ADVANCEMENTS IN SPECTROSCOPY AT APS-U BEAMLINE S-25

U.S. DEPARTMENT OF ENERGY

Argonne National Laboratory is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC.

Workshop for Future Science in Korea-4GSR
June 25 - 27, 2025

Argonne NATIONAL LABORATORY

OUTLINE

Spectroscopy Group, Beamlines and Science Examples

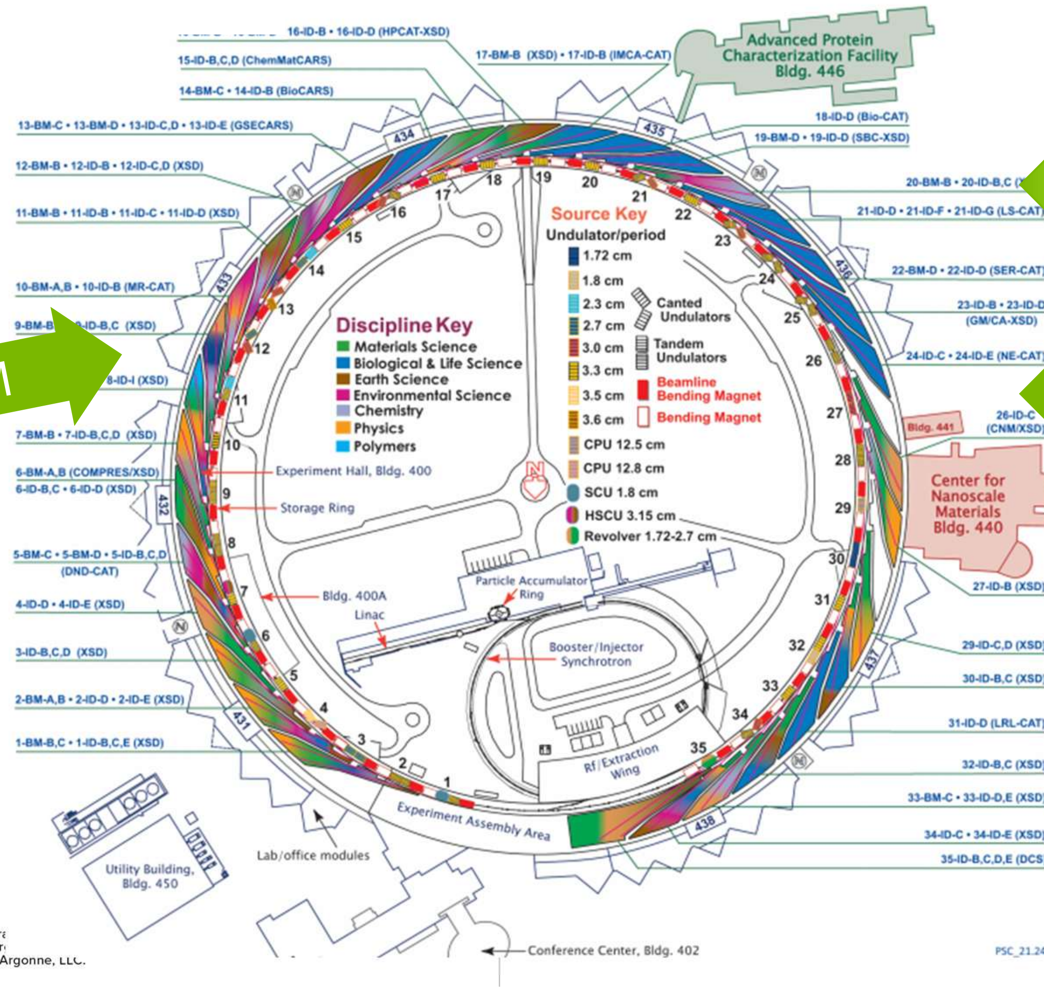
- Spectroscopy group and measurements
- Beamline design and specifications
- Science examples from early experiments

SPECTROSCOPY GROUP

Zou Finfrock
George Sterbinsky
Rishabh Ranjan
Jiaqi Wang
Anthony Gironda
M. Aleks Solovyev
Kamila Wiaderek
Debora Meira
Chengjun Sun
Yanna Chen
Mike Pape
Mark Wolfman
Shelly Kelly
Juanjuan Huang

SPC Group Beamlines: 20-BM, 9-BM, and 25-ID-C,D

9-BM



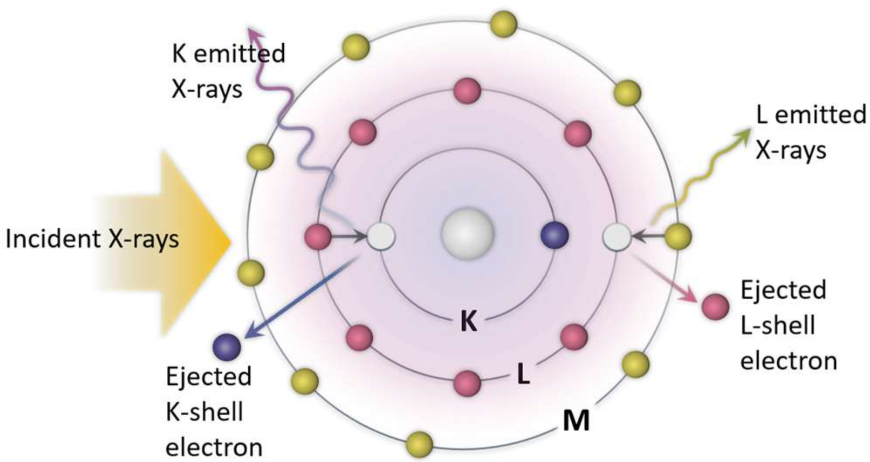
20-BM / 20-ID

New 25-ID!

SPECTROSCOPY MEASUREMENTS

Probing electronic and atomic environment of atoms

- Scan x-ray energy through absorption edge recording absorption or fluorescence (XAS) or partial fluorescence (HERFD)
- Set the x-ray energy above the absorption edge recording fluorescent x-ray energy (XES)
- Scan x-ray energy far above absorption edge recording x-rays with energy loss from interaction with core electrons (XRS)



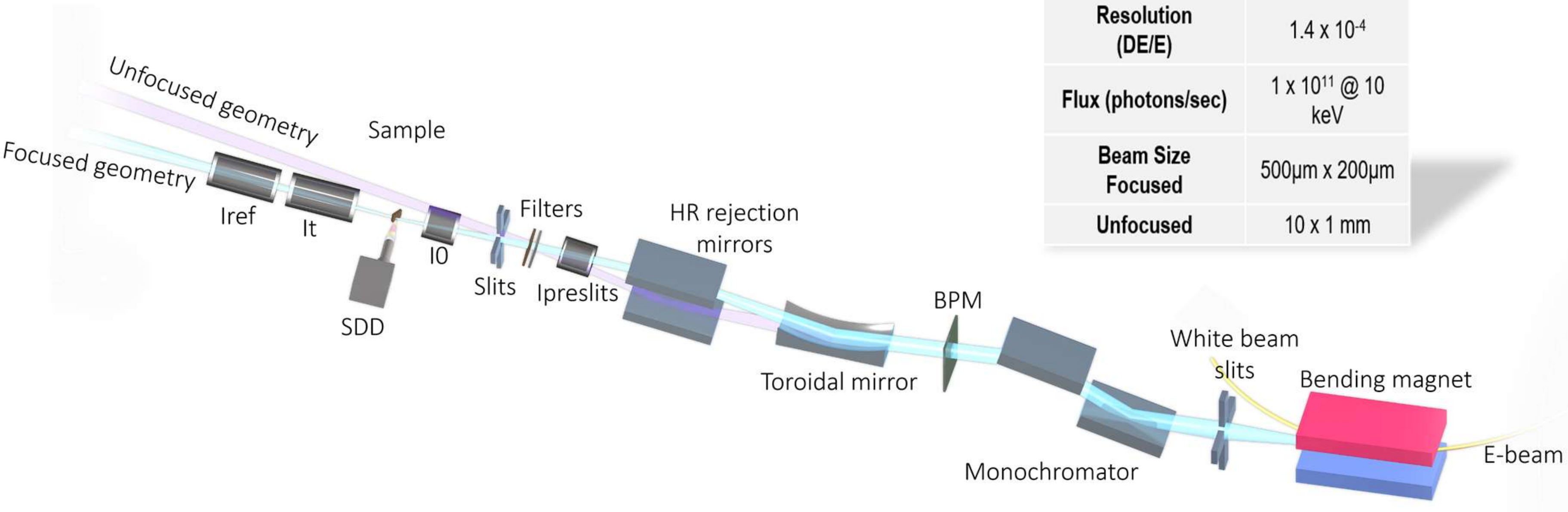
Combined with microprobe resolution and XRF mapping

The future will bring more image processing

20-BM X-RAY ABSORPTION SPECTROSCOPY

Highly productive XAS Beamline

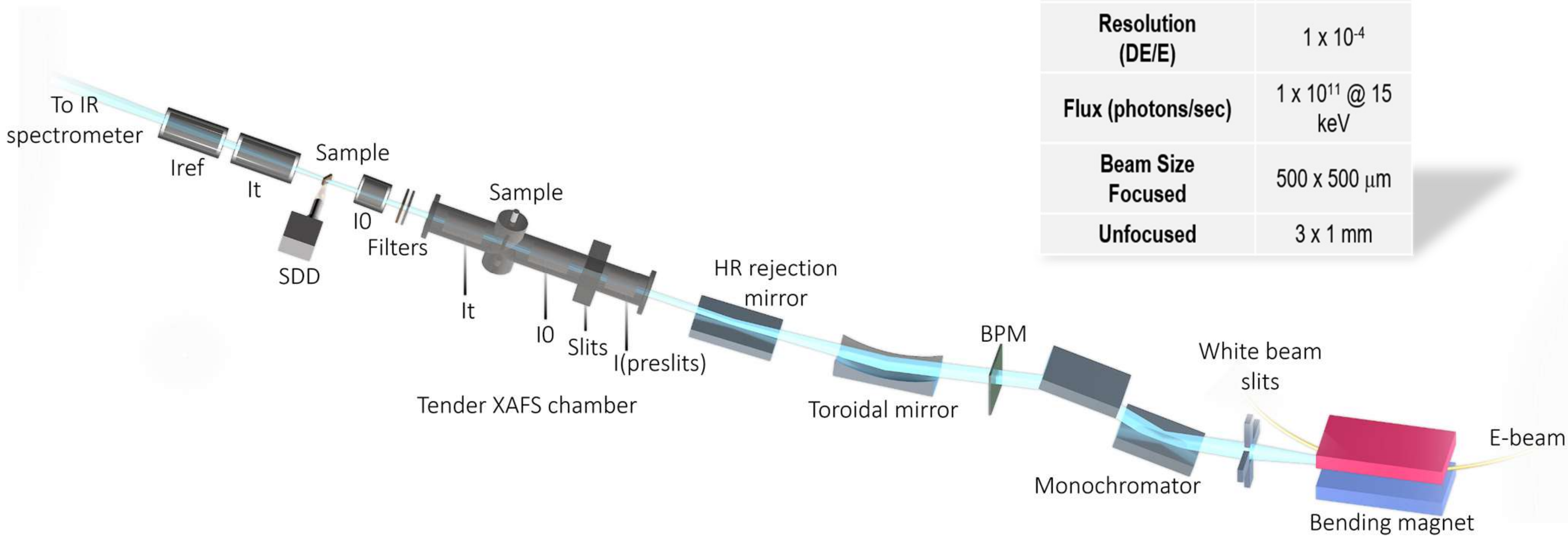
Source	20-BM
Monochromator	Si(111)
Energy Range	3.9 – 35 keV
Resolution (DE/E)	1.4 x 10^{-4}
Flux (photons/sec)	1 x 10^{11} @ 10 keV
Beam Size Focused	500μm x 200μm
Unfocused	10 x 1 mm



9-BM IN-SITU XAS BEAMLINE

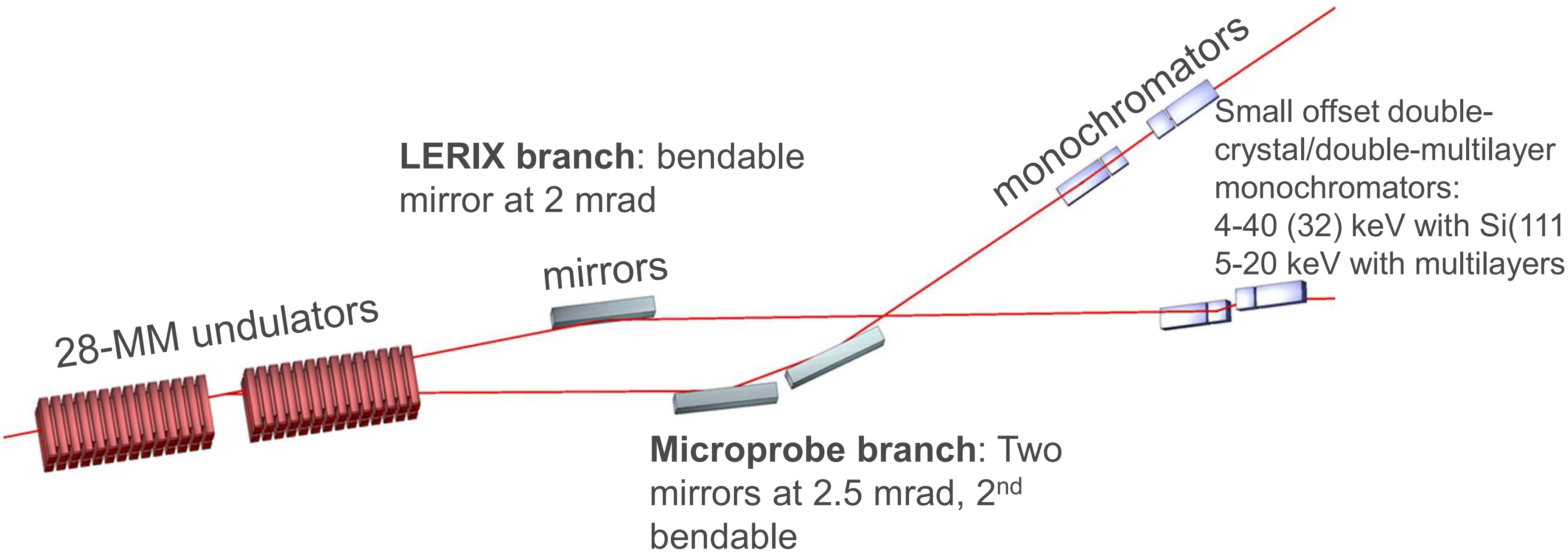
Fast scanning, wide energy range, In-situ

Source	9-BM
Monochromator	Si(111), Si(220)
Energy Range	2.1 – 40 keV
Resolution (DE/E)	1 x 10^{-4}
Flux (photons/sec)	1 x 10^{11} @ 15 keV
Beam Size Focused	500 x 500 µm
Unfocused	3 x 1 mm



S-25 BASIC OPTICAL LAYOUT

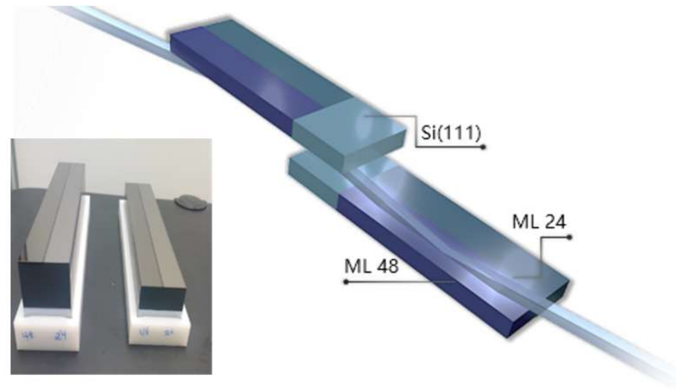
Horizontal deflecting mirrors to separate two beamlines



MONOCHROMATORS

Located in 25-ID-B

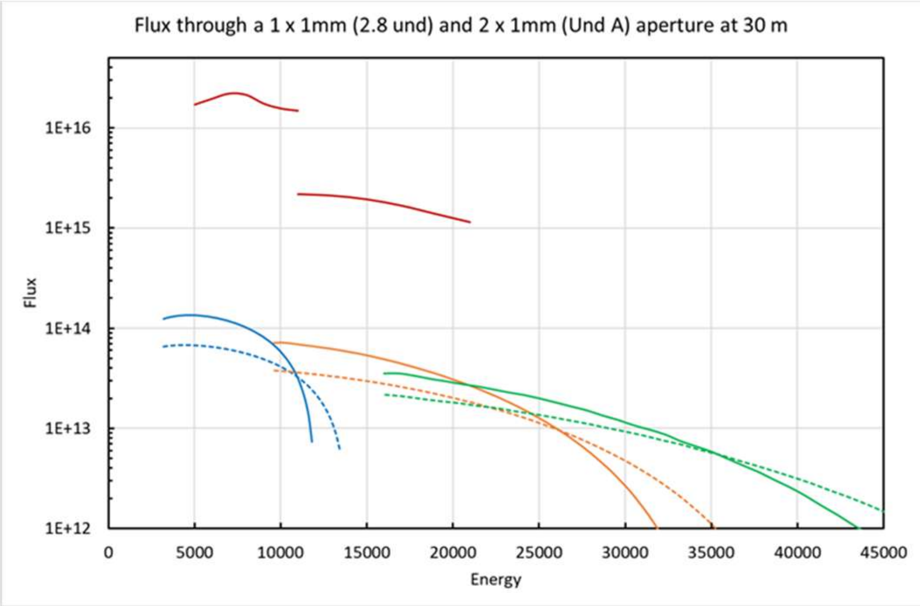
- Standard vertical deflection double crystal LN2 cooled
- Interferometers to monitor/correct crystal alignment
- Si(111) for entire energy range
- Small (10 mm) offset allows for multilayer
- Multilayers
  - 2 ML's (d=24 and 48 Å) to cover 5-21 keV
  - Accessed by small (~1 mm) vertical motion.
- Secondary mono Si (220 or 311) for higher energy resolution e.g. LERIX



Multilayers		Energy range	BW
ML 48 (d = 48 Å)	Mo (12 Å) + B_4C (36 Å)	4.9 – 10.7 keV	~ 3%
ML 24 (d = 24 Å)	Mo (10 Å) + B_4C (14 Å)	9.8 – 21.5 keV	~ 1%

MONOCHROMATORS

Located in 25-ID-B

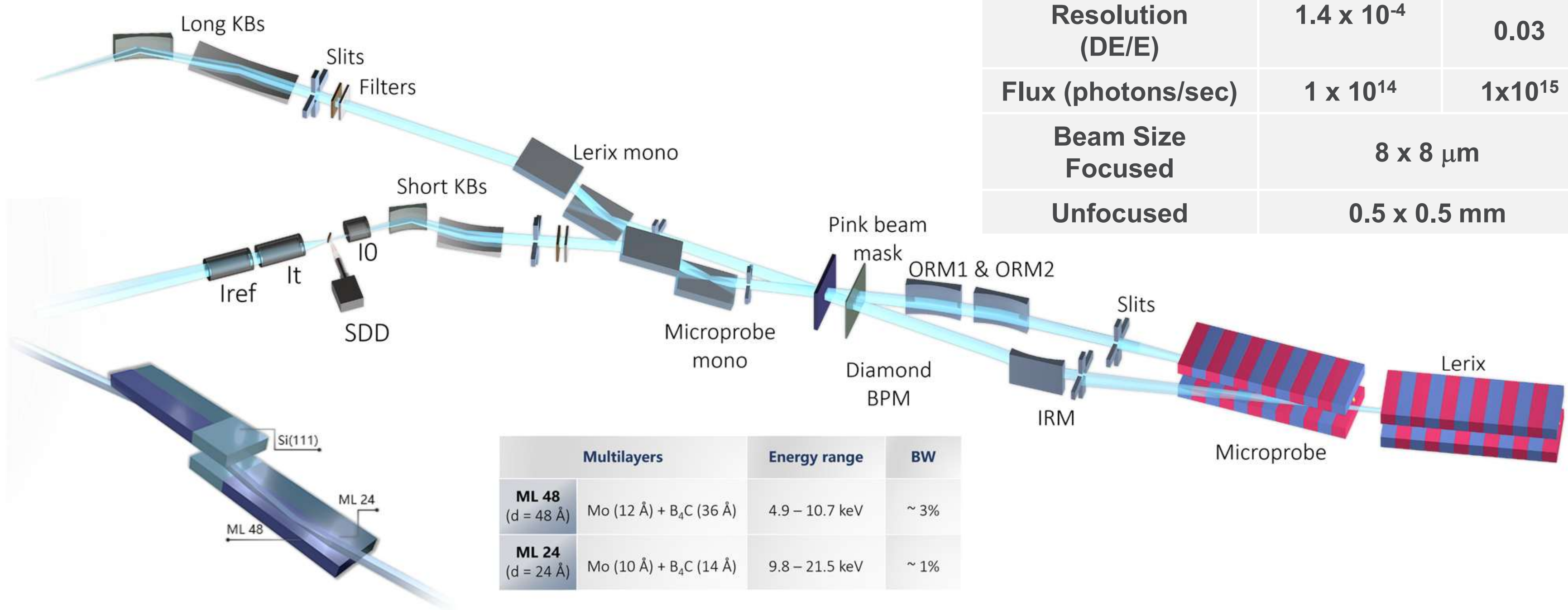


- Multilayers enable non-resonant applications with much higher flux

SPECTROSCOPY GROUP

S-25 Advanced Spectroscopy

Source	25-ID-C/D	
Monochromator	Si(111), 2nd Si(220)	Multilayer
Energy Range	4-40/32 keV	5-20 keV
Resolution (DE/E)	1.4×10^{-4}	0.03
Flux (photons/sec)	1×10^{14}	1×10^{15}
Beam Size Focused	$8 \times 8\ \mu m$	
Unfocused	0.5 x 0.5 mm	



Multilayers		Energy range	BW
ML 48 (d = 48 Å)	Mo (12 Å) + B_4C (36 Å)	4.9 – 10.7 keV	~ 3%
ML 24 (d = 24 Å)	Mo (10 Å) + B_4C (14 Å)	9.8 – 21.5 keV	~ 1%

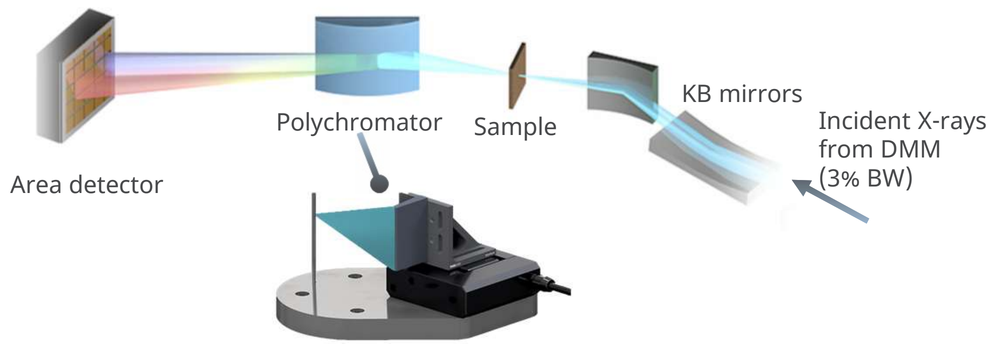
DISPERSIVE XAS DEMONSTRATION

Prototype success-fully commissioned

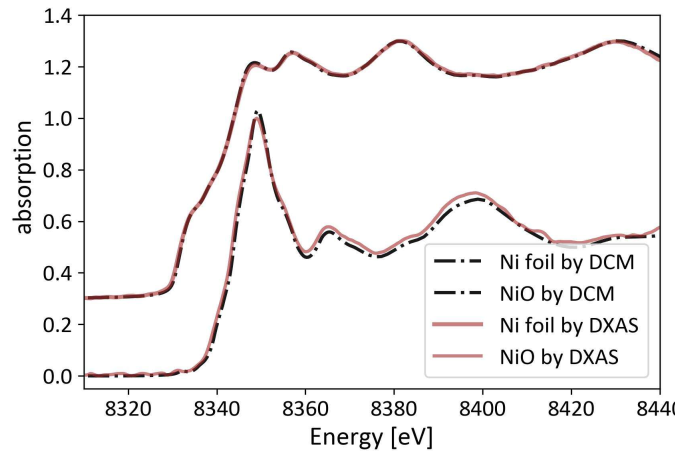
- DXAS, as a single-shot technique, offers significant advantages for XAS mapping and time-resolved measurements.
- Initial spectra measured on standard references samples replicate those from a DCM
- Combined with fly scanning of the sample stage to achieve rapid 2D XANES mapping capabilities, particularly *for in situ* and *in operando* measurements.

https://doi.org/10.1107/S1600577525004953.

DXAS setup

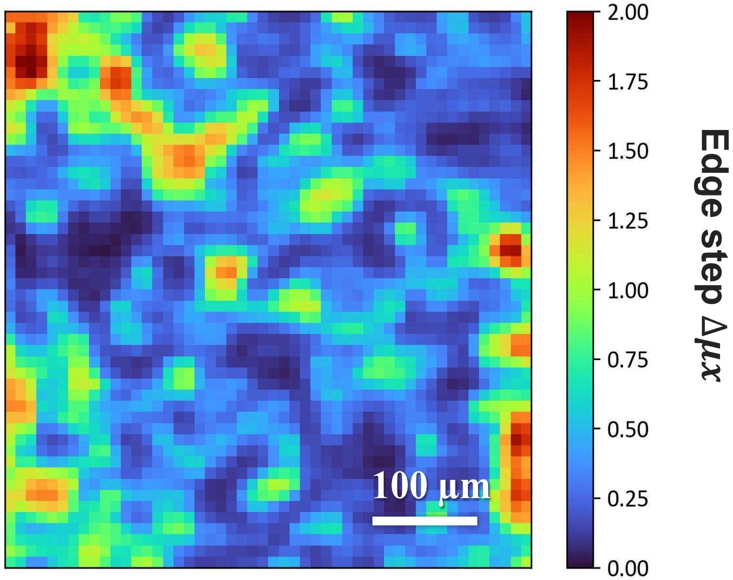


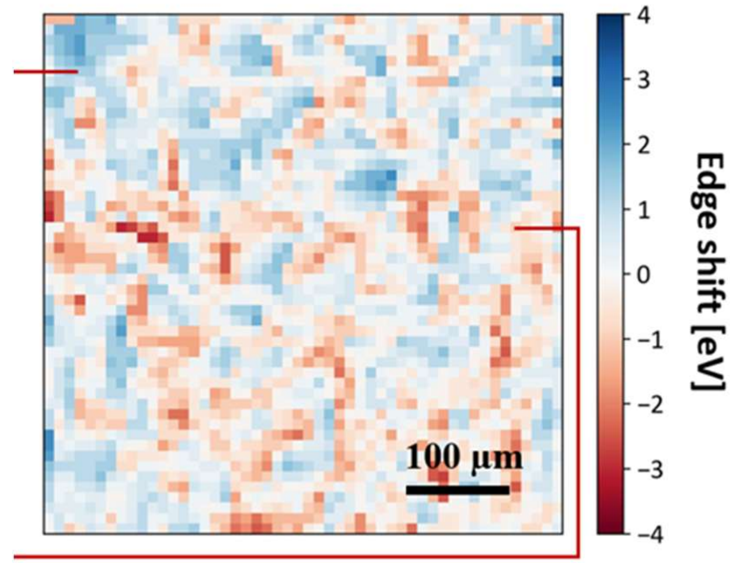
DXAS results



DISPERSIVE XANES MAPPING

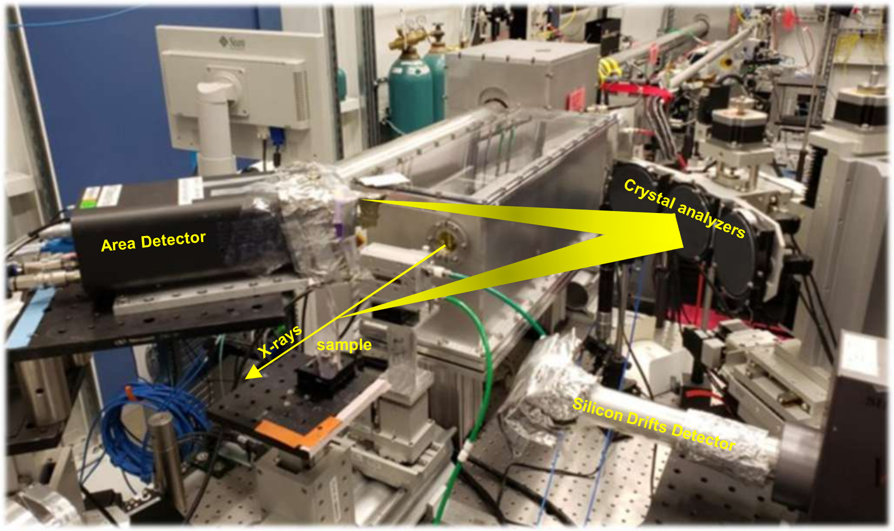
Spatial maps of absorption and edge-shift derived from spatially resolved Dispersive XAS on a $Mn_xNi_yO_z$ laminate.

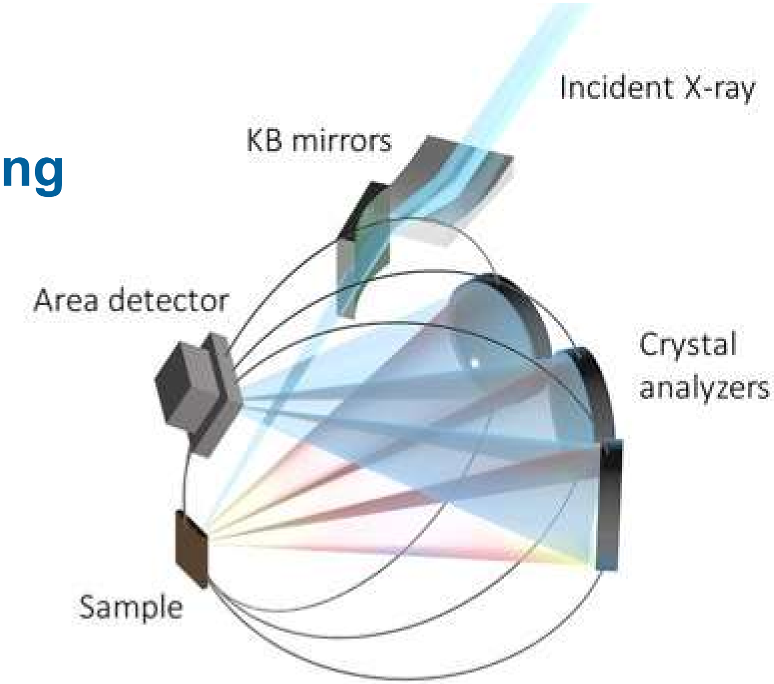




HERFD AT S-25

Three crystal spectrometer commissioning

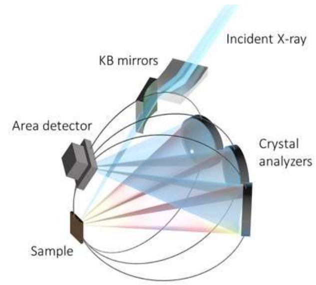




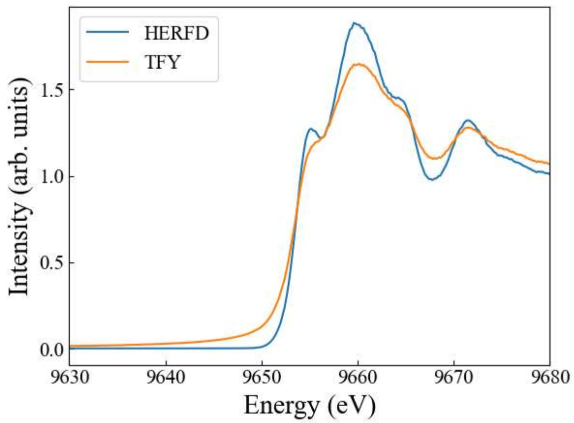
- Range of Si crystals available: Si(111), (100), (110), (211), (311), (773), (911)
- Common edges: Cr, Mn, Fe, Co, Ni, Cu, Zn, As, W, Au, Hg, Pb, U, Ce

HERFD EXAMPLES AT S-25

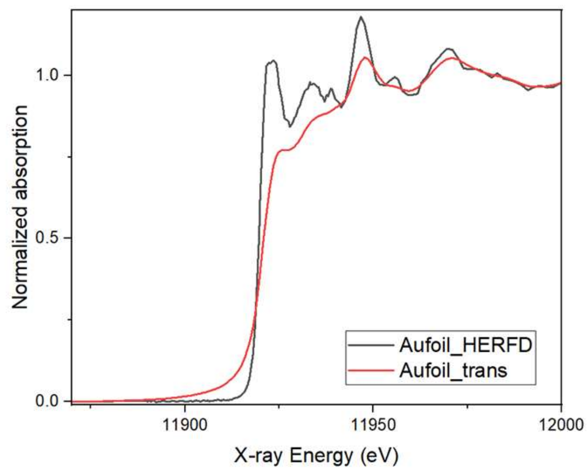
From thin films, bulk foils to dilute U-oxides



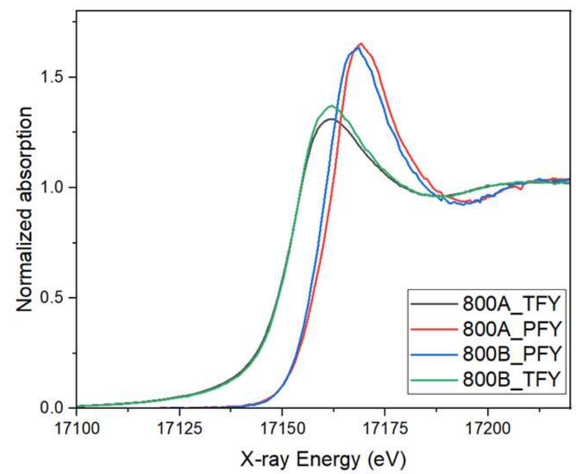
ZnO film



Au foil



U-oxides

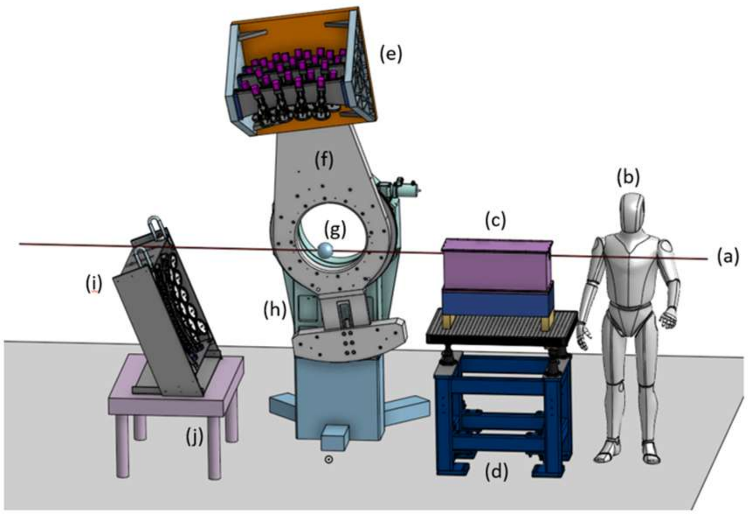


- Absorption edge features become more pronounced
- Sample differences are more apparent

X-RAY RAMAN SCATTERING (XRS)

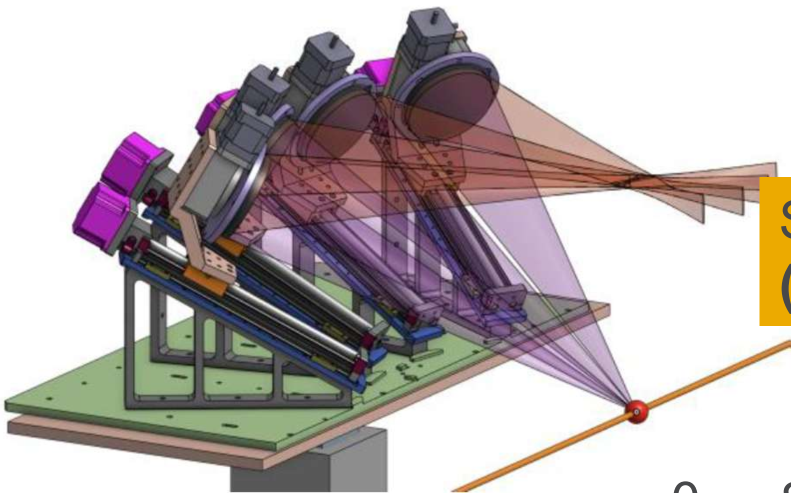
Probing soft x-ray transitions with hard x-rays

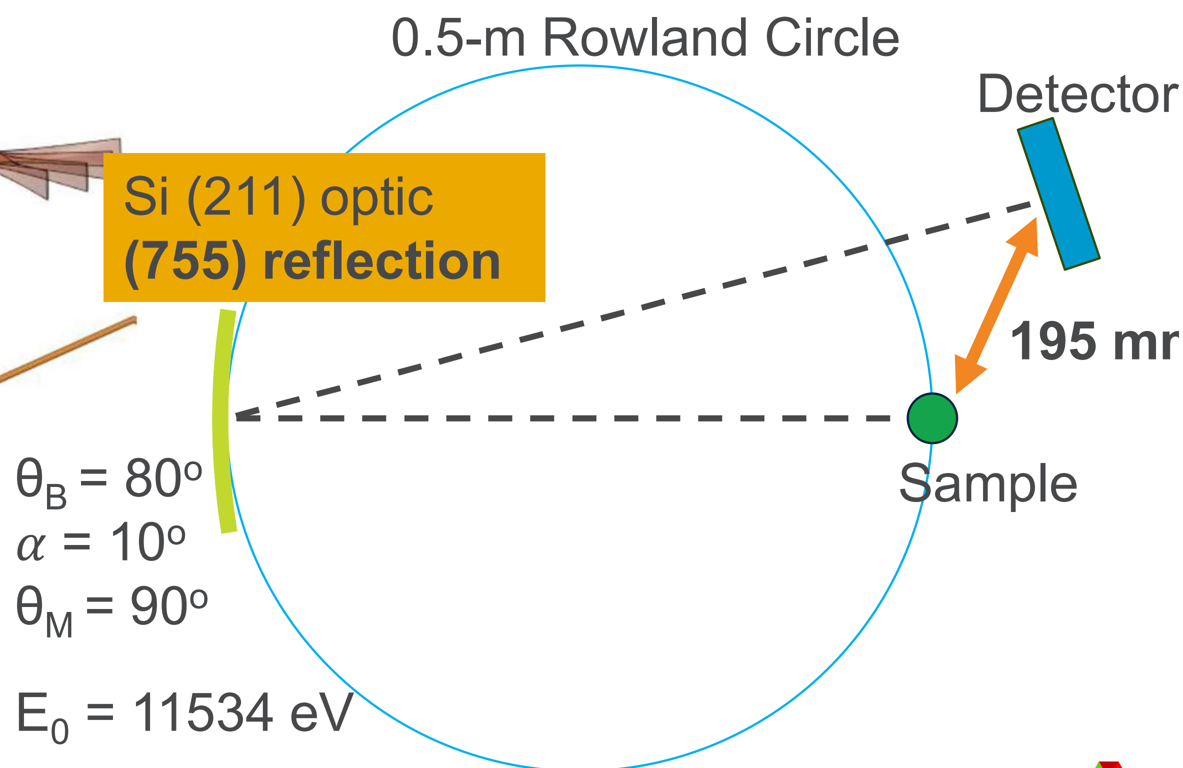
- Low energy electron transitions with hard x-rays
  - Transitions from core shells of light elements
  - Transitions from higher shells of heavier elements
- Eliminates several complications of soft x-ray absorption
  - Hard x-rays are more easily combined with complex sample environments such as in-situ, in-operando, high pressure (diamond anvil), and liquid cells
  - Bulk sensitive (hard x-rays)
  - Free of self absorption (non-resonant)
- Sensitive to non-dipolar transitions
  - Momentum transfer dependent, can be minimized or enhanced
  - Access aspects of electronic structure unavailable in XAS



PROOF OF PRINCIPLE XRS DESIGN

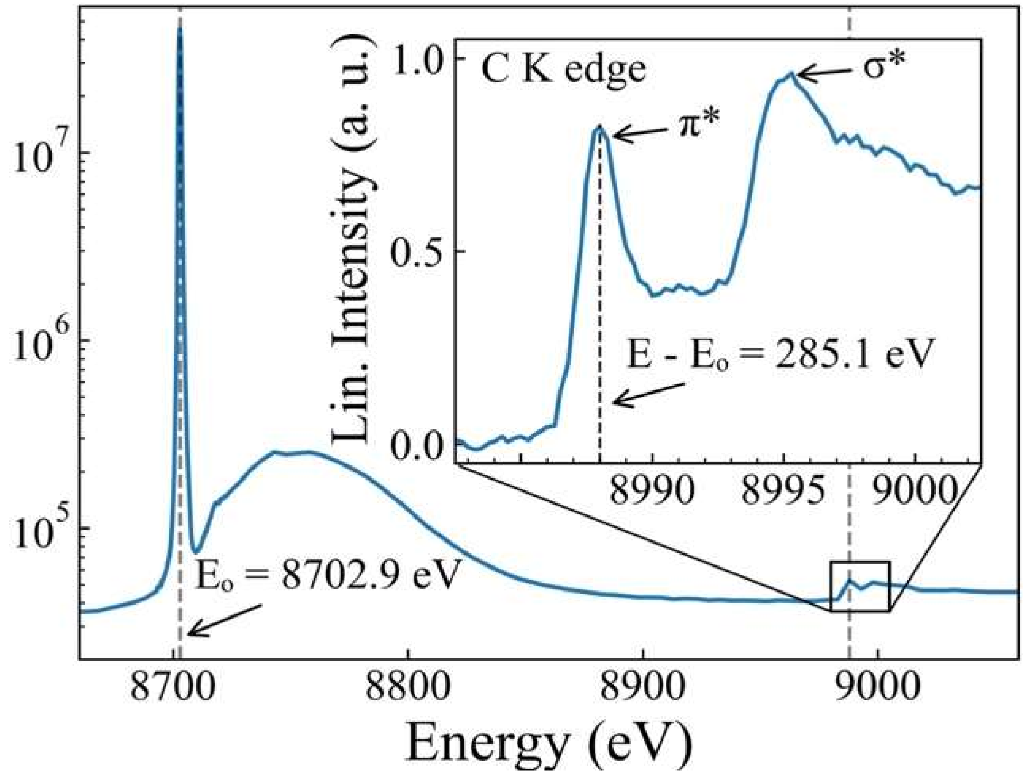
S-25 testing XRS design using half-meter analyzers





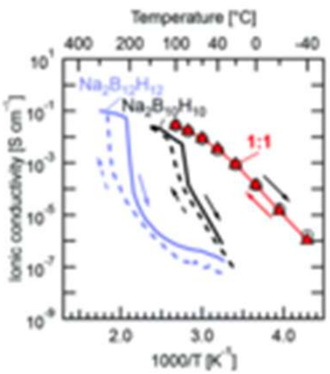
PROOF OF PRINCIPLE XRS DESIGN

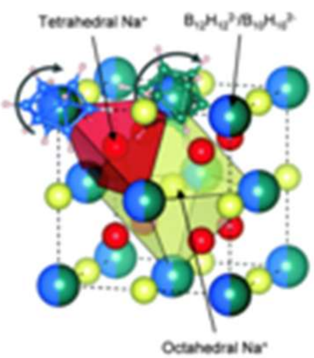
S-25 testing XRS design using half-meter analyzers

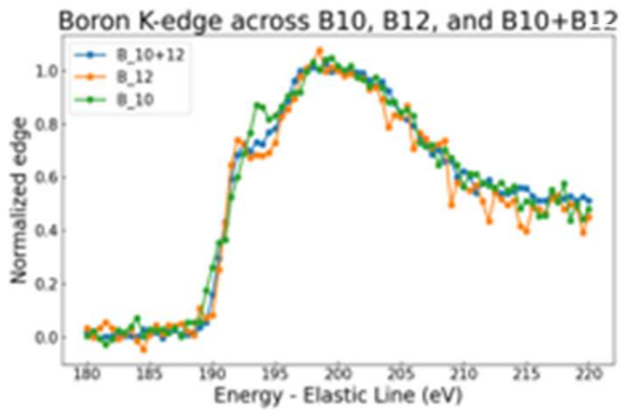


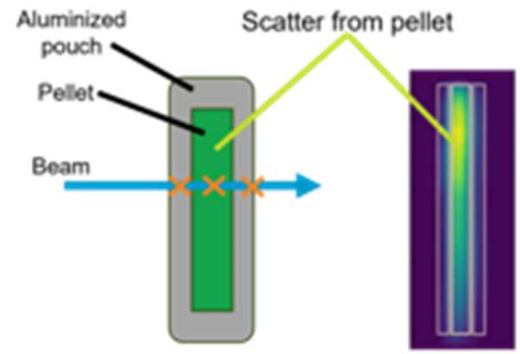
R&D ASYMMETRON FOR XRS AND HERFD

Single Optic used for 15 emission lines from 5 to 14 KeV









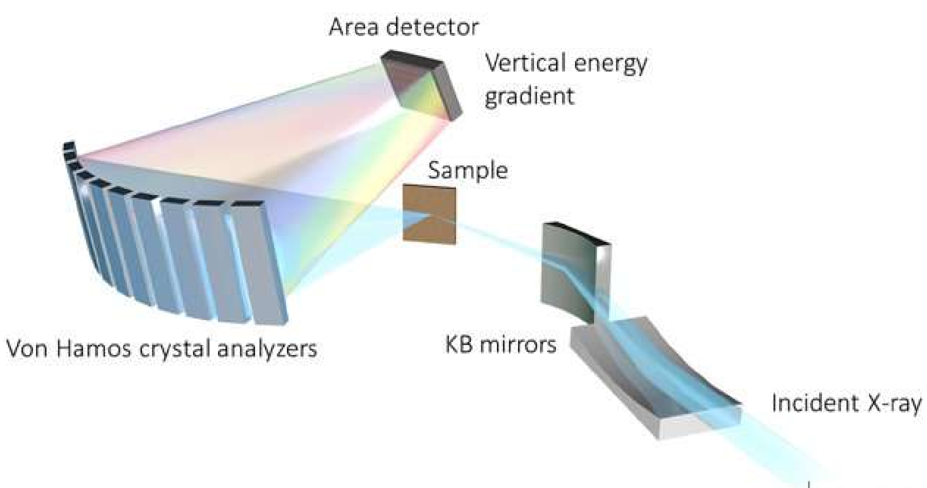
L. Duchêne et al. Chem. Commun., 53 (30), 4195-4198 (2017)

- Conductivity of Sodium Borates (B10 and B12) a promising class of solid-state electrolytes.
- X-ray Raman Scattering of Boron showing distinct chemical information for B10, B12 and mixture.
- Detector image of sample in pouch showing signal separation

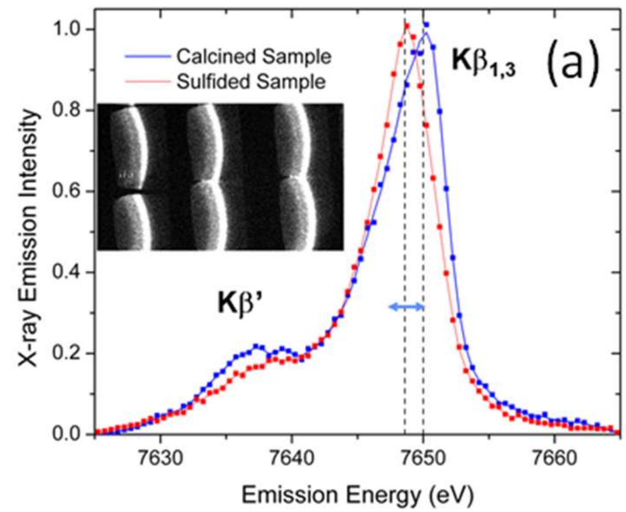
X-RAY EMISSION SPECTROSCOPY

Sensitive to spin state, valence, ligands

- Collection time from 30 sec to a few minutes
- Multilayer Monochromator after APS-U will allow sub-second integration time: mapping



Co emission from catalyst using miniXS – 30 sec



RESEARCH ARTICLE | FEBRUARY 08 2012

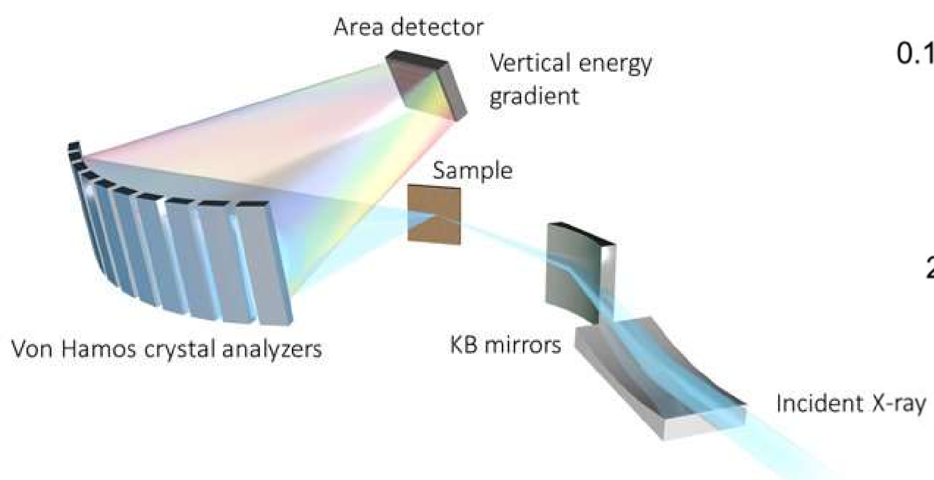
A plastic miniature x-ray emission spectrometer based on the cylindrical von Hamos geometry

B. A. Mattern; G. T. Seidler; M. Haave; J. I. Pacold; R. A. Gordon; J. Planillo; J. Quintana; B. Rusthoven

X-RAY EMISSION SPECTROSCOPY

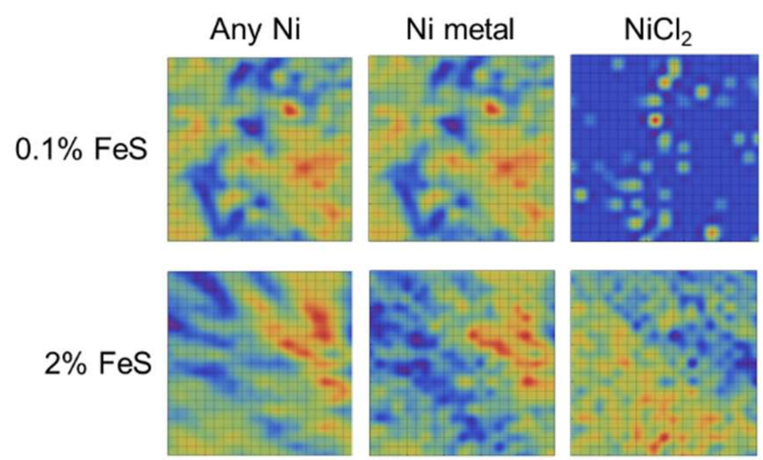
Sensitive to spin state, valence, ligands

- Collection time from 30 sec to a few minutes
- Multilayer Monochromator after APS-U will allow sub-second integration time: mapping



Example: distinguishing Ni and $NiCl_2$ in a battery electrode

Bowden et al, J. Power Sources 247, 517-526 (2014)



100 µm X 100 µm XES maps

RESEARCH ARTICLE | FEBRUARY 08 2012

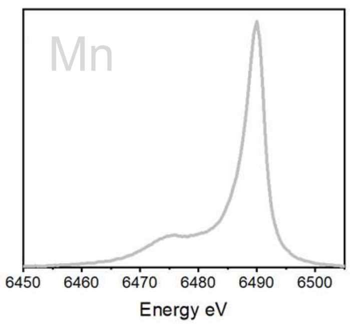
A plastic miniature x-ray emission spectrometer based on the cylindrical von Hamos geometry

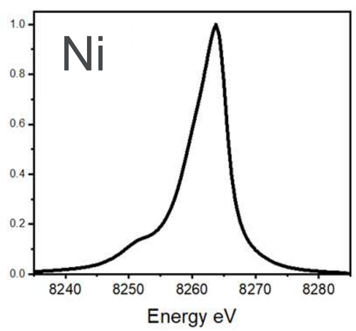
B. A. Mattern; G. T. Seidler; M. Haave; J. I. Pacold; R. A. Gordon; J. Planillo; J. Quintana; B. Rusthoven

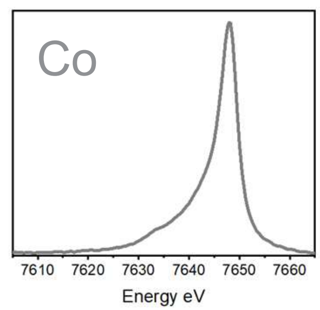
SPECTROMETER FOR MULTI-ELEMENT XES

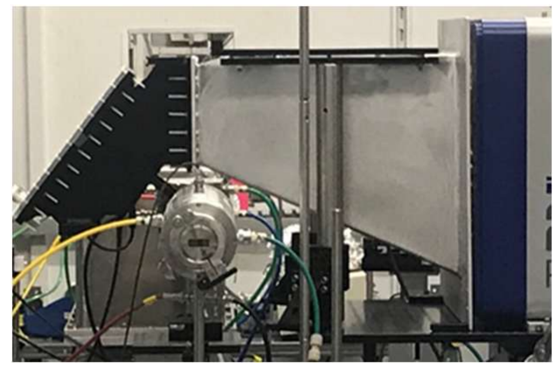
Large area detectors enable multiple element non-resonant XES

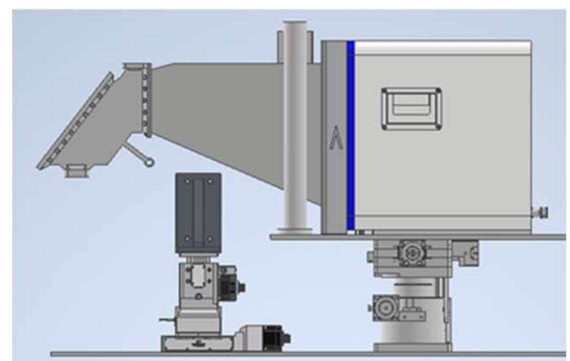
- Simultaneous XES spectra from nickel/manganese/cobalt on alumina cathode
- Simultaneous measurement
- Incident x-ray energy 8400 eV







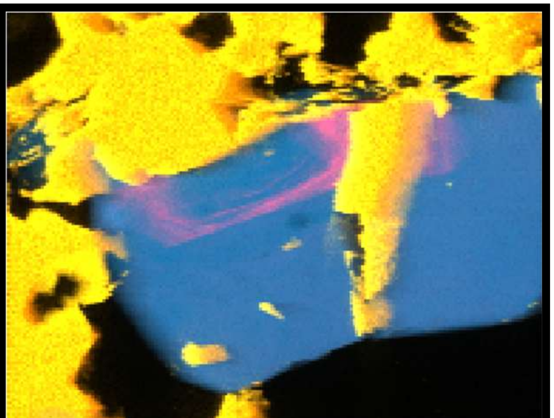




BONANZA GOLD MECHANISM

Microprobe XRF and Spectroscopy

Extremely high-resolution SR-µXRF mapping of arsenian pyrite reveals that bonanza-style gold mineralization was caused by gold flocculation from electron transfer near arsenic-rich bands.

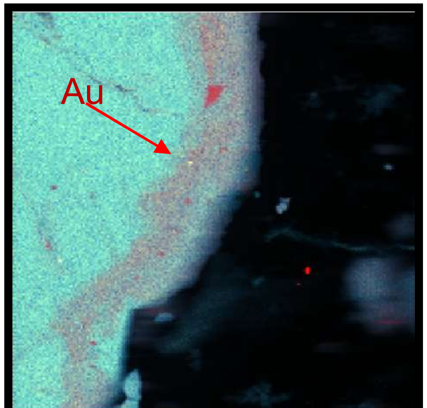


500 µm x 500 µm (50,451 pixels)

As K   Fe K   Au L   Ag K

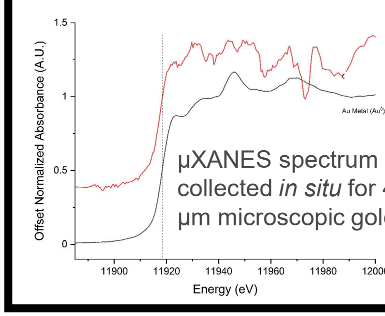
Colour - Colours scaled independently

The distribution of electrum (Au, ■ + Ag, ■) on the edges of corroded pyrite grains (Fe, ■) with As banding (As, ■) as fine as <2 µm (single pixel thickness!)



400 µm x 400 µm (40,401 pixels)

Microscopic metallic gold grain (2 pixels wide, ■) within the As band (As, ■) on the edge of a pyrite grain (Fe, ■).



Microscopic gold within arsenian pyrite growth zone is metallic Au^0 and not lattice bound Au^{+1}

U.S. DEPARTMENT OF ENERGY

Argonne National Laboratory is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC.

Dr. Neil R. Banerjee, P.Geo.
Dr. Lisa L. Van Loon, C.Chem.

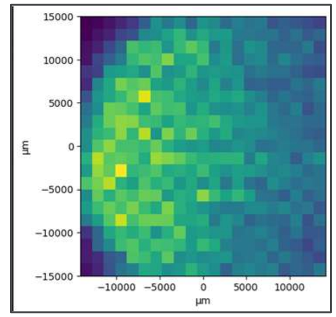
XRF data analysis in Peakaboo (https://peakaboo.org)
Beam spot size: <2 µm x <2 µm
Energy: 26 keV

Argonne NATIONAL LABORATORY

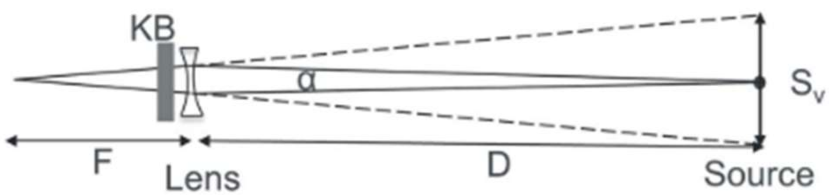
DEVELOPMENTS TOWARD LARGE MAPPING

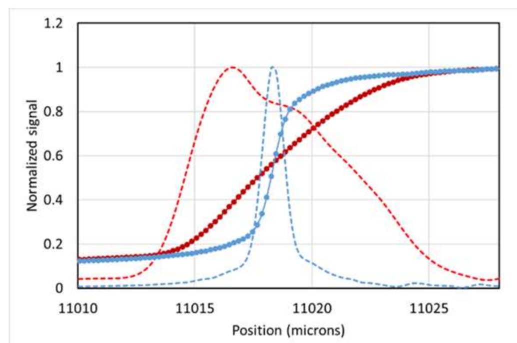
Fly scanning sample positioner and variable focus

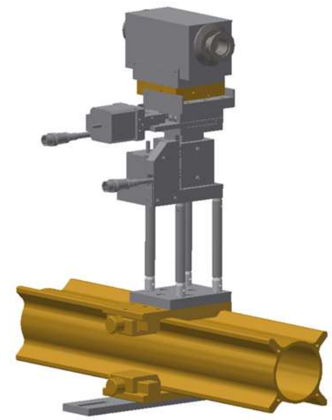
- Fly scanning sample positioner
  - 4 hour measurement using weak Fe-57 source with 18 minutes (7.5%) overhead
- Easy/rapid and reliable beam size adjustment using Be lenses
  - Initial measurements made at 20-ID



30mm x 30mm
21x21 points
30sec/point



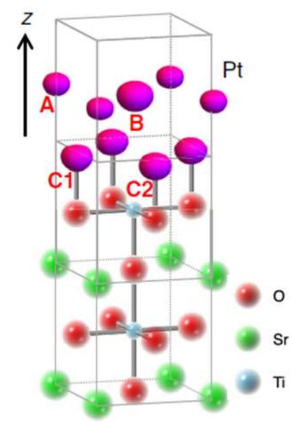


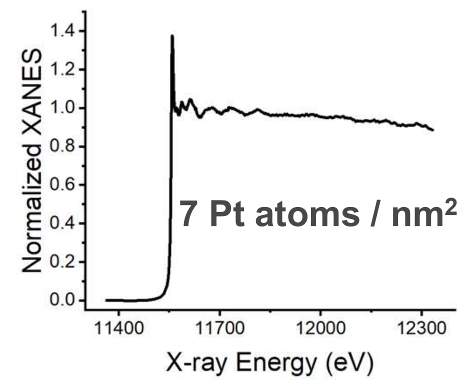


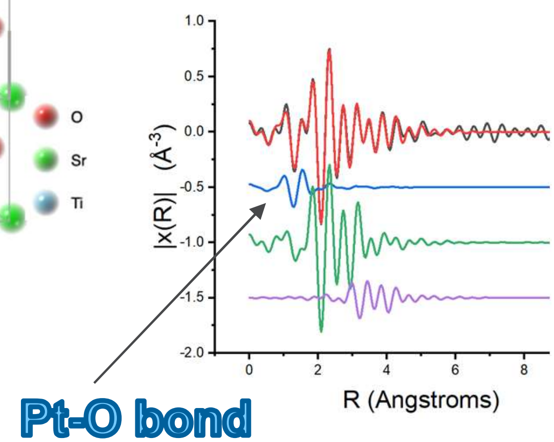
GRAZING INCIDENCE PT EXAFS

Pt monolayer on $SrTiO_3$ (001) substrate

- Oxide supported noble metal nanoparticles are widely used as heterogeneous catalysts; playing an important role for the societal shift from a fossil-fuel to renewable energy sources.
- Studies of highly diluted monolayer and single atom catalyst are difficult, but necessary with catalyst development at the atomic-scale.
- Initial measurements show full EXAFS scans can be used to determine interfacial Pt-O bond

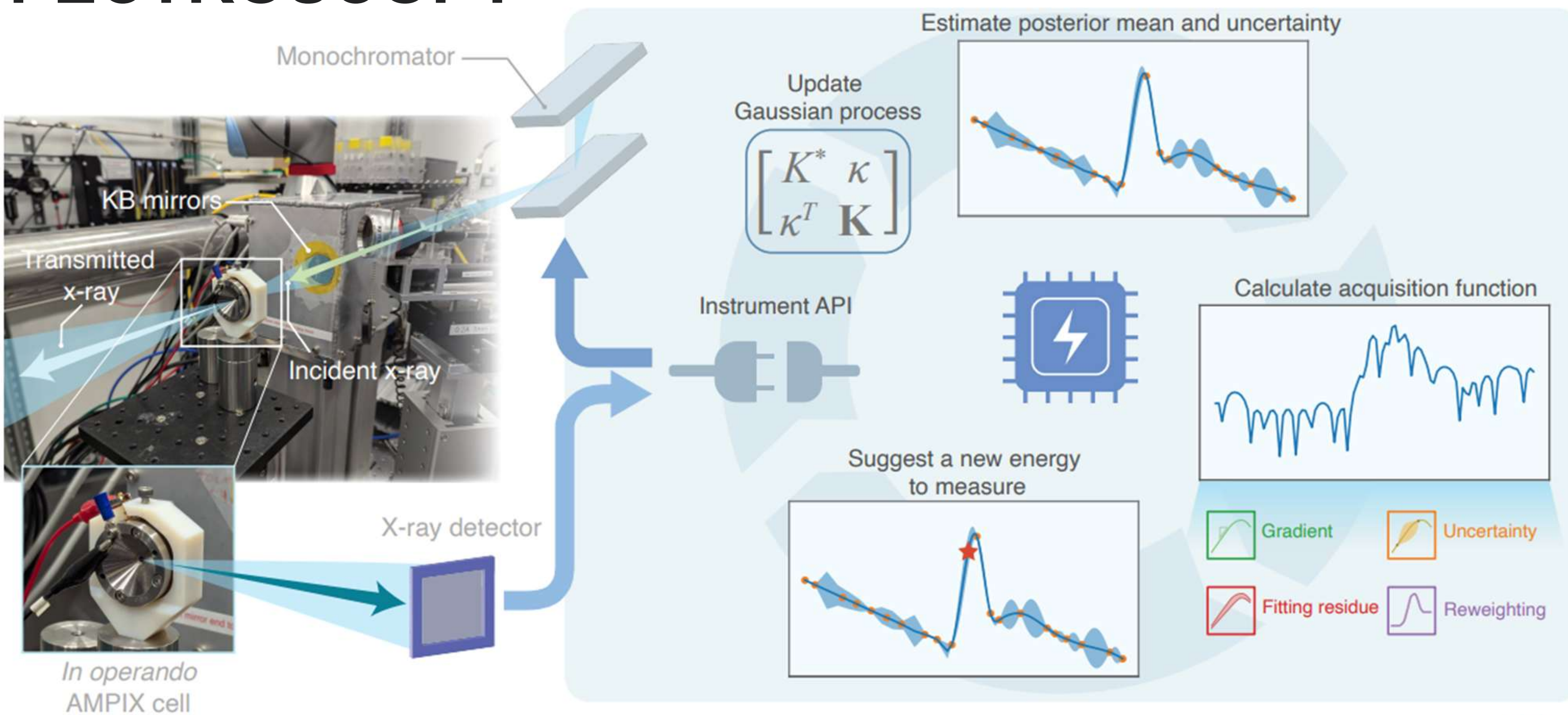






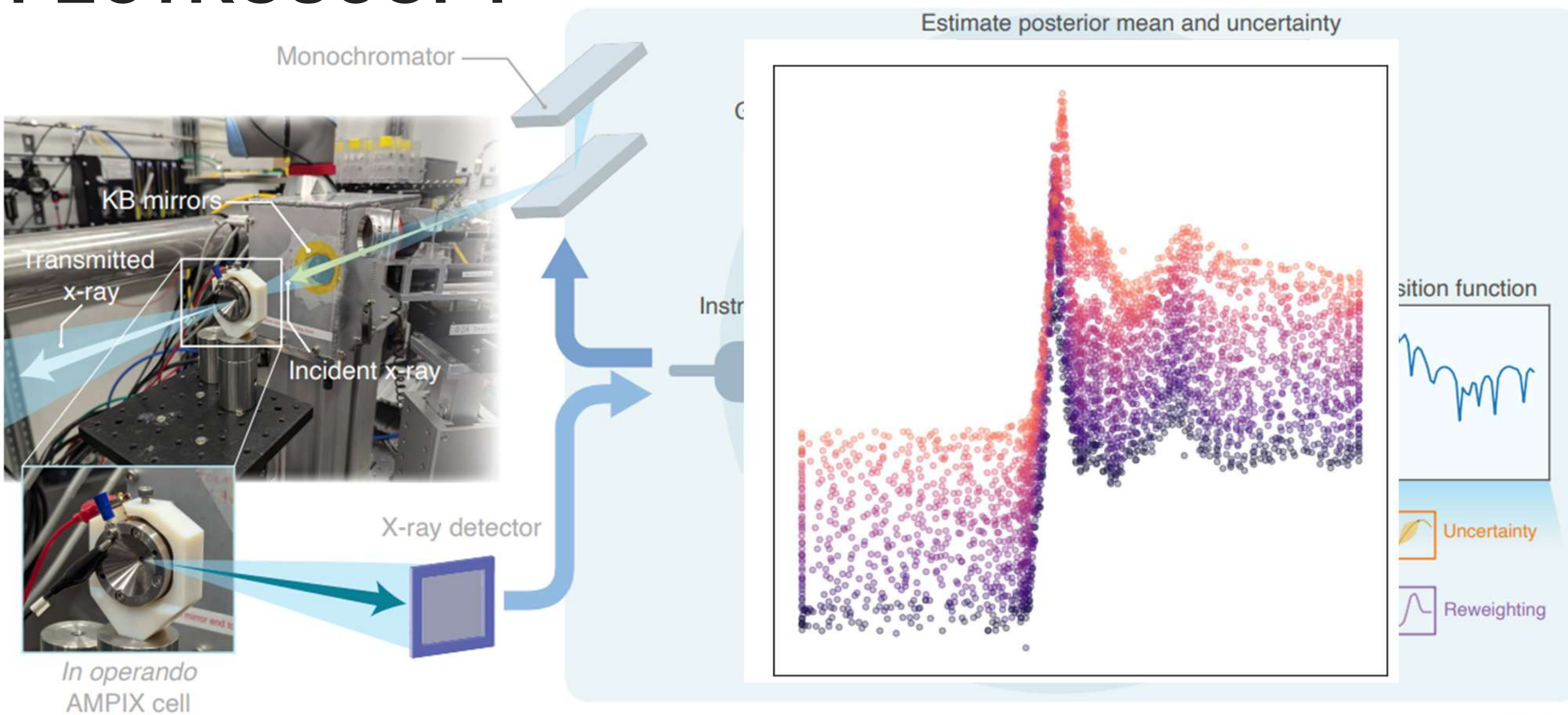
https://doi.org/10.1103/PhysRevLett.128.206801

AI DRIVEN WORKFLOW FOR DYNAMIC SPECTROSCOPY



https://doi.org/10.48550/arXiv.2504.17124

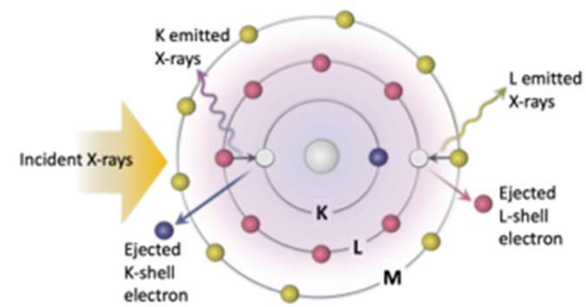
AI DRIVEN WORKFLOW FOR DYNAMIC SPECTROSCOPY

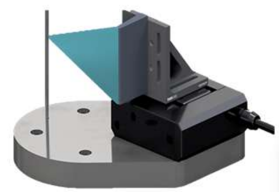


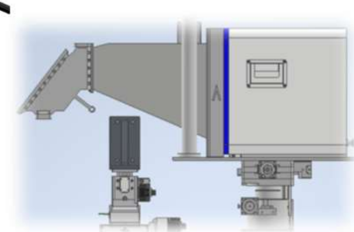
https://doi.org/10.48550/arXiv.2504.17124

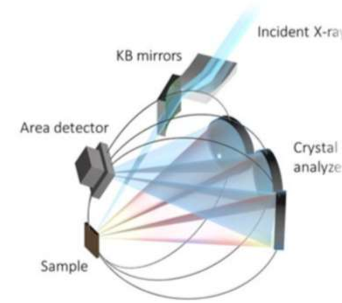
SPECTROSCOPY AT APS

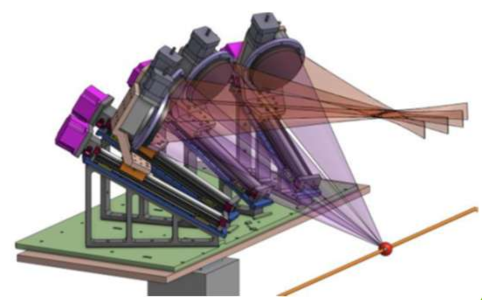
- X-ray absorption spectroscopy
  - **HERFD**
  - Dispersive XANES
  - Grazing incidence
- **X-ray emission spectroscopy**
- **X-ray Raman spectroscopy**
- Micro spectroscopy, XRF+
  - confocal
- In-situ and Operando
  - Temperature
  - Pressure: DAC
  - Heterogeneous Catalysis
  - Energy Materials
  - IR











THANK-YOU FOR YOUR ATTENTION