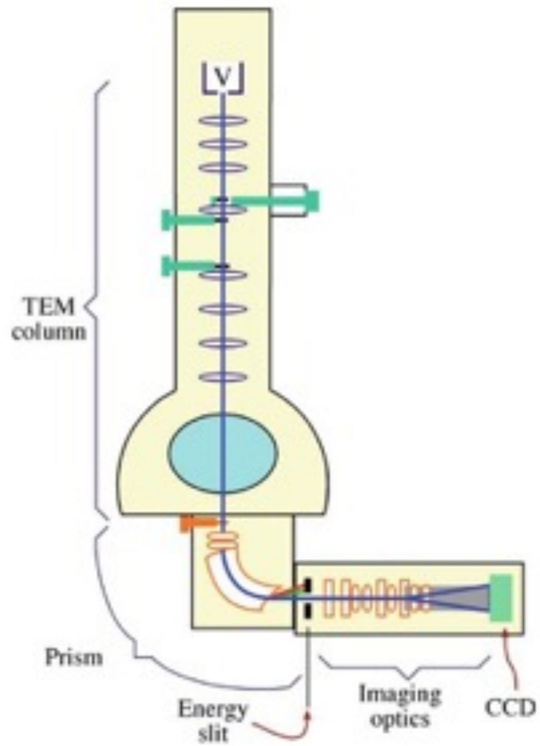
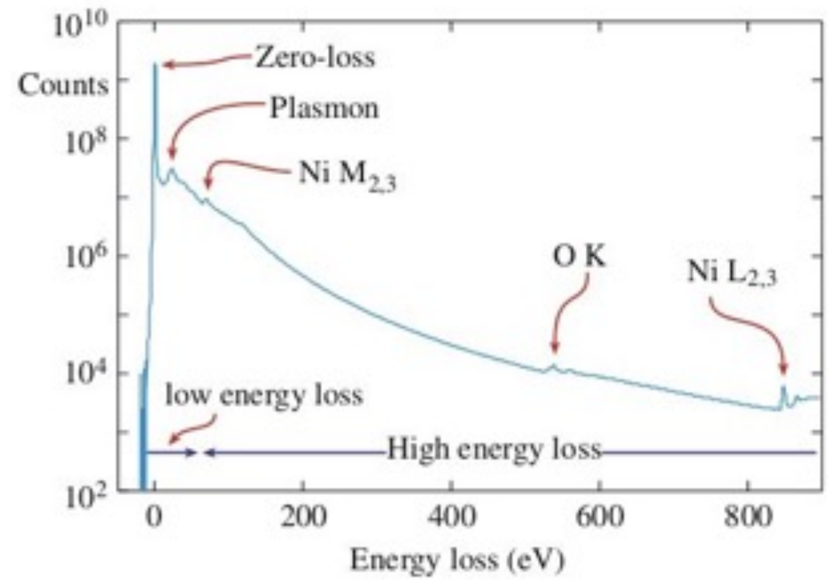
Electron Energy-Loss Spectrometry

Walid Hetaba
28.10.2016

Energy loss spectrum





Williams, Carter: Transmission Electron Microscopy, Springer 2009

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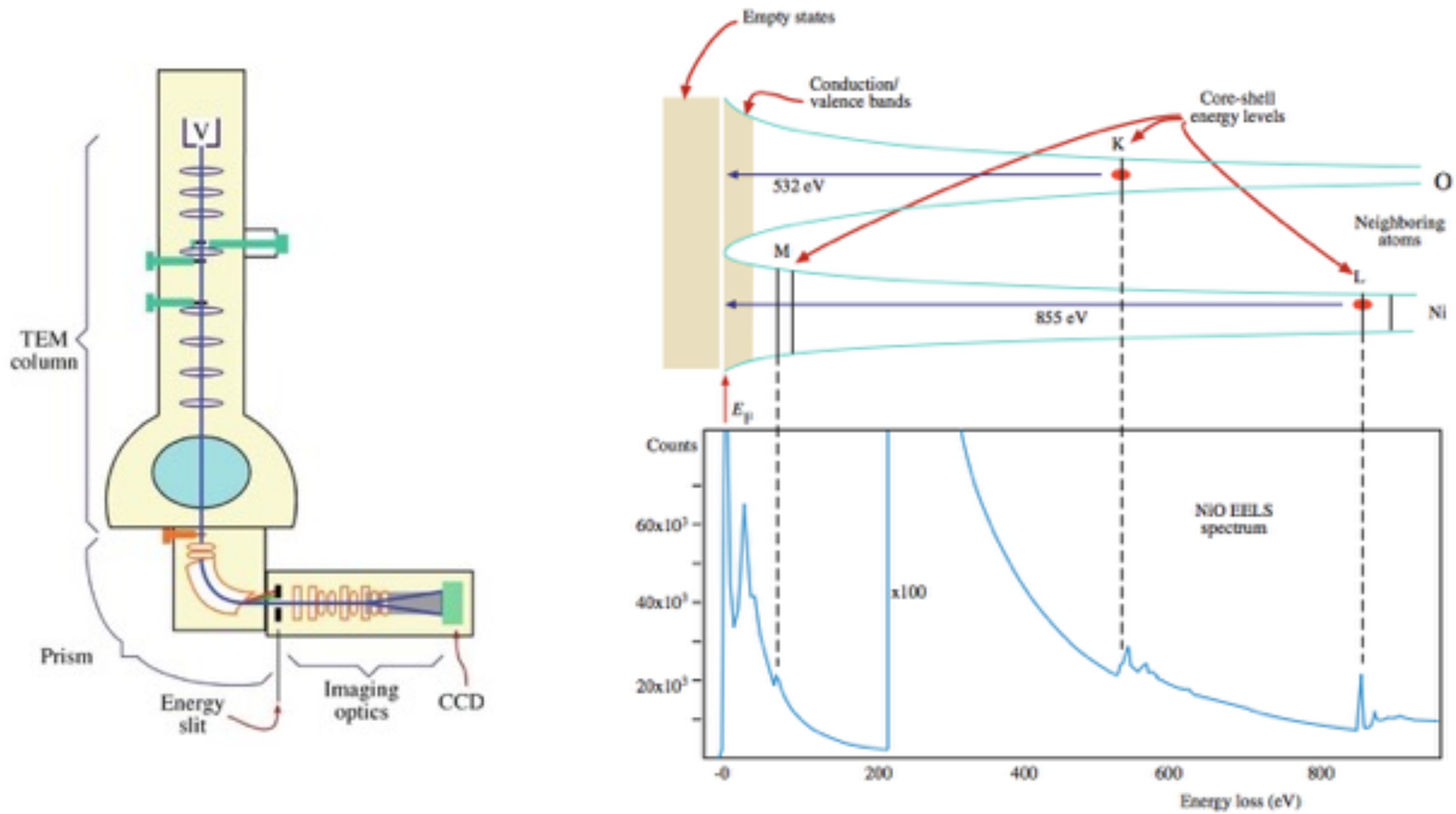
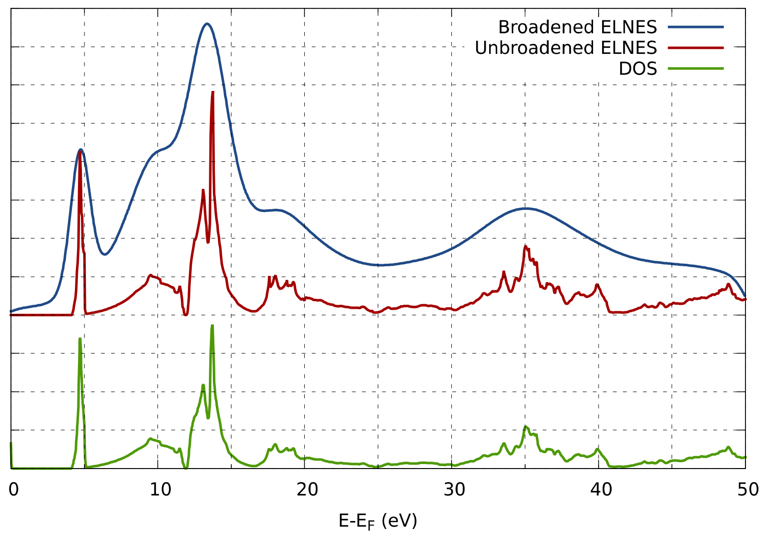


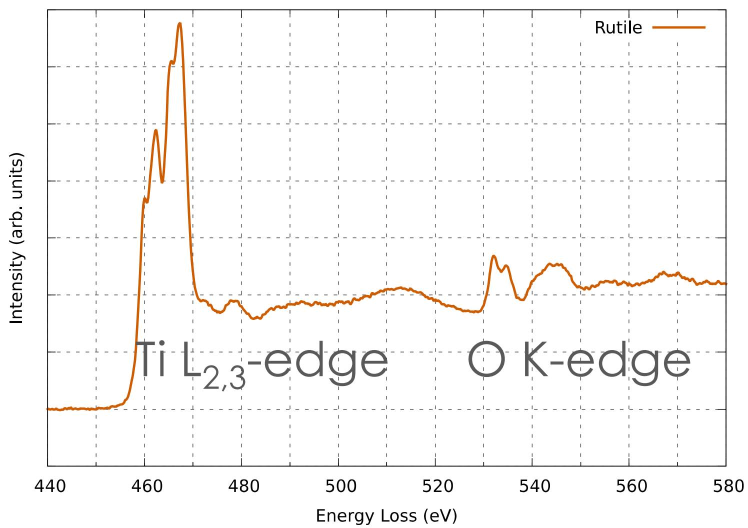
Williams, Carter: Transmission Electron Microscopy, Springer 2009

Energy loss near edge spectrum

ELNES



NiO, WIEN2k



TiO_2, exp.

Hetaba et al., PRB 85 (2012), 205108

Formalism

Schrödinger equation:

$$\hat{H}\Psi(t) = i\hbar \frac{\partial}{\partial t}\Psi(t)$$
$$\hat{H}\Psi = E\Psi$$
$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}, t)$$

Bra-Ket formalism:

$$\left|\Psi\right\rangle, \left\langle\Psi\right|, \left\langle\Psi\middle|\Phi\right\rangle$$

$$\left\langle x\middle|\Psi\right\rangle = \Psi(x)$$

$$\left\langle\Psi\middle|x\right\rangle = \Psi^*(x)$$

$$\left\langle\Psi\middle|\Psi\right\rangle = \int \Psi^*(x)\Psi(x)d^3x$$

Double differential scattering cross-section

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

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$$\left|\Psi_{i,f}\right\rangle = \left|\psi_{i,f}\right\rangle \otimes \left|i, f\right\rangle \quad \left\langle \mathbf{r} \middle| \psi_{i,f} \right\rangle = \left\langle \mathbf{r} \middle| \mathbf{k}_{i,f} \right\rangle = \frac{1}{\left(2\pi\right)^{3/2}} e^{i\mathbf{k}_{i,f}\mathbf{r}}$$

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$$\hat{V} = \frac{1}{4\pi\varepsilon_0}\left(\sum_k \frac{-Ze^2}{\left|\mathbf{r}-\mathbf{a}_k\right|} + \sum_j \frac{e^2}{\left|\mathbf{r}-\mathbf{R}_j\right|}\right)$$

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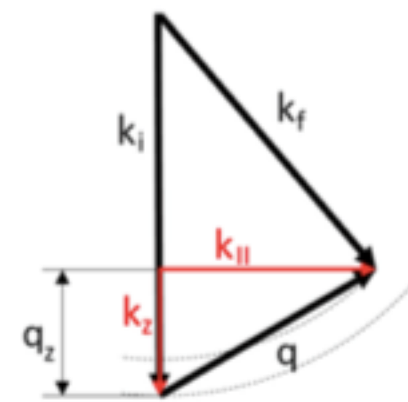

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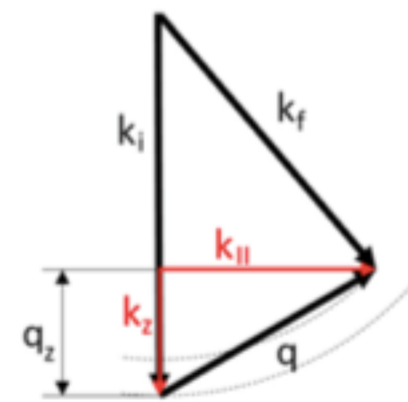
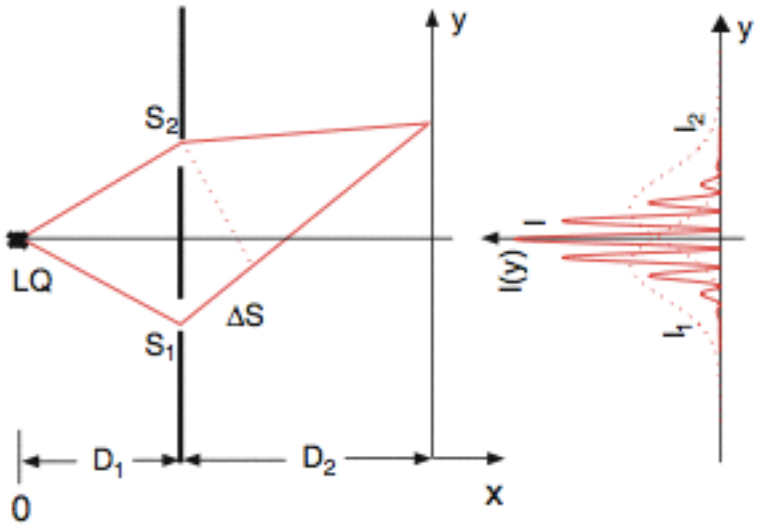


$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} = \frac{4\gamma^2}{a_0^2}\frac{k_f}{k_i}\frac{1}{Q^4}\underbrace{\sum_i\sum_f\sum_j\left|\left\langle f\middle| e^{i\mathbf{Q}\cdot\mathbf{R}_j}\middle| i\right\rangle\right|^2 \cdot \delta\left(E_{|f\rangle} - E_{|i\rangle} - E\right)}_{S(\mathbf{Q},E)}$$

Dynamic form factor (DFF)

Interferometric EELS (the mixed DFF)



$$I \propto A_1^2 + A_2^2 + 2\Re\left[A_1 A_2^* \cdot e^{i(\varphi_1-\varphi_2)}\right]$$

Demtröder, Experimentalphysik 3, Springer 2010

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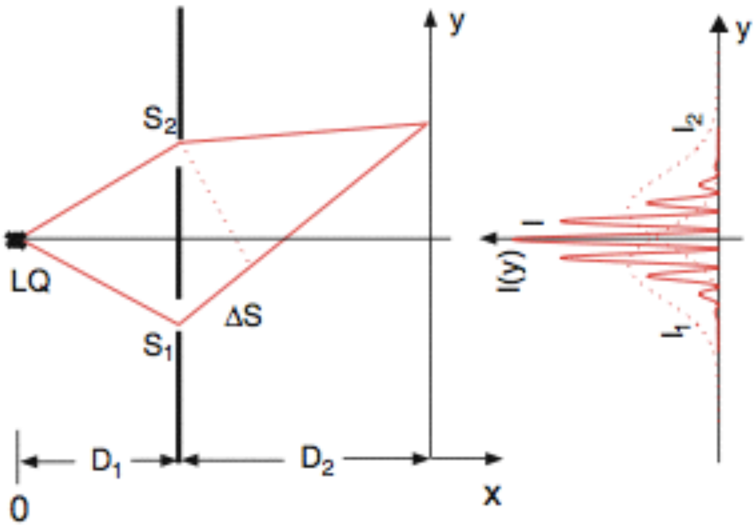

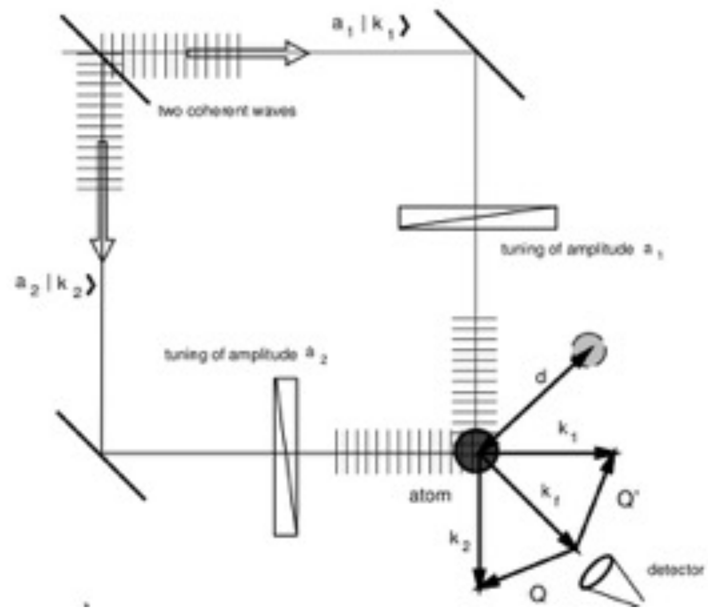

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$$\left|\psi_i\right\rangle = a_1\left|\mathbf{k}_1\right\rangle + a_2\left|\mathbf{k}_2\right\rangle$$

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Kohl & Rose, 1985

Nelhiebel, PhD thesis, 1999

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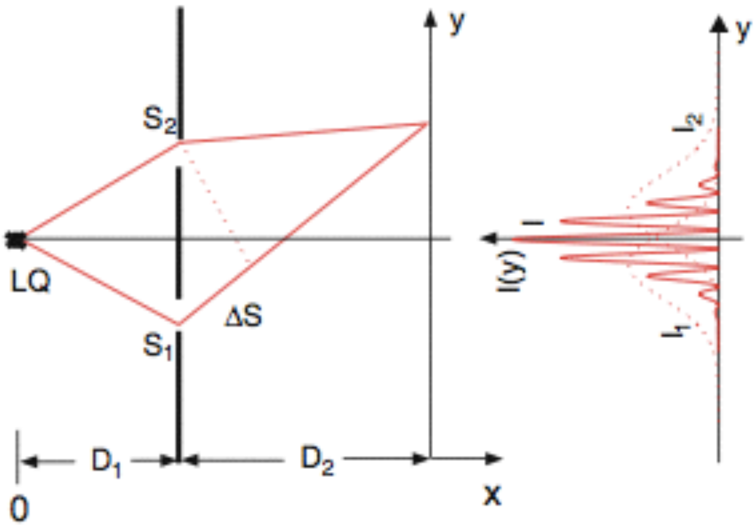

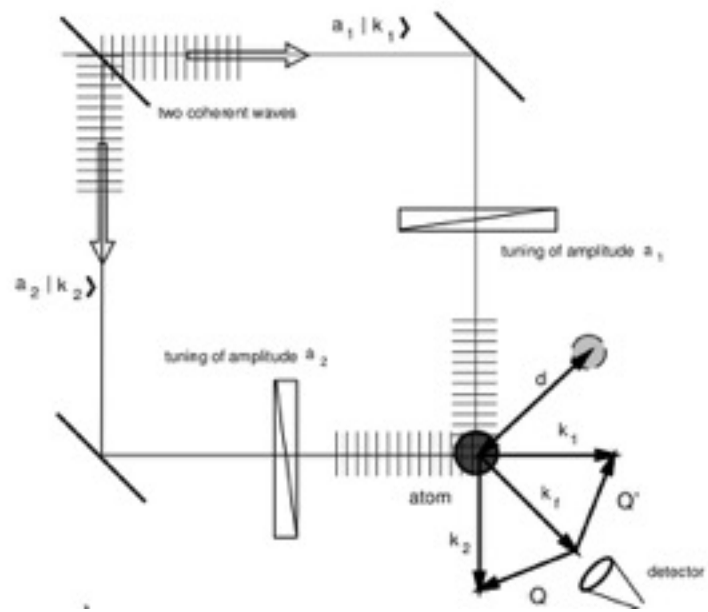

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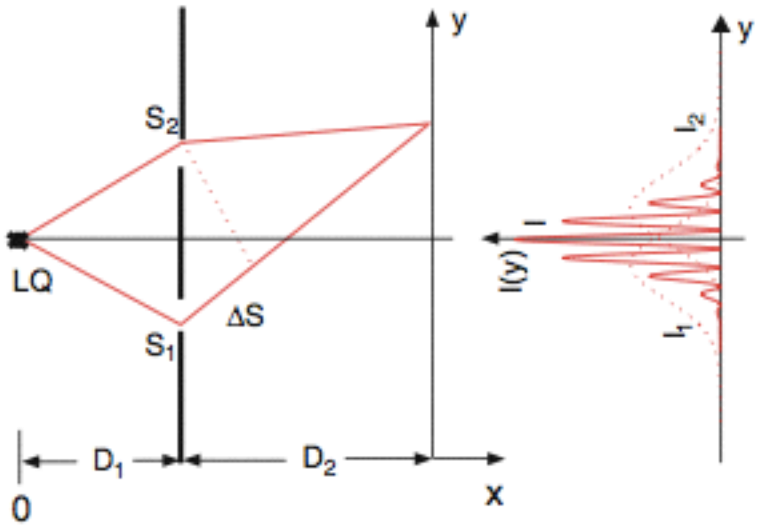

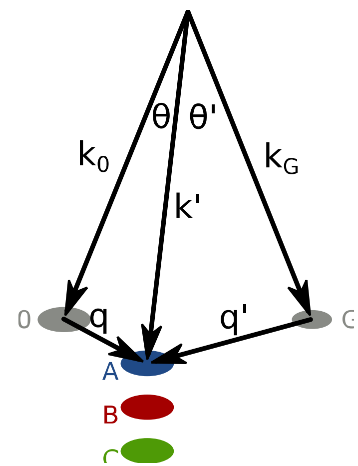

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Kohl & Rose, 1985

Demtröder, Experimentalphysik 3, Springer 2010

Nelhiebel, PhD thesis, 1999

The MDFF for crystals

$S(\mathbf{Q},\mathbf{Q}',E)$

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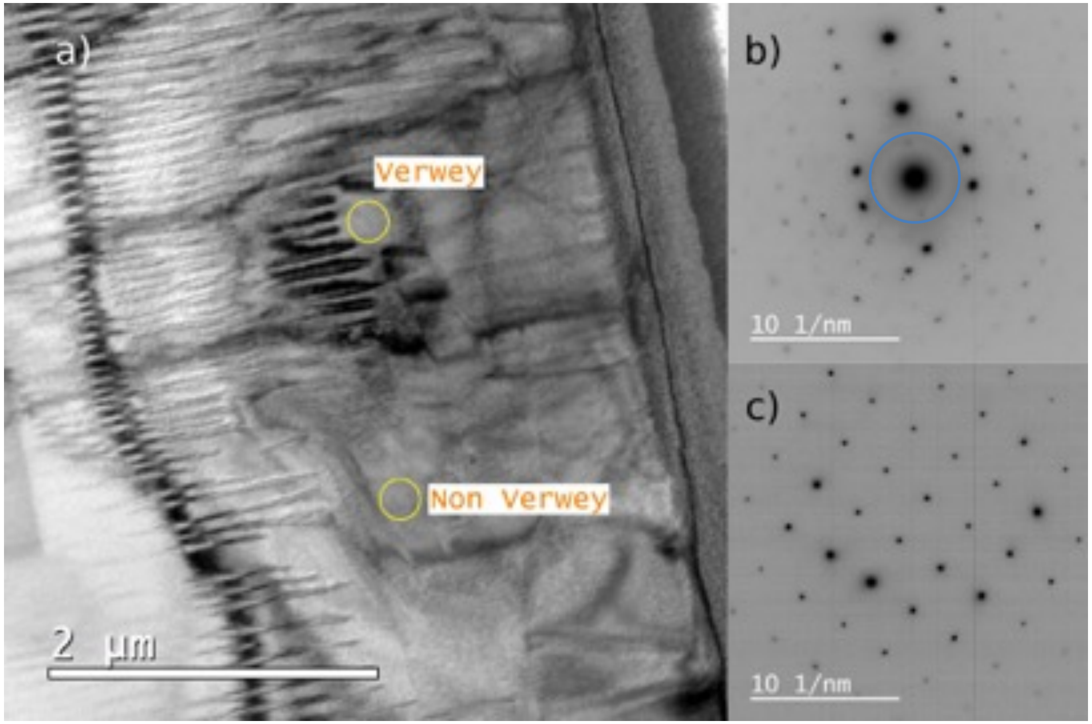
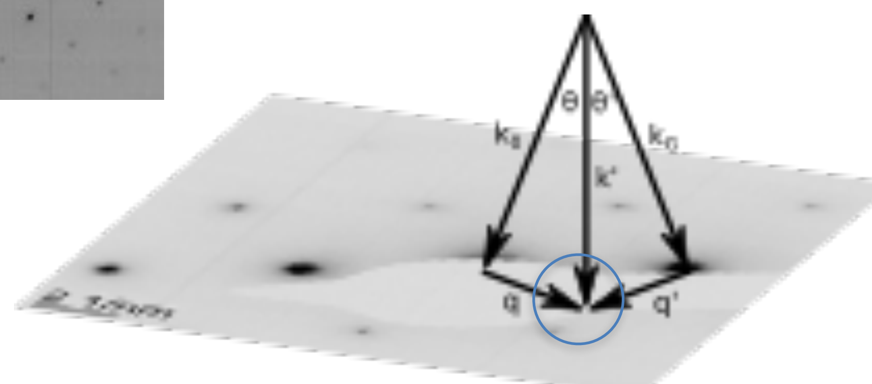
$$S\left(\mathbf{Q},\mathbf{Q}',E\right)$$

$$\left\langle j_\lambda\left(Q\right)\right\rangle_{\nu njLS} = \int_0^\infty u_{\nu LS}\left(R\right)^* j_\lambda\left(QR\right) u_{njS}\left(R\right) R^2\, dR$$

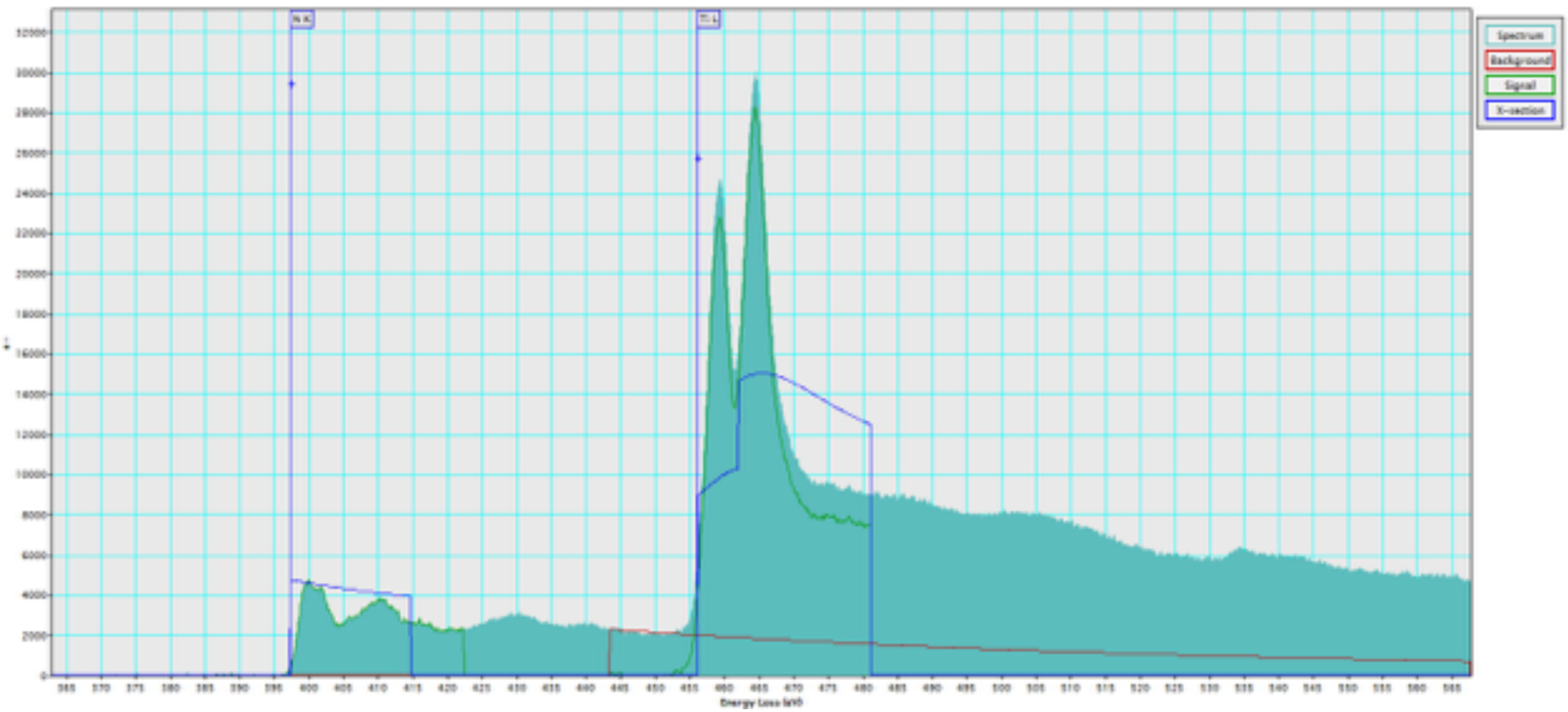
$$X_{LMS,L'M'S'}(E) \coloneqq \sum_\nu \left(D^\nu_{LMS}\right)^* D^\nu_{L'M'S'} \delta\left(E - E_\nu\right)$$

Experimental realisation





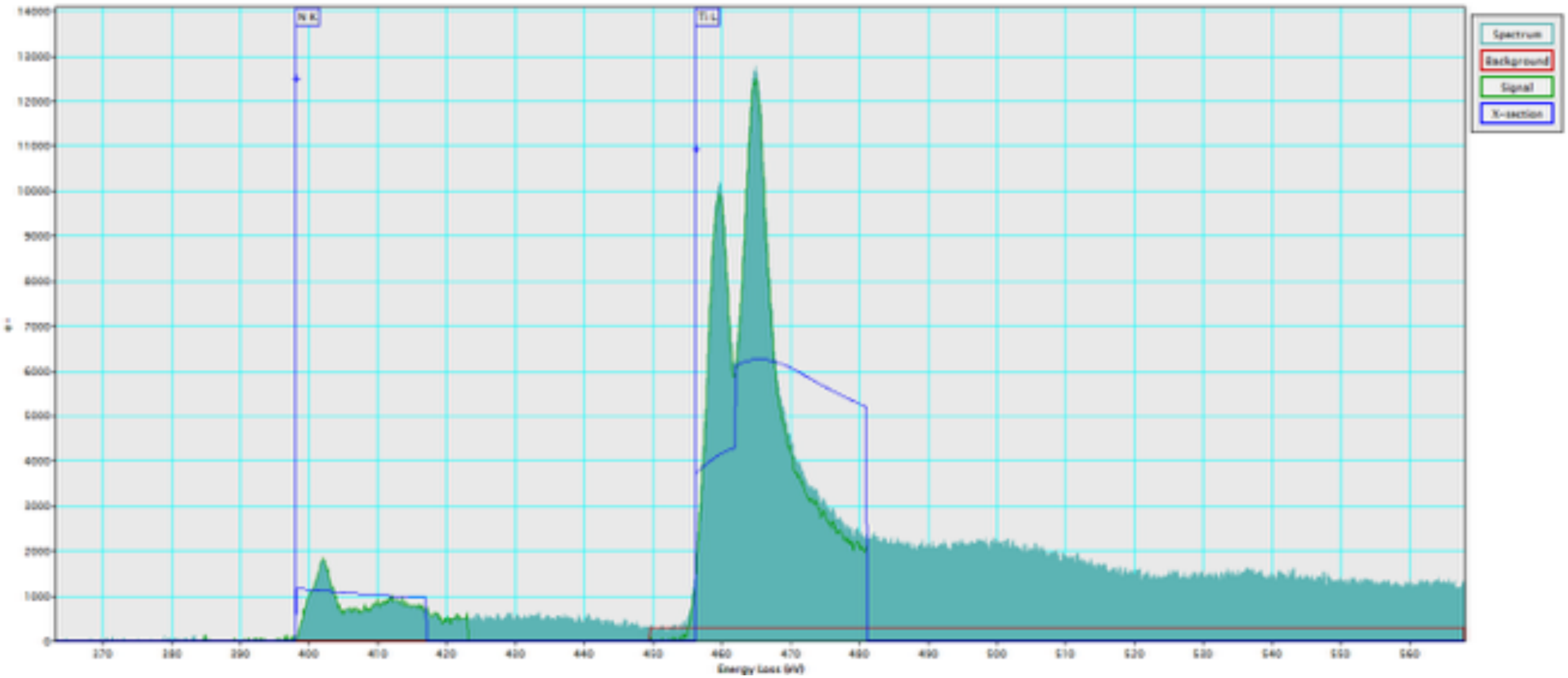
Experimental spectra



Relative quantification:

Elem.	Atomic ratio (/Ti)	Percent content
N	0.80 ± 0.113	44.34
Ti	1.00 ± 0.000	55.66

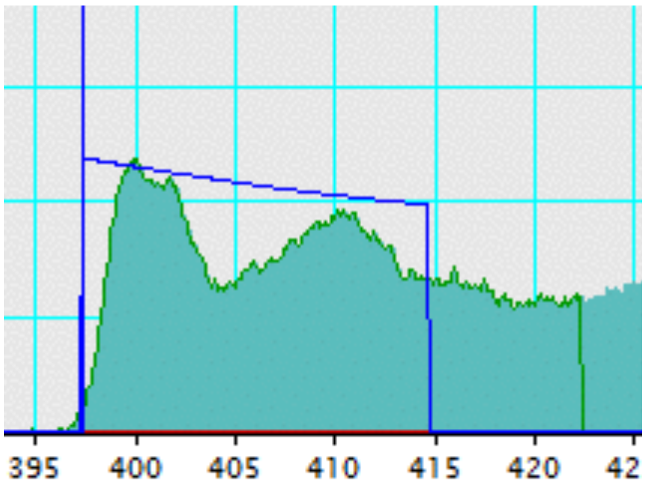
Experimental spectra

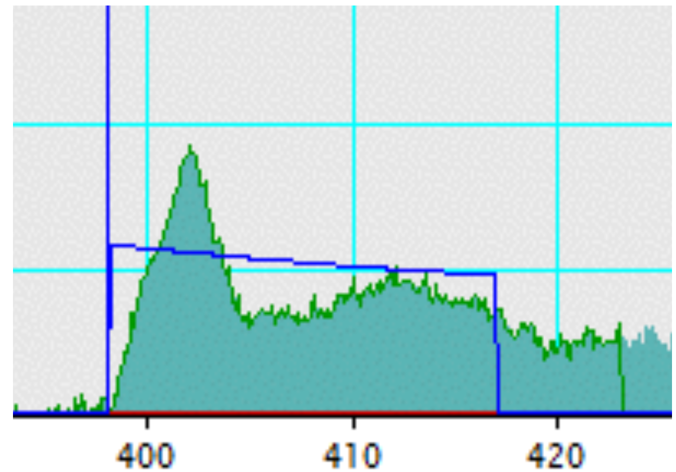


Relative quantification:

Elem.	Atomic ratio (/Ti)	Percent content
N	0.47 ± 0.067	32.01
Ti	1.00 ± 0.000	67.99

Experimental spectra

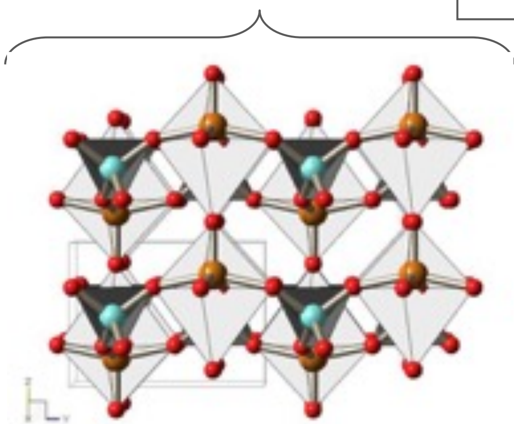




Differences in fine structure: different electronic structure

WIEN2k simulation

Input: Unit cell with atomic positions



→ Calculate starting density from atomic densities: ρ_{in}

→ Calculate potential from density $\hat{V}$

↓

Solve Kohn-Sham equation: $\left[-\nabla^2 + \hat{V}\right]\psi_k = E_k \psi_k$

↓ ψ_k, E_k

Calculate density from gained wave functions: $\rho_{val} = \sum \psi_k^* \psi_k$

↓ $\rho = \rho_{val} + \rho_{core}$

New density = old density?

no → (back to: Calculate potential from density)

yes

Payne *et al.*, Rev. Mod. Phys. 64, 1045 (1992)

WIEN2k simulation

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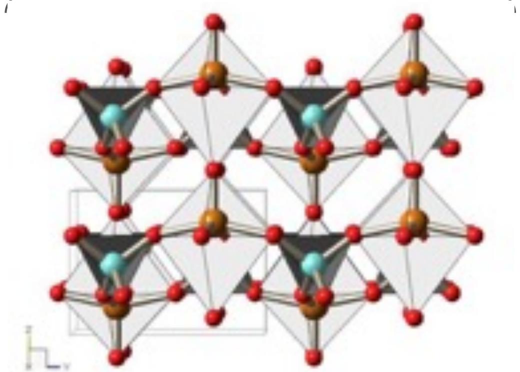

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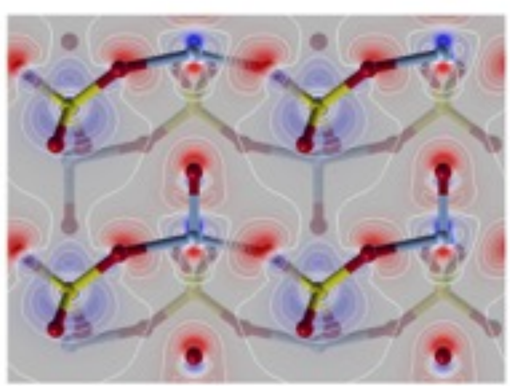
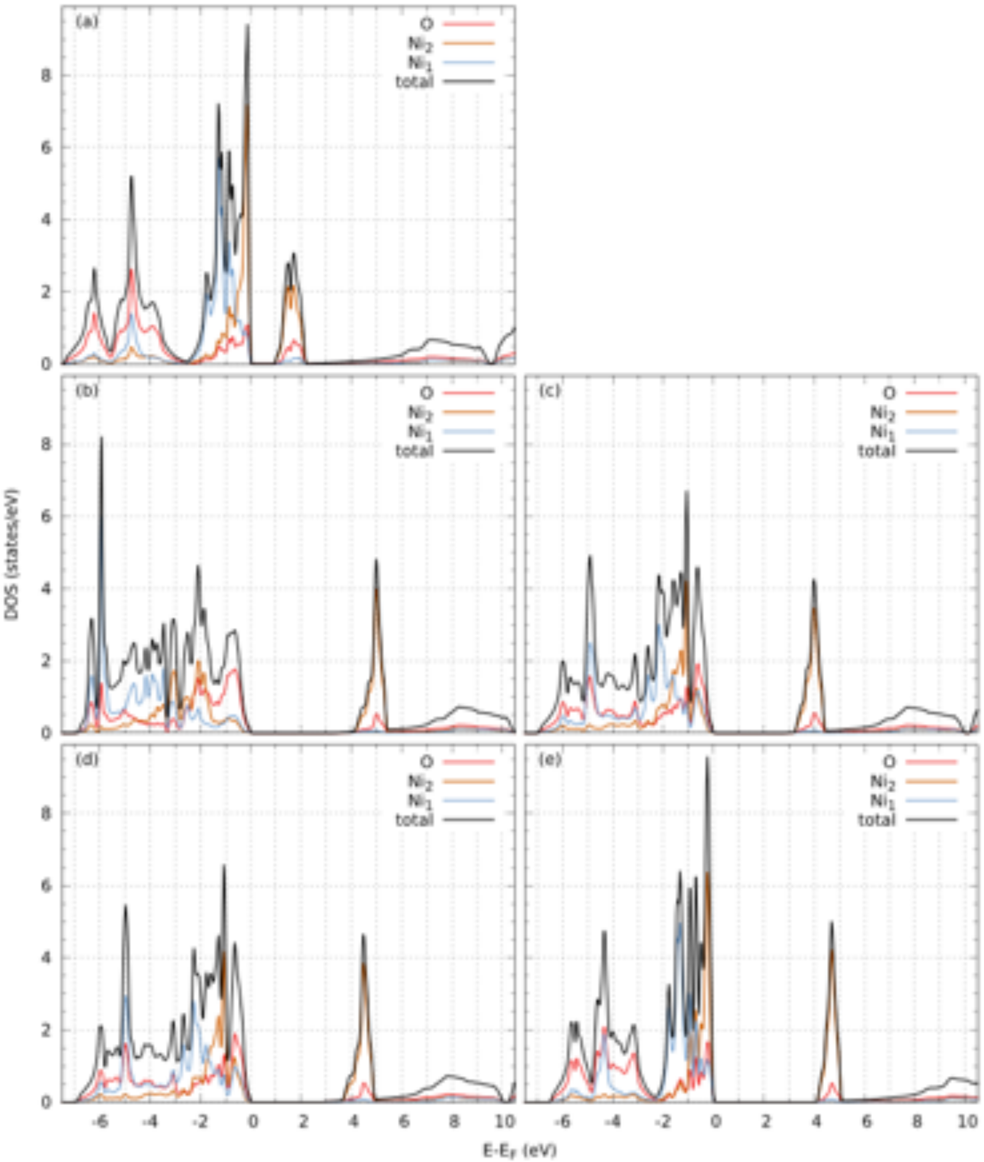
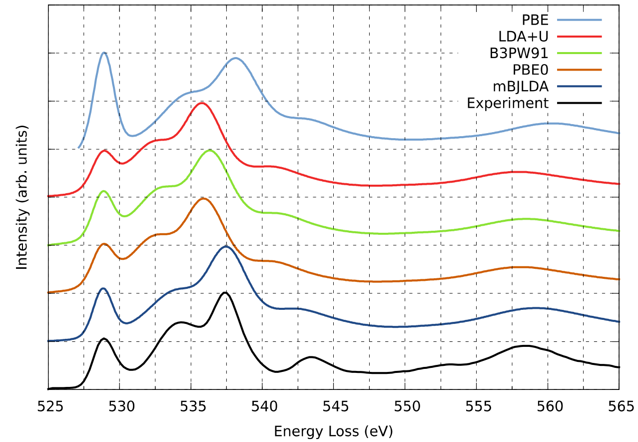
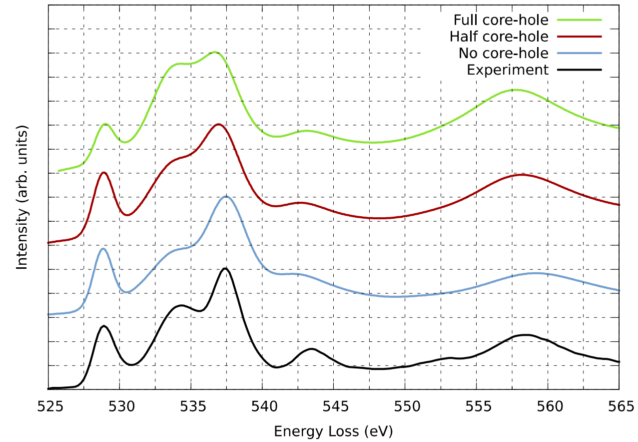


Payne *et al.*, Rev. Mod. Phys. 64, 1045 (1992)

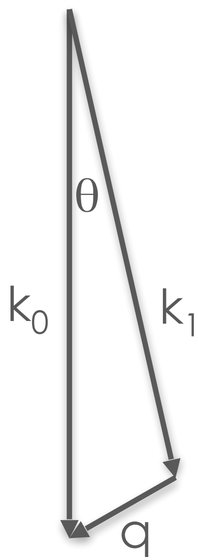
TELNES – calculation of spectra







Effects of anisotropy



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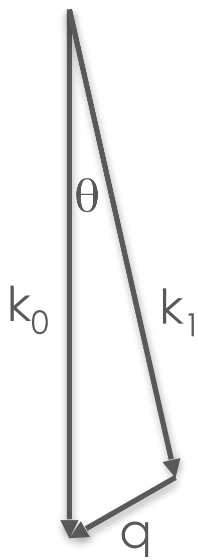

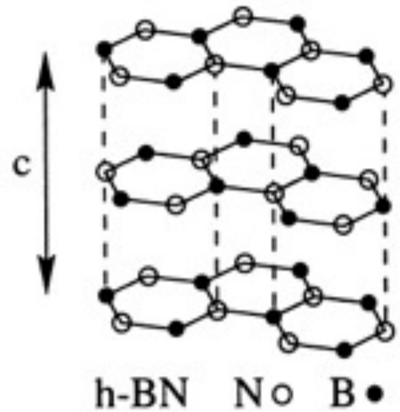

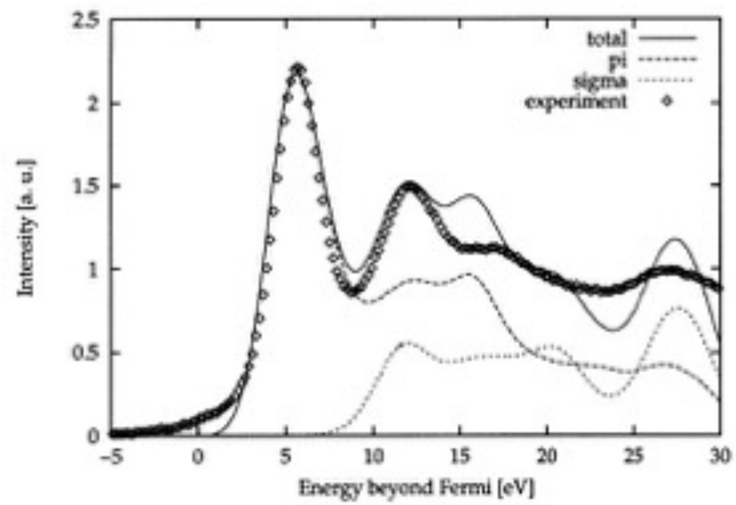

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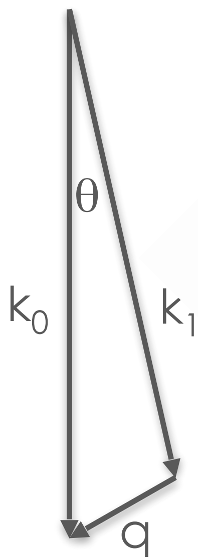
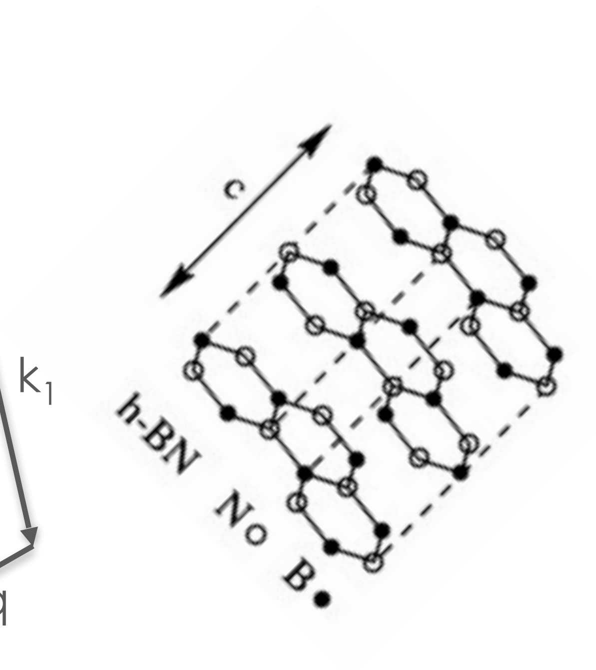
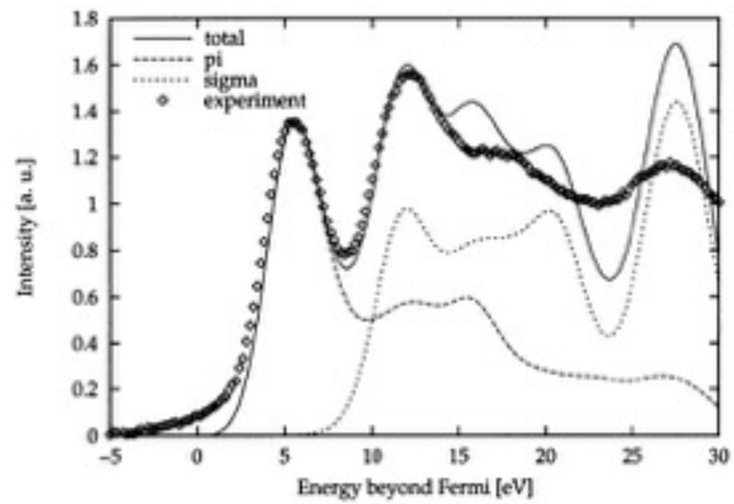


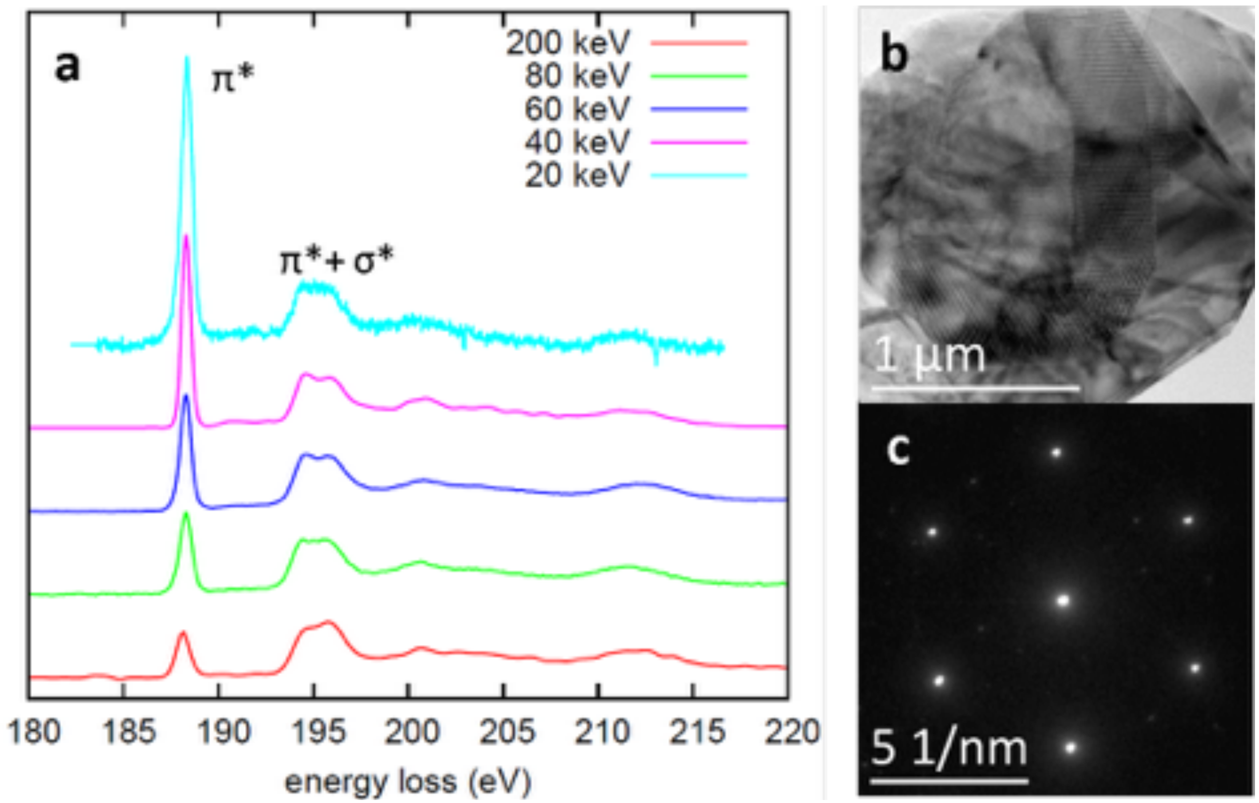




Hébert-Souche et al., UM 83 (2000), 9-16

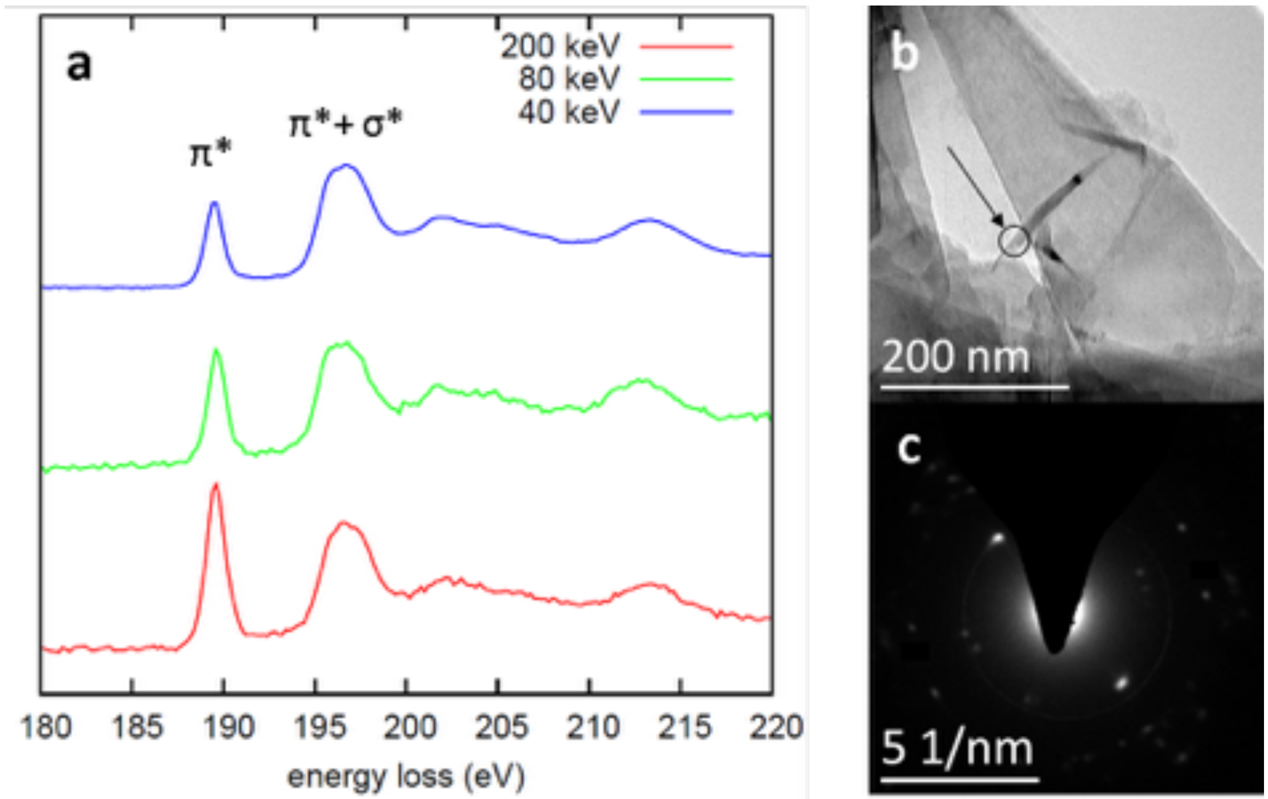
Anisotropy – experiment 1

Orientation: c-axis parallel to electron-beam



Anisotropy – experiment 2

Orientation: c-axis perpendicular to electron-beam



Energy-loss magnetic chiral dichroism

- EMCD, 2006
- Polarisation vector ⟷ momentum transfer vector

$$\varepsilon + i\,\varepsilon'$$

$$q + i\,q'$$

Energy-loss magnetic chiral dichroism

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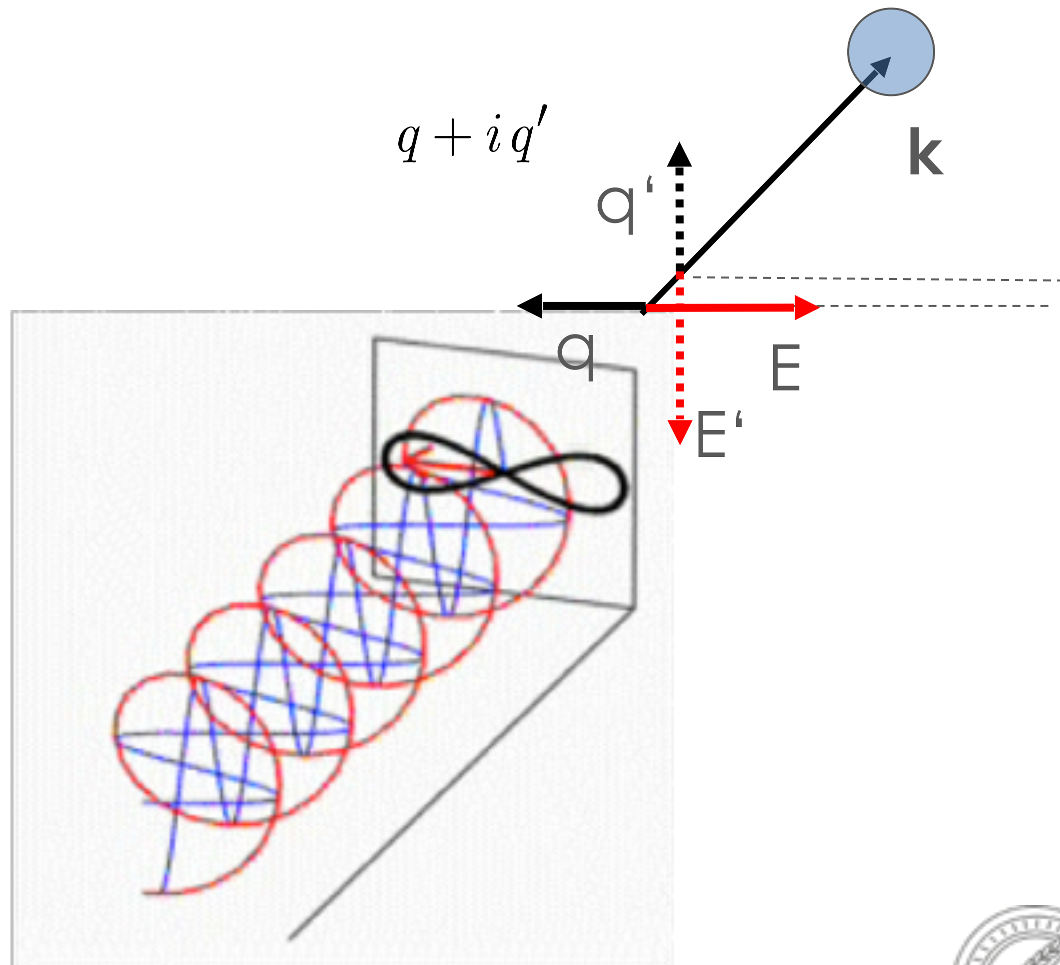
- Polarisation vector ⟷ momentum transfer vector

$\varepsilon + i\,\varepsilon'$ $\qquad$ $q + i\,q'$



Energy-loss magnetic chiral dichroism

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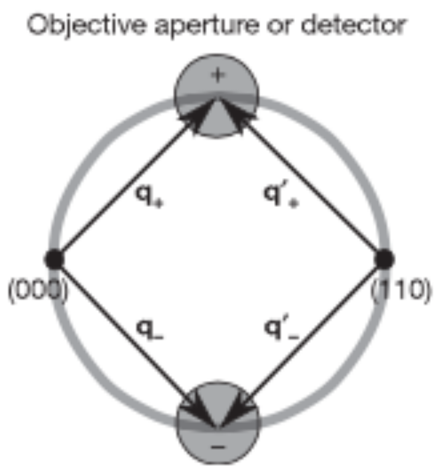

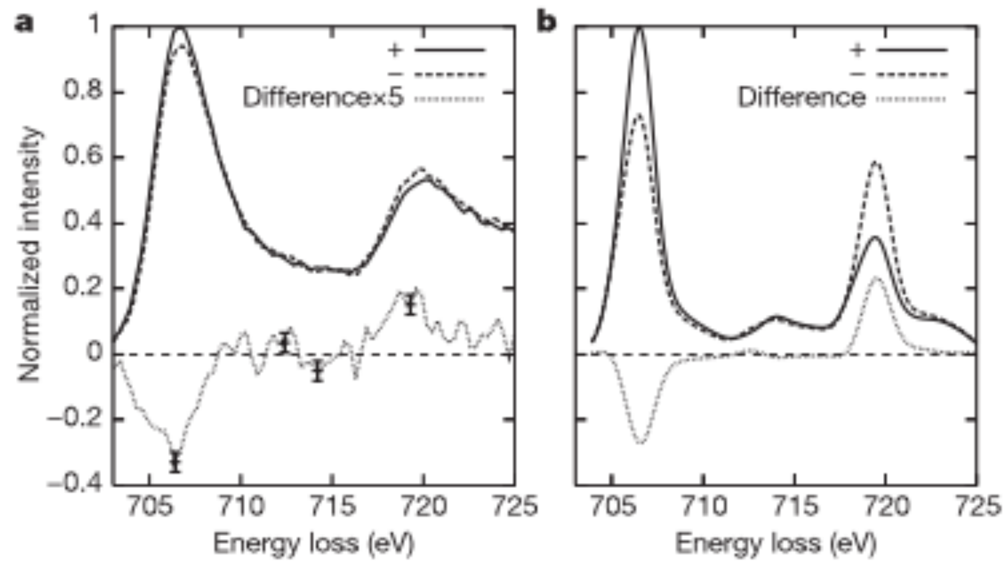

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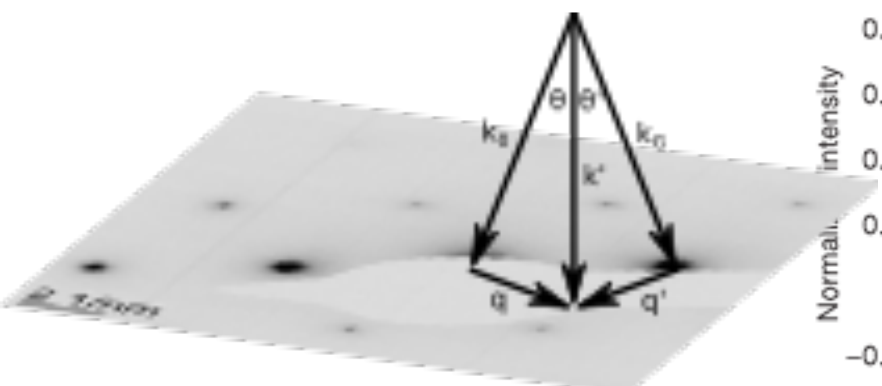
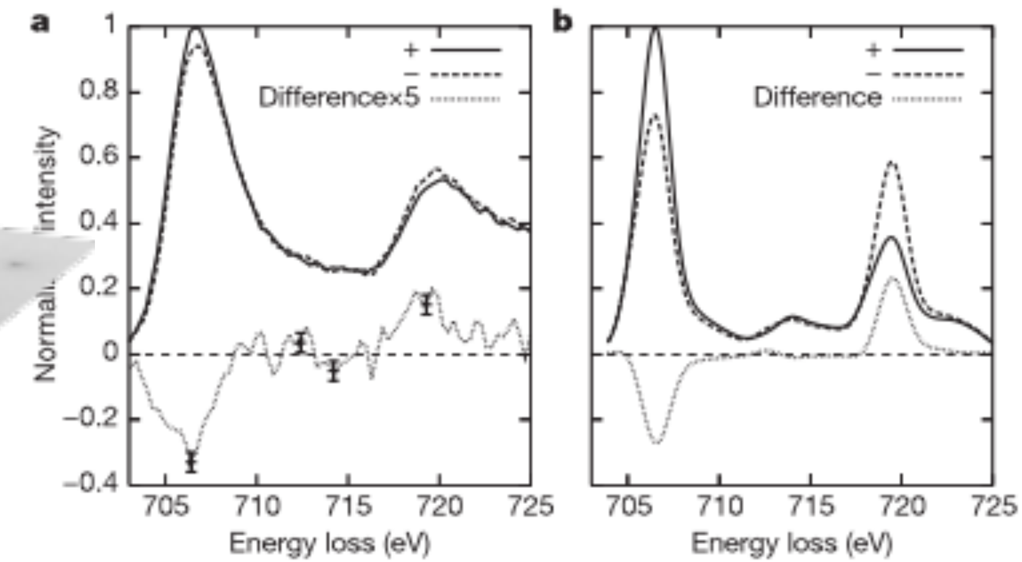
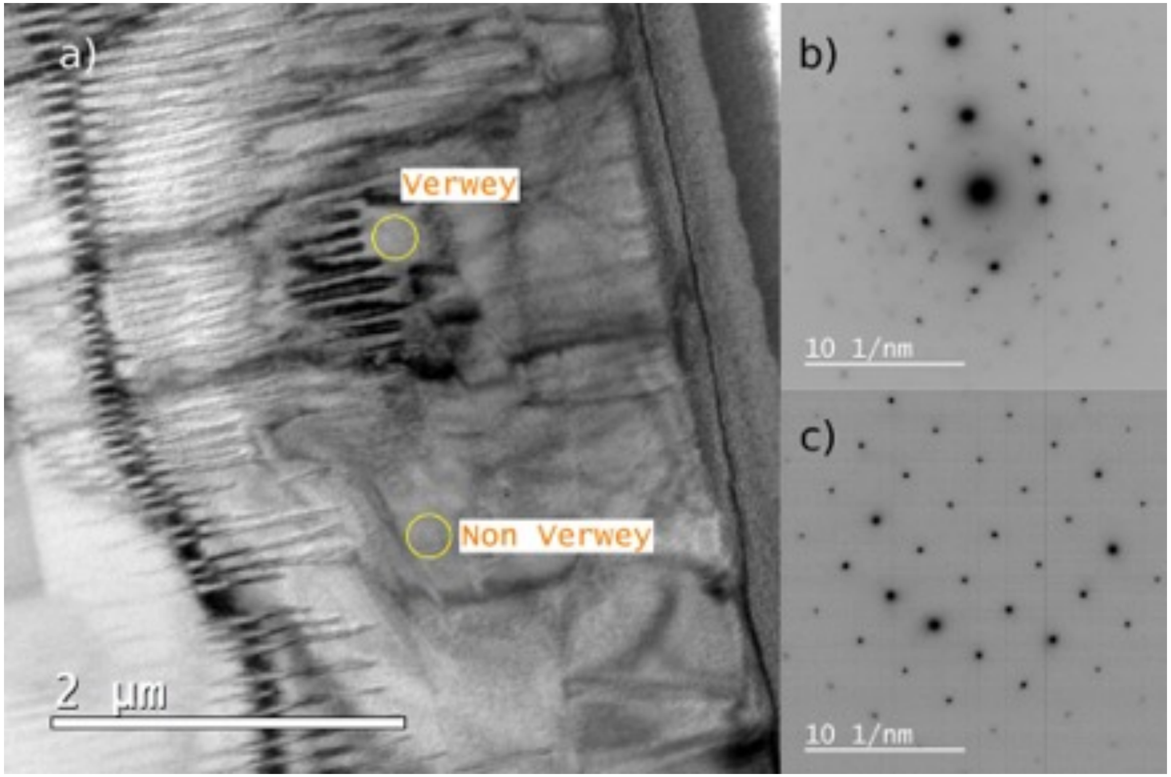




EMCD – example 1



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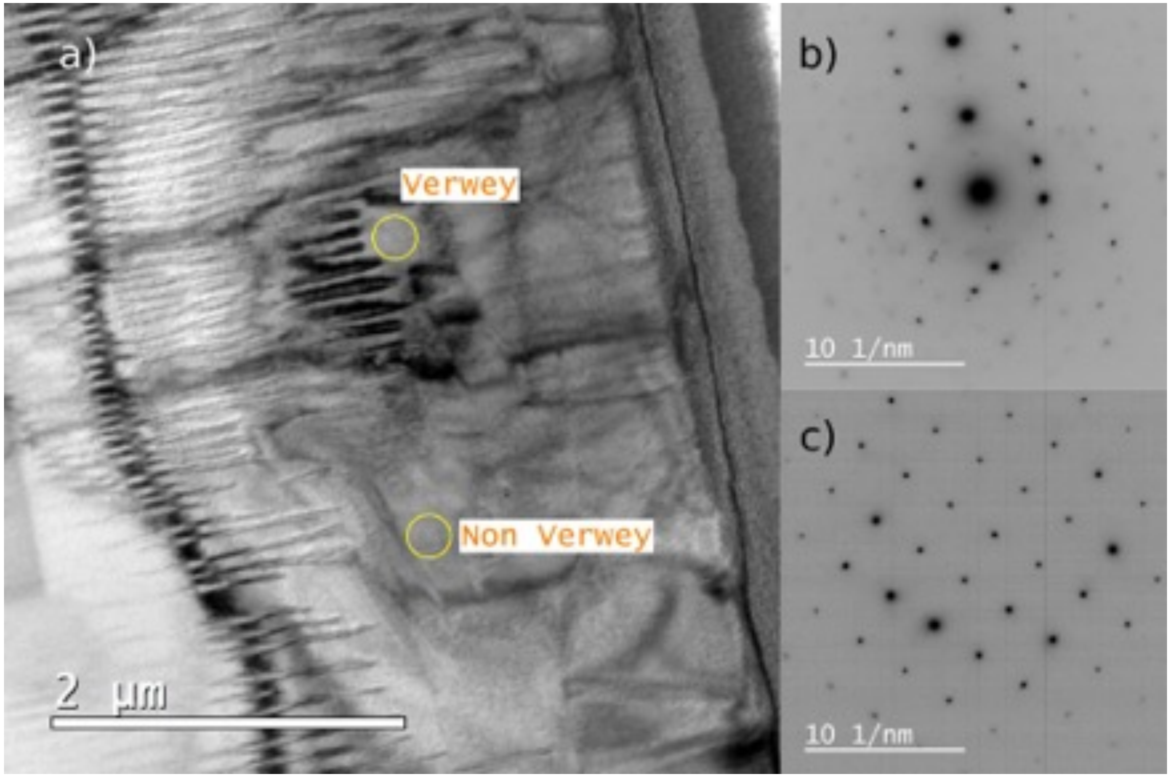
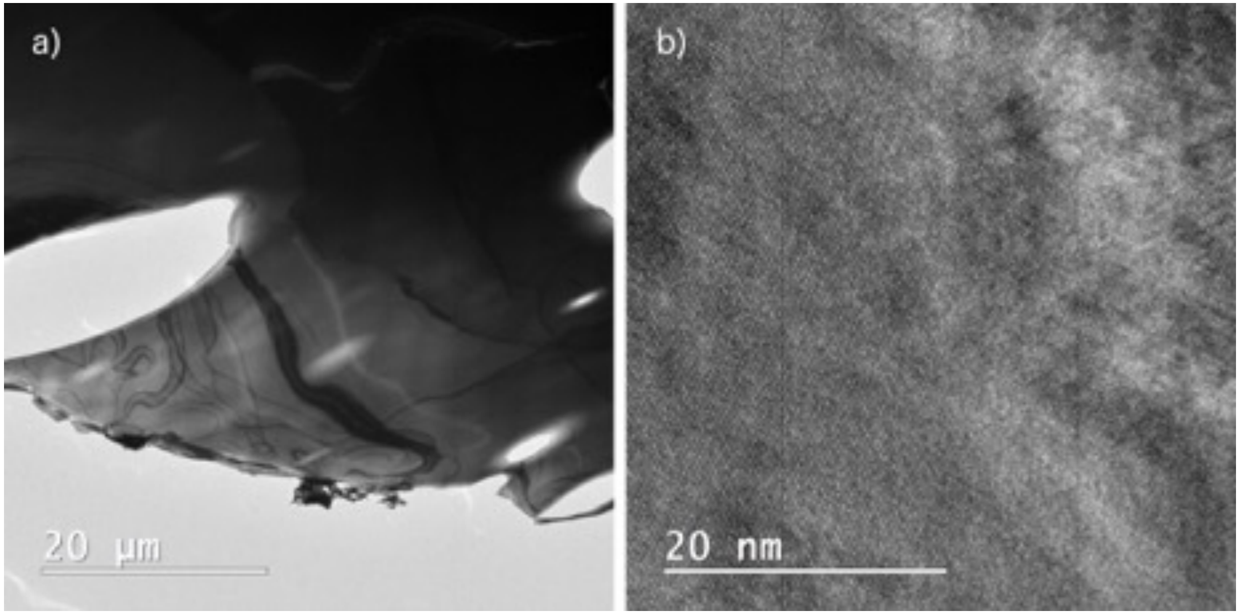
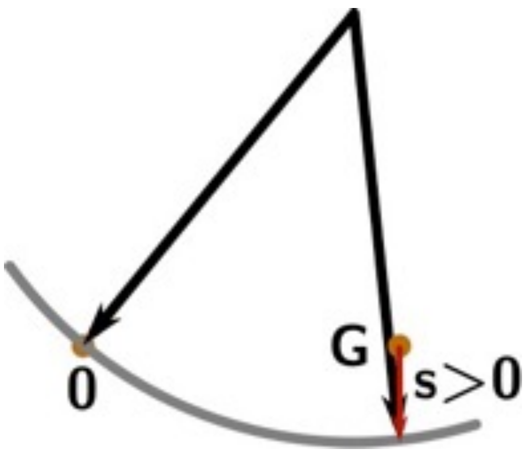


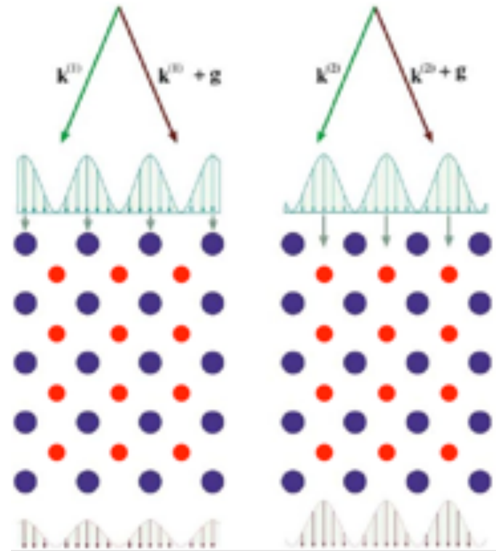
EMCD – example 2



Energy losses by channelled electrons

ELCE, 1982





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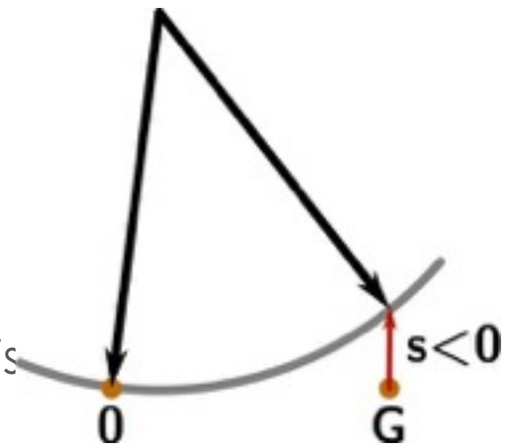
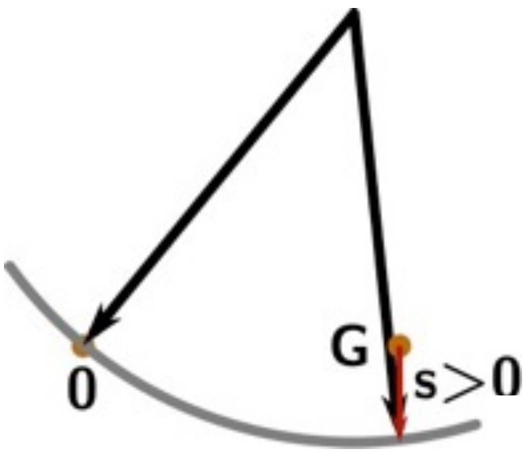
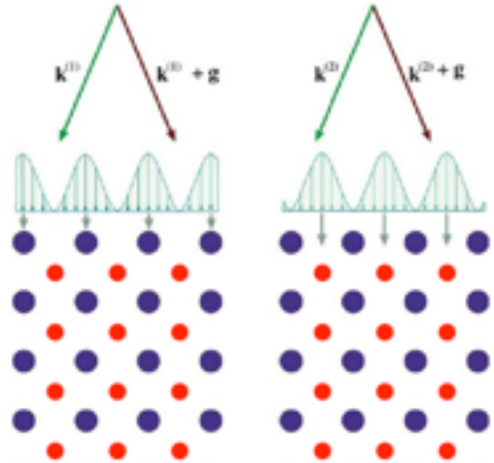


Energy losses by channelled electrons

ELCE, 1982





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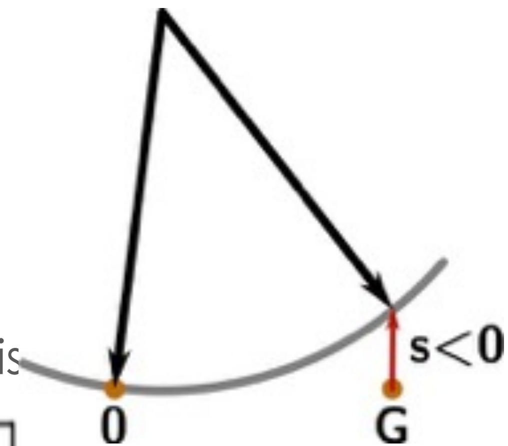

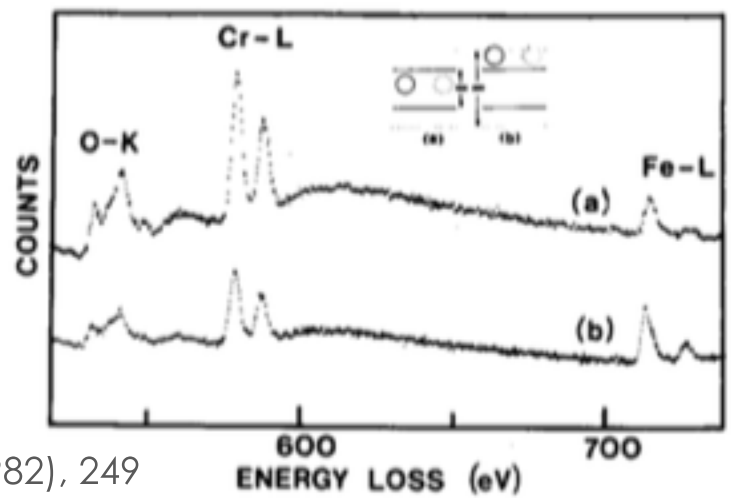

Fig. 7. EEL spectra from chromite. (a) Octahedral sites selected. (b) Tetrahedral sites selected.

Krivanek et al., Ultram 9 (1982), 249

ELCE simulations

Incoming wave, scattering, outgoing wave
Input: crystal, exp. paramters, scattering model
Output: Bloch waves, intensity maps, thickness dependence

Löffler & Schattschneider, Ultram 110 (2010), 831

Hetaba, Diploma-Thesis, 2011

ELCE simulations

Incoming wave, scattering, outgoing wave
Input: crystal, exp. paramters, scattering model
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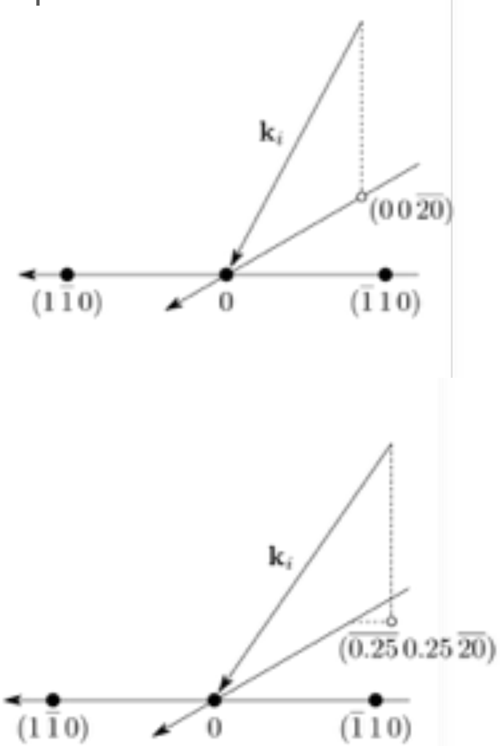

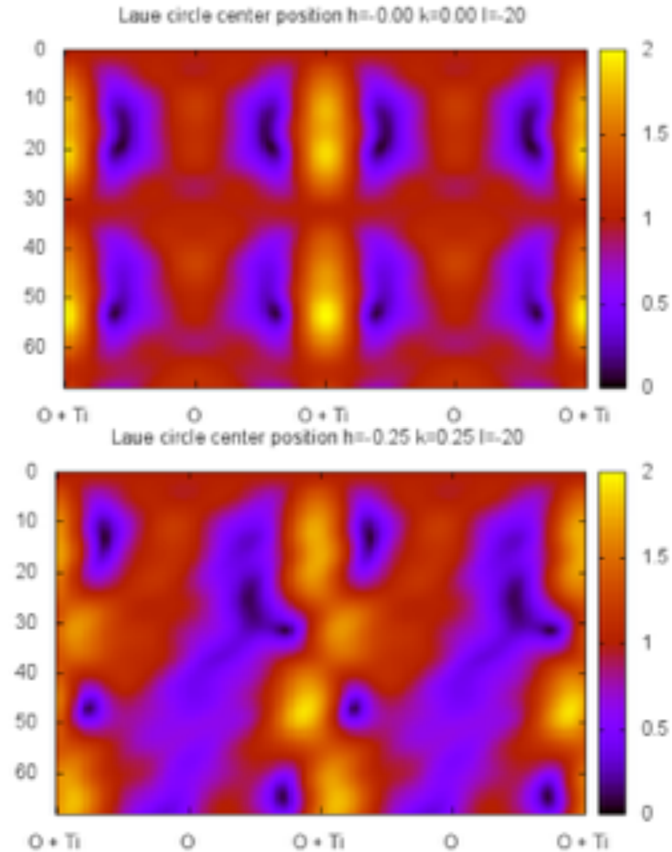

Löffler & Schattschneider, Ultram 110 (2010), 831

Hetaba, Diploma-Thesis, 2011

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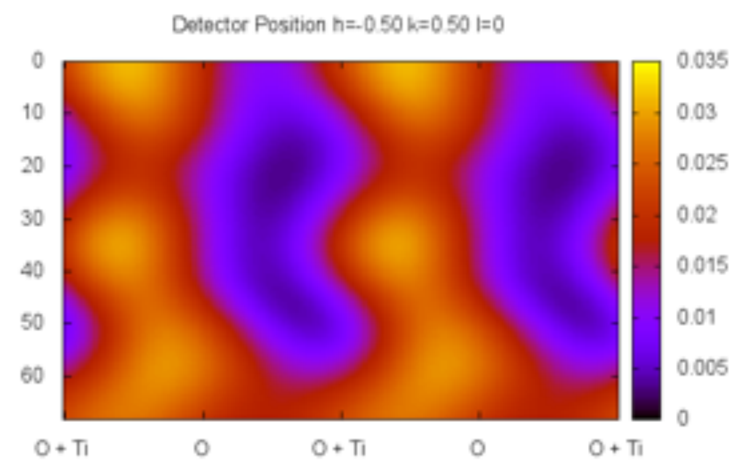

Löffler & Schattschneider, Ultram 110 (2010), 831

Hetaba, Diploma-Thesis, 2011

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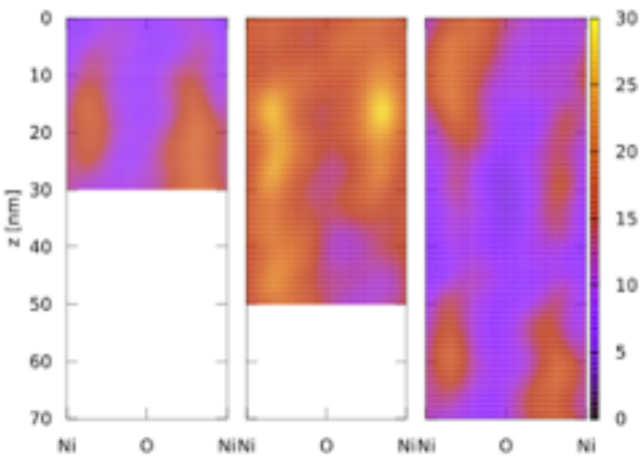

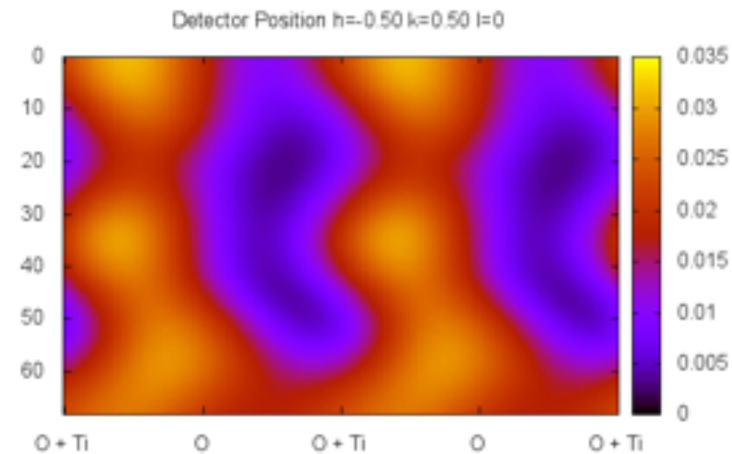

Löffler & Schattschneider, Ultram 110 (2010), 831

Hetaba, Diploma-Thesis, 2011

ELCE simulations

Incoming wave, scattering, outgoing wave
Input: crystal, exp. paramters, scattering model
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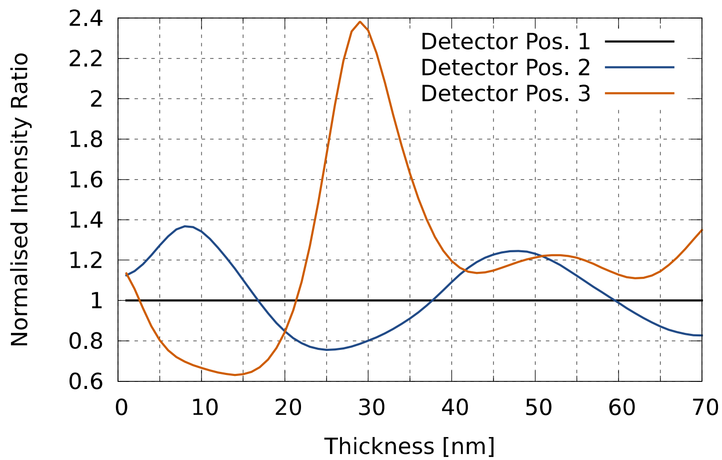
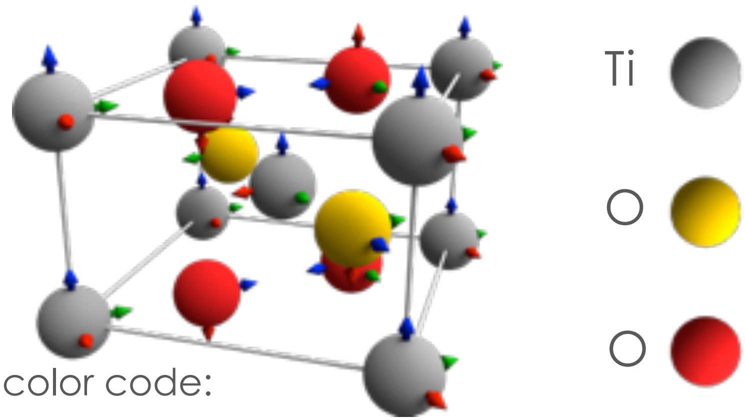


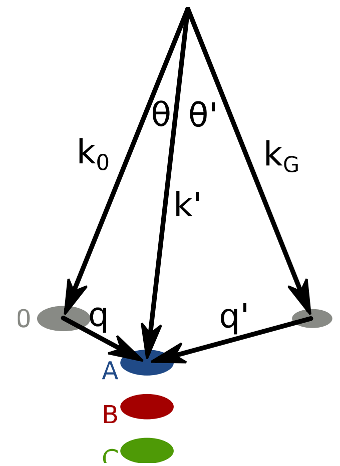
Löffler & Schattschneider, Ultram 110 (2010), 831

Hetaba, Diploma-Thesis, 2011

ELCE experiments & simulations

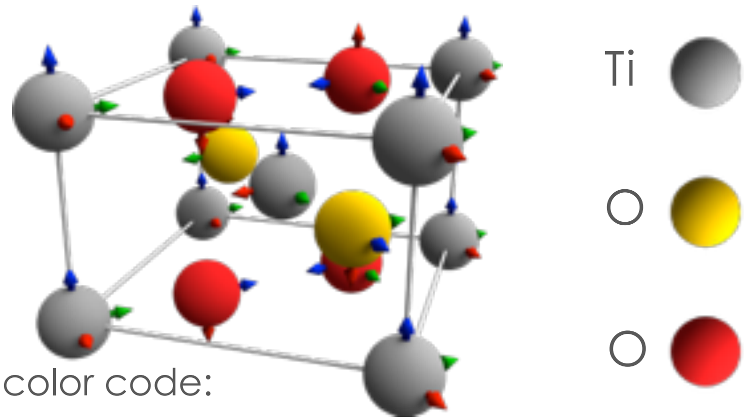


Axis color code:
x, y, z



Hetaba, Micron 63 (2014), 15

ELCE experiments & simulations



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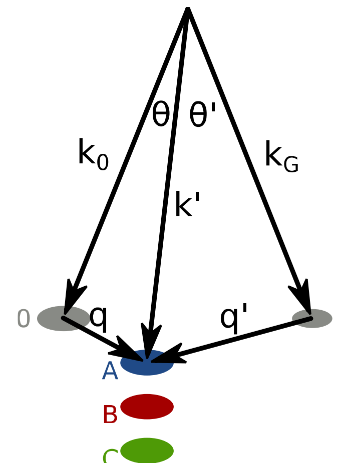
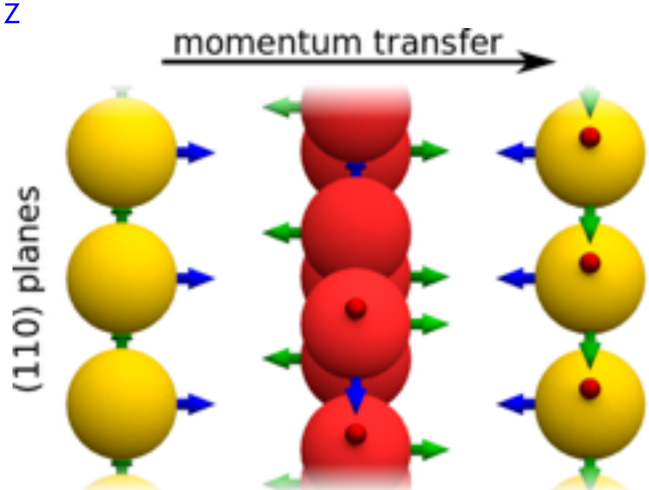
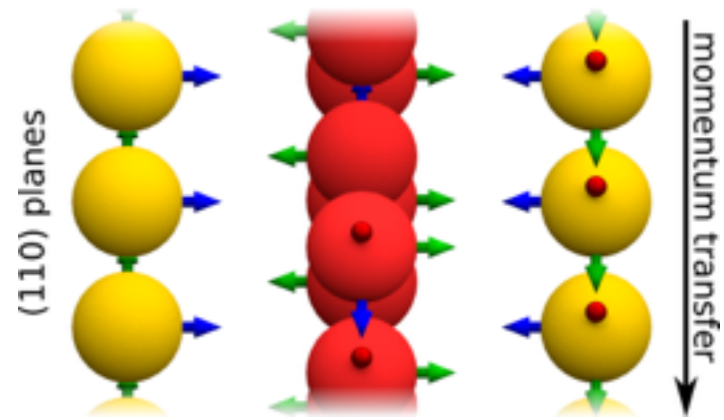
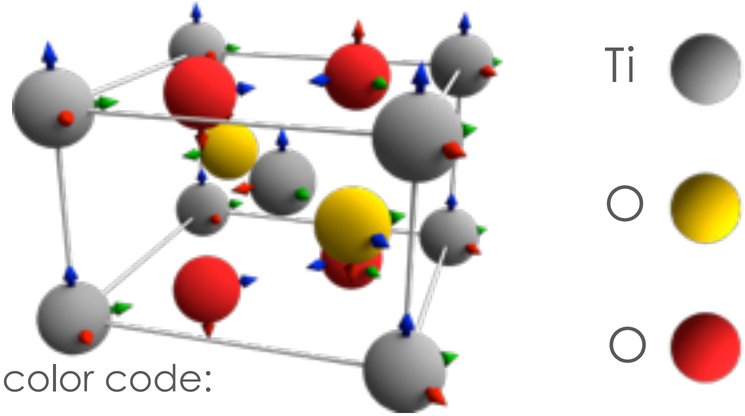






Hetaba, Micron 63 (2014), 15

ELCE experiments & simulations



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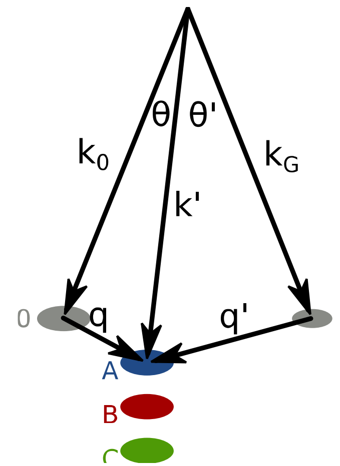
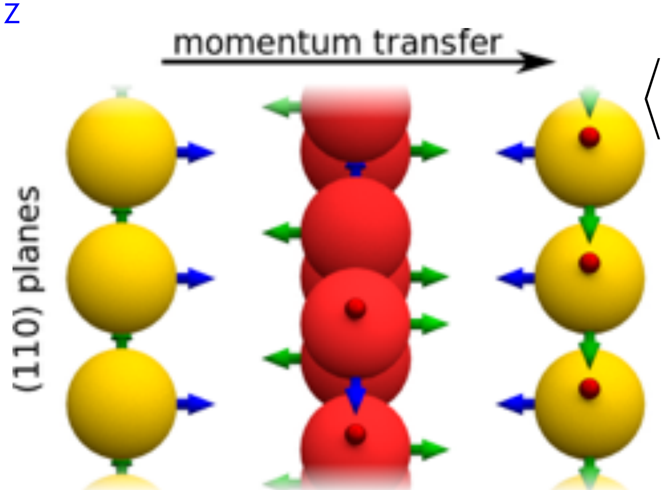
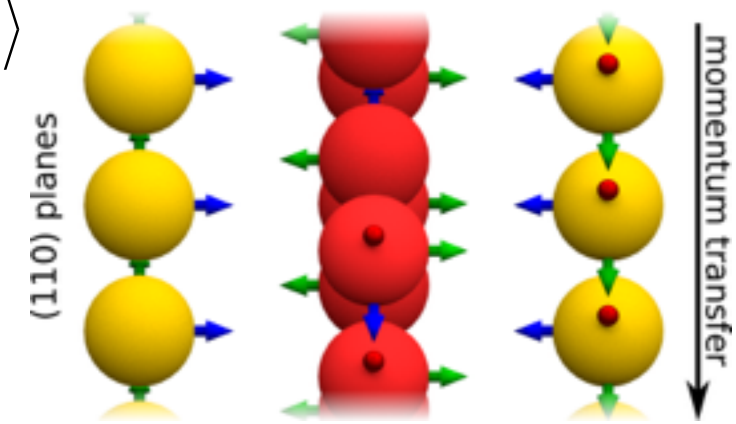


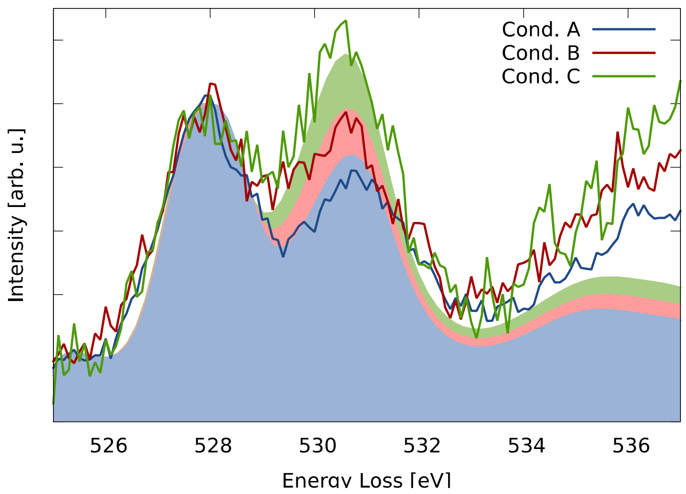


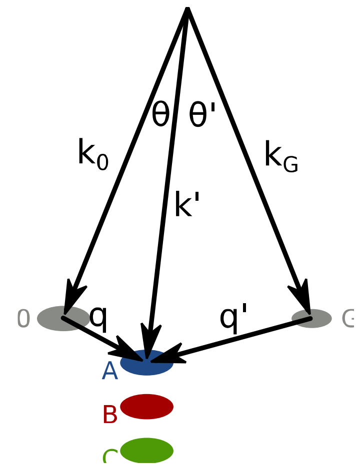
$$\left\langle f \middle| e^{i\mathbf{Q}\cdot\mathbf{R}} \middle| i \right\rangle$$

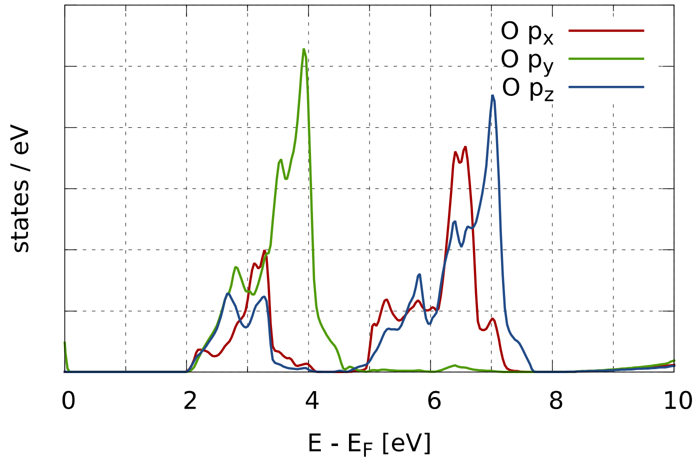


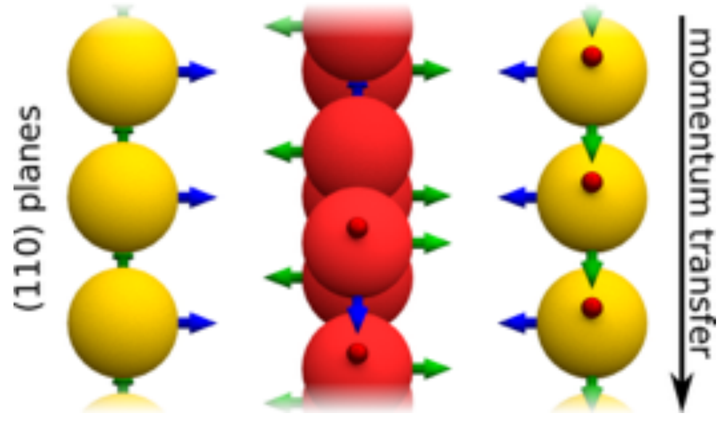
Hetaba, Micron 63 (2014), 15

ELCE experiments & simulations



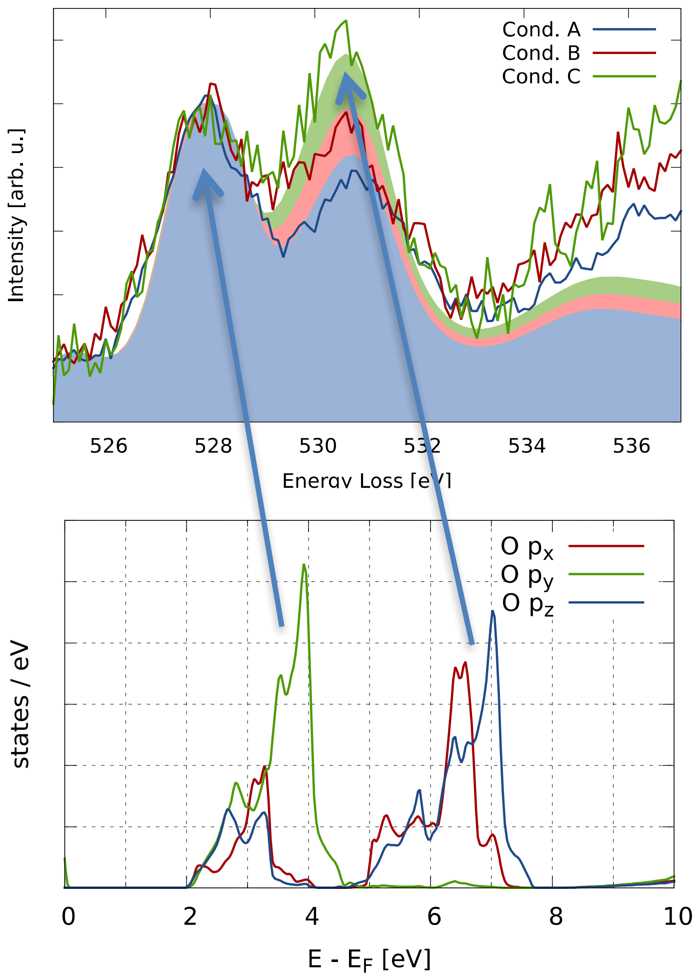


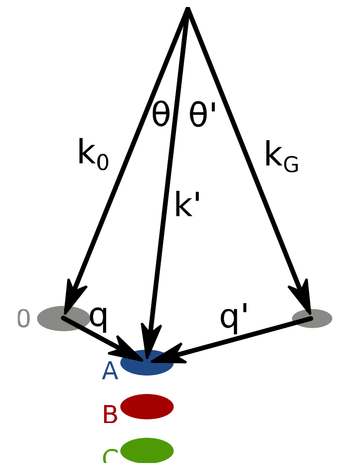


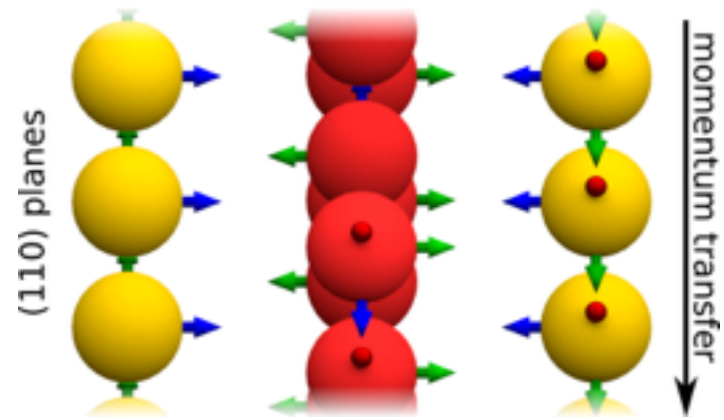


Hetaba, Micron 63 (2014), 15

ELCE experiments & simulations







Hetaba, Micron 63 (2014), 15

Summary

- EELS comparable to XAS
- Available at lower costs
- Almost all TEMs have EELS-capability
- Usually less energy-resolution but higher spatial resolution

- EELS is a versatile analytical methods
- Information about:
  - Elemental composition
  - Thicknes
  - Electronic structure
  - Optical properties
  - Magnetic properties