Analytical Electron Microscopy

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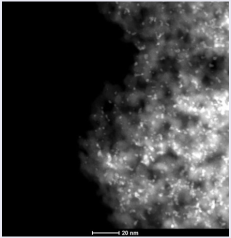
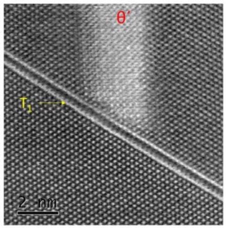
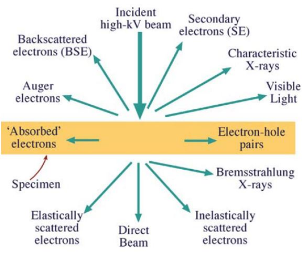
10.11.2017

Analytical Electron Microscopy

- Imaging
- Diffraction
- Spectrometry

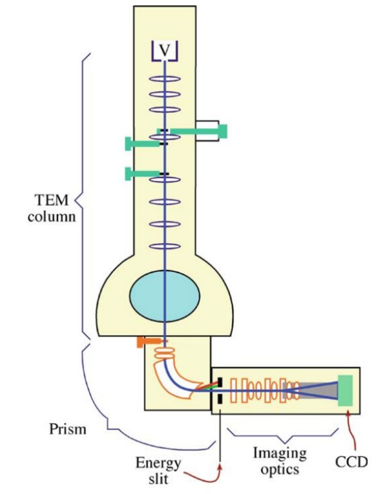


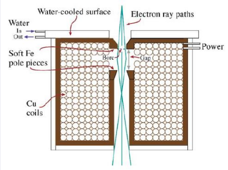


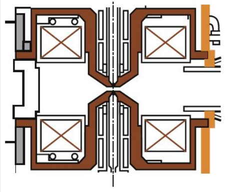


Williams, Carter: "Transmission Electron Microscopy - A Textbook for Materials Science", Springer 2009

Mode of Operation

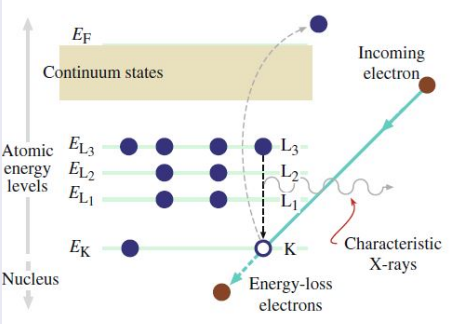






Williams, Carter: "Transmission Electron Microscopy - A Textbook for Materials Science", Springer 2009

Introduction to EDX



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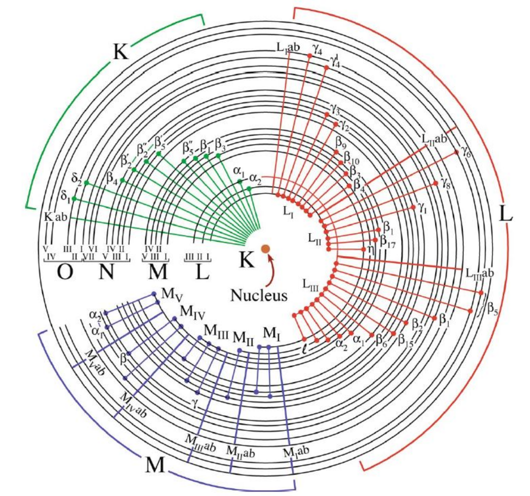
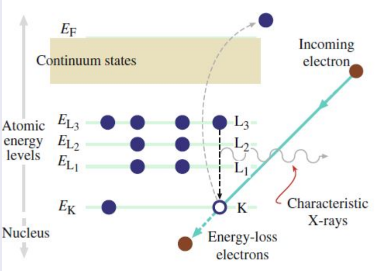
EDX

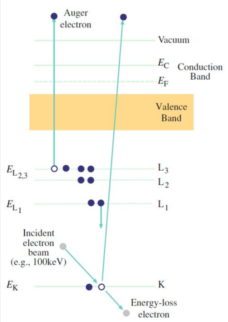
Introduction to EDX

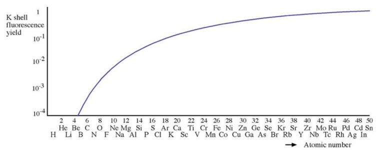


Williams, Carter: "Transmission Electron Microscopy - A Textbook for Materials Science", Springer 2009

Fluorescence Yield



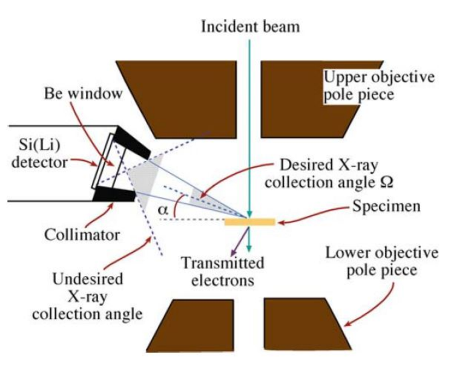




Williams, Carter: "Transmission Electron Microscopy - A Textbook for Materials Science", Springer 2009

Detectors

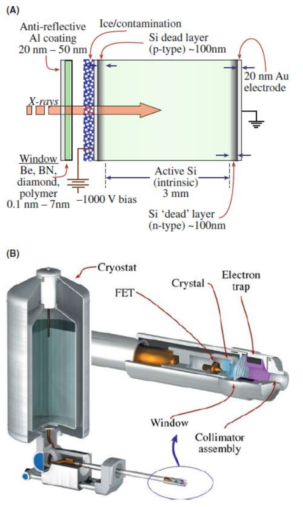
EDX-Setup

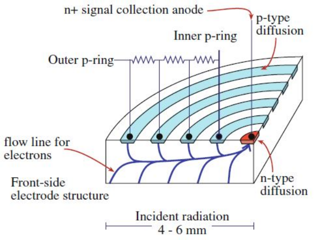


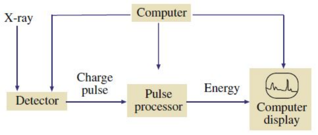
Detector area, collection angle
SuperX (ChemiSTEM): 4 detectors

Williams, Carter: "Transmission Electron Microscopy - A Textbook for Materials Science", Springer 2009

EDX Detectors

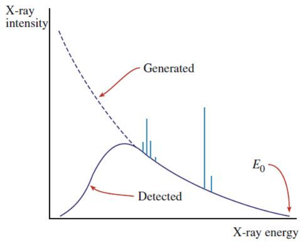


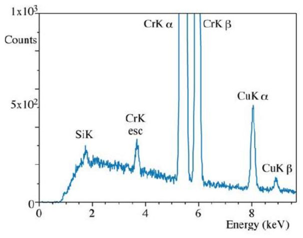


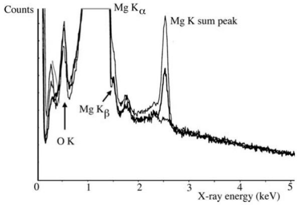


- Dead Time
- Live Time
- Clock Time

EDX Signal







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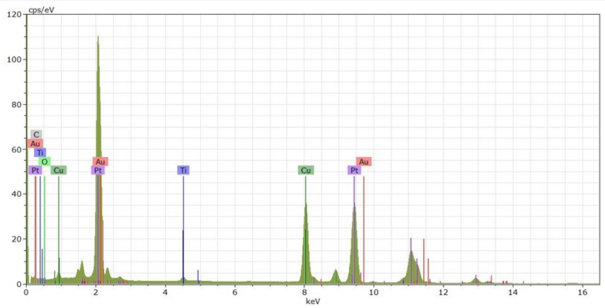
Qualitative Analysis

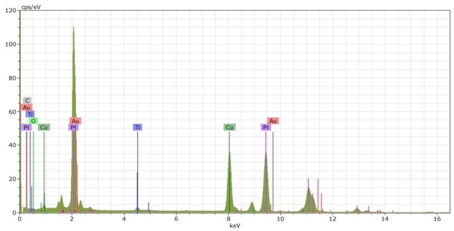
EDX-Spectra

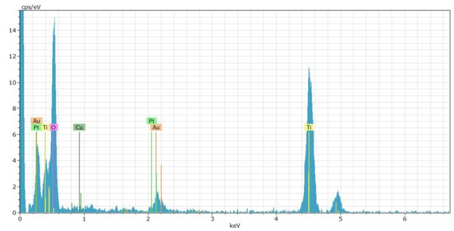


- Cu from System
- Be for low background sample holder

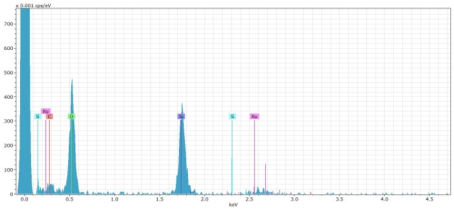
Qualitative Analysis

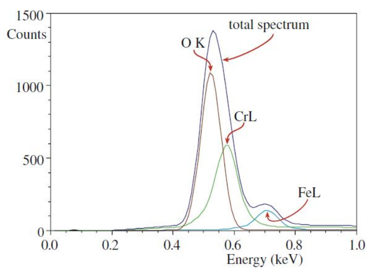
EDX-Spectra





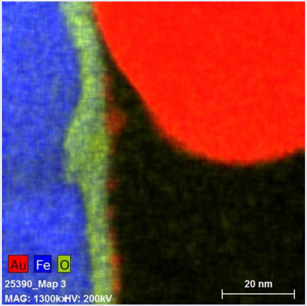
EDX-Spectra

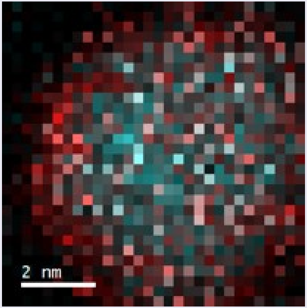

x 0.001 cps/eV
700
600
500
400
300
200
100
0
S
Ru
C
O
Si
S
Ru
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
keV


1500
Counts
1000
500
0
total spectrum
O K
CrL
FeL
0.0
0.2
0.4
0.6
0.8
1.0
Energy (keV)

Qualitative Analysis

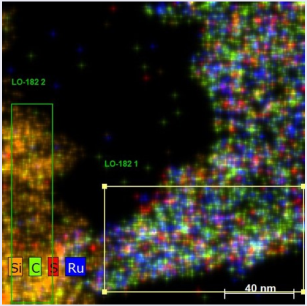
EDX-Maps

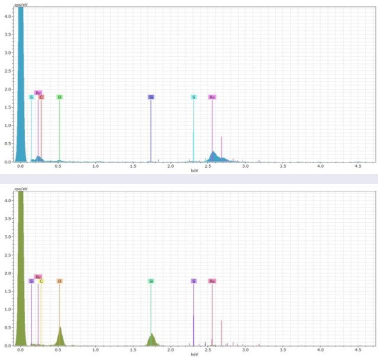




Qualitative Analysis

EDX-Maps





Quantitative Analysis

Cliff-Lorimer Ratio Technique

- $C_A/C_B = k_{AB} \cdot I_A/I_B$
- $k_{AB} \ldots$ Cliff-Lorimer factor
- $C_A + C_B = 1$
- For thin specimen, absorption can be neglected
- k_{AB} either measured using standards or calculated

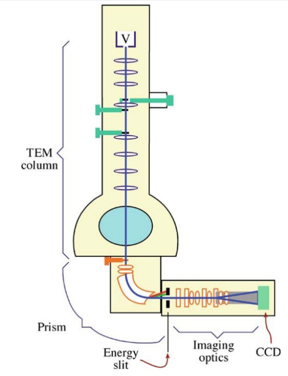
Quantitative Analysis

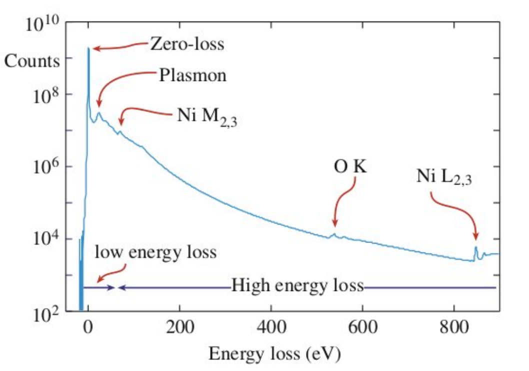
ζ-Factor Method

- $\rho t = \zeta_A \cdot I_A / C_A$
- $C_A / C_B = (I_A \zeta_A)/(I_B \zeta_B)$
- ζ-factors either measured using standards or calculated
- For both techniques absorption correction (ZAF) possible

Electron Energy Loss Spectrometry

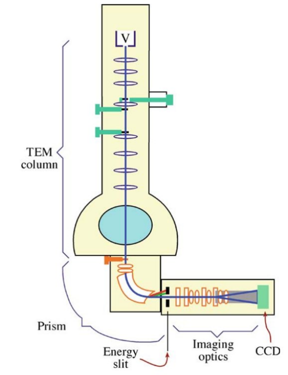
EELS

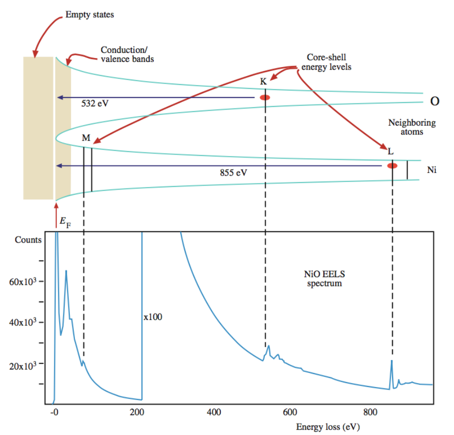




Williams, Carter: "Transmission Electron Microscopy - A Textbook for Materials Science", Springer 2009

EELS





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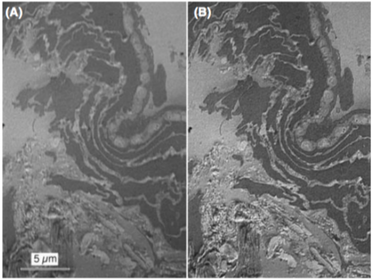
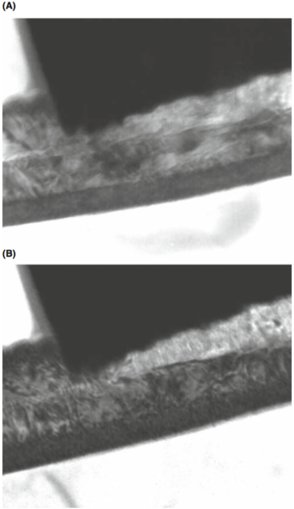
Electron Energy Loss Spectrometry





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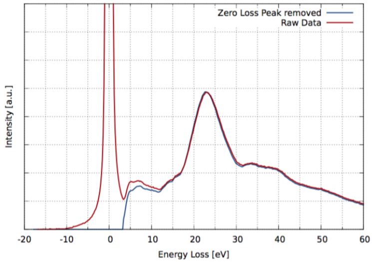
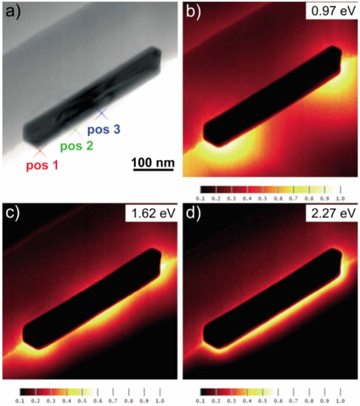
Electron Energy Loss Spectrometry



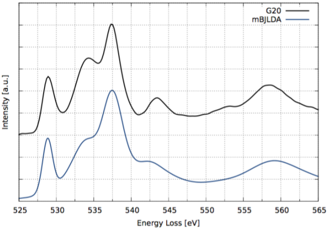


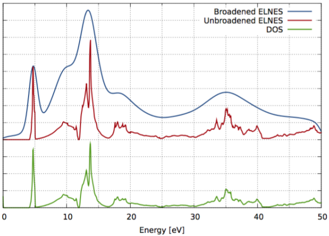
Hetaba: Fine Structure and Site Specific Energy Loss Spectra of NiO, Diploma Thesis, TU Wien 2011

Schaffer et al., Phys. Rev. B, 79, 041401(R), 2009

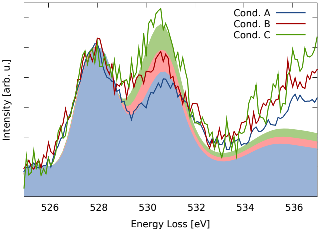
Electron Energy Loss Spectrometry

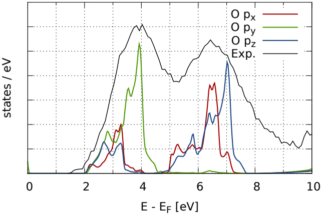
NiO





TiO_2





Hetaba: Fine Structure and Site Specific Energy Loss Spectra of NiO, Diploma Thesis, TU Wien 2011

Hetaba: The Theory and Application of Inelastic Coherence in the Electron Microscope, PhD Thesis, TU Wien 2015

Classical Scattering Theory

- Elastic vs. inelastic scattering
- Differential scattering cross section $\mathrm{d}\sigma/\mathrm{d}\Omega$ to describe scattering

Elastic Scattering

- Transfer of momentum
- Transfer of kinetic energy
- No change of internal energy of particle and target

Inelastic Scattering

- Transfer of momentum
- Transfer of energy
- Internal energy of target changed

Elastic vs. Inelastic Scattering

interaction	$\Delta E[eV]$	target apparatus	crystal	atom	electron
Bragg	10^{-23}	in	**el**	-	-
phonon	0.01	in	in	**el**	-
at. displacement	> 10	in	in	**el**	**el**
interband	1	in	in	in	**el**
exciton	< 10	in	in	in	**el**
plasmon	> 10	in	in	-	**el**
ionization	~ 100	in	in	in	**el**
Compton	~ 1000	in	in	in	**el**

Schattschneider, Werner, Hébert: Lecture Notes “Electron Beam Techniques for Nanoanalysis”, TU Wien 2007

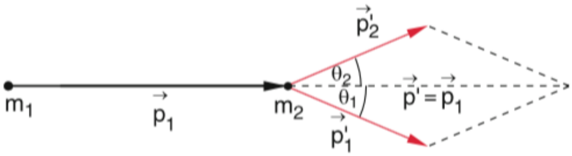
Elastic Scattering

Classical scattering

$\boldsymbol{p}_0 = \boldsymbol{p}_1 + \boldsymbol{p}_2$

$E_0 = \frac{p_0^2}{2m} = \frac{p_1^2}{2m} + \frac{p_2^2}{2M}$

$\Delta E = \frac{p_2^2}{2M} = \frac{4mM}{(M+m)^2} E_0 \approx 4\frac{m}{M} E_0$, with $m \ll M$



Demtröder: Experimentalphysik 1, Springer 2013

Elastic Scattering

Rutherford scattering

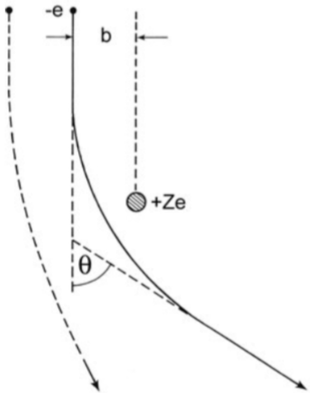
$\mathrm{d}\sigma/\mathrm{d}\Omega = |f(q)|^2$, $f(q)\ldots$ scattering factor

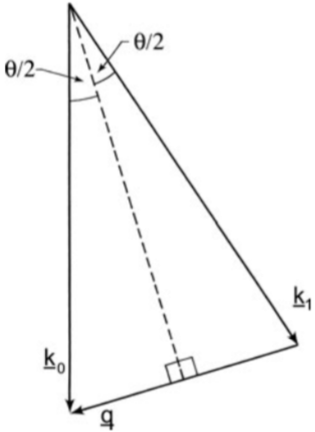
$f(q)$ proportional to $FT[V(r)]$, $V(r)\ldots$ atomic potential

Coulomb potential yields Rutherford cross section:

$\mathrm{d}\sigma/\mathrm{d}\Omega = \frac{4\gamma Z^2}{a_0^2 q^4}$, $q = 2k_0 \sin(\theta/2)$

Elastic Scattering





Egerton: Electron energy-loss spectroscopy in the electron microscope, Plenum Press 1996

Elastic Scattering

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Coulomb potential yields Rutherford cross section:

$\mathrm{d}\sigma/\mathrm{d}\Omega = \frac{4\gamma Z^2}{a_0^2 q^4}$, $q = 2k_0 \sin(\theta/2)$

- Unscreended potential
- Overestimates elastic scattering at small θ (large b)

Elastic Scattering

Yukawa potential

Screened potential:

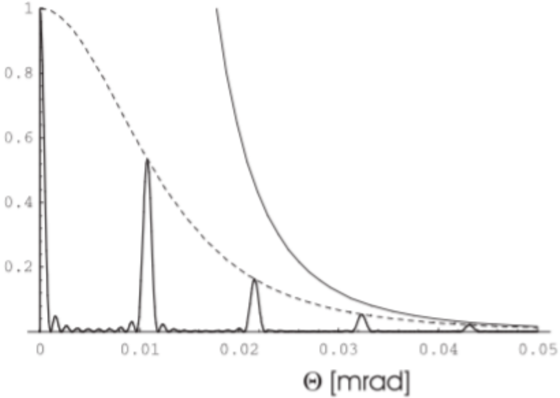
$$V(r) = (Ze/4\pi\epsilon_0 r)\exp(r/r_0)$$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{4\gamma^2 Z^2}{a_0^2 k_0^4} \frac{1}{(\theta^2+\theta_0^2)^2}$$

Characteristic scattering angle: $\theta_0 = (k_0 r_0)^{-1}$

Screening radius: $r_0 = a_0 Z^{-1/3}$

Elastic Scattering



Schattschneider, Werner, Hébert: Lecture Notes “Electron Beam Techniques for Nanoanalysis”, TU Wien 2007

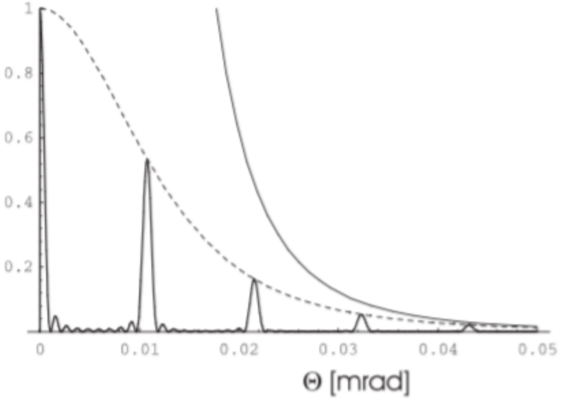
Elastic Scattering

Diffraction and channelling effects

- Bragg scattering in crystals
- Modifies scattering cross section
- Channelling effects: redistribution of electron flux inside crystal

- Elastic scattering changes probabilites for inelastic scattering

Elastic Scattering



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Elastic Scattering

Diffraction and channelling effects

- Bragg scattering in crystals
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- Elastic scattering changes probabilites for inelastic scattering

Inelastic Scattering

Inelastic differential scattering cross section

$$\frac{\mathrm{d}\sigma_i}{\mathrm{d}\Omega} = \frac{4\gamma^2 Z}{a_0^2 q^4}\left\{1 - \frac{1}{[1+(qr_0)^2]^2}\right\}$$

$$q^2 = k_0^2(\theta^2 + \theta_E^2)$$

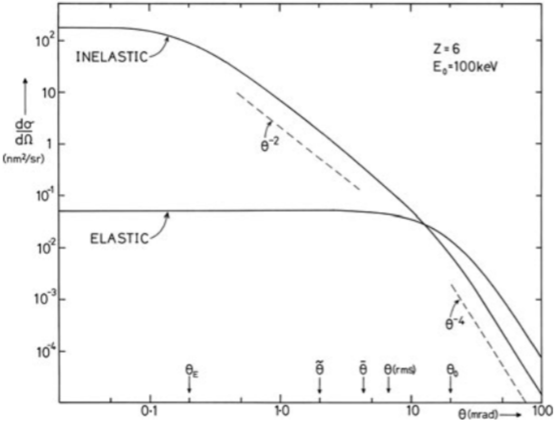
$\theta_E = E/(\gamma m_0 v^2)$, characteristic inelastic scattering angle

$$\theta_0 = (k_0 r_0)^{-1}$$

$\theta_E < \theta < \theta_0$: $\mathrm{d}\sigma/\mathrm{d}\Omega \propto \theta^{-2}$

$\theta > \theta_0$: $\mathrm{d}\sigma/\mathrm{d}\Omega \propto \theta^{-4}$

Inelastic Scattering



Egerton: Electron energy-loss spectroscopy in the electron microscope, Plenum Press 1996

Quantum Mechanical Description

Double differential scattering cross section

$$W_{i\to f} = \frac{2\pi}{\hbar} \left| \langle \Psi_f | \hat{V} | \Psi_i \rangle \right|^2 dv_f \cdot \delta \left(E_{|\Psi_f\rangle} - E_{|\Psi_i\rangle} \right)$$

$$dj = d\sigma(E, \Omega) \cdot j_i$$

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} = \left(\frac{2\pi}{\hbar} \right)^4 m^2 \frac{k_f}{k_i} \sum_i p_i \sum_f \left| \langle \psi_f | \langle f | \hat{V} | i \rangle | \psi_i \rangle \right|^2 \cdot \delta \left(E_{|f\rangle} - E_{|i\rangle} - E \right)$$

Models for the DDSCS

Single plane wave

$\psi_{i,f}(\boldsymbol{r}) = \frac{1}{(2\pi)^{3/2}} \exp[i\boldsymbol{k}_{i,f}\boldsymbol{r}]$

$\frac{\partial^2\sigma}{\partial E \partial \Omega} = \frac{4\gamma^2}{a_0^2}\frac{k_f}{k_i}\frac{1}{Q^4}\sum_i p_i \sum_f \sum_j \left|\langle f \mid e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_j} \mid i\rangle\right|^2 \cdot \delta\left(E_{|f\rangle} - E_{|i\rangle} - E\right)$

Dynamic Form Factor (DFF):

$S(\boldsymbol{Q}, E) = \sum_i p_i \sum_f \sum_j \left|\langle f \mid e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_j} \mid i\rangle\right|^2 \cdot \delta\left(E_{|f\rangle} - E_{|i\rangle} - E\right)$

$\frac{\partial^2\sigma}{\partial E \partial \Omega} = \frac{4\gamma^2}{a_0^2}\frac{k_f}{k_i}\frac{1}{Q^4} S(\boldsymbol{Q}, E)$

Models for the DDSCS

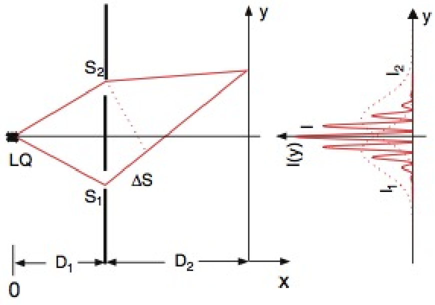
Superposition of plane waves

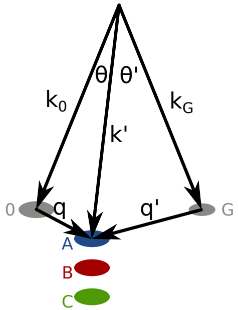
$$|\psi_i\rangle = a_1 |\boldsymbol{k}_1\rangle + a_2 |\boldsymbol{k}_2\rangle, \; |a_1|^2 + |a_2|^2 = 1$$

$$\frac{\partial^2\sigma}{\partial E \partial \Omega} = \frac{4\gamma^2}{a_0^2}\frac{k_f}{k_i}\left[|a_1|^2 \frac{1}{Q^4} S(\boldsymbol{Q}, E) + |a_2|^2 \frac{1}{Q'^4} S(\boldsymbol{Q}', E) + \right.$$
$$\left. + 2\Re\left[a_1 a_2^* \frac{1}{Q^2 Q'^2} S(\boldsymbol{Q}, \boldsymbol{Q}', E)\right]\right]$$

Mixed Dynamic Form Factor (MDFF):
$$S(\boldsymbol{Q}, \boldsymbol{Q}', E) = \sum_i \sum_f \langle f|e^{i\boldsymbol{Q}\cdot\boldsymbol{R}}|i\rangle \langle i|e^{-i\boldsymbol{Q}'\cdot\boldsymbol{R}}|f\rangle \cdot \delta\left(E_{|f\rangle} - E_{|i\rangle} - E\right)$$

Models for the DDSCS





$$I \propto A_1^2 + A_2^2 + 2\Re[A_1 A_2^* \cdot \exp i(\phi_1 - \phi_2)]$$

Demtröder: Experimentalphysik 1, Springer 2013

Hetaba: The Theory and Application of Inelastic Coherence in the Electron Microscope, PhD Thesis, TU Wien 2015

Models for the DDSCS

Bloch waves

$$\frac{\partial^2\sigma}{\partial E\partial\Omega} = \frac{4\gamma^2}{a_0^2}\frac{k_f}{k_i}\sum_{\mathbf{x}}\sum_{\substack{j,j',l,l' \\ \mathbf{g},\mathbf{g}',\mathbf{h},\mathbf{h}'}} X^{jlj'l'}_{\mathbf{g}\mathbf{h}\mathbf{g}'\mathbf{h}'}(\mathbf{x})\frac{S_x(\mathbf{Q},\mathbf{Q}',E)}{Q^2Q'^2}$$

MDFF for Crystals

$$S(\mathbf{Q},\mathbf{Q}',E)=\sum_{\nu}\sum_{mm'}\sum_{\lambda\lambda'}\sum_{\mu\mu'}\sum_{LMS}\sum_{L'M'S'} i^{\lambda-\lambda'}4\pi(2l+1)\times$$
$$\sqrt{(2L+1)(2L'+1)(2\lambda+1)(2\lambda'+1)}\times$$
$$Y_{\lambda}^{\mu}(\mathbf{Q}/Q)^{*}\,\langle j_{\lambda}(Q)\rangle_{\nu njLS}\,Y_{\lambda'}^{\mu'}(\mathbf{Q}'/Q')\,\langle j_{\lambda'}(Q')\rangle_{\nu njL'S'}\times$$
$$\begin{pmatrix} L & \lambda & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L' & \lambda' & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & \lambda & l \\ -M & \mu & m \end{pmatrix}\begin{pmatrix} L' & \lambda' & l \\ -M' & \mu' & m' \end{pmatrix}\times$$
$$\sum_{j_z}(-1)^{M+M'}(2j+1)\begin{pmatrix} l & \frac{1}{2} & j \\ m & S & -j_z \end{pmatrix}\begin{pmatrix} l & \frac{1}{2} & j \\ m' & S' & -j_z \end{pmatrix}\times$$
$$(D_{LMS}^{\nu})^{*}(D_{L'M'S'}^{\nu})\delta(E_{|f\rangle}-E_{|i\rangle}-E)$$

Löffler: Study of real space wave functions with electron energy loss spectrometry, PhD Thesis, TU Wien 2013

WIEN2k Simulations

Features of WIEN2k

- Density Functional Theory, Kohn-Sham equation
- Electronic properties of crystal
  - Electron density
  - Bandstructure
  - DOS
- TELNES.3

Density Functional Theory

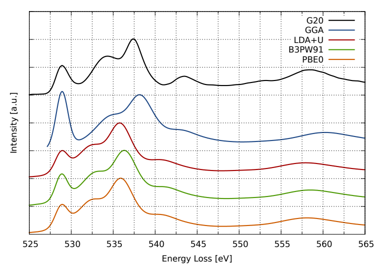
Kohn-Sham equation

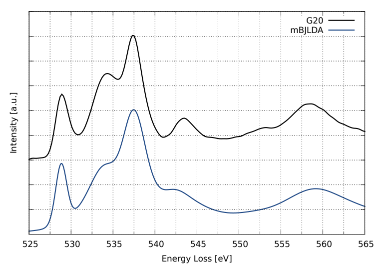
$$\hat{H} = -\frac{\hbar^2}{2}\sum_i^N \frac{\nabla^2_{\vec{R}_i}}{M_i} - \frac{\hbar^2}{2}\sum_i^N \frac{\nabla^2_{\vec{r}_i}}{m_e}$$
$$-\frac{1}{4\pi\epsilon_0}\sum_{i,j}^N \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0}\sum_{i\neq j}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0}\sum_{i\neq j}^N \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}$$

$$\begin{aligned}\hat{H}_{KS} &= \hat{T} + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext} \\ &= -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \hat{V}_{xc} + \hat{V}_{ext}\end{aligned}$$

Calculated Spectra

NiO

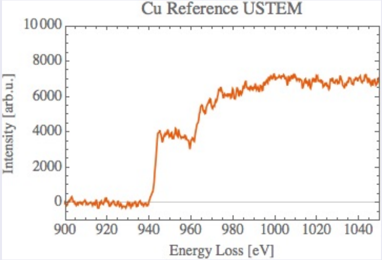


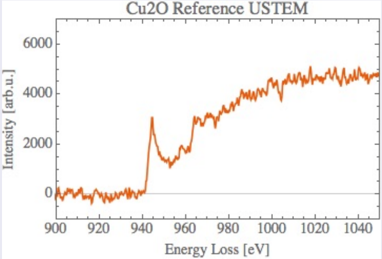


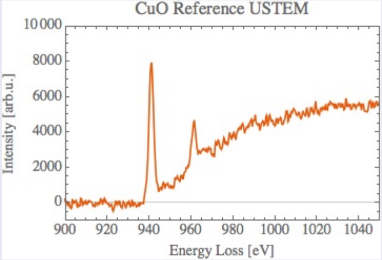
Hetaba: Fine Structure and Site Specific Energy Loss Spectra of NiO, Diploma Thesis, TU Wien 2011
Hetaba et al., Phys. Rev. B 85, 205108, 2012

Applications

Oxidation State

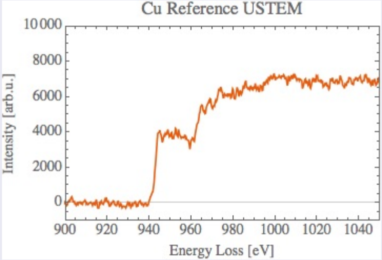


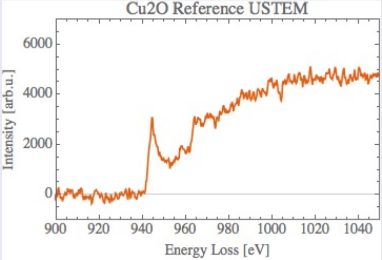


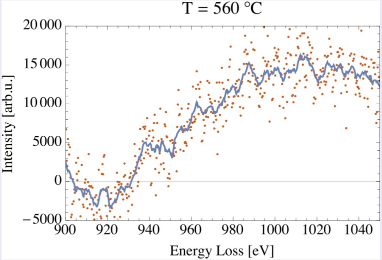


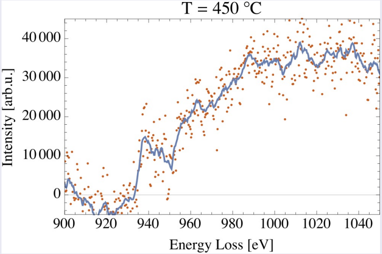
Applications

Oxidation State



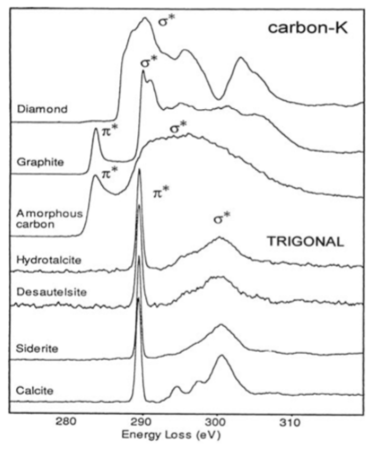






Applications

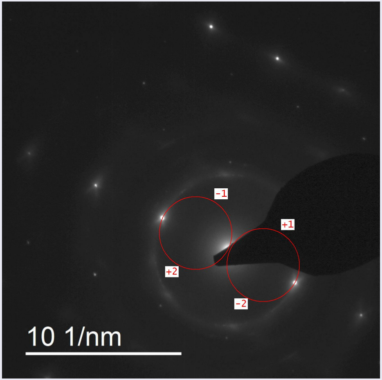
Crystallographic Structure - Coordination

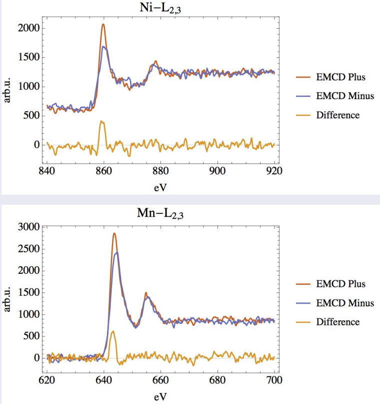


Egerton: Electron energy-loss spectroscopy in the electron microscope, Plenum Press 1996

Applications

EMCD

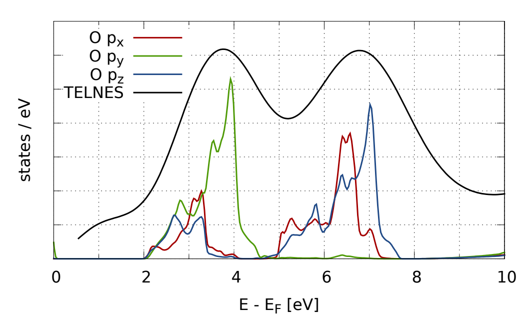




Hetaba: The Theory and Application of Inelastic Coherence in the Electron Microscope, PhD Thesis, TU Wien 2015

Applications

Channelling effects



Hetaba: The Theory and Application of Inelastic Coherence in the Electron Microscope, PhD Thesis, TU Wien 2015

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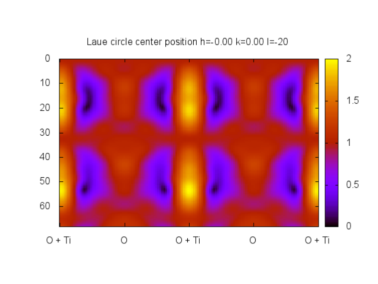

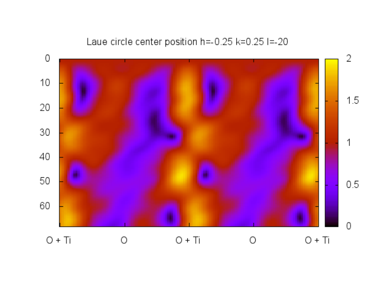

Hetaba: The Theory and Application of Inelastic Coherence in the Electron Microscope, PhD Thesis, TU Wien 2015

Hetaba et al., Micron 63, 15-19, 2014

Applications

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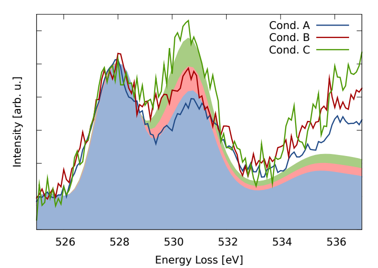

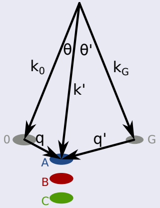

Hetaba: The Theory and Application of Inelastic Coherence in the Electron Microscope, PhD Thesis, TU Wien 2015

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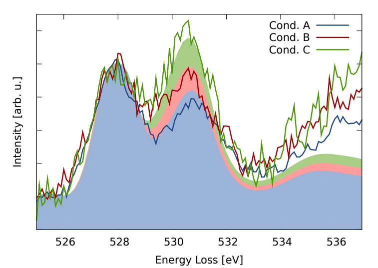

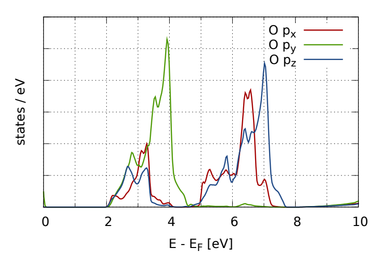

Hetaba: The Theory and Application of Inelastic Coherence in the Electron Microscope, PhD Thesis, TU Wien 2015

Hetaba et al., Micron 63, 15-19, 2014

Conclusion

- EDX and EELS complimentary techniques
- Understanding of theory necessary for interpretation
- Lots of different properties accessible
- Analytical Electron Microscopy versatile tool

Literature

Useful books (linked)

Analytical electron microscopy in general:

- Williams, Carter: Transmission Electron Micrsocopy - A Textbook for Materials Science

Everything about EELS:

- Egerton: Electron energy-loss spectroscopy in the electron microscope

Theory:

- Schattschneider: Fundamentals of Inelastic Electron Scattering
- Schattschneider: Linear and Chiral Dichroism in the Electron Microscope

Literature

Links to cited articles and EELS Databases

- Schaffer et al., Phys. Rev. B, 79, 041401(R), 2009
- Hetaba et al., Phys. Rev. B 85, 205108, 2012
- Hetaba et al., Micron 63, 15-19, 2014
- Demtröder: Experimentalphysik 1, Springer 2013
- PhD thesis Löffler
- PhD thesis Hetaba

EELS Database:

- Gatan EELS.info, EELS-Atlas
- EELS Data Base

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- A. Hütten