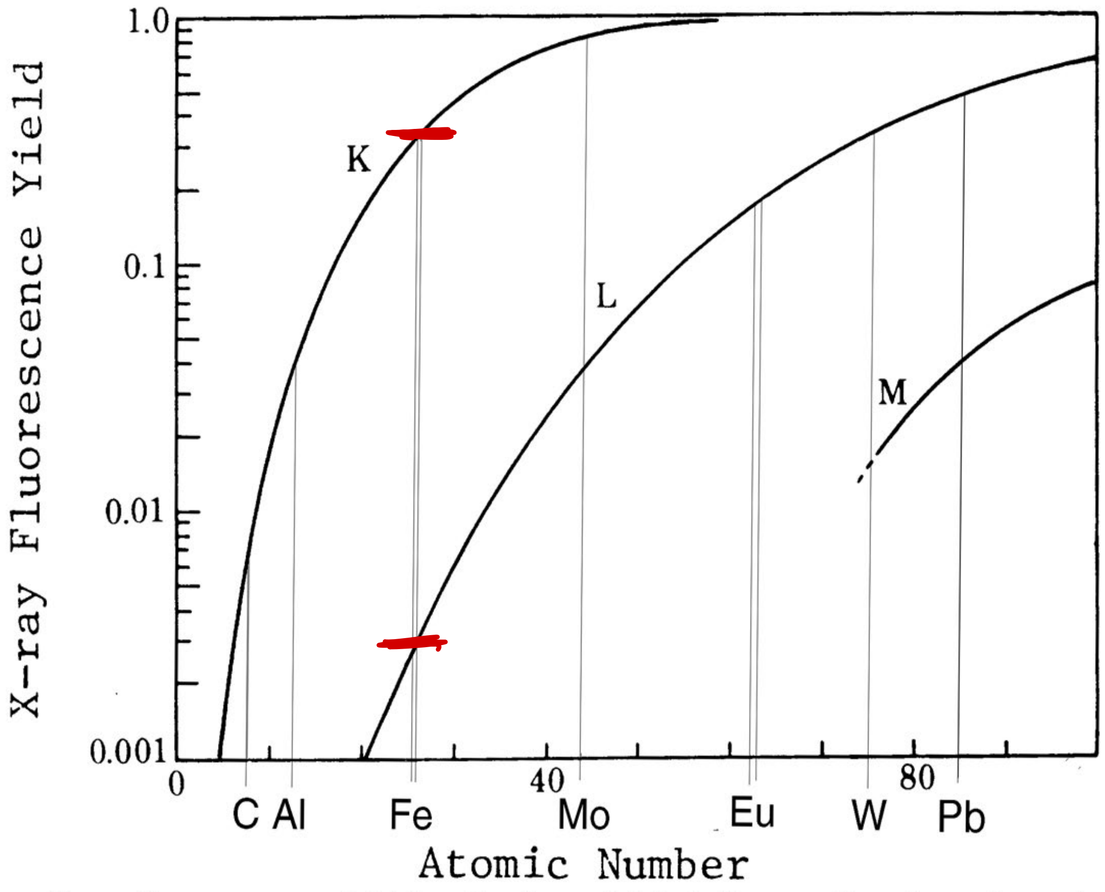
X-ray generation ↑ as Z ↑



To ionise an atom, the incident electron MUST have an energy larger than the core shell level U>1. To be efficient, it should have about twice the edge energy U>2.

(S)TEM: U ≥ 60 keV
⇒ All X-rays excited

Fluorescence yield



X-ray fluorescence yield for *K*-, *L*-, and *M*-shells, as a function of atomic number.

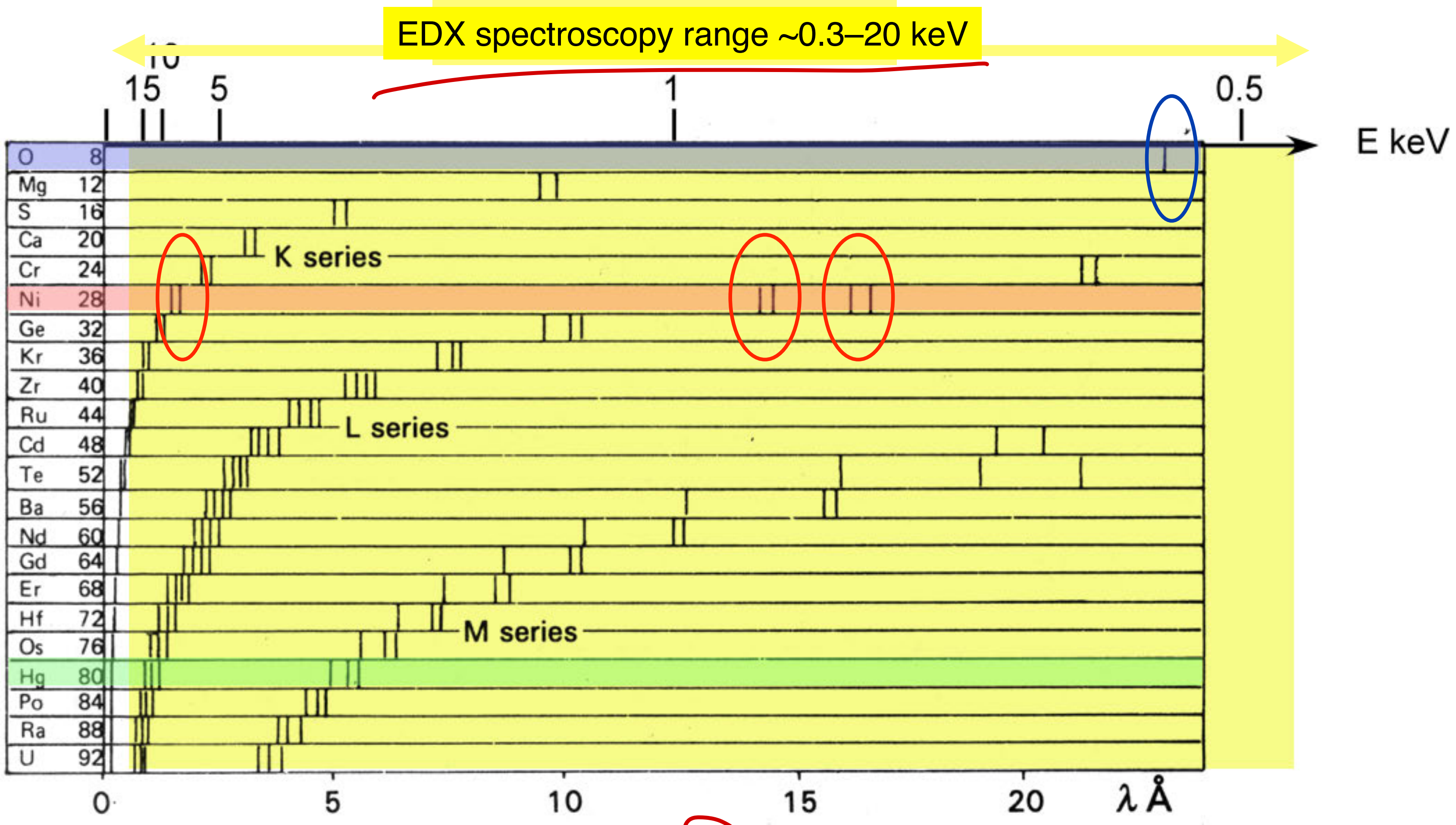
Probability of ionization
+ prob. of de-excitation as X-ray emission

↓

Peak intensity

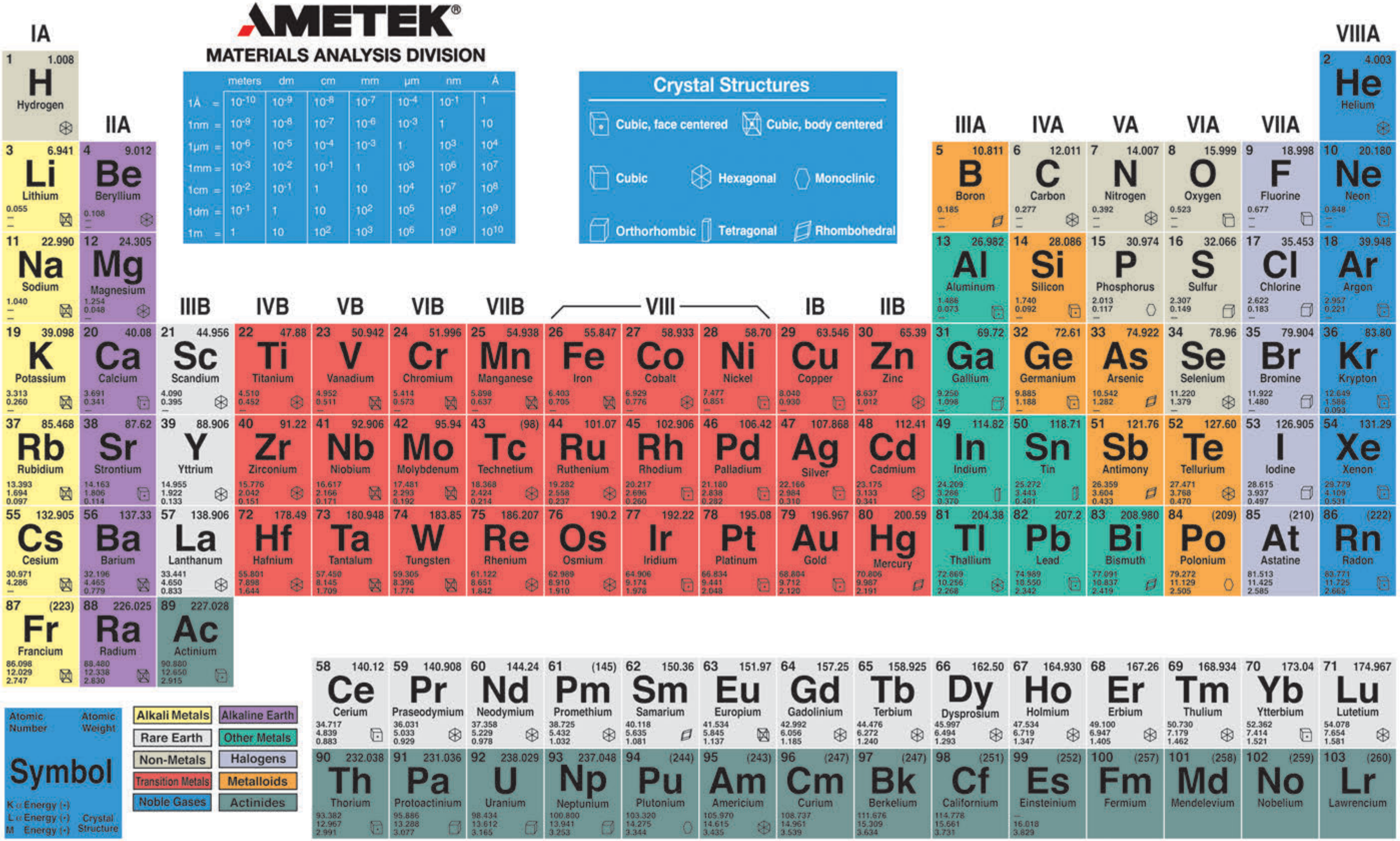
For each Z:
"Fixed" intensity ratios between their peaks
e.g. Kα : Kβ
L : K

Separation of EDX peaks



[↑ Wavelength-dispersive X-ray spectroscopy – (WDXS)]

Periodic table of X-ray peaks



Periodic table of X-ray peaks

Energies in keV

IIIA	IVA	VA	VIA	VIIA	
					2 4.003 **He** Helium
5 10.811 **B** Boron 0.185	6 12.011 **C** Carbon 0.277	7 14.007 **N** Nitrogen 0.392	8 15.999 **O** Oxygen 0.523	9 18.998 **F** Fluorine 0.677	10 20.180 **Ne** Neon 0.848
13 26.982 **Al** Aluminum 1.486 0.073	14 28.086 **Si** Silicon 1.740 0.092	15 30.974 **P** Phosphorus 2.013 0.117	16 32.066 **S** Sulfur 2.307 0.149	17 35.453 **Cl** Chlorine 2.622 0.183	18 39.948 **Ar** Argon 2.957 0.221
31 69.72 **Ga** Gallium 9.250 1.098	32 72.61 **Ge** Germanium 9.885 1.188	33 74.922 **As** Arsenic 10.542 1.282	34 78.96 **Se** Selenium 11.220 1.379	35 79.904 **Br** Bromine 11.922 1.480	36 83.80 **Kr** Krypton 12.649 1.586 0.093
49 114.82 **In** Indium 24.209 3.286 0.370	50 118.71 **Sn** Tin 25.272 3.443 0.401	51 121.76 **Sb** Antimony 26.359 3.604 0.433	52 127.60 **Te** Tellurium 27.471 3.768 0.470	53 126.905 **I** Iodine 28.615 3.937 0.497	54 131.29 **Xe** Xenon 29.779 4.109 0.531

No X-ray because no 2s... e^- only 1s

← K peaks

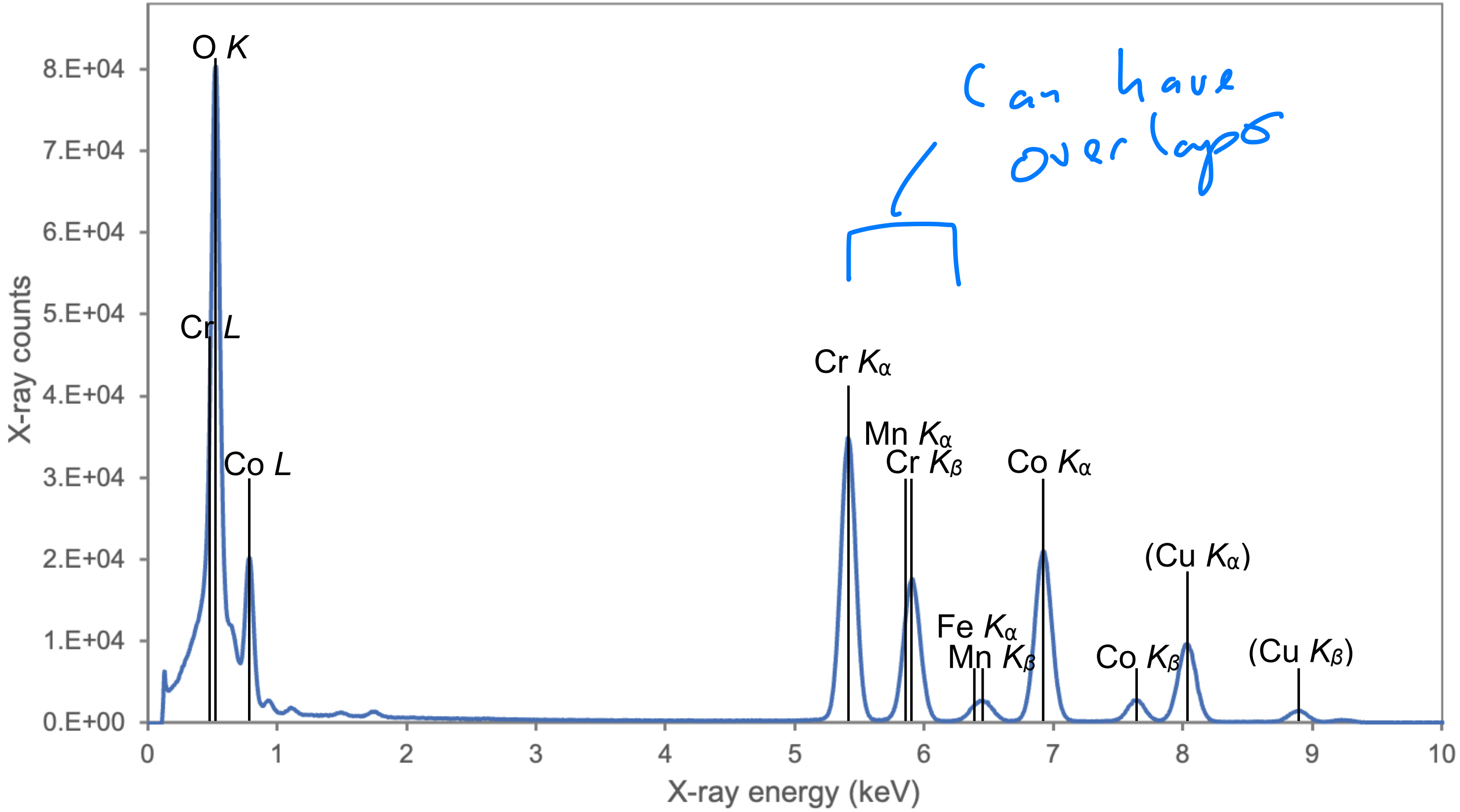
← K ← L

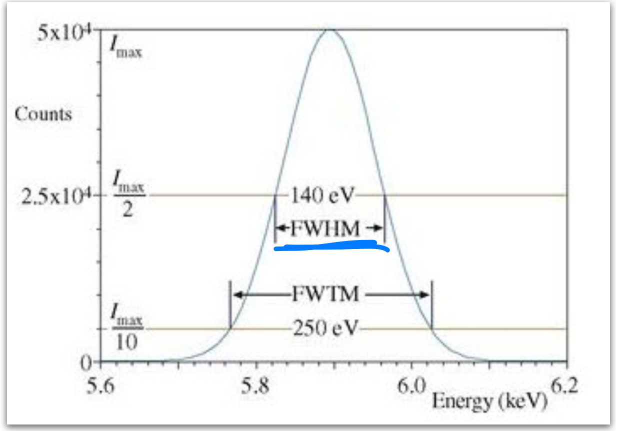
K L M

As Z ↑ X-ray energy ↑ because core-shell e^- goes down to deeper level

The EDX spectrum

- Example spectrum from fuel cell sample containing O, Cr, Mn, Fe, Co
- Spectrum of mostly well-defined peaks that e.g. can be fitted with Gaussians



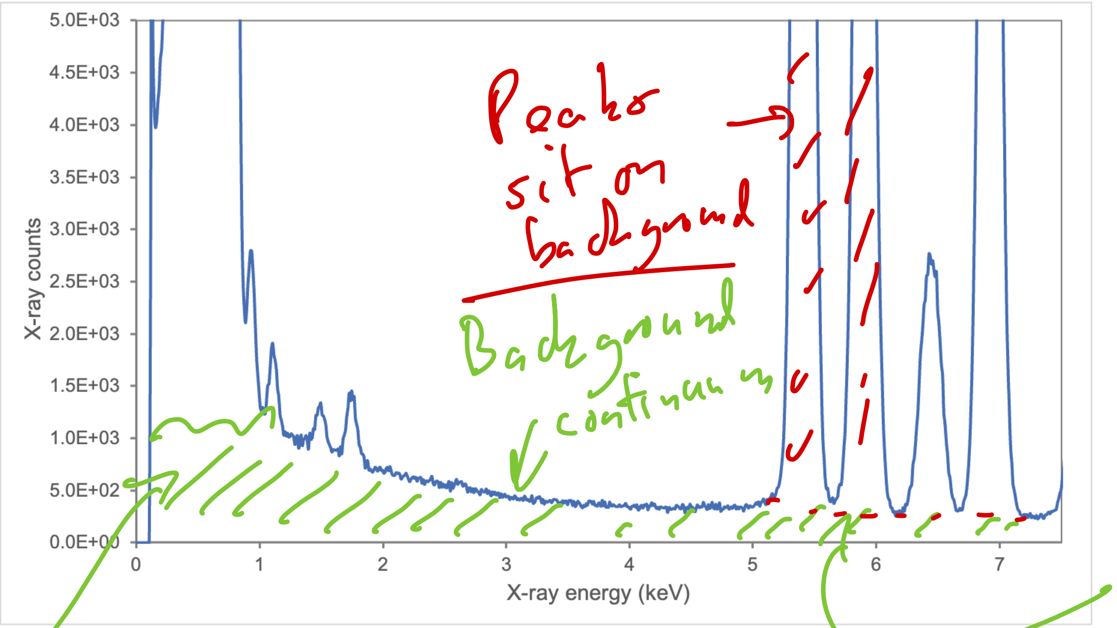


Width of peak determined by detector

typically 120-140eV in width

Bremsstrahlung background

- Continuum background of radiation emitted when e⁻ velocity changed by atomic field
- Stronger at low keV; depends on atomic number *Z*



Fitting error

Transmitting e⁻ changes momentum

emission of radiation

"braking radiation"

Fitting challenge

"State-of-the-art" model by Chapman (down to 1 keV): $I_{\text{brem}} = \dfrac{\beta_0}{E_{\text{X-ray}}} + \beta_1 + \beta_2 E_{\text{X-ray}}$

$\beta_0, \beta_1, \beta_2$: empirical values

EDXS quantification

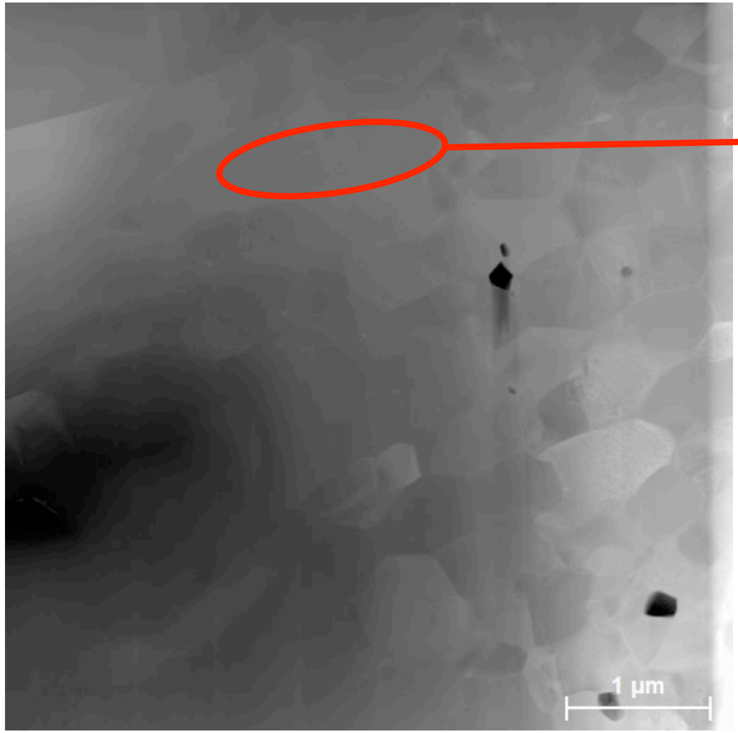
- To go from qualitative to quantitative: measure the intensities I_j of the X-ray peaks (area under the peak)
- Typically apply "Cliff-Lorimer" approach where calculate ratios of constituent elements:

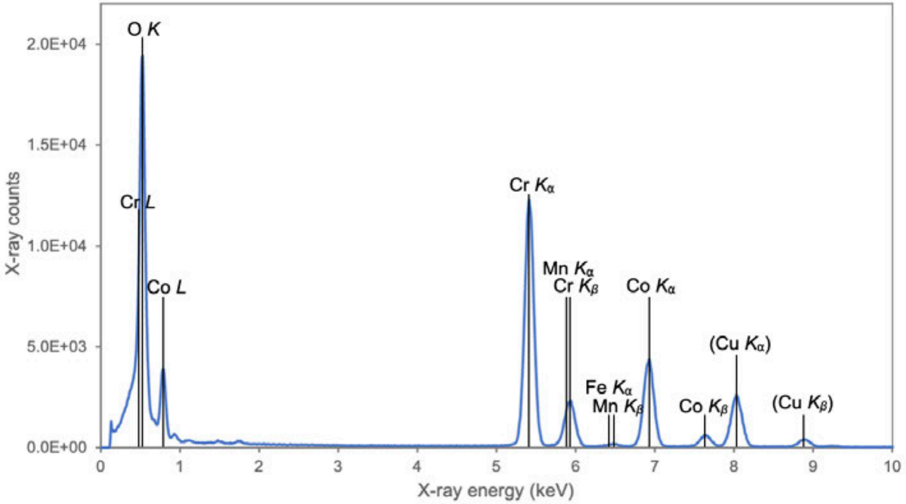
$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B}$$

- k_{AB}: *k*-factor
  – determined empirically by: standards / theoretical calculations / empirical models
- *k*-factors relate to probability of X-ray emission, probability of X-ray absorption and probability of unabsorbed X-ray being detected
- Rule of thumb: quantification accuracy 10–20%. However, much better (e.g. 1%) can be achieved in certain cases
- Detection limit: ~0.1 – a few at. %

EDXS quantification

- Example: Cr-rich grain in fuel cell spinel layer





Element	Peak series	At. %
Cr	K	33.7
Co	K	13.8
Mn	K	2.5
Fe	K	0.1
O	K	49.9

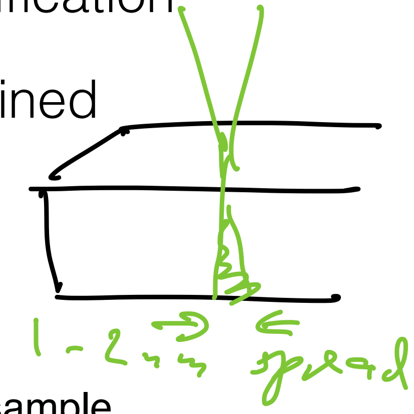
Spinel : AB_2O_4
A, B, transition metals
→ 57 at% O

Better relative accuracy

14% error

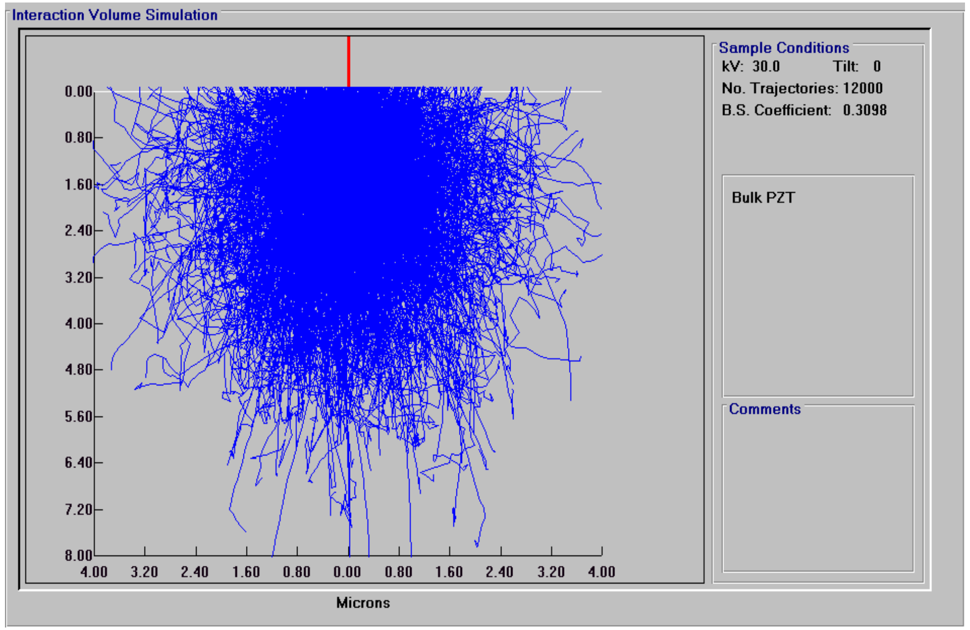
Compared to SEM-EDXS

- (Can) Neglect correction factors for absorption and fluorescence in quantification
- High energy e⁻-beam and thin sample ⟹ X-rays emitted from narrow/confined volume of sample in beam path direction

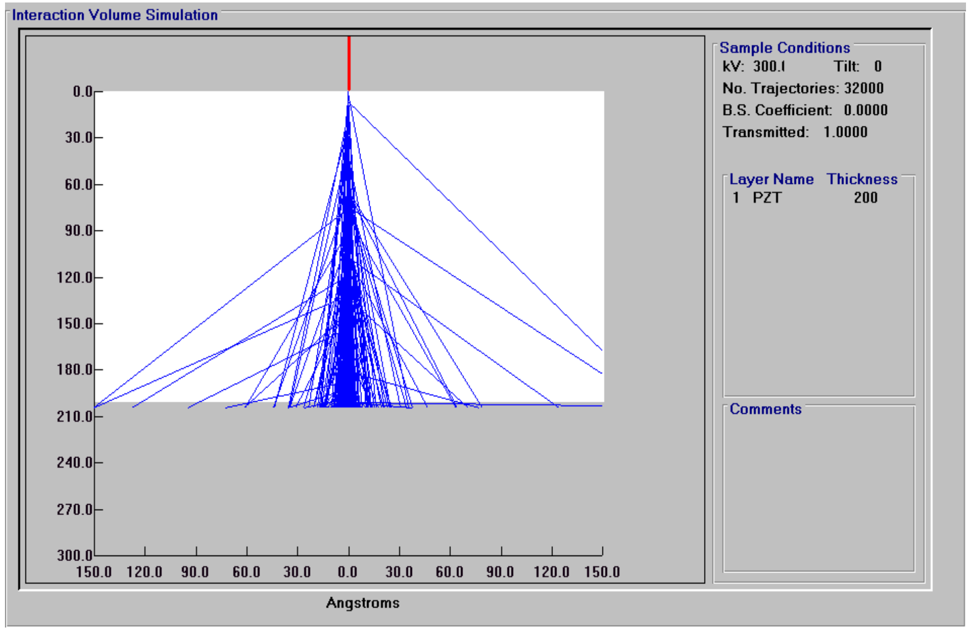


Pb(Zr,Ti)O_3 scattering models

SEM: 30 keV beam, bulk sample



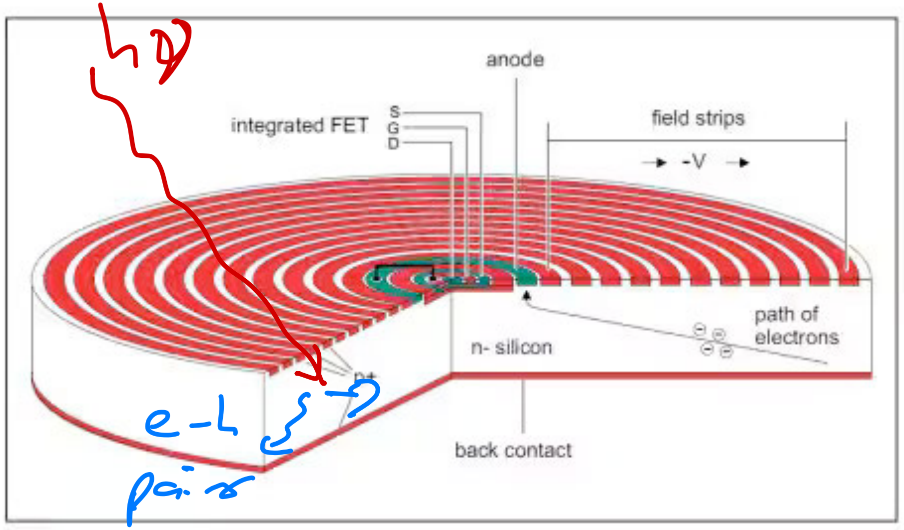
STEM: 300 keV beam, thin sample



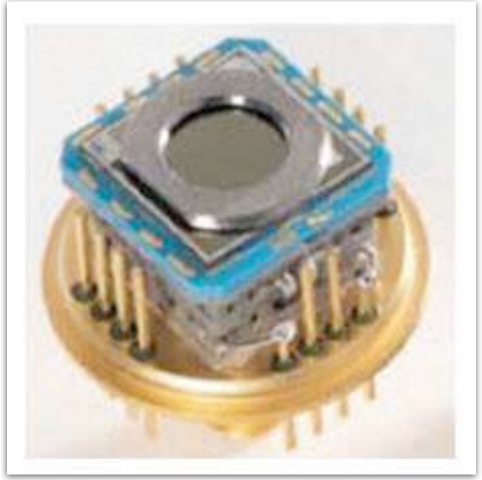
EDX detection

- Modern standard is the *Silicon Drift Detector (SDD)*
- Incident X-ray absorbed in Si creates e^{-}-h^{+} pairs
- Internal electric field drifts e^{-} charge towards anode
- Accumulated charge converted to voltage by a pre-amplifier
- Quantity of charge carriers depends on X-ray energy
  ⟹ measured voltage corresponds to energy of detected X-ray

Detector v. compact, v. fast

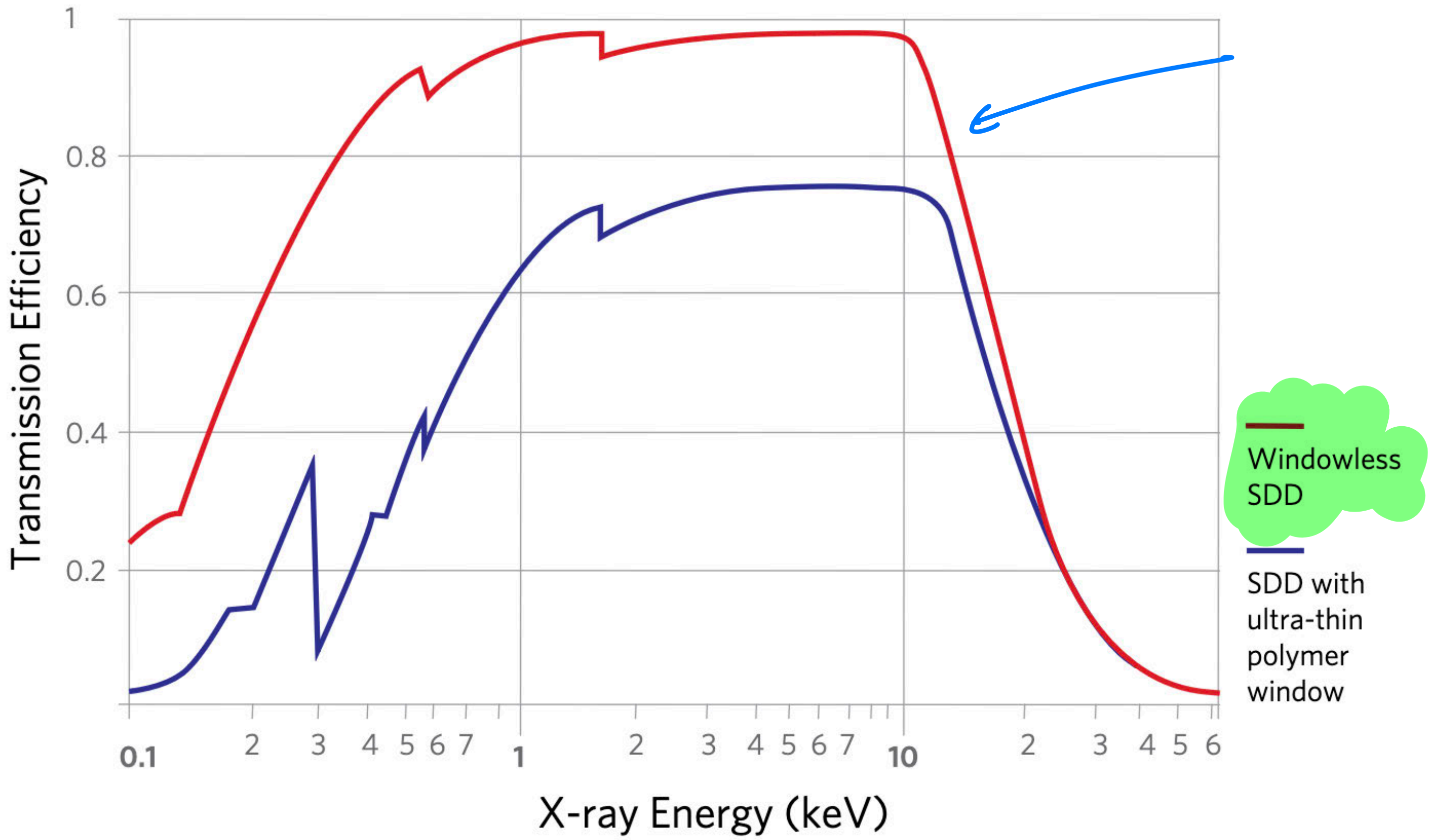


Example SDD detector design



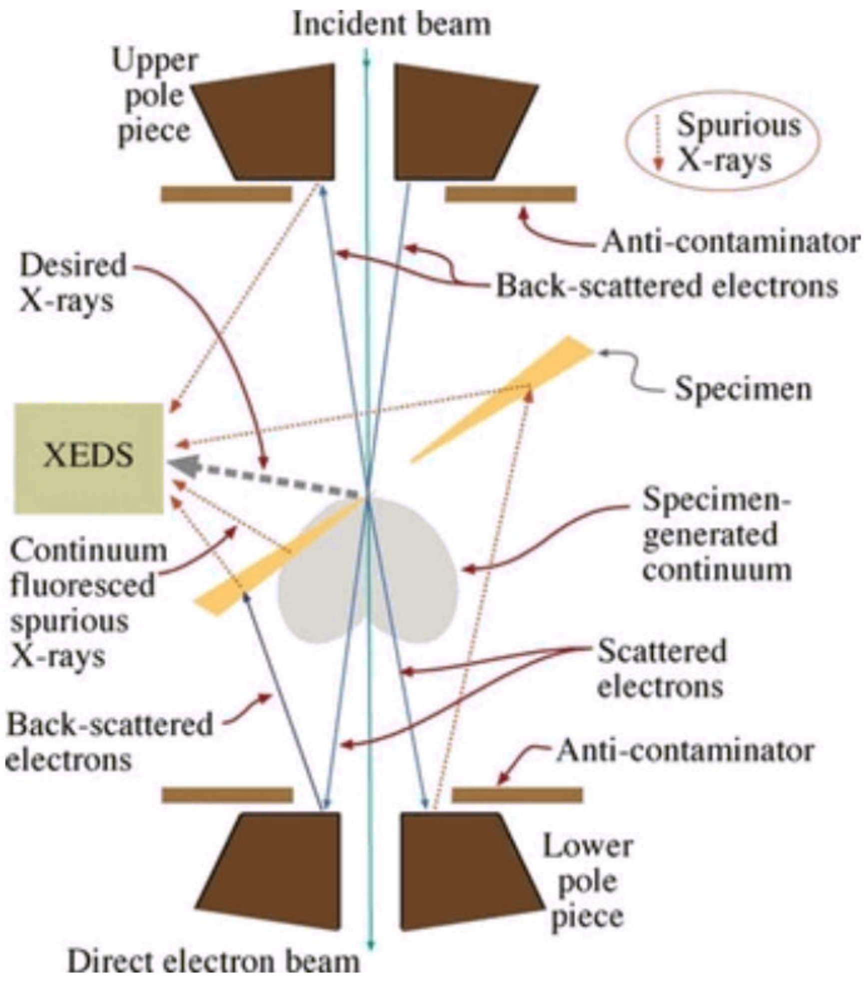
Detective quantum efficiency (DQE)

- SDD detectors are compact and fast, but poor DQE for X-rays ≳ 20 keV



Mostly use 0 - 20 keV range

Detection geometry



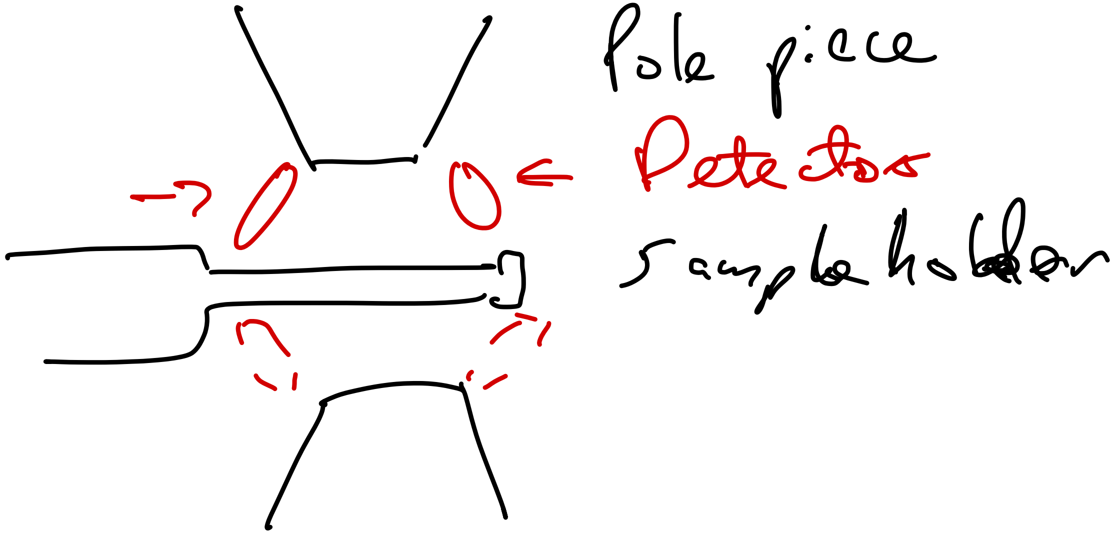
- Take care of spurious artefact X-ray peaks

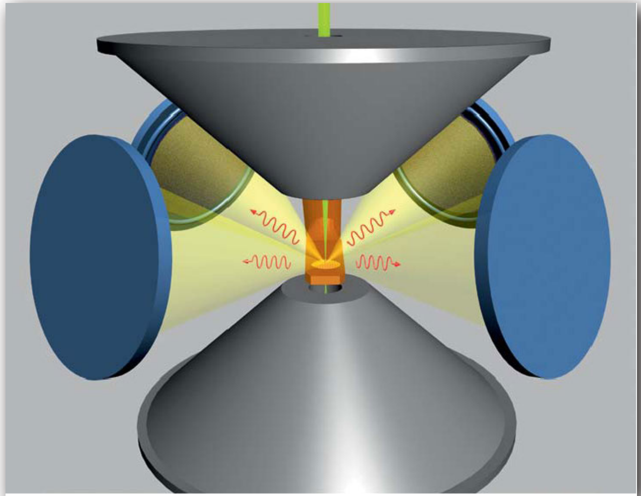
- Flourescence of X-rays from support grid (e.g. Cu K_α, K_β)
- Pole piece (Fe, Co, Cr) ?

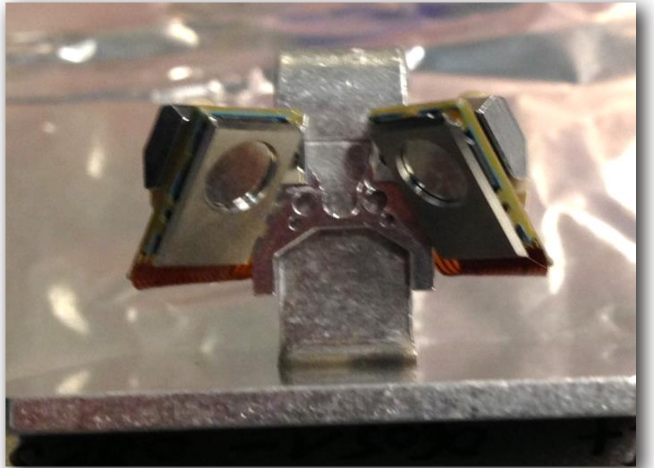
EPFL Detection geometry

SDD: up to 50'000 counts/s

- New standard is to use multiple SDDs to increase solid angle of collection and hence detection efficiency
- For example: “Super-X” on Osiris, Titan with 4 quadrants giving ~1 Sr solid angle of collection
- State-of-the-art: Thermo Fisher Scientific Ultra with ~4 Sr

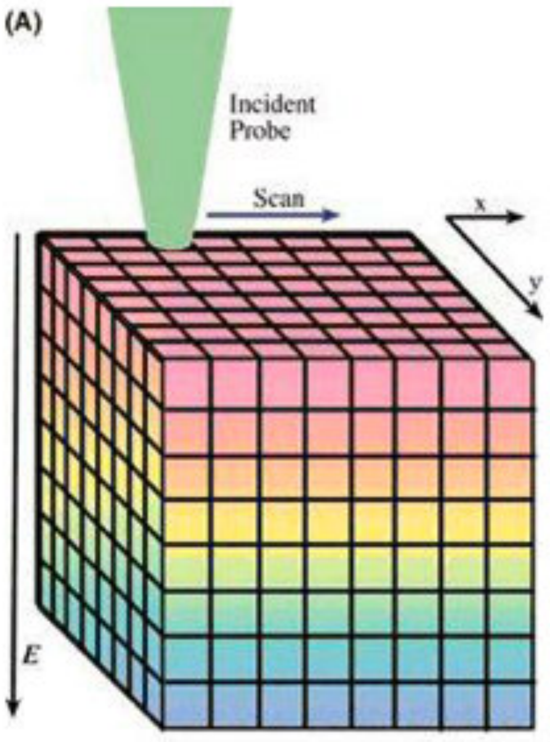




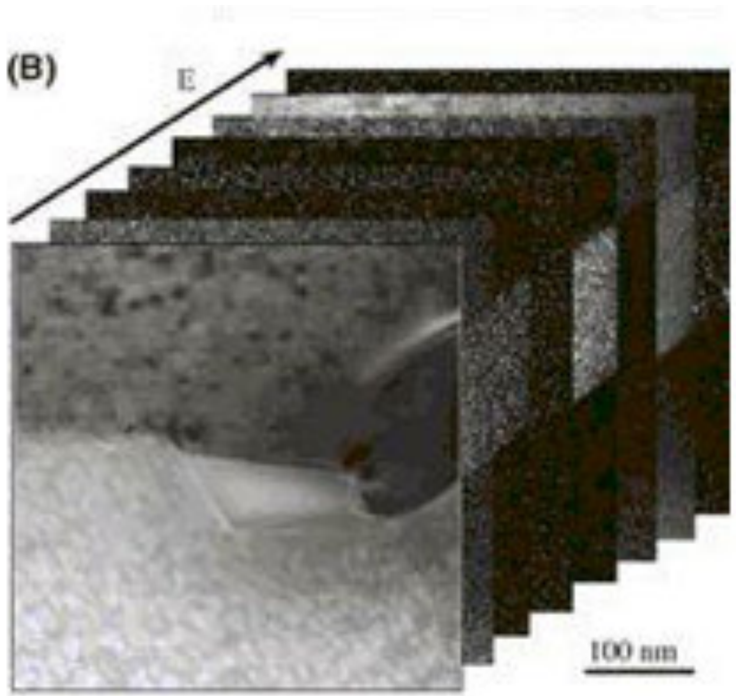


STEM-EDXS data-cube

- EDXS map: acquire one spectrum per pixel position (x, y)
- Gives 3D data-cube of information with axes (x, y, E) "Spectrum image"
- Data can be post-processed – integrate area under peak to generate qualitative elemental map



Each position (x,y) Spectrum



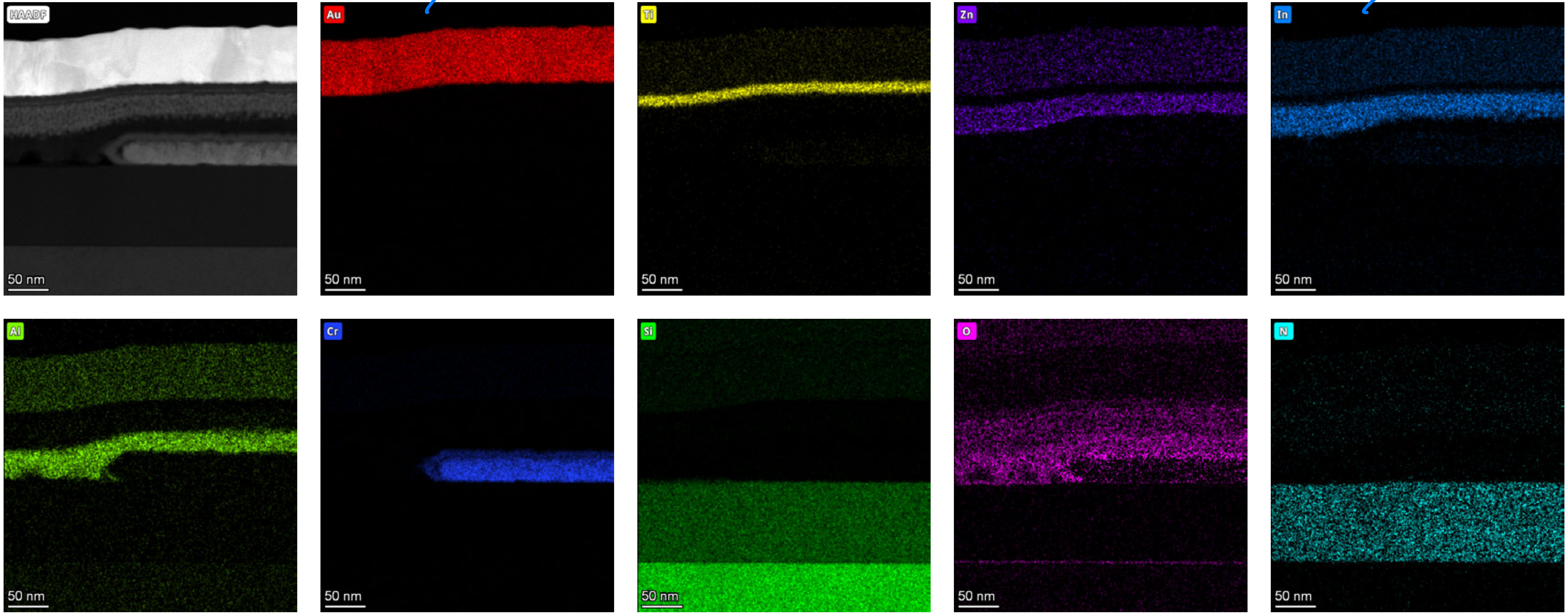
EDXS mapping: applications

- Multilayer sample – *net counts* maps

→ Extract integrated signal from peaks

L peaks

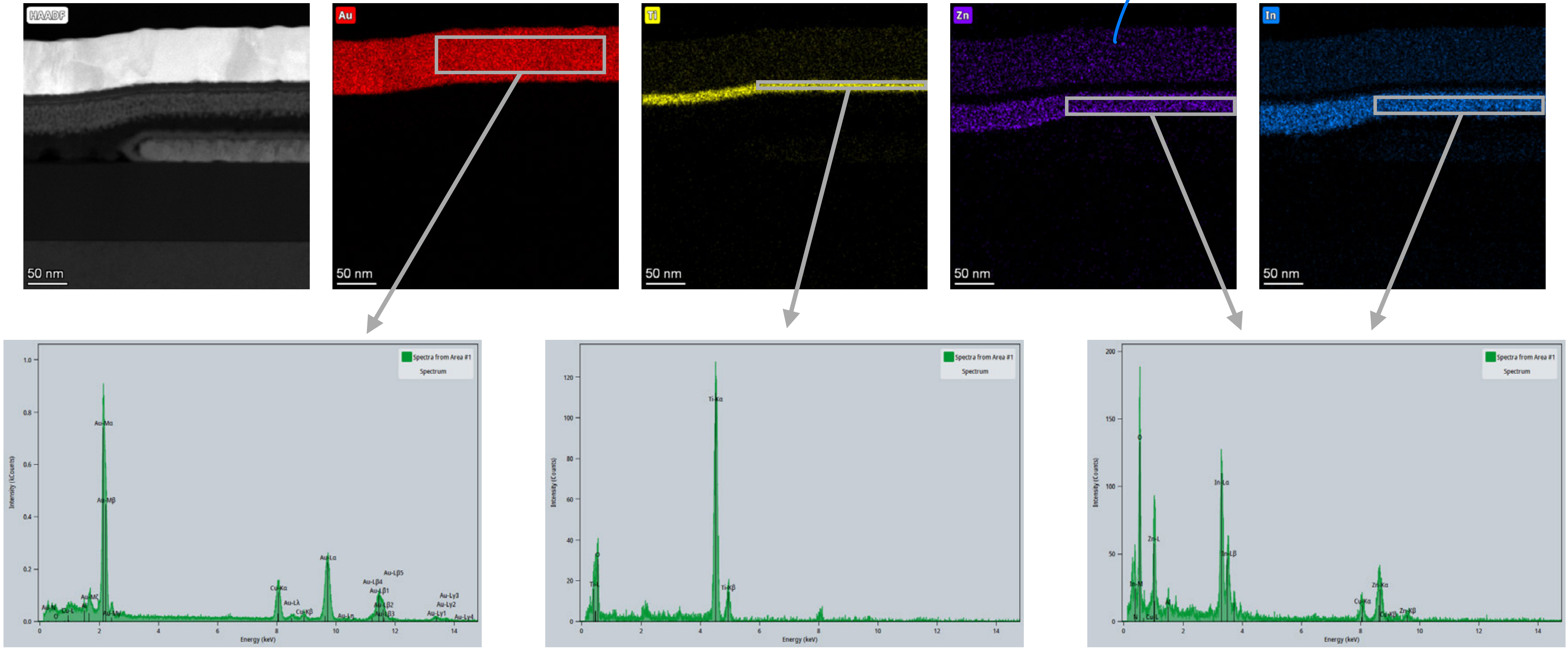
K-peaks



EPFL EDXS mapping: applications

- Multilayer sample – *integrated counts* EDX spectra

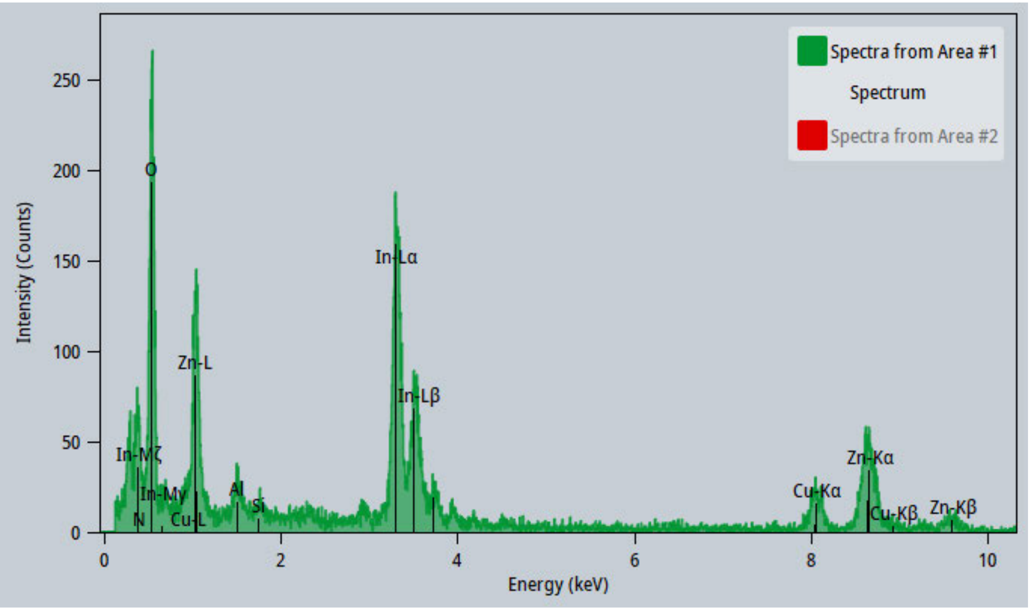
Fictive signal from Bremsstr. background



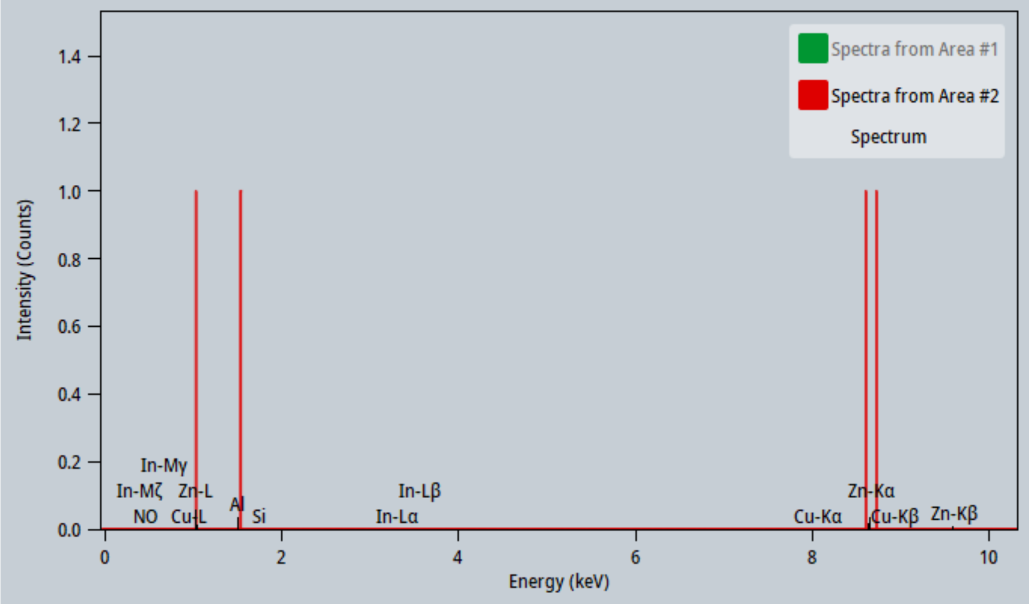
Why integrate counts across spatial ROI?

- In-Zn-O layer:

Integrated from 270 x 25 = 6'750 px²



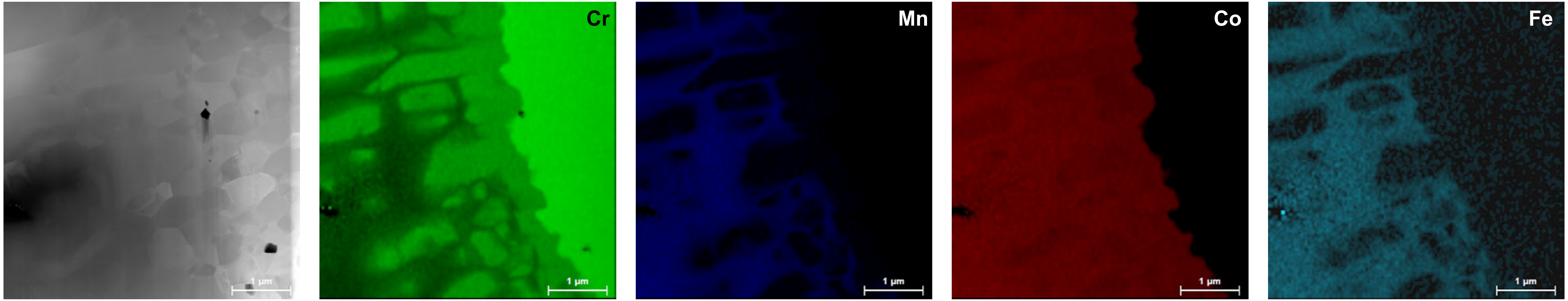
Single pixel spectrum

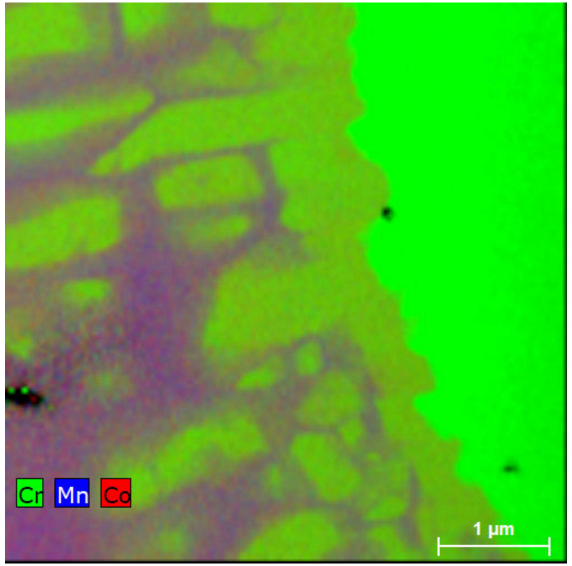


Poisson statistics: peak with counts N
noise $= \sqrt{N}$
$\Rightarrow$ Need $N = 10{,}000$ for 1% accuracy

EDXS mapping: applications

- Fuel cell sample: Fe-doped $MnCo_2O_4$ spinel layer





EDXS mapping: applications

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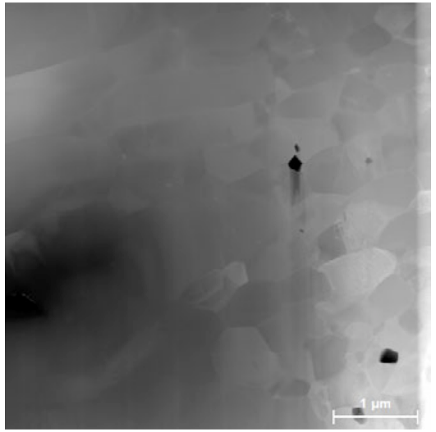
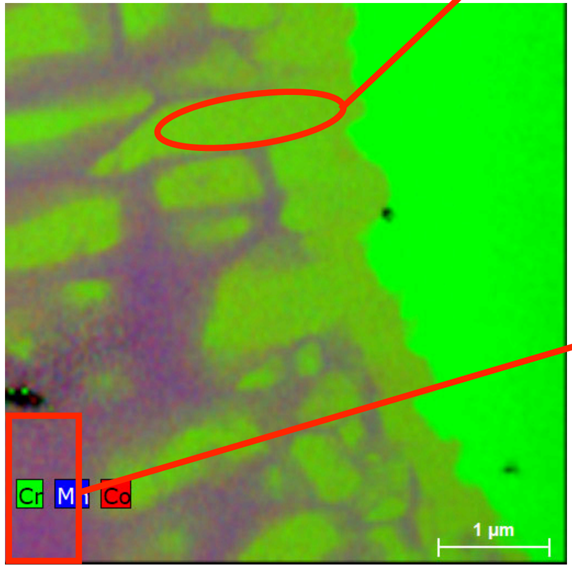
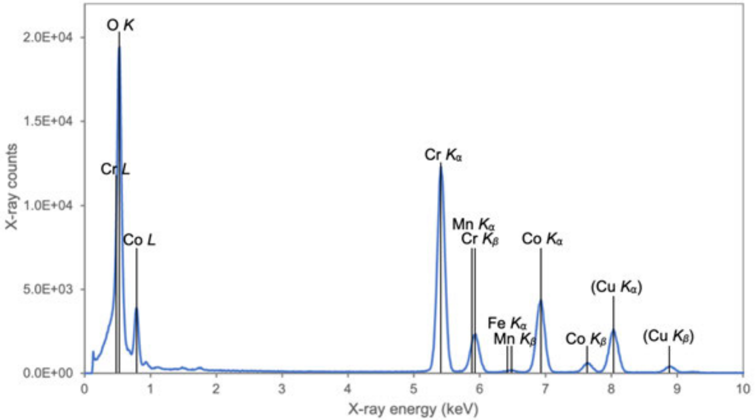
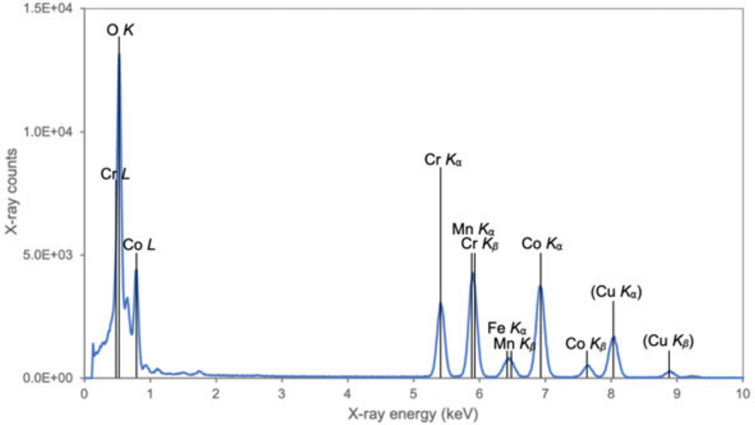






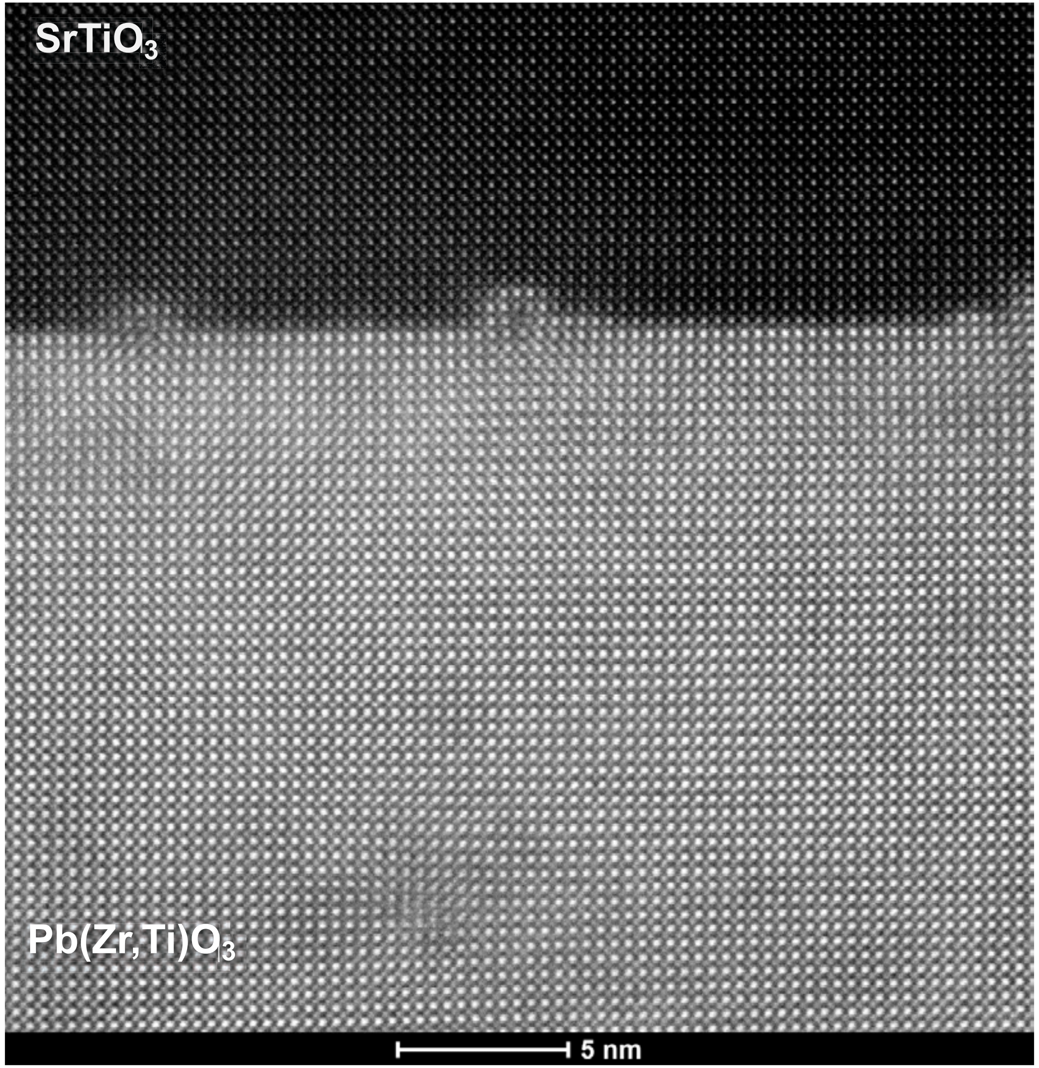
Element	Peak series	At. %
Cr	K	33.7
Co	K	13.8
Mn	K	2.5
Fe	K	0.1
O	K	49.9



Element	Peak series	At. %
Cr	K	12.5
Co	K	18.3
Mn	K	17.2
Fe	K	2.2
O	K	49.8

Atomic resolution EDXS with Cs-STEM

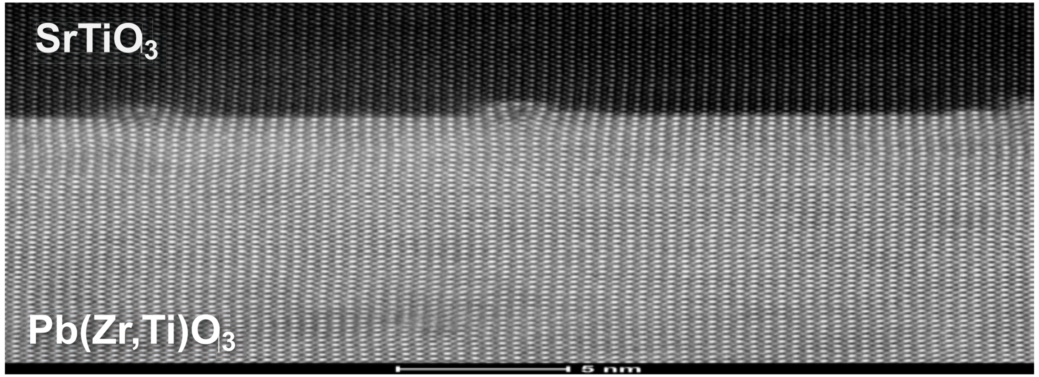
- Sample of $Pb(Zr,Ti)O_3$ on $SrTiO_3$



Atomic resolution EDXS with Cs-STEM

- Sample of $Pb(Zr,Ti)O_3$ on $SrTiO_3$

Misfit dislocation



Atomic resolution EDXS with Cs-STEM

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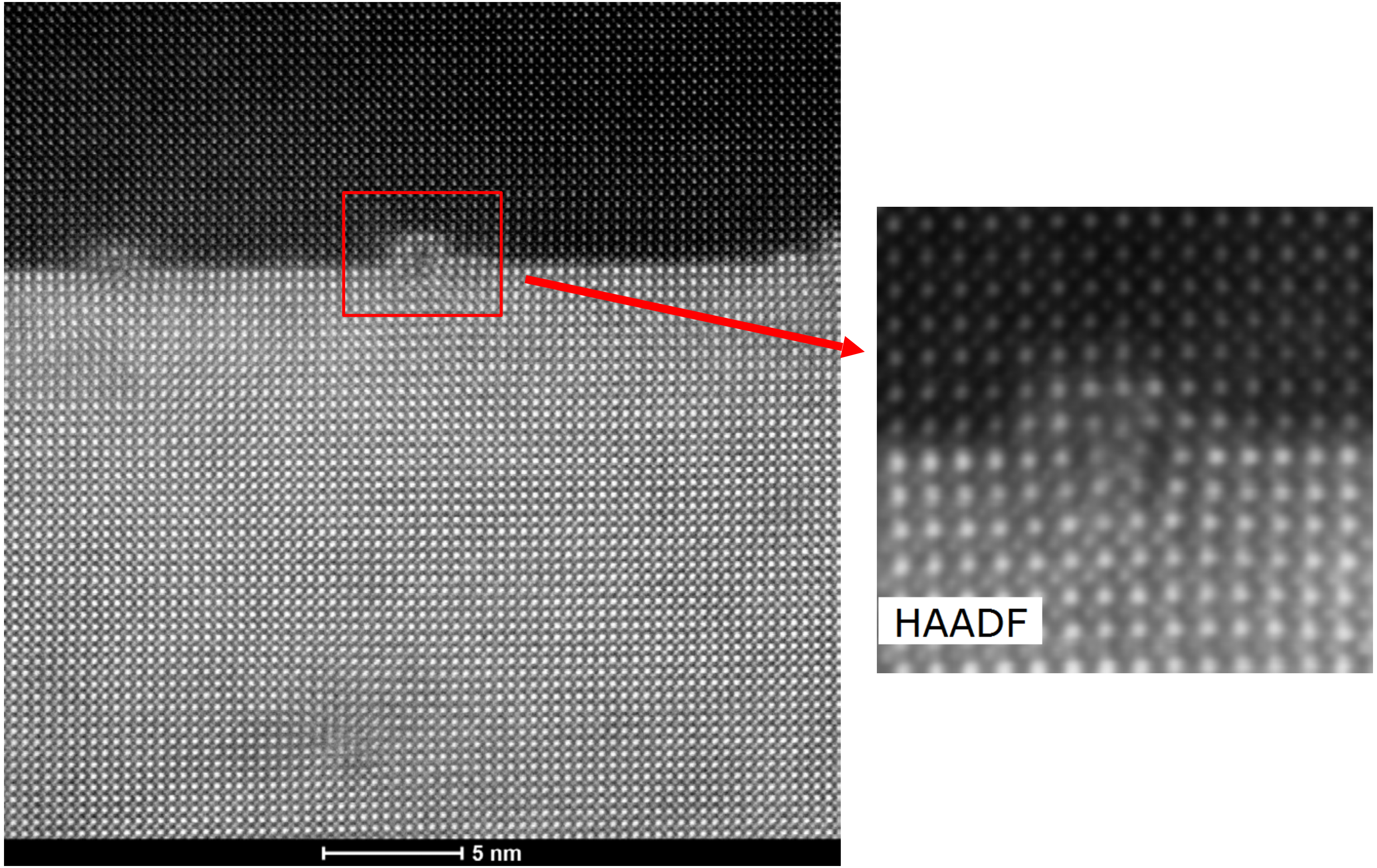

Atomic resolution EDXS with Cs-STEM

- Sample of Pb(Zr,Ti)O_3 on $SrTiO_3$ – atomic resolution elemental mapping