Coherence, speckle, and imaging for atomic and nanoscale studies of materials

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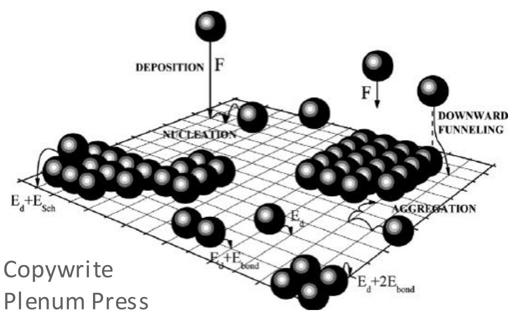
Topics

- What can we learn about materials with x-rays?
- What is coherent x-ray diffraction?
- How do x-rays interact with crystals?
- Imaging strain in single nanocrystals with phase retrieval.
- Principles of ptychography.
- Measuring time evolution of atomic structure with XPCS

Materials behavior and properties at the nanoscale

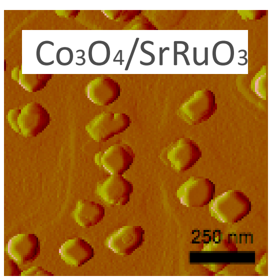
- Materials design enters new realms of possibility and flexibility at 10-100 nm.
- Properties are often different than the bulk, and interfaces play a huge role.
- Atomic-scale dynamics dictate behavior.

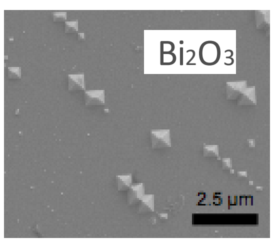
Materials synthesis



Copywrite Plenum Press 1997

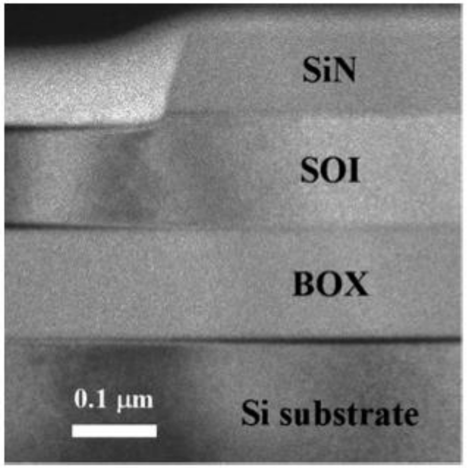
Epitaxial Heterostructures





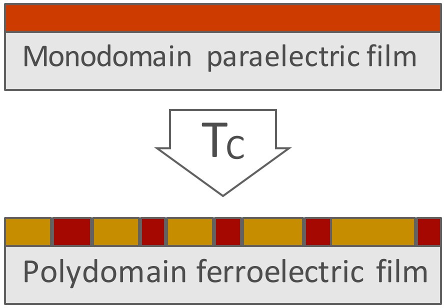
Device physics

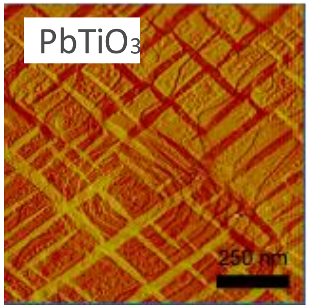
Strained silicon-on-insulator



Murray et.al., J. Appl. Phys. **104,** 013530,2008

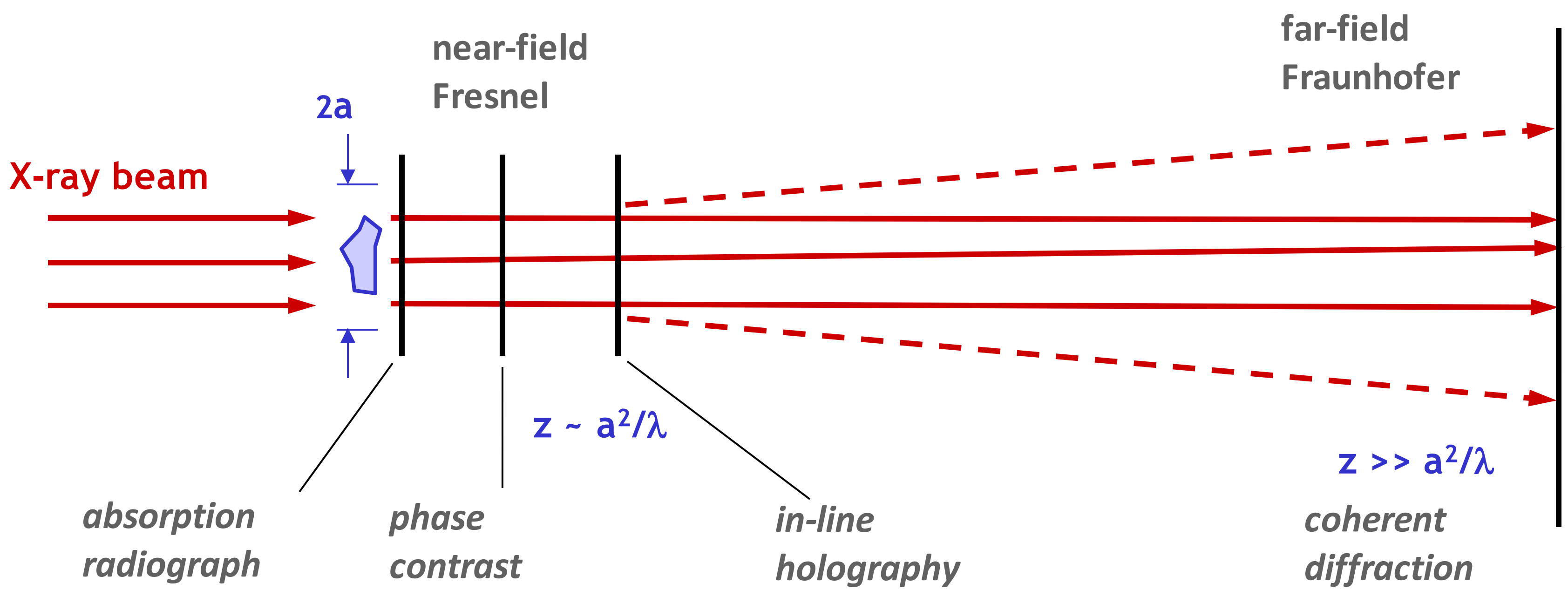
Phase transitions



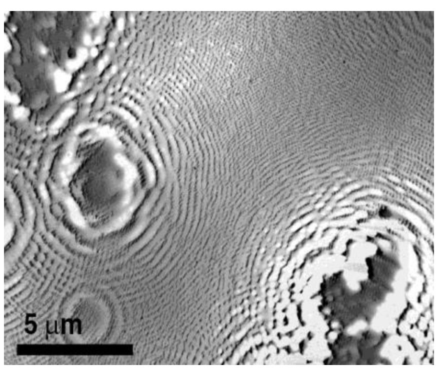


Visualizing lattice behavior and measuring dynamics in these materials is key!

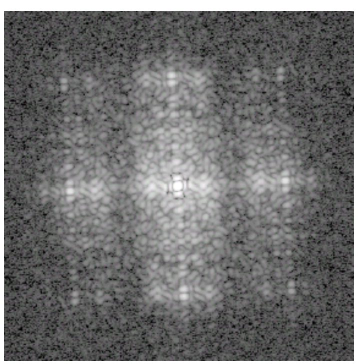
Interaction regimes with coherent x-rays



Kagoshima (1999)

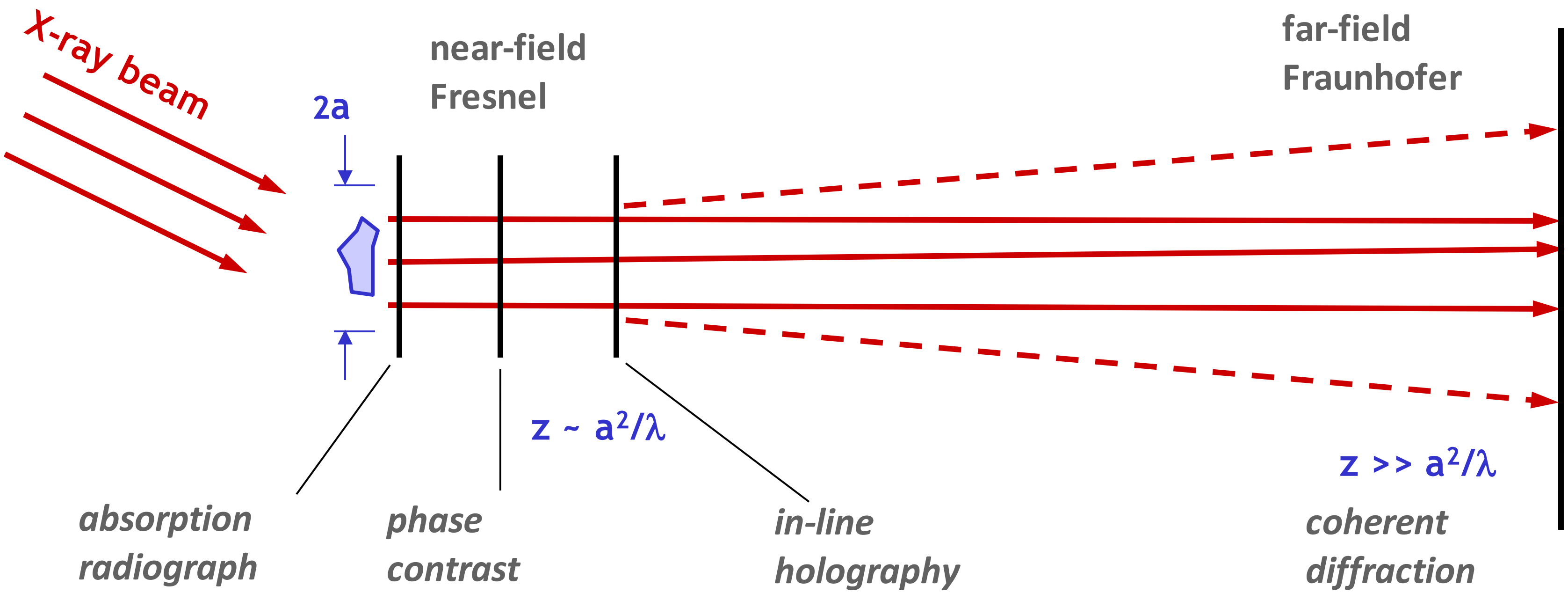


Jacobsen (1990)

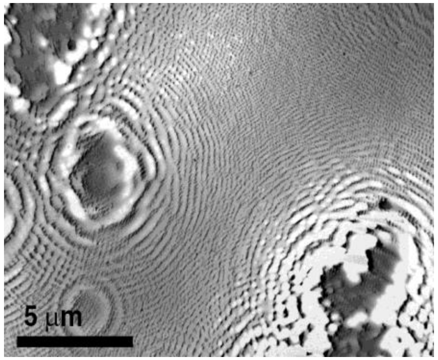


Miao (1999)

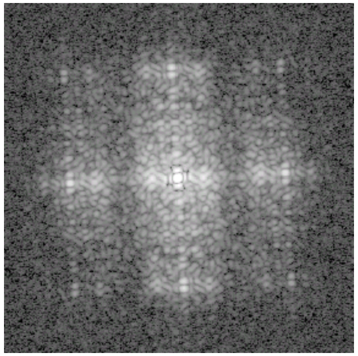
In crystals, regimes also apply in the Bragg geometry



Kagoshima (1999)



Jacobsen (1990)

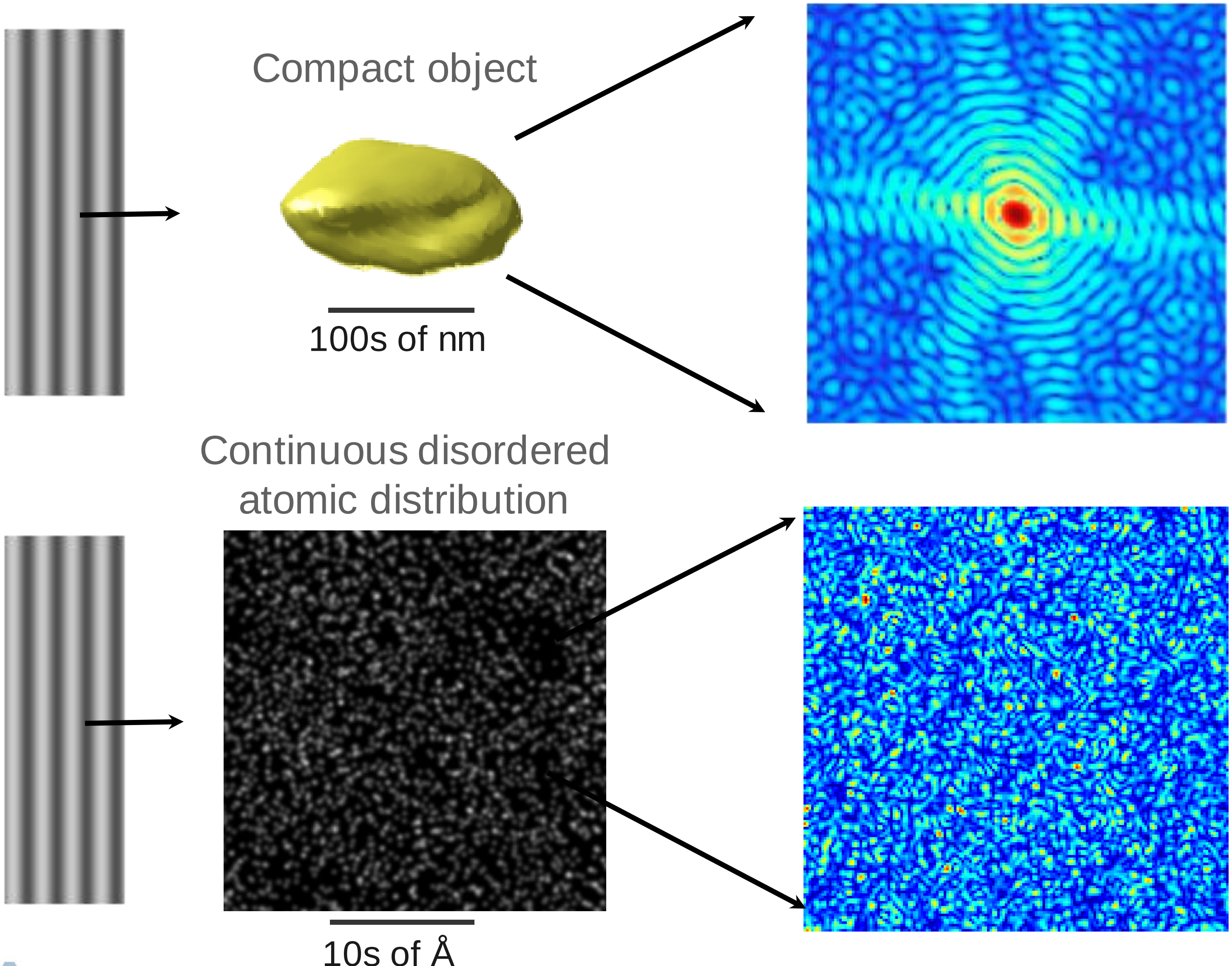


Miao (1999)

Coherent speckle in high-angle scattering

Incident x-ray coherent wavefront

Complex wavefront exits sample



Basis of coherent imaging

Basis of photon cross-correlation spectroscopy

X-ray and materials science

Advantages:

- **Wavelengths commensurate with typical unit cell size.**
  - **Diffraction-based techniques can link material structure to properties and dynamics**
- Weakly interacting with matter.
  - Multi-keV x-rays can penetrate gaseous and liquid sample environments and can access buried regions of interest in solid samples.
- Coherence lengths achievable from angstroms to tens of microns
  - Enables visualization of structure over these length scales
- Hard x-ray energies correspond to electron binding energies in elements
  - Enables elemental and band structure sensitivity via spectroscopy
- X-ray pulse widths available commensurate with atomic-scale dynamics

Disadvantages:

- Weakly interacting with matter
  - Techniques often require extremely bright x-ray sources for signal-starved experiments
- Low scattering cross-sections for low-Z elements

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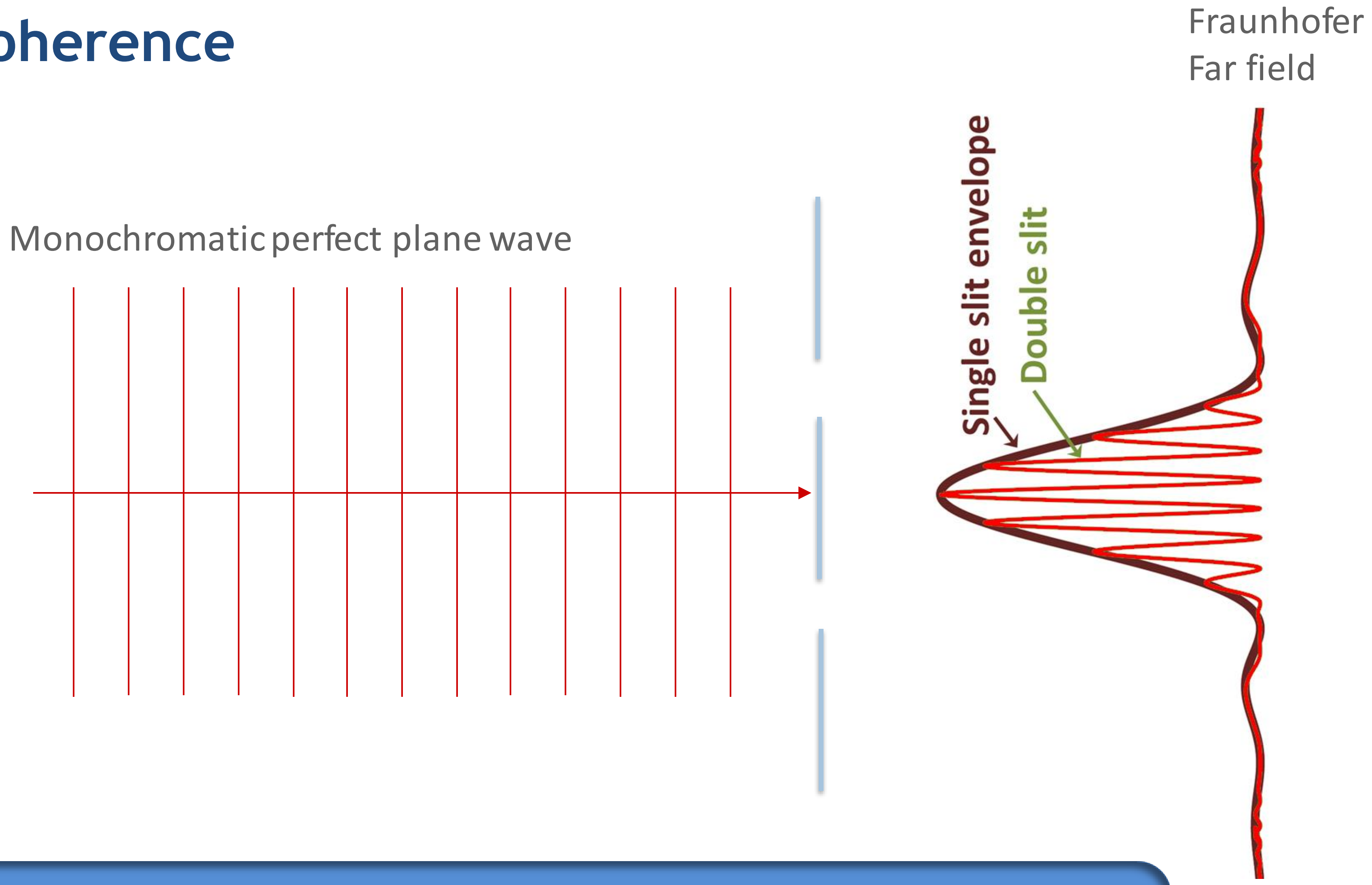
Coherence

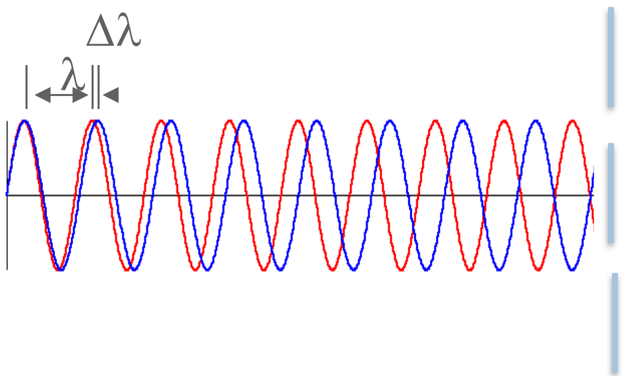


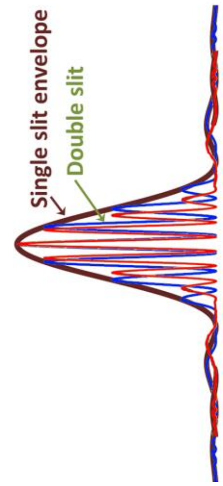
If the beam is coherent across the slit spacing, a Fourier Transform of the slit structure is created downstream.

In real life coherence is limited

Modeled as superposition of independent sources

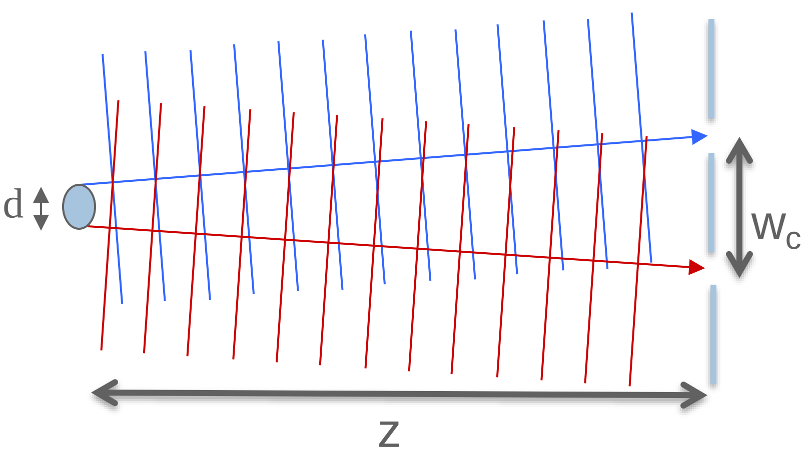
longitudinal coherence

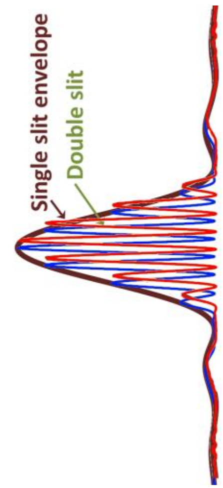




$$l_c \sim \frac{\lambda^2}{\Delta\lambda}$$

transverse coherence





$$w_c \sim \frac{l\,z}{d}$$

3rd gen synchrotron sources produce coherence lengths of tens of microns that dictate experimental design.

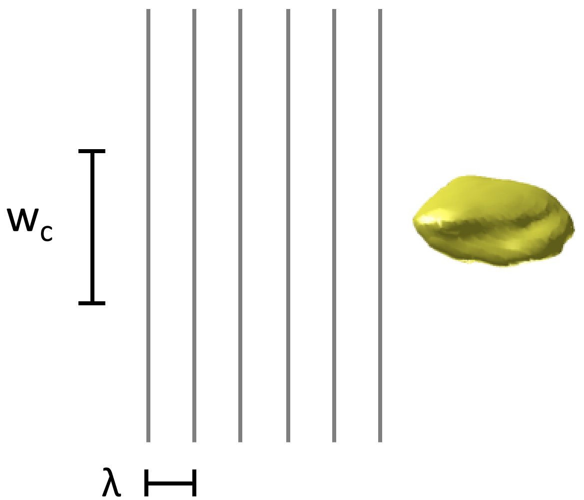
The Advanced Photon Source, your local synchrotron

The Advanced Photon Source at Argonne contains a relativistic electron orbit dedicated to generating x-ray photons.

The x-ray coherence will greatly improve with the planned APS Upgrade

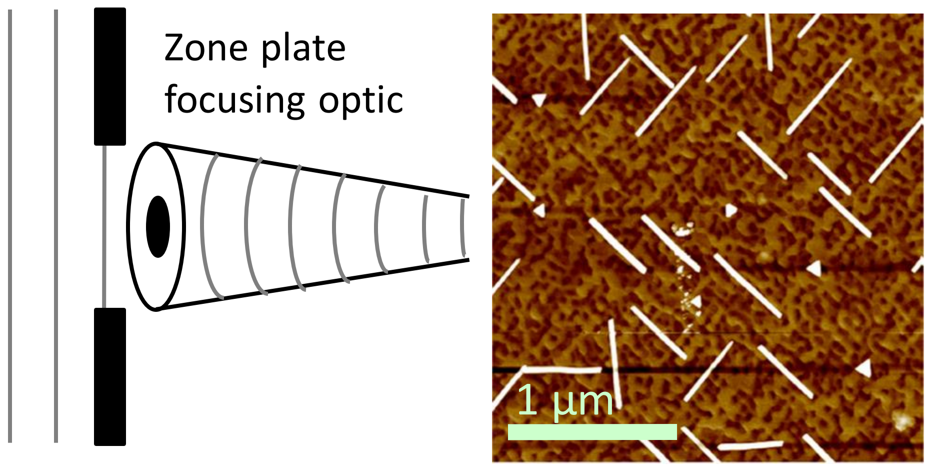
Designing imaging experiments with coherent beams

Coherently illuminating a small single crystal



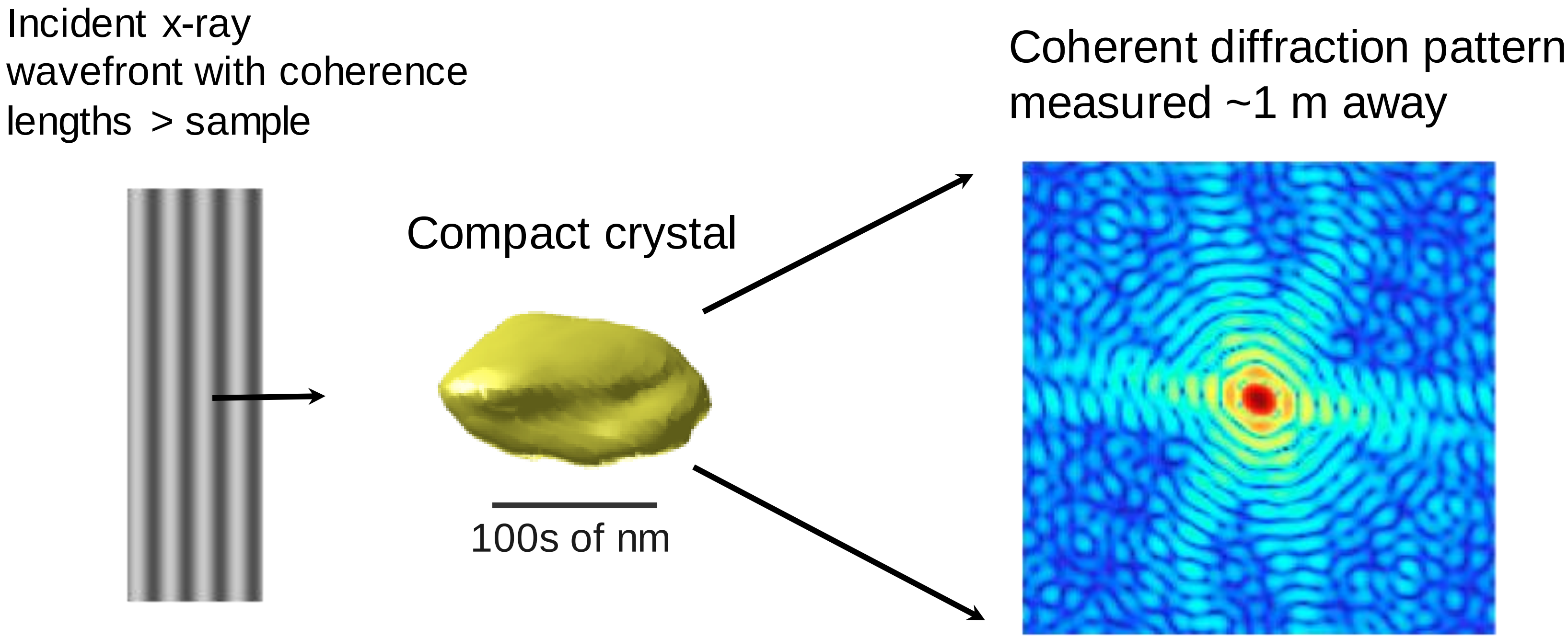
3D imaging with Bragg coherent diffraction imaging (BCDI)

Tightly focusing the beam



Diffraction-limited spot for Bragg coherent nanodiffraction of extended crystals

Coherent diffraction imaging



Direct inversion of pattern is not possible.

Phase retrieval reconstructs image from diffraction pattern.

Why phase retrieval? The phase problem

- X-ray diffraction could be easily convertible to real space because of the Fourier relationship between reciprocal space (where we do the measurement) and real space (where we desire structural information).

- Problem: x-ray detectors pixel area are only capable of measuring the energy deposited by an x-ray.

$$\Psi = A \times \exp[i\phi] \qquad E \propto |\Psi|^2$$

The phase is not measured, making phase retrieval a classic and ever-present challenge in x-ray crystallography.

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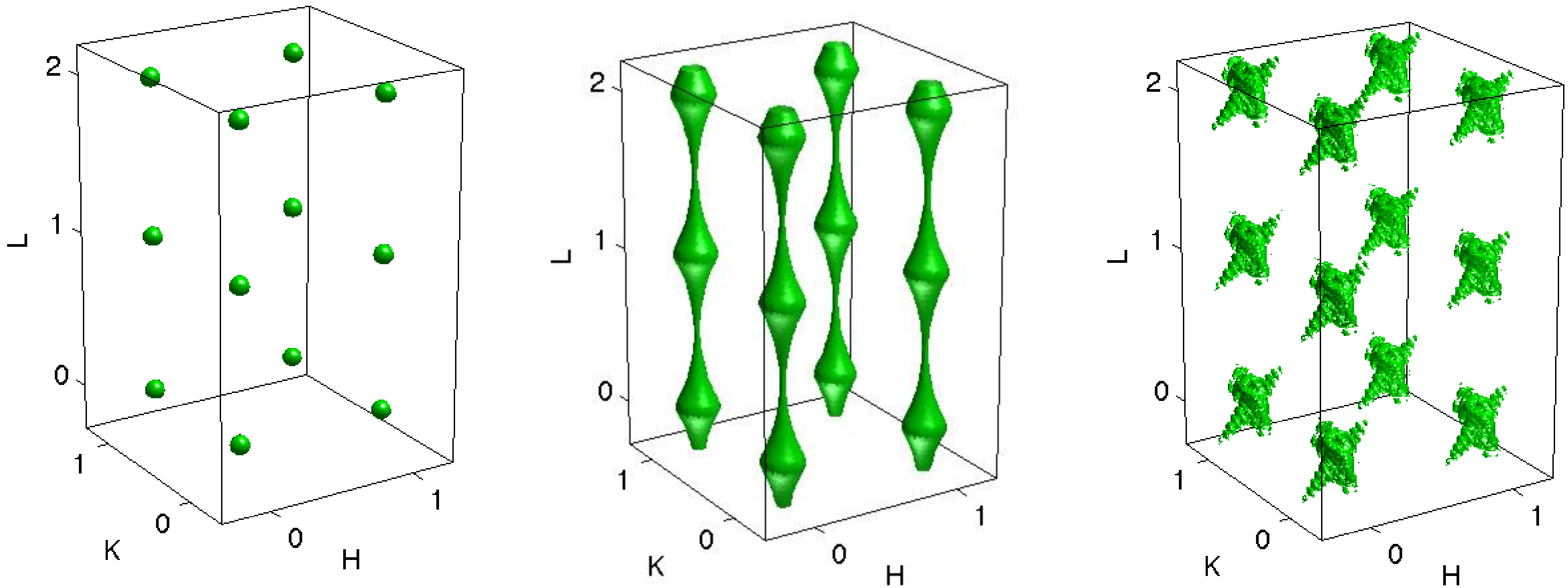
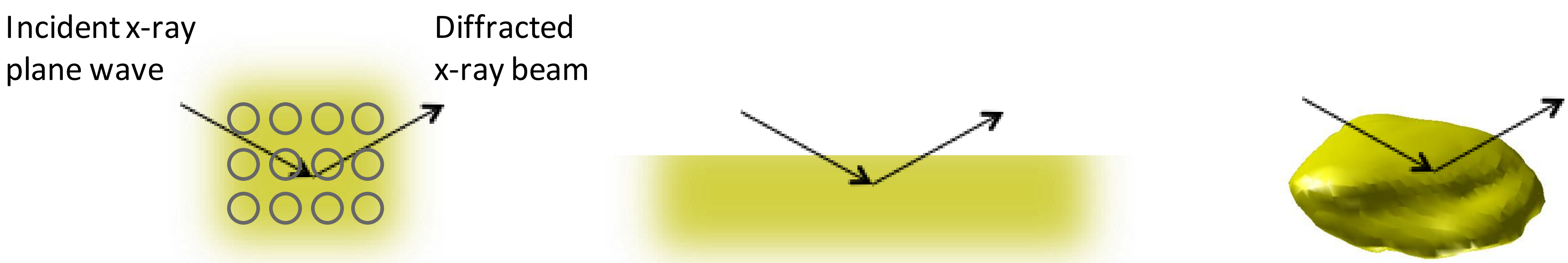
Reciprocal space with single crystal x-ray diffraction



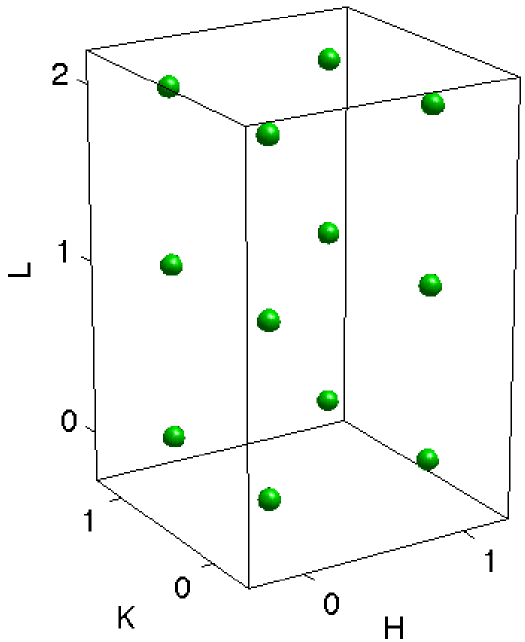


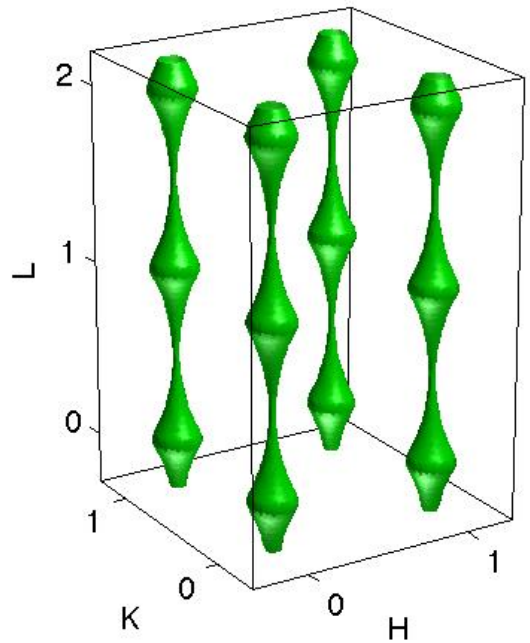
Diffraction from a bulk single crystal

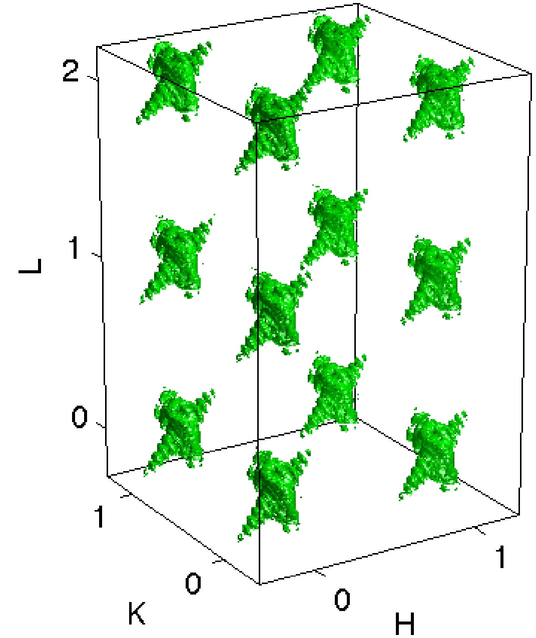
Diffraction from a truncated crystal

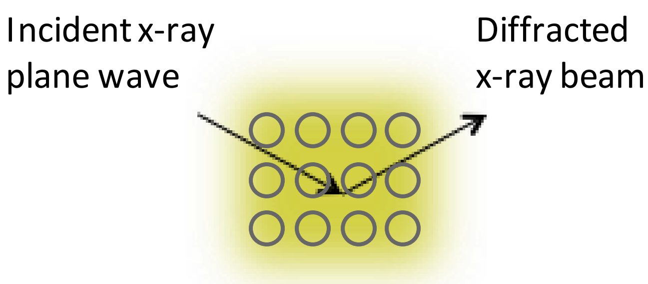
Diffraction from an isolated nanocrystal

Reciprocal space with single crystal x-ray diffraction

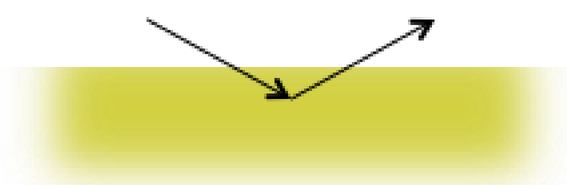




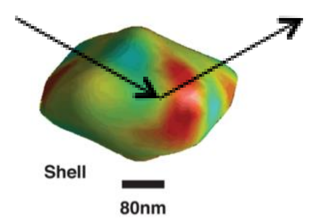




Diffraction from a bulk single crystal



Diffraction from a truncated crystal



Diffraction from an isolated nanocrystal

Structural sensitivity with coherent Bragg diffraction

- Coherent Bragg diffraction imaging maps the structure factor for a given Bragg peak.

$$F_{HKL} = \Sigma f_n \exp[i \mathbf{G}_{HKL} \cdot \mathbf{r}_n] \exp[i \mathbf{G}_{HKL} \cdot \mathbf{u}_n]$$

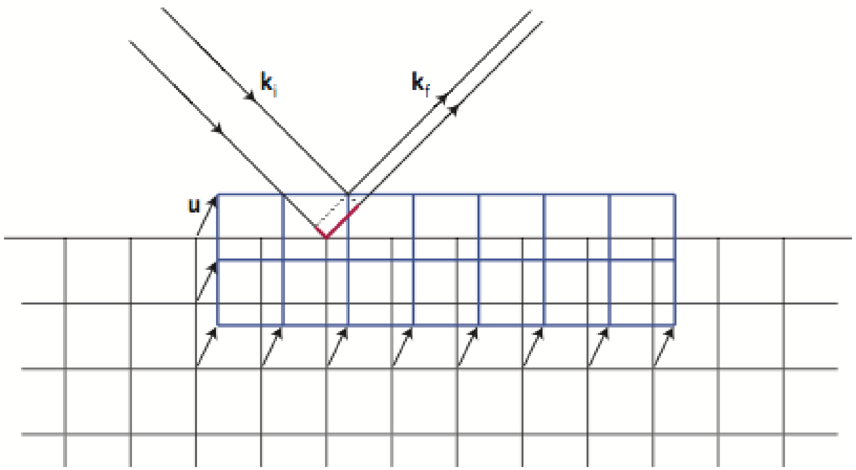
↑ Phase of Bragg peak

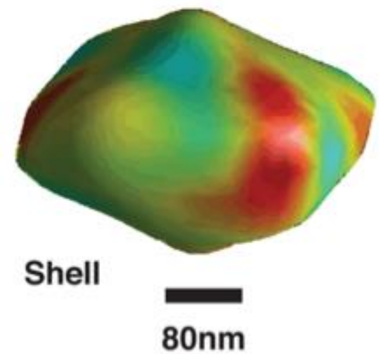
↑ Phase due to atomic deviations

- Phase encodes scalar component of displacement vector (**u**) at each atomic site.
  - More complex behavior requires model

Phase of Bragg structure factor sensitive to picometer-scale atomic displacement.

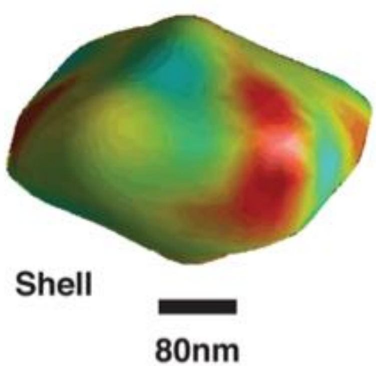
Lattice displacement due to strain:

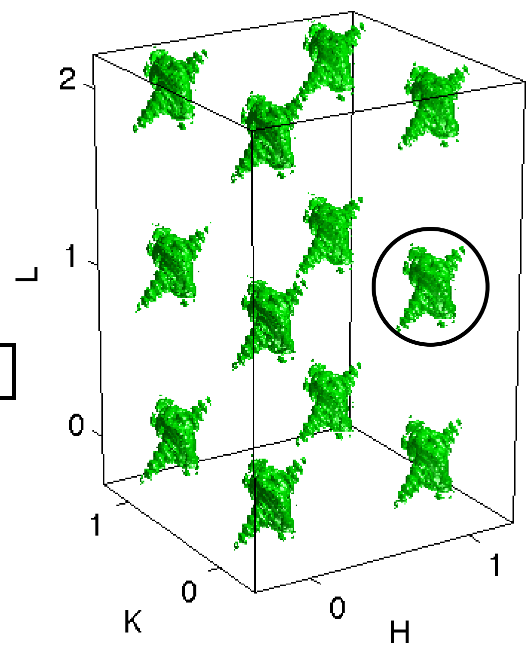




Robinson & Harder, Nat. Mater., 8 (291), 2009
Hruszkewycz et. al., PRL 110 (177601) 2013

So what do we need?





Measurement of 3D fringe pattern about a Bragg peak can yield 3D image reconstruction

Ulvestad, et.al. , Nano Lett.., 2014

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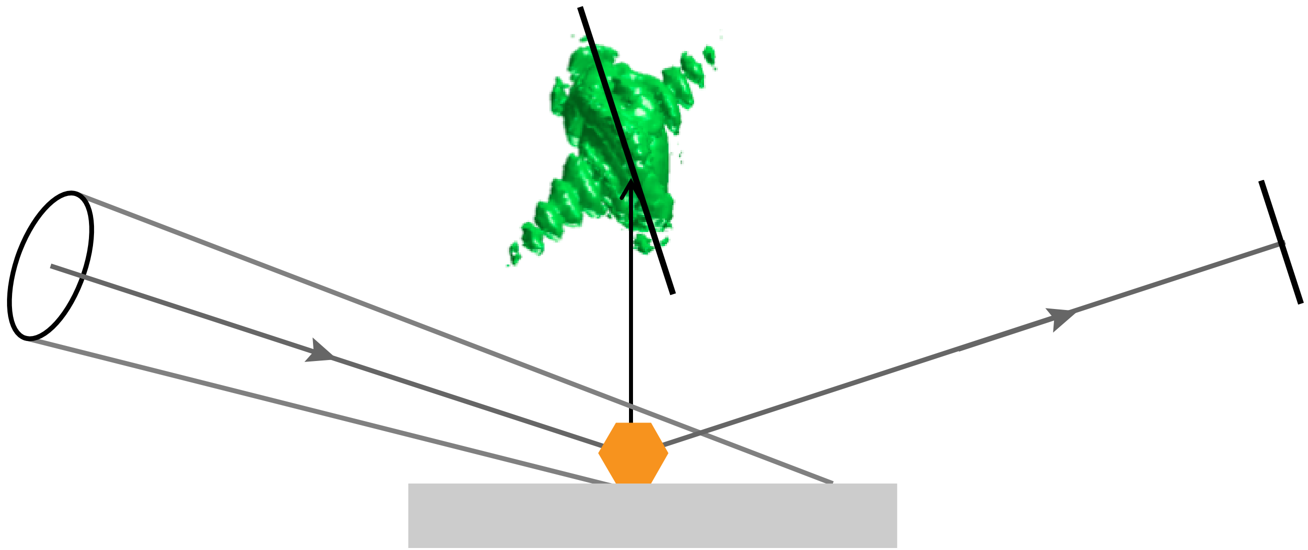
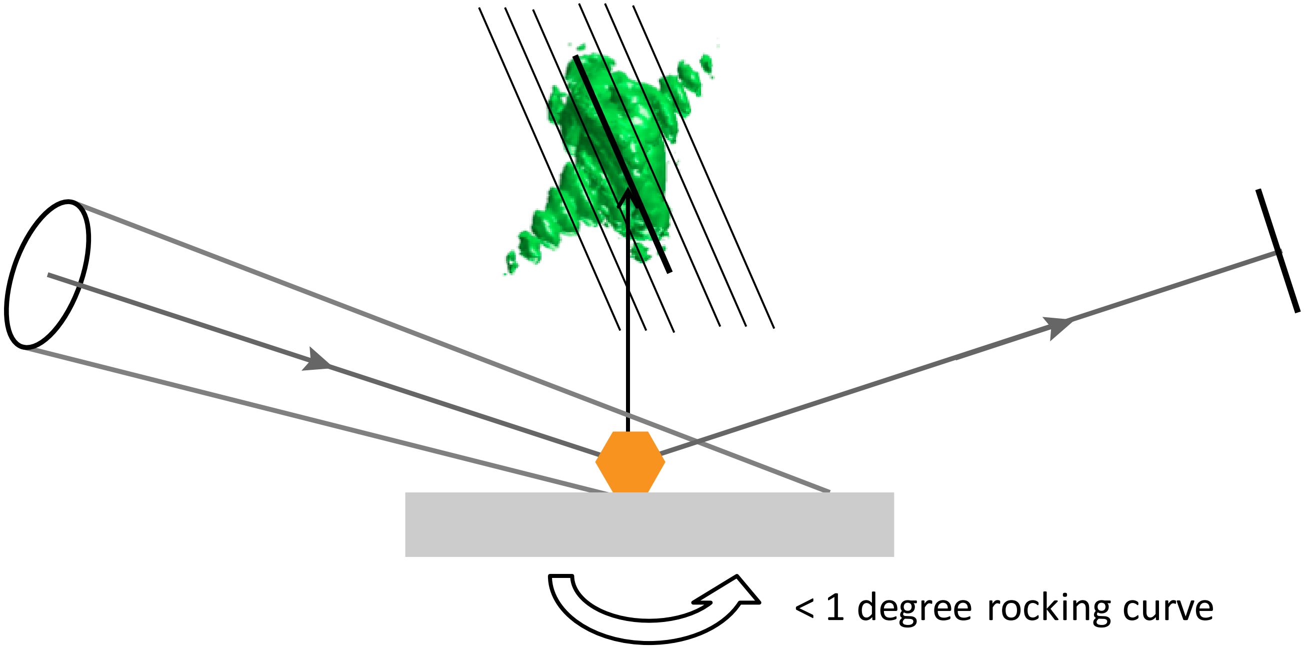
Measuring a coherent Bragg peak



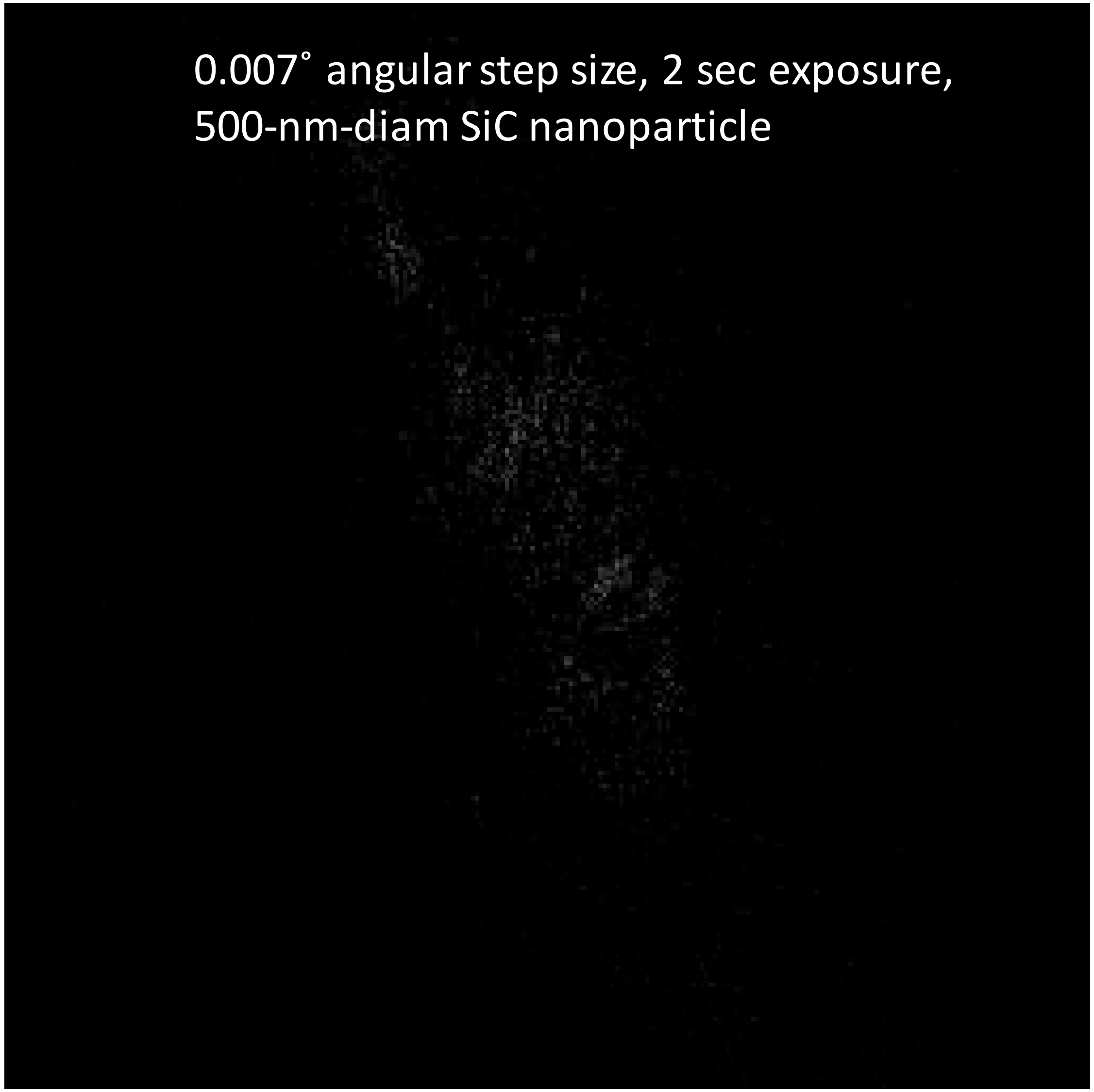
Once the crystal and incident beam are aligned to a Bragg condition, a 2D area detector measures a cut through the 3D intensity distribution

3D Bragg CDI measurement with a rocking curve

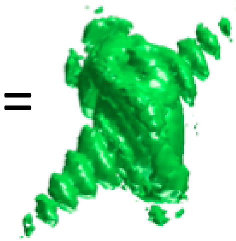


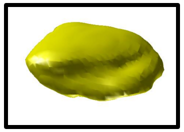
3D Bragg peak is measured slice-by-slice by varying sample angle in fine increments.

What does such a data set look like?



Finding a solution

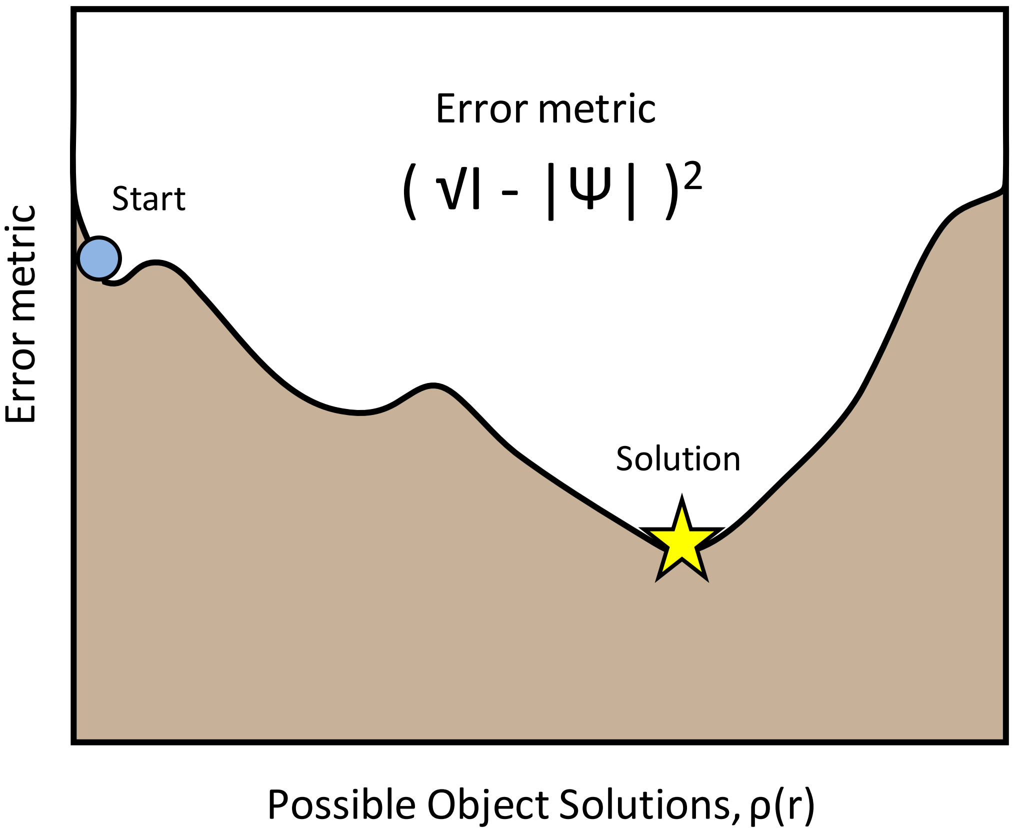
I = 

S = 

Unknown object ρ

$\Psi = F\,\boldsymbol{\rho}$

- Constraints:
  - 3D measured intensity pattern (I), oversampled
  - Rough size and shape of particle (support, S)
- Optimization approach:
  - Initialize guess of particle as random numbers
  - Error metric (ε^2) indicates how far away from the solution you are.
  - Gradient WRT ε^2 used to move "downhill" incrementally, together with support.
  - Iteratively change sample according to gradient



Avoid local stagnation! Use mix of optimization algorithms

BCDI phase retrieval

- Calculate gradient for current iteration:

$$\partial_k = \mathcal{F}^{-1}\left(\psi_k - \sqrt{I}\angle\psi_k\right)$$, where: $$\psi_k = \mathcal{F}\rho^{(k)}$$

- Error reduction (steepest descent)

$$\rho^{(k+1)} \longleftarrow S(\rho^{(k)} - \frac{1}{2}\partial_k)$$

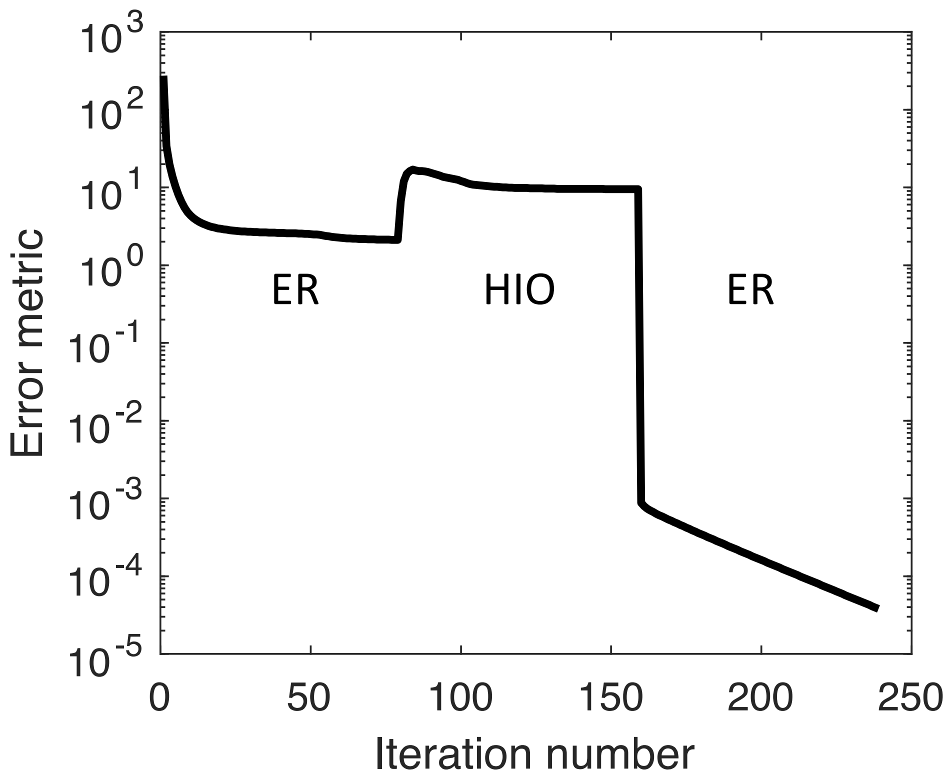
- Hybrid input-output (saddle point search)

$$\rho^{(k+1)} \longleftarrow \begin{cases} \rho^{(k)} - \frac{1}{2}\partial_k & \mathbf{r} \in S \\ \rho^{(k)} - \beta(\rho^{(k)} - \frac{1}{2}\partial_k) & \mathbf{r} \notin S \end{cases}$$

Alternate ER with HIO to avoid stagnation in local minima

Marchesini, RSI, 78 (011301) 2007

BCDI phase retrieval

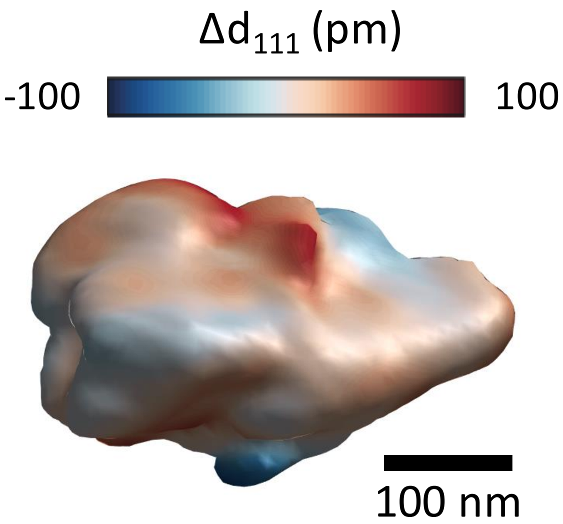


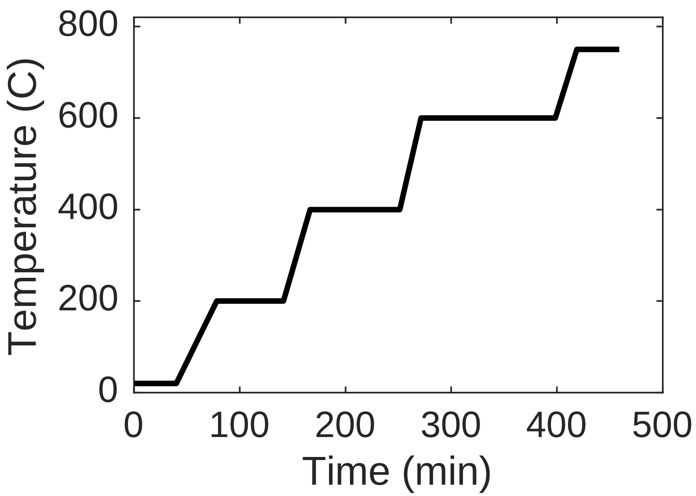
Alternate ER with HIO to avoid stagnation in local minima

BCDI of materials transformations: Strain annealing of nanodiamonds

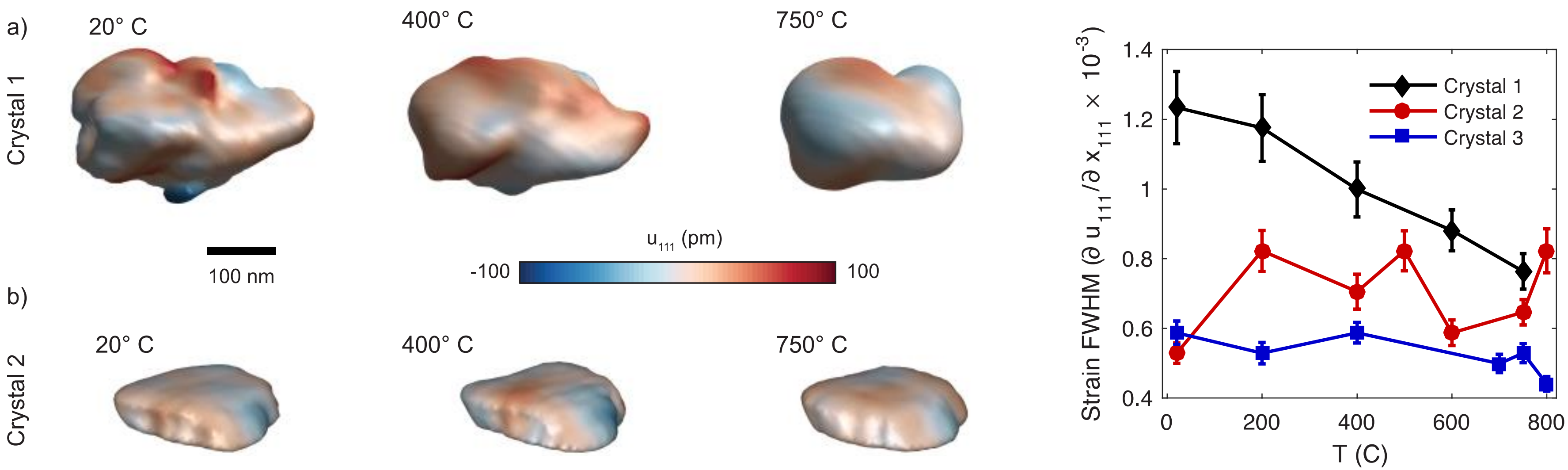
- Inexpensive commercial nanodiamonds
  - Potential for quantum sensing applications with nitrogen-vacancy centers.
  - Contain inhomogeneous internal strain distributions detrimental to performance.
  - High-temperature annealing provides strain relaxation suitable for applications.

Can we visualize strain annealing processes in-situ with BCDI?





Strain annealing of nanodiamonds



- We measured 3D strain fields within individual nanodiamond crystals during annealing up to 850 C and find that improvements in lattice homogeneity depend on initial strain.

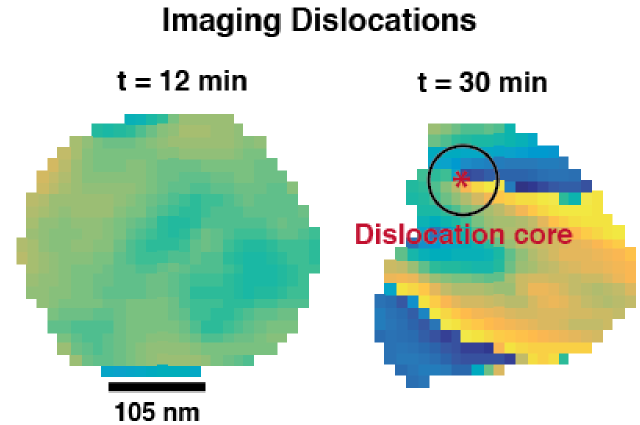
This helps develop scalable methods of processing nanodiamonds for quantum sensing and information processing

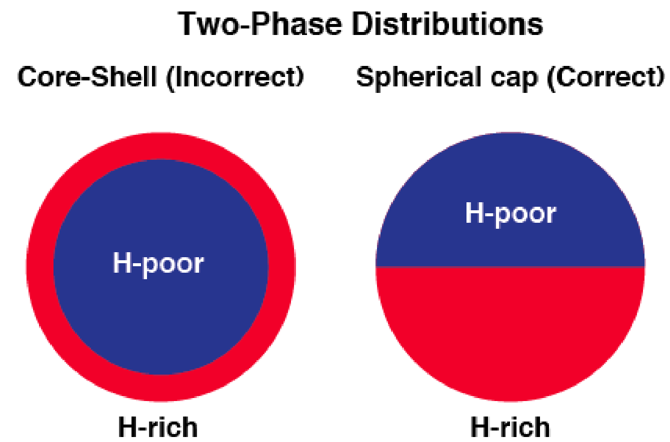
Hruszkewycz, et al., APL Materials, 5, 026105 (2017).

BCDI of materials transformations

- Gas-phase hydriding of Pd nanoparticles
  - Applications for hydrogen storage, sensing, and purification technology
  - Mechanism of hydriding phase transition thought to proceed as core-shell.
  - In-situ BCDI reveals a critical particle size for dislocation formation that affects H uptake.
  - Additionally, two-phase distributions adopted spherical cap geometry rather than core-shell.

BCDI gives access to 3D strain and dislocation distributions in environments critical to the processing and functioning of nanomaterials.





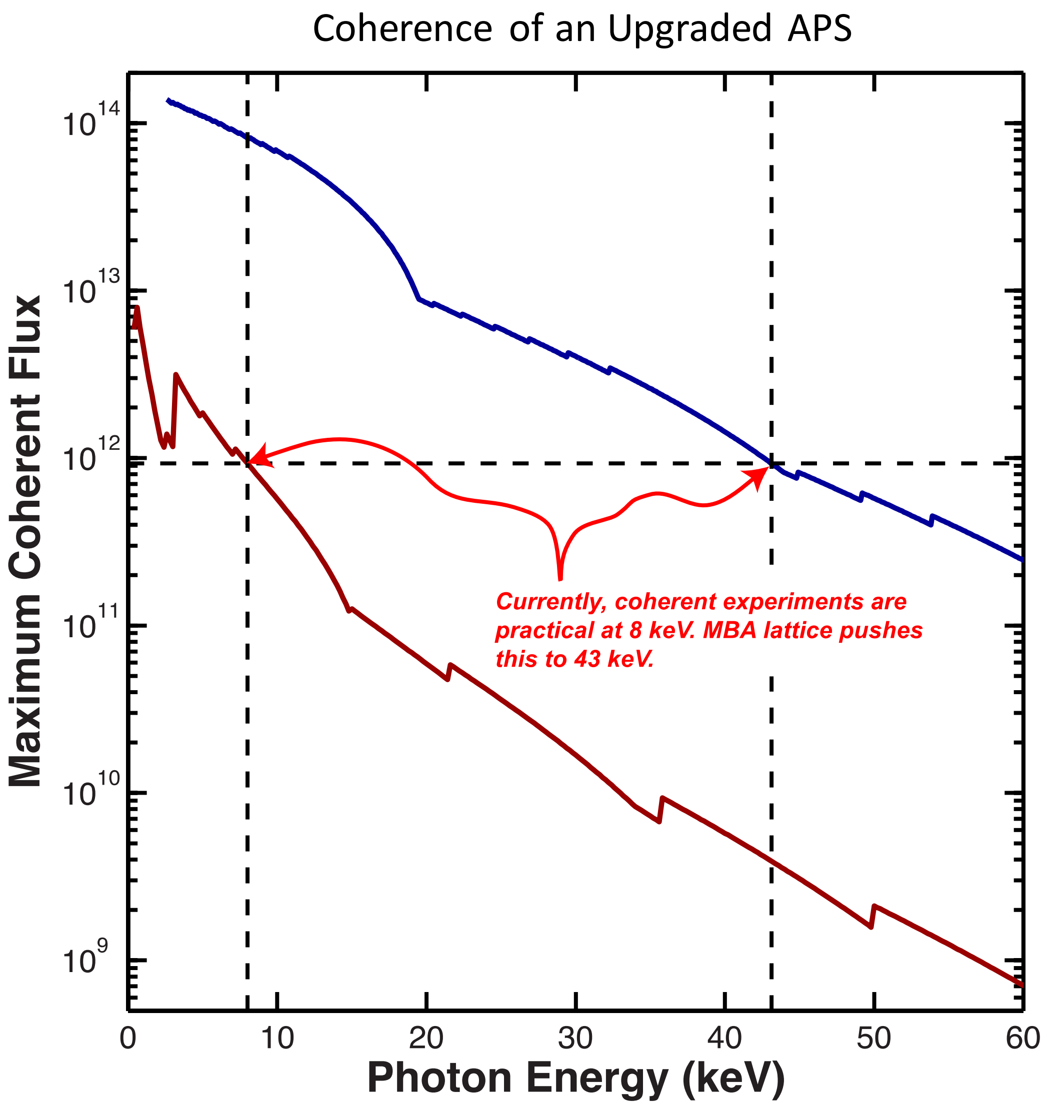
Ulvestad, et.al., Nature Materials, 2017

See also, Ni nanoparticle dissolution: Liu, et al., Nano Letters, 2017, DOI: 10.1021/acs.nanolett.6b04760

The Advanced Photon Source Upgrade

- What is now possible with 8 keV x-rays can be done at 43 keV with an MBA lattice.
- Today's coherent imaging can be done at highly penetrating x-ray energies.

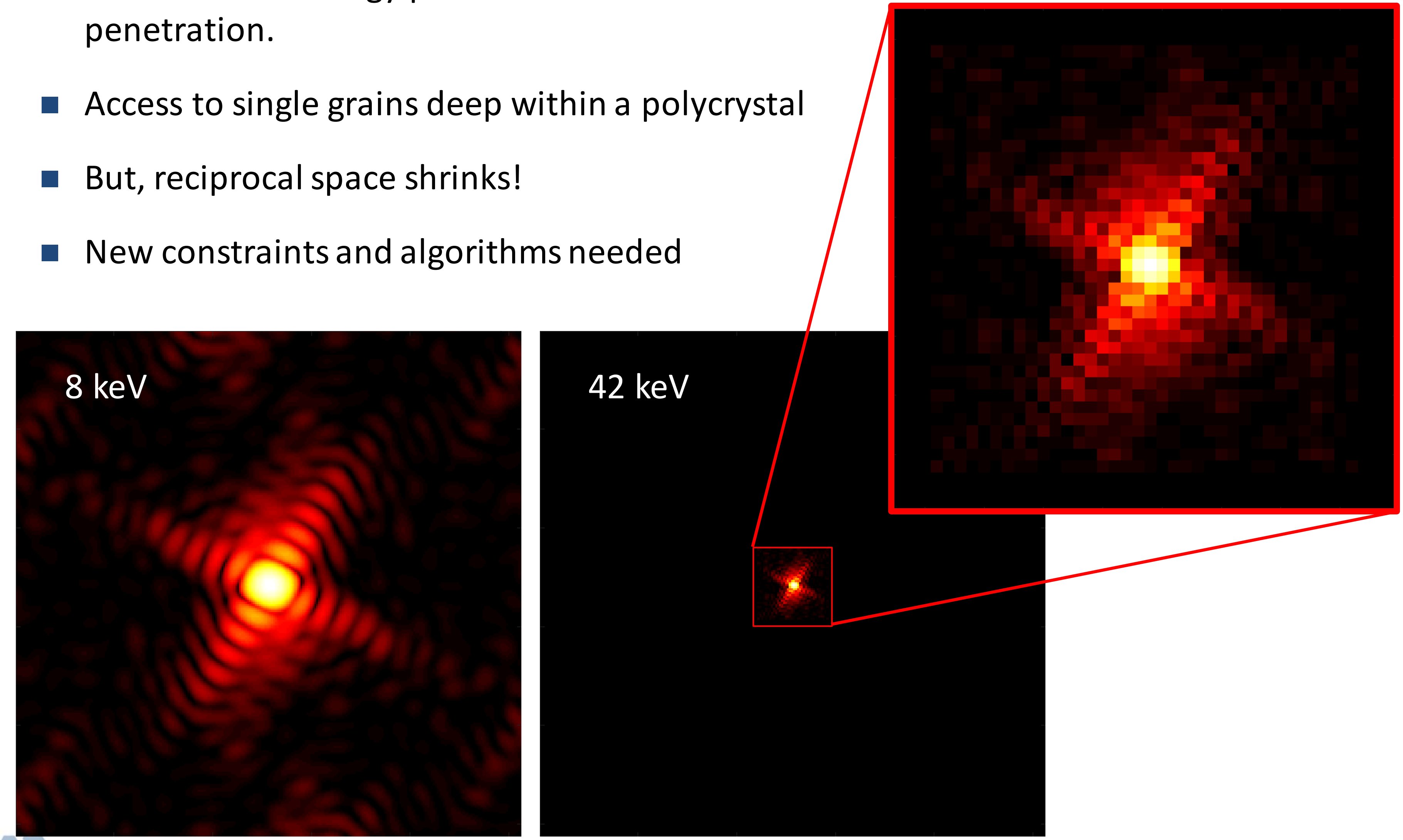
Key question for BCDI: What about the scaling of reciprocal space?



Courtesy of M. Borland

What about higher x-ray energies?

- 5x increase in energy provides much more penetration.
- Access to single grains deep within a polycrystal
- But, reciprocal space shrinks!
- New constraints and algorithms needed



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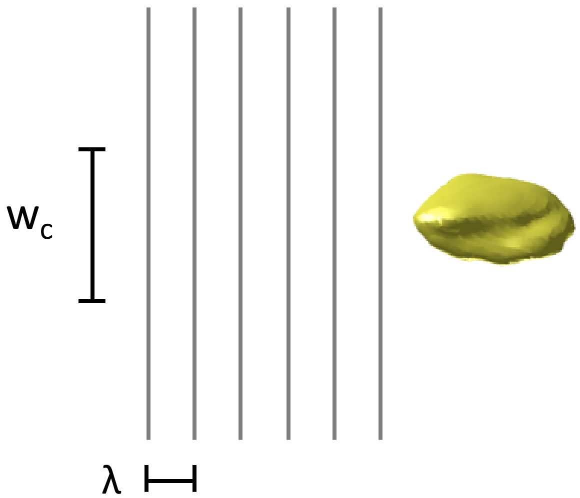
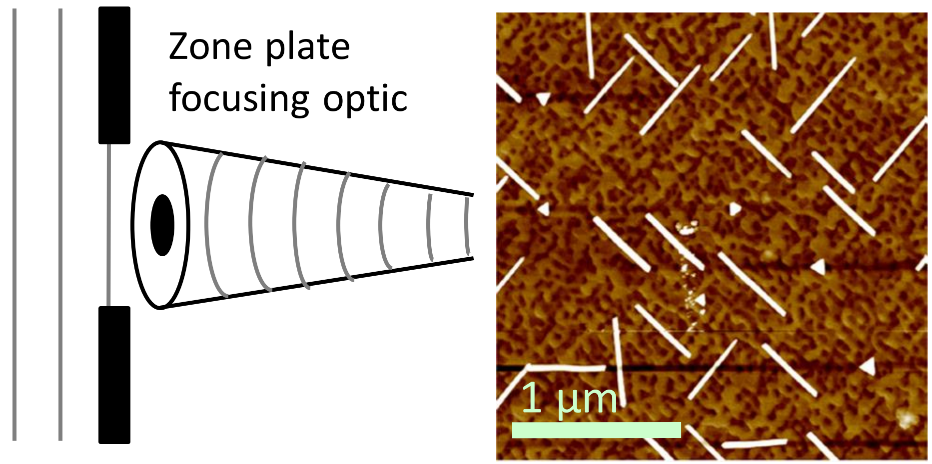
Designing experiments with coherent beams

Coherently illuminating a small single crystal



3D imaging with Bragg coherent diffraction imaging (BCDI)

Tightly focusing the beam



Diffraction-limited spot for Bragg coherent nanodiffraction of extended crystals

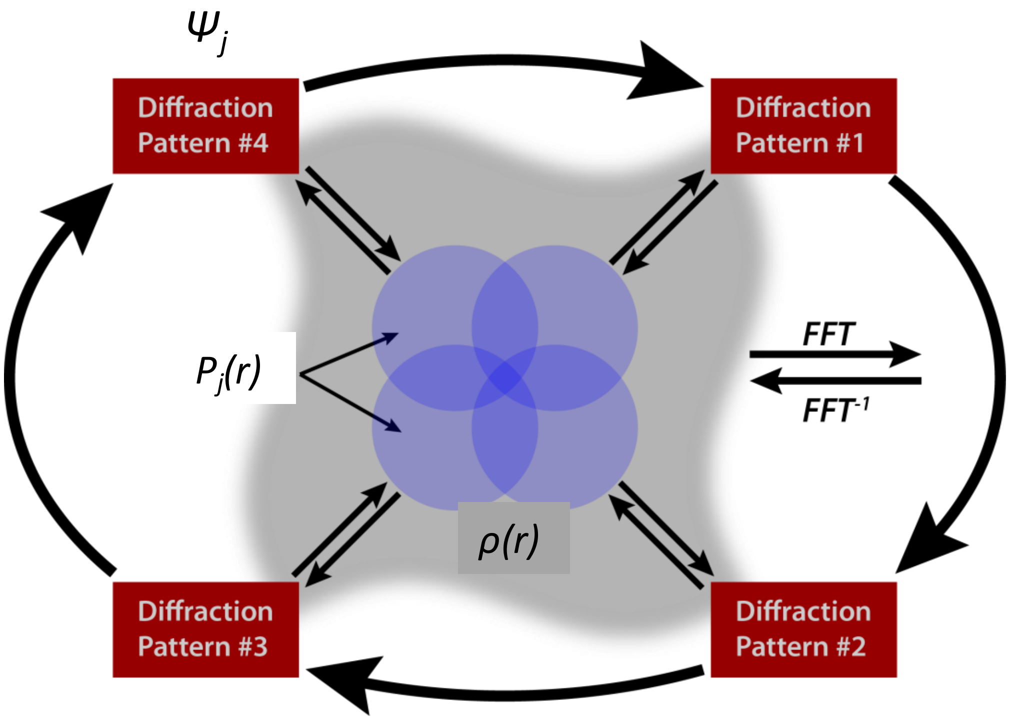
Collect diffraction from multiple sample positions with focused x-rays

Key concepts of ptychography

Unknown phases ↓ Unknown object ↓

$$\Psi_j = F\, P_j\, \rho$$

- Measure far field diffraction patterns from overlapping beam positions.
- Diffracting object is unknown, as are the phases of the measured coherent diffraction patterns.
- Local structure is encoded in at least two diffraction patterns.
- Iterative optimization algorithms find solution that agrees best with the measured diffraction.



Ptychography leverages the real-space overlap of a localized beam rastered over a sample to reconstruct a complex object.

Rodenburg, et. al., PRL 98 (034801) 2007

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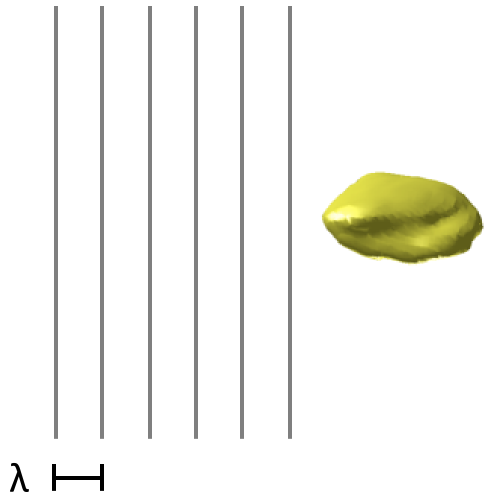
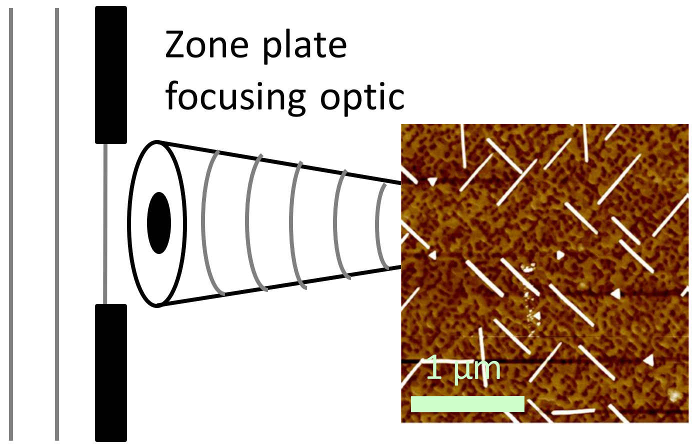
X-ray experiments with coherent beams

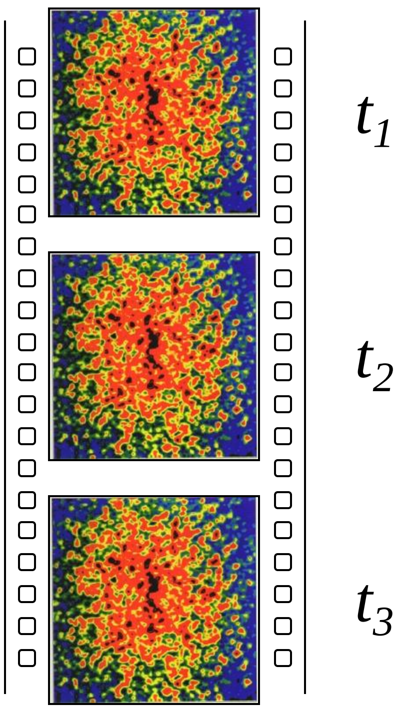
Bragg coherent diffraction imaging



X-ray nanodiffraction



X-ray photon Correlation spectroscopy

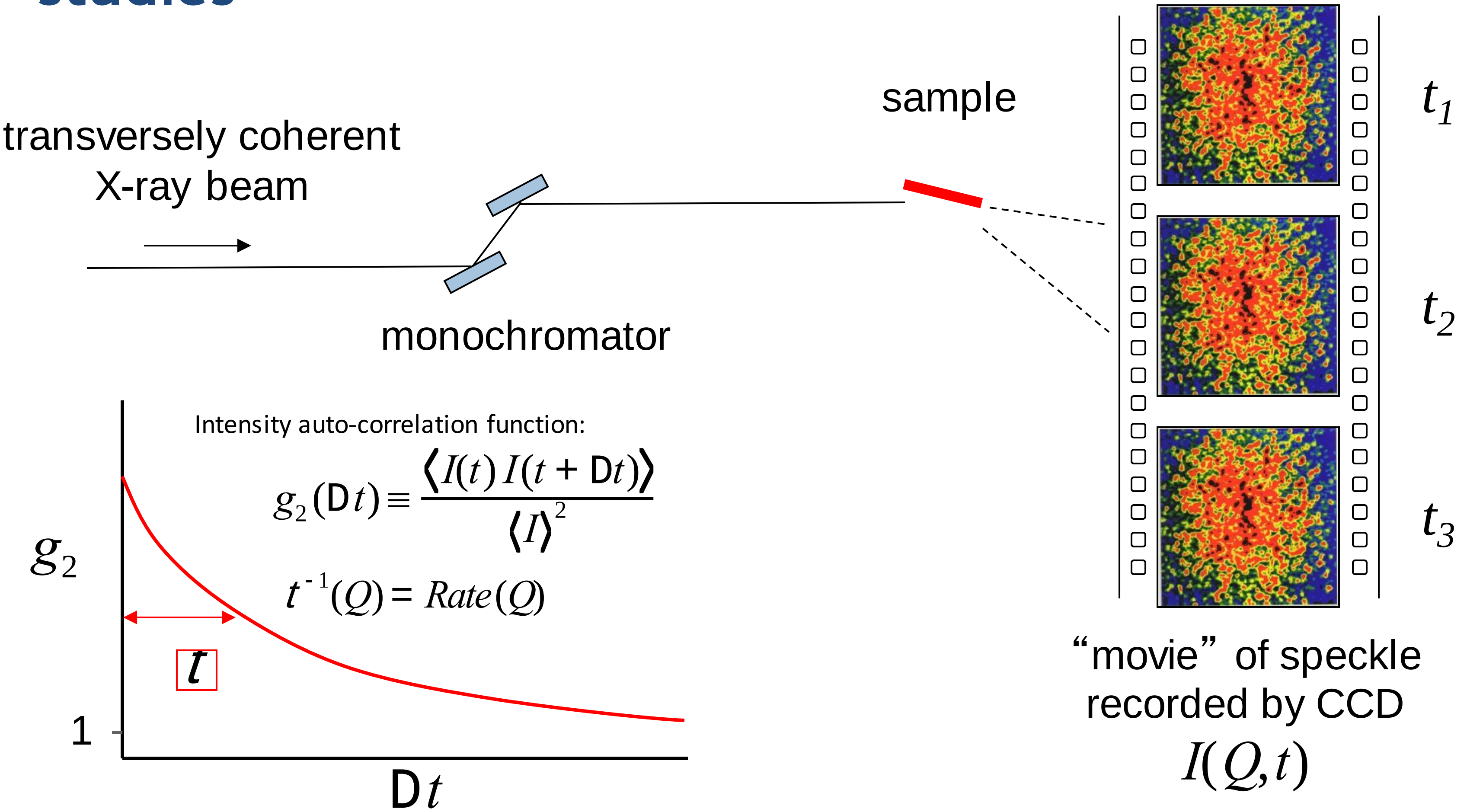


"movie" of speckle

$I(Q,t)$

Third way to exploit coherence: X-ray photon correlation spectroscopy

X-ray photon correlation spectroscopy for synthesis studies



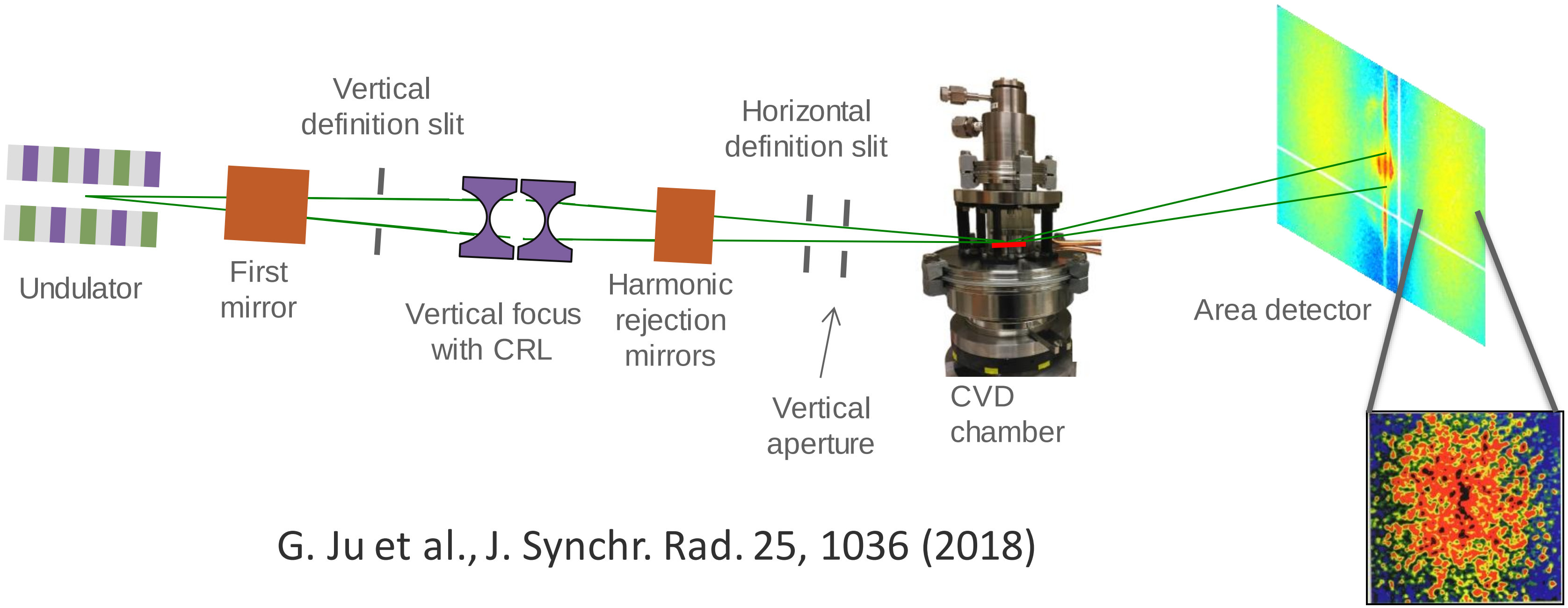
➢ **Intensity fluctuations of the speckle pattern reflect sample dynamics.**

Review of XPCS: O. Shpyrko, *J. Synchr. Rad*. **21**, 1057 (2014)

Combine strengths of high energy and coherence of x-rays

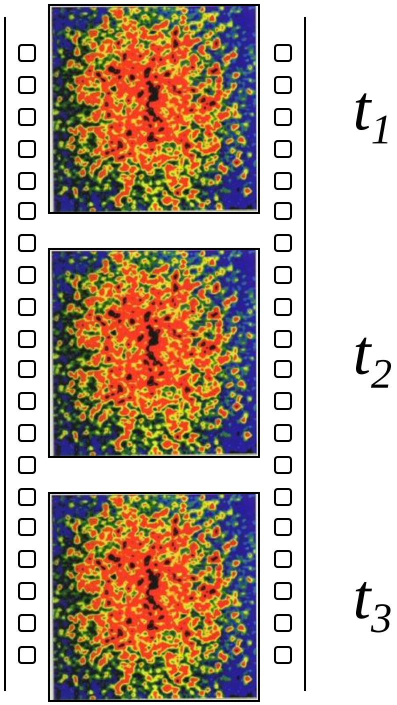
- Chemical vapor deposition can be used to grow single crystals one atomic layer at a time
- Process critical to wide bandgap semiconductor industry
- How do atoms arrange themselves as deposition proceeds?

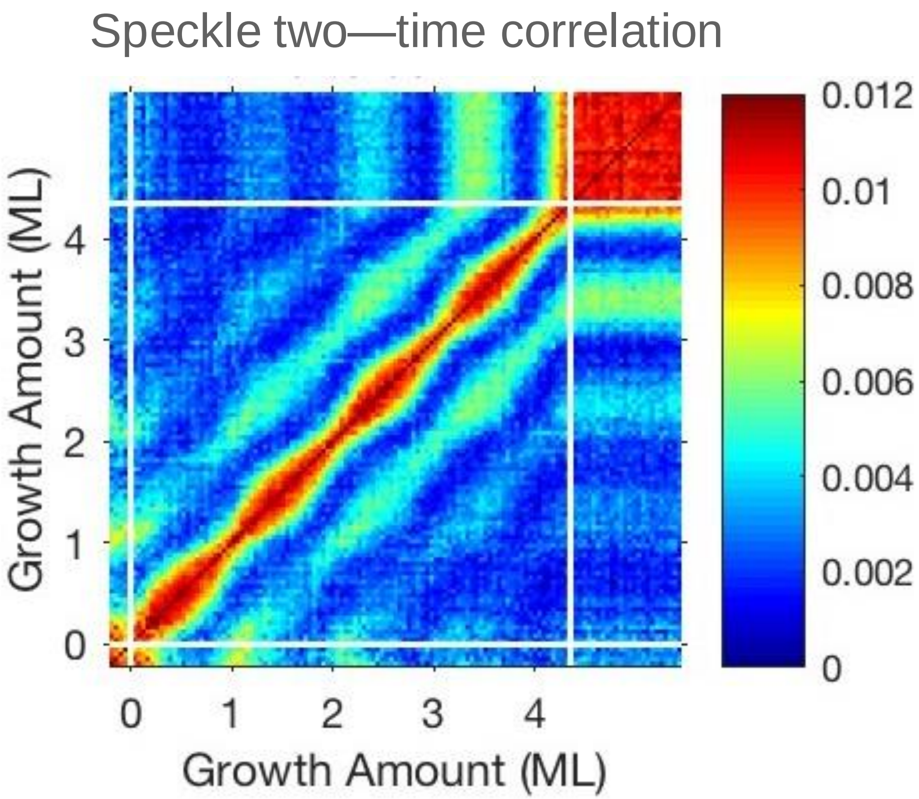
- High energy coherent x-rays and XPCS provide an opportunity
- Diffuse scattering from monolayer island formation offer the key



G. Ju et al., J. Synchr. Rad. 25, 1036 (2018)

Example: Observing surface growth dynamics in Gallium nitride using two-time correlation functions

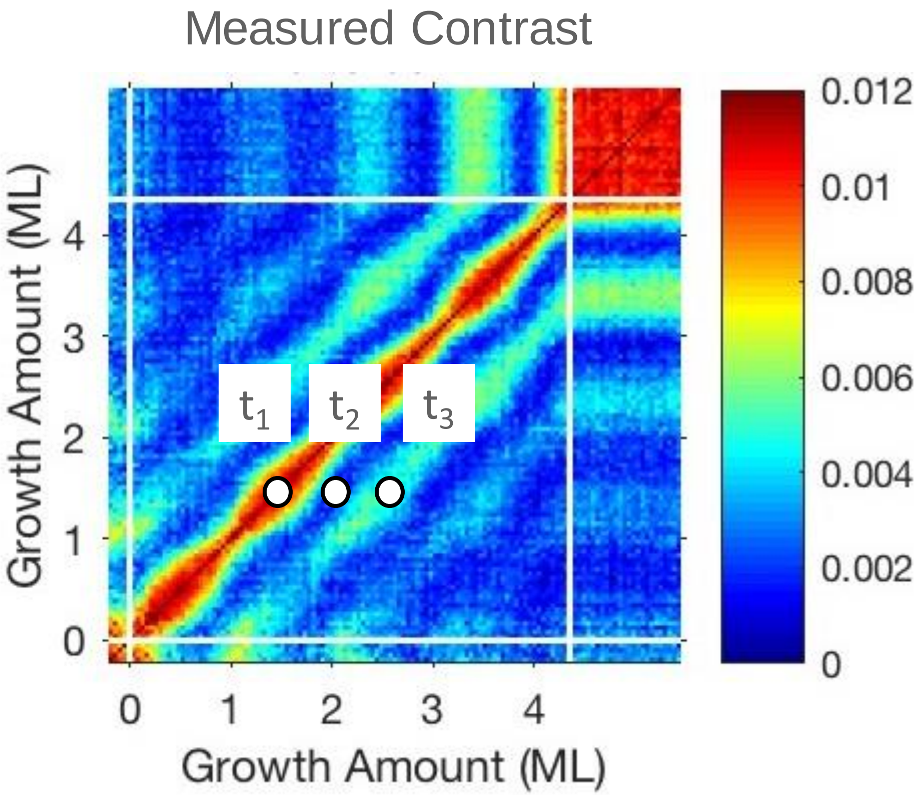


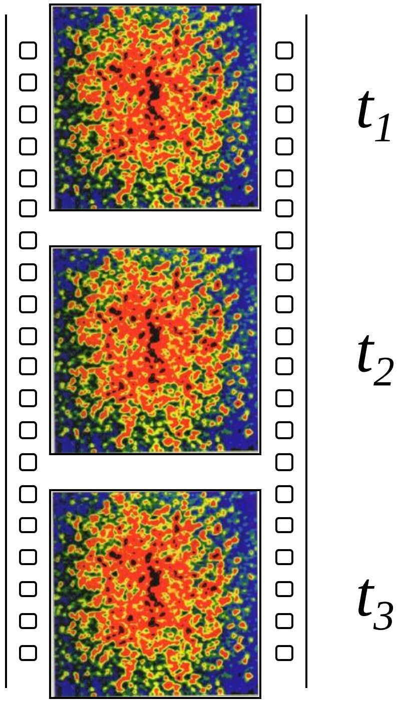


- "Striped" pattern in two-time correlation indicates a specific type of dynamics because speckle has temporal pattern of decorrelation and re-correlation

G. Ju et al., Nature Physics 15, 589 (2019)

What information is contained in a two-time correlation?





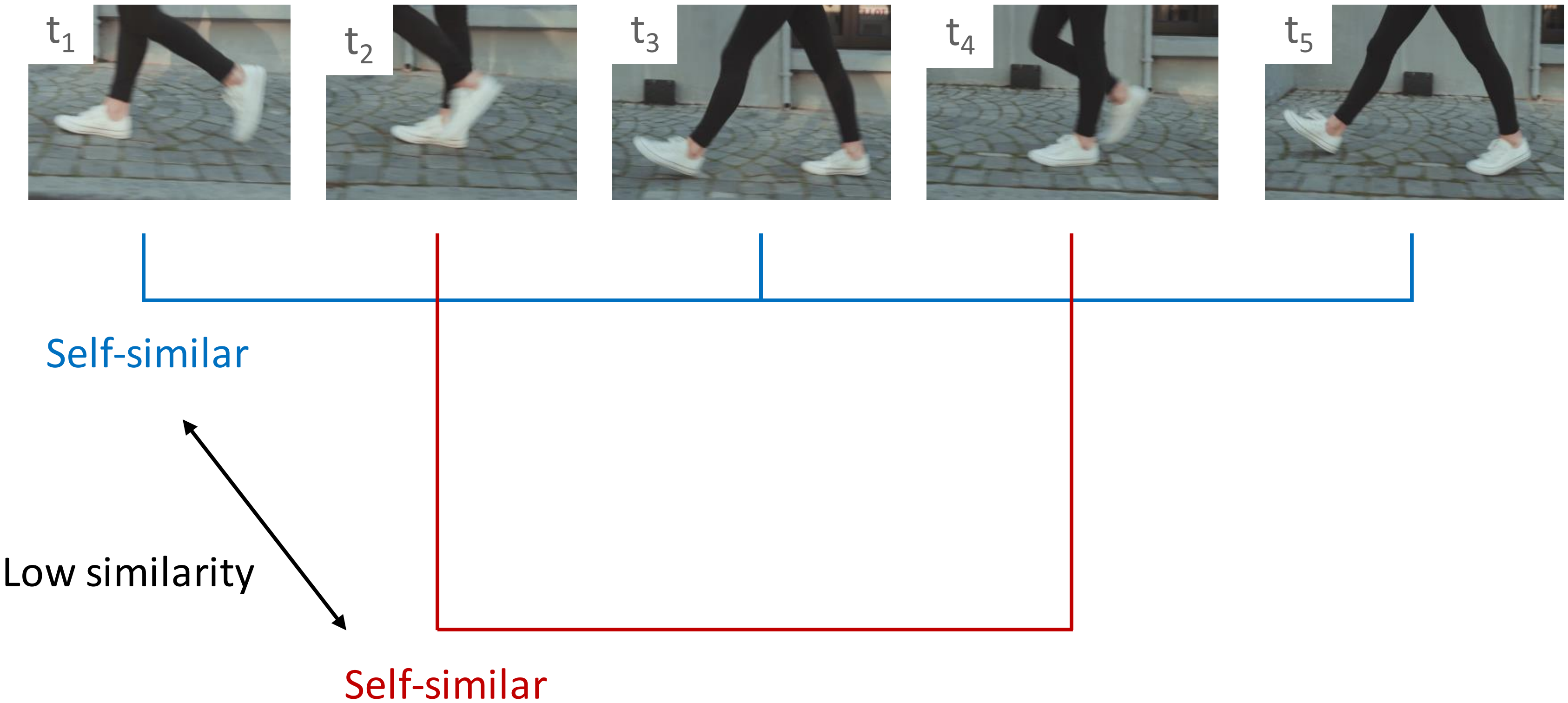
- Color on the TTCF map indicated degree of similarity of two speckle patterns
- The speckle "movie" has a certain characteristic.

G. Ju et al., Nature Physics 15, 589 (2019)

Let's look at a movie clip for insight

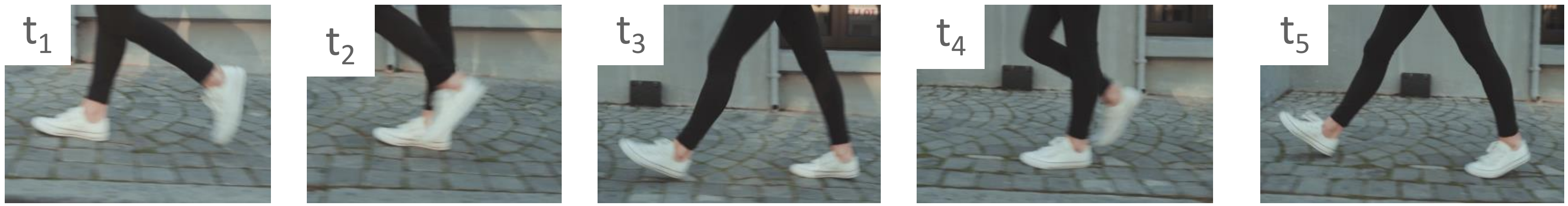
- Walking is a cyclic process.
- Expect that many frames of a movie will be self-similar in time

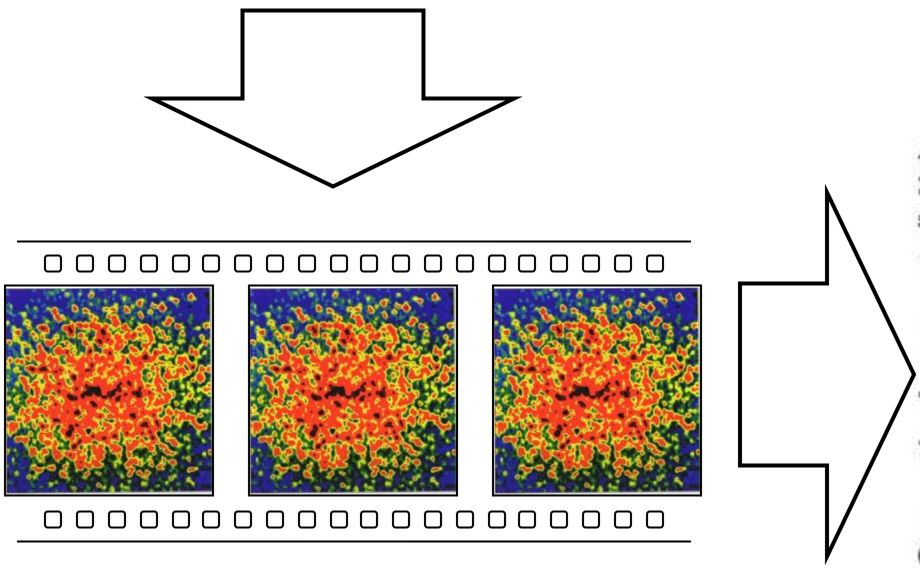
Take frame-by-frame view

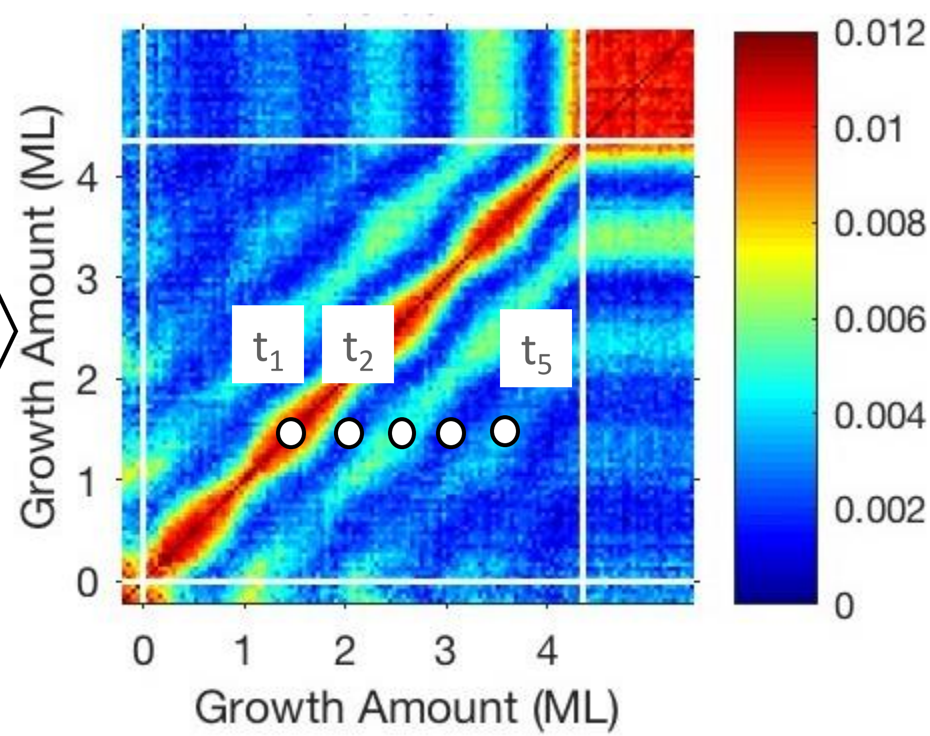


- Two states of the system display similar states (full stride vs legs together)
- Correlation between these two states relatively low

How does this connect to TTCF in XPCS?

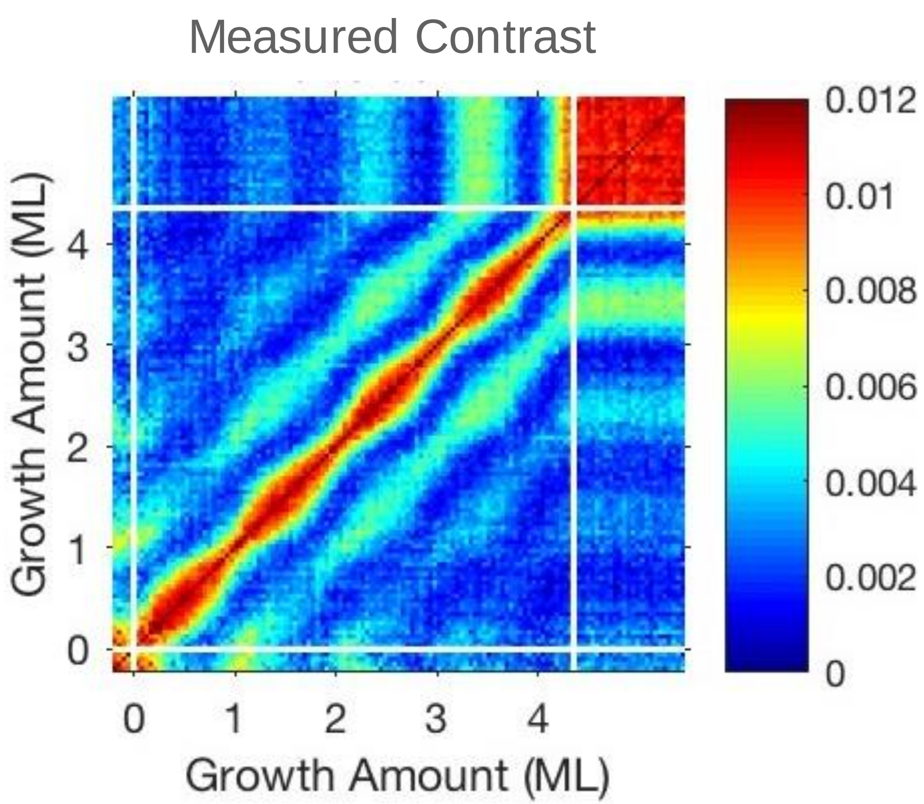


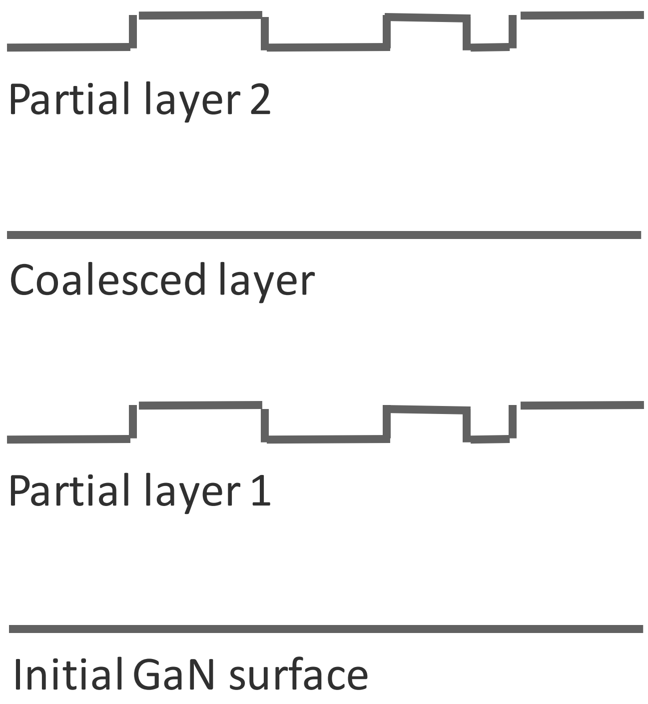




- This is a fingerprint of a cyclic process!

During deposition, monolayer-height islands form in the same spatial pattern from layer to layer in GaN





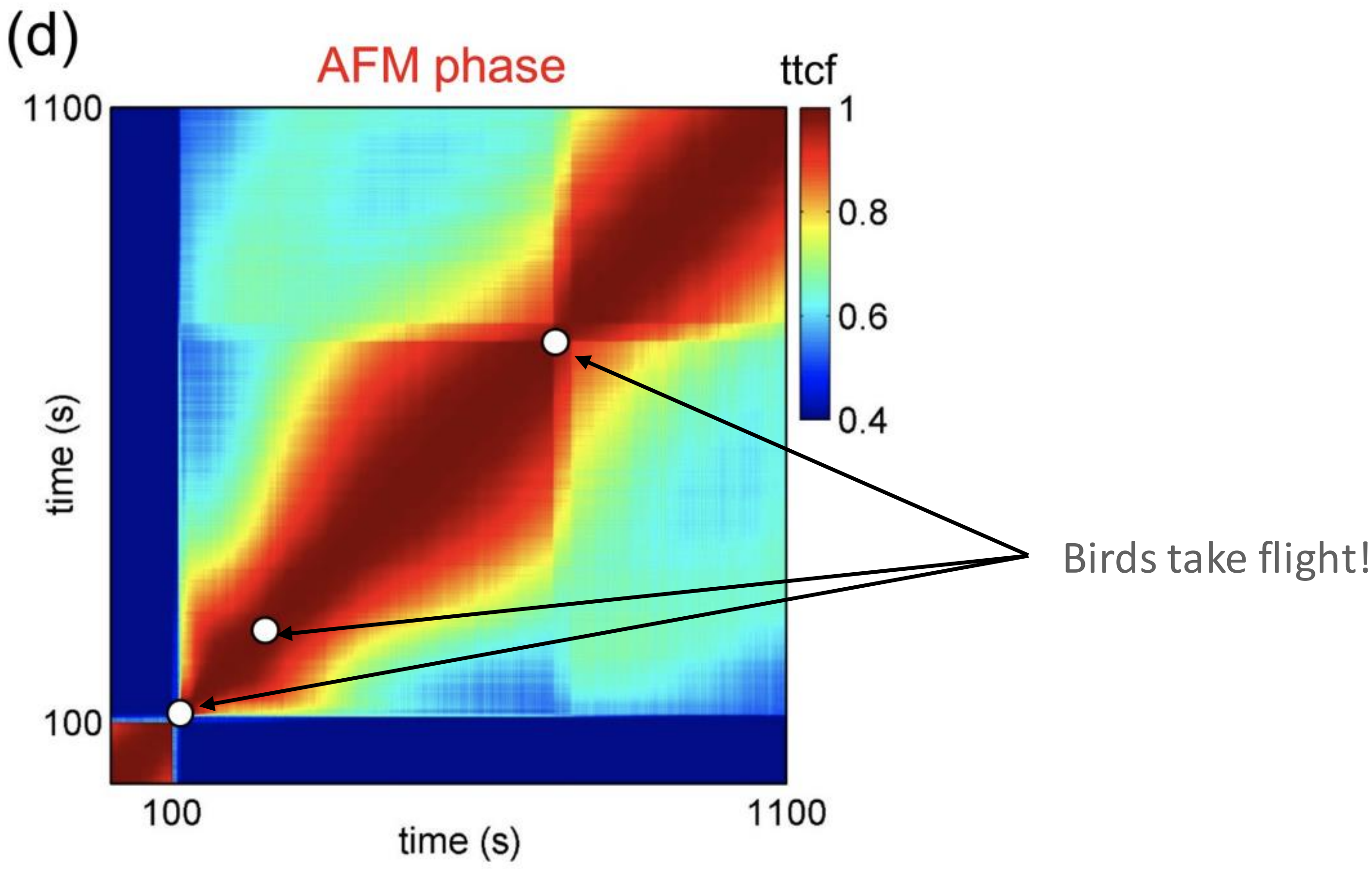
- "striped" pattern in two-time correlation indicates that island arrangement does indeed persist from layer to layer

G. Ju et al., Nature Physics 15, 589 (2019)

What other dynamics exist in nature?

- Stochastic rearrangements punctuated by periods of relative stillness

Fingerprints of stochastics nanostructures in TTCF



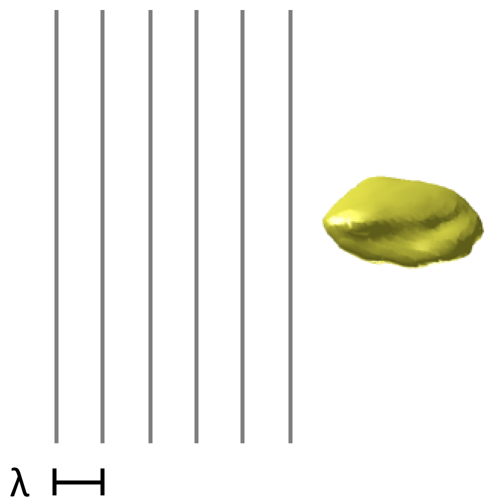
- Anti-ferromagnetic to ferromagnetic phase transformations
- Non equilibrium dynamics observed as system responds to temperature increase near transition temperature

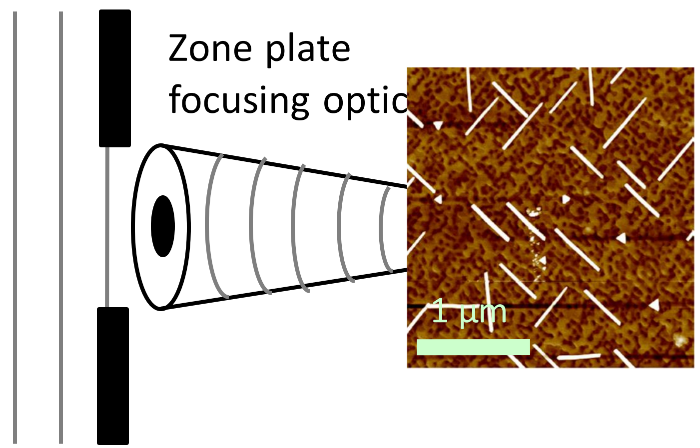
Graphical summary of coherent x-ray diffraction for materials science

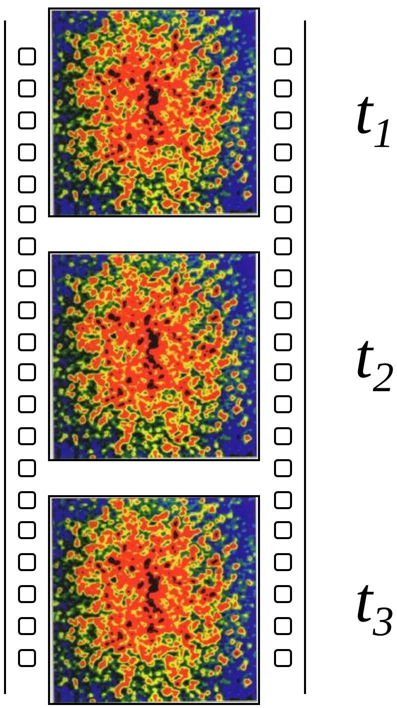
X-ray photon Correlation spectroscopy

Bragg coherent diffraction imaging

X-ray nanodiffraction







“movie” of speckle

$I(Q,t)$

Summary

- What can we learn about materials with x-rays?
- What is coherent x-ray diffraction?
- How do x-rays interact with crystals?
- Imaging strain in single nanocrystals with phase retrieval.
- Principles of ptychography.
- Measuring time evolution of atomic structure with XPCS

Outlook

- APS synchrotron to undergo major upgrade in spring 2023
- Results in 500-1000x increase in coherent flux
- With novel application of coherent x-ray diffraction and analysis, pioneering experiments of materials structure and dynamics await!