Electron Energy-Loss Spectroscopy

Or as…

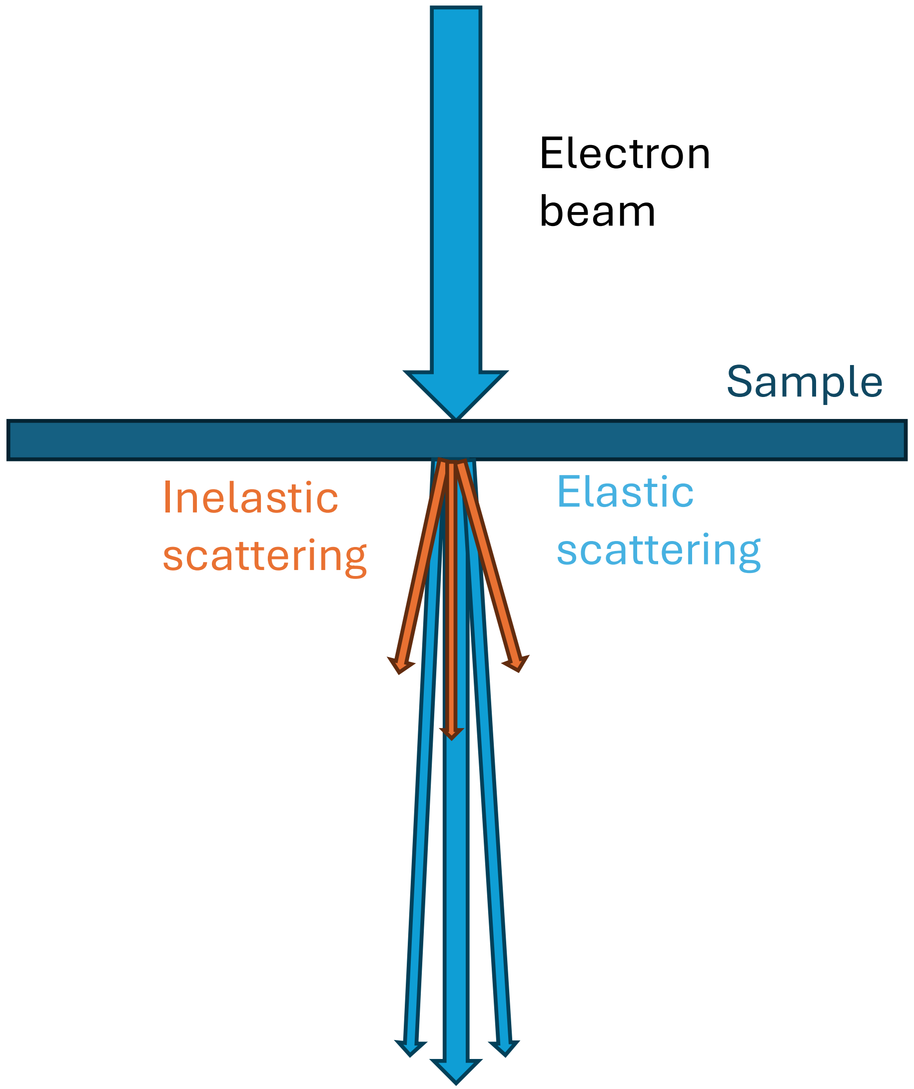
Miklós Nemesszeghy

EELS

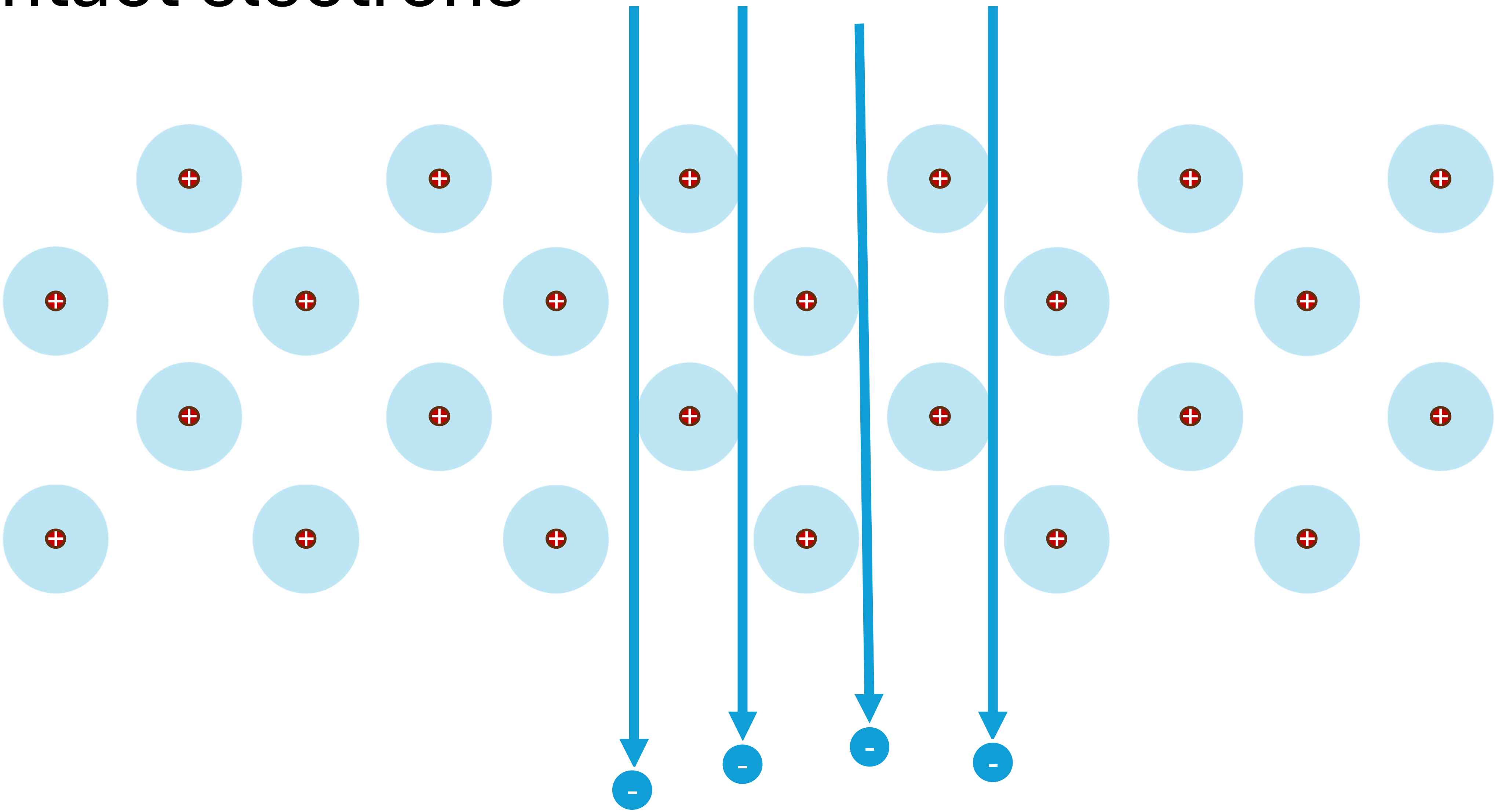
Southern Shortfin Eel, Anguilla australis Richardson 1841
Gomon, M.F. & Bray, D.J. 2024
FISHES OF AUSTRALIA

EELS

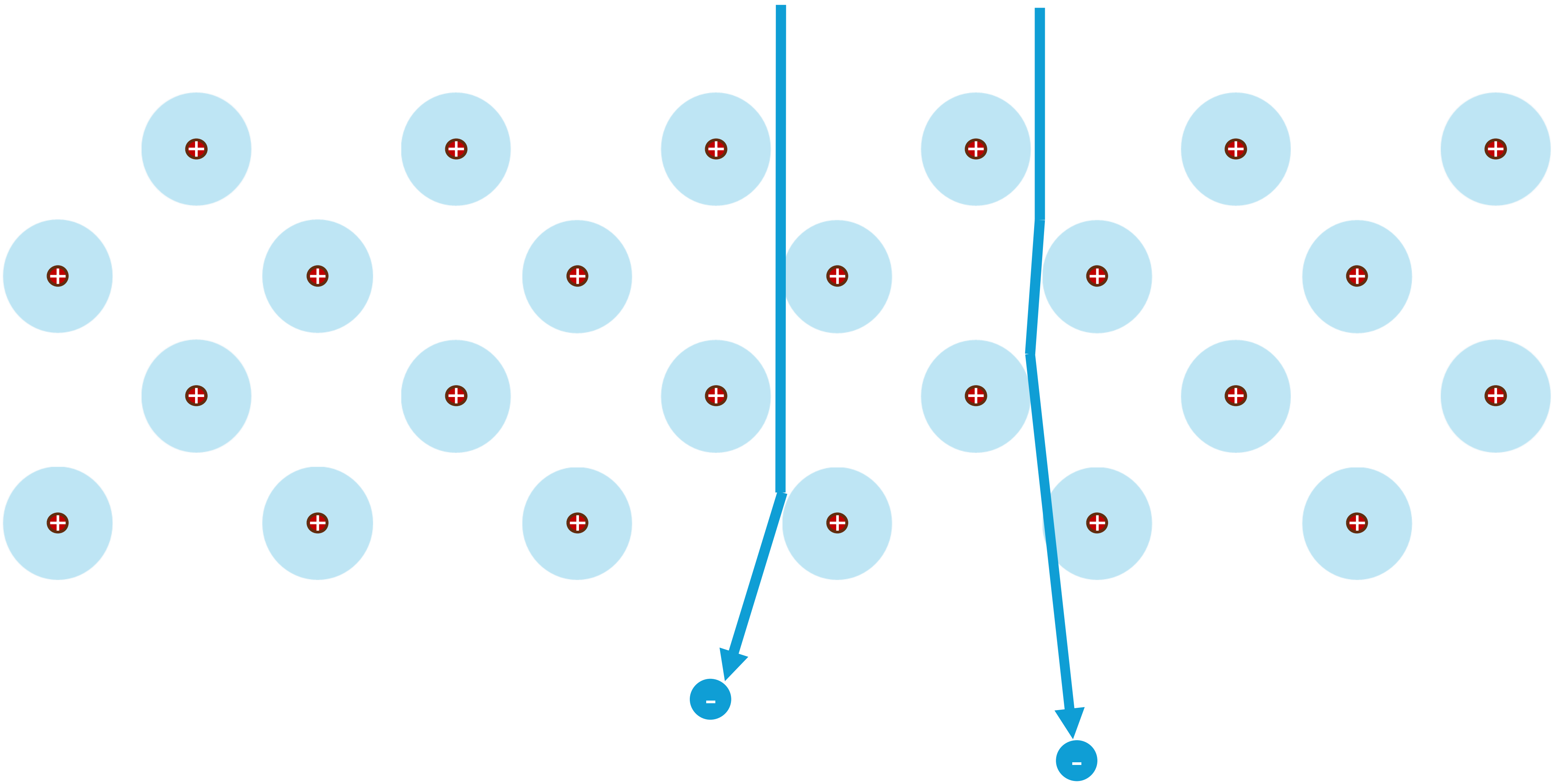
- Energy loss of transmitted electrons
- Used in TEM instruments
- Acquired data quite similar to XAS
- Elastic scattering
- Inelastic scattering



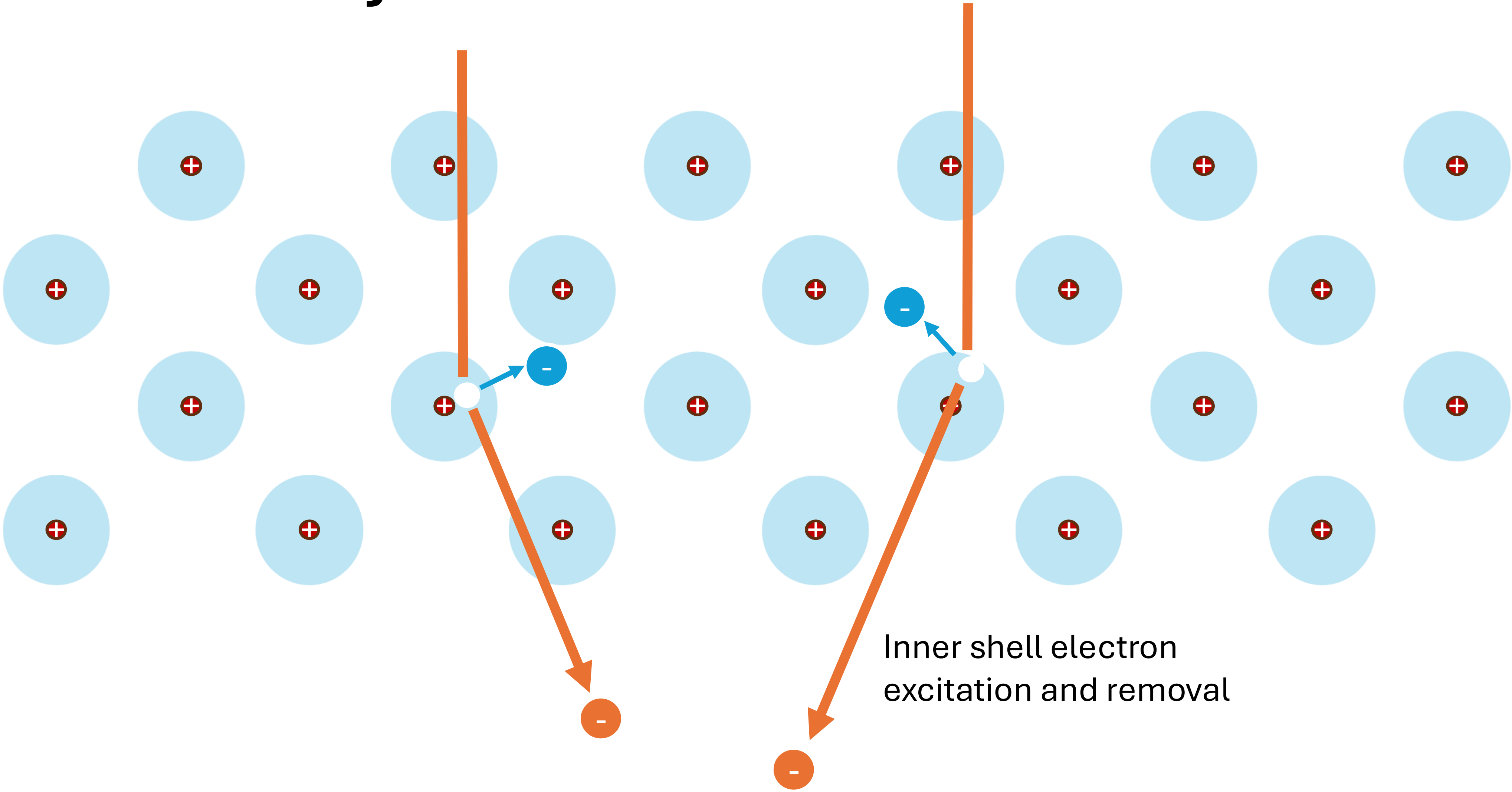
Intact electrons



Elastically scattered electrons



Inelastically scattered electrons:



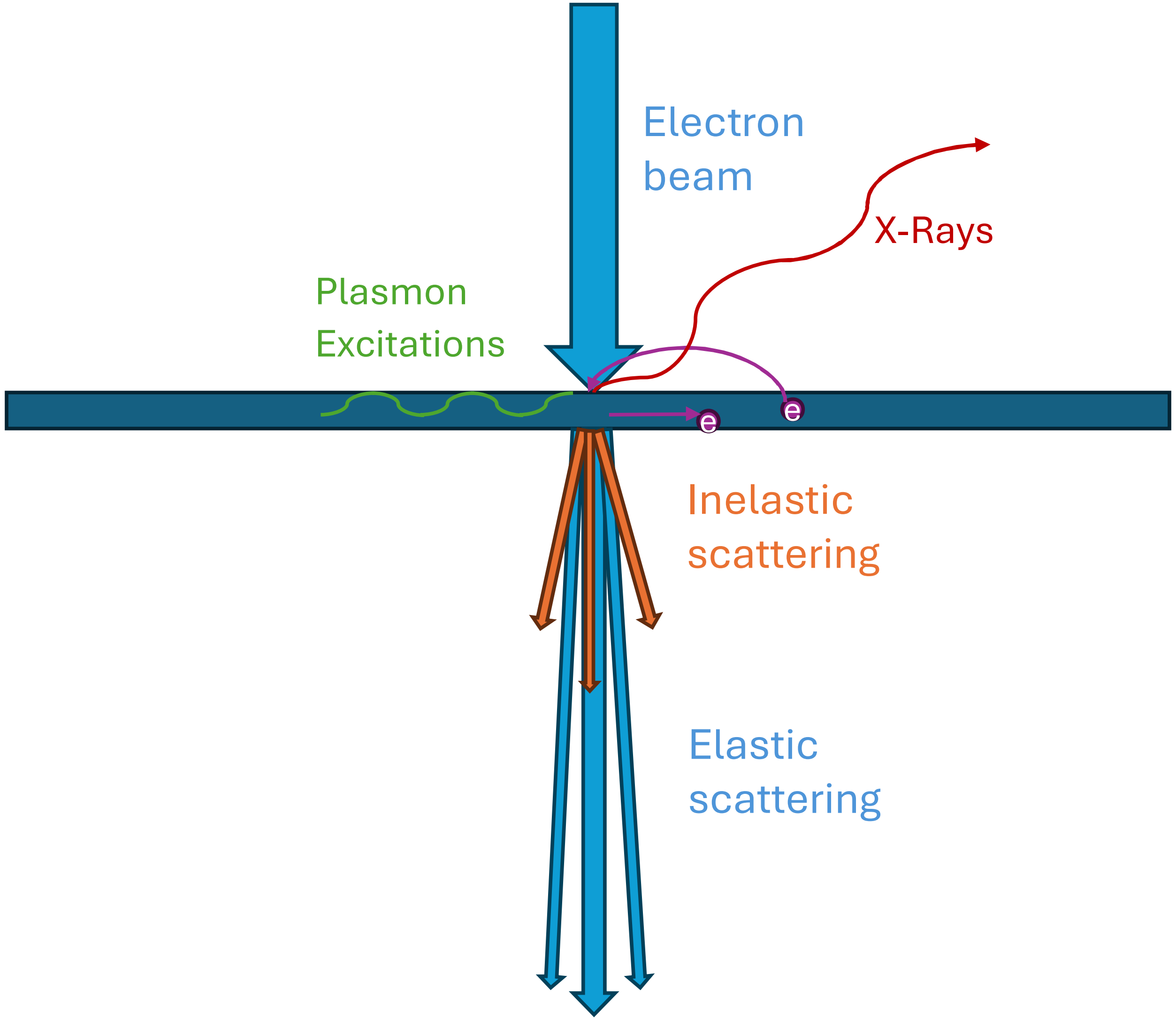
Inner shell electron
excitation and removal

Plasmon excitations and “band hopping”

- Plasmon: oscillation waves in electron density
- Low in energy
- Possible source for electron scattering
- “Band hopping”: electron excitations from valence band to conduction band

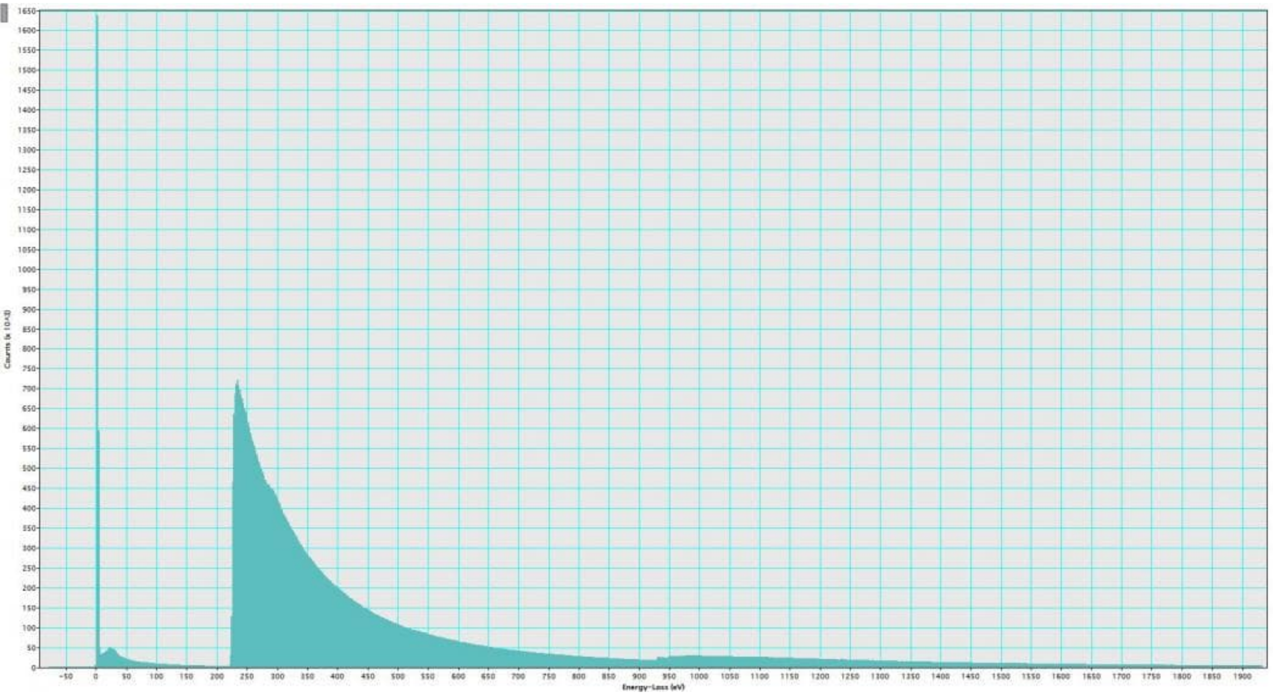
Summary of Scattering Events

- Elastically scattered and undisturbed electrons
- Electron excitations and removal
- Plasmon excitations
- (Phonon excitations are counted as elastic)
- Multiple scattering events possible

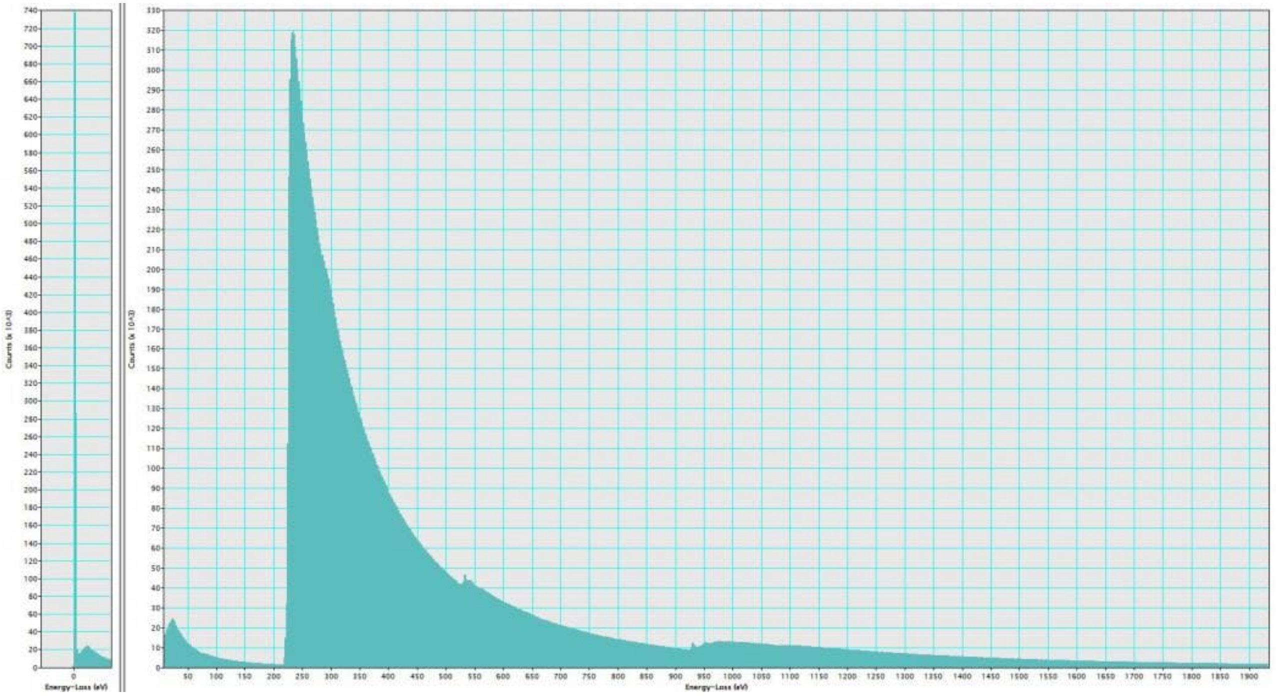


EELS Spectrum

Cu



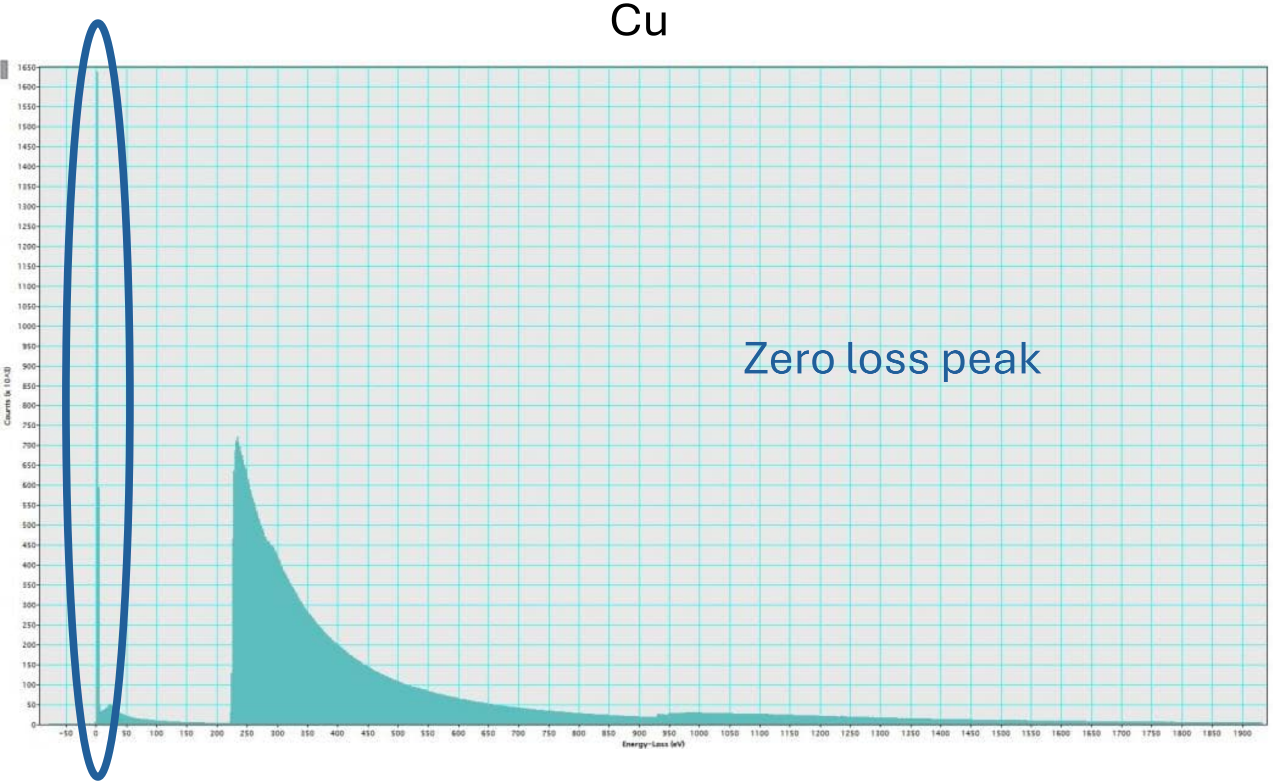
CuO



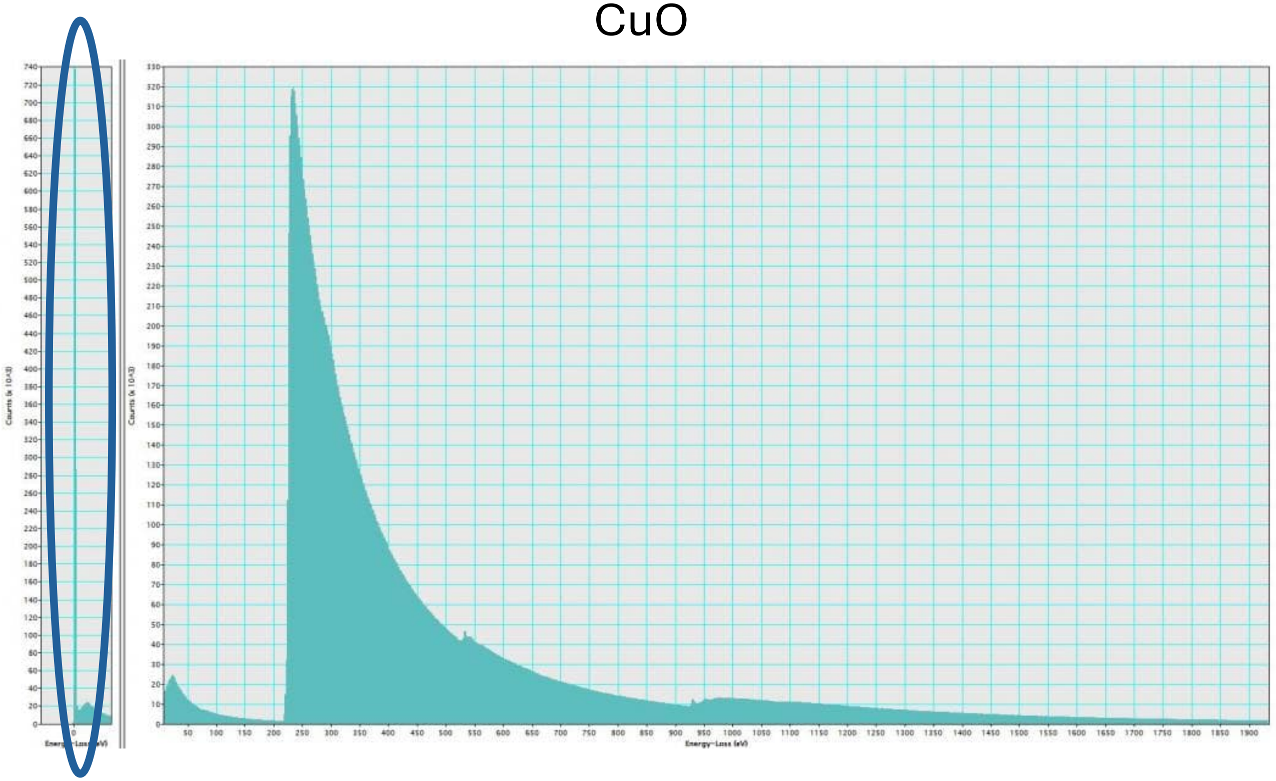
EELS atlas, EELS.info, Gatan corporate, EELS Atlas | EELS.info

EELS Spectrum

Cu



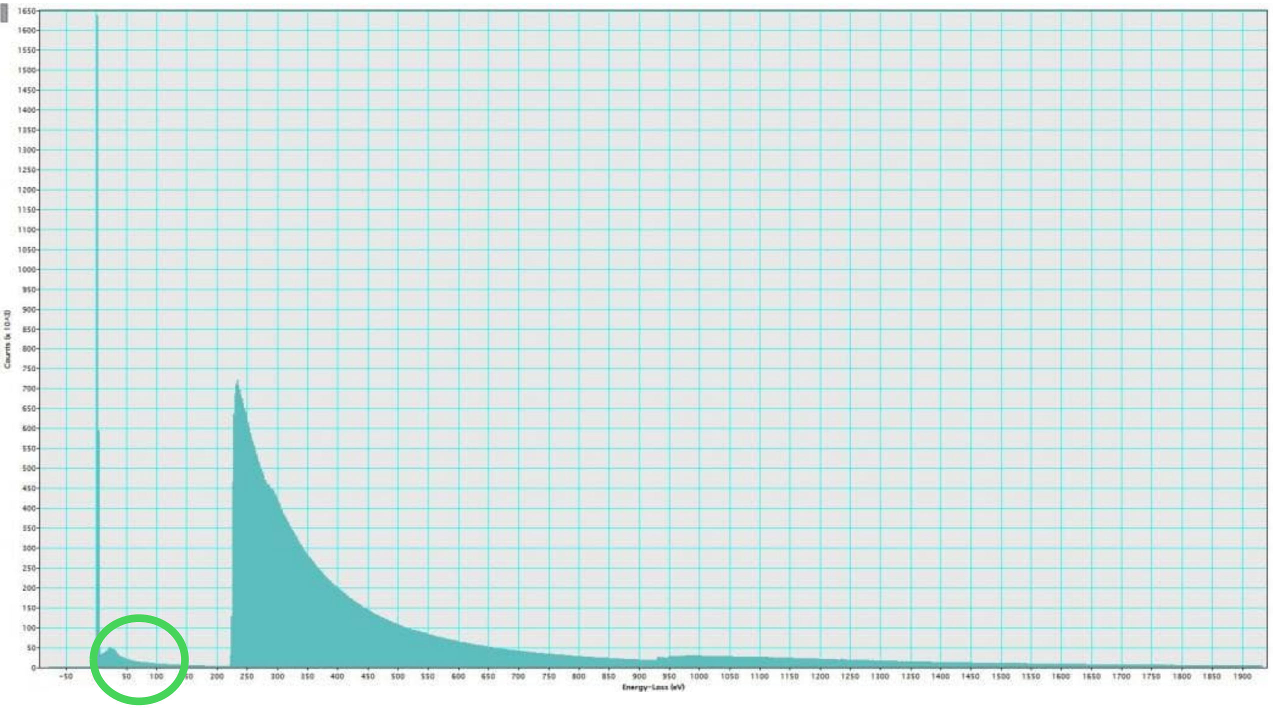
CuO



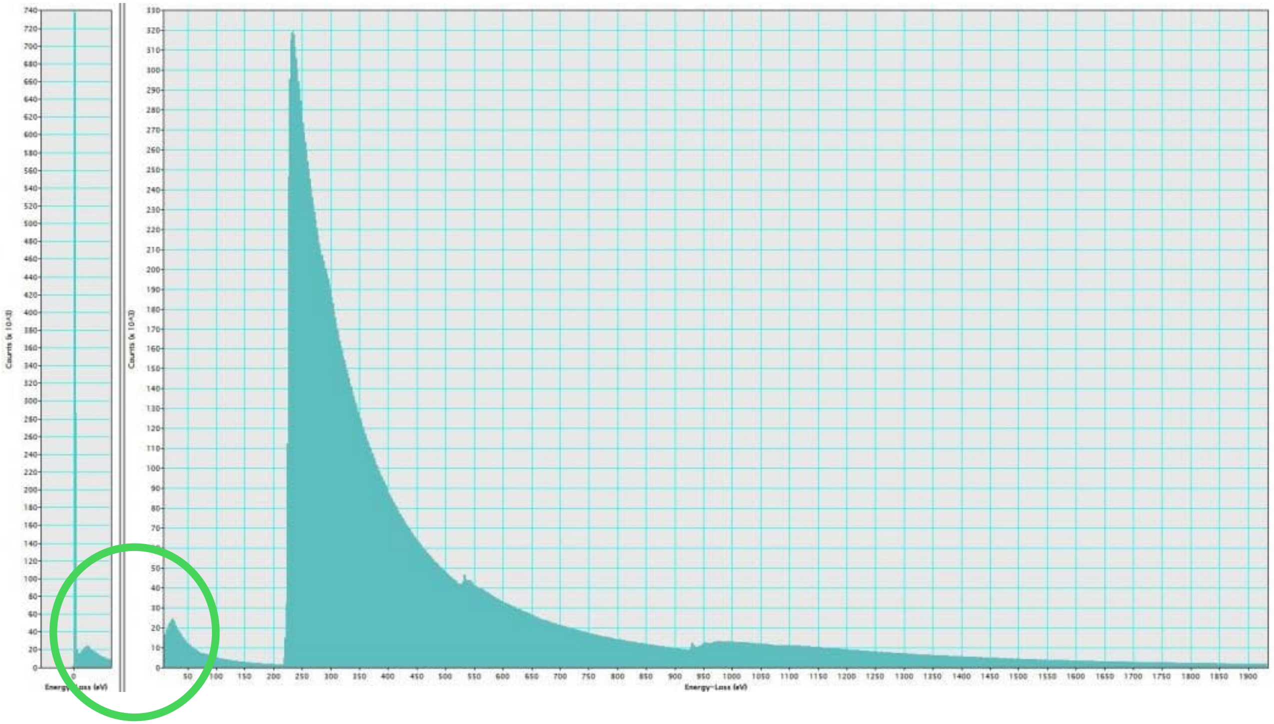
EELS atlas, EELS.info, Gatan corporate, [EELS Atlas | EELS.info]

EELS Spectrum

Cu



CuO

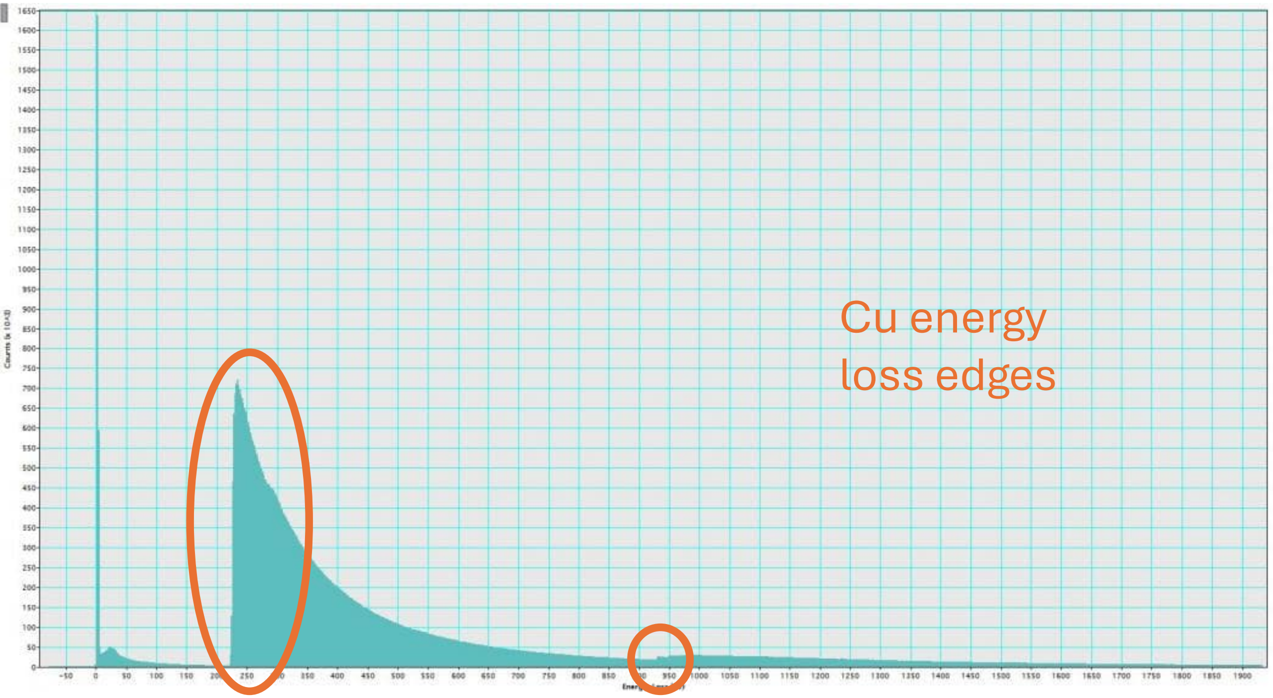


Plasmon peaks

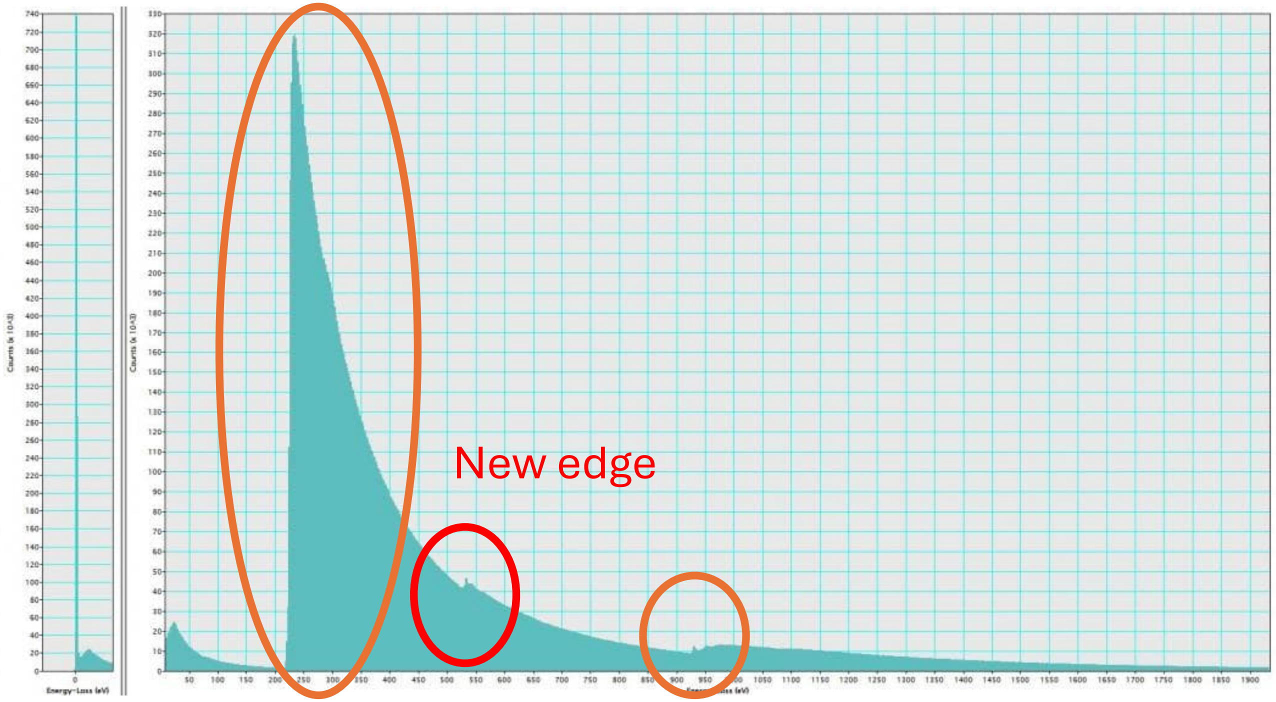
EELS atlas, EELS.info, Gatan corporate, [EELS Atlas | EELS.info]

EELS Spectrum

Cu



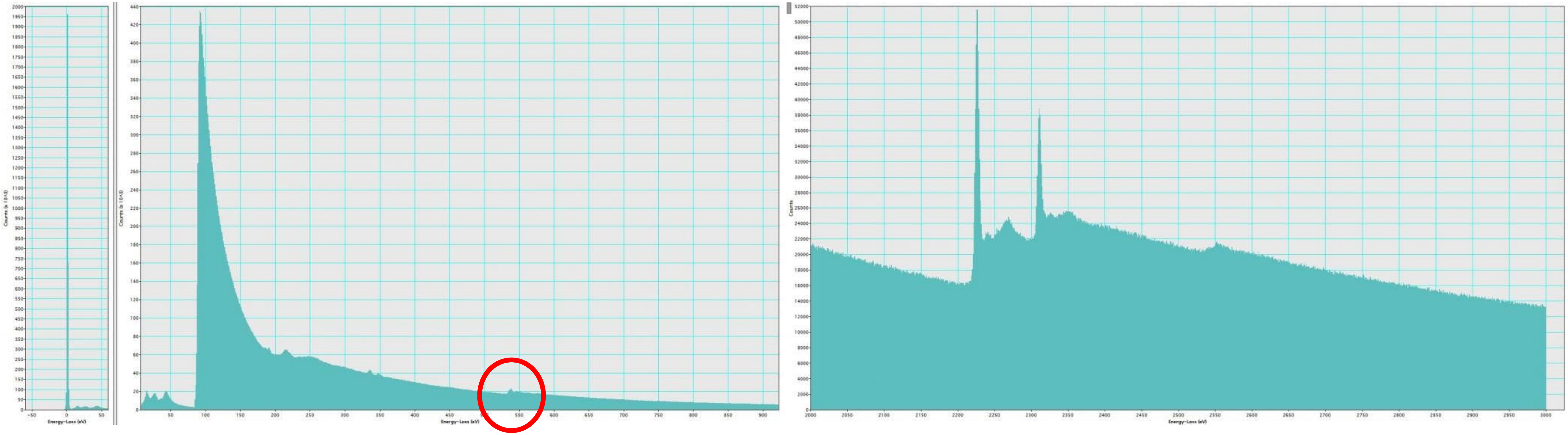
CuO



EELS atlas, EELS.info, Gatan corporate, [EELS Atlas | EELS.info]

EELS Spectrum

ZrO_2



EELS atlas, EELS.info, Gatan corporate, [EELS Atlas | EELS.info]

What we can get

- Elemental composition
- Sample thickness
- Chemical environment (EXELFS)
- Oxidation states (ELNES)
- Valence electron density (VEELS)

Elemental Composition

- Qualitative: characteristic edges for elements
- Quantitative:
  - Pick two edges of the same shell to compare (for different elements)
  - Remove background
  - Get the area of the (now) peak (by integrating)
  - Peak areas reflect atom density (more of the element -> more scattering)
  - Fit reference spectra (B_a, B_b)
  - Element-element ratio: $\frac{N_a}{N_b} = \frac{B_a I_{ka}(\beta, \Delta)\sigma_{kb}(\beta, \Delta)}{B_b I_{kb}(\beta, \Delta)\sigma_{ka}(\beta, \Delta)}$
- Small and noisy edges are difficult

Sample thickness

- If independent scattering events ⇒ Poisson distribution
- Average scattering events per electron: $\frac{t}{\lambda} = \ln \frac{I_{\mathrm{total}}}{I_0}$
- Approximation of mean free path λ
- Other, more complicated, methods exist

Extended Energy-Loss Fine Structure (EXELFS)

- Same as EXAFS
- Choose edge
- Remove background
- Remove smooth edge structure
- Transform energy loss to electron wave number k
- Weigh by k^n
- Preform Fourier transform
- Curve-Fitting for coordination environment
  - $\chi(k) = \sum_j \frac{N_j}{r_j^2} \frac{f_j(k)}{k} e^{-\frac{2r_j}{\lambda_i} - 2\sigma_j^2 k^2} \sin\left(2kr_j + \phi(k)\right)$

Energy-Loss Near-Edge Structure (ELNES)

- Same as XANES
- Element oxidation state
- Energy loss from electron excitations
- Reflects the available excitation paths and thus the occupied/unoccupied orbitals
- Valence state induction from edge positions

Valence Electron Energy-Loss Spectroscopy (VEELS)

- Low loss region: Plasmon peaks
- Possible to identify materials with reference spectra if the plasmon peaks are sharp enough
- Possible plasmon excitation energies from peak position
- Plasmon damping effects from peak width
- Material band gap theoretically obtainable

Together with STEM

- Unique contrast effects
- Elemental maps
- Zero- and Low-loss images
- Etc.
- Points of interest to measure

Pros and Cons

Pros

- High resolution
- Various information gained and multitude of uses
- Works well together with TEM
- No synchrotron needed

Cons

- Requires TEM setup
  - High vacuum, electron optics, etc.
- Sample preparation
  - Thin, electron transparent (same as TEM)
- Difficulty of quantitative analysis, reference heavy

Research Example #1

Journal of Power Sources 354 (2017) 41–47

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

ELSEVIER

High-power durability of $LiCoO_2$ thin film electrode modified with amorphous lithium tungsten oxide

CrossMark

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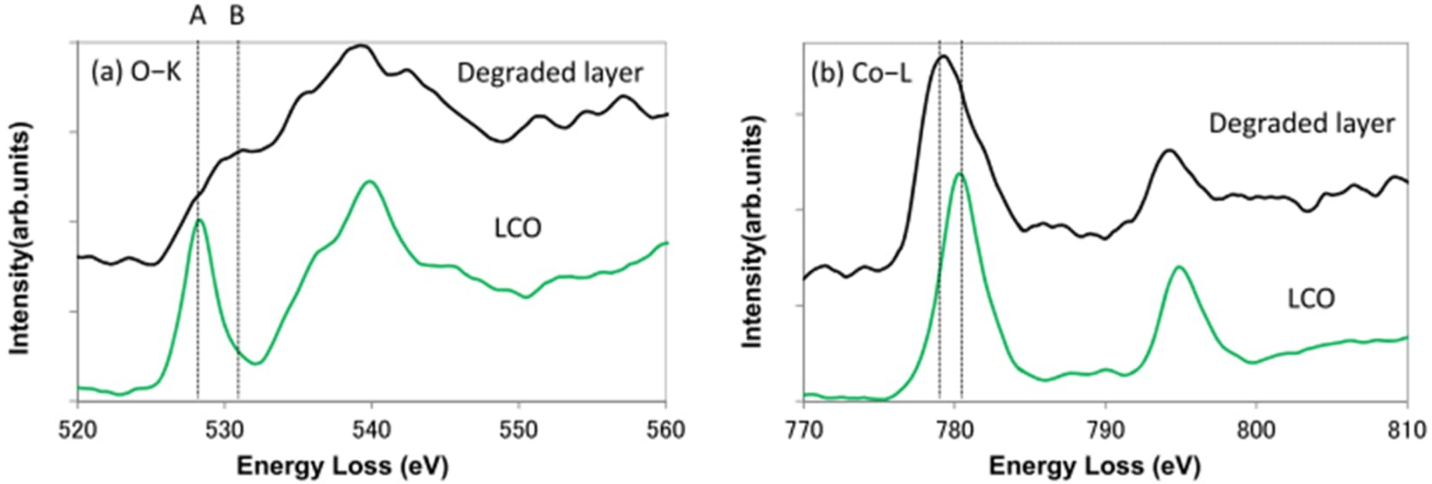
High-power durability of $LiCoO_2$ thin film electrode modified with amorphous lithium tungsten oxide

- Amorphous Li_2WO_4 on $LiCoO_2$ electrode
  - Li_2WO_4 Li-ion conductive
  - Can protect the electrode from the electrolyte
- Only done under very controlled environment
- Effects of moist air on Li_2WO_4 coated $LiCoO_2$
- EELS (and XPS) for composition and contaminations
  - Spots to measure with STEM
  - 2 nm thick layer

T. Hayashi, Y. Matsuda, N. Kuwata, and J. Kawamura, "High-power durability of LiCoO2 thin film electrode modified with amorphous lithium tungsten oxide," *Journal of Power Sources, vol. 354, pp. 41-47, 2017/06/30/ 2017, doi: 10.1016/j.jpowsour.2017.04.036.*

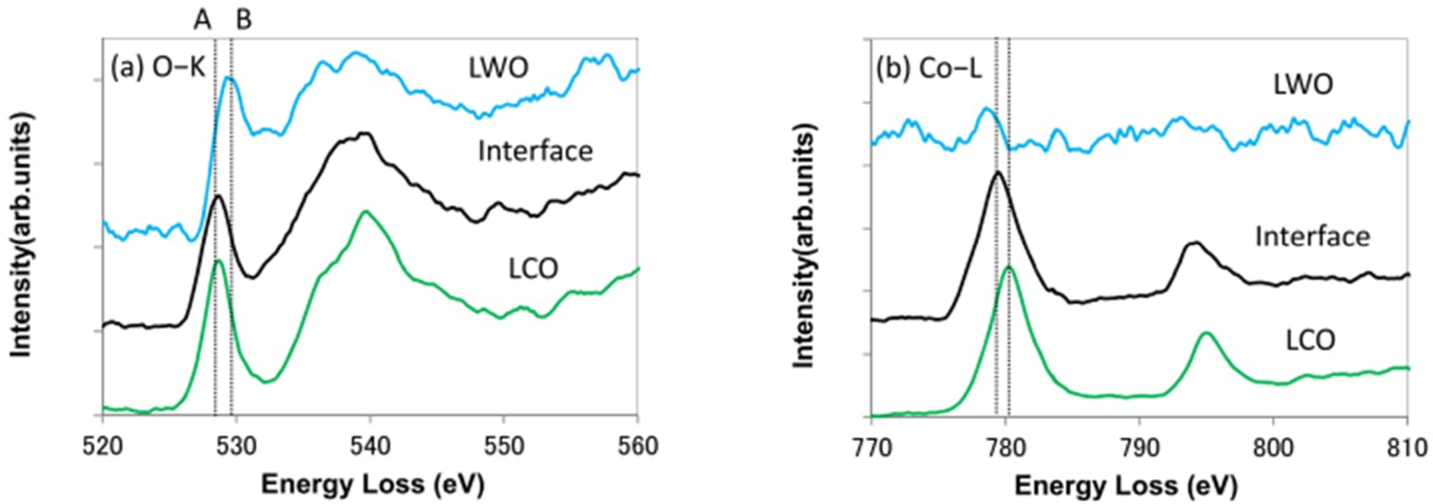
High-power durability of $LiCoO_2$ thin film electrode modified with amorphous lithium tungsten oxide



- Layer on $LiCoO_2$ after electrochemical tests
- B: CoO peak
- Co-L peak shifts to lower energy -> valence reduction from 3+

T. Hayashi, Y. Matsuda, N. Kuwata, and J. Kawamura, "High-power durability of LiCoO2 thin film electrode modified with amorphous lithium tungsten oxide," *Journal of Power Sources, vol. 354, pp. 41-47, 2017/06/30/ 2017, doi: 10.1016/j.jpowsour.2017.04.036.*

High-power durability of $LiCoO_2$ thin film electrode modified with amorphous lithium tungsten oxide



- Interface between $LiCoO_2$ and Li_2WO_4 after electrochemical tests
- A, and Co-L energy shift -> Li deficient phase
  - $Li_{1-x}CoO_{2-y}$

Research Example #2

Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

PAPER

Check for updates

Cite this: *Dalton Trans.*, 2017, **46**, 4796

Atomic layer deposition of nickel–cobalt spinel thin films

D. J. Hagen, T. S. Tripathi and M. Karppinen *

We report the atomic layer deposition (ALD) of high-quality crystalline thin films of the spinel-oxide system $(Co_{1-x}Ni_x)_3O_4$. These spinel oxides are ferrimagnetic p-type semiconductors, and promising material candidates for several applications ranging from photovoltaics and spintronics to thermoelectrics. The spinel phase is obtained for Ni contents exceeding the $x = 0.33$ limit for bulk samples. It is observed that the electrical resistivity decreases continuously with x while the magnetic moment increases up to $x = 0.5$. This is in contrast to bulk samples where a decrease of resistivity is not observed for $x > 0.33$ due to the formation of a rock-salt phase. From UV-VIS-NIR absorption measurements, a change from distinct absorption edges for the parent oxide Co_3O_4 to a continuous absorption band ranging deep into the near infrared for $0 < x \leq 0.5$ was observed. The conformal deposition of dense films on high-aspect-ratio patterns is demonstrated.

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DOI: 10.1039/c7dt00512a

rsc.li/dalton

Atomic layer deposition of nickel–cobalt spinel thin films

- Semiconducting thin films from available elements
  - Applications: Transparent conductors, photocatalysts, thermoelectric generators, electrodes
- P-type oxides have low conductivity
- $(Co_{1-x}Ni_x)_3O_4$, $x \in [0, 1]$ was investigated
- ALD for deposition
- EELS for determining the mean oxidation state of Co

D. J. Hagen, T. S. Tripathi, and M. Karppinen, "Atomic layer deposition of nickel–cobalt spinel thin films," *Dalton Transactions, 10.1039/C7DT00512A vol. 46, no. 14, pp. 4796-4805, 2017, doi: 10.1039/C7DT00512A.*

Atomic layer deposition of nickel–cobalt spinel thin films

- Relativistic quantum chemistry
  - Energy difference in p-orbitals
  - L = 2nd electron shell
  - Assumption: $L_1 = 2s$, $L_2 = 2p_{1/2}$, $L_3 = 2p_{3/2}$
- Figure: 2p electrons excited to 3d
- Empirical:
  - $\frac{L_3}{L_2} \approx 4.8$ for Co^{3+}
  - $\frac{L_3}{L_2} \approx 3.3$ for $Co^{2.67+}$
- $\frac{L_3}{L_2} = 3.5$ => Oxidation < 3+

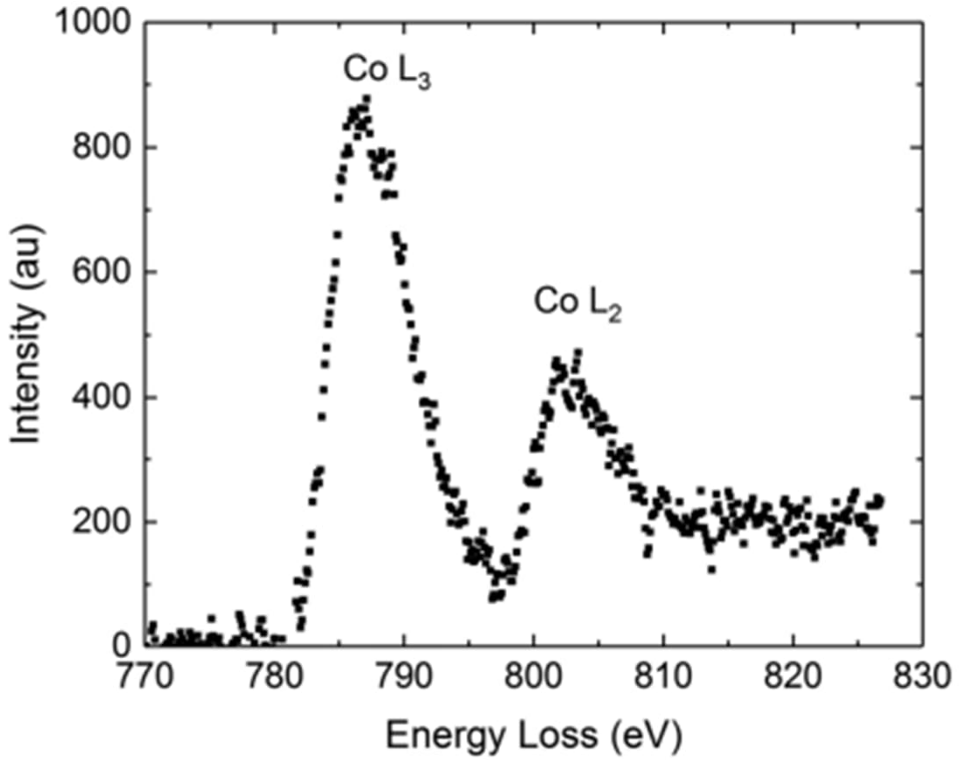

Fig. 4 EELS graph for the $(Co_{1-x}Ni_x)_3O_4$ film with x = 0.33: the ratio of the Co L_3 and L_2 peaks strongly indicates a valence lower than +3.

D. J. Hagen, T. S. Tripathi, and M. Karppinen, "Atomic layer deposition of nickel–cobalt spinel thin films," *Dalton Transactions, 10.1039/C7DT00512A vol. 46, no. 14, pp. 4796-4805, 2017, doi: 10.1039/C7DT00512A.*

Research Example #3

Microsc. Microanal. 20, 1246–1253, 2014
doi:10.1017/S1431927614000543

Microscopy and Microanalysis

Local Band Gap Measurements by VEELS of Thin Film Solar Cells

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[4]*Institut für Festkörperphysik, TU Dresden, D-01062, Germany*

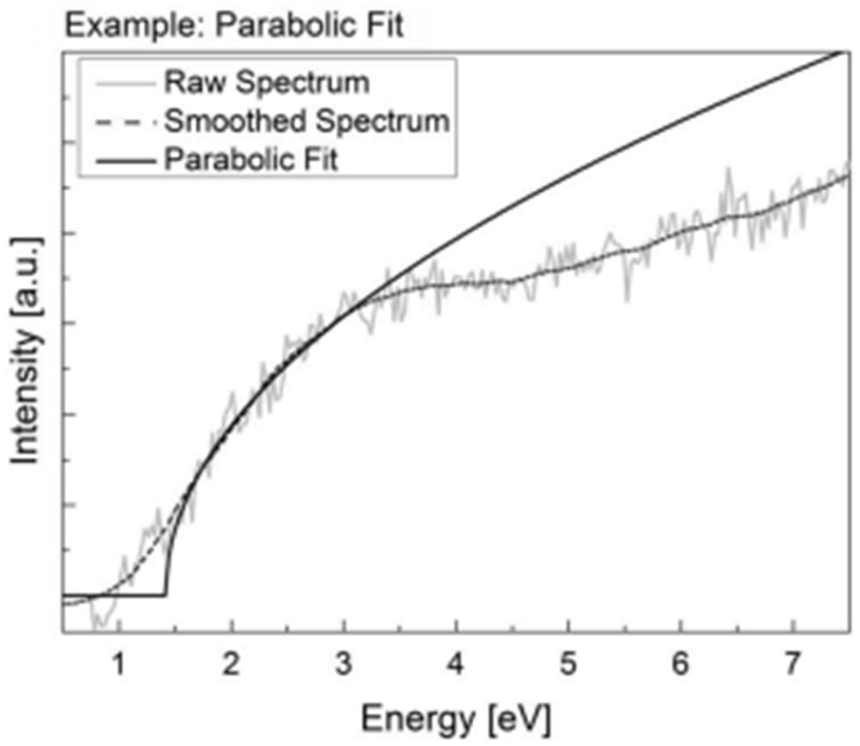
Local Band Gap Measurements by VEELS of Thin Film Solar Cells

- VEELS for local band gap measurements
  - For solar cells
- $Cu(In, Ga)Se_2$ with varying Cu, In and Ga
- Two methods:
  - “Parabolic fit”
  - “Inflection point”

D. Keller *et al., "Local Band Gap Measurements by VEELS of Thin Film Solar Cells," Microscopy and Microanalysis, vol. 20, no. 4, pp. 1246-1253, 2014, doi: 10.1017/S1431927614000543.*

Parabolic fit

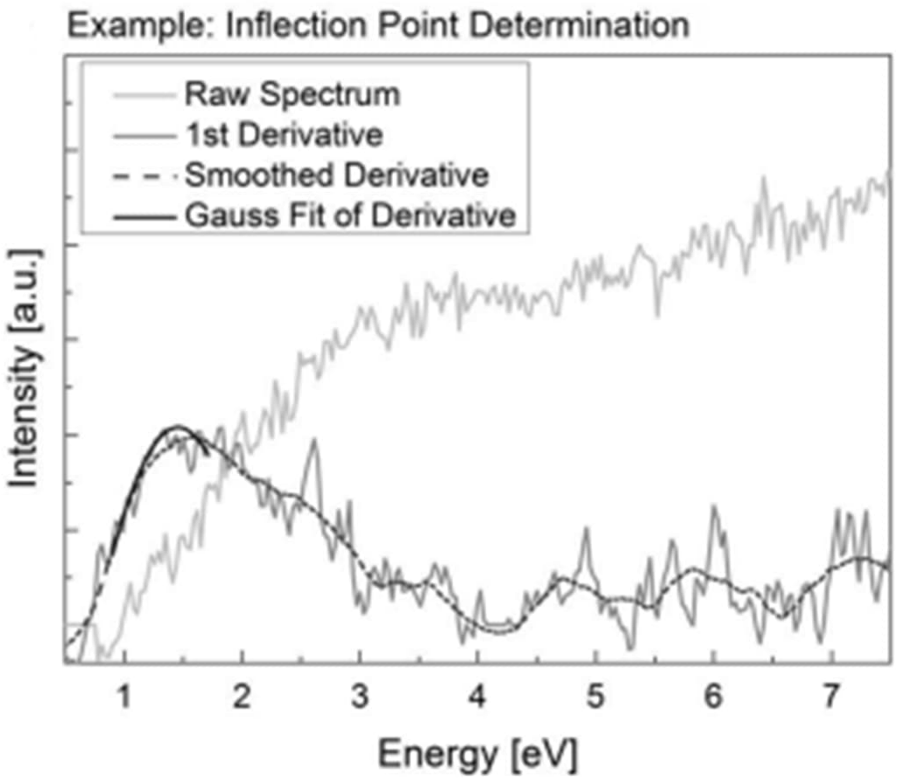
- Parabolic start for direct band gap semiconductors.
- Parabola, opening right, fitted
- Parabola-energy axis intersection gives the band gap



D. Keller *et al.*, *"Local Band Gap Measurements by VEELS of Thin Film Solar Cells," Microscopy and Microanalysis, vol. 20, no. 4, pp. 1246-1253, 2014, doi: 10.1017/S1431927614000543.*

Inflection point

- The first maximum of the derivative gives the band gap.
- Three different ways tried



D. Keller *et al.*, *"Local Band Gap Measurements by VEELS of Thin Film Solar Cells," Microscopy and Microanalysis, vol. 20, no. 4, pp. 1246-1253, 2014, doi: 10.1017/S1431927614000543.*

Local Band Gap Measurements by VEELS of Thin Film Solar Cells

- Issues in reproducing results -> high error
- Both methods overestimated the band gap.
  - Measured composition beforehand
- Possible reasons:
  - Sample damage (from 300 keV electron beam)
  - Too much noise
  - Measurement too sensitive to local structure

D. Keller *et al.*, *"Local Band Gap Measurements by VEELS of Thin Film Solar Cells," Microscopy and Microanalysis, vol. 20, no. 4, pp. 1246-1253, 2014, doi: 10.1017/S1431927614000543.*

Further information

- Gatan corporate: EELS.info
- R. F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope.* Springer New York, NY, 2011.
    - More than you would ever want to know about EELS

Here’s another eel

Reedfish
Michal Zalewski 2006
Wikipedia