Mapping of strain in nanocrystals in three dimensions

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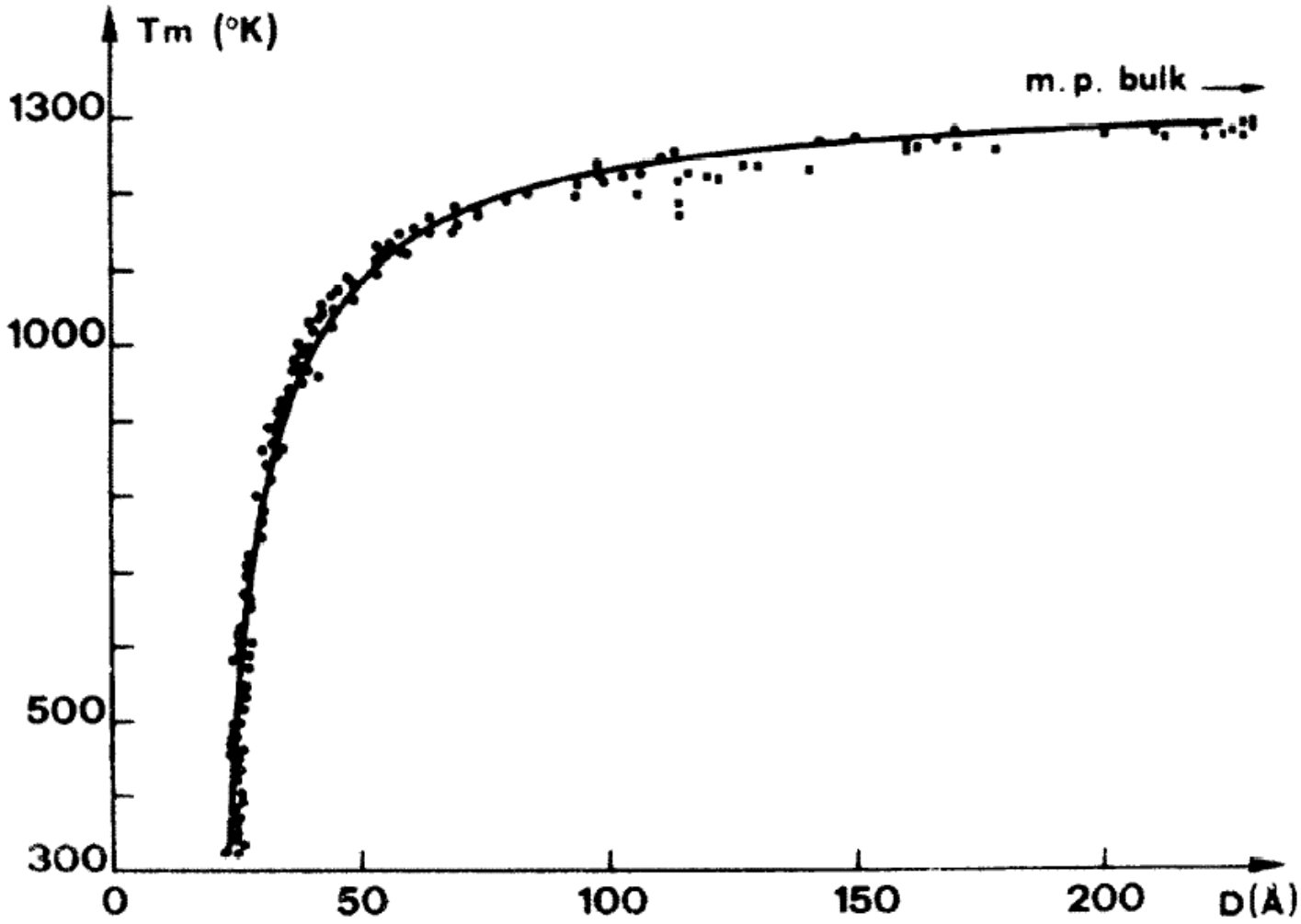
Outline

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

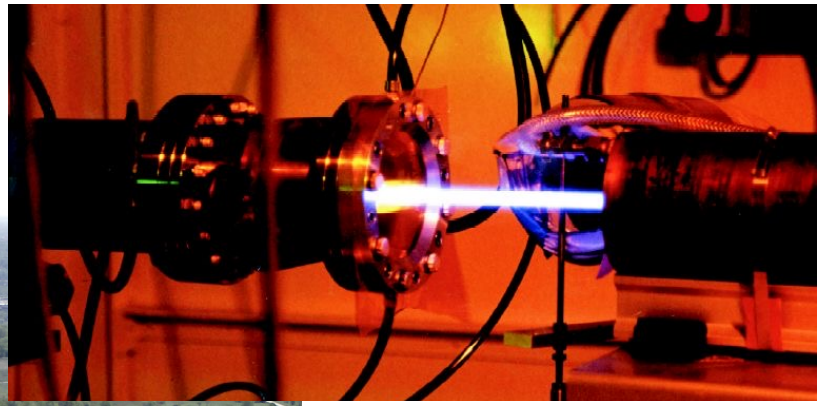
Size-dependent Melting of Au Particles

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



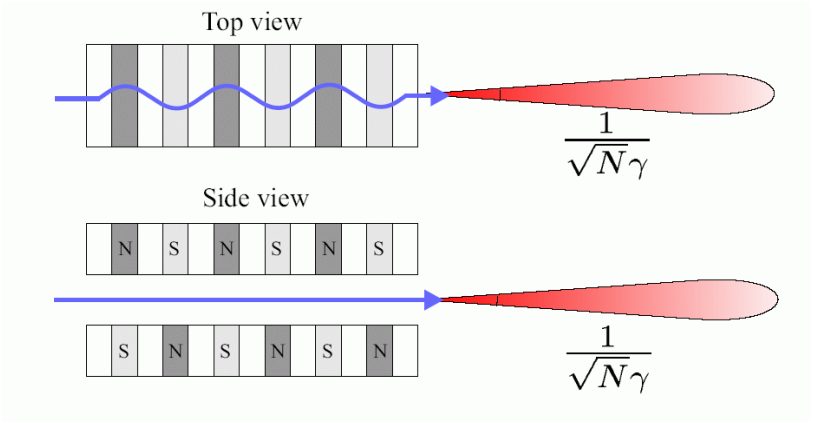
Synchrotron Radiation

Urbana

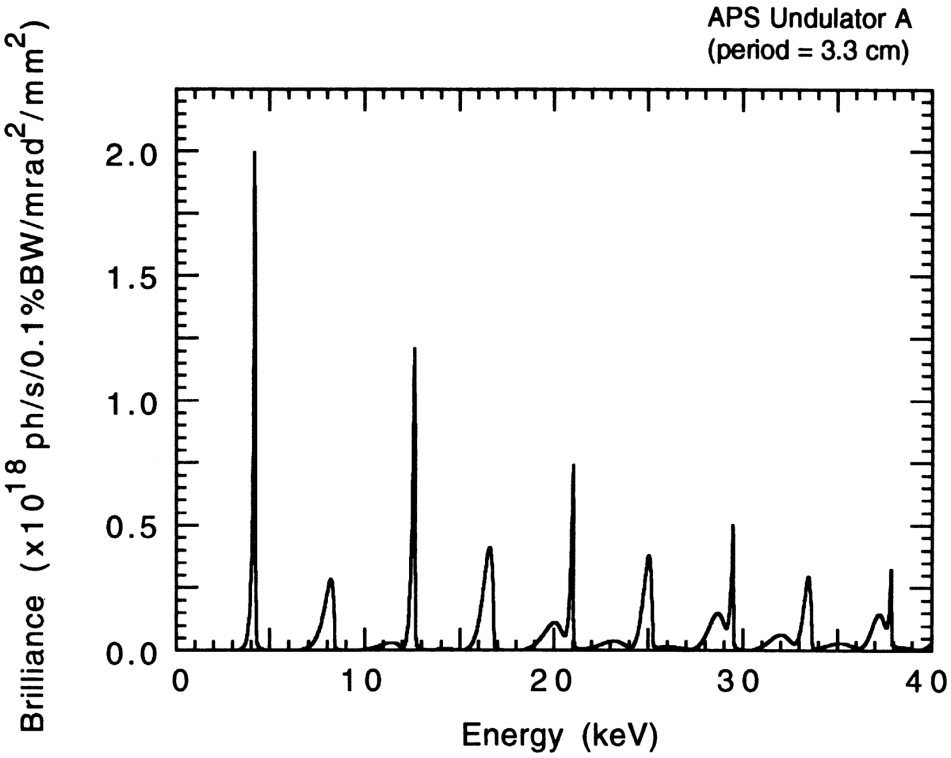


34-ID-C

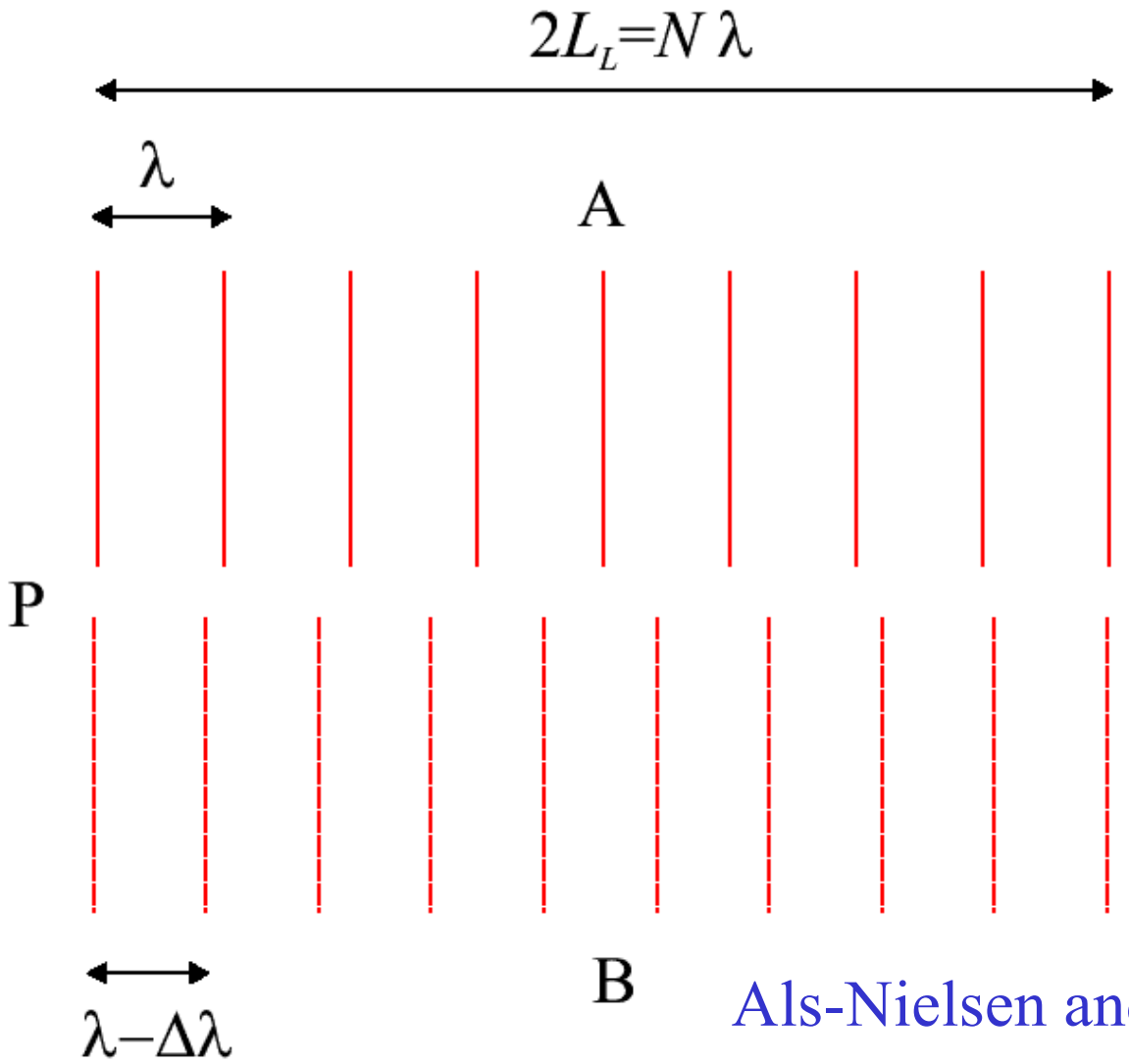
X-ray Undulator at APS



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



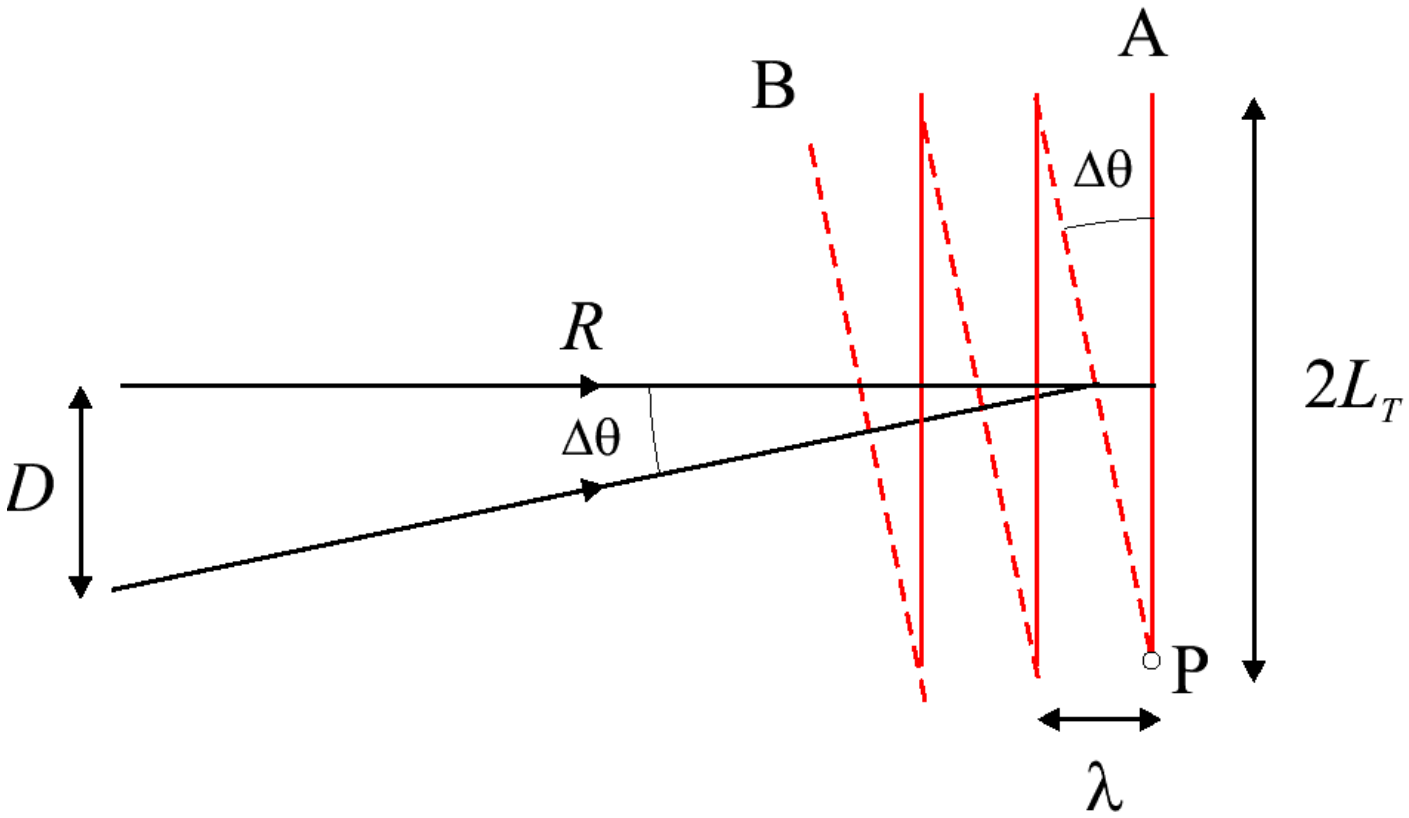
Longitudinal Coherence



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

Als-Nielsen and McMorrow (2001)

Lateral (Transverse) Coherence



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

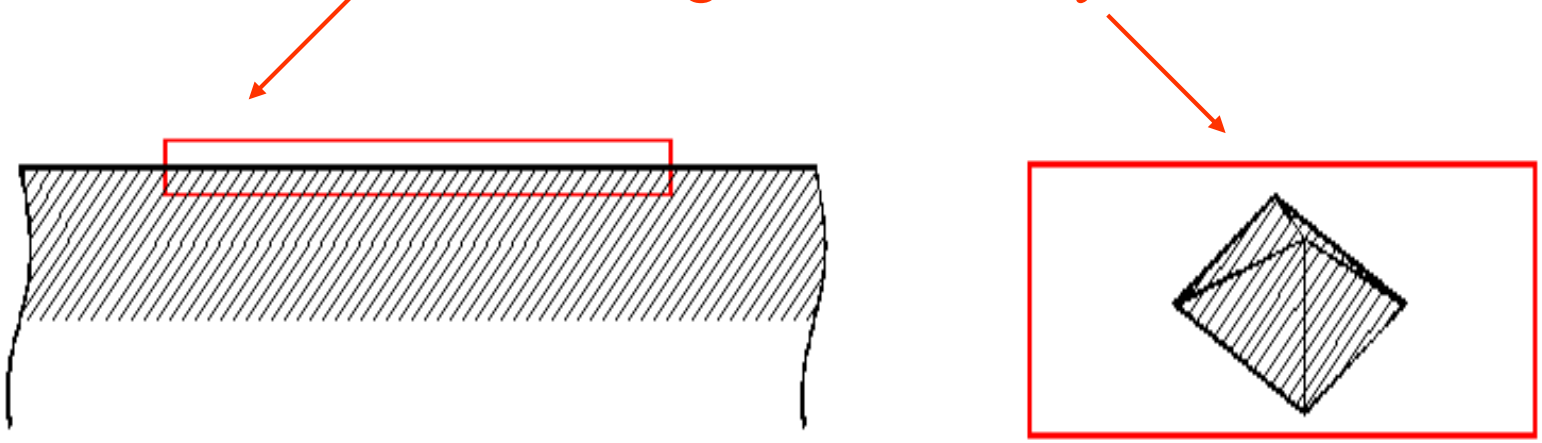
Als-Nielsen and McMorrow (2001)

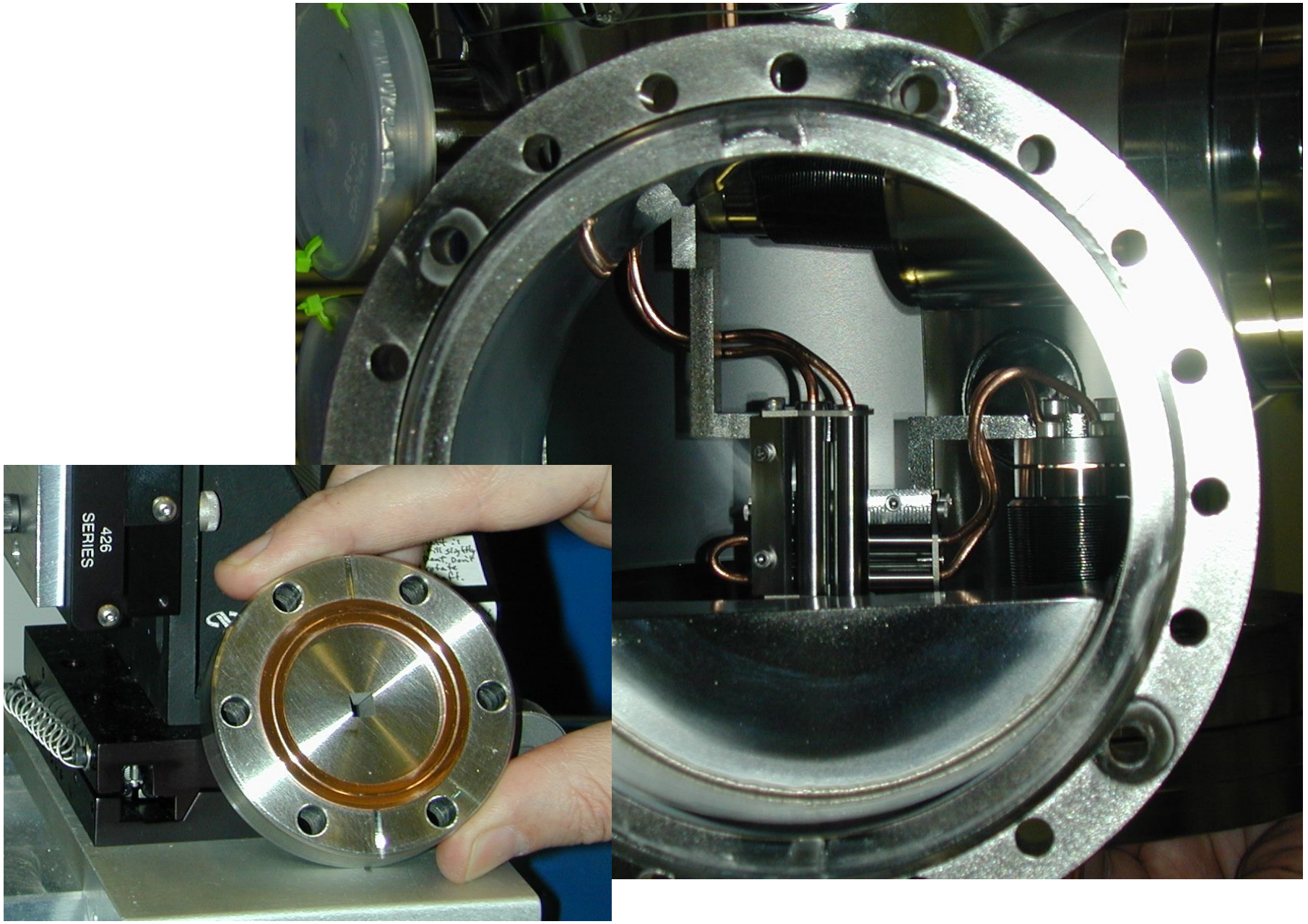
Coherence at APS, ESRF or DLS

Typical of 3rd Generation (undulator) Synchrotron Source

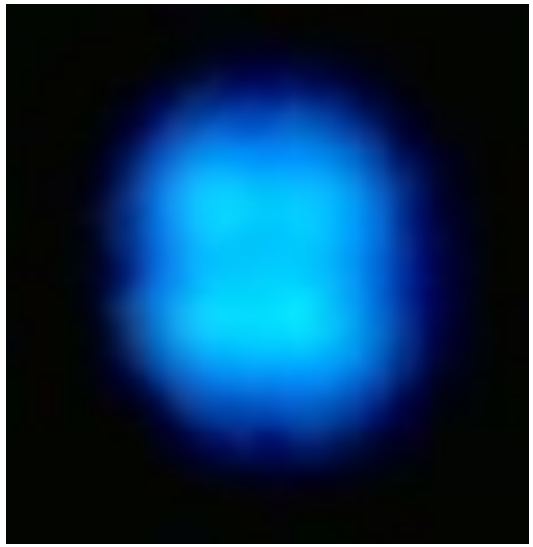
Coherence of	ξ_{VER}	ξ_{HORIZ}	ξ_{LONG}	Flux
Raw Undulator	35μm	9μm	0.004μm	2×10^{12}
Si(111) Monochromator	35μm	9μm	1μm	1×10^{10}
C(111) Monochromator	35μm	9μm	3μm	3×10^{9}

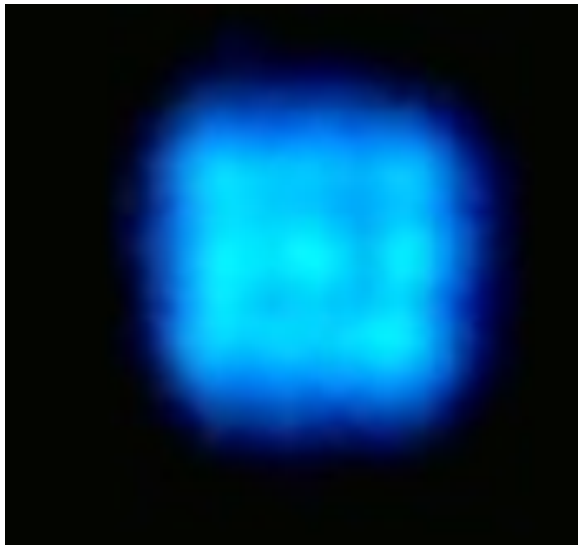
Coherent region defined by slits



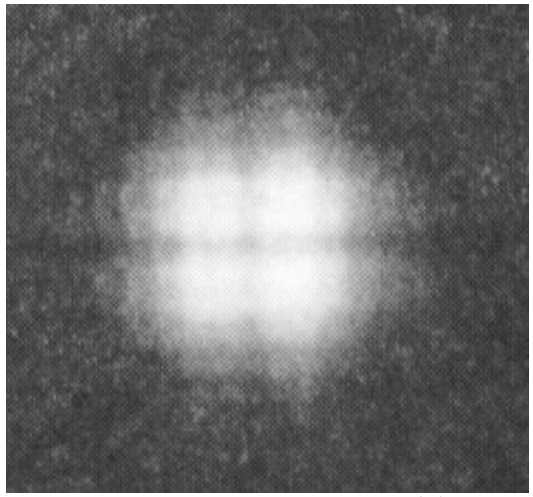

426
SERIES

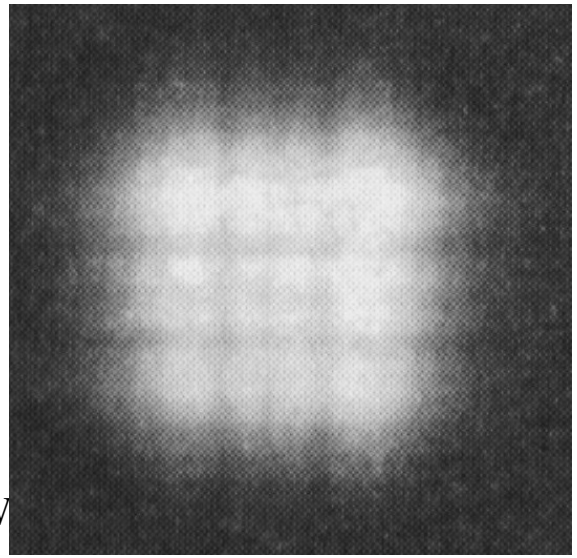
Fresnel Diffraction when $d^2 \sim \lambda D$





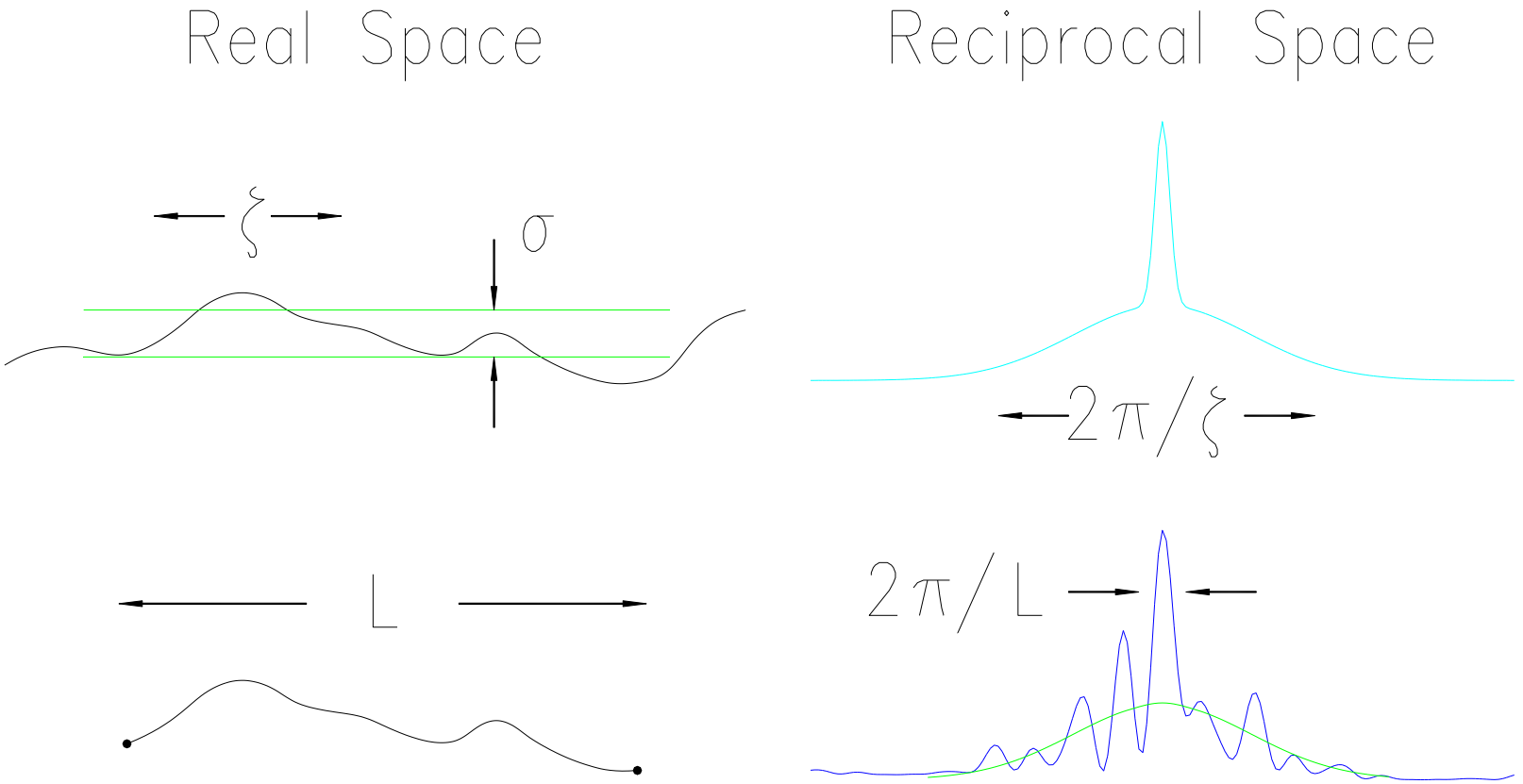
X-ray beam defined by RB slits





Visible Fresnel diffraction from Hecht "Optics"

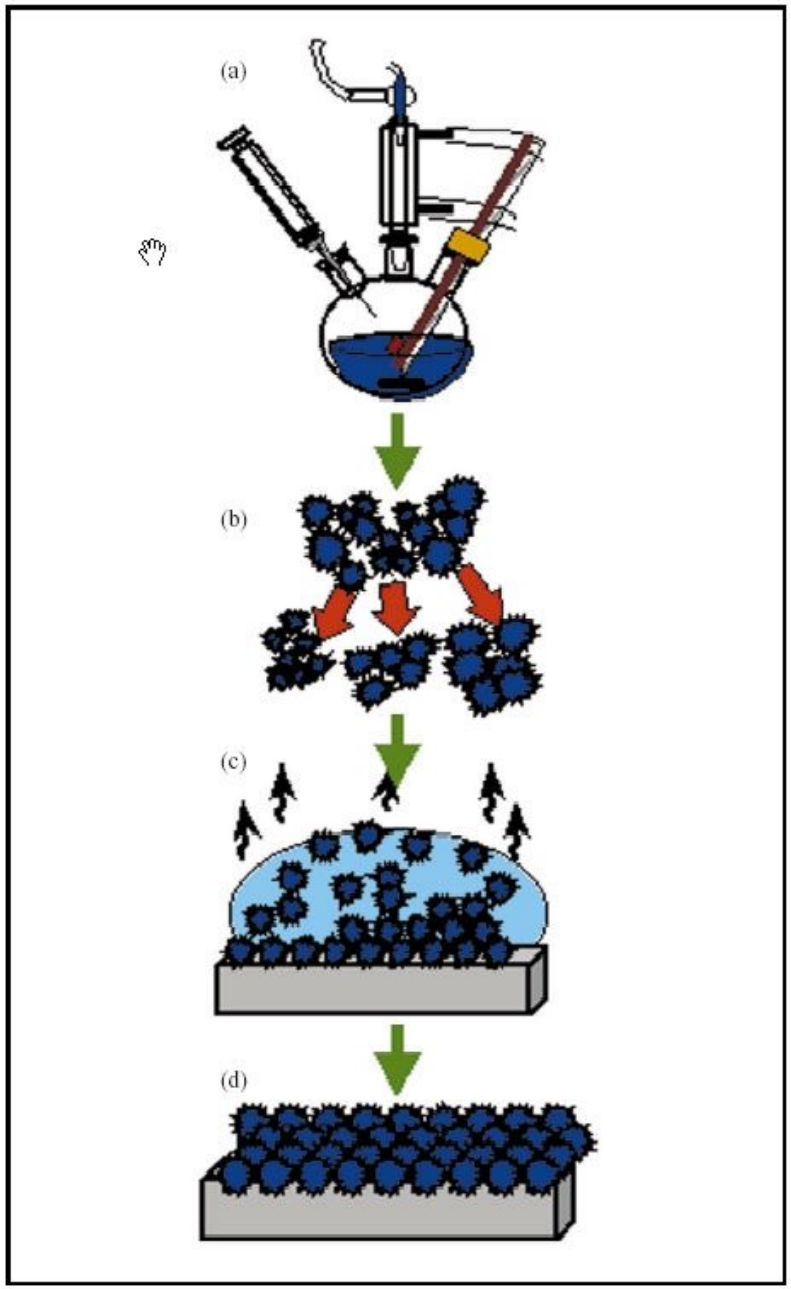
Diffuse Scattering acquires Structure using CXD



Facts of Life with Coherence

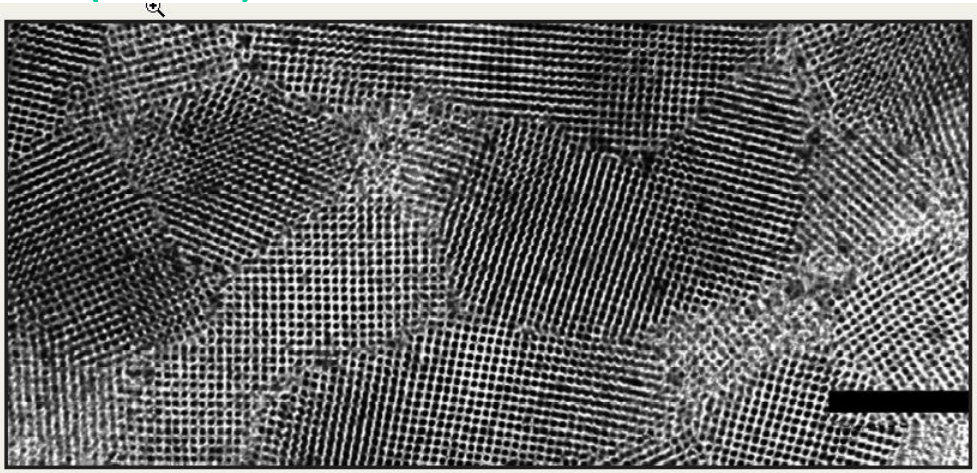
- No more diffuse scattering
- No more ensemble averaging
- Coherence is indestructible
  - everything following your (coherence-defining) entrance slit is your 'sample'
- If something moves, the whole interference pattern changes

Chemical Synthesis of Nanocrystals



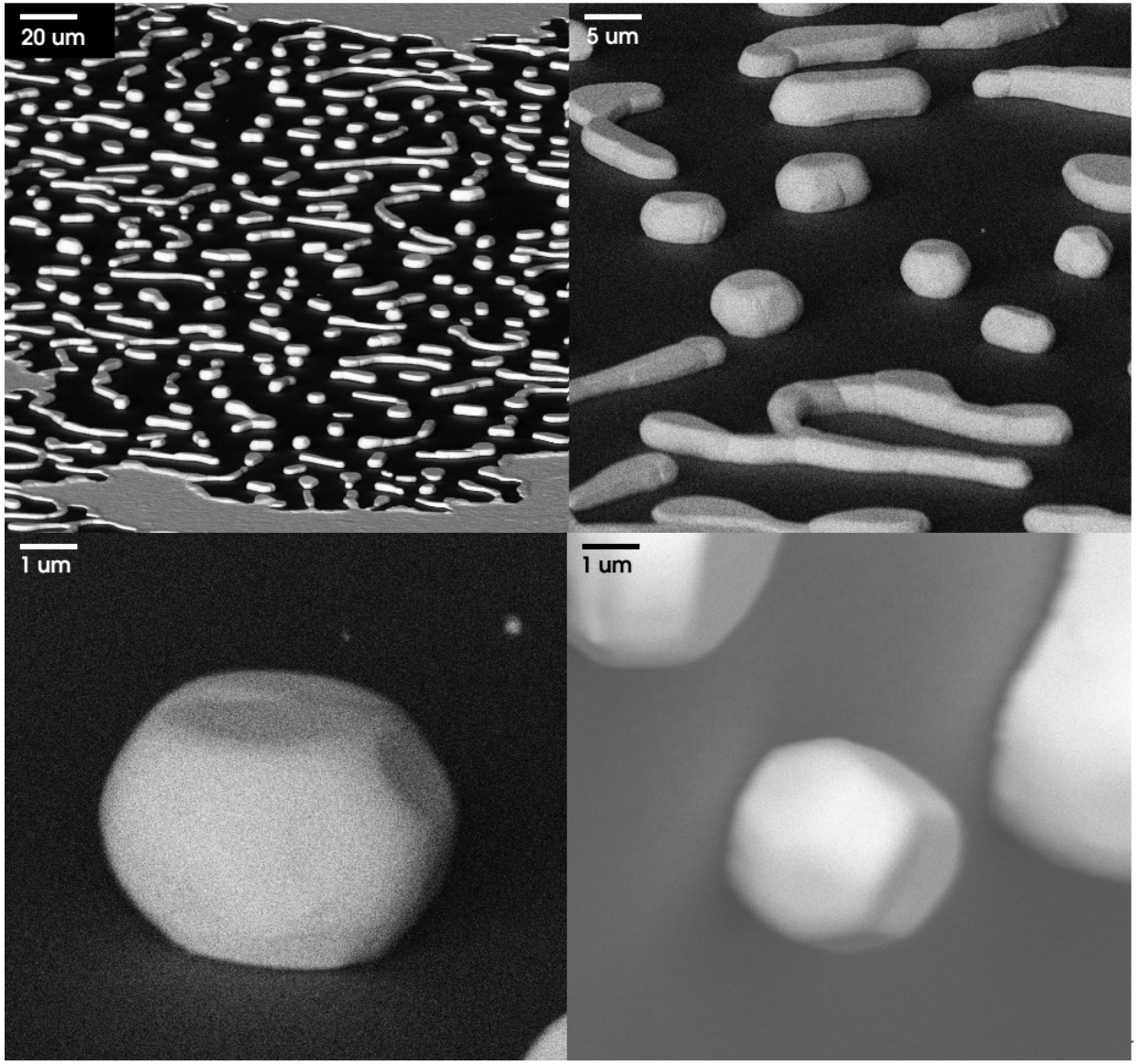
- Reactants introduced rapidly
- High temperature solvent
- Surfactant/organic capping agent
- Square superlattice (200nm scale)

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

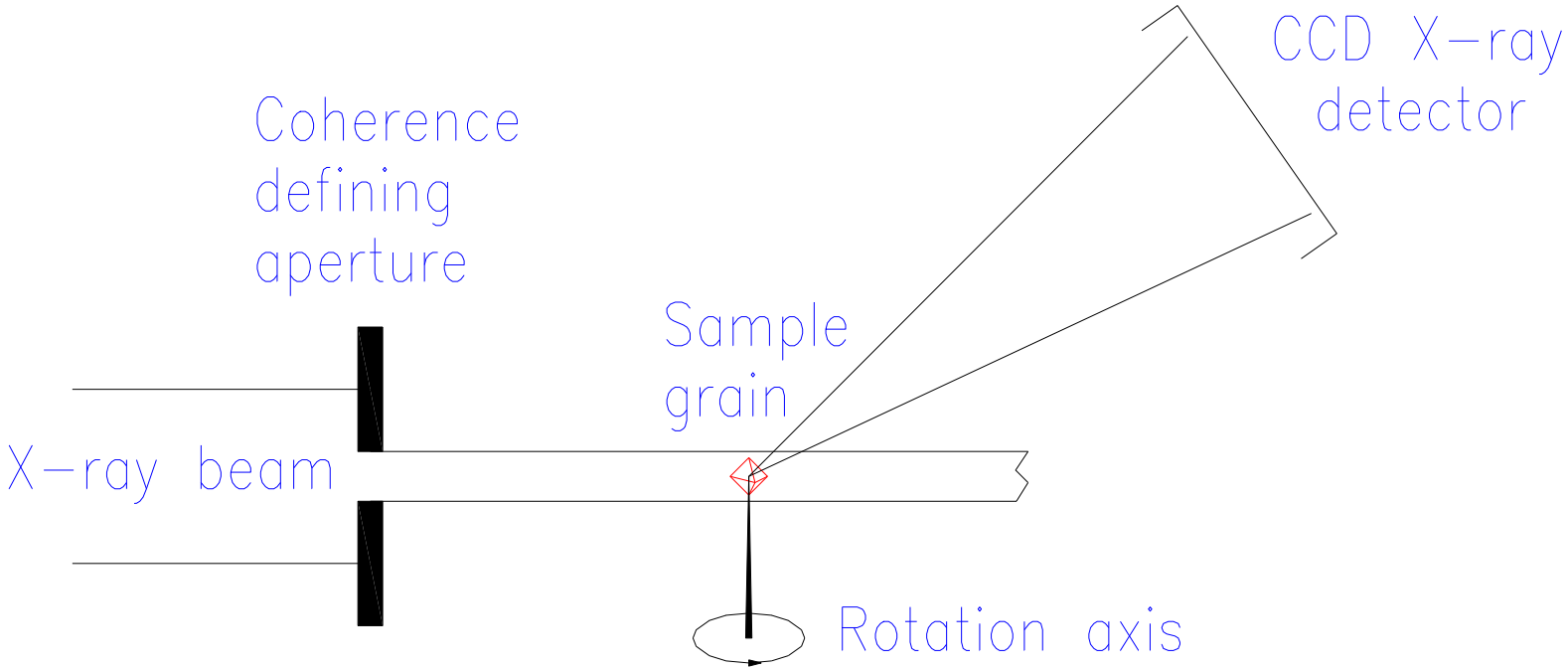


SEMS

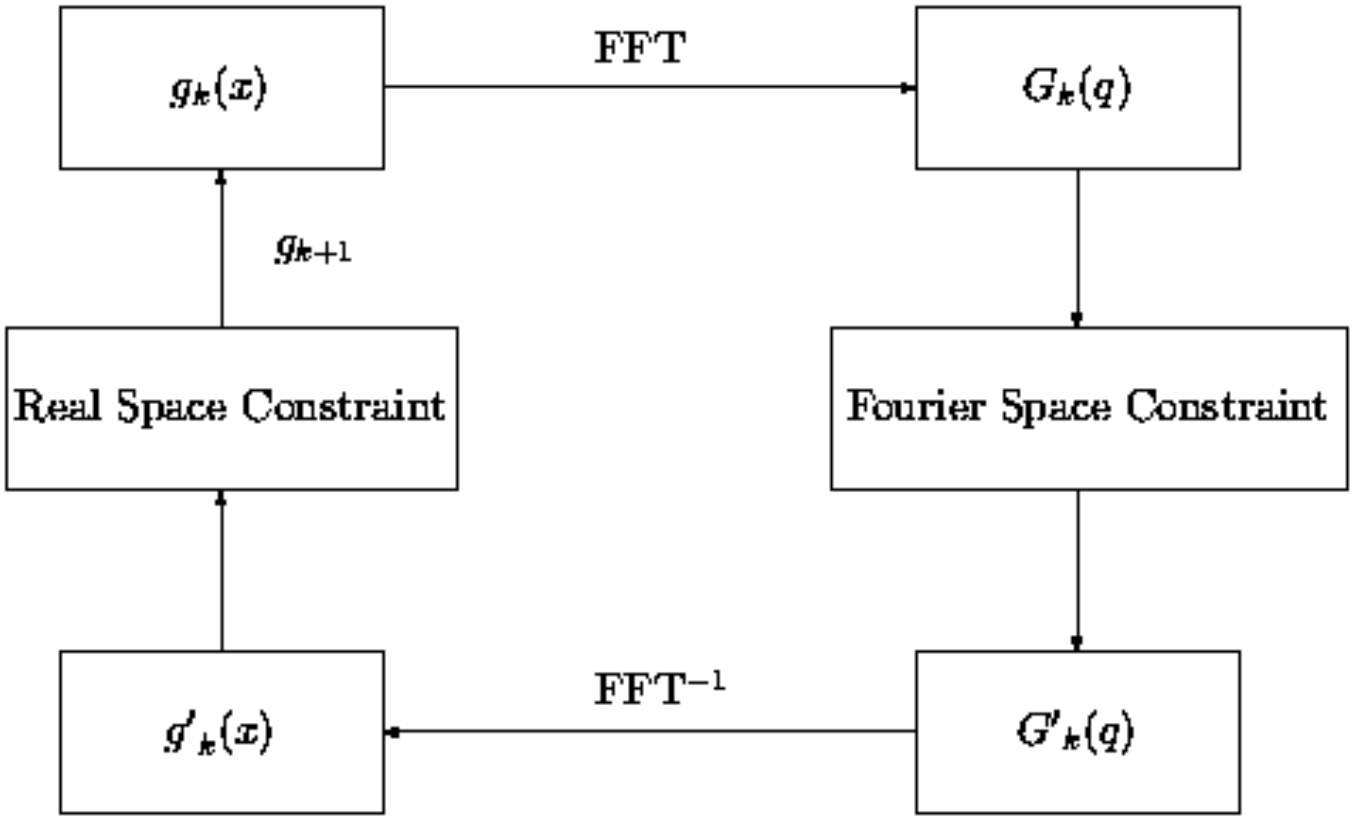
- Au blanket film
- Quartz substrate
- Annealed at 950°C for 70 hrs.



Lensless X-ray Microscope



Generic "Error Reduction" method



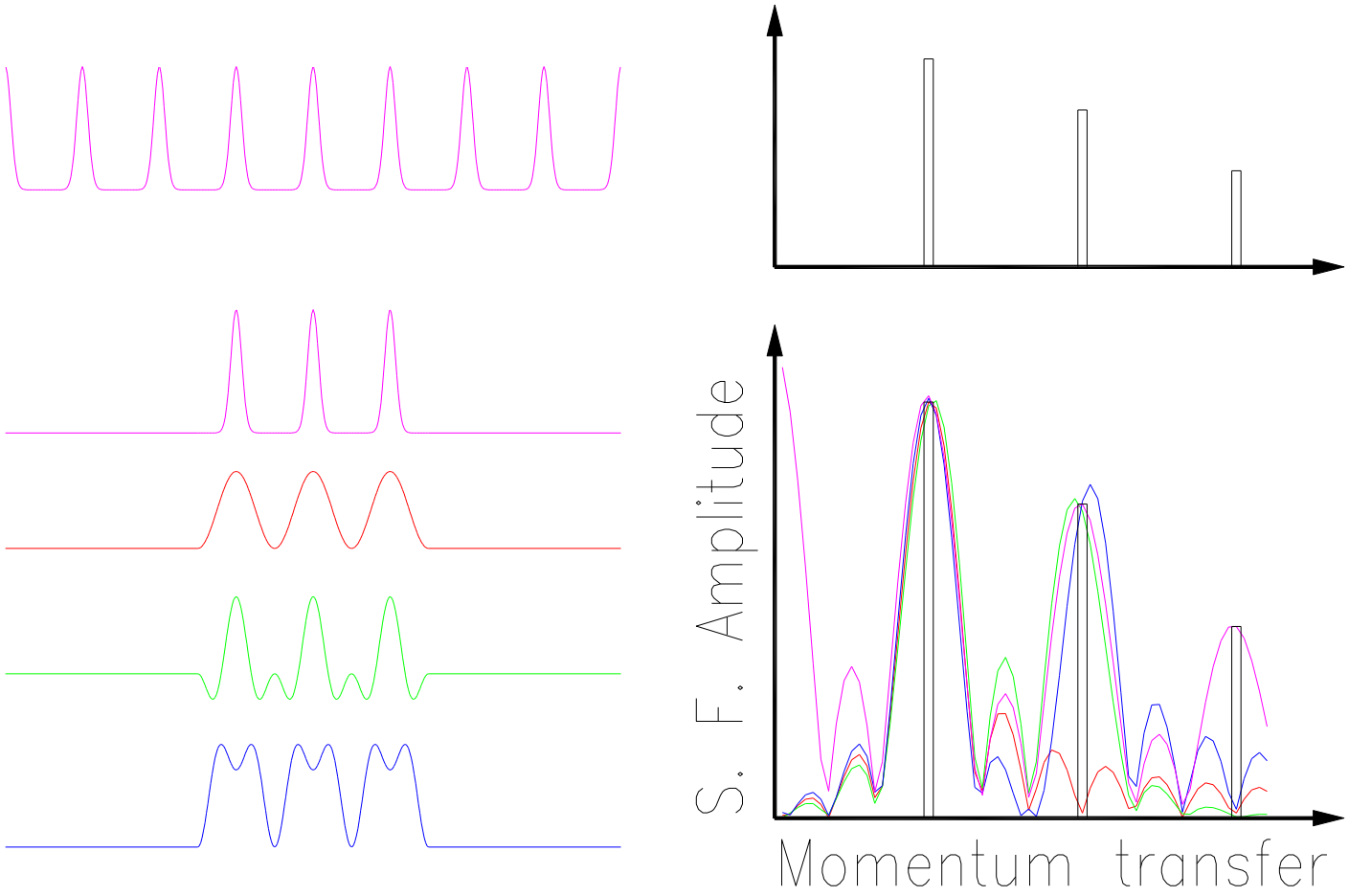
J. R. Fienup Appl. Opt. 21 2758 (1982)
R. W. Gerchberg and W. O. Saxton Optik 35 237 (1972)

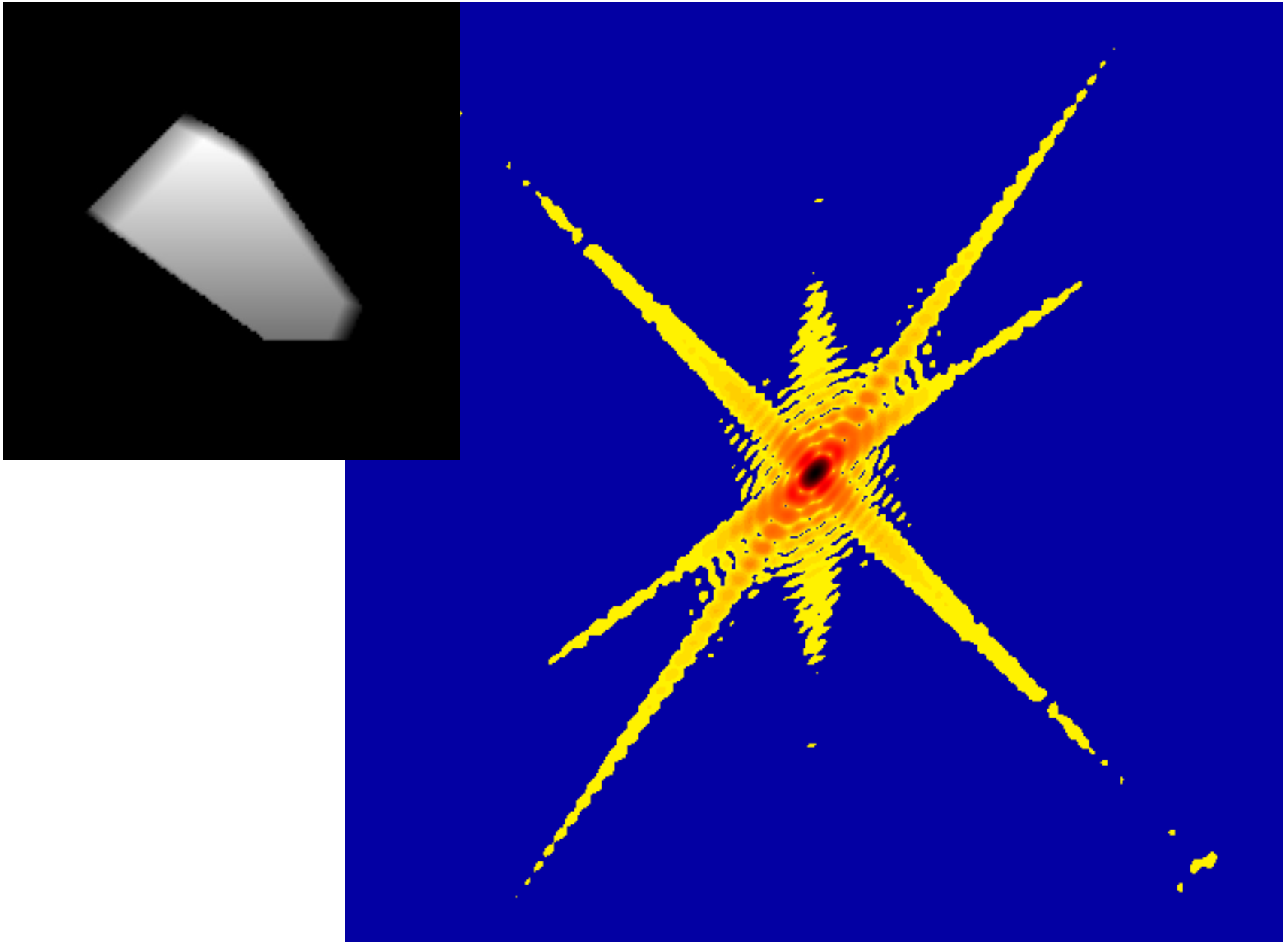
Real-space Constraints in Crystallograhy

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)

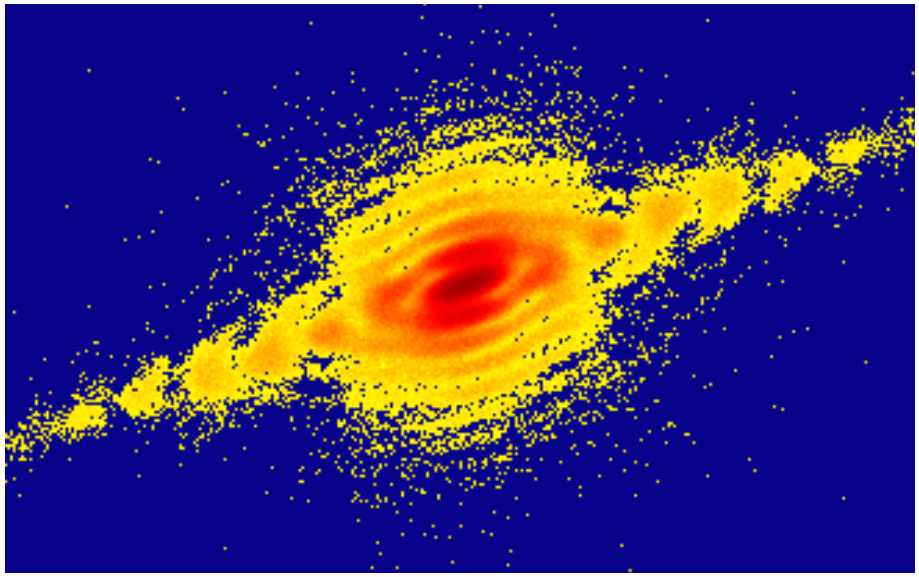
Phase Problem: Finite-size Effect

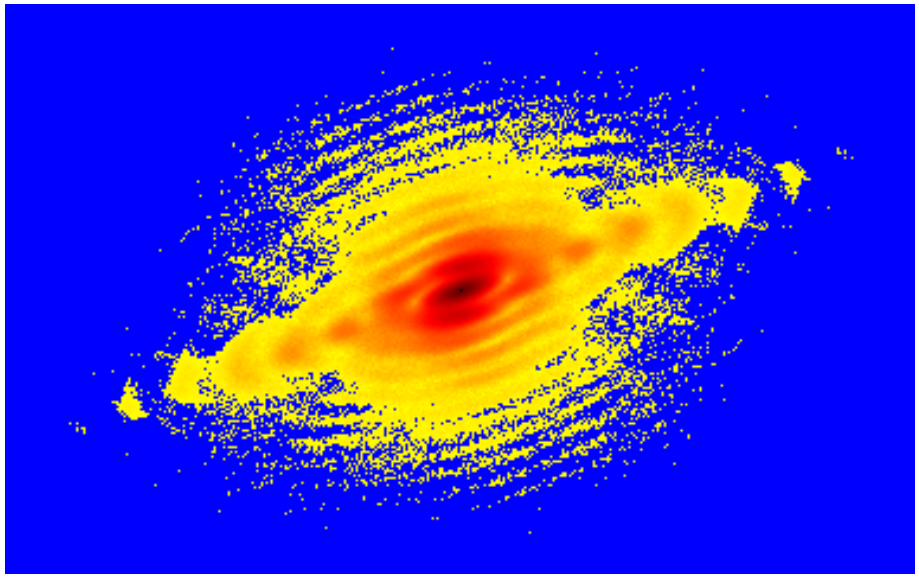


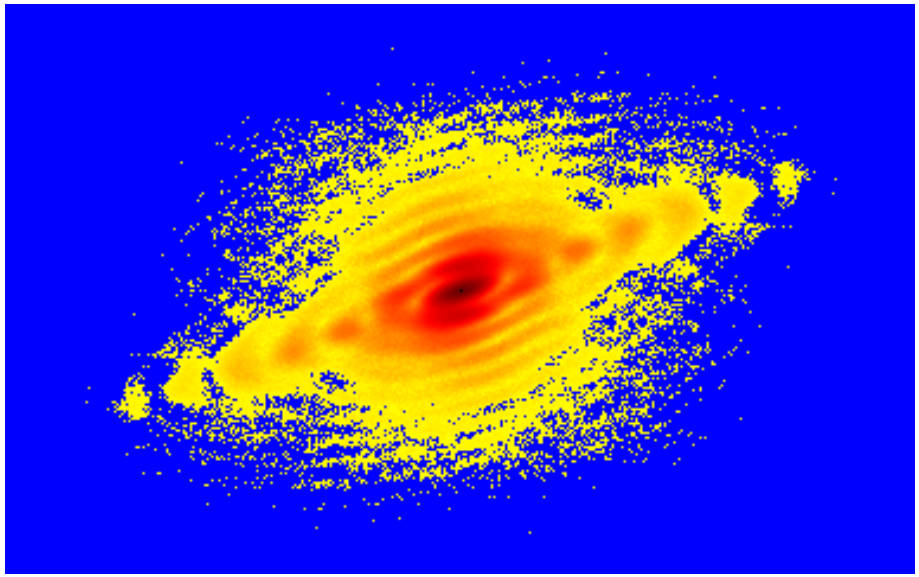


Symmetrized Data and two best fits

Chisq=0.0005

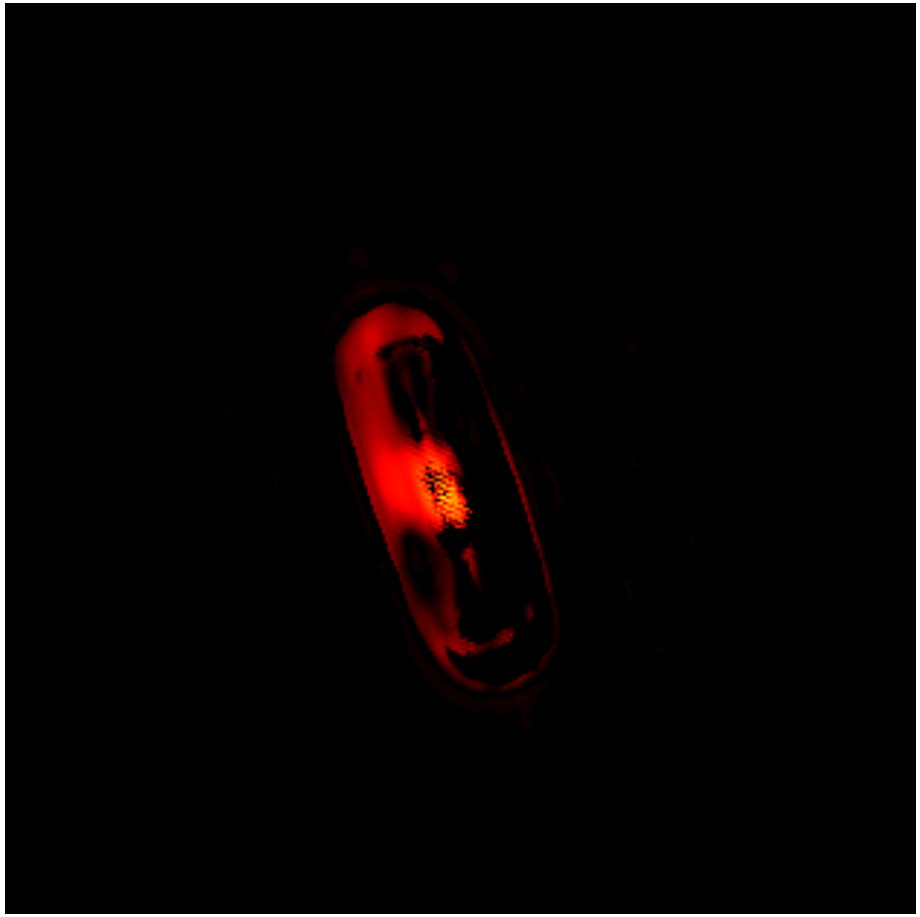


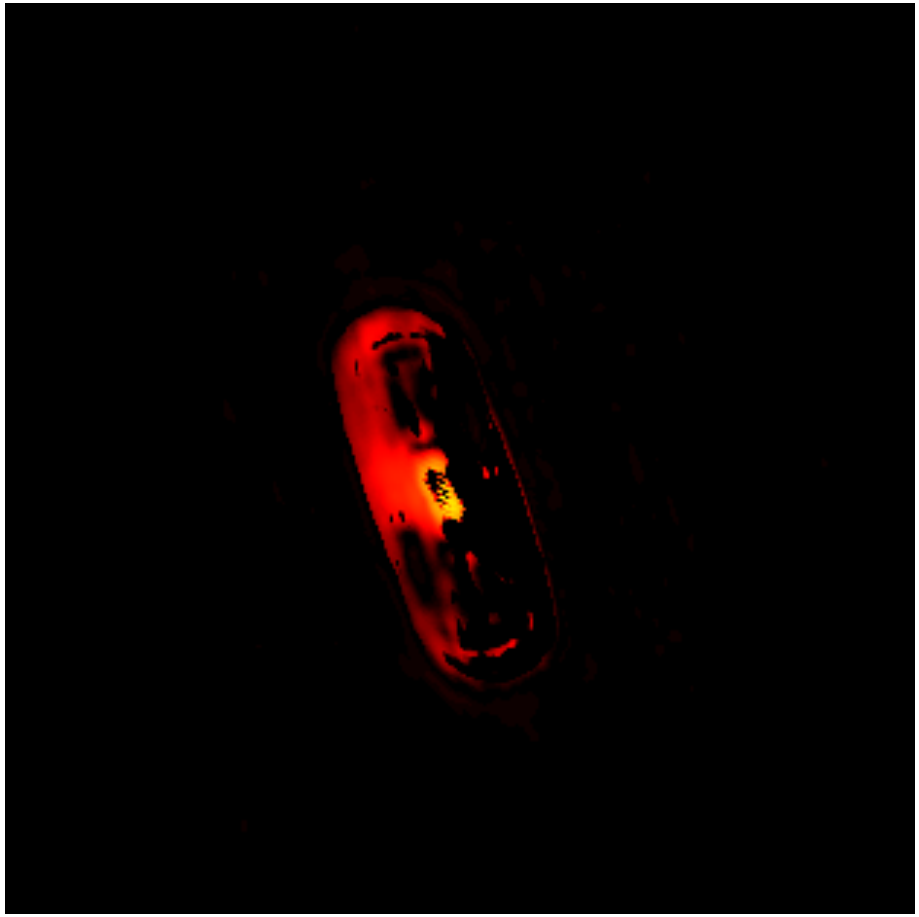




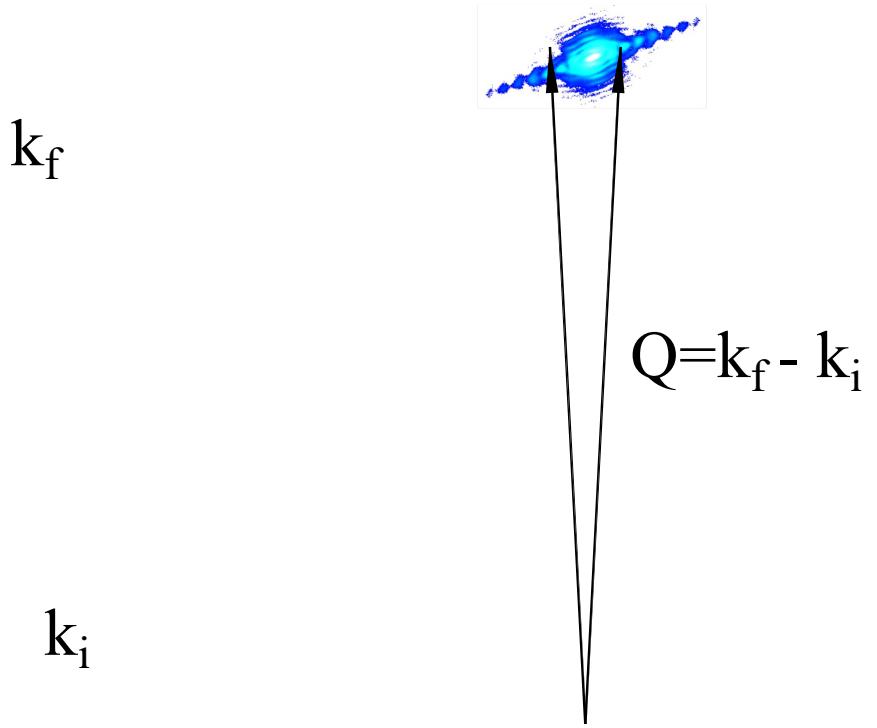
2D Reconstructions

chisquare = 0.0005

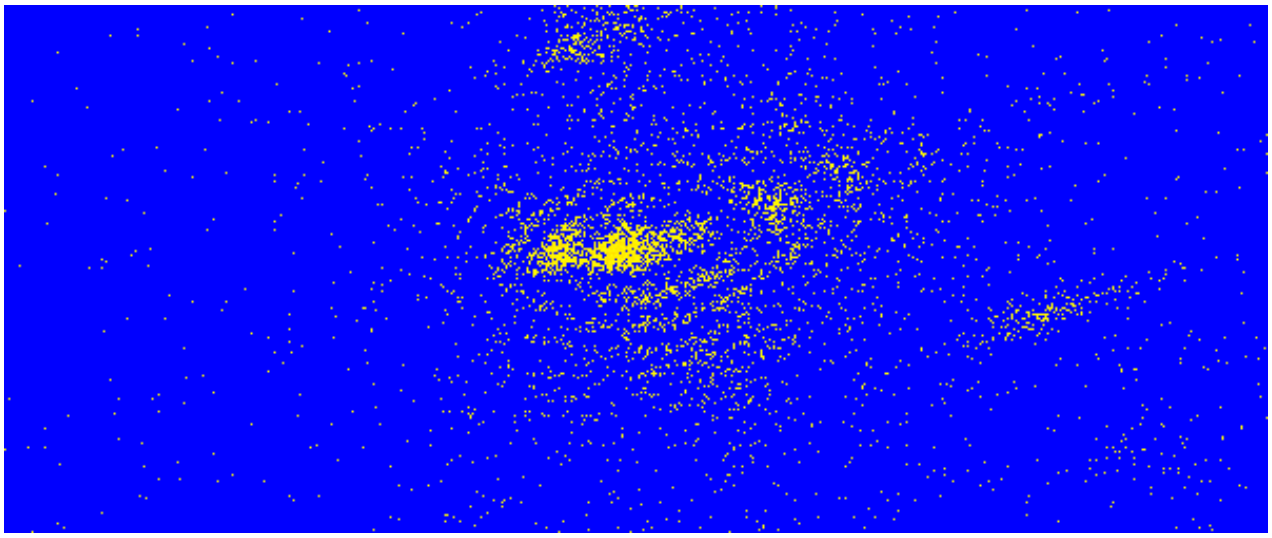


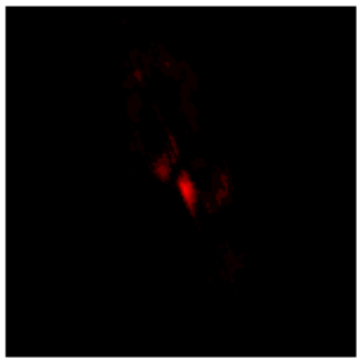
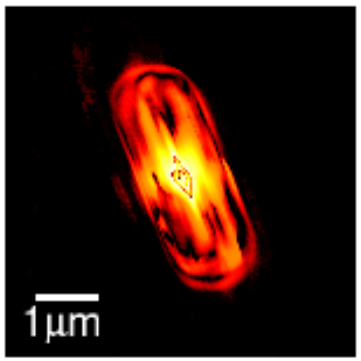


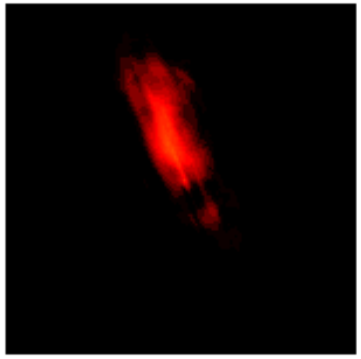
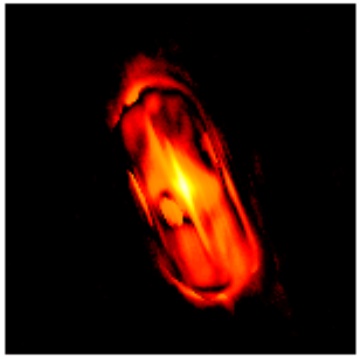
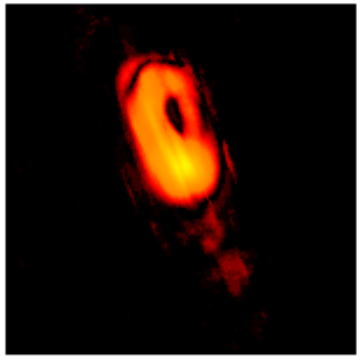
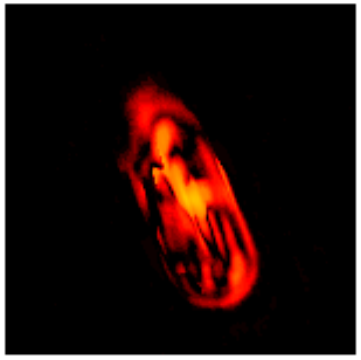
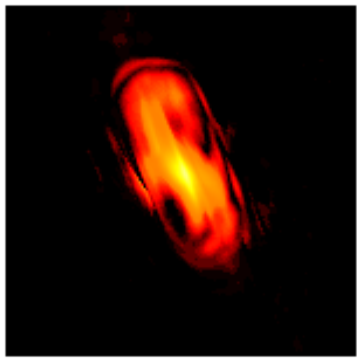
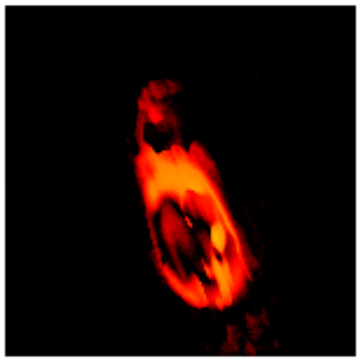
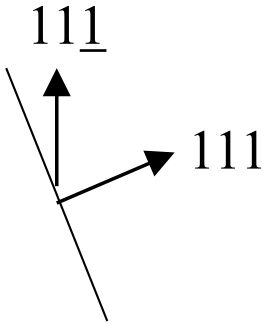
3D Diffraction Method

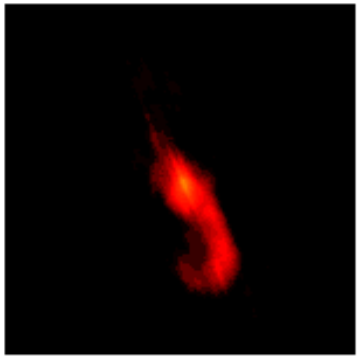
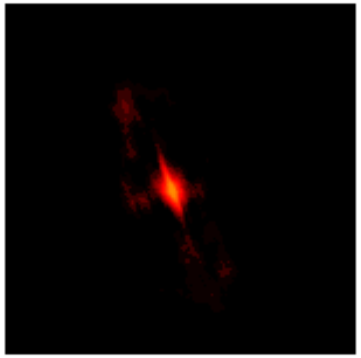


3D Diffraction Data
1 micron Au crystal

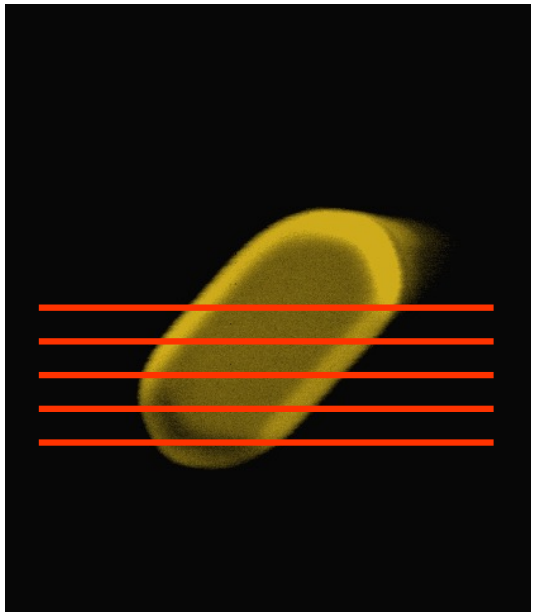


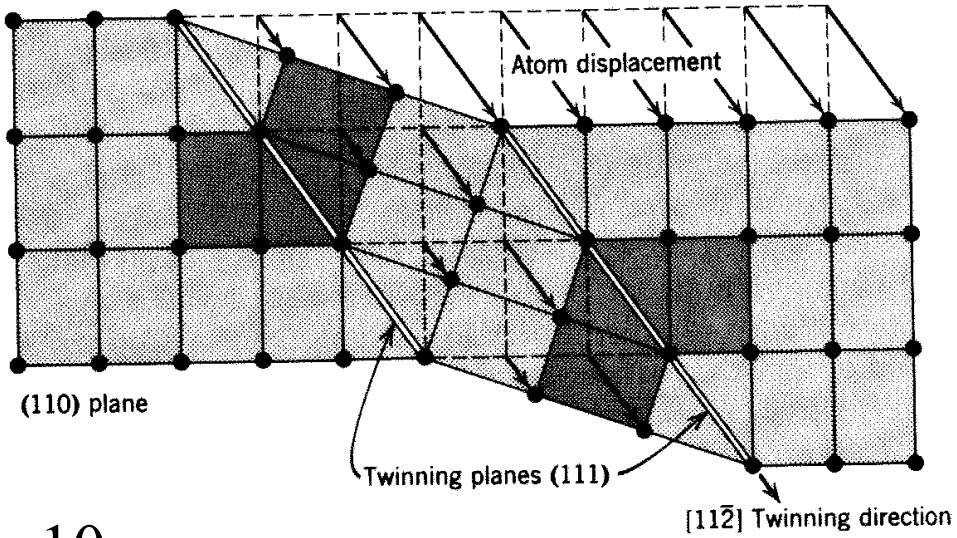



Slices through plan view SEM:

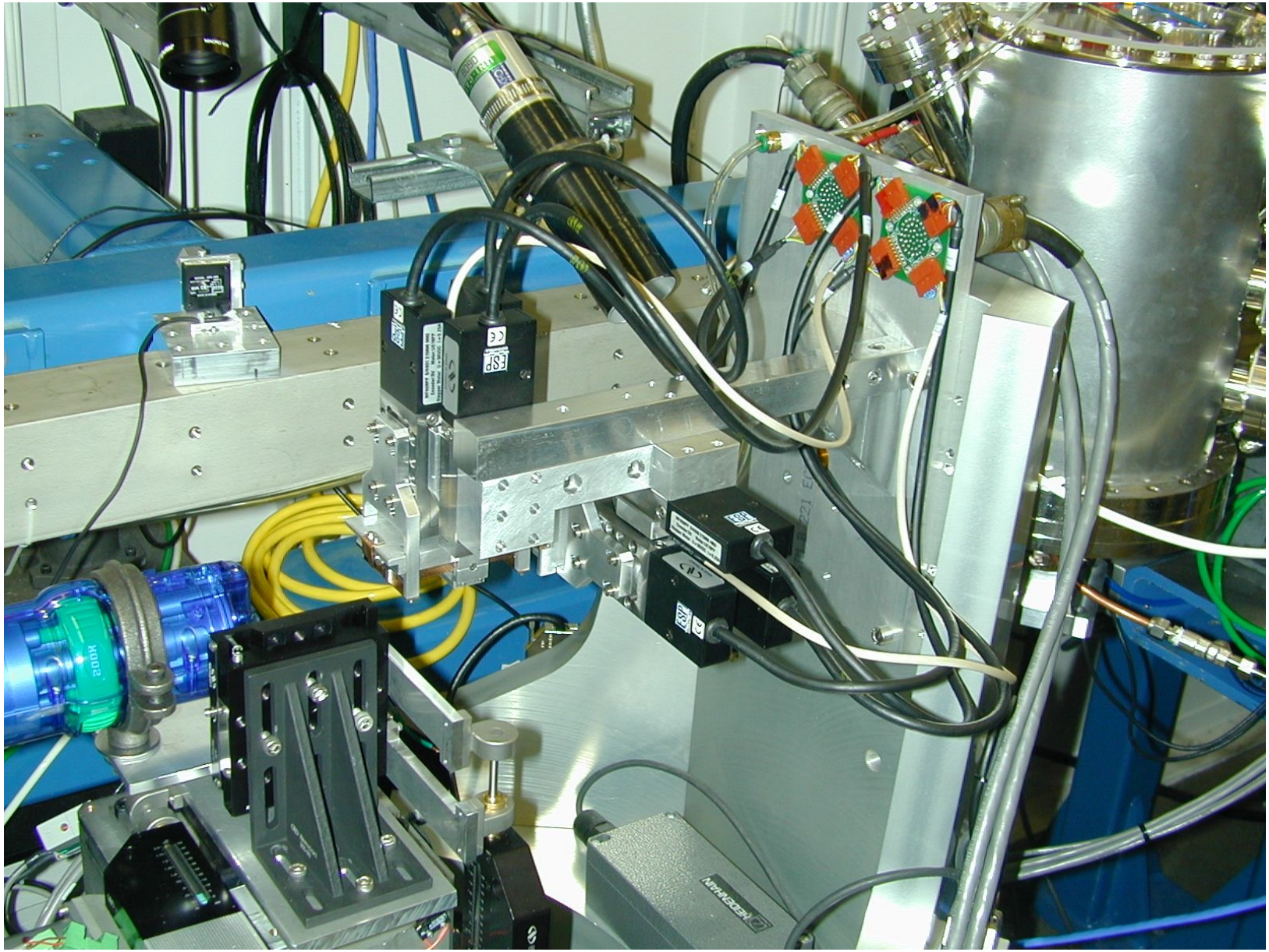


Twinning in deformed FCC metals

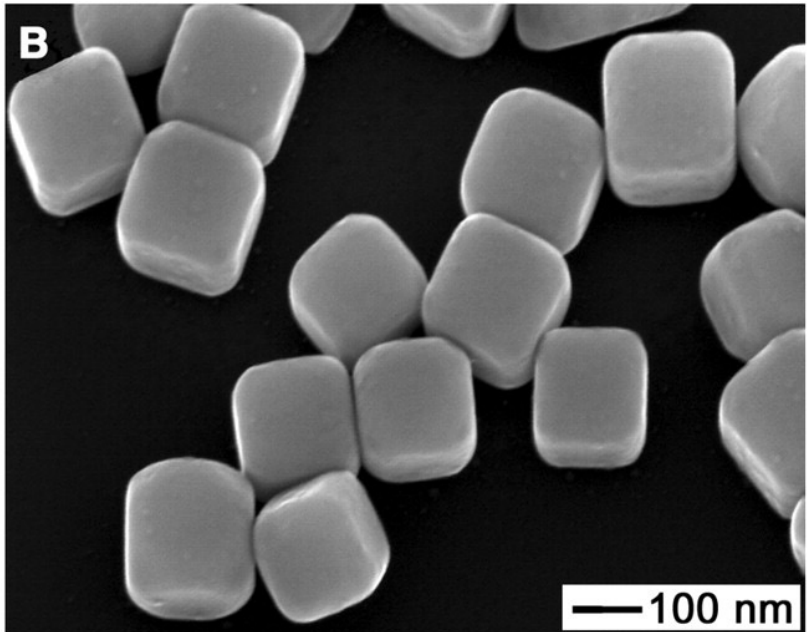
J. Wulff, "Structure and Property of Materials III" (1965)

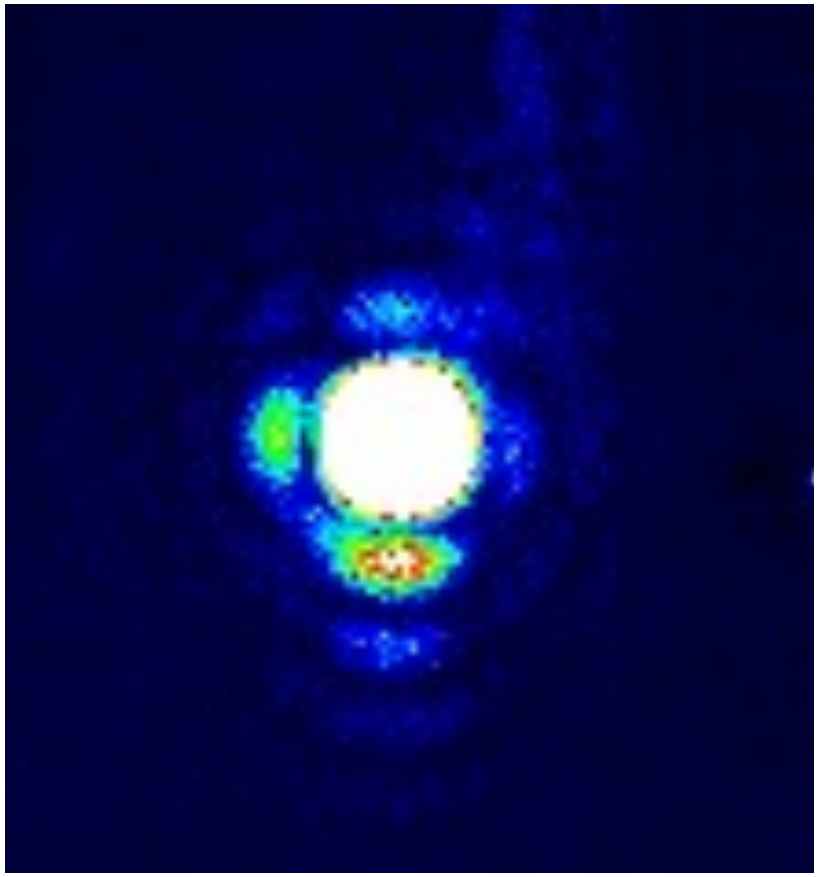


~10μm
Cu



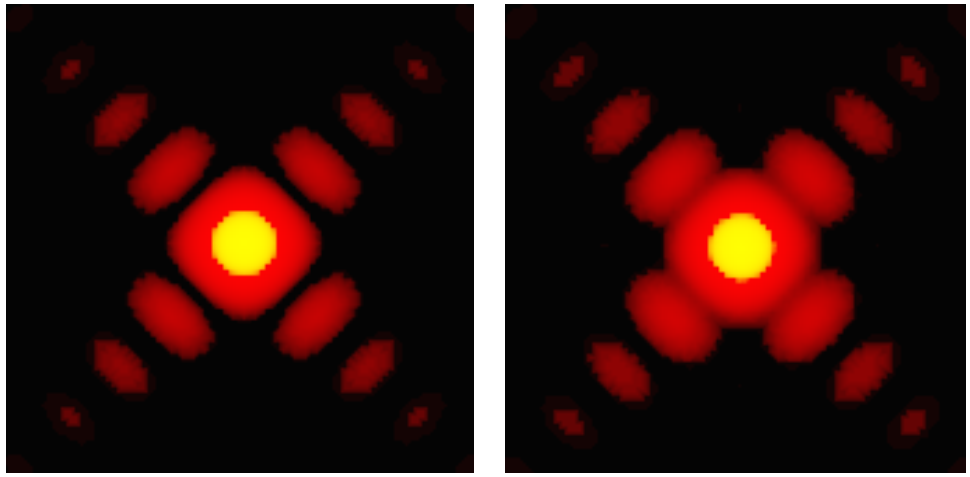
Chemically Synthesized Silver Nanocubes



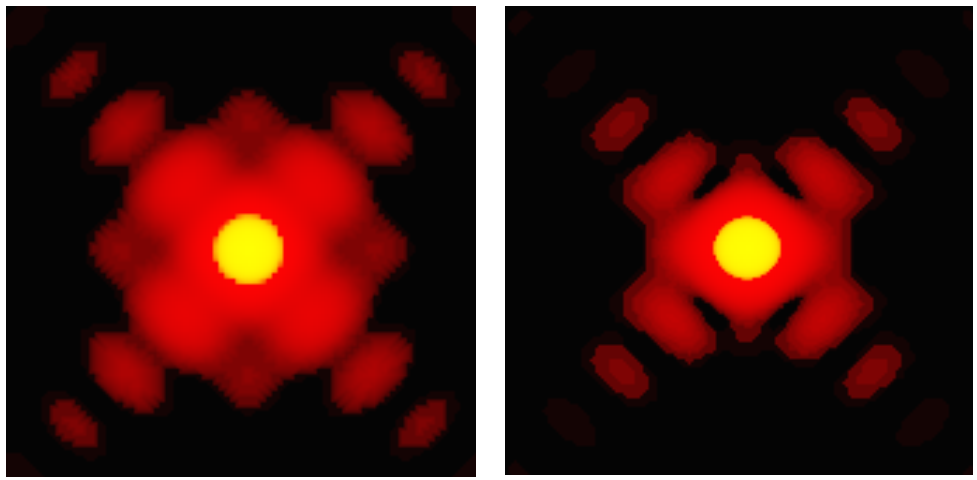


Yugang Sun and Younan Xia,
Science 298 2177 (2003)

Spherical and cylindrical waves



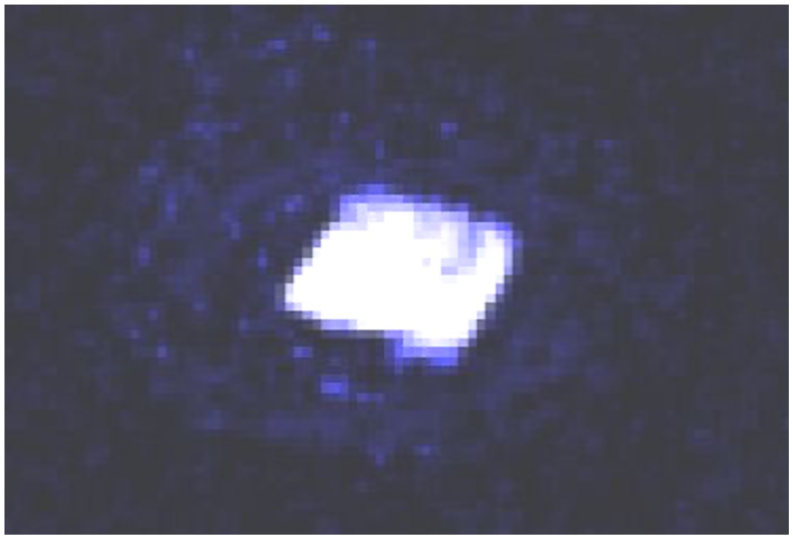
π/4



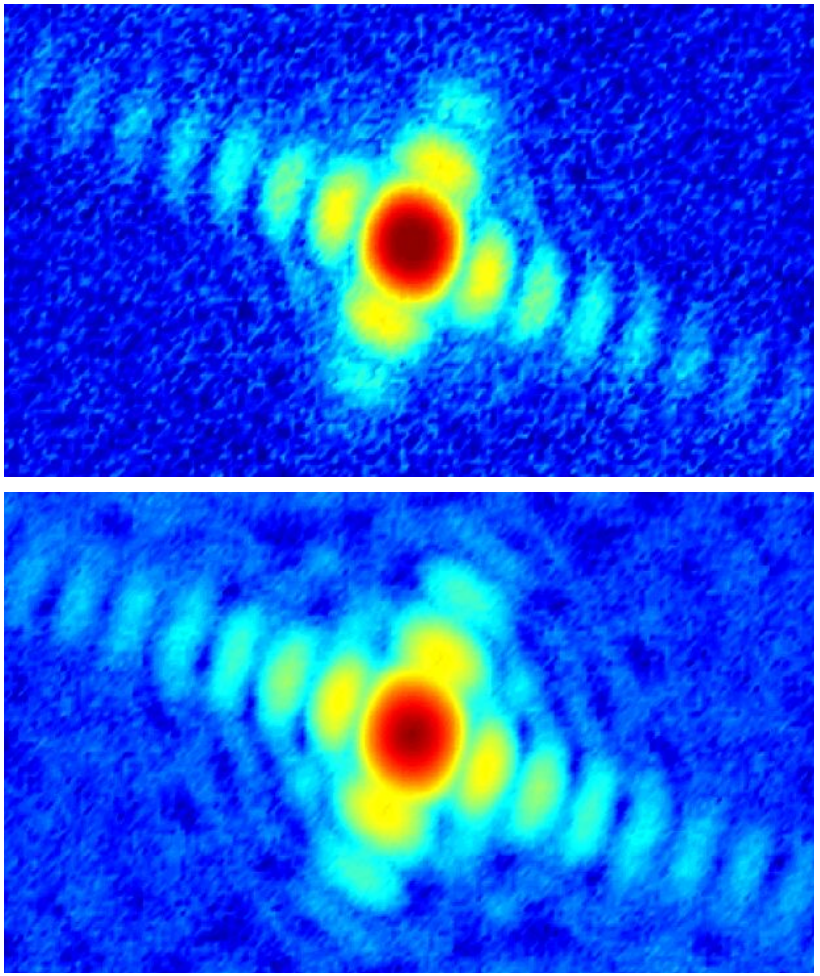
π/2

π/4 (x)

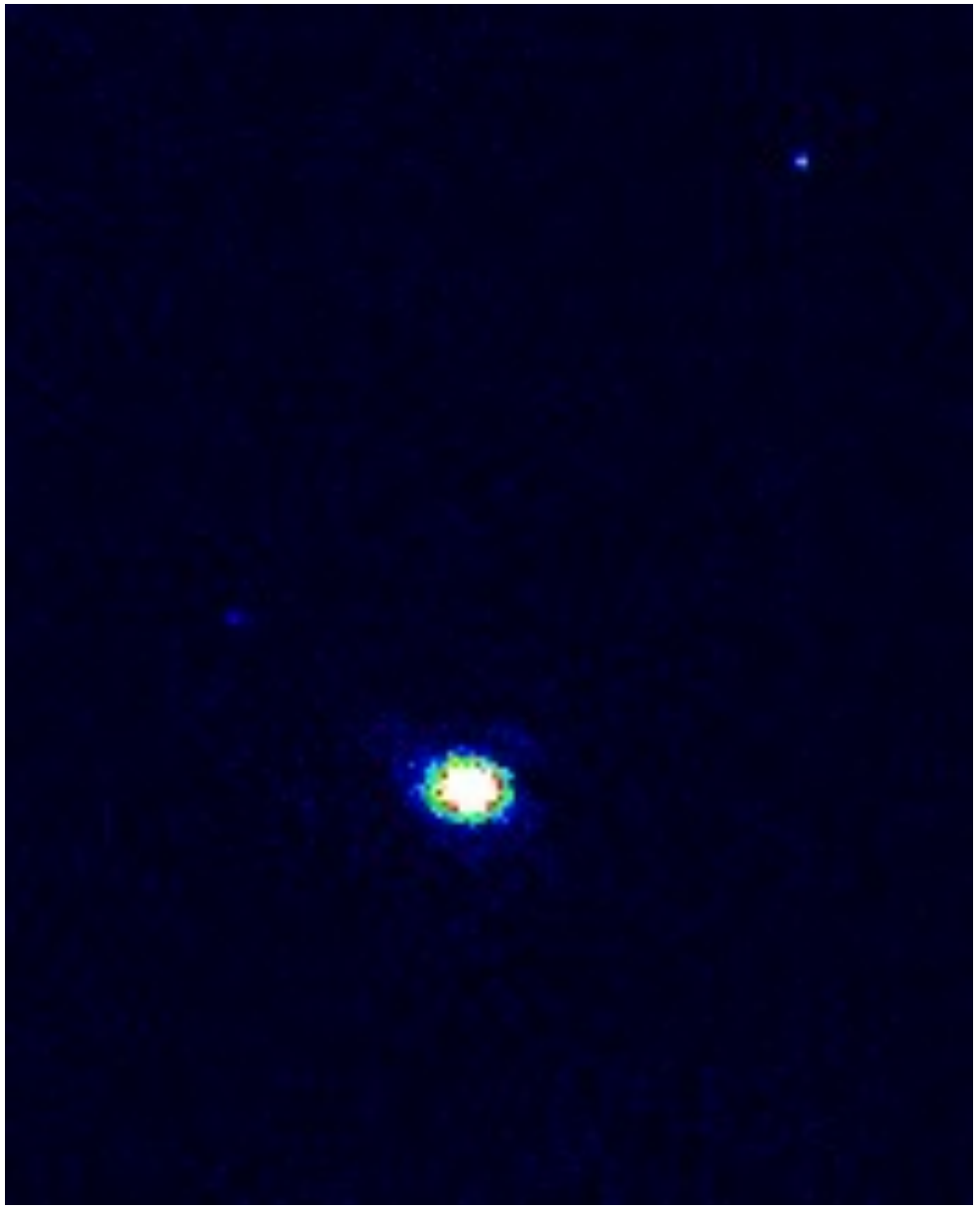
Reconstruction of Ag Nanocrystal

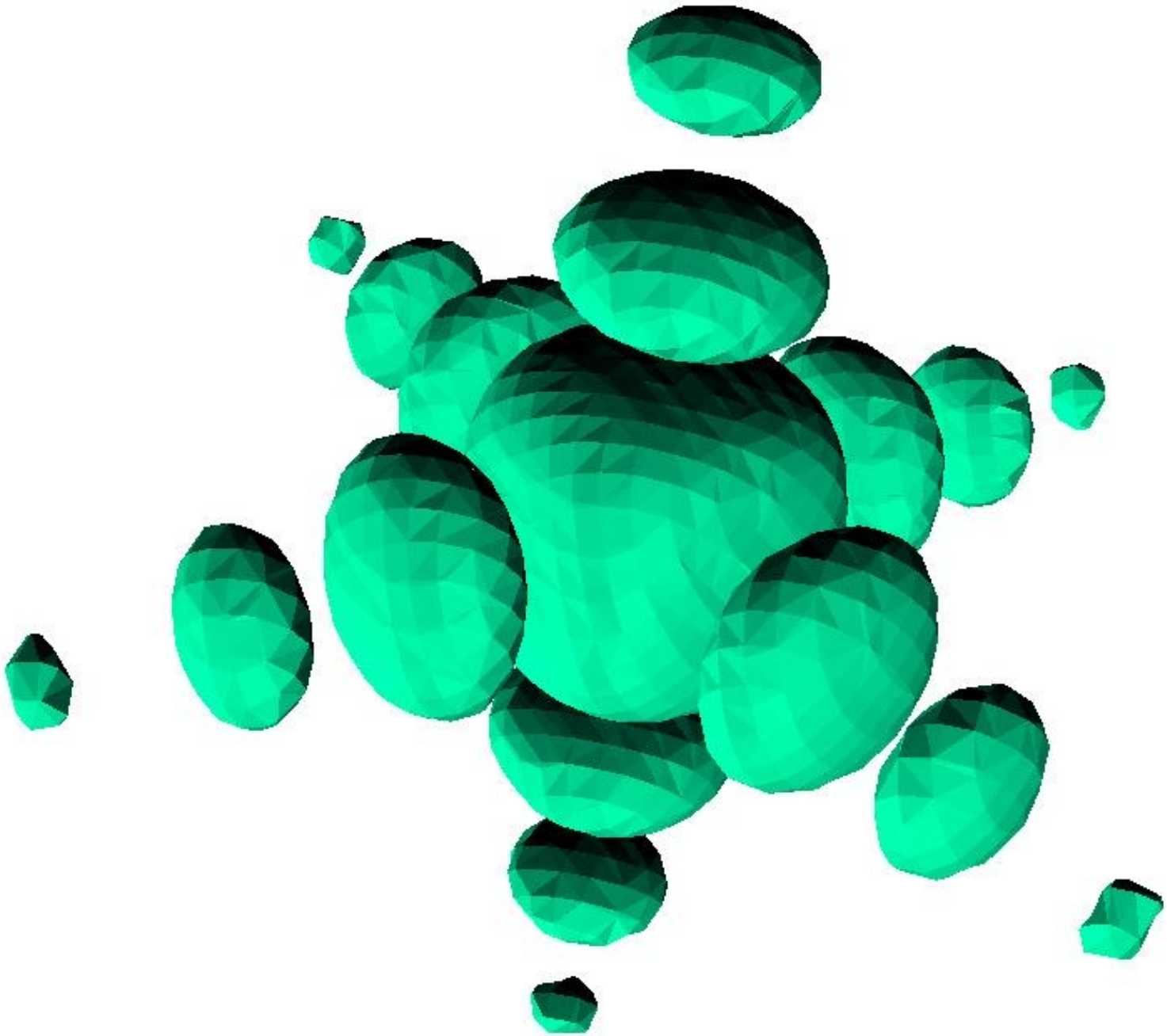


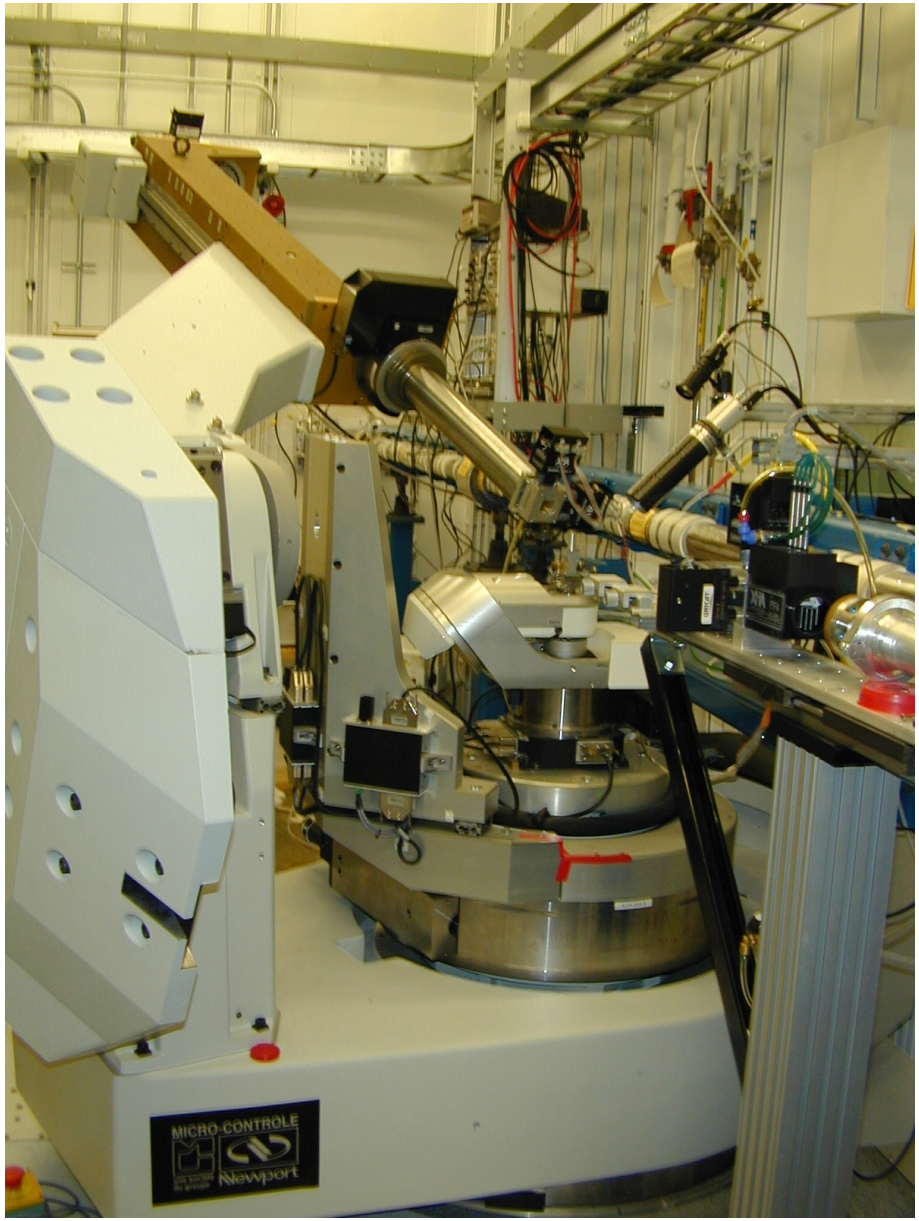
200nm

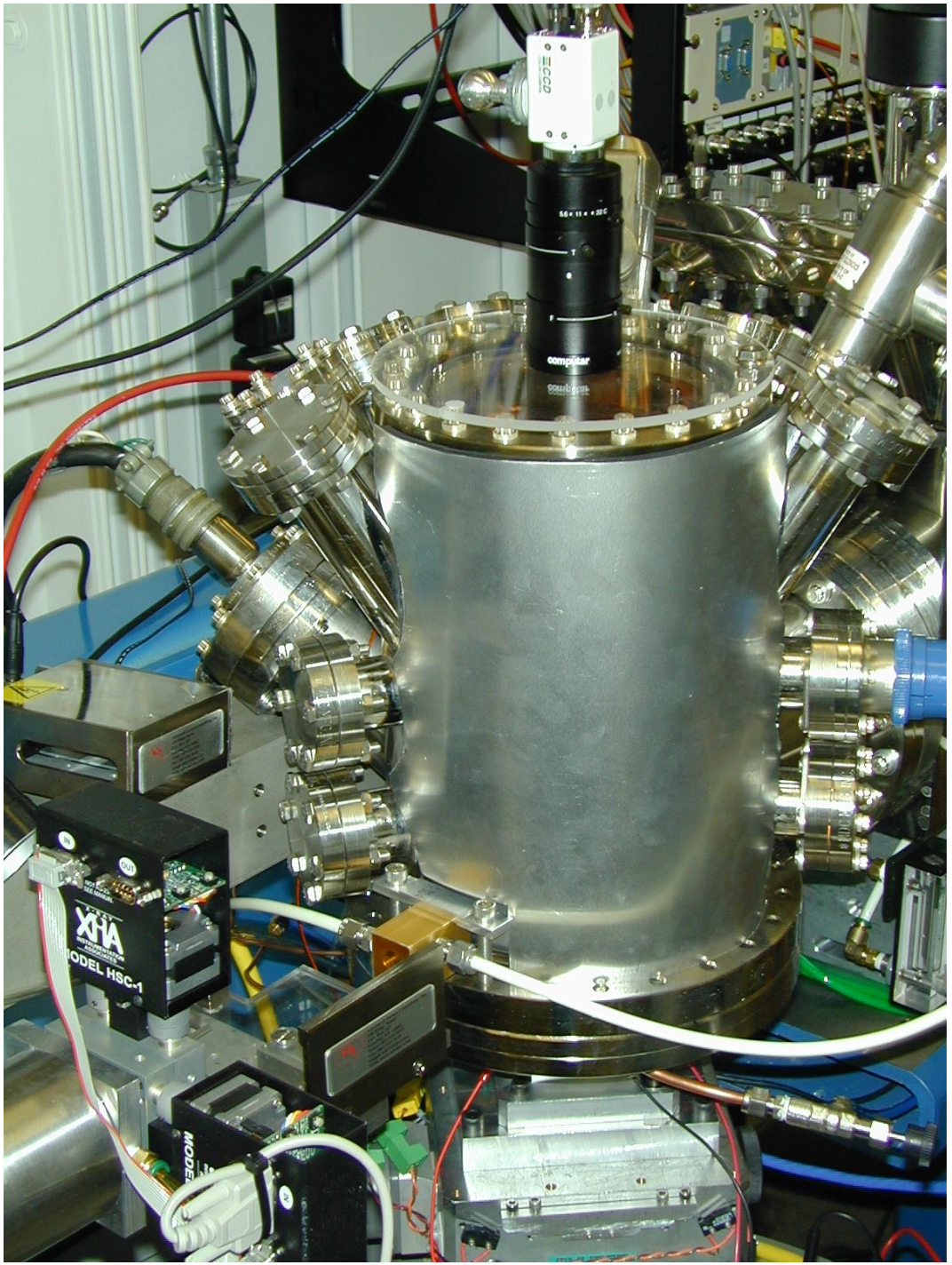


Rocking scan of Ag cubes with 0.01° steps

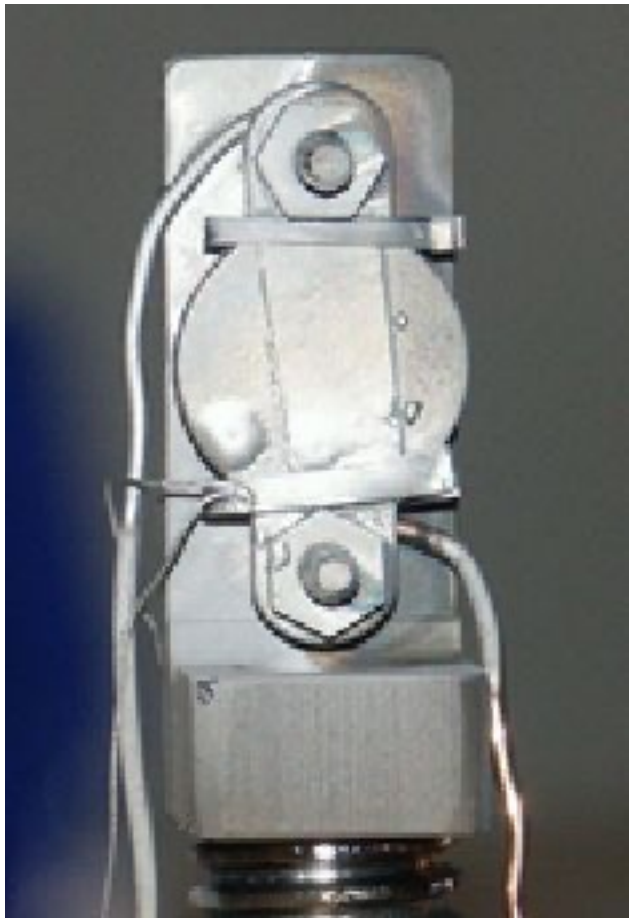


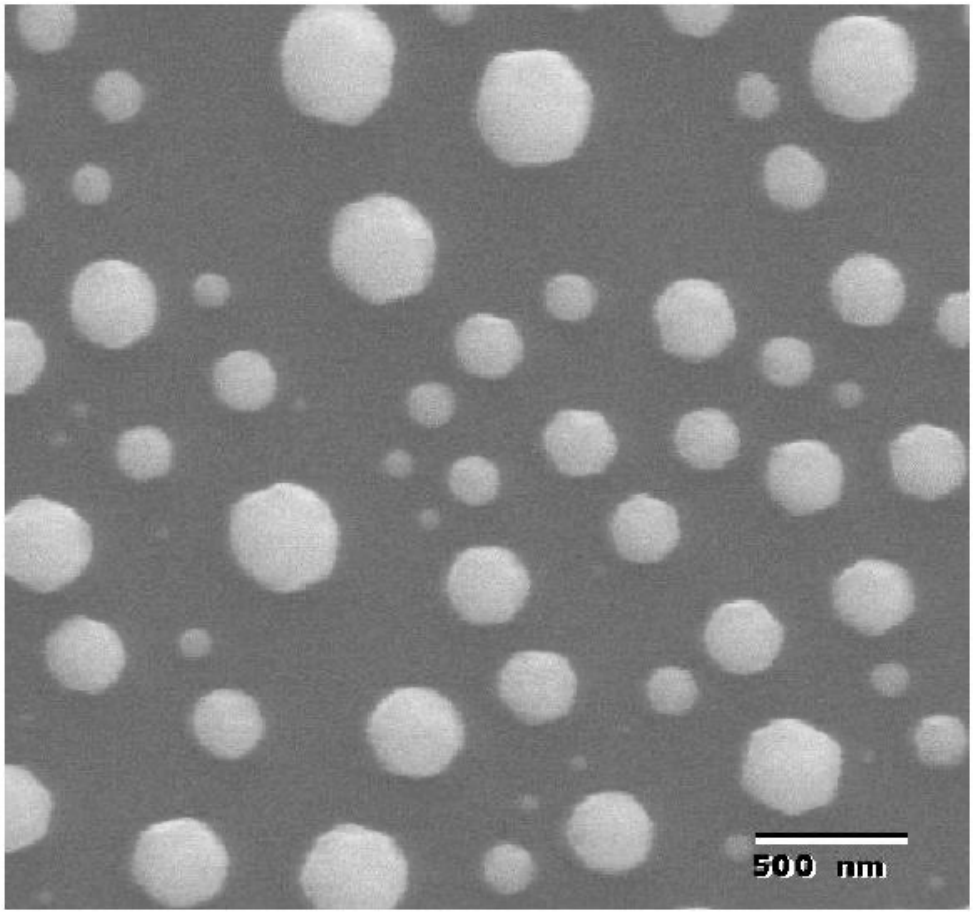



MICRO-CONTROLE
Newport

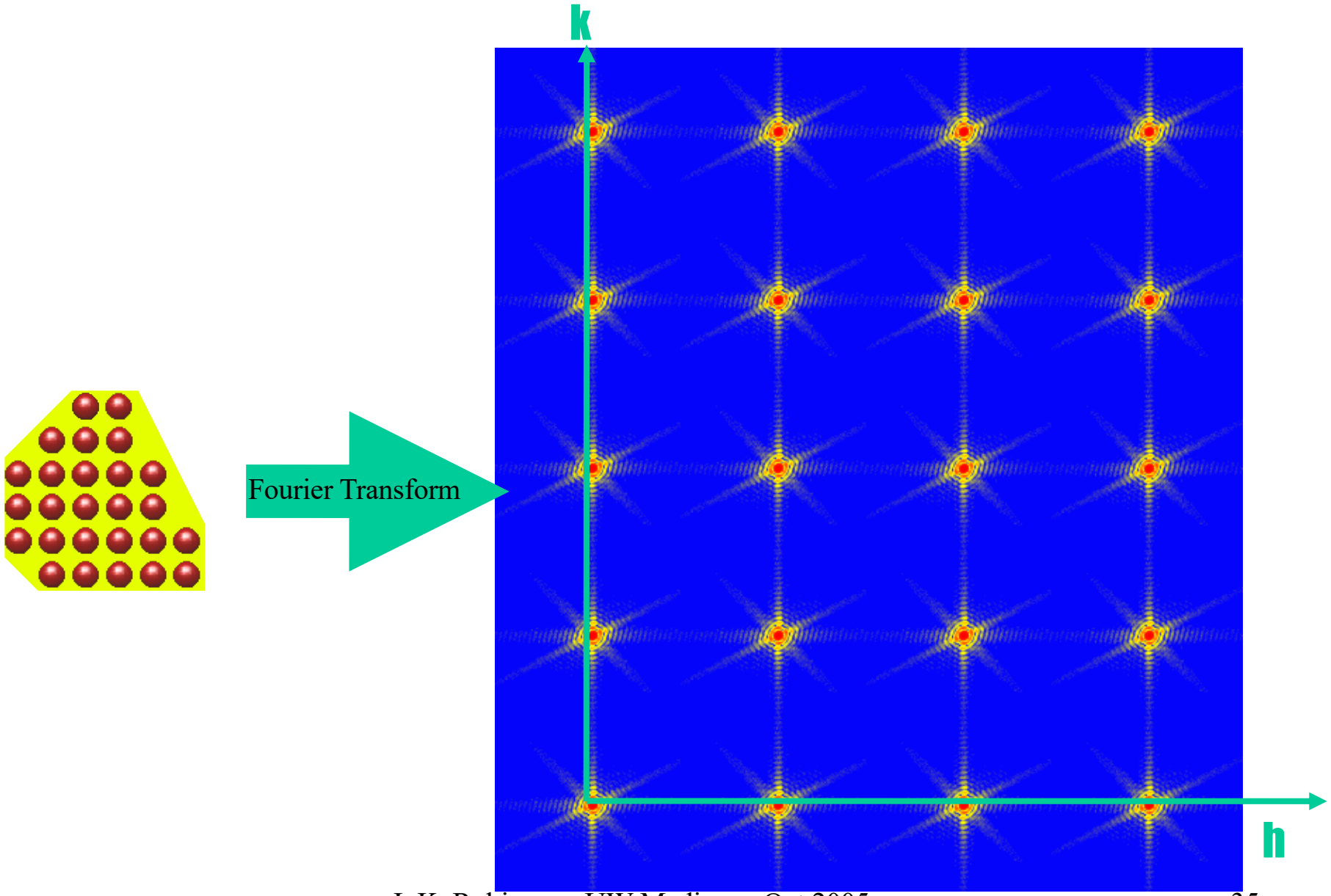

computar
MODEL HSC-1

In situ growth of Pb crystals





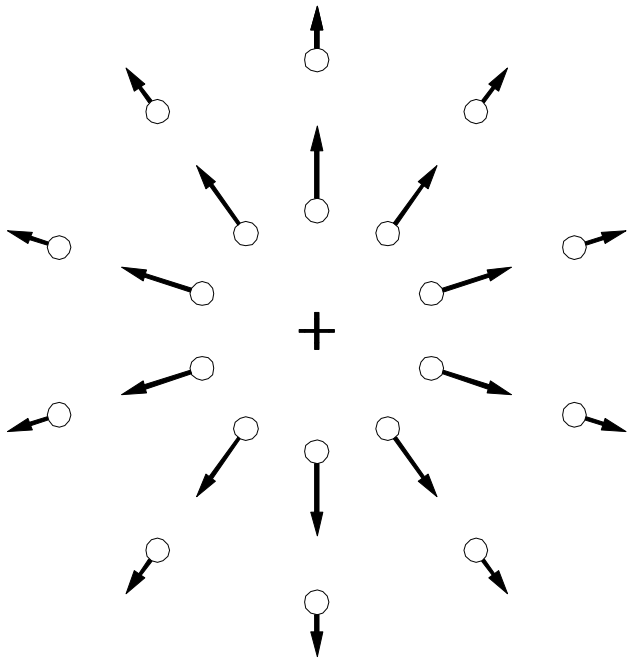
Coherent Diffraction from Crystals

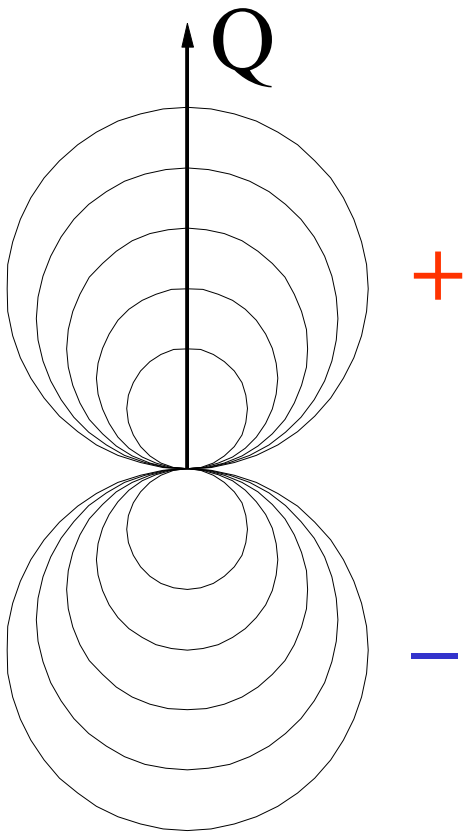


Diffraction by Strain of Point Defect

$$A \sim \sum e^{iQ\cdot(R_j+u_j)}$$
$$\approx \sum e^{iQ\cdot R_j}(1+iQ\cdot u_j)$$

Imaginary density





Good statistics, 3D diffraction data

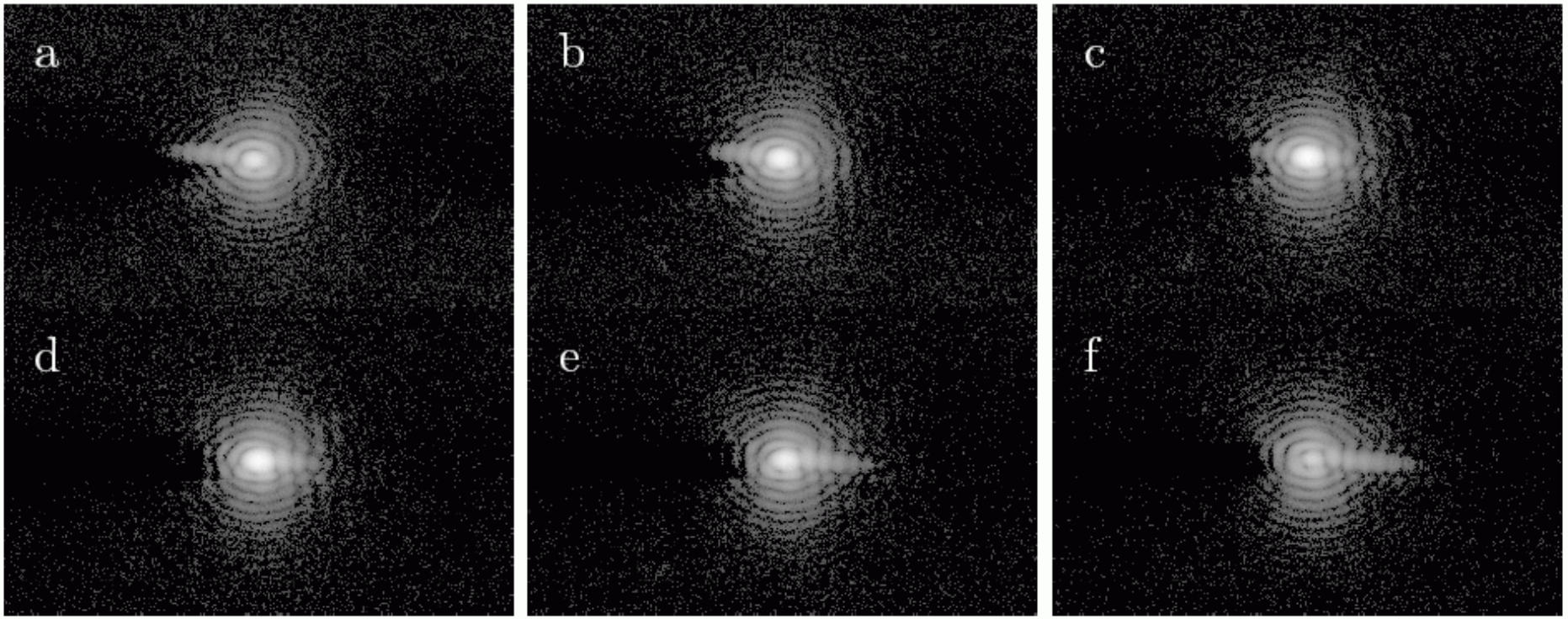
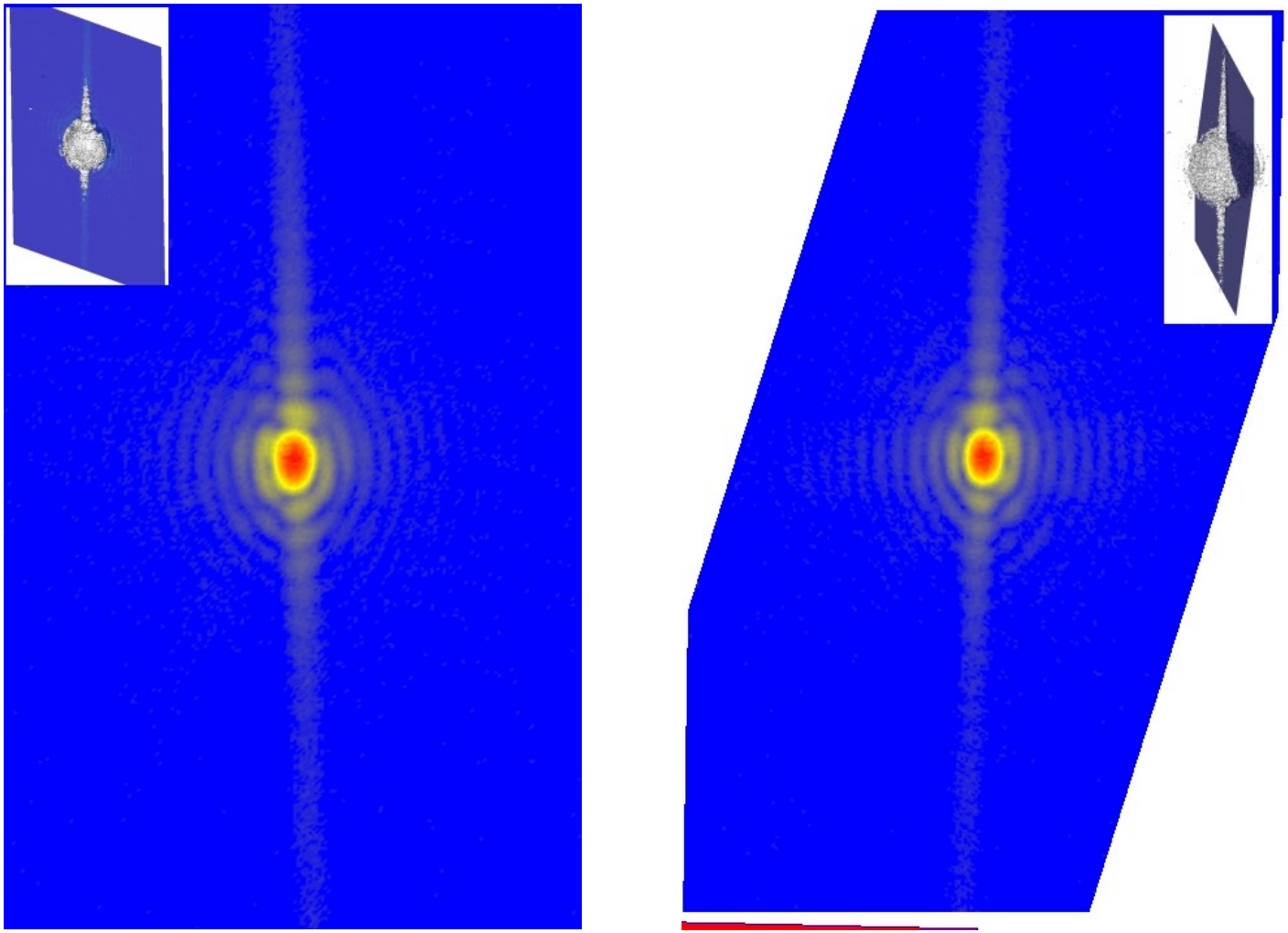
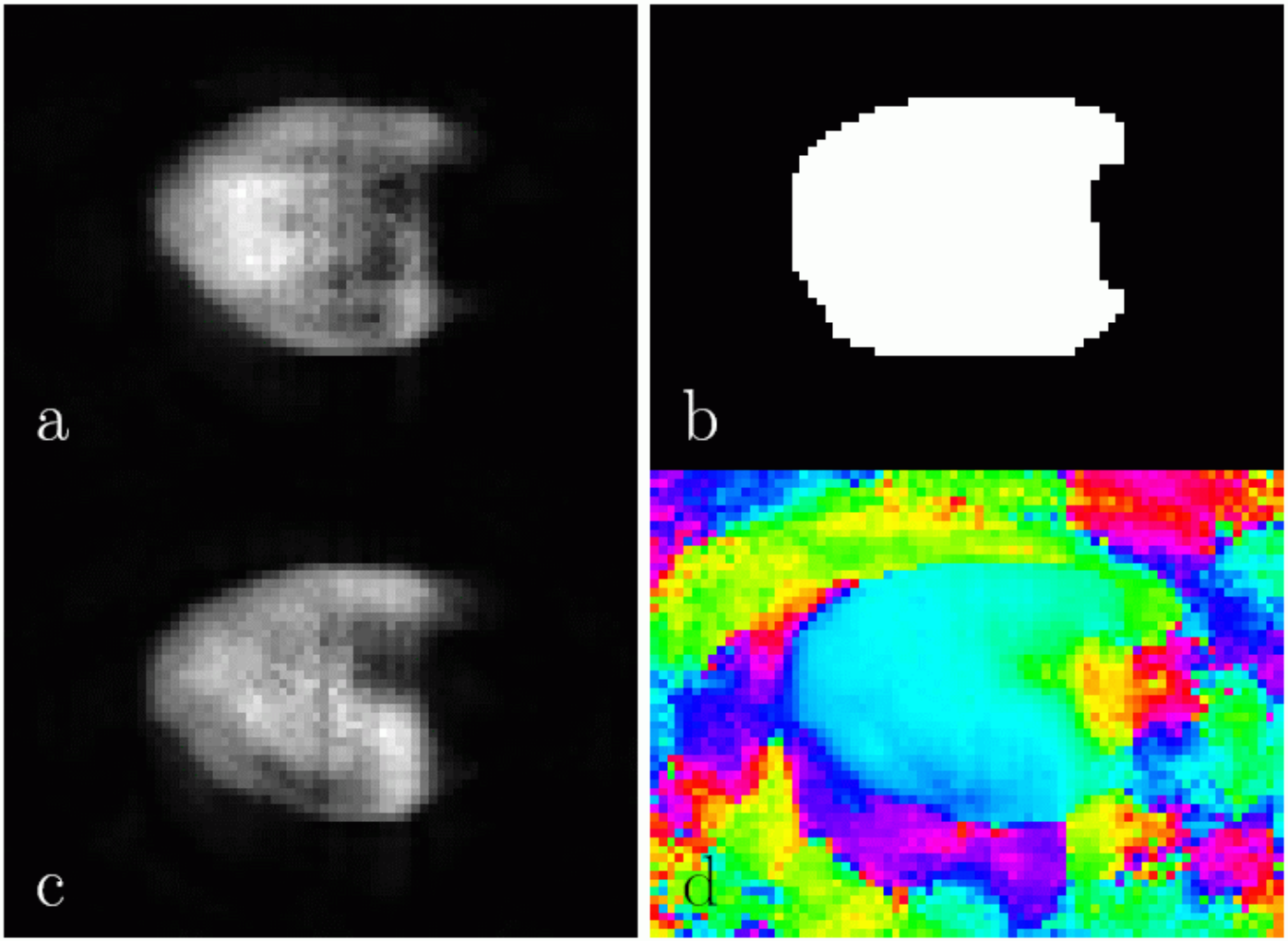


Figure 4.12: Center slices from 3D CXD pattern from Pb sample, on a log scale. Data file 296 from 10/03.

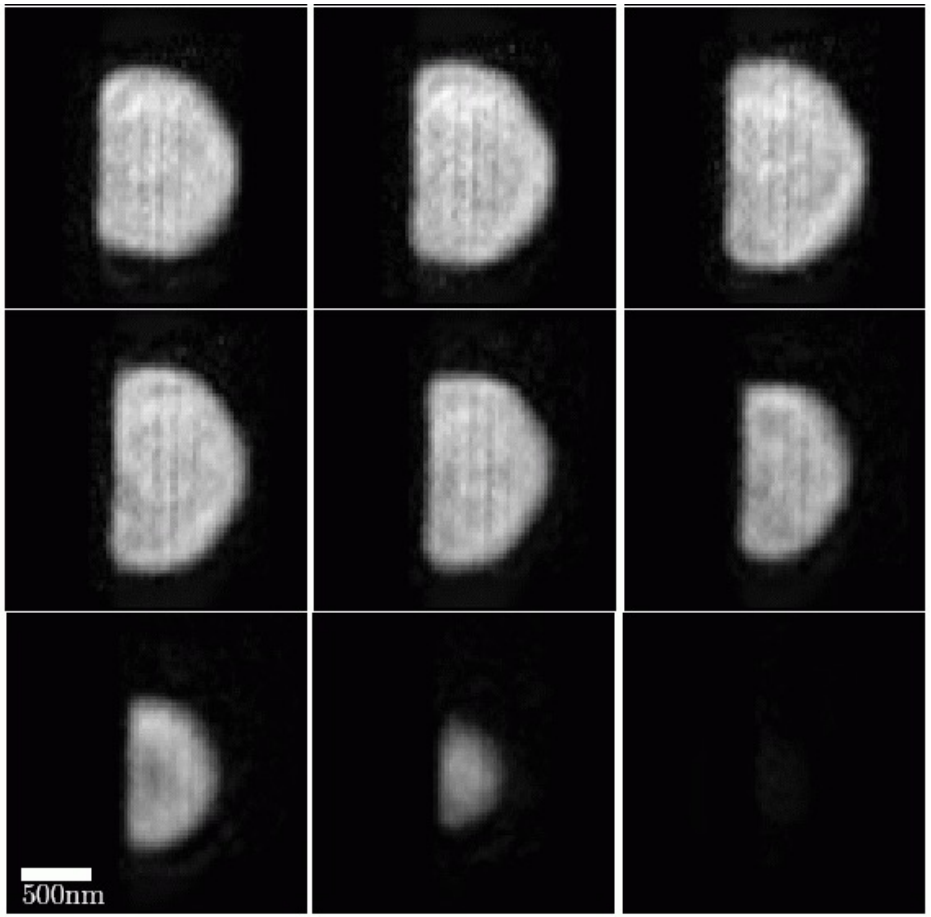
3D data along special directions

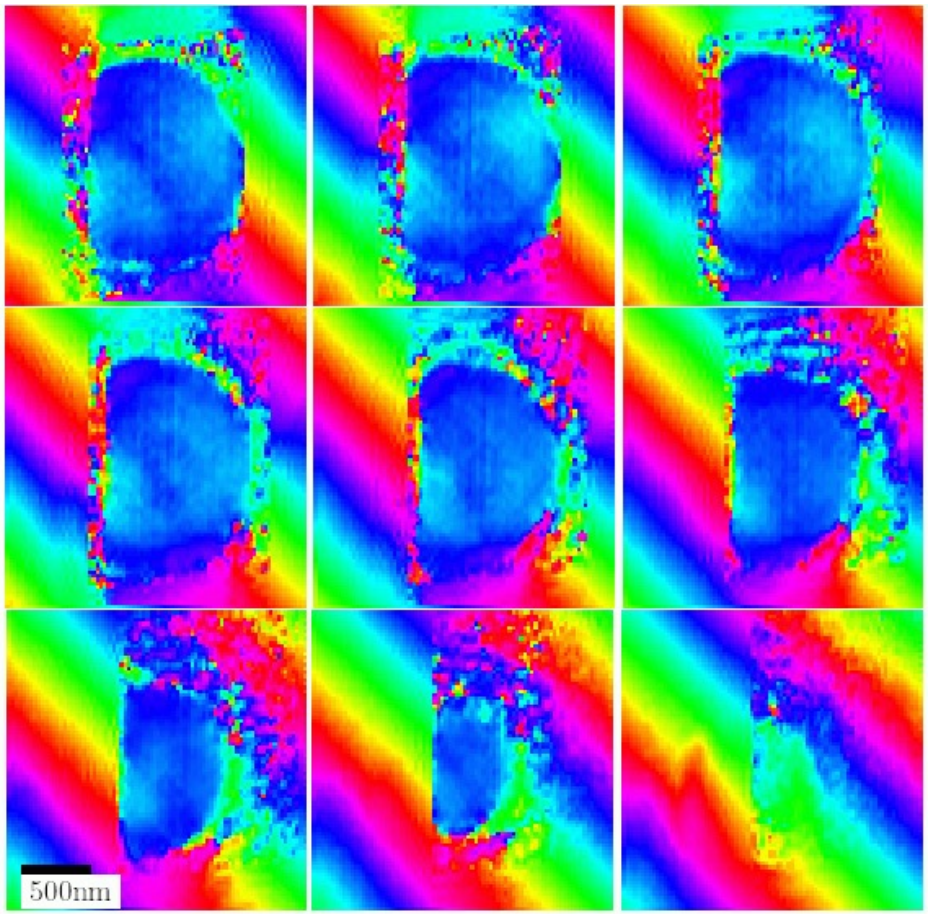


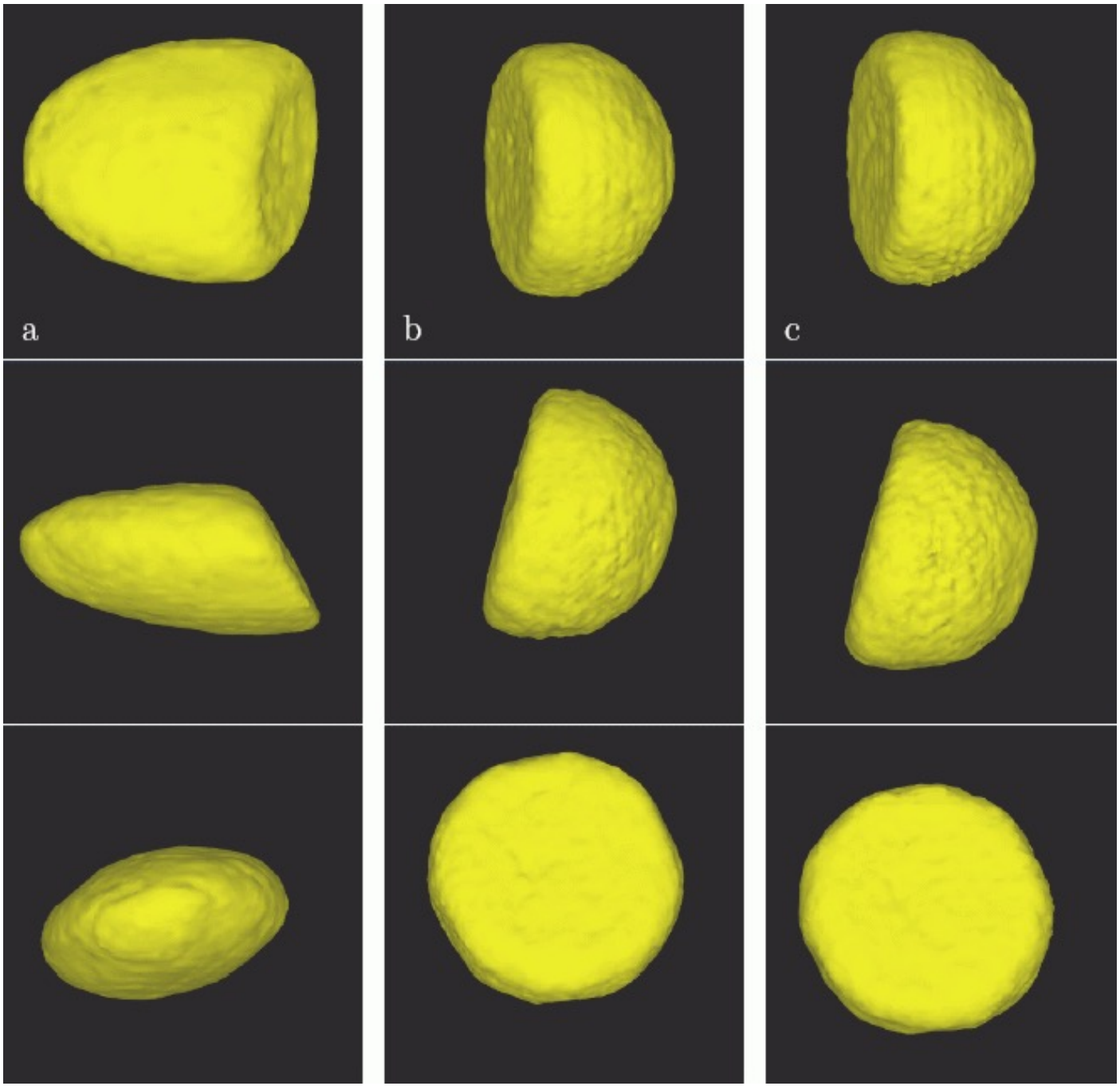
Learn shape of “tight” support



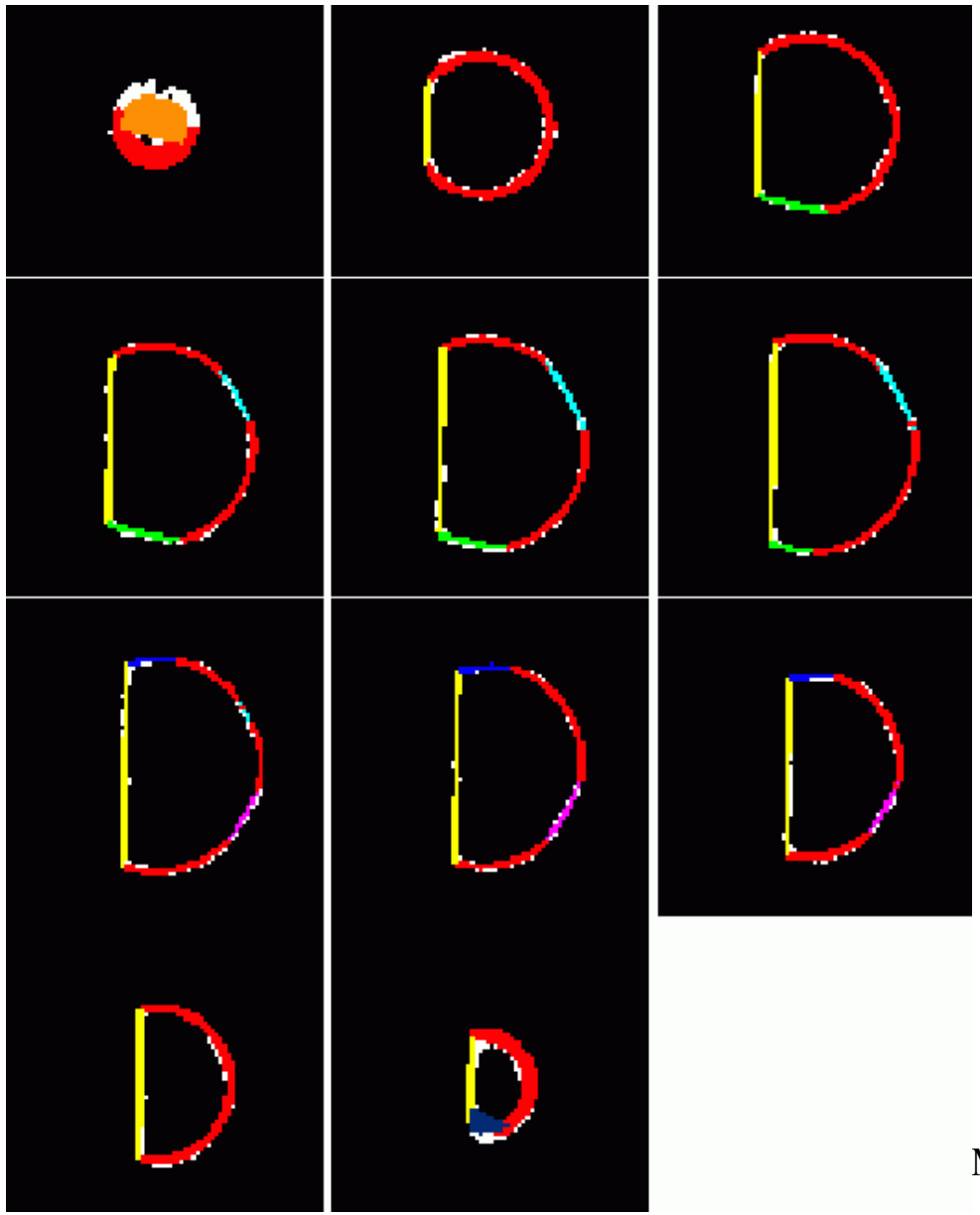
Then refine amplitude *and* phase





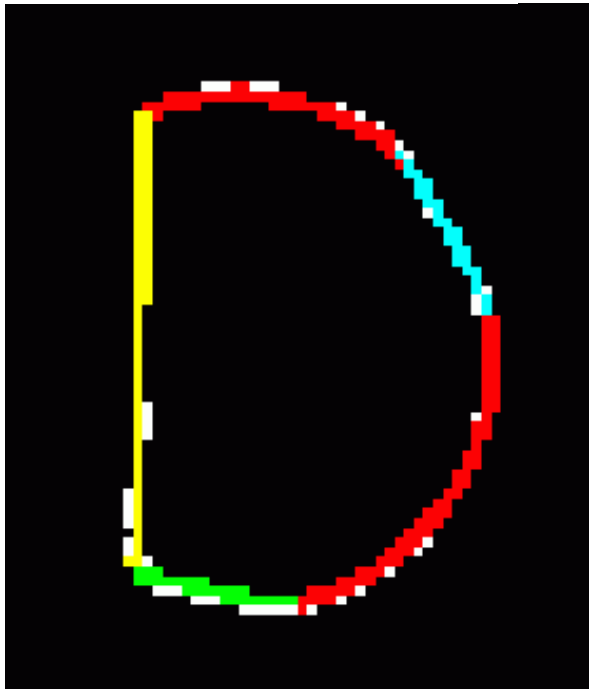

a
b
c

Fitting to facetted shape



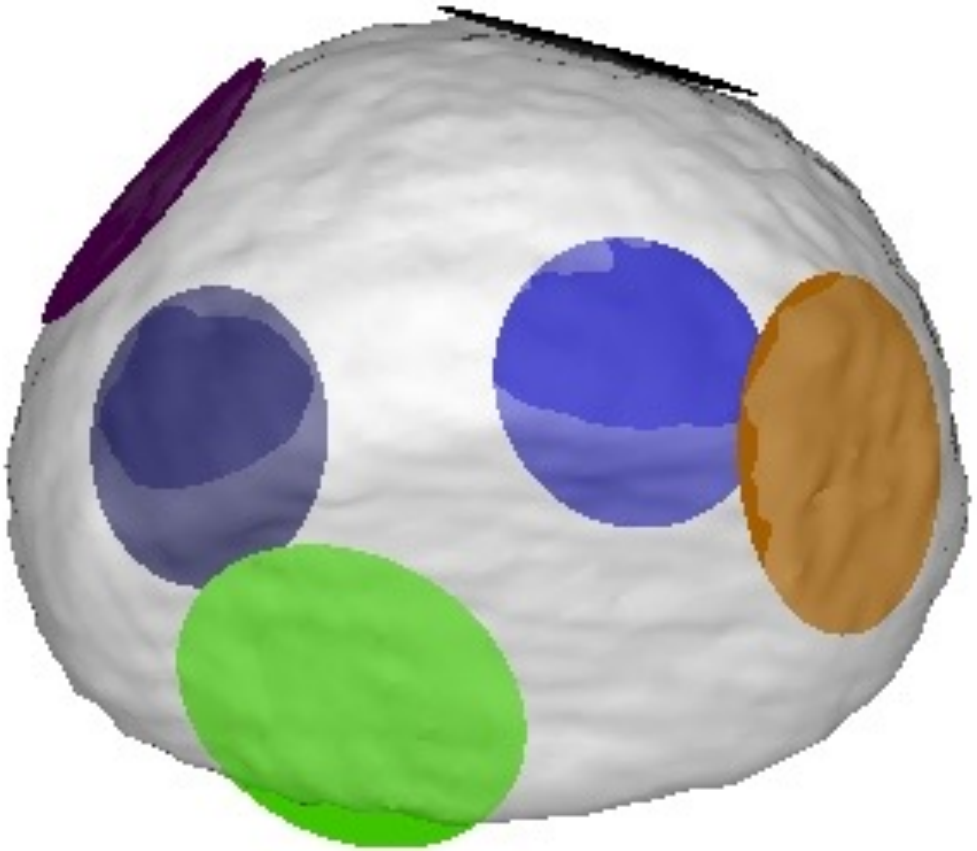
	$\|R\|$		P0	P1	P2	P3	P4	P5	P6
	9.4	P0	0	85	149	79	134	106	71
	25.7	P1		0	123	164	83	76	102
	25.1	P2			0	72	67	74	110
	25.9	P3				0	111	106	76
	25.4	P4					0	113	68
	25.4	P5						0	176
	26.0	P6							0 0

Angles between facets

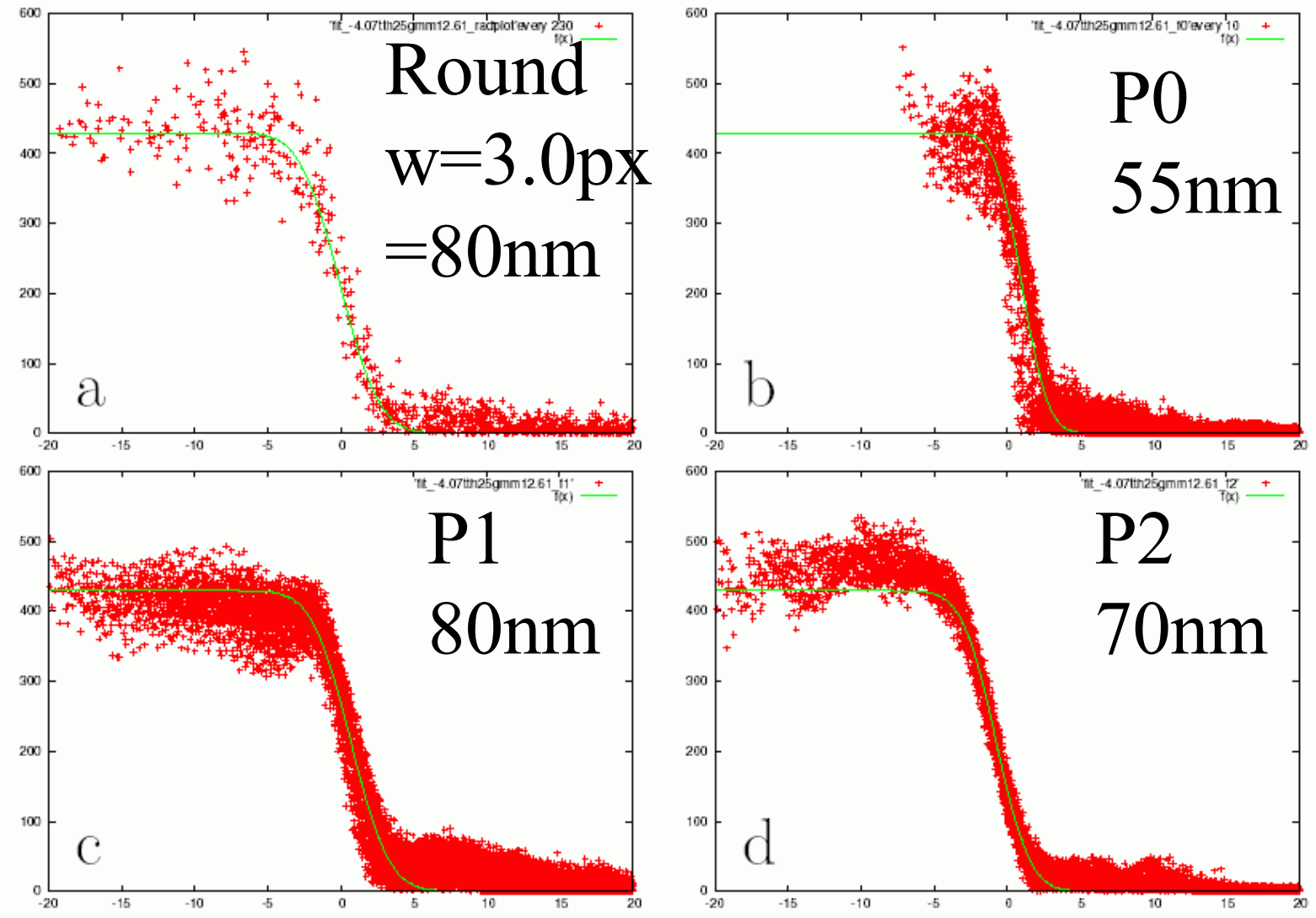


Madison, Oct 2005

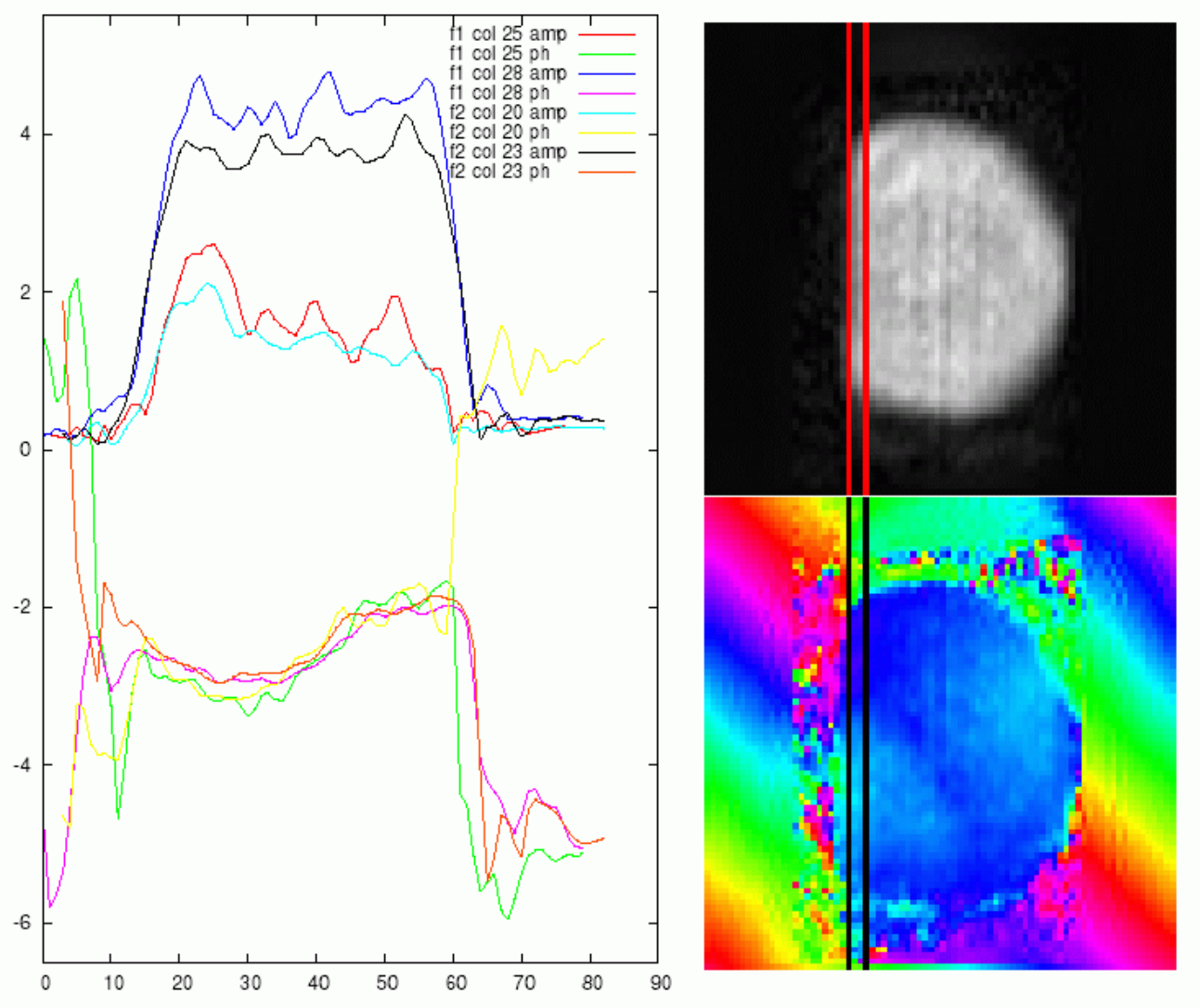
Facets of Equilibrium Crystal Shape



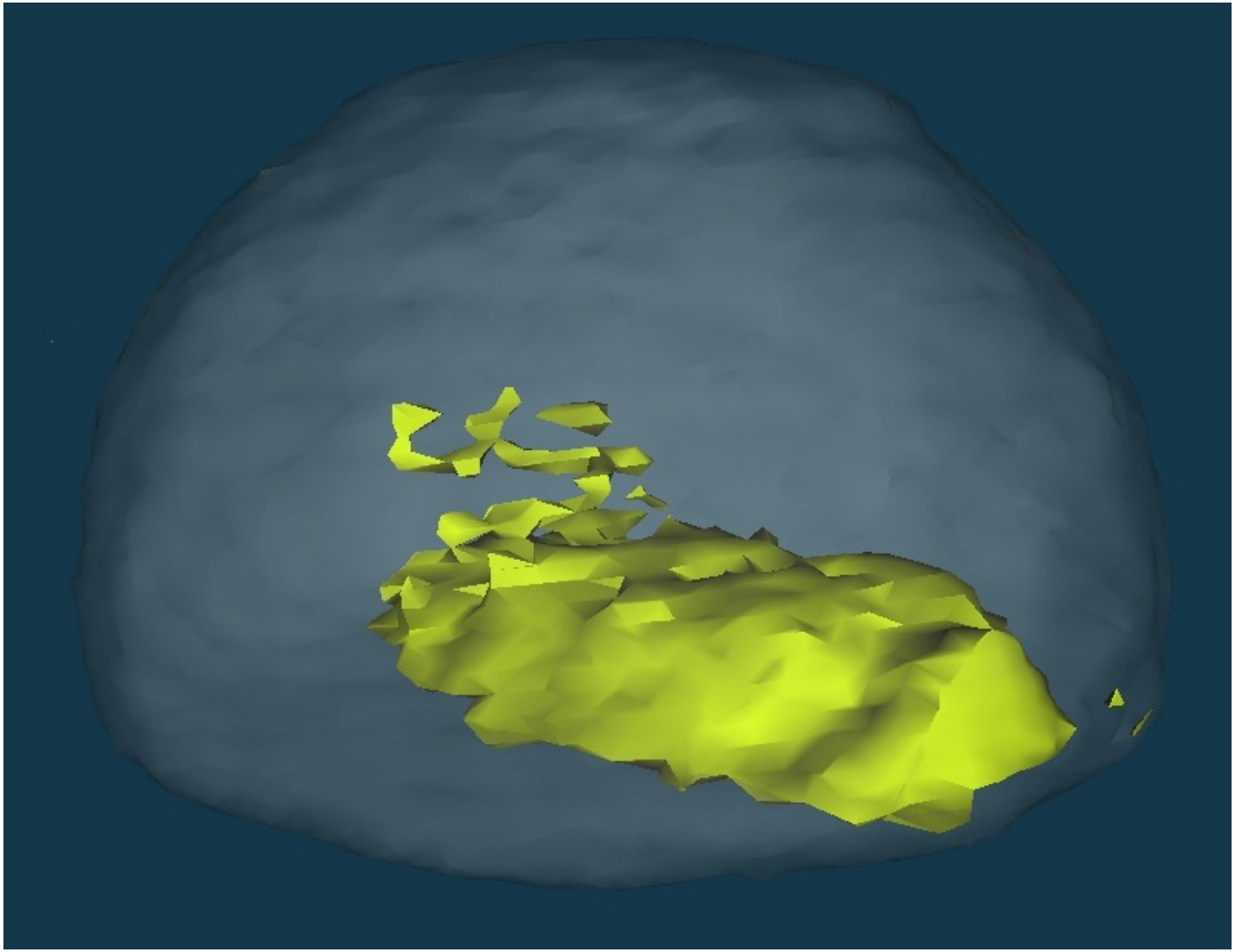
Density distribution across surface



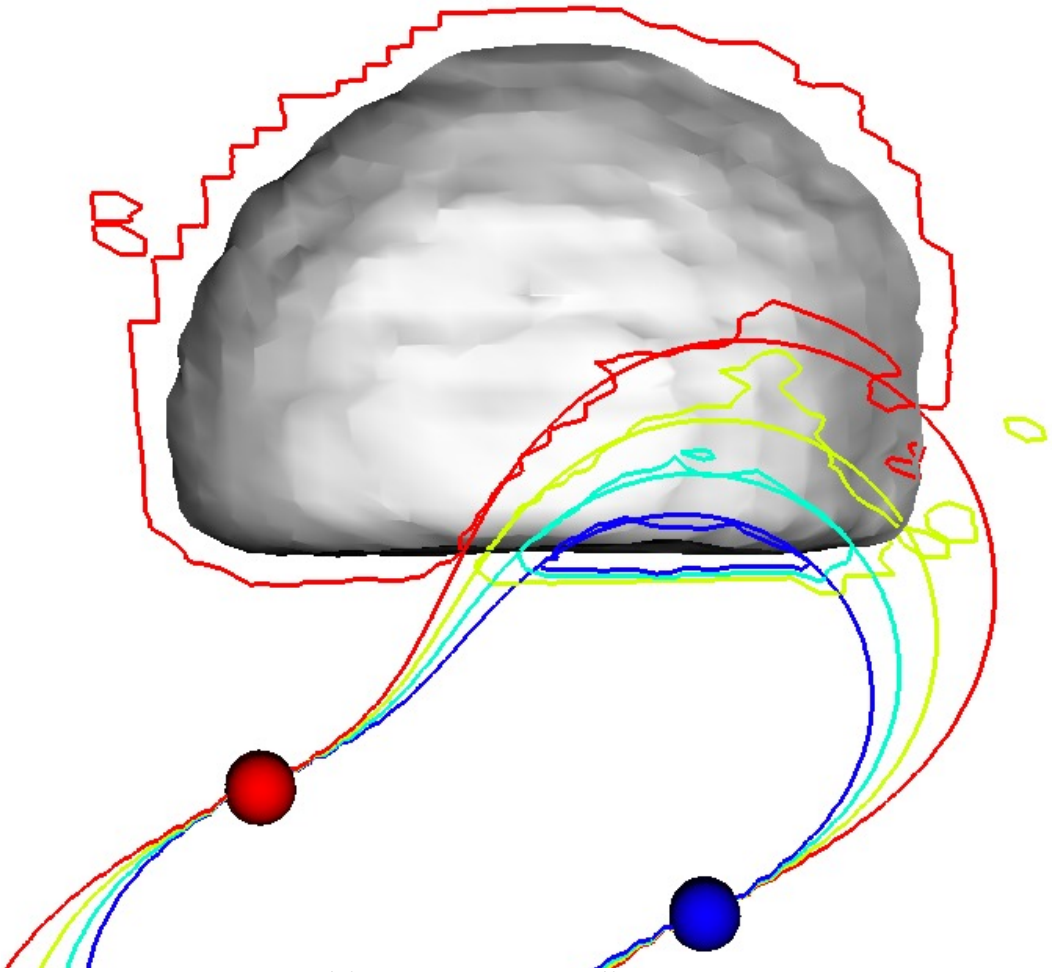
Phase structure near substrate interface



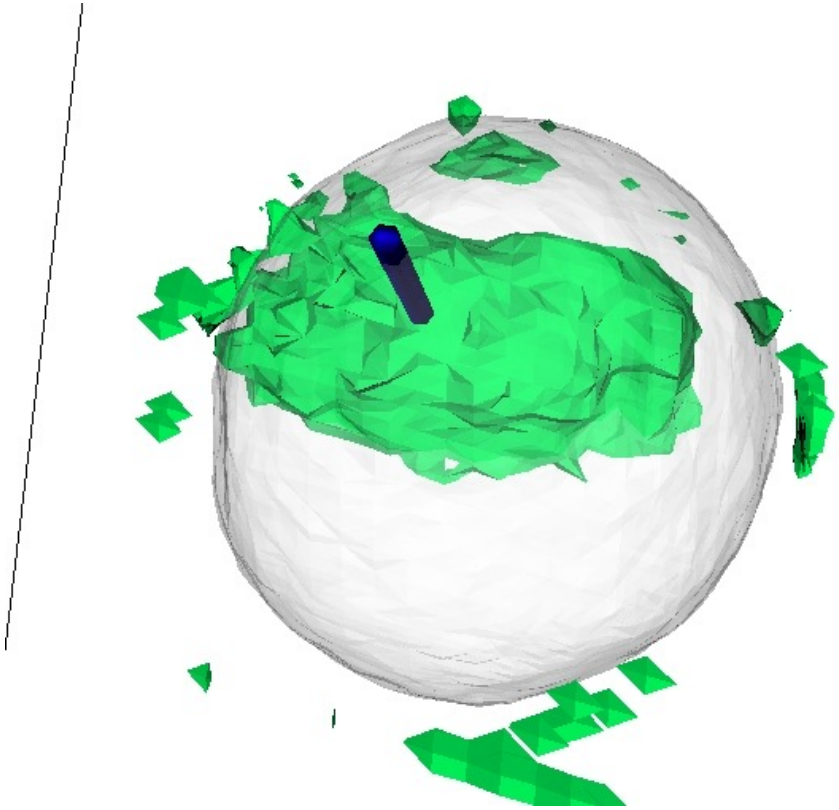
Modeling of 3D Phase Bump

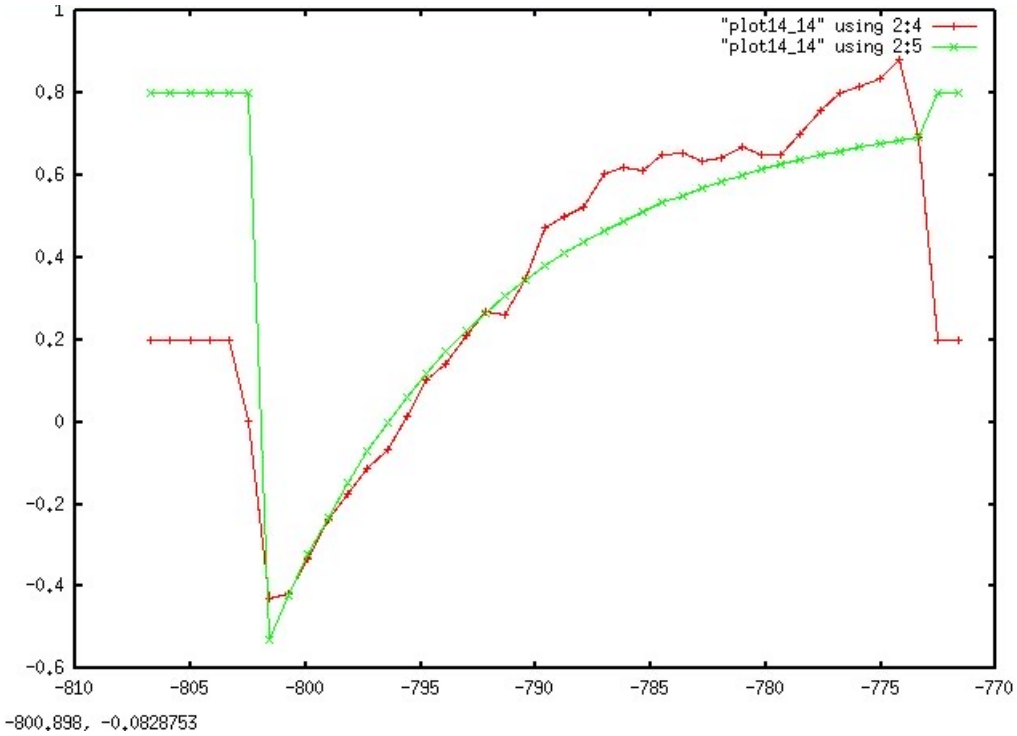


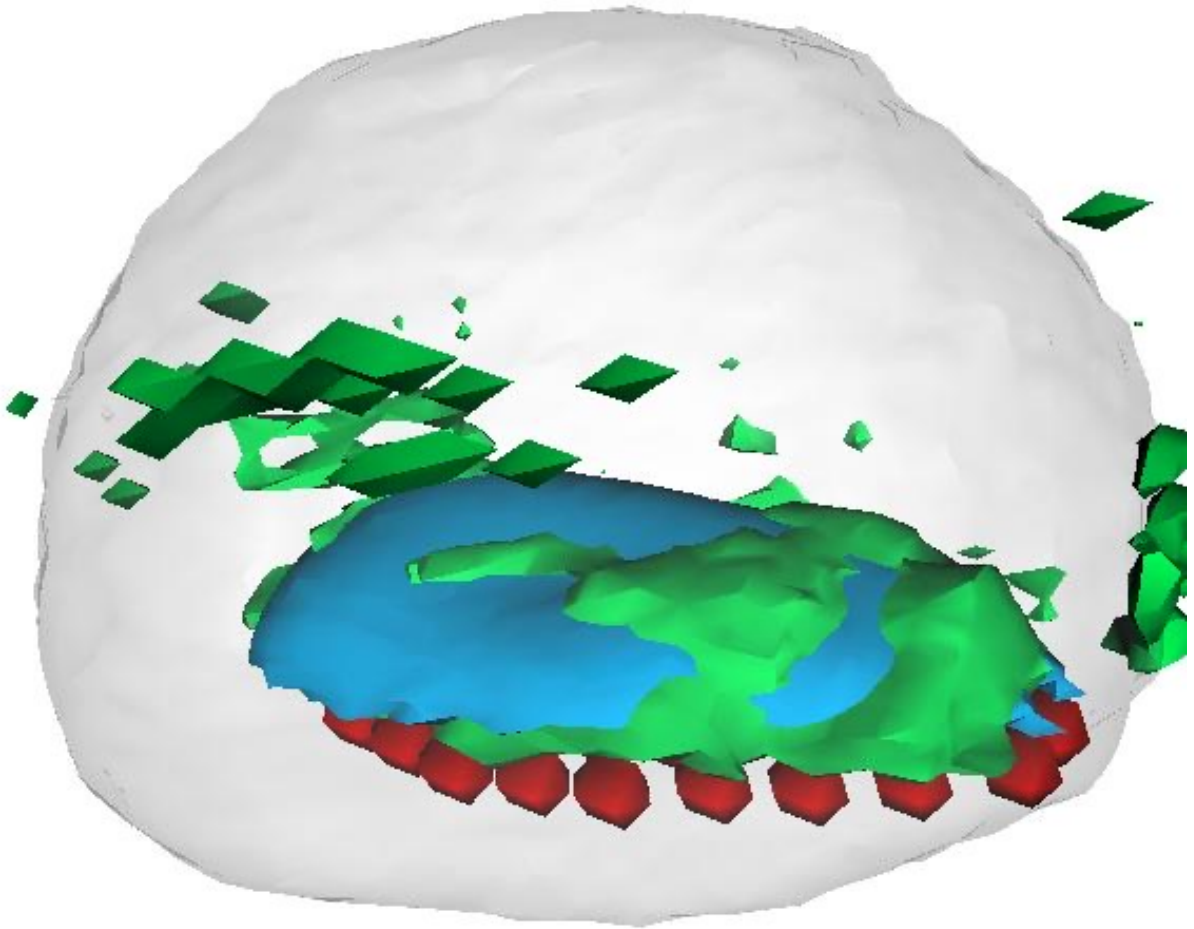
Field lines of Point Charges



Line scan through phase

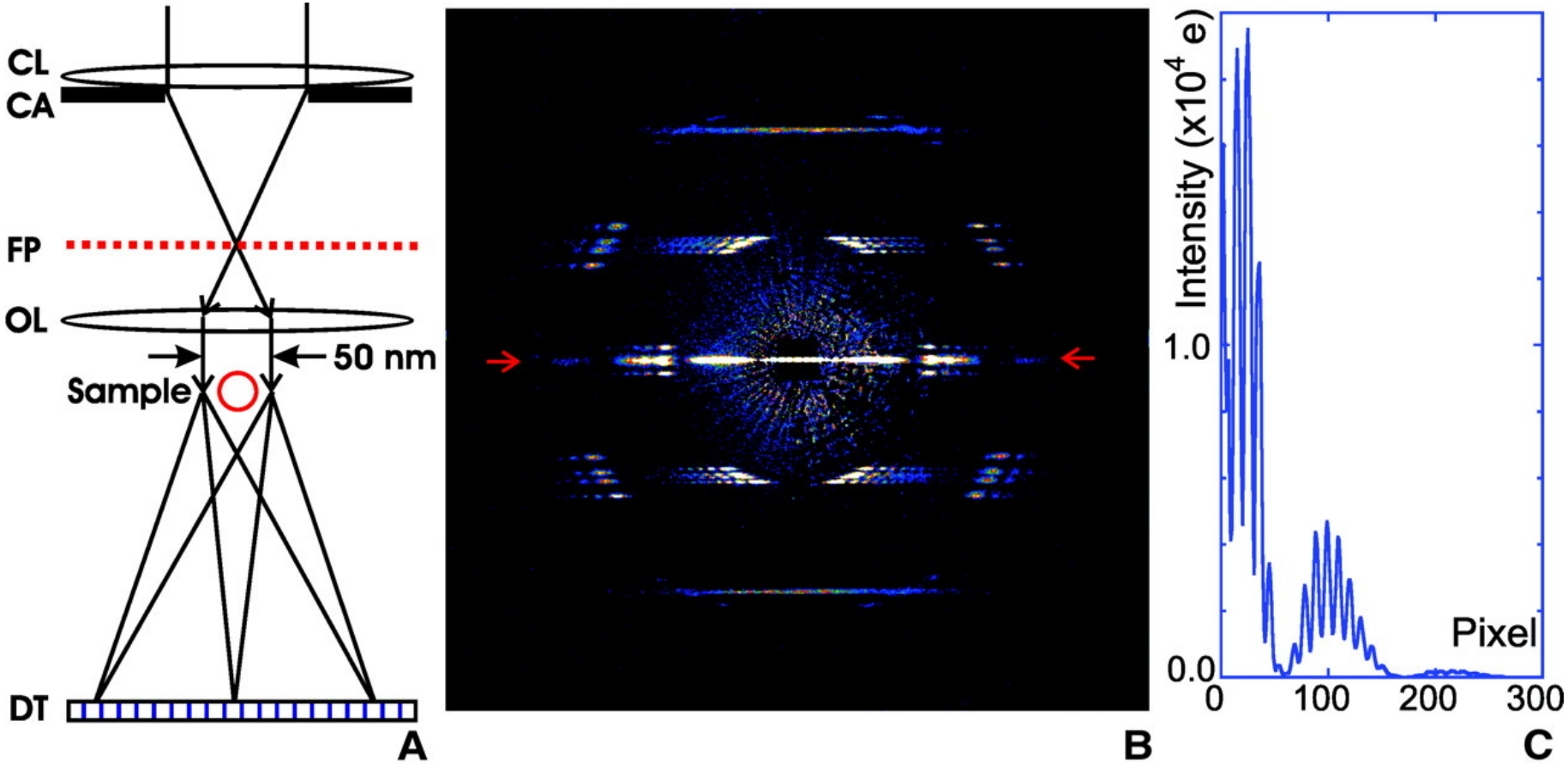






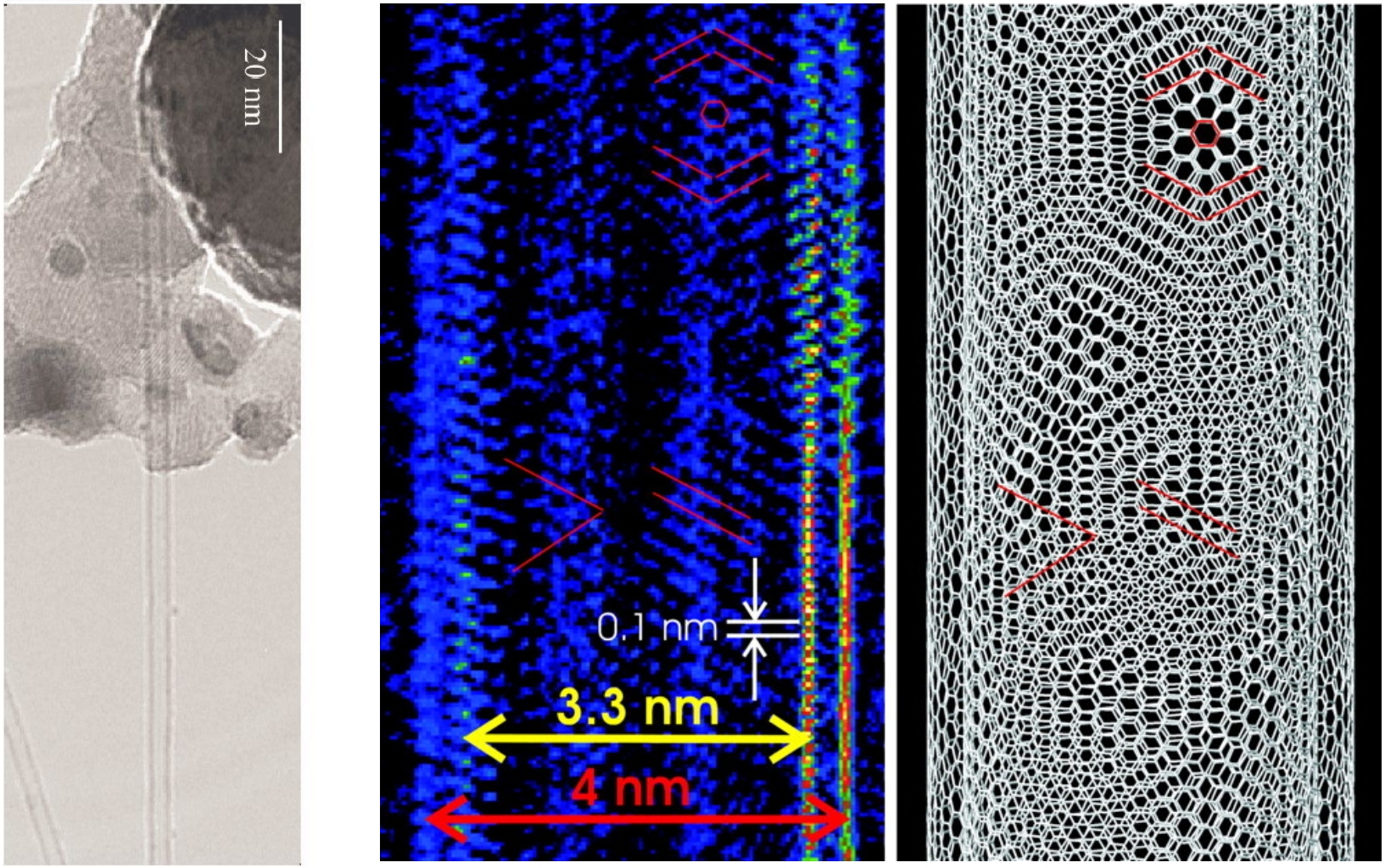
Electron Diffraction from C-nanotube

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

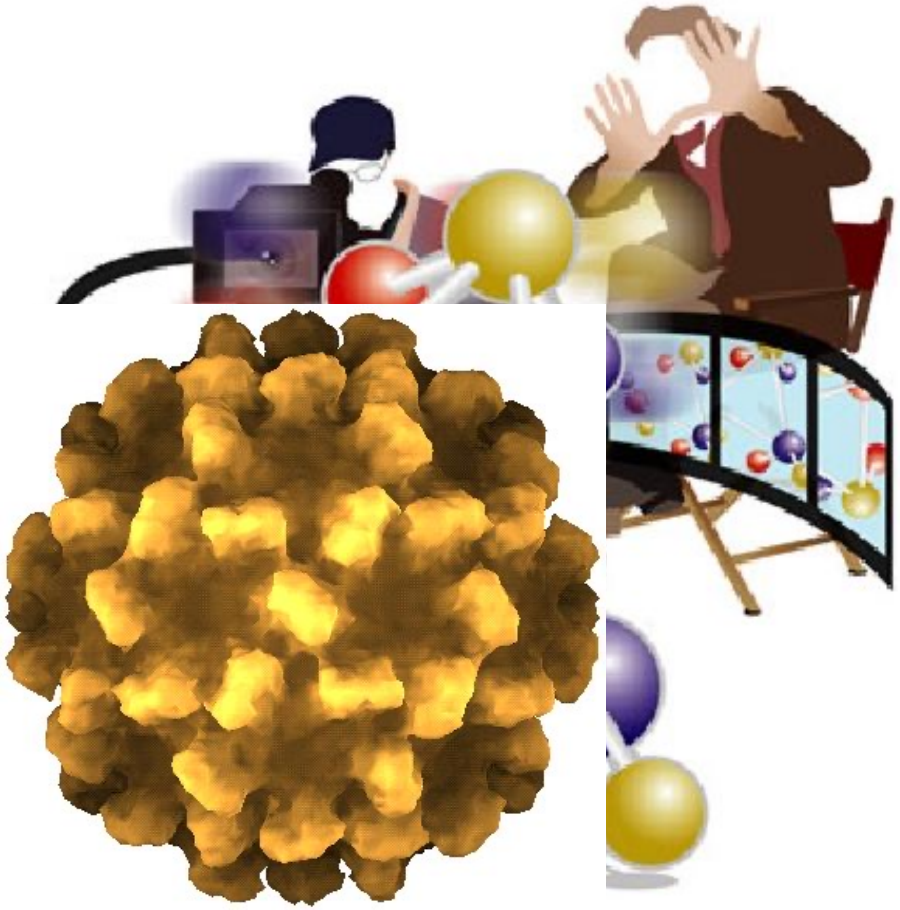


Images of DW C-nanotube

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