Inelastic scattering - II

Core loss spectroscopy

Cécile Hébert IPHYS-LSME

Layout

- Introduction
- Double differential scattering cross section
- Quantification
- ELNES
- Angular resolved EELS
- Dichroisim in the TEM

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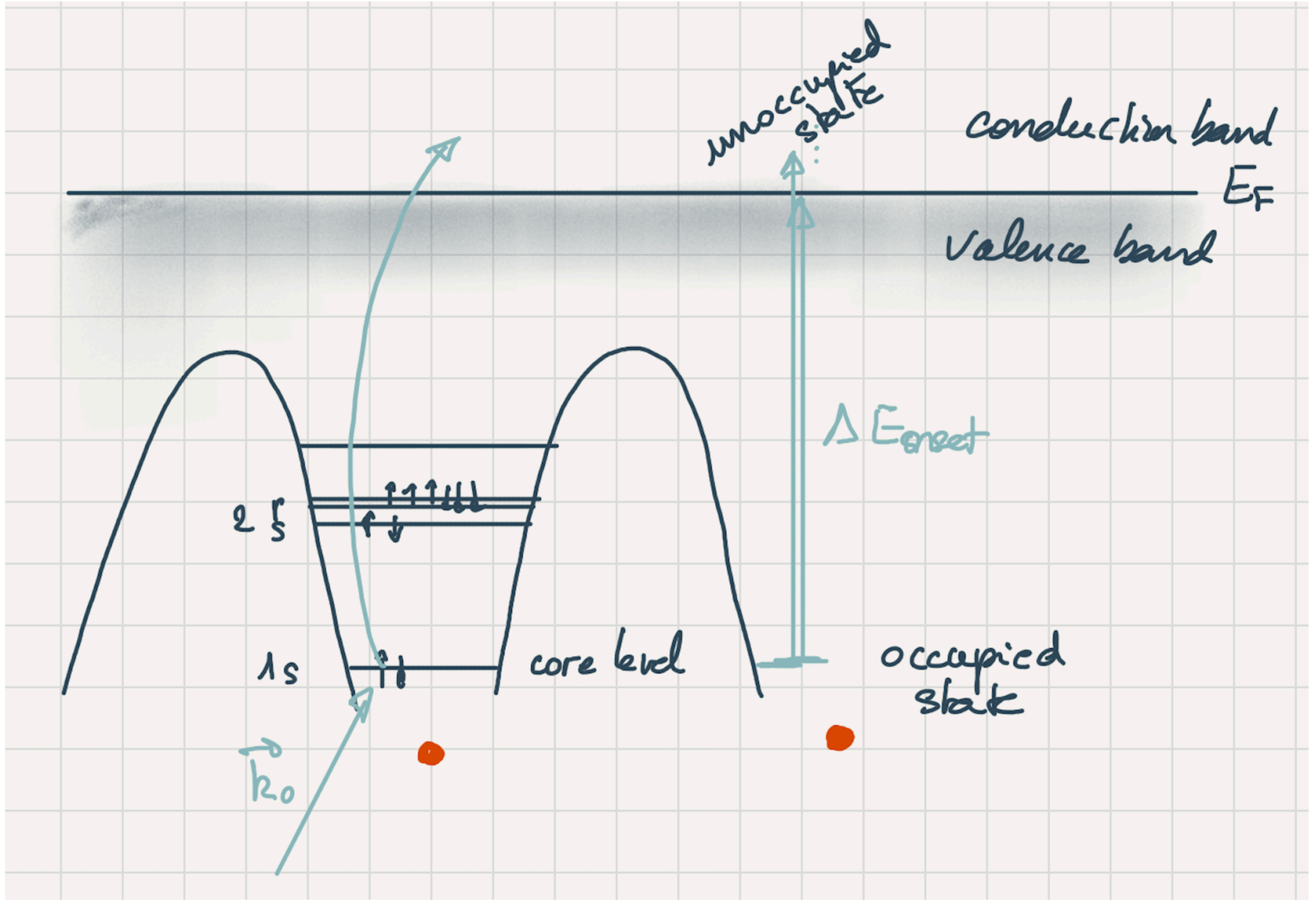
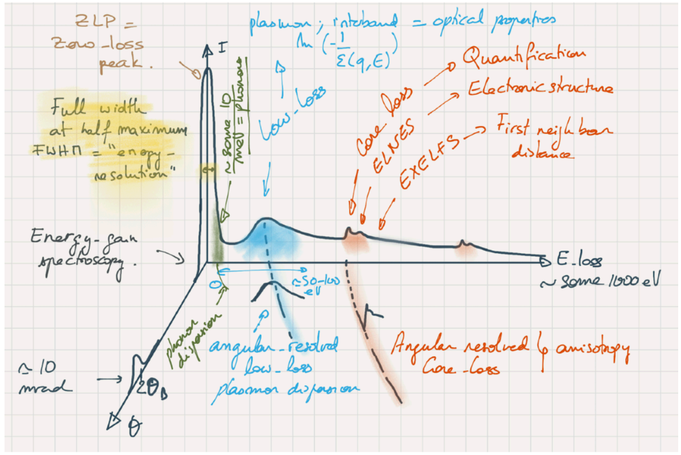
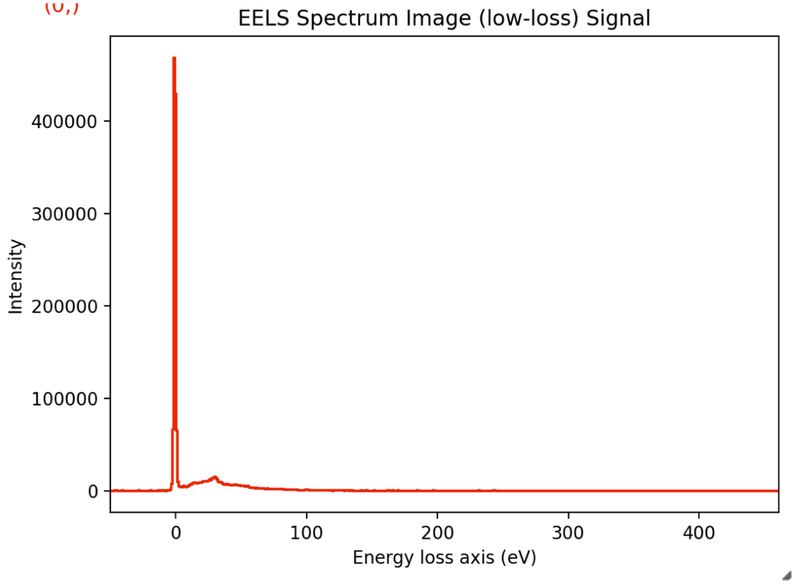
Introduction

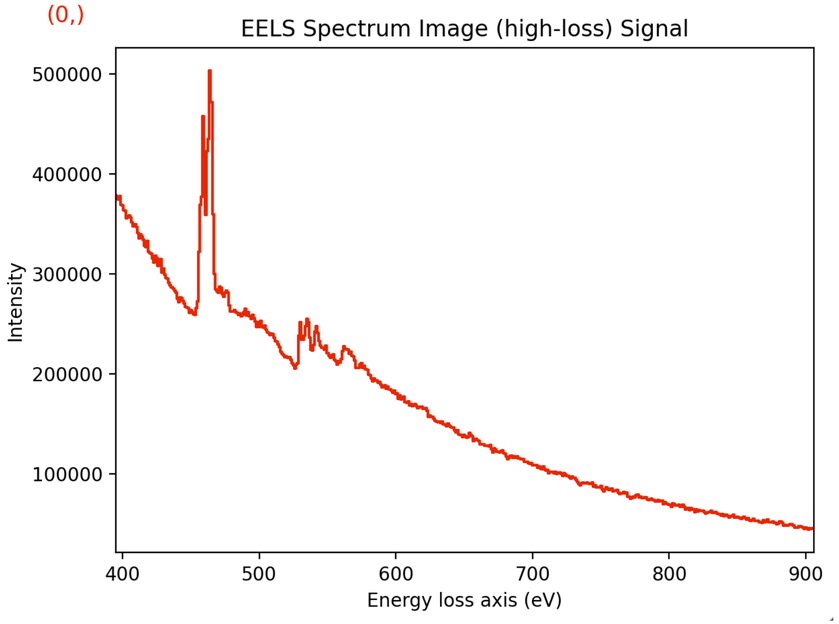


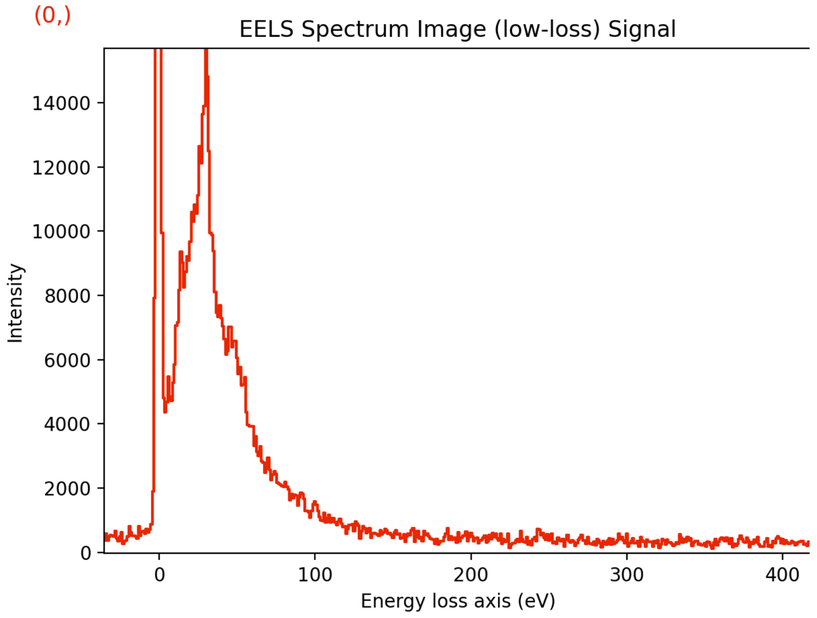
- Core electron: transition from a localised core state to an unoccupied state
- Onset: energy needed to reach Fermi level
- Transition possible above onset

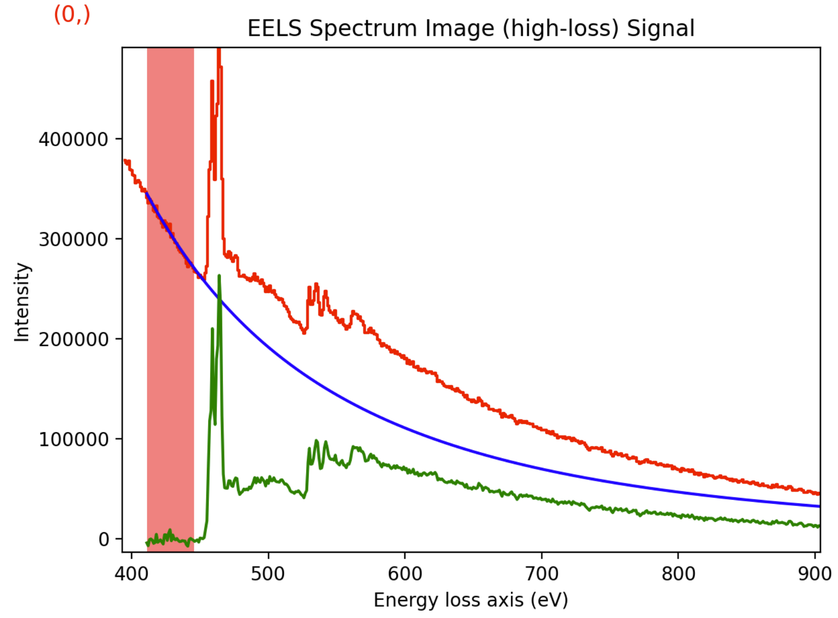
Introduction











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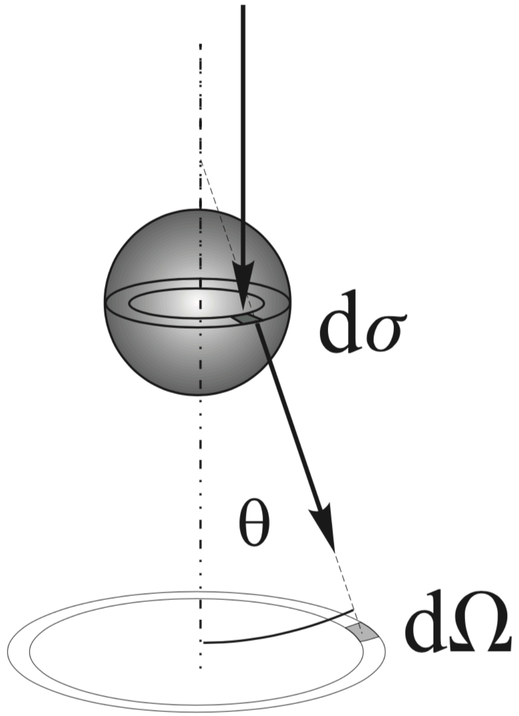
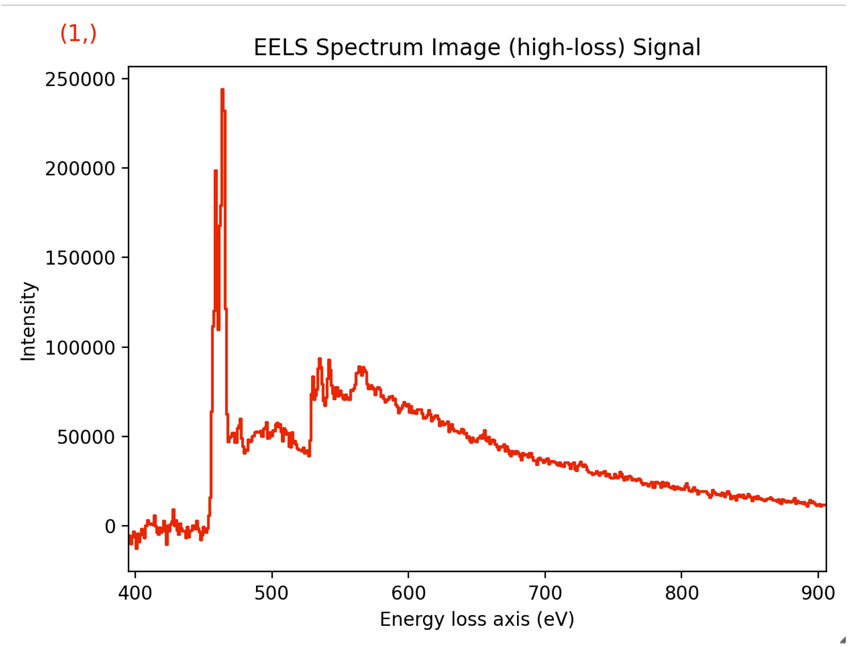
Double differential scattering cross section

Definition





- Apparent area relevant for the scattering
- Function of scattering angle and energy loss
- per unit of solid angle and energy

Double differential scattering cross section

- System: fast (incoming) electron + target electron
- Interaction potential: Coulomb
- First order perturbation theory, first Born approximation

H.A.Bethe: 1930:

Zur Theorie des Durchgangs schneller Korpuskularstrahlen durch Materie

Annalen der Physik, vol. 397, Issue 3, pp.325-400

Double differential scattering cross section

The fast electron and target electron are distinguishable. Exchange are neglected. Energy exchange small compared to energy of scattered electron.

$$|i\rangle = |\vec{k}_0\rangle \otimes |I\rangle \qquad |f\rangle = |\vec{k}'\rangle \otimes |F\rangle$$

Transition from an initial state at one energy to a group of energy in a continuum

Transition probability per unit of time, according to Fermi golden rule, time independent perturbation theory.

$$dP_{if} = \frac{2\pi}{\hbar} |\langle i | V | f \rangle|^2 dv_f \, \delta(E_f - E_i)$$

Double differential scattering cross section

Cross section ?

$$d\sigma = \sum_{i,f} \frac{dP_{i,f}}{j_0}$$

j_0 current density of the incident electron plane wave $j_0 = \frac{2\pi\hbar k_0}{m}$

$$dv_f = dv_{k'}\, dv_F = \frac{k'm}{(2\pi\hbar)^2}\, dE\, d\Omega \cdot 1$$

$$d\sigma = \sum_{i,f} \frac{2\pi}{\hbar} |\langle i | V | f \rangle|^2 \frac{k'm}{(2\pi\hbar)^2}\, dE\, d\Omega\, \delta(E_f - E_i) \frac{m}{(2\pi\hbar)k_0}$$

$$\frac{\partial^2\sigma}{\partial E\, \partial\Omega} = \sum_{i,f} \frac{m^2}{\hbar^4(2\pi)^2} \frac{k'}{k_0} |\langle i | V | f \rangle|^2 \delta(E_f - E_i)$$

details of calculation (1)

$k = \frac{1}{\lambda}$ $\quad p = hk$ $\quad$ plane wave: $e^{2\pi i \vec{k}.\vec{r}}$

$$dv_{k'} = \frac{(hk')^2 d\Omega(hk') d\theta_E}{h^3} = \frac{(hk')^2 d\Omega(hk')}{h^3} \frac{mdE}{h^2 k'^2} = \frac{mk' d\Omega dE}{h^2} \qquad dv_f = dv_{k'} dv_F = \frac{k'm}{(2\pi\hbar)^2} dE\, d\Omega \cdot 1$$

$$j_0 = |\vec{j}_0| \qquad \vec{j}_0 = \frac{\hbar}{2mi}(\psi^* \overrightarrow{\nabla} \psi - \psi \overrightarrow{\nabla} \psi^*) \qquad \overrightarrow{\nabla} \psi = 2\pi i \vec{k} e^{2\pi i \vec{k}.\vec{r}} \qquad j_0 = \frac{2\pi\hbar k_0}{m} = \frac{hk_0}{m}$$

details of calculations (2)

$$\langle i \,|\, V \,|\, f \rangle = \langle I | \otimes \langle \vec{k}_0 \,|\, V \,|\, \vec{k}' \rangle \otimes | F \rangle$$

$$V = \frac{1}{4\pi\epsilon_0}\left(\frac{-Ne^2}{|\,\vec{r}\,|} + \sum_1^N \frac{e^2}{|\,\vec{r} - \vec{r}_i\,|}\right)$$

Interaction with one atom, independent from its neighbours

First term will vanish as initial and final states of core electrons are orthogonal

$e^{2\pi i \vec{k}_0 \cdot \vec{r}}$ Plane wave

$$\int \frac{e^{2\pi i \vec{q}\cdot\vec{r}}}{|\,\vec{r} - \vec{r}_i\,|} d^3r = \frac{4\pi}{(2\pi q)^2} e^{2\pi i \vec{q}\cdot\vec{r}_i}$$

$$\langle \vec{k}_0 \,|\, V \,|\, \vec{k}' \rangle = \frac{e^2}{(4\pi)\epsilon_0} \frac{4\pi}{(2\pi q)^2} e^{2\pi i \vec{q}\cdot\vec{r}_i}$$

Detail of calculation (3)

$$\langle i\,|\,V\,|f\rangle = \langle I\,|\otimes\langle\vec{k}_0\,|\,V\,|\,\vec{k}'\rangle\otimes|\,F\rangle$$

$$V = \frac{1}{4\pi\epsilon_0}\left(\frac{-Ne^2}{|\,\vec{r}\,|} + \sum_1^N \frac{e^2}{|\,\vec{r}-\vec{r}_i\,|}\right)$$

$\vec{r}_i$ coordinate of electron number i in atom

I and F functions of $\vec{r}_i$. Plane waves $e^{2\pi i\vec{k}_0.\vec{r}}$ and $e^{2\pi i\vec{k}'.\vec{r}}$ functions of $\vec{r}$

Double differential scattering cross section

$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} = \frac{m^2}{\hbar^4(2\pi)^2}\frac{k'}{k_0}\left(\frac{e^2}{(4\pi)\epsilon_0}\frac{4\pi}{(2\pi q)^2}\right)^2 \sum_F |\langle I|\, e^{2\pi i\vec{q}\vec{r}_i}\,|F\rangle|^2\,\delta(E_F - E_I - \Delta E)$$

Bohr's radius: $a_0 = \dfrac{4\pi\epsilon_0\hbar^2}{m_0 e^2}$

$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} = \left(\frac{\gamma}{2\pi^2 a_0}\right)^2 \frac{k'}{k_0}\frac{1}{q^4}\sum_F |\langle I|\, e^{2\pi i\vec{q}\vec{r}_i}\,|F\rangle|^2\,\delta(E_F - E_I - \Delta E)$$

Double differential scattering cross section

$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} = \left(\frac{\gamma}{2\pi^2 a_0}\right)^2 \frac{k'}{k_0}\frac{1}{q^4}\sum_F |\langle I|\, e^{2\pi i\vec{q}\cdot\vec{r}_i}\,|F\rangle|^2\,\delta(E_F - E_I - \Delta E)$$

two pi or not two pi in EELS

$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} = \left(\frac{2\gamma}{a_0}\right)^2 \frac{k'}{k_0}\frac{1}{q^4}\sum_F |\langle I|\, e^{i\vec{q}\cdot\vec{r}_i}\,|F\rangle|^2\,\delta(E_F - E_I - \Delta E)$$

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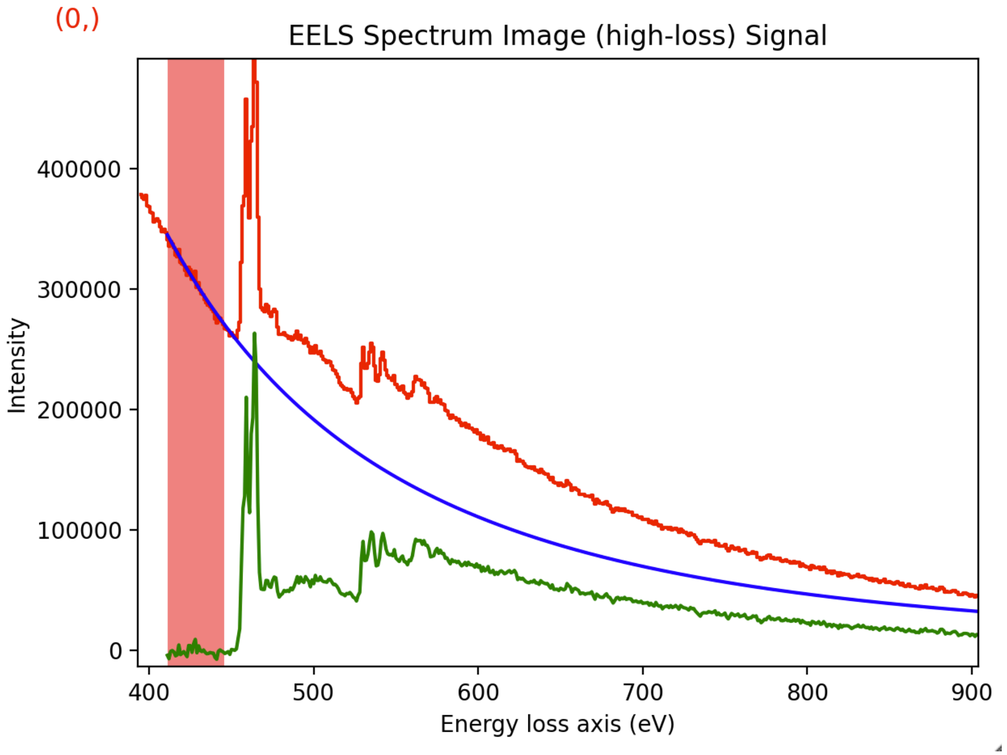
Chemical quantification



$$\sum_F |\langle I | e^{2\pi i \vec{q}\vec{r}_i} | F \rangle|^2$$

Hydrogenic model

Hartree-Slater model

challenges in accuracy (depending on edges)

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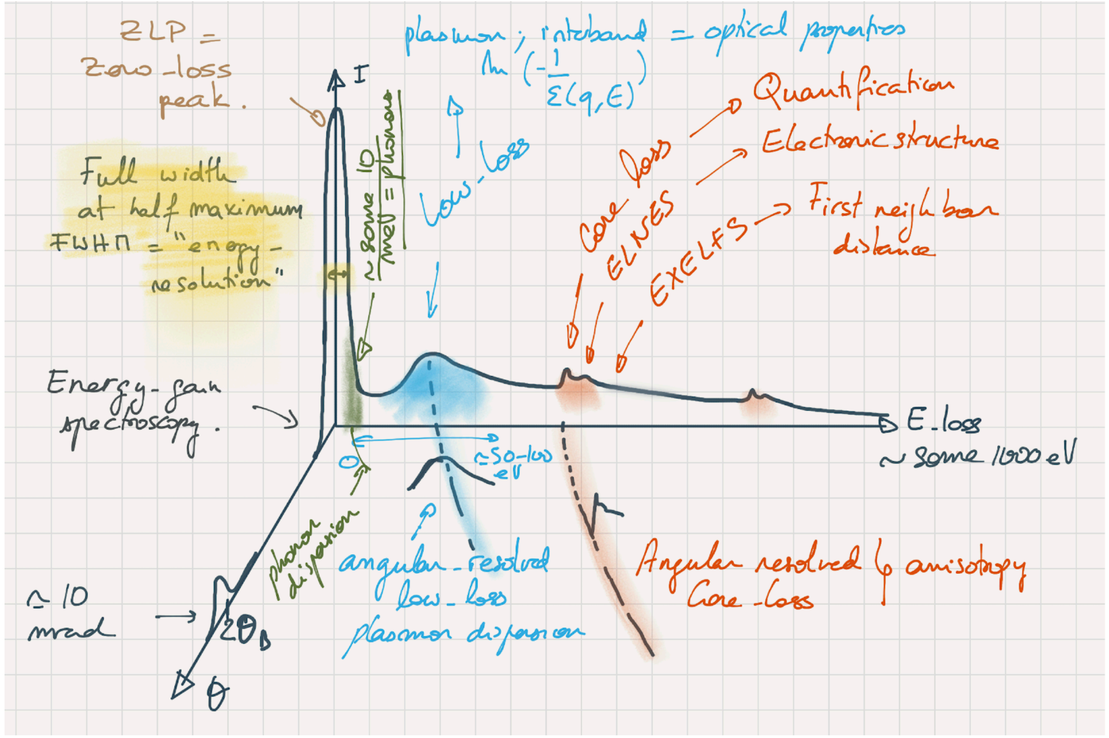
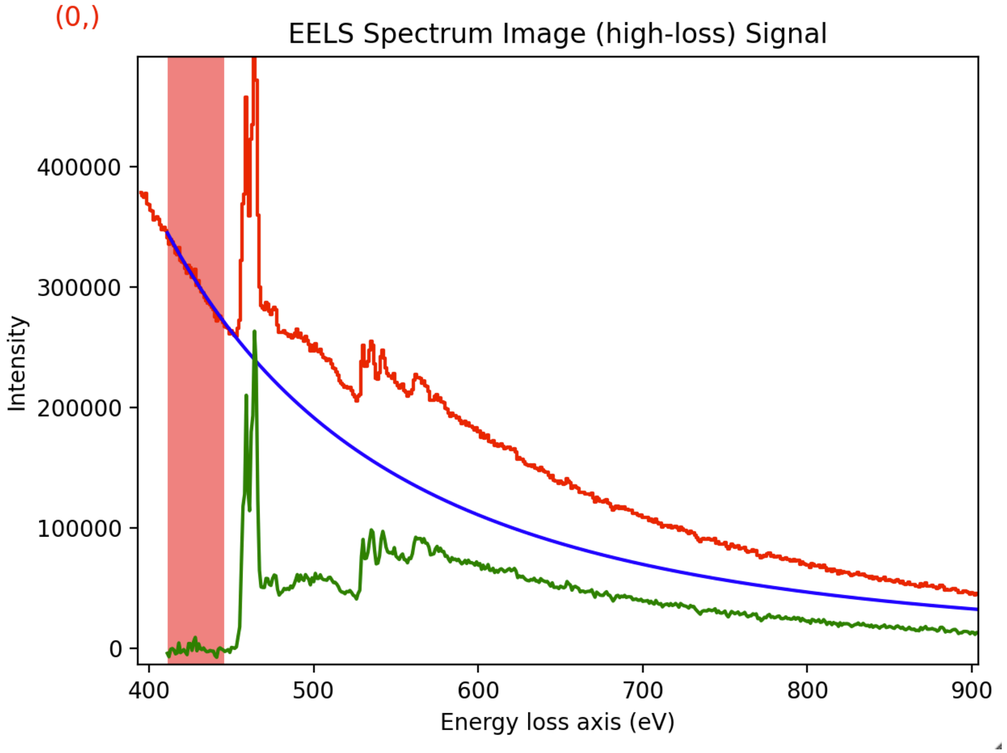
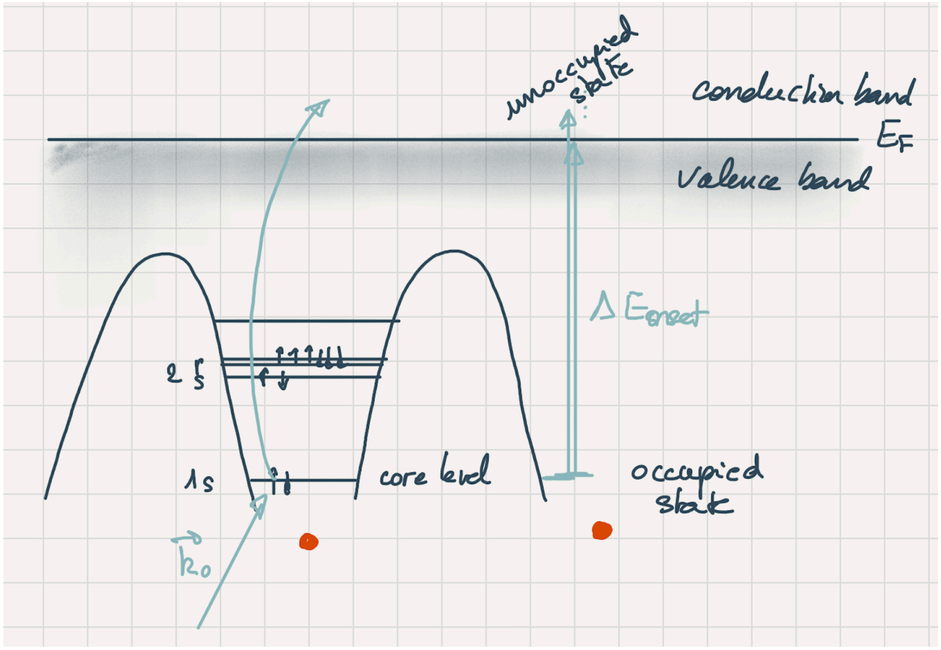


Fine structure analysis



$$\sum_F |\langle I | e^{2\pi i \vec{q}\vec{r}_i} | F \rangle|^2$$

Challenge: calculate the matrix element.

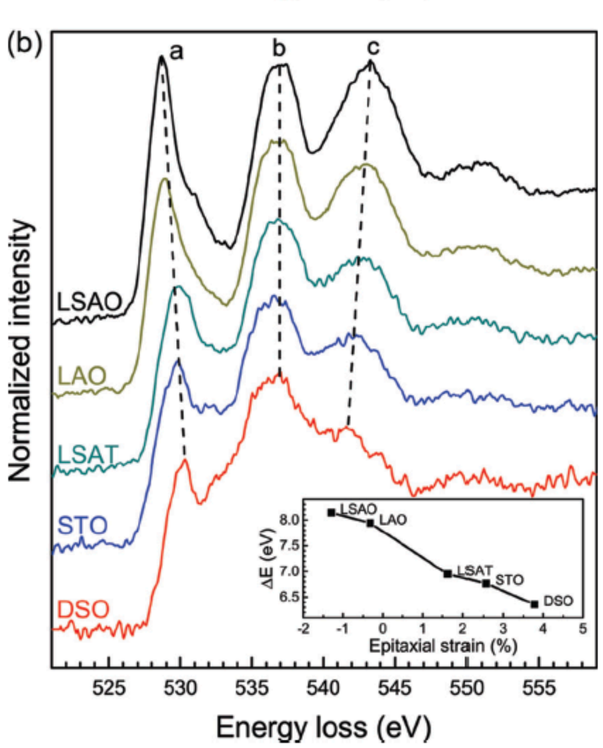


Fine structure analysis

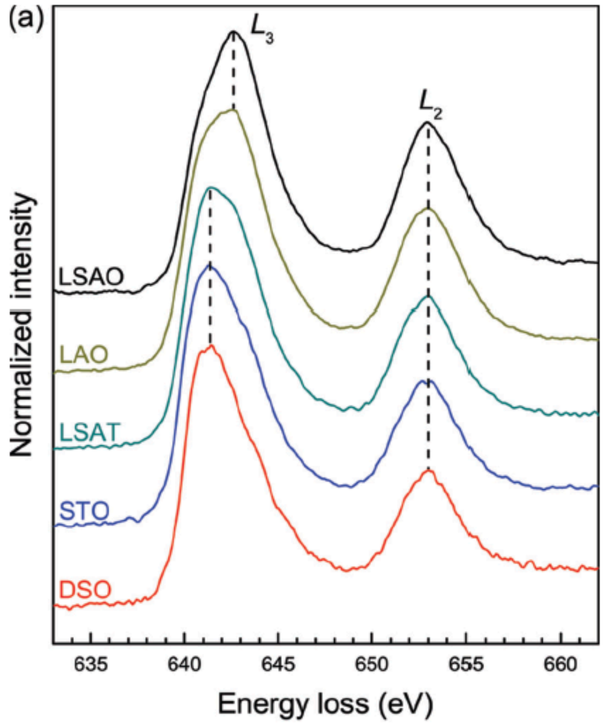
PHYSICAL REVIEW B **94**, 104101 (2016)

Strain-driven oxygen deficiency in multiferroic $SrMnO_3$ thin films

P. Agrawal,[1,2] J. Guo,[3] P. Yu,[3] C. Hébert,[4] D. Passerone,[2] R. Erni,[1] and M. D. Rossell[1,*]



O-K edge



Mn L edges

- SMO film grown on different substrates

TABLE I. Experimental lattice parameters and optimized out-of-plane parameters calculated for strained SMO structures without oxygen vacancies.

Substrate	$a=b$ (Å)	c (Å)	Optimized c parameter (Å)
LSAO	3.756	3.927	3.935
LSAT	3.868	3.803	3.624
DSO	3.955	3.826	3.626

Fine structure analysis

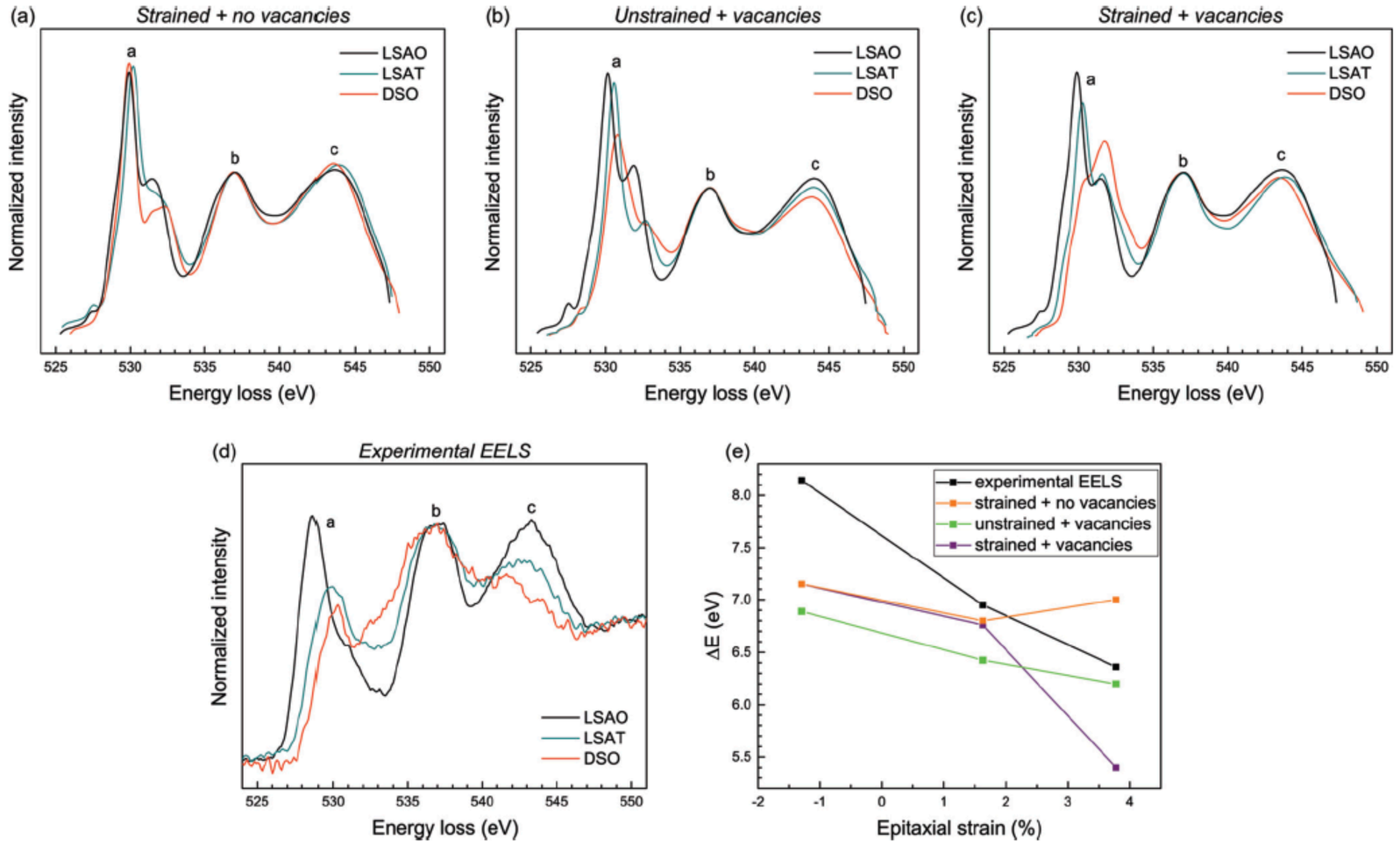


FIG. 5. O-K edge EEL spectra of SMO structures on LSAO, LSAT, and DSO. (a) The O-K edge spectra are calculated assuming strained lattice parameters and no oxygen vacancies. (b) The O-K edge spectra are calculated assuming unstrained lattice parameters and the presence of oxygen vacancies. (c) The O-K edge spectra are calculated assuming strained lattice parameters and the presence of oxygen vacancies. (d) Experimental O-K edge spectra. (e) Energy difference between the O-K_a prepeak and the O-K_b main peak as a function of epitaxial strain for all four cases.

Fine structure calculation using DFT theory (FPLAPW code Wien2k)

Core hole approximation

“supercell”

Trends more important than absolute values

Fine structure calculations: challenges

- One electron scheme. No correlation. OK for “reasonable” systems
- real space (multiple scattering methods) vs reciprocal space
- Workaround for the excited state: core hole
- Time dependent DFT, etc

“workaround”: fingerprints

Example: determination of the oxidation state of transition metals

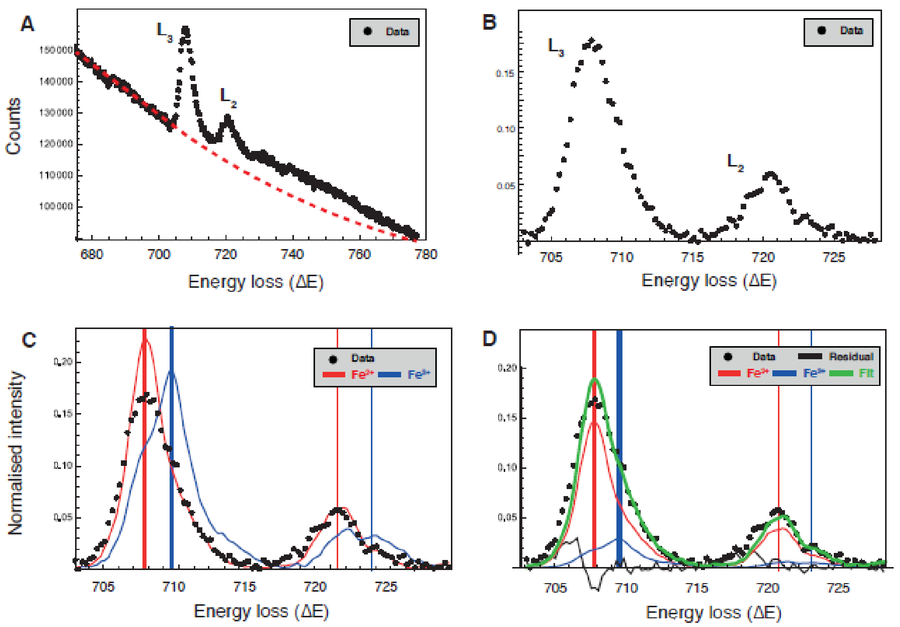
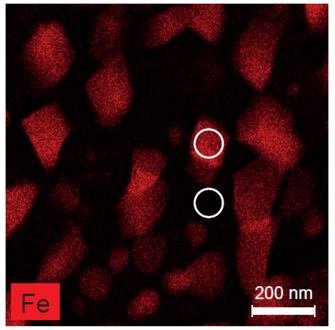
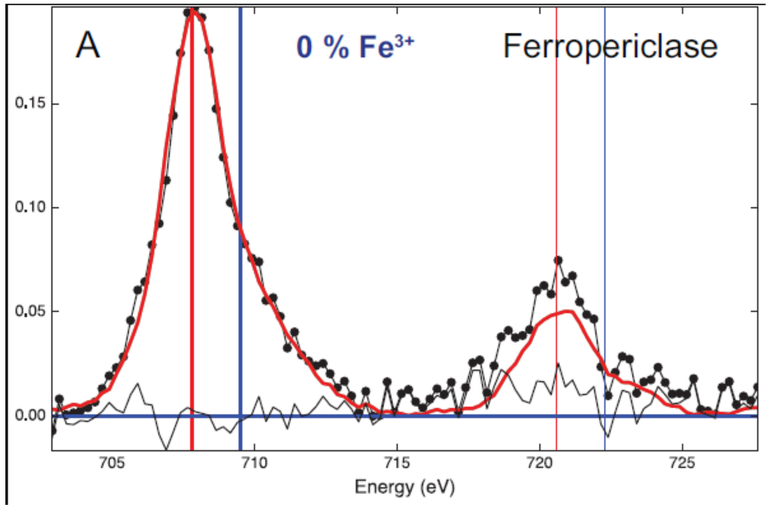


Figure 3.25 – **Procedure for Fe^{2+}/Fe^{3+} ratios spectra quantification**. a) Typical acquired EEL spectrum showing ionisation (L_2, L_3) edges of iron. We first proceed to data binning for better spectral intensity, and then background subtraction (red dashed line). b) Data normalised to peak intensities c) Data with reference spectra for pure ferrous and pure ferric iron. We processed these spectra following the same procedure as for the data. d) Calculated fit (in green) obtained by a least-squares fit using the two standards (blue and red curves). The fit indicates the presence of 15.9 ± 4% Fe^{3+}.



$Fe^{3+}/\sum Fe$ = 0%

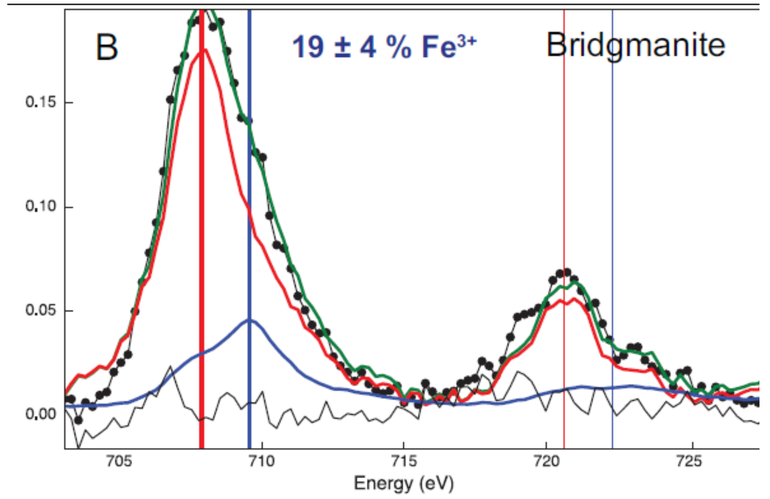
$Fe^{3+}/\sum Fe$ = 19%



Spin and valence dependence of iron partitioning in Earth’s deep mantle

Piet & al.

www.pnas.org/cgi/doi/10.1073/pnas.1605290113



van Aken PA, Liebscher B, (2002) *Phys Chem Miner* 29(3):188–200.

Dipole approximation

$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} \propto \frac{k'}{k_0}\frac{1}{q^4}\sum_F |\langle I|\, e^{2\pi i\vec{q}\cdot\vec{r}_i}\,|F\rangle|^2\,\delta(E_F - E_I - \Delta E)$$

$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} \propto \frac{1}{q^4}\sum_F |\langle I|\,\vec{q}\cdot\vec{r}_i\,|F\rangle|^2\,\delta(E_F - E_I - \Delta E)$$

Dipole selection rule. Usually OK.

Dipole approximation: angular distribution

$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} \propto \frac{1}{q^4}\sum_F |\langle I|\vec{q}\cdot\vec{r}_i|F\rangle|^2\,\delta(E_F - E_I - \Delta E) \propto \frac{1}{q^2} \propto \frac{1}{\theta^2+\theta_E^2}$$

Lorenzian distribution, HWHM θ_E

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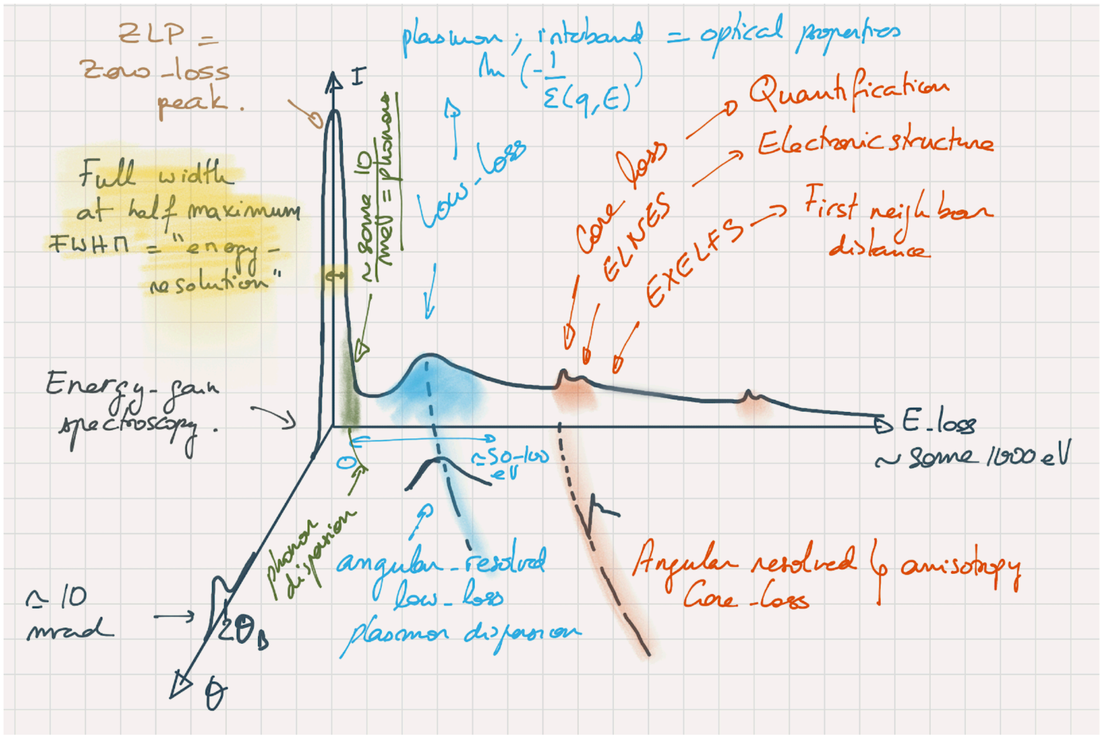
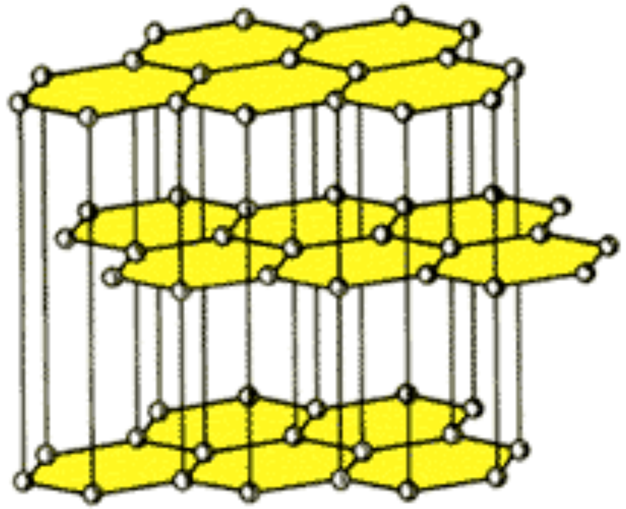


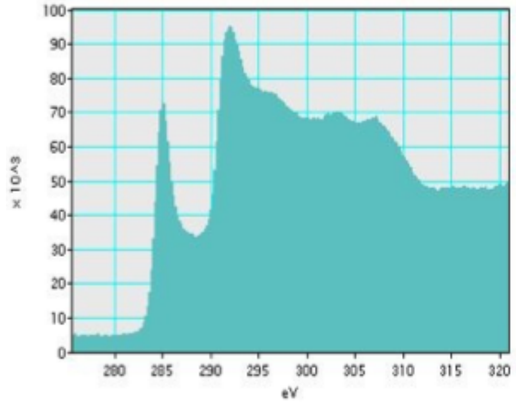
Linear dichroism

If the final state is anisotropic

$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} \propto \frac{k'}{k_0}\frac{1}{q^4}\sum_F |\langle I|\vec{q}\cdot\vec{r}_i|F\rangle|^2\,\delta(E_F - E_I - \Delta E)$$

Example: HOPG or h-BN





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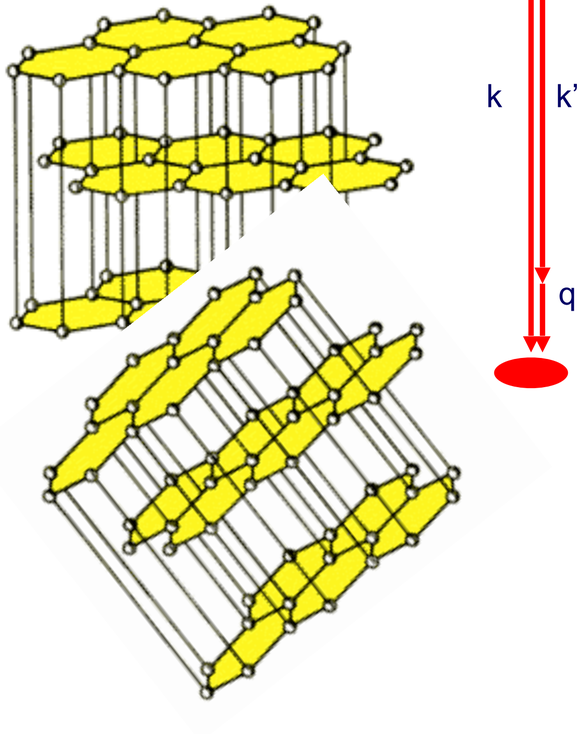
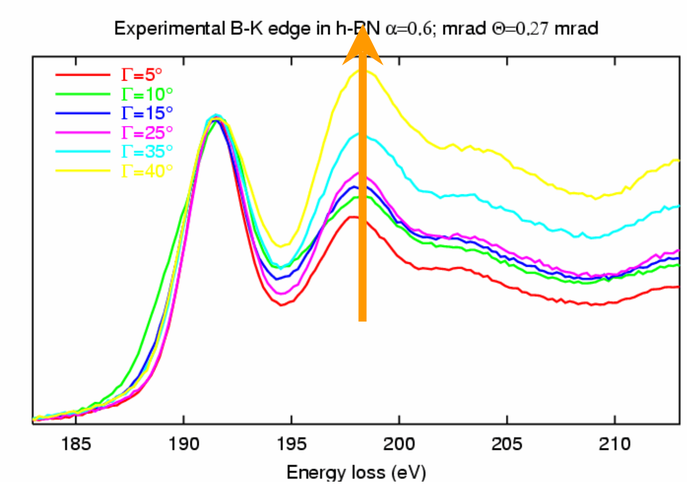
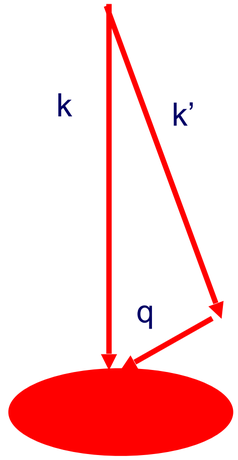
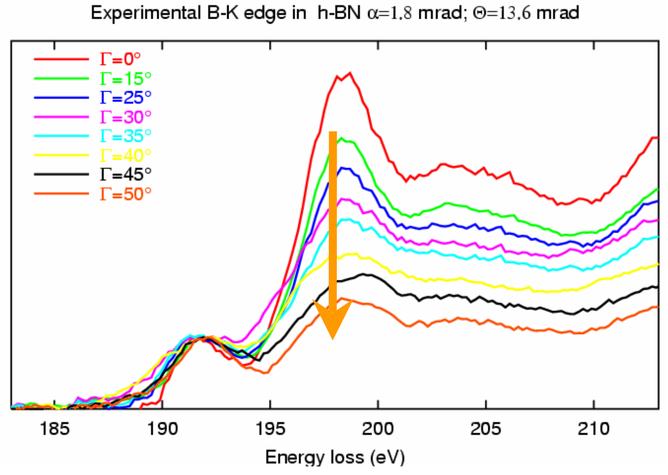
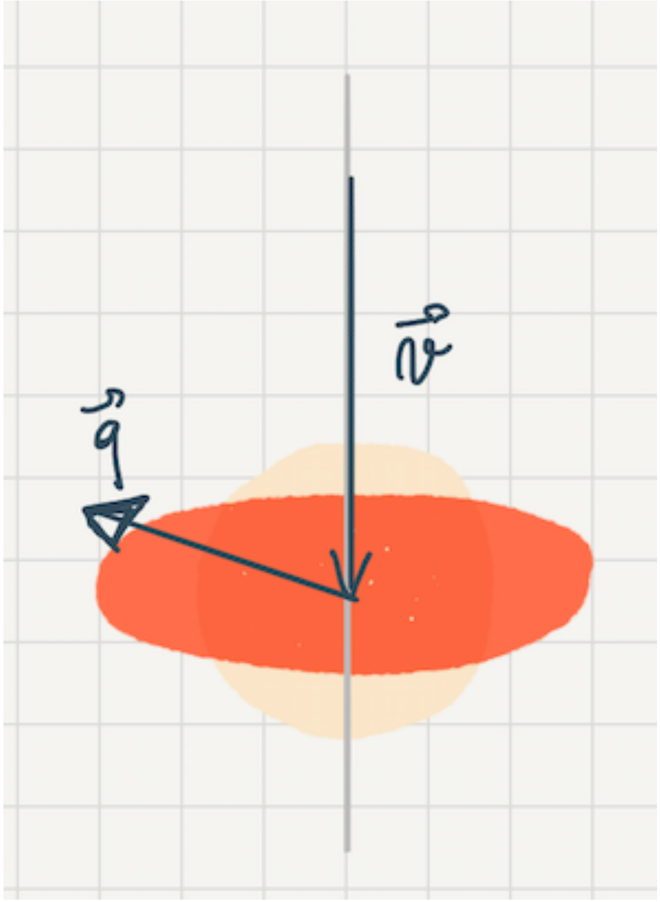








Anisotropy: Relativity fires back



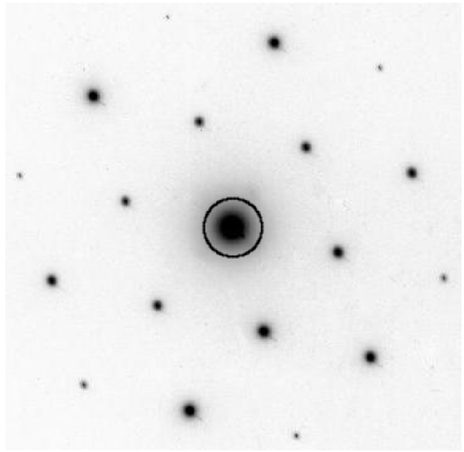
Electric field of a moving charge is compressed in the direction of movement

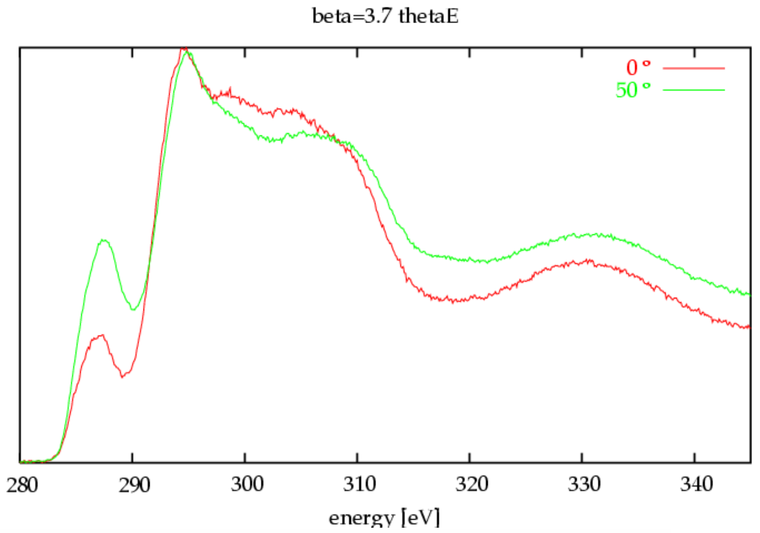
Coulomb coupling becomes anisotropic

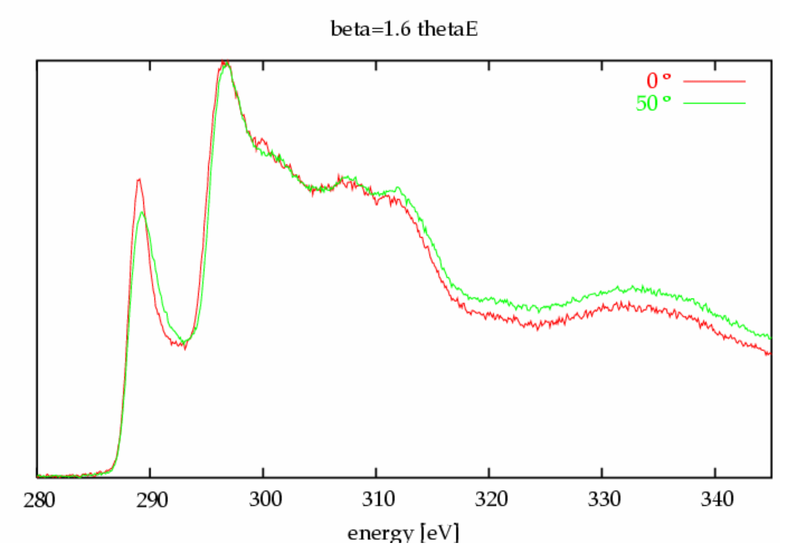
Coupling with momentum transfer parallel to the electron's trajectory becomes smaller

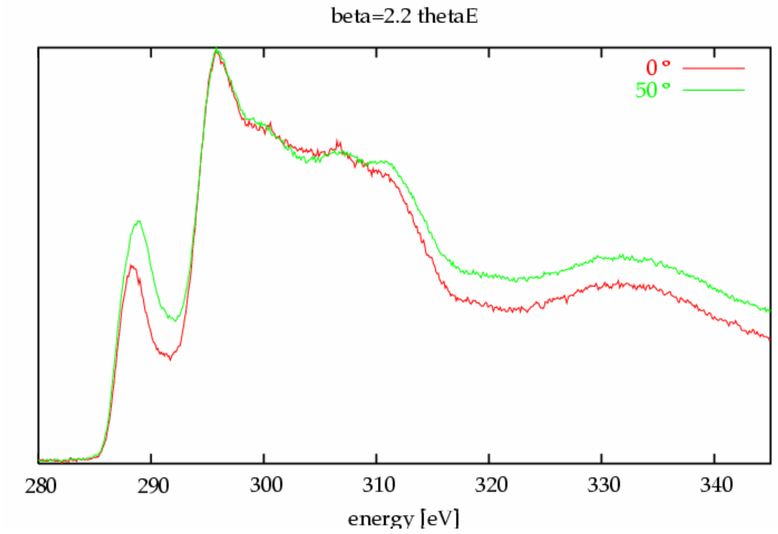
Coupling with momentum transfers perpendicular to the electron's trajectory becomes larger

Anisotropy: Relativity fires back









non-relativistic “magic angle”: $3.8\,\theta_E$

experimental value: $\approx 1.6\,\theta_E$

relativistic value at 200 kV $1.6\,\theta_E$