Electron energy loss spectroscopy (EELS) and Energy Filtering TEM (EFTEM)

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2.46 Å
Outline

Basics of EELS
EELS/EFTEM-Instrumentation
STEM-EELS
ELNES / Bonding Information
Elemental Mapping
Cc-correction: PICO
EFTEM / EELS Analysis
Analytical TEM: Electron Intensity Distribution

$I = \text{const.}$

5 - 50 nm

specimen

$I = I(x, y, \theta_x, \theta_y, \Delta E)$

conventional TEM

EELS

Electron Spectroscopic Imaging (ESI)

Diffraction (ESD)

Energy Filtering TEM
Inelastic Scattering, low energy losses: phonon and plasmon excitation

$$\Delta E = 1 \ldots 50 \text{ meV}$$

$$\Delta E = 1 \ldots 50 \text{ eV}$$
Inelastic Scattering: Inner Shell Excitation

\[ E_0 - \Delta E, \quad \Delta E = E_B + E_{\text{kin}} \]
Schematical Energy Loss Spectrum

- Zero-loss
- Plasmon-loss region
- Inner-shell losses

Energy Loss ($\Delta E$)

Intensity ($I$)

$E_0 - \Delta E$, $\Delta E = E_B + E_{\text{kin}}$
Inelastic Scattering: Solid State Model
HR-ELNES

HR-EELS of Co L\textsubscript{2,3} of CoO

![Graph showing energy loss spectra with peaks at different energies.]

- CM20
- TF20
- TF20+ mono.
- XAS
- Calc.

With crystal-field multiplet theory (FMF de Groot)

LaB\textsubscript{6} \sim 0.65 eV

FEG \sim 0.55 eV

\sim 0.20 eV

Mitterbauer, Kothleitner & Hofer, Ultramicroscopy
NiO EELS

<table>
<thead>
<tr>
<th>Feature</th>
<th>Integrated counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero loss peak</td>
<td>$8 \times 10^8$</td>
</tr>
<tr>
<td>Plasmon peak</td>
<td>$2 \times 10^8$</td>
</tr>
<tr>
<td>Ni M edge</td>
<td>$2 \times 10^7$</td>
</tr>
<tr>
<td>O K edge</td>
<td>$9 \times 10^5$</td>
</tr>
<tr>
<td>Ni L edge</td>
<td>$3 \times 10^5$</td>
</tr>
</tbody>
</table>

Log$_{10}$(Counts)

Energy-Loss (eV)
<table>
<thead>
<tr>
<th></th>
<th>EELS</th>
<th>EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Count rate</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Background</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Quantification</td>
<td>tricky</td>
<td>easy</td>
</tr>
<tr>
<td>Mapping</td>
<td>fast</td>
<td>slow</td>
</tr>
<tr>
<td>Spatial res.</td>
<td>atoms</td>
<td>columns</td>
</tr>
<tr>
<td>Bonding info</td>
<td>yes</td>
<td>no</td>
</tr>
</tbody>
</table>
Instrumentation
Energy Loss Spectrometer
(magnetic prism)

\[ \mathbf{F}_L = -e(\mathbf{\hat{v}} \times \mathbf{B}) \]
The Omega Energy Filter
Energy Filtering Transmission Electron Microscopy

elemental distribution images

convergent beam electron diffraction

$\Omega$-filter

spatially resolved energy loss spectroscopy

bonding charge densities
Optical elements of Gatan post-column filters

*200 kV and higher filters only
The Gatan Imaging Filter

Models: GIF 2000 series, new GIF Tridiem
Wien Filter Monochromator

2 crossed fields perpendicular to each other

Two forces act on the particles:
\[ F_E = qE, \text{ electrostatic field} \]
\[ F_B = qvB, \text{ magnetic field} \]

For electron moving with \( v \) and \( E \) parallel to optic axis the forces are balanced and the electron travels straight

Any other electron travelling with different \( v \) or at some angle to the axis execute a cycloidal motion
What is the best way to water flowers?

EFTEM

STEM
HAADF - STEM Imaging

Example: individual Sb atoms in doped Si

High Resolution Z-Contrast Imaging
Mn-Doped GB in SrTiO$_3$

G. Duscher, Solid State Division, ORNL
Atomic Column Resolved EELS at SrTiO$_3$ 36.7° Grain Boundary Doped with Mn

G. Duscher, Solid State Division, ORNL
Electronic Band Structure

Energy Level Diagram

Conduction Band
Defect Band
Valence Band

transitions to unfilled states

Core levels
Energy Loss Near Edge Structure (ELNES)

Energy Level Diagram

Core levels

.transitions to unfilled states

Valence Band

Defect Band

Conduction Band

Binding Energy

Typical EELS

Near Edge Structure

low-loss region

core-loss region

x 10
ELNES-Interpretation
(one electron approximation)

1) Fermi's Golden Rule:
\[ I(E) \propto |M(E)|^2 N(E) \]
   • local density of unoccupied states (LDOS)

2) Dipole selection rule:
\[ \Delta l = \pm 1 \]
   • symmetry projected DOS

3) Momentum resolved spectroscopy:
\[ \vec{q} = \vec{q}_{//} + \vec{q}_{\perp} \]
   • excitation into specific orbitals
Chemical Shifts

![Diagram showing chemical shifts for different compounds](image)

- TiO$_2$: Ti$^{4+}$
- Ti$_2$O$_3$: Ti$^{3+}$
- Pyrolusite Mn$^{4+}$
- MnO Mn$^{2+}$
- Hematite Fe$^{3+}$
- Ilmenite Fe$^{2+}$

Count / 1000

Energy loss (eV)
TiO$_2$ - Polymorphs

(F. Hofer, TU Graz)
Molecular Orbital (MO) Term Scheme

Example: Ti

Leapman et al & Grunes 1983, 1984
$\text{BaTiO}_3$: Ti in octahedral coordination

$\text{Ba}_2\text{TiO}_4$: Ti in tetrahedral coordination
Dislocations at SrTiO$_3$ low-angle tilt grain boundary

- Controllable type and density of dislocations.
- Model system for in-depth study of the relationship between structure and property.

Frank's Formula

\[ D = \frac{b}{2 \sin(\theta/2)} \]
EDX spectrum imaging @200 kV

<table>
<thead>
<tr>
<th>Sr</th>
<th>Ti</th>
<th>Sr+Ti</th>
<th>HAADF (51)</th>
<th>HAADF+Sr+Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="a" alt="Image" />.jpg)</td>
<td><img src="b" alt="Image" />.jpg)</td>
<td><img src="c" alt="Image" />.jpg)</td>
<td><img src="d" alt="Image" />.jpg)</td>
<td><img src="e" alt="Image" />.jpg)</td>
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1 nm

- **EDX**: Extra Ti-intensity at the tensional side of the dislocation cores
- **HAADF**: altered coordination at tensional side
Core Structure

HAADF PICO@80 kV

- EDX: Extra Ti-intensity confirms the presence of the FCC TiO phase at the tensinal side of the dislocation cores.
- Result of strain energy (lattice constant of FCC TiO: 0.42 nm, SrTiO$_3$: 0.39 nm).

Edge-sharing TiO$_6$ octahedra associated with the FCC TiO phase at the tensinal side of the dislocation cores.
Energy loss near edge fine structure

\[ \delta \] estimated by the free carrier density (Hall effect)

Valence/Bonding state mapping

Reduction of Ti-valency state makes dislocation core electrically active!
Analytical TEM: Electron Intensity Distribution

\[ I = \text{const.} \]

5 - 50 nm

\[ I = I(x, y, \theta_x, \theta_y, \Delta E) \]

- conventional TEM
- EELS

Electron Spectroscopic Imaging (ESI)
Diffraction (ESD)

Energy Filtering TEM
Energy Filtering TEM vs. STEM

Image mode: $I = I(x, y, \Delta E)$

specimen

STEM

EFTEM

EELS

$x \times 100$

$\Delta E$
Elemental Distribution Images:
Three Window Technique
Sintered polymer derived Si3N4/SiC-composite
red: C, green: N, blue: O

Sintered polymer derived Si3N4/SiC-composite
Aberration corrected electron optics

$C_S = 0$

- TU Darmstadt (H. Rose)
- EMBL Heidelberg (M. Haider)
- Forschungszentrum Jülich (K. Urban)

Volkswagen Stiftung

Chromatic Aberration
Correction Principle: Wien Filter

Harald Rose and Max Haider
Correction Principle: Crossed Electrostatic/Magnetic Quadrupoles

Harald Rose and Max Haider
Cc-Corrector: 10 multipole elements + 4 coupling lenses
Cc-Corrector: 10 multipole elements + 4 coupling lenses
CCOR in Heidelberg, CEOS

828 mm, 470 kg, 160 channels
PICO upgrades

- 2011
- 2012
- 2013
- 2014
- 2015

CCOR power supplies

CCOR and power supplies

CCOR+
Chromatic Aberration

\[ d_c = \frac{1}{2} C_c \frac{dE}{E} \theta \]

Biggest impact of Cc-correction expected for:

- large energy spread \( dE \) (EFTEM)
- low accelerating voltages (low \( E \))
### Energy Filtering TEM

**EFTEM resolution:**

\[ d_{\text{tot}} = \sqrt{d_c^2 + d_s^2 + d_d^2 + d_{\text{del}}^2} \]

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td><strong>Spherical Aberration</strong></td>
<td><strong>0</strong></td>
</tr>
<tr>
<td><strong>Chromatic Aberration</strong></td>
<td><strong>0</strong></td>
</tr>
<tr>
<td><strong>Diffraction Limit</strong></td>
<td>[ d_d = 0.6 \frac{\lambda}{\theta} ]</td>
</tr>
<tr>
<td><strong>Delocalisation</strong></td>
<td>[ d_{\text{del}} = 0.5 \frac{\lambda}{\theta_{E}^{3/4}} ]</td>
</tr>
</tbody>
</table>
21%
BMBF-project
SINOVA

21%

60%
Si/SiO₂-Superlattices: Fabrication by RPECVD at 250°C and Rapid Thermal Annealing at 900 to 1100°C

Sample: B. Spangenberg, H. Kurz, IHT, RWTH Aachen, TEM: A. Sologubenko, M. Beigmohamadi
Fabrication by RPECVD and Laser annealing

Sample: B. Spangenberg, H. Kurz, IHT, RWTH Aachen, TEM: M. Beigmohamadi
PICO: Energy Filtering TEM
Si-L edge, 3 window meth.

Maryam Beigmohamadi, Jörg Jinschek
EFTEM Resolution & Cc-Correction

Cs corrected

Cc=1.4 mm
W=10 eV

Cs and Cc corrected

Cc=10 μm
W=50 eV

-> optical resolution better than delocalisation
-> large windows possible

As in Krivanek et al, J. Microsc. 180 (1995) 277
High Resolution EFTEM of Si

EFTEM, Si-L edge at 99 eV, energy window 40 eV

(a) Pre edge

(b) Post edge

(c) Post edge

Preservation of Elastic Scattering Contrast

Elastic Wave Field: Channeling and Pendellösung

ψ_{el}  

ψ_{inel}  

EFISTEM vs. hollow cone illumination and STEM

(a) EFISTEM
(b) Precession EFTEM (over solid angle)
(c) STEM EELS

Scan
Energy filter
Spectrometer
Energy Filtering Image STEM (EFISTEM)

Les Allen
(Melbourne)
A. Rosenauer
(Bremen)
SrTiO$_3$: EFISTEM zero loss
SrTiO$_3$: EFISTEM oxygen map

Ultramicroscopy, to be published
Tsinghua University: Xiaoyan Zhong, Zechao Wang, Hanbo Jiang

Ernst Ruska-Centre: Amir Tavabi, Lei Jin, Juri Barthel, Les Allen

LEFT circular polarized X-ray

RIGHT circular polarized X-ray

Nature Materials (DOI:10.1038/s41563-017-0010-4)
Energy Loss Spectroscopic Profiling (ELSP)

Image mode: $I = I(x,y,\Delta E)$

specimen

STEM

EFTEM

EELS

$\Delta E$

x 100
Atomic Resolution ELSP of CaTiO₃/ SrTiO₃ interface

[a: HRTEM of CaTiO₃/SrTiO₃ interface
b&c: Ca and Ti edge ELSP after background subtraction
d: raw ELSP data without background subtraction under (100) 3beam condition
Ca edge and Ti edge are mainly localized at Ca-O and Ti-O2 crystal planes respectively. There is no much delocalization at Ca L3,2 edge at CTO/STO interface.]

Cc corr. needed!
Material: Sr$_2$FeMoO$_6$ Room-Temperature Ferrimagnetic T$_c$: 426K

Schematic of Atomic Scale ELSP+EMCD (SFMO)

External Magnetic Field direction (2T) strong enough to get SFMO saturated along z axis, EMCD measure M$_z$, spin direction of all Fe atoms // external field

In SFMO case, the B site contained the ordered Fe and Mo atom
Conclusions

• Despite technical complexity, the Cc-corrector does not harm the TEM performance in any mode.

• The resolution in many different TEM-modes can greatly be improved.

• Low voltage HRTEM: resolution improvement to 16 \( \lambda \).

• Examples in spectroscopy: atomically resolved EFTEM + EFISTEM, atomic scale EMCD.
solution...