Introduction to EELS data analysis

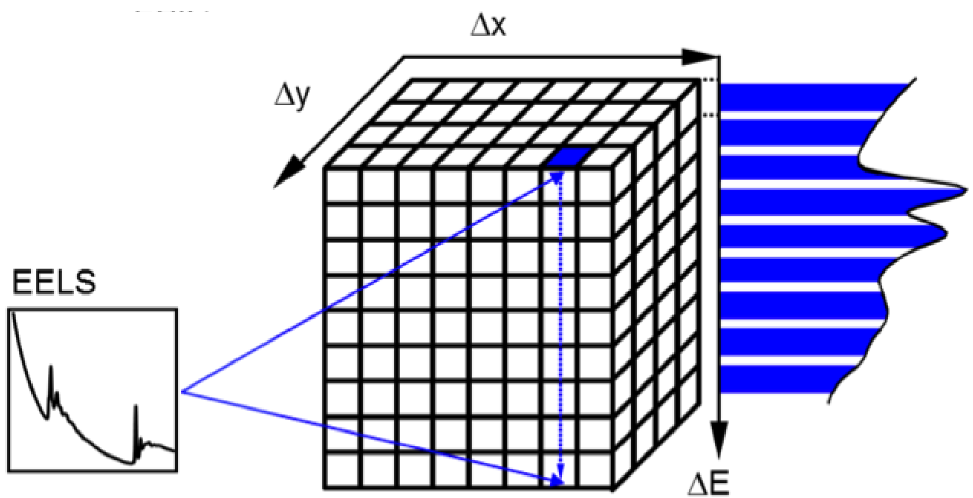
Eric Prestat

Department of Materials, University of Manchester, Manchester, UK

SuperSTEM Laboratory, SciTech Daresbury Campus, Daresbury, UK

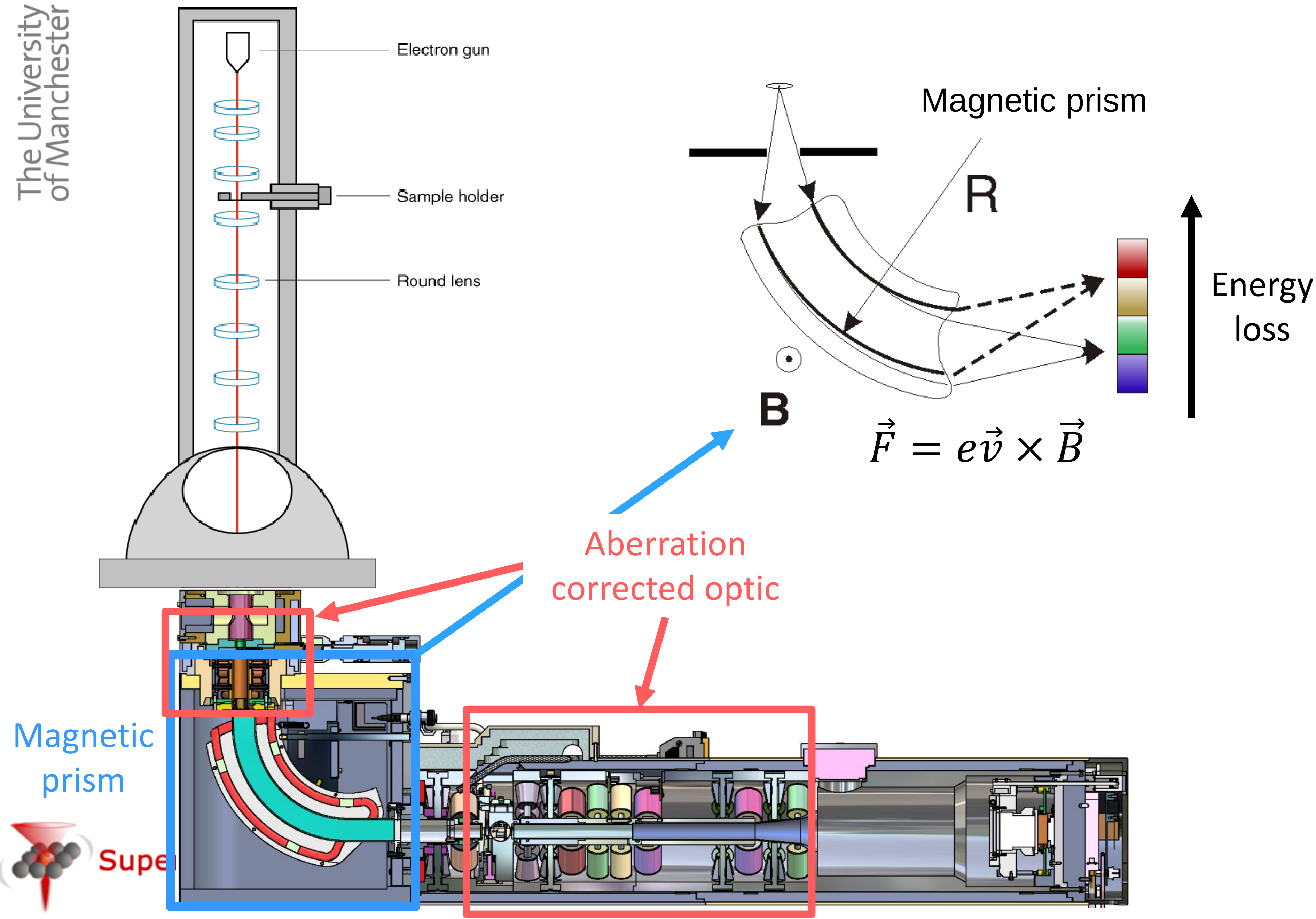
eric.prestat@manchester.ac.uk

- Introduction to EELS
- Elemental quantification
  - Integration method
  - Curve fitting method



EELS measures the energy that electrons have lost in the specimen

The University of Manchester



EELS

- Core-loss edges can be used to estimate the elemental composition of the specimen
- Low loss contains plasmon, phonon, band gap, etc.

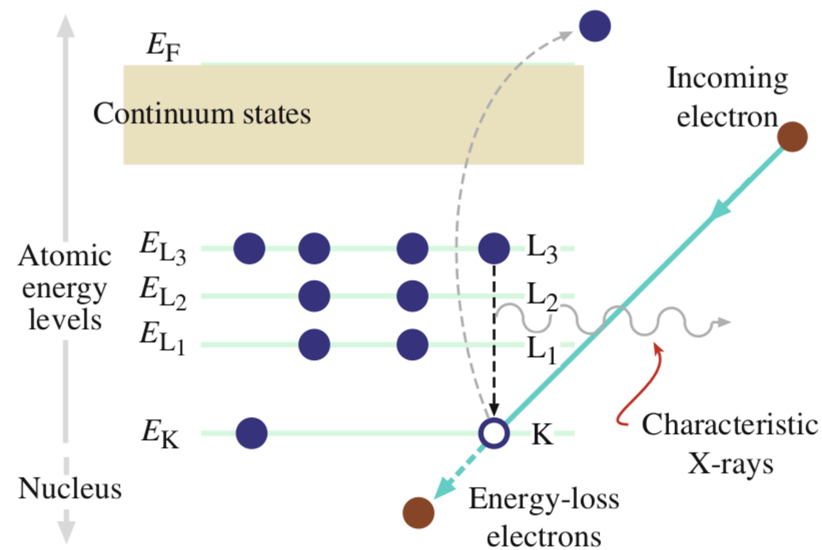
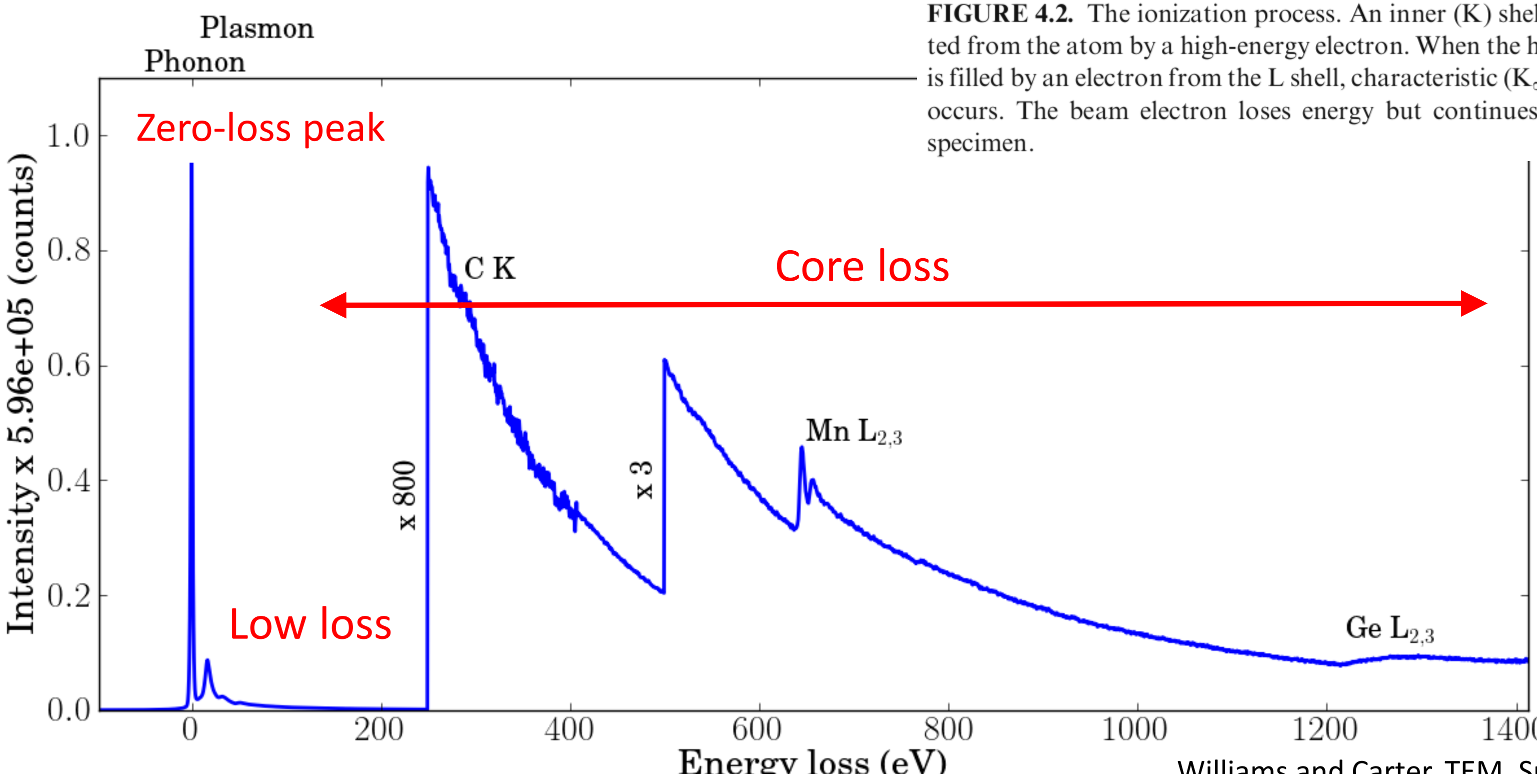


FIGURE 4.2. The ionization process. An inner (K) shell electron is ejected from the atom by a high-energy electron. When the hole in the K shell is filled by an electron from the L shell, characteristic (K_α) X-ray emission occurs. The beam electron loses energy but continues on through the specimen.



Williams and Carter, TEM, Springer (2009)

The feature of the edge (the so-called *fine structure*) is related to the band structure

The University of Manchester

EELS maps empty states above the Fermi level

Low-loss region is from plasmon excitation. Lies at energy level of conduction / valence bands

Ionization results in electrons which are ejected from core states into empty states above the Fermi level

This is why these are ‘edges’, and not ‘peaks’ - there is an onset

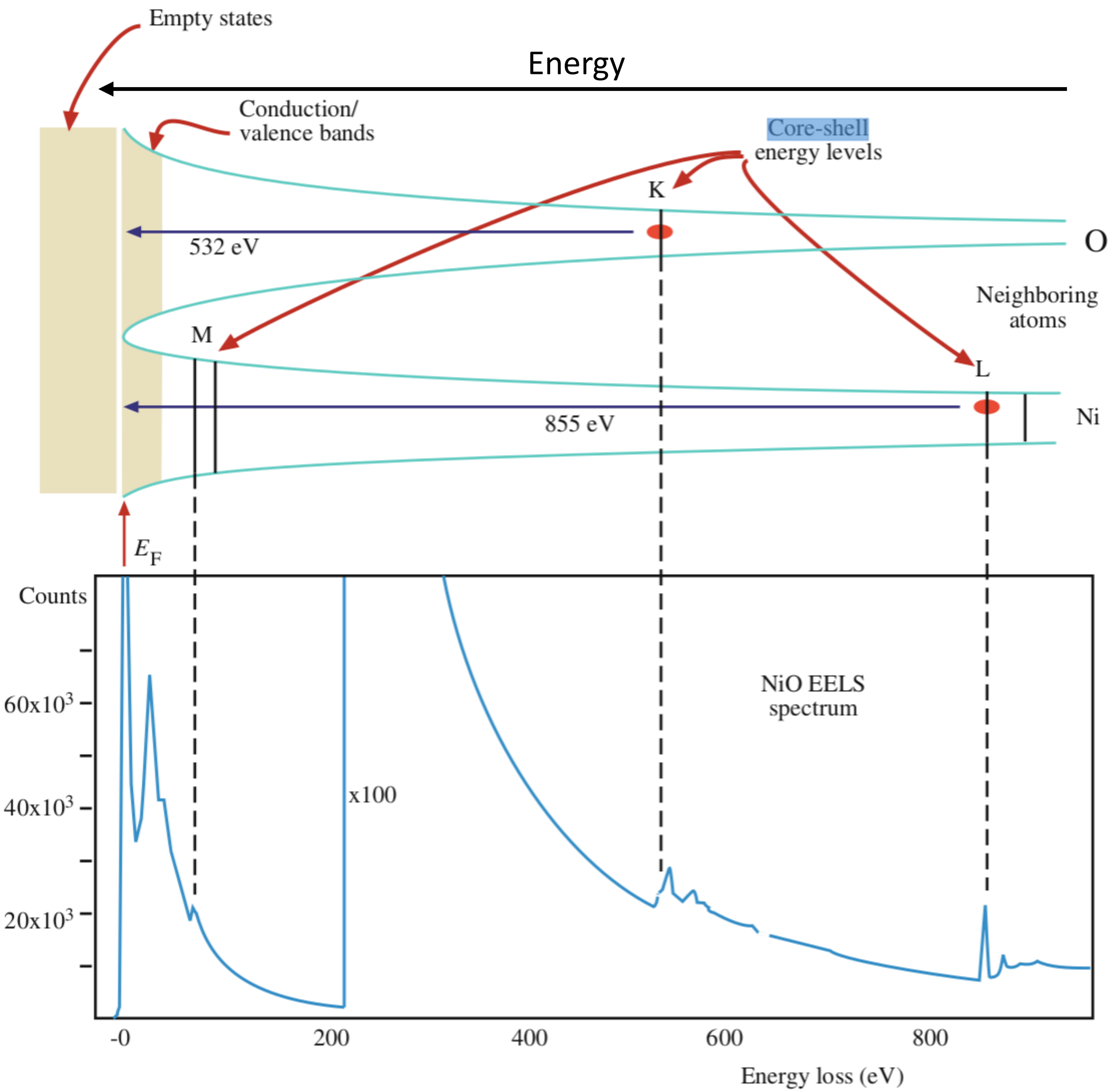


FIGURE 39.6. The correspondence between the energy levels of electrons surrounding adjacent Ni and O atoms and the energy-loss spectrum. The deeper the electrons sit in the potential well the more the energy needed to eject them. The ZLP is above the Fermi energy E_F, the plasmon peak is shown at the energy level of the conduction/valence bands where plasmon oscillations occur in the loosely bound electrons. The critical ionization energy required to eject electrons in specific shells is shown (Ni L: 855 eV and O K: 532 eV).

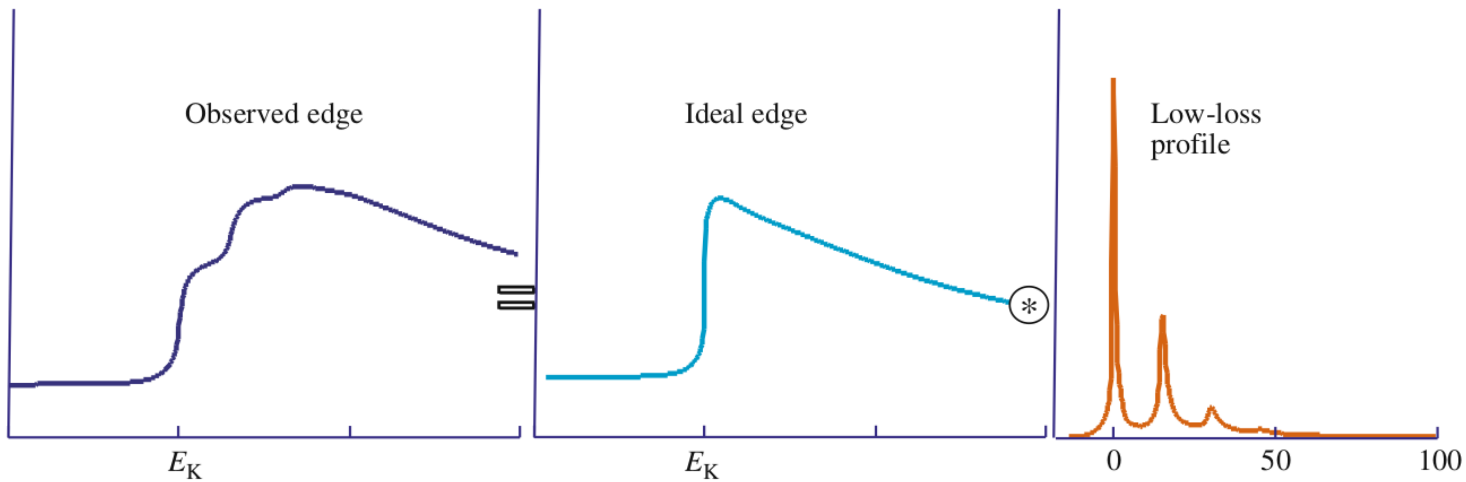
SuperSTEM DARESBURY

Williams and Carter, TEM, Springer (2009) p 720

The University of Manchester

How does an edge generally looks like? Well, it depends on a few things…

- On the thickness of your specimen
  - Plural scattering in thick specimen changes background
  - Core-loss scattering followed by plasmon scattering ⇒ Convolution of the edge feature with the plasmon peak



It also depends on the band structure of your materials

Some element are know to have sharp peak called “white line”

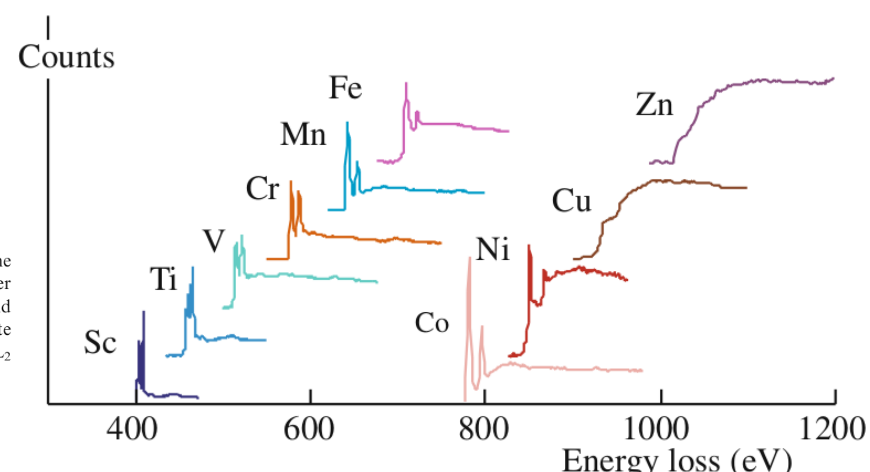


FIGURE 40.4. Spectra from the transition metals show a variation in the L_3 and L_2 white-line intensity ratios reflecting the variation in the number of core L-shell electrons ejected into unfilled d states. Note that Cu and Zn show no white lines because their d shells are full. The L_3 and L_2 white lines in the Fe L edge are the only ones that show the expected L_3:L_2 of ~2:1.

SuperSTEM DARESBURY

Williams and Carter, TEM, Springer (2009) p731 and p744

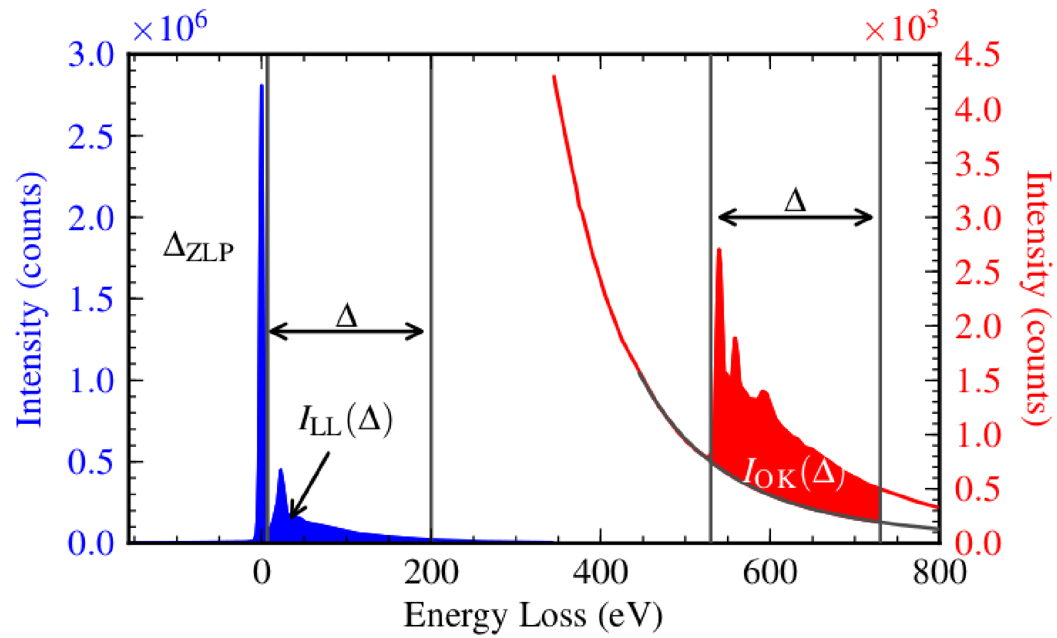
Elemental analysis of EELS spectrum

The University of Manchester

- EELS can be used to estimate the relative composition of a specimen
  - Similar to EDS
- Integration method

1. Subtract the background by extrapolation (usually, we use a power-low)
2. Integrate the number of count I_K in the edge within a limited energy range after the edge onset
3. Compute the cross-section σ_K for this specific experimental conditions based on theoretical model; alternatively use own calibrated experimental factors

$$\frac{C_A}{C_B} = \frac{I_K^A}{I_K^B}\frac{\sigma_K^A}{\sigma_K^B}$$



de la Peña (2010) PhD thesis

SuperSTEM DARESBURY

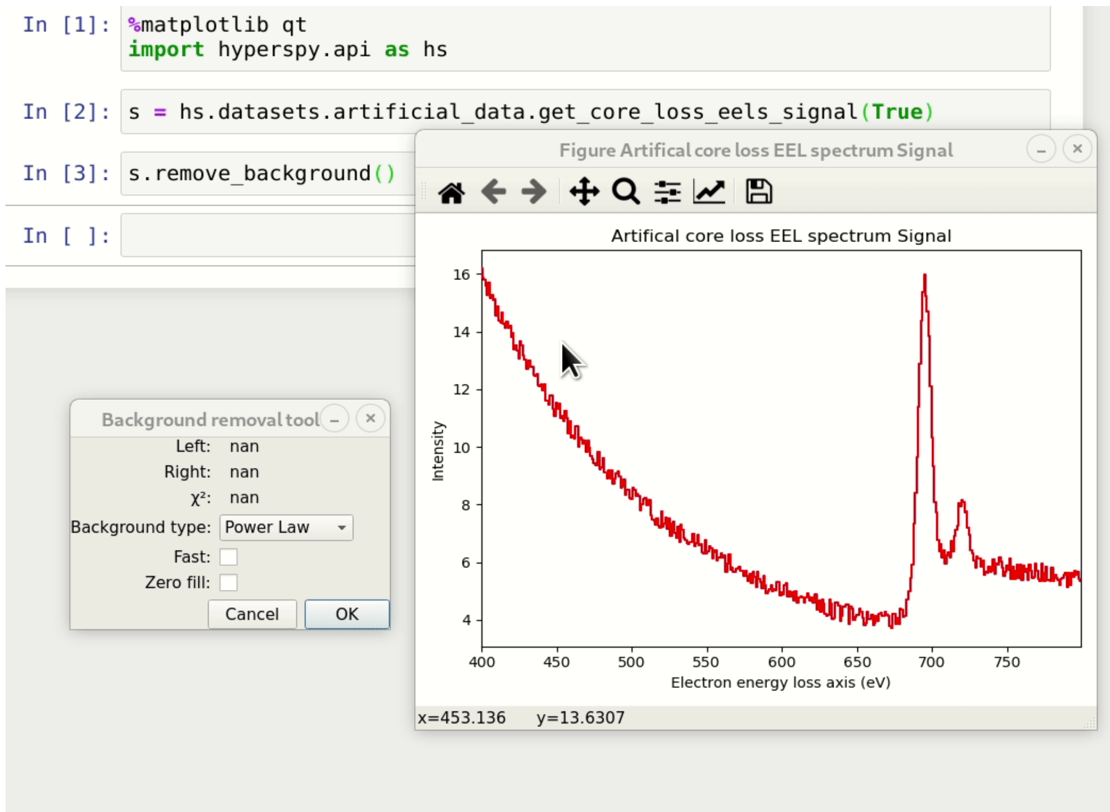
Integration method

Advantage

- Fast
- Simple

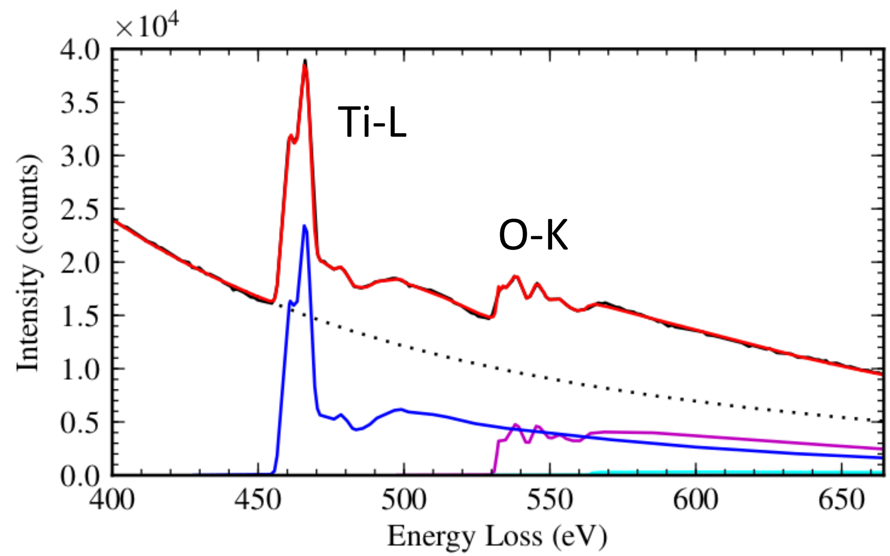
Drawback

- Background extrapolation inaccuracy
- User bias: where should the windows be?
- Issue when edges are overlapping
- Plural scattering needs to be removed



The University of Manchester

- Model
  - Combination of functions describing the spectrum
  - Noise model
  - Set of initial parameters
- Non-linear fitting
  - Optimise parameters
- A typically EELS model to quantify elemental composition consists of
  - A power background
  - Core-loss edge
  - Convolution with low-loss spectrum to model plural scattering



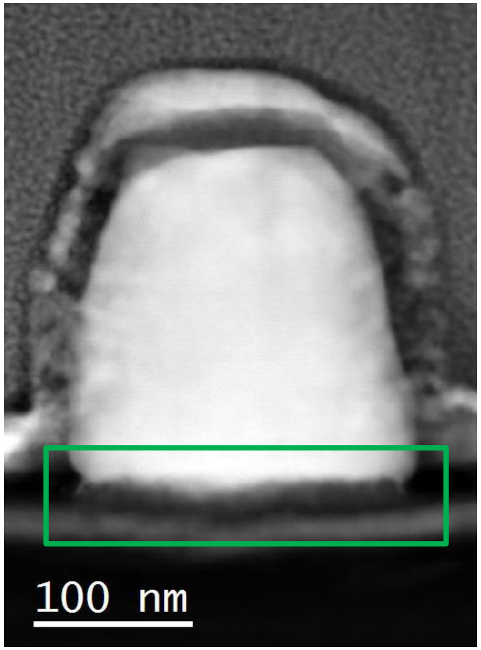
de la Peña (2010) PhD thesis

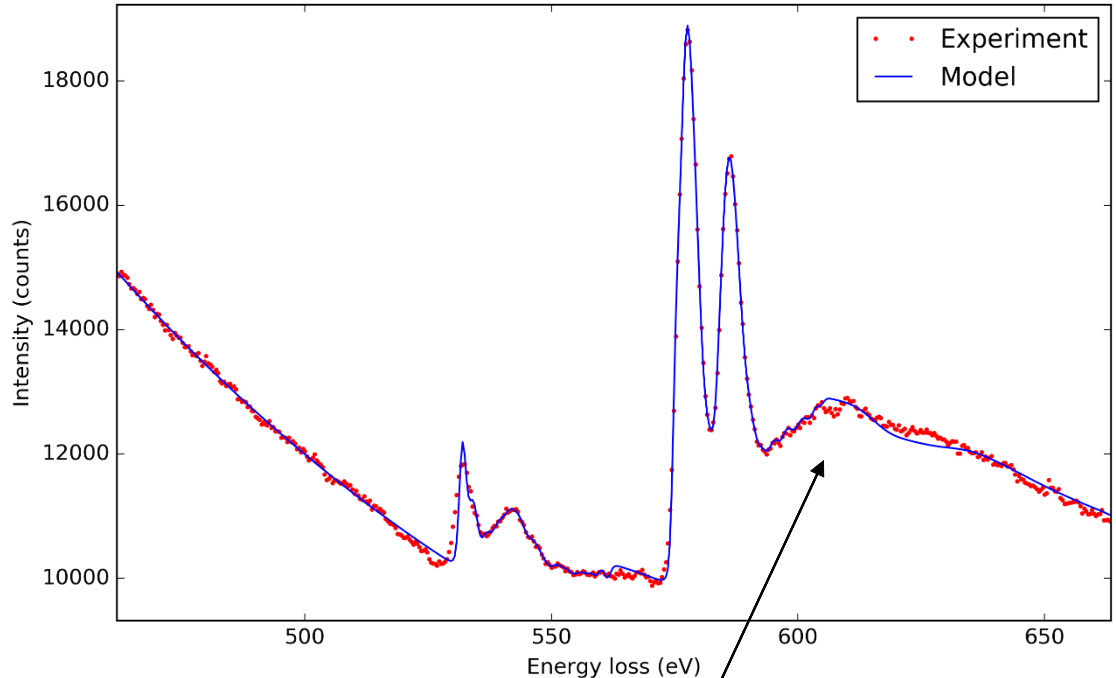
SuperSTEM DARESBURY

Plasmon induced conductive filament in CrO_x

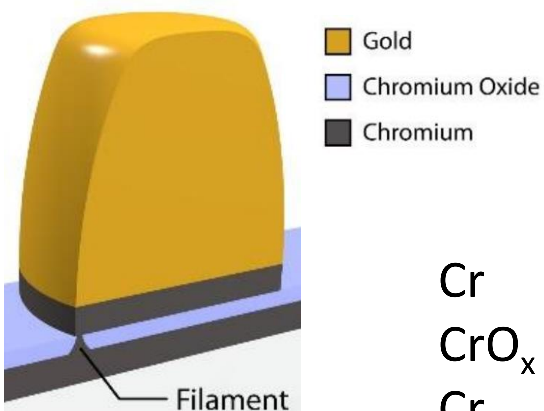
The University of Manchester

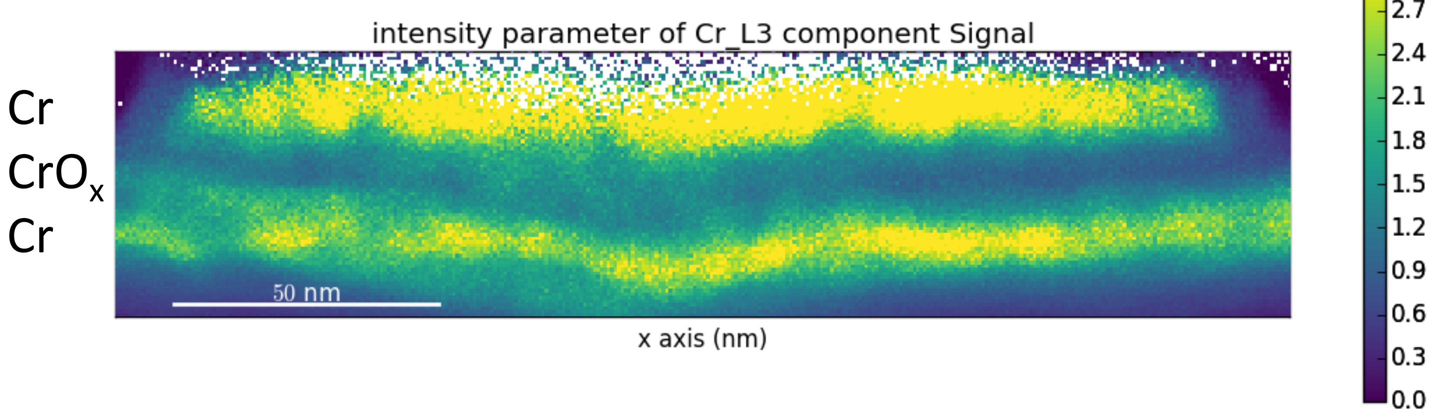
Au dots on Cr/CrO/Cr





“Thick specimen”: significant plural scattering



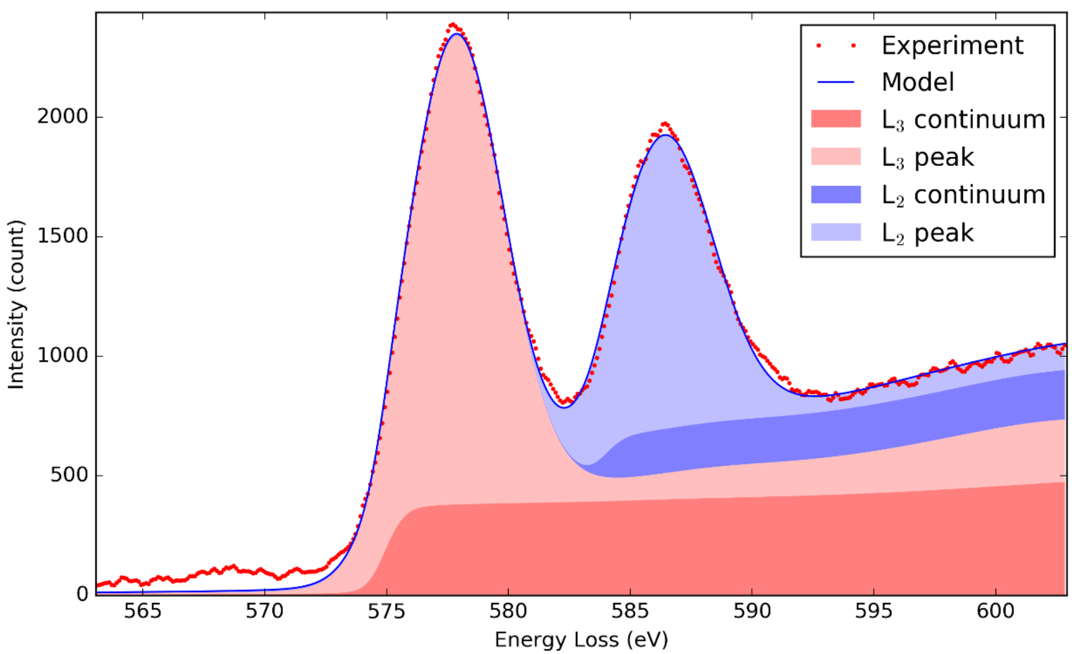


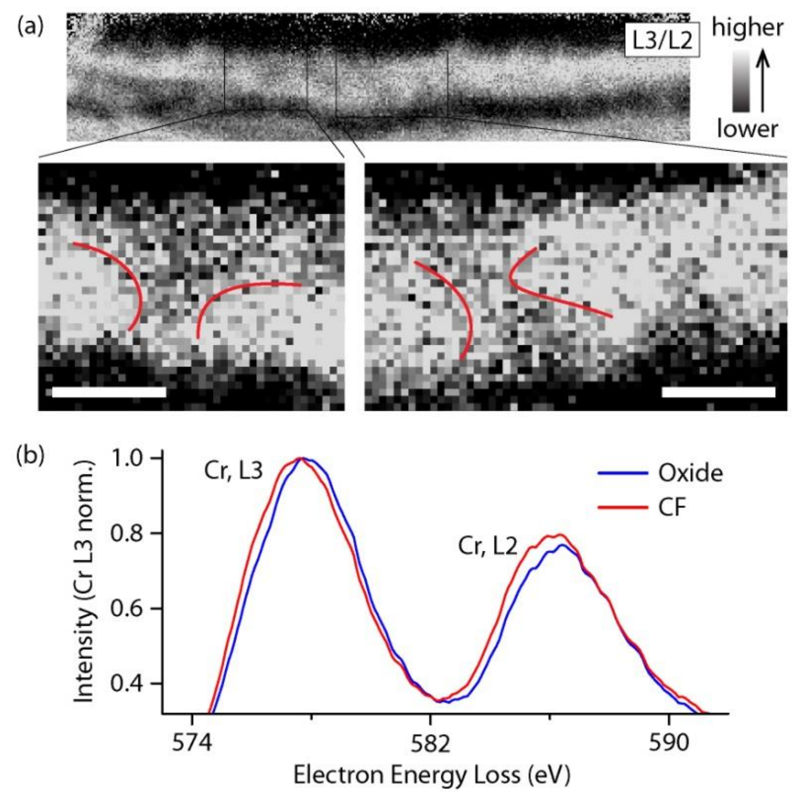
SuperSTEM DARESBURY

The University of Manchester

Curve fitting of white line

- Convolution with low-loss to model plural scattering
- Hartree-Slater cross section to model continuum
- Gaussian function to model L_3 and L_2 peak
  - Data acquired with end-of-life X-FEG: energy resolution ~ 1.2 eV





SuperSTEM DARESBURY

The University of Manchester

Curve fitting method

Advantage

- Work well with overlapping edges
- Highly flexible
- Model plural scattering
- Model noise
- Error calculation
- Use all data points

Drawback

- Slow
- Complex
- Non-linear problem
  - convergence issue
  - Very sensitive to starting parameters

SuperSTEM DARESBURY

The University of Manchester

Reference

- Integration method
  - Transmission Electron Microscopy , Williams & Carter (2009) Springer, chapter 39
  - Electron Energy-Loss Spectroscopy in the Electron Microscope, Egerton (2011) Springer
- Curve fitting method
  - Steele *et al.* (1985) A single-stage process for quantifying electron energy-loss spectra. Ultramicroscopy, 17: 273
  - Manoubi *et al.* (1990) Curve fitting methods for quantitative analysis in electron energy loss spectroscopy. Microscopy Microanalysis Microstructures, 1: 23
  - Verbeeck and Aert (2004) Model based quantification of EELS spectra. Ultramicroscopy, 101: 207
  - Verbeeck and Bertoni (2008) Model-based quantification of EELS: is standardless quantification possible? Microchim Acta, 161: 439
  - de la Peña (2010) Advanced methods for Electron Energy Loss Spectroscopy core-loss analysis, PhD thesis, University Paris-Sud 11

SuperSTEM DARESBURY