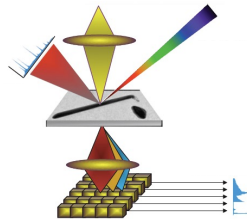


The X-ray Perimeter Array Detector (XPAD): a New Resource for Atomic Resolution and High Sensitivity Microanalysis in the Analytical Electron Microscope



0.5 Å in TEM/STEM $\Rightarrow$ 5 Å in 5D [X, Y, Z, S, τ]

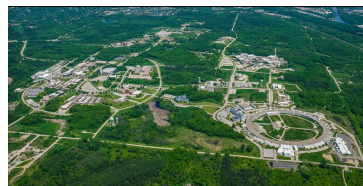
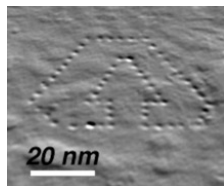


Nestor J. Zaluzec
Photon Science Directorate
zaluzec@aaem.amc.anl.gov
zaluzec@microscopy.com



1

Acknowledgements



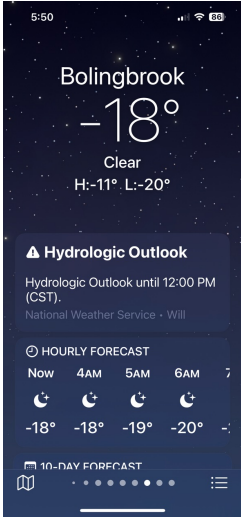
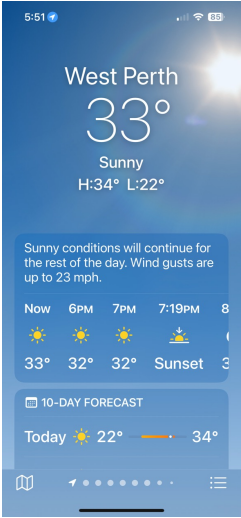
ANL LDRD Projects
ANL/ThermoFisher(FEI) CRADA #1300701

ThermoFisher
SCIENTIFIC

Permission Given to Photograph/Capture Slides or Request a PDF Copy by Email

2

This Morning's Traditional Weather Report



3

Last's Years Weather Report

The Year there was no meeting
Feb 2, 2022



4

Jan 25 2023
1 day prior to leaving for Oz



5

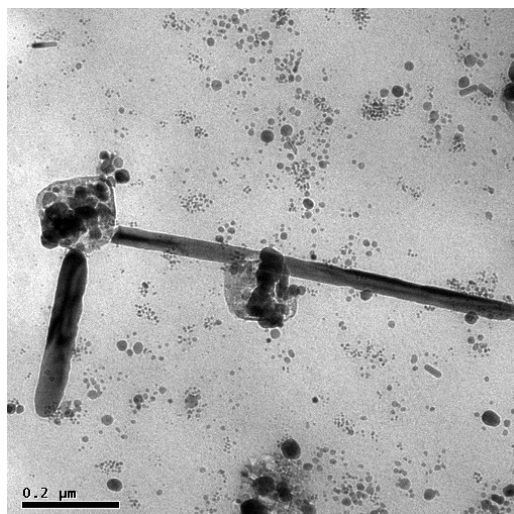
Jan 27 2023



But you managed once again to depart just in time to get out of shoveling the driveway

6

Microanalytical Challenges

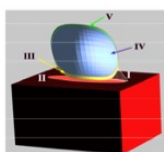


You can't measure it, if you can't detect it

7

Small Particles: Catalysts, Nanomaterials , Quantum Structures

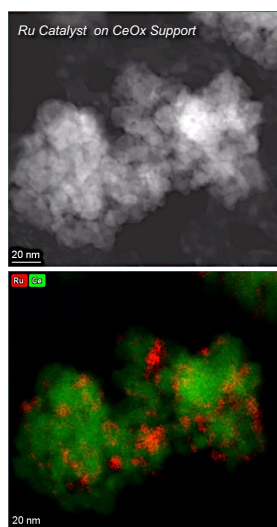
Nanomaterials and processes challenge our ability to understand them:



Catalytic Nanoparticles

Key Challenges:

- ◆ Quantification - nanocrystallography at atomic resolution (automated w/ real time modeling and simulation)
- ◆ Atomic scale 3D imaging and diffraction
- ◆ In situ: controlled environments for simultaneous imaging and spectroscopy during reactions
- ◆ Dynamics: real-time observation



8

Spectroscopic Detectability Limits

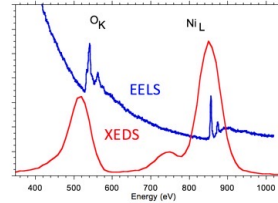
Signal in the Presence of Background

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

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:

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

$$MMF \sim \frac{2.33}{\sqrt{I * \left[\frac{I}{B}\right]}}$$

*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

9

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

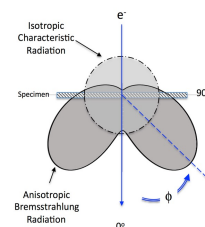
(I_x/B_x) = Peak to Background ratio for X

η_o = Incident electron flux

J_o = Incident electron current density

d = Probe diameter

τ = Analysis time



10

Bremsstrahlung Emission due to electron excitation

$$I_{Bgnd}(\phi, E_o, E_{Bgnd}, Z, \dots) = I_\phi \cdot \left\{ \frac{C_z \cdot N_o \cdot \rho}{W_Z} \right\} \cdot \xi_o \cdot t \cdot \epsilon_{Bgnd} \cdot \left\{ \frac{dE_{Bgnd} \cdot d\phi}{E_{Bgnd}} \right\}$$

$$I_\phi = I_i \cdot \left\{ \frac{\sin^2(\phi)}{[1 - \beta \cdot \cos(\phi)]^4} \right\} + I_j \cdot \left\{ 1 + \frac{\cos^2(\phi)}{[1 - \beta \cdot \cos(\phi)]^4} \right\}$$

$$I_i, I_j \Rightarrow f(Z, E_o, E_{Bgnd}, \dots), \quad \beta = \frac{v}{c}$$

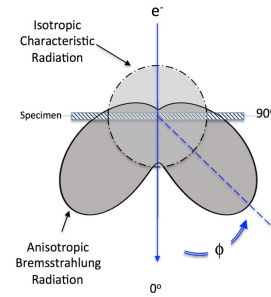
I_{Bgnd} = Bremsstrahlung intensity

E_o = incident electron energy (I),

ϕ = observation angle

E_{Bgnd} , dE_{Bgnd} the continuum x-ray energy being measured and its window

I_i , I_j = continuum radiation components

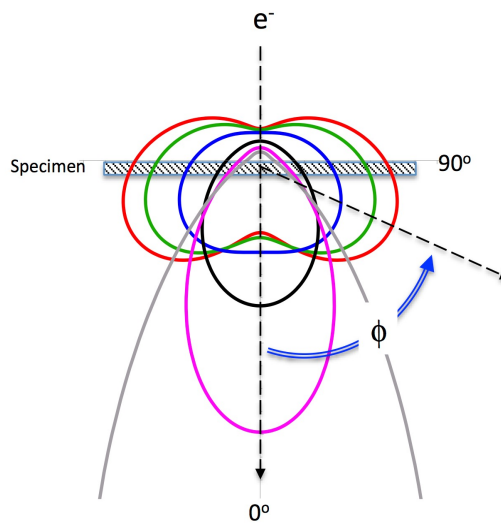


Note: Traditional
Detector Elevation Angle
 $\theta = \phi - 90^\circ$

Sommerfeld, 1931; Scherzer, 1932, Motz and Placious, 1958

11

Bremsstrahlung at fixed Background Energy window (7.48 keV) vs E_o



E_o (keV)	V_o (kV)
9.71	10
11.59	12
18.88	20
43.51	50
76.78	100
123.52	200
$E_{Bgnd} = 7.48 \text{ keV}$	

Calculations for Ni

12

Early Days of XEDS 1973

Hamish Fraser, John Woodhouse,...

13

Early Days of XEDS 1978

Ray Carpenter, Jim Bentley, Ed Kenik ...

14

Argonne
NATIONAL LABORATORY

XEDS Geometries Vary

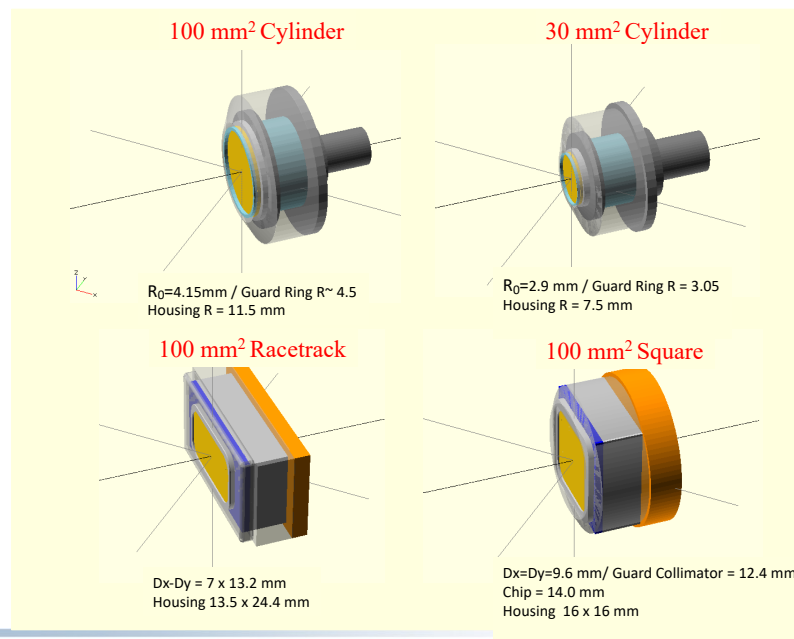
Hartmut Wiedersich, Charlie Allen, Mark Kirk, Dean Miller, Russ Cook, JG Wen.....

15

One of the First SDD's - ANL AAEM Project

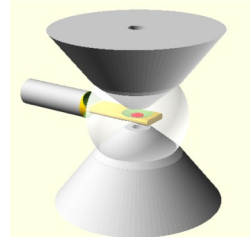
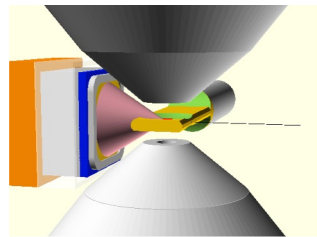
16

Today Detectors come in various sizes and shapes

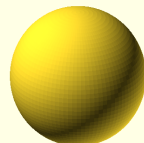


17

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

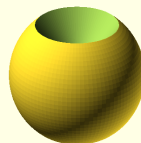


$4\pi \text{ sR}$



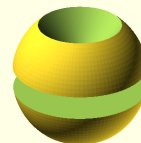
Theoretical Maximum

$\sim 2.5 \pi \text{ sR}$



Eliminate Pole Piece Volume

$> \pi^+ \text{ sR}$

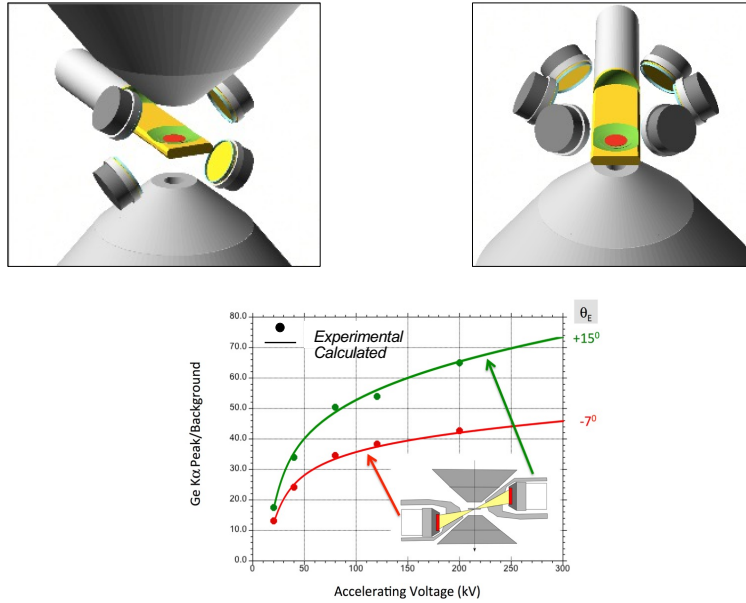


Eliminate Specimen Holder

The collection solid angle Ω is a key parameter

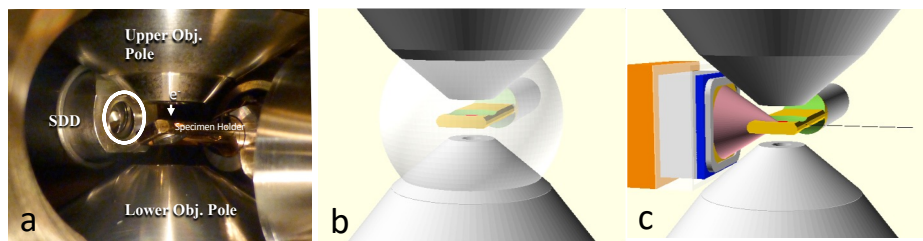
18

Non Traditional Geometries are now also possible



19

Traditional XEDS/AEM Geometry
Additional Limitations?

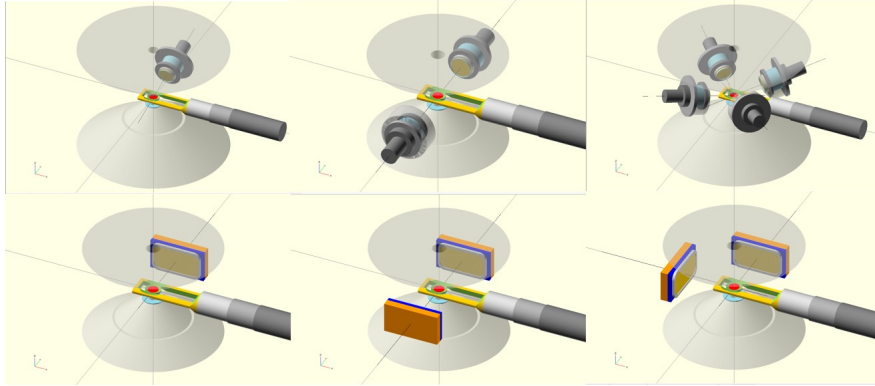


$$MDM \sim \frac{2.33}{\sqrt{I}}$$

20

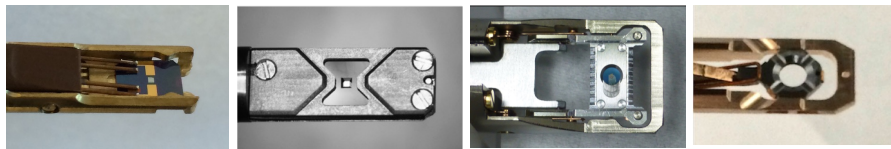
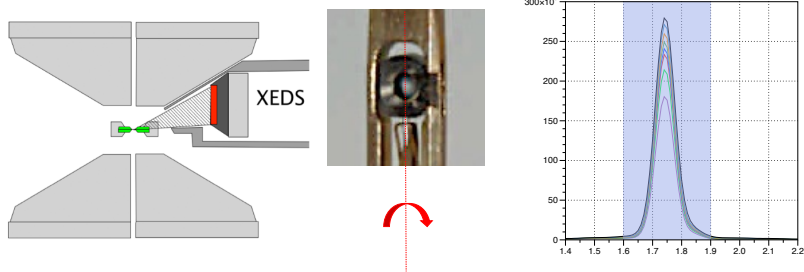
SDD Geometries are extremely varied today

Using the simple tilt series protocol, individual configurations can now be directly characterized and compared on equal and unbiased basis.

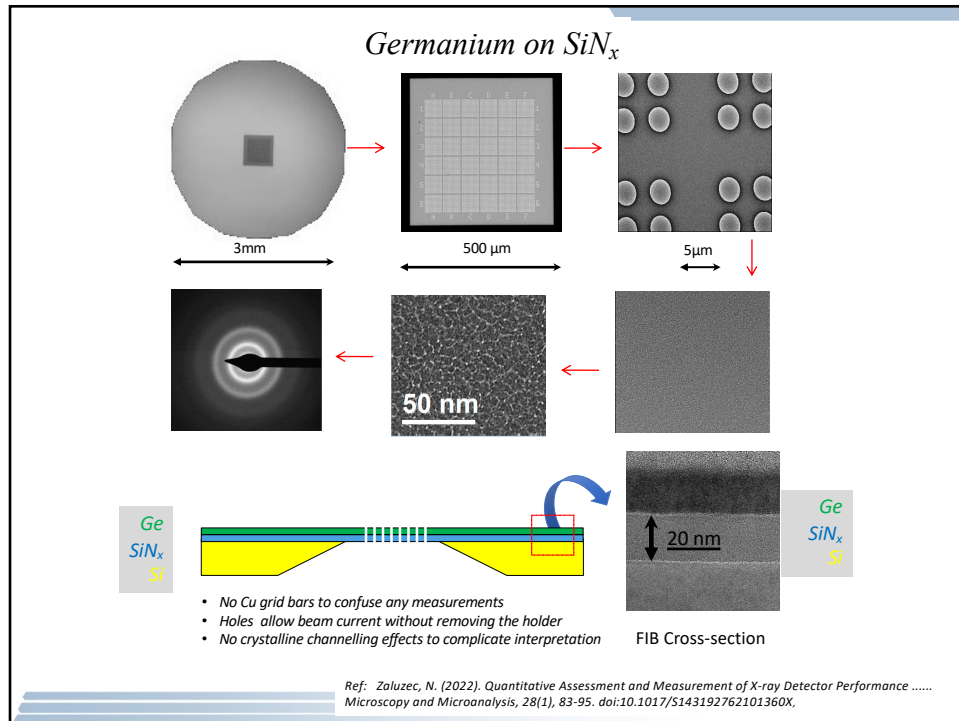


21

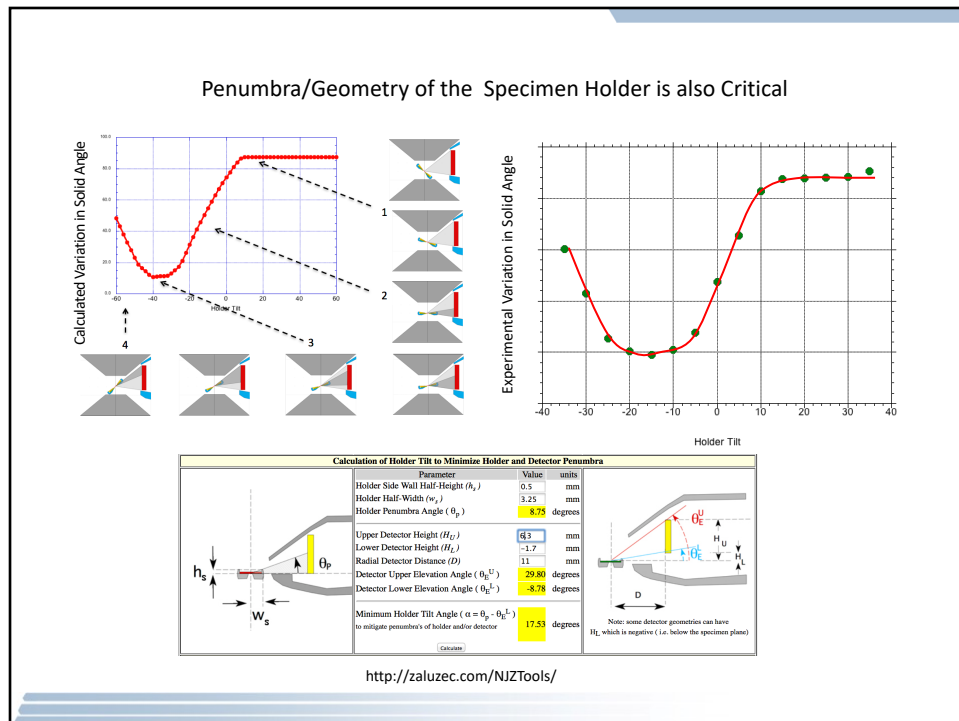
Penumbra of the specimen holder
is a limiting factor for XEDS in virtually all experiments
How do you determine it's real extent and minimize it or correct for it?



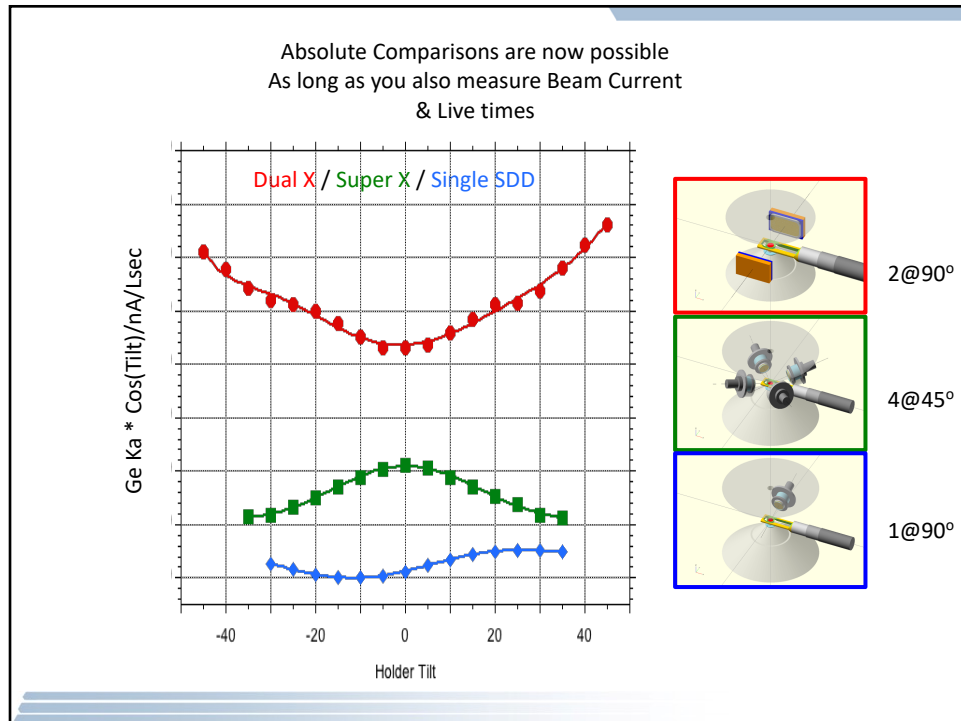
22



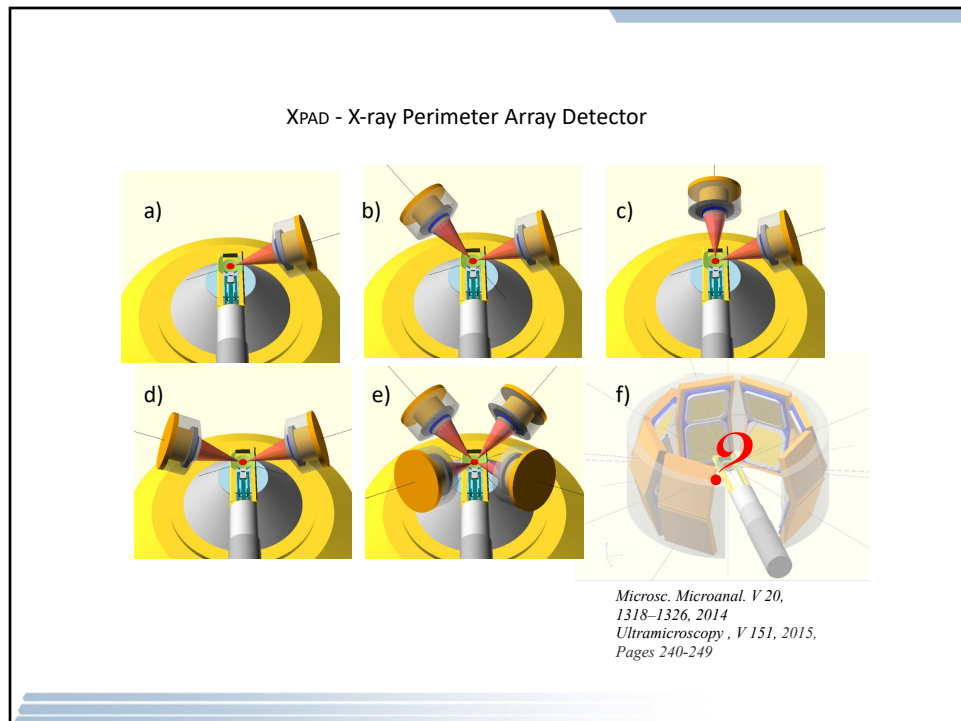
23



24

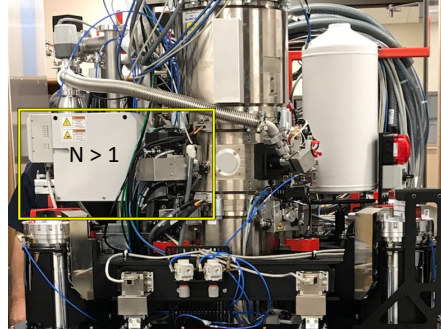


25



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ANL/UofC PicoProbe

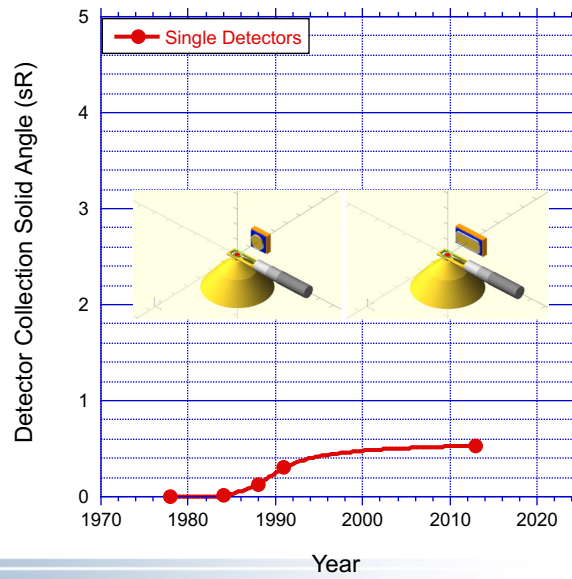


ANL LDRD Projects
ANL/ThermoFisher(FEI) CRADA #1300701

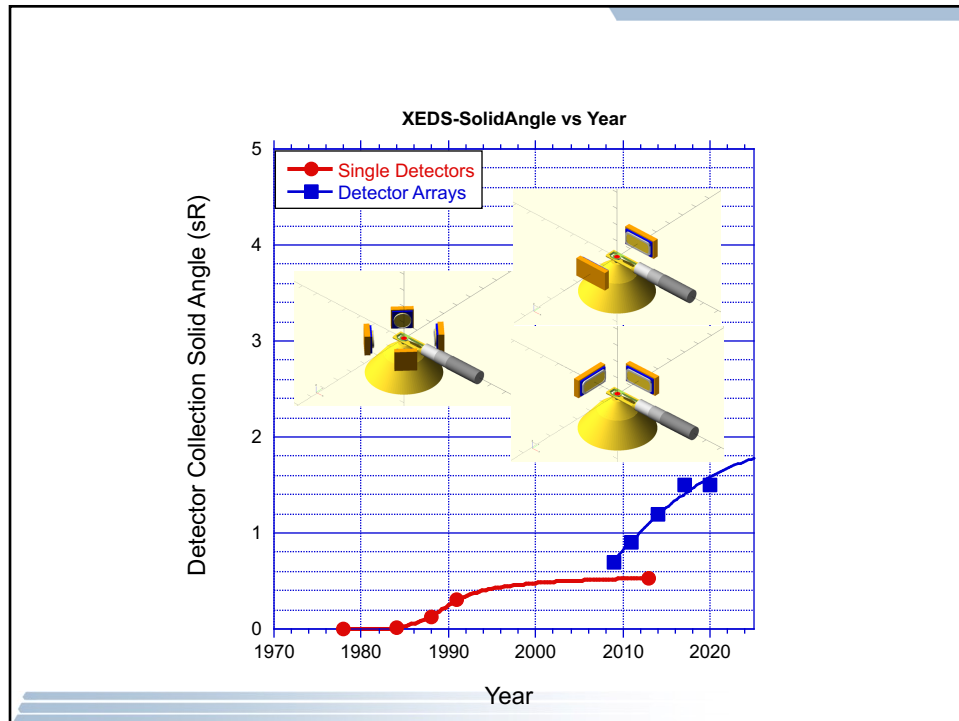
ThermoFisher
SCIENTIFIC

27

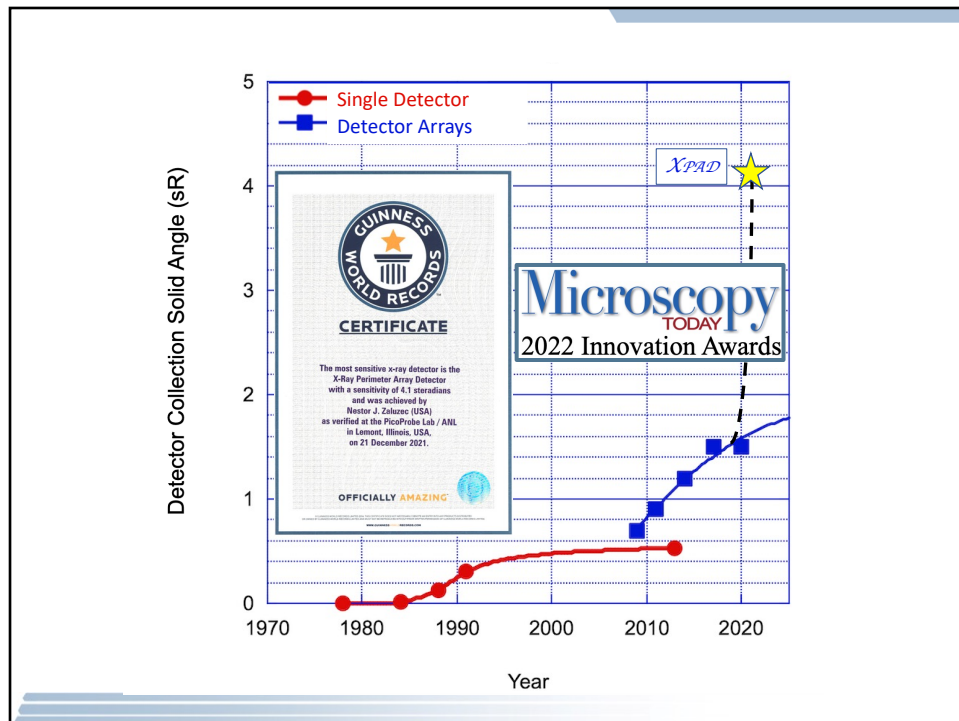
XEDS-SolidAngle vs Year



28

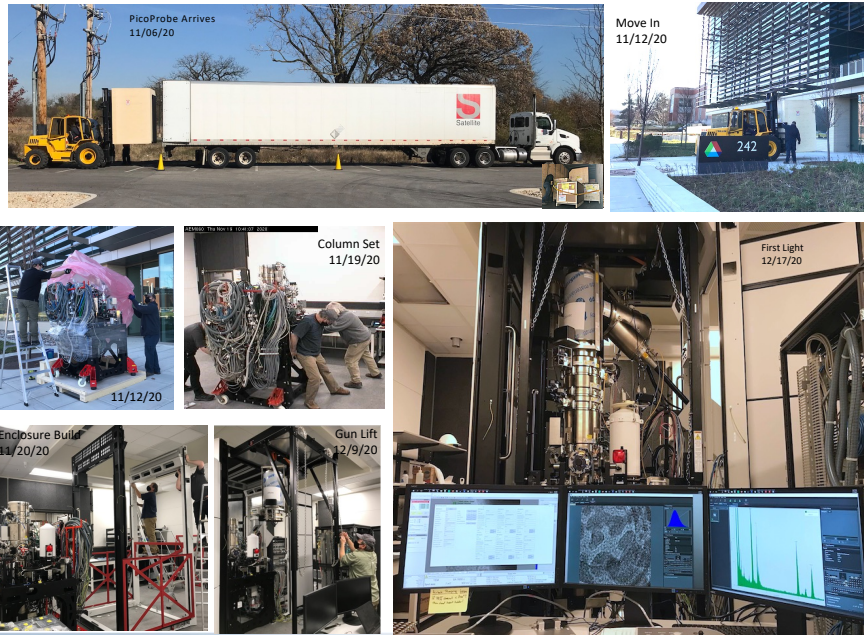


29

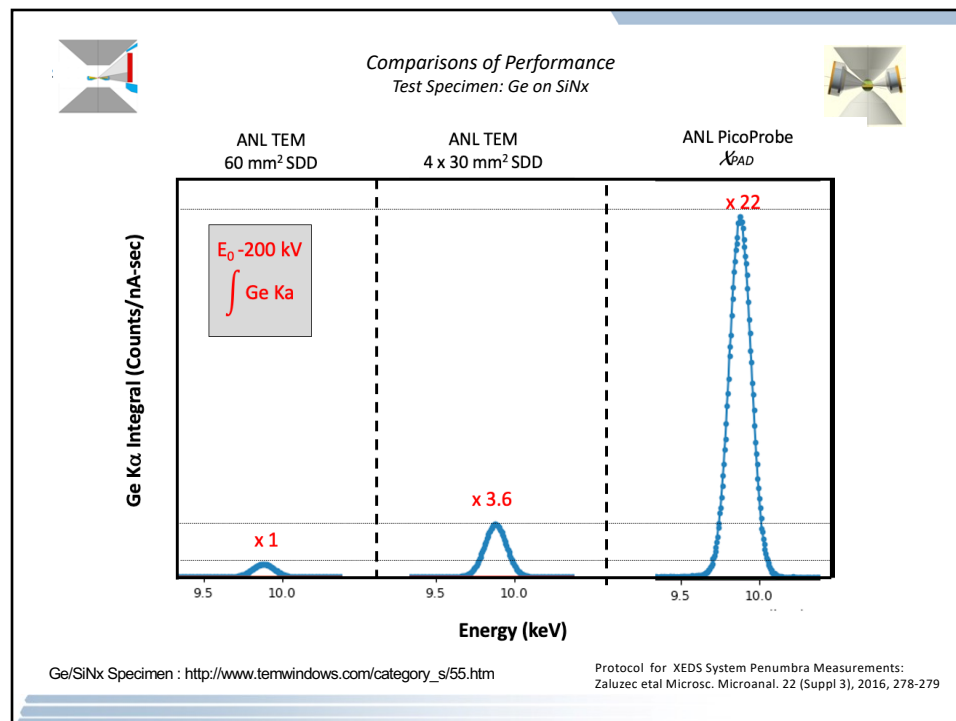


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Analytical PicoProbe Arrival → Assembly → First Light



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Quantitative Detector Configuration Comparisons

$$\Omega = 4\pi \cdot \frac{I_{K\alpha}}{\{\sigma_K \cdot \omega_K \cdot \Gamma_{K\alpha}\} \cdot \left\{ \frac{C_Z \cdot N_o \cdot \rho_Z}{W_Z} \right\} \cdot t_Z \cdot \eta_o \cdot \tau \cdot \varepsilon_{K\alpha}}$$

Detector Configuration	Experimental Ge Ka Intensity (Integrated counts/nA-sec)	Theoretical Cross-section (Barns)	Experimental Ω (sR)
Single 60 mm ² SDD	610	157.8-182.7	0.18-0.16
Quad 30 mm ² SDD	2105	157.8-182.7	0.62-0.54
Dual 100 mm ² SDD	4310	157.8-182.7	1.27-1.10

$I_{K\alpha}$ = Net integrated full K α peak intensity
 σ_K = Kth shell x-ray ionization cross-section
 ω_K = Kth shell x-ray fluorescence yield
 $\Gamma_{K\alpha}$ = Radiative partition function for the K α signal
 C_Z = Composition of the volume producing the signal
 N_o = Avogadro's Number

ρ_Z = Density of the volume producing the signal
 W_Z = Atomic weight of the species producing the signal
 t_Z = Thickness the volume producing the signal
 η_o = Incident electron beam current
 τ = Acquisition live time
 $\varepsilon_{K\alpha}$ = X-ray detector efficiency for $I_{K\alpha}$.

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

Accelerating Voltage (kV)	Average Ge Ka Intensity (Integrated counts/nA-sec)	Theoretical Cross-section (Barns)	Experimental Ω (sR)
200	15570	157.8-182.7	4.28 $\pm$ 0.3
300	15160	144.0-167.5	~ 4.55 $\pm$ 0.3

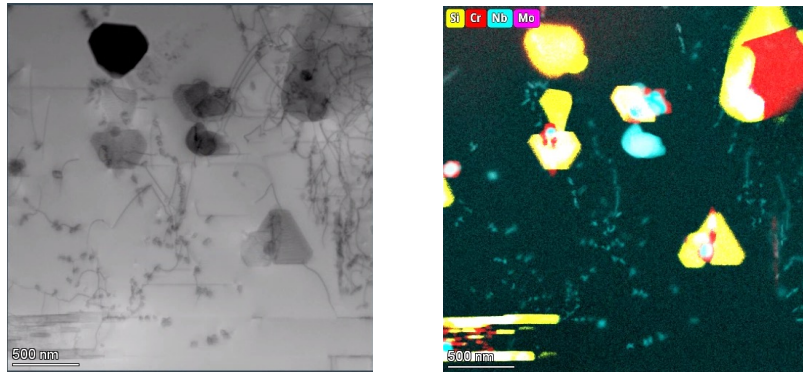
Experimentally determined solid angle for XPAD on the ANL PicoProbe. The designed solid angle was 4.47 sR and is within the errors of the cross-section models used.

Zaluzec N.J. , (1984) "K and L Shell Cross Sections for X-ray Microanalysis in an AEM" Analytical Electron Microscopy, ed. D. Williams, San Francisco Press, 279-284,

Llovet, X, Powell, C.J., Salvat, F. and Joblonski A, (2014) "Cross Sections for Inner-Shell Ionization by Electron Impact, Journal of Physical and Chemical Reference Data 43, 13102

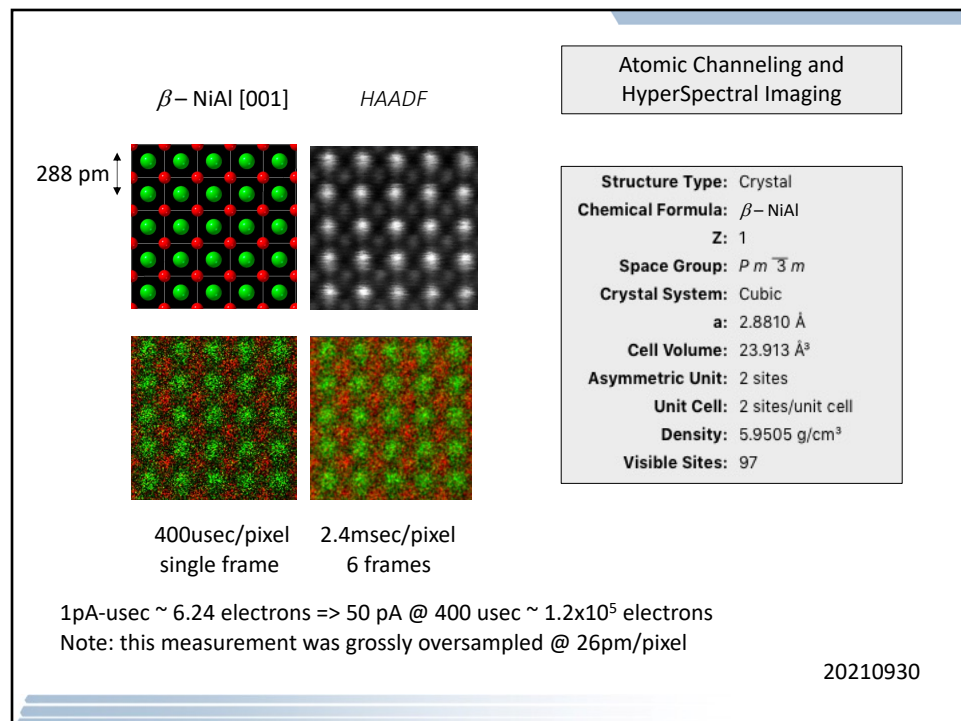
34

HyperSpectral Image Carbide Precipitates in Type 709 Steel

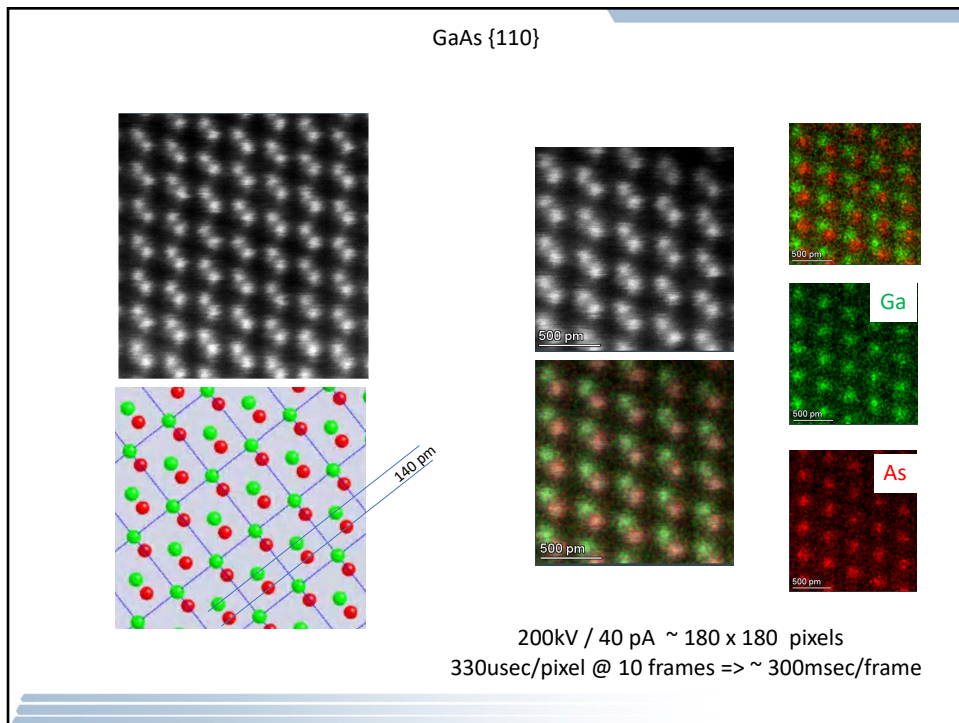


ElectroPolished Type 709 Steel
 ANL PicoProbe/XPAD
 300 kV, 400 pA @ 40 kX
 2K x 2K @ 13.7 ms/pixel
 Conventional background subtracted
 0.7 pixel Gaussian Blur to minimize noise

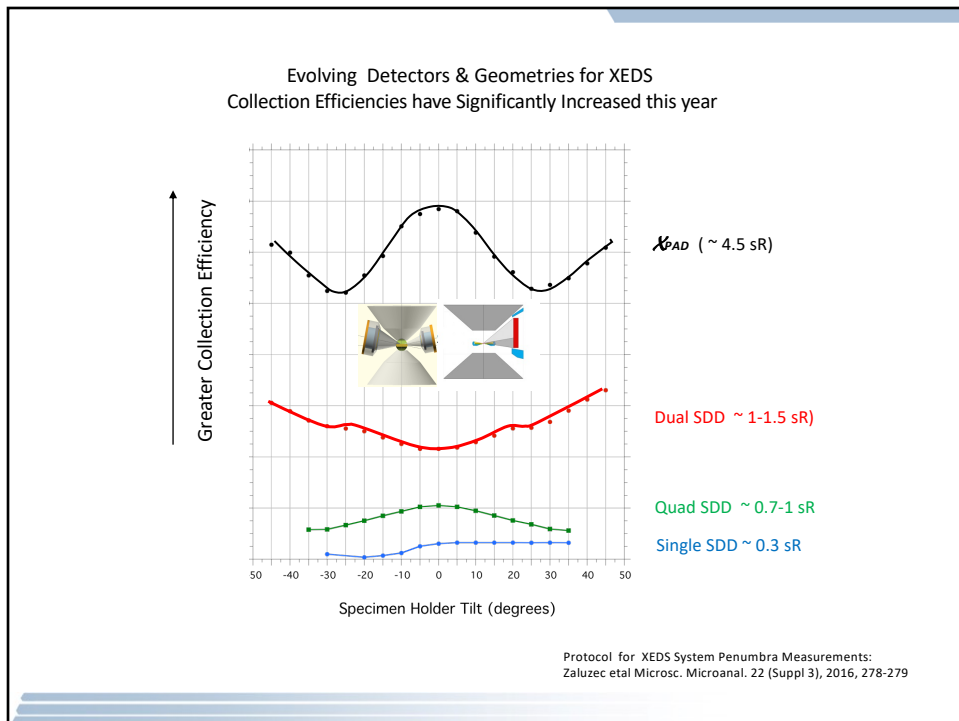
35



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37



38

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_k = Characteristic (Peak) Signal from X

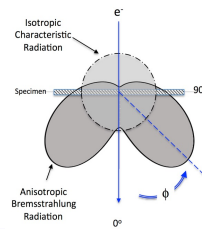
(I_x/B_x) = Peak to Background ratio for X

η_o = Incident electron flux

J_o = Incident electron current density

d = Probe diameter

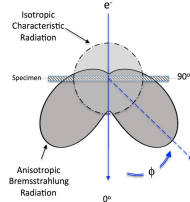
τ = Analysis time



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Spectroscopic Detectability Limits

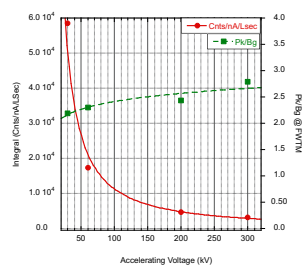
Signal in the Presence of Background



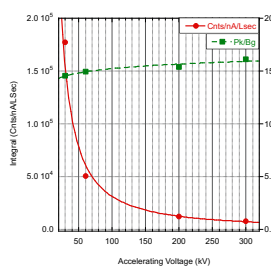
$$I_\alpha = \{ \sigma_\alpha(E_o, Z) \cdot \Gamma_\alpha \cdot \omega_\alpha \} \cdot \left\{ \frac{C_Z \cdot N_o \cdot \rho}{W_Z} \right\} \cdot \xi_o \cdot t \cdot \left\{ \varepsilon_\alpha \cdot \frac{\Omega}{4\pi} \right\}$$

$$I_{Bg} = I_i \cdot \left\{ \frac{\sin^2(\phi)}{[1 - \beta \cdot \cos(\phi)^4]} \right\} + I_j \cdot \left\{ 1 + \frac{\cos^2(\phi)}{[1 - \beta \cdot \cos(\phi)^4]} \right\}$$

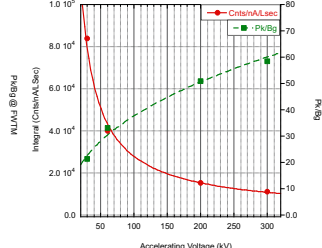
N K vs Accelerating Voltage



Si Ka vs Accelerating Voltage



Ge Ka vs Accelerating Voltage



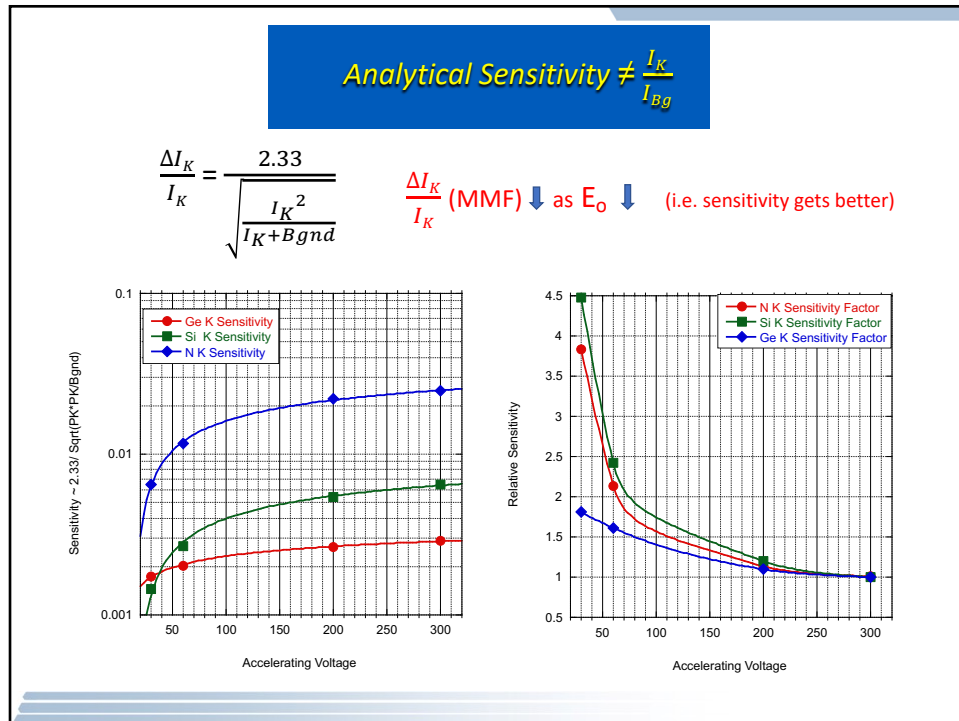
$$I_k \uparrow \text{ as } E_o \downarrow$$

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

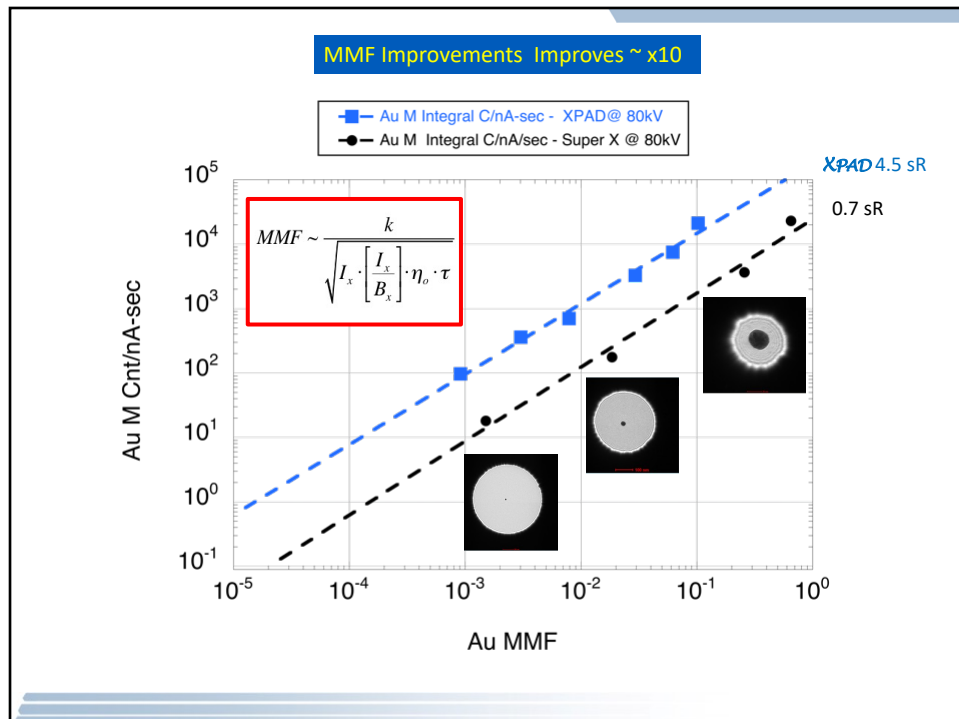
$$\frac{I_k}{I_{Bg}} \downarrow \text{ as } E_o \downarrow$$

$$MMF \sim \frac{2.33}{\sqrt{I \cdot \left[\frac{I}{B} \right]}}$$

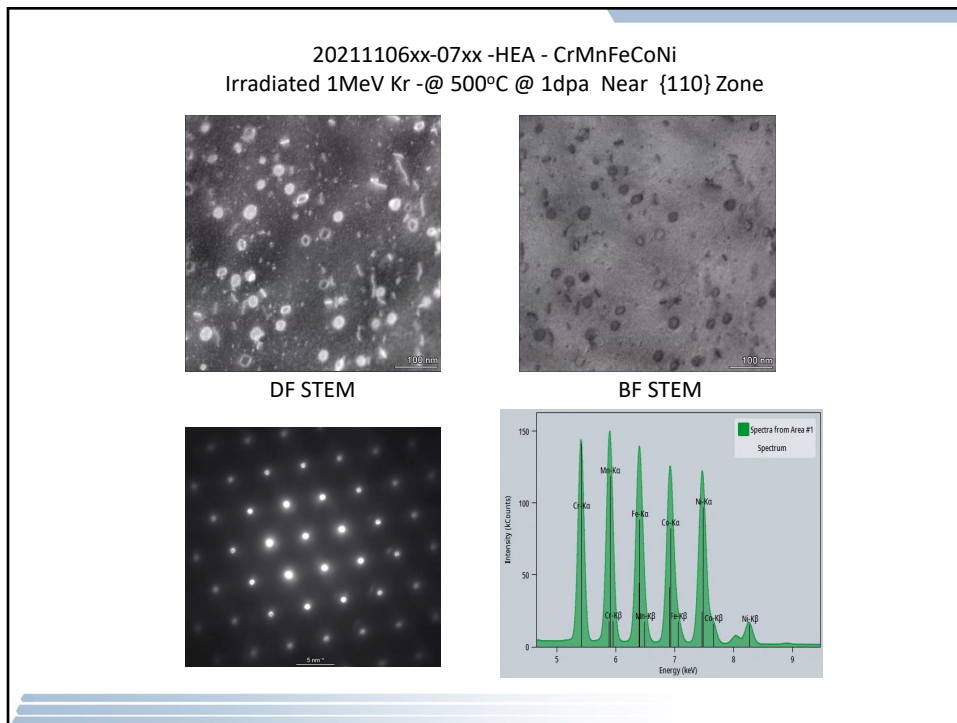
40



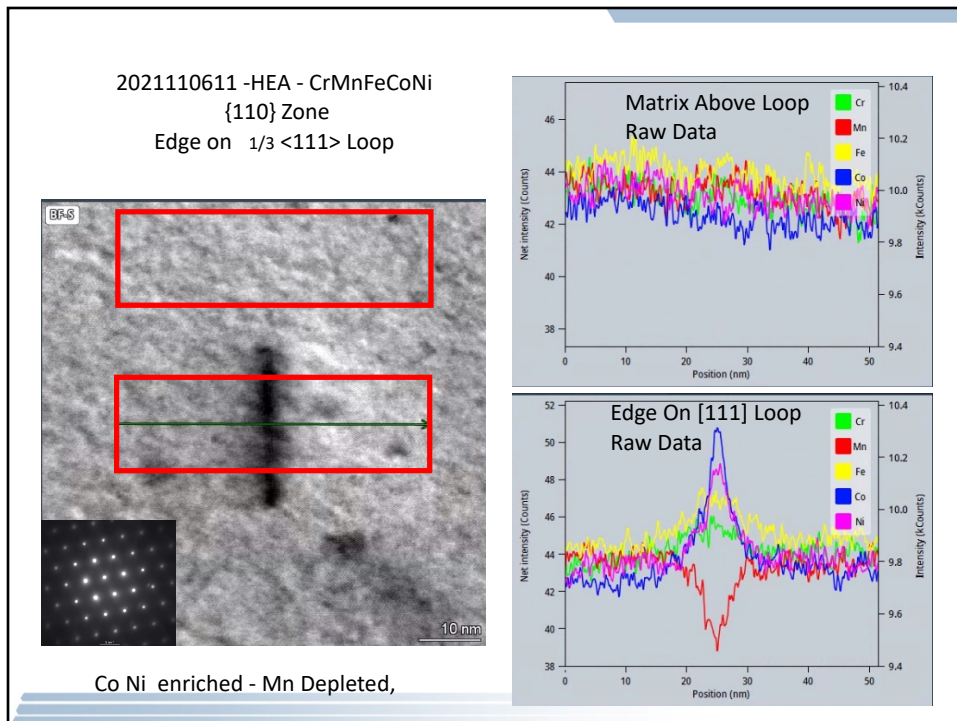
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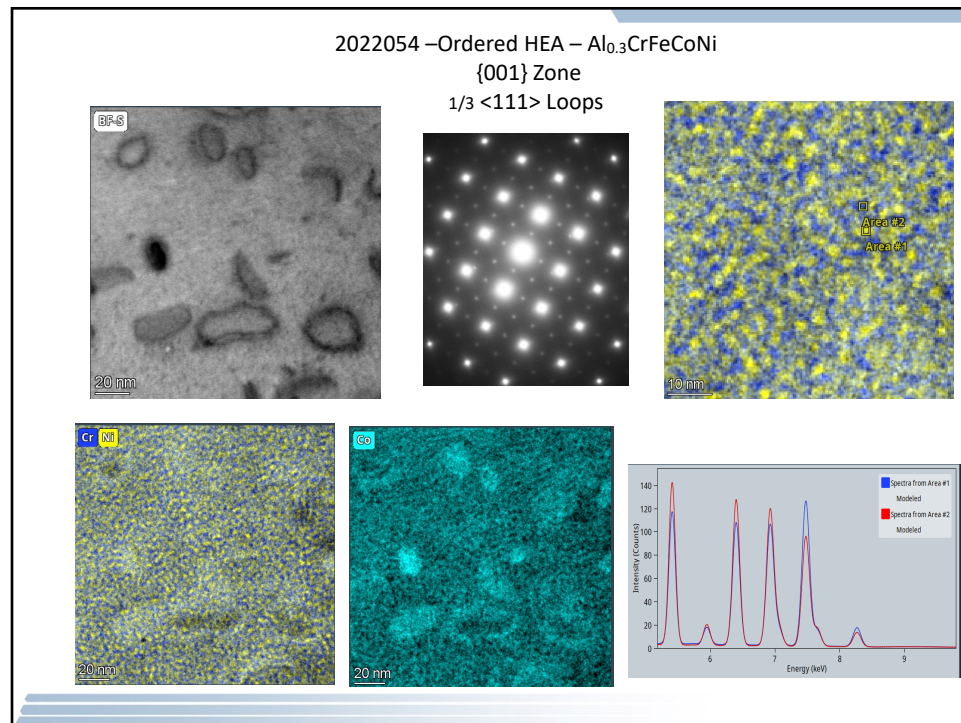
42



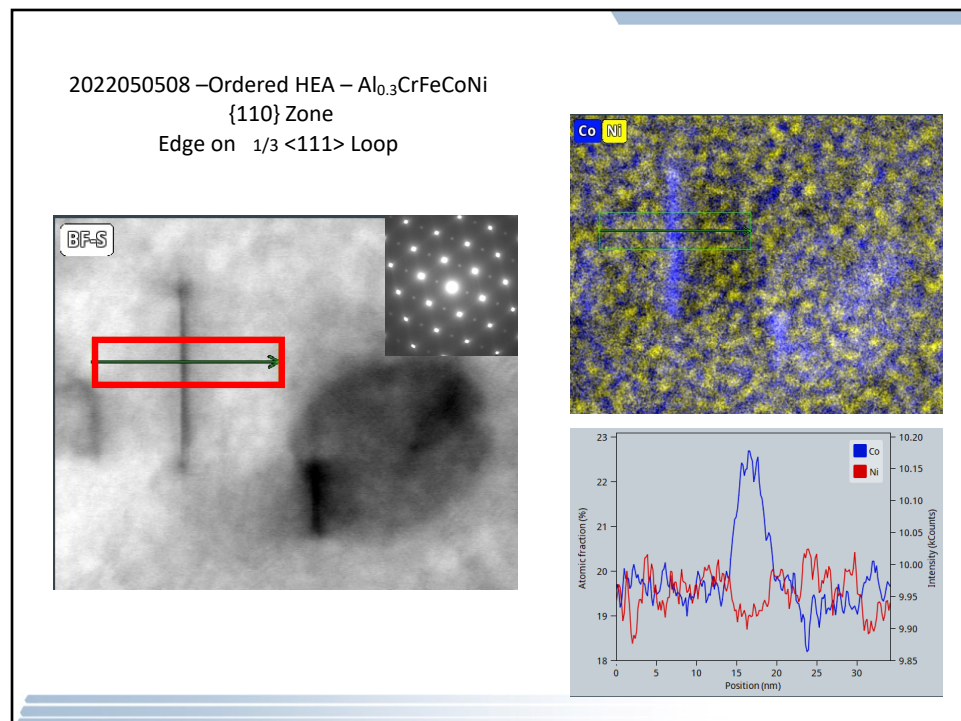
43



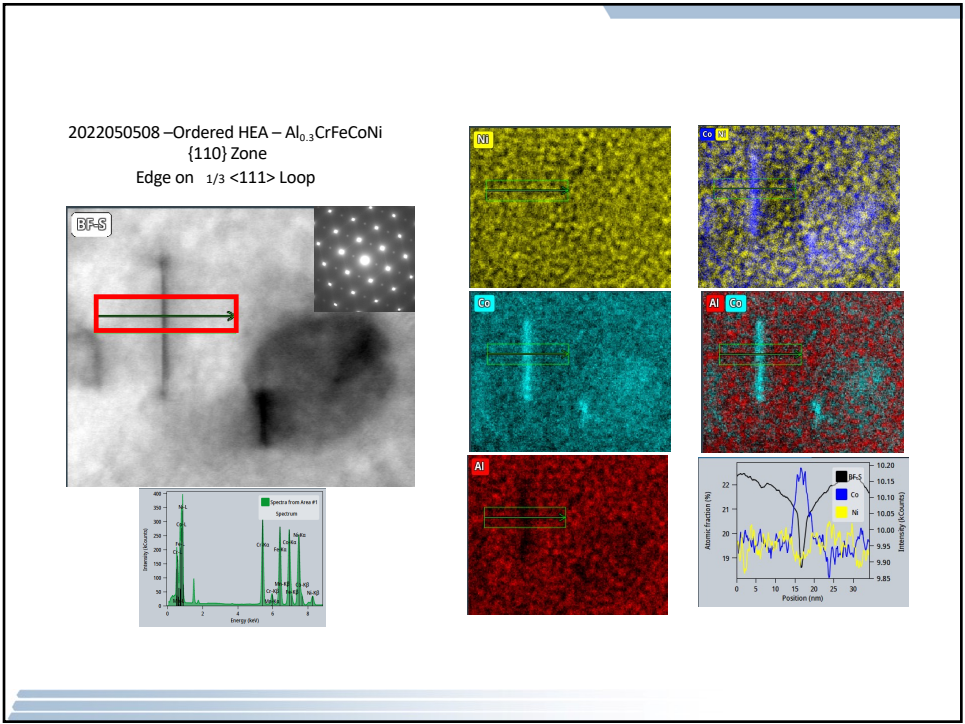
44



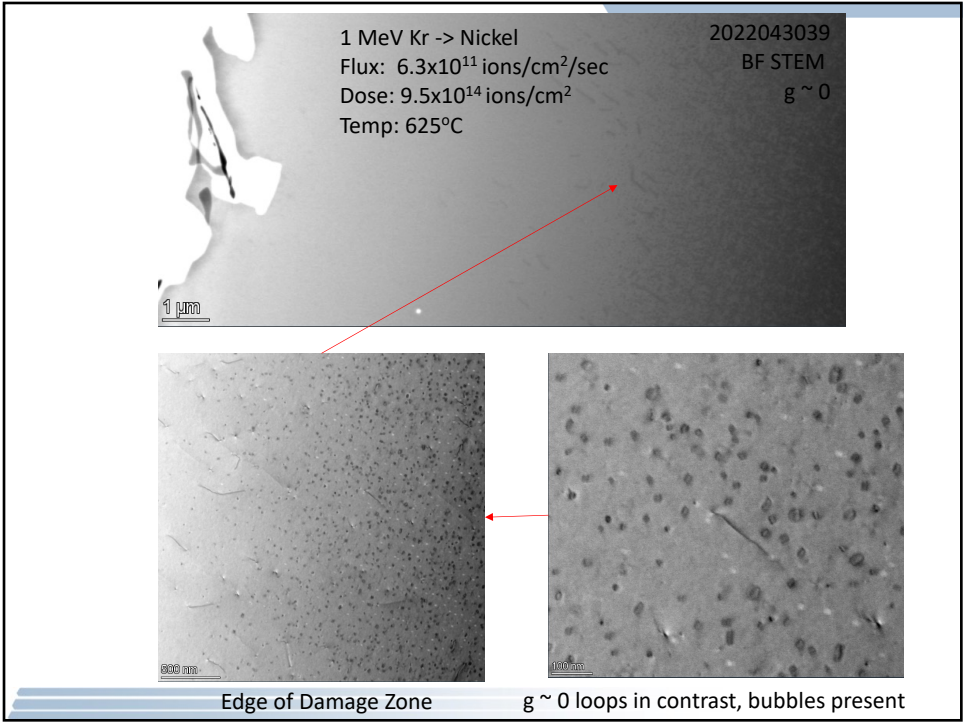
45



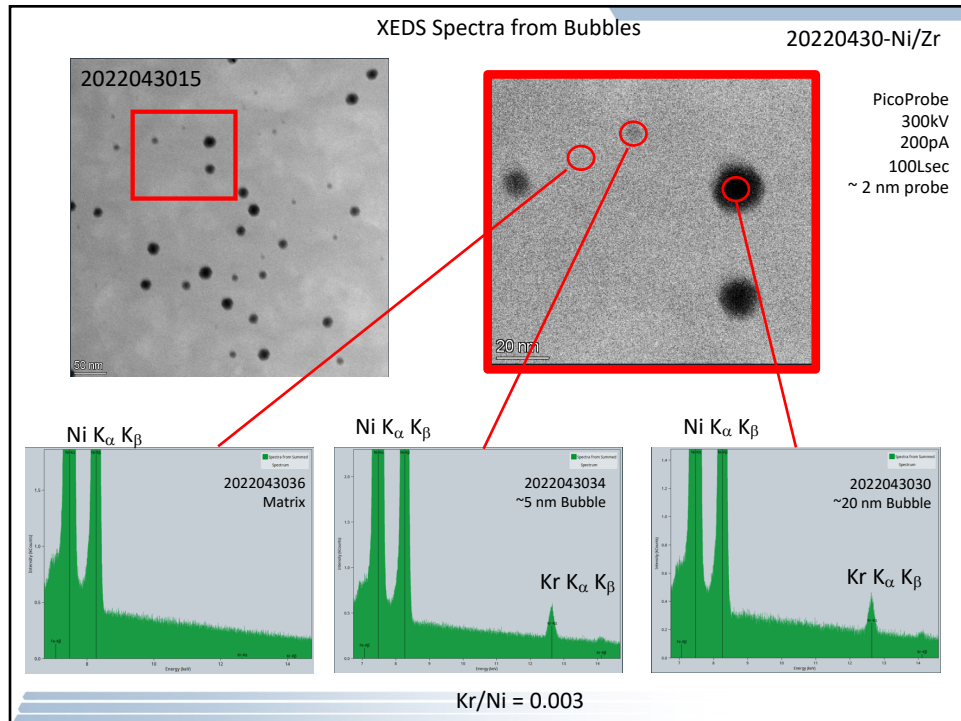
46



47

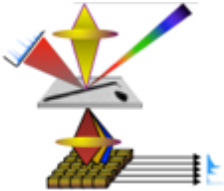


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If you can't detect it, then you can't measure it.



Thanks !

Questions ?





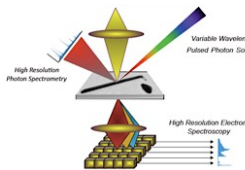
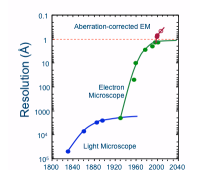
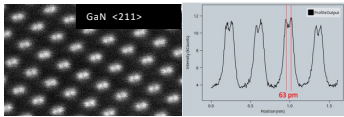
Zaluzec@aaem.amc.anl.gov
Zaluzec@Microscopy.com



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The Analytical PicoProbe Electron Optical Beam Line

**<211> GaN sub-atomic image
Ga-Ga = 63 pm**

Key Features/Attributes at Commissioning

- Eo: 30-300 kV Electron Source
- High Brightness Coherent Field Emission Gun
- Probe Corrector ($\delta x < 55 \text{ pm}$)
- Monochromator ($\delta E \leq 30 \text{ meV}$)
- XRD 4.5 sR X-ray Spectrometer
- ZTwin Lens
- Next Generation Multi-Port Octagon
- HR/LowDrift Piezo Goniometer
- 4Kx4Kx16 bit CMOS Imaging Detector
- 128x128x30bit Diffraction Camera
- CTEM/STEM/iDPC /4DSTEM Modes
- Analytical LBHV DTilt Holder
- Ambient Tomography Holder
- Ptychography/Tomography Holder
- Ambient Liquid Cell Holder
- Cryo Tomography/Spectroscopy Holder
- Dynamic Imaging ~ 0-300 fps
- Multi-Modal Enabled
- Telepresence Enabled
- [Electron Energy Filter / UltraMono](#) - Spring 2023

Image Resolution
CTEM < 100 pm / STEM ~ 55 pm

Temporal Resolution
0-300+ fps (CTEM) 1 usec/pixel (STEM)

Spectroscopy
- Worlds most sensitive AEM XEDS detector (>4sR)
- **HR Energy Filter-Spectrometer** - (< 30 meV)

Environmental
Commercial and Custom (Ambient) In-Situ Holders
Direct Electron Detectors
Cryo EM Imaging for Soft/Hard, Energy & Quantum Materials
Cryo EM Prep / Inert transfer

Future
In-situ Gaseous Media @ Temperature
In-situ Photonics/UV/IR/NIR
Adaptive Holographic Optics



ANL/ThermoFisher
CRADA #1300701
ANL LDRD #2017-153
ANL PR/# 1006014
NSF MRI #2117896

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