Electron Energy-Loss Spectroscopy (EELS) Basics

CIME
Interdisciplinary
Centre for
Electron
Microscopy

Based on the previous workflow
from
Duncan Alexander
IPHYS-LSME

MSE-735 Scanning and Analytical Transmission Electron Microscopy

EELS Basics

PRESEDENTED BY
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November 2025

École
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fédérale
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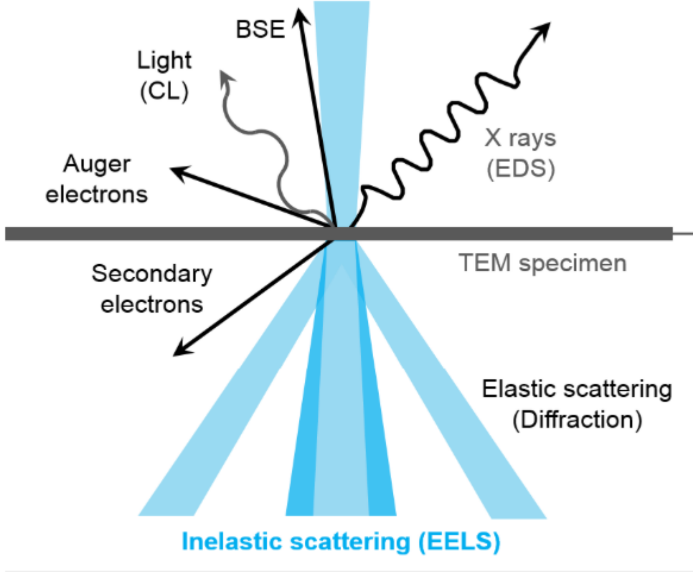
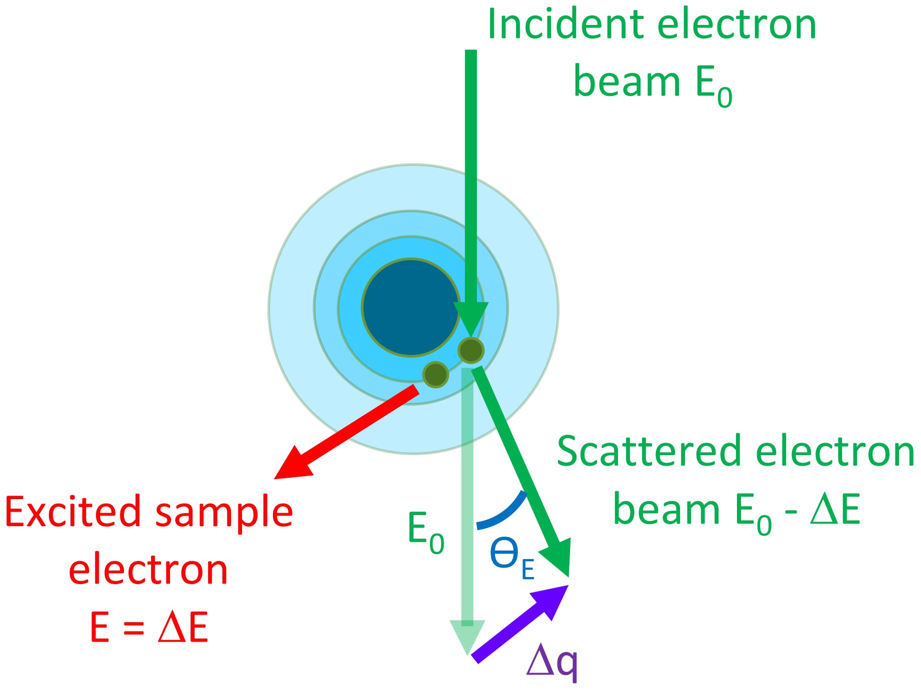
OUTLINE

- What is EELS?
- Ionization energy loss
- Spectrometers
- Key parameters
- Spectrum imaging
- The Electron Energy-loss spectrum
- Low-loss EELS
  - Spectral deconvolution
  - Volume plasmon
  - Plasmonic resonance
  - Light elements
- Ionization edges / core–loss
  - Elemental distribution
  - Elemental quantification
  - ELNES
  - Fine structure
  - White lines
  - EELS spatial resolution
  - What we should retain?
  - References

What is EELS?





Incident electron beam E_0

Excited sample electron $E = \Delta E$

E_0

θ_E

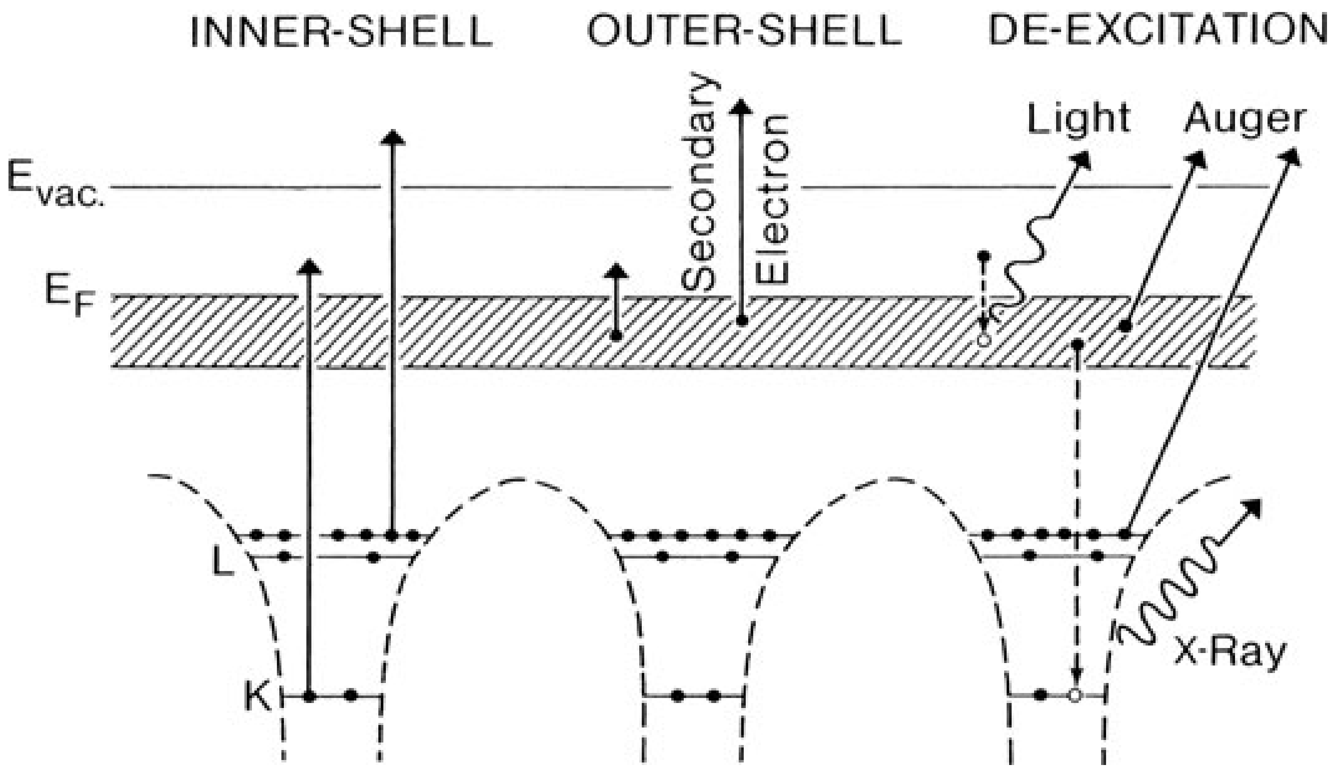
Scattered electron beam $E_0 - \Delta E$

Δq

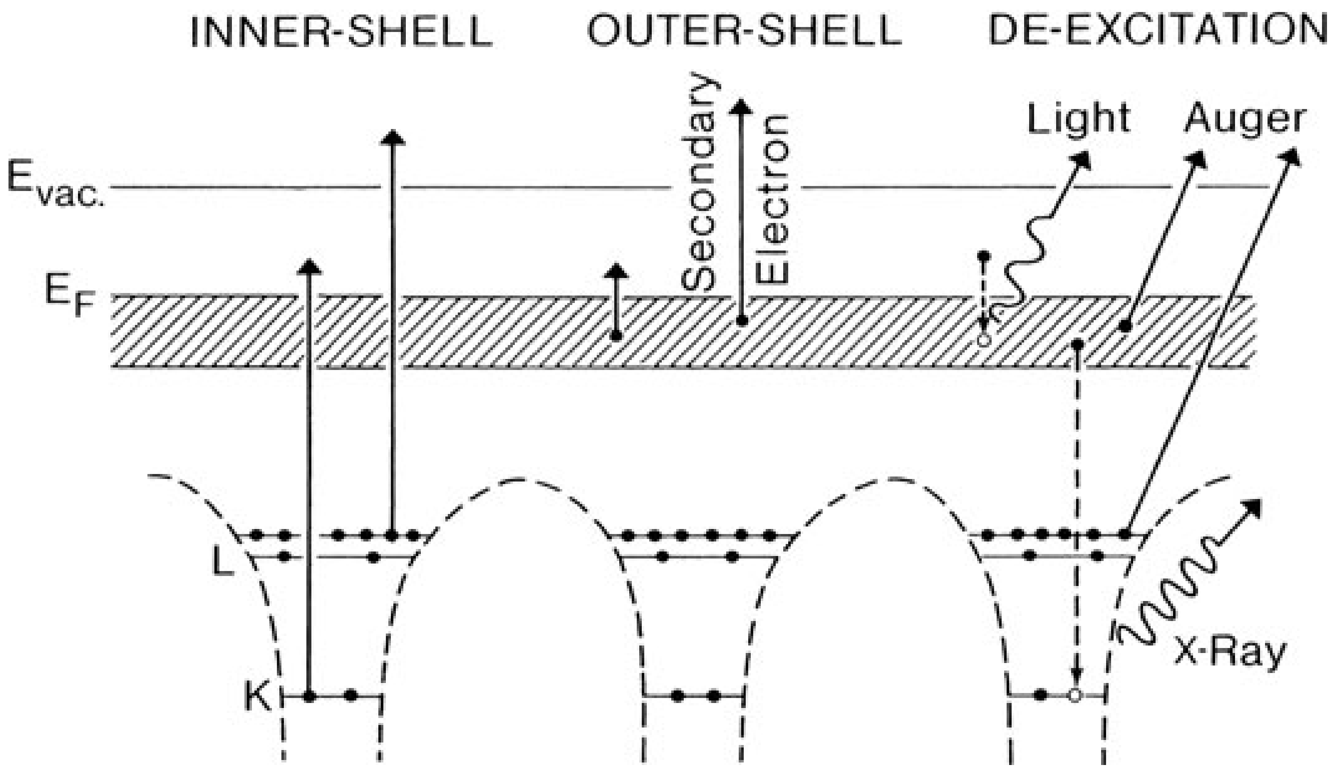
$$\theta_E = \frac{\Delta E}{2F_g E_0}$$

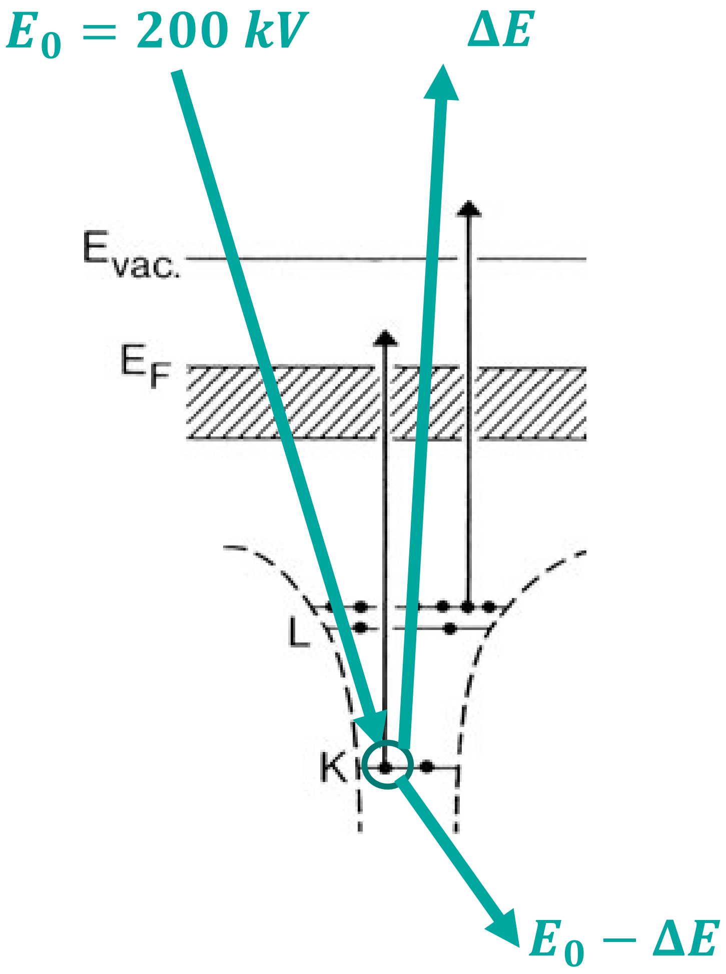
- The primary electron transfers both energy and momentum (angle)
- The primary electron is then measured in the EELS system.
- Both, the final energy and scattering angle are important.
- EELS probes primary events
- EELS is highly localized
  - No peripheral “fluorescence” or interactions
  - The only delocalization is that due to the quantum nature of the interaction
- EELS features reflect specimen electronic structure and excitations.

Ionization energy loss



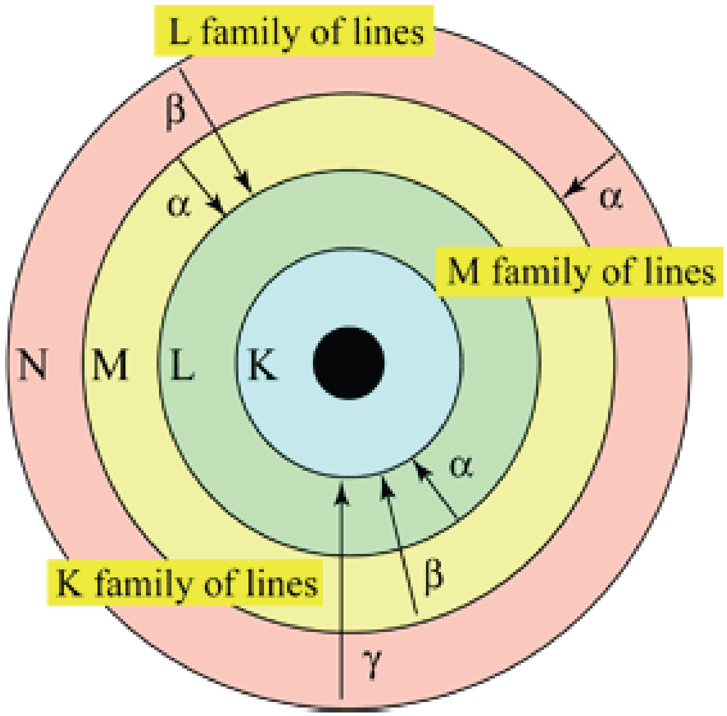
Ionization energy loss

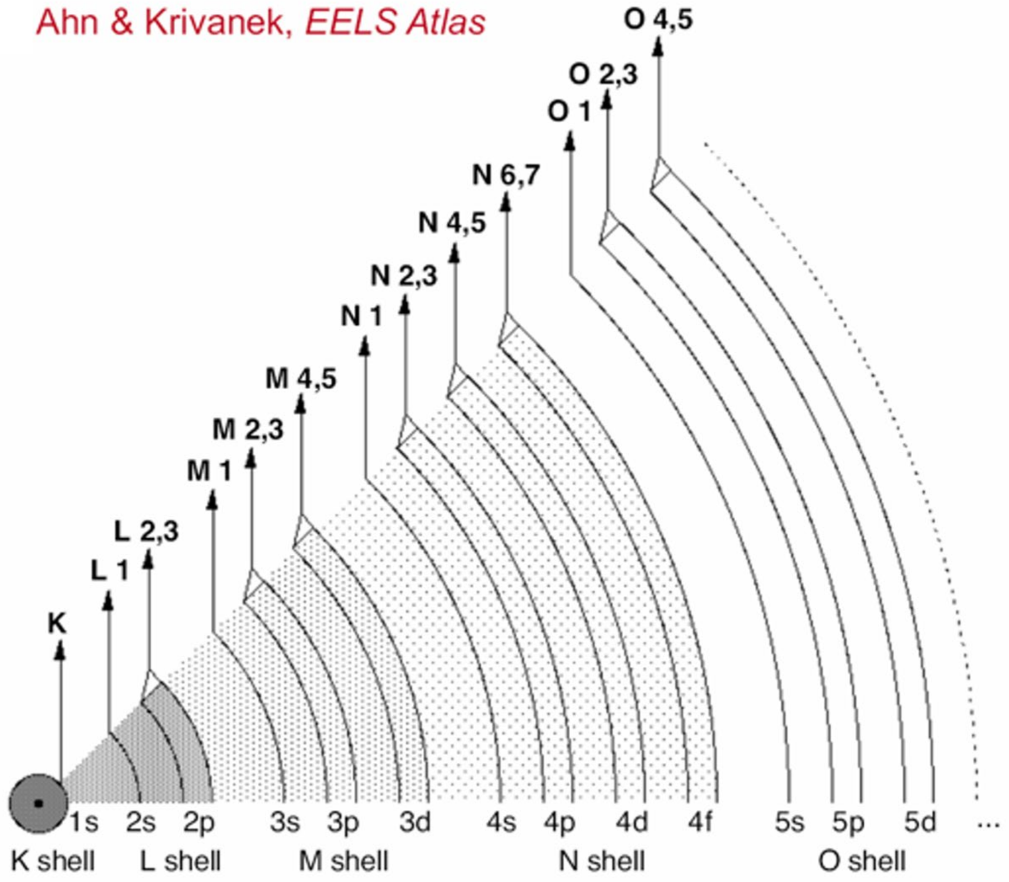




Energy-loss K-edge

Nomenclature of EELS ionization edges




Ahn & Krivanek, *EELS Atlas*

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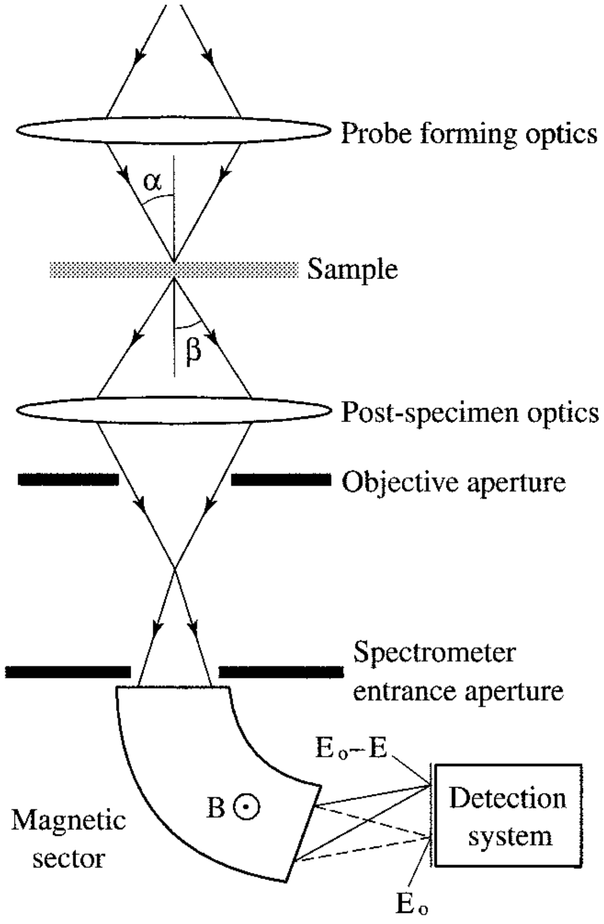
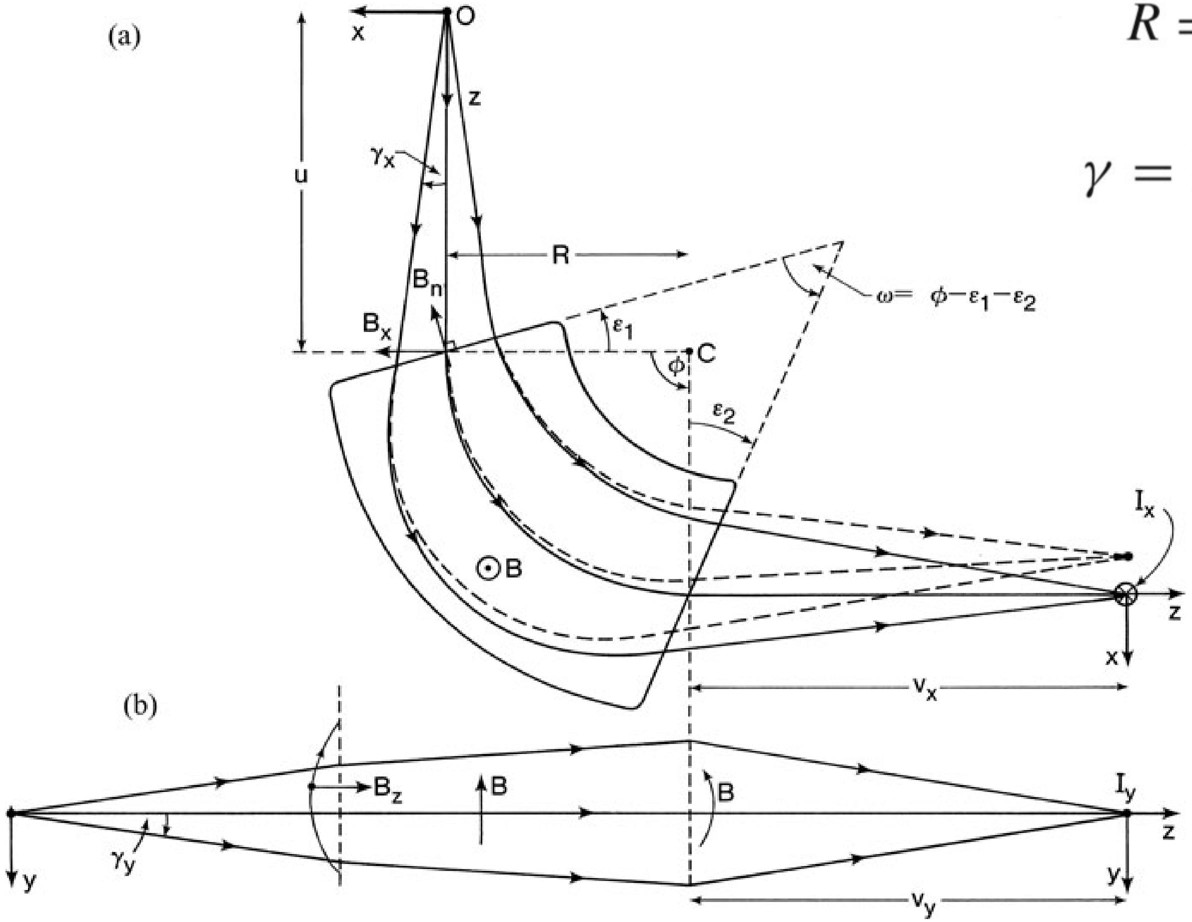
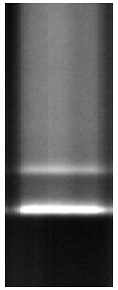
Electron energy-loss spectrometer



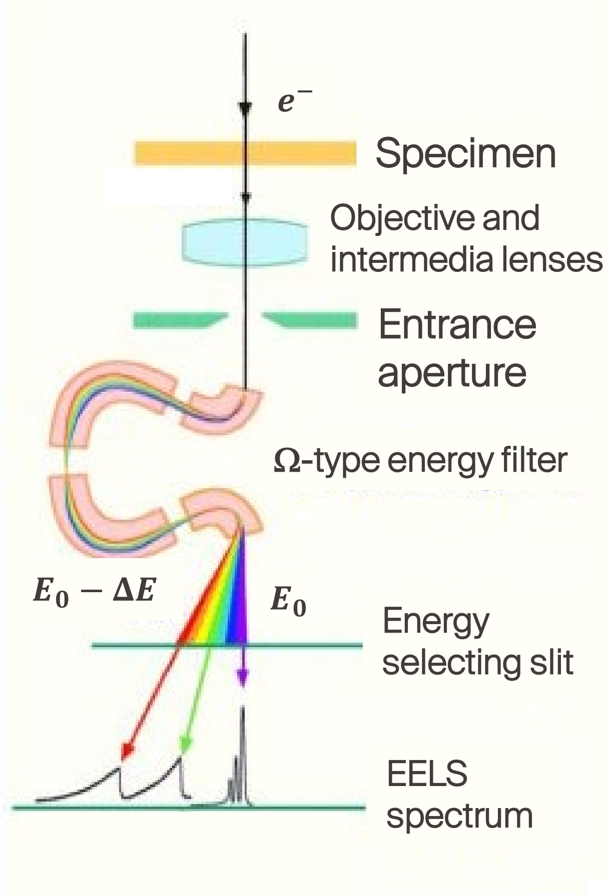


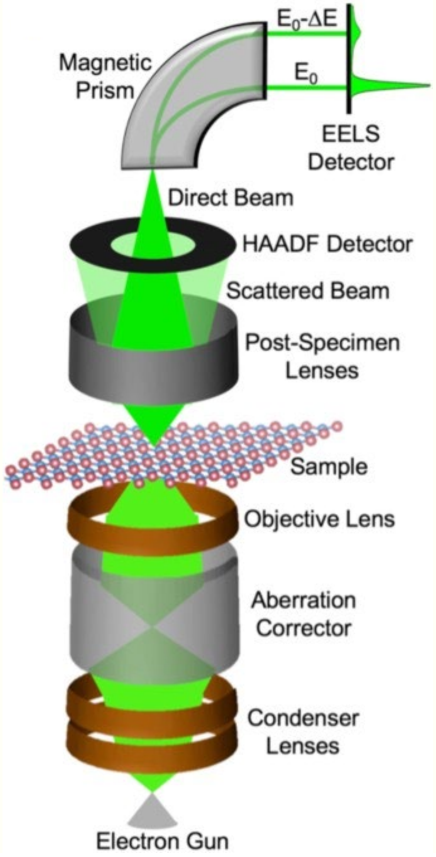
$$R = (\gamma m_0 / eB) v$$

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



Spectrometers



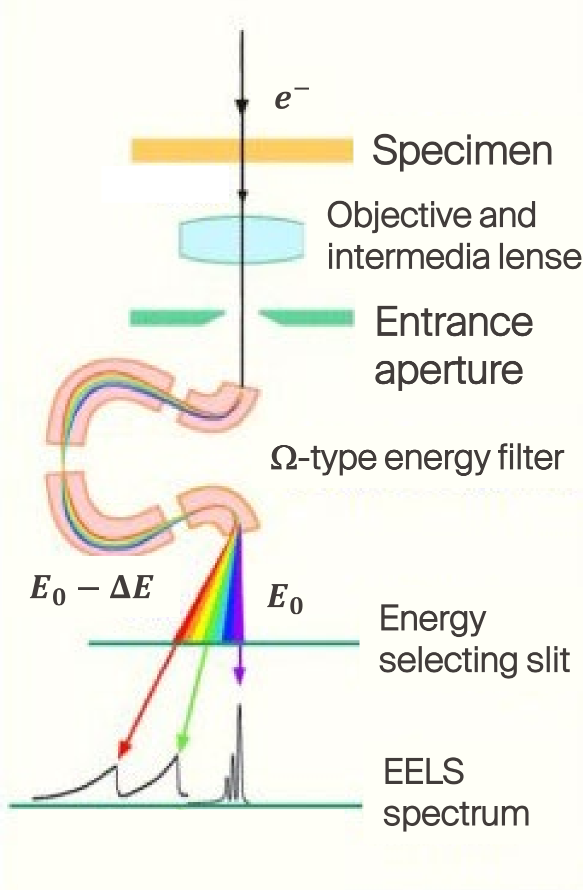


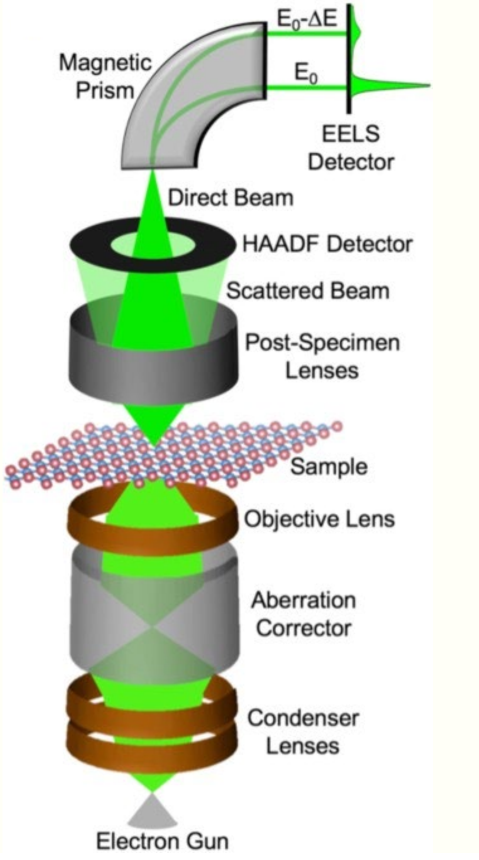
In-column

Post-column

Jordan A. Hachtel et al. *Scientific Reports volume 8, 5637 (2018)*

Spectrometers





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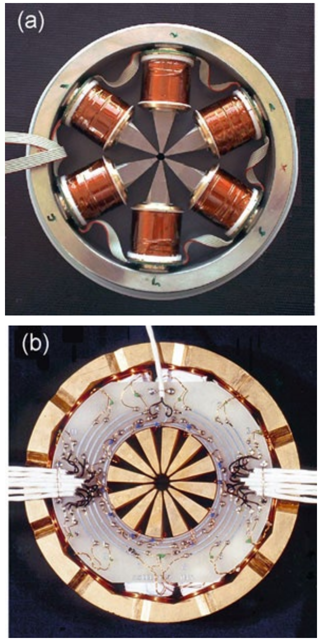

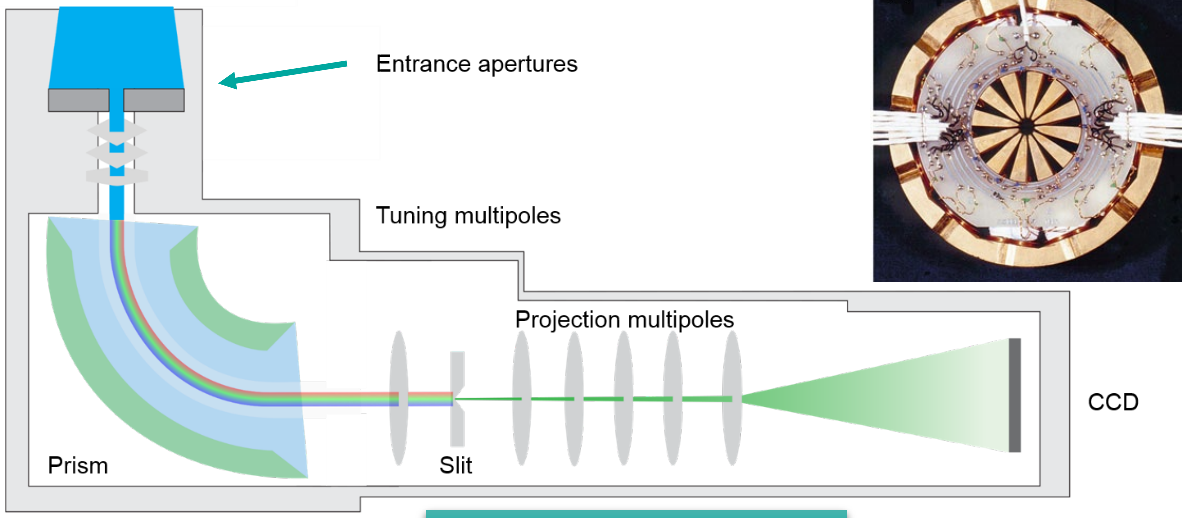

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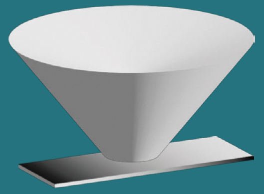
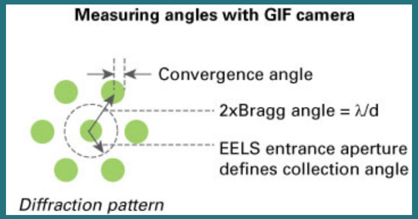
Key parameters

Semi Convergence angle: α





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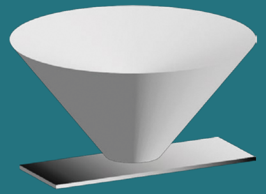
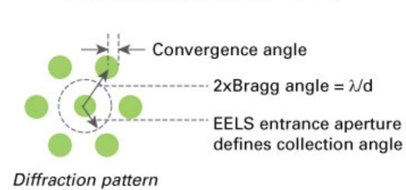
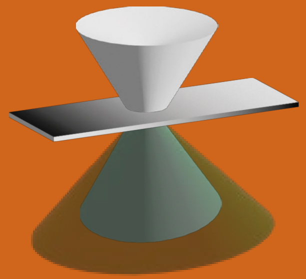
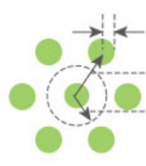
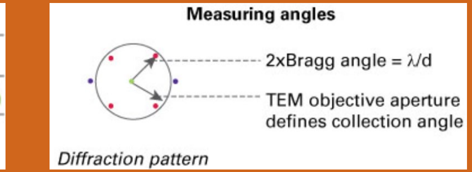




Semi Collection angle: β







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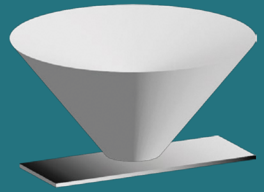

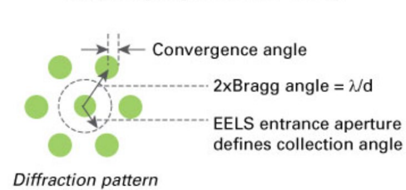

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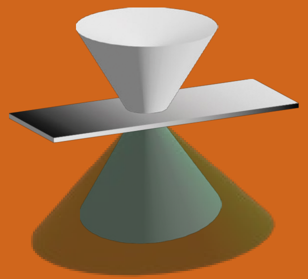
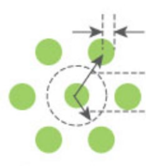
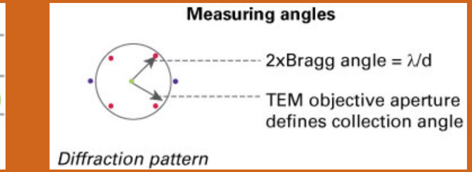
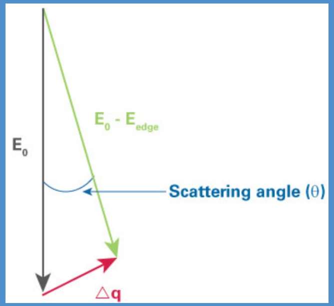






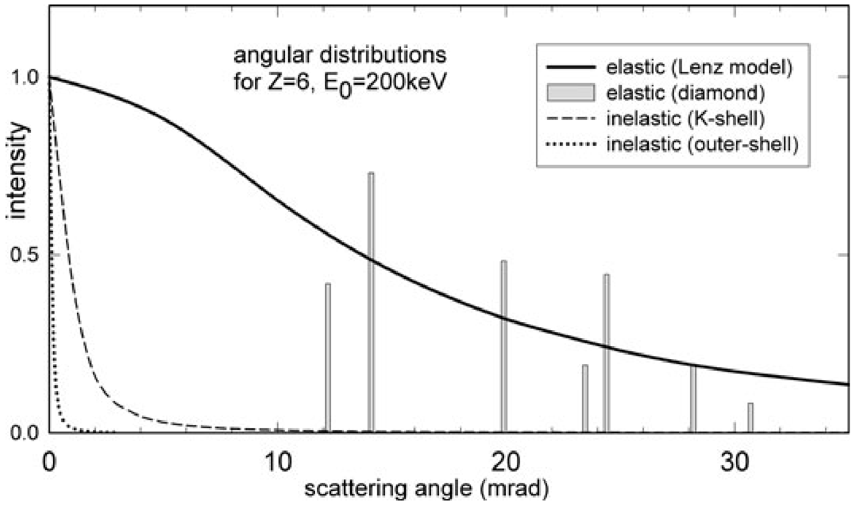
Innelastic scattering angle: θ_E

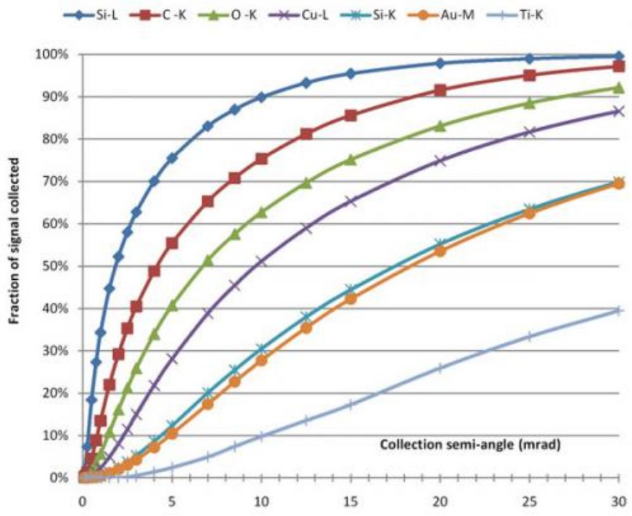


$$\theta_E = \frac{\Delta E}{\gamma m_0 v^2} \sim \frac{\Delta E}{2E_0}$$

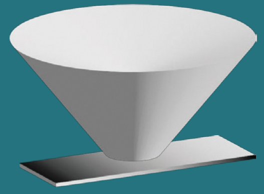
Recommended $2\theta_E$ or $3\ \theta_E$

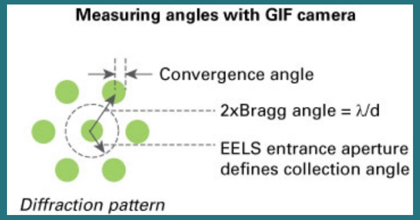
Key parameters



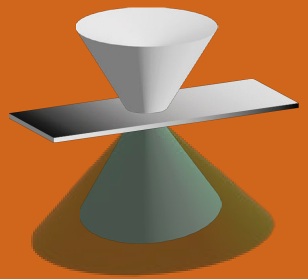


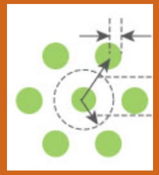
Semi Convergence angle: α

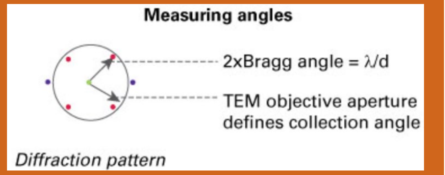




Semi Collection angle: β







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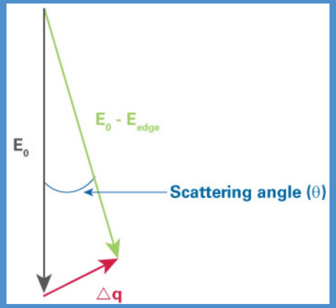


$$\theta_E = \frac{\Delta E}{\gamma m_0 v^2} \sim \frac{\Delta E}{2E_0}$$

Recommended $2\theta_E \ or \ 3\ \theta_E$

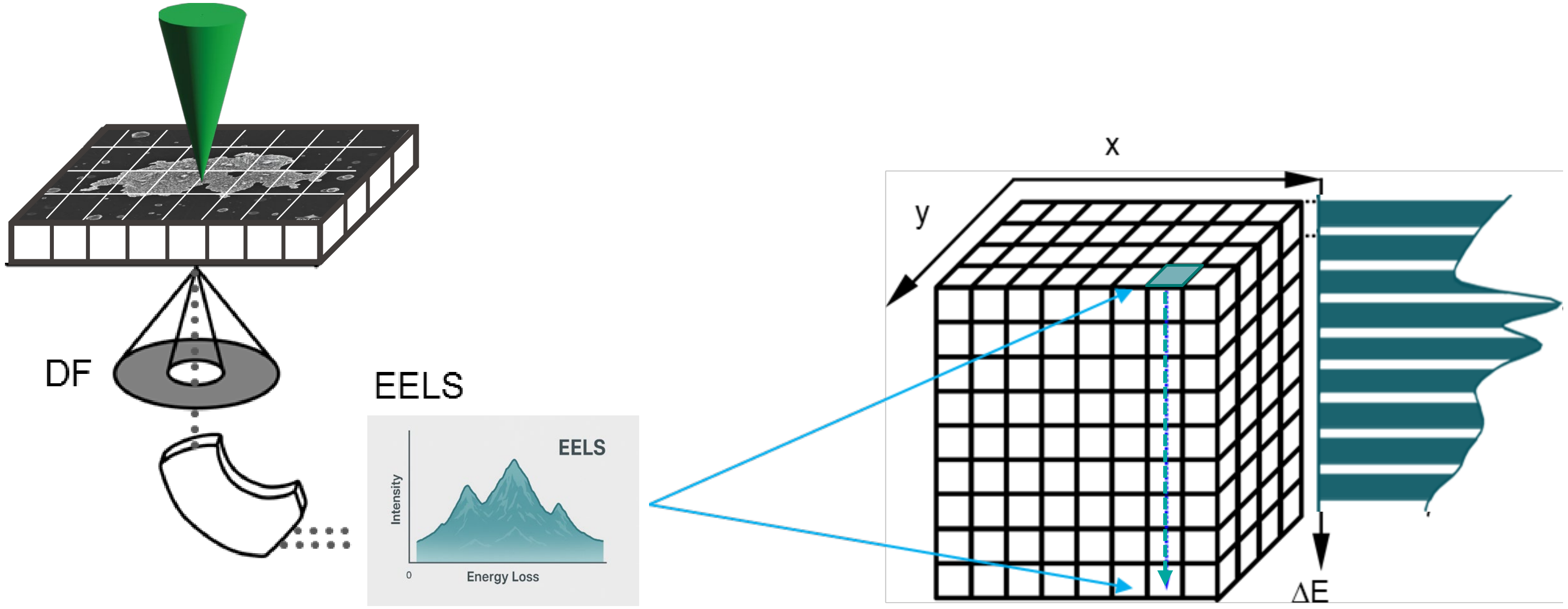
Carbon

C-K$_{\text{edge}}$= 284 eV

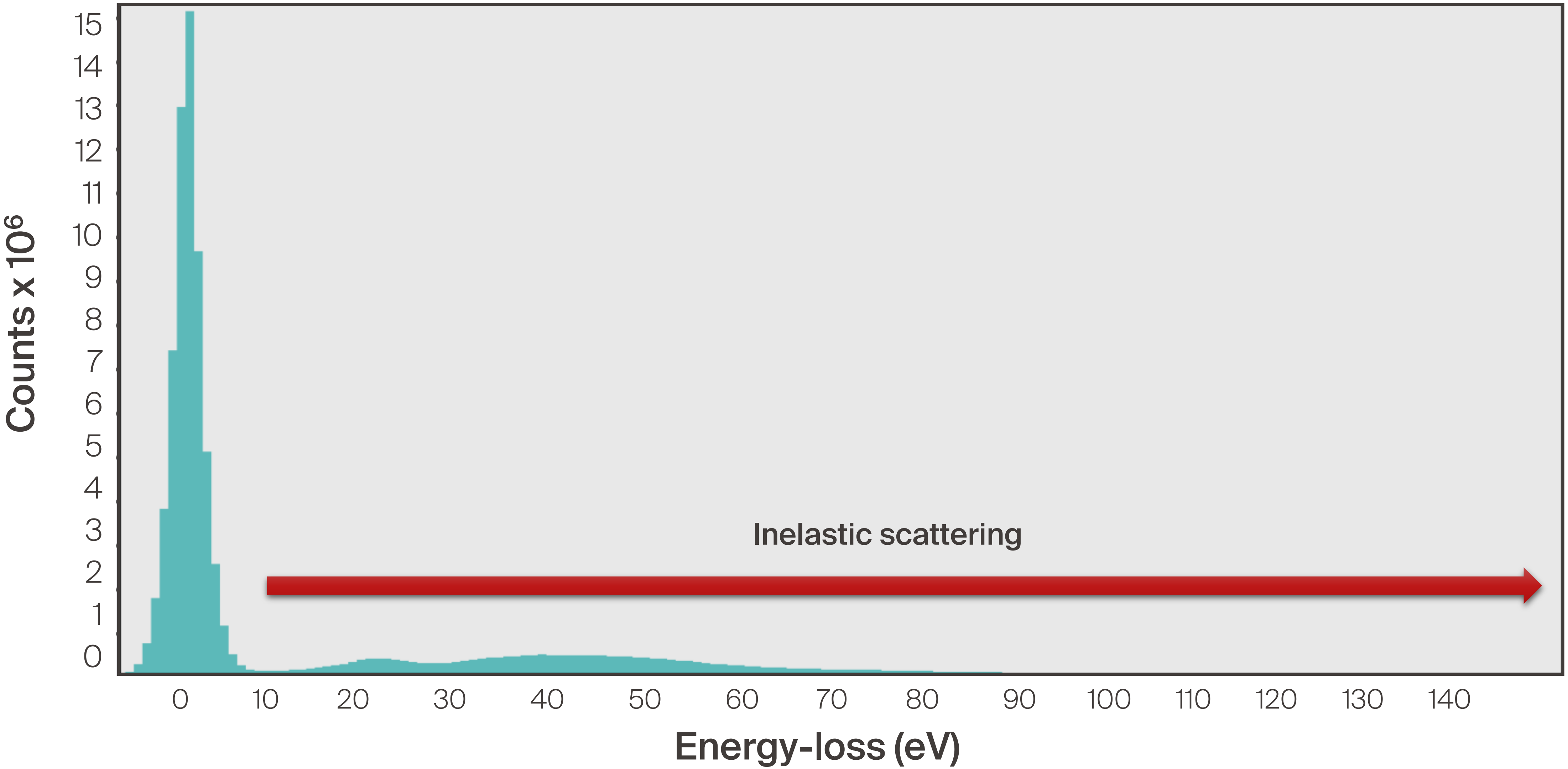
$$E_0 = 200\ kV$$

$$\theta_E \sim 0.71\ mrad$$

STEM-EELS spectrum imaging



The Electron Energy-Loss Spectrum



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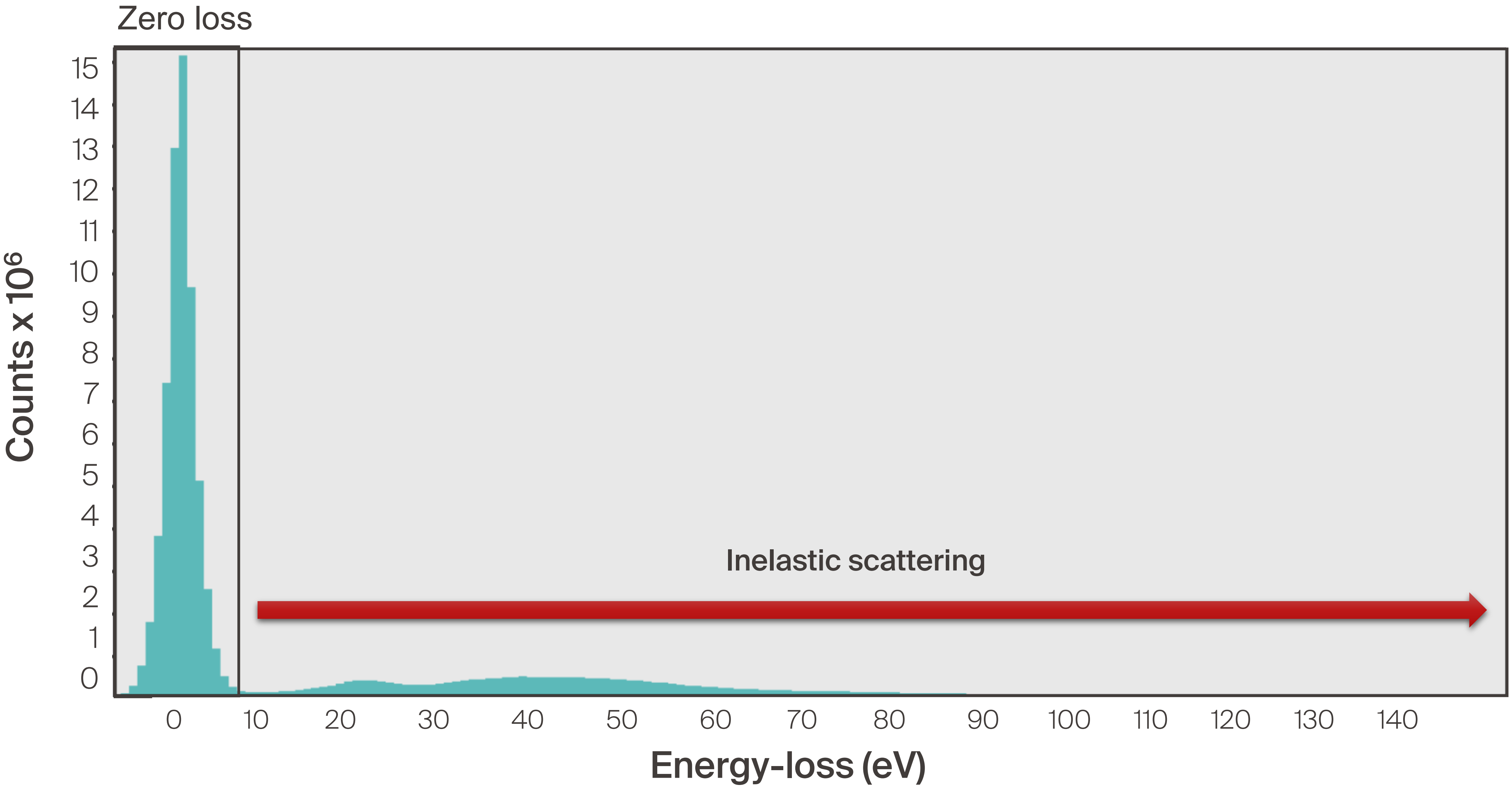

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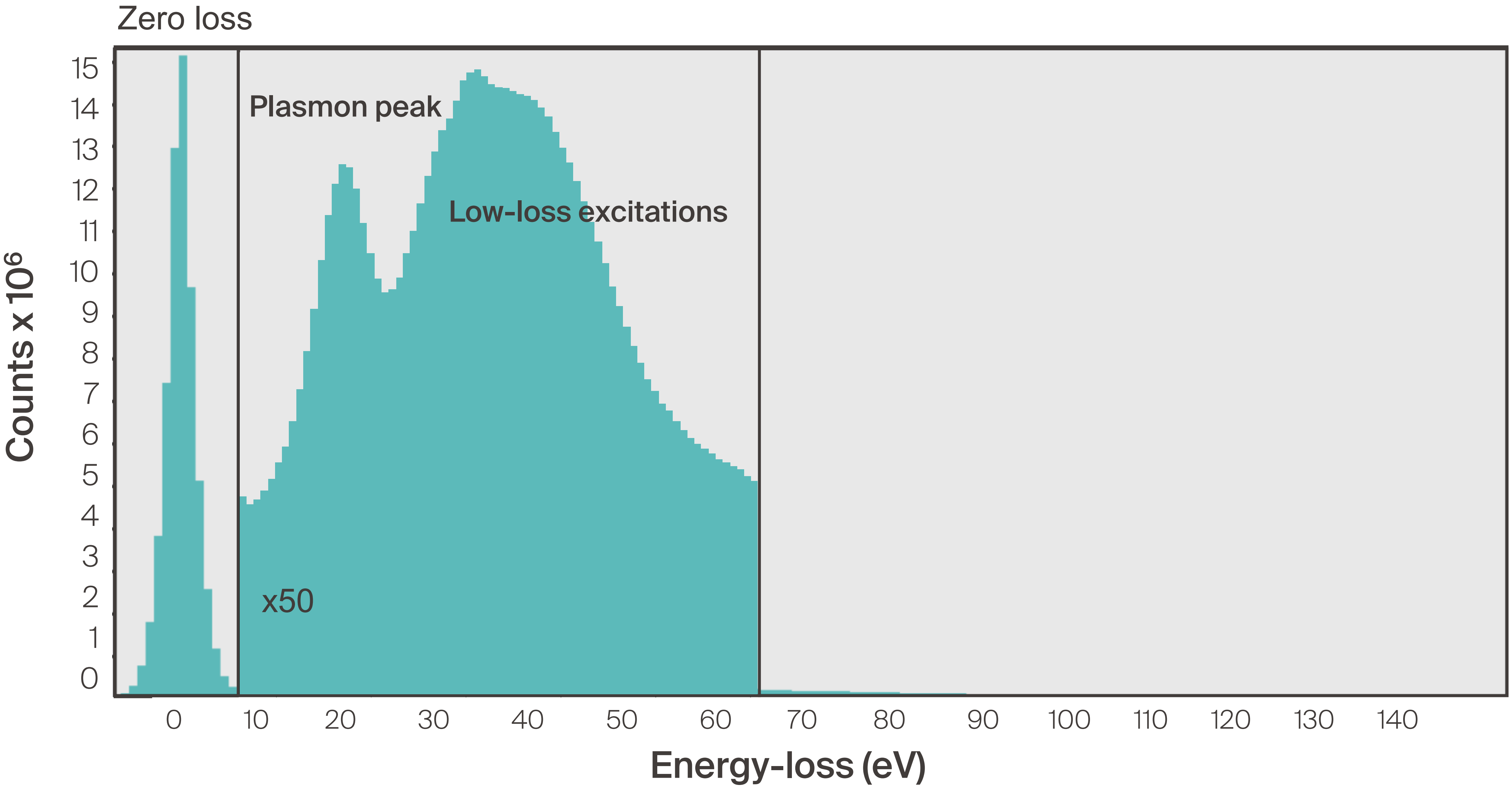

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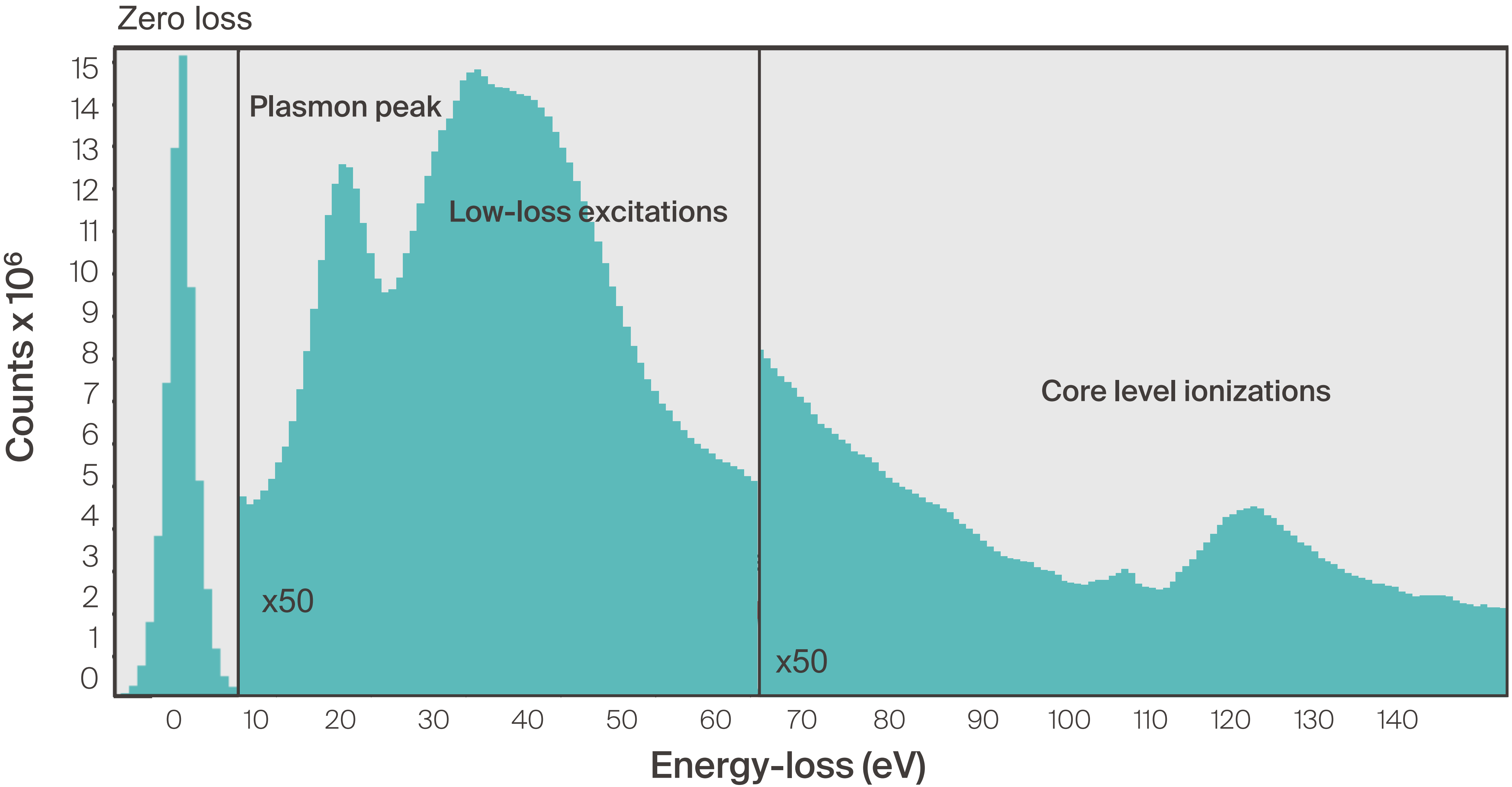

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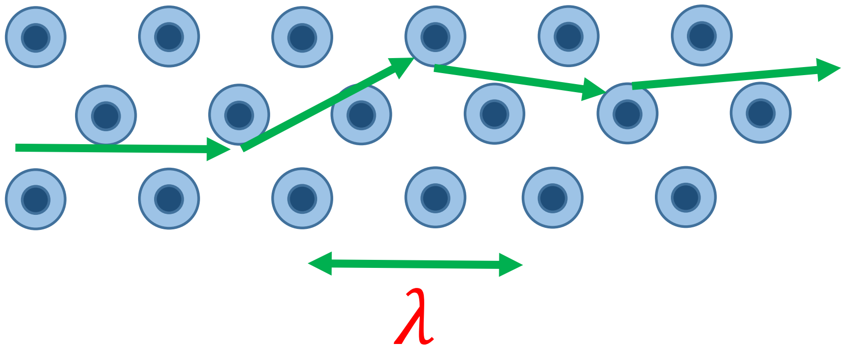
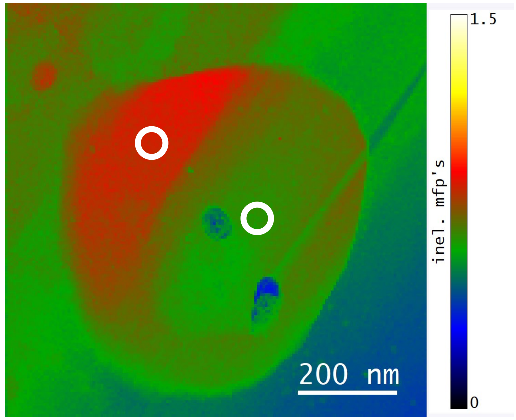
Low-loss EELS

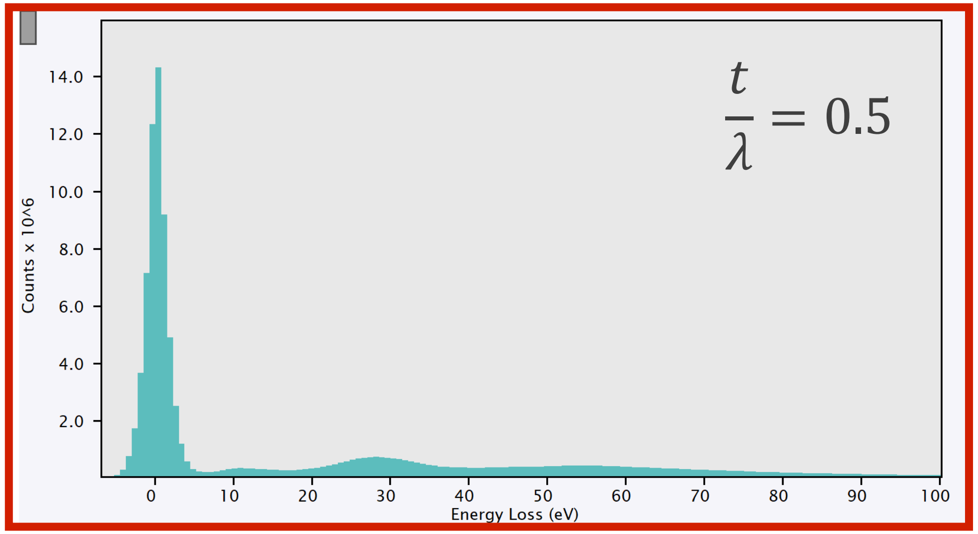
Specimen thickness

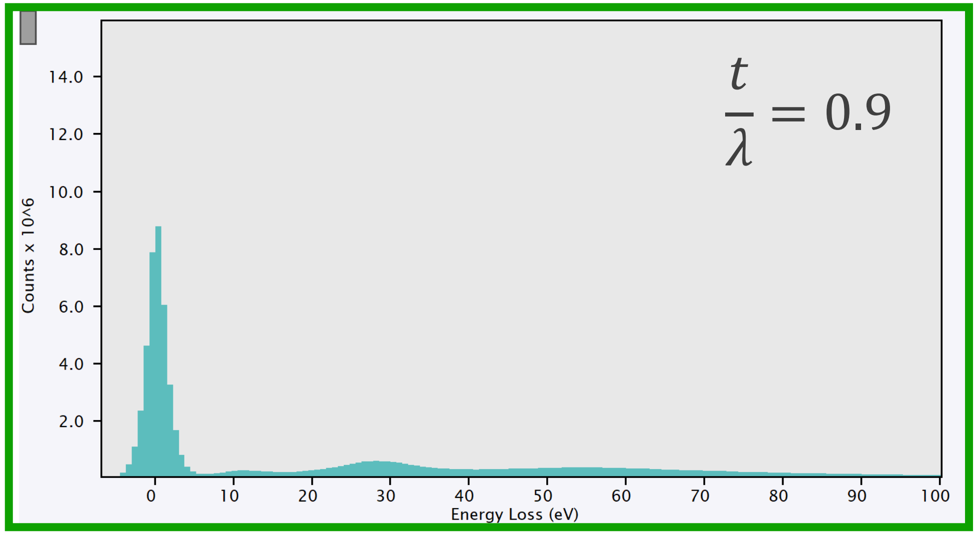
- As thickness specimen increase → multiple scattering is produce
- Inelastic scattering

$$\frac{t}{\lambda} = \ln(I/I_0)$$









t: thickness of the sample

λ: inelastic mean free path

I: Total spectrum integral

I_0: Zero-loss peak integral

$\lambda \sim 100\ nm$

Low-loss EELS

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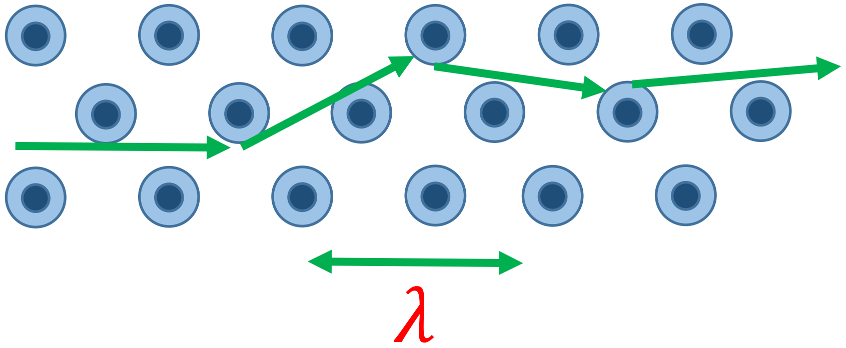

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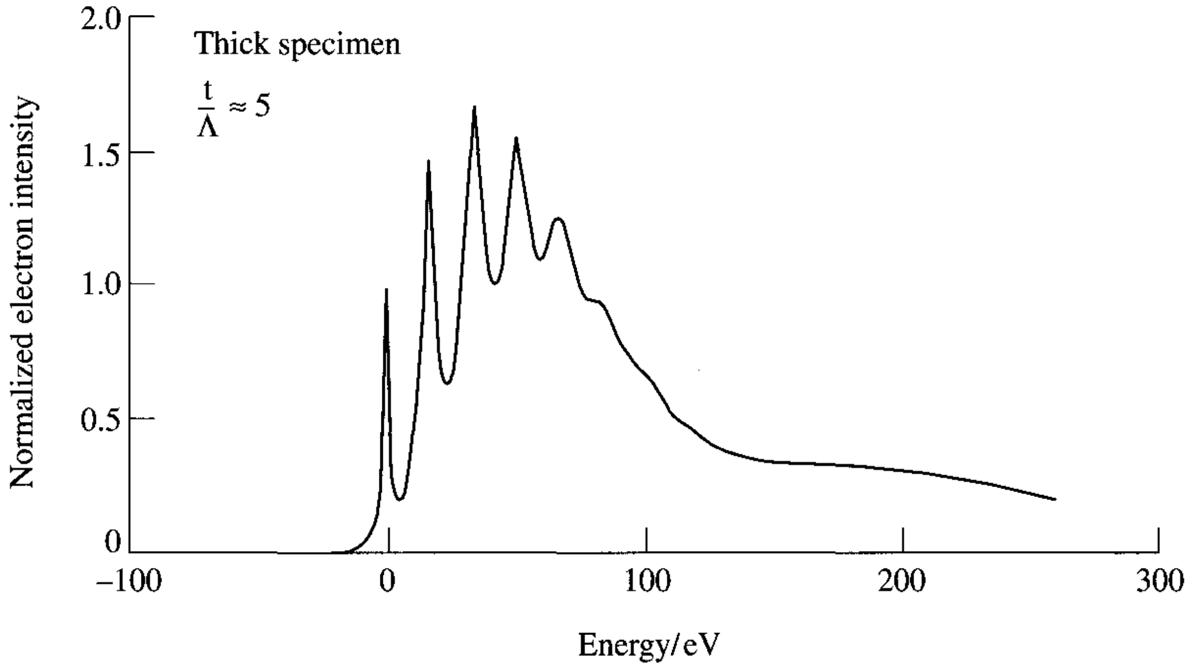

$\lambda \sim 100\ nm$

Low-loss EELS

Specimen thickness

Log-ratio (absolute)

$$\lambda = \frac{106F(E_0/E_m)}{\ln(2E_0\beta^*/E_m)}$$

$$E_m \sim 7.6Z_{eff}^{0.36}$$

$$Z_{eff} = \frac{\sum_i f_i Z_i^{1.3}}{\sum_i f_i Z_i^{0.3}}$$

α β

Low-loss EELS

Specimen thickness

Log-ratio (absolute)

$$\lambda = \frac{106F(E_0/E_m)}{\ln(2E_0\beta^*/E_m)}$$

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α β

Kramers-Kronig Sum Rule

$$t = \frac{4a_0FE_0}{I_0(1-1/n^2)}\int\frac{S(E)dE}{E\ln\left(1+\beta^2/\theta_E^2\right)}$$

$S(E)$: **Single-scattering distribution**

a_0: **Bohr radius**

n : **Refractive index**

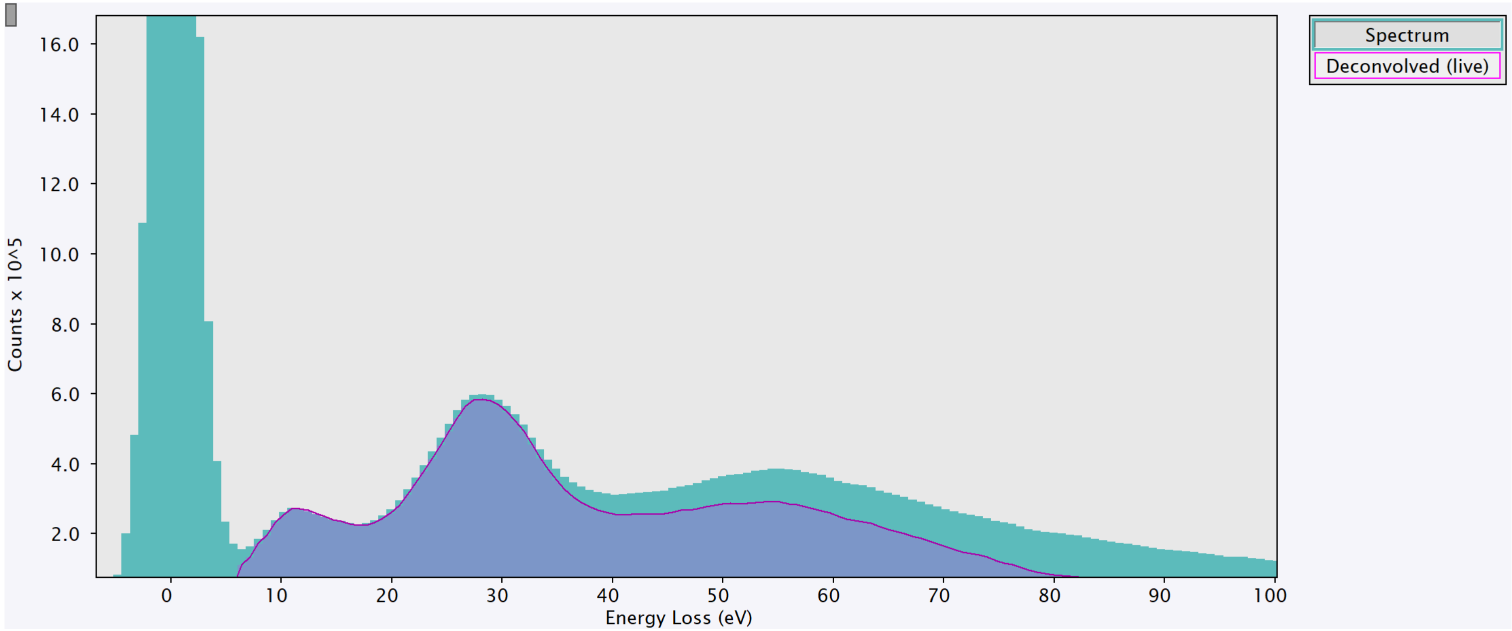
θ : **Scattering angle at an energy E**

α β

Spectral deconvolution

Single-scattering distribution (SSD):

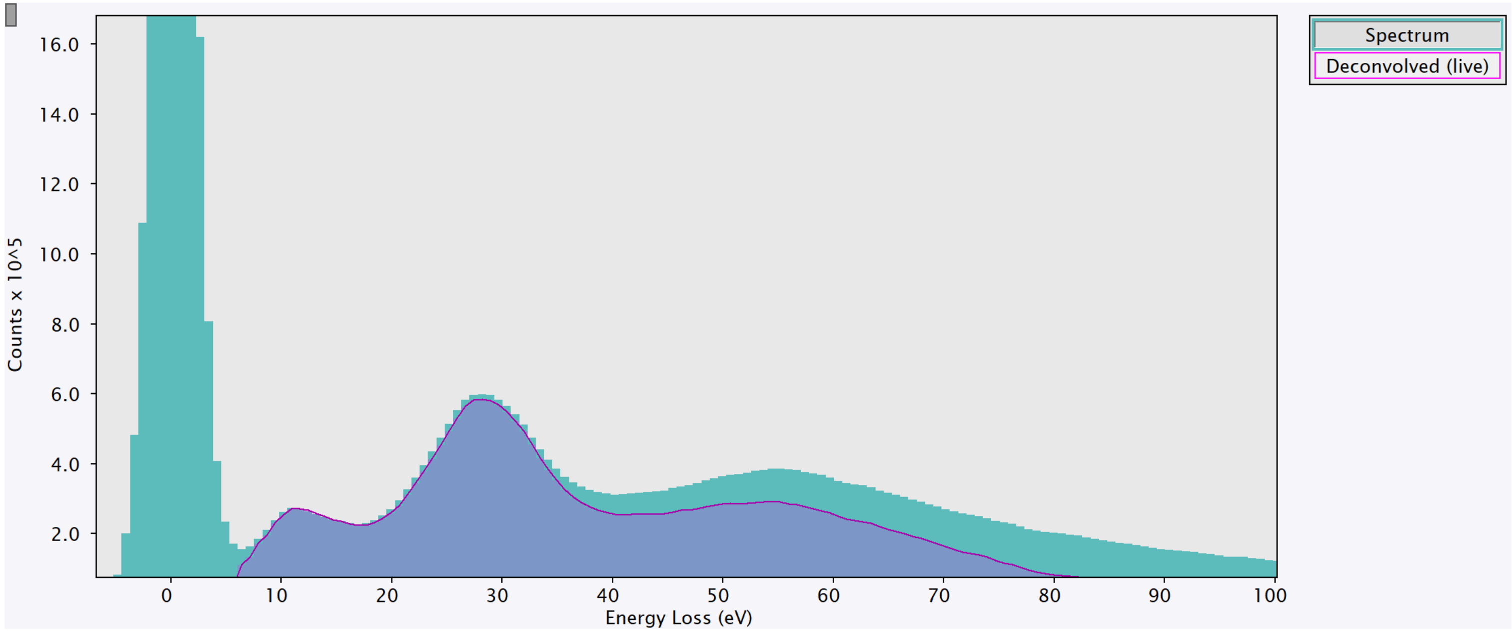
- Core-loss spectra → Fourier-log deconvolution → need the low-loss spectrum
- Low-loss spectra → Fourier-ratio deconvolution



Spectral deconvolution

Single-scattering distribution (SSD):

- Core-loss spectra → Fourier-log deconvolution → need the low-loss spectrum
- Low-loss spectra → Fourier-ratio deconvolution



$$S(E) = K * Im\left[\frac{-1}{\varepsilon(E)}\right]\ln\left[1 + \frac{\beta}{\theta_E^2}\right]$$

$S(E)$: Single scattering distribution

K: Proportional constant

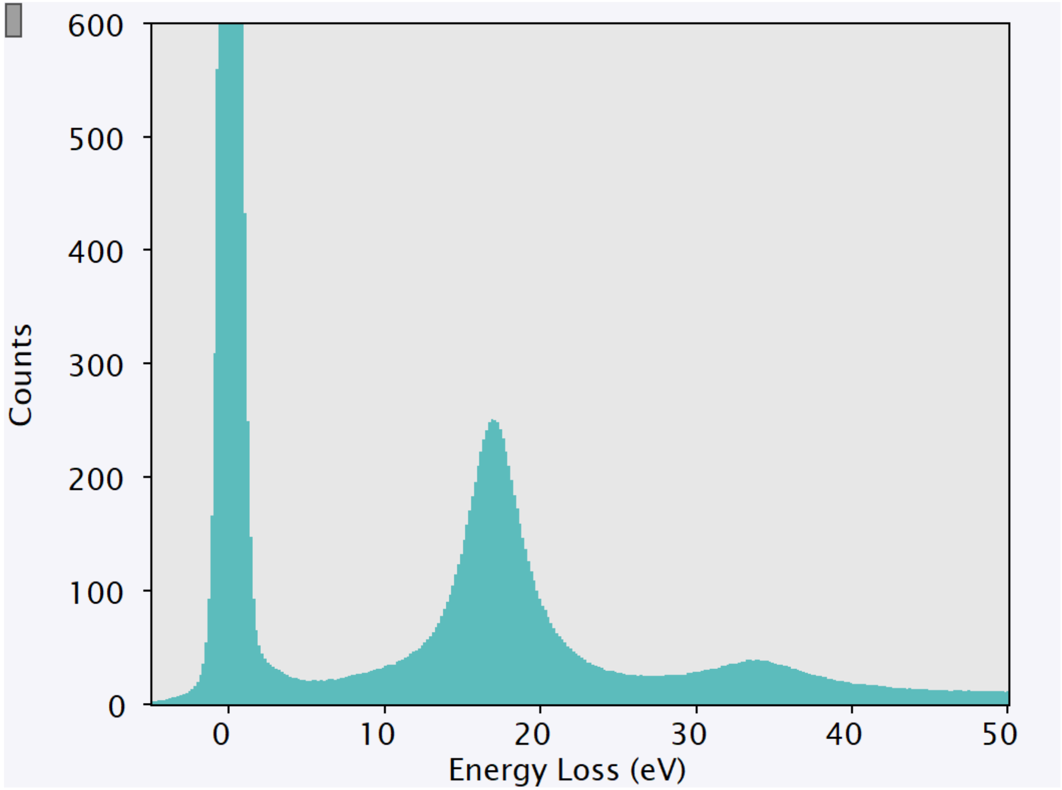
$\varepsilon(E)$: dielectric function

β, θ_E: Collection and characteristic angles

$$\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$$

Volume Plasmon

Oscillation of valence electrons → Drude-Lorentz model



Plasmon Energy

$$E_p = \hbar\sqrt{\frac{Ne^2}{\varepsilon_0 m_e}}$$

N: conduction / valence electron density

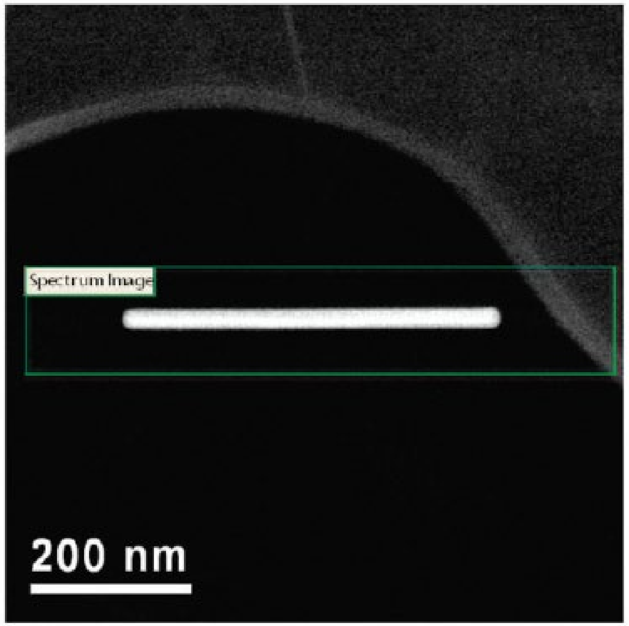
e: electron (hole) charge

m_e: electron (hole) effective mass

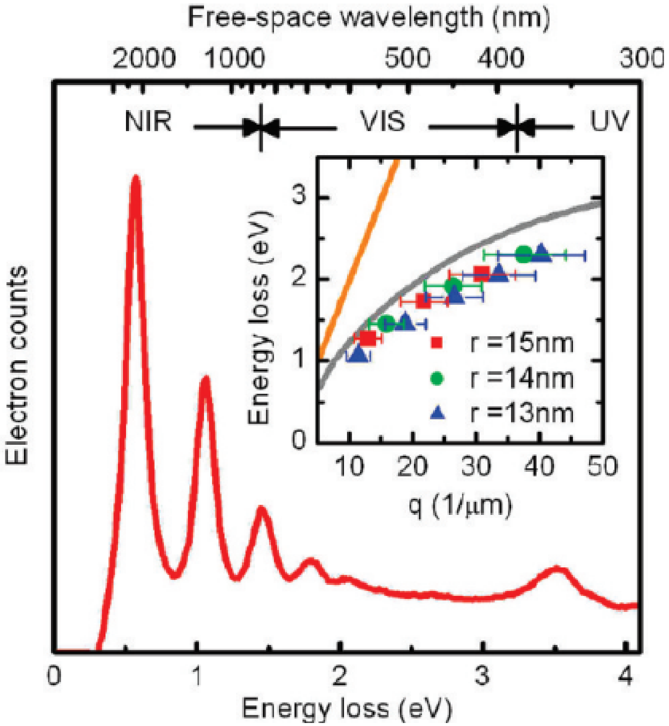
h: Plank's constant

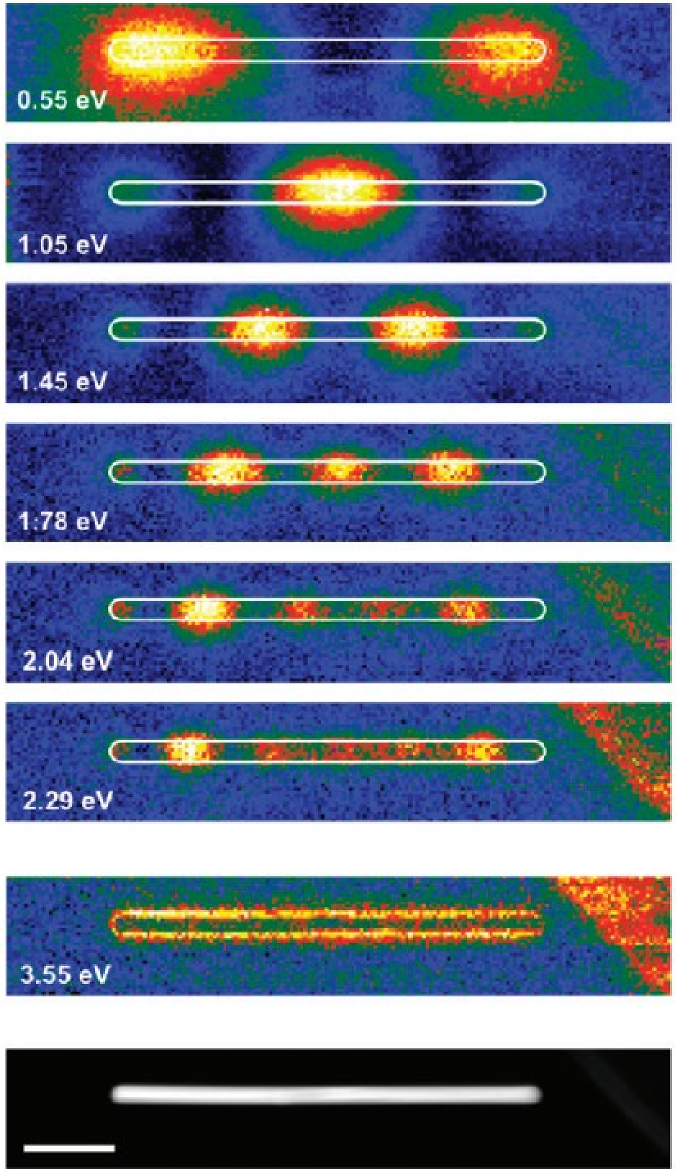
Plasmonic resonance

Optical properties



Silver Nanowire Antenna

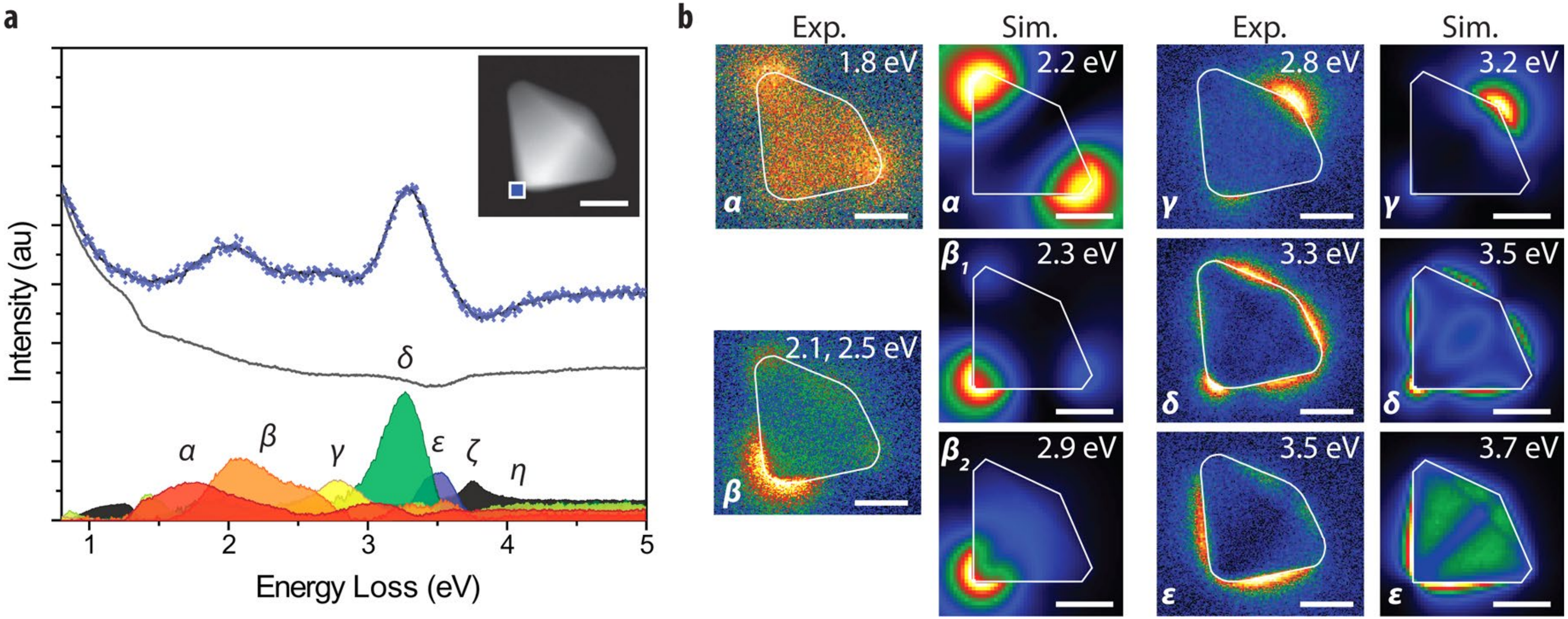




D. Rossouw et al. *Nano Lett. 11, 1499-1504 (2011)*

Plasmonic resonance

Optical properties

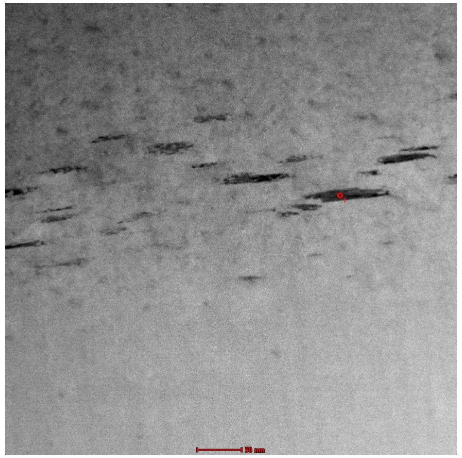


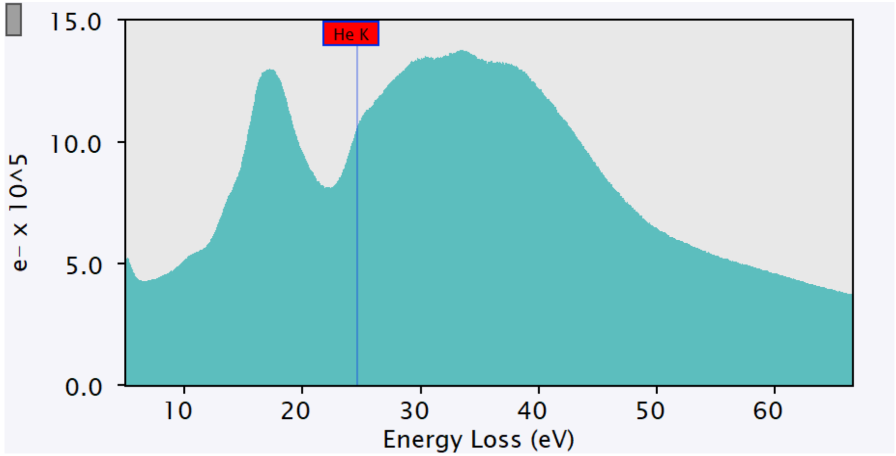
Sean M. Collins et al. *ACS Photonics 2015, 2, 1628–1635*

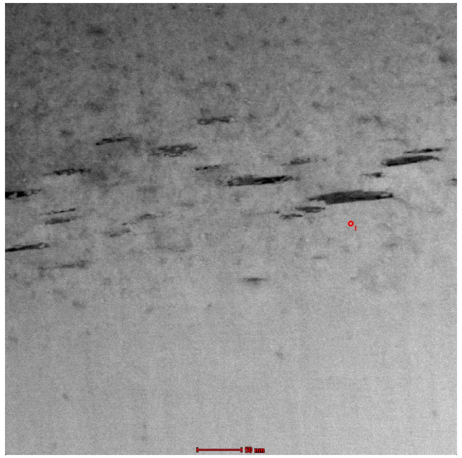
Monochromated EELS to achieve such Energy resolution

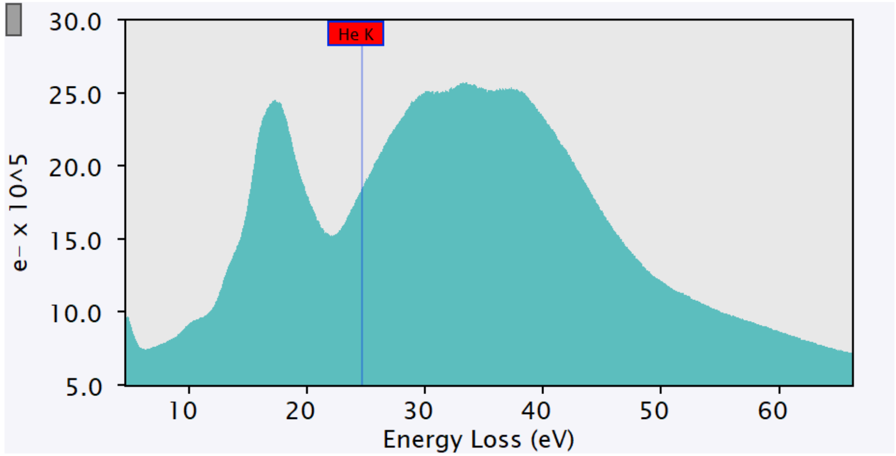
Light elements

In-situ experiment to release Helium bubbles (platelet shape)



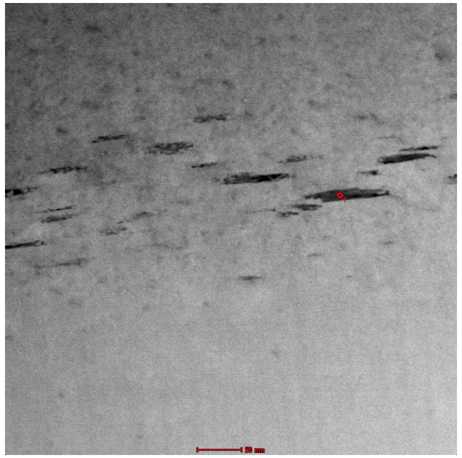


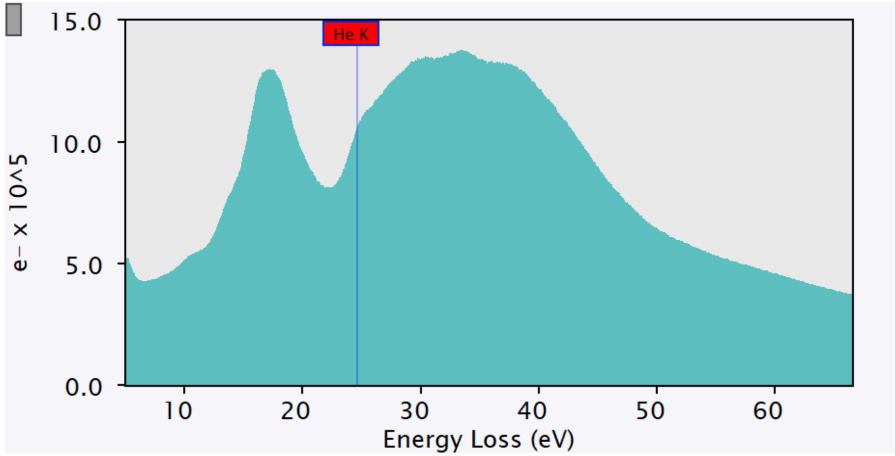


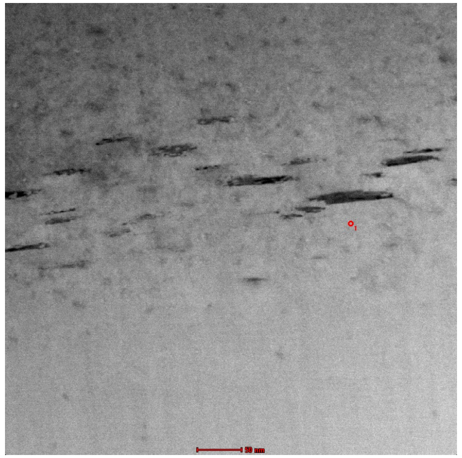


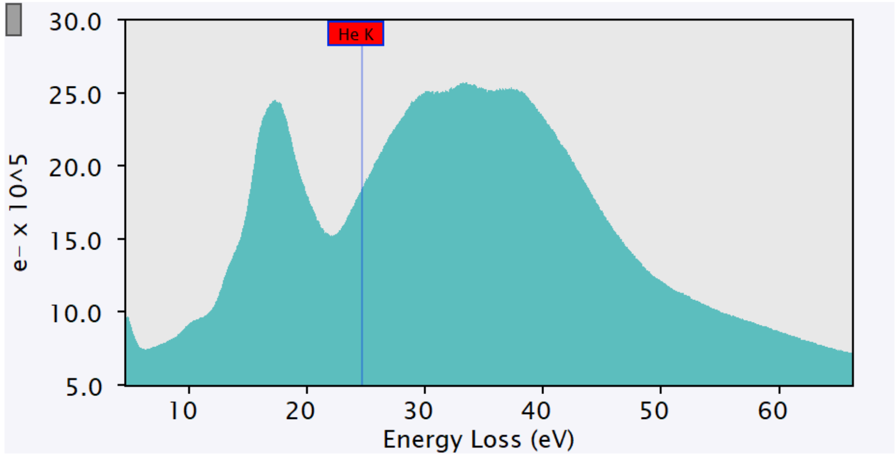
Light elements

In-situ experiment to release Helium bubbles (platelet shape)

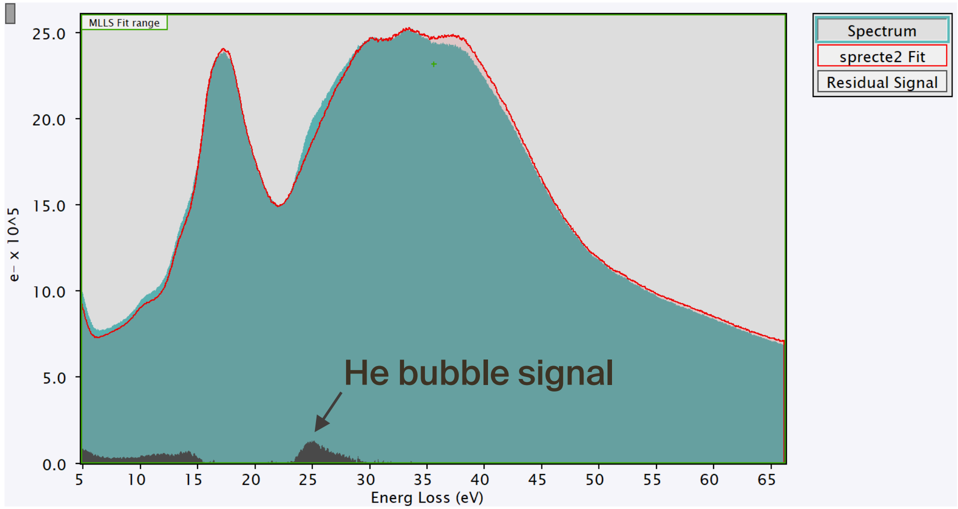








Multiple Linear Least Squares MLLS Fitting



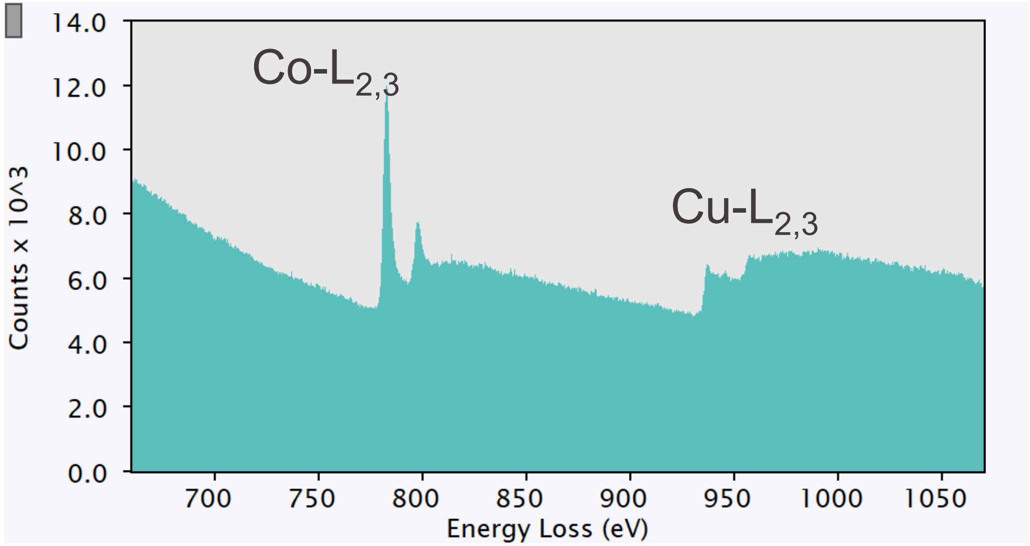
He bubble signal

OUTLINE

- What is EELS?
- Ionization energy loss
- Spectrometers
- Key parameters
- Spectrum imaging
- The Electron Energy-loss spectrum
- Low-loss EELS
  - Spectral deconvolution
  - Volume plasmon
  - Plasmonic resonance
  - Light elements
- Ionization edges / core –loss
  - Elemental distribution
  - Elemental quantification
  - ELNES
  - Fine structure
  - White lines
  - EELS spatial resolution
  - What we should retain?
  - References

Ionisation edge / core-loss analysis

- Elementa ionization edges superimposed on exponentially decaying background → “normally” fit with power-law model
- Signal intensity proportional to projected atomic concentration and elemental partial ionization scattering cross-section $\Delta\sigma$



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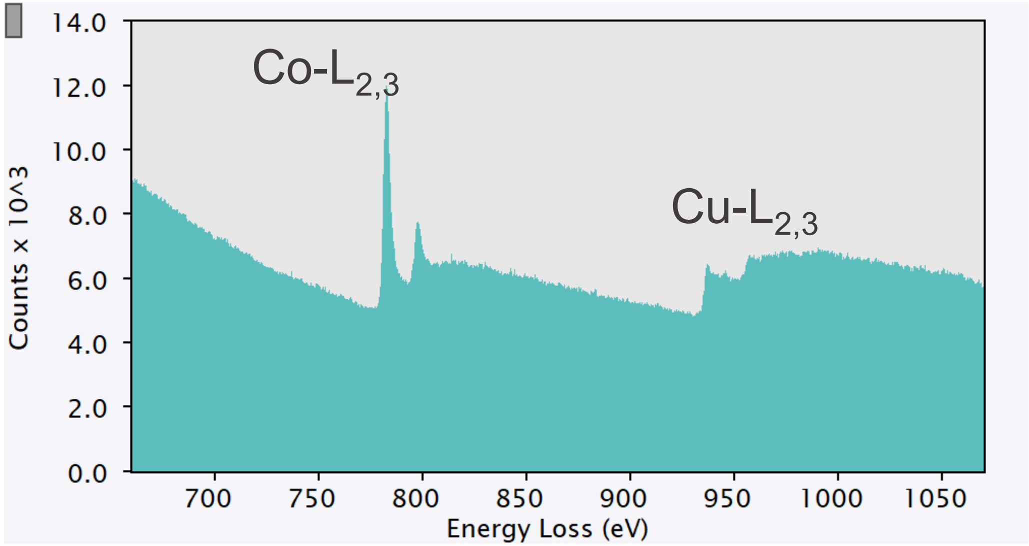

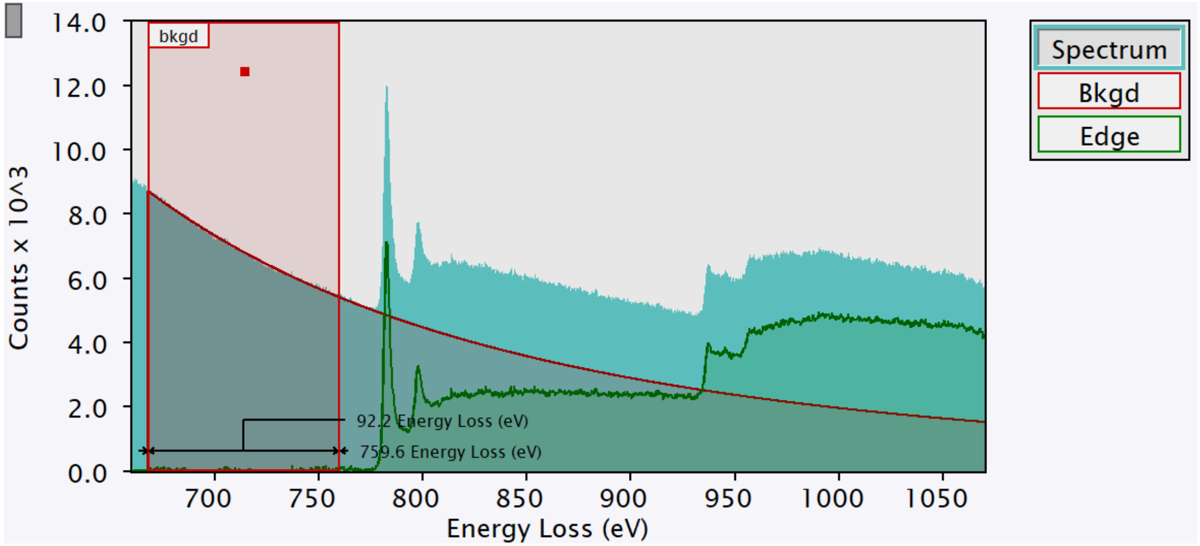

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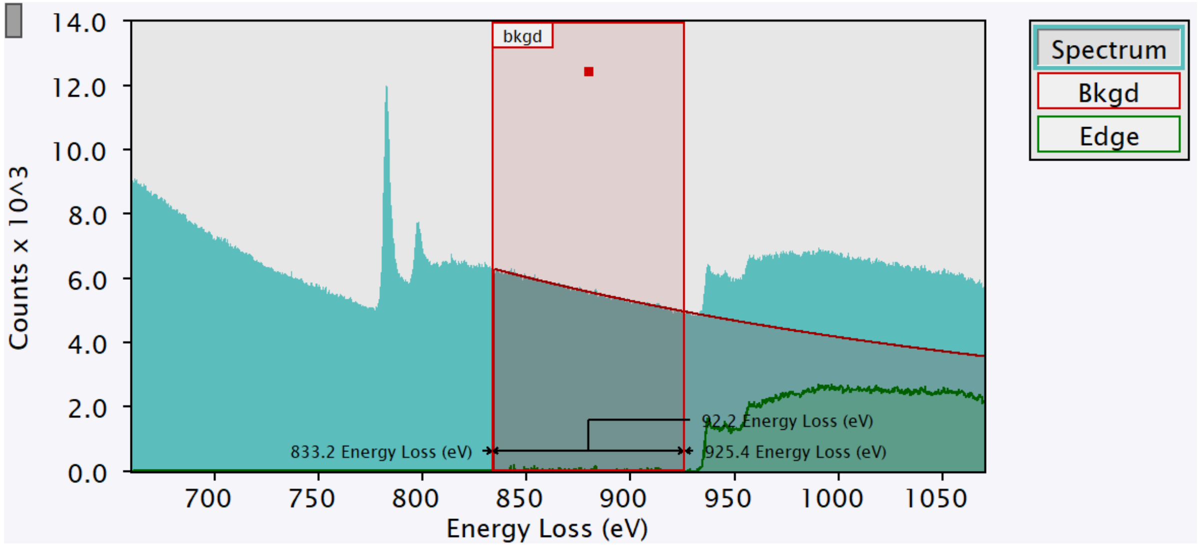
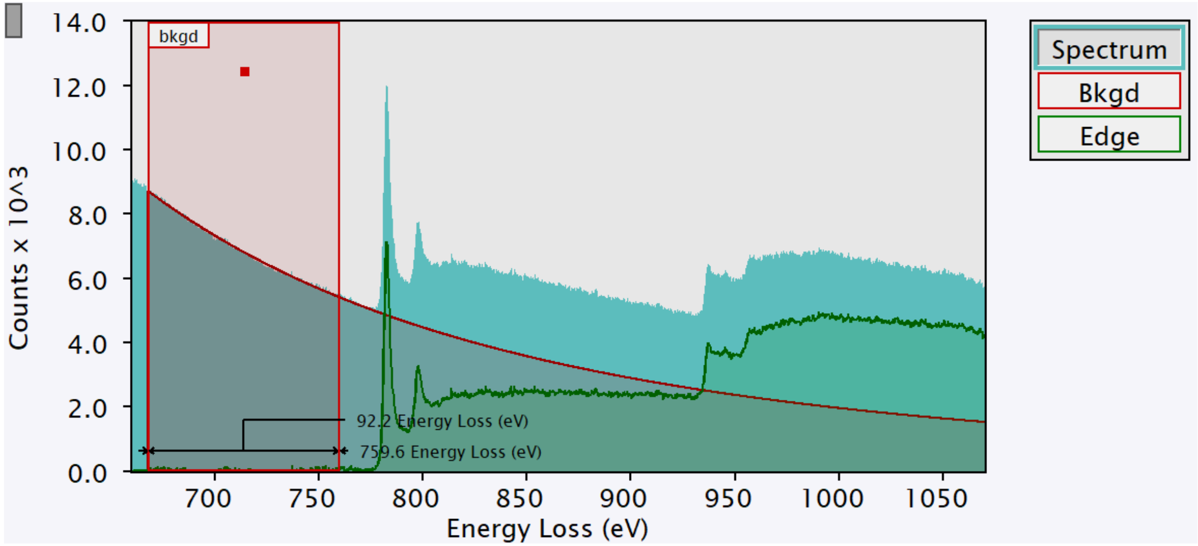
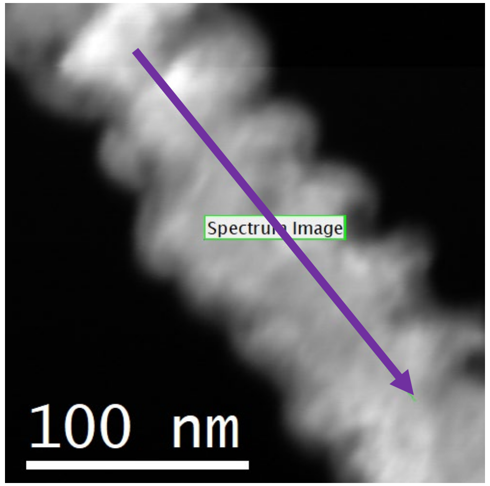
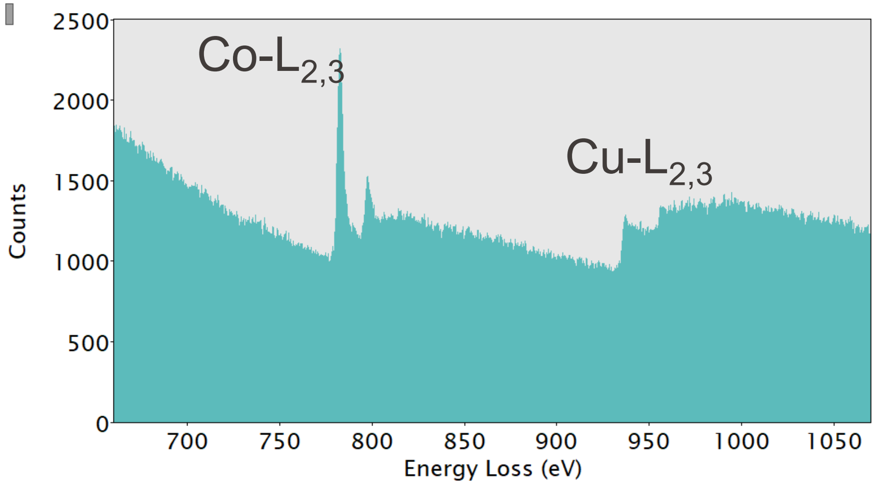
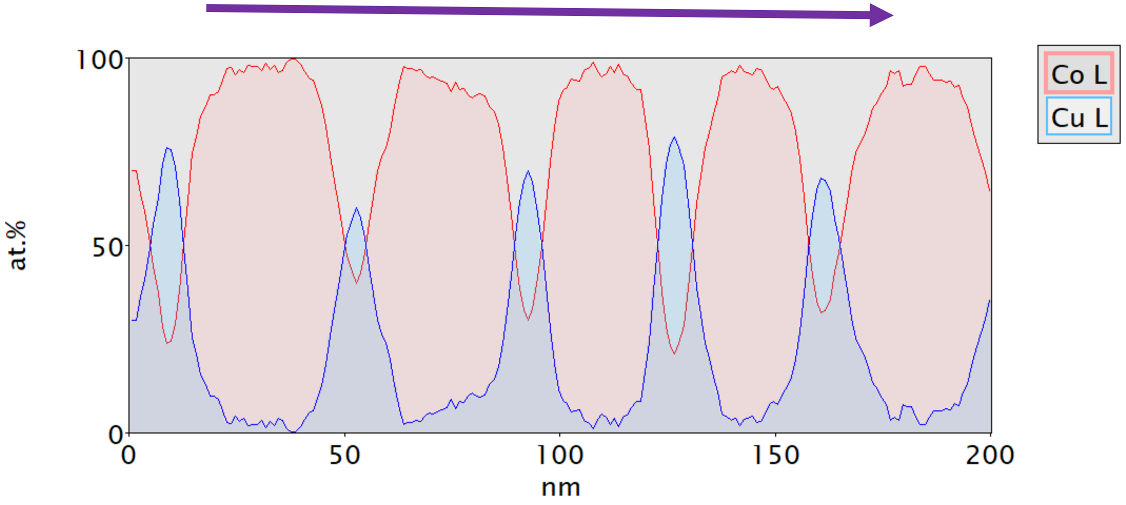


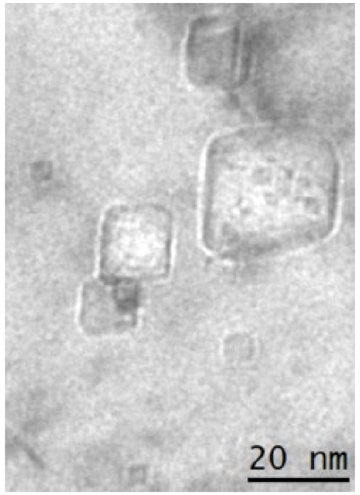


Elemental distribution

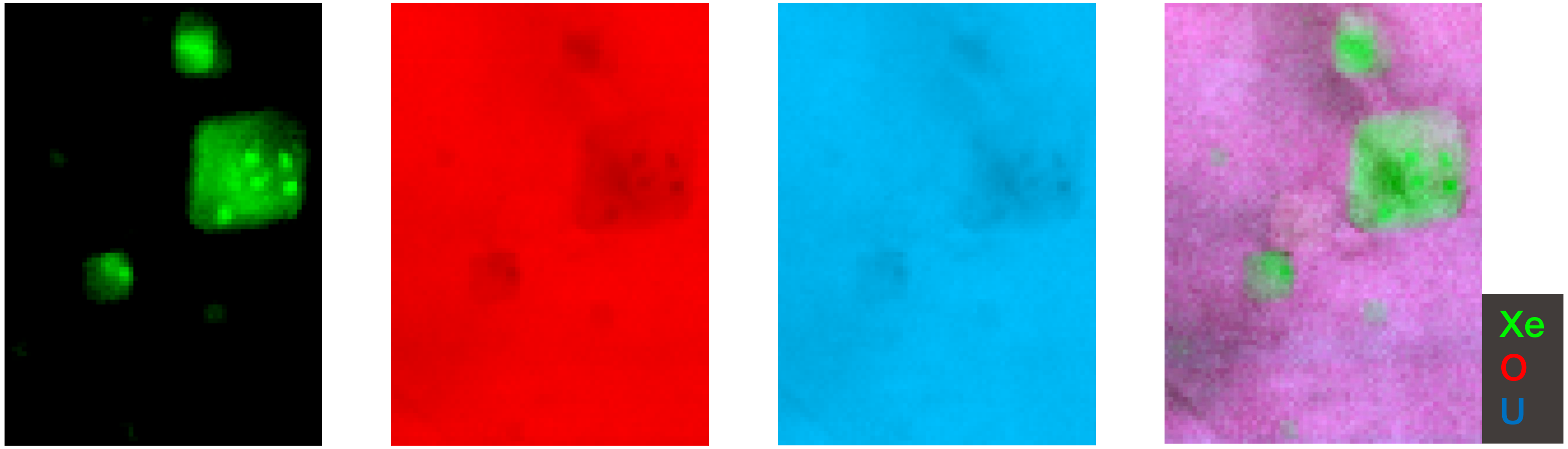








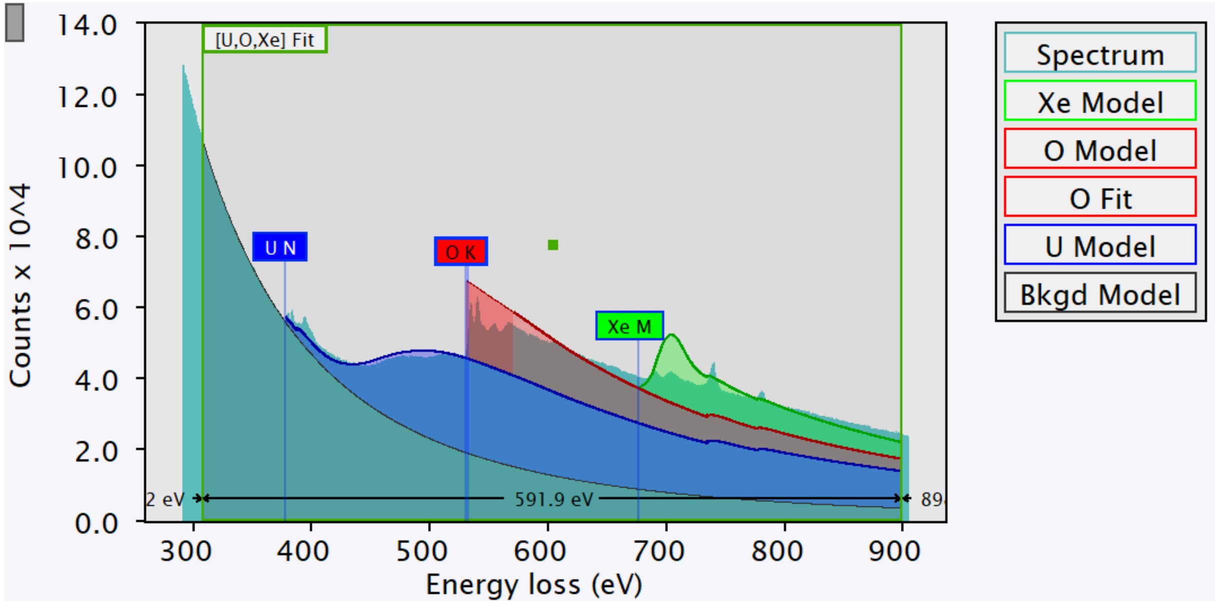
Defocused TEM image



Elemental EELS maps

Elemental mapping

- Previous information about EELS edges to be observed → **EELS Atlas**
- What are the energy losses of your elements?
- Which ionization edges can you fit on one spectrum?
- Check Possible overlaps or “difficult” edges



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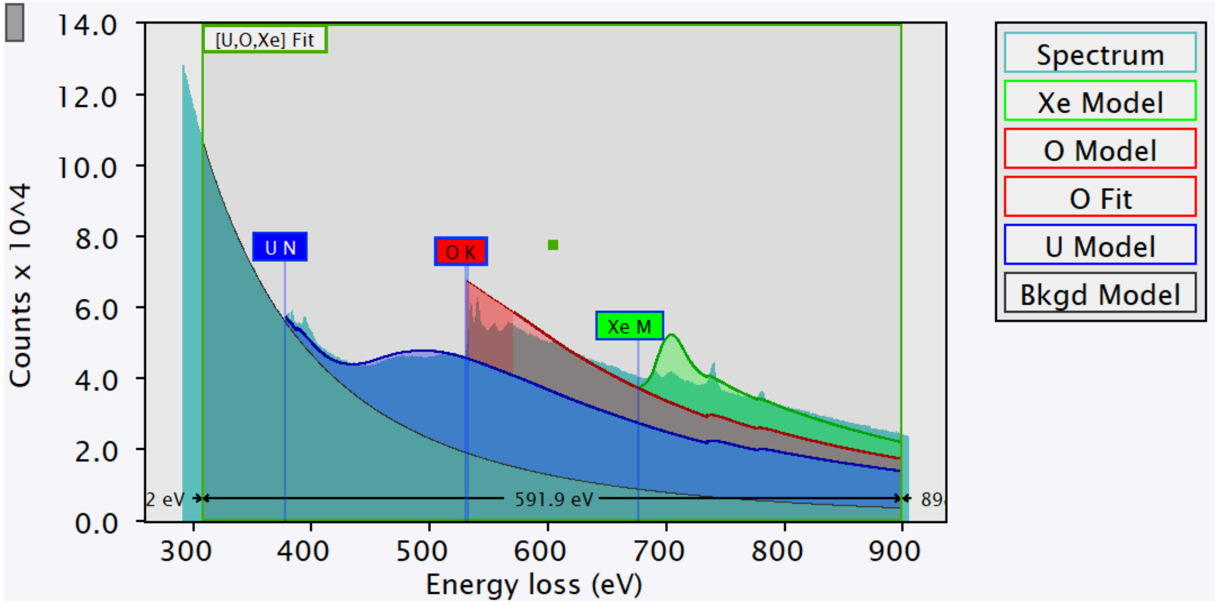
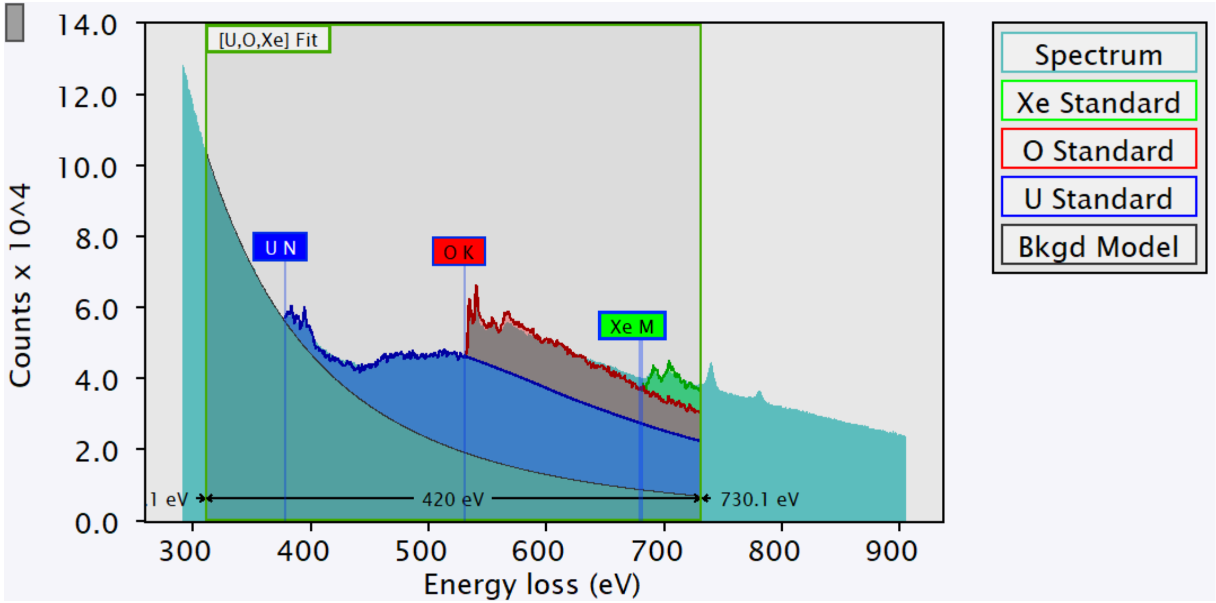


Fitting using standards



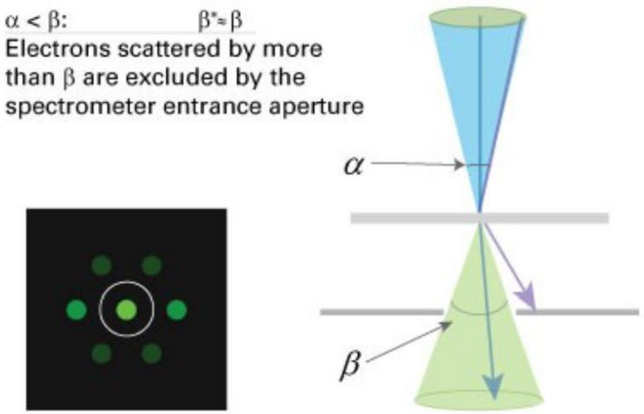
Elemental quantification

- Elemental percentage → Relative quantification $\frac{N_A}{N_B} = \frac{conc.A}{conc.B} \approx \frac{I_A \Delta\sigma_B}{I_B \Delta\sigma_A}$ **σ**: Cross-section → The probability for a scattering event to take place → $\boxed{\frac{d^2\sigma}{d\Omega dE} = \frac{8a_0^2R^2}{Em_0v^2}\left(\frac{1}{\theta^2+\theta_E^2}\right)\frac{df_n}{dE}}$

To be calculated!

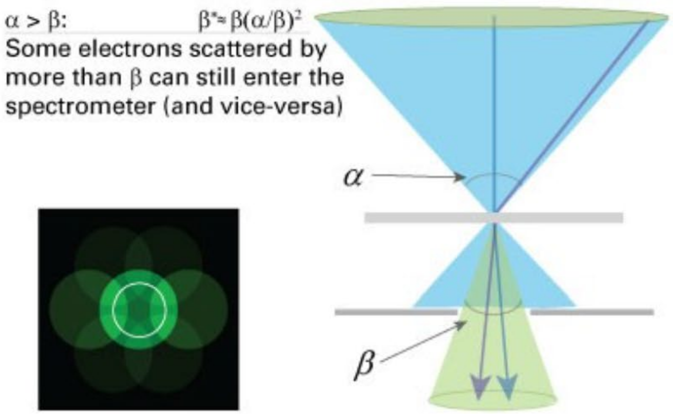
- Density of atoms (atoms/nm^2) → Absolute quantification $N = \frac{I_k^1}{I_0 \Delta\sigma_k}$ **σ**: Integral edge k with no plural scattering integrated over a window Δ

- Good quantification depends on the correct choice of the convergence semi-angle **α** and the signal collected with the spectrometer with a certain collection semi-angle **β**.



$\alpha < \beta$: $\beta^* \approx \beta$

Electrons scattered by more than β are excluded by the spectrometer entrance aperture



$\alpha > \beta$: $\beta^* \approx \beta(\alpha/\beta)^2$

Some electrons scattered by more than β can still enter the spectrometer (and vice-versa)

β^*: effective collection angle

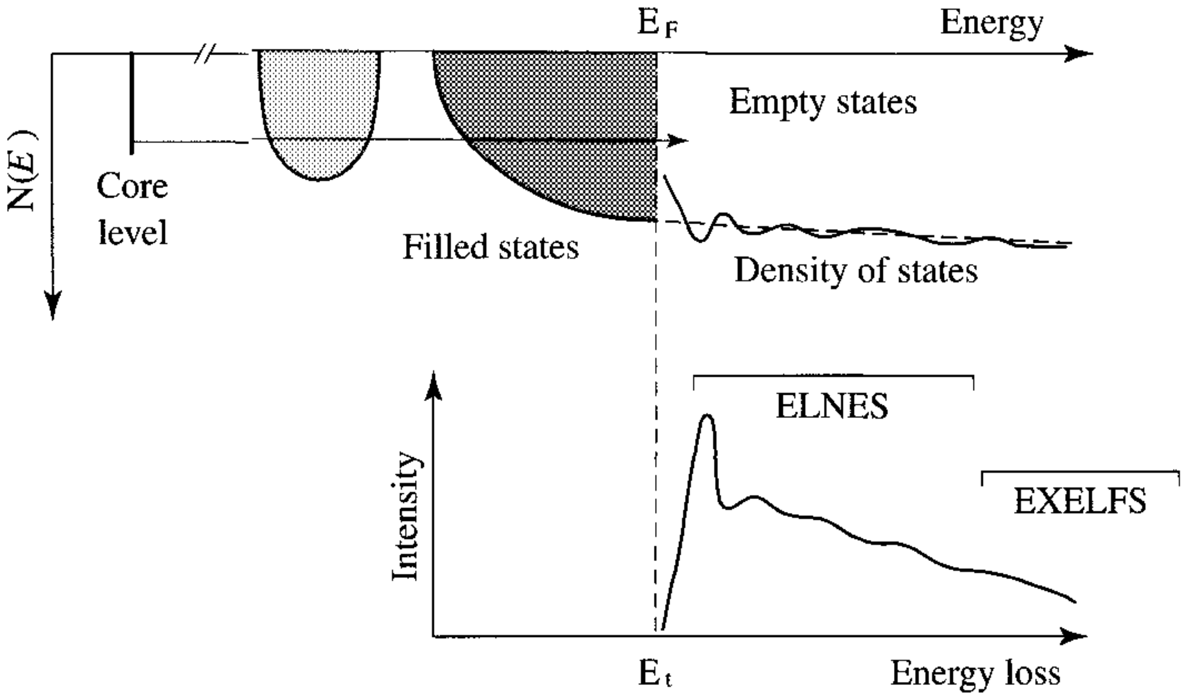
$$\theta_E \sim \frac{\Delta E}{2E_0}$$

$\alpha \approx 0$ for TEM

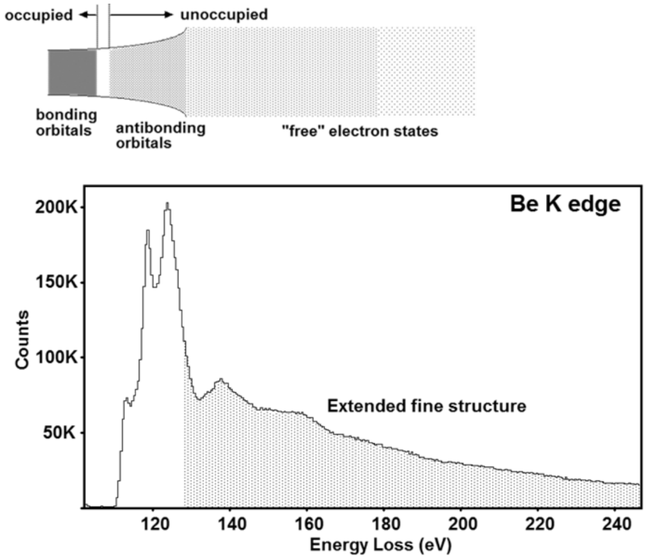
Recommended $2\theta_E$ or $3\ \theta_E$

Energy-loss Near Edge Structure (ELNES)

- ELNES reflects the unoccupied density of states (DOS) probed by an inner-shell electron excited from a deep core level.
- Fine structure comparable to X-ray absorption spectroscopy (XAS) data
- **ELNES** can be simulated using Density functional theory (DFT)

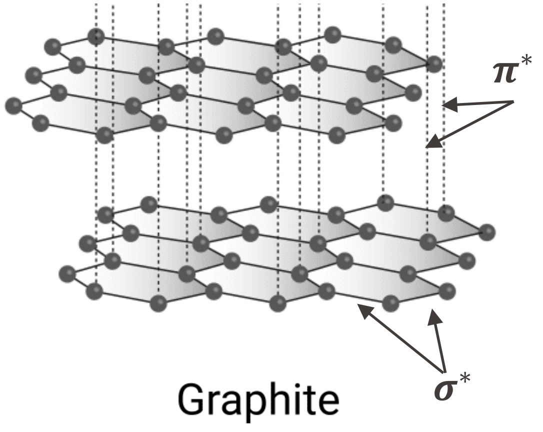


DOS: the number of different states at a particular energy level that electrons are allowed to occupy, i.e. the number of electron states per unit volume per unit energy

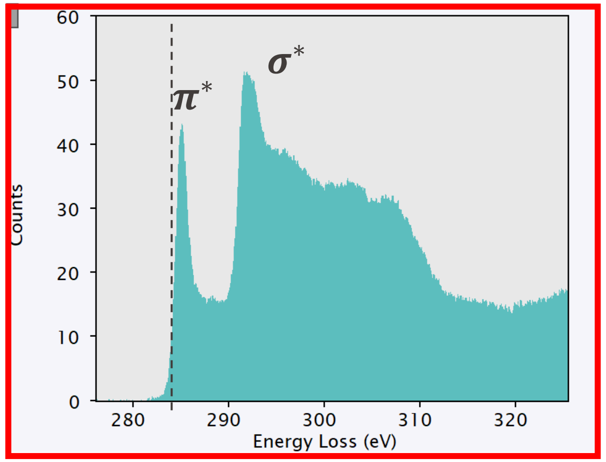


The extended fine structure represents transitions from the core level to states above the vacuum level. This creates a source of free electrons in the material centered at the interacting atom. These electrons scatter and interact giving rise to interference terms in the tail of the scattering

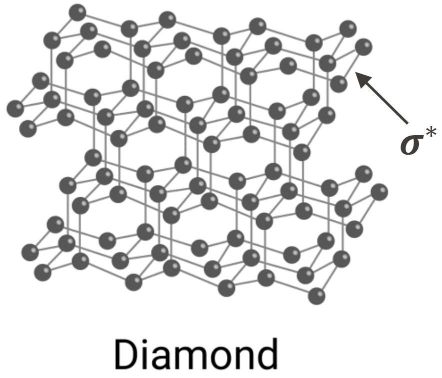
Core-loss fine structure : Carbon K-edge

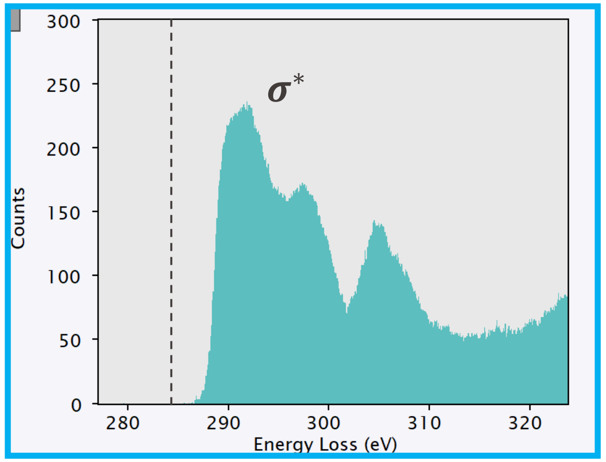


Pure sp^2 hybridization



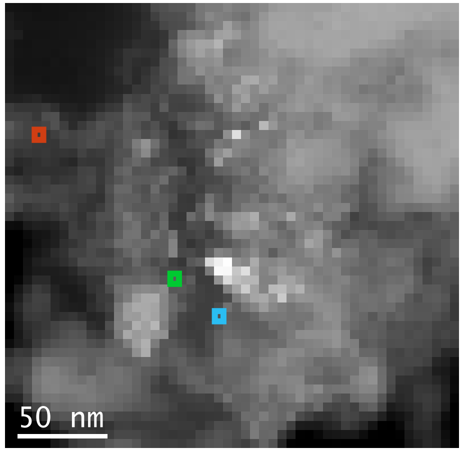
C K-edge 284eV

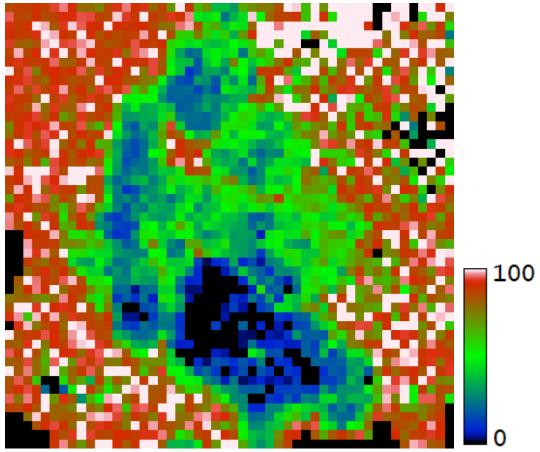




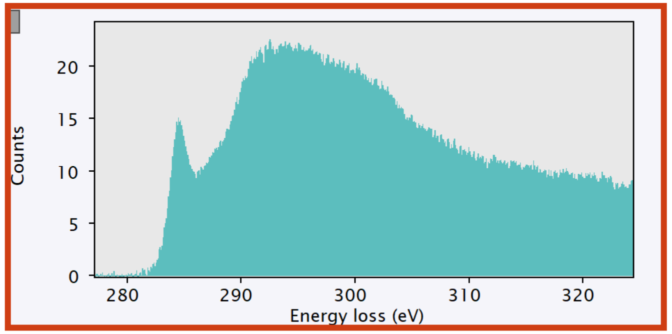
Pure sp^3 hybridization

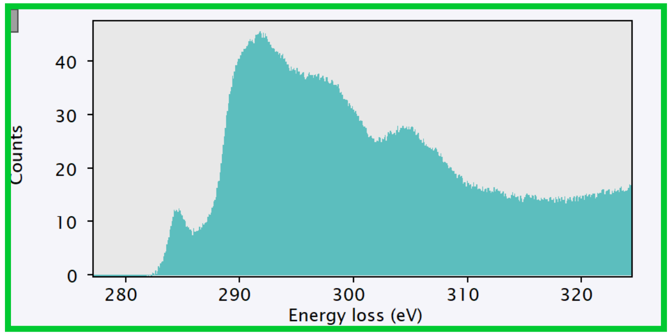
Possible to map the % of the sp^2 hybridization

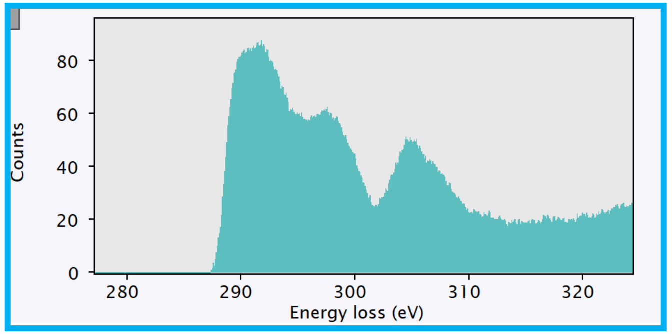




Map of $\%sp^2$ for a non-pure nano-diamond sample

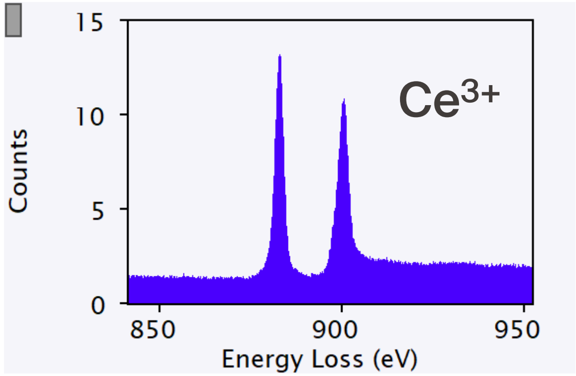


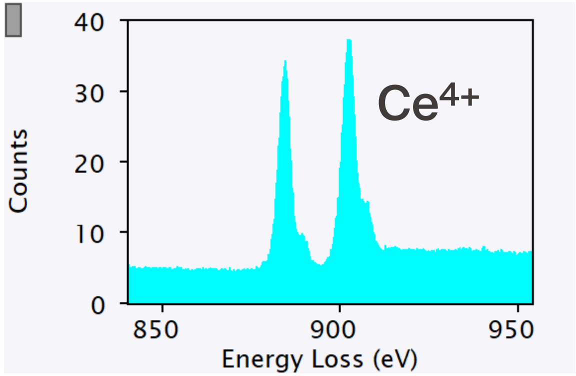


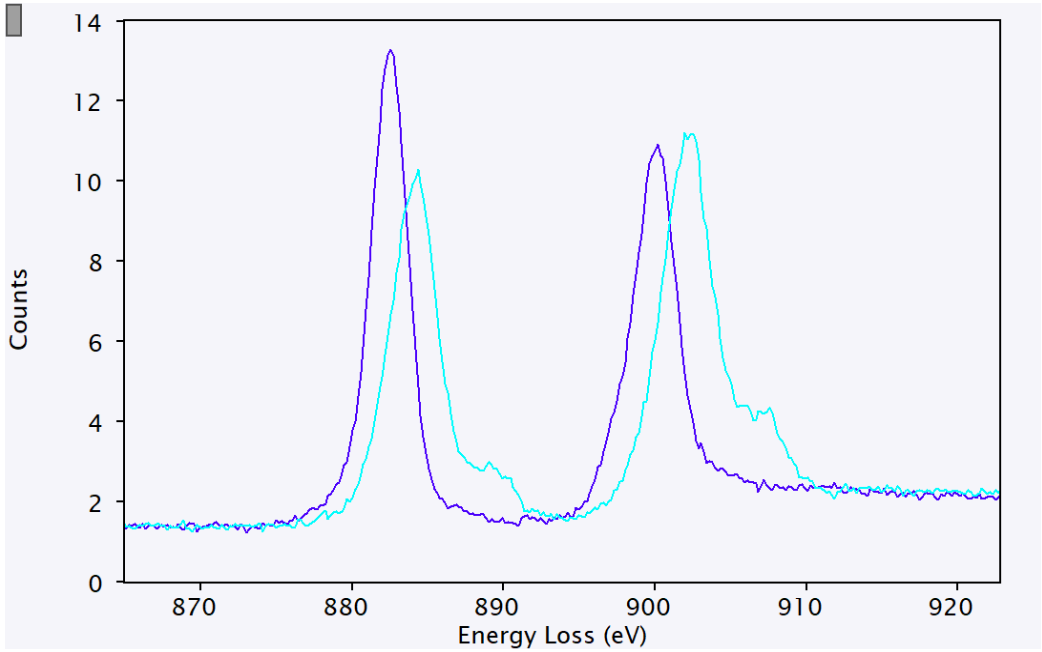


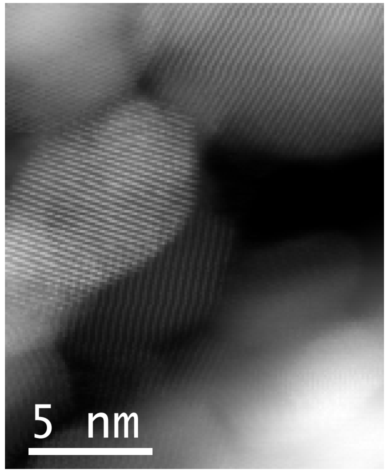
White lines

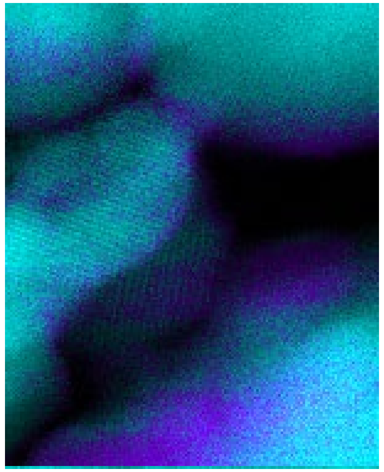
- ELNES can be used to determine the valence/oxidation state
- Strategies to detect the change on the valence state: shift on energie peaks postion, ratio between L-edge peaks, shape of the peaks







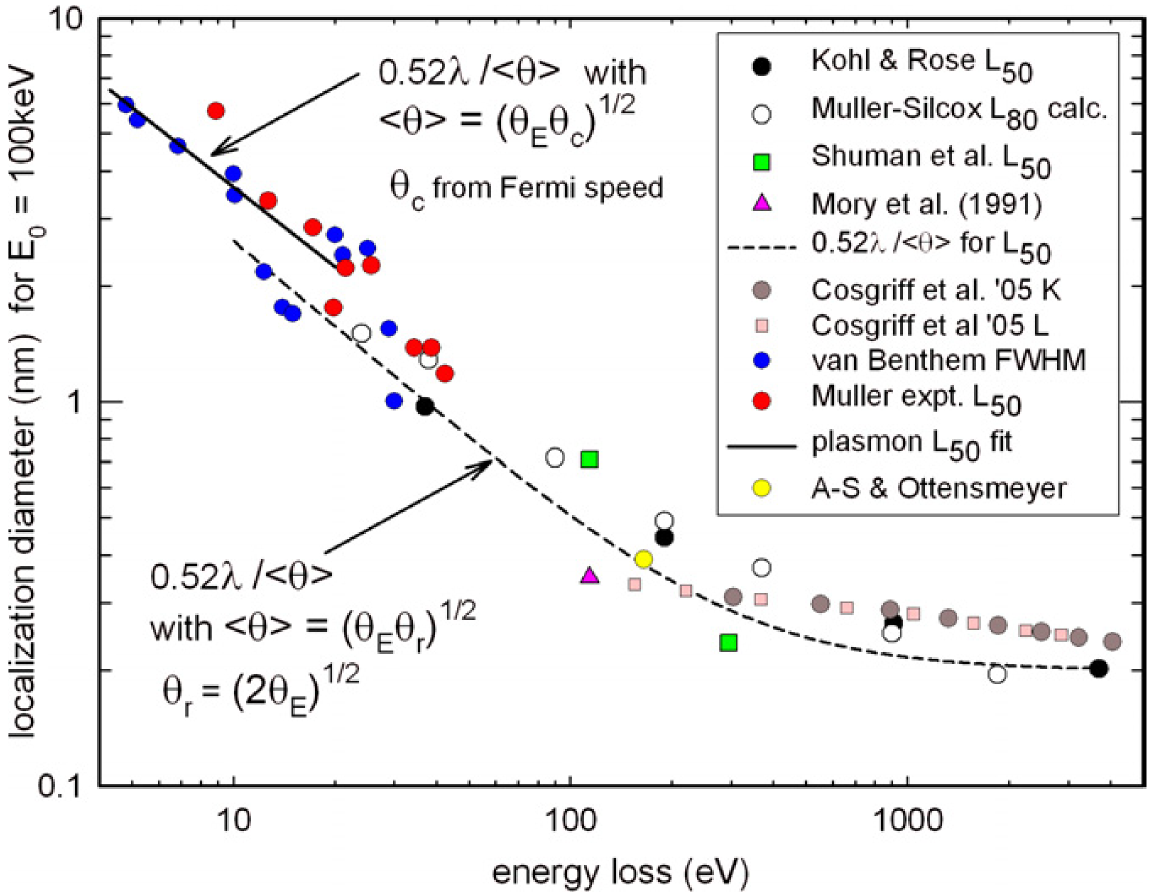




EELS spatial resolution

- **Instrumental** and electron optic on TEM
- Physics of electron scattering: **Elastic scattering** causes a **broadening of a focused electron probe** → wort for thick samples → can be reduced by using an aperture limiting electrons scattered at high angles.
- Decreasing energy loss $\boldsymbol{\Delta E}$ → increasing **spatial delocalization**

How far from a certain atom must the electron probe be before an ionization edge can be detected?

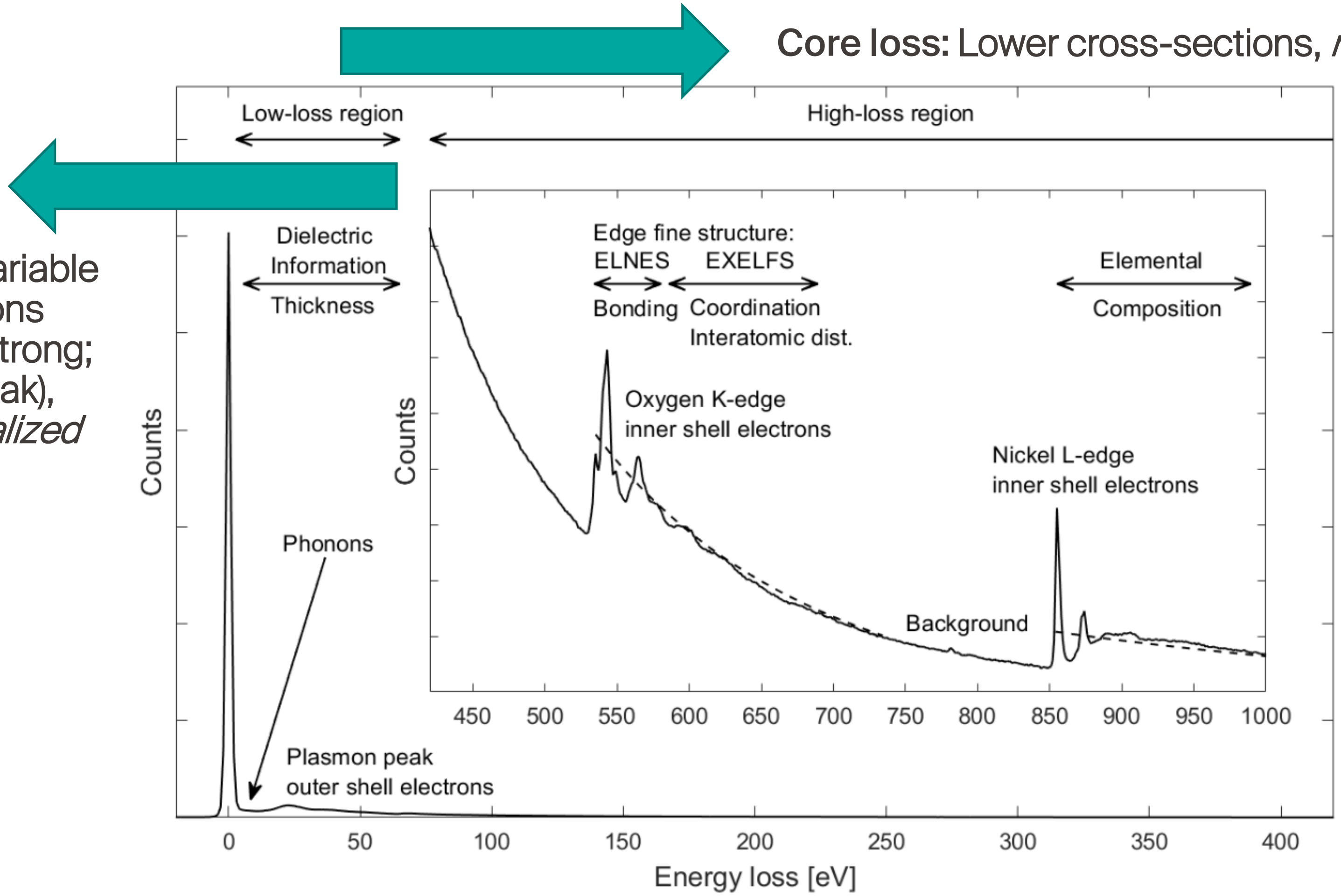


Egerton Rep. Prog. Phys. **72** 016502 (2009)

What we should retain?

Core loss: Lower cross-sections, *more localized*

Low loss: Variable cross-sections (plasmons strong; phonons weak), *more delocalized*



https://lampz.tugraz.at/~hadley/ss2/quasiparticles/eels/eels.php

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Electron Energy Loss Spectroscopy | R. Brydson | Taylor & Francis eBoo

- Electron energy-loss spectroscopy in the TEM. **Ray. F. Egerton:**

Electron energy-loss spectroscopy in the TEM – IOPscience

- Gatan website: EELS.info

- Doctoral school **PHYS-637:**

Electron-Matter Interactions in Transmission Electron Microscopy