EPFL

Analytical Electron Microscopy (EELS & EFTEM)

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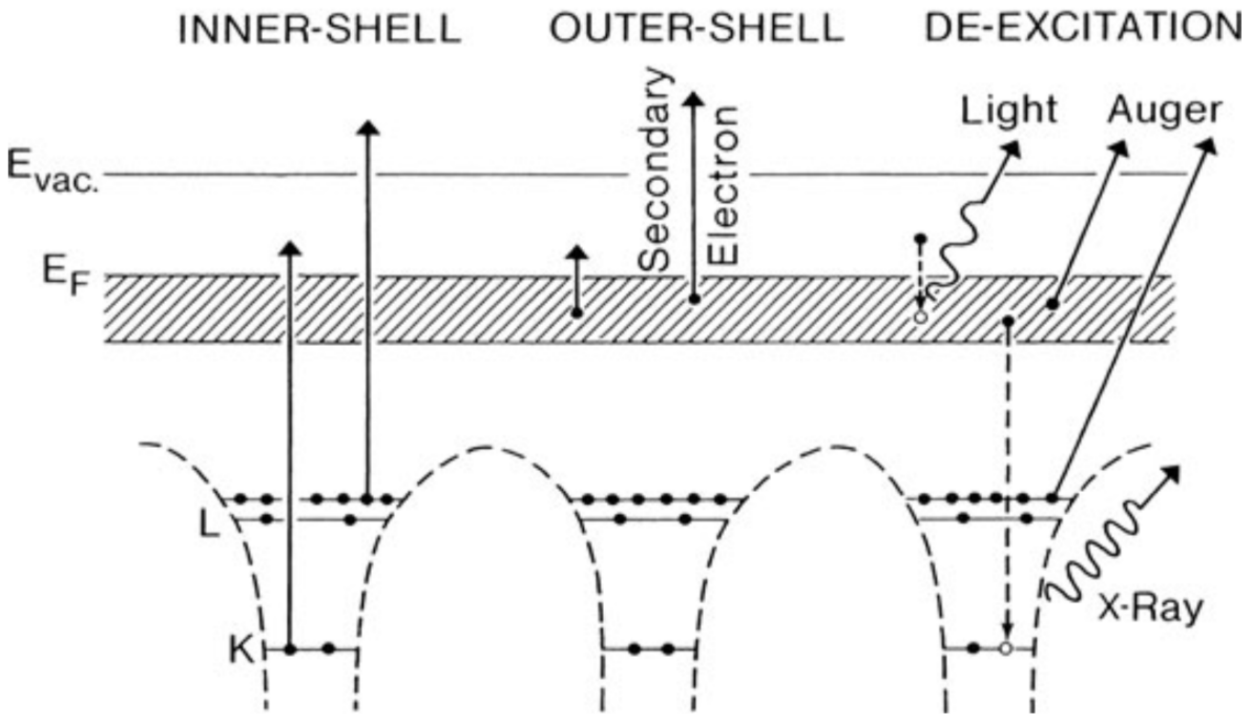
  - Elemental detection and mapping
  - Elemental quantification
  - ELNES
- References

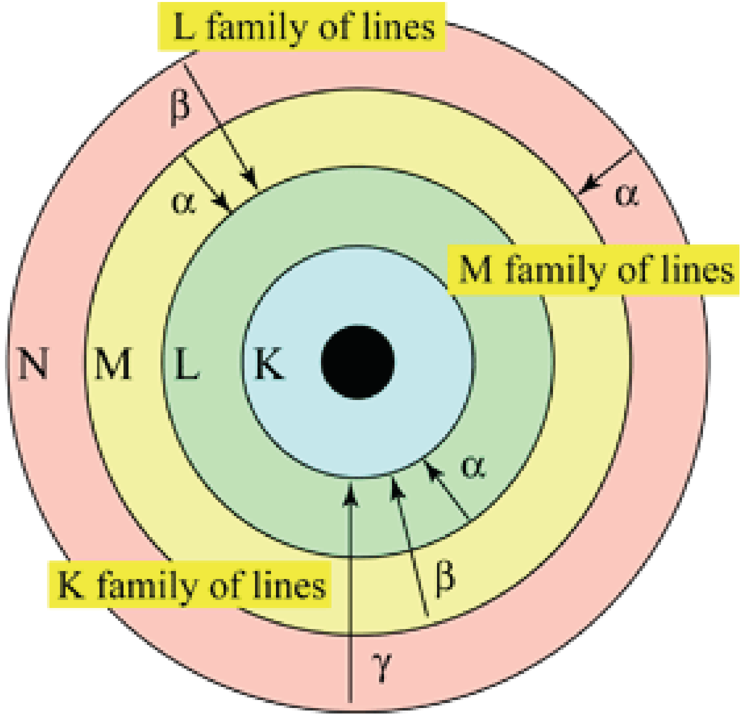
Ionisation energy loss

- Atomic ionisation leading to X-ray emission $\Longleftrightarrow$ energy loss of transmitted e^-

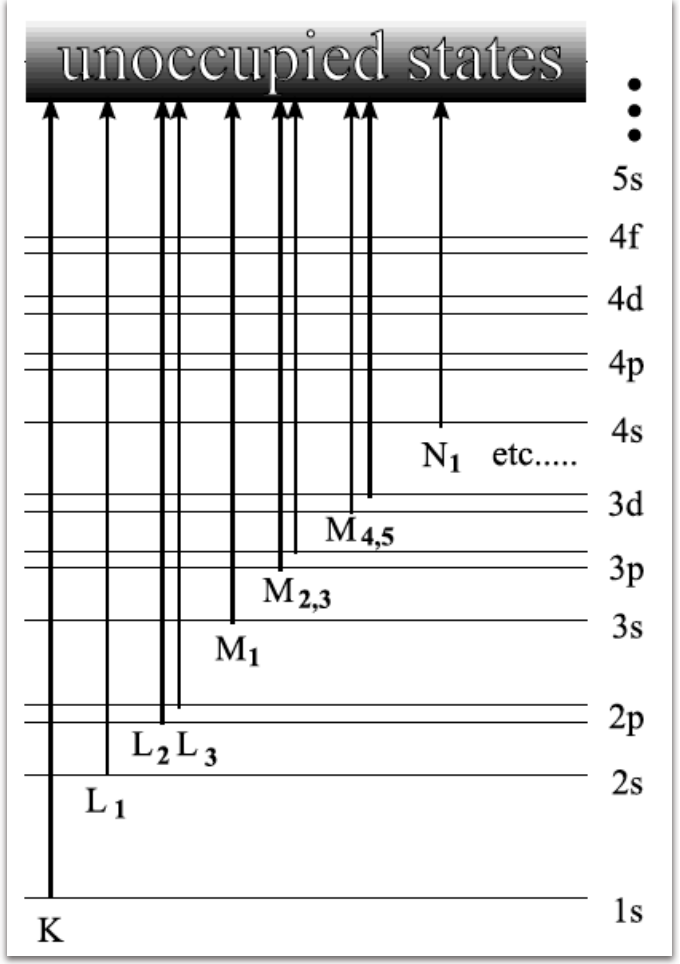


Ionisation edge naming

Energy-dispersive X-ray spectroscopy (EDXS)



Electron energy-loss spectroscopy (EELS)



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Features of the EEL spectrum

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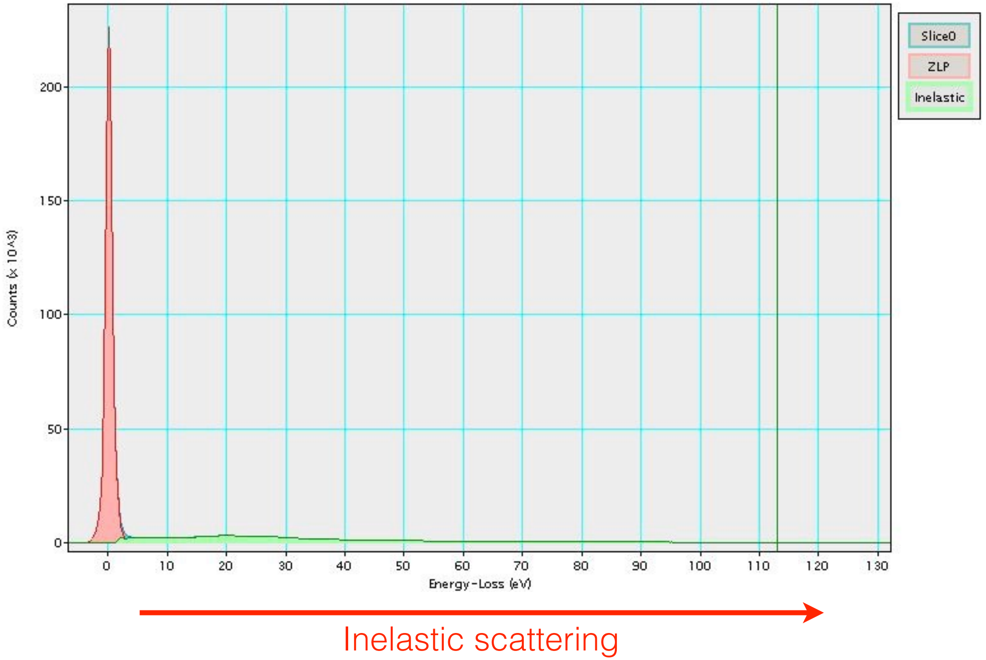
- Energy loss > 0 $\Longrightarrow$ *Inelastic scattering*



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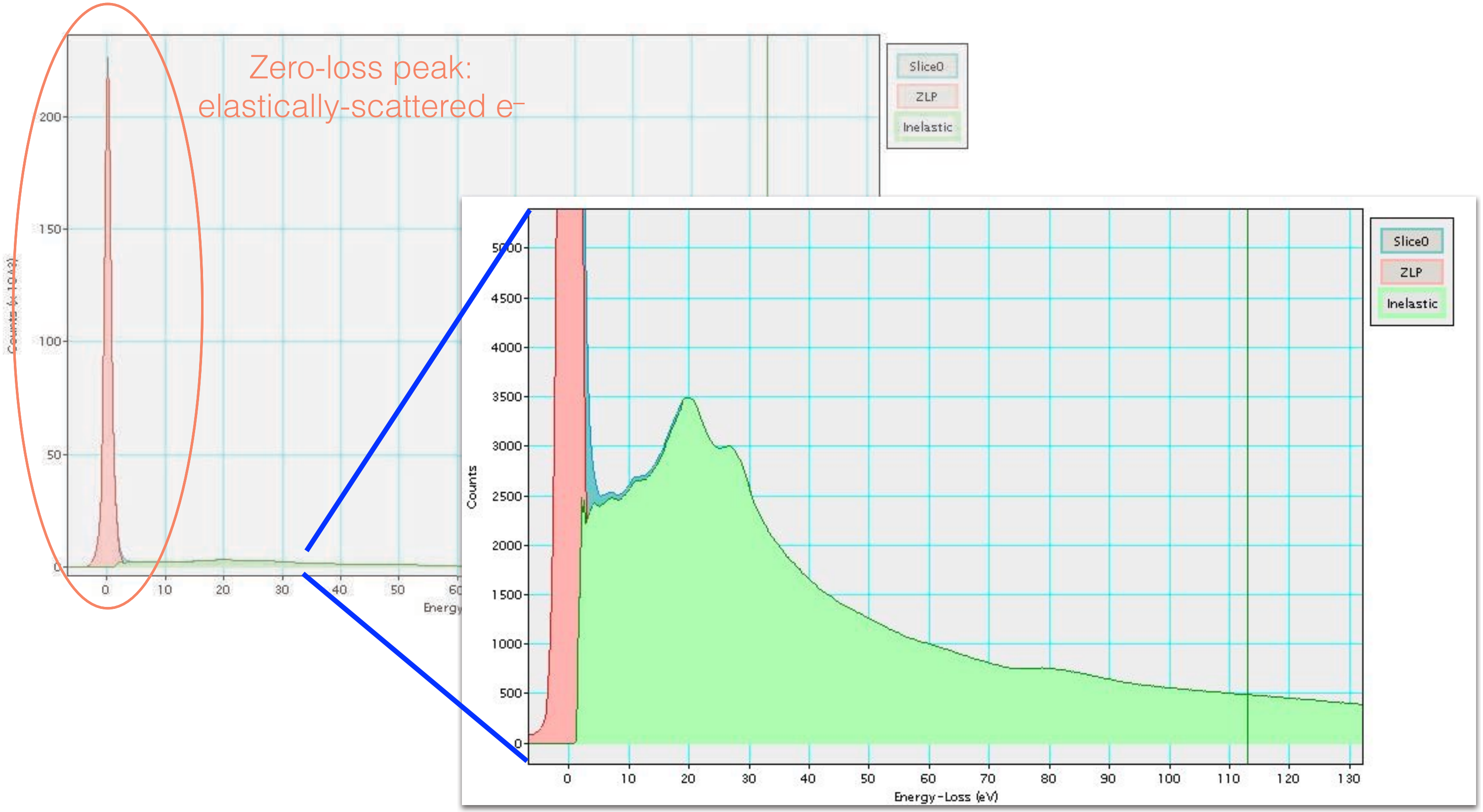

Low-loss spectrum 0-50 eV:
phonons; valence excitations - plasmons (bulk & surface);
interband transitions

Features of the EEL spectrum

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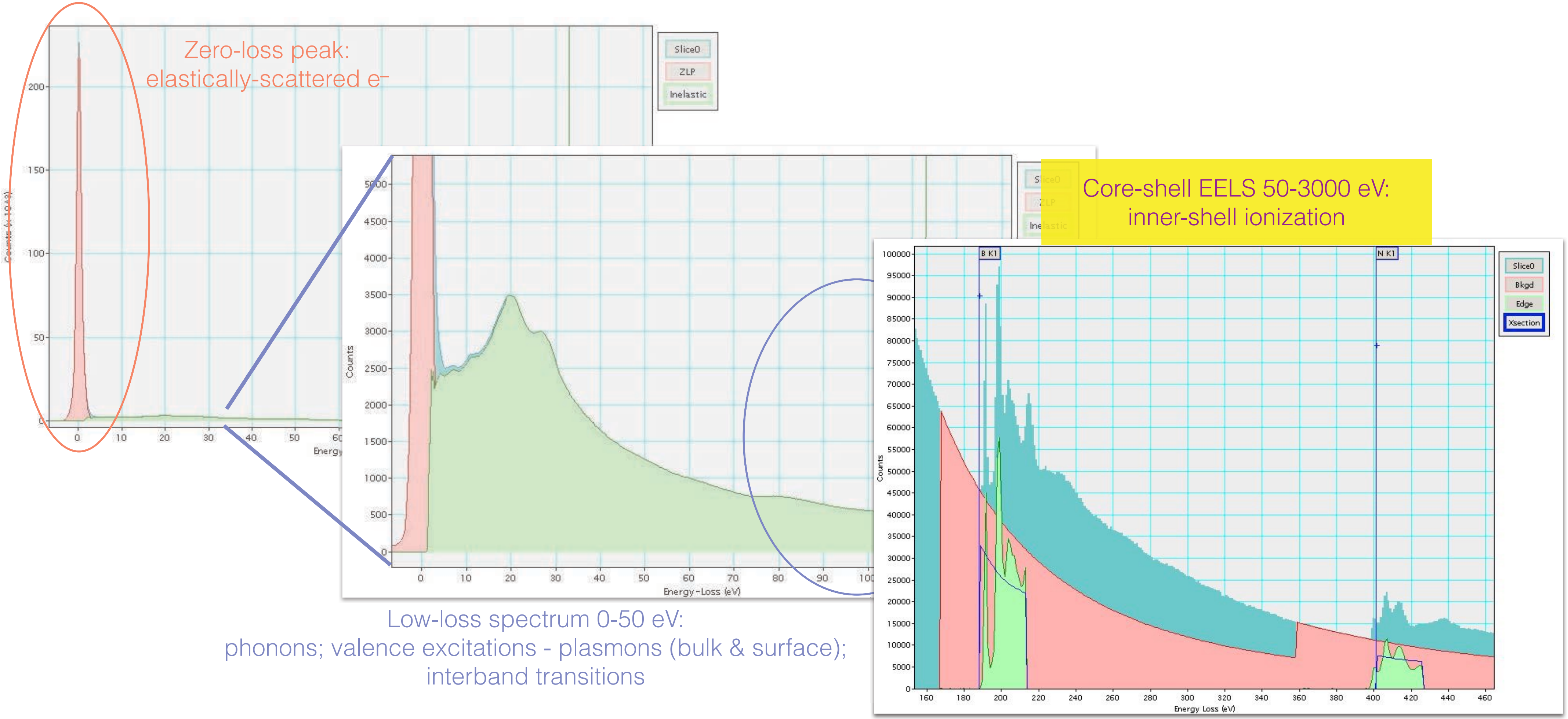
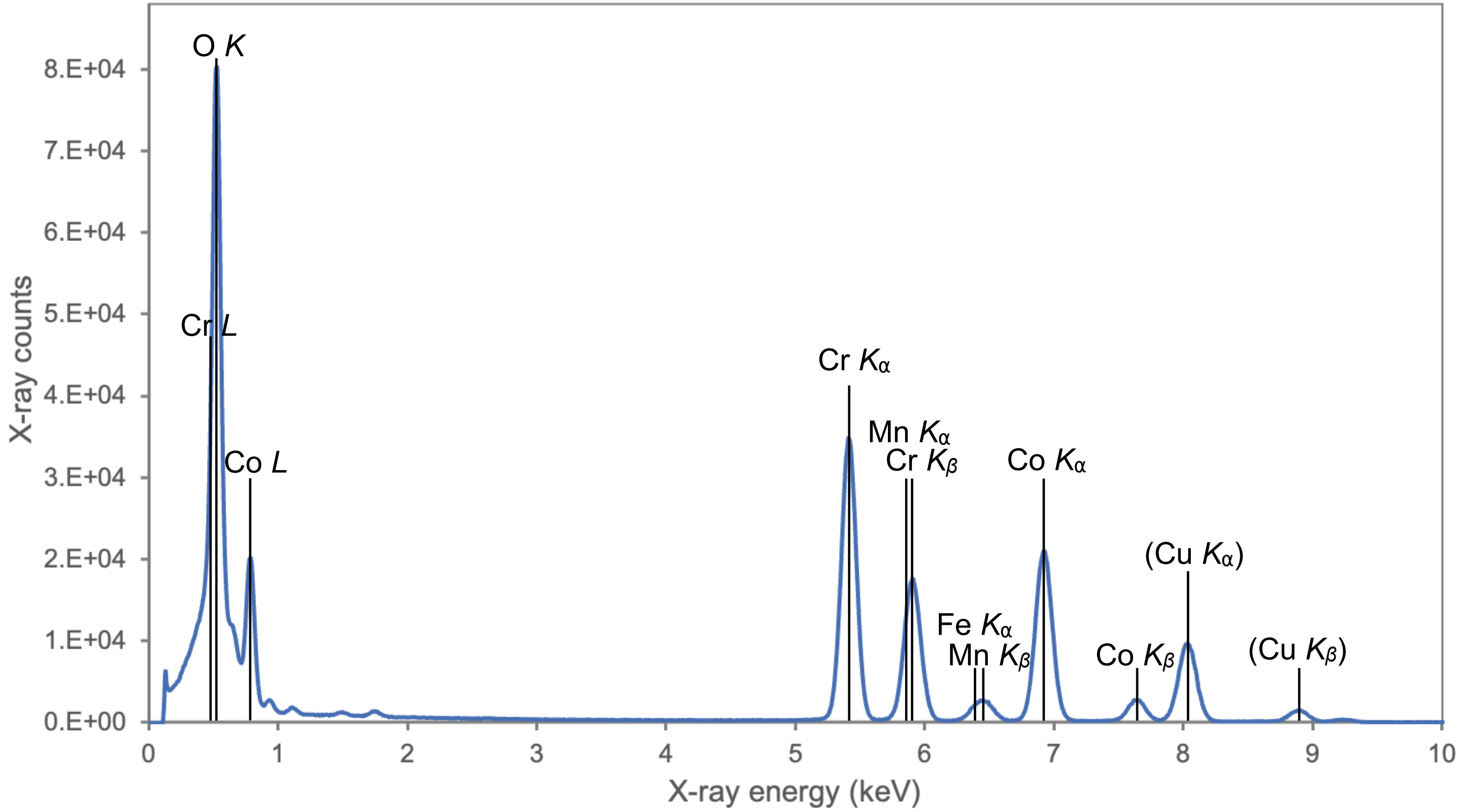


Comparison with EDX spectrum

- EDX 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



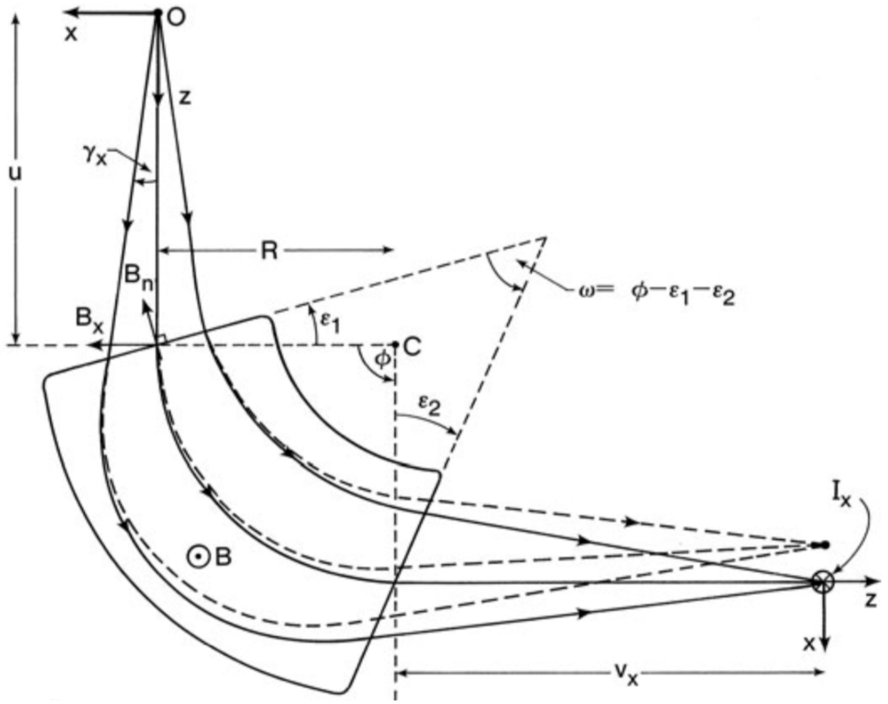
Contents

Electron energy-loss spectrometer

- Typical EEL spectrometer: magnetic prism

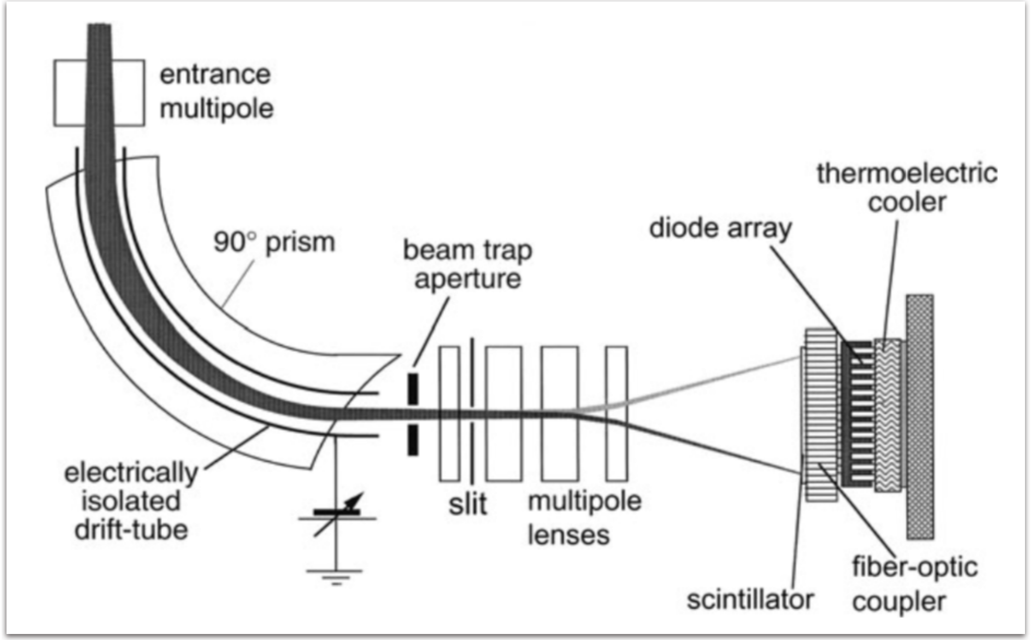
$$R = (\gamma m_0/eB)v$$

$$\gamma = 1/(1-v^2/c^2)^{1/2}$$



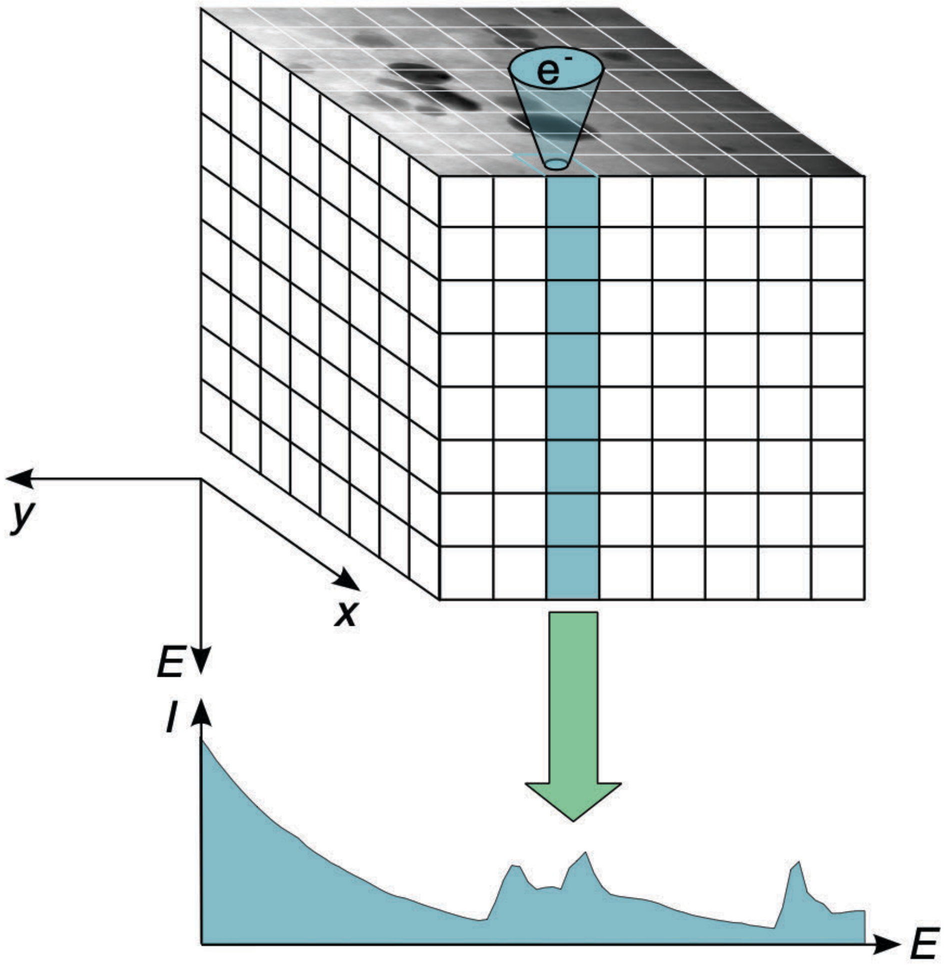
Post-column spectrometer

- Post-column spectrometer most common type used for materials science/physics
- For instance: Gatan EEL spectrometer
- In-column energy filters (e.g. JEOL omega) also exist



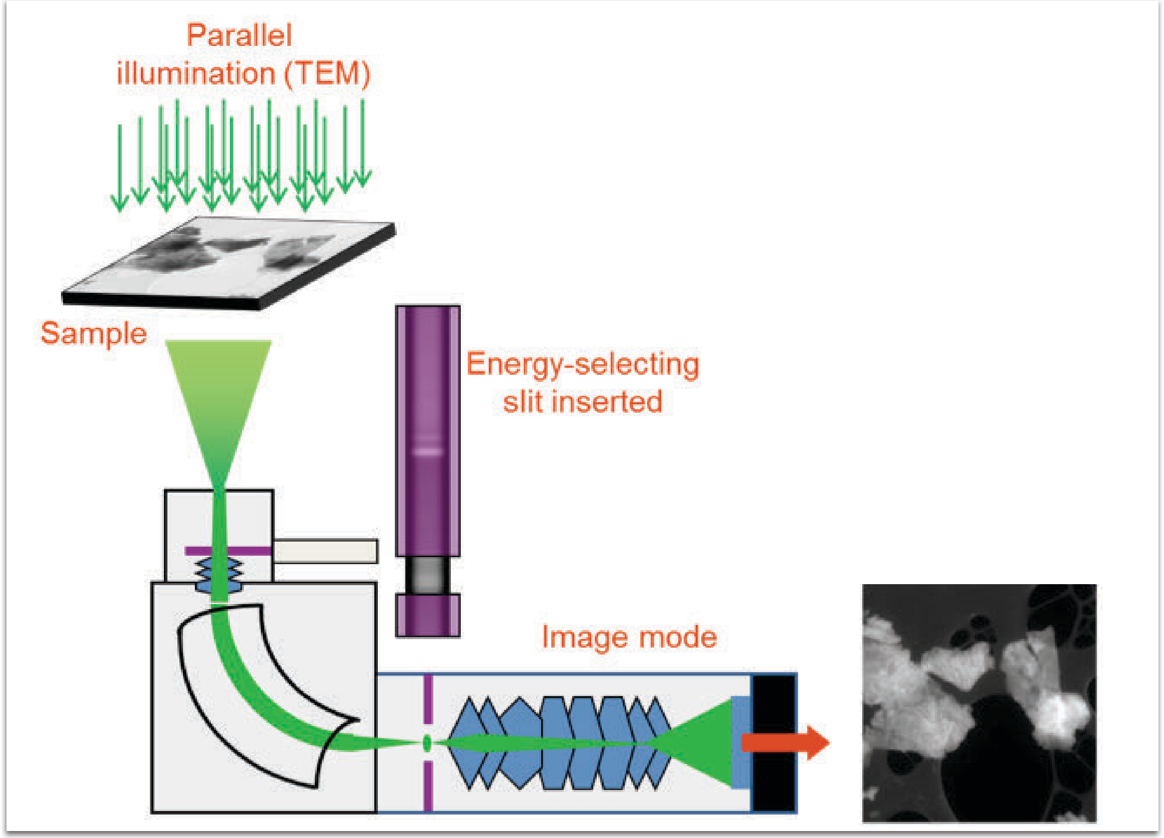
STEM-EELS spectrum imaging

- During STEM imaging, collect the *forward-scattered* electrons in the spectrometer entrance aperture
- Record 3D data cube with a spectrum for each probe position (*x*, *y*)



Energy-filtered TEM (EFTEM)

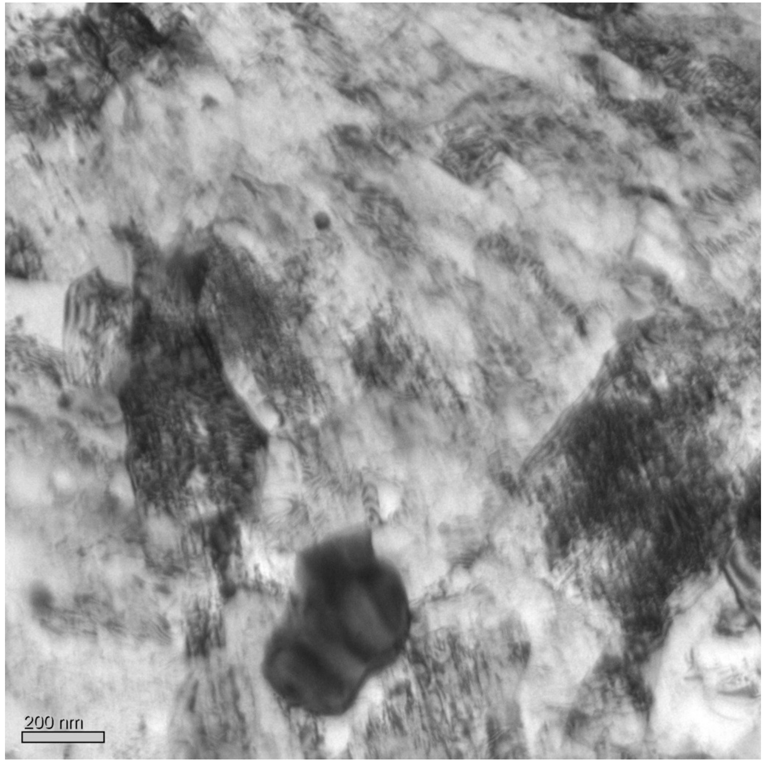
- Record TEM image(s) made from transmitted electrons having certain energy
- Images defined by energy-loss *ΔE* and energy window
- *Zero-loss* filtering: TEM image of elastically-scattered electrons with no energy loss



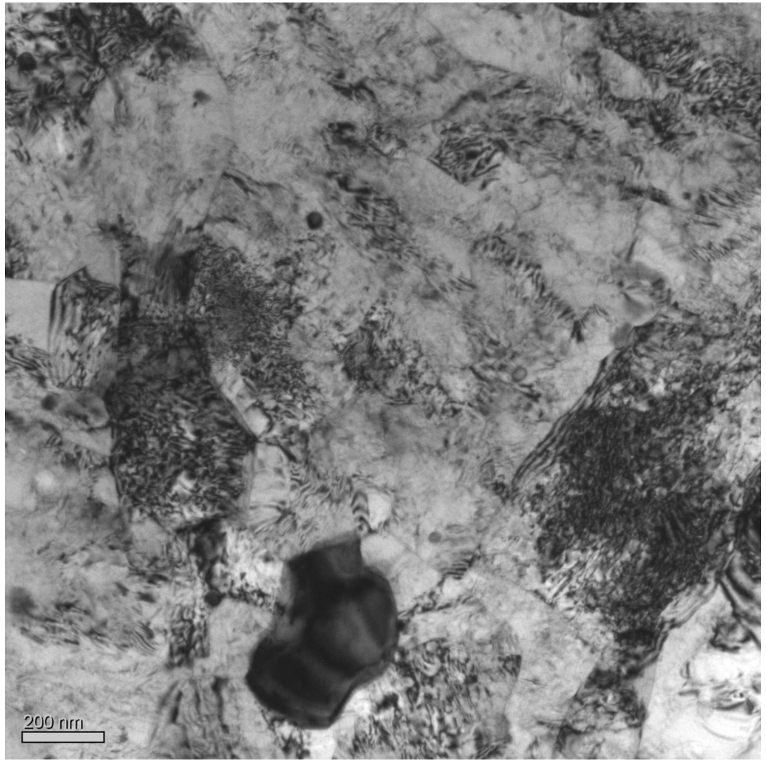
Zero-loss EFTEM

- Zero-loss filtering can be used to remove diffuse inelastic scattering in TEM images of thick samples and in diffraction patterns
- Example – ODS reinforced steel, sample ~250 nm thick:

Unfiltered bright-field TEM:



Zero-loss TEM:



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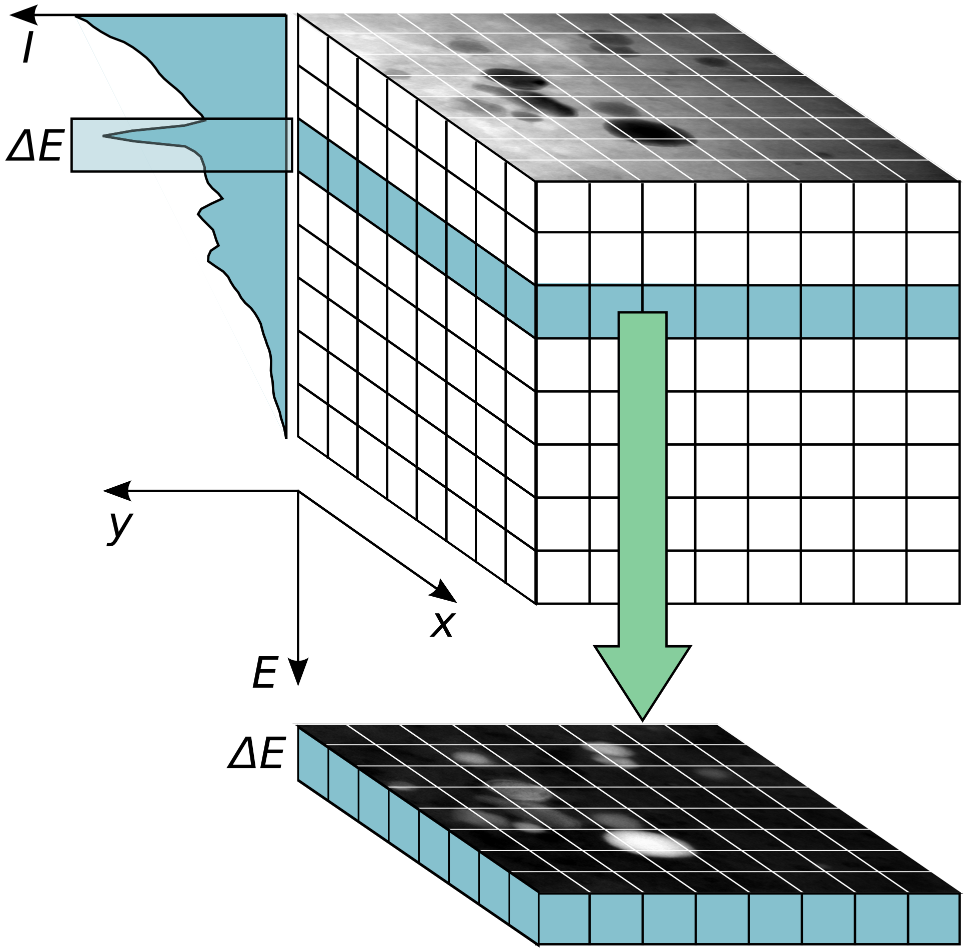
- EFTEM spectrum imaging:
  create 3D data-cube by recording image series at consecutive energy losses



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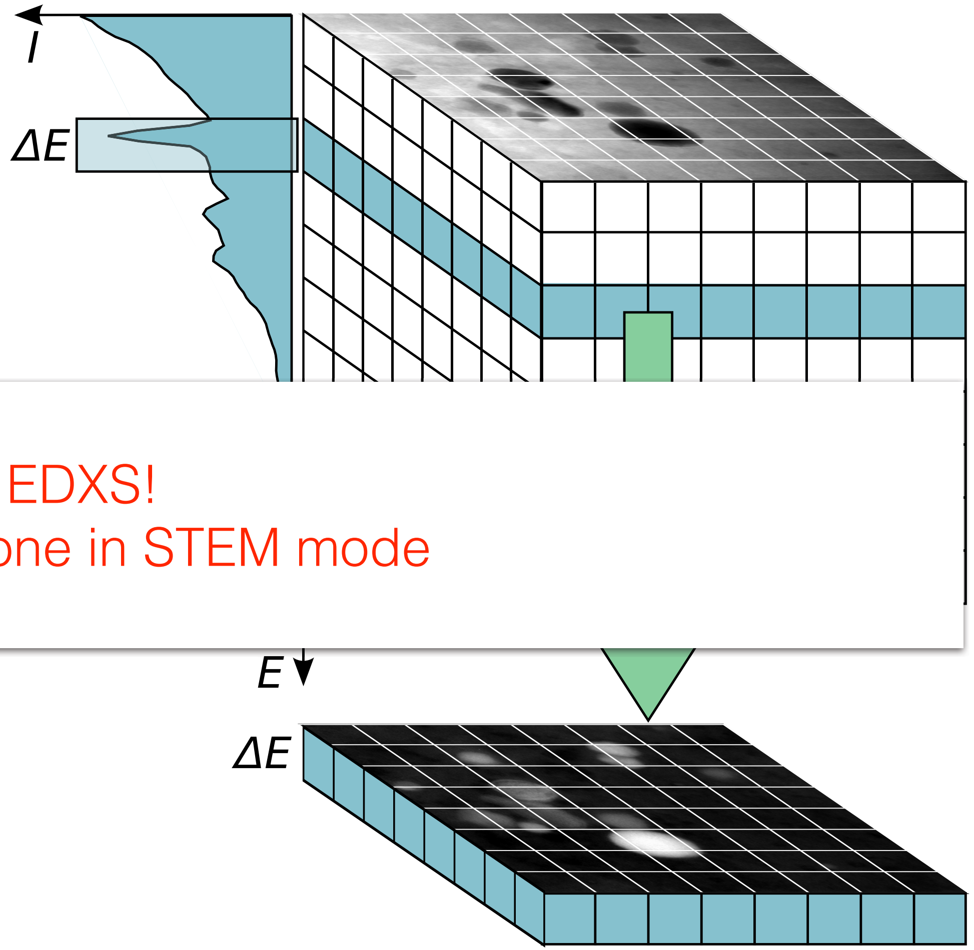
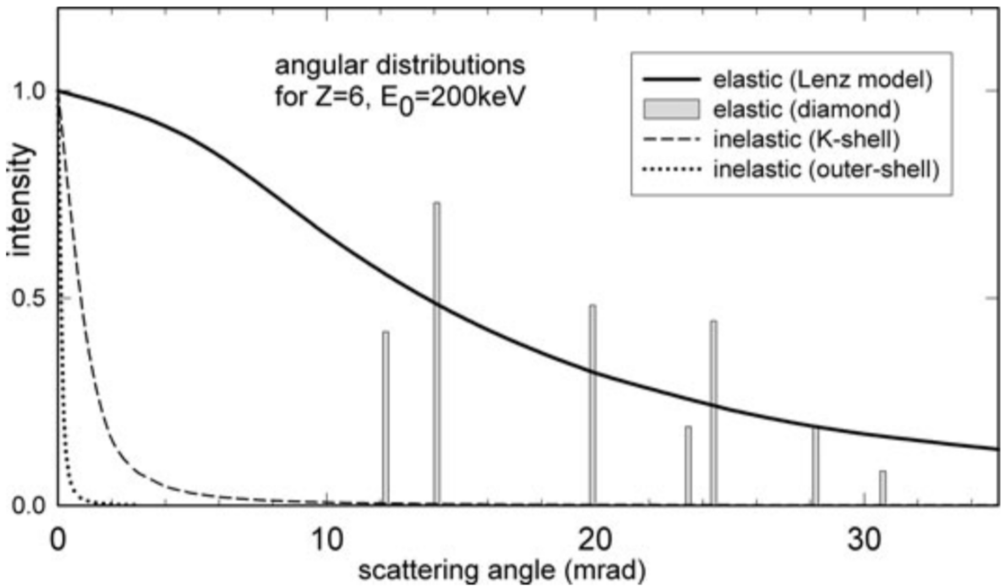


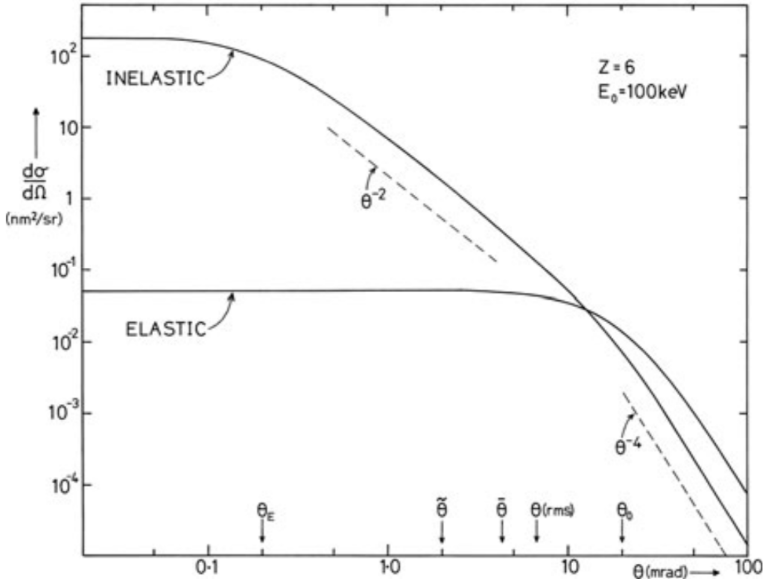
No equivalent with EDXS!
EDXS mapping can only be done in STEM mode

- EFTEM spectrum imaging:
create 3D data-cube by recording image series at consecutive energy losses

Inelastic scattering angular range

- Inelastic scattering concentrated into much smaller angles than elastic scattering
- Characteristic angle for scattering: $\theta_{\mathrm{E}} = \dfrac{\Delta E}{\gamma m_0 v^2} \sim \dfrac{\Delta E}{2E_0}$



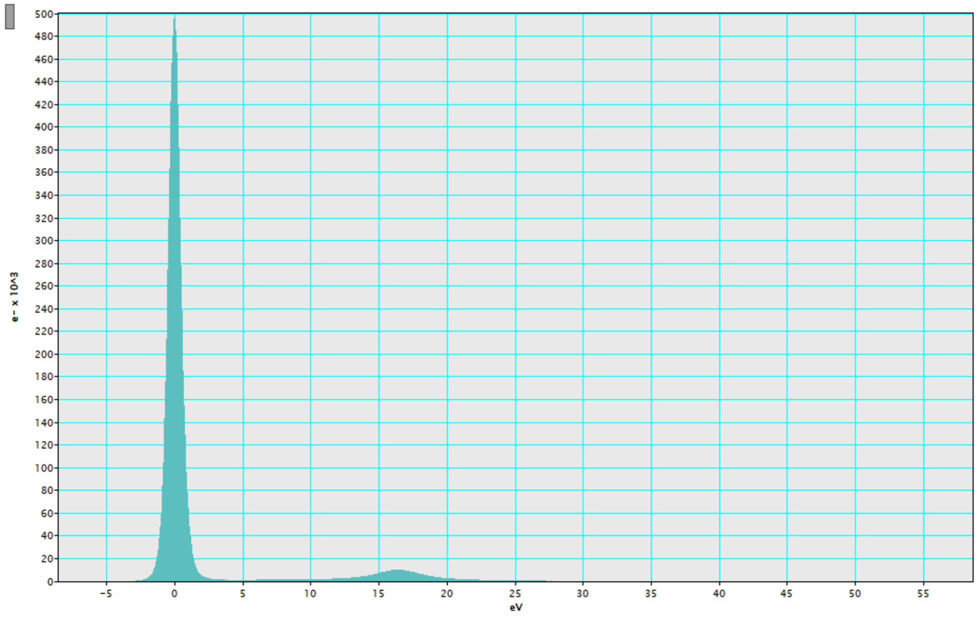


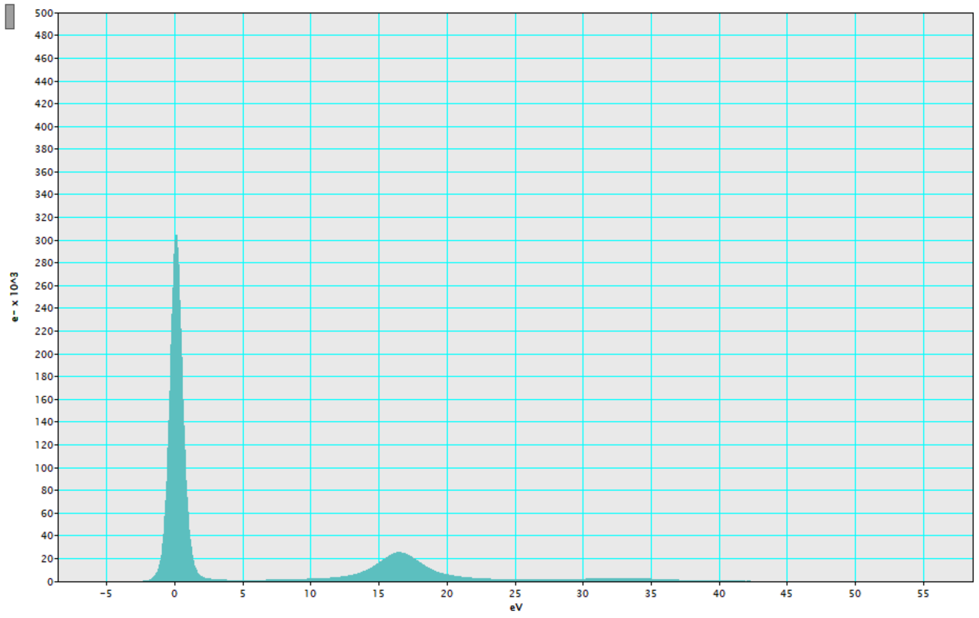
Contents

Low-loss EELS

- For ΔE ~1–50 eV: excitation of plasmons
- Volume/bulk plasmon: oscillation of valence electrons

Example low-loss: crystalline Si





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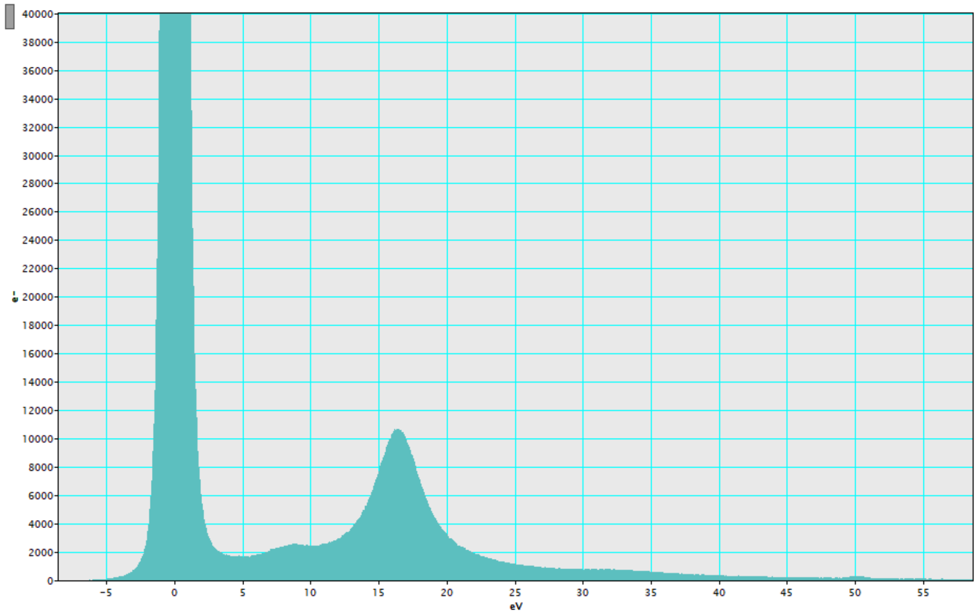
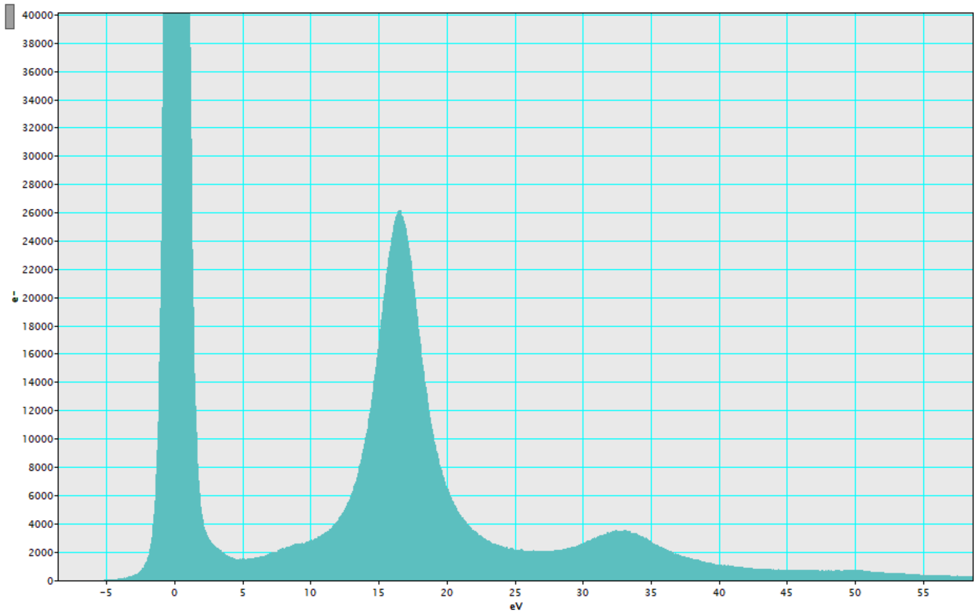
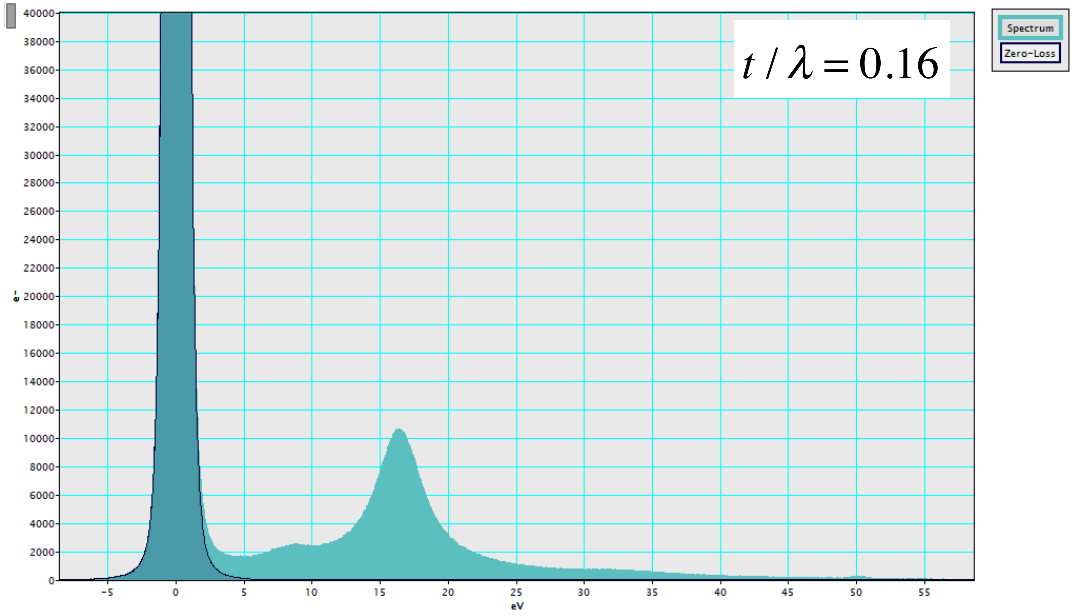
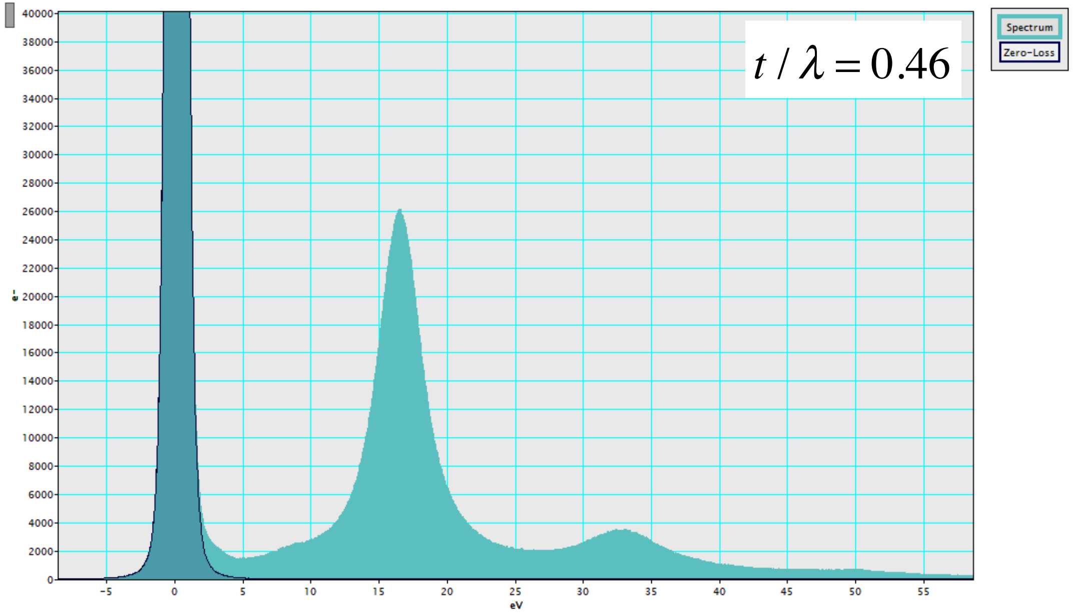




Multiple scattering

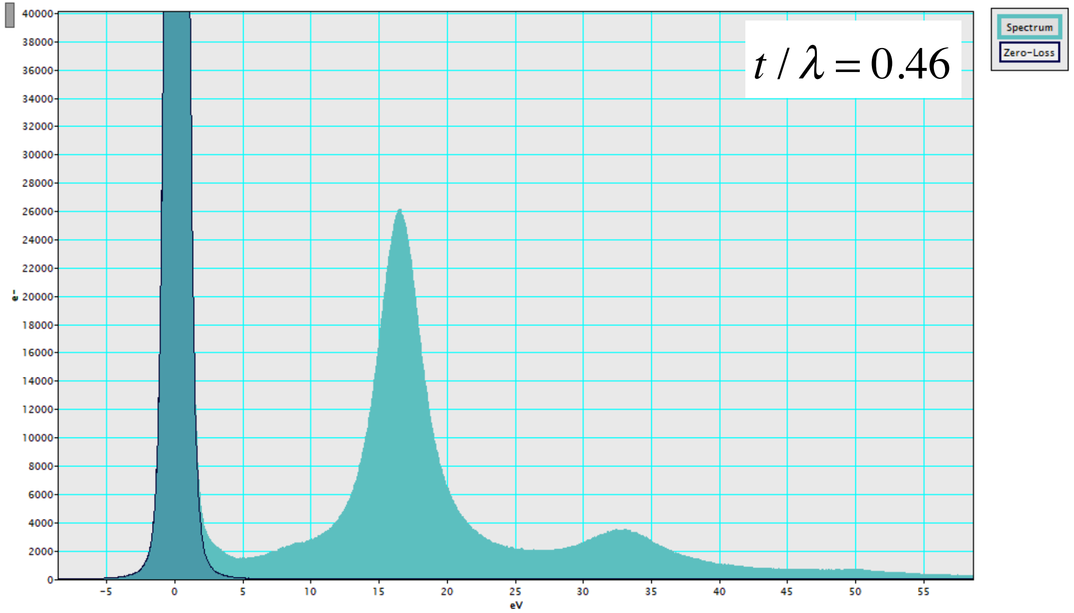
- As specimen thickness increases, have multiple scattering
- Inelastic scattering mean free path: λ
- From Poisson statistics: $t/\lambda = \ln(I_t/I_0)$





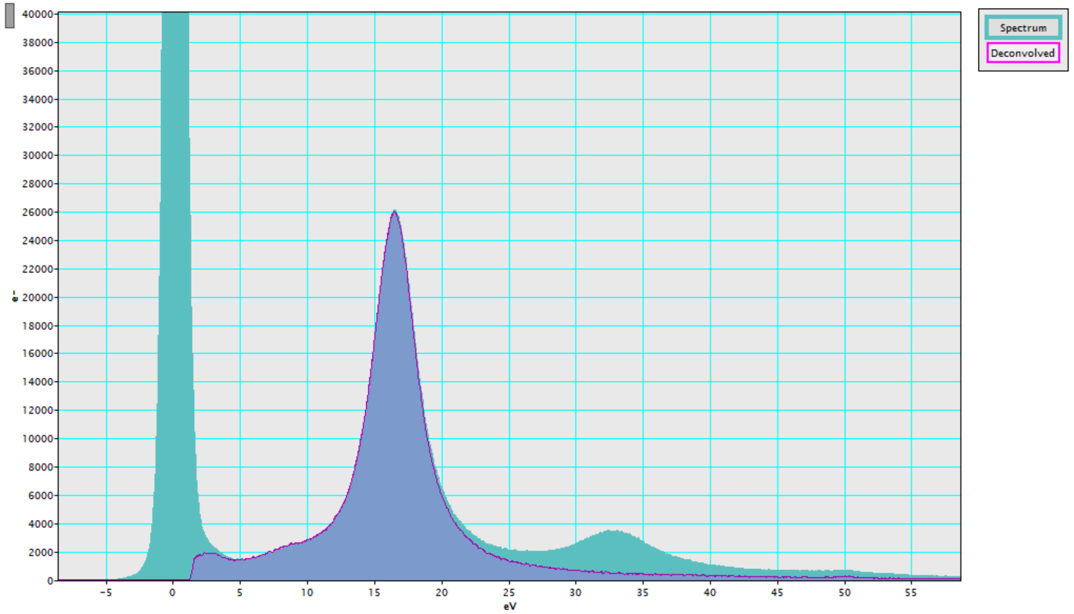
Sample thickness measurement

- By calculating λ the sample thickness t can be estimated
- Two routines in Digital Micrograph:
  - Kramers-Kronig sum rule
  - Log-ratio (absolute) – Bethe sum rule
- Accuracy ~ ± 5–10 nm



Spectral deconvolution

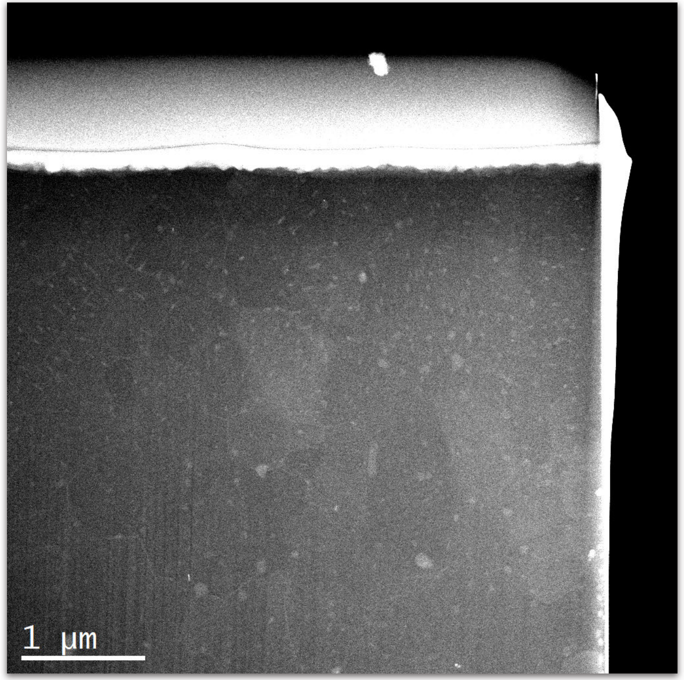
- Deconvolution can be used to retrieve the *single-scattering distribution* (SSD)
- Core-loss spectra: use Fourier-ratio deconvolution (needs low-loss spectrum)
- Low-loss spectra: use Fourier-log deconvolution:

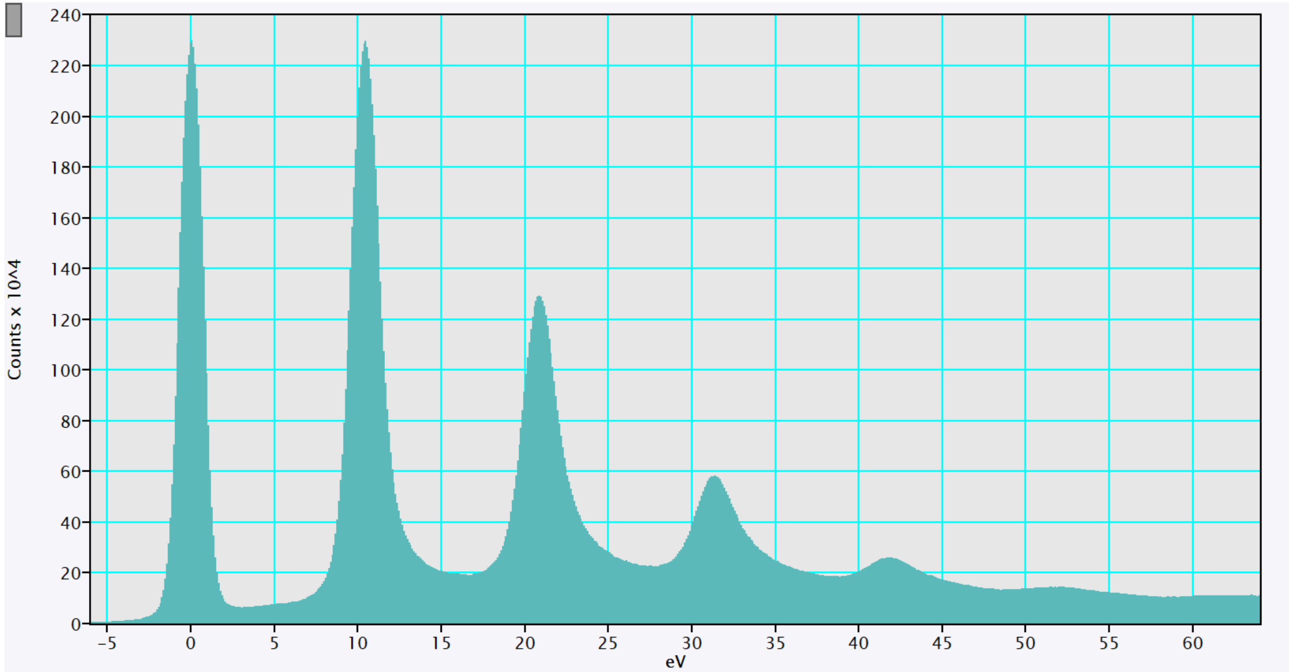


- Intensity of SSD: $S(\Delta E) = \frac{I_0 t}{\pi a_0 m_0 v^2} \mathrm{Im}\left[\frac{-1}{\varepsilon(\Delta E)}\right] \ln\left[1 + \left(\frac{\beta}{\theta_E}\right)^2\right]$

Multiple scattering: Mg sample

- Thick sample: $t / \lambda \approx 2.3$
- Well-defined plasmon peak (free electron gas)
- Multiple orders of plasmon peak excitation





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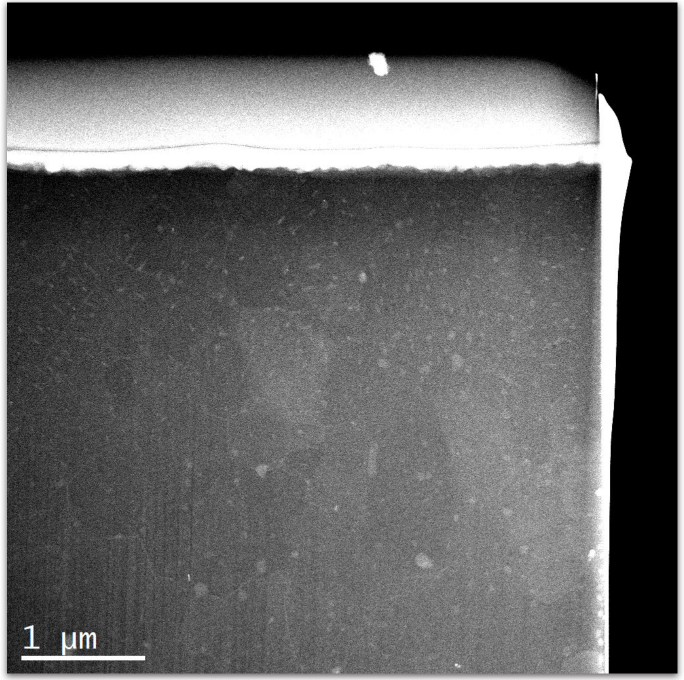
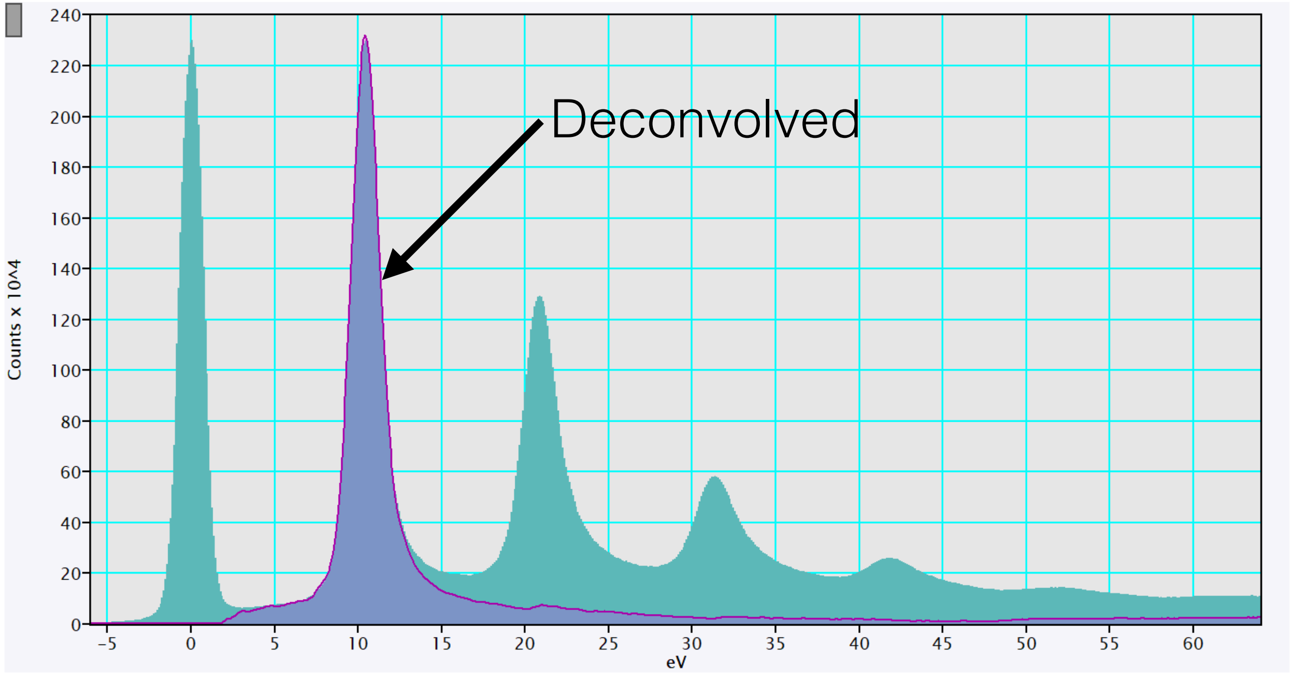


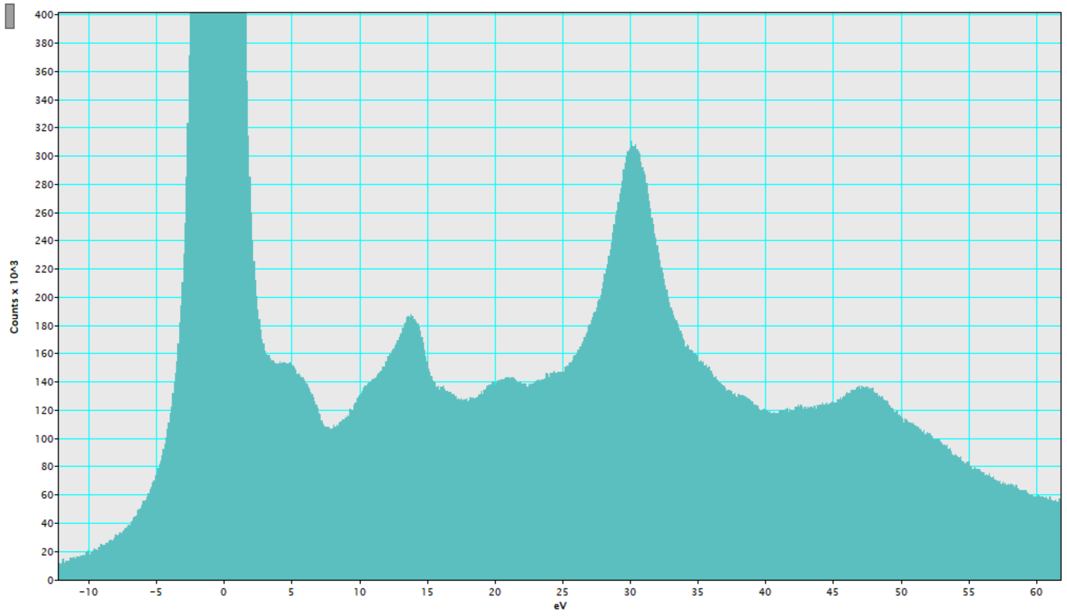


Complexity in the low-loss spectrum

- As well as bulk plasmons, can have surface plasmons, Cherenkov losses

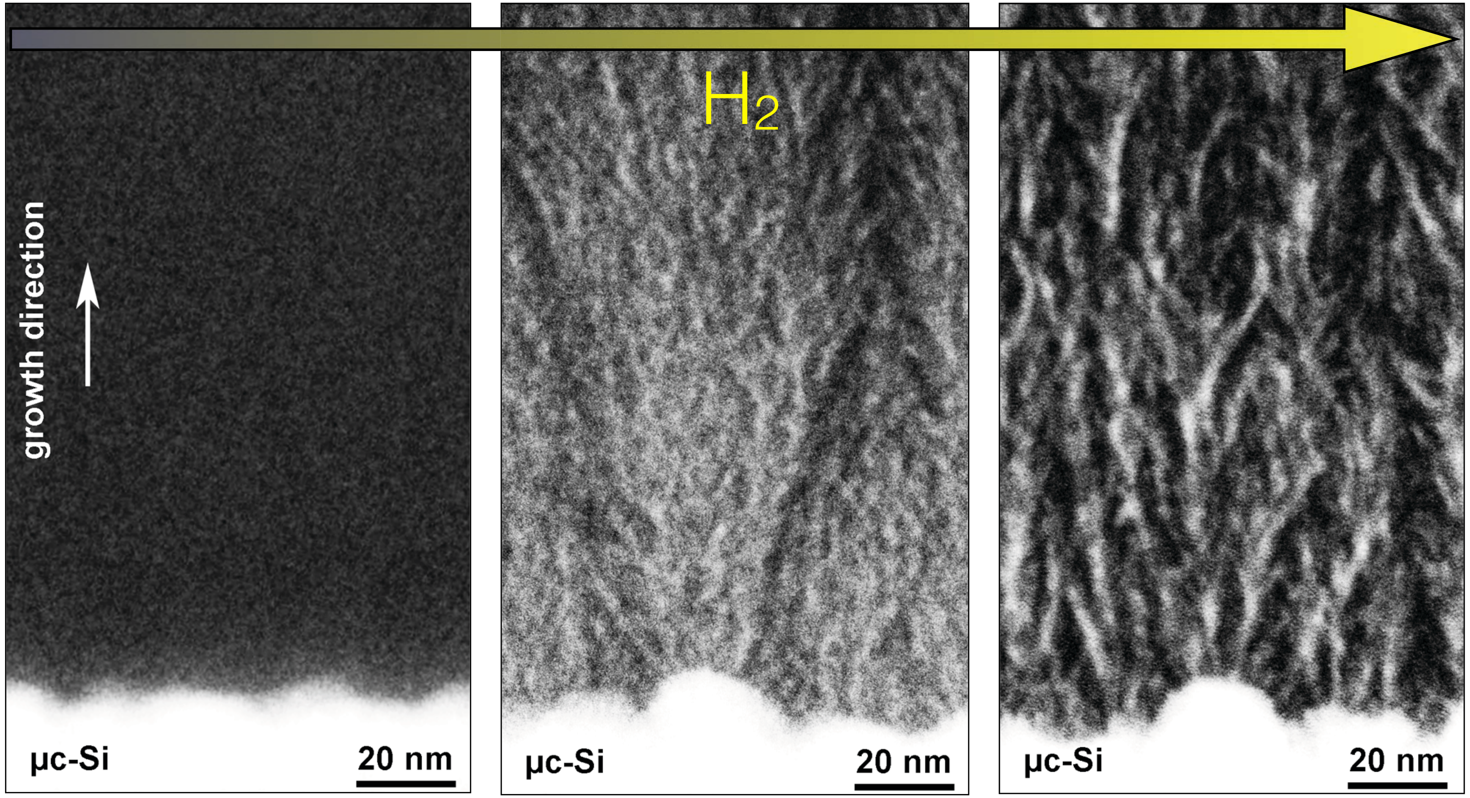
- Bulk plasmon region can also show single electron excitations
  $\Longrightarrow$ Low-loss spectrum has features related to phase electronic structure

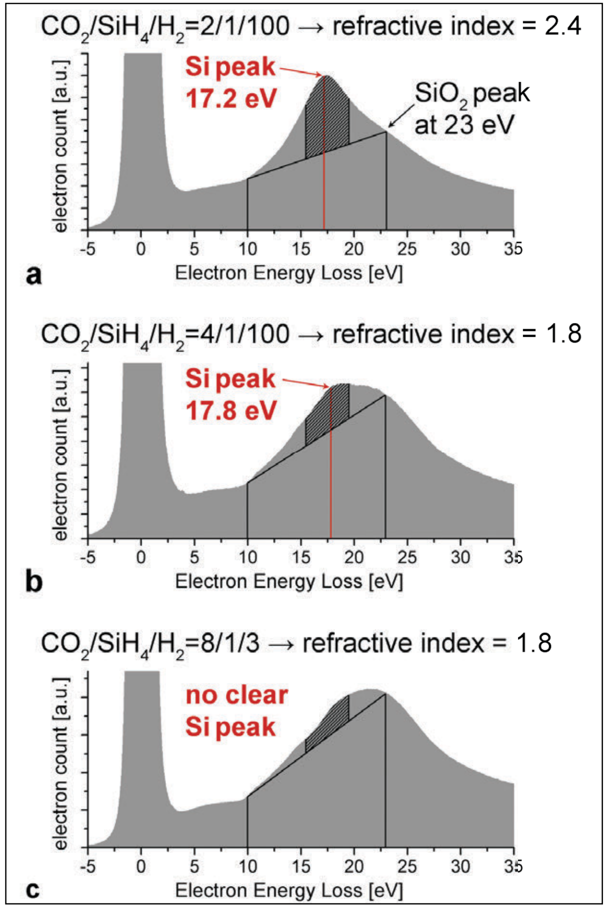
$SrTiO_3$ low-loss:



Ex. plasmon use: mapping elemental Si

- Use plasmon peak to map elemental Si nano-filaments in SiO_x thin films





- Increasing H_2 plasma ⟹ increased phase separation

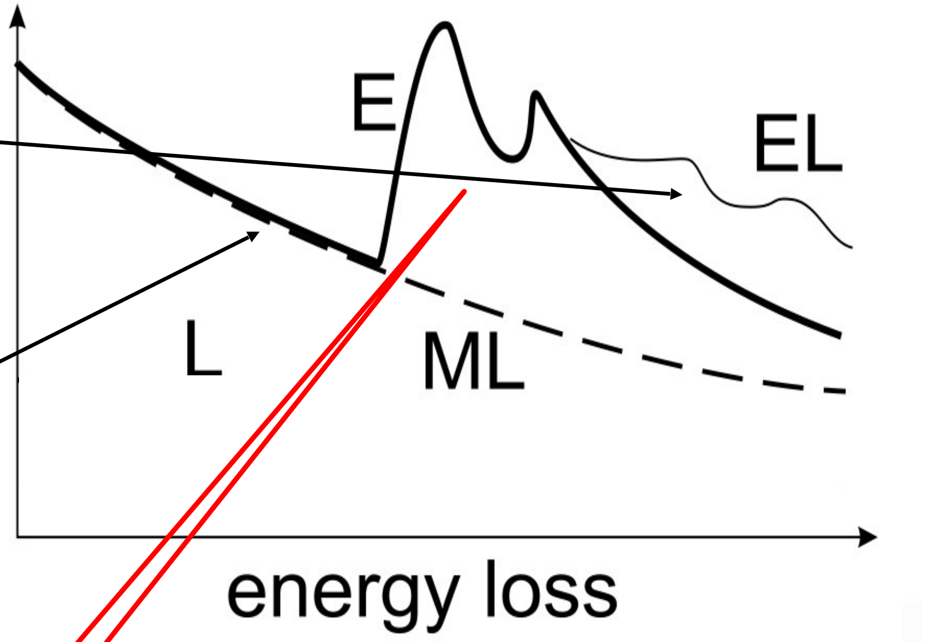
Cuony *et al.* Adv. Mater. **24** 1182 (2012)

Contents

Ionisation edge / “core-loss” analysis

Multiple scattering:
Fourier-ratio deconvolution

High energy tail of lower energy losses: background removal



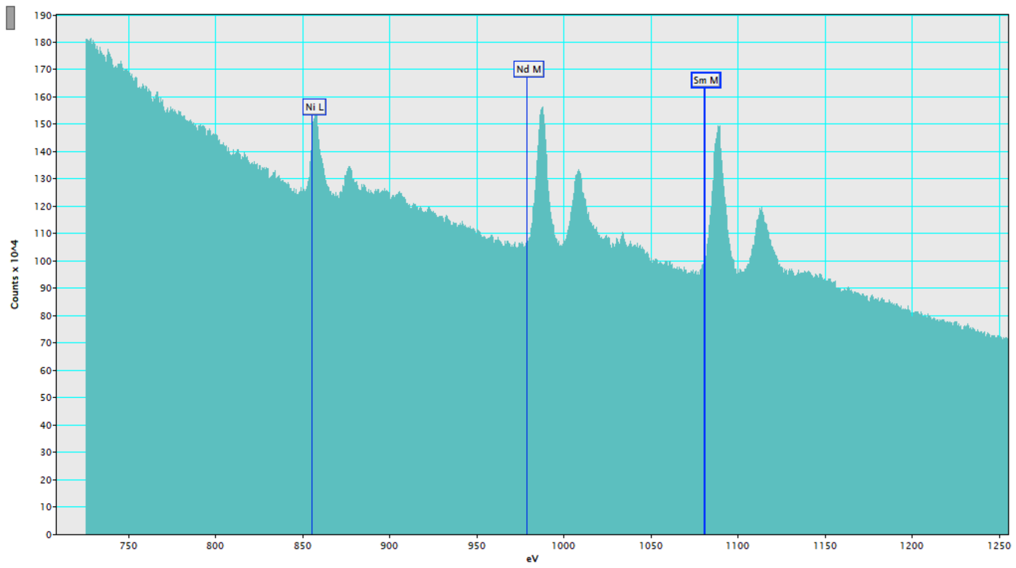
$$N = \frac{\boxed{I}}{j_0 \boxed{\Delta\sigma}}$$

Theoretical model –
e.g. hydrogenic, Hartree-Slater
(Digital Micrograph)

Ionisation edge / “core-loss” analysis

- Elemental ionisation edges superimposed on exponentially decaying background (fit with power-law model)
- Signal intensity proportional to projected atomic concentration and elemental partial ionisation scattering cross-section $\Delta\sigma$

(Nd, Sm)NiO_3 spectrum:



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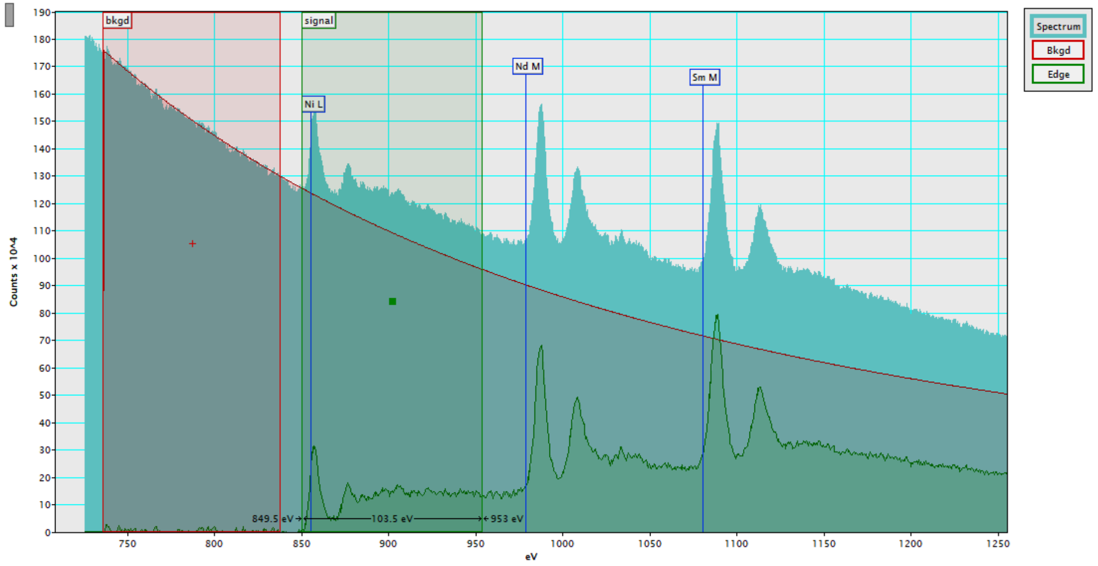
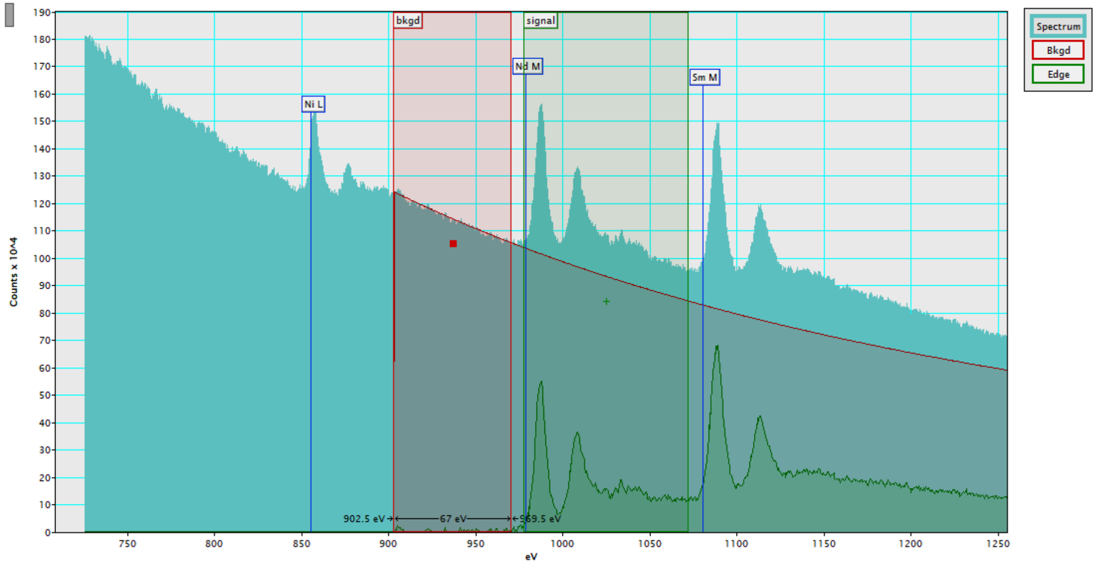
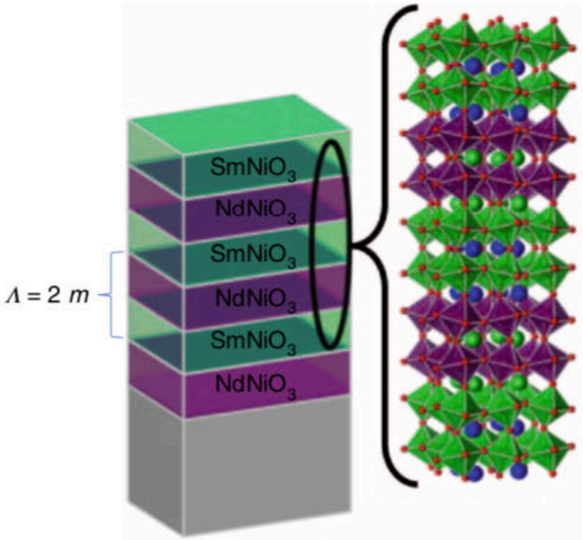


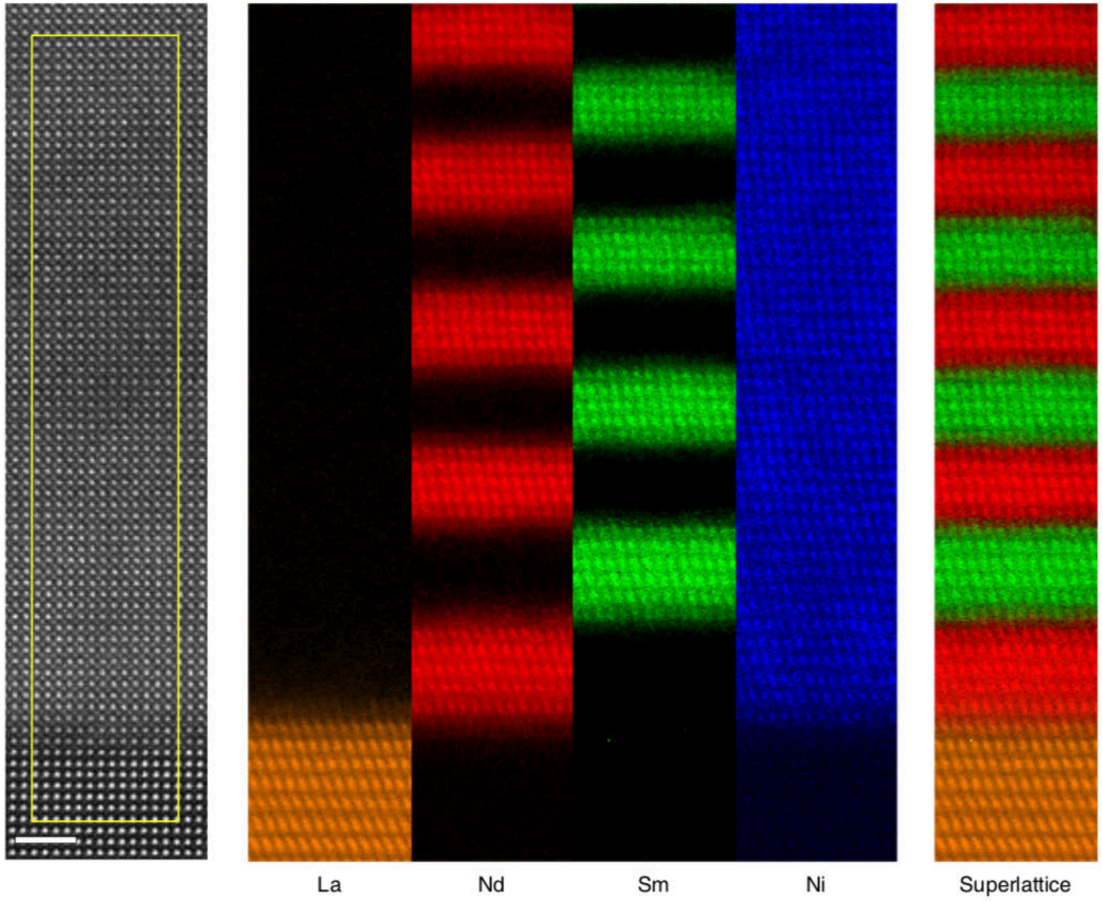


Elemental mapping – STEM-EELS

- Produce elemental maps by plotting integrated intensity in background-subtracted energy-loss "windows" that select different ionisation edges

Example: $NdNiO_3$ / $SmNiO_3$ superlattice on $LaAlO_3$

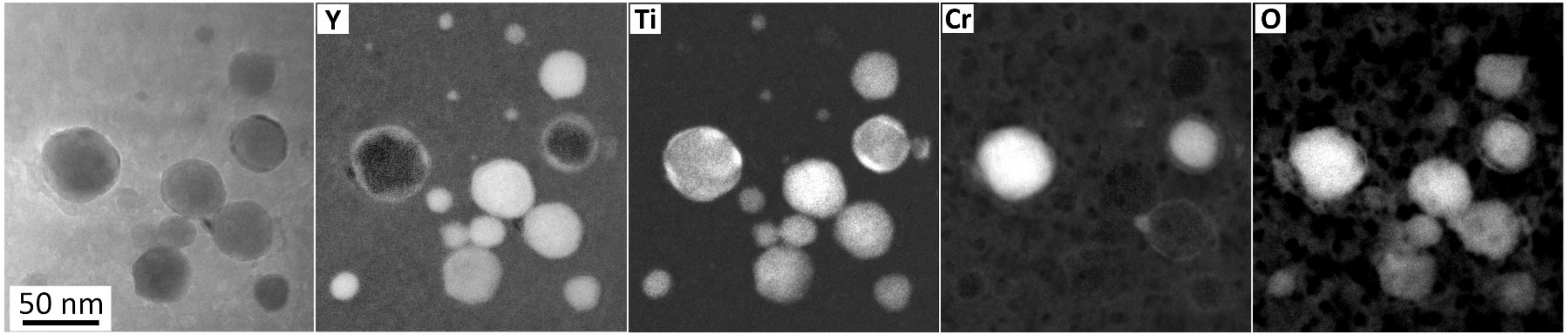




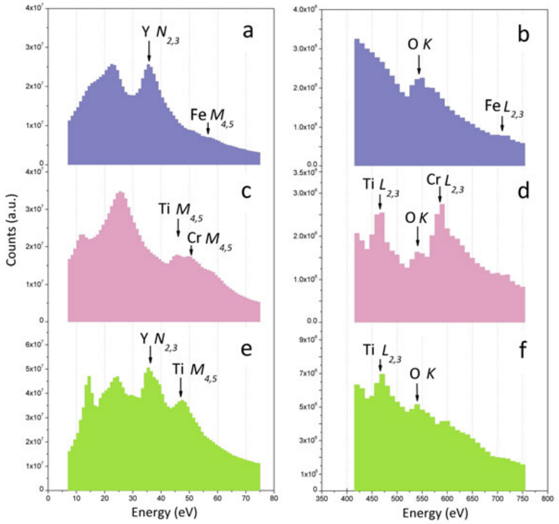
Dominguez et al. Nature Mater. **19** 1182 (2020)

Elemental mapping – EFTEM

- Example: EFTEM spectrum imaging of ODS reinforced steel
- Statistics obtained on spatial distribution of different particle types



Spectral fingerprints:



← Y-O particles: 6%, 16 nm

← Ti-Cr-O particles: 4%, 33 nm

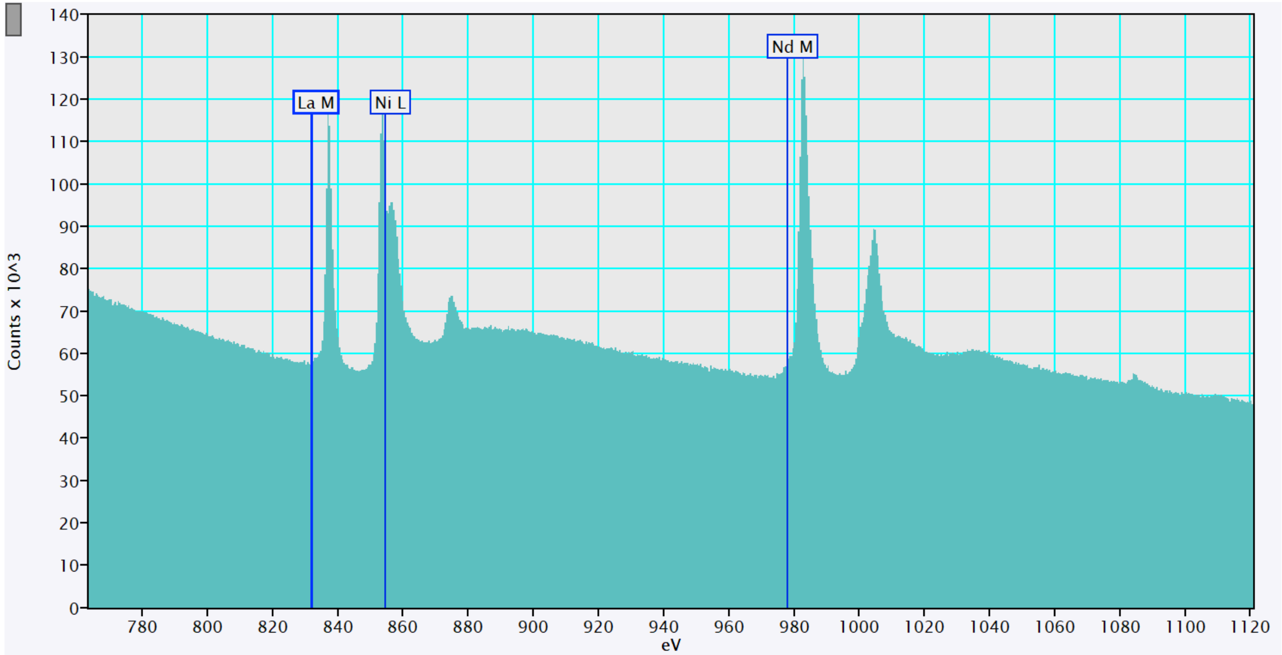
← Y-Ti-O particles: 90%, 6 nm

Unifantowicz et al. J. Nuclear Mater. **422** 131 (2012)

Mapping: choose your elements wisely!

- First step: look at the EELS Atlas!
- What are the energy losses of your elements?
- Which ionisation edges can you fit on one spectrum?
- Do you have any overlaps?

(La, Nd)NiO_3 alloy



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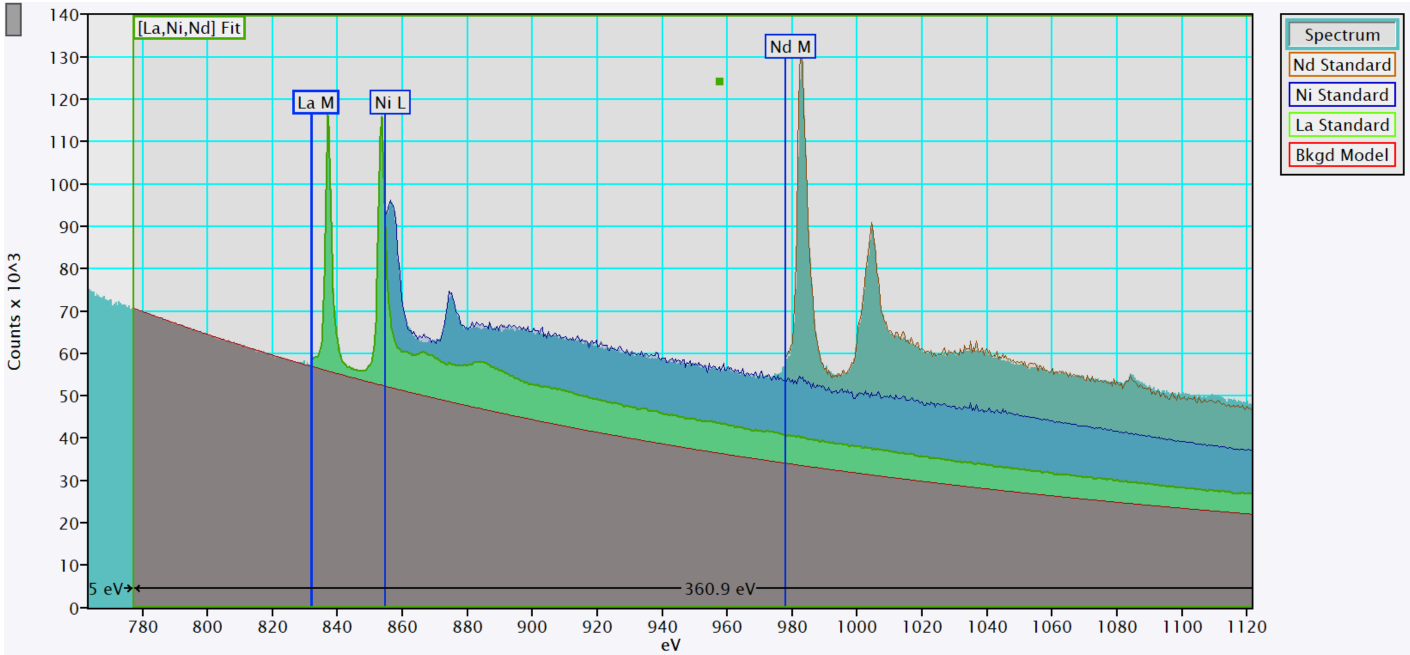

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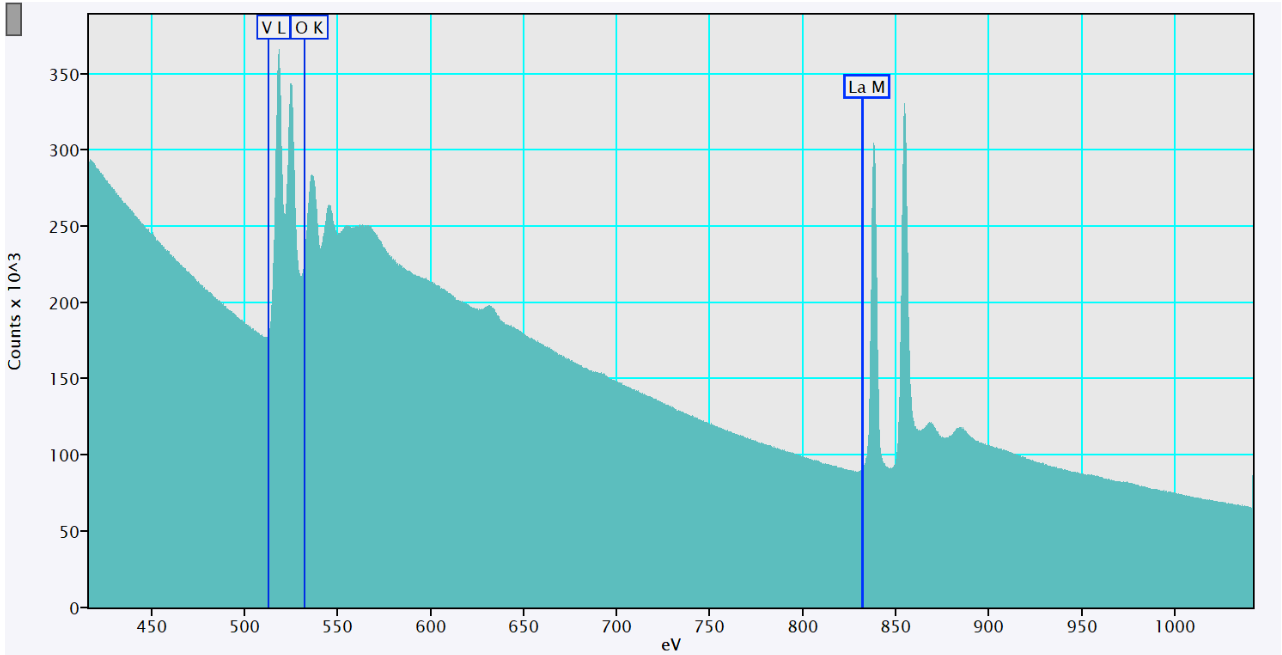
$LaVO_3$



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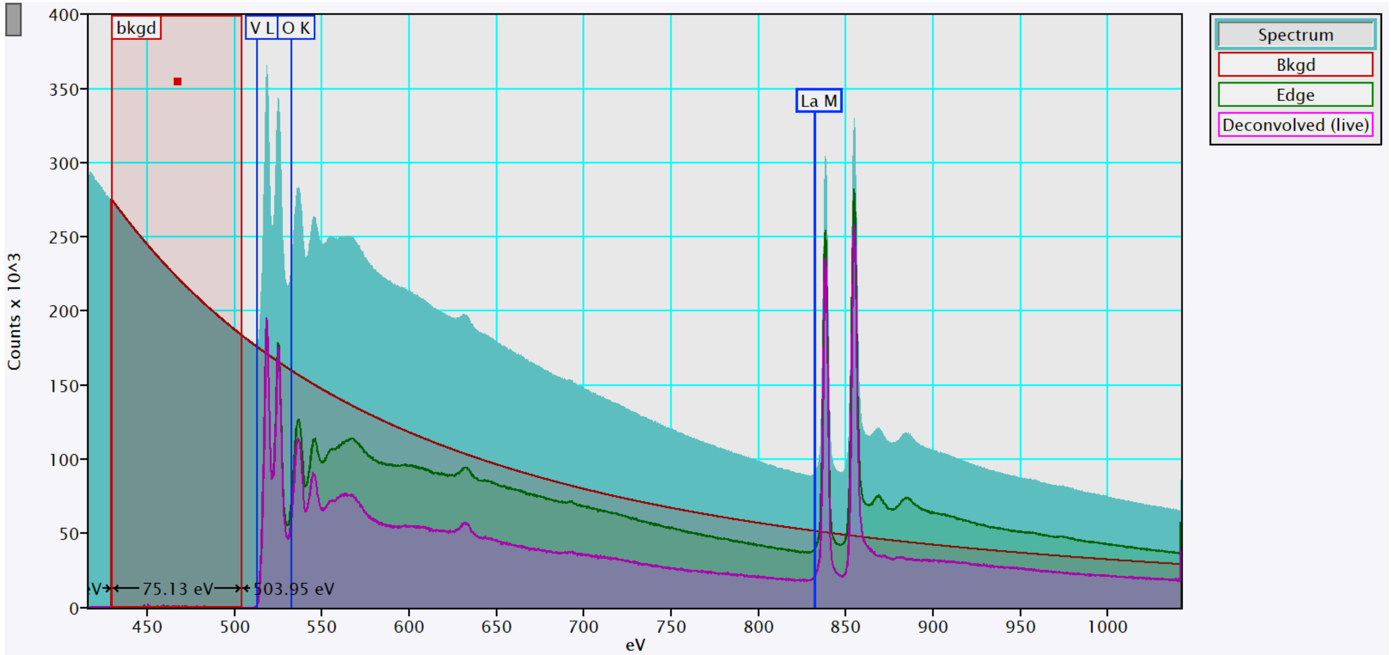
Fourier-log deconvolution to remove plural scattering (needs extra low-loss spectrum)

LaVO$_3$



Elemental quantification

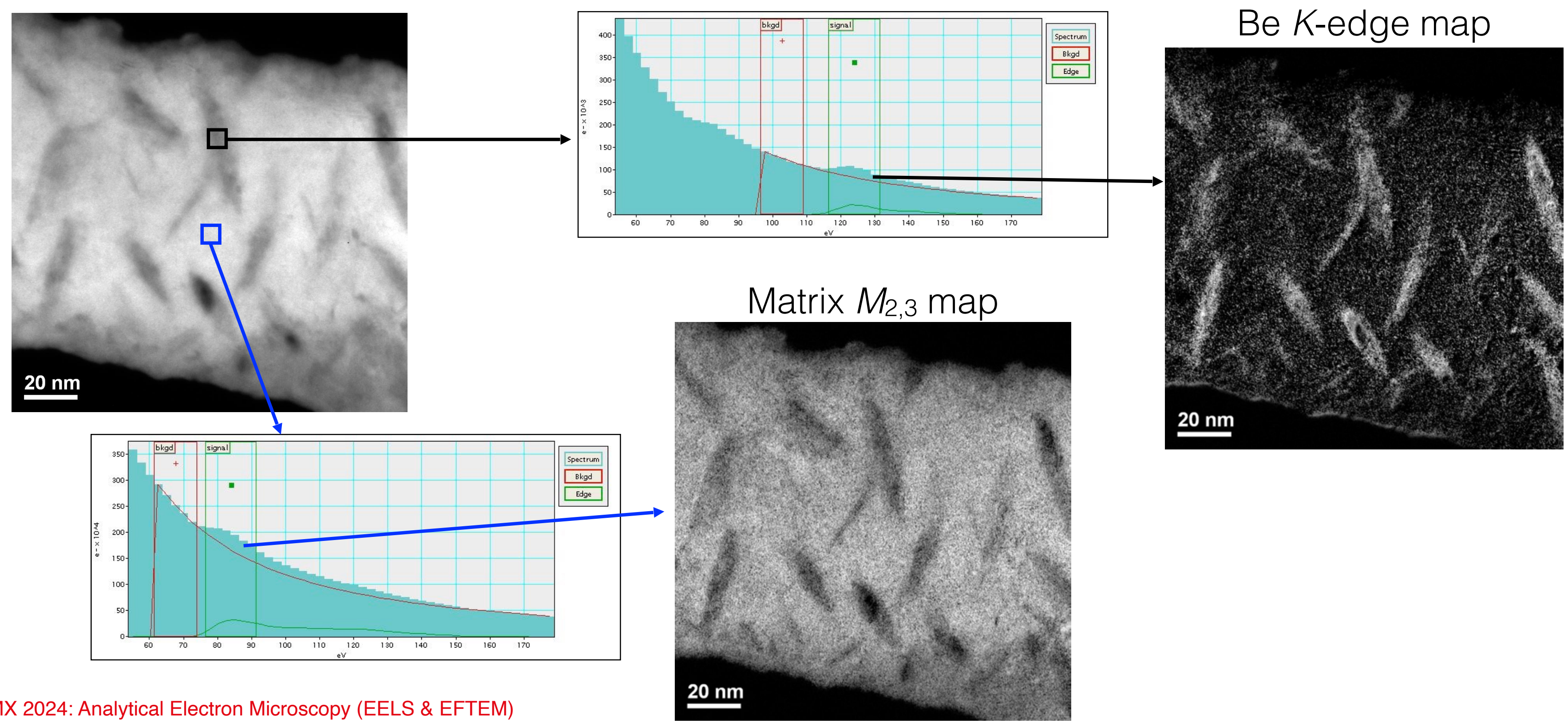
- Number of atoms per unit area N given by: $$N = \frac{I}{j_0 \Delta\sigma}$$
- Elemental percentages calculated using: $$\frac{N_a}{N_b} = \frac{I_a}{I_b}\frac{\Delta\sigma_b}{\Delta\sigma_a}$$
- For good quantification, need knowledge and correct choice of convergence semi-angle α and EEL spectrometer collection semi-angle β
- Example: BN measured in TEM mode ($\alpha \approx 0$) at 200 keV:
  - $\beta = 100$ mrad: 47 at.% B / 53 at.% N

→ Consider characteristic angle of scattering $\theta_\mathrm{E} \sim \Delta E / 2E_0$

Benefits of EELS vs EDXS

- No artefacts from fluorescence/stray emission
- Physics and chemistry: ELNES, plasmons (see later)
- Light elements: relatively strong intensity in EELS

Example:
Be mapping



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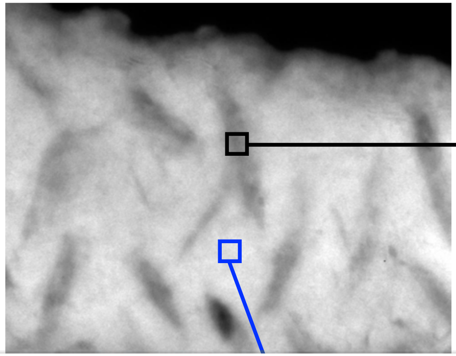
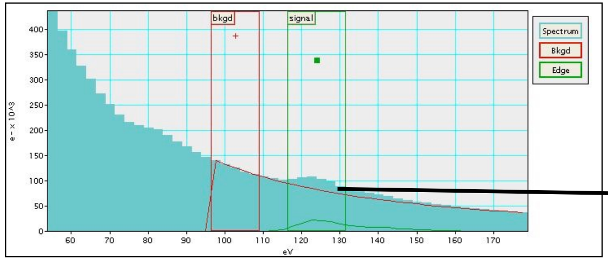
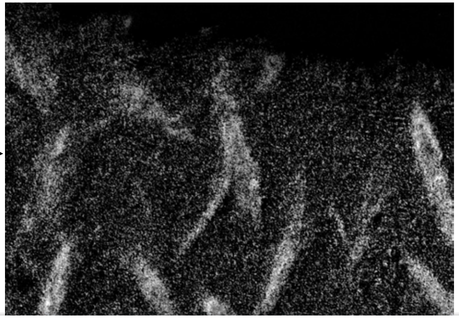




Be K-edge map



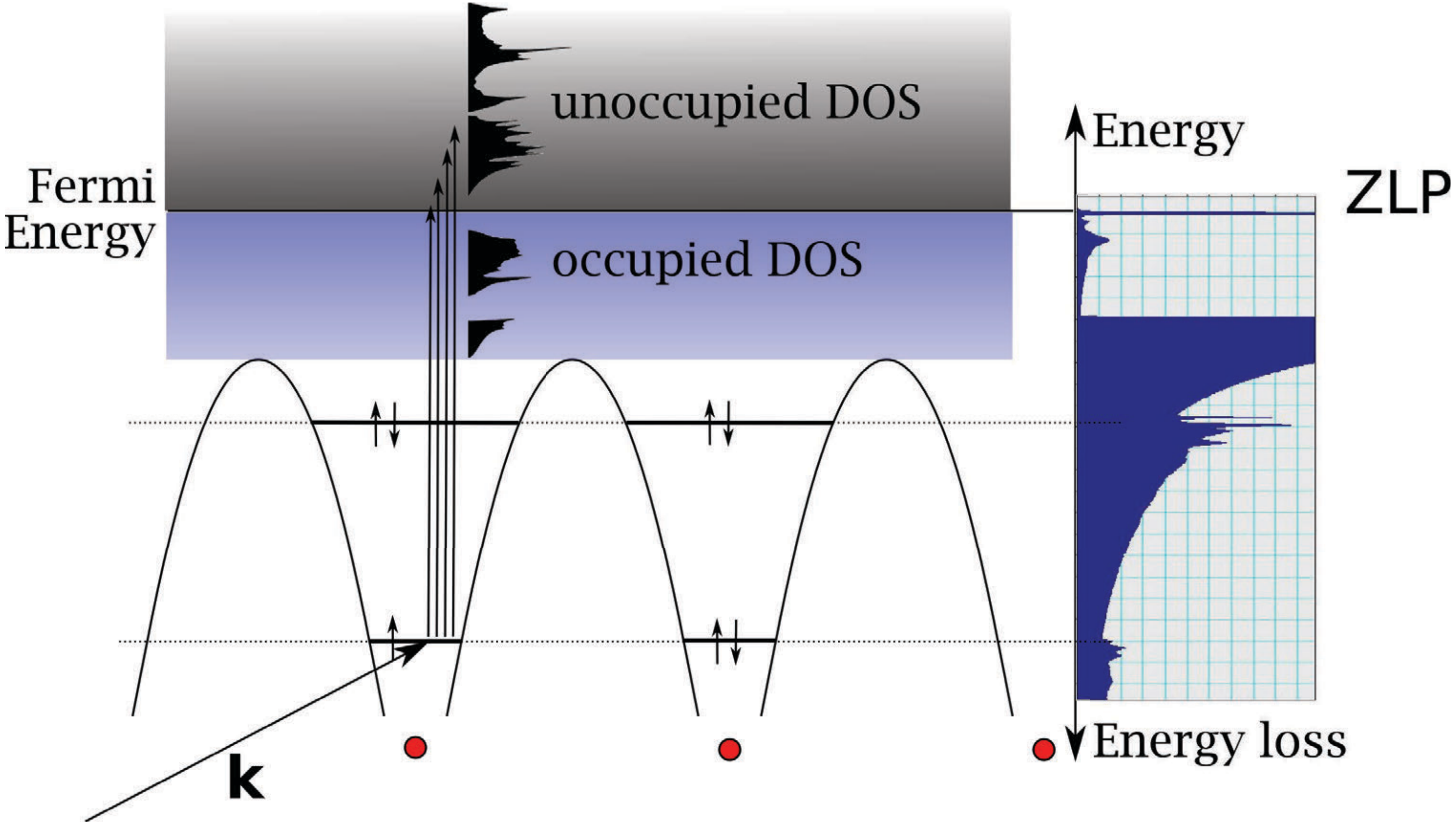
Matrix $M_{2,3}$ map

1. EELS: limited spectral range
→ (S)TEM-EDXS: large spectral range (e.g. 0–20 keV)

2. EELS: need thin samples (ideally $t / \lambda < 1$)
→ (S)TEM-EDXS much better than EELS for thick samples!

Energy-loss near edge structure (ELNES)

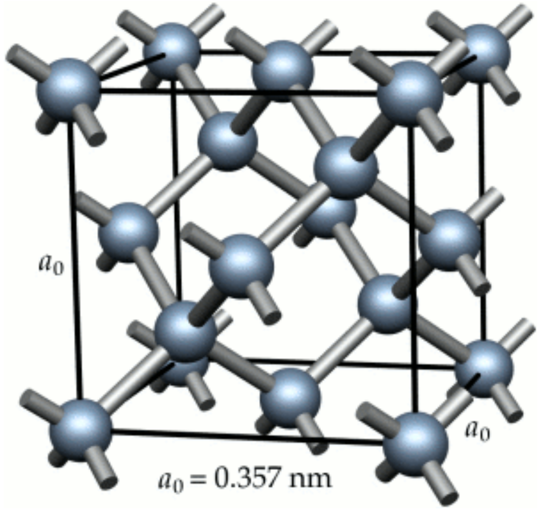
- Ionisation edge onsets show peaks related to unoccupied density of states (DOS)
- Fine structure comparable to X-ray absorption spectroscopy (XAS) data

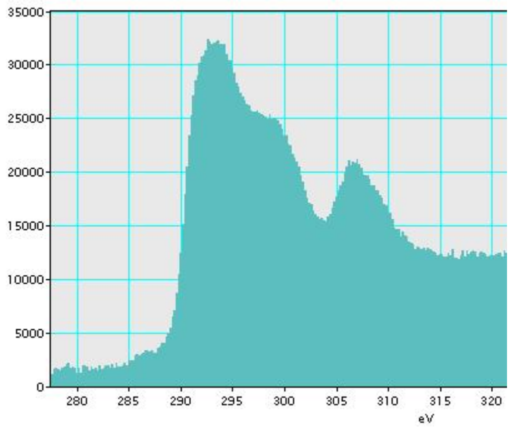


Core-loss fine structure

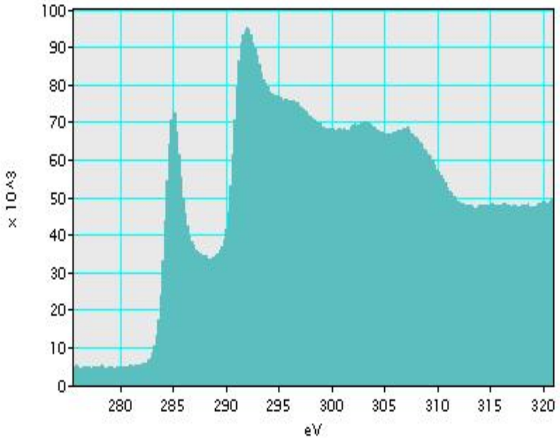
- Example: carbon *K*-edge

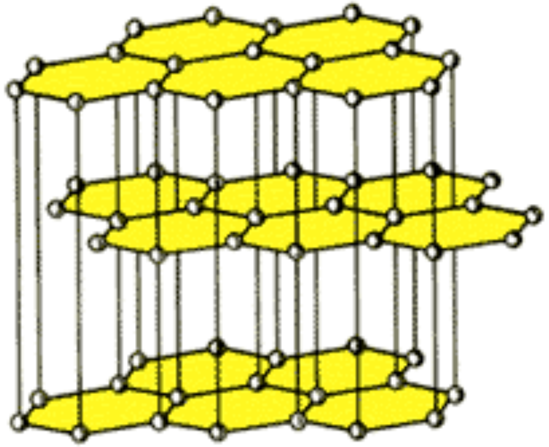
Diamond





Graphite

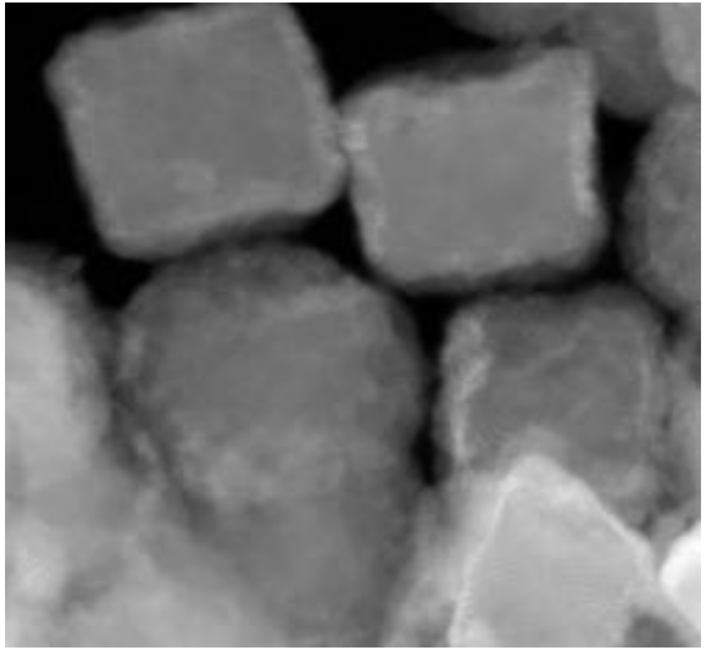




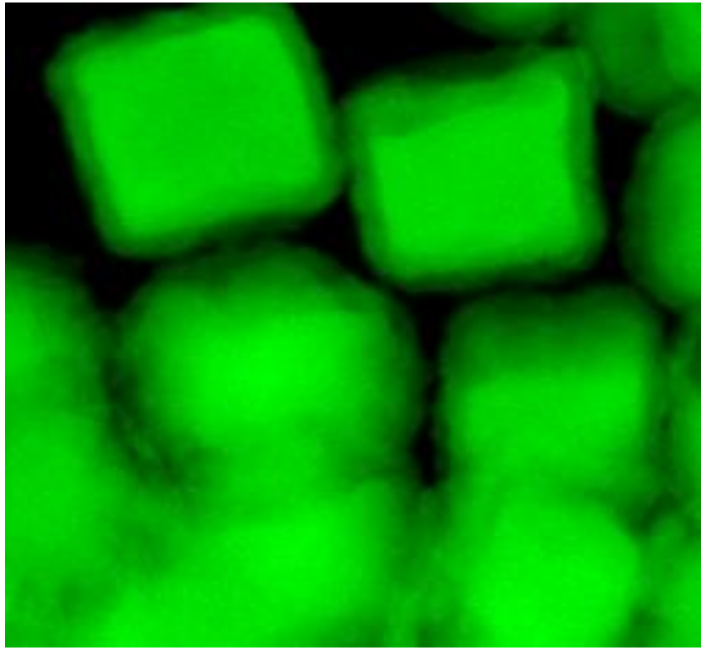
Core-loss fine structure analysis

- Cu nanocubes with oxide surface shell

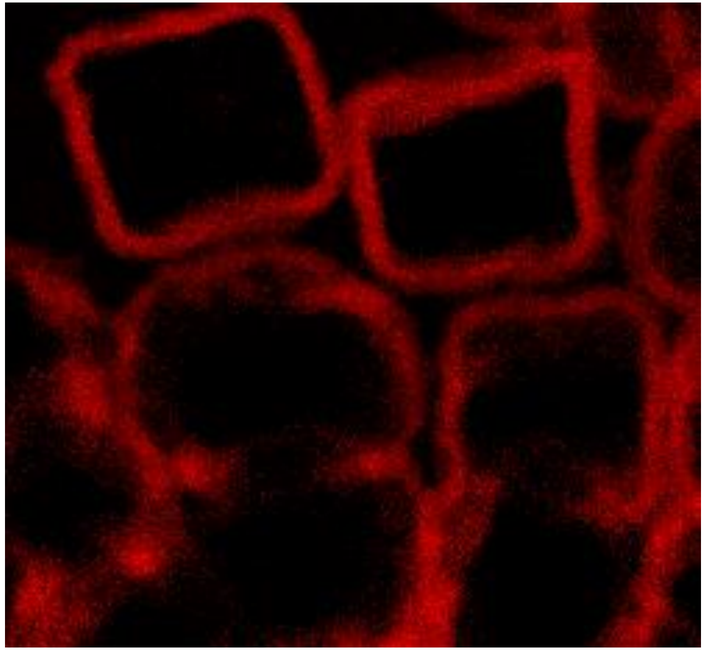
STEM image



Cu *L*-edge map



O *K*-edge map

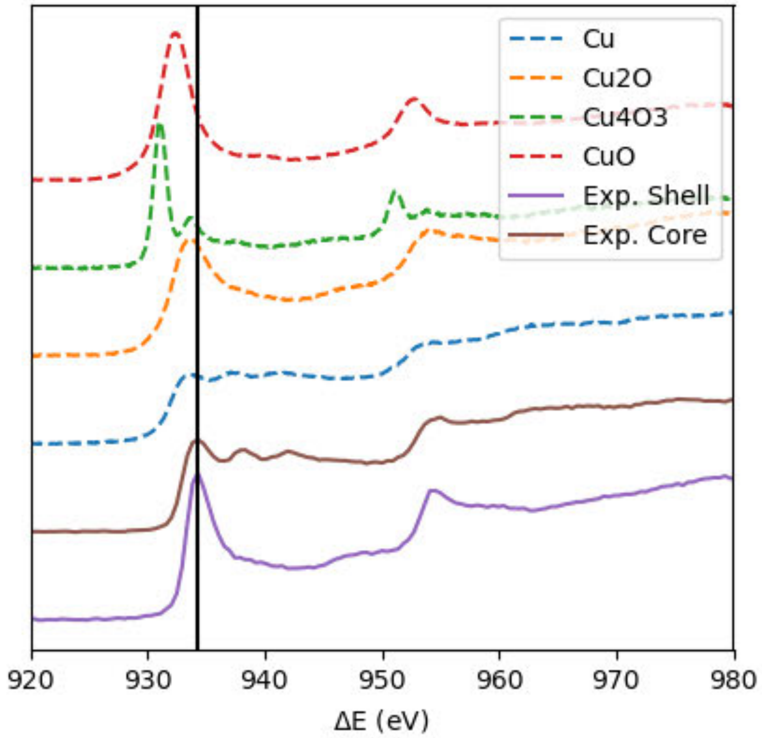


Analysis by Pau Torruella, LSME, EPFL

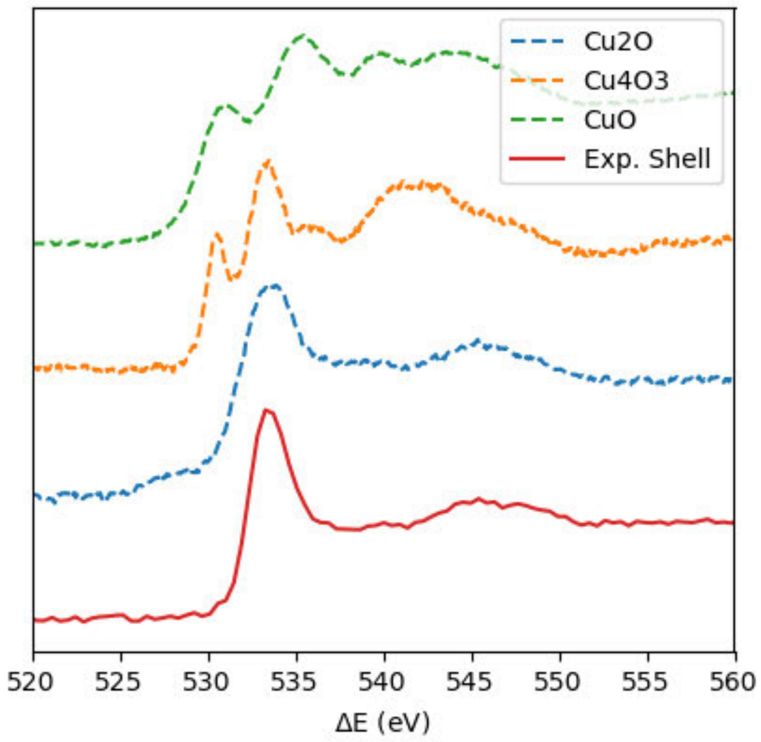
Core-loss fine structure analysis

- Cu nanocubes with oxide surface shell
- Compare experimental EELS fine structure to reference spectra from database

Cu *L*-edge



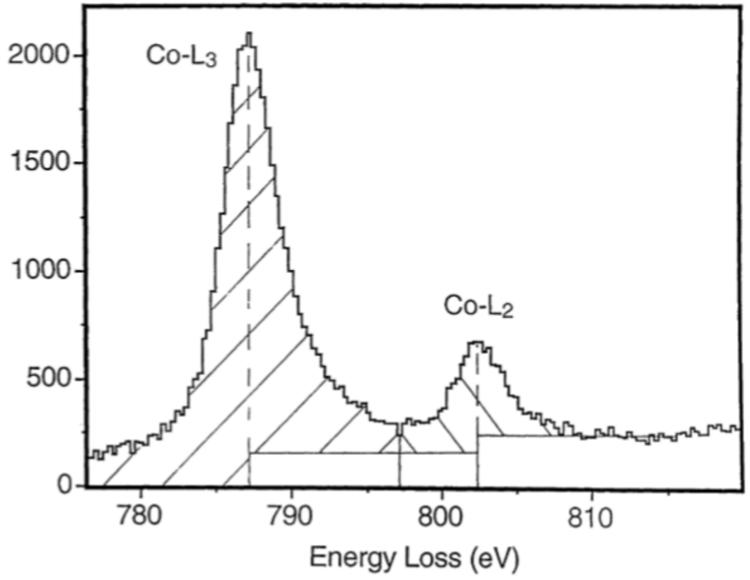
O *K*-edge

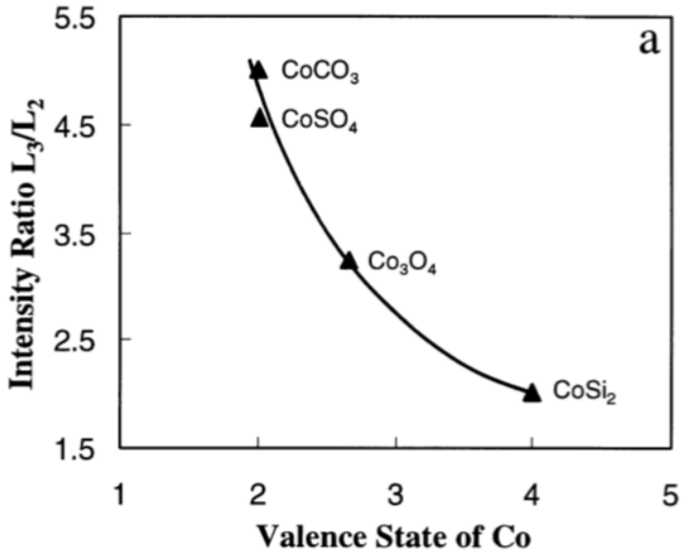


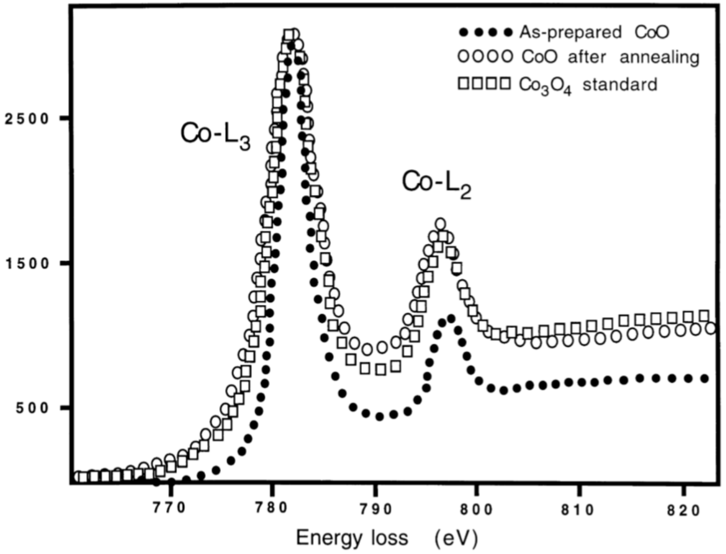
Analysis by Pau Torruella, LSME, EPFL

“White line” analysis

- ELNES peaks used to determine valence/oxidation state e.g. of transition metals
- Example: Co oxidation state



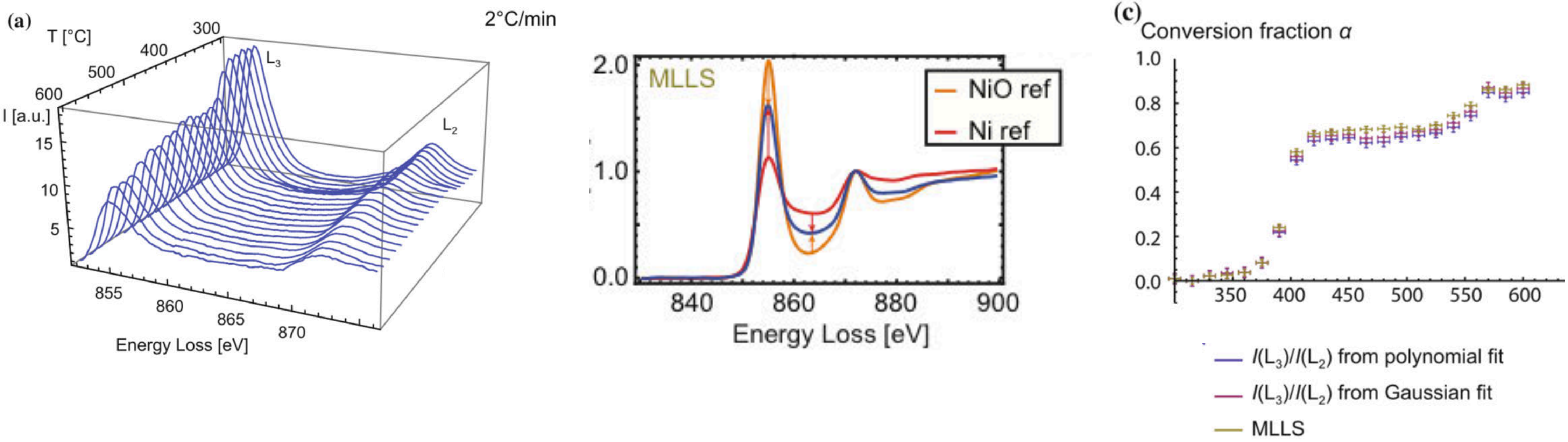




Wang et al. Micron **31** 571 (2000)

“White line” analysis

- ELNES peaks used to determine valence/oxidation state e.g. of transition metals
- Example: Ni oxidation state during *in-situ* reduction of NiO



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  Ray. F. Egerton: https://link.springer.com/book/10.1007%2F978-1-4419-9583-4
- EELS Atlas
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  A. Polman et al., Nature Mater. **18**, 1158 (2019):
  https://doi.org/10.1038/s41563-019-0409-1