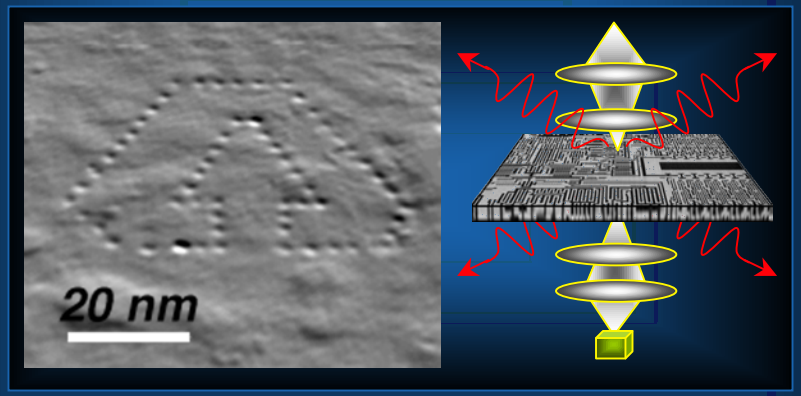
Introduction to EELS in the AEM

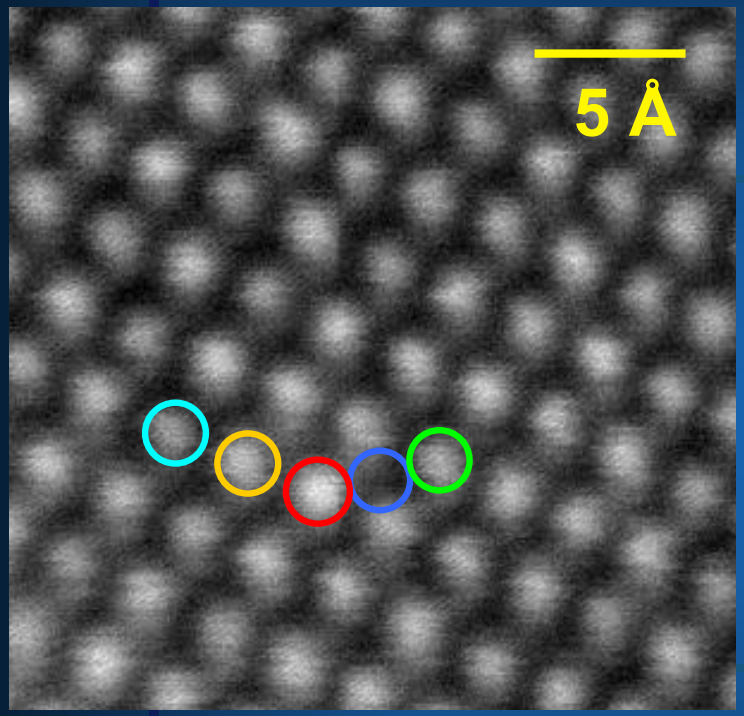


Nestor J. Zaluzec

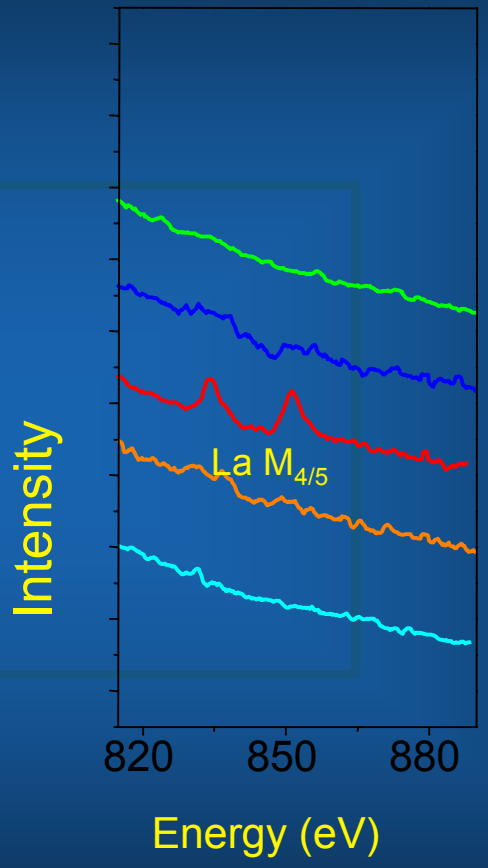
zaluzec@microscopy.com

zaluzec@aaem.amc.anl.gov

What are the Limits - Today?



La in $CaTiO_3$ grown by MBE

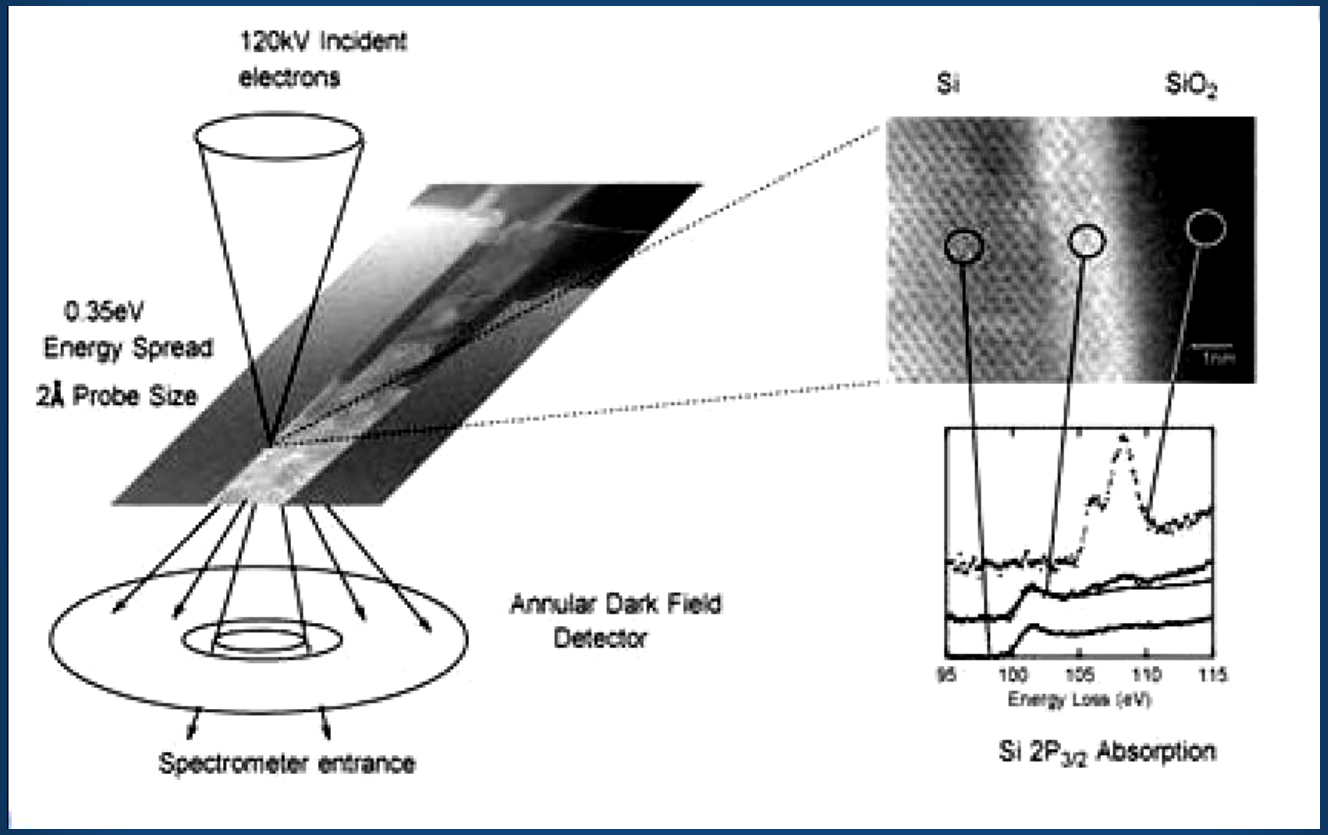


Spectroscopic identification at subnanometer resolution.

8% collection efficiency

S. Pennycook etal from the TEAM Project Report

AEM - High Spatial Resolution Analysis



Electronic Structure changes at the Si/SiO2 Interface

P.E. Batson IBM Yorktown, Jan 2004

Brief Review of Energy Loss Processes

Instrumentation: Detector Systems

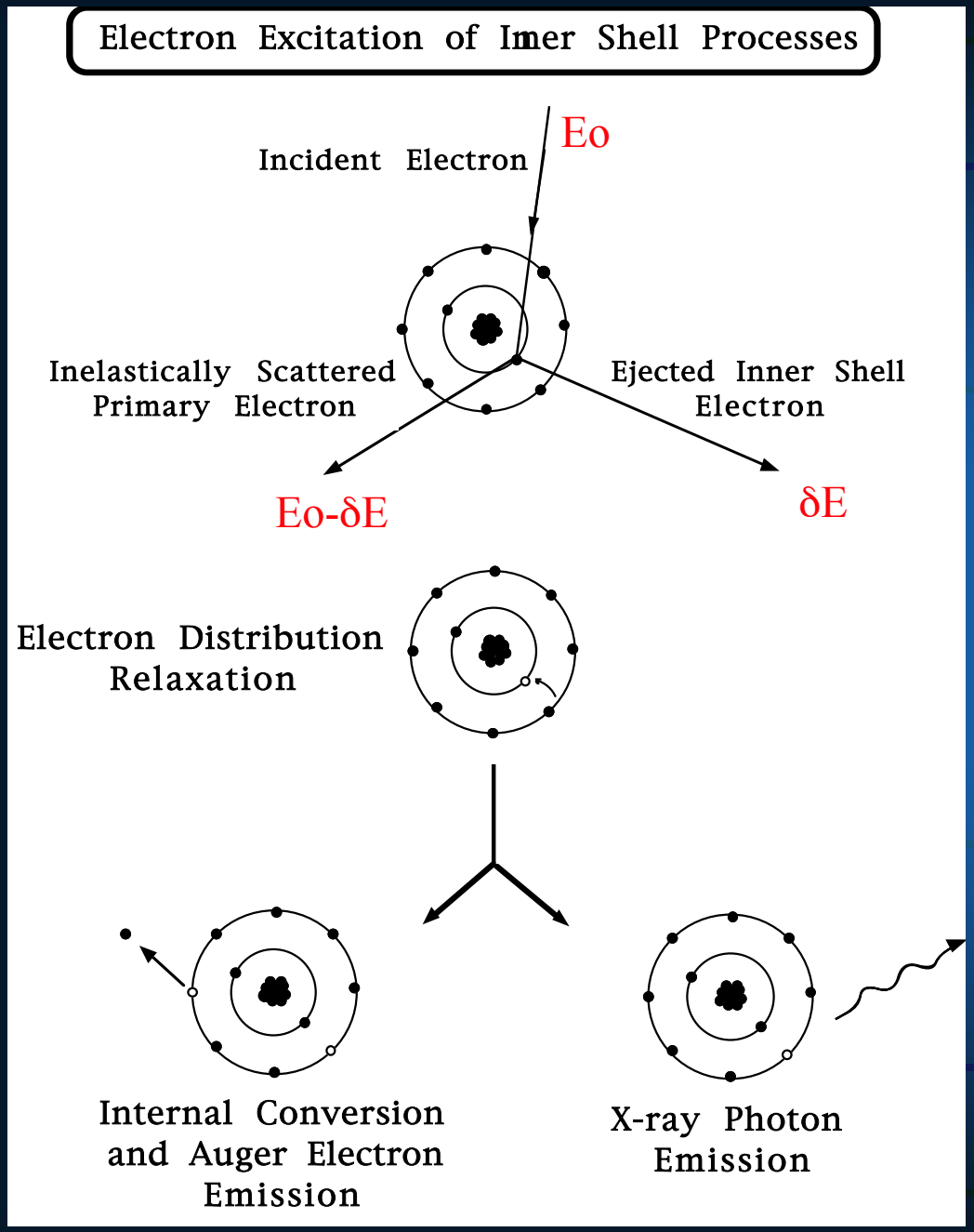
Instrumentation: AEM Systems

Data Analysis and Quantification:

Advanced Topics

Brief Review of Energy Loss Processes

Electron Excitation of Inner Shell & Continuum Processes
Spectral Shapes
Notation of Edges
Electron Scattering Angular Distributions



The Emission Process:

1-Excitation
2-Relaxation
3-Emission

Electron Energy Loss Spectroscopy

Measure the changes in the energy distribution of an electron beam transmitted through a thin specimen.

Each type of interaction between the electron beam and the specimen produces a characteristic change in the energy and angular distribution of scattered electrons.

The energy loss process is the primary interaction event. All other sources of analytical information (i.e. X-rays, Auger electrons, etc.) are secondary products of the initial inelastic event. Thus, EELS has the highest potential yield of information/inelastic event

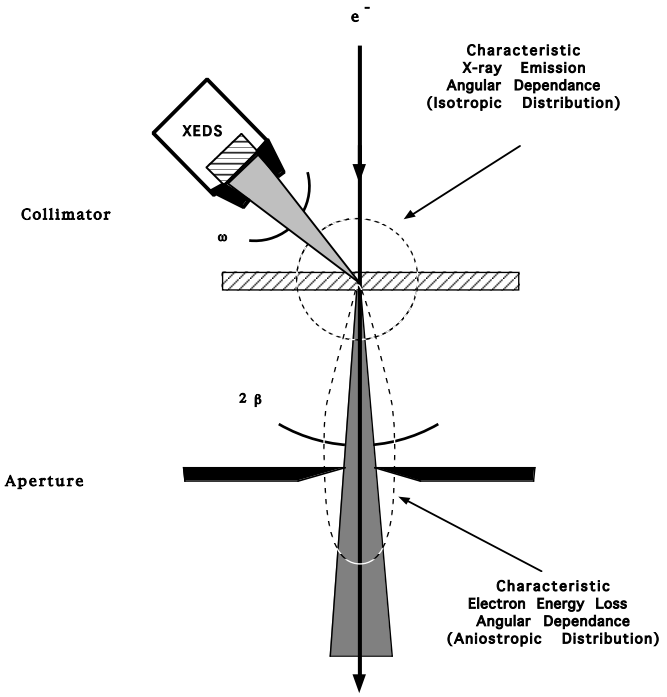
Geometrical Collection Efficiency in XEDS

$$\varepsilon_\omega = \frac{\omega}{4\pi} = \frac{1}{4\pi}\frac{A}{R^2}$$

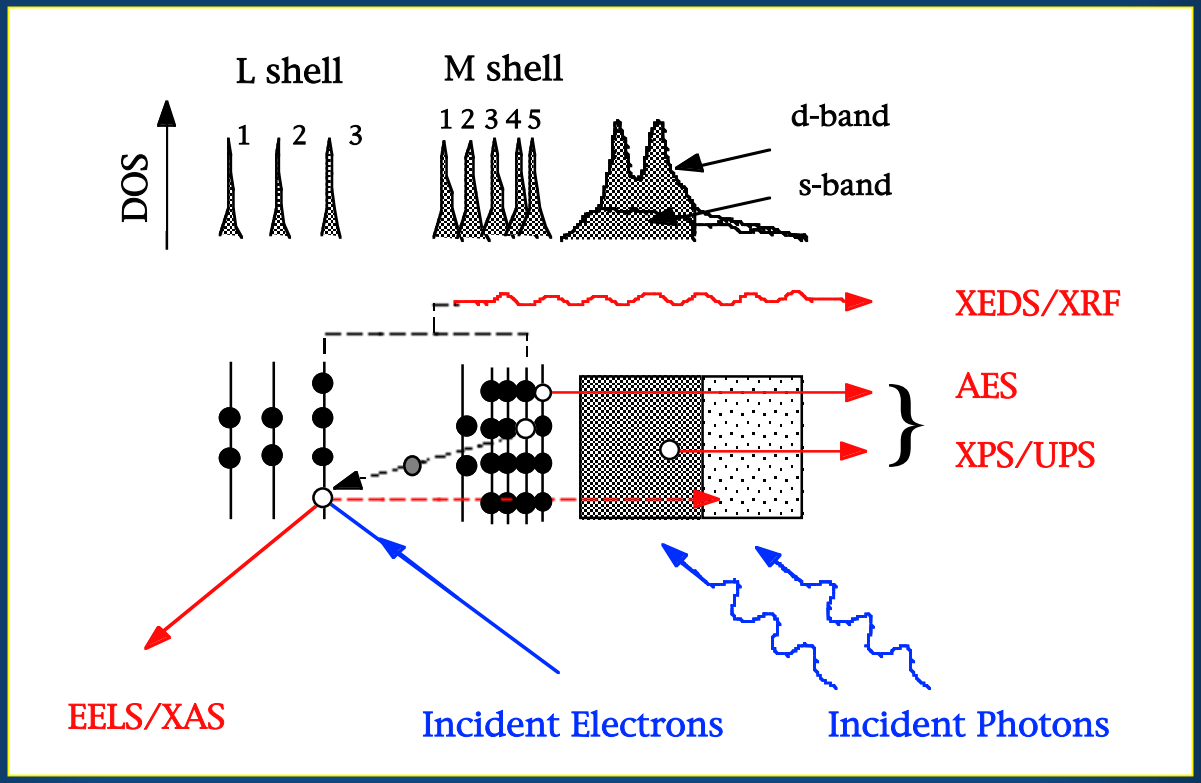
Geometrical Collection Efficiency in EELS

$$\varepsilon_\beta = \frac{\ln\left(1 + \left[\frac{\beta}{\theta_E}\right]^2\right)}{\ln\left(\frac{2}{\theta_E}\right)}$$

$$\theta_E = \frac{\Delta E}{2\gamma_o T_o}; \quad \gamma_o = \frac{1}{\sqrt{1-\beta^2}}; \quad T_o = \frac{1}{2} m_o v^2 = 255.530\left[1 - \left(\frac{1}{1+\frac{V_o(kV)}{511.060}}\right)^2\right] keV$$

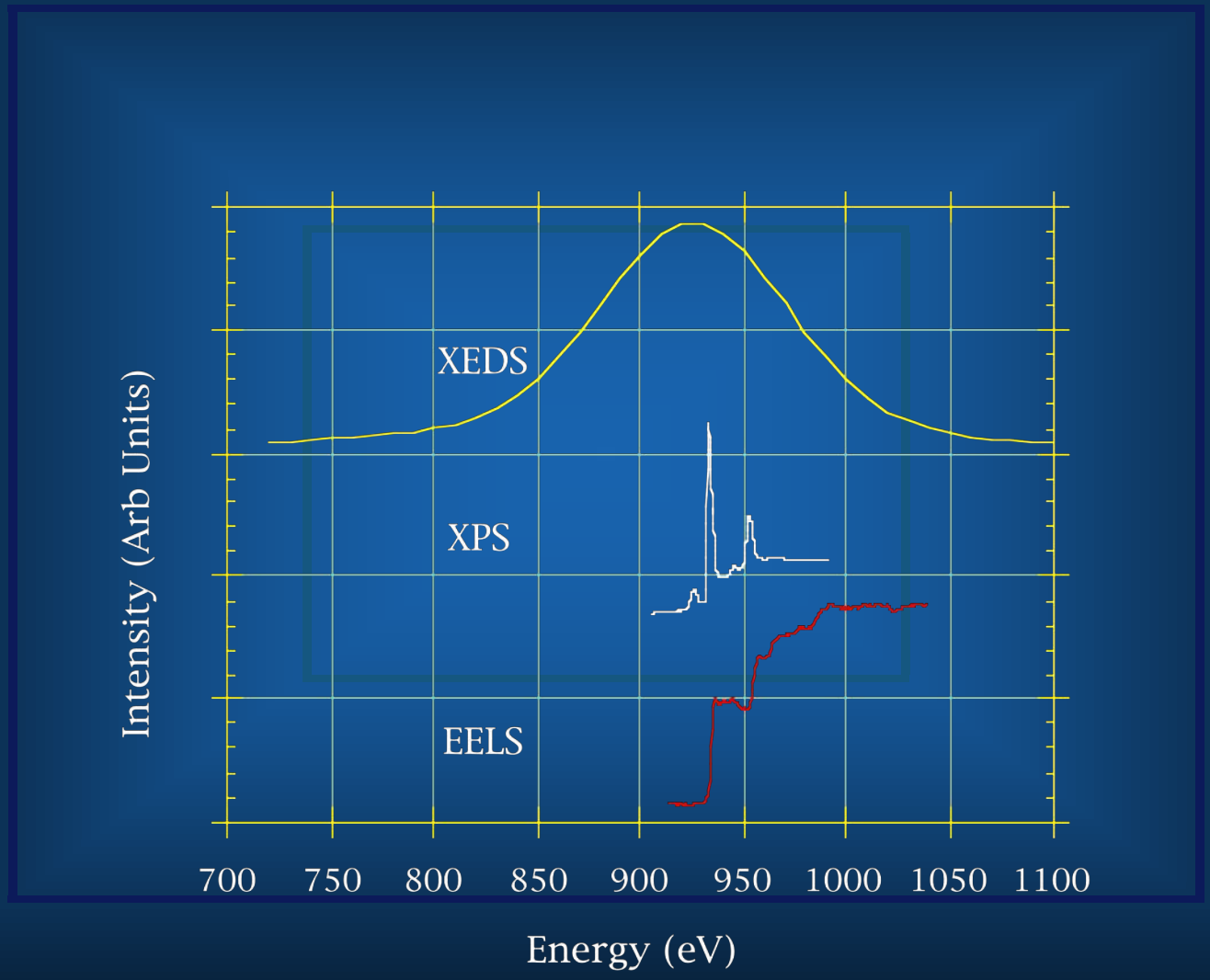


Accelerating Voltage V_o (kV)	$T_o = \frac{1}{2} m_o v^2$ (keV) •	Energy Loss ΔE (eV)	Accelerating Voltage (kV)	Scattering Angle θ_E (mr)
50	43.5	10	120	0.057
100	76.8	100	120	0.569
120	87.9	200	120	1.14
150	102.8	500	120	2.84
200	123.5	1000	120	5.69
250	140.3	500	100	3.26
300	153.8	500	200	2.02
350	165.5	500	300	1.62
400	175.1	500	400	1.43
1000	226.3	500	1000	1.10

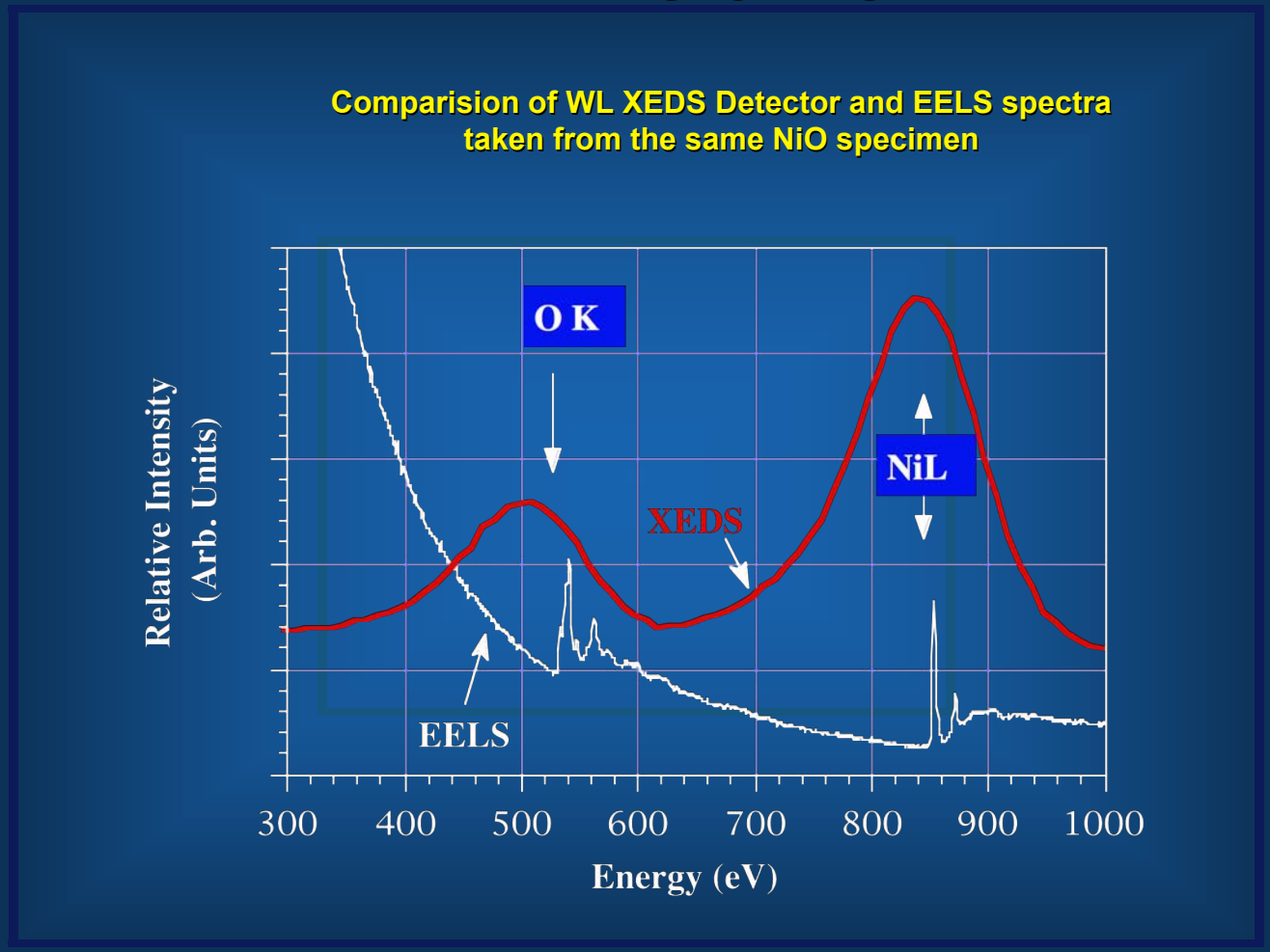


Schematic Diagram Illustrating Sources of Inelastic Scattering Signals

Experimental XEDS, XPS, and EELS data from the Copper L shell. Note the differences in energy resolution, and spectral features.



Comparision Light Element Spectroscopy Resolution
XEDS vs EELS



Note the enhanced spectral information in the EELS data. Vertical scale is arbitrary and chozen for clarity of presentation.

Edges for EELS Microanalysis
(0 - 3 keV)

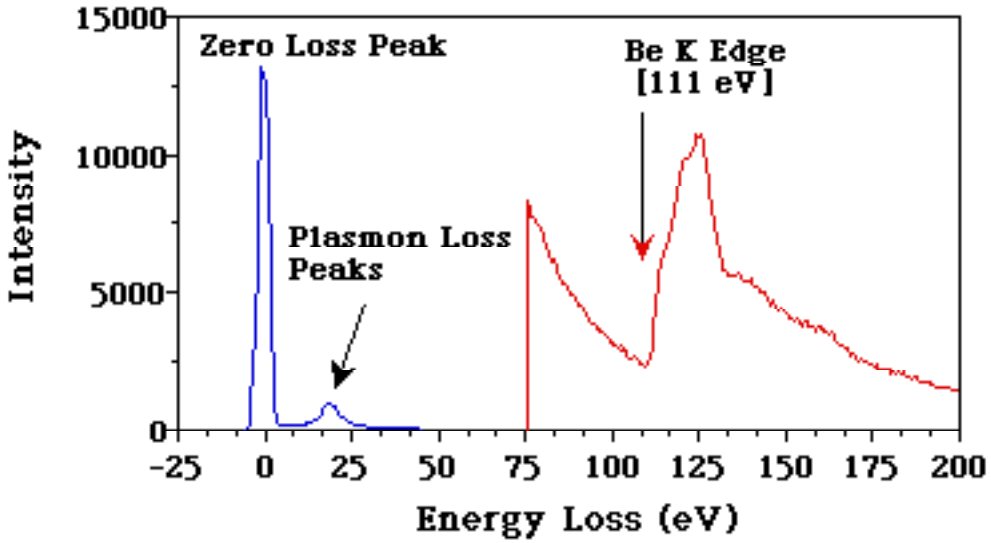


Table 1. Edges Suitable for EELS Microanalysis for the Energy Range 0-3 keV

Atomic Number	Inner Shell	Spectroscopic Notation
Z = 1-11	K	1s
Z = 12-17	K L_3, L_2, L_1	1s $2p_{3/2}, 2p_{1/2}, 2s$
Z = 19-45	L_3, L_2, L_1 M_{54}, M_{32}, M_1	$2p_{3/2}$ ---> $3d_{5/2}, 3d_{3/2}, 3d_{1/2}$, $3p_{3/2}, 3p_{1/2}, 3s$
Z = 46-79	M_{54}, M_{32}, M_1 N_{45}, N_{32}, N_1 O_{32}, O_1	$3d_{5/2}$ ---> $4d_{5/2}, 4d_{3/2}, 4d_{1/2}$, $4p_{3/2}, 4p_{1/2}, 4s$ $5p_{3/2}, 5p_{1/2}, 5s$
Z > 80	$N_{67}, N_{45}, N_{32}, N_1$ O_{45}, O_{32}, O_1	$4f_{7/2}$ ---> $5p_{3/2}$ --->

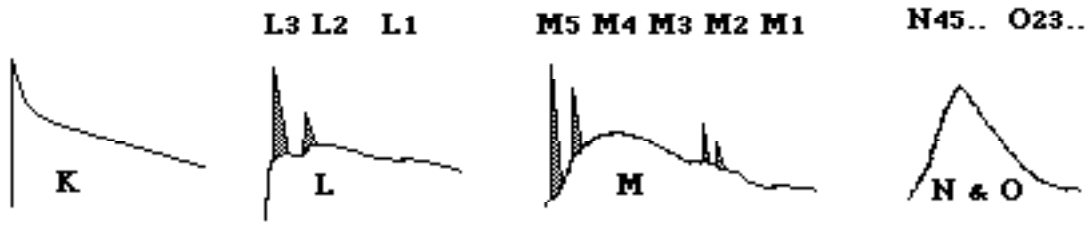


Figure 5. Schematic illustration of K, L, M, N and O Edge shapes, the "white lines" sometimes detected on L and M shells are shown shaded peaks at the edge onsets. In all sketches the background shape has been omitted for clarity. These profiles should be compared with experimental profiles of figure 6.

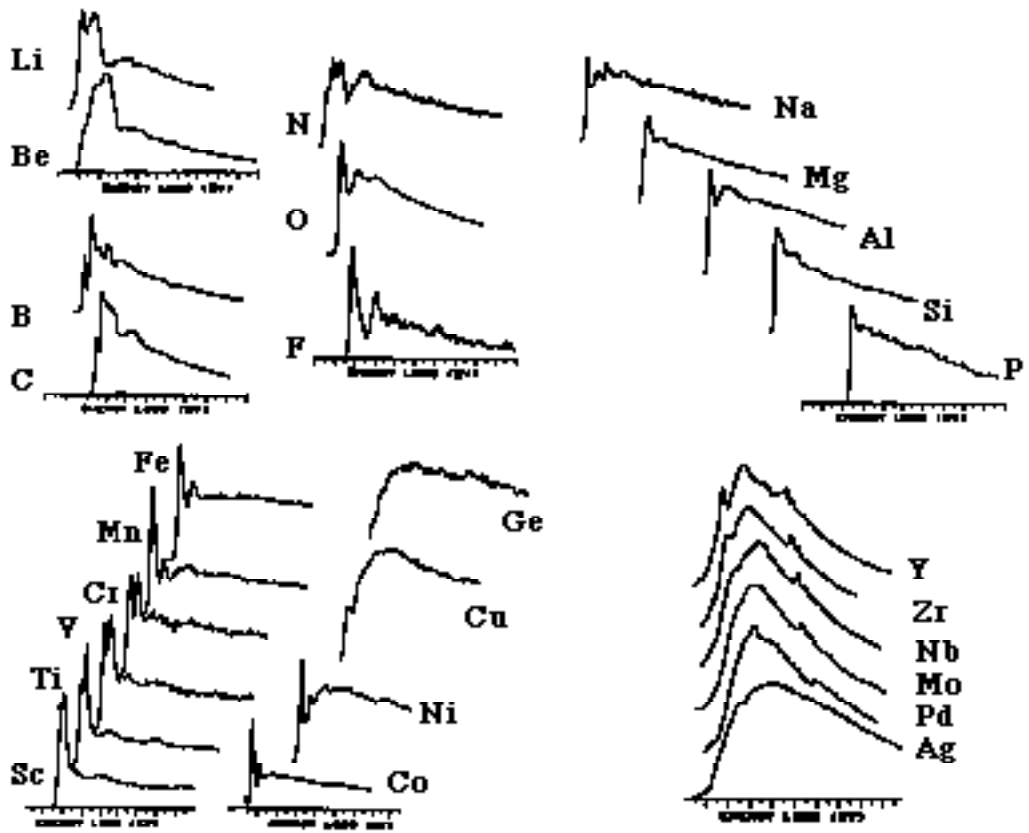
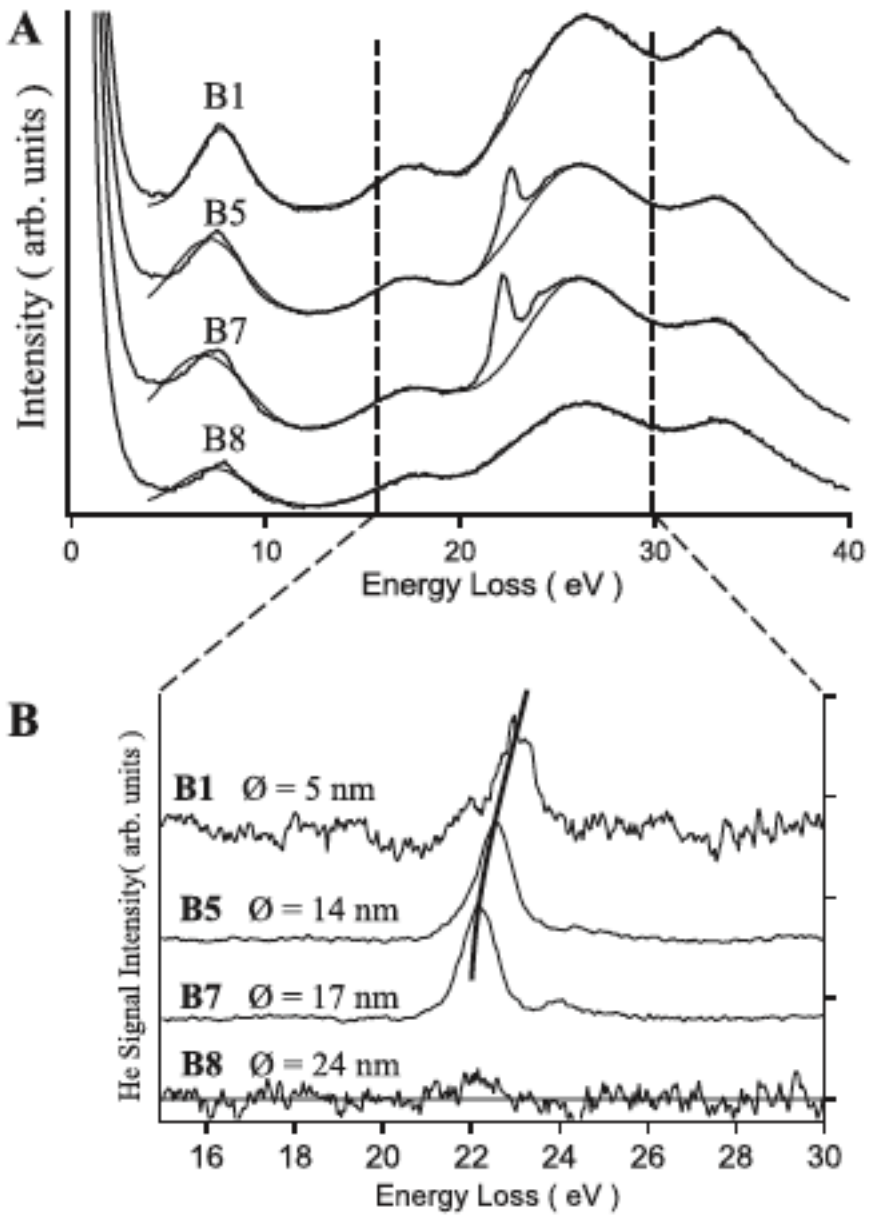


Figure 6. Selection of representative K-Shell [Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P]; L-shell [Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ge]; and M-shell [Y, Zr, Nb, Mo, Pd, Ag] experimental spectral profiles (all background subtracted).



Helium
In Pd

D. Taverna etal
PRL 100, 035301 (2008)

Electron Scattering

Elastic Scattering

Single Atoms:

$$I(\theta) \sim |f(\theta)|^2 = |f_o|^2 \bullet \frac{1}{(\theta^2 + \theta_o^2)^2}$$

$$\theta_o = \frac{1}{2\pi(0.885 a_o Z^{-1/3})}$$

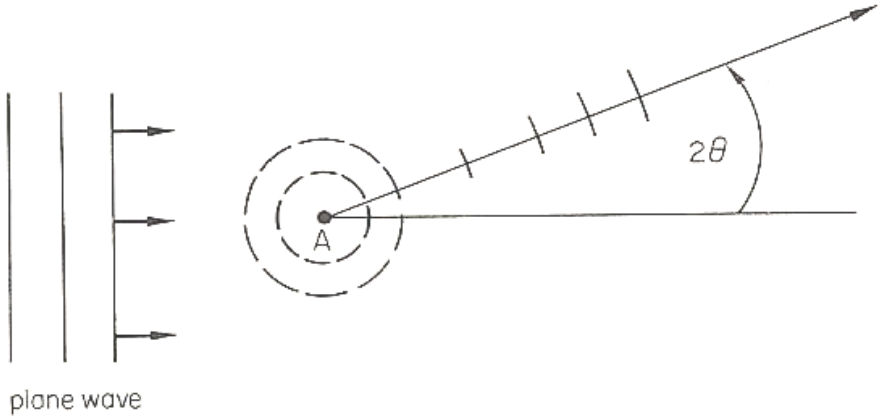


Figure 2.2 The scattering of a plane wave at an atom A through the formation of spherical wavelets travelling at an angle 2θ to the original direction of motion

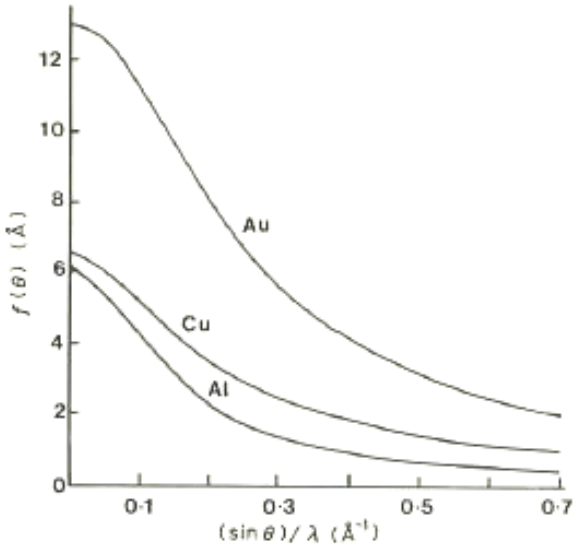


Fig. 2.2 Relationship between the atomic scattering factor $f(\theta)$ (in Å) and the scattering angle $(\sin\theta)/\lambda$ (in $Å^{-1}$) for aluminium, copper and gold calculated using equation (2.1).

Scattering from an isolated atom in free space

Elastic Scattering

Single Atoms:

$$I(\theta) \sim |f(\theta)|^2 = |f_o|^2 \bullet \frac{1}{(\theta^2 + \theta_o^2)^2}$$

$$\theta_o = \frac{1}{2\pi(0.885 a_o Z^{-1/3})}$$

Amorphous Solids:

$$I(\theta) \sim |f(\theta)|^2 \bullet \left(1 + \frac{\sin(kR)}{kR}\right)$$

$$k = \frac{4\pi}{\lambda} \sin(\theta)$$

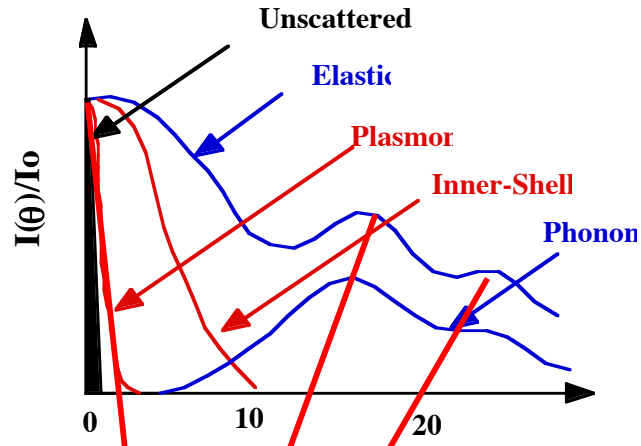
Scattering from an collection of an amorphous collection of atoms
- neighboring atoms give rise to interference

Amorphous Solids:

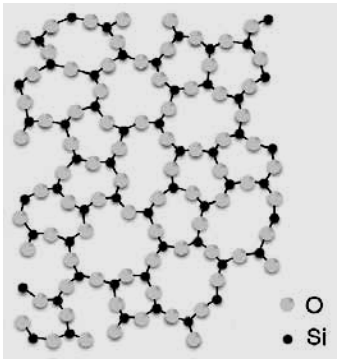
$$I(\theta) \sim |f(\theta)|^2 \cdot \left|1 + \frac{\sin(kR)}{kR}\right|$$

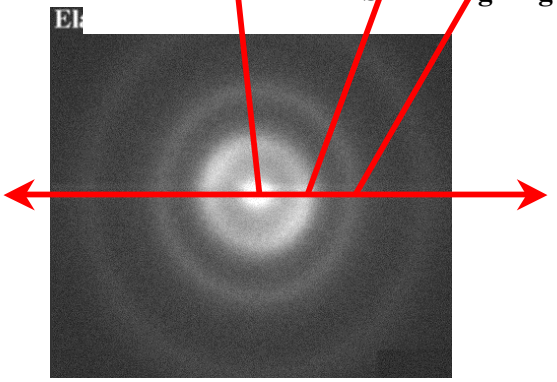
$$k = \frac{4\pi}{\lambda}\sin(\theta)$$

R = Average Interatomic Spacing



Amorphous Silica (SiO_2)





Phonons:

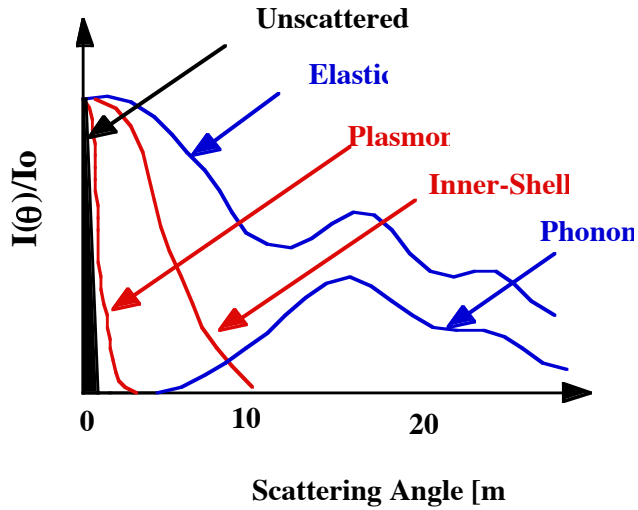
$$I(\theta) \sim |f(\theta)|^2 \cdot \{1 - e^{-2M}\}$$

$$M = \frac{8\pi \langle u^2 \rangle \sin(\theta)}{\lambda}$$

Inelastic:

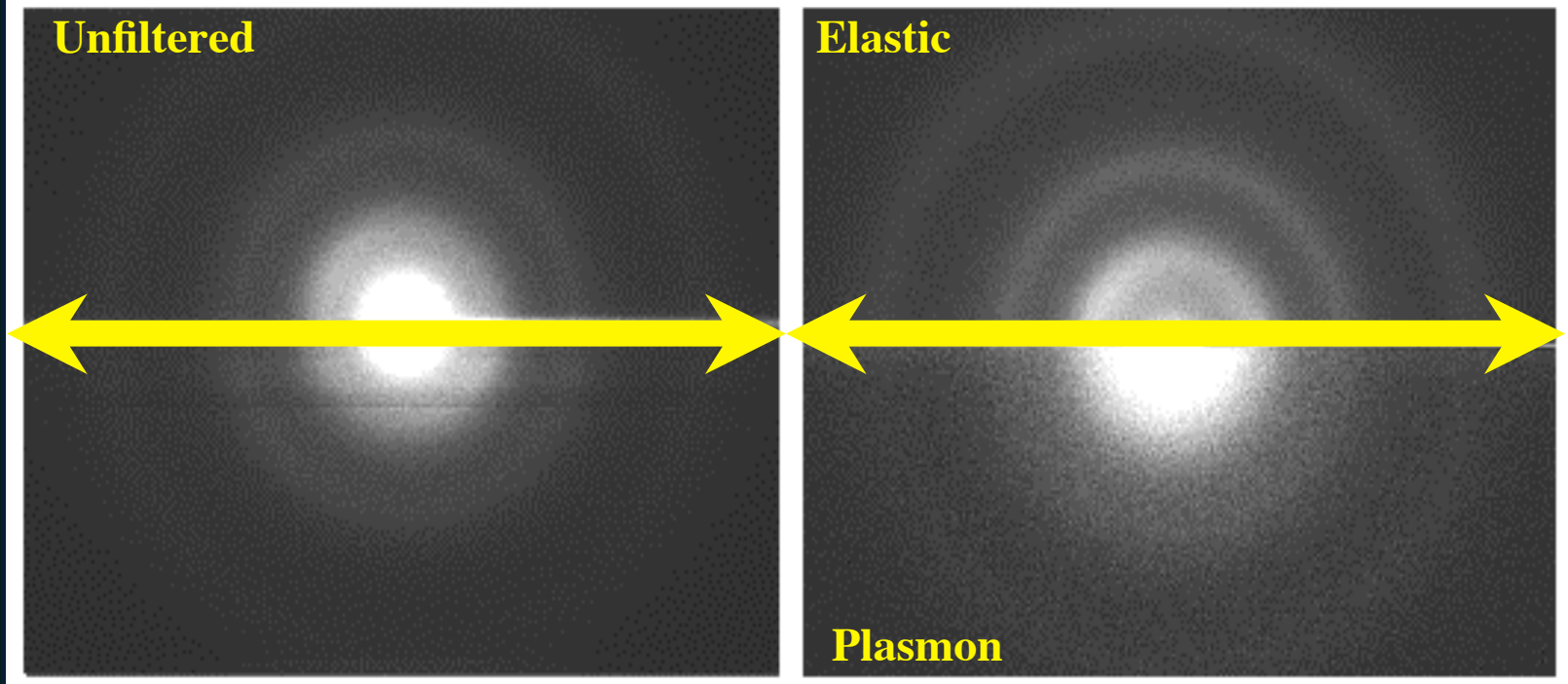
$$I(\theta) = \Gamma(\delta E, \theta) \cdot \frac{1}{\theta^2 + \theta_E^2}$$

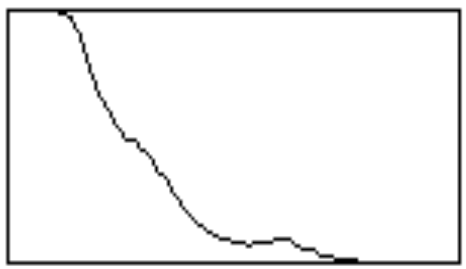
$$\theta_E = \frac{\Delta E}{2\gamma_o T_o} \qquad \gamma_o = \frac{1}{\sqrt{1-\beta^2}}$$

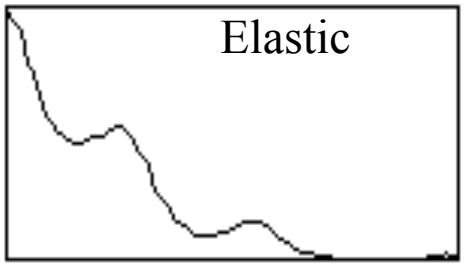


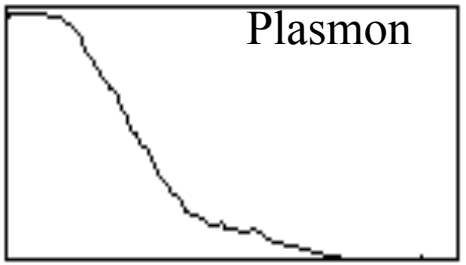
$\Gamma(\delta E,\theta)$: Imaginary Part of the Complex Dielectric constant(ε)

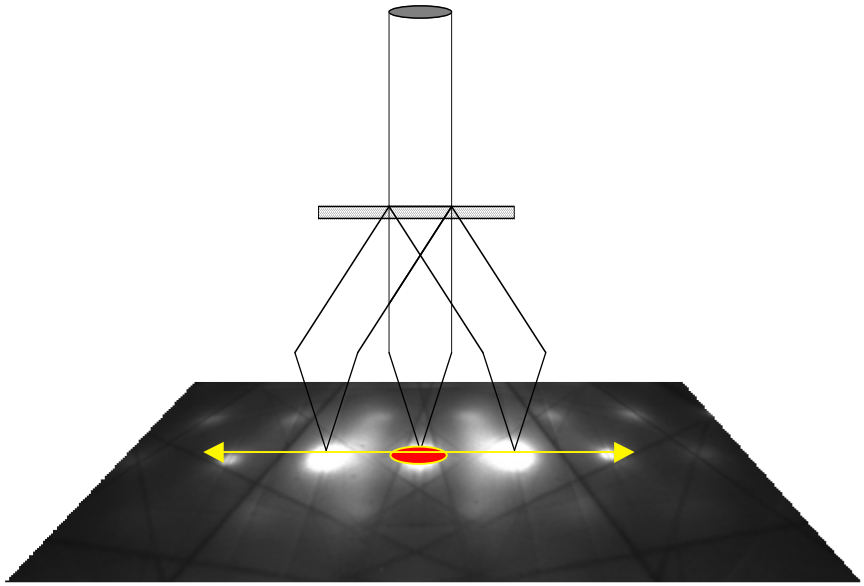
: Generalized Oscillator Strength

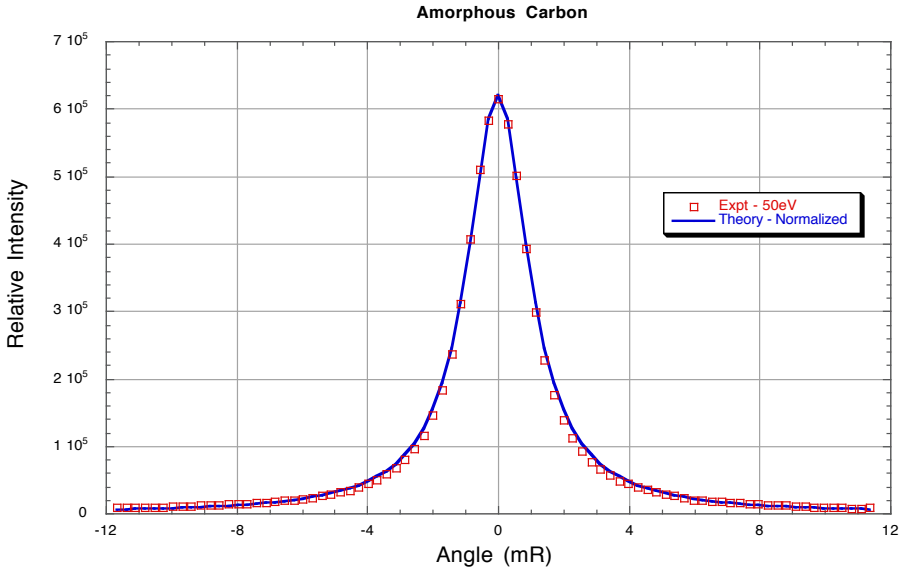

Unfiltered
Elastic
Plasmon




Elastic


Plasmon





Inelastic:

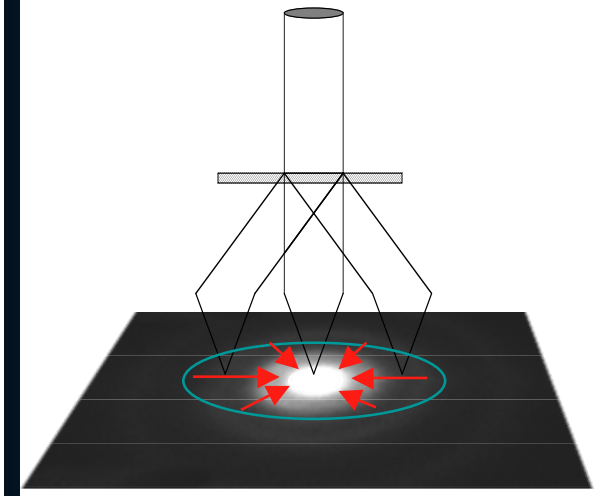
$$I(\theta) = \Gamma(\delta E,\theta) \bullet \frac{1}{\theta^2 + \theta_E^2}$$

$$\theta_E = \frac{\Delta E}{2\gamma_o T_o} \qquad \gamma_o = \frac{1}{\sqrt{1-\beta^2}}$$

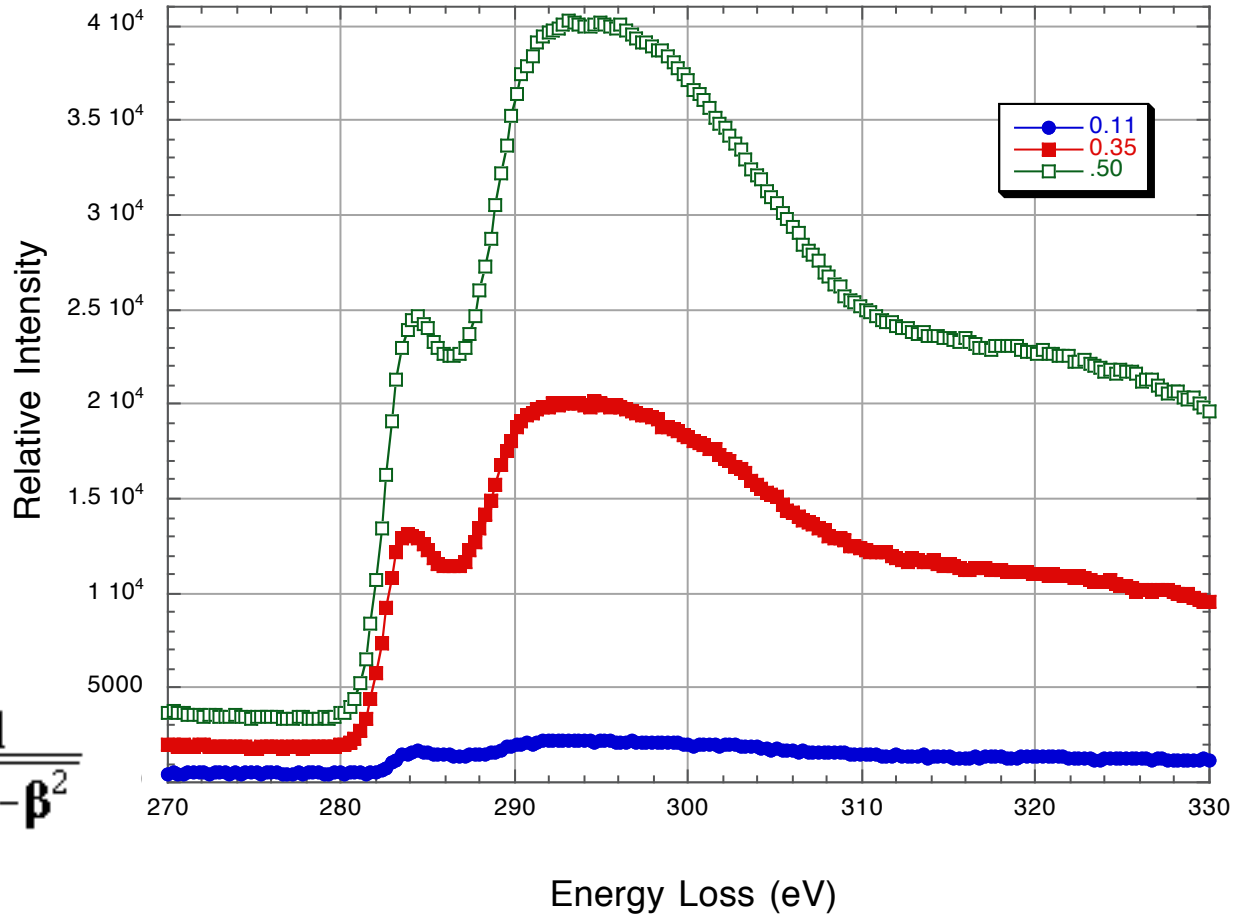
$\Gamma(\delta E,\theta)$: Imaginary Part of the Complex Dielectric constant(ε)

: Generalized Oscillator Strength

Intensity of Edges is Directly Related to Mean Scattering Angle
Example: Amorphous Carbon

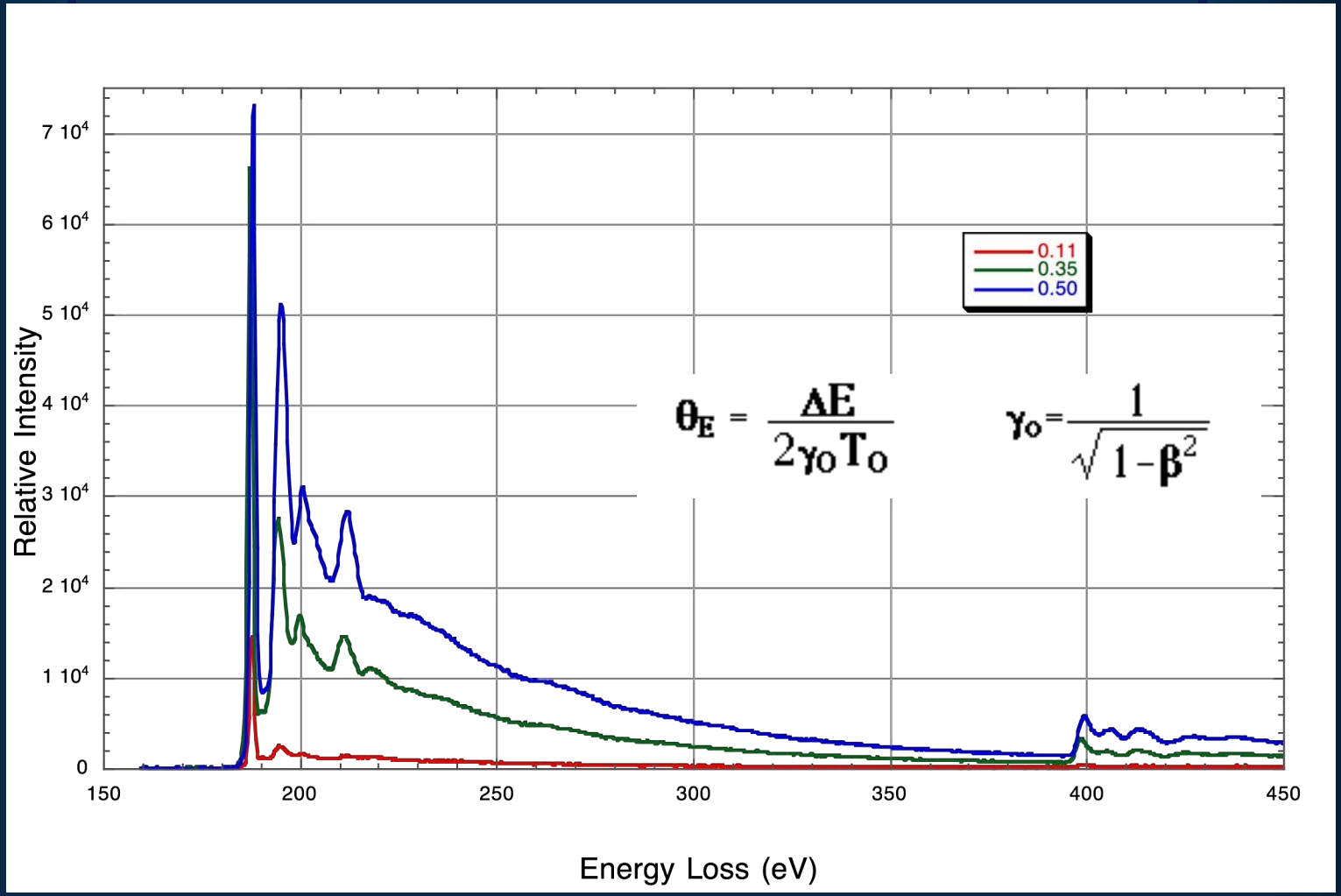


$$\theta_E = \frac{\Delta E}{2\gamma_0 T_0} \qquad \gamma_0 = \frac{1}{\sqrt{1-\beta^2}}$$



θ_E ~1.15 mR

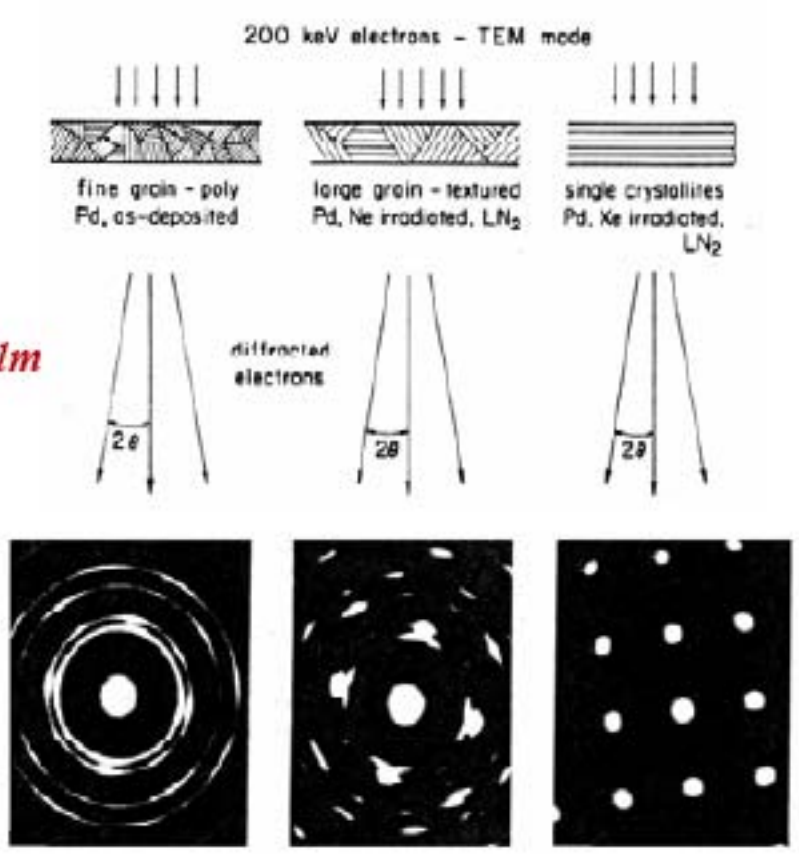
Intensity of Edges is Directly Related to Mean Scattering Angle
Example: Boron - Nitride



θ_E ~0.777 mR

θ_E ~1.62 mR

Electron Beam Diffraction of a Pd film



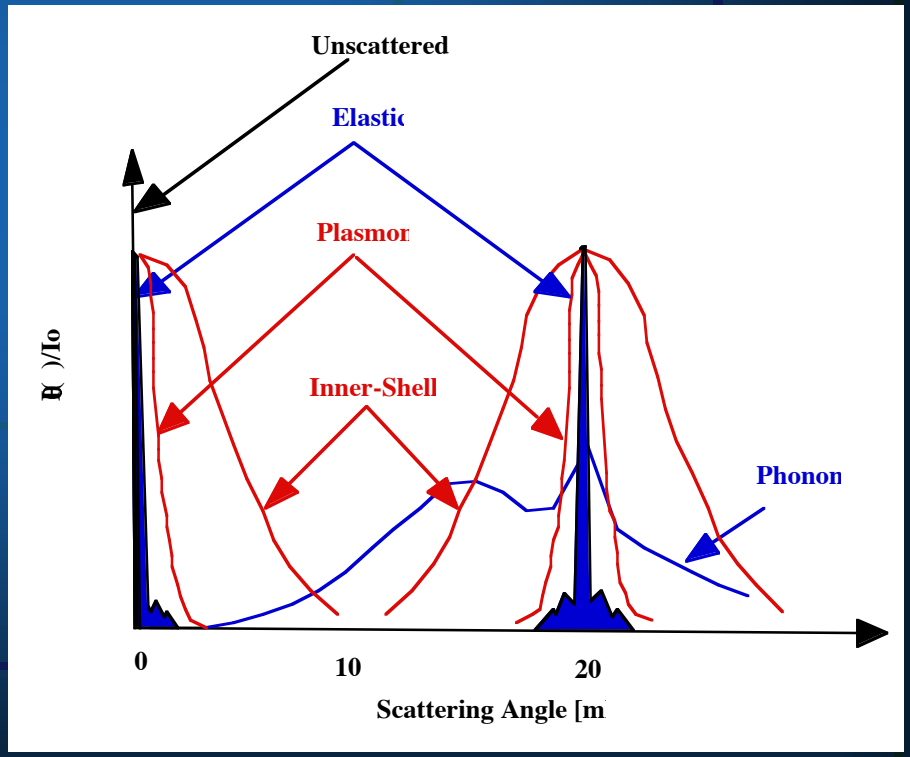
Type of Electron Scattering	Angular Range	Energy Loss
Unscattered	0	0
Elastic	10's-100's mR	~0
Phonon	10's-100's mR	<.025 eV
Inelastic	10's mR	everything else
Plasmon	< 1mr	10's of eV
Inner-Shell	~10's of mR	10's-1000's eV

Elastic Scattering

Crystalline Solids:

$$I(\theta) \sim |F(hkl)|^2$$

$$F(hkl) = \sum_j f_j(\theta)\ e^{(-2\pi i \vec{k}\cdot\vec{r})}$$



Phonons:

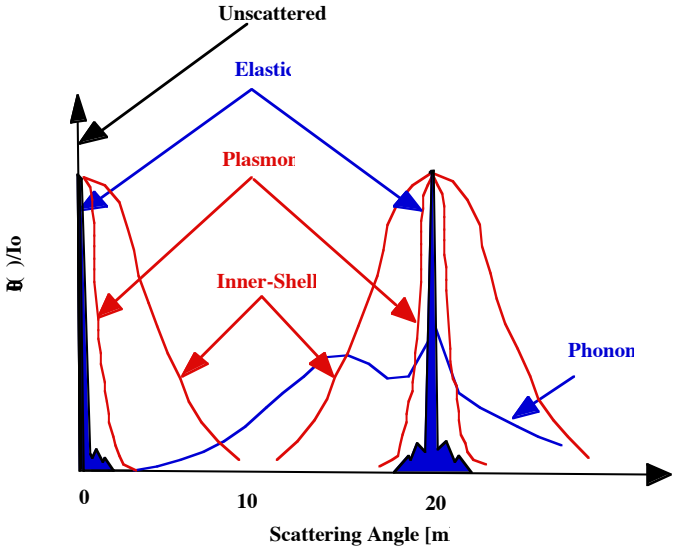
$$I(\theta) \sim |f(\theta)|^2 \bullet \{1 - e^{-2M}\}$$

$$M = \frac{8\pi \langle u^2 \rangle \sin(\theta)}{\lambda}$$

Inelastic:

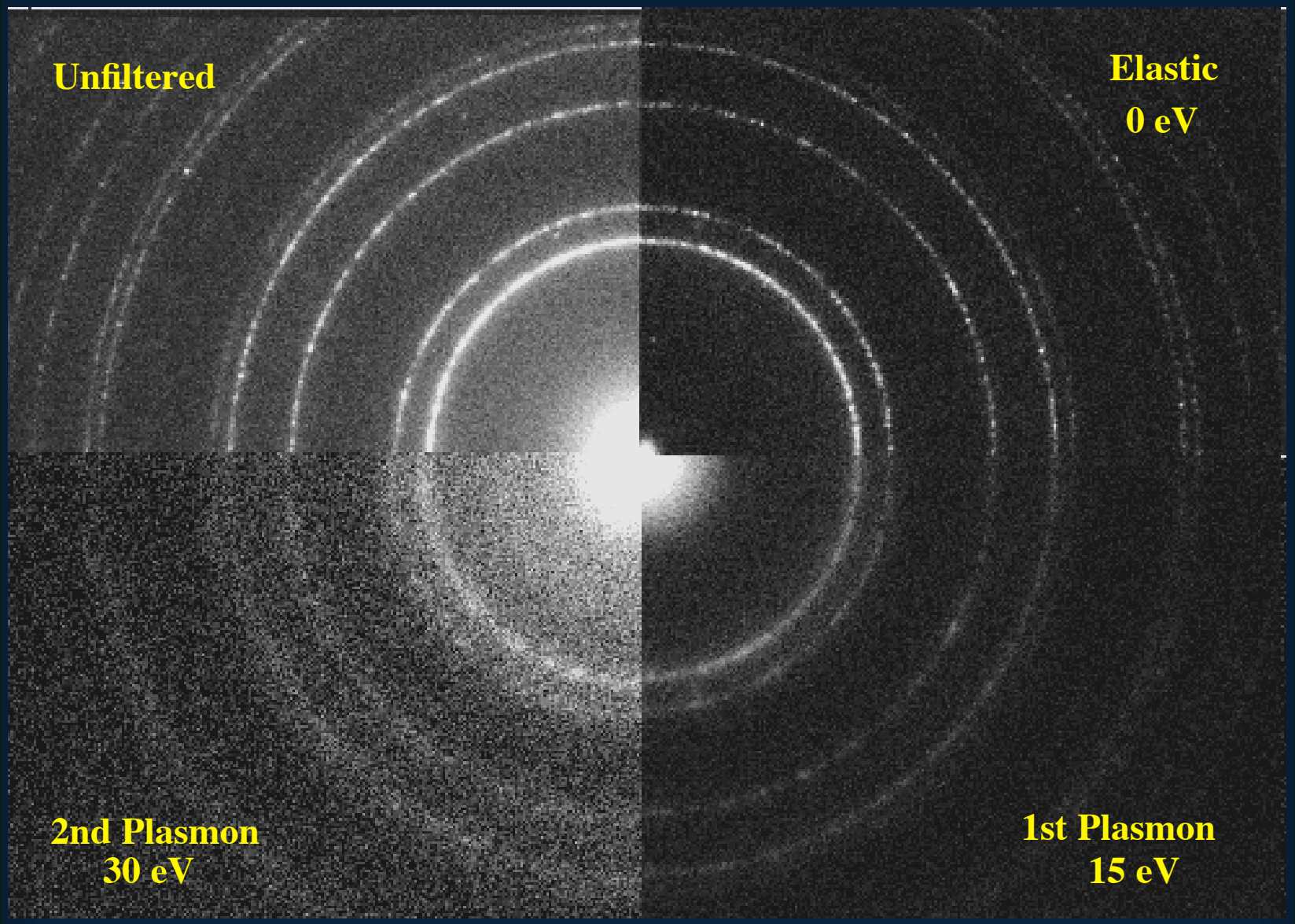
$$I(\theta) = \Gamma(\delta E, \theta) \bullet \frac{1}{\theta^2 + \theta_E^2}$$

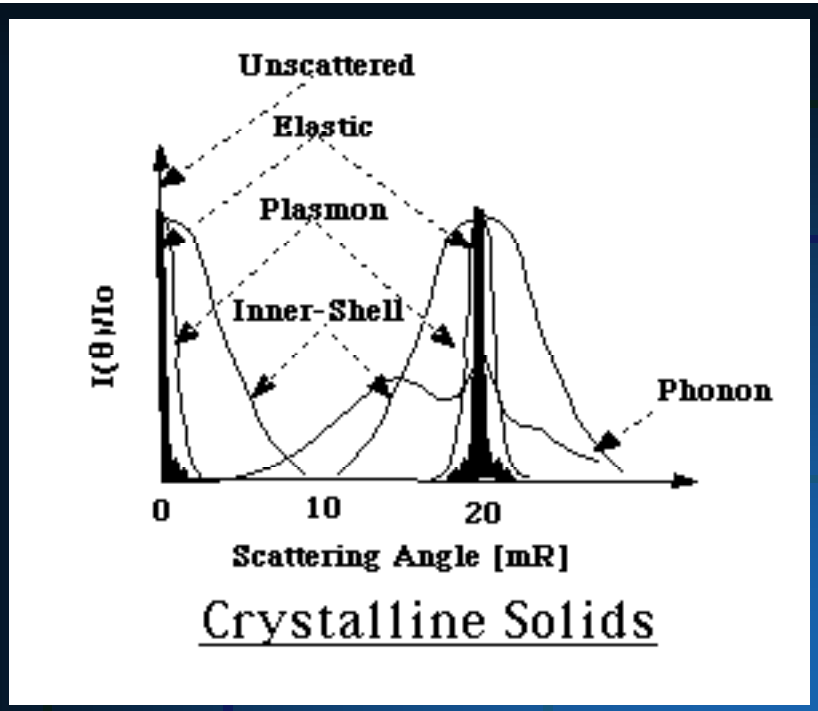
$$\theta_E = \frac{\Delta E}{2\gamma_0 T_0} \qquad \gamma_0 = \frac{1}{\sqrt{1-\beta^2}}$$



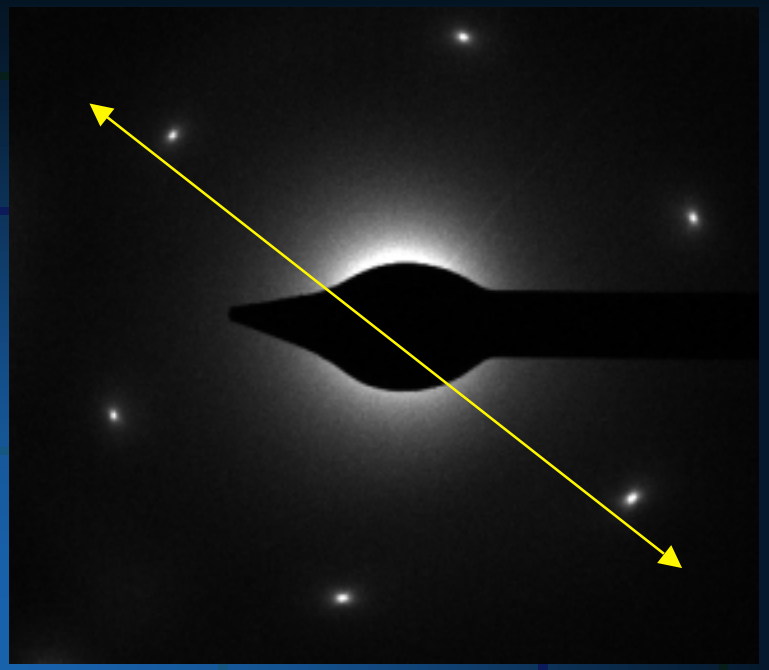
$\Gamma(\delta E,\theta)$: Imaginary Part of the Complex Dielectric constant(ε)

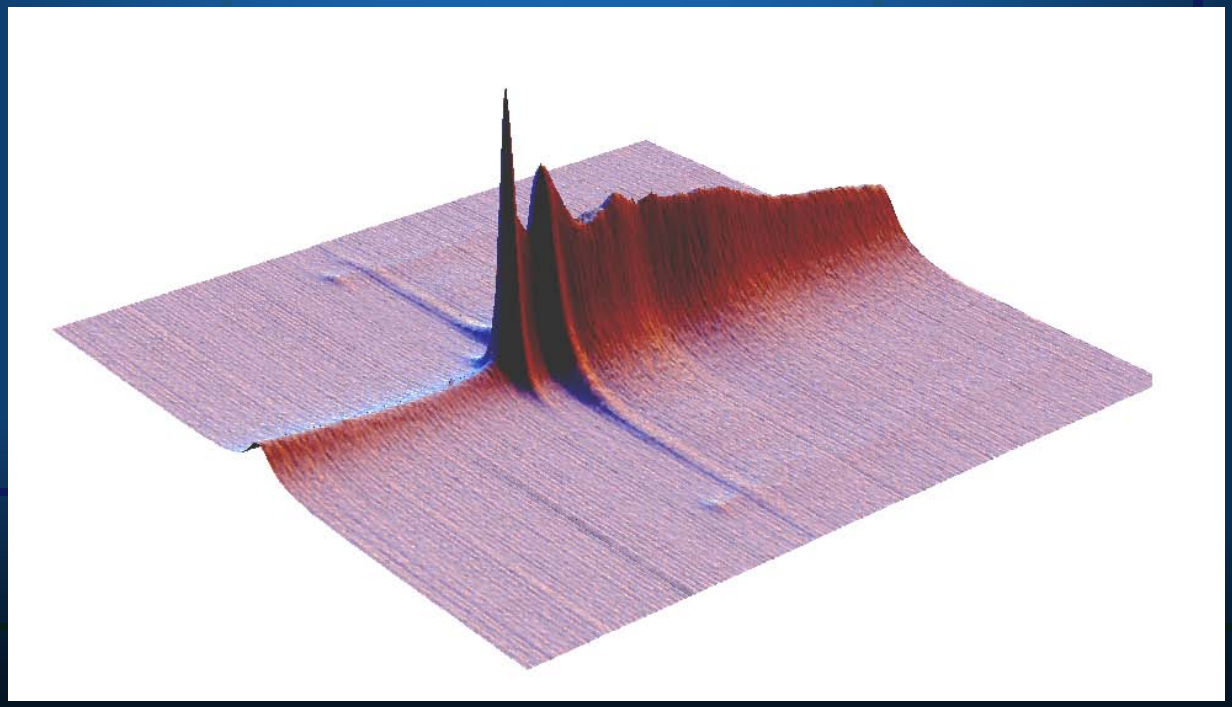
: Generalized Oscillator Strength


Unfiltered
Elastic
0 eV
2nd Plasmon
30 eV
1st Plasmon
15 eV



Crystalline Solids





Instrumentation: Detector Systems

Energy Loss Spectrometers
- Basic Principles
- Electrostatic/Electromagnetic
- Serial/Parallel Detector Systems
- Spectral Artifacts

Multichannel Analyzers

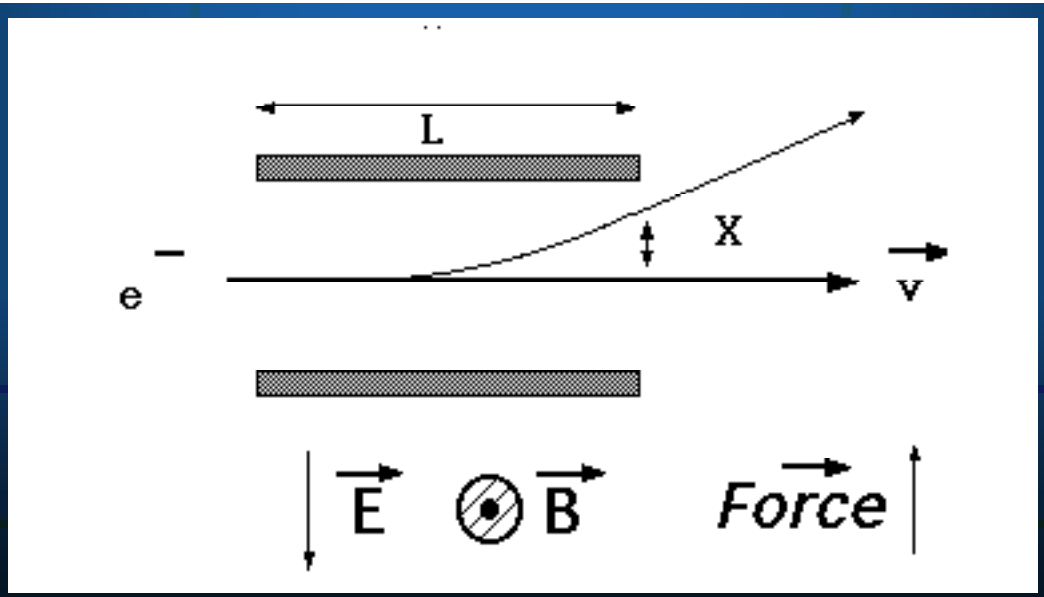
Force (F) and displacements (X) on electrons by different types of fields yields a deflection in their trajectory. In a uniform field region the electrons drift at a characteristic radius (R).

Electrostatic

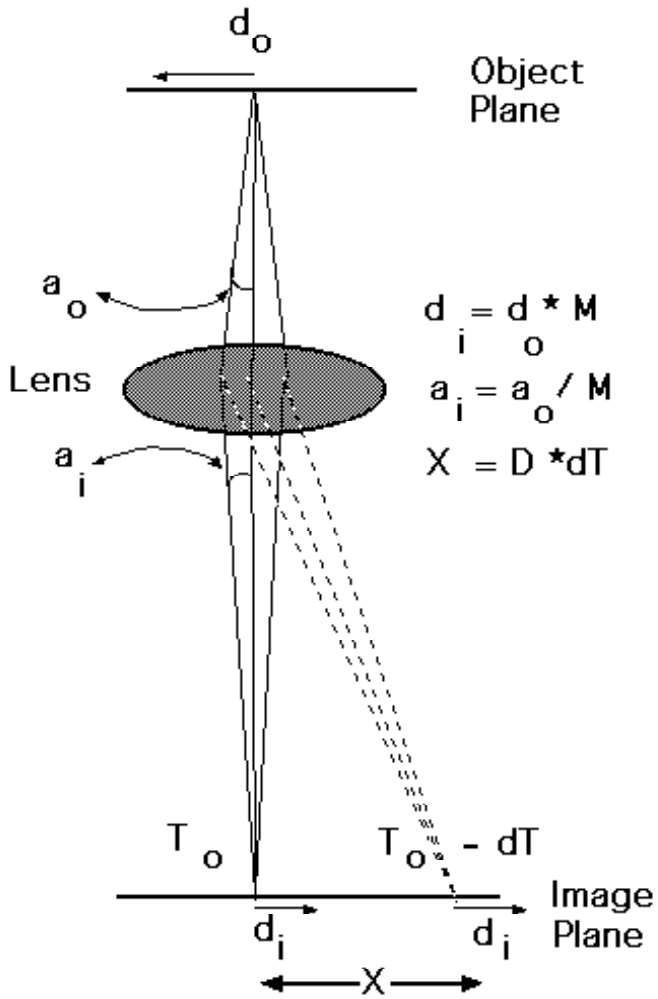
$$\vec{F_E} = q\,\vec{E} \qquad X_E = \frac{1}{2}\frac{qEL^2}{m_0 v^2} \qquad R_E = \frac{m_0 v^2}{qE}$$

Electromagnetic

$$\vec{F_B} = q\left[\vec{v} \times \vec{B}\right] \qquad X_B = \frac{1}{2}\frac{qBL^2}{m_0 v} \qquad R_B = \frac{m_0 v}{qB}$$

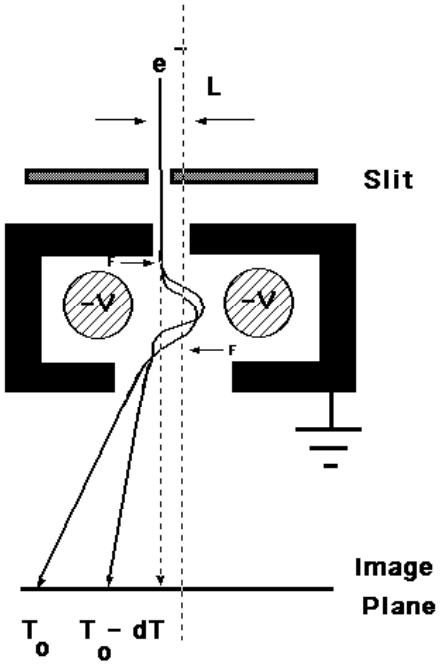


Basic Spectrometer

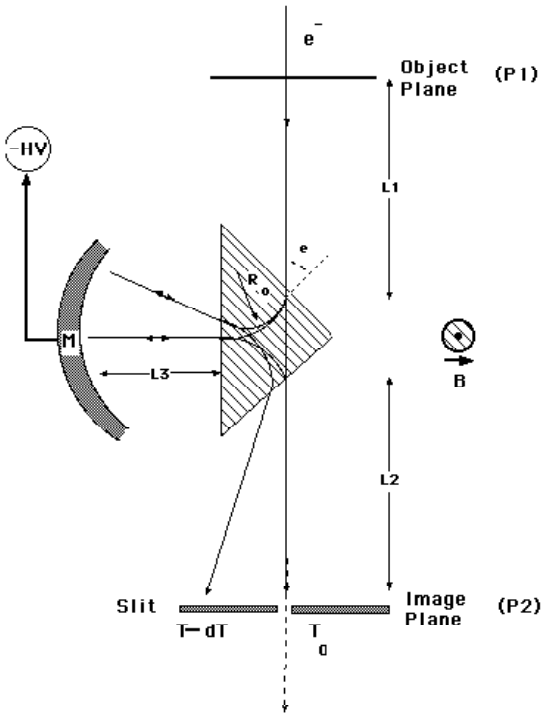


Types of Electron Spectrometers:

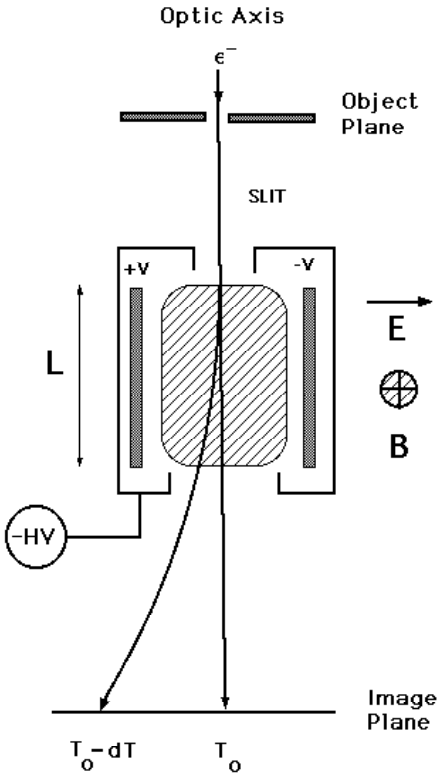
Electrostatic:	**Mollenstedt**
Electrostatic/magnetic:	**Wien, Castaing-Henry**
Electromagnetic:	**Cylindrical, Omega, Sector**



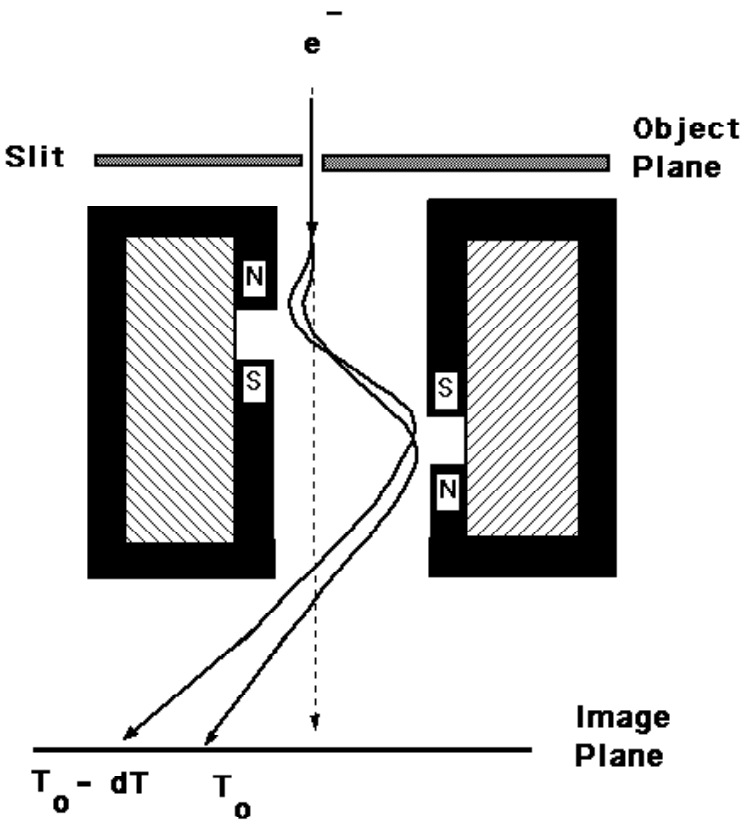
Mollenstedt Analyzer



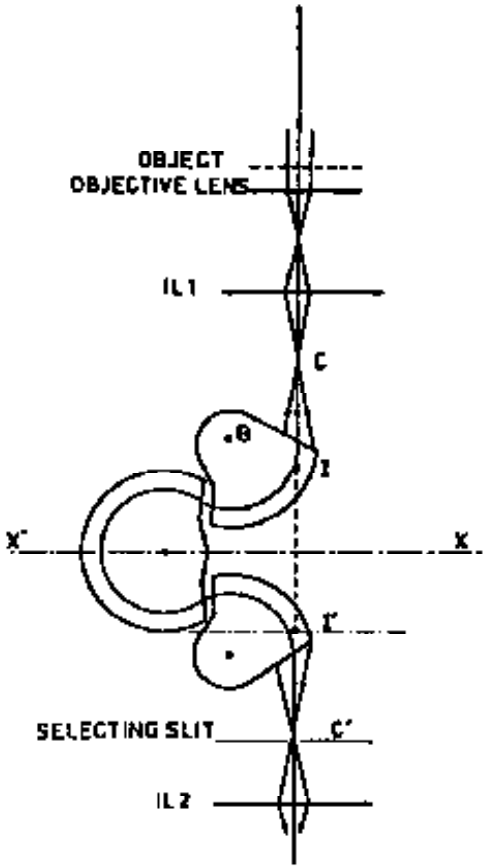
Castaing-Henry Filte



Wien Filter

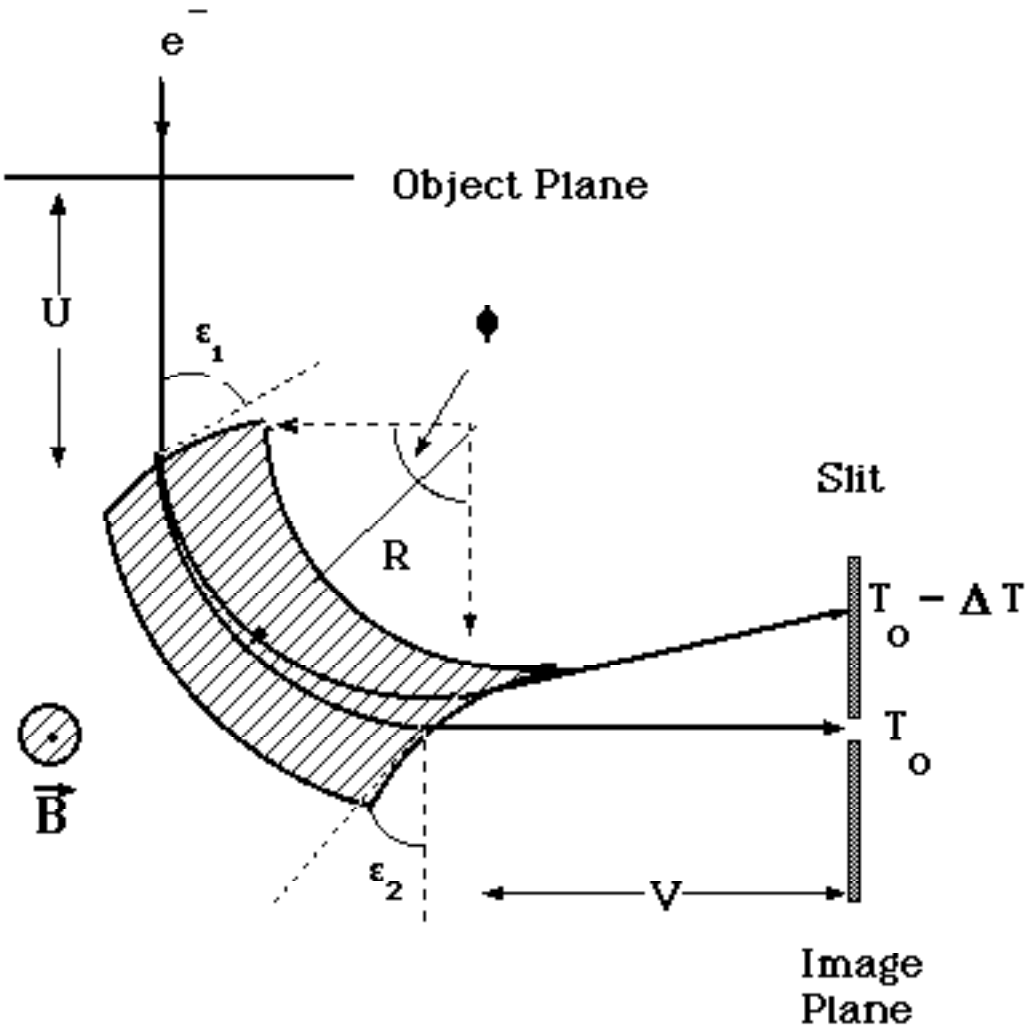


Cylindrical Magnetic Analyzer



Omega Filter

Magnet Sector Analyzer



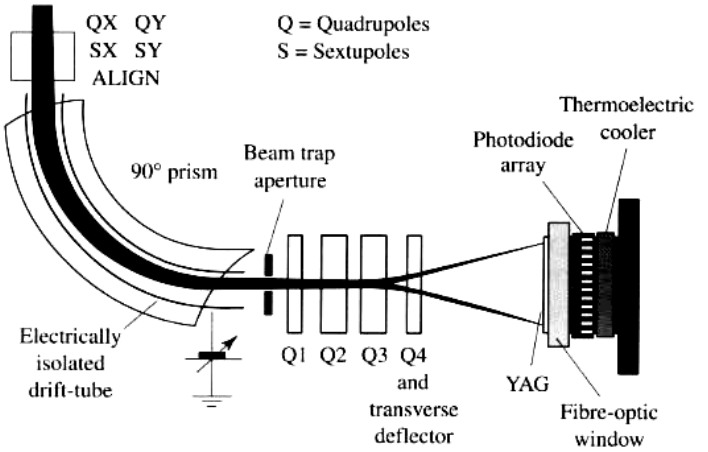


Figure 3.3. Schematic diagram of a Gatan PEELS system. Redrawn from Egerton (1996) *Electron Energy Loss Spectroscopy in the Electron Microscope*, 2nd Edn, with permission of Plenum Publishers.

Commerical Spectrometers Vs Imaging Filters

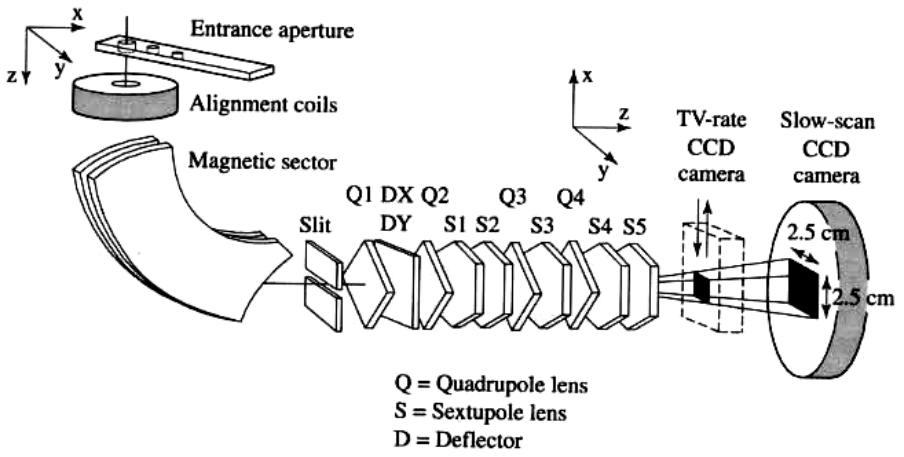
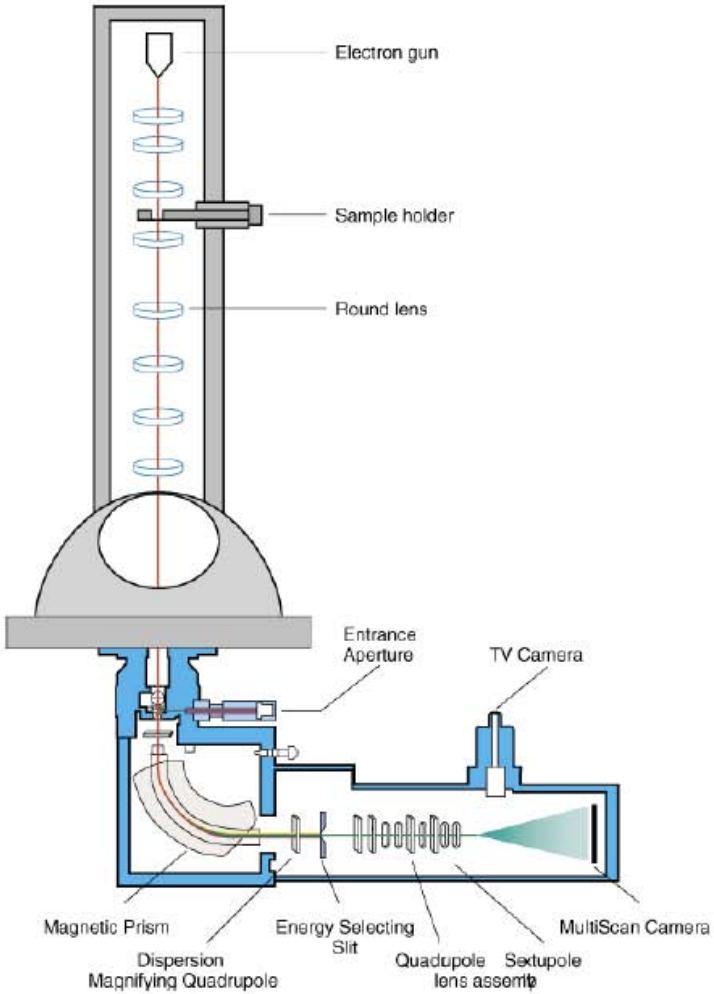


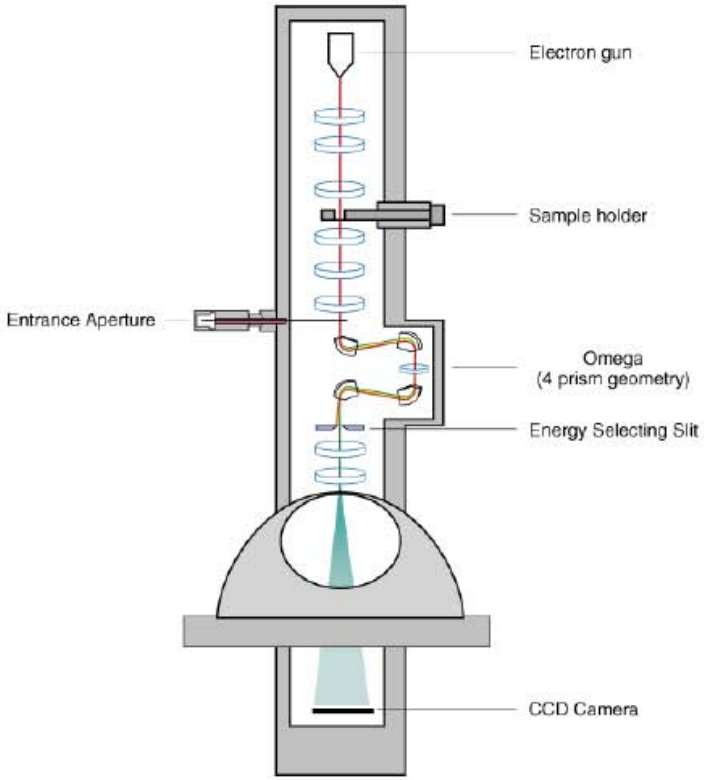
Figure 3.4. Schematic diagram of a Gatan imaging filter. Redrawn from Egerton (1996) *Electron Energy Loss Spectroscopy in the Electron Microscope*, 2nd Edn, with permission of Plenum Publishers.

Imaging Filters vs Spectrometers

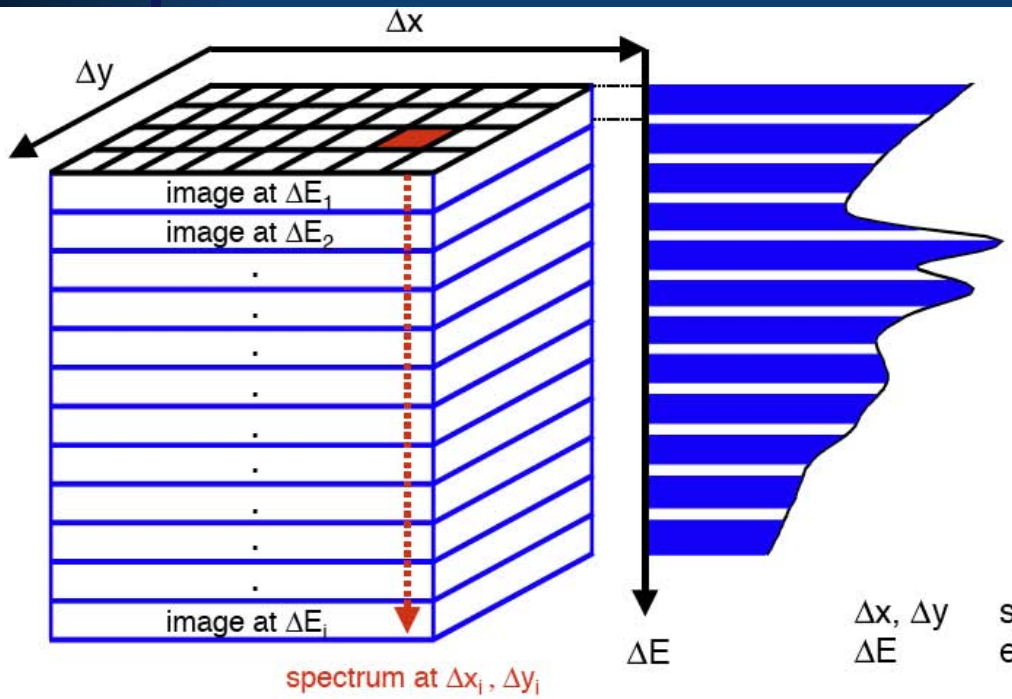
Post-column filter (Gatan)



In-column filter (LEO, JEOL)



Spectral Imaging
Slice-by-Slice vs Point-by-Point

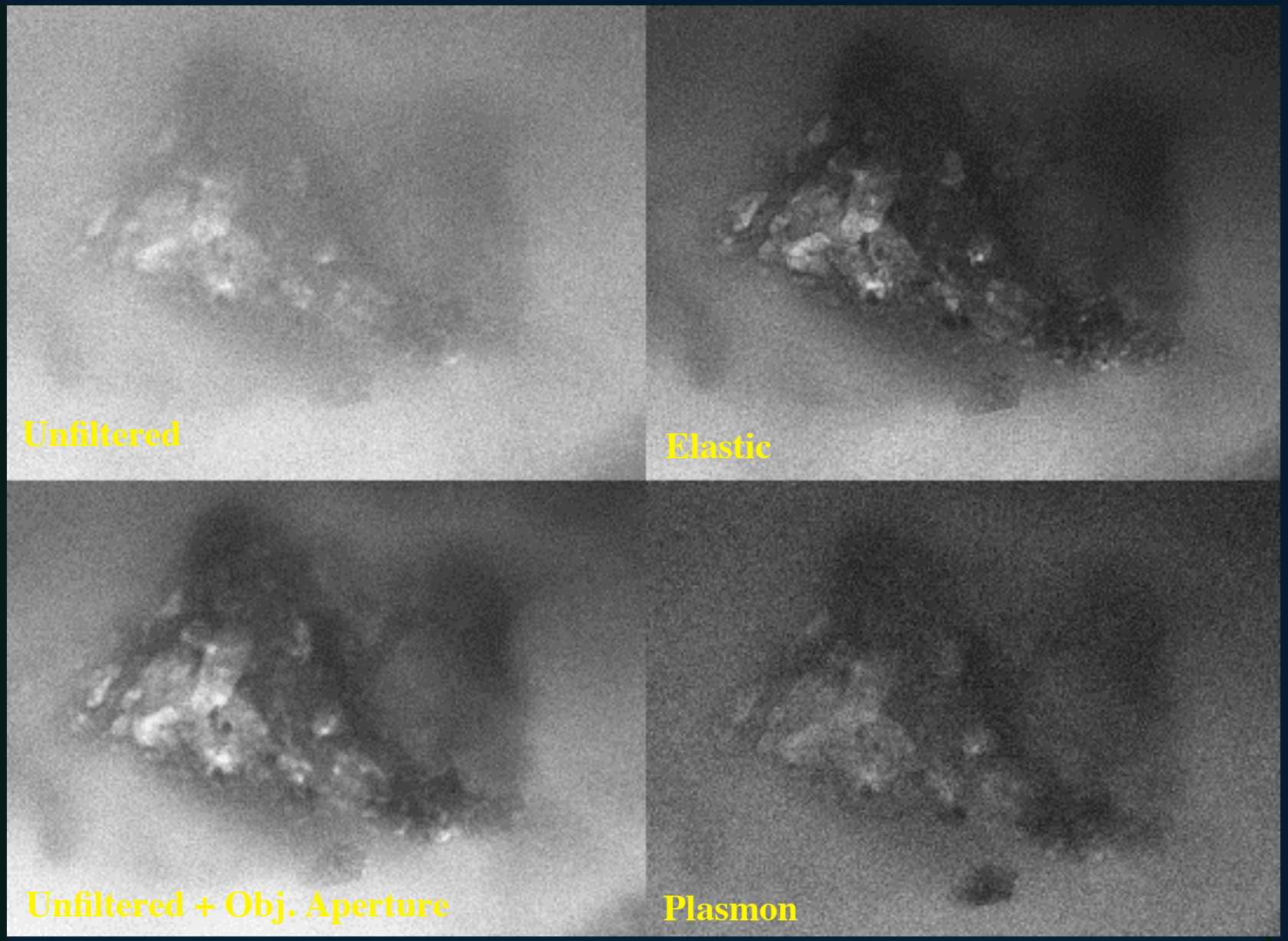


The technique of building up a more or less complete data cube is termed **Spectrum Imaging**

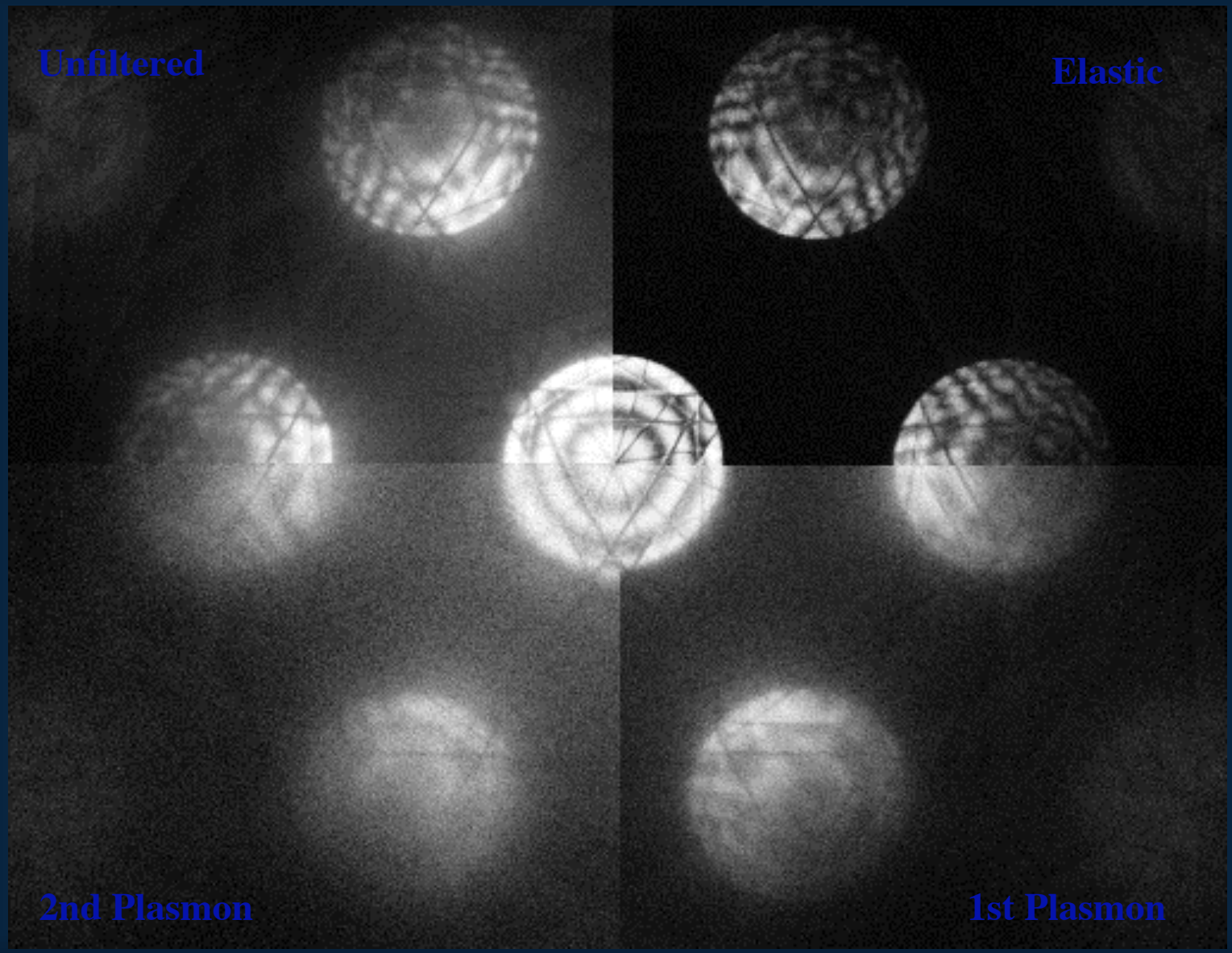
Δx, Δy spatial dimensions
ΔE energy-loss dimension

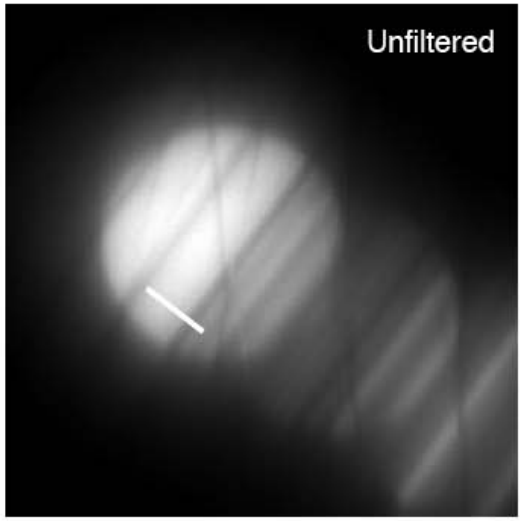
EFTEM Spectrum Imaging:
- Energy filtered broad beam technique
- fills data cube one image plane at a time
- less time

STEM Spectrum Imaging:
- Focused probe method
- fills data cube one spectrum at a time
- less dose

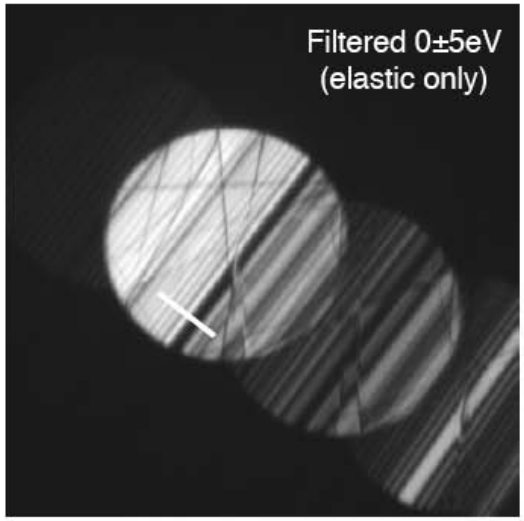

Unfiltered
Elastic
Unfiltered + Obj. Aperture
Plasmon

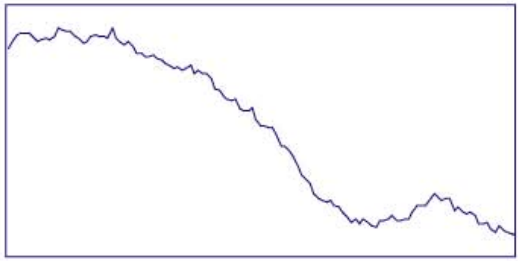
Silicon 111 ZAP- Gamma Corrected



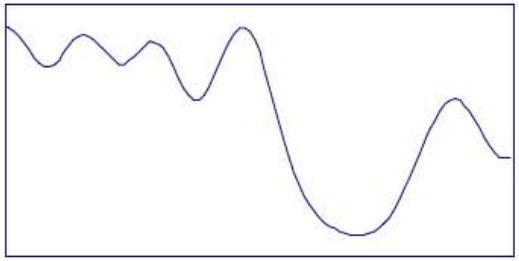


Silicon [110]



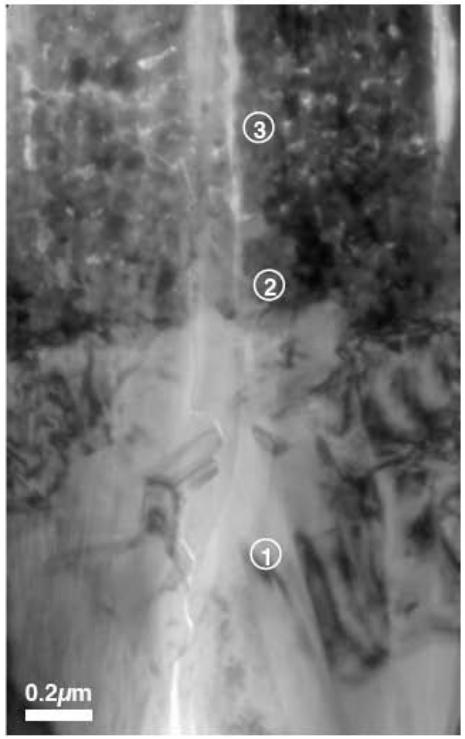


essential for
quantitative CBED



Spectroscopy vs Filtered Imaging

Information without EFTEM

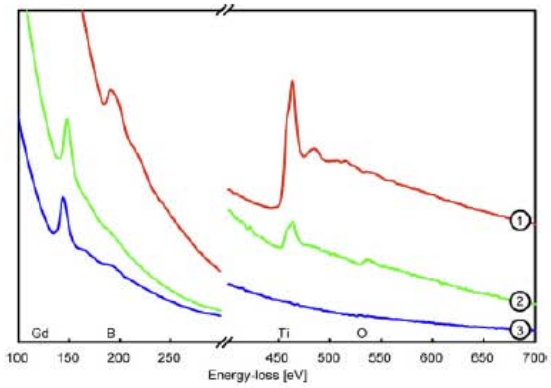


Unfiltered bright field image - structural contrast only

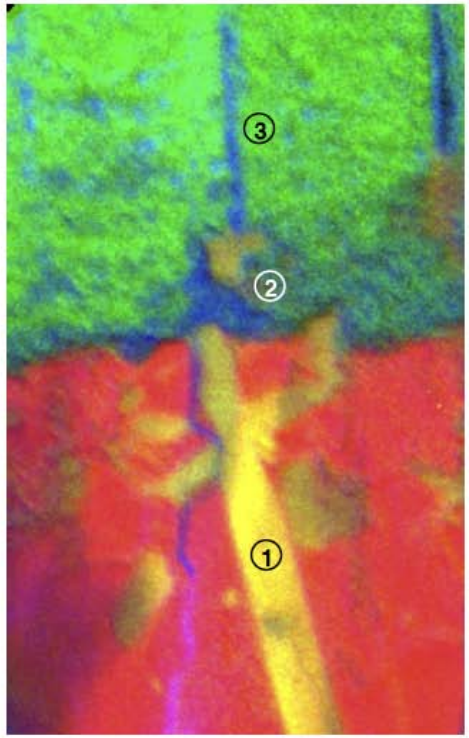
Information gain with EELS + EFTEM

Interface Titanium alloy and PVD-grown Gadoliniumboride

EELS spectra



from conventional TEM images
via EEL-spectra
to energy-filtered images
showing elemental distributions



Titanium Boron Oxygen

EFTEM - Elemental contrast

- What are the goals of the experiment?
  - Detection or quantification
    - Detection
      - What threshold is of interest?
    - Quantification
      - What threshold is of interest?
      - What accuracy & precision needed
  - What kind of data is requested: point analysis, line scans, maps

- Choose analysis technique
  - Select spectrum features to analyze
    - Predict feature overlaps in advance
  - Estimate required S/N for desired detection threshold or quantification precision
    - How long will this take? Are line scans and maps still practical?
    - Determine if unusual techniques or effort is required
  - Determine needed equipment parameters
    - What energy and spatial resolution is required?
    - What equipment configuration allows this?

- Other questions
  - Would another spectroscopy work better for this application?

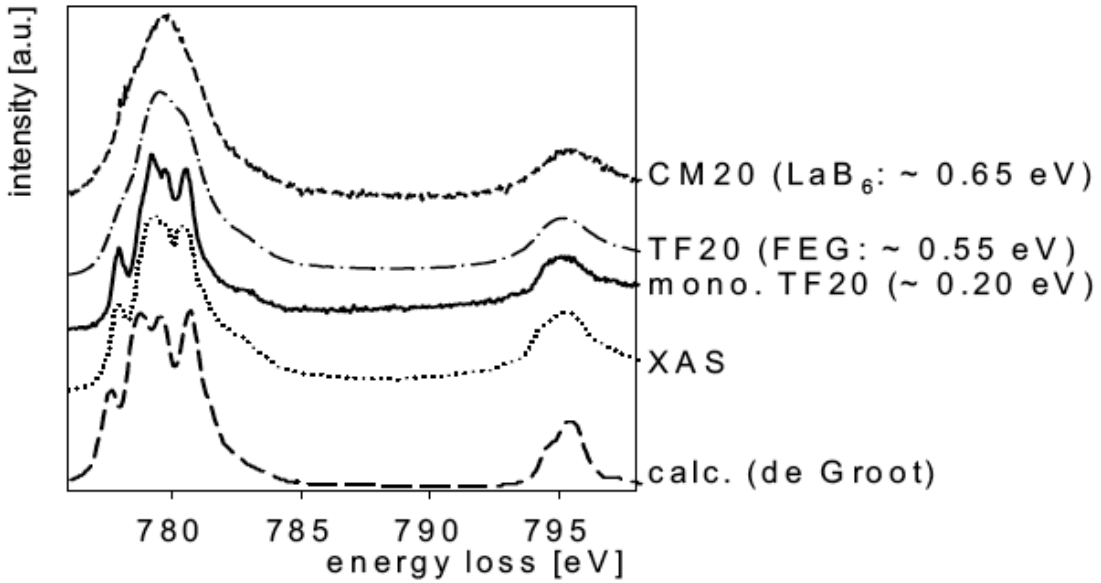


Fig. 2: Comparison of the Co L_{23} ELNES of CoO measured on different microscopes with X-ray absorption data and calculated values. The energy resolution values given are FWHM values of the zero-loss peak.

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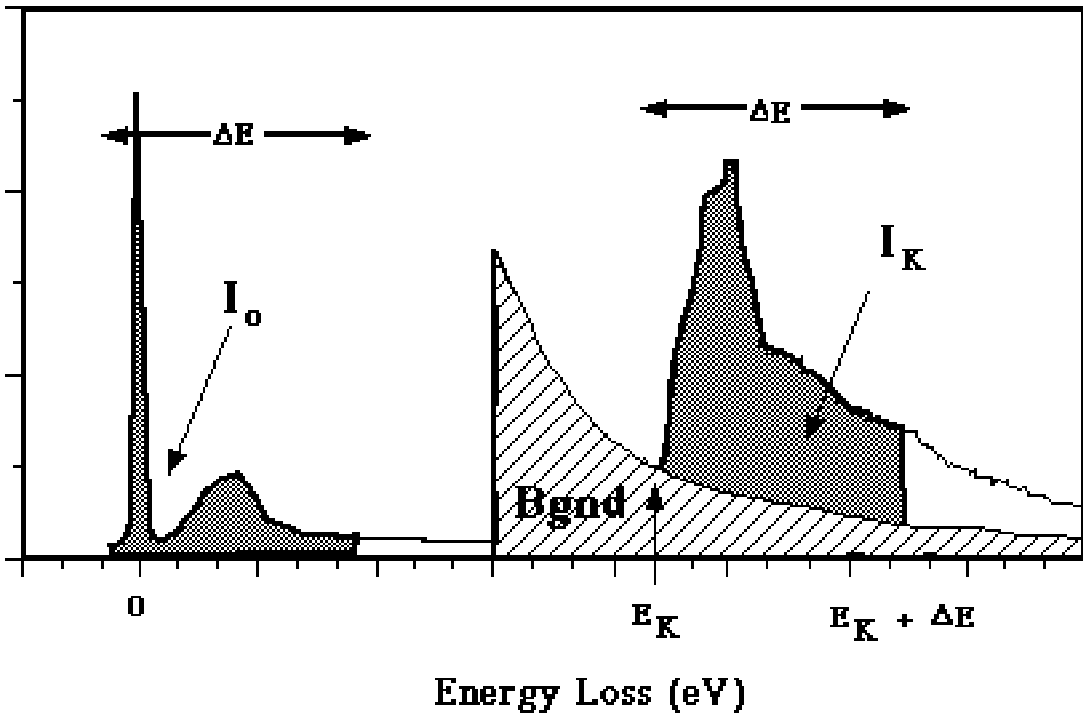
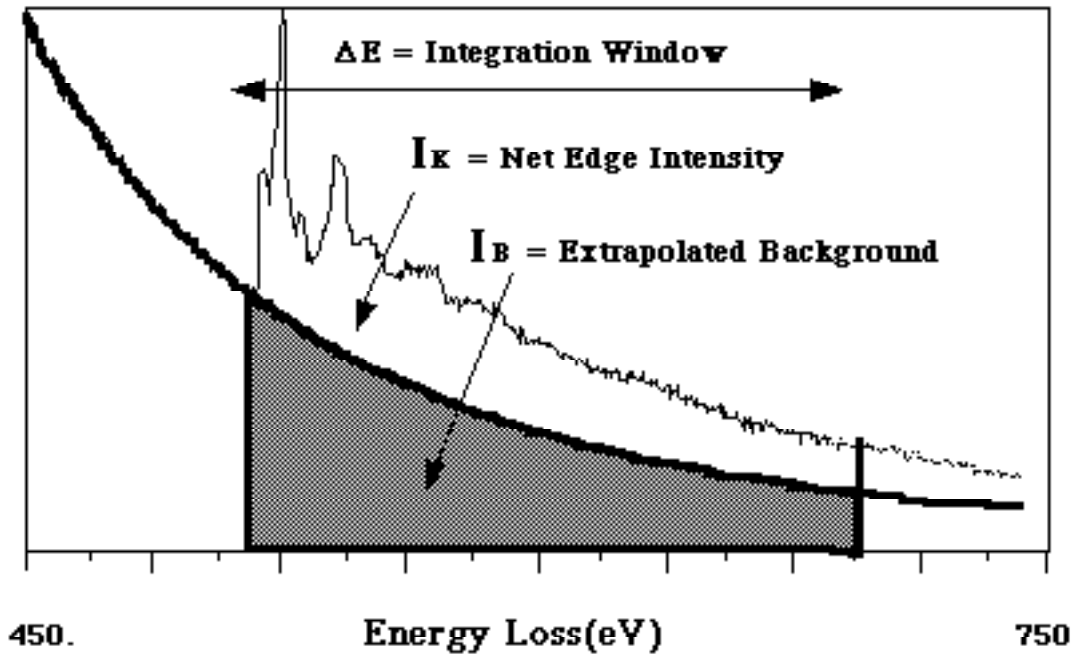
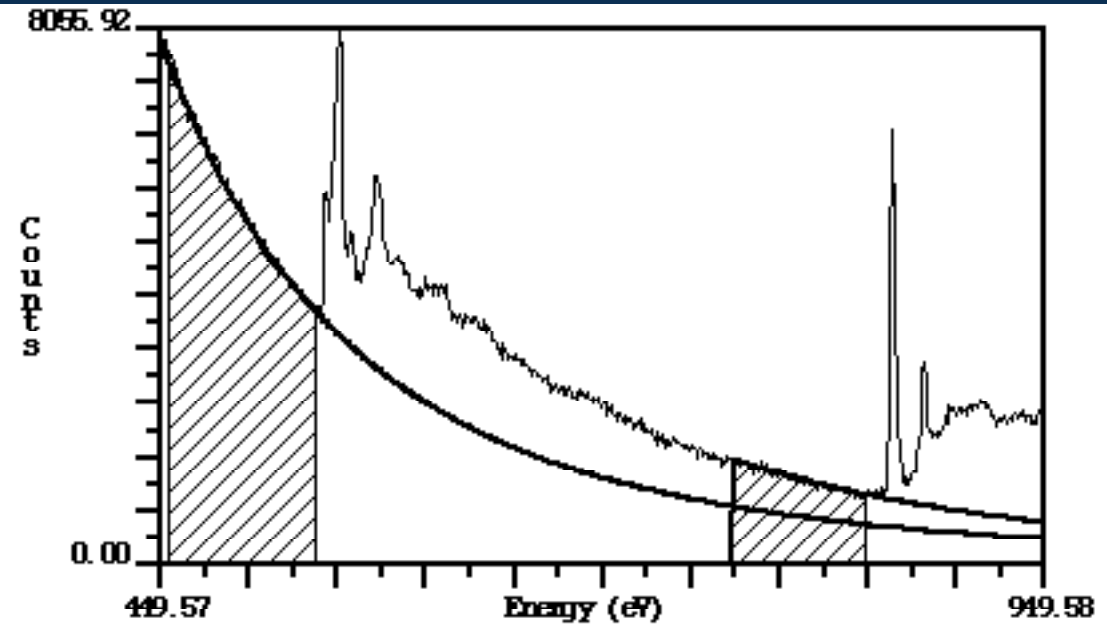
Data Analysis and Quantification:

Spectral Processing
Thin Film Quantification Methods
Specimen Thickness Effects

Measurement of Parameters required for EELS Quantification




ΔE = Integration Window
I_K = Net Edge Intensity
I_B = Extrapolated Background
450.
Energy Loss(eV)
750



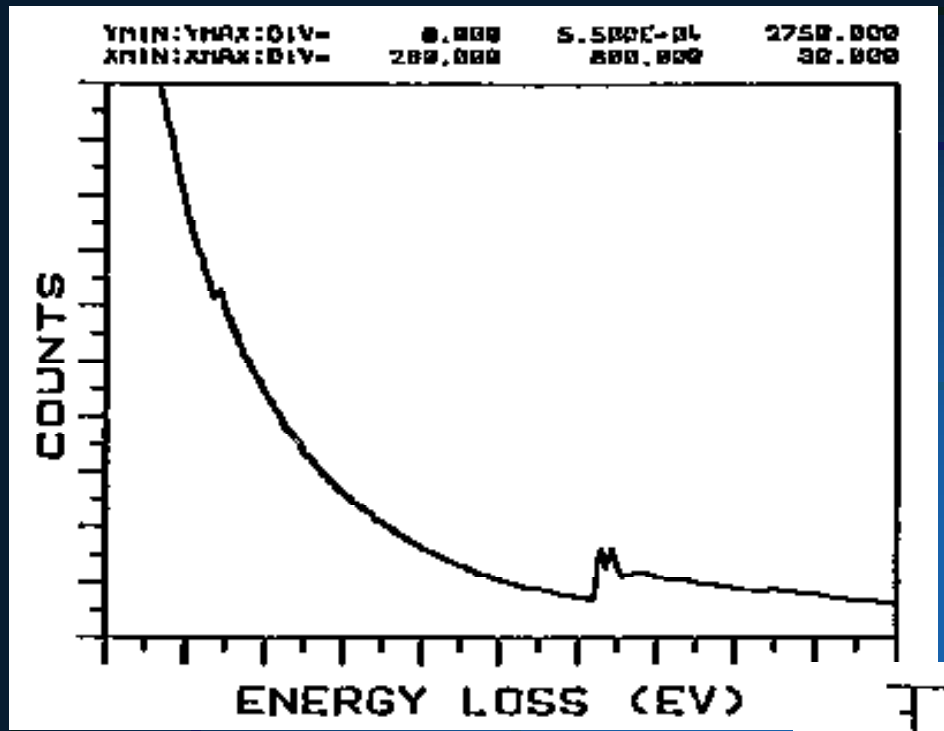
Most Frequently Used Model in the Medium Loss Regime

$$I_{Bgnd} = A\ E^{-R}$$

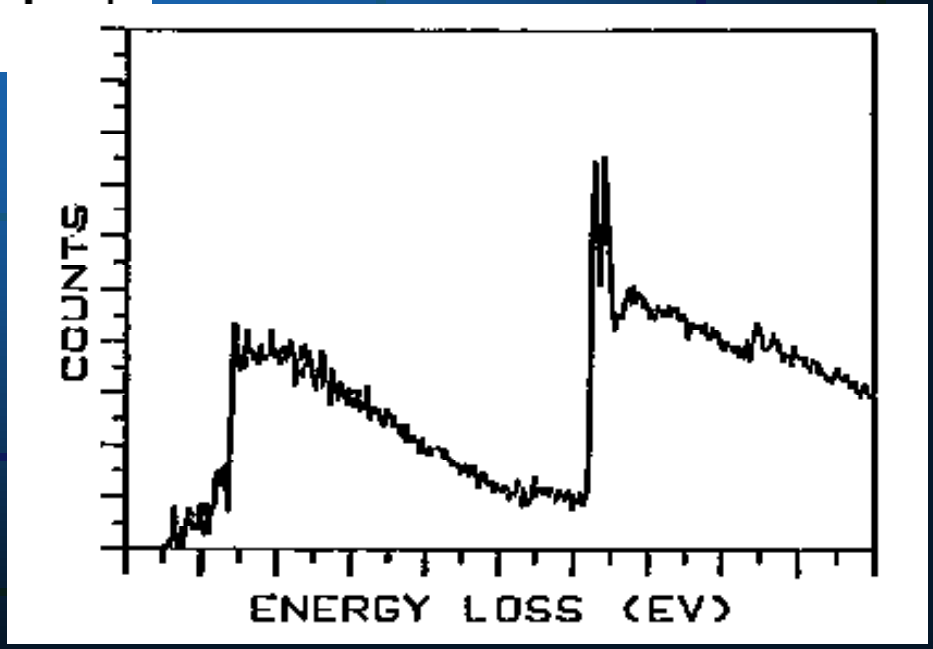
$2 \leq R \leq 7$ typical values for $200\ eV < E < 1500\ eV$

Other Background Models Used are Phenomenological

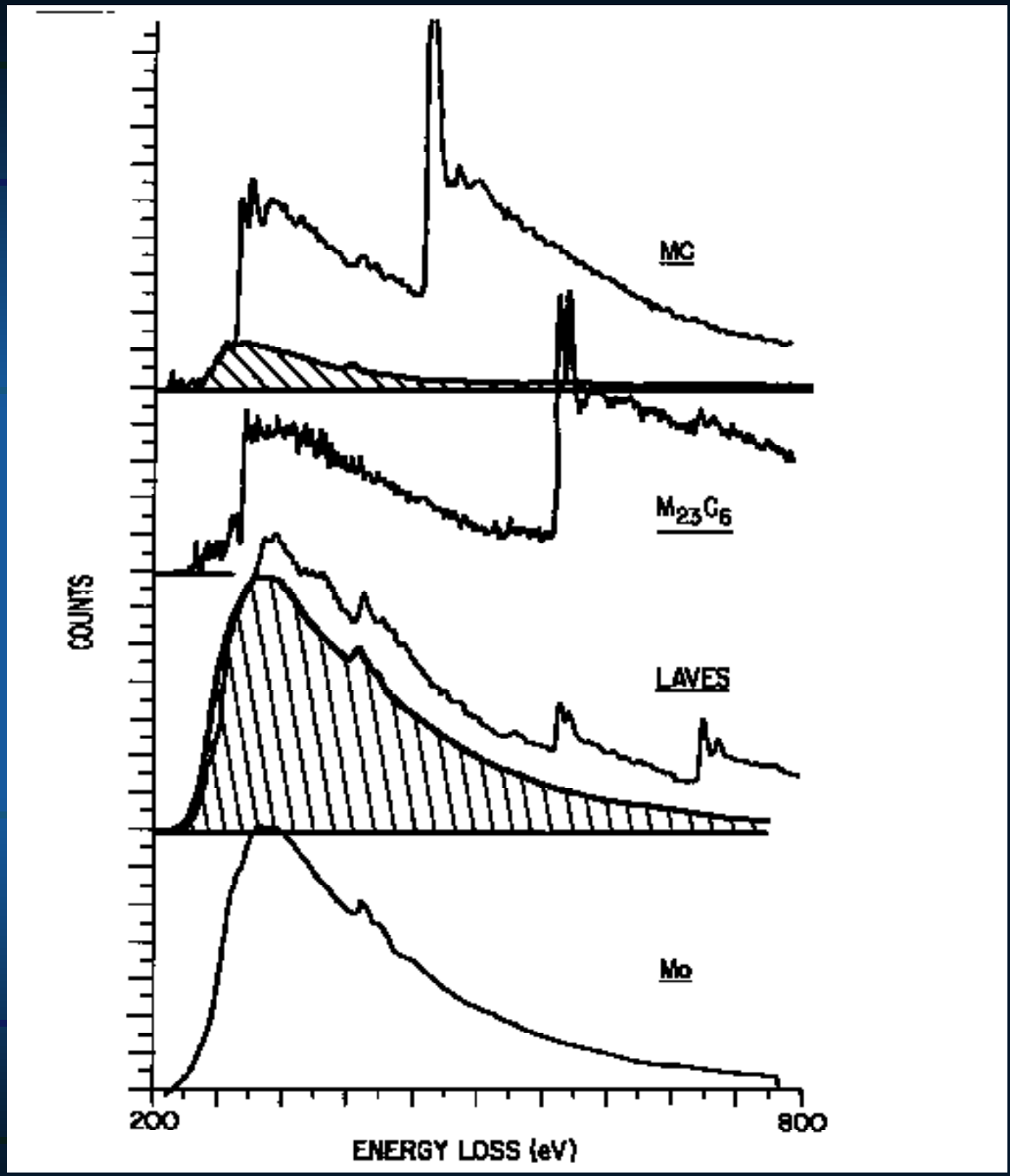
N^{th} Order Polynominal & Log-Polynominal mainly used < 200 eV Loss

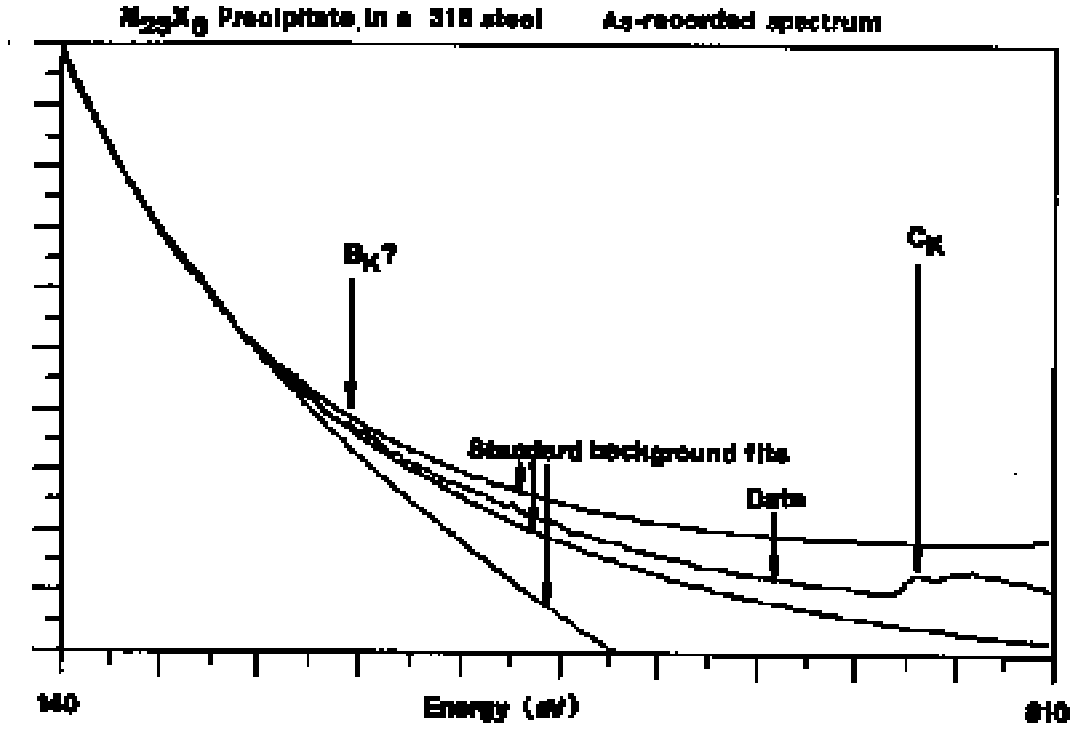


$M_{23}C_6$ in Steel : Spectral Overlap



Spectral OverLap Problems also exist in EELS





Conventional Background Fitting does not always allow the user to find small peaks in high background areas.

Two Related Methods are sometimes used:

Second Difference Filtering (Shuman etal MAS,1983)

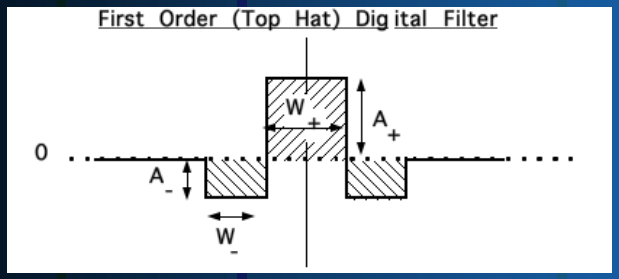
Record 3 Energy Loss Spectra which are displaced in energy by dE Mathematically combine in computer to form the Second Difference (SD) Spectrum

$$SD(E) = I_1(E-dE) - 2\,I_2(E) + I_3(E+dE)$$

Spectrum has the appearance of a derivitive, removes channel to channel gain variation in parallel EELS and slowly varying backgrounds. Sharp features are enhanced in visibility.

Digital Filtering

This is related to a simple numerical differentiation of a single spectrum



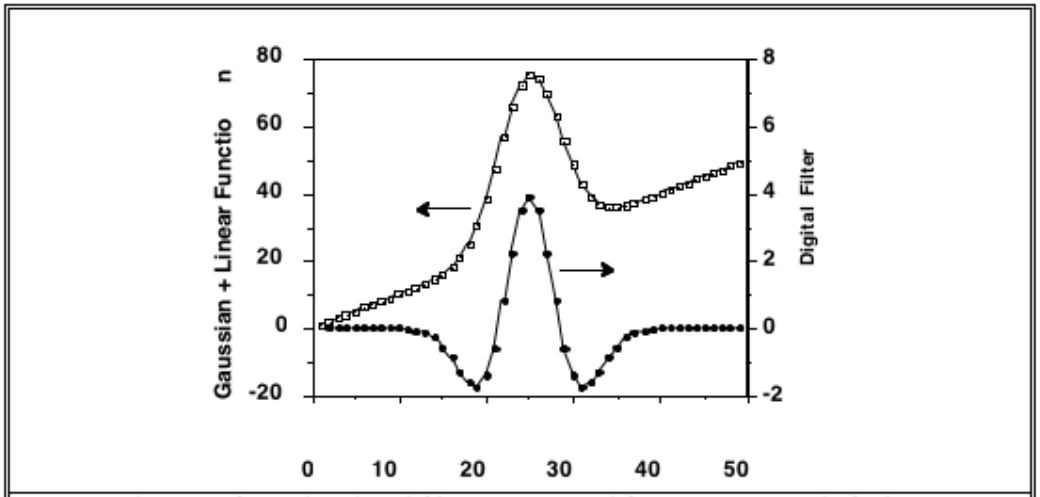


Fig 1.6 Application of a tophat digital filter to a spectral function composed of a linear + Gaussian distribution. Note removal of linear component and distortion of the Gaussian.

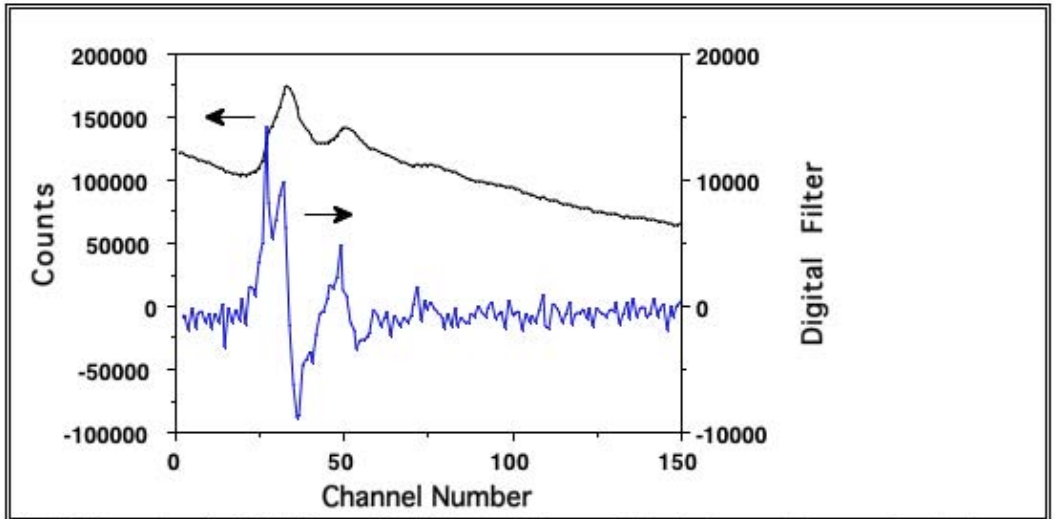
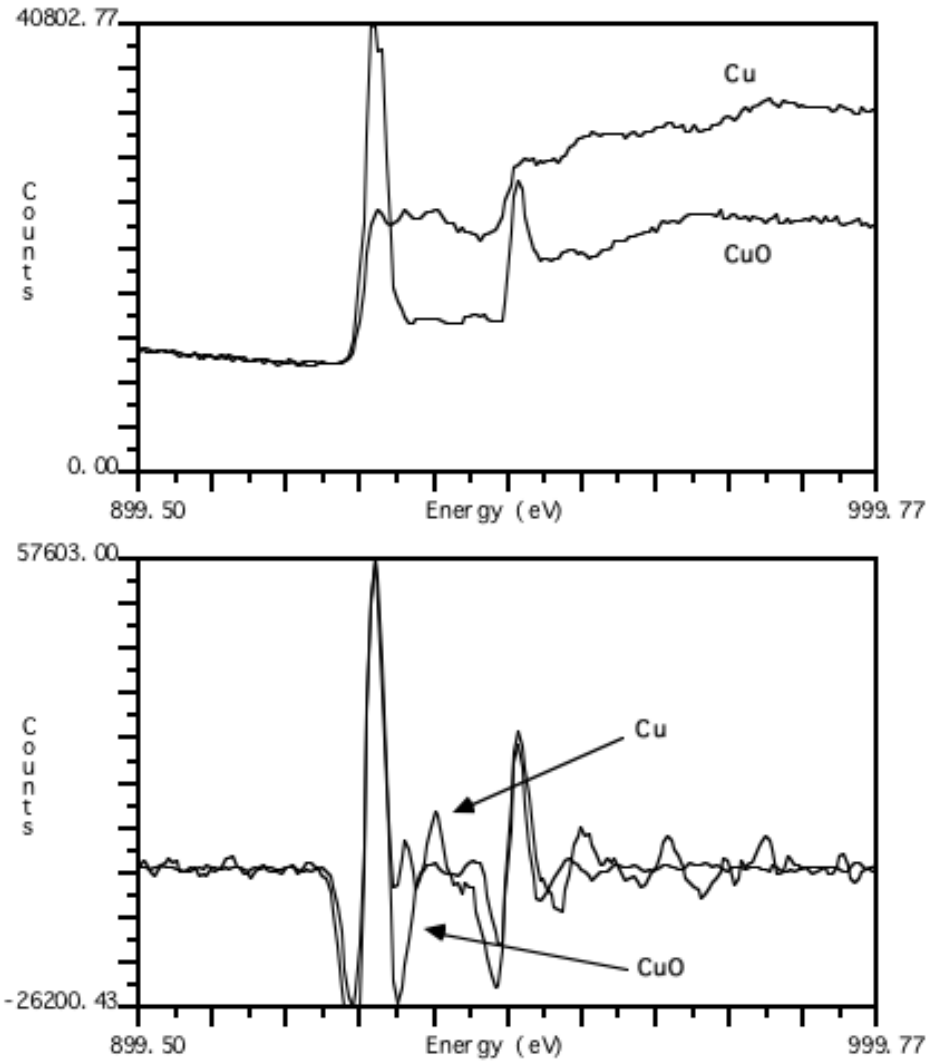
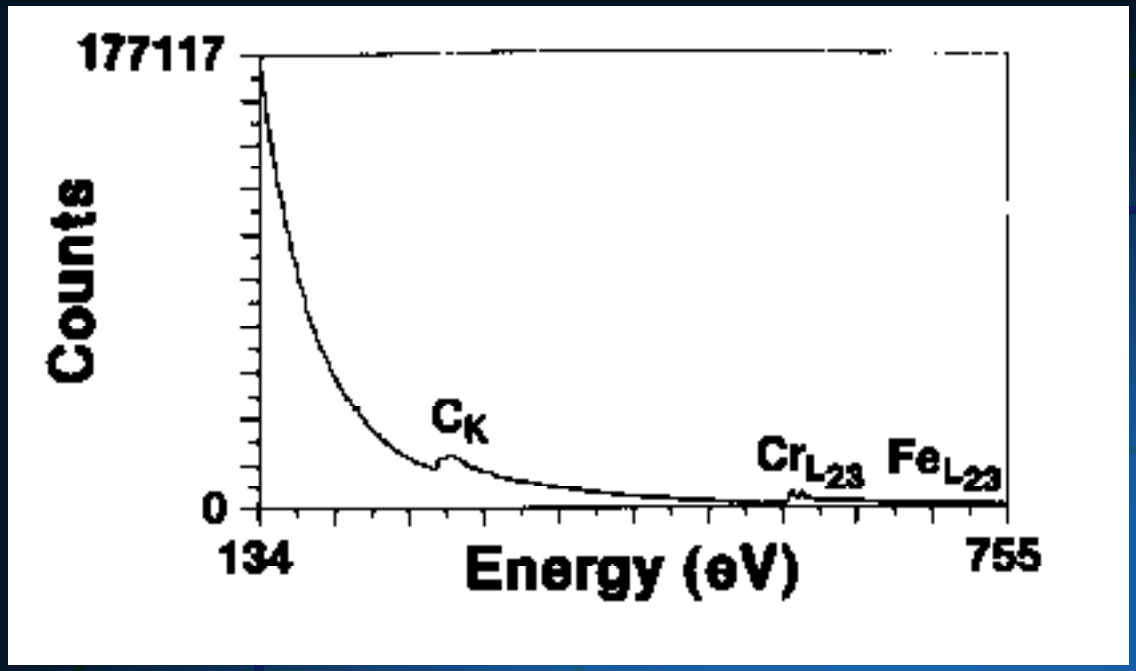
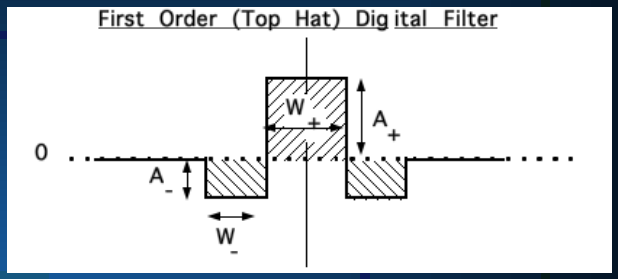


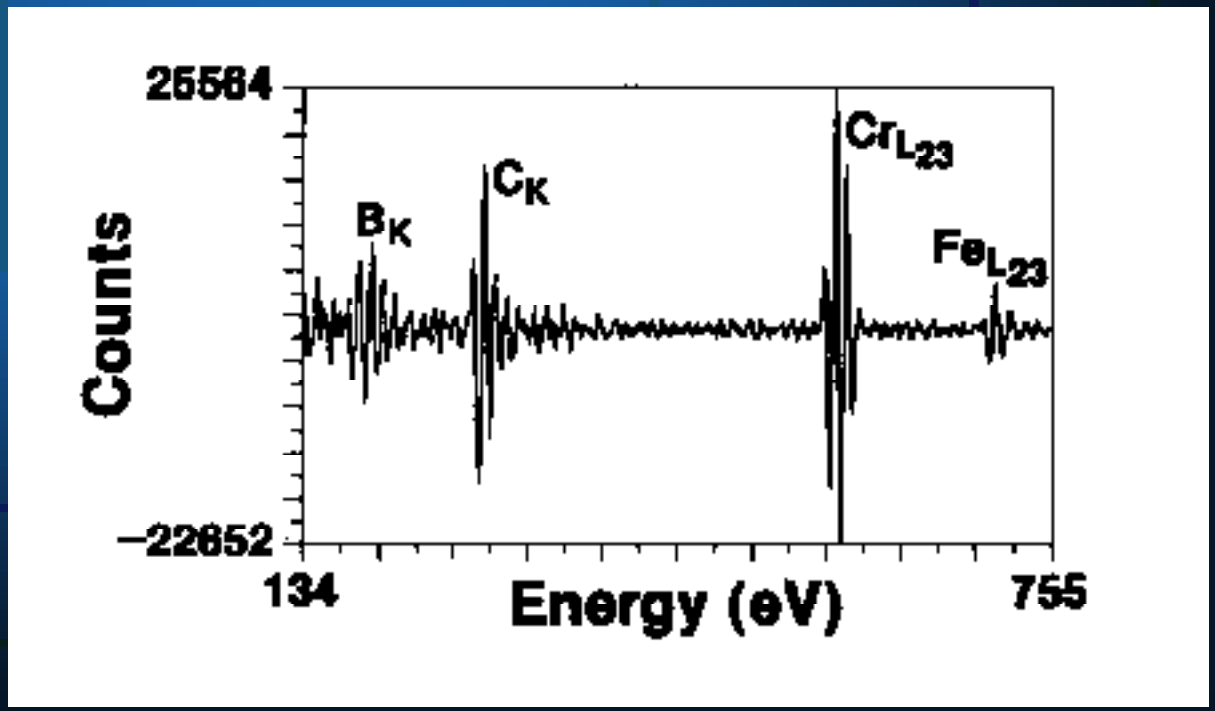
Fig 1.7 Example of digital filter of EELS data. Note complete background supression, but severe spectral distortion.

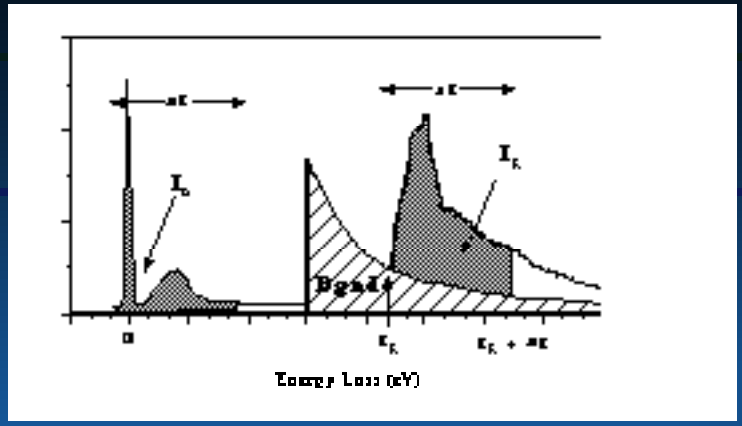
Filtering of EELS Spectra




177117
Counts
0
134
Energy (eV)
755
C_K
$Cr_{L_{23}}$
$Fe_{L_{23}}$


First Order (Top Hat) Digital Filter
0
A_-
W_-
W_+
A_+


25584
Counts
−22652
134
Energy (eV)
755
B_K
C_K
$Cr_{L_{23}}$
$Fe_{L_{23}}$



$$I_k = P_k * I_o$$

I_k = Number of electron having excited a kth inner shell

P_k = Probability of excitation of the kth shell

I_o = Incident electron current

$$P_k = N \sigma_k$$

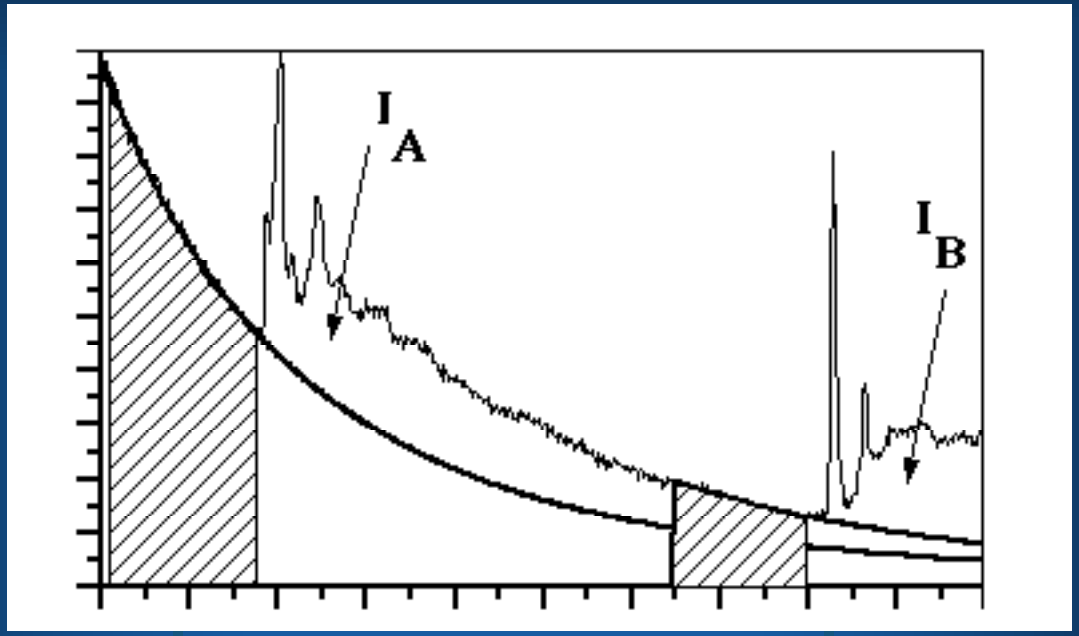
N = Number of atoms of the element analyzed

σ_k = Ionization cross-section for the kth shell

$$N = \frac{I_k}{\sigma_k \; I_o}$$

Alternatively;

Consider the ratio of Intensities of any two Edges in the same spectrum I_A and I_B



Invoke the Ratio Method and obtain the exact equation:

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

Note the similiarity of this equation with that of Thin Film XEDS

But in the real world the assumptions used in the above simple arguments are never realized:

- Measure all scattered electrons($\beta=\pi=180^0$)
- Integration over all energy Losses

Because we must measure over a finite energy window (δE) we modify the expression to:

$$N_A = \frac{I_A(\delta E)}{\sigma_A(\delta E) * I_0}$$

we also measure over a finite angular window (β) and therefore, we modify the expression to:

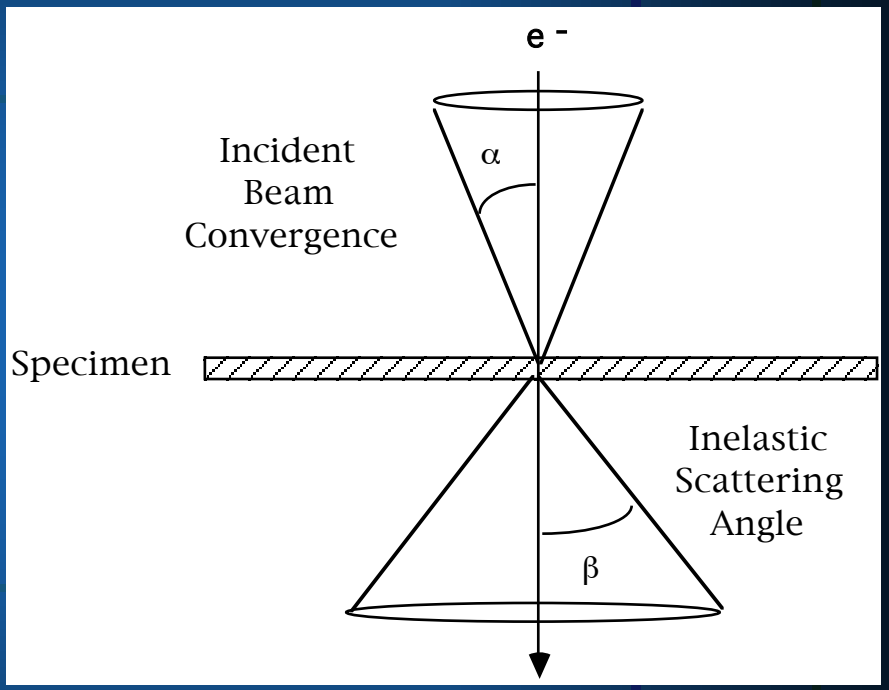
$$N_A = \frac{I_A(\delta E, \beta)}{\sigma_A(\delta E, \beta) * I_0}$$

and the ratio equation becomes:

$$\frac{N_A}{N_B} = k_{AB} \frac{I_A(\delta E, \beta)}{I_B(\delta E, \beta)}$$

with

$$k_{AB} = \frac{\sigma_B(\delta E, \beta)}{\sigma_A(\delta E, \beta)}$$



By measuring $\mathcal{N}$ edges we have $\mathcal{N}-1$ equations, if we invoke the argument that the compositions must sum to unity

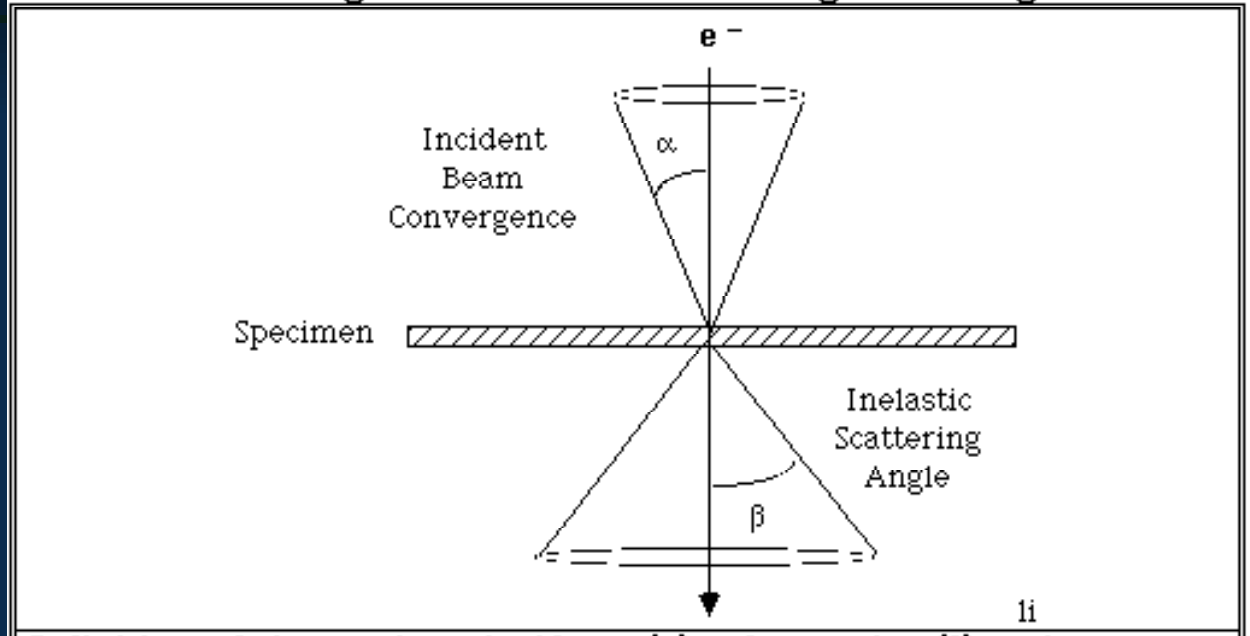
$$\sum_{i=1}^{\mathcal{N}} C_i = 1$$

we arrive at a set of $\mathcal{N}$ equations and $\mathcal{N}$ unknowns which can be solved by simple algebra.

For example:

- if $N_A/N_B = 2.$; then $N_A = 2\,N_B$
- if $N_A + N_B = 1$; then $3N_B = 1$ or $N_B = 0.33$
- and $N_A = 1 - N_B = 0.67$

Measuring Incident and Scattering Solid Angles



Definitions of electron beam incidence (α) and scattering (β) angles

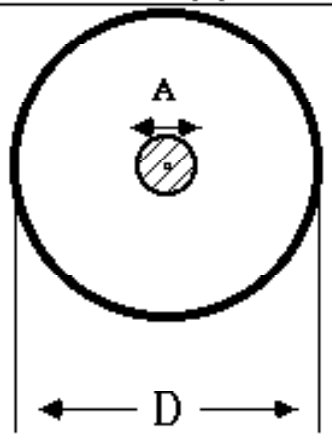
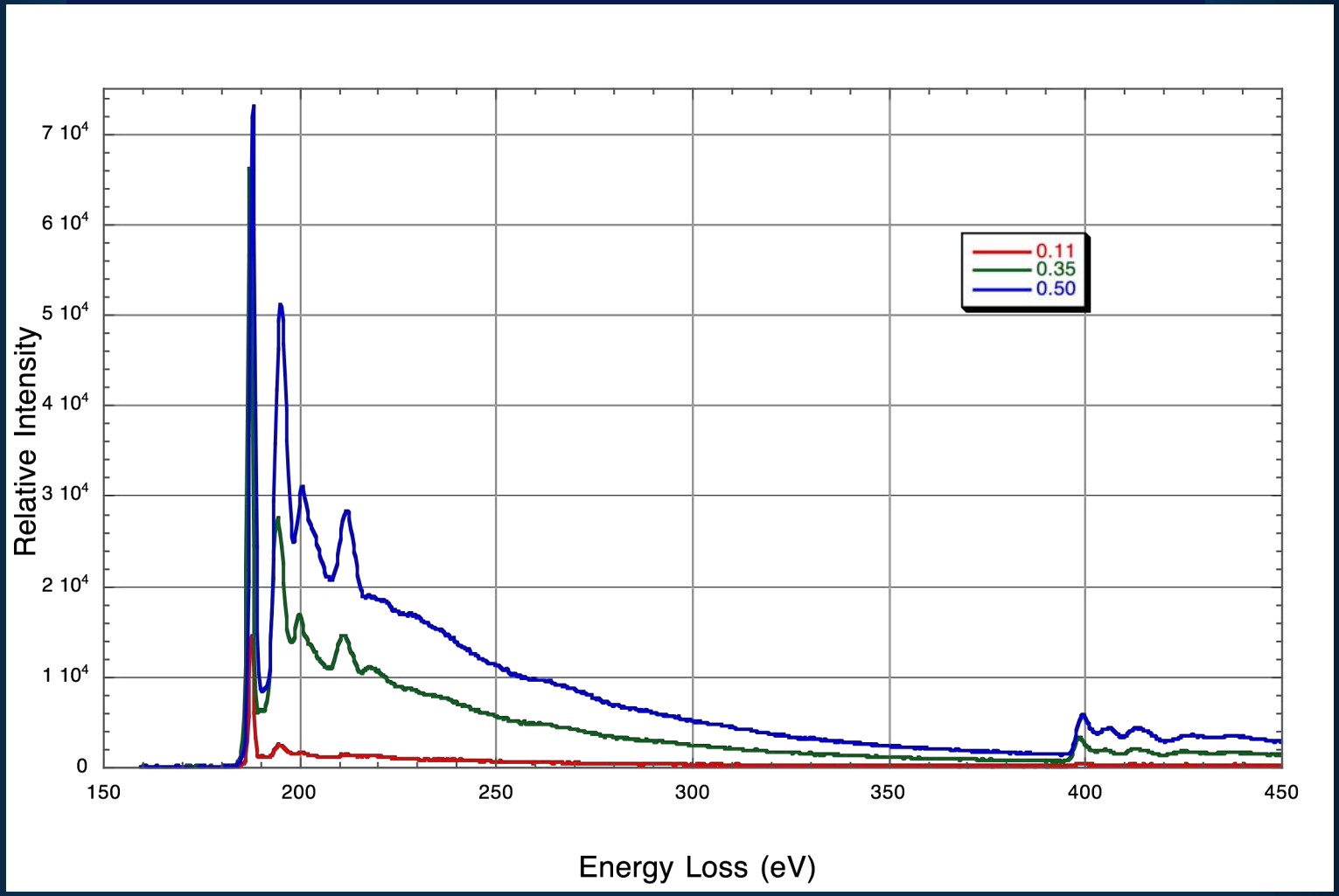


Figure 1.4 Measurement of convergence or scattering angles by comparison to a polycrystalline diffraction pattern of a standard.

$$\alpha \text{ or } \beta = \frac{A}{D} * 2\,\text{Arcsin}\left(\frac{\lambda}{2d}\right) \qquad \lambda = \frac{12.27}{\sqrt{V_o(1+0.978x\,10^{-6}V_o)}}$$

Hexagonal Boron- Nitride



θ_E ~0.777 mR

θ_E ~1.62 mR

Problems in EELS Quantification
Cross-section Calculations

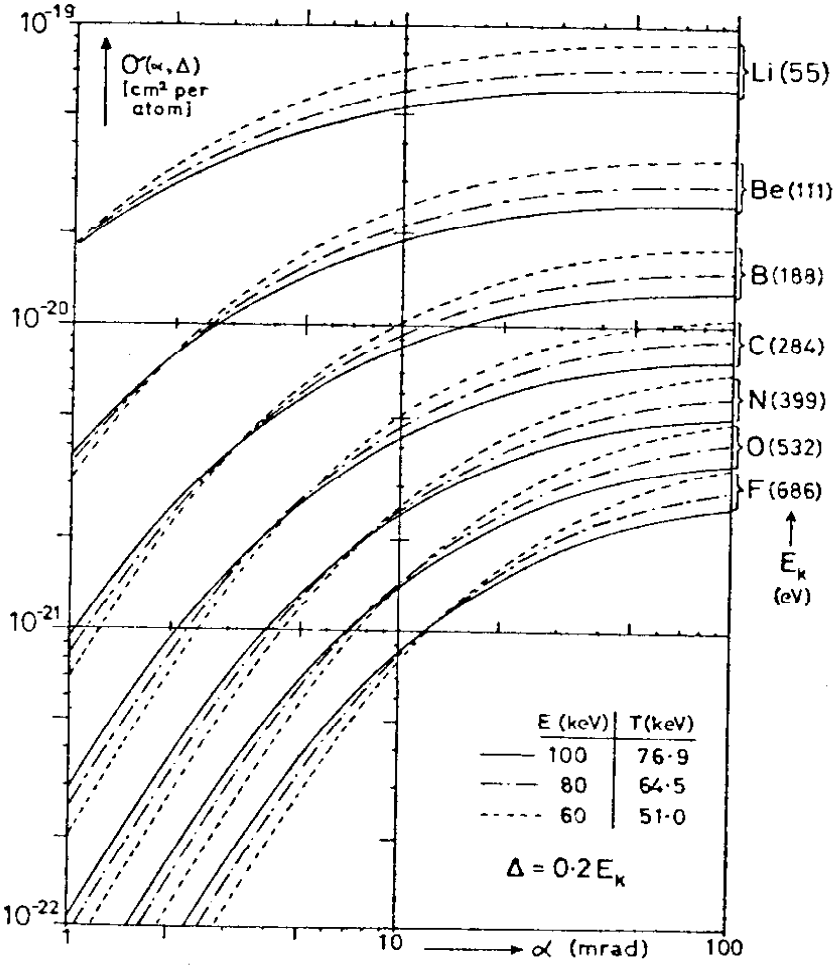


Fig. 3. K-shell partial cross-sections for first-row elements with $\Delta = 0.2\,E_K$ and incident electron energies of 60, 80 and 100 keV.

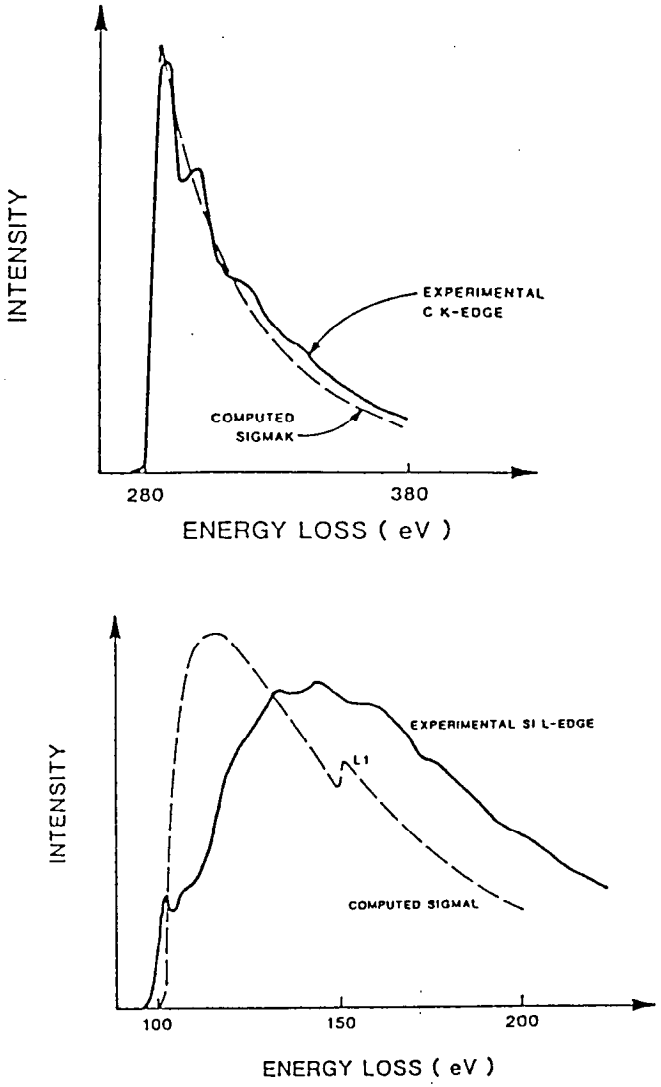
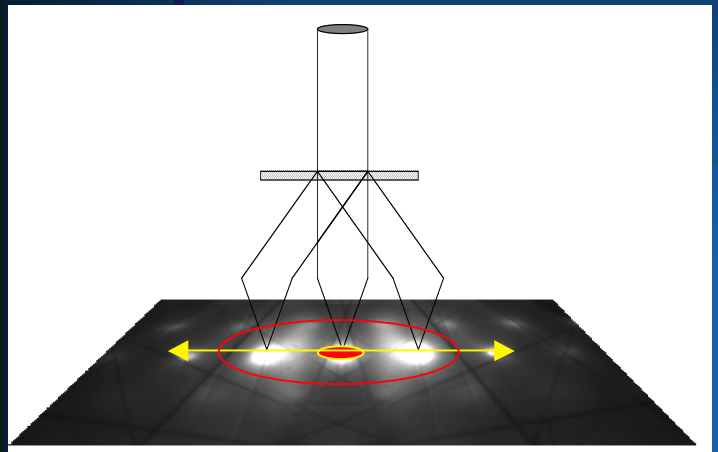
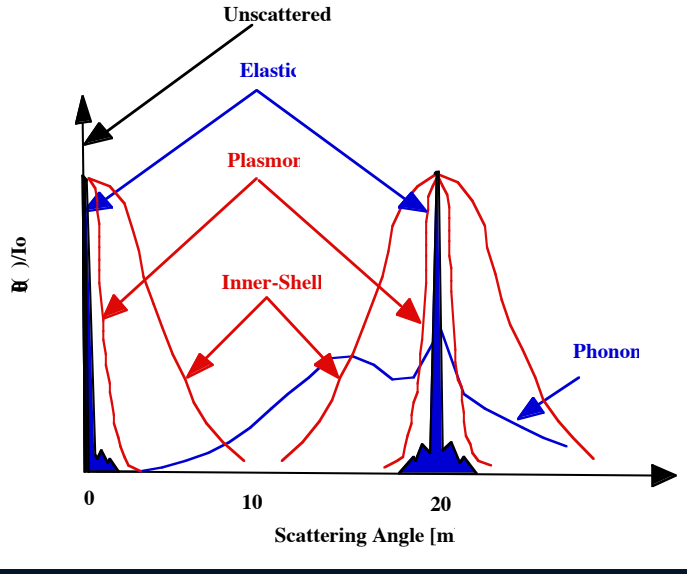
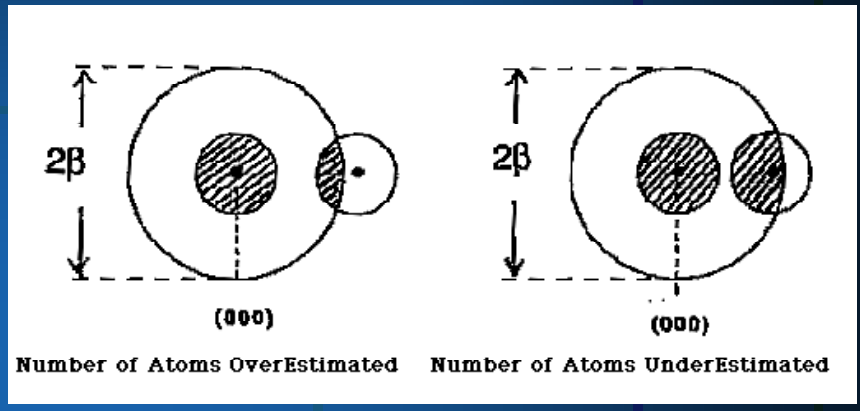


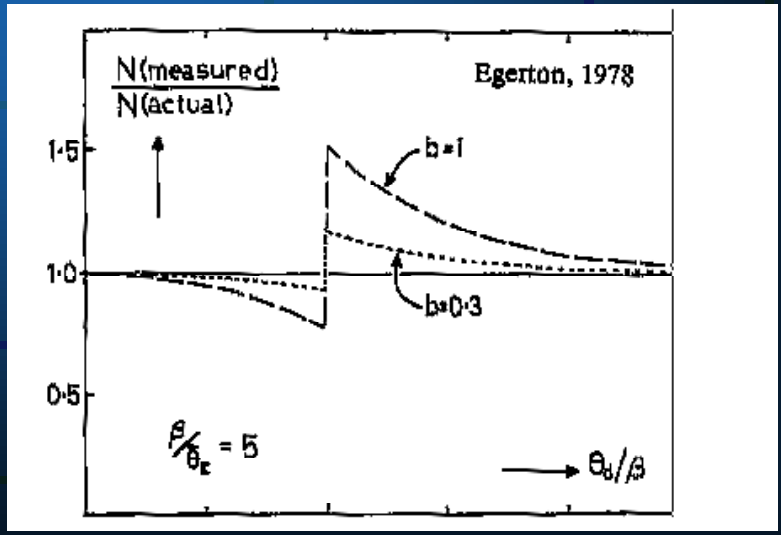
Figure 5 Comparison of an experimental L edge profile with the equivalent profile calculated by using the SIGMAL model.

Problems In EELS Quantification
Collection Angle Errors

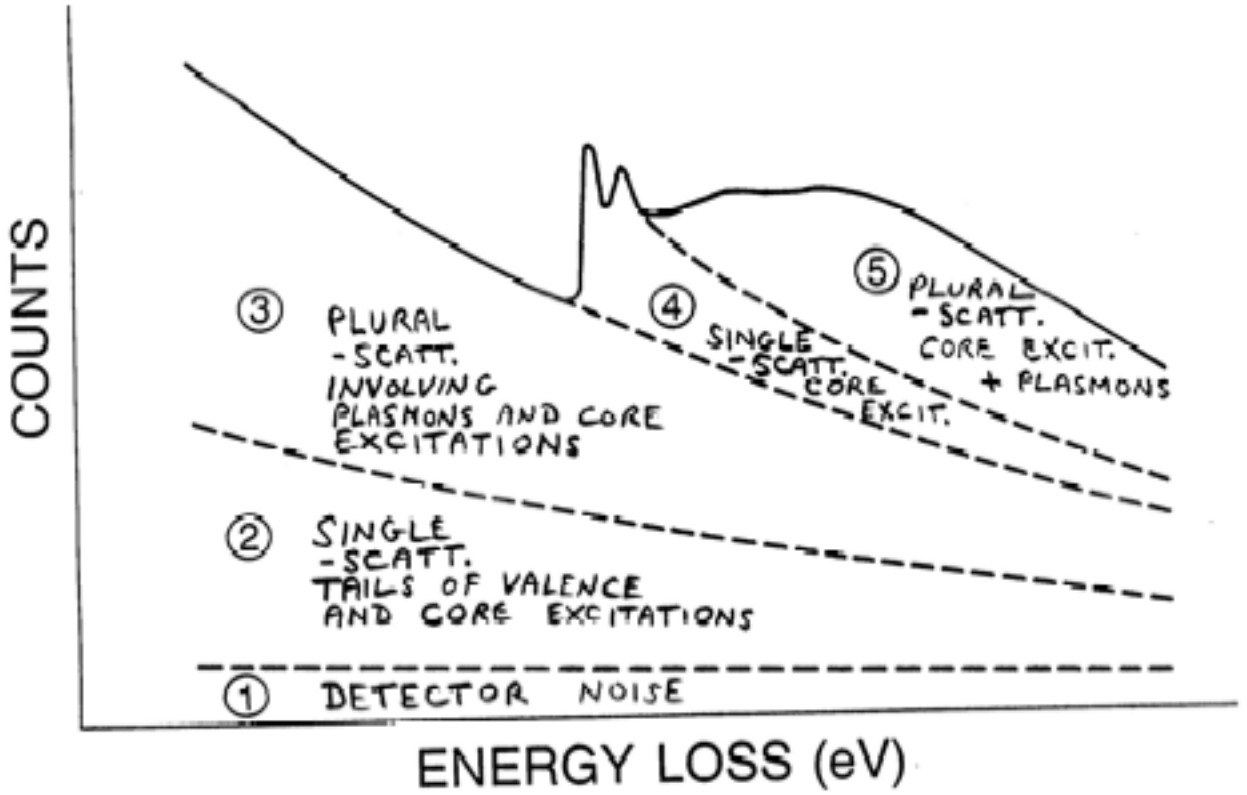








Problems In EELS Quantification
Multiple Scattering



Leapman, 1991

Effects of Specimen Thickness

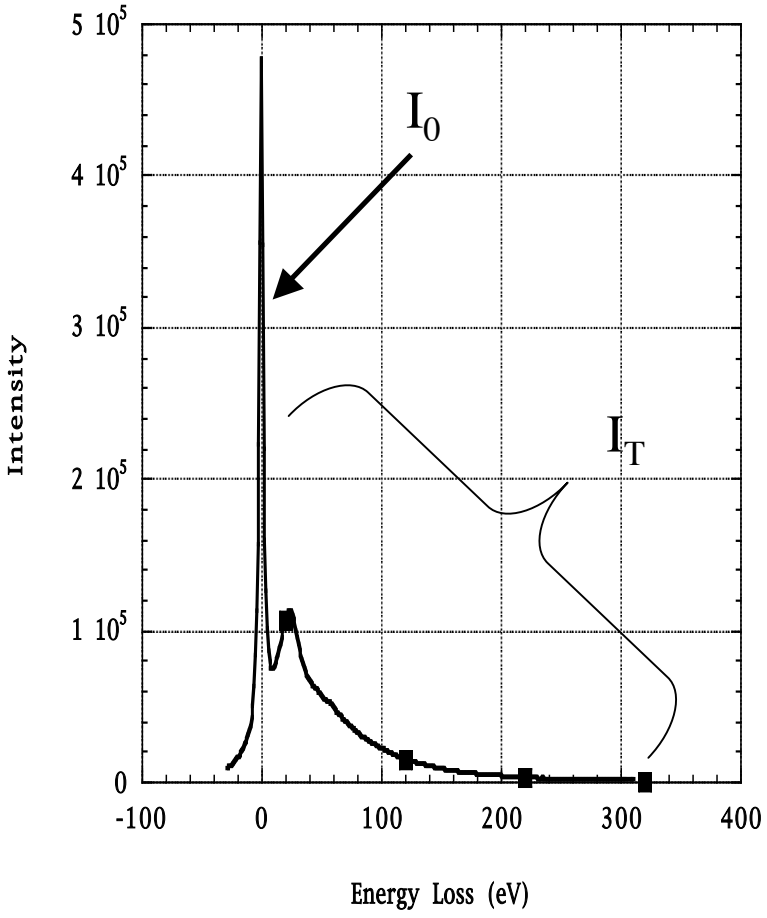
- **Multiple Scattering**
  - **Low Loss**
  - **Core Loss -Visiblity**
  - **Quantification Effects**

- To measure the thickness of compare the intensity of the zero loss (I_0) to the total integrated intensity in the spectrum (I_T).

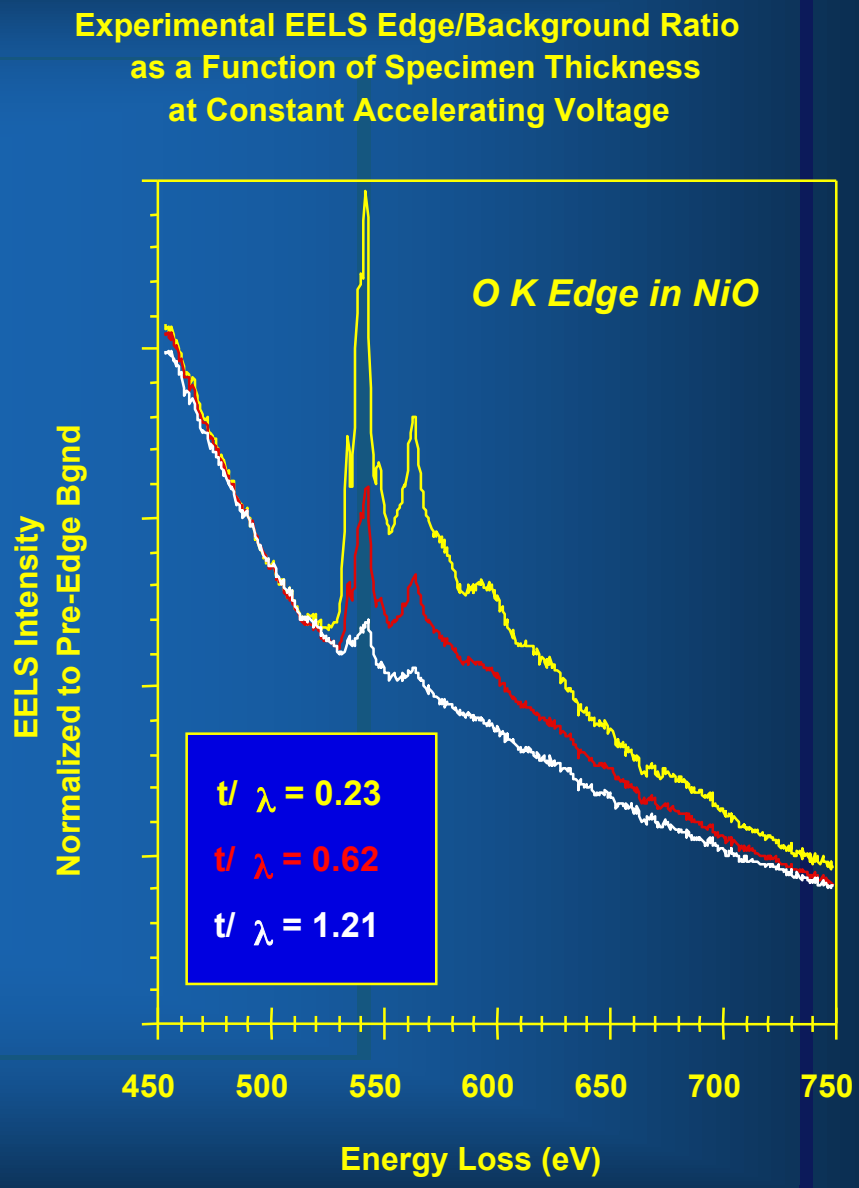
- This ratio is directly proportional to the local thickness of the specimen.

$$t = \lambda * \ln (I_o / I_T)$$

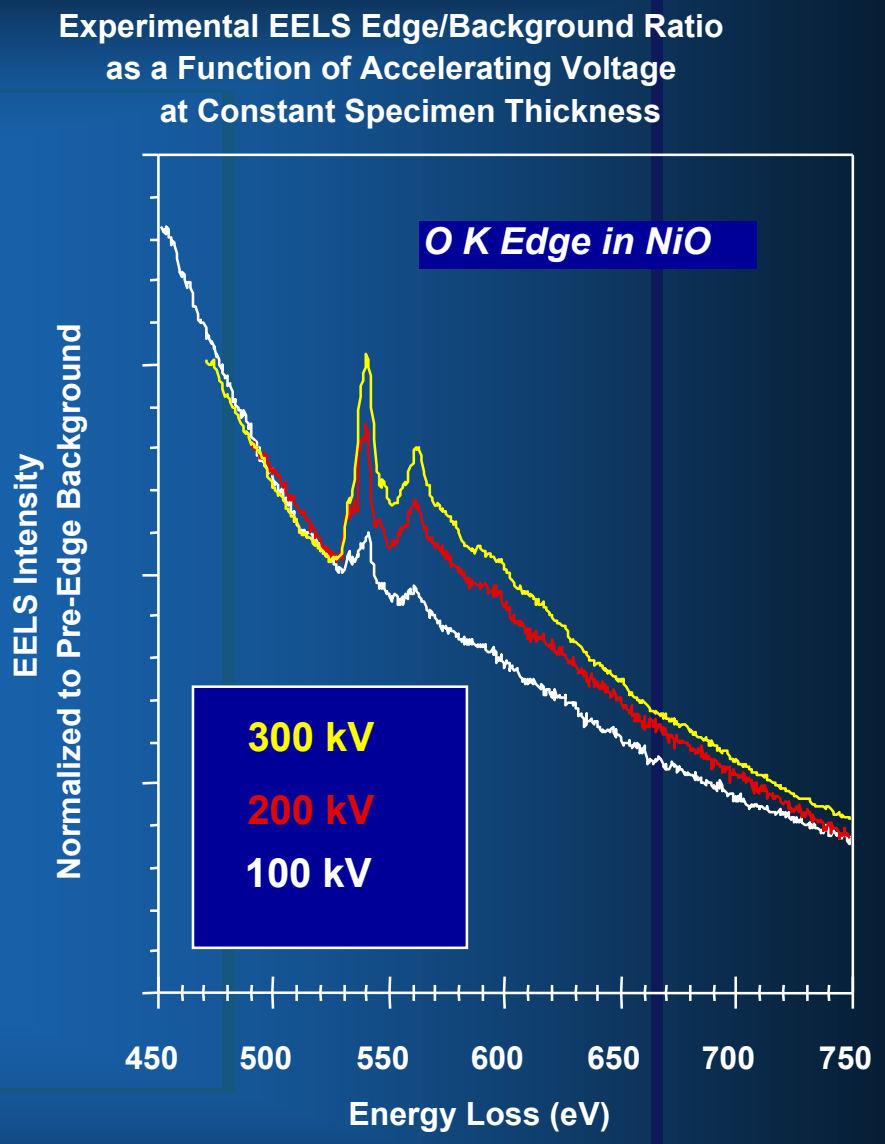
λ = mean free path



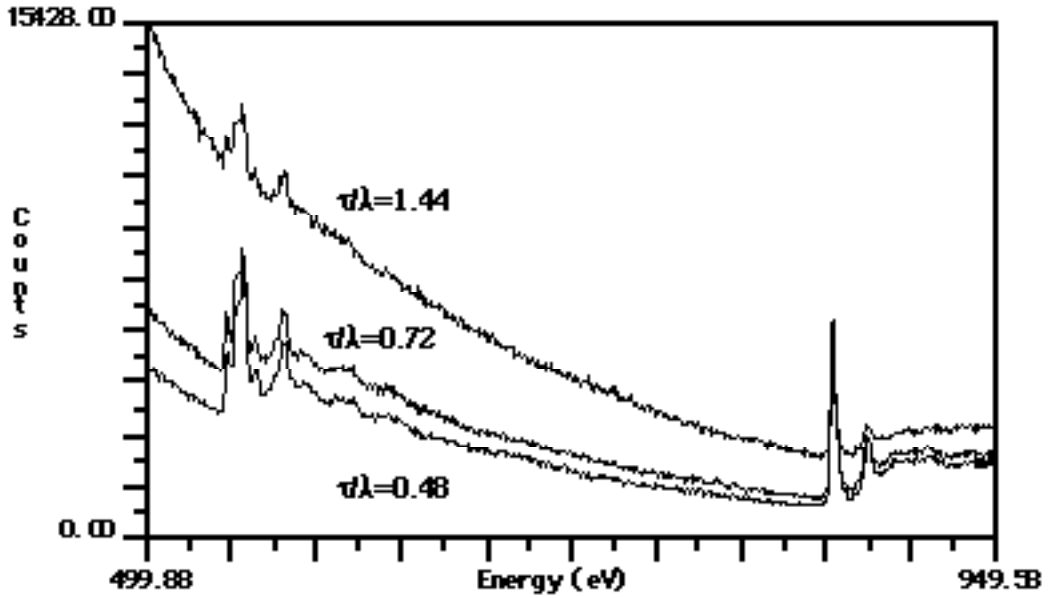
Variation in EELS Edge P/B with Thickness

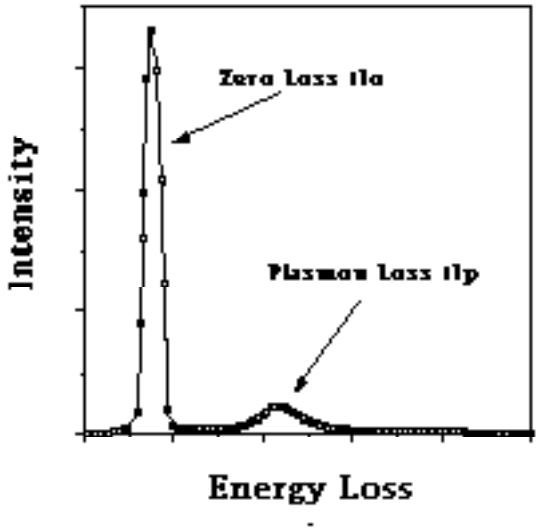


Variation in EELS Edge P/B with kV



Specimen Thickness Effects on EELS

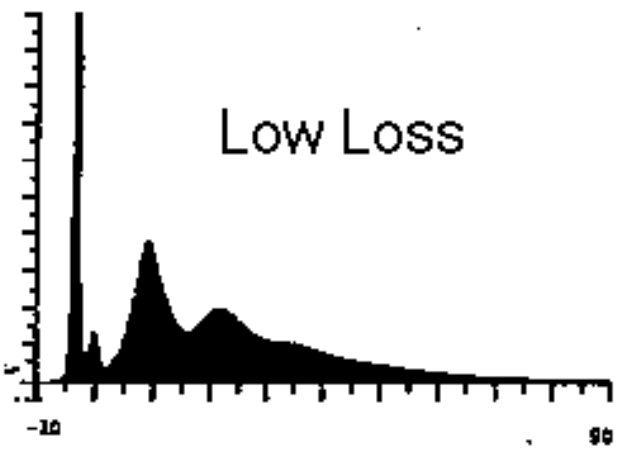


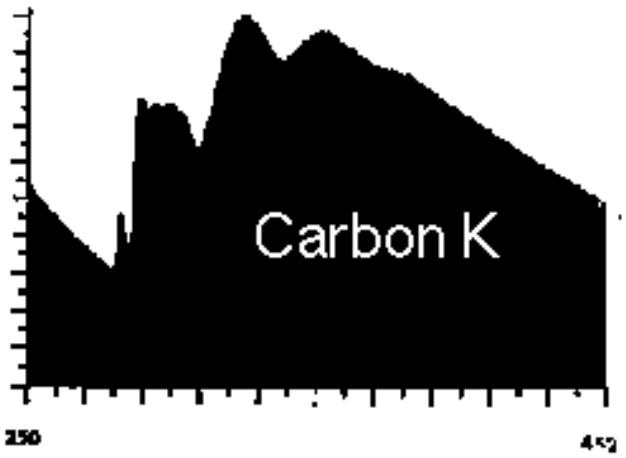


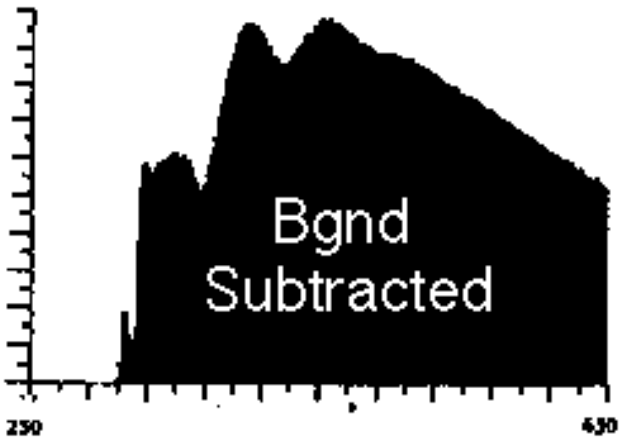
$$\frac{I_P}{I_o} = \frac{t}{\lambda} \leq 0.1$$

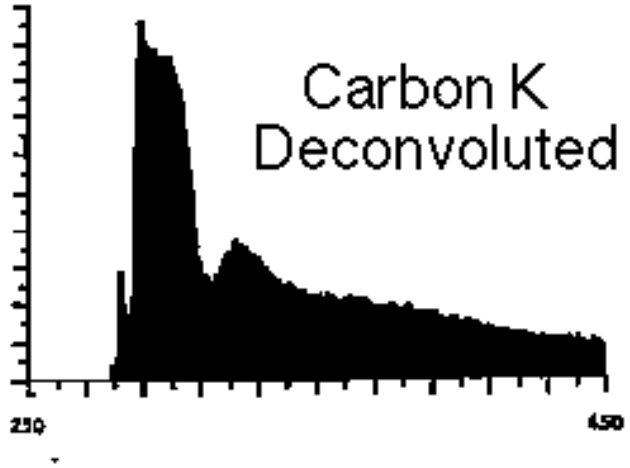
$$\ln\left(\frac{I_T}{I_o}\right) = \frac{t}{\lambda} \leq 1.0$$

Deconvolution of Multiple Scattering using Leapman/Swyt Method







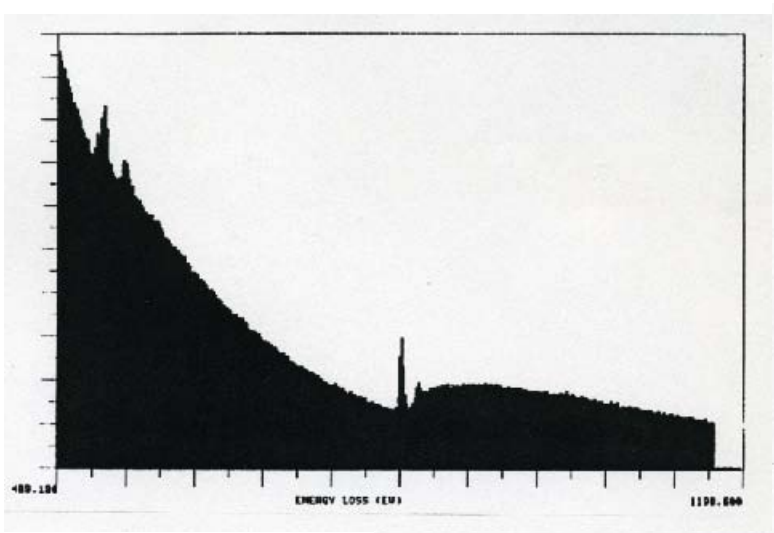


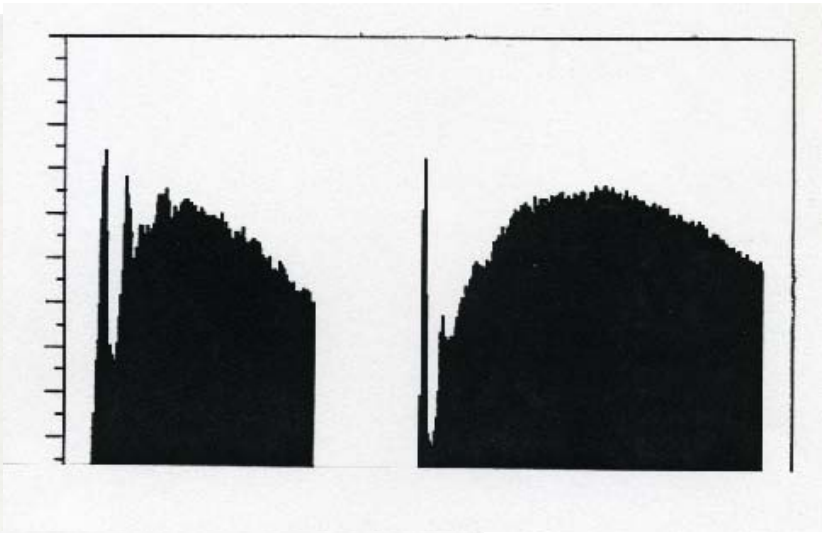
$$MS = SS * LL \qquad SS = \mathcal{F}^{-1}\left\{\frac{\mathcal{F}(MS)}{\mathcal{F}(LL)}\right\}$$

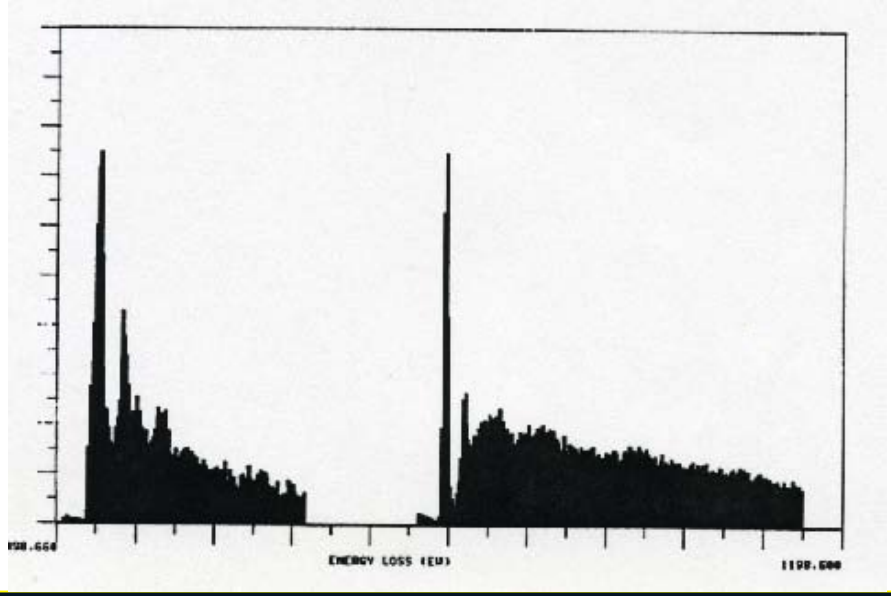
$\mathcal{F}$ = *Fourier Transform* $\qquad$ $\mathcal{F}^{-1}$ = *Inverse Fourier Transform*

Does Deconvolution Help Quantification?

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







Does Deconvolution Help Quantification?

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

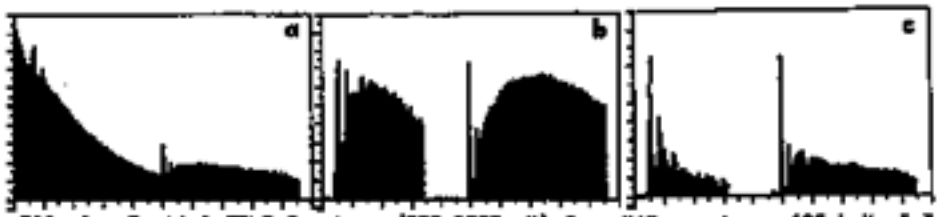
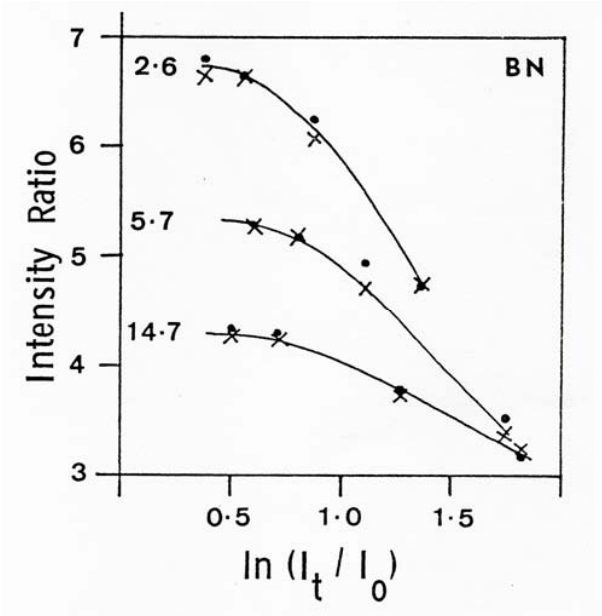
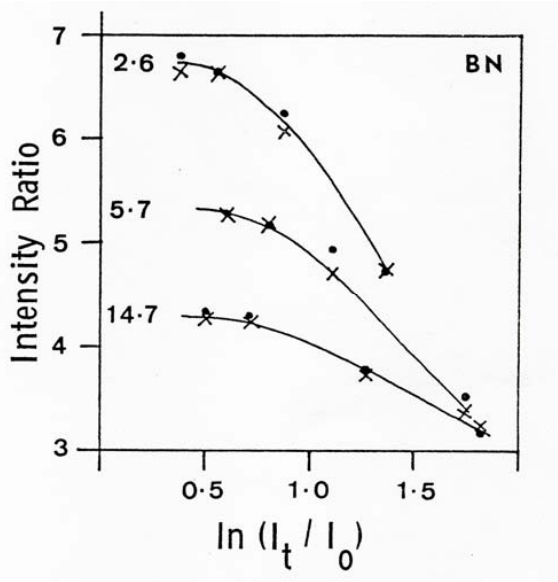
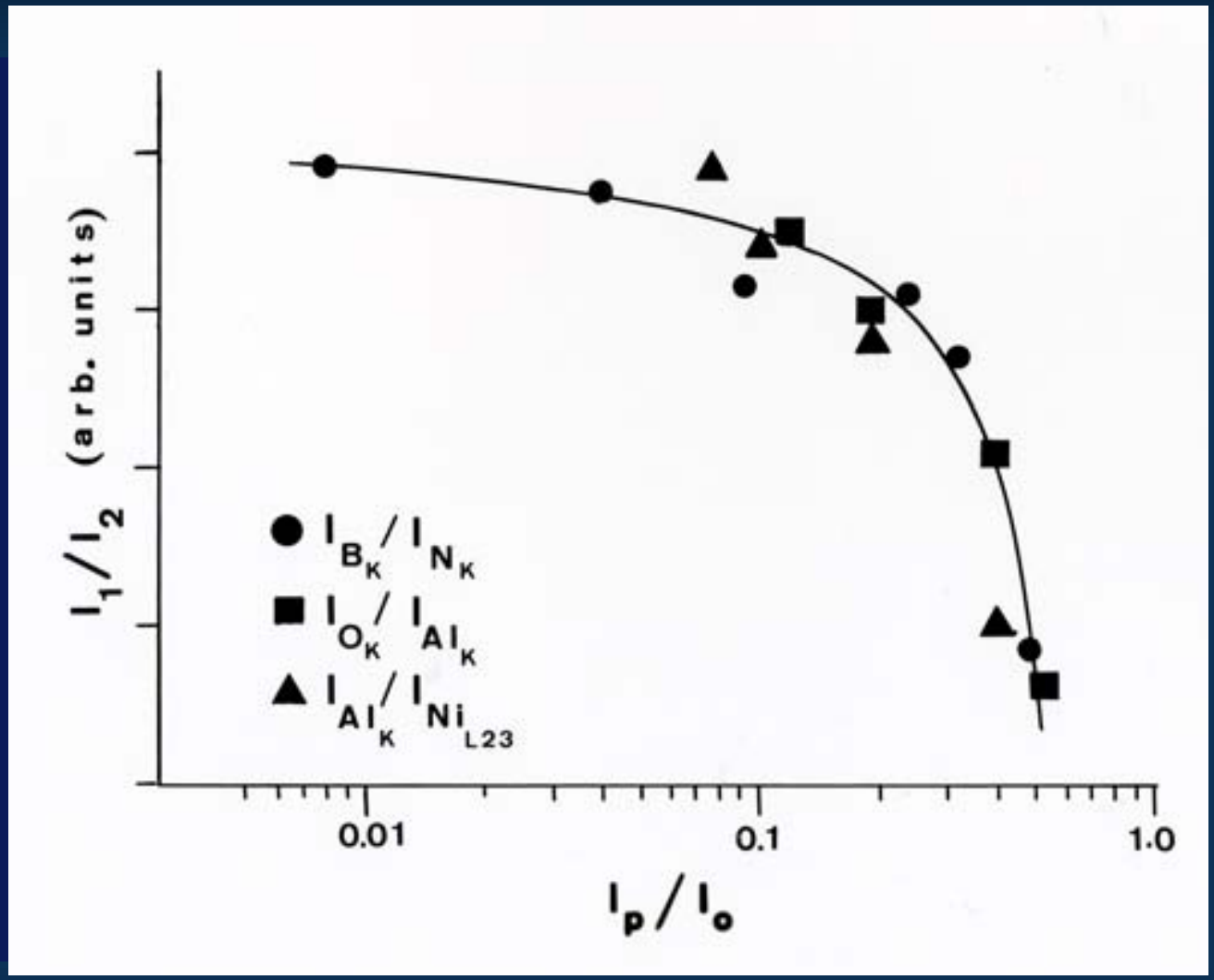


FIG. 1.--Partial EELS Spectrum (500-1200 eV) from NiO specimen: 100 keV, 5.7 mr scattering angle, a) unprocessed data b) background stripped, c) deconvoluted.

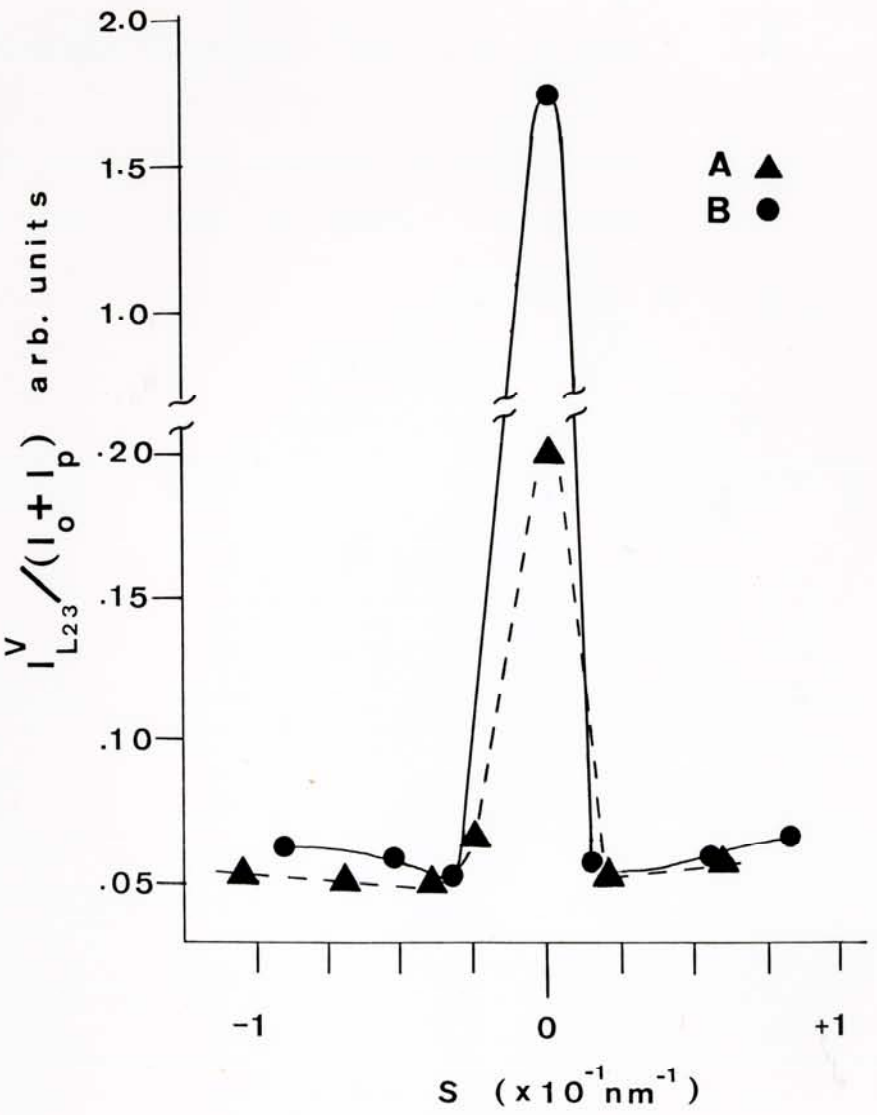




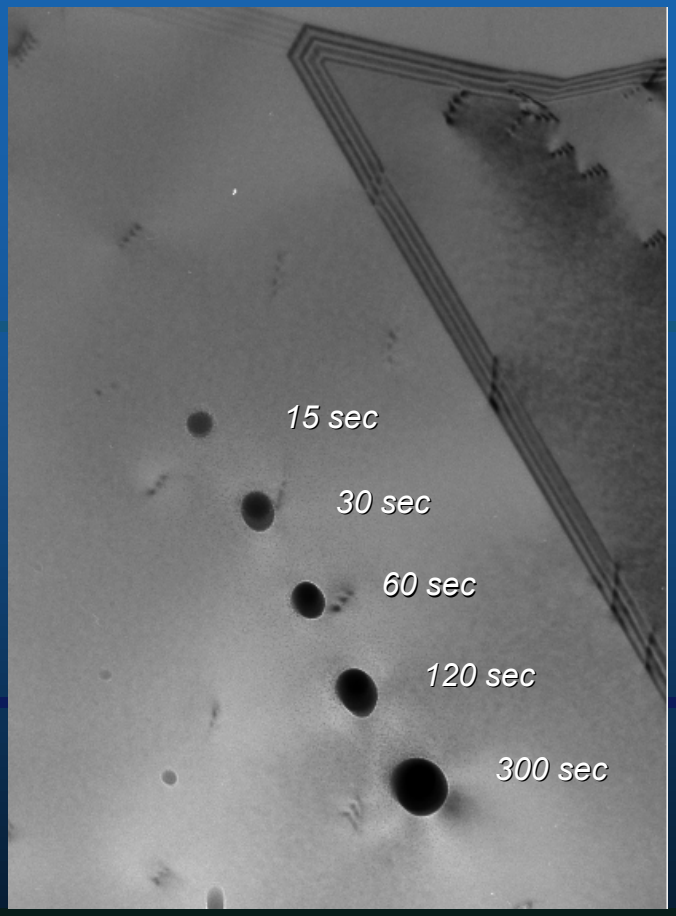
This defines a "Thin Film Approximation" for EELS i.e. $\frac{t}{\lambda} < 1.0$

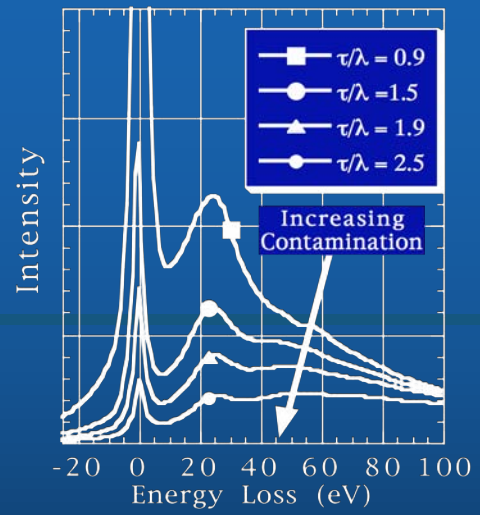

I_1/I_2 (arb. units)
I_{B_K}/I_{N_K}
I_{O_K}/I_{Al_K}
$I_{Al_K}/I_{Ni_{L23}}$
0.01
0.1
1.0
I_p/I_o

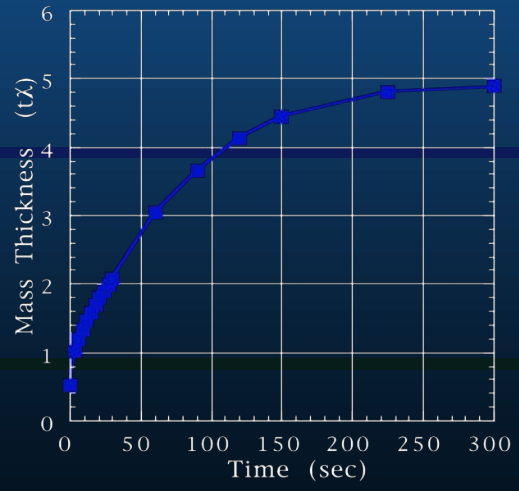
Orientation & Thickness Effects on EELS Signals



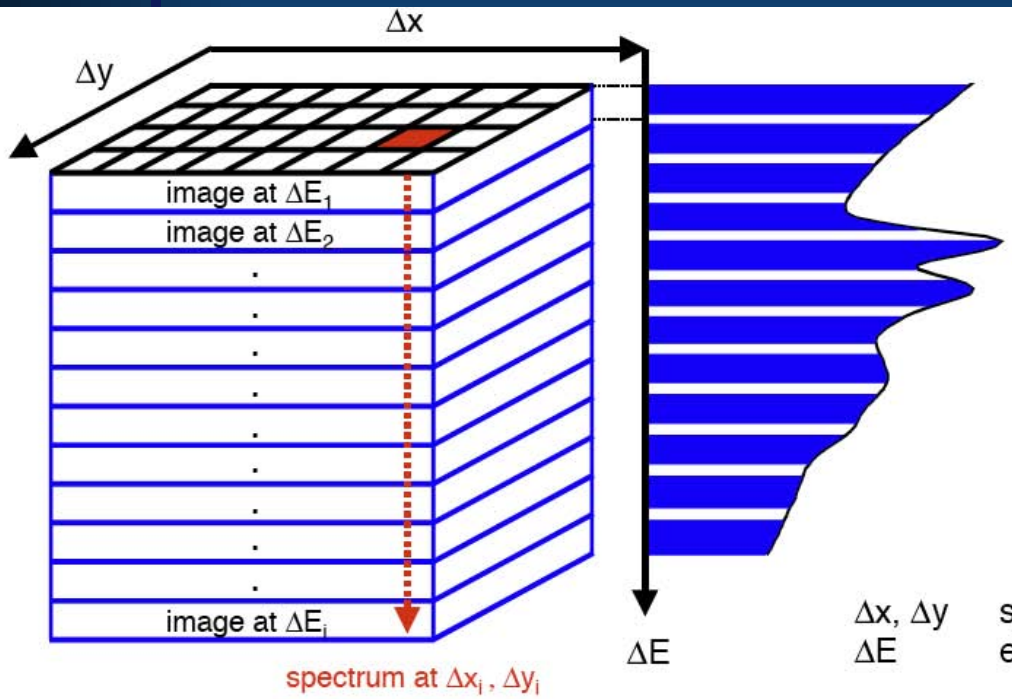
Specimen Contamination
The Microscopists Bane







Spectral Imaging
Slice-by-Slice vs Point-by-Point



The technique of building up a more or less complete data cube is termed **Spectrum Imaging**

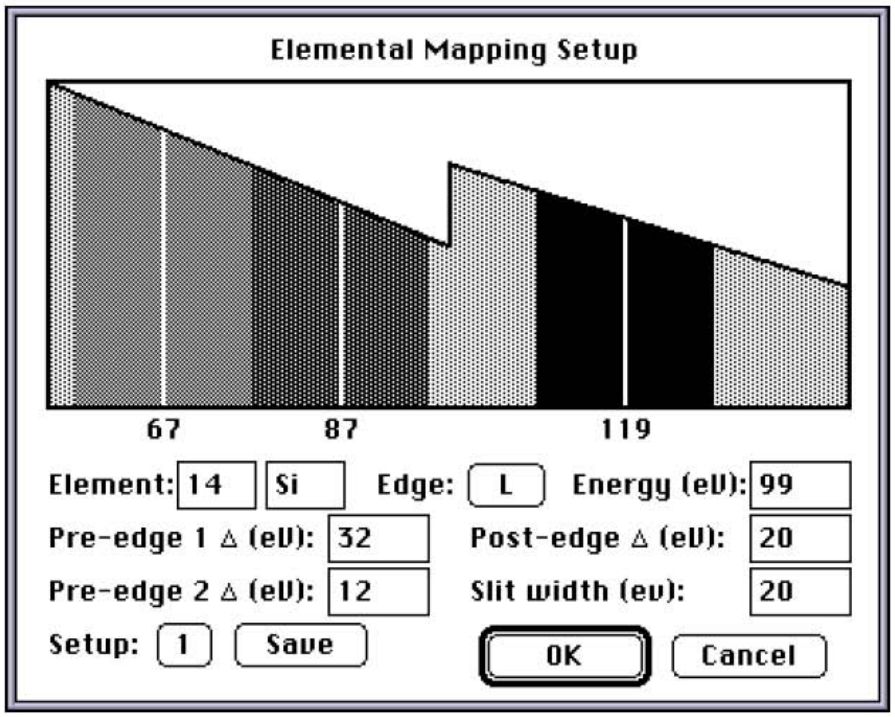
Δx, Δy spatial dimensions
ΔE energy-loss dimension

EFTEM Spectrum Imaging:
- Energy filtered broad beam technique
- fills data cube one image plane at a time
- less time

STEM Spectrum Imaging:
- Focused probe method
- fills data cube one spectrum at a time
- less dose

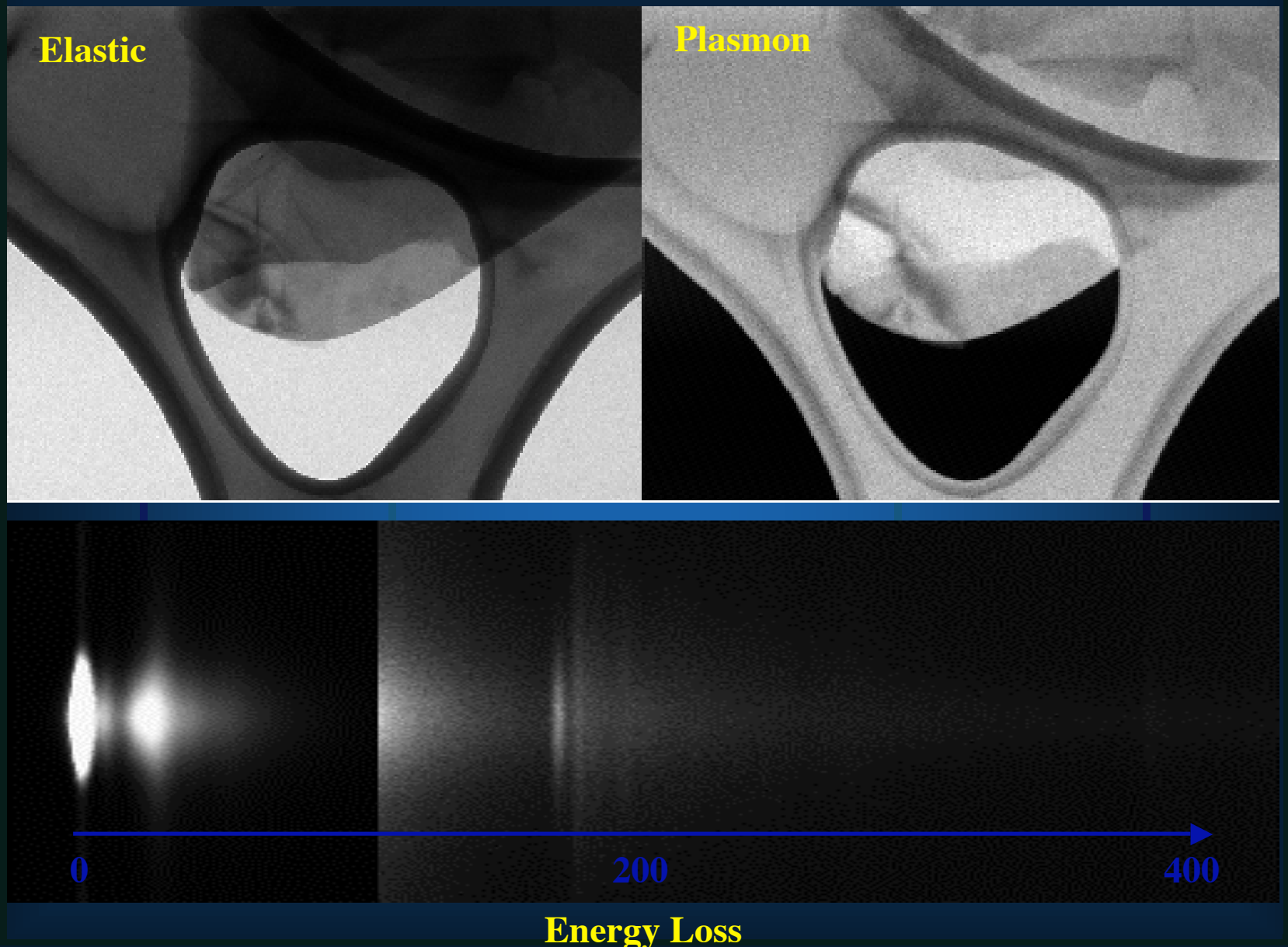
Elemental Mapping

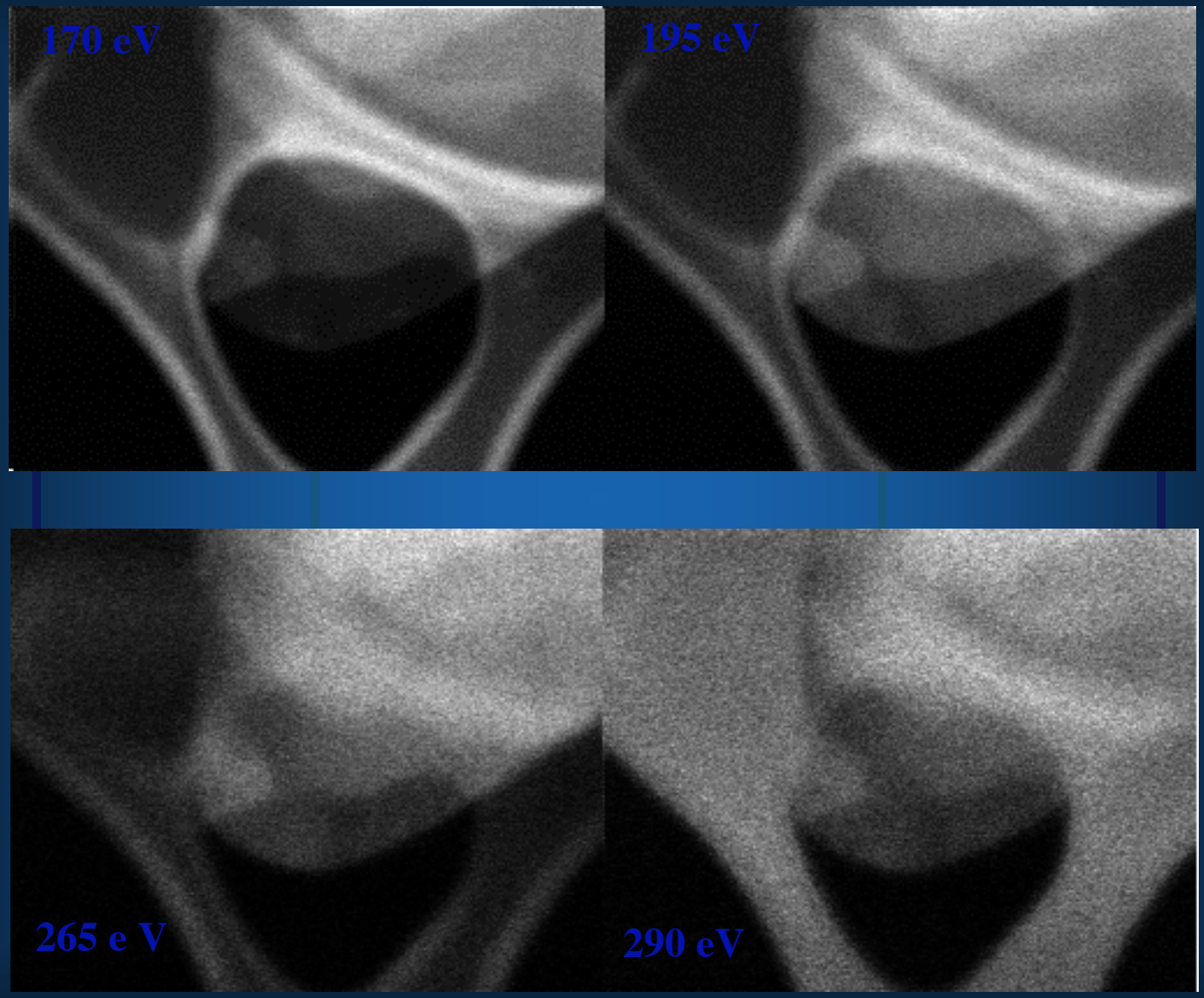
Determine and subtract edge background using two pre-edge images to obtain the true edge signal



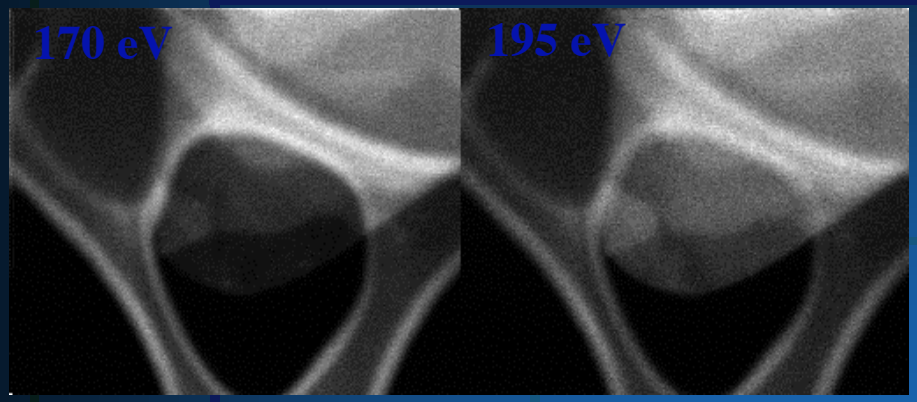
- Minimum of two background windows are necessary
- Map intensity is directly proportional to projected concentration
- Map-intensity can be related to absolute concentration if thickness and elemental cross-sections are known

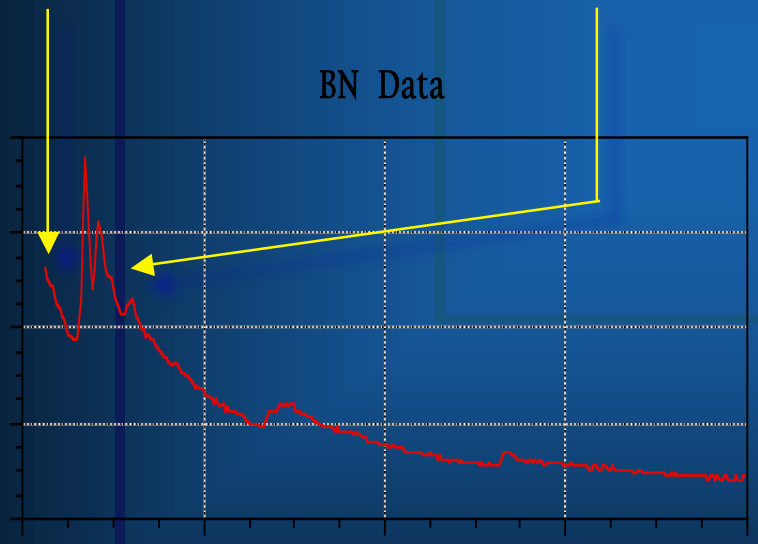
Boron Nitride on Holey Carbon

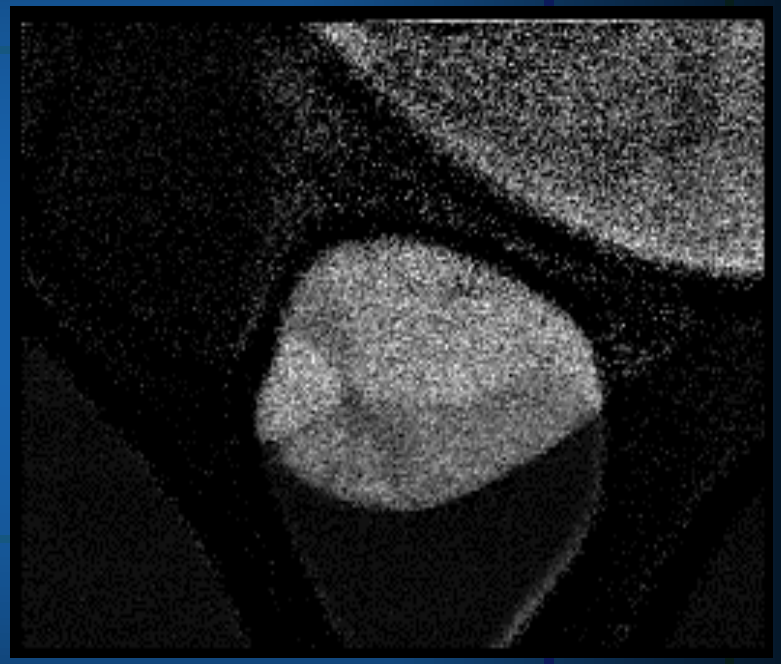



170 eV
195 eV
265 e V
290 eV

Filtered Elemental Imaging

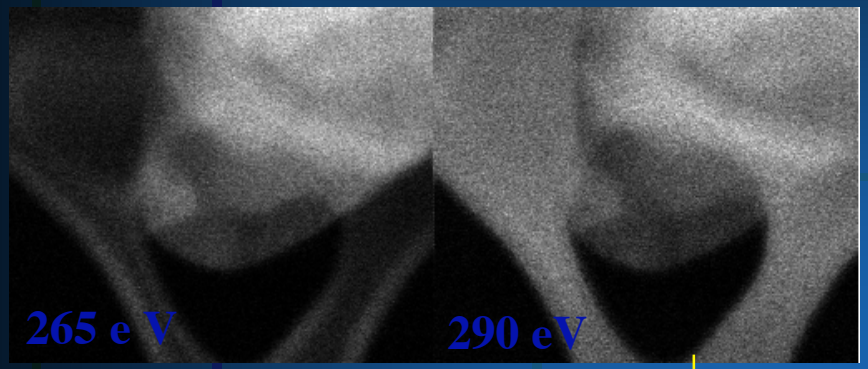


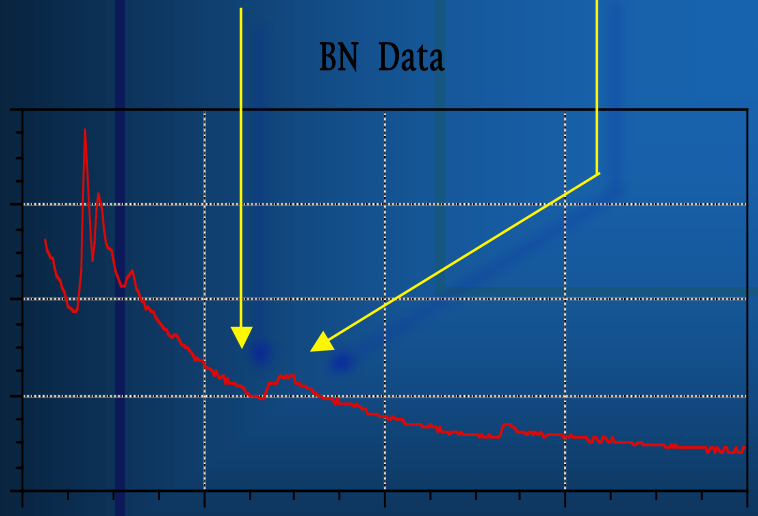


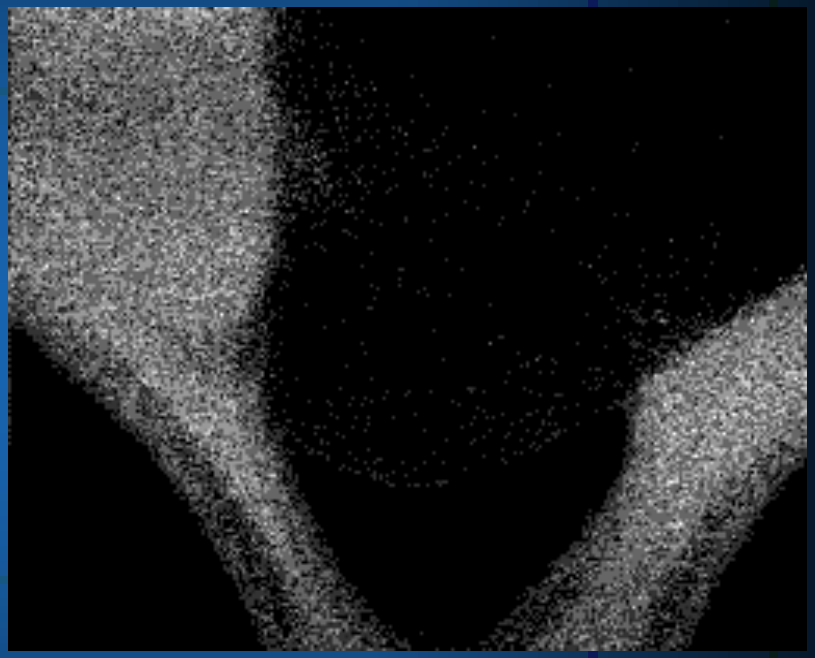


Net Boron K Image

Filtered Elemental Imaging







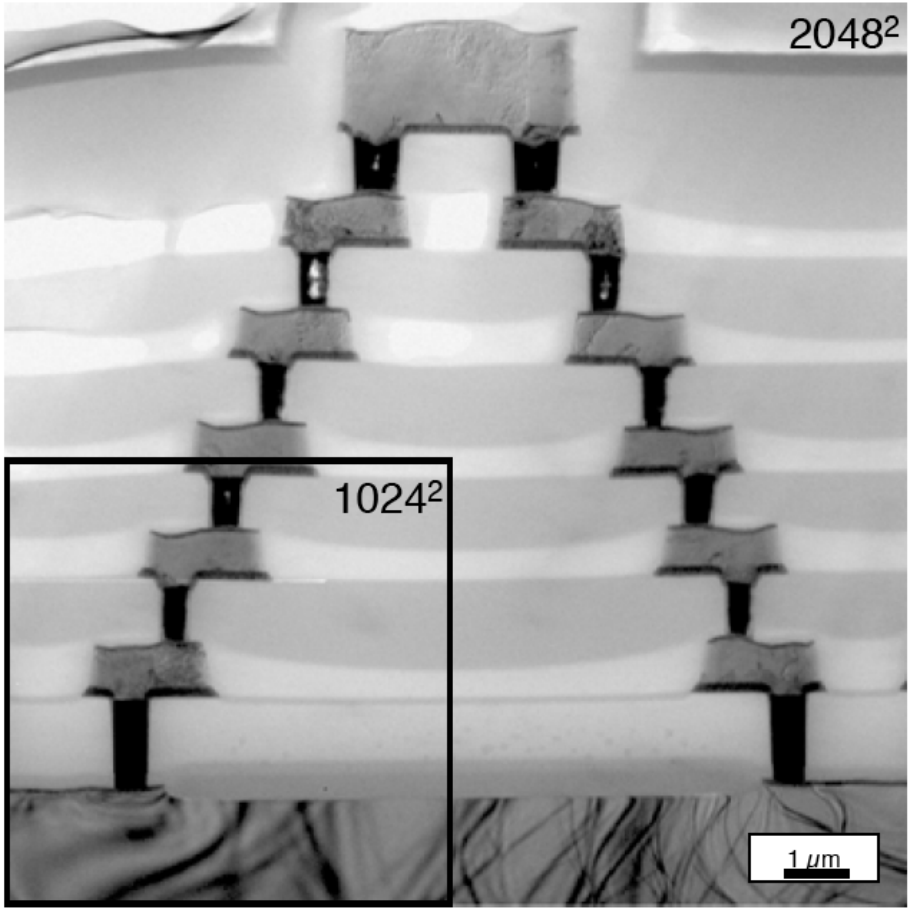
Net Carbon K Image

Elemental Mapping

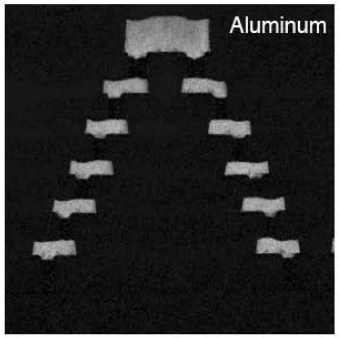
6 layer metallization
test structure

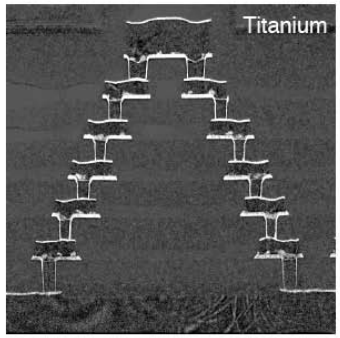
recorded on a CM200, LaB6
with a GIF2002 (2K CCD)

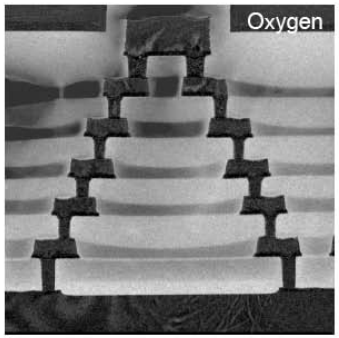
field of view: 12 μm
number of pixels: 4.2 x 10^6

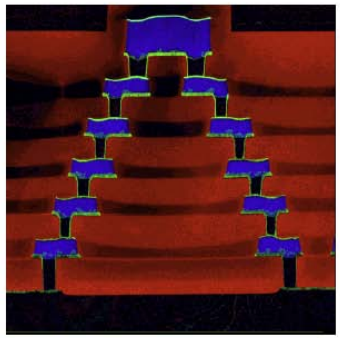


Gerald Kothleitner









O Ti Al

3 images each around:

O K edge:	@ 532 eV
Ti L_{23} edge:	@ 455 eV
Al K edge:	@ 1560 eV

Color overlays,RGBimages:

- assign a color to each elemental map: O red, Ti green and Al blue

- superimpose three color layers to form RGB composite

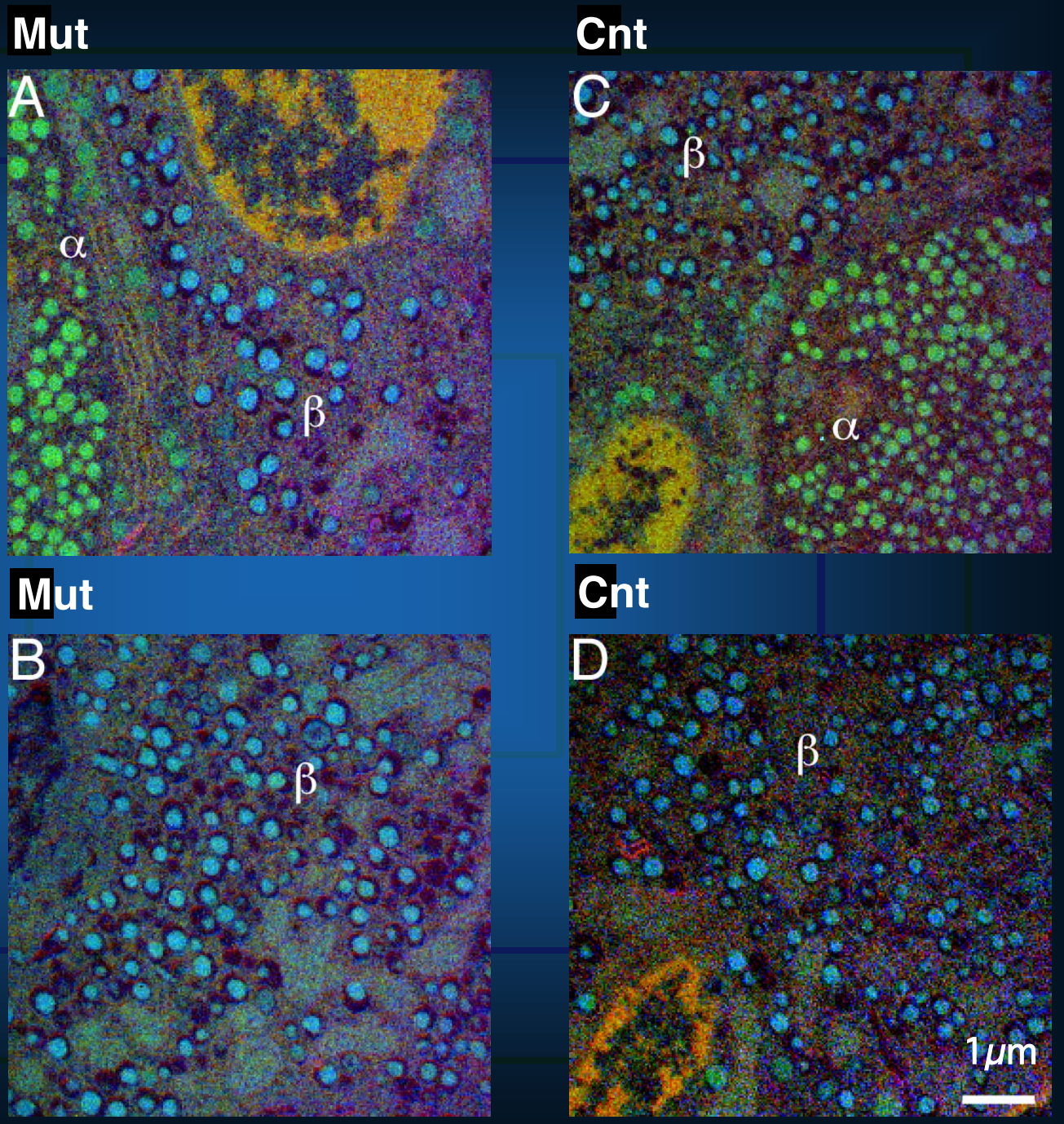
Gerald Kothleitner

Leapman et al. (2003)

EFTEM elemental maps of mouse pancreatic Islet cells

Shows sulfur-rich insulin granules in β cells

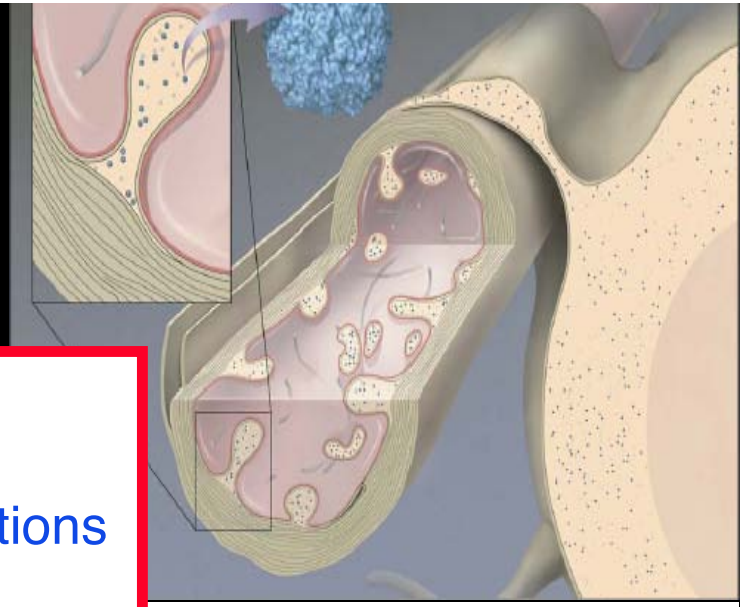
Nitrogen
Phosphorus
Sulfur



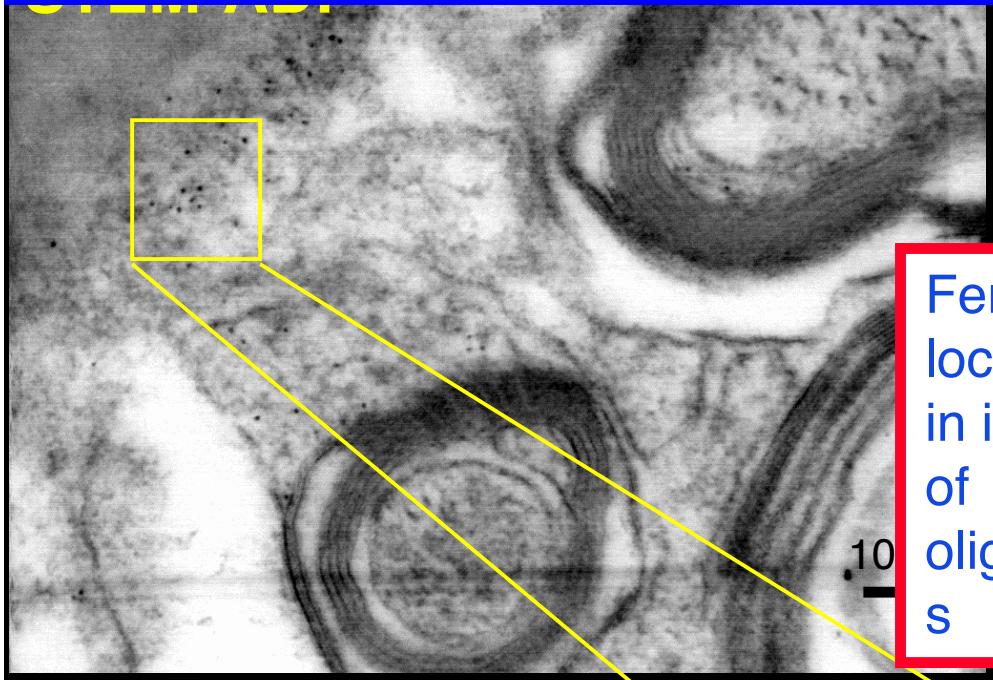
Mapping Ferritin in Brain: Misregulation of Iron Metabolism in IRP Knockout Mice

(P. Zhang et al., J. Struct. Biol. 2005)

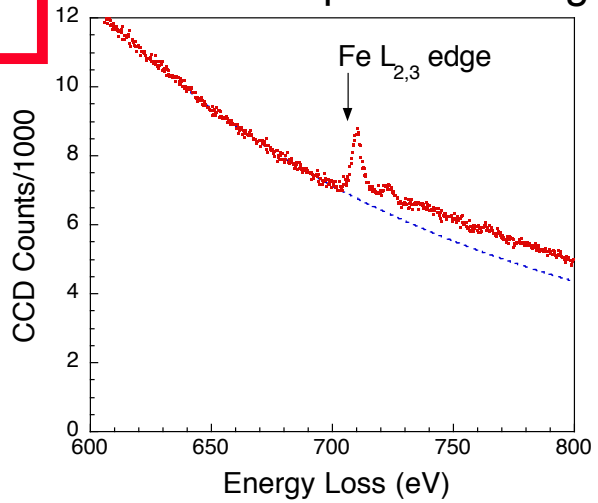
Model of axon and oligodendrocyte showing anatomy of degeneration



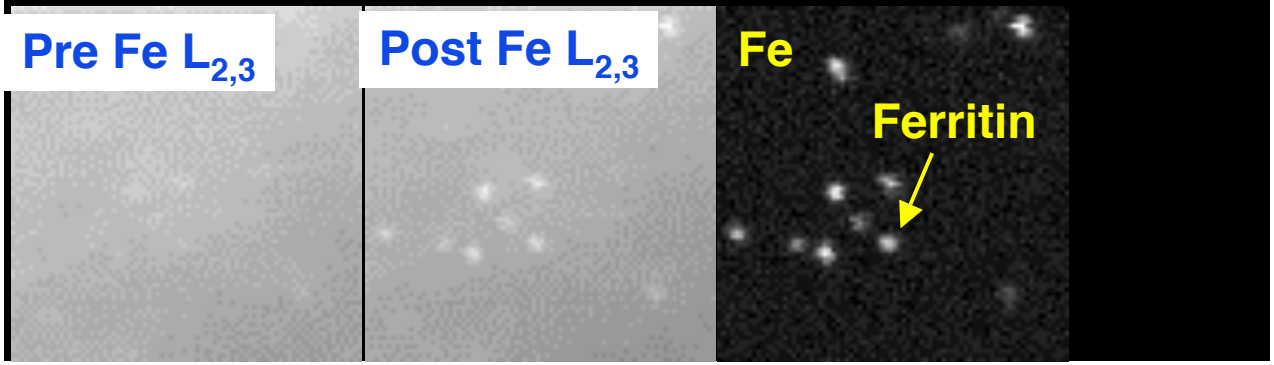
Ferritin localized in invaginations of oligodendrocytes



EELS of ferritin molecule extracted from spectrum-image



STEM-EELS



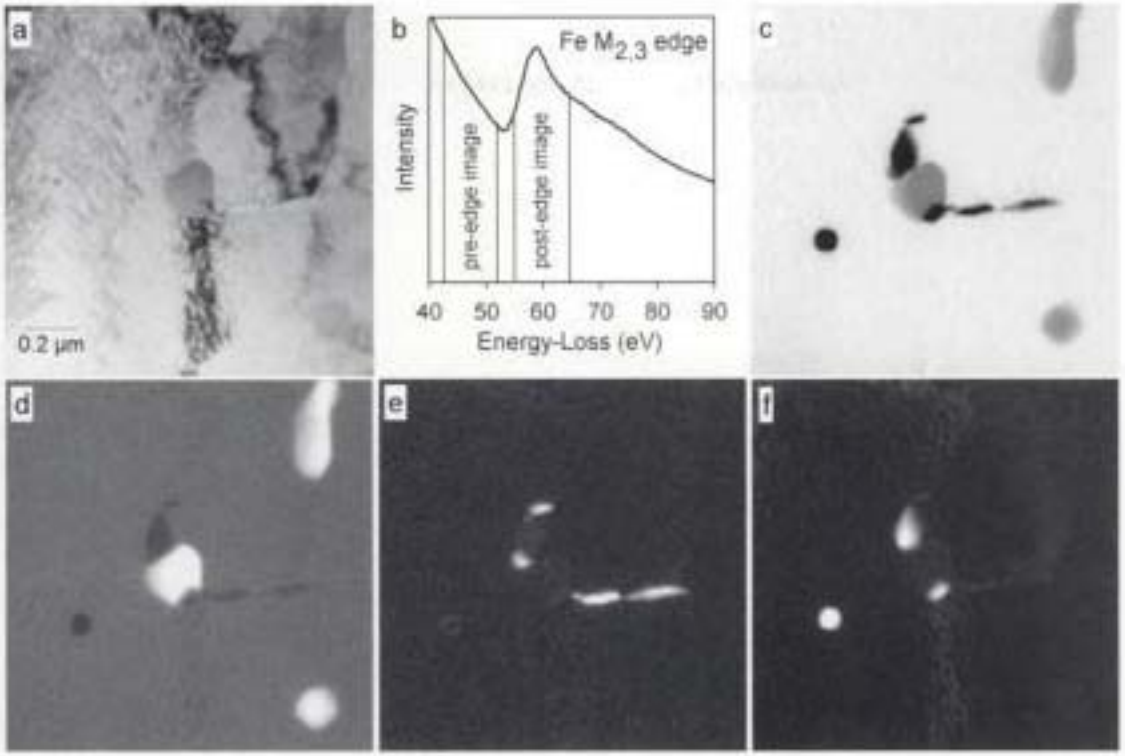


Fig. 6.14 Imaging of precipitates in a steel specimen; (a) TEM-bright field image of a 10% Cr steel with $Cr_{23}C_6$, VN and Nb(C,N) precipitates; (b) EELS spectrum with the Fe M_{23} edge; (c) Fe M_{23} jump-ratio image recorded under rocking beam illumination; (d) Cr L_{23} jump ratio image; (e) V L_{23} jump ratio image; (f) Nb M_{45} jump ratio image.

Hofer & Warbichler - Graz TU

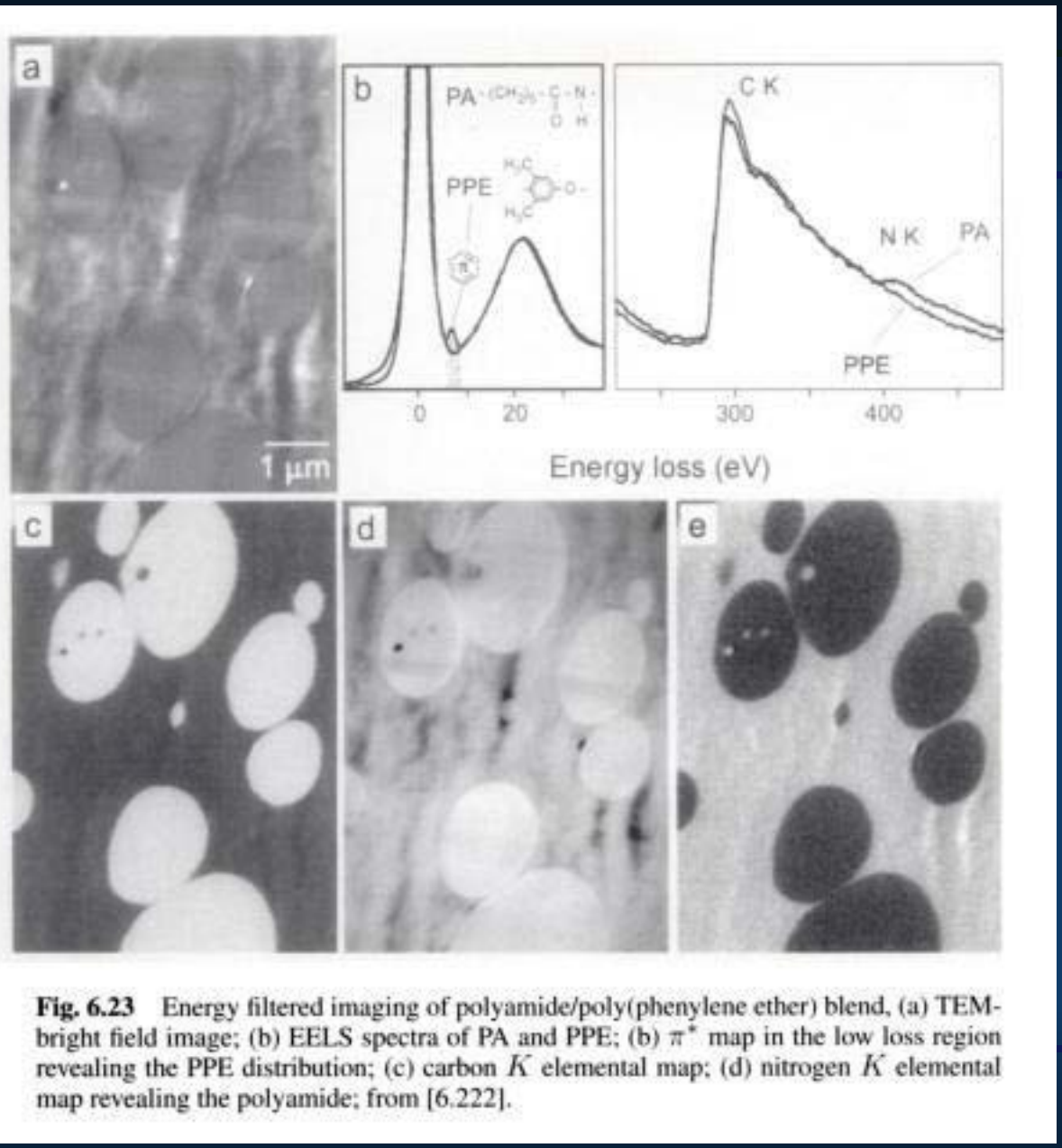


Fig. 6.23 Energy filtered imaging of polyamide/poly(phenylene ether) blend, (a) TEM-bright field image; (b) EELS spectra of PA and PPE; (b) π^* map in the low loss region revealing the PPE distribution; (c) carbon K elemental map; (d) nitrogen K elemental map revealing the polyamide; from [6.222].

Steps in Quantitative (Elemental) Analysis

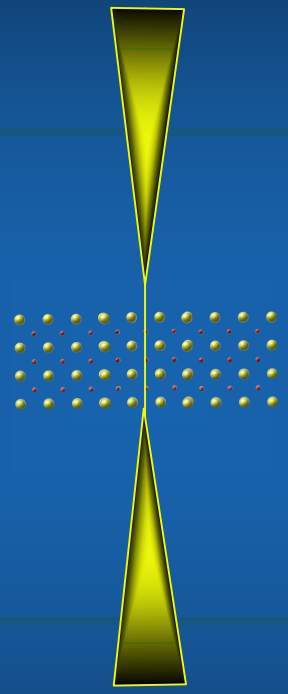
- Select the operating mode: Is it appropriate?
  - CTEM, STEM.....
  - Image Coupled, Diffraction Coupled
- Obtain a typical spectrum
- Optimize the experimental conditions
  - Accelerating Voltage (maximum consistent with your specimen)
  - Chooze the best Edges to analyze (K, L, M,....)
  - Optimize β for the weakest edges ($\theta_E = \delta E/2Eo$)
  - Optimize α to minimize problems ($\alpha < \beta/2$)
  - Optimize the Acquisition Mode
    - Normal - High Concentrations
    - Difference - Low Concentrations
  - Optimize the Data Acquisition
    - Select Energy Resolution and Range
    - DQE & Statistics
- Process the Data to Extract Intensities
    - Normal
    - Difference
    - Reference Spectra
- Check the relative specimen thickness ($t/\lambda < 1$)
- Calculate the compositions
  - Absolute # of atoms
  - Relative # of atoms
  - Standards/Standardless?
- ReCheck for Artifacts/Problems
  - Diffraction
  - Orientation/Channeling
  - Unidentified Edges
  - Spectral Overlaps
  - Radiation Damage

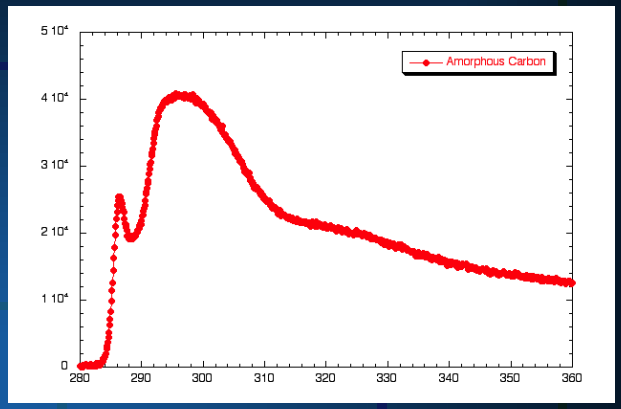
Linear Dichroism and Core Loss Electron Spectrosopy

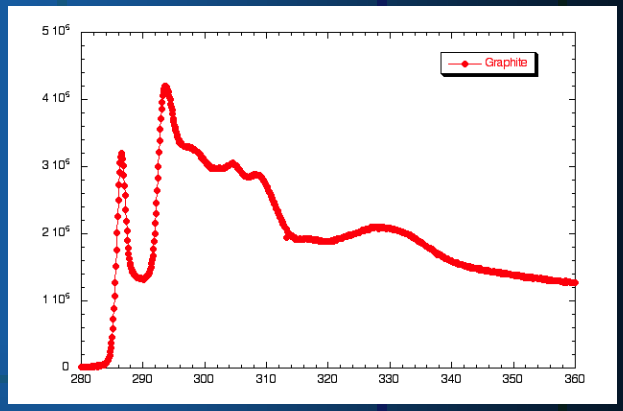
Linear dichroism:

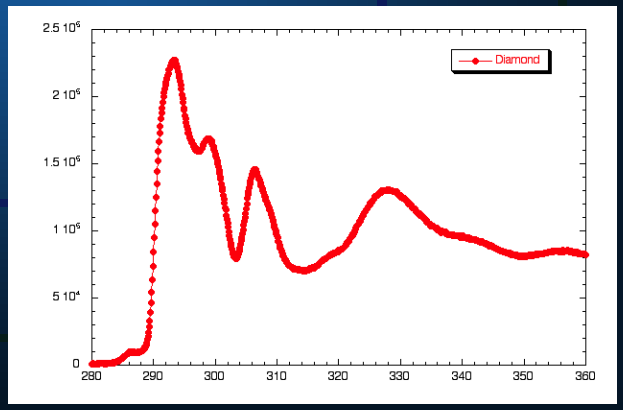
The linear polarization of the incident electrons parallel to the direction of momentum transfer. This polarization can be used sense the anisotropy of the valence states involved in the core excitation process. It can detect the number or changes in the number of the valence holes in different directions of the atomic volume.

In many cases, the anisotropy of the charge in the atomic volume is caused by crystal-field interaction and is due to an anisotropy in the bonding.

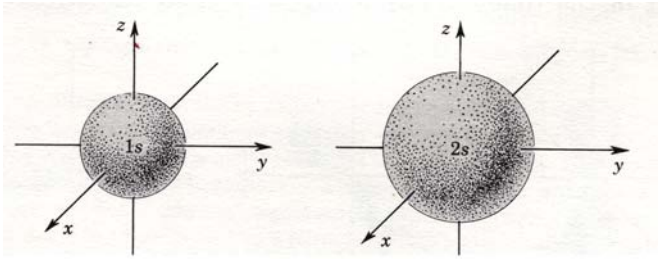




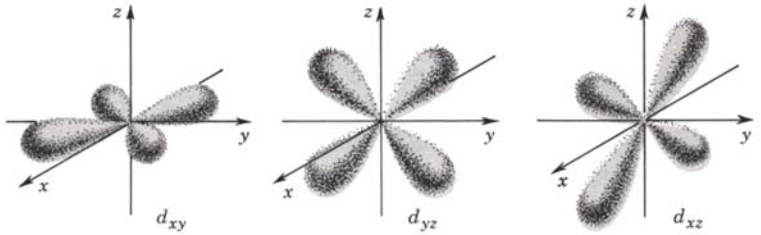




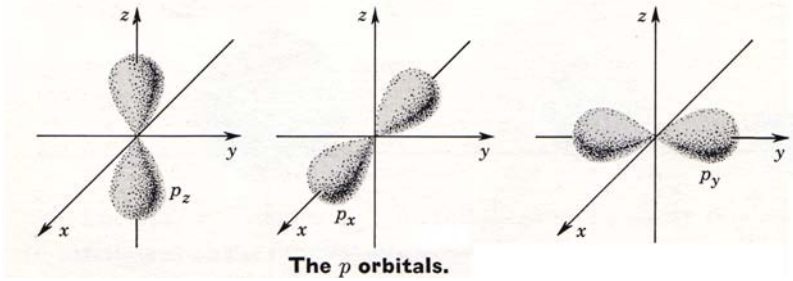
Momentum Resolved EELS (MREELS) in Core Loss Spectroscopy derives its information from transitions from initial to final states



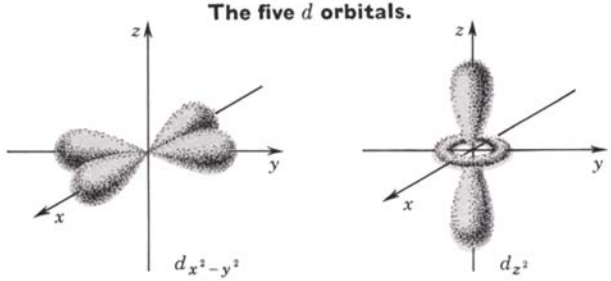
1s and 2s orbitals.



The five d orbitals.

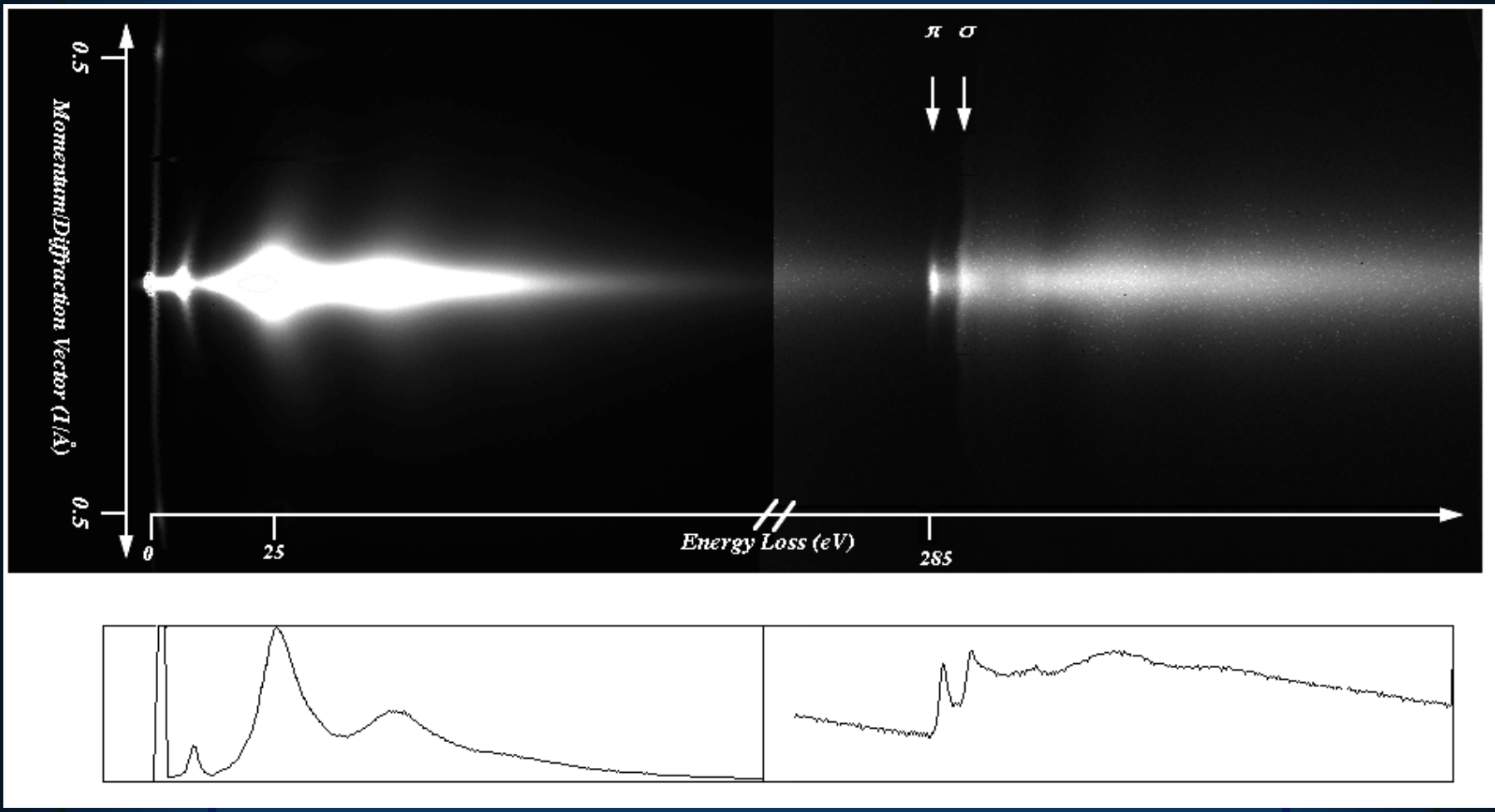


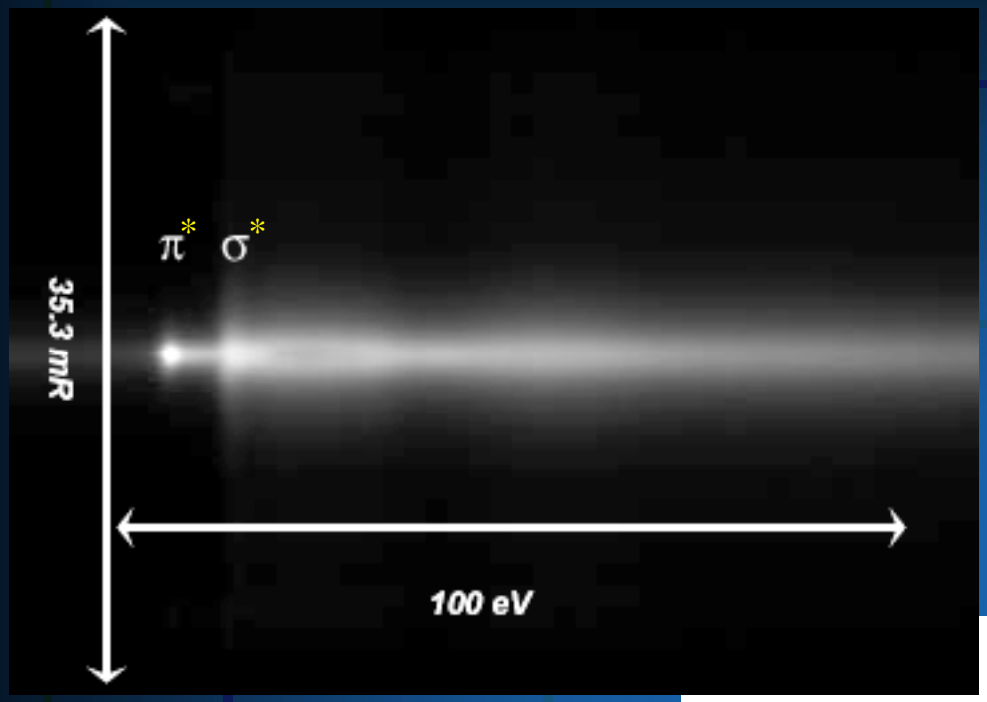
The p orbitals.

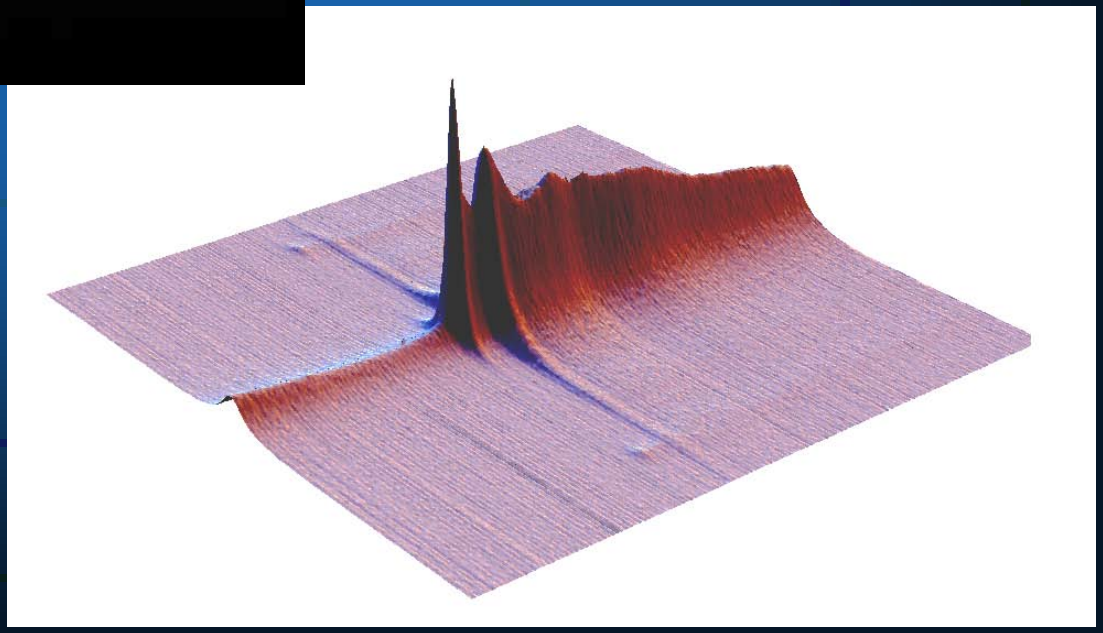


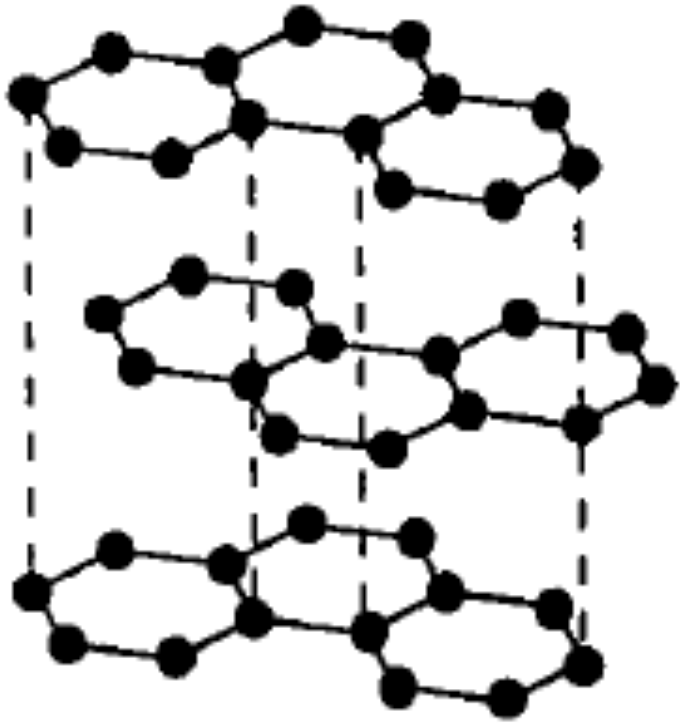
K shell p-> s

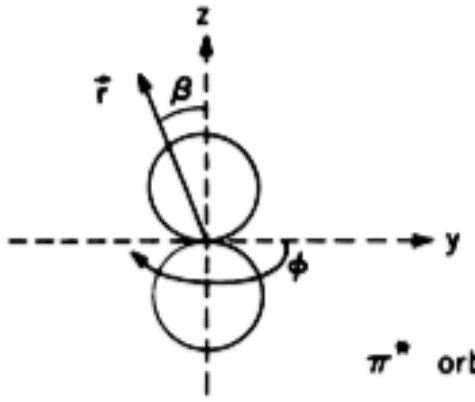
L shell p->s and p->d


π σ
0.5
Momentum/Diffraction Vector (1/Å)
0.5
0
25
Energy Loss (eV)
285

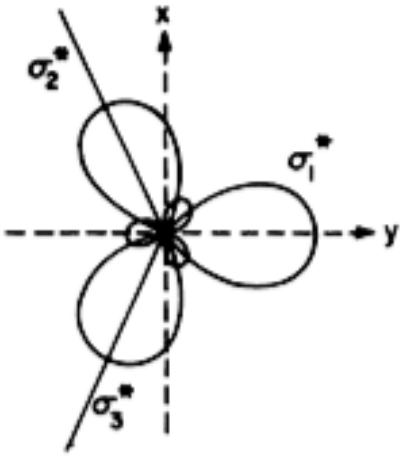

π*
σ*
35.3 mR
100 eV

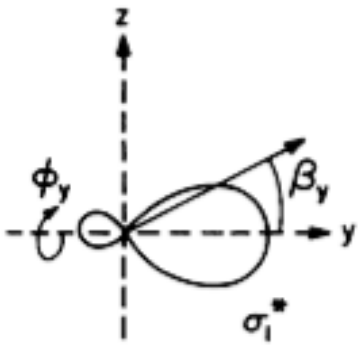






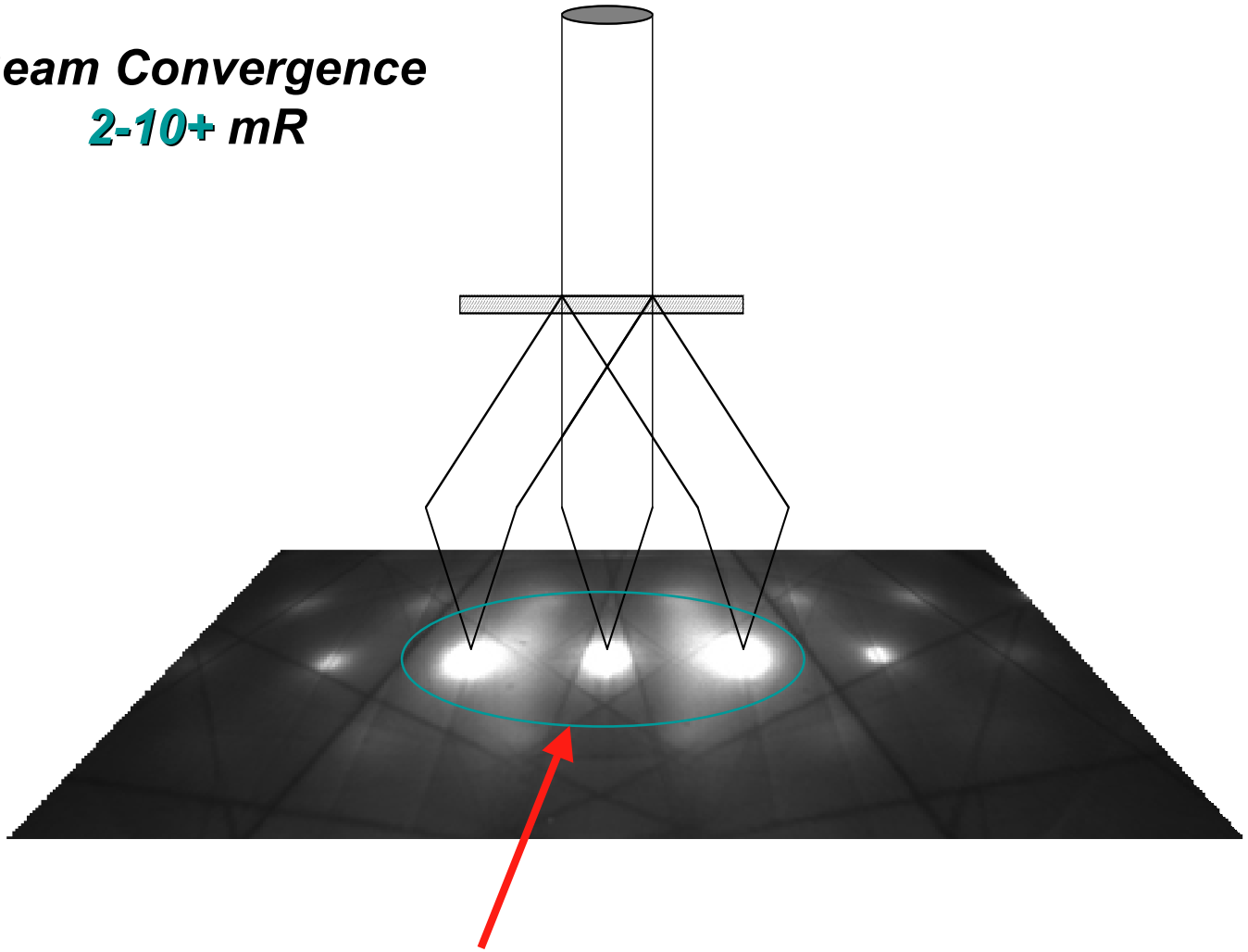
π^* orbital



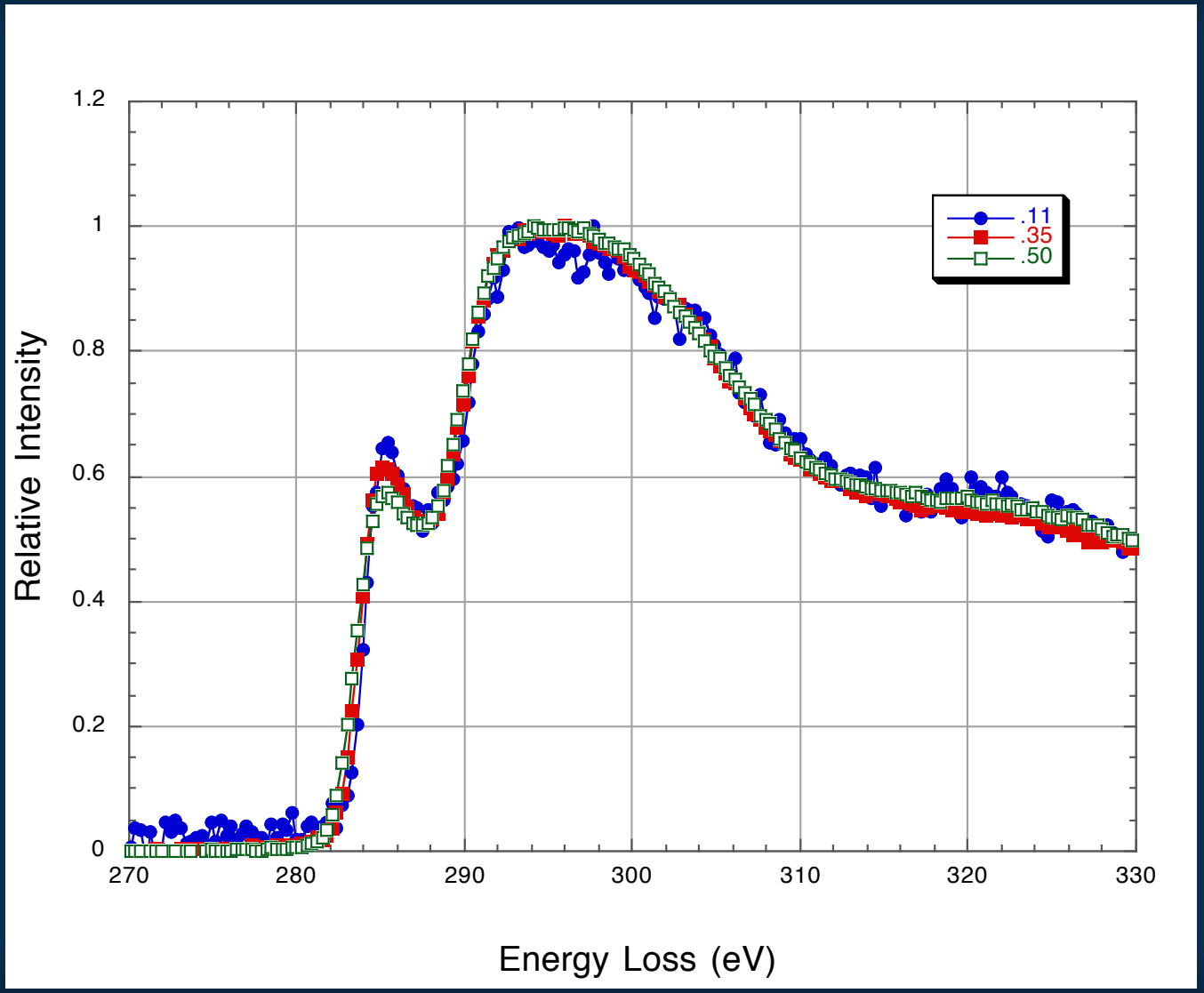


σ^* orbitals

A Conventional EELS experiment in the TEM

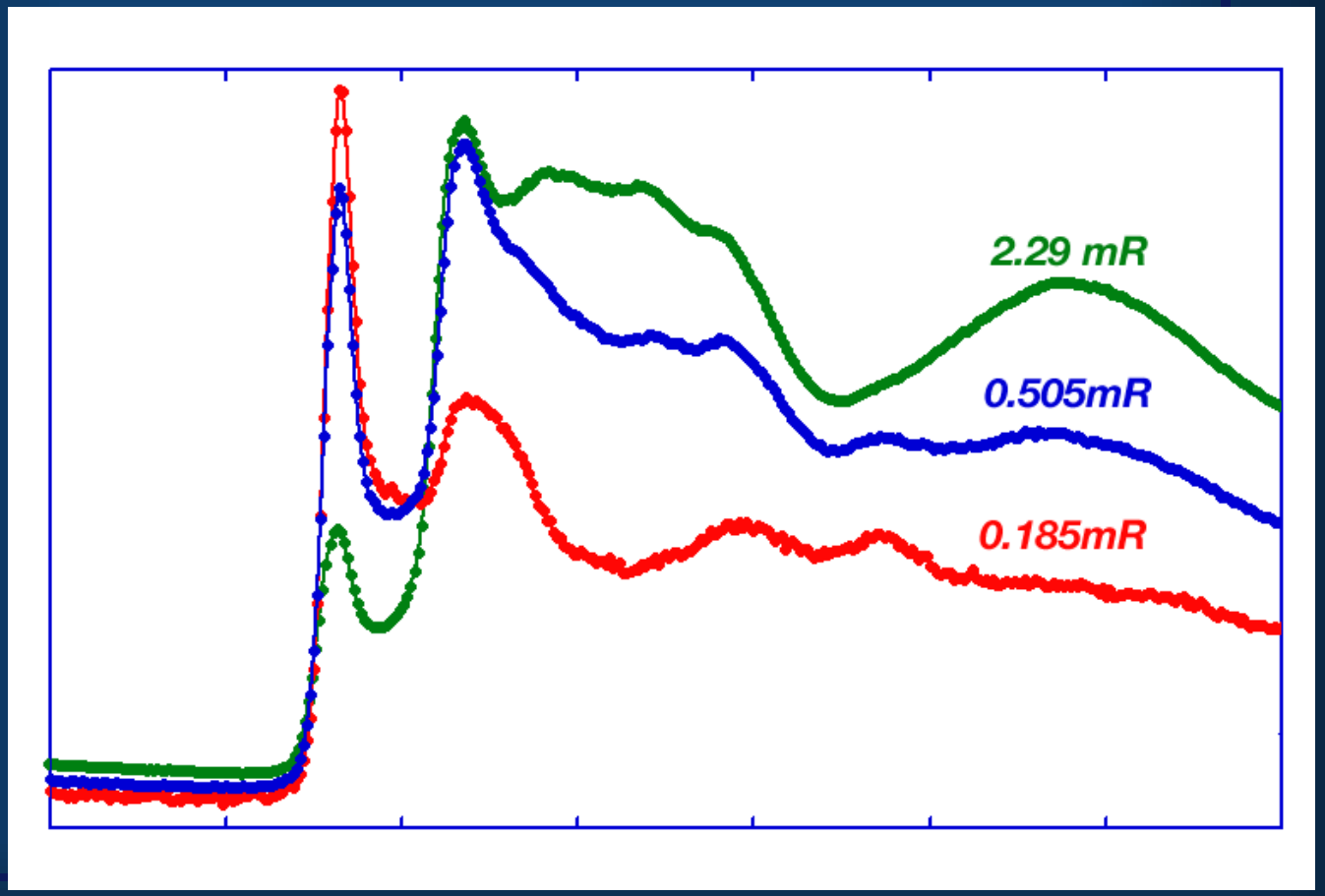


Variation of Amorphous Carbon NES with Collection Angle (β)



In some systems/conditions the difference is subtle
But …. this also depends upon what your looking for.

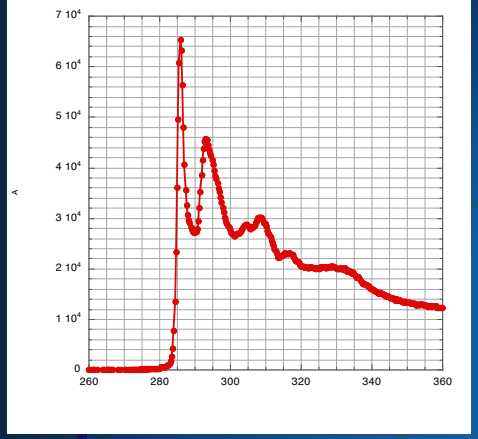
Variation of Graphite NES with Collection Angle (β)



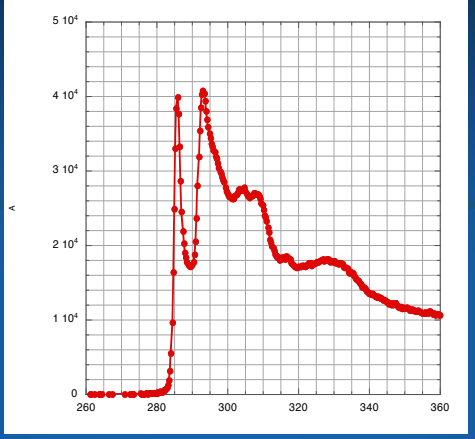
For Anisotropic Materials there can be large variations in the relative intensities of spectral features as a function of Angle (Momentum)

Variation of C_K (π^* σ^*) in Graphite with Scattering Angle

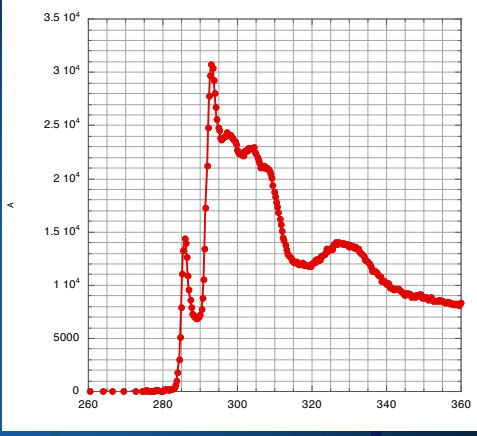
0 mR



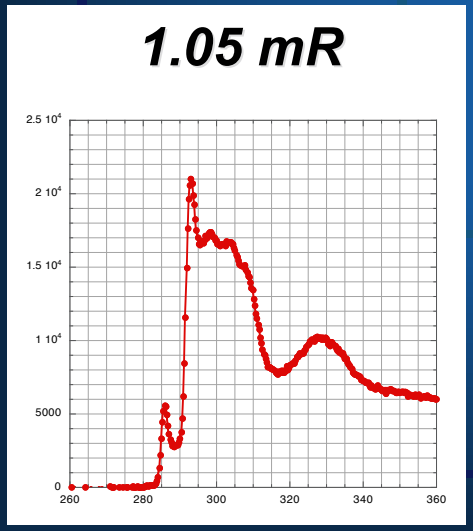
0.35 mr



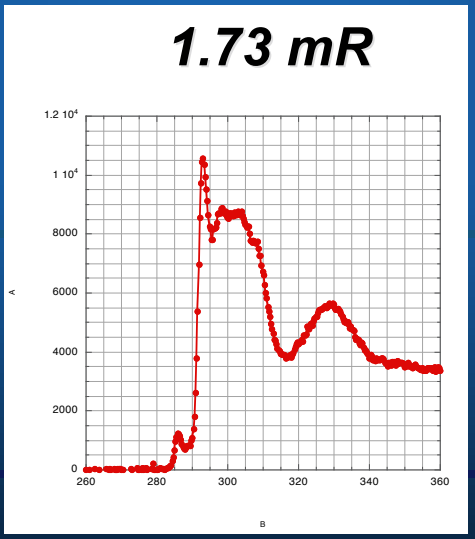
0.7mr



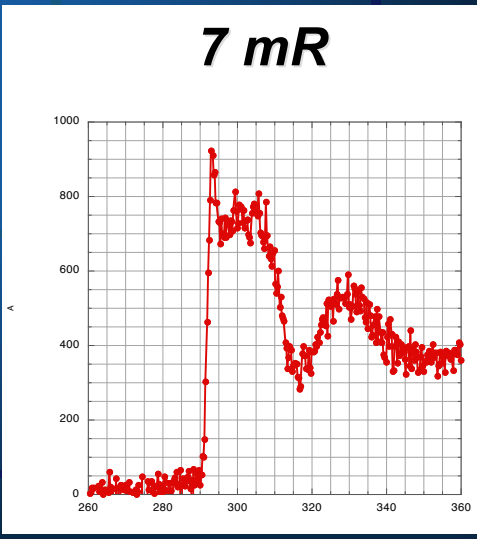
1.05 mR



1.73 mR



7 mR

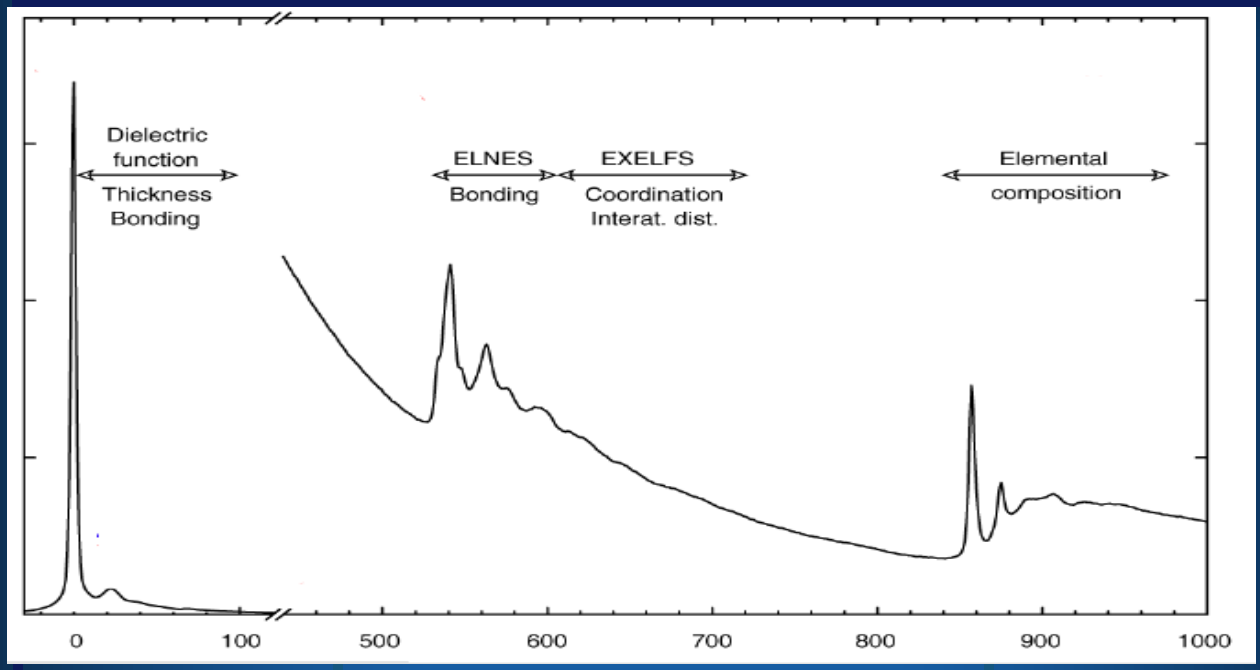


$\alpha_{1/2}$ ~ 0.025 mR $\beta_{1/2}$ ~ 0.1 mR

θ_E ~1.15 mR

Advanced Topics

- Low Loss Spectroscopy
  - Plasmon Losses Studies
  - Dielectric Properties
- Core Loss Spectroscopy
  - Near Edge Structure
  - Extended Fine Structure
- Radiation Damage



Low Loss Regime

Optical, Dielectric, Electronic, Magnetic Properties

Core Loss Regime

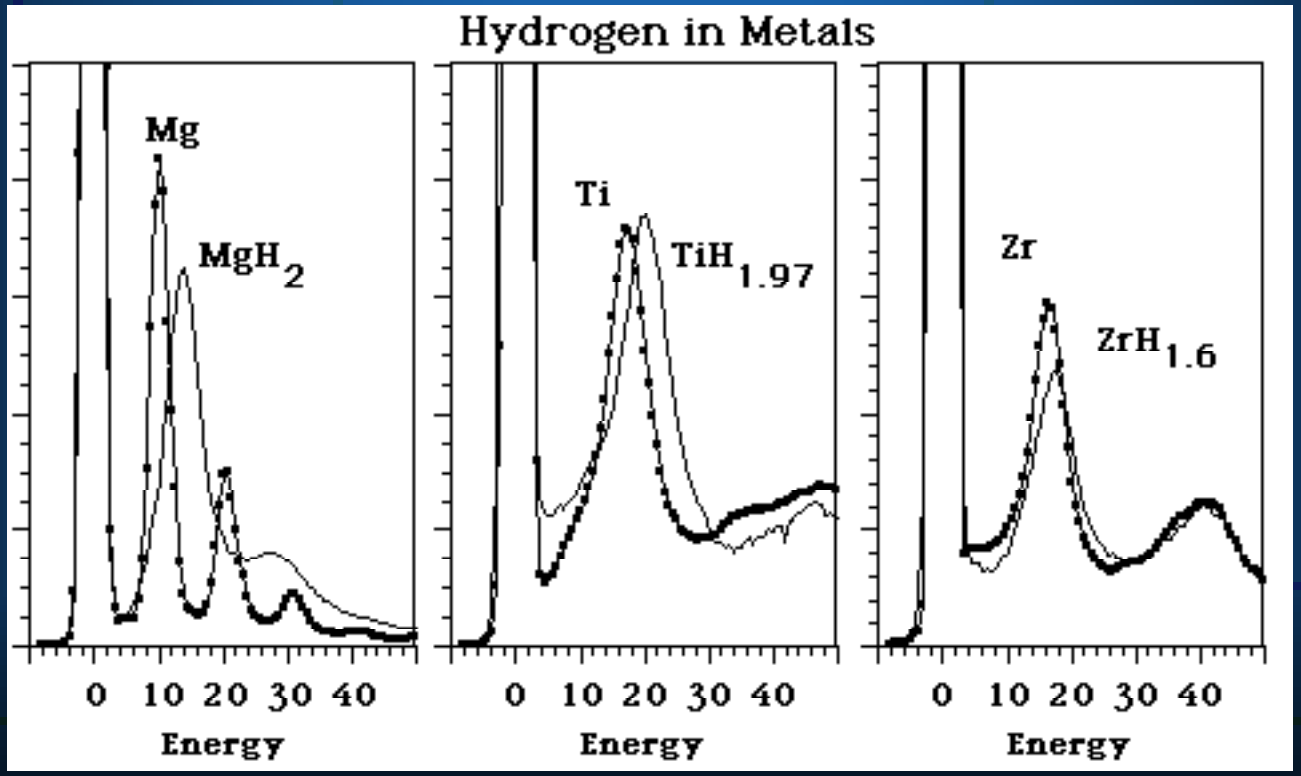
Composition, Bonding, Electronic, Magnetic , Structural Properties

Structure in EEL Spectra is a manifestation of:
Bonding (Chemistry/Physics) and/or Crystallography (Structure)

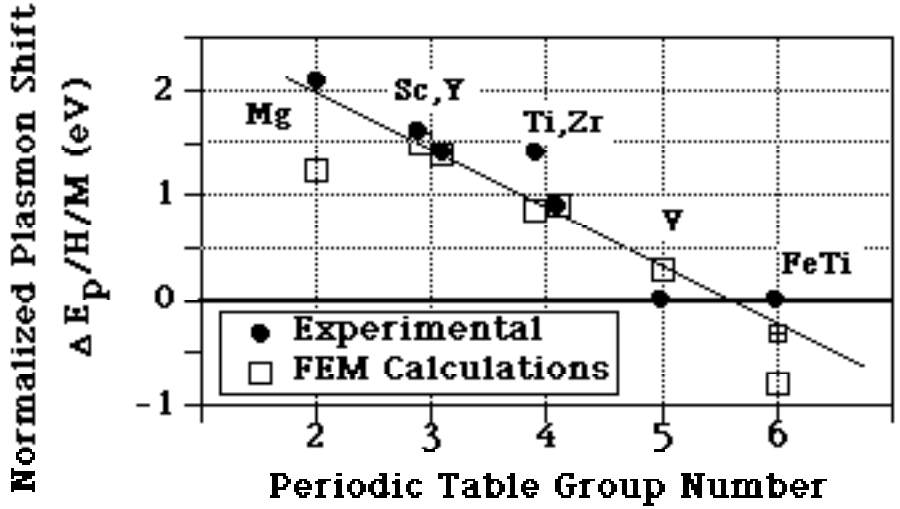
EELS Measurements of Valence Electron Densities

$$\text{Plasmon Energy} = E_p = \hbar\omega_p = \sqrt{\eta \frac{\hbar^2 e^2}{m \varepsilon_o}}$$

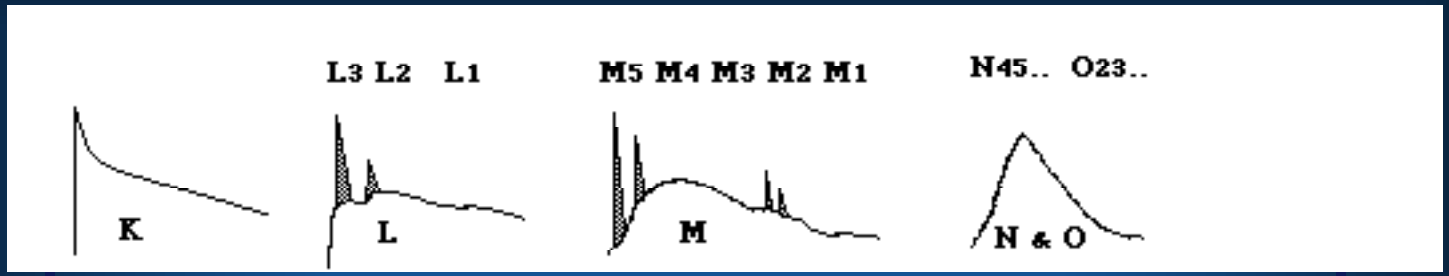
e is the elctron charge,
m its mass,
ε_o the vacuum dielectric constant,
$\hbar$ = Planck's constant/2π
η the valence electron density

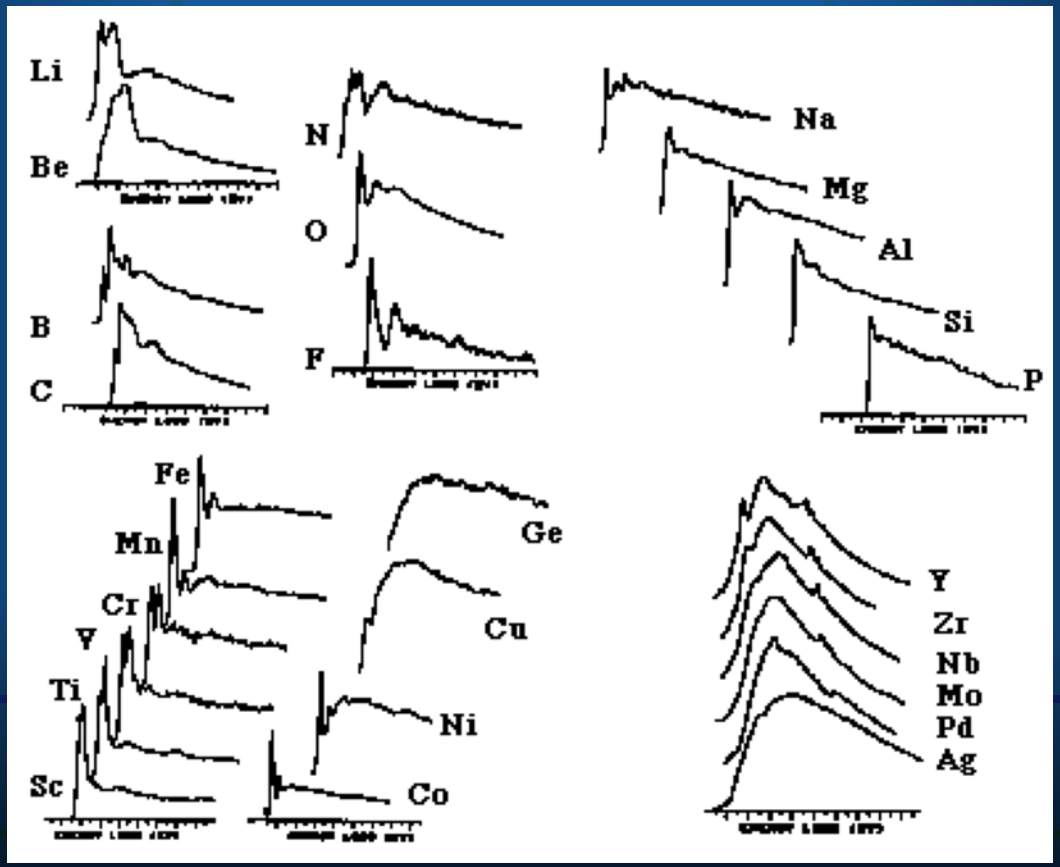


$$E_p = \hbar\omega_p = \sqrt{\frac{\hbar^2 e^2}{\varepsilon_o}\left(\frac{n_s}{m_s} + \frac{n_d}{m_d}\right)}$$



Information in Core-Loss Profiles

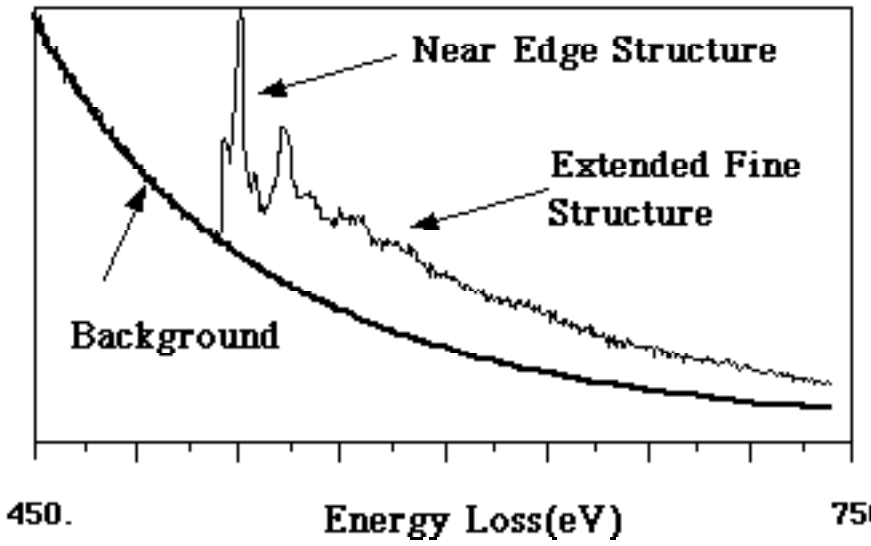




Additional EELS Information

Excitation of core levels by the transmitted electron beam can be used to measure the elemental composition of the solid, Near Edge Structure (NES) and EXtended Energy Loss Fine Structure (EXELFS) can be used to elucidate the density of states above the Fermi level and nearest neighbor configurations.

Oxygen K Shell in NiO



ELNES

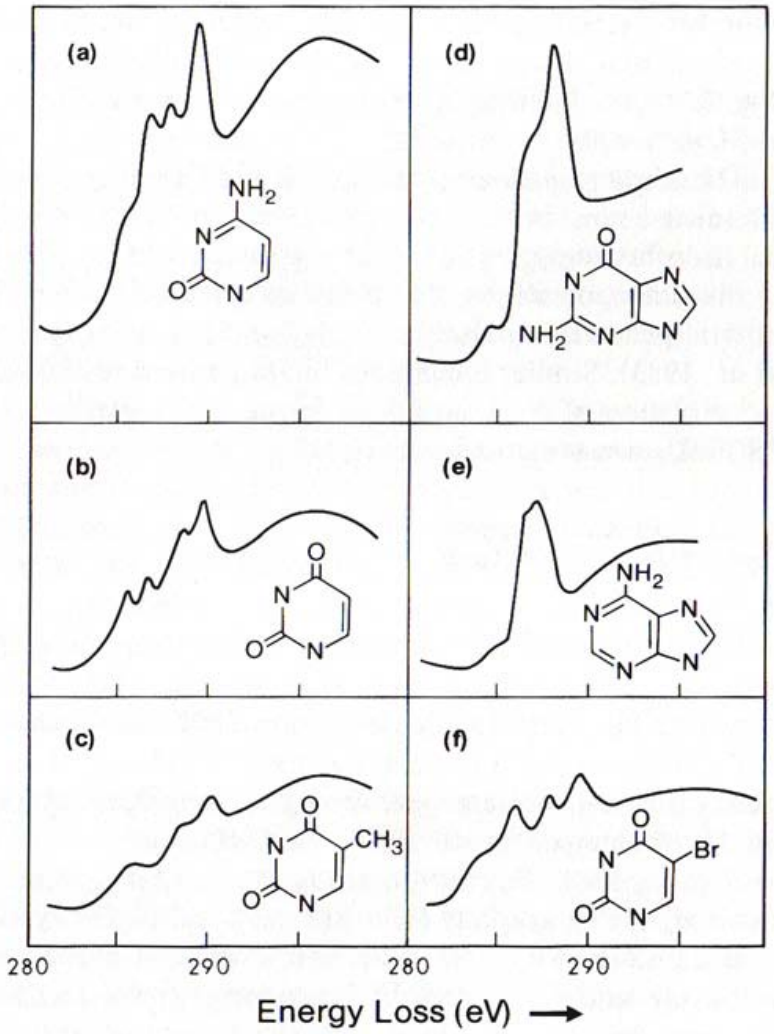
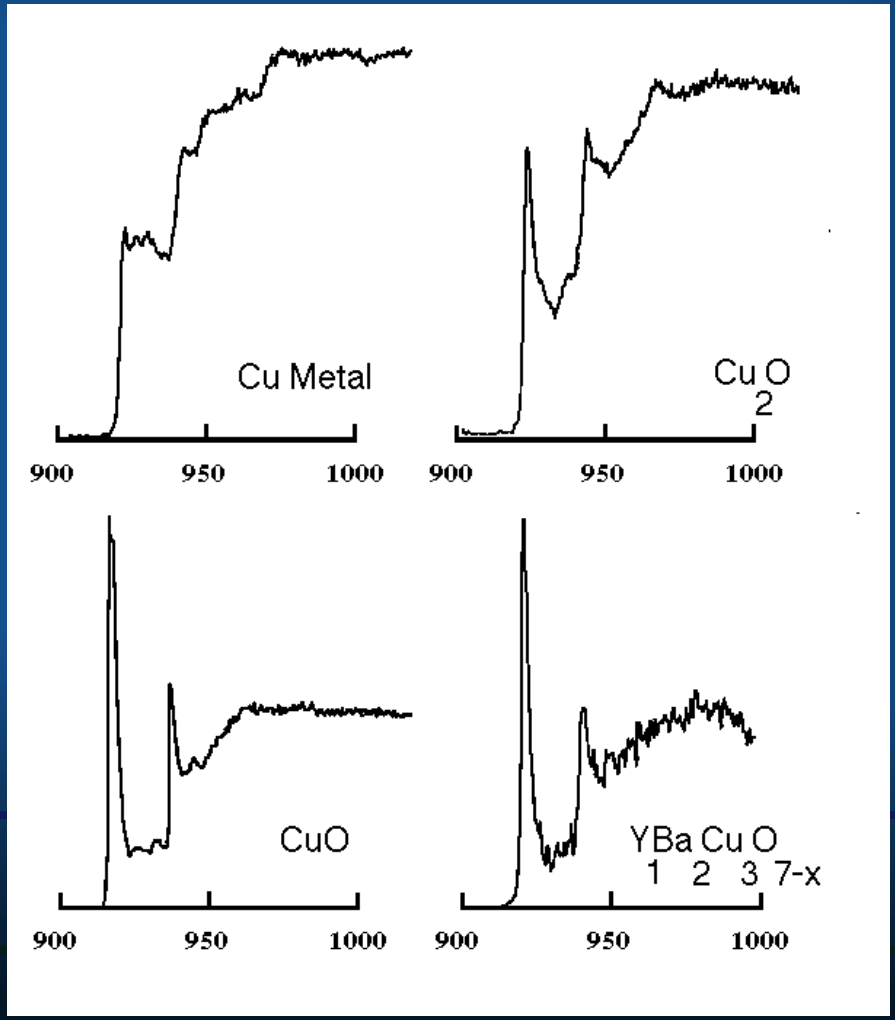


Figure 5.25. Carbon *K*-edge fine structure measured from thin films of (a) cytosine, (b) uracil, (c) thymine, (d) guanine, (e) adenine, and (f) bromothymine. Data from Isaacson (1972b) and Johnson (1972).

Copper L-shell Core Loss Spectroscopy in Metallic, Oxide and High Tc Superconductor Phases



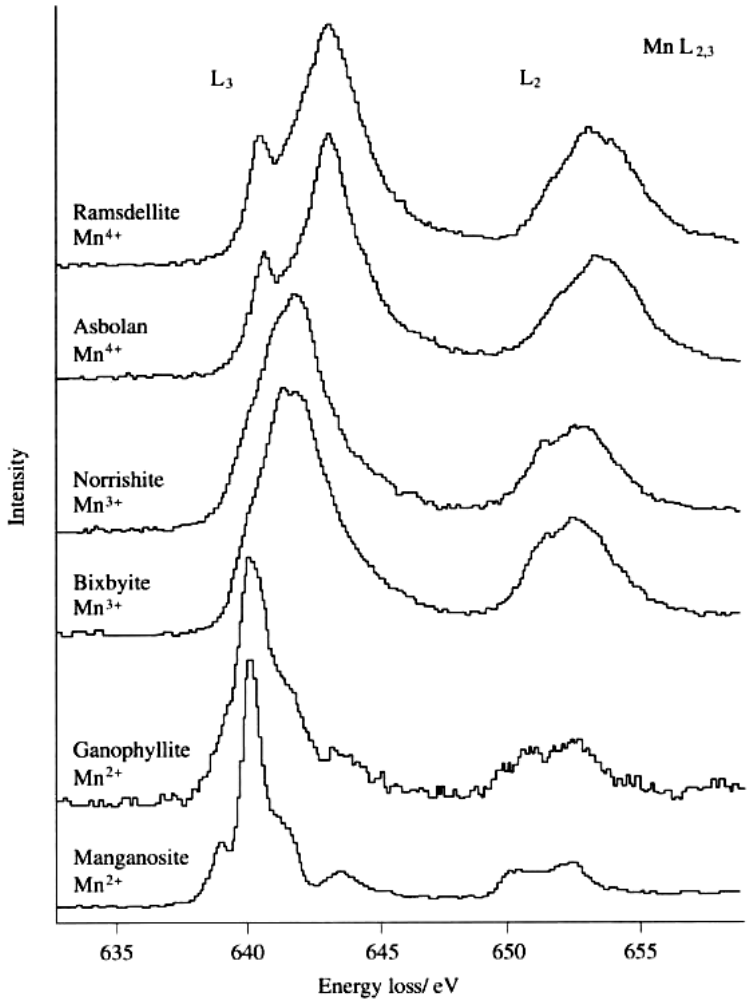
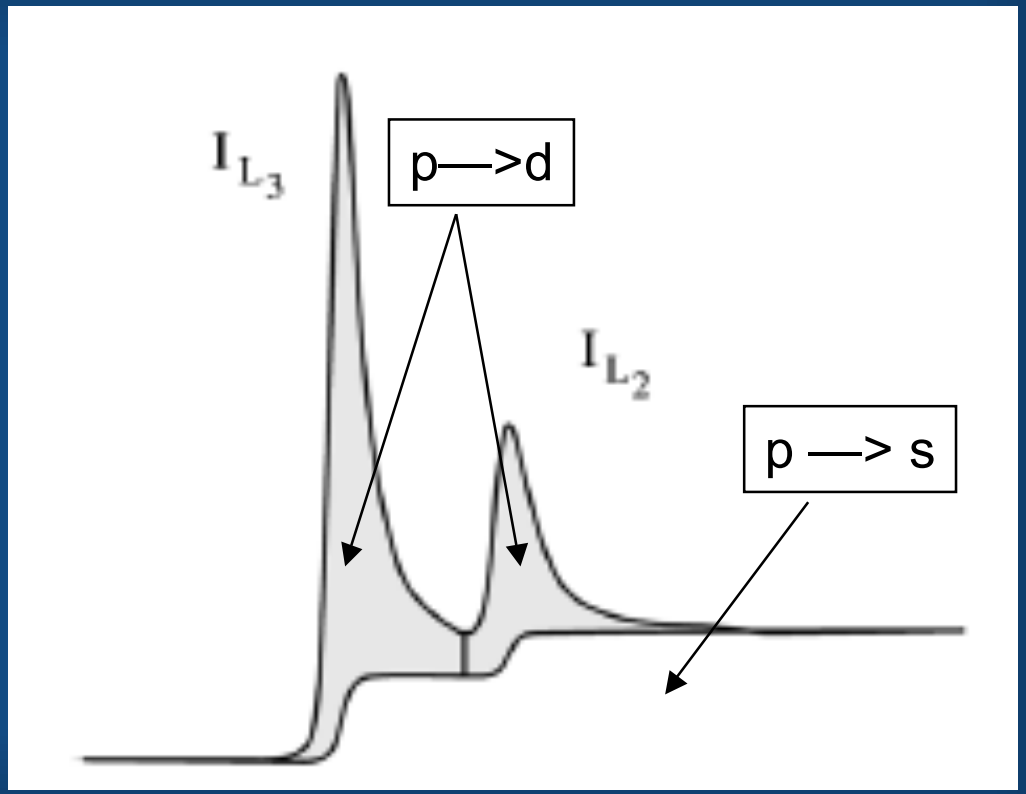


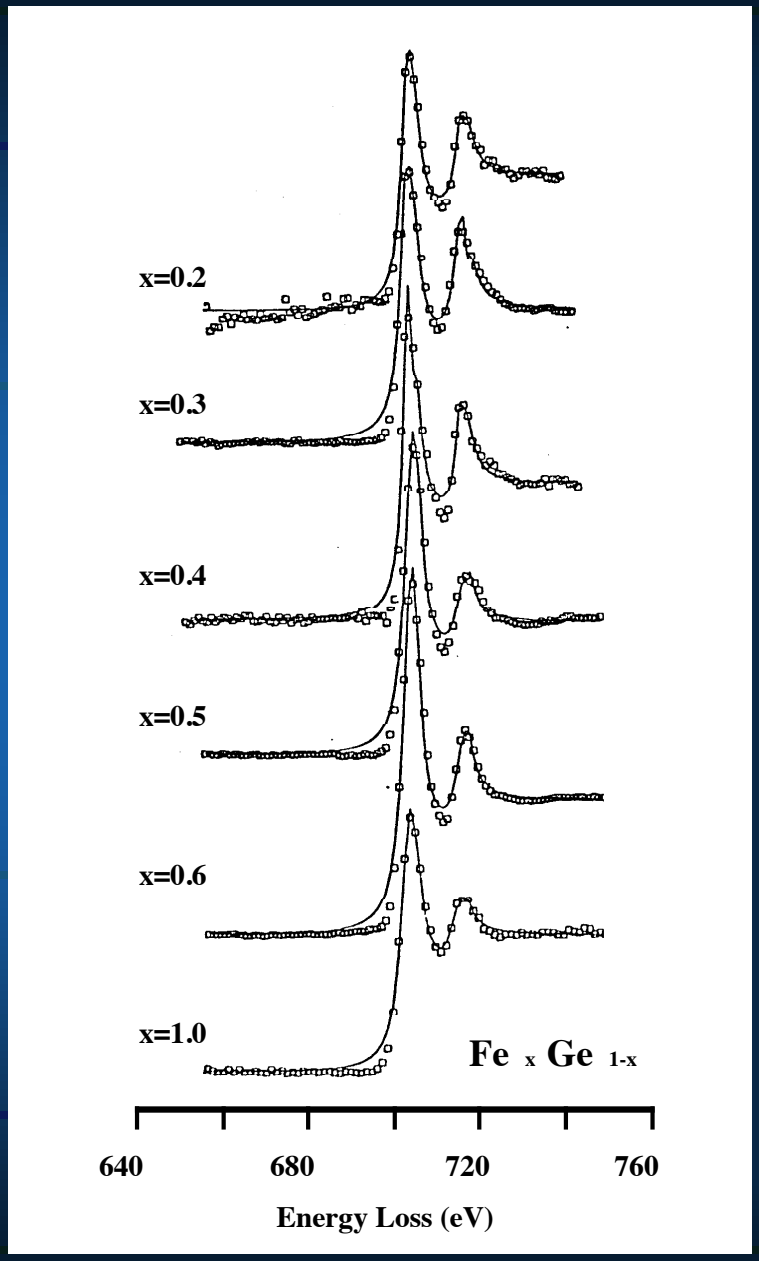
Figure 6.7. Comparison of Mn $L_{2,3}$-ELNES from a range of manganese minerals showing the systematic change in the L_3 peak position, the L_3/L_2 white-line intensity ratio and the detailed fine structure as a function of the oxidation state of Mn.

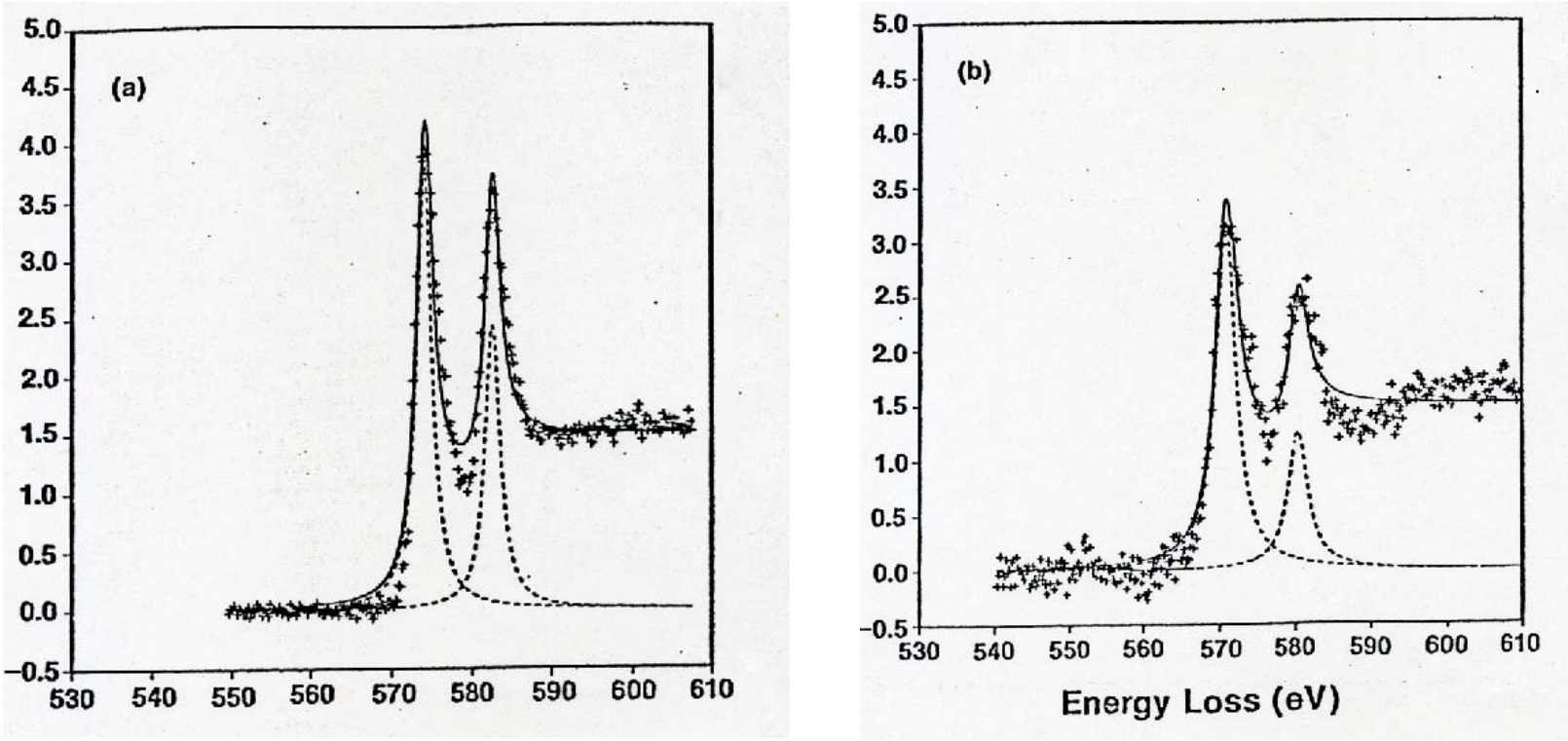
Magnetism in EELS is detectable using the L shell transitions



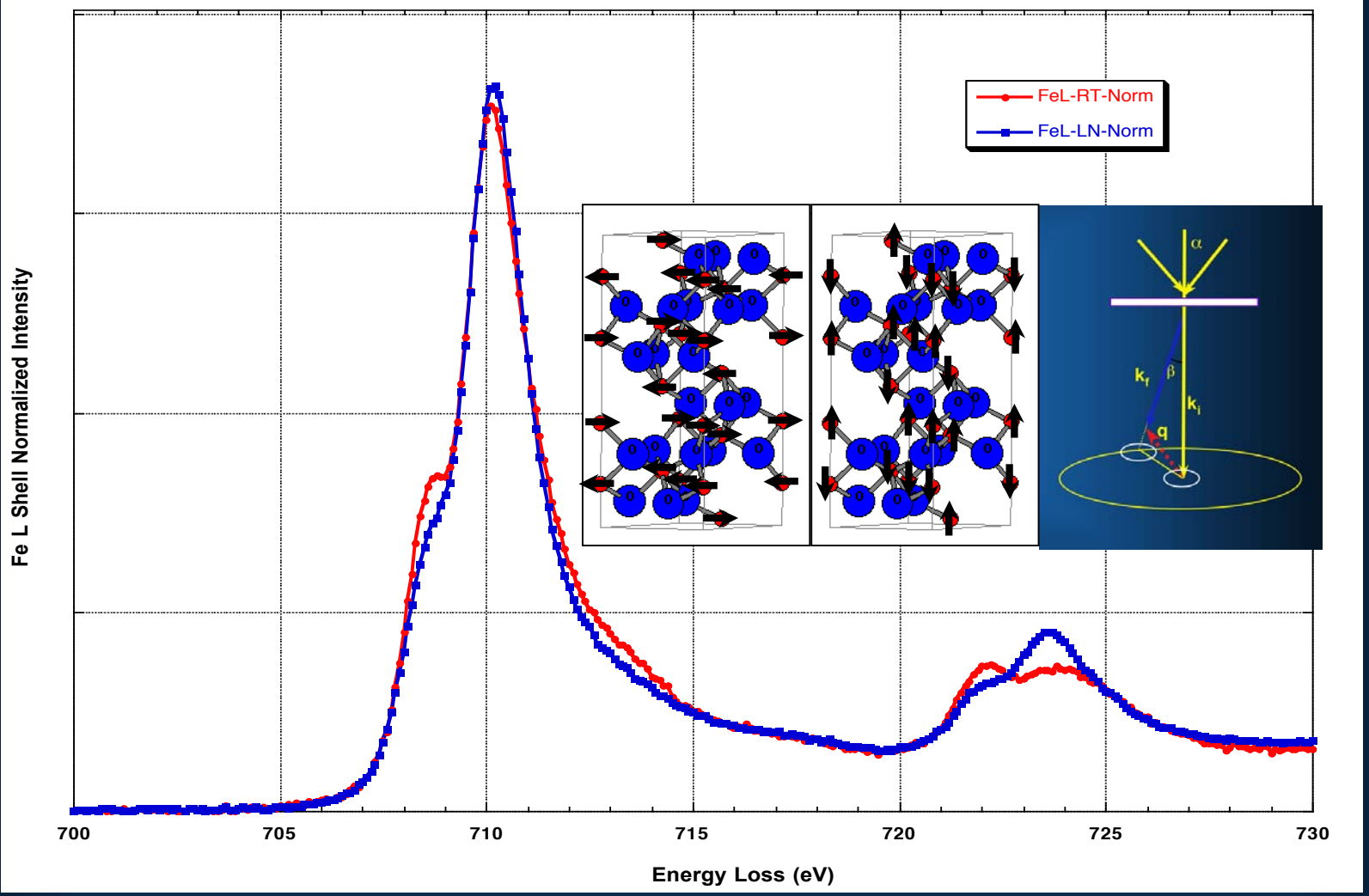
- d electrons are dominant in determining magnetic properties
- the L_3/L_2 "white lines" are the principle signals used to measure magnetism

Amorphous Fe_xGe_{1-x} Magnetic Materials




(a)
(b)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
530
540
550
560
570
580
590
600
610
Energy Loss (eV)

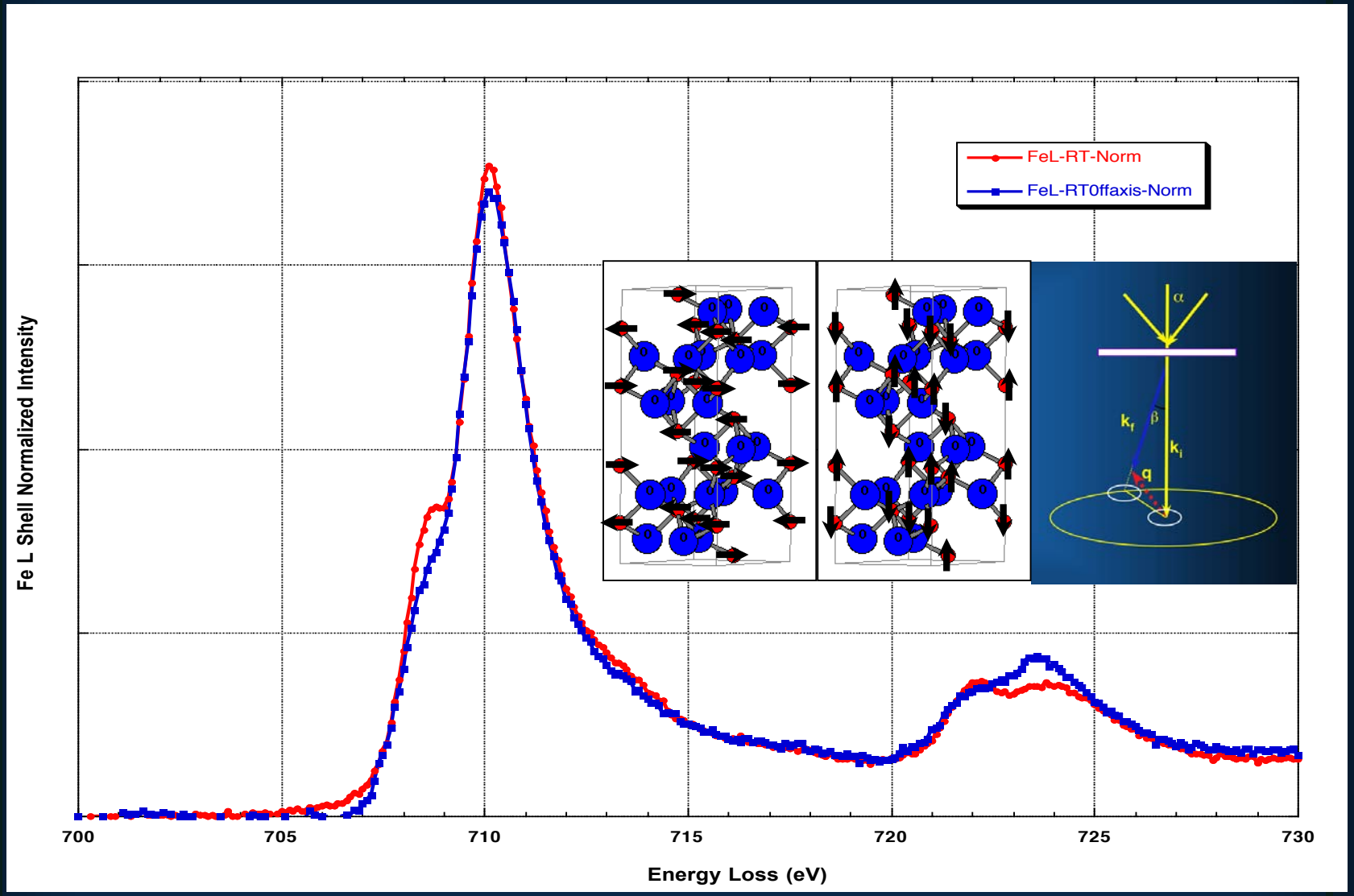
Fe_2O_3 (hematite)



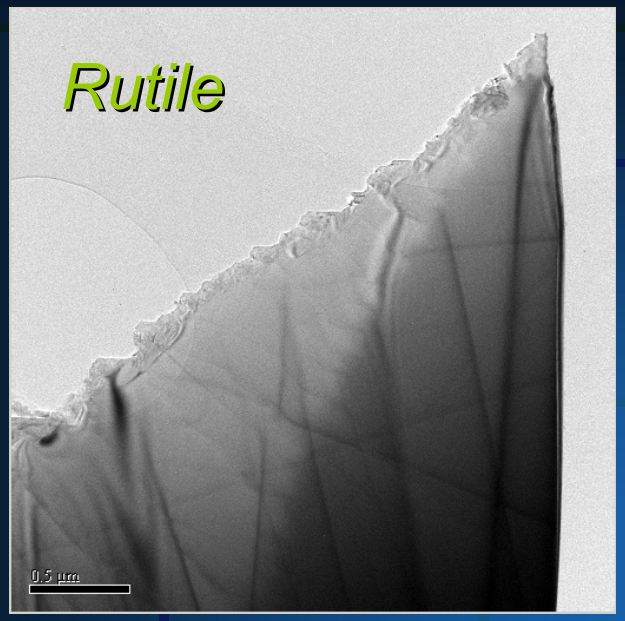
Normalized to LShell Integral

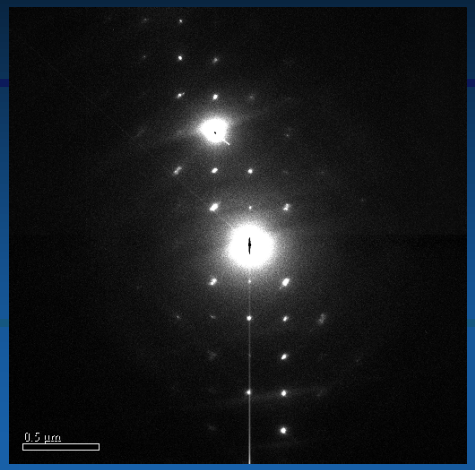
Summed Spectra 4 x 300 sec ~ 200KCnts at L3 Pk

Momentum Resolved On-Axis vs Off-Axis



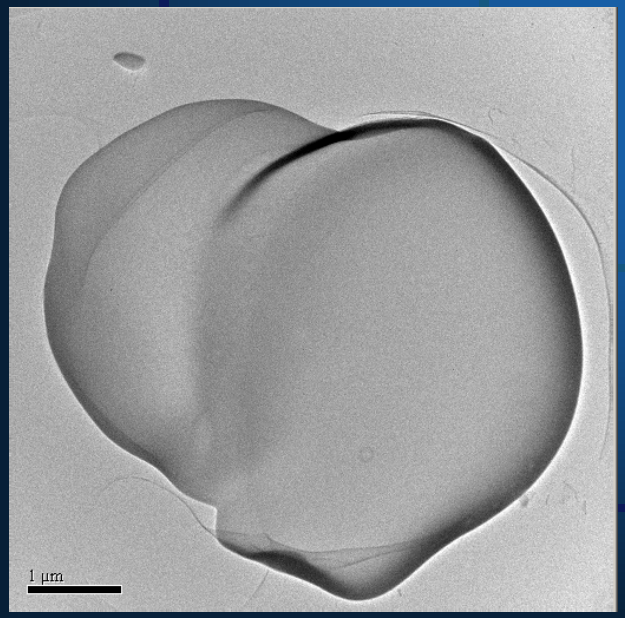
Normalized to LShell Integral

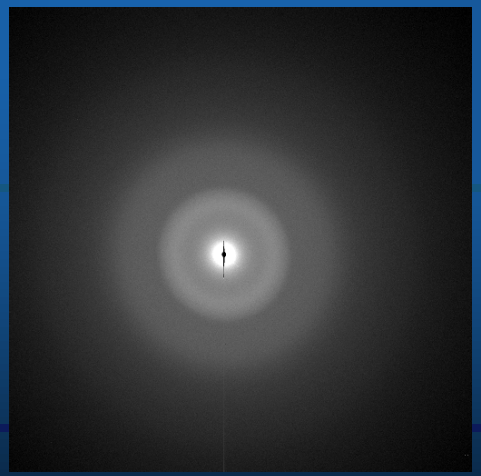




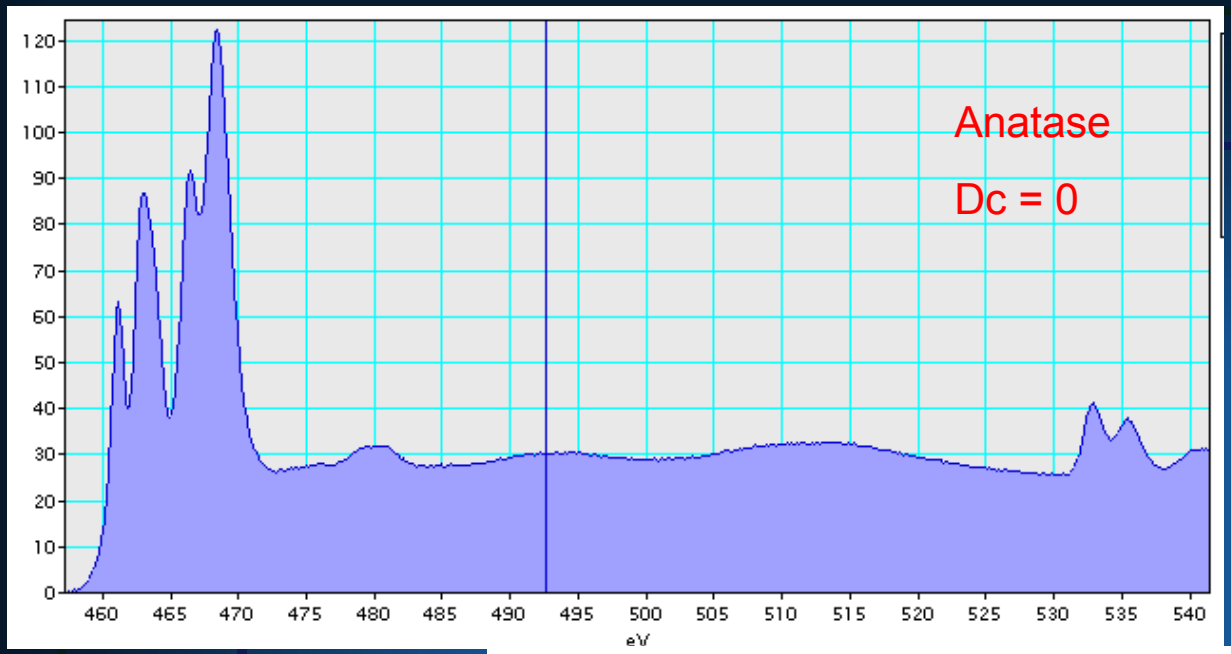
Typical Specimen
used in the EELS work

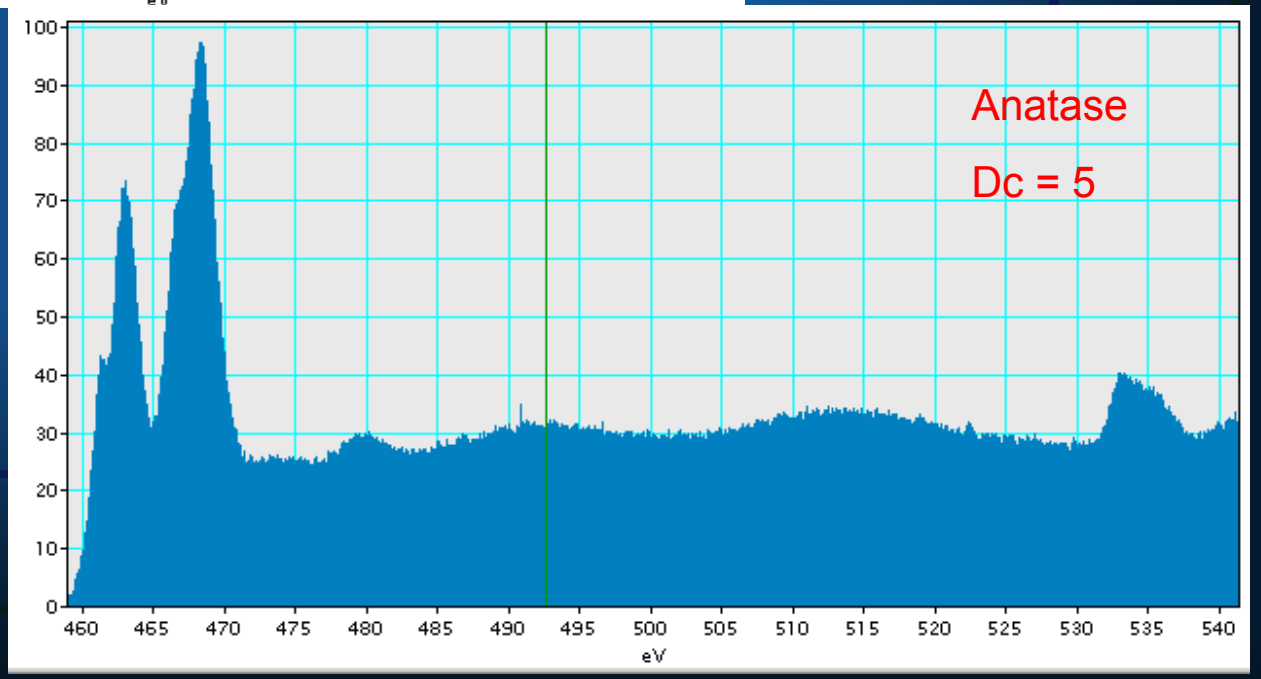
Dc = 0
Native
State



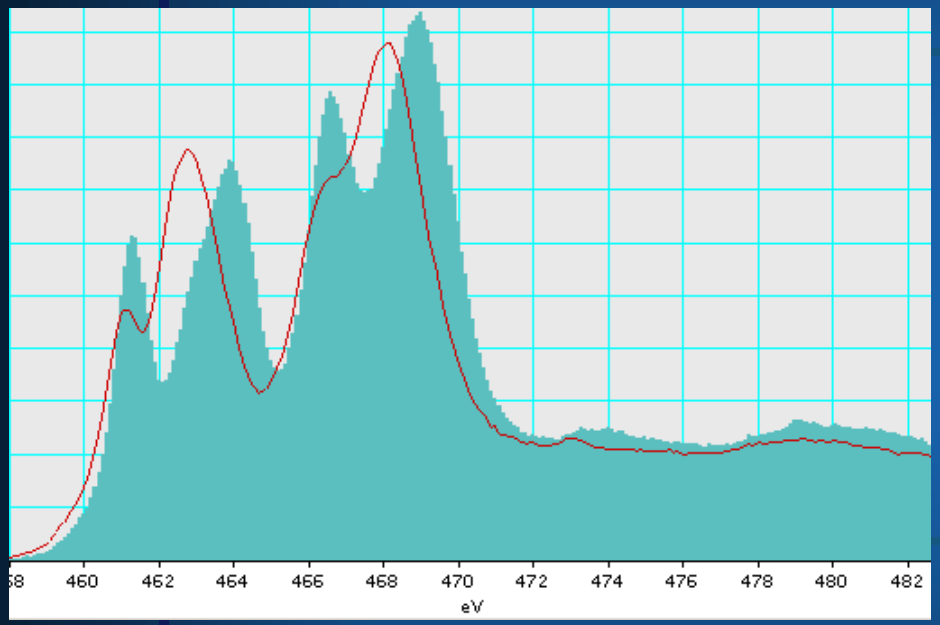


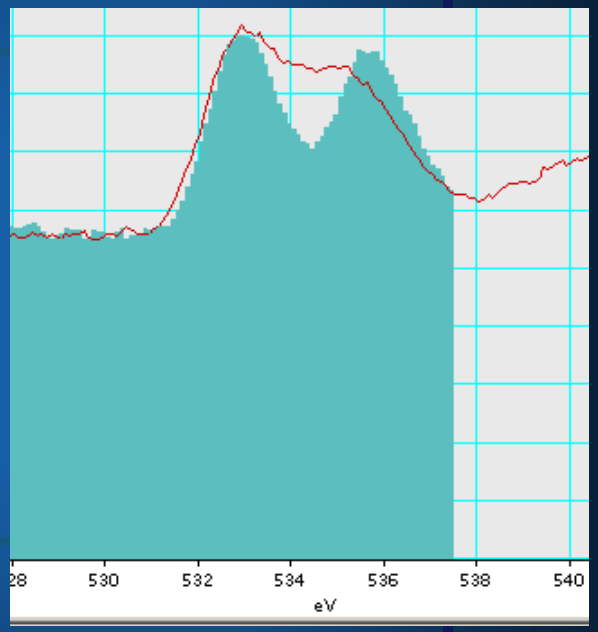
Dc = 5
Fully
Amorphized
State


Anatase
Dc = 0
120
110
100
90
80
70
60
50
40
30
20
10
0
460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540
eV


Anatase
Dc = 5
100
90
80
70
60
50
40
30
20
10
0
460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540
eV

Rutile Comparison Dc = 0 / 5





TiL

OK

Table 2.1. Summary of the analytical uses of EELS

Property determined	Spectral region	Processing required	Uses/limitations
Sample thickness	Full spectrum or low loss region	Integration of intensities	Rapid measure of relative thickness; need Λ (inelastic) for absolute values.
Valence electron density	Low loss – plasmon peak position	Peak fitting if required	Phase Identification/ Effects of alloying
Surface/interface states	Low loss – surface plasmons	Need model of dielectric function based on geometry	Surface properties
Joint DOS	Low loss – energy loss function	Deconvolution/fitting of ZLP/Kramers Kronig analysis/sum rules	Band gaps/interband transitions/comparison with optical results
Elemental concentration/ elemental distributions (EFTEM)	High loss – ionization edge intensities	Background subtraction/ deconvolution/ integration/calculation of partial cross-sections	Good for light elements with edges in range 0–2.5 keV/ often high detection limits/limited to thin sample areas
Element specific local coordination and/or valency	High loss – ELNES	Deconvolution/ comparison with reference materials – fingerprinting/peak fitting	Need good energy resolution and determination of absolute energy loss
Element specific unoccupied DOS	High loss – ELNES	Deconvolution/modelling of electronic structure	Need good energy resolution/effect of the core hole
Element specific radial distribution function	High loss – EXELFS	Standard EXAFS data processing	Low SNR – requires good statistics and large edge separations
Anisotropic DOS	High loss – ELNES/ low loss	Deconvolution/modelling of electronic structure	Need small collection angles and well-defined specimen orientation
Site specific DOS	High loss – ELNES/ALCHEMI	Deconvolution/modelling of electronic structure	Need well-defined diffraction and collection conditions
Ground state electron momentum distribution at large momentum transfer	Compton profile	Standard Compton scattering data processing	Low SNR/diffraction conditions