

Analytical Electron Microscopy

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1 Introduction

2 EDX

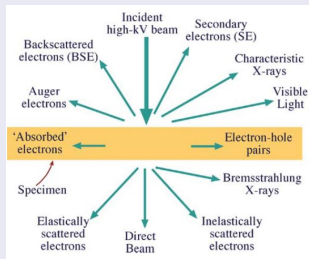
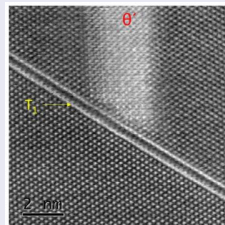
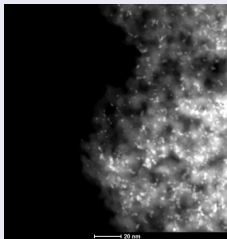
3 EELS

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Introduction

Analytical Electron Microscopy

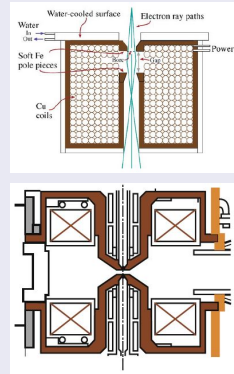
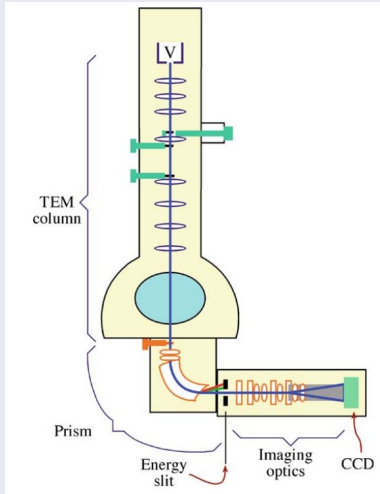
- Imaging
- Diffraction
- Spectrometry



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

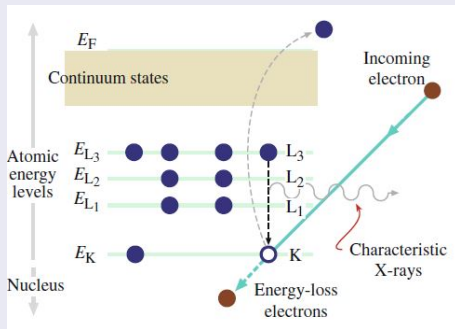
Introduction

Mode of Operation



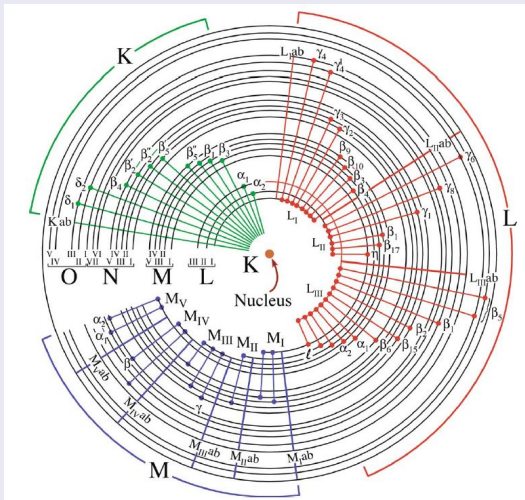
Williams, Carter: "Transmission Electron Microscopy - A Textbook for Materials Science", Springer 2009

Introduction to EDX



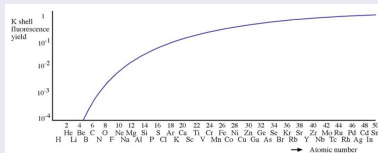
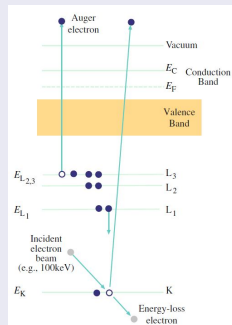
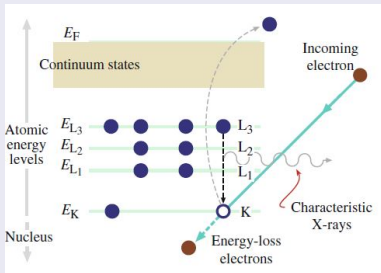
Williams, Carter: "Transmission Electron Microscopy - A Textbook for Materials Science", Springer 2009

Introduction to EDX



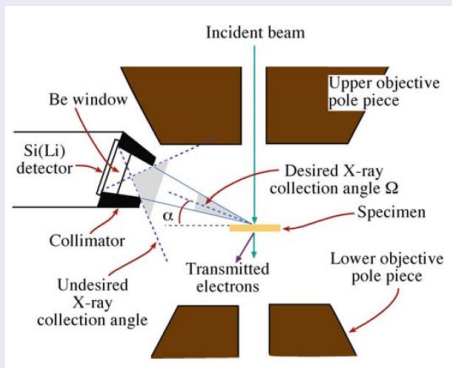
Williams, Carter: "Transmission Electron Microscopy - A Textbook for Materials Science", Springer 2009

Fluorescence Yield



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

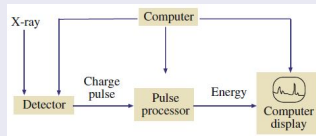
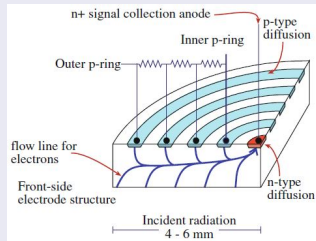
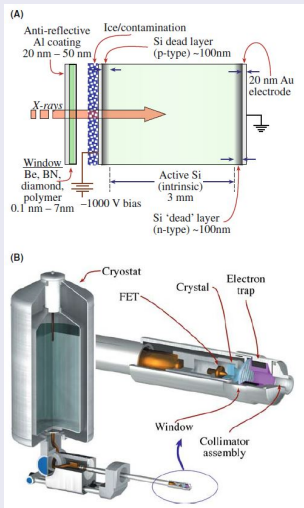
EDX-Setup



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

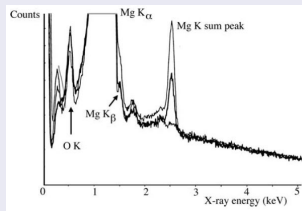
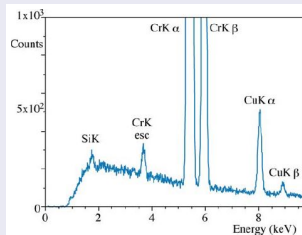
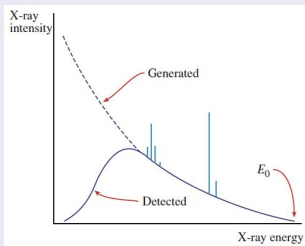
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EDX Detectors



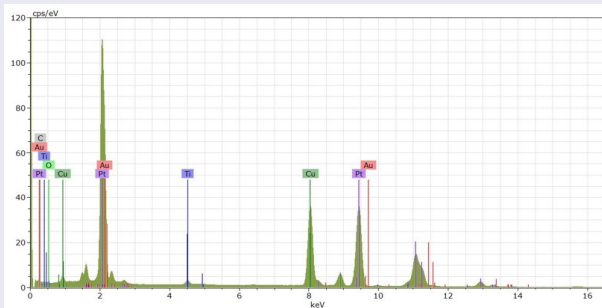
- Dead Time
- Live Time
- Clock Time

EDX Signal



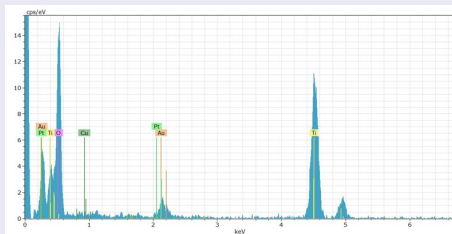
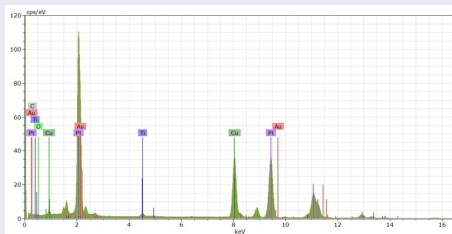
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EDX-Spectra

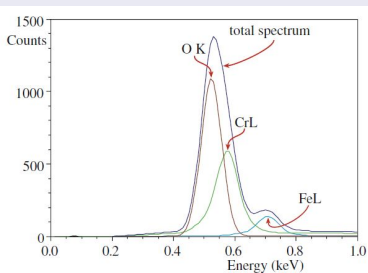
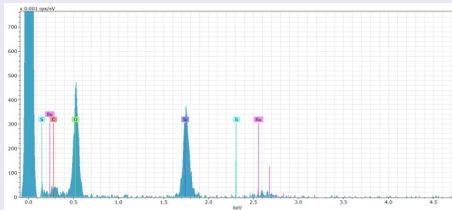


- Cu from System
- Be for low background sample holder

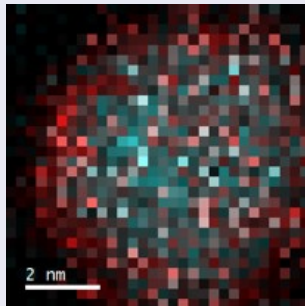
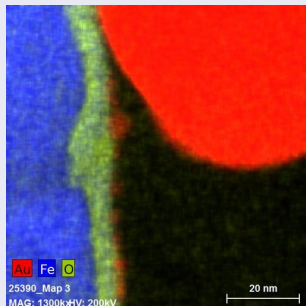
EDX-Spectra



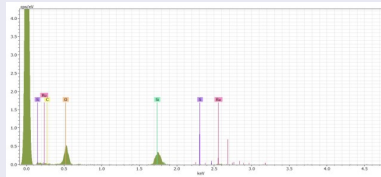
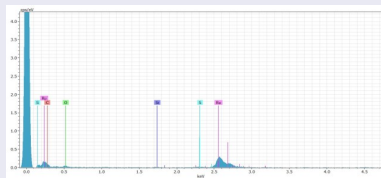
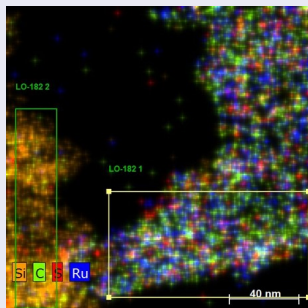
EDX-Spectra



EDX-Maps



EDX-Maps



Cliff-Lorimer Ratio Technique

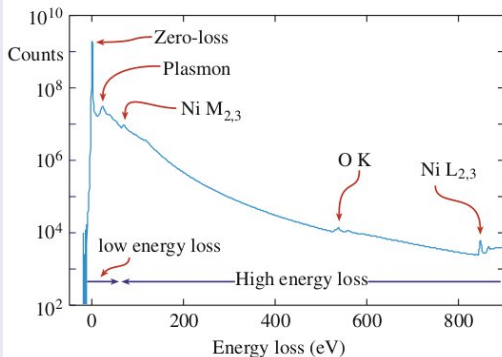
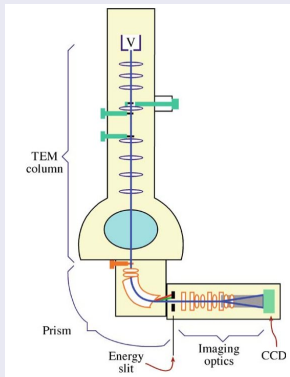
- $C_A/C_B = k_{AB} \cdot I_A/I_B$
- k_{AB} ... Cliff-Lorimer factor
- $C_A + C_B = 1$
- For thin specimen, absorption can be neglected
- k_{AB} either measured using standards or calculated

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

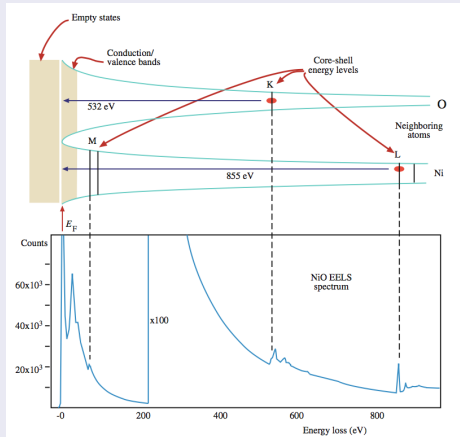
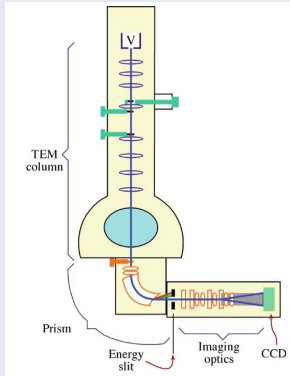
EELS



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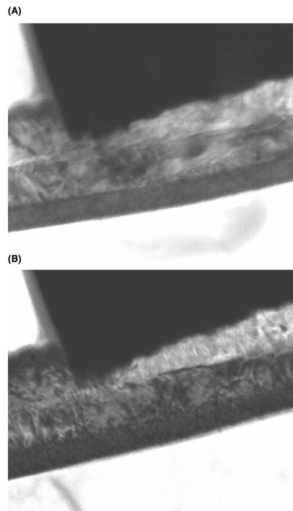
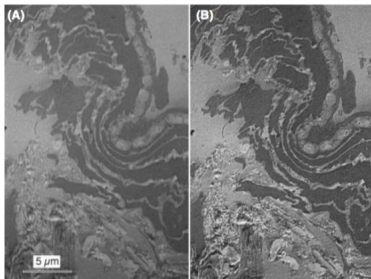
Electron Energy Loss Spectrometry

EELS



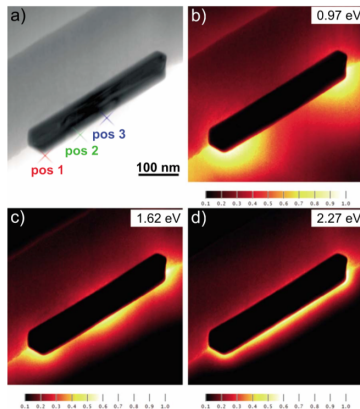
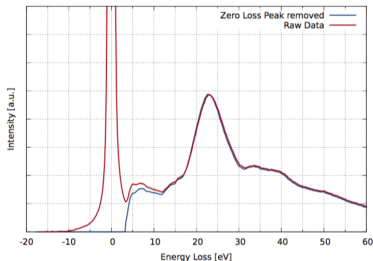
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Electron Energy Loss Spectrometry



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Electron Energy Loss Spectrometry

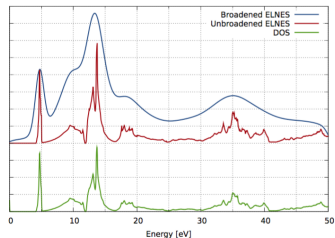
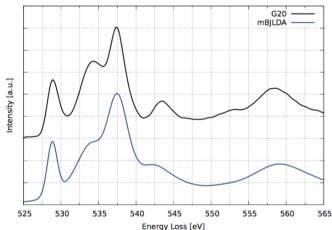


Hetaba: Fine Structure and Site Specific Energy Loss Spectra of NiO, Diploma Thesis, TU Wien 2011

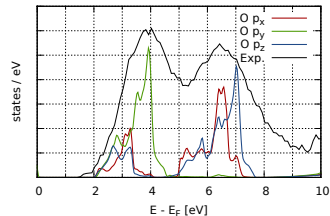
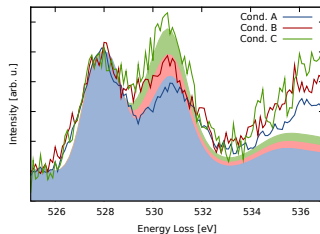
Schaffer et al., Phys. Rev. B, 79, 041401(R), 2009

Electron Energy Loss Spectrometry

NiO



TiO₂



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 $d\sigma/d\Omega$ 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 phonon	10^{-23}	in	el	-	-
	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

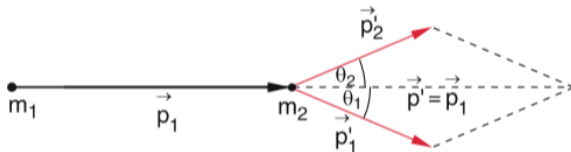
Elastic Scattering

Classical scattering

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

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

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



Demtröder: Experimentalphysik 1, Springer 2013

Rutherford scattering

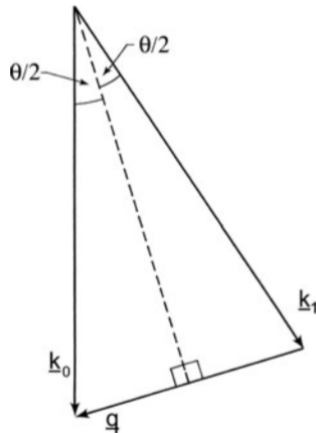
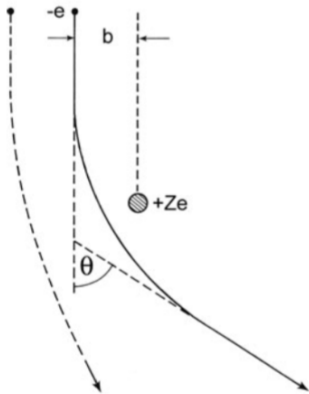
$d\sigma/d\Omega = |f(q)|^2$, $f(q) \dots$ scattering factor

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

Coulomb potential yields Rutherford cross section:

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

Elastic Scattering



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

Rutherford scattering

$d\sigma/d\Omega = |f(q)|^2$, $f(q) \dots$ scattering factor

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Coulomb potential yields Rutherford cross section:

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

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

Yukawa potential

Screened potential:

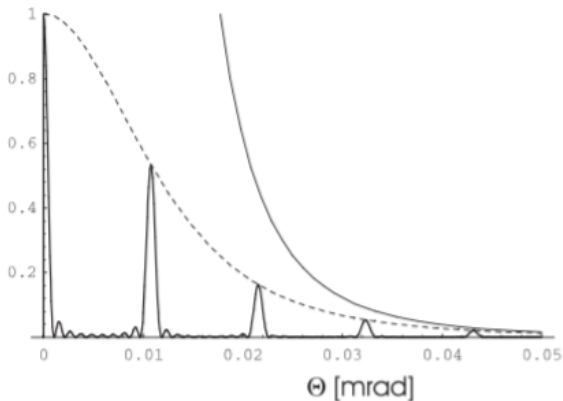
$$V(r) = (Ze/4\pi\epsilon_0 r) \exp(r/r_0)$$

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

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

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

Elastic Scattering

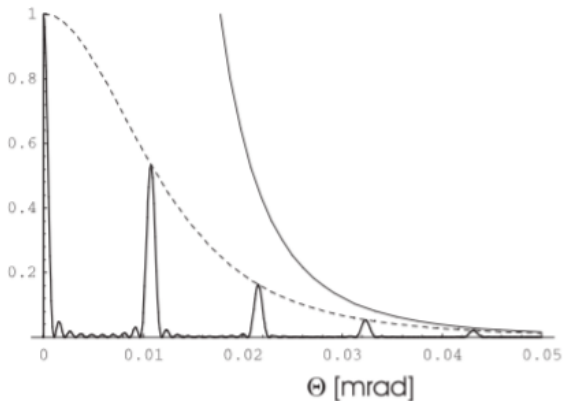


Schattschneider, Werner, Hébert: Lecture Notes "Electron Beam Techniques for Nanoanalysis", TU Wien 2007

Diffraction and channelling effects

- Bragg scattering in crystals
- Modifies scattering cross section
- Channelling effects: redistribution of electron flux inside crystal
- Elastic scattering changes probabilities for inelastic scattering

Elastic Scattering



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

Diffraction and channelling effects

- Bragg scattering in crystals
- Modifies scattering cross section
- Channelling effects: redistribution of electron flux inside crystal
- Elastic scattering changes probabilities for inelastic scattering

Inelastic differential scattering cross section

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

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

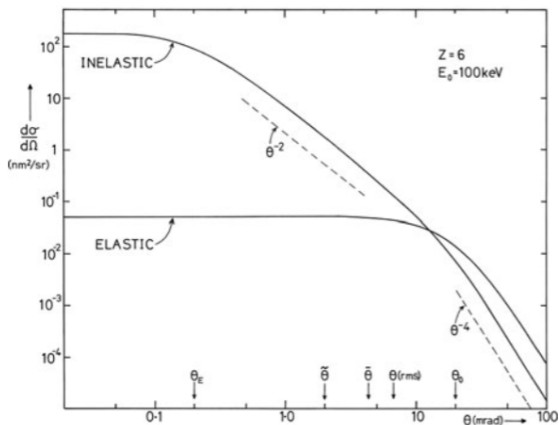
$\theta_E = E/(\gamma m_0 v^2)$, characteristic inelastic scattering angle

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

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

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

Inelastic Scattering



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

Double differential scattering cross section

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

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

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

Single plane wave

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

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

Dynamic Form Factor (DFF):

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

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

Superposition of plane waves

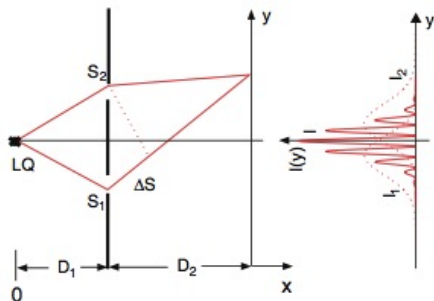
$$|\psi_i\rangle = a_1 |\mathbf{k}_1\rangle + a_2 |\mathbf{k}_2\rangle, |a_1|^2 + |a_2|^2 = 1$$

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

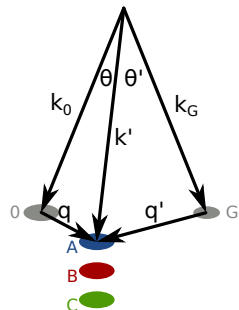
Mixed Dynamic Form Factor (MDFF):

$$S(\mathbf{Q}, \mathbf{Q}', E) = \sum_i \sum_f \langle f | e^{i\mathbf{Q} \cdot \mathbf{R}} | i \rangle \langle i | e^{-i\mathbf{Q}' \cdot \mathbf{R}} | f \rangle \cdot \delta(E_{|f\rangle} - E_{|i\rangle} - E)$$

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

Bloch waves

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

MDFF for Crystals

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

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

Features of WIEN2k

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

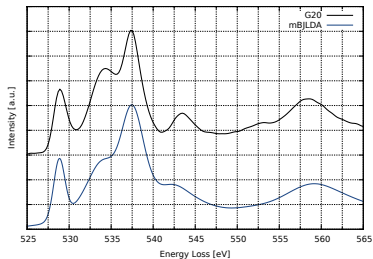
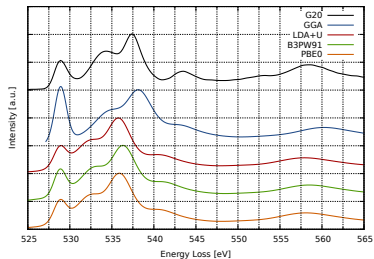
Kohn-Sham equation

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

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

Calculated Spectra

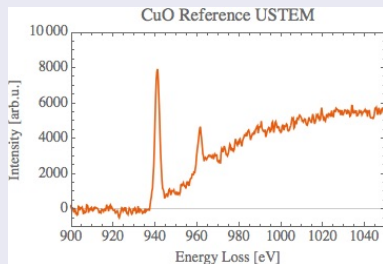
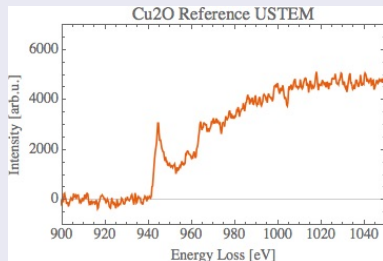
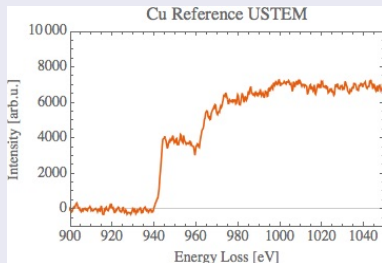
NiO



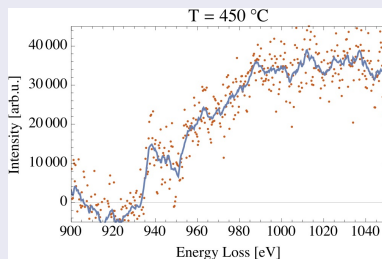
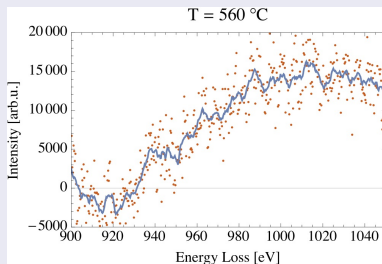
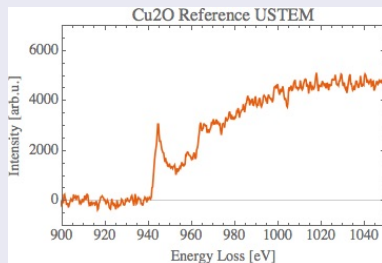
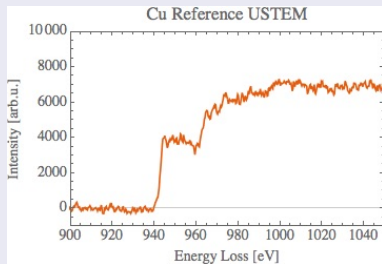
Hetaba: Fine Structure and Site Specific Energy Loss Spectra of NiO, Diploma Thesis, TU Wien 2011

Hetaba et al., Phys. Rev. B 85, 205108, 2012

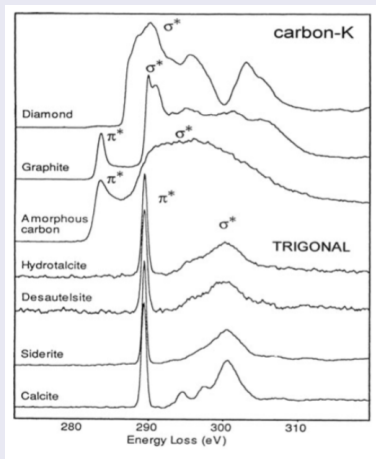
Oxidation State



Oxidation State

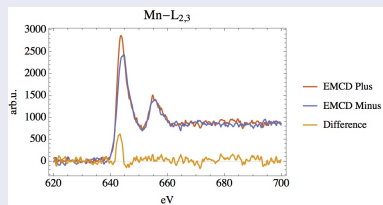
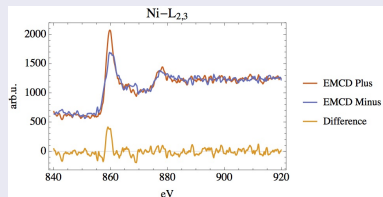
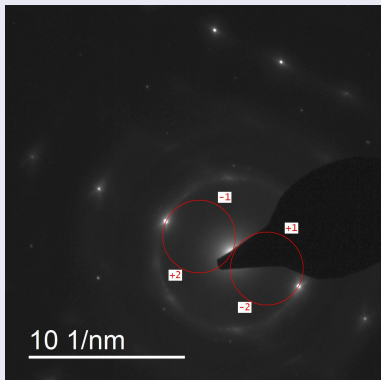


Crystallographic Structure - Coordination



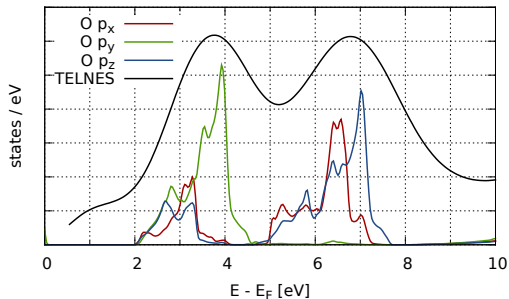
Egerton: Electron energy-loss spectroscopy in the electron microscope, Plenum Press 1996

EMCD



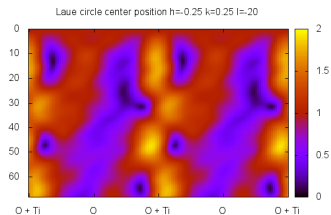
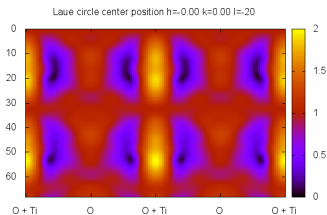
Hetaba: The Theory and Application of Inelastic Coherence in the Electron Microscope, PhD Thesis, TU Wien 2015

Channelling effects



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

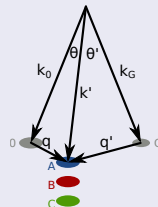
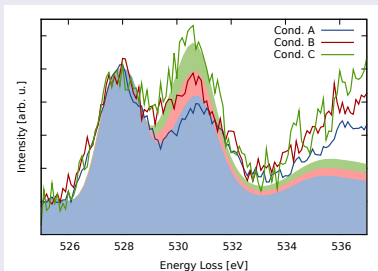
Channelling effects



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

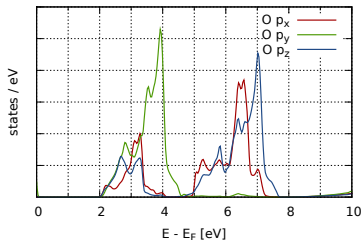
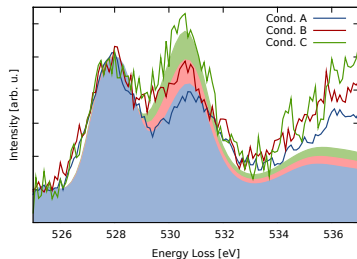
Channelling effects



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

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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

Useful books (linked)

Analytical electron microscopy in general:

- Williams, Carter: Transmission Electron Microscopy - 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

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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