EELS

Electron Energy Loss Spectroscopy

(Thanks to Steve Pennycook, Quan Li, Charlie Lyman, Ondre Krivenak, David Muller, David Bell, Natasha Erdman, Nestor Zaluzec and many others)
**EELS - AN INTRODUCTION**

*Zero loss* - elastically scattered electrons

*Low loss* - interactions with weakly bound outer shell electrons (includes plasmons - resonance of valence electrons)

*High loss* - interactions with inner shell electrons, causing excitation into an unoccupied shell above the Fermi level & resulting in characteristic elemental energy loss ‘edges’ (e.g. $K$ & $L_{1}/L_{2,3}$ edges are excited by $1s$ & $2s/2p$ electrons; ELNES & EXELFS yield fine structures related to bonding)
Comparison

**EDS**
- Low collection efficiency (small solid angle)
- Good peak/background
- Good for high-Z elements
- SEM (~500 nm) or TEM (~10 nm)
- Stray x-rays in the column can be mistaken for trace elements

**EELS**
- TEM only & thin samples
- High collection efficiency (~90%)
- Poor peak/background (esp in thick samples)
- Best for low-Z elements (large signals)
- Bonding information for Z<33
- High spatial resolution (0.1 – 1 nm)
Auger vs X-ray Yield

Below ~10 keV, Auger emission dominates and very few x-rays are emitted. X-ray fluorescence is most efficient for detecting high-Z elements.

David Muller 2006

Eqn 3.13 of Rev. Mod. Phys. 44, 716 - 813 (1972)
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Experimental XEDS, XPS, and EELS data from the Copper L shell. Note the differences in energy resolution, and spectral features.
Electron energy filter/spectrometer configurations in TEM

Post-column filtering

In-column filtering
FEG STEM at UIC

bias electrode
filament

acceleration tube and beam deflection coils
electrostatic gun lens
condenser lenses, C1 & C2

STEM objective aperture
condenser stigmators and deflection coils (STEM scan coils)
specimen
objective lens (on), objective stigmator (on) and objective mini-lens (off)

deflection coils
collector aperture
post-specimen lens system, stigmator coils and deflection coils

removable annular dark-field detector

GIF for EELS, brightfield and energy-filtered CBED
LIBRA 200® C_s and Monochromator

- FEG
- Condenser (C1, C2 & C3)
- Objective
- C_s Corrector
- Projector 1 (P1, P2 & P3)
- Corrected Omega Filter
- Projector 2 (P4, P5 & P6)
- Viewing chamber + Detectors

Monochromator

- Dispersion free
- Ease of use
- 30% of intensity at 0.2eV
Electron Energy Loss Spectrum of SiO$_2$

Each edge sits on the tails of the preceding edges \( \rightarrow \) Backgrounds are large

![Graph showing electron energy loss spectrum with labels for Incident Beam, Valence Excitations, Si L edge, and O-K edge.](image-url)
Energy Levels and Energy-Loss Spectrum

Basic formalism

• Ignore diffraction effects, not really right but OK for now
• Consider inelastic scattering as completely incoherent – 99% correct
• Ignore relativistic effects, not correct and over the last decade they have been shown to be critical
• Assume that processes are not dependent upon the electron energy, good for swift electrons
• Consider a simple probability $P(dE,q)$, for $dE$ change in energy and $q$ wavevector change
• Many simplifications if we integrate over all $q$, collection angle (experimental variable)
Basic formalism

\[ \frac{dI(E,q,z)}{dz} = \int I(E - E', q - q', z)P(dE', dq')dE'dq \]

Simplest case when energies do not overlap leads to a Poisson distribution solution:

\[ I(E, q, t) = \exp \left( -\frac{t}{\lambda} \right) \delta(E) + tP(dE, q) \exp \left( -\frac{t}{\lambda} \right) \delta(E - dE) + \ldots \]

\[ I(E - ndE, nq, t) = \left( \frac{1}{n!} \right) t^n P^n(dE, q) \exp(-t/\lambda) \]

\[ 1/\lambda = \int P(dE, q)dEdq \]

We call \( \lambda \) the mean free path. Note that the zero-loss peak has an intensity of \( \exp(-t/\lambda) \), so if we divide by this we get \( tP(dE,q) \) for single scattering.

With multiple scattering the result is slightly more complicated, but one can do a log deconvolution to clean up the data.
Figure 38.2. (A) The low-loss spectrum from a very thin sample of pure Al showing the intense zero-loss peak ($I_0$) and a small plasmon peak ($I_p$) at about 15 eV. (B) The low-loss spectrum from a thick specimen of pure Al showing several plasmon peaks.
Al → free electron metal

Fe → Transition metal

NiO – ZrO$_2$ interface

Plasmon peak

NiO – ZrO$_2$ 6 nm interface

Low loss spectrum from Al and Al compounds
→ The differences in the spectra are due to differences in bonding
Intraband transition characteristic of Polystyrene

Band gap differences manifesting itself in the low loss region of the EELS spectrum

Low loss region before Plasmon peak
Core Losses

![Core Losses Graph]

- **Counts x 10^3**
- **eV**
- **bkgd**

- Spectrum
- L2
- L3
- L1

**Idealized edge**

**Edge superimposed on plural scattering**

**Bonding Effects**

**ELNES**

**EXELFS**

**Thick Specimen → Combination of ionization and plasmon losses**

**Ionization loss**

**Plasmon loss**

Diffraction Effects from atoms surrounding the ionized atom
The L edge of transition metals
Chemical bonding

Cu and CuO

3d$^{10}$
3p$^{6}$
3s$^{2}$
2p$^{6}$
2s$^{2}$
1s$^{2}$
Diamond, graphite and fullerene all consist of only carbon. All of these specimens have absorption peaks around 284 eV in EELS corresponding to the existence of carbon atoms. From the fine structure of the absorption peak, the difference in bonding state and local electronic state can be detected. The sharp peak at absorption edge corresponds to the excitation of carbon K-shell electron (1s electron) to empty anti-bonding pi-orbital. It is not observed for diamond, because of no pi-electron in it.
Is low friction associated with $\pi$-bond formation?

Merkle et al, Carbon, in press

**Energy Loss (eV)**

- **σ**
- **82% sp²**
- **π**

**Intensity (counts)**

- **σ**
- **N**
- **C:N:O=1:0.17:0.46**
- **O**

**dried bovine serum**

**C:O=1:0.07**

**tribiological layer**

**graphite**
FEI monochromator
(Tiejmeier et al.)
Additional fine structure seen with monochromation

(a) Titanium $L_{23}$ and oxygen $K$-edge showing splitting between $t_{2g}$ and $e_g$ levels in rutile (courtesy J. Auerhammer). (b) High resolution spectrum of Ti $L_{23}$-edge in rutile (courtesy R. Brydson).
Monochromator / Energy-Filter Performance

No Monochromator @ 200KV

FWHM = 600 meV

Monochromator 1um Slit @ 200KV

FWHM = 81 meV

Monochromator 1um Slit @ 80KV

FWHM = 62 meV
Schematic of the Nion high resolution monochromator


un-dispersed outgoing beam

EELS 1
energy-dispersed beam

Energy dispersion at slit is variable from ~ 2 µm/eV to ~ 200 µm/eV

EELS 2
monochromated beam

incoming beam

The Nion monochromator is equivalent to 2 parallel EEL spectrometers arranged back-to-back, with an energy-selecting slit in the mid-plane, plus (next slide):
More recent zero loss peaks

MC in final position, stabilization schemes not yet connected up.

Stabilization scheme 1 connected, but not making much difference: short exposure time is needed to avoid broadening the ZLP.

The instability is due to elements outside the stabilization scheme, e.g. the quadrupoles of the MC or the quads of the EELS. The probe on the sample does not jitter, and this points to the EELS as the source of the problem.
Stainless steel specimen

2.761 Å

No visible Grain Boundary

Fourier filtered image

Dislocation structures at the Grain boundary

~8° TILT BOUNDARY IN THE SrTiO₃ POLYCRYSTAL

EELS

Si peak at 1839 eV

Sr L₂,₃ peaks

Grain Boundary

Grain

VG microscope
Single $B_xS_{1-x}$TO nanocubes EELS

7 nanocubes are detected as EELS, and the $\text{Ba}/O=0.16-0.19$
$\text{Ti}/O=0.33-0.36$, $X$ average value is close is 0.5.

Relative quantification:

<table>
<thead>
<tr>
<th>Elem.</th>
<th>Atomic ratio ((\text{/}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>0.33 ± 0.046</td>
</tr>
<tr>
<td>O</td>
<td>1.00 ± 0.000</td>
</tr>
<tr>
<td>Ba</td>
<td>0.15 ± 0.022</td>
</tr>
</tbody>
</table>
Elemental mapping

Three-window method

• \[
\frac{W_3}{W_1 + W_2} = \text{Elemental map}
\]
What is Spectrum Imaging?

- Spectrum imaging is the technique of acquisition, storage, processing, and analysis of spectroscopic data at each pixel in a digital image.
- Conventional image pixels contain one intensity value only.
- Spectrum image pixels contain complete spectra.
- Produces quantitative elemental maps and profiles.

Spectrum image schematic:

- $\Delta x$, $\Delta y$: Spatial dimensions.
- $\Delta E$: Energy-loss dimension.

Vertical columns are spectra.

Horizontal planes are energy filtered images.

spectrum at pixel $\Delta x_i$, $\Delta y_i$
Acquisition of Spectrum Images

- A spectrum image is typically acquired in STEM mode by stepping a focused electron probe from one pixel to the next.

- The spectrum image data cube is filled one spectrum column at a time.

- In STEM it is possible to collect EELS, X-ray or both spectra simultaneously.

- Use of the DF or SE signal during acquisition permits spatial drift correction and assurance that information is coming from the desired area.
Multilayer coating
Carbon Nanotube
Electron Microscopy Methods for the Characterization of Nanomaterials (Example: Vanadium Oxide Nanotubes)

SEM: characterization of tubular morphology

EELS: composition

Cross-sections of VO_x nanotubes: TEM and elemental maps obtained by electron spectroscopic imaging

TEM: characterization of the wall structure
Column-by-column EELS?

Dynamical effects
Beam broadening
Localization
Interpretation

Column by column image

Prism

IBF = 1-ADF

Scanned Incident Probe
Specimen

Column by column EELS?
Atomic resolution chemical analysis

- Edge resolution test on CoSi$_2$/Si(111) interface
- VG Microscopes HB501UX, 100 kV, ~ 2.2 Å probe

Browning, Chisholm, Pennycook, Nature 1993
Single Atom Spectroscopy


La-doped CaTiO$_3$

EELS ~ XAS with atomic resolution and sensitivity to 1 atom
~ STM but below the surface
An example

D. A. Muller, Nature 399, 58 (1999)
Chemical Imaging in 2D
(Integrated counts above background)

EELS map
Of LaMnO$_3$/SrTiO$_3$
recorded
on the Nion SuperSTEM

28 seconds live time
(10 seconds overhead)
Simultaneously acquired EELS and EDS maps from a LaFeO$_3$/SrTiO$_3$ interface. Principal component analysis was used to remove random noise. Data acquired in a JEOL JEM-ARM200F at 200 kV, courtesy of E. Okunishi (JEOL) and M. Varela (ORNL). Sample courtesy of Jacobo Santamaria's group (Complutense University, Spain).
Atomic resolution Imaging and EELS map with High Energy Resolution

\[ \text{Ca}_3\text{Co}_4\text{O}_9 \]
(110)

Annular Bright Field (ABF)

HAADF

EELS SI
- Ca
- Co
- O

Data courtesy of Dr. Robert Klie, University of Illinois at Chicago
Atom by atom spectroscopy


Materials Science and Engineering and Scientific User Facilities Divisions
Some $3d$ states in Si-C$_4$ structure are missing!
EELS Theory

In the first Born approximation, the partial cross section for the inelastic scattering of an electron wave packet (with initial group velocity $v$), undergoing a momentum transfer $\vec{q}$ and losing energy $E$, is given by

$$\frac{d^2 \sigma(E,q)}{dEDq} = \frac{8 \pi e^4}{\hbar^2 v^2} \sum_{q, i, f} |\hat{\epsilon}_q \cdot \langle f | \hat{r} | i \rangle|^2 \delta(E - E_f + E_i) + \cdots$$

Some subtleties as to which density of states is measured see Muller, Singh and Silcox, Phys Rev B57, 8181 (1998)

This is very important if you want to measure charge transfers (you don’t – there is no unique definition).

Dipole selection rules: $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$

K-edge: $1s \rightarrow p$  L-edge: $L_1: 2s \rightarrow p$;  $L_{2,3}: 2p \rightarrow d, s$;

David Muller 2006
Calculation of the Final States

- **Cluster Methods**: good for defects & clusters, often easier to run
  - Muffin-Tin Potential (OK for Metals, bad for semiconductors)
    - FEFF7 – no self-consistency: must guess charge transfers
    - FEFF8 – self-consistent: good for metals
  - Full Potential
    - FDMNES – no self-consistency, but it can input potentials from Wien2k

- **Bandstructure methods**: (3D periodic structures or supercells)
  - Almost all bandstructure codes are self-consistent now
  - Muffin-Tin Potential
    - LMTO – good for close-packed structures, esp. metals
  - Full Potential
  - FP-LAPW
    - Wien2k – easy to calculate matrix elements & core hole effects
  - Plane-wave codes (faster and less prone to artifacts than APW codes)
    - ABINIT (free, open-source and downloadable from abinit.org)
    - VASP (commercial)
    - CASTEP (commercial, fancy user interface)

David Muller 2006
Wien2k vs FEFF8

Lionel Celmels, Claude Mirguet, and Yolande Kihn
PHYSICAL REVIEW B 73, 024207 (2006)