EELS: Electron Energy-Loss Spectroscopy

- avoid confusion with “EELS” of surface science techniques (meV energy losses of electrons reflected at surfaces in UHV)

- EELS in the TEM:
  - complimentary to XEDS
  - however: no “routine” method – interpretation less straight forward
  - on the other hand: more information (local composition, oxidation state, interatomic bonding, local density of state, band gaps)

- principle of an EELS spectrometer for TEM (magnetic prisma):
• requirements:
  – energy-discriminating ray path → energy-dispersive plane
  – focus all electron of the same kinetic energy on one line (independent of the angle their path makes with the optic axis)
    → “lens”, rounded surfaces at entrance an exit plane
  – conjugate plane of the energy-dispersive plane:
    · TEM: back focal plane of the projective lens (⇒ spectrometer largely independent of microscope settings)
    · DSTEM: plane of the object (⇒ align specimen height)
    ⇒ focus spectrometer

• realization (GATAN 666 PEELS, “parallel” EELS spectrometer)

• only one manufacturer (GATAN)

• evaluation of spectra requires computer system with adequate software (EL/P, GATAN)
SEELS und PEELS

- formerly: serial EELS spectrometers → SEELS
  - detector: slit + scintillator + photo-multiplier
  - “ramp” magnetic field
  - inefficient: drift, contamination
• later development: parallel EELS spectrometer → PEELS

- detector: diode array
- 100- to 1000 times more efficient than SEELS
EELS in TEM-Image and TEM-Diffraction Mode

• remember:
  – the conjugate plane of the energy-dispersive plane in the spectrometer is the back focal plane of the projective lens
  ⇔ the “object” of the spectrometer is the intensity pattern in the back focal plane of the projective lens

• TEM imaging mode:
  – image on the TEM screen
  ⇒ diffraction pattern at the back focal plane of the projective lens
  ⇒ spectrometer “views” a diffraction pattern, “diffraction coupling”

• TEM-diffraction mode:
  – diffraction pattern on the TEM screen
  ⇒ image at the back focal plane of the projective lens
  ⇒ spectrometer “views” an image, “image coupling”

Parameters Characterizing an EELS Spectrometer

• dispersion
  – definition: \( \frac{dx}{dE} \)
    
    \( x \): spatial coordinate in the energy-dispersive plane; \( E \): energy of the electron.
  – dispersion varies with
• energy of the primary electrons
• strength of the magnet in the prism

– typical value of the dispersion for SEELS:

\[
\frac{dx}{dE} \approx 2 \ \mu m/eV
\]

– PEELS: larger (≈ 1,5 μm/eV)

• energy resolution ΔE

– definition: ΔE equals full width at half of the maximum that corresponds to the primary electrons (FWHM of zero-loss peak)

→ focus (!) spectrometer to back focal plane of the projective lens (or plane of the object in STEM)

– ΔE depends on the electron source of the microscope (ΔE[W] > ΔE[LaB₆] > ΔE[FEG])

– example: for cold FEG, ΔE can be as small as ≈ 0,3 eV

– energy resolution drops with increasing energy loss of the electrons being analyzed

• point-spread function

– cross-talk of the YAG scintillator in the PEELS

– example: even if the width of the zero-loss maximum corresponds to only one channel, a signal also appears in neighboring channels

→ “delocalization” of information in the EELS spectrum

• spectrometer collection semiangle, β

– definition:
• most important parameter (for example, when comparing spectra)

- large collection angles $\beta$ will give high intensity in the spectrum

- $\beta$ depends on the mode of the microscope:
  - DSTEM:
    
    $$\beta = \frac{d}{2h}$$

  - TEM:
    
    - TEM imaging mode $\Leftrightarrow$ spectrometer “views” diffraction pattern
    - entrance aperture $\Leftrightarrow$ objective aperture
    - “without” objective aperture $\Rightarrow \beta \approx 100$ mrad
– with objective aperture
(spurious Bremsstrahlung excludes simultaneous XEDS!):

\[ \beta = \frac{\beta_{\text{Ob}}}{M} \]

\( \beta \): aperture semiangle at the objective lens; \( M \): magnification.
- TEM-diffraction mode $\Leftrightarrow$ spectrometer “views” image

specimen

$f \approx 3\text{mm}$

objective aperture

intermediate lens(es)

projector lens

back focal plane of projector lens, IMAGE

diffraction pattern

d_{\text{eff}}

effective spectrometer entrance aperture

d_{\text{eff}}$

$\beta$

$D$

$D$

$hkl$

CBED disks

$2\alpha$

$2\beta$

$2\beta_B$
– in this case,

\[ \beta = \frac{d_{\text{eff}} \cdot 2 \theta_B}{2R} \]

– large aperture (high intensity, large \( \beta \)) degrades the energy resolution

• spatial resolution

– depends on operating mode (TEM imaging or TEM diffraction)

– TEM imaging mode: origin of the signal corresponds to the demagnified image of the spectrometer aperture in the object plane

– example:
  - magnification 100.000 \( \times \)
  - aperture of the EELS spectrometer = 1 mm
  \[ \Rightarrow \] diameter of the object area contributing to the spectrum: 10 nm

– however: at large energy losses the chromatic aberration of the objective lens introduces contributions from object regions outside of this region (typical offset: 100 nm)

\[ \Rightarrow \] TEM imaging mode is appropriate for recording EELS spectra with large acceptance angle \( \beta \) and high energy resolution; the spatial resolution, however, may be only moderate

– for highest spatial resolution use TEM-diffraction mode!
  (resolution \( \leftrightarrow \) beam diameter at the specimen)

– TEM: limit the region that contributes to the EELS spectrum by means of the area-selecting aperture (SAD aperture in the image plane of the intermediate lens)

– DSTEM: focused electron beam, limits the object region that contributes to the spectrum

– feasible: spatial resolution approaching single atomic columns
EELS Spectra

- processes of inelastic electron scattering, ordered according to probability / increasing energy loss:

<table>
<thead>
<tr>
<th>process</th>
<th>energy loss $E$ [eV]</th>
<th>scattering angle $\theta_E$ [mrad]</th>
</tr>
</thead>
<tbody>
<tr>
<td>phonons</td>
<td>$\approx 0.02$</td>
<td>5-15</td>
</tr>
<tr>
<td>intraband transitions</td>
<td>5-25</td>
<td>5-10</td>
</tr>
<tr>
<td>plasmons</td>
<td>5-25</td>
<td>$&lt;0.1$</td>
</tr>
<tr>
<td>ionization</td>
<td>10-1000</td>
<td>1-5</td>
</tr>
</tbody>
</table>

- scattering angle $\theta_E$ (semitangle of scattering cone) varies with energy $E$ of the electrons and with the energy loss, $E$:

$$\theta_E = \frac{E}{2E} = \sqrt{1 - \frac{v^2}{c^2}}$$

$E$: energy loss; $E$: total energy of the primary electrons (rest energy + kinetic energy); $m_0$: rest mass of the electron; $v$: velocity of the electron; $c$: velocity of light (vacuum).

The Zero-Loss Peak

- main feature in EELS spectra of thin specimens

- originates from electrons that have lost no energy on their way through the specimen (except for small losses owing to phonon scattering)
• corresponds to undiffracted beam in the diffraction pattern (Bragg reflections do not contribute to the EELS spectrum, owing to the large diffraction angles)

• width of the zero-loss peak: energy spread of the electron source (thermal emitter, field-emission gun)

• zero-loss peak contains no analytical information about the specimen

Low-Loss Region

• energy losses up to 50 eV

• reflects excitation of
  – plasmons
  – interband transitions
**Plasmons**

- dominant in materials with "weakly bound", "quasi-free" electrons

→ pronounced plasmon peaks from metals
   (however also from polymers – not understood yet)

- plasmonen energy:
  \[ E_P = \frac{h}{2\pi} \omega_P = \frac{h}{2\pi} \sqrt{\frac{nen^2}{\epsilon_0 m}} \]

  \(\omega_P\): Plasmonenfrequenz; \(n\): lokale Dichte schwach gebundener Elektronen; \(\epsilon_0\): Influ-
  enzkonstante; \(m\): Elektronenmasse; \(e\): Elementarladung; \(h\): Planck-Konstante.

→ depends on local density \(n\) of weakly bound electrons
  - varies with composition
  - use for microanalysis

- consider plasmons in the interior of a material (longitudinal charge-
  density waves)

- however: excitation of plasmons at the surface of the TEM specimen can
  play a role, too (transversal charge-density waves)

- typical lifetime of plasmons: \(10^{-15}\) s

→ localized to \(\approx 10\) nm

- mean free path length for electron scattering at plasmons: \(\approx 100\) nm

→ plasmon losses always occur – except, maybe, in ultra-thin specimens
• thicker samples: multiple plasmon losses interfere with straightforward interpretation of the EELS spectrum

• example: Al
in general: easiest interpretation of for single electron scattering
⇒ thin TEM specimen!

**Band-Band Transitions**

- interband transitions
- intraband transitions

- “one electron” interaction with small energy losses
  ⇒ excitation of an electron to an orbital of higher quantum number

- typical energy loss of the primary electron: 25 eV

- example: electron energy losses at π-orbitals of carbon molecules produce characteristic “fingerprint” in the EELS spectrum

- physical understanding still underdeveloped

- quantitative predictioin of the EELS spectrum in the low-loss region not yet possible

- fingerprints: “EELS-Atlas” (library of spectra)

- enables identification of characteristic features in the low-loss region of the spectrum
- example:
  Al atoms in different environments

![Graph showing energy loss for different substances](image)

- excitation that frees a weakly bound electron from the coulomb field of the atomic nuclei:
  - secondary electron
  - typical energy loss of the primary electron: $E < 20\,\text{eV}$

- outer electrons determine the "response" of the material to an outer electrical field
→ typical excitations in the region $E<10\,\text{eV}$ of the EELS spectrum

→ information about the dielectric function

**High-Loss Region**

• energy losses $E>50\,\text{eV}$

• remember: the closer a primary electron approaches the nucleus of an atom, the larger can be the energy loss during inelastic scattering

→ $E>50\,\text{eV}$ ↔ inelastic scattering in *inner* regions of atoms

• in particular: ionisation of inner shells (K, L, M, …)

⇒ element-characteristic energy losses → ATEM

• advantage of EELS versus XEDS:
  – energy loss of the primary electron does not depend on the way in which the atom returns to the ground state

⇒ unlike XEDS, detection of inner-shell ionization by EELS does not depend on fluorescence yield (ratio of X-ray emission and emission of Auger electrons)

⇒ suitable to detect *light* elements

• inner-shell ionization

  ⇒ EELS spectrum features “absorption edges”
- examples of absorption edges:

![Graphs showing examples of absorption edges](image1)

- EXELFS
- ELNES
- ionization + plasmons
- increased background
• absorption edges:
  – onset energy ↔ *minimum* energy transfer $E = E_c$ for ionization
    (binding energy of the inner-shell electron to the nucleus of atom)
  – at this energy the scattering cross-section reaches its maximum
  – however, ionization occurs also with larger energy losses: $E > E_c$
  – scattering cross-section decreases with increasing energy loss $E$
    ⇒ intensity of the absorption edge *decreases* with increasing energy loss

• nomenclature of absorption edges (or “ionization” edges):
• background
  – origin:
    · *multiple* inelastic electron scattering
    · extension of previous absorption edges
  – decays rapidly (power law)

• absorption edges feature *fine structure*
  – from $E = E_c$ to $E_c + 50 \text{ eV}$ (by definition): *near-edge structure*
    $\rightarrow$ ELNES, “electron loss near-edge structure”
    $\rightarrow$ information on local density of empty states, oxidation state, …
  – $E > E_c + 50 \text{ eV}$: extended fine structure
    $\rightarrow$ EXELFS, “extended energy-loss fine structure”
    $\rightarrow$ information on local coordination of the respective atom
  – multiple inelastic scattering
    · ionization followed by plasmon scattering
      $\rightarrow$ modulation at $E_c + 15..25 \text{ eV}$

\[
\begin{array}{c}
N \\
\hline
\text{ELNES} \quad \text{EXELFS} \\
\begin{array}{c}
\text{plasmons} \\
50 \text{ eV}
\end{array}
\end{array}
\]
• correlation between ELNES and electron band structure?

• example: NiO

⇒ electron-loss near-edge structure (ELNES):
  − probes local density of unoccupied states (DOS)
  − example NiO:
    • $L_2$ and $L_3$ yield two sharp maxima ("white lines")

⇔ empty 3d states
– counterexample: metallic Cu
  · 3d states occupied
  · no white lines

⇒ advantage of EELS versus XEDS:
  – more information
  – enables not only identification of elements and quantification of local composition, but also analysis of electronic structure (density of empty states, oxidation state, local coordination, bandgap, …)
  – disadvantage: interpretation of EELS spectra can be difficult
    · absorption edges have complex shape
    · quantification of local concentrations requires evaluation of extended absorption edges, which typically have a complex shape
    · problems: rapid variation of the background, overlap of absorption edges

• further advantage of EELS: more efficient than XEDS
  – typical inner-shell energy loss: $E \approx 1000$ eV

⇒ $\theta_E \approx 5$ mrad for 100 keV electrons
  (see expression for $\theta_E$ above)

  – compare plasmons: 10-15 mrad
  – phonon scattering and elastic scattering: scattering angles much larger

⇒ electrons with energy losses by inner-shell ionization or plasmon scattering:
  scattering mainly in forward direction
– scattering mainly in *forward* direction enables much more *efficient* detection than with XEDS:

• further example: EELS spectrum of BN (boron nitride)
Qualitative EELS

- interpretation of EELS spectra is often more difficult than in XEDS
- evaluation of EELS spectra is less straight-forward than in XEDS

Optimization of experimental parameters

- with increasing accelerating voltage
  - the scattering cross-section for ionization decreases
  $\Rightarrow$ signal decreases – but background decreases even quicker!
  $\Rightarrow$ to maximize the signal-to-background ratio, increase the accelerating voltage
- convergence semiangle $\alpha$ of the primary electron beam
  - only matters if $\alpha > \beta$ (acceptance angle of the spectrometers)
  - no problem in TEM-diffraction mode
  - TEM-image mode with $\alpha > \beta$:
    quantification requires correction factor for ionization cross-section
- beam diameter and beam current:
  - trade-off between spatial resolution and signal-to-noise ratio
- specimen thickness
– thick specimens ⇒ multiple scattering, quantification requires deconvolution of spectrum (⇒ loss of information)
⇒ specimen should be as thin as possible!

• acceptance angle $\beta$ of the spectrometer
  – trade-off between intensity, spatial resolution, and energy resolution
  – $\beta$ large in TEM-image mode, small in TEM-diffraction mode
    (controlled by entrance aperture)

• energy resolution
  – limited by energy spread of the electron source
  – field-emission gun better than thermal emitter
  – cold FEG better than Schottky emitter

• indicator of spectrum quality: “jump ratio”

– jump ratio should exceed 5 for C K edge (film thickness $\approx$ 50nm)
Qualitative Interpretation of EELS Spectra

- EELS spectra hardly feature artifacts one could misinterpret as ionization edges (≠ XEDS)

- compare spectrum with reference spectra (EELS Atlas)

- edges must occur in families
  (corresponding to families of peaks in XEDS)

- for quantification choose K or L edges
  (for elements with atomic numbers below 13 (Al) the spectrum only feature K edges)

- problem: onset energy $E_c$ of edges often not sharp, particularly for M, N, and O edges
Quantitative EELS

- consider: K edge of an element in an EELS spectrum (special case, but method works in general)
- intensity $I_K$ above the background follows from incident intensity $I_T$ by multiplication with the ionization probability $P_K$:
  $$I_K = P_K I_T$$
- this equation neglects that fact that one only detects electrons in a limited solid angle
- assumption: only single inelastic scattering
- this leads to the Ansatz
  $$P_K = N \sigma_K \exp \left[ \frac{t}{\lambda_K} \right]$$

$\sigma_K$: ionization cross-section of the K shell; $\lambda_K$: mean free path length for inelastic scattering; $N$: specimen atoms per unit area in the projection; $t$: specimen thickness.
- assume that mean free path length $\lambda_K$ is large compared to the specimen thickness $t$; required to justify assumption of single inelastic scattering
  $$\Rightarrow$$ the exponential function adopts a value close to 1 an, such that gild:
  $$I_K \approx N \sigma_K I_T$$
- this implies
  $$I_K = P_K I_T$$
• this means: one can determine the number density $N$ of atoms (in the illuminated region and projected to two dimensions) by
  – measuring the intensity $I_K$ of the K edge above the background,
  – dividing this intensity by the total intensity $I_T$, and
  – dividing by the ionization cross-section, $\sigma_K$

• to quantify the relative amounts of only two elements A and B, one does not need to know the total intensity:

\[
\frac{N_A}{N_B} = \frac{I_K^A \sigma_K^B}{I_K^B \sigma_K^A}
\]

• corresponding expressions describe the concentration ratio of A and B to other elements or the intensity ratios between different ionization edges of the same element

• problems
  – background not precisely known
  – integration of intensity in absorption edges only possible over a limited range $\Delta$ of energies; typical width: $\Delta \approx 50$ eV

• this leads to

\[
I_K[\Delta] = N\sigma_K[\Delta]I_l[\Delta]
\]

• in this equation, $I_T$ was replaced by $I_l$, the intensity in an energy window of finite width $\Delta$, which includes the zero-loss region and part of the low-loss region

• moreover, detection of electrons is limited to a limited solid angle $\beta$, thus:
\[ I_K[\beta \Delta] = N \sigma_K[\beta \Delta] I_l[\beta \Delta] \]

\( \sigma_K[\beta \Delta] \): “partial” ionization cross-section.

- this leads to the following expression for the concentration ratio of two elements, A and B:

\[
\frac{N_A}{N_B} = \frac{I^K_A[\beta \Delta]}{I^K_B[\beta \Delta]} \frac{\sigma_K^B[\beta \Delta]}{\sigma_K^A[\beta \Delta]}
\]

\( \rightarrow \) the ratio

\[
\frac{\sigma_K^B[\beta \Delta]}{\sigma_K^A[\beta \Delta]}
\]

of the partial cross-sections corresponds to the \( k \) factor in XEDS

- experimental experience:
  - requirement of single inelastic scattering is easy to fulfill
  - however: already for relatively thin TEM specimens, multiple scattering becomes an issue (10..20% error owing to multiple scattering)
  - thicker specimens: “de-convolute” spectrum

**Background Subtraction**

- origin of background:
  - multiple scattering
  - extension of absorption edges with onset at lower energies
• so far, there is no physical theory to predict the background (corresponding to the Kramers relation in XEDS)

→ phenomenological description

• methods of background subtraction:
  – fit an analytical function to the experimentally observed background
  – differentiate

Background subtraction by Fitting an Analytical Function

![Background subtraction diagram]

• Ansatz for function describing the background:

\[ I_U = A \cdot E^{-r} \]

E: energy loss; \( I_U \): background intensity in the channel that corresponds to the energy loss \( E \); \( A, r \): fitting parameters, depending on \( E \) (!).
• exponent parameter $r$:
  – typical value: between 2 and 5
  – decreases with increasing specimen thickness $t$
  – decreases with increasing acceptance angle $\beta$ of the spectrometer
  – decreases with increasing energy loss $E$

• intensity variation of absorption edges can be described accordingly:

\[ I_A = B \cdot E^{-s} \]

• however: power law with constant parameters matches the true intensity variation only across small energy intervals $[E_1, E_2]$

• the width $\Delta$ of the energy window $[E_1, E_2]$ should be small enough to satisfy $E_2 / E_1 < 1.5$

• example Ni-L$_{2,3}$ edge:
Background Subtraction by Differentiation

- corresponds differentiation of the EELS spectrum

- record two spectra with small relative shift along the energy axis (relatively simple with PEELS)

- difference of the two spectra
  - vanishes in regions of slow intensity variation → background
  - regions of rapid variation appear as maxima → edges

- example: background subtraction in the EELS spectrum of Al–Li
Integration of Absorption Edges

- method depends on method of background subtraction
  - background subtraction differentiation: comparison with reference spectra (library)
  - background subtraction by fitting an analytical function: proceed as follows

- energy window $\Delta$ for background subtraction should not be too large

- often the onset of subsequent absorption edges limits the width of the energy window $\Delta$

- normally, one chooses $E_1 = E_c$

- exception: pronounced pre-edge structure or ELNES (is not accounted for in present theories of ionization cross-section)

- *absolute* quantification of atom number $N \Rightarrow$ determine $I_1$ by integrating over the zero-loss peak and the low-loss region for determining a concentration *ratio*, $I_1$ is not required

Determination of the Partial Scattering Cross-Section $\sigma$

- “sensitivity factor”: ratio of the partial scattering cross-sections $\sigma[\beta \Delta]$ the two elements A and B possess for ionization (corresponds to $k$ factor in XEDS)

- determine $\sigma[\beta \Delta]$
  - theoretically (computer programs SIGMAK and SIGMAL)
– experimentally, by comparing the experimental EELS spectrum with standard spectrum

• model on which the programs SIGMAK and SIGMAL are based:
  – consider the respective atom of atomic number $Z$ as H atom with charge $Z$ in the nucleus, but without outer electrons
  – owing to the neglect ion of the outer electrons this theory is best suited for describing K edges
  – this Ansatz does not allow for any fine structure of absorption edges
  → if the experimentally observed edge actually possesses a pronounced fine structure, do not choose $E_1 = E_c$ but $E_1 > E_c$
  – apart from the fine structure, SIGMAK yields a reasonable approximation for experimental observations
  – example: N-K edge
Experimental *Determination of Scattering Cross-Sections*

- by mean of standard specimens
- analogy with “standard” method for determining the k factor in XEDS
- why is comparison with standard specimens not as popular in EELS as in XEDS?

→ EELS spectra depend on a larger number of parameters, all of which would have to be met by the standard specimen:
– chemistry
  · nature of interatomic bonds
  · electron band structure
  · oxidation state
– specimen thickness $t$
– experimental conditions of EELS
  · $\Delta$
  · $\beta$
  · $E_0$

• particularly important: thickness of the TEM specimen

• remarkable trend:
  – in EELS the comparison with “standard” specimens gains more and more importance
    (particularly for analyzing light elements)
  – in XEDS, on the other hand, theoretical methods for determining $k$ factors gain more and more importance