Part 3

Energy-Filtering Transmission Electron Microscopy
Energy-Filtering TEM

**Principle of “EFTEM”**

- expose specimen to mono-energetic electron radiation

- *inelastic* scattering in the specimen ⇒ poly-energetic electron beam.

- remember CTEM:
  - image-forming electrons are selected by scattering angle (via objective-lens aperture)
  ⇒ diffraction contrast
  ⇒ CTEM image is formed with the full range of electron energies

- EFTEM:
  - the transmitted electrons pass an energy filter
  - energy filter:
    - electron path depends on kinetic energy
    - energy-dispersive *plane*
  - slit aperture in energy dispersive plane
  ⇒ *energy* selection
    (in addition to scattering-angle selection)
  - admit only electrons with kinetic energy (or energy loss) within a particular interval \([E_1,E_2]\) to the image or diffraction pattern
Instrumentation

- two fundamentally different constructions: in-column and post-column

- in-column filter
  - present generation: “omega” type
  - future: “mandoline” filter, W-filter, ...
  - omega (Ω) filter:

  - advantages:
    - mirror symmetry reduces aberrations
    - filtered images and diffraction patterns can be recorded on photographic film
    - future generation filters enable extremely large scattering angles and fields of view with the same energy loss
• post-column filter
  – Gatan “GIF” (Gatan imaging filter)
- advantages:
  - can be retrofitted to many microscopes
  - images and diffraction patterns can also be recorded \textit{without} the filter

- CSAM’s new instrument: Tecnai F30 (FEI)

- 300kV field-emission gun
- XEDS with selected Si-Li detector
- scan unit
- Gatan post-column imaging filter (GIF 2002)
EFTEM Techniques

• operating modes of the energy filter
  – zero-loss filtering
  – energy-loss “window”

• overview of important EFTEM techniques:
  – EELS
  – zero-loss filtering
  – quantitative CBED
  – electron-spectroscopic imaging (ESI)
  – tomography

EELS

• imaging the energy-dispersive plane of the energy filter onto the image plane (viewing screen) of the microscope:

→ electron energy-loss spectrum of the illuminated specimen area

• record with CCD camera ⇒ EELS spectrum, ELNES

→ elemental analysis, electronic structure
Zero-Loss Filtering

- position slit aperture on zero-loss peak of the EELS spectrum

⇒ only those electrons that suffered \textit{(practically)} no energy loss in the specimen can pass

⇒ only elastically scattered electrons (electrons that have not suffered any energy loss) arrive at the electron detector (viewing screen, photographic plate, or CCD camera).

- two major applications:
  - imaging of thick specimens
  - quantitative electron diffraction, particularly with a highly convergent electron beam (CBED)

- demonstration of zero-loss filtering:
  - CTEM image without (left) and with energy filter (right)
example: microstructure of a Ti-Al-V alloy

specimen was not perfectly thin

⇒ a substantial fraction of the transmitted electrons has suffered energy losses in the specimen

⇒ without filter:
  · inelastically scattered electrons also reach the image plane
  · chromatic aberration of the objective lens
⇒ image part due to inelastically scattered electrons is out of focus
⇒ diffuse background
⇒ image appears blurred and has poor contrast

⇒ same image with zero-loss filtering:
  · only elastically scattered electrons contribute to the image
⇒ no effect of chromatic aberration
⇒ image is much sharper
⇒ image has substantially better contrast

⇒ zero-loss filtering enables TEM imaging of thicker specimens

• significance:
  − preparation of TEM specimens often imposes severe problems
  − example: specimens from multi-component materials
    · mechanical pre-preparation difficult
    · different sputtering rates during ion-beam milling

⇒ ability to image thicker specimens constitutes a major advantage for TEM of many types of structural and electronic materials
• zero-loss filtering also improves TEM diffraction patterns

• conventional diffraction patterns:
  • diffuse background
  • particularly in thicker regions of the specimen

• this problem is particularly evident in CBED
  – CBED usually must be carried out in thicker regions of the specimen in order to obtain enough fine detail
  – fine detail is particularly sensitive to diffuse background

• zero-loss filtering removes the diffuse background

⇒ much clearer and “sharper” diffraction patterns

• demonstration of zero-loss-filtered CBED:

  – cubic BN (boron nitride) in [110] direction
- left: unfiltered pattern
  - blurred
  - poor contrast
  - line scan of diffracted intensity at the bottom features pronounced background intensity

- right: filtered pattern
  - sharp
  - fine detail
  - high contrast
  - line scan of diffracted intensity exhibits substantially smaller background

- zero-loss filtered CBED patterns can be quantitatively evaluated
  - requires recording the pattern with a CCD camera
  - conventional diffraction patterns: diffuse background inhibits quantitative evaluation

- quantification of diffracted intensities
  ⇒ electron structure factors

⇒ assessment of the nature of chemical bonds in crystals:
  - convert electron structure factors to X-ray structure factors (Mott formula)
  - perform a Fourier transformation
  ⇒ charge density reflects nature of interatomic bonds
  ⇒ distinguish, for example, between ionic and covalent interatomic bonding
– however: small effect

⇒ subtract charge density of inner shells to obtain “bonding” charge density

• it is not possible to invert the diffracted intensities and directly extract the underlying parameters

→ compare experimental CBED patterns with and simulated patterns

• optimize the model (parameters) by computer-based refinement algorithm

→ minimization of

$$\chi^2 = \sum_{i=1}^{n} \frac{w_i (c f_i^{\text{sim}} - f_i^{\text{exp}})}{\sigma_i^2}$$

i: pixel index; N: total number of pixels; $f_i^{\text{exp}}, f_i^{\text{sim}}$: experimental and simulated pixel intensity, respectively; $w_i (\neq 1)$: weighing factor; $\sigma_i$: standard deviation of pixel intensity in the experimental data ↔ noise; c: scaling constant.

• example of recent research: interatomic bonding in NiAl
  – B2 structure (CsCl)
  – primitive cubic
  – zero-loss-filtered CBED patterns
  – recorded $\approx 5^\circ$ away from the [110] zone axis (avoid Bragg contrasts)
  – diffraction geometry and example of CBED pattern:
- scans along S1, S2, S3, S4
- result of the fitting procedure:
– measured structure factors:

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– map of bonding charge density:
result:
- concentration of electrons along the nearest neighbor (NN) axis
  ⇒ partial formation of a covalent bond
- electrons are drawn away from the core regions, in particular from the Al core
- both atoms are equally charged and do not have opposite ionicities
  ← donate their electrons to covalent or metallic bonds in the crystal

- second important application of energy-filtered, quantitative CBED: highly precise measurement of lattice spacings with nanometer resolution

  ⇒ determination of stress and strain fields on the nanoscale
  - position of higher-order Laue-zone lines can be determined with substantially less uncertainty
  - the determination of the strain state from the higher-order Laue zone (HOLZ) line positions can be automated by of digital image processing
  - local lattice parameter can be determined with high accuracy
  - recent experiments demonstrated an accuracy of about $10^{-4}$
  ⇒ variety of applications
  - thermal expansion
  - lattice misfit strain
  - transformation strain
  - stress fields of particles, crack tips, etc.
Electron Spectroscopic Imaging

• chemical analysis by imaging with particular, element-specific energy-loss windows

• advantage of ESI over STEM-EELS (EELS with scanning electron probe): fast!

• comparison between EELS and ESI

• two-dimensional data acquisition

• STEM-EELS: sequential recording
• high spatial resolution obtained only with field-emission gun instruments

• early work exists, but rapid development of EFTEM began when omega-type and post-column energy filters became available

• full spectra extending from the zero-loss up to energy loss of 1..2 keV can be retrieved from extended series of ESI-images.

• quantitative analysis of the resulting intensity distribution

• ideally, intensity $I(x, y, E_1, \Delta E)$ should be independent of the sequence in which the data are acquired

**Basics of Quantification**

• after background subtraction, the integrated intensity under an inner-shell loss edge is given by

$$I_k[E_1,E_2] = N_A \sigma_k[E_1,E_2] l_1[E_2 - E_1]$$

$N_A$: number of of A-atoms per unit area, $\sigma_k[\Delta]$: inelastic scattering cross-section for the K-edge of element A in a spectral integration interval $[E_1, E_2]$, $l$: intensity in the low-loss region integrated up to the energy loss $E_2 + E_1$.

• starting point of the integration window: 10..20 eV above the edge onset

  $\Rightarrow$ omit strong oscillations of the near-edge structure

• density $N_a$(atoms/nm$^2$):

$$t = \frac{N_A}{n_A}$$
\[ n_A: \text{number of atoms per volume unit of element } A. \]

- atom density \( n_a \) of element A in a compound \( A_xR \) is related to the mass density \( \rho \) of the compound by

\[
n_A = x \cdot n \]

and

\[
n = \frac{\rho N_A}{A} \]

\( n \): number of atoms per formula unit per unit volume; \( A \): molar mass; \( N_A \): Avogadro number (6.023 \( 10^{23} \)).

- if only concentration ratios between two elements A and B need to be determined, the low-loss intensity \( I_l[E_2-E_1] \) does not have to be measured

- result is determined by the ratio of the intensities under the core-loss edges after background subtraction:

\[
\frac{N_B}{N_A} = \frac{\sigma_k^B[E_1,E_2] I_k^A[E_1,E_2]}{\sigma_k^A[E_1,E_2] I_k^B[E_1,E_2]} \]

- specimen thickness \( t \) can be computed from the inelastic mean free path length for inelastic electron scattering with energy losses smaller than an integration limit \( E_{\text{int}} \)

\[
t = \lambda \ln \left[ \frac{I_{\text{tot}}}{I_0} \right] \]

- integration limit \( E_{\text{int}} \) should be chosen in the range of 150 to 200eV

108
Elemental Mapping Images

- characteristic edges in the energy-loss spectrum
- onset energy characteristic of atomic species
- concentration of an element can be determined from EELS spectrum
- if the pre-edge background must be extrapolated and subtracted from the signal above the edge
- ESI images: subtract background for each pixel
- efficient method for background subtraction: *three-window* technique
• two ESI images are acquired in the background region, before the edge

• extrapolate background and subtracted from the ESI image containing the signal above the edge

• result: difference image
  – contains intensity only in regions where the corresponding element is present in the sample
  – maps the distribution of this element

• however, intensity in the difference image not only depends on concentration of the element but on grain orientation

⇒ artifacts usually referred to as “preservation of elastic scattering contrast”

• intensity of the individual ESI images is low 100 to 1000 times smaller than the corresponding bright-field image

⇒ ESI images tend to be very noisy

⇒ difficult to detect elements in very small concentrations (below 1 at.%) 

• noise can be reduced by image processing techniques

• however, this may result in loss of resolution

• optimum position and width of the three energy windows depend on:
- the intensity in the energy-loss spectrum, which decreases strongly with increasing energy
- the shape of the edge, which shows a sharp onset only for light elements
- the width of the unstructured background region before the edge

• often, the relative amount and spatial distribution of several elements has to be studied in a given region of the specimen

• elemental distribution images can be combined in one image by using different colors for each element and overlaying the individual images

• if several elements are present in some region, mixed colors will result

⇒ mixed colors reveal important information about the occurrence of particular (stoichiometric) phases or compounds

• straight-forward quantitative analysis of three-window ESI images is possible if only concentration ratios of two elements are required:
  - divide the ESI image of one element by the image of the other
  - normalize by the ratios of the core-loss scattering cross-section

⇒ quantitative two-dimensional maps of concentration ratios
demonstration of elemental mapping via ESI:

- oxygen maps of Si₃N₄ ceramics
- grain boundaries contain amorphous film
- film thickness can be controlled by Ca doping
- ESI images show grain boundary film for three different film thicknesses

**Detection Limits**

- cross-sections for inner-shell excitations are small

⇒ detection limit is governed by the signal-to-noise ratio

- signal intensity in the presence of element A:

  \[ I_A = \frac{1}{e} j_0 n_A \sigma_A \tau \]

  \( j_0 \): current density of incident beam; \( n_A \): number of A atoms per unit area; \( \tau \): integration time (exposure time of the image); \( \sigma_A = \sigma_A(E_1, E_2, \delta E, \Theta_c, \theta_0) \): integrated elastic scattering cross-section for the chosen energy window \((E_1, E_2)\), width \( \delta E \); \( \Theta_c \): illumination aperture; \( \theta_0 \): objective aperture.

- intensity \( I_A \) is superimposed on a background:
\[ I_b = \frac{1}{e} j_0 \left( n_A \sigma_A + \sum_{X} n_X \sigma_X^b \right) \tau, \]

to which the element A and all other elements contribute according to their densities \(n_X\).

- the two images acquired at energy losses \(\Delta E_1\) and \(\Delta E_2\) below the edge show only this background intensity

- extrapolate background by power law:
  \[ I_b = a(\Delta E)^{-r} \]

- subtract from third image, \(I_3 = I_A + I_b\) to obtain \(I_A\), the elemental map of element A

- signal-to-noise level for the above example of grain boundary films in Si\(_3\)N\(_4\) ceramics:

  - empirical rule: detection requires \(S/N > 5\)
• theoretical curve: result of quantitative consideration of Poisson noise statistics (not derived here)

• the $S/N$ ratio can be improved by integrating parallel to the boundary (upper curve)

• theoretical curve $\Rightarrow$ even one monolayer of oxide should be detectable in integrated line scans!!

• effect of increasing the high voltage:
  - inelastic scattering cross-sections $\sigma_X$ decrease
  - this can be countered to some extent by using a greater specimen thickness
    (this also reduces the influence of surface layers)
  - accelerating voltages above 1MeV, however, are clearly disadvantageous

**Spatial Resolution of ESI**

• spatial resolution is controlled by a number of factors:
  - the ultimate limit $\leftrightarrow$ aberrations of the electron optical elements of the instrument (spherical aberration, aperture, instabilities)

    $\rightarrow$ instrumental resolution limit

    - however, the resolution is further *degraded* by the inherent *delocalization* of inelastic scattering (a consequence of the quantum mechanical uncertainty principle):
\[ d_{\text{del}} = \frac{\lambda}{2\theta_E^{3/4}} M \]

\( \lambda \): de Broglie wavelength; \( \theta_E \): acceptance angle; \( M \): magnification.

- calculations show that this contribution is small and can be ignored for inner-shell losses of 100eV and higher

- resulting resolution \( d_{\text{ges}} \) as a function of the maximum scattering angle \( \alpha \):

\( d_s, d_c, d_b \): contribution from spherical aberration, chromatic aberration, aperture.

- often, however, the dominant limitation arises from the *statistical nature* of inelastic scattering and the weakness of the signal
structures close to the instrumental resolution limit remain unresolved in ESI images because of poor signal-to-noise ratio

⇒ object-related resolution limit

• often two to five times worse than the instrumental resolution limit!

• demonstration of highly resolved ESI imaging:

- ESI map of Si in a SiGe multilayer with 1.5nm layer thickness
- left: bright-field image (conventional TEM)
- right: ESI image
- individual layers are resolved
⇒ spatial resolution on the order of 1nm
Tomography

- principle of tomography
  - reconstruct a volume of material from a series of two-dimensional *projections* (sections)

- complication with TEM:
  - dynamical diffraction \(\rightarrow\) non-linear contrast formation
  - image contrast changes dramatically with specimen orientation

- solution: ESI
  - form image only with electrons that have undergone a particular energy loss, typical for a chemical element in the specimen

- demonstration:
- $\text{Y}_2\text{O}_3$ nanoparticles at FeAl grain boundaries
- electron-spectroscopic imaging with oxygen edge
- images in different directions, spanning a tilt-angle range of 120°
- recorded under energy losses of 0, 20, 40, and 60eV
- 360 views of Y$_2$O$_3$ a nanoparticle ensemble, computer-reconstructed from multiple elemental maps over a tilt-angle range of 120°:
The Future of Analytical TEM
• SESAM stands for “sub-eV sub-Å microscope”

• prototype is presently being installed in Stuttgart/Tübingen (Germany)

• features:
  - electron monochromator
    (electrostatic omega filter in the illumination system)
    → limit the energy spread of the primary electrons down to 0.2eV
  - mandoline filter
    → superior transmissivity

• potential applications:
  - fine structure in EELS spectra with superior energy resolution
  - electronic structure of crystal defects

• examples:
  - distinguish solute atoms in different environments
    (e.g. cations in inverse spinel versus normal spinel)
  - effect of crystal defects on the bandstructure of semiconductor crystals
  - examples:
    - electronic effect of crystal dislocations, stacking faults, grain boundaries, …
    - electronic effect of misfit strain in semiconductor heterostructures