

Nanocrystals and how to study them with Coherent X-ray Diffraction

- Ian Robinson
- Ivan Vartanyants
- Franz Pfeiffer
- Mark Pfeifer
- Garth Williams
- Wei Zhang
- Curtis Benson

Departments of Physics
and Materials Science
University of Illinois

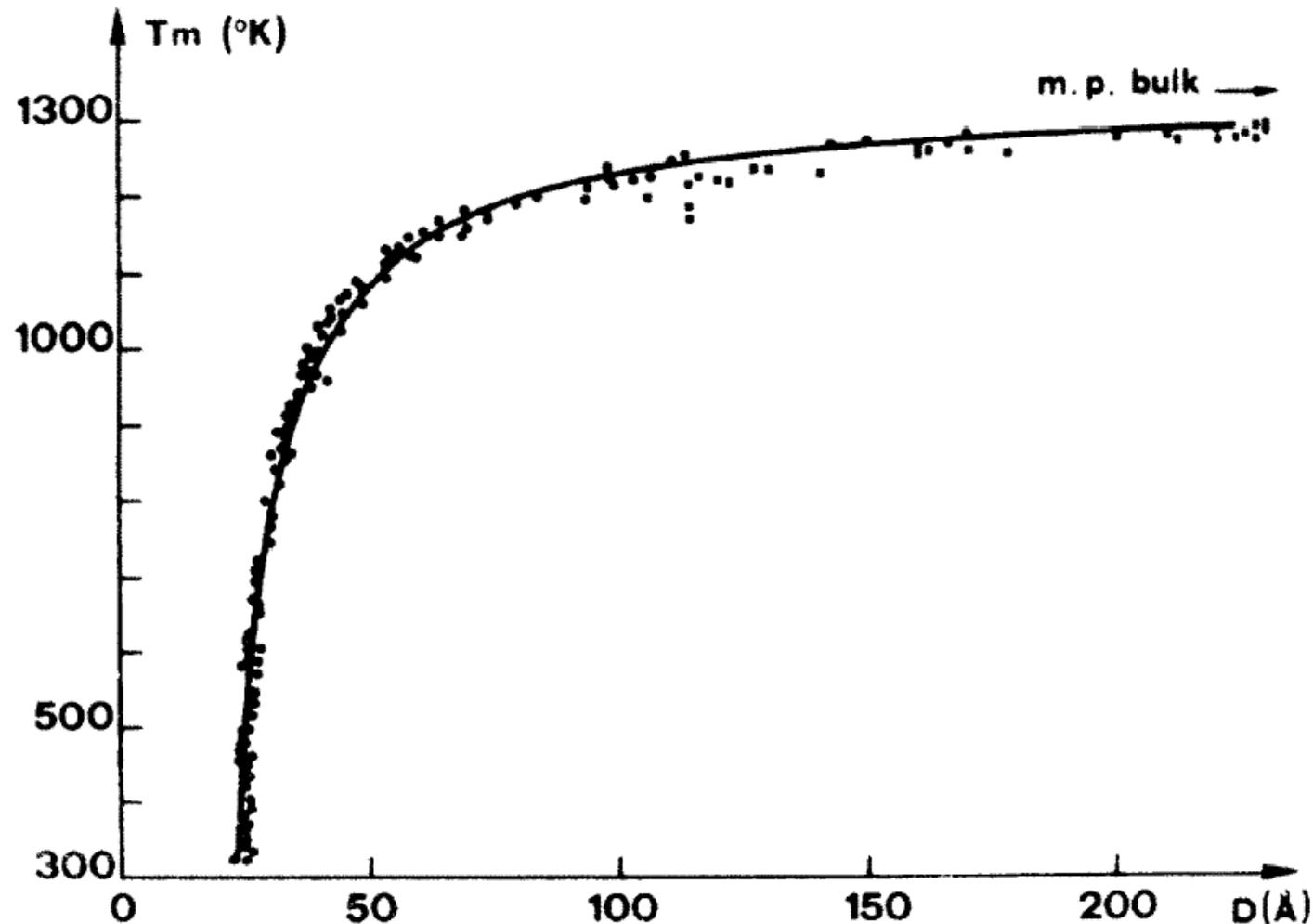
MatSE Colloquium, June 2003

Outline

- Nanocrystals
- Coherence in Diffraction
- The **Phase** Problem
- Nanocrystal Shapes
- How small can we go?
- Future Applications of CXD

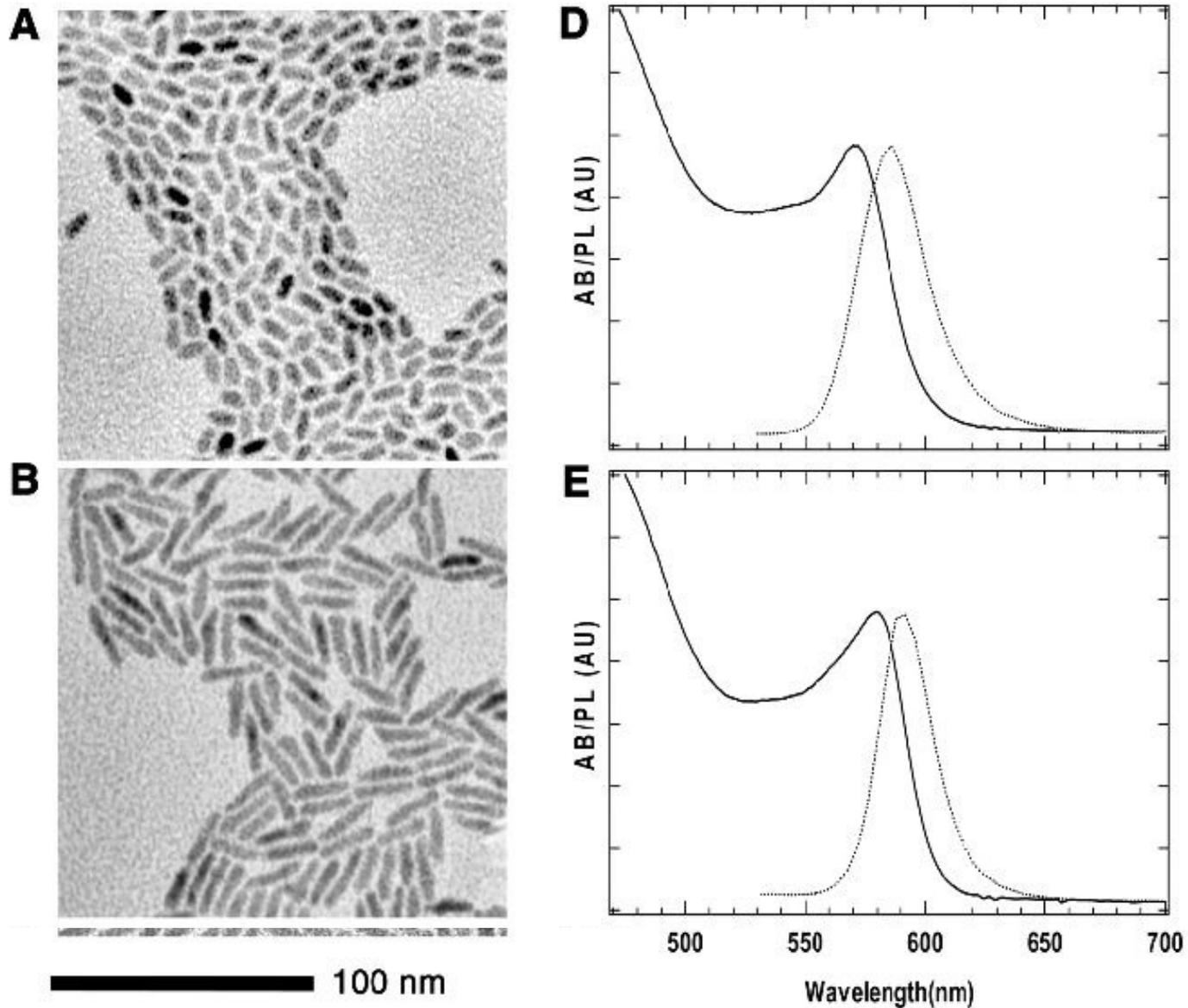
Size-dependent Melting of Au Particles

P. Buffat and J-P. Borel, Phys. Rev. A 2287-97 (1975)



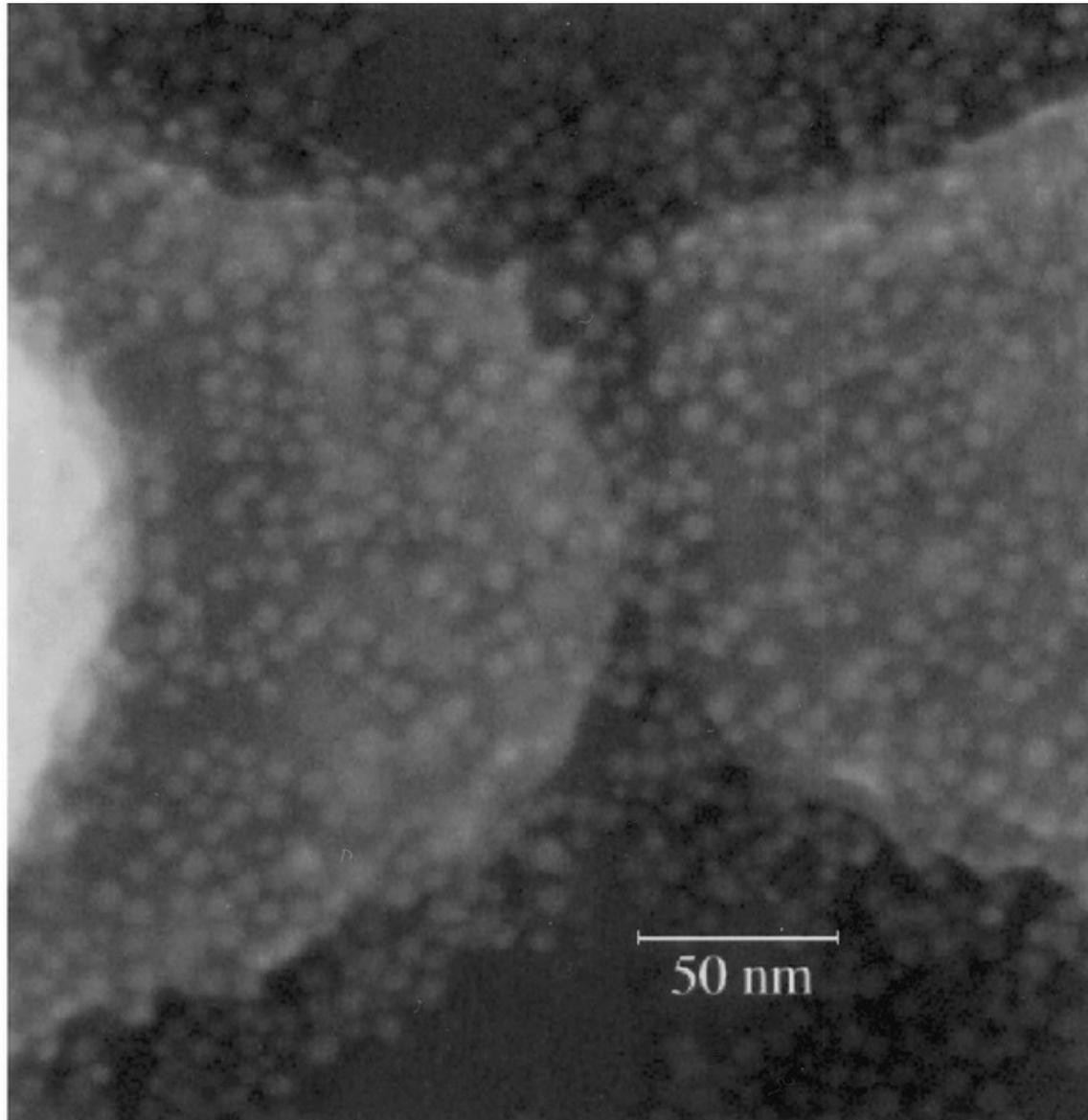
Rod-like Nanocrystals of CdSe

J. Hu et al., Science **292** 2060 (2001)



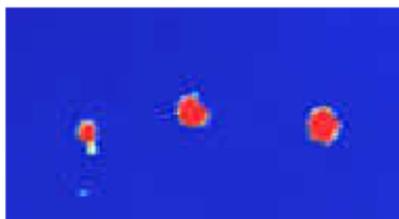
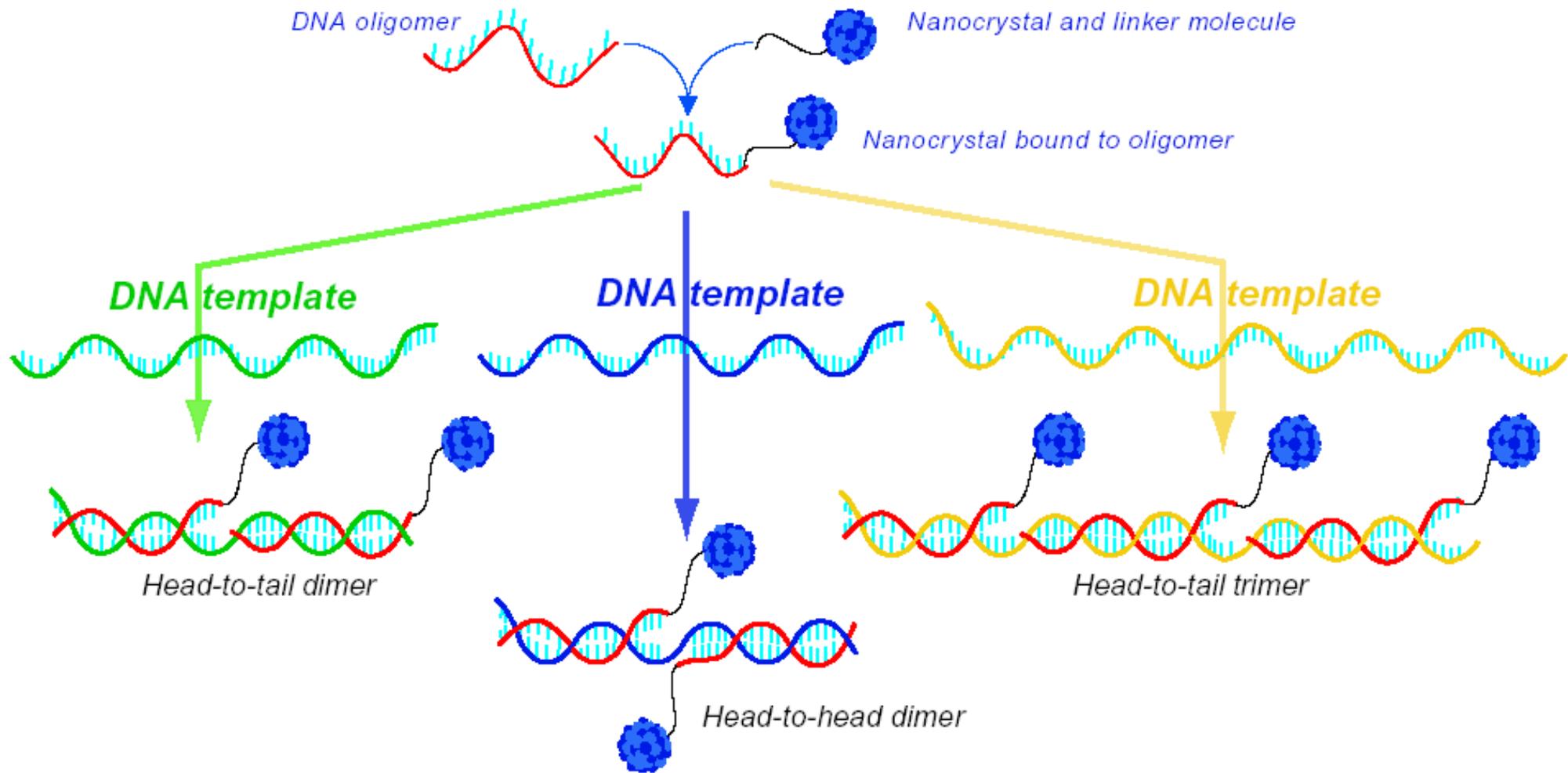
CdSe Single-Electron Transistor

D. L. Klein et al, *Nature* **389**, 699 - 701 (1997)



Nanocrystal Structures Built on a DNA Scaffold

Defined Geometries Achieved through Watson-Crick Base Pairing



7.0nm

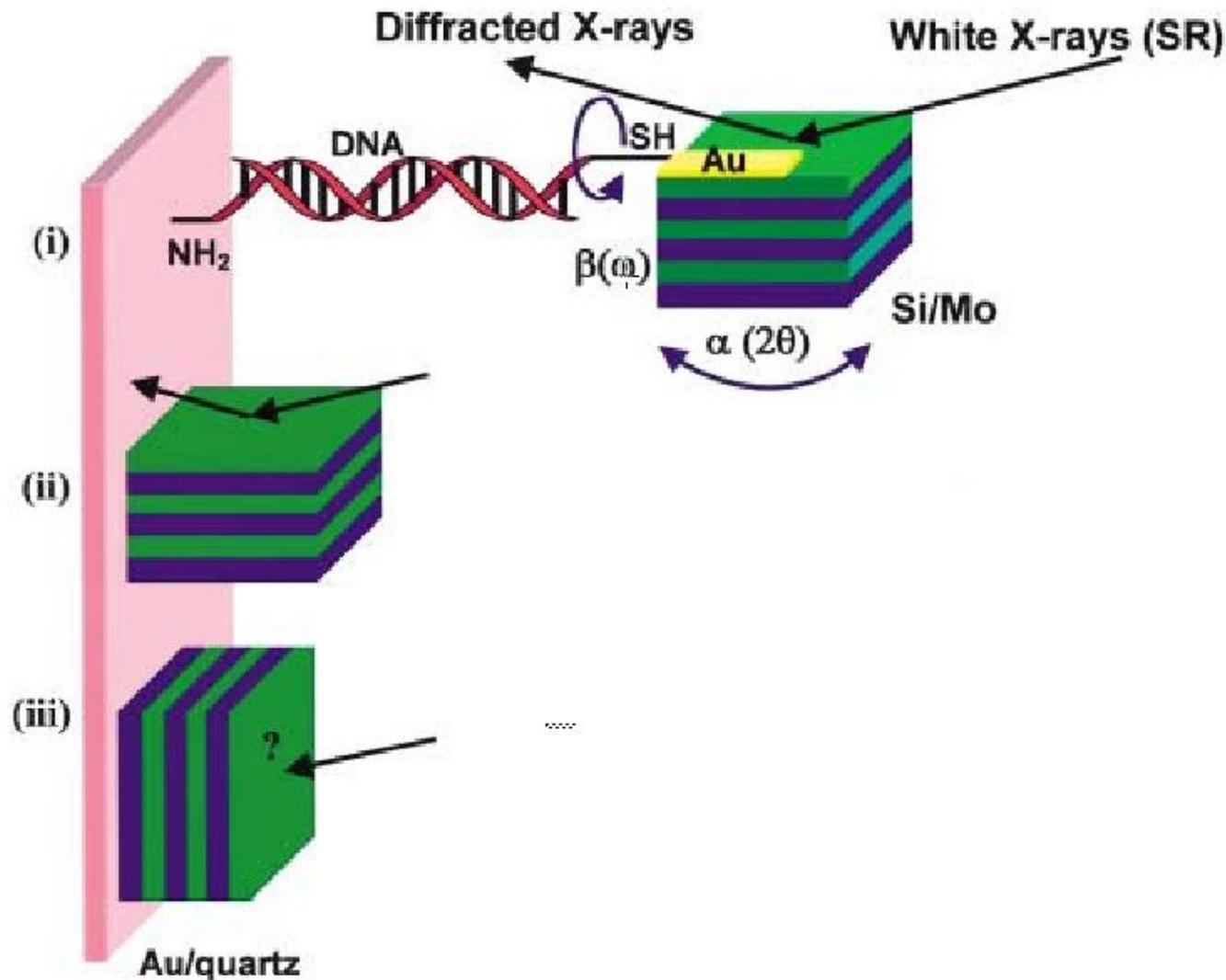
TEM image of gold-nucleic acid head-to-tail trimer complex.

Peter Schultz, Paul Alivisatos
Molecular Design Institute
Materials Sciences Division
Berkeley Lab

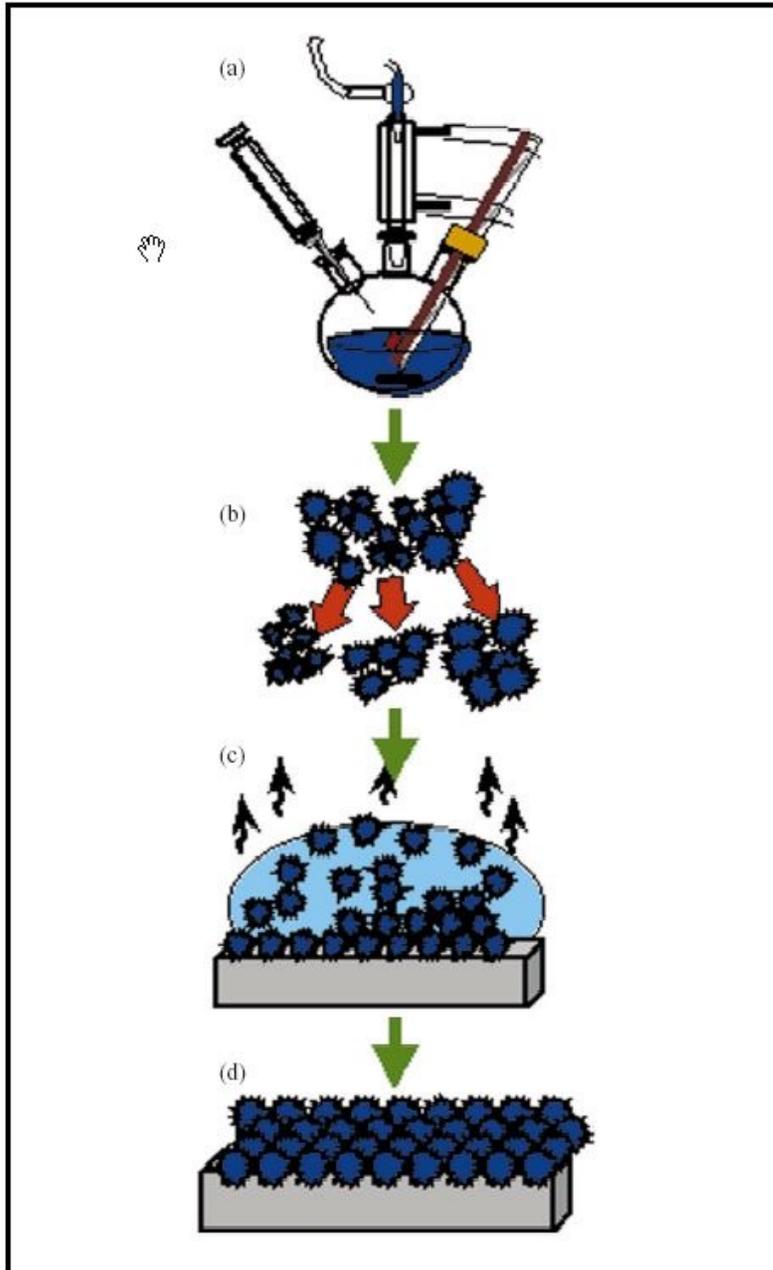
Funded by Office of Naval Research

Nanocrystal-DNA complex

J. Sasaki et al, Phys. Rev. Lett. 87 248102 (2001)

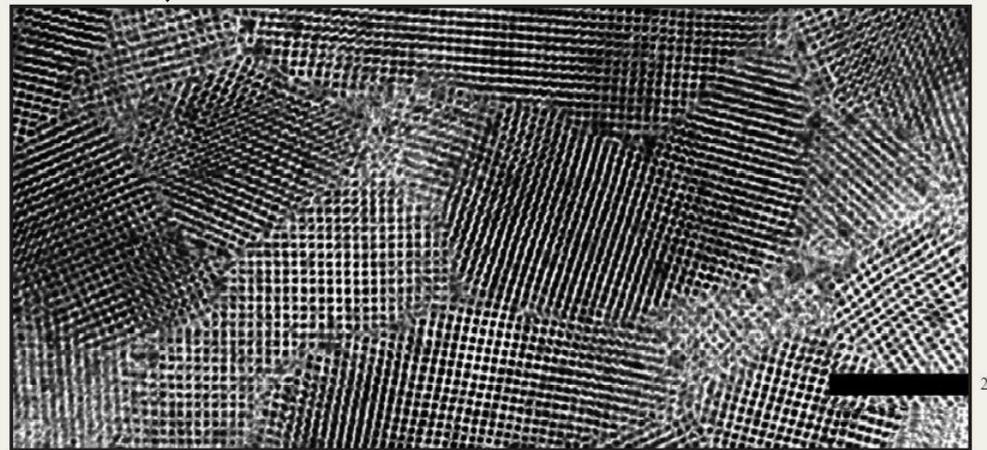


Chemical Synthesis of Nanocrystals

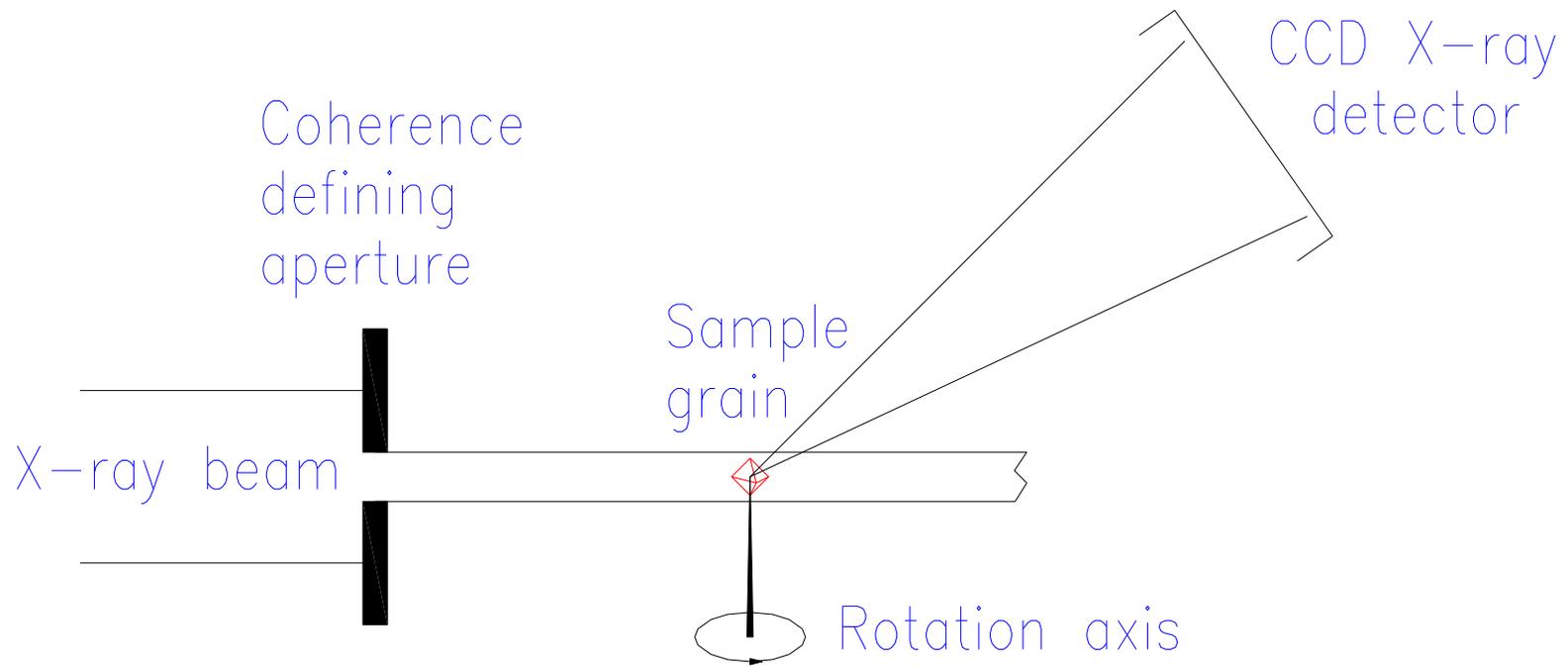


- Reactants introduced rapidly
- High temperature solvent
- Surfactant/organic capping agent
- Square superlattice (200nm scale)

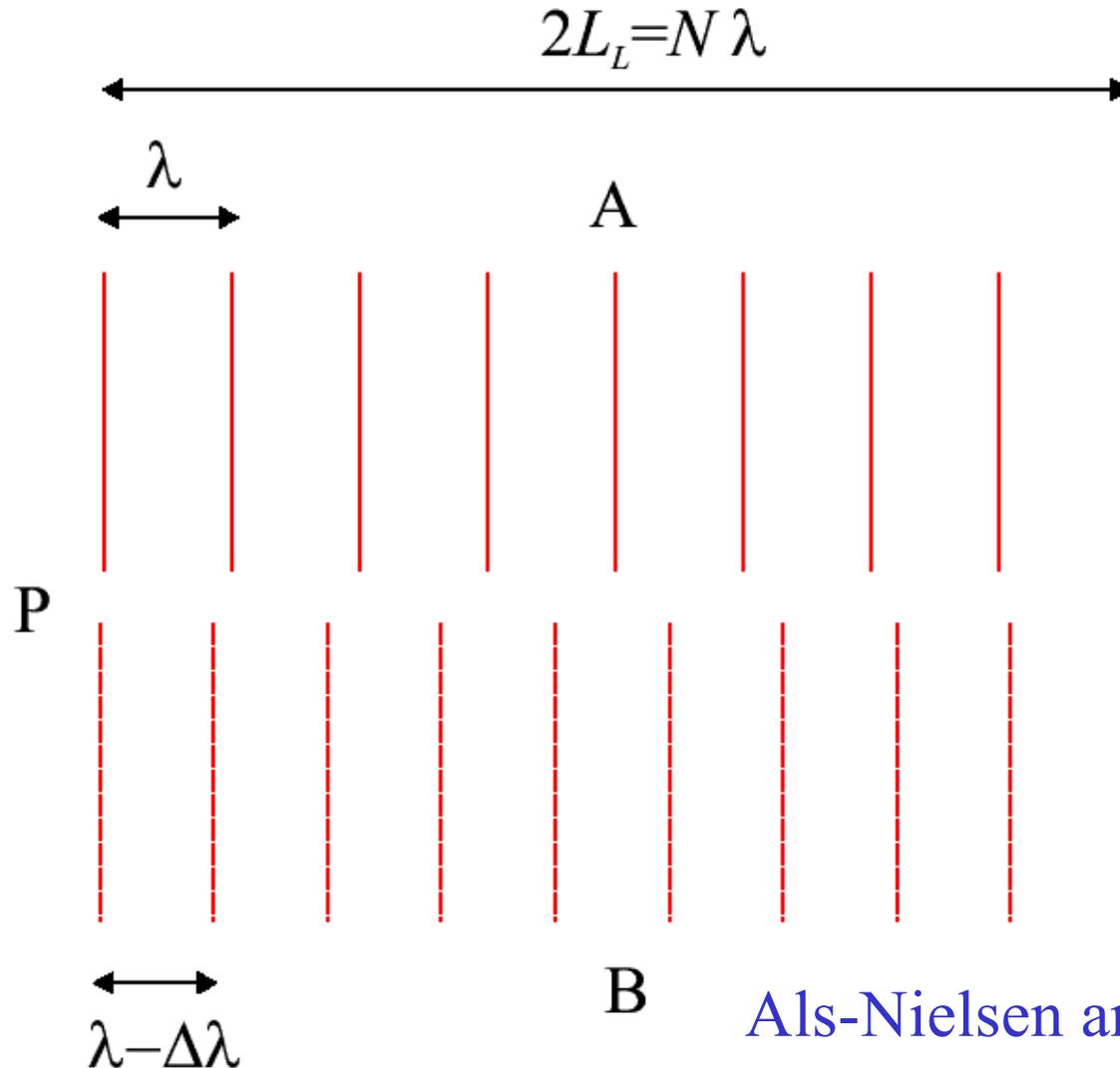
C. B. Murray, IBM J. Res. & Dev. **45**
47 (2001)



Lensless X-ray Microscope



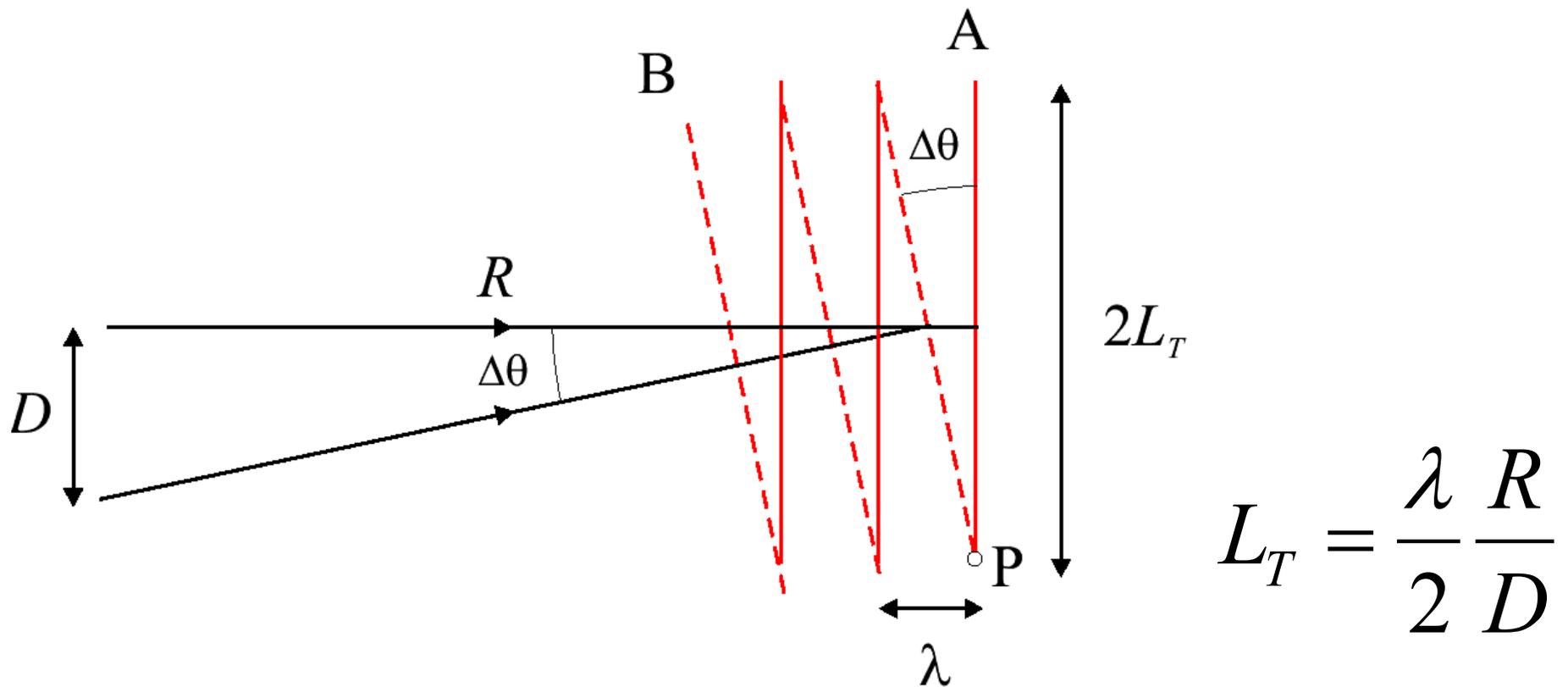
Longitudinal Coherence



$$L_L = \frac{1}{2} \frac{\lambda^2}{\Delta\lambda}$$

Als-Nielsen and McMorro (2001)

Lateral (Transverse) Coherence



$$L_T = \frac{\lambda R}{2 D}$$

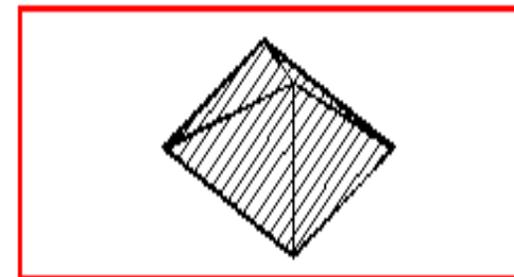
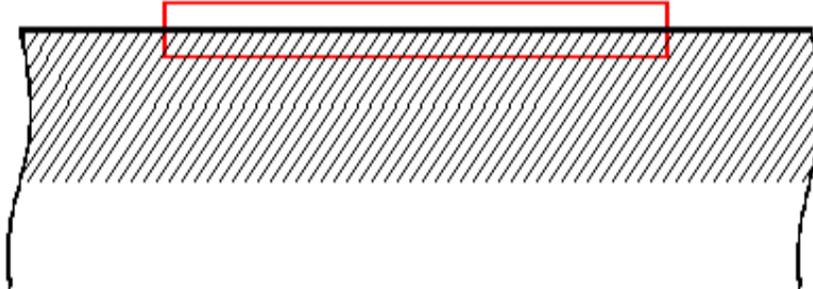
Als-Nielsen and McMorrow (2001)

Coherence at the APS

Typical 3rd Generation (undulator) Synchrotron Source

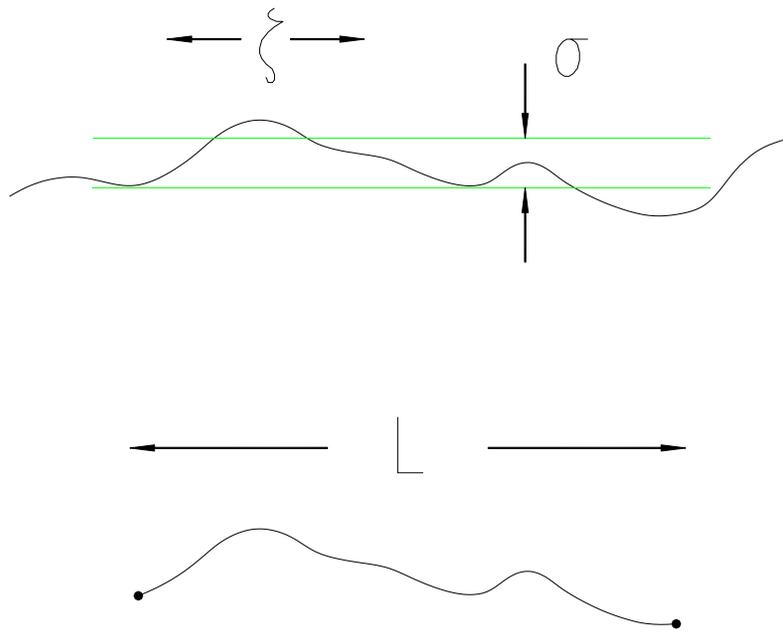
| Coherence of | ξ_{VER} | ξ_{HORIZ} | ξ_{LONG} | Flux |
|-----------------------|--------------------|----------------------|---------------------|--------------------|
| Raw Undulator | 35 μm | 9 μm | 0.004 μm | 2×10^{12} |
| Si(111) Monochromator | 35 μm | 9 μm | 1 μm | 1×10^{10} |
| C(111) Monochromator | 35 μm | 9 μm | 3 μm | 3×10^9 |

Coherent region defined by slits

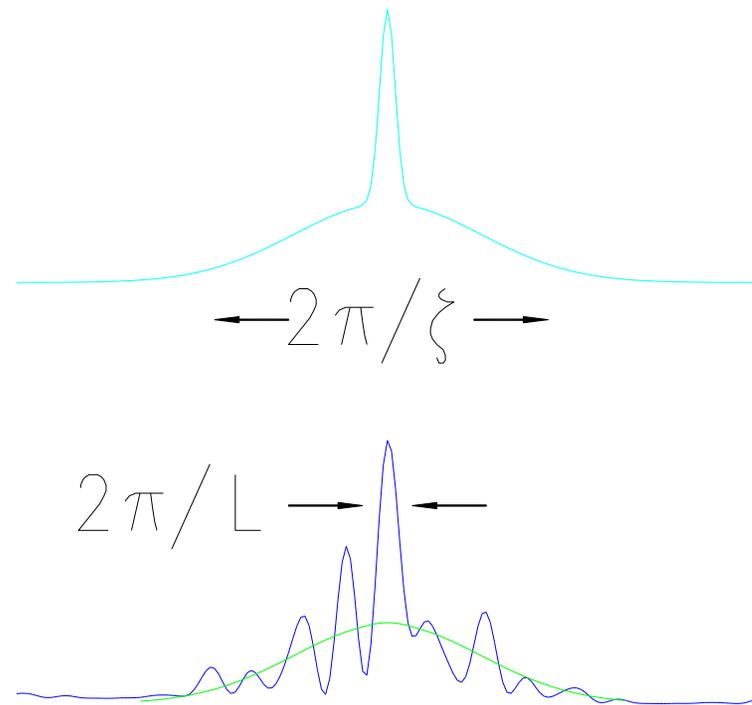


Diffuse Scattering acquires Structure using CXD

Real Space



Reciprocal Space

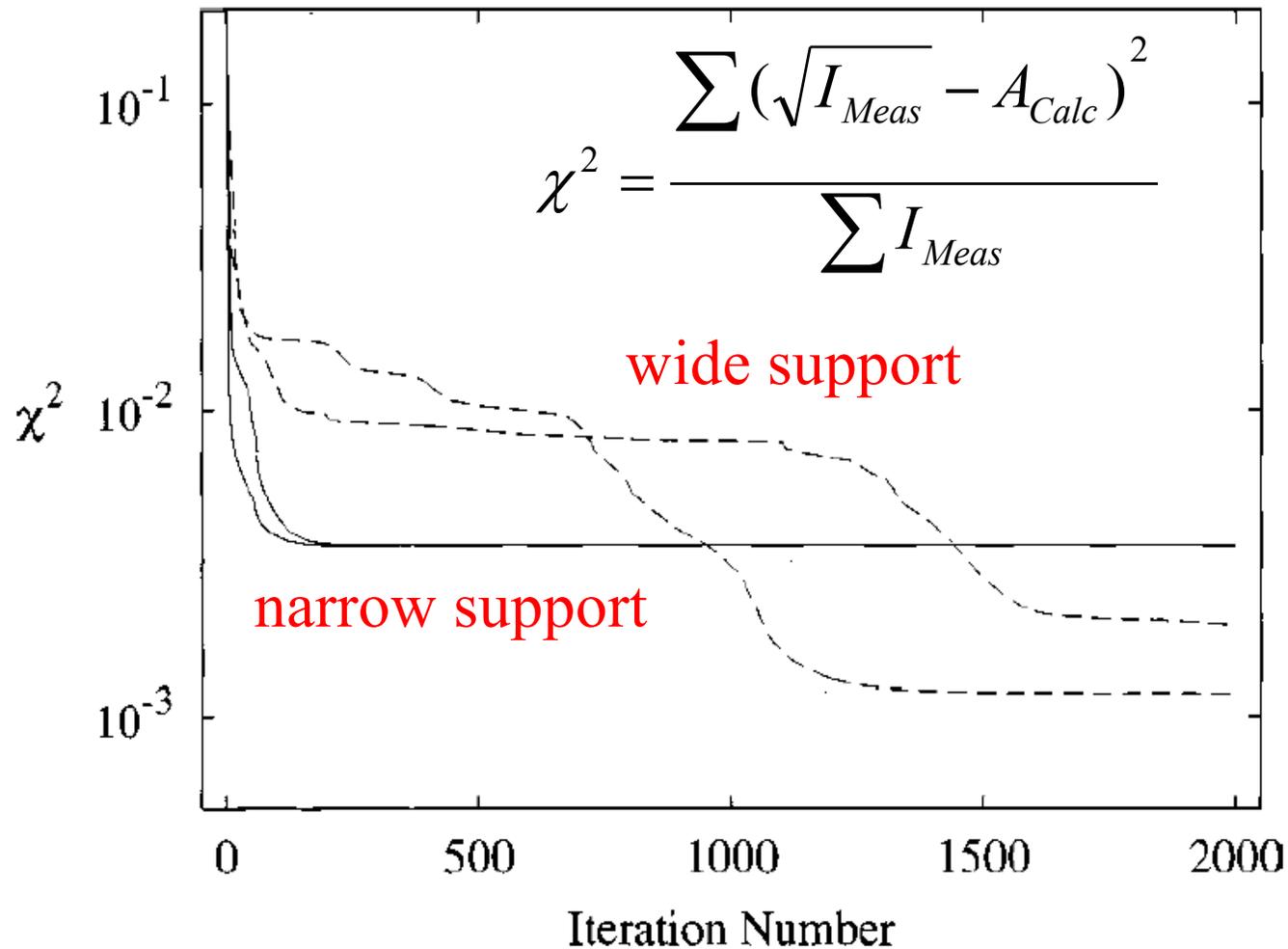


Real-space Constraints in Crystallography

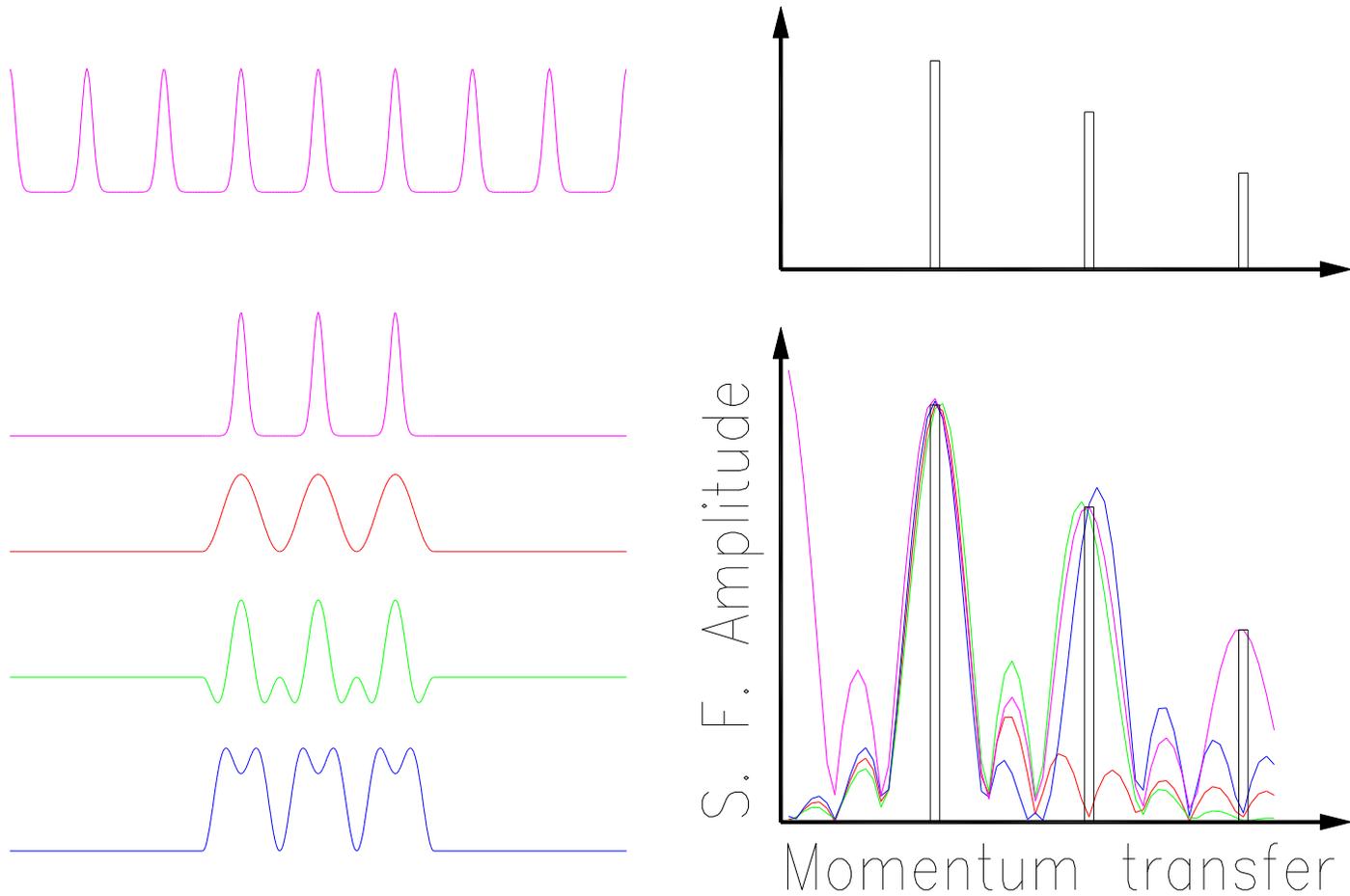
R. P. Millane, J. Opt. Soc Am. A 13 725 (1996)

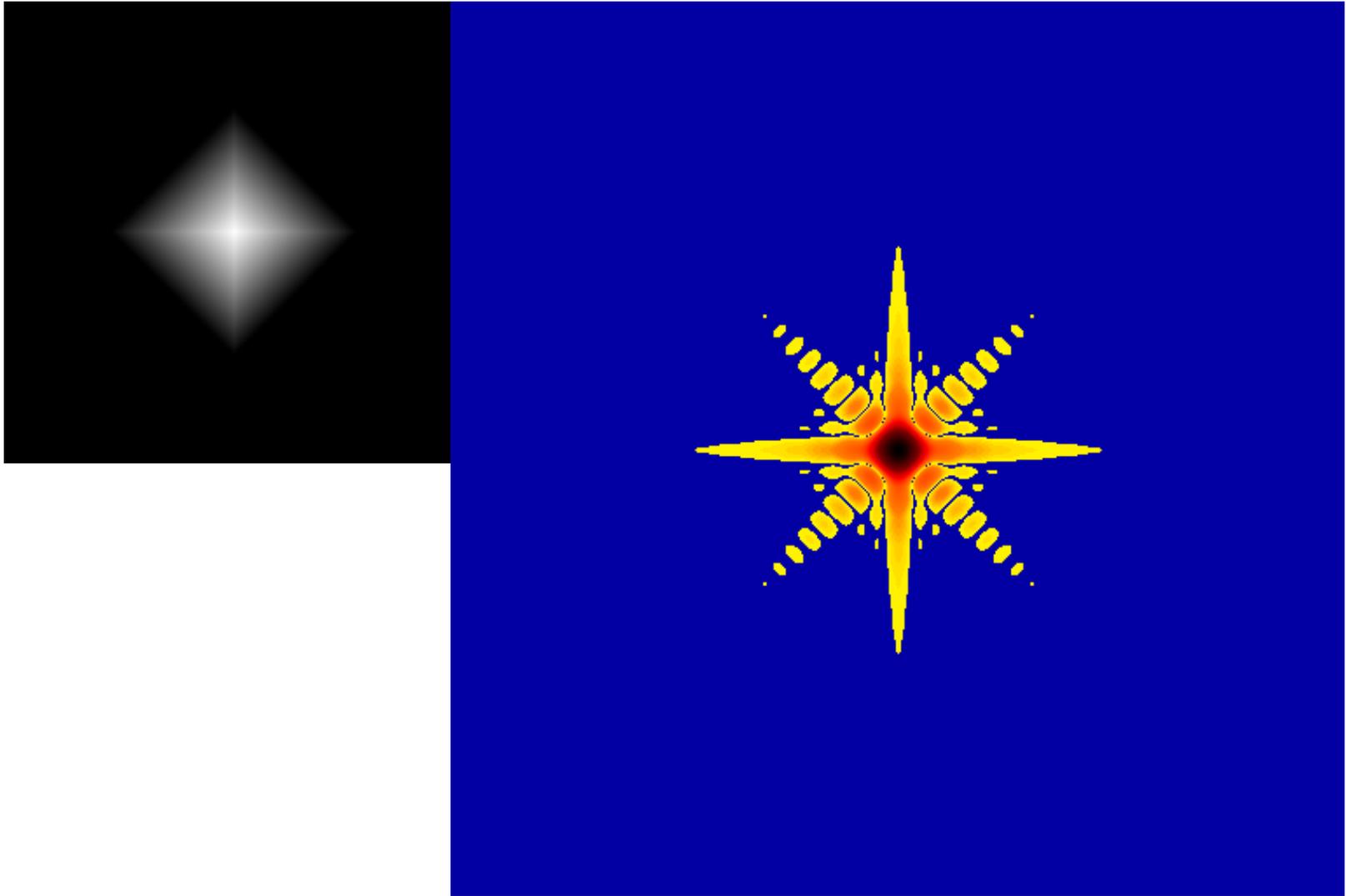
- ‘Positivity’, ‘Atomicity’ constraints (Sayre)
- Solvent flattening
- Non-crystallographic symmetry
- Molecular replacement
- Finite **support** = molecular envelope
- Non-uniqueness is ‘pathologically rare’ ($d > 1$)

Convergence Trajectory



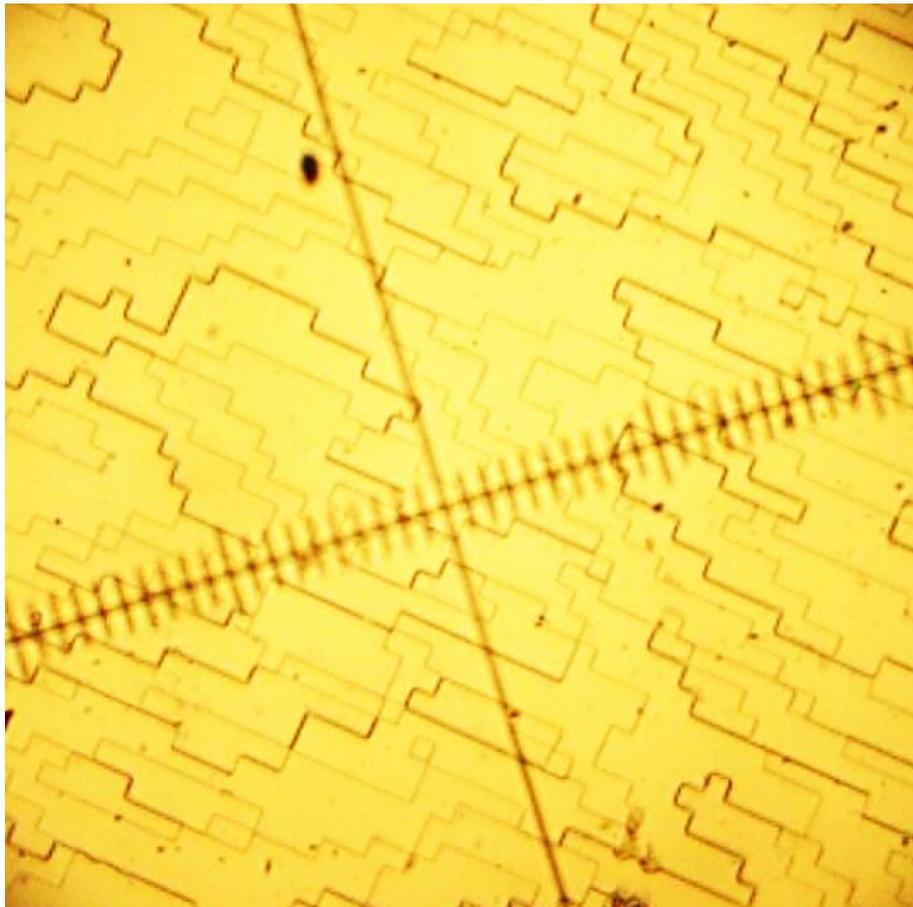
Phase Problem: Finite-size Effect



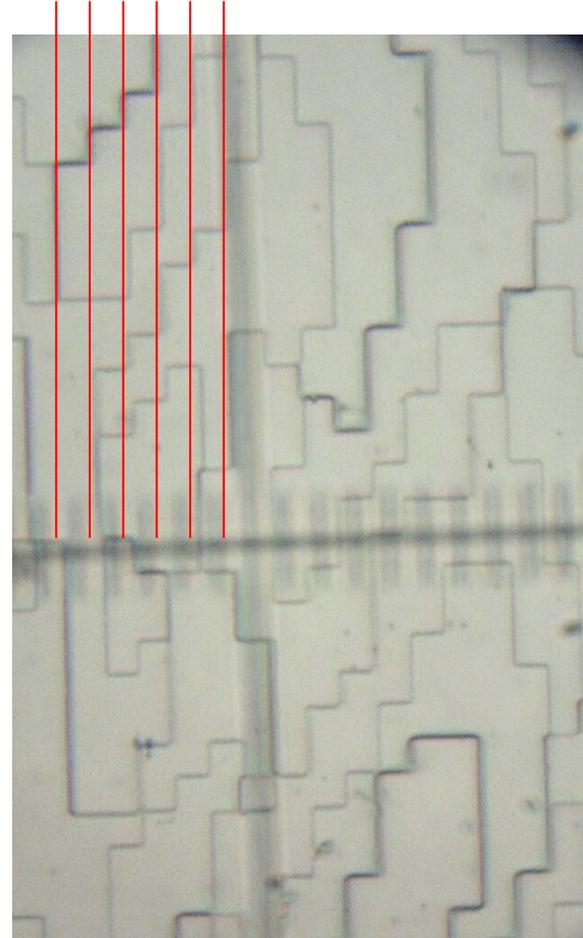


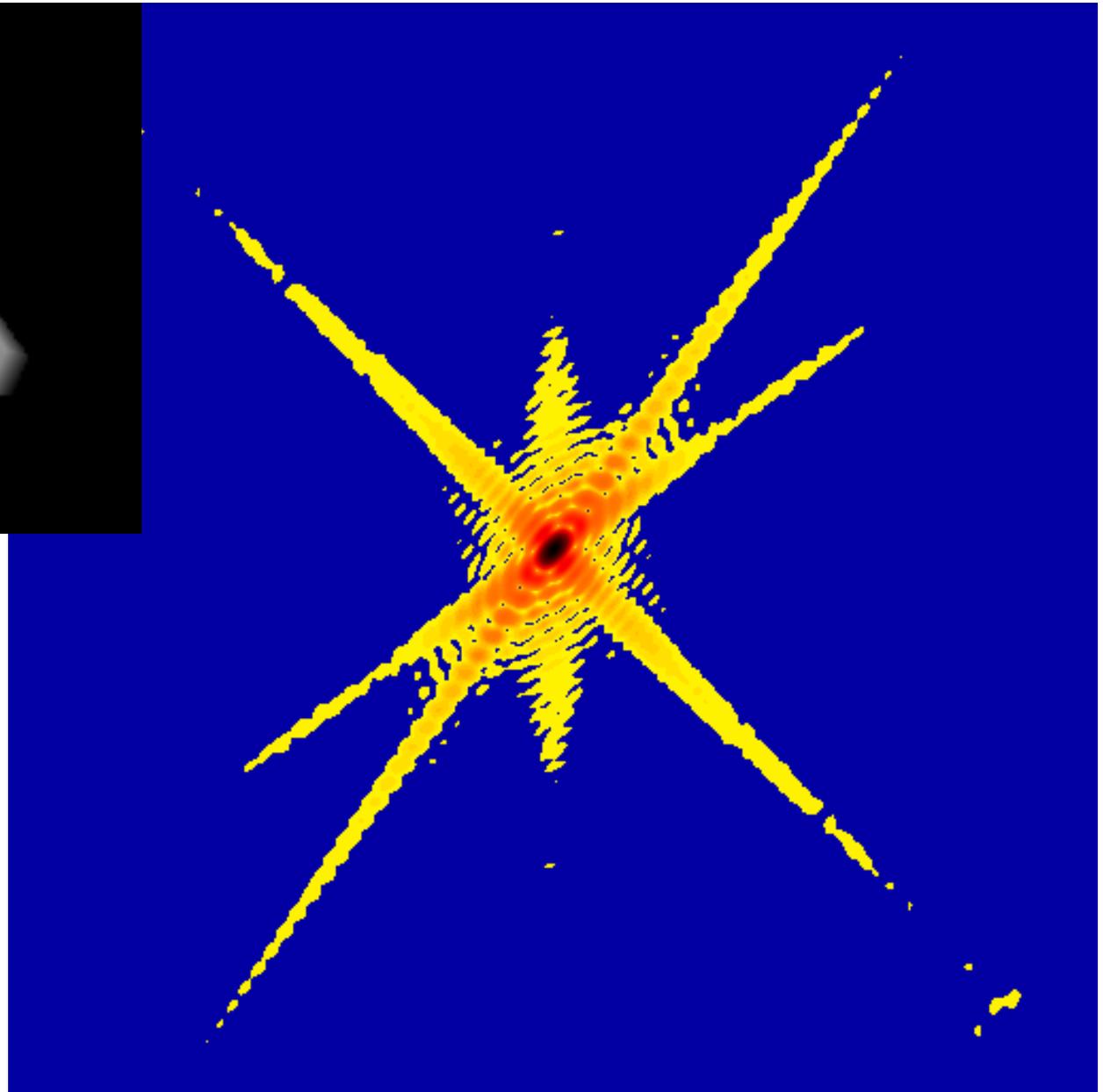
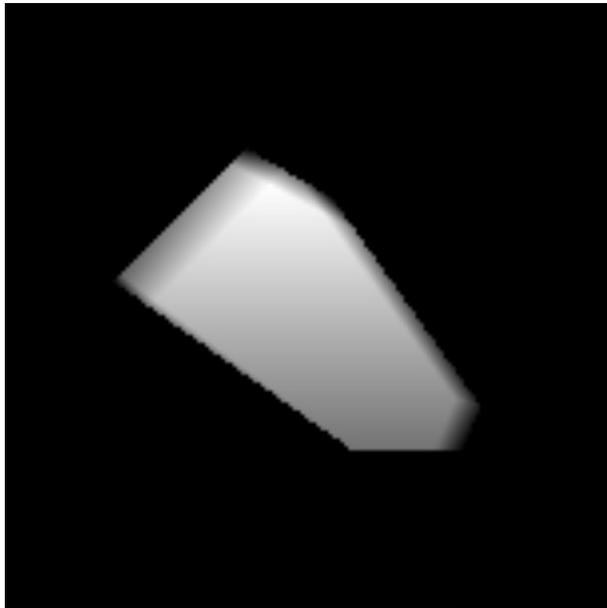


Microscope Images of Gratings



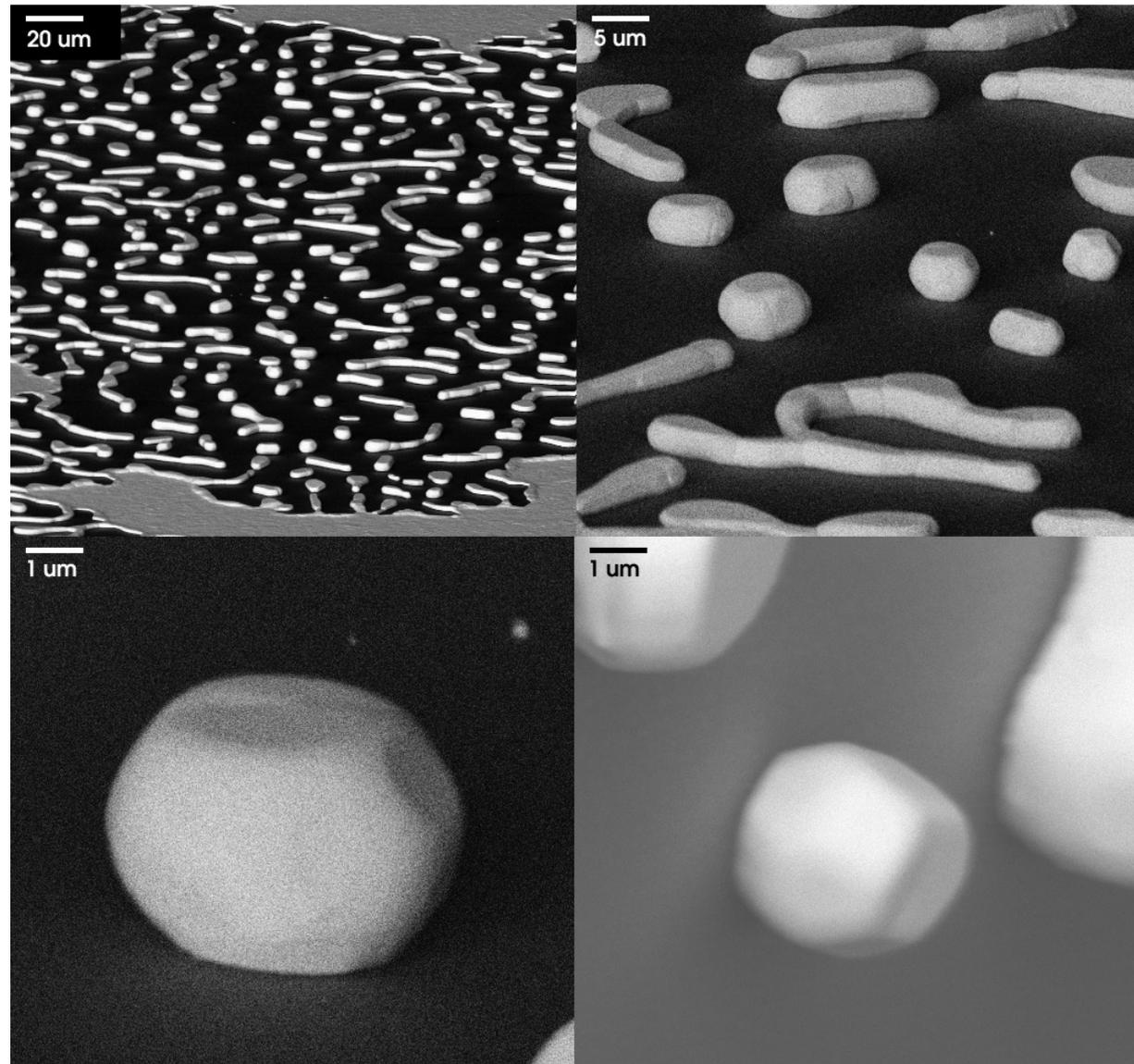
5 μ m grid lines



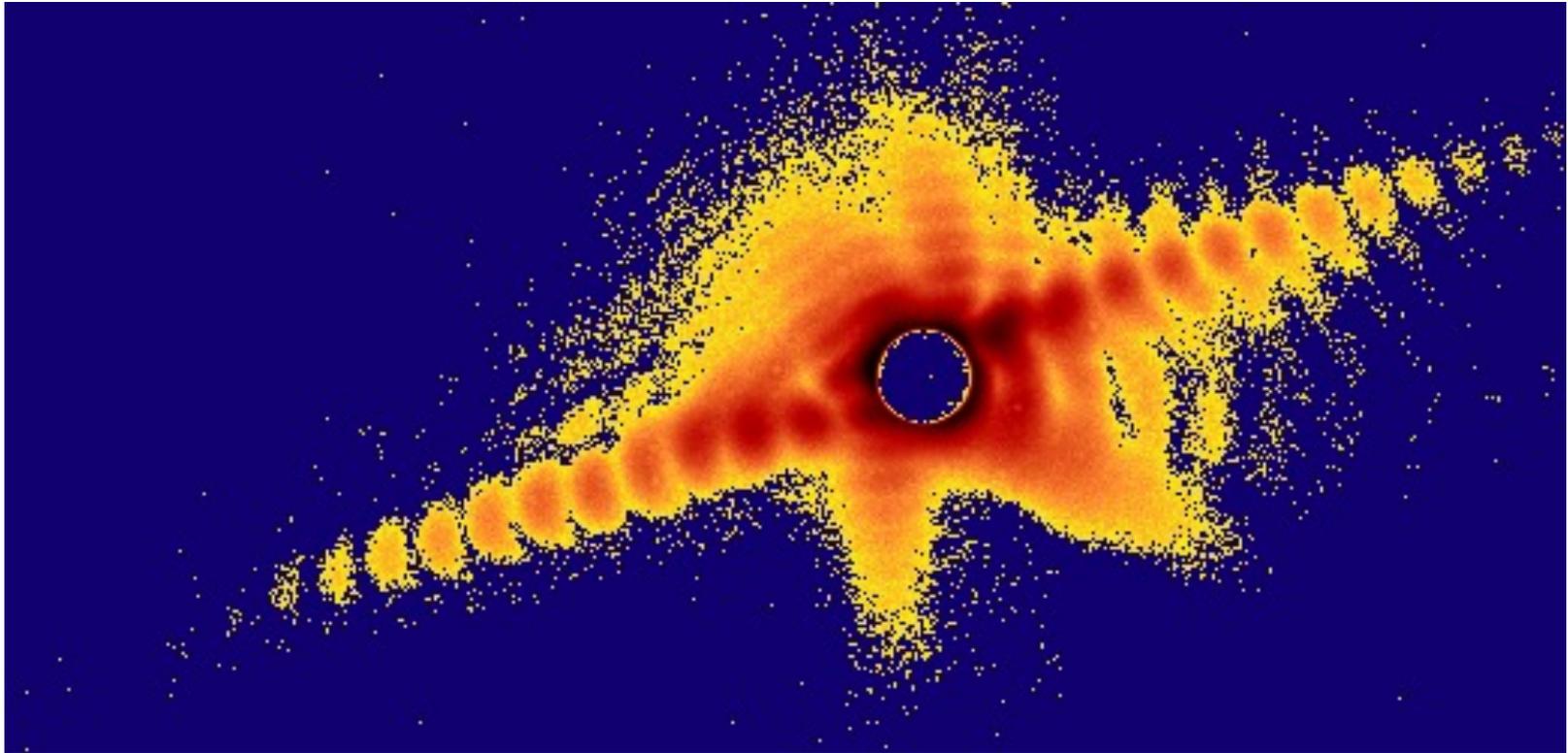


SEMS

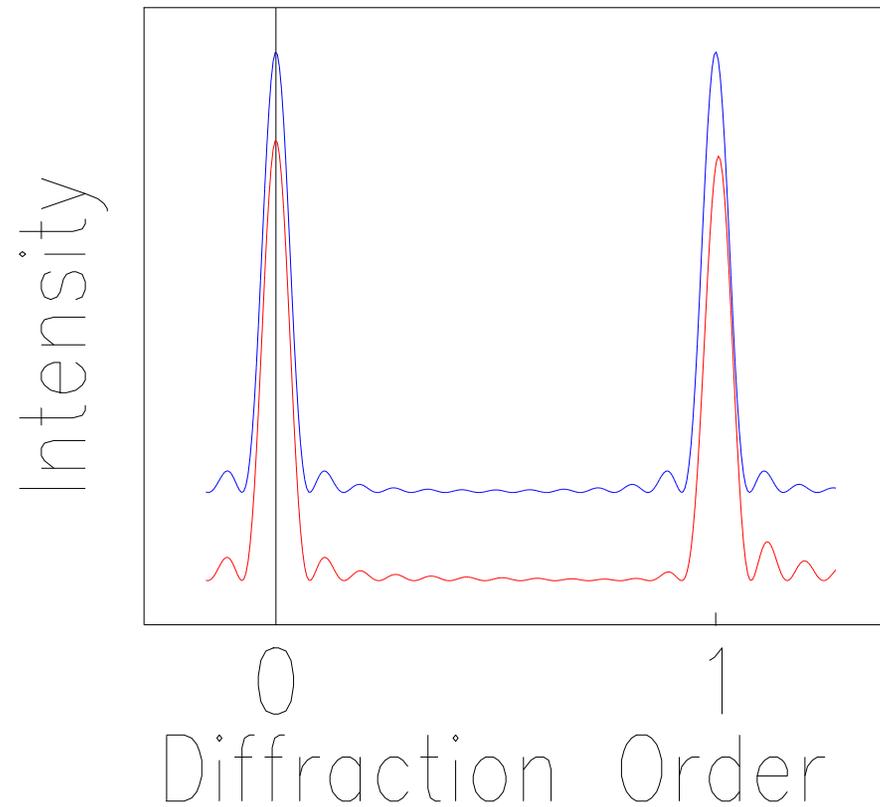
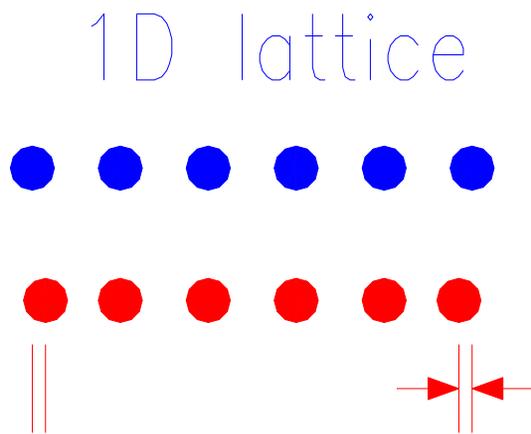
- Au blanket film
- Quartz substrate
- Annealed at 950°C for 70 hrs.



Micron-sized gold crystal: (111) Bragg reflection

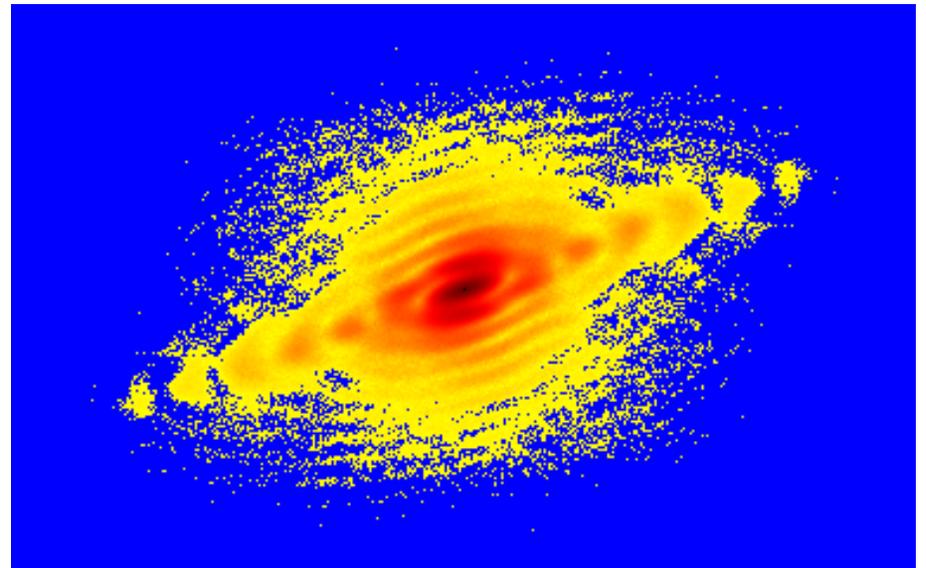
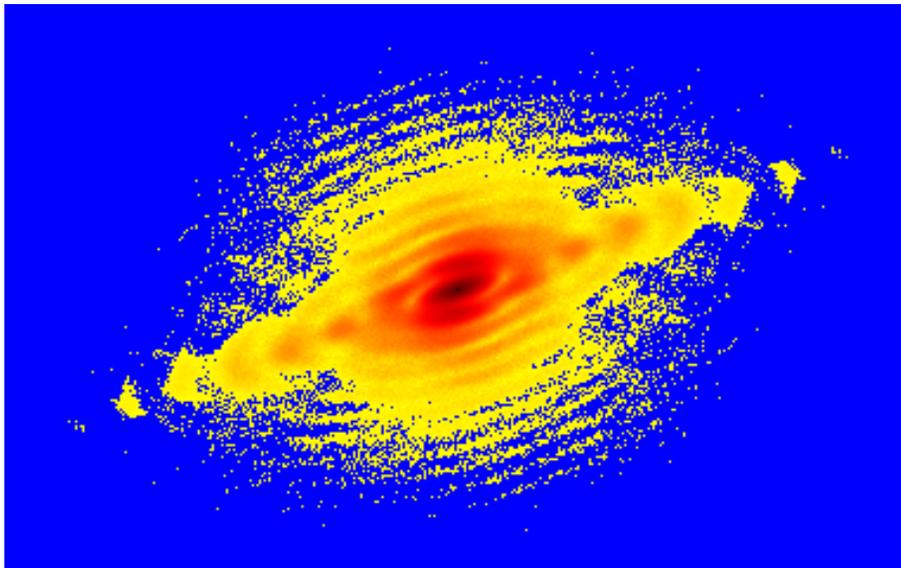
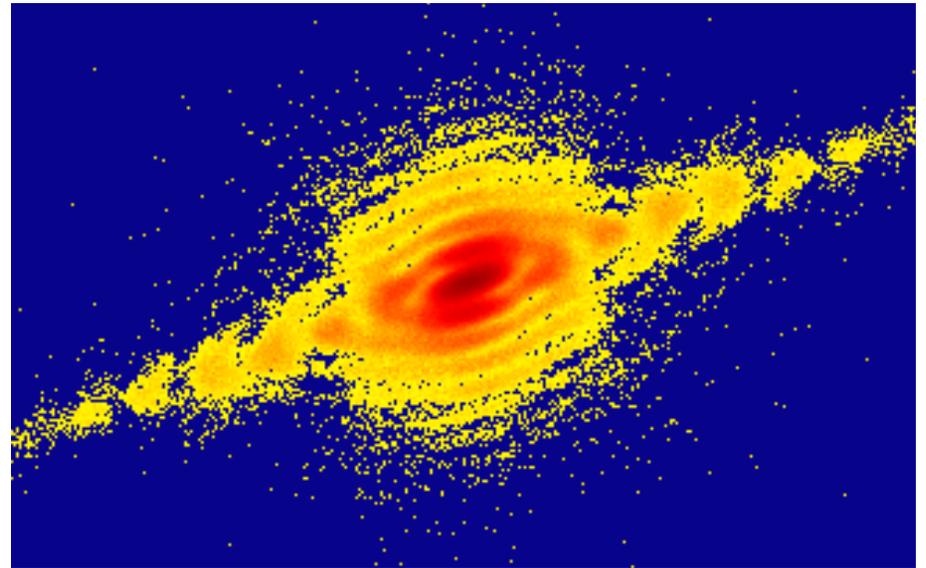


Imaging of Lattice Strains



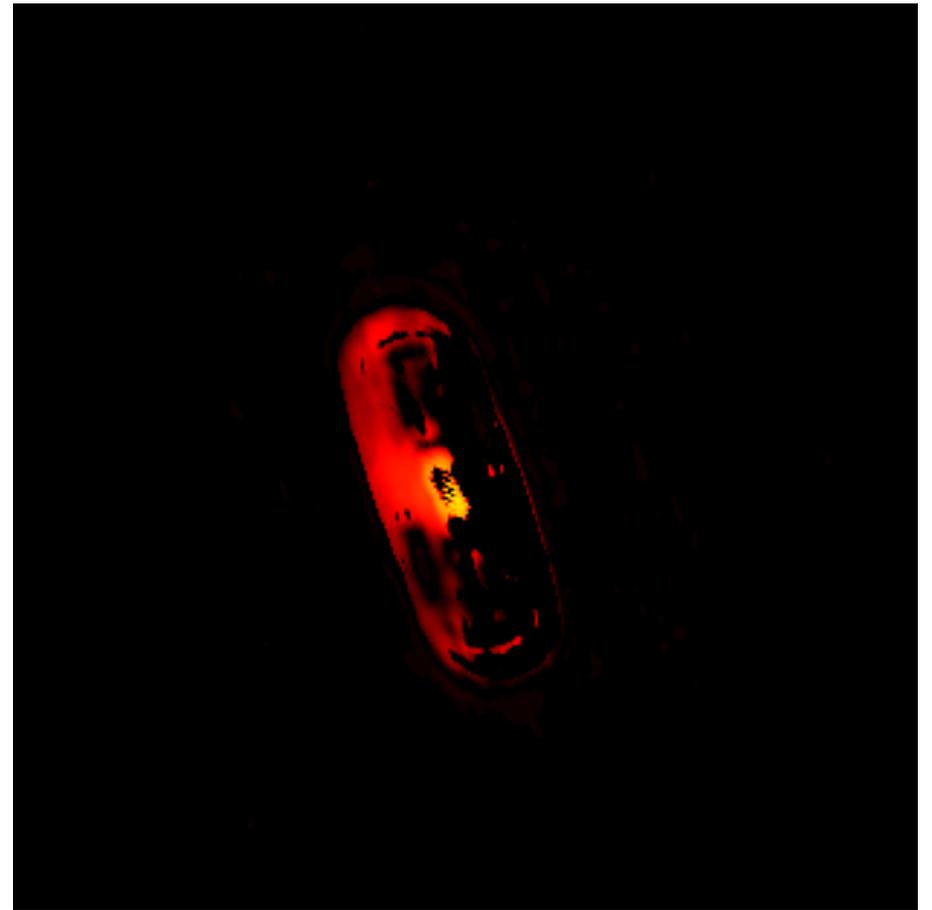
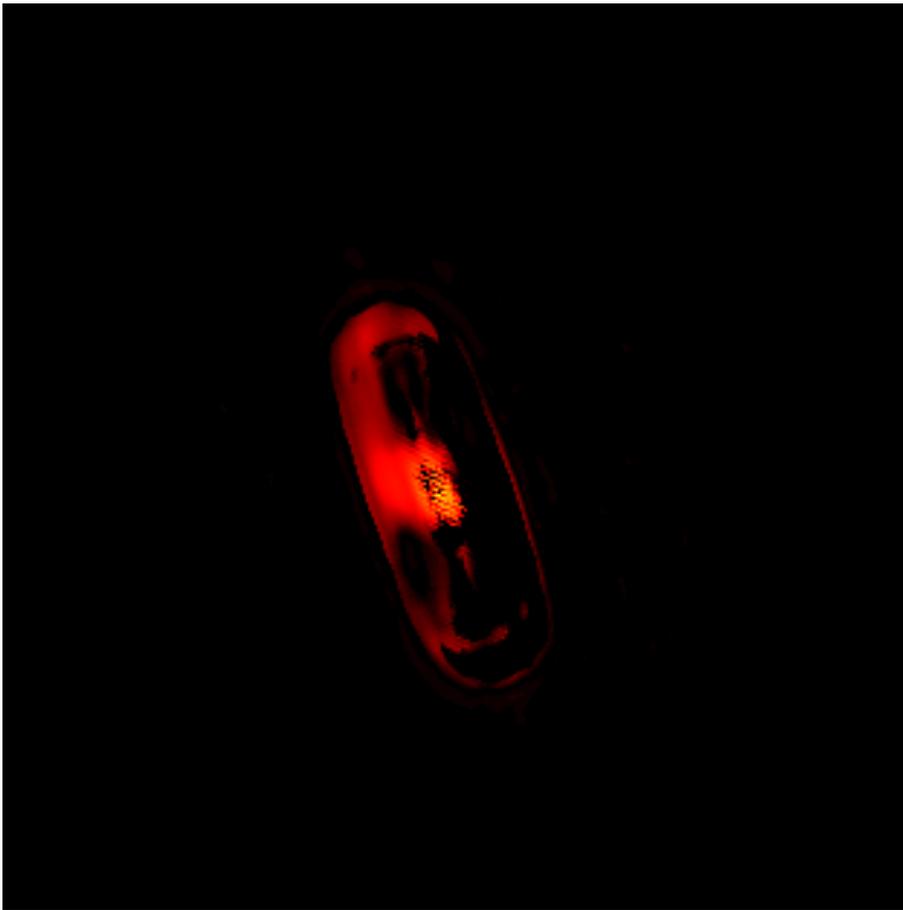
Symmetrized Data and two best fits

Chisq=0.0005

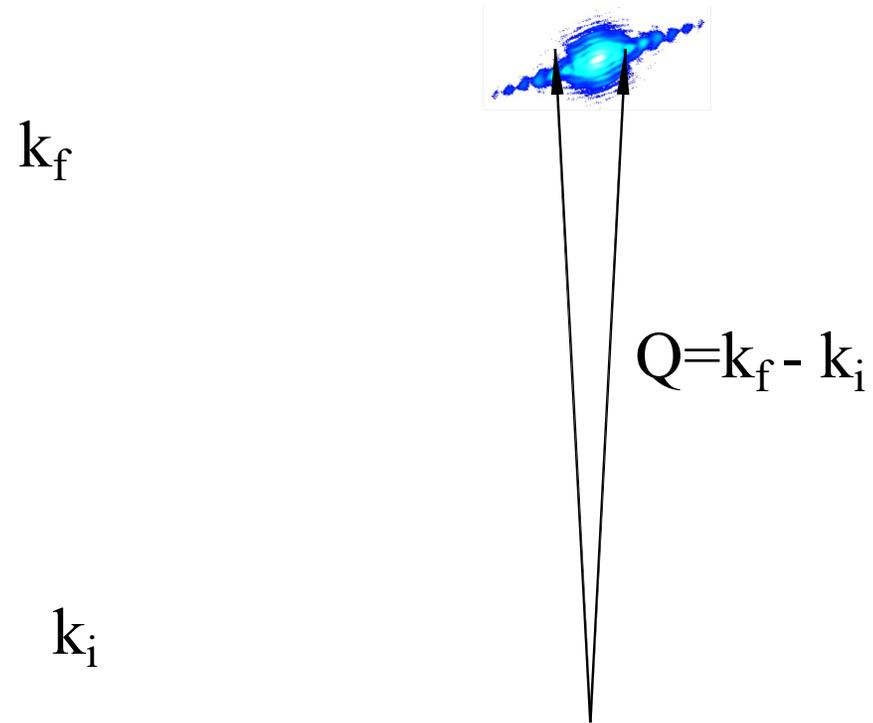


2D Reconstructions

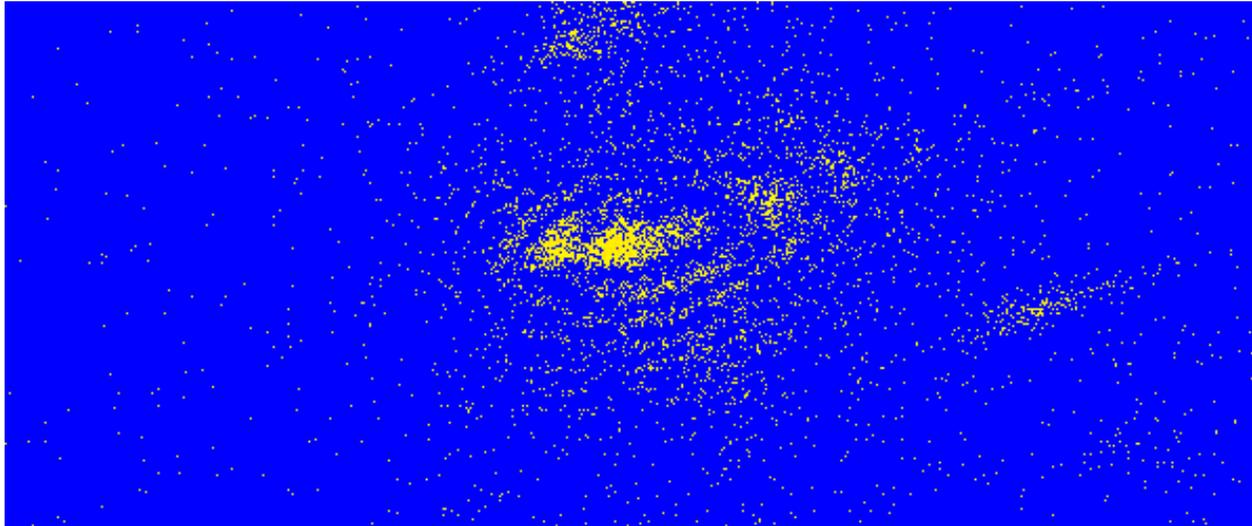
chisquare = 0.0005



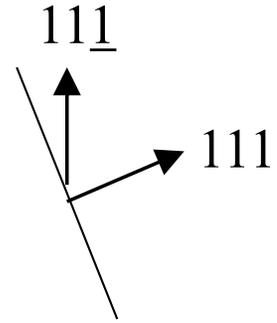
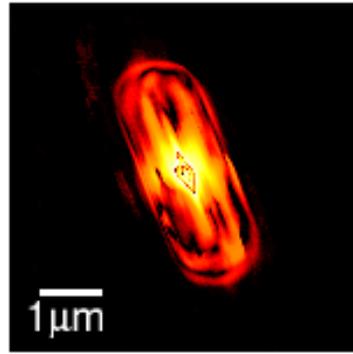
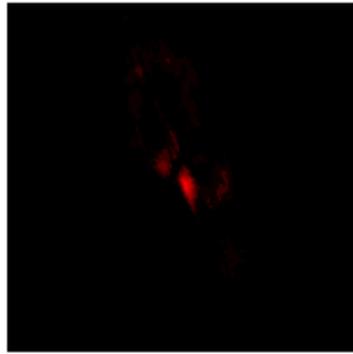
3D Diffraction Method



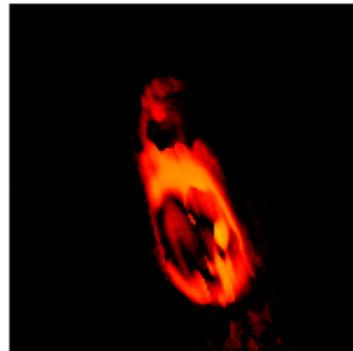
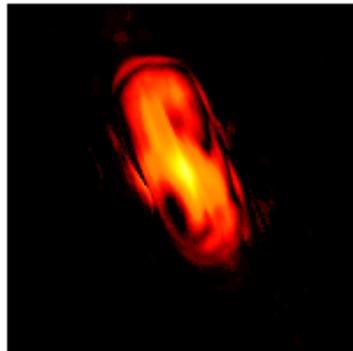
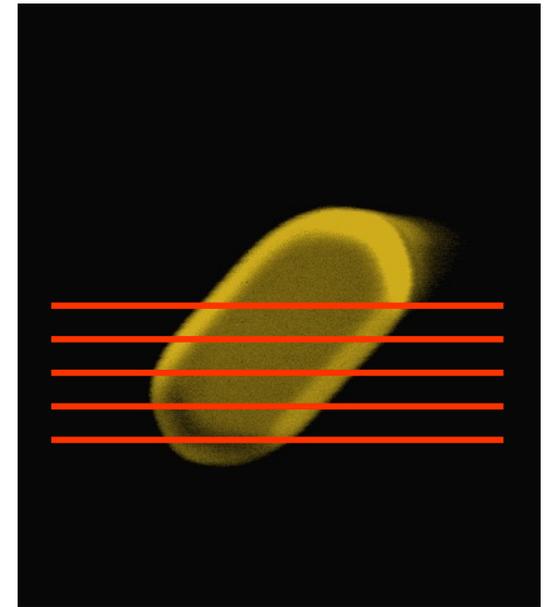
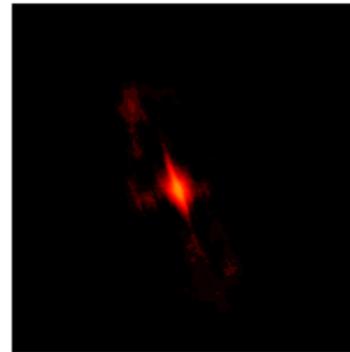
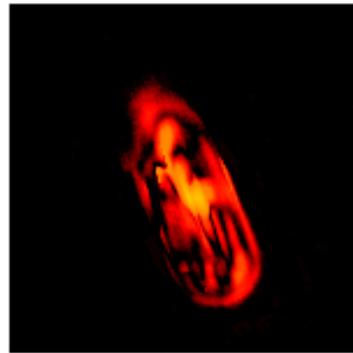
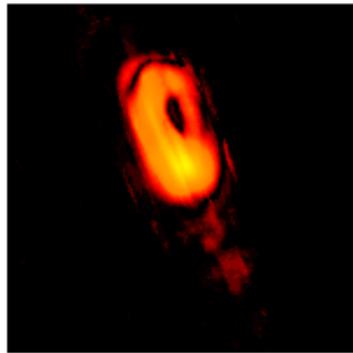
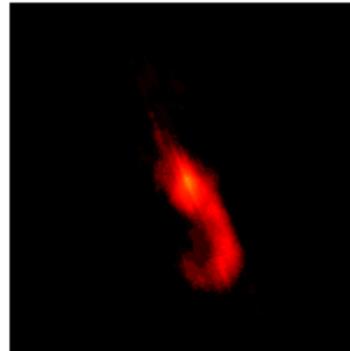
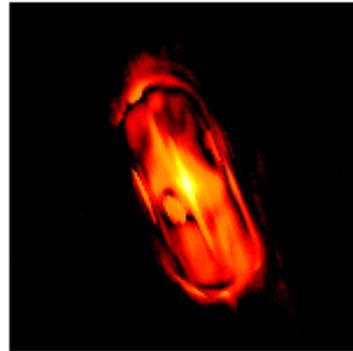
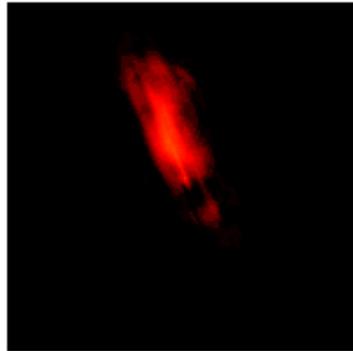
3D Diffraction Data 1 micron Au crystal



* Center is Symmetric *

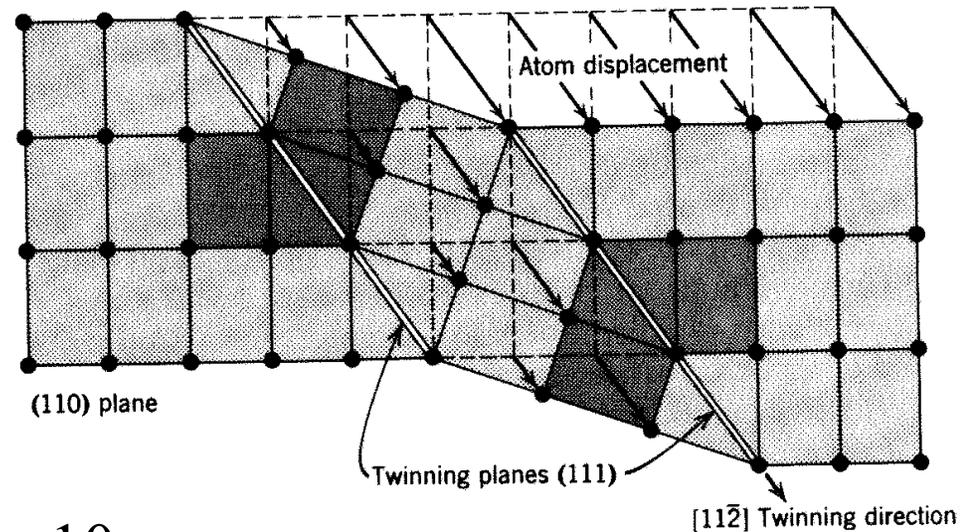
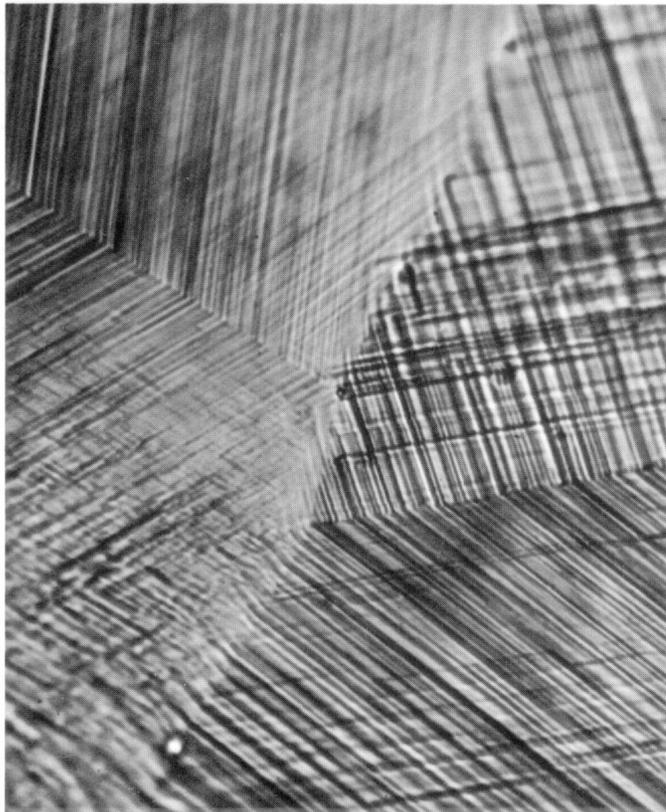


Slices through
plan view SEM:



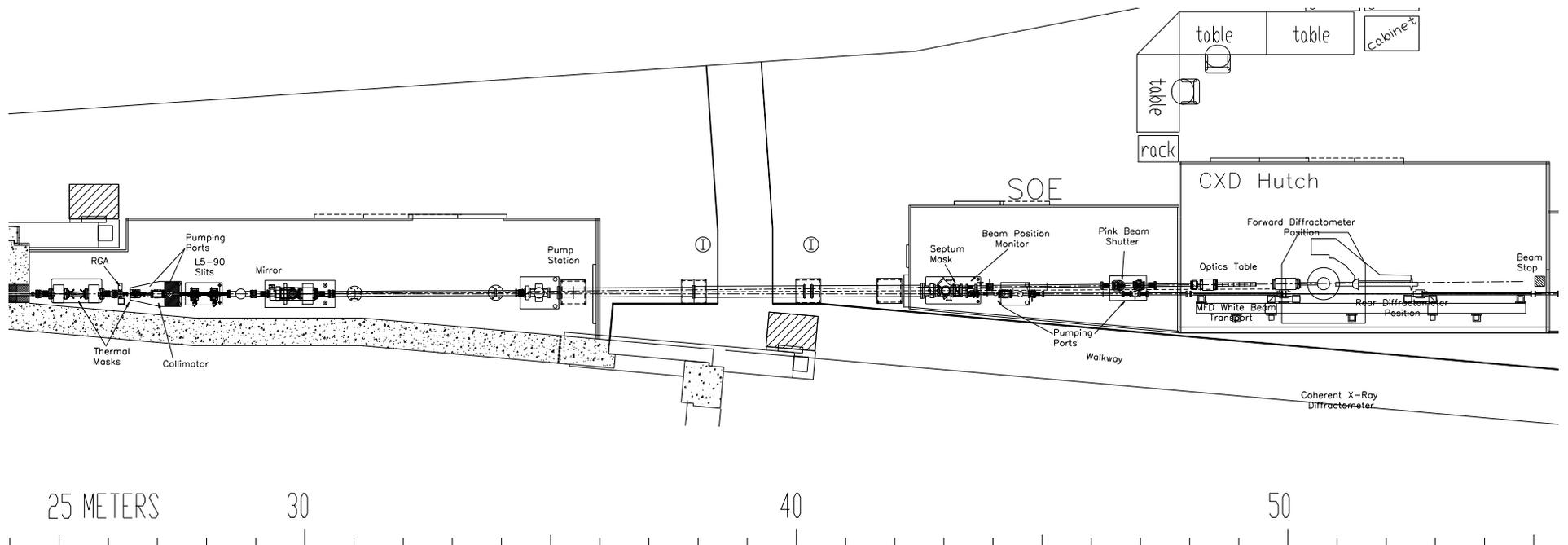
Twinning in deformed FCC metals

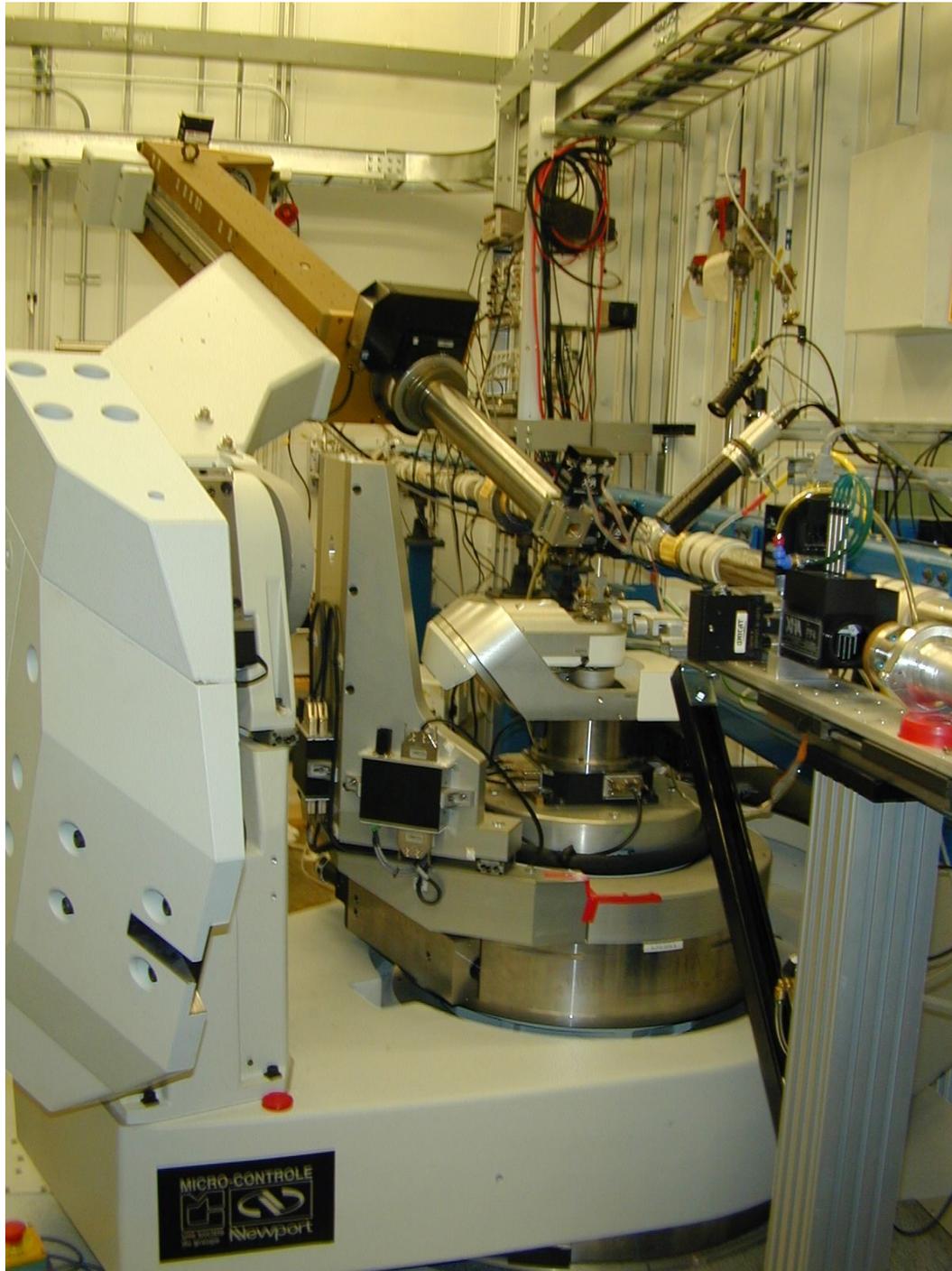
J. Wulff, "Structure and Property of Materials III" (1965)



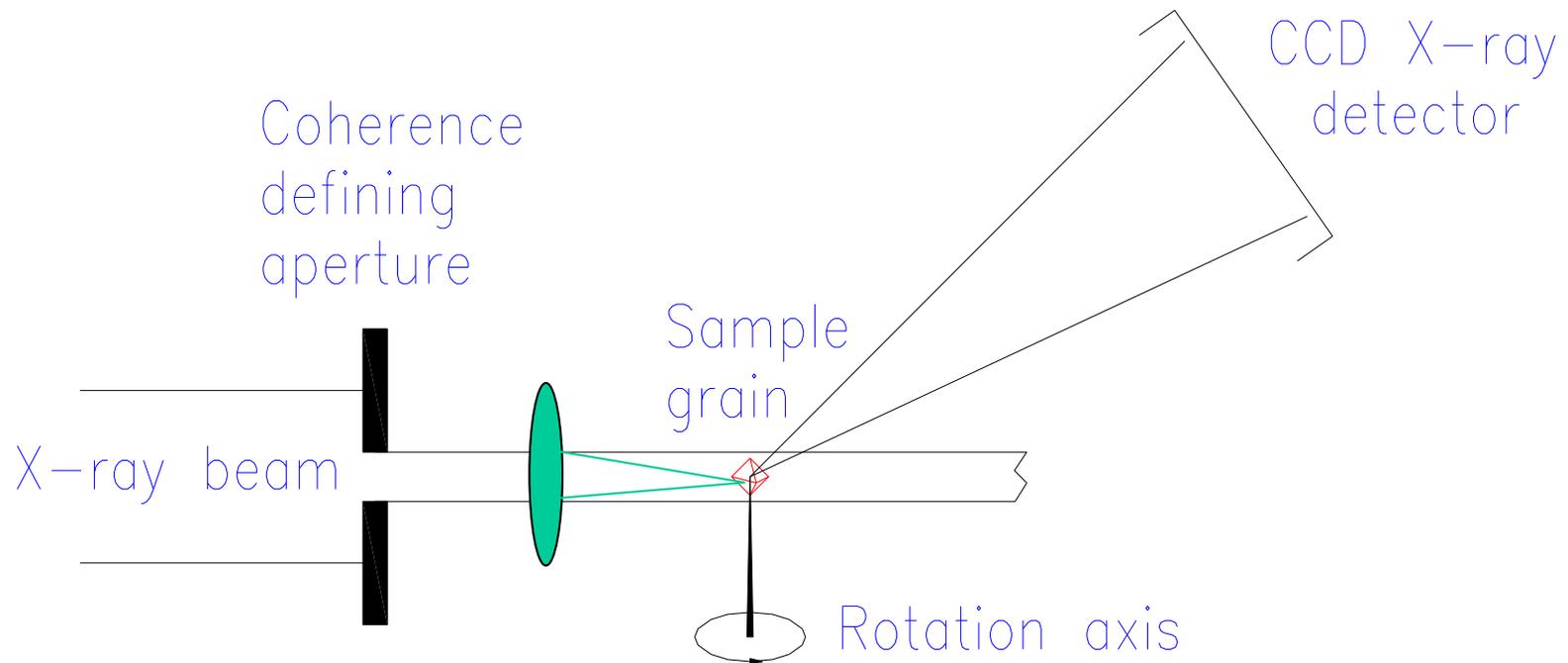
■ $\sim 10\mu\text{m}$
Cu

CXD Beamline at APS Sector 34

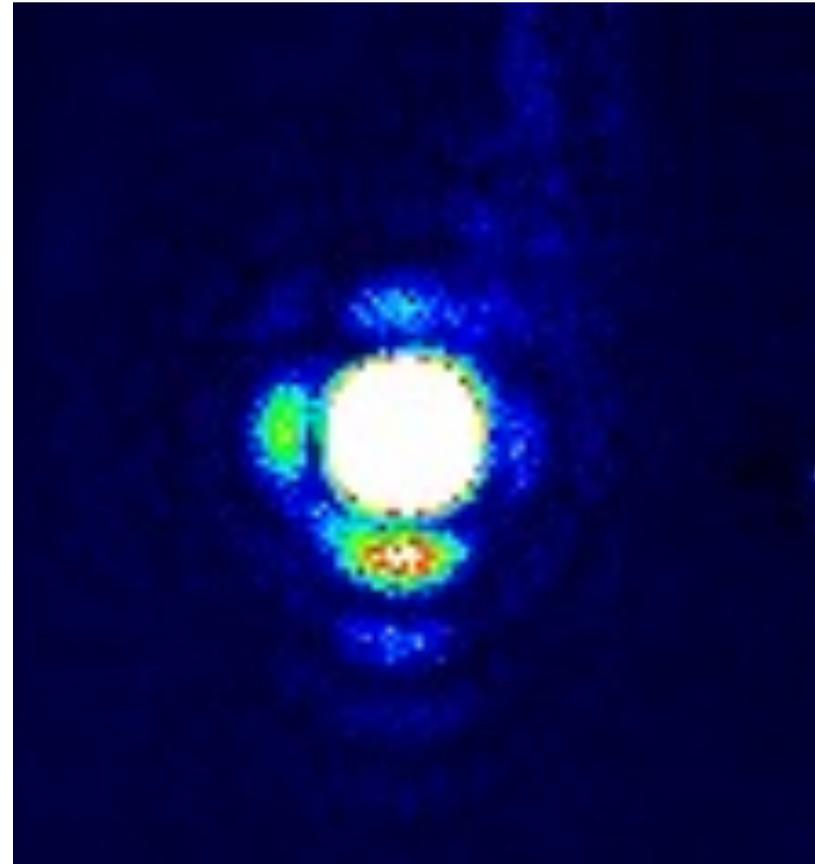
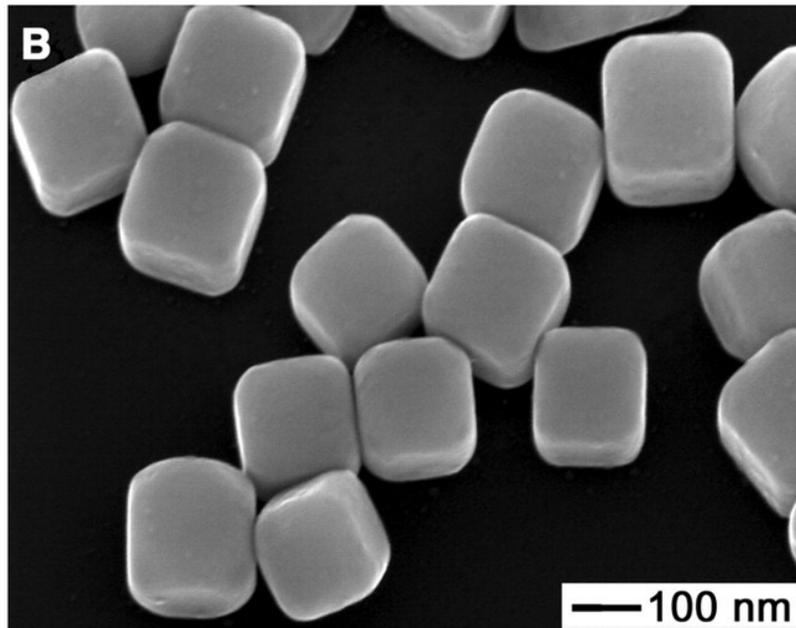




Lensless X-ray Microscope

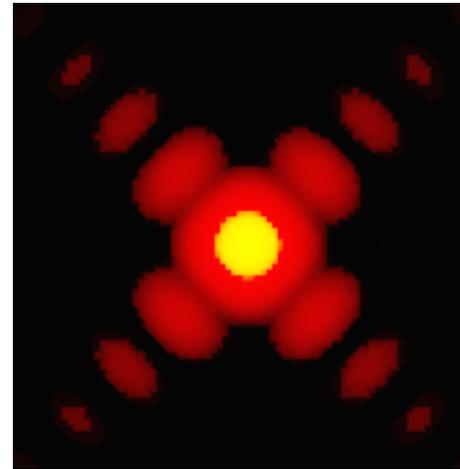
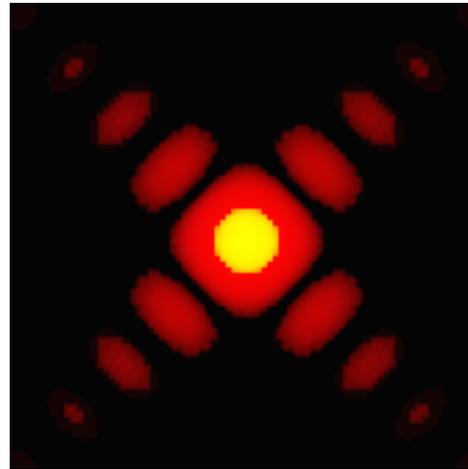


CXD from Silver Nanocubes



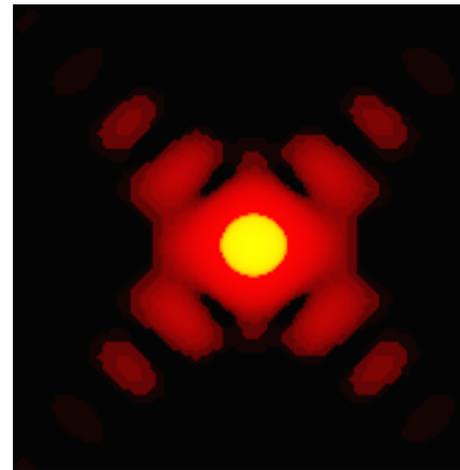
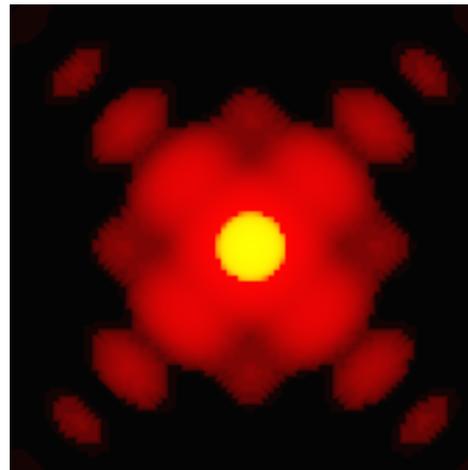
Yugang Sun and Younan Xia,
Science 298 2177 (2003)

Spherical and cylindrical waves



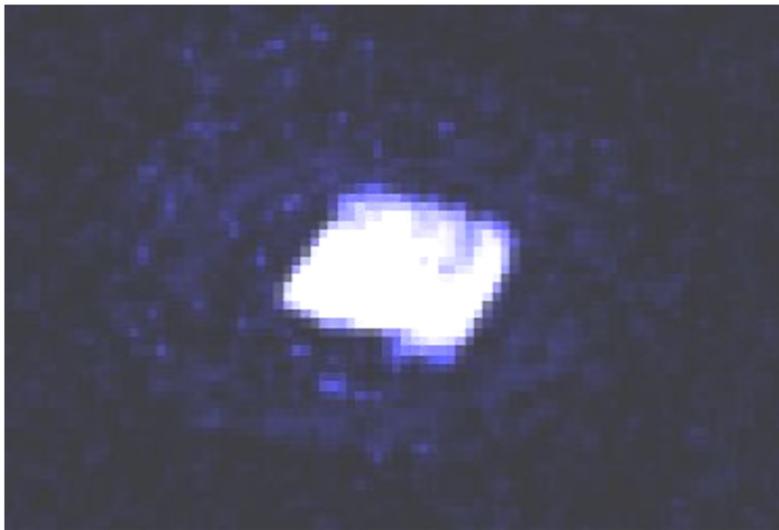
$\pi/4$

$\pi/2$

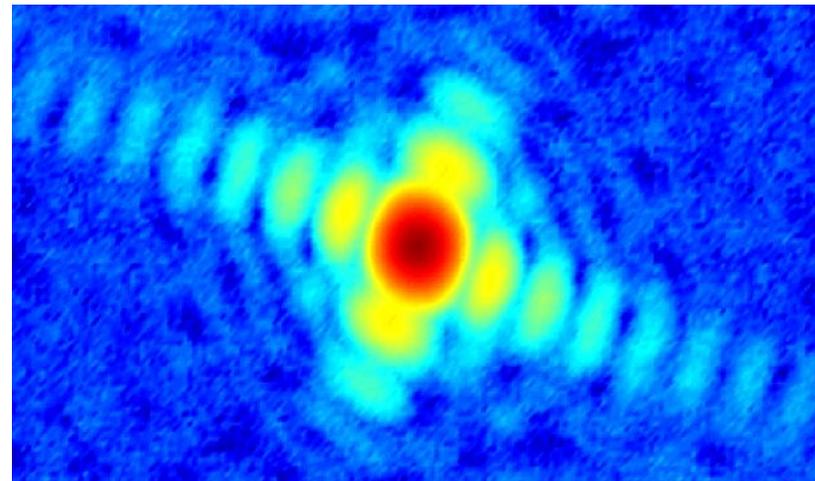
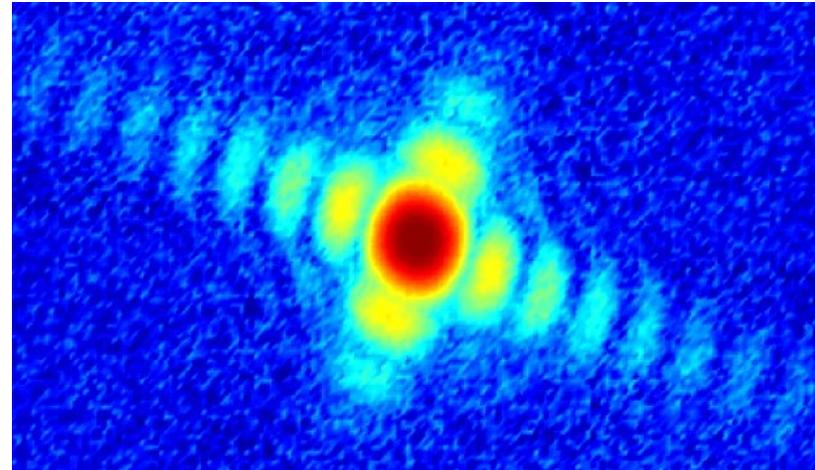


$\pi/4$ (x)

Reconstruction of Ag Nanocrystal

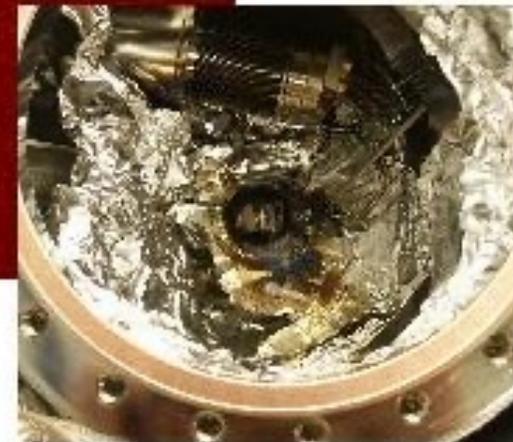
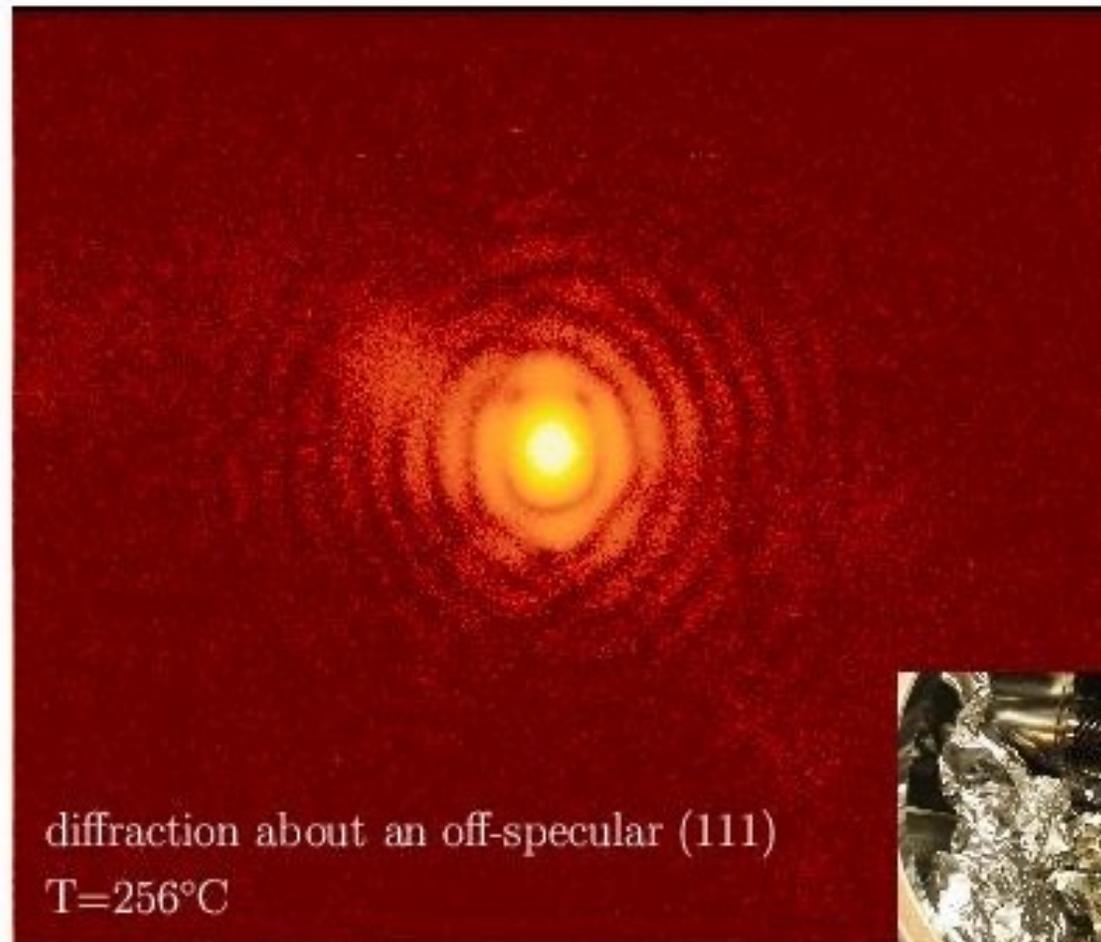


←→
200nm

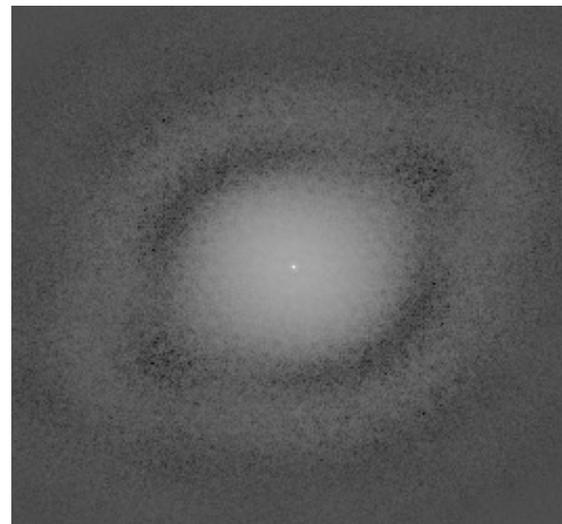
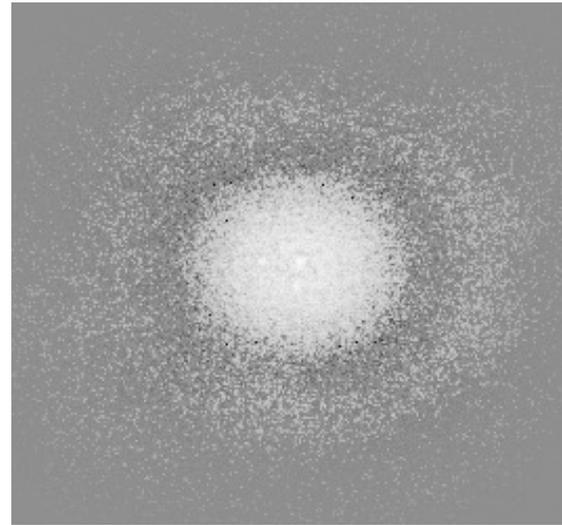
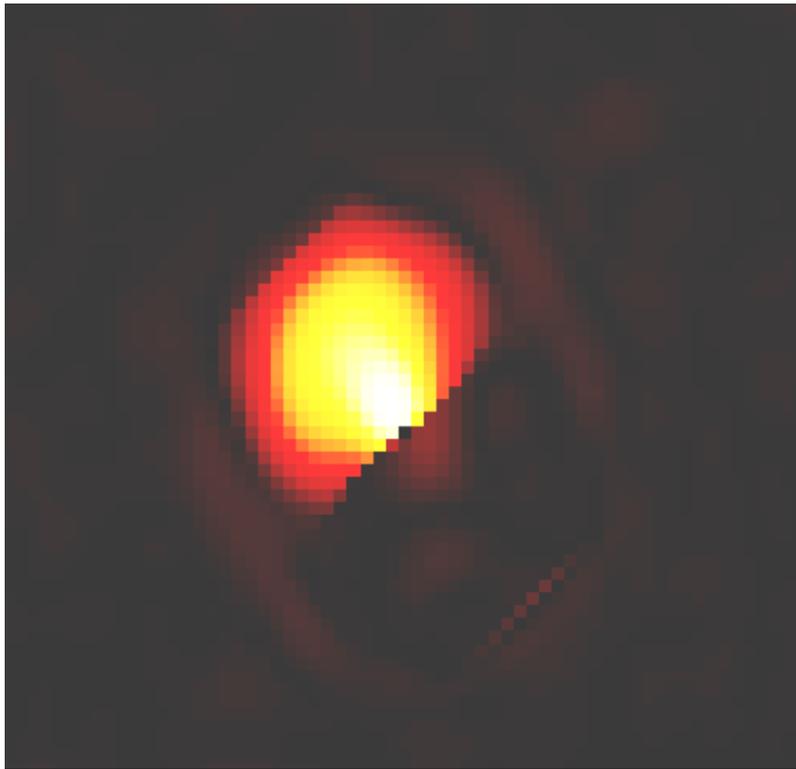


0.7 μm Pb Nanocrystal

In-situ growth at APS sector 34

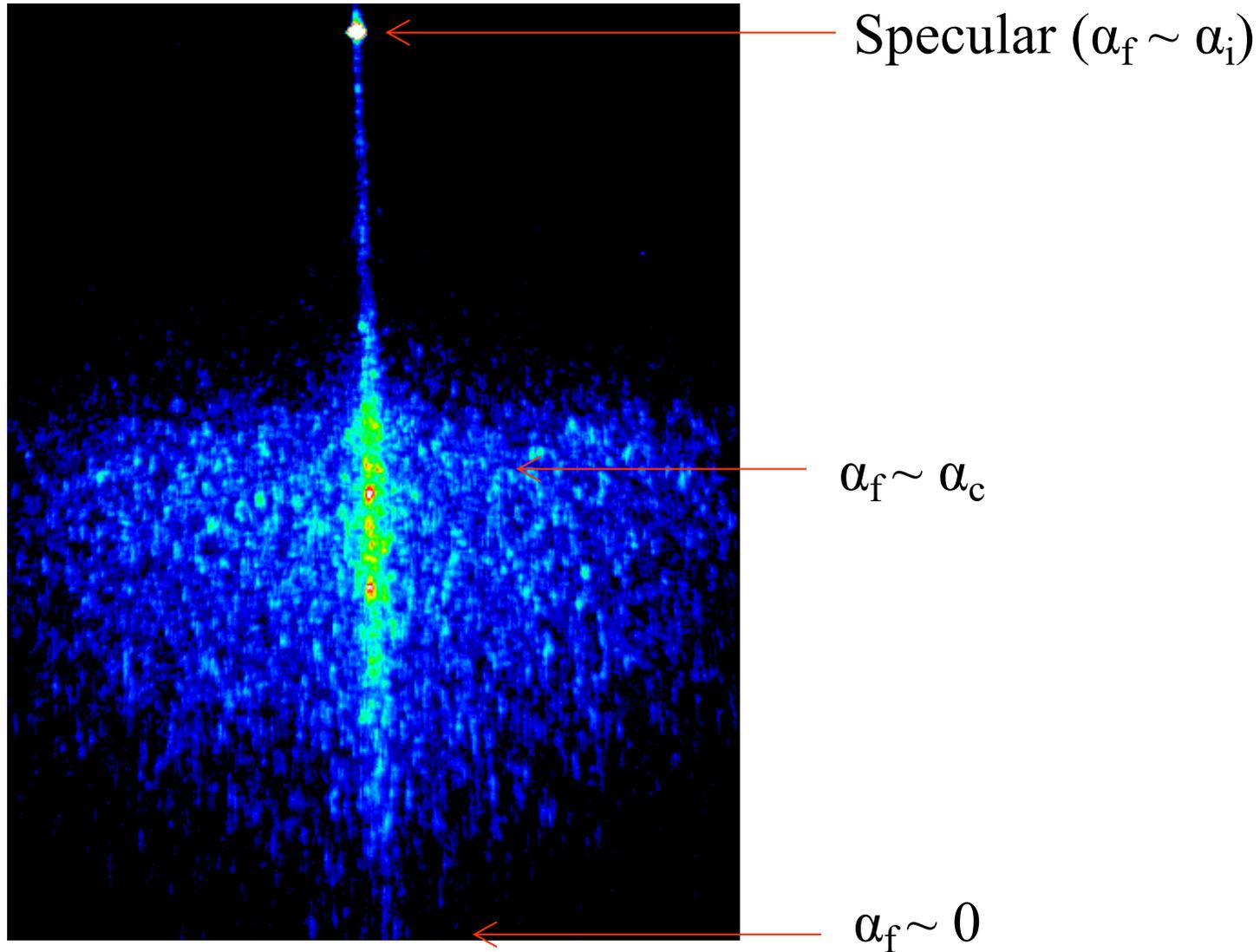


Reconstruction of Pb Nanocrystal



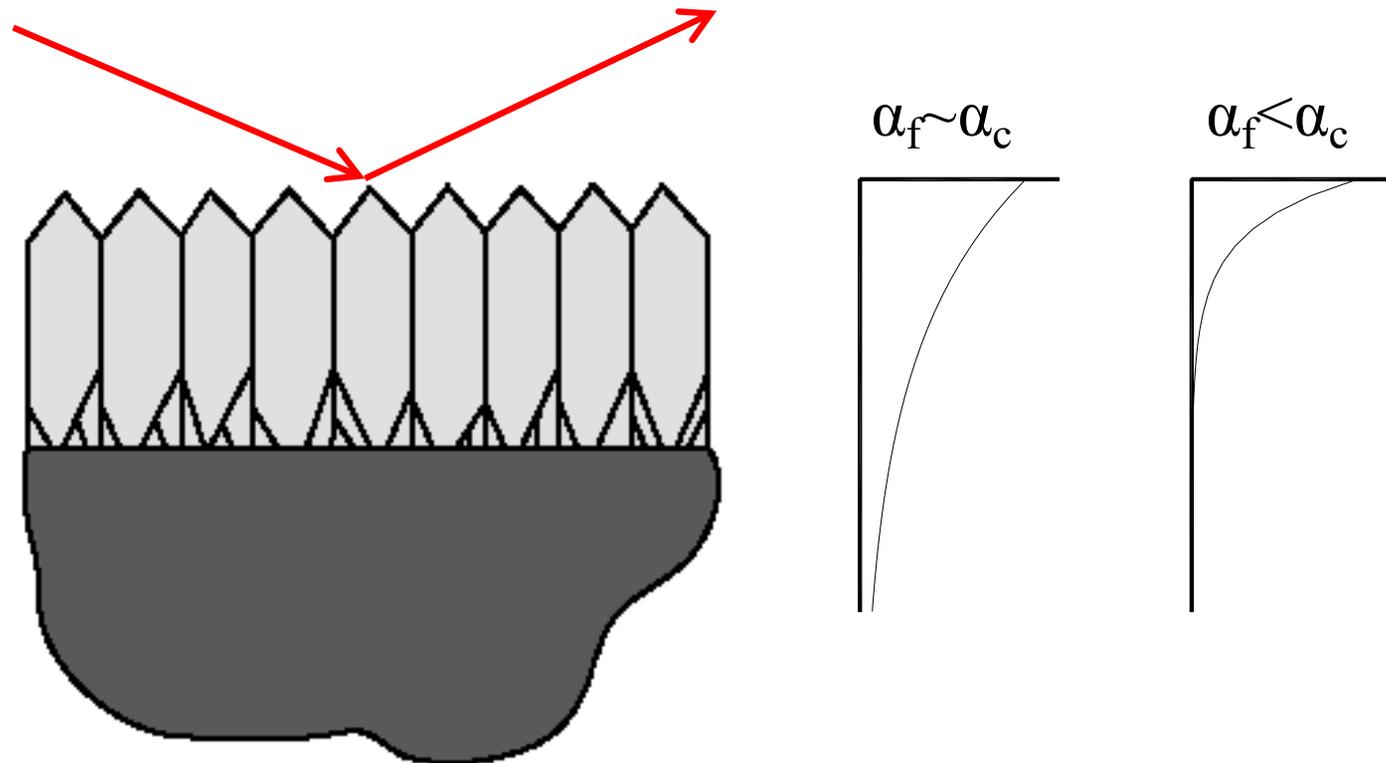
Structure in “Yoneda” Peak

Grazing-exit diffraction from a 1000Å Au polycrystalline film

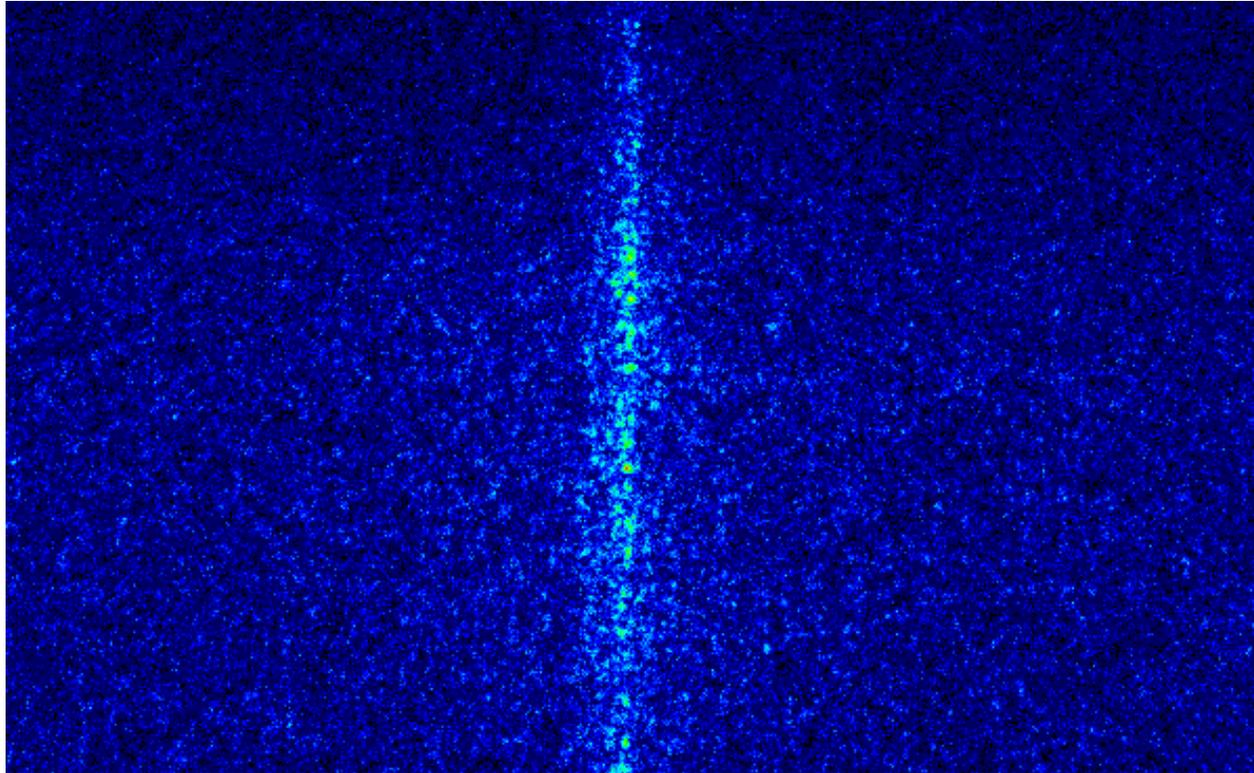


Competitive Grain Growth

C. V. Thompson, *Ann. Rev. Mat. Sci.* **30** 159 (2000)



Angle series, 0.01° steps

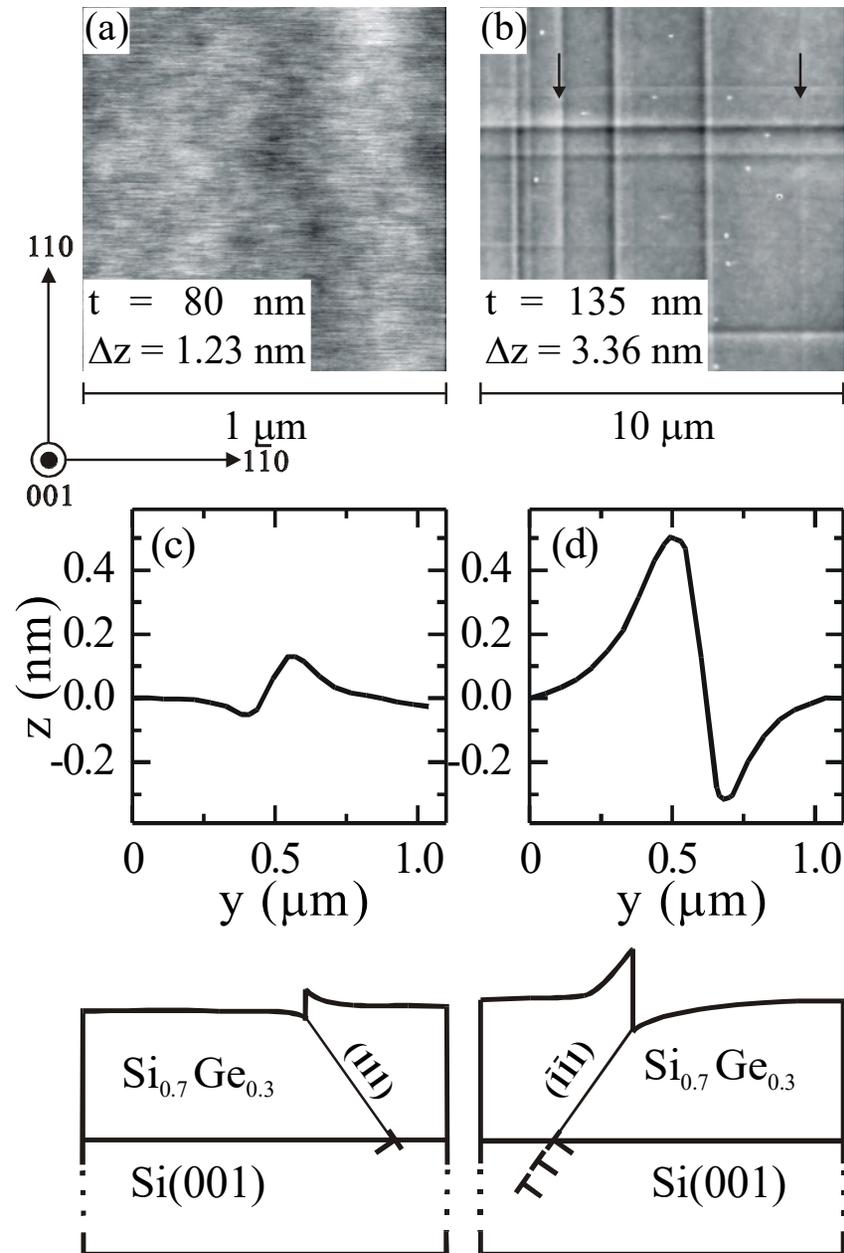


Low dislocation density GeSi films

Thickness close to critical thickness

Dislocations aggregate at interface and glide to surface along {111}

T. Spila, UIUC Thesis

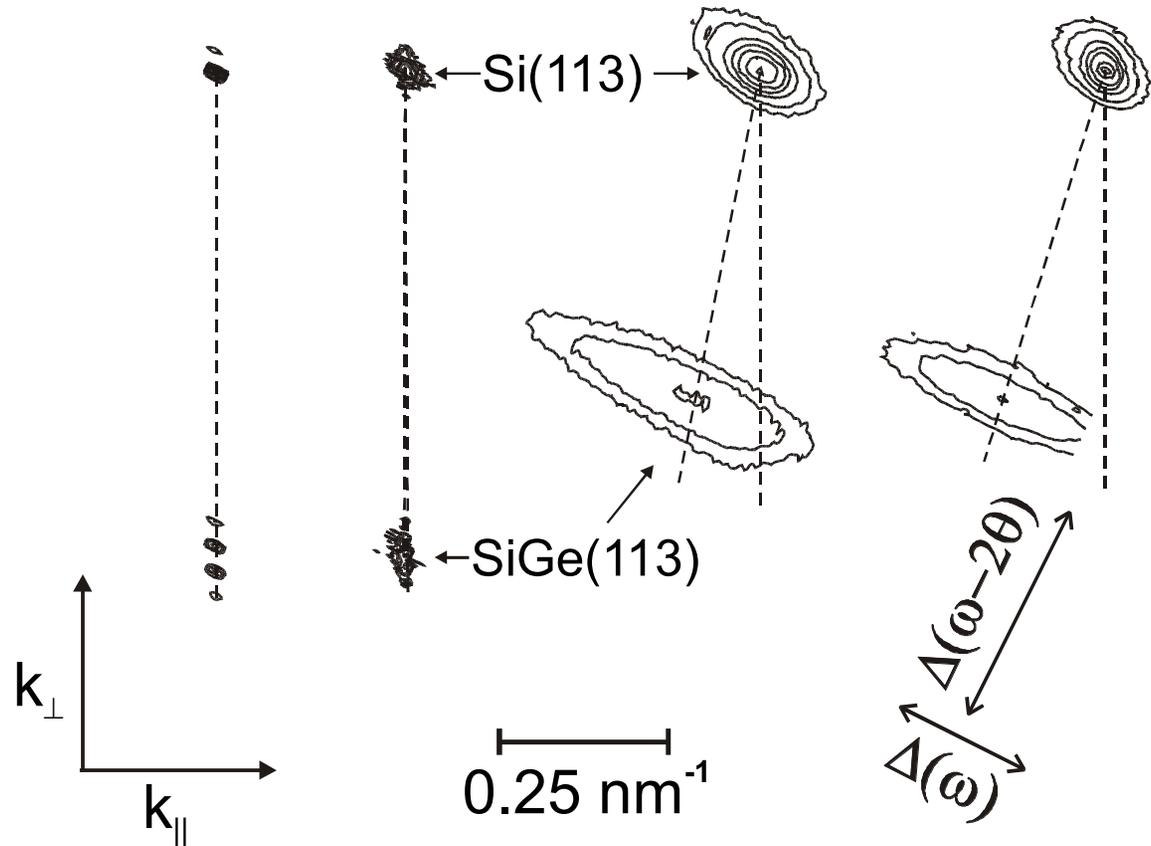


$\text{Si}_{0.7}\text{Ge}_{0.3}/\text{Si}(001)$

$T_s = 450^\circ\text{C}$

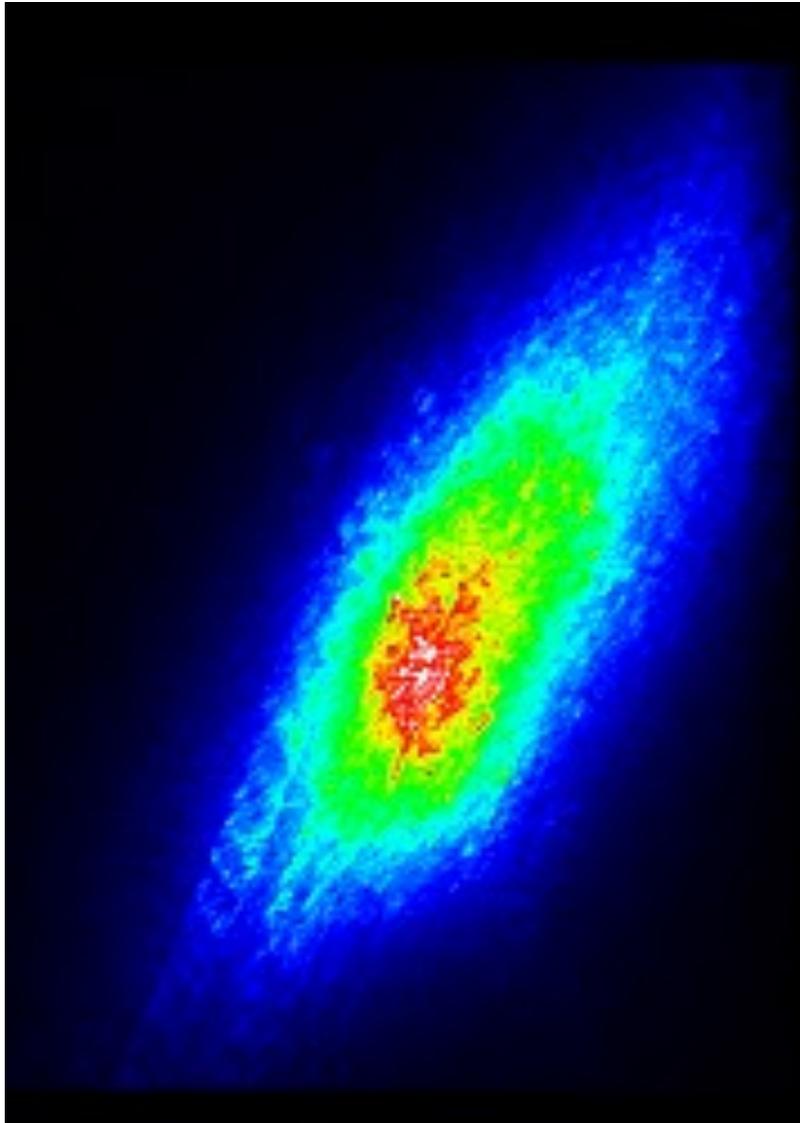
$t =$ 80 135 350 440 nm

$R =$ 0 1 51 78 %



I. K. Robinson, MatSE Colloquium, Sept 2003

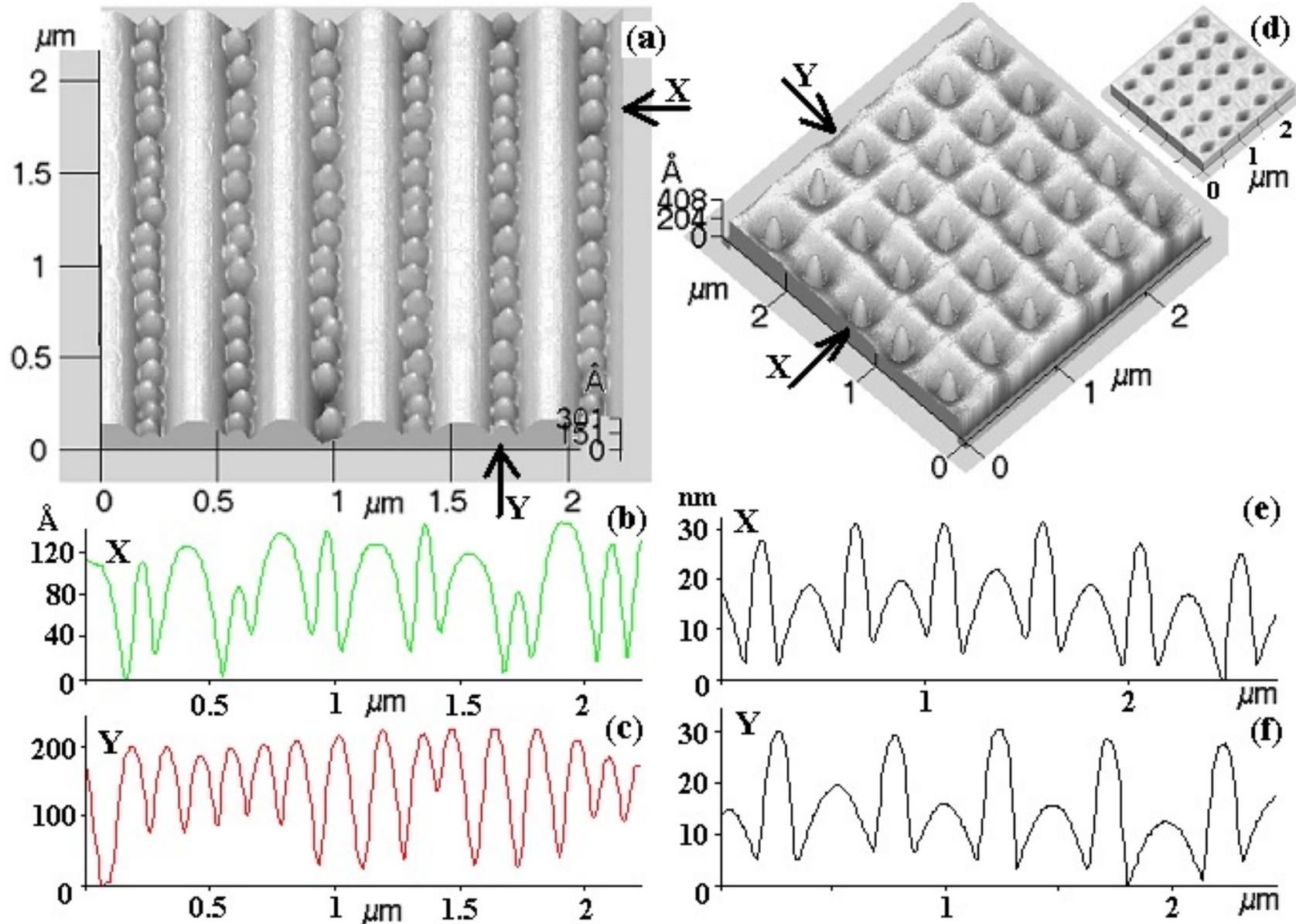
$\text{Ge}_x\text{Si}_{1-x}$ Film Diffraction



- 202 Bragg Peak
- 2800Å film
- 2° incidence angle
- 8.5 keV
- 20μm × 40μm beam
onto KB mirror
- 1μm × 1μm focus
- 0.5μm sample steps
- APS 34-ID-C

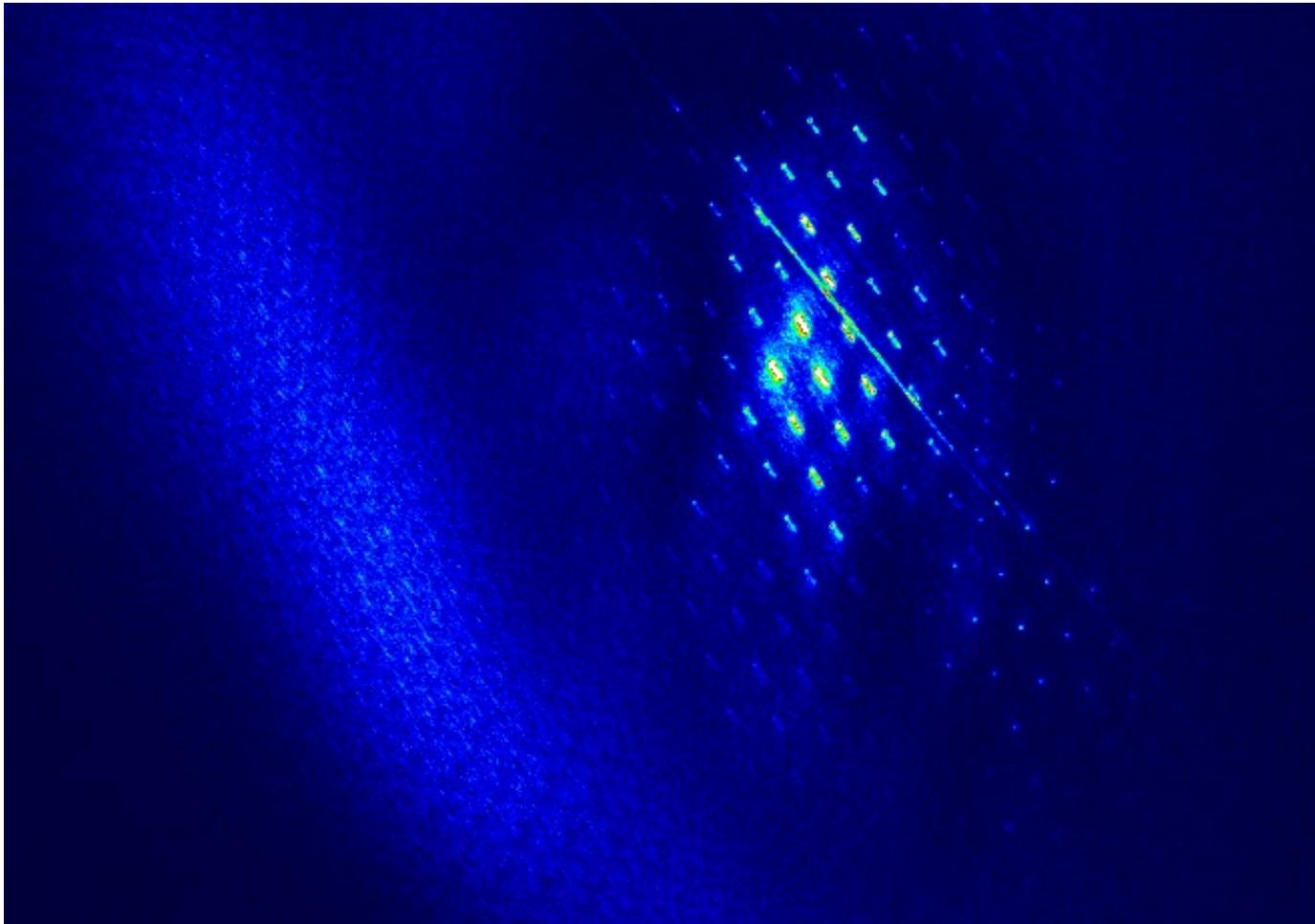
1D and 2D Quantum Dot Arrays

Zhenyang Zhong, G. Bauer, Johannes Kepler Universität Linz

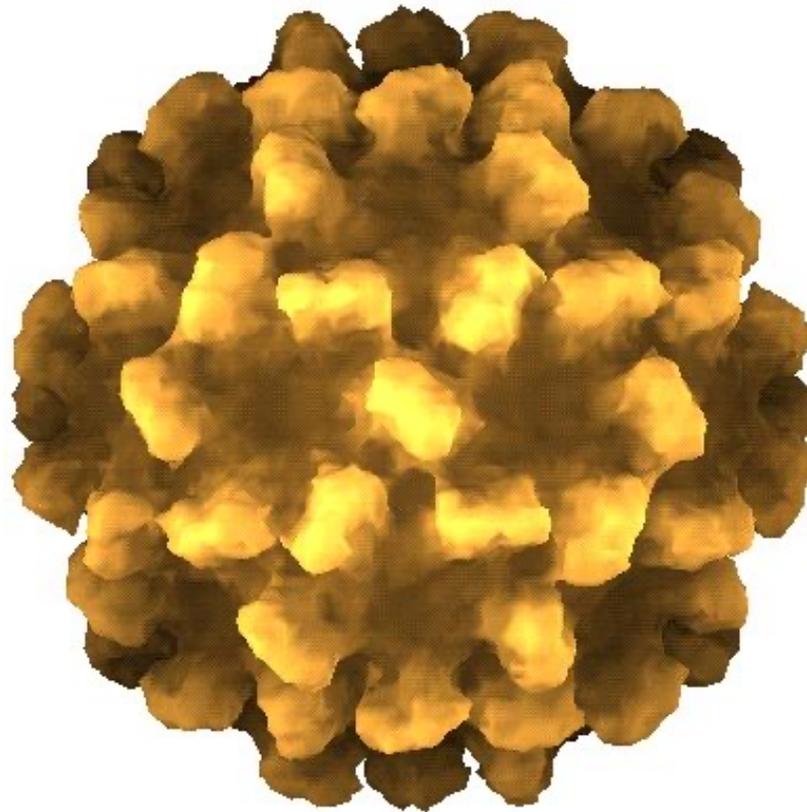


202 Diffraction from Ge QD array

with G. Bauer, Z. Zhong and T. H. Metzger



Tomato Bushy Stunt Virus 1980



Conclusions and Outlook

- Inversion of CXD demonstrated
- Diffuse scattering acquires fine structure
- Internal structure of Au Nanocrystals
- Preservation of coherence upon focussing
- Dislocations, Quantum Dots all possible now
- Single molecules one day