

# 3D Mapping of Strain in Nanocrystals

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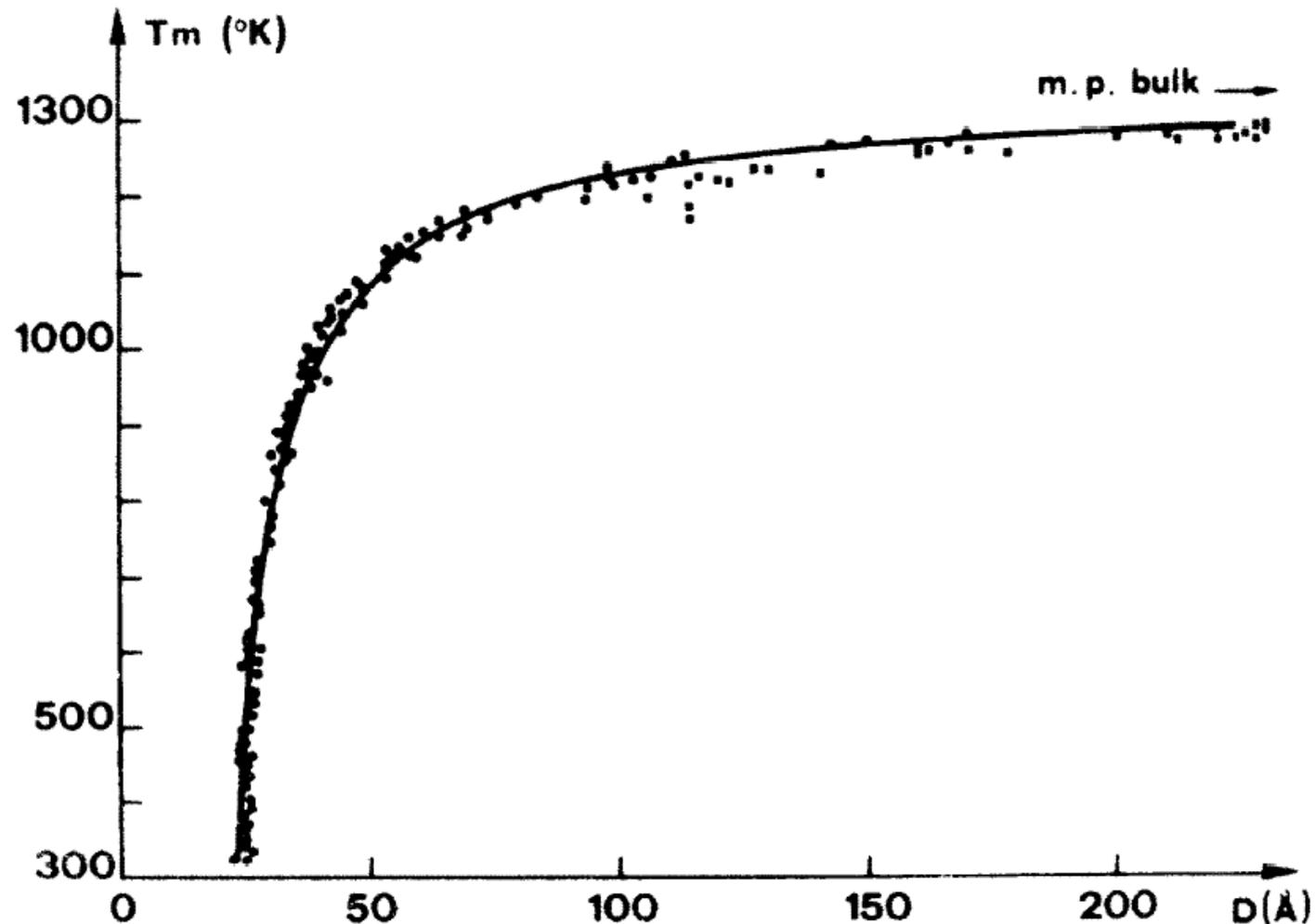
Materials Science Seminar  
University of Pittsburgh  
September 2005

# Outline

- Coherent X-ray Diffraction
- How to Solve the Phase Problem
- Nanocrystal Shapes
- Extension to Phase Objects
- Opportunities with Electrons and FELs

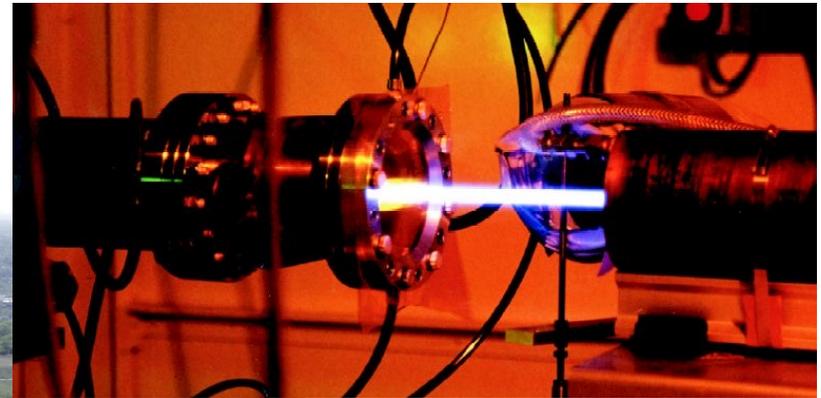
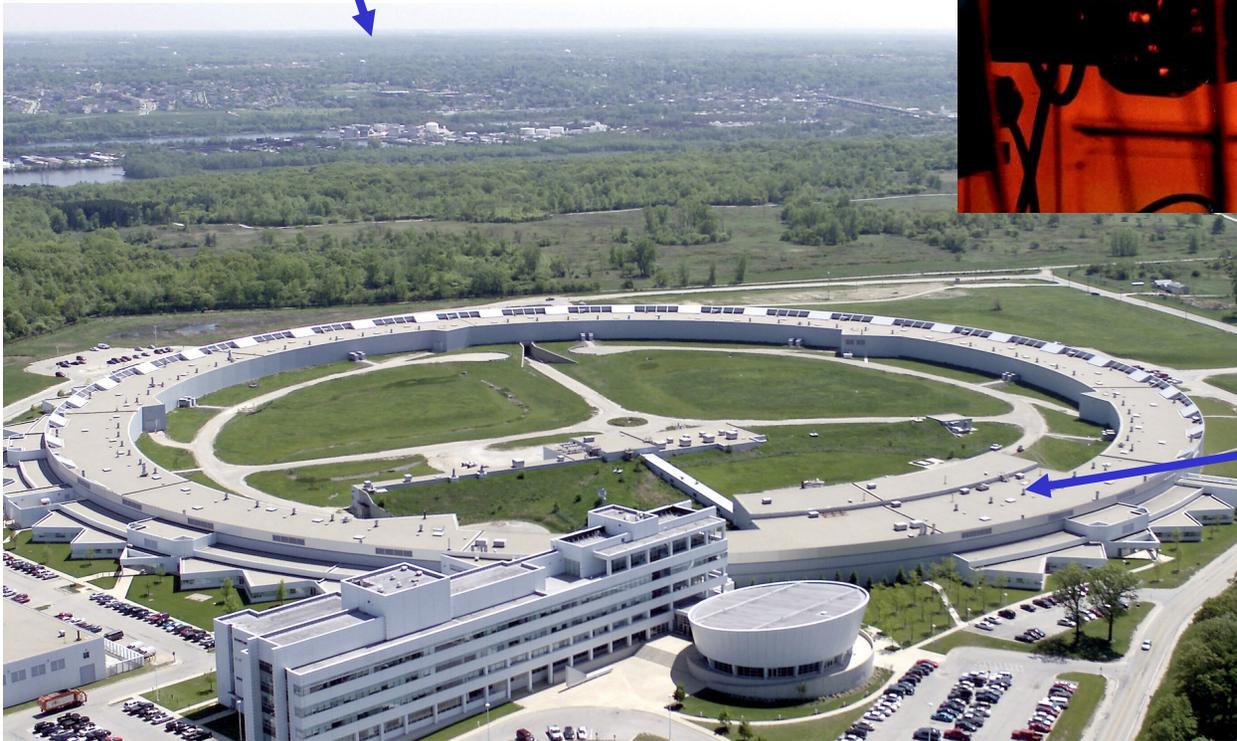
# Size-dependent Melting of Au Particles

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



# Synchrotron Radiation

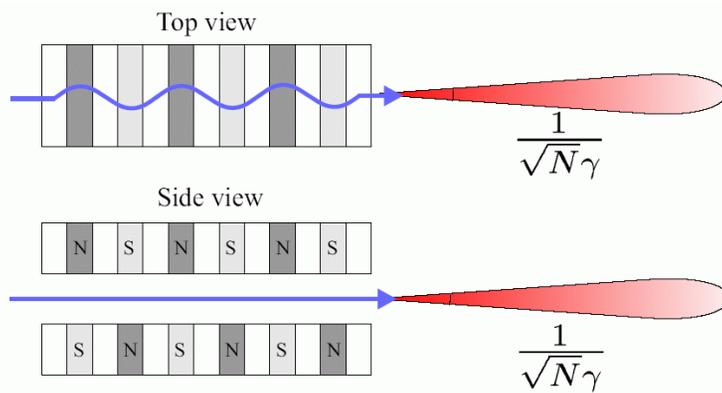
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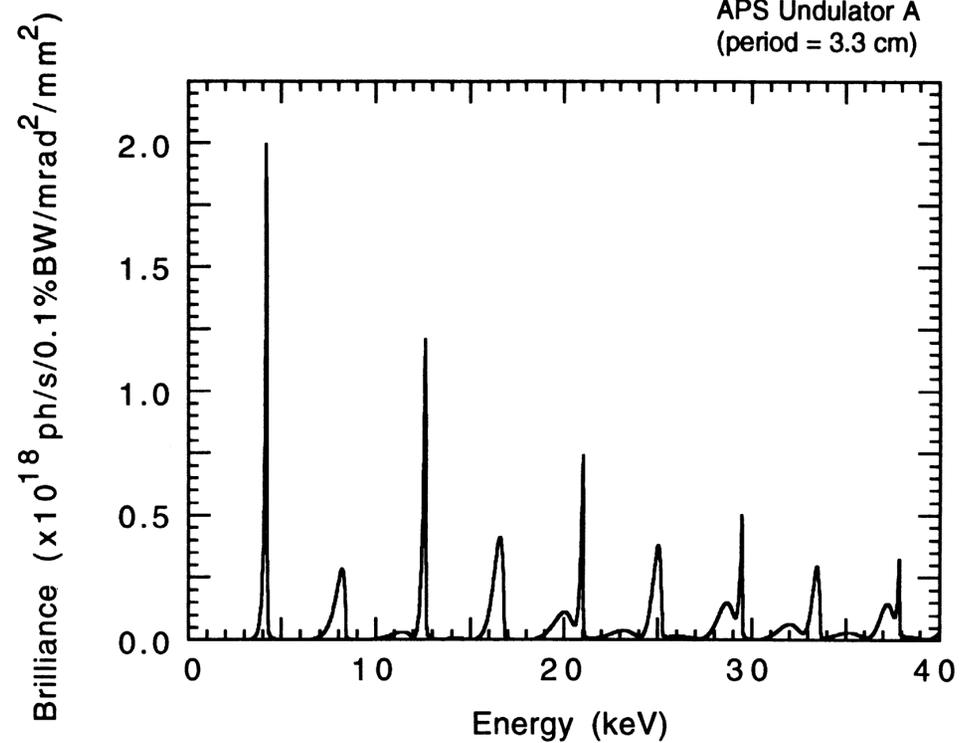
34-ID-C



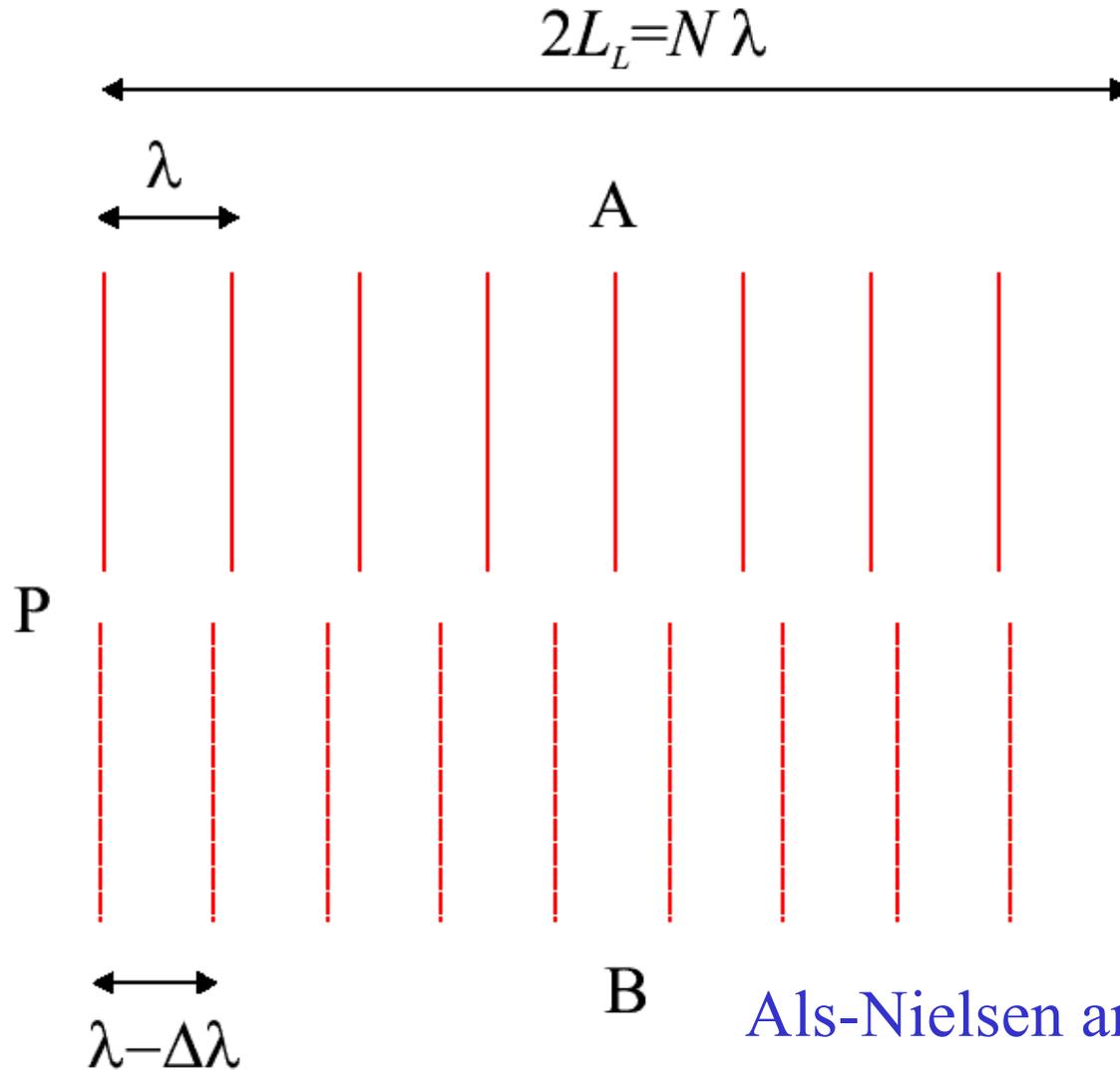
# X-ray Undulator at APS



$$\lambda_X = \frac{\lambda_U}{2\gamma^2} \left\{ 1 + \frac{K^2}{2} + (\gamma\theta)^2 \right\}$$



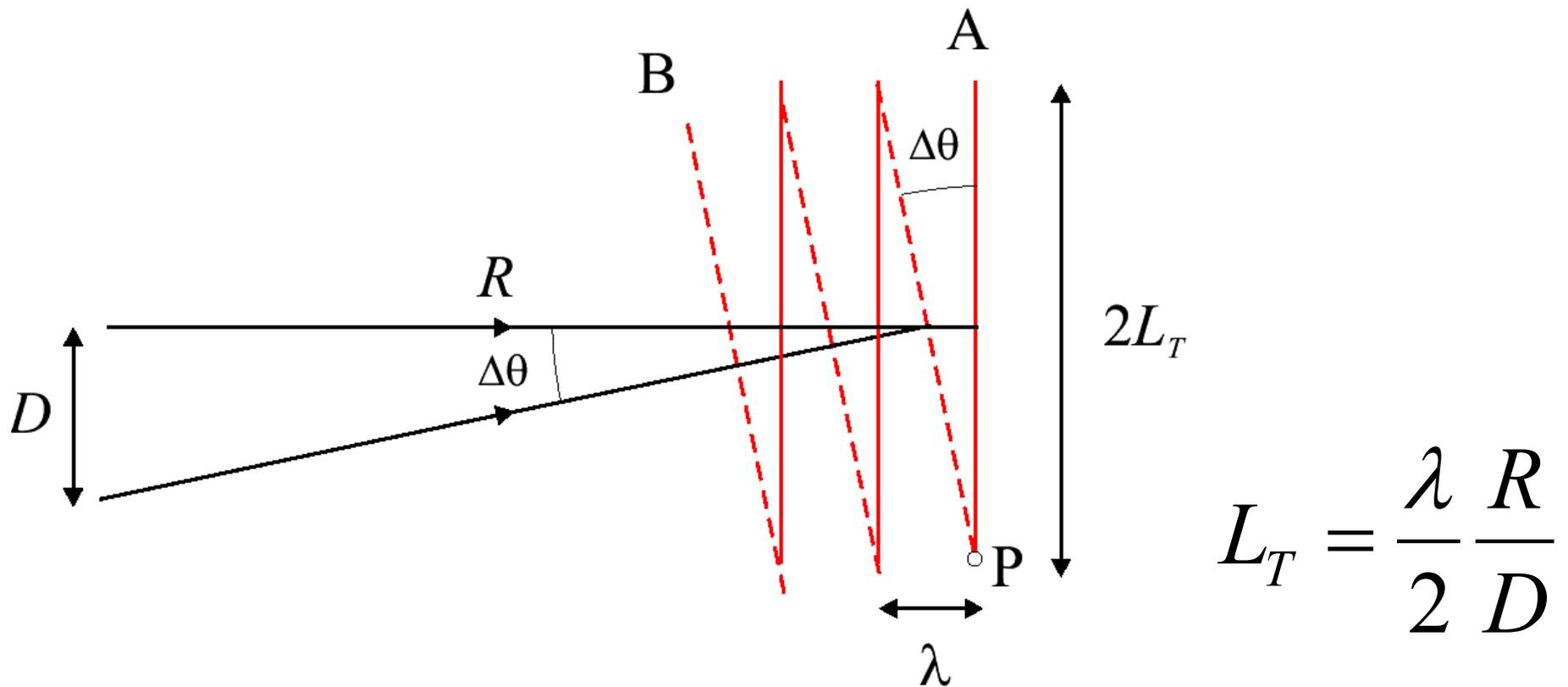
# Longitudinal Coherence



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

Als-Nielsen and McMorro (2001)

# Lateral (Transverse) Coherence



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

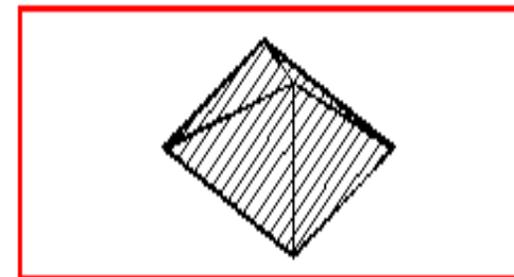
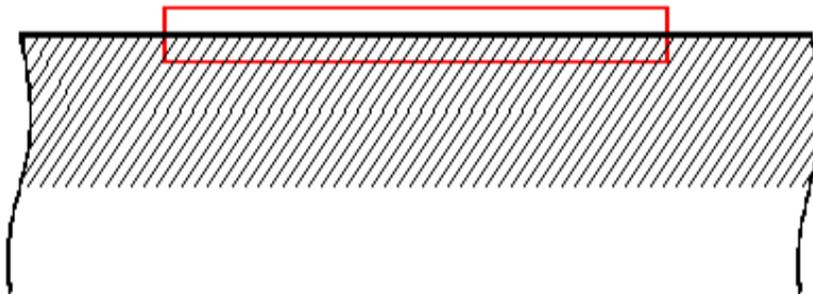
Als-Nielsen and McMorrow (2001)

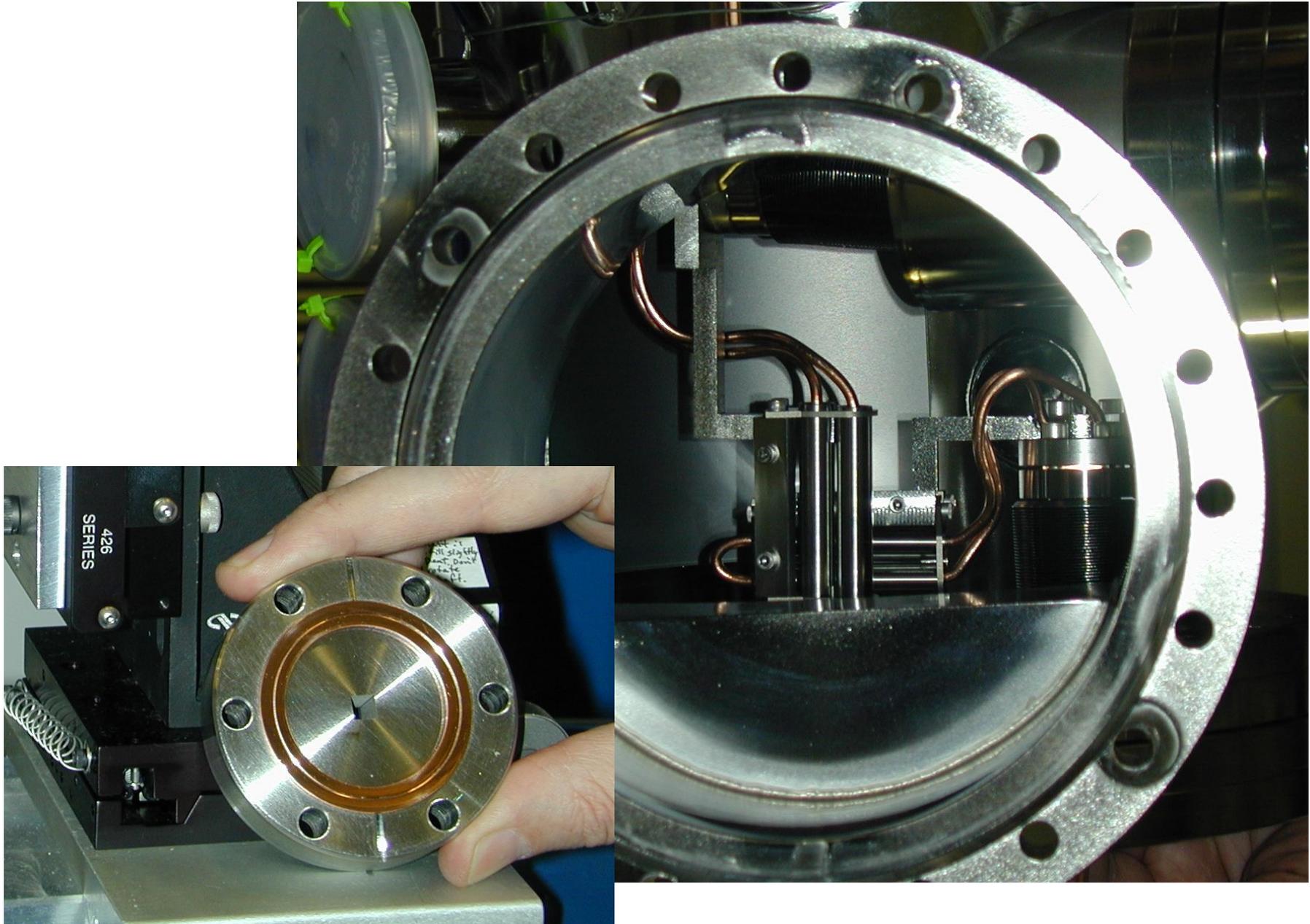
# Coherence at APS, ESRF or DLS

Typical of 3rd Generation (undulator) Synchrotron Source

Coherence of	$\xi_{\text{VER}}$	$\xi_{\text{HORIZ}}$	$\xi_{\text{LONG}}$	Flux
Raw Undulator	35 $\mu\text{m}$	9 $\mu\text{m}$	0.004 $\mu\text{m}$	$2 \times 10^{12}$
Si(111) Monochromator	35 $\mu\text{m}$	9 $\mu\text{m}$	1 $\mu\text{m}$	$1 \times 10^{10}$
C(111) Monochromator	35 $\mu\text{m}$	9 $\mu\text{m}$	3 $\mu\text{m}$	$3 \times 10^9$

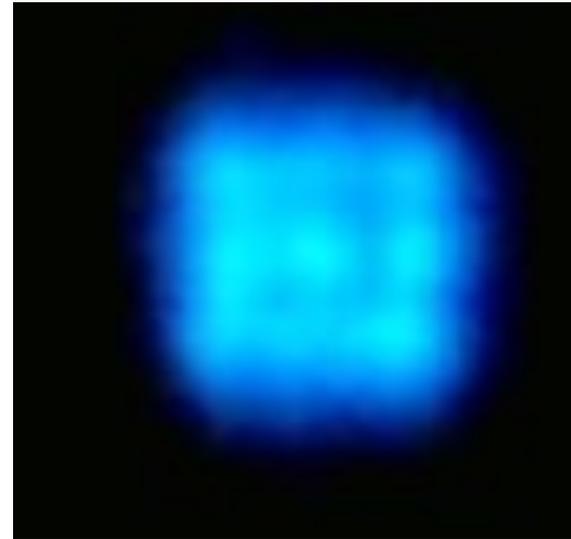
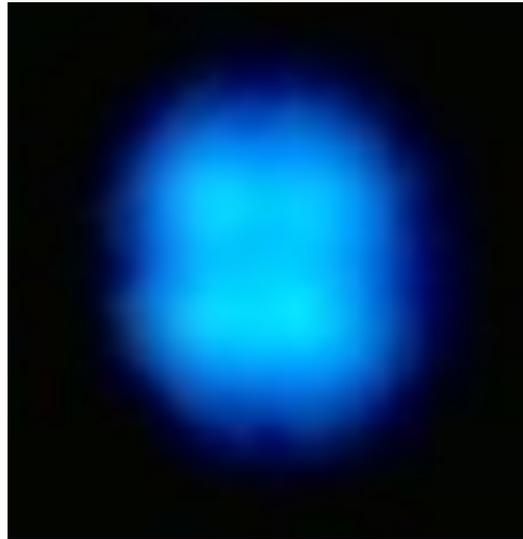
Coherent region defined by slits



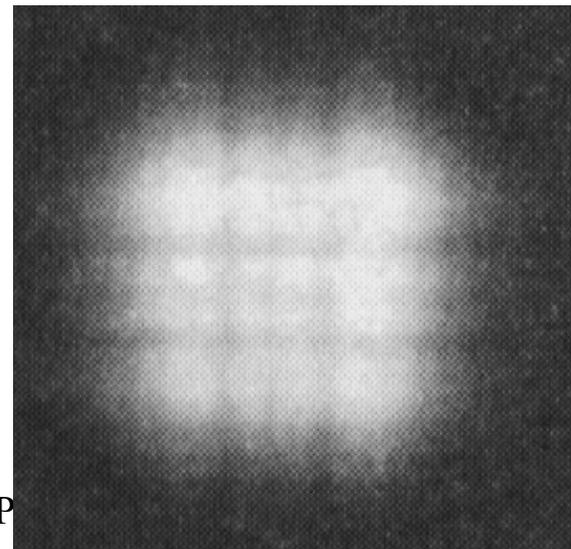
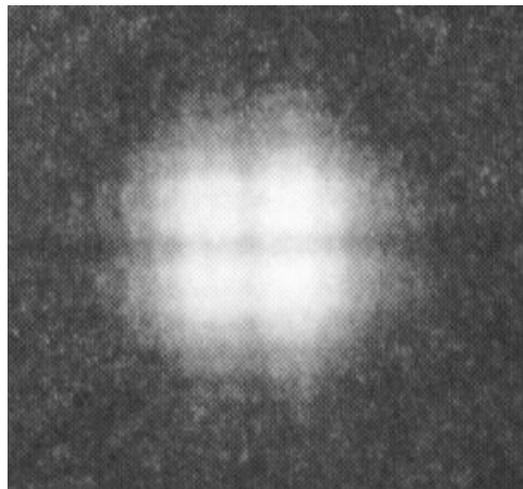


I. K. Robinson, U. Pittsburgh, Sept 2005

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



X-ray  
beam  
defined  
by RB  
slits

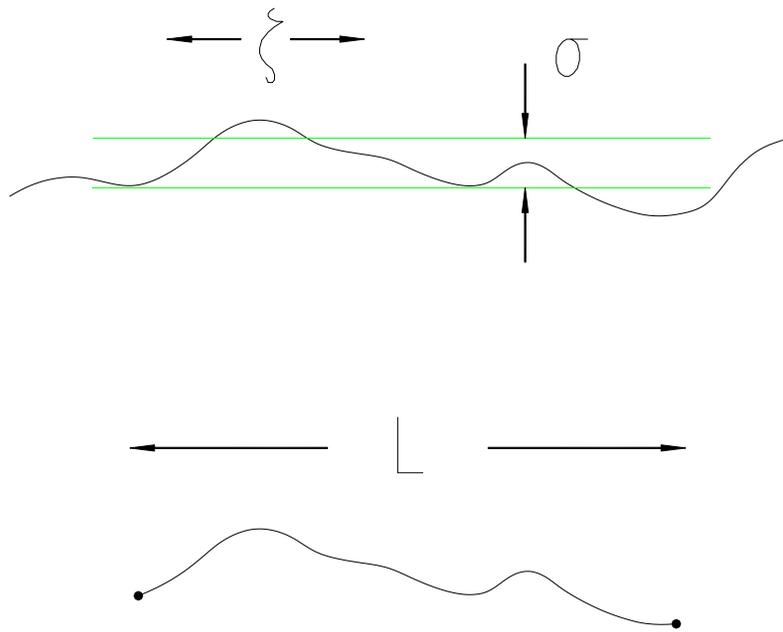


Visible  
Fresnel  
diffraction  
from  
Hecht  
“Optics”

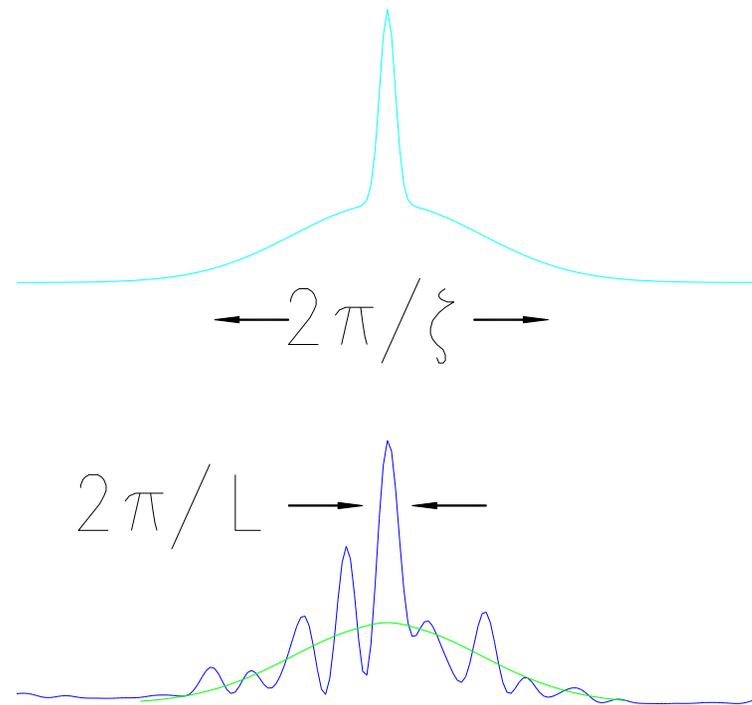
I. K. Robinson, U. P.

# Diffuse Scattering acquires Structure using CXD

Real Space



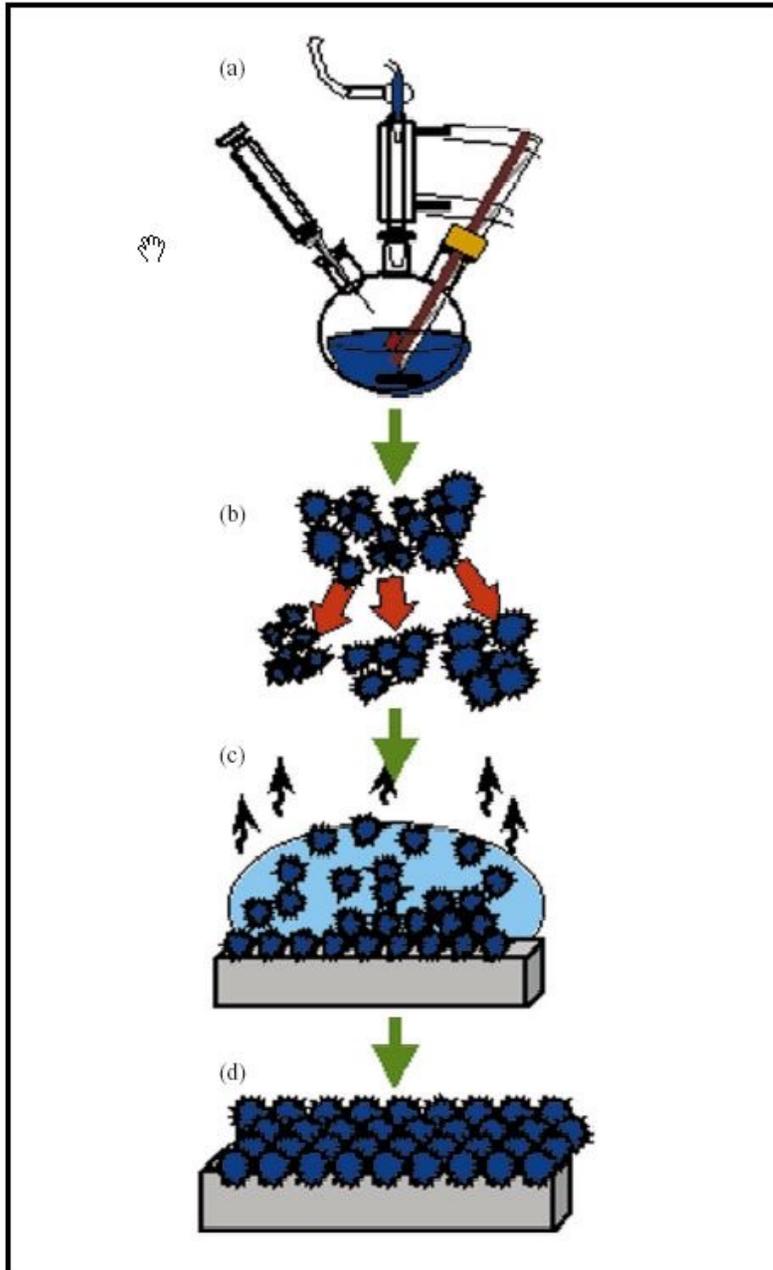
Reciprocal Space



# Facts of Life with Coherence

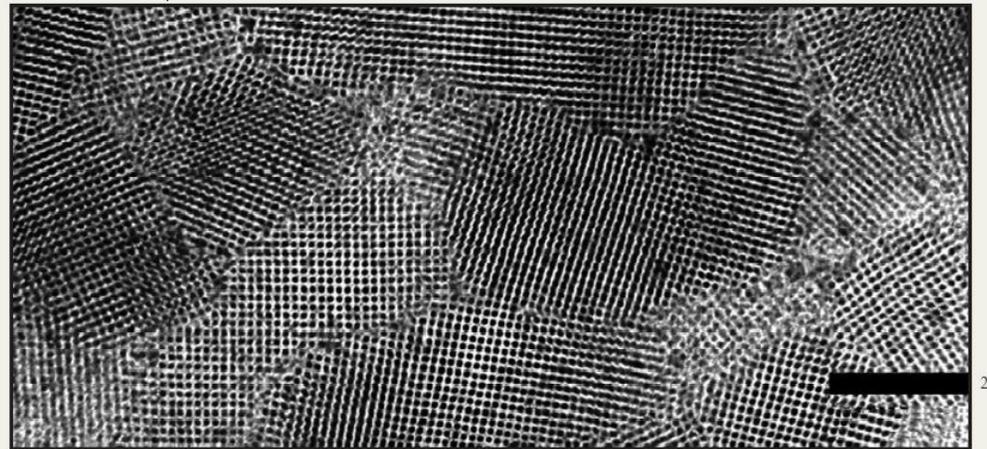
- No more diffuse scattering
- No more ensemble averaging
- Coherence is indestructible
  - everything following your (coherence-defining) entrance slit is your ‘sample’
- If something moves, the whole interference pattern changes

# Chemical Synthesis of Nanocrystals



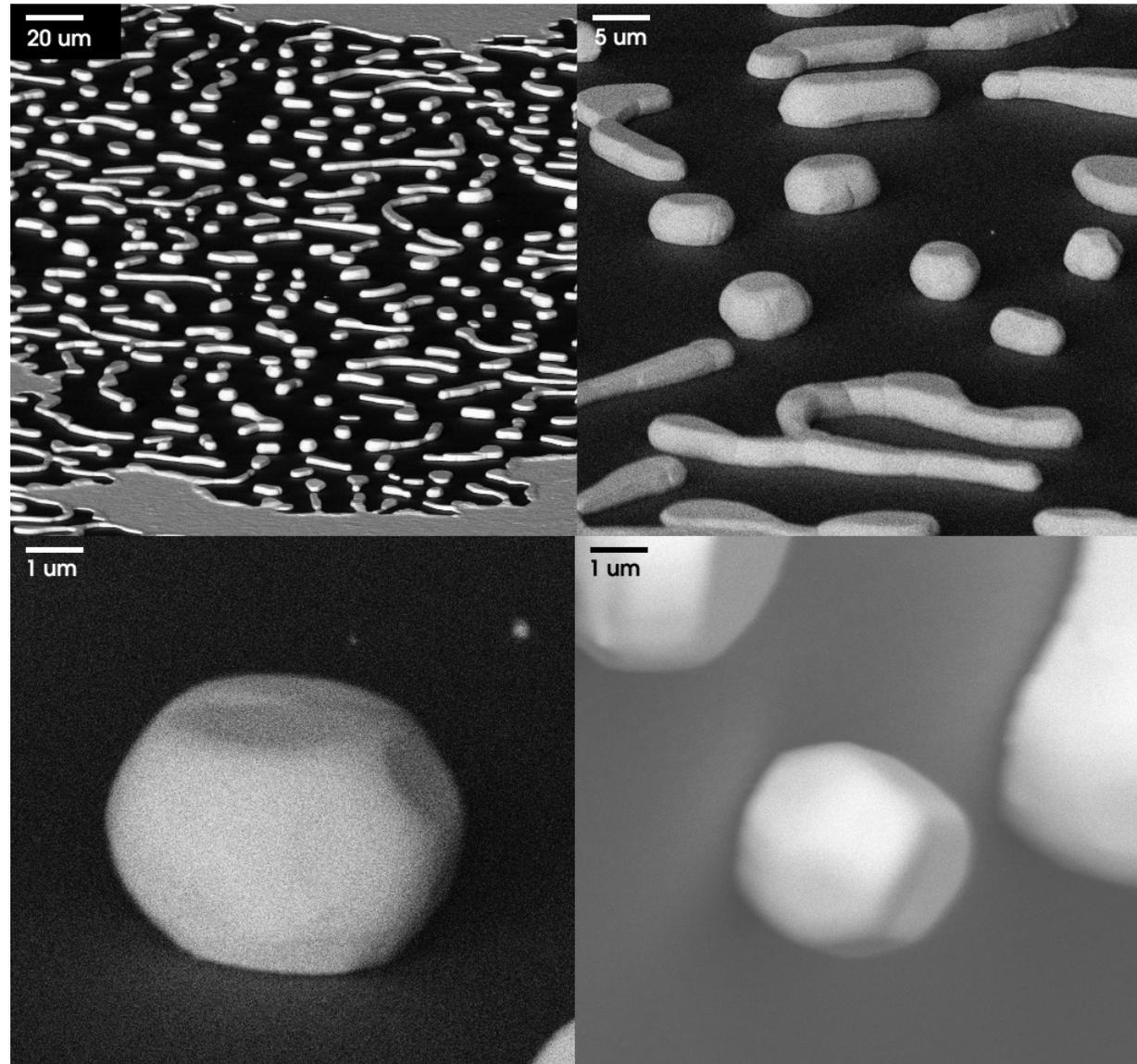
- Reactants introduced rapidly
- High temperature solvent
- Surfactant/organic capping agent
- Square superlattice (200nm scale)

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

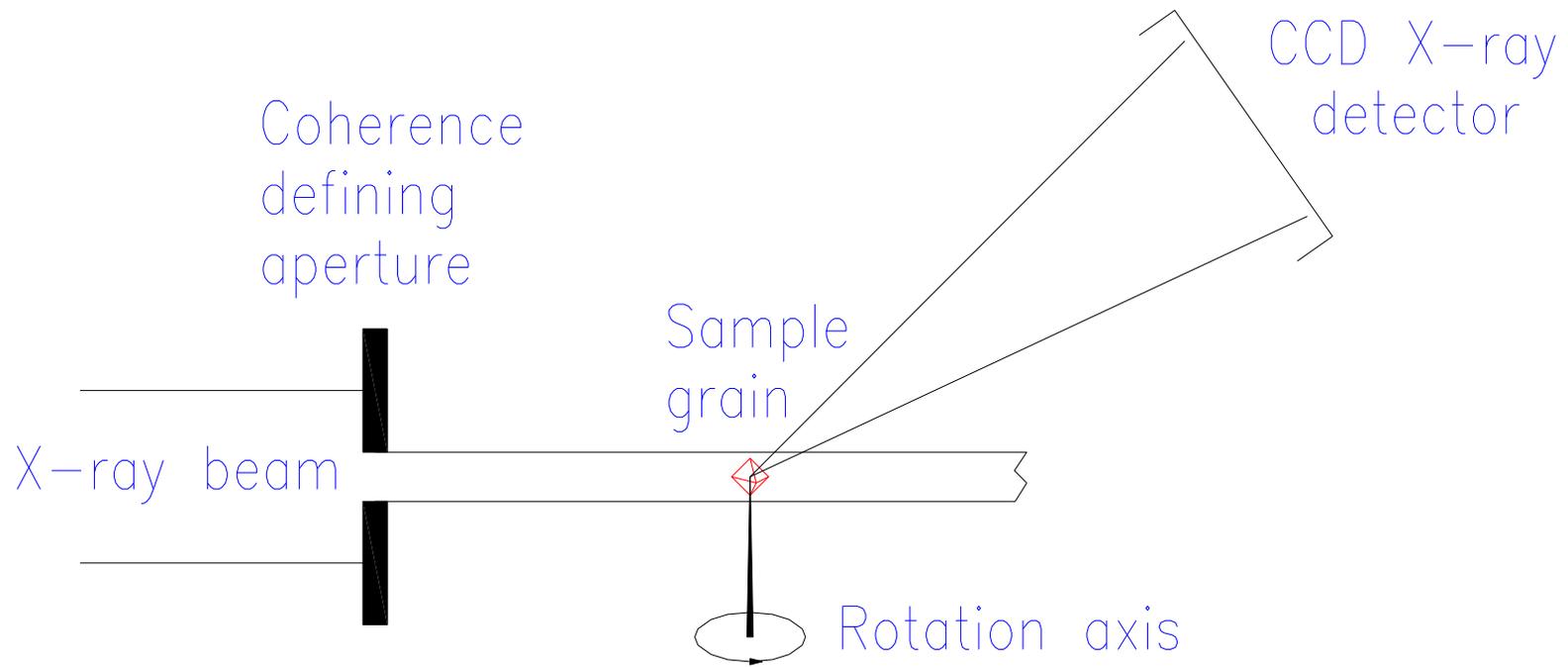


# SEMS

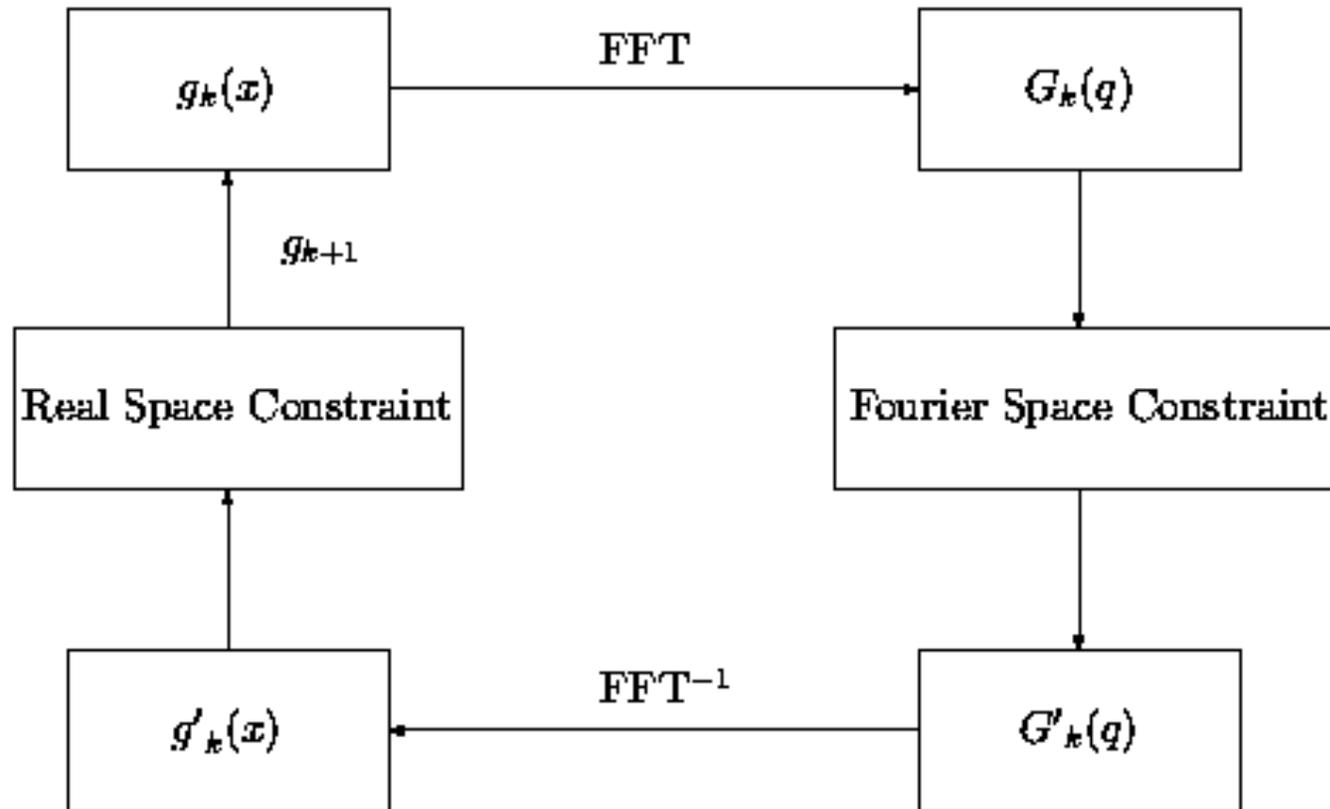
- Au blanket film
- Quartz substrate
- Annealed at 950°C for 70 hrs.



# Lensless X-ray Microscope



# Generic “Error Reduction” method



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

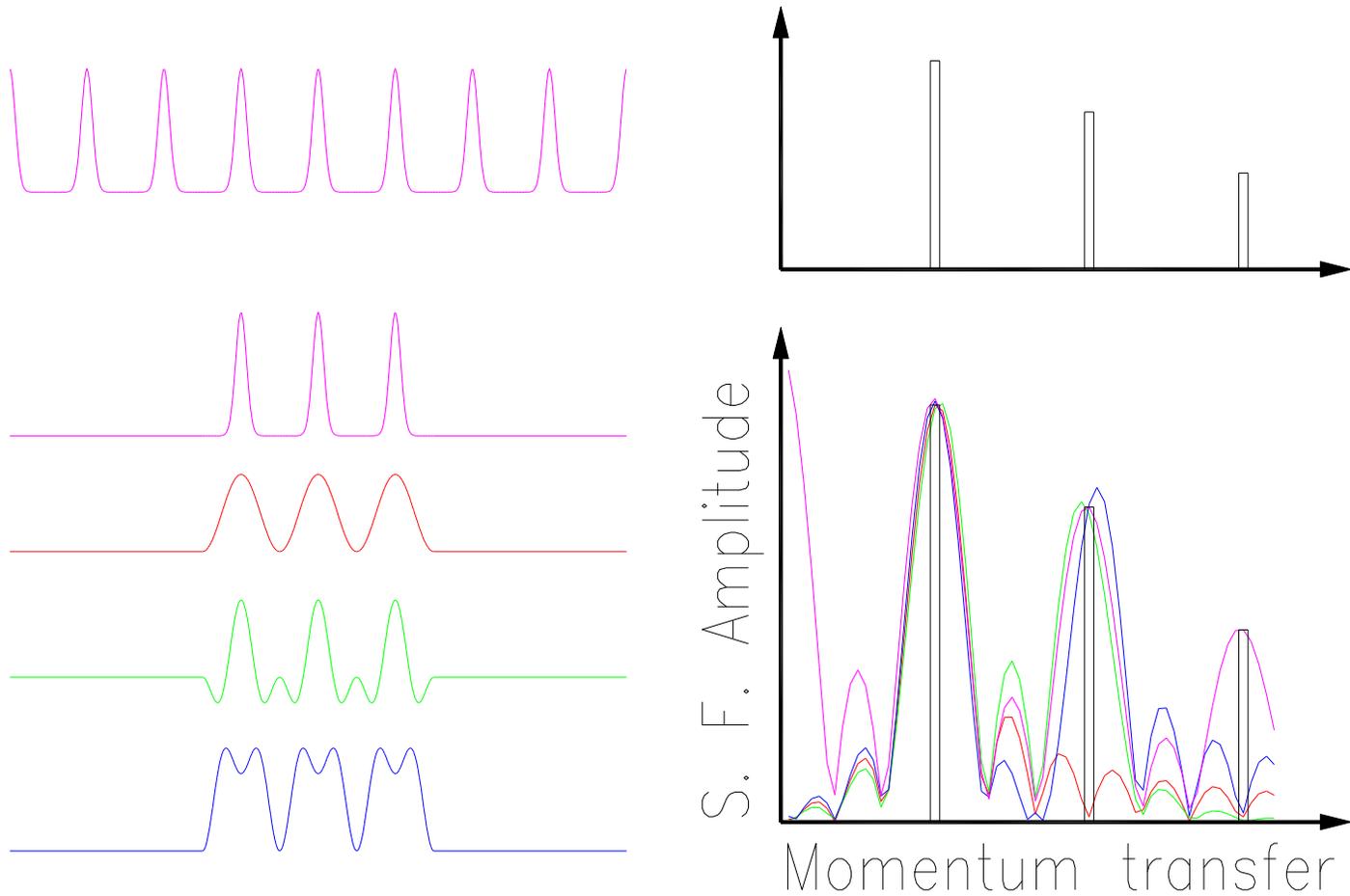
R. W. Gerchberg and W. O. Saxton *Optik* 35 237 (1972)

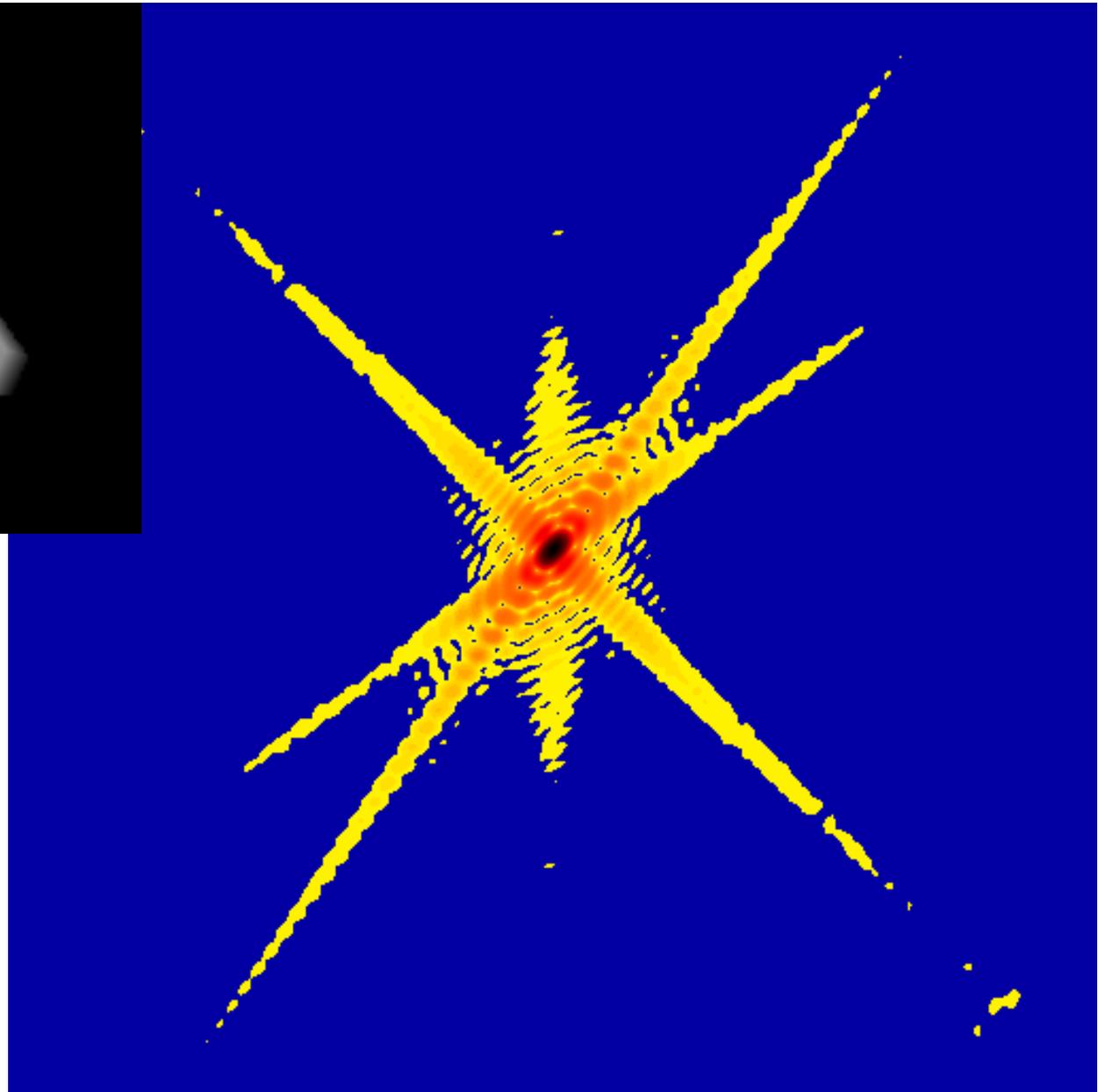
# Real-space Constraints in Crystallography

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)

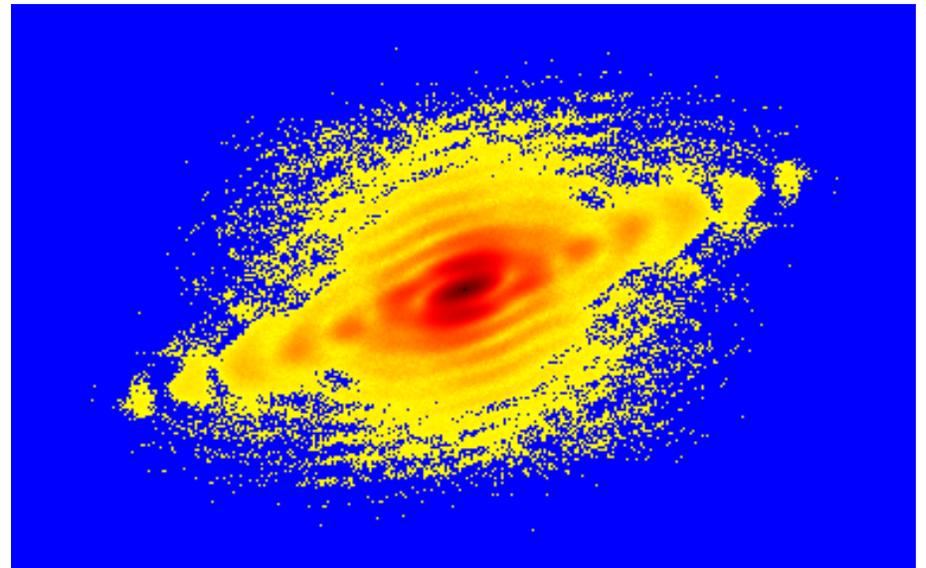
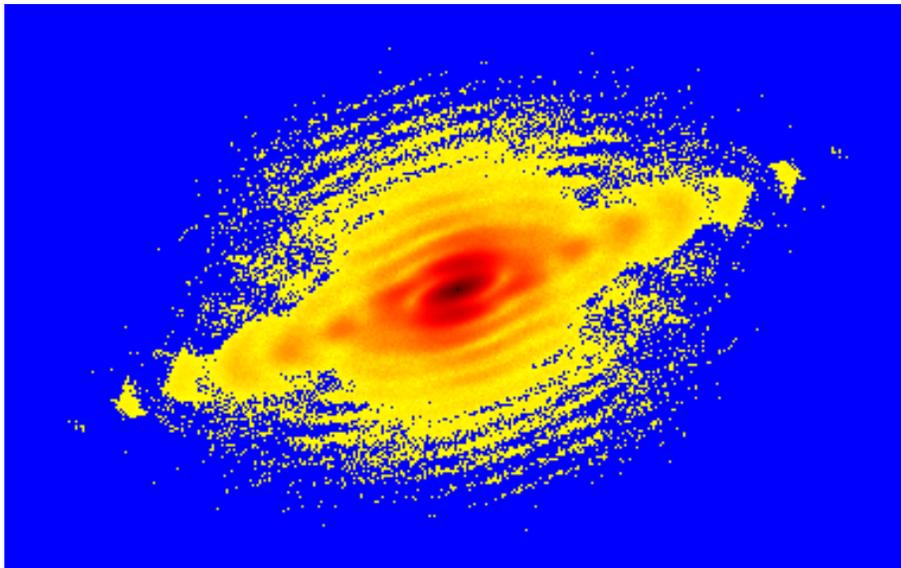
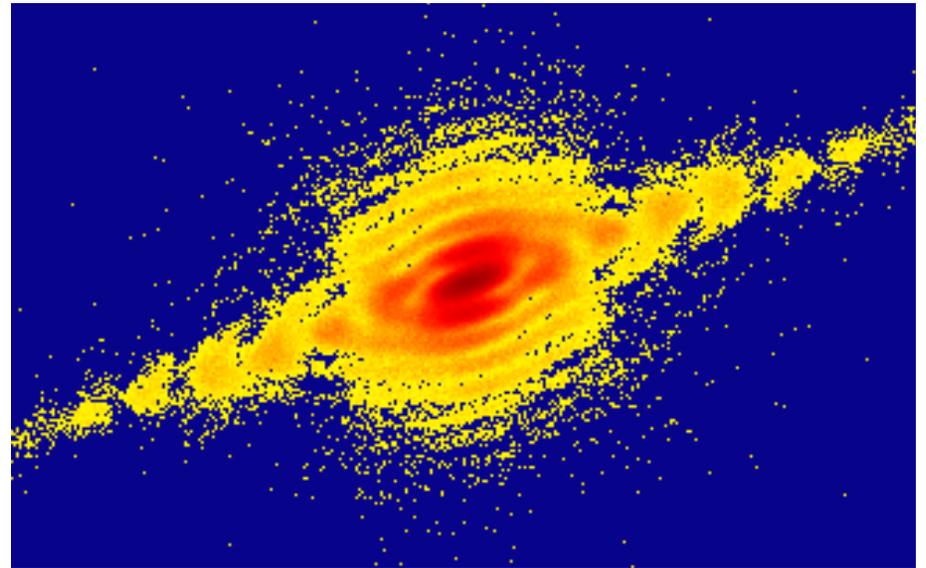
# Phase Problem: Finite-size Effect





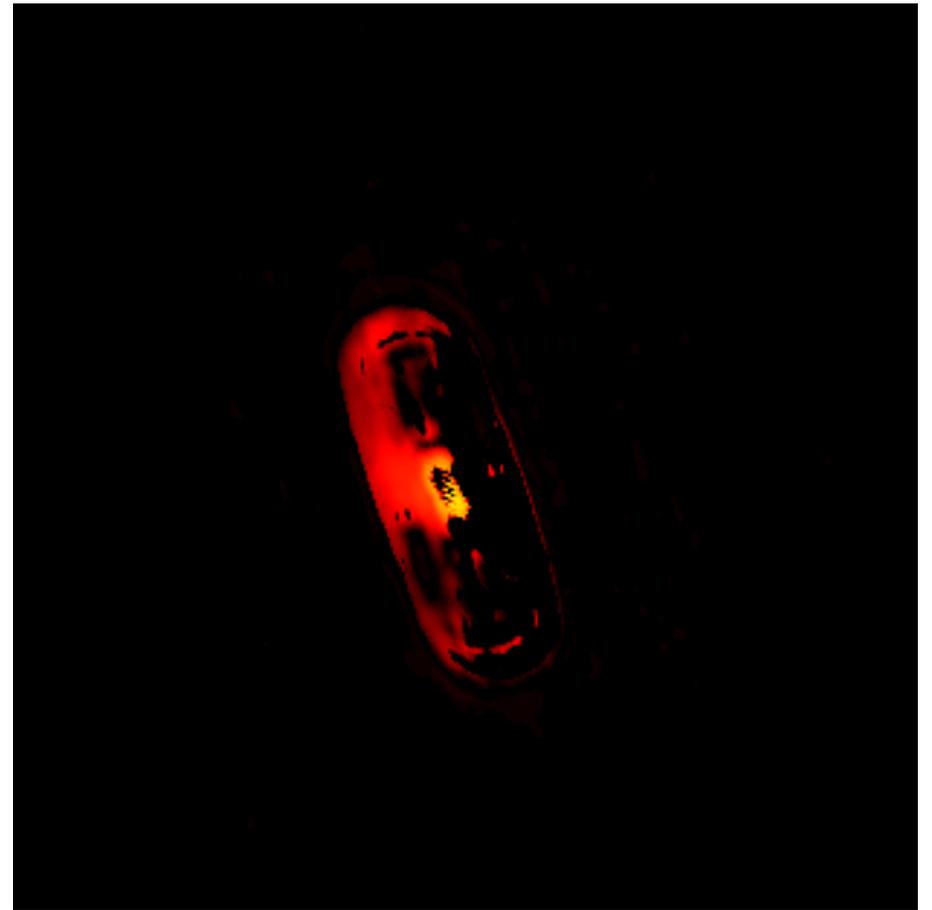
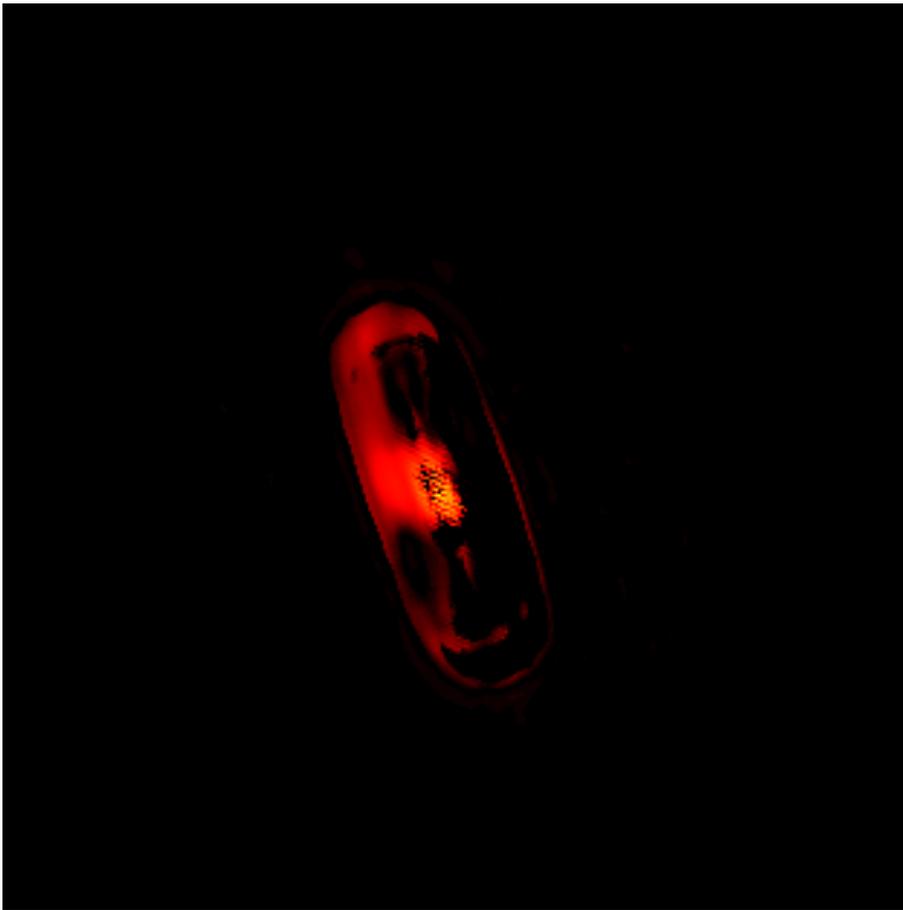
# Symmetrized Data and two best fits

Chisq=0.0005

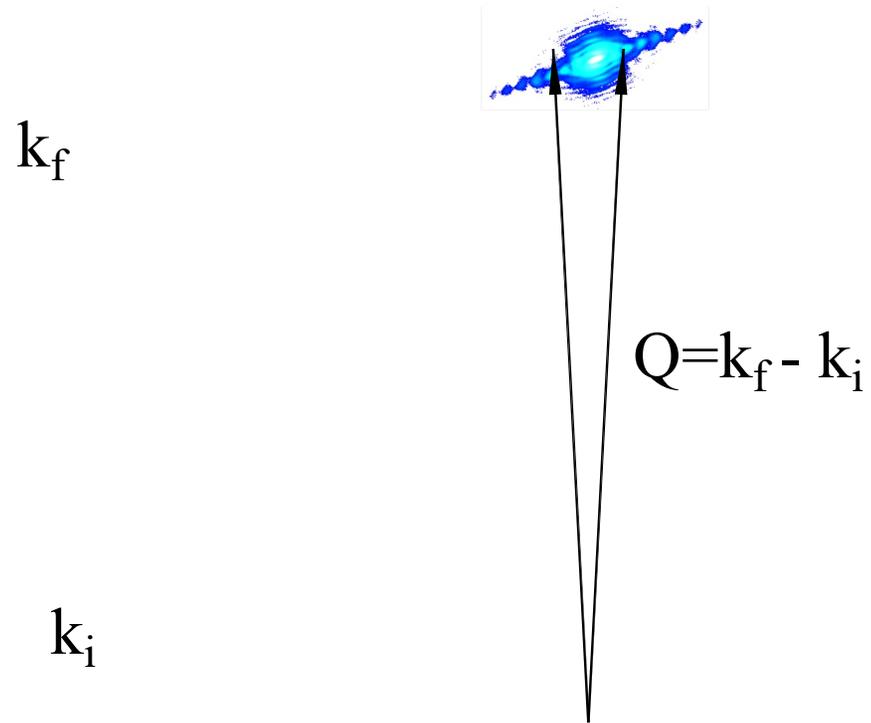


# 2D Reconstructions

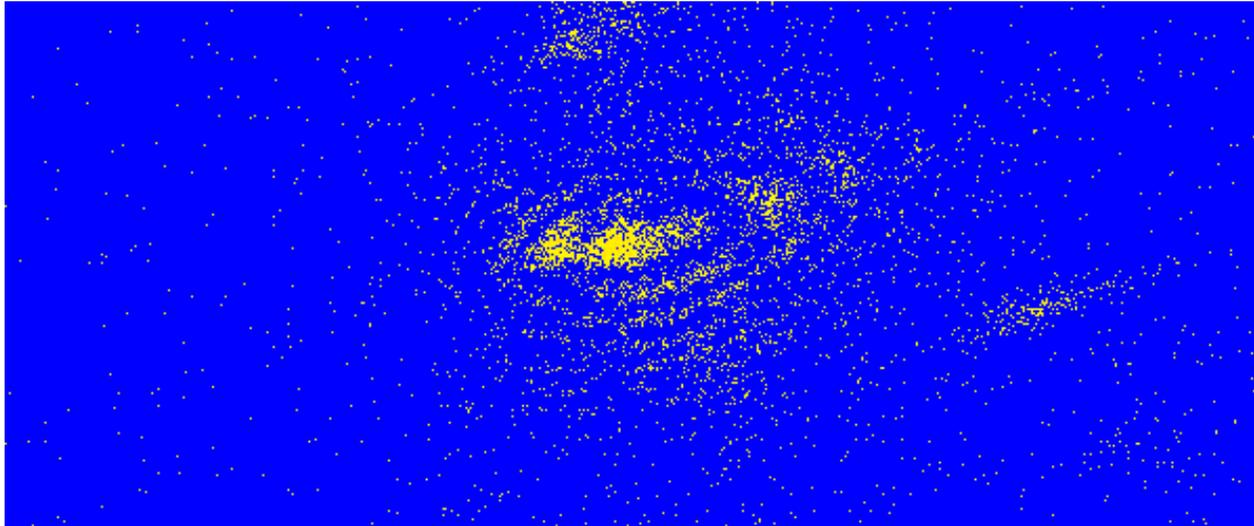
chisquare = 0.0005

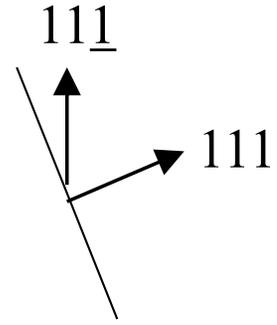
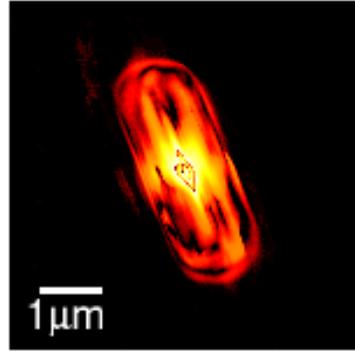
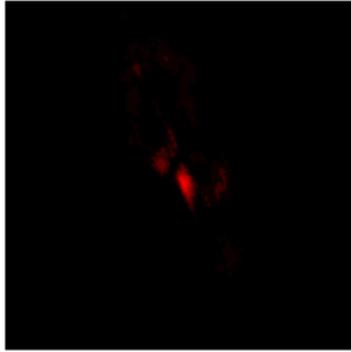


# 3D Diffraction Method

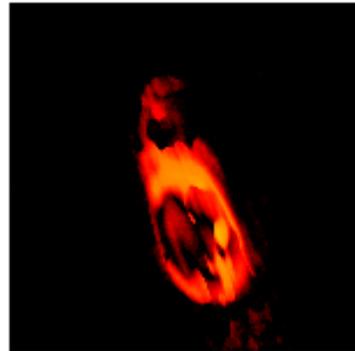
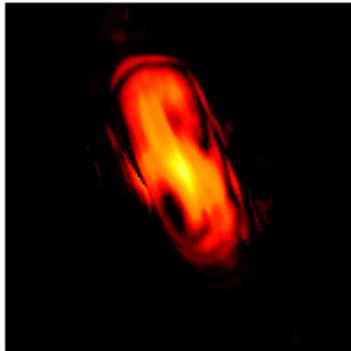
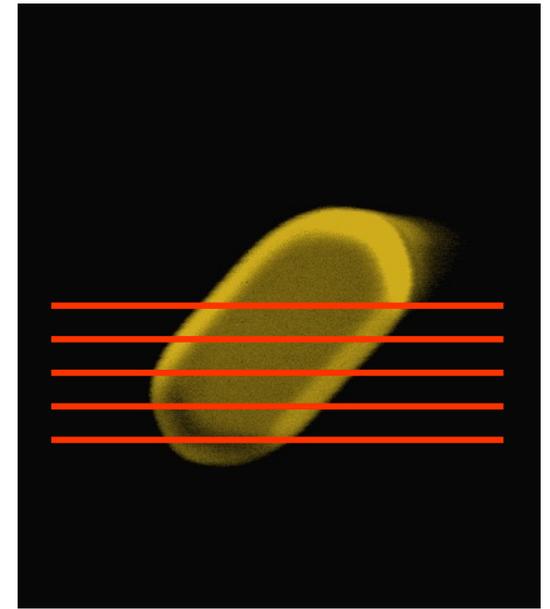
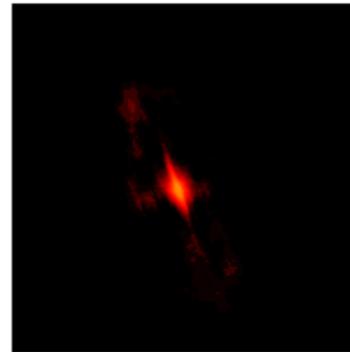
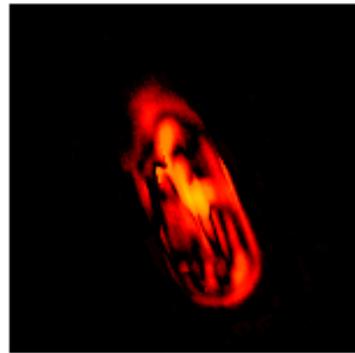
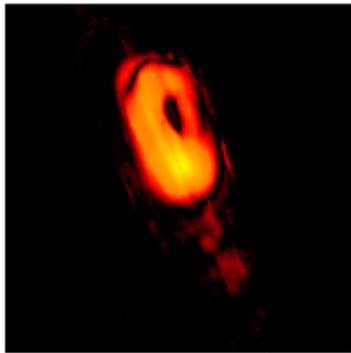
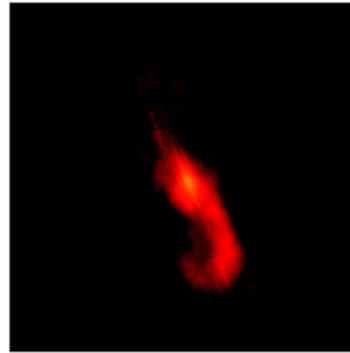
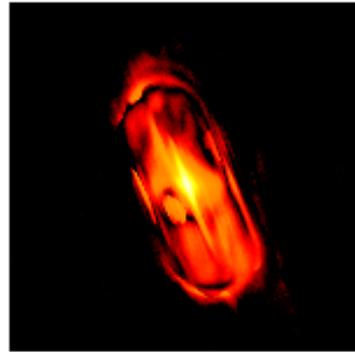
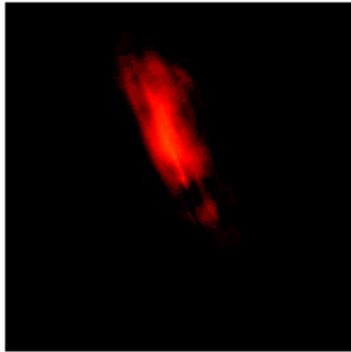


# 3D Diffraction Data 1 micron Au crystal



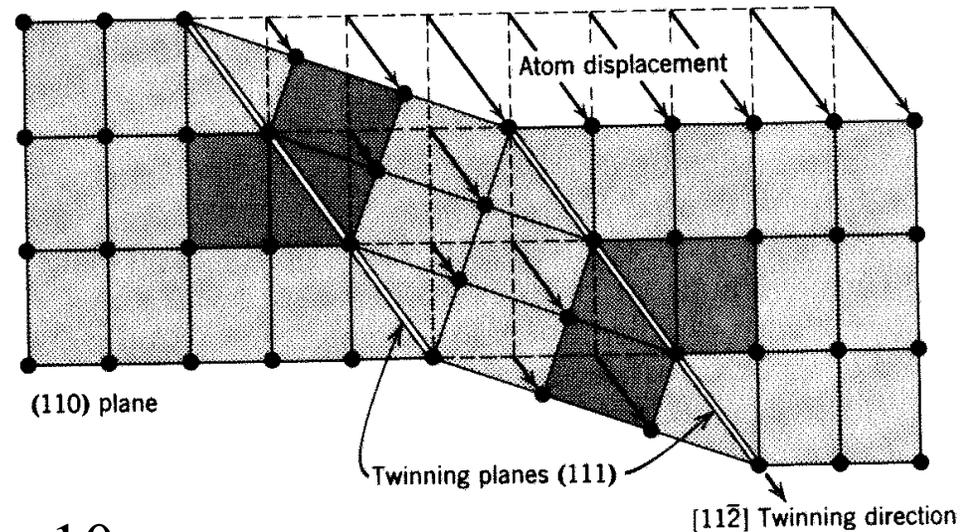


Slices through  
plan view SEM:

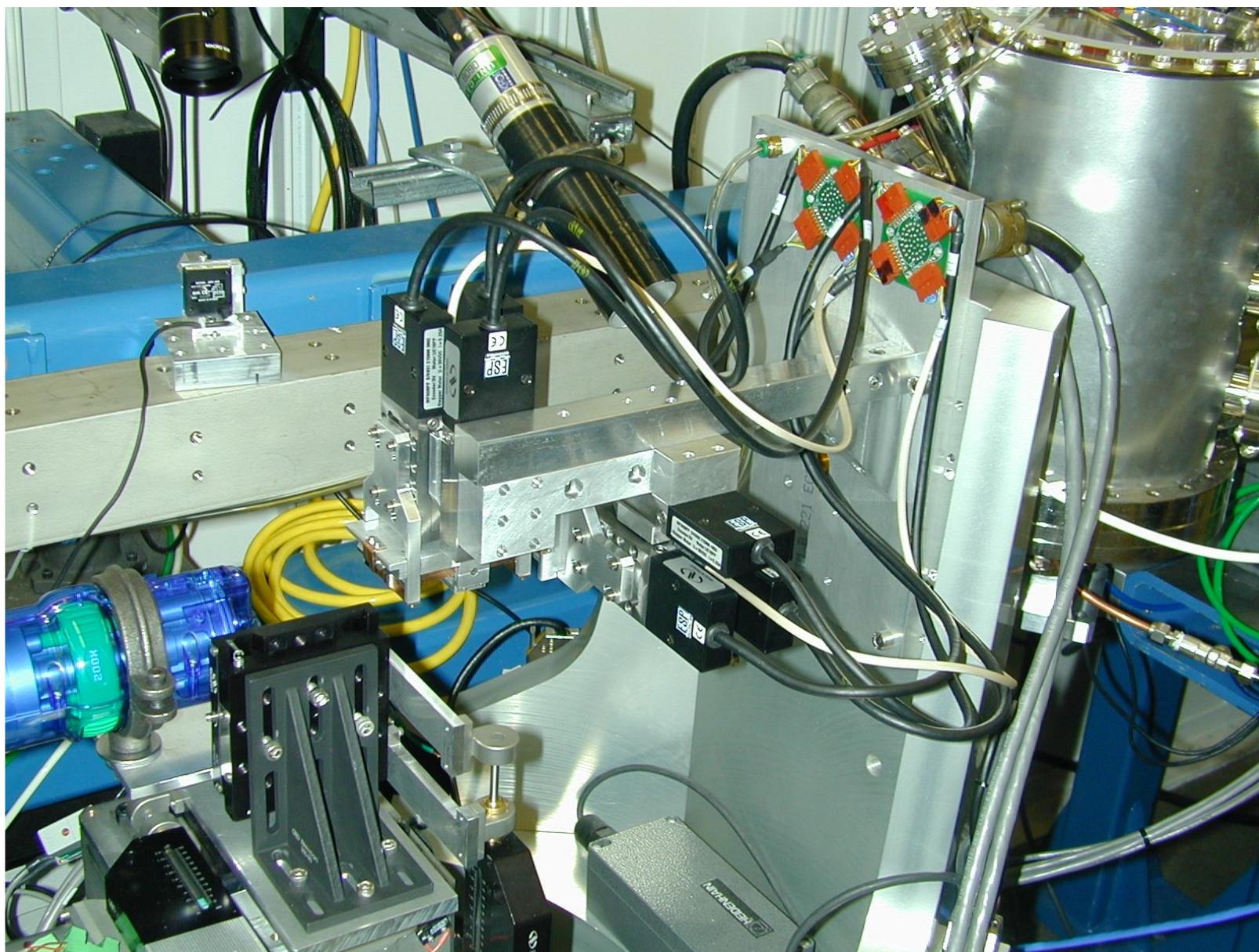


# Twinning in deformed FCC metals

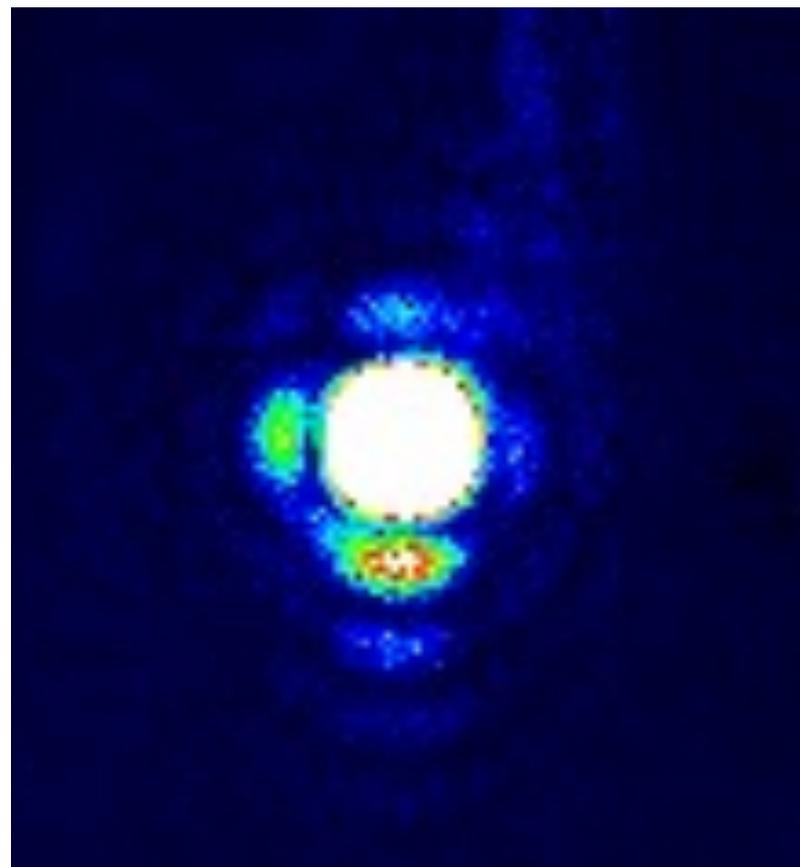
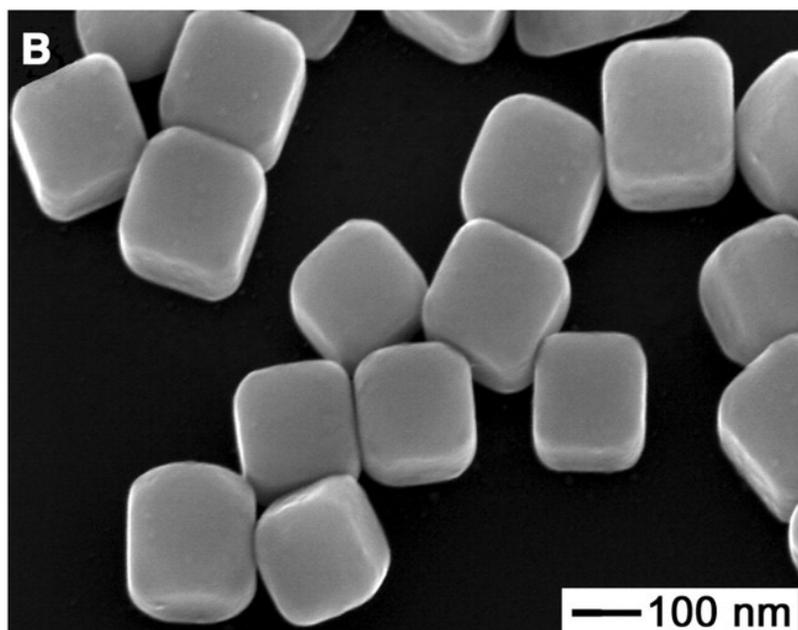
J. Wulff, "Structure and Property of Materials III" (1965)



■  $\sim 10\mu\text{m}$   
Cu

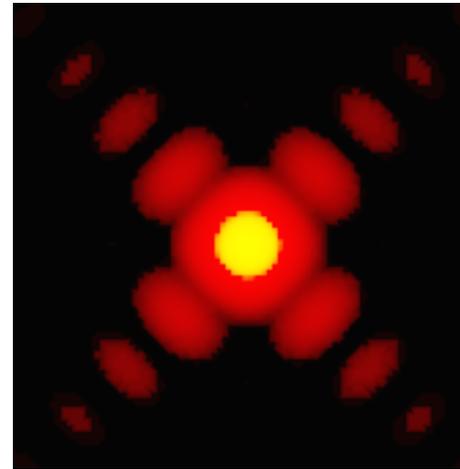
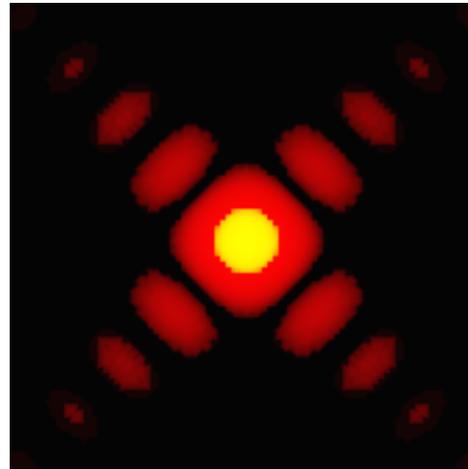


# Chemically Synthesized Silver Nanocubes



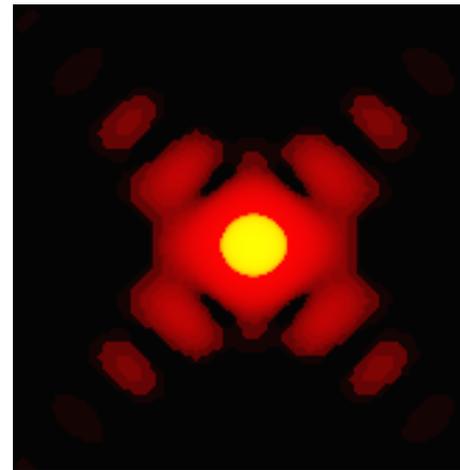
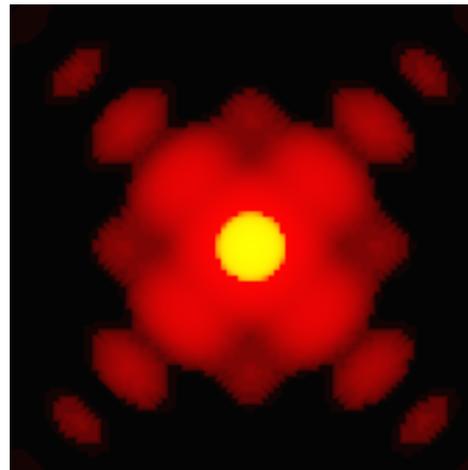
Yugang Sun and Younan Xia,  
*Science* 298 2177 (2003)

# Spherical and cylindrical waves



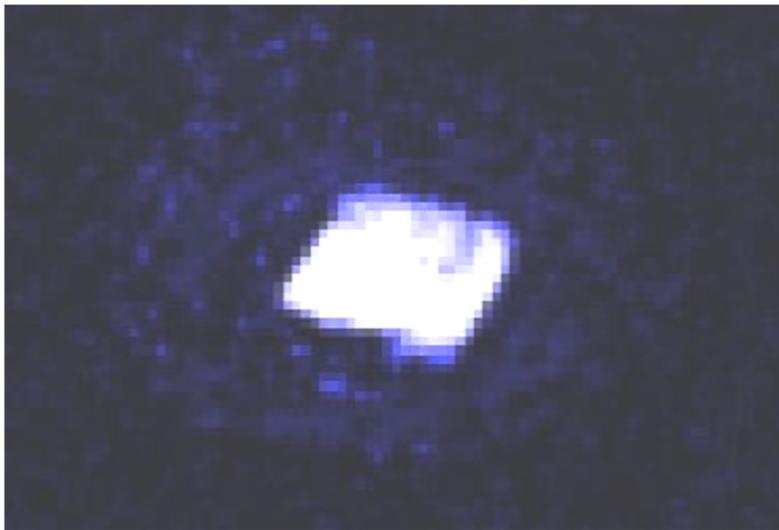
$\pi/4$

$\pi/2$

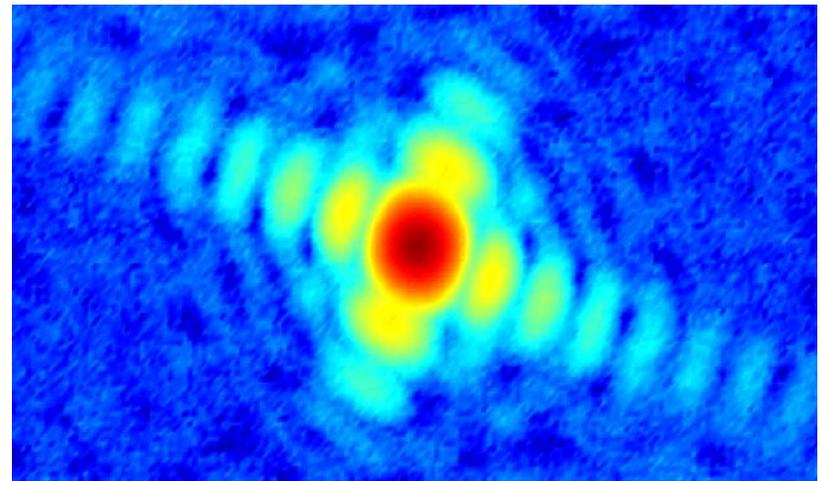
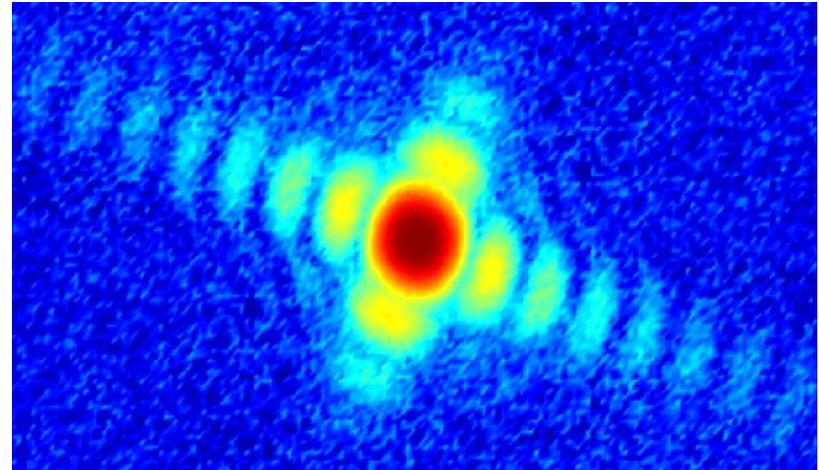


$\pi/4$  (x)

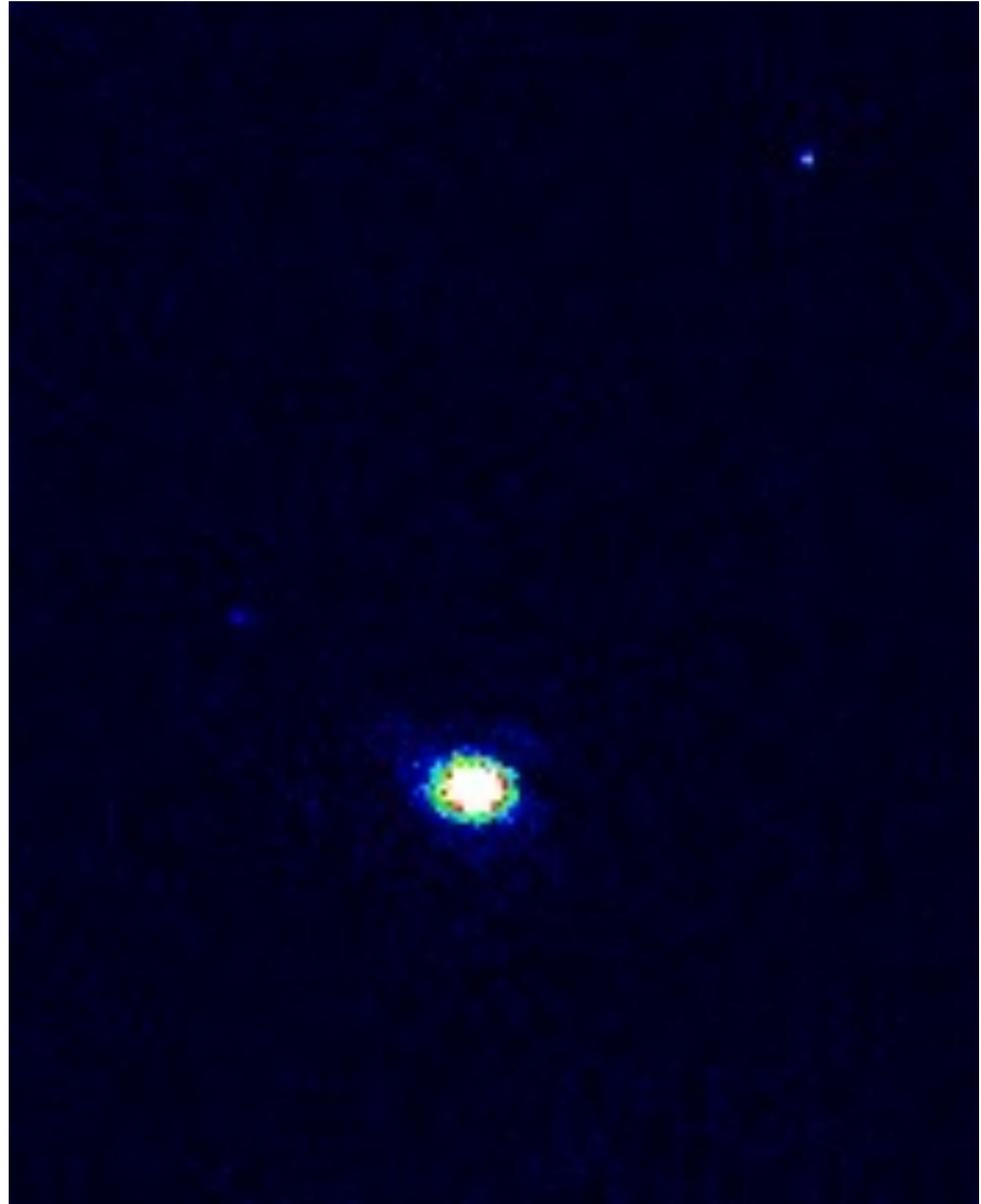
# Reconstruction of Ag Nanocrystal

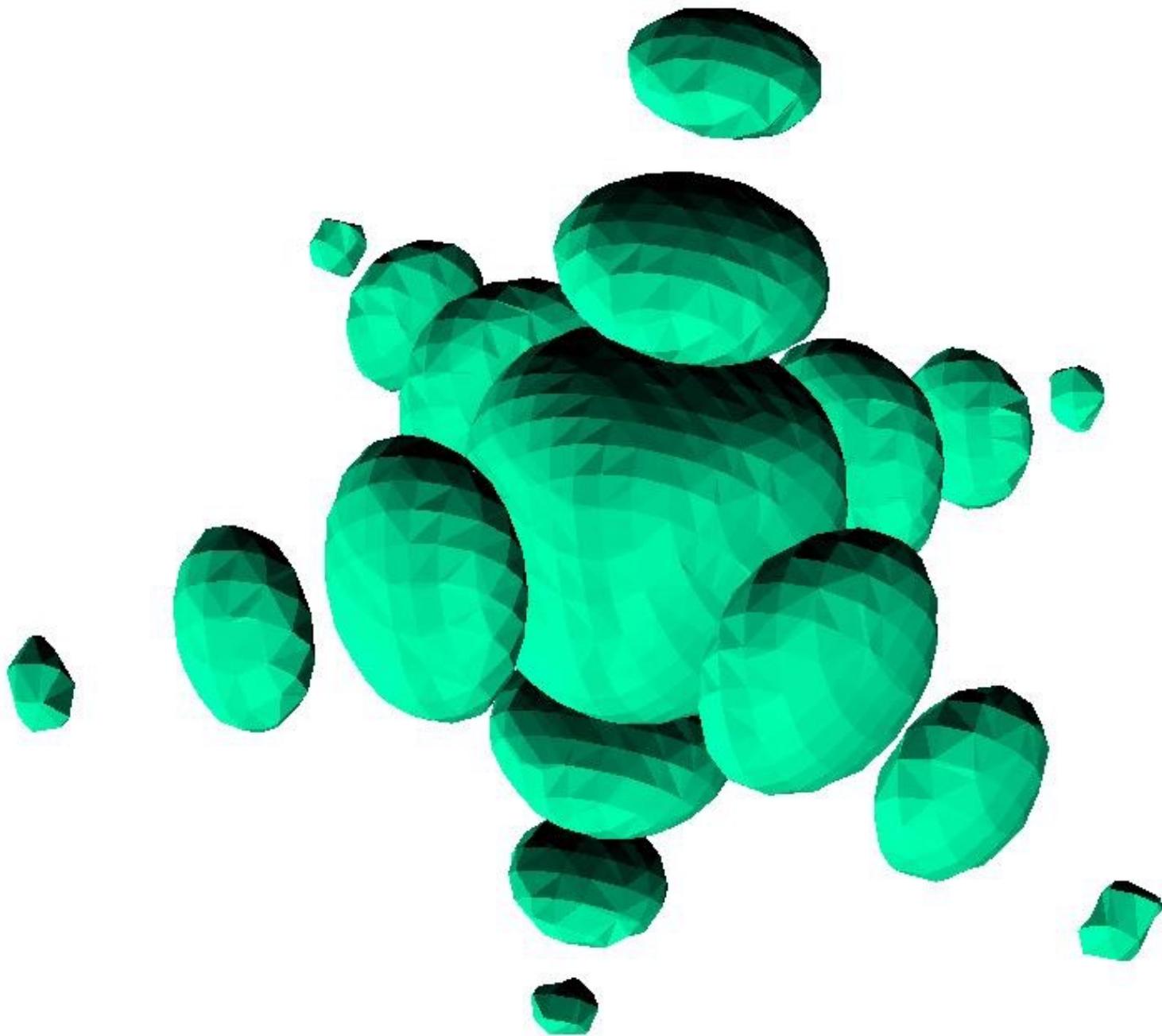


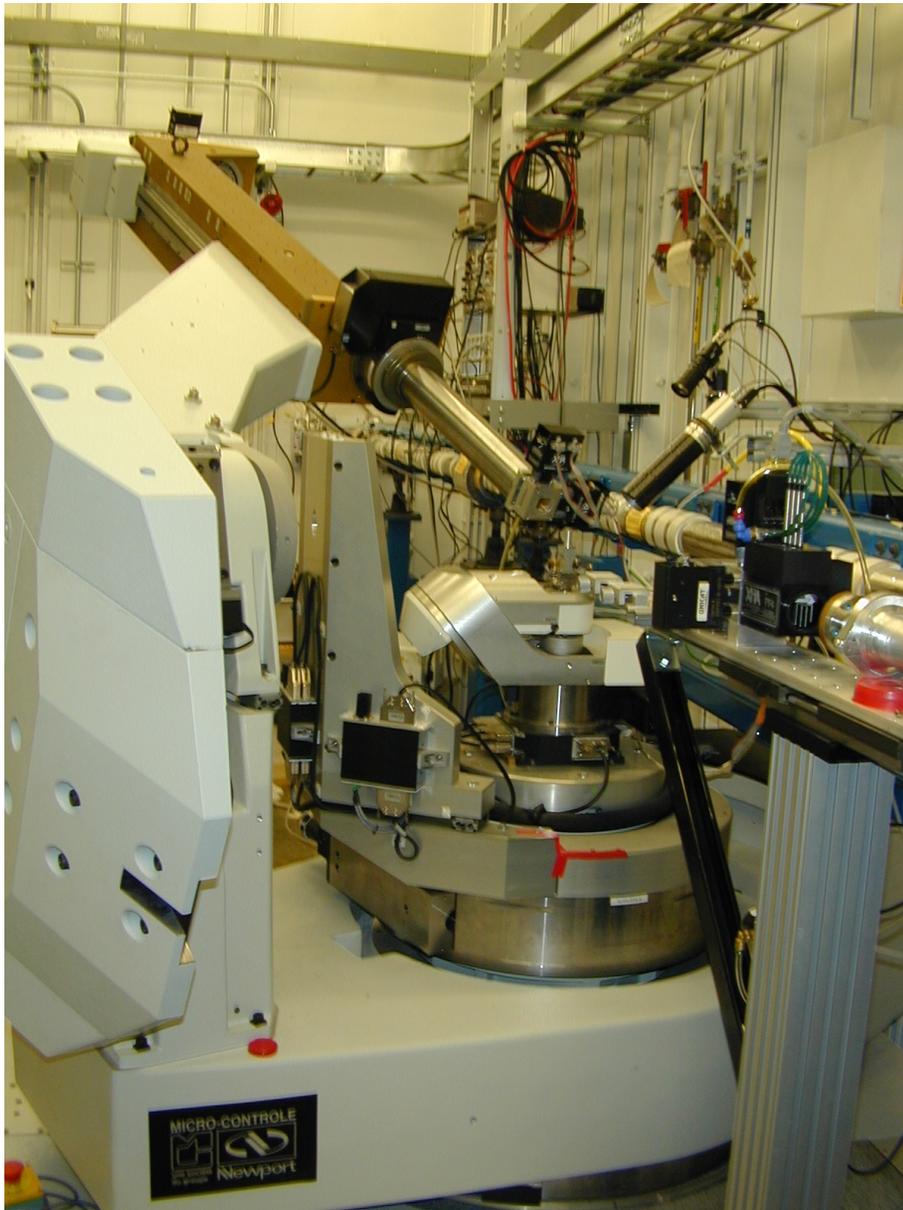
←→  
200nm

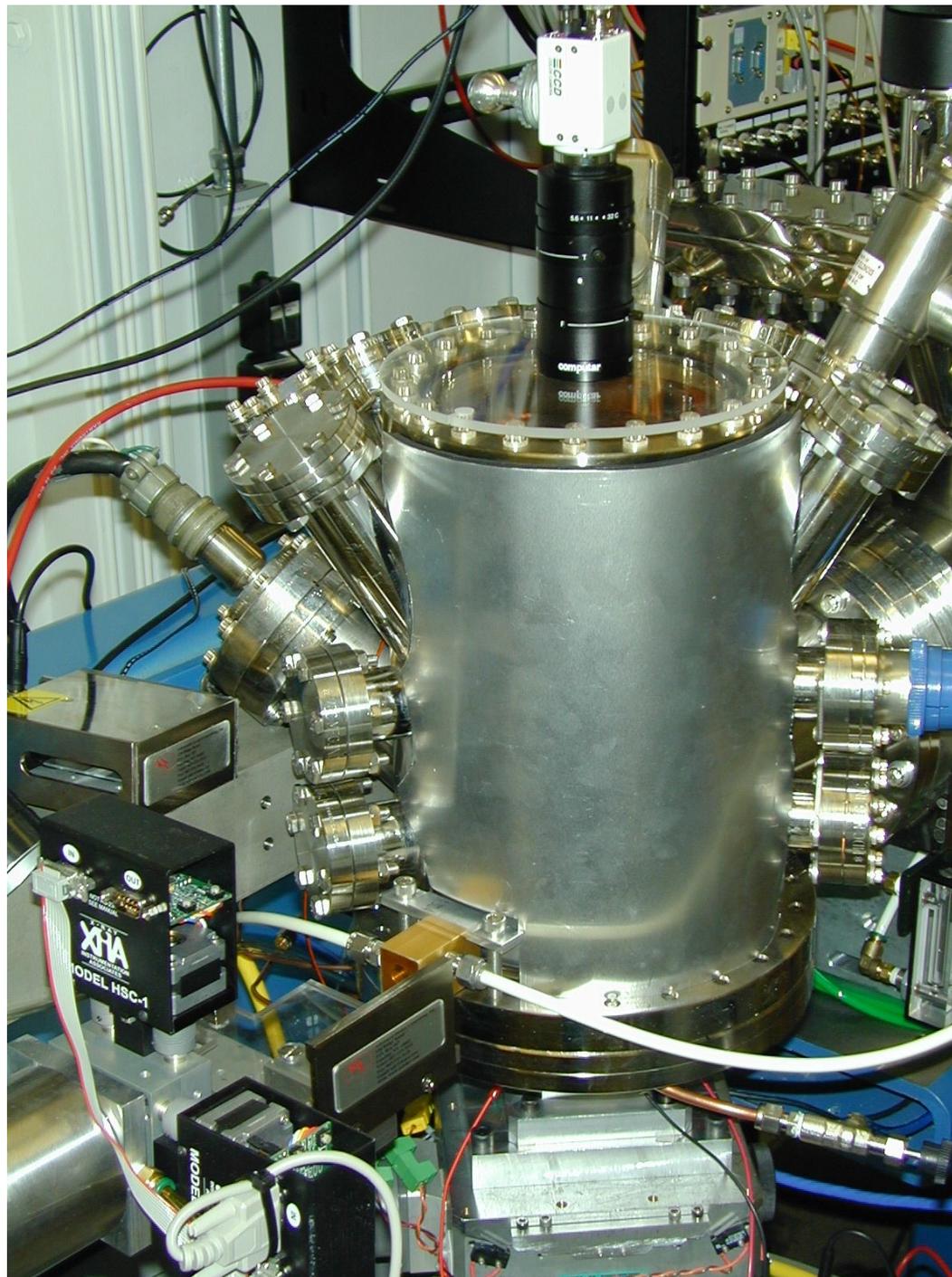


Rocking  
scan of Ag  
cubes with  
 $0.01^\circ$  steps

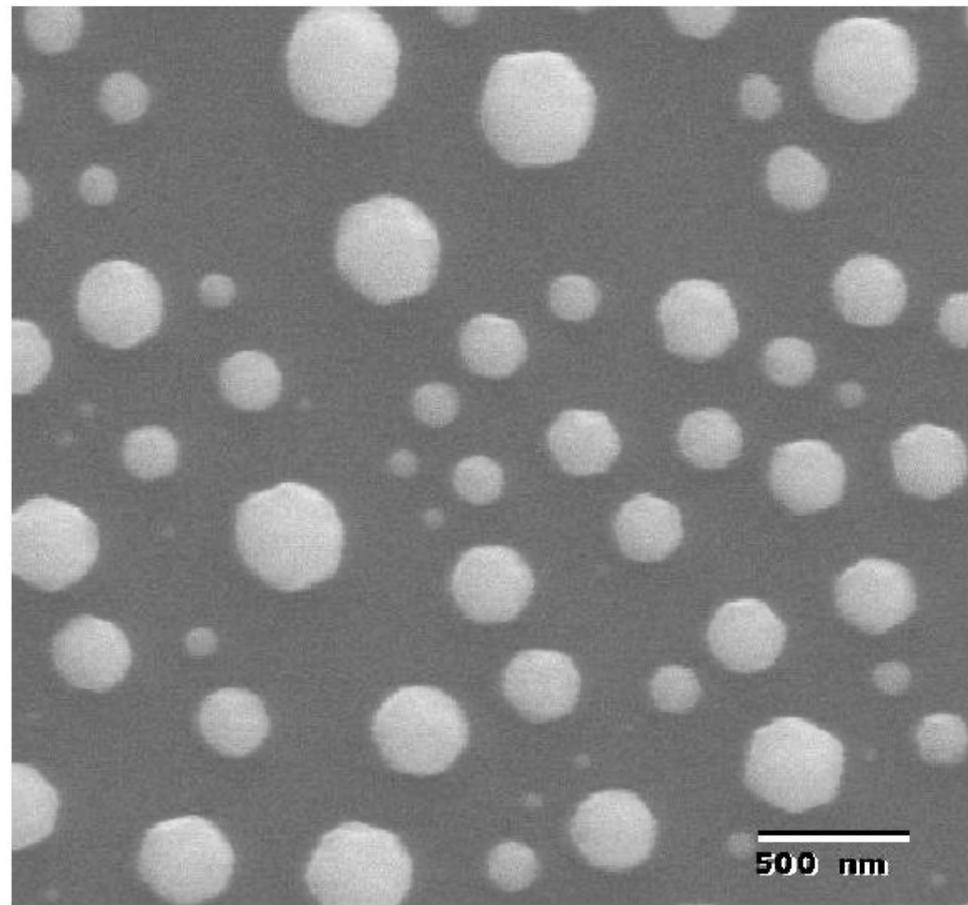
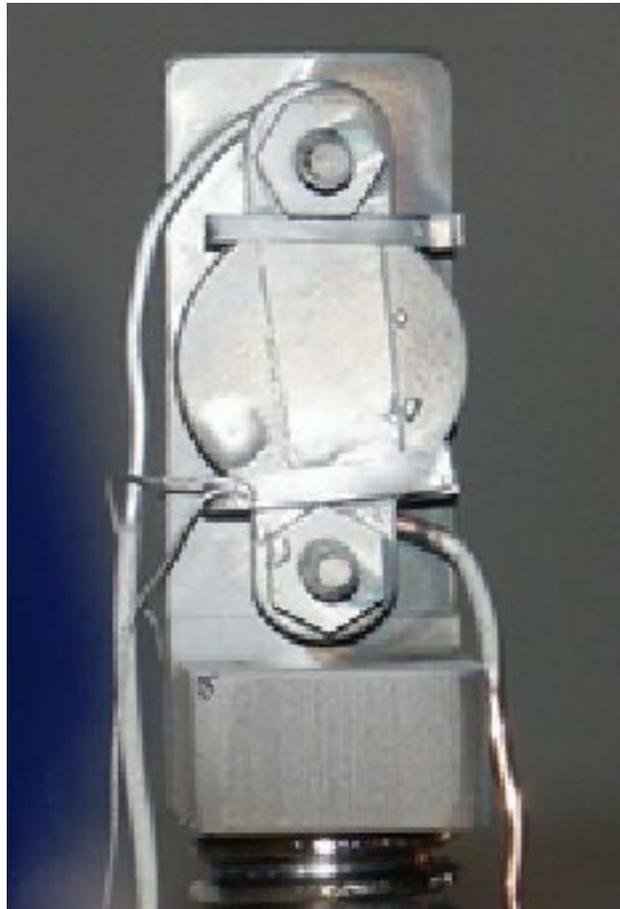




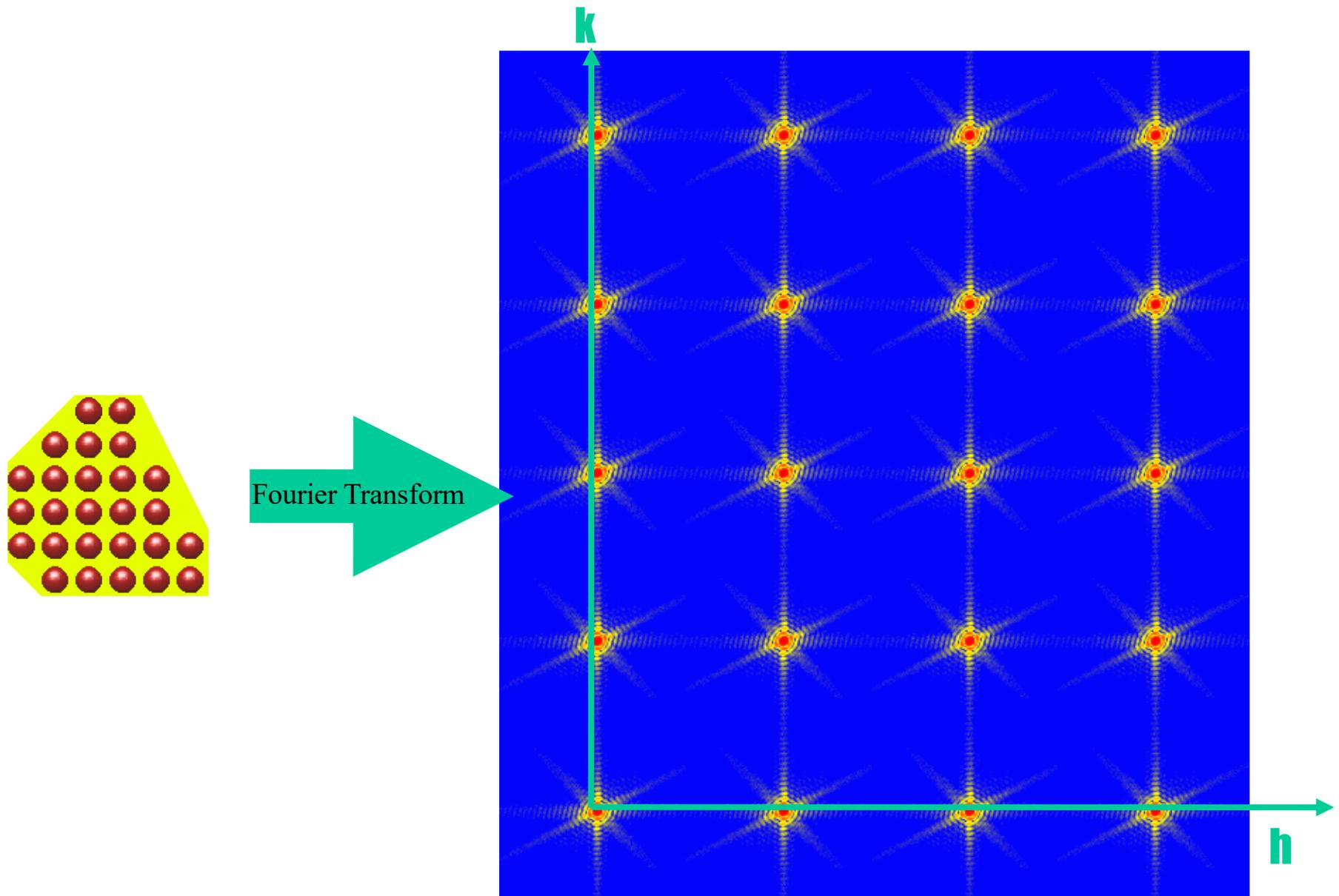




# In situ growth of Pb crystals



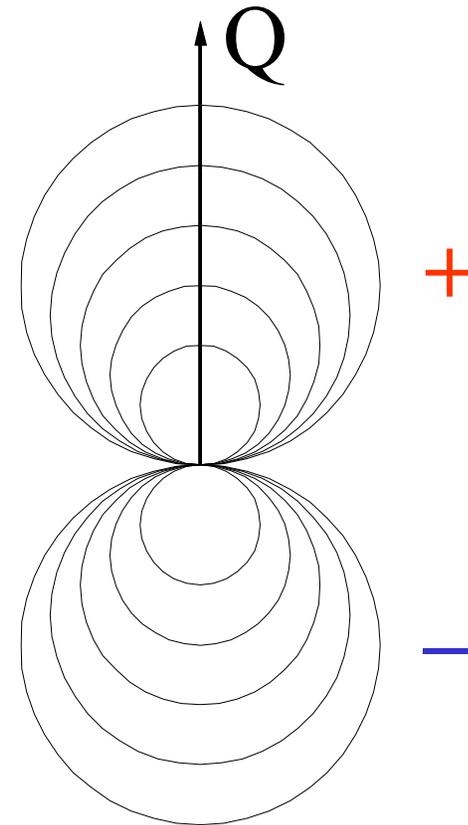
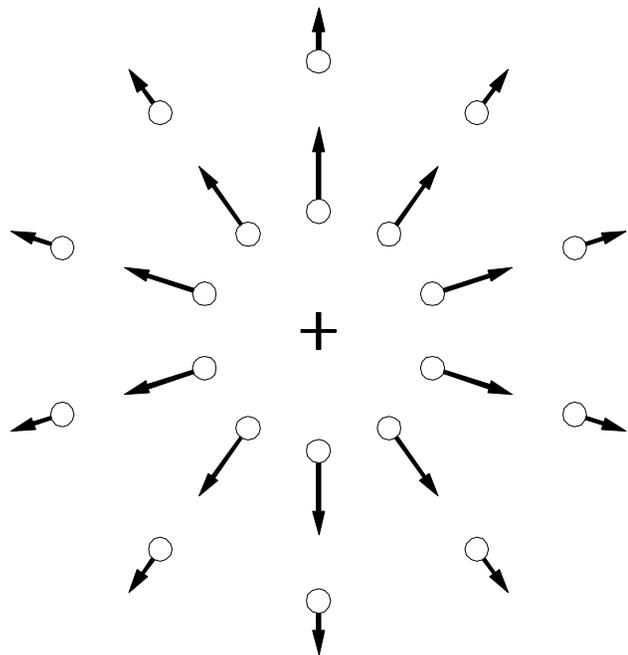
# Coherent Diffraction from Crystals



# Diffraction by Strain of Point Defect

$$A \sim \sum e^{i\mathbf{Q}\cdot(\mathbf{R}_j+\mathbf{u}_j)}$$
$$\approx \sum e^{i\mathbf{Q}\cdot\mathbf{R}_j} (1+i\mathbf{Q}\cdot\mathbf{u}_j)$$

Imaginary density



# Good statistics, 3D diffraction data

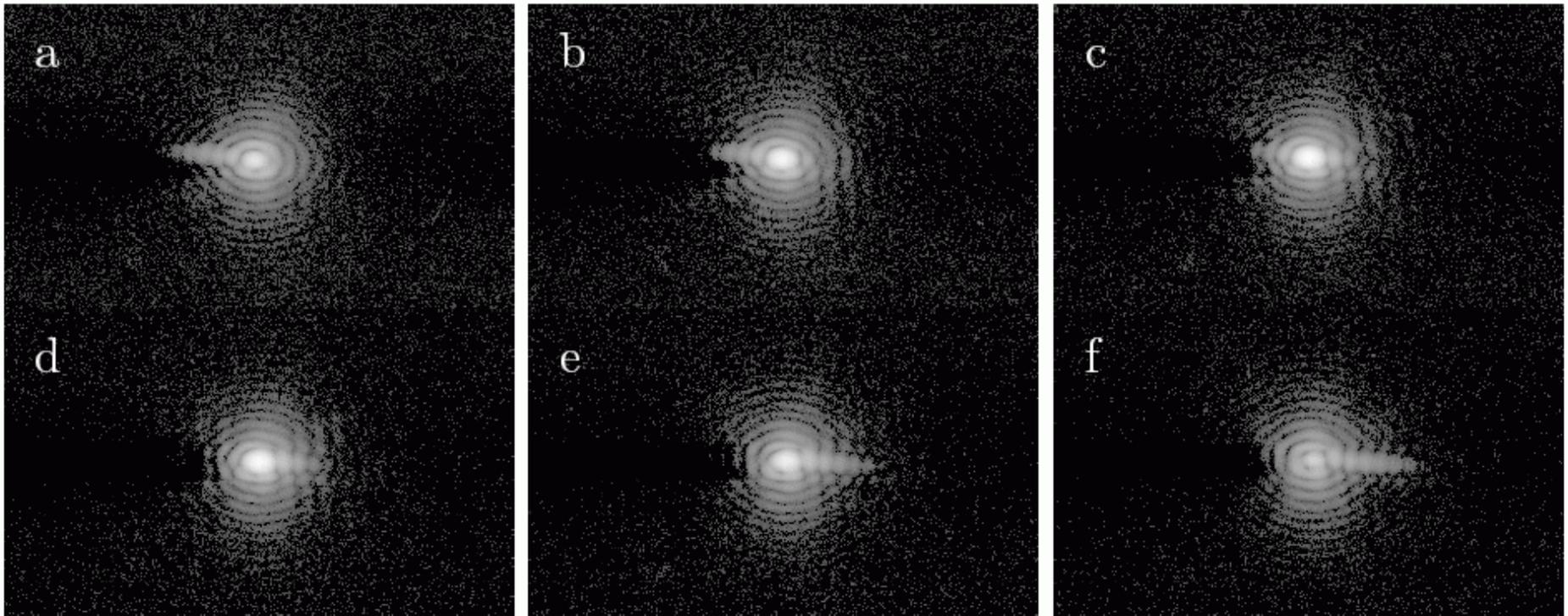
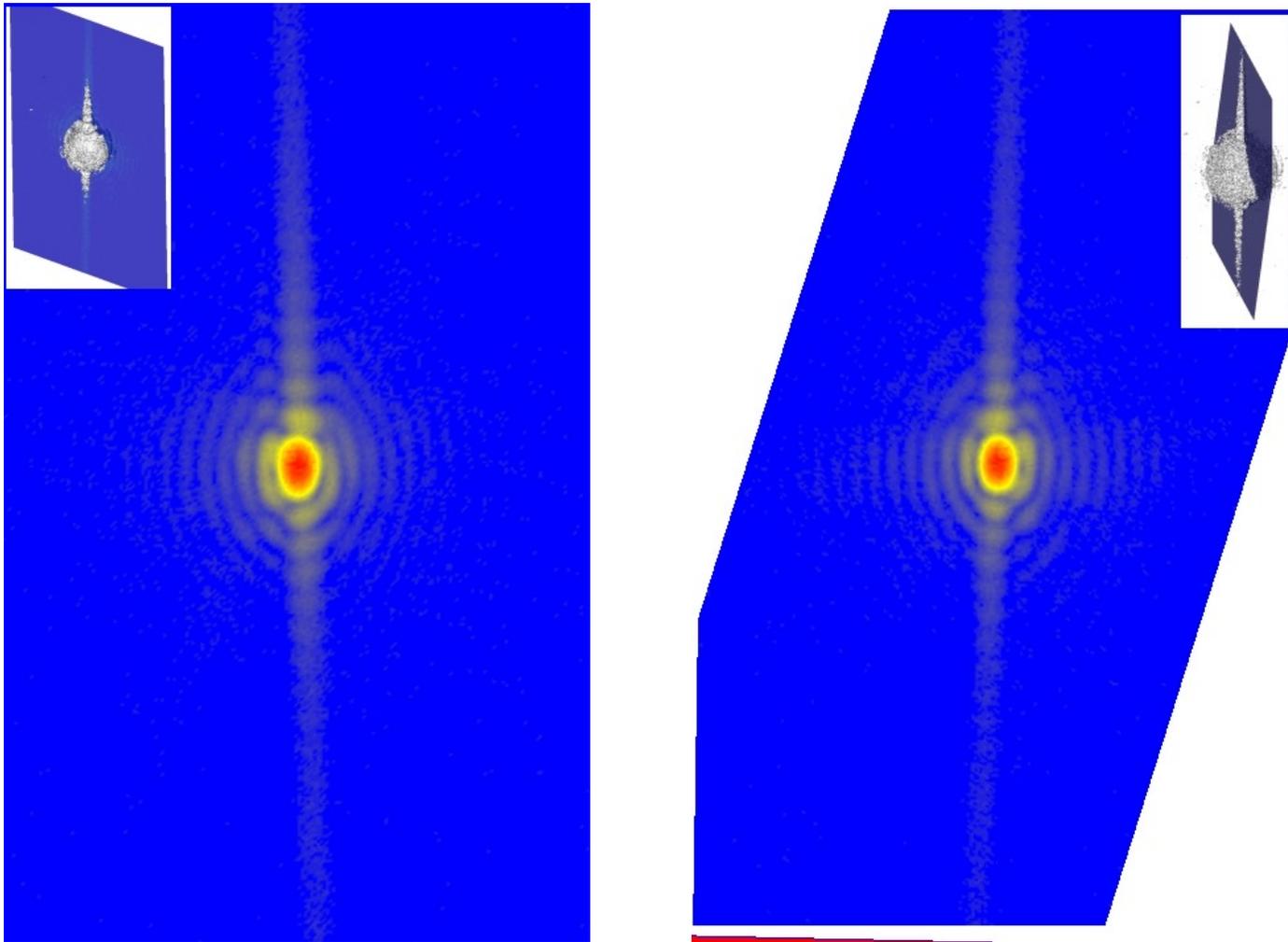
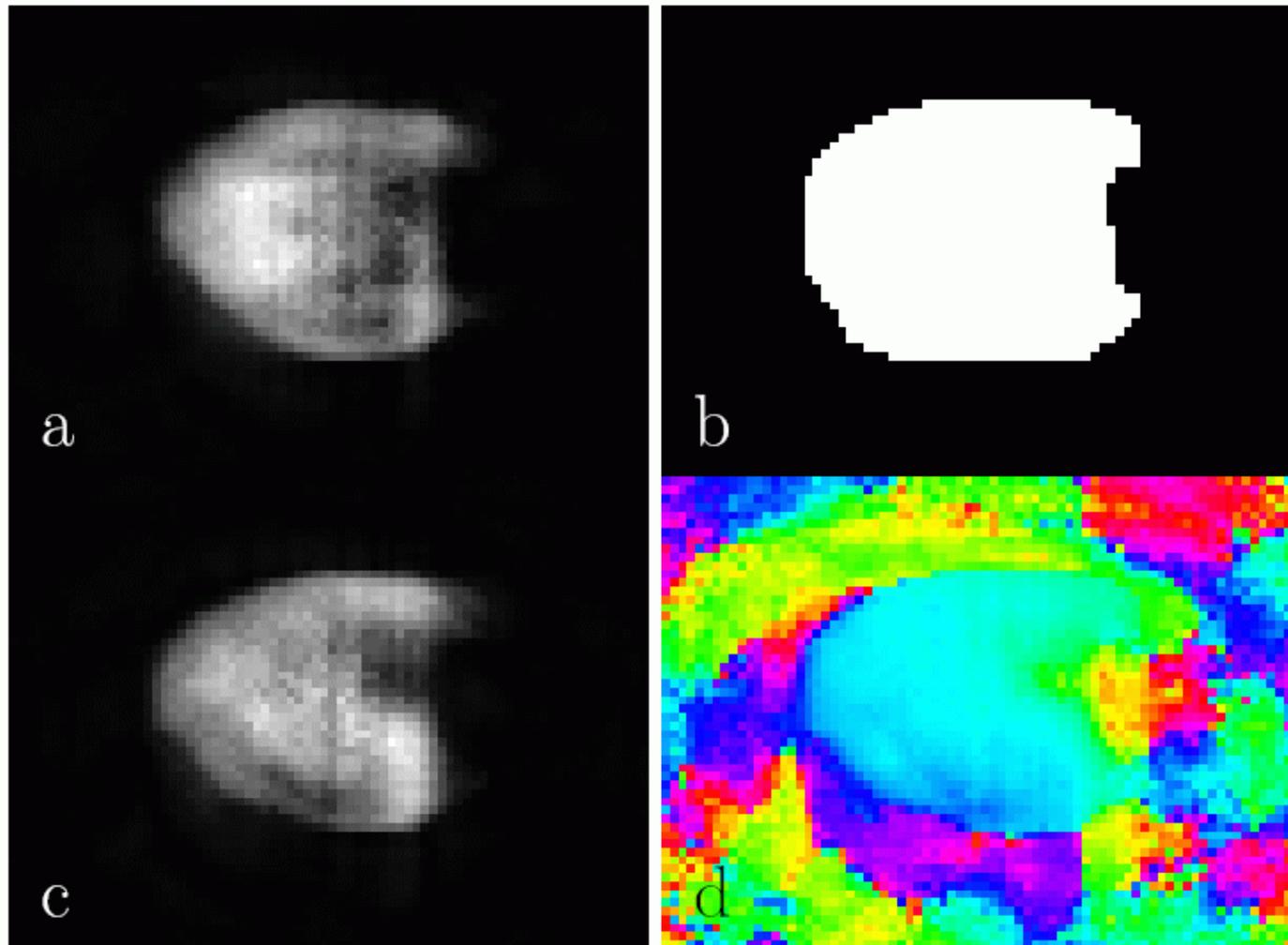


Figure 4.12: Center slices from 3D CXD pattern from Pb sample, on a log scale. Data file 296 from 10/03.

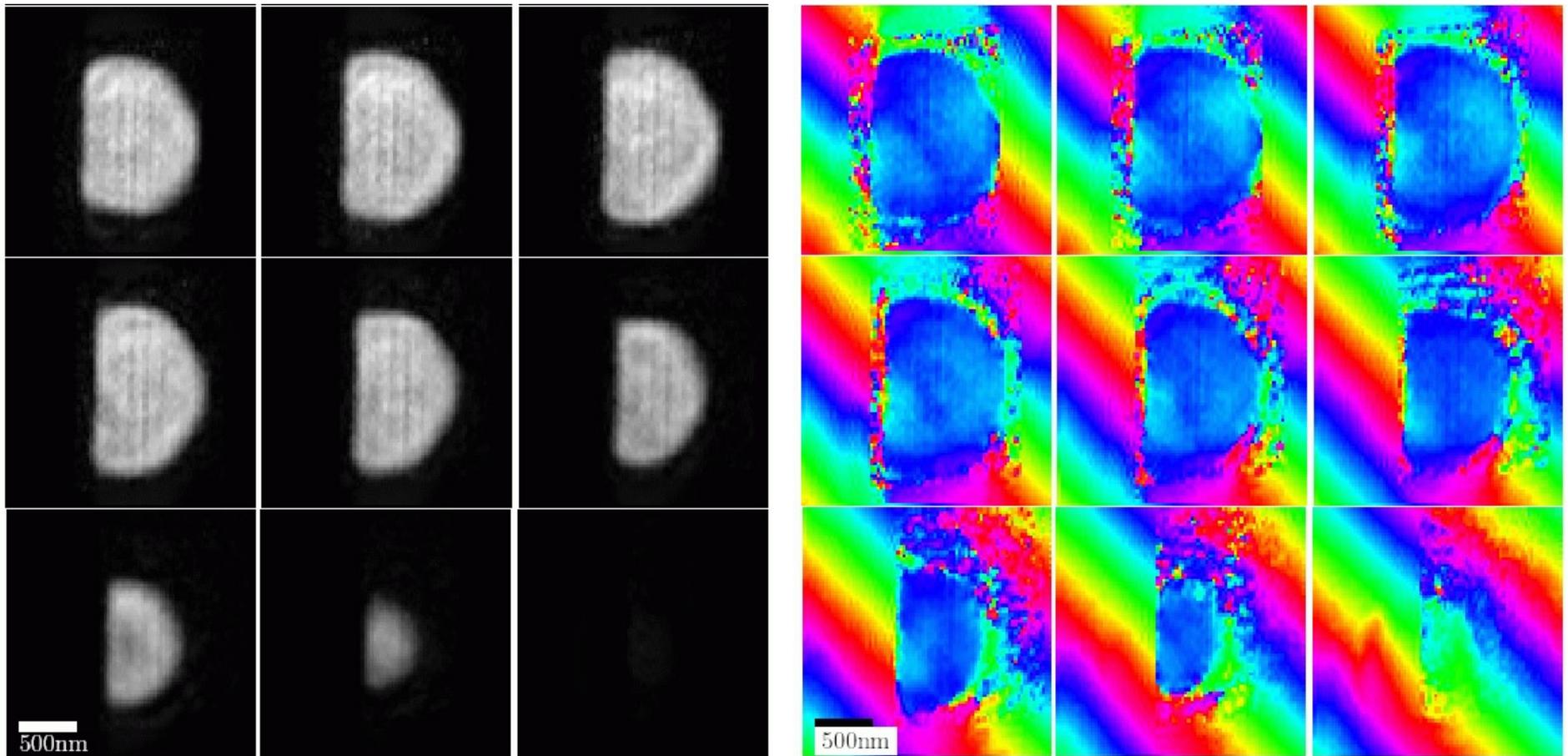
# 3D data along special directions

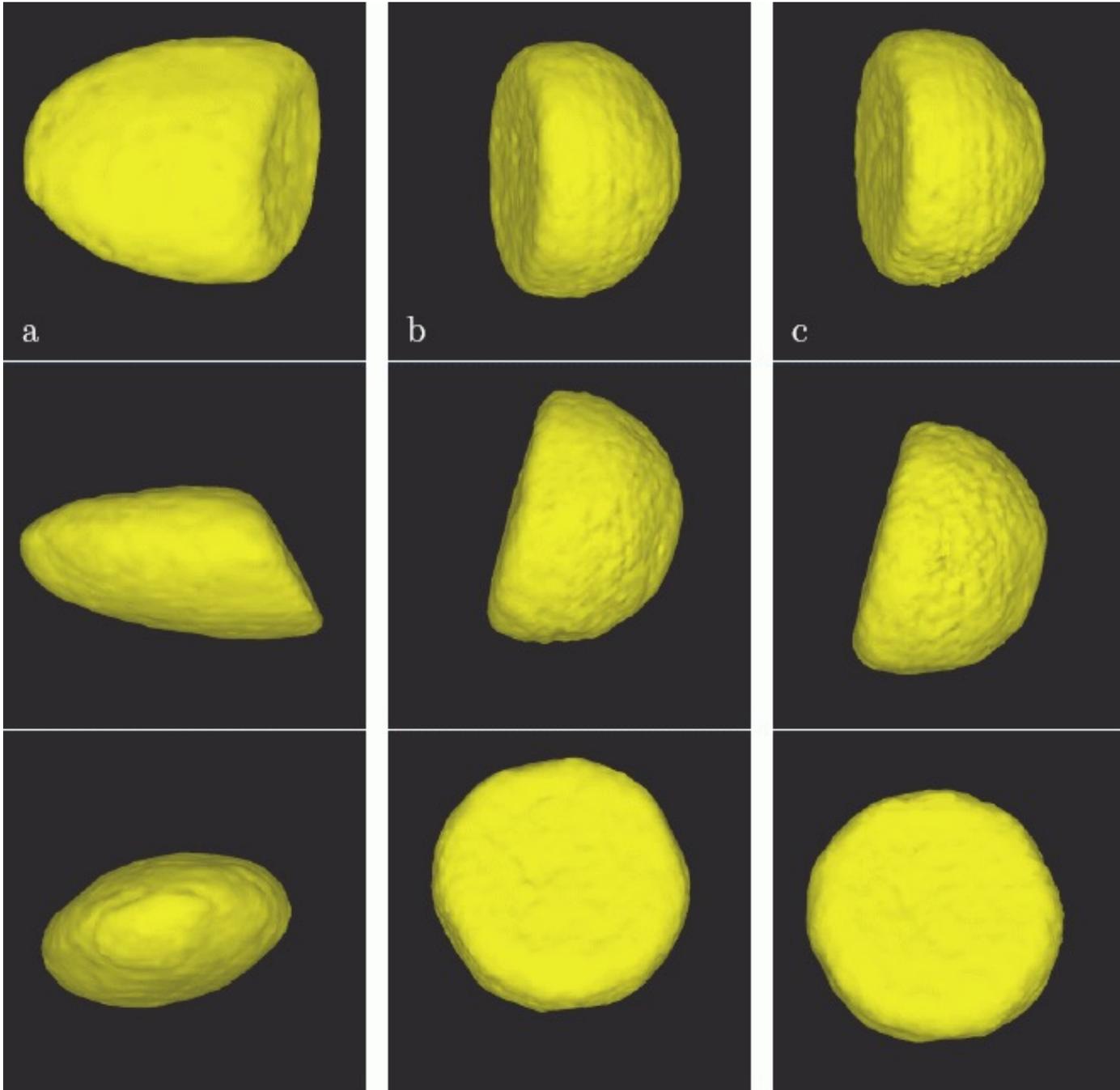


# Learn shape of “tight” support

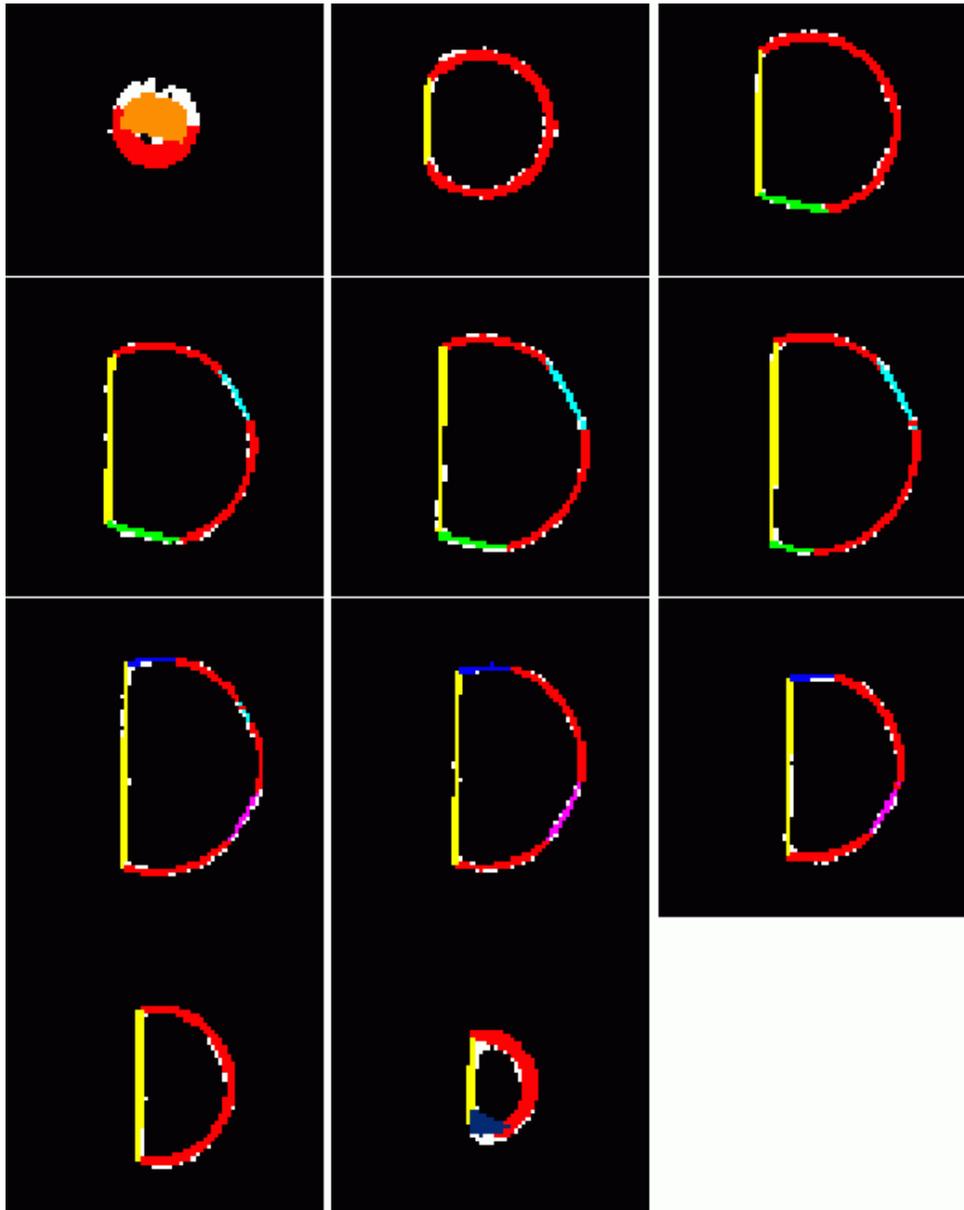


# Then refine amplitude *and* phase



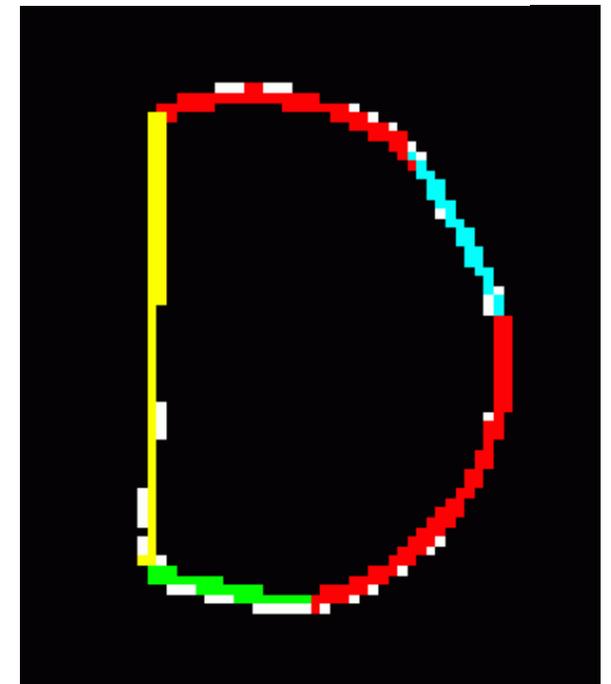


# Fitting to faceted shape



	$ R $		P0	P1	P2	P3	P4	P5	P6
	9.4	P0	0	85	149	79	134	106	71
	25.7	P1		0	123	164	83	76	102
	25.1	P2			0	72	67	74	110
	25.9	P3				0	111	106	76
	25.4	P4					0	113	68
	25.4	P5						0	176
	26.0	P6							0 0

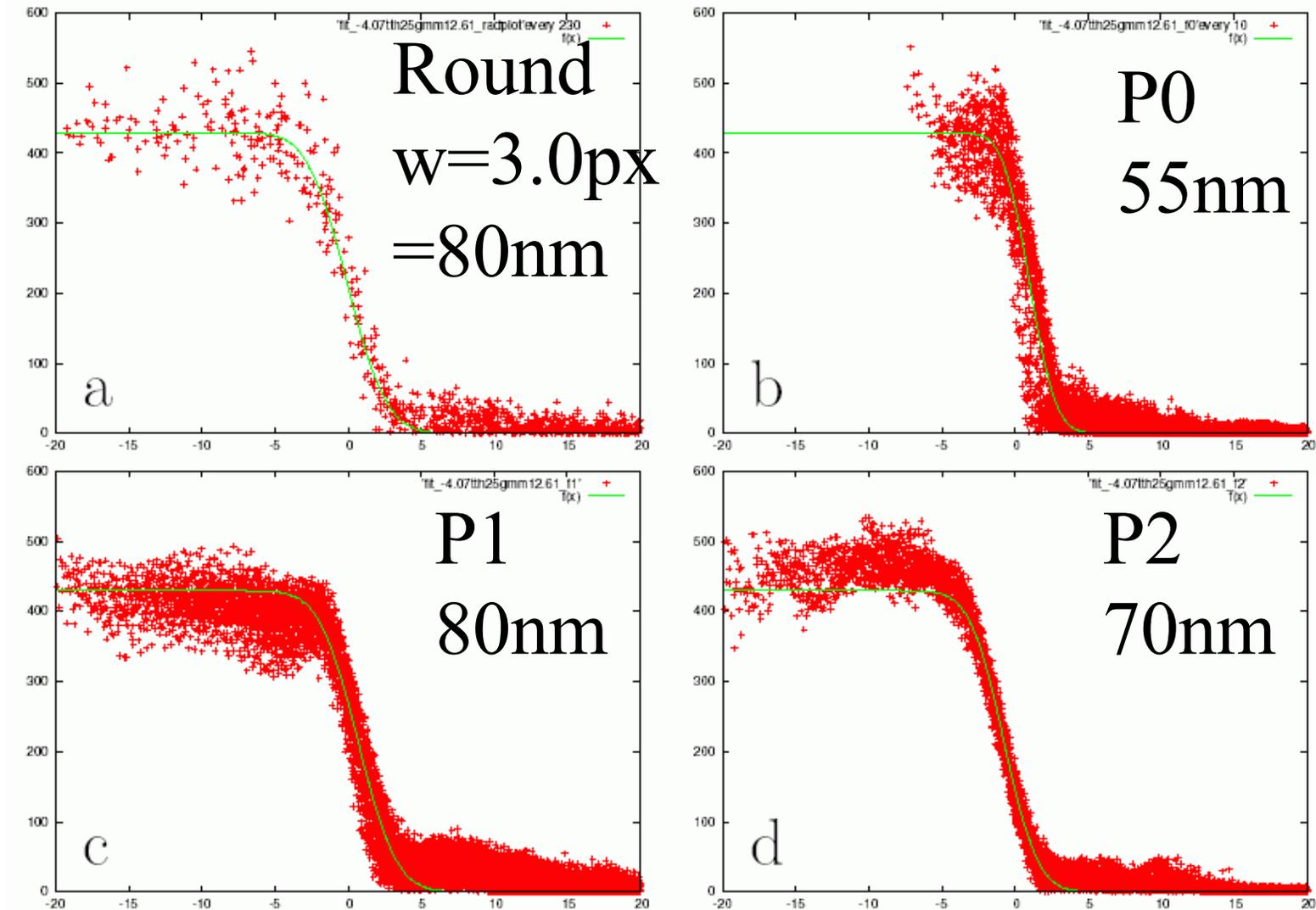
Angles between facets



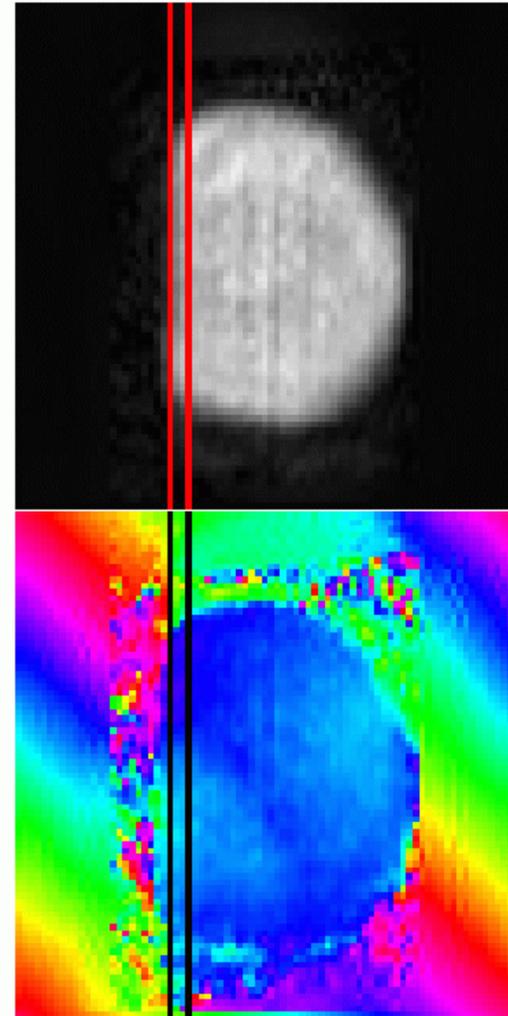
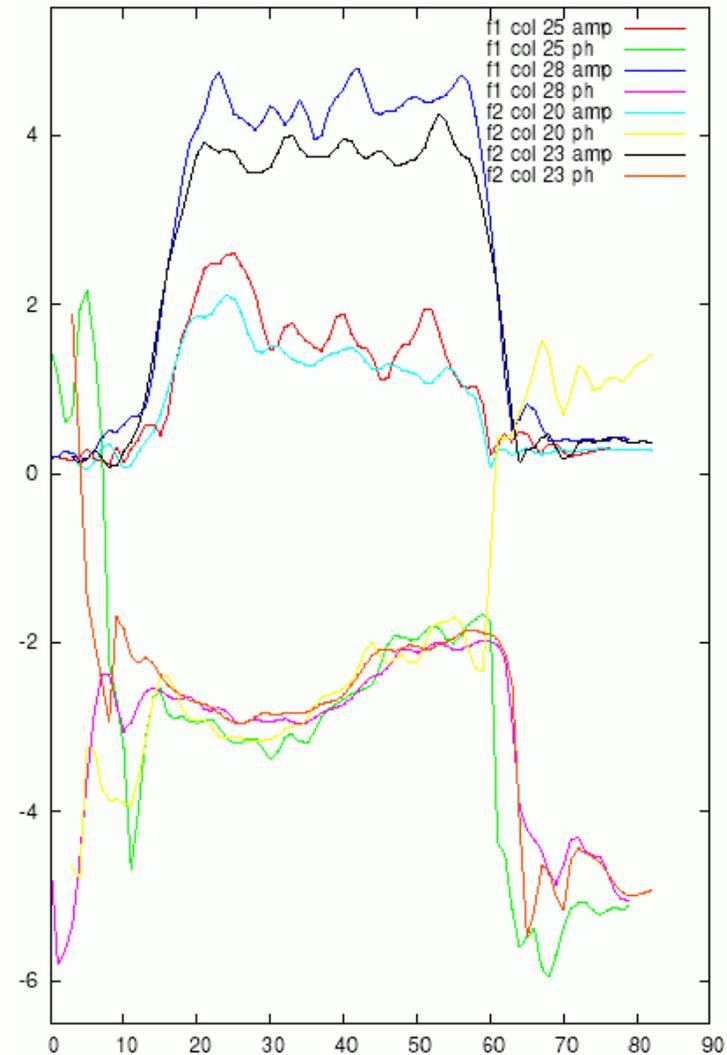
# Facets of Equilibrium Crystal Shape



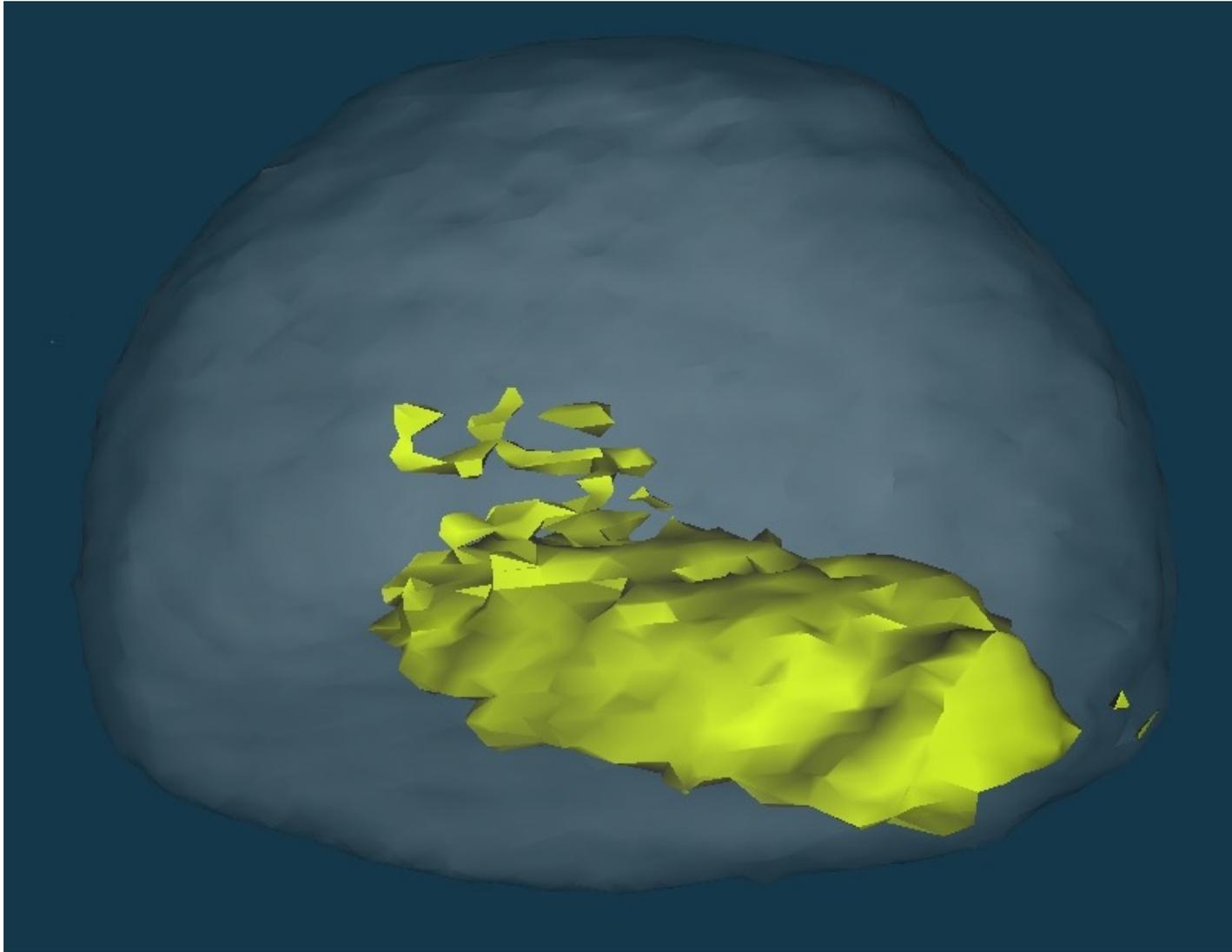
# Density distribution across surface



# Phase structure near substrate interface

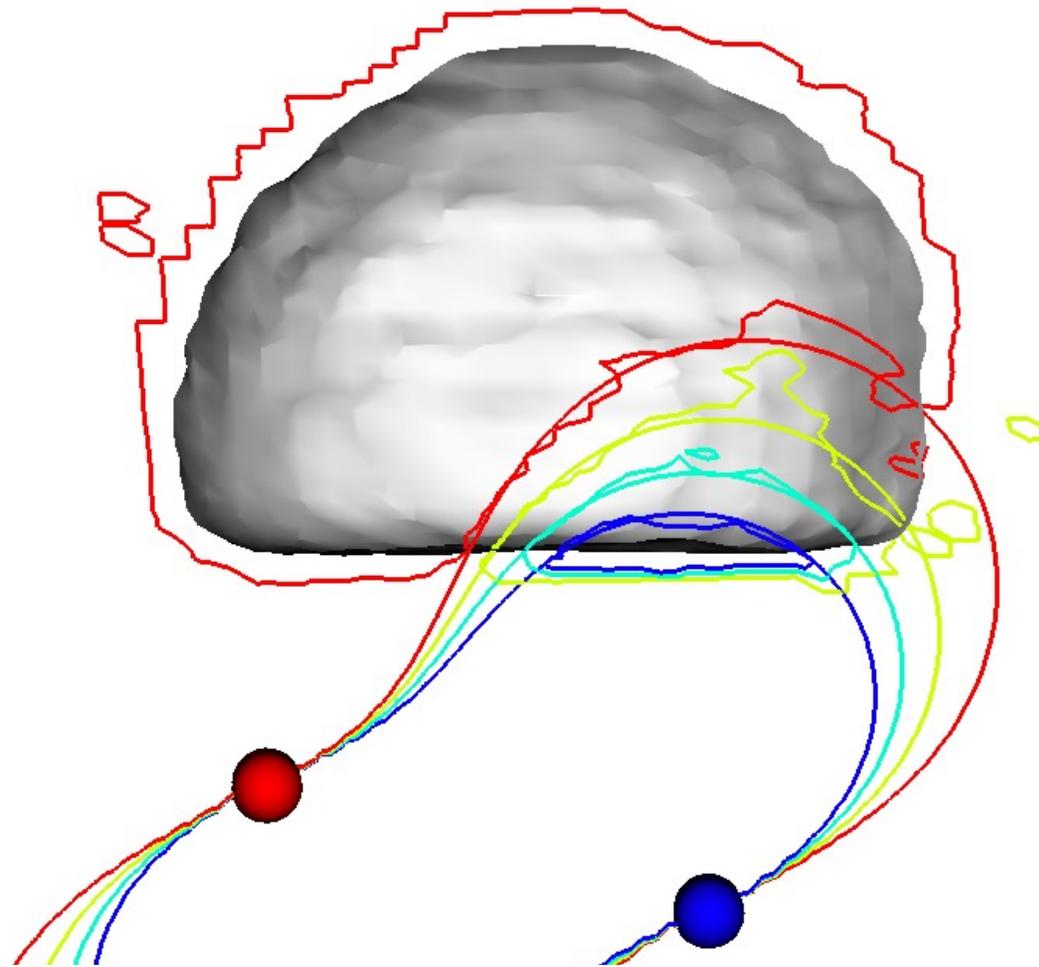


# Modeling of 3D Phase Bump



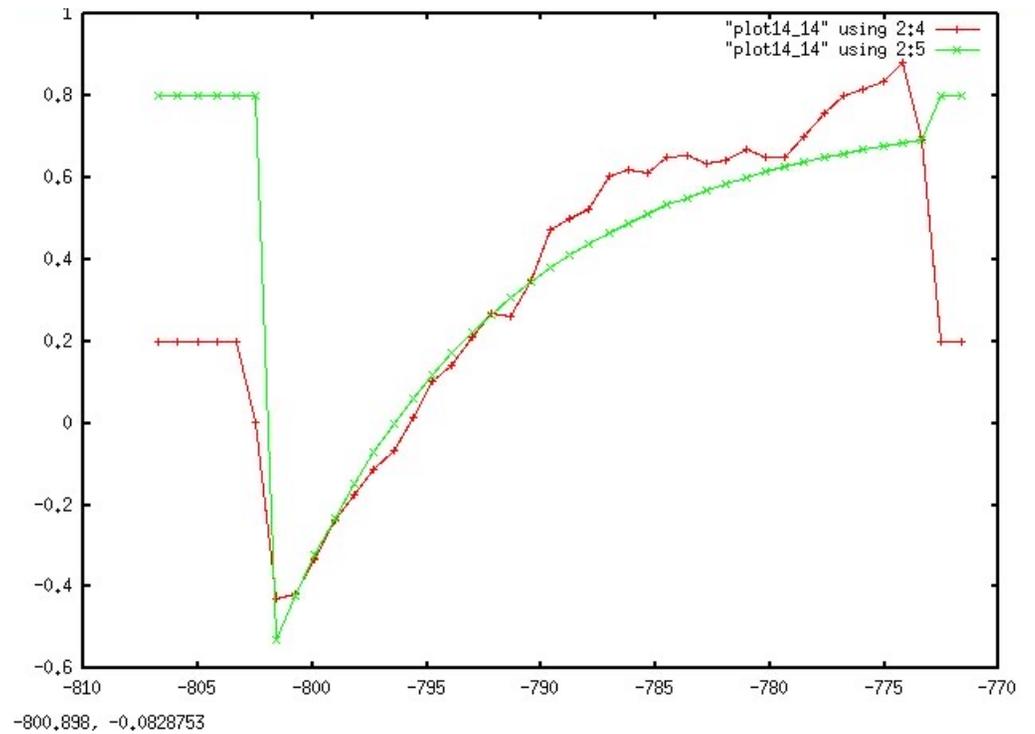
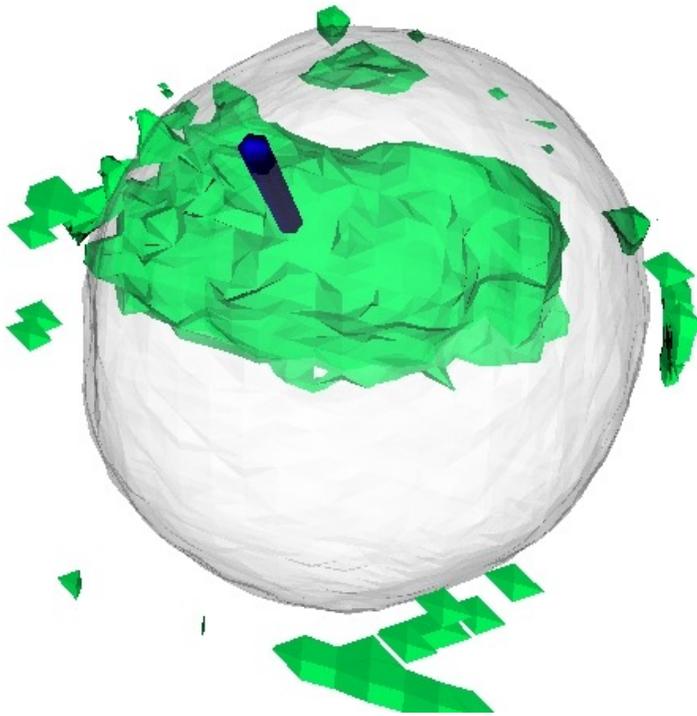
I. K. Robinson, U. Pittsburgh, Sept 2005

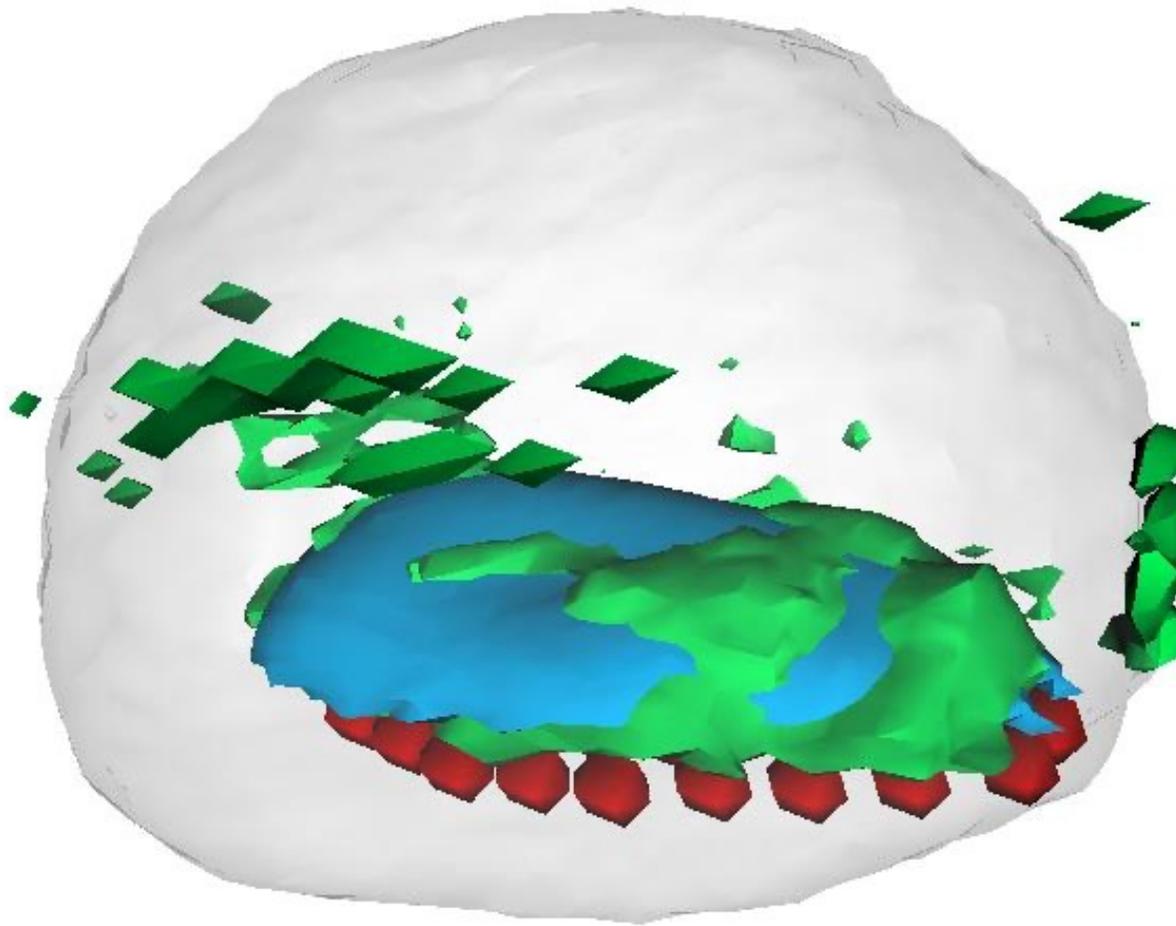
# Field lines of Point Charges



I. K. Robinson, U. Pittsburgh, Sept 2005

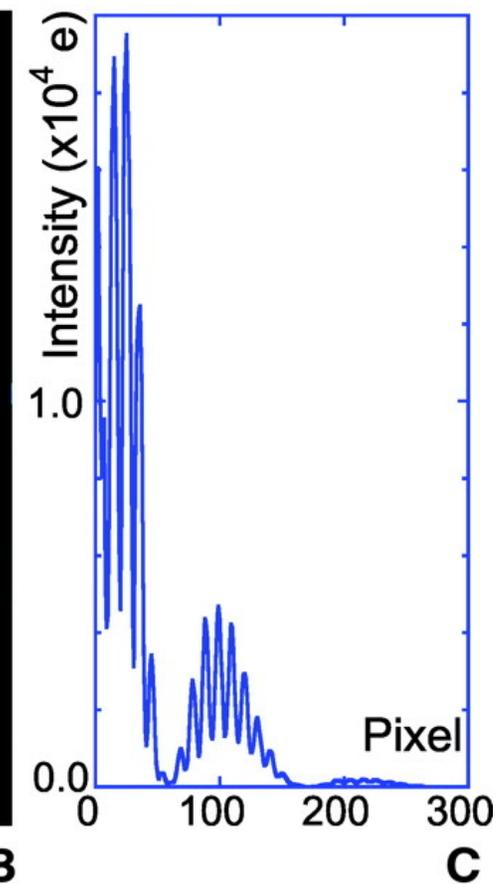
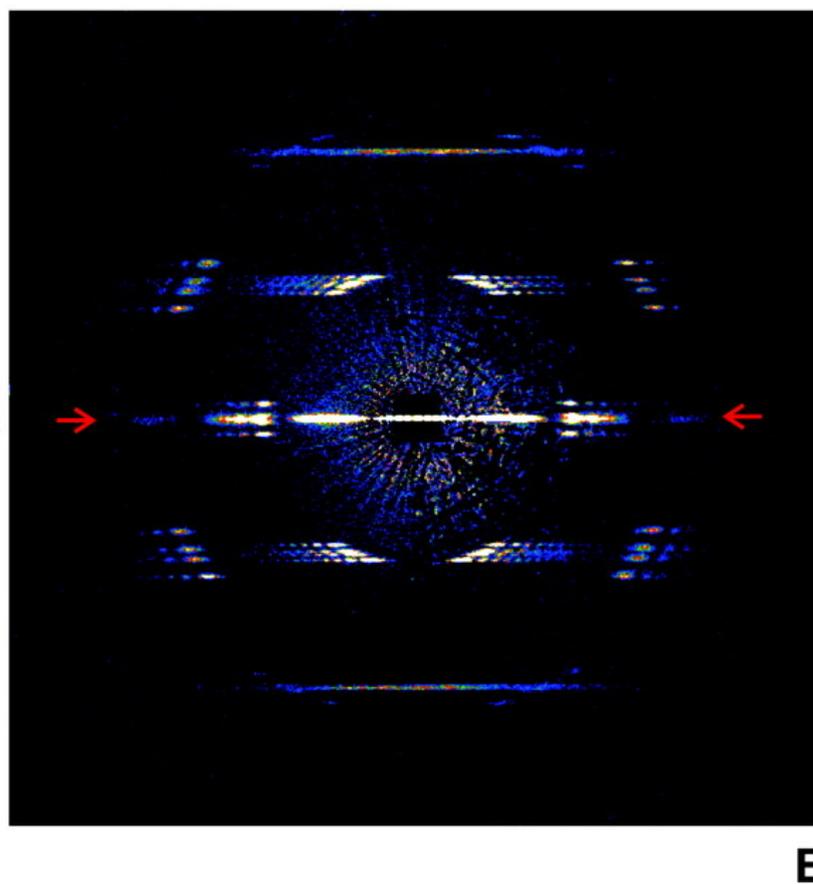
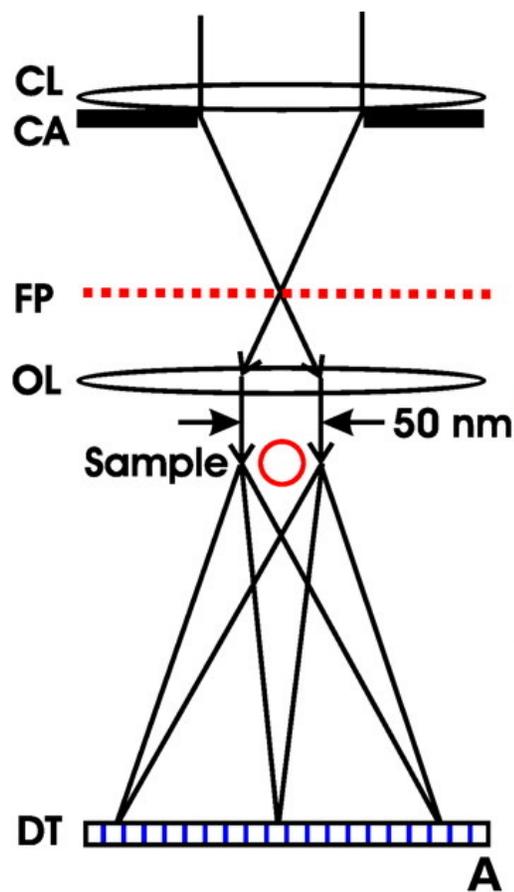
# Line scan through phase





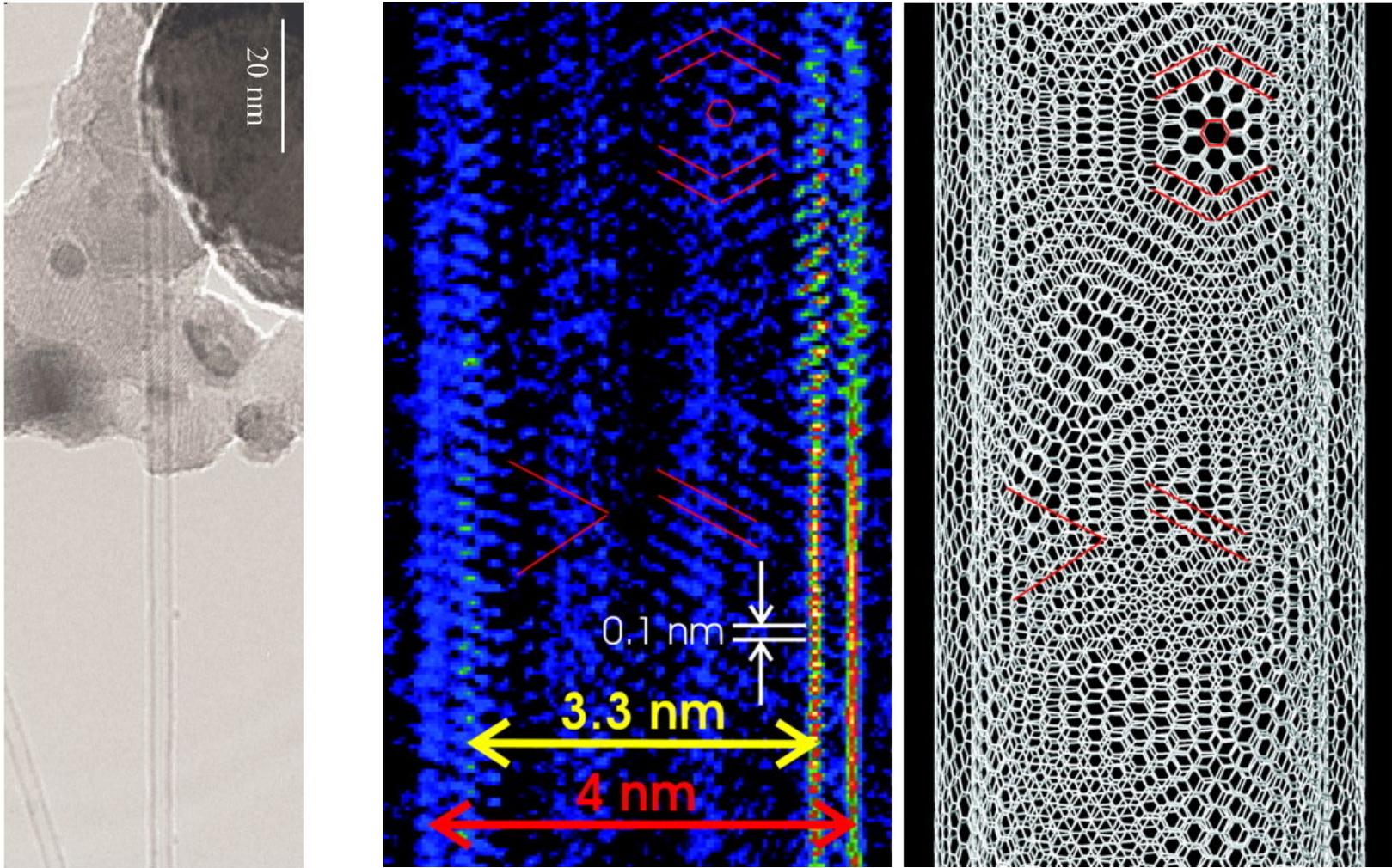
# Electron Diffraction from C-nanotube

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



# Images of DW C-nanotube

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



# Molecular Movies using XFEL



# Conclusions and Outlook

- Internal structure of Au Nanocrystals
- 3D imaging practical for nanocrystals
- Phasing by computation instead of lens
- Strain fields imaged from asymmetric patterns
- Atomic resolution with electron diffraction
- Single molecules using XFEL