UiO : Department of Physics
University of Oslo

Core losses: Quantification and electronic structure

FYS5310/FYS9320
Lecture 6
23.02.2016

FYS5310 teaching schedule

Preliminary schedule only! You should keep the class-times on Wednesdays and Thursdays open unless notified by email (or in this schedule) that there is no class
References to the textbook to Fultz & Howe unless stated otherwise.

Date		Time	Lecture/lab	Topic	Chapters	Homework
Wednesday	18.01.2017	14:15-16:00	Lecture	Introduction to the course. Derivation of the structure factor (01)	4.1, 4.3.1, 6.1	Exercise set 1 (handout)
Thursday	19.01.2017	12:15-14:00	Lecture	No class (SMN seminar)		
Wednesday	25.01.2017	13:15-16:00	Lab/Colloquium	Going through exercise set 1 + Lecture: The atomic form factor (02)	4.3	Excercise set 2 (handout)
Thursday	26.01.2017	12:15-14:00	Lecture	No class		
Wednesday	01.02.2017	14:15-16:00	Lab/colloquium	Going though exercise set 2		
Thursday	02.02.2017	12:15-14:00	Lecture	Uses of EELS and EELS instrumentation (03)	5.1, 5.2; W&C 37	Exercise set 3 (handout)
Wednesday	08.02.2017	14:15-16:00	Lab/colloquium	Going though exercise set 3		
Thursday	09.02.2017	12:15-14:00	Lecture	Inelastic form factors (04)	5.4.1-5.4.3 + primer on Dirac notation	
Wednesday	15.02.2017	12:15-16:00	Lab/colloquium	No class		
Thursday	16.02.2017	12:15-14:00	Lecture	Inelastic form factors, scattering cross sections, dipole selection rules (05)	5.4.4-5.4.7, W&C 39, plus Brehm and Mullin on parity and dipole selectrion rules	
Wednesday	22.02.2017	12:15-16:00	Lab/colloquium	No class		
Thursday	23.02.2017	12:15-14:00	Lecture	Core losses: Quantification and electronic structure (06)	5.4, W&C 39+40	Exercise set 4 (handout)
Wednesday	01.03.2017	12:15-16:00	Lab/colloquium	Going through excercise set 4		
Thursday	02.03.2017	12:15-14:00	Lecture	Low energy loss; electronic structure and dielectric properties pt 1 (07)		
Wednesday	08.03.2017	12:15-16:00	Lab/colloquium	Computer lab		
Thursday	09.03.2017	12:15-14:00	Lecture	Low energy loss; electronic structure and dielectric properties pt 2 (08)	5.3, W&C 38	
Wednesday	15.03.2017	12:15-16:00	Lab/colloquium	No class		
Thursday	16.03.2017	12:15-14:00	Lecture	No class		
Wednesday	22.03.2017	12:15-16:00	Lab/colloquium	Computer lab		

Elemental quantification

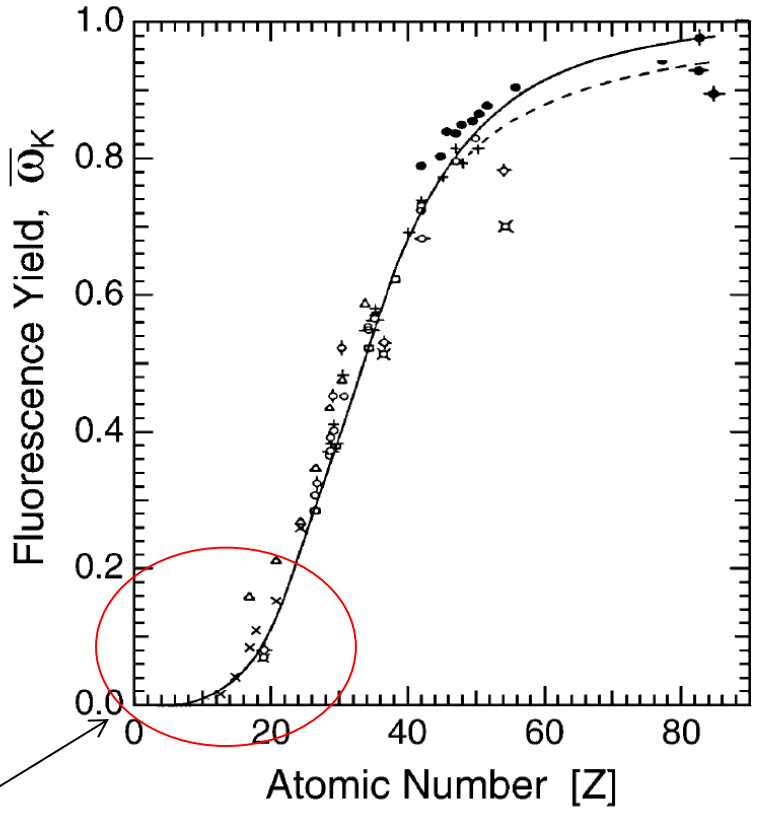
- The core loss EELS edges can be used to quantify the composition of your specimen
- In particular useful for low-Z elements

The fluorescence yield in EDS analysis

The probability for generating a characteristic X-ray is given by the fluorescence yield ω

$$\omega = \frac{Z^4}{a + Z^4}$$

The probability of generating an Auger electron is the 1- ω.



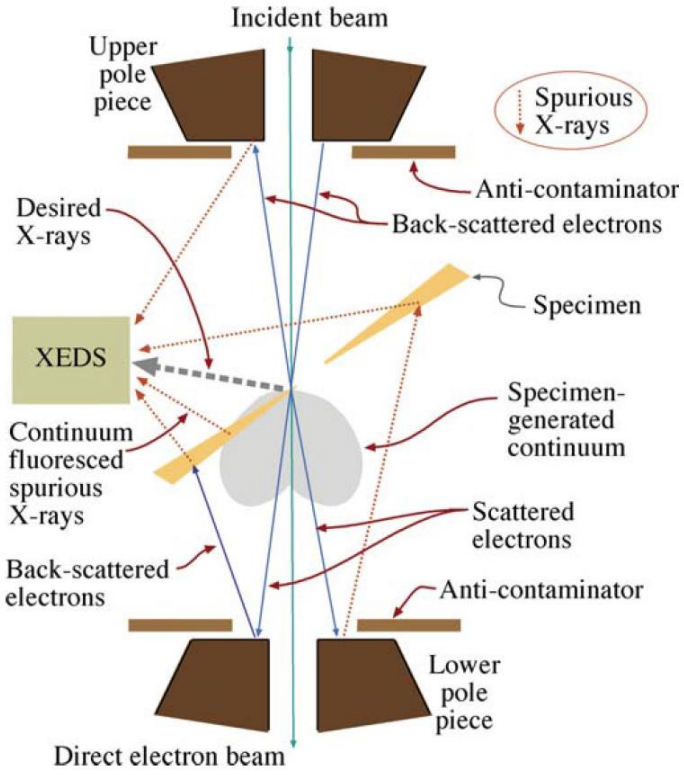
Very few X-ray generated

Elemental quantification

- The core loss EELS edges can be used to quantify the composition of your specimen
- In particular useful for low-Z elements
- You also avoid some of the experimental errors of EDS

Spurious and system X-rays in EDS analysis

- Spurious X-rays from the specimen, but not the region of interest
- System X-rays from the sample holder, specimen support grid, microscope itself (Cu, Fe)



Elemental quantification

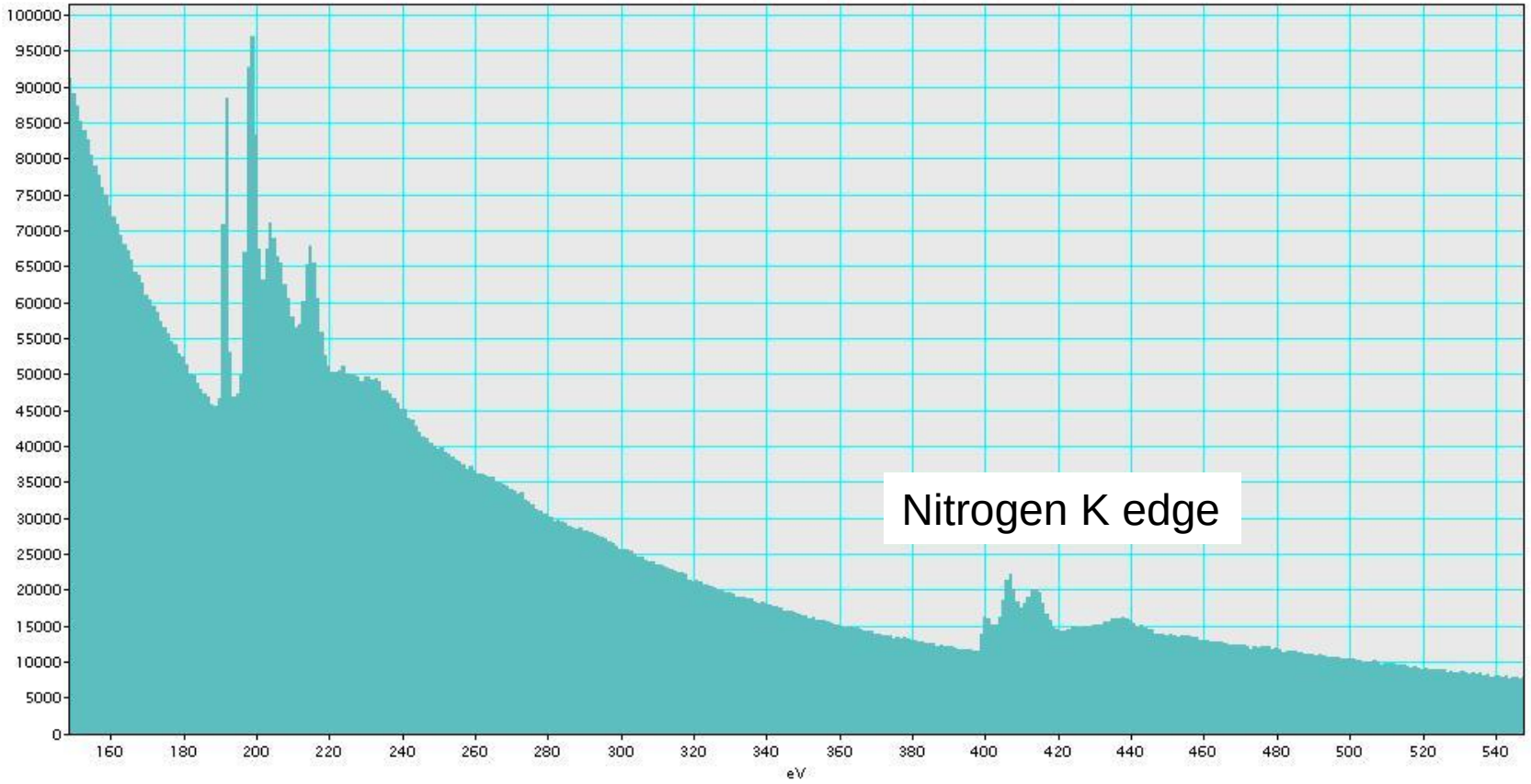
- The core loss EELS edges can be used to quantify the composition of your specimen
- In particular useful for low-Z elements
- You also avoid some of the experimental errors of EDS (spurious and system X-rays)
- In the first approximation, the observed intensity *I* of edge *i* of element A is:

$$I_A^i = I_0 N_A \sigma_A^i$$

- Relative composition is then

$$\frac{N_A}{N_B} = \frac{I_A^i}{I_B^j}\frac{\sigma_B^j}{\sigma_A^i}$$

Boron K edge


100000
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50000
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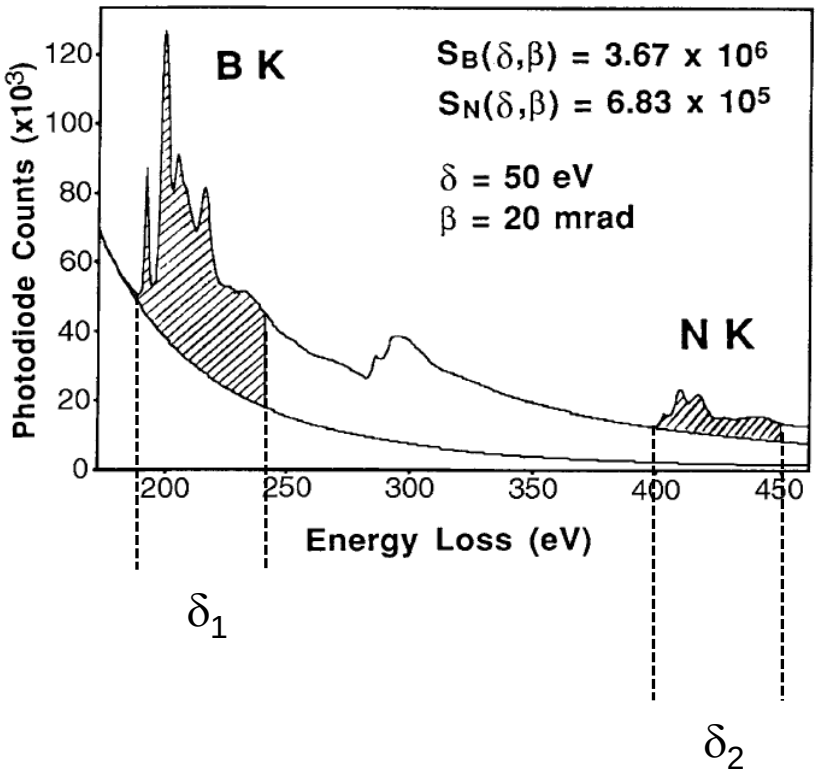
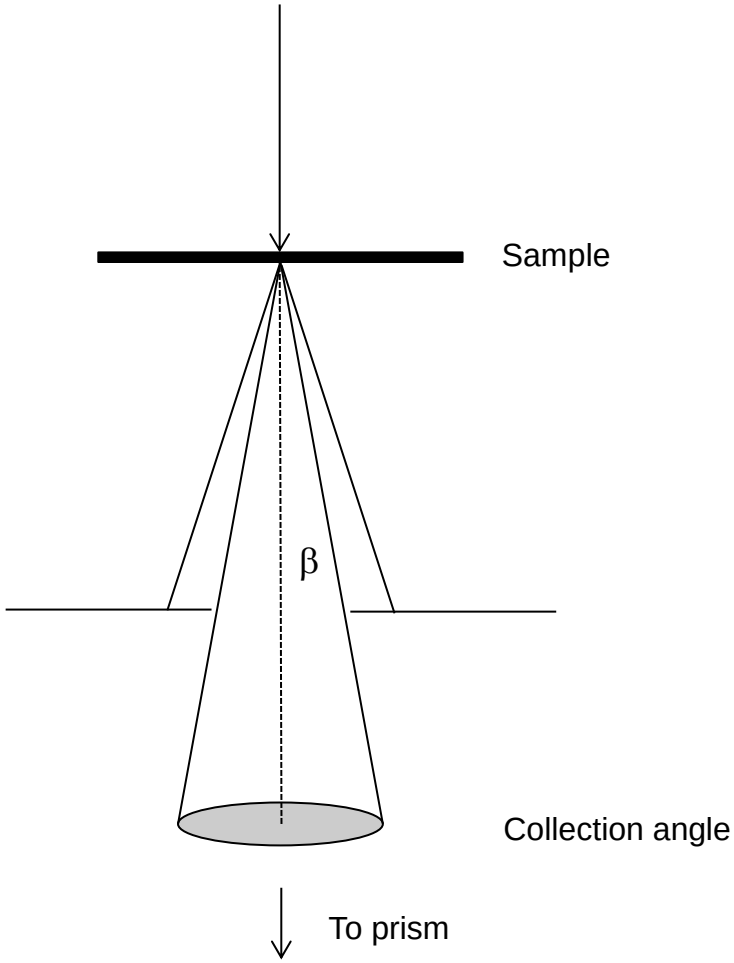
25000
20000
15000
10000
5000
0
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
520
540
eV
Nitrogen K edge

What scattering cross section do we use?



What scattering cross section do we use?

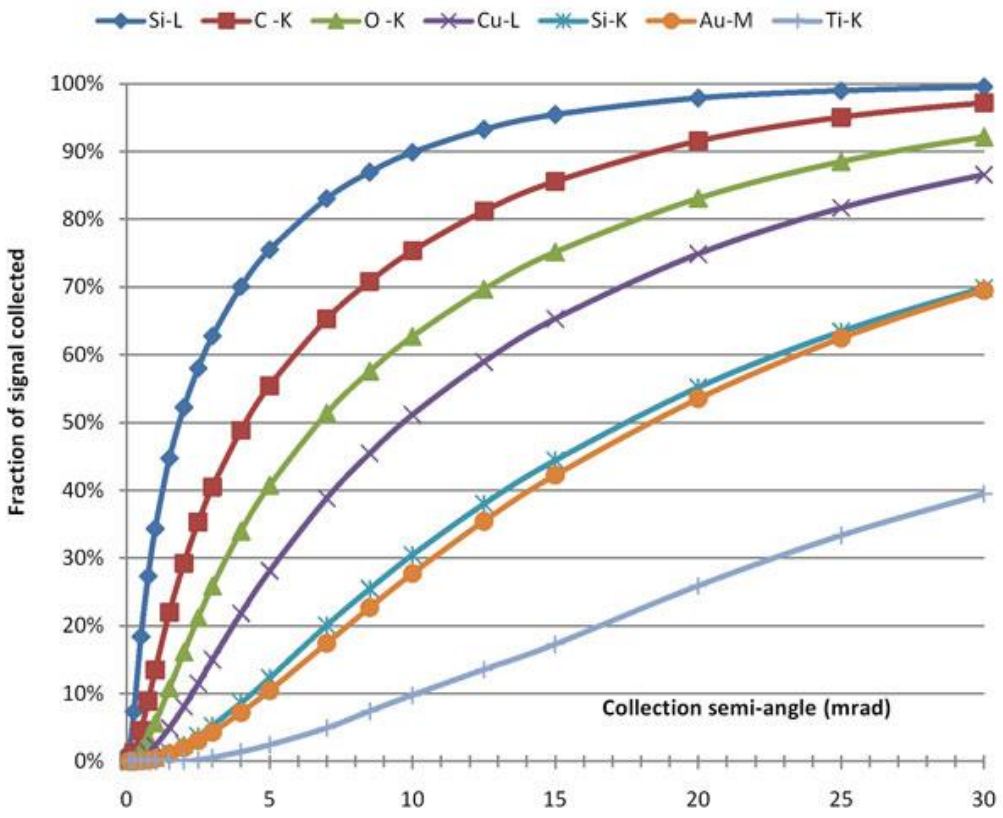


What scattering cross section do we use?

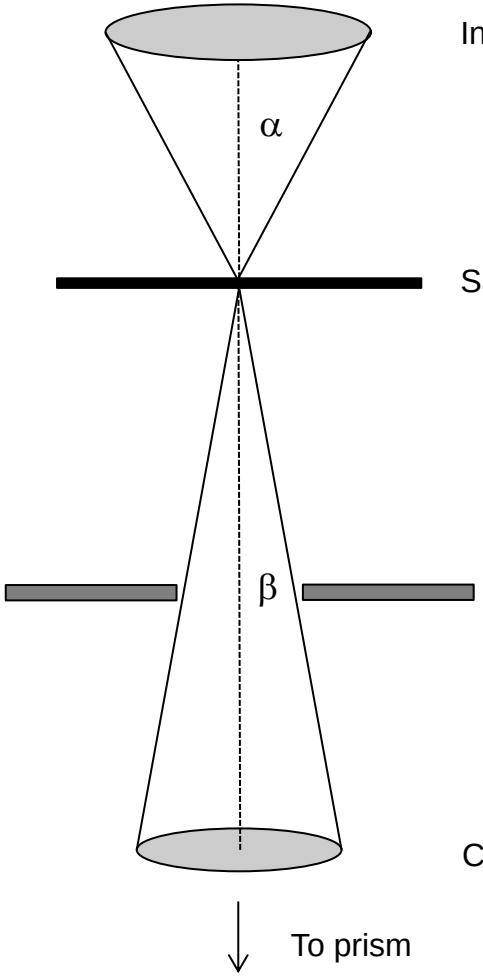
- In practice, our experiment looks only at inelastic scattering in an energy range [E,E+δ] and scattering angle [0,β]
- Partial cross section $\sigma(\delta,\beta)$ must be used

$$\sigma_A^i(\delta,\beta) = \int_0^{\beta} \int_{E_i}^{E_i+\delta} \frac{\mathrm{d}^2\sigma(\phi,E)}{\mathrm{d}\phi \mathrm{d}E} \mathrm{d}E \mathrm{d}\phi$$

$$\frac{N_A}{N_B} = \frac{I_A^i(\delta,\beta)\sigma_B^j(\delta,\beta)}{I_B^j(\delta,\beta)\sigma_A^i(\delta,\beta)}$$


Si-L
C -K
O -K
Cu-L
Si-K
Au-M
Ti-K
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Fraction of signal collected
0
5
10
15
20
25
30
Collection semi-angle (mrad)

Geometry of the experiment



Incident beam convergence angle

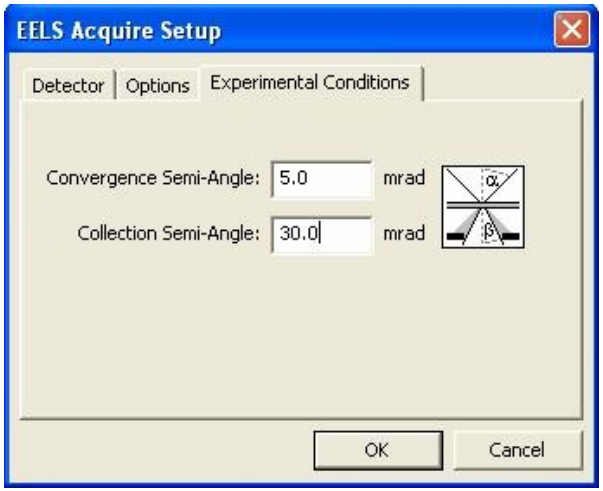
Sample

GIF entrance apperture or
Microscope objective apperture

Collection angle

To prism

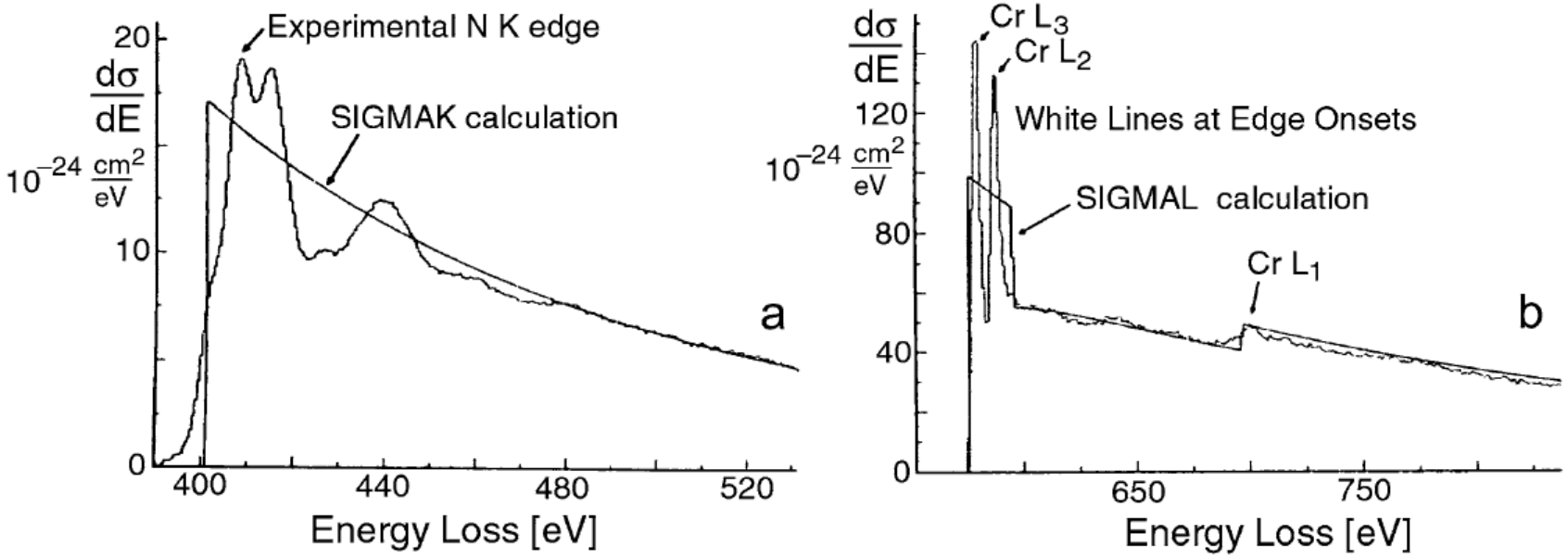
Microscope in	Collection angle determined by
imaging mode	size of microscope objective apperture
diffraction mode	size of spectrometer entrance apperture



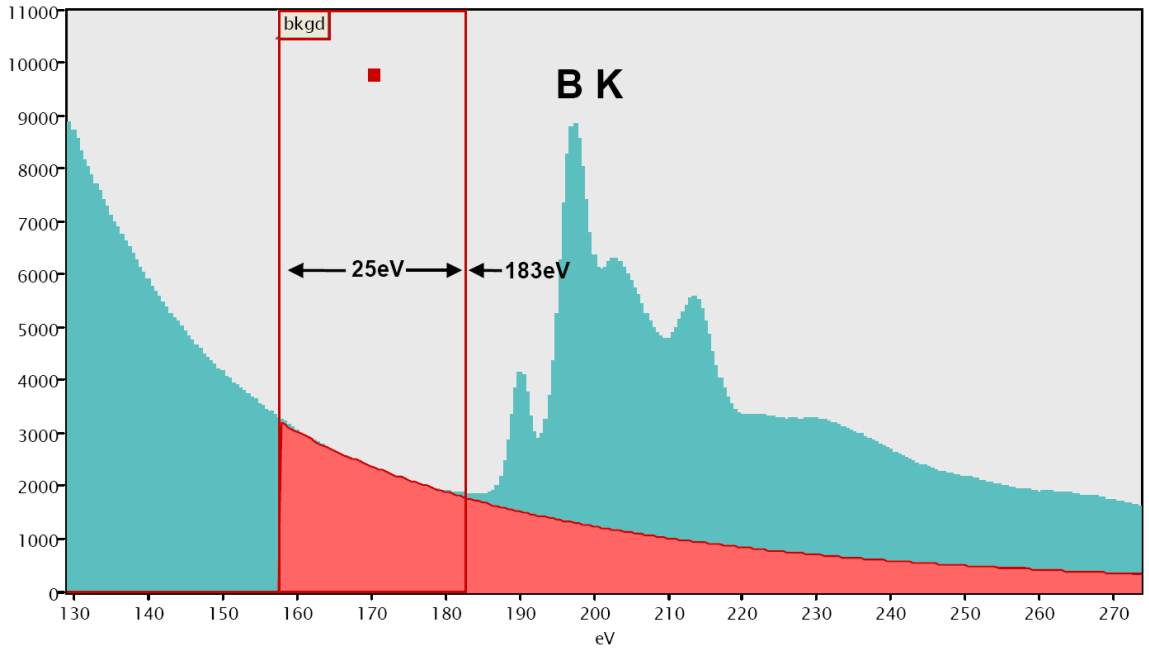
$$\beta^* \approx \beta(\alpha/\beta)^2$$

How to determine partial cross sections

- Calculations
  - Hydrogenic model
  - Hartree-Slater model
- Experimentally



Background removal



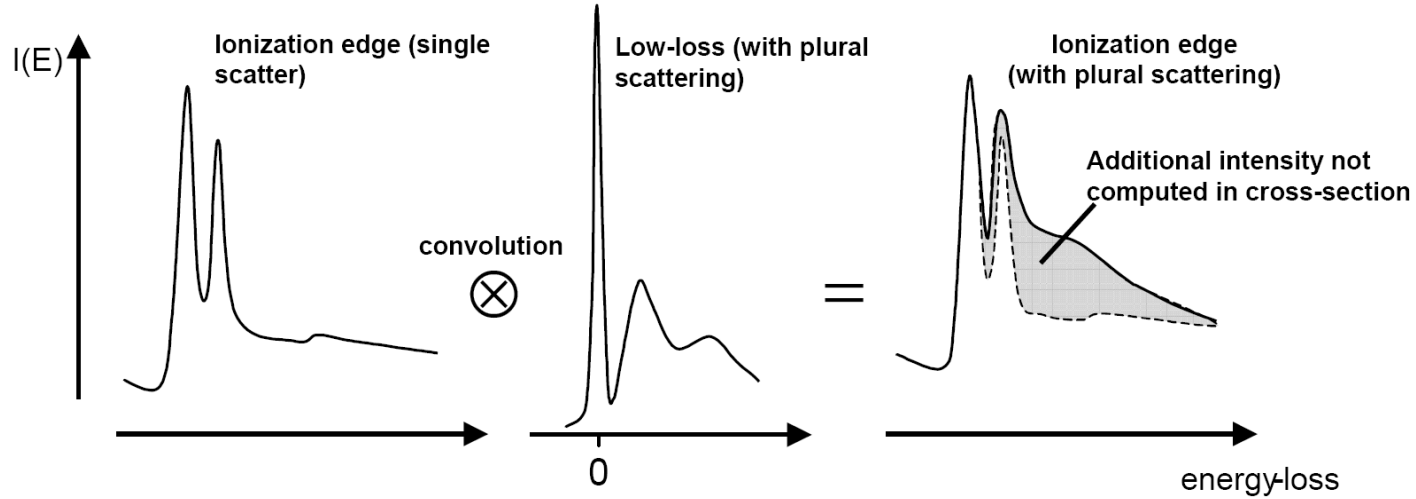
Power law model:

$$J(E) = AE^{-r}$$

where A = scaling constant

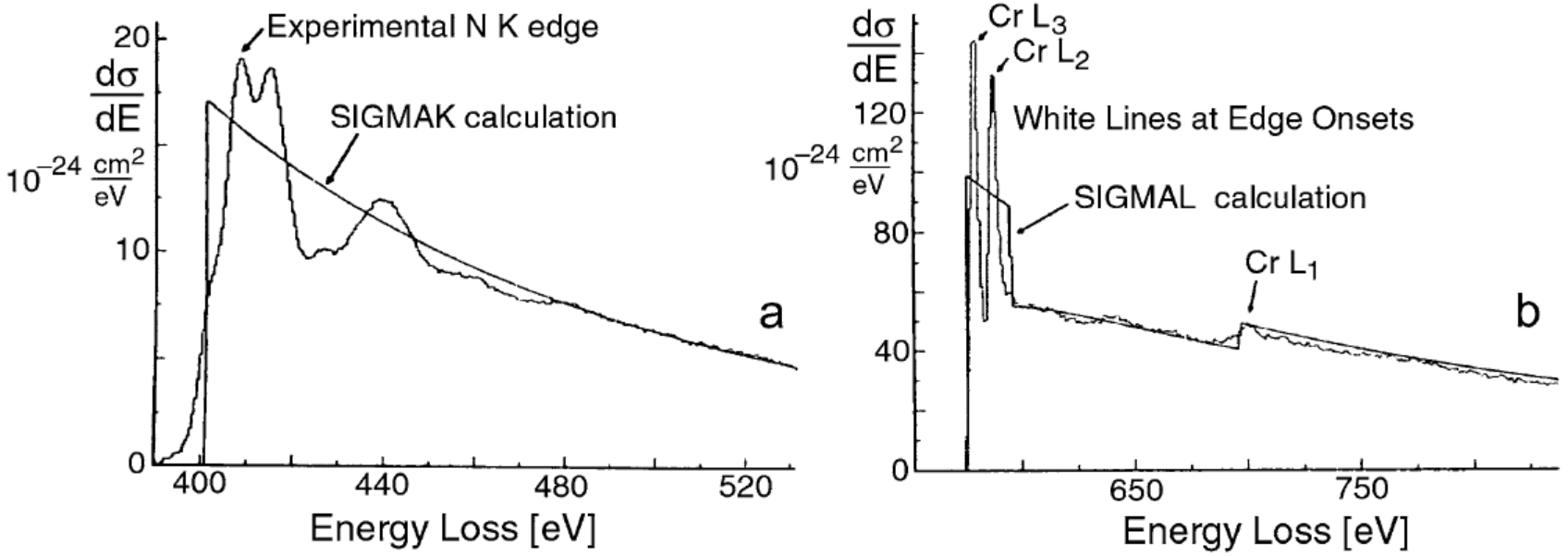
r = slope exponent (usually 2-5)

Plural scattering



- Remove using Fourier-ratio or Fourier-log methods

Free atom cross sections compared to spectra from materials



$$\frac{\mathrm{d}^2\sigma(\phi,E)}{\mathrm{d}\phi\mathrm{d}E} = \frac{2\pi\hbar^4}{a_0^2 m_2^2 E_{\alpha\beta} T} \overbrace{\frac{\phi}{\phi^2+\phi_E^2}}^{\text{exp. scatt. angles}} \underbrace{\rho(E)}_{\text{sol. state eff.}} \overbrace{G_{\alpha\beta}(\Delta k,E)}^{\text{atomic osci. str.}}$$

$$G_{\alpha\beta}(\Delta k,E) = E_{\alpha\beta}\frac{2m_e}{\hbar^2\Delta k^2}\left|\int_{-\infty}^{\infty}\Psi_\beta^*(\mathbf{r})e^{-i\mathbf{\Delta k}\cdot\mathbf{r}_2}\Psi_\alpha(\mathbf{r}_2)\mathrm{d}^3\mathbf{r}\right|^2$$

Under usual assumtions, the core loss EELS spectrum probes the

- local density of states around the excited atom…
- with symmetry *l±1…*
- above the Fermi-level

The site and symmetry selected DOS

$$\frac{\mathrm{d}^2\sigma(\mathbf{\Delta k}, E)}{\mathrm{d}\Omega \mathrm{d}E} = \frac{4}{a_0^2 \Delta k^4} \rho(E) \left| \langle \beta | e^{-i\mathbf{\Delta k}\cdot\mathbf{r}} | \alpha \rangle \right|^2$$

Titanium Formula: Ti Core Loss

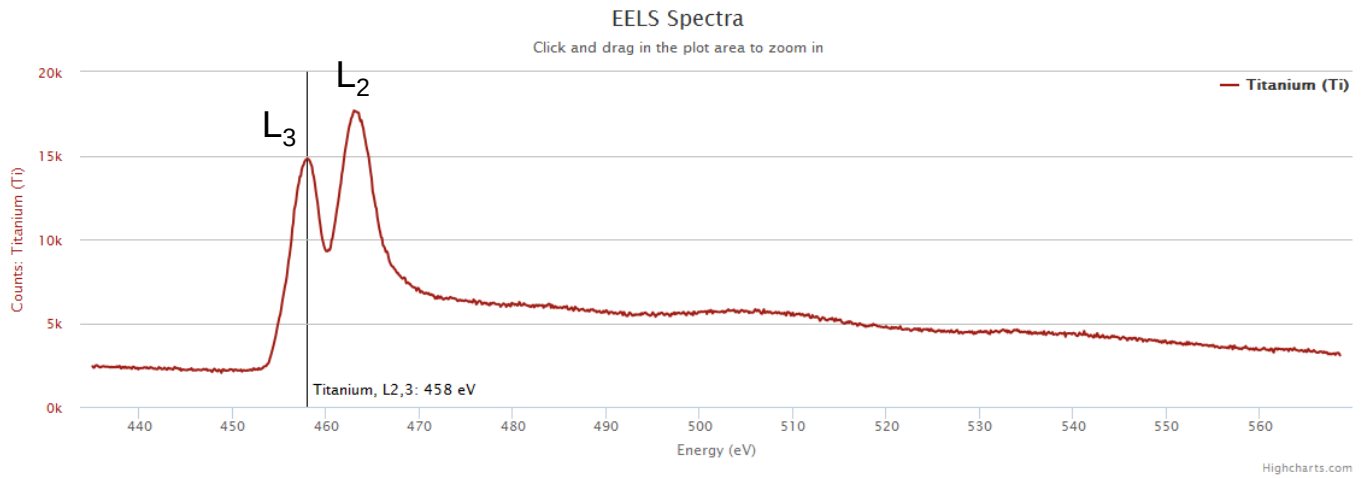
View in Materials Explorer | Remove from Favourites | Download

Submitted by Wilfried Sigle, January 21, 2008.

Source / Purity: Ti substrate

Author Comments: Analyst: Zaoli Zhang. Temperature: Room.

Select overlay plot: Titanium Dioxide: TiO2 (anatase) Show



Titanium Dioxide Formula: TiO_2 (anatase) Core Loss

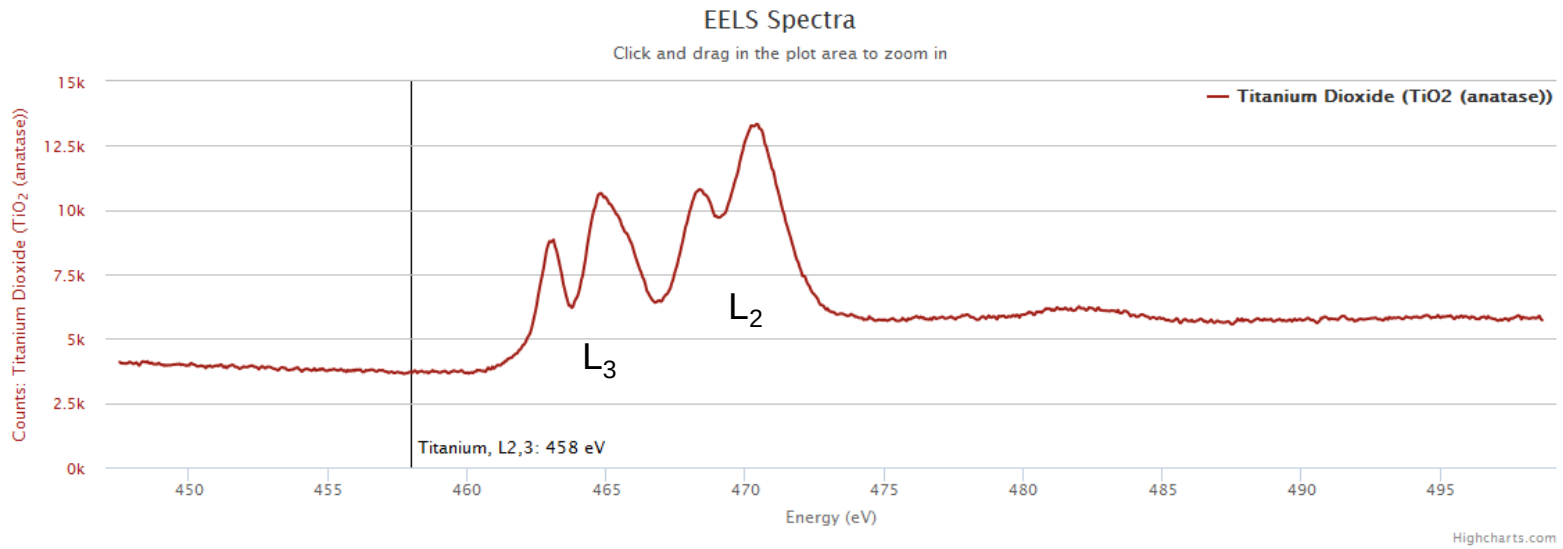
Remove from Favourites | Download

Submitted by Giovanni Bertoni, November 12, 2007.

Source / Purity: Aldrich powder

Author Comments: Polycrystalline sample Analyst: Giovanni Bertoni. Temperature: Room.

Select overlay plot: Titanium Dioxide: TiO2 (anatase) Show



Titanium Formula: Ti Core Loss

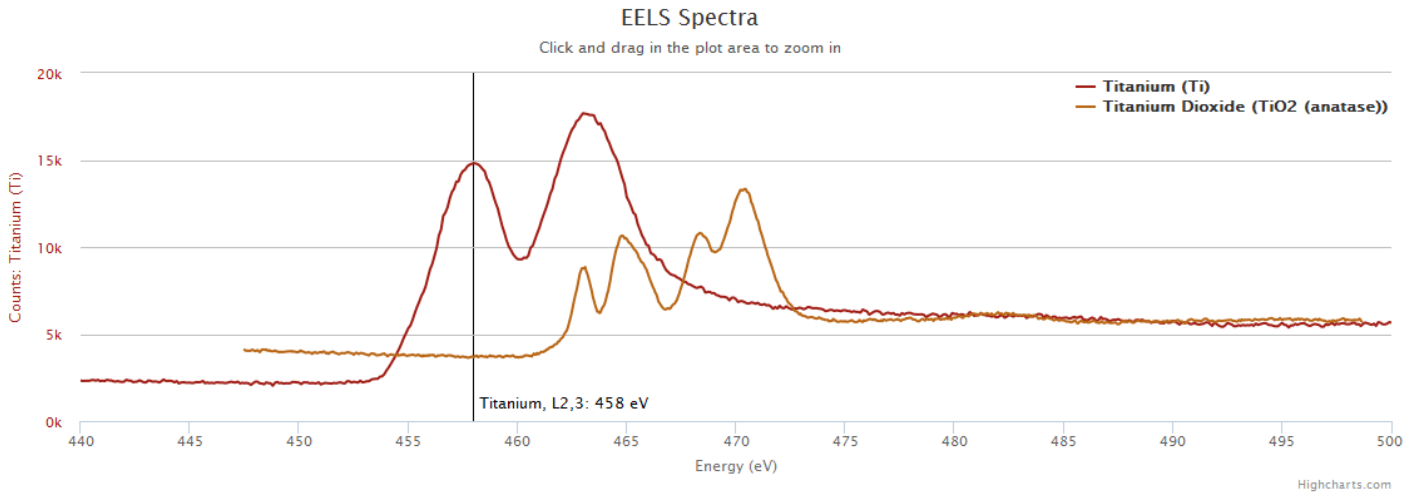
View in Materials Explorer | Remove from Favourites | Download

Submitted by Wilfried Sigle, January 21, 2008.

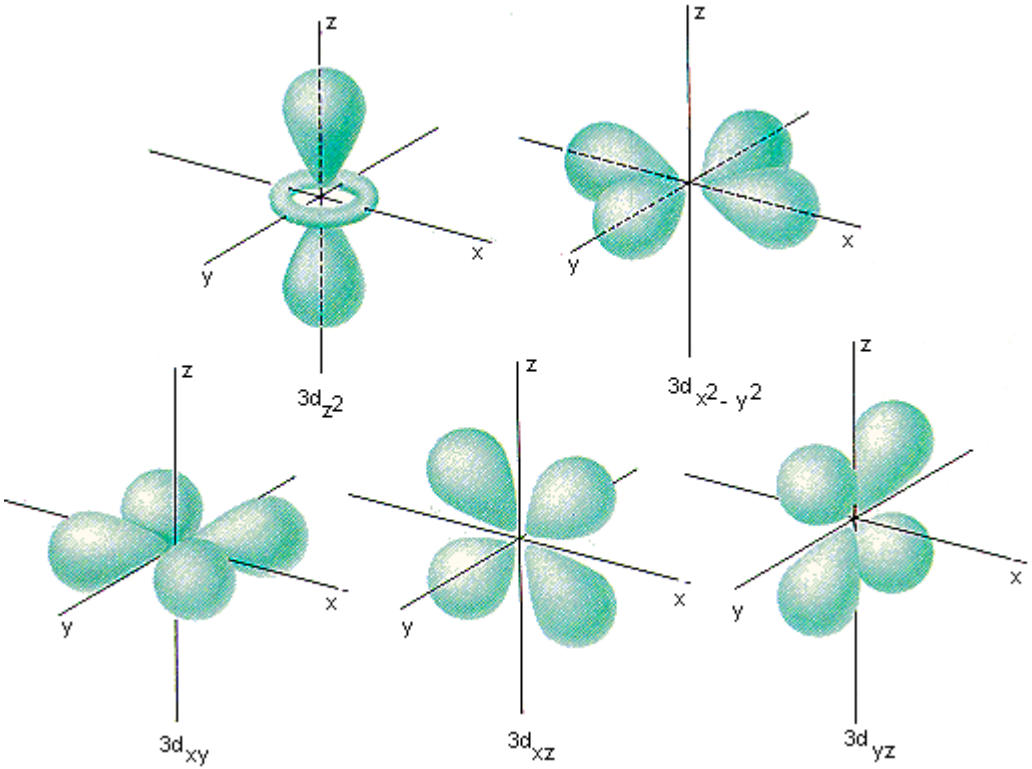
Source / Purity: Ti substrate

Author Comments: Analyst: Zaoli Zhang. Temperature: Room.

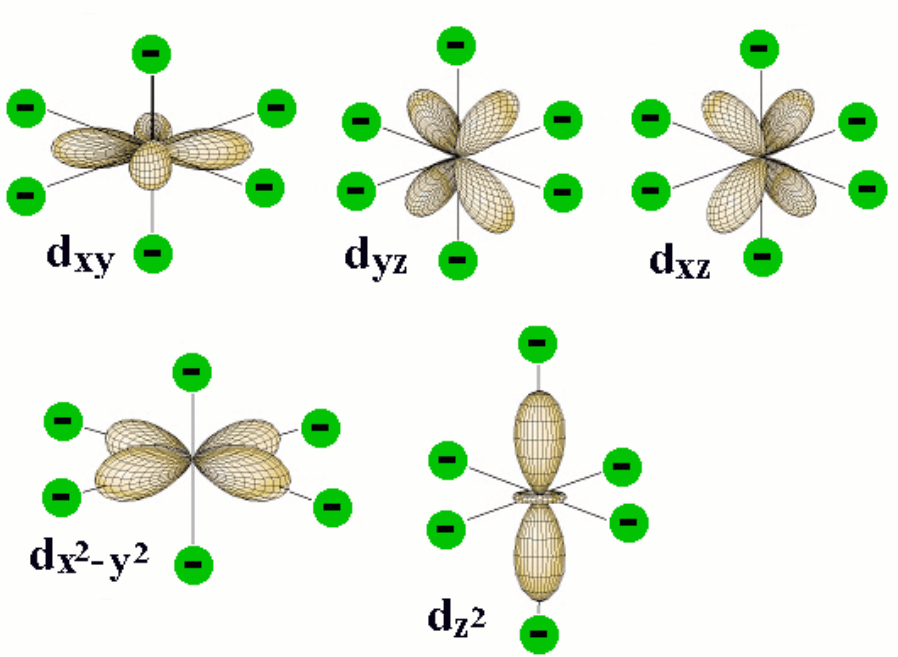
Independent Axes | Remove overlay plot

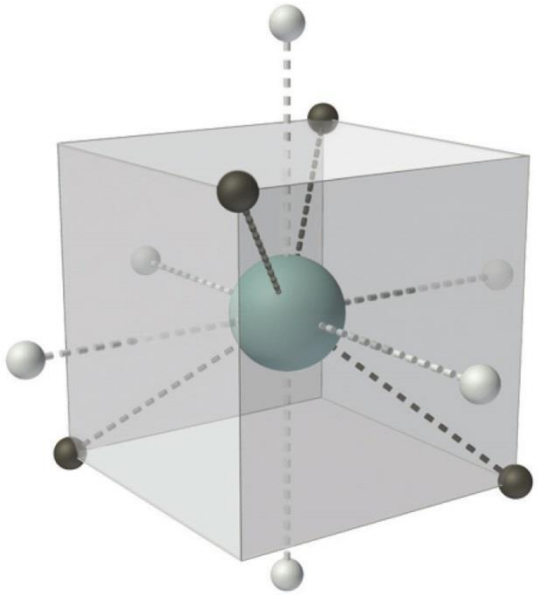


The 3d orbitals

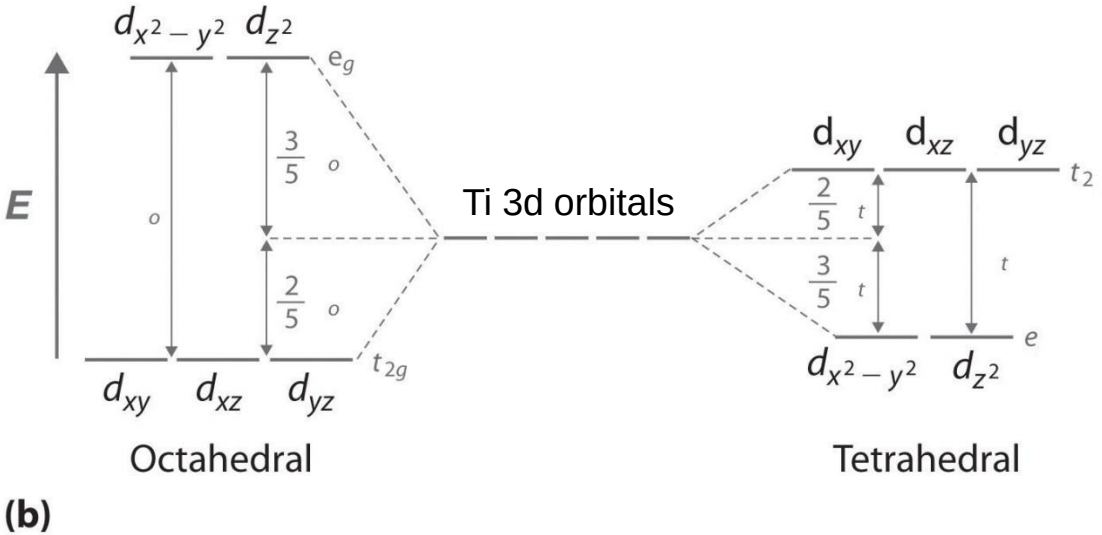


Let’s imagine octahedral coordination





(a)


E
$d_{x^2-y^2}$
d_{z^2}
e_g
o
$\frac{3}{5}$ o
$\frac{2}{5}$ o
t_{2g}
d_{xy} d_{xz} d_{yz}
Octahedral
Ti 3d orbitals
d_{xy} d_{xz} d_{yz}
t_2
$\frac{2}{5}$ t
$\frac{3}{5}$ t
t
e
$d_{x^2-y^2}$ d_{z^2}
Tetrahedral

(b)

Titanium Dioxide Formula: TiO_2 (anatase) Core Loss

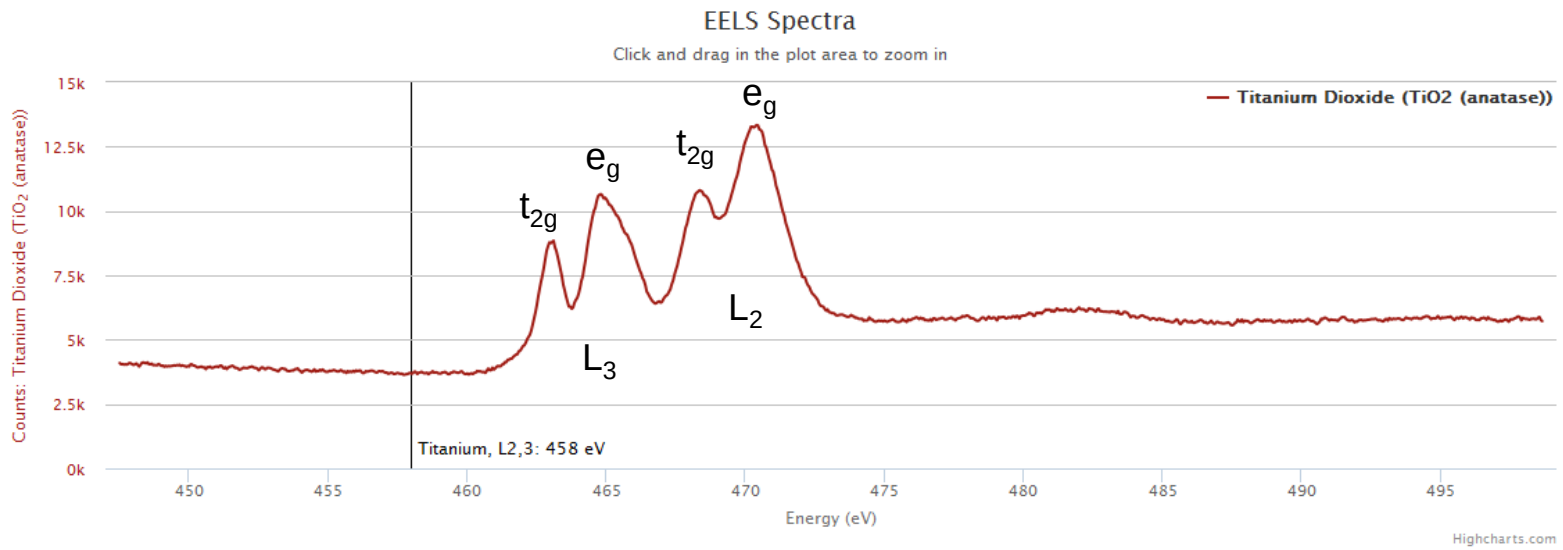
Remove from Favourites | Download

Submitted by Giovanni Bertoni, November 12, 2007.

Source / Purity: Aldrich powder

Author Comments: Polycrystalline sample Analyst: Giovanni Bertoni. Temperature: Room.

Select overlay plot: Titanium Dioxide: TiO2 (anatase) Show

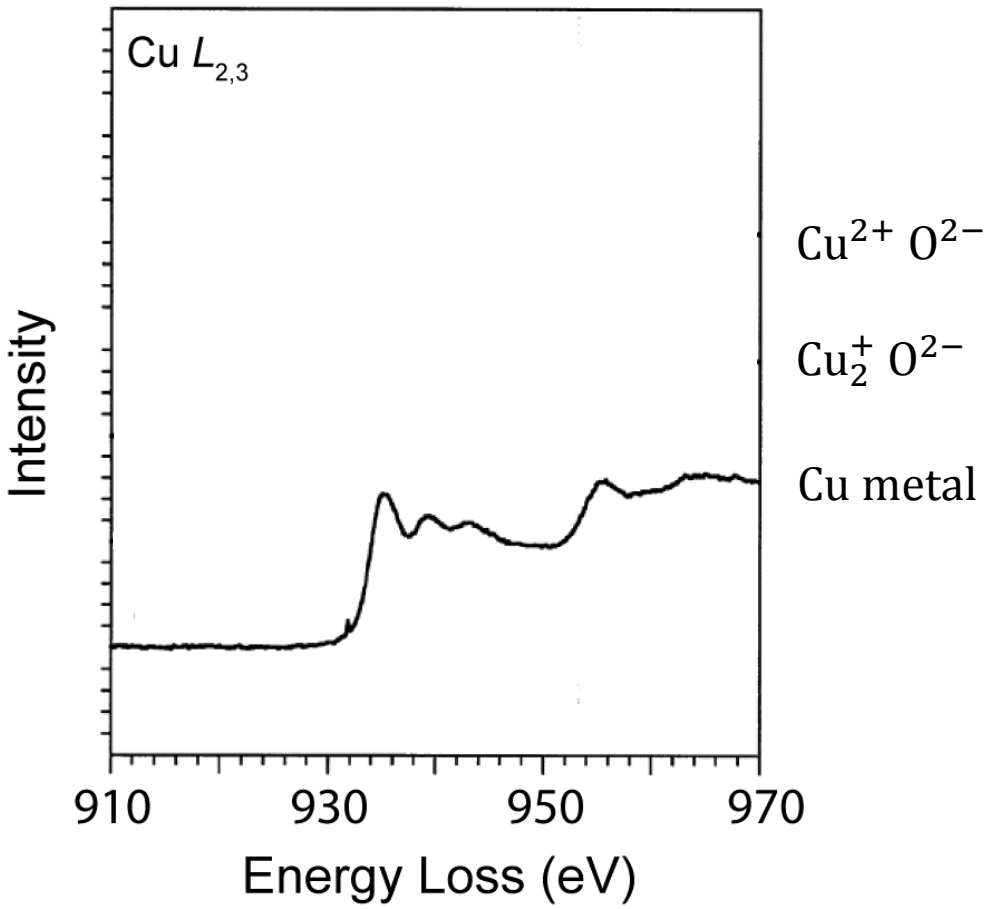


Direct comparison with calculated density of states (DOS)

$$\frac{\mathrm{d}^2\sigma(\mathbf{\Delta k}, E)}{\mathrm{d}\Omega \mathrm{d}E} = \frac{4}{a_0^2 \Delta k^4} \rho(E) \left| \langle \beta | e^{-i\mathbf{\Delta k}\cdot\mathbf{r}} | \alpha \rangle \right|^2$$

- The transition matrix determines the underlying edge shape
- Usually slowly varying with energy
- The density of states gives more rapid variations on top of this
- Allows comparison with calculated DOS, e.g. from density functional theory (DFT)

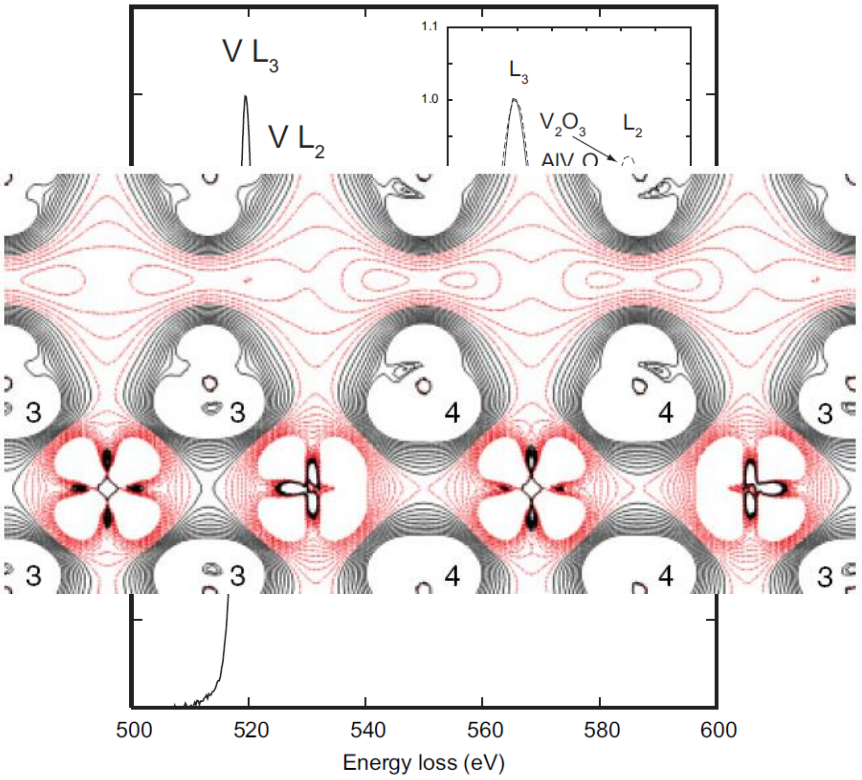
Direct observations of charge transfer in copper oxide

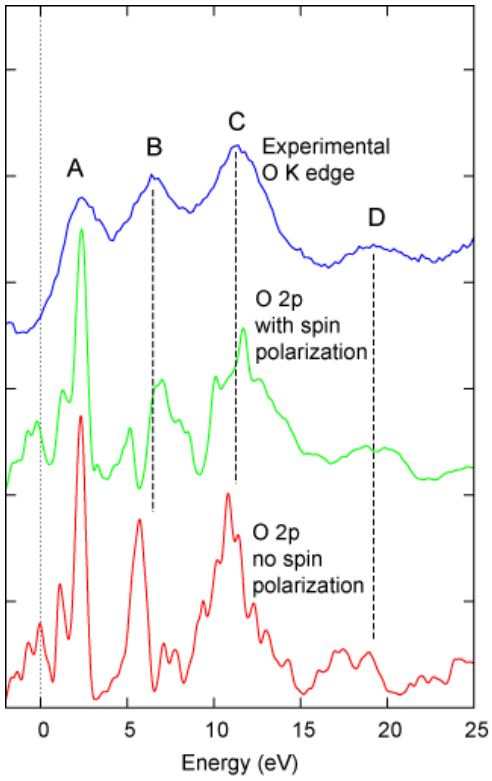


Charge is transferred from copper atom towards oxygen because of greater electronegativity

V. J. Keast *et al.* J. Microsc. (2001)

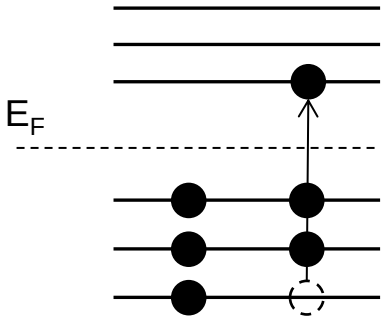
Oxygen 2p DOS of AlV_2O_4





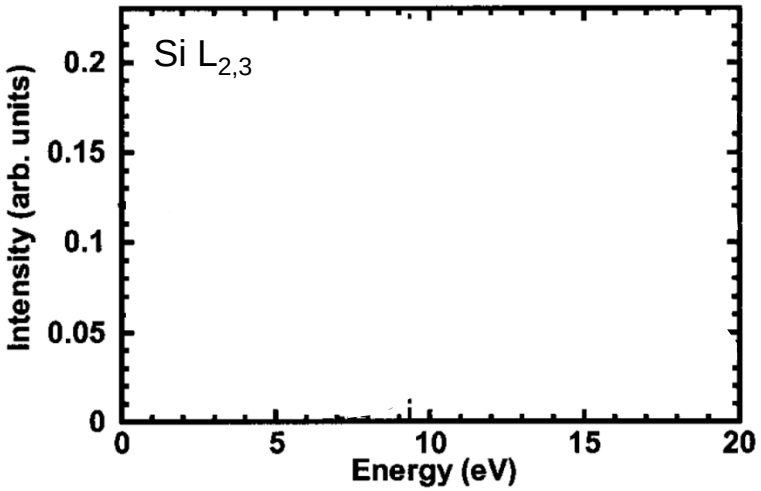
The core hole problem

- We have so far assumed that the probed DOS is the *ground state* DOS
- But we are explicitly exciting the system out of the ground state
- Coloumb interaction between electron and hole
- Change in electrostatic potential $\Rightarrow$ change in the DOS and rearrangement of charge



The core hole problem

SiO_2 as an example

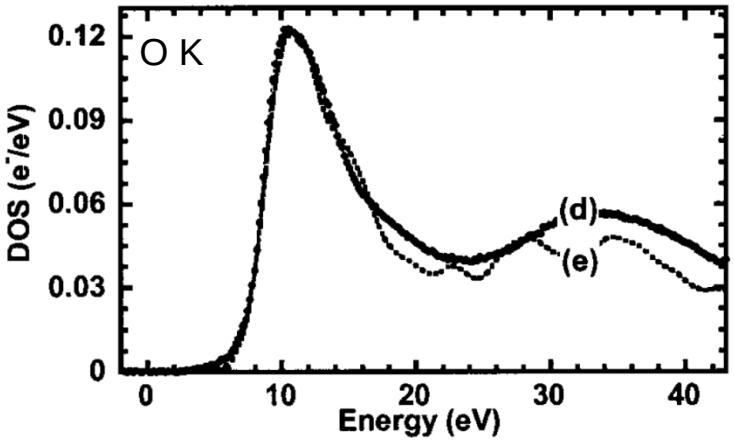


$p \rightarrow s,d$

Experiment

s and d DOS with core hole

s and d ground state DOS



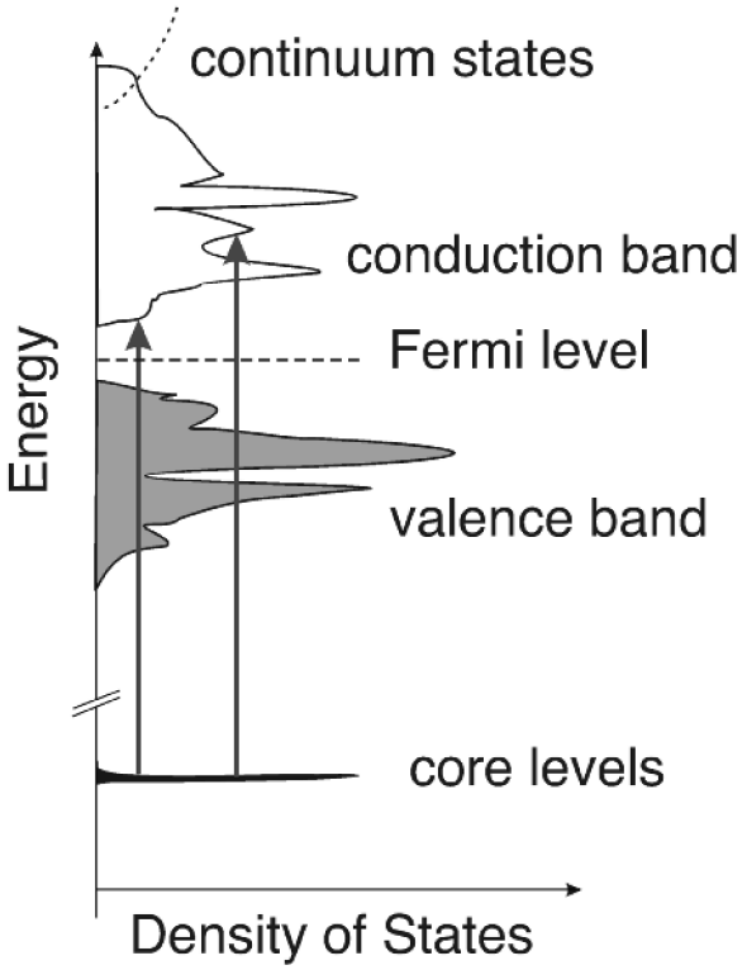
$s \rightarrow p$

p ground state DOS

Experiment

- The core hole should in principle always be accounted for
- Neglecting the core hole sometimes works well or even better (metals), other times not (insulators and oxides)

J. B. Neaton *et al*. Phys. Rev. Lett. (2000)



- If the initial states are sharply peaked in energy, then all transitions originate at this energy
- One particular E_i and one particular E takes you to a single point in the conduction band E_f
- In effect we are convoluting the conduction band DOS with a delta function

$$Delta\ function \otimes cDOS = cDOS$$

- But what if the initial states are in the valence band?

$$vDOS \otimes cDOS = ?$$

- Topic for next time