Electron Energy-Loss Spectroscopy (EELS) – Basics

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EPFL-IPHYS-LSME

EELS basics: contents

- Ionisation energy loss
- Electron energy-loss spectrometer
- Features of the EEL spectrum
- Ionisation edge Core-loss analysis
  - Elemental detection and mapping
  - Elemental quantification
  - ELNES
- Low-loss EELS
  - Bulk plasmon
  - Multiple scattering, thickness measurement and deconvolution
- EELS spatial resolution
- References

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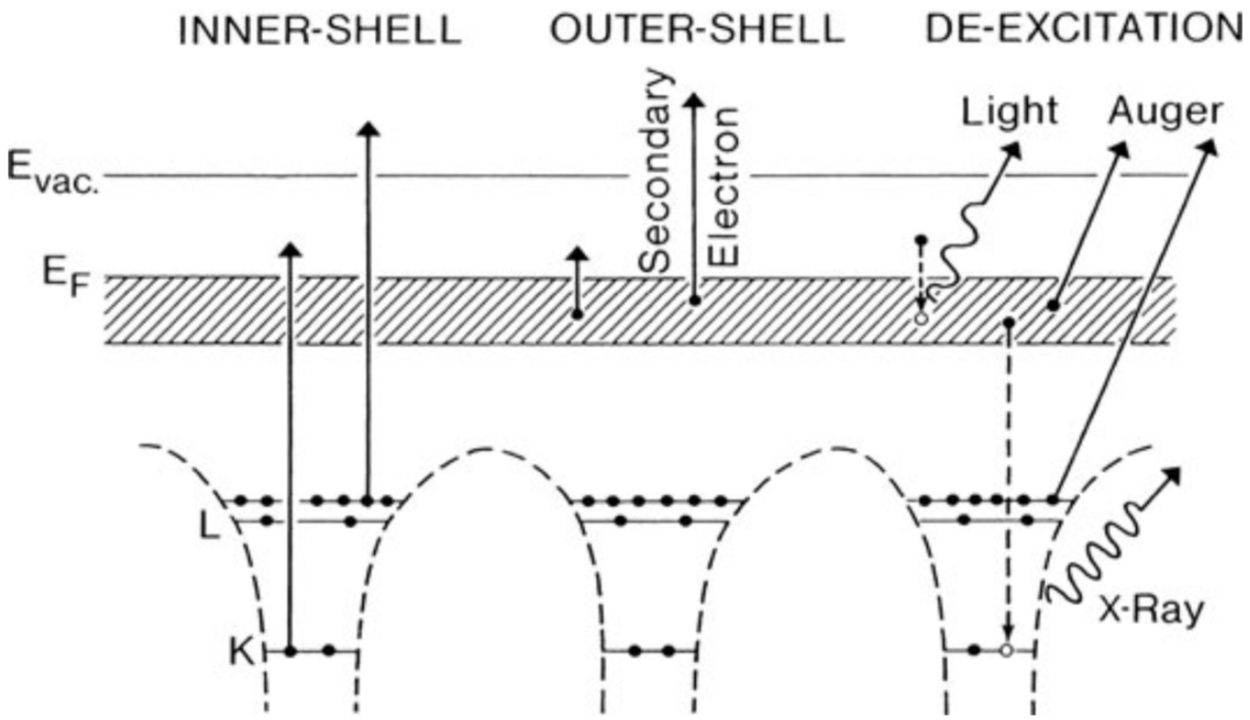
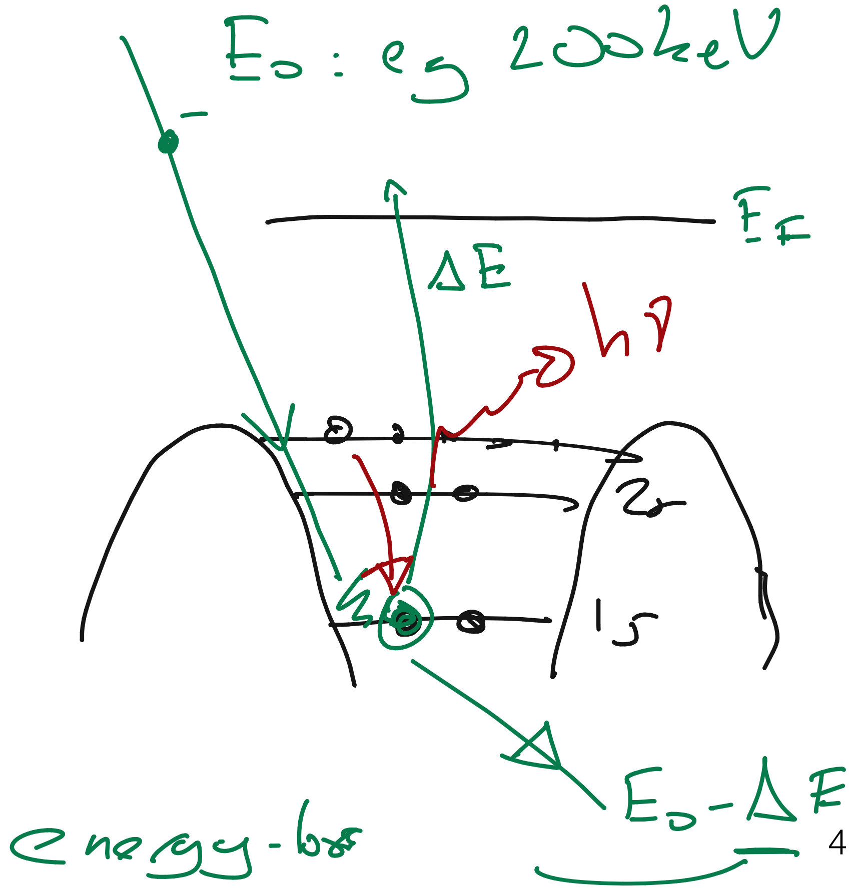
Ionisation energy loss

- Atomic ionisation leading to X-ray emission ⟺ energy loss of transmitted e⁻

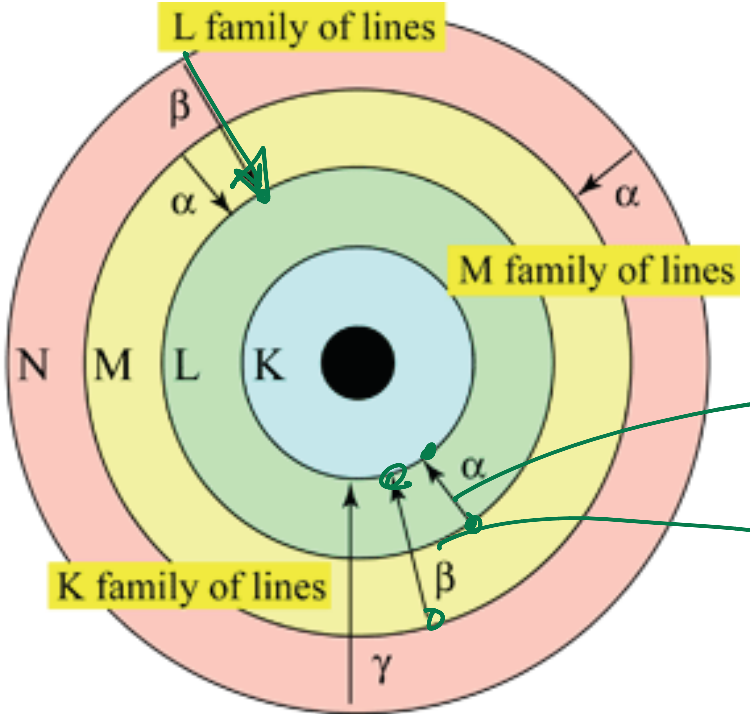




Ionisation edge naming

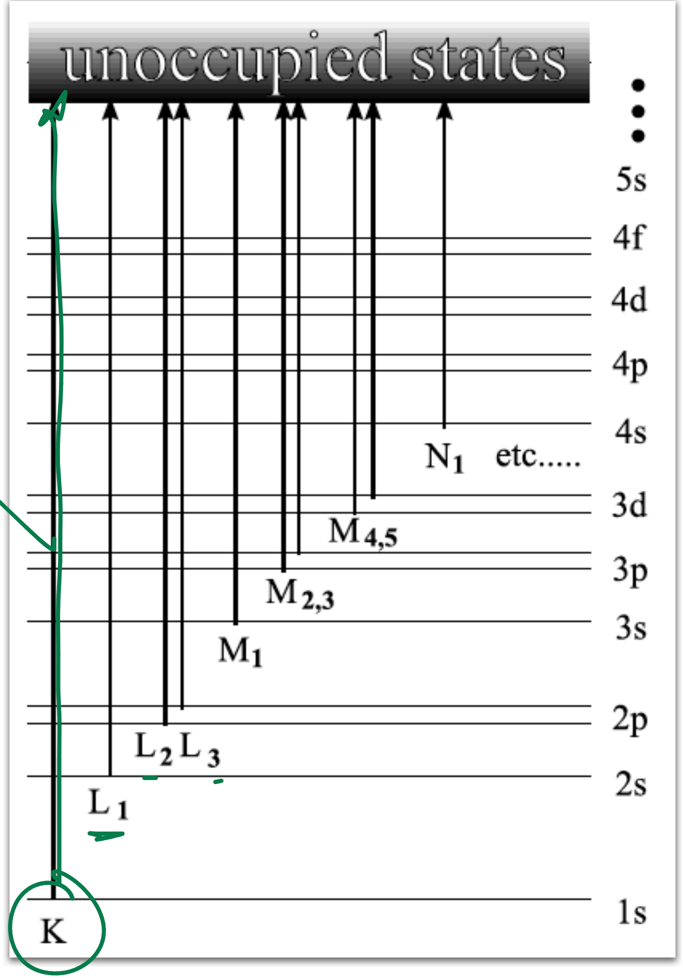
ΔE K > L
L1 > L2 > L3

EDXS



energy of Kβ > Kα ...
- Peaks

EELS



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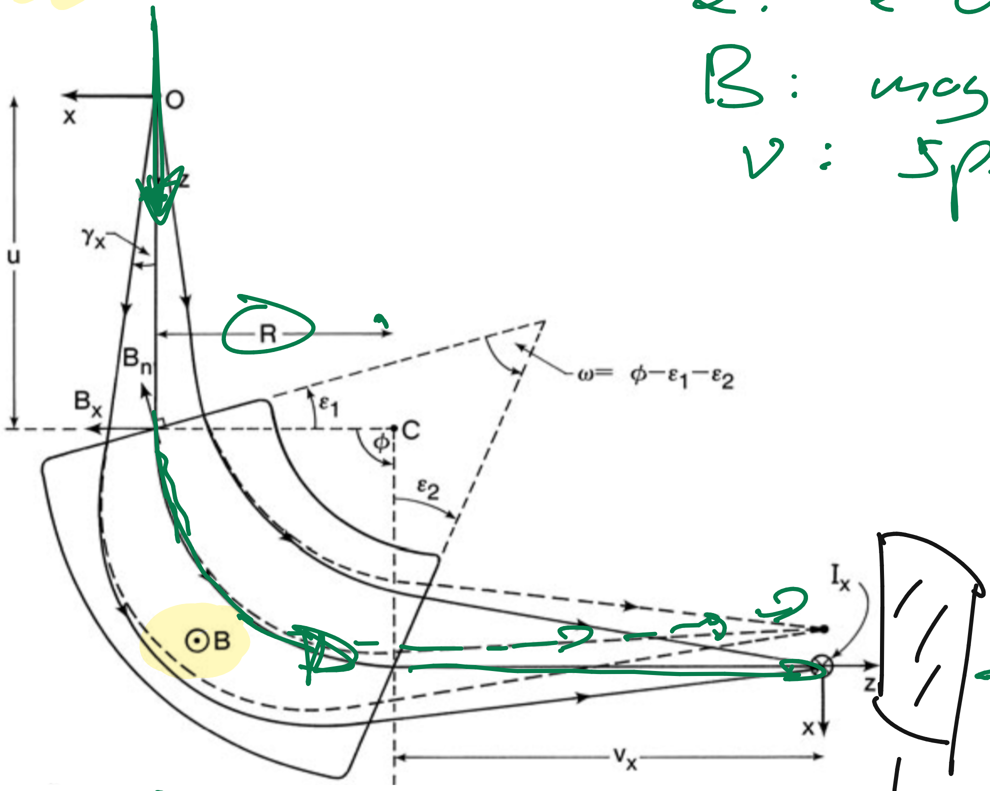
Electron energy-loss spectrometer

- Typical EEL spectrometer: magnetic prism

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

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

Relativistic factor



m_0: rest mass of e^-
e: e^- charge
B: mag. field
v: speed of e^-

Detector
ΔE
E_0

Lorentz force: $\vec{F} = e.\vec{v} \times \vec{B}$

Post-column spectrometer

- Post-column spectrometer most common type used for materials science/physics
- For instance: Gatan Image Filter (GIF)

STEM-EELS

ADF in STEM

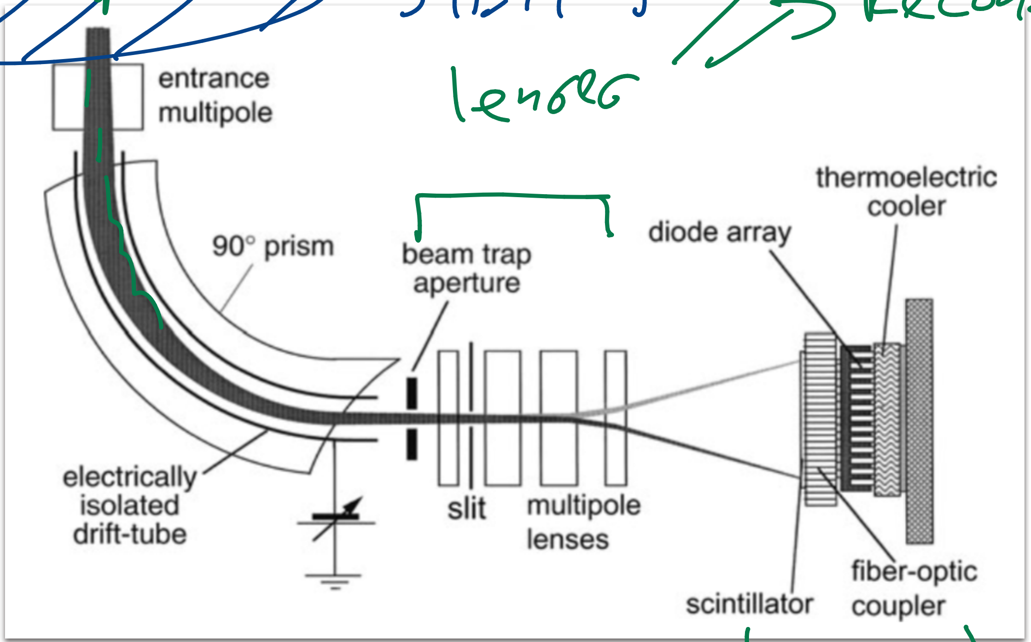
correct aberrations in spectrum

Reconstruct TEM image (energy-filtered TEM)

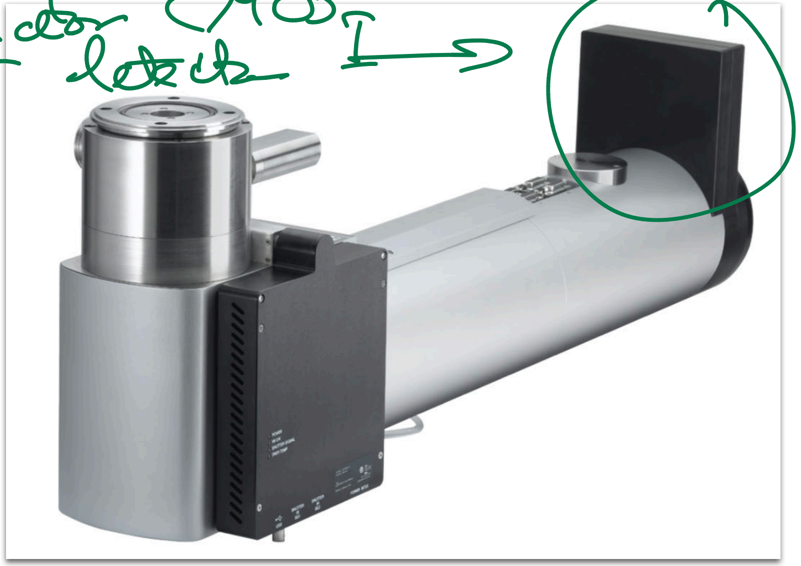
lenses

Scintillator CMOS

Direct e⁻ detector



CCD



Inelastic scattering angular range

Lorentz dist^n of inelastic scattering

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

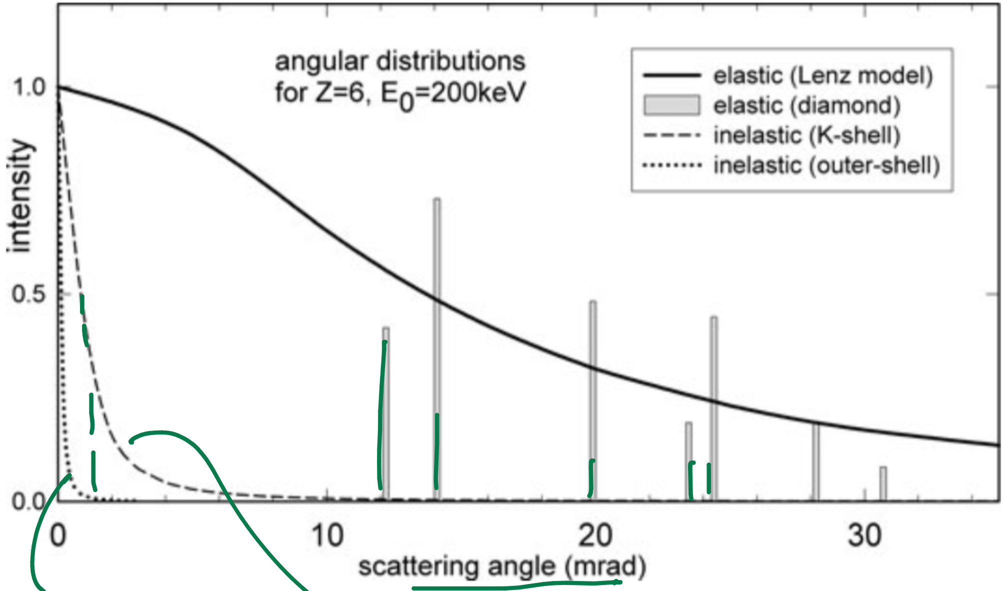
Rule of thumb

For carbon

ΔE : 800eV

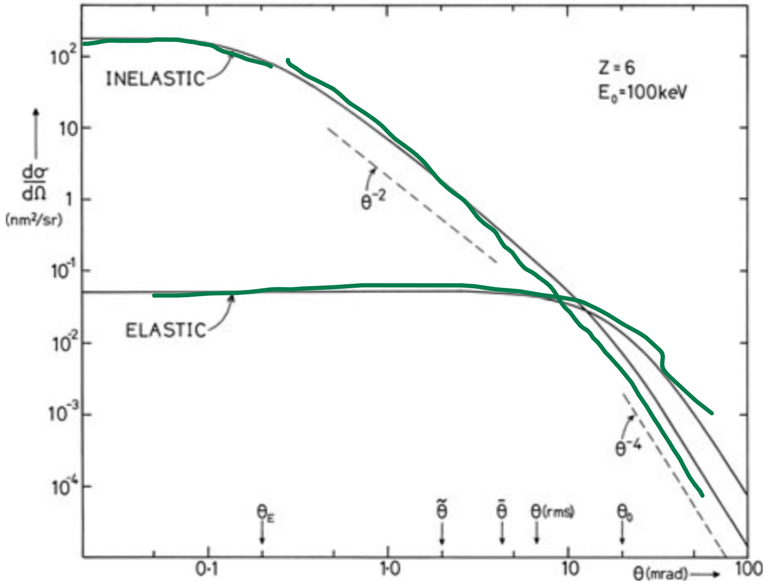
E₀ : 200 keV

θE ~ 2 mrad



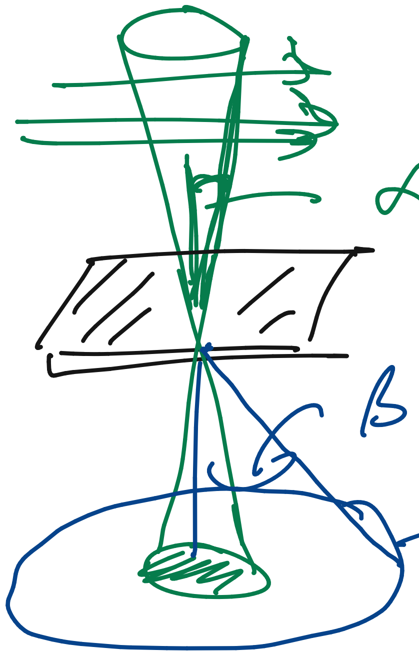
ΔE: 30eV

ΔE: 300eV



EPFL STEM-EELS spectrum imaging

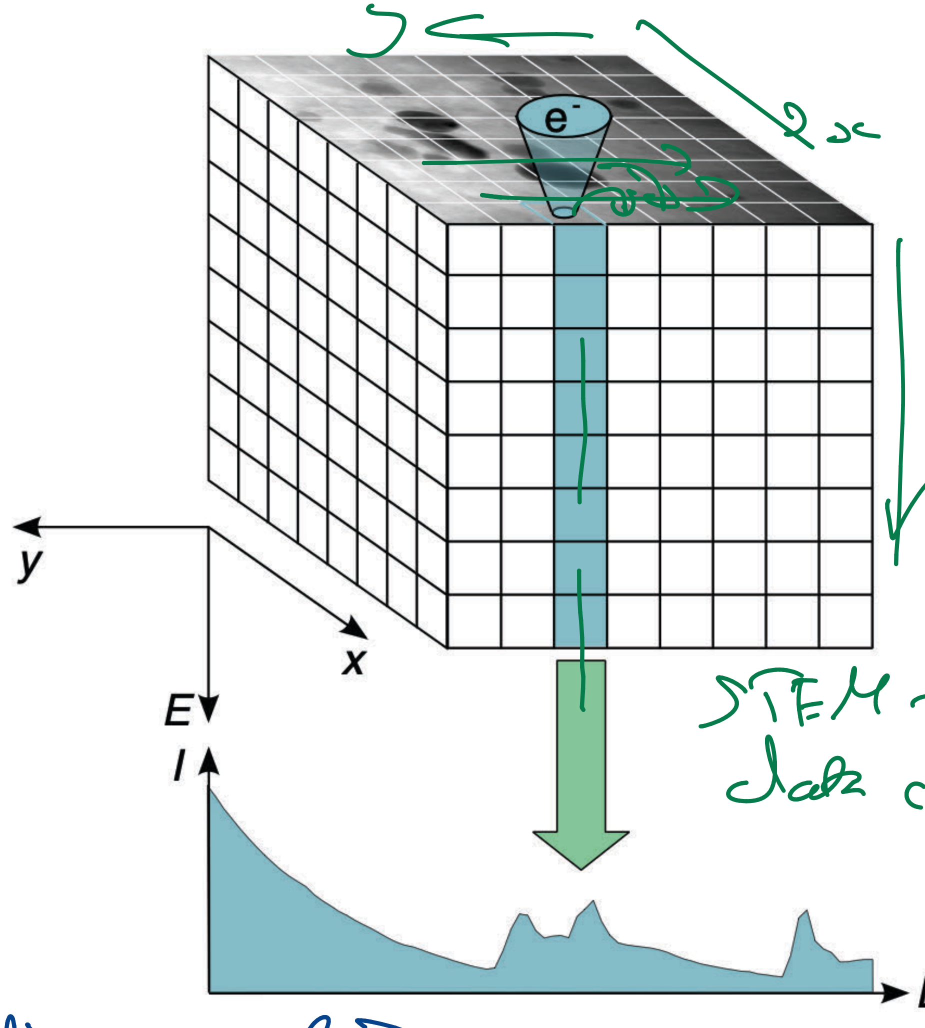
- During STEM imaging, collect the *forward-scattered* electrons in the spectrometer entrance aperture
- Record 3D data cube with a spectrum for each probe position (*x*, *y*)



α : semi-angle of convergence

β: semi-angle of collection

Entrance aperture for EELS



Ionization : $\beta > \alpha$

Quant. EELS : $\beta \gtrsim 2\alpha$

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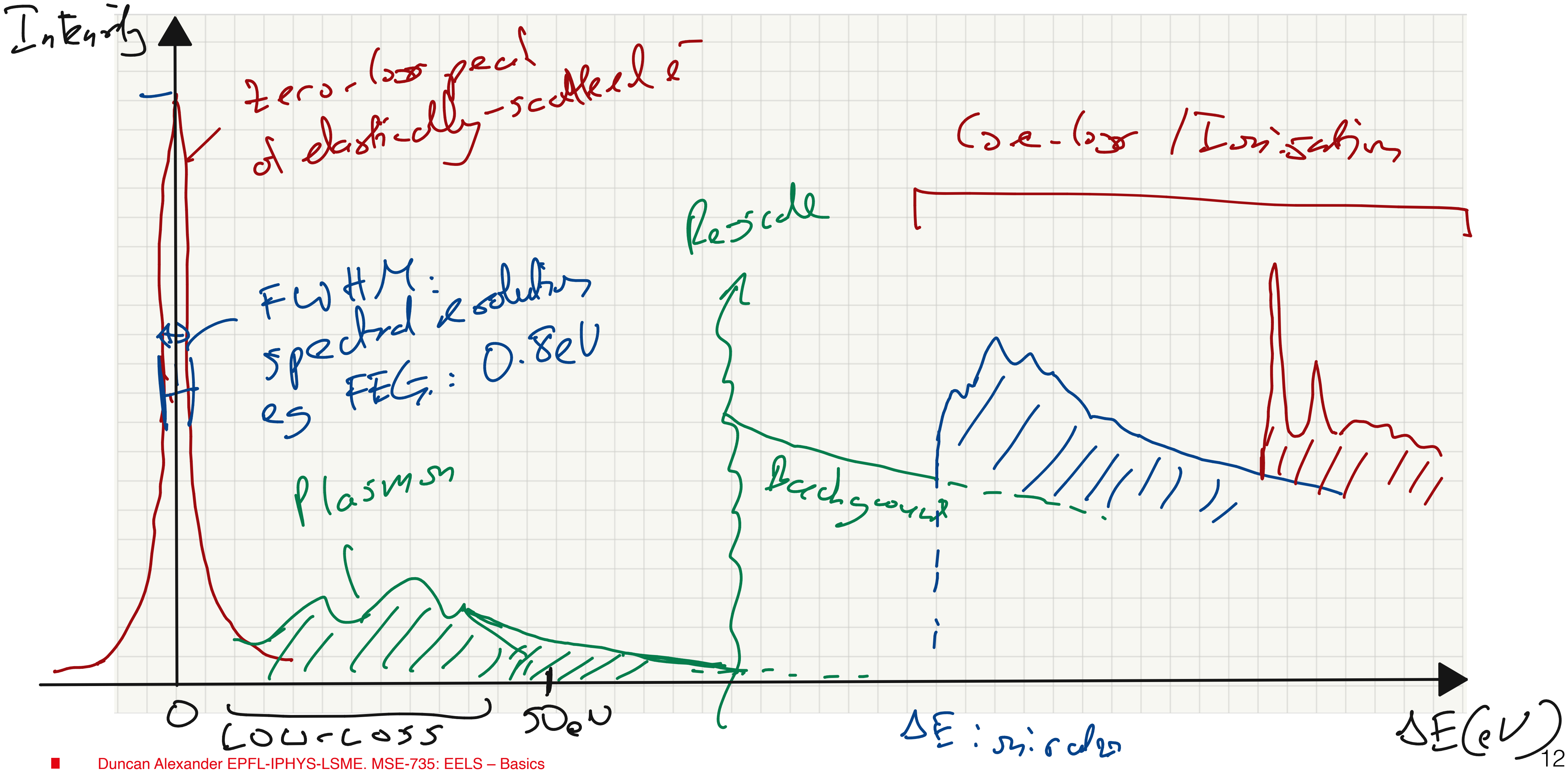
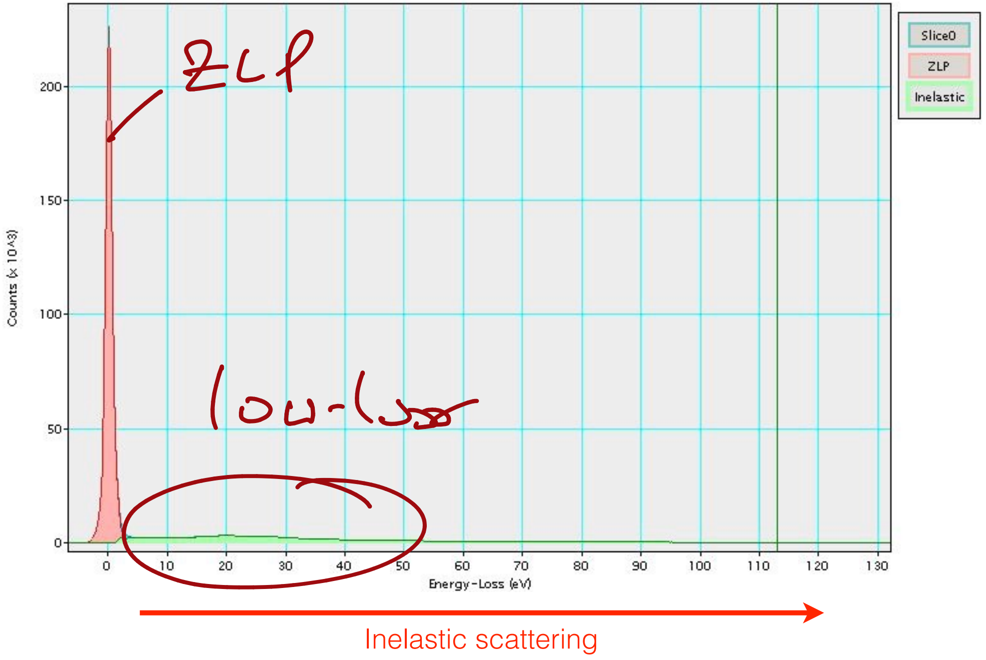
Features of the EEL spectrum



Features of the EEL spectrum

- Energy loss > 0 ⟹ *Inelastic scattering*



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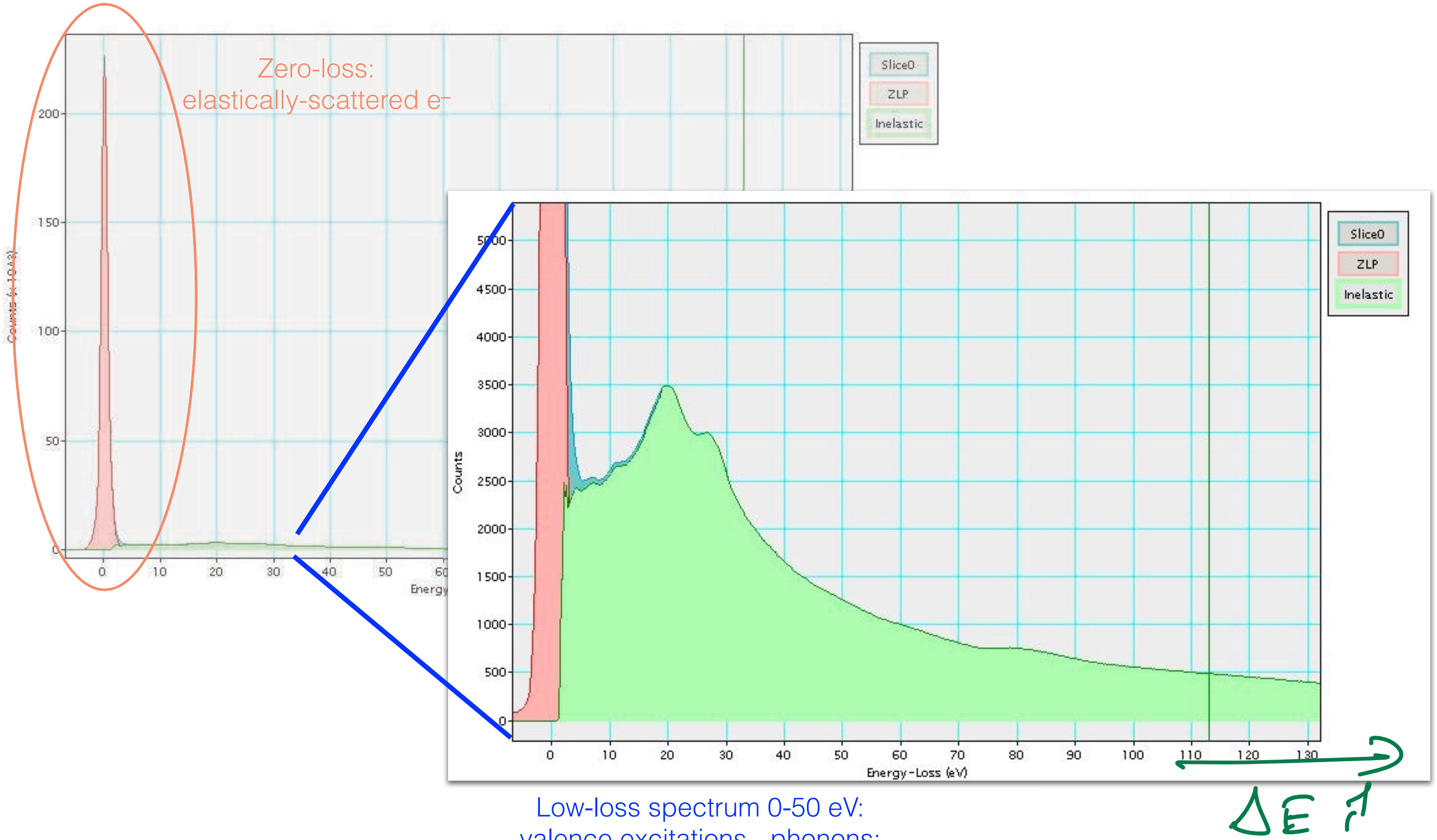
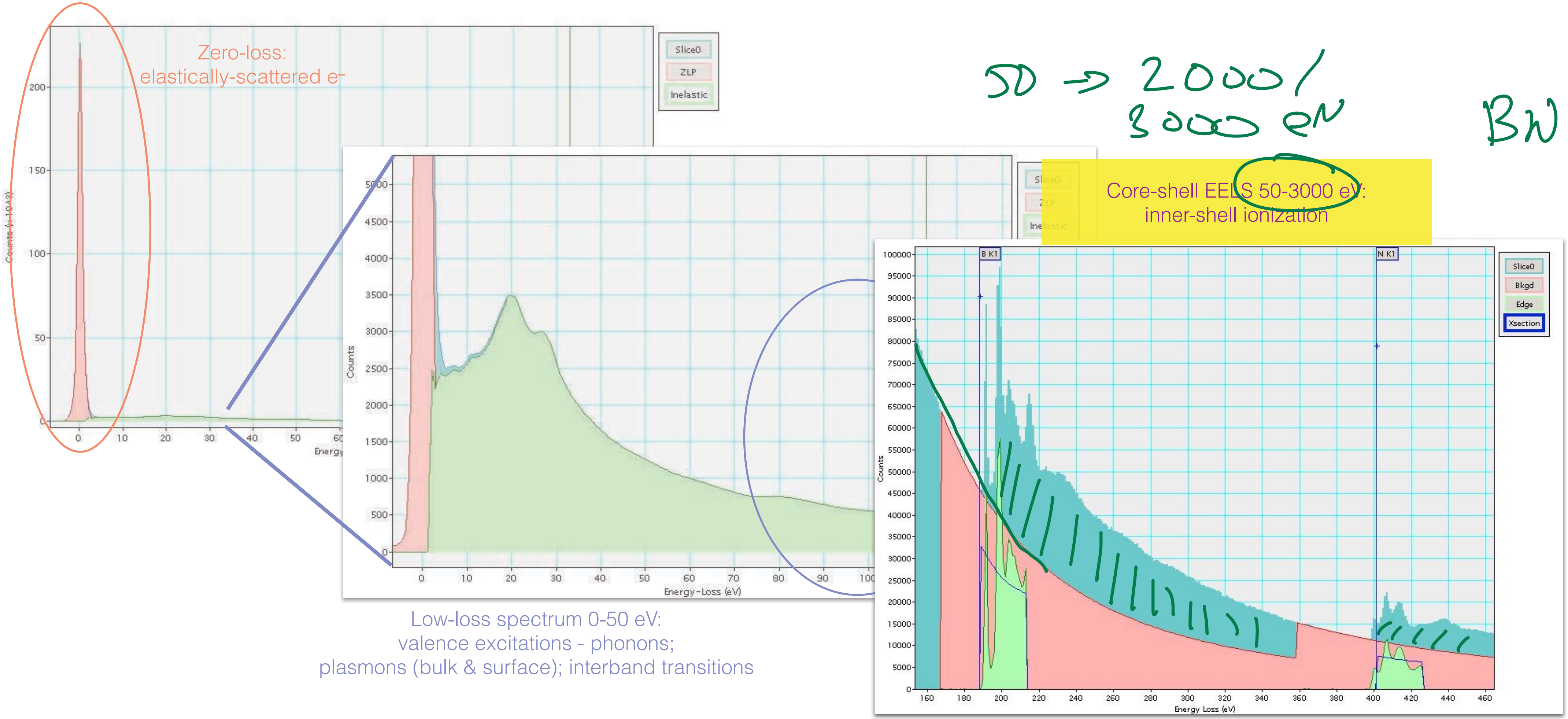


Low-loss spectrum 0-50 eV:
valence excitations - phonons;
plasmons (bulk & surface); interband transitions

Features of the EEL spectrum

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



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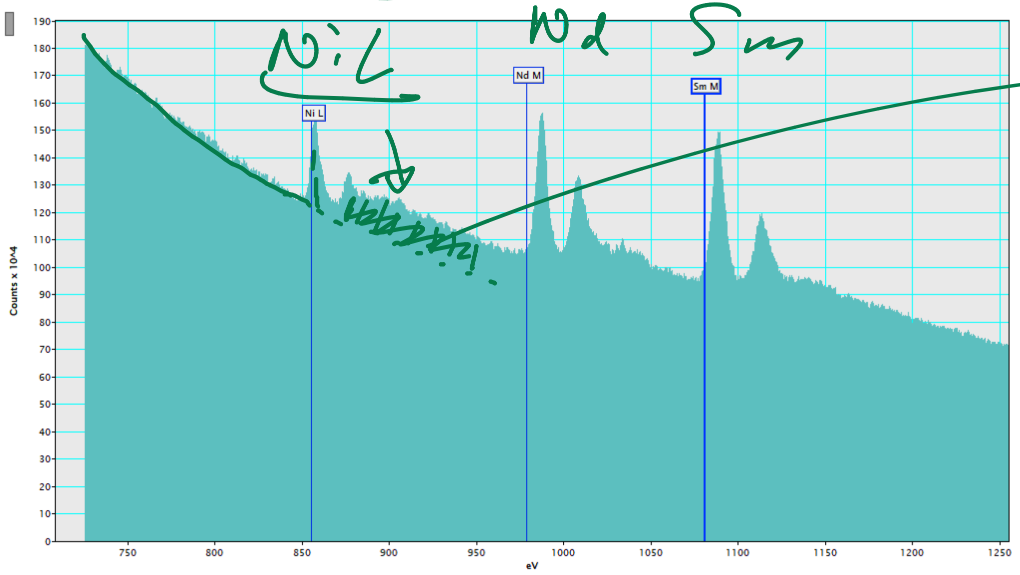
Ionisation edge / “core-loss” analysis

- 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 Δσ

(Nd, Sm)NiO_3 spectrum:



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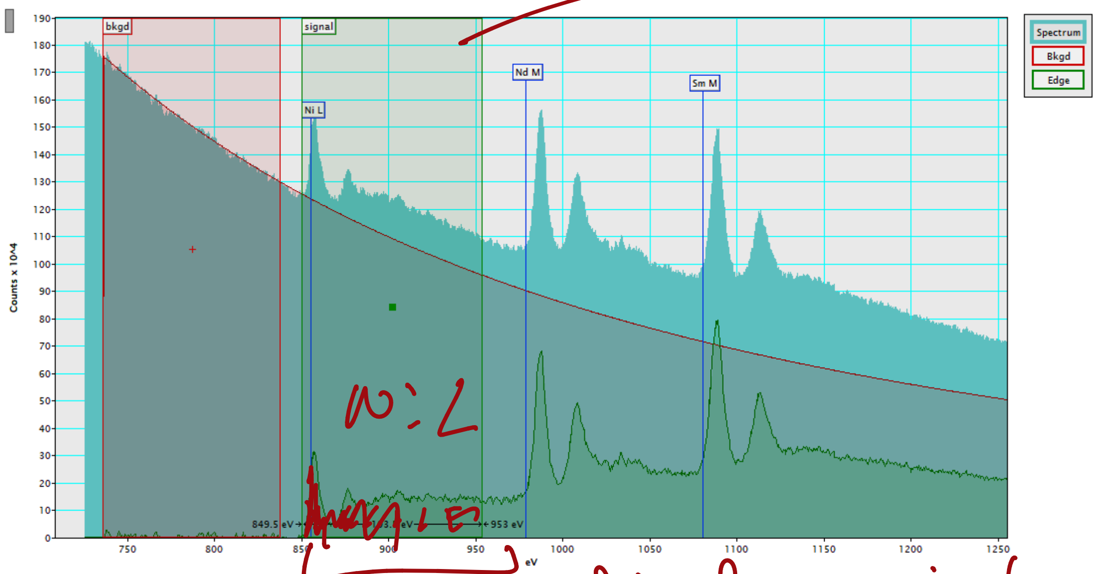
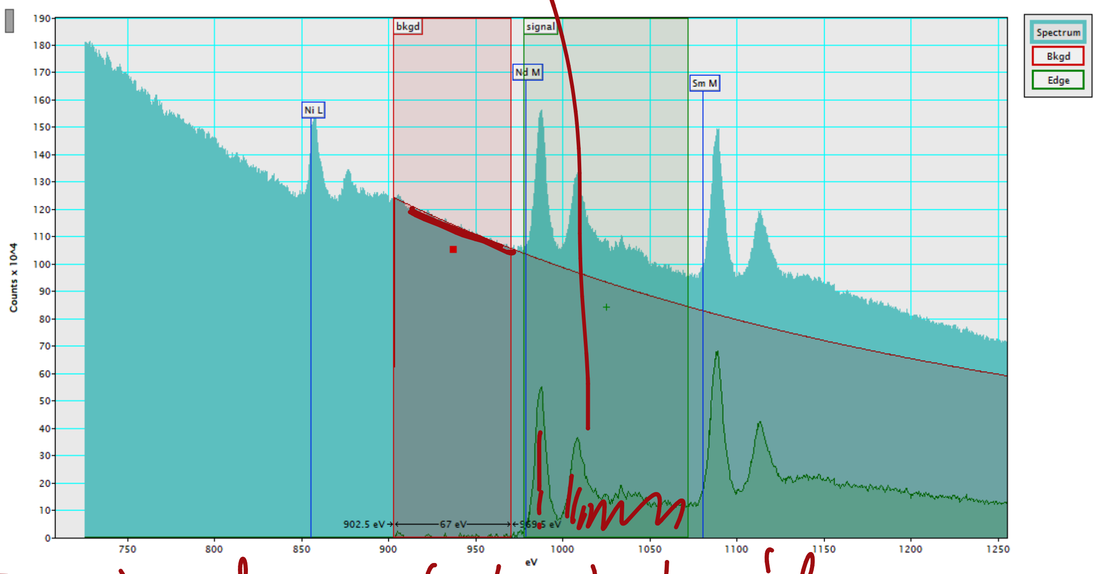


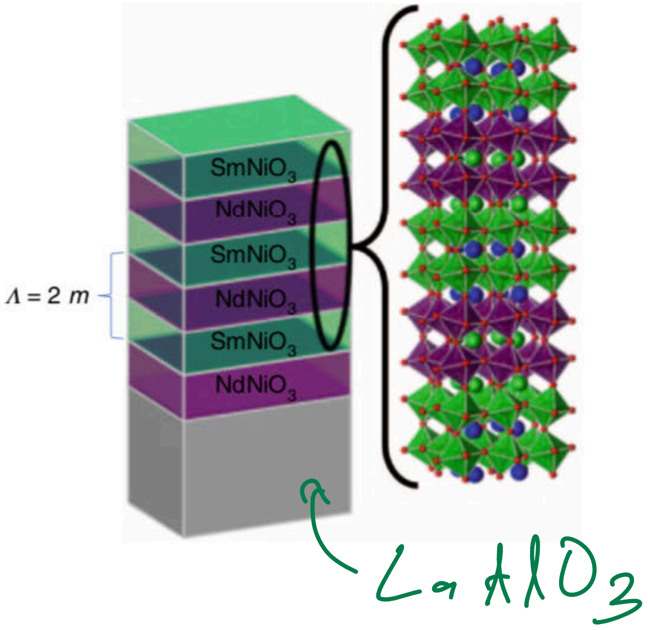


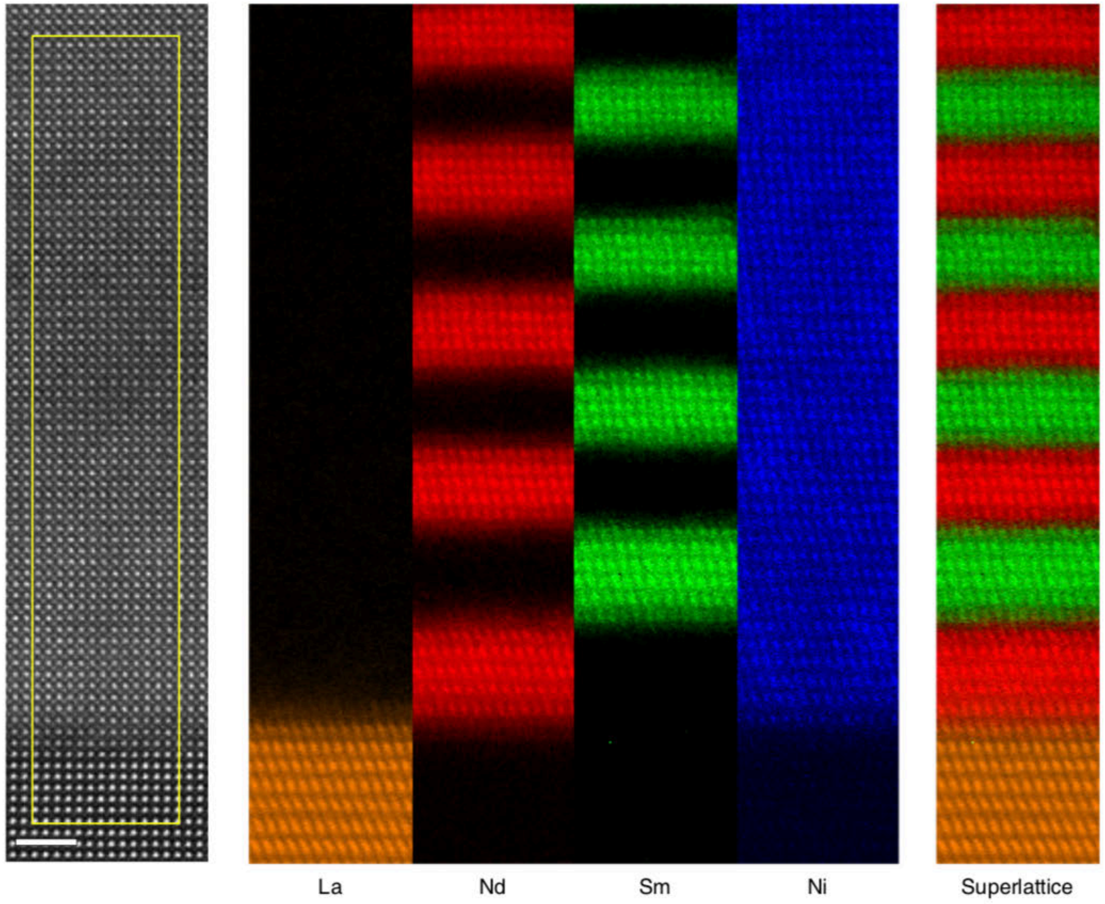
Window - integrate signal - plot intensity → Elemental map

Elemental mapping

- Produce elemental maps by plotting (x, y) integrated intensity in background-subtracted energy-loss "windows" selecting different ionisation edges

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





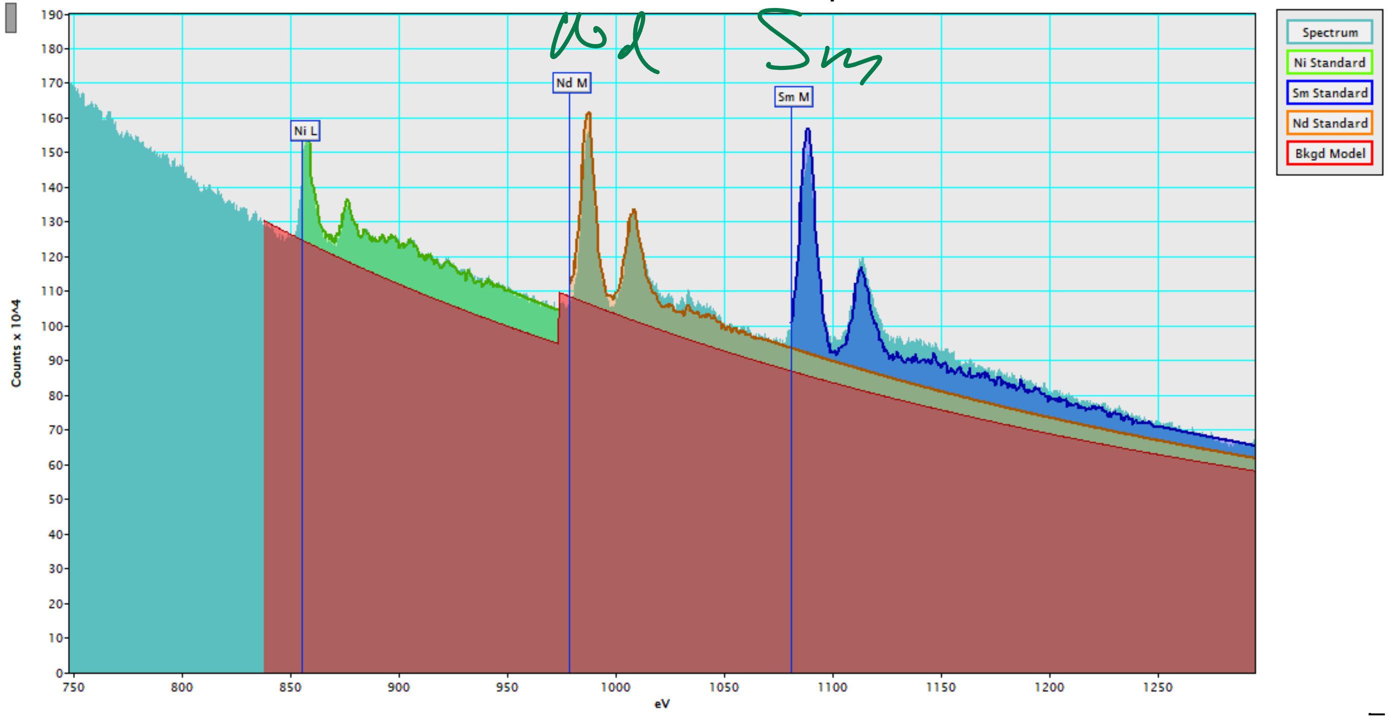
Dominguez et al. Nature Mater. **19** 1182 (2020)

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?

Model-based fitting for Sm →

NiNdO$_3$ / NiSmO$_3$ superlattice



Mapping: choose your elements wisely!

- First step: look at the EELS Atlas!
- What are the energy losses of your elements?
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- Do you have any overlaps?

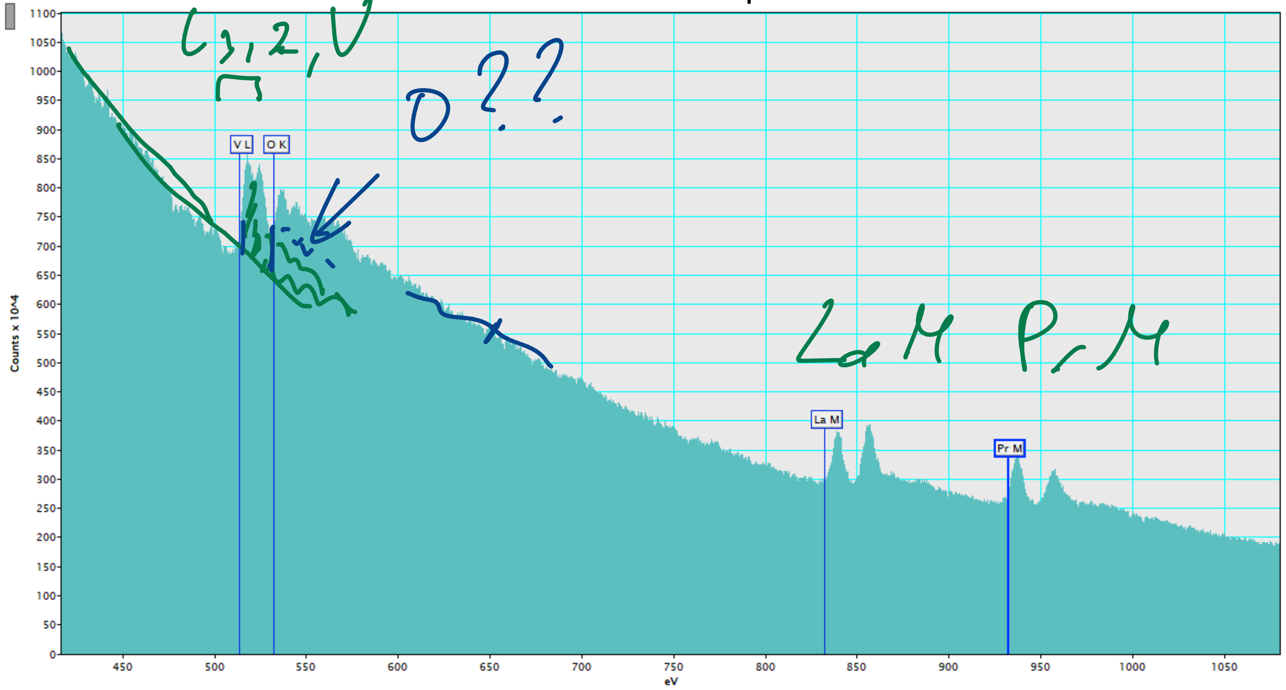
V, O

L: 525eV

K: 532eV

Cannot separate unique signature of Ok from V L

$LaVO_3$ / $PrVO_3$ superlattice



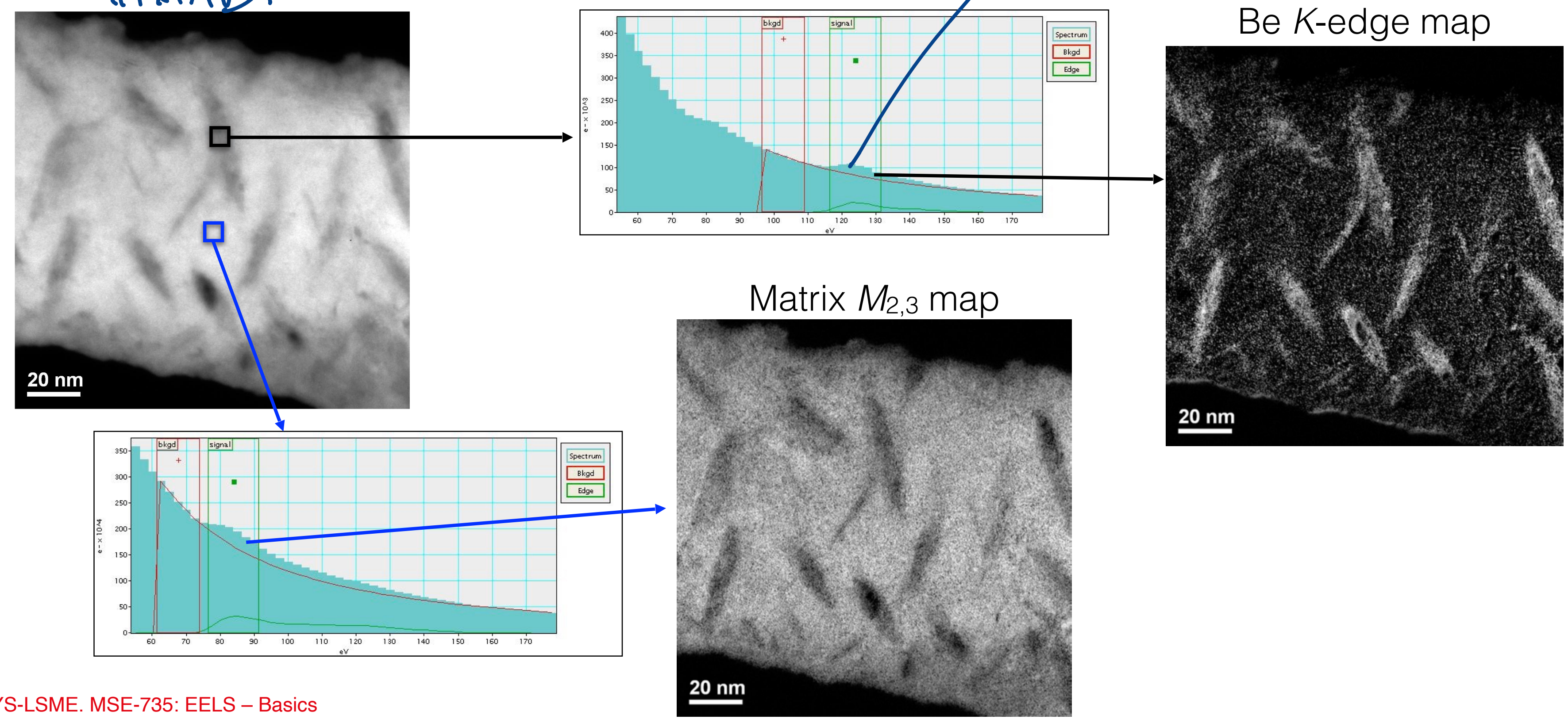
Benefits of EELS vs EDXS

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

Example:
Be mapping

(EFTEM)

HAADF



Elemental quantification

- Number of atoms per unit area N given by: $N = \dfrac{I}{j_0 \Delta\sigma}$

- Elemental percentages calculated using: $\dfrac{N_a}{N_b} = \dfrac{I_a}{I_b}\dfrac{\Delta\sigma_b}{\Delta\sigma_a}$

- For good quantification, need knowledge and correct choice of convergence semi-angle α and EEL spectrometer collection semi-angle β

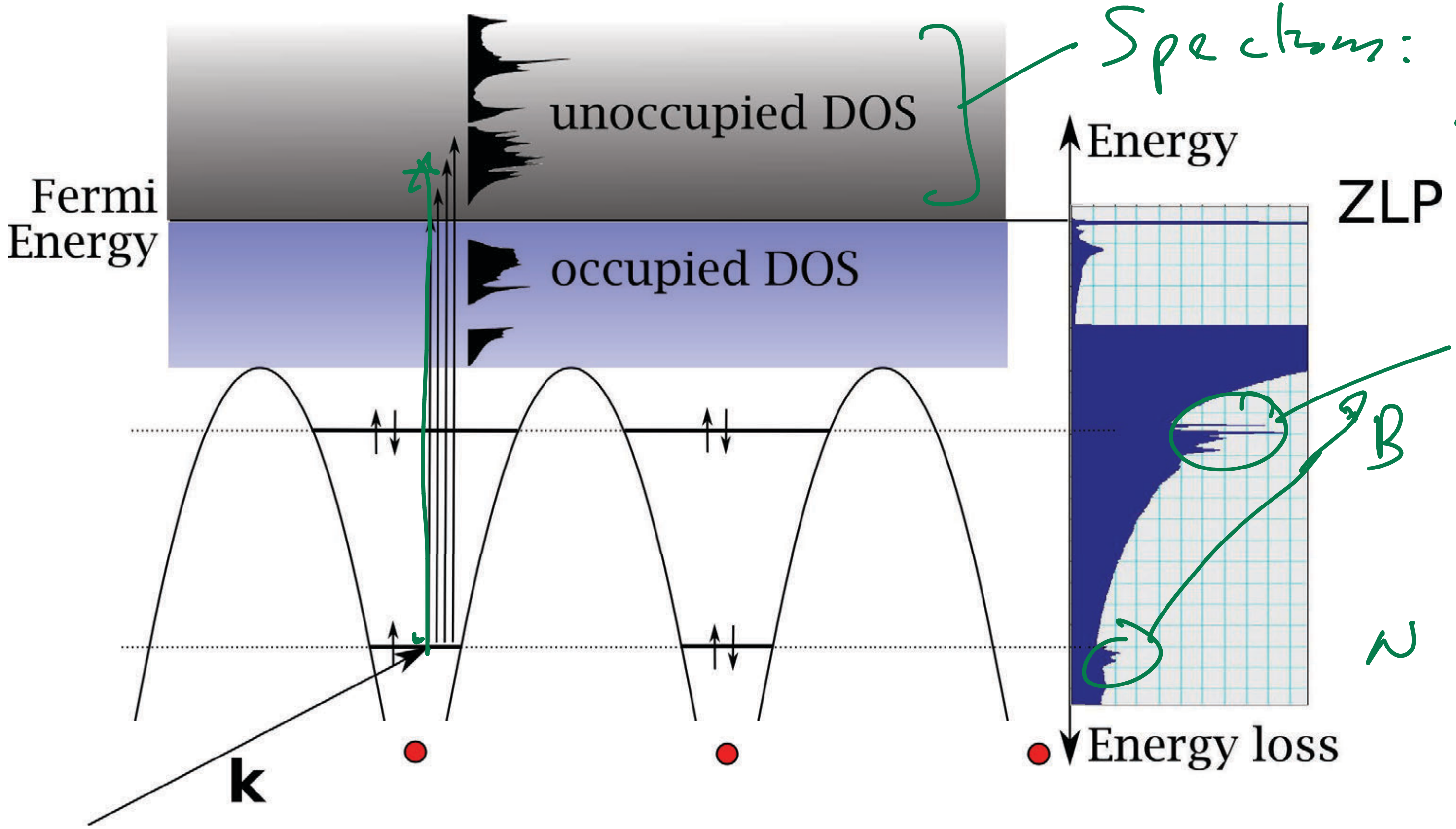
- Example: BN measured in TEM mode ($\alpha \approx 0$) at 200 keV:
  - $\beta = 100$ mrad: 47 at.% B / 53 at.% N ✓
  - $\beta = 0.5$ mrad: 23 at.% B / 77 at.% N ✗

  → Consider characteristic angle of scattering $\theta_E \sim \Delta E / 2E_0$

j_0: incident current density
I: ionisation edge intensity
$\Delta\sigma$: scat. x-section
≡ k-factor in EDX
DM: calculate $\Delta\sigma$
Accuracy ~10–20%
Wrong β
β: 100 mrad
B: 200 eV
N: 400 eV
$\theta_E \sim 1$ mrad

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



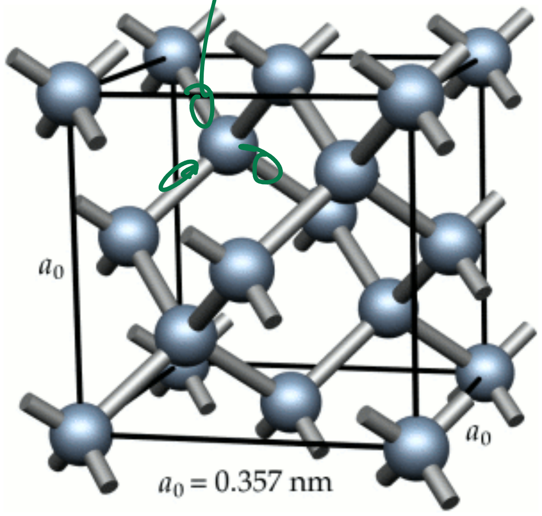
Spectrum: structure which mirrors the unocc. DOS

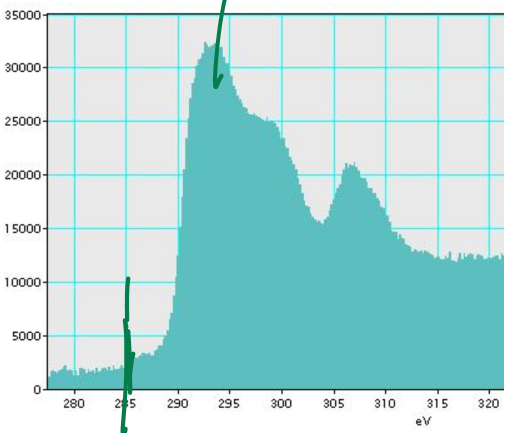
ELNES

Core-loss fine structure

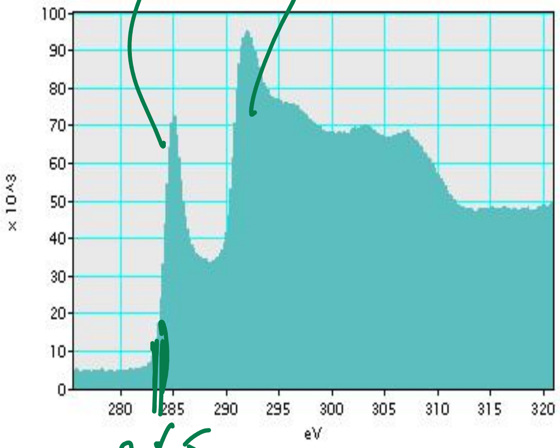
- Example: carbon *K*-edge

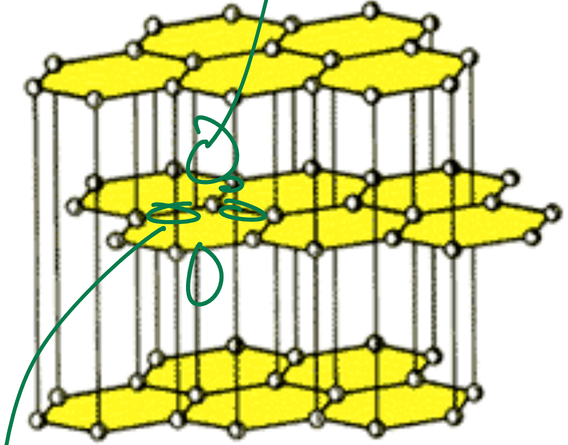
Diamond





Graphite

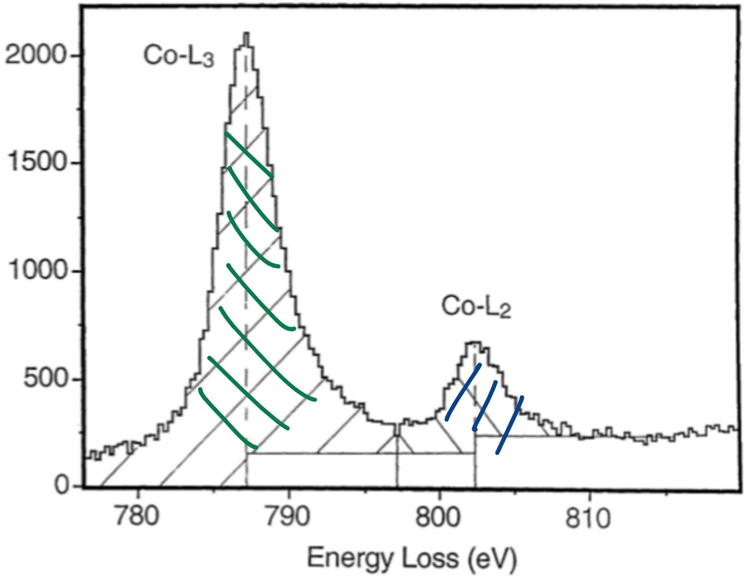


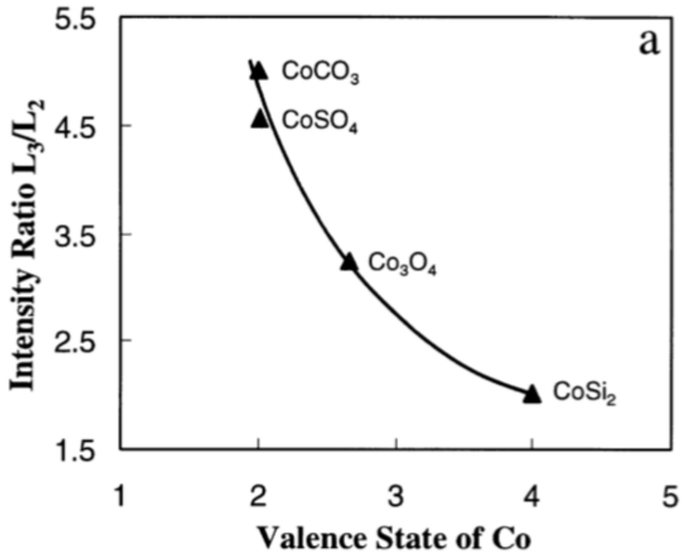


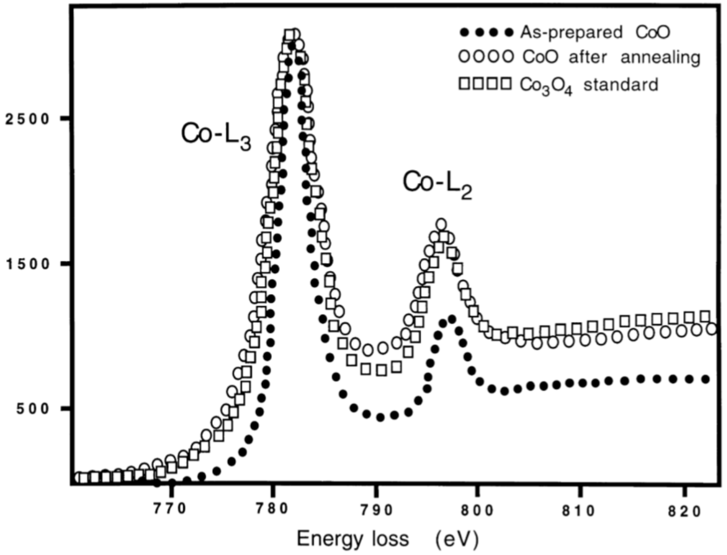
“White line” analysis

- L3, L2 peaks

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





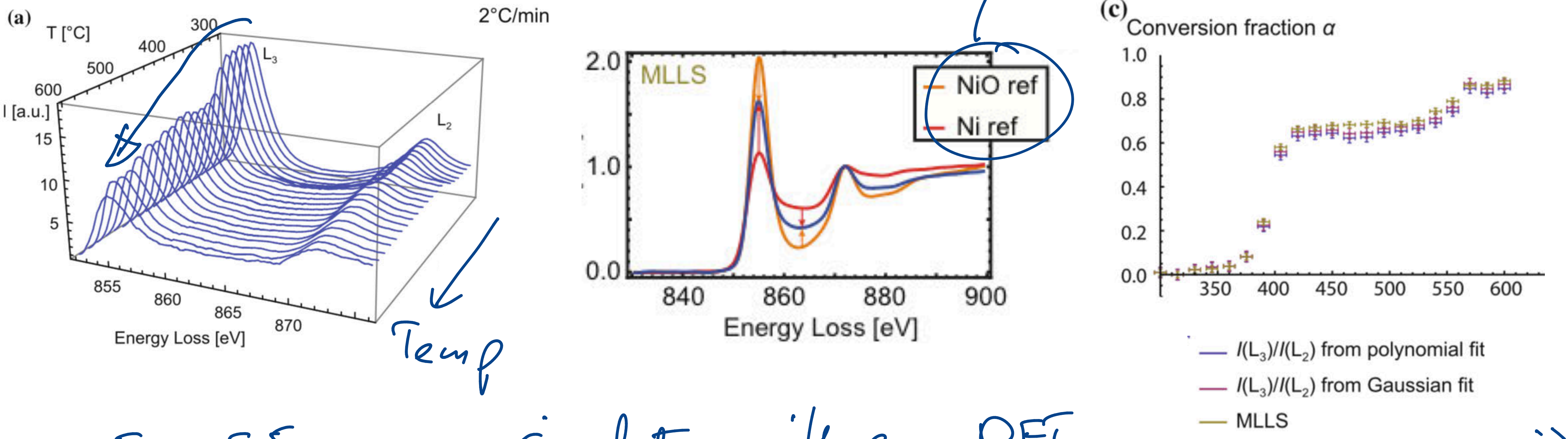


Wang et al. Micron **31** 571 (2000)

“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

standards to calibrate



Temp

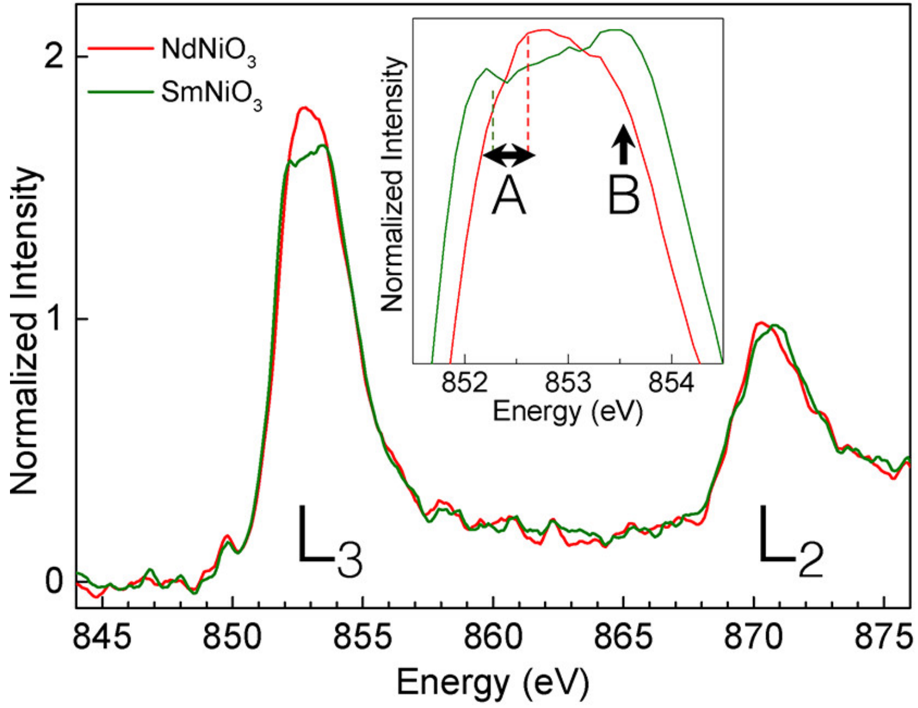
ELNES: can simulate with e.g. DFT + code “Wien 2k”

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

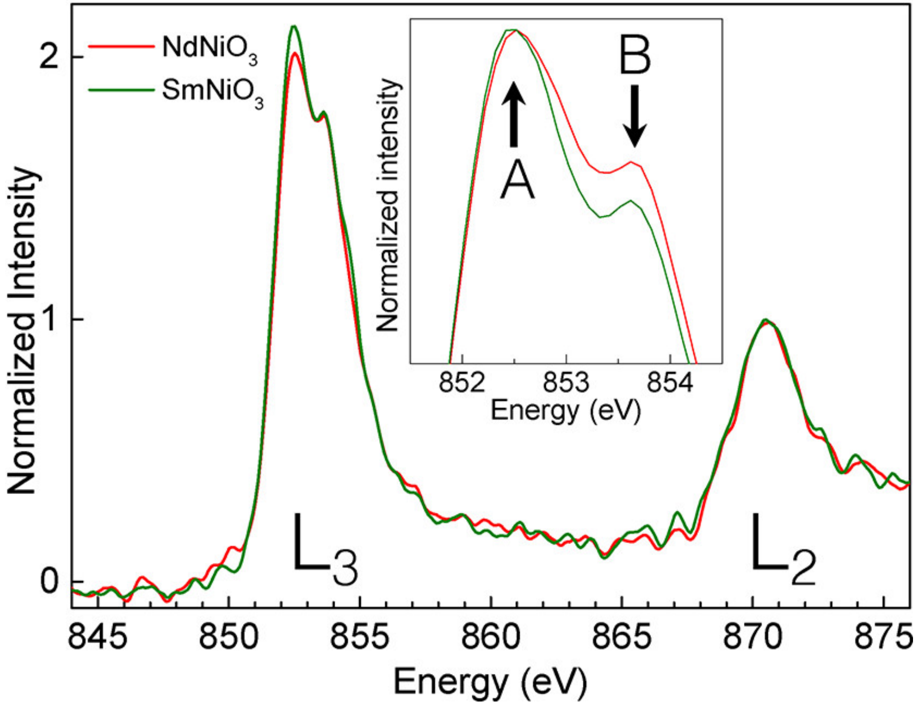
Probing electronic states in nickelates

- Small modulations in EELS Ni L_3 peak used to measure electronic state

30/30 lattice: $NdNiO_3$ metallic; $SmNiO_3$ insulating



5/5 lattice: both $NdNiO_3$ and $SmNiO_3$ metallic

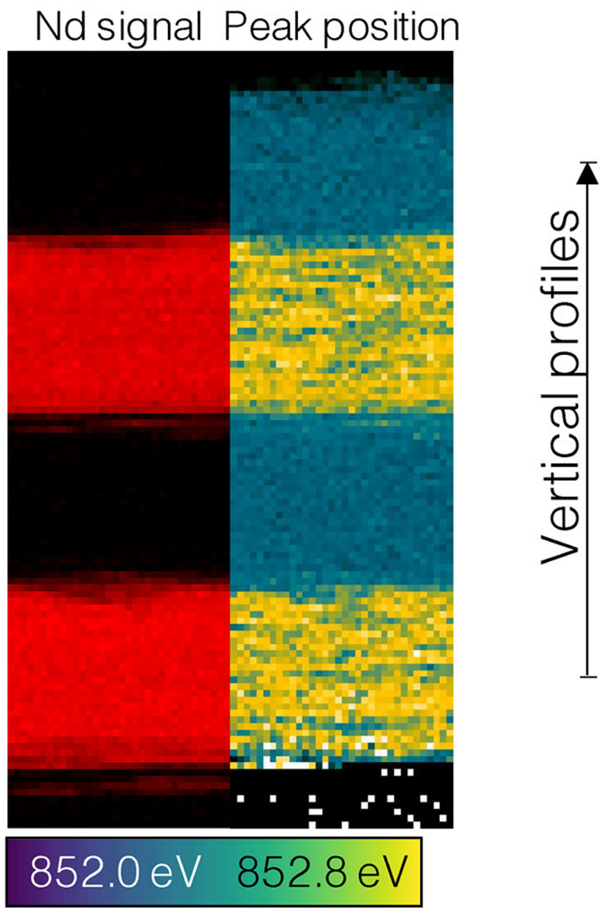


Mundet et al. Nano Lett. **21**, 2436 (2021)

Probing electronic states in nickelates

- Map Ni L_3 peak A position ⟹ electronic state mapping

30/30 lattice NdNiO$_3$ SmNiO$_3$



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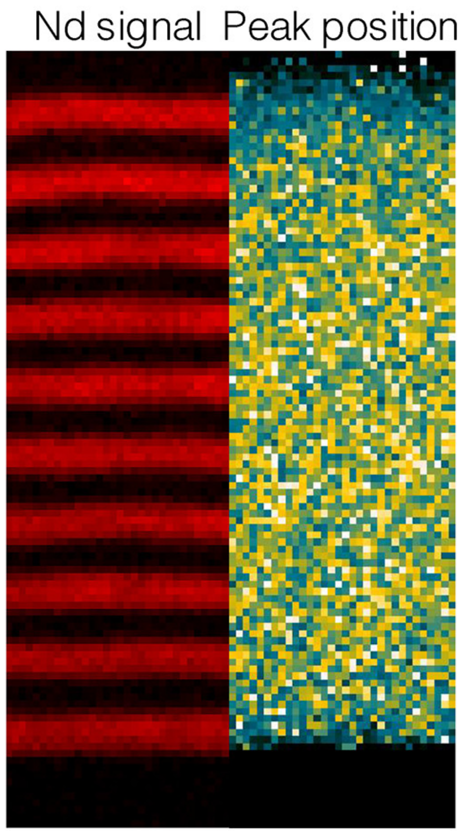

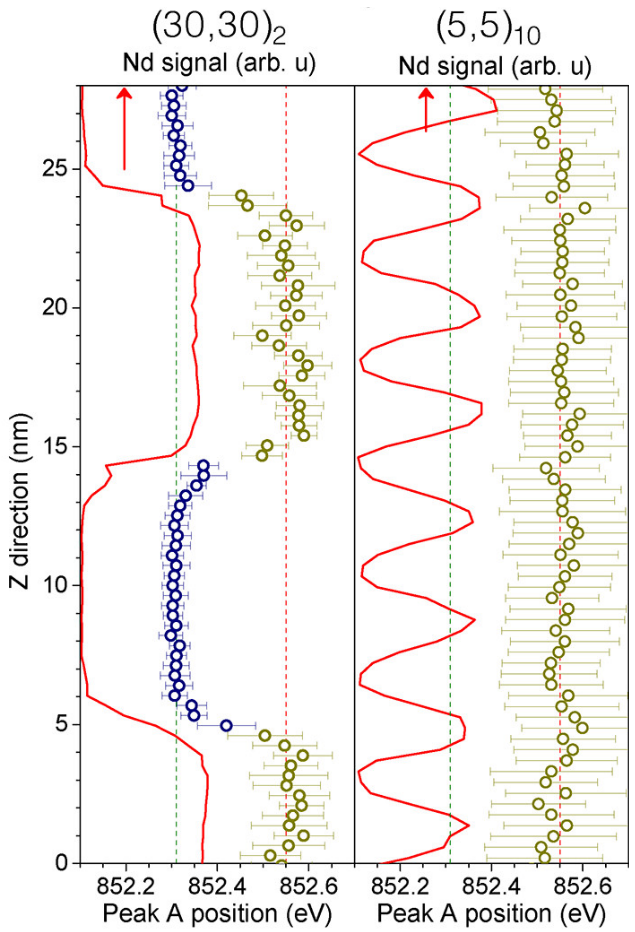

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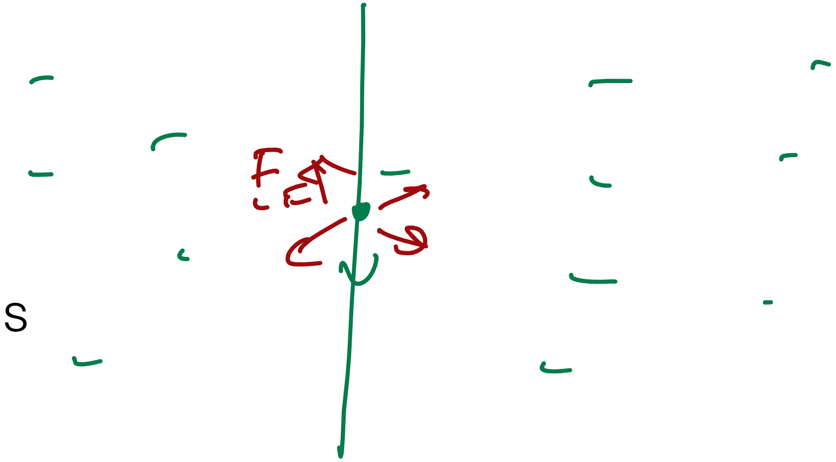
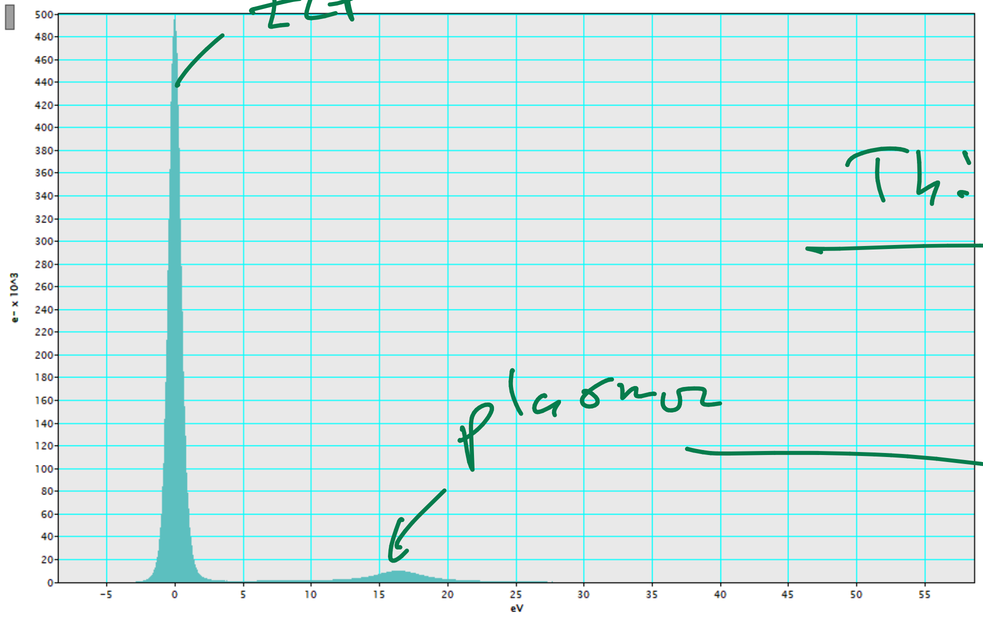
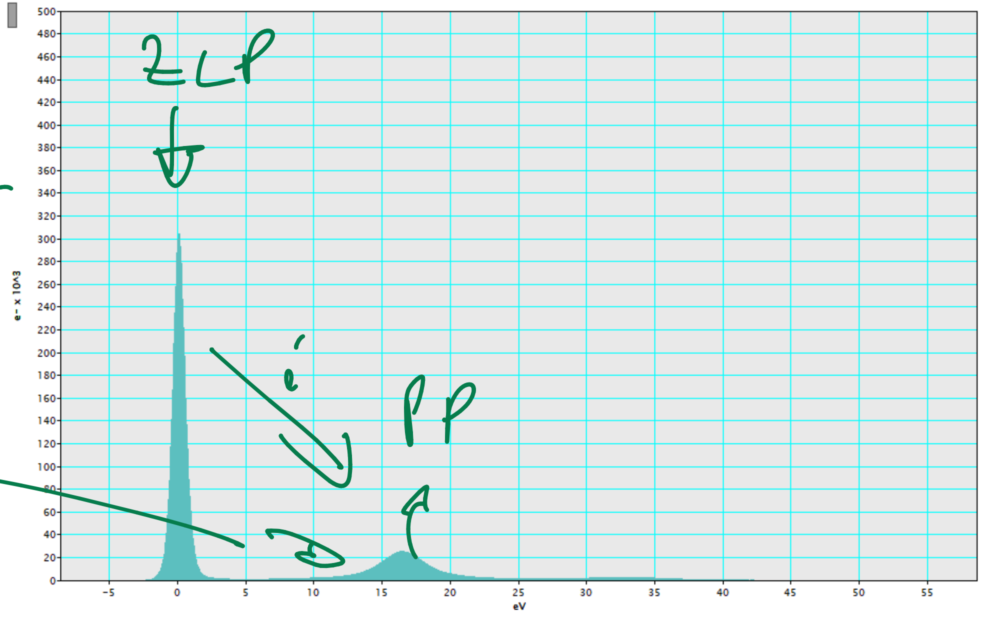
Low-loss EELS

- 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

Free e⁻ model
(Drude model)
-> Lorentzian p.p.

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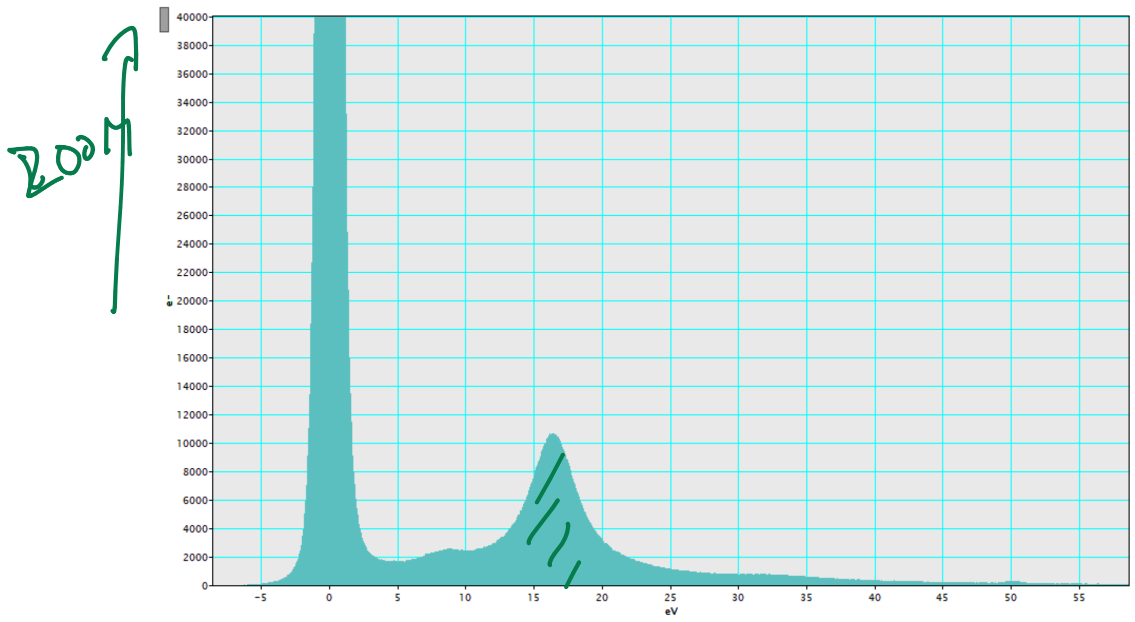
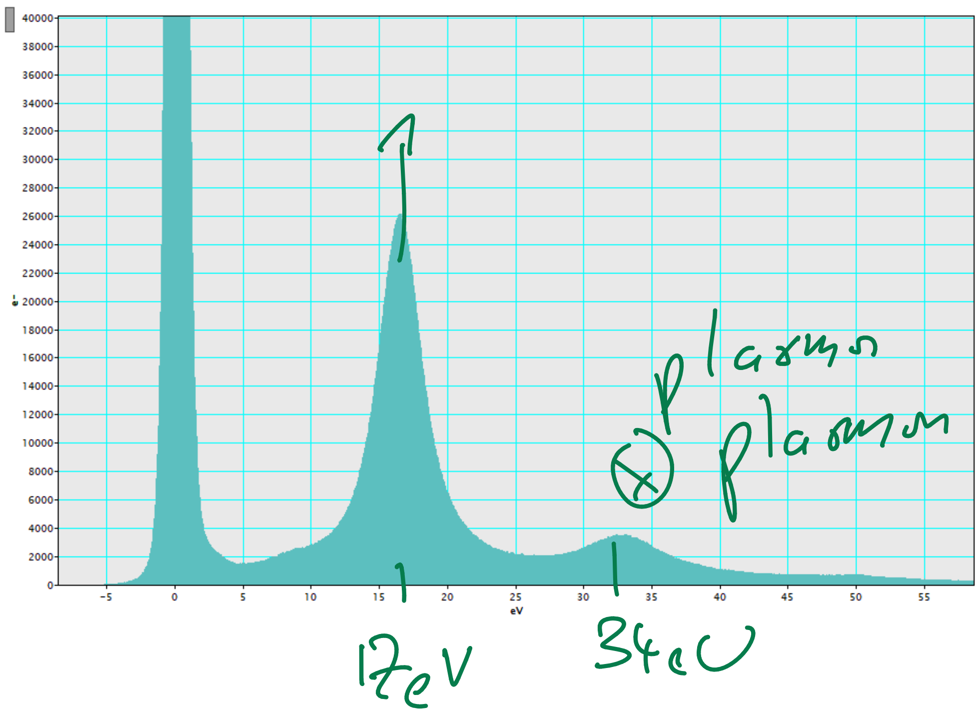


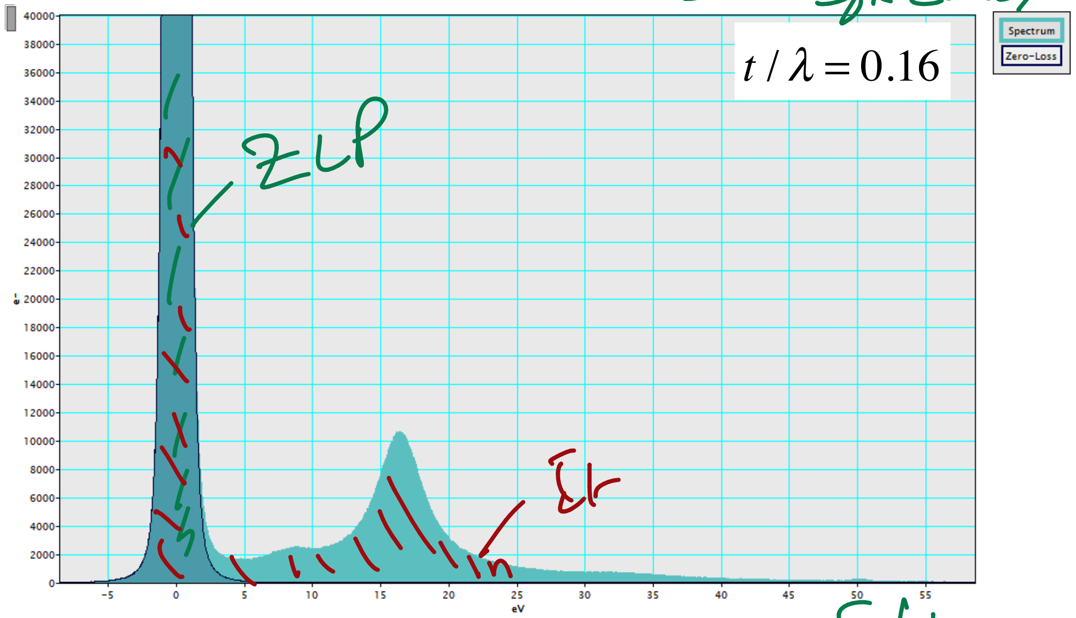


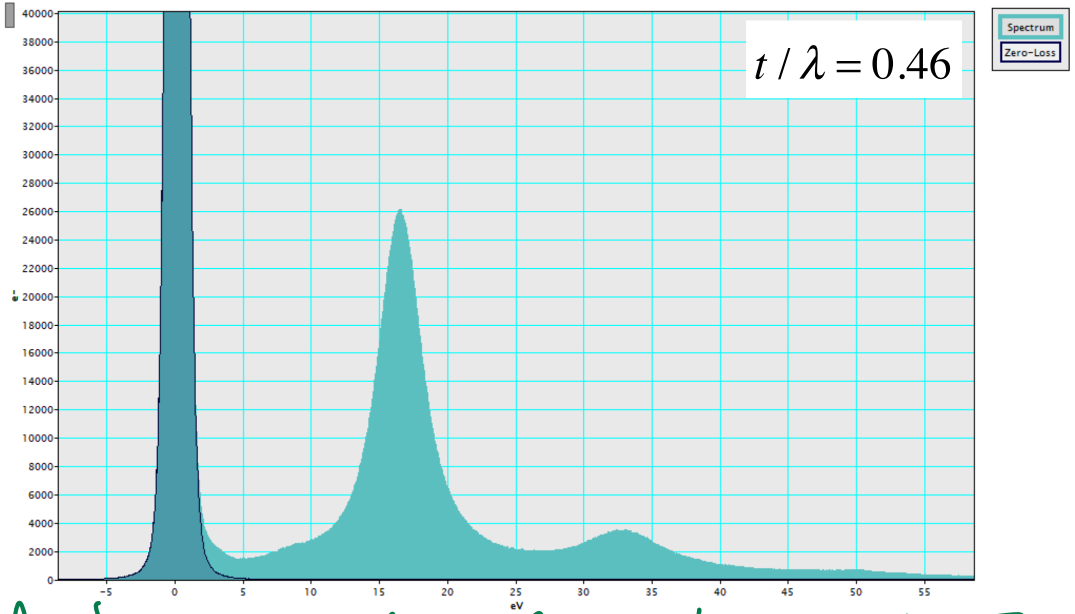
Multiple scattering

Sample thickness t

- As specimen thickness increases, have multiple scattering
- Inelastic scattering mean free path: λ → Av. distance between inel. sca. events
- From Poisson statistics: $t/\lambda = \ln(I_t/I_0)$

Int. spectrum (I_t); Int. ZLP (I_0)





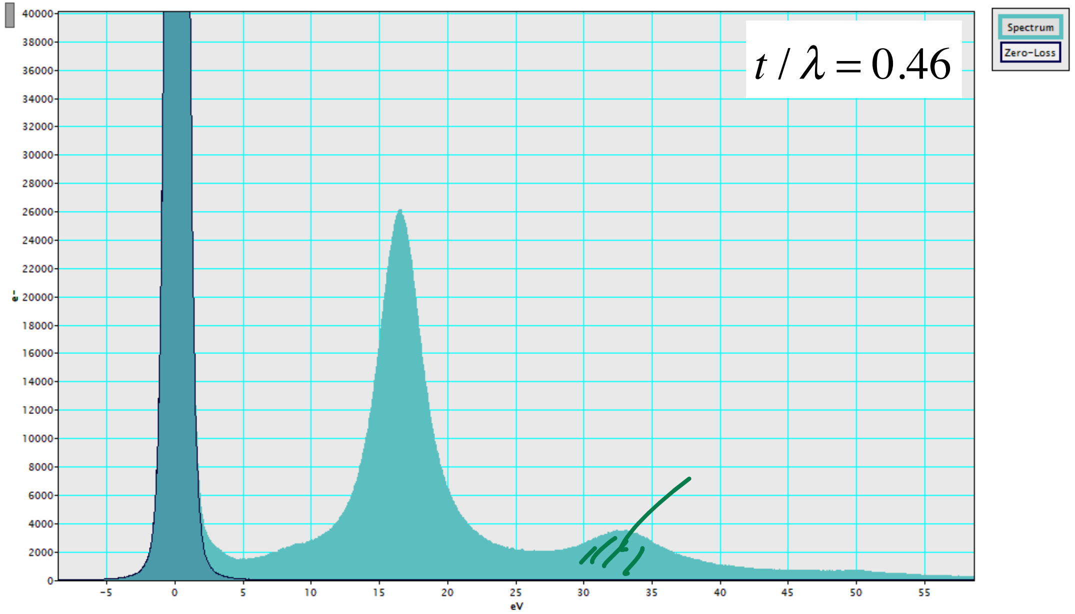
Elt. analysis want $0.3 \leq t/\lambda \leq 0.7$

Sample thickness measurement

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

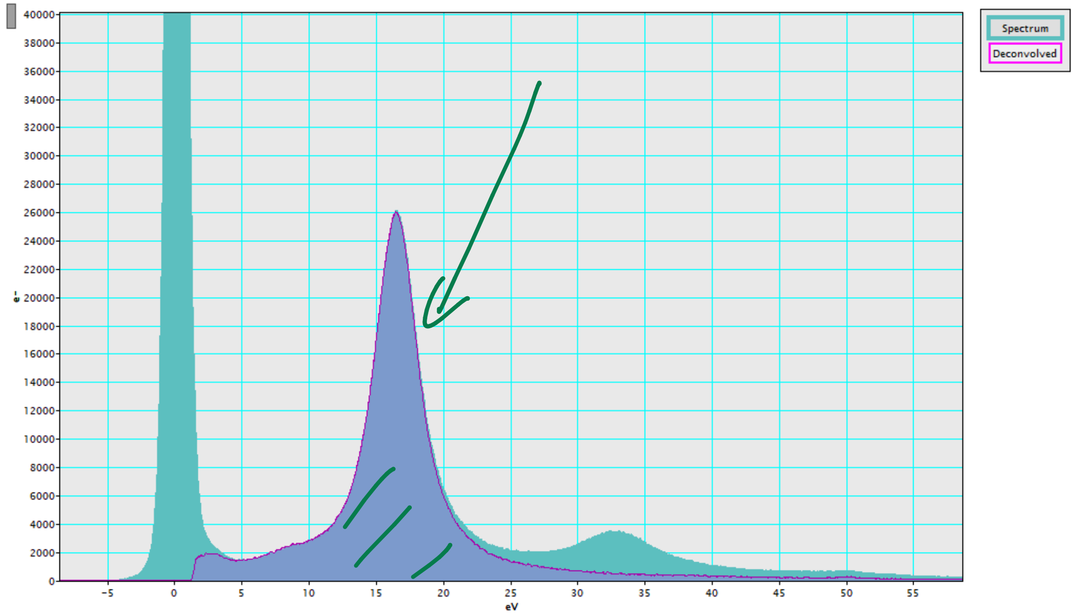
$\lambda \sim 100$ nm

Need α, β



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:



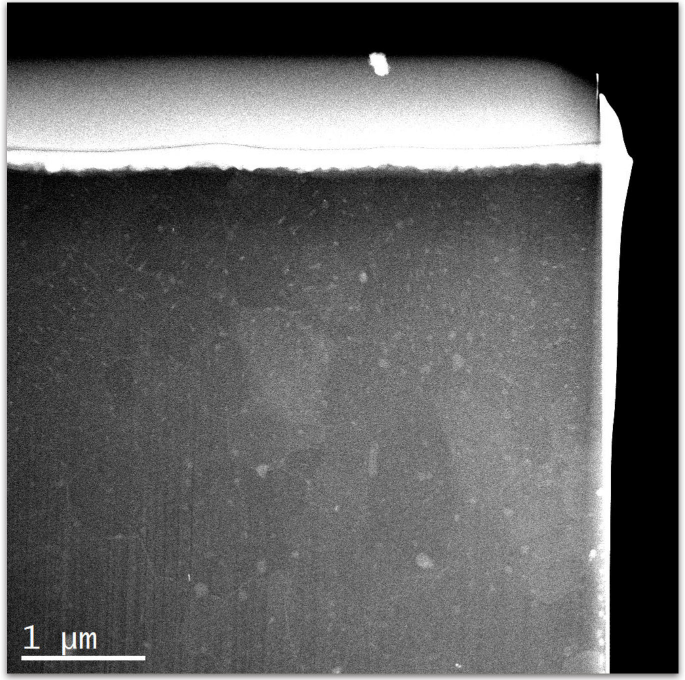
- Intensity of SSD: $\Gamma(\omega) \propto \mathrm{Im}\left\{ -\frac{1}{\epsilon(\omega)} \right\}$

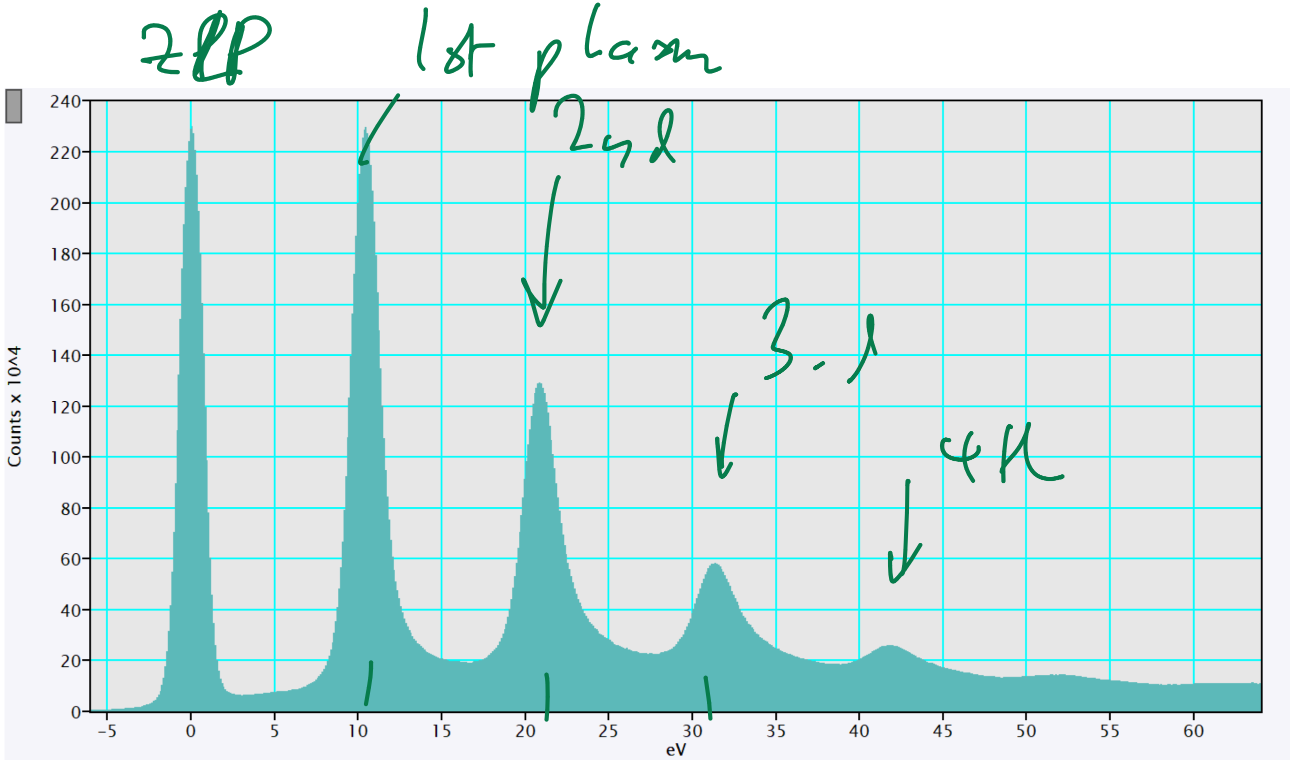
low loss

$\epsilon = \epsilon' + i\epsilon''$

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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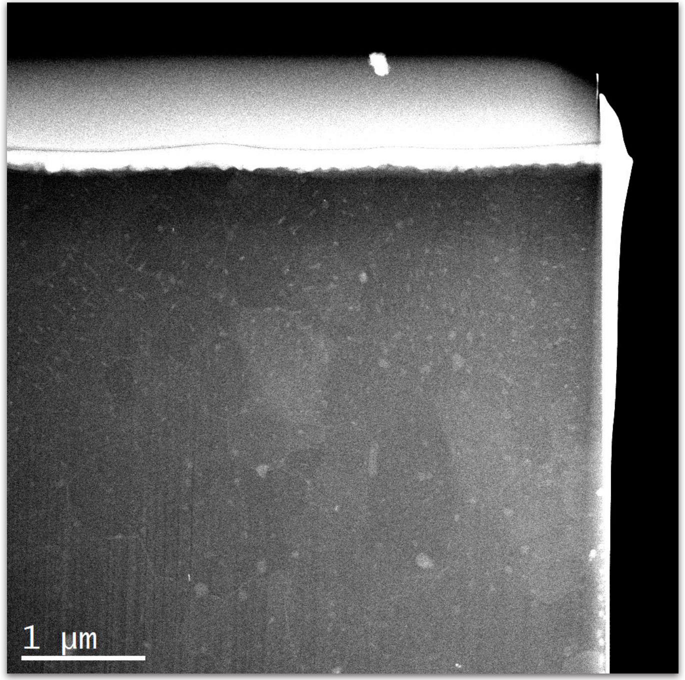
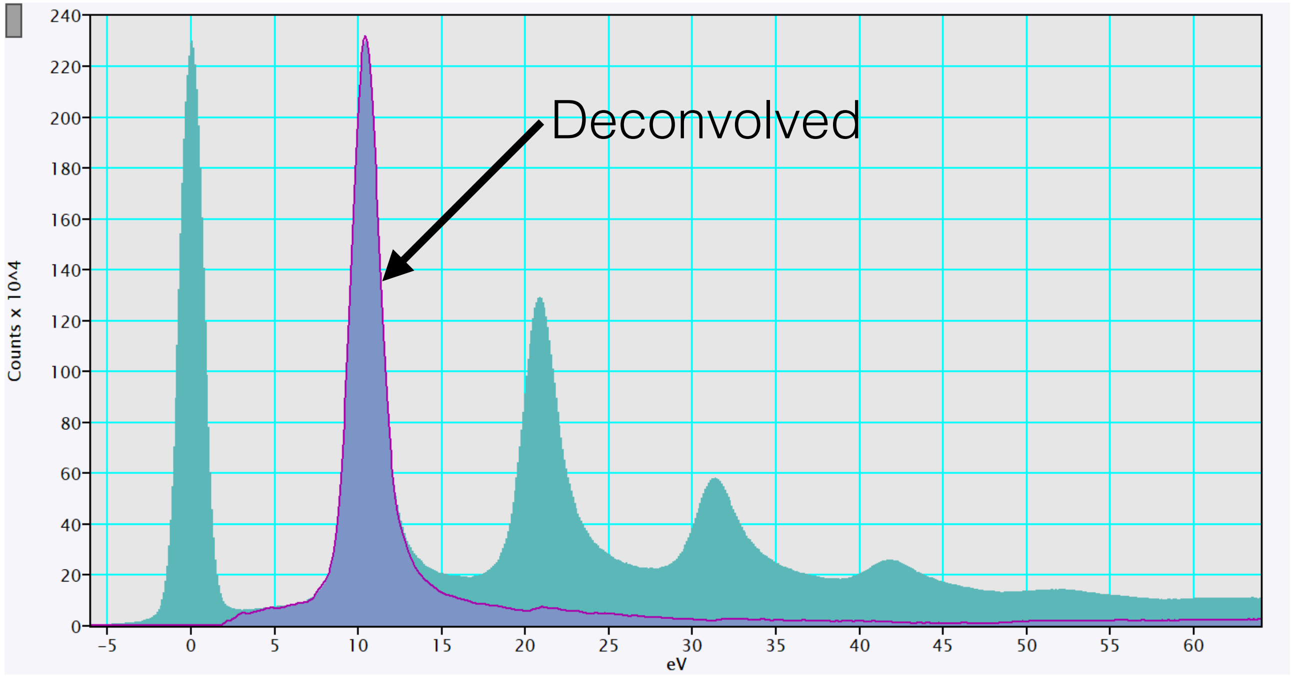
- Multiple orders of plasmon peak excitation



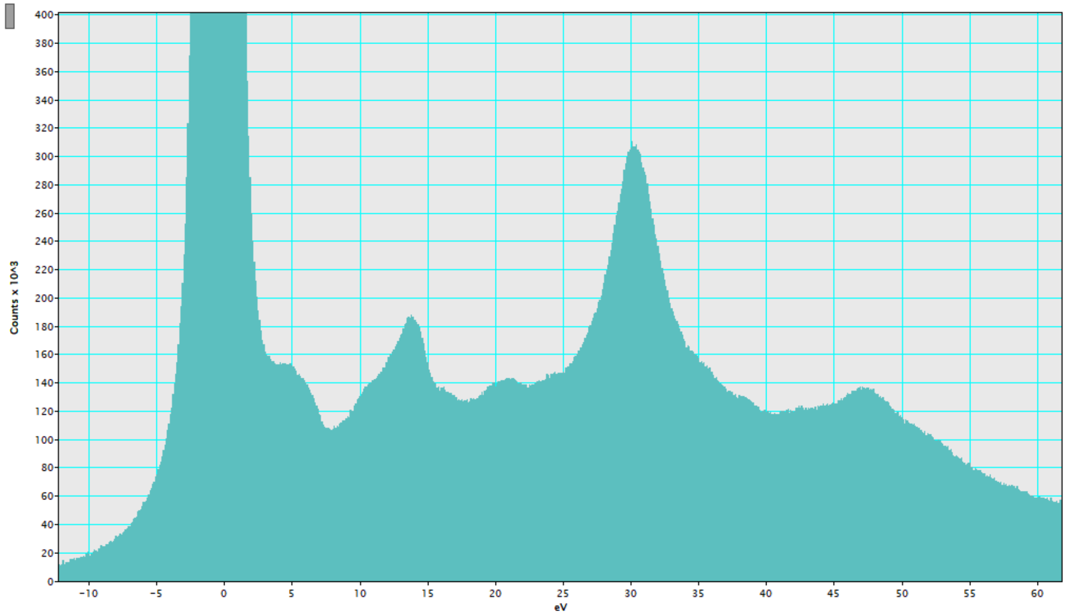


Complexity in the low-loss spectrum

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

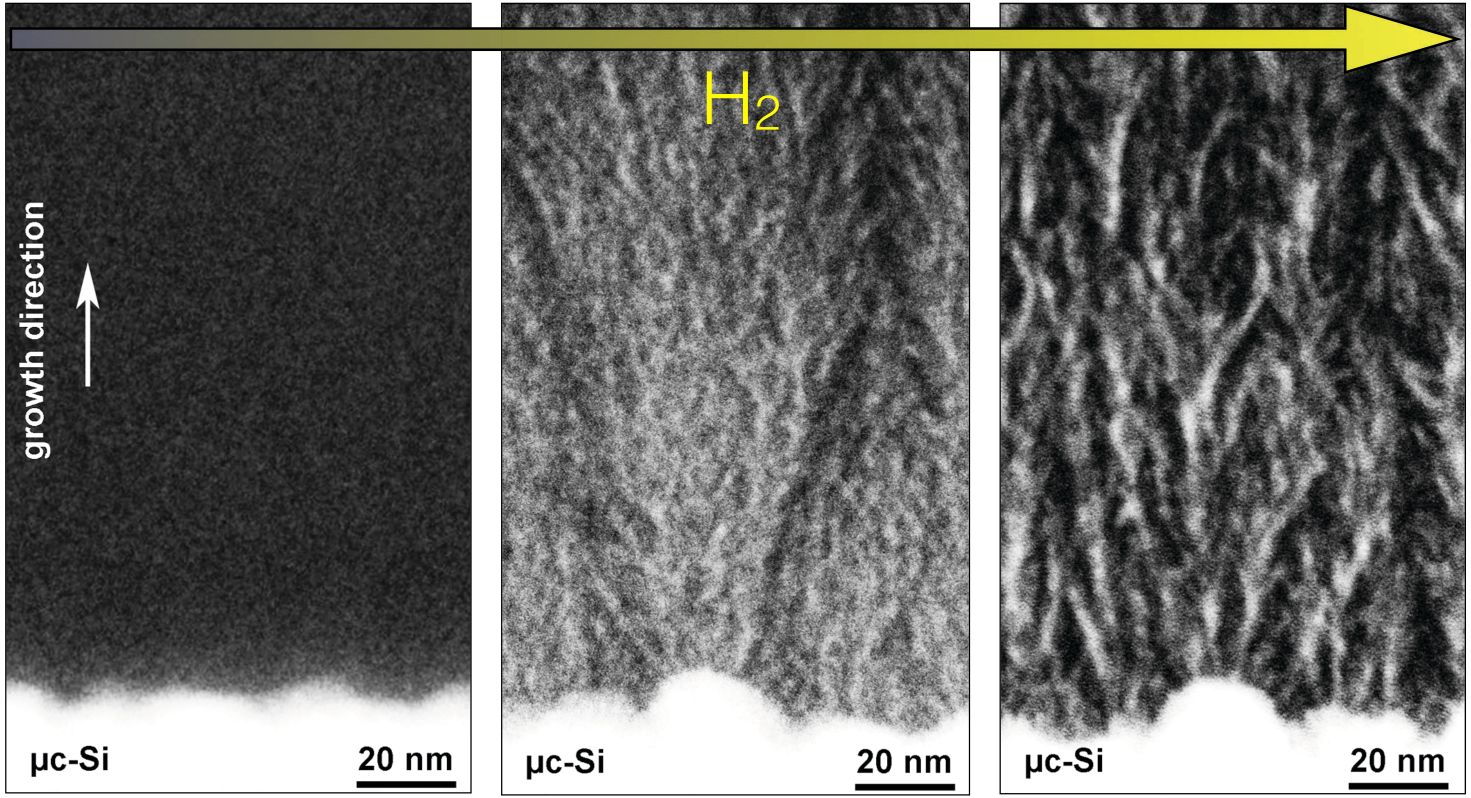
- Bulk plasmon region can also show single electron excitations
  ⟹ Low-loss spectrum has features related to phase electronic structure

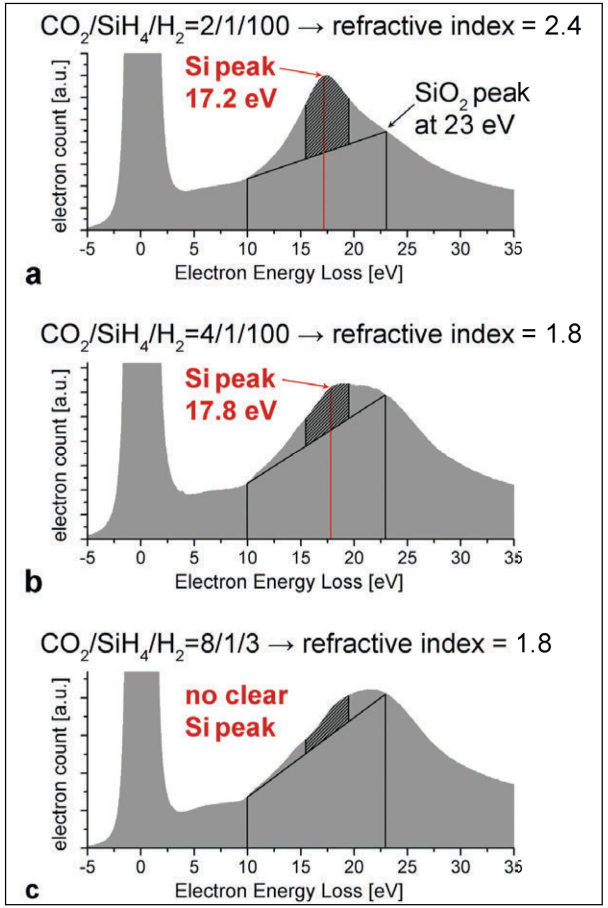
$SrTiO_3$ low-loss:



Example plasmon use: mapping Si

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





- Increasing H_2 plasma ⟹ increased phase separation

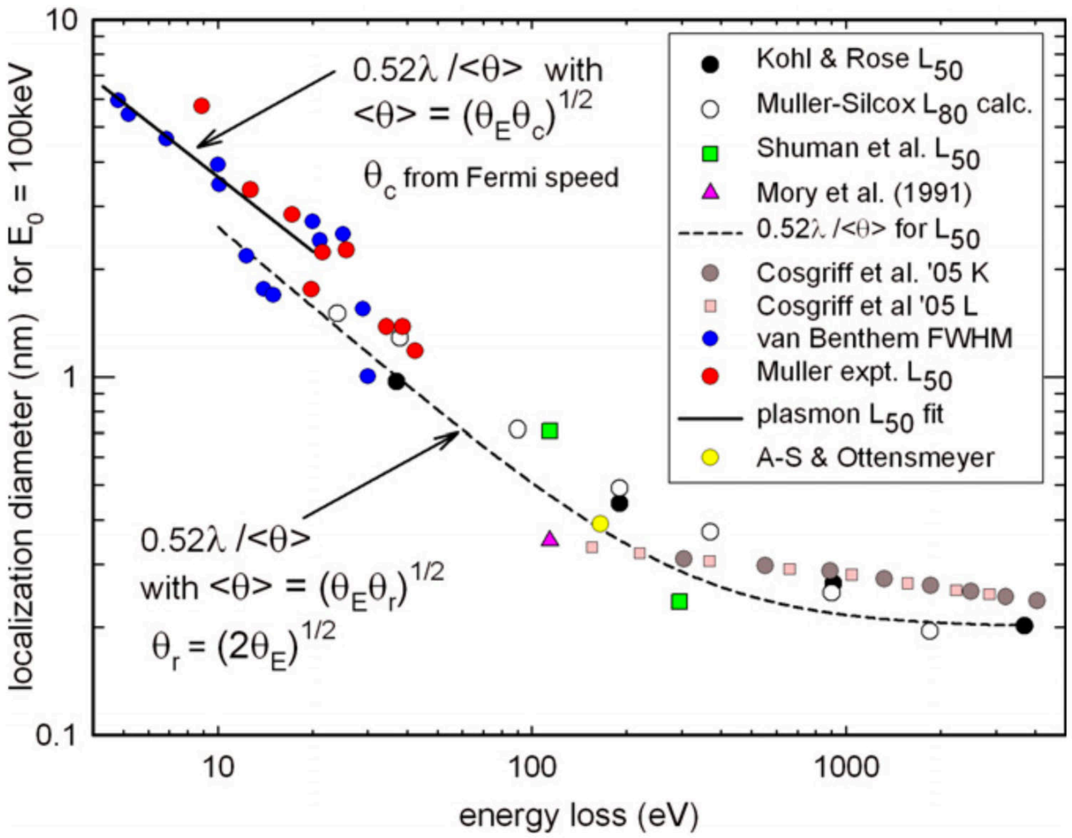
Cuony *et al*. Adv. Mater. **24** 1182 (2012)

EELS basics: contents

- Ionisation energy loss
- Electron energy-loss spectrometer
- Features of the EEL spectrum
- Ionisation edge Core-loss analysis
  - Elemental detection and mapping
  - Elemental quantification
  - ELNES
- Low-loss EELS
  - Bulk plasmon
  - Multiple scattering, thickness measurement and deconvolution
- EELS spatial resolution
- References

EELS spatial resolution

- Attainable spatial resolution of EELS signal depends on the nature of the scattering process
- Decreasing energy loss ΔE
  $\Longrightarrow$ increasing spatial *delocalisation*
- (Exception: acoustic phonon excitations with high momentum transfer)



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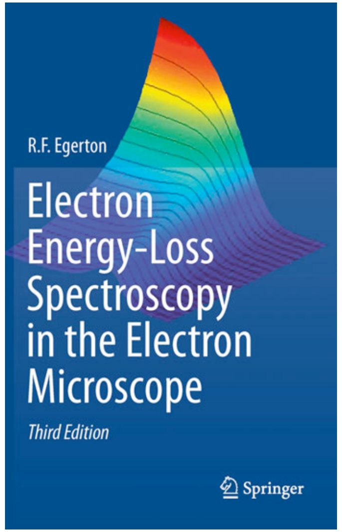

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