Analytical electron microscopy

Lecture 12

Outline

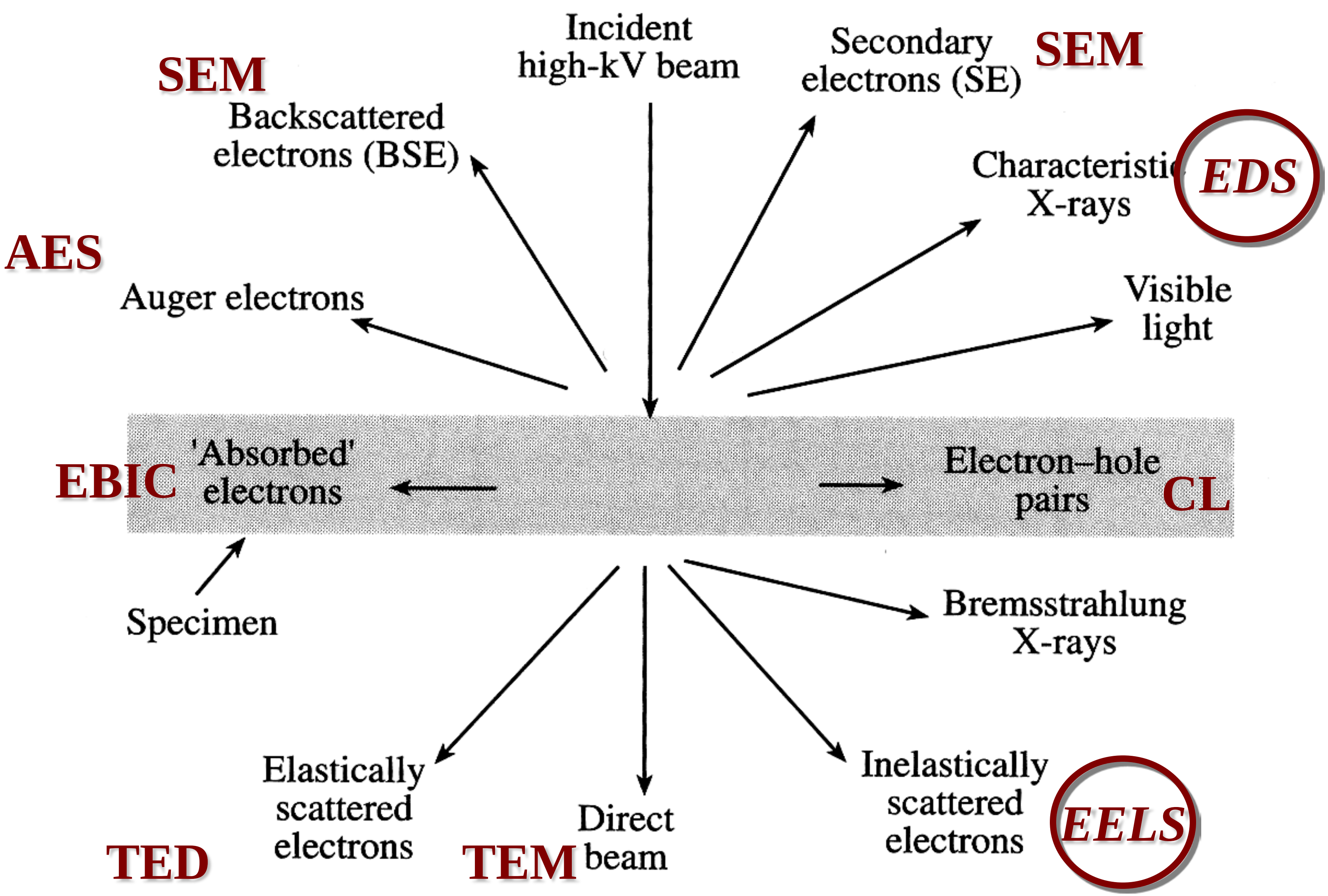
Elastic and inelastic scattering of electrons

Energy dispersive spectroscopy (EDS)

Electron energy loss spectroscopy (EELS)

Energy filtered imaging (EFTEM)

Scattering in the TEM



Energy Dispersive Spectroscopy (EDS)

Ionization cross sections

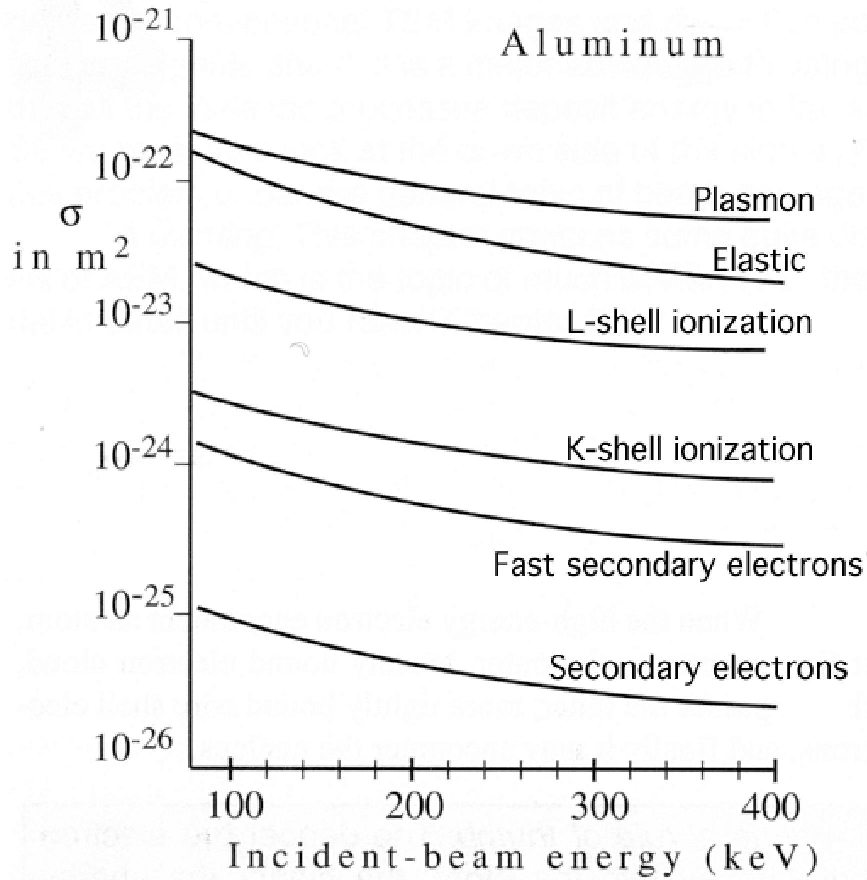
What are the chances of each type of interaction?

Plasmons most common, elastic common, ionization interactions, less so.

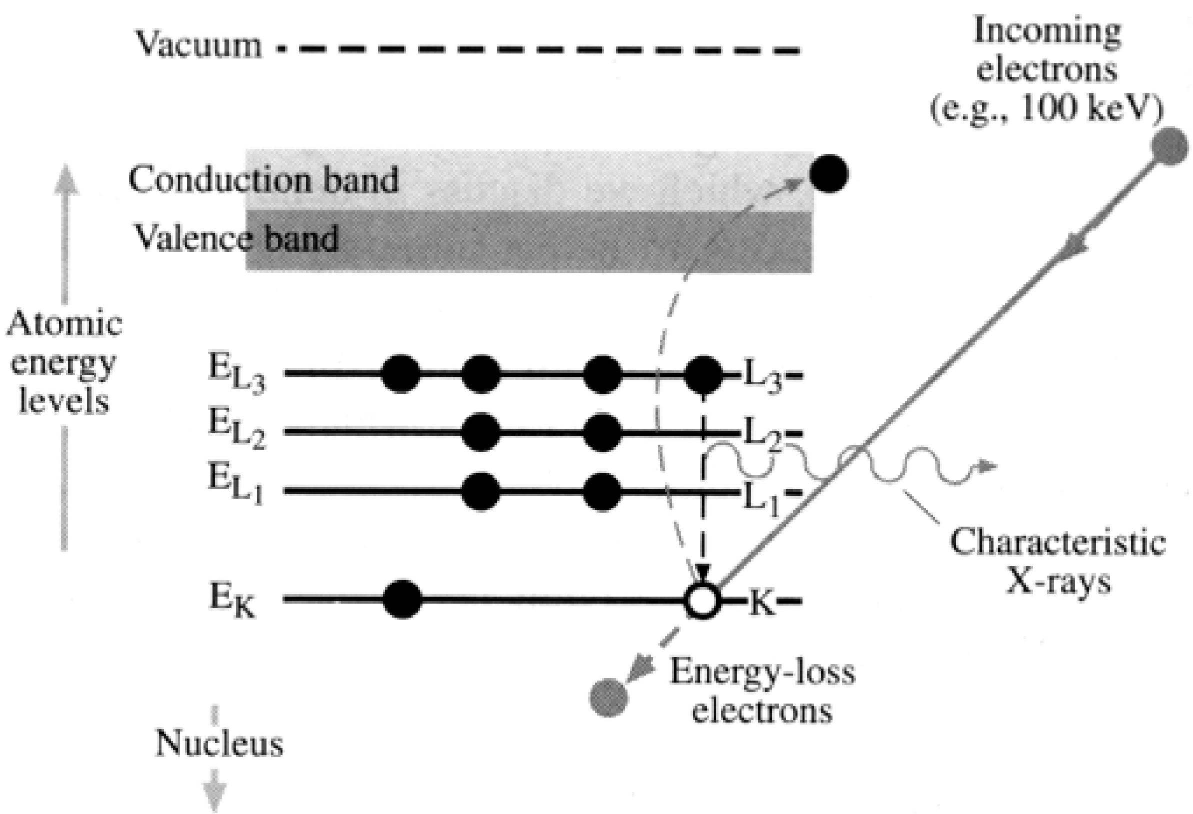
O, N, M, L, K …

- Makes sense

But generally, we use K, L, & M



X-ray production



High energy electron scatters inner shell electron ($E > E_c$)

Atom ionized. Can return to ground state by outer shell electron filling empty state.

Accompanied by either x-ray emission or Auger electron emission.

- **Characteristic of the particular energy states of the atom!**

Possible electron transitions that generate X-rays

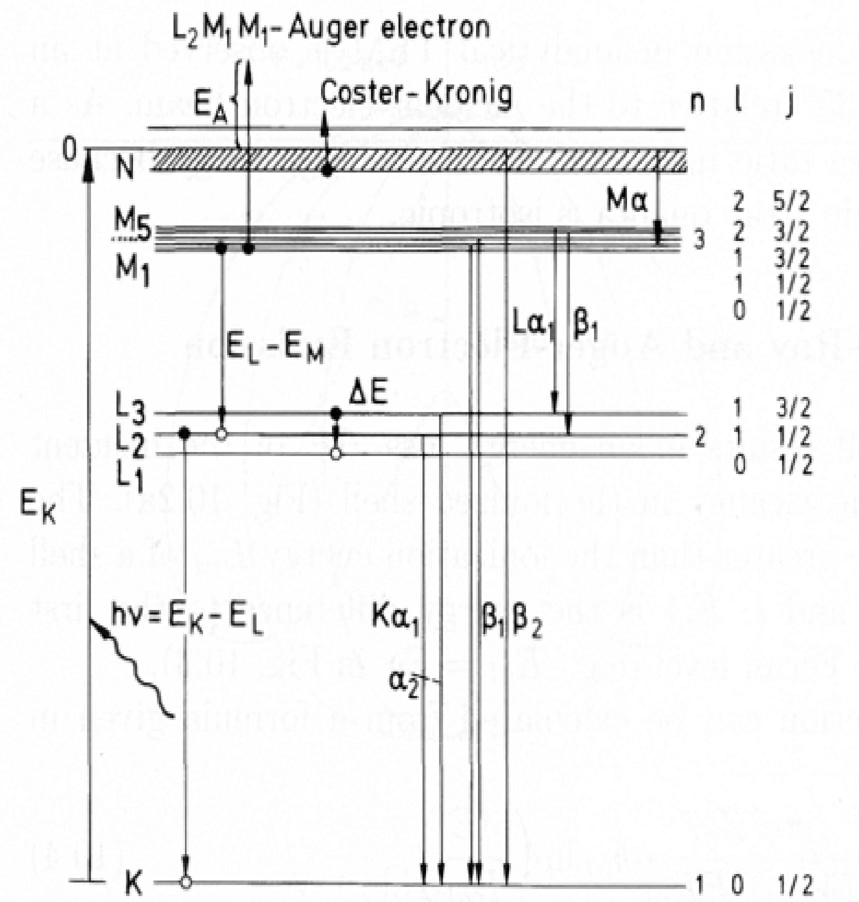
Very complex process with many possible transitions

Not all these can be observed in TEM

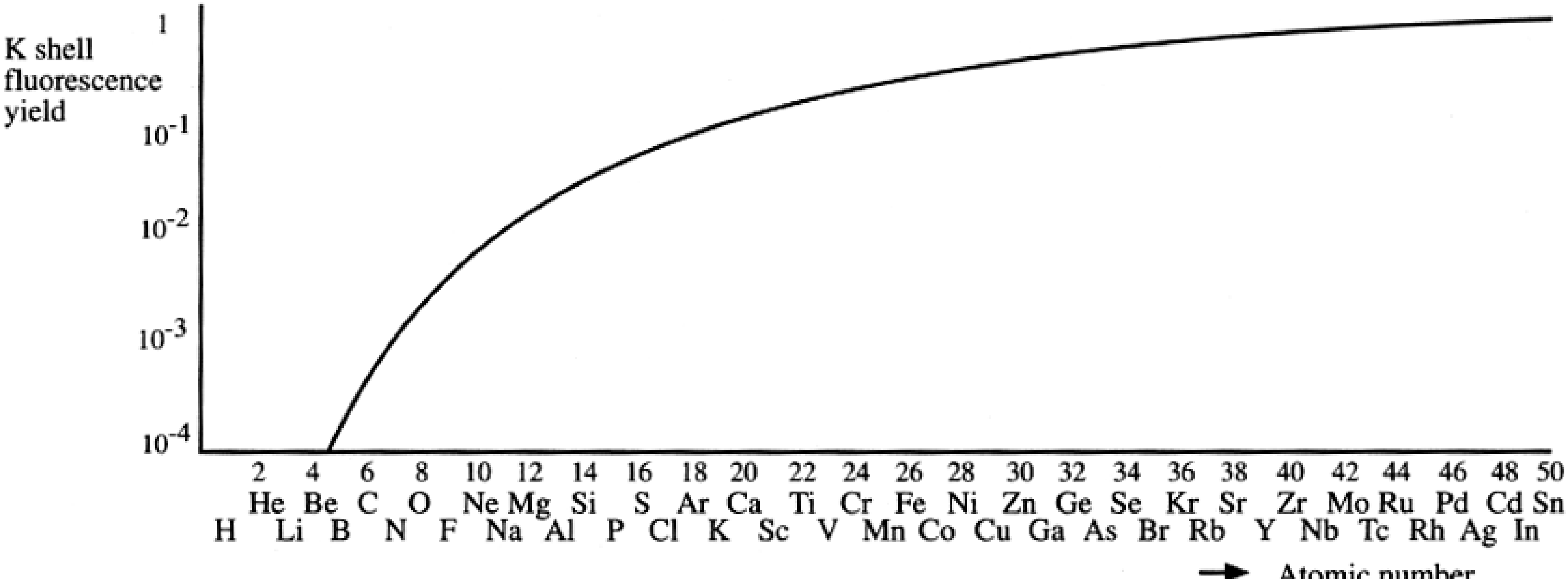
Commonly observe:

- K, L, M

Resolution of spectrometer, nature of edges determines if α, β, γ, δ can be resolved.



Fluorescence yield



Key point

- EDS cannot be used for elements below boron

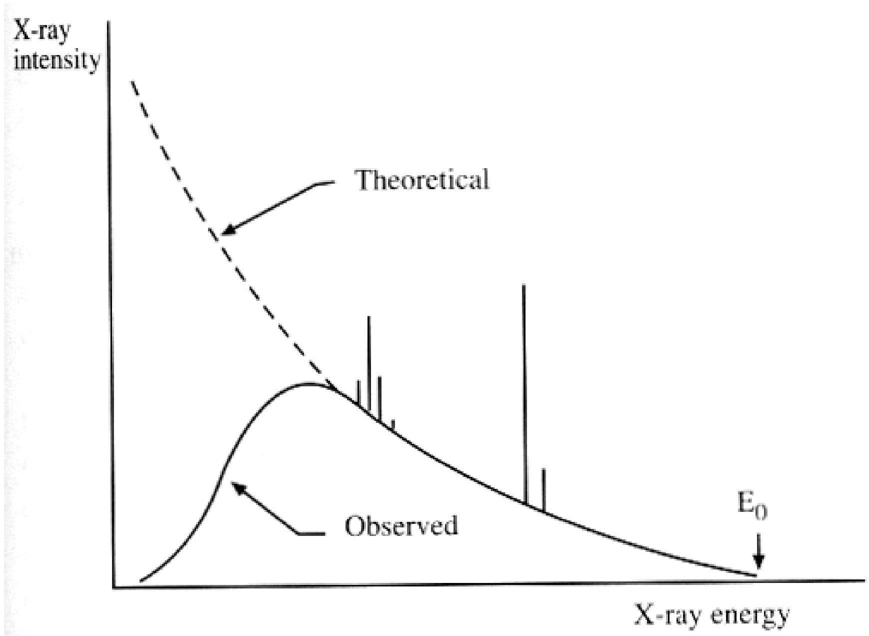
Can be used for C, N, O but it's difficult

- Probably best to do EELS instead

Continuous Background
Bremsstrahlung

Electron interaction with nucleus results in continuous background radiation

At low energies, attenuated by absorption by specimen & detector



Excited volume

Where do the x-rays come from in the specimen?

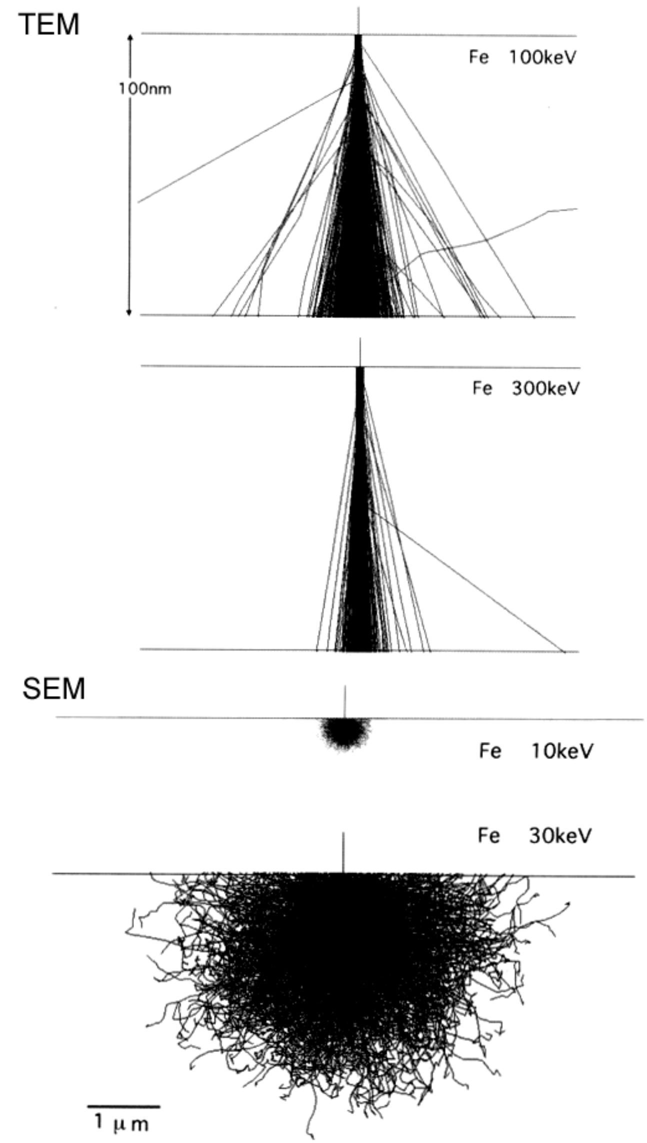
Depends …

TEM:

- 200 to 300 kV normally
- Scattering quite localized to electron probe

Not so in SEM of bulk materials

- Comparatively poor spatial resolution

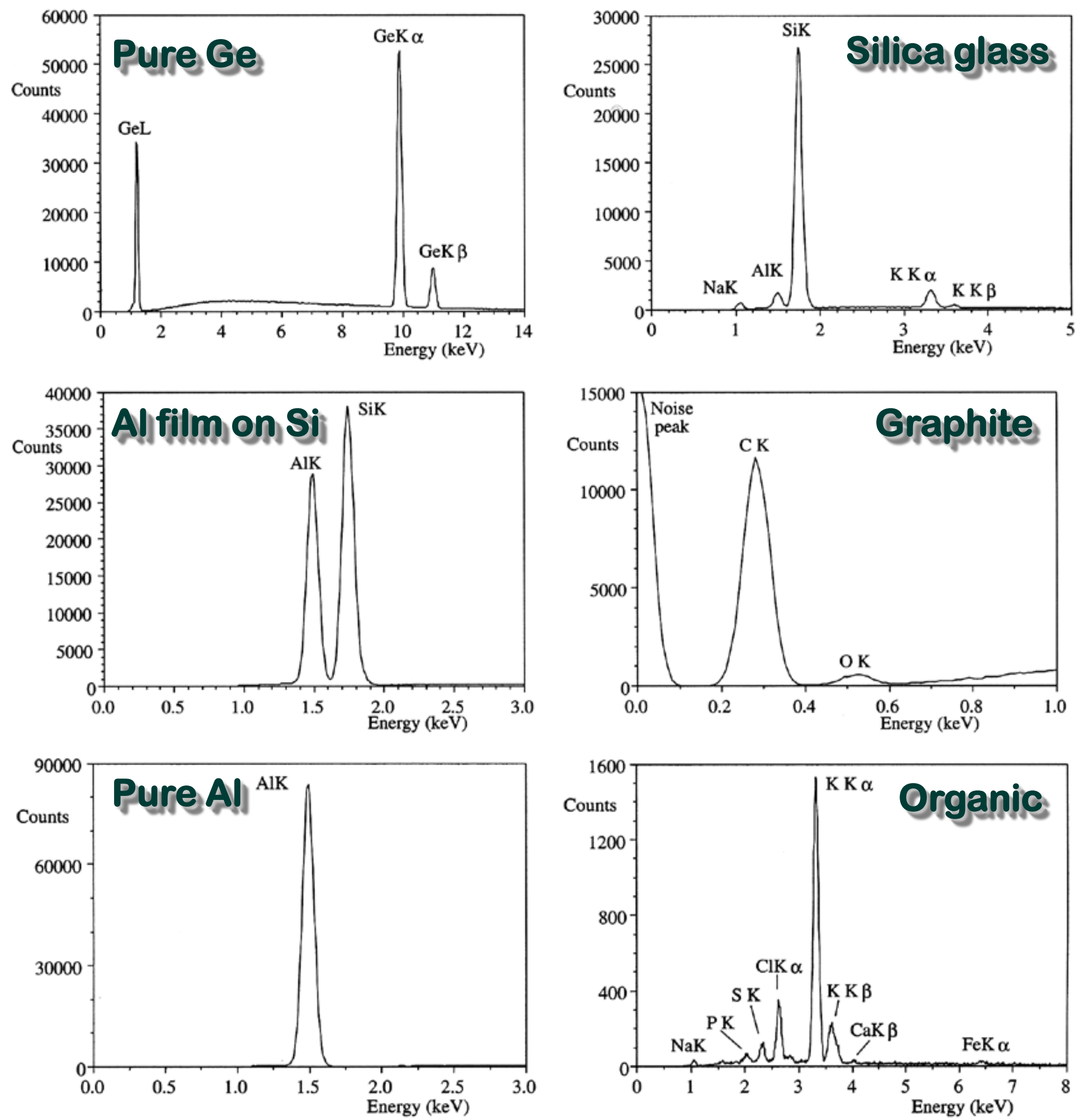


Example x-ray spectra (EDS)

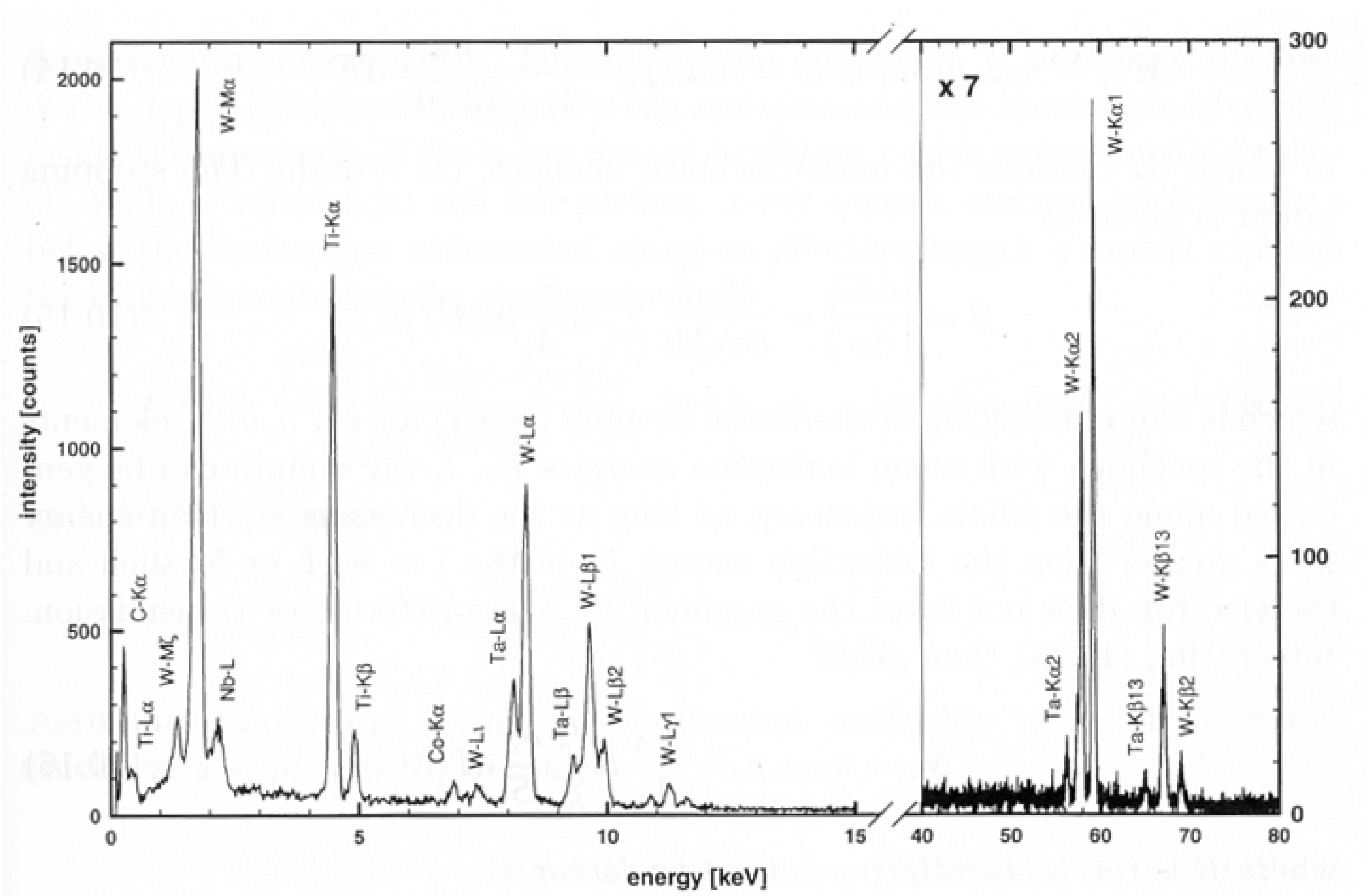
Several examples of EDS spectra

Note:

- Relative # of counts
- Energy range of each spectrum



EDS Example



x 7
intensity [counts]
energy [keV]
2000
1500
1000
500
0
300
200
100
0
0
5
10
15
40
50
60
70
80
C-Kα
Ti-Lα
W-Mζ
W-Mα
Nb-L
Ti-Kα
Ti-Kβ
Co-Kα
W-Lι
Ta-Lα
W-Lα
Ta-Lβ
W-Lβ1
W-Lβ2
W-Lγ1
Ta-Kα2
W-Kα2
W-Kα1
Ta-Kβ13
W-Kβ13
W-Kβ2

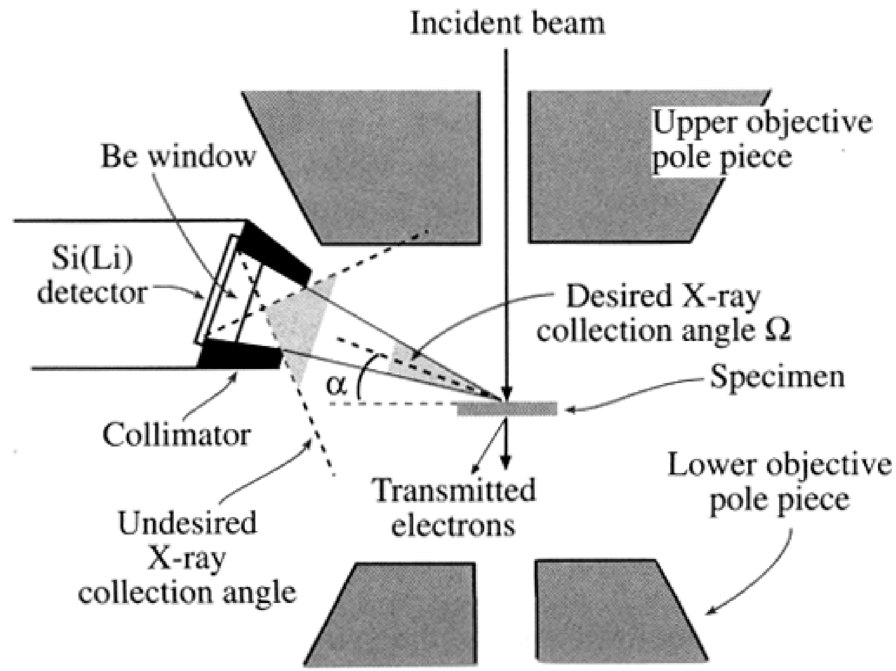
EDS geometry

X-rays produced from all angles.

The detector is a small crystal, and subtends only a small angle.

EDS is not efficient.

Specimen tilted to the appropriate angle to maximize collection efficiency.



X-ray spectrometers

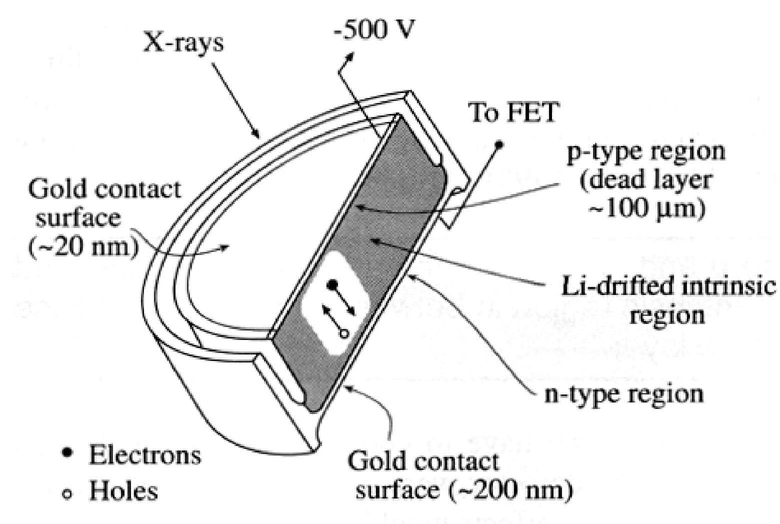
Detector: Li doped (drifted) Si reversed bias p-i-n device

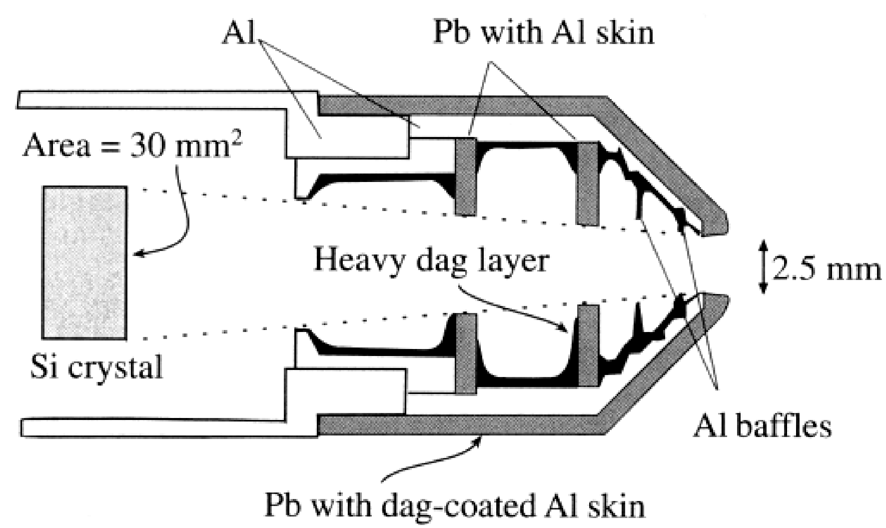
X-rays enter, create e-h pairs

Number of e-h pairs generated directly proportional to x-ray energy

These are swept to the collector contacts

Done in series, but quickly. Appears parallel





Spurious x-rays

Recall, x-rays generated at all angles.

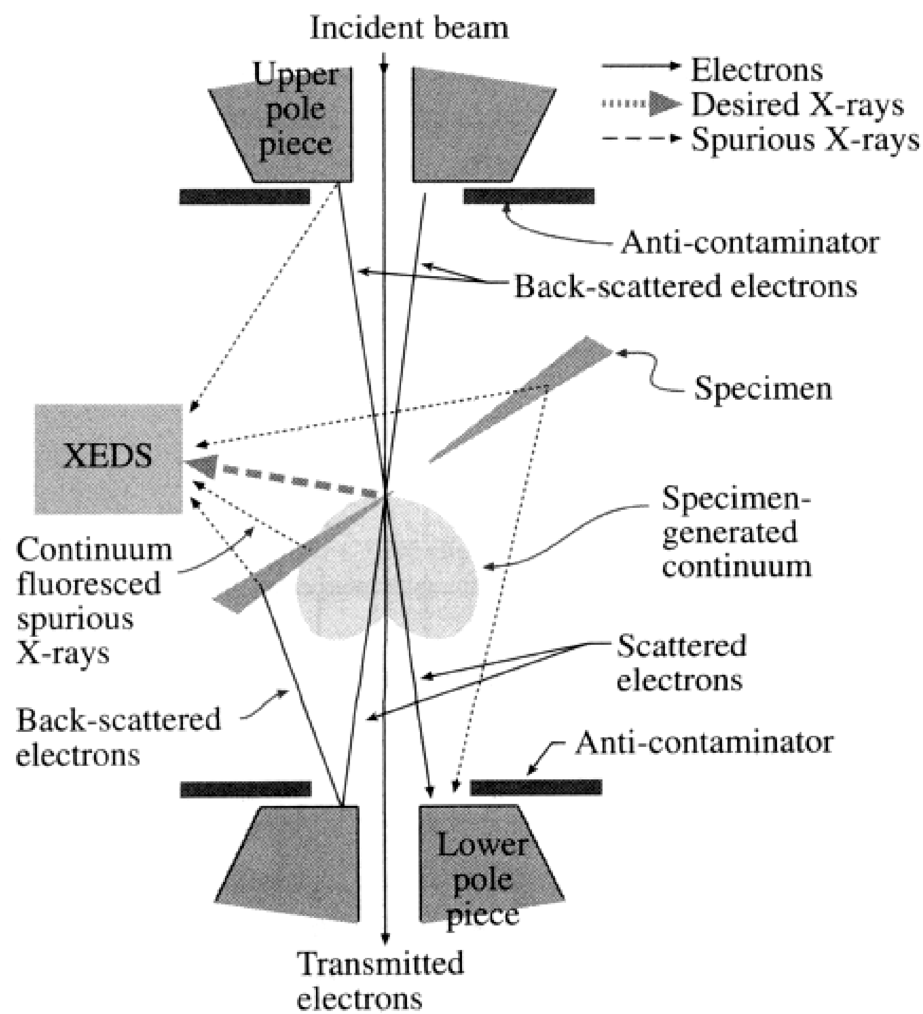
They are high energy.

Can excite further x-ray production from:

- Microscope parts
- Sample holder
- Other regions of sample

Be careful!

- Do not modify microscope without working w/ radiation safety technicians



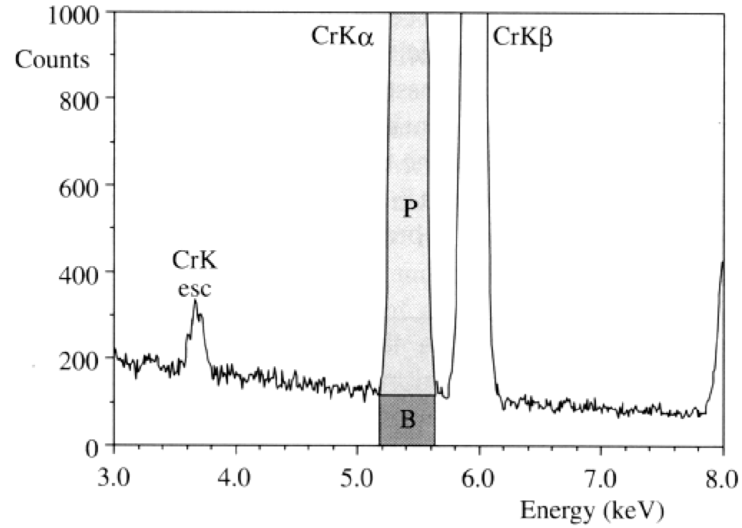
Quantification
background subtraction

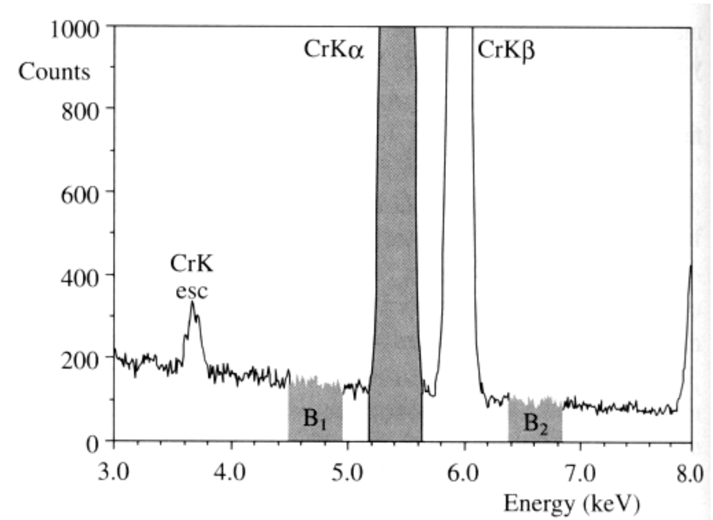
EDS is readily *quantifiable*.

- i.e. can determine the relative proportion of one element to another.

Need to subtract the Bremsstrahlung background to find real number of counts.

Most modern software does this for you.





Quantification
Cliff-Lorimer method

Relatively simple idea - it works!

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}$$

But this means you have to have a *standard.*

Standards:

- Ideally, well characterized single phase
- Thin sample that is representative, stable
- Want very high counts: 10^4 above background

k_{AB} is a function of the EDS / TEM combination.

- It is **NOT** a constant (but can be theoretically estimated)
- Best if experimentally determined for a given system
  - TEM + Detector + Geometry

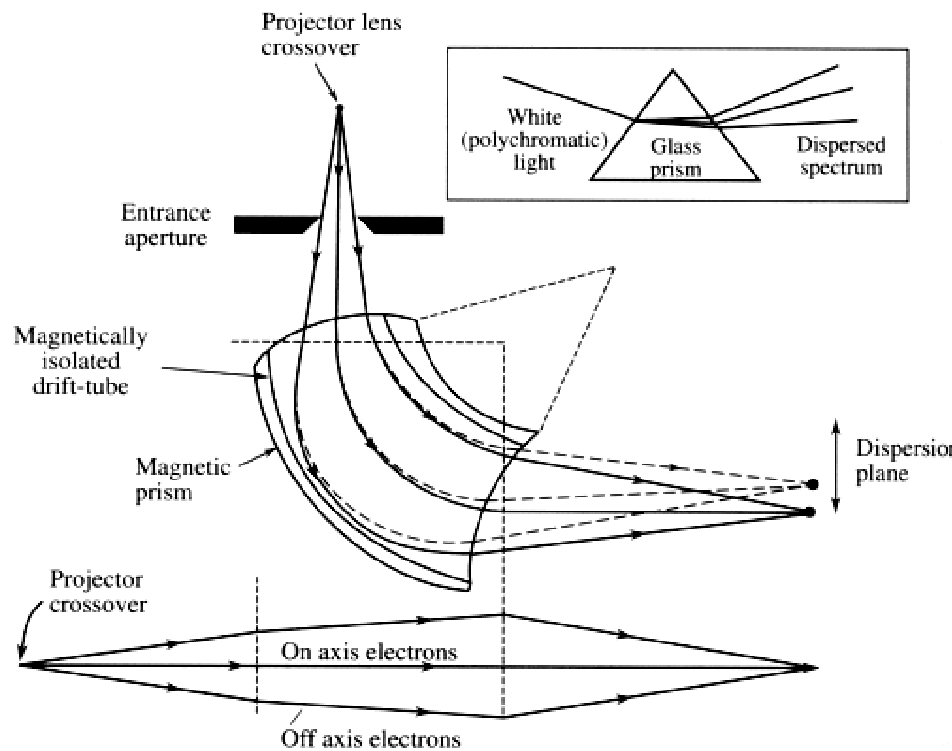
Electron Energy Loss Spectroscopy (EELS)

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.



What an EELS edge looks like

Well, it kind of depends…

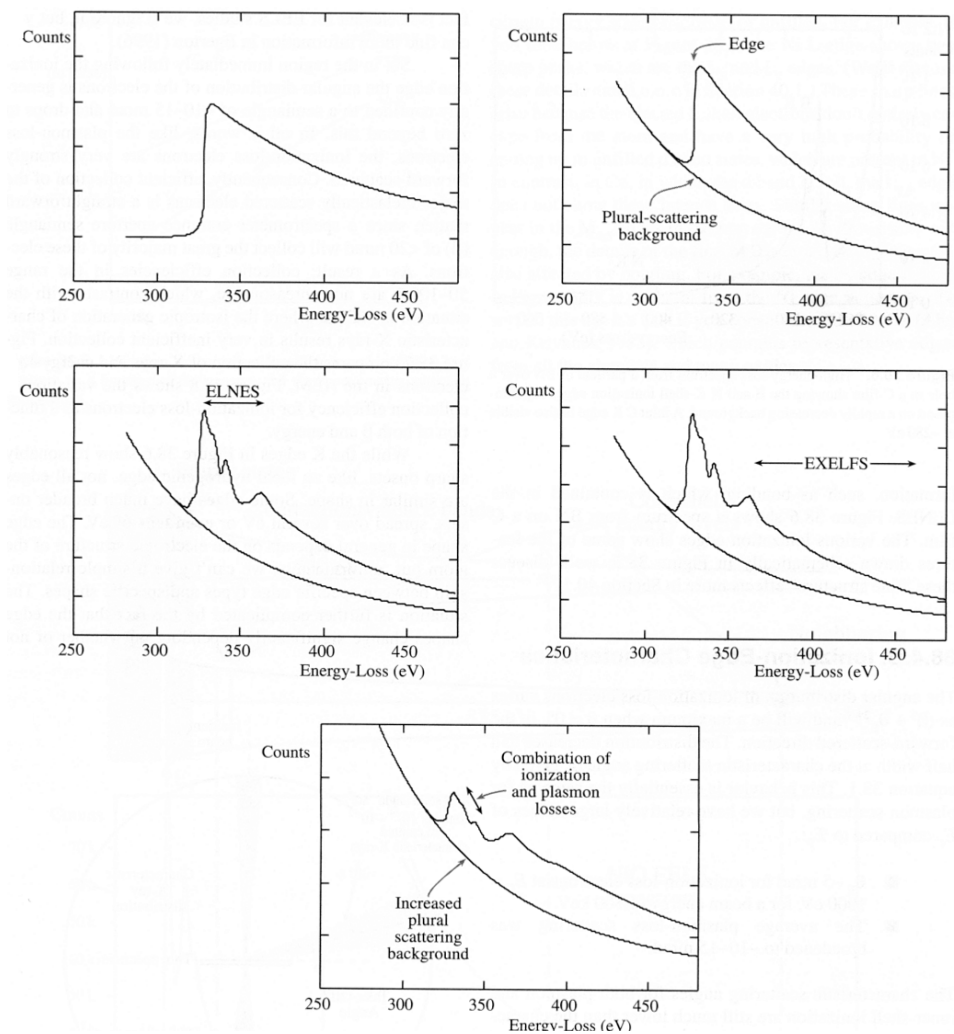
How thick is your sample?

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

Plasmon peaks can be convoluted

So ⇒ use a *thin* sample

- **< 1 mfp, ≈ 500 Å is great**



Example EELS Spectra

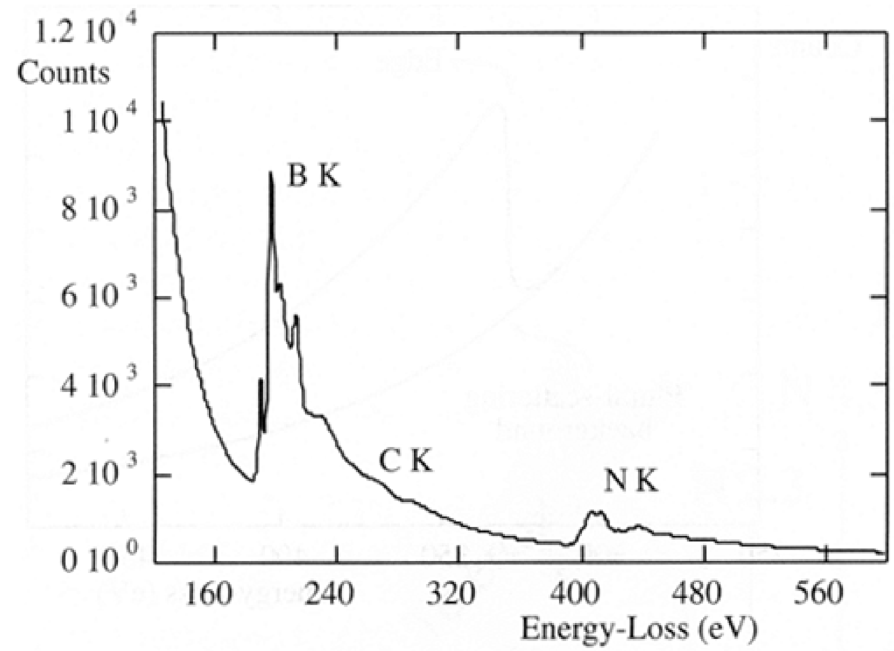
This is from boron nitride (with some carbon contamination)

Note sharp onset of the K-edges.

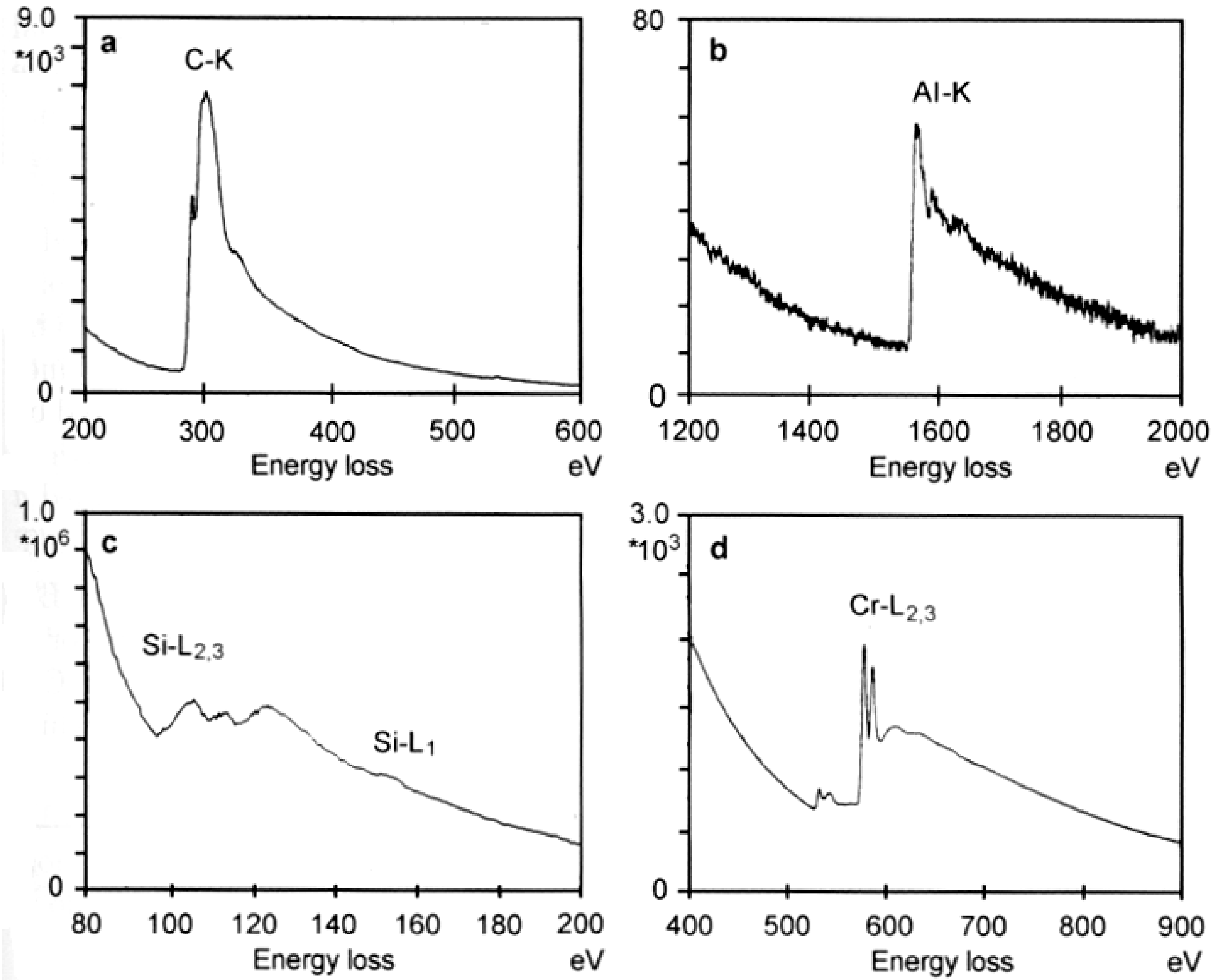
Note the 'white lines' in the boron edge.

Broad range of energy

Huge number of counts vs. those in EDS

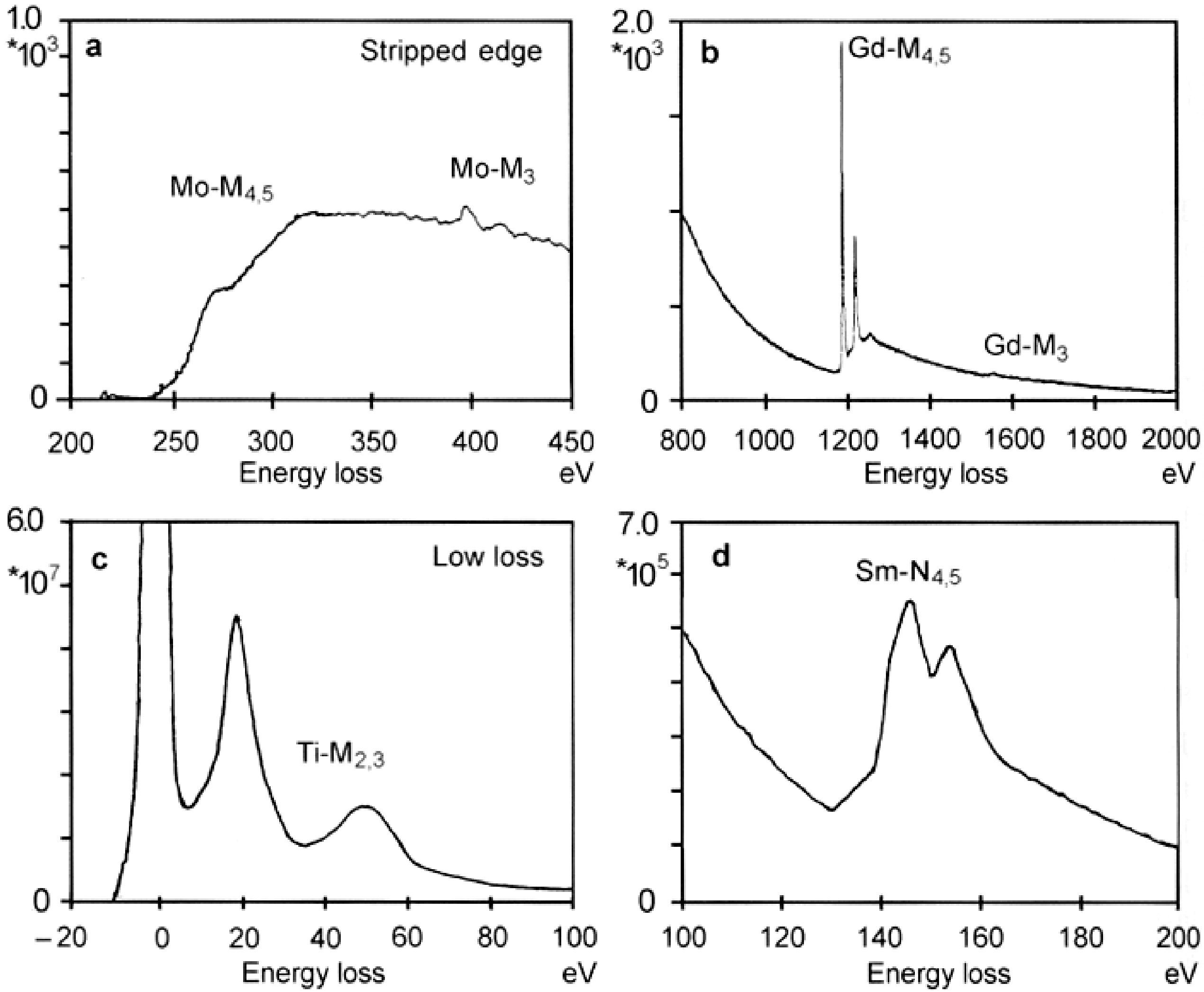


K and L Edges



a
C-K
9.0
*10^3
0
200
300
400
500
600
Energy loss
eV
b
Al-K
80
0
1200
1400
1600
1800
2000
Energy loss
eV
c
Si-L2,3
Si-L1
1.0
*10^6
0
80
100
120
140
160
180
200
Energy loss
eV
d
Cr-L2,3
3.0
*10^3
0
400
500
600
700
800
900
Energy loss
eV

M and N edges



1.0
*10³
a
Stripped edge
Mo-M4,5
Mo-M3
0
200 250 300 350 400 450
Energy loss
eV
2.0
*10³
b
Gd-M4,5
Gd-M3
0
800 1000 1200 1400 1600 1800 2000
Energy loss
eV
6.0
*10⁷
c
Low loss
Ti-M2,3
0
– 20 0 20 40 60 80 100
Energy loss
eV
7.0
*10⁵
d
Sm-N4,5
0
100 120 140 160 180 200
Energy loss
eV

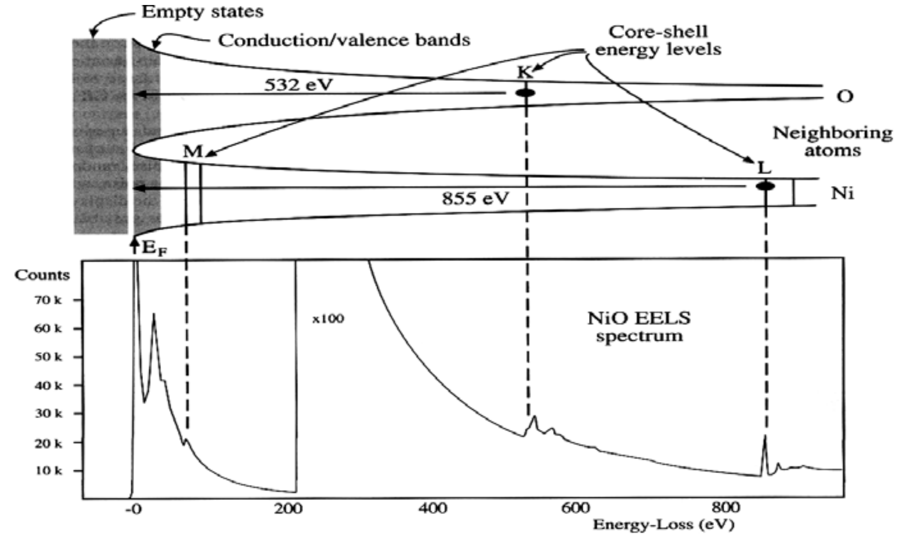
EELS vs. Band structure

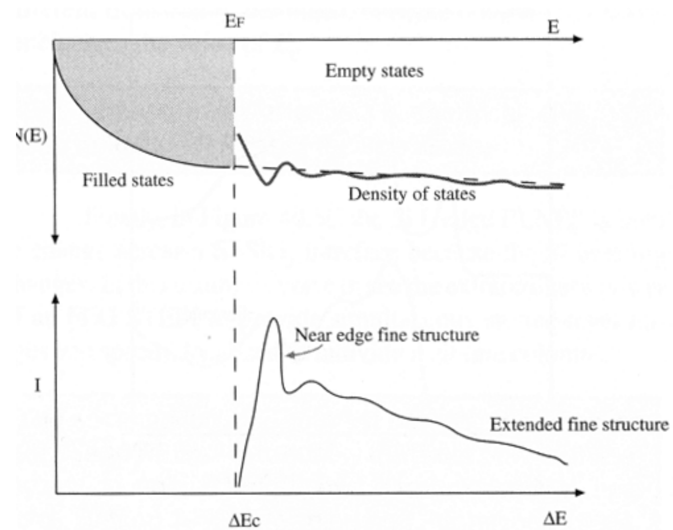
EELS maps empty states above the Fermi level.

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.



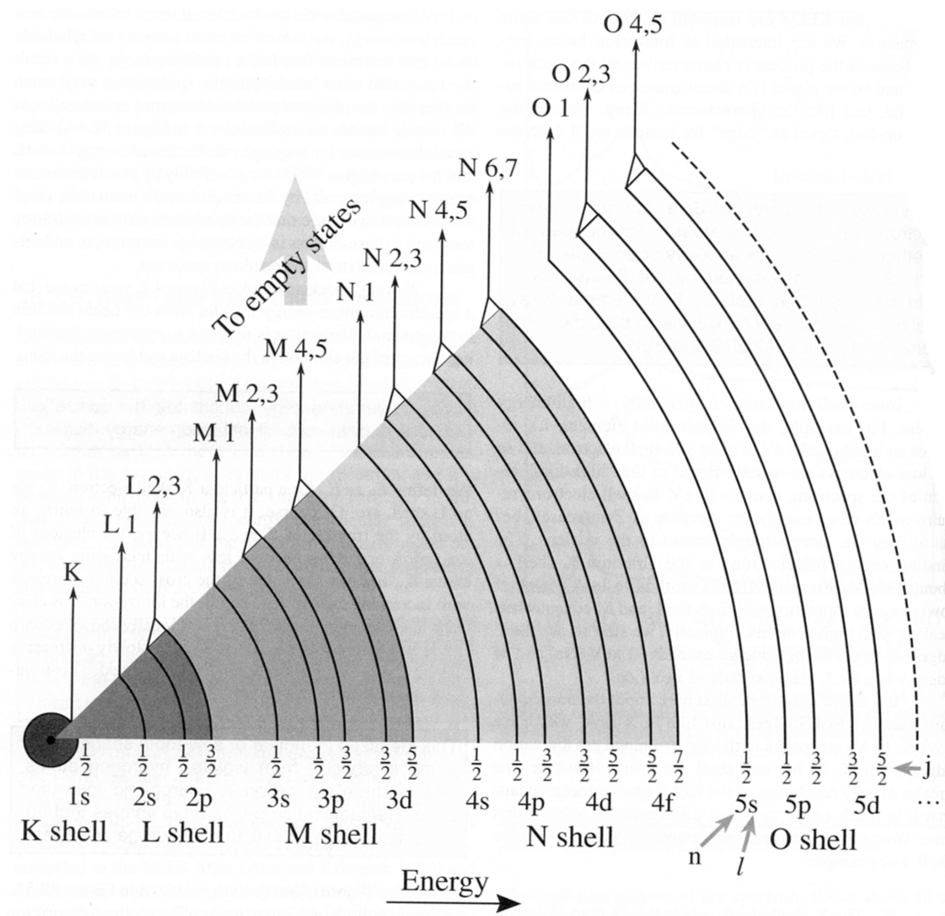


Allowed transitions

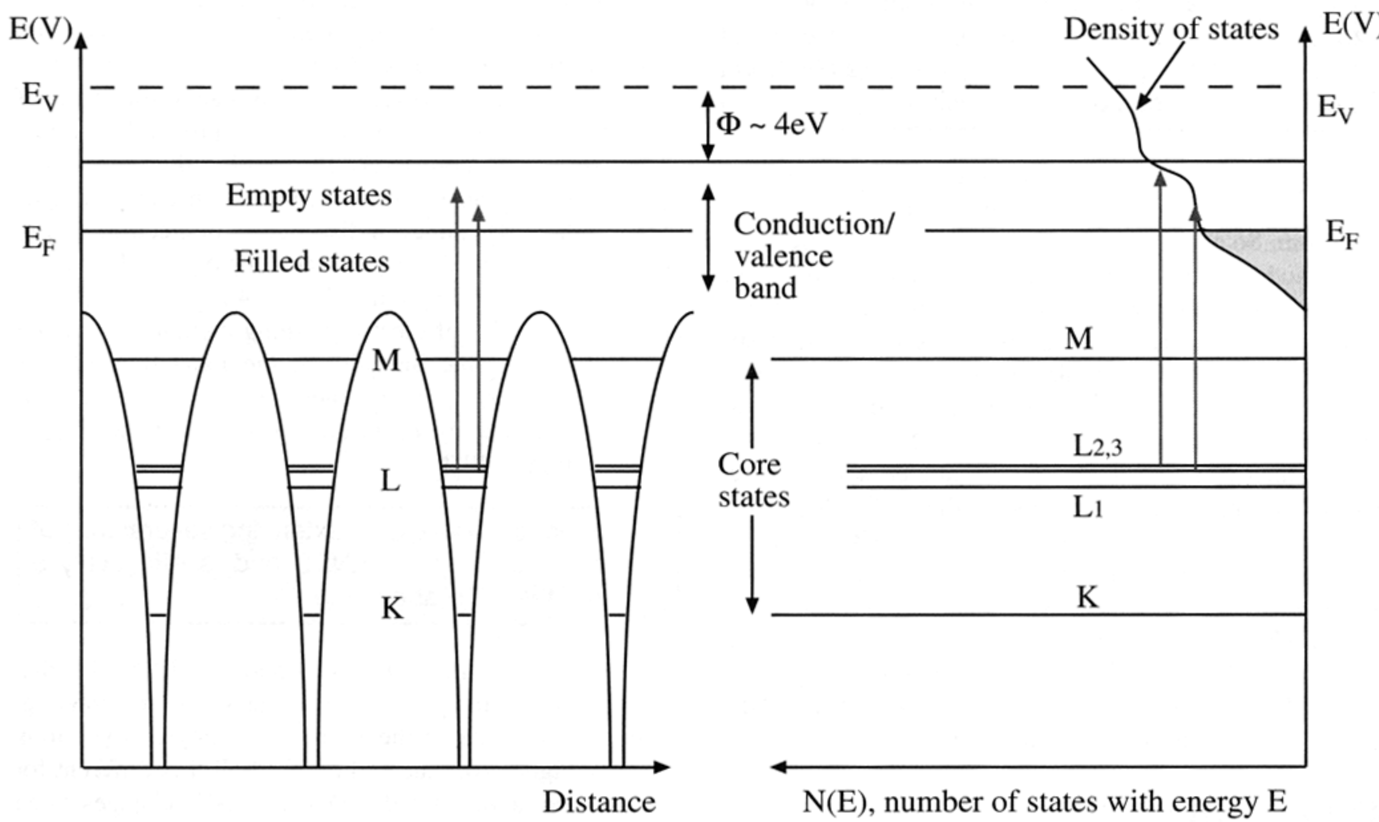
Like EDS, the observable edges can be directly related to the electron shells.

You will observe K, L, M edges

Depends on the atomic weight of your material, which you see.



ELNES / EXELFS



Near edge structure probes DOS in conduction band (ELNES)

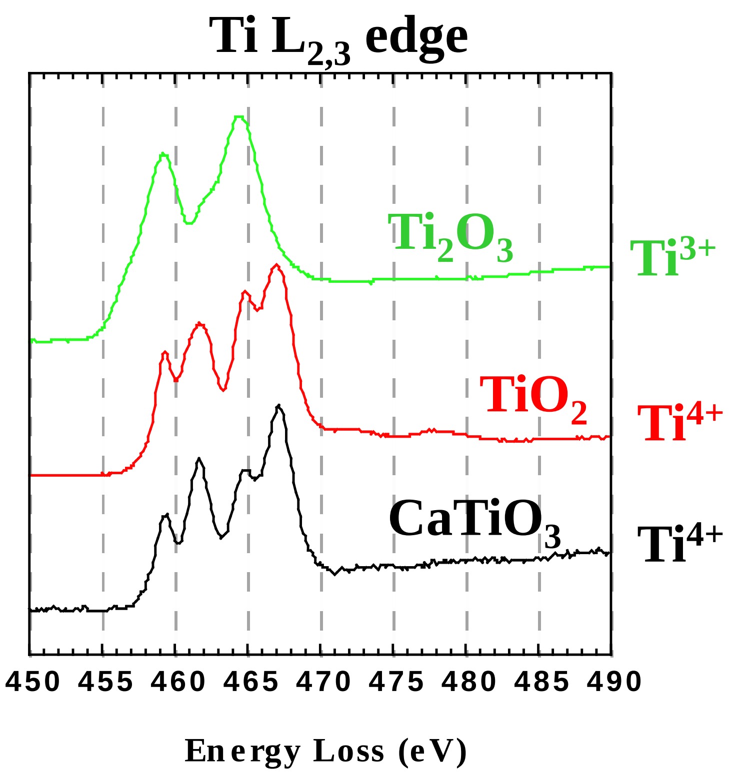
- Increasing well understood, experiments becoming more routine

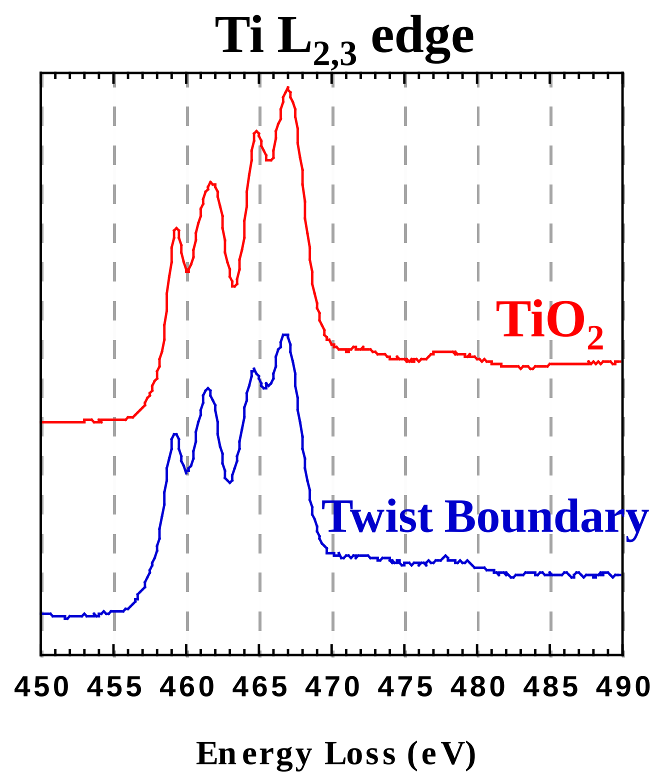
Extended structure probes chemical bonding (EXELFS)

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

ELNES - "Fingerprinting"

Ti valence determination using EELS





Ti $L_{2,3}$ edge from trivalent Ti_2O_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, GE Central Research

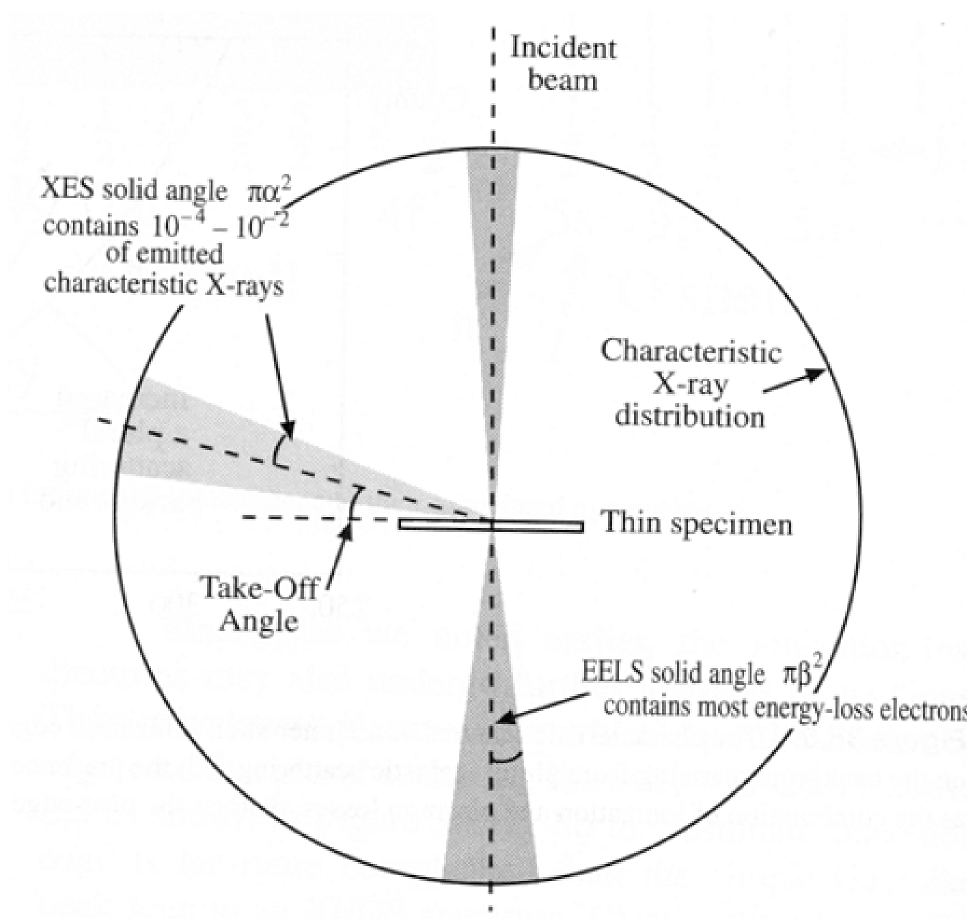
Comparison of collection EDS / EELS

As you've seen the number of counts in EELS >> EDS

Function of collection angle.

EDS collects small angular distribution of all emitted x-rays

Inelastic scattering of electrons is largely forward ⇒ most collected.



Spatial resolution

For best performance:

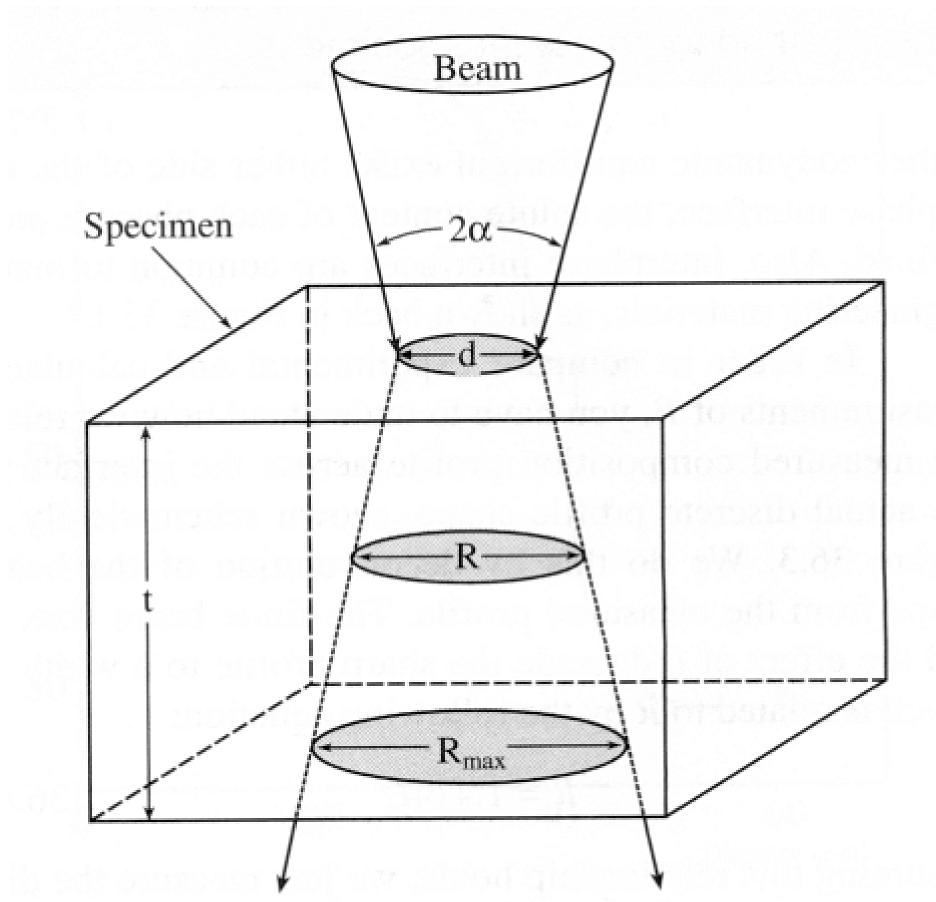
- Thin sample
- FEG: high brightness, coherent ⇒ small probe

Probe size:

- Thermionic: 2 nm
- FEG: < 1Å demonstrated, 2Å soon at NCEM

EDS: need to worry about beam spreading, spurious x-rays

EELS: can be same size as probe



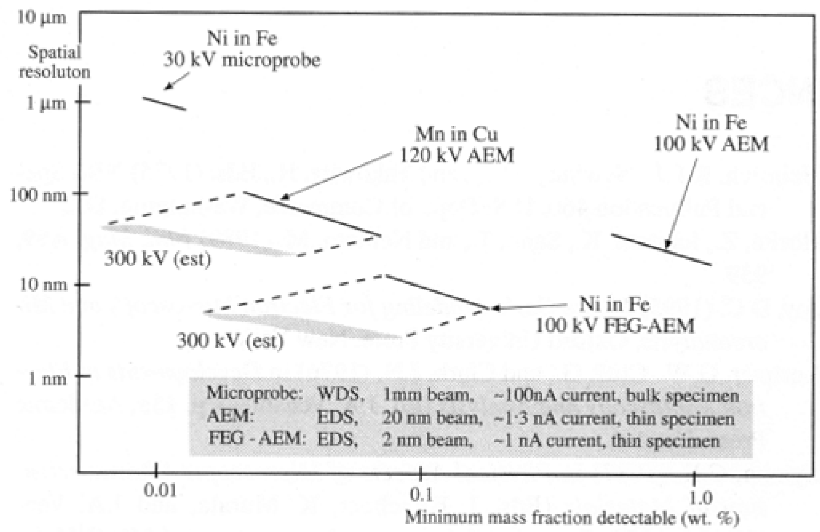
Sensitivity of EDS & EELS

"Minimum Mass Fraction" - minimum detectability

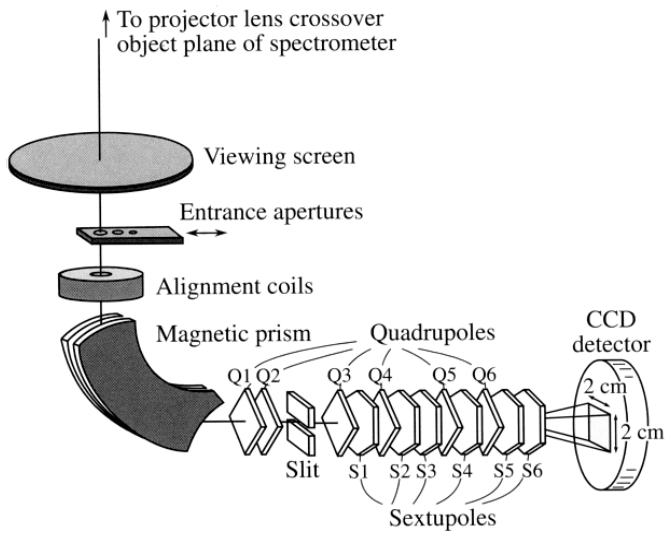
- 0.01% to 1% for EDS & EELS
- Depends on microscope & sample

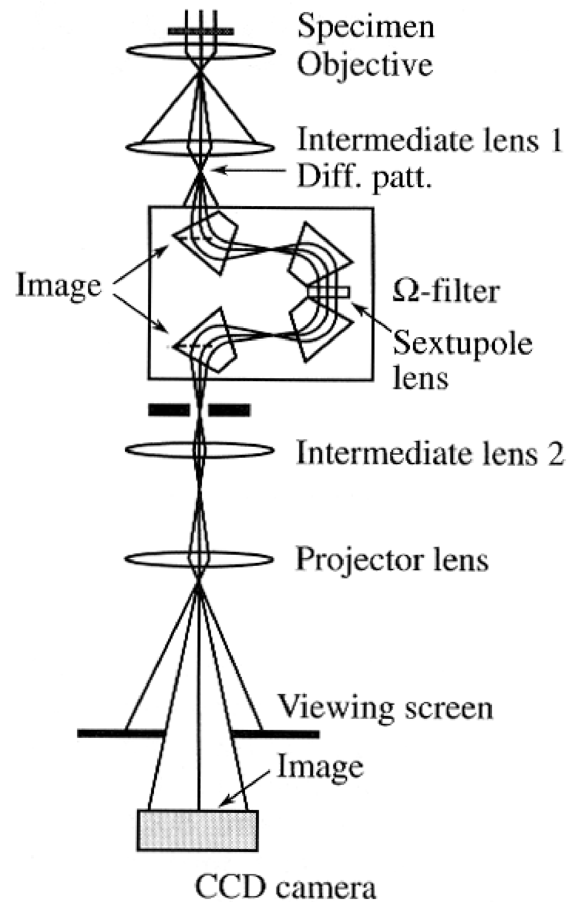
"Minimum Detectable Mass"

- We're talking about a *small* volume
- 10's to 100's of atoms do-able with EDS
- 100's of atoms with EELS.



Energy filtered imaging (EFTEM)





Additionally, can image inelastically scattered electrons

Spatial distribution of chemistry possible

- High spatial resolution
- Short collection time

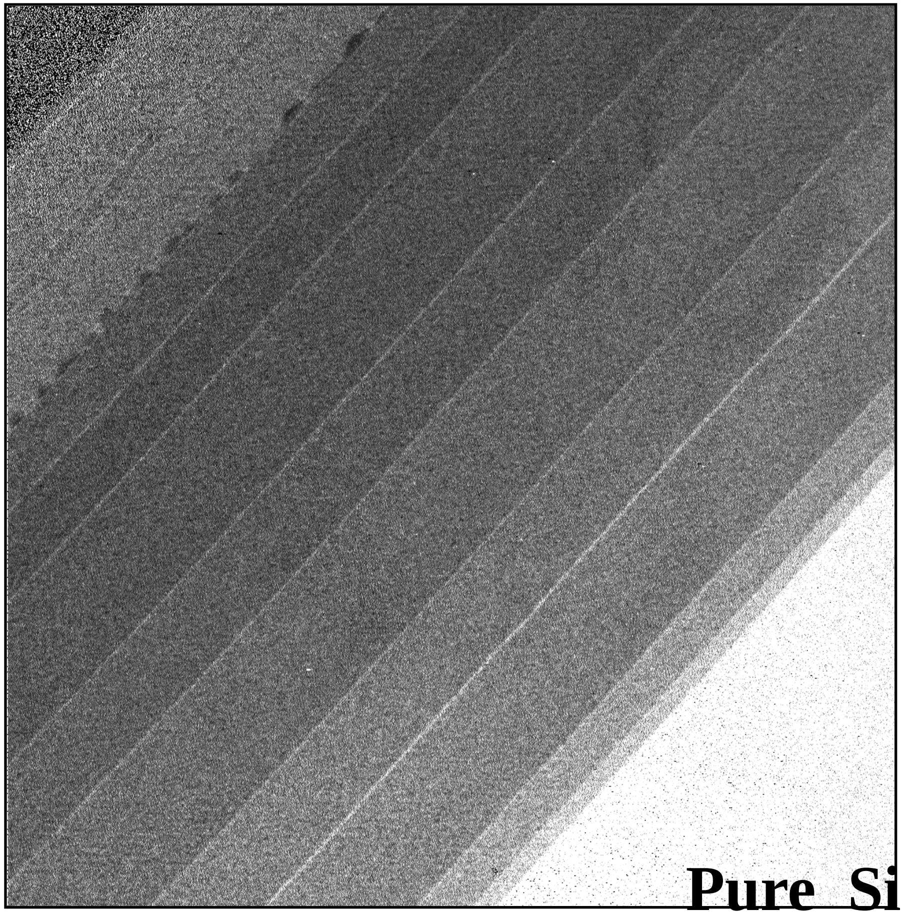
EFTEM - example

From an Omega filtered machine

Graded SiGe multilayer, not Si layer in between - only two monolayers.

Single monlayer detection has been demonstrated.

Rapid acquisition, high counts, quantifiable with work



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” D.B. Williams and C. B. Carter, Plenum Press, NY 1996.

- Great introductory text covering every major topic. Loads of references and figures.
- Spend the money for the hardbound text - indices and figure refs are only in Vol. 1 of softbound which is incredibly annoying.

“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.