MOLECULAR FOUNDRY

Programmatic and Deep Learning Analysis Pipelines for 4D-STEM Materials Science Experiments

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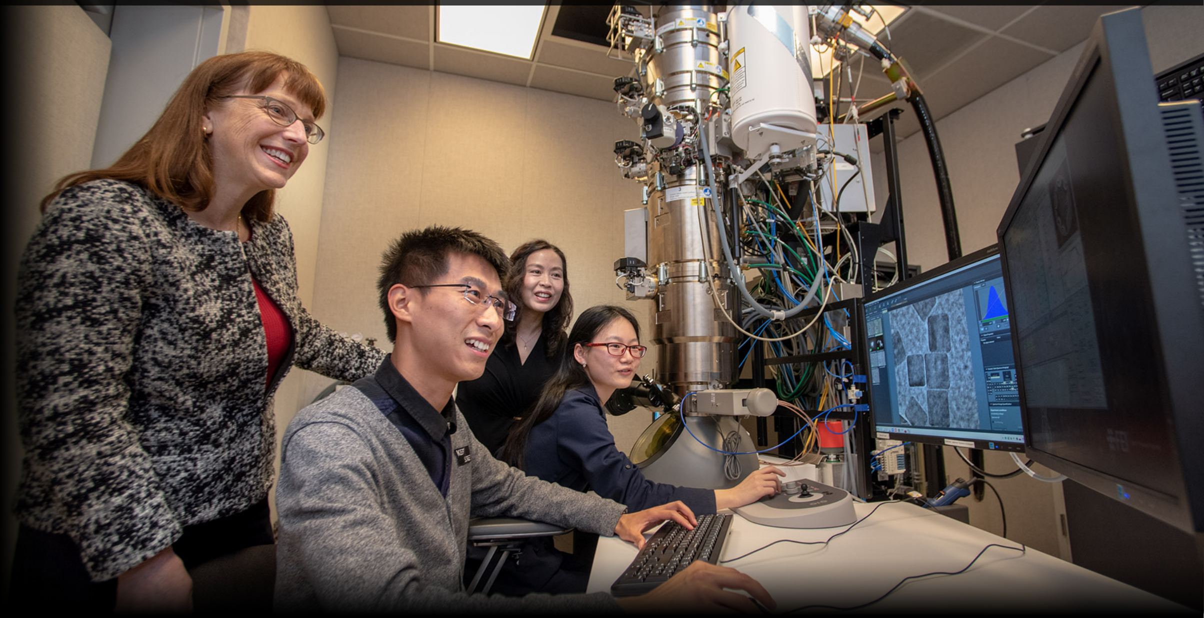
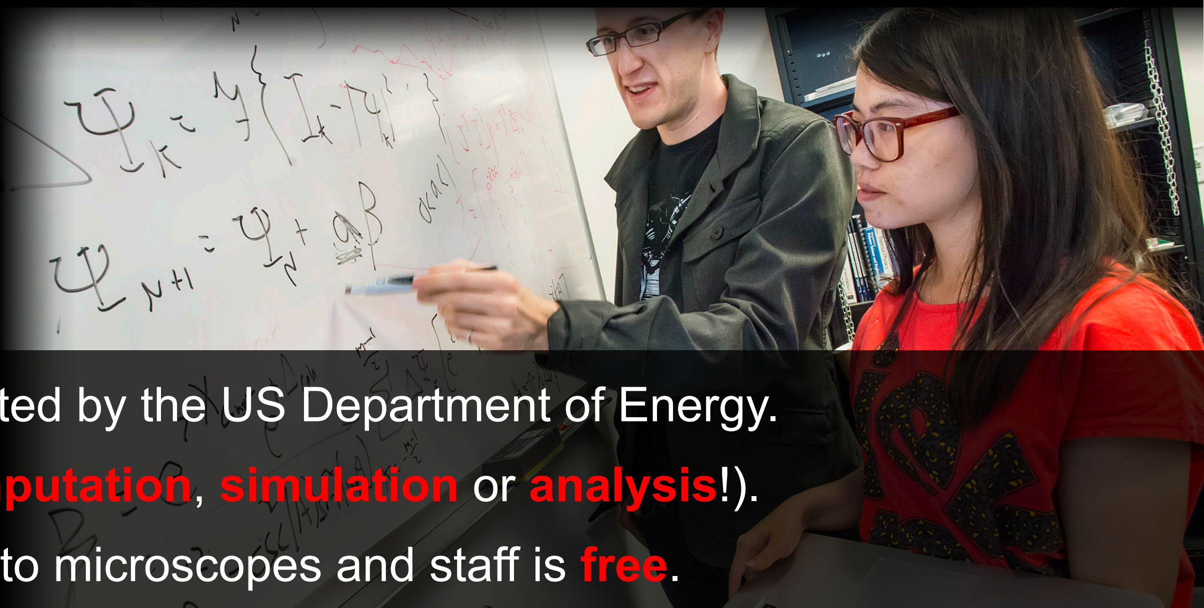
NCEM, Molecular Foundry, Lawrence Berkeley National Laboratory

2023 June 21 – Thursday 15:00
University of Maryland – AI for Scattering Workshop

Open Call for Proposals – September 2023 – foundry.lbl.gov

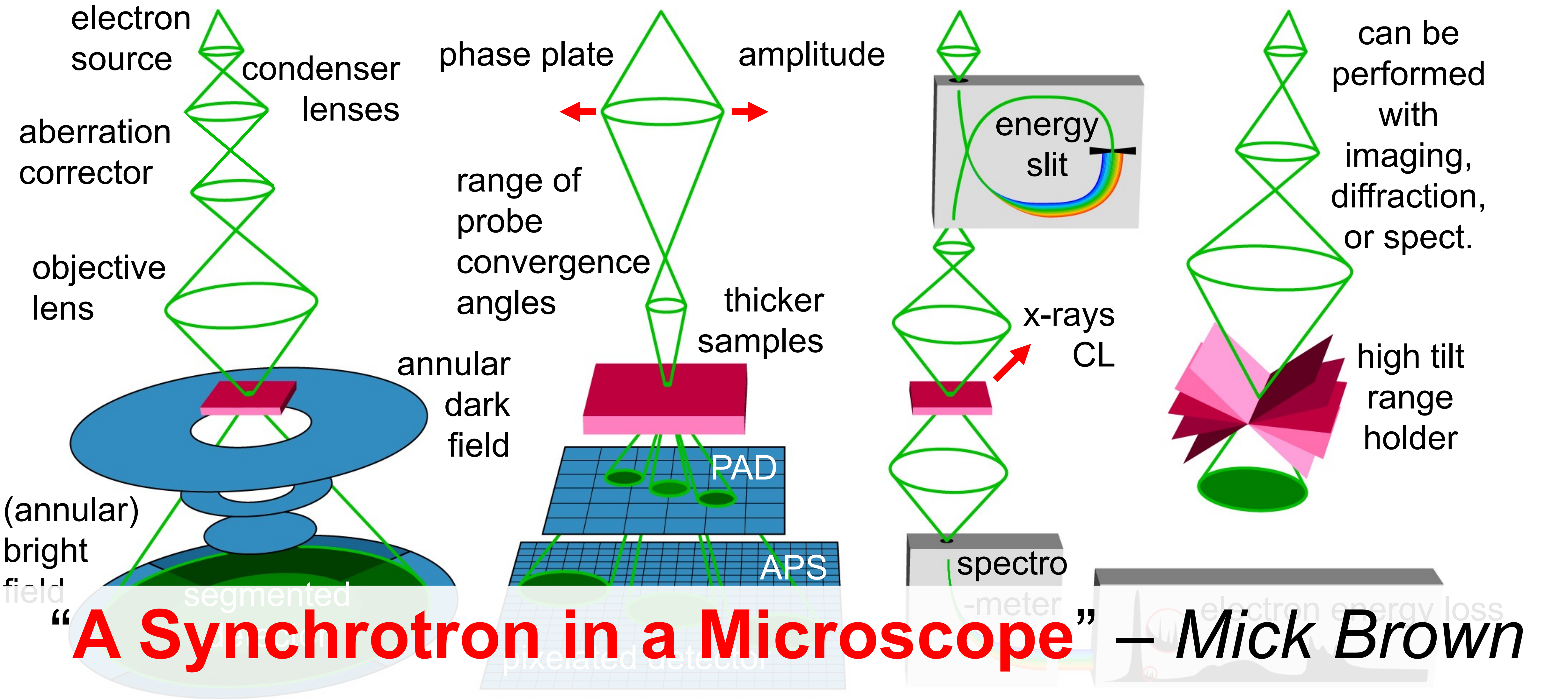




- We are a **user facility** at the Berkeley Lab, operated by the US Department of Energy.
- **Anyone** can submit a proposal (including for **computation**, **simulation** or **analysis**!).
- If accepted by independent review board, access to microscopes and staff is **free**.

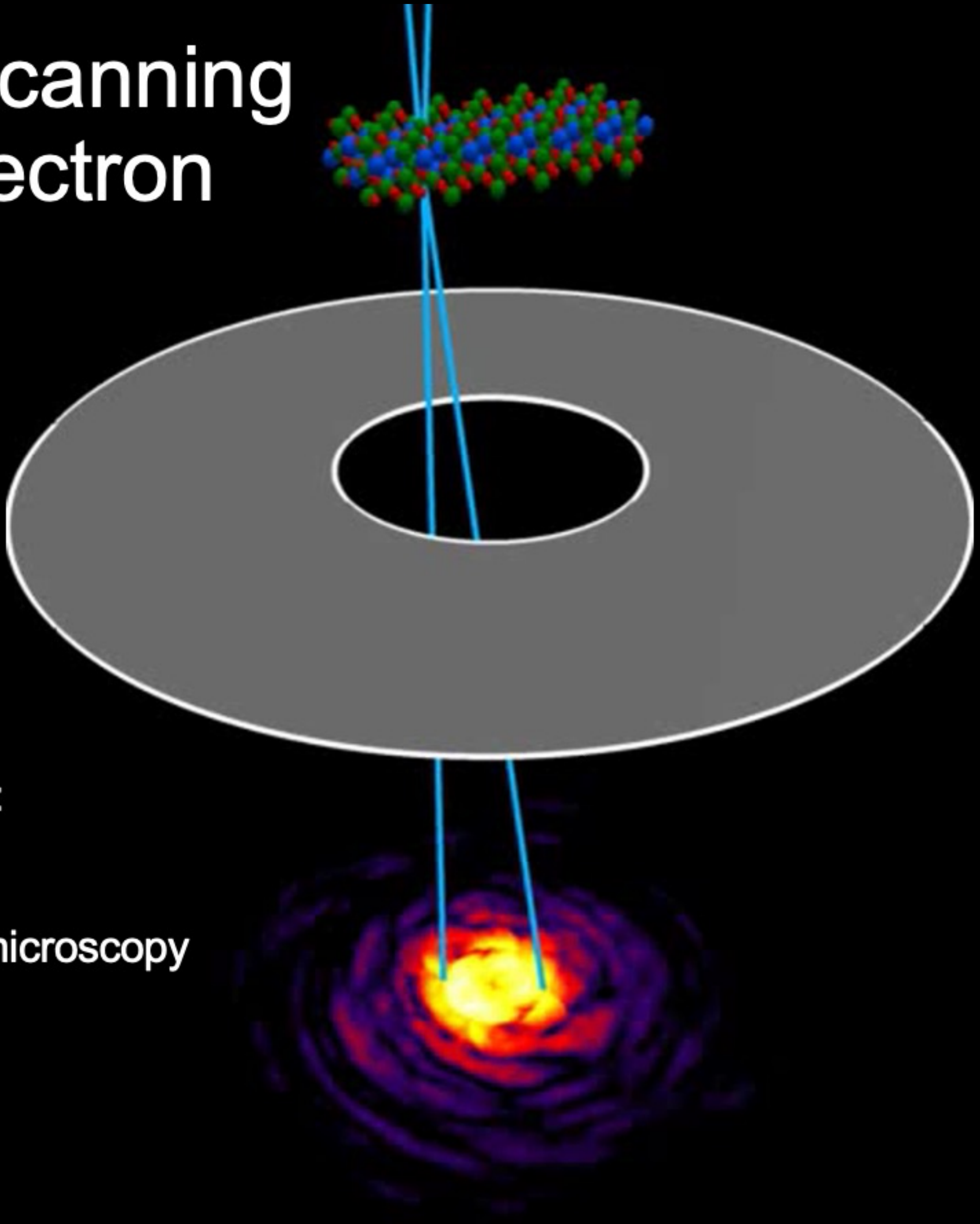
Scanning Transmission Electron Microscopy

Imaging | **Diffraction** | **Spectroscopy** | **Tomography**



"**A Synchrotron in a Microscope**" – *Mick Brown*

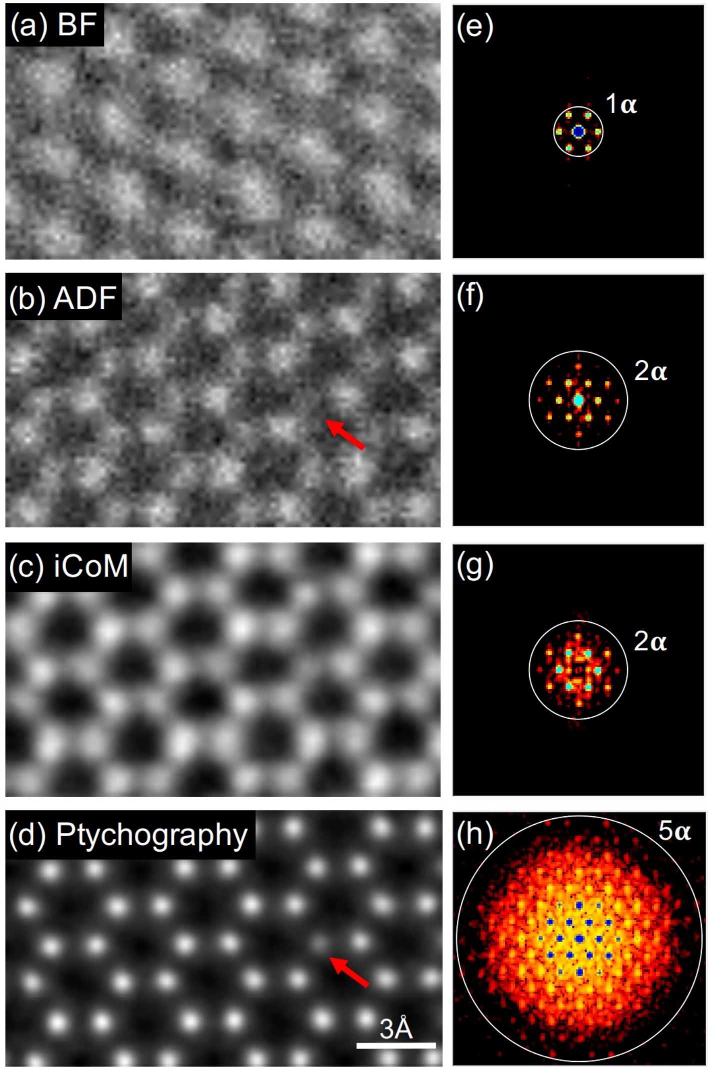
Introduction to Scanning Transmission Electron Microscopy



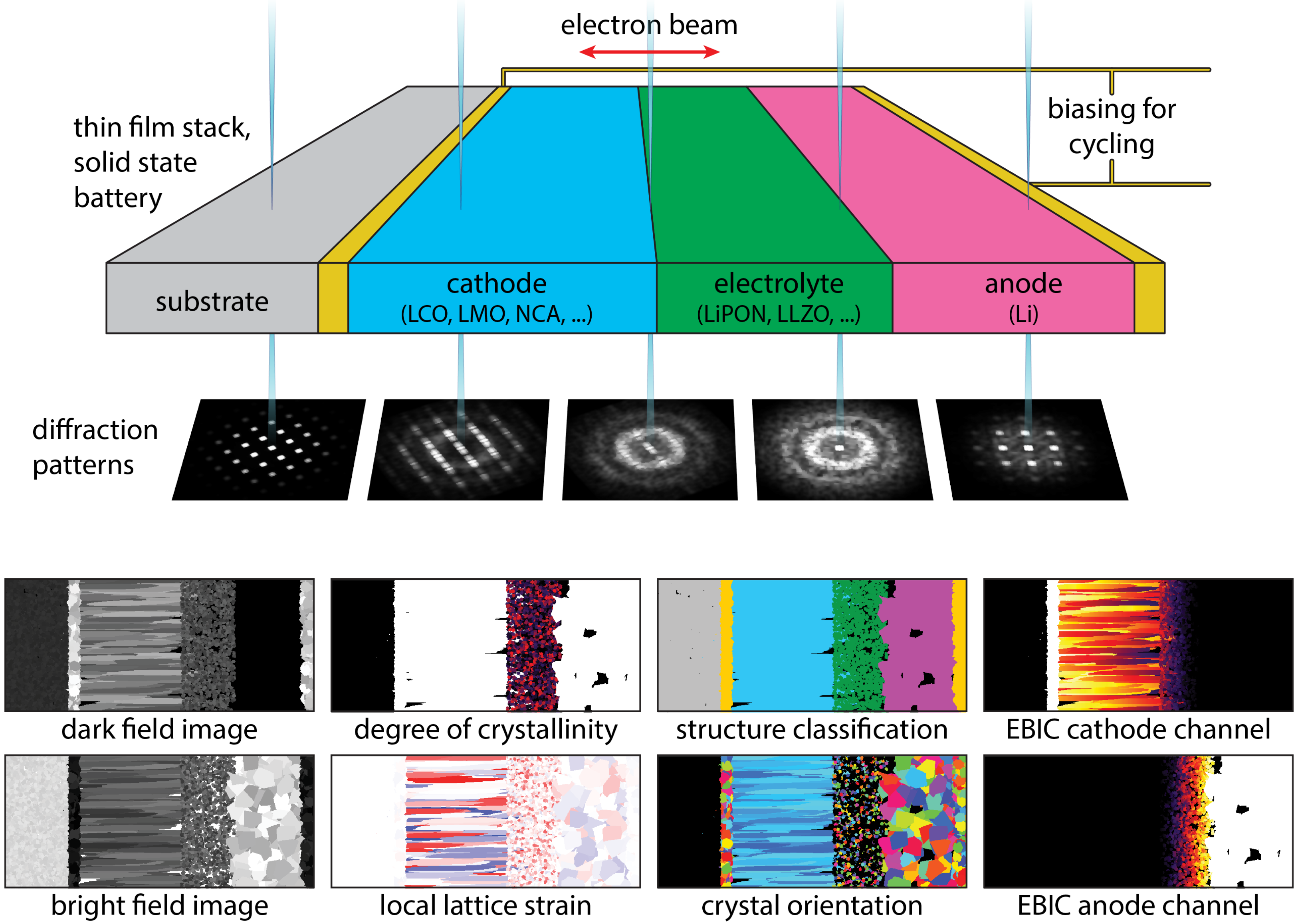
2D images recorded
over a 2D grid of probe positions:

Four dimensional
scanning transmission electron microscopy
(4D-STEM)

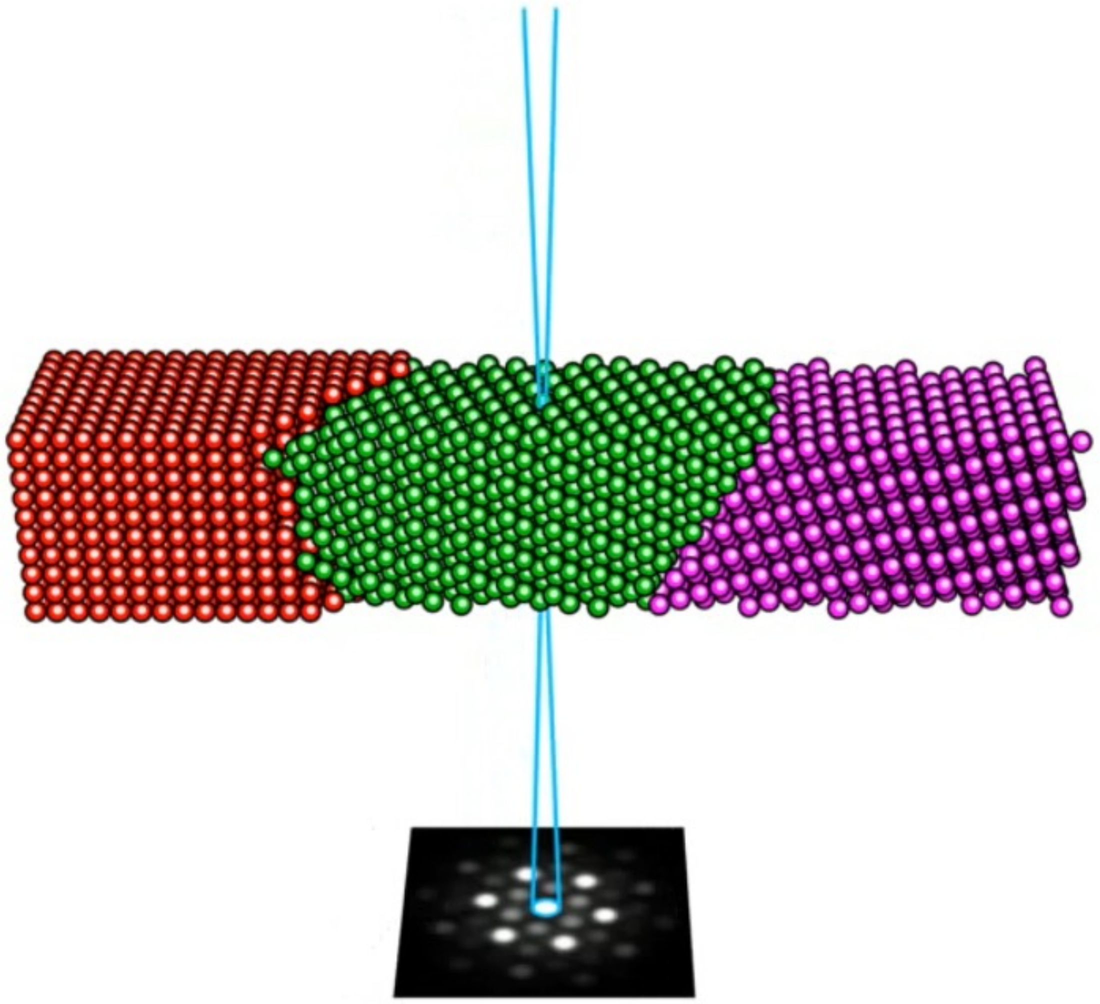
Motivation – Why do 4D-STEM?



Jiang et al., Nature 559, 343 (2018)

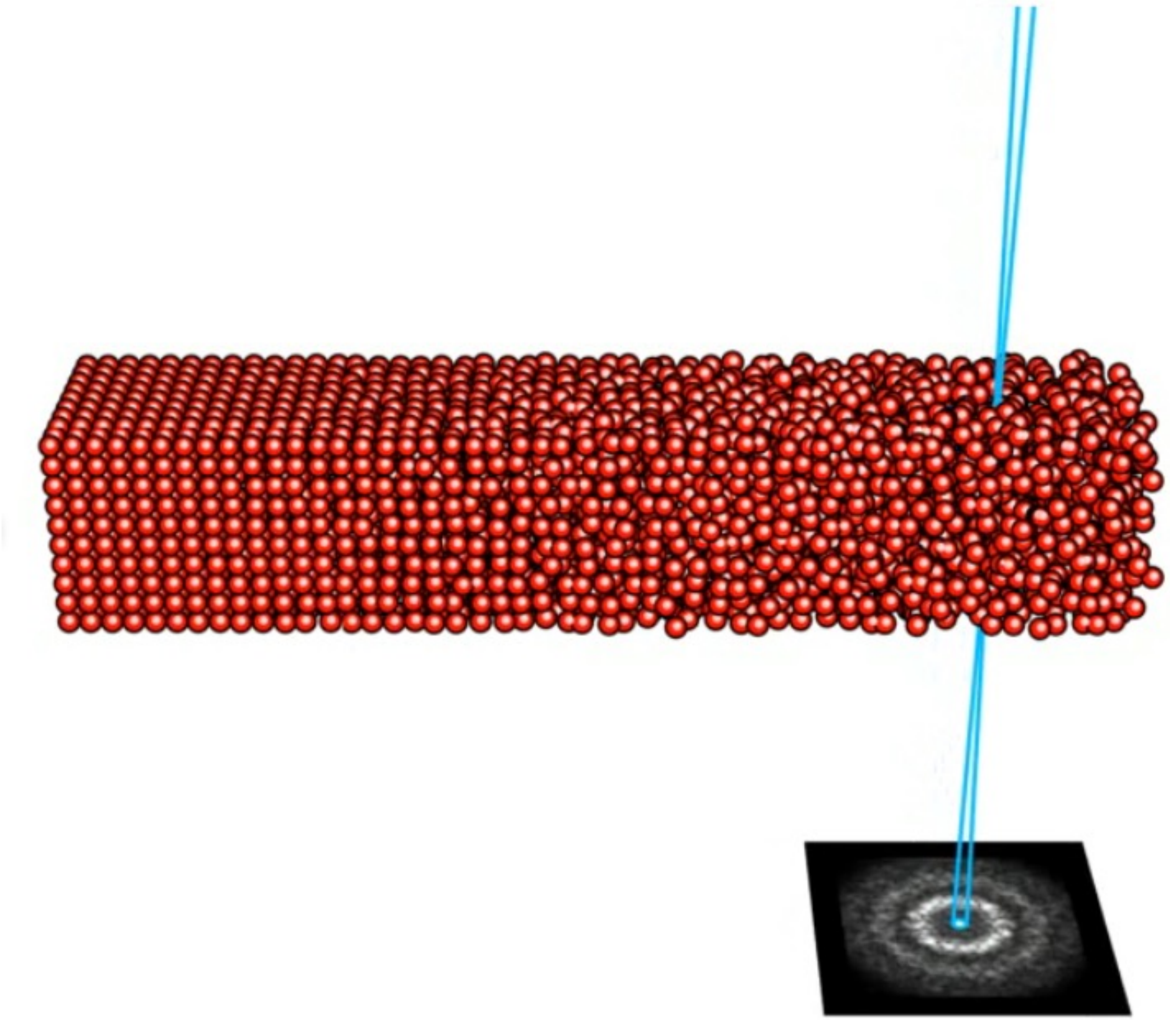


STEM Diffraction from Crystalline Samples



- Ideally, the diffracted signal is simply a 2D **Fourier transform** of the projected potential, multiplied by the probe intensity.
- Thus the position and intensity of **Bragg disks** of each diffraction pattern acts as a **fingerprint** for the local structure and orientation of the (crystal) sample.
- Interpretation is complicated by multiple / dynamical scattering (thickness effects), overlapping grains, background signals.

4D-STEM Diffraction from Amorphous Samples

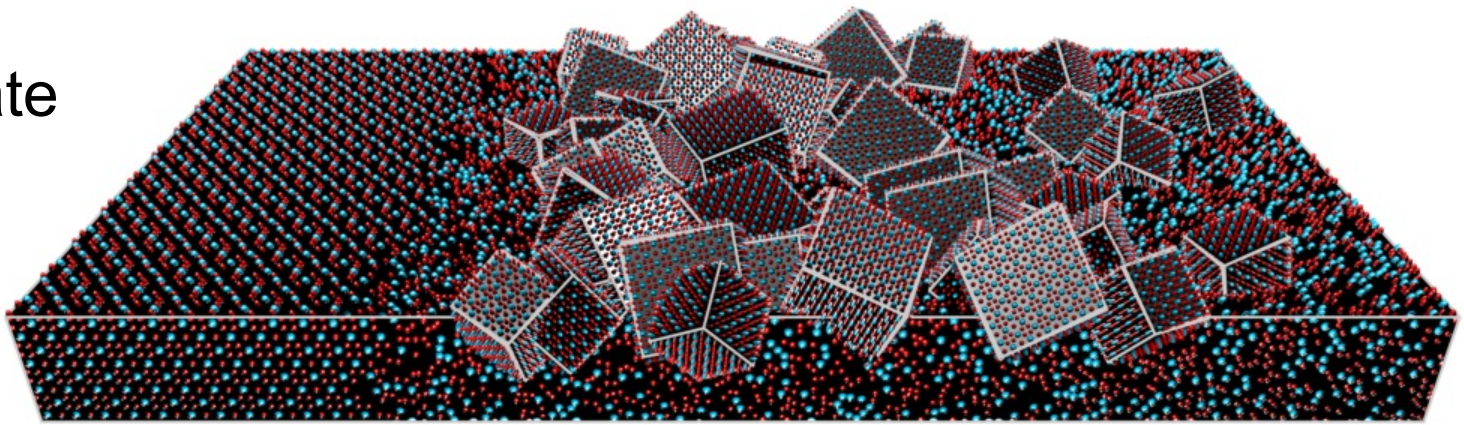


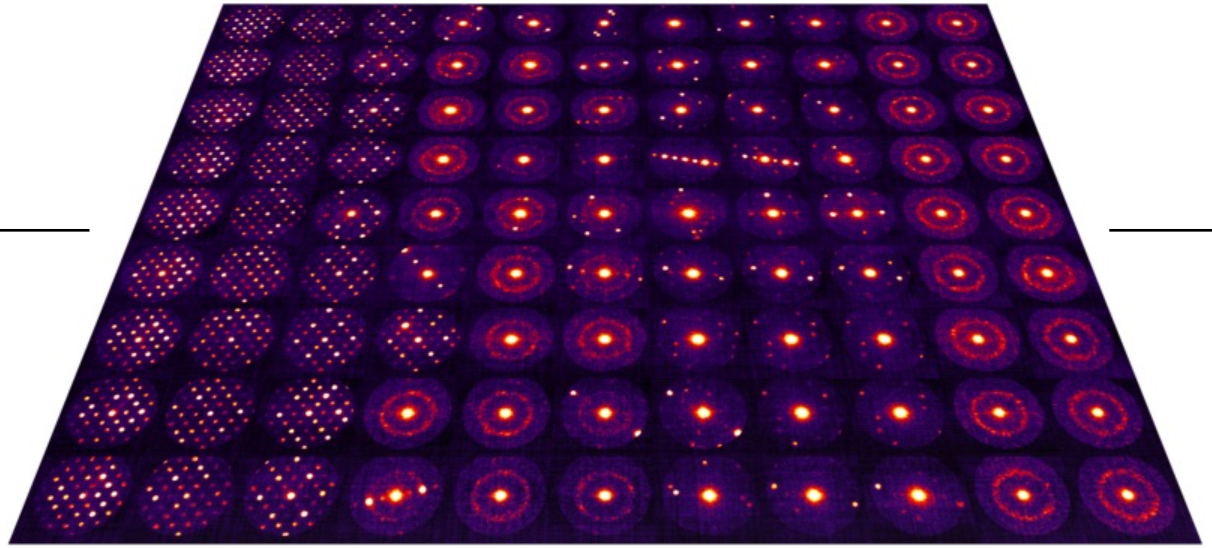
- Ideally, the diffracted signal is simply a 2D **Fourier transform** of the projected potential, multiplied by the probe intensity.
- The position and shape of **amorphous halos** of each diffraction pattern acts as a **fingerprint** for the local structure factor, given by the mean atomic arrangement.
- Interpretation is **complicated** by multiple / dynamical scattering (thickness effects), background, **more** than crystal diffraction!

Complex Sample Analysis with 4D-STEM

Gadolinium Titanate

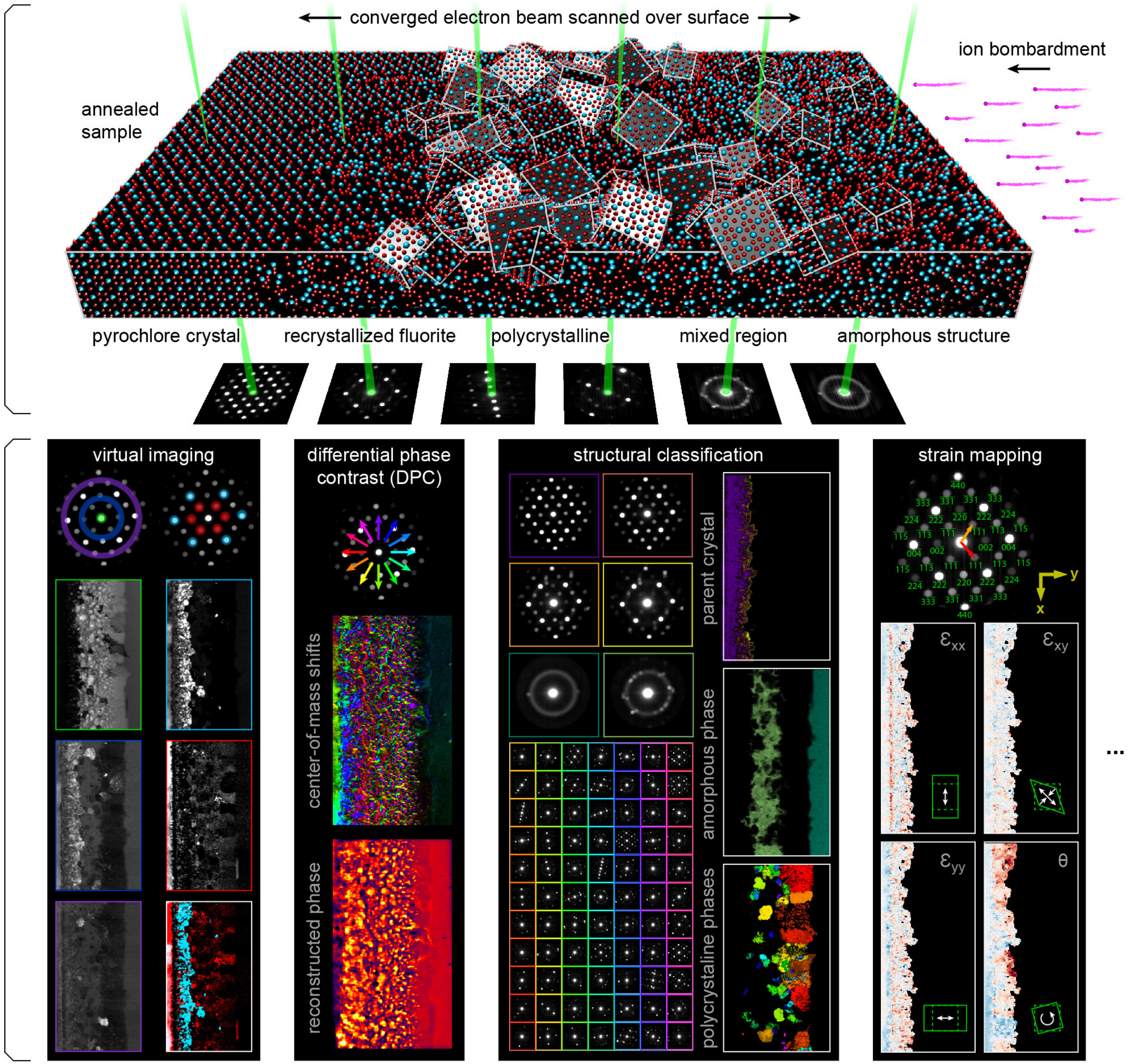
4D-STEM experiment





B Savitzky et al., Microscopy and Microanalysis 27, 712 (2021)

4D-STEM

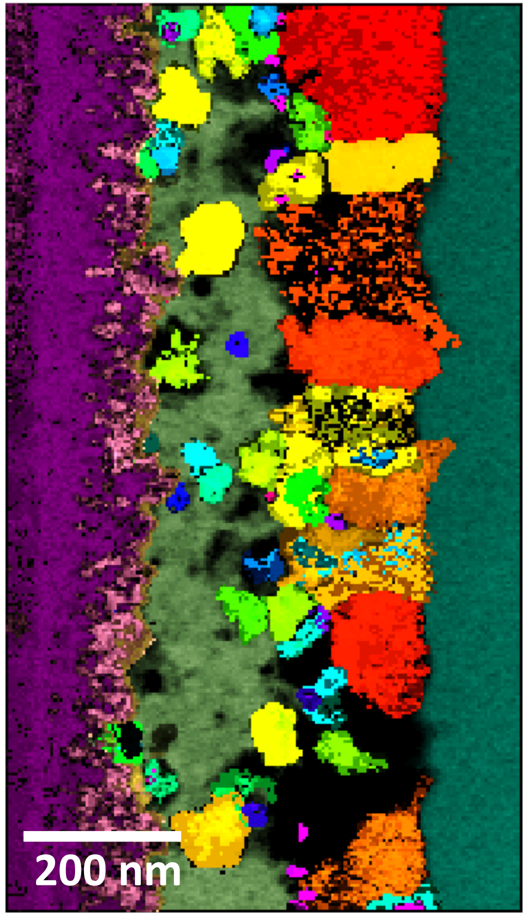


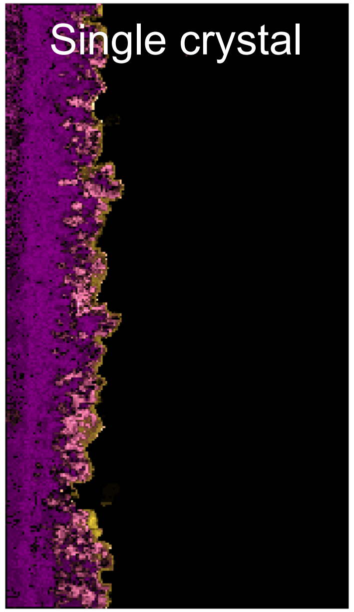
py4DSTEM

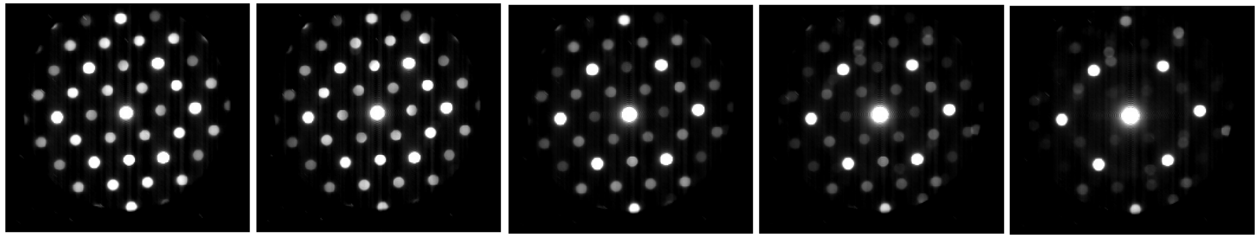
B Savitzky et al., Microscopy and Microanalysis 27, 712 (2021)

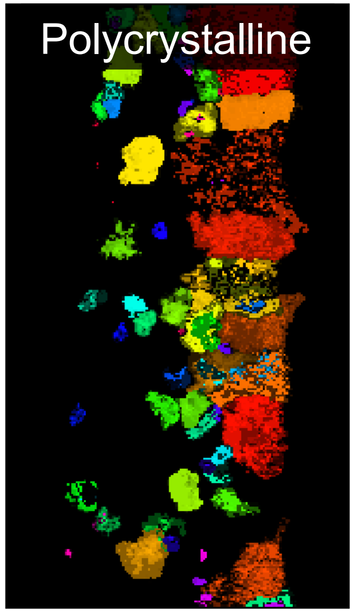
4D-STEM – Classification and Segmentation

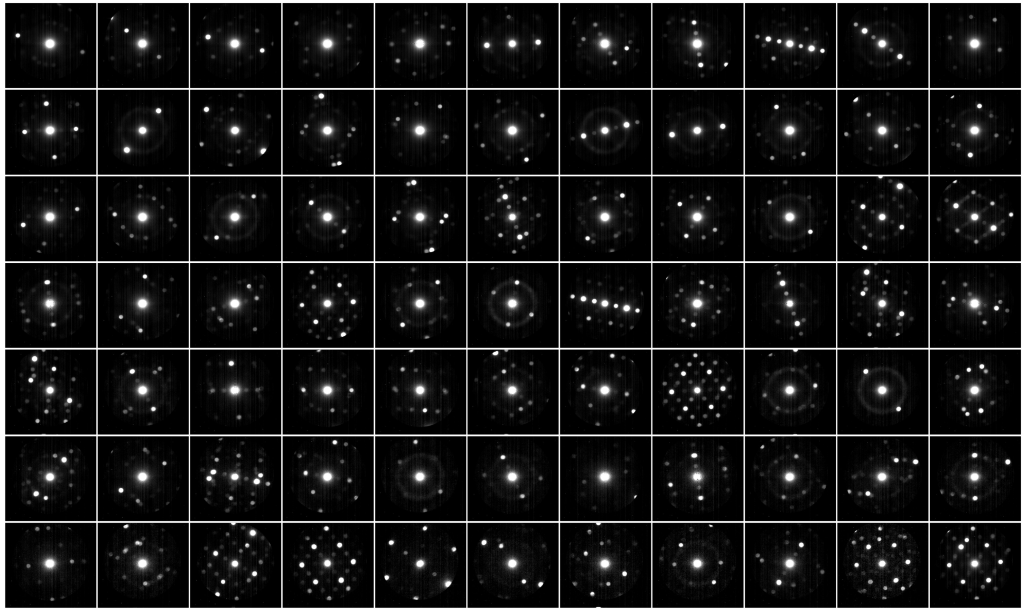
Unsupervised classification of the GTO sample:

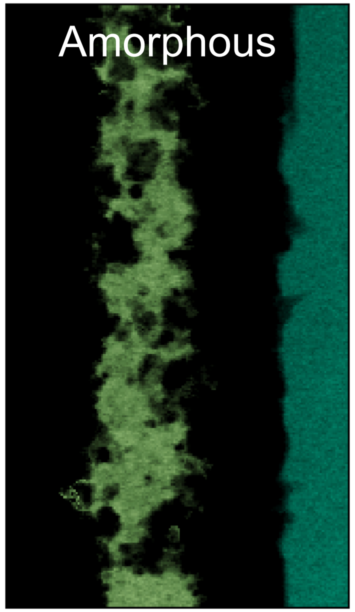


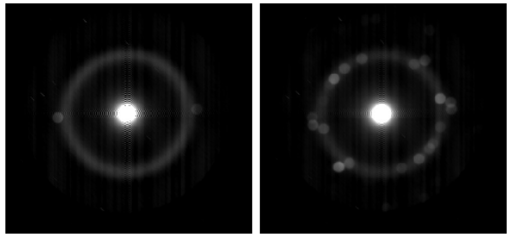






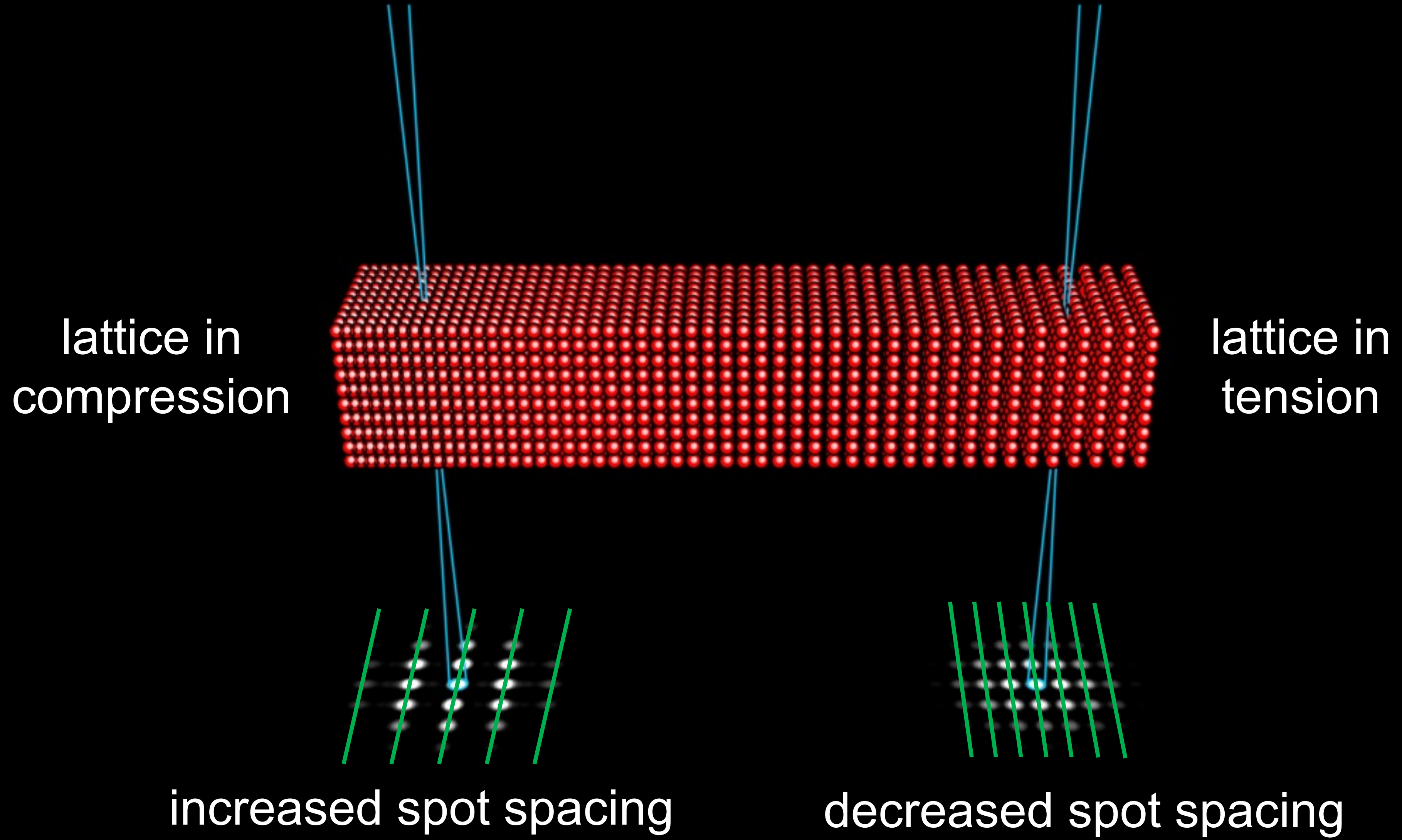






General classification is performed by using **NNMF** on **feature vectors**, constructed from Bragg vector maps, amorphous signals, virtual images, etc.

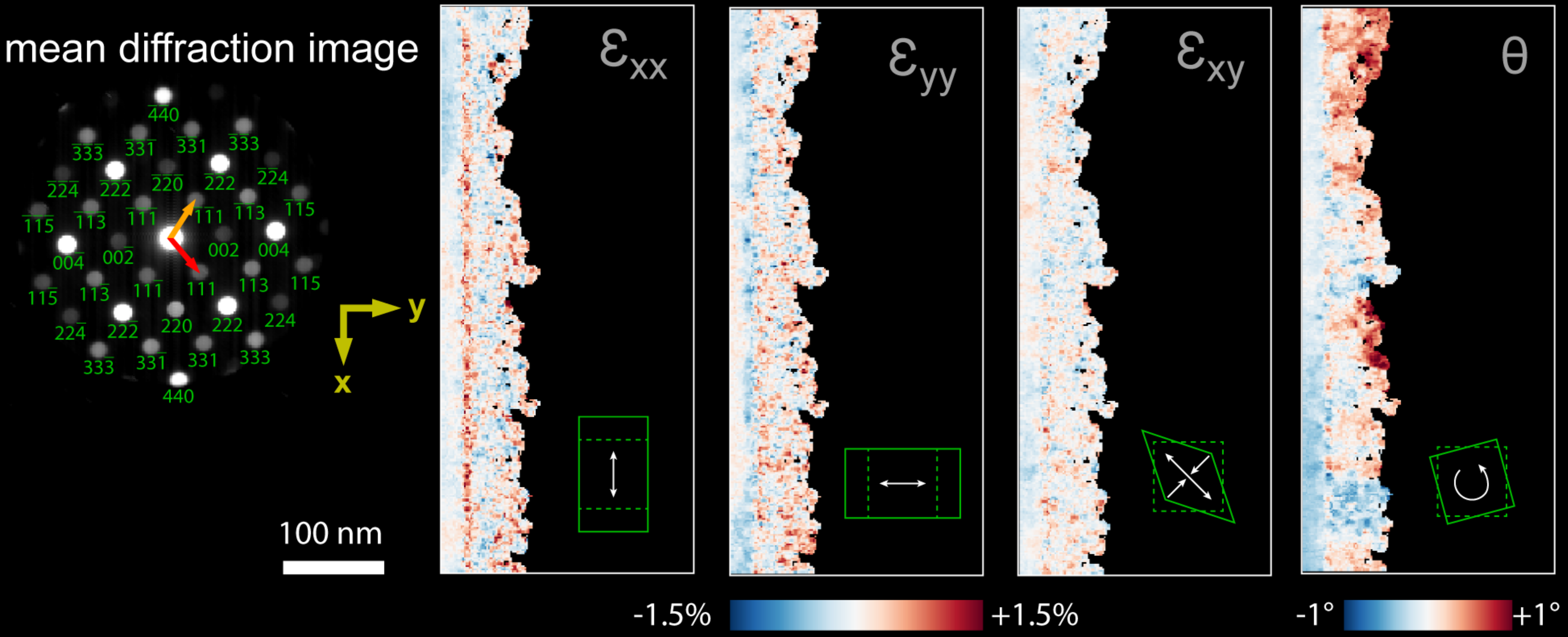
4D-STEM – Crystalline Strain Mapping



4D-STEM – Crystalline Strain Mapping

Strain measured in single-crystal GTO pyrochlore / recrystallized fluorite

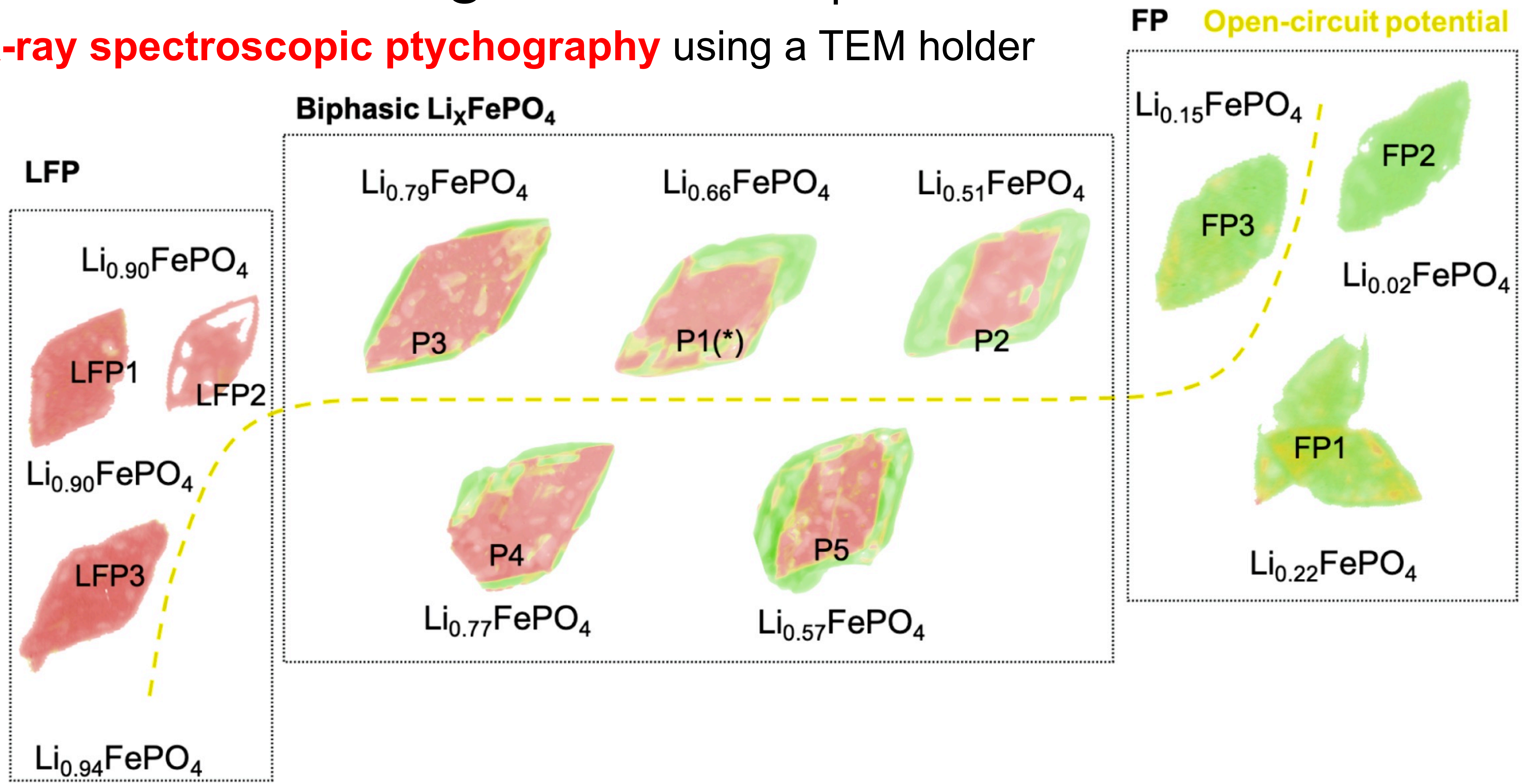
mean diffraction image



B Savitzky et al., Microscopy and Microanalysis (2021).

Inverse Learning of $LiFePO_4$ Chemo-Mechanics

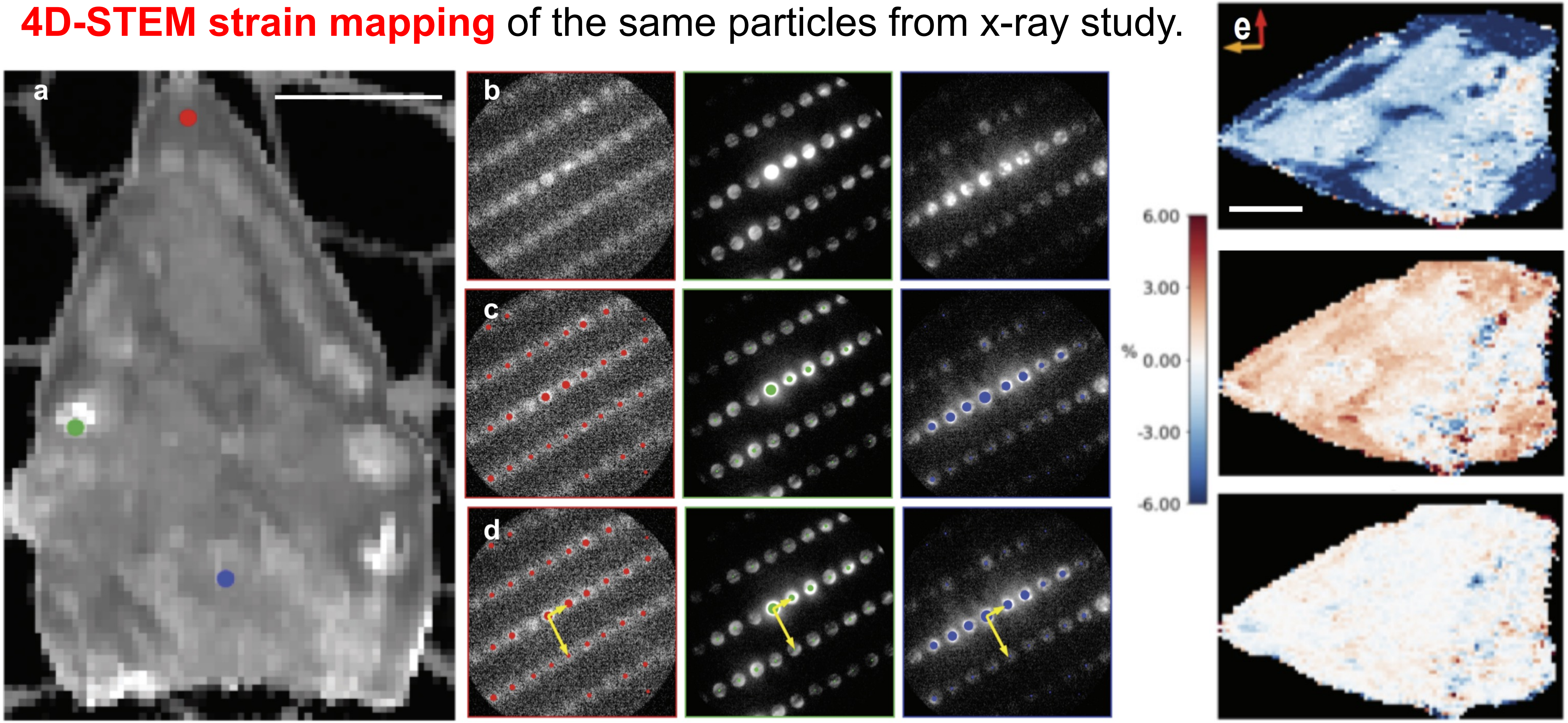
X-ray spectroscopic ptychography using a TEM holder



HD Deng et al., Nature Materials 21, 547 (2022). Hughes et al., Materials Today 52, 102 (2022)

Inverse Learning of $LiFePO_4$ Chemo-Mechanics

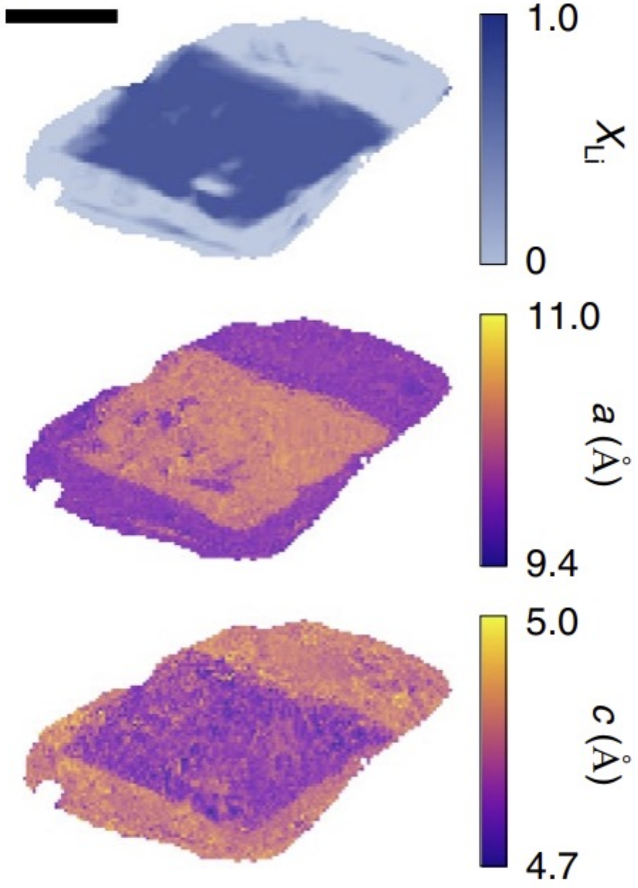
4D-STEM strain mapping of the same particles from x-ray study.

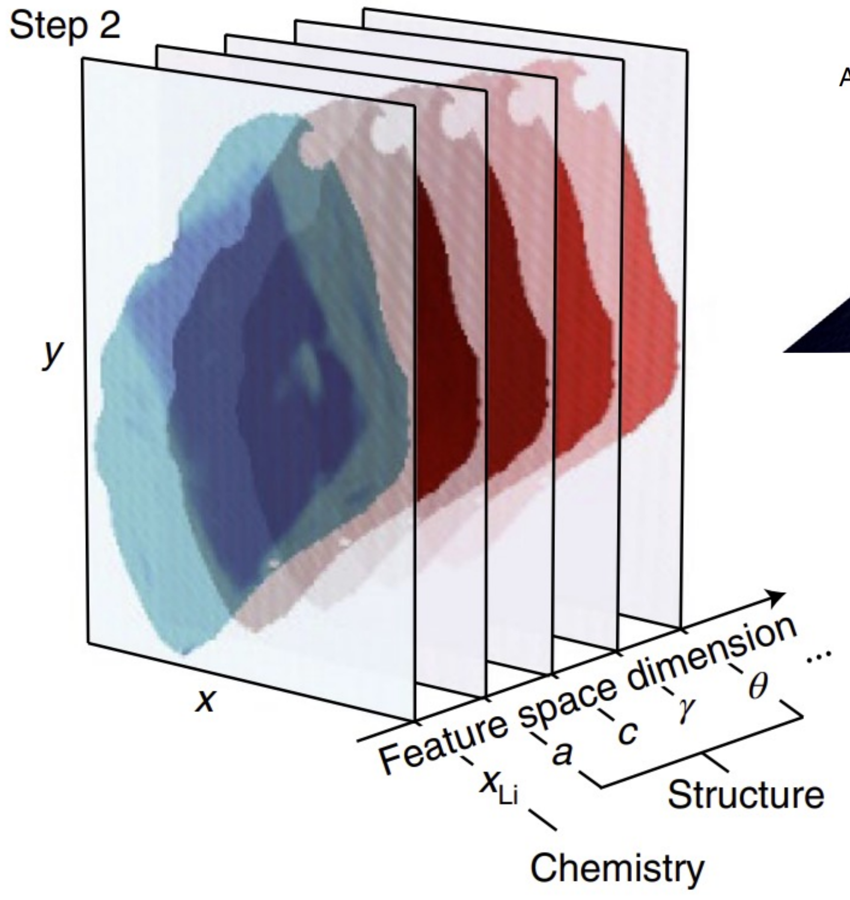


HD Deng et al., Nature Materials 21, 547 (2022). Hughes et al., Materials Today 52, 102 (2022)

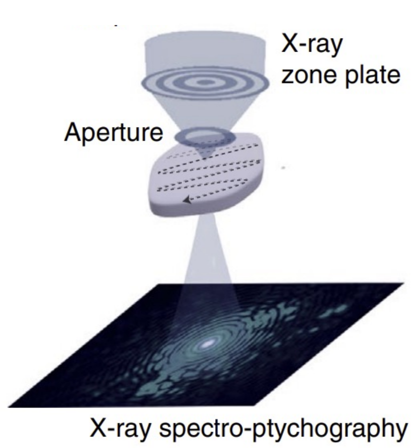
Inverse Learning of $LiFePO_4$ Chemo-Mechanics

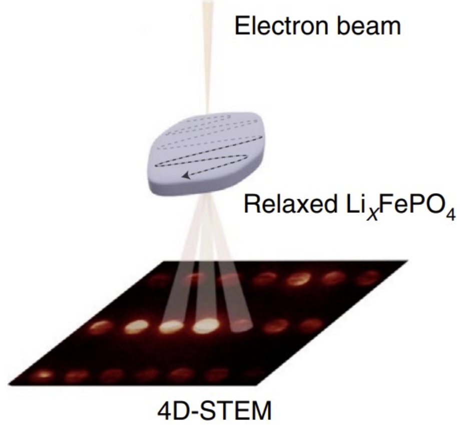
Alignment and correlation of all channels → **inverse learning of constitutive law**

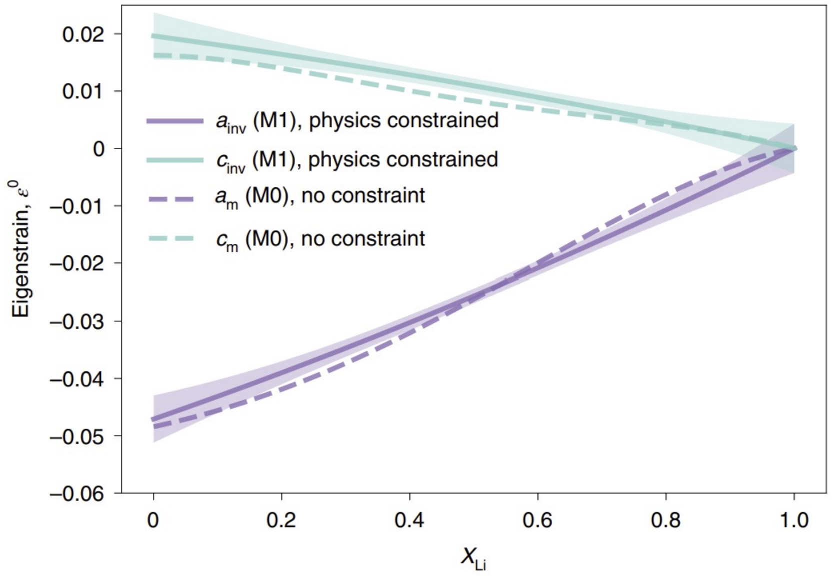




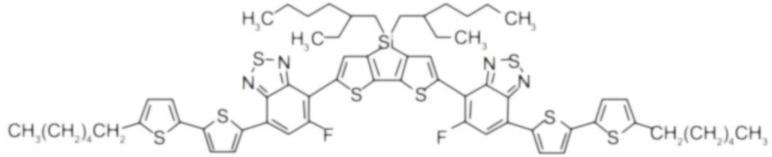
Multi-featured image stack ($\hat{s}$)

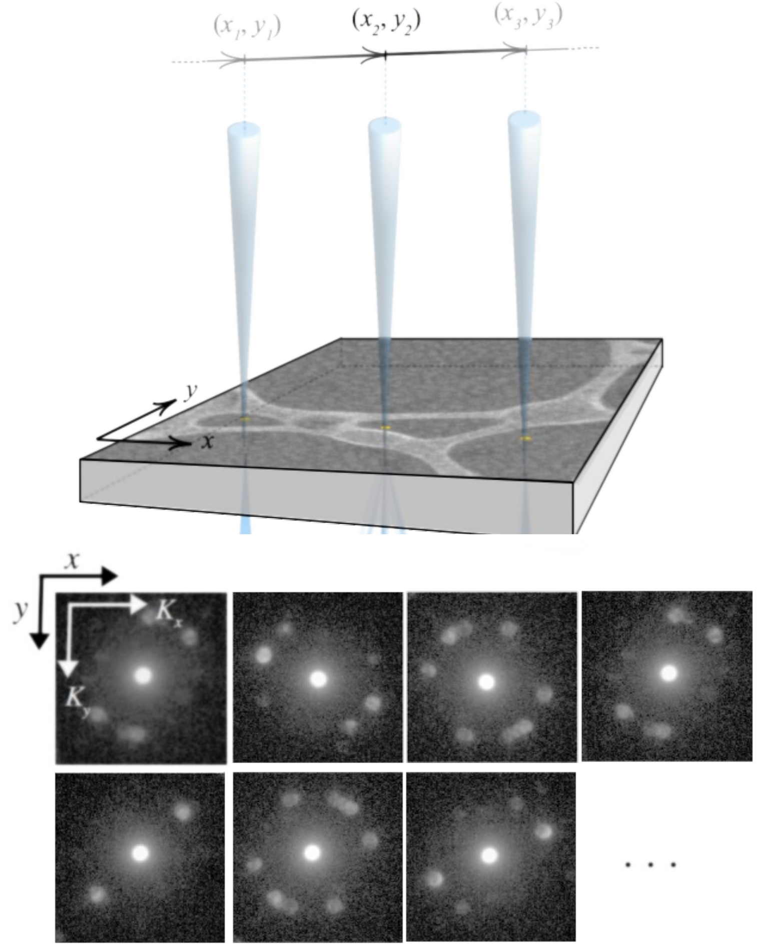




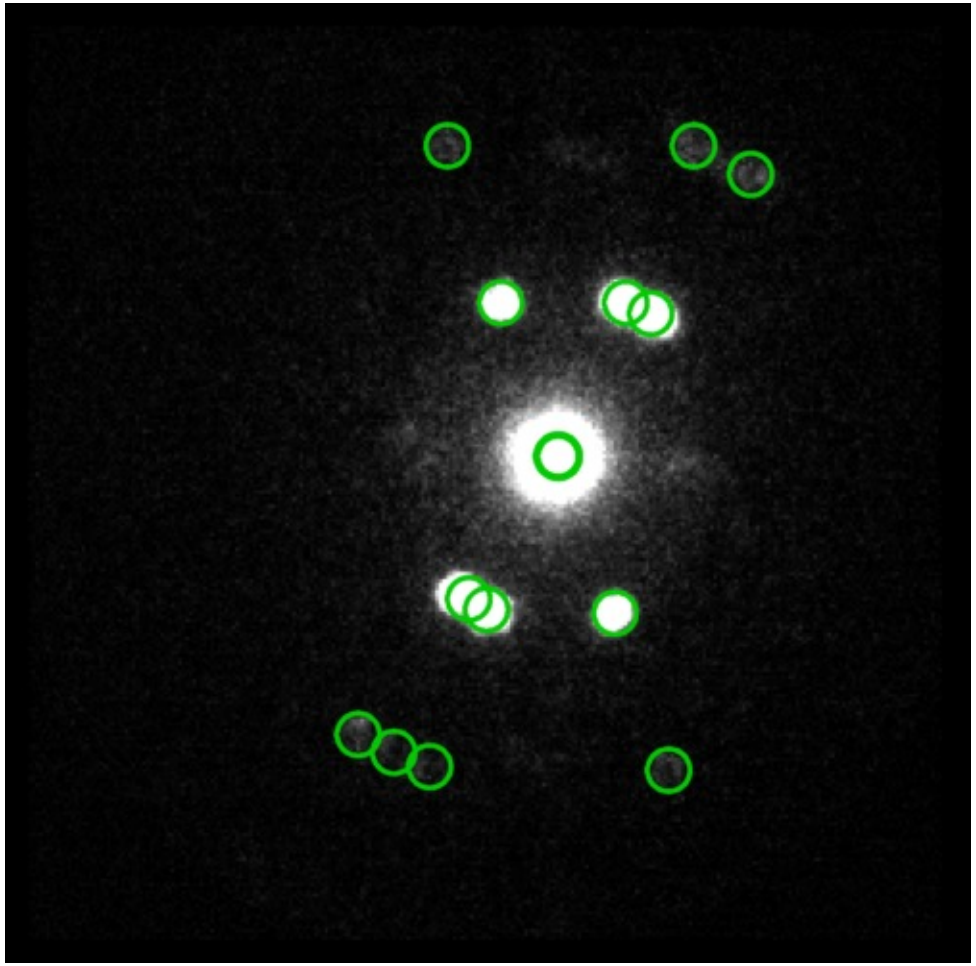


4D-STEM – Orientation Mapping of Soft Matter





Bragg peaks detected in each diffraction pattern:



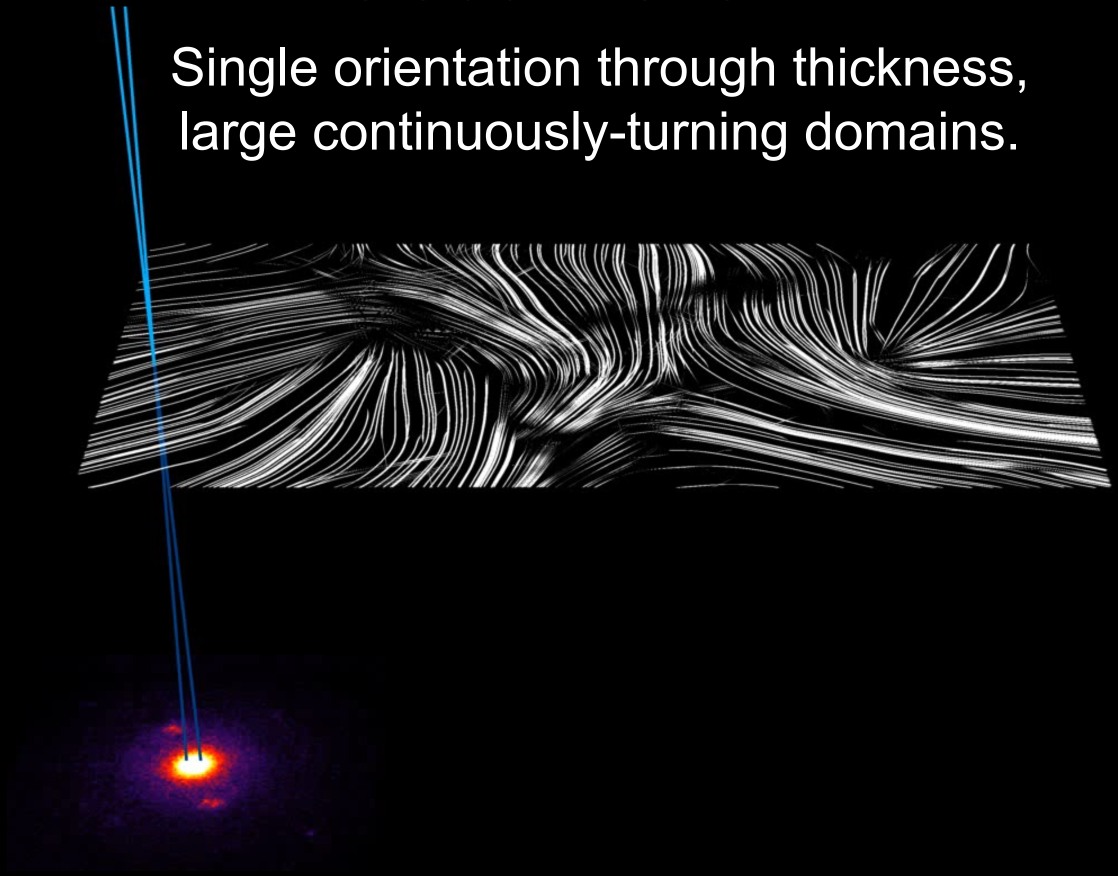
- Image template from vacuum reference probe or synthetic disk.
- Use template matching / image correlation to identify peaks.
- Record data, move onto next image.

4D-STEM – Orientation Mapping of Soft Matter

Visualization of the two morphologies:

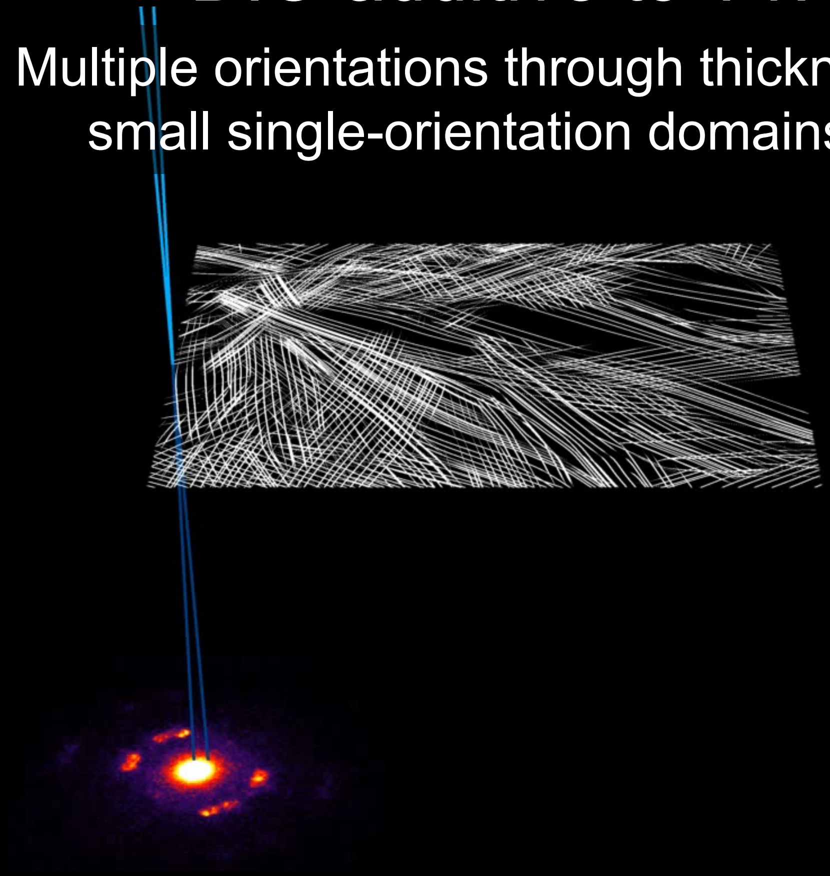
No additive to T1:

Single orientation through thickness, large continuously-turning domains.



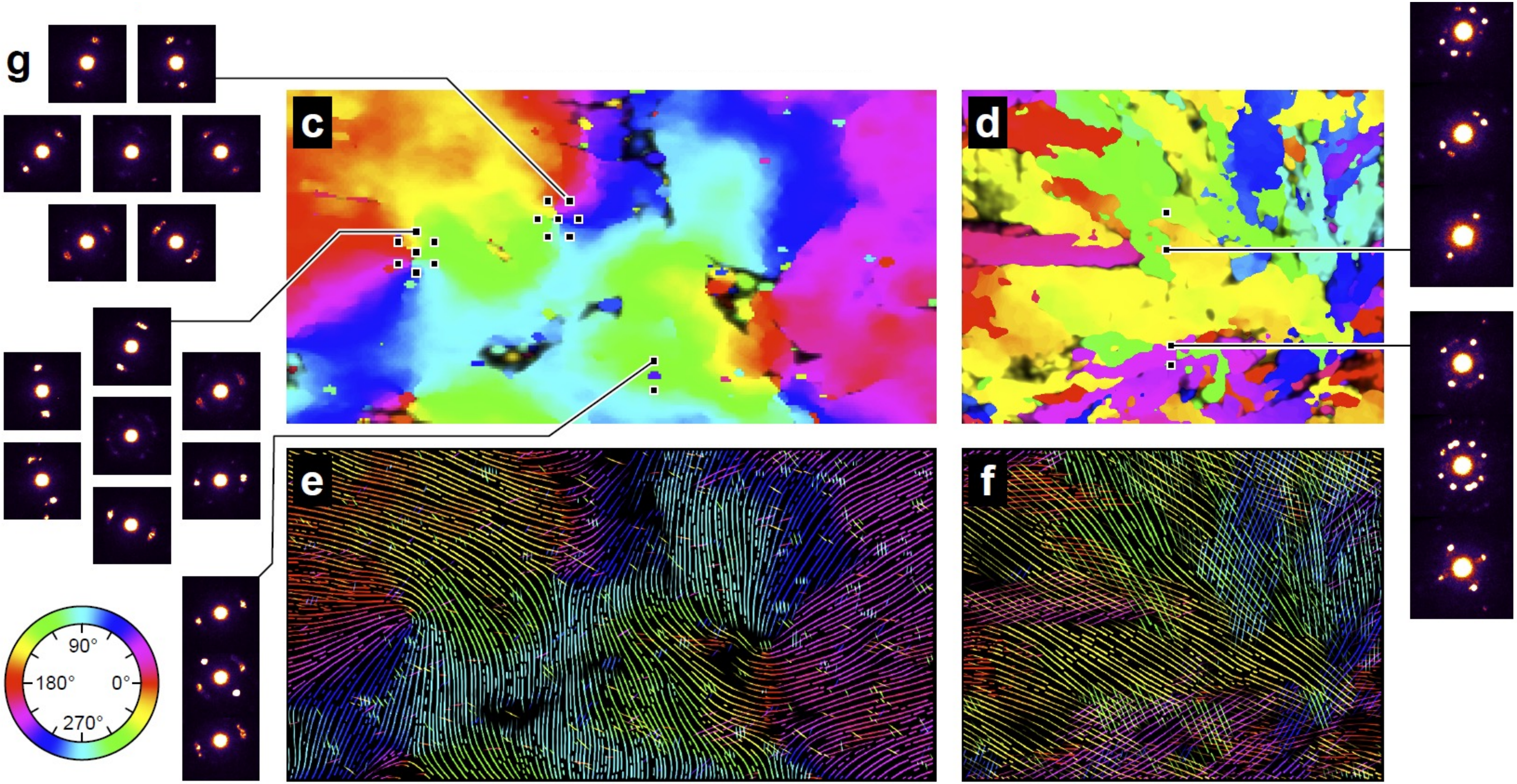
DIO additive to T1:

Multiple orientations through thickness, small single-orientation domains.



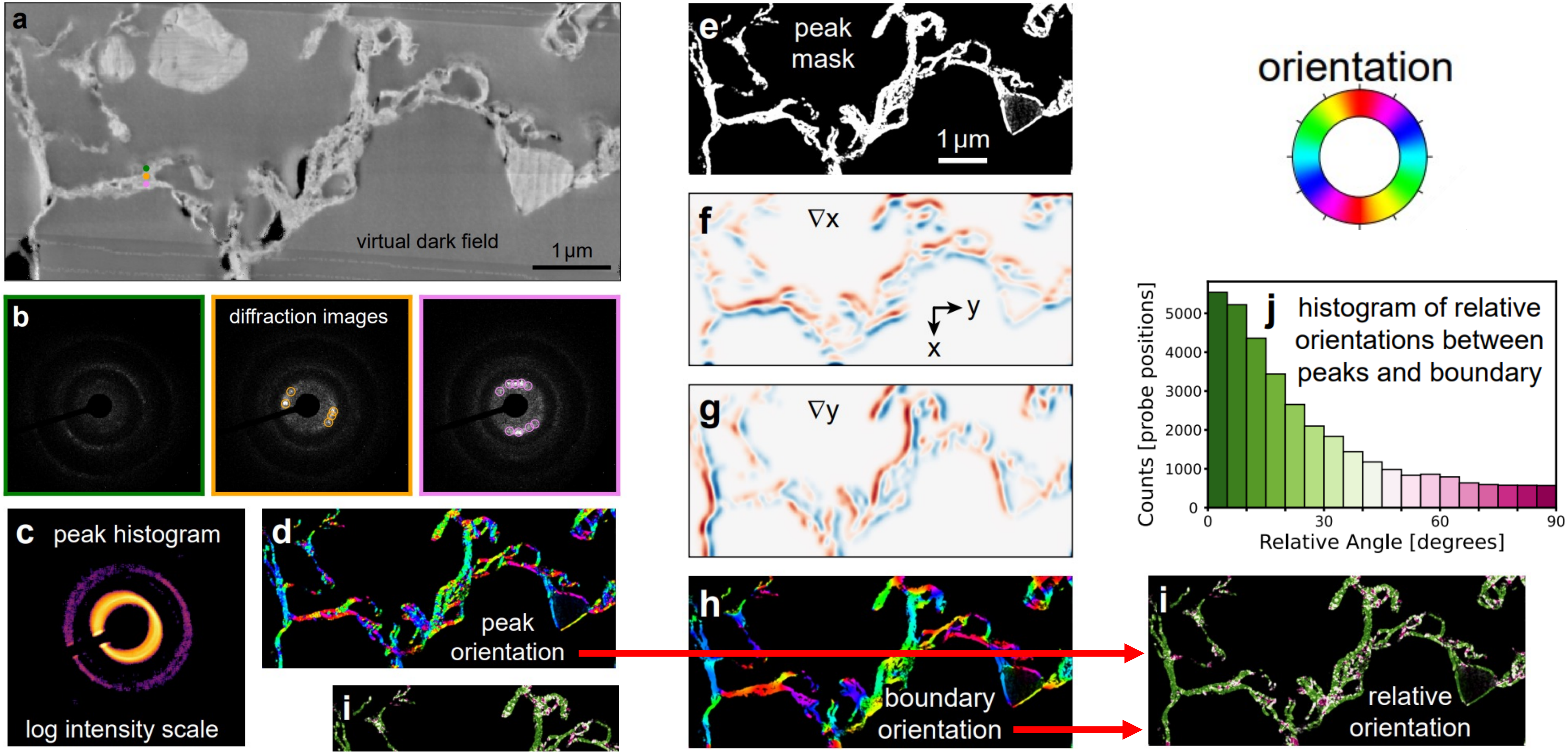
C Ophus*, O Panova* et al., Nature Materials 18, 860 (2019)

4D-STEM – Orientation Mapping of Soft Matter



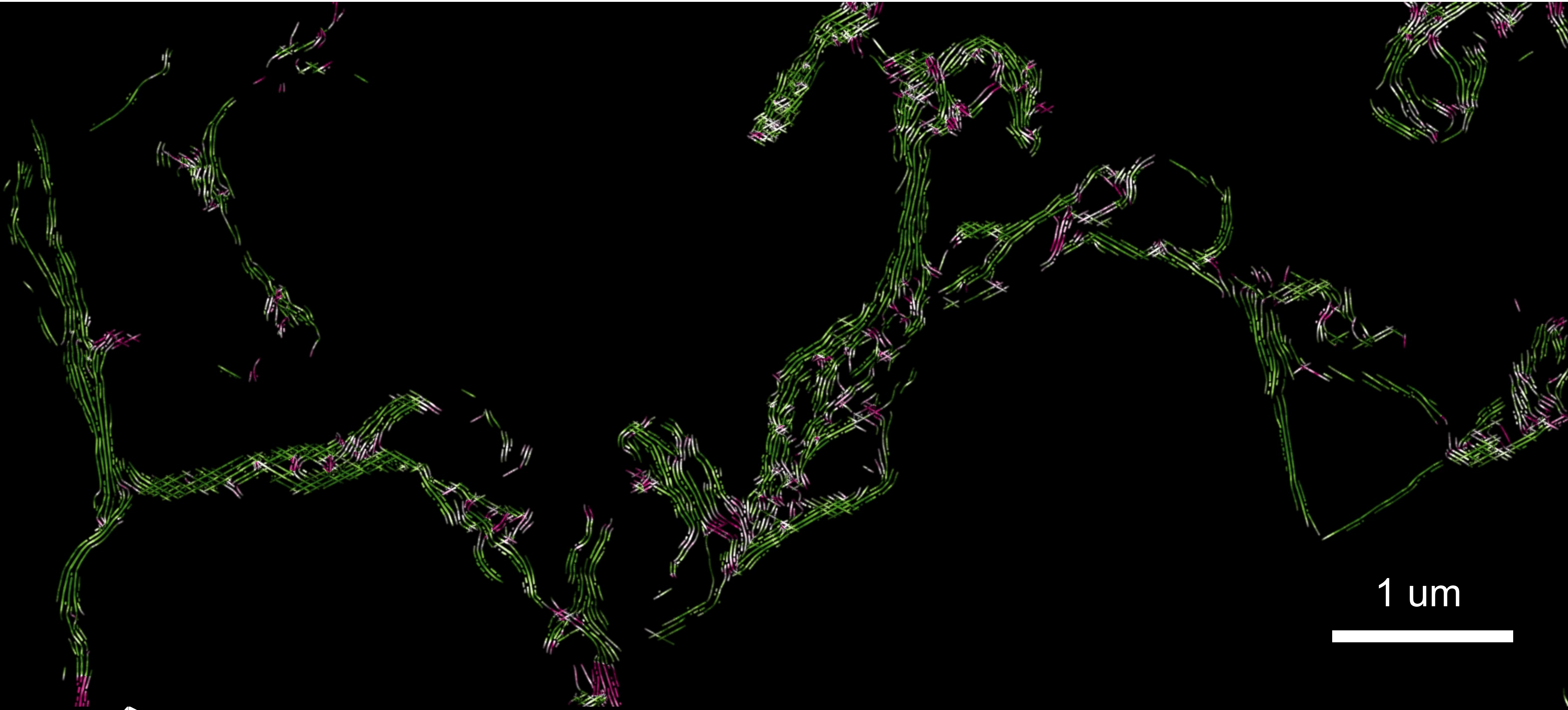
C Ophus*, O Panova* et al., Nature Materials 18, 860 (2019)

Carbon Basal Plane Orientations, Color Relative to Pores



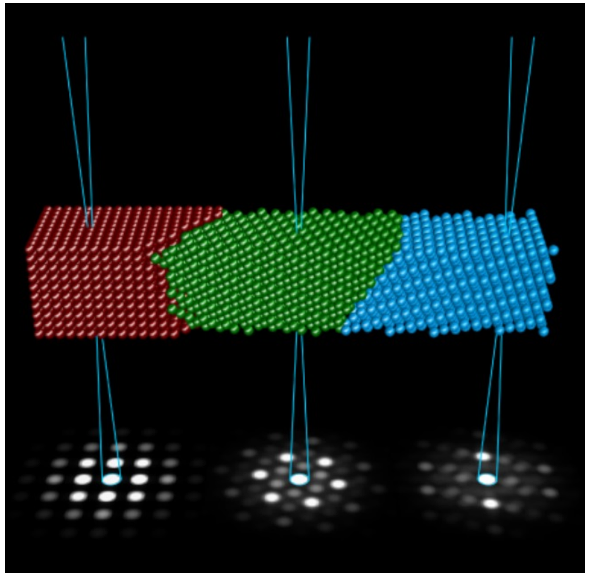
Huize Wang, Charles Otieno Ogolla et al., **Advanced Functional Materials** 2207406 (2022)

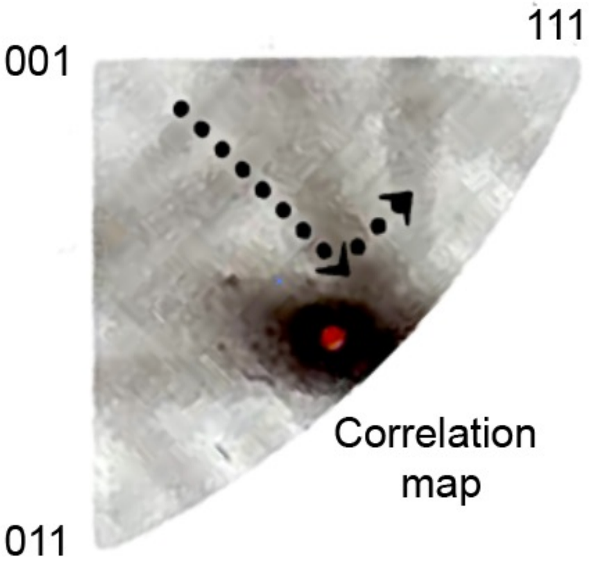
Carbon Basal Plane Orientations, Color Relative to Pores

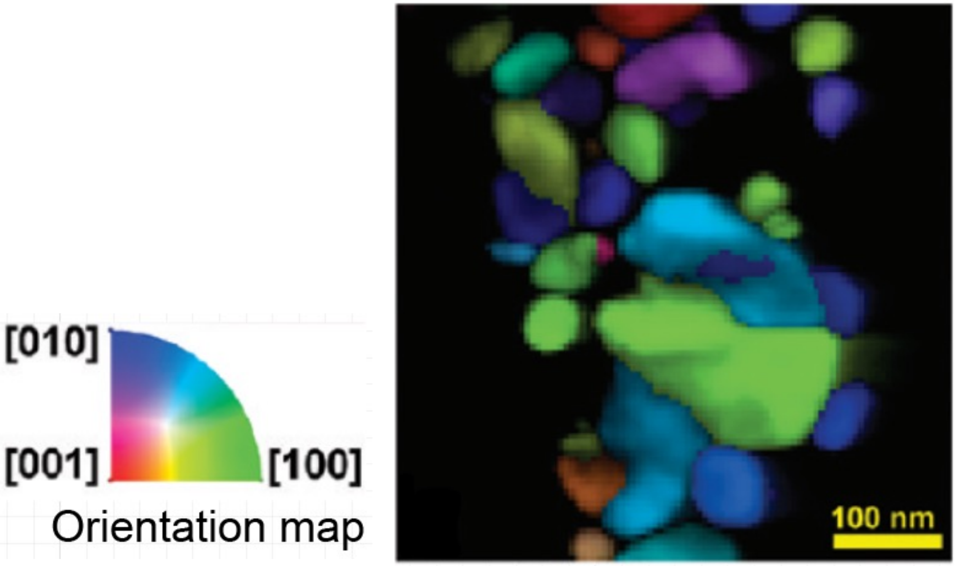


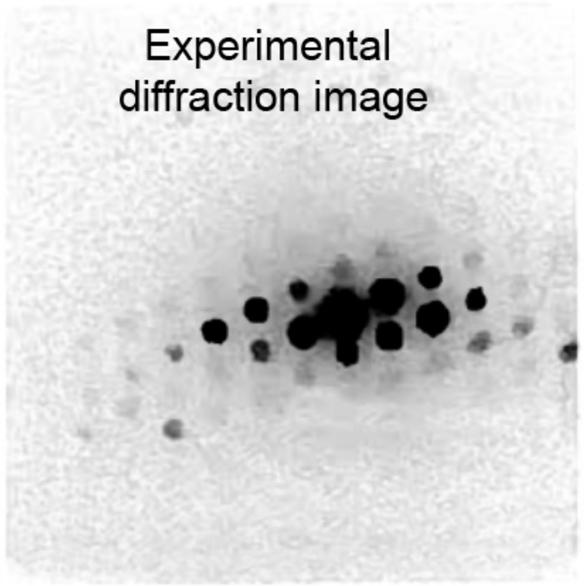
Huize Wang, Charles Otieno Ogolla et al., **Advanced Functional Materials** 2207406 (2022)

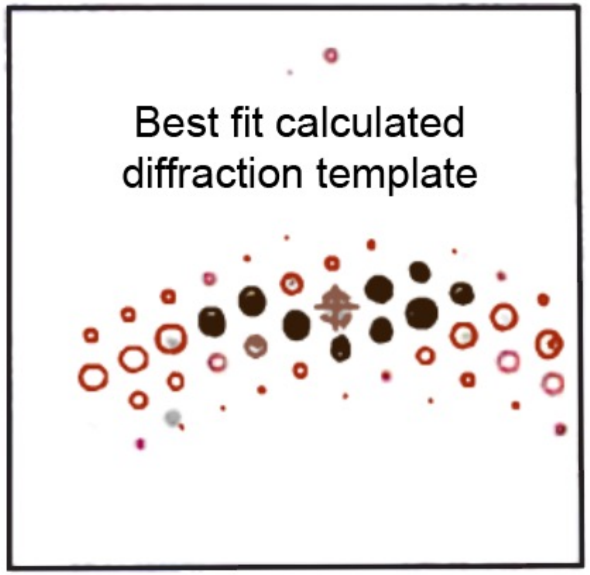
Orientation / Phase from a Diffraction Pattern Library

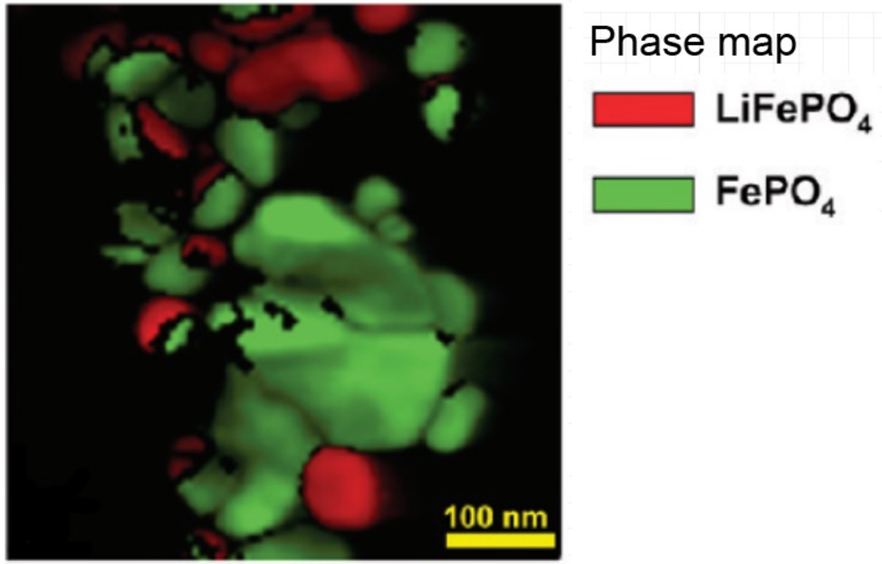








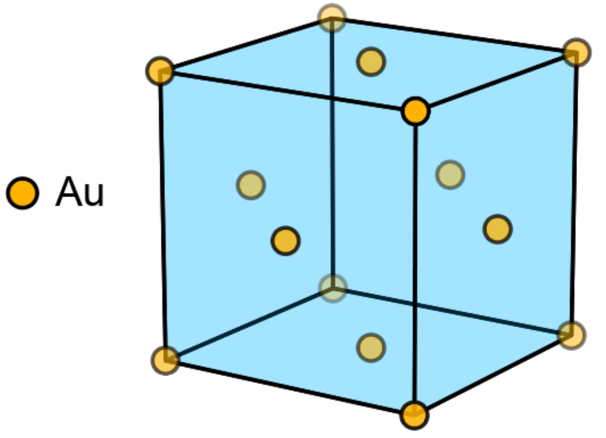




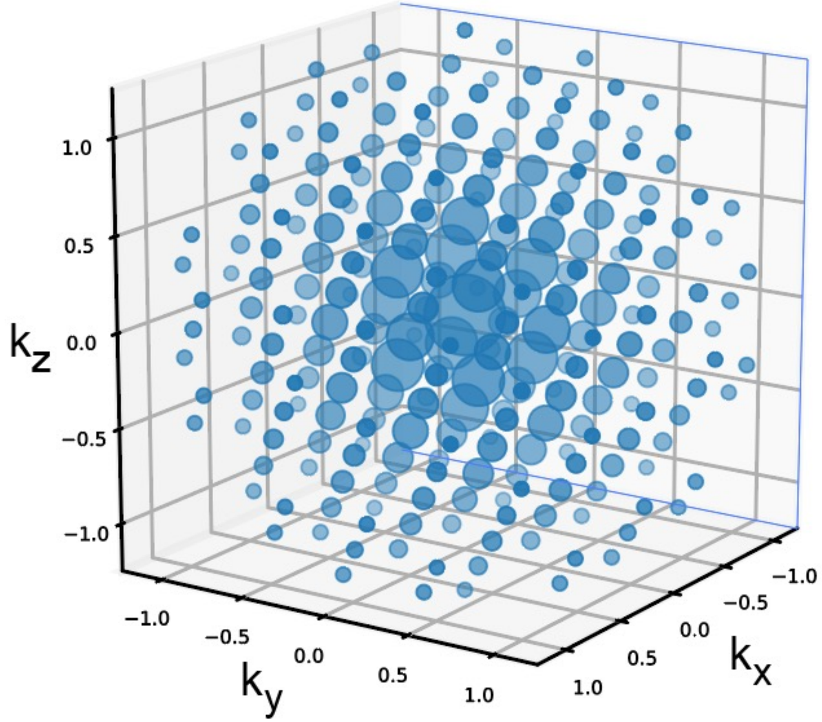
C Ophus, M and M 25, 563 (2019)   E Rauch et al., Arch Metall Mater 50, 87, (2005)   G Brunetti et al., Chem Mater 23, 4515, (2011)

Kinematical / Dynamical Diffraction Patterns

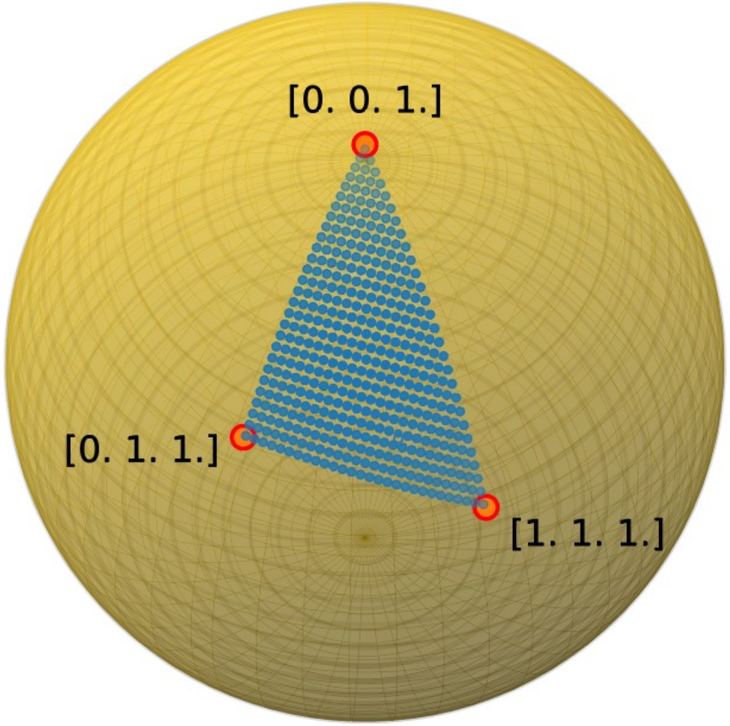
Unit Cell Structure



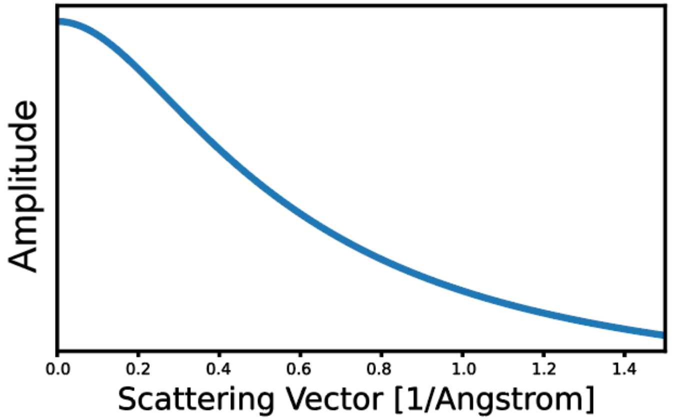
Structure Factors



Zone Axis Range



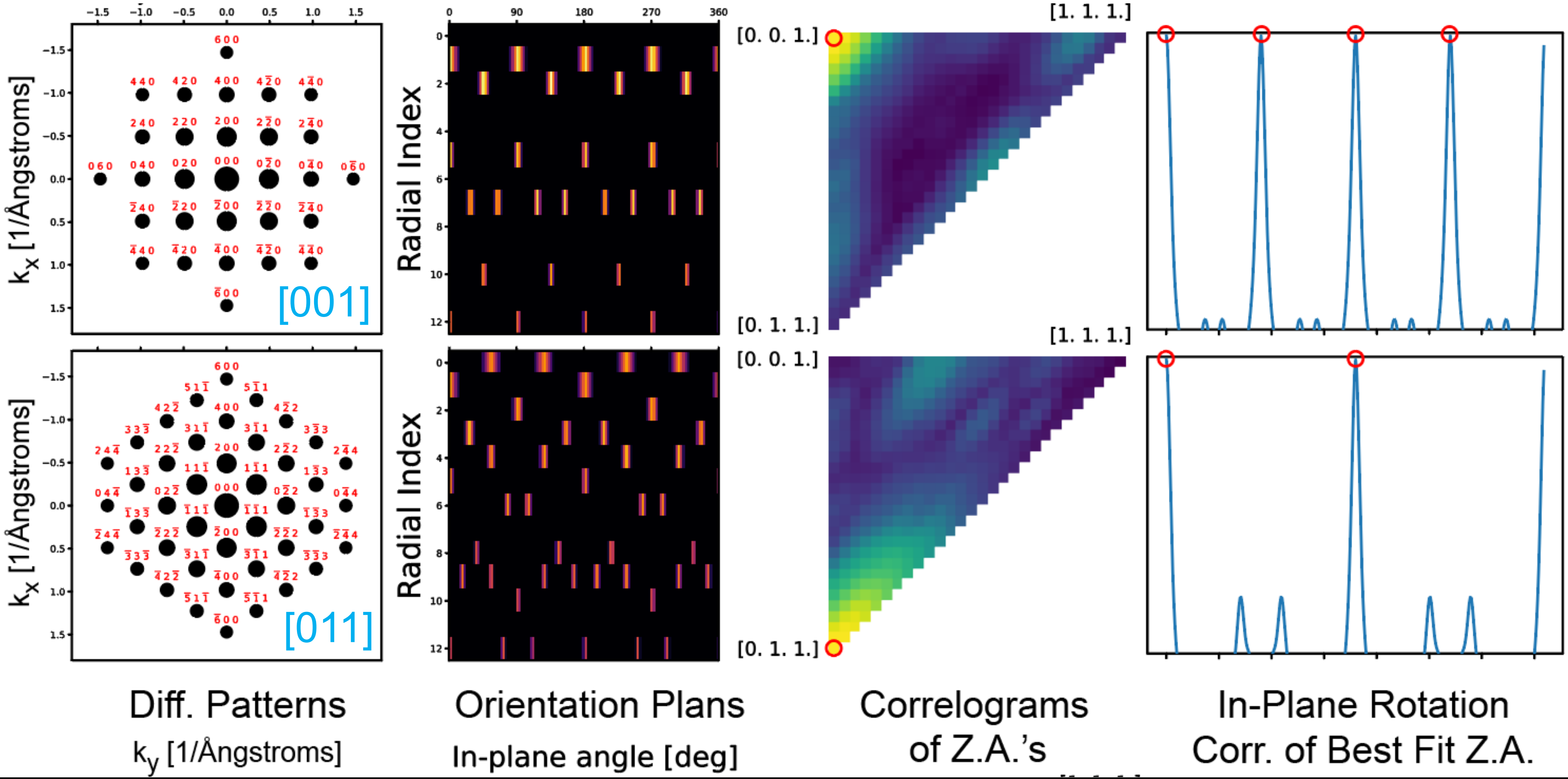
Single Atom Scattering



$$F_{hkl} = \sum_{n=1}^{N} f_n(\|\boldsymbol{q}\|) \exp\left[-2\pi i (h,k,l) \cdot \boldsymbol{p}_n\right]$$

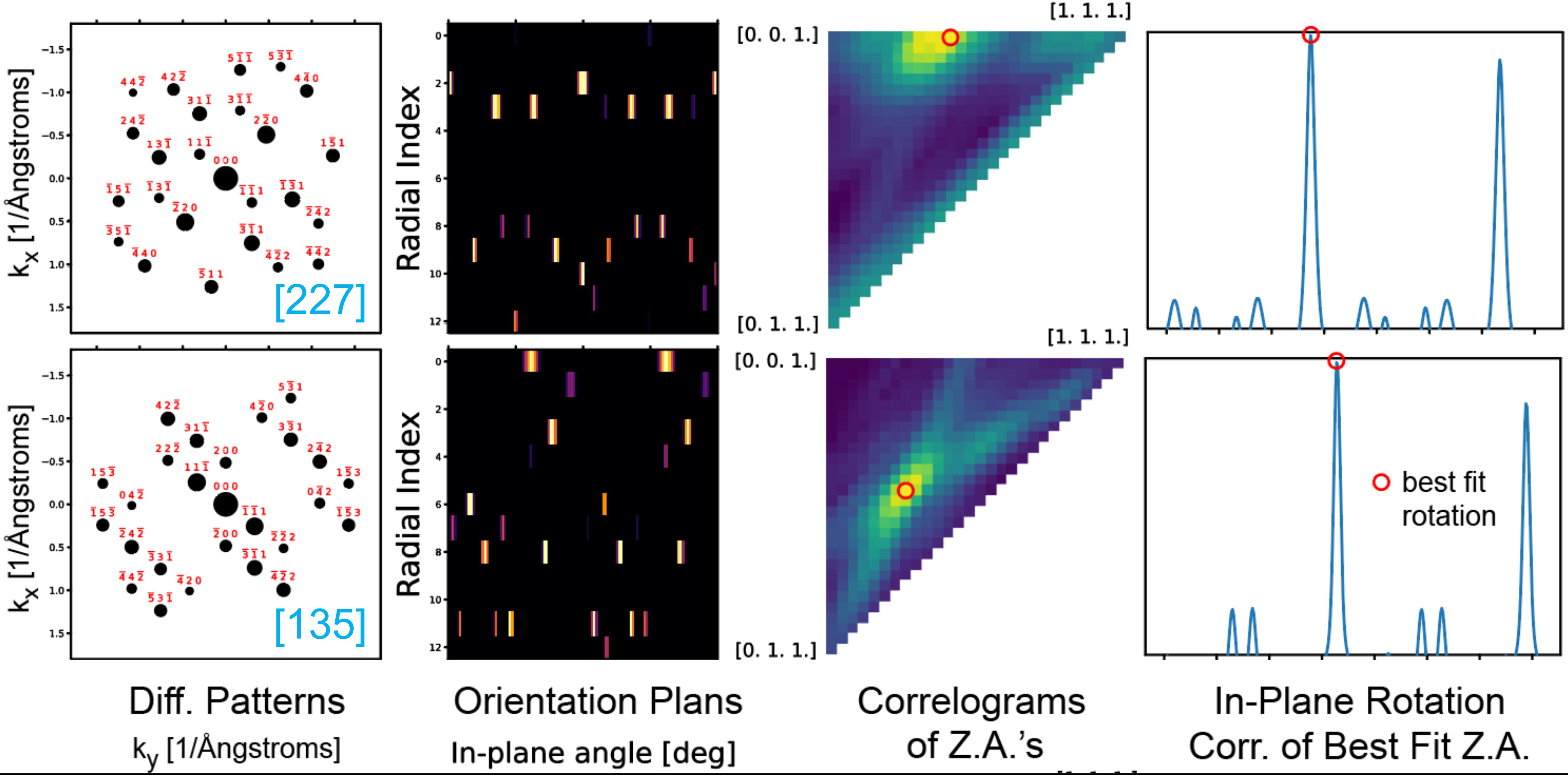
$$\mathrm{Slerp}(p_0, p_1; t) = \frac{\sin\left[(1-t)\Omega\right]}{\sin\Omega} p_0 + \frac{\sin[t\Omega]}{\sin\Omega} \varpi_1$$

Orientation Mapping via Sparse Correlation



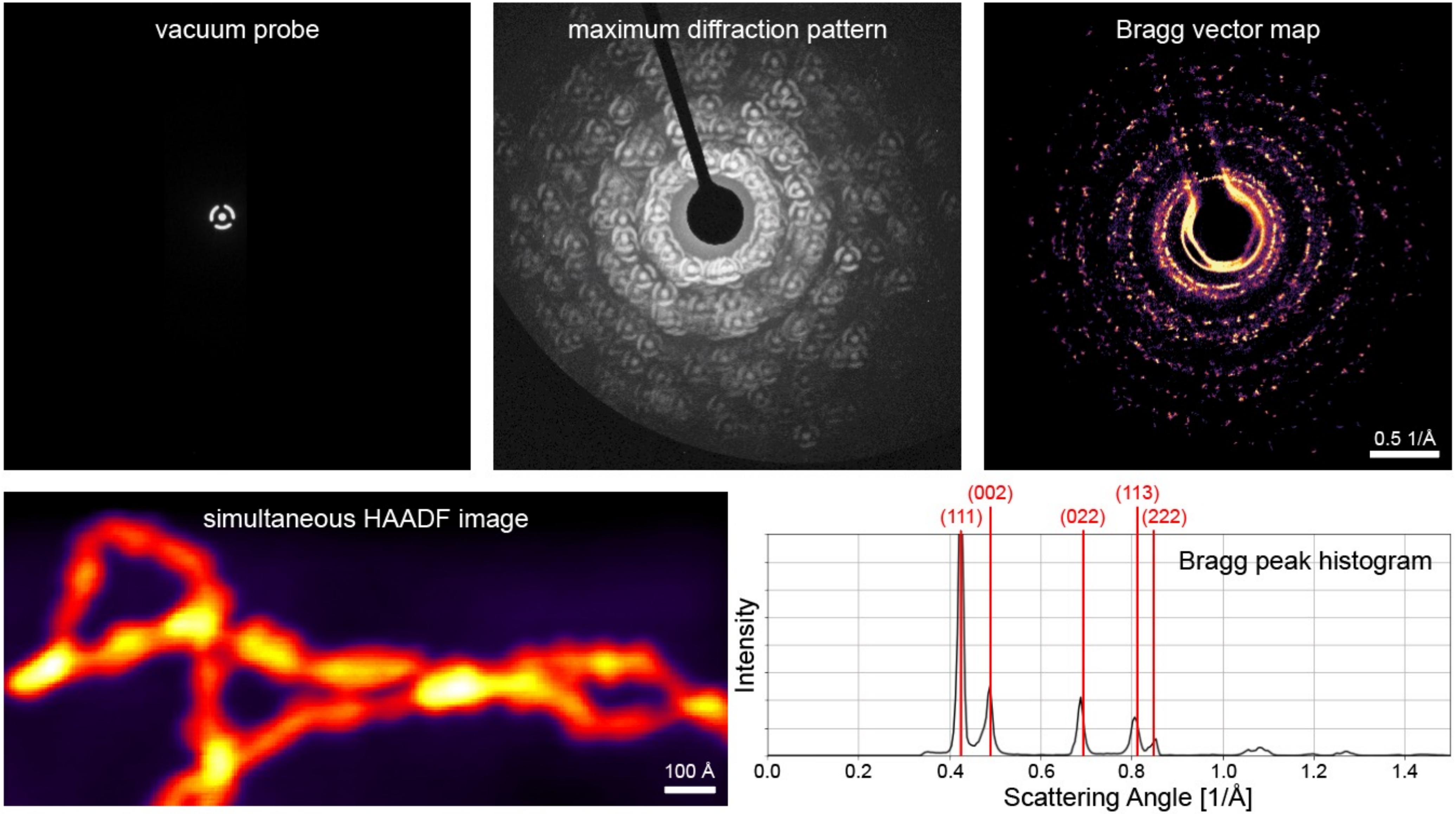
C Ophus et al., Microscopy and Microanalysis 28, 390 (2022).

Orientation Mapping via Sparse Correlation



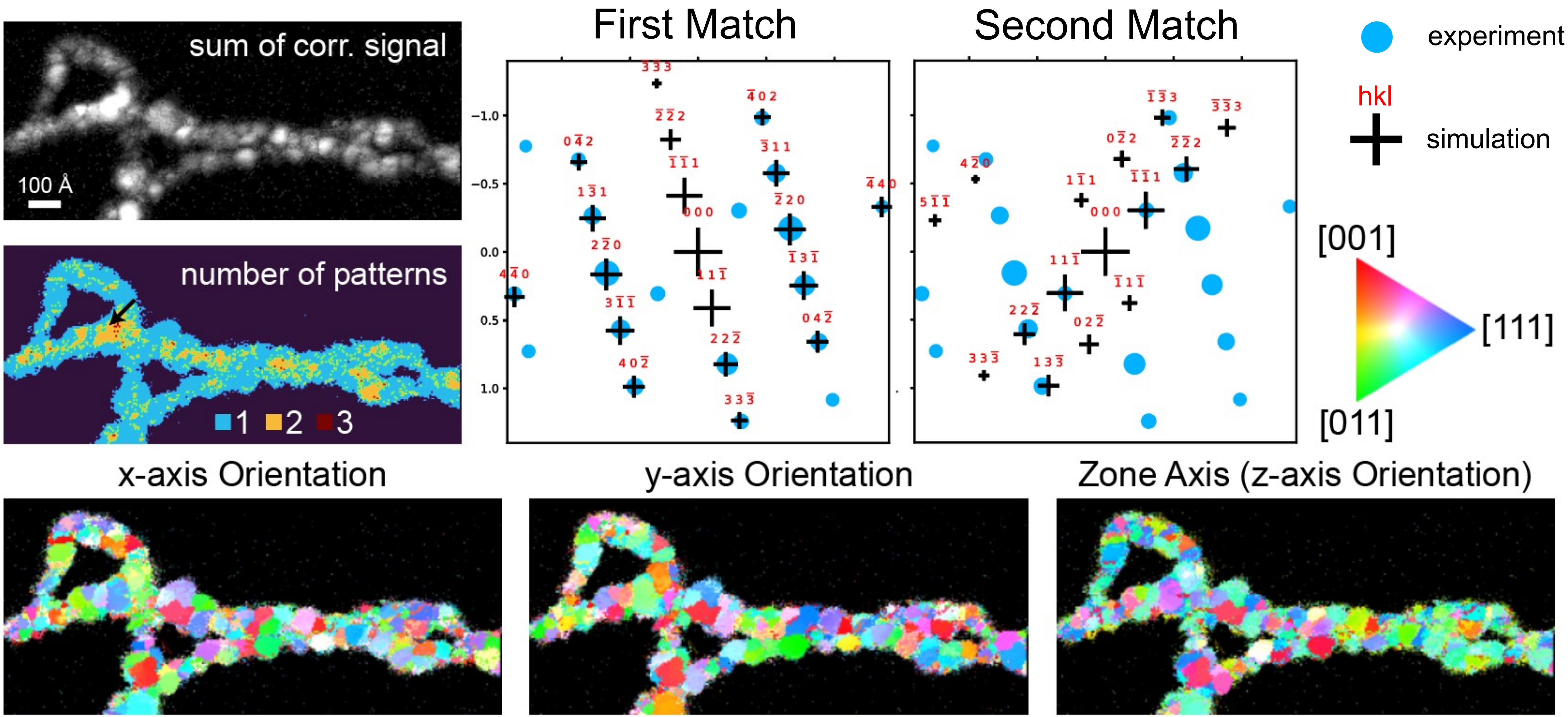
C Ophus et al., Microscopy and Microanalysis 28, 390 (2022).

4D-STEM of Twisted AuAgPd Nanowires



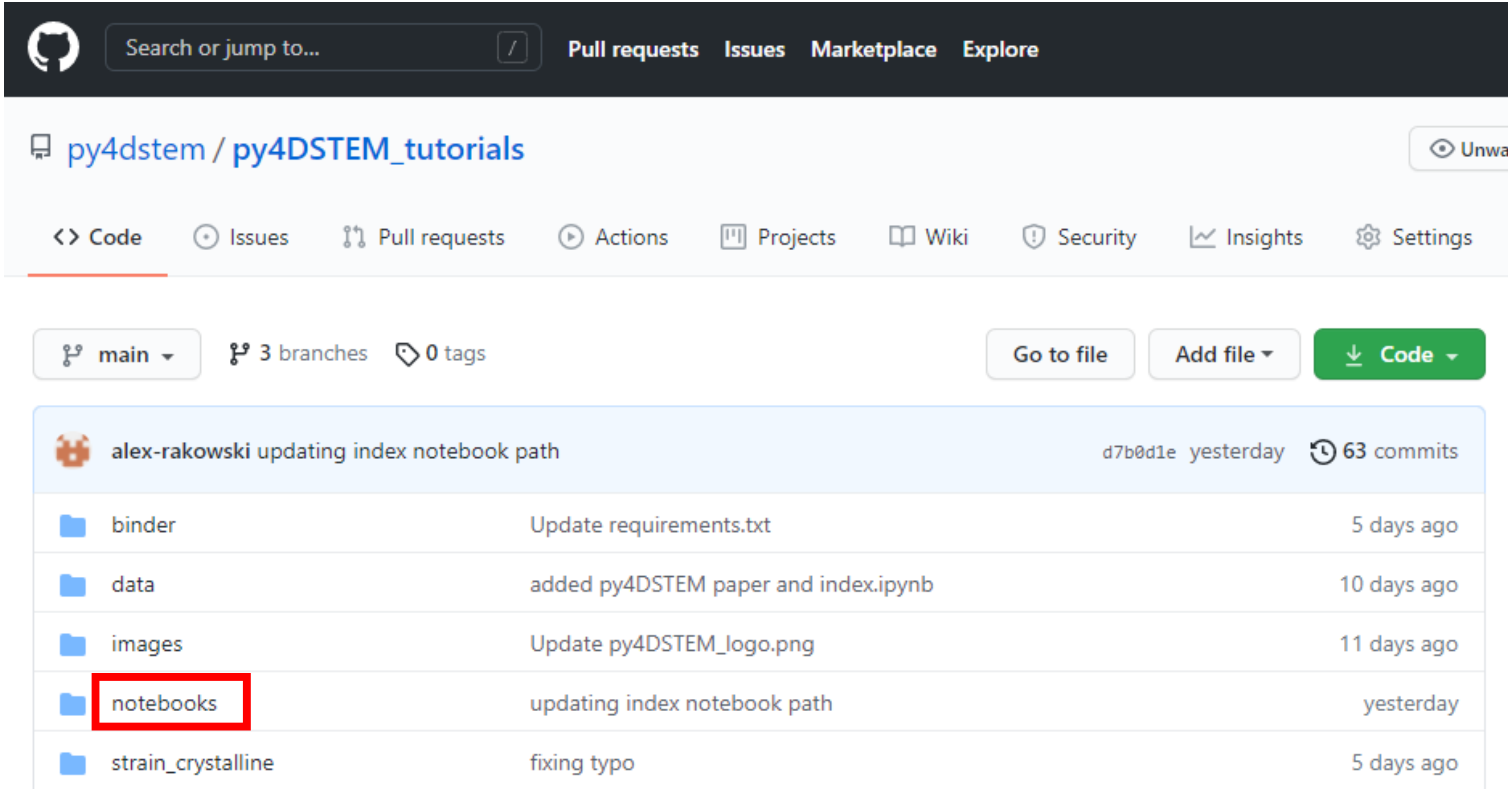
C Ophus et al., Microscopy and Microanalysis 28, 390 (2022).

Orientation Mapping of AuAgPd Nanowires



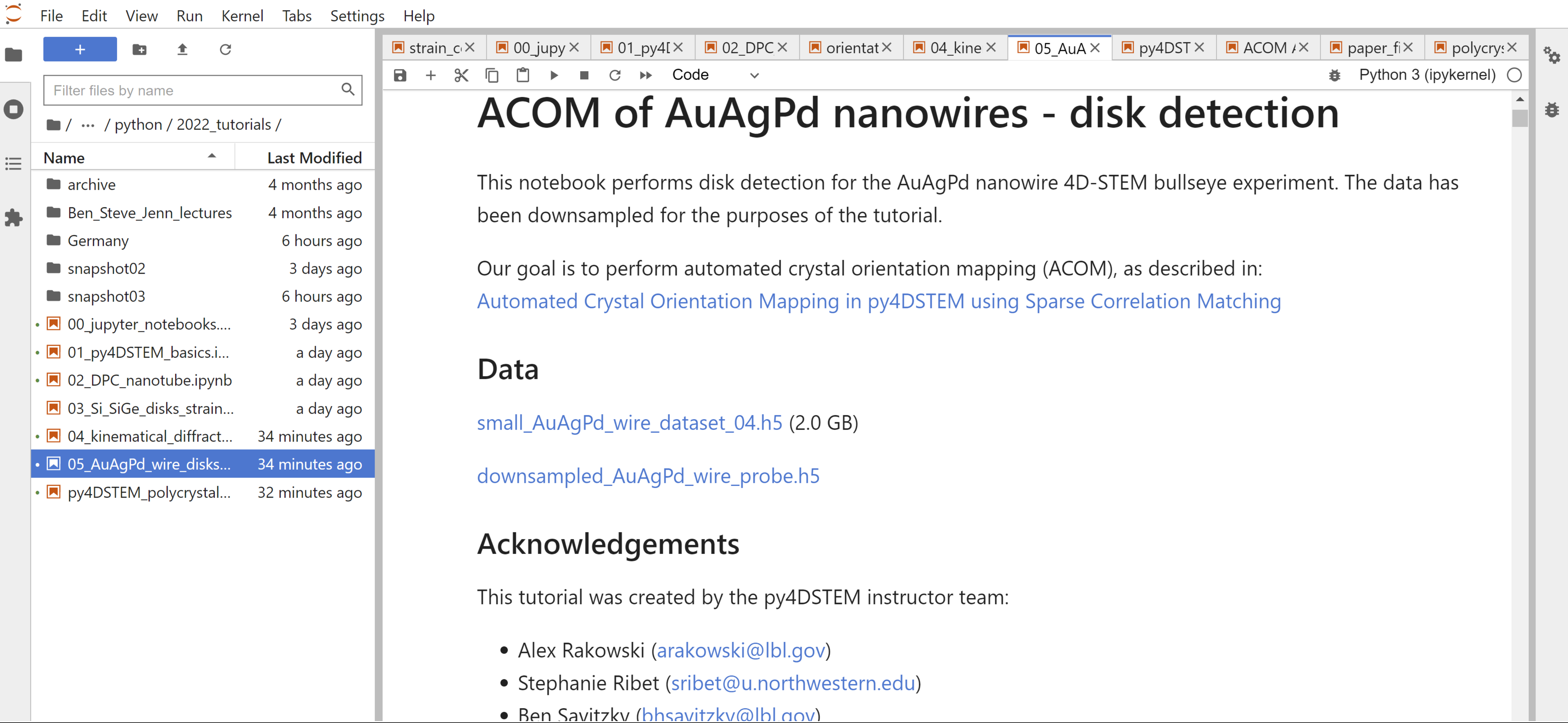
py4DSTEM Tutorials

Tutorial repository – https://github.com/py4dstem/py4DSTEM_tutorials

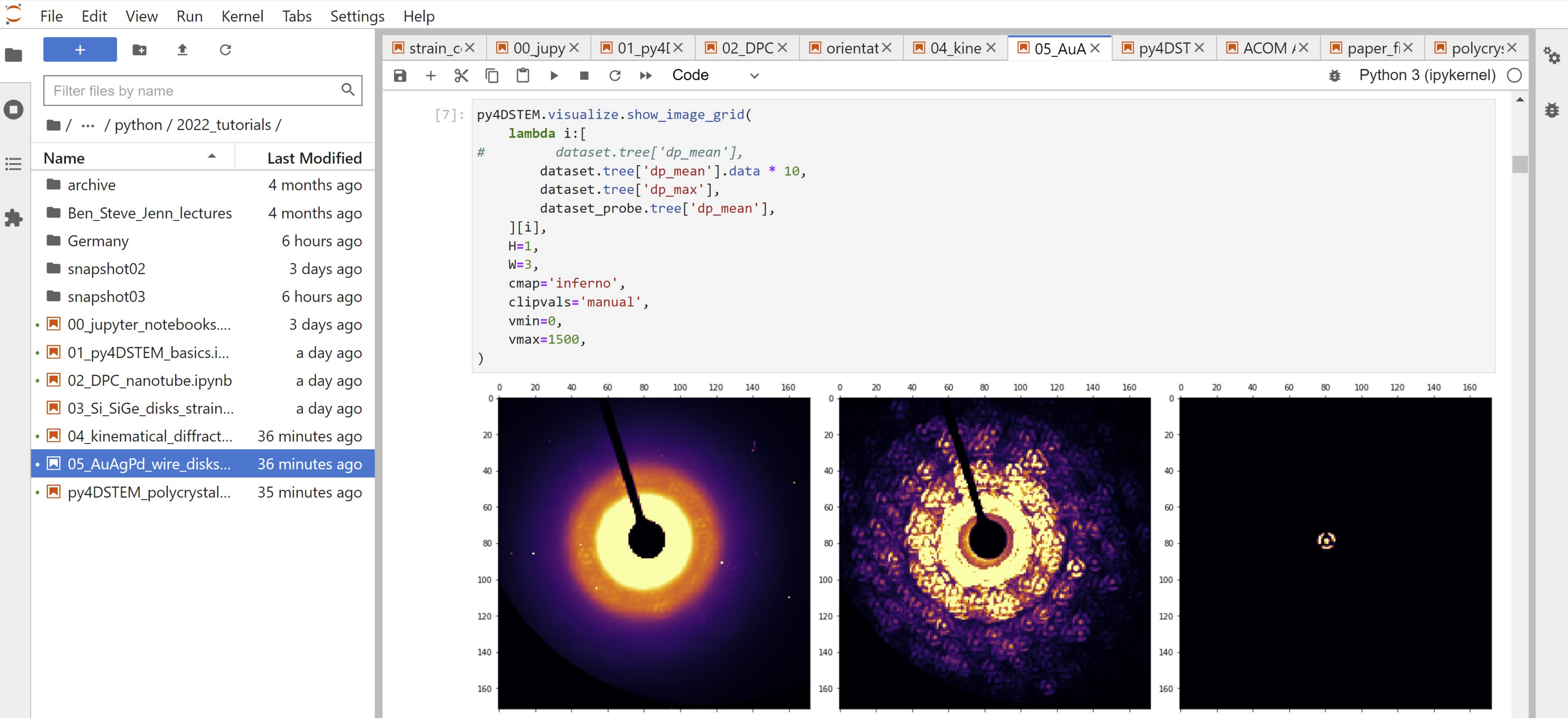


py4DSTEM

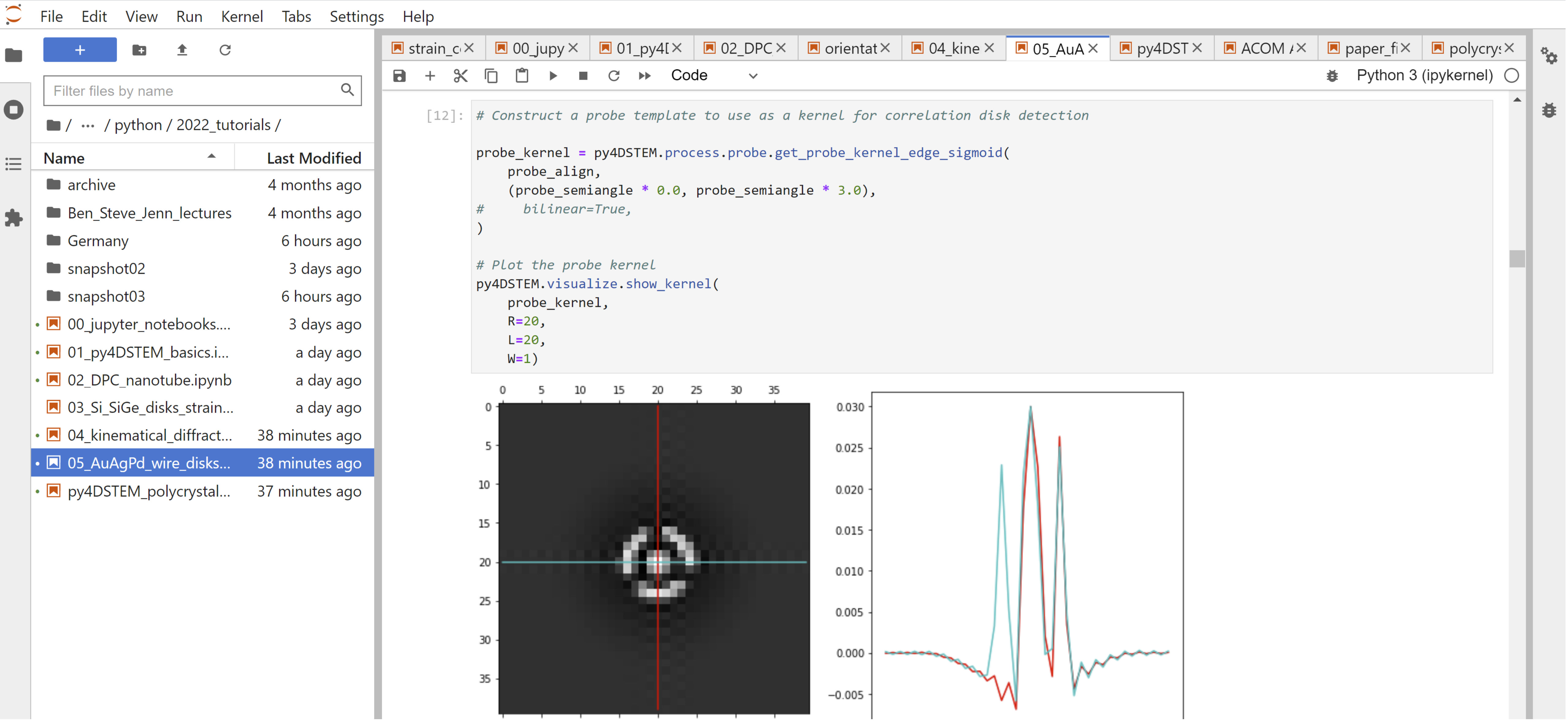
Crystalline Orientation Mapping in py4DSTEM



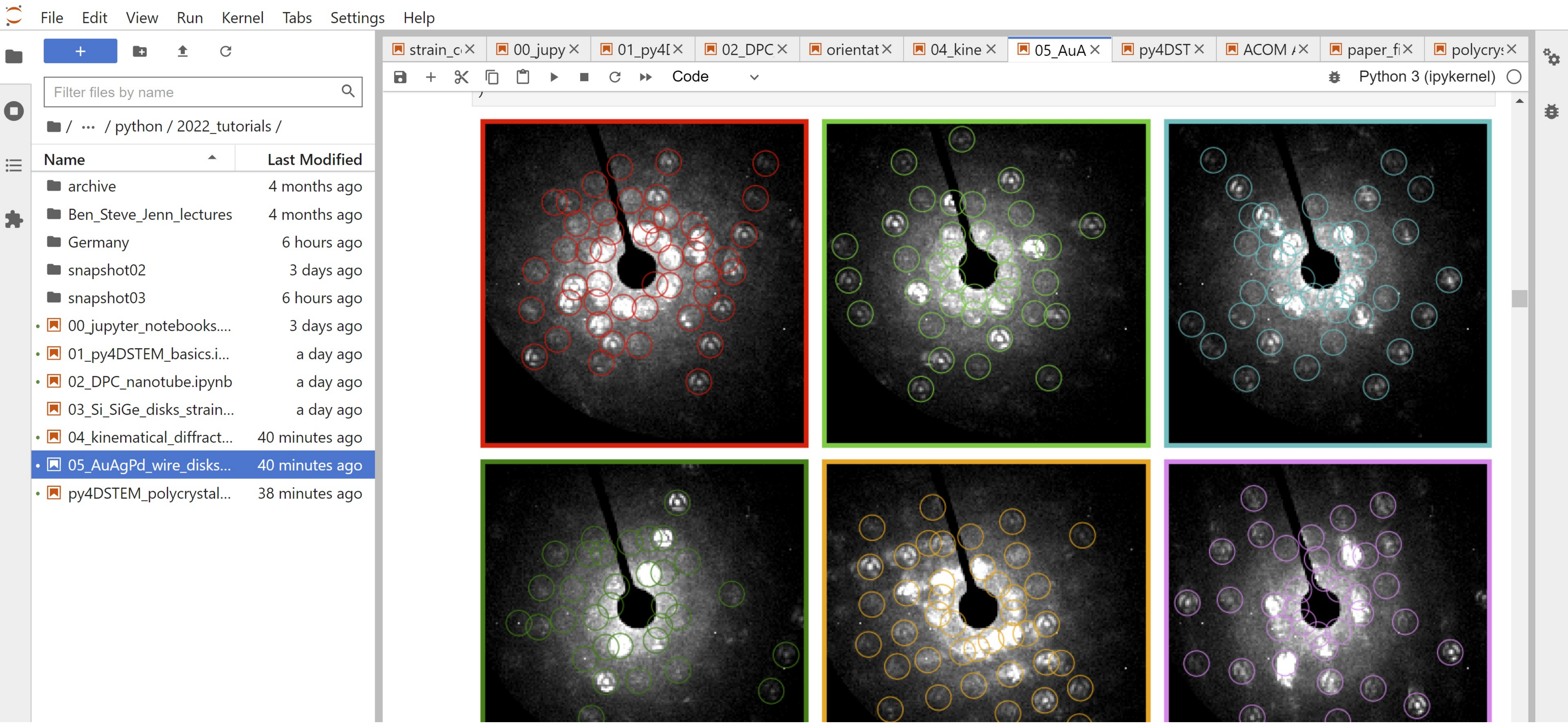
Crystalline Orientation Mapping in py4DSTEM



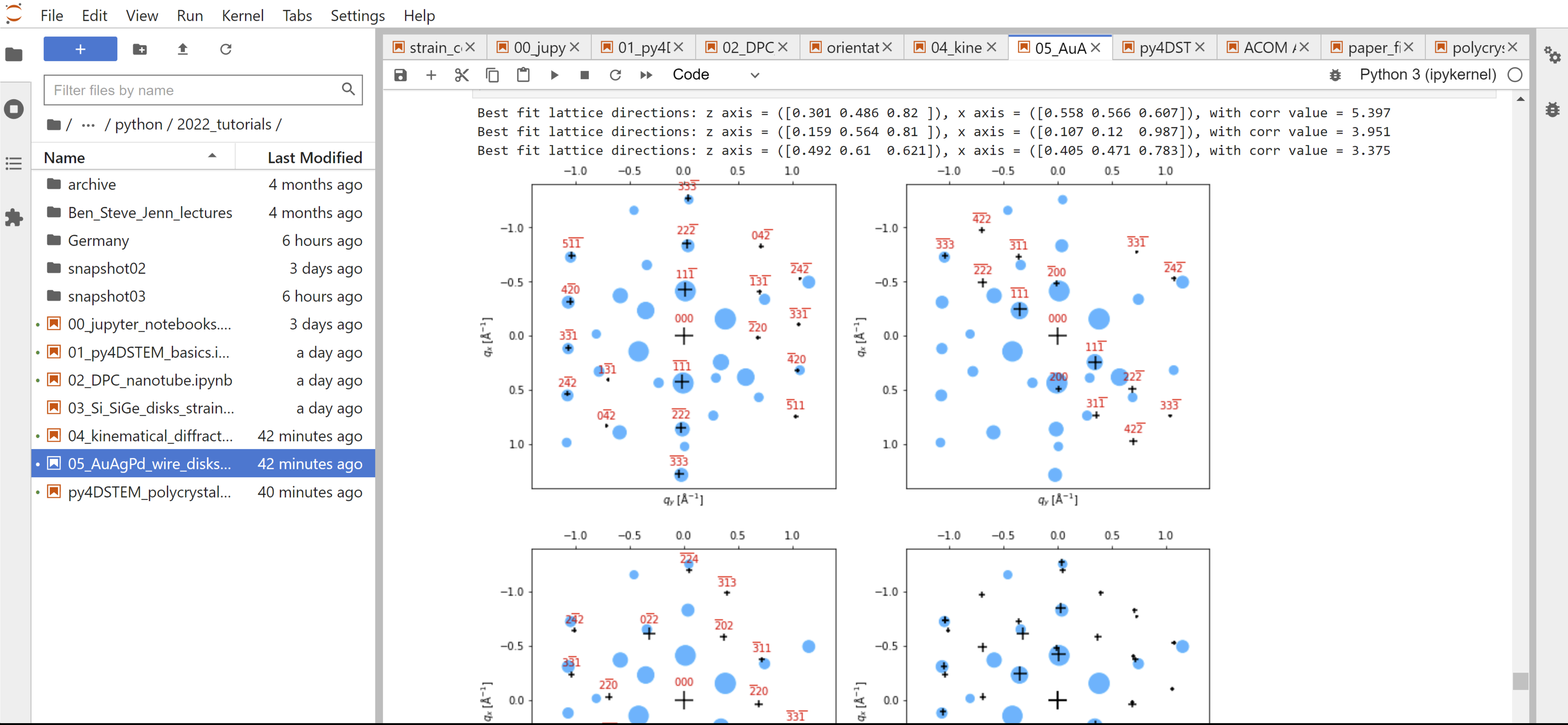
Crystalline Orientation Mapping in py4DSTEM



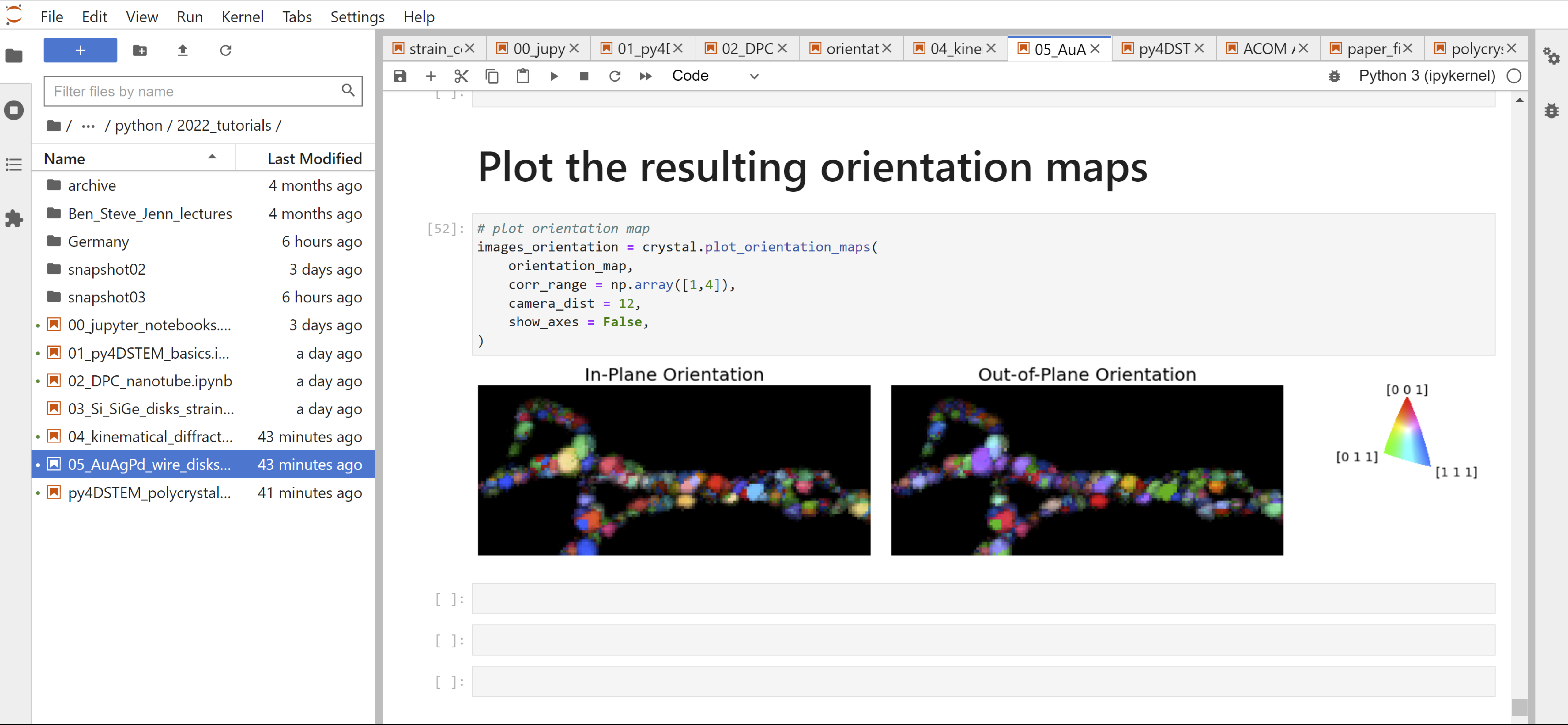
Crystalline Orientation Mapping in py4DSTEM



Crystalline Orientation Mapping in py4DSTEM

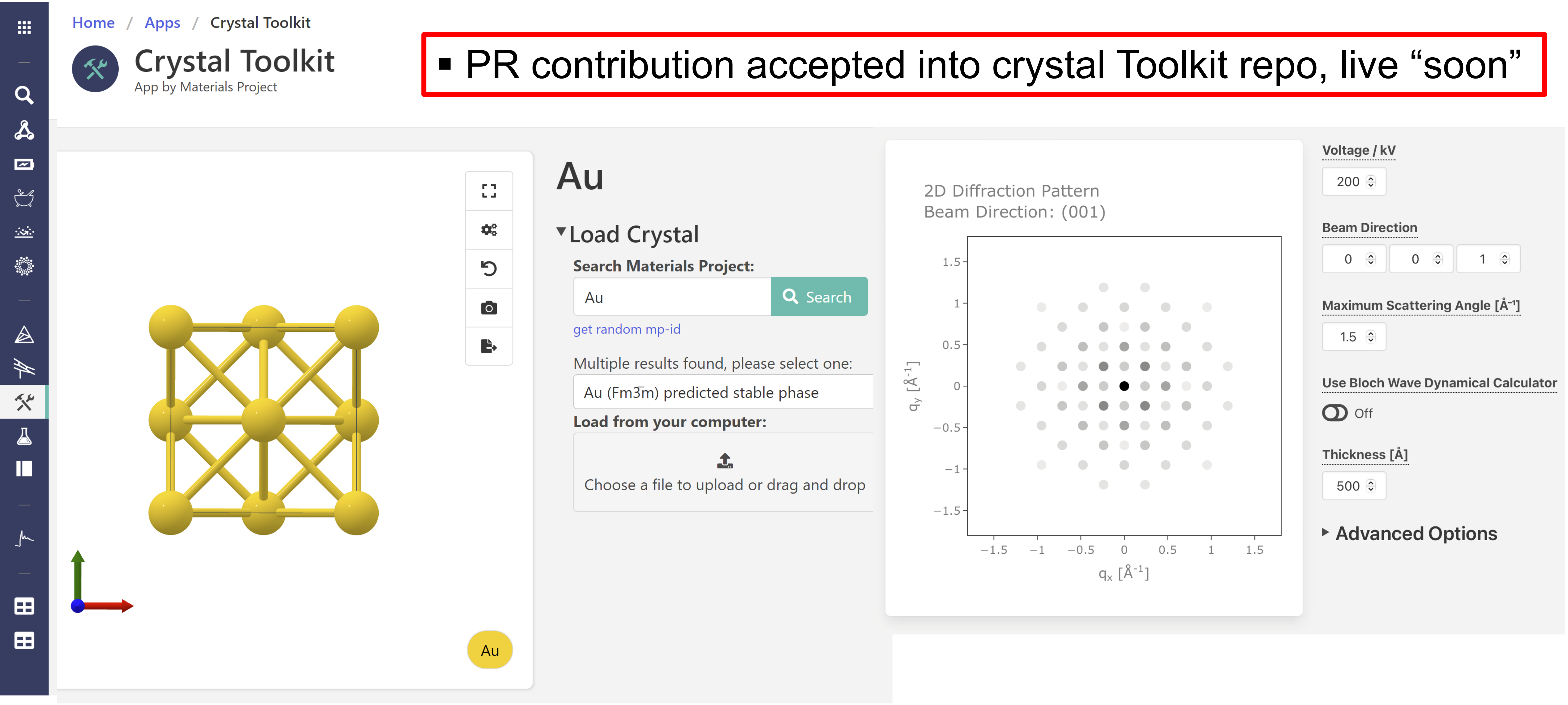


Crystalline Orientation Mapping in py4DSTEM



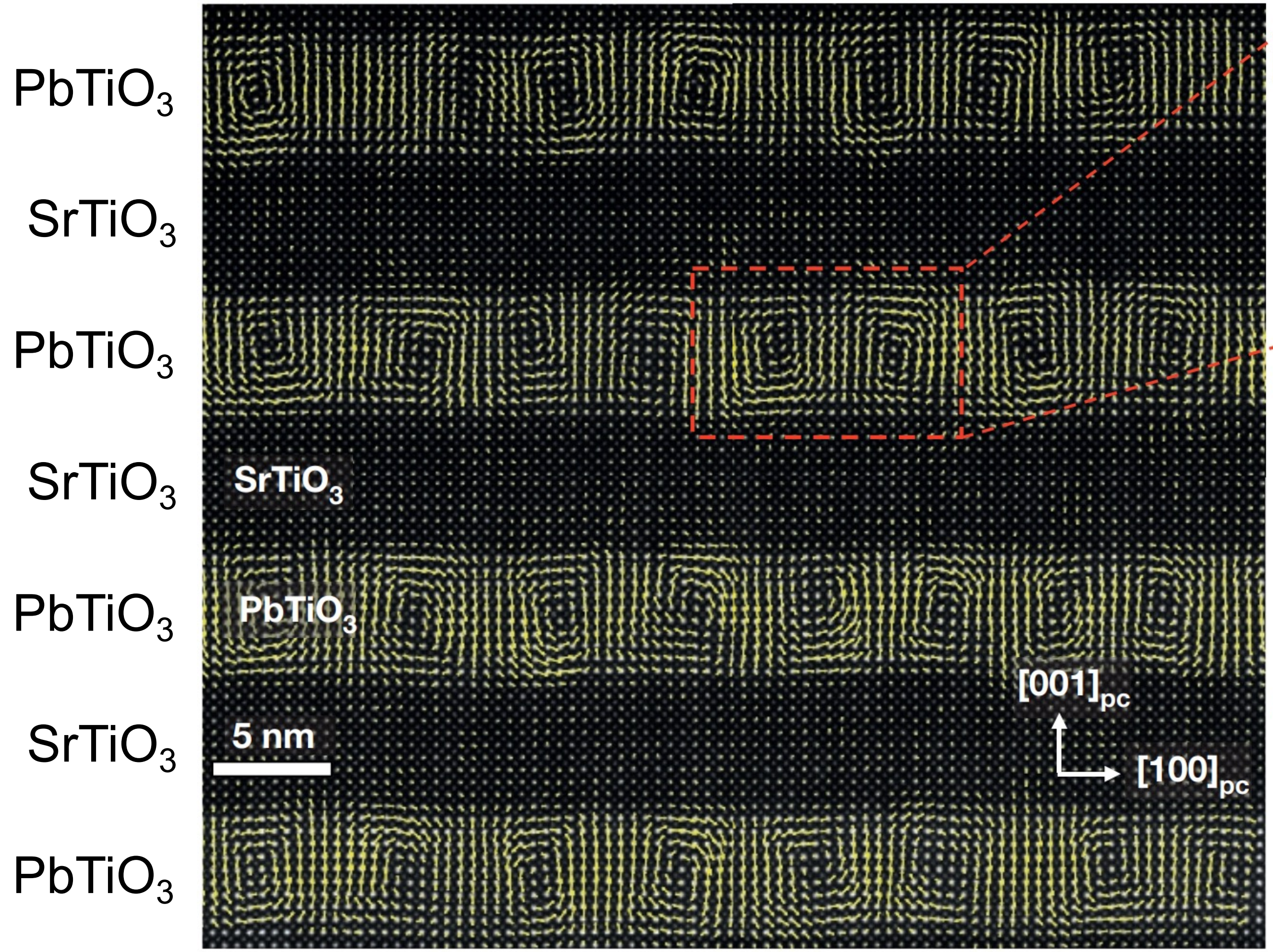
Deploying py4DSTEM into the Materials Project

- PR contribution accepted into crystal Toolkit repo, live “soon”



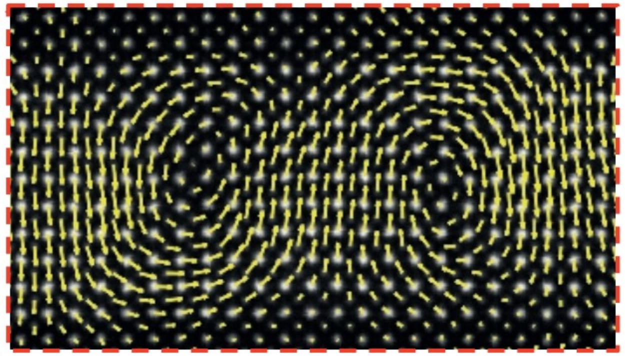
Vortex Structures in STO/PTO Superlattices

High angle annular dark field (HAADF) image



Multilayers grown on $SrRuO_3/DyScO_3$ substrate

vortex-antivortex pair

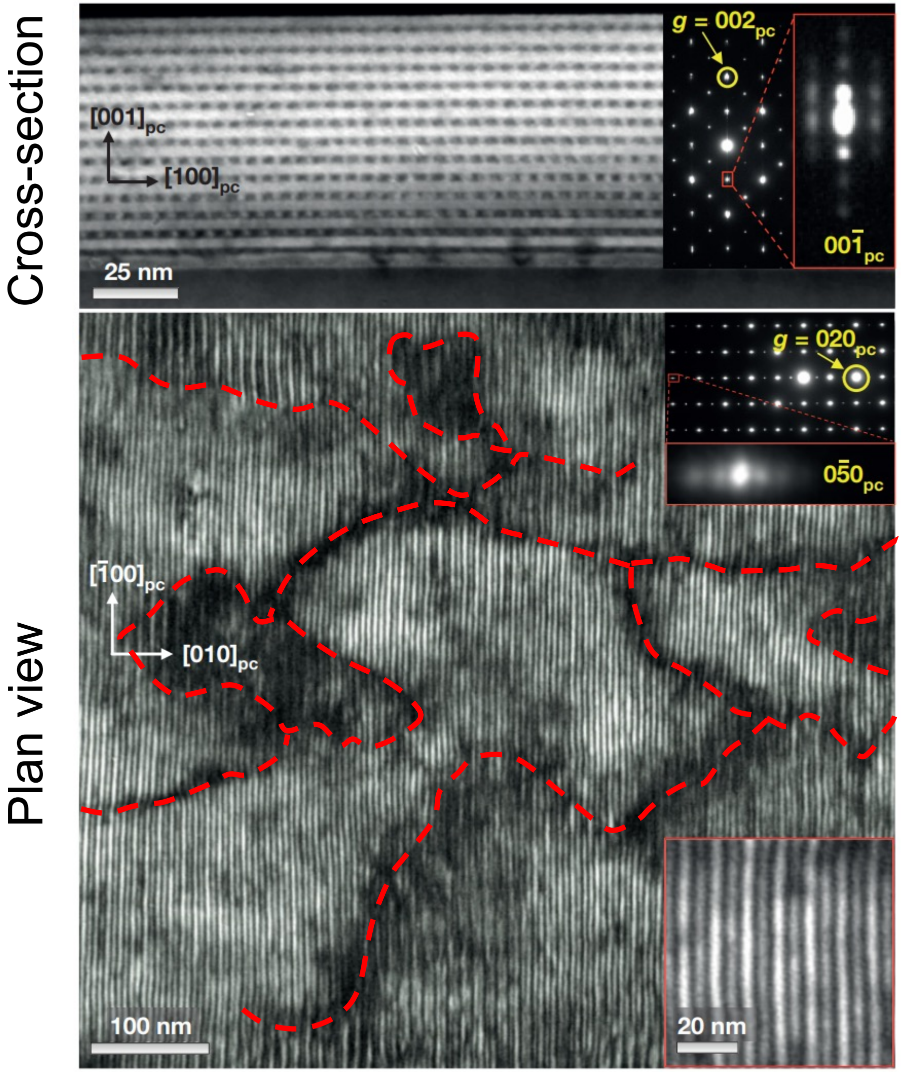


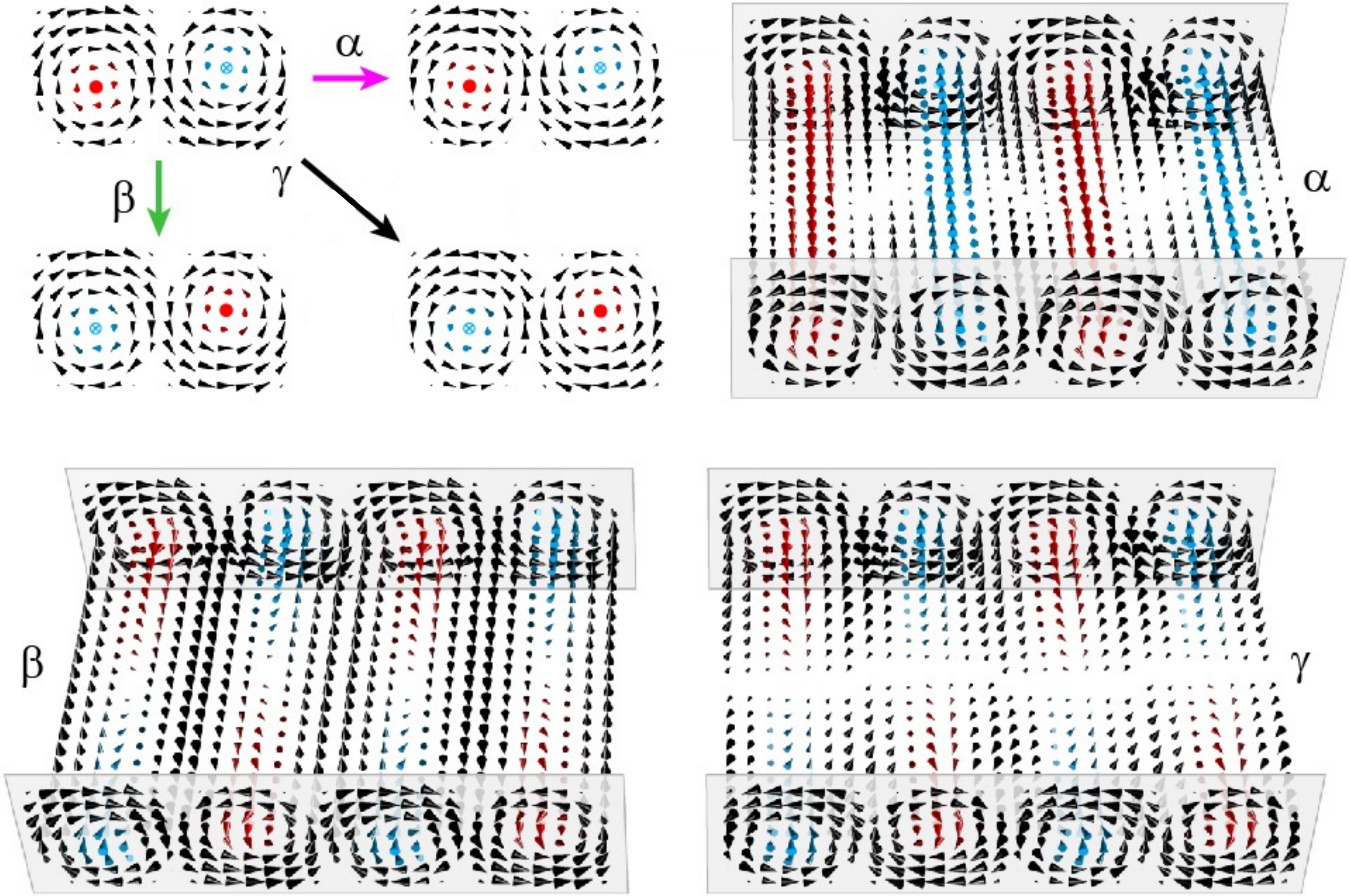
Polar displacements overlaid on HAADF image, from A sites.

AK Yadav*, CT Nelson*, *Observation of polar vortices in oxide superlattices*, **Nature 530**, 198 (2016)

Domain Wall Configuration of STO/PTO Layers

Dark field TEM





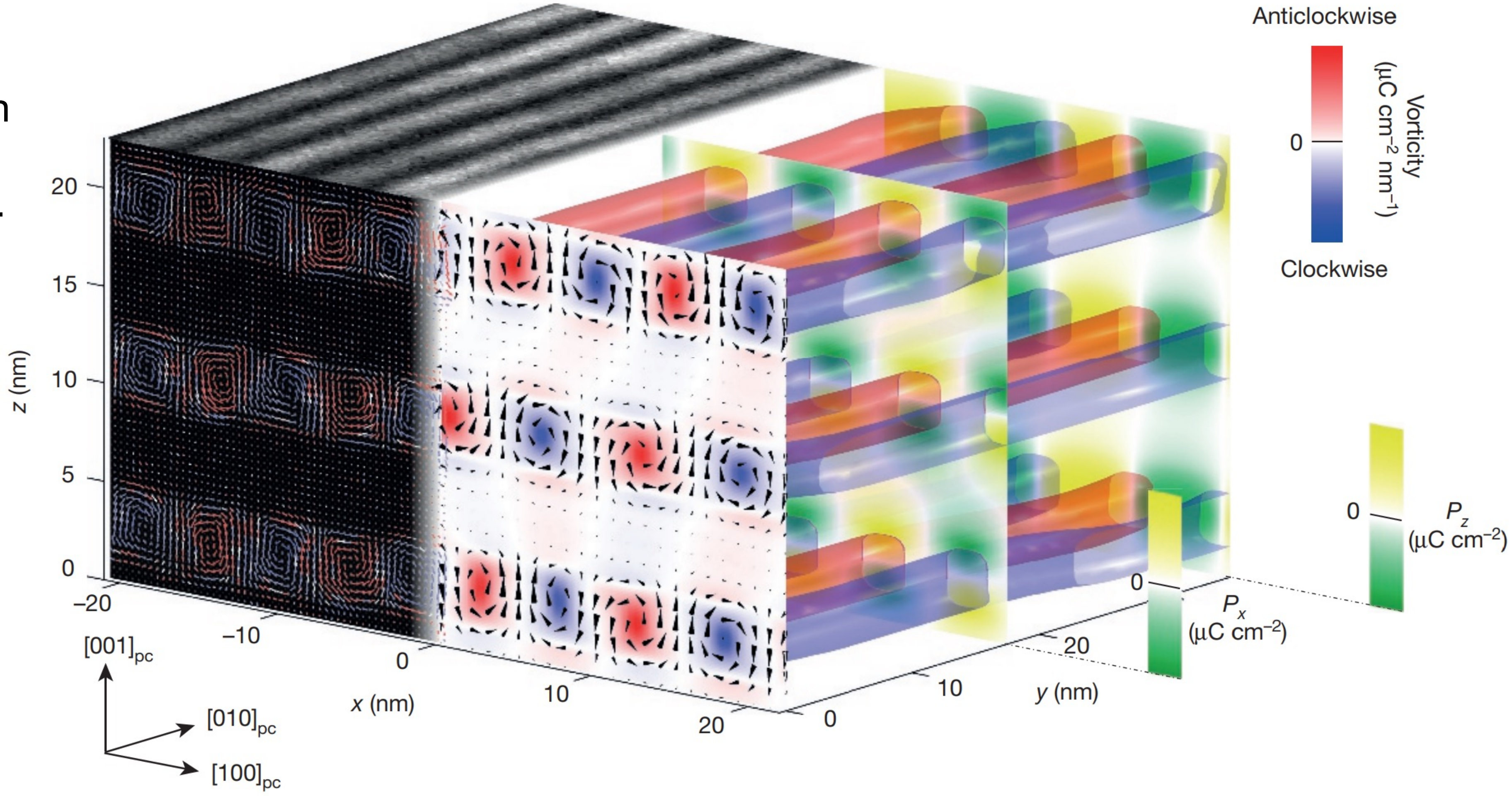
3D Vortex Structures in STO/PTO Superlattices

Large gradient energy of vortices is balanced by:

- Electrostatic energy reduction by removing polar **discontinuities** at interfaces.
- Elastic energy from with **epitaxial** constraints.

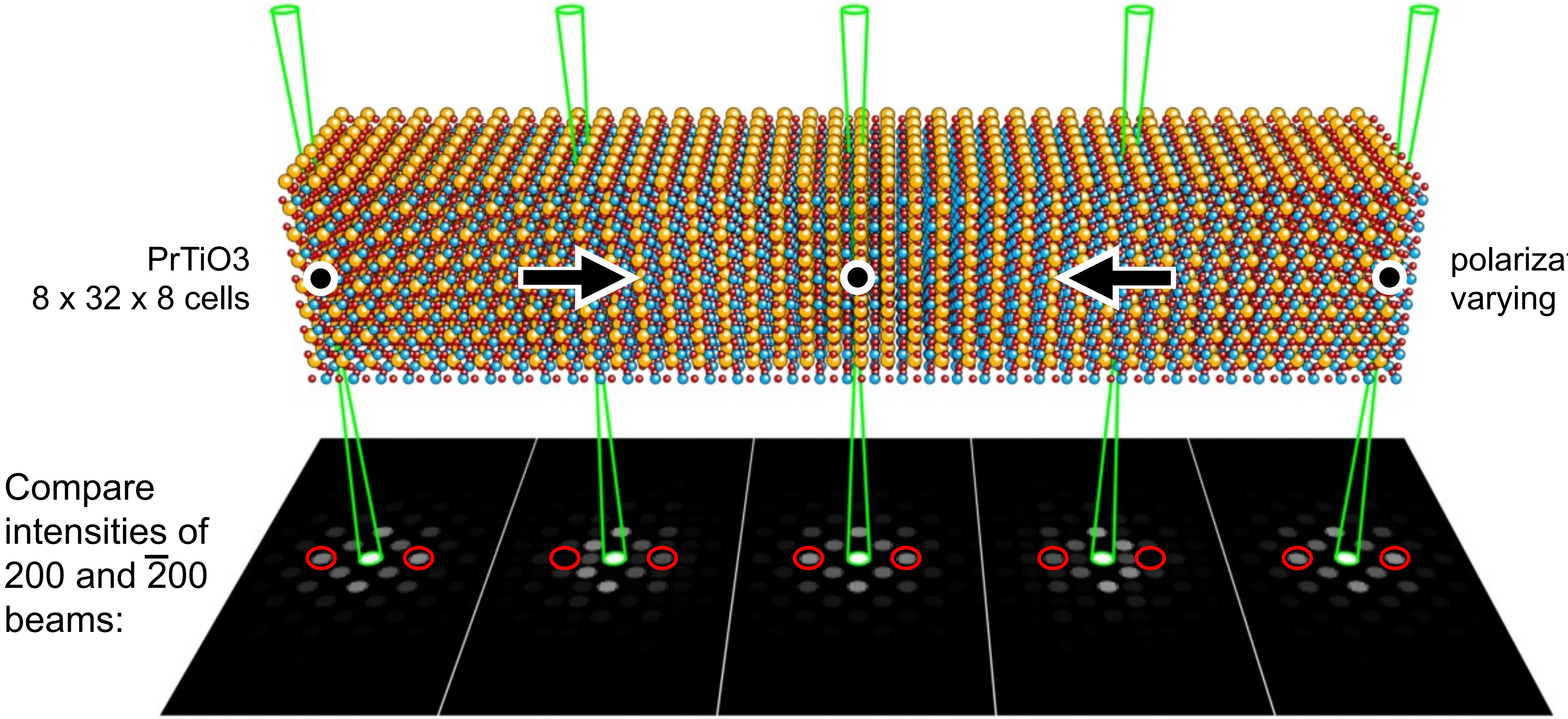
Open questions about vortex structure in 3D:

- Vertical [001] **asymmetry in position** of vortex cores?
- Non-zero **polarization** vectors along **vortex cores**?

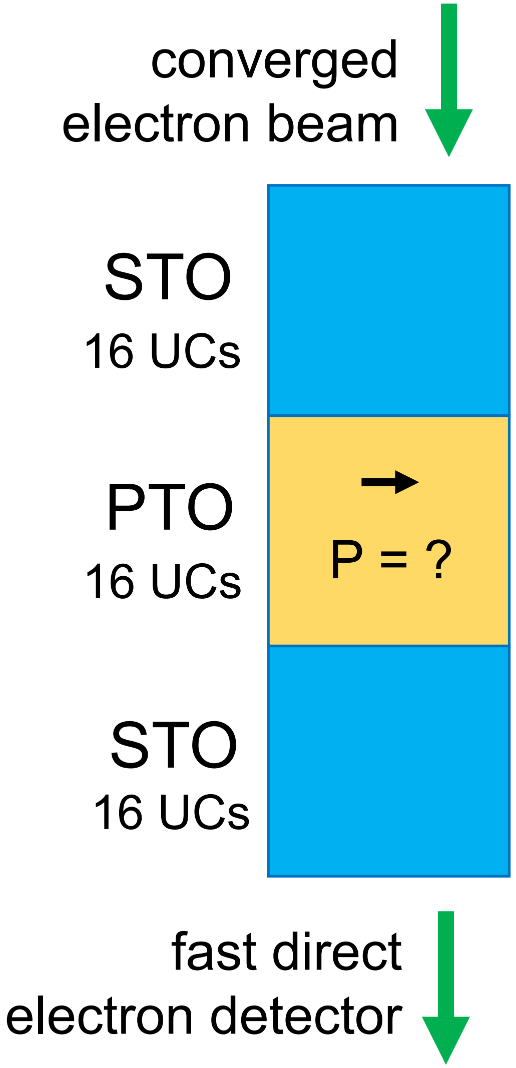


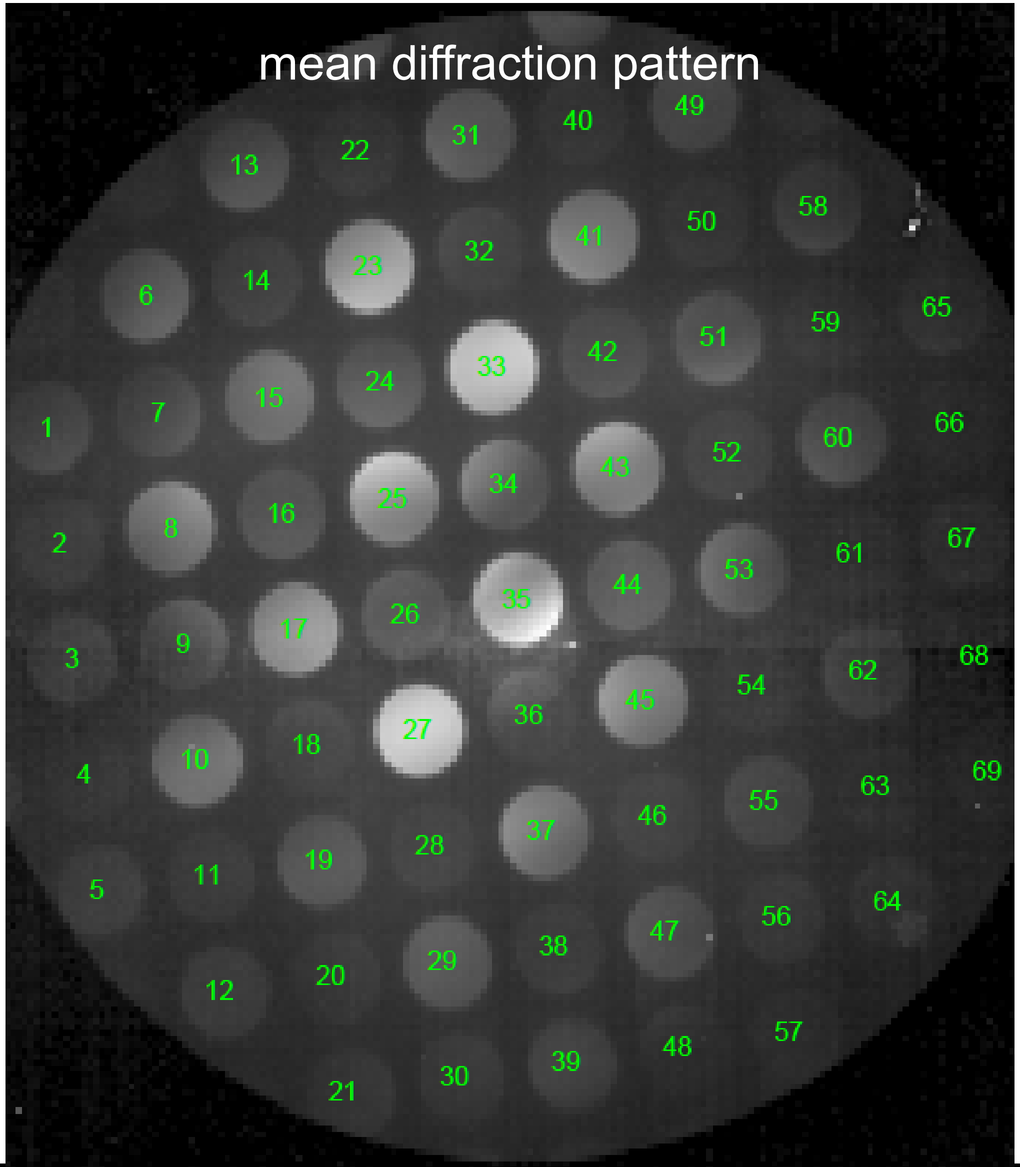
Atomic-resolution imaging uses 2D projections – difficult if structure varies along beam direction. **Alternatives?**

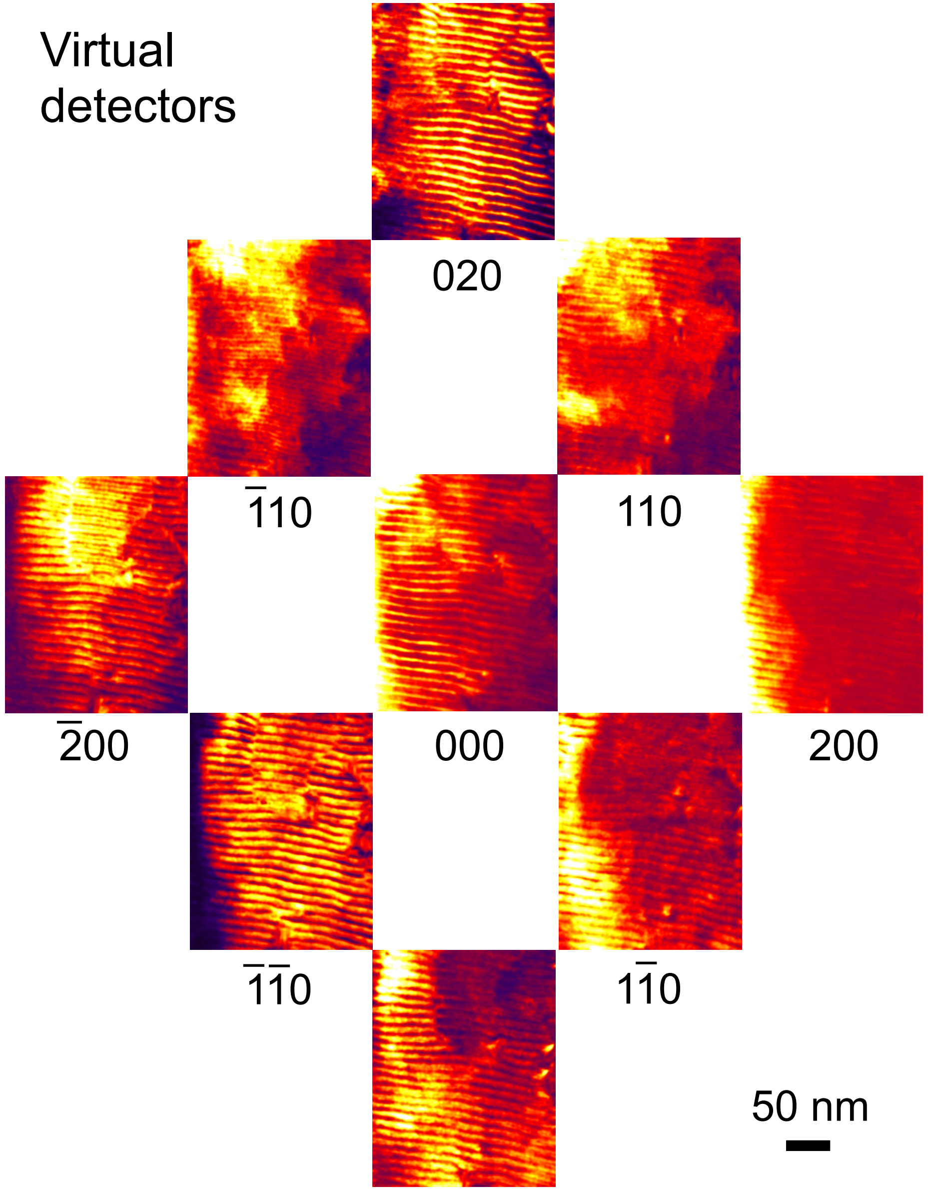
Measuring $PbTiO_3$ Polarization using 4D-STEM



STO/PTO/STO Multilayer – 4D-STEM Experiments







S Zeltmann et al., Ultramicroscopy 250, 113732 (2023).

$PbTiO_3$ Polarization with Dynamical Diffraction

4D-STEM measurements of intensities differences in **Friedel pairs** of Bragg disks works for **kinematical diffraction** (thin samples).

But what about **dynamical diffraction** (thick samples)?

Investigate with **Bloch wave** simulations:

$$\bar{\mathcal{A}}\mathcal{C} = 2k_n\gamma\mathcal{C}$$

Bloch wave coefficients ($\mathcal{C}$)

normal comp. wavevectors (γ)

structure matrix:

$$\bar{\mathcal{A}} = \begin{bmatrix} 0 & U_{-\mathbf{g}} & \cdots & U_{-\mathbf{h}} \\ U_{\mathbf{g}} & 2k_0 s_{\mathbf{g}} & \cdots & U_{\mathbf{g}-\mathbf{h}} \\ \vdots & \vdots & \ddots & \vdots \\ U_{\mathbf{h}} & U_{\mathbf{h}-\mathbf{g}} & \cdots & 2k_0 s_{\mathbf{h}} \end{bmatrix}$$

electron wave at depth *z* in sample:

$$\Psi(z) = \mathcal{C}\mathcal{E}(z)\mathcal{C}^{-1}\Psi(0)$$

where:

$$\mathcal{E}(z) = \mathrm{e}^{2\pi \mathrm{i}\gamma^{(j)}z}\delta_{ij}$$

Scattering matrix (**S-matrix**)

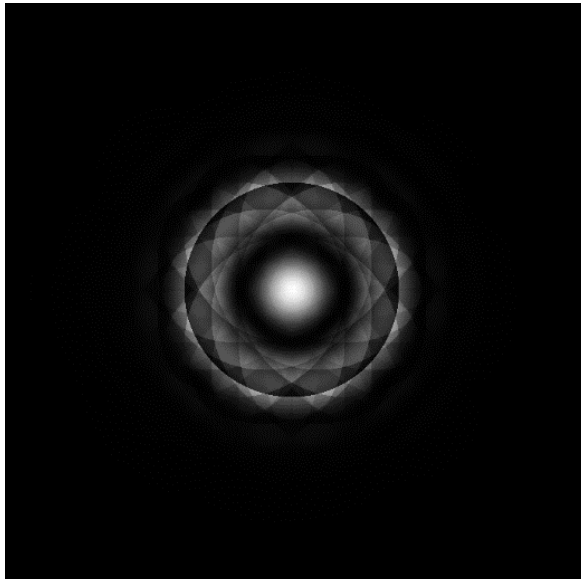
Simulating multilayers with an **S-matrix** is straightforward: $\mathcal{S} = \mathcal{S}_{\mathrm{STO}}\,\mathcal{S}_{\mathrm{PTO}}\,\mathcal{S}_{\mathrm{STO}}$

What is a Scattering Matrix?

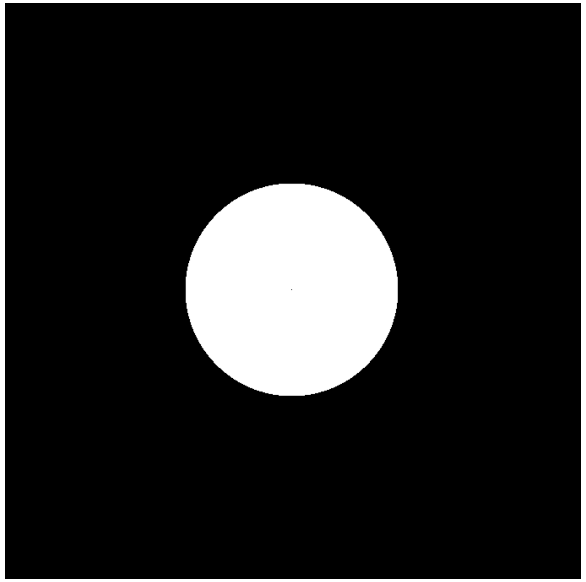
Probe at exit surface **Initial probe**

$$\Psi(x,y,z) = \exp\left\{\int_0^z \left[i\sigma V(x,y,z) + \frac{i\lambda}{4\pi}\nabla_{x,y}{}^2\right]\right\}\Psi(x,y,0)$$

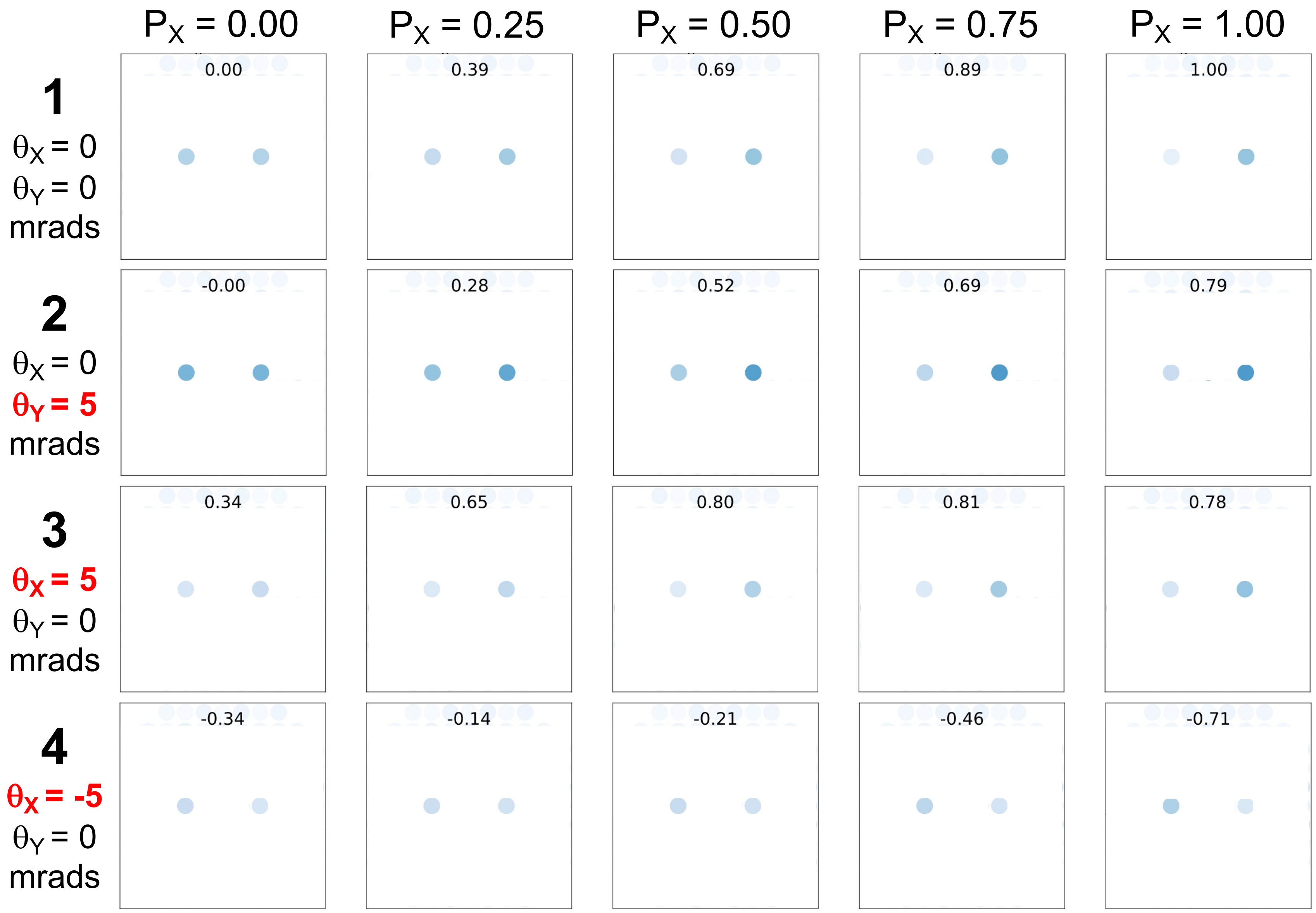
S



$$= \begin{bmatrix} S_{\mathbf{g}_1,\mathbf{g}_1} & S_{\mathbf{g}_1,\mathbf{g}_2} & \cdots & S_{\mathbf{g}_1,\mathbf{g}_n} \\ S_{\mathbf{g}_2,\mathbf{g}_1} & S_{\mathbf{g}_2,\mathbf{g}_2} & \cdots & S_{\mathbf{g}_2,\mathbf{g}_n} \\ \vdots & \vdots & \ddots & \vdots \\ S_{\mathbf{g}_n,\mathbf{g}_1} & S_{\mathbf{g}_n,\mathbf{g}_2} & \cdots & S_{\mathbf{g}_n,\mathbf{g}_n} \end{bmatrix}$$



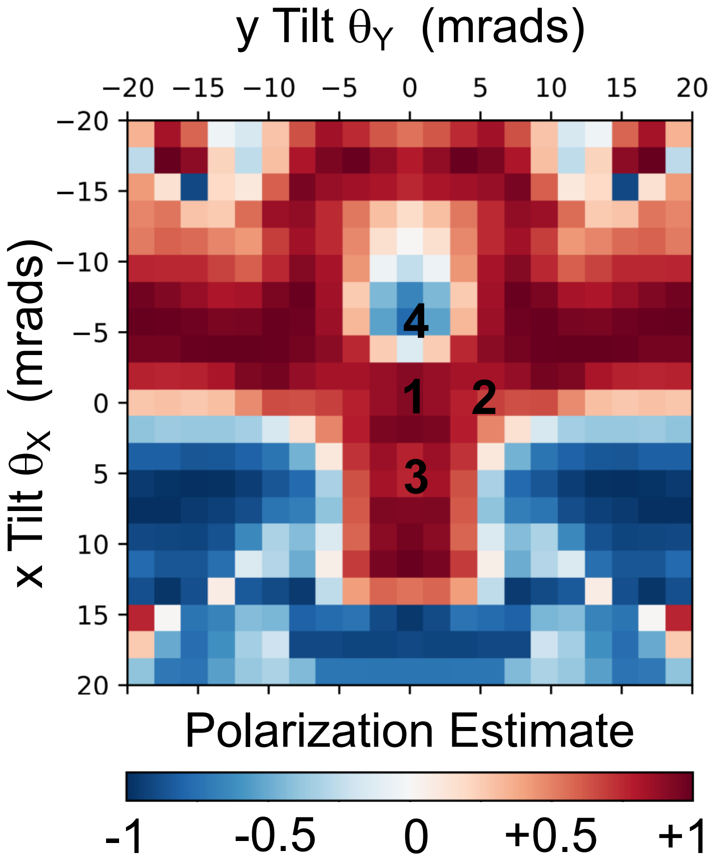
PTO Polarization in 16/16/16 STO/PTO/STO



→ polarization vector

$$P_X = \frac{I_{200} - I_{\bar{2}00}}{I_{200} + I_{\bar{2}00}}$$

polarization estimate
(inset, normalized to P_X=1)



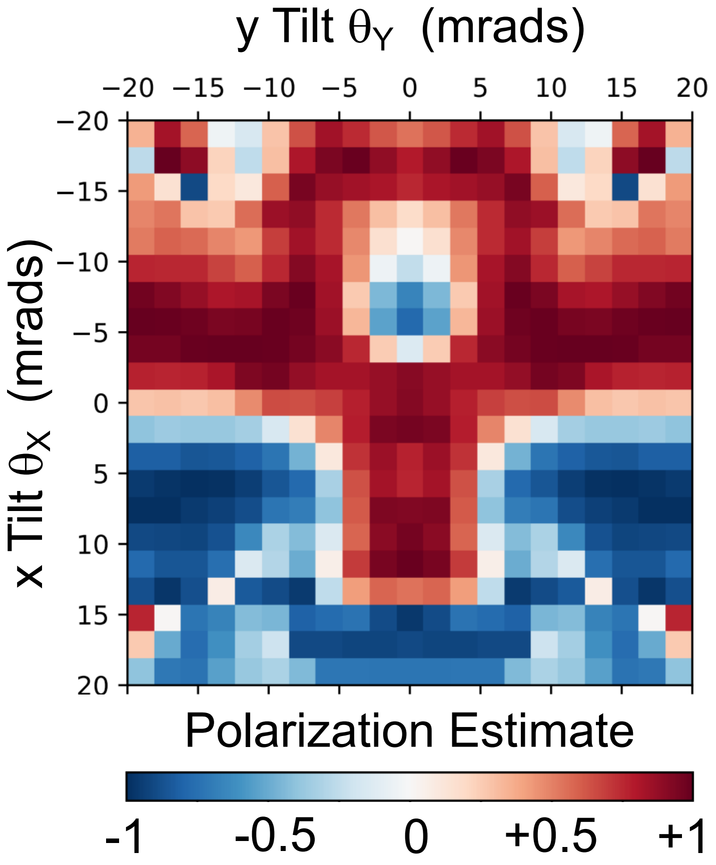
S Zeltmann et al., Ultramicroscopy 250, 113732 (2023).

PTO Polarization in 16/16/16 STO/PTO/STO

Under dynamical diffraction conditions, **tilt** and **polarization** are **not orthogonal**.

Multiple scattering leads to complex nonlinear intensity response, contrast decrease, even **contrast reversals**.

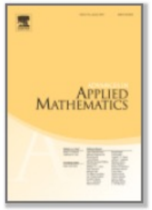
How can we measure **polarization** in complex structures, locally tilted, **thick samples**?



Flexible Inversion of Dynamical Scattering Data

ELSEVIER

Advances in Applied Mathematics



Volume 16, Issue 3, September 1995, Pages 321-375

Regular Article

Derivatives of the Matrix Exponential and Their Computation

Najfeld, I., Havel, T.F.

$$D_{\boldsymbol{V}}(t, \boldsymbol{A}) \equiv \lim_{h \to 0} \frac{1}{h}\left(e^{t(\boldsymbol{A}+h\boldsymbol{V})} - e^{t\boldsymbol{A}}\right)$$

Directional **derivative** of matrix exponential.

$$D_{\boldsymbol{V}}(t, \boldsymbol{A}) = \boldsymbol{U}\left(\left(\boldsymbol{U}^{-1}\boldsymbol{V}\boldsymbol{U}\right) \odot \boldsymbol{\Phi}(t)\right)\boldsymbol{U}^{-1}$$

Derivative of matrix after **spectral decomposition**.

where $$\Phi_{ij}(t) = \begin{cases} (e^{t\lambda_i} - e^{t\lambda_j})/(\lambda_i - \lambda_j) & \text{if } \lambda_i \neq \lambda_j \\ t e^{t\lambda_i} & \text{if } \lambda_i = \lambda_j \end{cases}$$

$$\frac{d\mathcal{S}}{d\theta} = \sum_i^N \left[\prod_{j=0}^{j=i-1} \mathcal{S}^{(j)} \cdot \frac{d\mathcal{S}^{(i)}}{d\theta} \cdot \prod_{k=i+1}^{k=N} \mathcal{S}^{(k)}\right]$$

Product rule for **multiple S-matrices**

Sample **tilt** derivatives

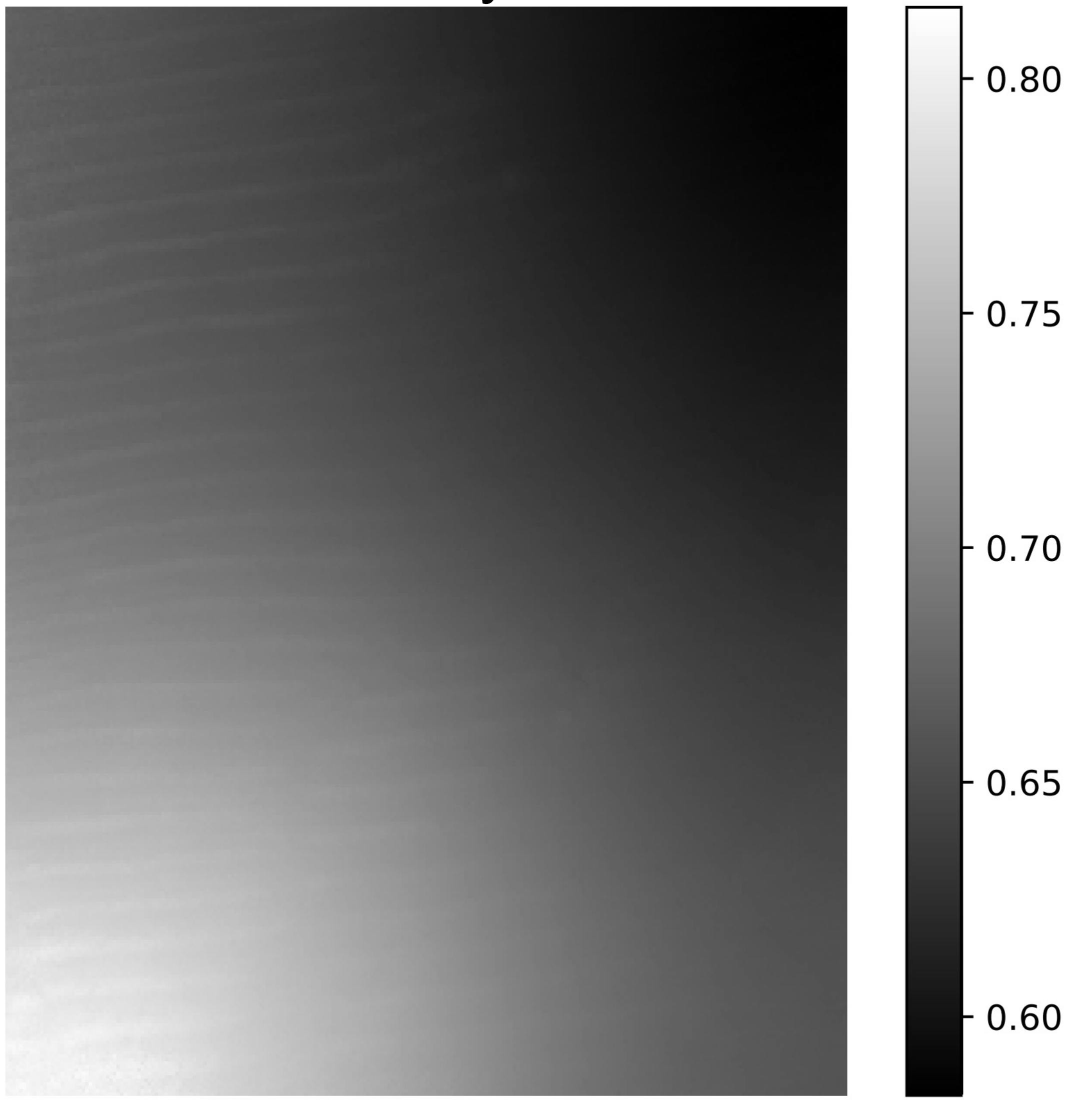
$$\frac{ds_{\boldsymbol{g}}}{dk_{\{x,y\}}} = -\frac{g_{\{x,y\}}}{|\boldsymbol{g} + \boldsymbol{k_0}|} + \frac{(g_{\{x,y\}} + k_{\{x,y\}})(\boldsymbol{g} \cdot (2\boldsymbol{k} + \boldsymbol{g}))}{2|\boldsymbol{g} + \boldsymbol{k}|^3}$$

Sample **polarization** derivatives

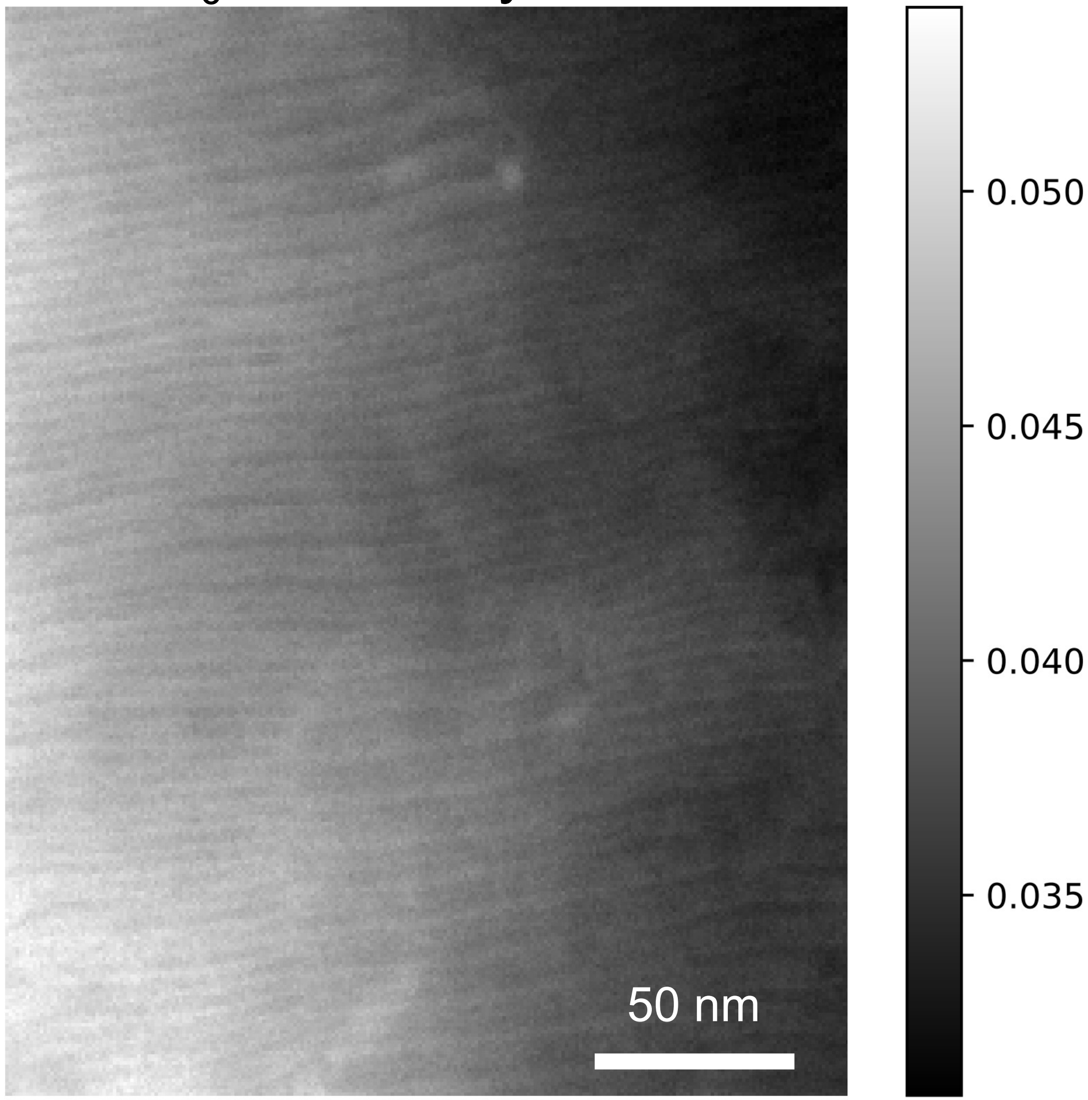
$$\frac{dU_{\boldsymbol{g}}}{d\rho_a} = \frac{1}{\Omega}\sum_j 2\pi i f_e^{(j)}(\boldsymbol{g} \cdot \delta\boldsymbol{r}_a) e^{2\pi i((\boldsymbol{r}^{(j)} + \rho_a \delta\boldsymbol{r}_a^{(j)} + \rho_b \delta\boldsymbol{r}_b^{(j)}) \cdot \boldsymbol{g})}$$

Preliminary 16/16/16 STO/PTO/SRO Inversion

ΔI – intensity scale

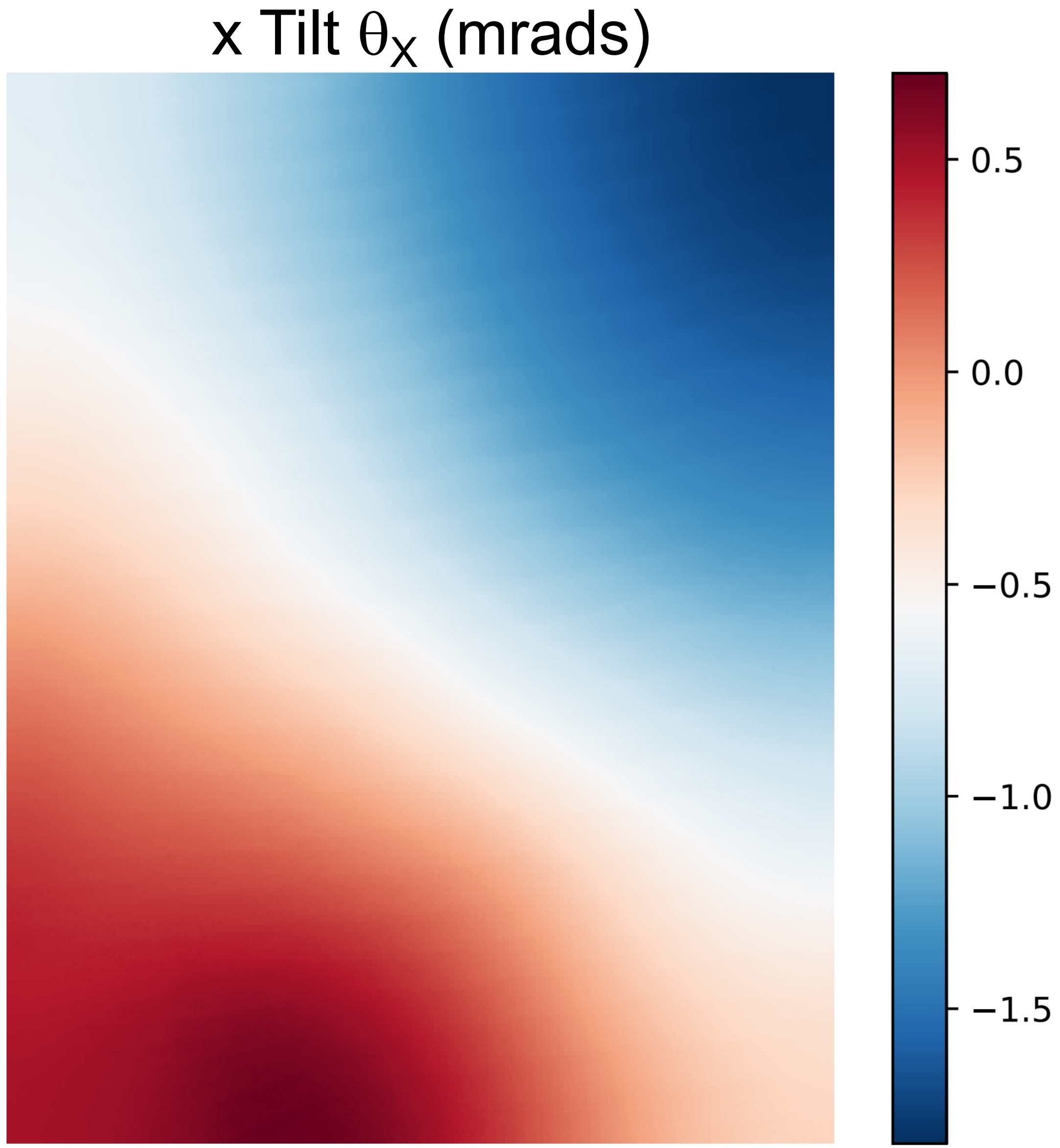


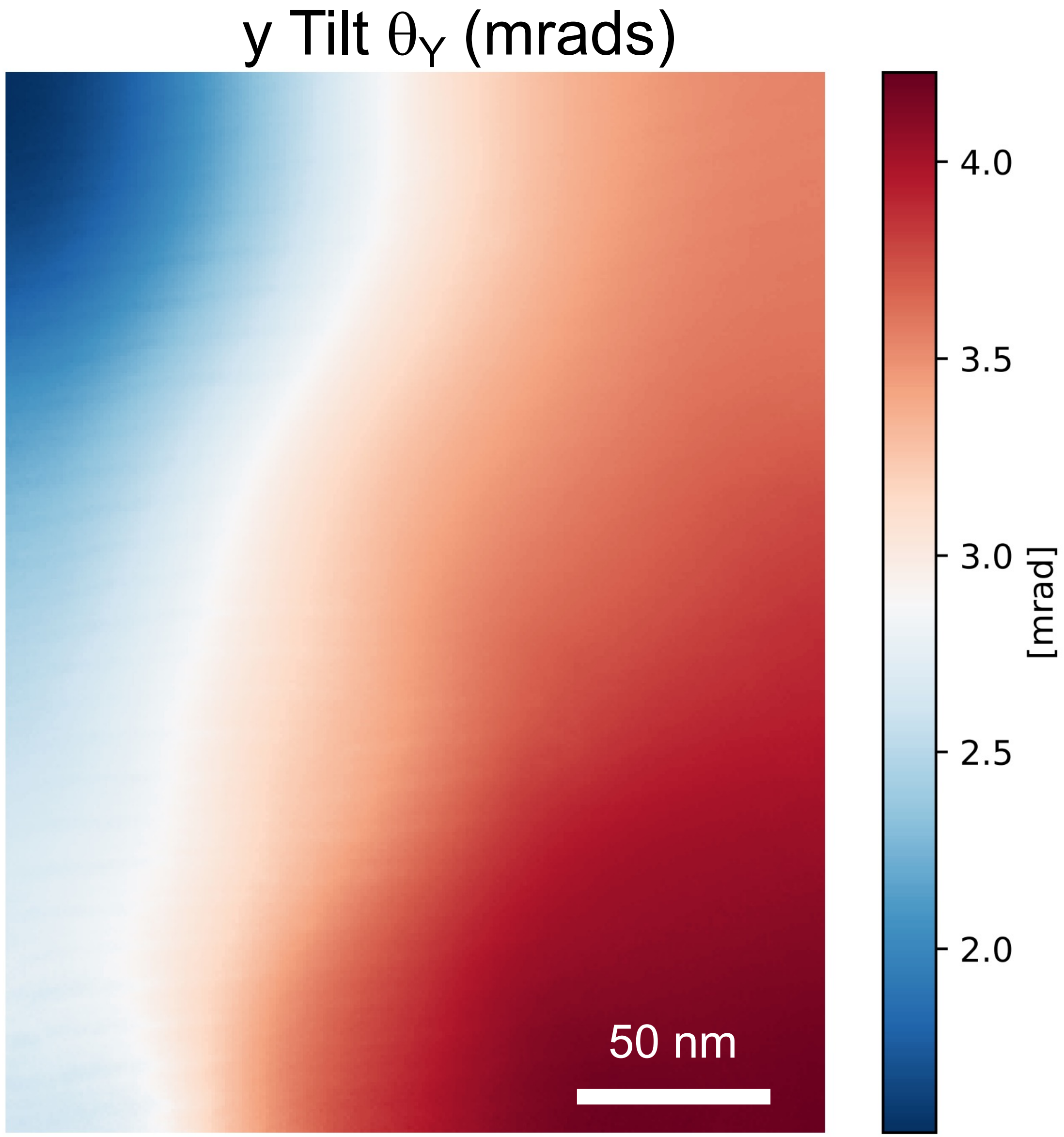
I_0 – intensity offset



S Zeltmann et al., Ultramicroscopy 250, 113732 (2023).

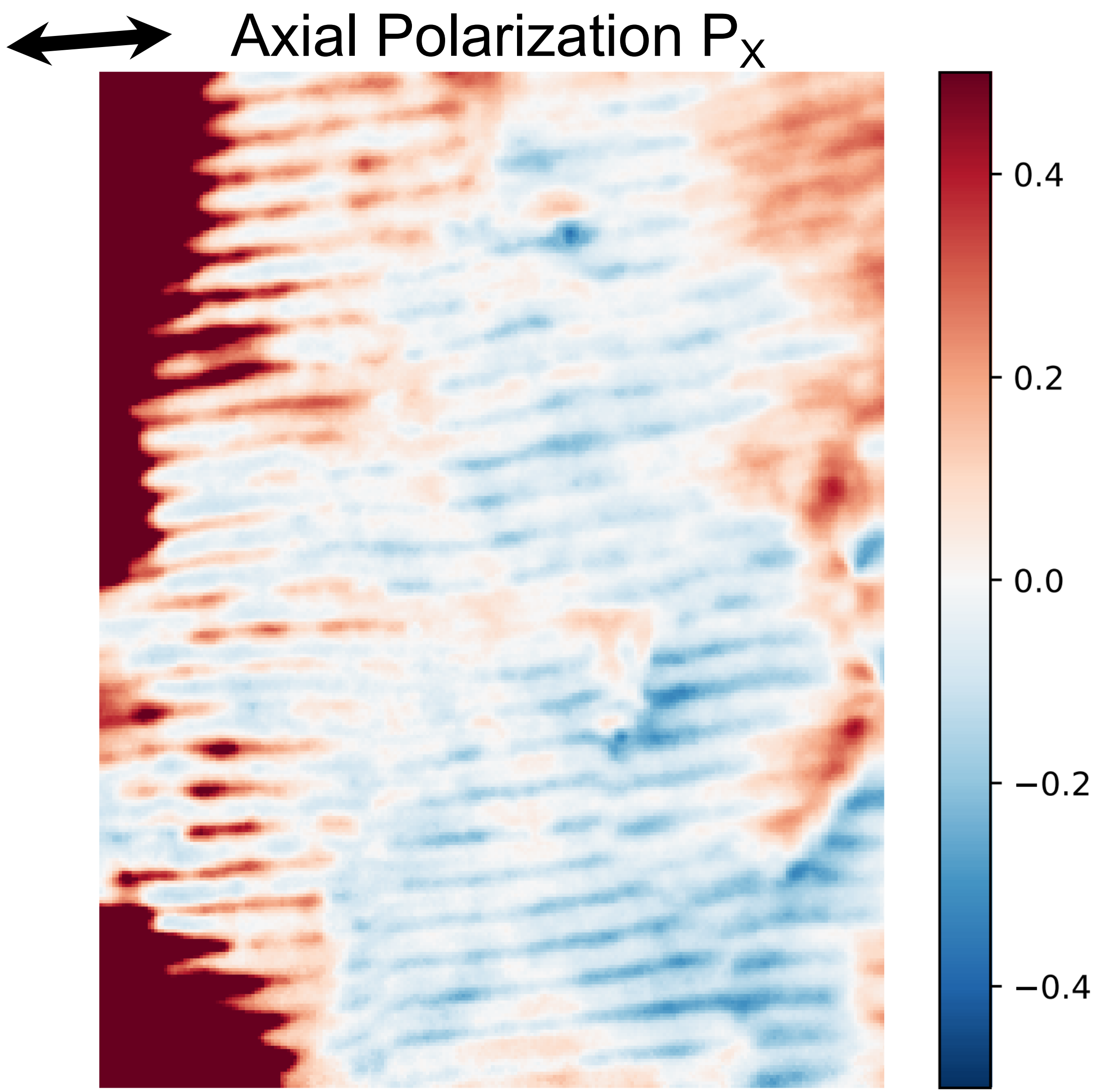
Preliminary 16/16/16 STO/PTO/SRO Inversion

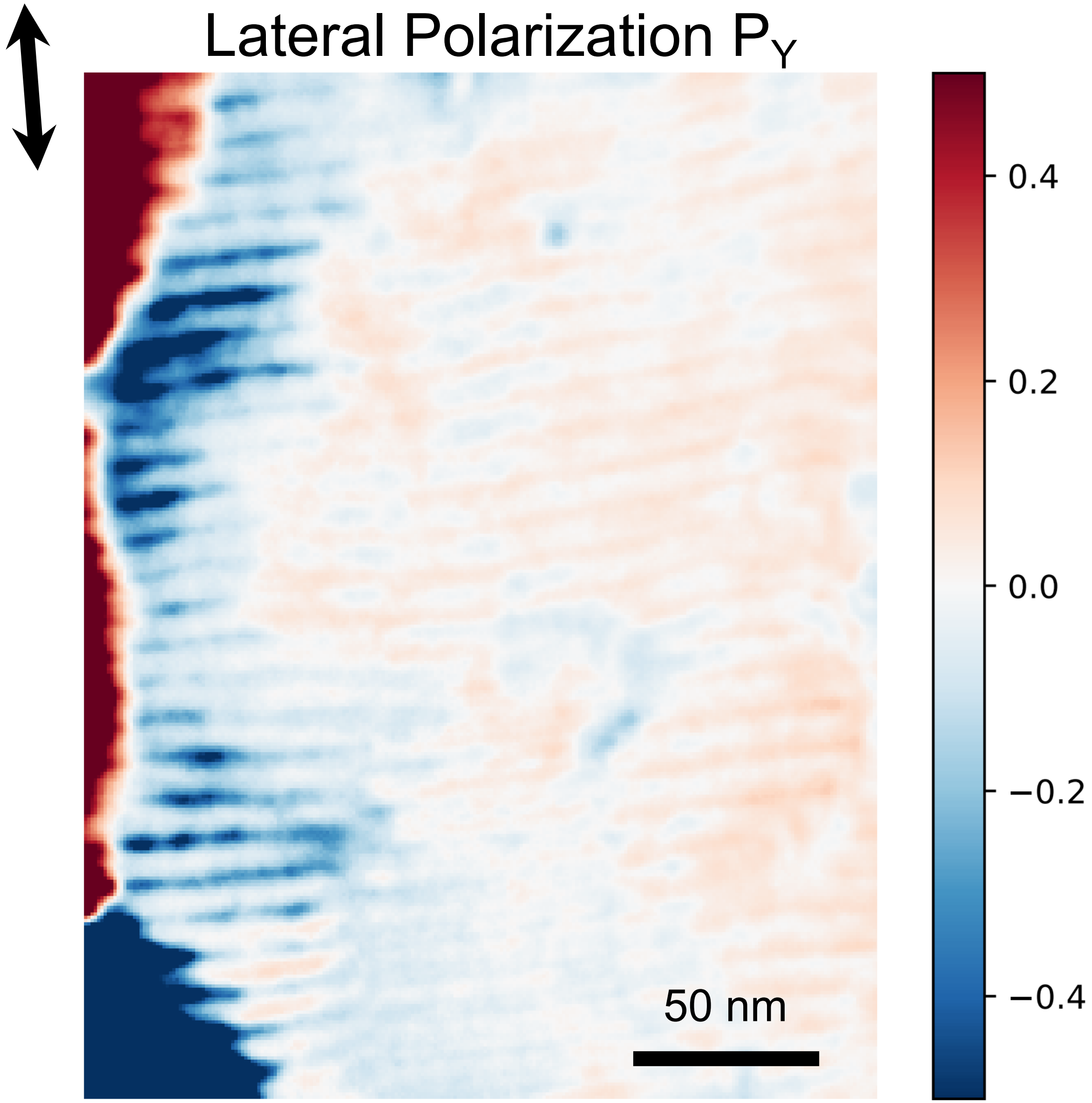




S Zeltmann et al., Ultramicroscopy 250, 113732 (2023).

Preliminary 16/16/16 STO/PTO/SRO Inversion

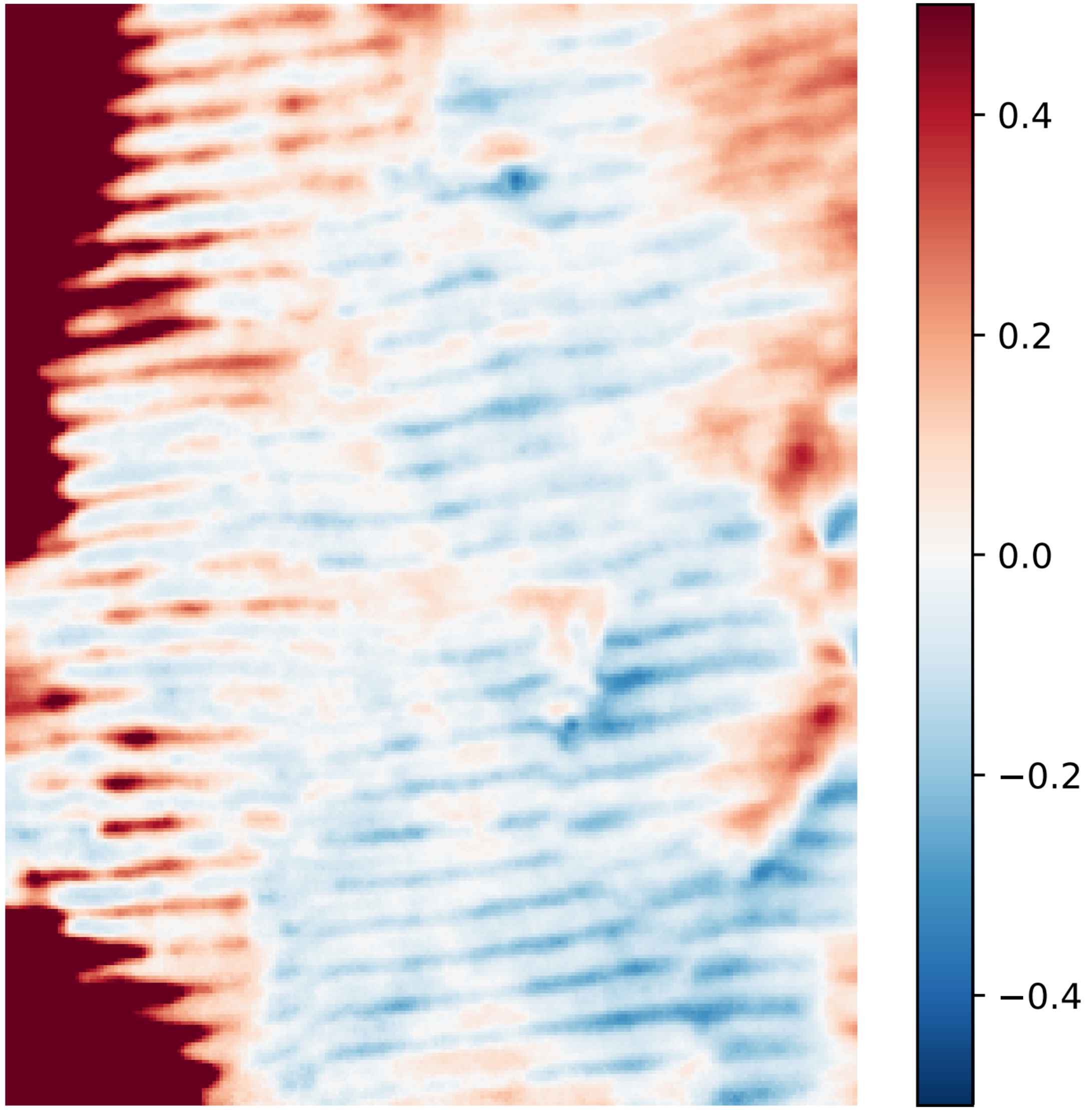




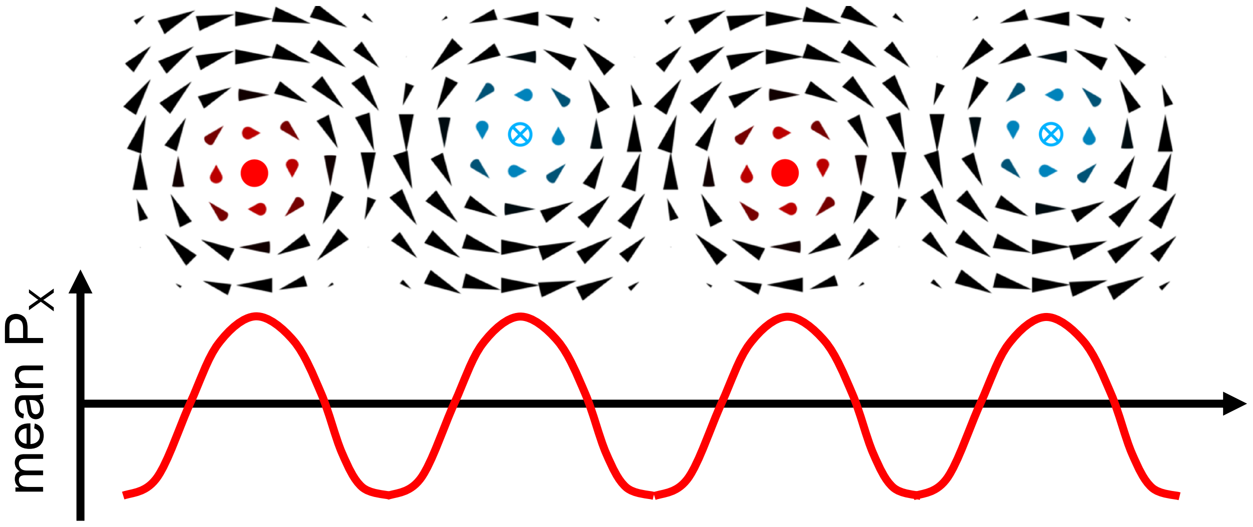
S Zeltmann et al., Ultramicroscopy 250, 113732 (2023).

Preliminary 16/16/16 STO/PTO/SRO Inversion

Axial Polarization P_X

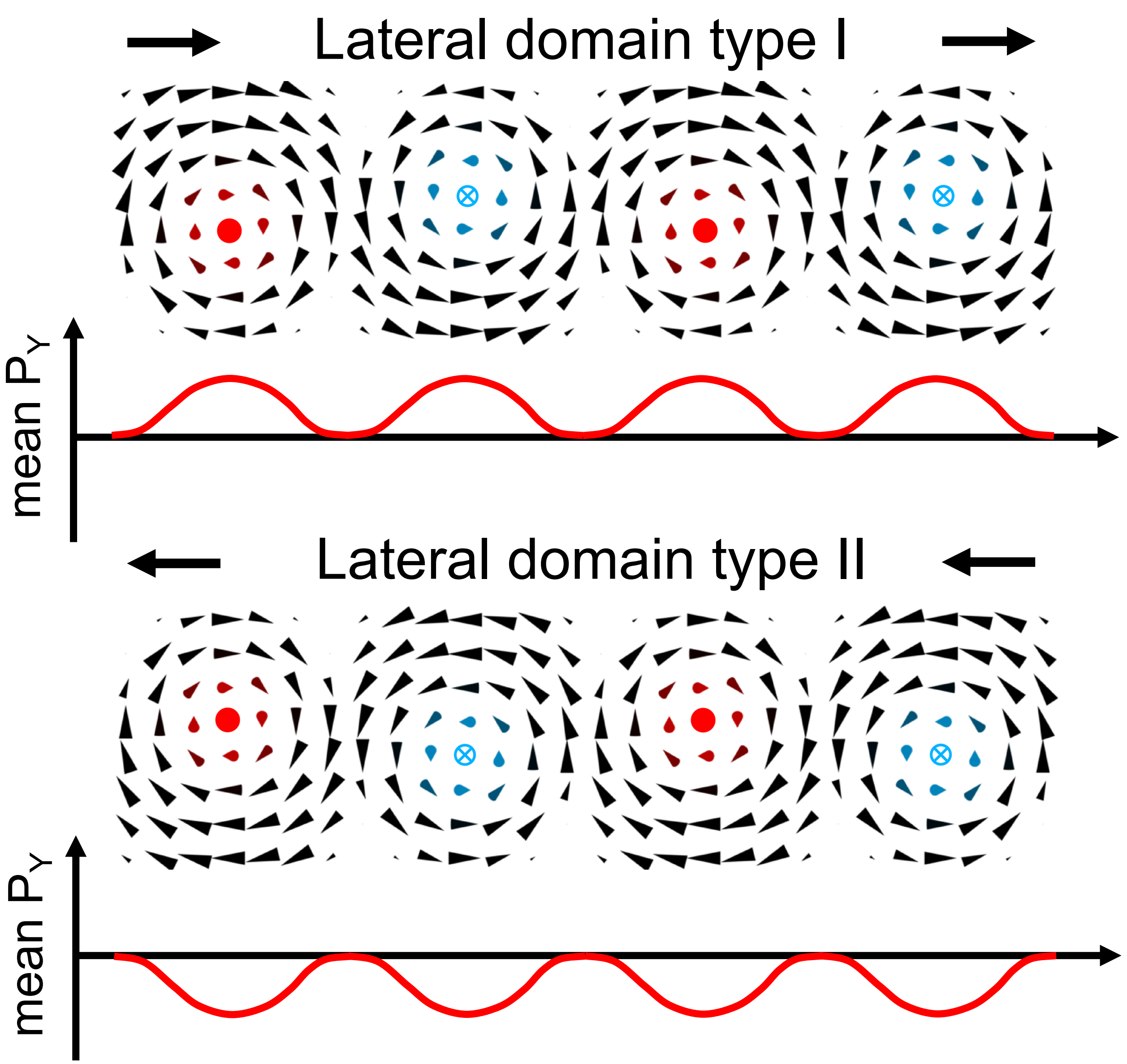


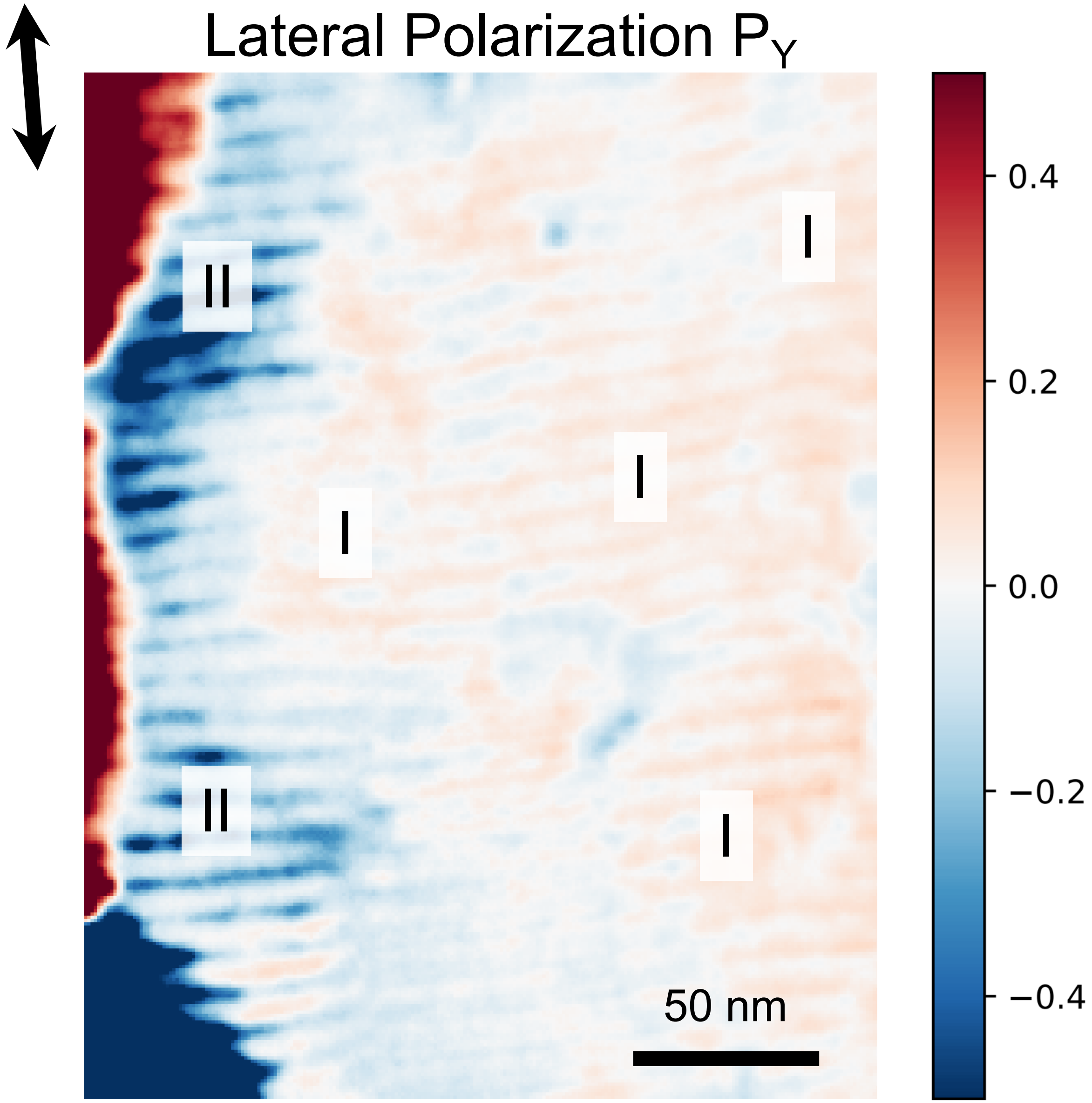
Axial Polarization – expected to alternate



- Oscillating behavior observed everywhere.
- However, many domains show net polarization in one direction.
- Need a more complex 3D model of P?

Preliminary 16/16/16 STO/PTO/SRO Inversion





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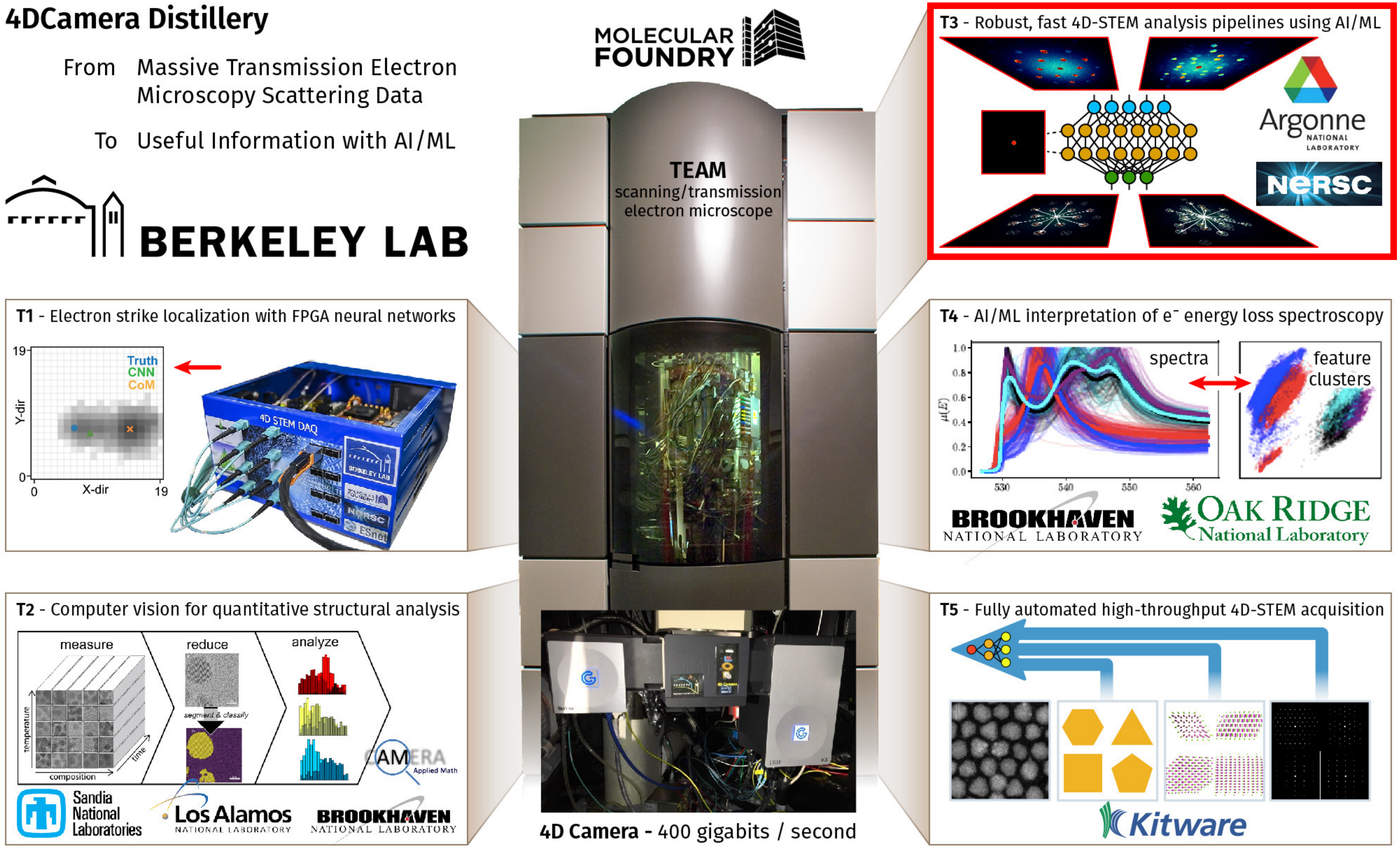
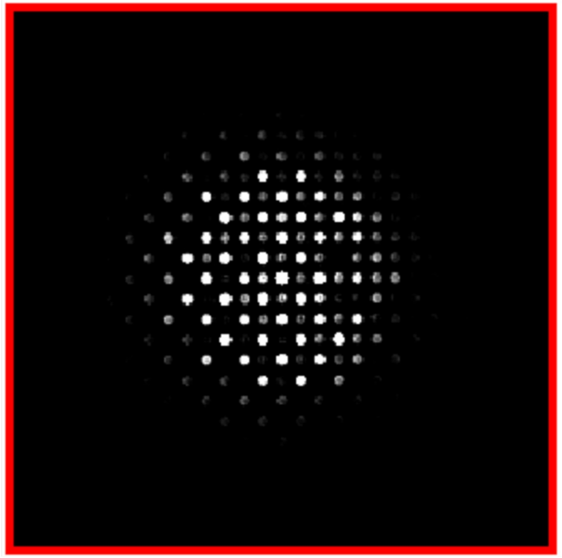
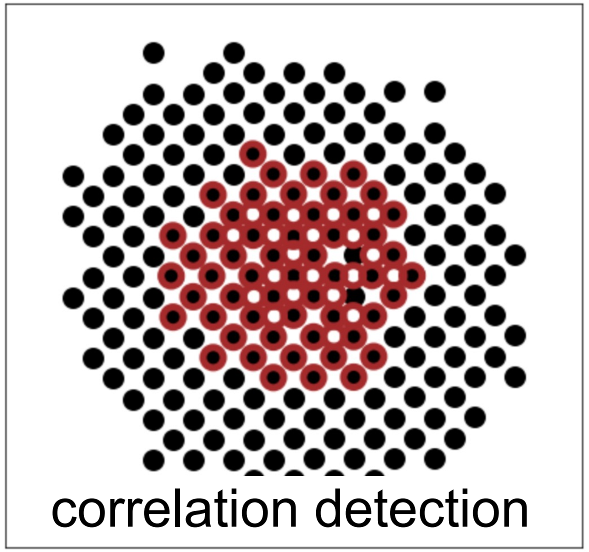

4DCamera Distillery
From Massive Transmission Electron Microscopy Scattering Data
To Useful Information with AI/ML
BERKELEY LAB
MOLECULAR FOUNDRY
TEAM
scanning/transmission electron microscope
T3 - Robust, fast 4D-STEM analysis pipelines using AI/ML
Argonne NATIONAL LABORATORY
NERSC
T1 - Electron strike localization with FPGA neural networks
Truth
CNN
CoM
Y-dir
X-dir
19
0
4D STEM DAQ
T4 - AI/ML interpretation of e⁻ energy loss spectroscopy
spectra
feature clusters
μ(E)
1.0
0.8
0.6
0.4
0.2
0.0
530
540
550
560
BROOKHAVEN NATIONAL LABORATORY
OAK RIDGE National Laboratory
T2 - Computer vision for quantitative structural analysis
measure
reduce
analyze
segment & classify
temperature
composition
time
CAMERA
Applied Math
Sandia National Laboratories
Los Alamos NATIONAL LABORATORY
BROOKHAVEN NATIONAL LABORATORY
4D Camera - 400 gigabits / second
T5 - Fully automated high-throughput 4D-STEM acquisition
Kitware

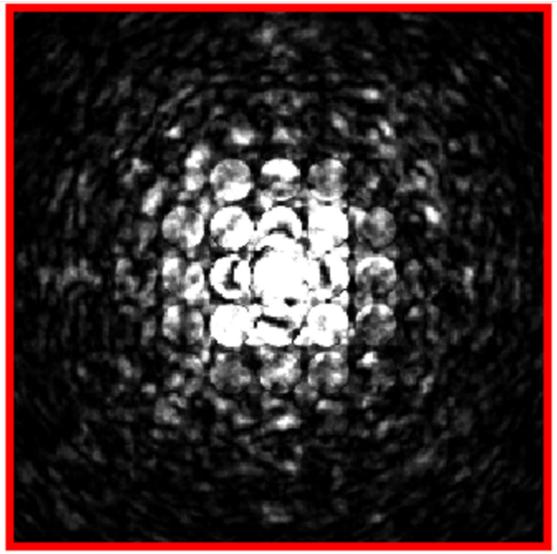
Dynamical Diffraction Complicates Disk Detection

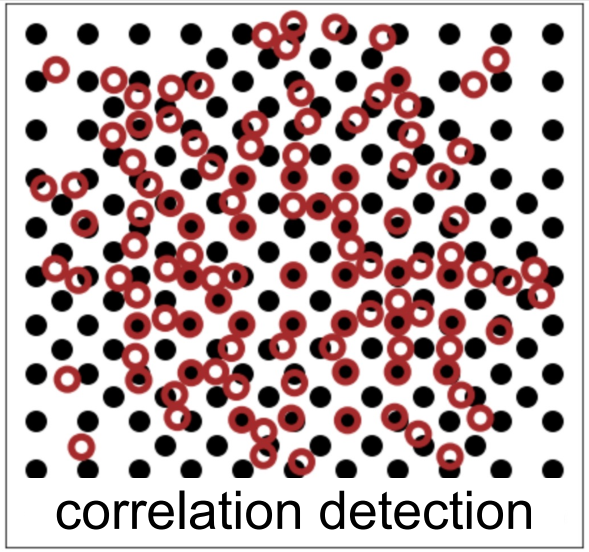
Diffraction pattern from using small convergence angle, thin sample





Diffraction pattern from using large convergence angle, thick sample





Can machine learning methods help us when our conventional image analysis pipelines fail?

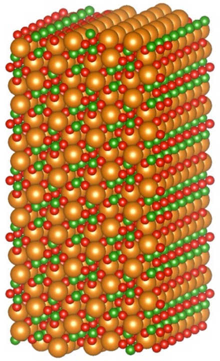
J Munshi*, A Rakowski*, et al., npj computational materials 8, 254 (2022)

Simulation Pipeline Infrastructure

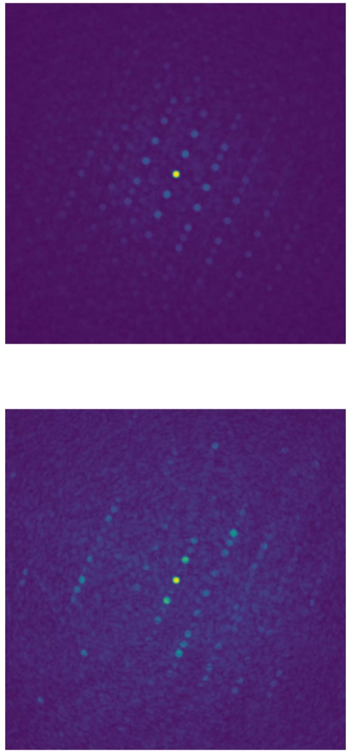
4D-SCRAPE & Manipulatt

The Materials Project
materialsproject.org

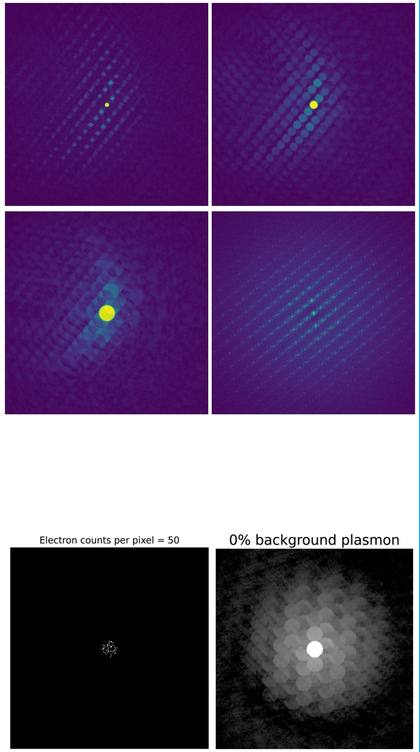
AFLOW
Automatic - FLOW for Materials Discovery



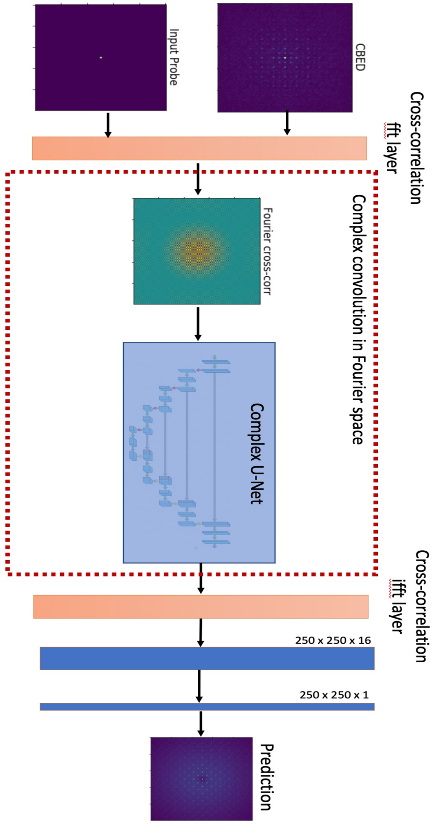
4D-MAKE



4D-PREP



4D-OPTIMIZE

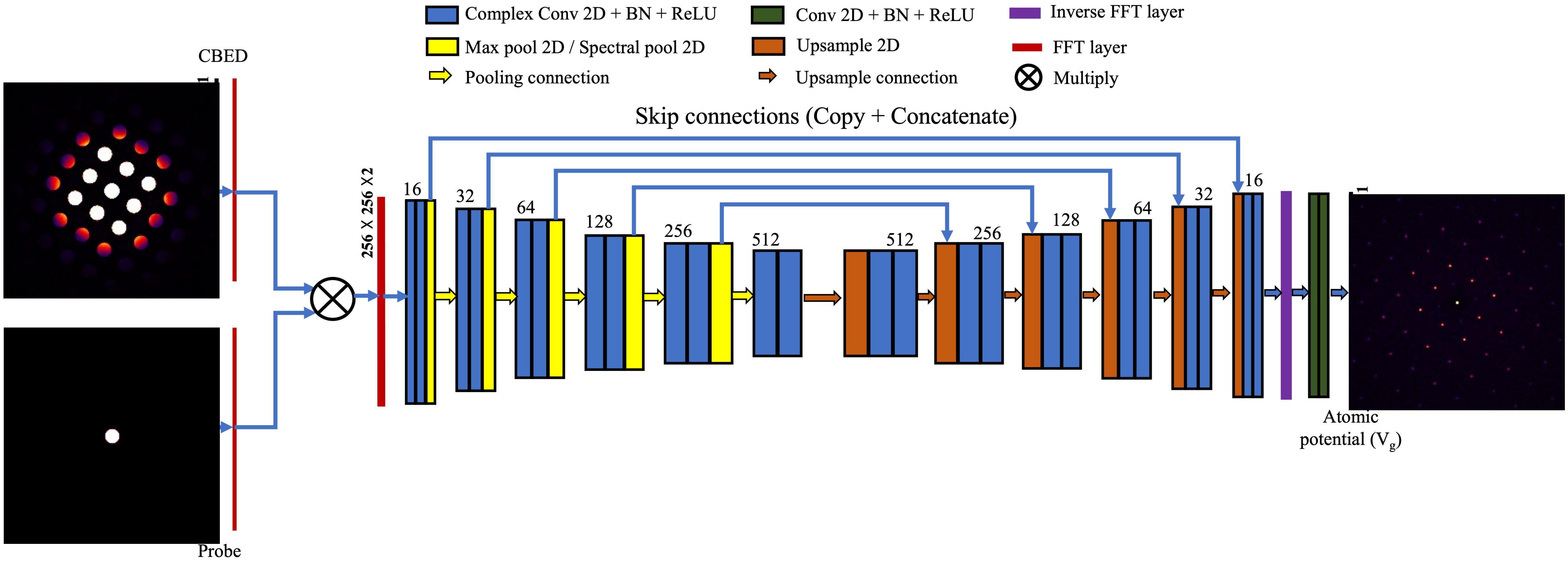


Many open source software tools used:

py4DSTEM
RAPIDS
DASK
SHIFTER
HOROVOD
TensorFlow
tune

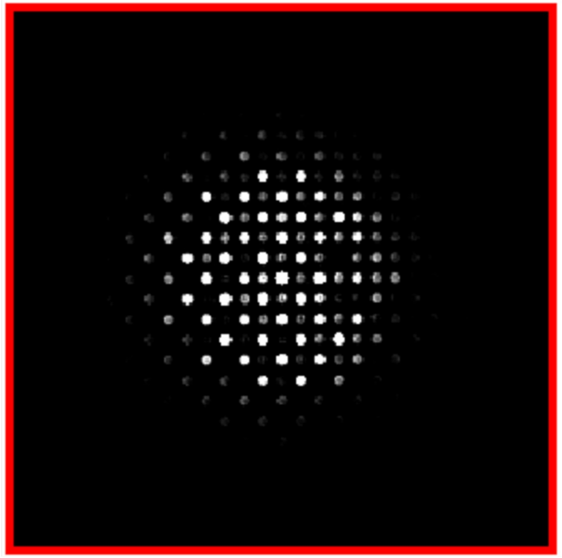
J Munshi*, A Rakowski*, et al., npj computational materials 8, 254 (2022)

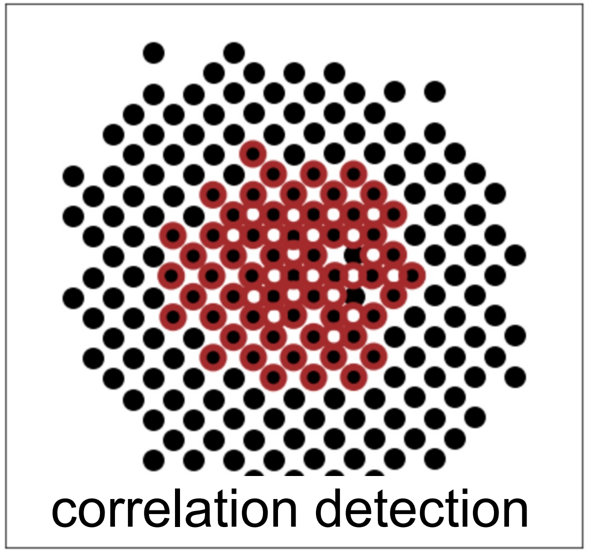
Solving Diffraction with Deep Learning

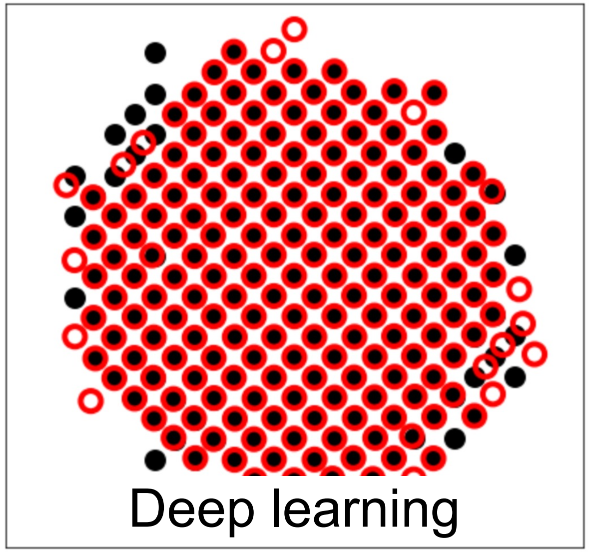


Dynamical Diffraction **Defeated** by Deep Learning

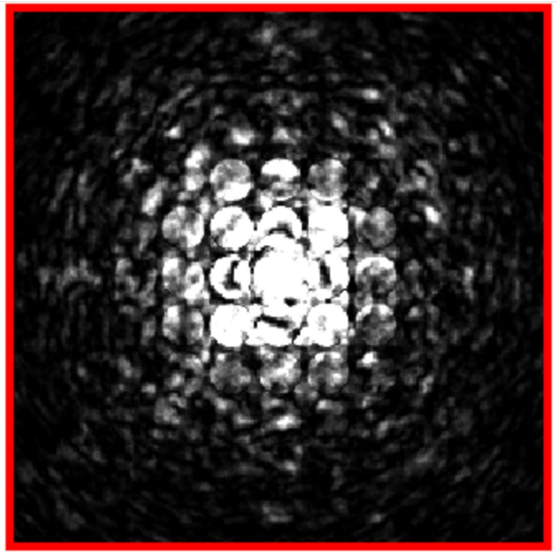
Diffraction pattern from using small convergence angle, thin sample

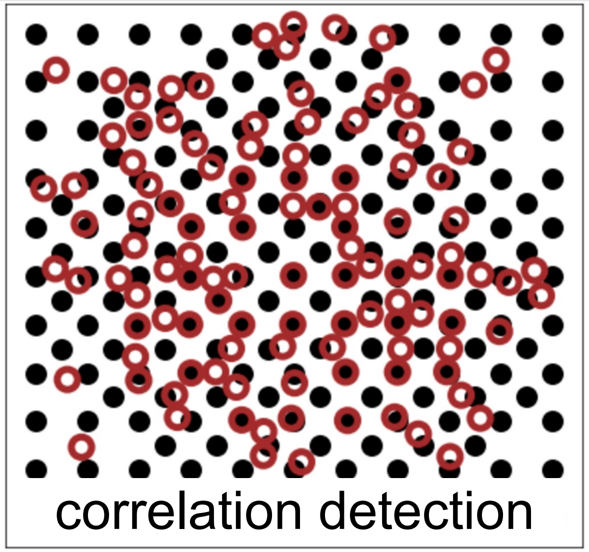


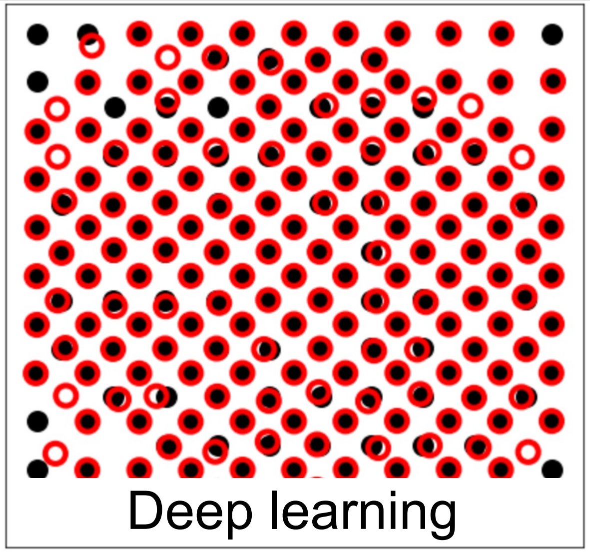




Diffraction pattern from using large convergence angle, thick sample







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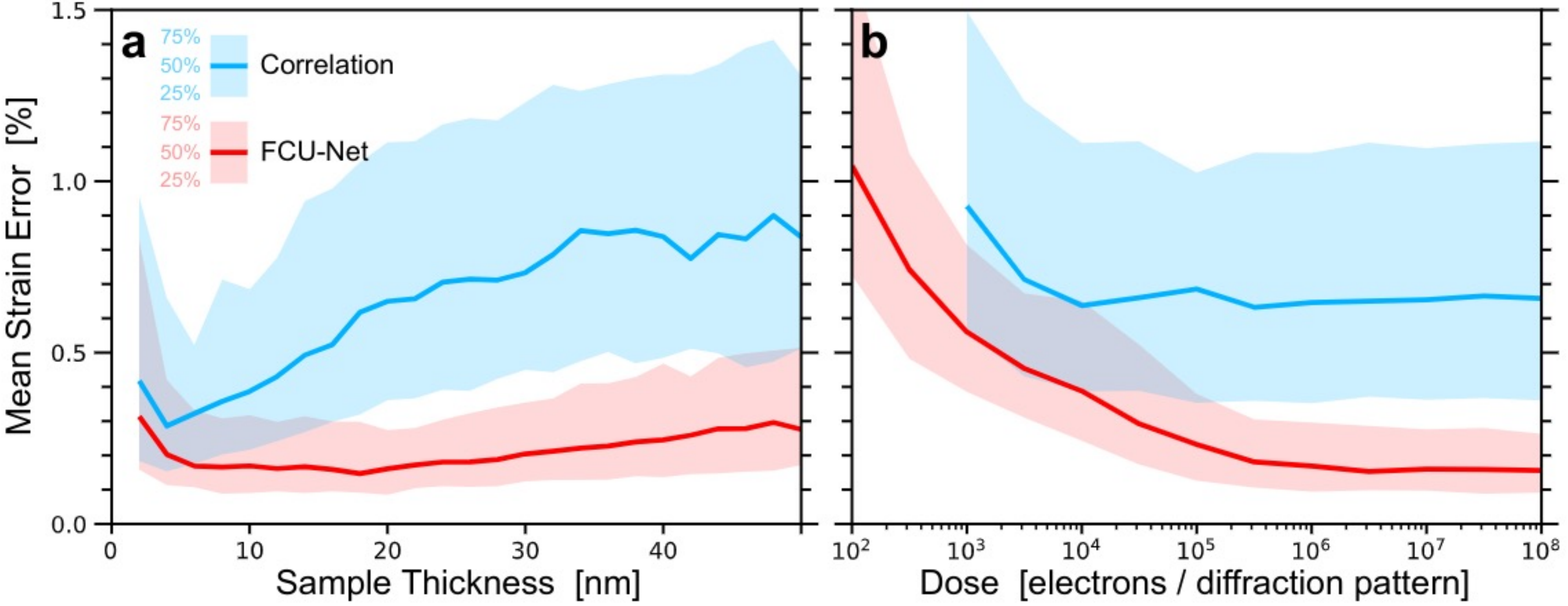
Solving Diffraction with Deep Learning – FCU-Net



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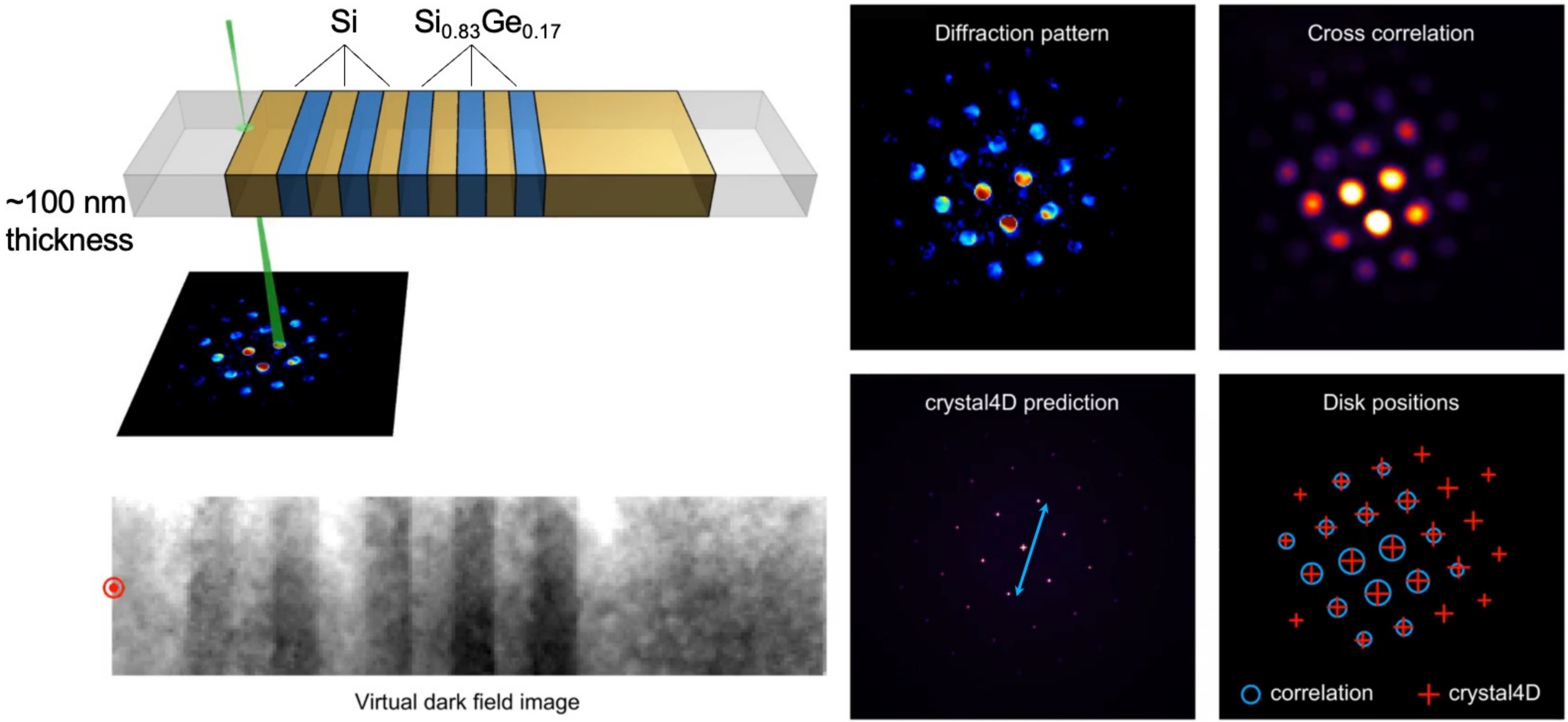
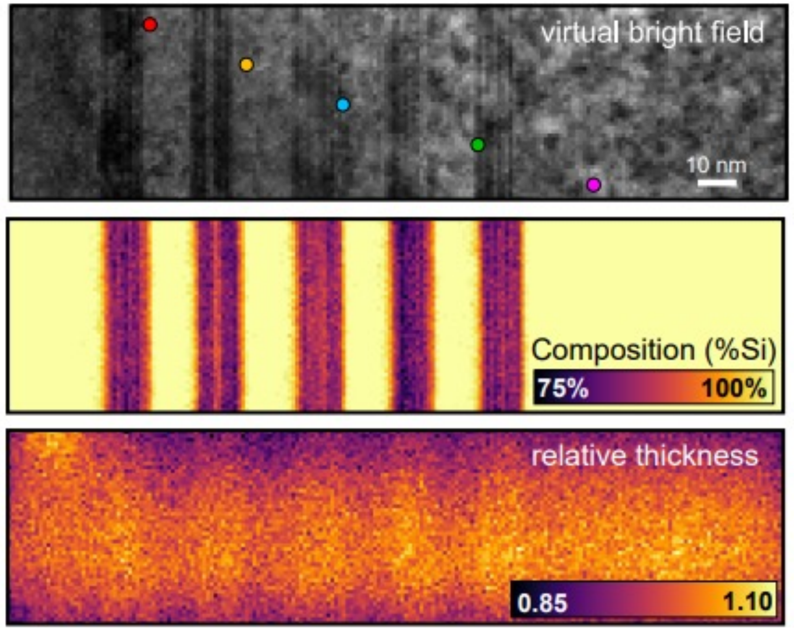
Strain Mapping of SiGe Multilayers w/ Deep Learning

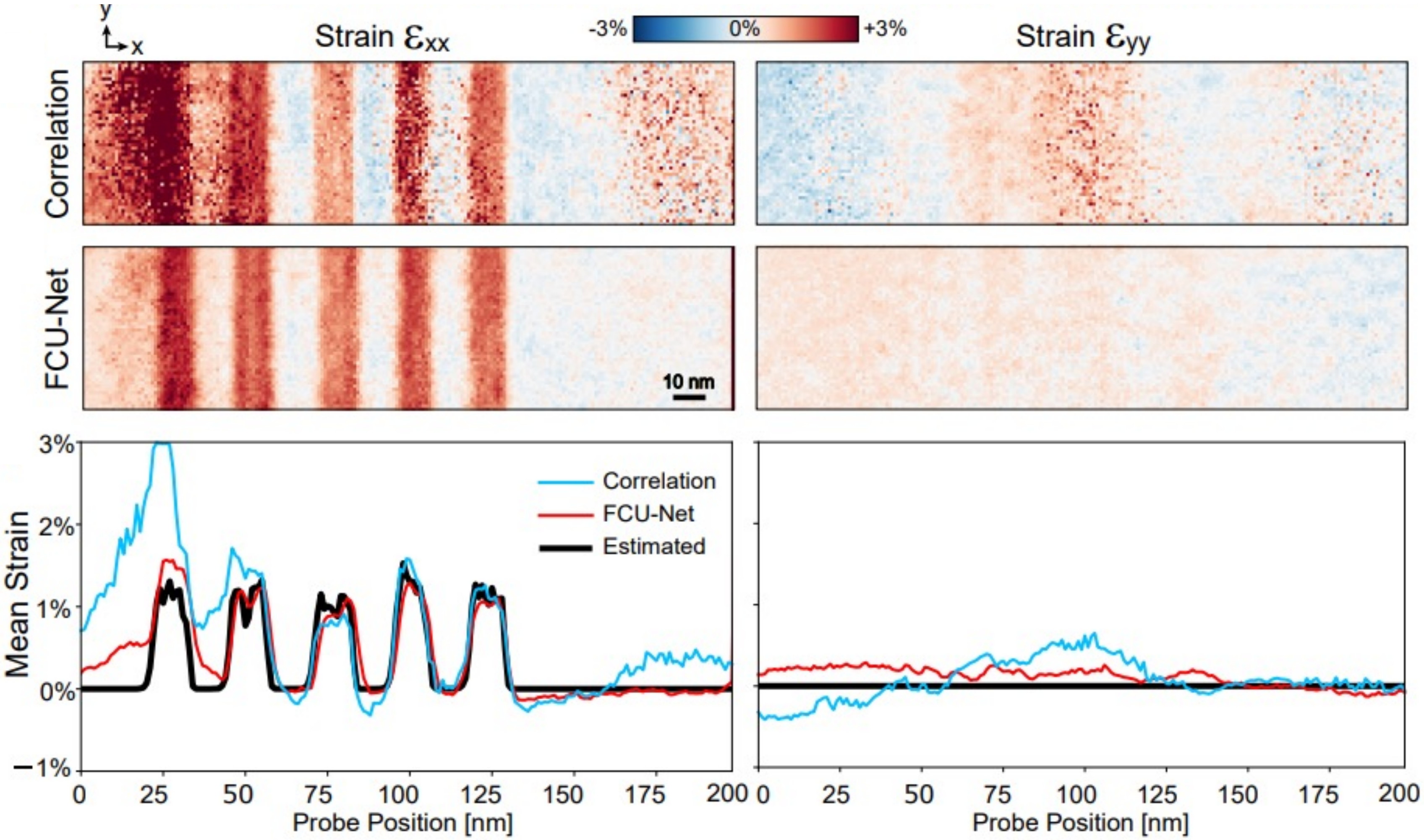


J Munshi*, A Rakowski*, et al., npj computational materials 8, 254 (2022)

Strain Mapping of SiGe Multilayers w/ Deep Learning



Strain mapping of alternating multilayers of Si and SiGe.

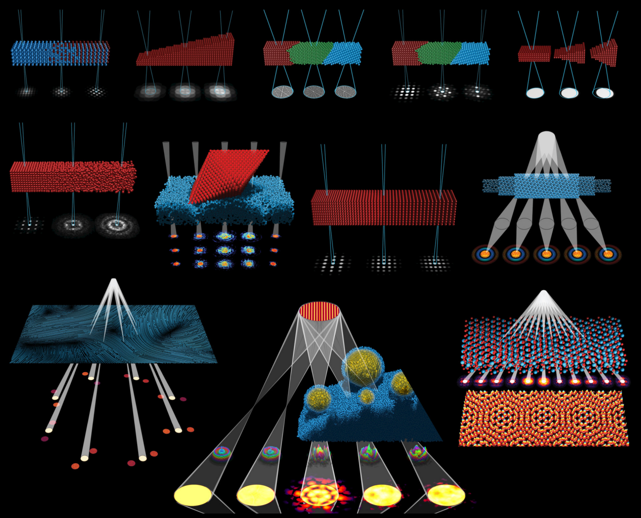


- Our deep learning approach significantly improves the **measurement accuracy** over conventional correlation, and **does not require** any **labeled training data**.

More Info – clophus@lbl.gov – ncem-lbl.slack.com

Volume 25, Number 3 June 2019

Microscopy AND Microanalysis

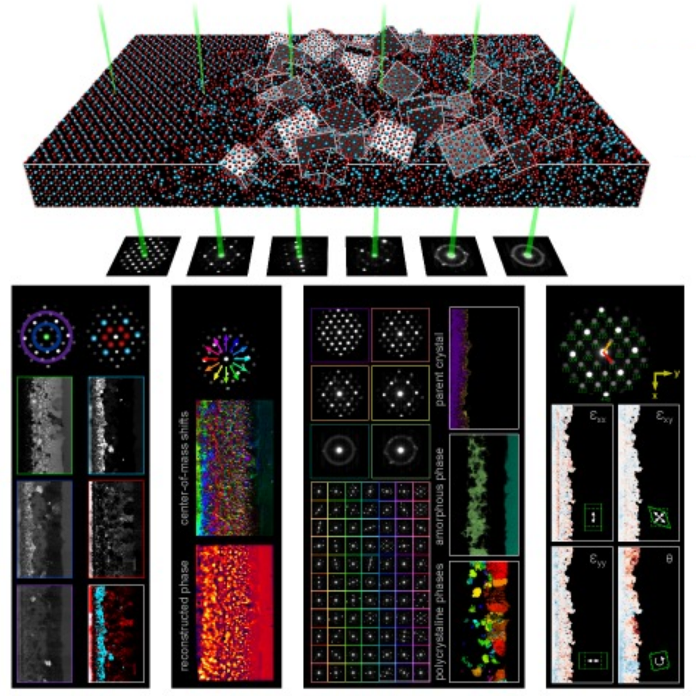


4D-STEM Review

C Ophus, Microscopy and Microanalysis **25**, 563 (2019)

4D-STEM analysis: **py4DSTEM**

github.com/py4dstem/**py4DSTEM**
github.com/py4dstem/**py4DSTEM_tutorials**



www.prism-em.com

Prismatic
STEM Image Simulation

Fast 4D-STEM Simulation Code

Source code, GUI programs for Windows, OSX, Linux, tutorials

Acknowledgements

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Benjamin Savitzky
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Luis Rangel DaCosta
Georgios Varanides
Min Chen
David Ren
Tiffany Chien
Laura Waller
Hannah Devyldere
Mary Scott
Nathanael Kazmierczak
Madeline Van Winkle
Isaac Craig
Kwabena Bediako
Scott Stonemeyer
Derek Popple
Alex Zettl
Jun Ding
Mark Asta

Northwestern Univ
Roberto dos Reis
Vinayak Dravid

U Erlangen Nürnberg
Mingjian Wu
Philipp Pelz
Christina Harreiss,
Erdmann Spiecker

Arizona State U
Sandhya Susarla

UC Los Angeles
Yao Yang
John Miao

University of Siegen
Charles Otieno Ogolla
Benjamin Butz

KAIST
Juhyeok Lee
Hyesung Jo
Yongsoo Yang

Monash University
E Terzoudis-Lumsden
Scott Findlay

University of Melboune
Hamish Brown

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Dean Deng
William Chueh
Alberto Salleo
Yi Cui

Humboldt U of Berlin
Thomas Pekin
Christoph Koch

Weizmann Institute
Shahar Seifer
Michal Elbaum

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U.S. DEPARTMENT OF ENERGY | Office of Science