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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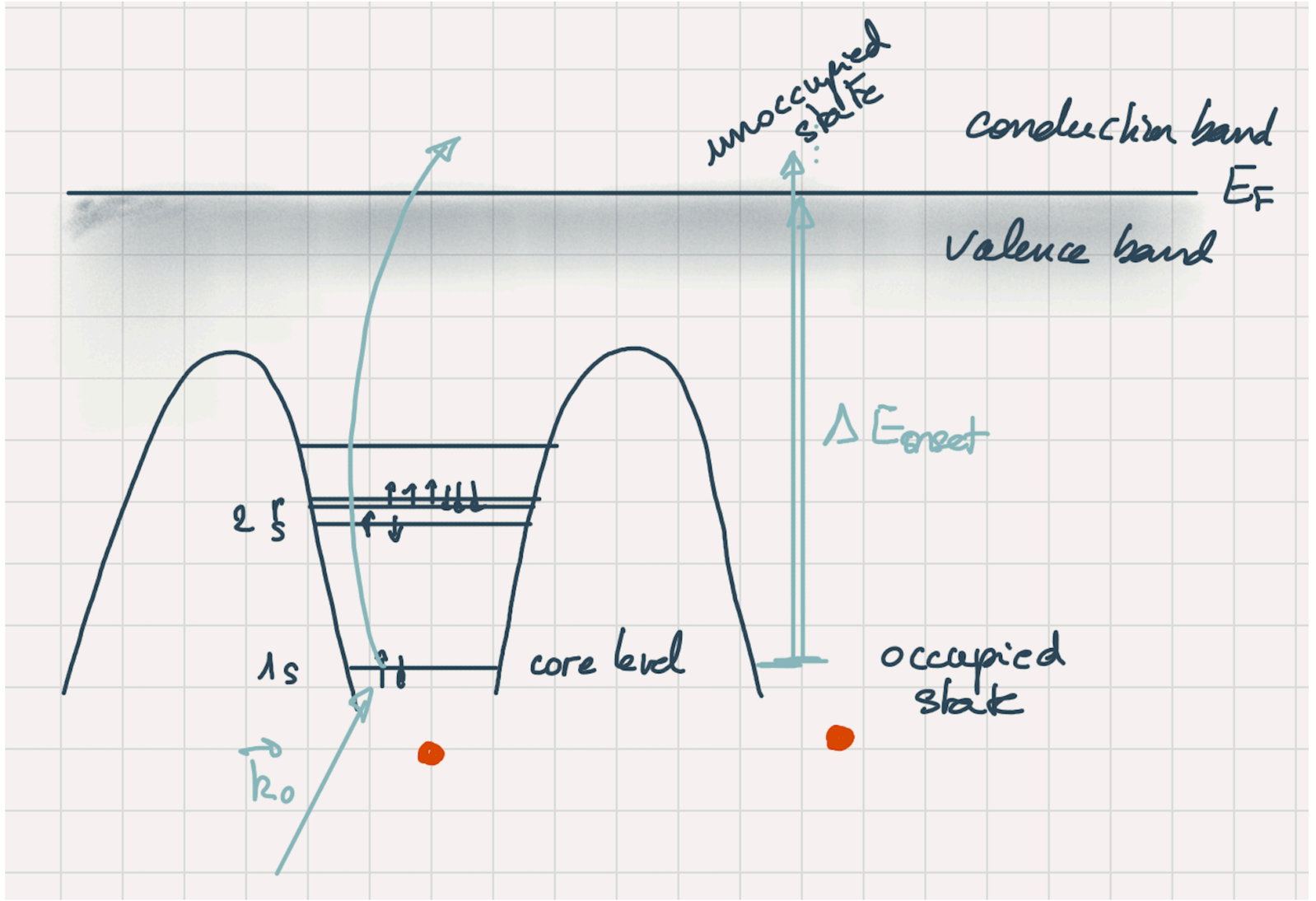
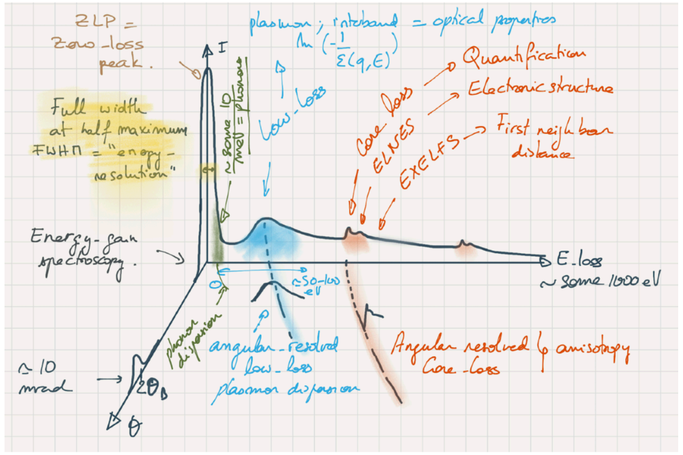
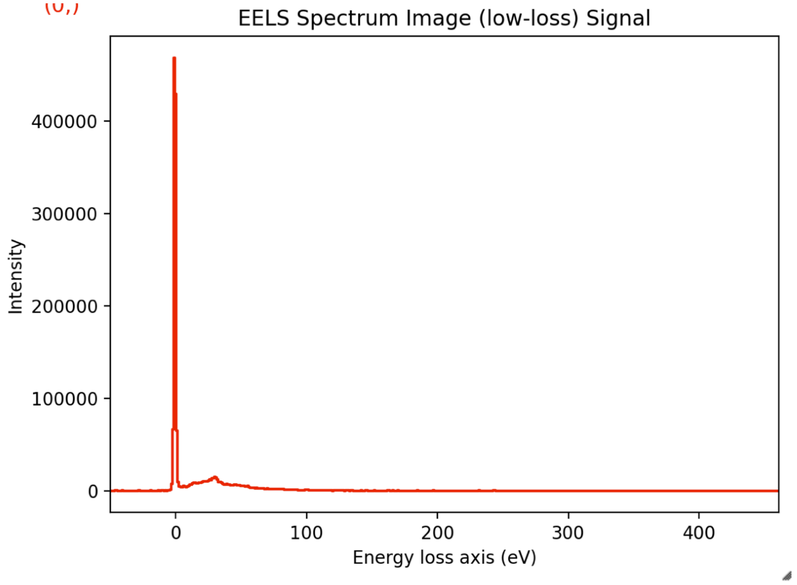
Introduction

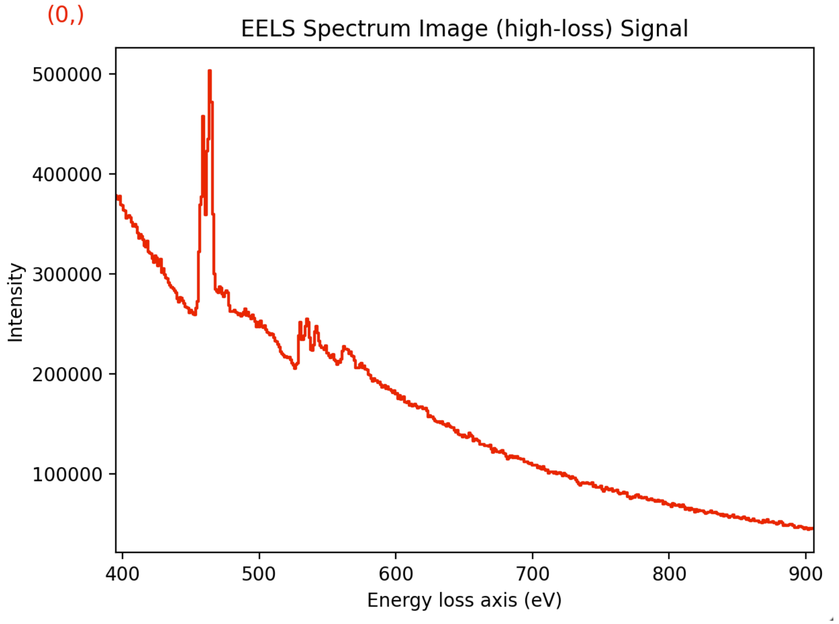


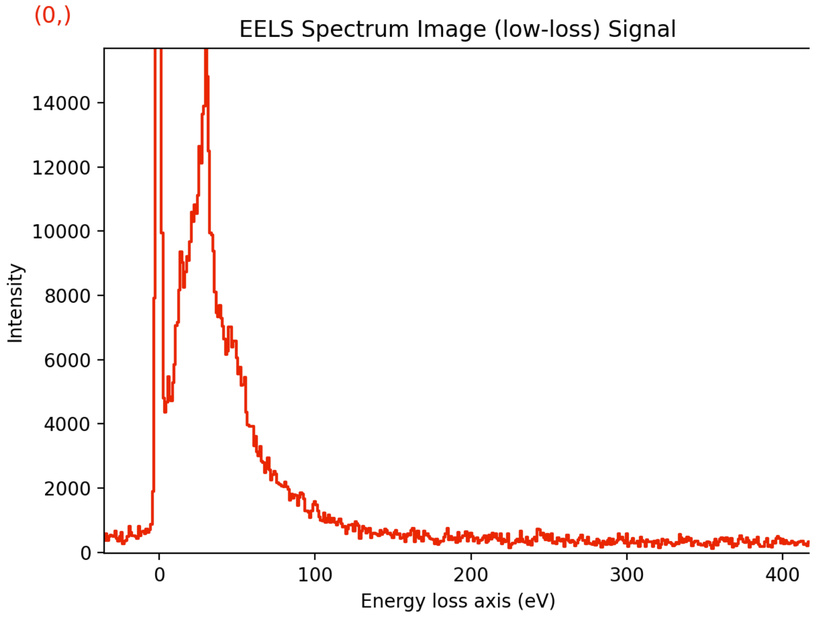
- Core electron: transition from a localised core state to an unoccupied state
- Onset: energy needed to reach Fermi level
- Transition possible above onset

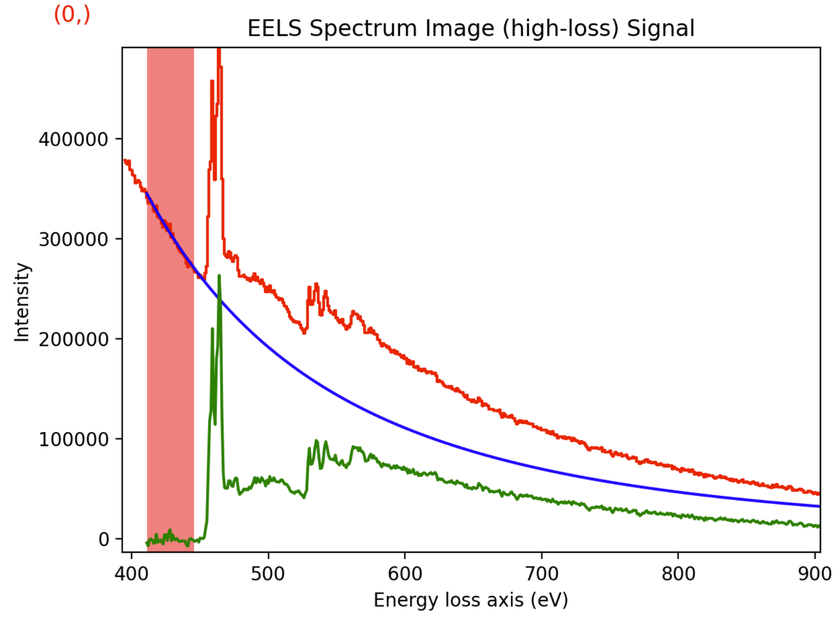
Introduction











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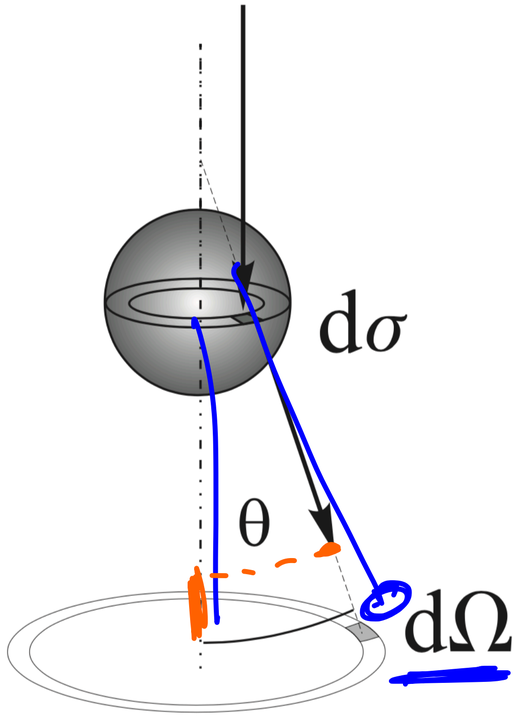
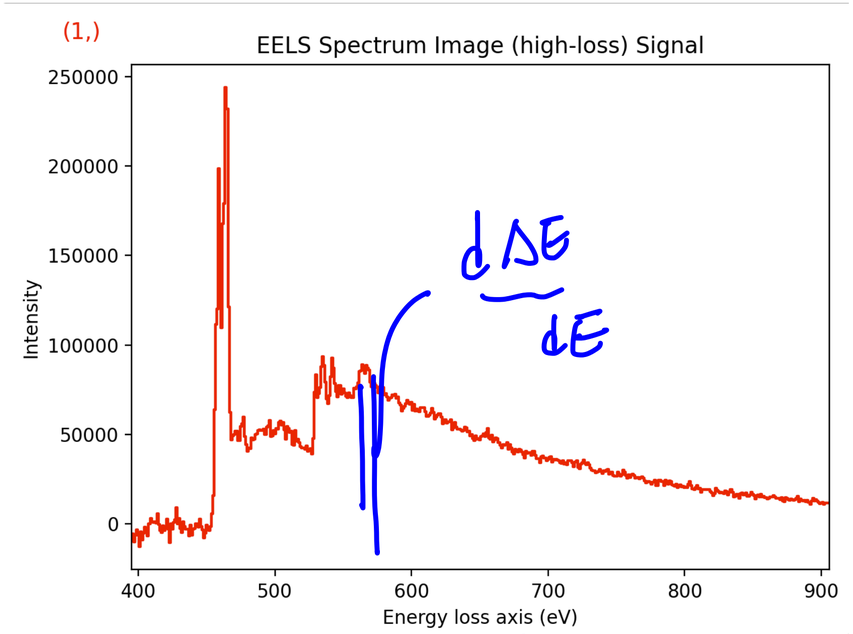
Double differential scattering cross section

Definition





Unit of m^2 per atom of the sample

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

$$\frac{\partial^2\sigma}{\partial\Omega\partial E}$$

Double differential scattering cross section

- System: fast (incoming) electron + target electron (atom)
- 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.

Coulomb potential

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

volume en phase space

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 $\quad j_0 = \frac{2\pi\hbar k_0}{m}$

next slide ②

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

next slide ①

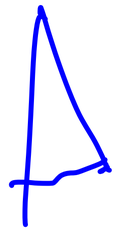
$$d\sigma = \sum_{i,f} \frac{2\pi}{\hbar} |\langle i|V|f\rangle|^2 \frac{k'm}{(2\pi\hbar)^2}\, dE\, d\Omega\, \delta(E_f - E_i) \frac{m}{(2\pi\hbar)k_0}$$

?

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

③

details of calculation (1)



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

m_0 rest mass $\quad m$ mass of moving particle

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

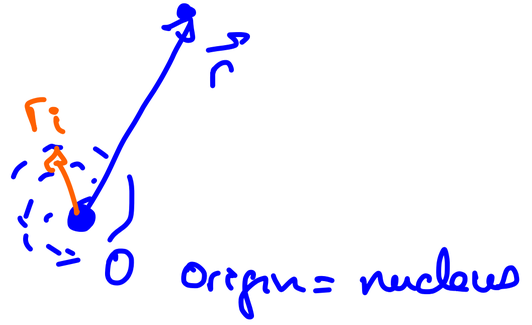
$\theta_E = \frac{k_0 - k'}{k_0} = 1 - \frac{k'}{k_0} = 1 - \frac{p'}{p_0}$ $\quad E_t$ of electron $\quad E_t^2 = (pc)^2 + (m_0 c^2)^2 = (E_{kin} + m_0 c)^2$

$p_0 = \sqrt{E_t^2 - (m_0 c^2)^2}$; $p' = \sqrt{(E_t - \Delta E)^2 - (m_0 c^2)^2} = \ldots$ $\quad \Delta E \ll E_t$; $\Delta E \ll E_k$; $p' = \sqrt{(E_t^2 - (m_0 c^2)^2)\left(1 - \frac{2\Delta E E_t}{E_t^2 - (m_0 c^2)^2}\right)}$

$\theta_E = 1 - \left[1 - \frac{1}{2} \frac{2\Delta E E_t}{E_k - (m_0 c^2)^2}\right]$ $\quad E_t = mc^2$ $\Rightarrow$ $\theta_\theta = \frac{\Delta E\, mc^2}{p^2 c^2} = \frac{m\Delta E}{h^2 k^2}$

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

details of calculations (2)



③

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

nucleus electrons

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

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

$$\left(e^{2\pi i\vec{k}'\cdot\vec{r}}\right)^* = e^{-2\pi i\vec{k}'\cdot\vec{r}} \rightarrow e^{2\pi i(\vec{k}_0-\vec{k}')\cdot\vec{r}}$$

$\vec{q}$

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

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

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 $\vec{r}$

function of $\vec{r}$

Matrix element $\int\!\!\int\!\!\int \ldots d^3r \} d^3r_i$

2 variables can be separated $\int \frac{1}{|\vec{r}|} e^{2i(\vec{q}.\vec{r})} \cdot \{ \underbrace{I(\vec{r}_i)\, f(r_i) d^3r_i}_{0}$

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

$m = \gamma m_0$

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

Double differential scattering cross section

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

Reimer

two pi or not two pi in EELS

Crystallo approach $|\vec{k}| = \frac{1}{\lambda}$ $\vec{a}.\vec{a}^* = 1$ $\vec{p} = h\vec{k}$ plane wave $e^{2\pi i \vec{k}.\vec{r}}$ $\theta_E = \frac{m\Delta E}{h^2 k^2}$

$p = \frac{h}{\lambda}$

Solid state $|\vec{k}| = \frac{2\pi}{\lambda}$ $\vec{a}.\vec{a}^* = 2\pi$ $\vec{p} = \hbar\vec{k}$ plane wave $e^{i\vec{k}.\vec{r}}$ $\theta_E = \frac{m\Delta E}{\hbar k^2}$

$p = \hbar k = \frac{h}{2\pi}\cdot\frac{2\pi}{\lambda} = \frac{h}{\lambda}$

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

Egerton

Schattschneider

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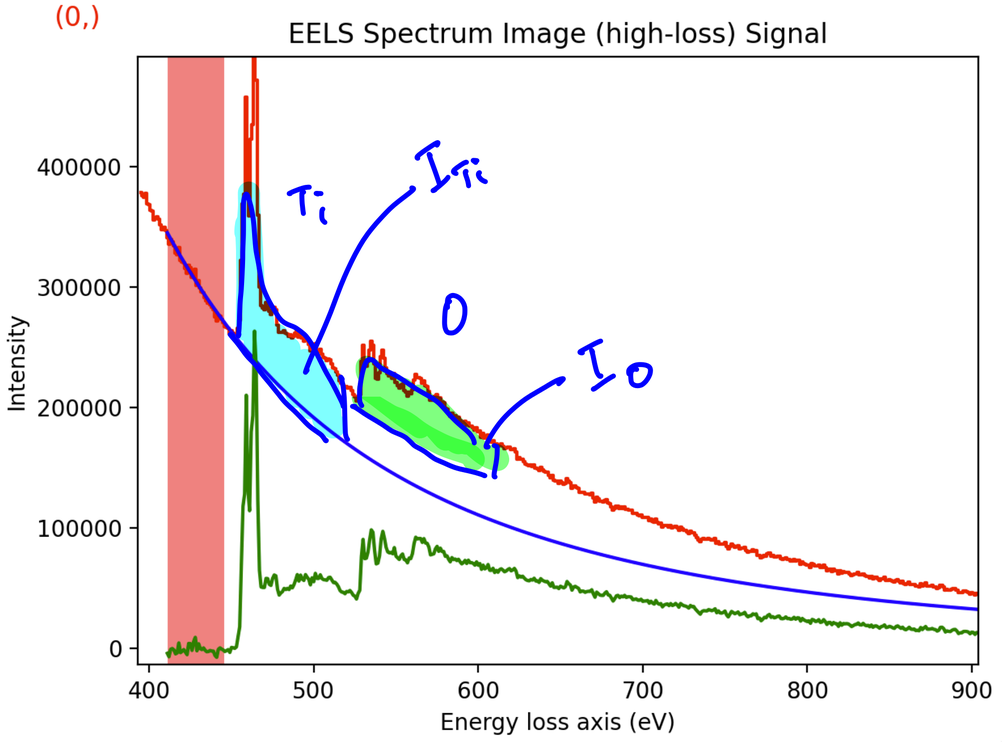
Chemical quantification



core state

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

final states above Fermi

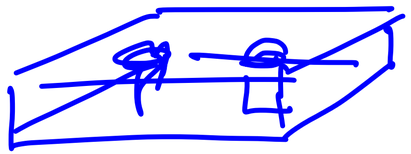
Hydrogenic model

Hartree-Slater model

atomic models!

challenges in accuracy (depending on edges)

≥ 10 - 20%



good for comparing areas observed under same condition

absolute quantification is hard!

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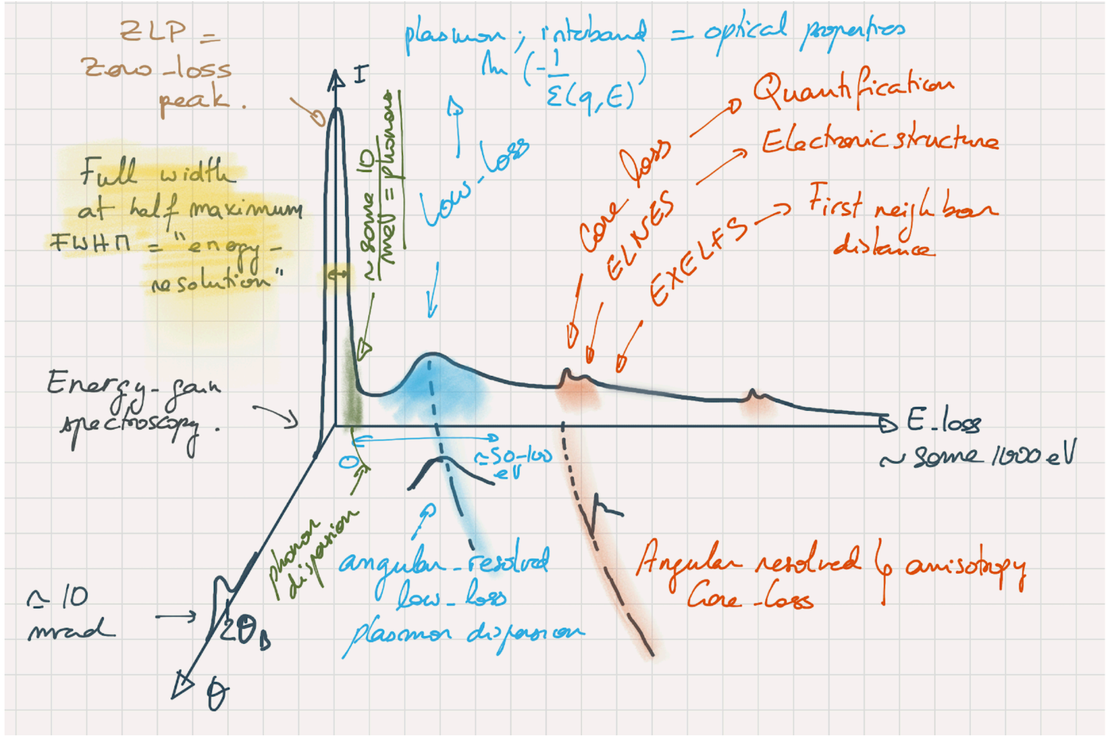
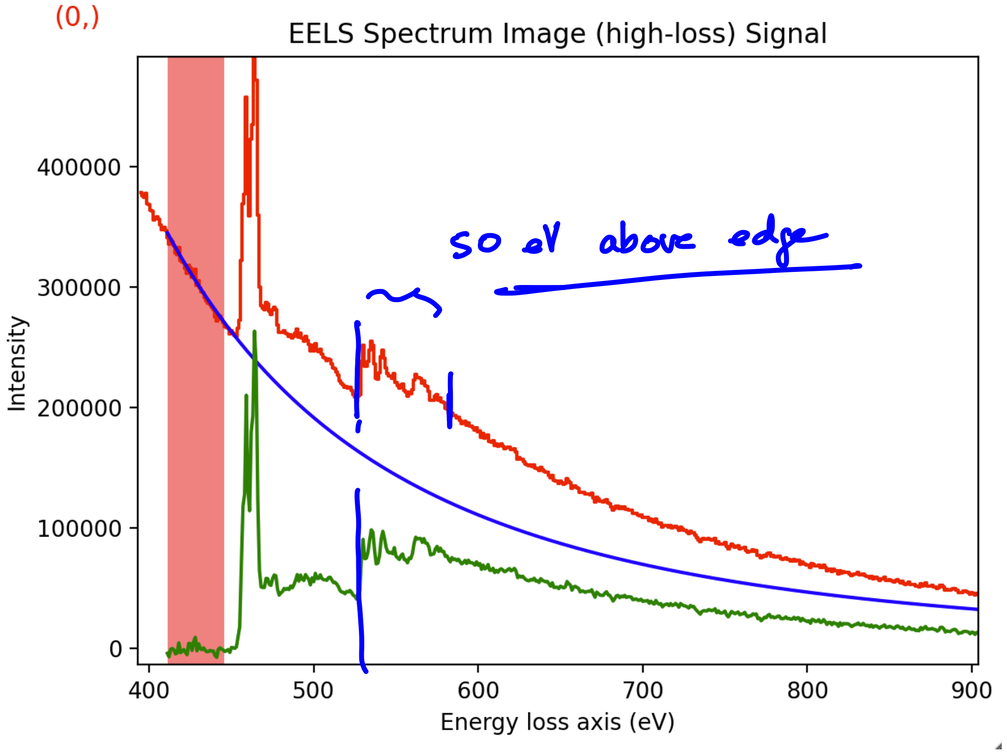


Fine structure analysis

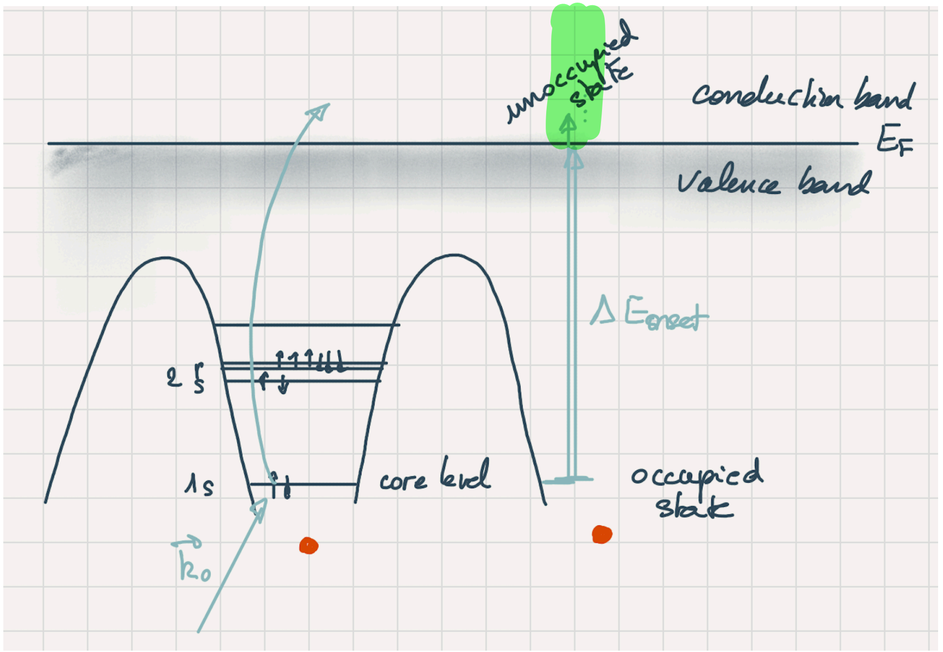
ELNES

EELS FINE STRUCTURES



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

Challenge: calculate the matrix element.

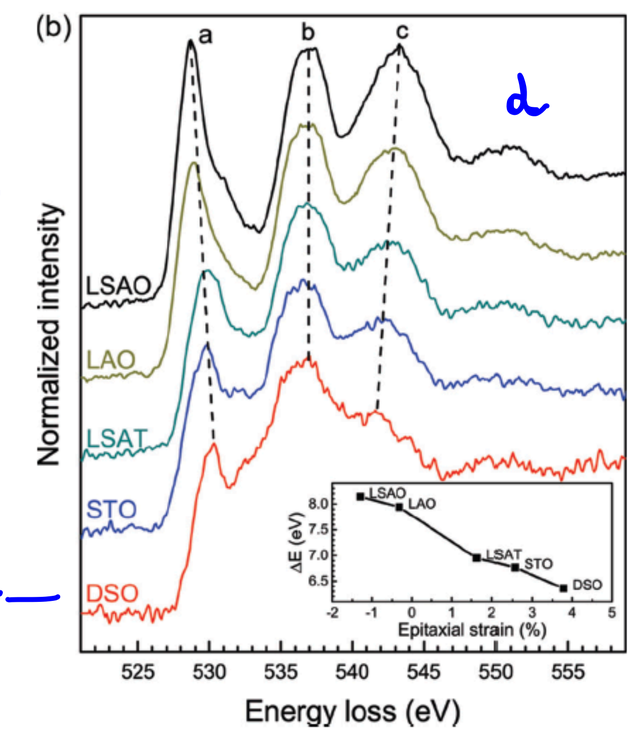


Fine structure analysis

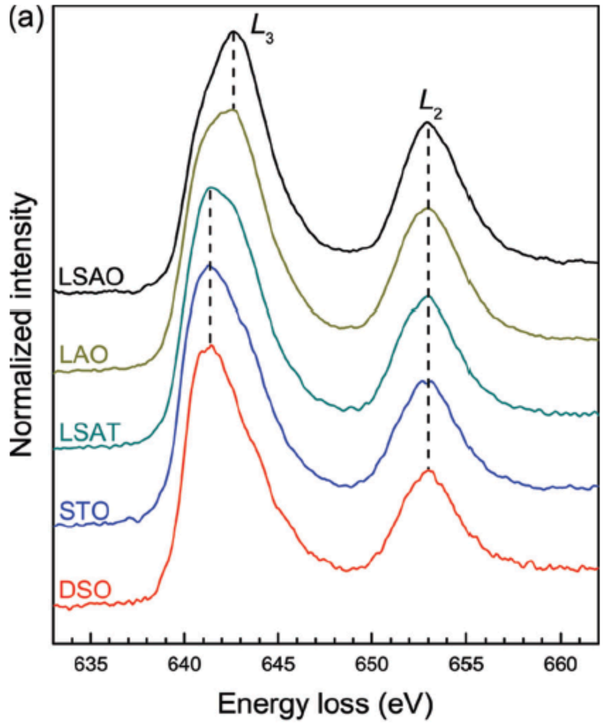
PHYSICAL REVIEW B **94**, 104101 (2016)

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

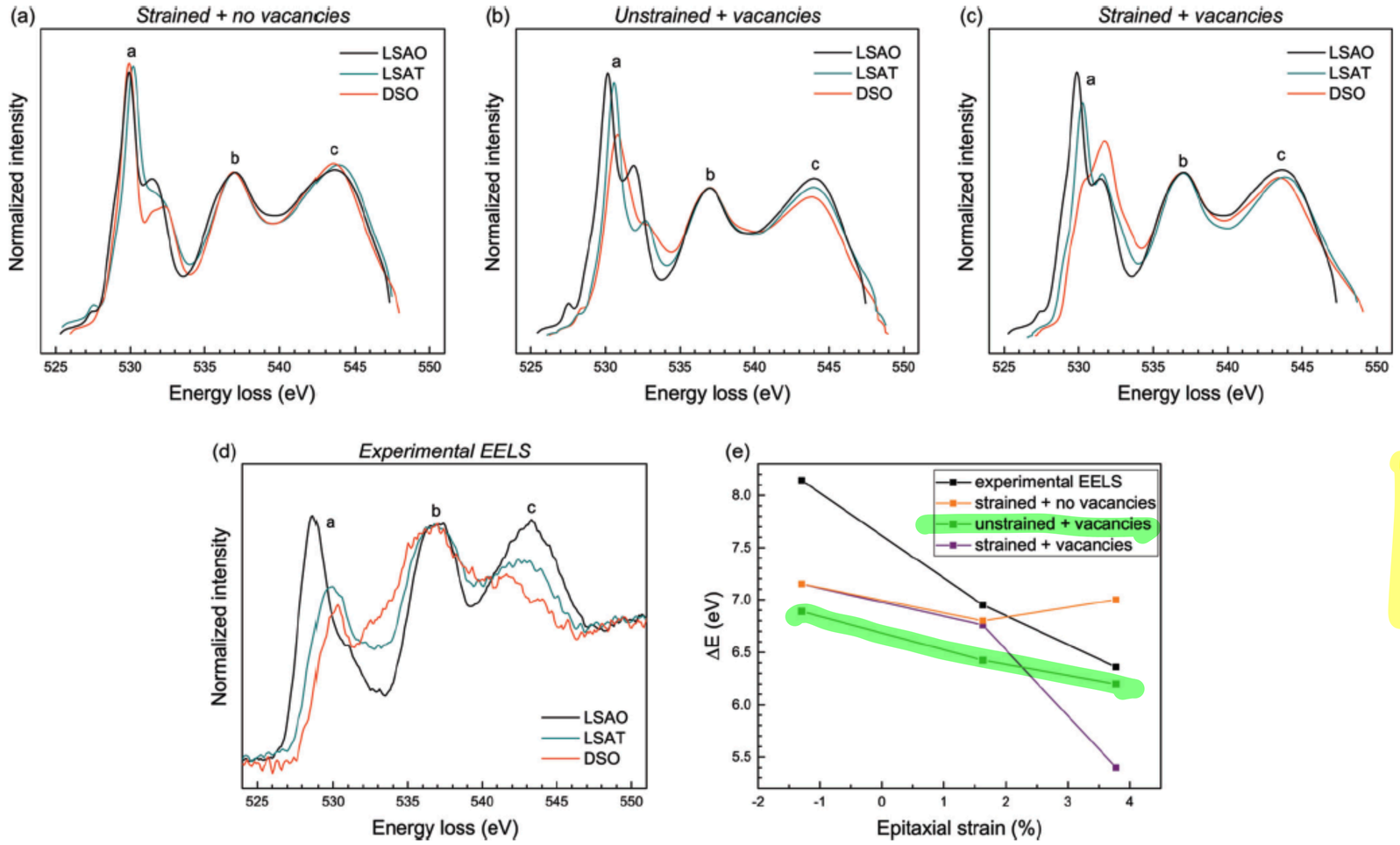


FIG. 5. O-K edge EEL spectra of SMO structures on LSAO, LSAT, and DSO. (a) The O-K edge spectra are calculated assuming strained lattice parameters and no oxygen vacancies. (b) The O-K edge spectra are calculated assuming unstrained lattice parameters and the presence of oxygen vacancies. (c) The O-K 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.

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

DFT

Fine structure calculation using DFT theory (FPLAPW code Wien2k)

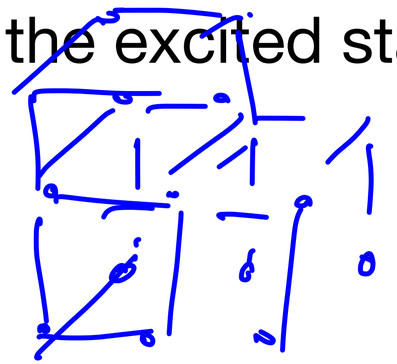
Core hole approximation

“supercell”

Trends more important than absolute values

Fine structure calculations: challenges

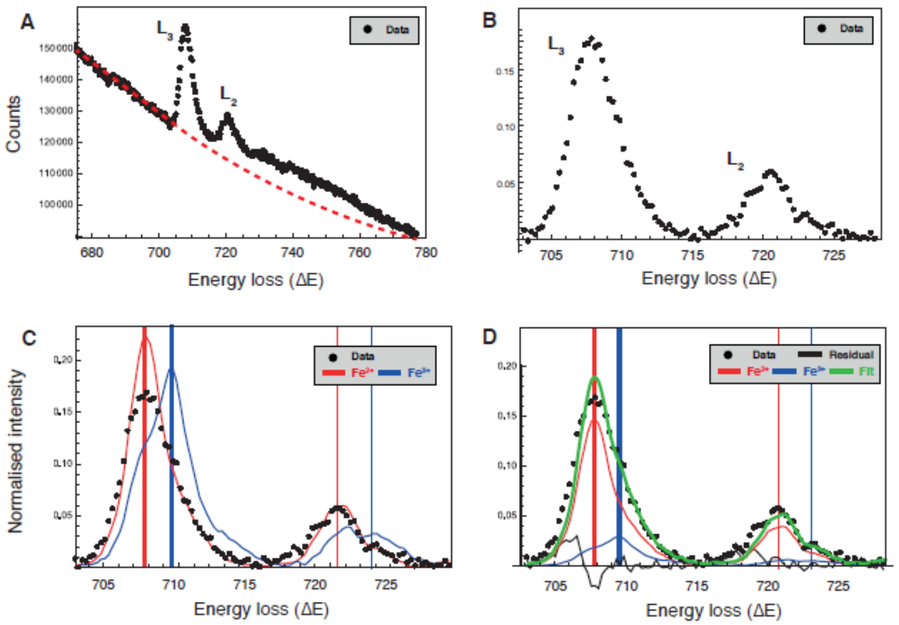
- One electron scheme. No correlation. OK for “reasonable” systems
- real space (multiple scattering methods) vs reciprocal space
  - ↳ FEFF
  - DFT
- Workaround for the excited state: core hole → "super cell"



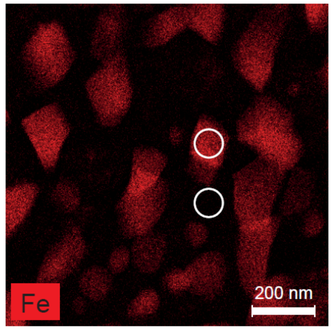
- Time dependent DFT, etc

“workaround”: fingerprints

Example: determination of the oxidation state of transition metals

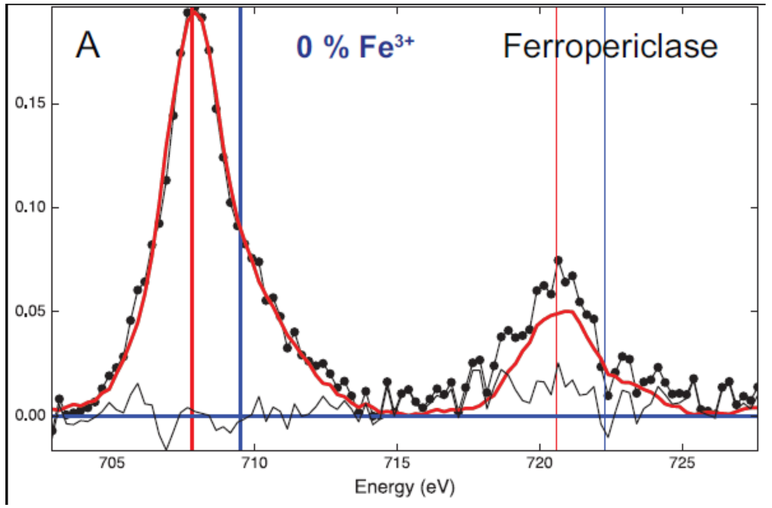


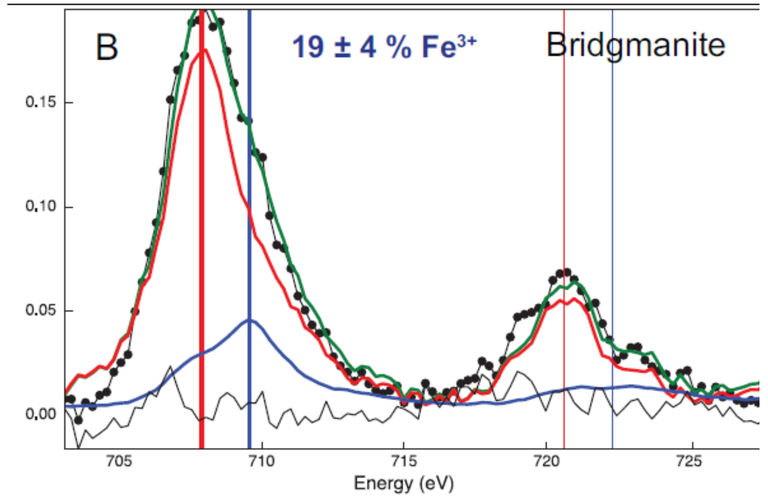
Fe L_{23}



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

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





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

Piet & al.

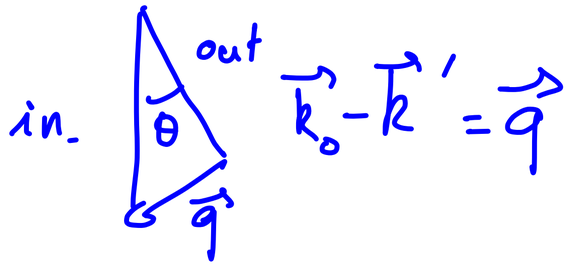
www.pnas.org/cgi/doi/10.1073/pnas.1605290113

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+}.

MLS fit
→ need standards.

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

Dipole approximation



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

$e^{\varepsilon} = 1 + \varepsilon$

$|\langle I|F\rangle|^{\varepsilon=0}$

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

Dipole selection rule. Usually OK.

$1s \rightarrow 2p$

$2s \rightarrow 3p$ L_1

$2p \rightarrow 3d$ L_{23}

$\rightarrow 3s$

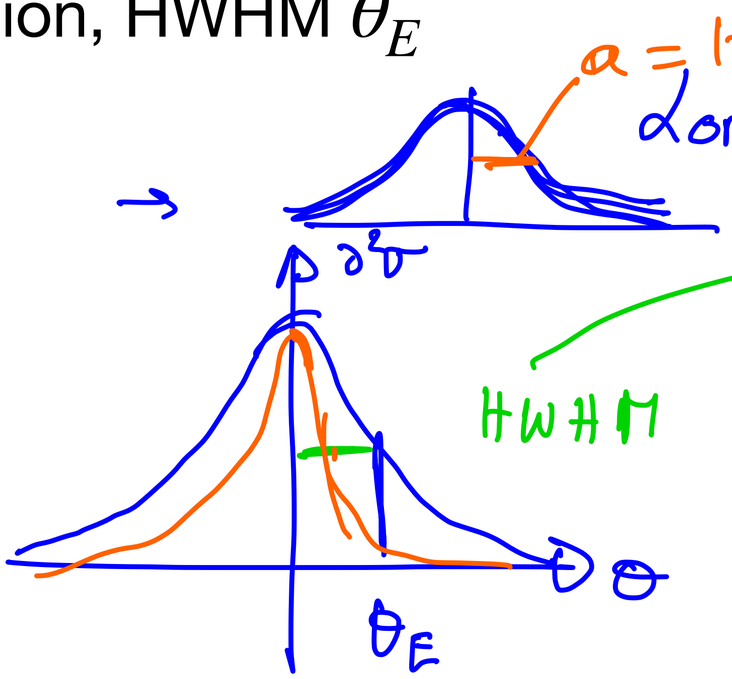
Dipole approximation: angular distribution

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

$\propto q^2 = k^2(\theta^2+\theta_E^2)$

Lorenzian distribution, HWHM θ_E

$f(x) = \frac{1}{a^2+x^2}$ →



$\theta_E \simeq \frac{\Delta E}{2E_0}$

$\frac{\partial^2\sigma}{\partial\Omega\partial E}(\theta)$

$\theta_E = cte$

BN N_K 400eV

B_K 200eV

200kV

$\theta_{E,N} = \frac{400}{2\times 200\cdot 10^3} = 1\,mrad$

$\theta_{E,B} = \frac{200}{2\times 200\cdot 10^3} = 0{,}5\,mrad$

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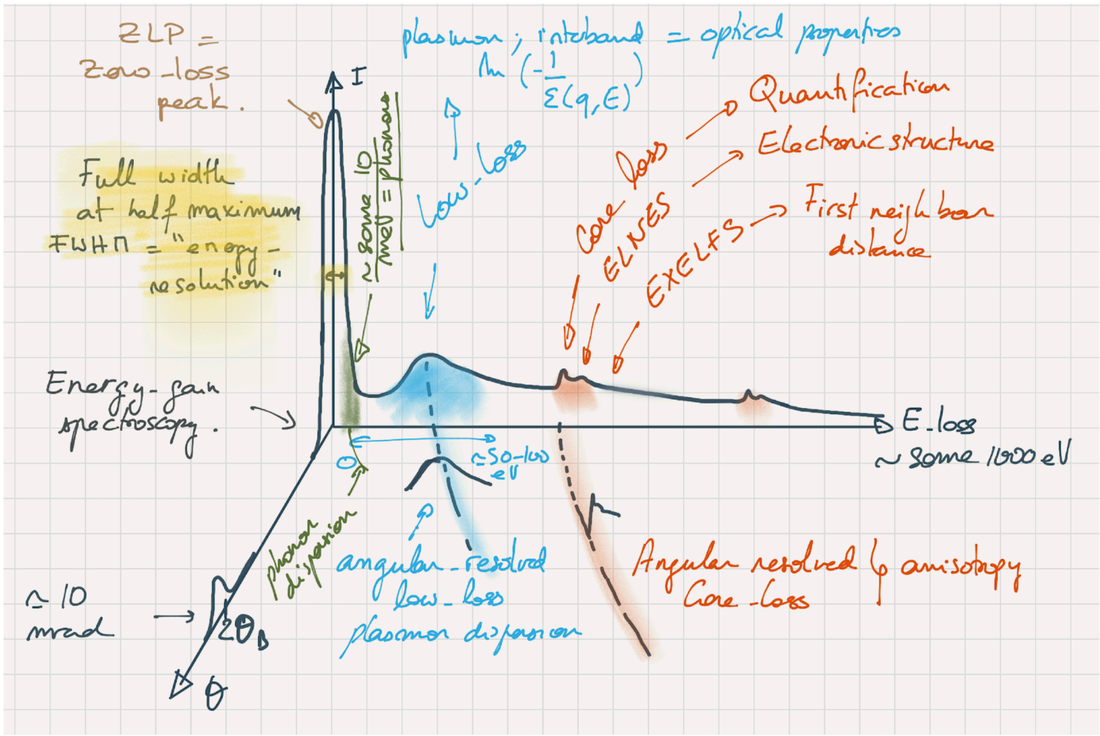
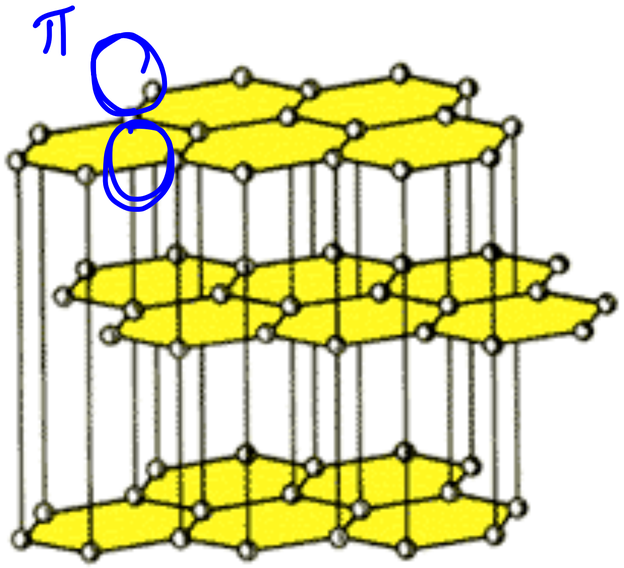


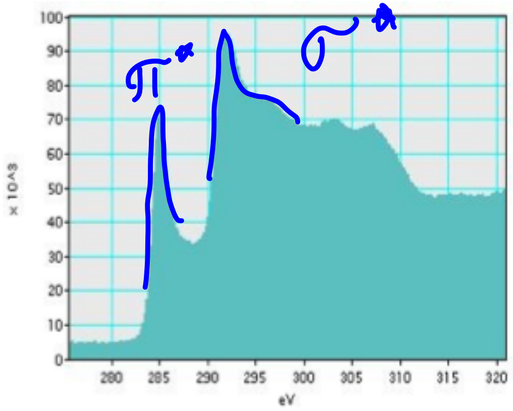
Linear dichroism

If the final state is anisotropic

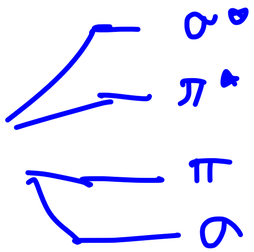
orientation

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





Carbon K-edge in HOPG

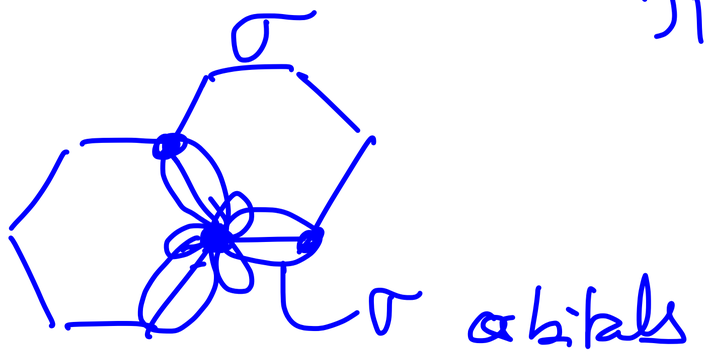


Example: HOPG or h-BN

sp^2 hybridization

2s ; 2px, 2py, 2pz

π



σ orbitals

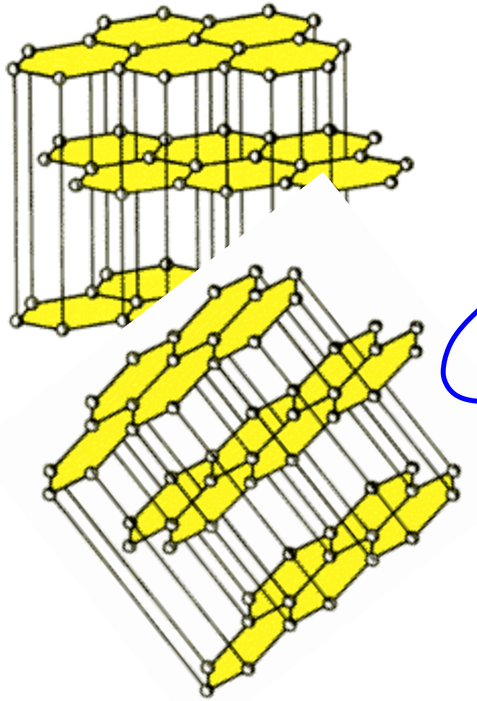
Linear dichroism

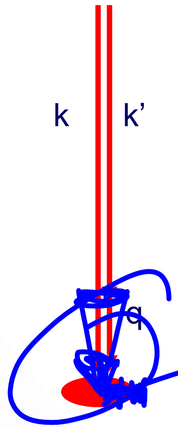
If the final state is anisotropic

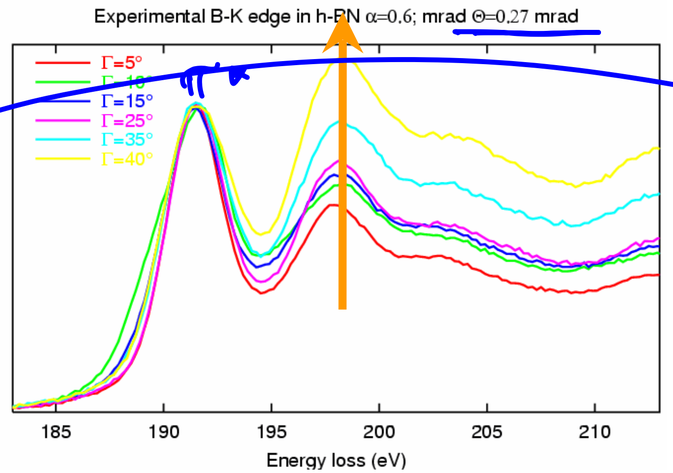
h-BN B-K edge

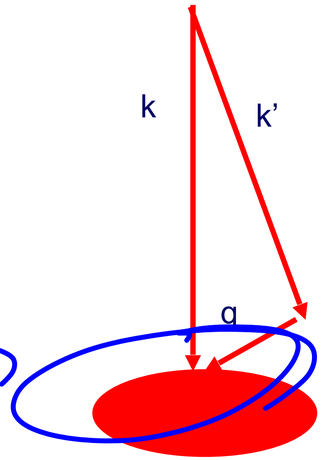
200kV θ_E = 0,5 mrad for B-K$_\alpha$

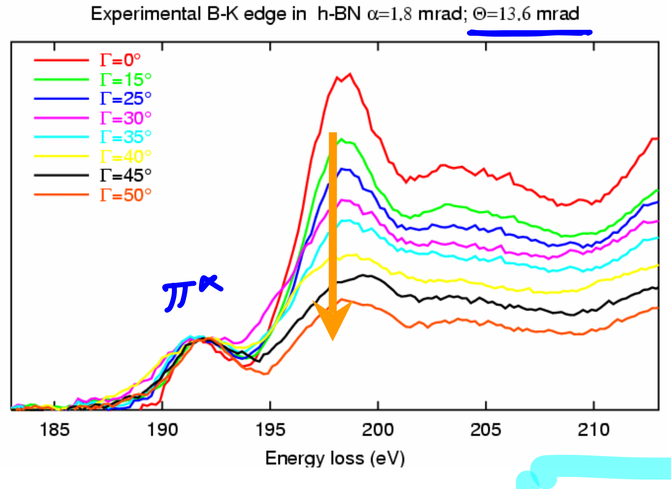
0,85 mrad







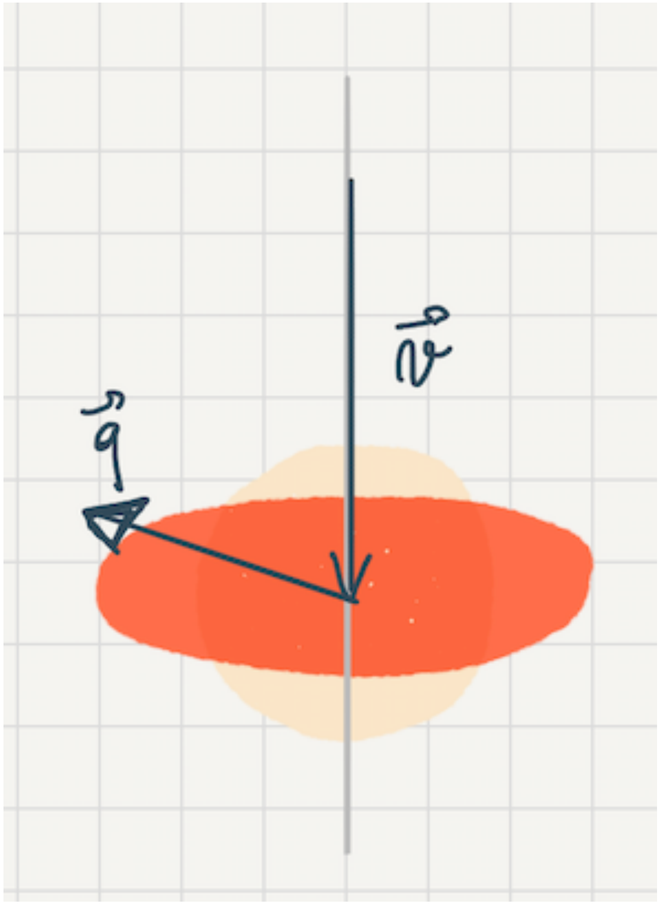




I> in between 0,27 & 13 mrad.

∃ one value of β such that No orientation effect] Magic Angle

Anisotropy: Relativity fires back



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

Coulomb coupling becomes anisotropic

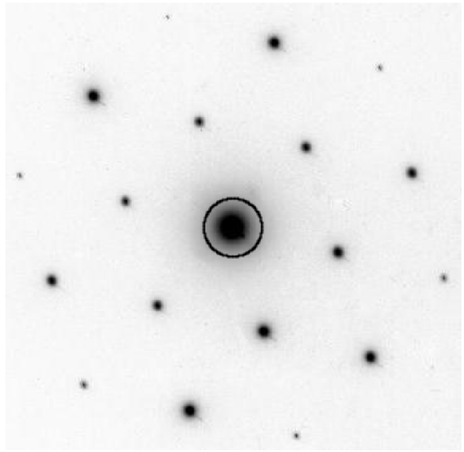
Coupling with momentum transfer parallel to the electron's trajectory becomes smaller

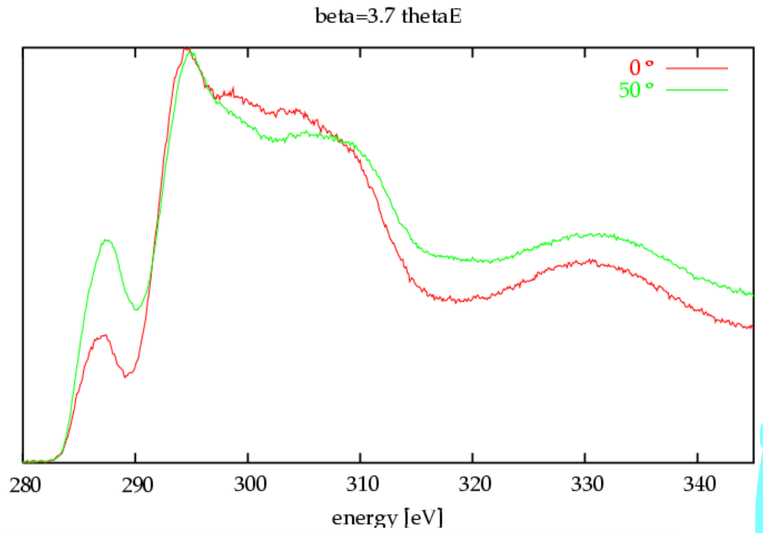
Coupling with momentum transfers perpendicular to the electron's trajectory becomes larger

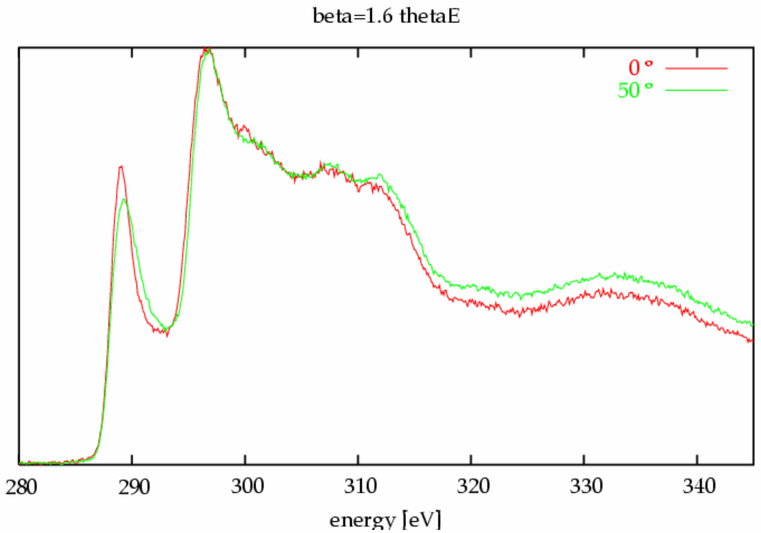
@ 20keV $v \simeq 97c$

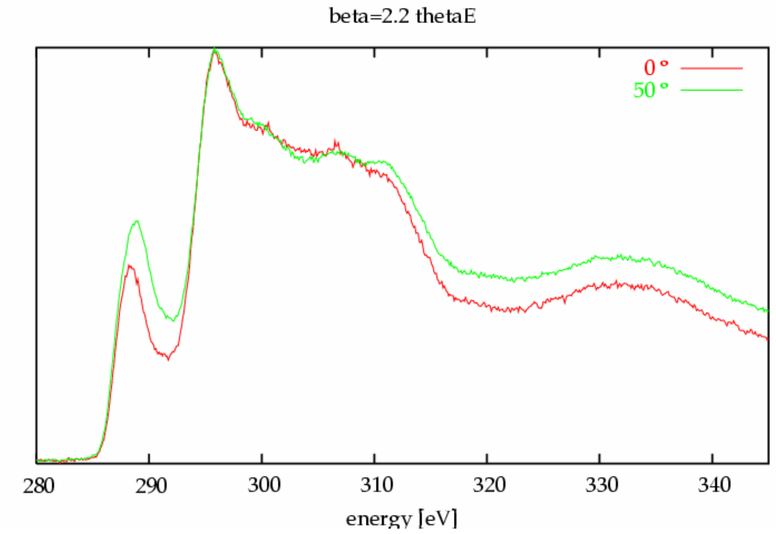
HOPG

Anisotropy: Relativity fires back









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

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

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