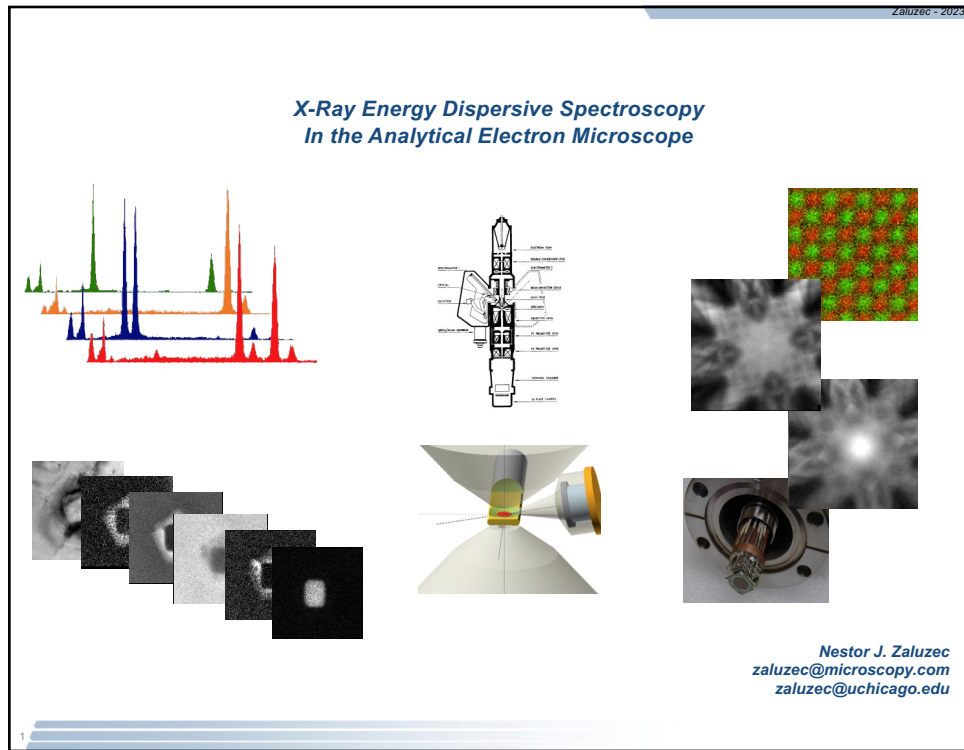
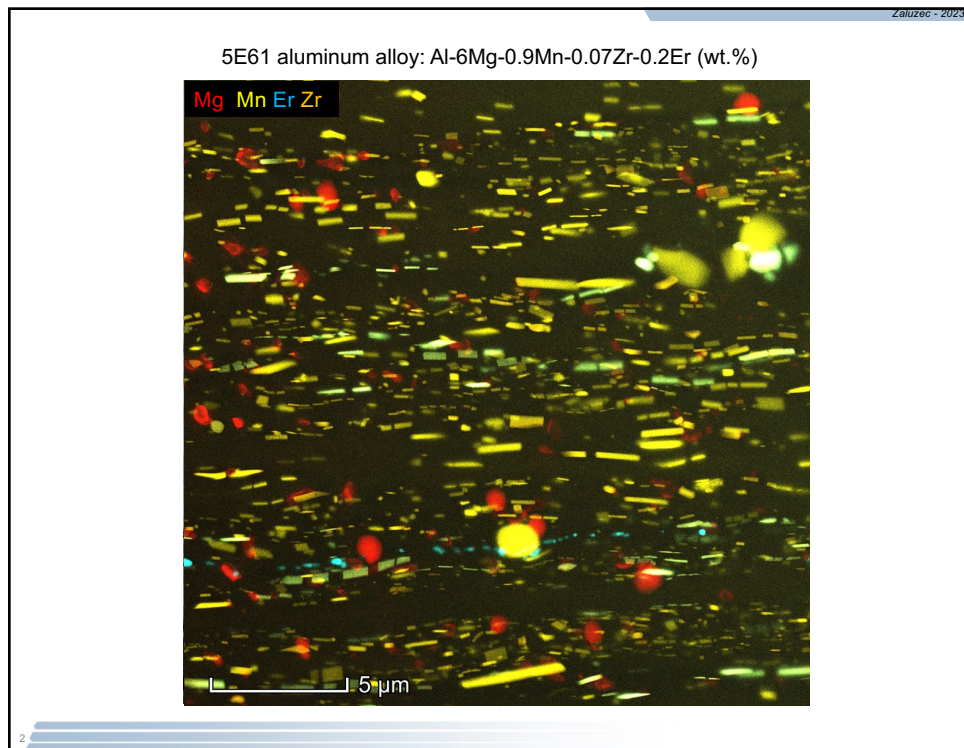


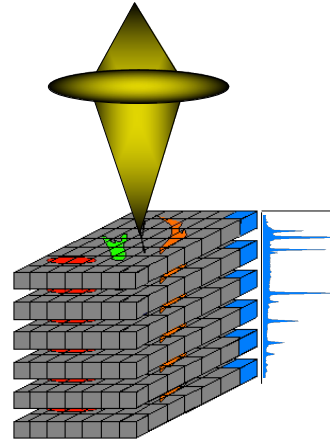
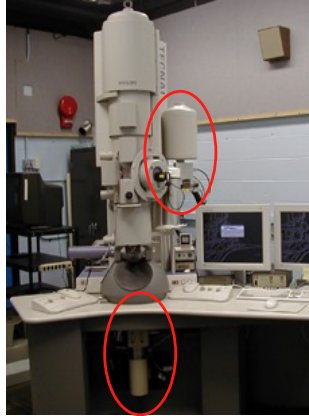


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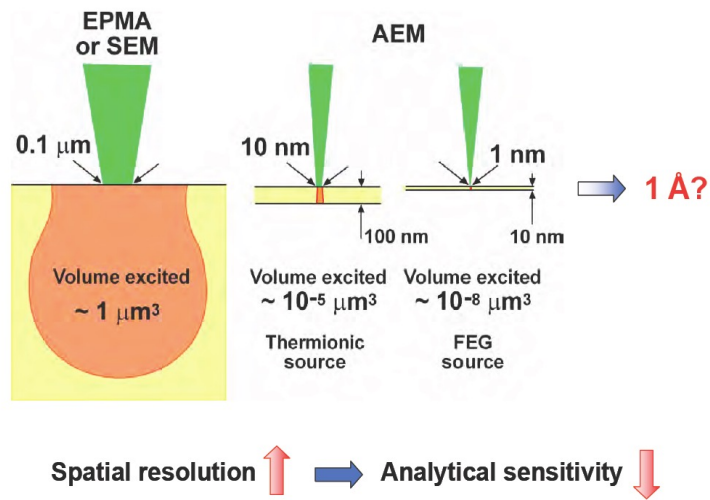
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Micro-Analytical Capabilities



3

3



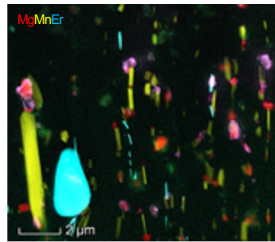
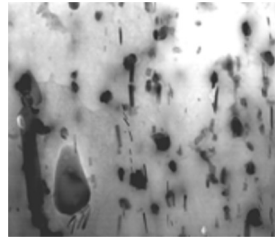
Williams & Carter

4

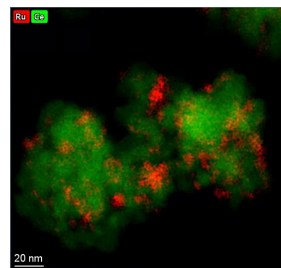
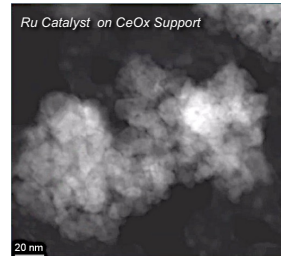
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Engineered Materials , Catalysts, Nanomaterials , Quantum Structures

Meso/Nanomaterials and processes challenge our ability to understand them:

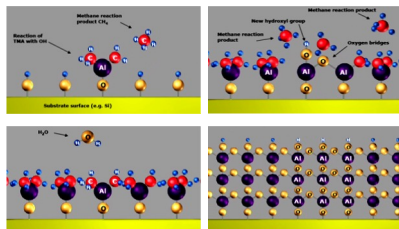


Materials Engineering at the Meso->Nanoscale



5

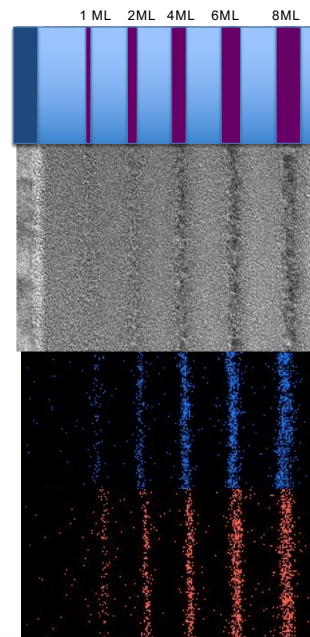
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Atomic Layer Deposition / $\text{MnO}_x:\text{TiO}_x$ with AlO_x spacers

Demonstrated ALD Reactions

1																	2																
H																	He																
Li	Be																B	C	N	O	F	Ne											
																		Na	Mg	Al	Si	P	S	Cl	Ar								
K	Ca																Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr																Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba																La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Fr	Ra																Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		
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Oxide
 Nitride
 Element
 S/Se/Te
 Ph/As
 C
 F
 Dopant

$$\begin{array}{c} \text{Si} \\ \text{AlO}_x \\ \text{MnO}_x / \text{TiO}_x \end{array}$$


1 msec/pixel !!!

6

6

Zoluzec - 2023

Brief Review of X-ray Generation

Instrumentation: Detector Systems

Instrumentation: EM Systems

Data Analysis and Quantification

Additional Topics

7

7

Zoluzec - 2023

Electron Excitation of Inner Shell Processes

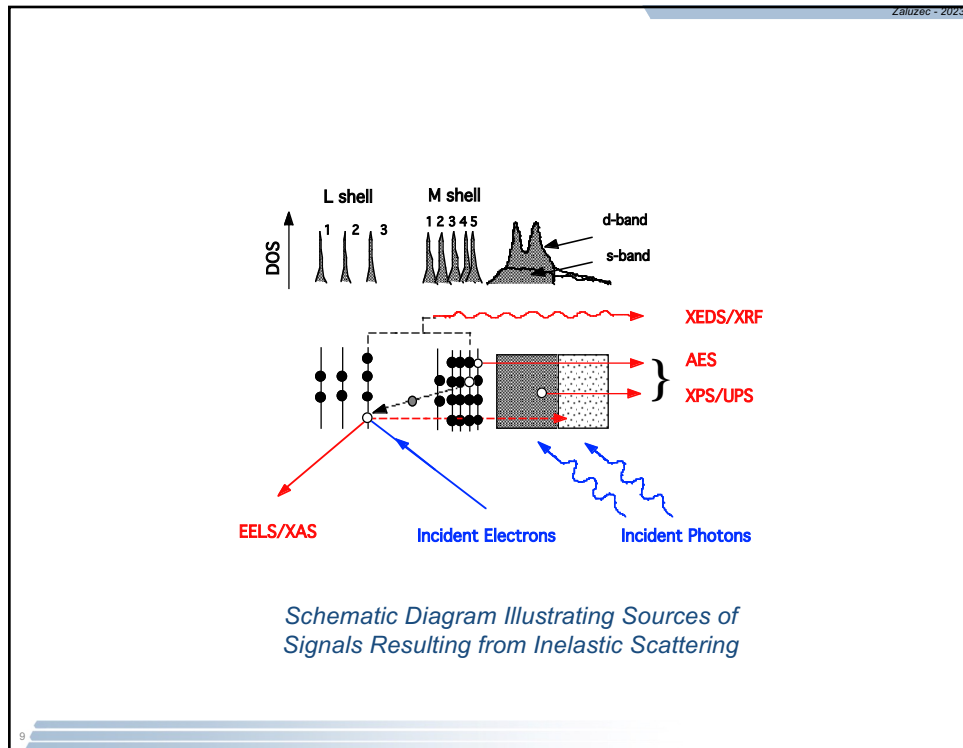
Non-radiative Emission Radiative Emission

Spectral Profiles

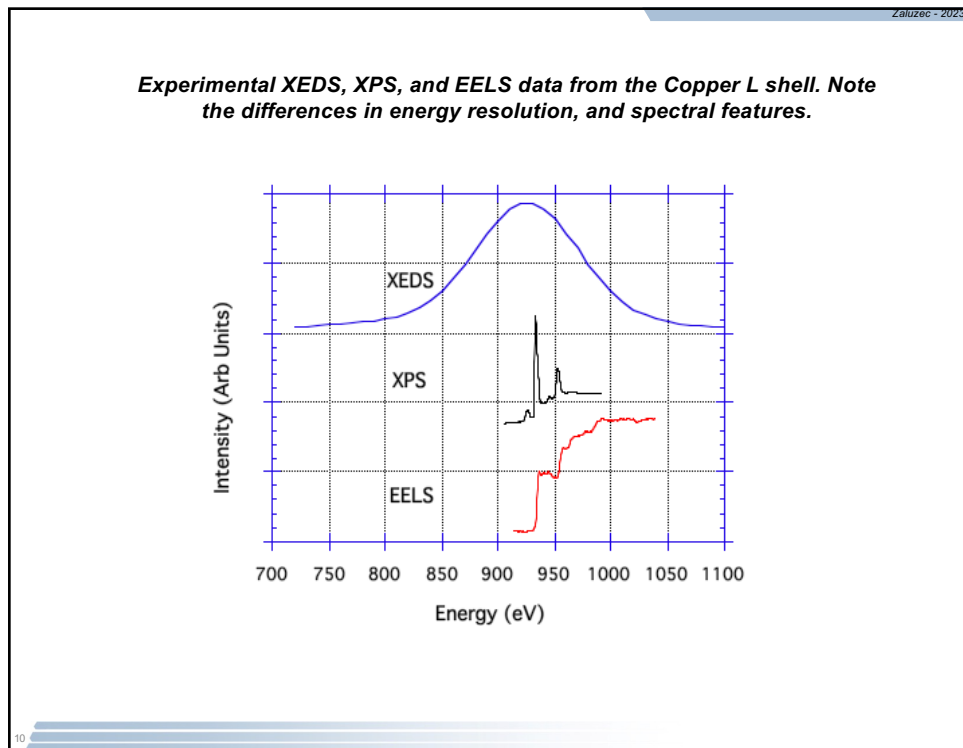
NiO : XEDS / EELS

8

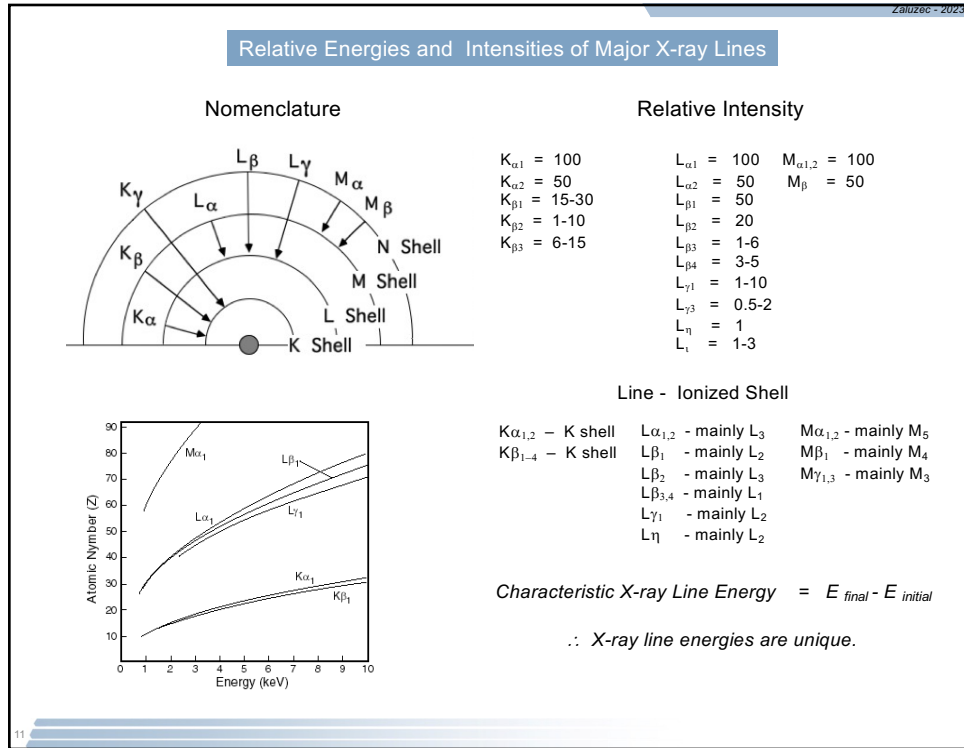
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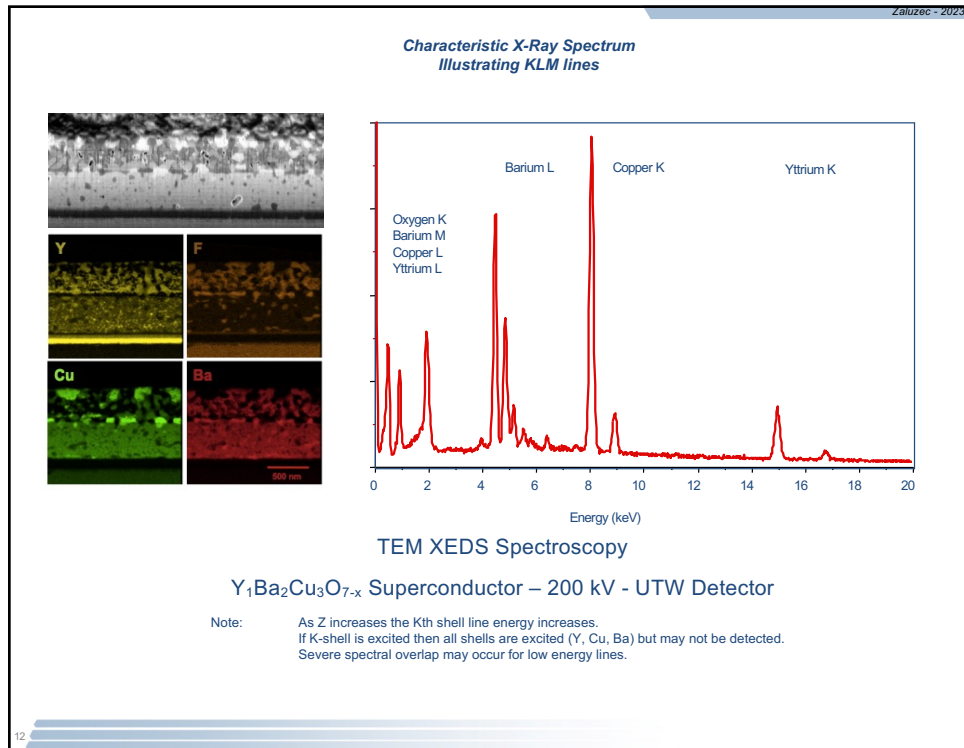
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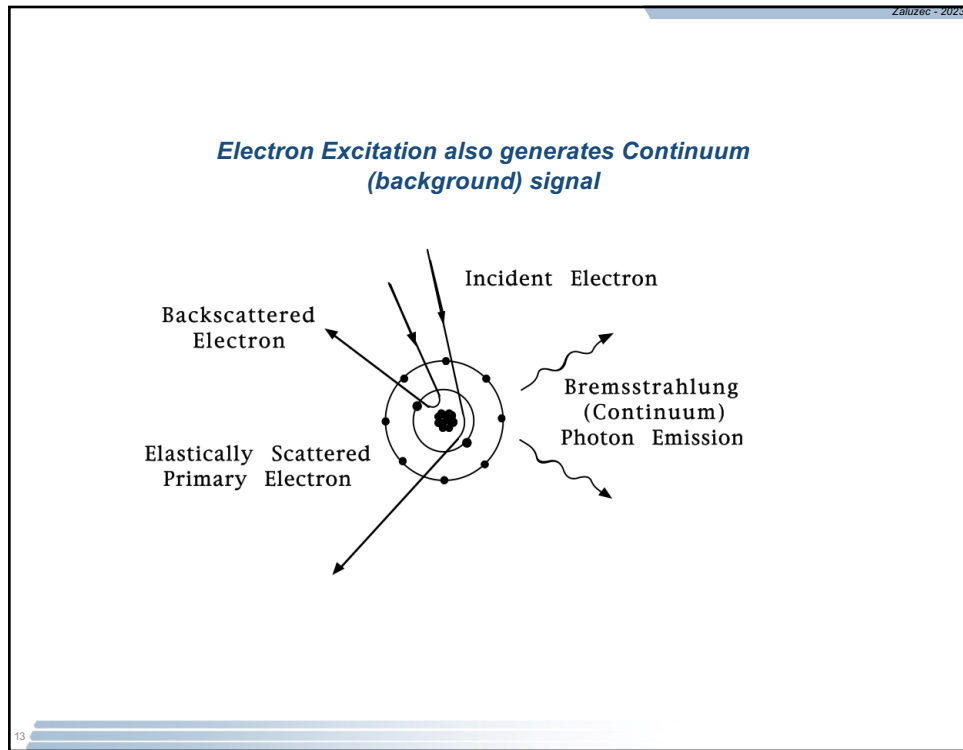
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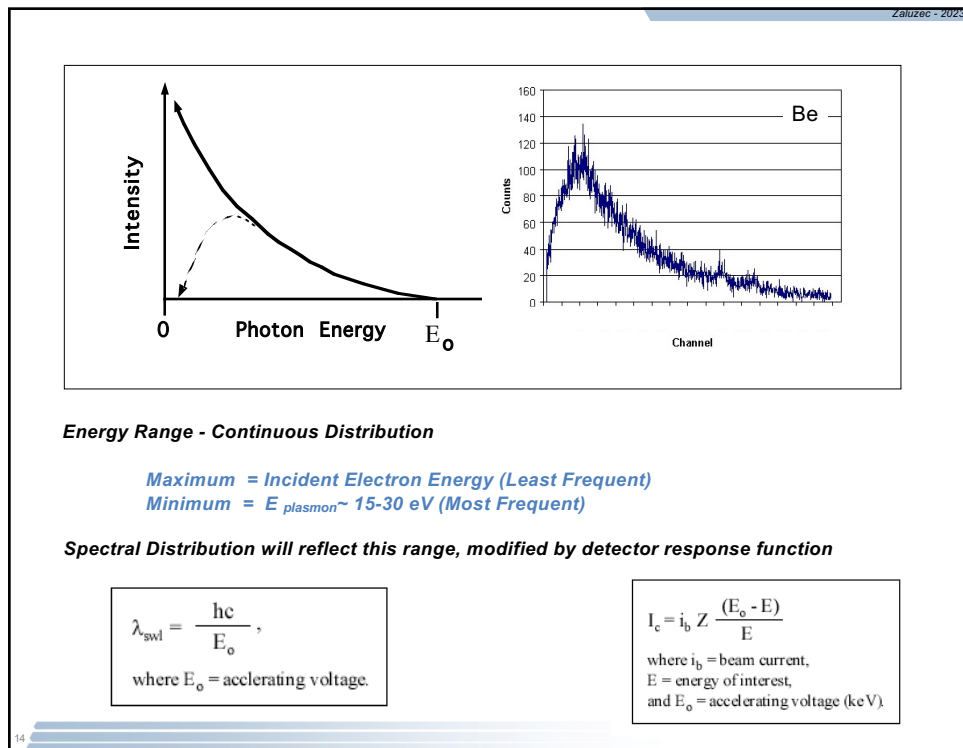
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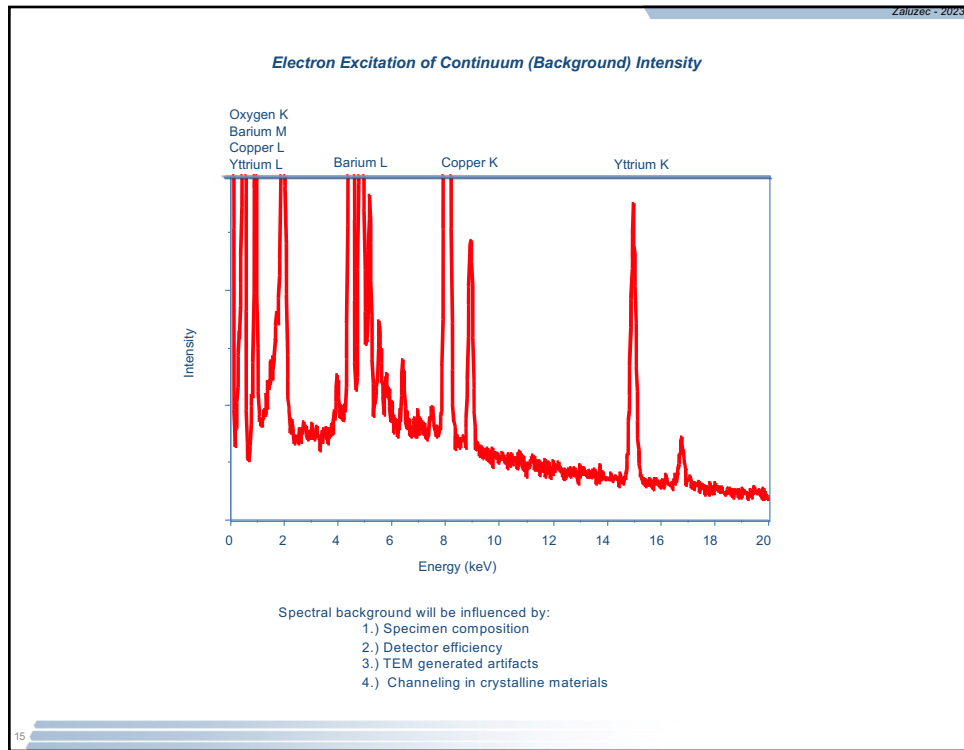
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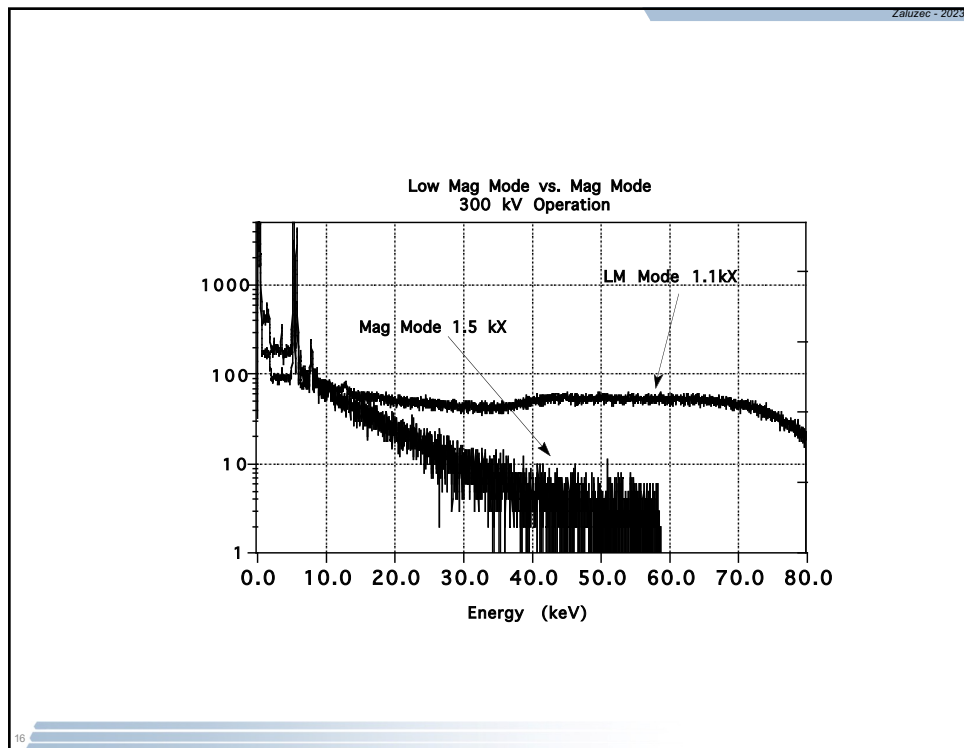
13



14



15



16

Instrumentation: Detector Systems

Wavelength Dispersive Spectrometers (WDS)
Energy Dispersive Spectrometers (EDS)
 Si(Li) Detectors
 HPGe Detectors
 Spectral Artifacts of the EDS System
 Detector Efficiency Functions
 Light Element Detectors
Superconducting Calorimeters/Bolometers
Silicon Drift Detectors

Multichannel Analyzers

17

17



18

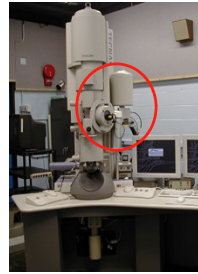
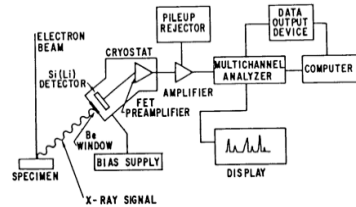
18

Energy Dispersive Spectrometers: (Solid State Detector)

Operates on Energy Deposition Principle

Simple, Nearly Operator Independent
 Large Solid Angles (0.05-1.0 sr)
 Virtually Specimen Position Independent
 No Moving Parts
 Pseudo-Parallel Detection
 Quantification by Standardless or Standards Methods

Poor Energy Resolution (~ 130 eV)
 Peak/Background Ratios (100:1)
 Detection Efficiency Depends upon X-ray Energy



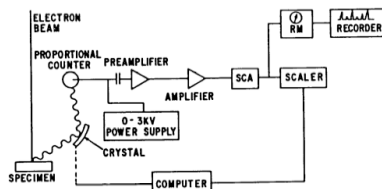
19

Wavelength Dispersive Spectrometers : (Diffractometer)

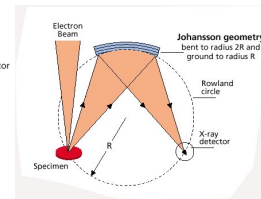
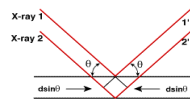
Operates using Diffraction Principles (Bragg's Law)

Excellent Energy Resolution (~ 5 eV)
 High Peak/Background Ratios (10000:1)
 Good Detection Efficiency for All X-rays
 High Counting Rates
 Good Light Element Capabilities

Complex Mechanical Devices, Operator Intensive
 Specimen Height dependant focus
 Moving Components in the AEM
 Limited Solid Angles (<0.01 sr)
 Serial Detection
 Quantification Requires Standards

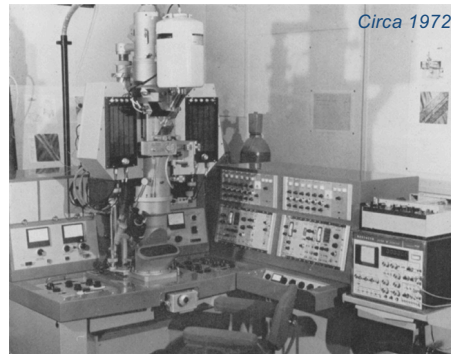
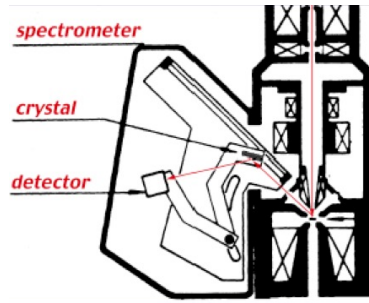
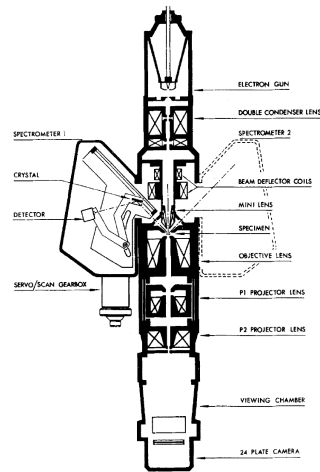


Bragg's Law as applied to x-ray diffraction
 $n\lambda = 2d \sin \theta$
 λ is the wavelength of interest
 d is the interplanar spacing of the diffractor
 θ is the angle of x-ray incidence on the diffractor
 n is an integer



20

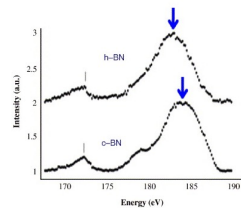
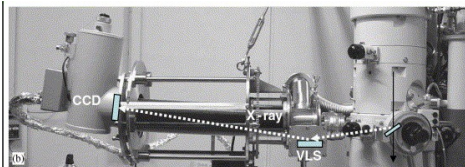
WDS system in a TEM EMMA-4 System



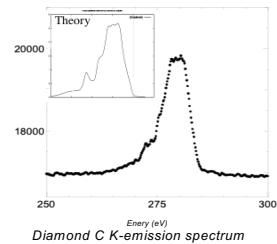
21

21

Modern Applications WDS Valence Band/Electronic Structure Measurements



M. Terauchi, M. Kawana – Tohoku University

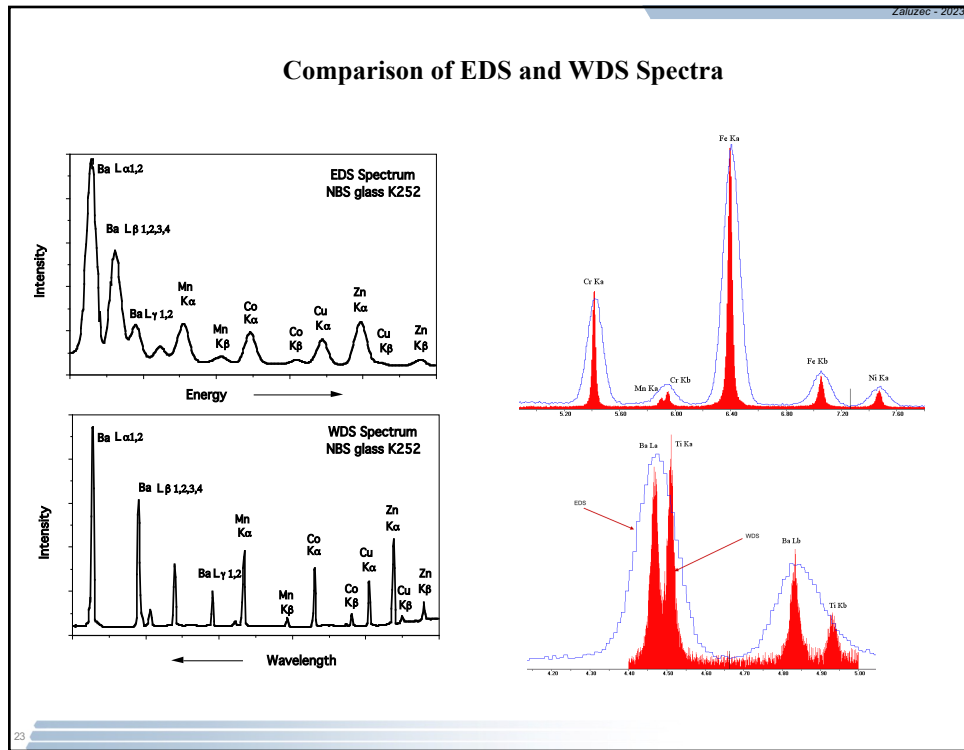


Diamond C K-emission spectrum

Y. Ito NIU Physics

22

22



23

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Comparison of EDS and WDS Spectrometers

Parameter	Wavelength Dispersive	Energy Dispersive
Construction	Mechanical Device moving components	Solid State no moving parts
Energy Resolution	5 eV	130 eV
Efficiency	≤ 30 %	100 % (3-10keV)
Input Count Rate	30-50 K cps	10 K cps
Peak/Background*	10000	100
Atomic Number Range	Z ≥ 4 (Be)	Z ≥ 11 (Na) Z ≥ 5 (B)
Number of Elements	1 per Detector	All in Energy Range
Solid Angle	0.001-0.01 sr	0.02- π sr
Collection Time	Tens of Minutes	Minutes
Beam Current	High Stability Required	Low Stability Required
Detector Stability	Good Short Term	Excellent
Spectral Artifacts	Negligible	Important
Operation	Skilled (?)	Novice

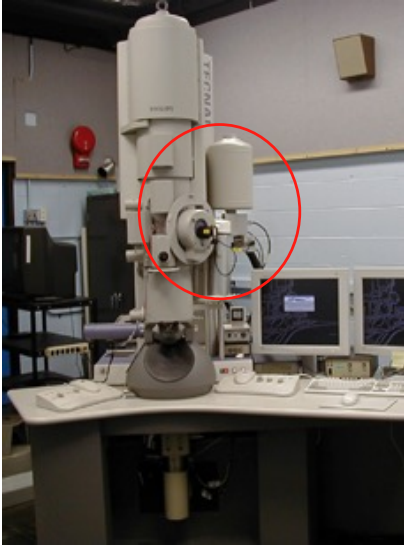
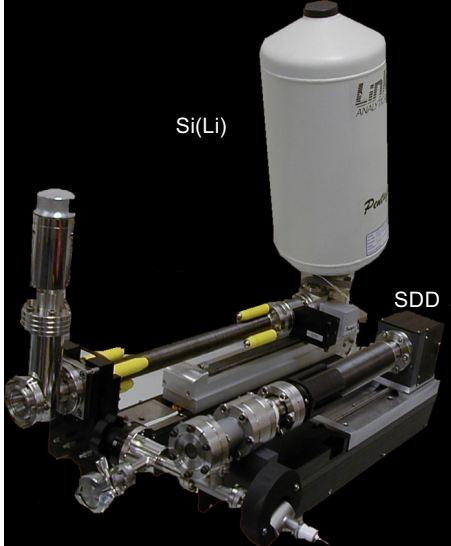
* Values depend on definition, specimen, and operating conditions

24

24

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Energy Dispersive Detectors

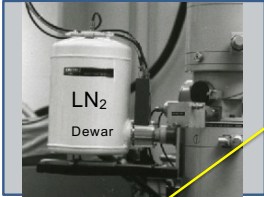
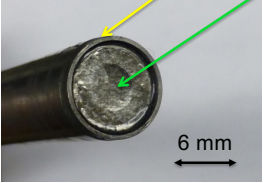
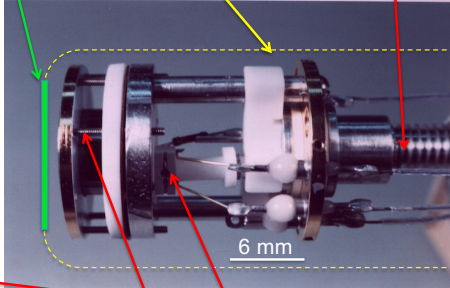
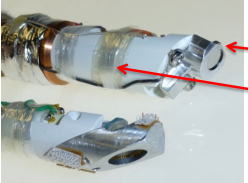
Si(Li) vs SDD

25

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Basic Construction of Si(Li) Detectors

Environmental Housing

Window

LN2 "Finger"

Si(Li)

FET

26

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Li Diffusion → **Initially p-type Silicon**

Thermally Induced Concentration Gradient

Apply a Reverse Biased Potential

Si(Li) Crystals

- P-type Silicon high conductivity due to impurities (usually Boron); Lithium acts as a compensating dopant neutralizing the Si giving it a high resistivity.
- Radiation deposits energy in the Si(Li) lattice & creates free electron-hole pairs in the crystal @ 1 electron-hole pair/3.8 eV of deposited energy @ 77K.
- Intrinsic semiconducting Si allows both electrons & holes to become mobile under application of a potential bias across the crystal

Cut Silicon Crystal on Intrinsic Boundaries

Si(Li) Intrinsic Silicon

27

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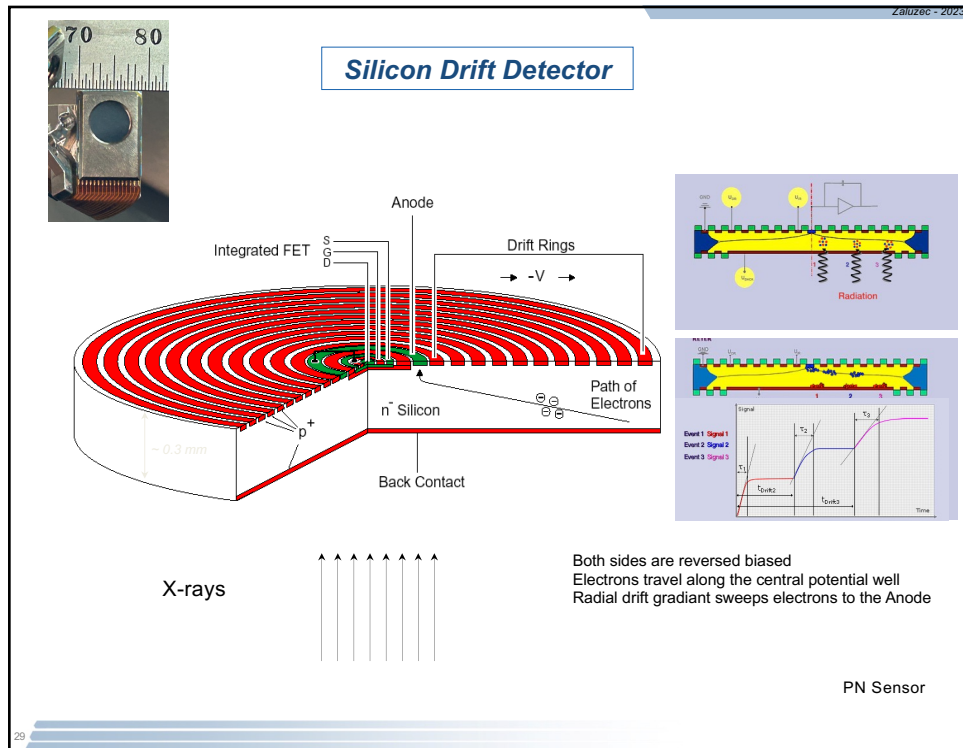
Silicon Drift Detectors

Environmental Housing

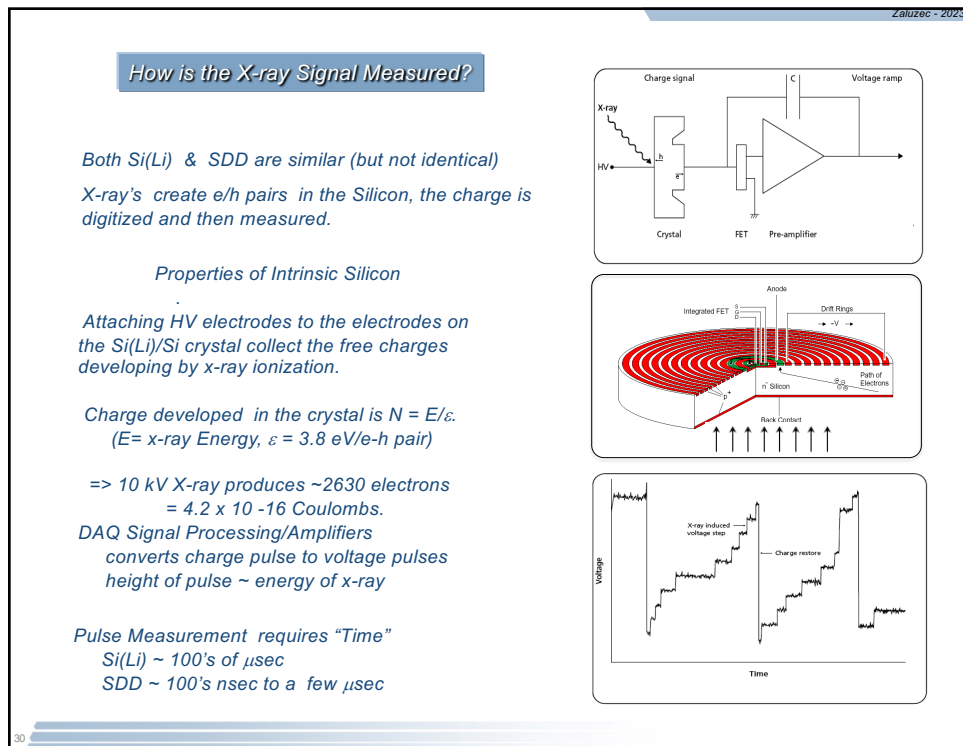
5 - 20 mm

28

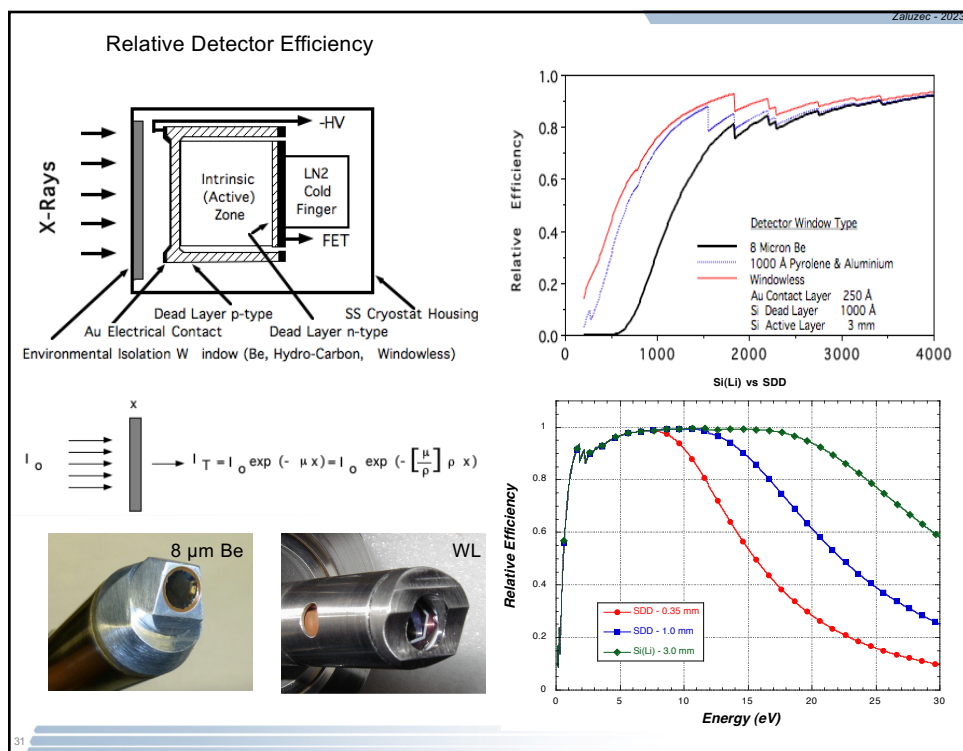
28



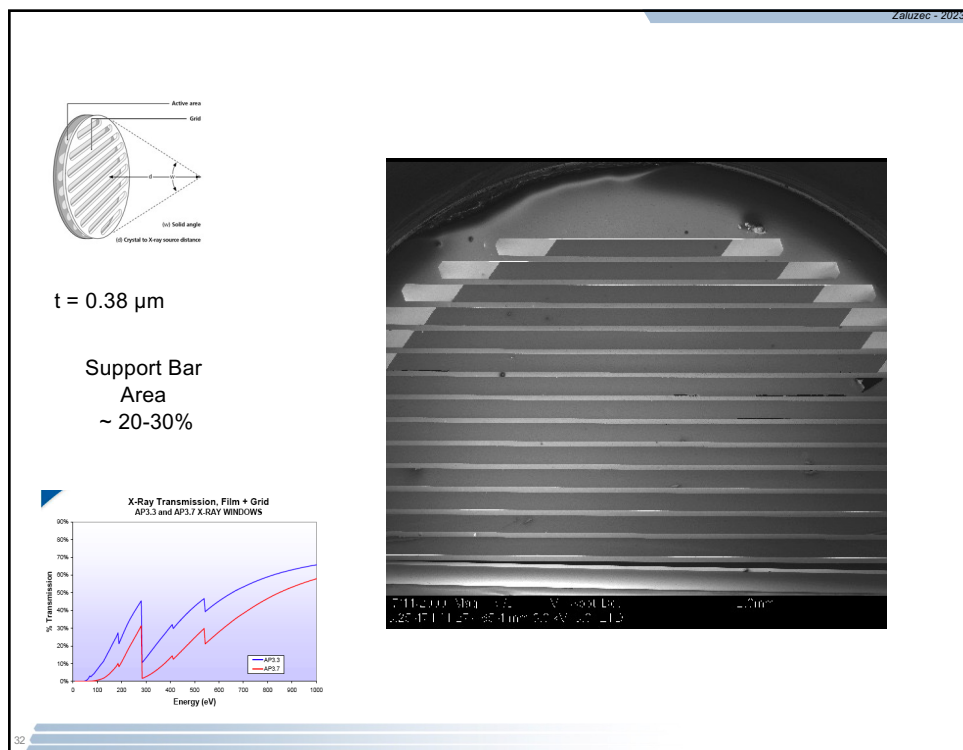
29



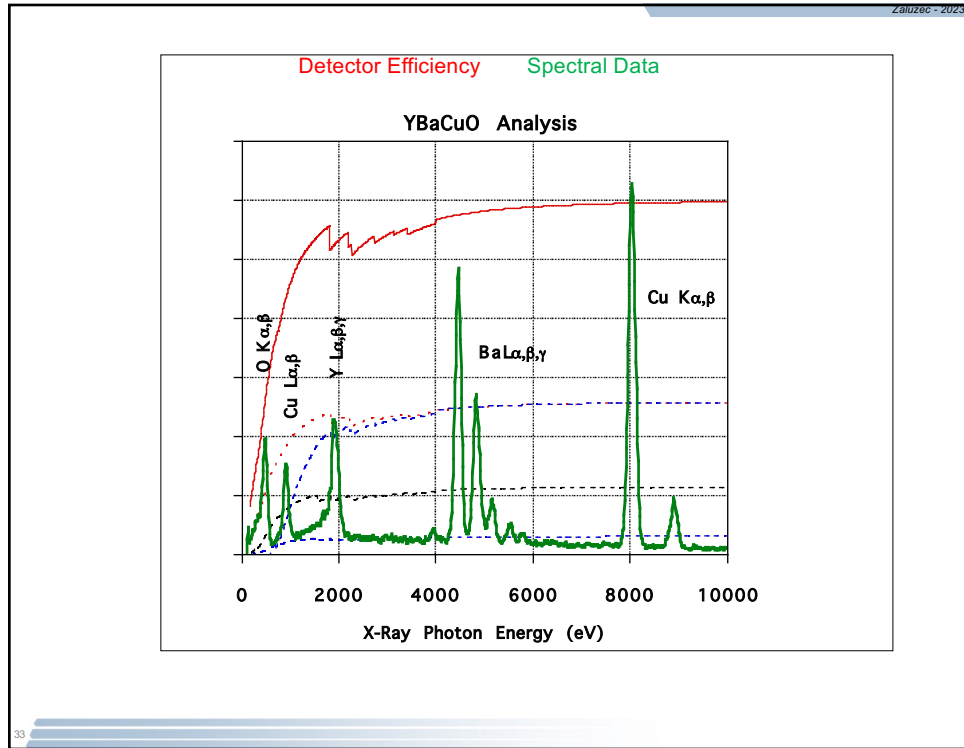
30



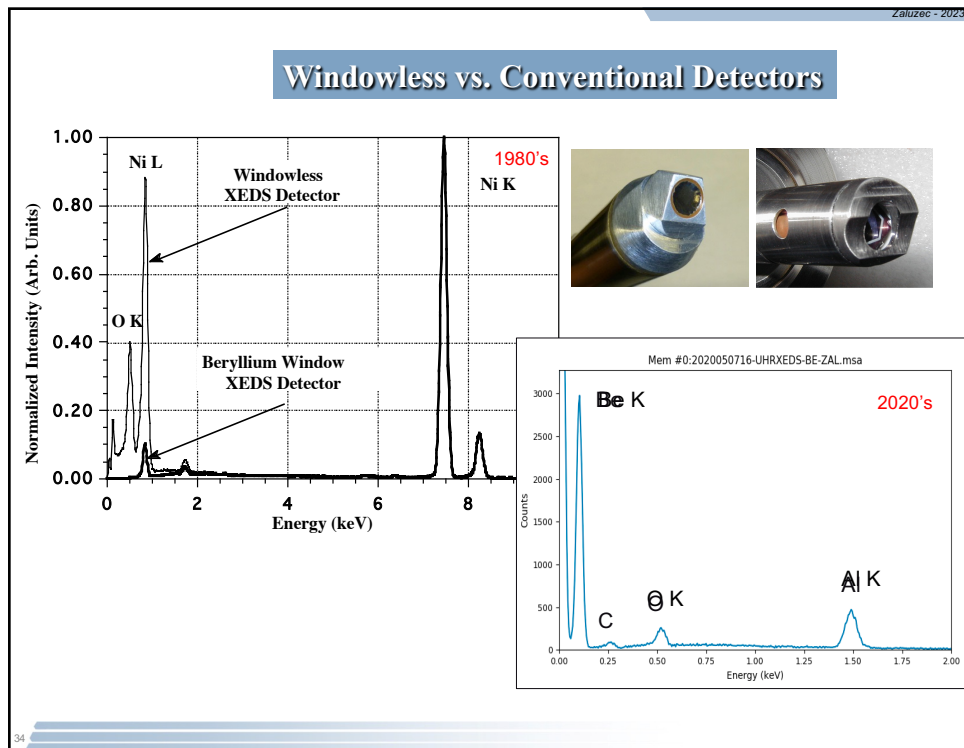
31



32

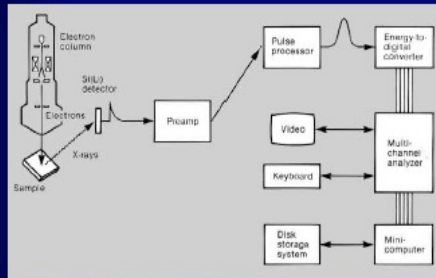


33



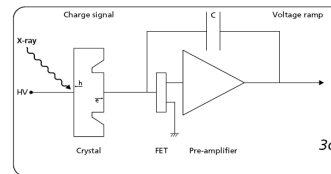
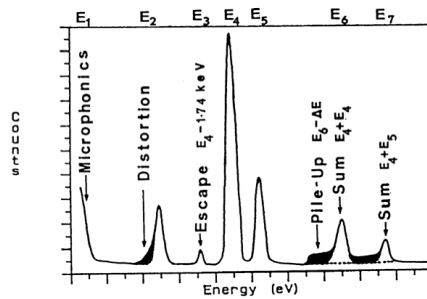
34

The Multi-Channel Analyzer



35

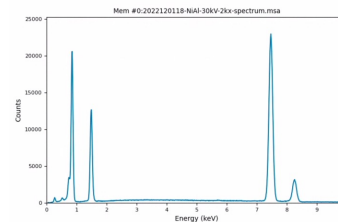
Detector Resolution & Facts/Artifacts



$$\Delta E_{FWHM} = \sqrt{\text{Electronic Noise}^2 + 2.35^2 \epsilon F E}$$

Detector Facts/Artifacts

- Resolution = $f(E, \text{DAQ}, T_c)$
- Spectral Overlap = $f(E, \text{Resolution}, \text{DAQ}, T_c)$
- Sum Peaks = $f(\text{Count rate}, E, T_c)$
- Escape Peaks = $f(\text{Counts}, E, \text{Geometry})$
- Distortion Tails = $f(E, \text{DAQ})$
- Microphonics = $f(\text{Environment})$

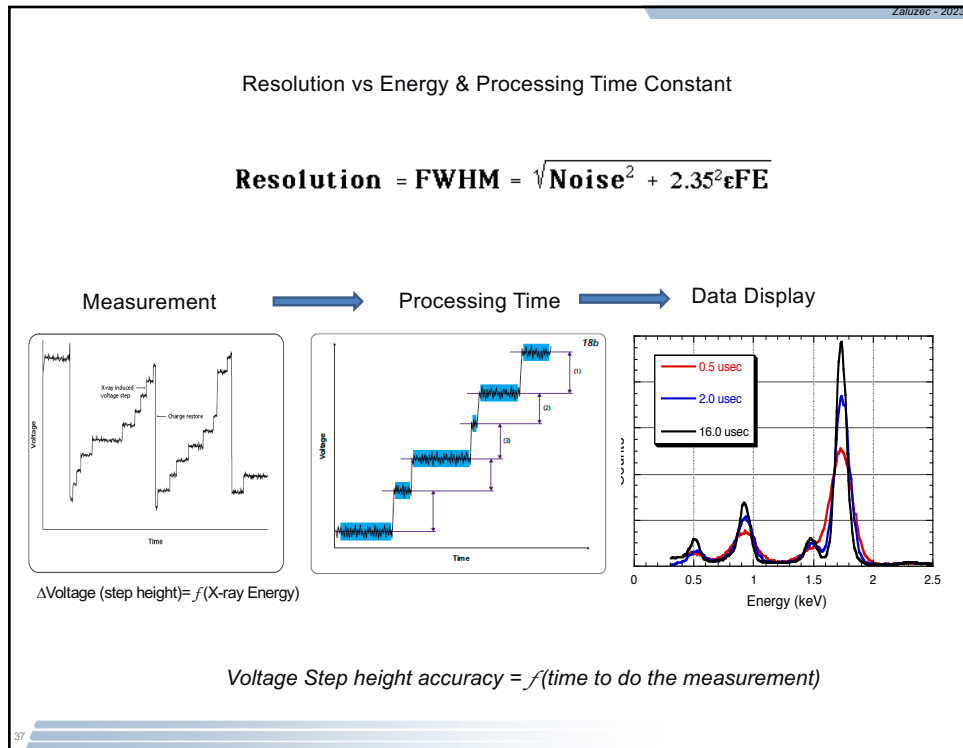


Nominal FWHM Values in Modern Silicon X-ray Detectors:

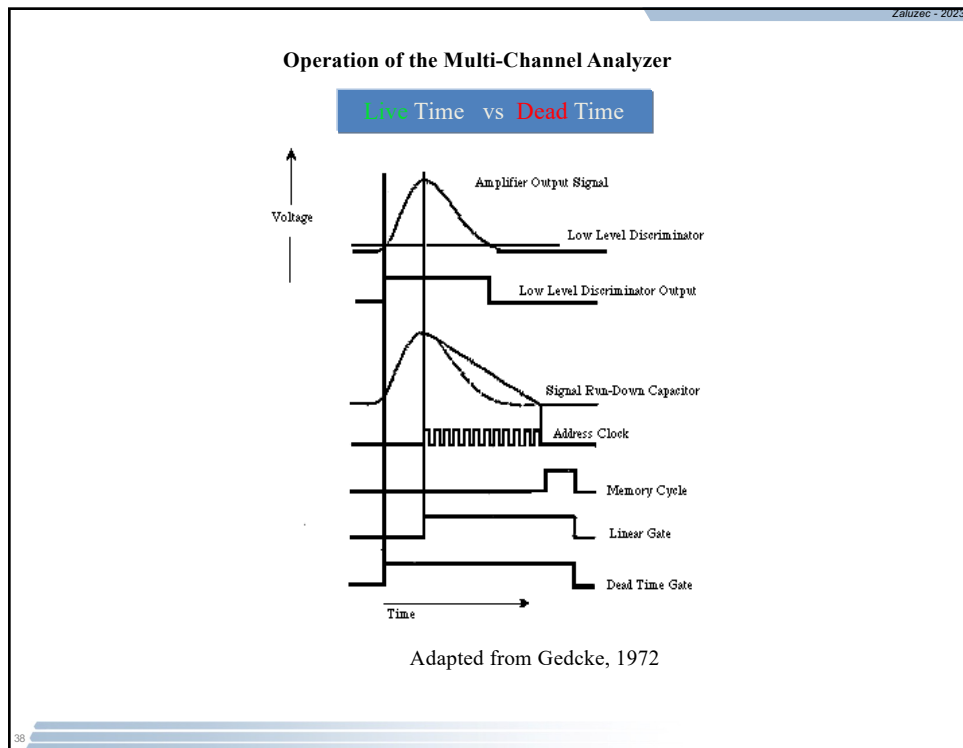
- O Kα (0.52 keV) = 60 to 100 eV
- Mn Kα (5.9 keV) = 120 to 160 eV
- Mo Kα (17.5 keV) = 210 to 230 eV

36

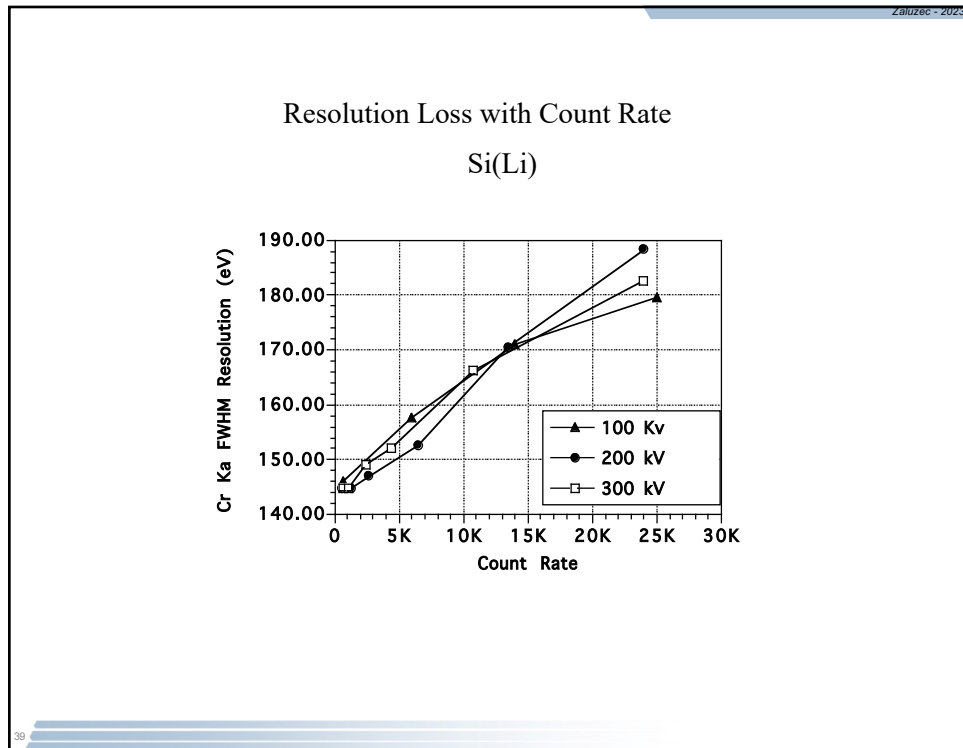
36



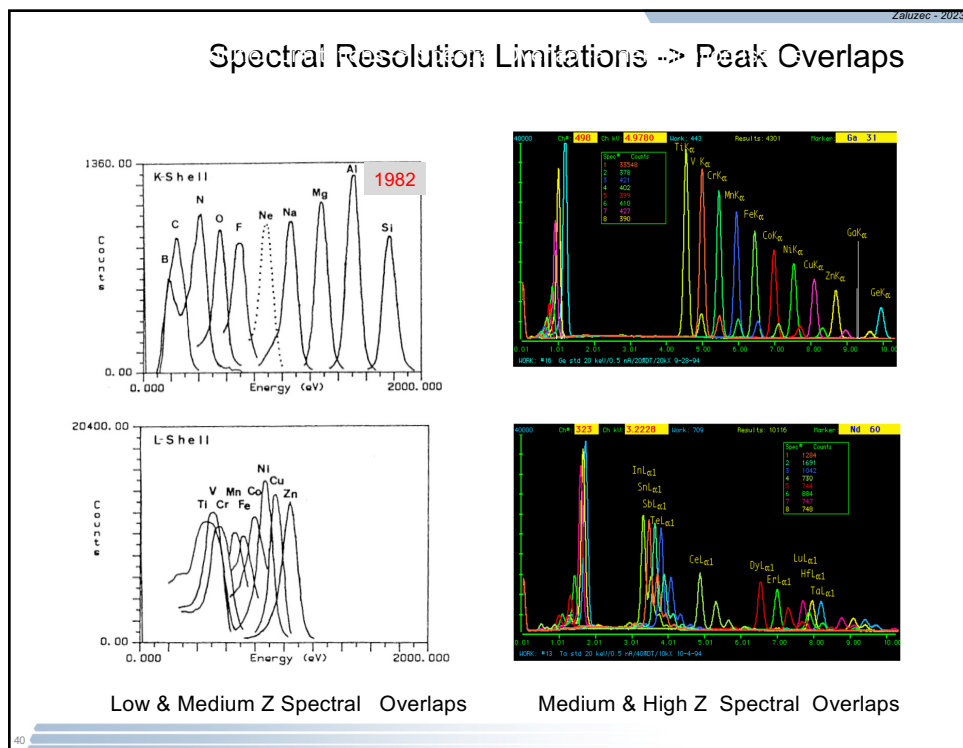
37



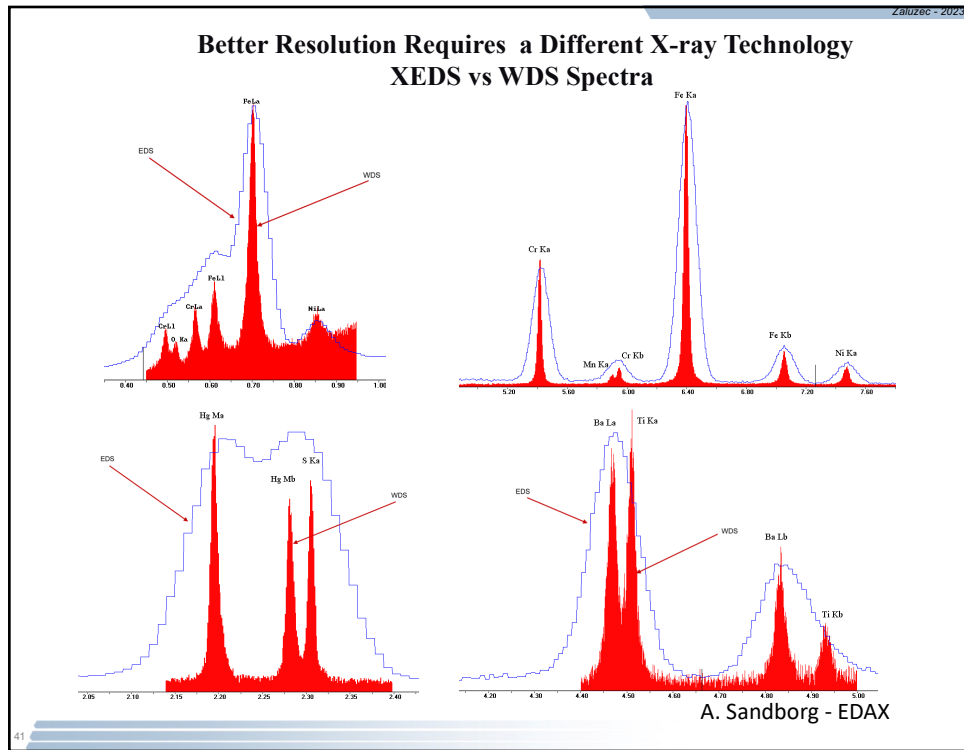
38



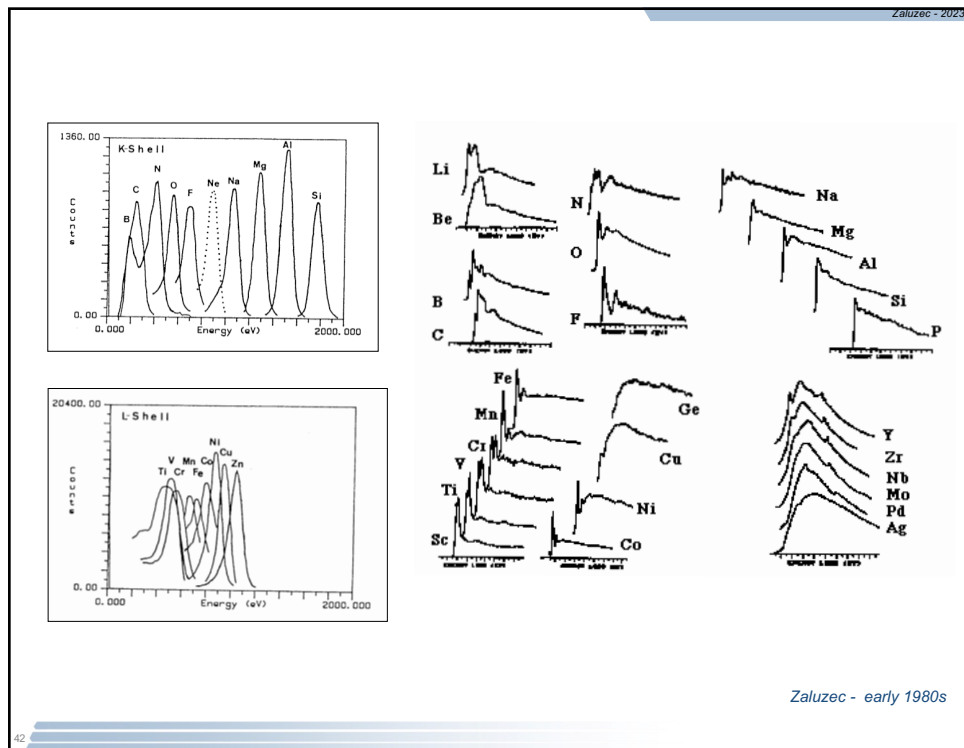
39



40

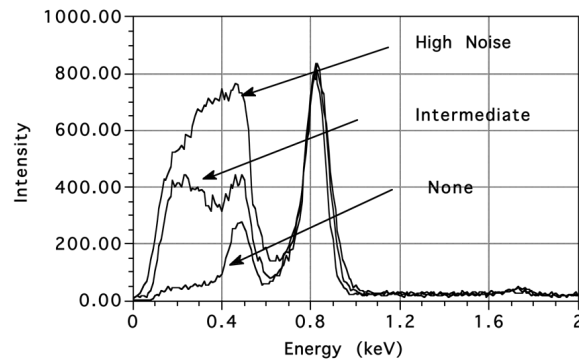


41



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Resolution will also vary with
Microphonic & Electronic Noise, IR/Visible Light!

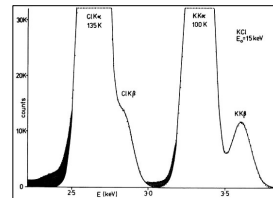
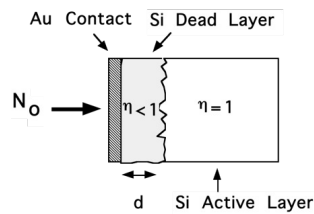


WL & UTW detectors are particularly sensitive to low energy noise and microphonics and *light all reflect energy added to the crystal*

Observe the changes in the spectra

43

Incomplete Charge Collection in Solid State Detectors : Low Energy Tails

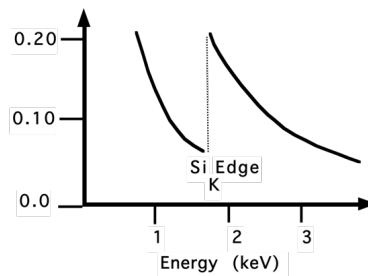


$$N_{\text{peak}} = N_0 \exp(-\mu d)$$

$$N_{\text{tail}} = N_0 (1 - \exp(-\mu d))$$

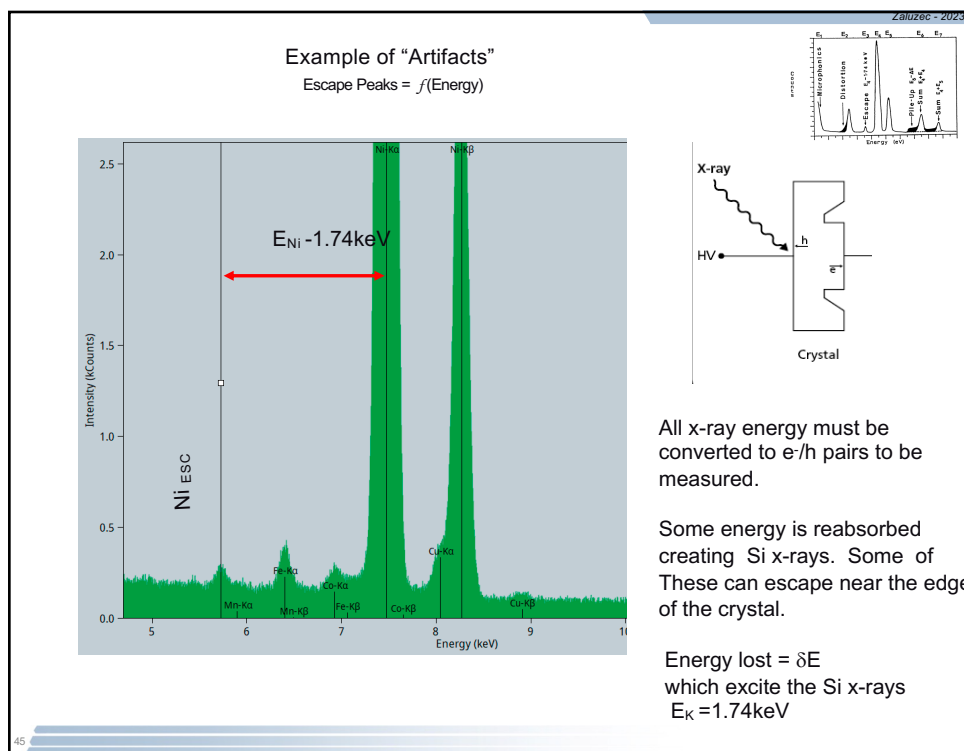
$$\frac{N_{\text{tail}}}{N_{\text{peak}}} = \frac{(1 - \exp(-\mu d))}{\exp(-\mu d)}$$

$\frac{N_{\text{tail}}}{N_{\text{peak}}}$

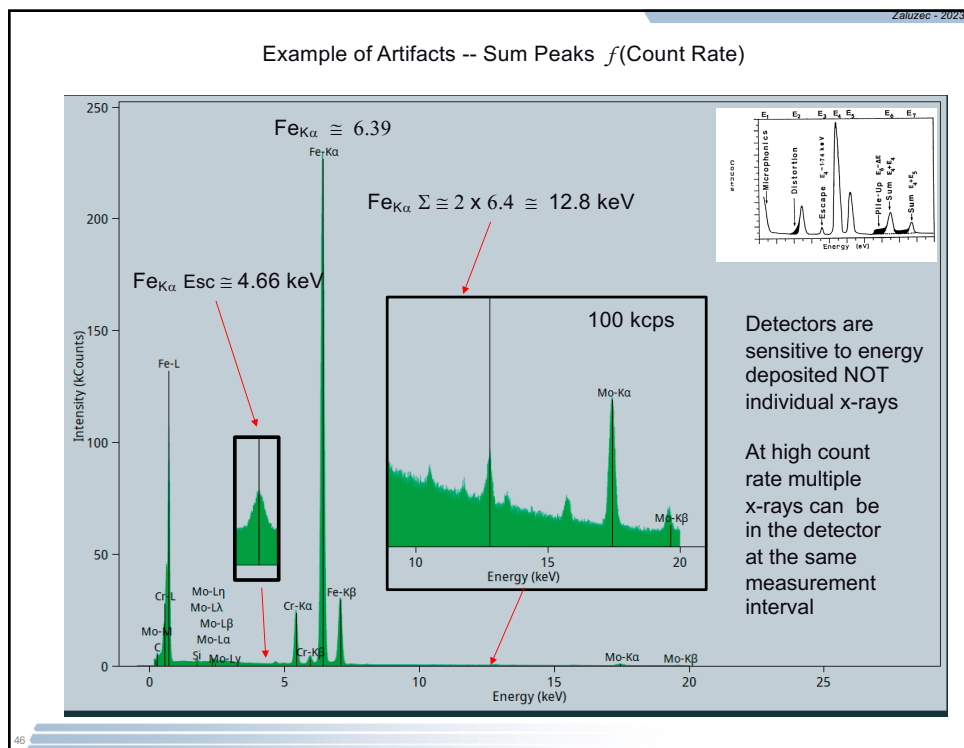


Most prominent at low energy Lines

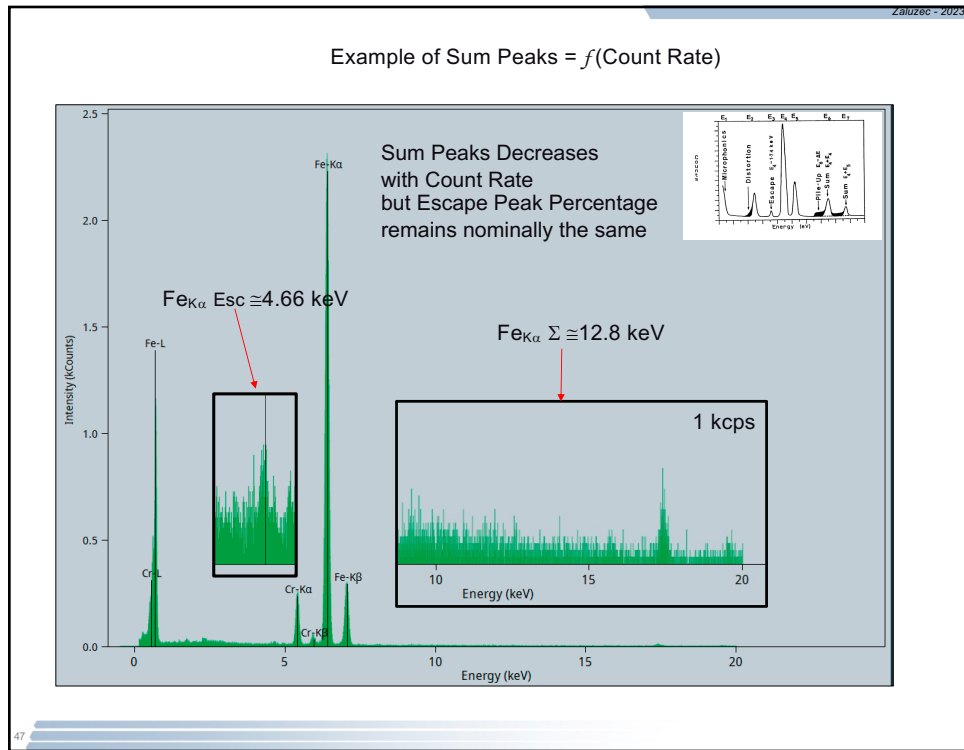
44



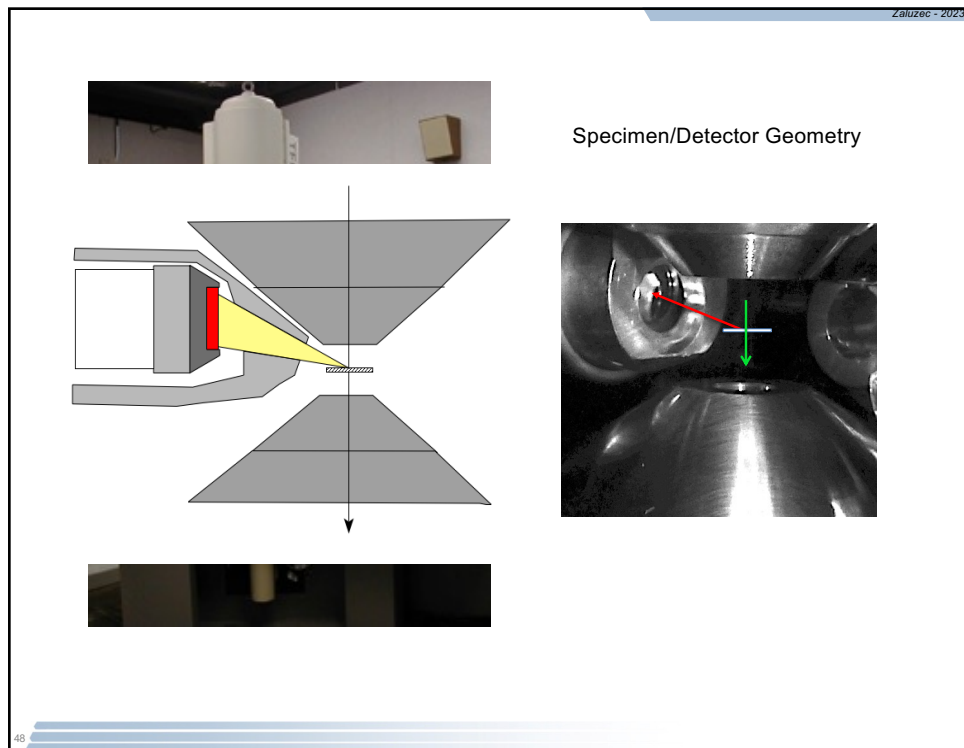
45



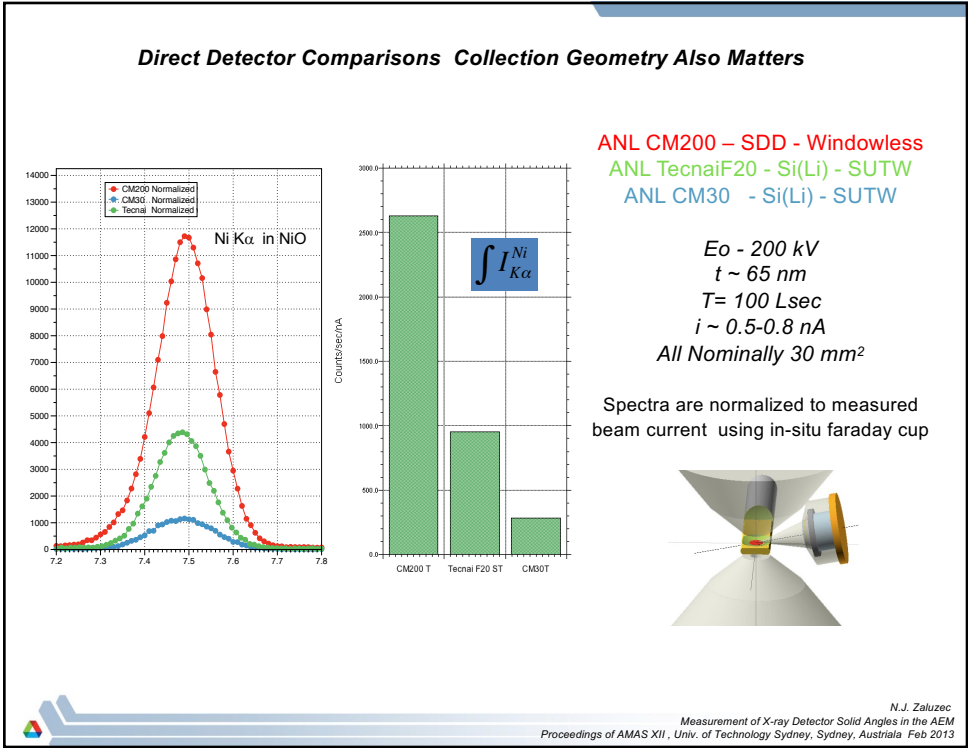
46



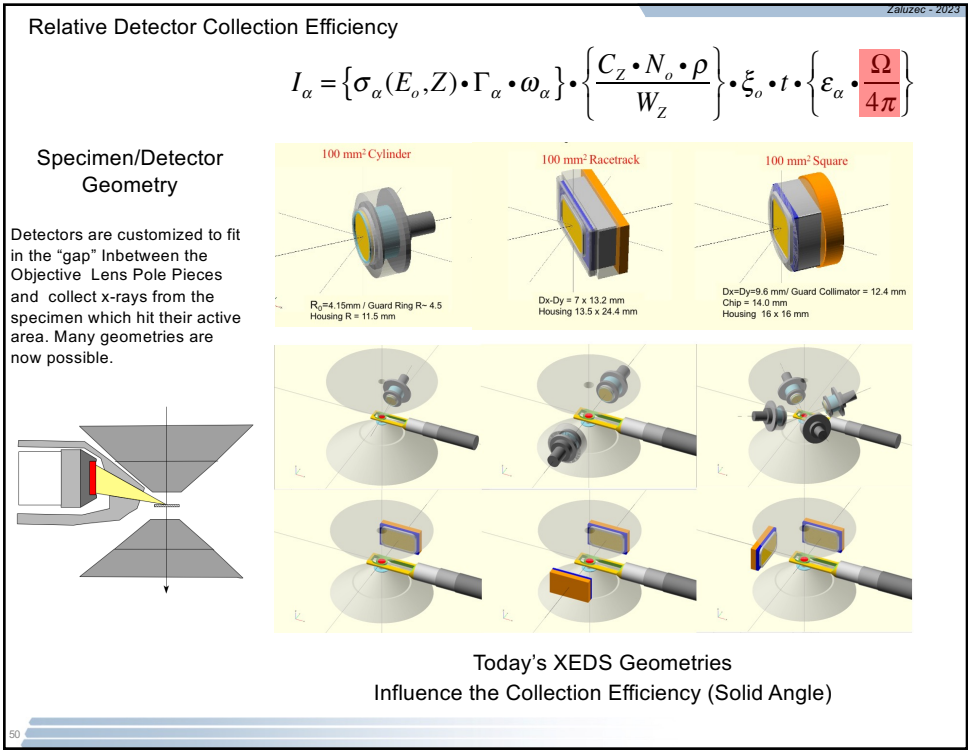
47



48



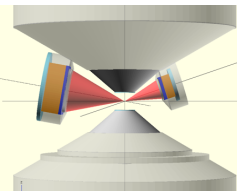
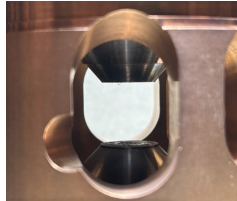
49



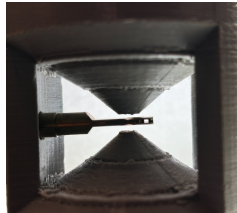
50

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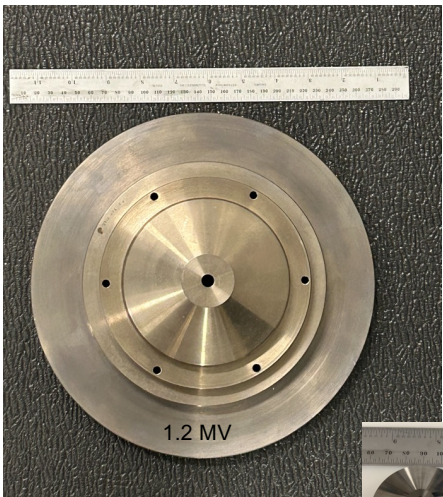
Pole Piece Configurations & Sizes

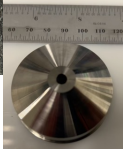
Large Gap
~ 8 - 10 mm



Typical Gap
~ 4-6 mm



1.2 MV



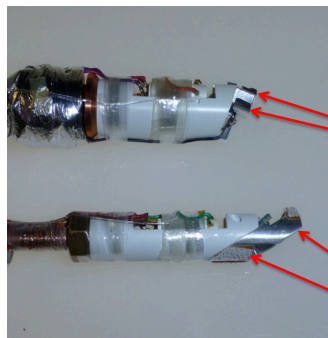
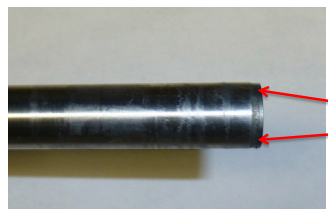
300 kV

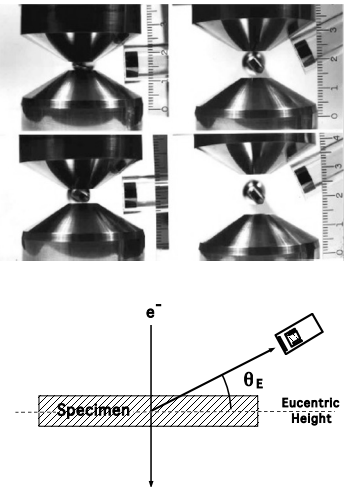
51

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Geometries Vary



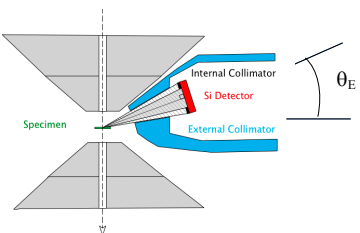
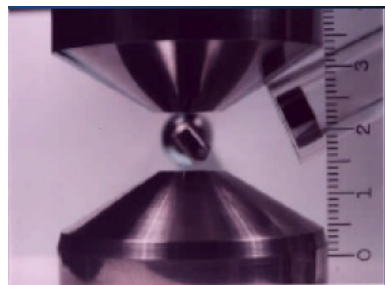
52

52

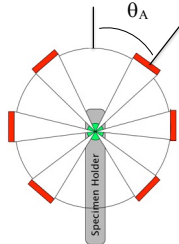
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Detector/Specimen Geometry

TEM

Designation	Elevation Angle θ_E	Azimuthal Angle θ_A
Low	0°	45°
	0°	90°
Intermediate	5 - 30°	90°, 45°
High	68-72°	0°

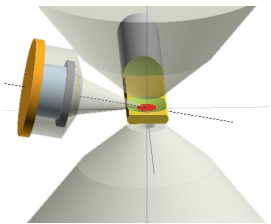


53

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Detector/Specimen Geometry – Collection Solid Angle

$$\Omega = \frac{S}{R^2} \neq \frac{A}{R^2}$$


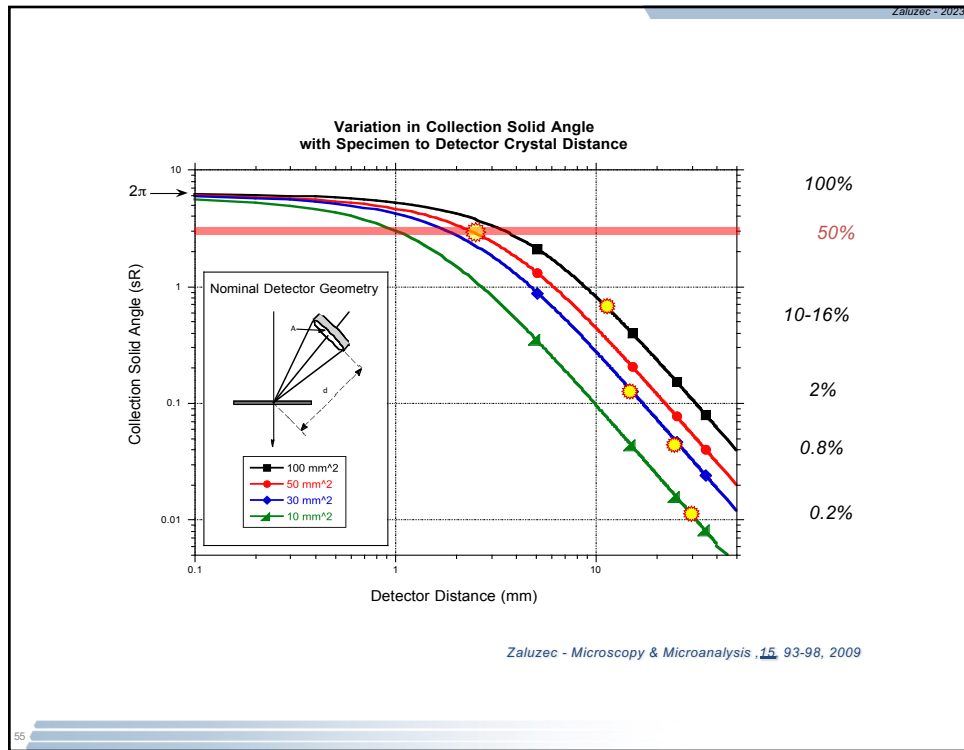
XEDS Tools
[Solid Angle Calculator](#)
 V-2014091607

Download M&M2014 Paper with calculation details
[Morse, Microanal., 30, 1318B \(1986\)](#)
[doi:10.1017/S153127610000956](#)

Circular Cross-section		
	Parameter	Value units
	Distance to Detector (d)	12 mm
	Detector Active Radius (r)	2.9 mm
	Detector Tilt Angle (theta)	15 degrees
	Fraction Obstructed (f)	0 0 <= f <= 1
	Nominal Active Area (A)	26.42 mm²
	Radial Detector Solid Angle (Omega)	0.176 sr
	Non-Radial Detector Solid Angle (Omega)	0.170 sr
	(Inaccurate)	
	Non-Radial Detector, Tilt Angle (theta) > 0	
Rectangular Cross-section		
	Parameter	Value units
	Distance to Detector (d)	12 mm
	Detector Active Height (h)	7 mm
	Detector Active Width (w)	13.2 mm
	Detector Tilt Angle (theta)	15 degrees
	Fraction Obstructed (f)	0 0 <= f <= 1
	Nominal Active Area (A)	92.40 mm²
	Radial Detector Solid Angle (Omega)	0.541 sr
	Non-Radial Detector Solid Angle (Omega)	0.524 sr
	(Inaccurate)	
	Non-Radial Detector, Tilt Angle (theta) > 0	
Annular Cross-section		
	Parameter	Value units
	Distance to Detector (d)	6 mm
	Outer Active Radius (r_o)	5 mm
	Inner Active Radius (r_i)	3 mm
	Fraction Obstructed (f)	0.1 0 <= f <= 1
	Nominal Active Area (A)	50.27 mm²
	Calculated Solid Angle (Omega)	0.714 sr
	(Inaccurate)	

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http://zaluzec.com/NJZTools
Zaluzec Microscopy & Microanalysis 2014

54



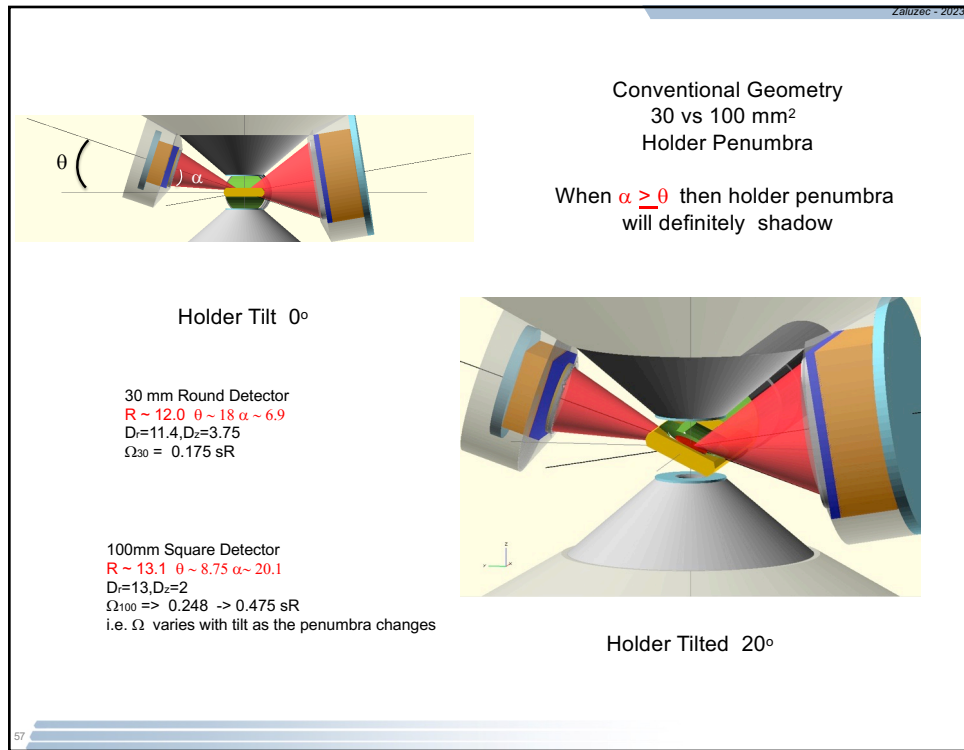
55

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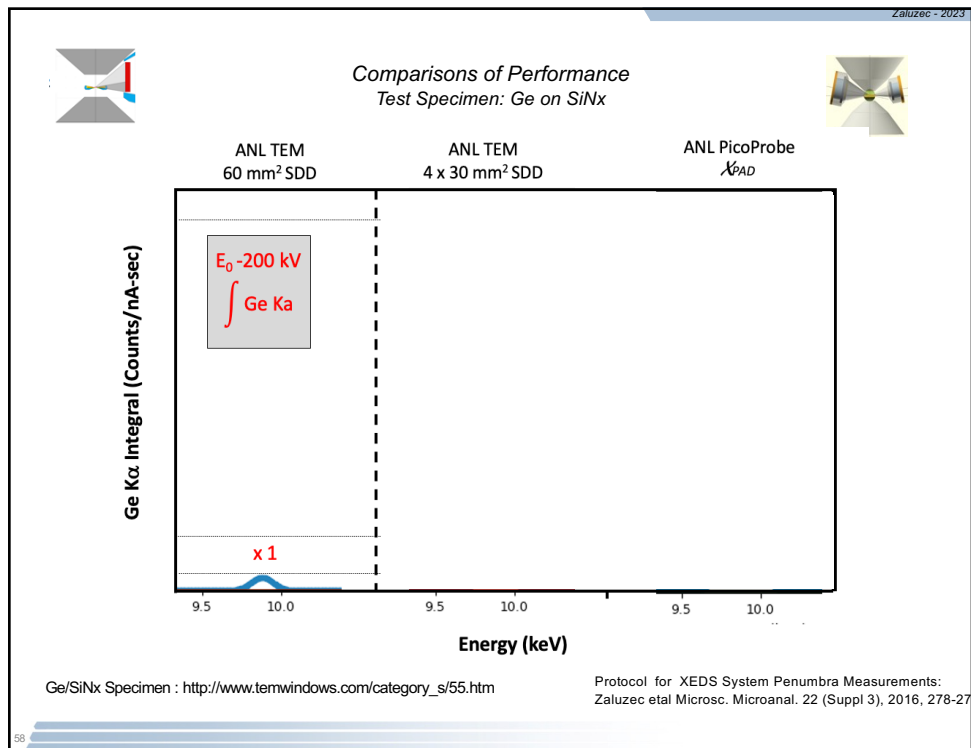
Shape	Geometry	Nominal Detector Area	Parameters	Calculated Solid Angle (sR)
Circular	Radial Windowless Eq. 2	30 mm ²	$A = 26.4 \text{ mm}^2$ $d = 12 \text{ mm}$ $\theta_E = 15$ $f_i = 0$	0.176
Circular	Non-Radial Tilted Windowless Eq. 11	30 mm ²	$A = 26.4 \text{ mm}^2$ $d = 12 \text{ mm}$ $\theta_E = 15$ $f_i = 0$	0.170
Circular	Non-Radial Tilted with Supported Window Eq. 11	30 mm ²	$A = 26.4 \text{ mm}^2$ $d = 12 \text{ mm}$ $\theta_E = 15$ $f_i = 0.2$	0.136
Circular	Non-Radial Windowless Eq. 11	60 mm ²	$A = 54.1 \text{ mm}^2$ $d = 19 \text{ mm}$ $\theta_E = 13.5$ $f_i = 0$	0.140
Circular	Non-Radial Windowless Eq. 11	100 mm ²	$A = 86.6 \text{ mm}^2$ $d = 20 \text{ mm}$ $\theta_E = 10$ $f_i = 0$	0.169
Rectangular	Radial Windowless Eqs. 4-6	100 mm ²	$A = 92 \text{ mm}^2$ $d = 12 \text{ mm}$ $\theta_E = 15$ $f_i = 0$	0.541
Rectangular	Non-Radial Tilted Windowless Eqs. 13-15	100 mm ²	$A = 92 \text{ mm}^2$ $d = 12 \text{ mm}$ $\theta_E = 15$ $f_i = 0$	0.529
Rectangular	Non-Radial Tilted with Supported Window Eqs. 13-15	100 mm ²	$A = 92 \text{ mm}^2$ $d = 12 \text{ mm}$ $\theta_E = 15$ $f_i = 0.2$	0.423

56

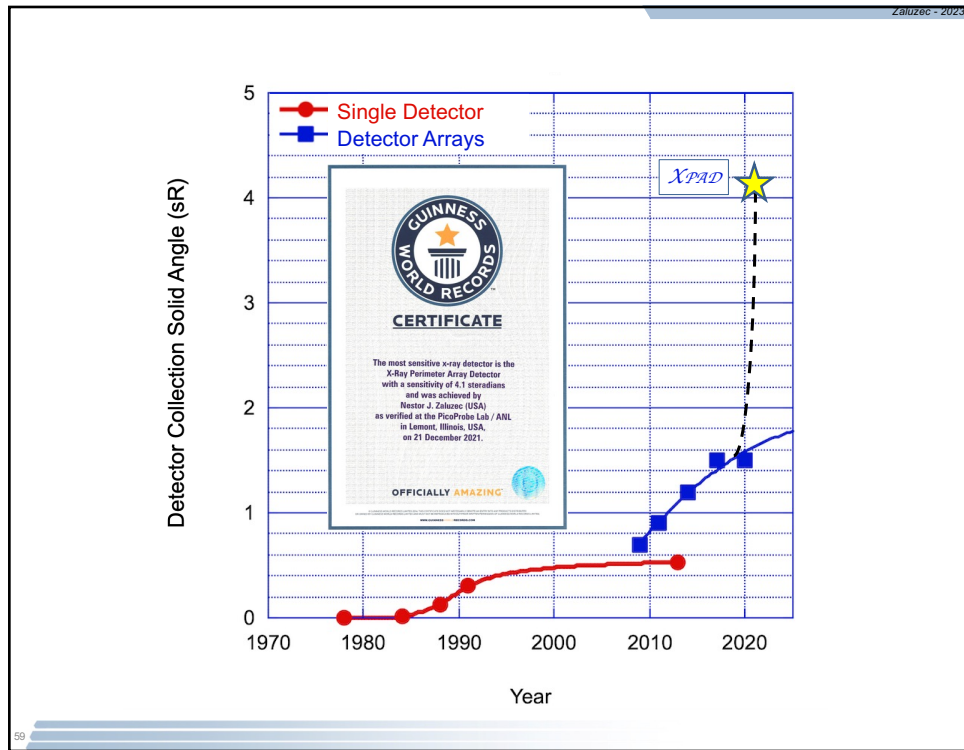
56



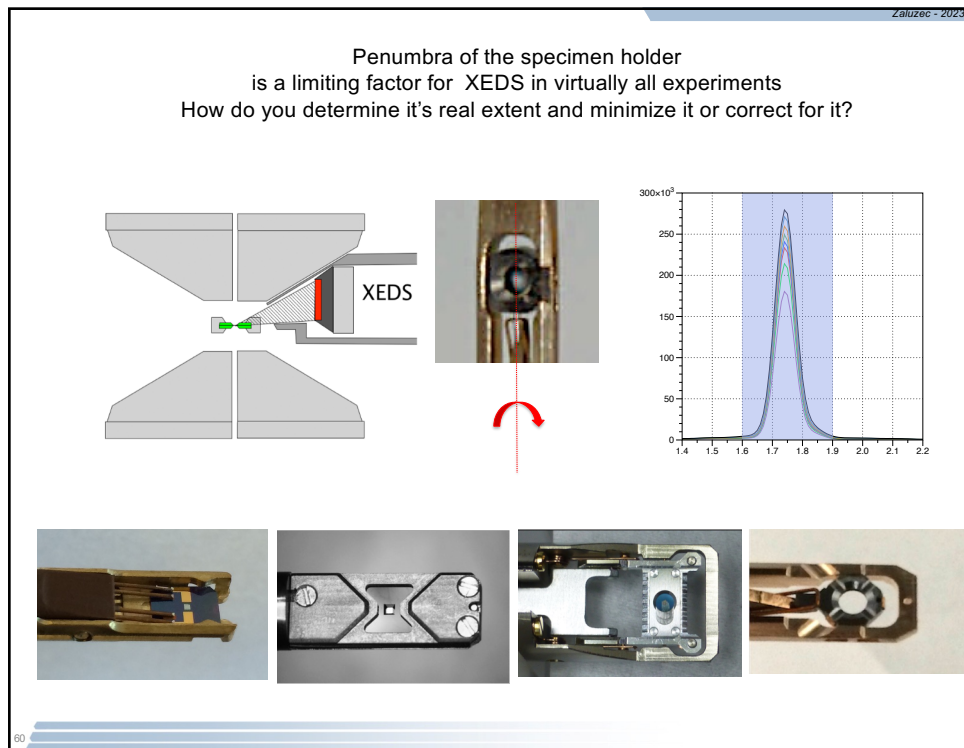
57



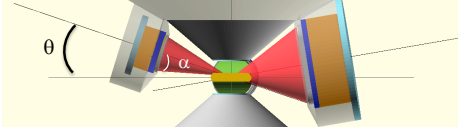
58



59



60



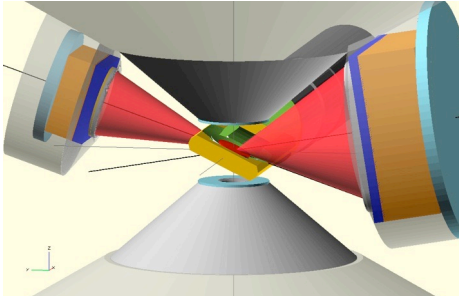
Holder Tilt 0°

30 mm Round Detector
 $R \sim 12.0$ $\theta \sim 18$ $\alpha \sim 6.9$
 $D_r=11.4, D_z=3.75$
 $\Omega_{30} = 0.175$ sR

100mm Square Detector
 $R \sim 13.1$ $\theta \sim 8.75$ $\alpha \sim 20.1$
 $D_r=13, D_z=2$
 $\Omega_{100} \Rightarrow 0.248 \rightarrow 0.475$ sR
 i.e. Ω varies with tilt as the penumbra changes

Conventional Geometry
 30 vs 100 mm²
 Holder Penumbra

When $\alpha \geq \theta$ then holder penumbra will definitely shadow

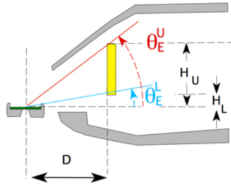


Holder Tilted 20°

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To estimate Penumbra of your Specimen Holder





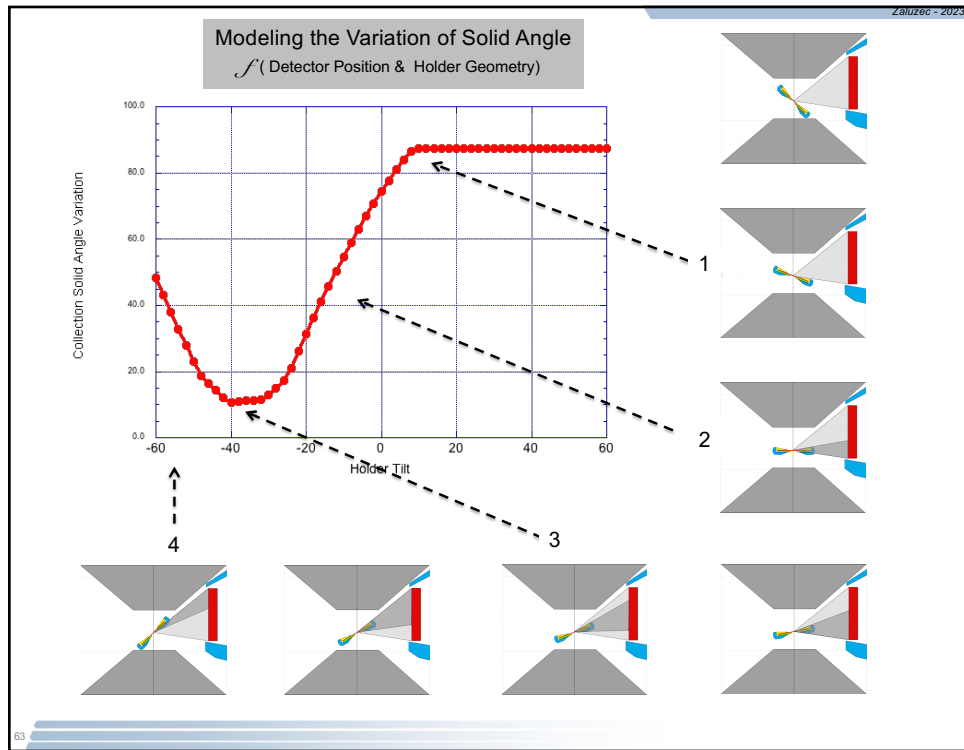
Calculation of Holder Tilt to Minimize Holder and Detector Penumbra

Parameter	Value	units
Holder Side Wall Half-Height (h_s)	0.5	mm
Holder Half-Width (w_s)	3.25	mm
Holder Penumbra Angle (θ_p)	8.75	degrees
Upper Detector Height (H_U)	6.3	mm
Lower Detector Height (H_L)	-1.7	mm
Radial Detector Distance (D)	11	mm
Detector Upper Elevation Angle (θ_E^U)	29.80	degrees
Detector Lower Elevation Angle (θ_E^L)	-8.78	degrees
Minimum Holder Tilt Angle ($\alpha = \theta_p - \theta_E^L$) to mitigate penumbra's of holder and/or detector	17.53	degrees

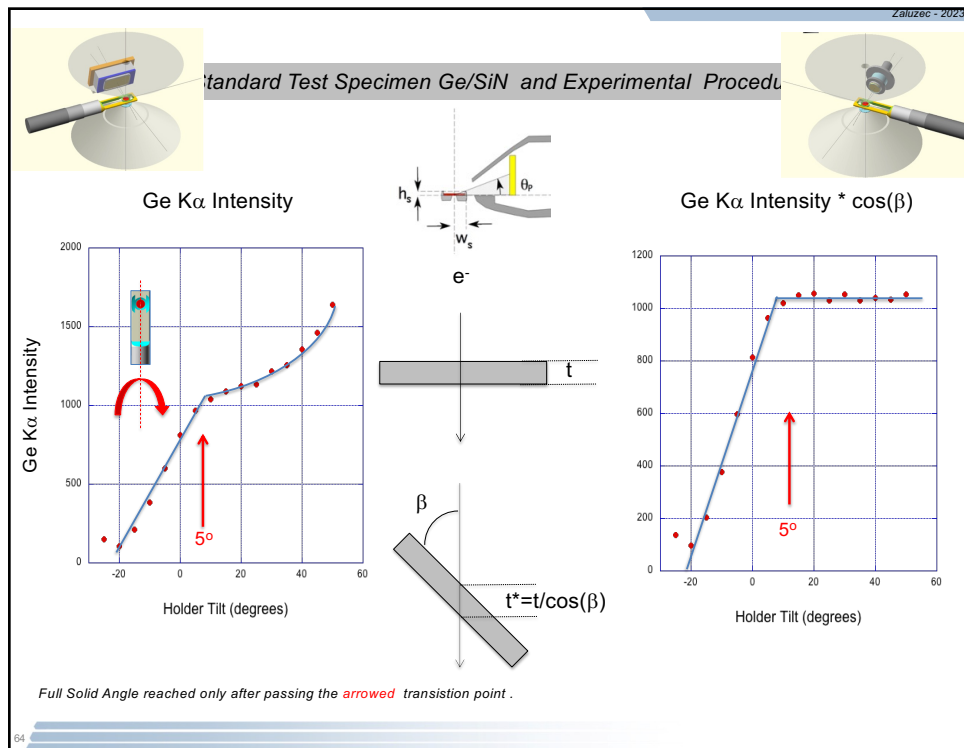
Note: some detector geometries can have H_L which is negative (i.e. below the specimen plane)

<http://tpm.amc.anl.gov/NJZTools/XEDSSolidAngle.html>

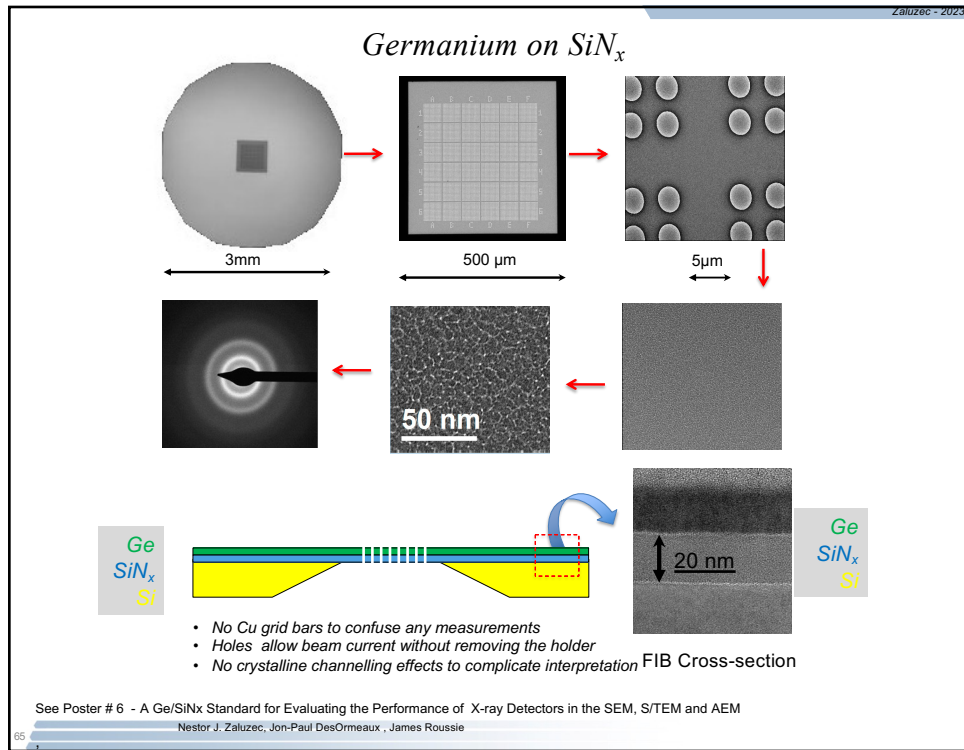
62



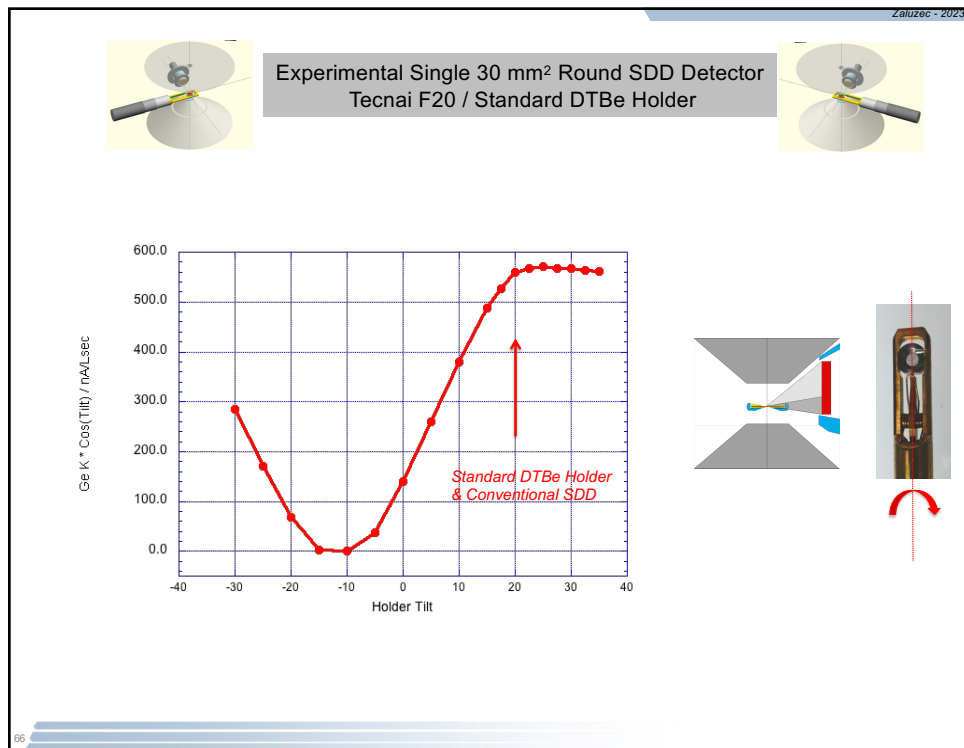
63



64

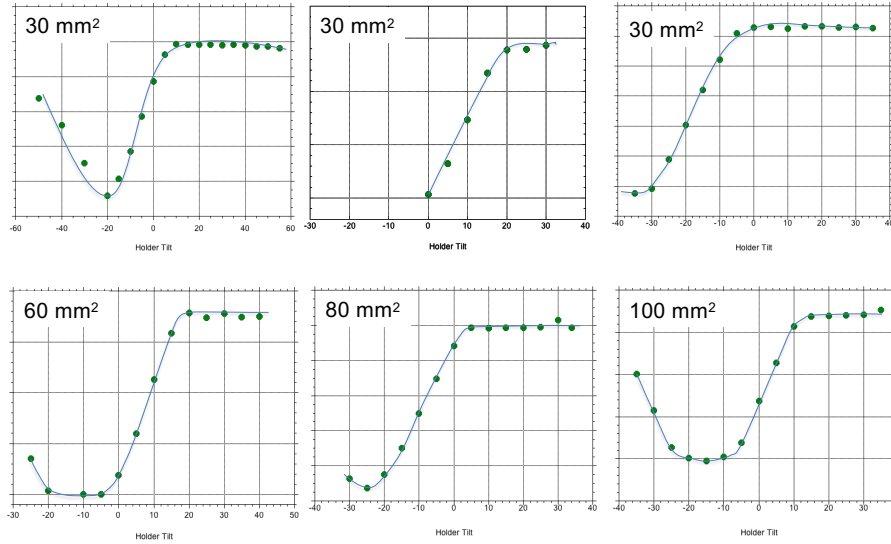


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Example 6 Different Instruments (2 Manufacturers) & Detectors (5 Manufacturers)
Notice Penumbra Differences

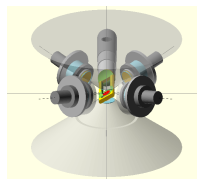
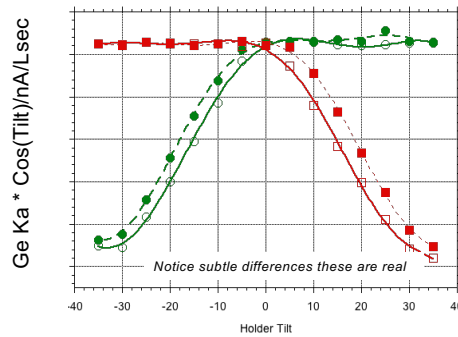


Ownership/Manufacturers Intentionally Obscured
Vertical Scales are NOT identical

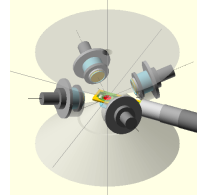
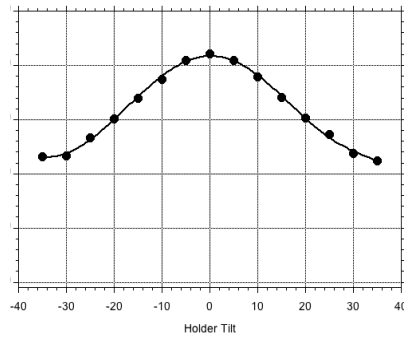
67

Detailed Example
Quad Super X Detector(s)

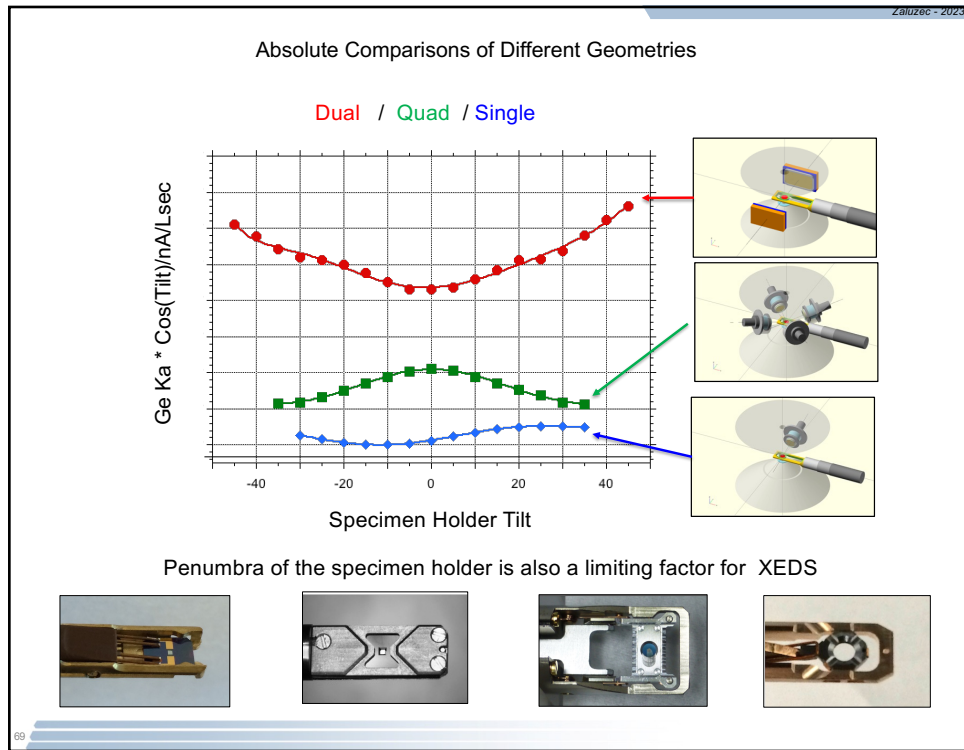
Four Individual Detectors



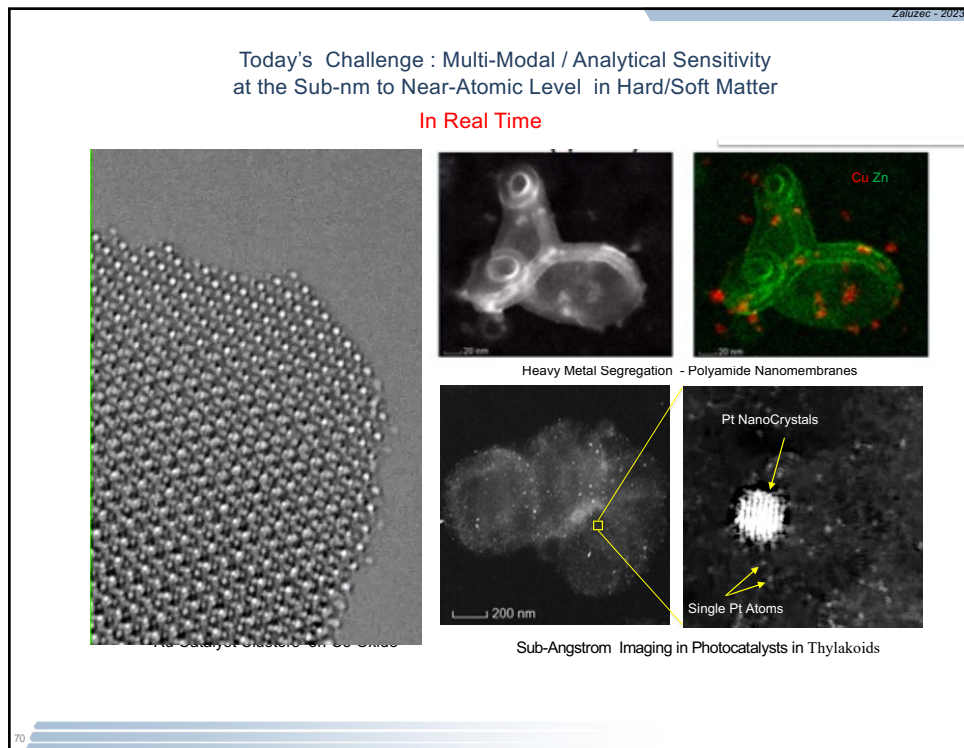
Detector Sum



68

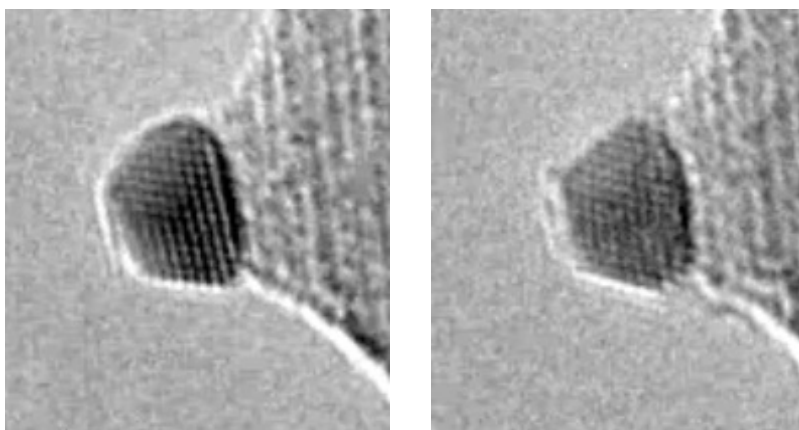


69



70

Heterogenous Catalysis “Atomic” Sensitivity at Site Specific Locations



How do we maximize analytical sensitivity?

71

71

Spectroscopic Detectability Limits

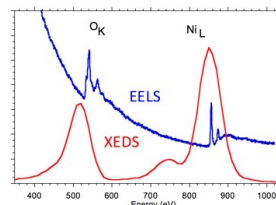
Signal in the Presence of Background

Detectability is related our ability to measure the change in signal that is statistically significant above random fluctuations

Student T-test Criterion

$$\Delta I > 2.33 * \sigma = 2.33 * \sqrt{I + B}$$

$$\frac{\Delta I}{I} > \frac{2.33}{\sqrt{\frac{I^2}{I + B}}}$$



if $B \ll I$ or $I \ll B$ or we can define the minimum detectable mass & mass fractional as:

$$MDM \sim \frac{2.33}{\sqrt{I}}$$

$$MMF \sim \frac{2.33}{\sqrt{I * \frac{I}{B}}}$$

*Notice the functional dependance on both I and I/B
This is not the traditional definition that has been used*

In the past only the I/B has been used as a measure to identify conditions for highest “sensitivity” today that is no longer appropriate because of the changes in our detector technologies.

Both cases you want to maximize I and minimize I/B

72

72

Detectability is Based on a Signal Measurement

$$I_x = f(Z, E_o, t, \eta_o, \tau, \varepsilon, \Omega, \theta \dots)$$

Minimum Detectable Mass

$$MDM \sim \frac{k}{I_x \cdot \eta_o \cdot \tau}$$

Minimum Mass Fraction

$$MMF \sim \frac{k}{\sqrt{I_x \cdot \left[\frac{I_x}{B_x} \right]} \cdot \eta_o \cdot \tau} =$$

k = Constant ... 2.33 (Student T-test)

I_x = Characteristic (Peak) Signal from X

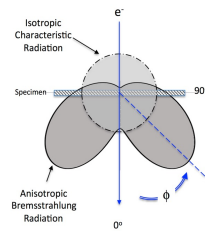
(I_x/B_x) = Peak to Background ratio for X

η_o = Incident electron flux

J_o = Incident electron current density

d = Probe diameter

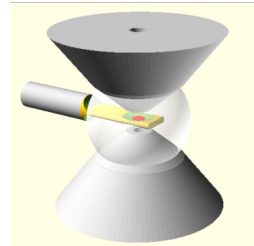
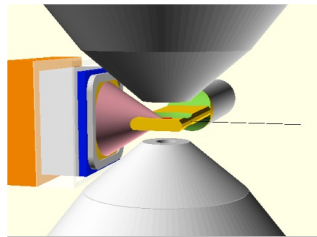
τ = Analysis time



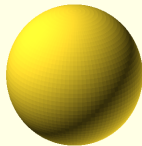
73

73

$$Intensity = \Gamma_{\text{scatteringprobability}} \cdot N_{\text{atoms}} \cdot \eta_{\text{electrons}} \cdot \tau_{\text{time}} \cdot \Omega_{\text{efficiency}}$$

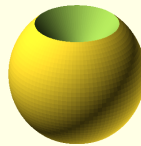


4π sR



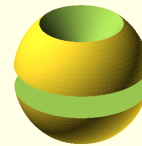
Theoretical Maximum

$\sim 2.5 \pi$ sR



Eliminate Pole Piece Volume

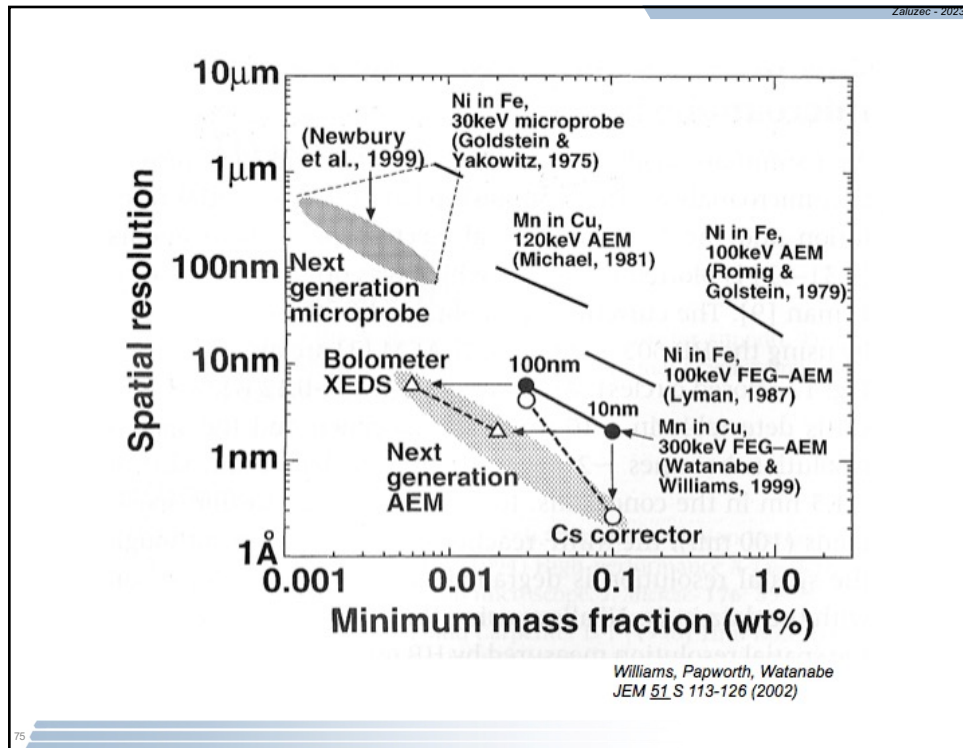
$> \pi^+$ sR



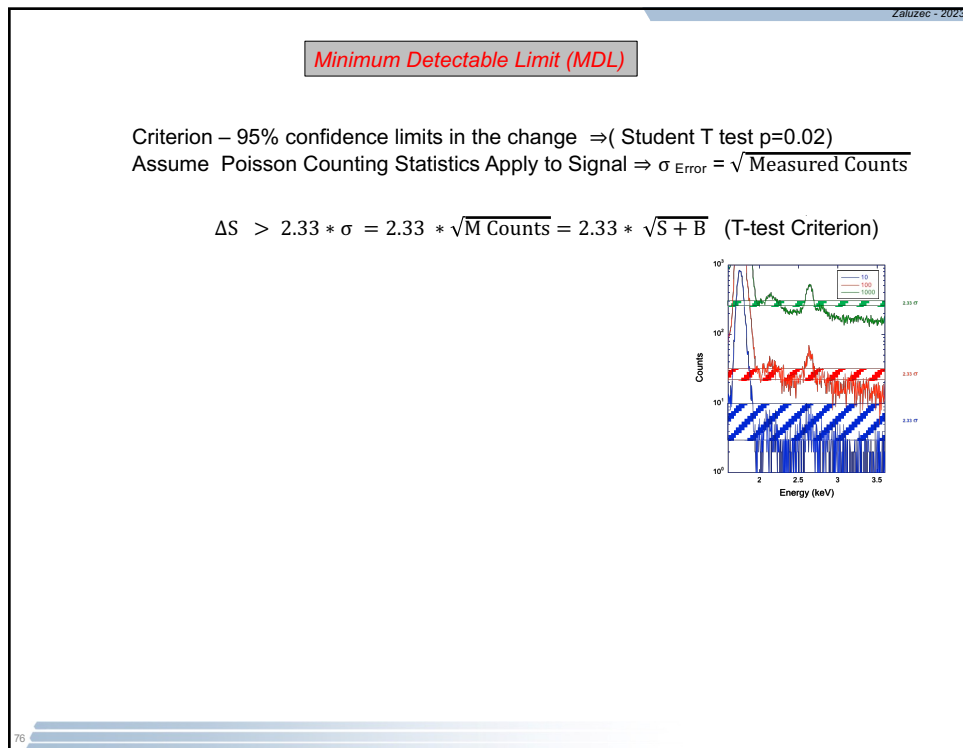
Eliminate Specimen Holder

74

74



75



76

Minimum Detectable Limit (MDL)

Criterion – 95% confidence limits in the change $\Rightarrow$ (Student T test $p=0.02$)
 Assume Poisson Counting Statistics Apply to Signal $\Rightarrow \sigma_{\text{Error}} = \sqrt{\text{Measured Counts}}$

$$\Delta S > 2.33 * \sigma = 2.33 * \sqrt{M \text{ Counts}} = 2.33 * \sqrt{S + B} \quad (\text{T-test Criterion})$$

$$\Delta S_A > 2.33 * \sqrt{S_A + B_A}$$

$$\frac{\Delta S_A}{S_A} > \frac{2.33}{\sqrt{\frac{S_A^2}{S_A + B_A}}}$$

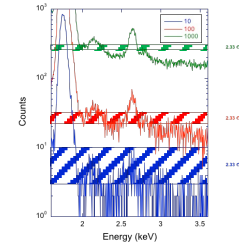
In the limit where $S_A \ll B_A$
(may not always be valid!)

$$\frac{\Delta S_A}{S_A} = \frac{2.33}{\sqrt{S_A \left(\frac{S_A}{B_A} \right)}}$$

$$S = P * \eta_o * \tau * \varepsilon * \Omega \Rightarrow \text{MDF/MDN/MDM} \sim \frac{2.33 k^*}{\sqrt{P * \left(\frac{P}{B} \right) * \eta_o * \tau * \varepsilon * \Omega}}$$

$P = N * Q * \omega * f$, η_o = beam current, τ = time, ε = detection efficiency Ω = collection efficiency
 k^* = term which depends upon measurement (Bulk $= \sqrt{1.2}$, Thin=1,)

To minimize $\Rightarrow$ must maximize $(P, P/B, \eta_o, \tau, \varepsilon, \Omega)$



77

Detectability is Based on a Signal Measurement

$$I_x = f(Z, E_o, t, \eta_o, \tau, \varepsilon, \Omega, \theta \dots)$$

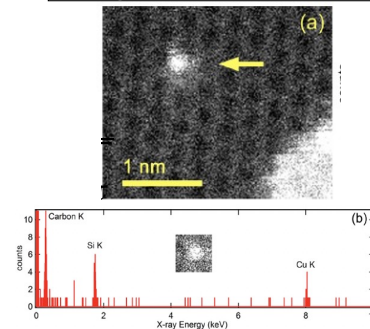
Minimum Detectable Mass

$$\text{MDM} \sim \frac{k}{I_x \cdot \eta_o \cdot \tau}$$

Minimum Mass Fraction

$$\text{MMF} \sim \frac{k}{\sqrt{I_x \cdot \left[\frac{I_x}{B_x} \right]} \cdot \eta_o \cdot \tau}$$

k = Constant ... (~ 3)
 I_x = Characteristic (Peak) Signal from X
 (I_x/B_x) = Peak to Background ratio for X
 η_o = Incident electron flux
 J_o = Incident electron current density
 d = Probe diameter
 τ = Analysis time



Lovejoy et al. APPLIED PHYSICS LETTERS 100, 154101 (2012)

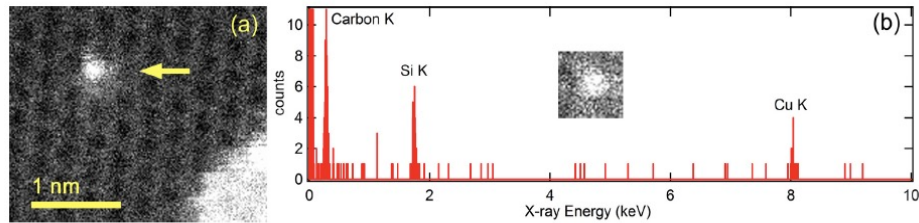
78

HyperSpectral Image Carbide Precipitates in Type 709 Steel



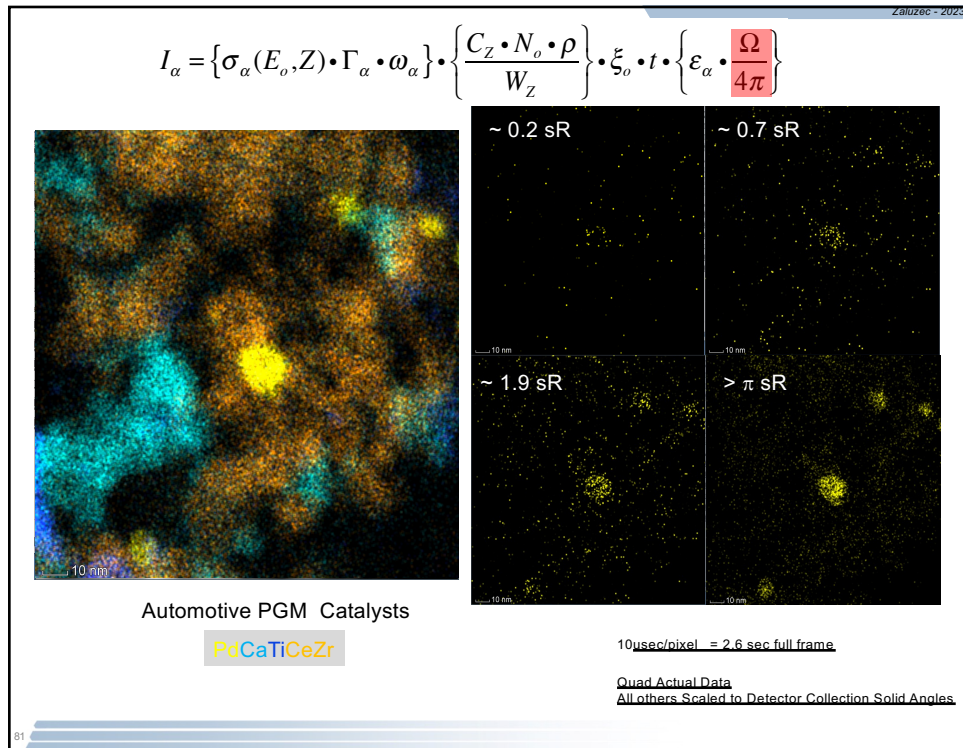
ElectroPolished Type 709 Steel
 ANL PicoProbe/XPAD
 300 kV, 400 pA @ 40 kX
2K x 2K @ 13.7 ms/pixel
 Conventional background subtracted
 0.7 pixel Gaussian Blur to minimize noise

79

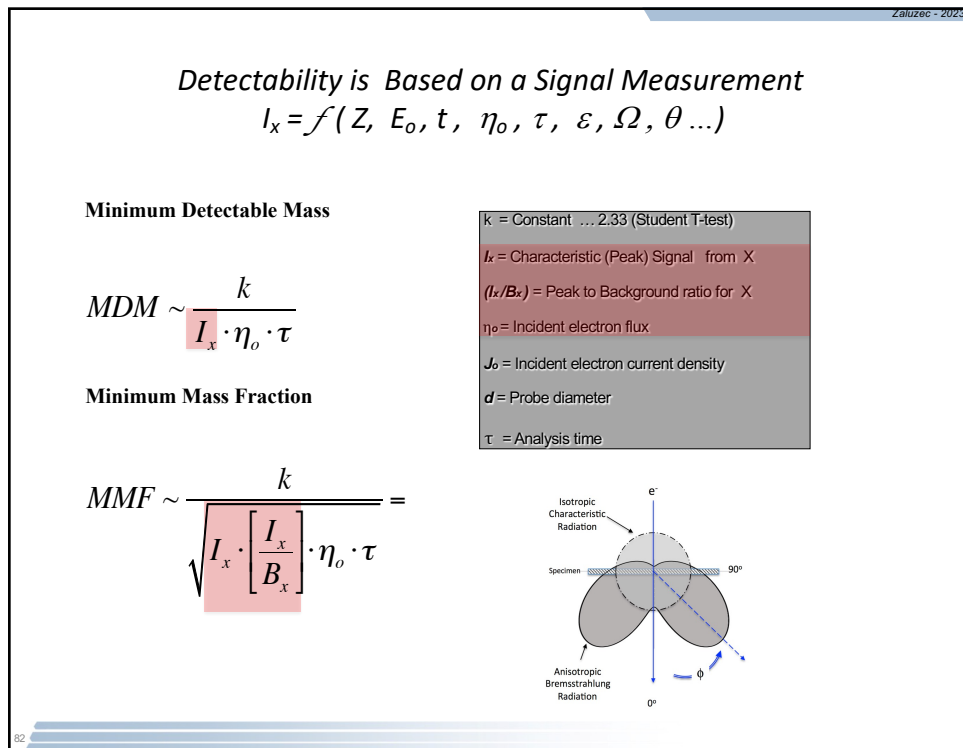


Lovejoy et al. APPLIED PHYSICS LETTERS 100, 154101
 (2012)

80



81



82

Detectability Limits

Minimum Detectable Mass

$$MDM \sim \frac{k}{I_x \cdot \eta_o \cdot \tau}$$

Minimum Mass Fraction

$$MMF \sim \frac{k}{\sqrt{I_x \cdot \left[\frac{I_x}{B_x} \right]} \cdot \eta_o \cdot \tau}$$

k = Constant ...

I_x = Characteristic (Peak) Signal from X

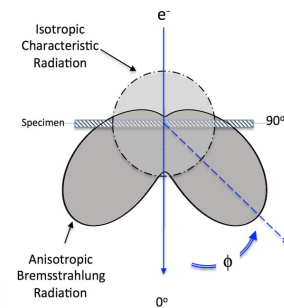
(I_x/B_x) = Peak to Background ratio for X

η_o = Incident electron flux

J_o = Incident electron current density

d = Probe diameter

τ = Analysis time



83

Characteristic X-ray Emission from a "thin film"

$$I_\alpha = \left\{ \sigma_\alpha(E_o, Z) \cdot \Gamma_\alpha \cdot \omega_\alpha \right\} \cdot \left\{ \frac{C_Z \cdot N_o \cdot \rho}{W_Z} \right\} \cdot \xi_o \cdot t \cdot \left\{ \varepsilon_\alpha \cdot \frac{\Omega}{4\pi} \right\}$$

I_α = measured x-ray intensity (counts) per unit area,

$\sigma_\alpha(E_o, Z)$ = α^{th} -shell ionization cross section

E_o = electrons of incident energy (eV),

ω_α = α^{th} -shell fluorescence yield,

Γ_α = α^{th} -shell radiative partition function,

W_Z and C_Z the atomic weight the composition

t = thickness

Z = atomic number

N_o = Avogadro's number,

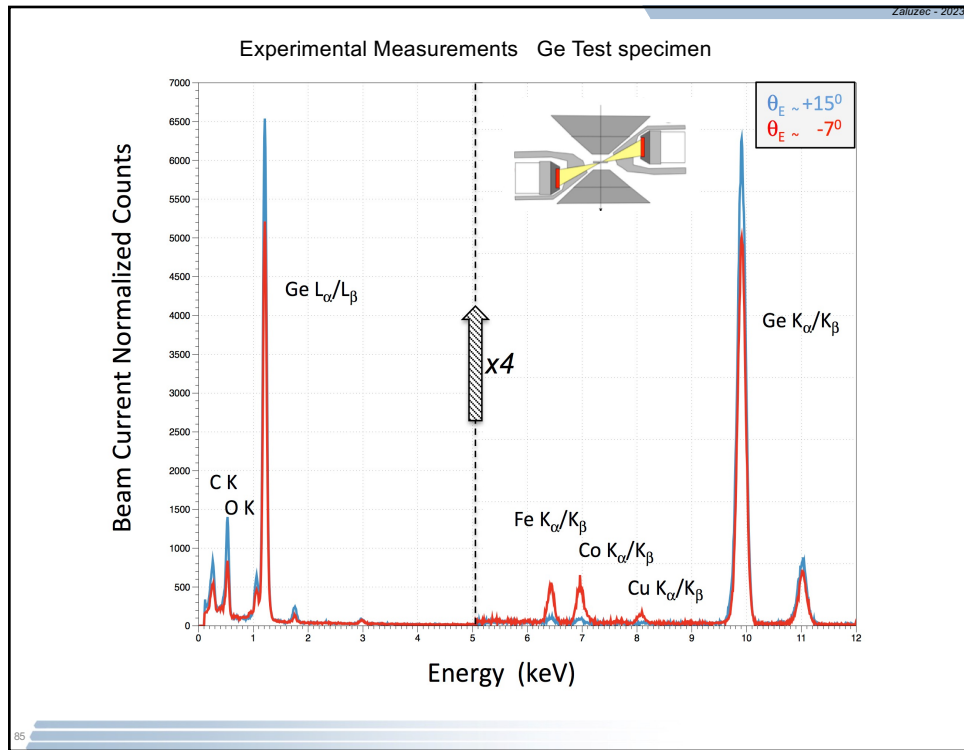
ρ = local specimen density,

$\xi_o = \eta_o \cdot t$ the incident electron flux,

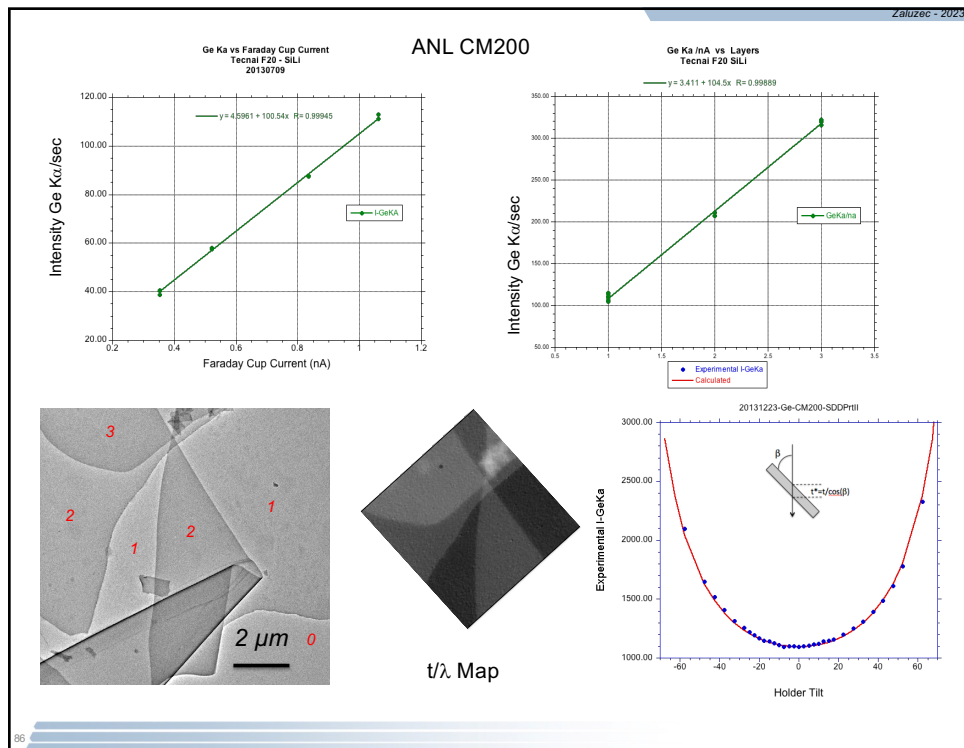
ε_α = the detector efficiency and

Ω_α = the detector collection solid angle.

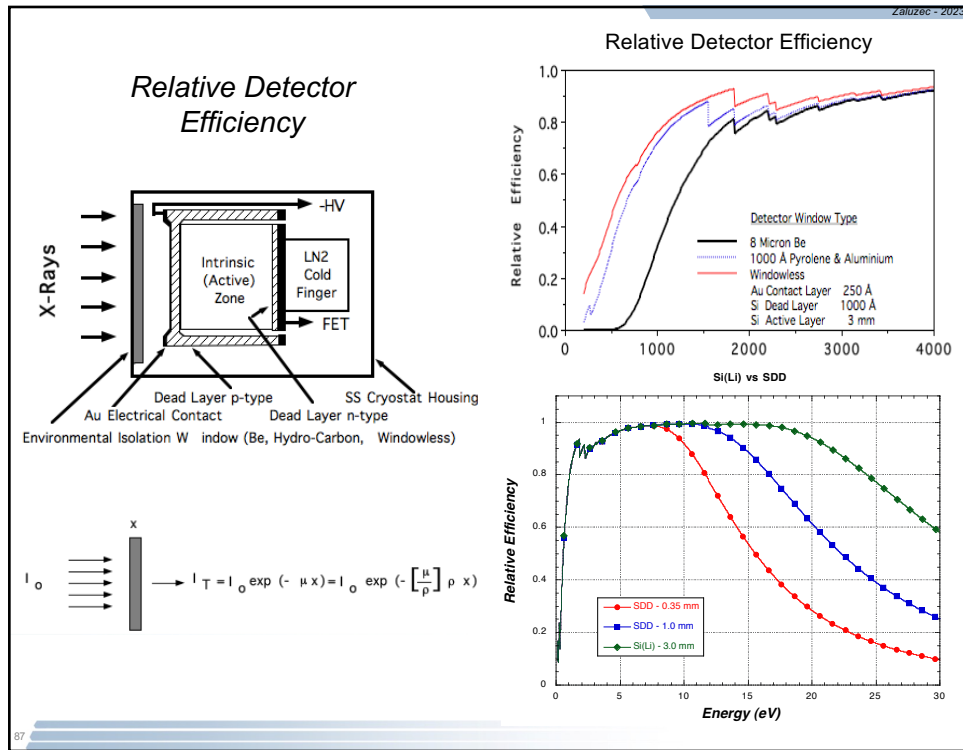
84



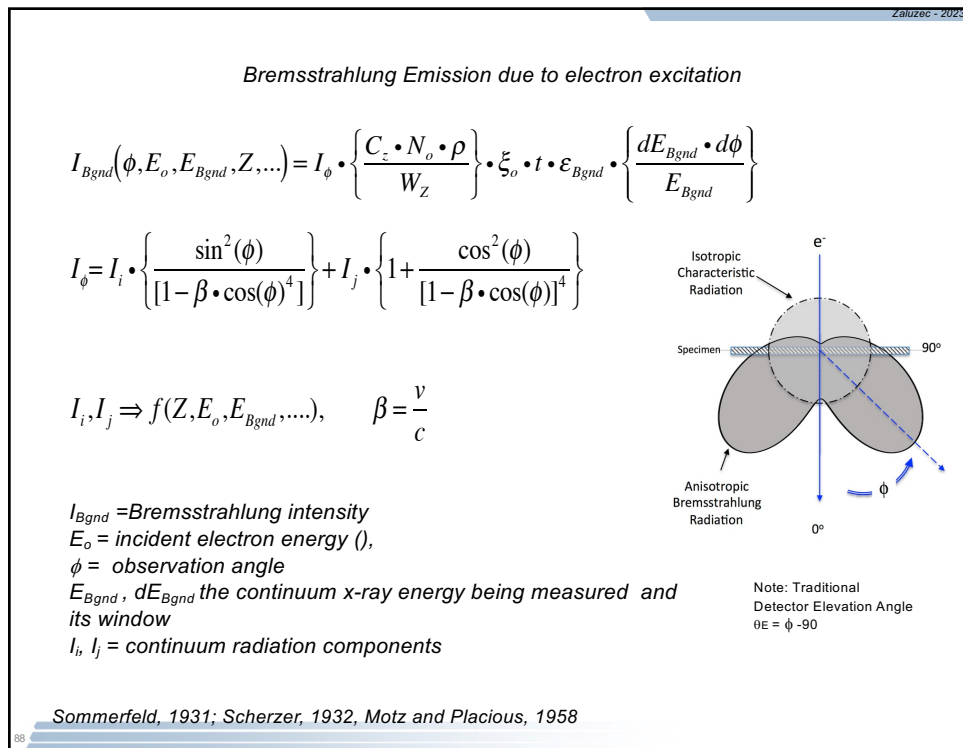
85



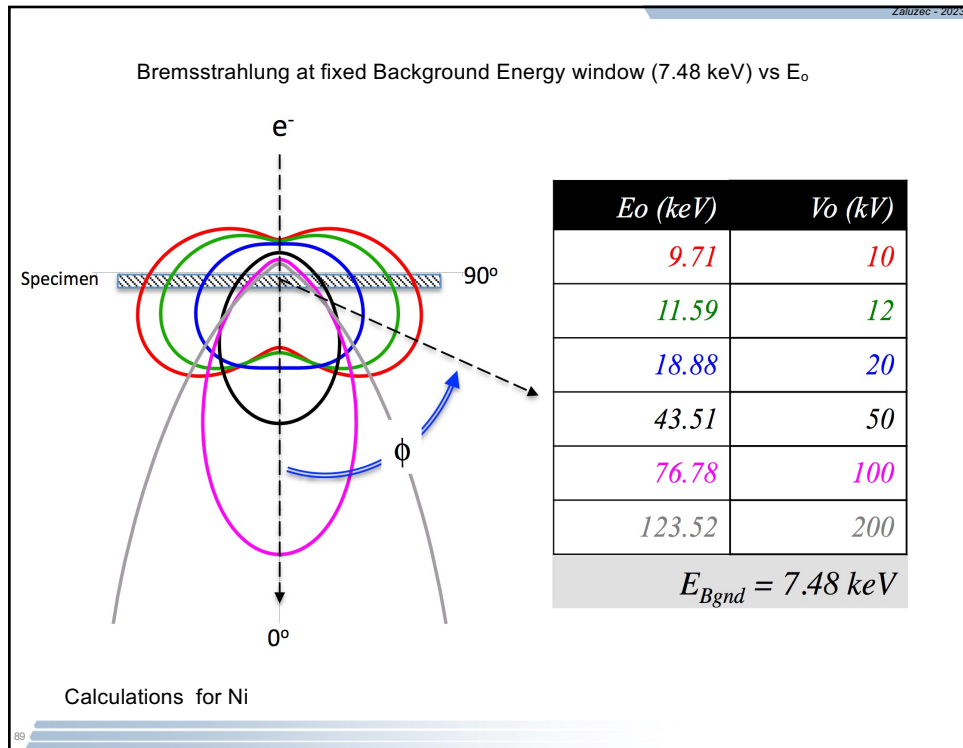
86



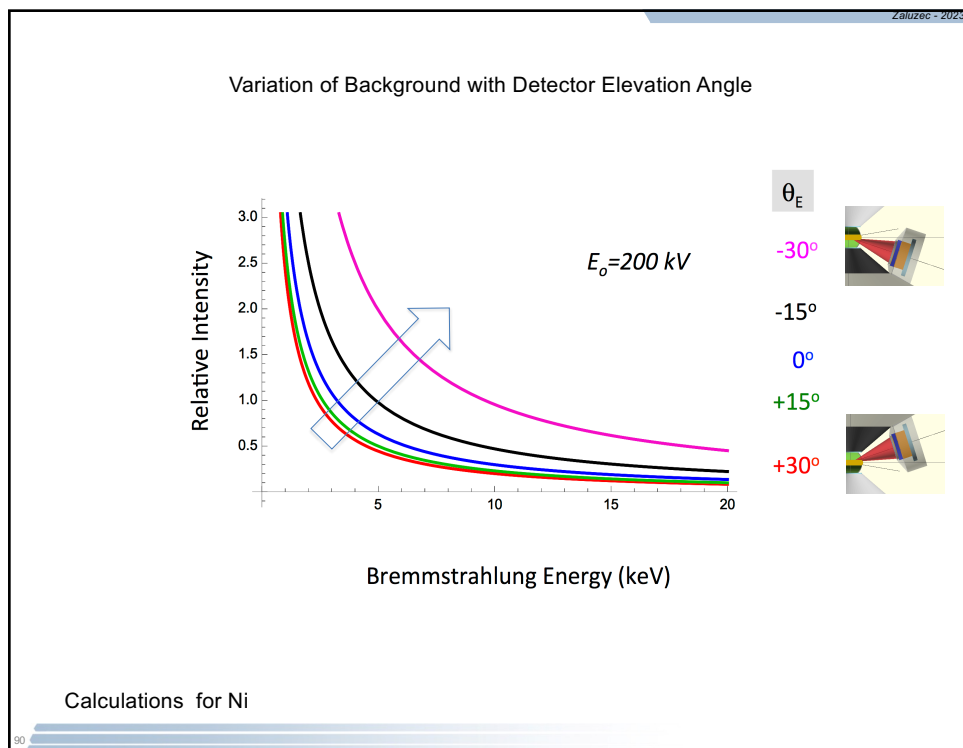
87



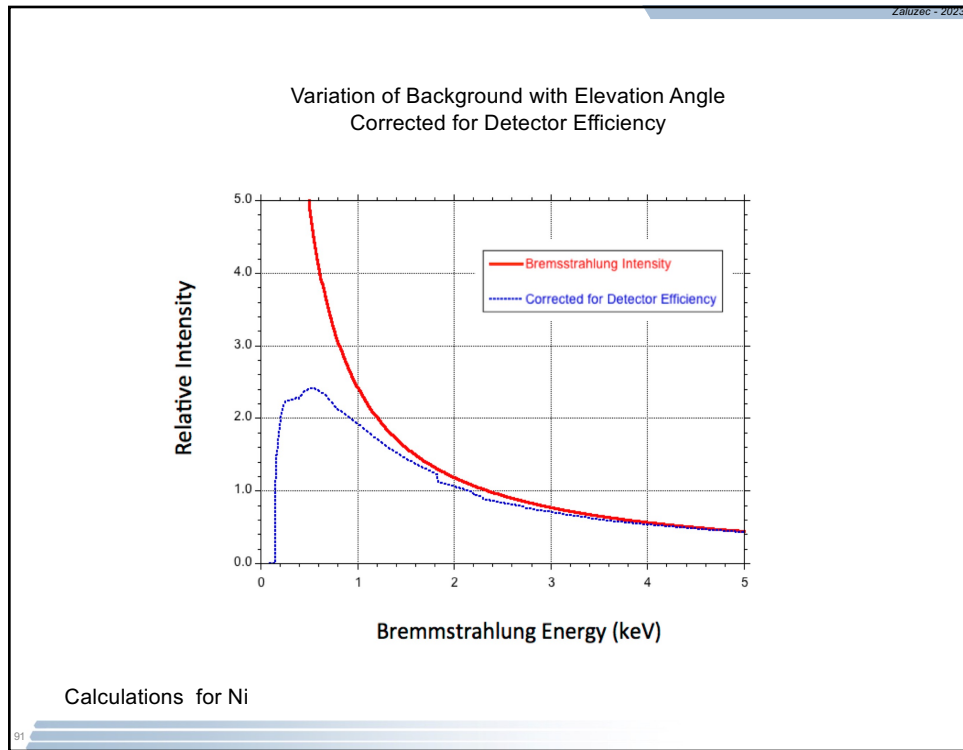
88



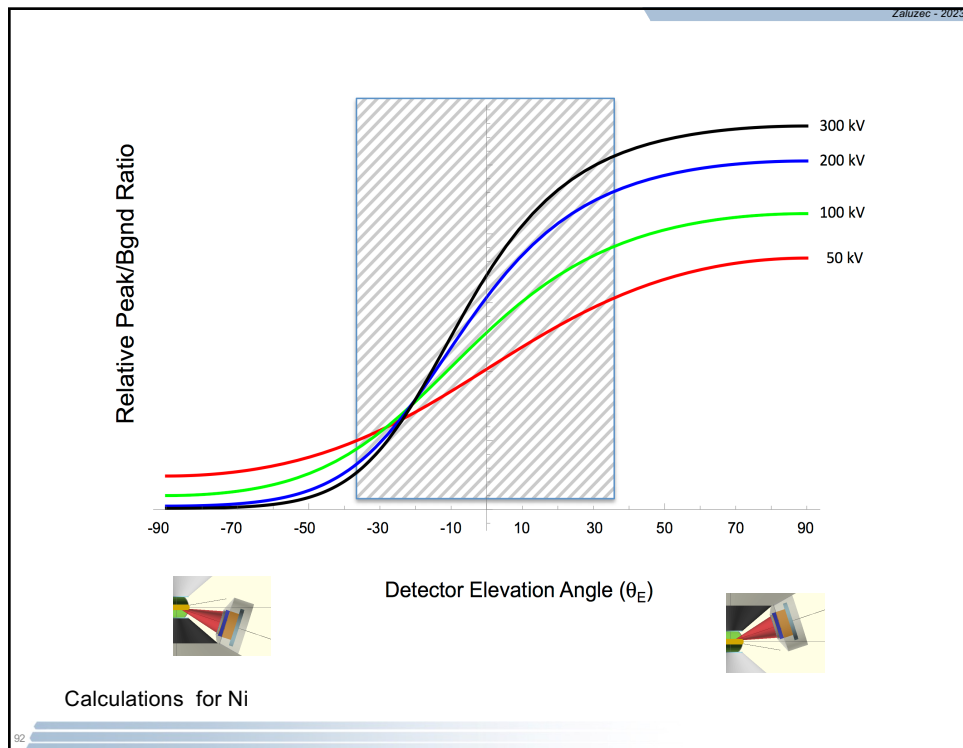
89



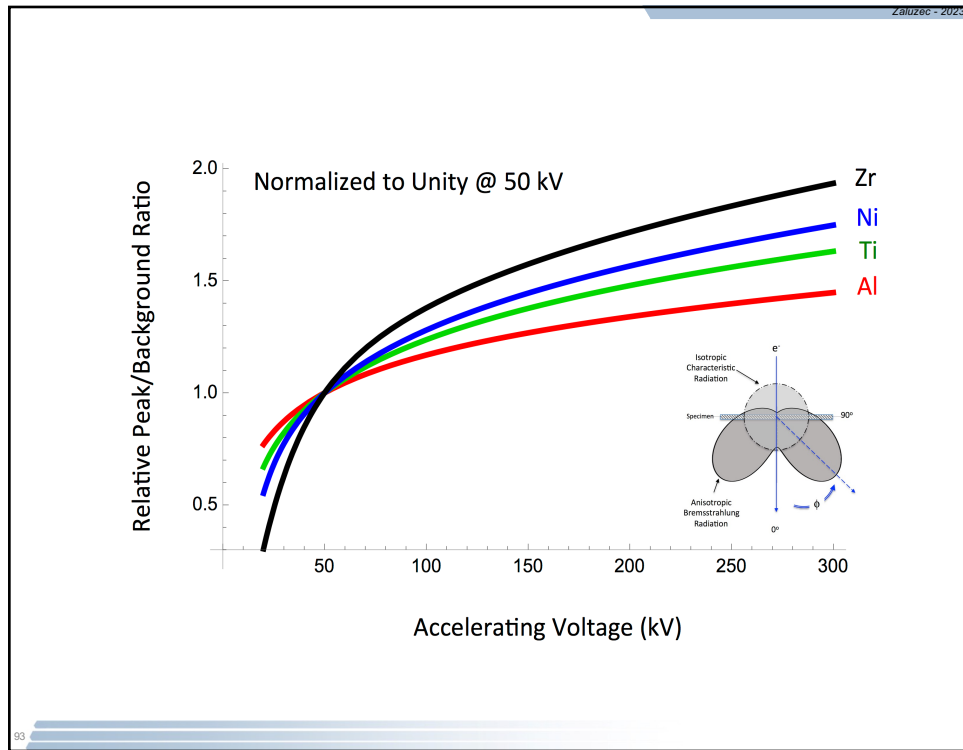
90



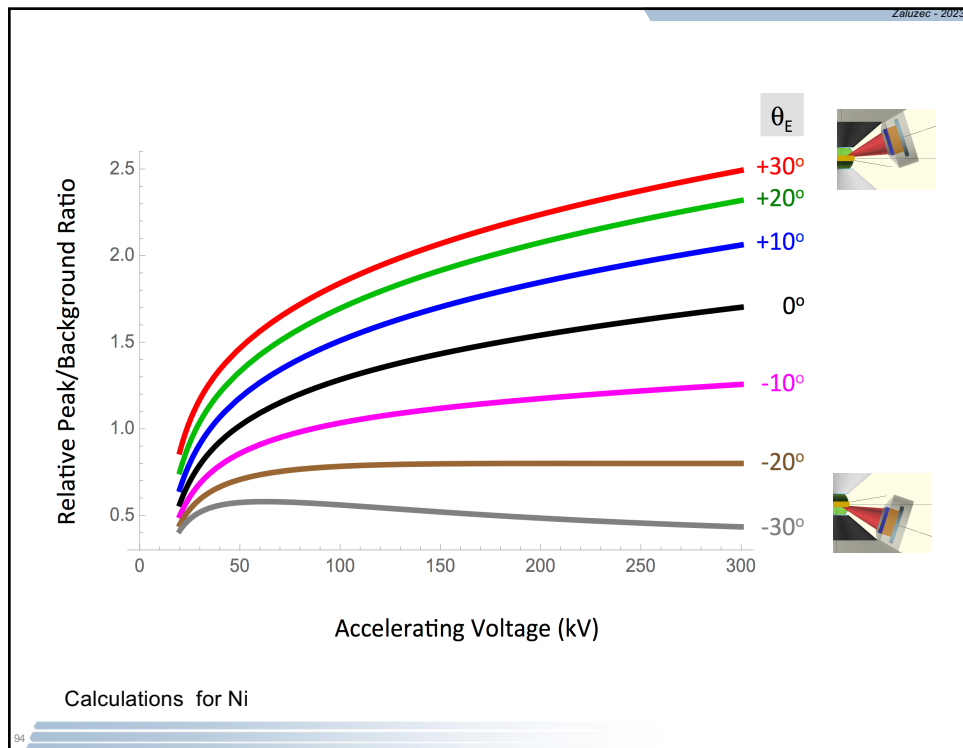
91



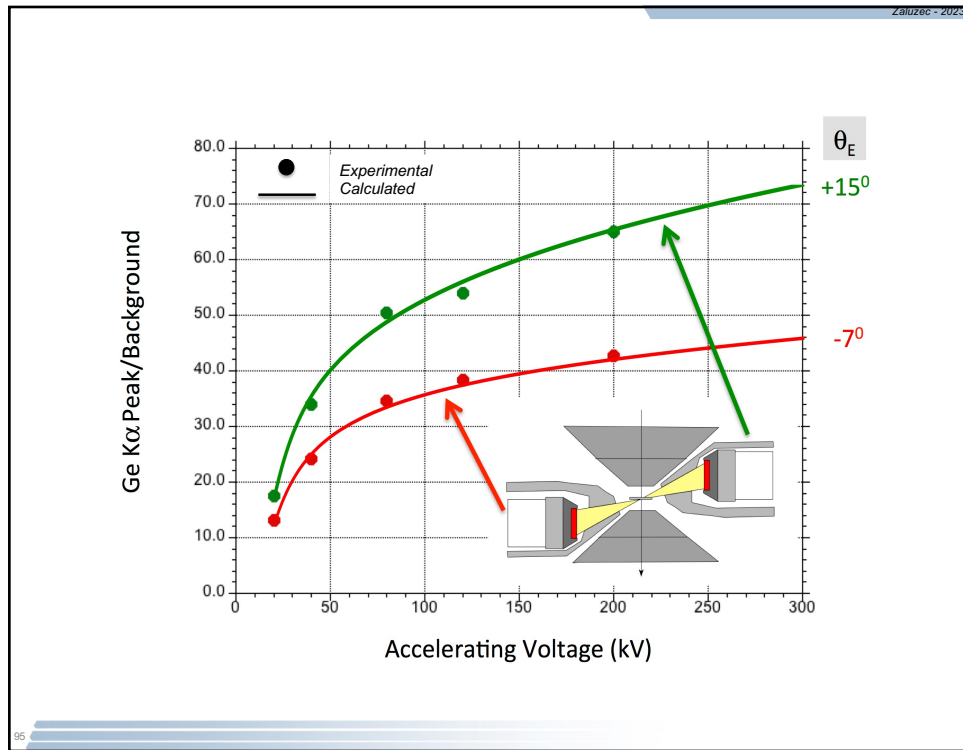
92



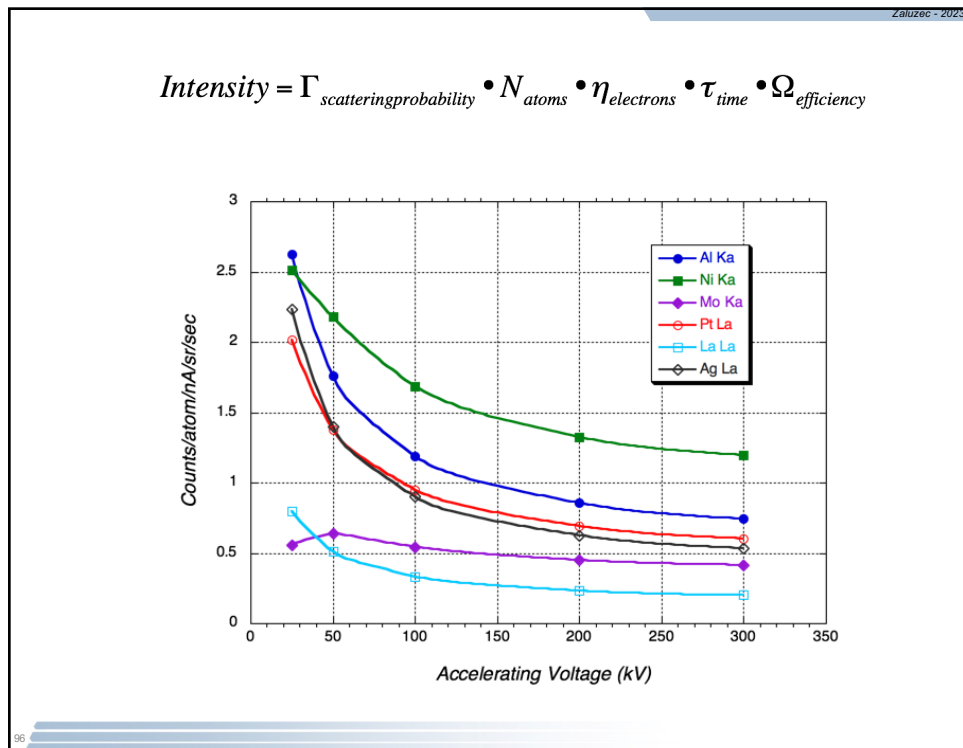
93



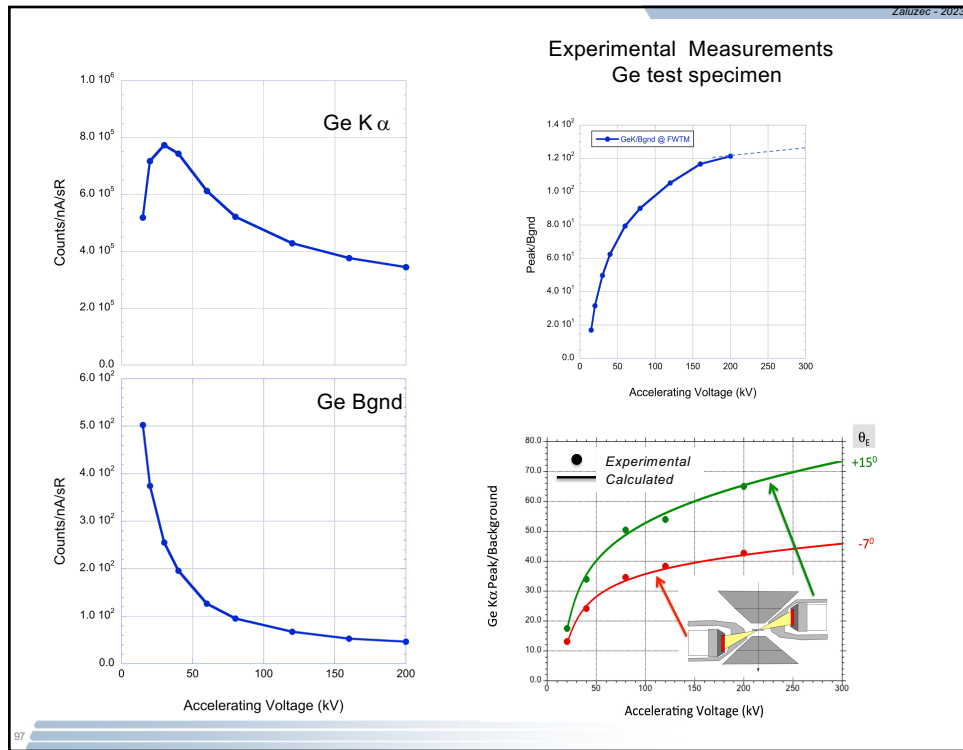
94



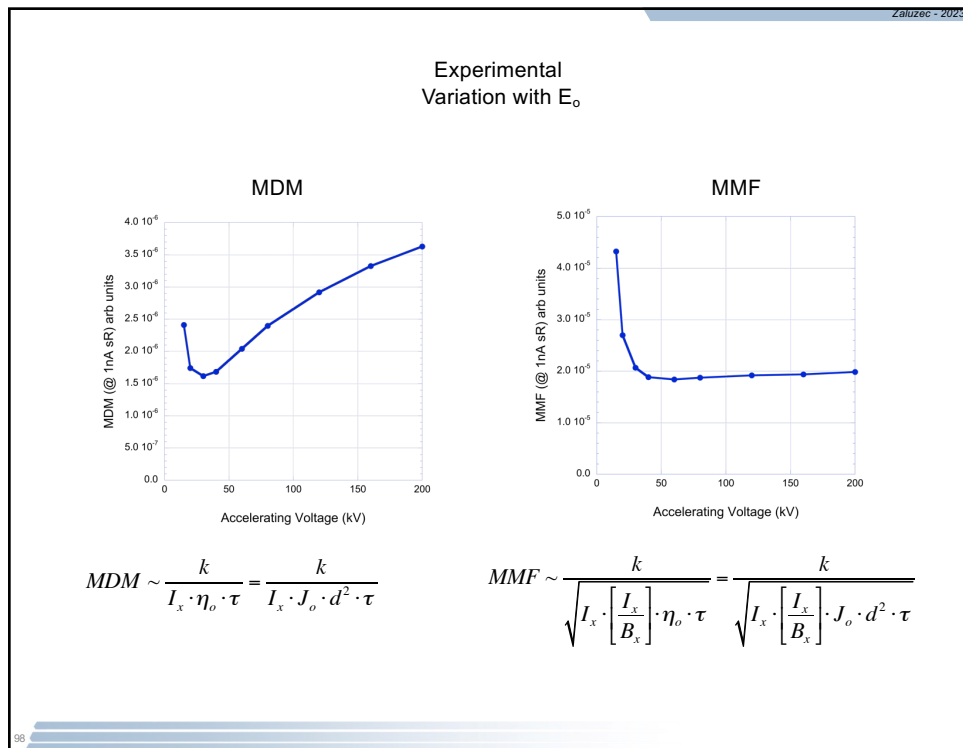
95



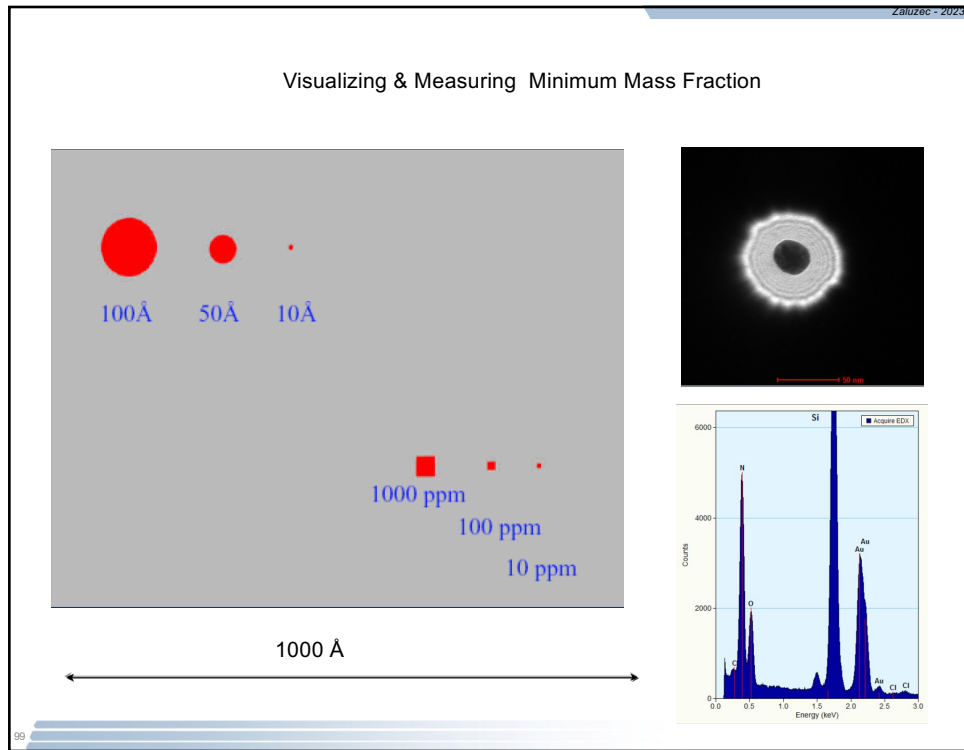
96



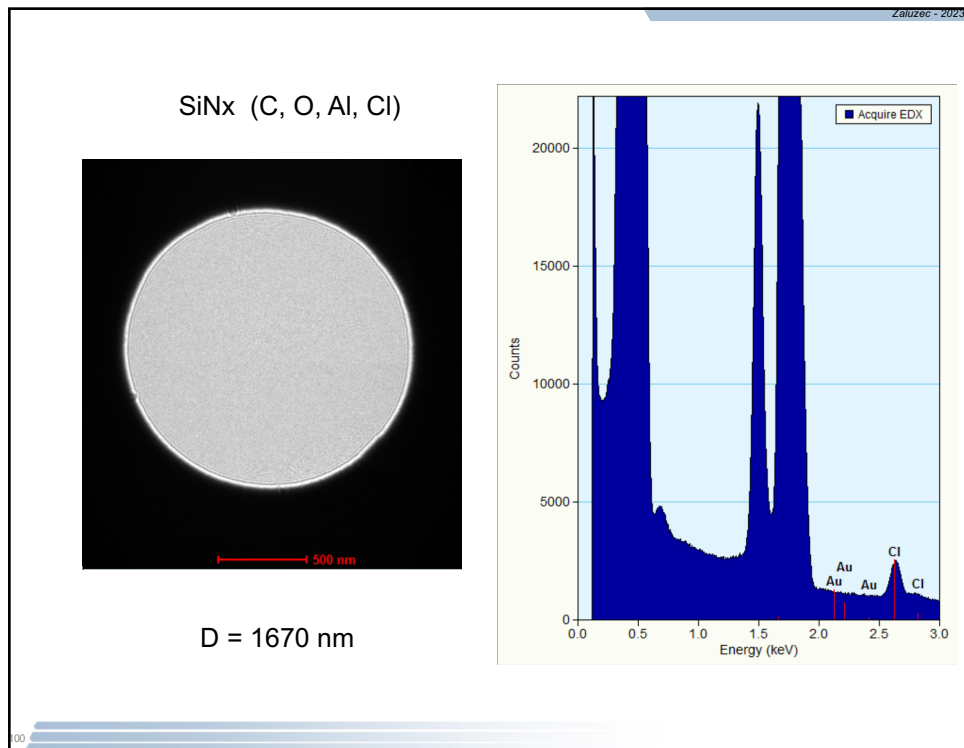
97



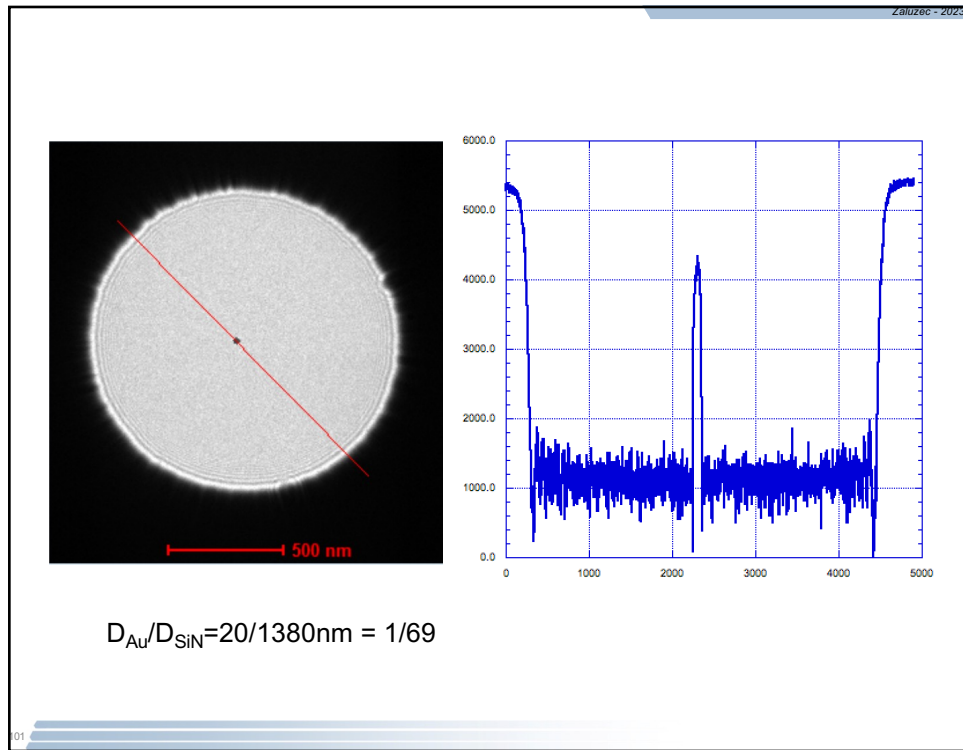
98



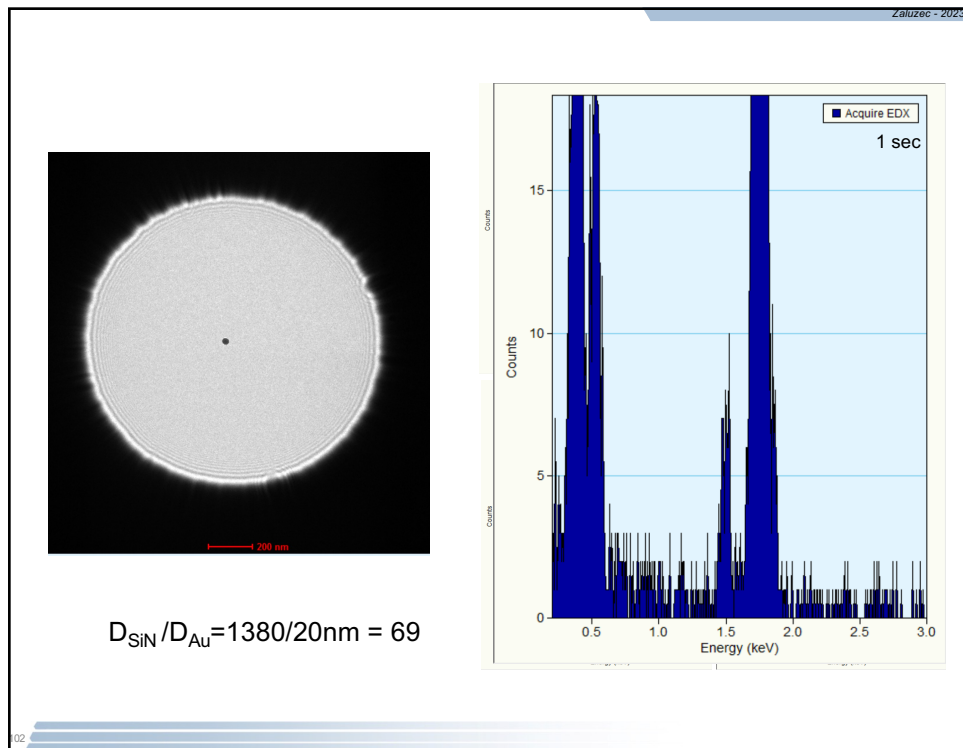
99



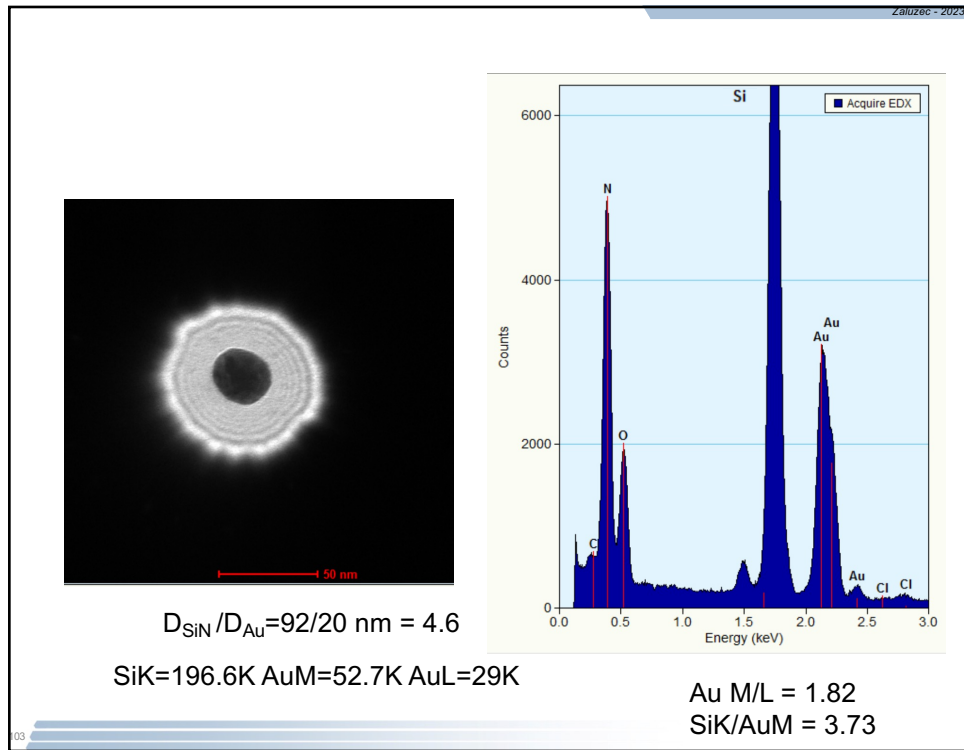
100



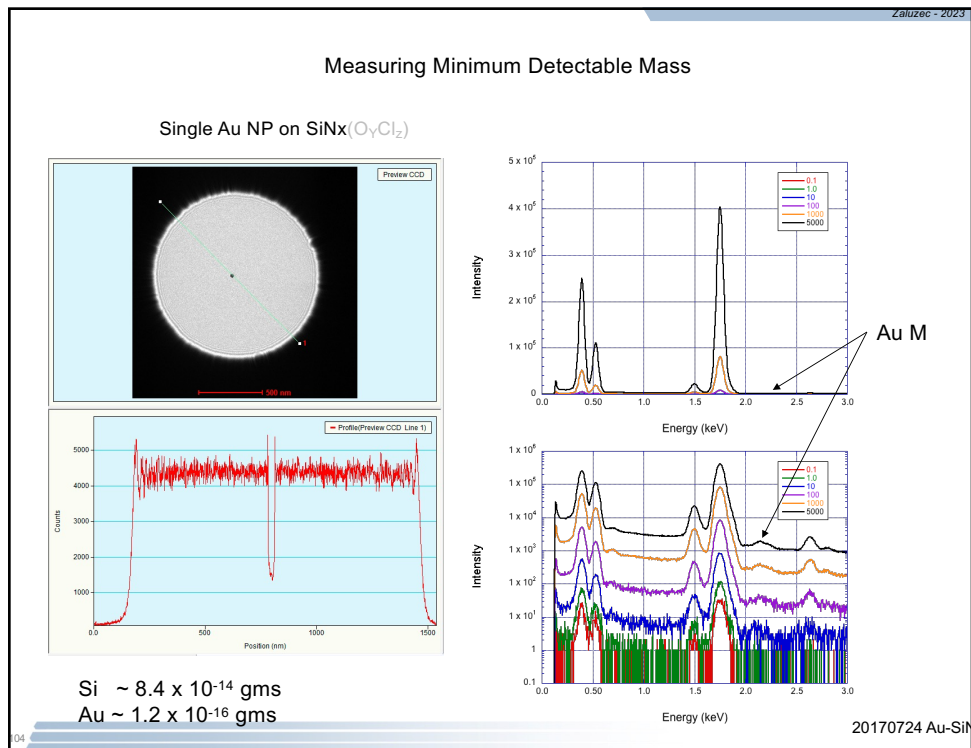
101



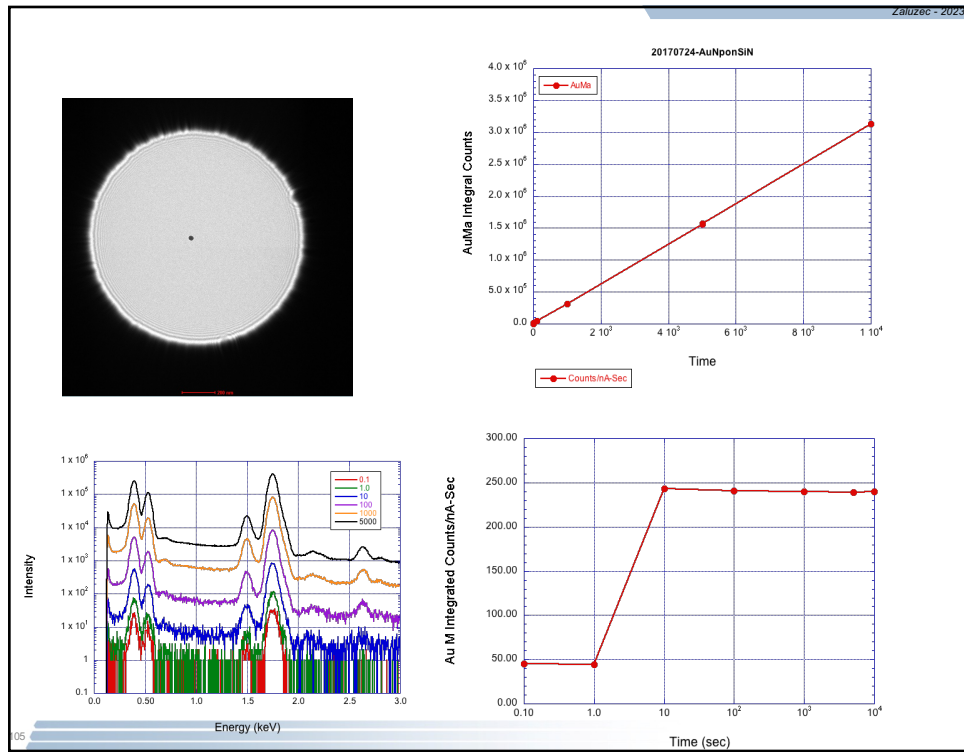
102



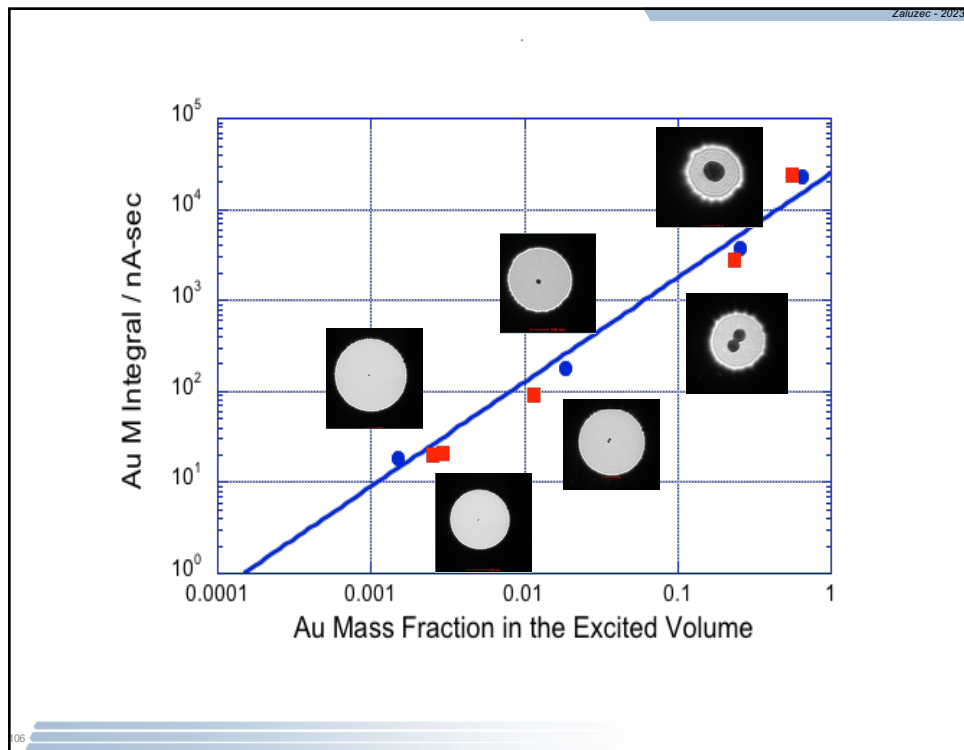
103



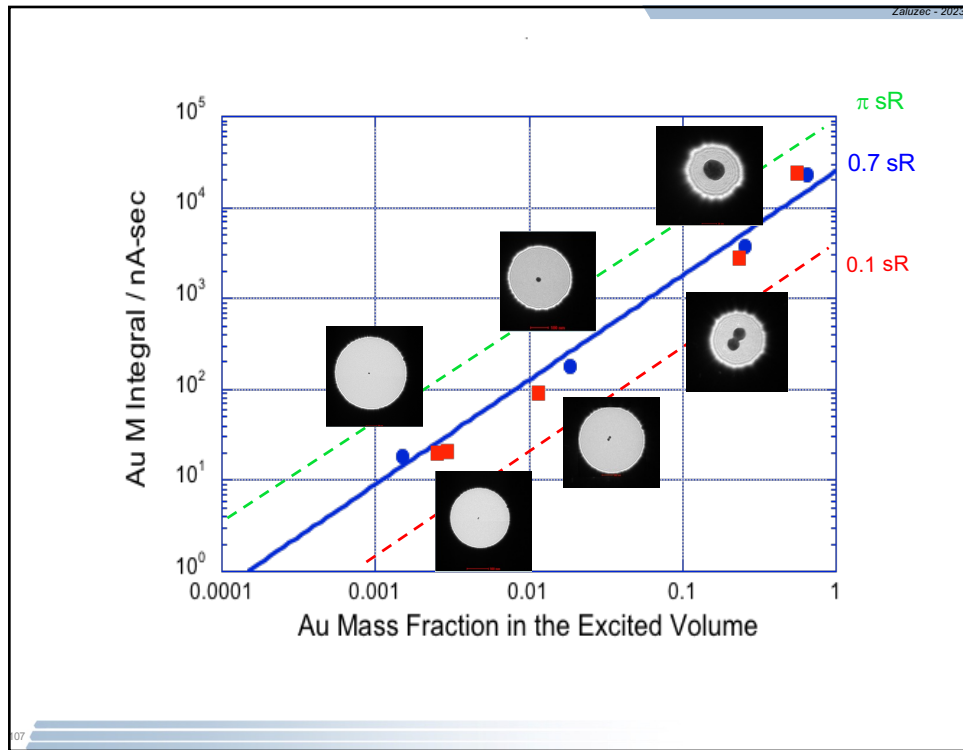
104



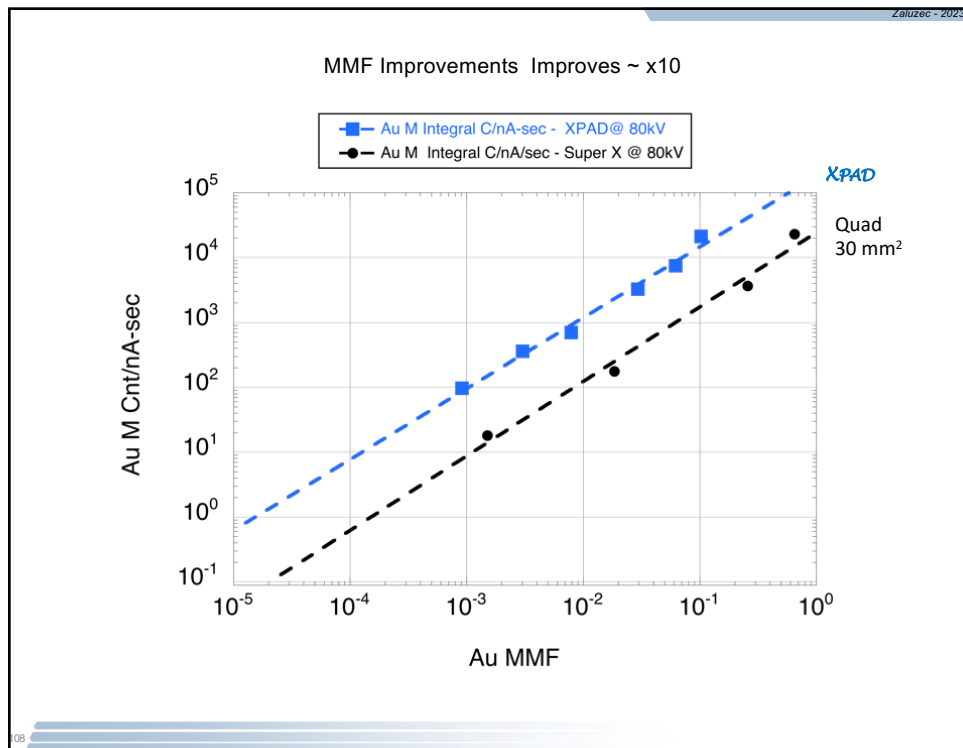
105



106



107



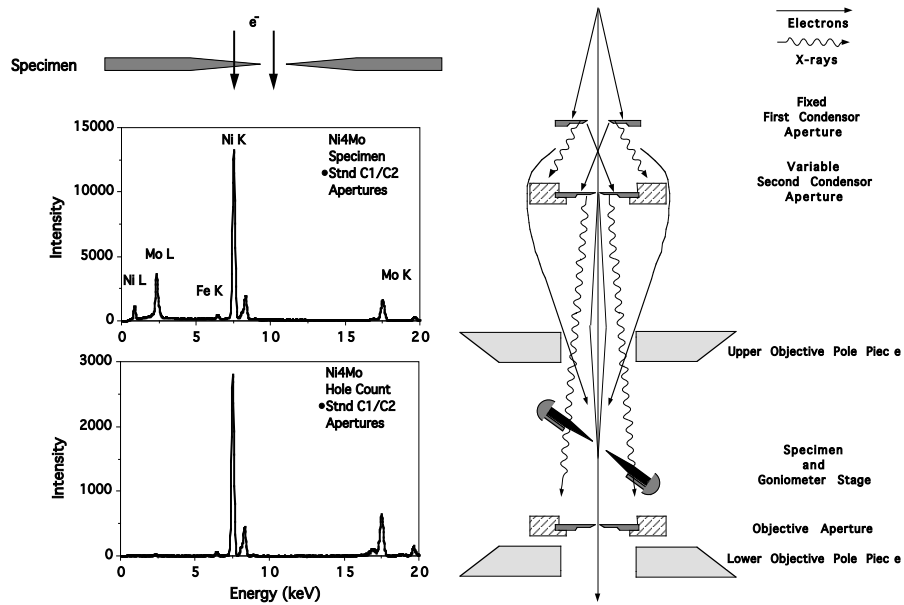
108

Instrumentation: AEM Systems

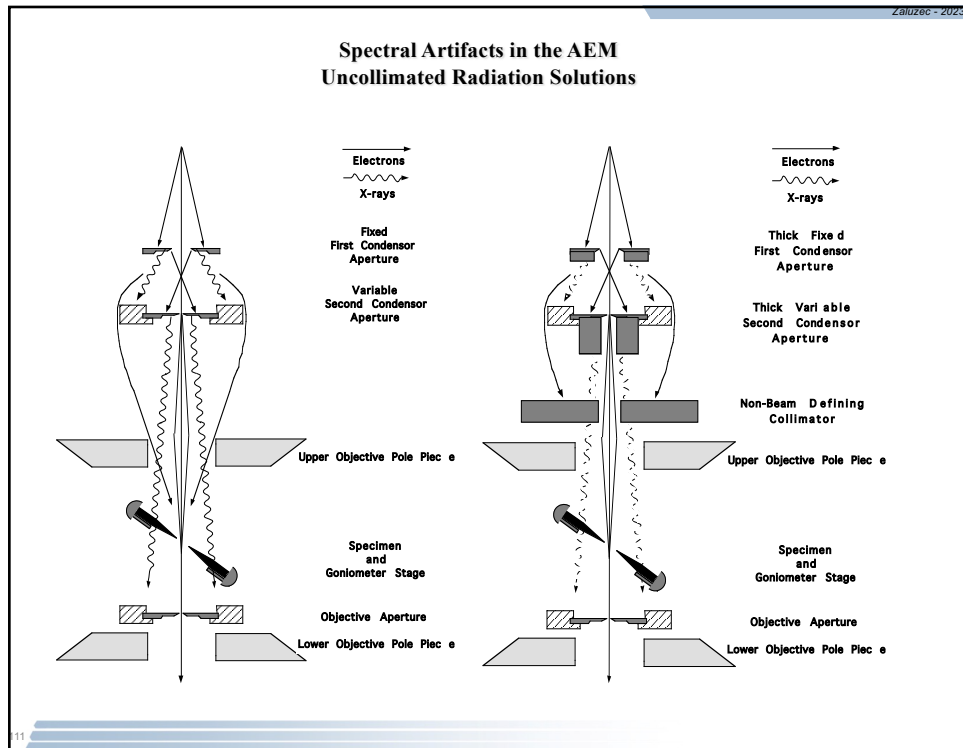
The AEM as a system
Spectral Artifacts in the AEM
Uncollimated Radiation
Systems Peaks
Artifacts at High Electron Energy
Specimen Contamination & Preparation
Optimizing Experimental Conditions

109

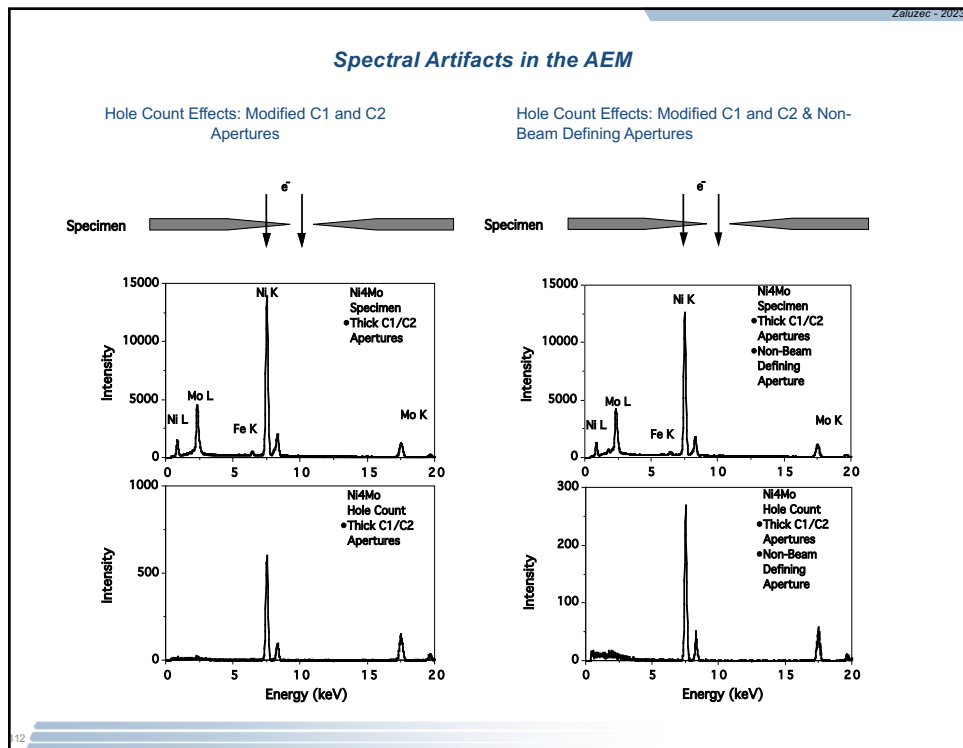
Spectral Artifacts in the AEM *Uncollimated Radiation: The Hole Count*



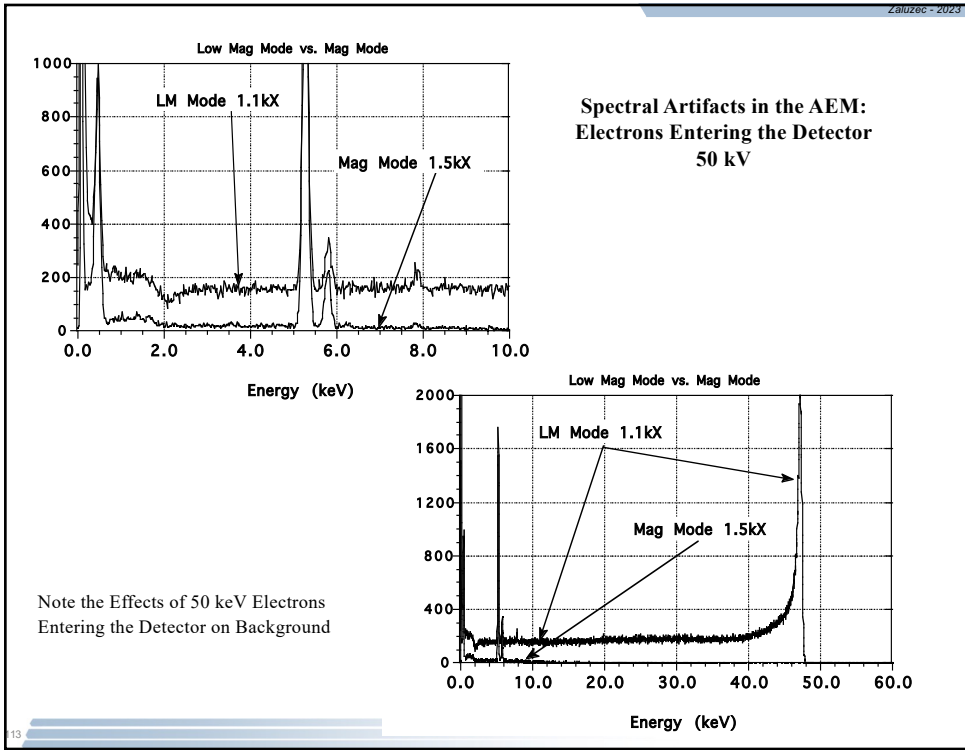
110



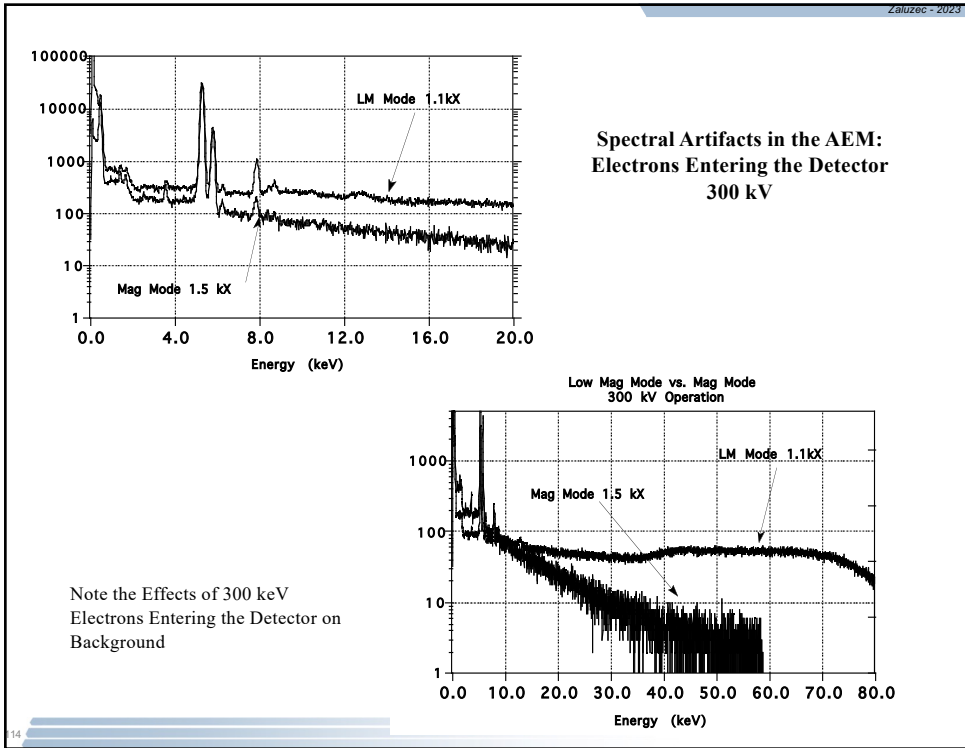
111



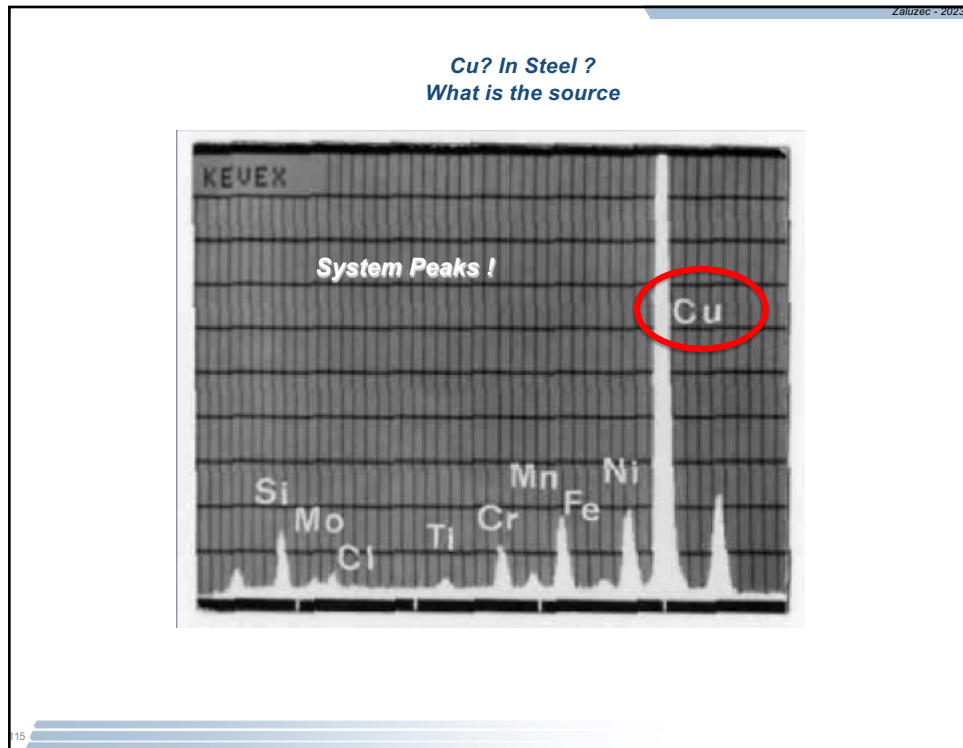
112



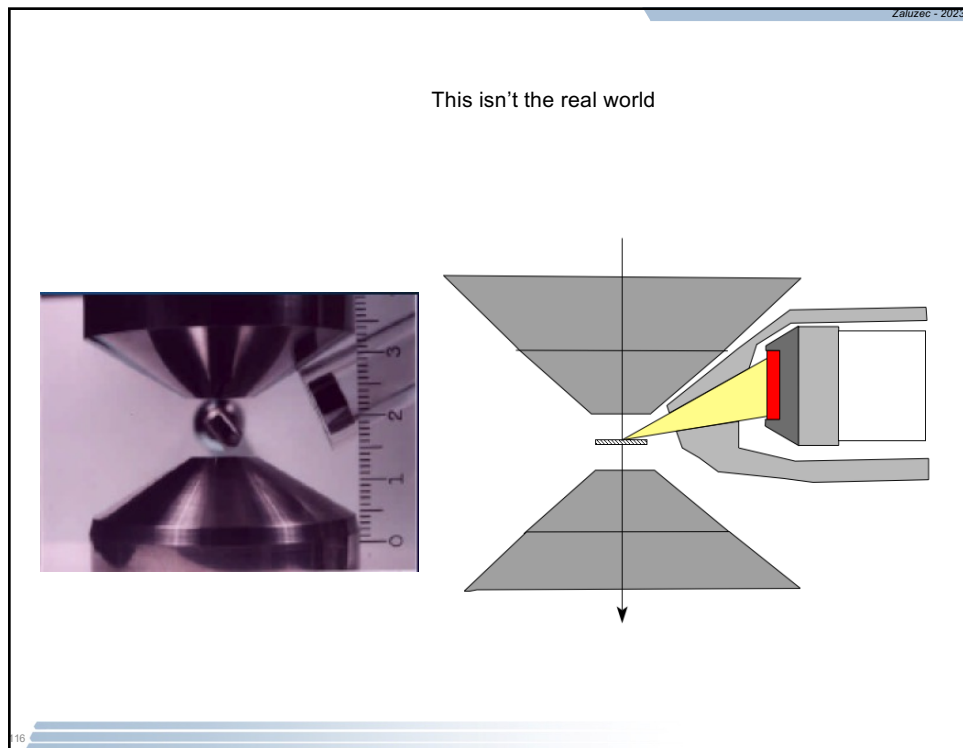
113



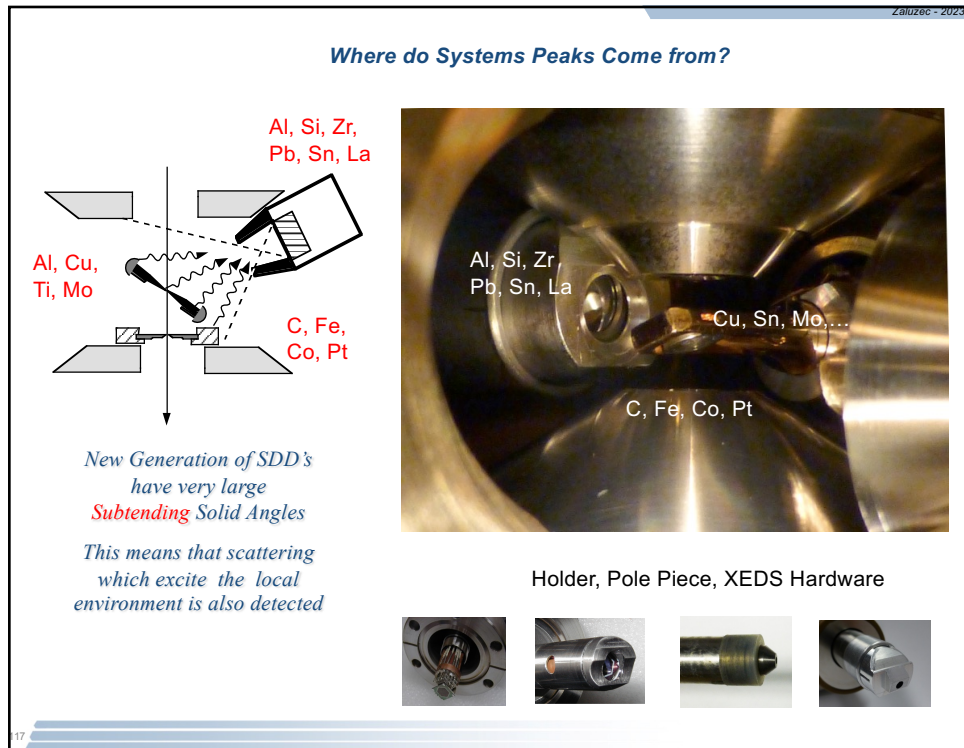
114



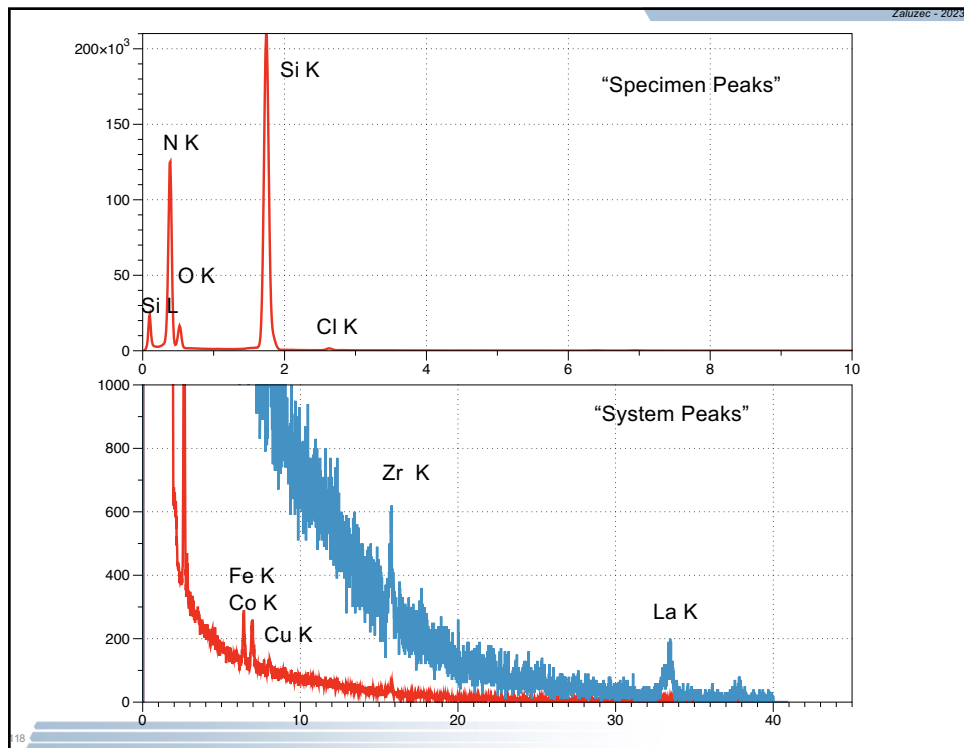
115



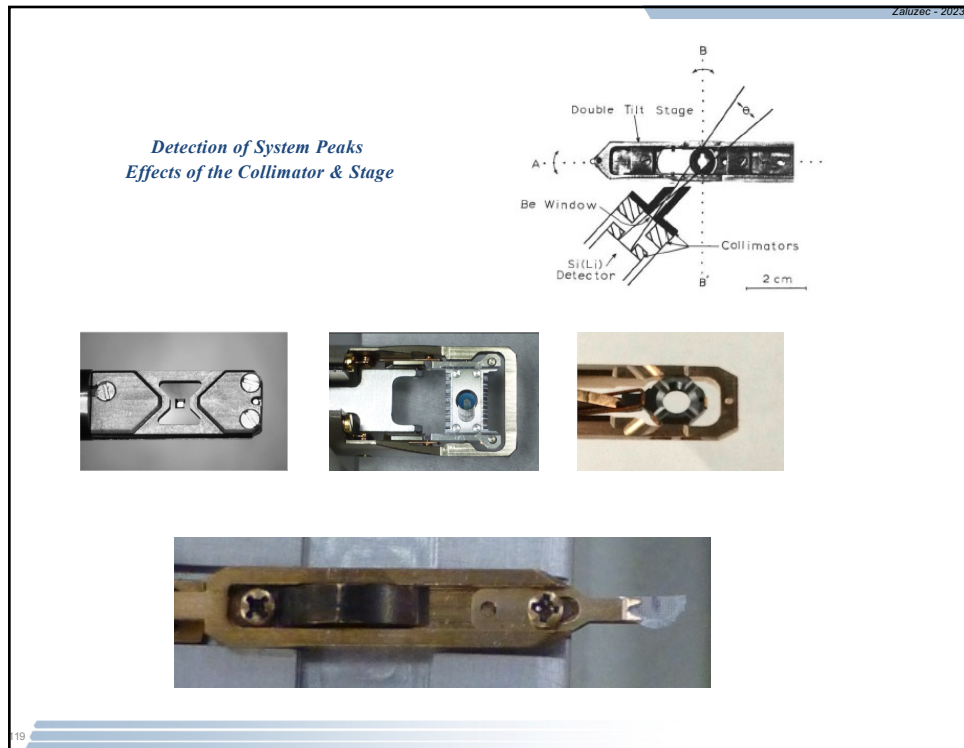
116



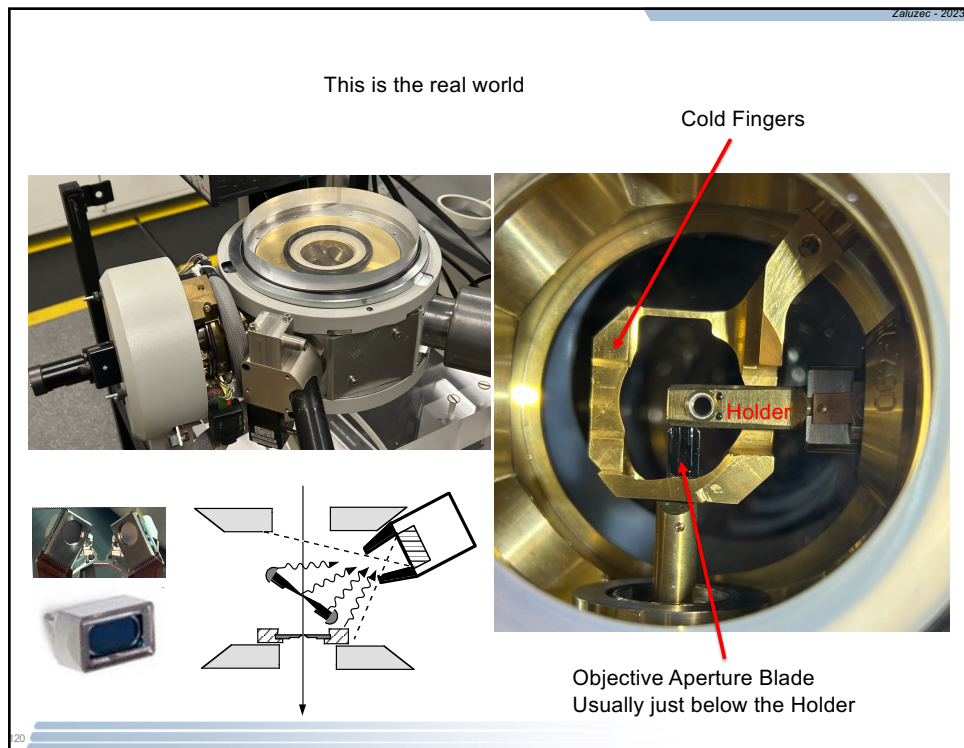
117



118

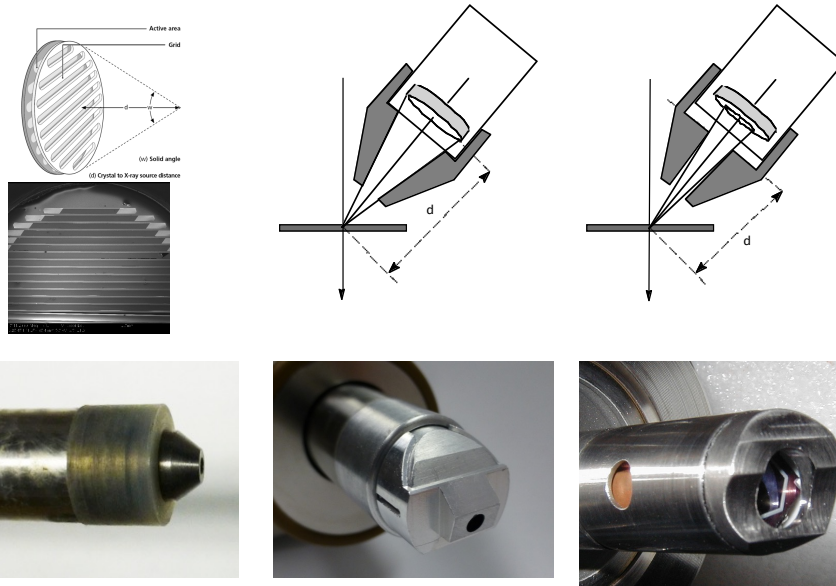


119



120

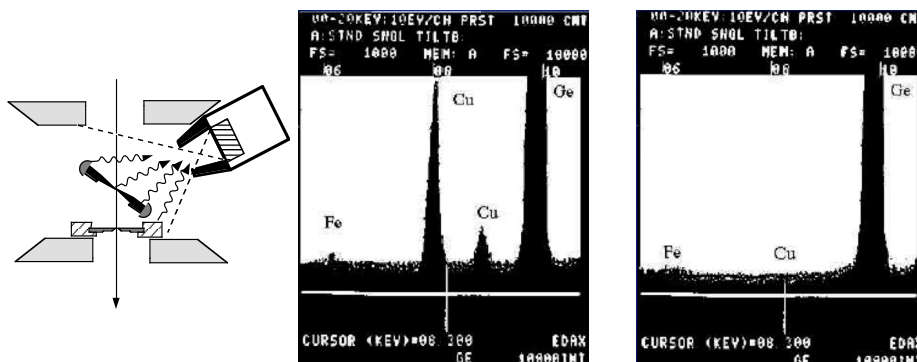
Collimators & Windows Vary



21

121

Detection & Minimization of System Peaks



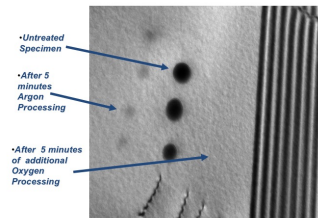
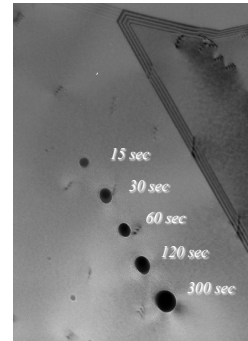
Minimization of Stage System Peaks by use of Beryllium Gimbals
 Ge specimen 10,000 in Ge K α peak in both spectra
 Left Standard Single Tilt Cu Stage, Right Be Gimbal DT Stage

22

122

Specimen Contamination

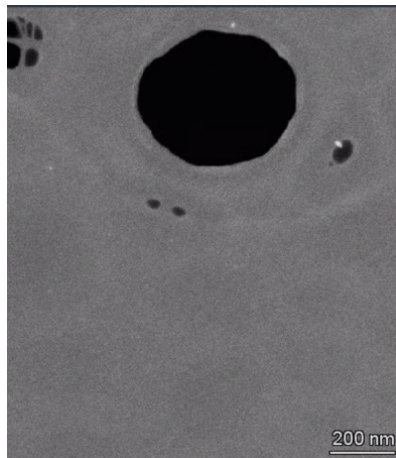
- The figure at the right shows the results of contamination formed when a 300 kV probe is focussed on the surface of a freshly electropolished 304 SS TEM specimen.
- The dark deposits mainly consist of hydrocarbons which diffuse across the surface of the specimen to the immediate vicinity of the electron probe. The amount of the contamination is a function of the time spent at each location. Here the time was varied from 15 - 300 seconds.
- Contamination decreases the spatial resolution and results in other peaks (Carbon ...) detected
- Plasma Cleaning with Ar, Ar/O, O, O/H gas mixtures removes mobile hydrocarbons



123

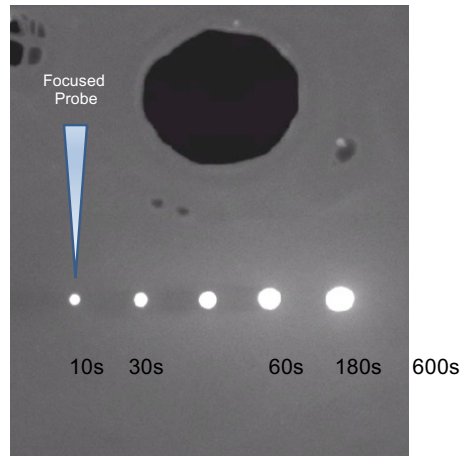
Does this work? Pre UVC Treatment

Before



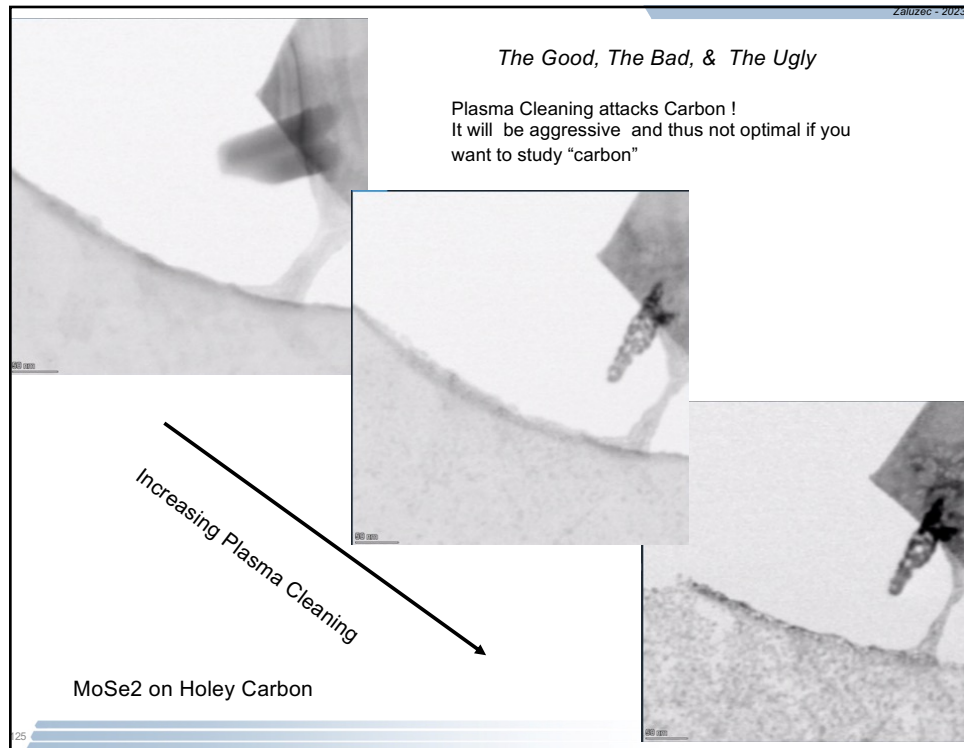
"Fresh (with mobile surface HC) Specimen "

After Focused Probe

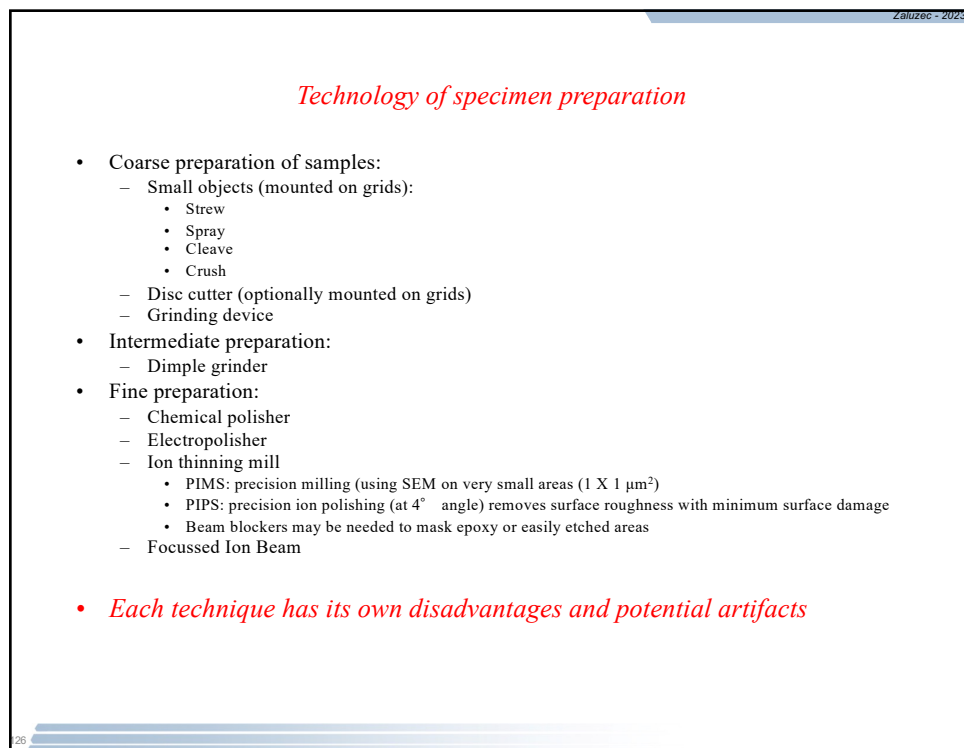


Post Spot Mode HC Accumulation

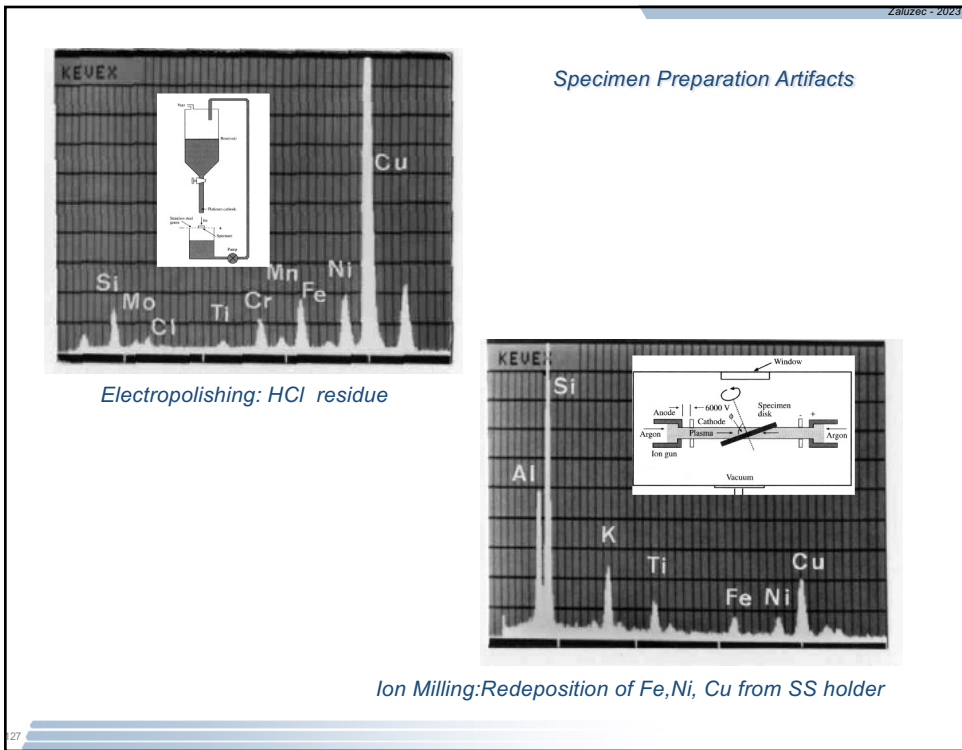
124



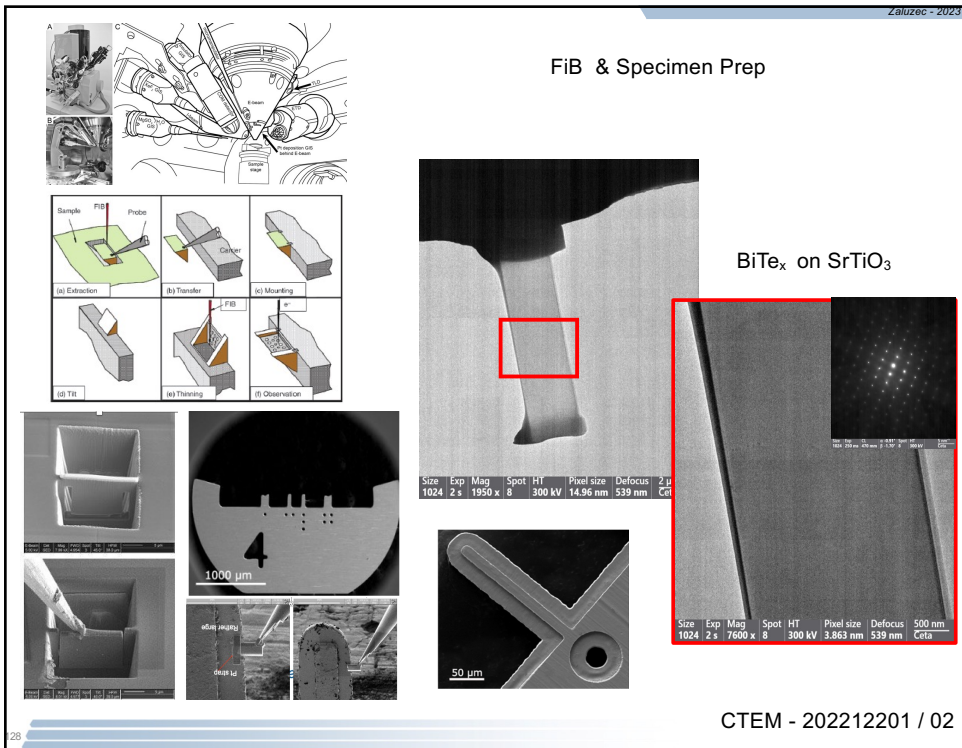
125



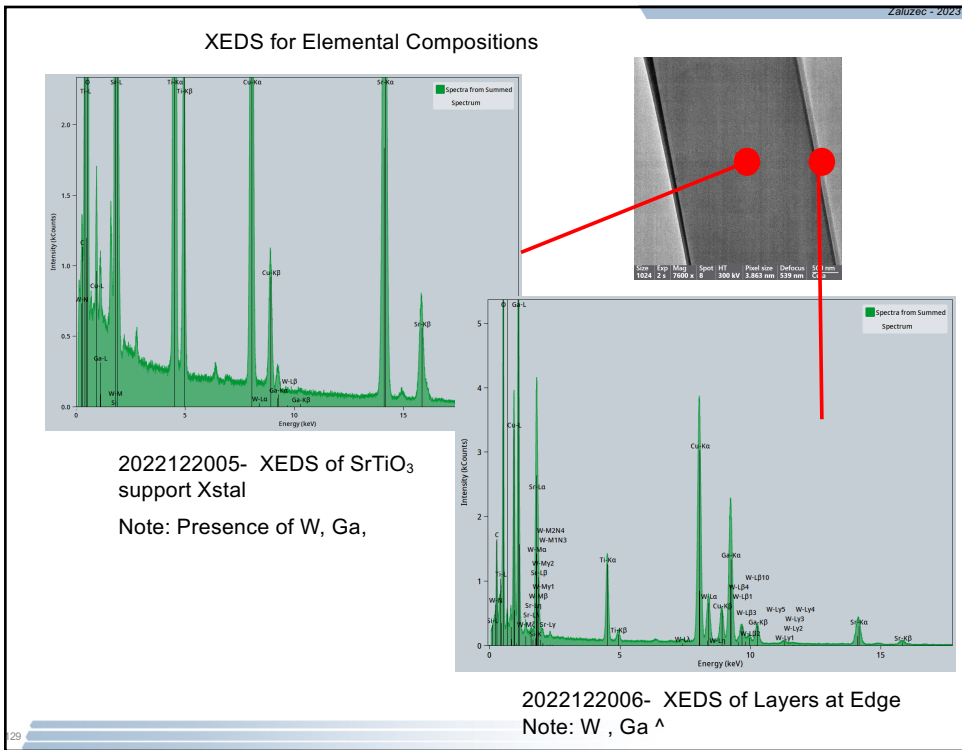
126



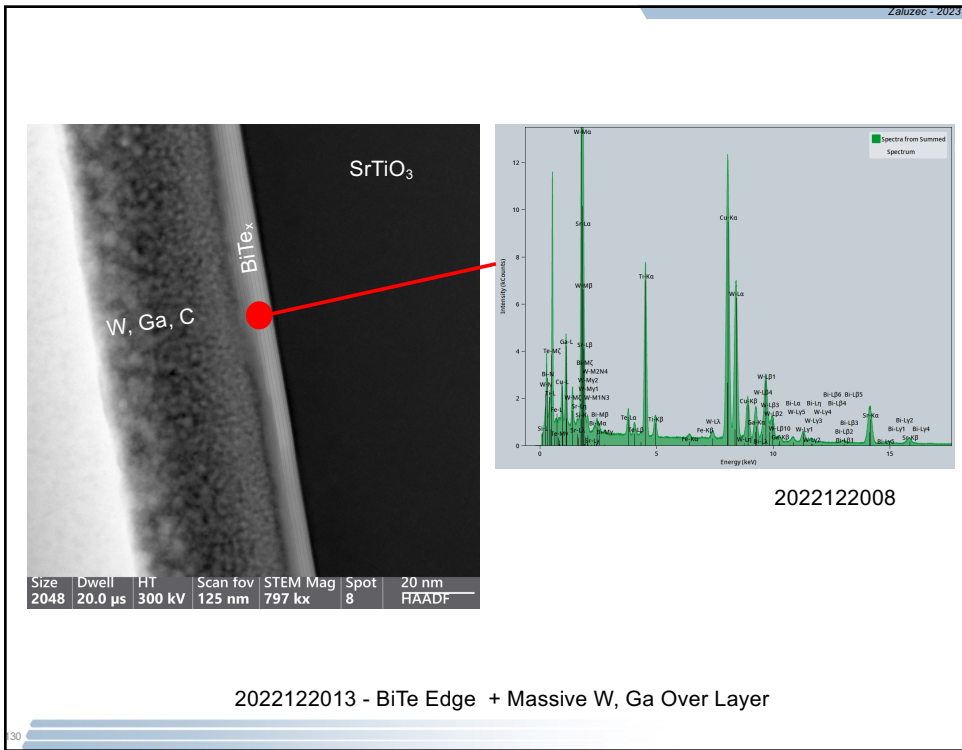
127



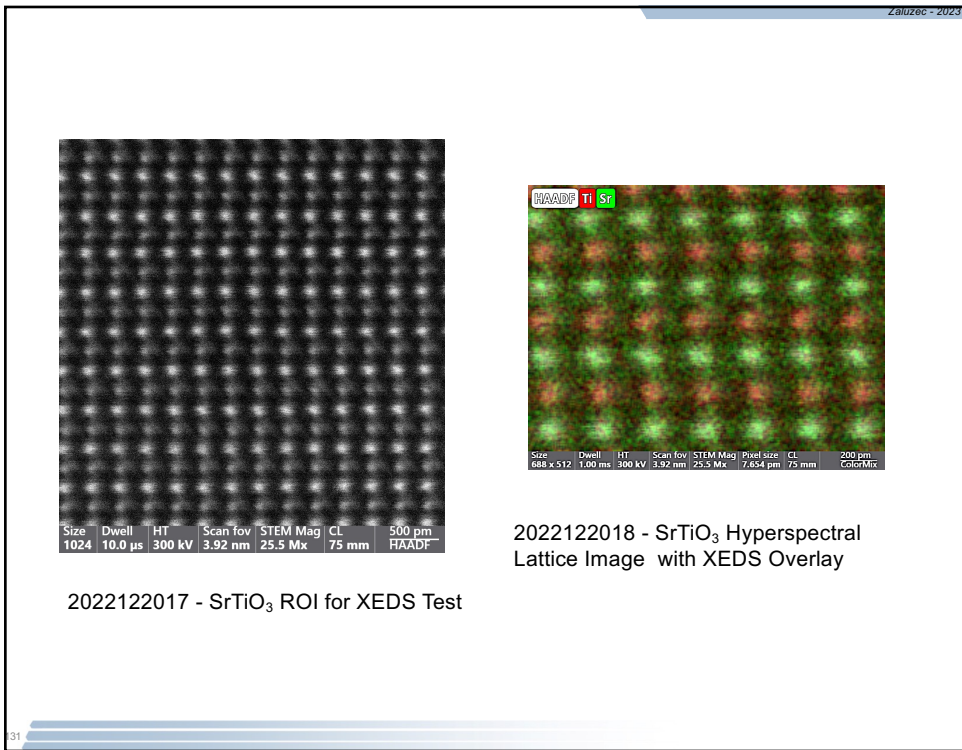
128



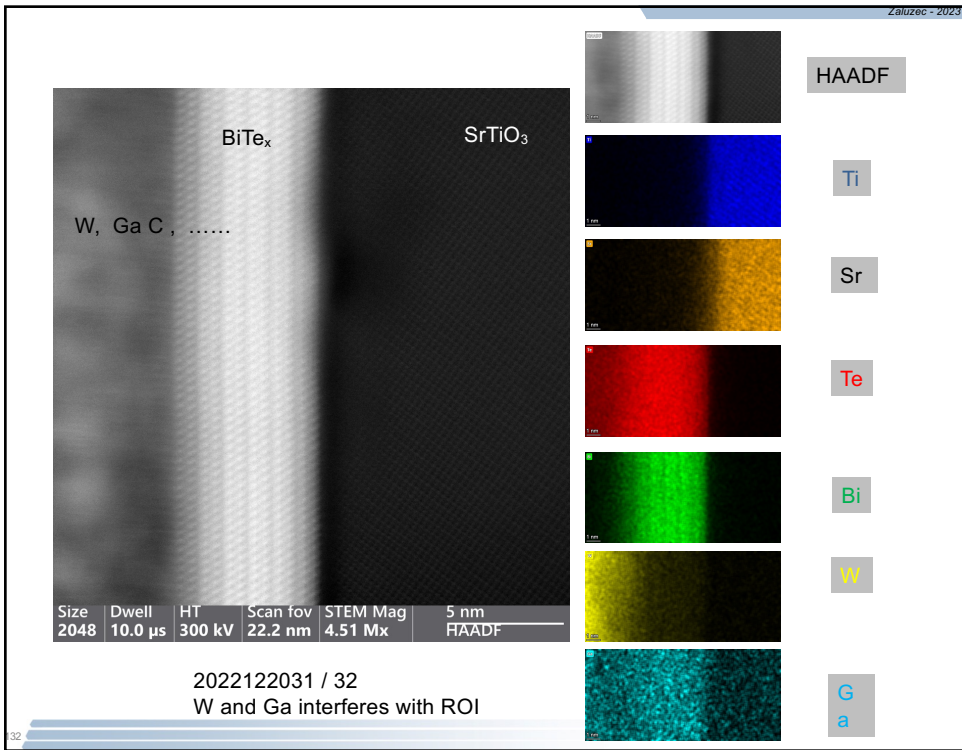
129



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Zakuzec - 2023

Support Grids and XEDS

Beryllium

Diamond

Plastic/Polymer

Aluminium

Titanium

Nickel

Copper

Molybdenum

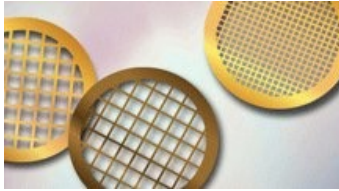
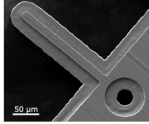
Silver

Gold

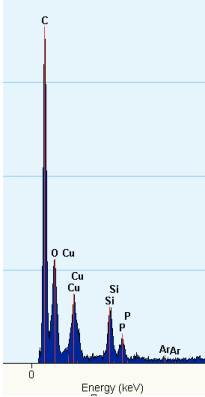
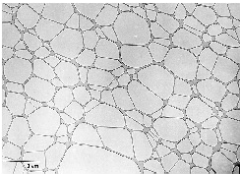
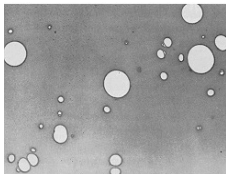
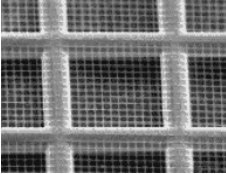
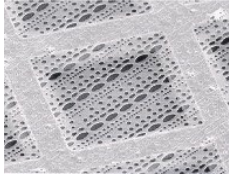
Pseudo-Carbon

Diamond

Si, SiN_x, SiO_x



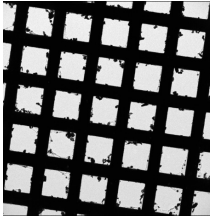
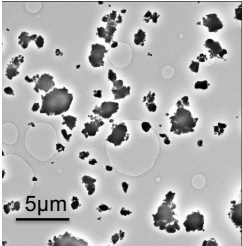






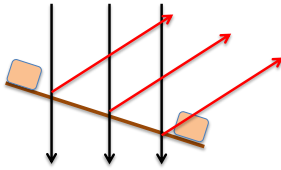
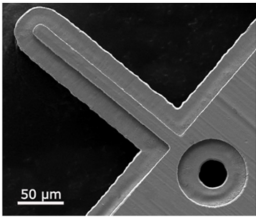
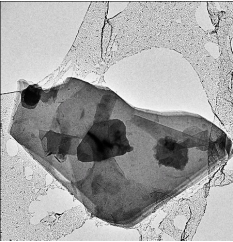
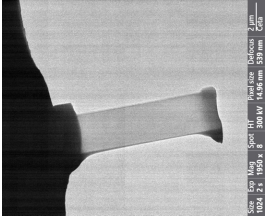
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Specimen's on Grids/TABS Where is the Detector

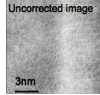
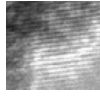



Post Plasma Cleaning

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	Geometrical Broadening $d_G \sim 2\alpha t$ (all probes)	α semiangle t thickness
	Beam Broadening $d_B \sim 625 \frac{Z}{E_o} \left(\sqrt{\frac{\rho}{A}} \right) t^{3/2}$ (general scattering)	d_B (cm) t thickness(cm) ρ density (gm/cm ³) E_o Accelerating Voltage (keV) Z, A atomic number & wt
	Chromatic Broadening $d_C \sim FC_c \beta \frac{\Delta_s}{E_o}$ (EFTEM)	C_c Chromatic Ab Coeff (um -> mm) β Scattering semiangle (mR) Δ_s Energy Window/Slit Width (eV) E_o Accelerating Voltage (keV) F Factor 0.1 (low loss) -0.3 (high loss)
	Inelastic Delocalization $d_L \sim 0.44 \frac{\lambda}{\theta_E^{3/4}}$	λ Electron Wavelength θ_E Mean Scattering angle ΔE Energy Loss $T_o = \gamma m_o c^2$
	Image/Diffraction Delocalization $d_R = C_s \square^5 g^5 + C_3 \square^3 g^3 + \square \square f g _{\max}$	$C_3 = C_s$ g diffract. vector Δf defocus

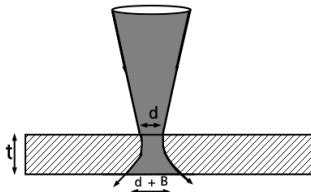
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Analytic Formulation (Elastic Scattering - Goldstein et al 1977)

$$B = 625 \frac{Z}{E_o} \sqrt{\frac{\rho}{A}} t^{3/2}$$

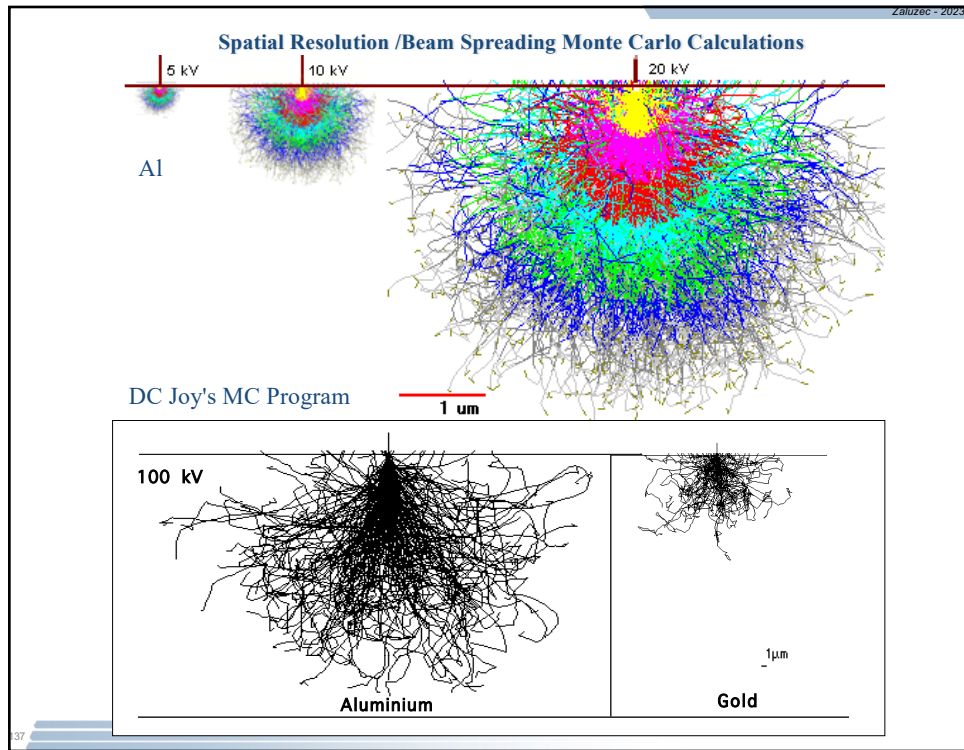
B = Beam Broadening [cm]
 E_o = Accelerating Voltage [kV]
 A = Atomic Weight
 Z = Atomic Number
 ρ = Density [gms/cm³]
 t = Thickness [cm]



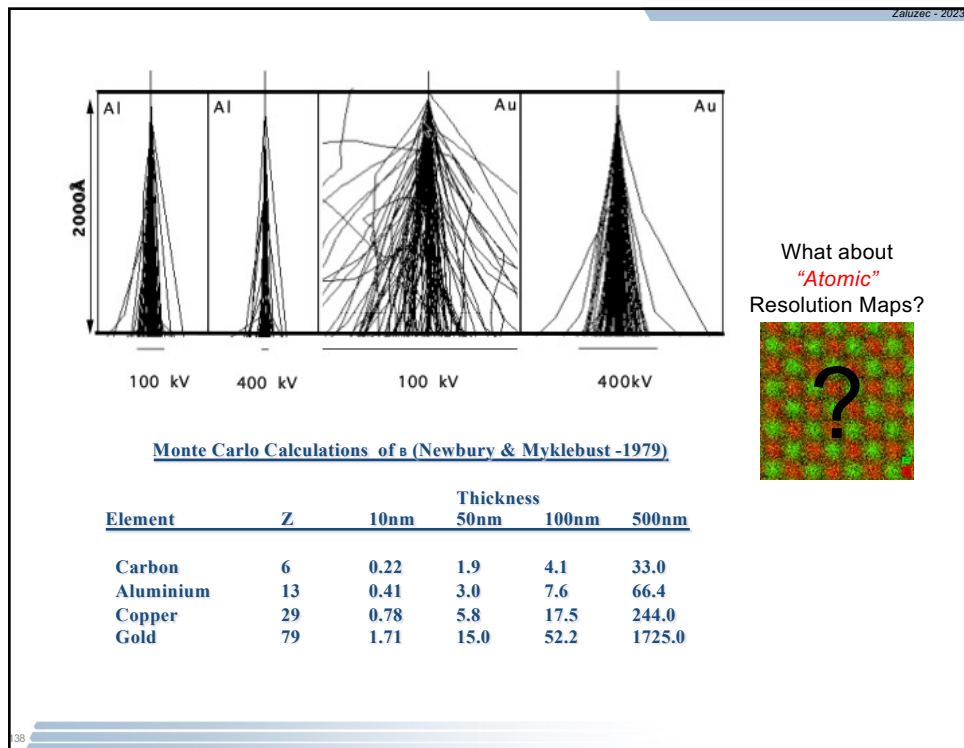
Element	Z	10nm	50nm	100nm	500nm
Carbon	6	0.16	1.8	5.13	57.4
Aluminium	13	0.26	1.9	8.12	90.9
Copper	29	0.68	7.6	21.4	*
Gold	79	15.5	17.3	*	*

*model invalid at higher kV and/or high scattering angles

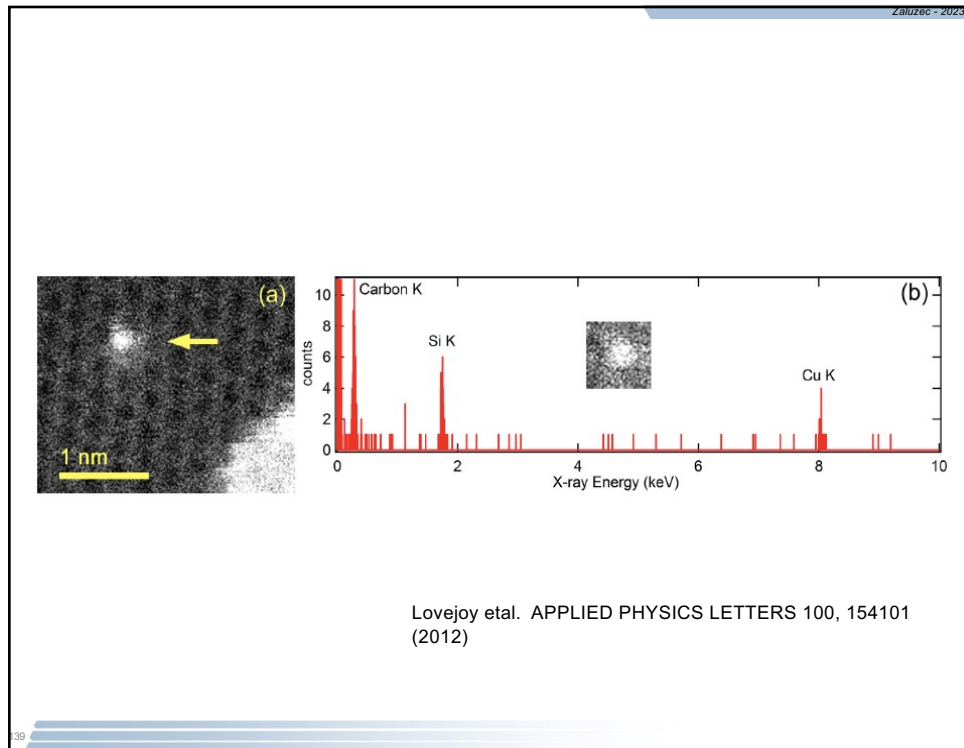
136



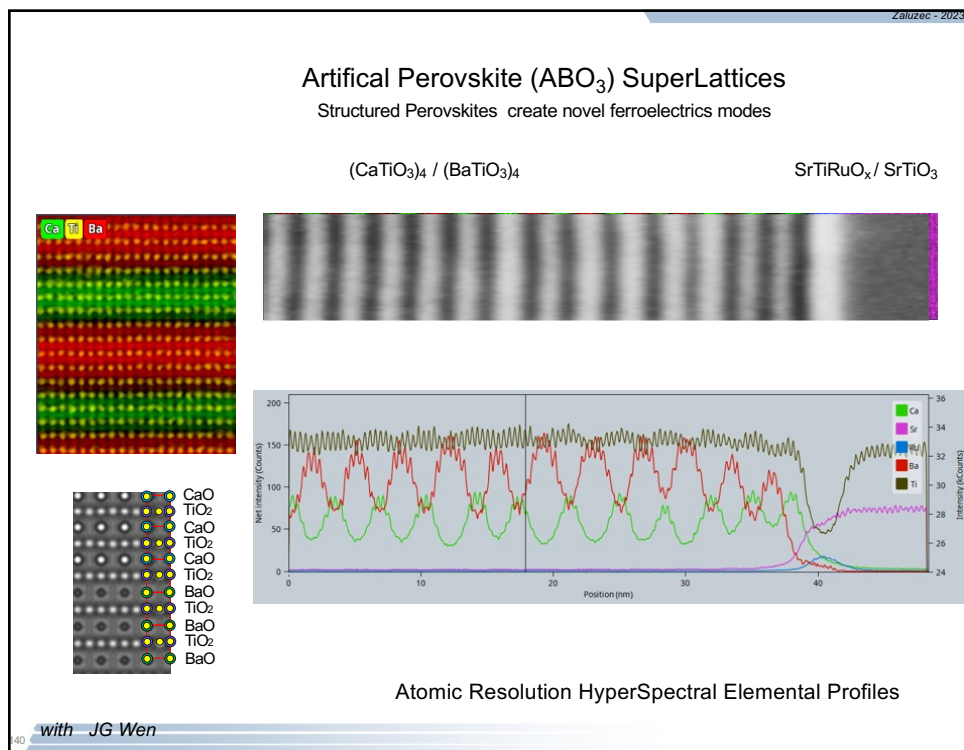
137



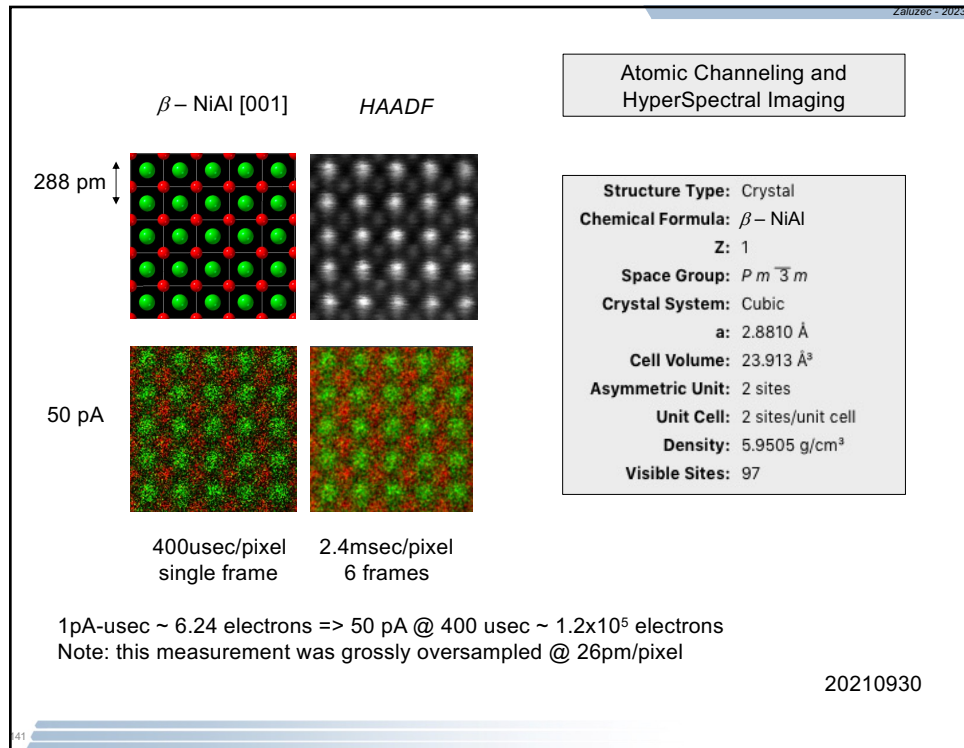
138



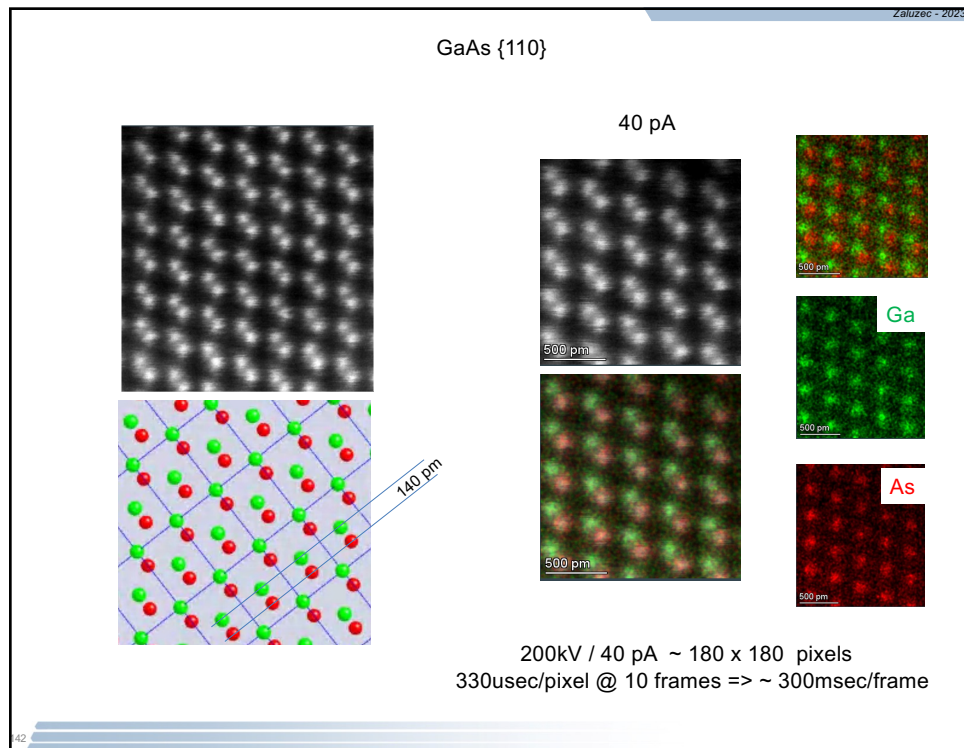
139



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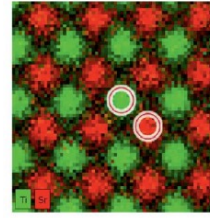
141



142

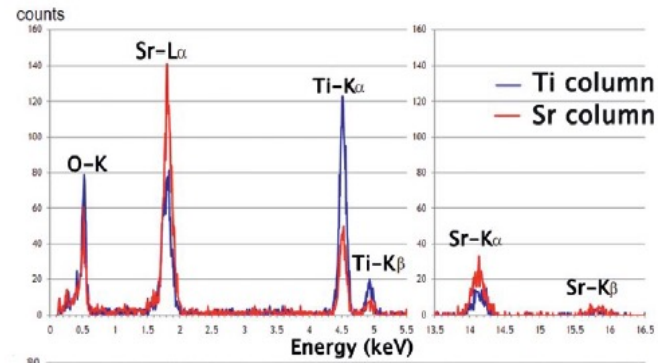
Atomic Resolution XEDS?

There is still work to be done !
Channeling is present
Calculations are needed to interpret

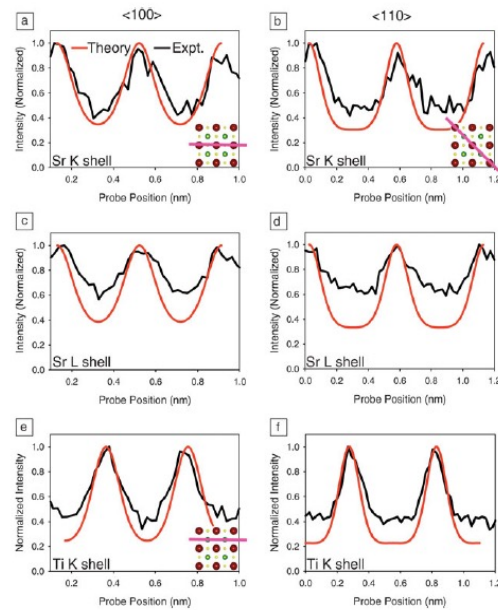


NB: These are NOT Chemical Maps

What about O₂ ?

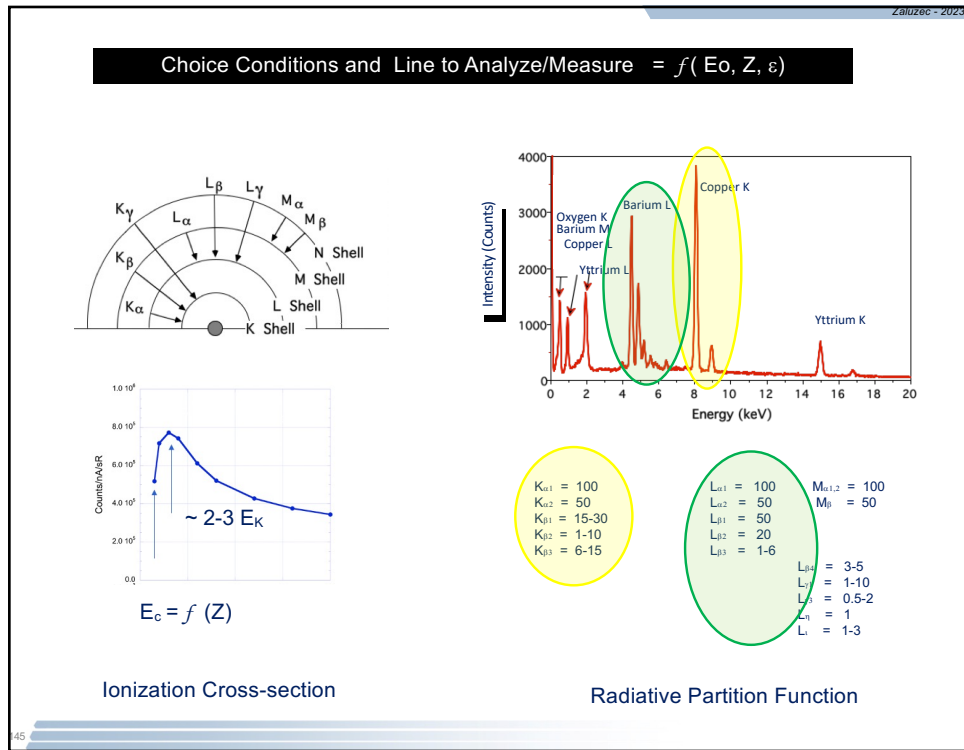


143

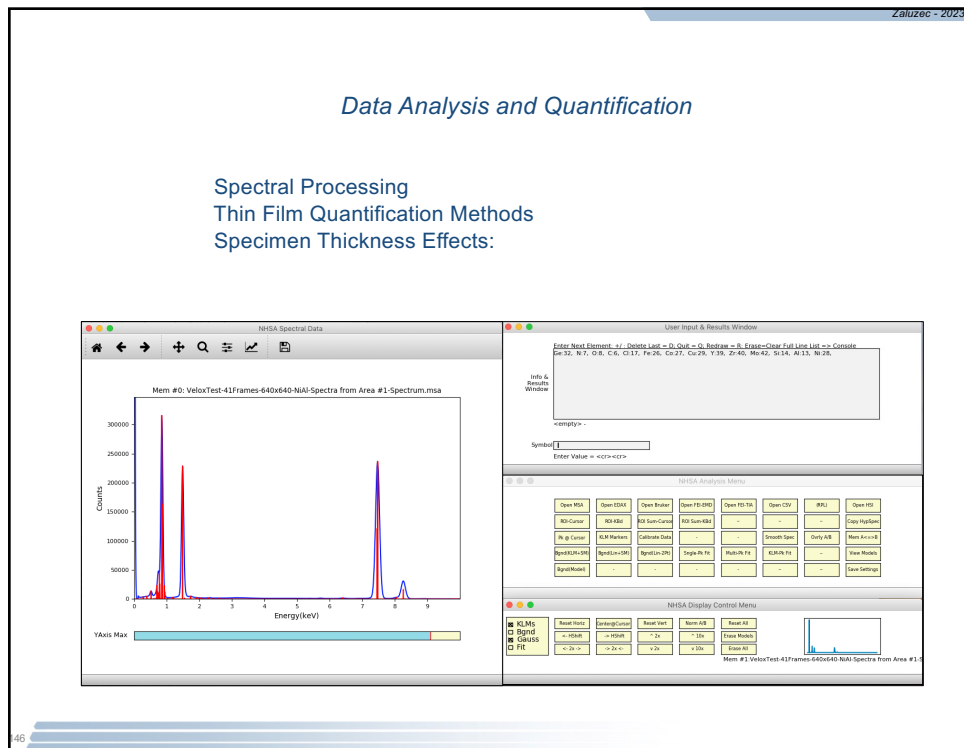


L. Allen et al
MRS Bulletin **37**, 47 (2012)

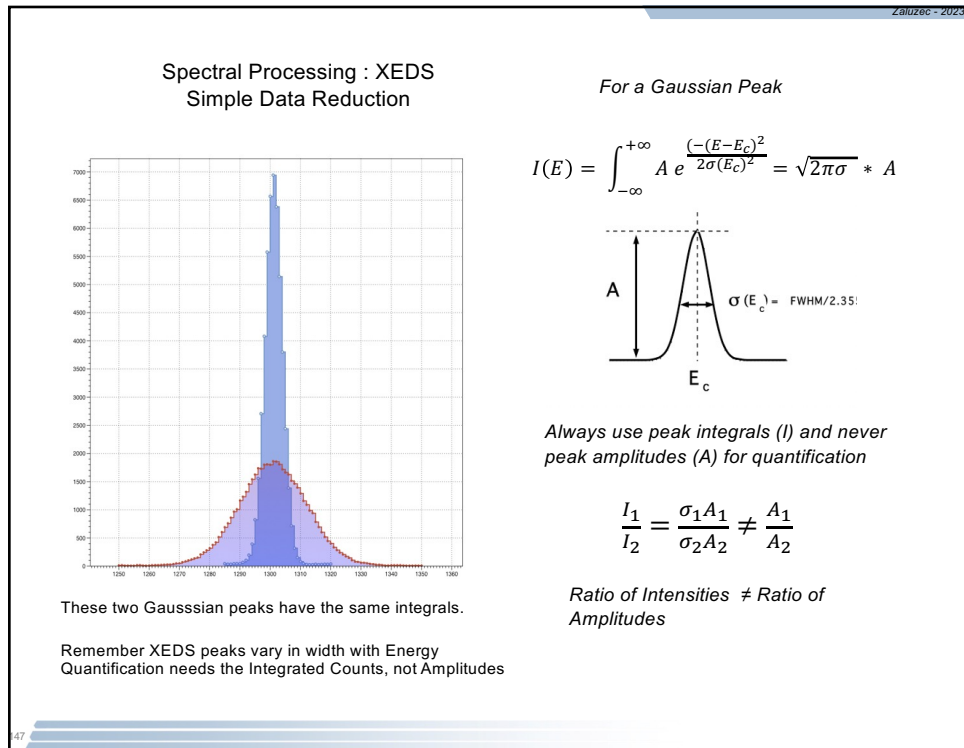
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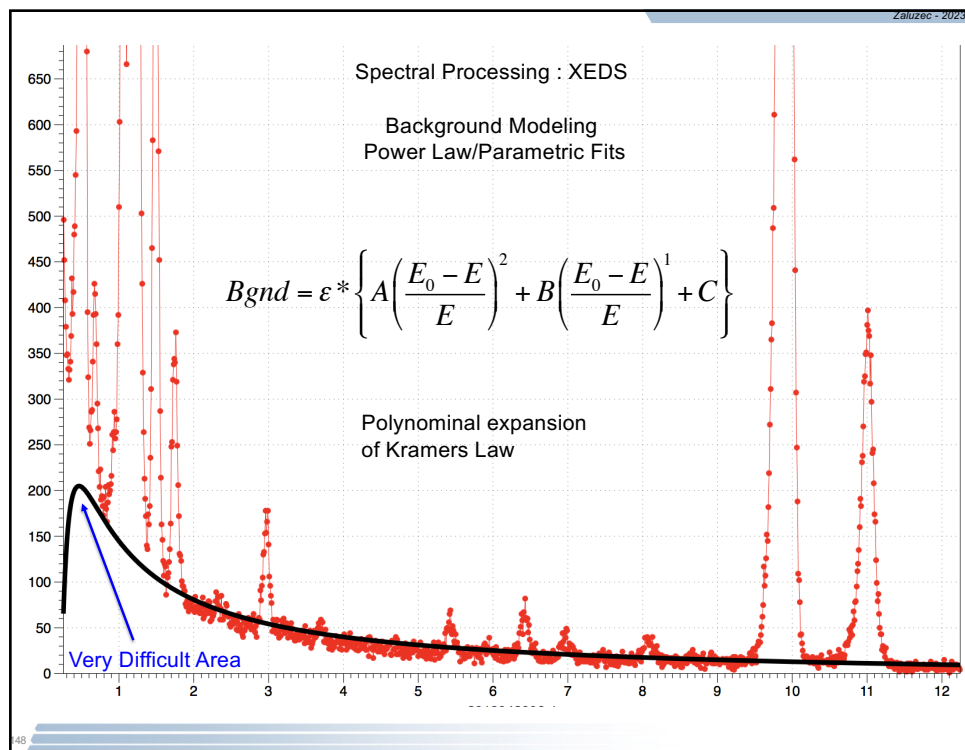
145



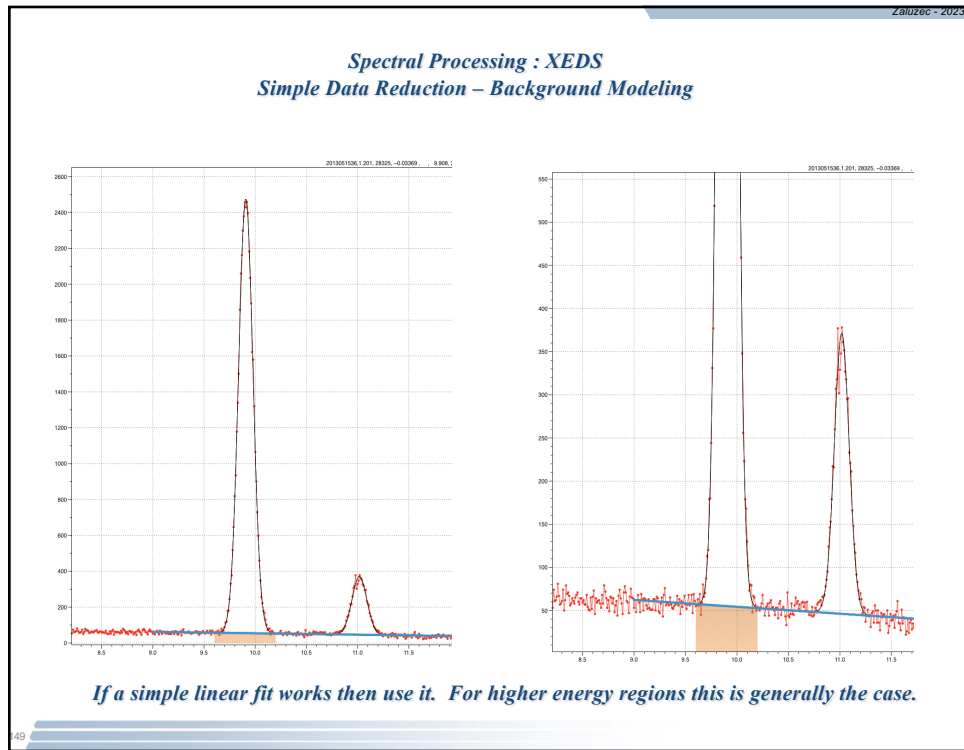
146



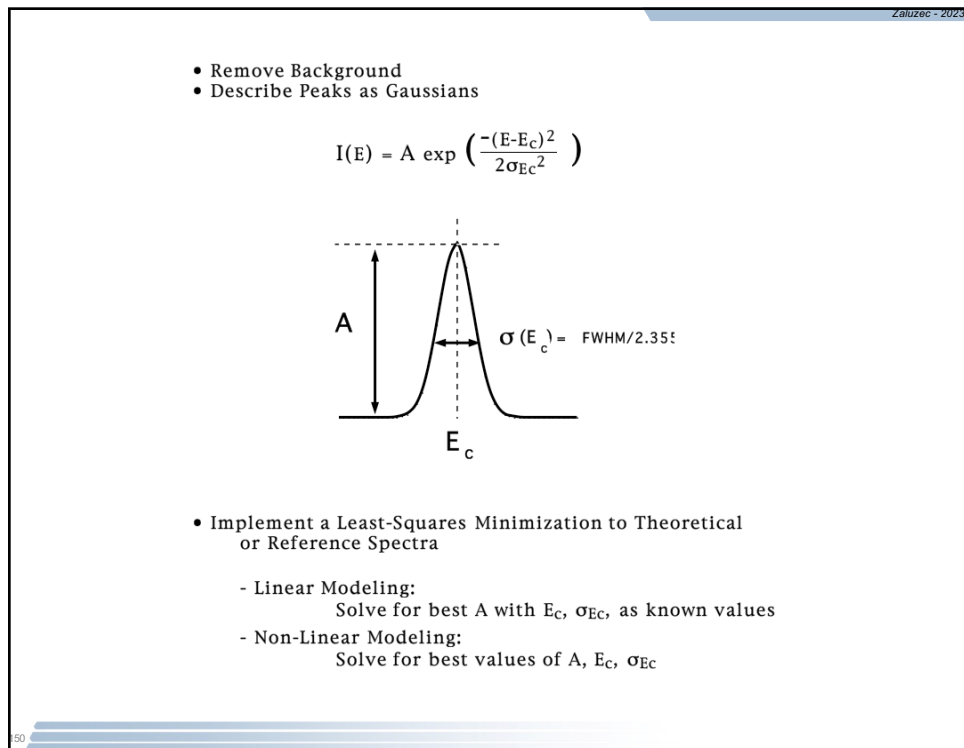
147



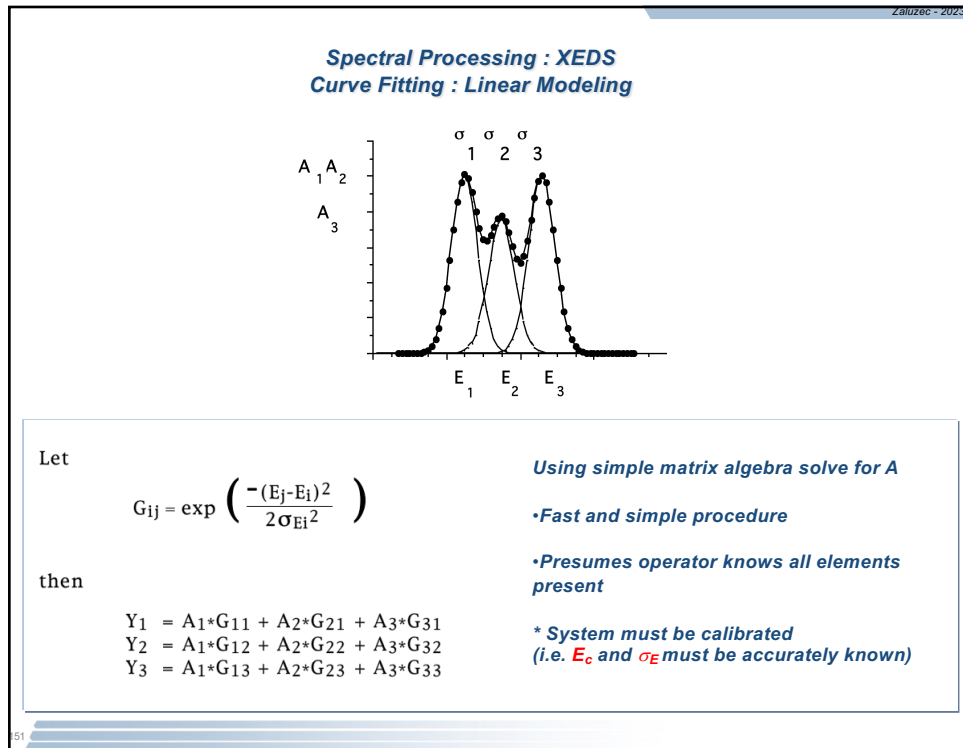
148



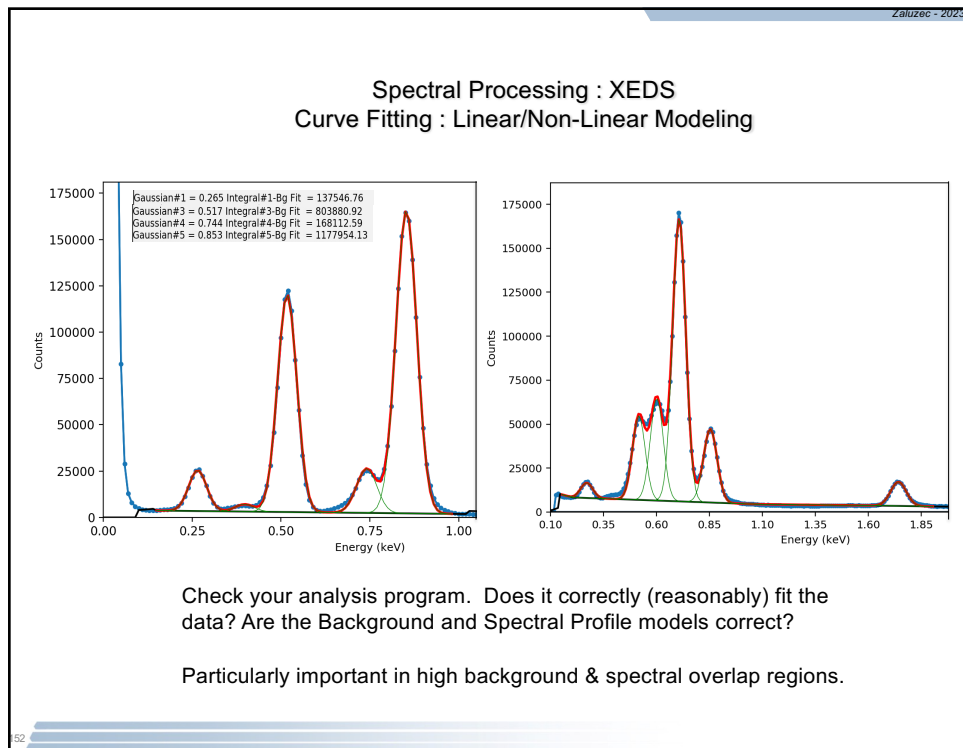
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Spectral Processing : XEDS
Curve Fitting : Non- Linear Modeling

Calculate and Minimize χ^2

$$\chi^2 = \sum_{k=1}^M \left(\sum_{i=1}^N \frac{(y_i - Y_k)^2}{y_i^2} \right) \quad \text{with } Y_k = A_k \exp \left(-\frac{(E_i - E_k)^2}{2\sigma^2(E_k)} \right)$$

and y_i = raw data

χ^2 is minimized by searching (E, σ , A) parameter space

- **Pattern Search**
 - Sequential method: mechanical iteration of each parameter until a local minimum is found.
 - Simplex method: simultaneous variation of all parameters.
- **Gradient Search**
 - Evaluate $\frac{\delta^2 \chi^2}{\delta p^2}$ and follow direction of steepest descent.
- **Multiple Least Squares with Derivative Reference**
 - Linearization of the above problem.
 $E \rightarrow E + \delta E \quad \sigma \rightarrow \sigma + \delta \sigma$

$$I'(E) = I(E) - \delta E \frac{\delta I(E)}{\delta E} + \left(\sigma \delta \sigma + \frac{(\delta E)^2}{2} \right) \frac{\delta^2 I(E)}{\delta E^2}$$

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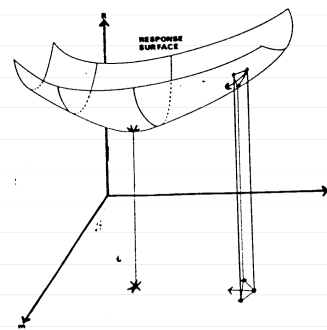
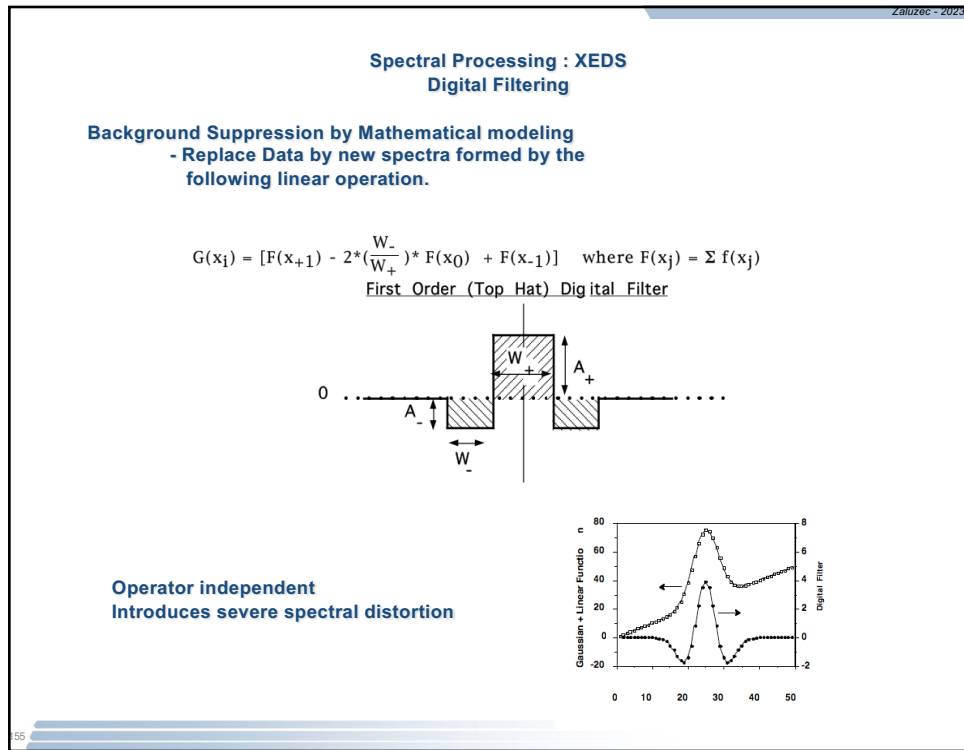


Figure 2. (a,b) plane and response surface showing a single, arbitrary, simplex.

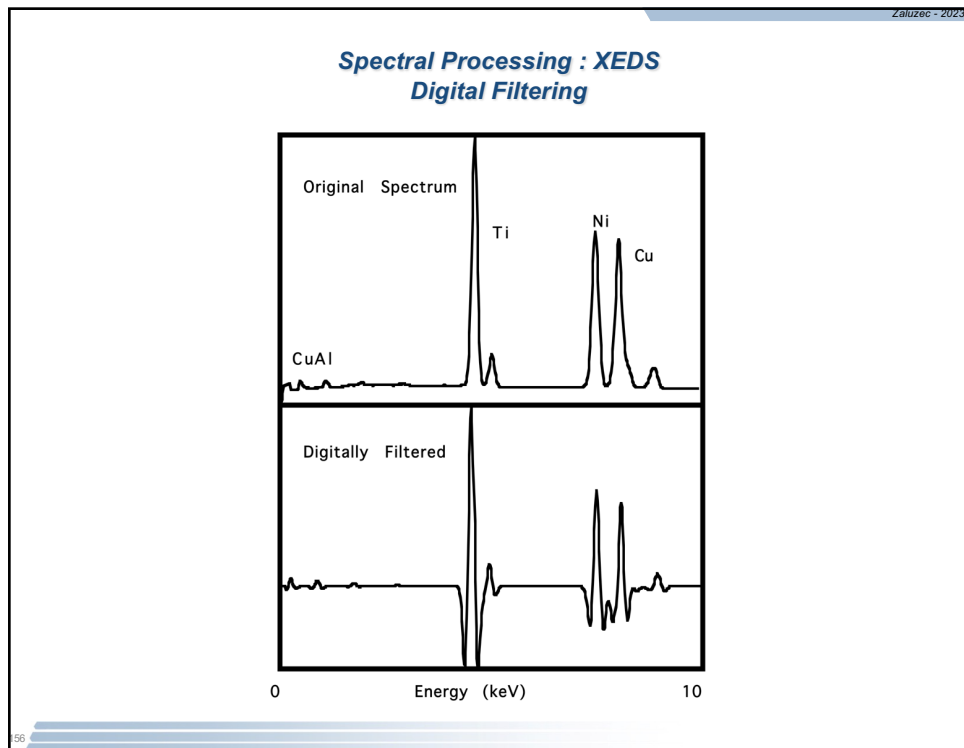
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Simplex search of Parameter Space after Fiori, NBS Special Pub. 604, 1979

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Data Analysis and Quantification:

Spectral Processing
Thin Film Quantification Methods
Specimen Thickness Effects:

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Quantitative X-ray Analysis

What should also be asked/understood?

- What is the Question?
- What Analysis Result is needed?
 - Qualitative
 - SemiQuantitative
 - Full Quantification
- What Resources are needed?

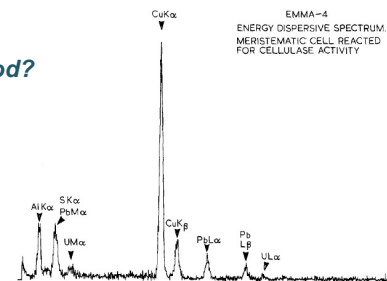
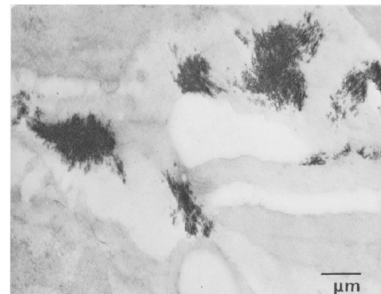


Figure 9. Energy dispersive spectrum of the final reaction product of cellulase activity (Bal, 1972; Weavers & Bal, 1972).

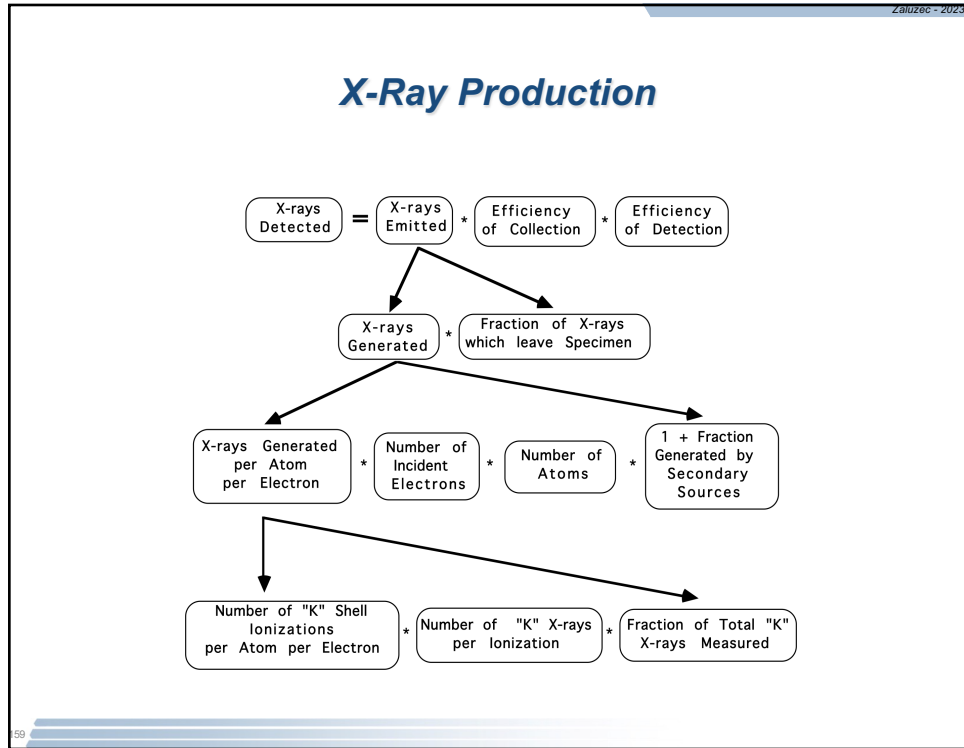
Did you plan the Experiment

- Is the Instrument suitable & calibrated
- Will Standards be Needed?
- Specimen & Standards Preparation
 - Depends on the Experiment
 - Mounting, Polish, Coat, ?
- Know your Instrument – Facts/Artifacts
- Survey the Specimen
- Optimize Instrument Parameters
 - E_0 , i_0 , Detectors.....
- Collect the Raw Data & Check for Other Artifacts
- Attempt to Quantify
 - Have you validated your protocols?
- Are the results Sensible?



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Data Analysis and Quantification:

Quantitative Analysis Equations

For a "thin" specimen of element A

$$I_A^{K\alpha} = \langle \sigma_A(E, Z) \Gamma_A \omega_A \rangle C_A \left(\frac{N_o \rho}{W_A} \right) \langle \eta_o t \rangle \langle \epsilon_A \Omega \rangle$$

I_A	=	Measured x-ray intensity per unit area	Function of ---
σ	=	K^{th} -shell ionization cross-section	E_o, Z, E_K
ω	=	K^{th} -shell fluorescence yield	Z, E_K
Γ	=	K^{th} -shell radiative partition function	Z, E_K
W	=	Atomic Weight	Z
N_o	=	Avagadro's number	---
ρ	=	Density	Sample
C	=	Composition (At %)	Sample
t	=	Specimen thickness	Sample
η_o	=	Incident electron flux	Probe current
ϵ	=	Detector efficiency	E_K , Detector
Ω	=	Detector solid angle	Detector

NB: no assumptions on: crystallinity, orientation, solid-state effects.....

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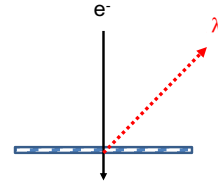
Quantitative Analysis Equations (minimalistic)

For an infinitely thin specimen

$$I_A^{K\alpha} = \sigma_{\alpha}(E, Z) * \Gamma_A * \omega_{\alpha} * C_A * \frac{N_o \rho t}{W_A} * \eta_o \tau * \varepsilon_A \frac{\Omega}{4\pi}$$

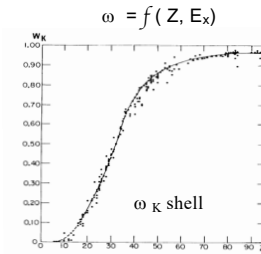
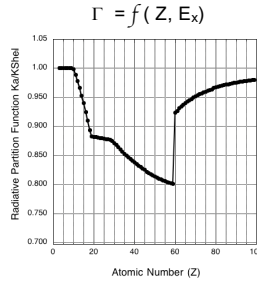
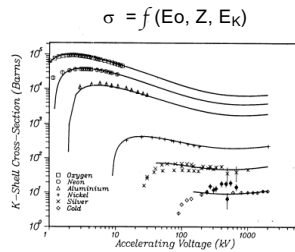
Probability X-ray/atom/electron * # Atoms * # Electrons * Probably of Detection

I_A = measured x-ray intensity (counts) per unit area,
 $\sigma_{\alpha}(E_o, Z)$ = α^{th} -shell ionization cross section
 E_o = electrons of incident energy (eV),
 ω_{α} = α^{th} -shell fluorescence yield,
 Γ_{α} = α^{th} -shell radiative partition function,
 W_z and C_z the atomic weight the composition
 Z = atomic number
 N_o = Avogadro's number,
 ρ = local specimen density,
 t = thickness of ROI
 η_o = the incident electron beam current,
 τ = acquisition (live) time
 ε_{α} = the detector efficiency and
 Ω_{α} = the detector collection solid angle.

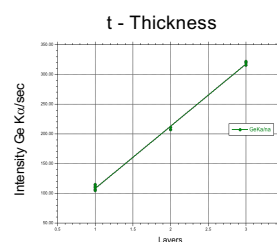
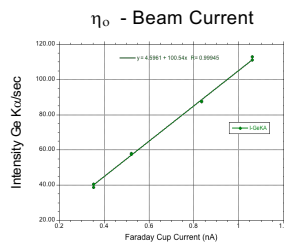
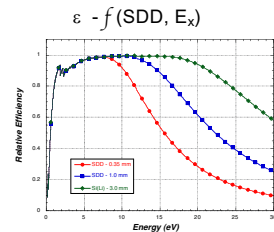


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$$I_A^{K\alpha} = \langle \sigma_{\alpha}(E, Z) \Gamma_{\alpha} \omega_{\alpha} \rangle C_A \left\langle \frac{N_o \rho}{W_A} \right\rangle \langle \eta_o t \rangle \langle \varepsilon_A \Omega \rangle$$



There are no analytical models that fits all experimental data. Virtually none include solid state effects !!!



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Quantitative Analysis using XEDS
Standardless Method

Invoke the Intensity Ratio Method, that is consider the ratio of x-ray lines from two elements

$$\frac{I_A}{I_B} = \frac{\kappa_A \epsilon_A C_A}{\kappa_B \epsilon_B C_B} = k_{AB}^{-1} \frac{C_A}{C_B}$$

$$\kappa_A = \frac{\sigma_A \omega_A \Gamma_A}{W_A}$$

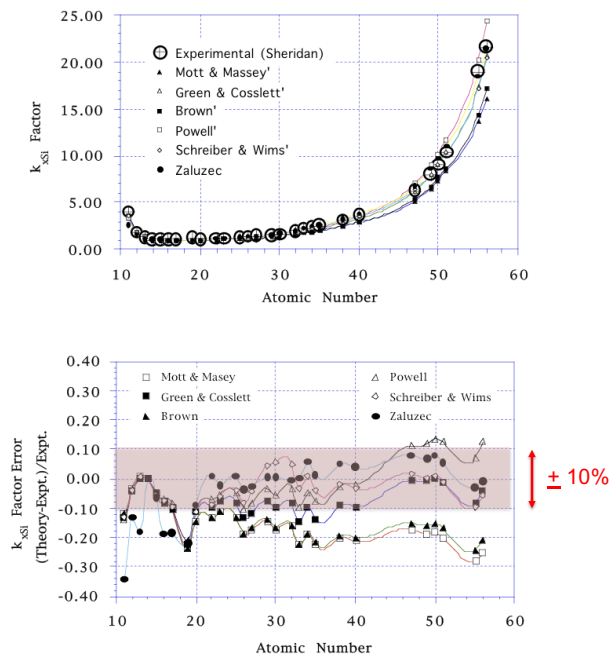
$$\frac{\kappa_A \epsilon_A}{\kappa_B \epsilon_B} = k_{AB}^{-1} \quad (\text{k-factor})$$

This simple equation states that the relative intensity ratio of any two characteristic x-ray lines is directly proportional to the relative composition ratio of their elemental components multiplied by some "constants" and is independent of thickness.

NOTE: The k_{AB} factor is not a universal constant!!
Only the ratio of κ_A/κ_B is a nominal physical constant and is independent of the AEM system. The ratio of ϵ_A/ϵ_B is not a constant since no two detectors are identical over their entire operational range.

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k-Factors
Experiment
vs
Theory



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The analysis to this point has only yielded the **relative compositions** of the specimen. We need one additional assumption to convert the relative intensity ratio's (I_i/I_j) into compositions namely:

$$\sum_{i=1}^N C_i = 1.0$$

One now has a set of N equations and N unknowns which be solved algebraically solved for the individual composition values.

Thus for a simple two element system we have:

and
$$\frac{I_A}{I_B} = k_{AB}^{-1} \frac{C_A}{C_B}$$

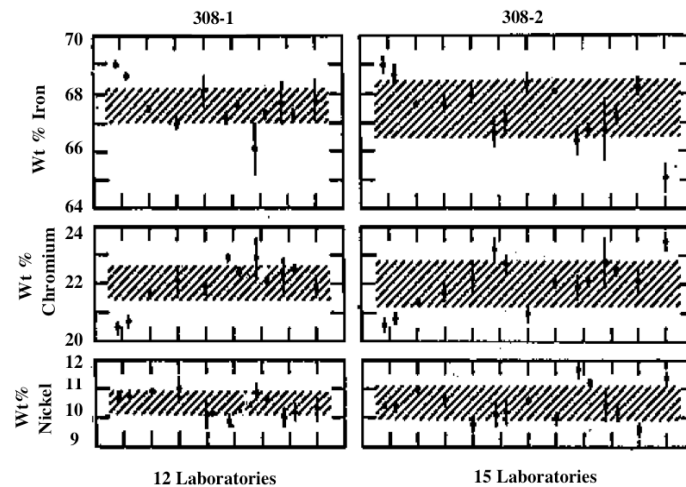
or
$$C_A + C_B = 1.$$

$$C_B \left(\frac{C_A}{C_B} + 1 \right) = 1$$

Solving for C_B and C_A

$$C_B = \left(\frac{1}{1 + \frac{C_A}{C_B}} \right) = \left(\frac{1}{1 + \frac{I_A}{I_B} * k_{AB}} \right) \text{ and } C_A = C_B - 1$$

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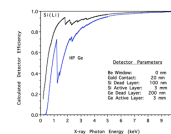


Vitek et al, AEM, 1984

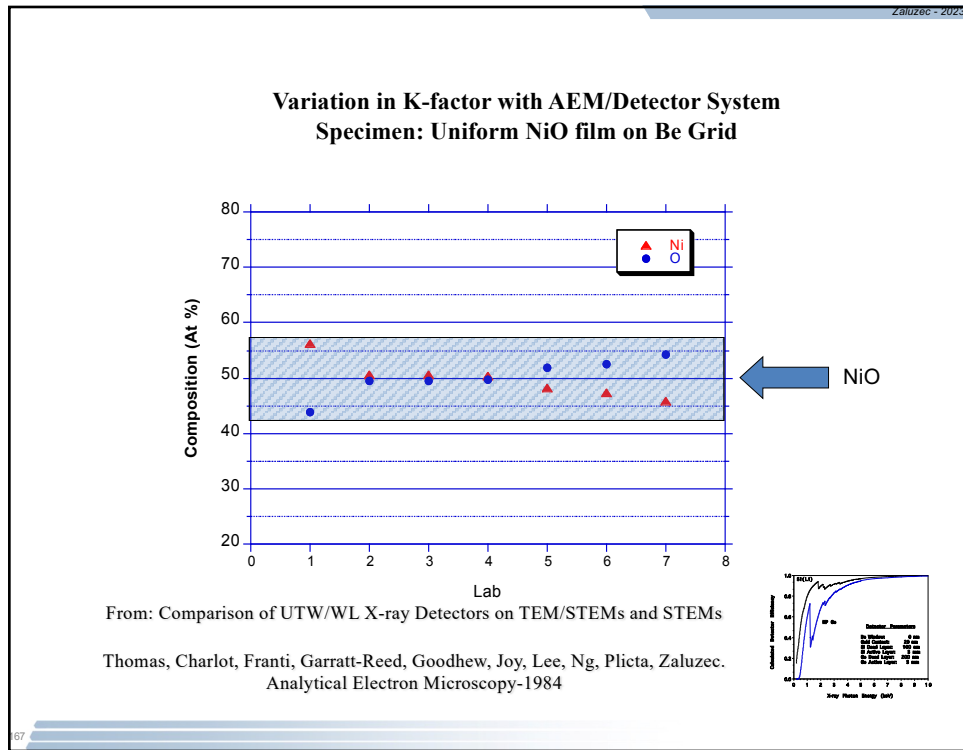
Variation in Measured Composition on 308 SS for Different Labs

Example in which K-factor is stable : Cr, Fe, Ni

Note: Detector efficiency ~ 100% in this energy range



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Determining the k_{AB}^{-1} Factor

Experimental Measurements

Prepare thin-film standards of known composition
then measure relative intensities and solve explicitly
for the k_{AB} factor needed. Prepare a working data base.

This is the "best" method, but

- specimen composition must be verified independently
- must have a standard for every element to be studied

Theoretical Calculations

Attempt first principles calculation knowing
some fundamental parameters of the AEM system

Start with a limited number of k_{AB} factor measurements,
then fit the AEM parameters to best match the data.
Extrapolate to systems where measurements and/or
standards do not exist.

- **Method 1.** (Goldstein et al) Assume values for $\Gamma_{i,0}, \epsilon$ and determine the best σ to fit k_{AB} . This procedure essentially iterates the fit of σ to the data.

Method 2. (Zaluzec) Assume values for $\Gamma_{i,0}, \sigma$ and determine the best ϵ to fit k_{AB} . This procedure essentially iterates the fit of ϵ (detector window parameters) to the data.

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Sources of values for k_{AB} Calculations

- W - International Tables of Atomic Weights
- $\Gamma(K)$ - Schreiber and Wims, X-ray Spectroscopy (1982)
Vol 11, p. 42
- $\Gamma(L)$ - Scofield, Atomic and Nuclear Data Tables (1974)
Vol 14, #2, p. 121
- $\omega(K)$ - Bambynek et al, Rev. Mod. Physics, Vol 44, p. 716
Freund, X-ray Spectrometry, (1975) Vol 4, p.90
- $\omega(L)$ - Krause, J. Phys. Chem. Ref. Data (1974) Vol 8,
p.307
- $\sigma(E_0)$ - Inokuti, Rev. Mod. Physics, 43, No. 3, 297 (1971)
- Goldstein et al, SEM 1, 315, (1977)
- Chapman et al, X-ray Spectrometry, 12, 153, (1983)
- Rez, X-ray Spectrometry, 13, 55, (1984)
- Egerton, Ultramicroscopy, 4, 169, (1969)
- Zaluzec, AEM-1984, San Fran. Press. 279, (1984)
- $\epsilon(E)$ - Use mass absorption coefficients from:
-Thinh and Leroux; X-ray Spect. (1979), 8, p. 963
-Henke and Ebsiu, Adv. in X-ray Analysis, 17, (1974)
-Holton and Zaluzec, AEM-1984, San Fran Press, 353, (1984)

Quantitative Analysis using XEDS Standards based Method

Invoke the Intensity Ratio Method, that is consider the ratio of x-ray lines from the same element in both the Unknown and a Standard

$$\frac{I_A^{Unknown}}{I_A^{Standard}} = \frac{C_A^U \eta^U \rho^U t_\rho^U}{C_A^S \eta^S \rho^S t_\rho^S} = K_S^U \left(\frac{C_A^U}{C_A^S} \right)$$

This simple equation states that the relative intensity ratio of the same characteristic x-ray lines is directly proportional to the relative composition ratio of the elemental components multiplied by a proportionality factor which, in the thin film approximation, is *dependent upon ρ , t and η*

NOTE: The K_S^U factor also is not a universal constant, and requires an accurate measurement/determination of density, thickness and beam current.

Quantitative Analysis using XEDS

 ζ = factor Method

Rearrange the Intensity Equation

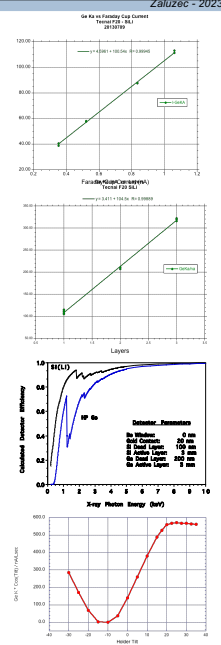
$$I_A^{K\alpha} = \left(\sigma_A(E, Z) \Gamma_A \omega_A \right) C_A \left(\frac{N_o \rho}{W_A} \right) \left(\eta_o t \right) \left(\epsilon_A \Omega \right)$$

Recognize

$$\rho t = \frac{I_A^{K\alpha} W_A}{\left(\sigma_A(E, Z) \Gamma_A \omega_A \right) \left(C_A N_o \right) \left(\eta_o t \right) \left(\epsilon_A \Omega \right)} = \zeta_A \frac{I_A^{K\alpha}}{C_A n_o}$$

With

$$\zeta_A = \frac{W_A}{\left(\sigma_A(E, Z) \Gamma_A \omega_A \right) \left(N_o \right) \left(\epsilon_A \Omega \right)}$$



M. Watanabe & D.B. Williams, J. Microsc. 221 (2006) 89-109.

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 ζ -Factor Method

LEHIGH

For element A: $\rho t = \zeta_A \frac{I_A}{C_A D_e}$

For element B: $\rho t = \zeta_B \frac{I_B}{C_B D_e}$

In binary system: $C_A + C_B = 1$

Thickness: $\rho t = \frac{\sum \zeta_j I_j}{D_e}$

Composition:

$$C_A = \frac{\zeta_A I_A}{\rho t} = \frac{\zeta_A I_A}{\sum \zeta_j I_j}$$

 D_e : total number of incident electrons

Features

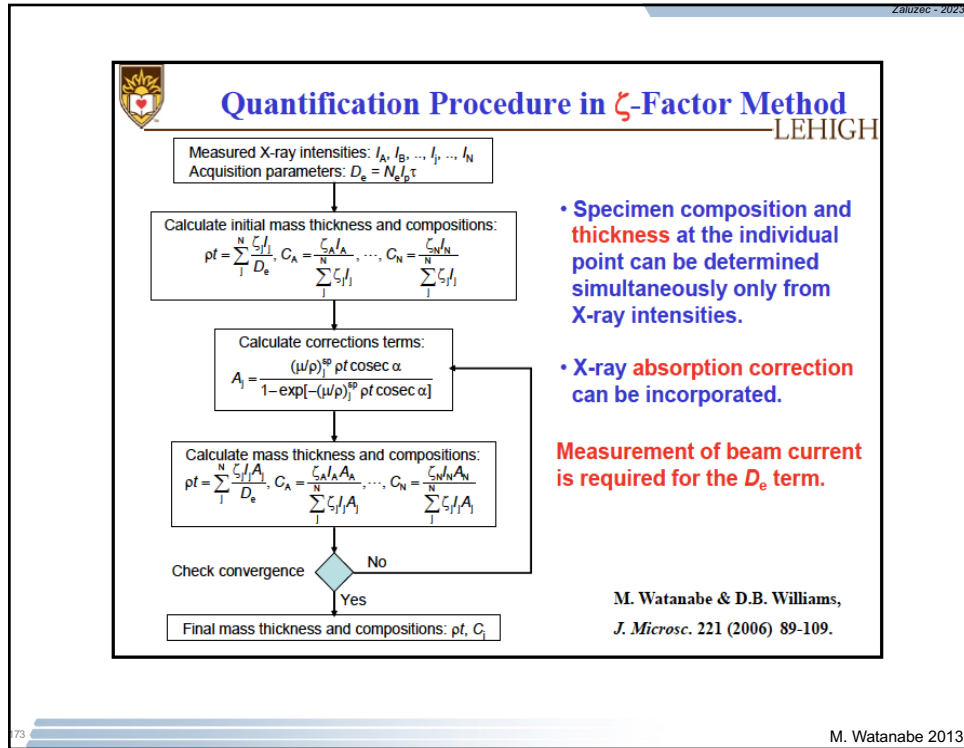
- Specimen composition and thickness at the individual point can be determined simultaneously only from X-ray intensities.
- X-ray absorption correction can be incorporated.
- Simultaneous estimation of spatial resolution and analytical sensitivity (MMF & MDM).

Measurement of beam current is required for the D_e term.

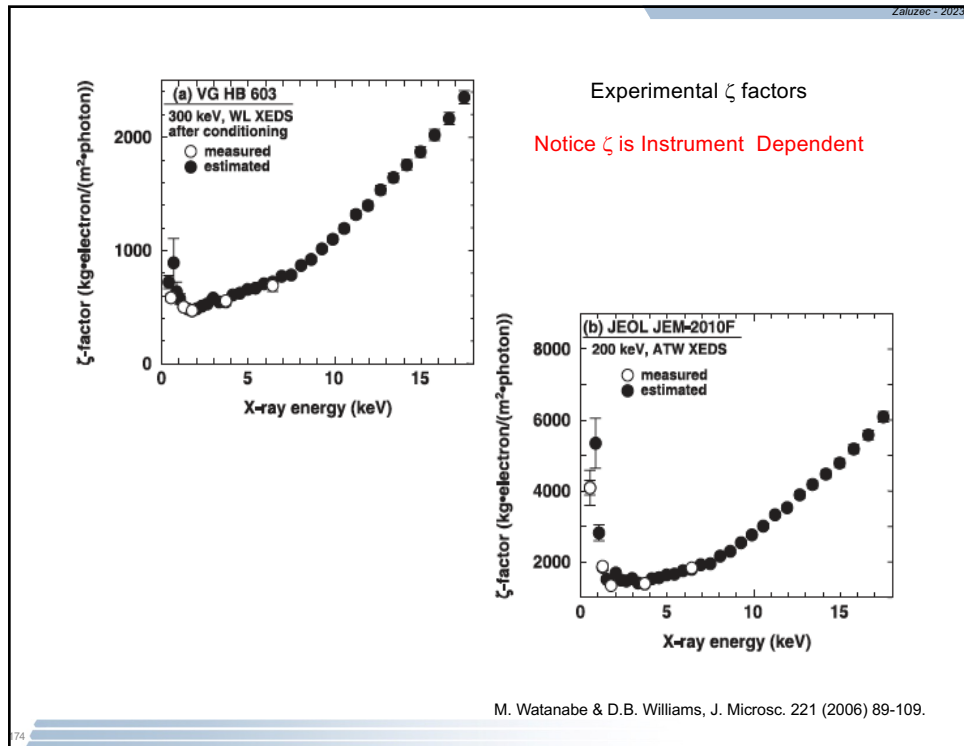
M. Watanabe & D.B. Williams, J. Microsc. 221 (2006) 89-109.

M. Watanabe 2013

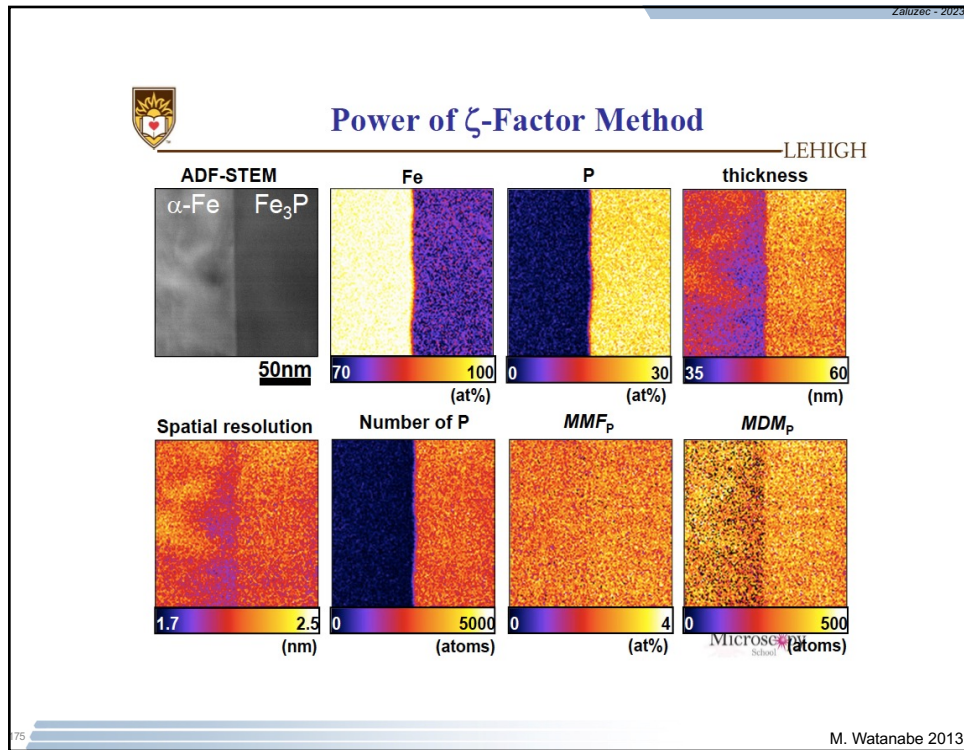
172



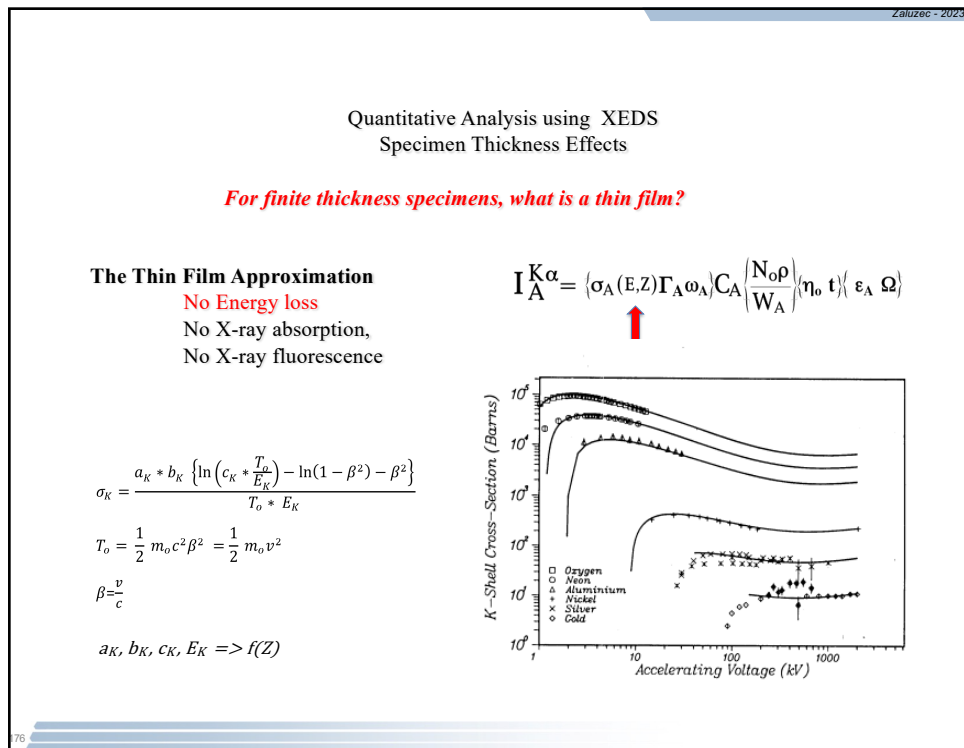
173



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Consider the mean energy loss of a electron beam ($\frac{dE}{ds}$) going through a film of thickness = "t". Let s = electron pathlength (~thickness) then (Inokuti -1971):

$$\frac{dE}{ds} = \frac{\pi e^4 N_0 \rho Z}{WE} \left\{ \ln \left(\frac{2ET_E}{J^2(1-\beta^2)} \right) - 2 \ln(2) \sqrt{(1-\beta^2)} + 1 - \beta^2 + \frac{(1-\sqrt{1-\beta^2})^2}{8} \right\}$$

with the following new definitions

$$E = \frac{1}{2} m_0 c^2 \beta^2, \quad T_E = eV_0, \quad J = 9.29 \times 10^{-3} Z (1 + 1.287 Z^{-2/3})$$

Calculated Energy Losses (eV) as a function of pathlength

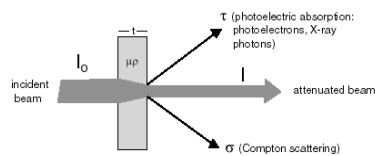
Voltage	Pathlength	Al	Ni
100 kV	100 nm	87	255
	400 nm	349	1020
300 kV	100 nm	51	150
	400 nm	203	60

∴ For conventional specimen thicknesses used in AEM, the effect of energy loss on characteristic x-ray production is negligible.

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When is the specimen "Thin" ?

- No Electron Energy loss
- No X-ray absorption
- No X-ray fluorescence



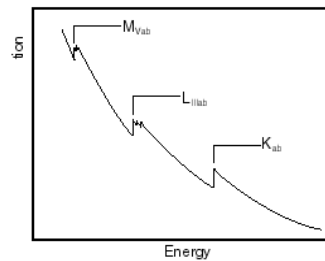
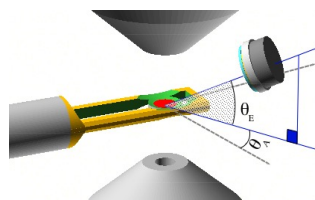
$$\mu = \tau + \sigma$$

where μ = bulk mass absorption coefficient,
 τ = photoelectric absorption coefficient,
 σ = Compton scattering coefficient

$$I = I_0 e^{-\mu \rho t}$$

where I_0 = initial intensity (cps),
 I = final intensity (cps),
 μ = bulk mass absorption coefficient of the material (cm^2/g),
 ρ = density of the material (g/cm^3),
and t = thickness of the material (cm).

$$I(\Omega, t) = \iint_{t, \Omega} I_0 \exp[-X \rho t(\Omega)] d\Omega$$

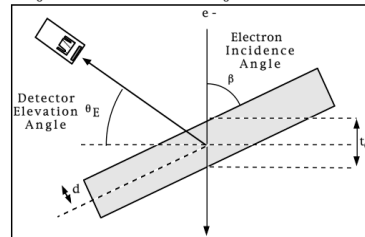


178

Quantitative Analysis using XEDS : Absorption Correction

Consider simple absorption model for x-rays leaving the specimen

$$I = \int_0^{t_0} I_0(t) \exp(-\mu^* d) dt = \int_0^{t_0} I_0(t) \exp(-\chi \rho t) dt$$



Parallel Slab Geometry

$$d = \text{Absorption Pathlength from the specimen to detector}$$

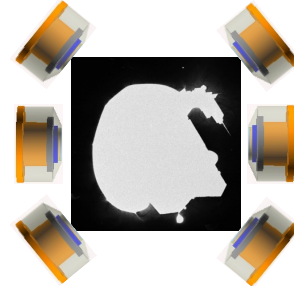
$$= t \frac{\sin(\beta)}{\cos(\beta - \theta_E)}$$

$$\chi = \text{Geometrical factor multiplied by average mass absorption coefficient for the measured x-ray line in the compound}$$

$$= \left(\frac{\mu}{\rho} \right)_{\text{Spec.}} \frac{\sin(\beta)}{\cos(\beta - \theta_E)}$$

$$\left(\frac{\mu}{\rho} \right)_{\text{Spec.}} = \text{Weighted average mass absorption coefficient}$$

$$= \sum_{i=1}^N \left(\frac{\mu}{\rho} \right)_i \cdot C_i \quad (\text{Note: composition dependent!})$$



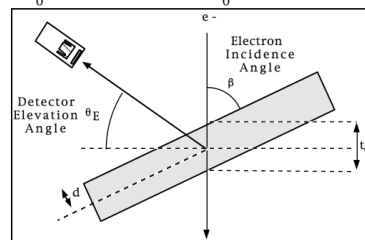
Where is the XEDS detector?
Are there multiple detectors?
What is the Geometry to each?

179

Quantitative Analysis using XEDS : Absorption Correction

Consider simple absorption model for x-rays leaving the specimen

$$I = \int_0^{t_0} I_0(t) \exp(-\mu^* d) dt = \int_0^{t_0} I_0(t) \exp(-\chi \rho t) dt$$



Parallel Slab Geometry

$$d = \text{Absorption Pathlength from the specimen to detector}$$

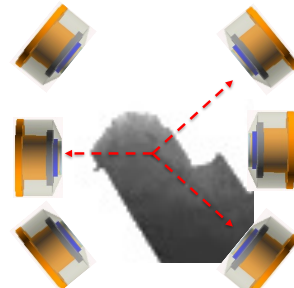
$$= t \frac{\sin(\beta)}{\cos(\beta - \theta_E)}$$

$$\chi = \text{Geometrical factor multiplied by average mass absorption coefficient for the measured x-ray line in the compound}$$

$$= \left(\frac{\mu}{\rho} \right)_{\text{Spec.}} \frac{\sin(\beta)}{\cos(\beta - \theta_E)}$$

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$$= \sum_{i=1}^N \left(\frac{\mu}{\rho} \right)_i \cdot C_i \quad (\text{Note: composition dependent!})$$



Where is the XEDS detector?
Are there multiple detectors?
What is the Geometry to each?

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Now rederive the standardless equations to include absorption.

$$\frac{I_A}{I_B} = \frac{\epsilon_A}{\epsilon_B} * \frac{\kappa_A}{\kappa_B} * \frac{\delta_A}{\delta_B} * \frac{C_A}{C_B}$$

with

$$\frac{\delta_A}{\delta_B} = \frac{\left(\frac{\mu}{\rho}\right)_{AB}^{B \text{ in}} (1 - \exp(-\chi \rho t^*))_{AB}^{A \text{ in}}}{\left(\frac{\mu}{\rho}\right)_{AB}^{A \text{ in}} (1 - \exp(-\chi \rho t^*))_{AB}^{B \text{ in}}}$$

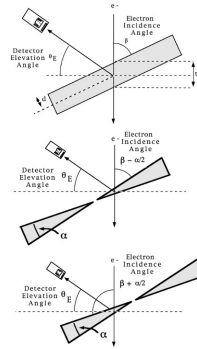
$$t^* = t_0 \frac{\sin(\beta)}{\cos(\beta - \theta_E)}$$

$$\chi = \left(\frac{\mu}{\rho}\right)_{\text{X-ray in Compound}} = \sum_{i=1}^N \left(\frac{\mu}{\rho}\right)_i * C_i$$

$$\beta = \text{Electron Incidence Angle} \Rightarrow \beta \pm \alpha$$

$$= \text{Function of Stage Tilts: } \phi_x, \phi_y, \text{ \& Detector Azimuth } \theta,$$

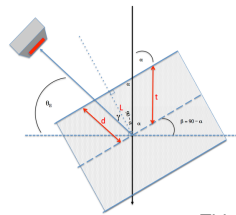
$$\theta_E = \text{Detector Elevation Angle}$$



Define the Thin Film approximation: $\chi \rho t^* < 0.1$

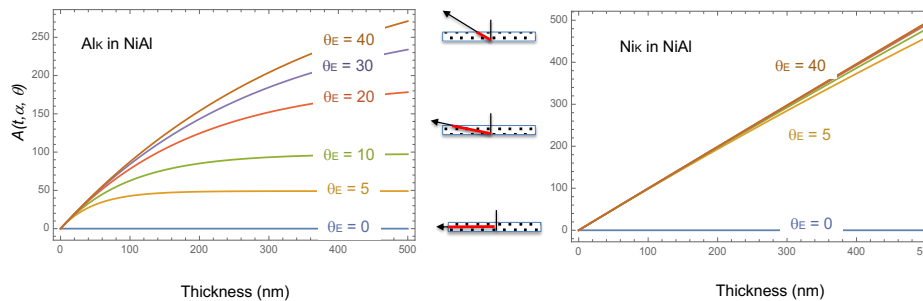
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X-ray Absorption $A(t, \alpha, \theta)$ for parallel slab film geometry with a "Point Detector"



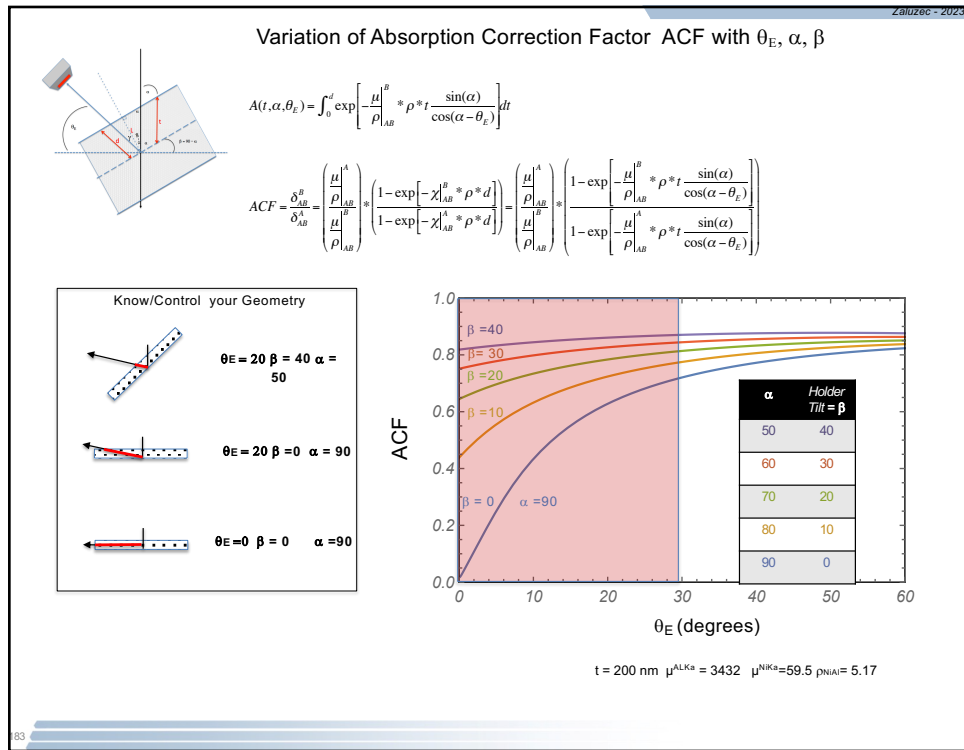
$$A(t, \alpha, \theta_E) = \frac{I(t, \alpha, \theta_E)}{I_0} = \int_0^t \exp\left[-\frac{\mu}{\rho}\right]_{AB} * \rho * t \frac{\sin(\alpha)}{\cos(\alpha - \theta_E)} dt$$

Thickness, geometry and μ/ρ are all important parameters

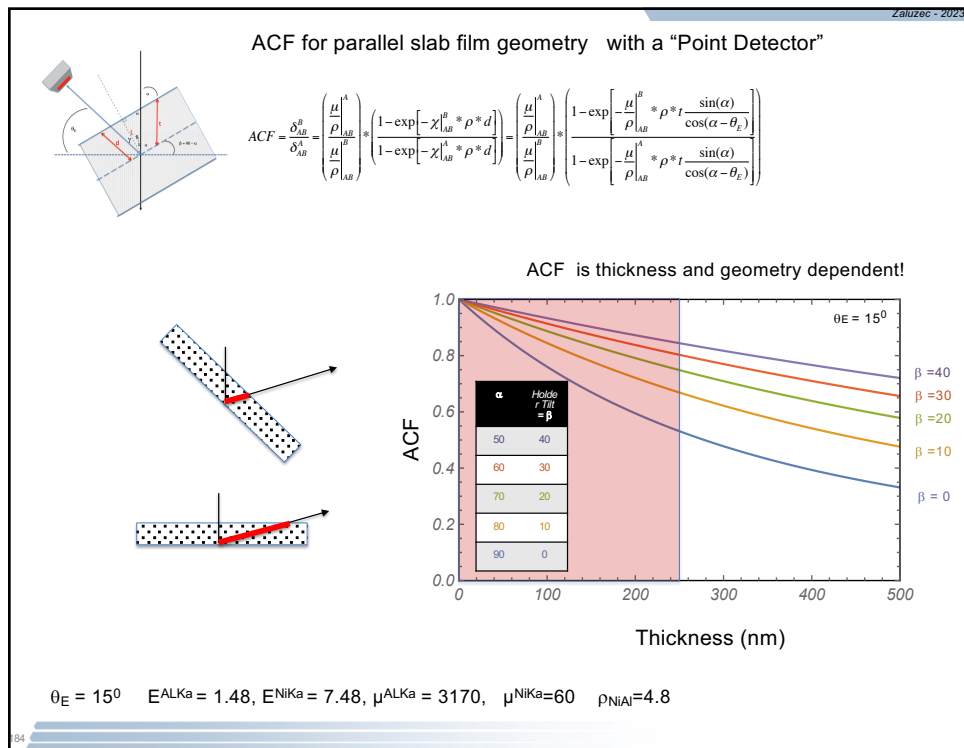


$$\mu^{AlK\alpha} = 3432 \quad \mu^{NiK\alpha} = 59.5 \quad \rho_{NiAl} = 5.17 \quad 0^\circ \leq \theta_E \leq 40^\circ \quad \alpha = 90^\circ \quad \beta = 0^\circ$$

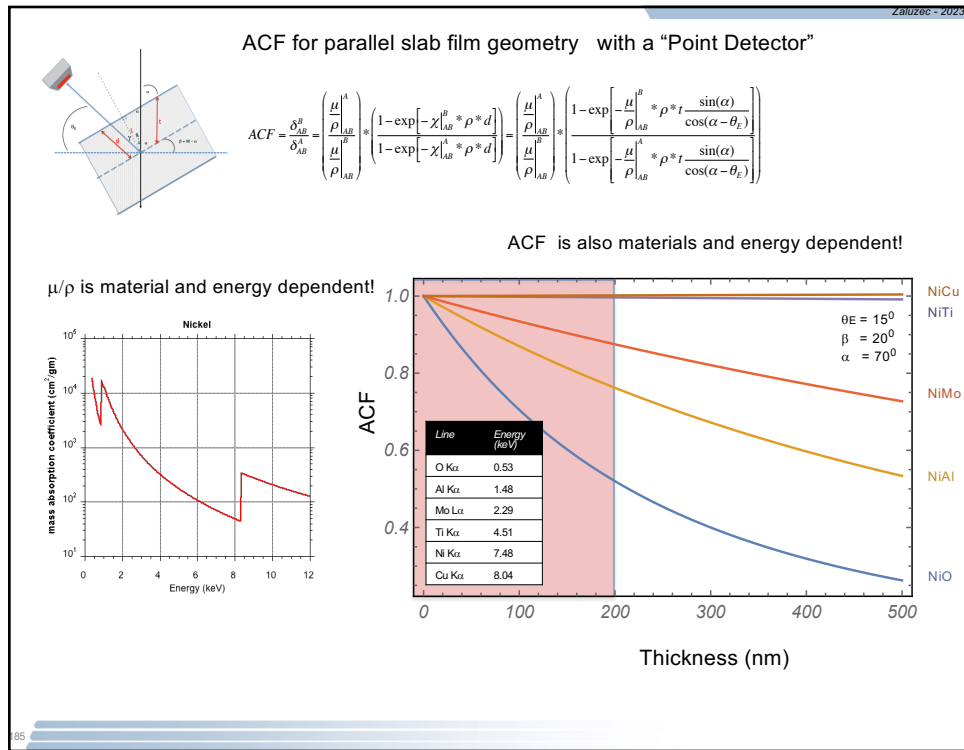
182



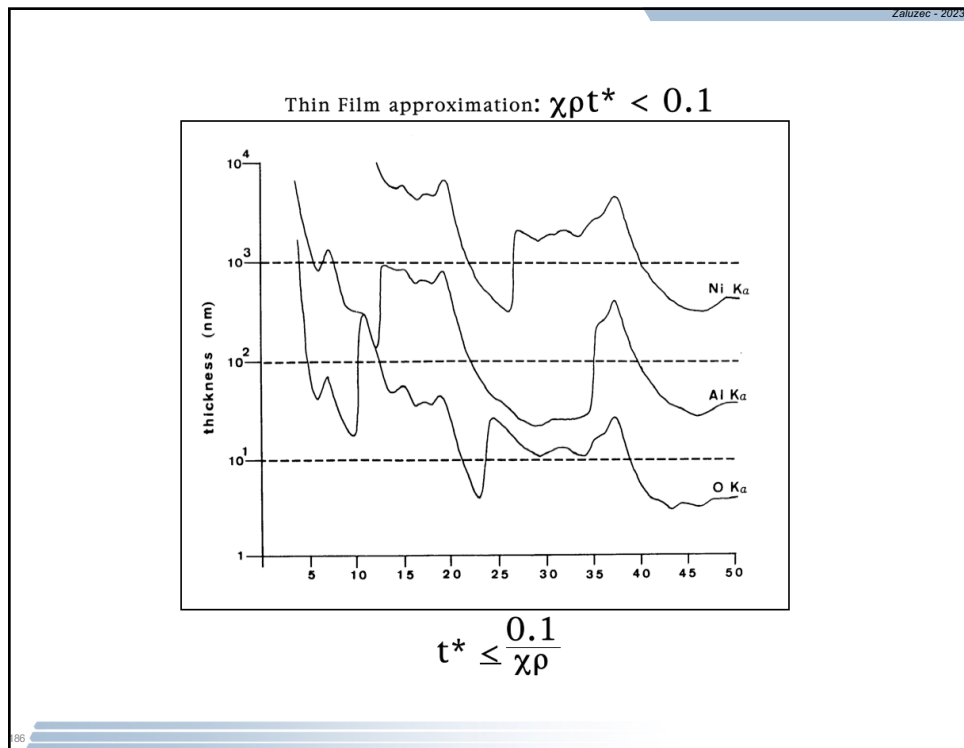
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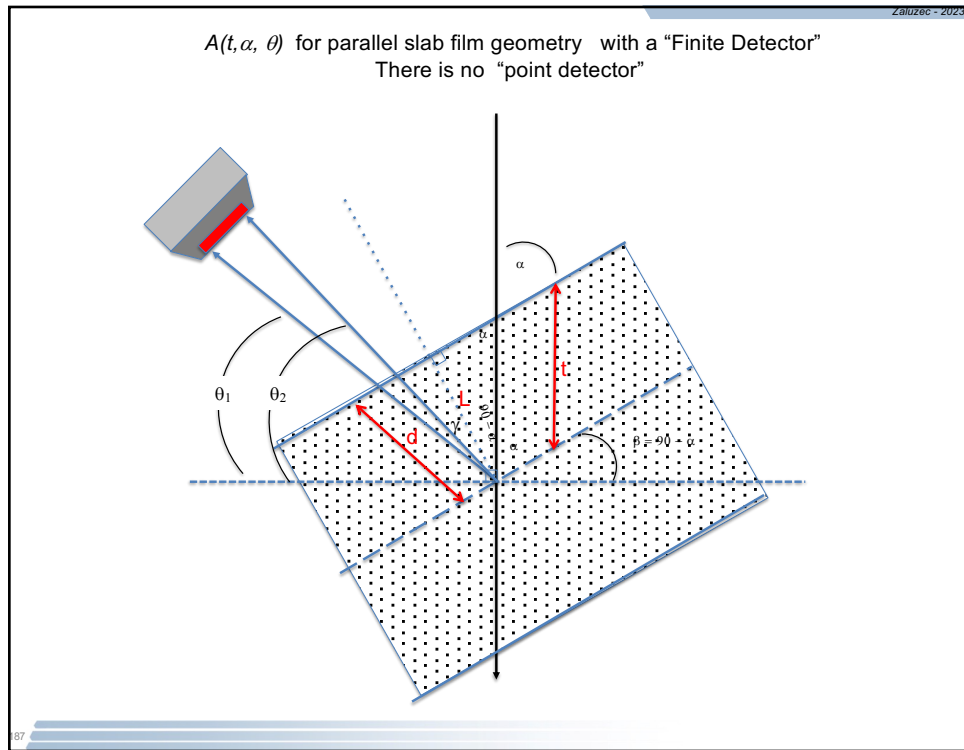
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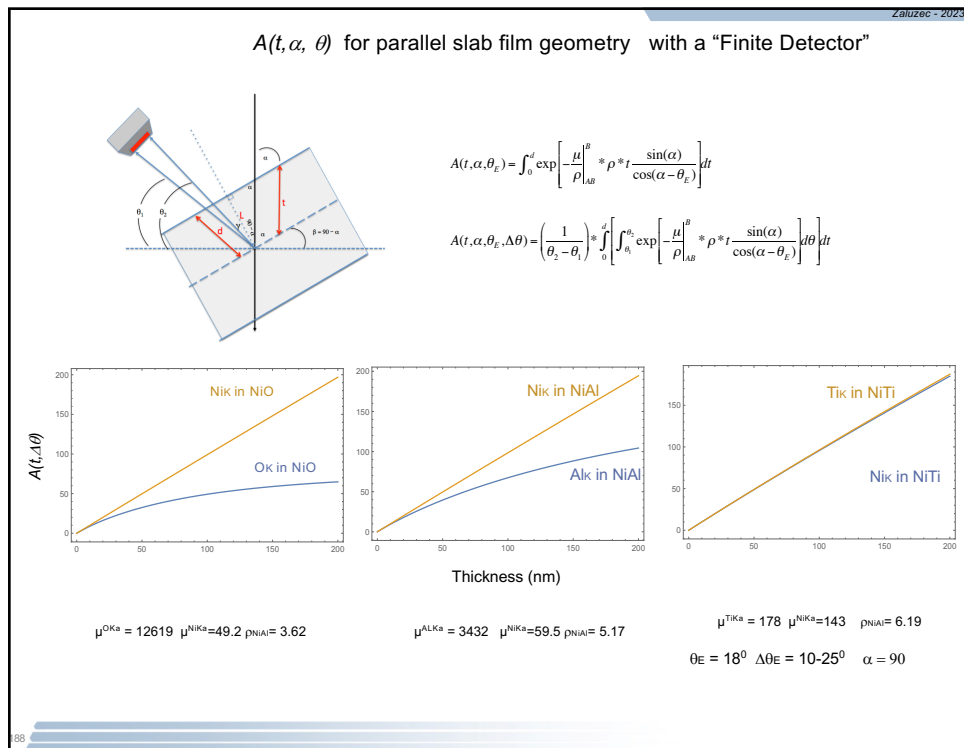
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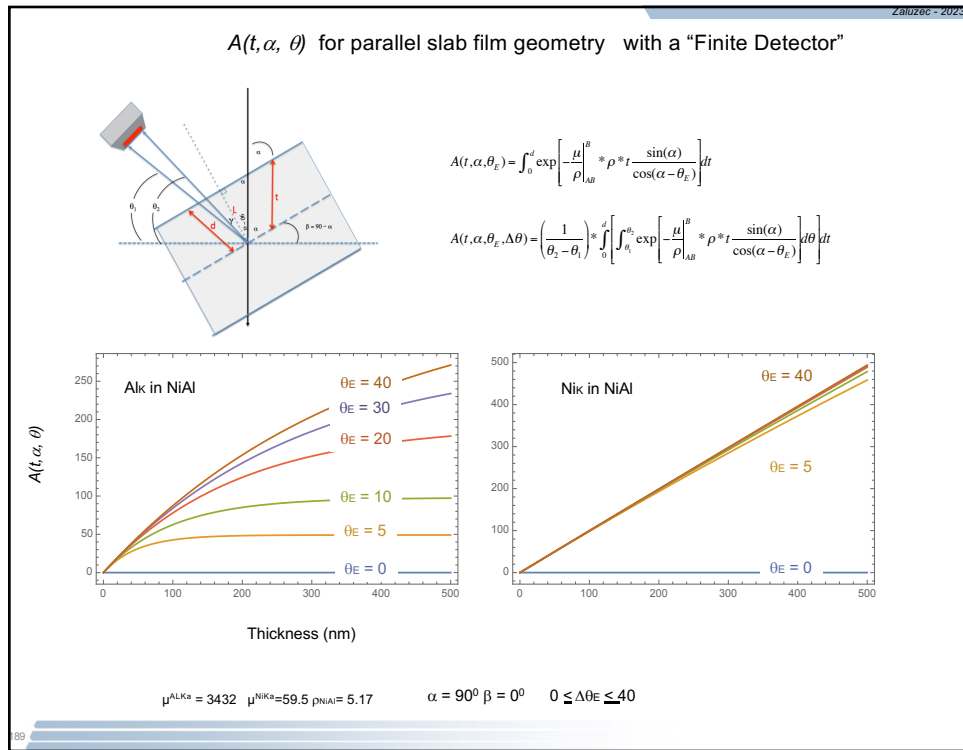
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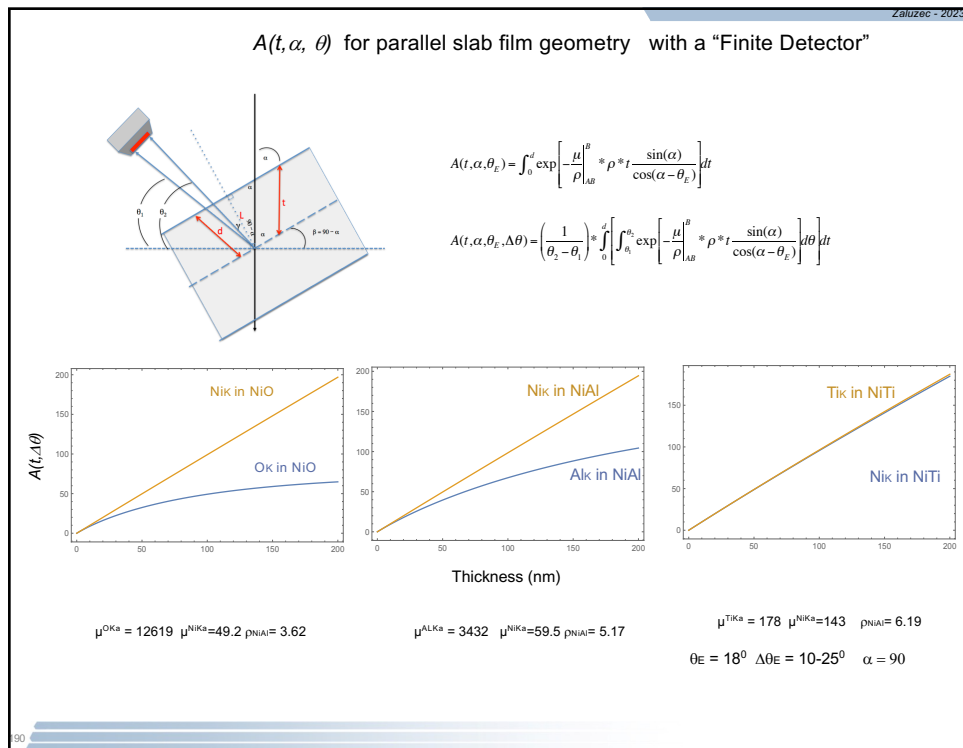
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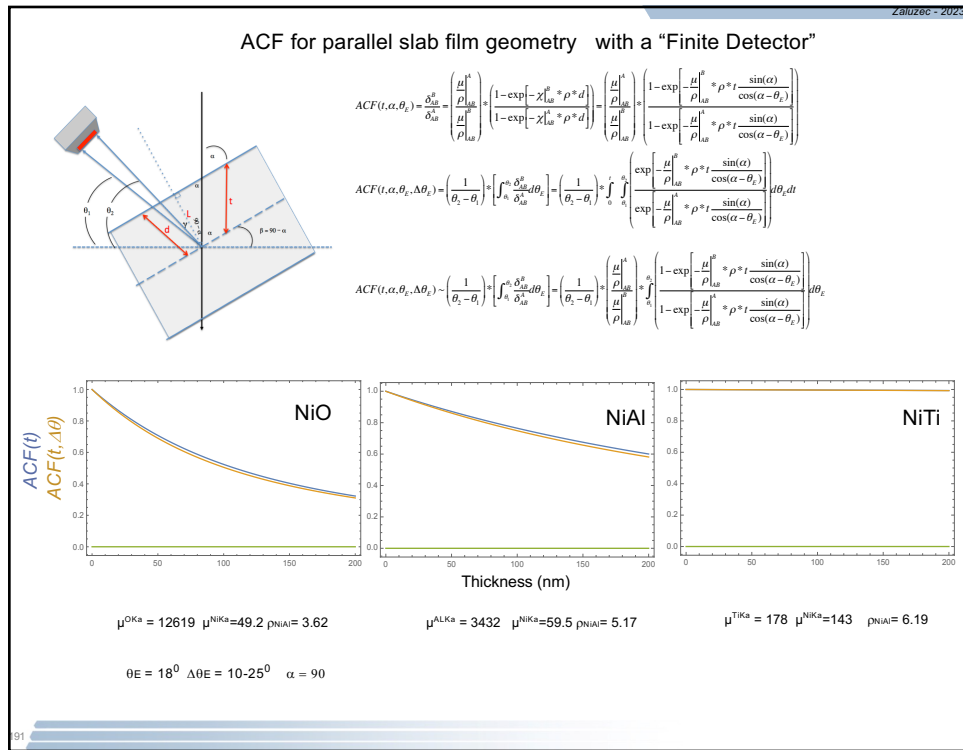
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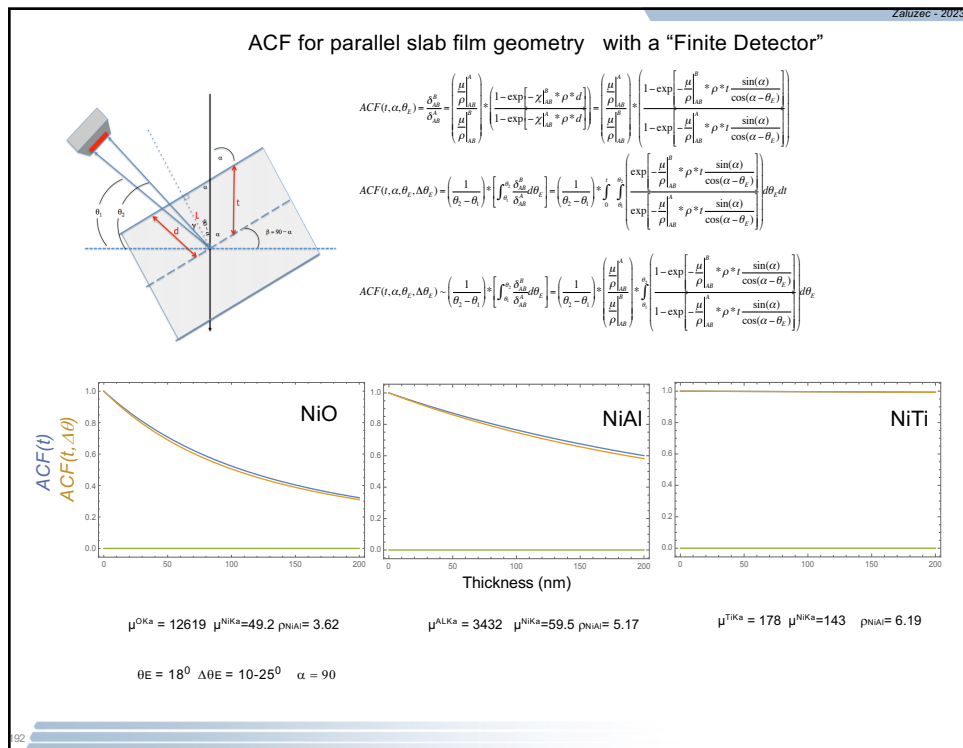
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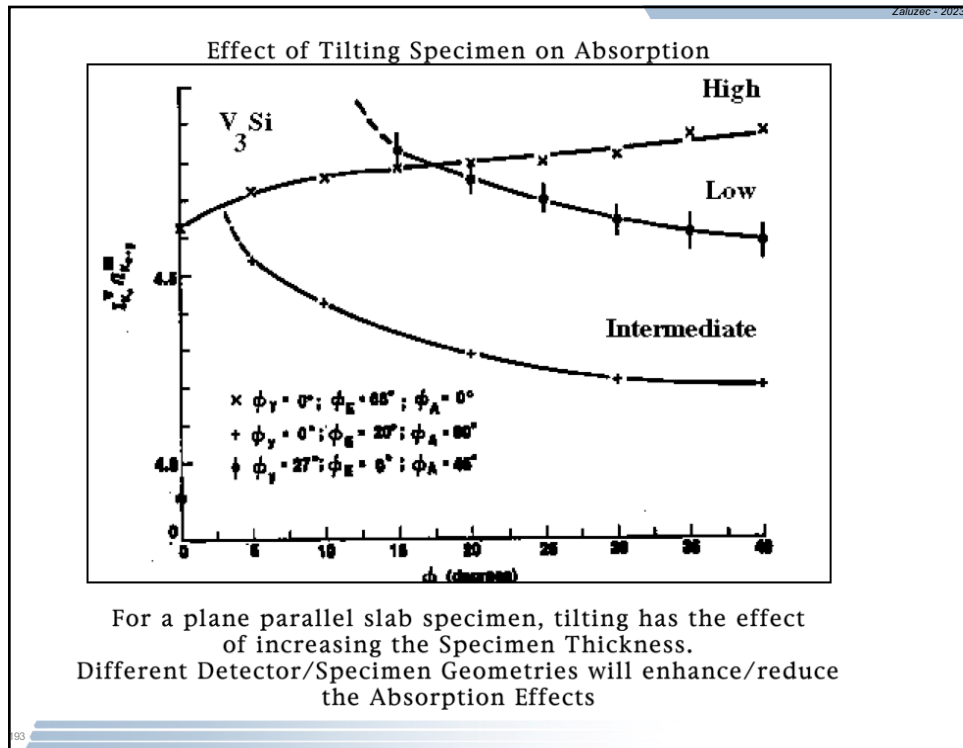
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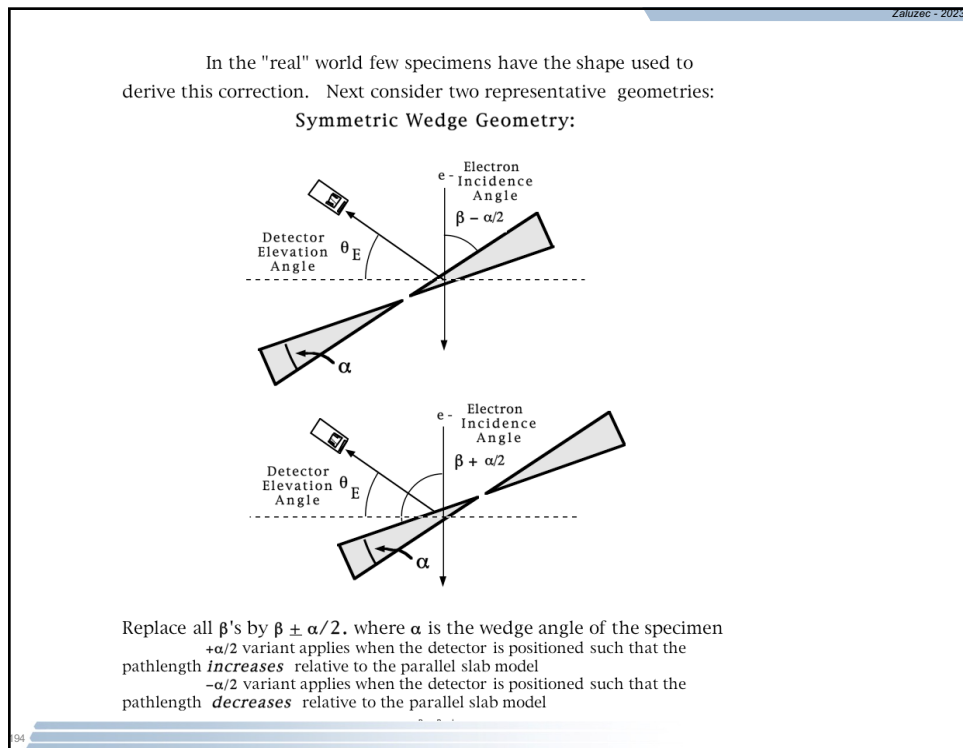
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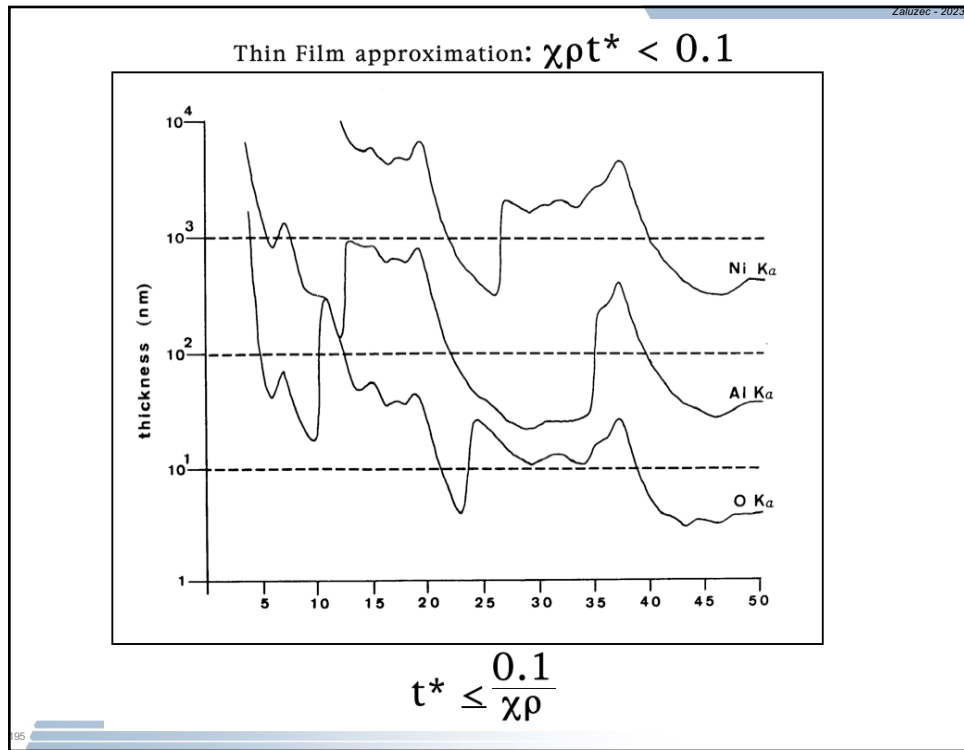
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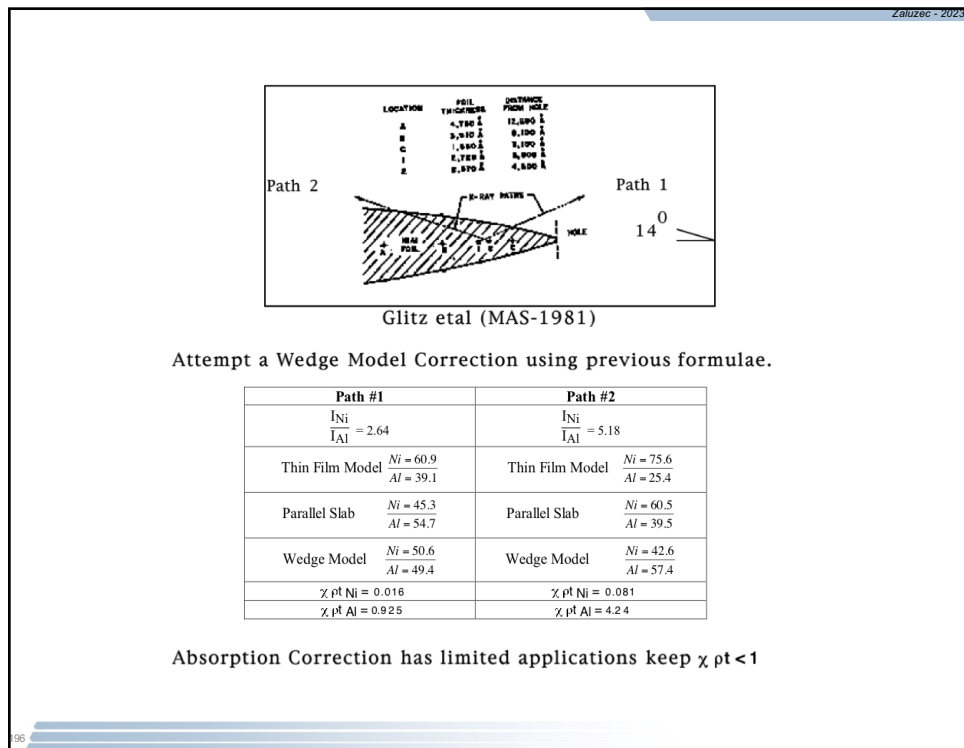
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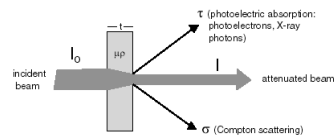
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Quantitative Analysis using XEDS Specimen Thickness Effects

For finite thickness specimens, what is a thin film?

Previous Assumptions:

Energy loss,
X-ray absorption,
No X-ray fluorescence

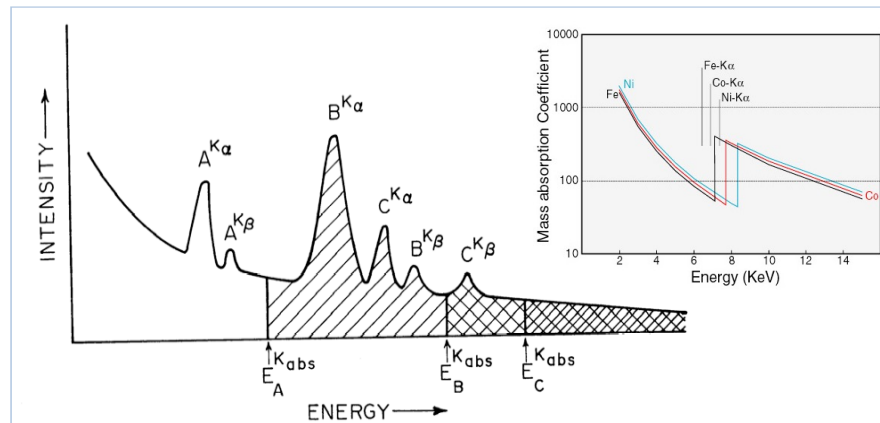


$$I = I_0 e^{-\mu \rho t}$$

where I_0 = initial intensity (cps),
 I = final intensity (cps),
 μ = bulk mass absorption coefficient of the material (cm^2/g),
 ρ = density of the material (g/cm^3),
and t = thickness of the material (cm).

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X-Ray Fluorescence Correction



$$I_A^{\text{Measured}} = I_A^{\text{Electron}} + I_A^{\text{XRF by B}}$$

$$I_A^{\text{Measured}} = I_A^{\text{Electron}} \left(1 + \frac{I_A^{\text{XRF by B}}}{I_A^{\text{Electron}}} \right)$$

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Calculation of the Intensity of I_A x-rays due to fluorescence by I_B

$$dI_A^{\text{XRF by B}} = I_B \cdot \left[\exp \left(-\left(\frac{\mu^B}{\rho}\right)_{AB} \rho z \csc \phi \right) \right] \cdot \left[\rho C_A \left(\frac{\mu^B}{\rho}\right)_A \csc \phi \right] \cdot \left[\left(\frac{\Delta \mu}{\mu}\right)_A \right] \cdot \left[\omega_A \cdot \Gamma_A \right]$$

$$dI_A^{\text{XRF by B}} = I_B \cdot P_A^{\text{XRF by B}} dz d\phi$$

$\left[\exp \left(-\left(\frac{\mu^B}{\rho}\right)_{AB} \rho z \csc \phi \right) \right]$	Fraction of B x-rays that are absorbed in the material AB on leaving at angle ϕ from depth z
$\left[\rho C_A \left(\frac{\mu^B}{\rho}\right)_A \csc \phi \right]$	Probability that B x-rays are absorbed by atoms of type A
$\left[\left(\frac{\Delta \mu}{\mu}\right)_A \right]$	Probability that upon absorption the K-Shell is ionized for A
$\left[\omega_A \cdot \Gamma_A \right]$	Probability that a $K\alpha$ x-ray is emitted

Now integrate this over the specimen geometry $\phi=4\pi$, T =thickness

$$I_A^{\text{XRF}} = \int_0^T \int_0^{4\pi} dI_A^{\text{XRF}} = \int_0^T \int_0^{4\pi} I_B \cdot P_A^{\text{XRF}} dz d\phi$$

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Substituting for I_B and dividing by I_A and generalizing to element i

$$\frac{I_A^{\text{XRF by } i}}{I_A} = C_i \omega_i \Gamma_i \frac{A_A}{A_i} \frac{Q_i}{Q_A} \left(\frac{\Delta \mu}{\mu}\right)_A \left(\frac{\mu^i}{\rho}\right)_{Ai} \int_0^T \int_0^{4\pi} (\text{terms in Exp \& cosec } \phi) dz d\phi$$

Solution depends on the geometric assumptions
(see for example Twigg & Fraser MAS, 1982)

$$\frac{I_A^{\text{XRF by } i}}{I_A} = C_i \omega_i \Gamma_i \frac{A_A}{A_i} \frac{Q_i}{Q_A} \left(\frac{\Delta \mu}{\mu}\right)_A \left(\frac{\mu^i}{\rho}\right)_A \frac{\rho T}{2} \left[1.12 + \left(\frac{\mu^i}{\rho}\right)_{Ai} \cdot \frac{\rho T}{4} - \ln \left(\left(\frac{\mu^i}{\rho}\right)_{Ai} \cdot \rho T \right) \right]$$

for a plane parallel slab specimen

$$\text{Define } \gamma_A = \left(1 + \sum_{i=1}^N \frac{I_A^{\text{XRF by } i}}{I_A^{\text{Electron}}} \right)$$

200

Next rederive the standardless equations to include x-ray fluorescence and you can show.

$$\frac{I_A}{I_B} = \frac{\epsilon_A}{\epsilon_B} * \frac{\kappa_A}{\kappa_B} * \frac{\delta_A}{\delta_B} * \frac{\gamma_A}{\gamma_B} * \frac{C_A}{C_B}$$

as in the case of x-ray absorption this requires iterative solution because the ratio of γ 's are composition dependent..

When is the XRF Correction important?

- When fluorescing line is near the absorption edge of the lower energy line. Typically within a few atomic numbers (i.e. Z+2 to Z+6)
- When specimen is thick or path length is long

Define a thin film approximation for XRF as:

$$\frac{I_A^{\text{XRF by i}}}{I_A^{\text{Electron}}} < 0.05$$

$$C_i \omega_i \Gamma_i \frac{A_A}{A_i} \frac{Q_i}{Q_A} \left(\frac{\Delta\mu}{\mu} \right)_A \left(\frac{\mu^i}{\rho} \right)_A \frac{\rho T}{2} \left[1.12 + \left(\frac{\mu^i}{\rho} \right)_{Al} \cdot \frac{\rho T}{4} - \ln \left(\left(\frac{\mu^i}{\rho} \right)_{Al} \cdot \rho T \right) \right] < 0.05$$

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Examples Absorption & Fluorescence Corrections

Assume 100 kV, $\theta_A = 90^\circ$, $\theta_E = 20^\circ$, $\beta = 35^\circ$, $\alpha = 0^\circ$ i.e. tilted parallel slab

Ni 90%, Fe 10%

Calculation of Thin Film approximation $\chi_{pt} \Rightarrow 1.25\mu\text{m}$ for Fe in the Alloy

$\therefore$ for TEM specimens we can almost always ignore absorption effects

What about XRF?

$$\text{Let } T = 5000\text{\AA} \quad \frac{I_{\text{Fe}}^{\text{XRF by Ni}}}{I_{\text{Fe}}^{\text{Electron}}} = 0.103 \text{ i.e. } \sim 10\%$$

$$\text{Let } T = 1000\text{\AA} \quad \frac{I_{\text{Fe}}^{\text{XRF by Ni}}}{I_{\text{Fe}}^{\text{Electron}}} = 0.028 \text{ i.e. } 2.8\%$$

$\therefore$ for TEM specimens we may be affected by XRF

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Specimen Homogeneity

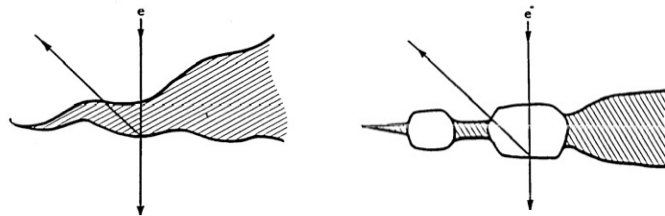
In this and all other derivations we have assumed that over the excited volume, as well as along the exiting pathlength, the specimen is homogeneous in composition. If this assumption is invalid, one must reformulate the absorption correction and take into account changes in μ/ρ , ρ , and t along the exiting pathlength.

Effects of Beam Broadening

Parallel Slab Model: No Change in absorption pathlength
 Wedge Model: There is a correction the magnitude of which varies with the wedge angle.

Effects of Irregular Surface

This cannot be analytically modeled but must be understood!



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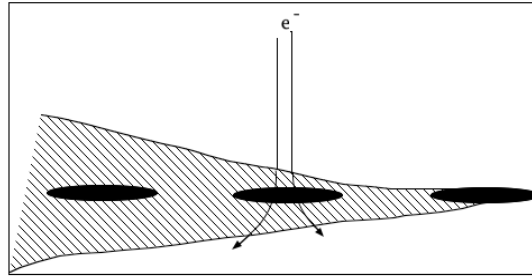
Additional Topics

Heterogeneous Specimens
 Composition Profiles
 Electron Channeling
 Spectral Imaging
 Radiation Damage

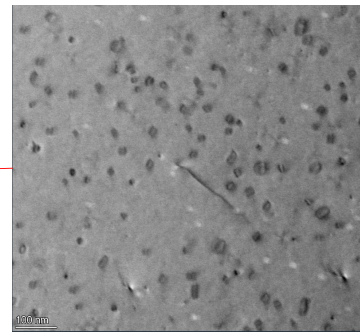
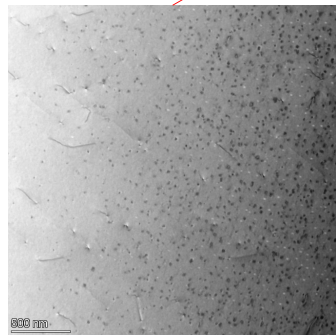
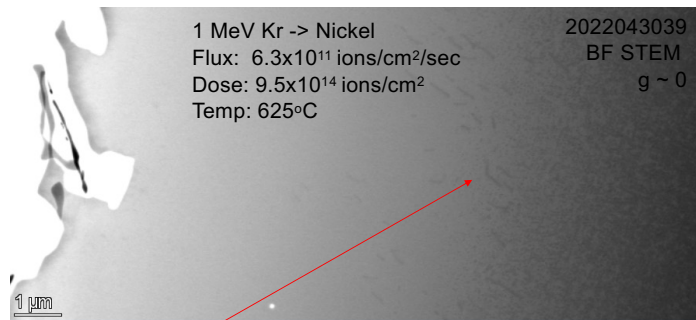
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All quantitative analysis equations were derived assuming that the specimen is homogeneous over the excited volume.

Application of these equations to heterogeneous specimens effectively averages the composition over the excited volume.



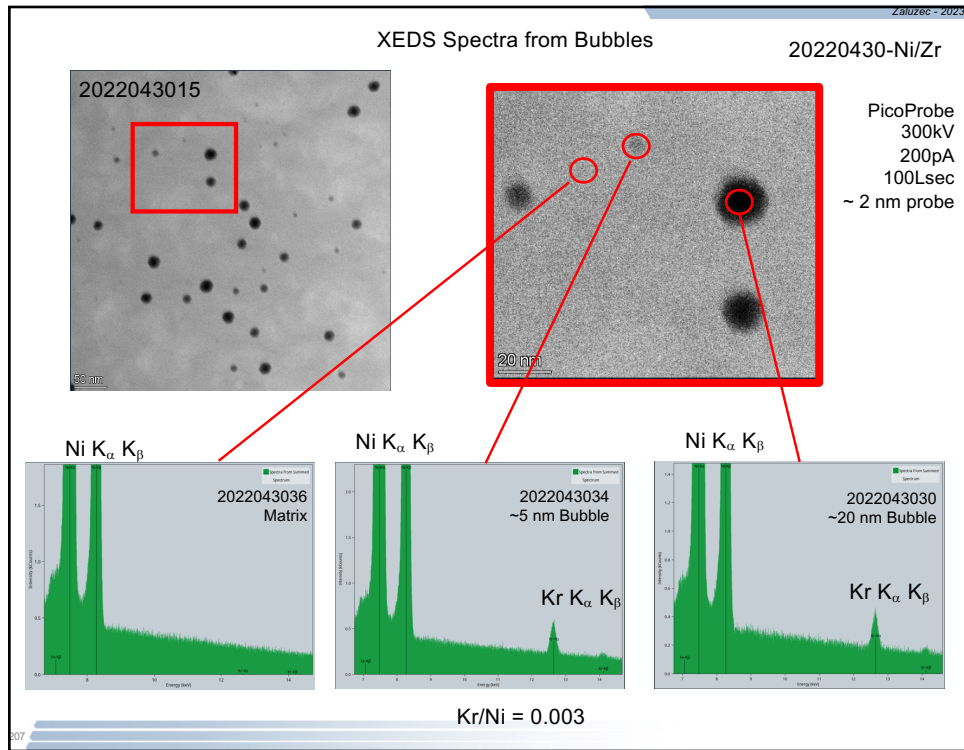
205



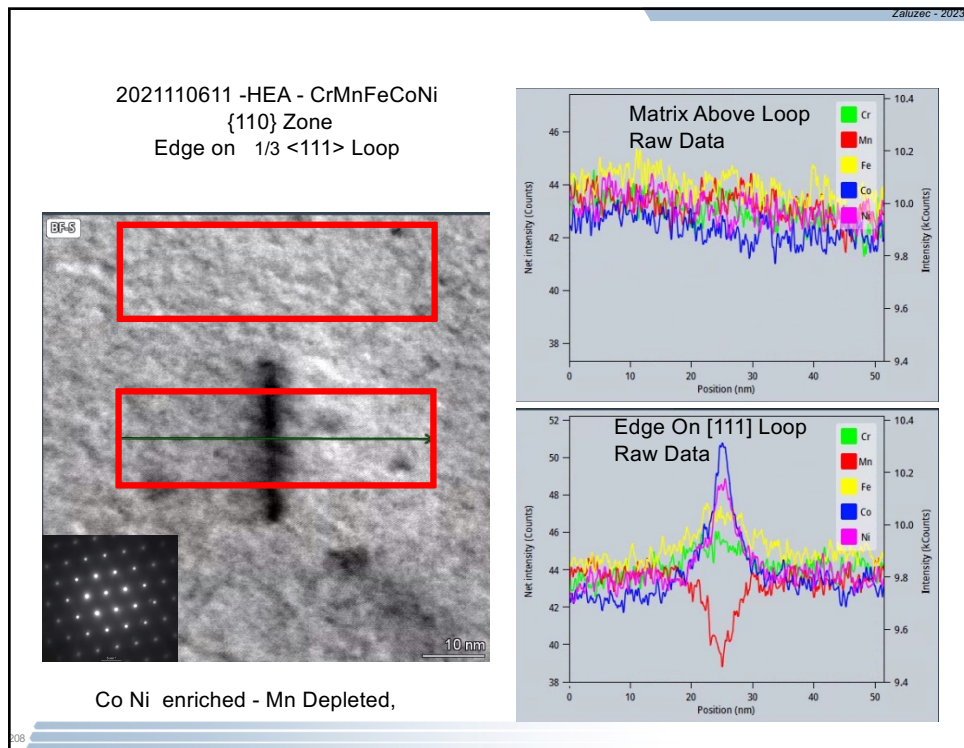
Edge of Damage Zone

g ~ 0 loops in contrast, bubbles present

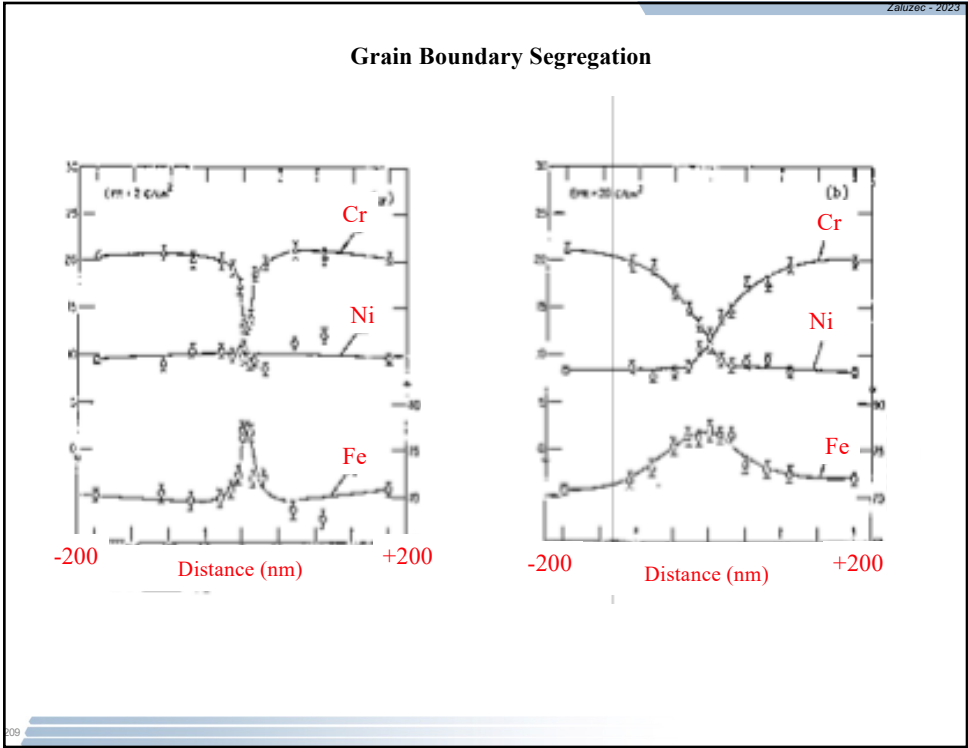
206



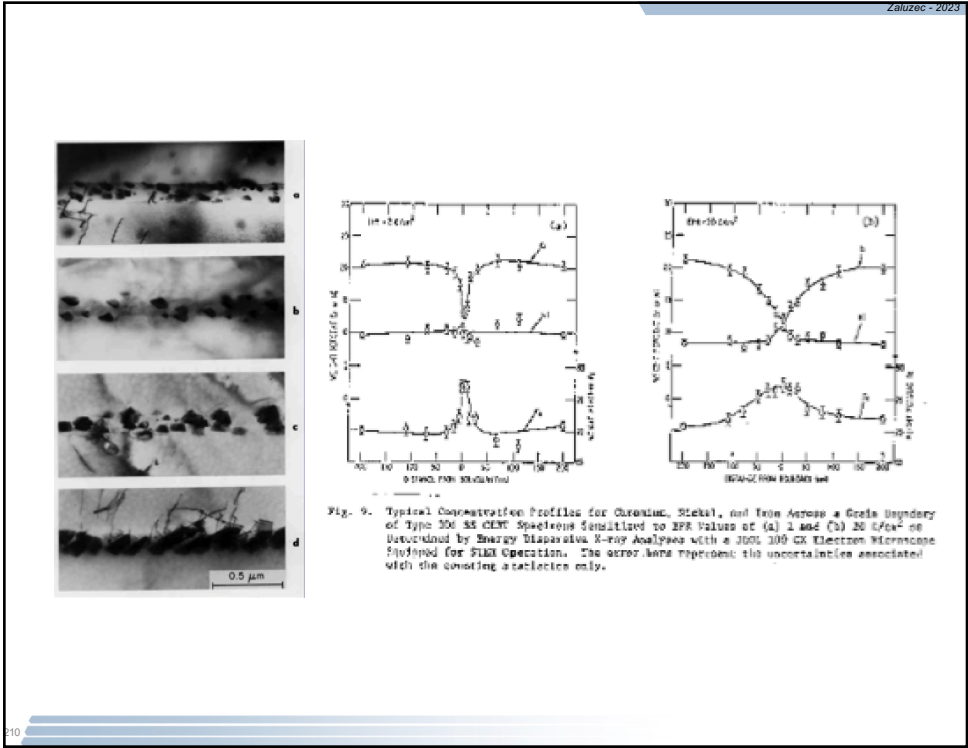
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$$C^*(x,y) = C(x,y,z) * d(x,y,z)$$

$C^*(x,y)$ = Apparent profile measured

$C(x,y,z)$ = Actual composition profile

$d(x,y,z)$ = Incident beam profile

$*$ = Convolution operator

F, F^{-1} = Fourier and Inverse Fourier Transforms

In the 2 dimensional limit one can deconvolute the measured profile using:

$$C(x,y) = F^{-1} \left\{ \frac{F\{C^*(x,y)\}}{F\{d(x,y)\}} \right\}$$

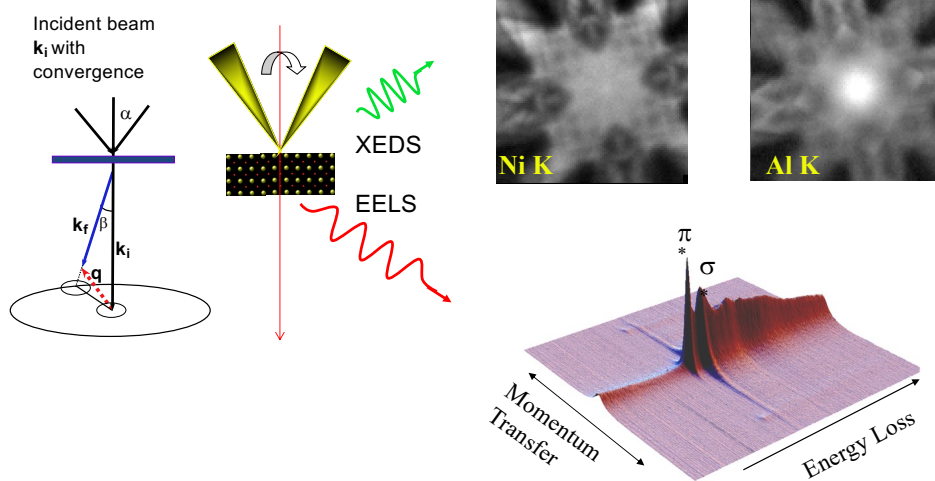
Realistically, it is better to decrease the probe diameter and specimen thickness

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High Angular Resolution (Momentum Resolved) Electron Channeling X-ray/Electron Spectroscopy

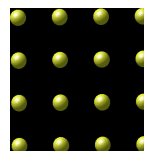
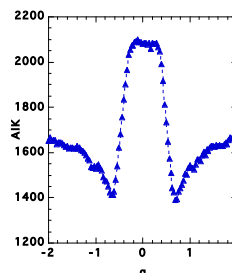


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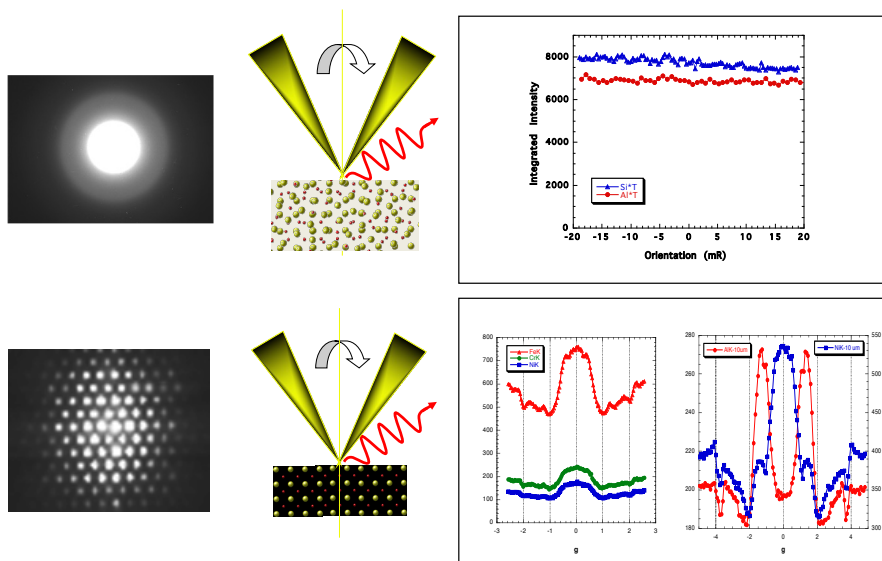
Electron Channeling Induced X-ray Emission

- Characteristic X-ray Emission is not truly isotropic in crystalline materials!
- Original Observations of Effect
 - Duncumb '62, Hall '66, Cherns et al '73
- Predicted Applications
 - Cowley '64, '70
- ACHEMI Technique -
 - Tafto '79, Spence & Tafto '83
- Multi-Variate Statistical Analysis -
 - Rossouw et al, Anderson and others late80' -90' s

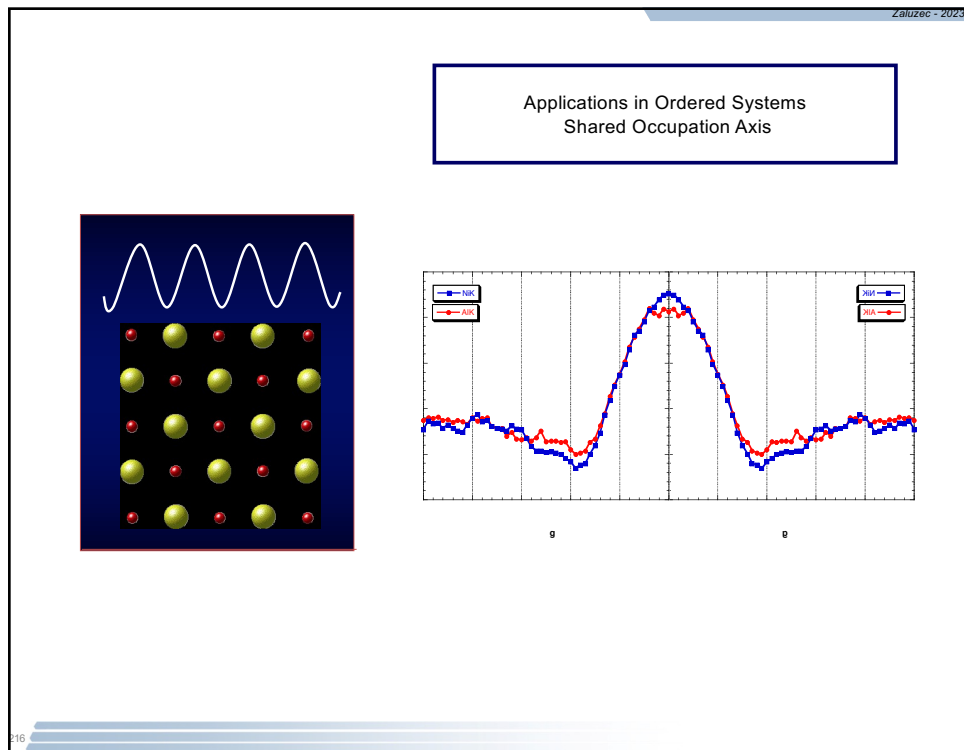
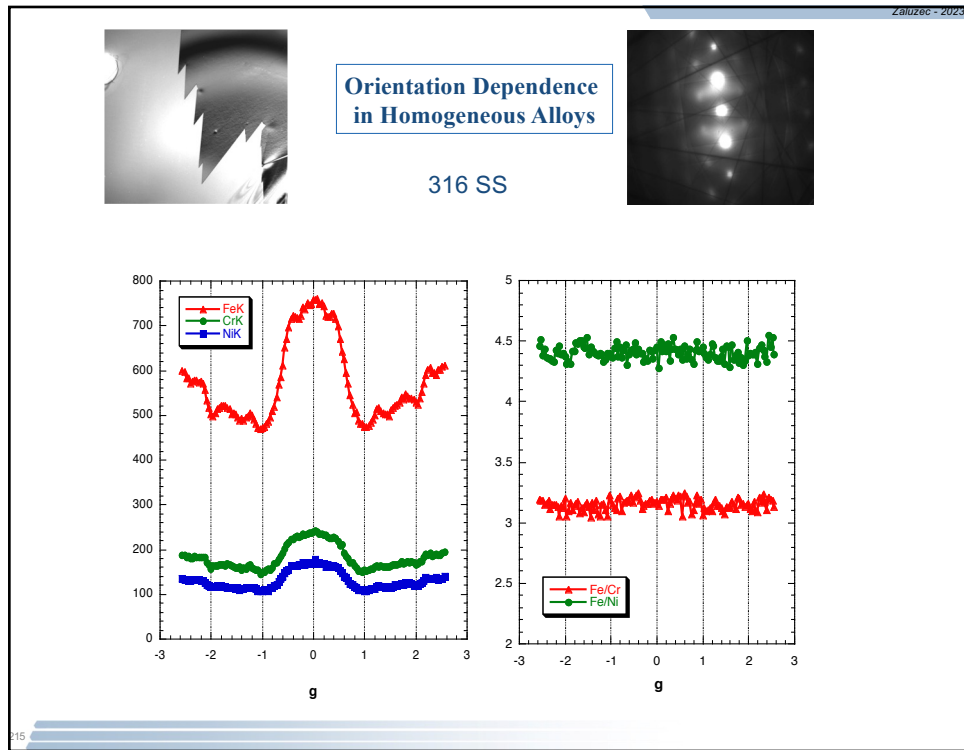


213

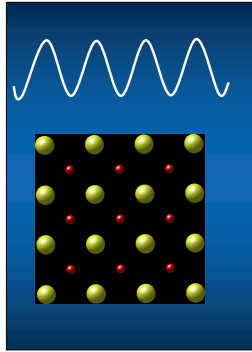
High Angular Resolution Electron Channeling X-ray Spectroscopy



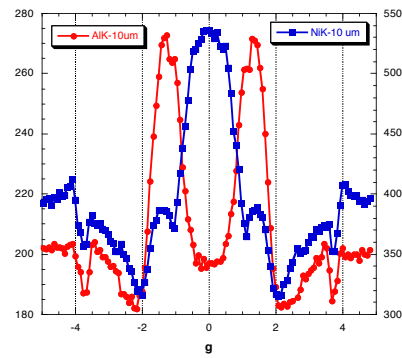
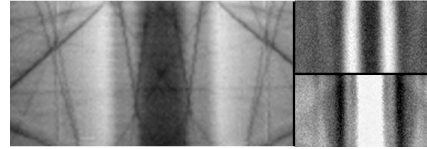
214



Applications in Ordered Systems
Independent Occupation Axis

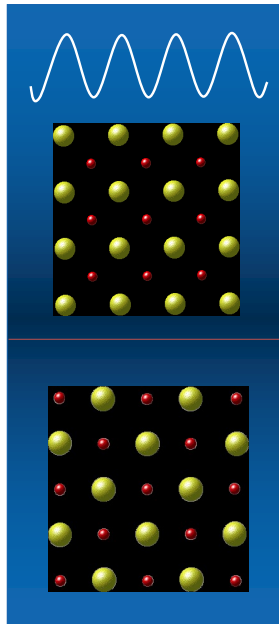


NiAl $\langle 100 \rangle$

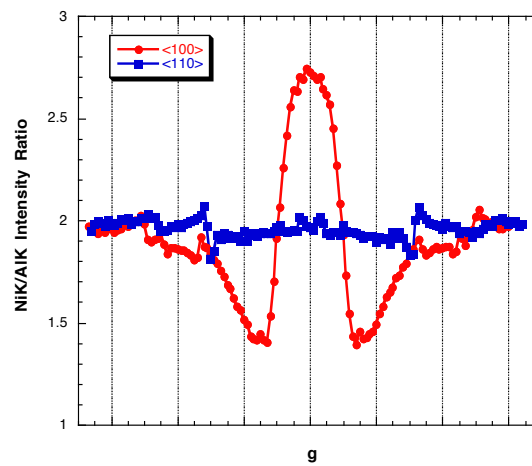


217

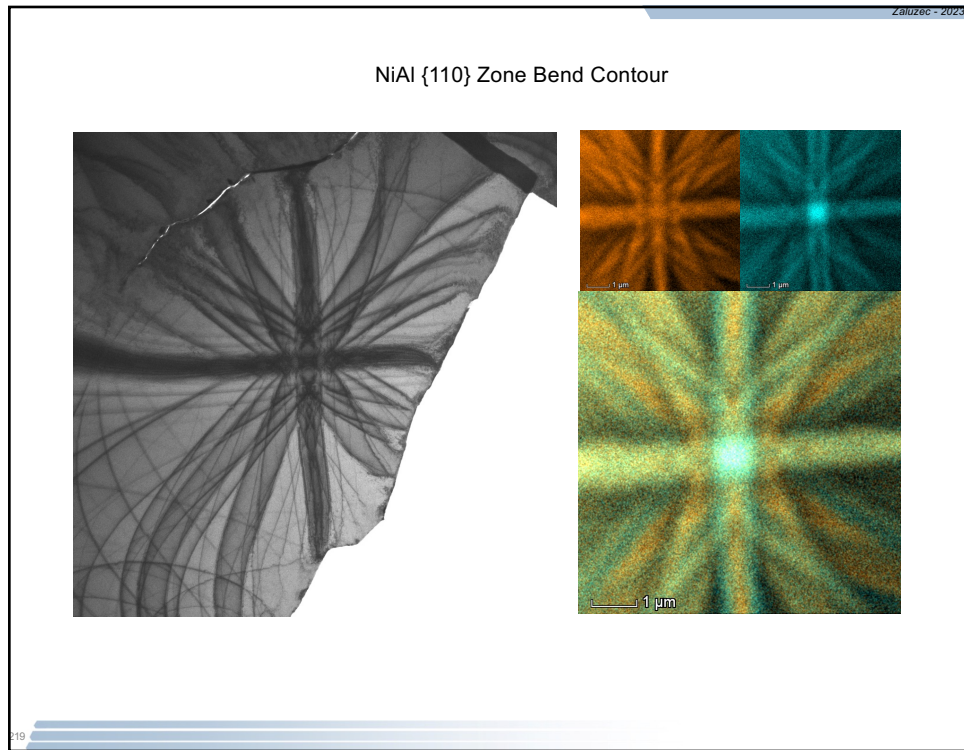
Applications in Ordered Systems



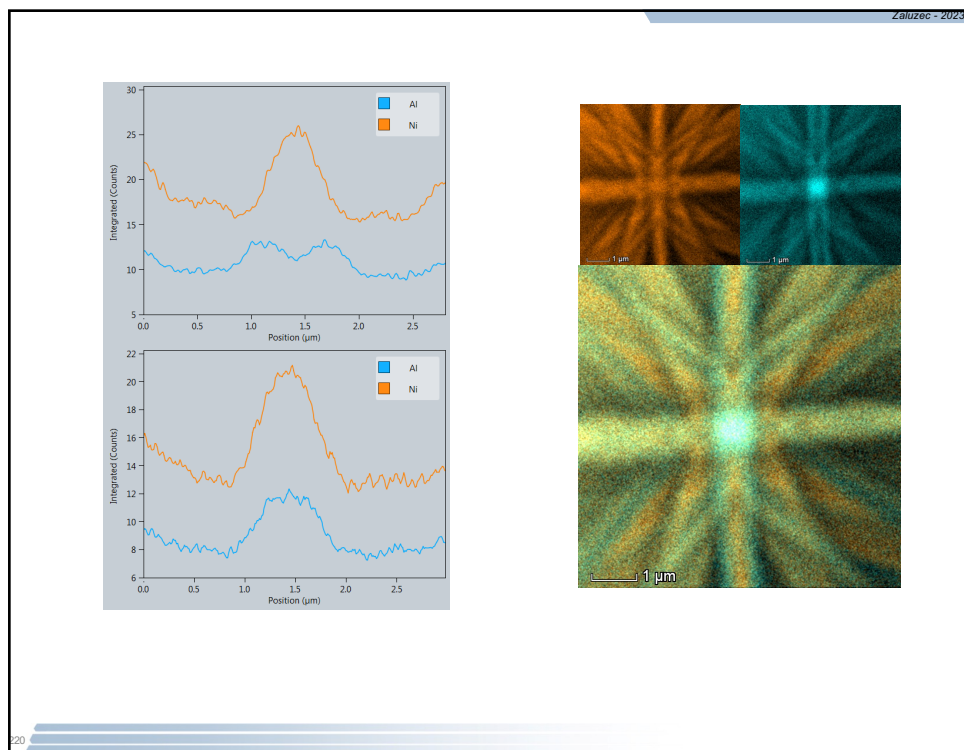
Compare Ni/Al $\langle 110 \rangle / \langle 100 \rangle$



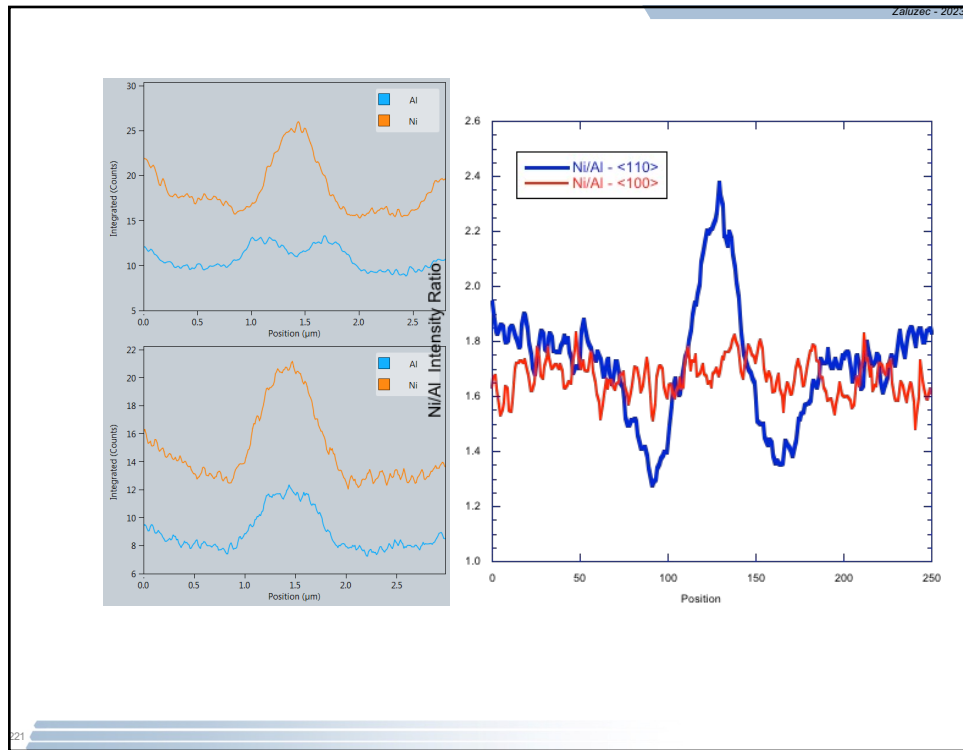
218



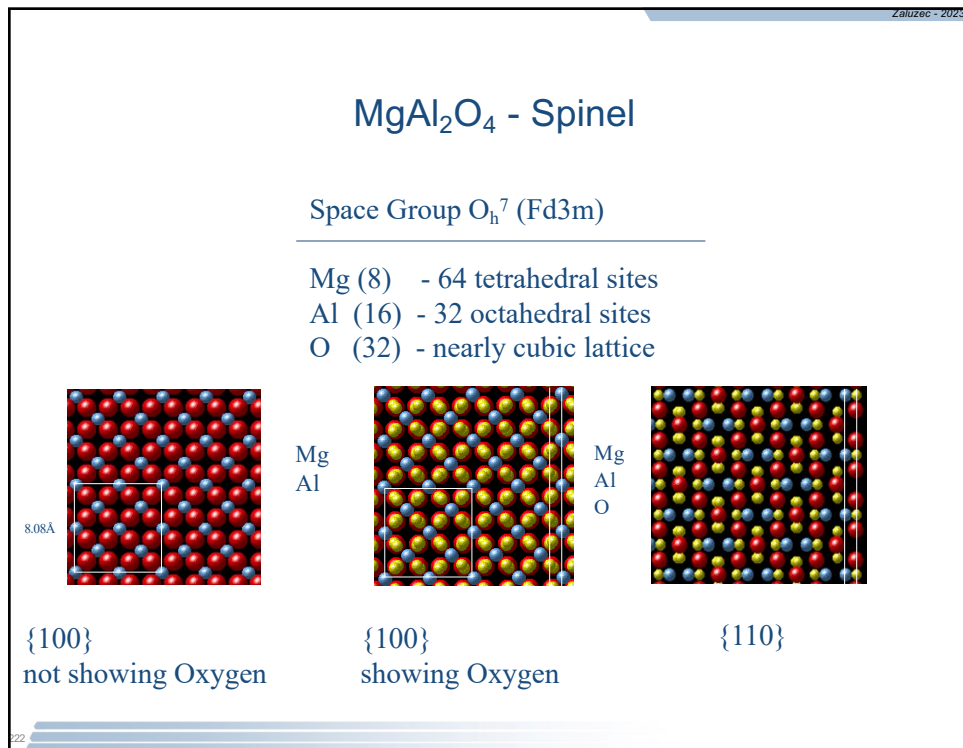
219



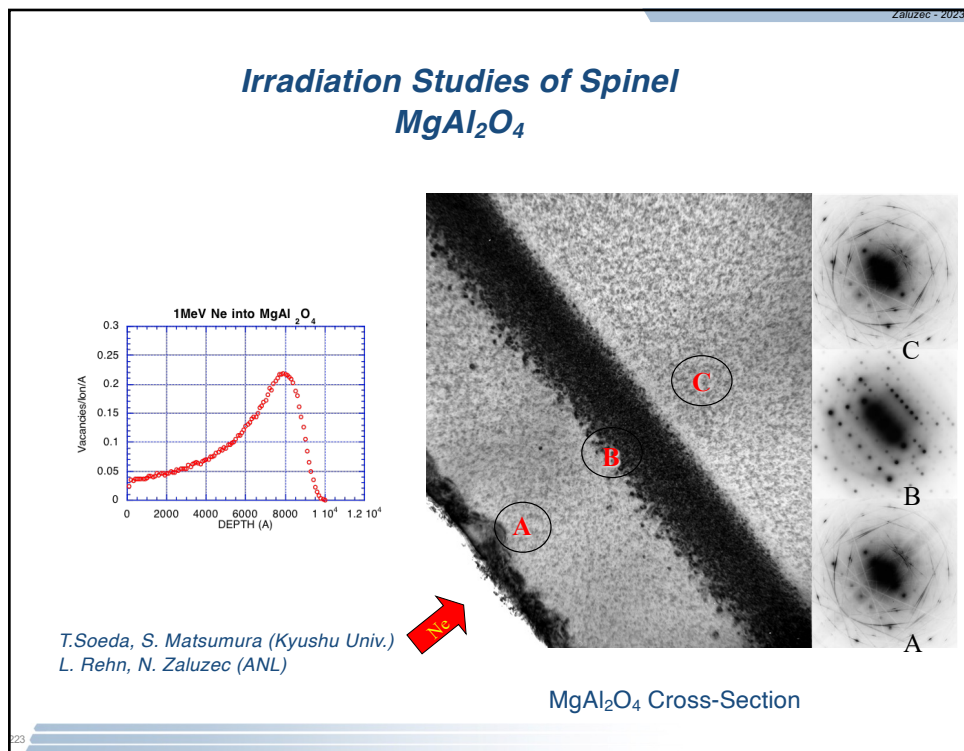
220



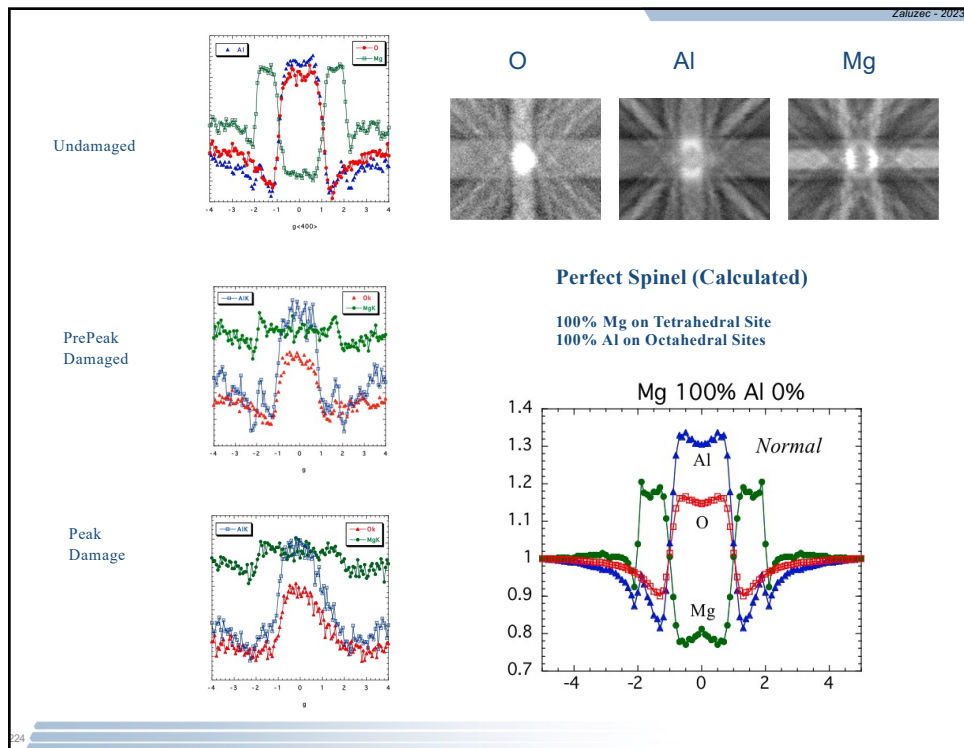
221



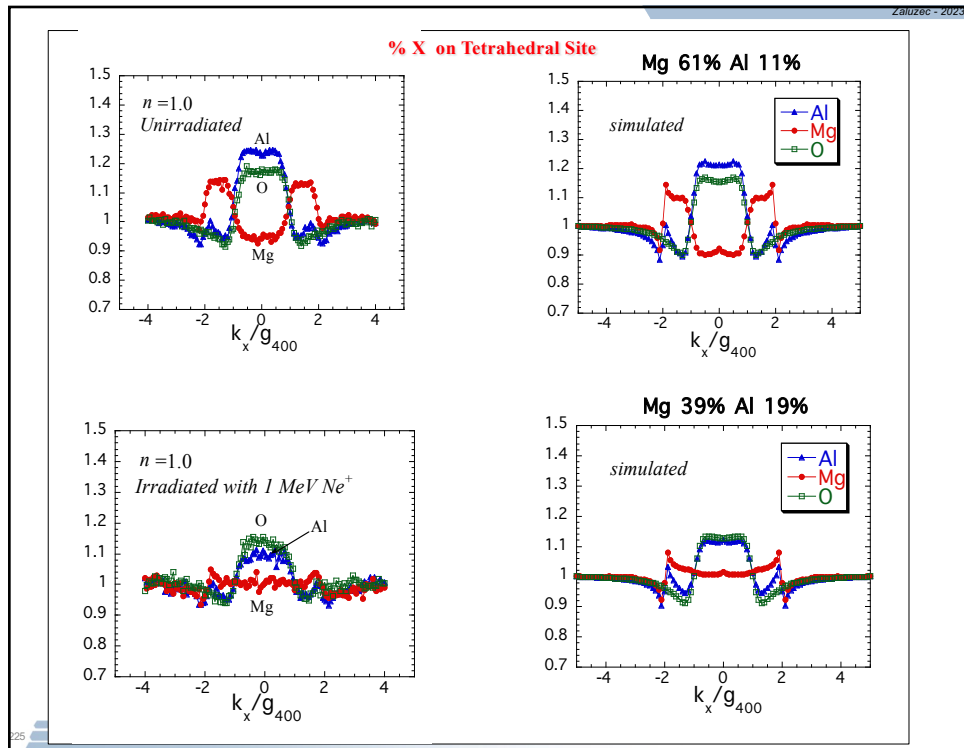
222



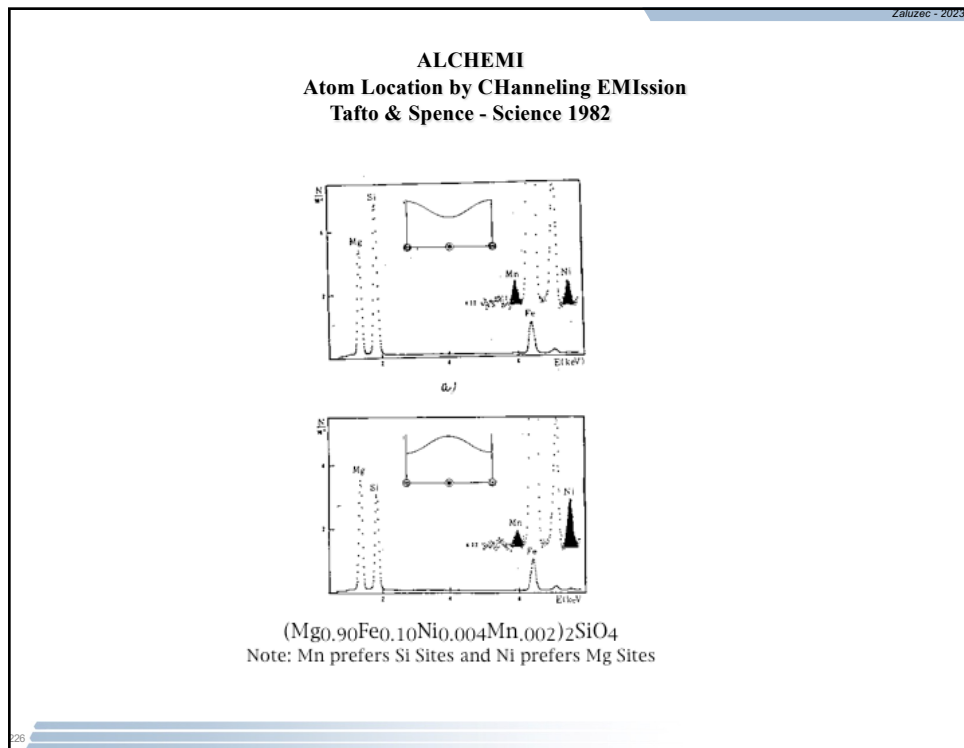
223



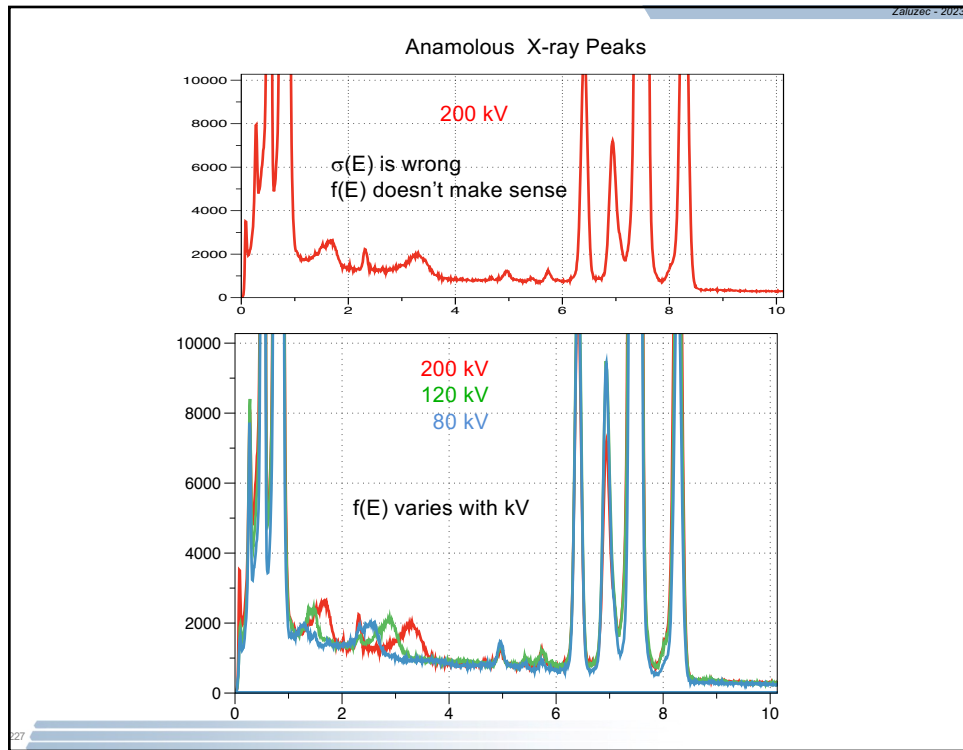
224



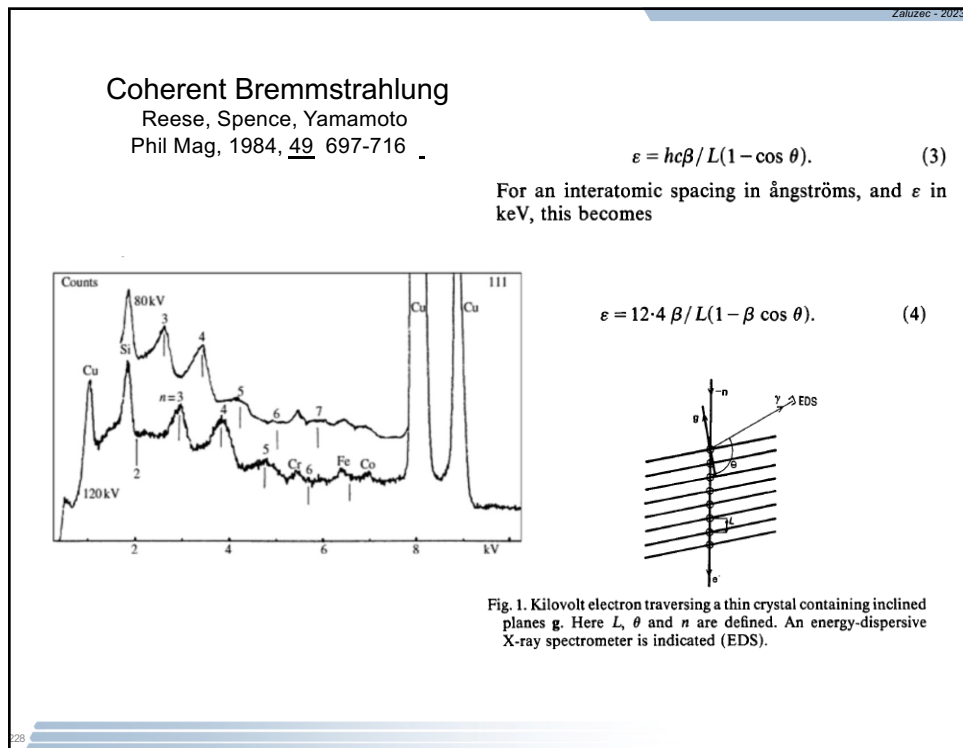
225



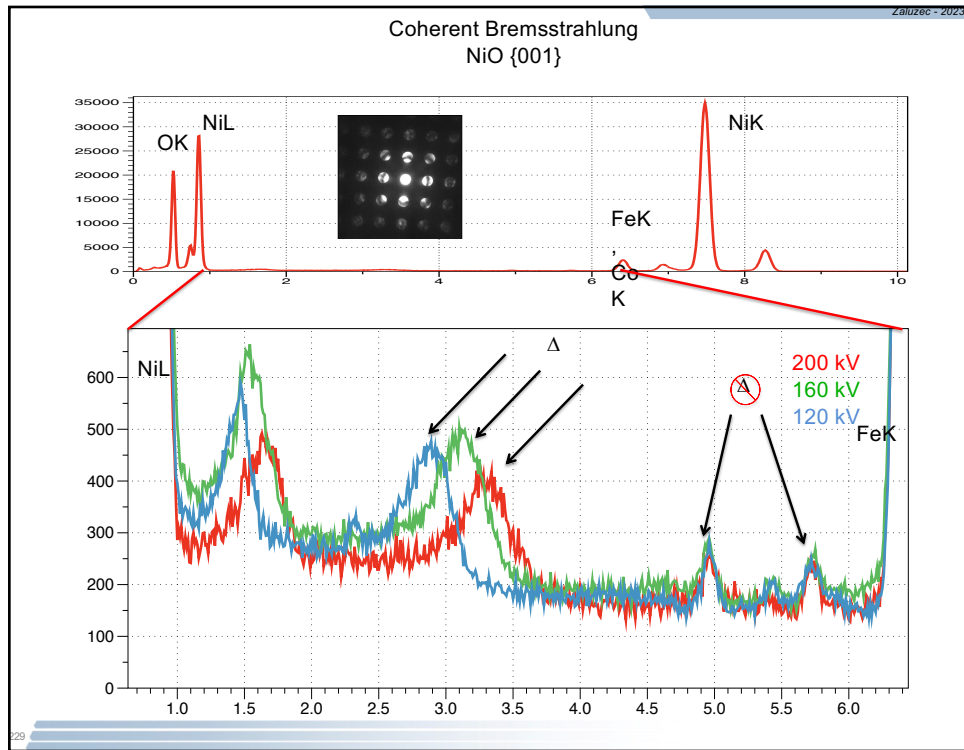
226



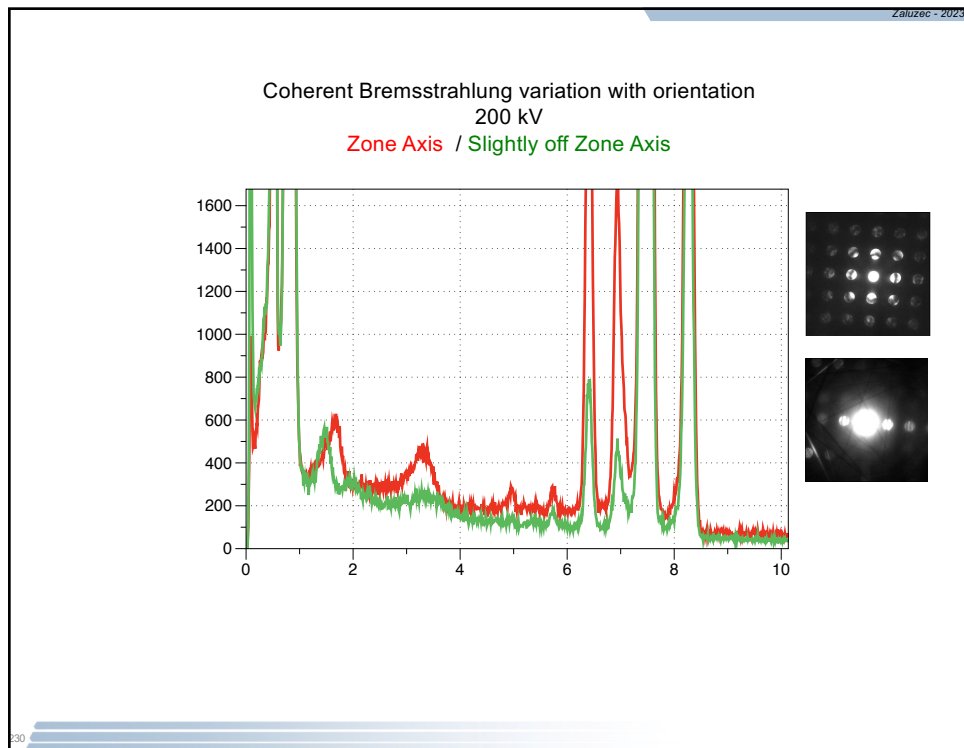
227



228

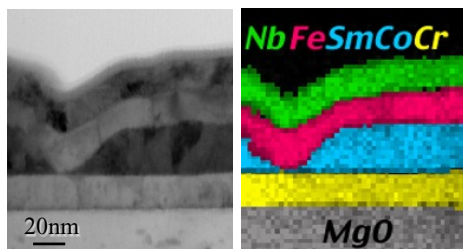
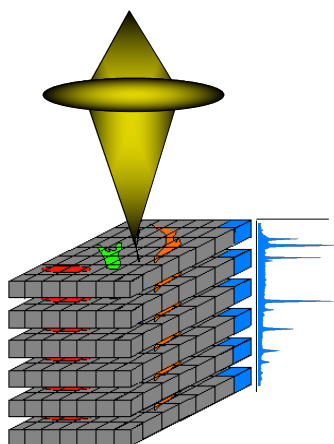


229



230

Significant amount of data is generated in SI Expt's

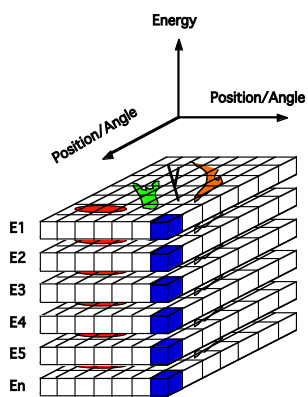


XY	128 ²	256 ²	512 ²	1024 ²
E	256	4M	16M	67M
256	4M	16M	67M	262M
512	8M	32M	134M	524M
1024	16M	64M	268M	1G

231

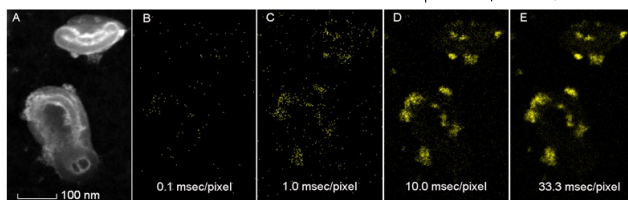
231

Significant amount of time is required in SI Expt's



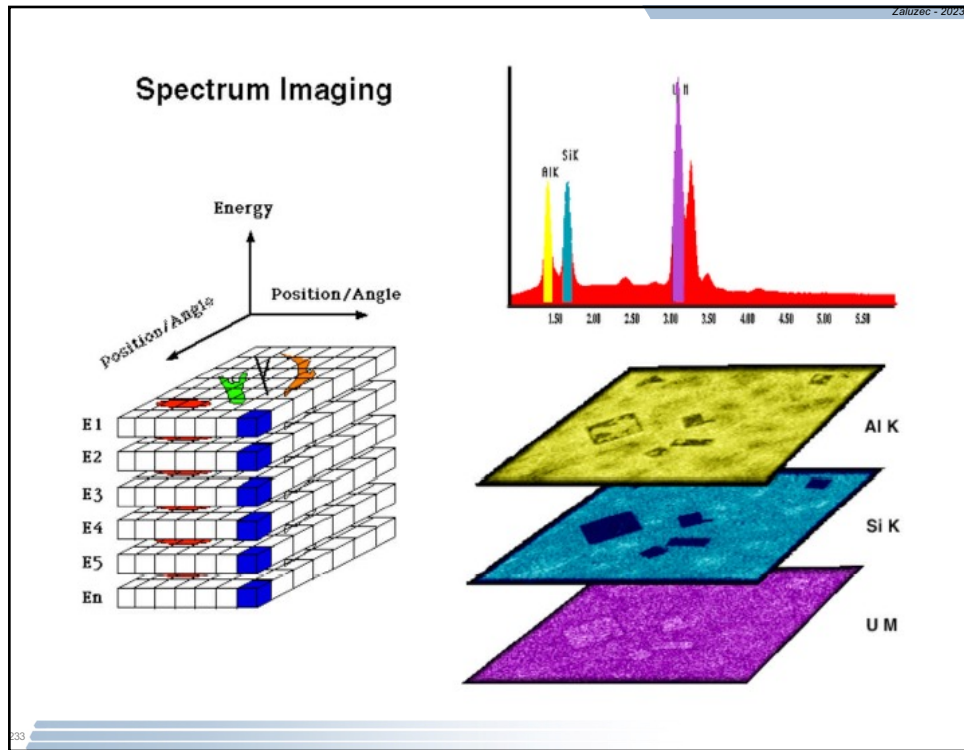
Temporally Resolved Multi-Frame
HyperSpectral Imaging
Is the new modality

XY	128 ²	256 ²	512 ²	1024 ²
t	128 ²	256 ²	512 ²	1024 ²
1μs	16 ms	65 ms	0.26 s	1.05 s
1ms	16 s	65 s	4.4 min	17.5 min
1 s	~4.5 hrs	~18 hrs	~3 days	~12 days
1 min	~11 days	~1.5 mnths	~6 mnths	~2 yrs

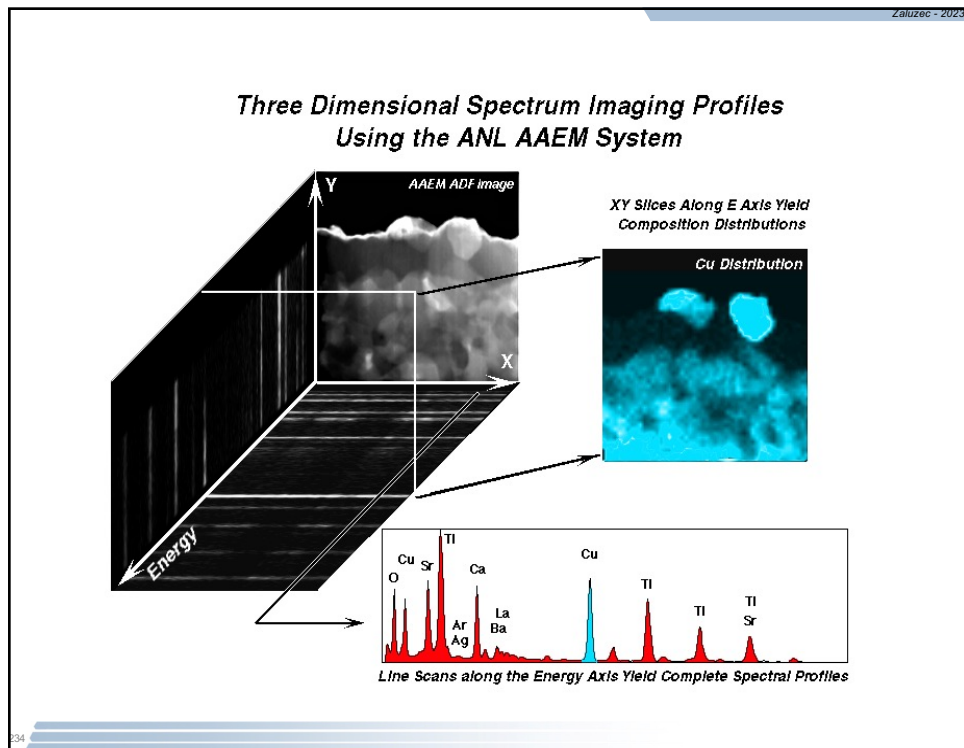


232

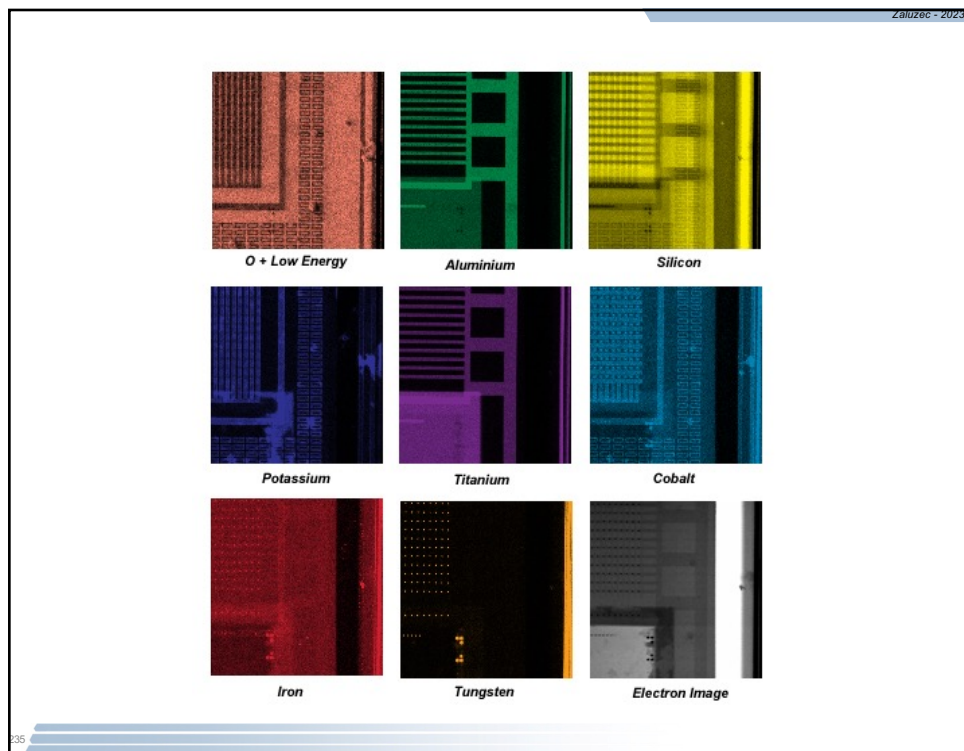
232



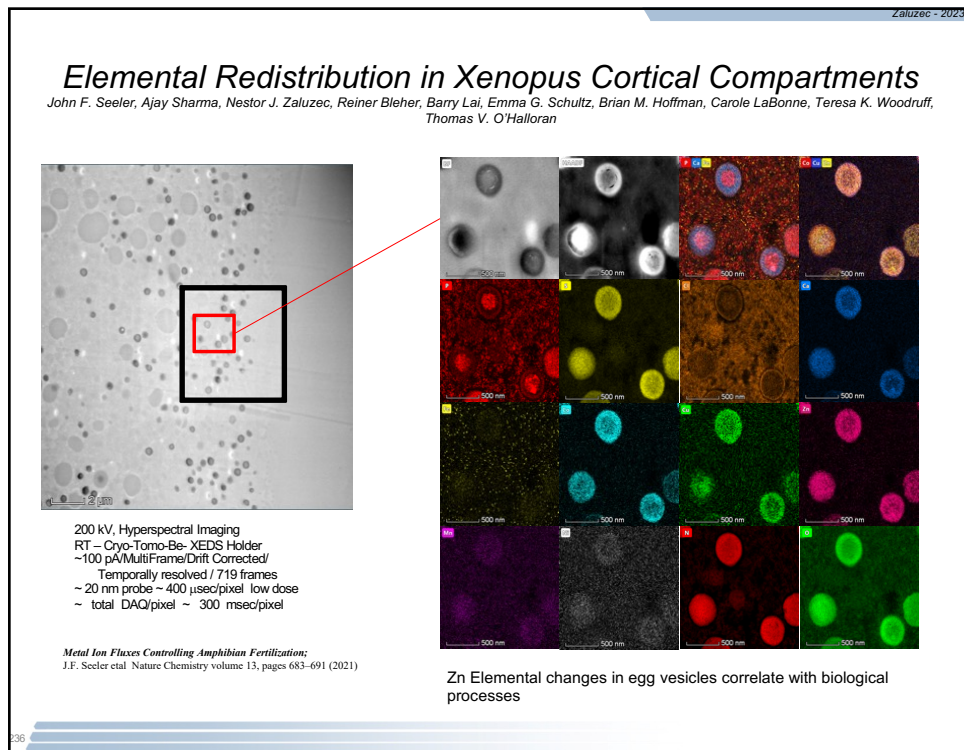
233



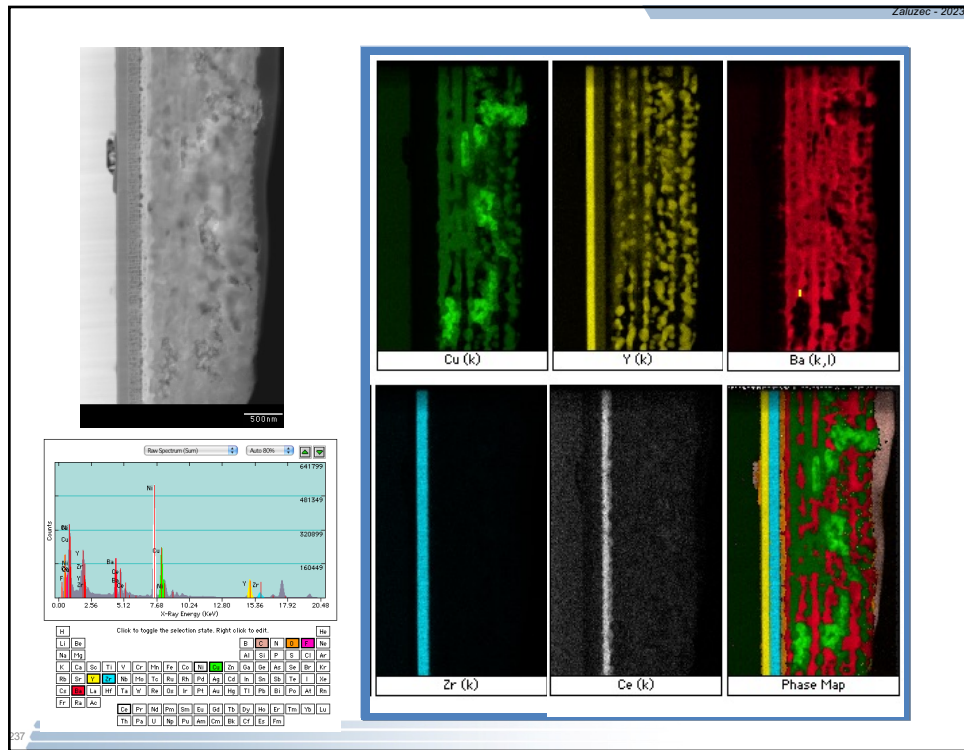
234



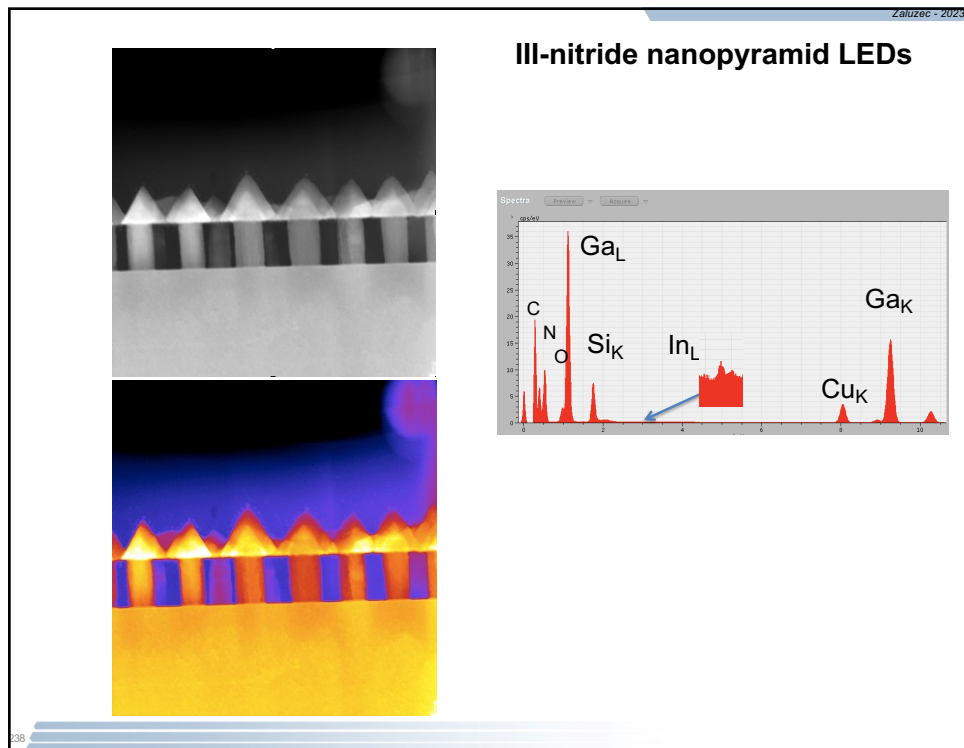
235



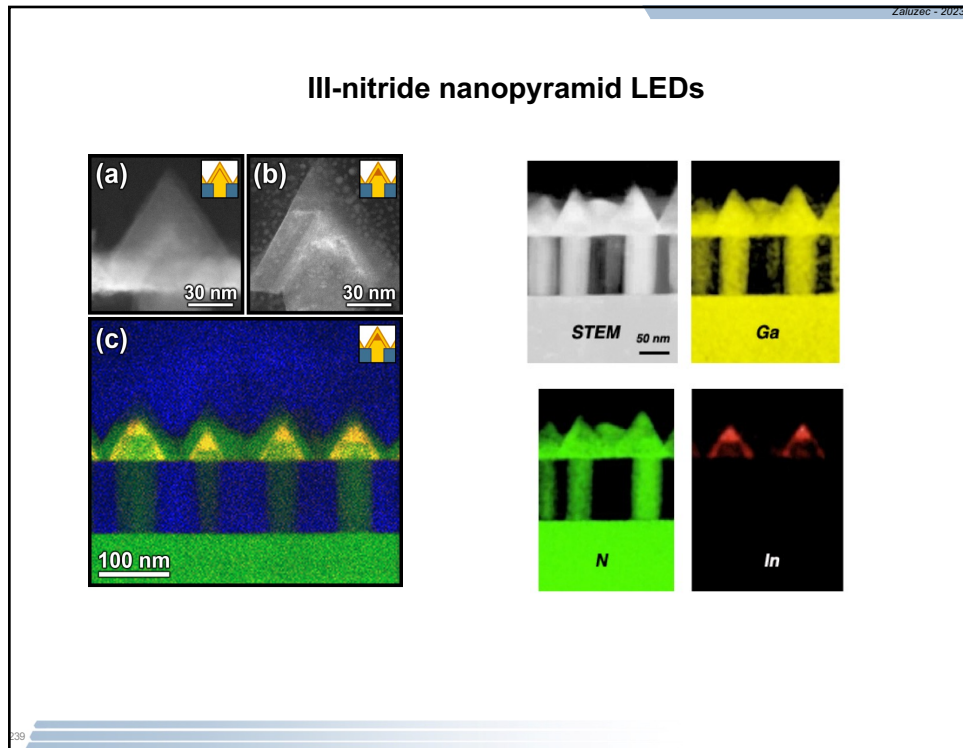
236



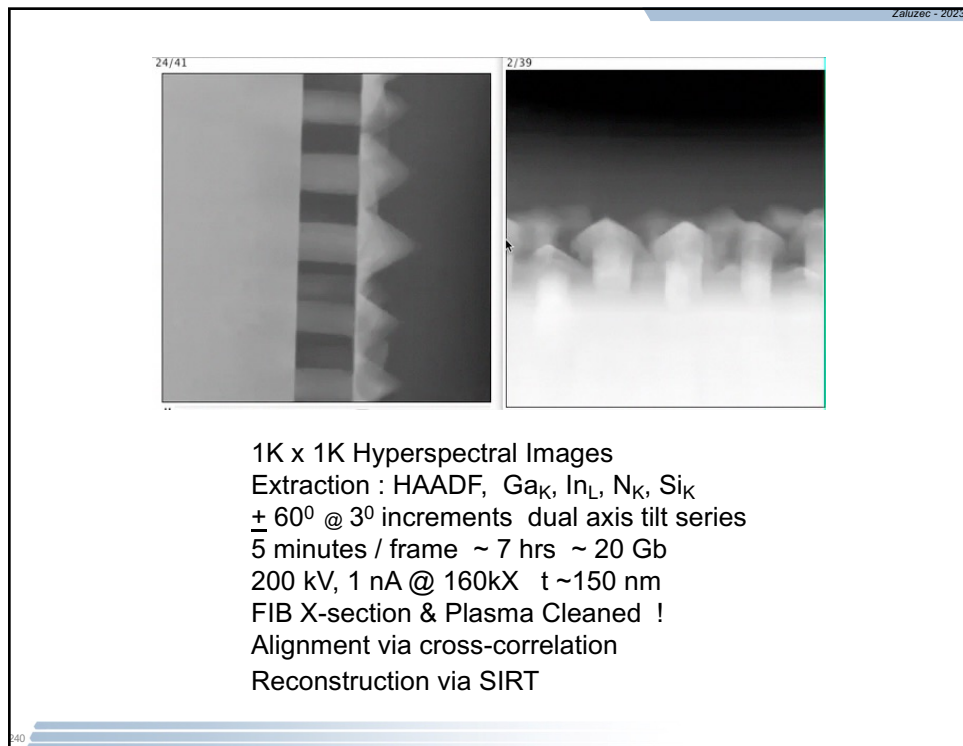
237



238

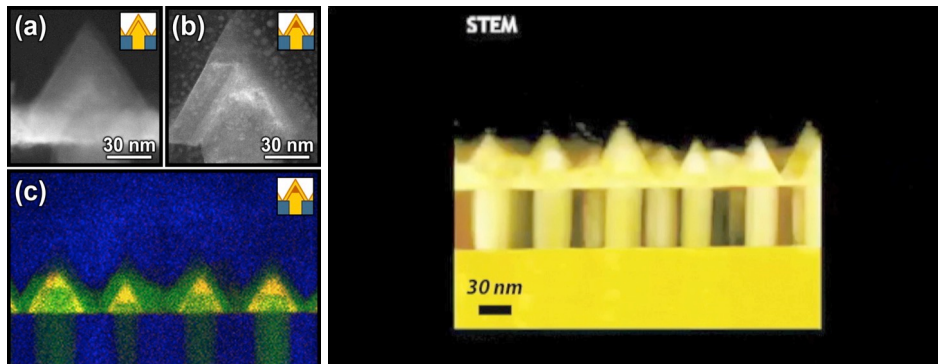


239



240

III-nitride nanopyramid LEDs

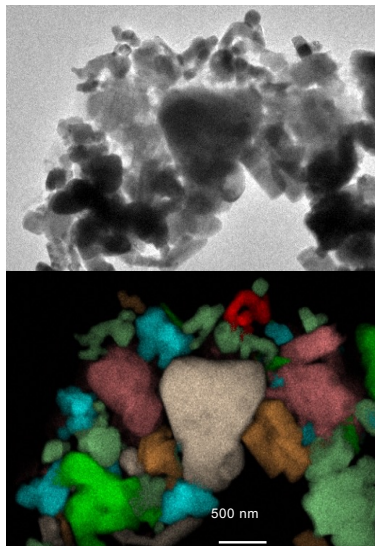


Tomographic reconstruction using Inspect 3D

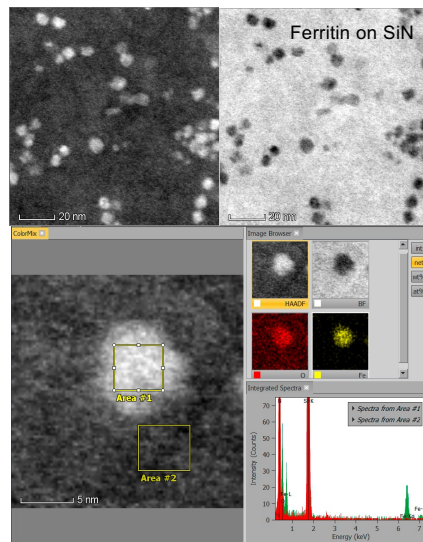
1K x 1K Hyperspectral Images
HAADF, Ga, In, N, Si
 $\pm 60^\circ$ @ 3° increments dual axis tilt series
5 minutes / frame ~ 7 hrs ~ 20 Gb
200 kV, 1 nA @ 160kX
FIB X-section & Plasma Cleaned !

241

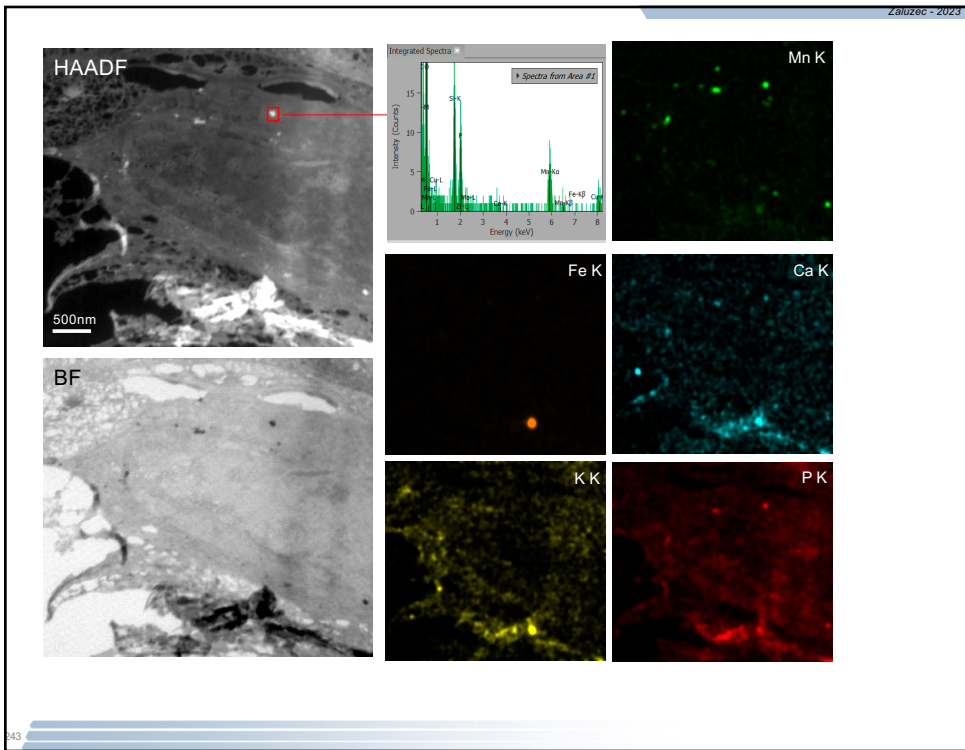
XEDS Hyperspectral Imaging in Materials



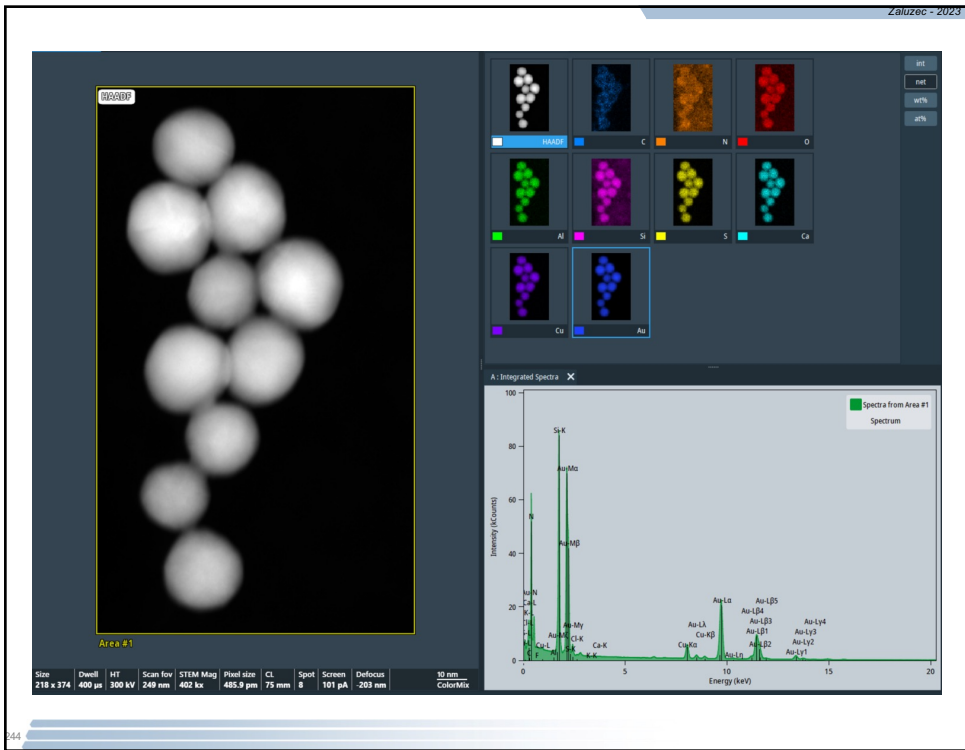
XEDS Hyperspectral Imaging of Soft Matter using Position Tagged Spectroscopy (x,y,E,t)



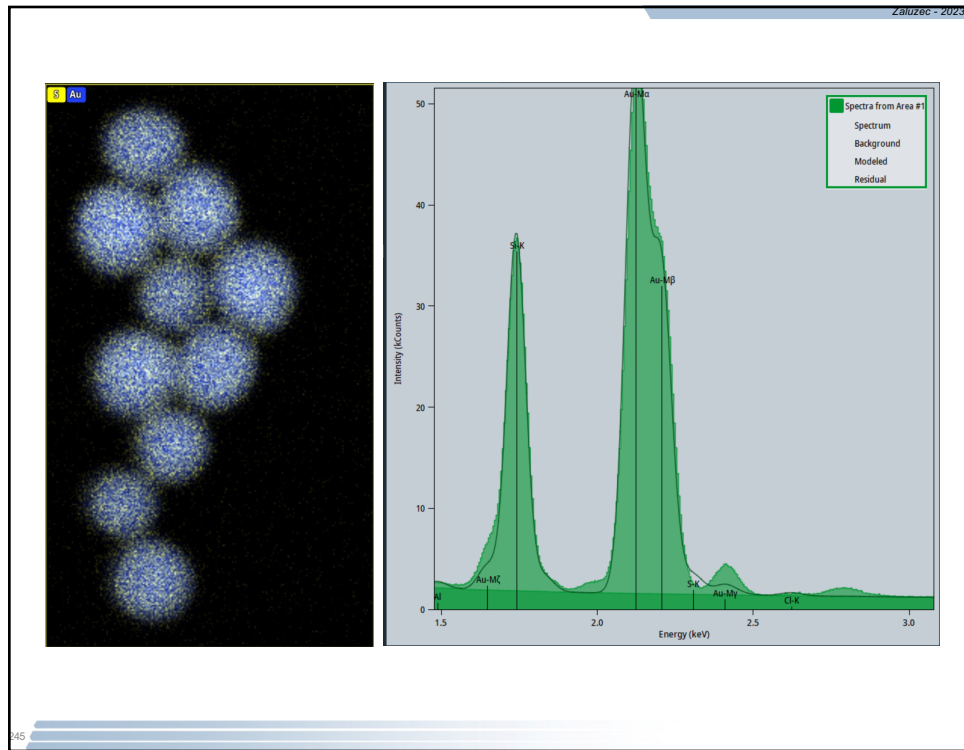
242



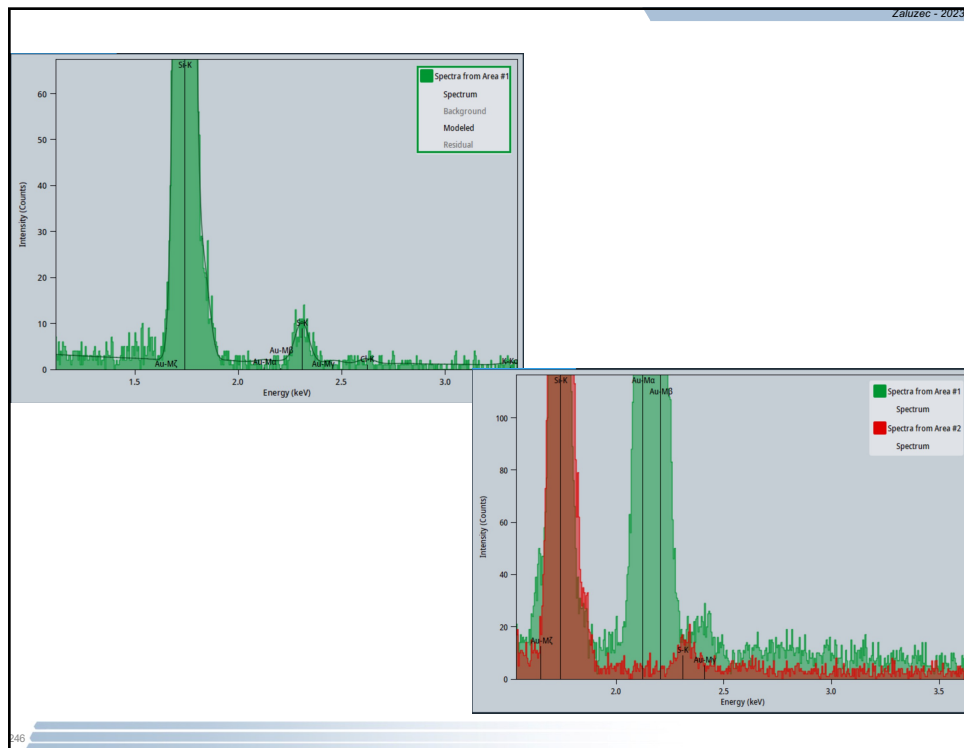
243



244



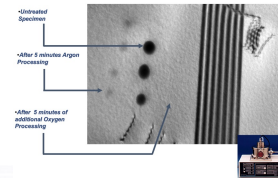
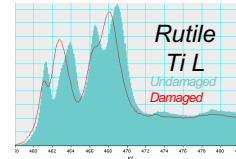
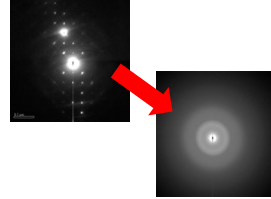
245



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The Microanalyst's Bane : Electron Radiation Damage & Contamination

- **Knock-on / Displacement Damage**
 - Mainly due to Elastic Scattering with Nucleus
 - Metals / Semiconductors / Ceramics /
 - Crystalline
 - Amorphous
 - Threshold Energy exists and varies with Materials
 - Increases with Beam Energy
 - Temperature dependence exists but is variable with Material
 - Sputtering / Melting are associated variants
 - Dose Dependent
- **Radiolysis / Ionization Damage**
 - Mainly due to Inelastic Events with electron shells
 - Most prominent in Organics, i.e. bond breakage
 - Decreases with Increasing Beam Energy
 - Very low Threshold for the onset (< 1 keV)
 - Some Evidence of decrease with specimen cooling
 - Dose Dependent
- **Secondary Electron Damage**
 - Emission of secondary's from inelastic scattering events
 - Increases radiolysis by additional low energy events
 - Also causes charging
 - Dielectric breakdowns
 - Coulomb explosion
 - Charging issues (drift, beam deflection)
- **HydroCarbon Contamination Mitigation**
 - Cryogenic operations
 - Plasma Cleaning
 - UVC Cleaning



247

247

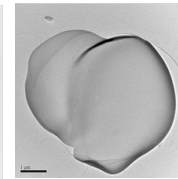
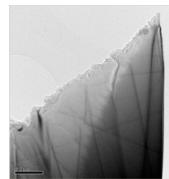
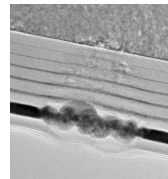
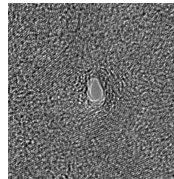
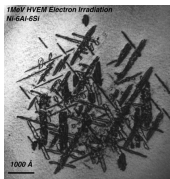
Radiation Damage in Hard AND Soft Materials

Atomic Displacement

Sputtering

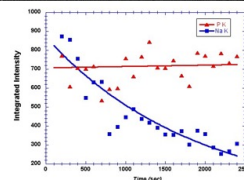
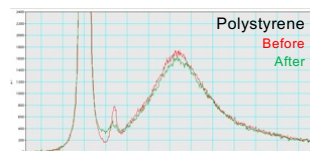
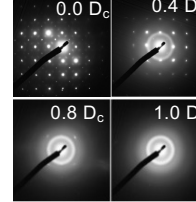
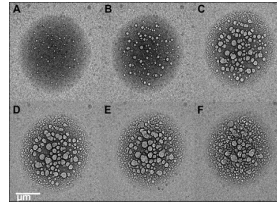
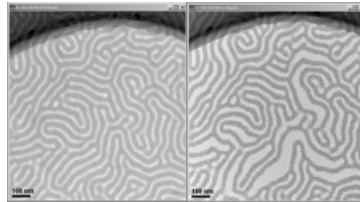
Melting

Amorphization



PS/PMMA Block CoPolymer

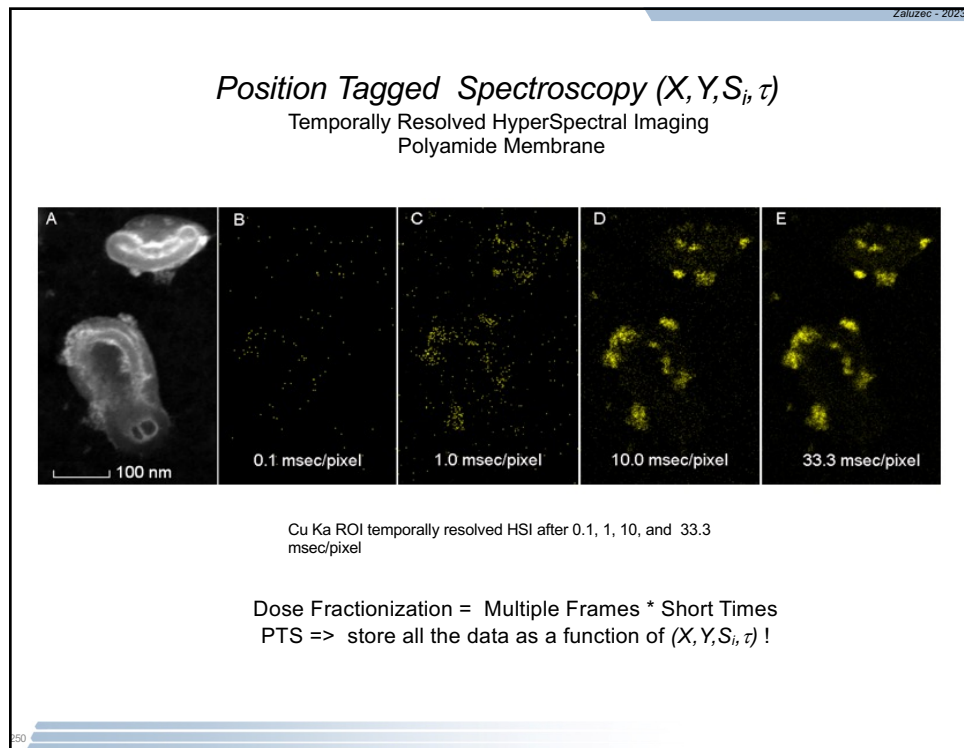
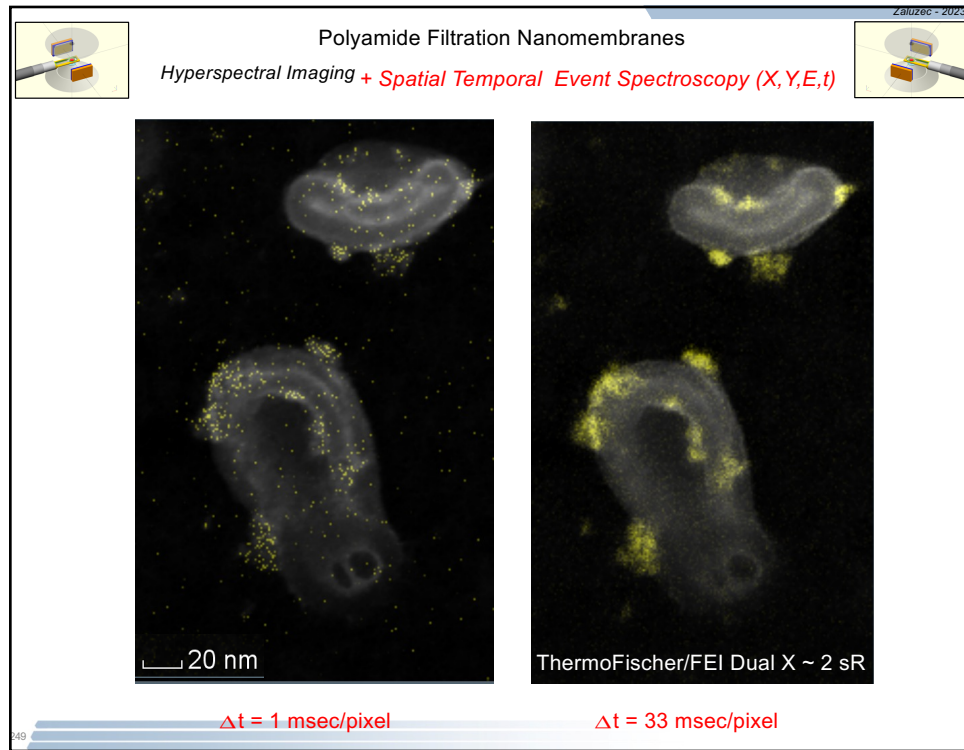
Sodium Phosphate

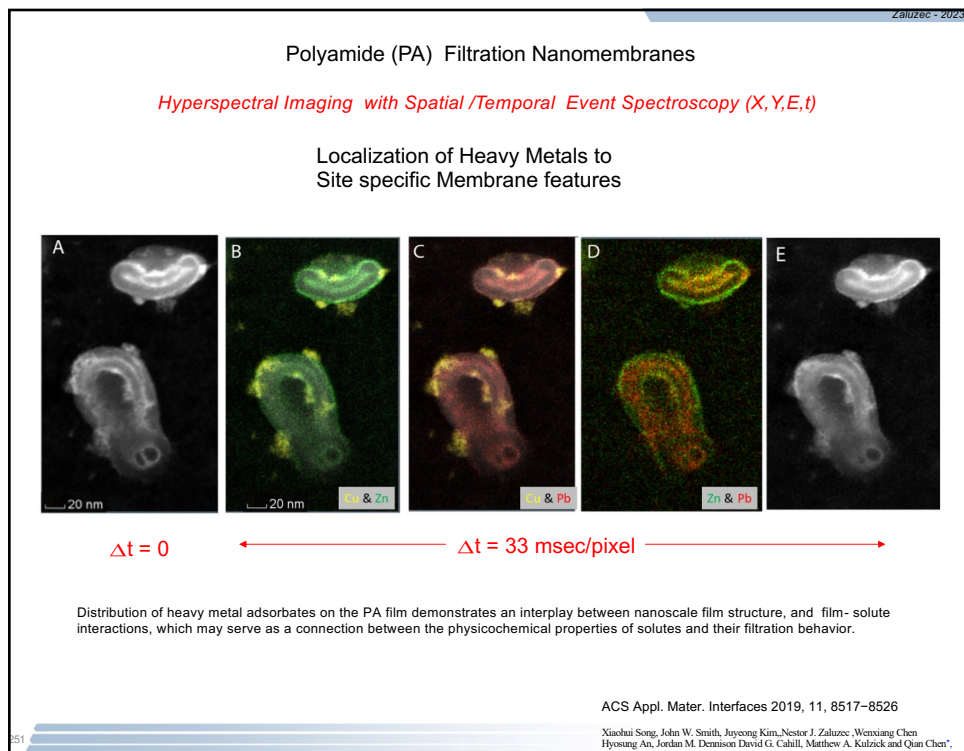


Radiation Damage to Organic
and Inorganic Specimens
Ray Egerton ;
Micron V119 73-87 (2019)

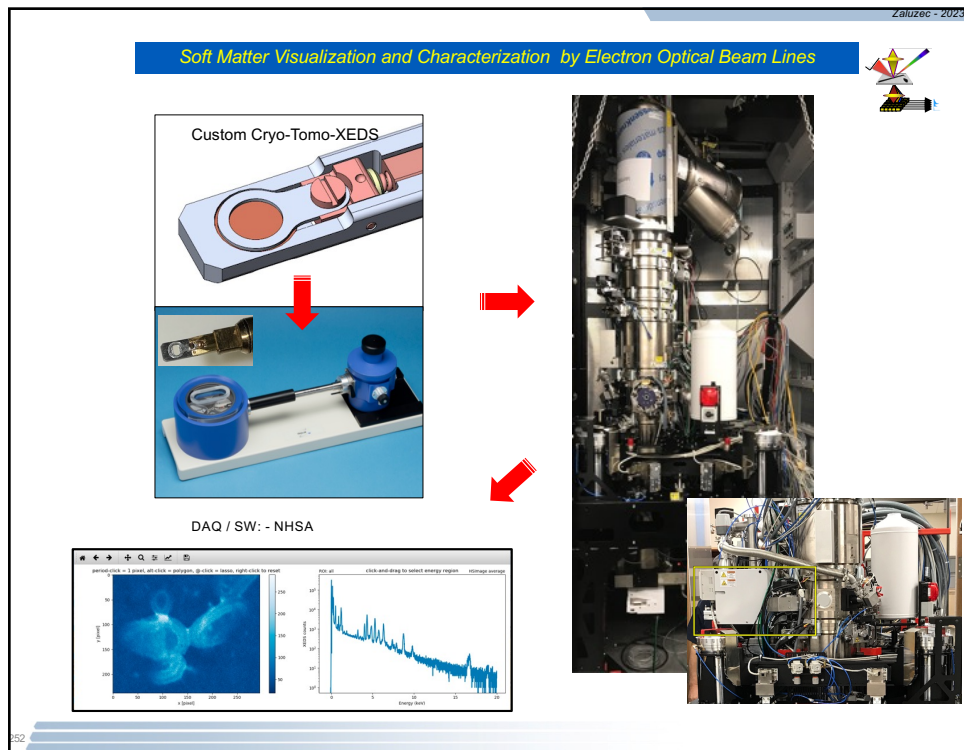
248

248



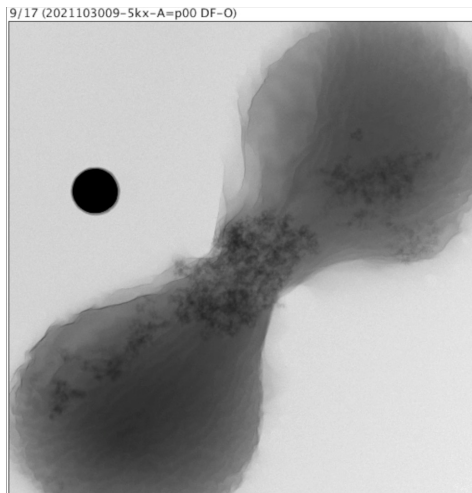


251



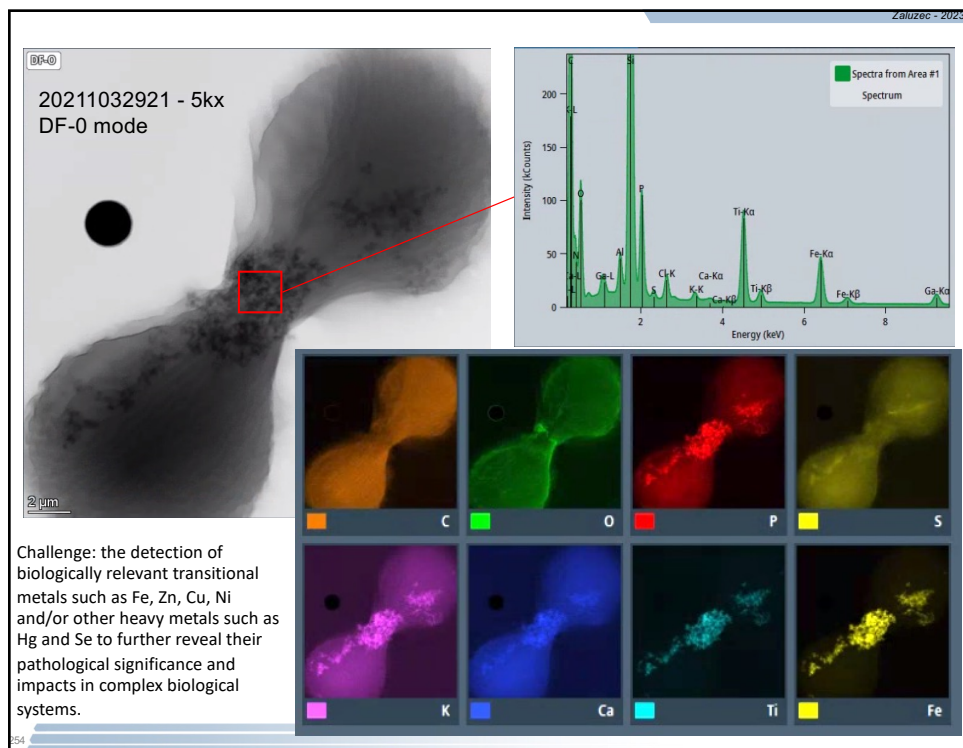
252

Nanotechnology, particularly with the usage of nanoparticles, has led to promising results in cancer diagnosis and treatment. Gaining insights into the interactions between nanomaterials and subcellular structures is crucial prior to their wide application *in-vivo*



Nanomaterial interactions within HeLa Cancer Cells

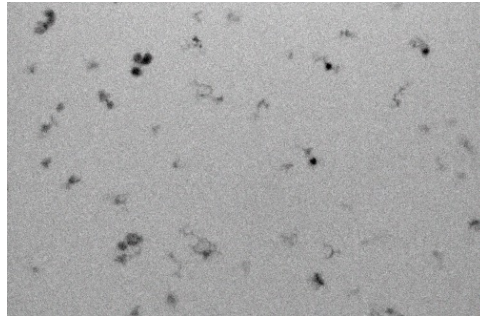
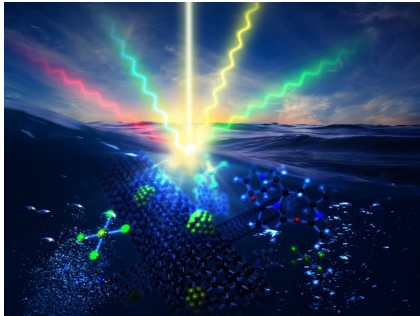
253



254

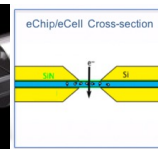
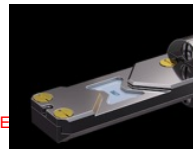
Environments: in-situ, growth processes and hard/soft materials

Materials behave differently in growth environments - understanding growth processes, especially self-assembly via organic or bio, presents a challenge for traditional Transmission/Scanning Electron Microscopy which operate under high vacuum conditions



Key Challenges:

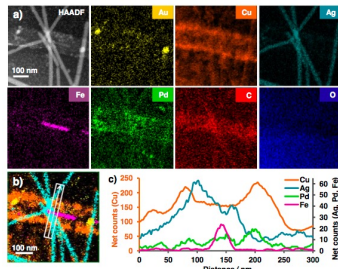
- ♦ In-situ observation of growth processes - at atomic resolution in Media
- ♦ In-situ (Gaseous/Liquid) high-spatial resolution chemical analysis
- ♦ Dynamics - Fast detection schemes, detectors, and sources
- ♦ In-Situ Operando Microscopy => Environmental EM / Environmental Cell E



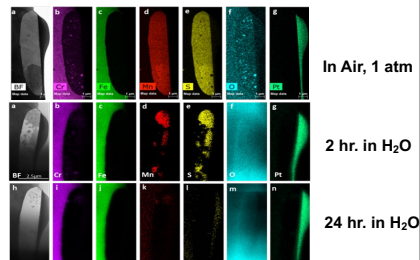
255

Hyperspectral Imaging in Liquids & Gases @ 1 ATM @ Temperature

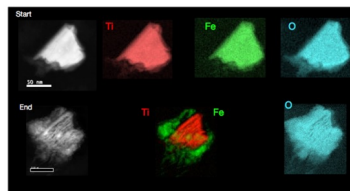
Characterization of nanoparticles in liquids



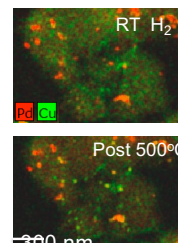
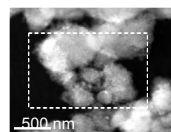
In Situ Metallurgical Studies
MnS Inclusion Dissolution in Water



Ilmenite reduction by hydrogen



Pd/Cu NP Catalysts on
TiO₂
Calcined vs Reduced
0.7 atm H₂

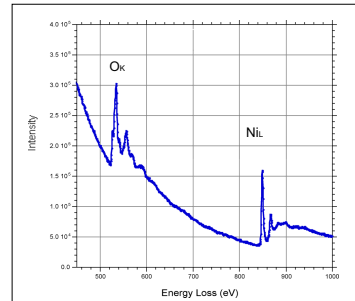
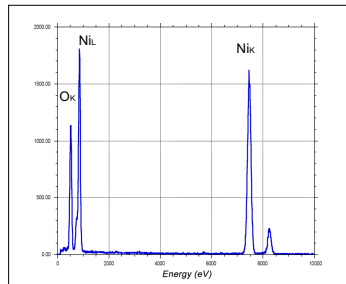
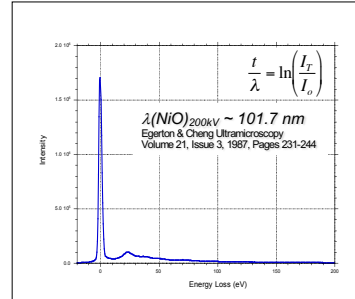


Collaborative work with Manchester & BP

256

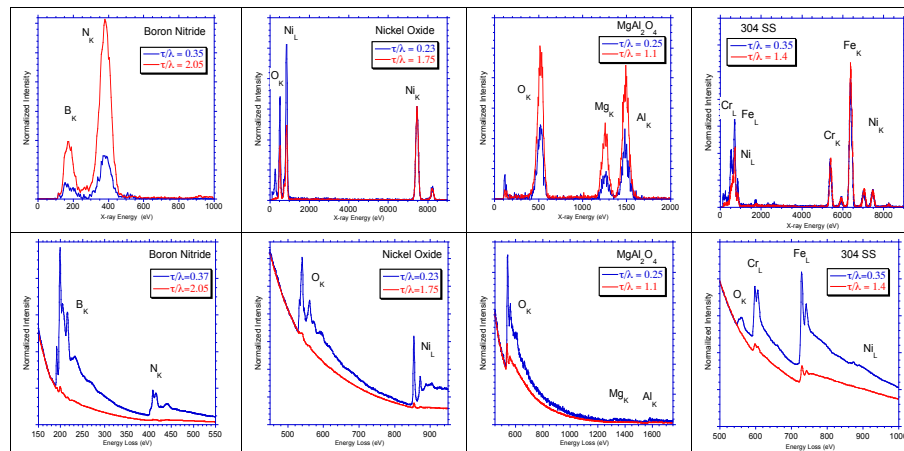
XEDS & EELS

Zakuzec - 2023

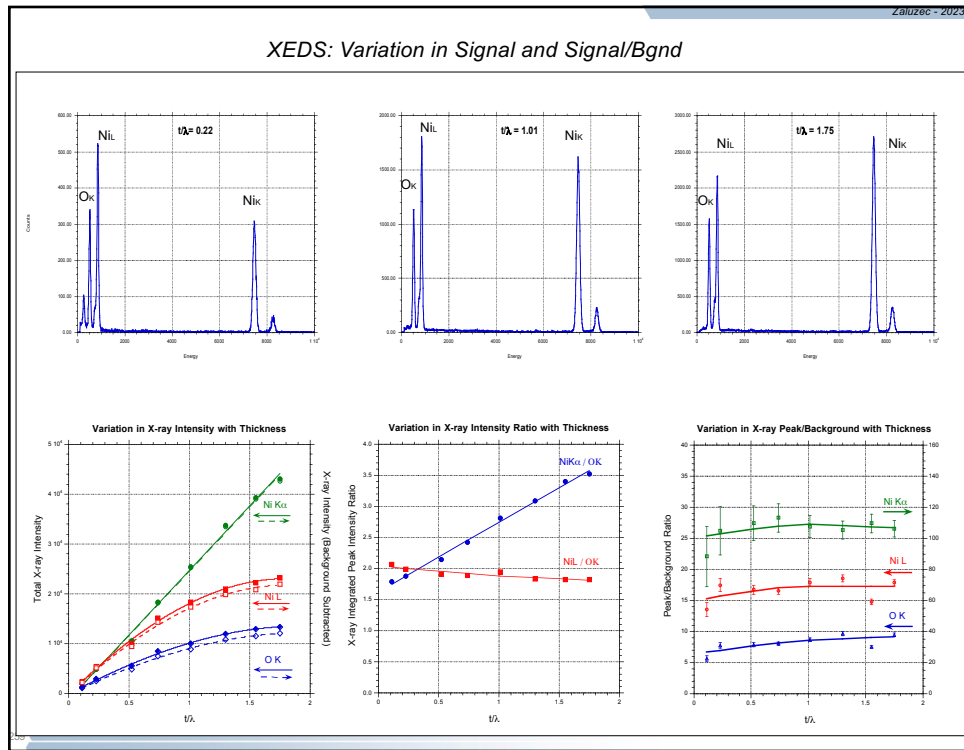


257

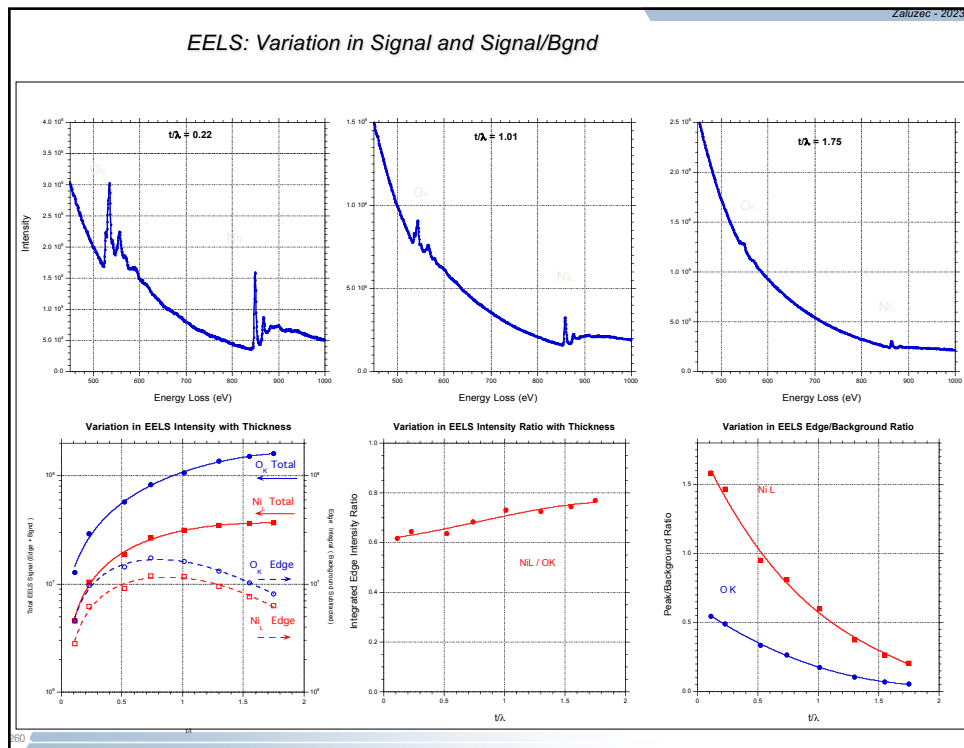
Zakuzec - 2023



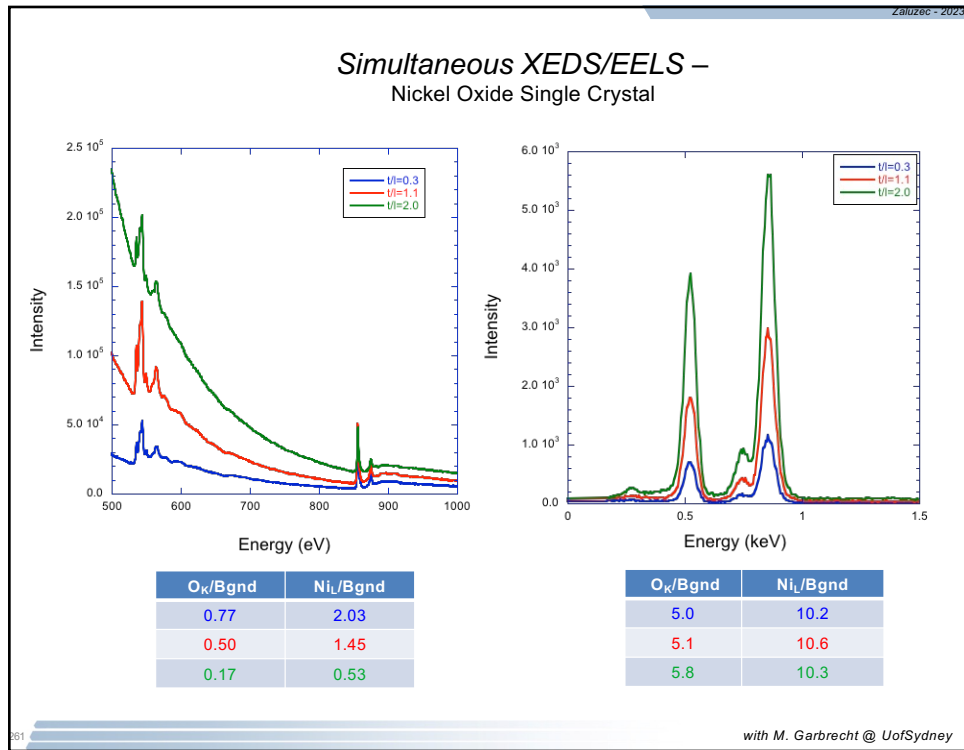
258



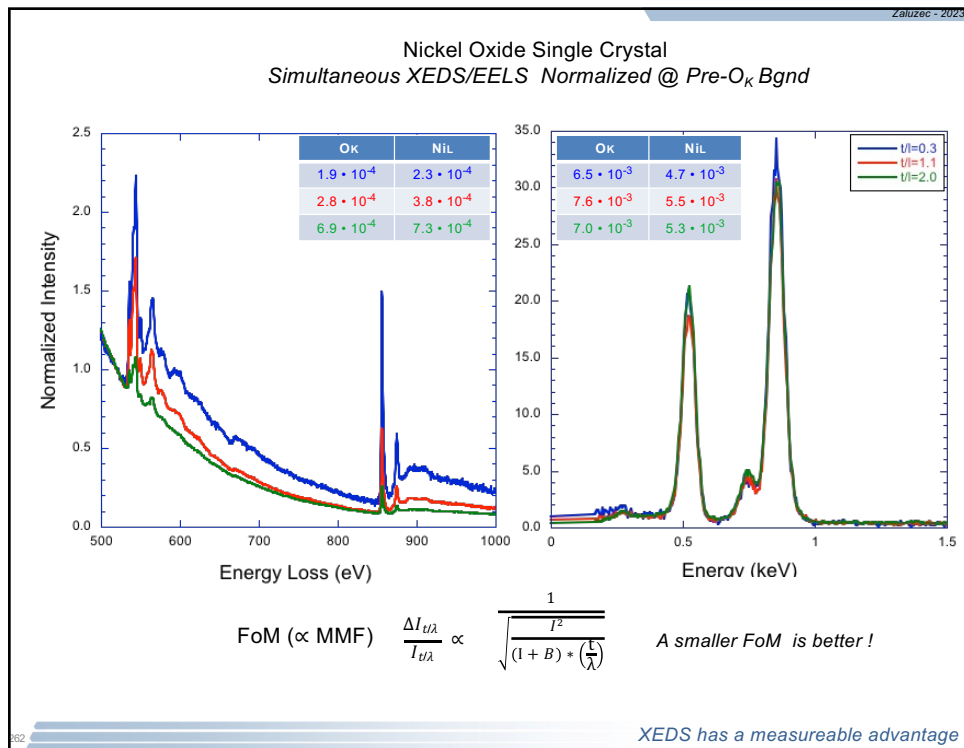
259



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Zoluzec - 2023

Thanks

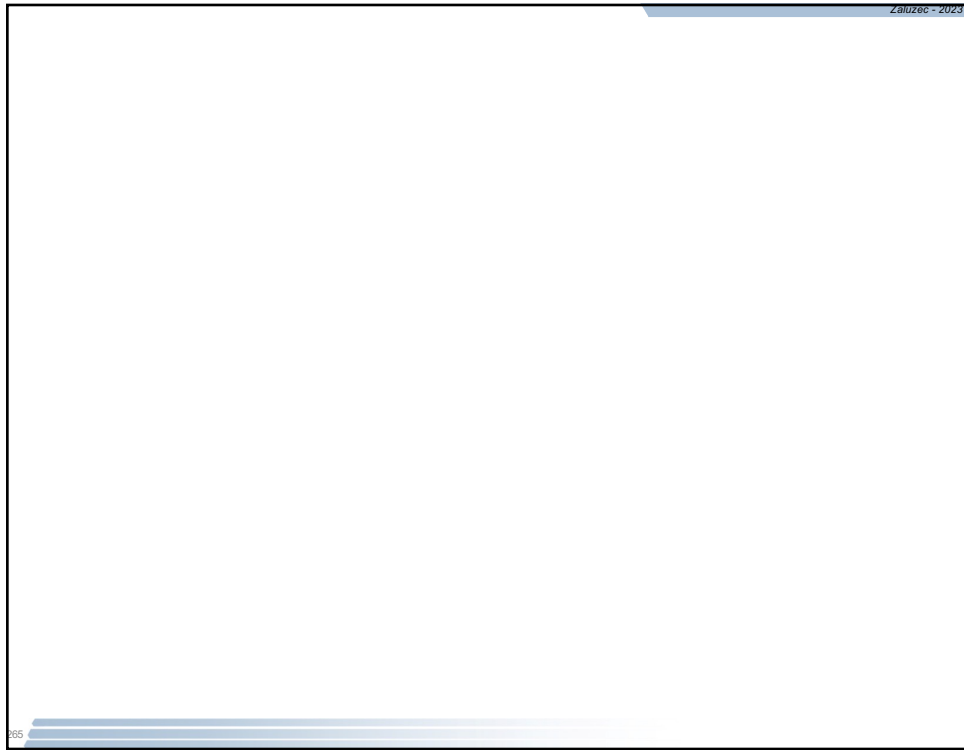


Questions?

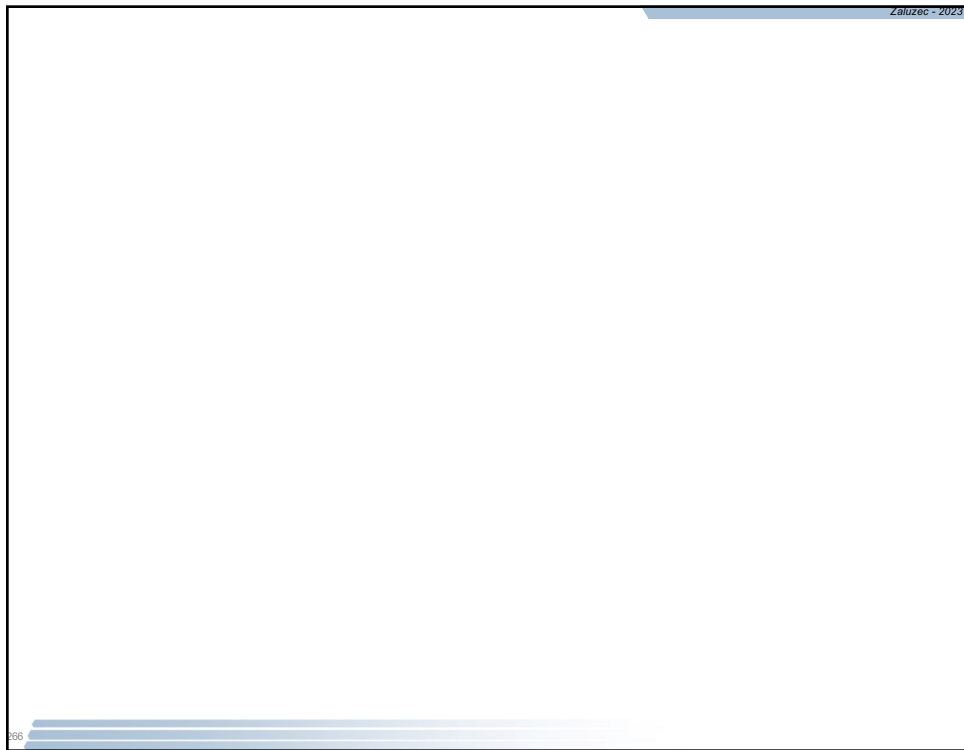
263

Zoluzec - 2023

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