EELS (electron energy loss spectrometry) is a technique used in TEM. It analyses the energy "lost" by the incoming fast electrons when they travel through the sample. While diffraction effects in the TEM are driven by the interaction of the fast electrons with the nucleus, in EELS, one deals with electron-electron interactions. This is the interaction between the electron of the beam and the electrons in the sample. Therefore EELS is able to provide information about the electronic structure of the sample. EELS can also be used for chemical analysis, and can provide quantitative information about the composition of the specimen. Since the energy lost is relatively small compared to the energy of the incoming electron (at most 2 to 3000 eV compared to 120 -300 keV in conventional microscopes), the electrons which have lost energy can still be "used" for imaging the specimen. Imaging the specimen with electrons which have lost energy characteristic for a certain atom will provide a cartographic picture of the repartition of this kind of atom in the sample. This is called chemical mapping.

Looking at the fine structure in the EELS spectrum will give information about the electronic state in the samples, and these results can be compared to theoretical calculations.
Outline

• Introduction: EELS in the TEM
• Instrumentation
• Core Loss EELS
  – Theory
  – Applications
• Low losses
• Imaging (EFTEM)
• ELNES
EELS in the TEM

Probe = electrons
100-300 kV
Velocity: 0.55-0.77 c
**Introduction**

**Excitation process**

**Scattering geometry**

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

0 \( < \theta < 100 \) mrad

To avoid aberrations

0 \( < \theta < 25 \) mrad

@200 kV [111] spot in fcc Cu: 11 mrad

\[ \theta \ll 1 \quad \Rightarrow \quad q^2 = k^2(\theta_E^2 + \theta^2) \quad \theta_E = \Delta mE\gamma/\hbar^2k^2 \]
Introduction

Bragg reflection
cluster excitations
interband transitions
Energy loss
q
0 to 100 eV
100 to 2000 eV
distributed
Bethe ridge

Elemental analysis
Bounds
Free orbitals
distances of atoms
coordination number
Energy loss
q-resolved ELNES

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Instrumentation

Gatan PEELS 666
Gatan digi-PEELS 766
Gatan Enfina
Instrumentation: energy filter

Cross over (chromatic object plane)

Image or diff. pattern on the SEA (achromatic object plane)

Filter

Achromatic image plane

Chromatic image plane (spectrum, energy selecting slit)

Sample

Filtered image or diffraction pattern

Operated as energy filter

Two possibilities: in- or post-column

Instrumentation: energy filter

Cross over (chromatic object plane)

Image or diff. pattern on the SEA (achromatic object plane)

Filter

Achromatic image plane

Chromatic image plane (spectrum, energy selecting slit)

Sample

Spectrum

Operated as spectrometer
Chapter 17: EELS/EFTEM

Instrumentation energy filter

Gatan Imaging Filter

Instrumentation: energy filter

1984: Zeiss 902

1962: Castaing-Henry filter
Instrumentation: energy filter

1992: Zeiss 912

Zanchi; Krahl: Omega filter

Instrumentation: energy filter

Zeiss libra: corrected omega

Jeol: omega
Instrumentation: energy filter

Mandoline:
SESAM project (Zeiss)

---

Instrumentation: 3D data cube

An energy filtered image \( I(x, y, \Delta E) \) is a slice from the 3D data cube.
In STEM mode the beam scans across the sample area and for each position \((x_i, y_i)\) the energy loss spectrum is recorded.

Each spectrum corresponds to a column in the 3D data cube.

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Core loss EELS

Which physics is needed?

- quantum mechanics
- Relativity (sometimes)

H.A. Bethe: 1930:

Zur Theorie des Durchgangs schneller Korpuskularstrahlen durch Materie

Annalen der Physik, vol. 397, Issue 3, pp.325-400

Core loss EELS: theory

\[
\frac{\partial^2 \sigma}{\partial E \partial \Omega} = \sum_{I,F} \frac{4\gamma^2 k_b}{a_0^2 q^4 k_a} \left| \langle F | e^{i\vec{q} \cdot \vec{R}} | I \rangle \right|^2 \delta(E_I - E_F + E) = \frac{4\gamma^2 k_b}{a_0^2 q^4 k_a} S(\vec{q}, E)
\]

\[
S(\vec{q}, E) = \sum_{F} \left| \langle F | e^{i\vec{q} \cdot \vec{R}} | I \rangle \right|^2 \delta(E_I - E_F + E)
\]

\[
f(\vec{q}, E) = \frac{2mE}{\hbar^2 q^2} S(\vec{q}, E)
\]

\[
f(\vec{q}, E) = \frac{2mE}{\hbar^2 q^2} \sum_{F} \left| \langle F | e^{i\vec{q} \cdot \vec{R}} | I \rangle \right|^2 \delta(E_I - E_F + E)
\]

Dipole approximation

q small

\[
\frac{\partial^2 \sigma}{\partial E \partial \Omega} = A \frac{1}{EE_0} \frac{1}{\theta^2 + \theta_e^2} f(\vec{q}, E).
\]
The partial cross section for ionization of shell n is

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

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

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

$$I = N \Delta \sigma j_0.$$  \hspace{1cm} (2)

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

The number $N$ of atoms irradiated by the probe is then

$$N = \frac{I}{j_0 \Delta \sigma}.$$  \hspace{1cm} (3)
Core loss EELS: theory

Multiple scattering: Fourier-ratio deconvolution

High energy tail of lower energy losses: Background removal

Dark signal correction

Theoretical model

Egerton’s programm (Digital micrograph)

Relative quantification: No need of $j_0$

\[
\frac{N_a}{N_b} = \frac{I_a}{I_b} \frac{\Delta \sigma_b}{\Delta \sigma_a} \text{ k-factor}
\]

Core loss EELS: theory

B-K: 1s -> p
N-K: 1s -> p
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Core loss EELS: applications


EELS study of interfaces in magnetoresistive LSMO/STO/LSMO tunnel junctions

La_{0.66} Sr_{0.33} MnO_3 /SrTiO_3 /La_{0.66} Sr_{0.33} MnO_3
Identification of ferritin molecules. Dark field STEM image (contrast reversed) of a thin tissue section from the IRP knockout mouse brain.

Core loss EELS: applications

Accuracy: - 15-20% under normal conditions
- can be lowered to a few % (standards, same thickness, same exp conditions)


Det. Limit Normally a few % (1 to 10).
Record: single atom detection

Varela et al PRL 92 (2004) 095502-1
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Low Loss

Visible light

UV

VUV

Extreme UV

Plasmons (collective oscillations)

Interband transitions

Scattering angle (momentum transfer)
Low Loss

SSD and loss function

\[ S(E) = \left( \frac{e^2}{\pi \hbar w} \right)^2 \cdot D \cdot \right) \left( \frac{-1}{\varepsilon(E)} \right) \cdot \ln \left[ 1 + \left( \frac{\beta}{\theta E} \right)^2 \right] \]

- Single scattering distribution
- Sample thickness
- Loss function
- Angular scattering distribution

Low Loss: KKA

From the experiment to the loss function: theory

Experiment

- EELS spectrum
- Single scattering distribution
- Loss function \( I(E) \)
- Normalized loss function \( \text{Im}(-1/s) \)
- \( \text{Re}(1/s) \), \( \varepsilon_1 \), \( \varepsilon_2 \), \( n \), \( k \), \( R \), \( T \)

Kramers-Kronig Analysis

Aperture correction

Normalization

Fourier-log deconvolution
Low Loss: the Kröger equation

The relation between the double differential cross section and the loss function is a "little bit" more complicated.

\[
\frac{\partial P(\omega, \mathbf{k}_l)}{\partial \omega \partial k_{l2}} = \frac{e^2}{\pi^2 \hbar^2} \cdot \left[ \frac{\mu^2}{\epsilon_0^2} \cdot D \right] \cdot \text{Volume term} \cdot \left[ 1 \right]
\]

Volume term

\[
- \frac{2k_0^2 (\epsilon - \epsilon_0)^2}{\epsilon_0 \epsilon_0} \cdot \left( \frac{\phi_{01}^2}{\epsilon_0} \cdot \left( \frac{\sin^2 \left( \frac{\omega D}{2} \right)}{L^+} + \frac{\cos^2 \left( \frac{\omega D}{2} \right)}{L^-} \right) \right) + \beta^2 \cdot \frac{\lambda_0^2 \omega^2}{\epsilon_0 v} \cdot \left( \frac{1}{L^+} - \frac{1}{L^-} \right) \cdot \sin \left( \frac{\omega D}{v} \right) - \beta^4 \cdot \frac{\omega^2}{v^2} \cdot \lambda_0 \lambda \left( \frac{\cos^2 \left( \frac{\omega D}{v} \right) \tanh (\lambda D/2)}{L^+} + \frac{\sin^2 \left( \frac{\omega D}{v} \right) \coth (\lambda D/2)}{L^-} \right) \right]
\]

Following abbreviations were used:

\[
\lambda = \sqrt{k_0^2 - \frac{\epsilon_0^2 \omega^2}{c^2}}, \quad \lambda_0 = \sqrt{k_0^2 - \frac{\epsilon_0 \omega^2}{c^2}}
\]

\[
L^+ = \lambda_0 \epsilon + \lambda_0 \epsilon \tanh (\lambda D/2), \quad L^- = \lambda_0 \epsilon + \lambda_0 \epsilon \coth (\lambda D/2)
\]

\[
\beta^2 = \frac{\nu^2}{c^2}, \quad \phi_{01}^2 = k_0^2 + \frac{\omega^2}{\nu^2} - (\epsilon + \epsilon_0) \frac{\omega^2}{c^2}
\]

\[
\phi^2 = \lambda^2 + \frac{\omega^2}{\nu^2}, \quad \phi_0^2 = \lambda_0^2 + \frac{\omega^2}{\nu^2}
\]

\[
\mu^2 = 1 - \epsilon \beta^2, \quad \mu_0^2 = 1 - \epsilon_0 \beta^2
\]

Z. Phys. 216 (1968), 115-135

Low Loss

Relativistic effects in semiconductors - Bulk

A lower TEM-acceleration voltage allows higher \( n \)-materials!

<table>
<thead>
<tr>
<th>kV</th>
<th>100</th>
<th>200</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>1.8242</td>
<td>1.4381</td>
<td>1.2878</td>
</tr>
<tr>
<td>( \epsilon_1 )</td>
<td>3.3278</td>
<td>2.0683</td>
<td>1.6584</td>
</tr>
</tbody>
</table>

Cerenkov losses

No Cerenkov losses
Low Loss: some solutions

Decrease TEM voltage (SiN$_x$H)

KKA – refractive index


Low Loss: some solutions

difference method (Si)

Si, 200 kV

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Imaging (EFTEM)

Operated as energy filter
Chapter 17: EELS/EFTEM

EFTEM: Zero-loss image

Frozen hydrated liposomes.

EFTEM: Plasmon images

Nerve section of about 500 nm in thickness.
EFTEM: Plasmon images

For this example a slit width of 1 eV was used

positiv: only short exposure times (0.1 - 0.5 s)

negativ: reduced lateral resolution due to delocalization

EFTEM: Core loss images

Al: 20 sec, Al-L edge
Si: 20 sec, Si-L edge
O: 60 sec, O-K edge
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Core Loss: fine structure

Diamond

Graphite

Carbon K edge
Core Loss: fine structure

**Thulium**
- **Ground state electron configuration:** [Xe]4f^{13}6s^{2}
- **Shell structure:** 2s,2p,3s,3p,3d
- **Term symbol:** ^2F_{7/2}

**Ytterbium**
- **Ground state electron configuration:** [Xe]4f^{14}6s^{2}
- **Shell structure:** 2s,2p,3s,3p,3d
- **Term symbol:** ^1S_{0}

Use the controls to display ground state electronic configurations of neutral gaseous atoms.
Core Loss: fine structure

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

\[
\begin{align*}
\text{Tm} & : Z=69 \\
\text{Energy levels} & \\
\text{Continuum} & \\
\text{E-loss} & \\
1s & 3d & E_F & 4f \\
\text{Yb} & : Z=70 \\
\text{Energy levels} & \\
\text{Continuum} & \\
\text{E-loss} & \\
1s & 3d & E_F & 4f
\end{align*}
\]

Core Loss: fine structure

\[
\begin{align*}
\text{Intensity [arb. u.]} & \\
\text{M 4.5} & \\
\text{Yb}_2\text{O}_3 & \\
\text{M 4.5} & \\
\text{Lu}_2\text{O}_3 & \\
1400 & 1500 & 1600 & 1700 & 1800 & 1900 & \text{eV} & 1500 & 1600 & 1700 & 1800 & 1900 & \text{eV}
\end{align*}
\]

\(\text{M}_{45}\) edges of Yb and Lu in their oxides, showing the disappearance of white line when the \(f\)-subshell is filled.

Charge transfer
Core Loss: theory

DFT

Core Loss: theory

Walter Kohn
Nobel prize laureate 1998
chemistry
Core Loss: theory

Electron density
-> Wave functions
-> Density of states
-> unoccupied density of states

EELS spectrum with fine structures!

Compare with experiment

C. Hébert, et al.
Core Loss: theory

Electron Energy-Loss Spectroscopy In The Electron Microscope
By: R. F. Egerton

C. Hébert, et al.