X-ray and Neutron Microdiffraction

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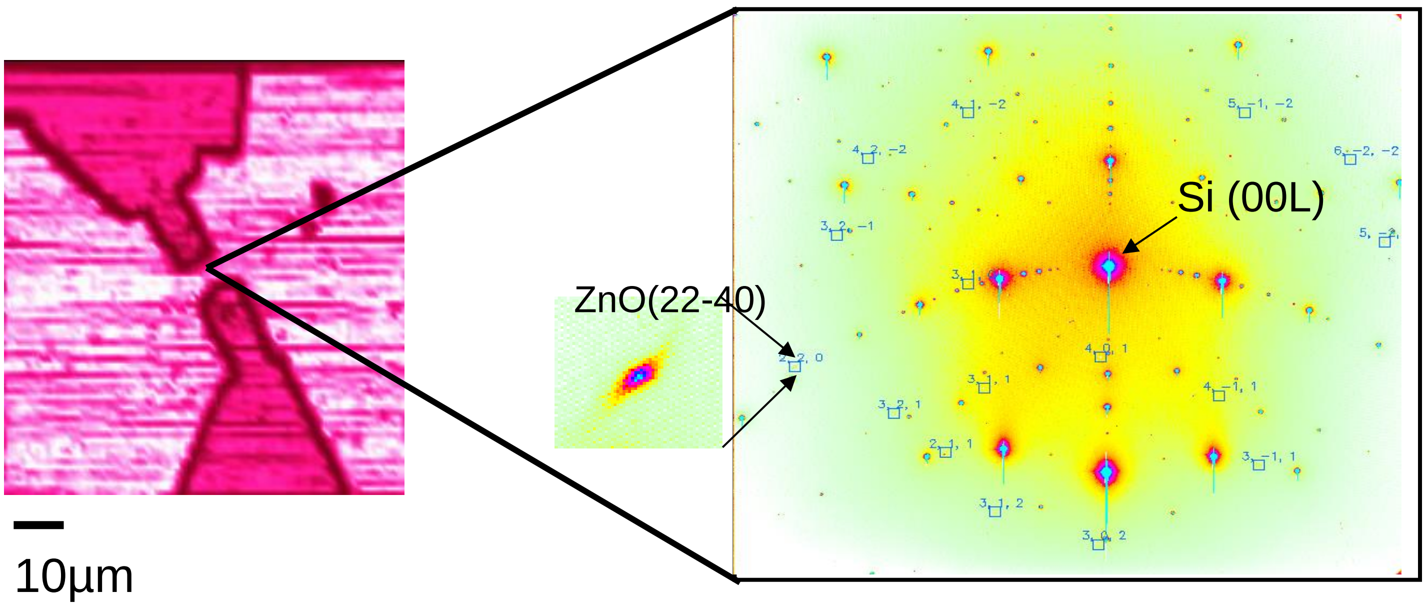


2013 Neutron X-ray Summer School

Oak Ridge National Laboratory

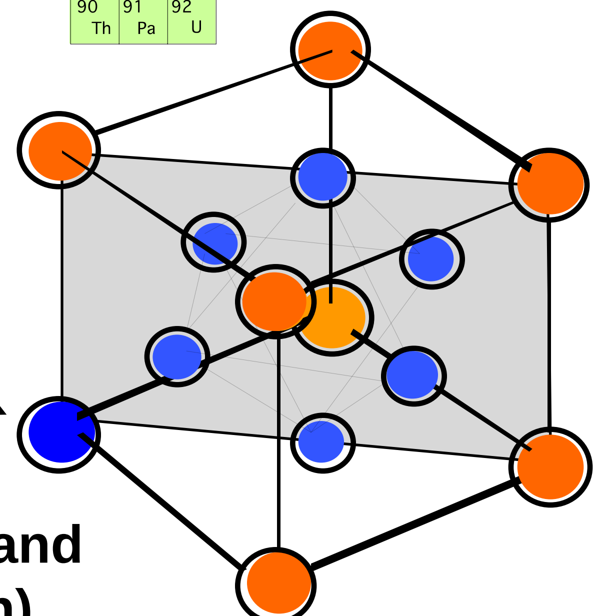
Two words

Spatial Resolution

Materials characterization begins 3 questions

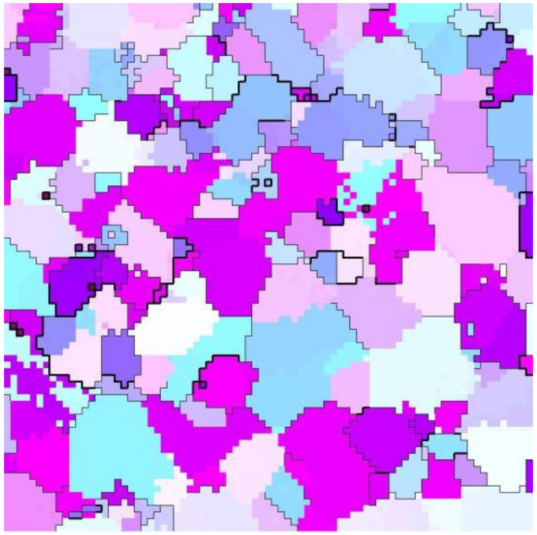
- **What is the elemental composition?**
- **What is the crystal/local structure?**
- **What are the defects?**

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 Ni	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 X
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U											

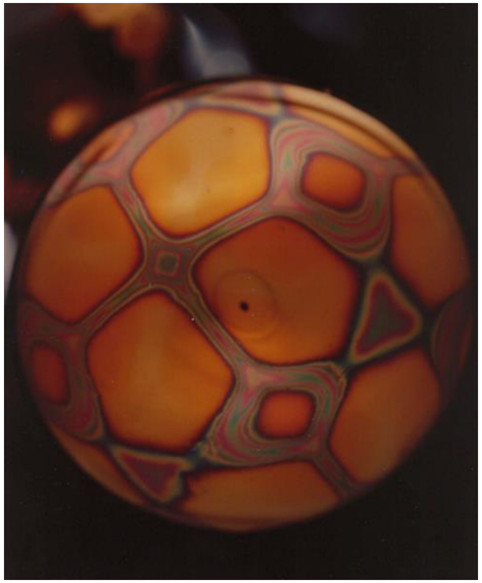


X-rays and neutrons probe structure and defects through scattering (diffraction)

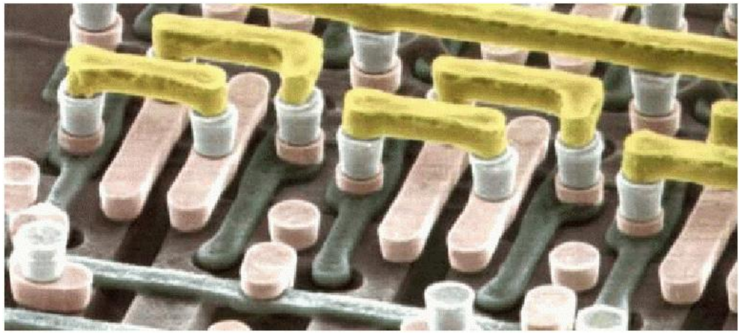
Spatial resolution essential!



- **Most materials** *polycrystalline* **(0.1-50 μm)**
  - **Anisotropic**
  - **Heterogeneous**
  - **Plastic/elastic deformation/ diffusion/ oxidation/**



- **Even** *within* **single and "perfect" crystal:**
  - **Strain**
  - **Defects**
  - **Spontaneously organize to reduce energy**



Spatial resolution essential for most advanced energy systems

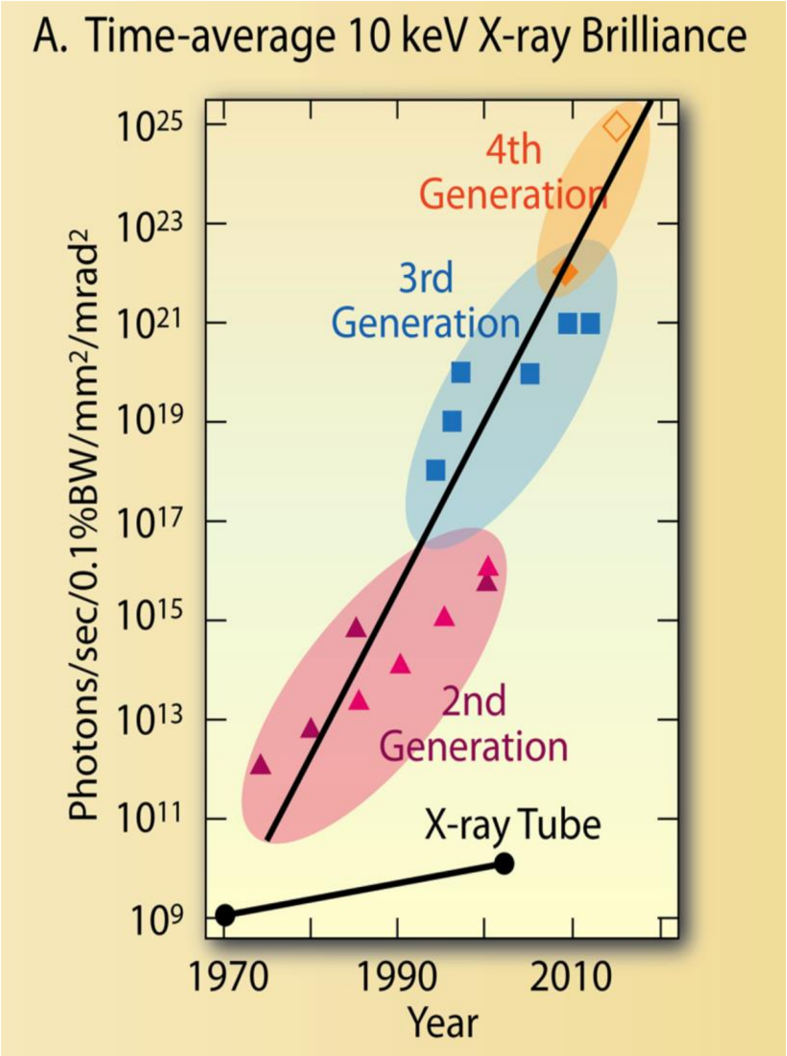




New X-ray/ Neutron Sources Changing the Possible

- **Brilliance figure-of-merit for spatially-resolved exp.**
- **X-ray brilliance doubling faster than Moore's law**
- **SNS with 10x brilliance 100x more efficient detectors**

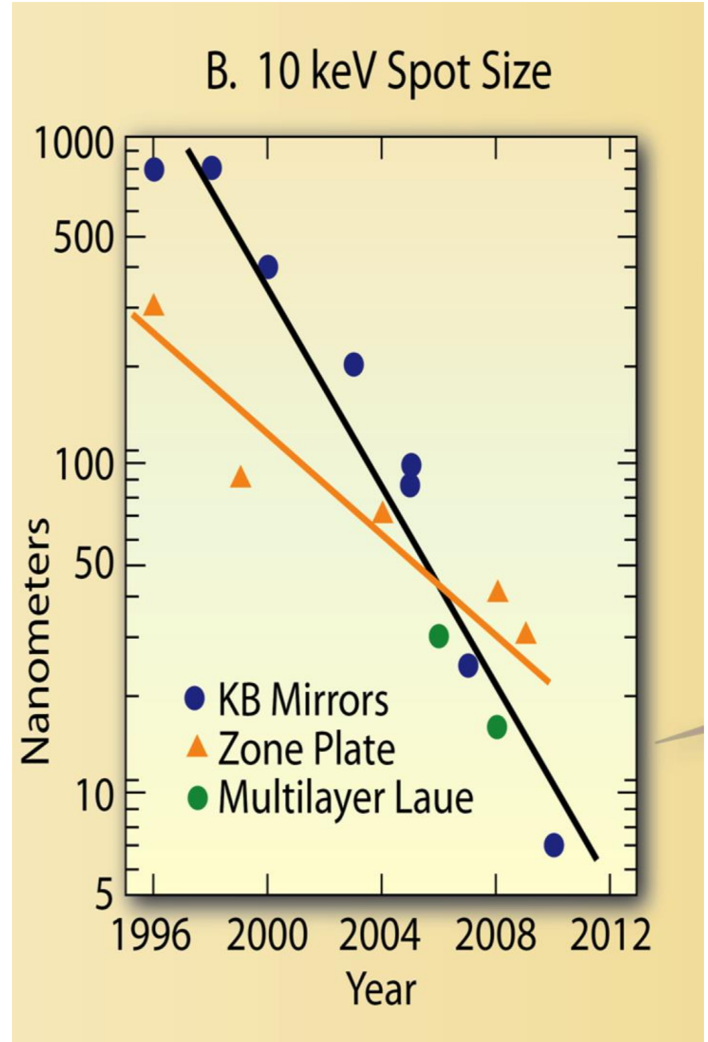
TOPAZ/ SNS



Spatial Resolving Optics Improving Rapidly

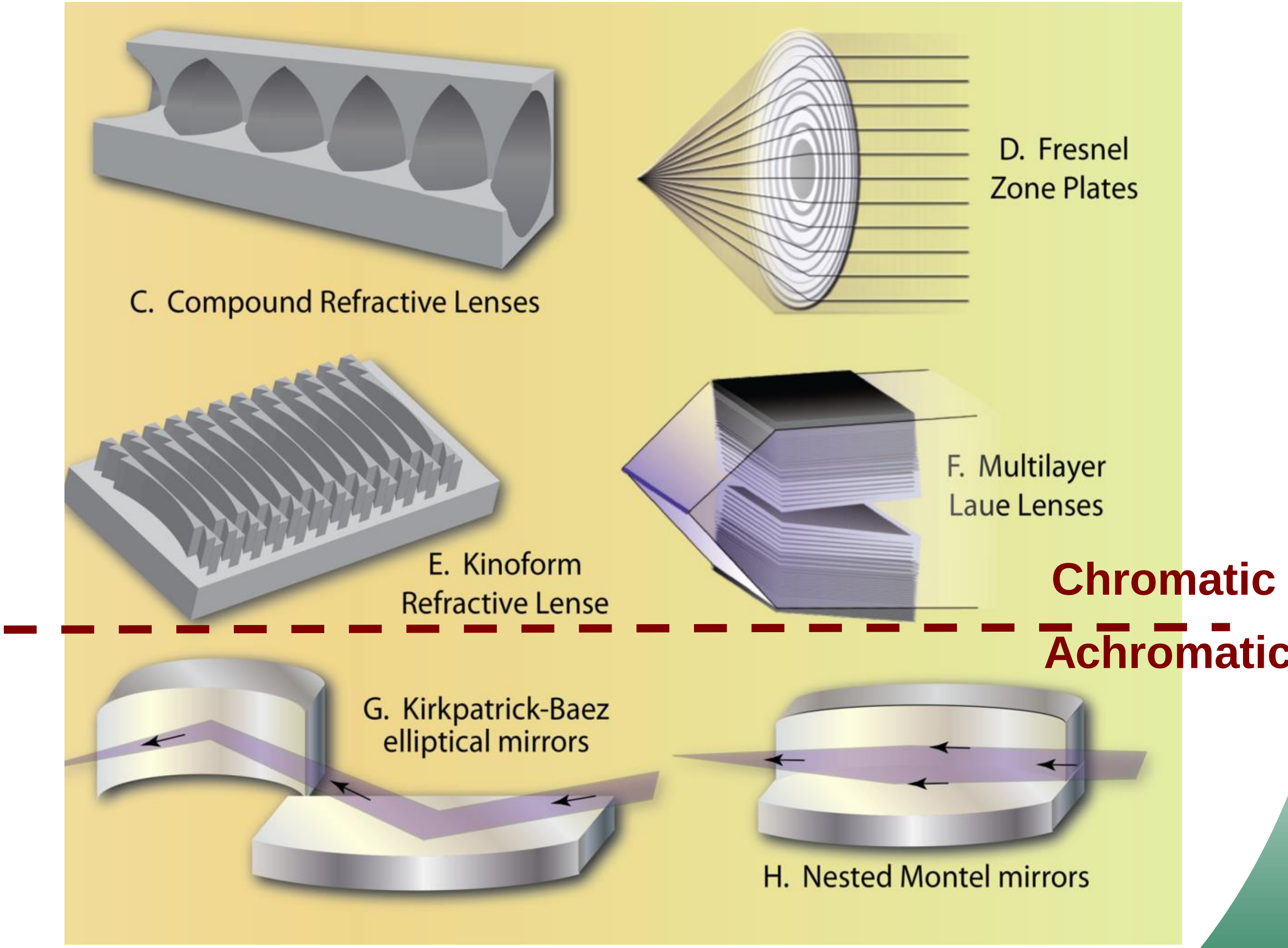
- **X-ray focal spot size routinely below 100 nm**
- **Neutron focusing optics below 100 µm**

Neutron optics with <70 µm Focus



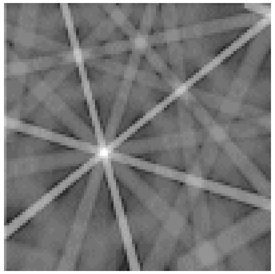
X-ray micro/nanofocusing optics rapidly evolving

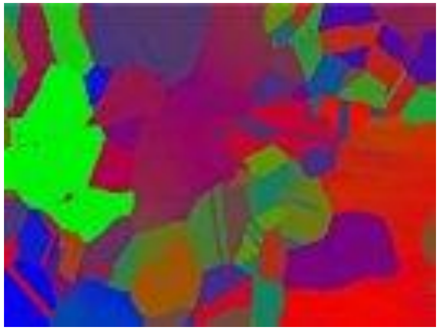
- CRL-50 nm
- FZP<30 nm
- Kinoform <70 nm
- MLL <15 nm
- KB <7 nm
- NMM<80 nm



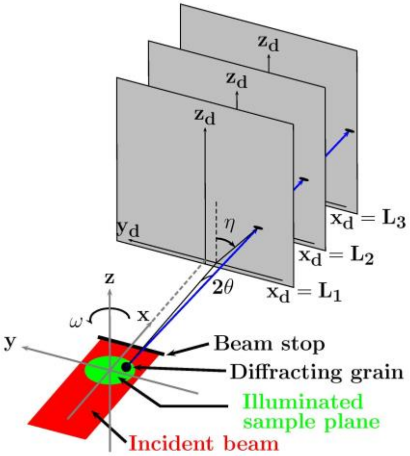
Diffraction mapping emerging area in electron and x-ray microscopy

- EBSD-transformed study of polycrystals
  - Surface phase
  - Surface orientation
  - FiB-3D mesoscale structure

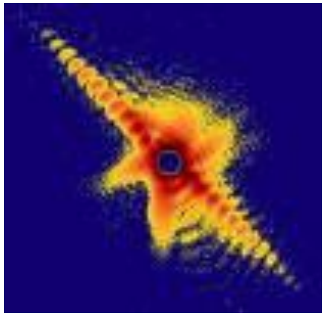




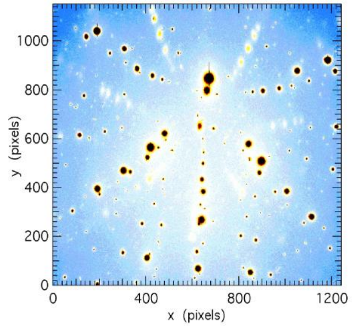
- 4D X-ray microscopy Lienert et al.
  - Time resolved
  - Deep penetration



- Coherent X-ray Diffraction (Robinson et al.)
  - Simple structures



- Polychromatic X-ray microdiffraction
  - Phase/texture/***strain***/
  - ***Nondestructive***
  - ***Submicron***



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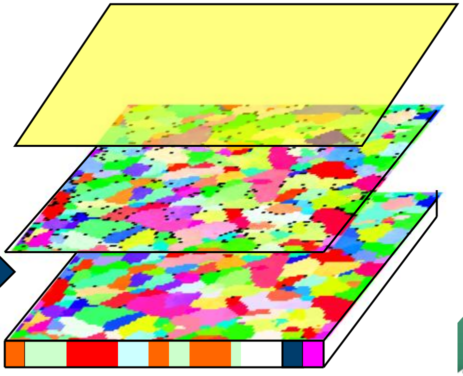
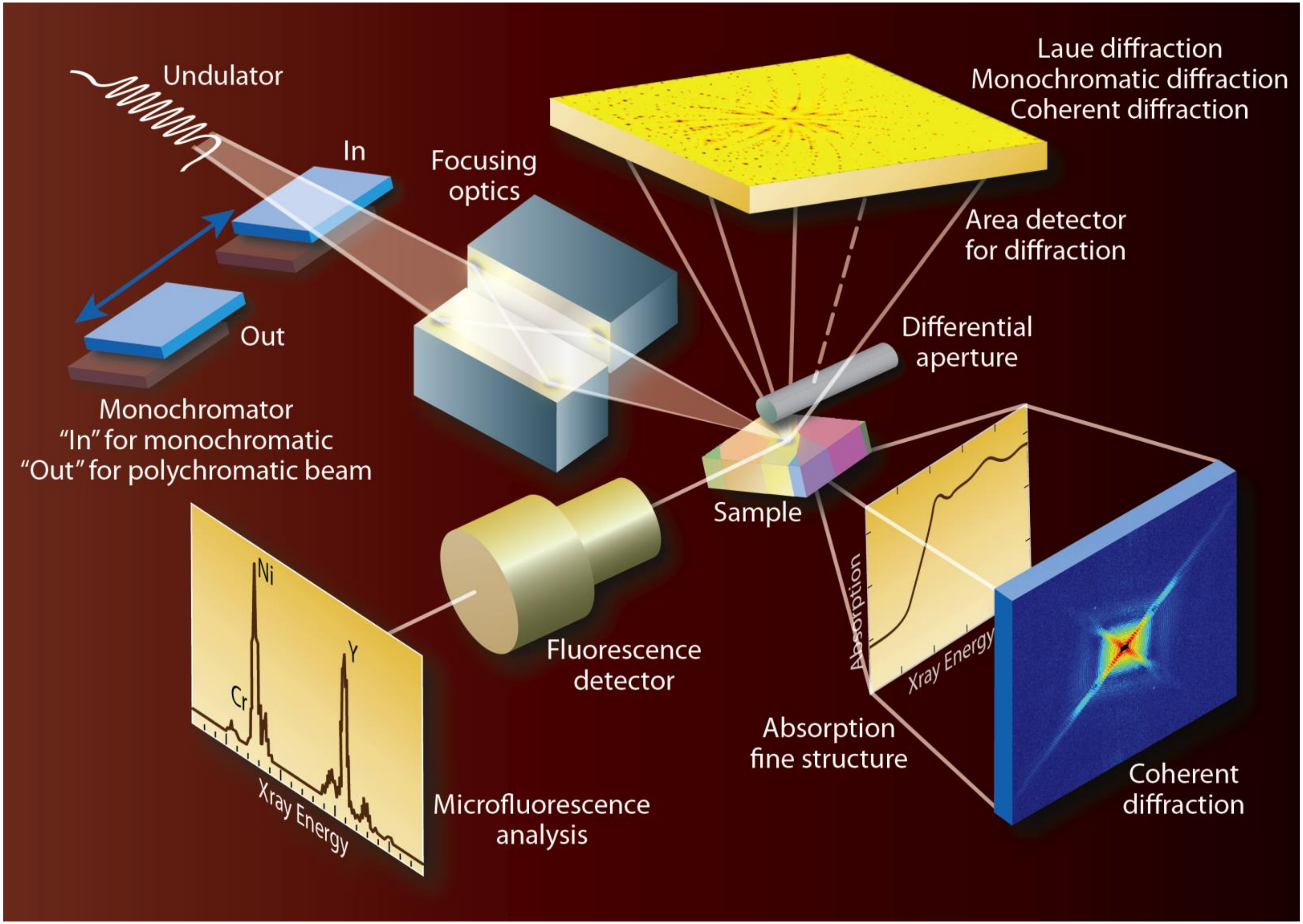
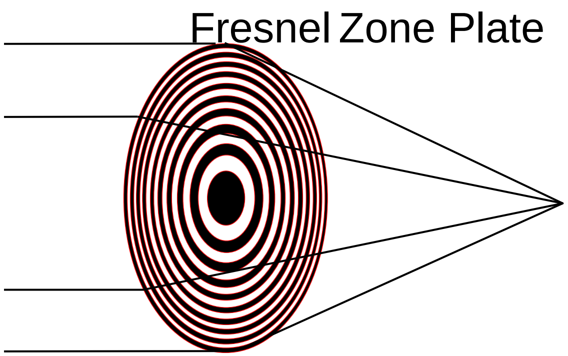


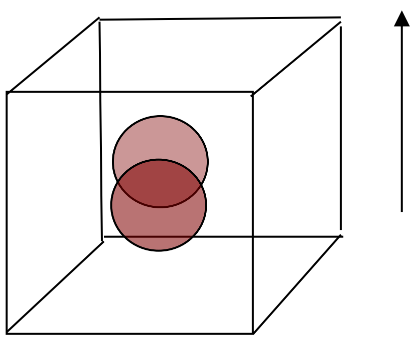
X-ray Micro/nanoprobe beams map chemistry and structure



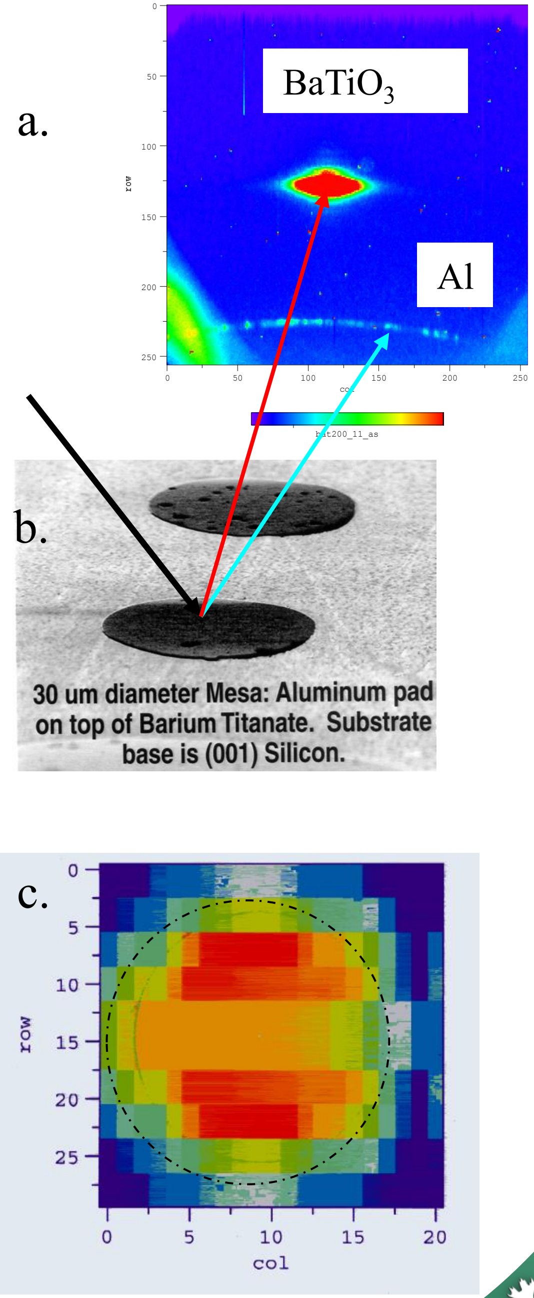
Monochromatic micro crystallography probes simple crystal systems



Wide-range of focusing choices

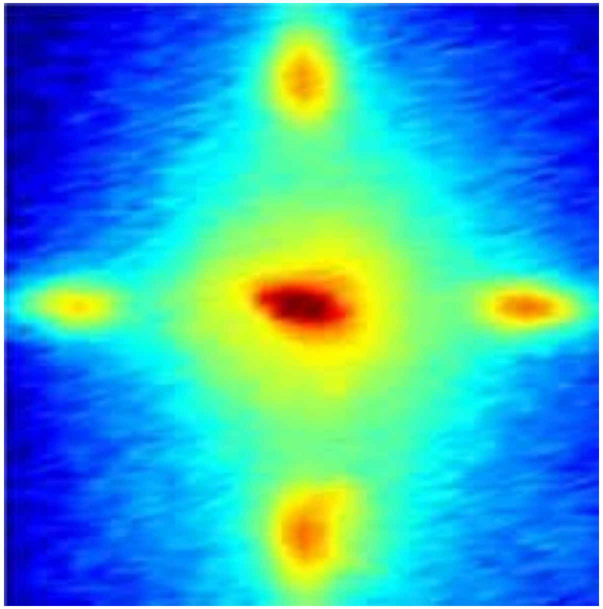


Ferroelectrics ideal samples



Thompson et al. study dimensionality of ferroelectricity

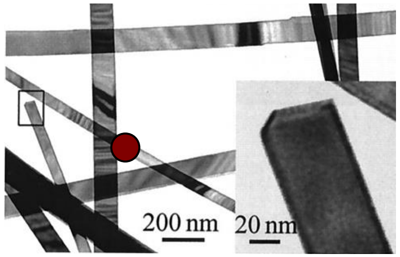
- Thickness
- Ribbons
- Dynamics



Diffraction from a ferroelectric stripe

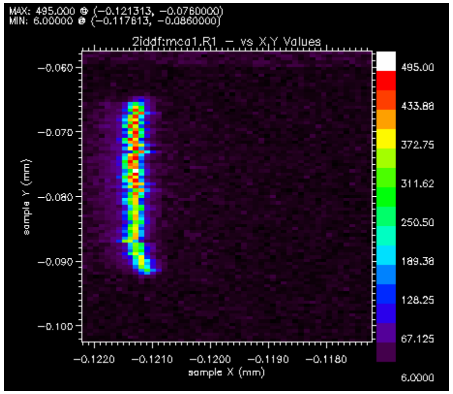
Ferroelectricity found with few unit cells

Cai et al. and others study ultra-small nanocrystalline volumes with existing microbeams

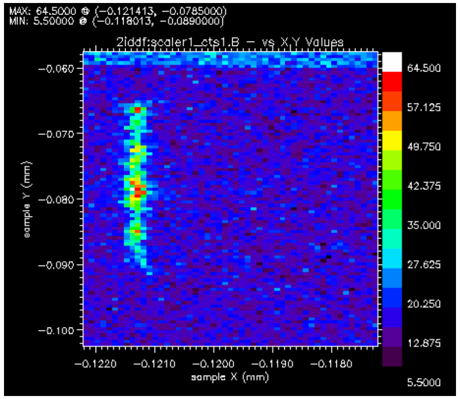


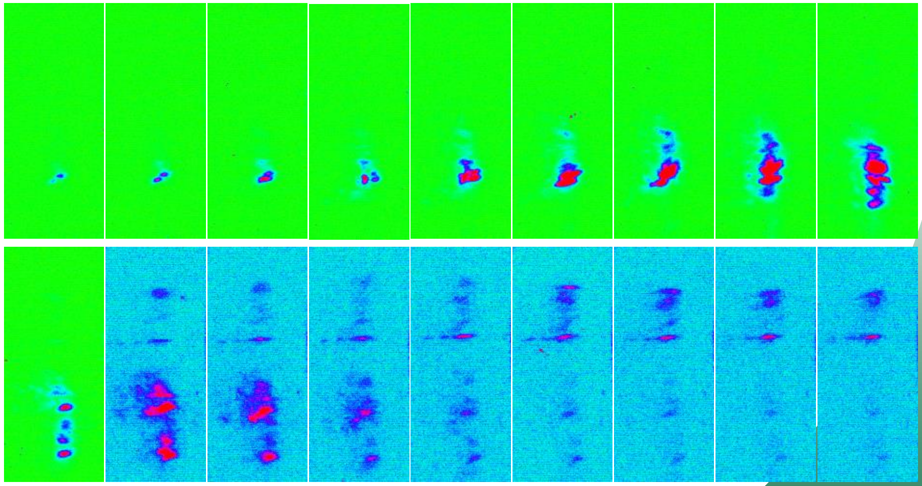
•150 nm beam resolves crystalline substructure in individual Sn_2O_3 nanobelts

Fluorescence map



Diffraction map





APS *Nanoprobe*- opens new opportunities for spatially resolved

- **Diffraction proposals compelling**
- **Physics of small**
- **Integrated circuit materials**

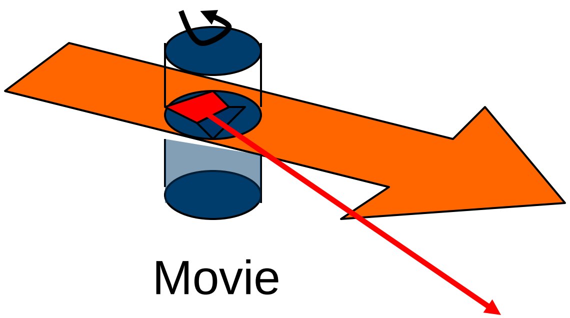
~30 nm now

<10 nm possible in future

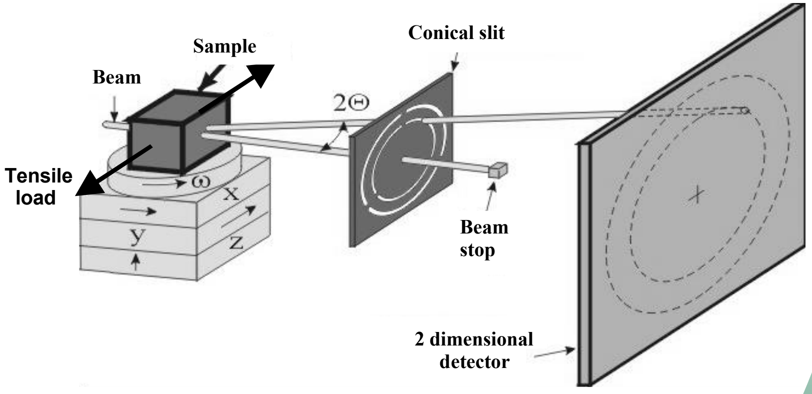
NSLSII ~1 nm!

4DXRD Microscope emerging tool for studying mesoscale dynamics-single rotations

- Singly focused monobeam illuminates numerous grains
  - Bragg condition satisfied by single rotation
  - *Time resolution! (4D)*



- Grain outline determined
  - Ray tracing
  - conical slit
  - Back-projection tomography

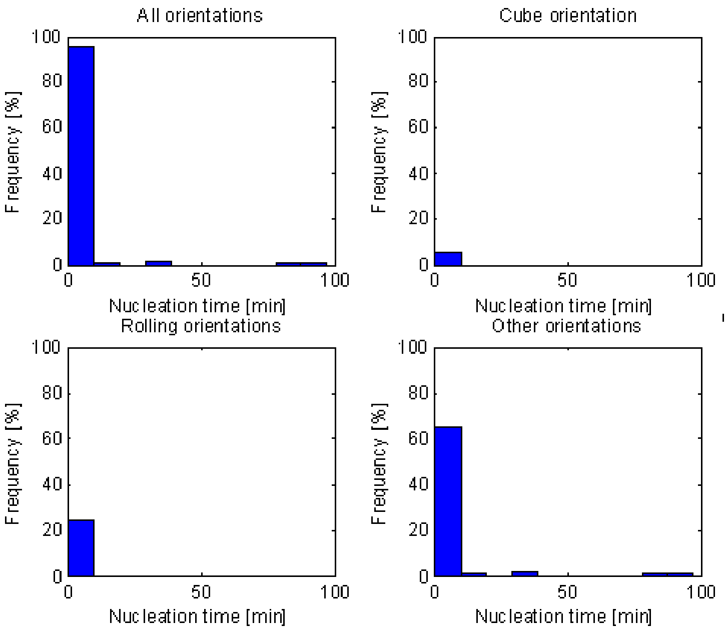


- E>50 keV allows deep measurements

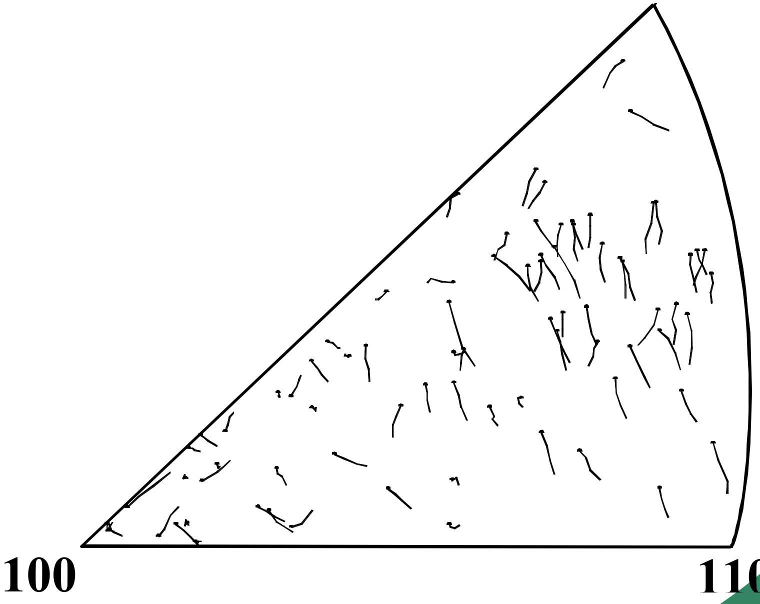
Best with high-energy beams/Beamline 1 at APS

4DXRD Microscope powerful dynamics probe

- **Recrystallization growth individual grains-deep**
  - **E. M. Lauridsen, D. Juul Jensen, U. Lienert and H.F. Poulsen (2000). *Scripta Mater.,* *43*, *561-566***

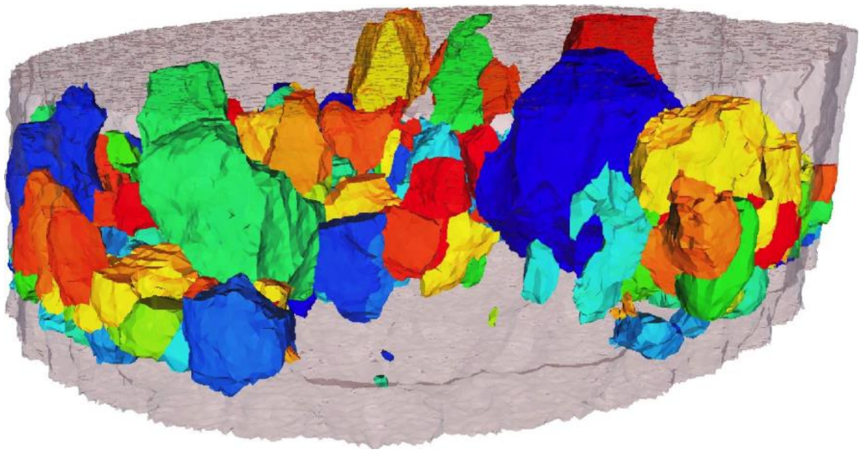


- **Rotations/texture evolution individual grains during deformation**
  - **Tests deformation models**
  - **L. Margulies, G. Winther and H.F. Poulsen, Science** 291, **2392-2394 (2001).**



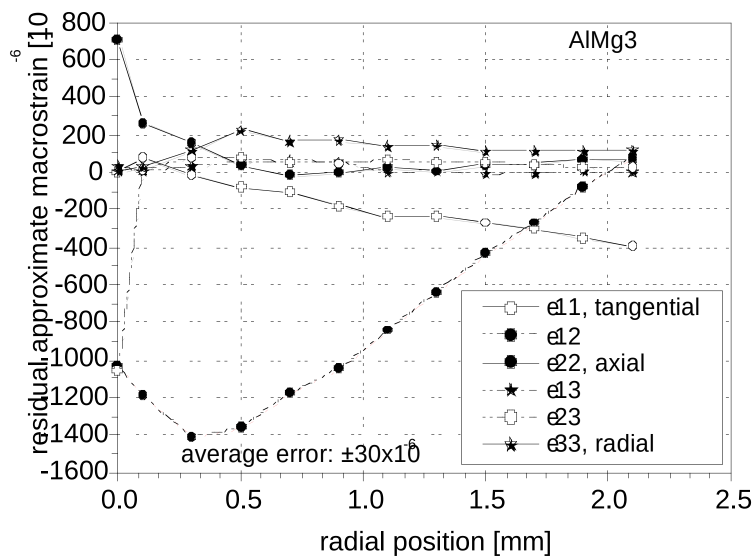
4DXRD Microscope provides additional powerful capabilities

- **Grain boundary mapping in coarse grained materials-5μm**
  - **Poulsen et al. J. Appl. Cryst. 34 751-756 (2001)**



- **Single crystal refinement for polycrystals**

- **Macro/microstrain**



Strain tensor elements in torsion sample

Ideal for neutrons! But needs high-resolution detectors!

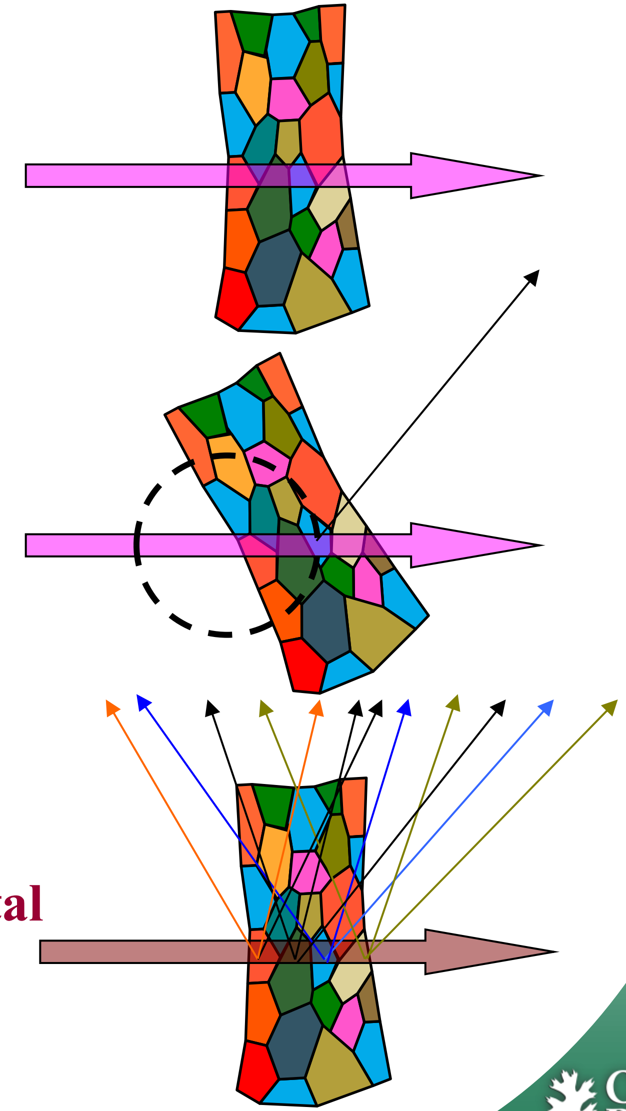
Polychromatic simplifies microdiffraction

Solves intrinsic problem with conventional microdiffraction-

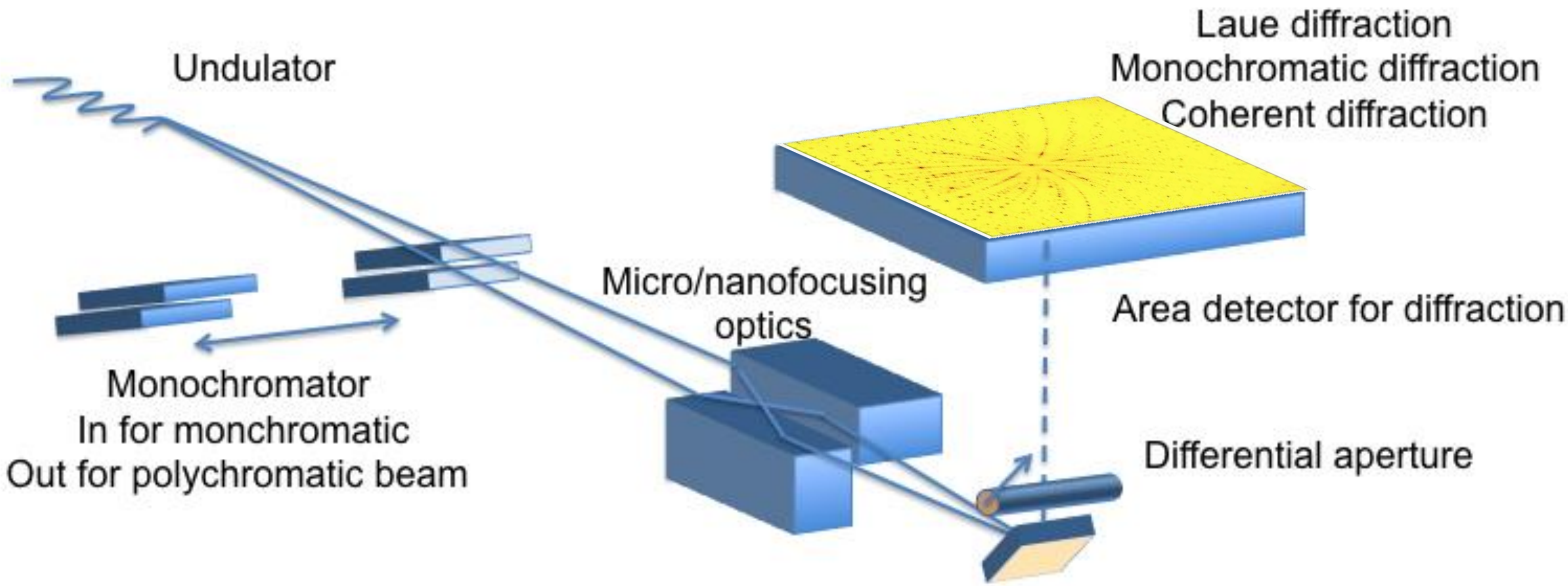
-Sample does not need to be rotated!

Special software required- Can index polycrystalline samples

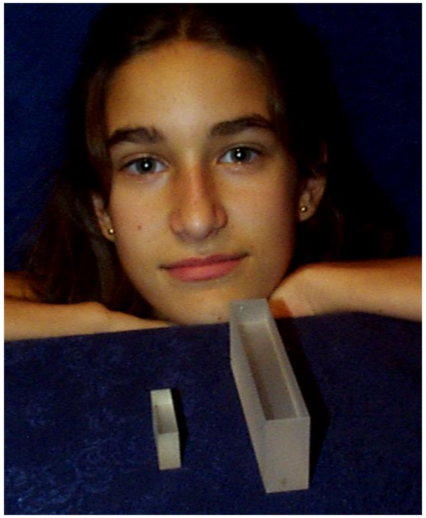
3D nondestructive probe of stress/strain/crystal structure!

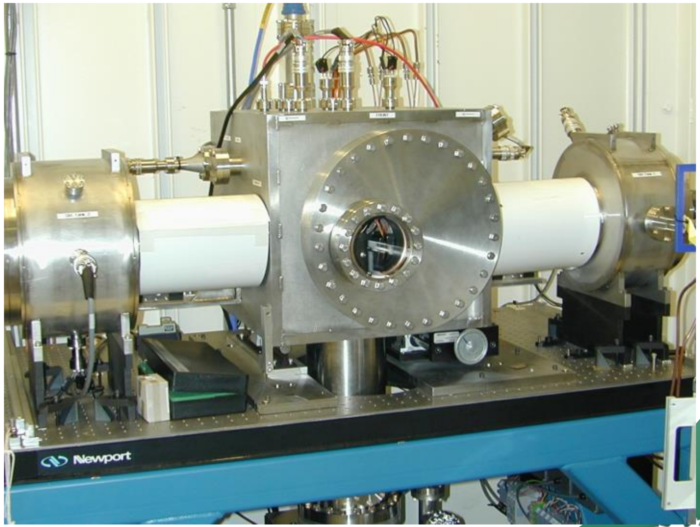


3-D X-ray Crystal Microscope has specialized elements



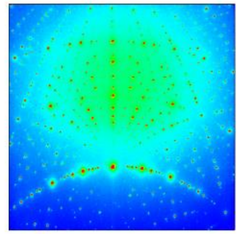
<0.25 x 0.25 x 0.5 μm^3
strain~10^{-4}-10^{-5}

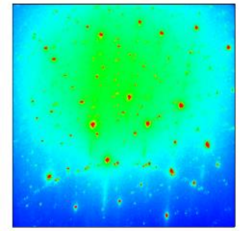


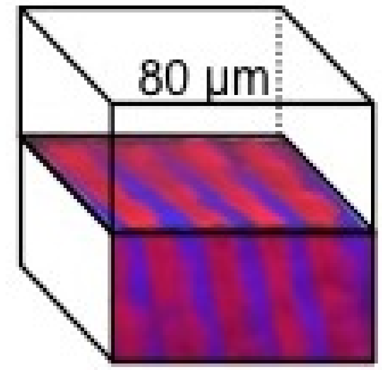


Provides Submicron 3D Maps With New Information

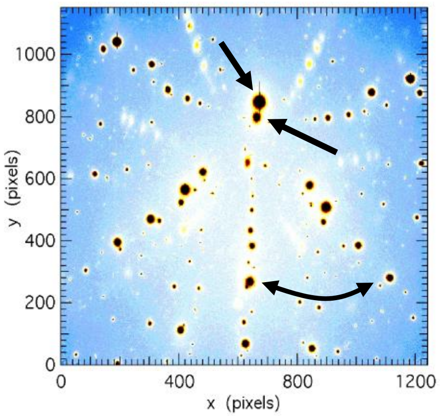
- **Phase boundaries**

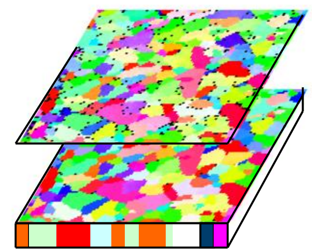


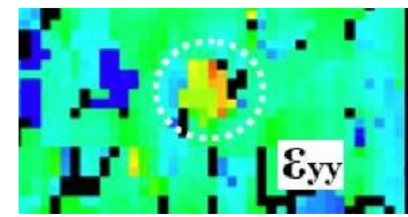




- **Grain boundaries(3D)**

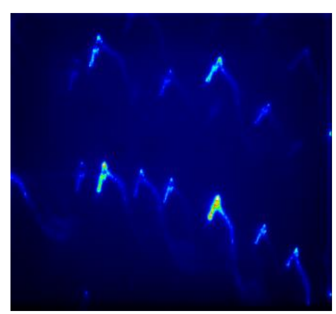


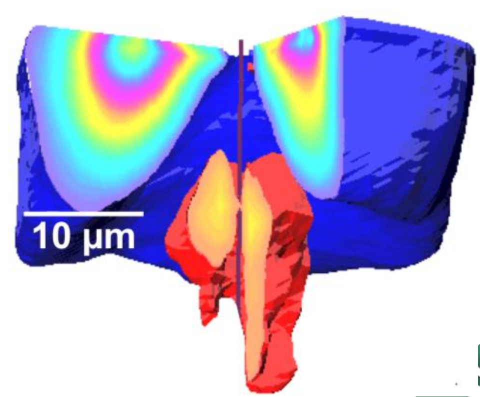




- **Elastic strain**

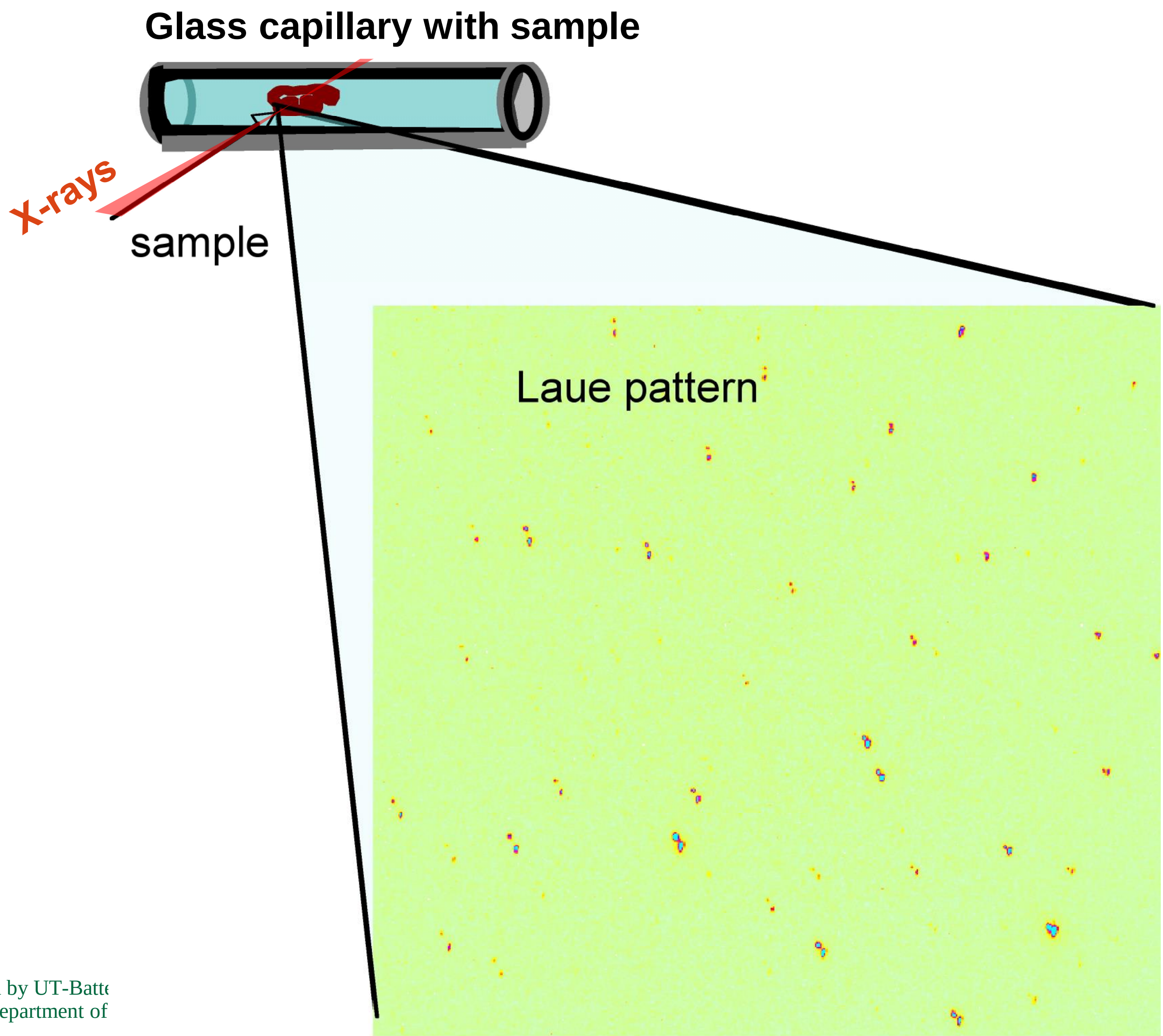
- **Deformation /Nye tensor**





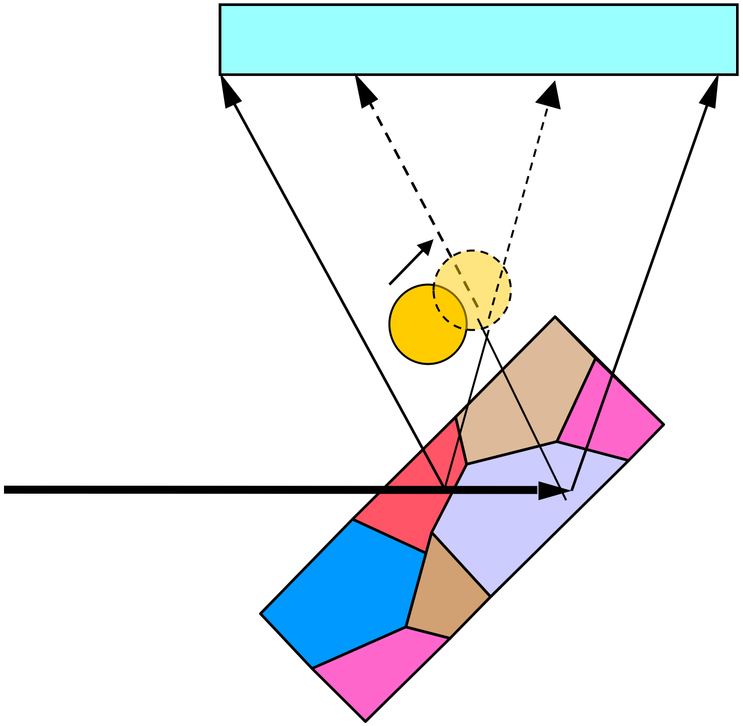
Nondestructive!

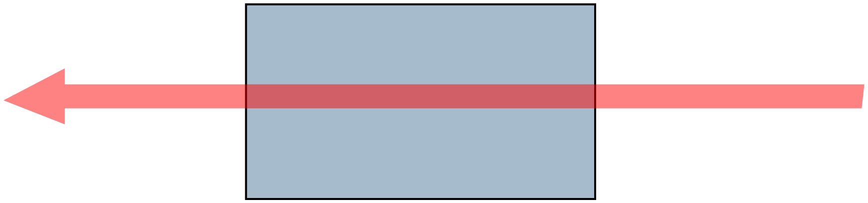
Laue methods essential for some samples



Differential aperture microscopy resolves submicron along incident beam!

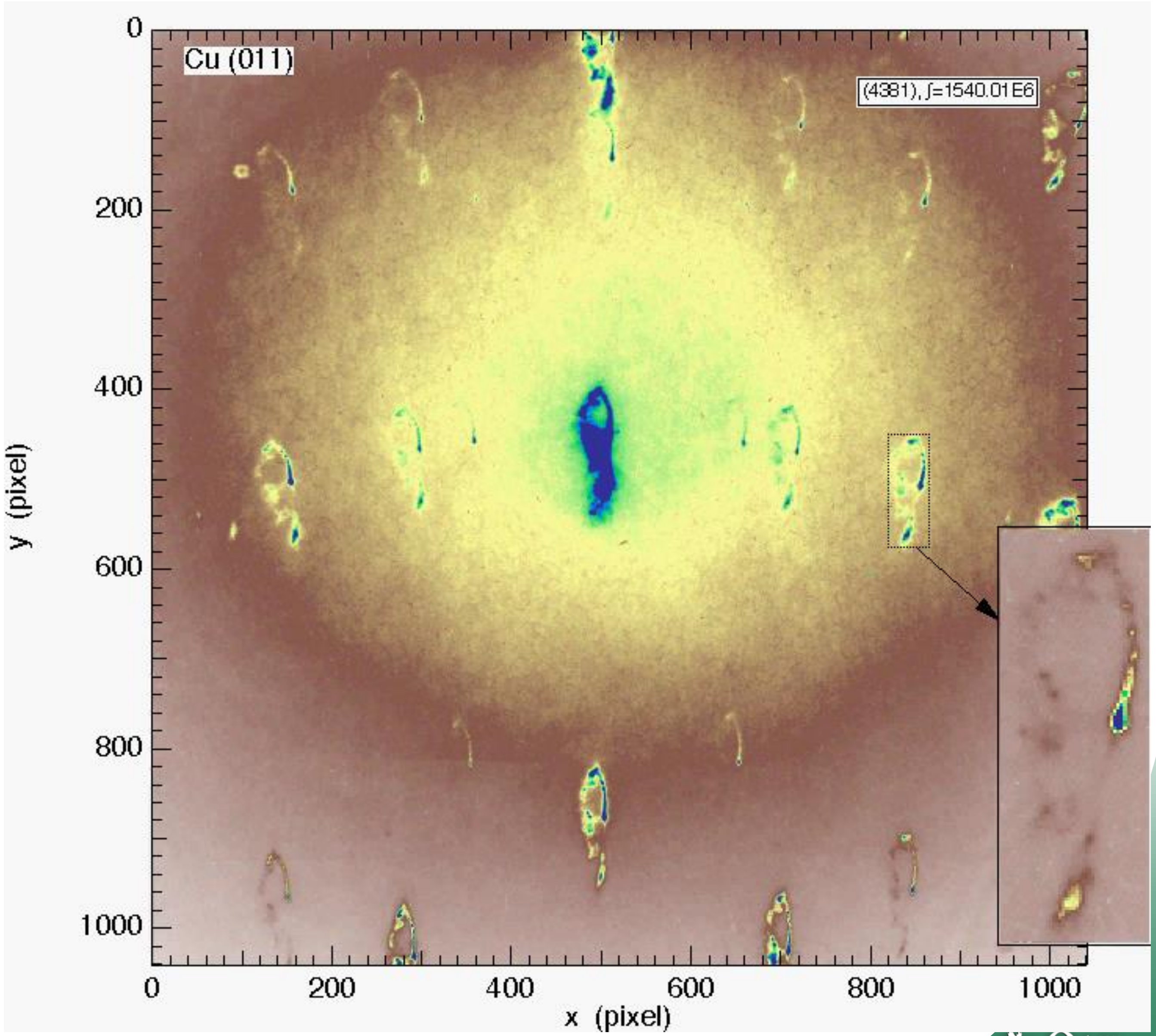
- Simplifies data interpretation
- Submicron Z resolution
- Isolates weak diffraction from strong
- First demonstration by Larson et al. on deformed Cu -



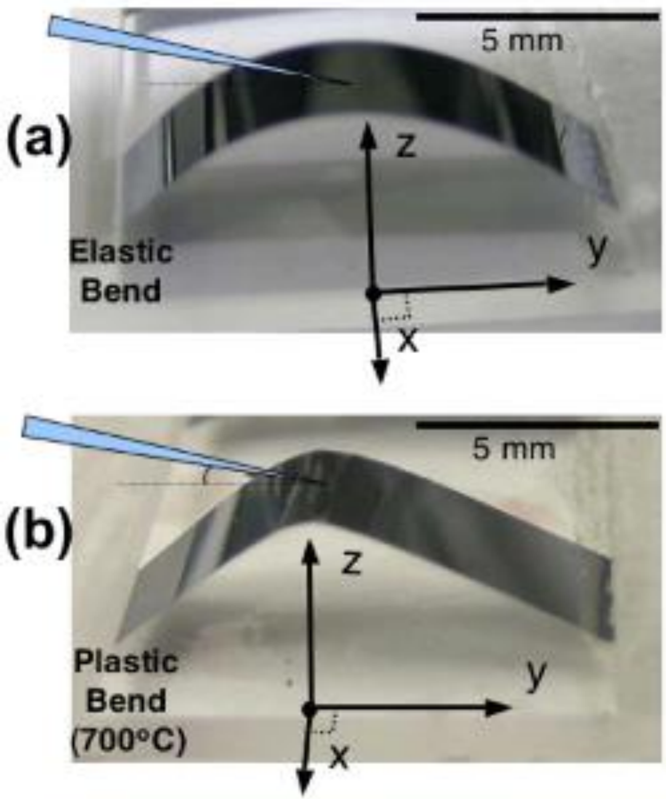


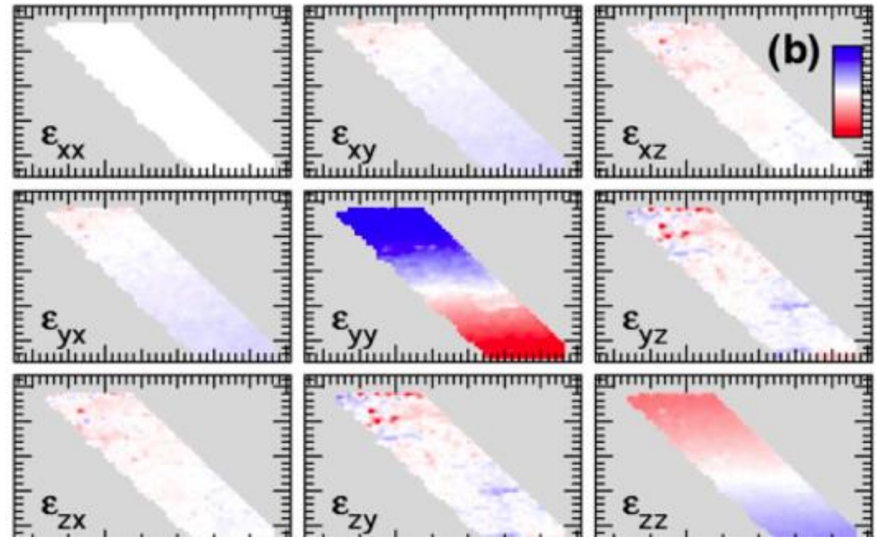
As wire moves its edge cuts through Laue spots

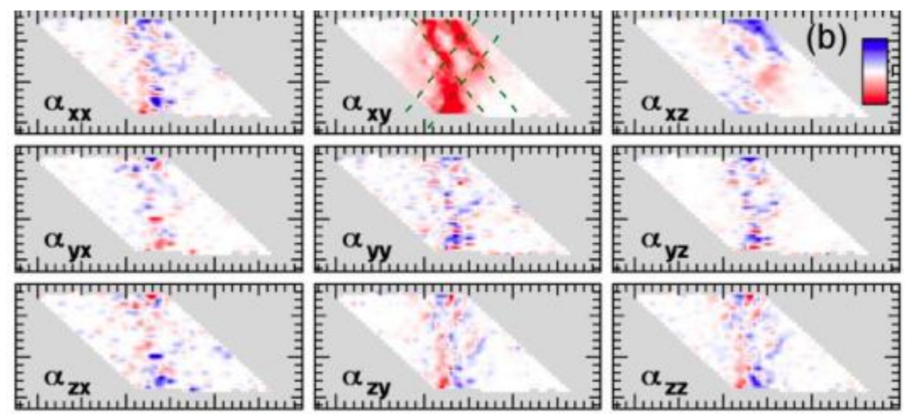
- **Near-surface fluorescence provides moving shadow**
- **Long scans needed for deep penetration**



Measurements of elastic strain tensor *inside* bent single crystal Si illustrate power of DAXM





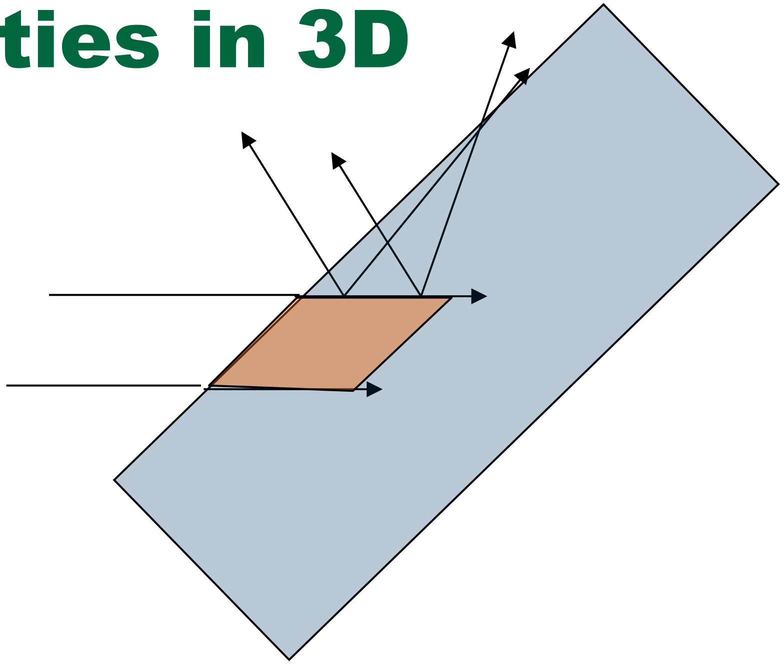


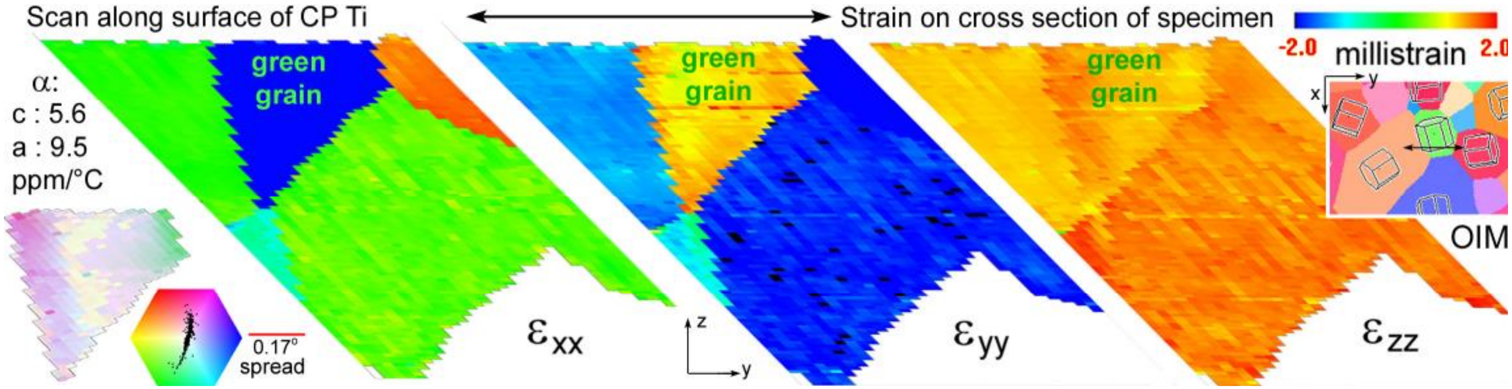
Orientations to 0.001°

Larson et al. J. Eng. Mat. and Tech. 130 021024 (2008) ORR award

Maps crystal properties in 3D

- **Phase**
- **Texture (orientation)**
- **Elastic strain tensor**
- **Nye tensor (deformation)**

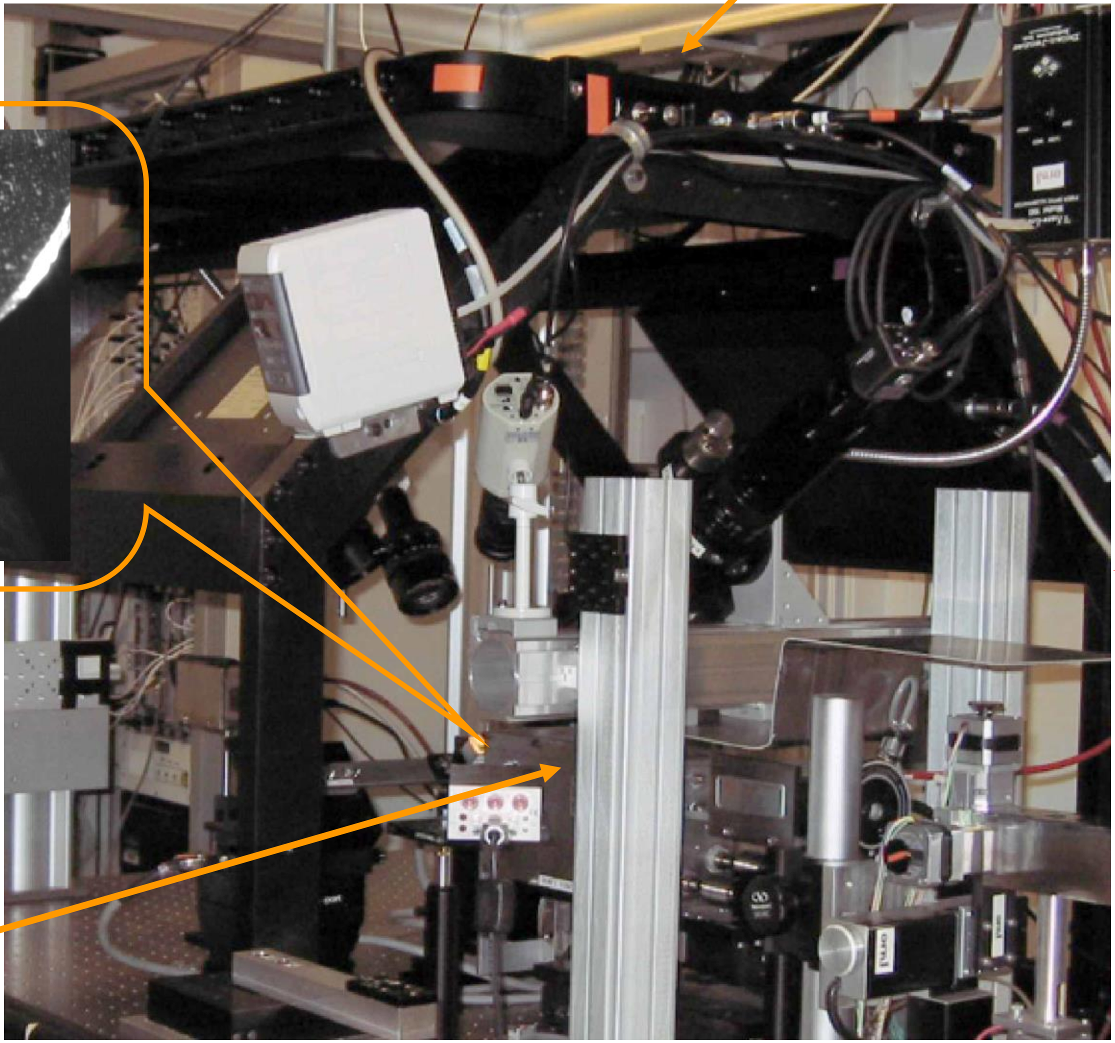




T. Bieler et al.

Experimental Hutch 34ID-E at UNICAT, Advance Photon Source

Amorphous Si
Area detector



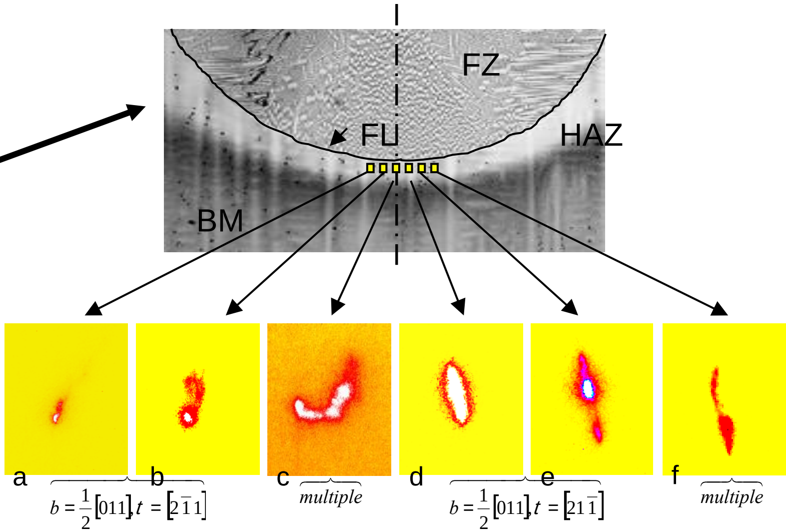
differential aperture

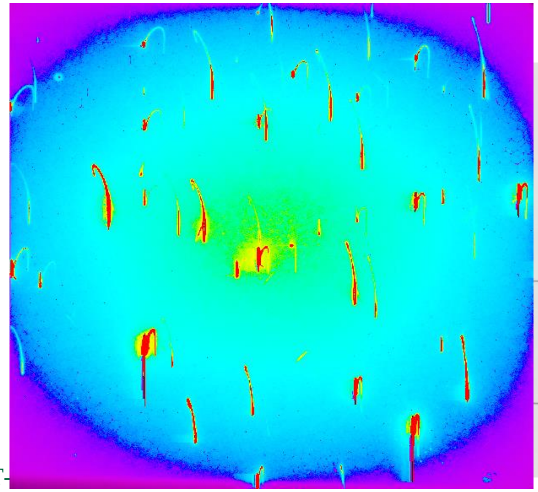
(wire scan, ~ 200 μm
above sample surface)

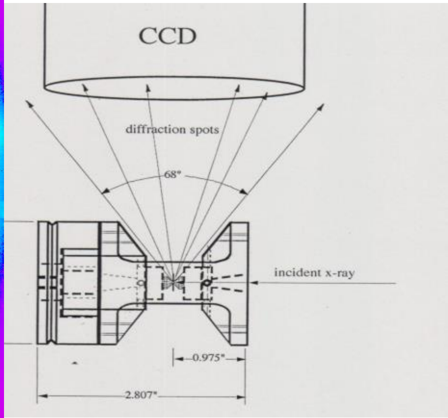
Mirror box

Ongoing research too extensive to cover

- **Fracture/stress localization in thin films**
- **Residual stresses/ deformation/ grain boundary network near welds**
- **Complex phase patterned materials**
- **Extreme environmental chambers**

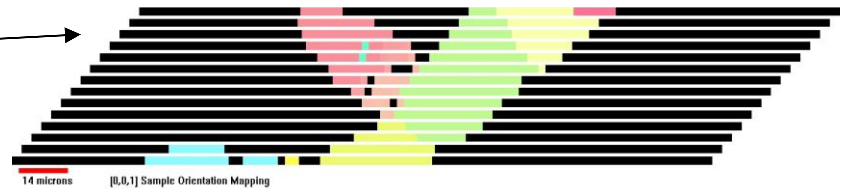


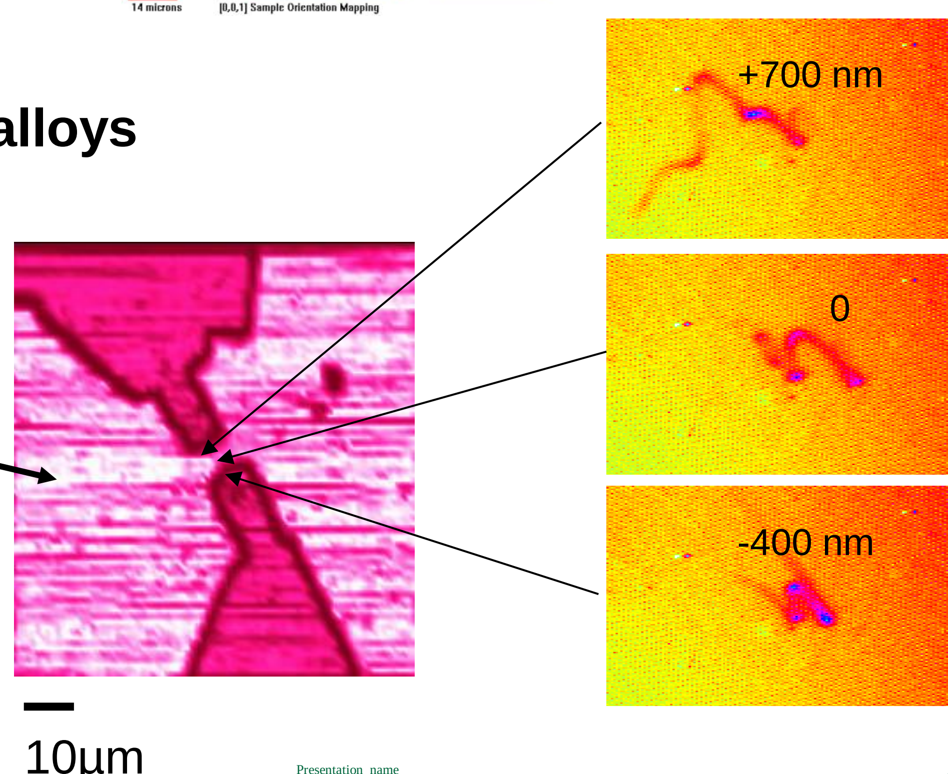




Ongoing too extensive continued..

- **Domain wall structure measurements**
- **Sn whisker growth**
- **High-performance alloys**
- **Nanomaterials**

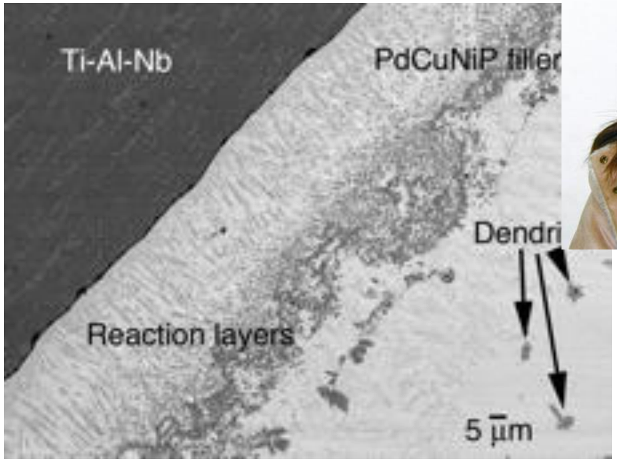




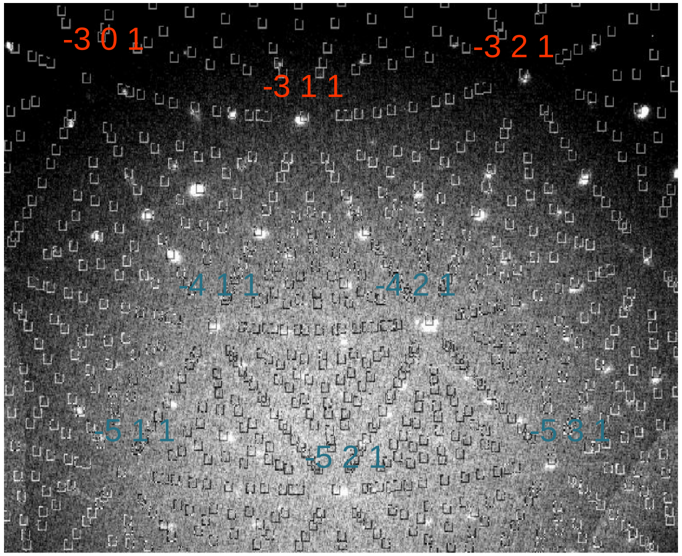
Energy scans allow structure determination

- **Generalization of orientation software can identify phases**
- **Energy scans provide integrated reflectivities.**
- **Identified two minor crystal phases tetragonal/hexagonal**

Cannot be found by powder

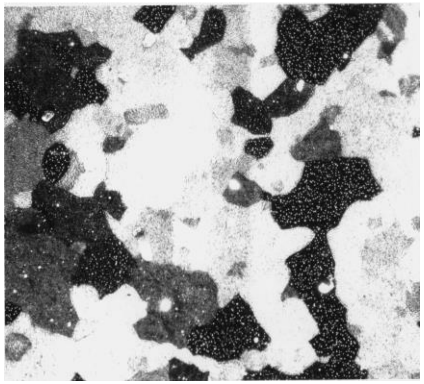


BAM braze $Pd_{40}Cu_{30}Ni_{10}P_{20}$

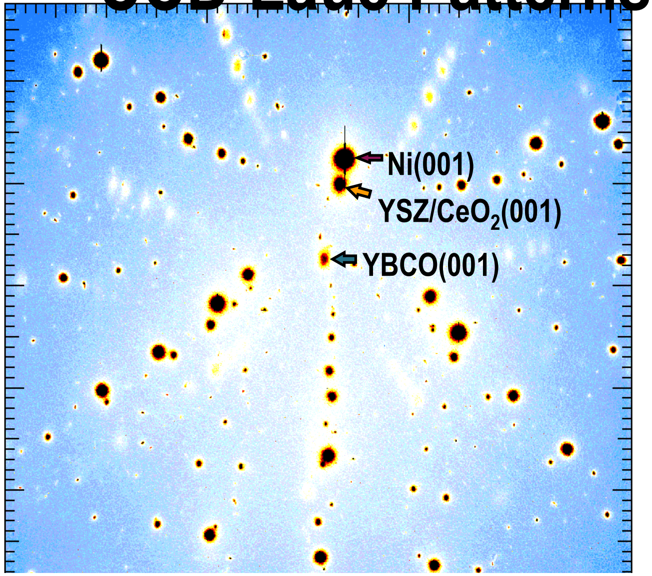


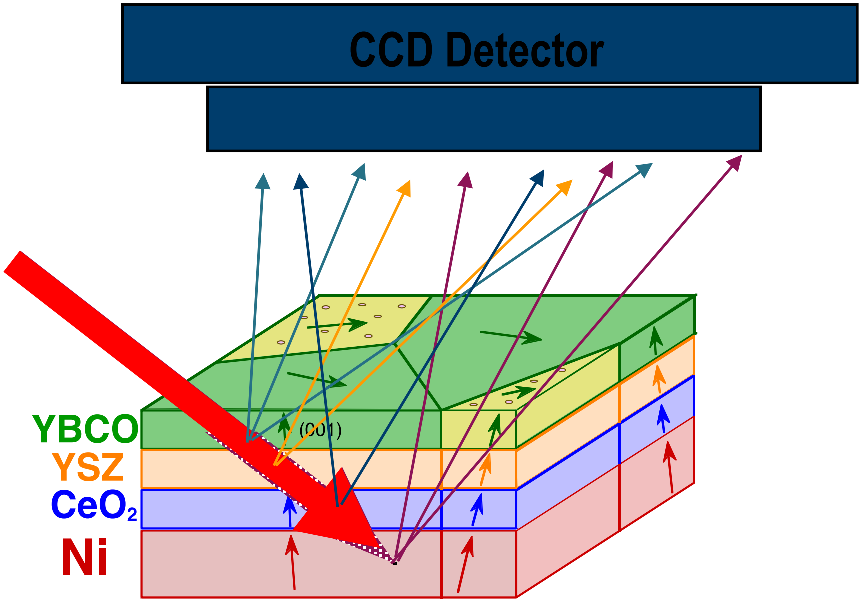
Grain-growth/ Budai et al. characterized epitaxial growth RABiTS

Optical: ~50μm grains



CCD Laue Patterns

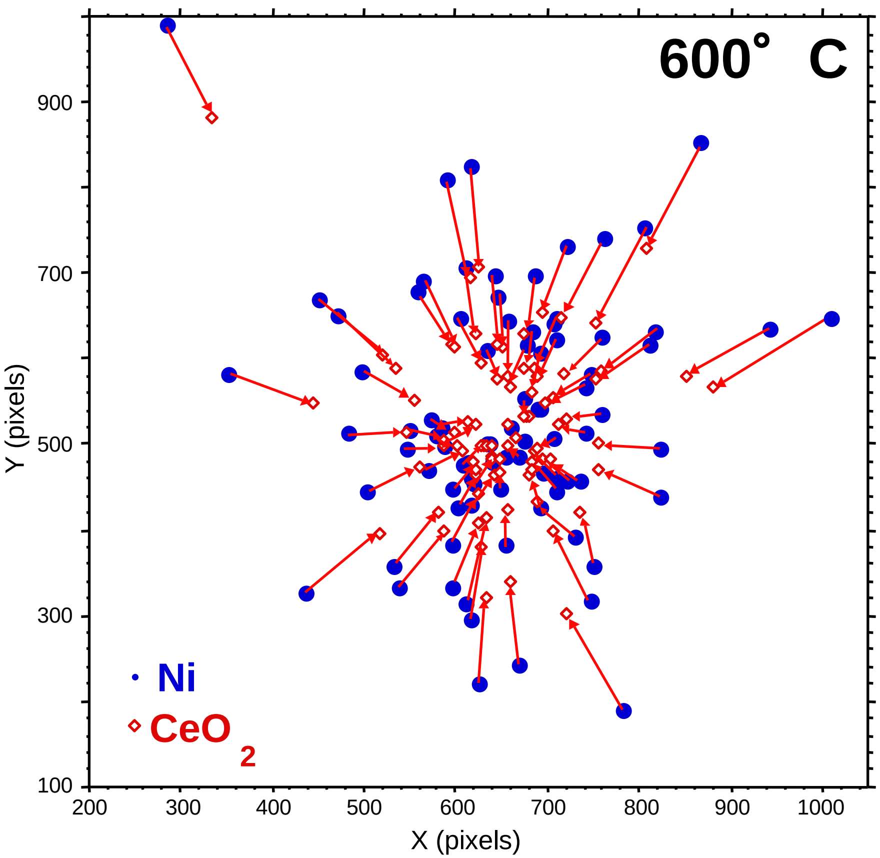


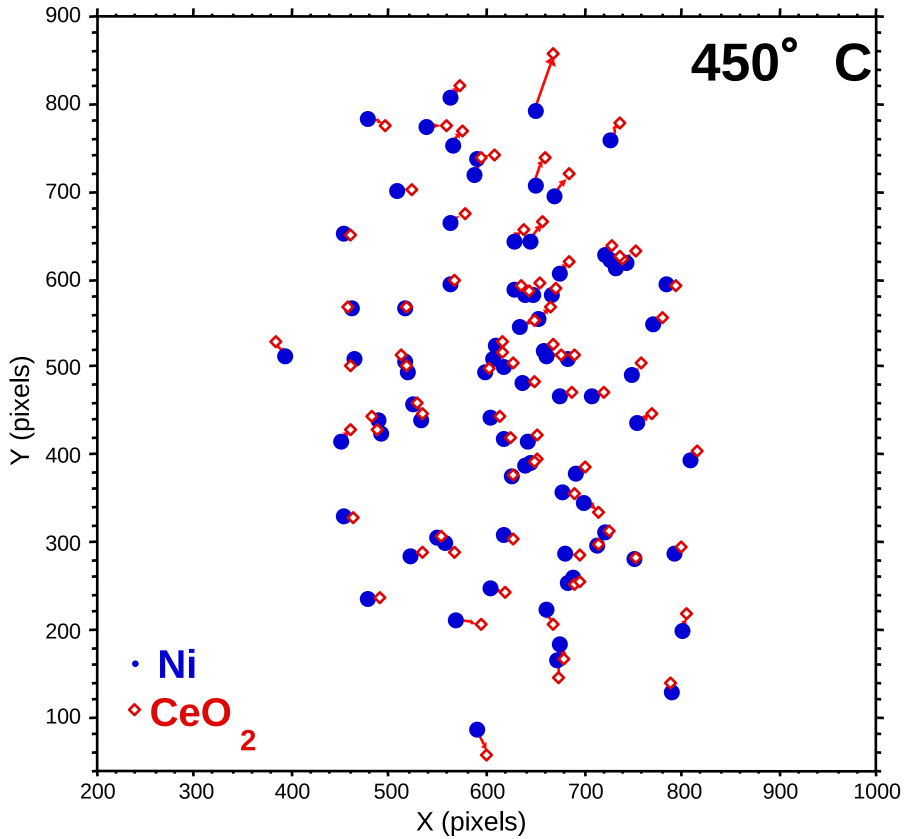


<u>CeO_2 Observation</u>:

Exact epitaxy for growth at low T; lattice tilts at high T

Relative CeO_2 orientation depends deposition temperature





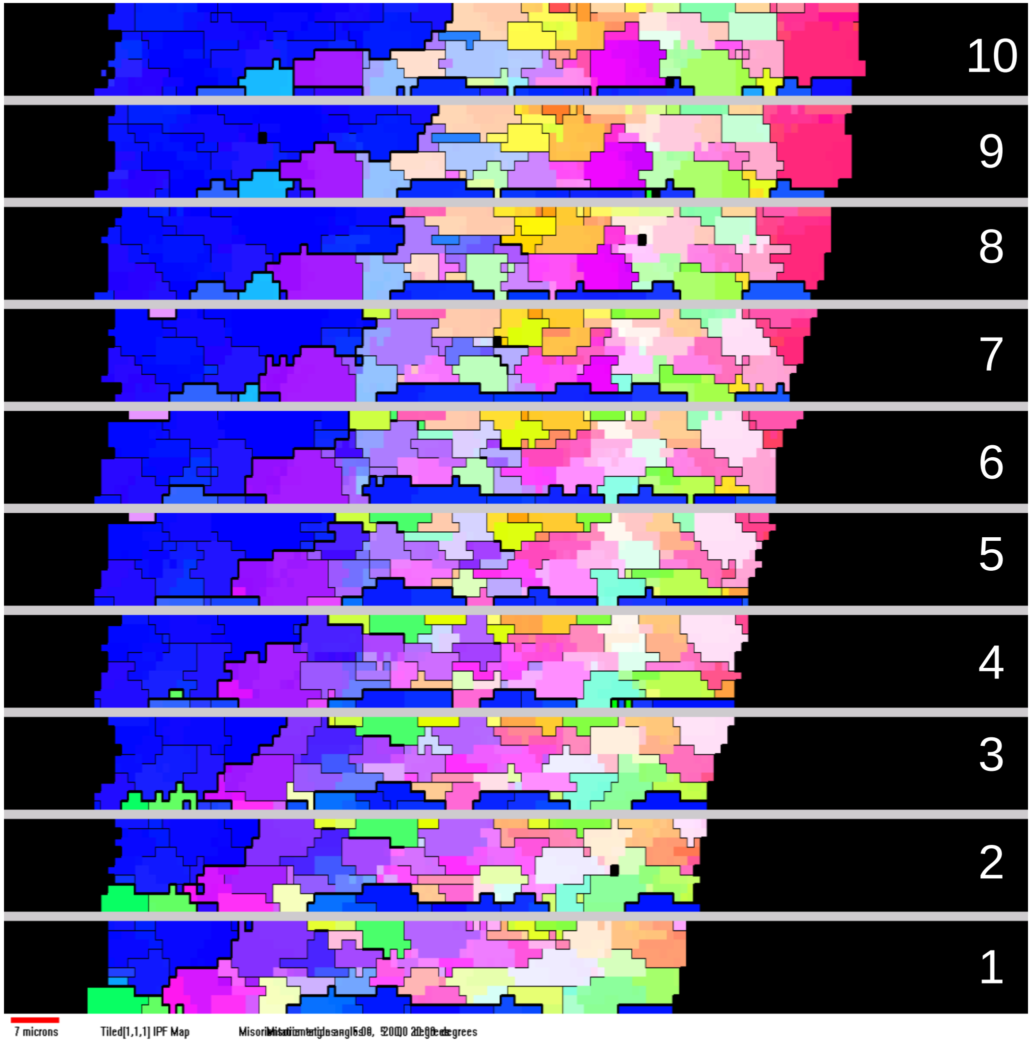
Step edge growth- good:

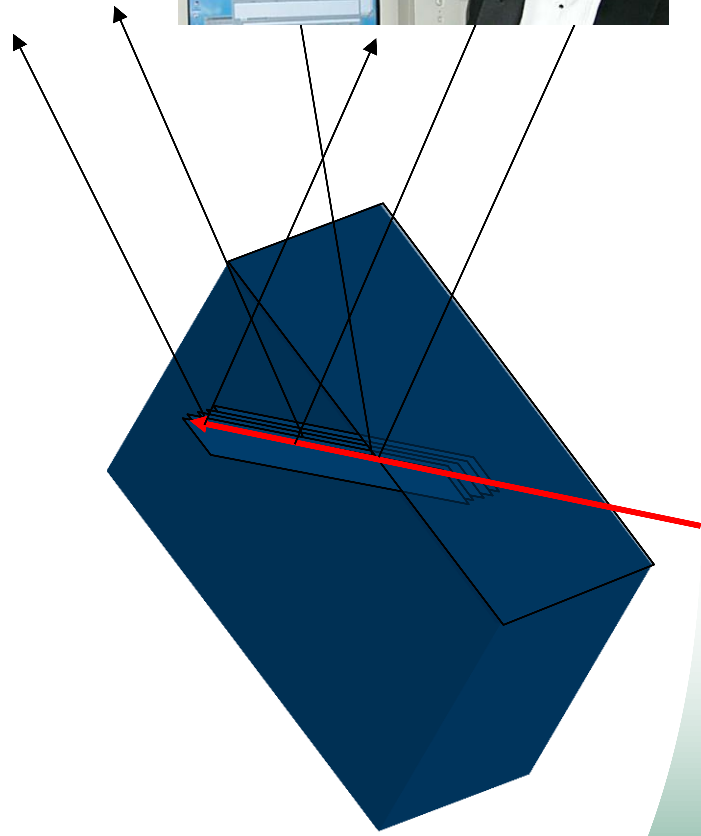
Crystallographic tilt towards ⊥

Tilt increases monotonically with miscut

Island growth-bad:

In-situ observations of 3D Grain Growth

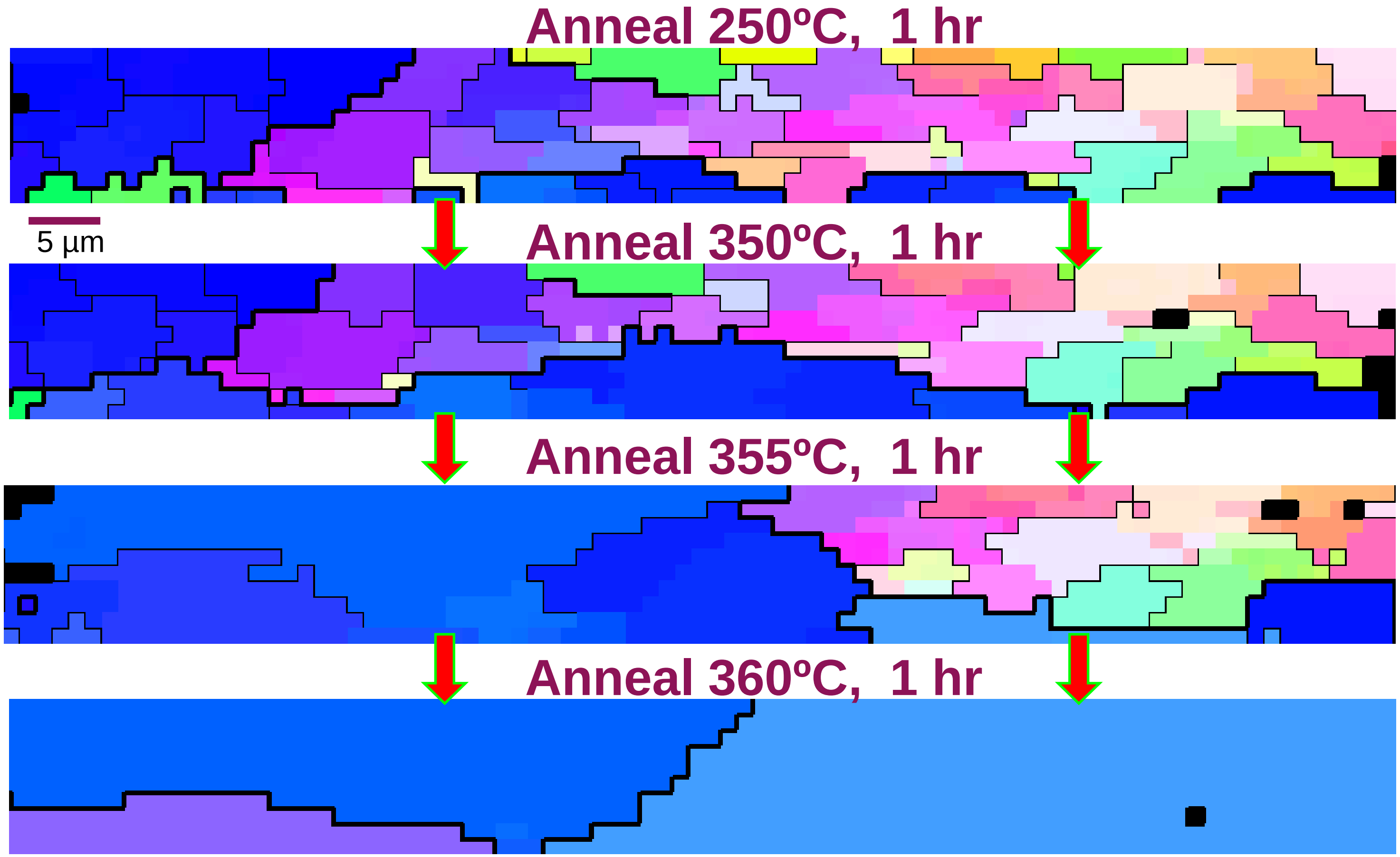




Hot-rolled (200˚ C
1xxx Al(~1%Fe,Si)
Alcoa Polycrystal

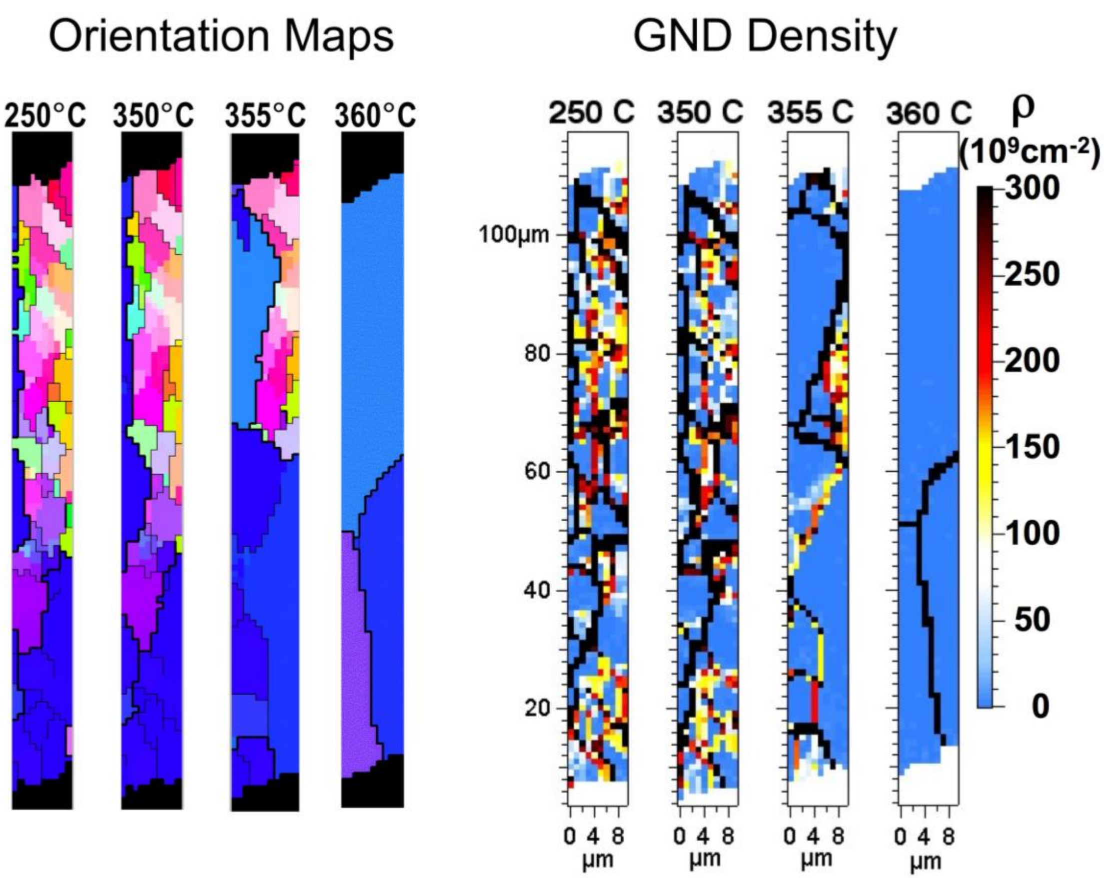
Thermal Grain Growth in Hot-Rolled Aluminum

1 µm pixels, Boundaries: 5˚ & 20˚



- GB motions include both high-angle and low-angle boundaries
- Complete and detailed 3D evolution needed for validation of theories.

Thermal Grain-Growth And Microstructure Refinement in Polycrystalline Al



- **3D X-ray Microscopy Measurements of Dislocation Density Finds Microstructure Refinement to Be Important**

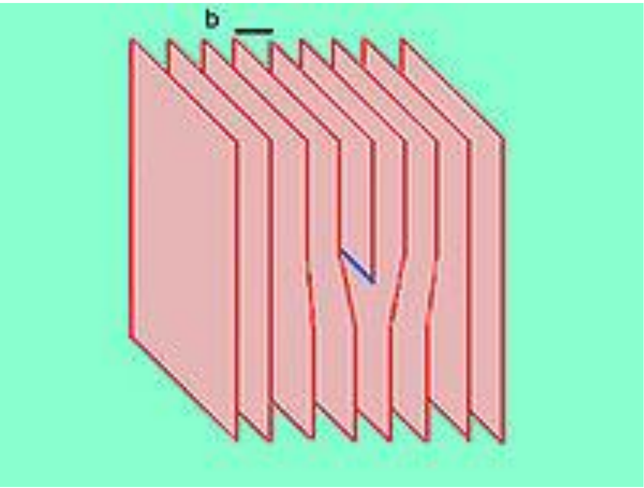
Deformation mediated by "dislocations"

- **Individual dislocations can be seen with TEM-but…**

X-ray people complain thin electron samples Fundamentally different

Neutron people complain thin X-ray samples Fundamentally different

What is "thin" and "bulk"?

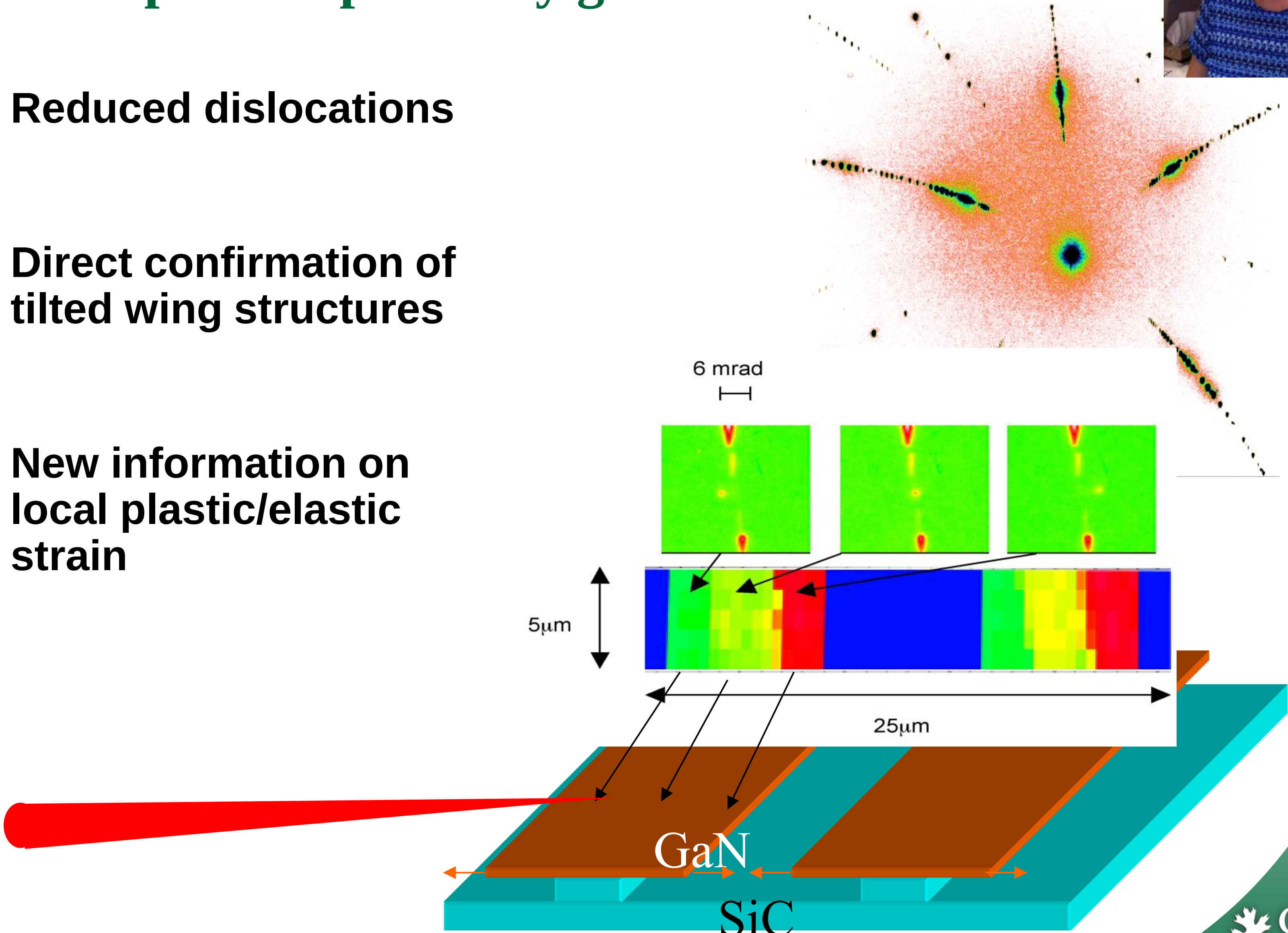


Edge dislocation

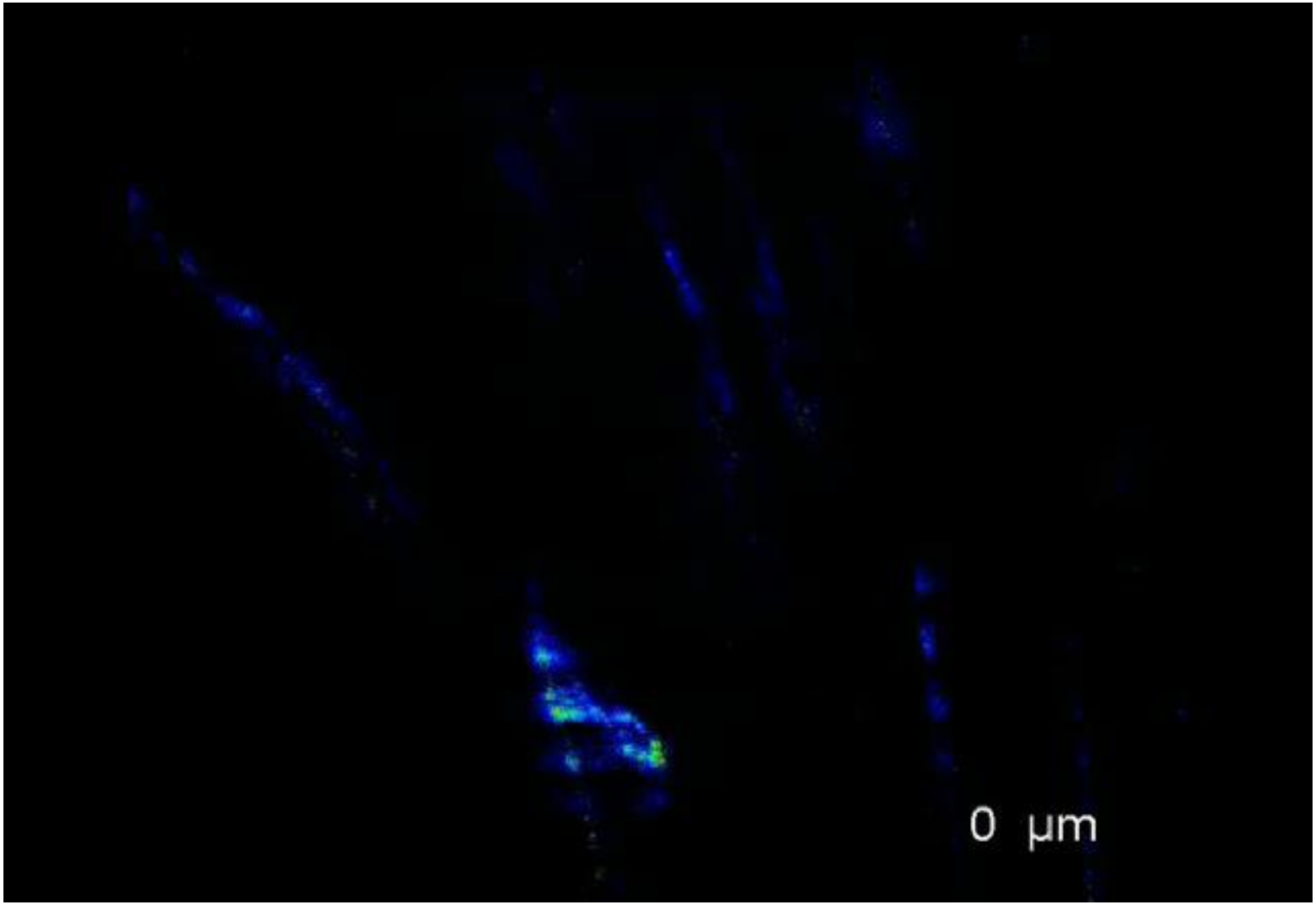
Screw Dislocation

Local orientation and plastic/elastic deformation mapped in pendeoepitaxially grown GaN

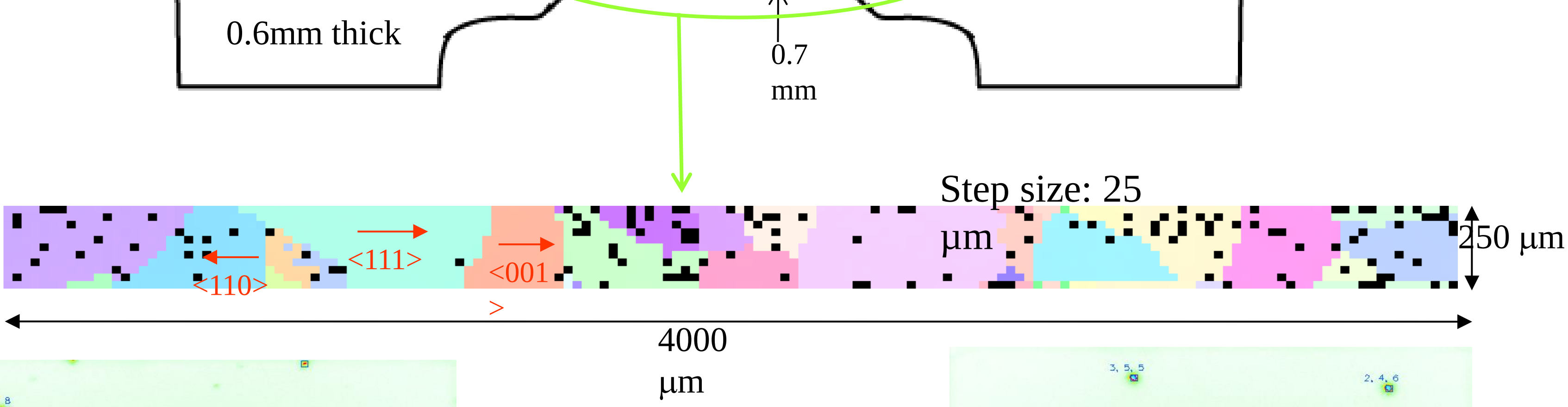
- Reduced dislocations
- Direct confirmation of tilted wing structures
- New information on local plastic/elastic strain

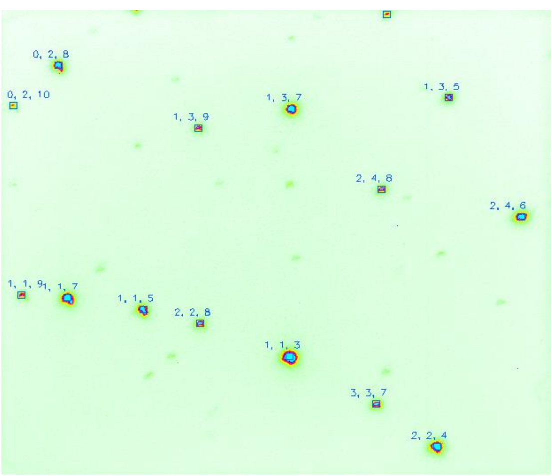


Deformation typically larger near surfaces/grain boundaries

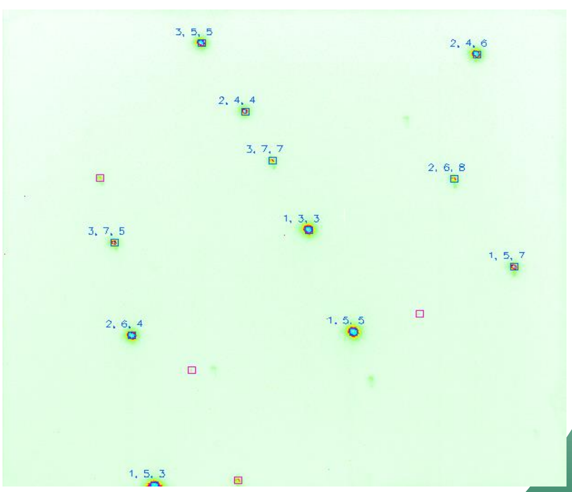


Deformation in polycrystals illustrates grain boundary behavior

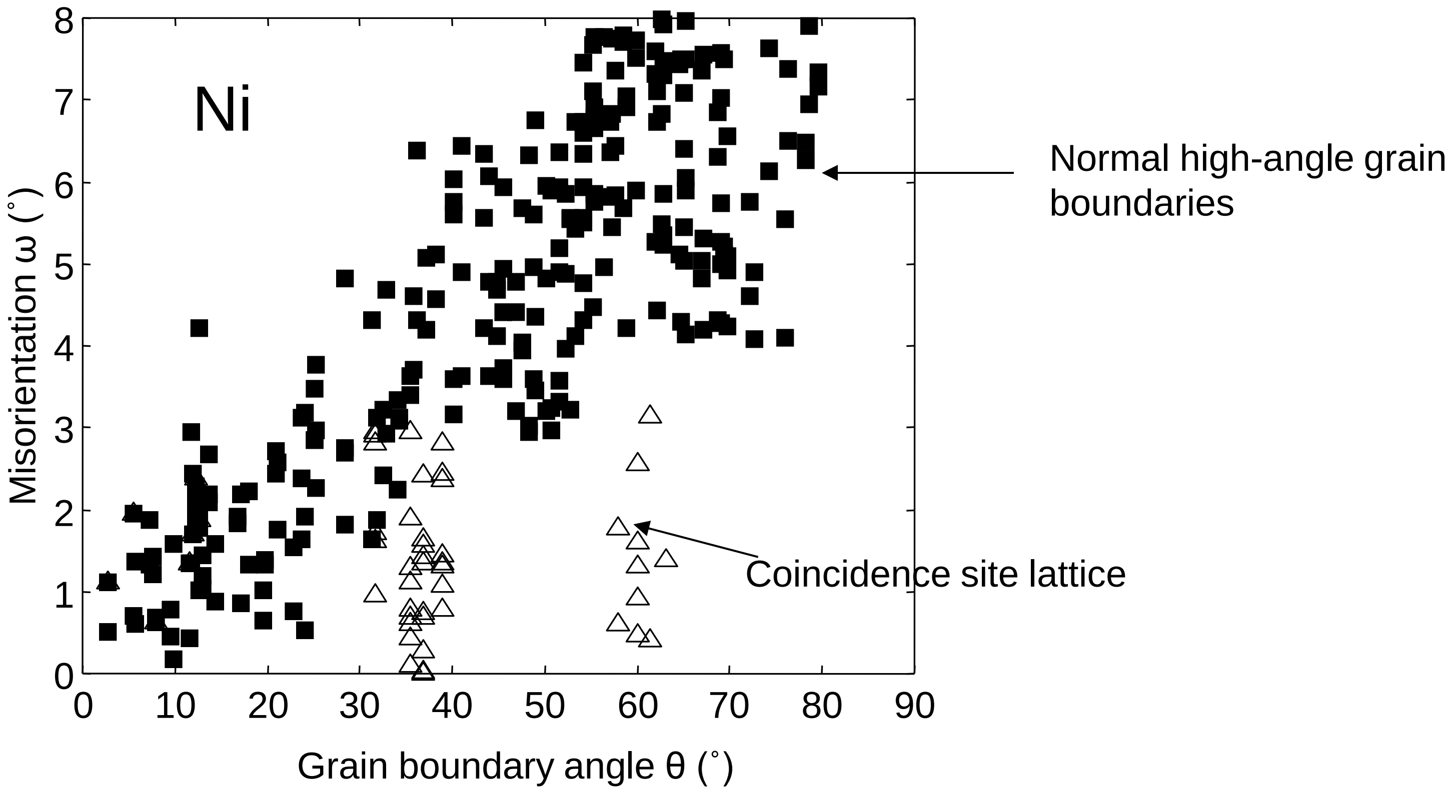




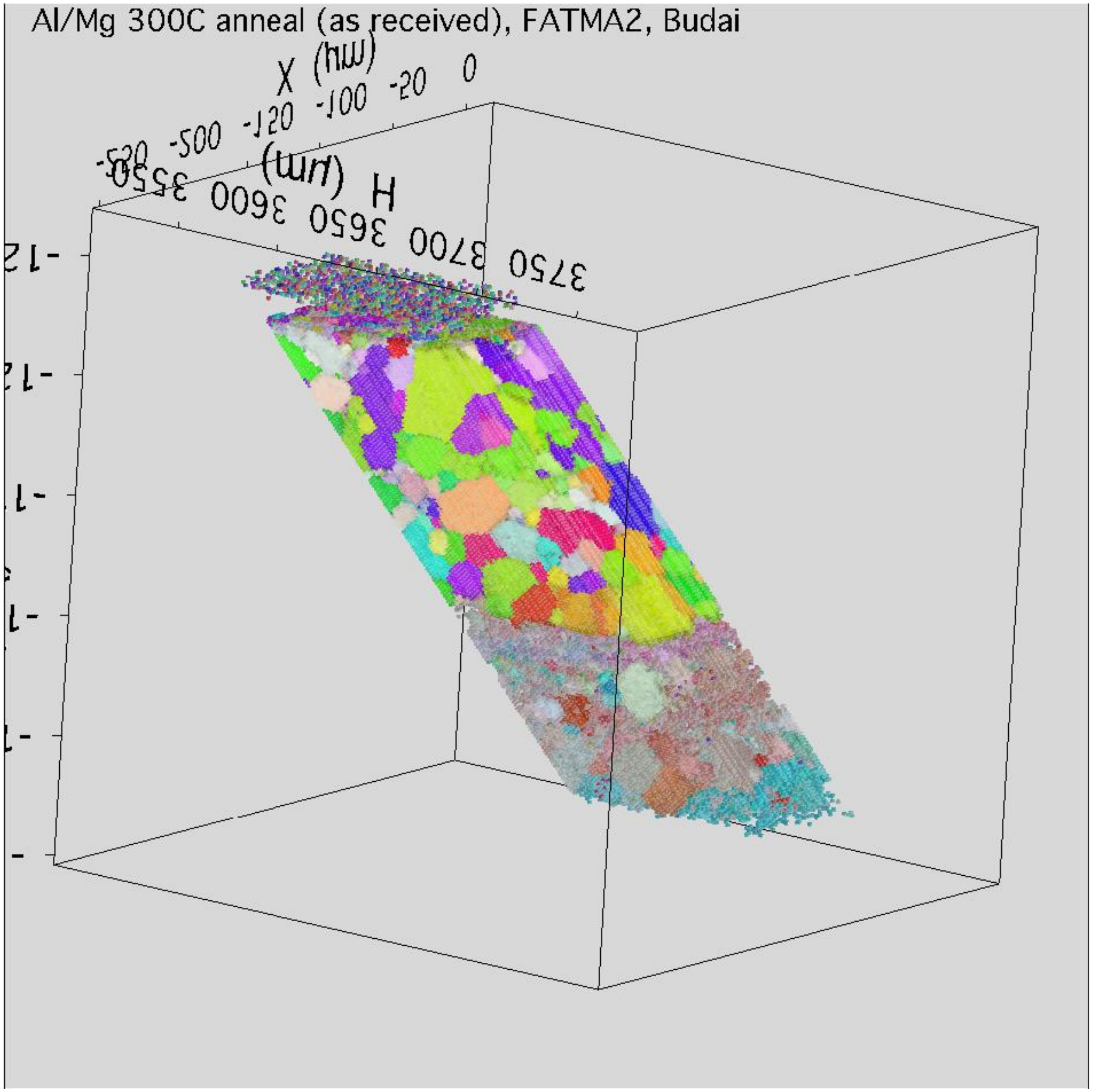
Indexation



Deformation induced rotations across grain boundaries sensitive to boundary type

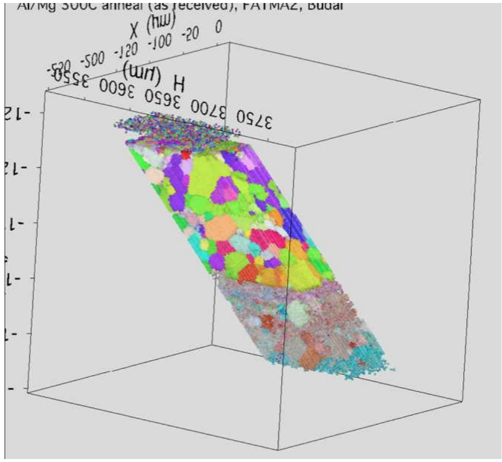


Submicron spatially-resolved crystallography opens new opportunities



Do neural networks provide a path forward?

- **Visualization of 3D tensor data unsolved problem**

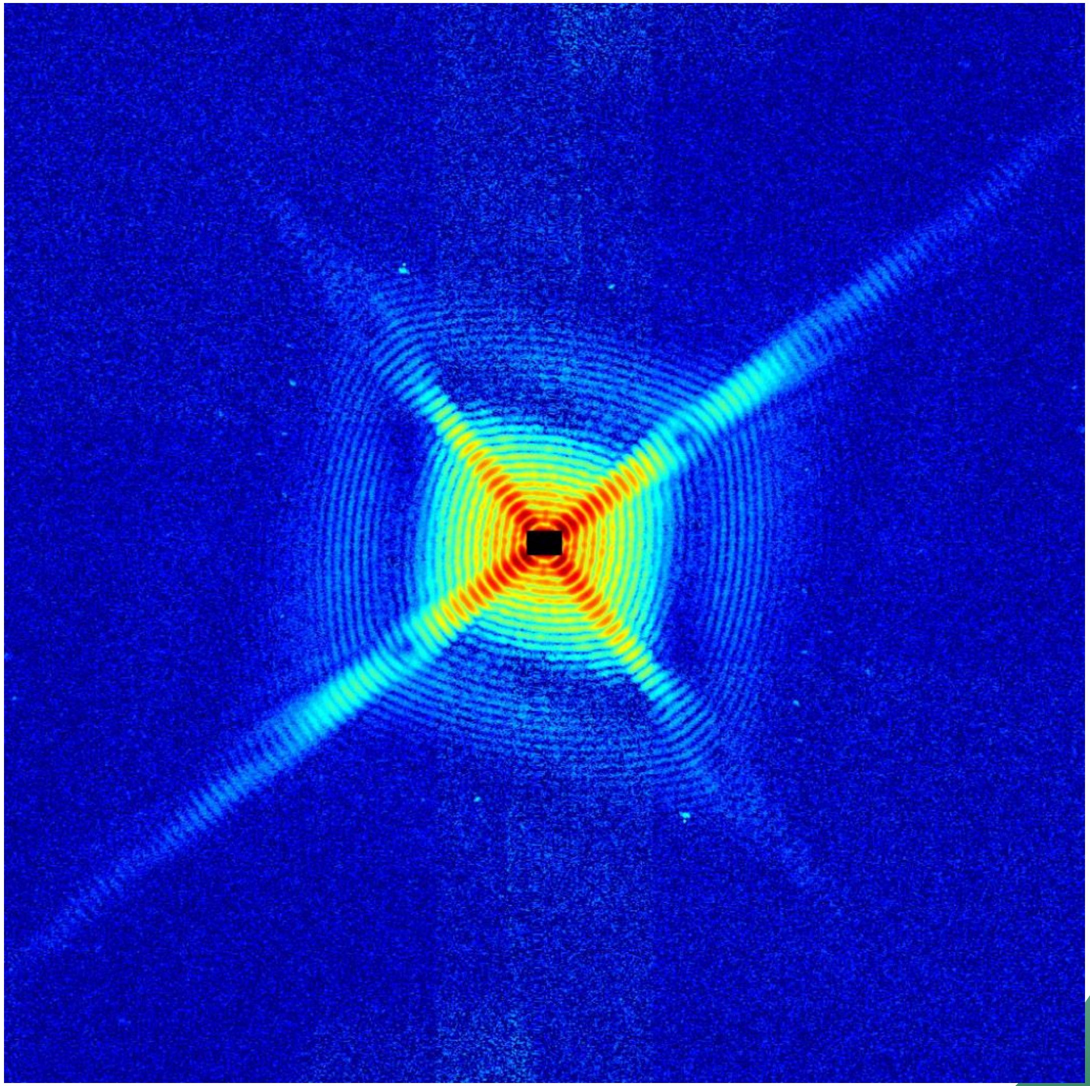


- **Human mind well adapted to 3D visualization based on binocular 3D data.**

- **Neural network not “limited” by streamlined processing of human brain**

Coherent diffraction offers promise for atomic resolution with focused beams

- Focusing
  - Better spatial resolution
  - Poorer field-of-view
- 2 nm with 3rd generation source and 1 µm focal spot
- 2 Å with 10 nm spot- or 4th generation source

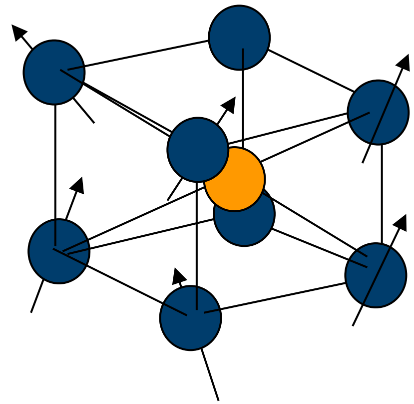


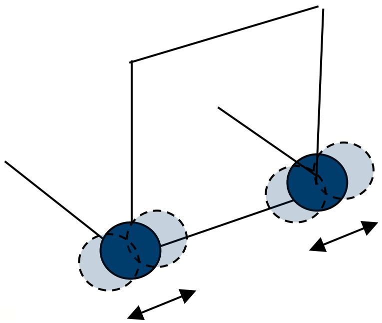
Neutron microdiffraction additional opportunities

Magnetism

Atomic motions

Low Z materials





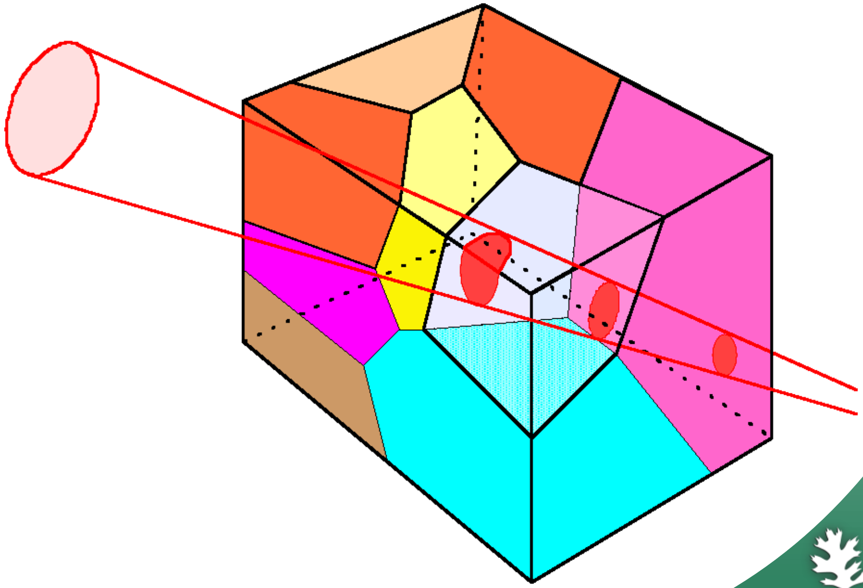
Nobel prize to Shull and Brockhouse

Focused beams extend neutron science

- **Inhomogeneous samples**

- **Small samples in environmental chambers**

- **Spatial resolved distributions deep in samples**



Even the most intense neutron source must be used efficiently

Neutron sources 10^{12} lower brilliance than advanced x-ray

Neutrons expensive 10^{13} more expensive!

10^{-16}\$ /x-ray

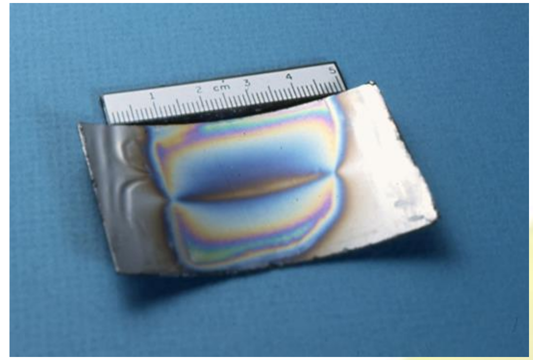
10^{-3}\$ /neutron

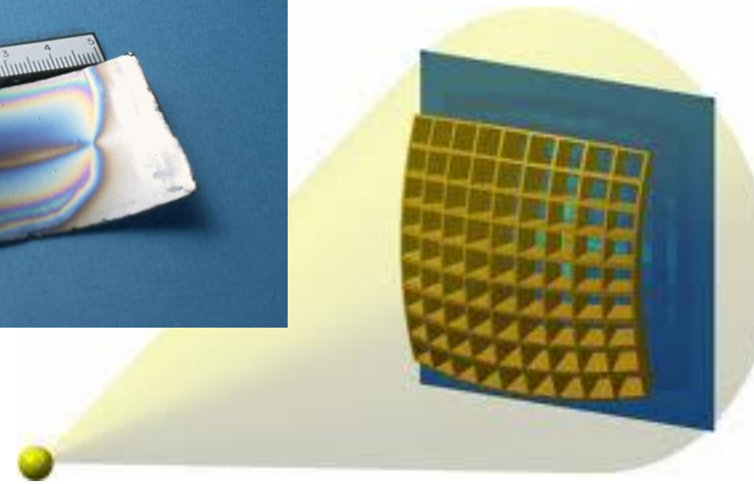
Increase divergence/bandpass

10^{-9}\$/ neutron

Neutron microfocusing optics evolving

- **Sagittal focusing optics < 300 μm**



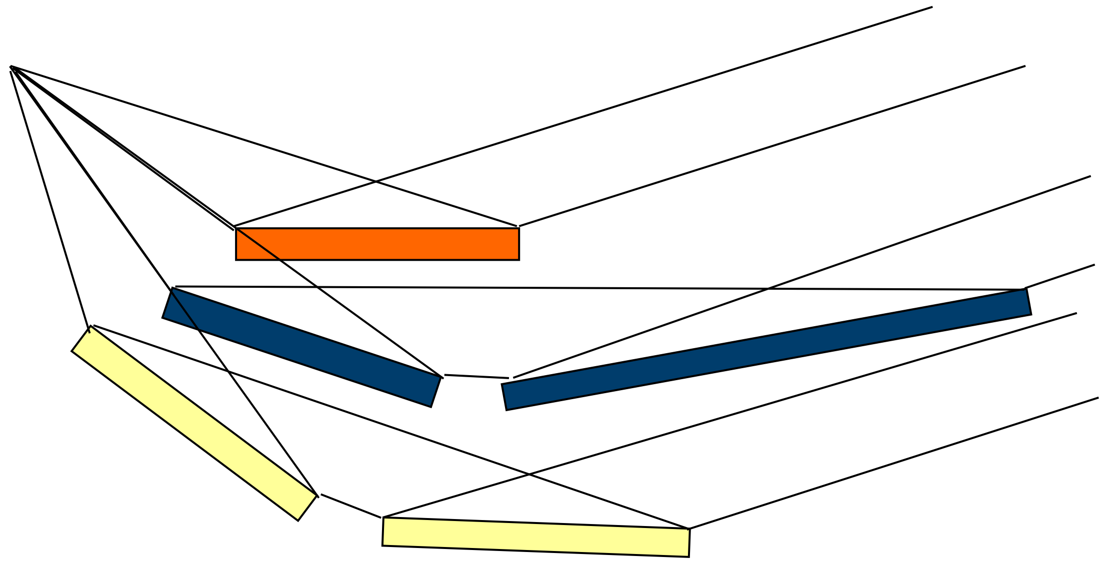


- **Lobster eye optics ?**

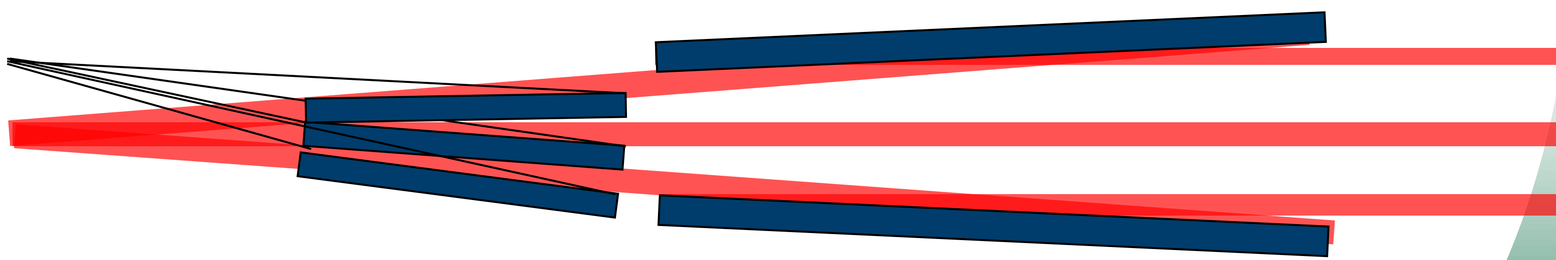
- **NMM <100 μm**

- **Wolter optics<200 μm**

"Deflected" KB™ can collect larger divergence



- **Basic element elliptical mirror**
- **Increase divergence with multiple reflections**
- **Optics within state-of-art**



2D Focusing complicated but possible

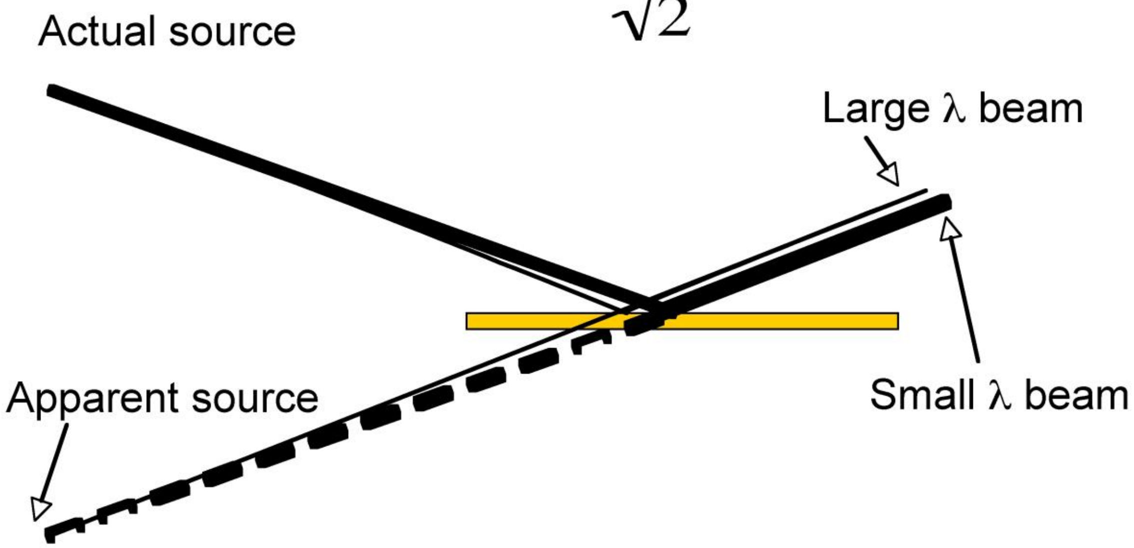
Gravity complicates polychromatic neutron microbeams

$$\Delta y_{total} \sim \frac{gF_1^2}{2v^2} M(1 - M)$$

Tricks to reduce dispersion

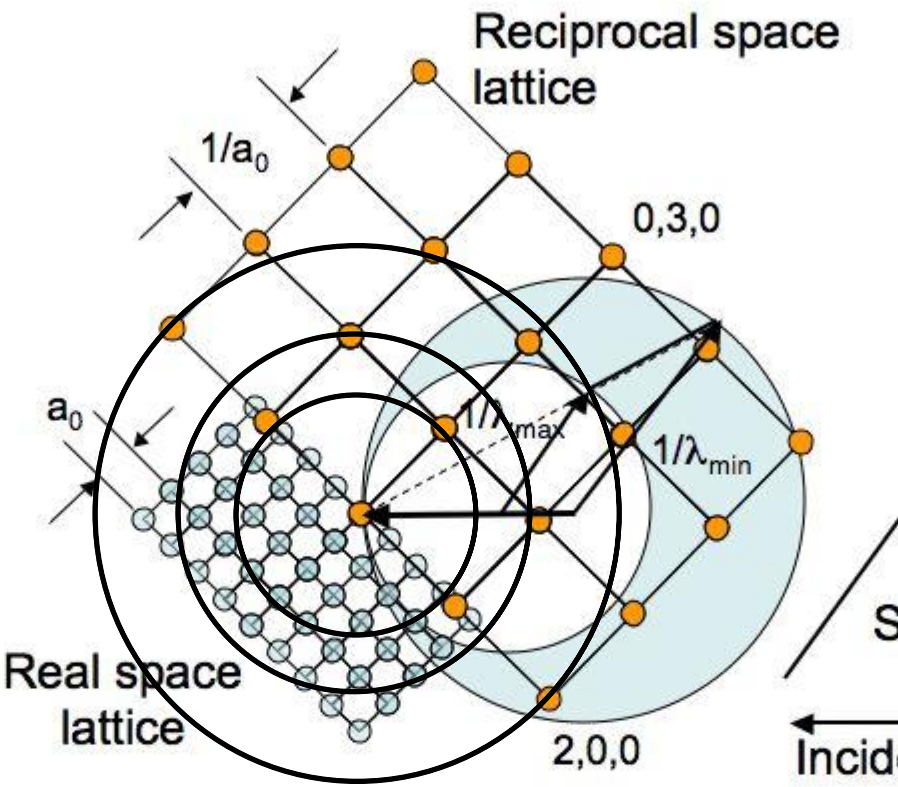
- M~1
- M small
- F_1 small
- Reflections

$$m = \frac{1 - \sqrt{2}}{\sqrt{2}}$$



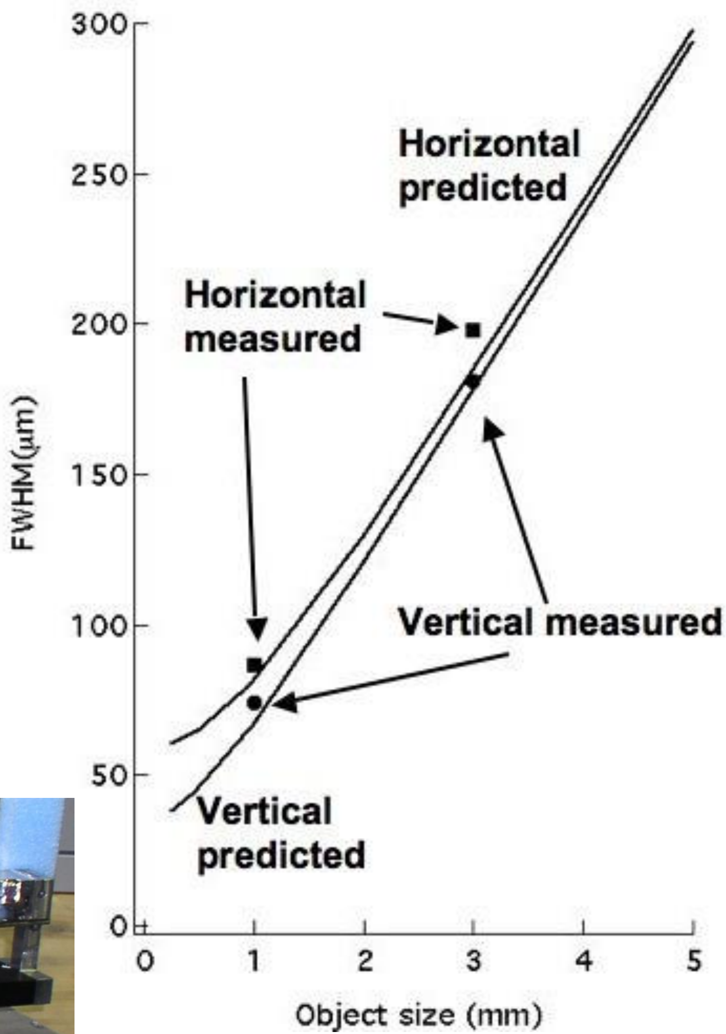
Spallation neutron science intrinsically polychromatic

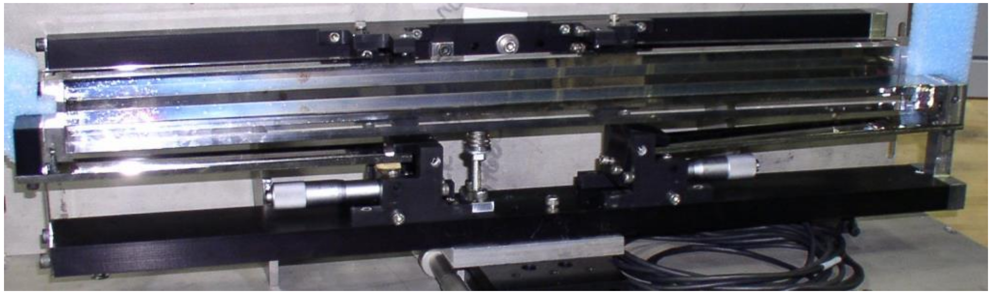
- **Analogous to polychromatic X-ray microdiffraction-*but includes* energy**
- **Allows for structure determination**
- **Absolute strain measurements**



SNAP experiments diffraction high pressure cells

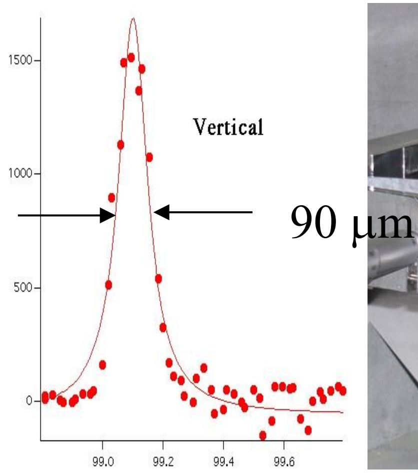
- **Focusing optics work near theoretical limit**
- **Minor improvements should enable 25 micron measurements**

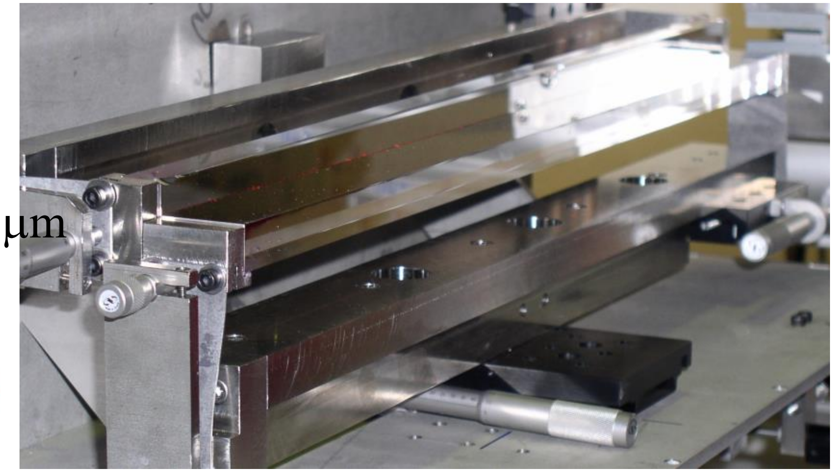


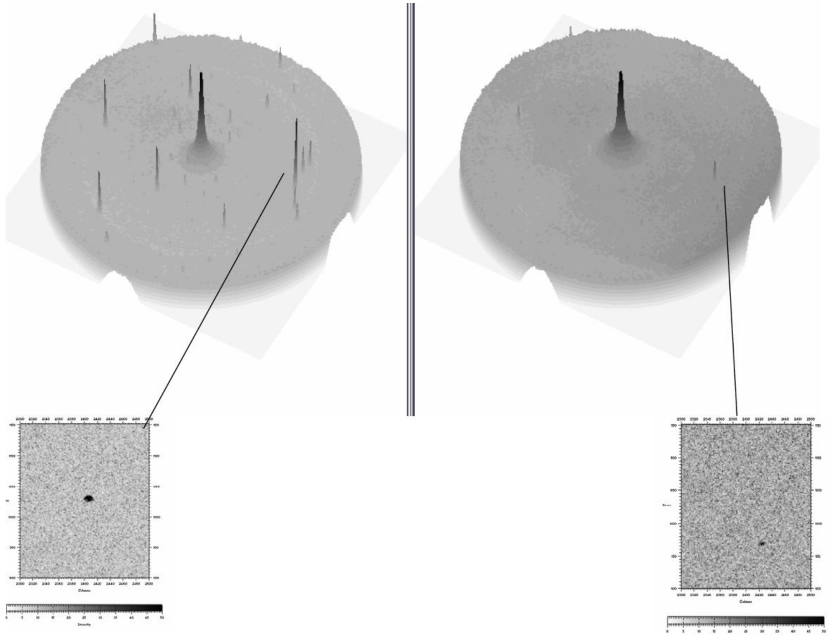


Neutron mirrors produce microbeams

- **Better signal-to-noise**
- **Resolve inhomogeneities**
- **Map crystal distributions**



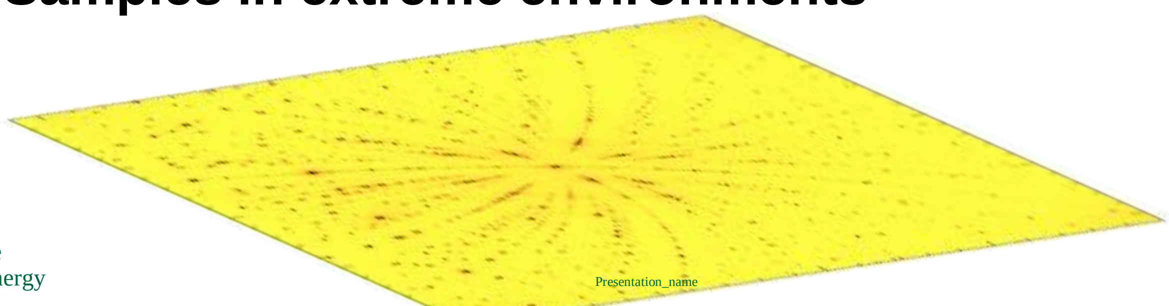




Useable 25 μm beams?

Conclusion: Microdiffraction

- Addresses long-standing issues materials physics
- Techniques and instrumentation rapidly evolving
- Answers specific questions about materials systems (Energy materials)
- Extend x-ray and neutron characterization to new classes of samples.
  - Dangerous
  - Inhomogeneous
  - Samples in extreme environments



Materials structure tiny- intrinsically 3D
And spatial resolution- is needed urgently
The frontiers moving quickly now-excitements in the air
Though ask the average person- they really couldn't care

CHORUS

Nondispersive - optics change what we can see
Mesostructure- resolved by crystallography
Atomic defects quantified - so that we can surmise
Emergent structures origins- at the mesoscopic size

New optics and new methods- extend what we can do
With spatial resolution- time resolution too
Nondestructive lets us watch- materials deep inside
Chambers or complex system - where once they could hide

Emerging applications- I've tried to show a few
Energy materials- have challenges quite new
With x-ray and neutron beams- we now are freed
To study these materials- on the scale that we need