Electron Energy Loss Spectroscopy (EELS)
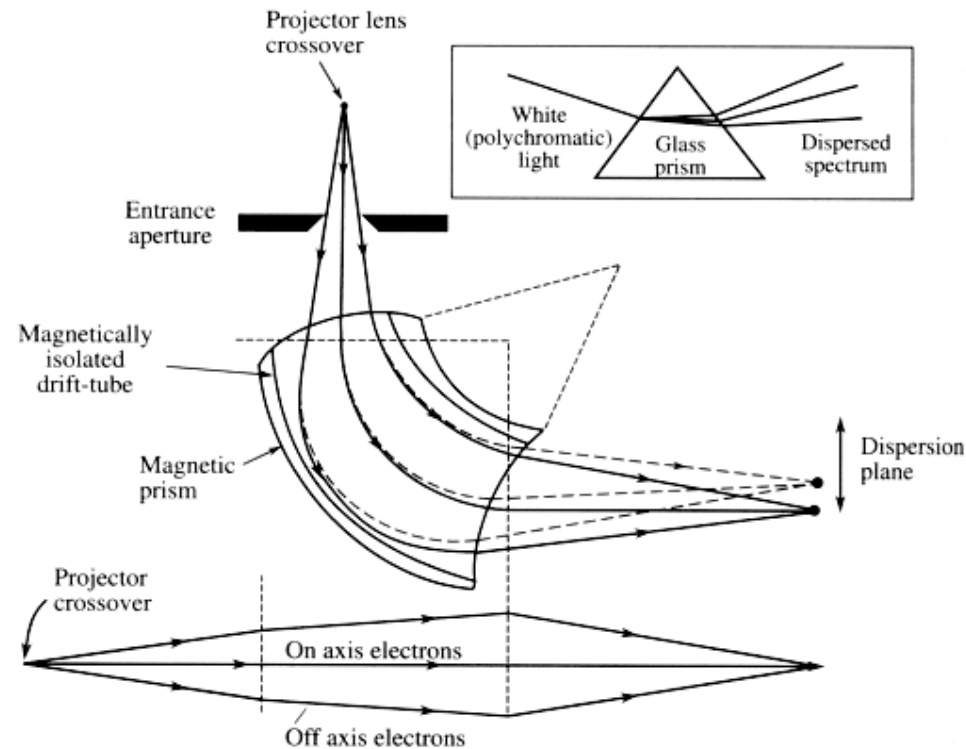
Lecture 20

EELS Spectrometer

Electrons lose energy due to inelastic scattering

Use a magnetic spectrometer to bend electrons

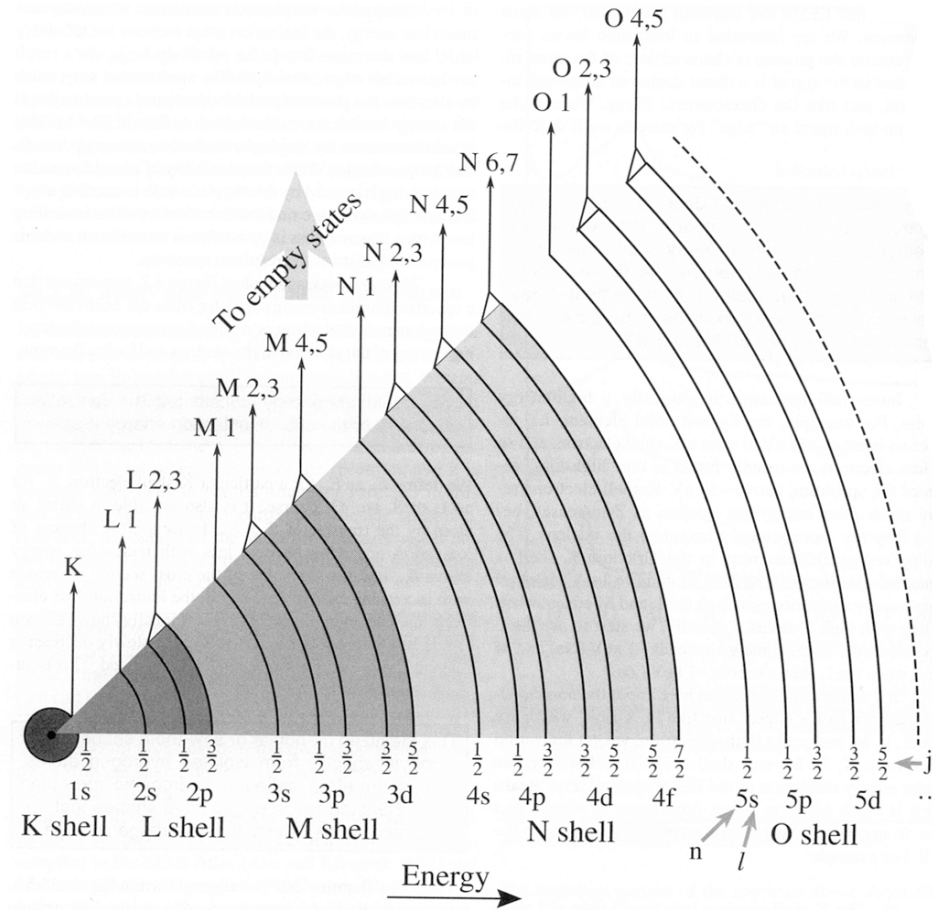Essentially acts as a prism, thereby 'coloring' electrons by energy loss
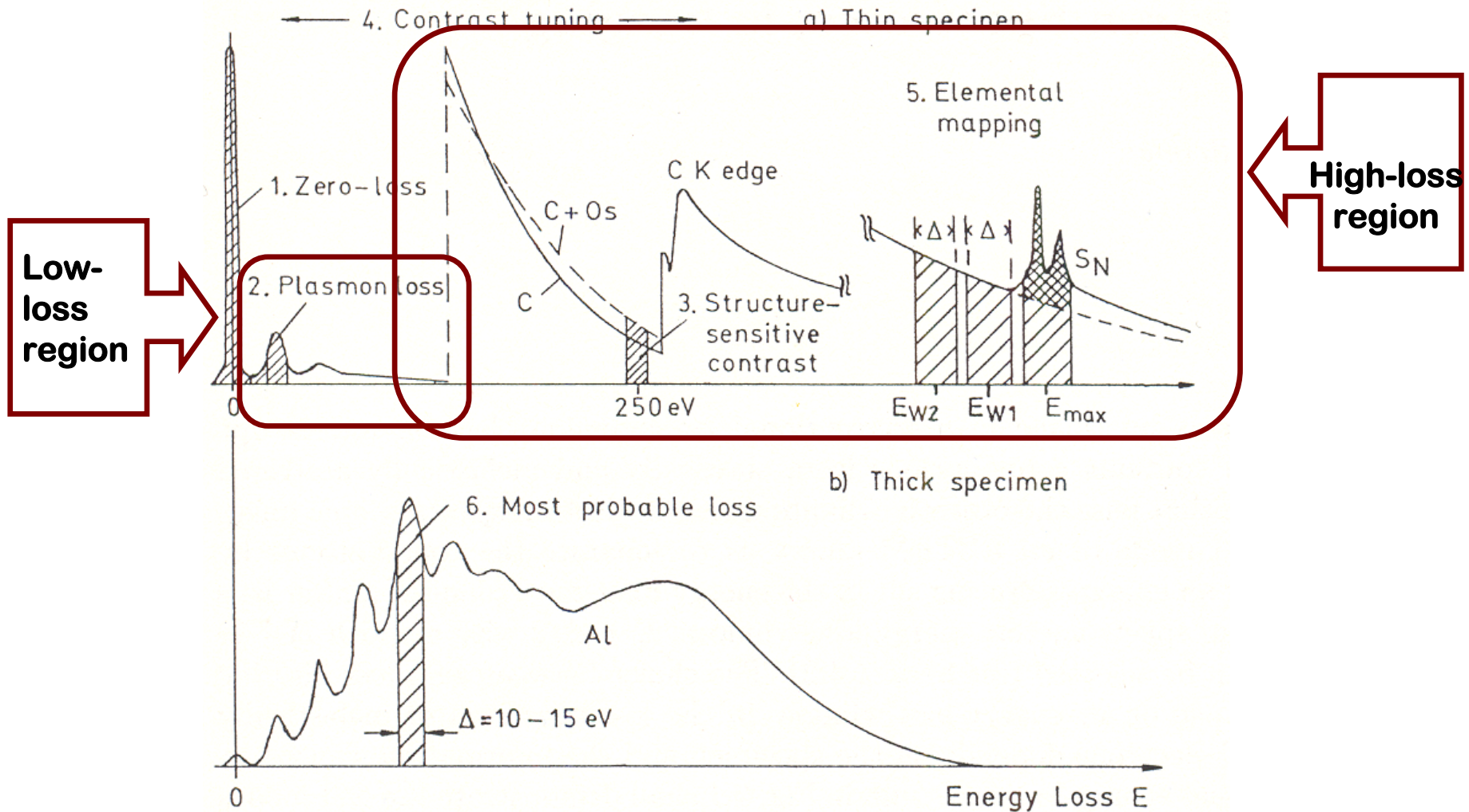
Allowed transitions

Like EDS, the observable edges can be directly related to the electron shells.

You will observe K, L, M and N edges

Which edges you see depends on the atomic weight of your material

The EELS spectrum

Effect of 'plural scattering'
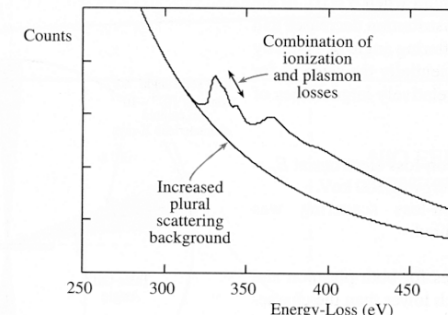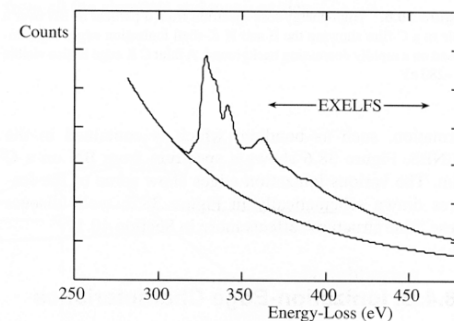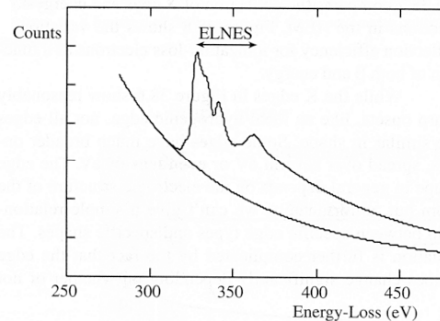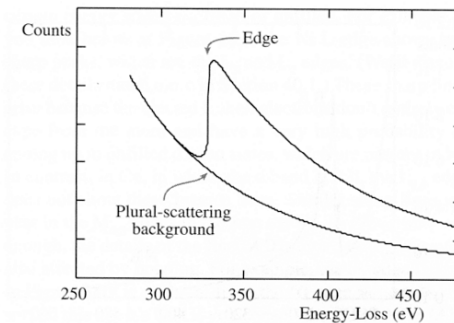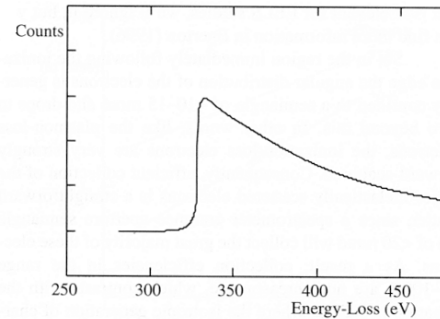
Well, it kind of depends…

How thick is your sample?

Plural scattering in thick samples changes background, which changes the edge

Plasmon peaks can be convoluted

So $\Rightarrow$ use a *thin* sample

- < 1 mfp, ≈ 500 Å is great

Zero Loss Peak

Predominant feature in thin specimen

- Electrons with beam energy

- Forward scattered

"Misnomer"

- There is a finite energy to the resolution of the spectrometer

- Can't produce monochromatic electrons

Problematic rather than useful

- Too intense

  - Damage scintillator

  - Saturate photodiode array

Zero loss peak

Start of usable informaiton
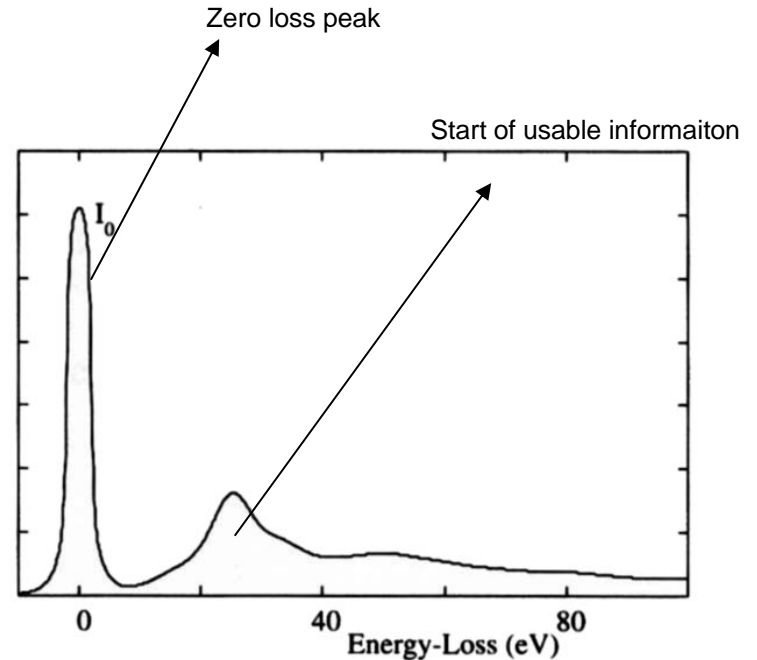
I_0

0   40   80
Energy-Loss (eV)

Figure 38.1. The intense zero-loss peak I_0 in a spectrum from stainless steel. The rest of the spectrum comprises energy-loss electrons which constitute a relatively small fraction of the total intensity in the spectrum.

Low-Loss Spectrum

Plasmons

- Longitudinal wavelike oscillations of weakly bound electrons
  - Small lifetime ≈ 10^{-15}s
  - Localized to < 10nm
- $\mathcal{E}_p$
  - Energy lost when plasmon is generated
  - Typical values: 5-25 eV
- Can give microanalytical information
  - $\mathcal{E}_p$ affected by free-electron density (n)
  - n may change with specimen chemistry
- Carries contrast information
  - Limit image resolution through chromatic aberration
  - Can remove through energy filtering
- Plasmon loss electrons strongly forward scattered

EDS Detector

Based on a p-i-n junction

- **Thick "intrinsic" region**
  - Li doped Si - Li fills acceptor states
  - Intrinic Ge - can make Ge more pure
- **p-layer on top**
- **n-layer on bottom**
- **Two thin ohmic Au contacts on outside**
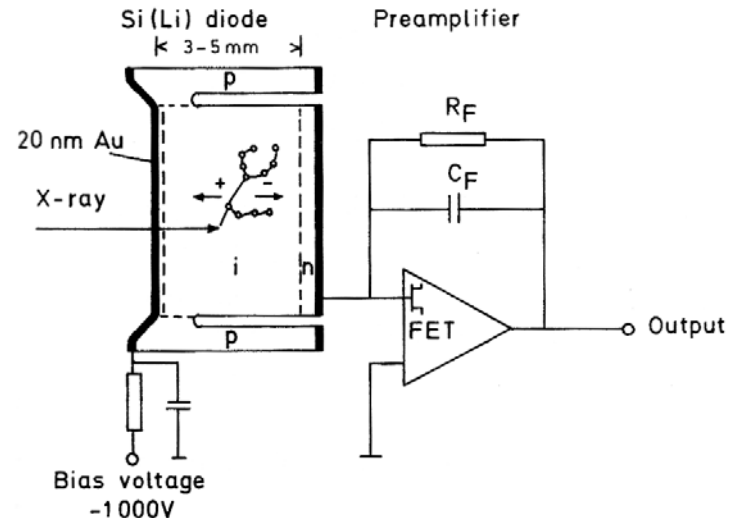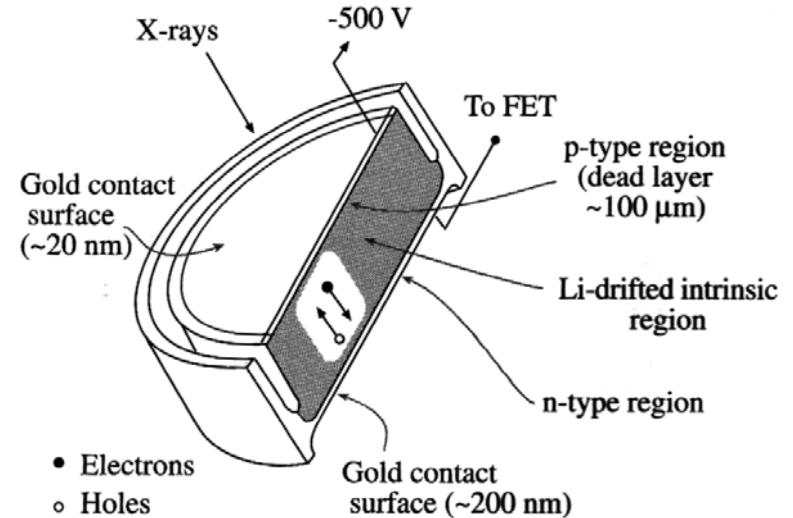
X-rays penetrate Au contact & p-region

- **Sufficient energy**

Create electron-hole pairs in the intrinsic region

- **Photoelectrons**
- **Same idea as a solar cell …**

p-i-n junction is under bias

- **Electron-hole pairs are swept to the contacts**
  - Electrons to p, holes to n

Low-Loss Spectrum

Plasmons

- Longitudinal wavelike oscillations of weakly bound electrons
  - Small lifetime ≈ 10^{-15}s
  - Localized to < 10nm
- $\mathcal{E}_p$
  - Energy lost when plasmon is generated
  - Typical values: 5-25 eV
- Can give microanalytical information
  - $\mathcal{E}_p$ affected by free-electron density (n)
  - n may change with specimen chemistry
- Carries contrast information
  - Limit image resolution through chromatic aberration
  - Can remove through energy filtering
- Plasmon loss electrons strongly forward scattered

Low-Loss Spectrum

Inter and Intra-Band Transitions

- Beam electron causes core electron to change orbital state

- Fingerprinting to identify particular specimen
    - Not well understood
    - Must have set of standards for comparison
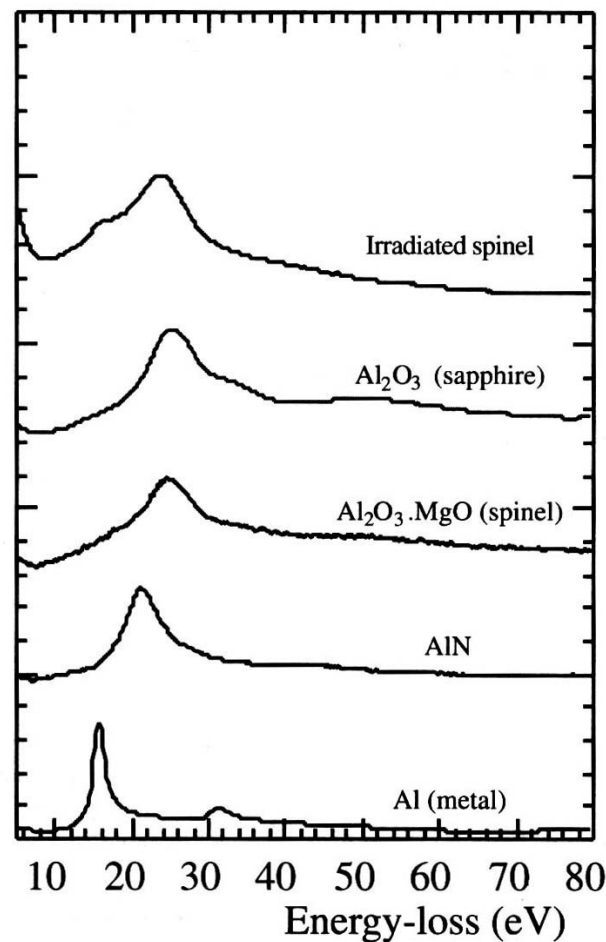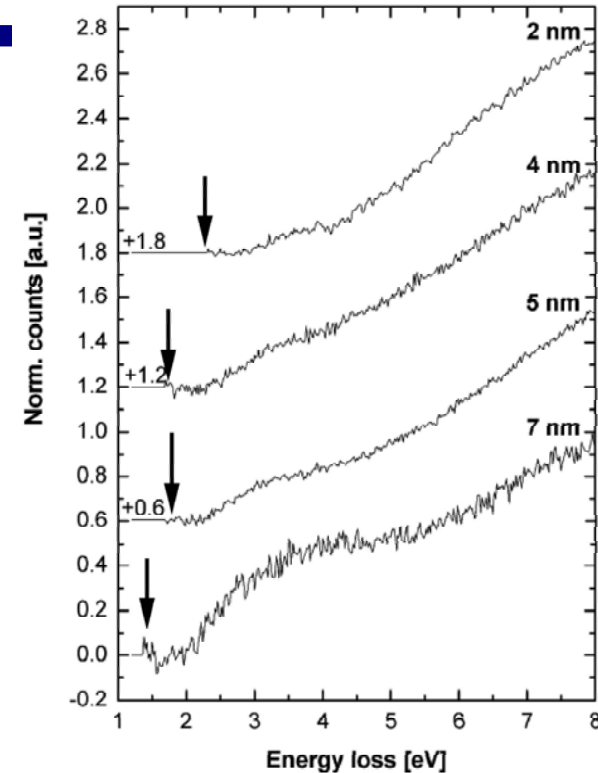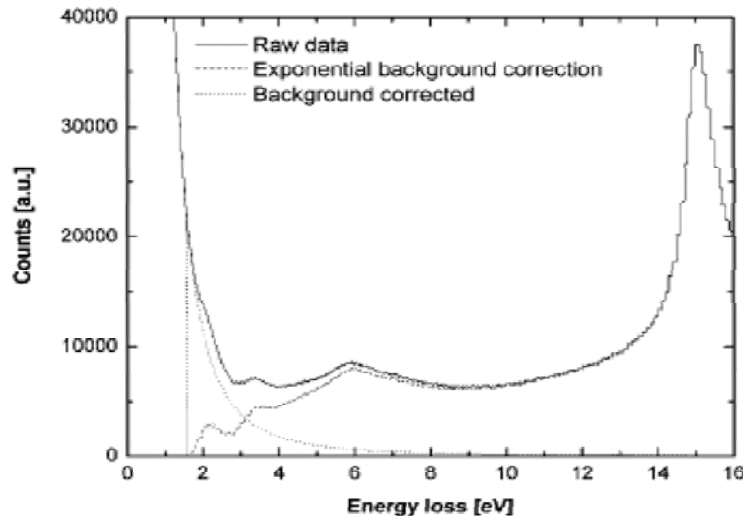
- May cause secondary electrons

Figure 38.3. The low-loss spectrum from specimens of Al and Al-containing compounds, showing differences in intensity that arise from differences between the bonding in the different materials. The spectra are displaced vertically for ease of comparison.
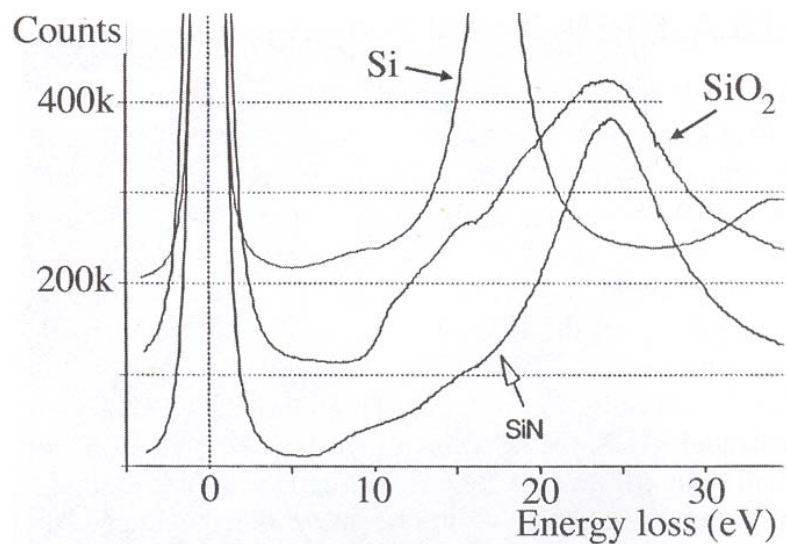
Valence EELS

"Monochromated" electrons sources allows high resolution EELS experimentation

Can be used to determine band gap, with ≈1 nm probe

Band gap measurements from CdSe quantum dots, as a function of dot diameter

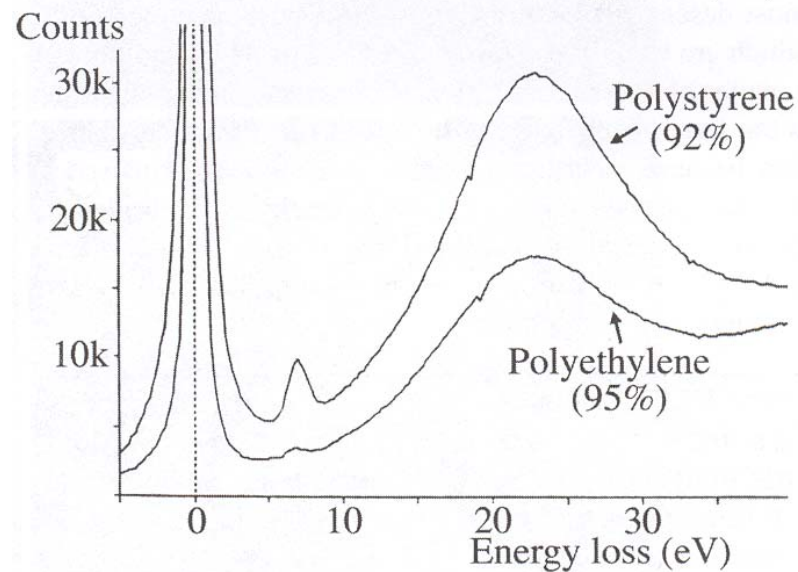Erni & Browning Ultramicroscopy, 2005.

Low Loss Spectrum

"Valence EELS" - VEELS

Band-gap measurement
- Between zero-loss peak and plasmon peak
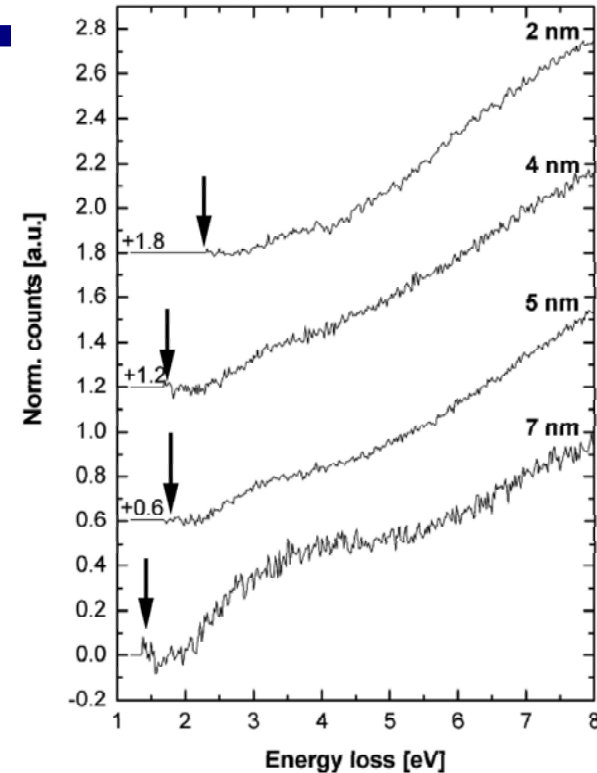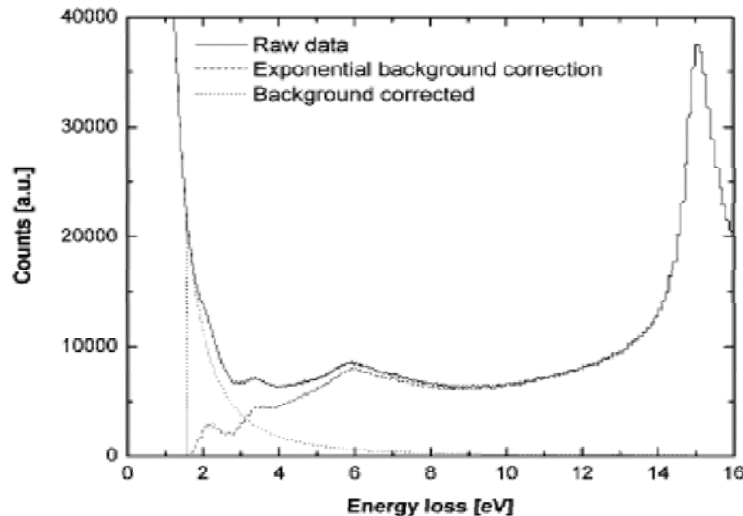- No electron-electron energy transfers occur

Identification of interband-transitions
- Visible on the rise of the plasmon peak

Valence EELS

"Monochromated" electrons sources allows high resolution EELS experimentation

Can be used to determine band gap, with ≈1 nm probe

Band gap measurements from CdSe quantum dots, as a function of dot diameter

High-Loss Spectrum

Inner-Shell Ionization

- **Ionization loss characteristic of element involved**

- **High energy processes**

- **Ionization edge intensity**
  - **Small compared to plasmons**
  - **Decreases as energy loss increases**

- **"Edge" Signal**
  - **Produces "triangular" shape**

- **More Complex spectra**
  - **From crystal lattice and amorphous structure**
  - **ELNES (energy-loss near-edge structure)**
  - **EXELFS (extended energy-loss fine structure)**
  - **From ionization-loss electrons undergoing further low-loss interactions**
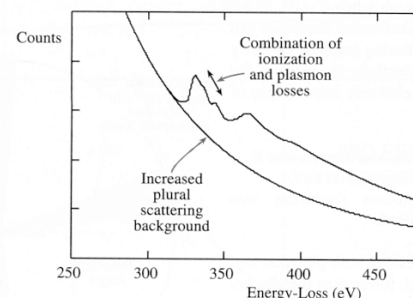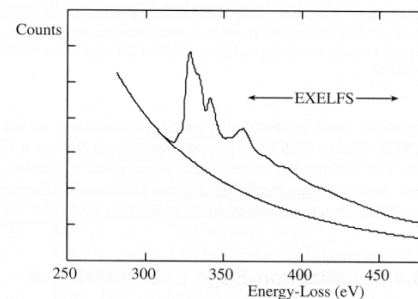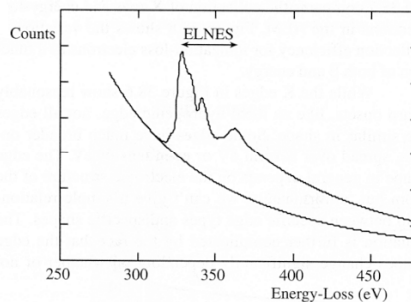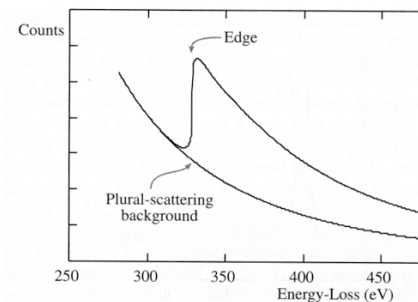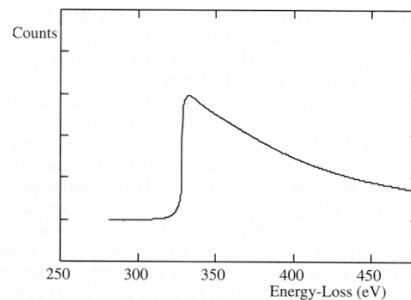
High-Loss Spectrum

Ionization Edge Characteristics

- Efficient collection of inelastically scattered electrons
  - Ionization-loss electrons are very-strongly forward scattered
  - Collection efficiencies of 50-100%

- Edge Shape
  - Depends on electronic structure of the atom
  - Changes significantly w/ filled/unfilled energy states
  - Affected by bonding
  - Best to consult EELS Atlas

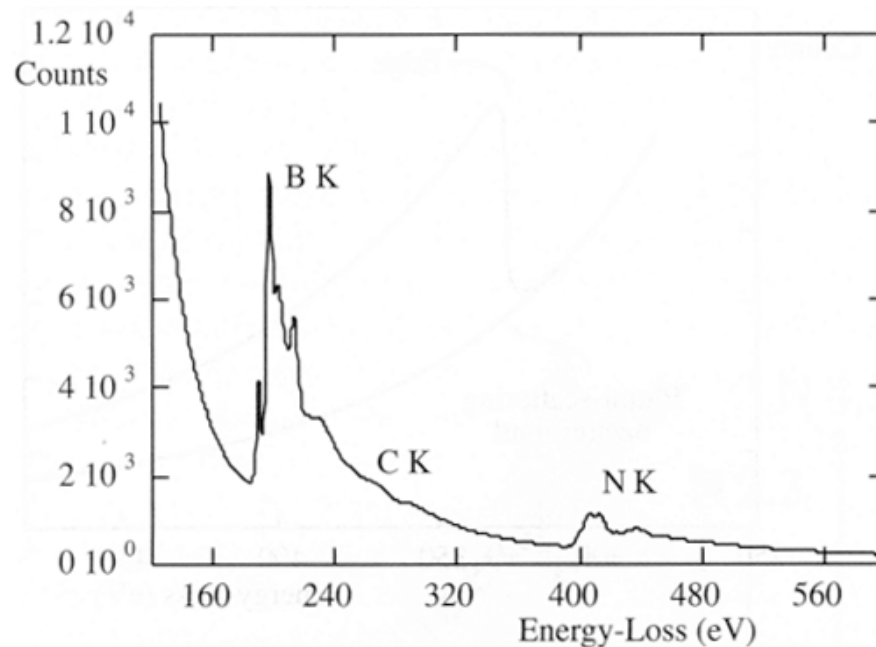- Qualitative microanalysis is difficult

Example EELS Spectra

This is from boron nitride (with some carbon contamination)

Note sharp onset of the K-edges.

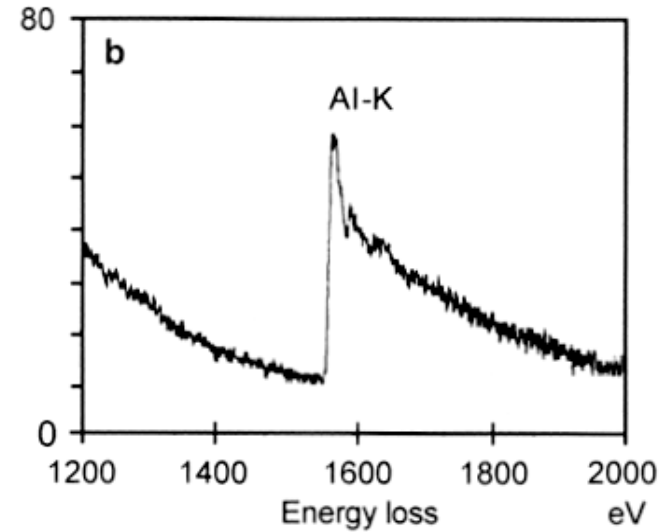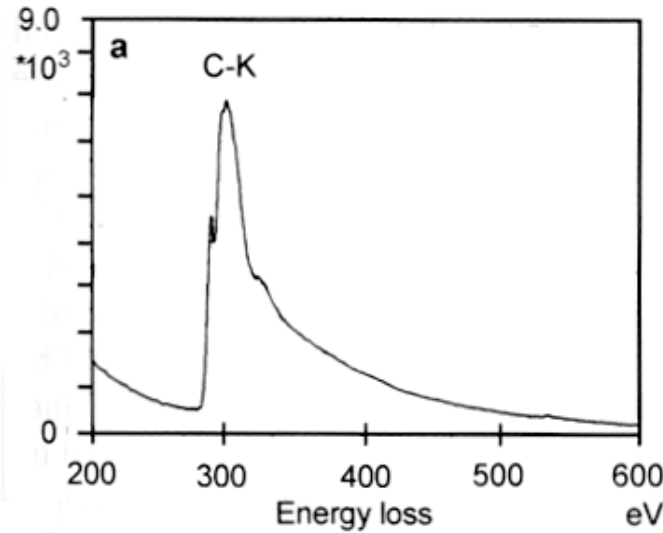Note the 'white lines' in the boron edge.

Broad range of energy
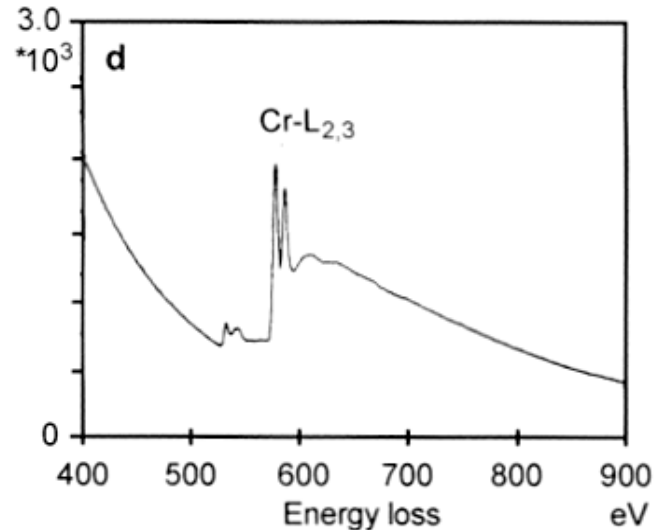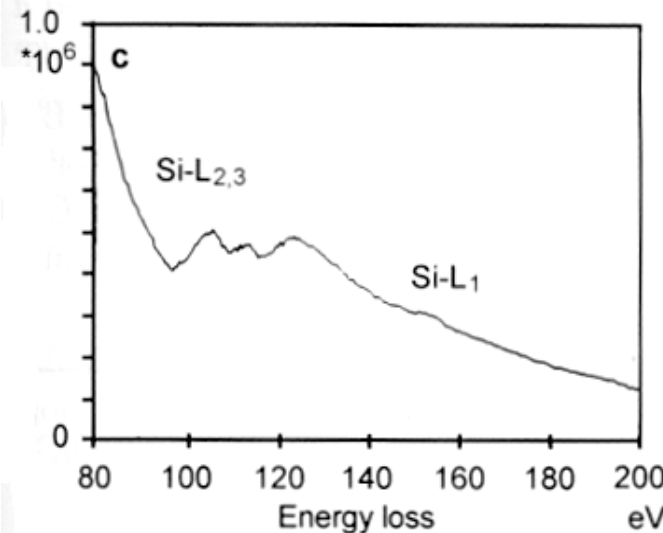
Huge number of counts vs. those in EDS

K and L Edges
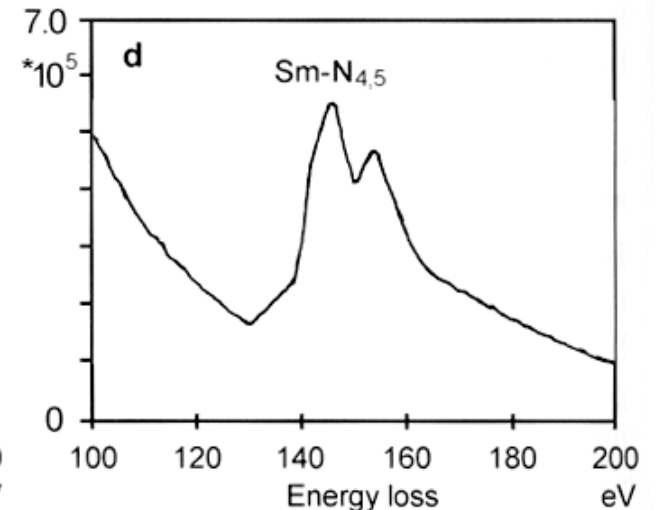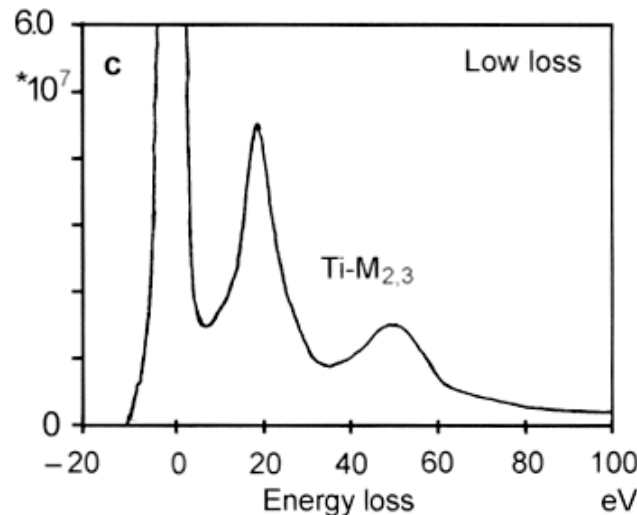
K edges:
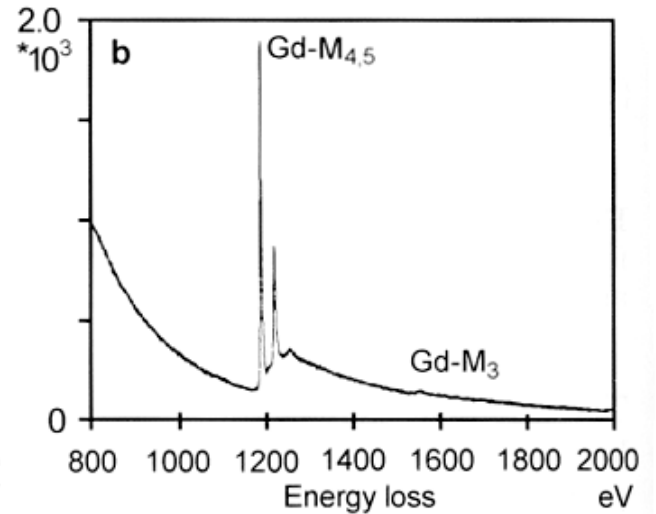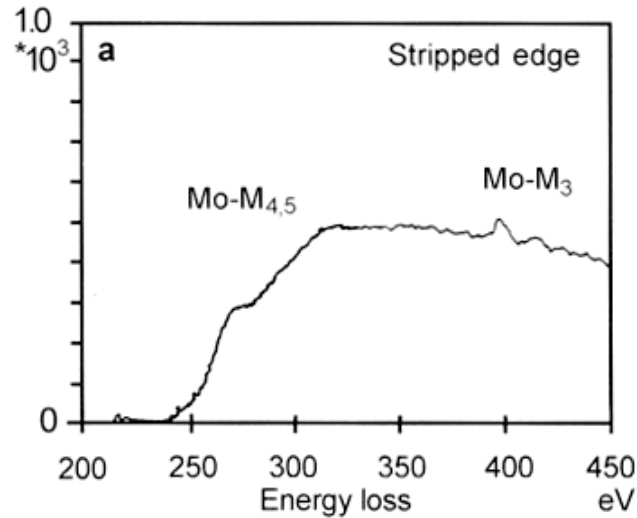- Sharp onsets

L edges:
- Can often resolve the the L1 and L2,L3 edges separately
- Leads to broader edges

M and N edges

M, N edges:

- Again, common to resolve separate sub-shell transitions

- Edges are again broadly dispersed in energy

EELS vs. Band structure

EELS maps empty states above the Fermi level

The electrons that are ejected from the core levels by the incident electron can scatter only into available states

Thus, the energy imparted by the incident electron to get them to make these transitions reflects the density of available states in the sample

ELNES / EXELFS

Near edge structure probes DOS in conduction band (ELNES)

– Increasing well understood, experiments becoming more routine

Extended structure probes chemical bonding (EXELFS)

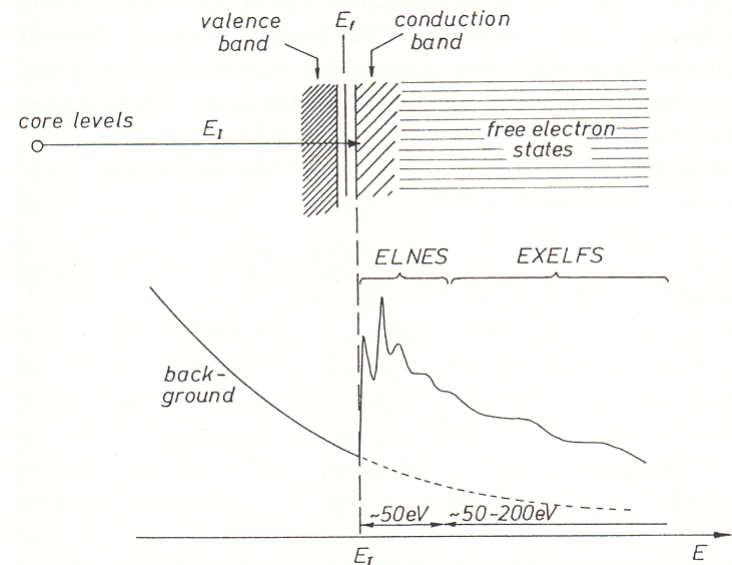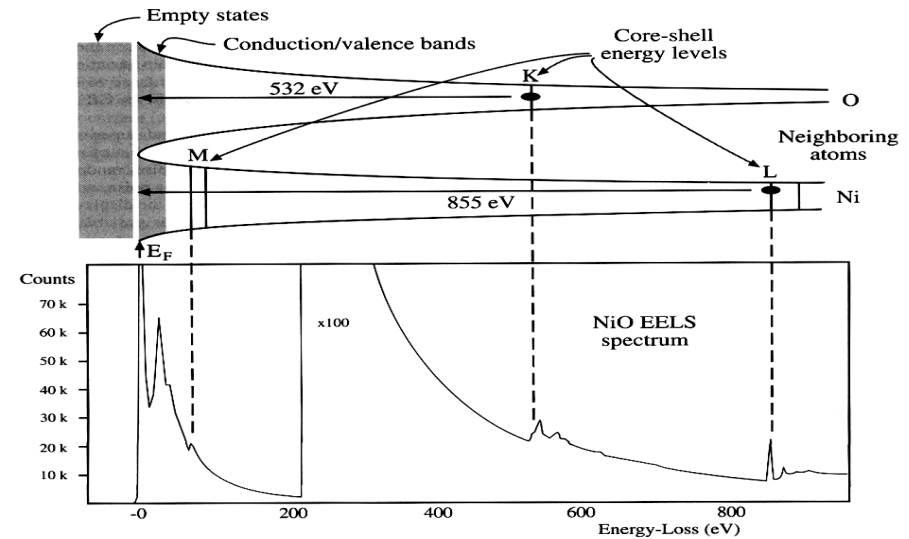– This is still largely a research topic in and among itself
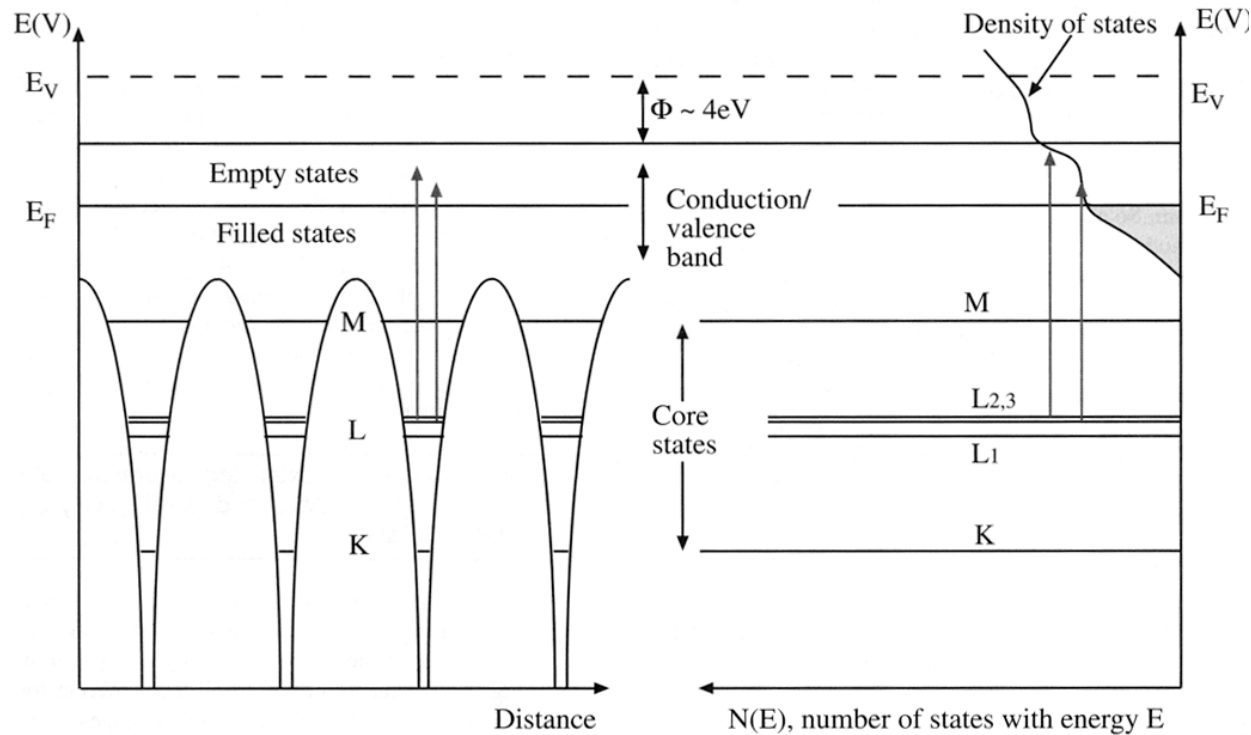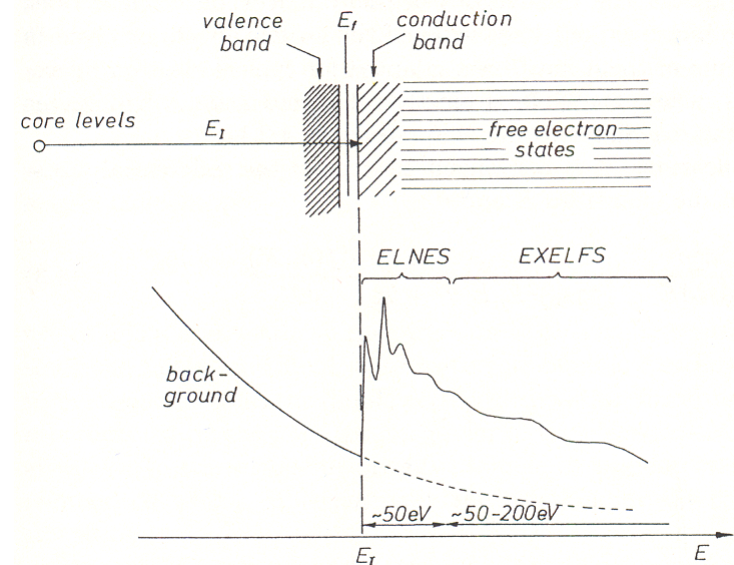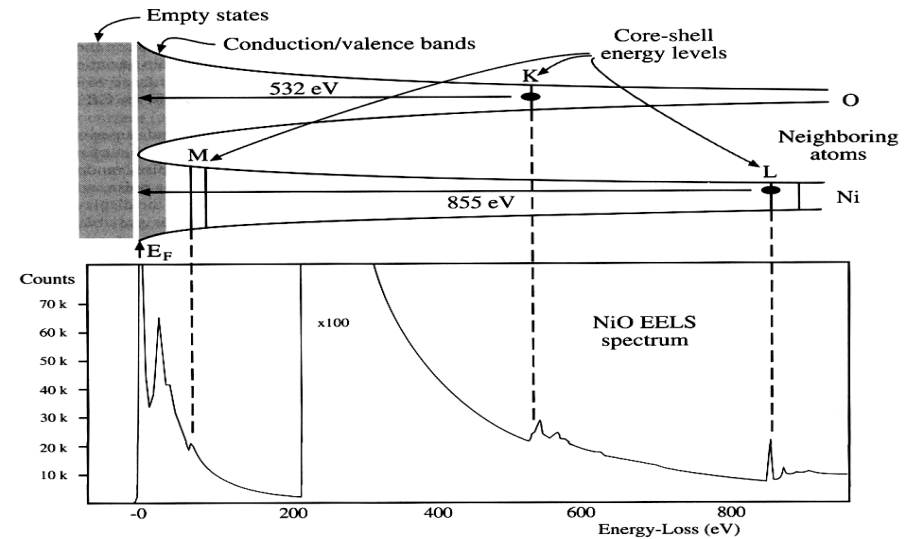
EELS vs. Band structure

EELS maps empty states above the Fermi level

The electrons that are ejected from the core levels by the incident electron can scatter only into available states

Thus, the energy imparted by the incident electron to get them to make these transitions reflects the density of available states in the sample
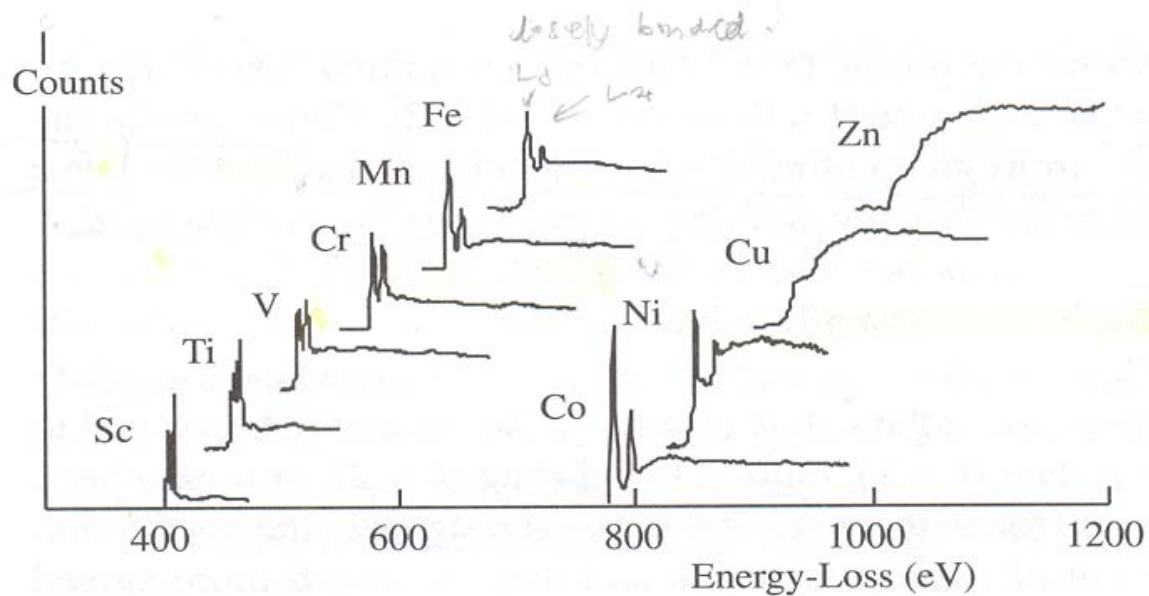
ELNES

Transition metal identification
- If d shell is empty, L_2 and L_3 are split
- Measure the ratio of L2 and L3 intensity
- Such separation called "spin-orbit splitting"

ELNES - "Fingerprinting"

Ti valence determination using EELS
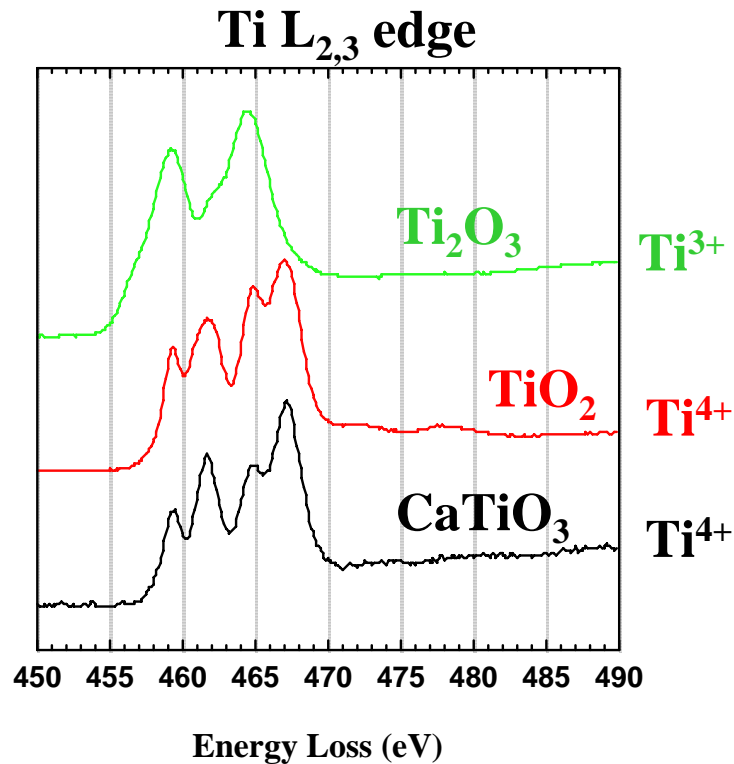
Ti L$_{2,3}$ edge from trivalent Ti$_2$O$_3$ differs markedly from tetravalent compounds TiO$_2$ and CaTiO$_3$.
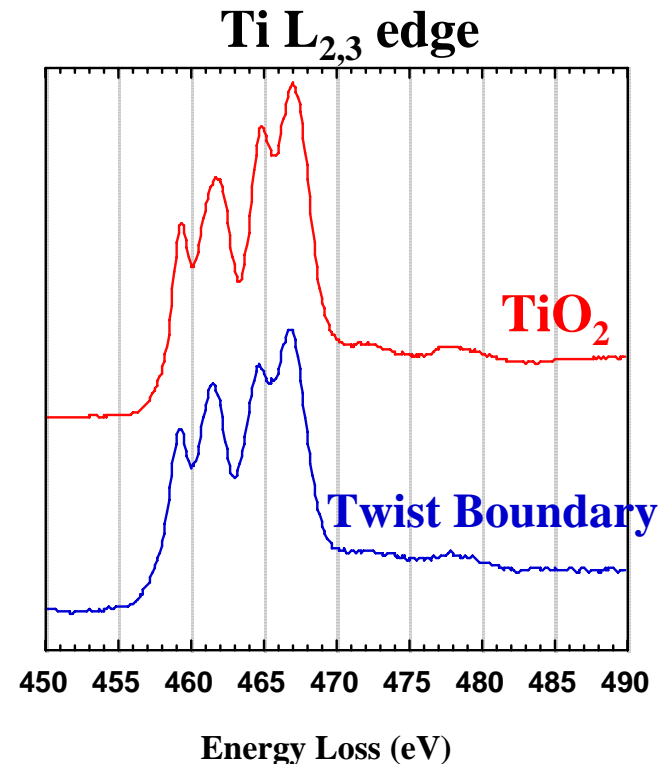
Ti L$_{2,3}$ edge from twist boundary closely matches edge structure of TiO$_2$ standard (Ti^{4+}).

Data courtesy Seth Taylor, Northrup Grumman

ELNES - Oxidation states

Identification of oxidation state

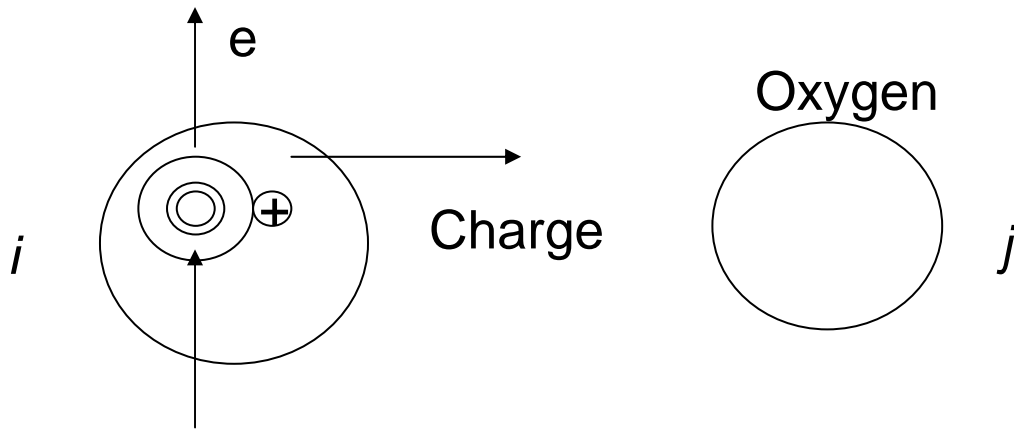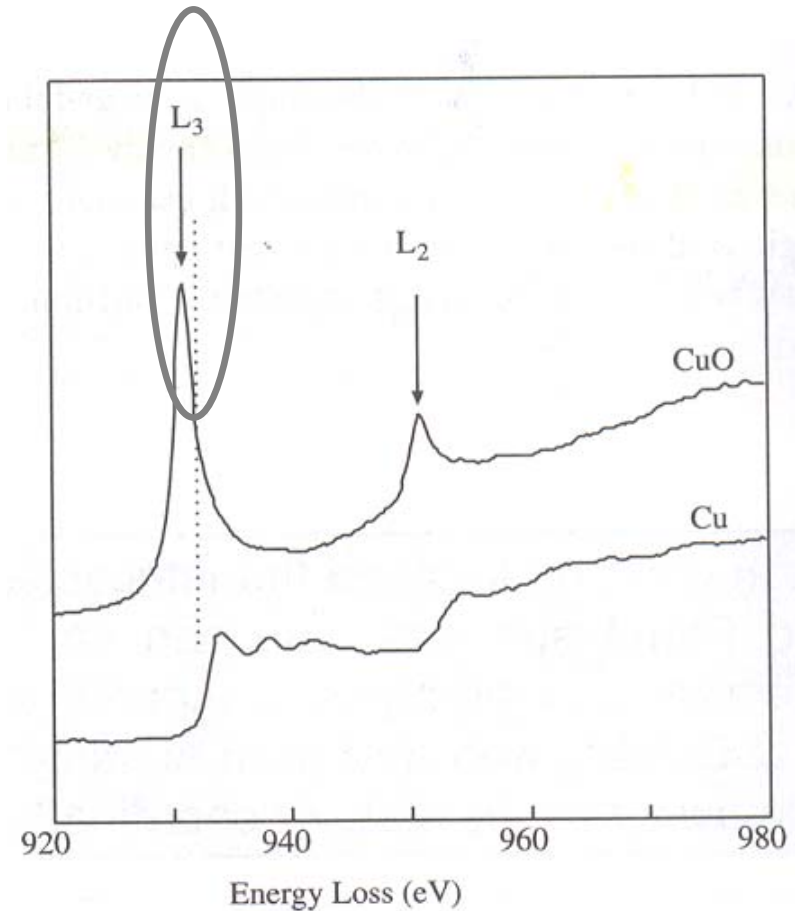**Chemical shift**: **Charge transfer from atom i to j due to oxidation by atom j reduces "screening effect" on the hole**
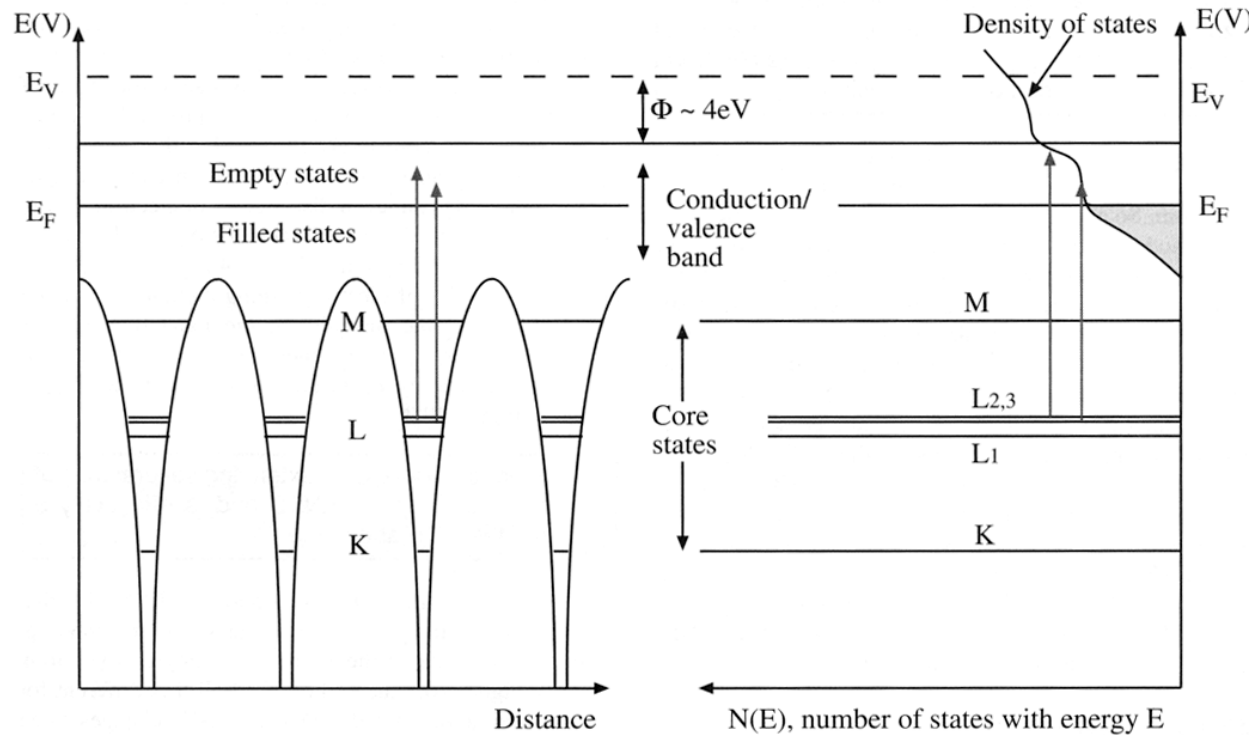→ **decrease kinetic energy**
→ **increase binding energy**
$(E_{KE} = h\nu - E_B, \quad E_{KE}\downarrow \quad \rightarrow \quad E_B\uparrow)$

ELNES / EXELFS

Near edge structure probes DOS in conduction band (ELNES)

– Increasing well understood, experiments becoming more routine

Extended structure probes chemical bonding (EXELFS)

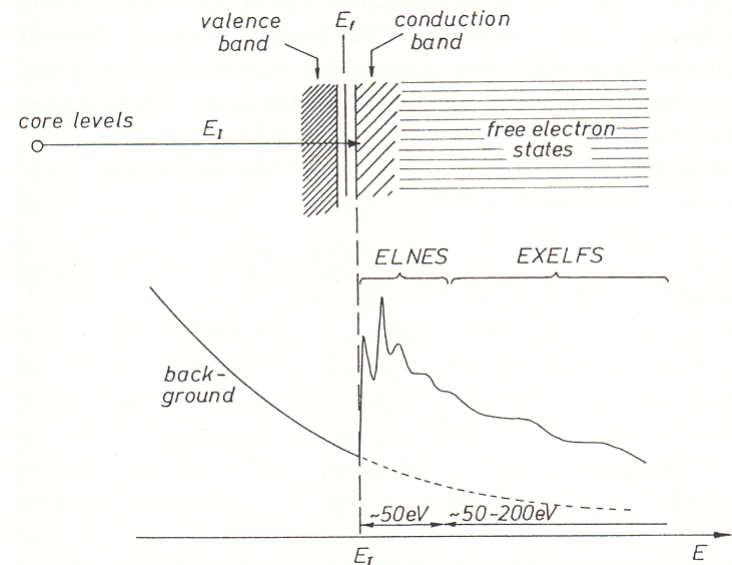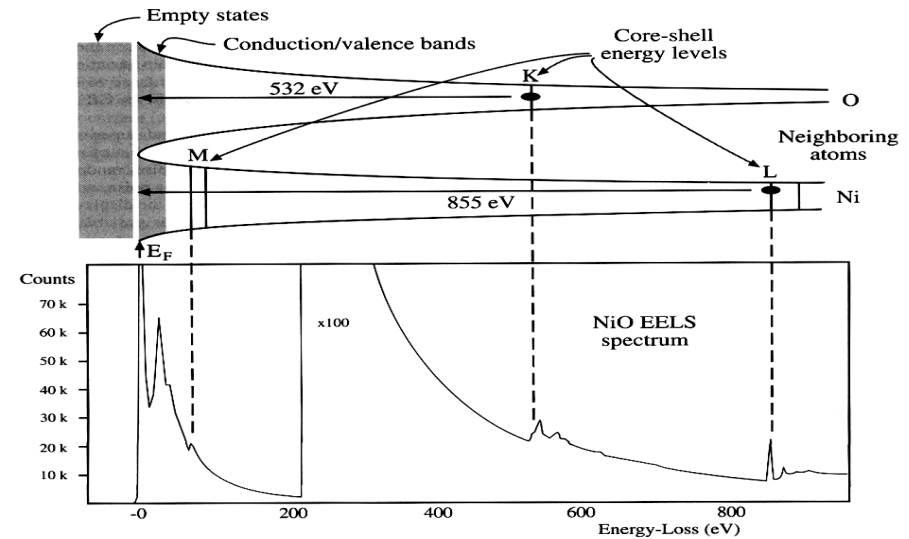– This is still largely a research topic in and among itself

EELS vs. Band structure

EELS maps empty states above the Fermi level

The electrons that are ejected from the core levels by the incident electron can scatter only into available states

Thus, the energy imparted by the incident electron to get them to make these transitions reflects the density of available states in the sample

Quantitative EELS

It is possible -- in limited cases -- to perform quantitative measurements of compositions using EELS

But it is difficult. Requires:

- Thin sample: good background subtraction

- Well separated edges

- A thoroughly calibrated and understood system (convergence angle, collection angle, beam current, etc.)

- In short: this is something that takes effort, knowledge, persistence and skill

Energy filtered imaging (EFTEM)
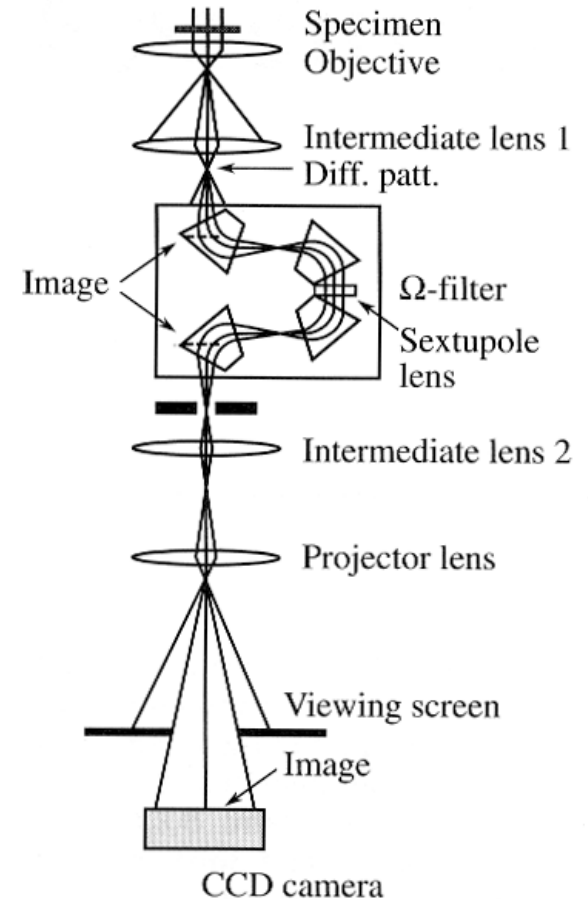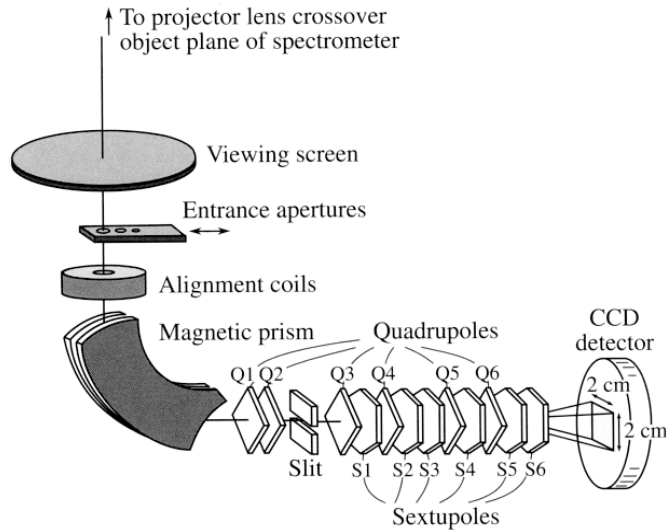
Additionally, can image inelastically scattered electrons

Spatial distribution of chemistry possible
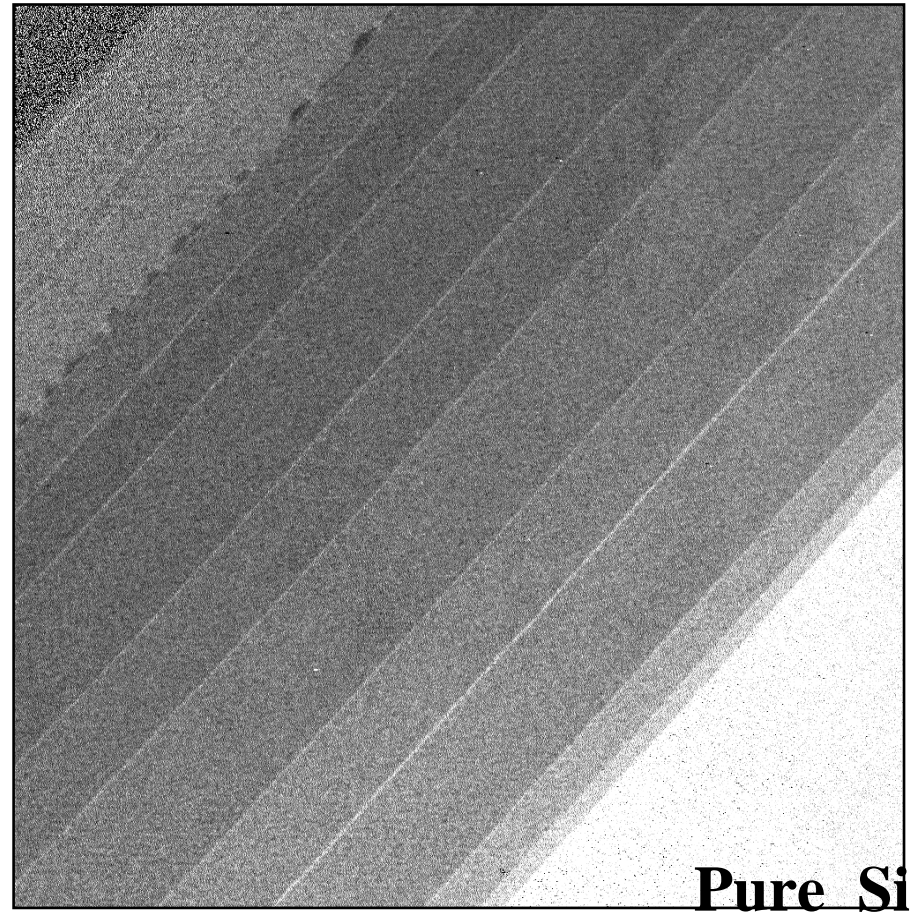
- High spatial resolution
- Short collection time

EFTEM - example

From an Omega filtered machine

Graded SiGe multilayer, note Si layer in between - only two monolayers

Single monlayer detection has been demonstrated

Rapid acquisition, high counts, quantifiable with work

Pure Si

Conclusions

AEM allows high spatial resolution determination of the chemistry of a material

EDS:

- **Quantifiable, simple, be careful of artifacts**

EELS:

- **Very powerful, harder to quantify, more than just chemistry$\Rightarrow$ DOS, bonding**

EFTEM:

- **Rapid spatial distribution of elements**

References

"Transmission Electron Microscopy" L. Reimer, Spriner, 1997

– Quite 'physics-ey'. But excellent, detail descriptions of scattering processes.

"Practical AEM in Materials Science"

– Older book, but still very useful if you're going to get into this area.

R.F. Egerton, Electron Energy-Loss Spectroscopy in the Electron Microscope, second edition (Plenum Press, New York, 1996).

– The EELS book.

Energy-Filtering Transmission Electron Microscopy, L. Reimer, Springer, 1994

– A compendium of chapters on EFTEM