

Nanocrystal Structure at the Diamond Light Source

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LCN Workshop on “Molecular
Scale Movies with X-rays
and Electrons”

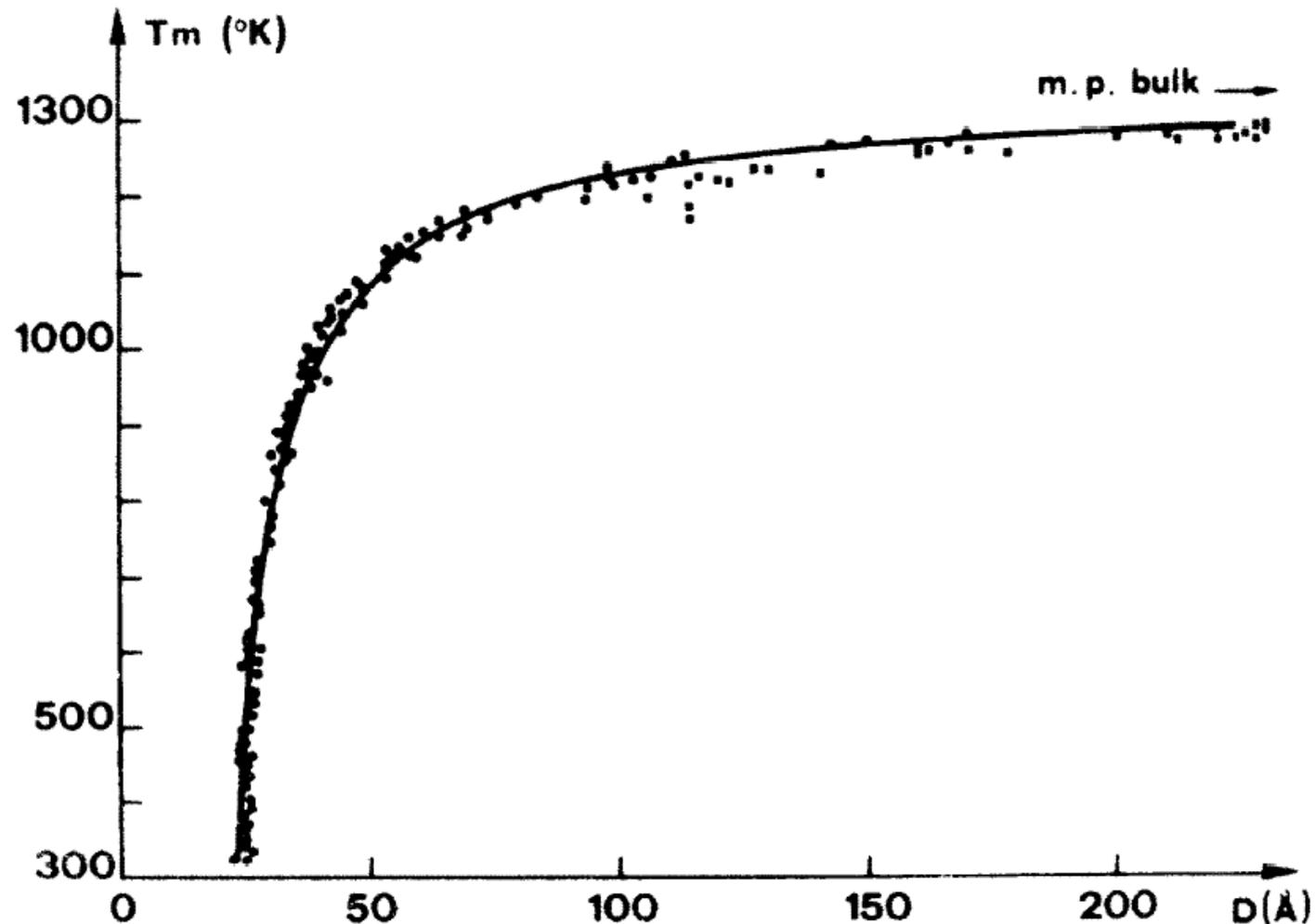
University College, London
July 2004

Outline

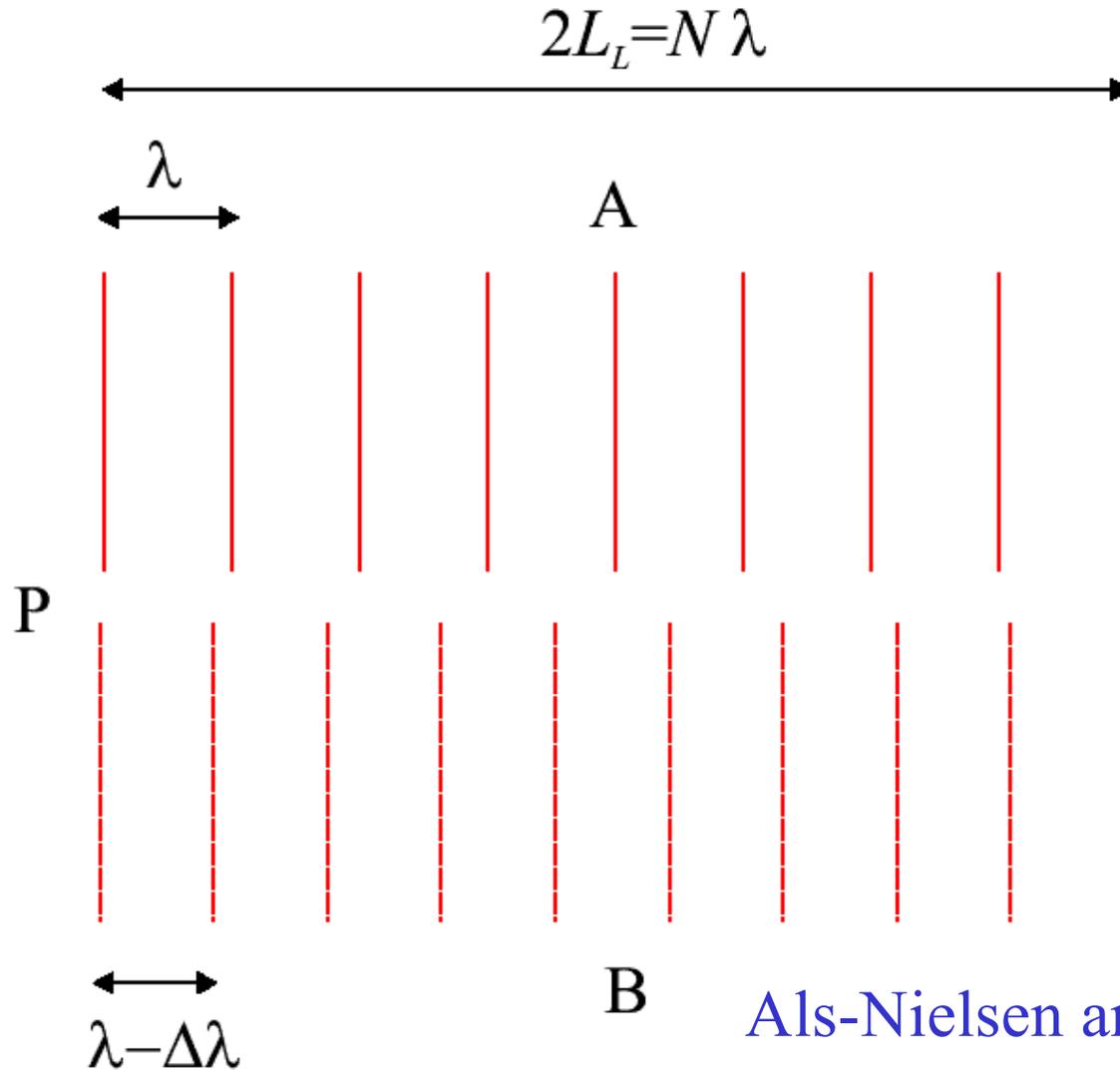
- Coherent X-ray Diffraction
- How to Solve the Phase Problem
- Nanocrystal Shapes
- Extension to Phase Objects
- Opportunities with Electrons
- Opportunities at Diamond Light Source

Size-dependent Melting of Au Particles

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



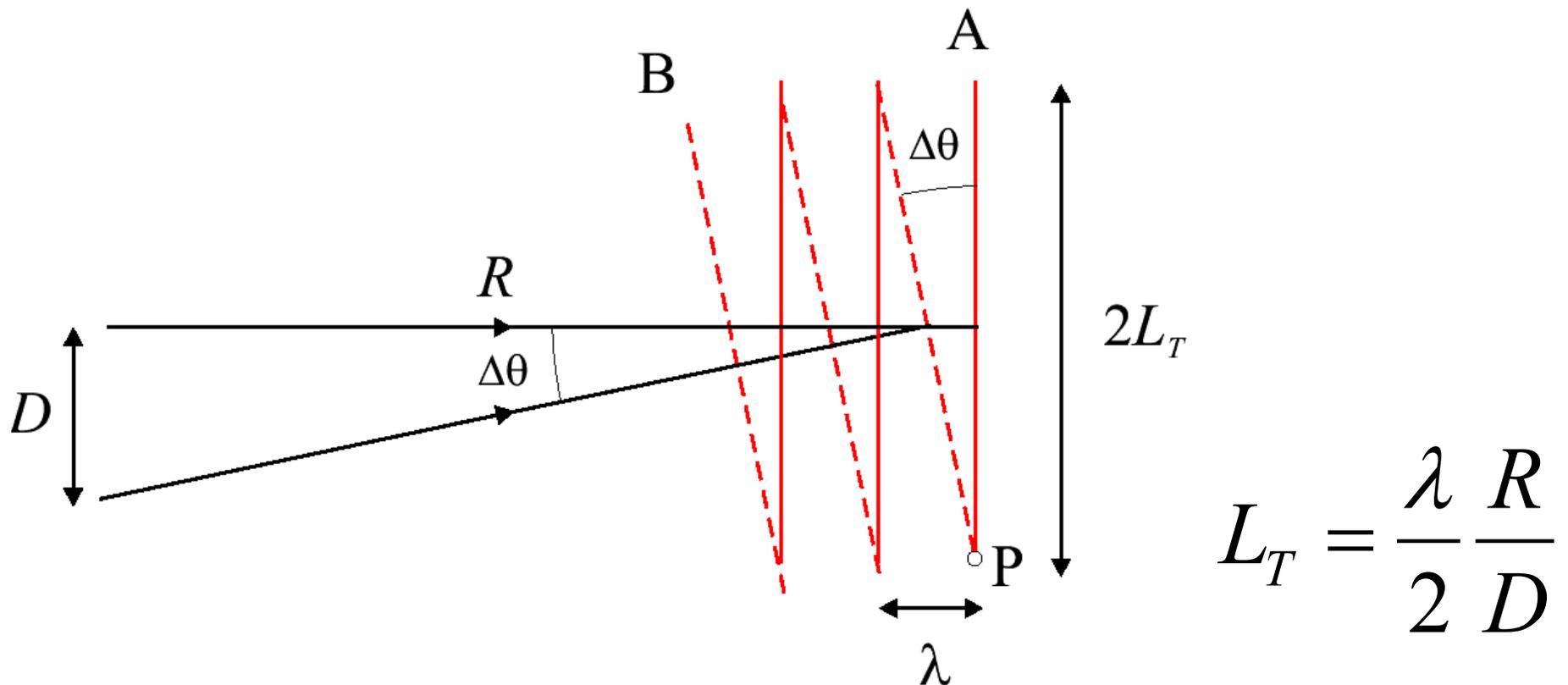
Longitudinal Coherence



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

Als-Nielsen and McMorrow (2001)

Lateral (Transverse) Coherence



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

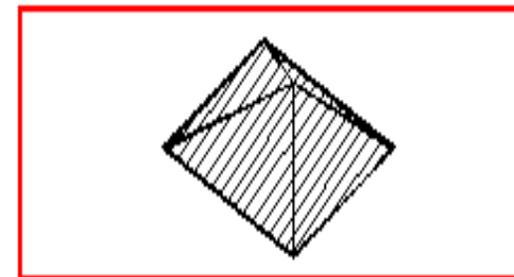
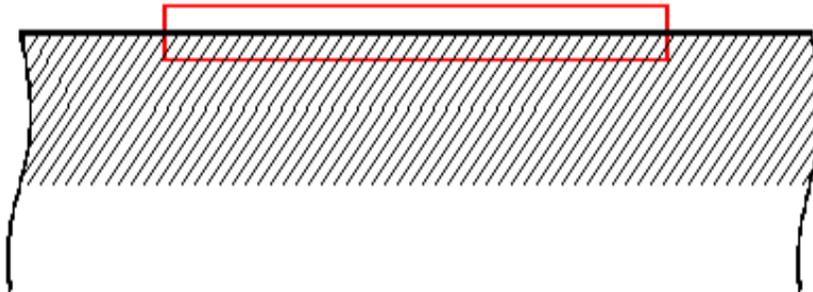
Als-Nielsen and McMorrow (2001)

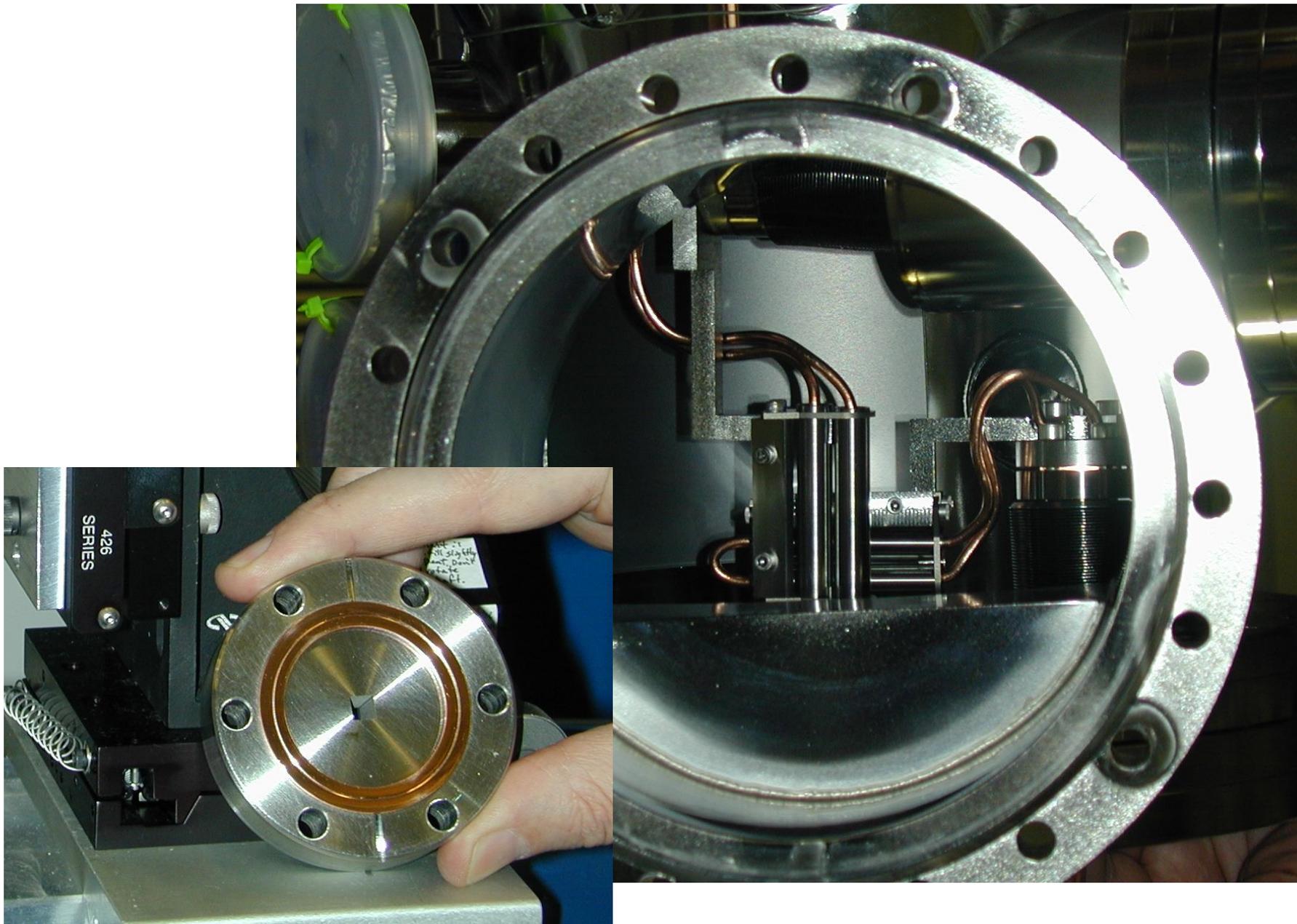
Coherence at APS, ESRF or DLS

Typical of 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

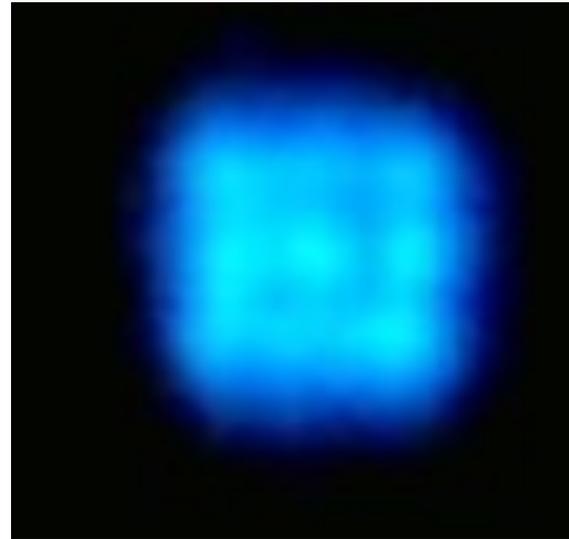
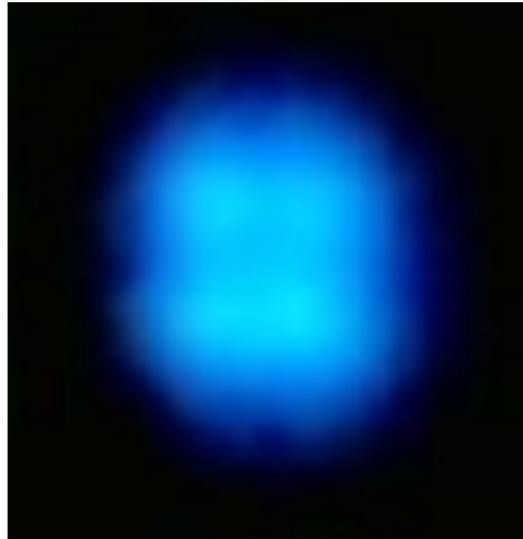
Coherent region defined by slits



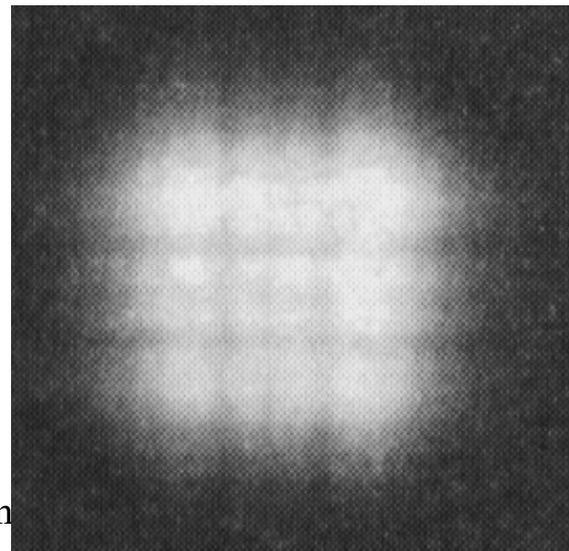
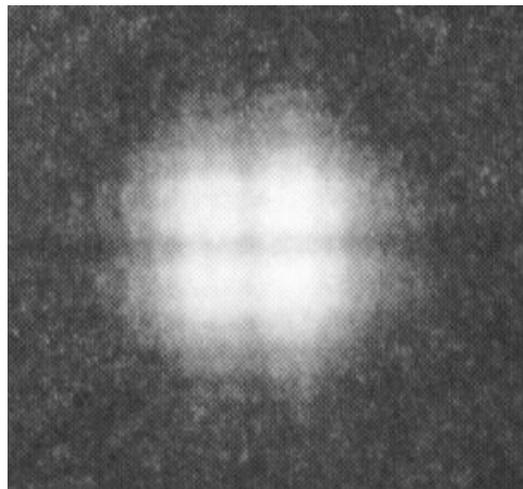


I. K. Robinson, Diamond CXD, July 2004

Fresnel Diffraction when $d^2 \sim \lambda D$



X-ray
beam
defined
by RB
slits

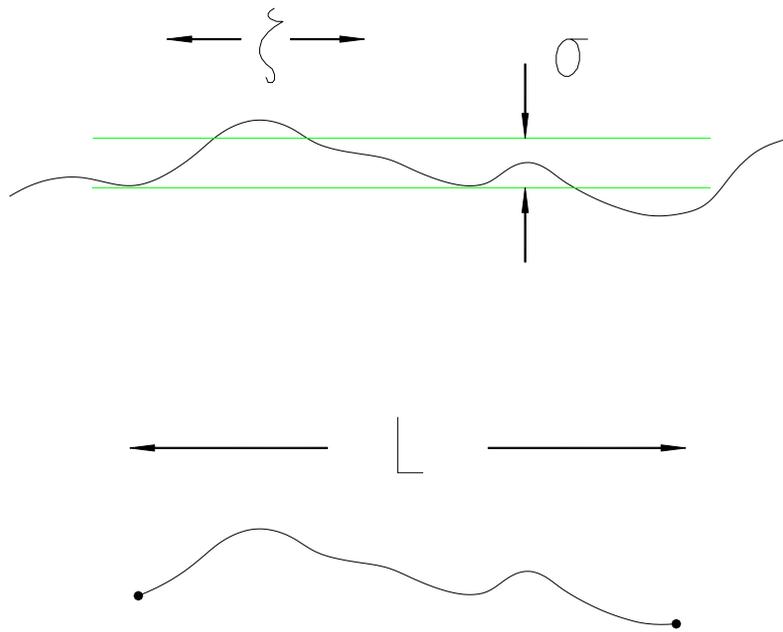


Visible
Fresnel
diffraction
from
Hecht
“Optics”

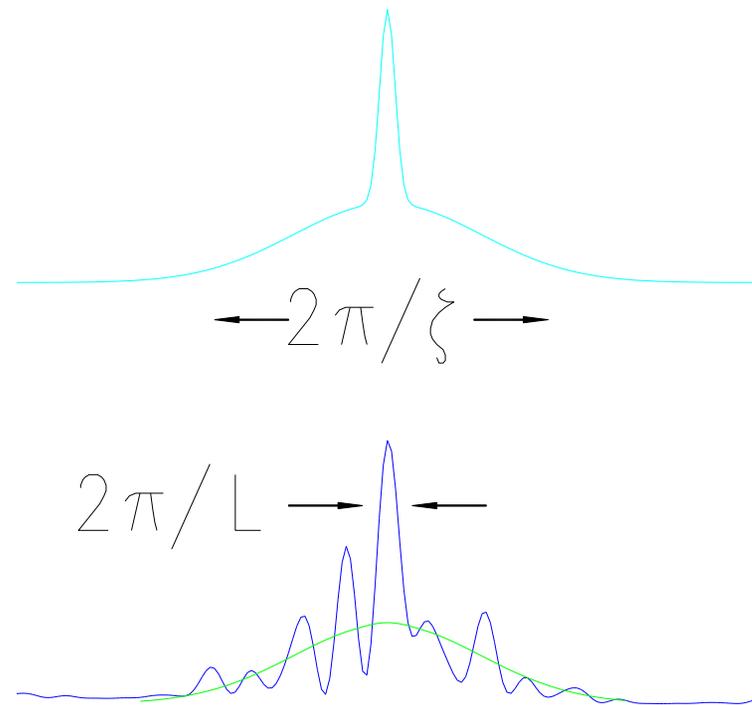
I. K. Robinson, Diam

Diffuse Scattering acquires Structure using CXD

Real Space



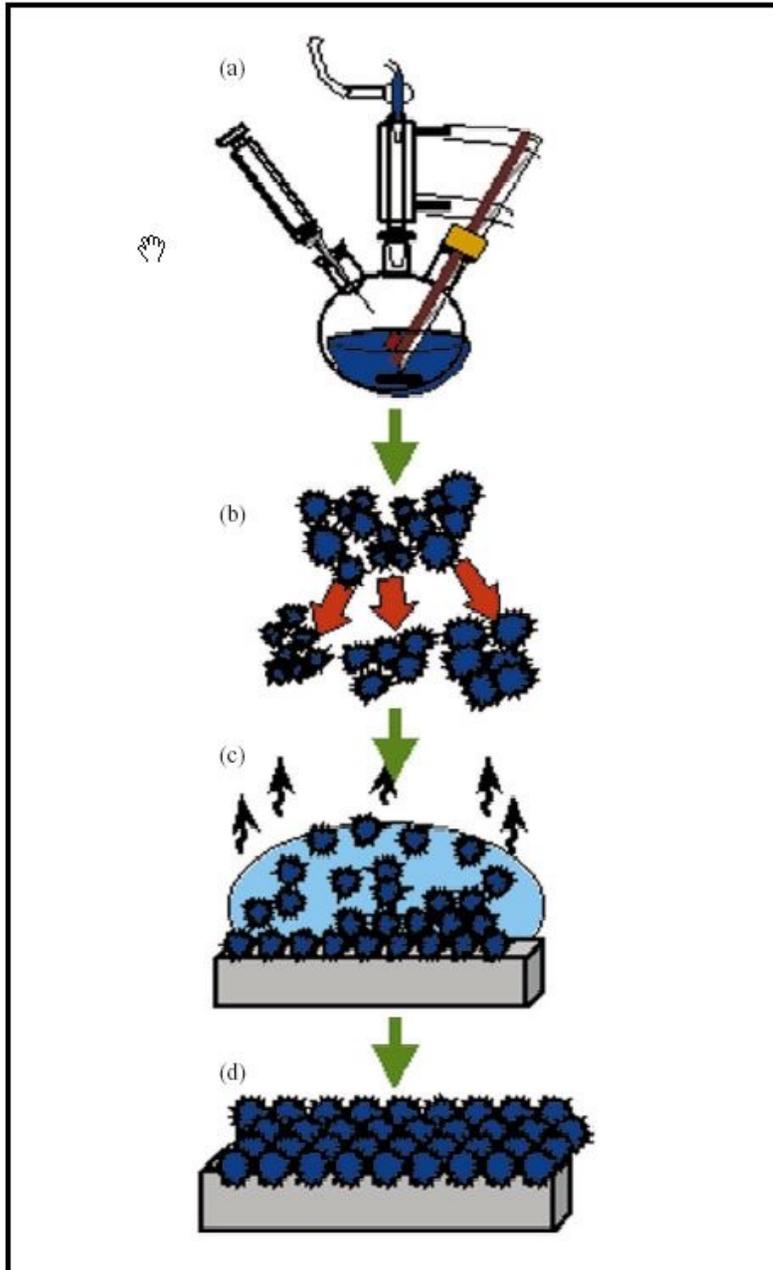
Reciprocal Space



Facts of Life with Coherence

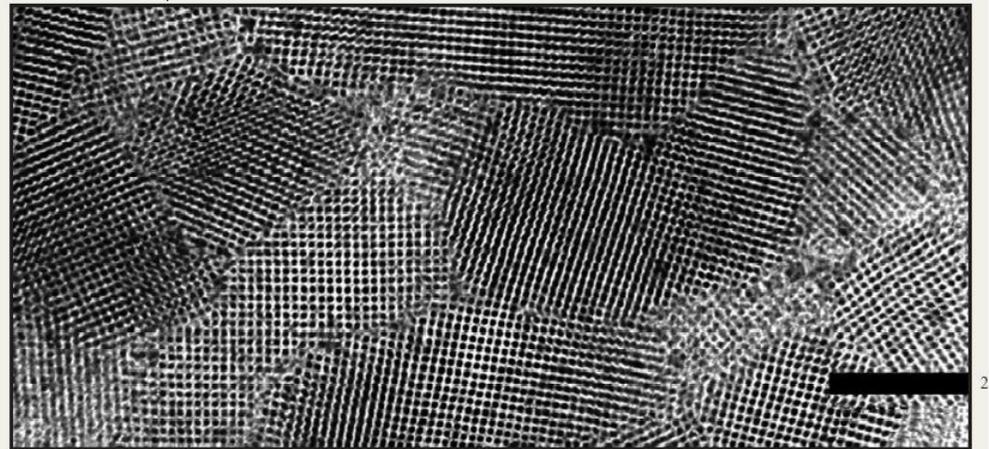
- No more diffuse scattering
- No more ensemble averaging
- Coherence is indestructible
 - everything following your (coherence-defining) entrance slit is your ‘sample’
- If something moves, the whole interference pattern changes

Chemical Synthesis of Nanocrystals



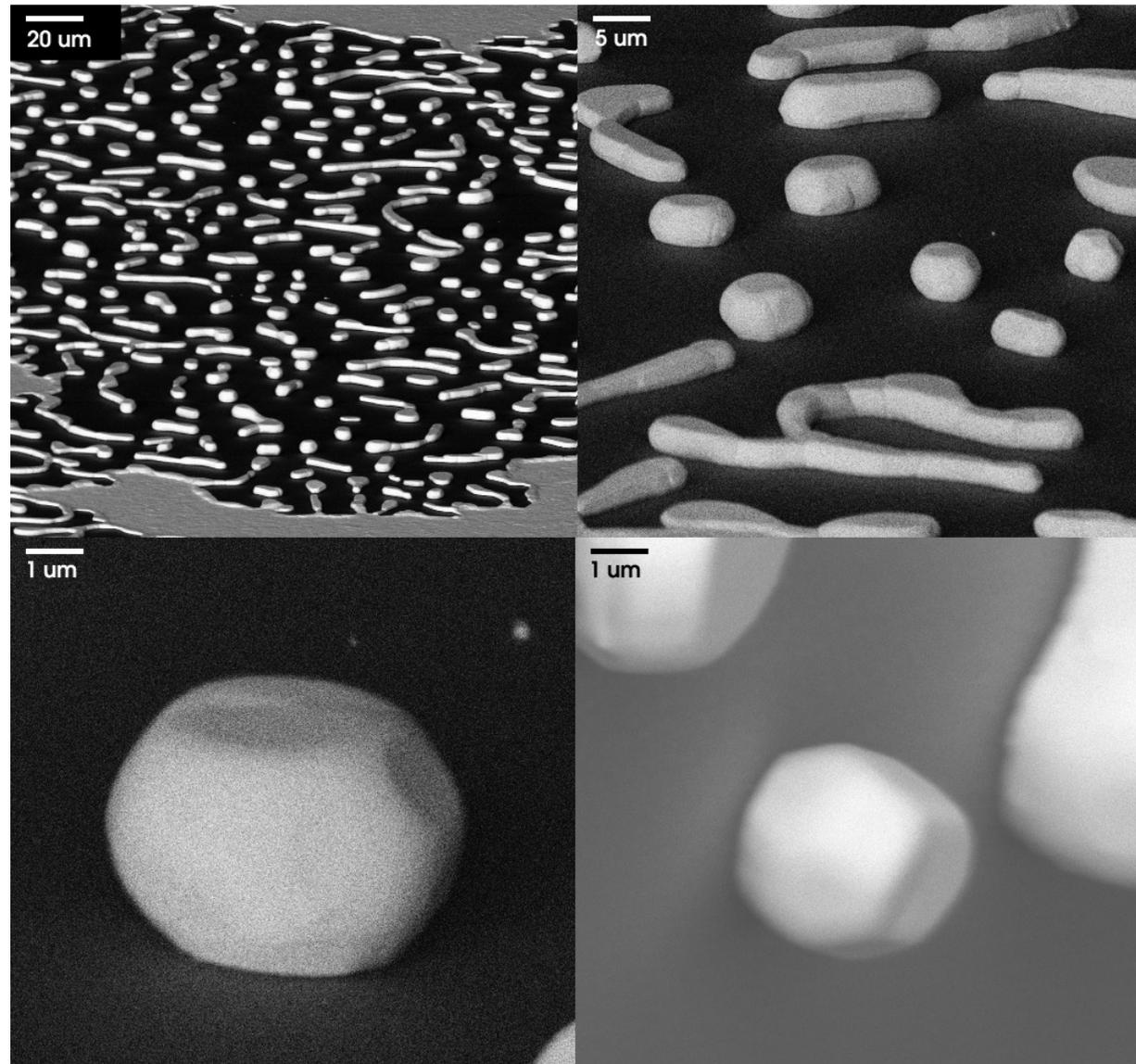
- Reactants introduced rapidly
- High temperature solvent
- Surfactant/organic capping agent
- Square superlattice (200nm scale)

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

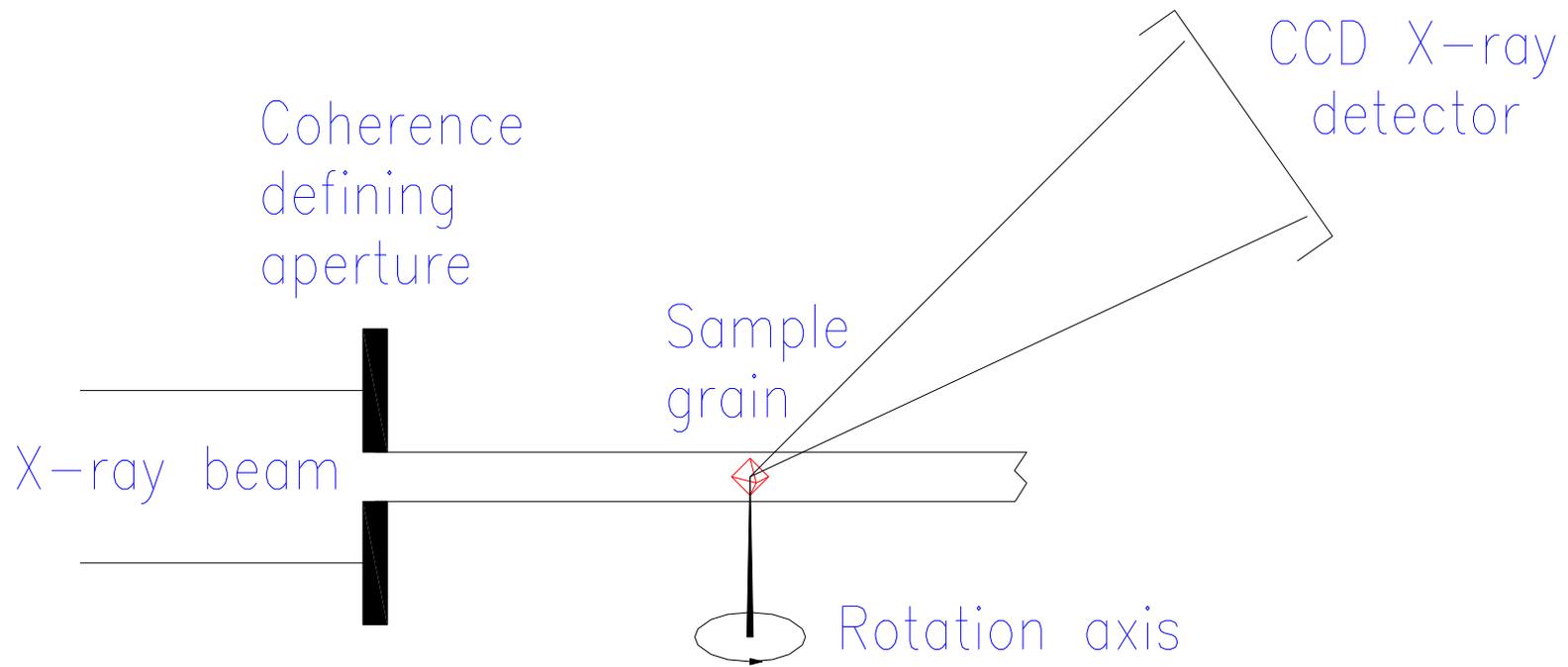


SEMS

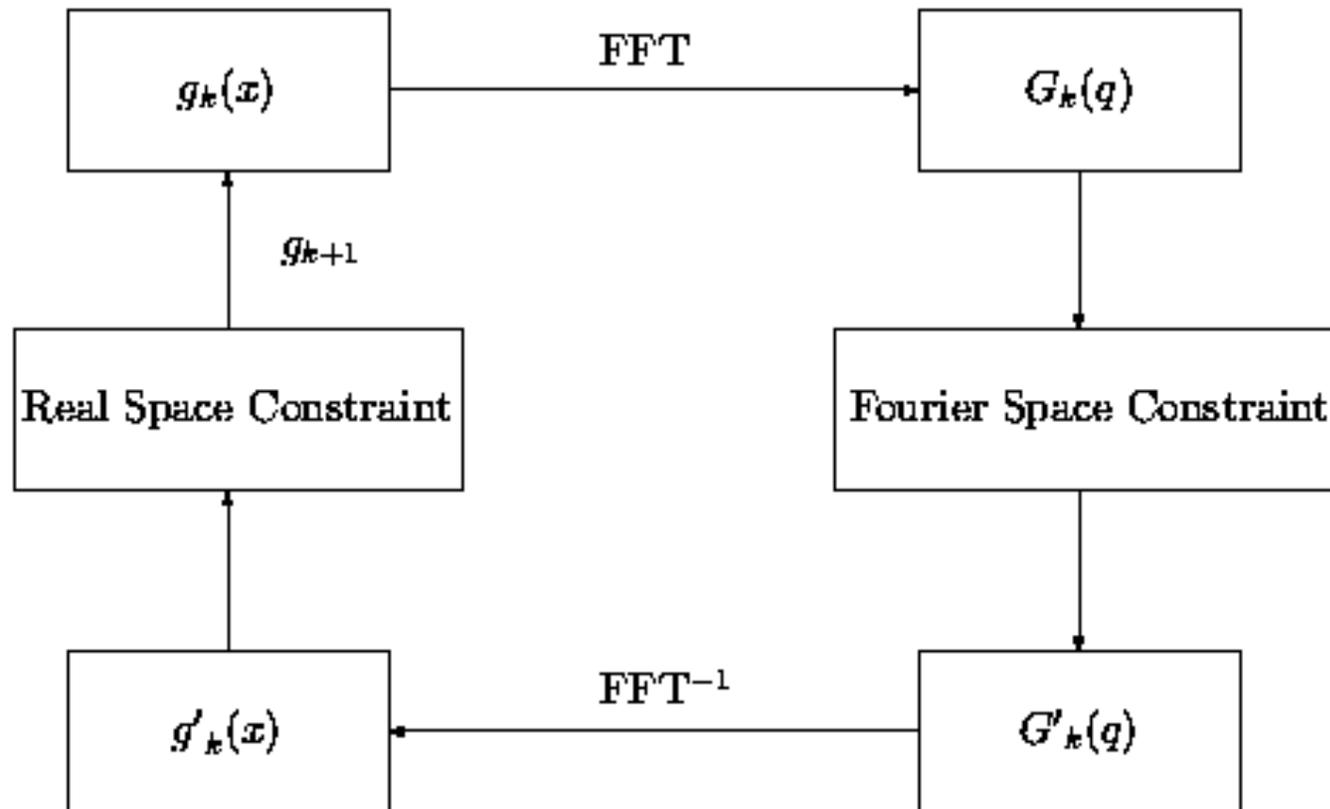
- Au blanket film
- Quartz substrate
- Annealed at 950°C for 70 hrs.



Lensless X-ray Microscope



Generic “Error Reduction” method



J. R. Fienup *Appl. Opt.* 21 2758 (1982)

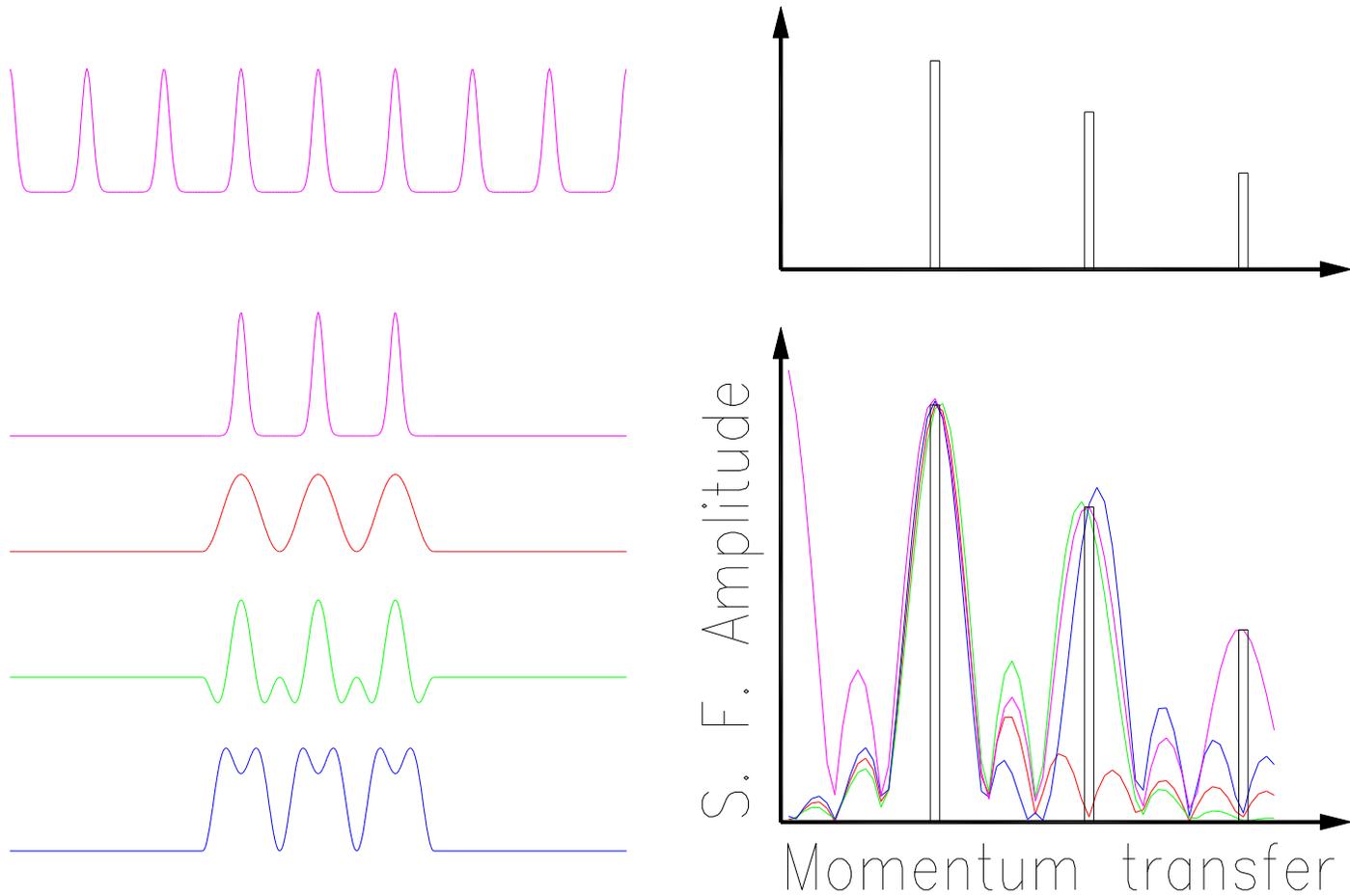
R. W. Gerchberg and W. O. Saxton *Optik* 35 237 (1972)

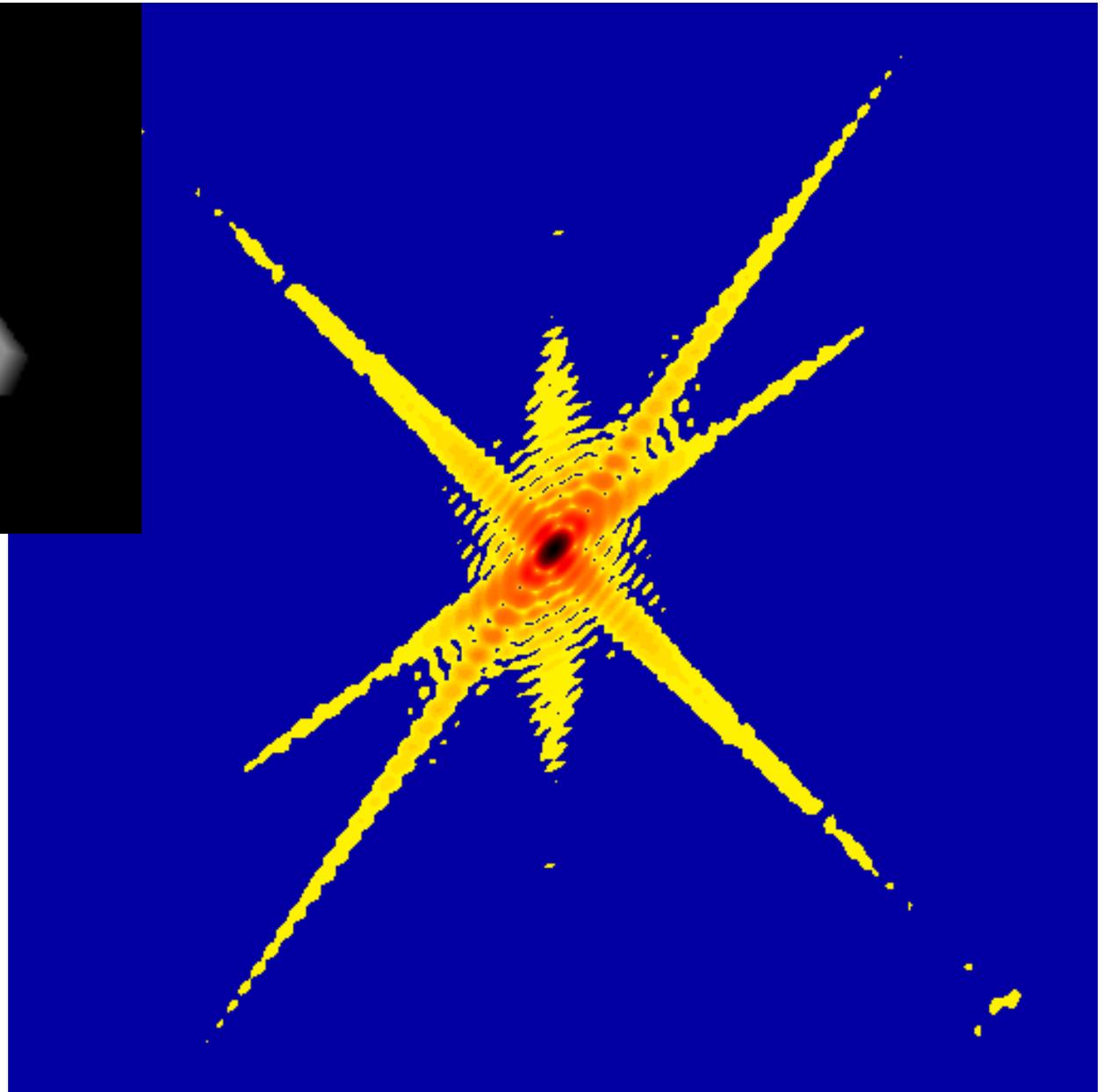
Real-space Constraints in Crystallography

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

- ‘Positivity’ and ‘Atomicity’ constraints (Sayre)
- Finite **support**, molecular envelope
- Solvent flattening/Molecular replacement
- Non-crystallographic symmetry
- Non-uniqueness is ‘pathologically rare’ ($d > 1$)
- Uses memory to avoid stagnation (Fienup HIO)

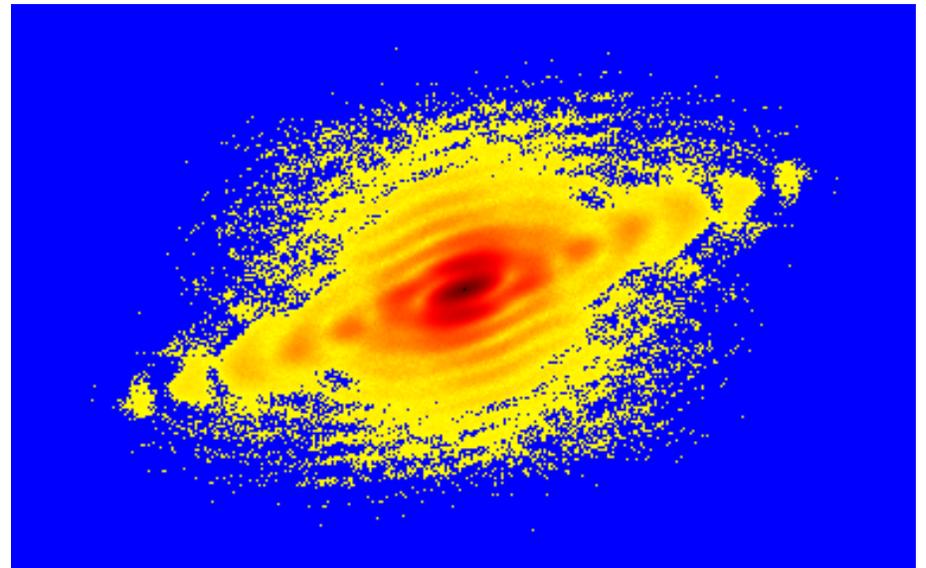
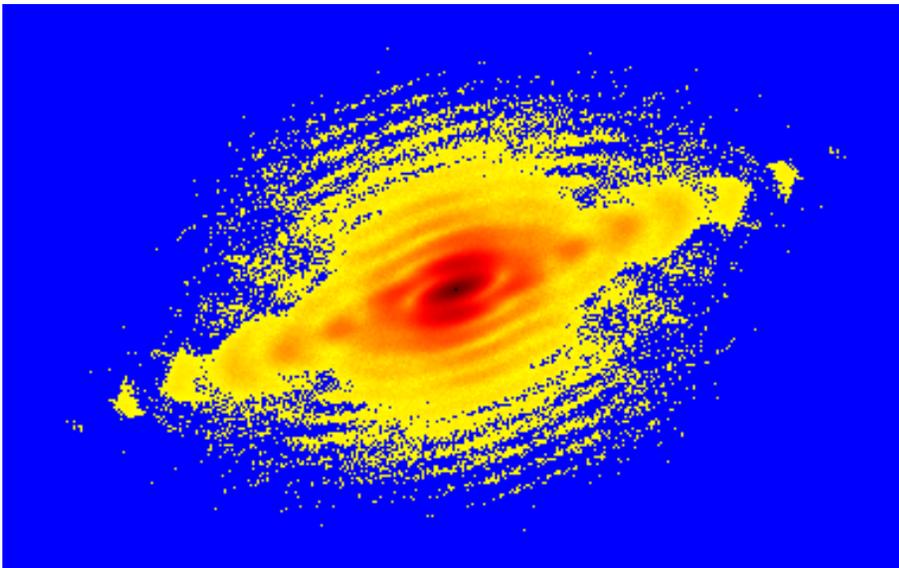
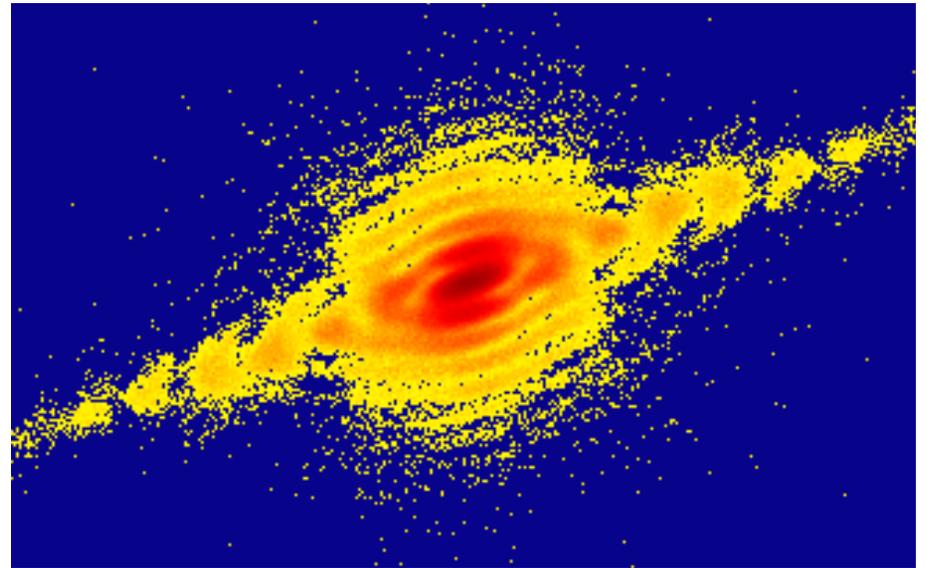
Phase Problem: Finite-size Effect





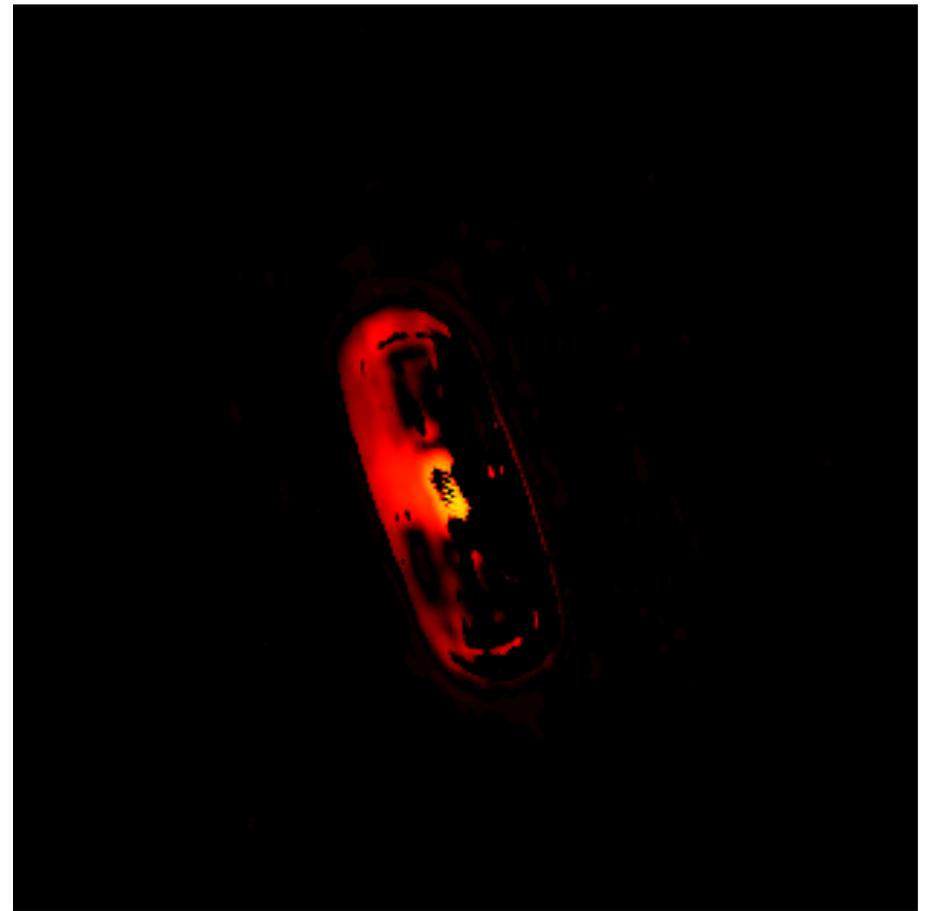
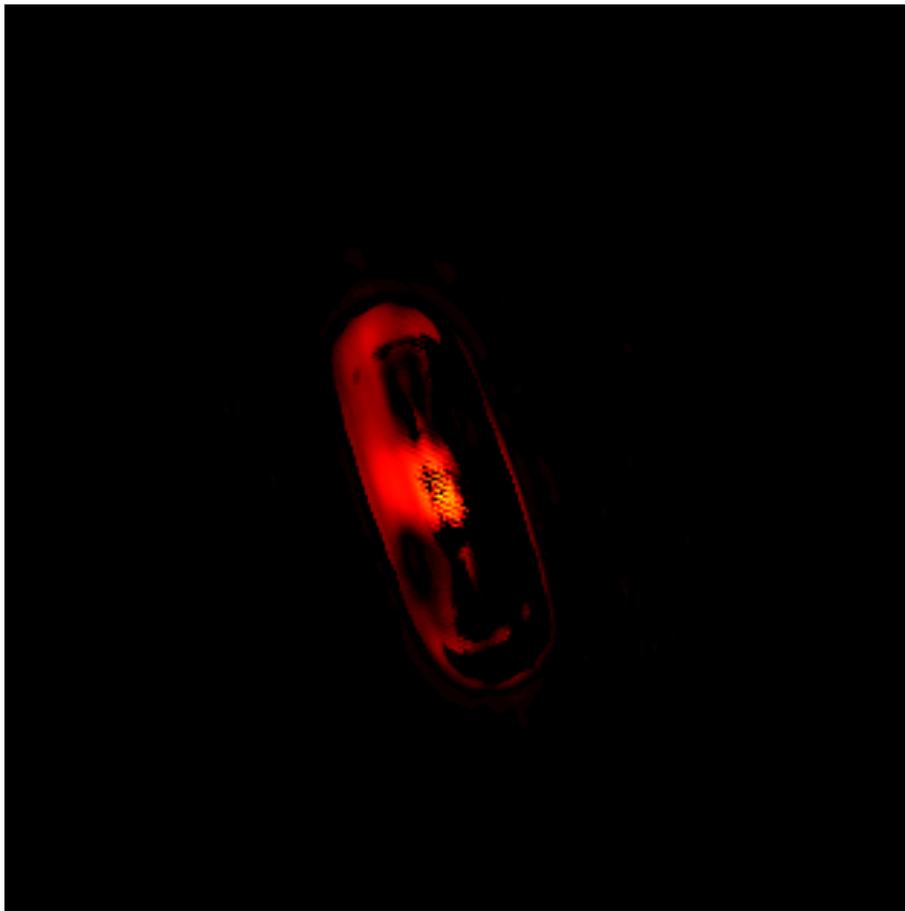
Symmetrized Data and two best fits

Chisq=0.0005

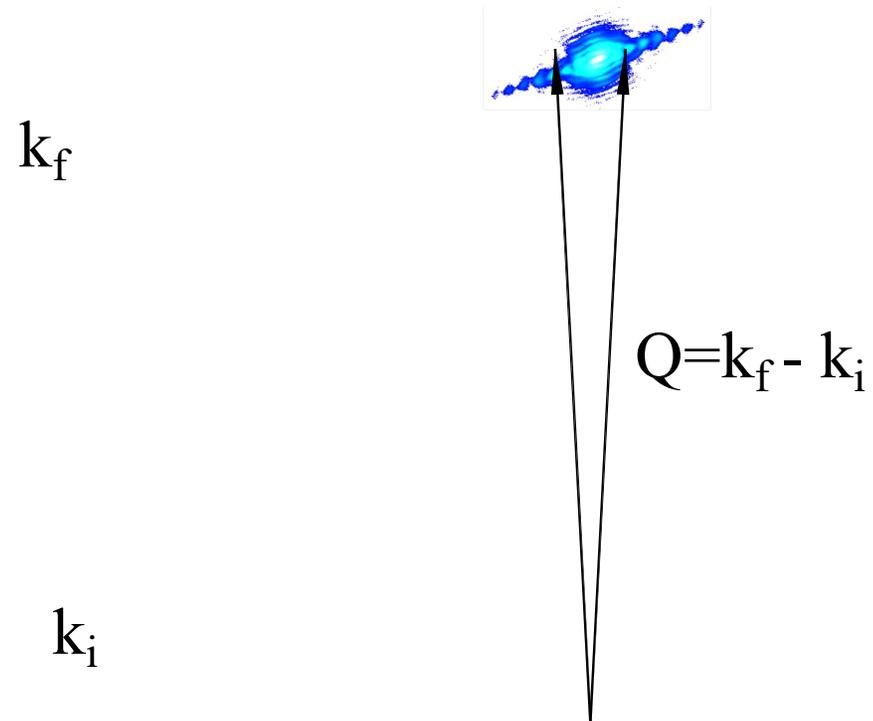


2D Reconstructions

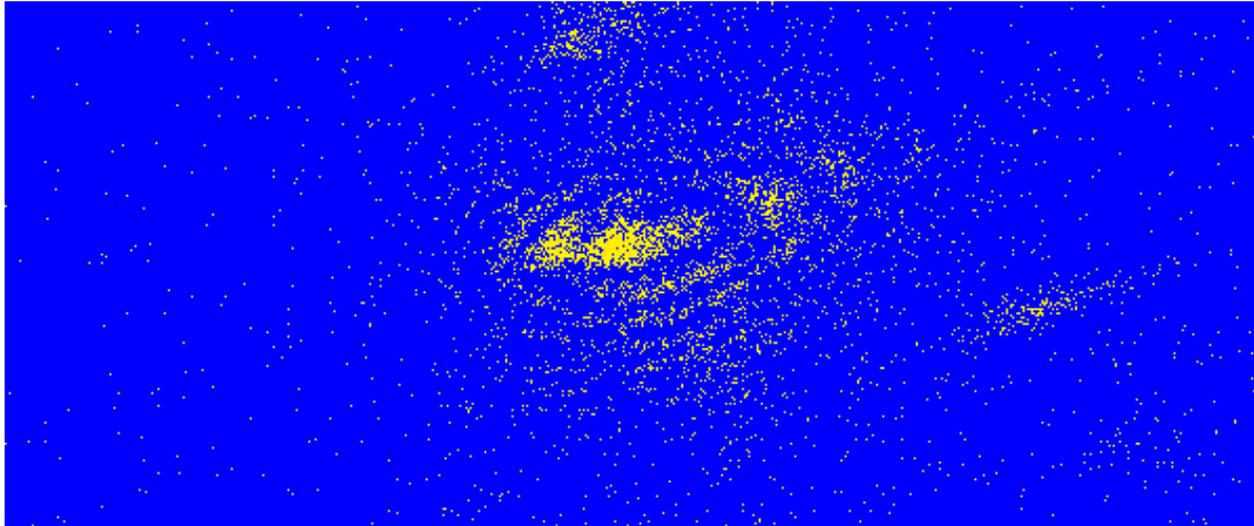
chisquare = 0.0005

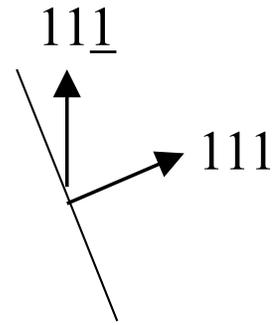
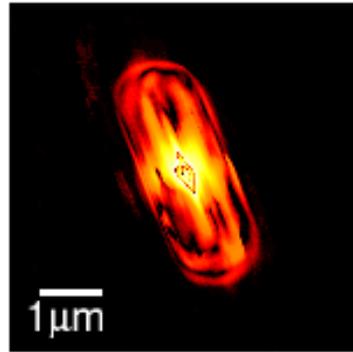
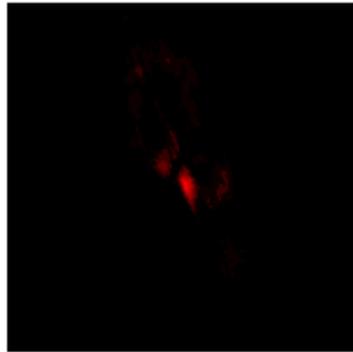


3D Diffraction Method

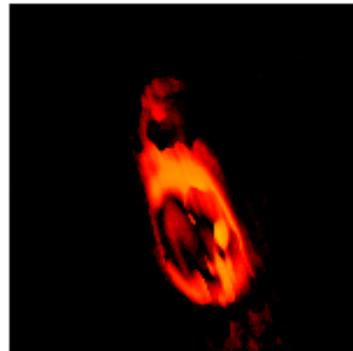
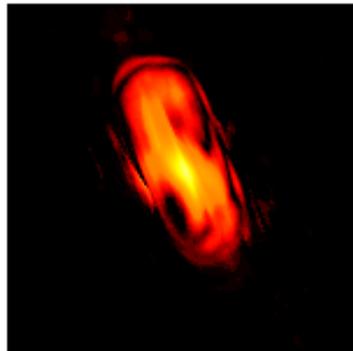
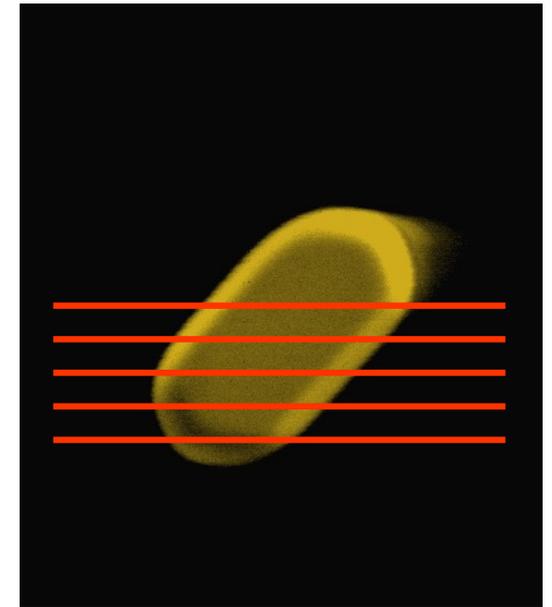
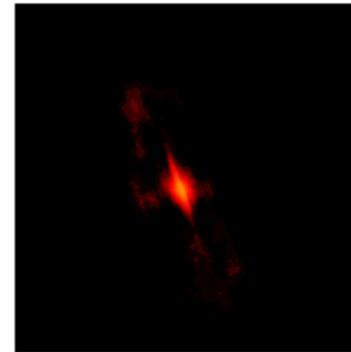
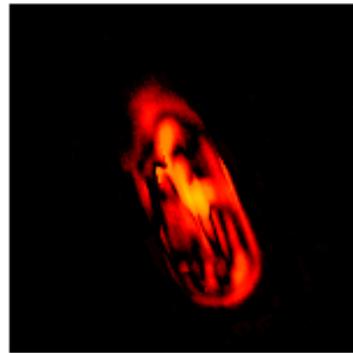
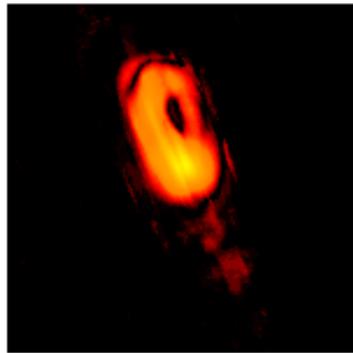
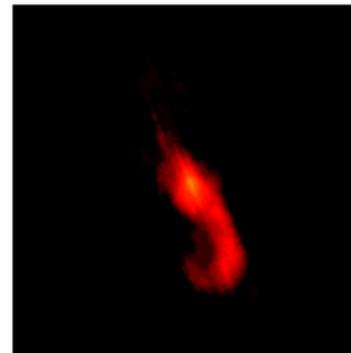
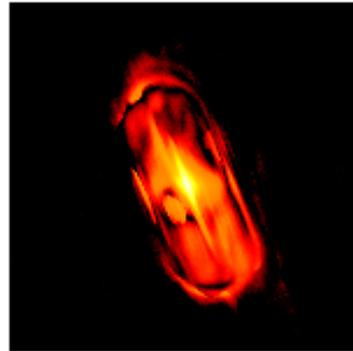
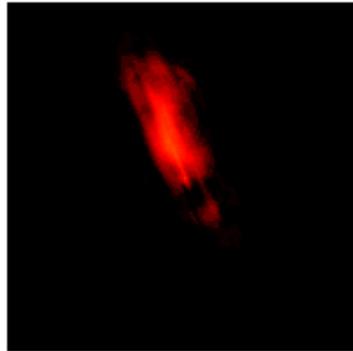


3D Diffraction Data 1 micron Au crystal



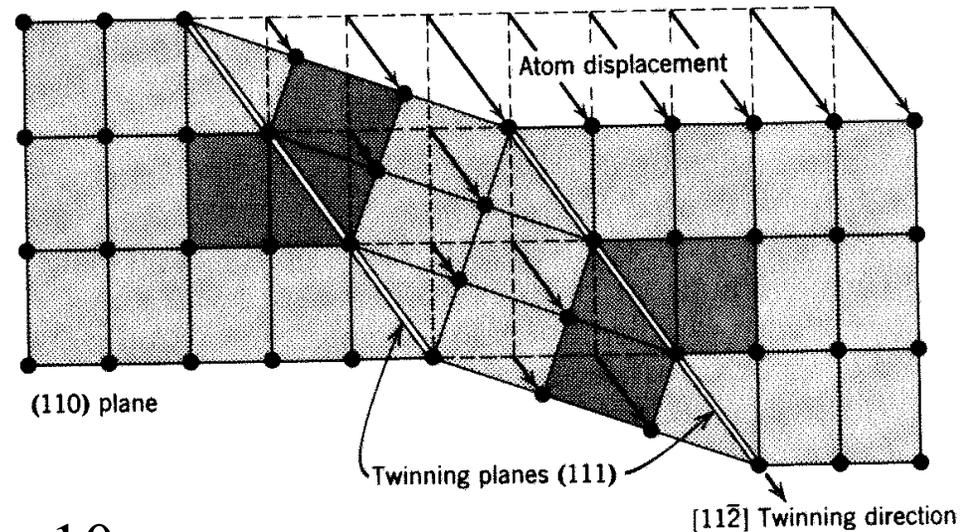
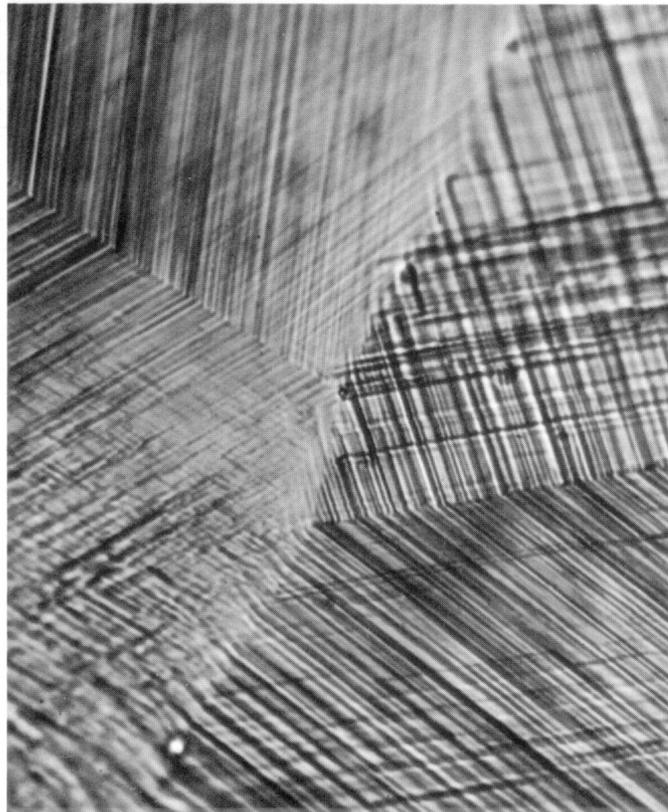


Slices through
plan view SEM:



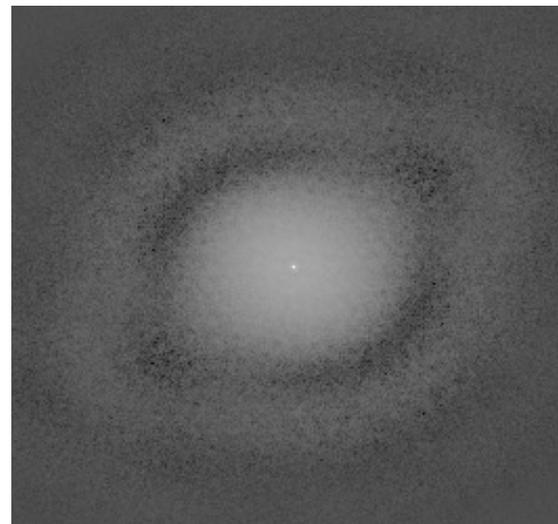
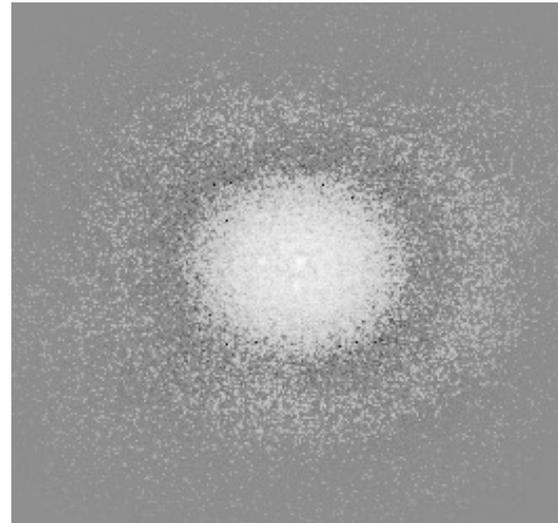
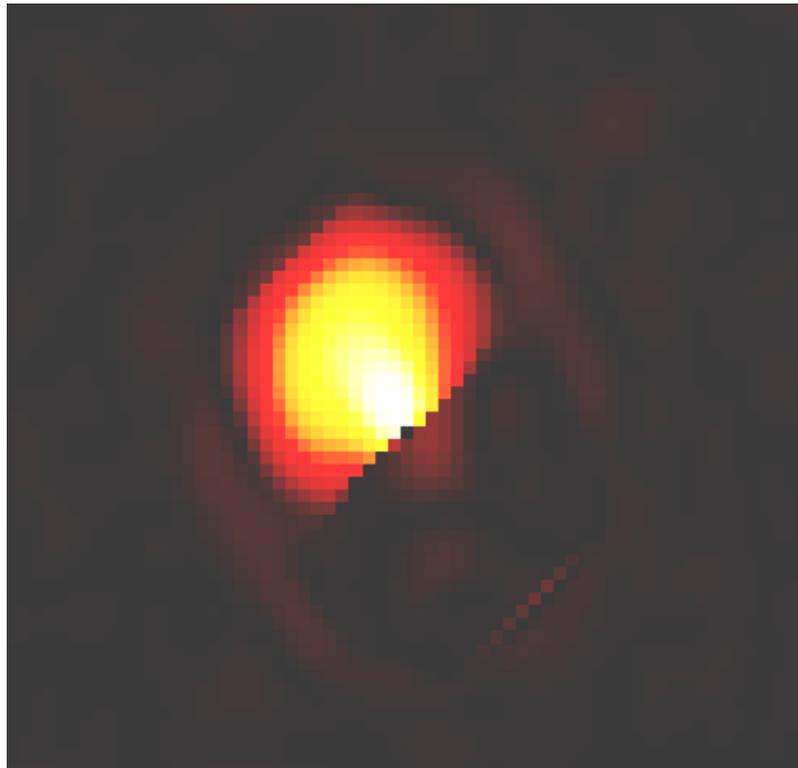
Twinning in deformed FCC metals

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

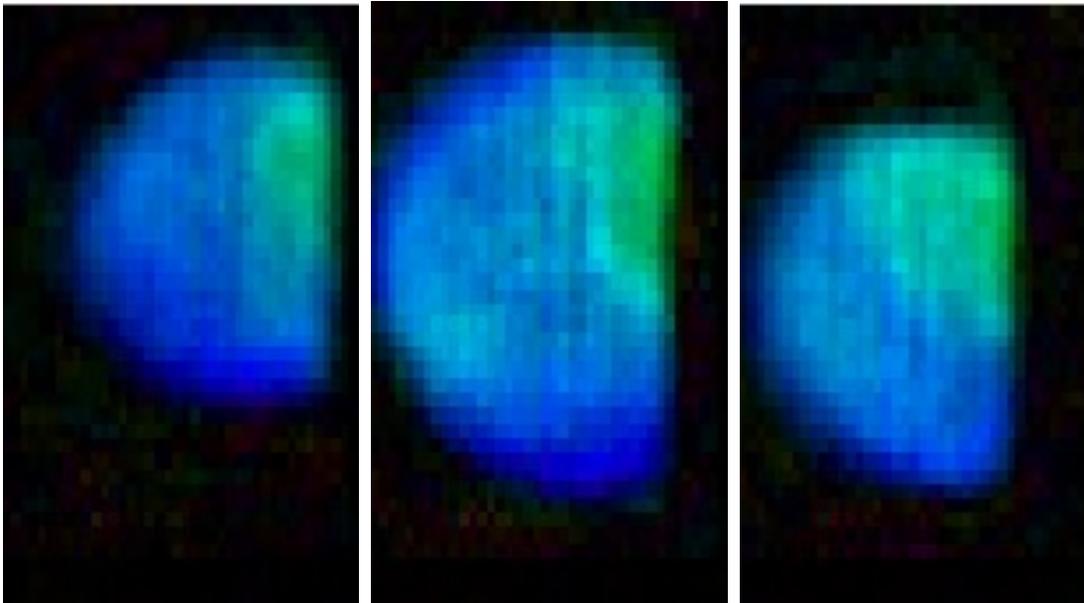


■ $\sim 10\mu\text{m}$
Cu

Reconstruction of Pb Nanocrystal



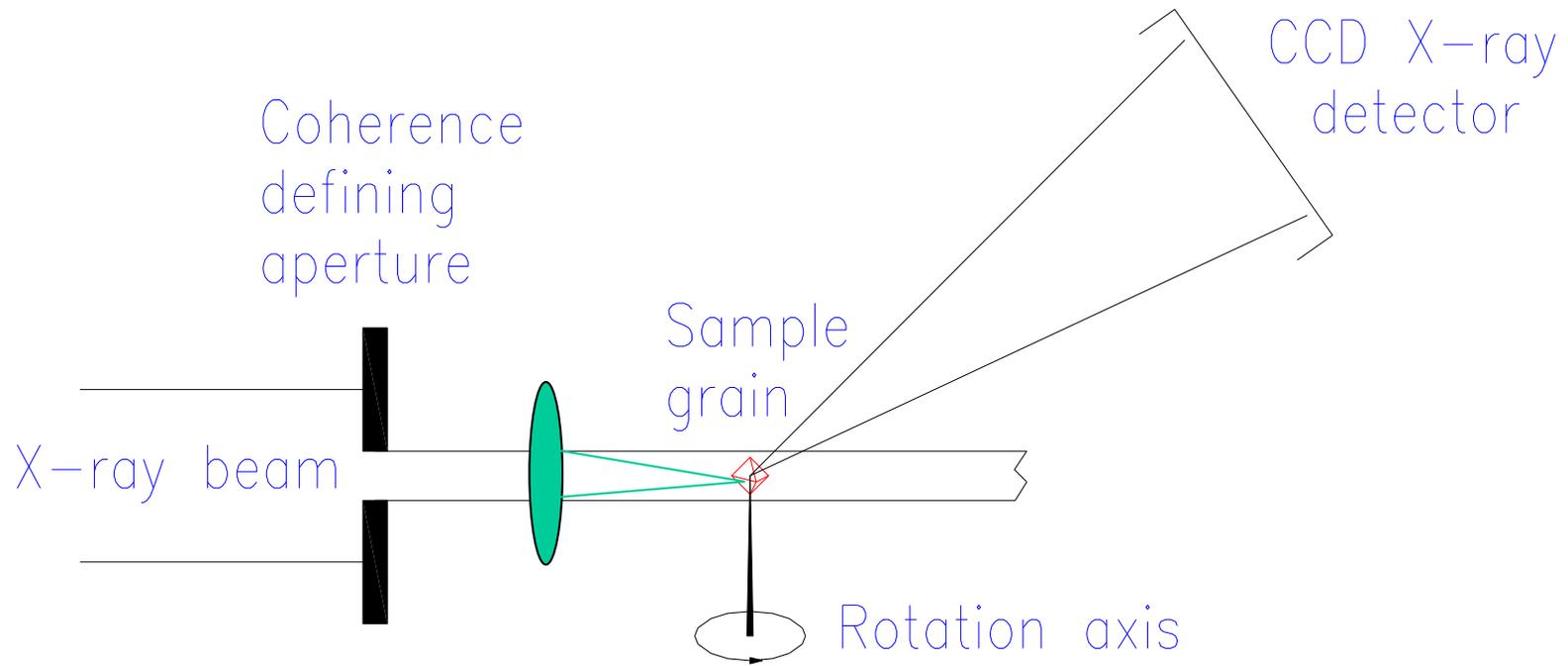
3D Images of Lead Nanocrystals

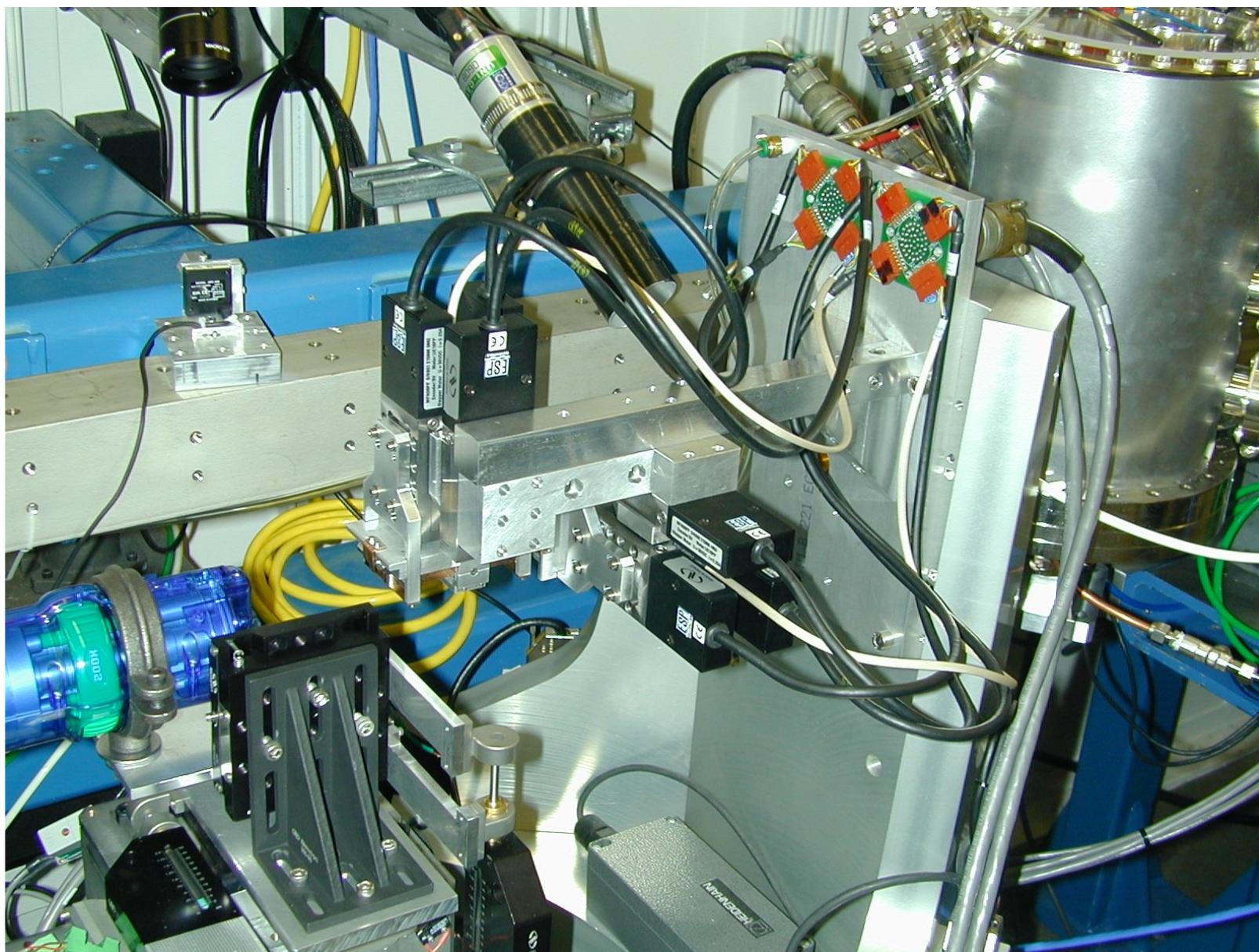


- 500nm Pb crystals grown in-situ in Sector 34 UHV system on a SiO₂ support (vertical).
- 3D diffraction data inverted into hemispherical cross-sections.

- These images are colored according to the **phase** of the density, which changes abruptly at an internal boundary.
- This plane is identified as a single deformation fault in the crystal.

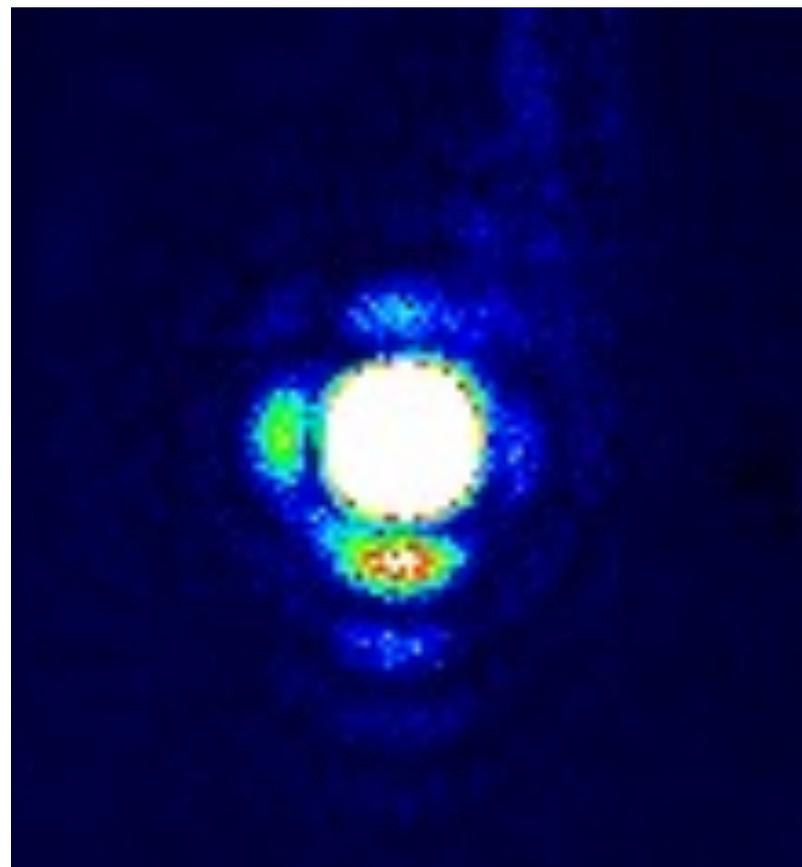
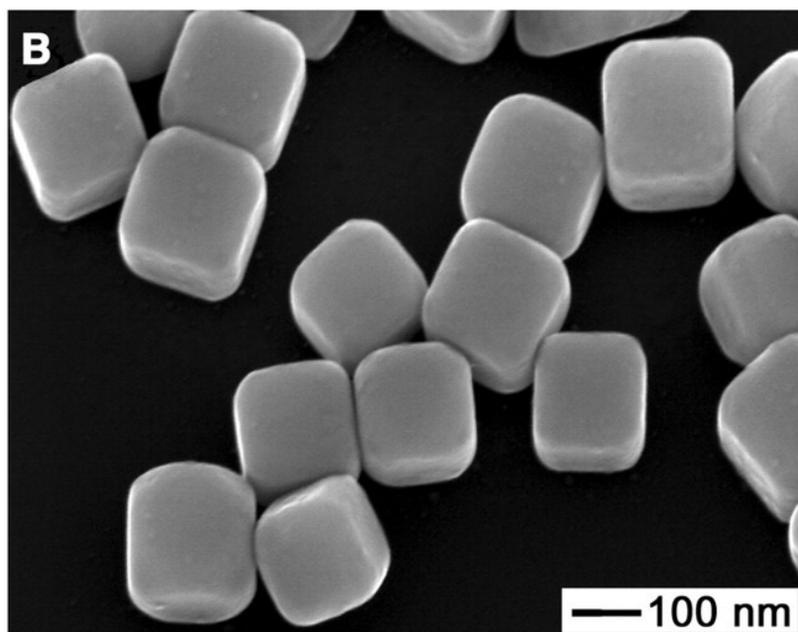
Lensless X-ray Microscope





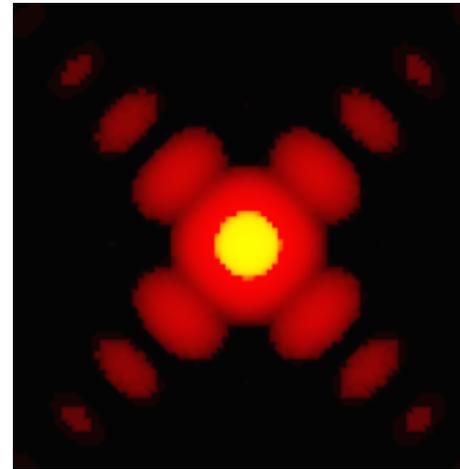
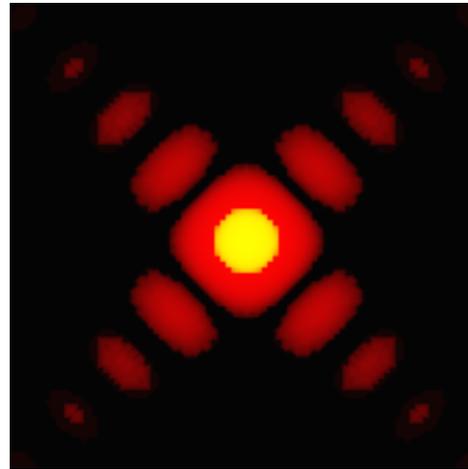
I. K. Robinson, Diamond CXD, July 2004

Chemically Synthesized Silver Nanocubes



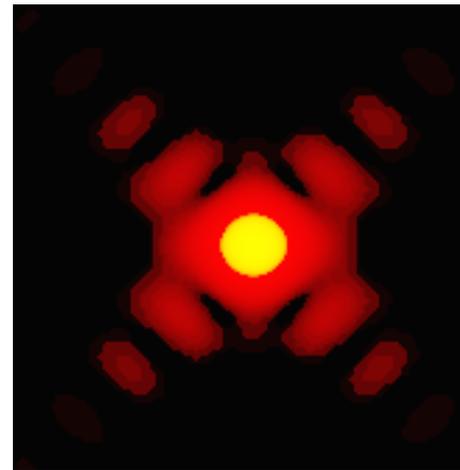
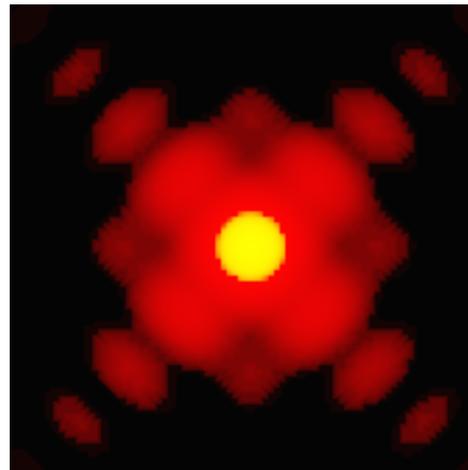
Yugang Sun and Younan Xia,
Science 298 2177 (2003)

Spherical and cylindrical waves



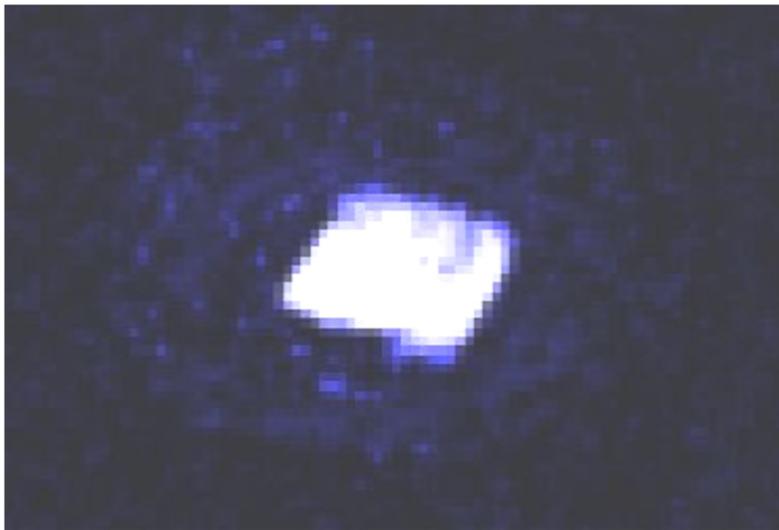
$\pi/4$

$\pi/2$

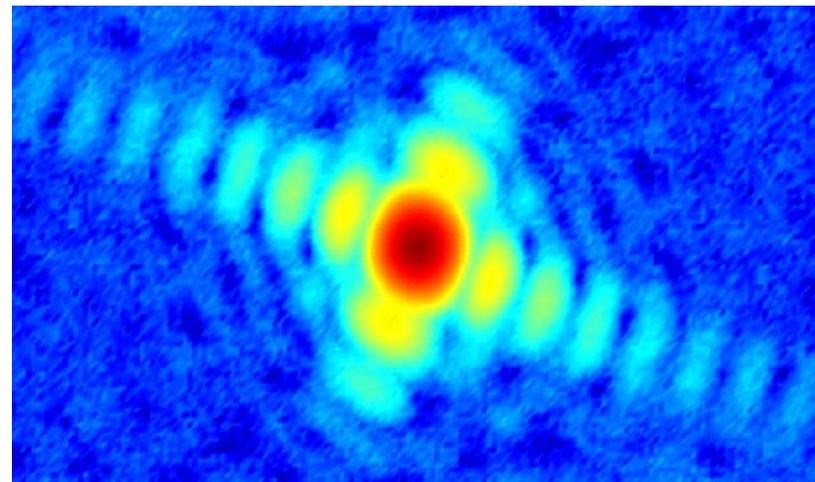
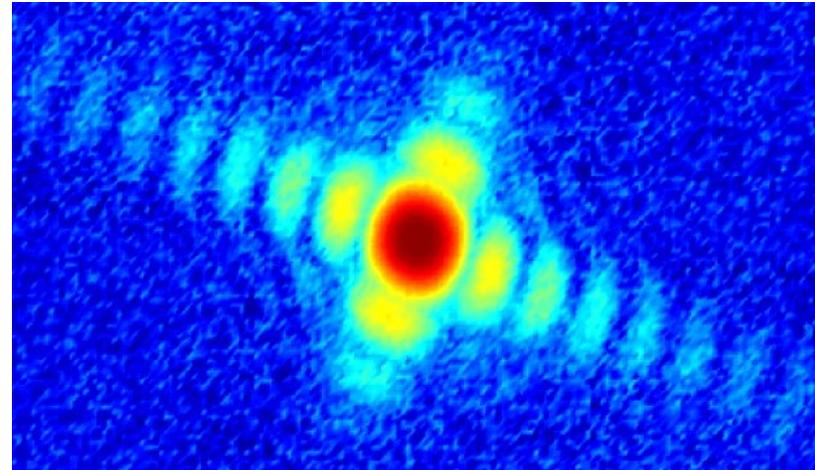


$\pi/4$ (x)

Reconstruction of Ag Nanocrystal



←→
200nm

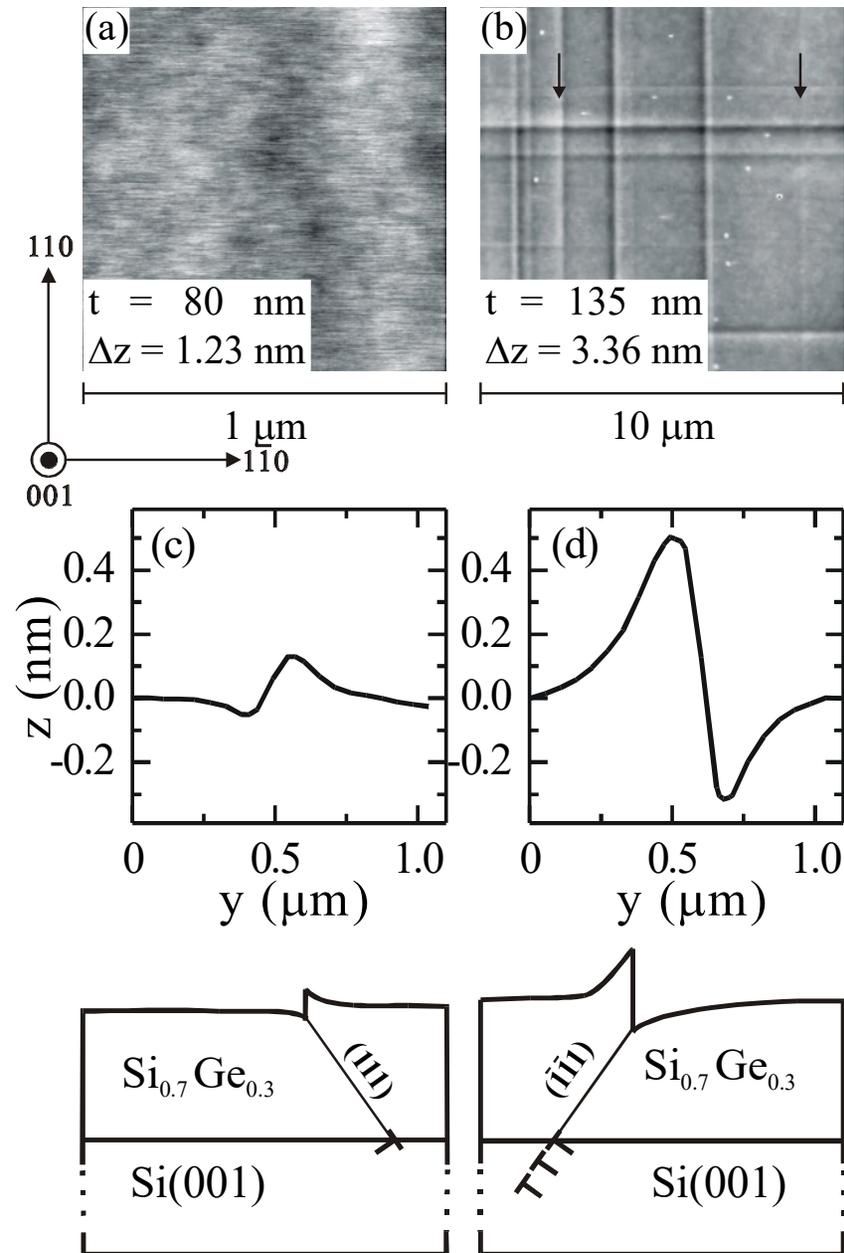


Low dislocation density GeSi films

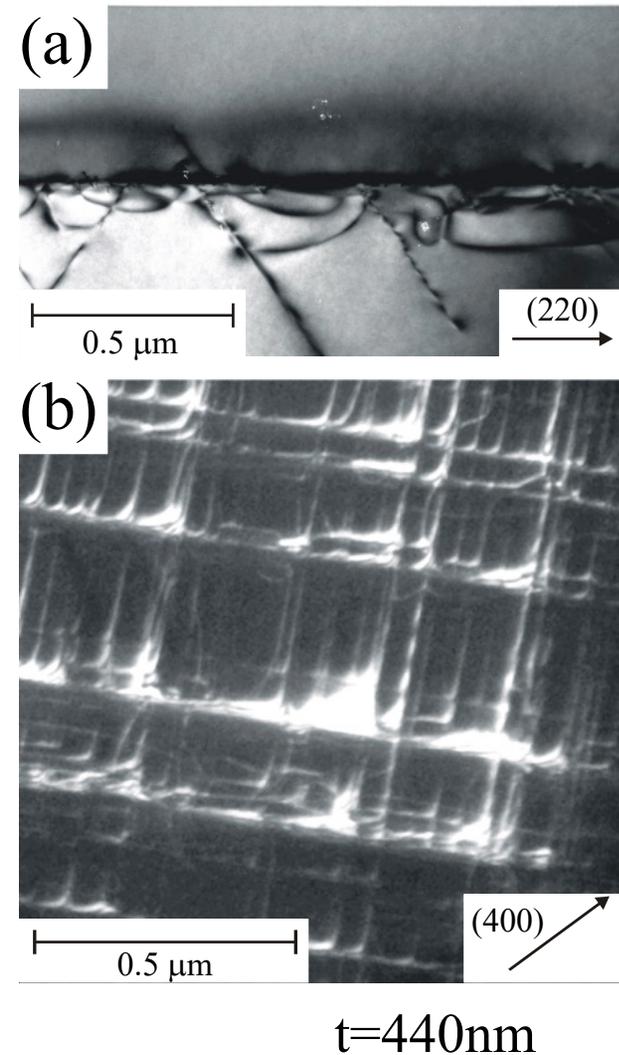
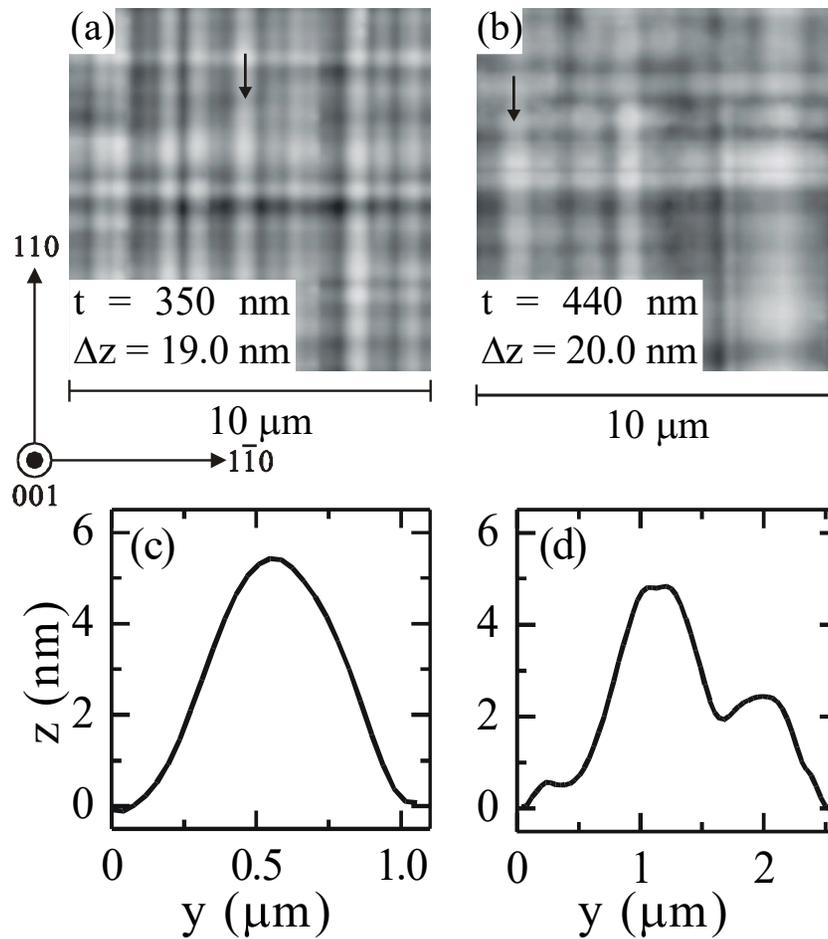
Thickness close to critical thickness

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

T. Spila, UIUC Thesis

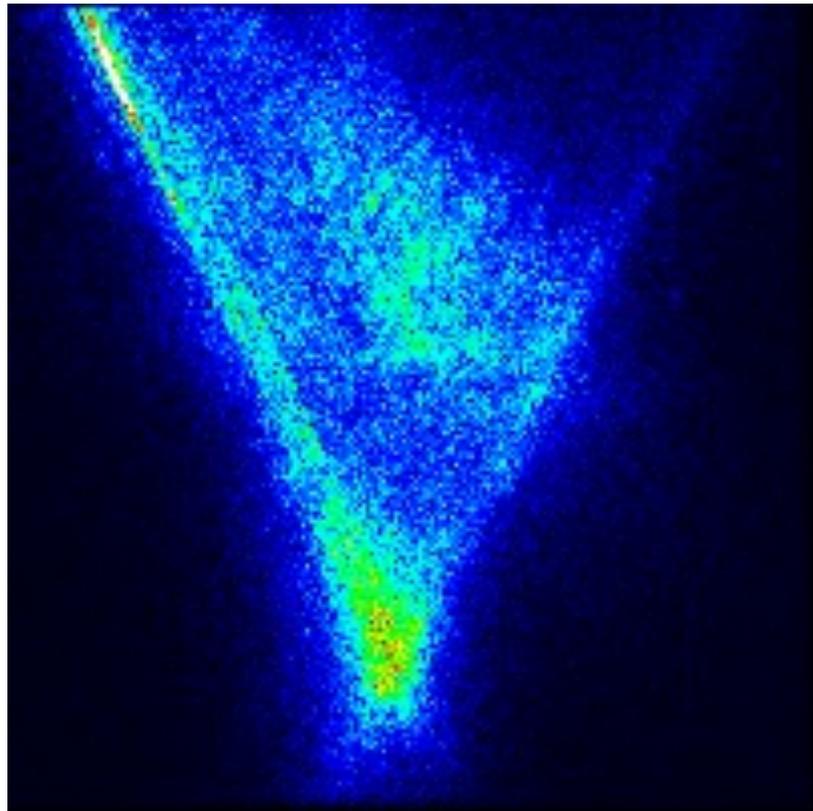


Higher Dislocation Density $\text{Ge}_{0.3}\text{Si}_{0.7}$

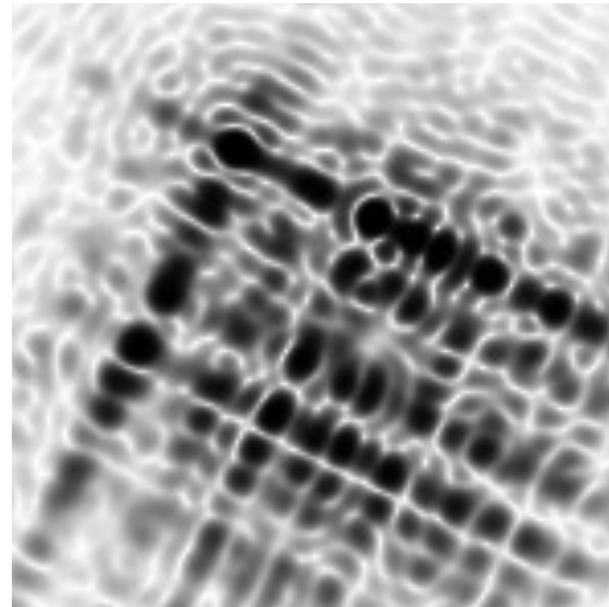


Use CCD and scan sample position

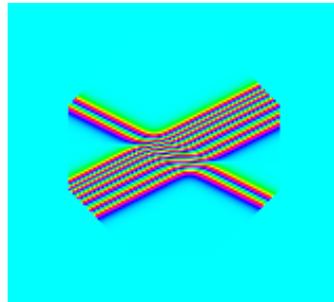
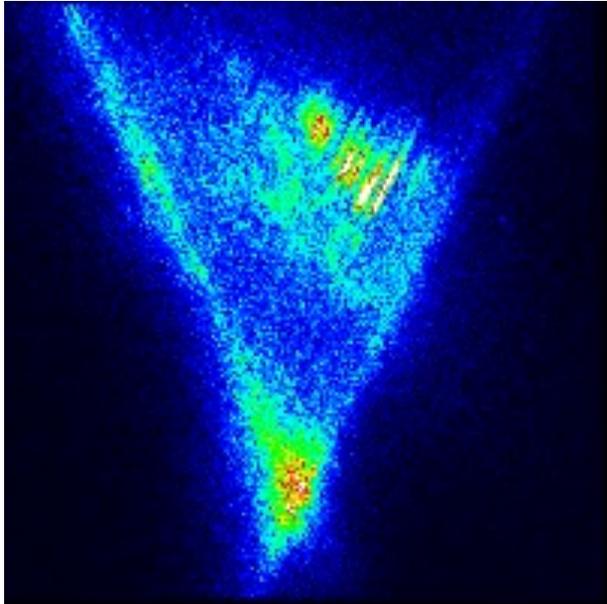
(2,0,1.92) 280nm thick $\text{Ge}_{0.3}\text{Si}_{0.7}$



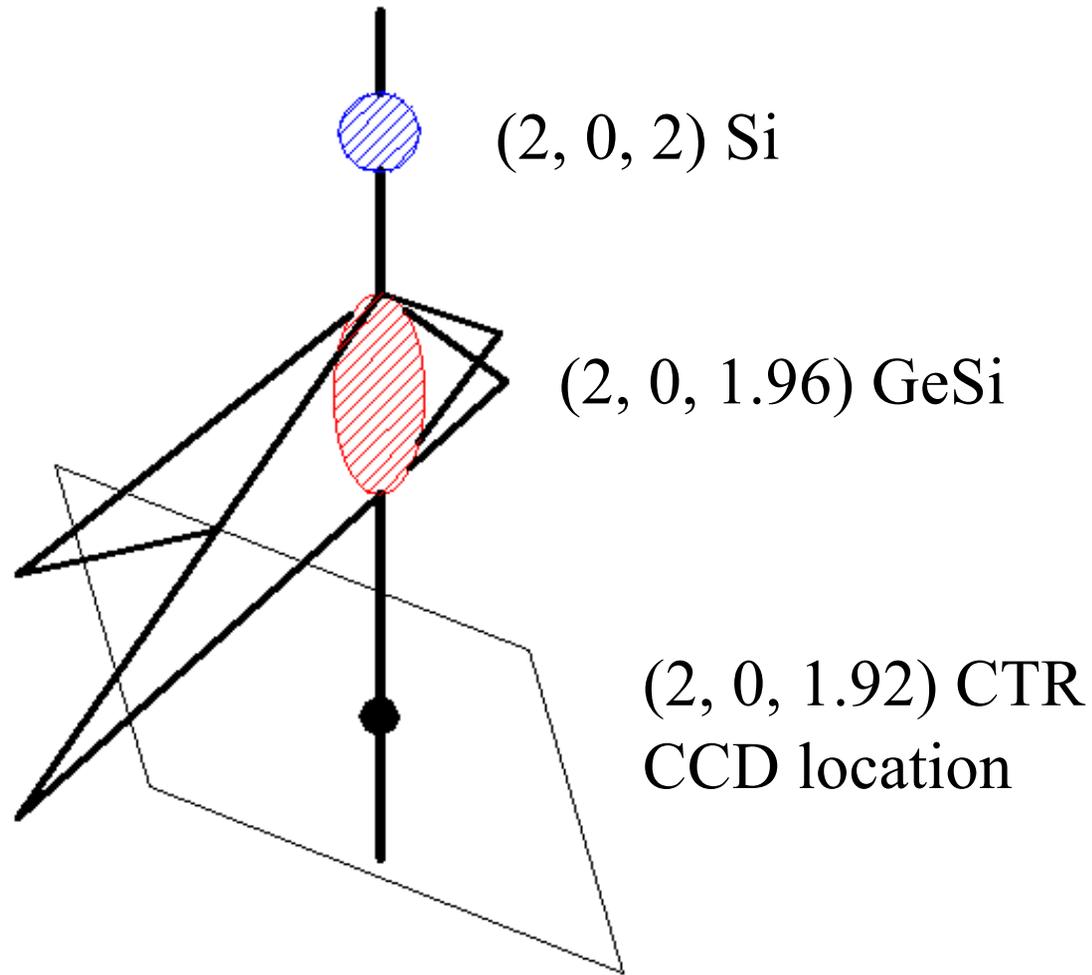
Dislocation Diffraction



Multiple Dislocations

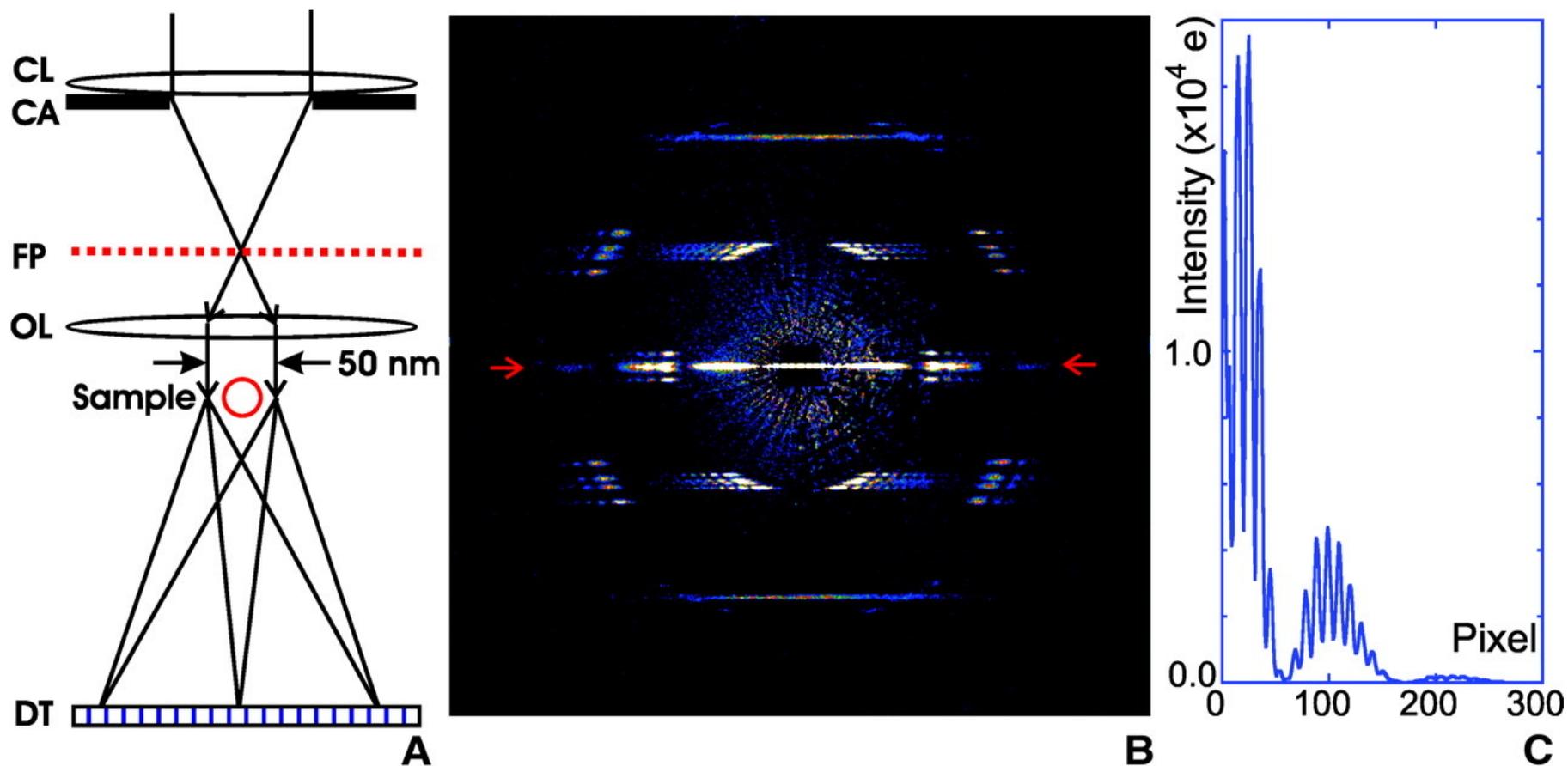


Dislocations in Reciprocal Space



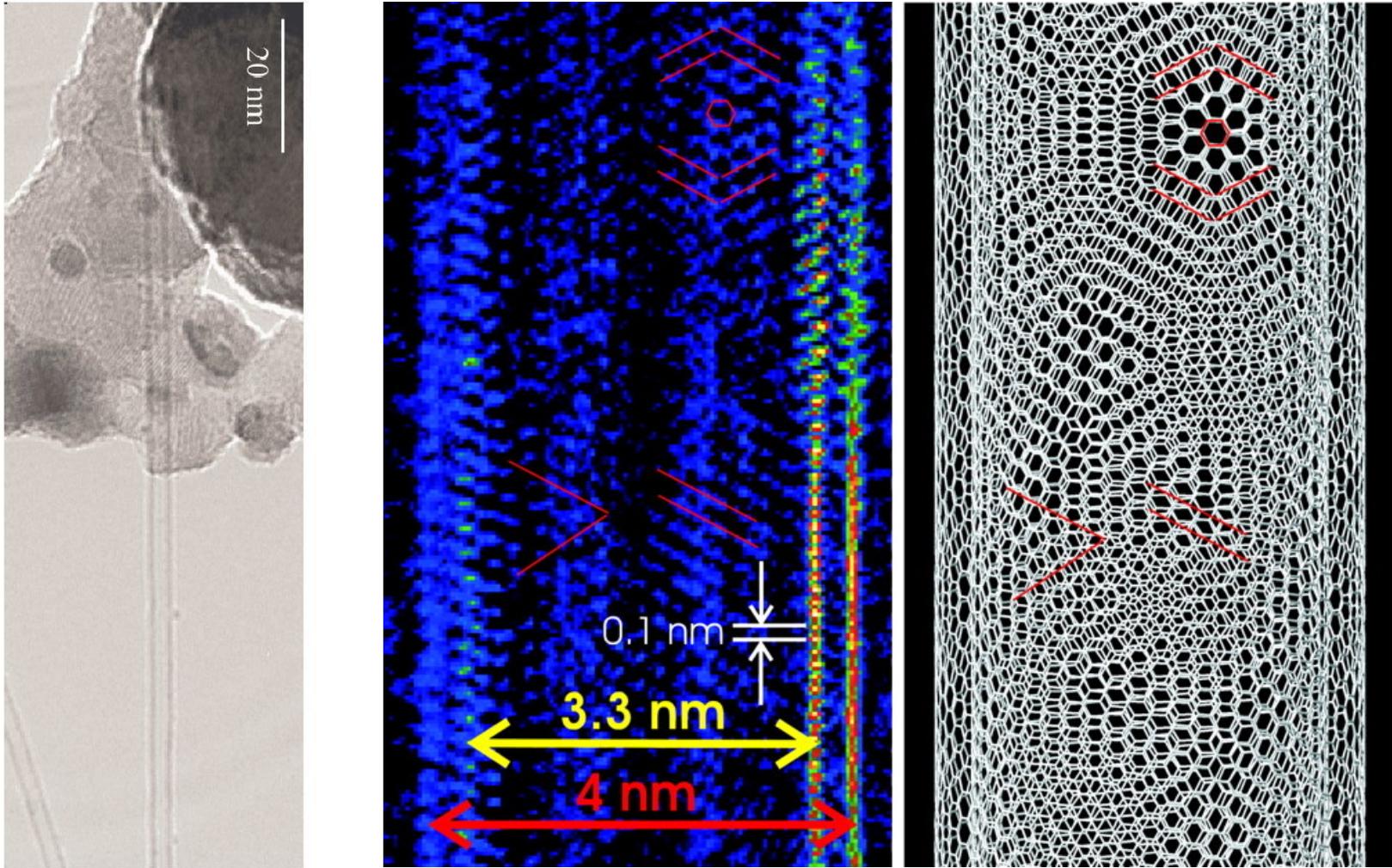
Electron Diffraction from C-nanotube

Jim Zuo et. al. Science 300 1419 (2003)



Images of DW C-nanotube

Jim Zuo et. al. Science 300 1419 (2003)



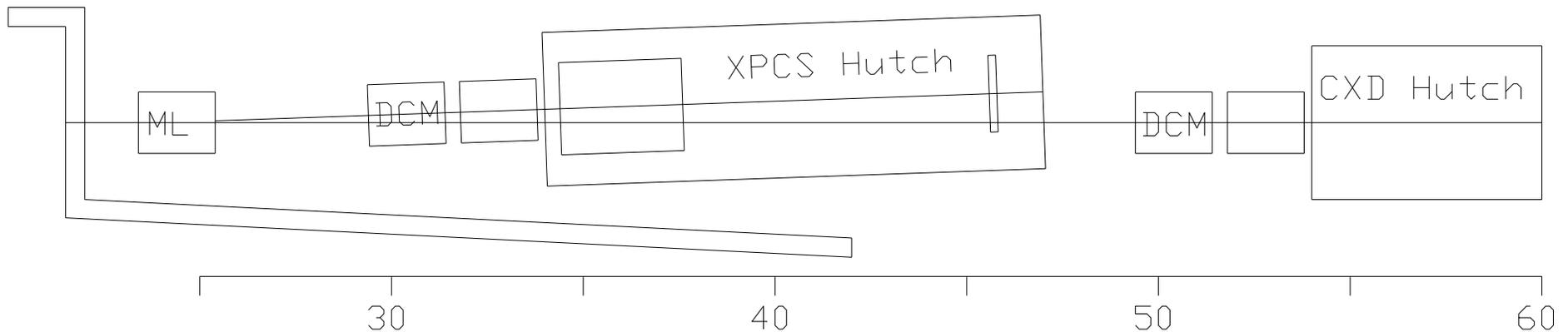
CXD and XPCS at Diamond

Call for “Expressions of Interest”

- Dynamics of Polymers, Colloids, Complex Fluids, Soft Matter and Nanocomposites on time scales down to Nanoseconds by XPCS.
- Structures of Granular Materials, Biominerals, Protein Crystals, Self-assembled and Semiconductor Nanostructures by CXD.
- Single-molecule Structure Determination.

CXD and XPCS at Diamond

Call for “Expressions of Interest”



- Simultaneous operation of both stations
- Fixed energy operation at $\sim 7\text{keV}$
- Multilayer (ML) beam splitter

Conclusions and Outlook

- Internal structure of Au Nanocrystals
- Phasing by computation instead of lens
- Dislocations give asymmetric patterns
- Atomic resolution with electron diffraction
- Future CXD facility at Diamond Light Source

Today's Programme

Ian Robinson	Coherent X-ray Diffraction
Gerhard Grübel	XFEL Project
Mike Horton	Bone Structure
Dave McComb	Ceramic Nanocrystals
Tim Jones	Semiconductor Nanostructures
Geoff Thornton	Nanostructuring Oxide Surfaces