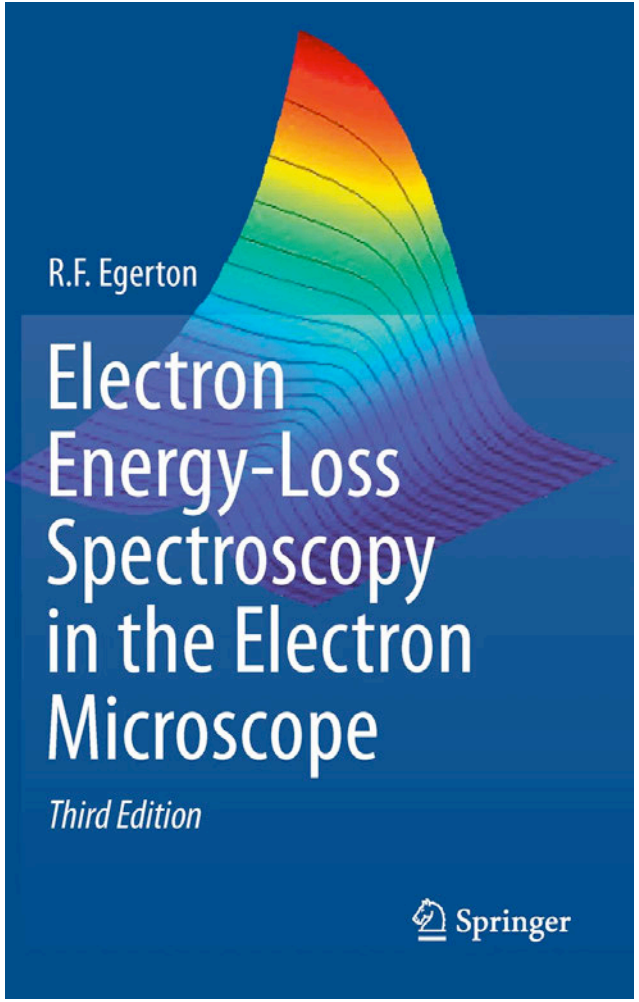
Analytical TEM part II

Duncan Alexander
EPFL-IPHYS-LSME

The reference book on EELS

- Electron Energy-Loss Spectroscopy in the Electron Microscope
  Ray F. Egerton
  https://link.springer.com/book/10.1007/978-1-4419-9583-4

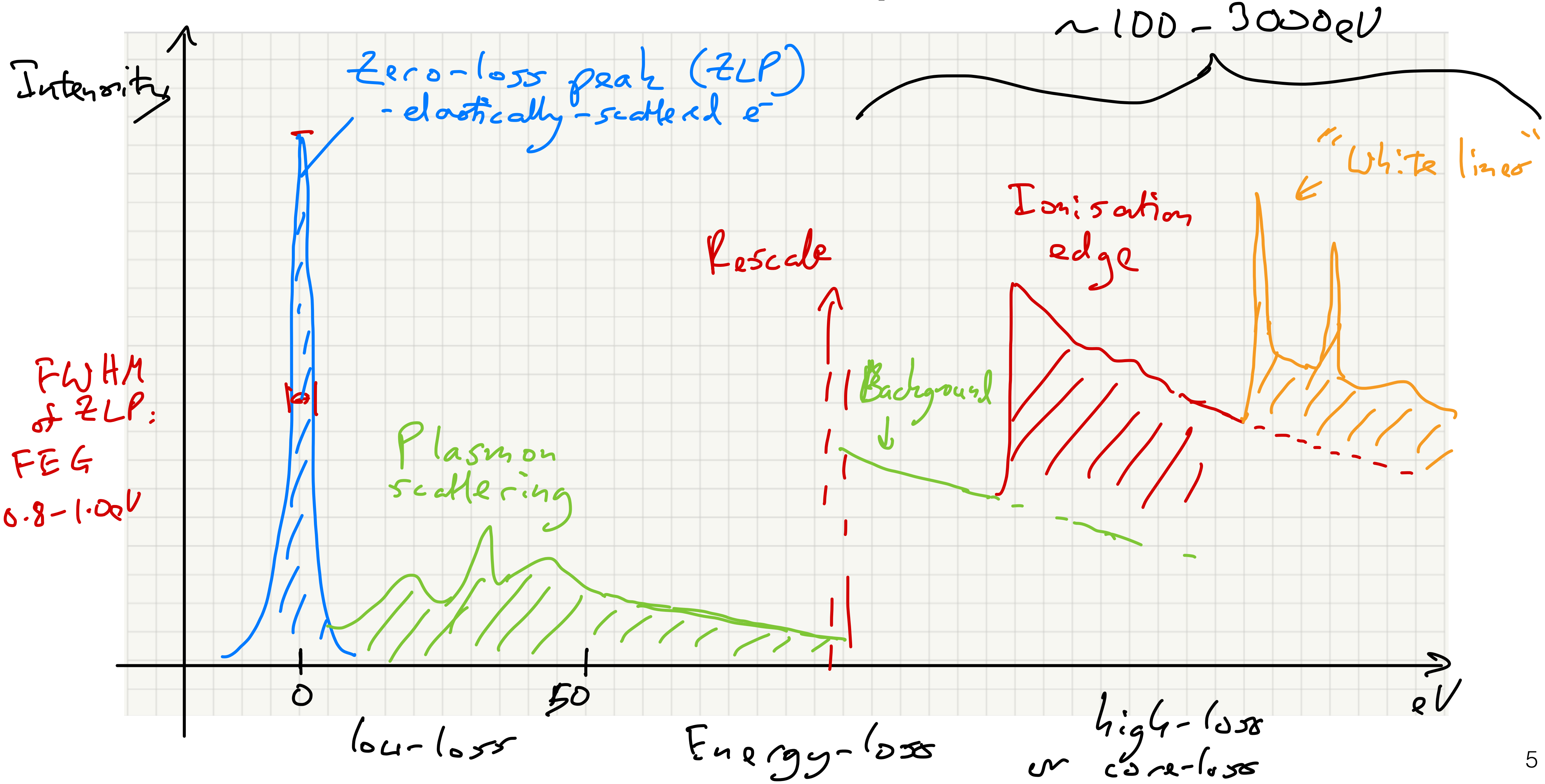


Contents

- Features of the EEL spectrum
- EELS instrumentation
- Energy-filtered TEM (EFTEM)
- Inelastic scattering geometry
- Low-loss EELS
- Thickness measurements
- Ionisation edge EELS
- Elemental quantification
- ELNES / “fine structure”

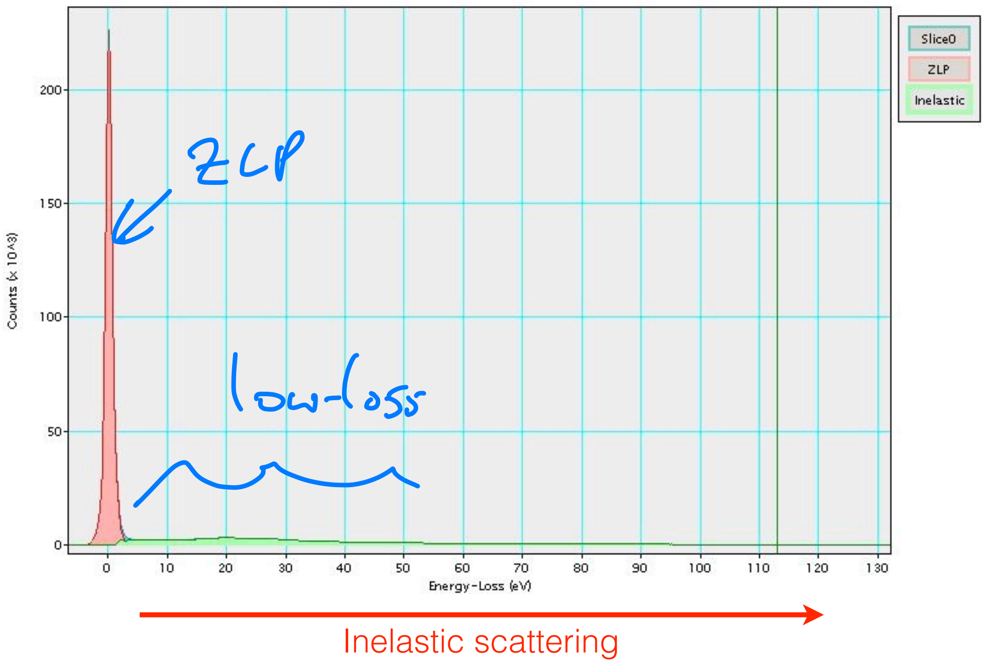
Contents

Features of the EEL spectrum



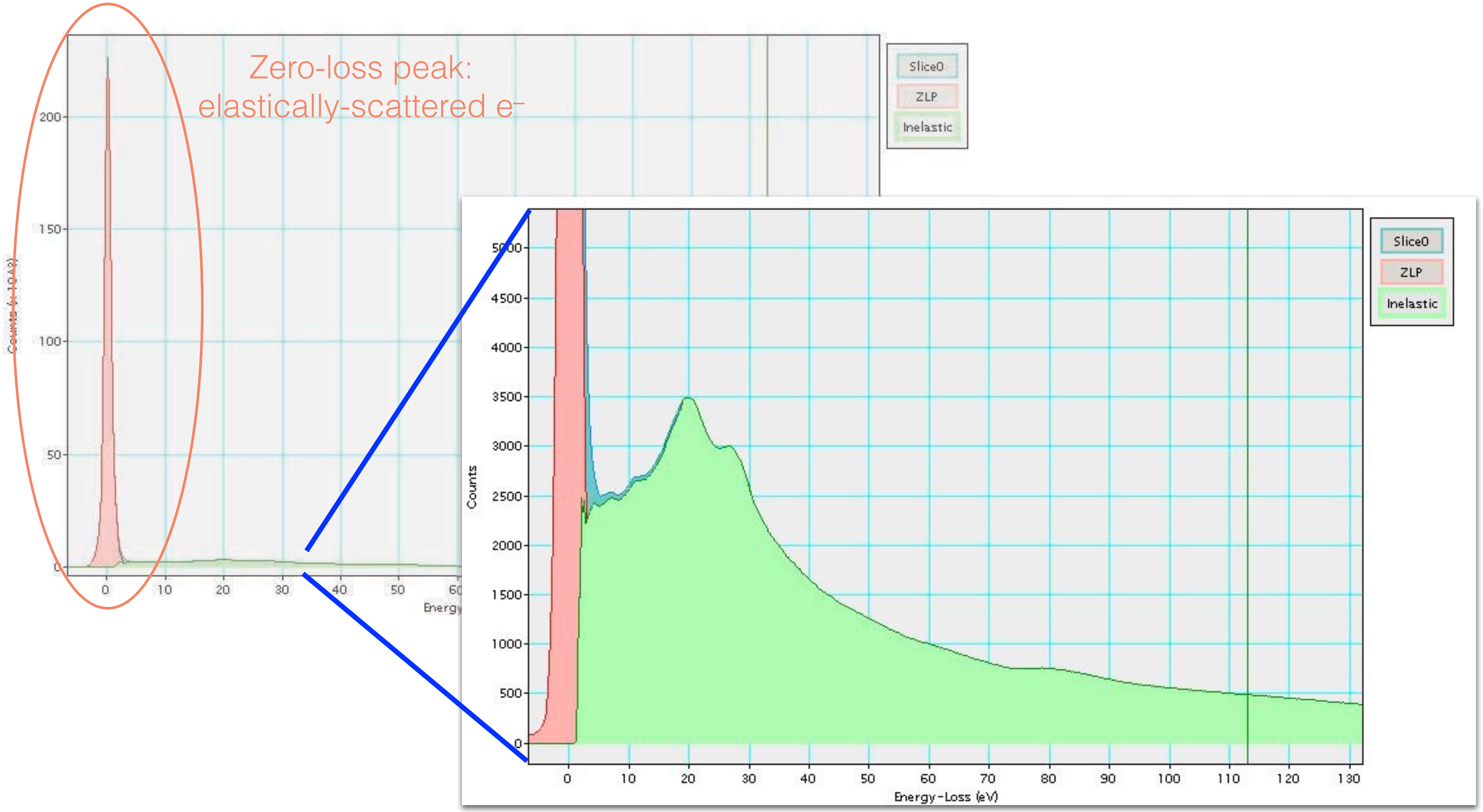
Features of the EEL spectrum

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



Features of the EEL spectrum

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

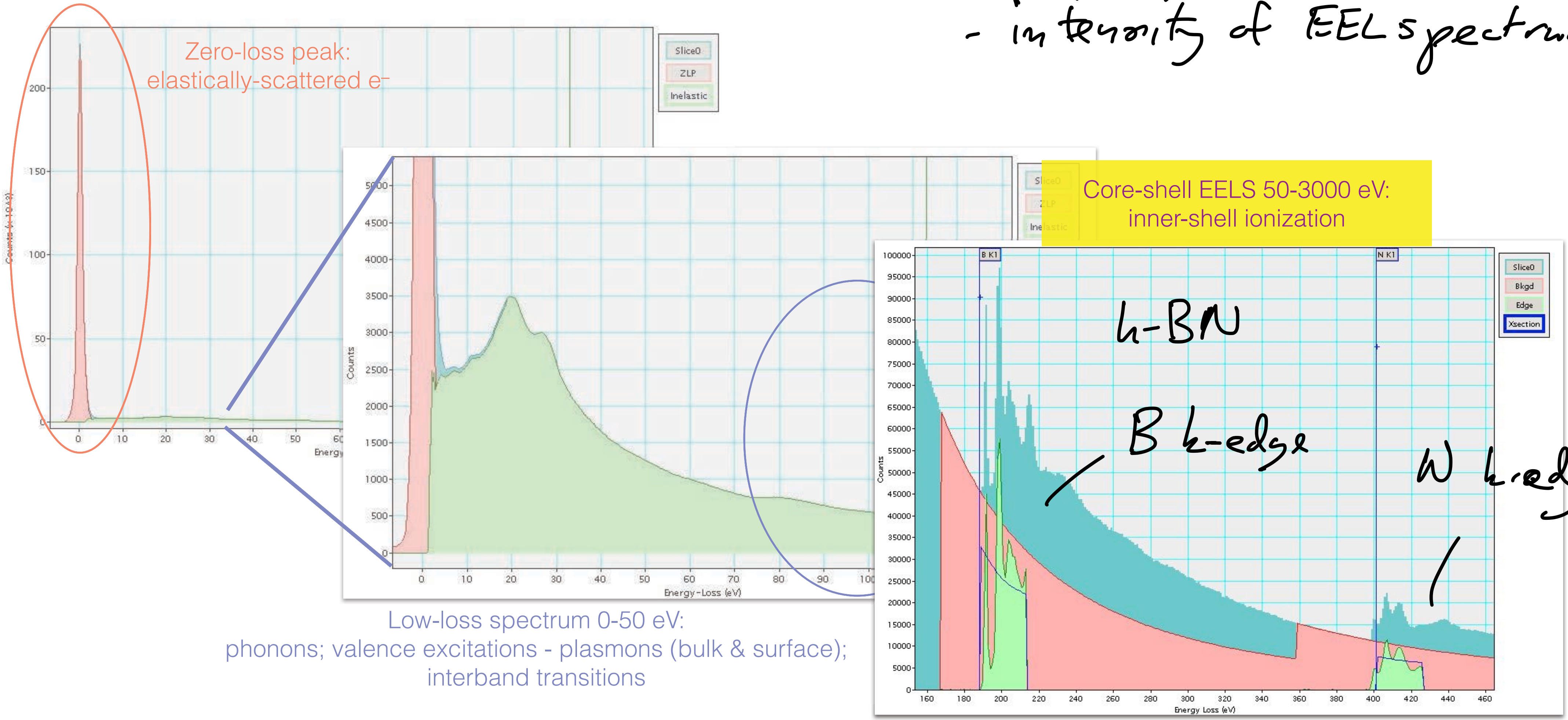


Low-loss spectrum 0-50 eV:
phonons; valence excitations - plasmons (bulk & surface);
interband transitions

Features of the EEL spectrum

- Energy loss > 0 ⟹ *Inelastic scattering*

Higher energy-loss ΔE
- intensity of EEL spectrum ↓



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

Contents

- Features of the EEL spectrum
- EELS instrumentation
- Energy-filtered TEM (EFTEM)
- Inelastic scattering geometry
- Low-loss EELS
- Thickness measurements
- Ionisation edge EELS
- Elemental quantification
- ELNES / “fine structure”

Electron energy-loss spectrometer

- Typical EEL spectrometer: magnetic prism

Radius of curvature

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

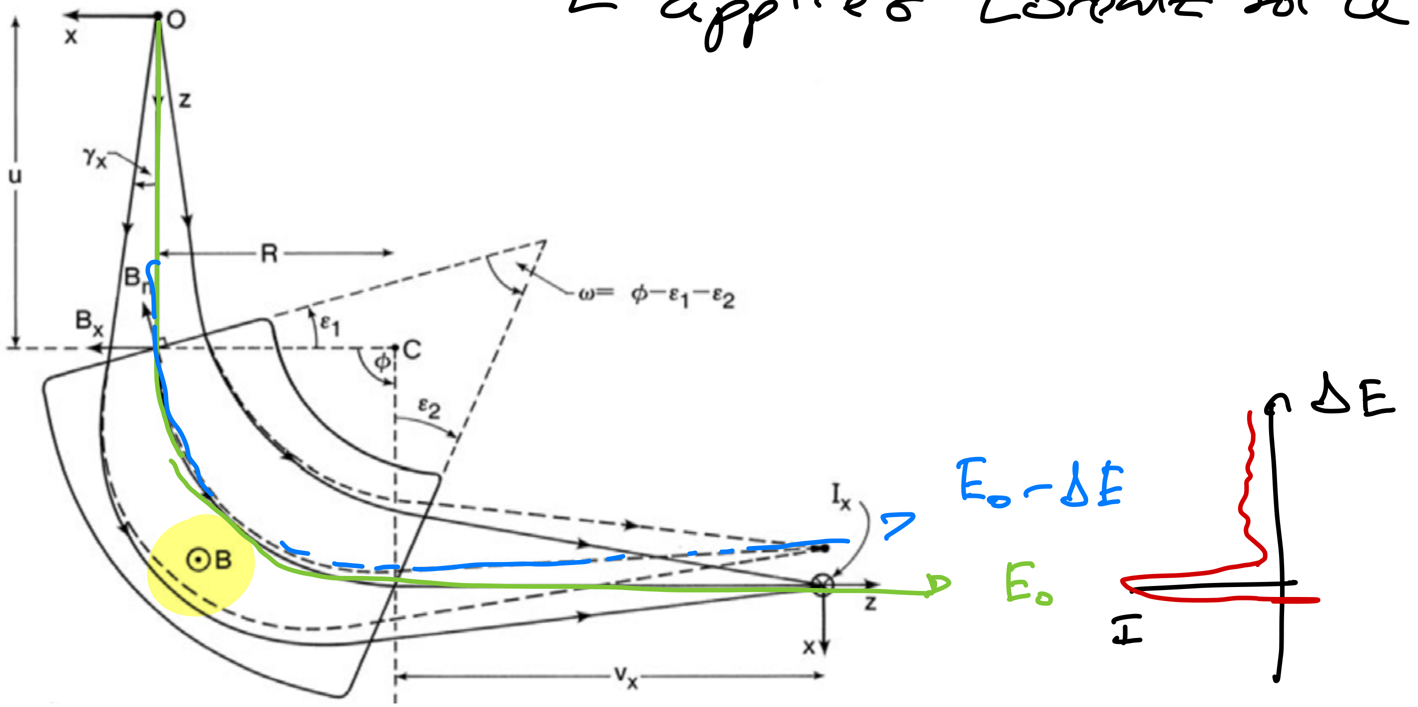
← speed of e⁻

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

m_0 : rest mass of e⁻

$\Delta E \Rightarrow R \downarrow$

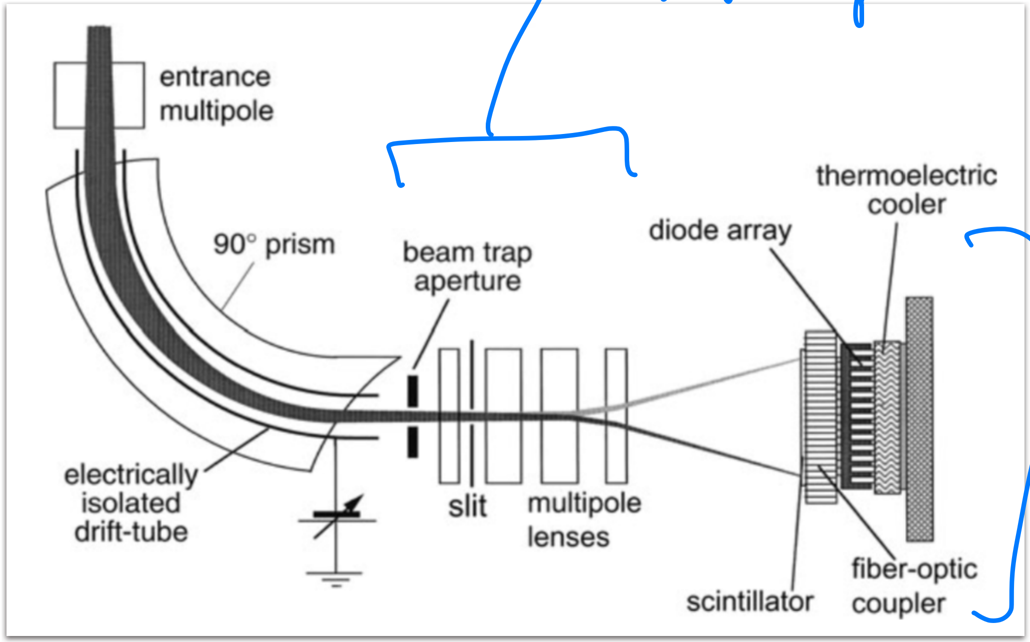
- applies $\vec{B}$ ⊥ to $\vec{v}$ of transmitted e⁻
  L applies Lorentz force



Post-column spectrometer

- Post-column spectrometer most common type used for materials science/physics
- For instance: Gatan EEL spectrometer

Correct distortions from prism

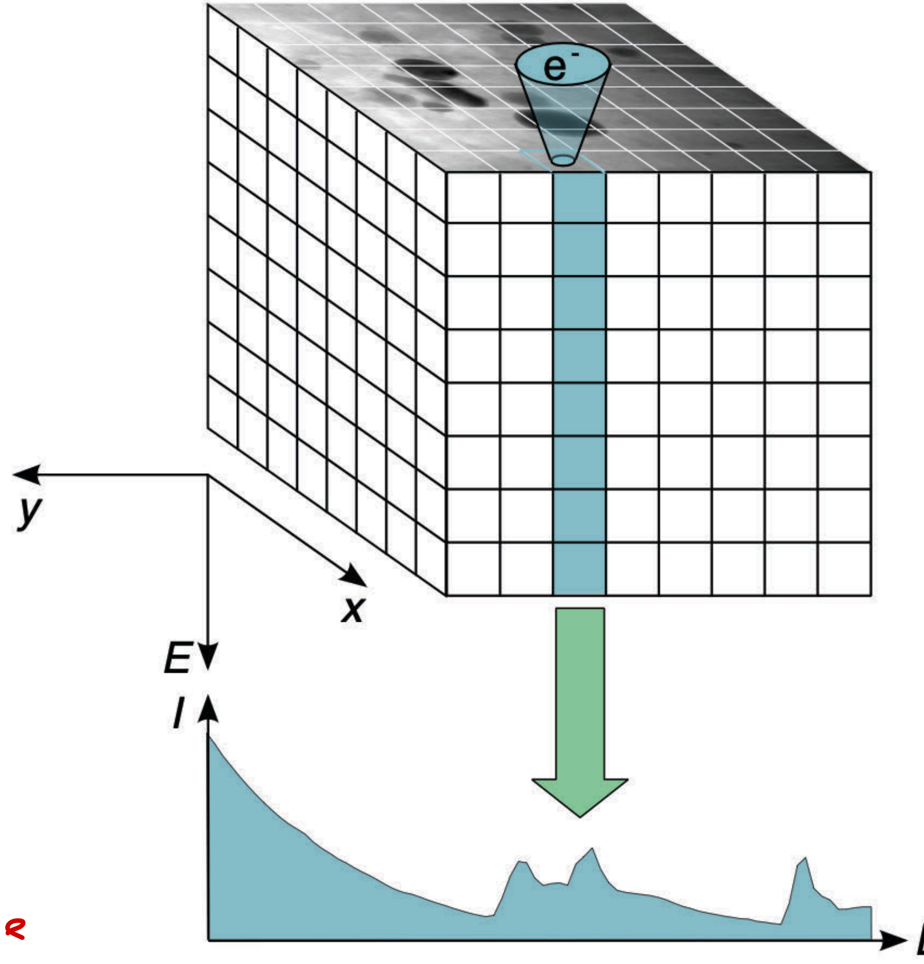


TEM column

EPFL

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*)



Contents

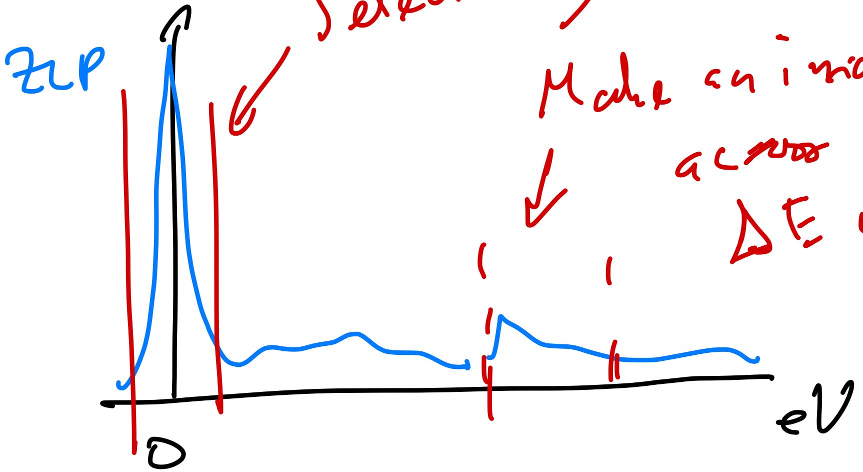
- Features of the EEL spectrum
- EELS instrumentation
- Energy-filtered TEM (EFTEM)
- Inelastic scattering geometry
- Low-loss EELS
- Thickness measurements
- Ionisation edge EELS
- Elemental quantification
- ELNES / “fine structure”

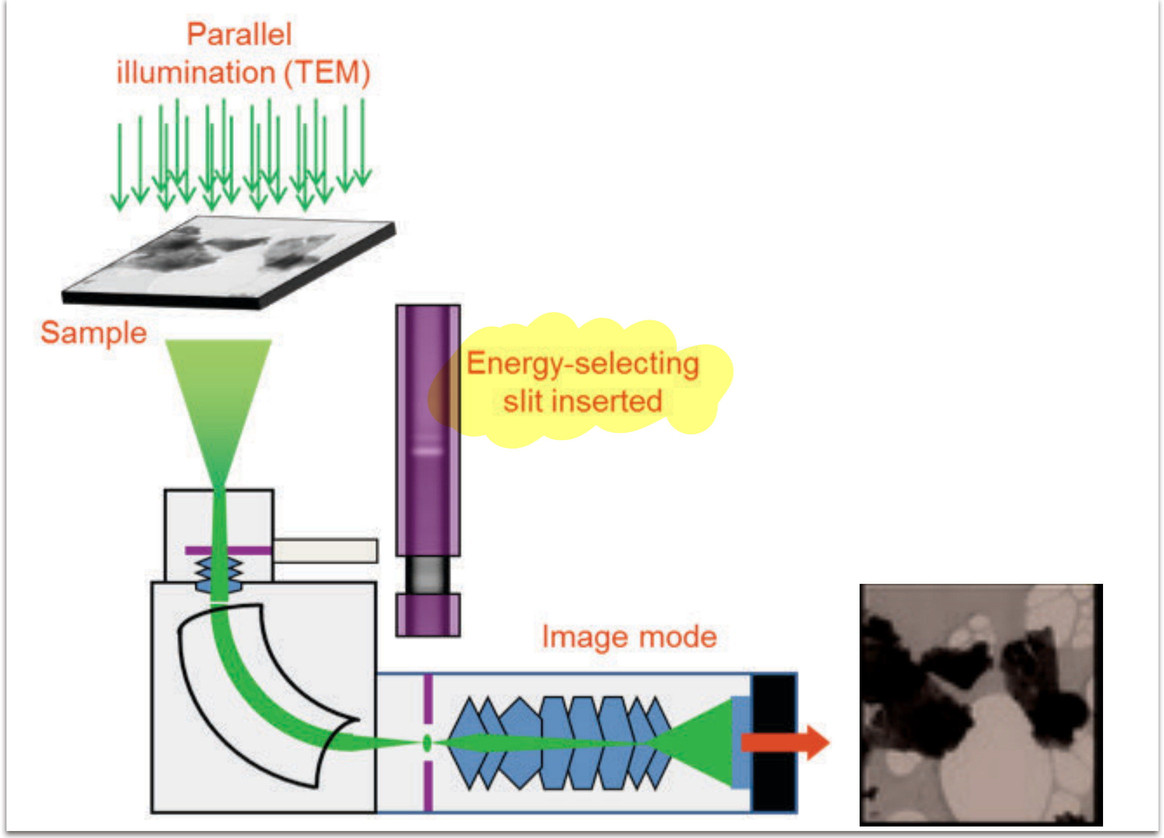
Energy-filtered TEM (EFTEM)

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

Select only ZLP

Make an image across some ΔE window

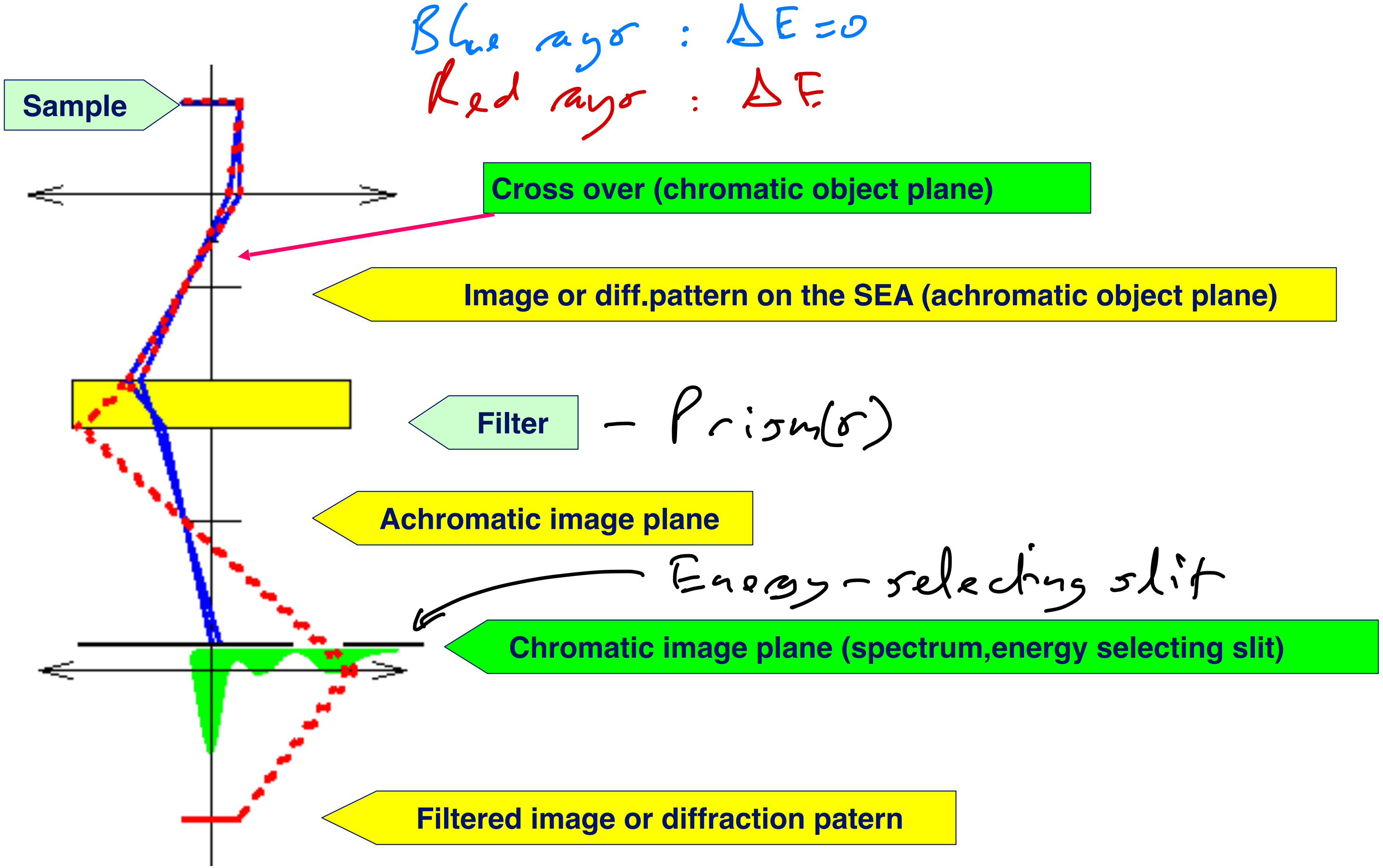




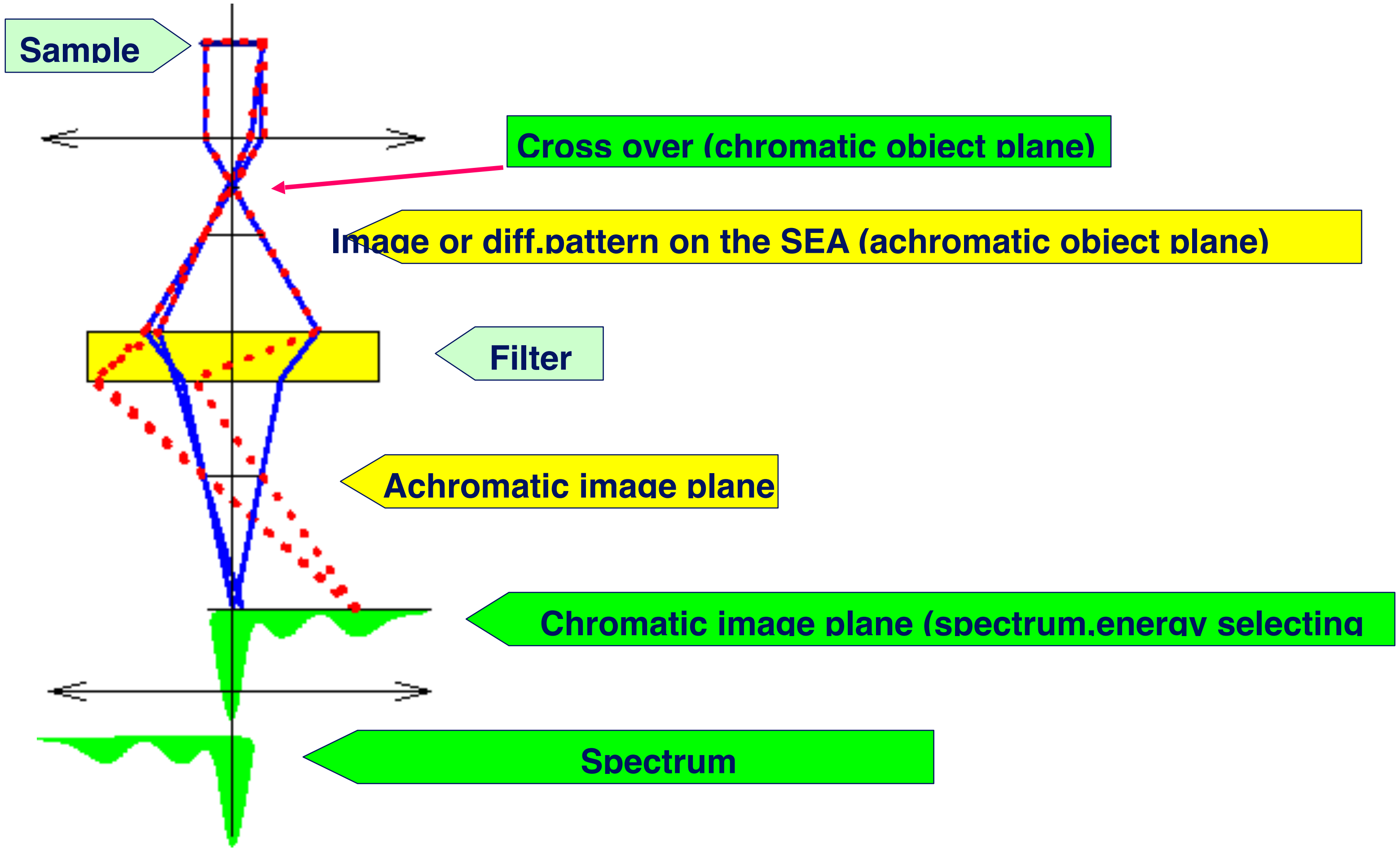
Energy-dispersed e⁻

- Select e⁻ with defined ΔE

Energy-filtered TEM ray diagram



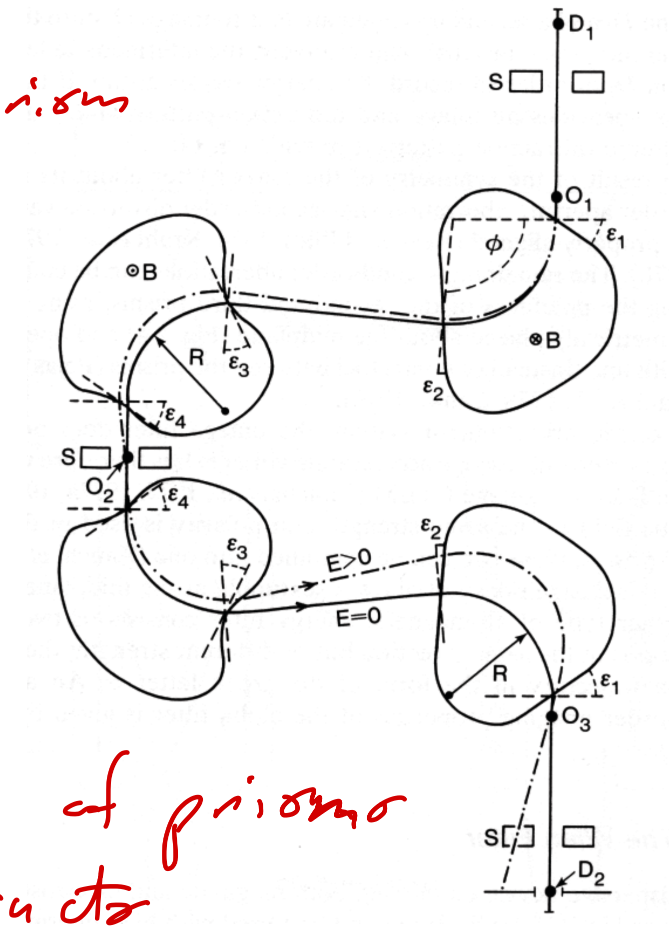
Spectroscopy mode ray diagram



Two possibilities: in-column or post-column

In-column Omega filter – e.g. JEOL 2200FS

4 × 90° prism



Symmetry of prisms reconstructs TEM image

ILs

Projector lenses

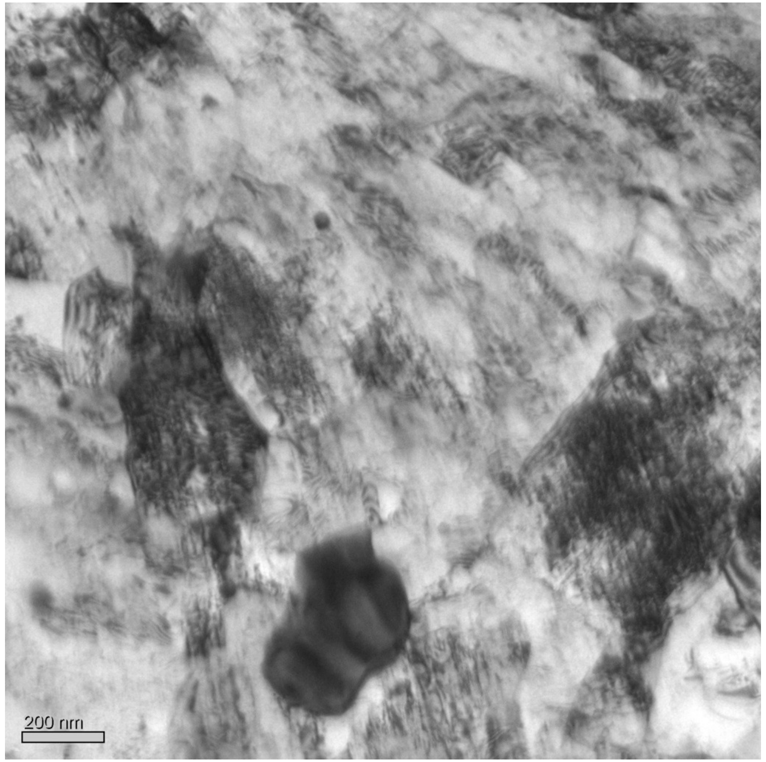
Zero-loss EFTEM

ΔE => inelastic sca.
=> incoherent sca.

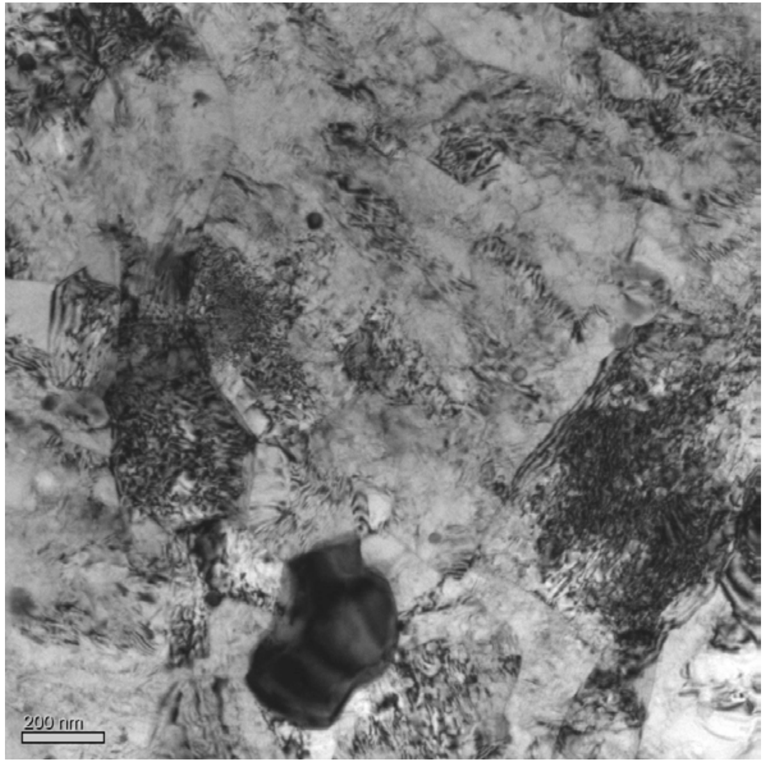
- Zero-loss filtering can be used to remove diffuse inelastic scattering in TEM images of thick samples and in diffraction patterns

- Example – ODS reinforced steel, sample ~250 nm thick:

Unfiltered bright-field TEM:

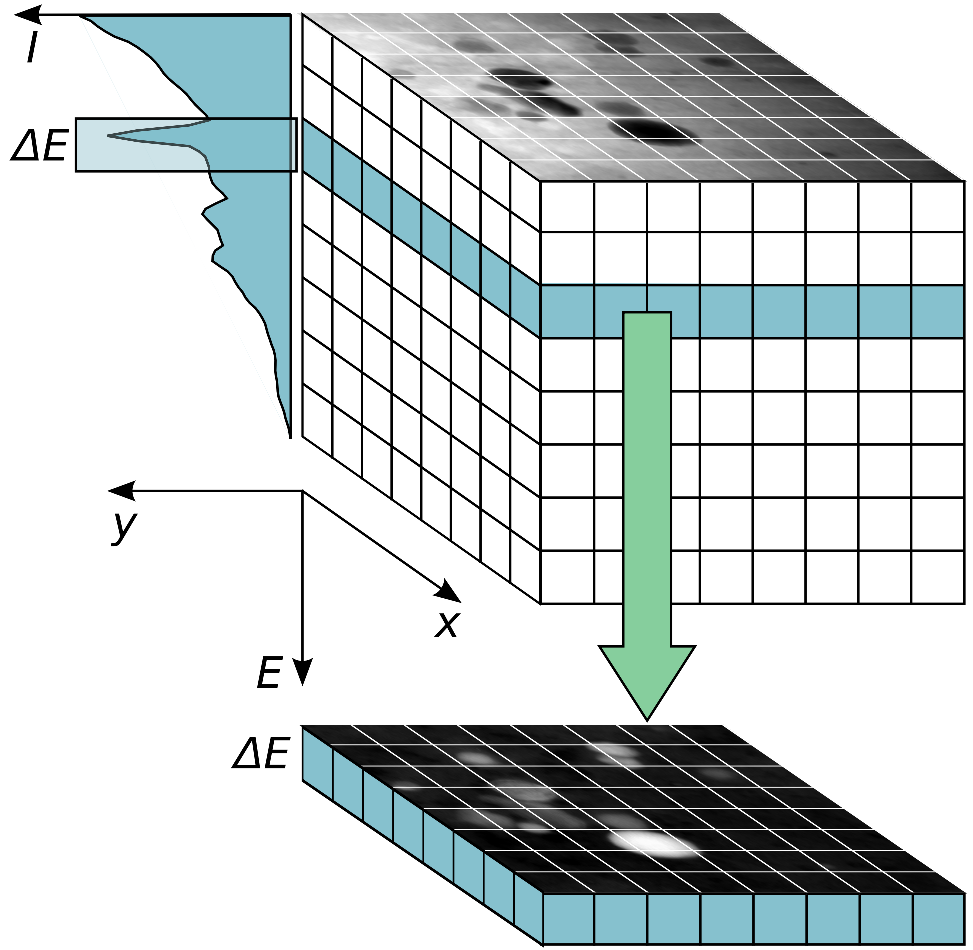


Zero-loss TEM:



Energy-filtered TEM (EFTEM)

- Record TEM image(s) made from transmitted electrons having a defined energy
- Images defined by energy-loss *E* and energy window
- *Zero-loss* filtering: TEM image of elastically-scattered electrons with no energy loss
- EFTEM spectrum imaging:
  create 3D data-cube by recording image series at consecutive energy losses

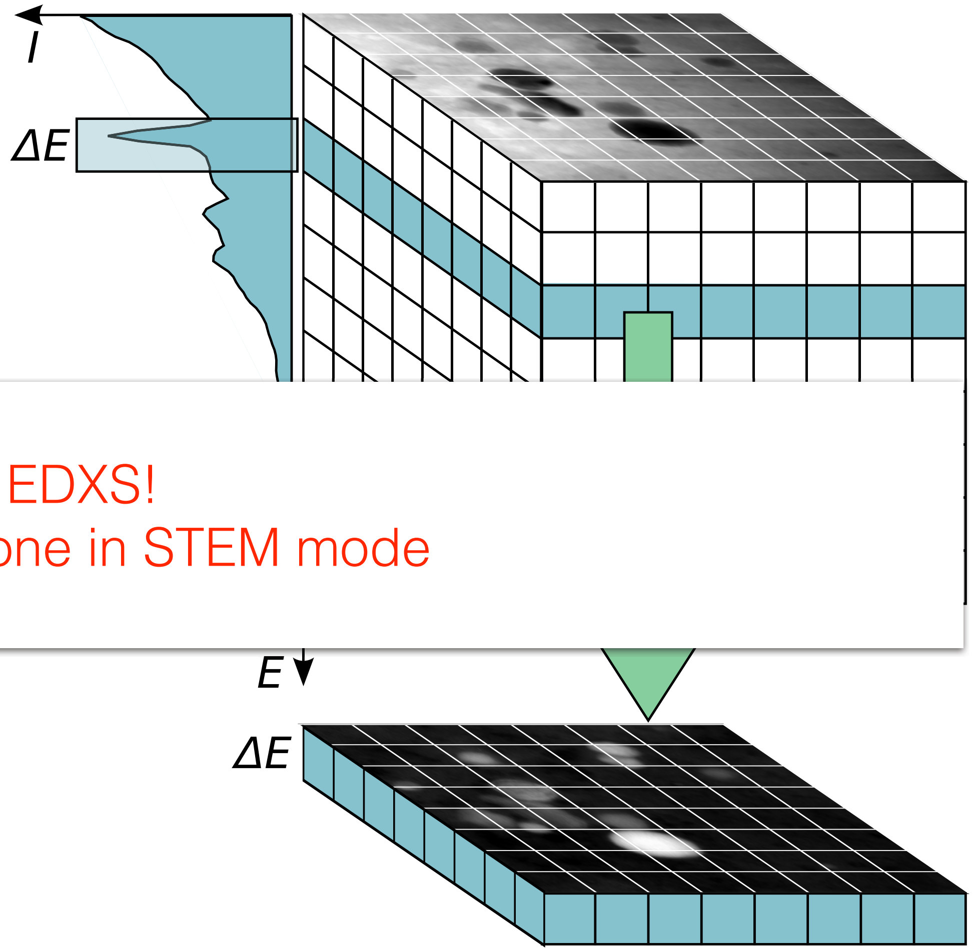


Energy-filtered TEM (EFTEM)

- Record TEM image(s) made from transmitted electrons having a defined energy
- Images defined by energy-loss *E* and energy window

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



Contents

Inelastic scattering geometry

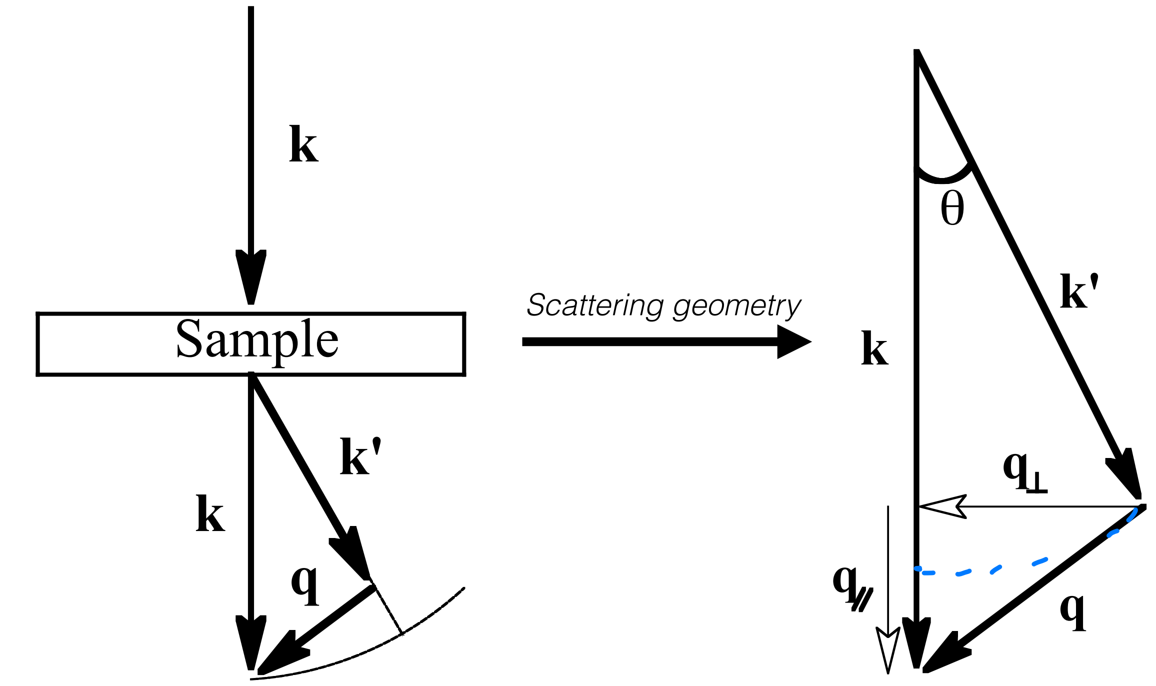
$E_0 \rightarrow E_0 - \Delta E$

$\lambda \uparrow \Rightarrow k \downarrow$

$|\vec{k}'| < |\vec{k}|$

$\vec{k}$ – incident wave-vector

$\vec{k}'$ – scattered wave-vector



q: momentum transfer of inelastic scattering

$$q^2 = k^2 + (k')^2 - 2kk'\cos\theta$$

$q_\parallel$: represents shortening of $\vec{k}'$ relative to $\vec{k}$

$$\theta_E = \frac{\Delta E m \gamma}{\hbar^2 k^2}$$

$|\vec{k}| = \frac{2\pi}{\lambda}$

$q_\perp = k\vartheta$ (geometry)

$q_\parallel = k\vartheta_E$ (definition of ϑ_E)

θ_E: represents shortening of k

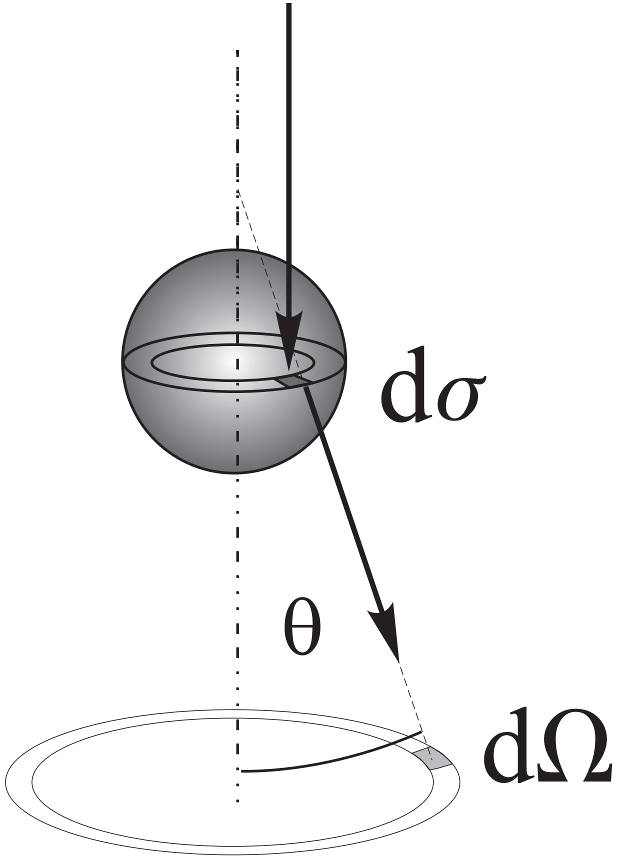
$\vartheta \ll 1$ therefore $q^2 = k^2(\vartheta_E^2 + \vartheta^2)$

Double differential scattering cross section

Relevant quantity: the *double differential scattering cross-section* (DDSCS) as a function of angle θ and energy loss *E*.

It is given for one atom.

We consider a transition from initial state | I > to final state | F > for the core electron of the atom



σ : scattering cross-section

- Probability of scattering : $\dfrac{\partial^2 \sigma}{\partial \Omega \, \partial E}$

Angular distribution of the ionisation edge

With quantum mechanical derivation, find that DDSCS for inelastic events varies as $\dfrac{1}{q^2}$

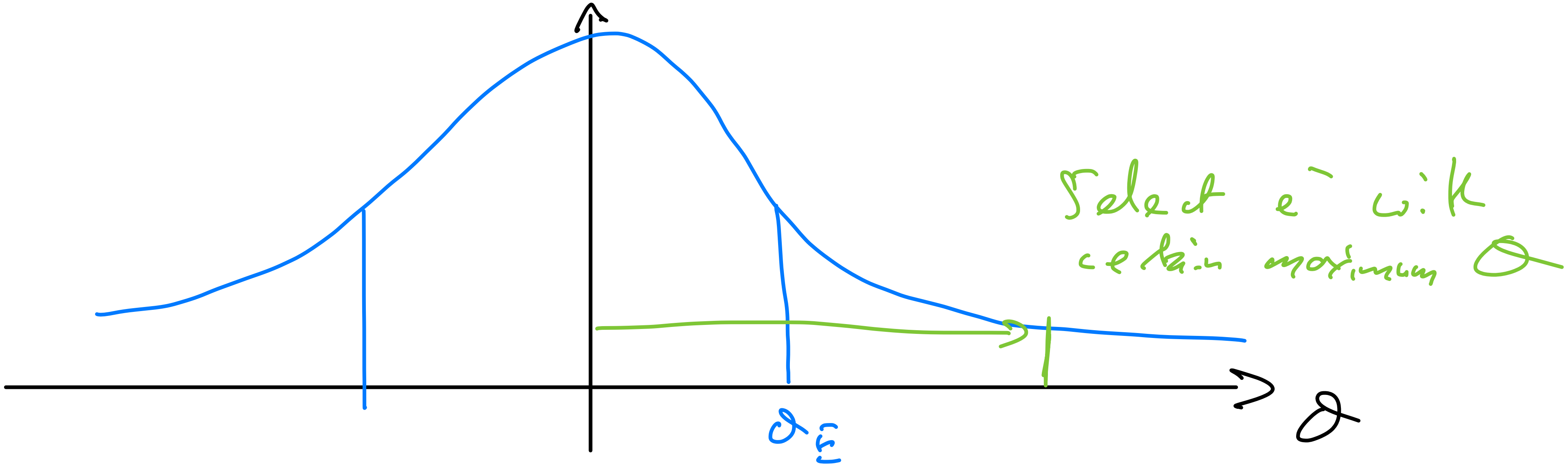
Since: $$q^2 = k^2(\theta^2 + {\theta_E}^2)$$

DDSCS has an angular dependence: $$\text{DDSCS}(\theta) \propto \frac{1}{\theta^2 + {\theta_E}^2}$$

Therefore the ionisation edge has an angular distribution of intensity that is **Lorentzian**

Angular distribution of the ionisation edge

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} \propto \frac{1}{\theta^2 + {\theta_E}^2}$$



θ_E is the scattering angle for the half width at half maximum (HWHM) of this Lorentzian

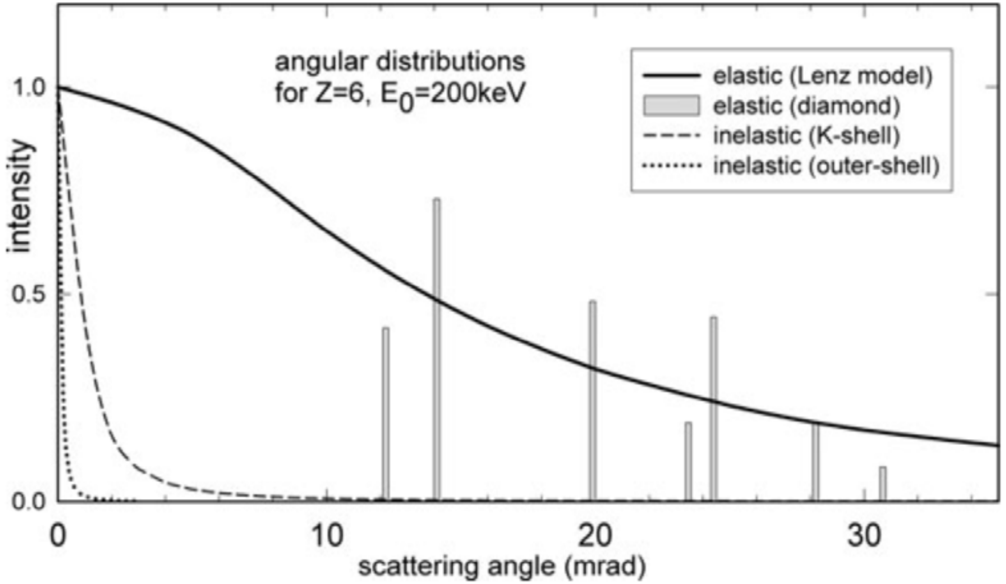
θ_E is therefore considered as the *characteristic angle of scattering*, because most of the ionisation edge intensity will fall within a collection aperture of this angle

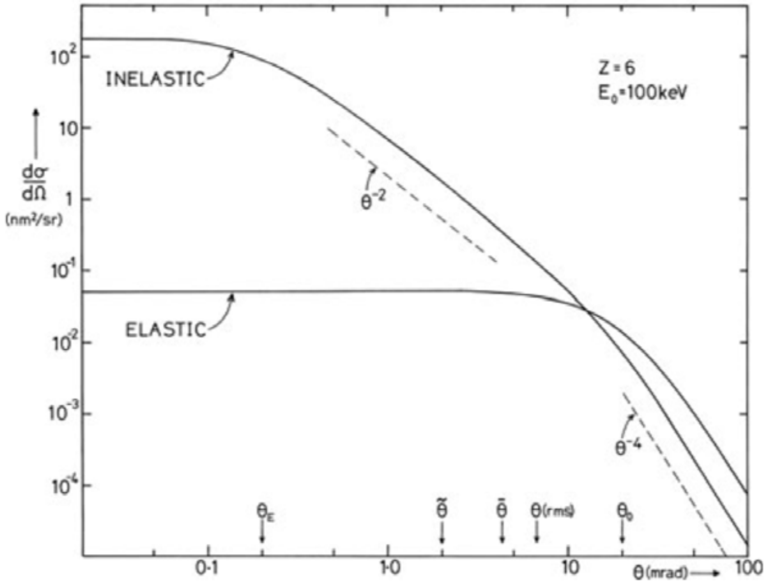
Inelastic scattering angular range

– ΔE forward scattered in small angular range

- Inelastic scattering concentrated into much smaller angles than elastic scattering
- Characteristic angle for scattering: $\theta_E = \frac{\Delta E m\gamma}{\hbar^2 k^2} = \frac{\Delta E}{\gamma m v^2} \sim \frac{\Delta E}{2E_0}$

within ~20%





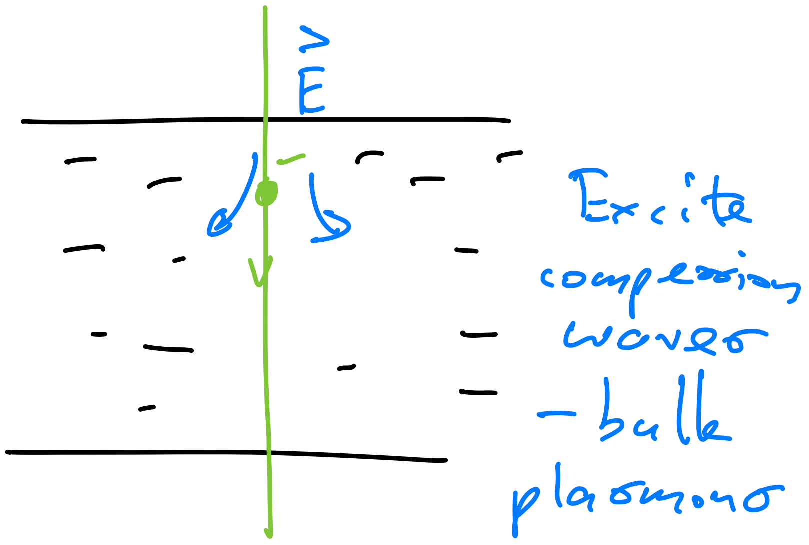
Suppose consider W K-edge: ΔE ~ 400 eV
Suppose E0 200 keV → $\theta_E \sim 1$ mrad

Contents

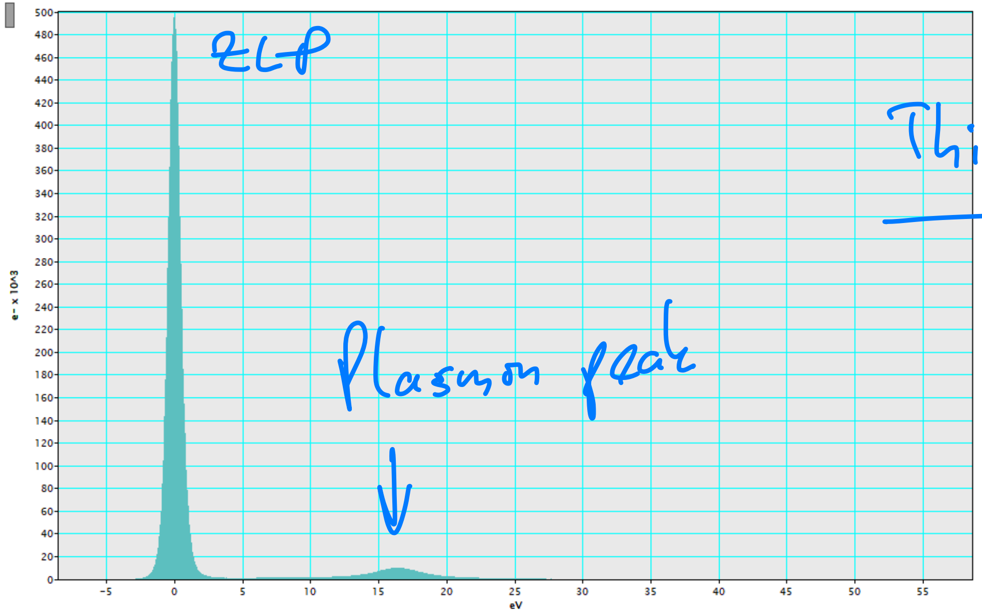
- Features of the EEL spectrum
- EELS instrumentation
- Energy-filtered TEM (EFTEM)
- Inelastic scattering geometry
- Low-loss EELS
- Thickness measurements
- Ionisation edge EELS
- Elemental quantification
- ELNES / “fine structure”

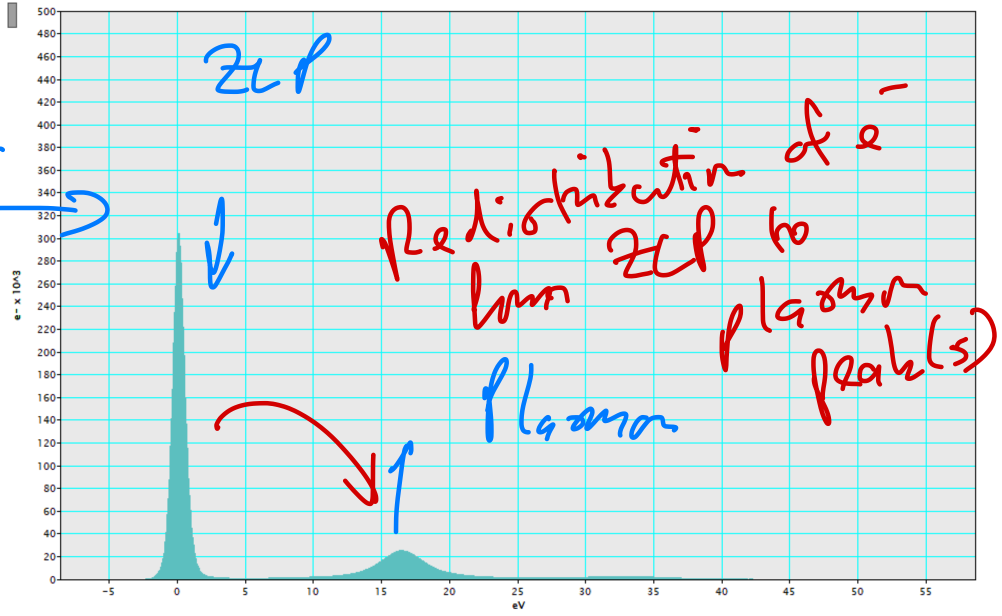
Low-loss EELS

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



Example low-loss: crystalline Si

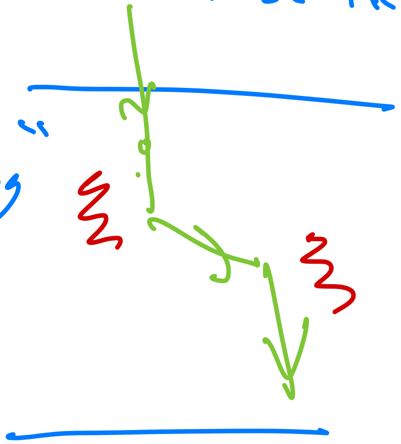




Low-loss EELS

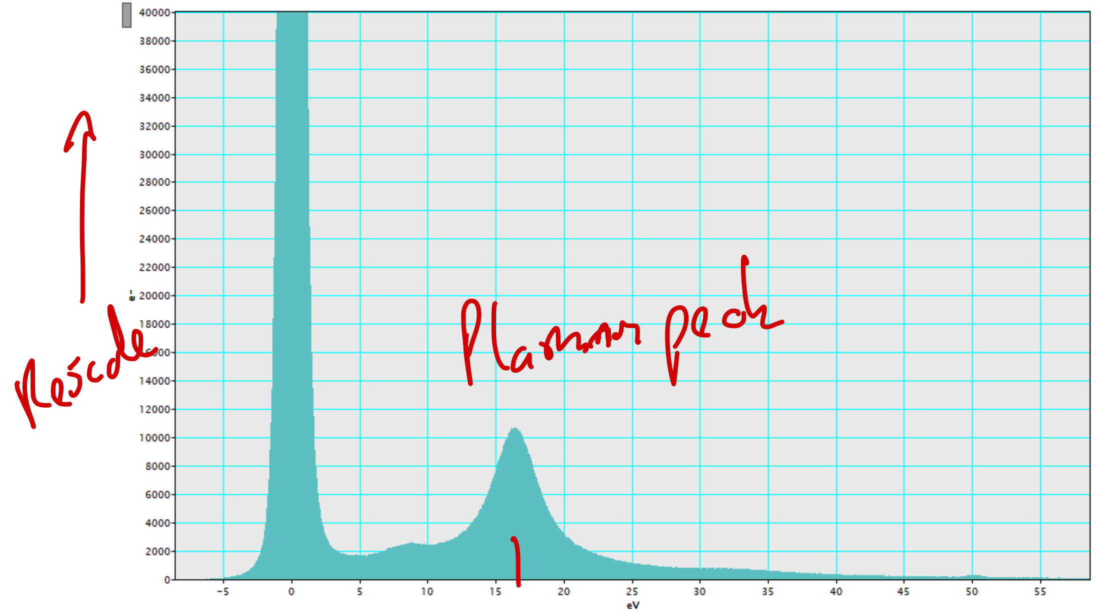
- For ΔE ~1–50 eV: excitation of plasmons
- Volume/bulk plasmon: oscillation of valence electrons

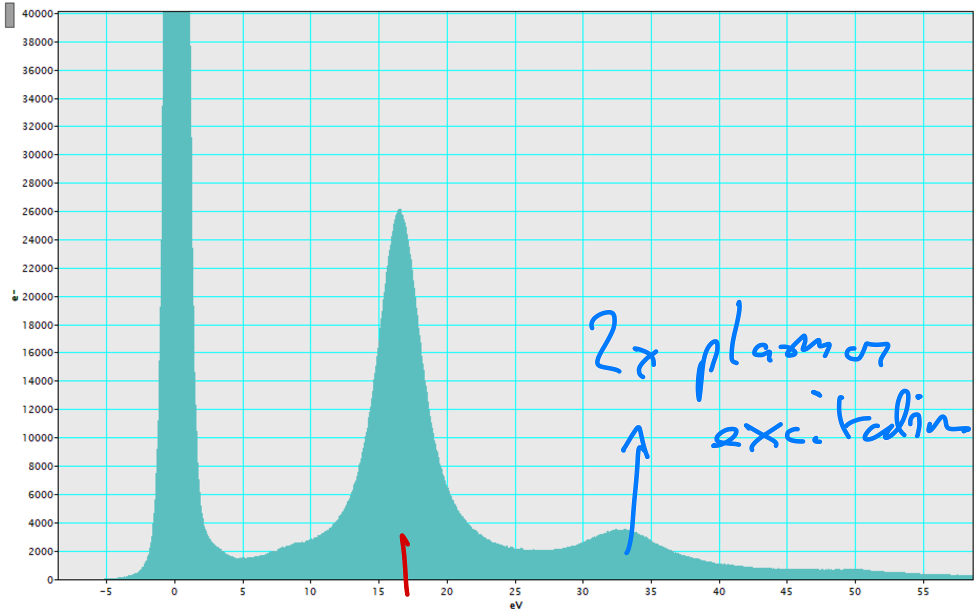
Convolution of scattering → "Multiple scattering"



Example low-loss: crystalline Si

ZOOMED





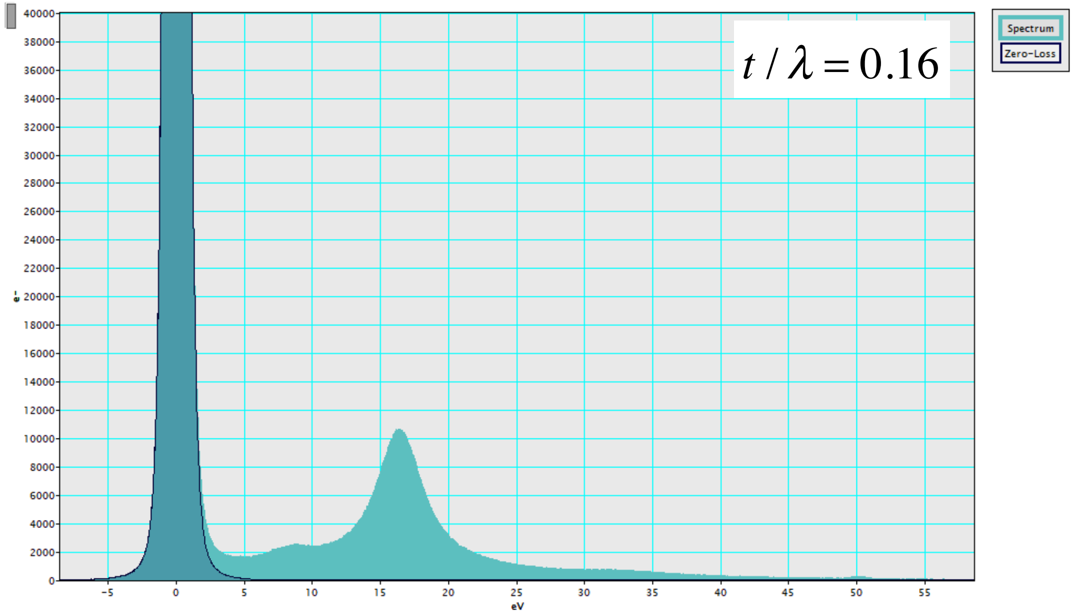
Plural scattering

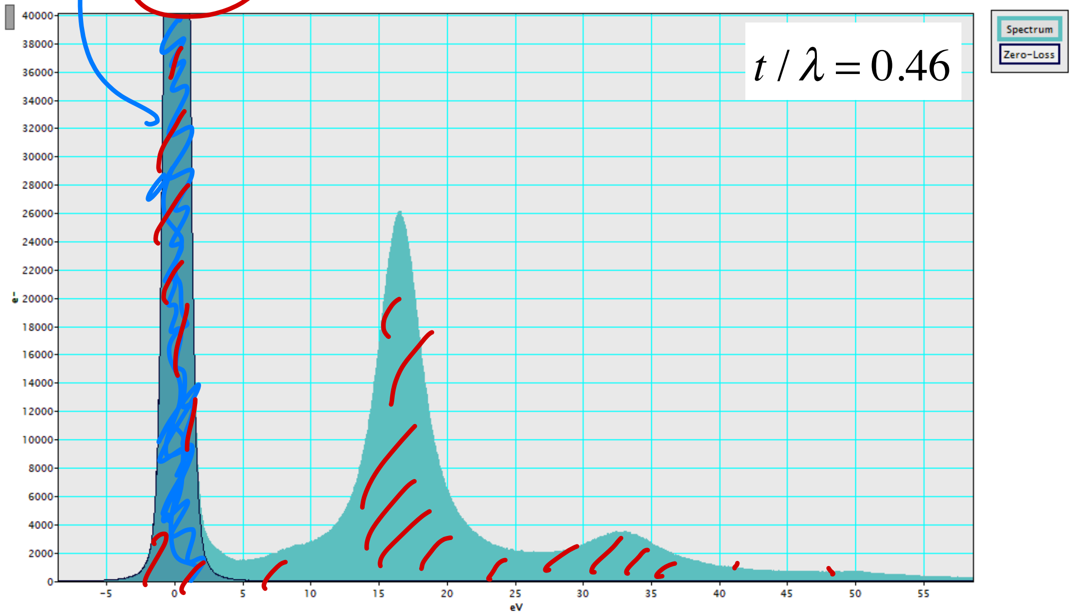
- As specimen thickness increases, can have multiple scattering: *plural scattering*
- **Inelastic scattering mean free path: λ**
- From Poisson statistics: $t/\lambda = \ln(I_t/I_0)$

t : sample thickness

I_0 : elastic-scattered intensity (ZLP)

I_t : all incident intensity





For EELS : like $t/\lambda \leq 0.7$

Plural scattering; mean free path

- What is likely to influence the inelastic scattering mean free path?

$E_0 \uparrow \quad \lambda \uparrow$

$Z \uparrow \quad \lambda \downarrow$

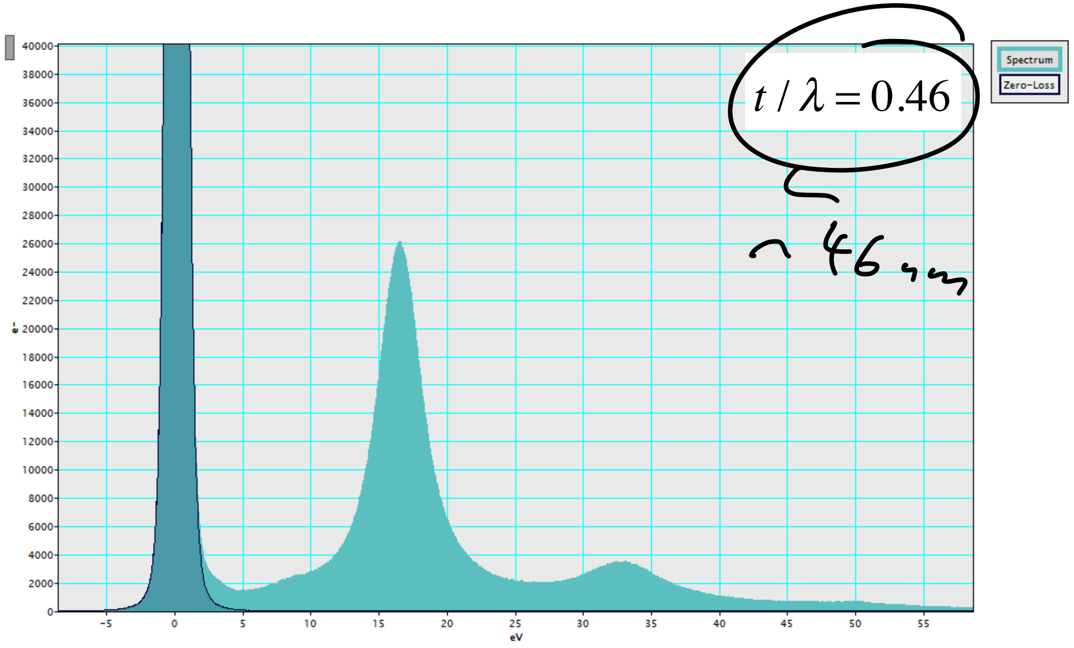
Sample thickness measurement

- 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

Si: $\lambda \sim$ 100nm

Need to know E, β

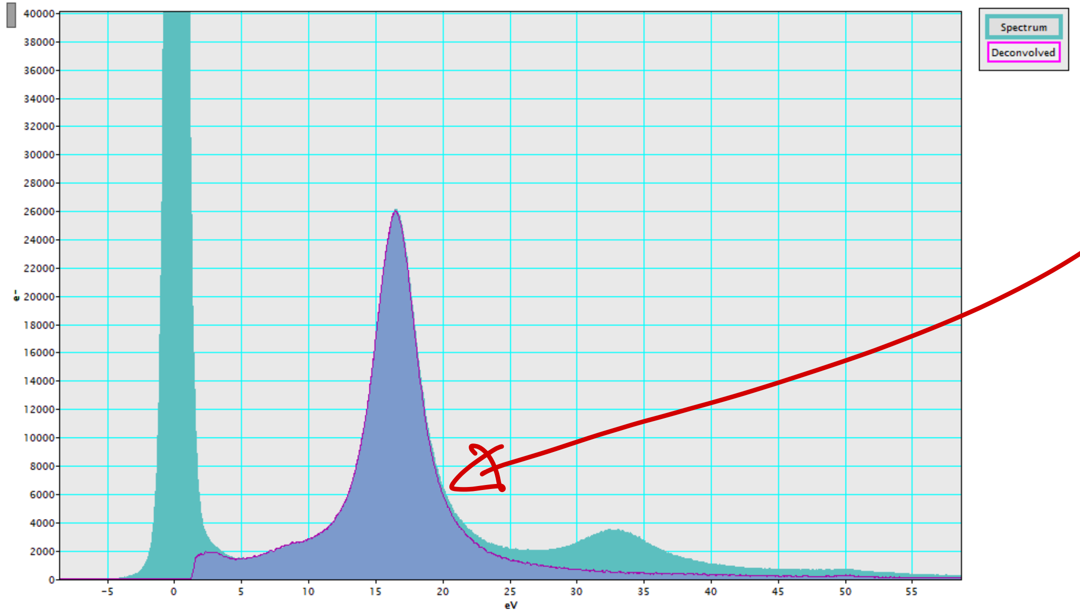
Spectrometer collection semi-angle



~ 46nm

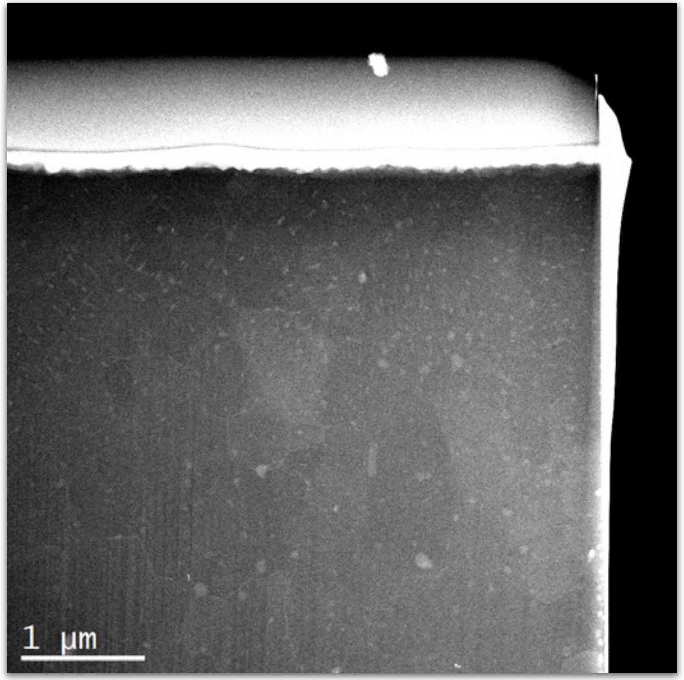
Spectral deconvolution

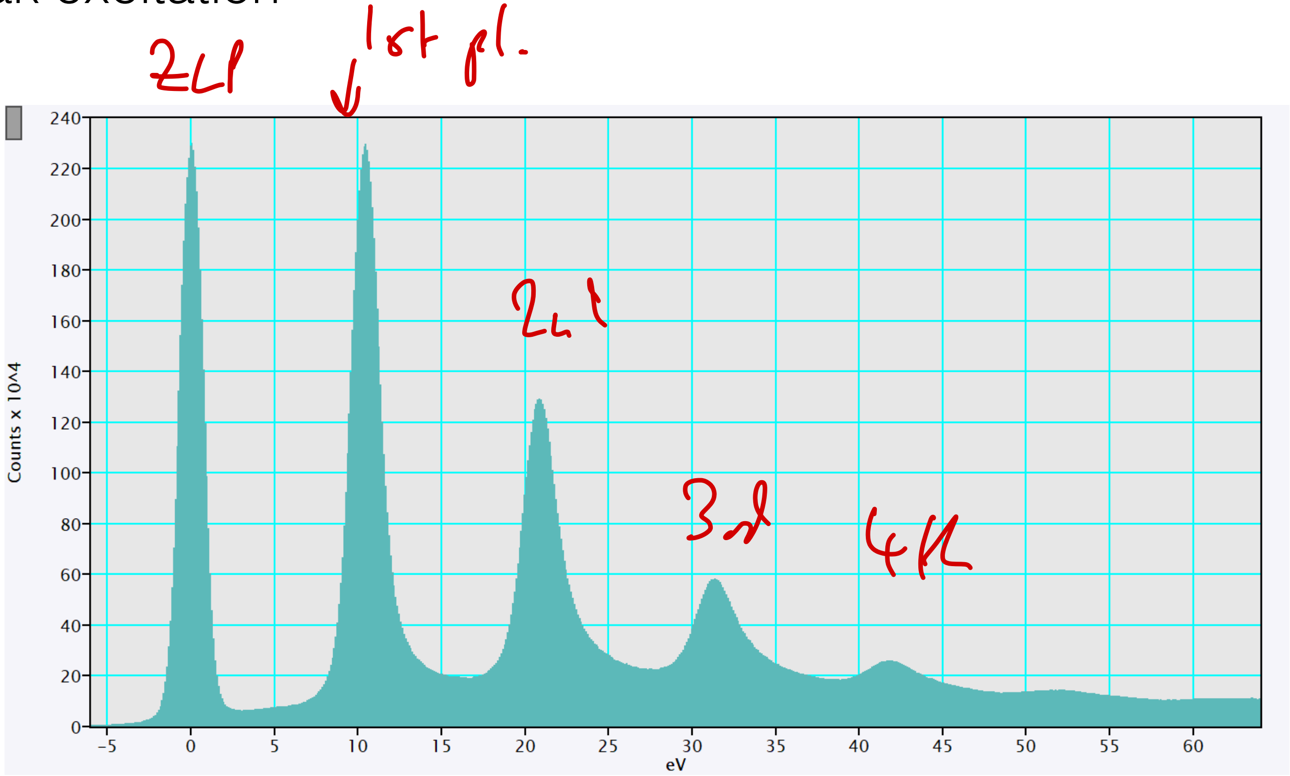
- Deconvolution can be used to retrieve the *single-scattering distribution* (SSD)
- Core-loss spectra: use Fourier-ratio deconvolution (needs low-loss spectrum)
- Low-loss spectra: use Fourier-log deconvolution:



Multiple scattering: Mg sample

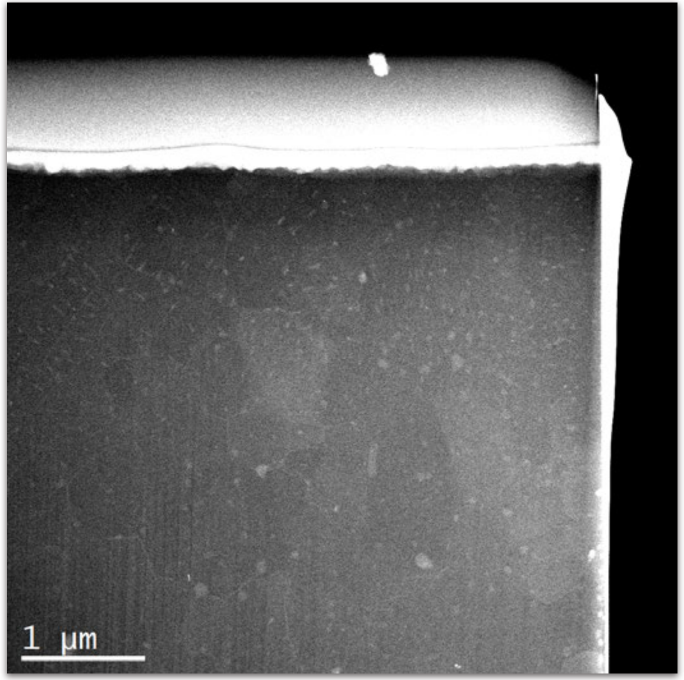
- Thick sample: $t / \lambda \approx 2.3$
- Well-defined plasmon peak (free electron gas)
- Multiple orders of plasmon peak excitation

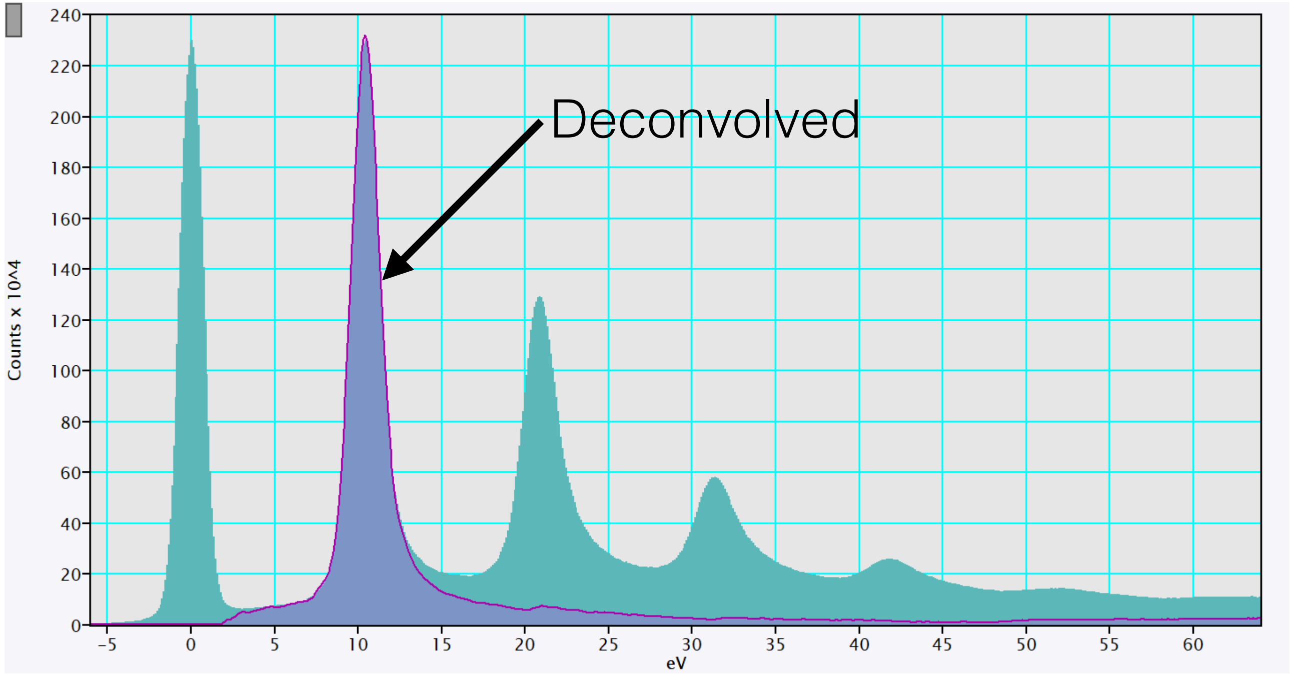




Multiple scattering: Mg sample

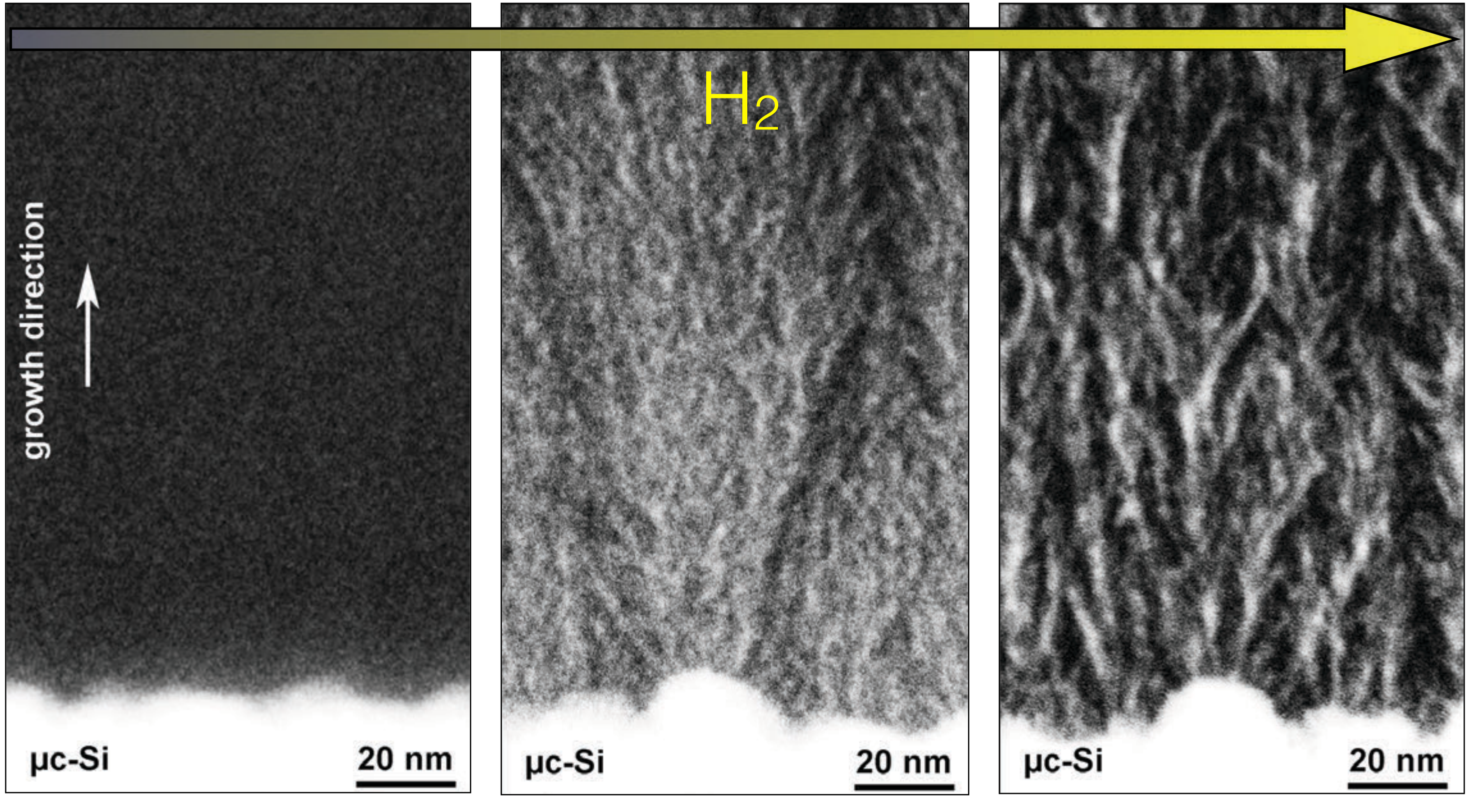
- Thick sample: $t / \lambda \approx 2.3$
- Well-defined plasmon peak (free electron gas)
- Multiple orders of plasmon peak excitation

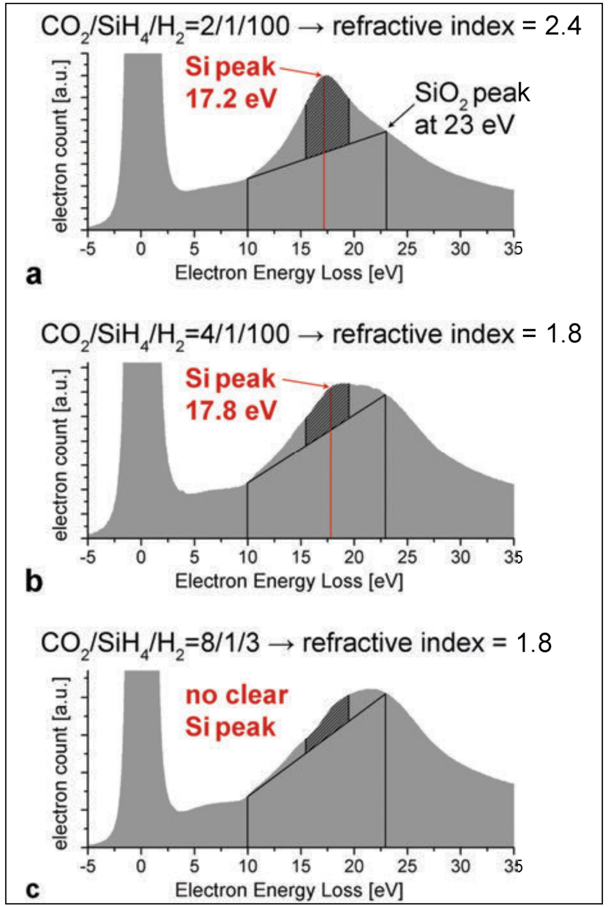




Ex. plasmon use: mapping elemental Si

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



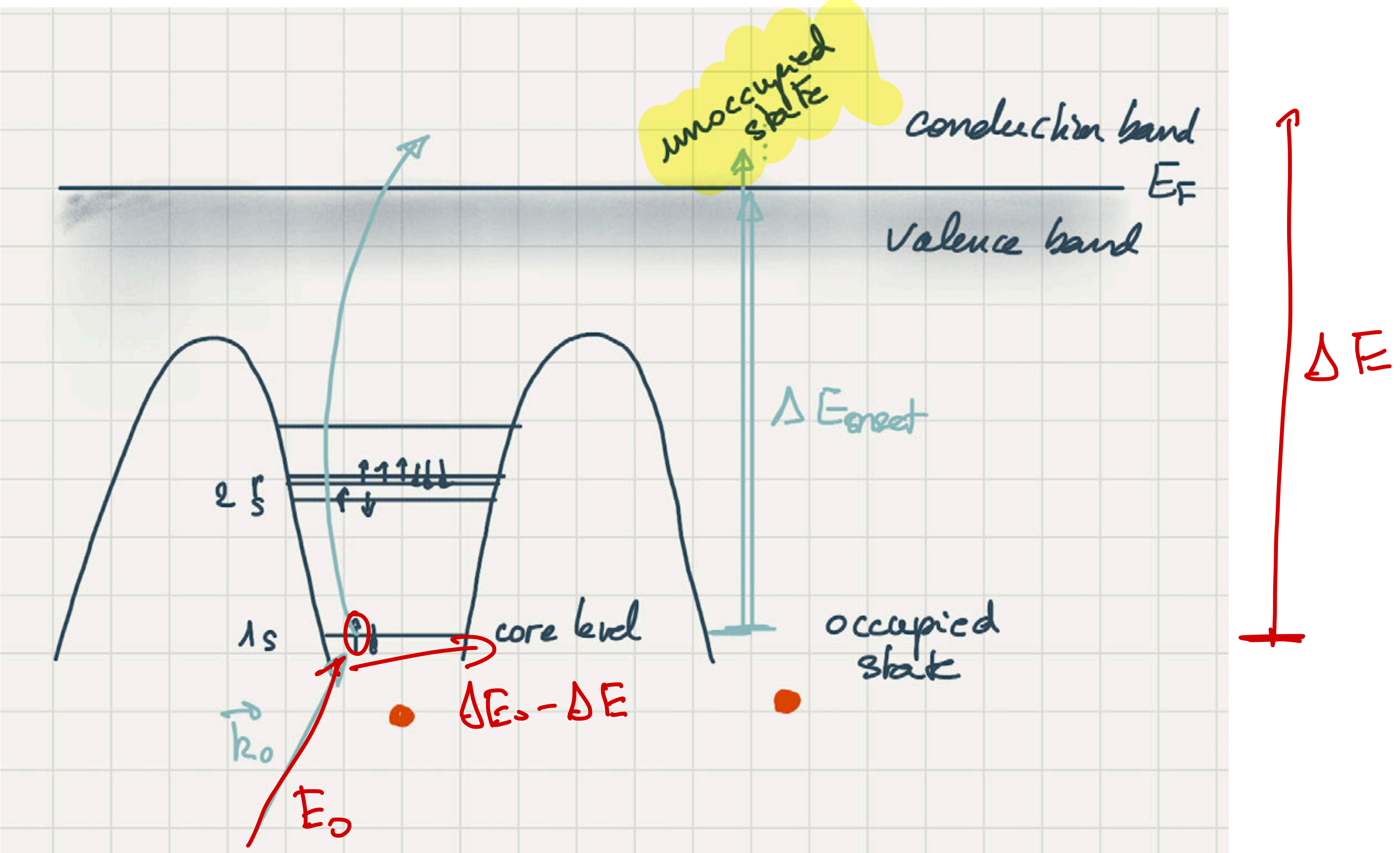


- Increasing H_2 plasma ⟹ increased phase separation

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

Contents

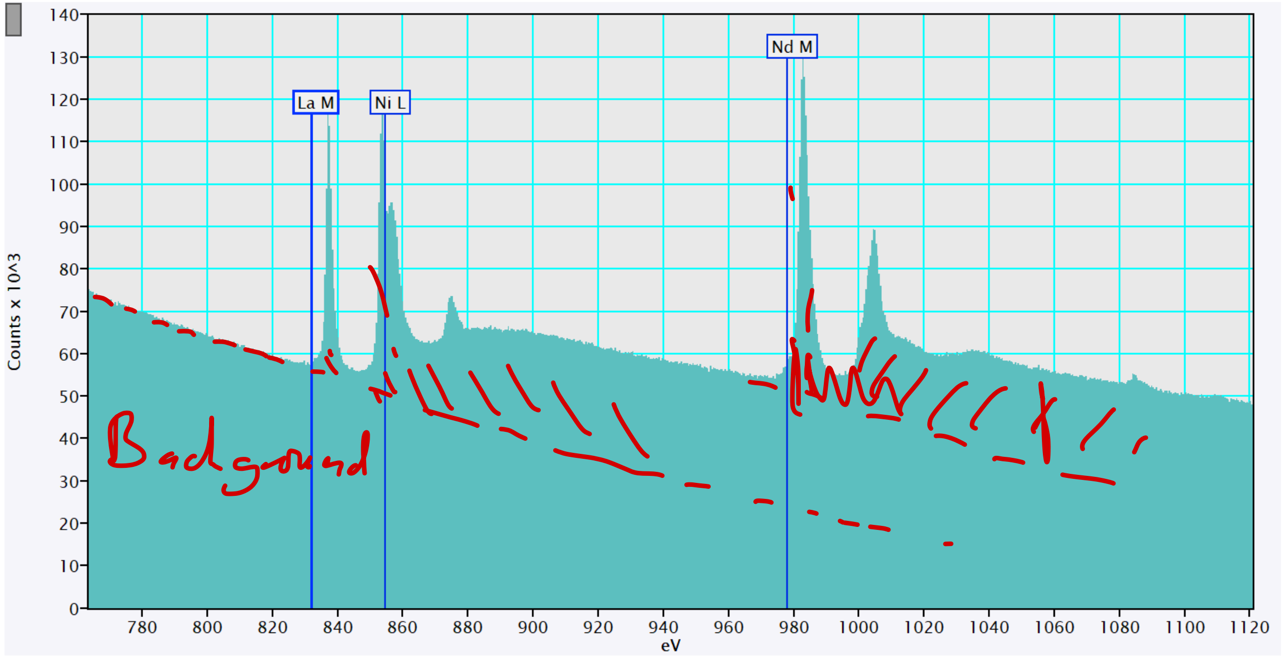
Ionisation edge / "core-loss" EELS



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 $\Delta\sigma$

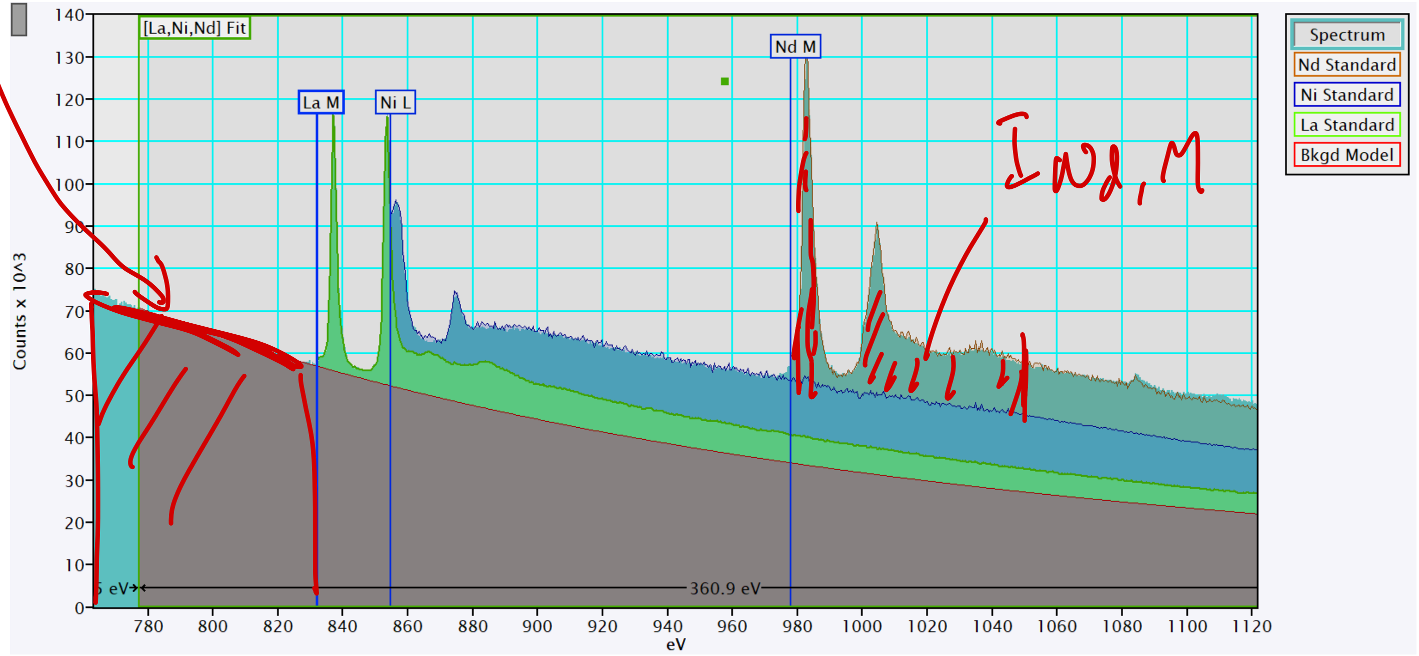
(La, Nd)NiO_3 alloy



Ionisation edge / "core-loss" analysis

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

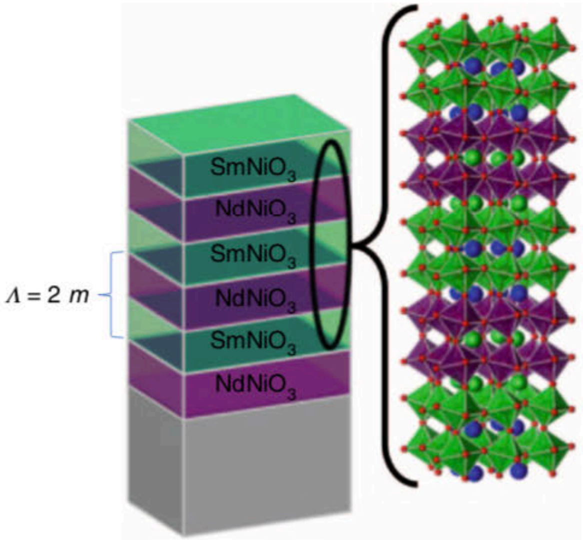
(La, Nd)NiO_3 alloy

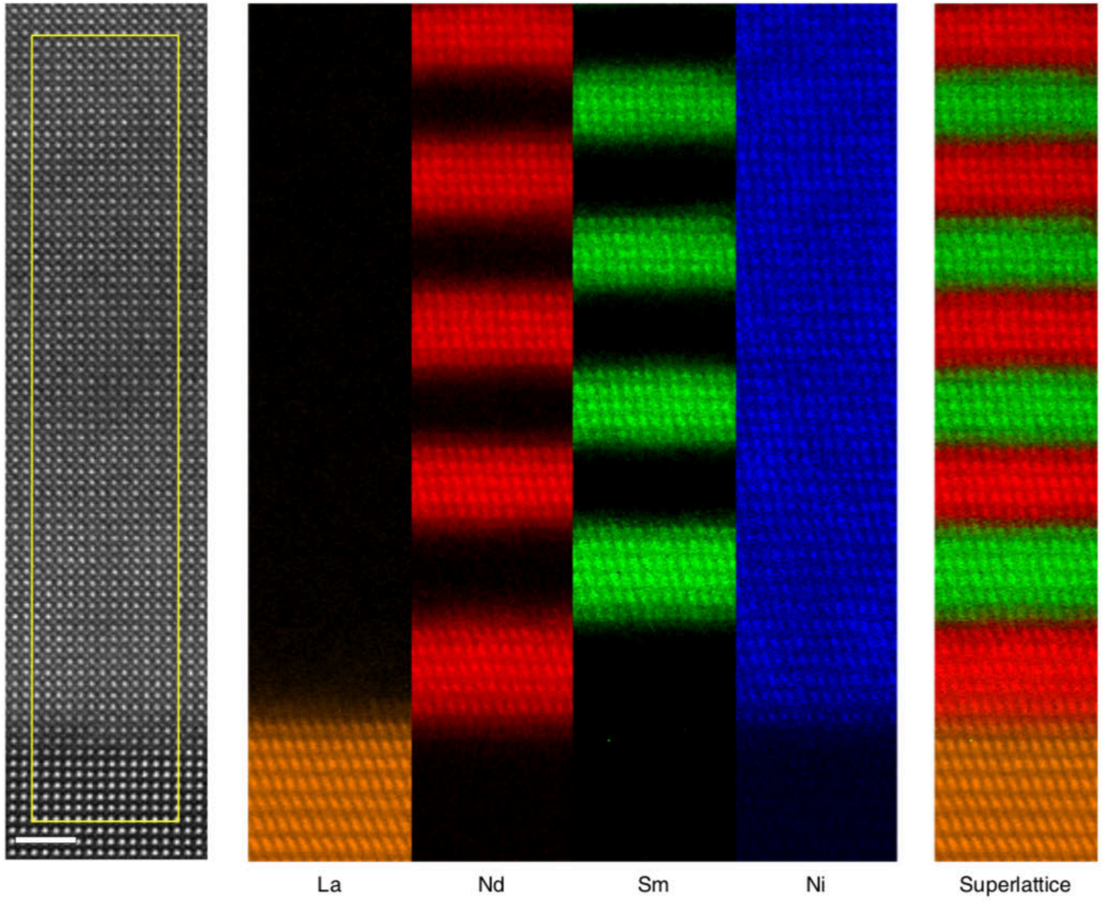


Elemental mapping – STEM-EELS

- 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 $LaAlO_3$

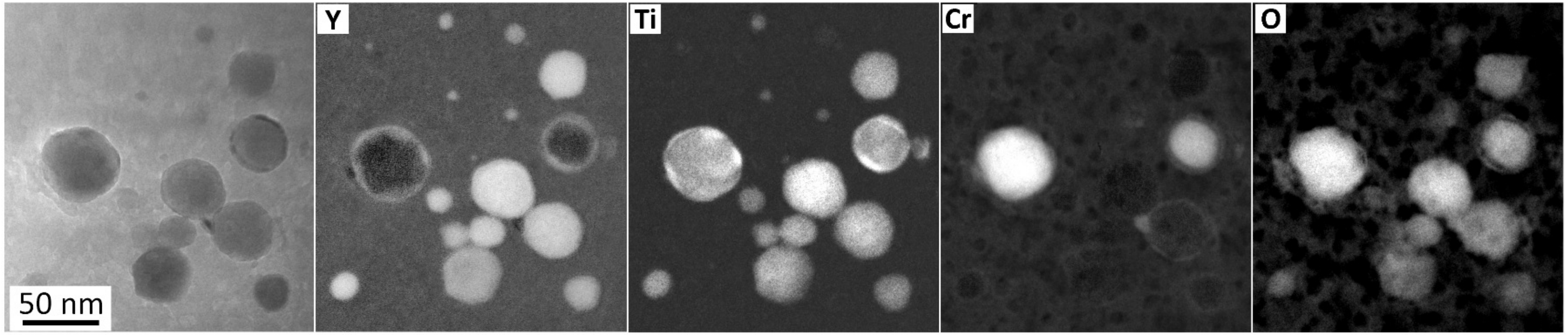




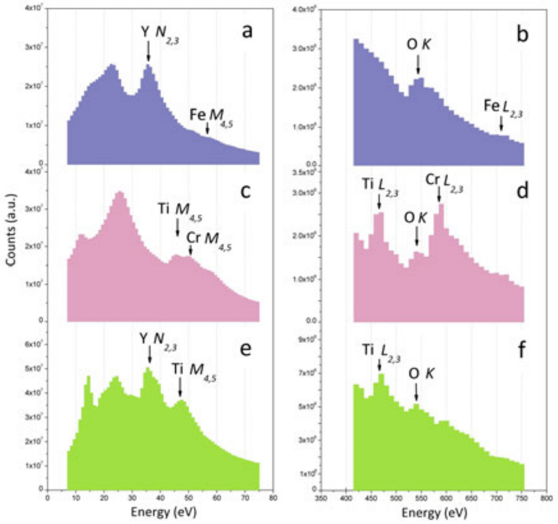
Dominguez et al. Nature Mater. **19** 1182 (2020)

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)

Partial scattering cross section

The partial cross section for ionization of shell n is

$$\Delta\sigma = \int_{E_n}^{E_n+\Delta E} \int_{\Delta\Omega} dE d\Omega \frac{\partial^2\sigma}{\partial E \partial\Omega}. \qquad (1)$$

$\Delta\sigma$ has dimension m^2/atom.

An incident beam *current density* j_0 causes, in a specimen with number of atoms N irradiated by the beam, within $\Delta E \Delta\Omega$ a probe current

$$I = N \Delta\sigma j_0. \qquad (2)$$

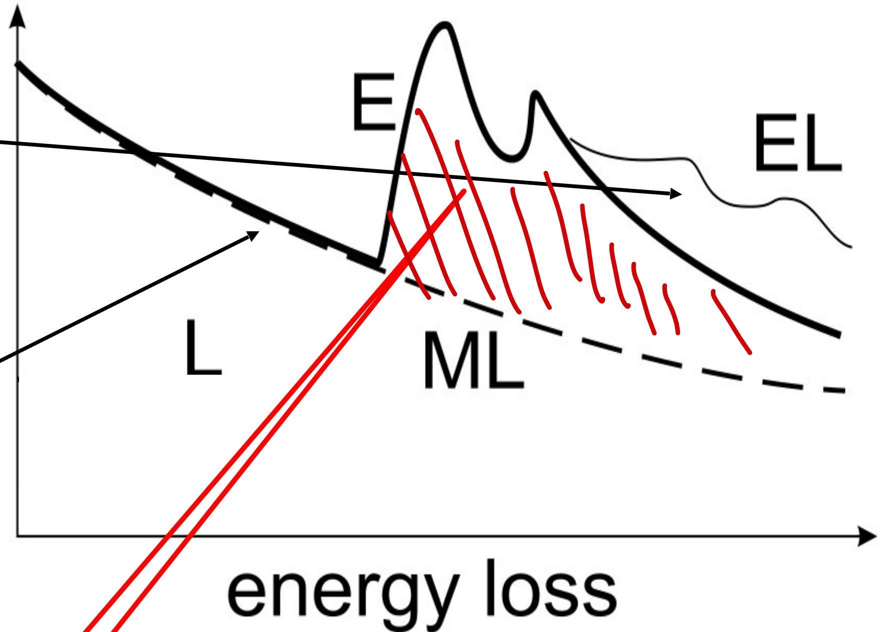
Here, we have ignored the background signal, as well as multiple scattering.

The number N of atoms irradiated by the probe is then

$$N = \frac{I}{j_0 \Delta\sigma}. \qquad (3)$$

Ionisation edge / "core-loss" analysis

Multiple scattering:
Fourier-ratio deconvolution



High energy tail of lower energy losses: background removal

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

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

Elemental quantification

- Number of atoms per unit area N given by: $$N = \frac{I}{j_0 \Delta\sigma}$$
- Elemental percentages calculated using: $$\frac{N_a}{N_b} = \frac{I_a}{I_b}\frac{\Delta\sigma_b}{\Delta\sigma_a}$$

Accuracy
~10-20%

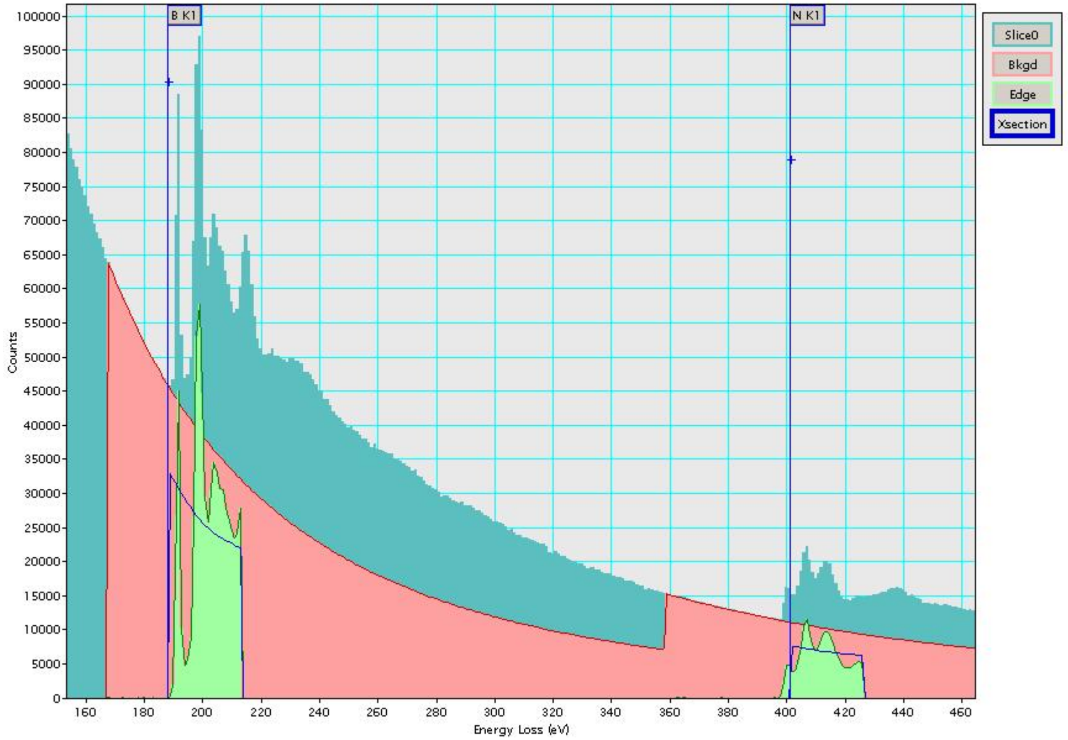
- For good quantification, need knowledge and correct choice of convergence semi-angle α and EEL spectrometer collection semi-angle β
- Fit background with power-law model: $I_B = AE^{-r}$

EPFL

Elemental quantification

- Example: BN measured in TEM mode at 200 keV:
- B K-edge at 188 eV
- N K-edge at 401 eV
- TEM mode: $\alpha \approx 0$ mrad; $\beta = 100$ mrad
- Quantification: 47 at.% B / 53 at.% N

Needed for $\Delta\sigma$



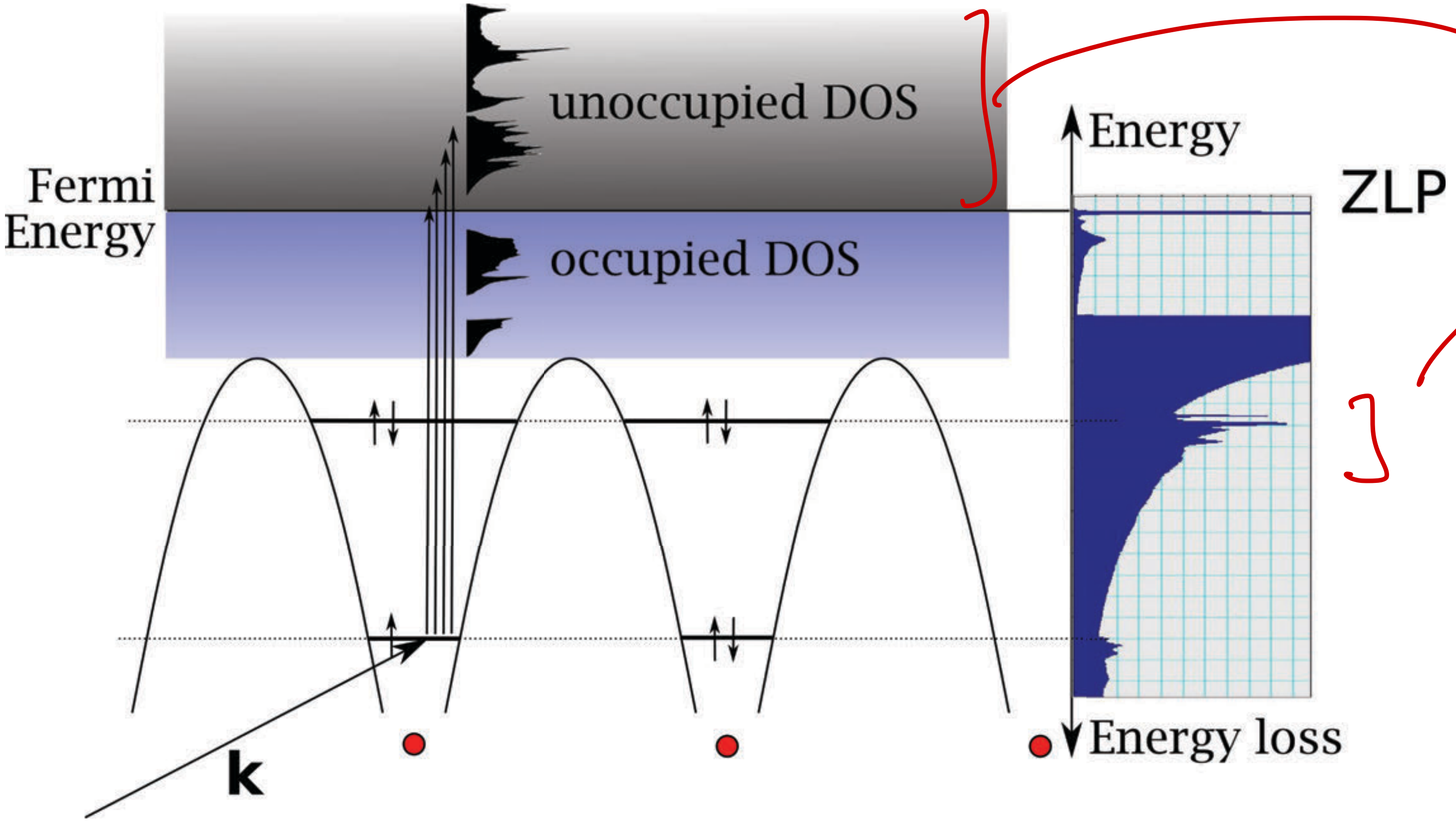
Note: Consider characteristic angle of scattering: $\theta_E \sim \dfrac{E}{2E_0}$

For light elements: EELS usually more accurate than EDXS

Contents

EPFL Energy-loss near edge structure (ELNES)

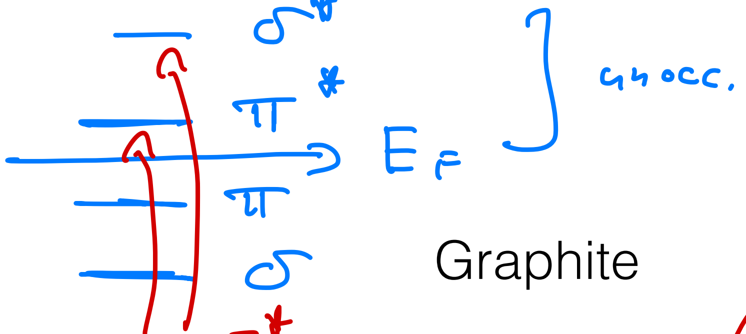
- Ionisation edge onsets show peaks related to unoccupied density of states (DOS)
- Also called “fine structure”



EEL spectrum has features that "reflect" unocc. DOS

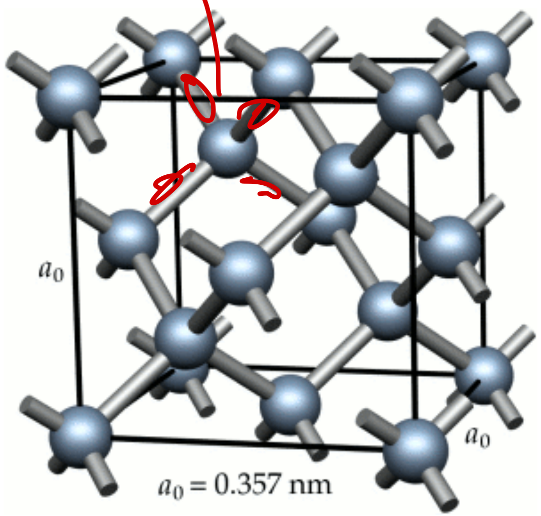
Core-loss fine structure (ELNES)

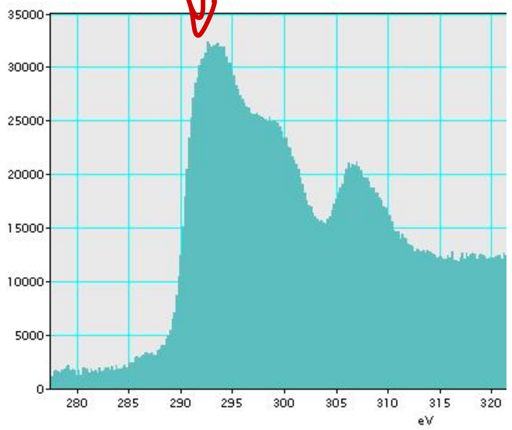
- Example: carbon *K*-edge

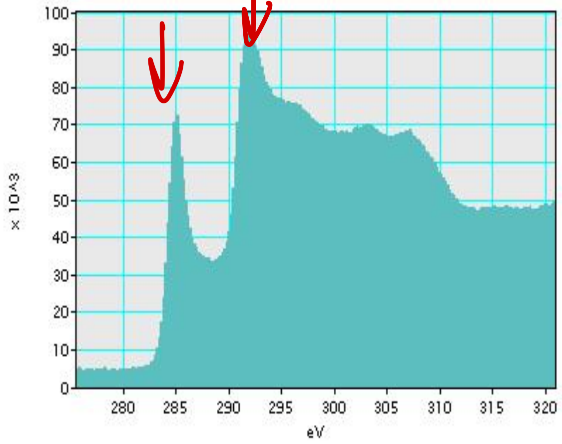


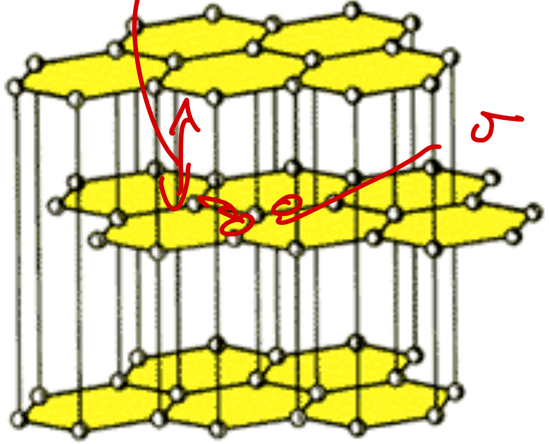
Diamond

Graphite





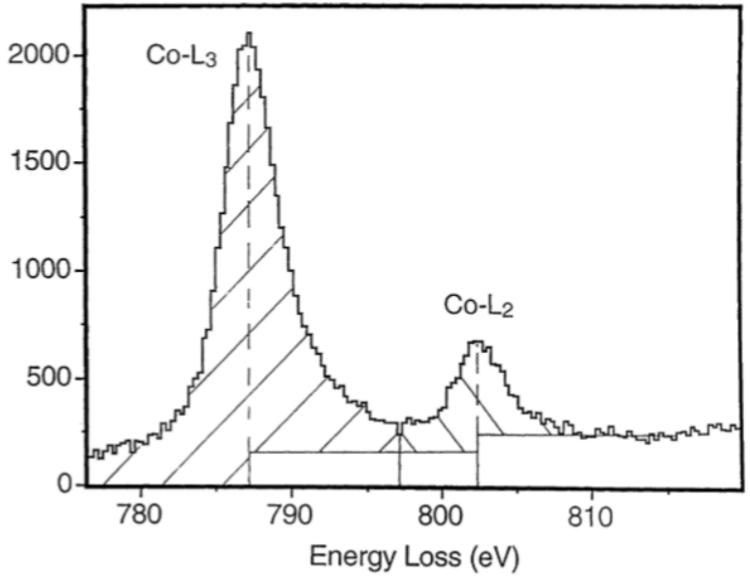


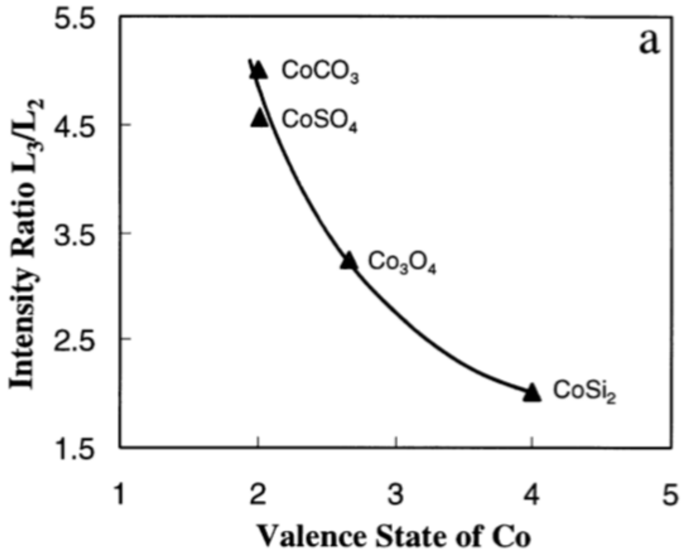


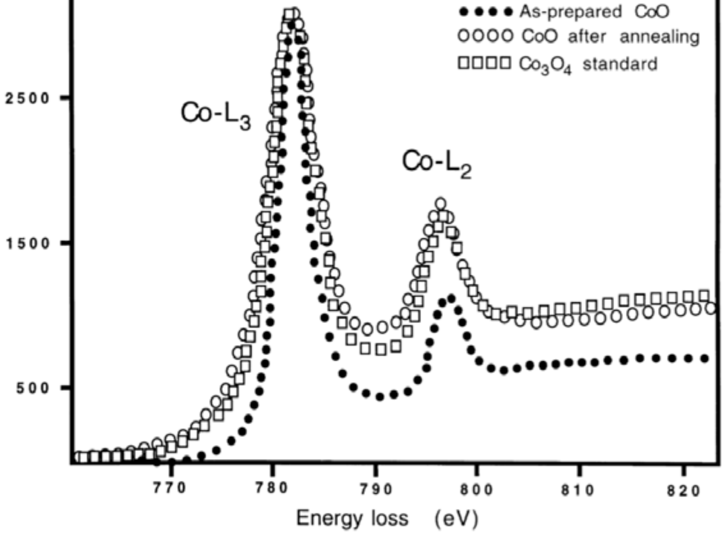
[Simulate edge structure from full electronic structure]

ELNES "White line" analysis

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





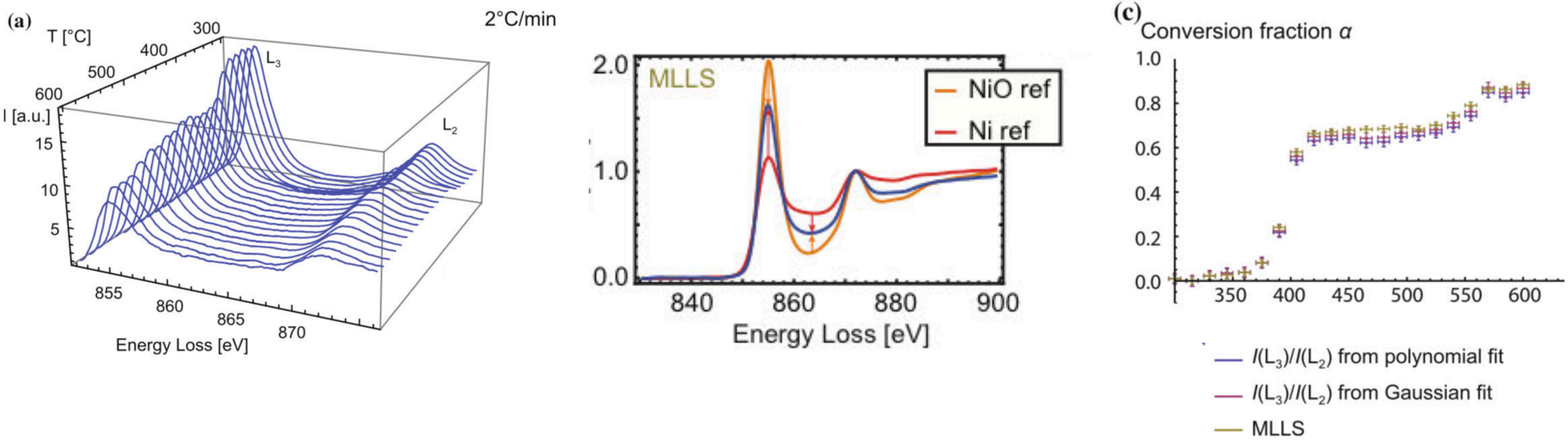


Wang et al. Micron **31** 571 (2000)

Local analysis of oxidation state

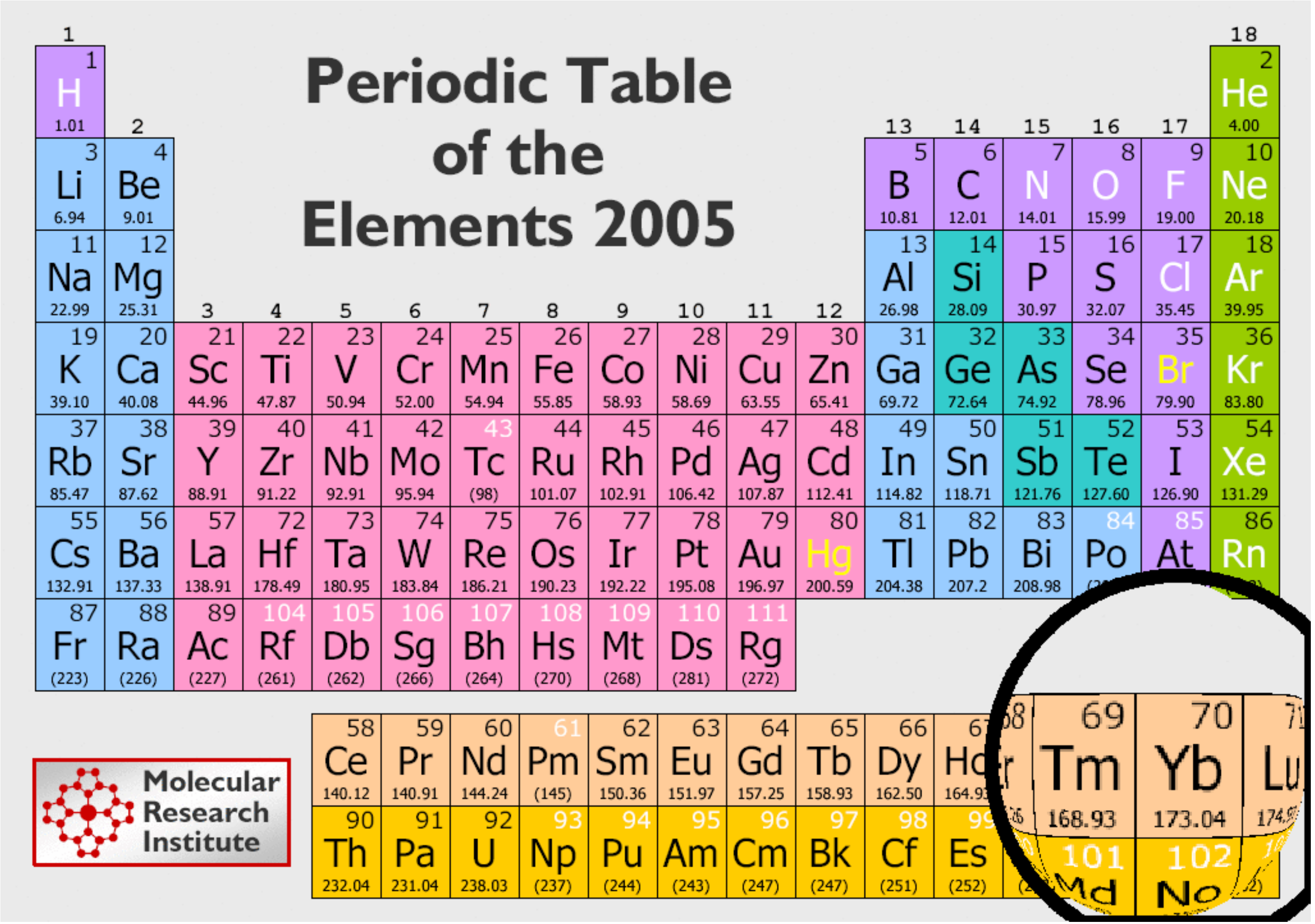
ELNES “White line” analysis

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



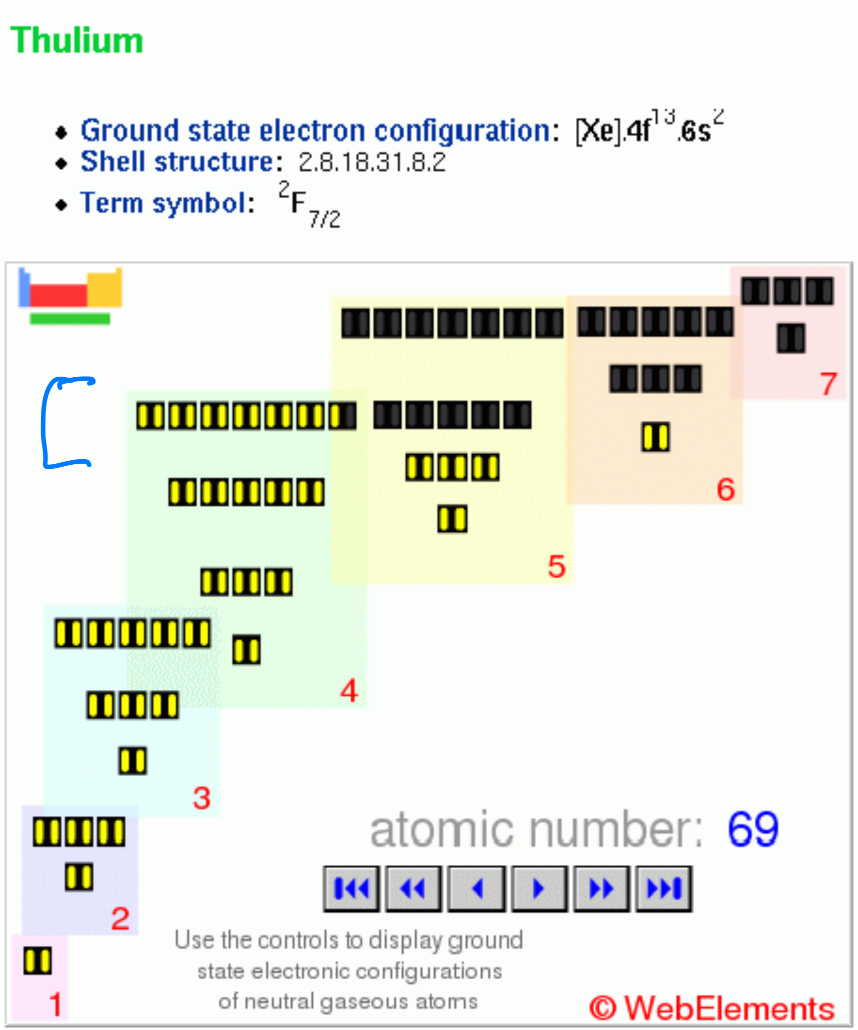
Jeangros et al. J. Mater. Sci. **48** 2893 (2013)

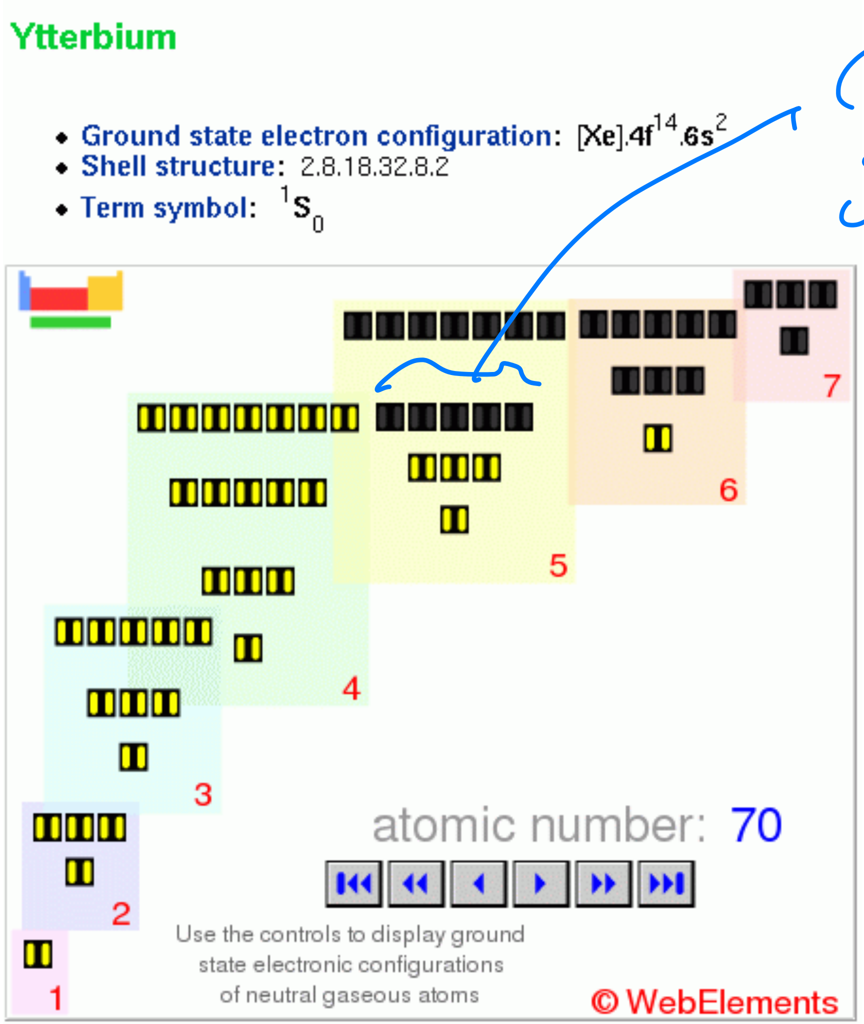
ELNES fine structure



ELNES fine structure

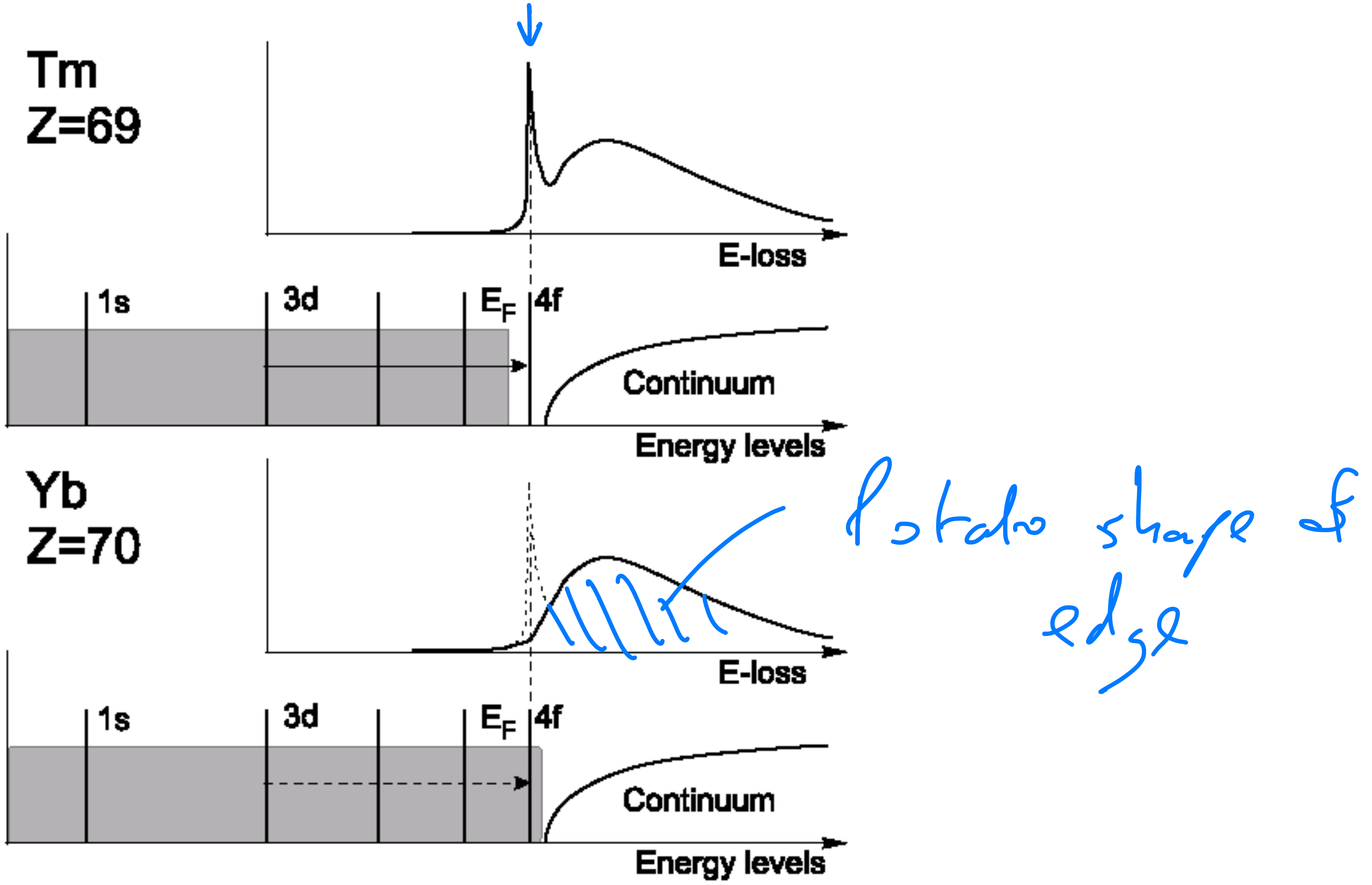
4f





Continuum of unocc. DOS

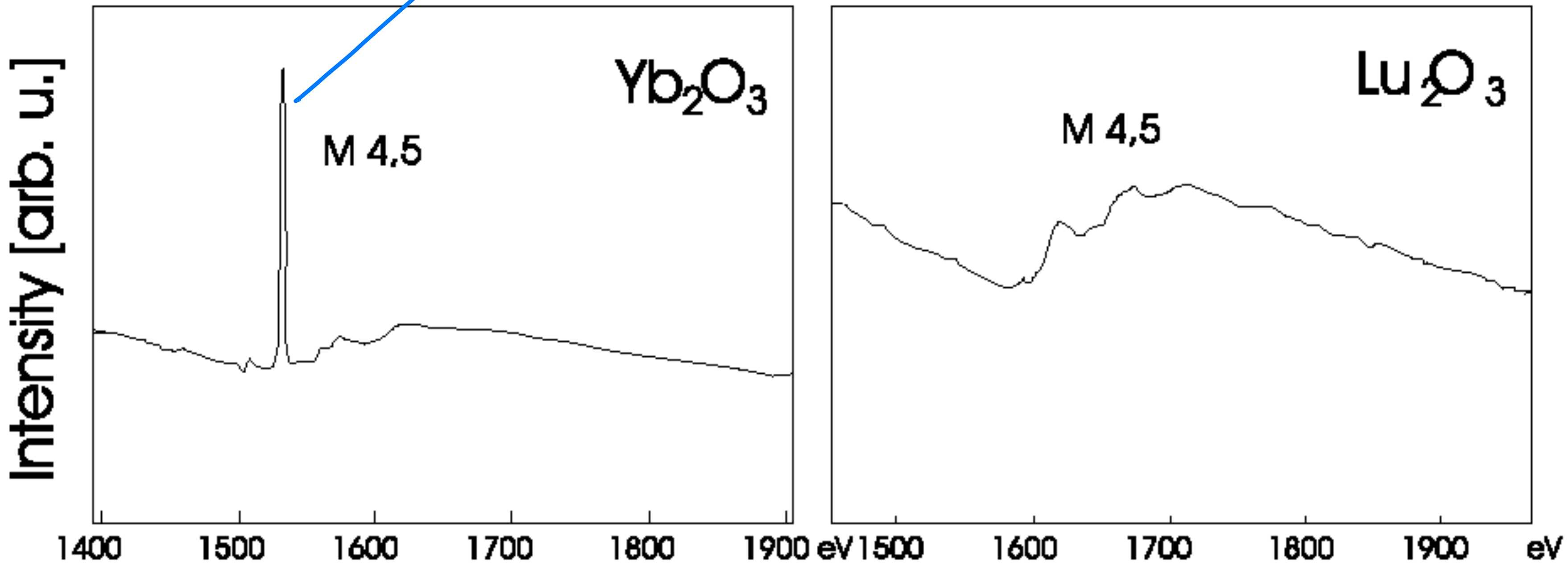
ELNES fine structure



For Yb (Z=70) and higher atomic number, the f-shell is completely filled, and white lines cannot occur.

ELNES fine structure

Given e^- to oxygen ⇒ created [illegible] w. DOS



M_{45} edges of Yb and Lu in their oxides, showing the disappearance of white line when the f-subshell is filled.