

Use of Coherence in X-ray Diffraction Studies of Phase Objects

- Ian Robinson
- Ivan Vartanyants
- Franz Pfeiffer
- Mark Pfeifer
- Garth Williams
- Meng Liang
- Ross Harder

Department of Physics
University of Illinois

ANKA Seminar
30 May 2005

Outline

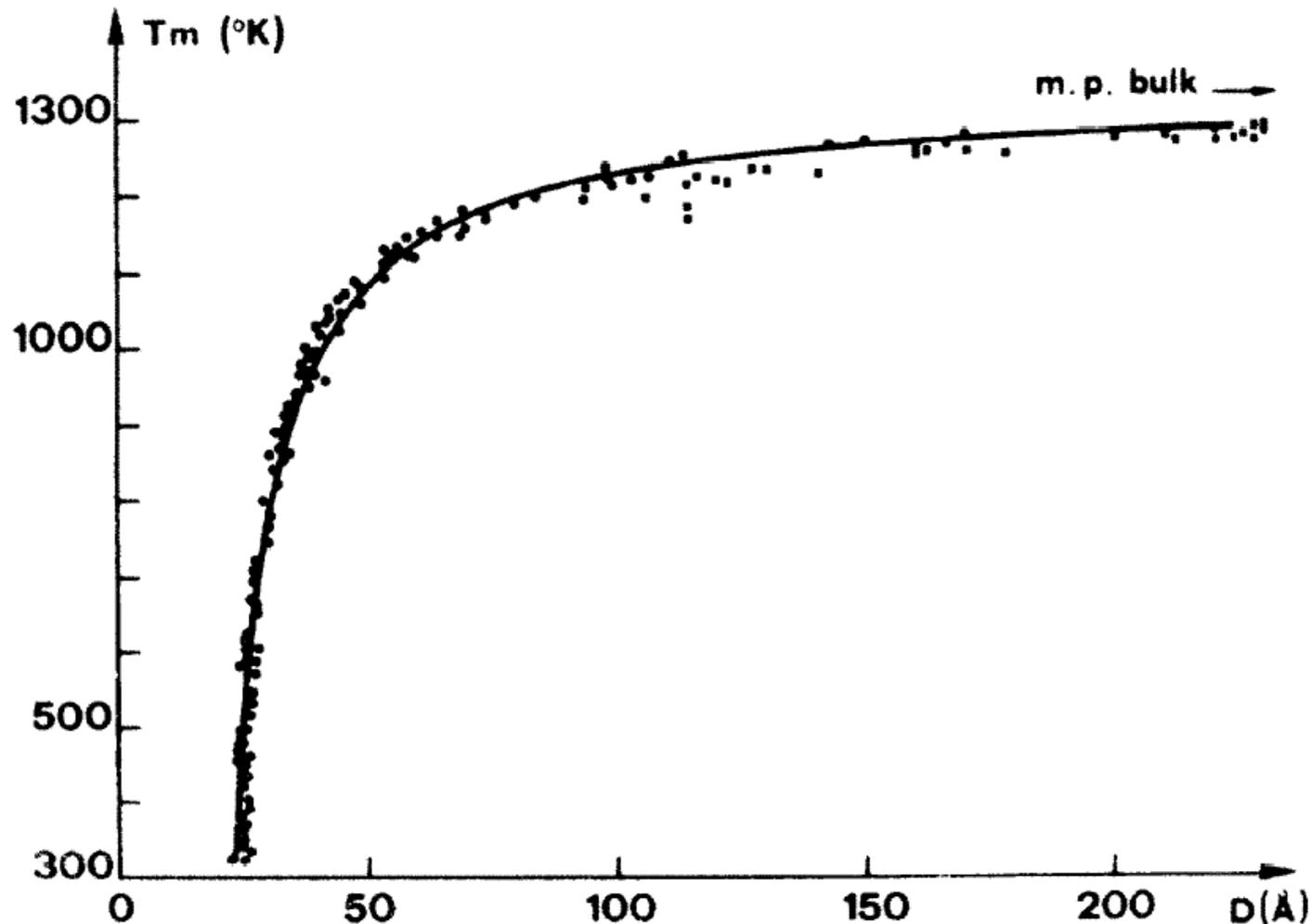
- Coherence in Diffraction
- The **Phase** Problem
- Nanocrystal Shapes
- Imaging of **Phase** Objects
- Strain fields within nanocrystals
- Explanation of off-center images

Goals of Coherent Diffraction

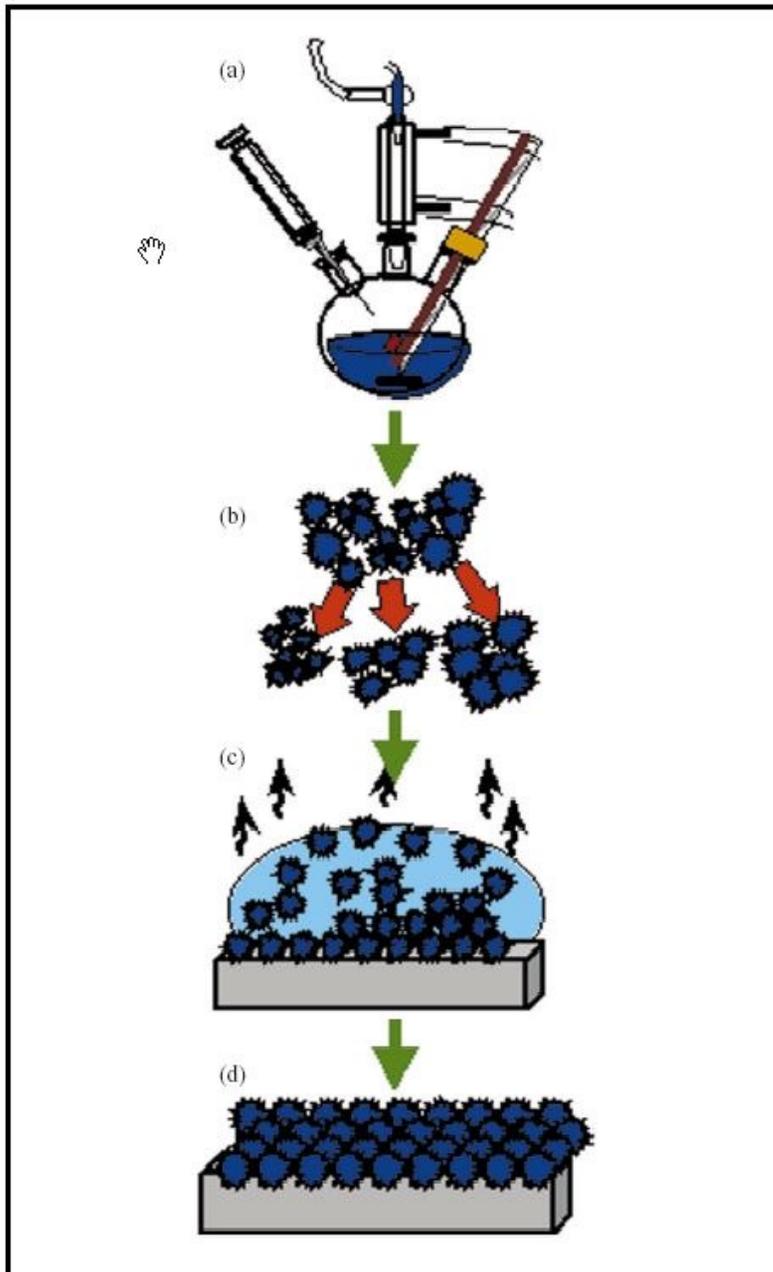
- Thermodynamic fluctuations
 - No ensemble average in CXD
- Probe of structure on **nm** scale
 - 1D, 2D and 3D
 - non-periodic object gives **continuous** $F(\mathbf{q})$
- **Oversampling** (in reciprocal space) permits solution of the **phase** problem

Size-dependent Melting of Au Particles

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

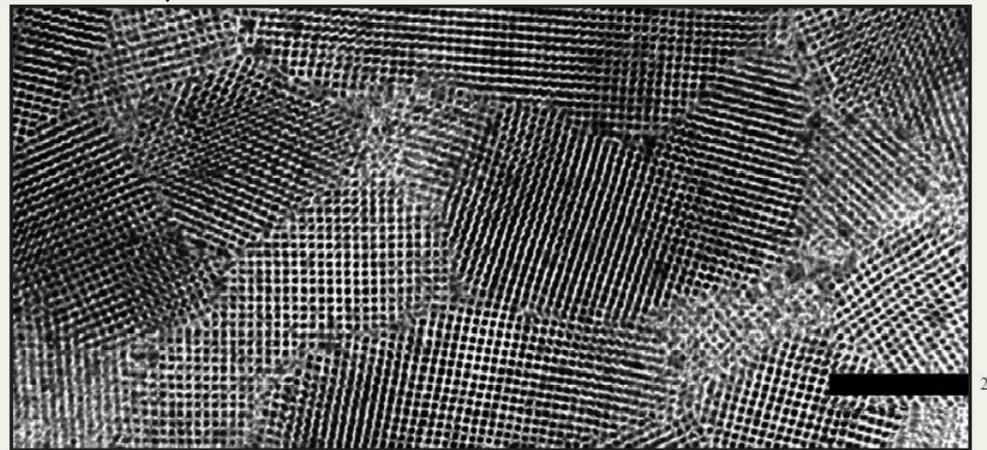


Chemical Synthesis of Nanocrystals

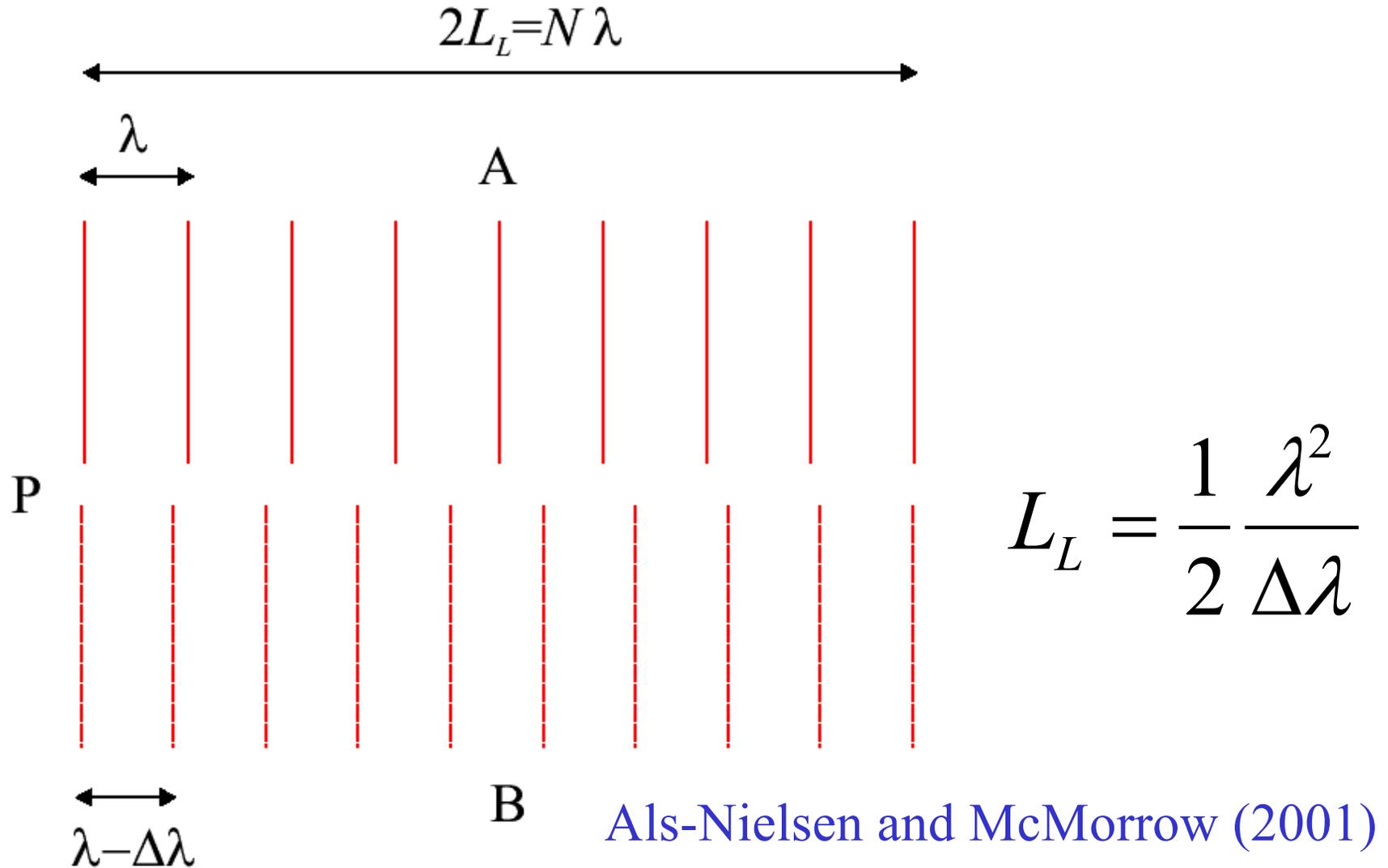


- Reactants introduced rapidly
- High temperature solvent
- Surfactant/organic capping agent
- Square superlattice (200nm scale)

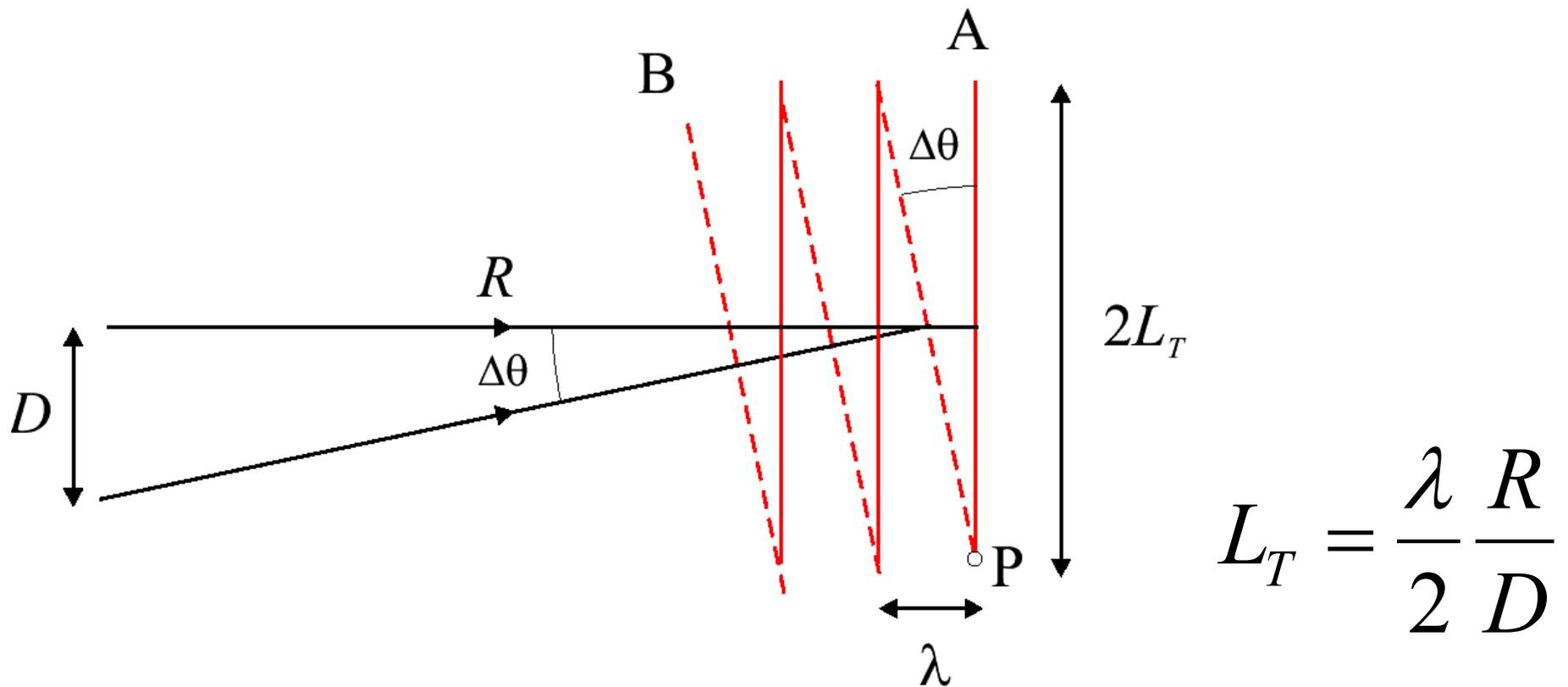
C. B. Murray, IBM J. Res. & Dev. **45**
47 (2001)



Longitudinal Coherence



Lateral (Transverse) Coherence



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

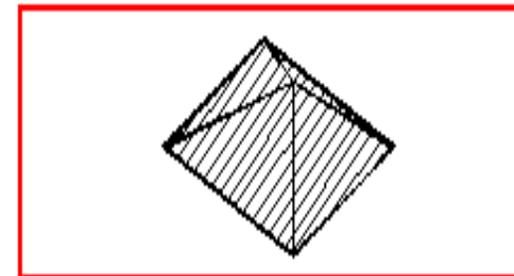
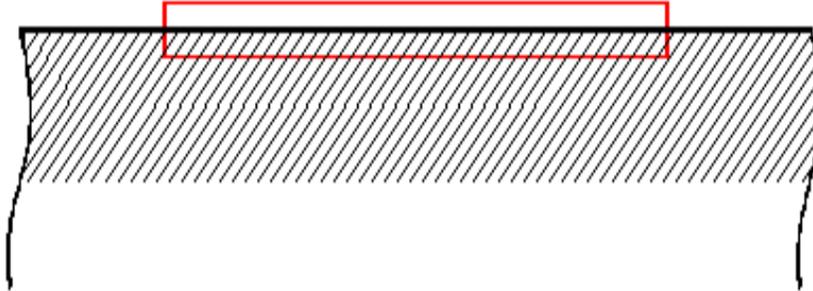
Als-Nielsen and McMorrow (2001)

Coherence at APS, Spring8 or ESRF

Typical of 3rd Generation (undulator) Synchrotron Source

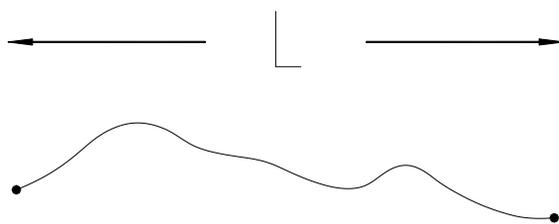
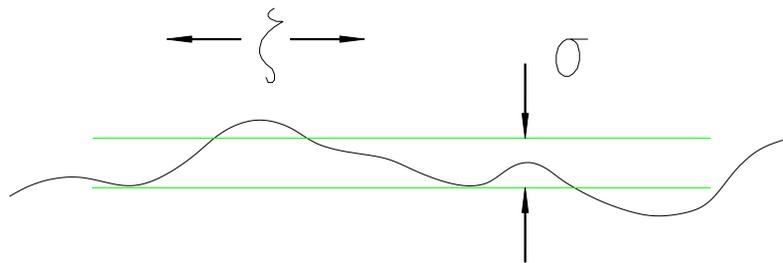
Coherence of	ξ_{VER}	ξ_{HORIZ}	ξ_{LONG}	Flux
Raw Undulator	35 μm	9 μm	0.004 μm	2×10^{12}
Si(111) Monochromator	35 μm	9 μm	1 μm	1×10^{10}
C(111) Monochromator	35 μm	9 μm	3 μm	3×10^9

Coherent region defined by slits

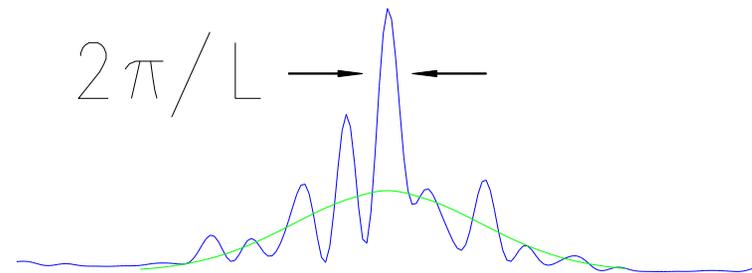
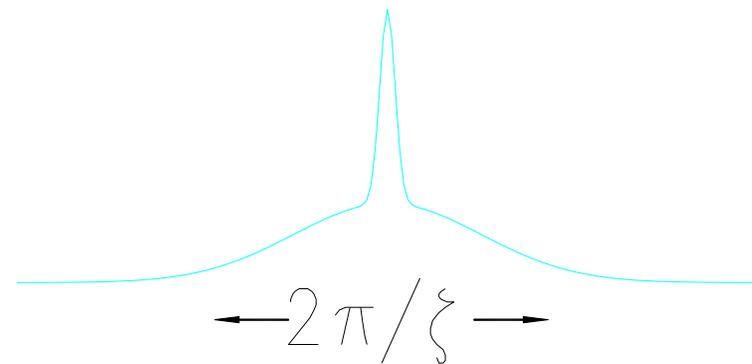


Diffuse Scattering acquires Structure using CXD

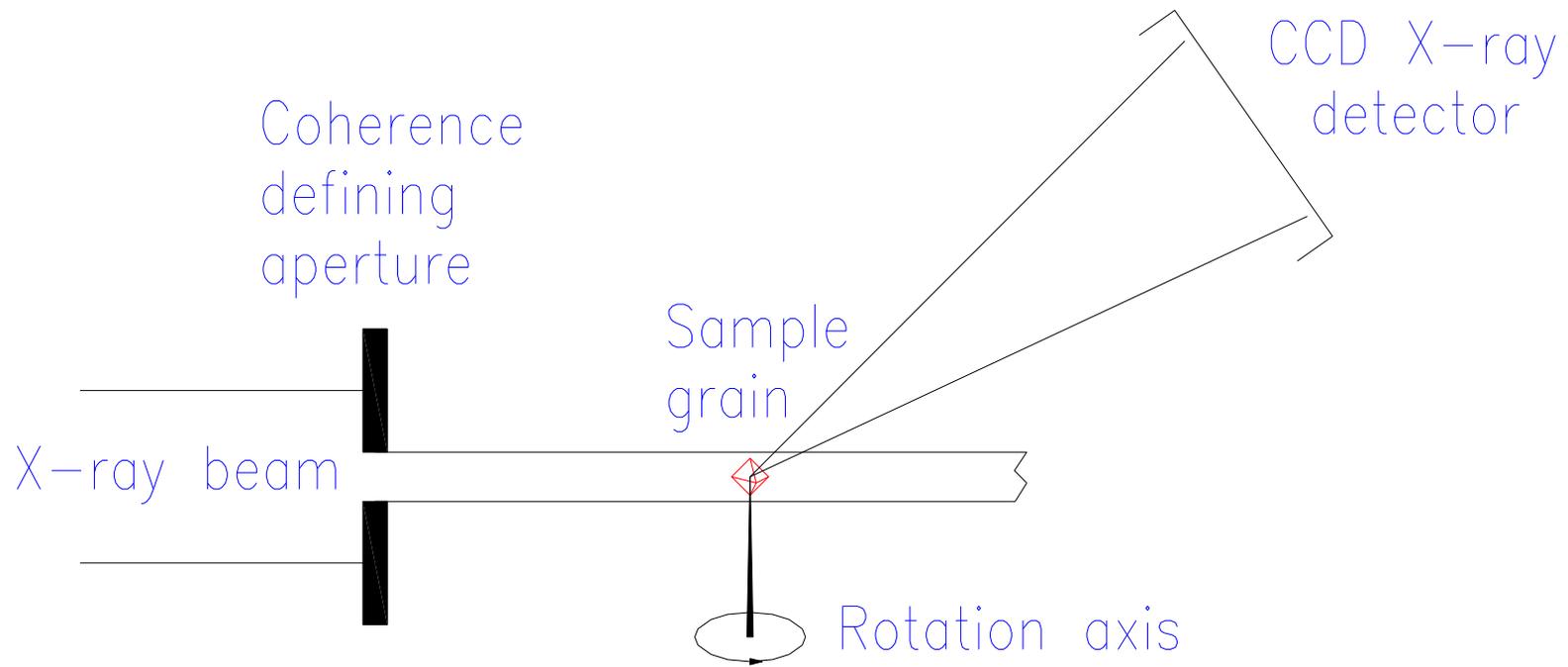
Real Space



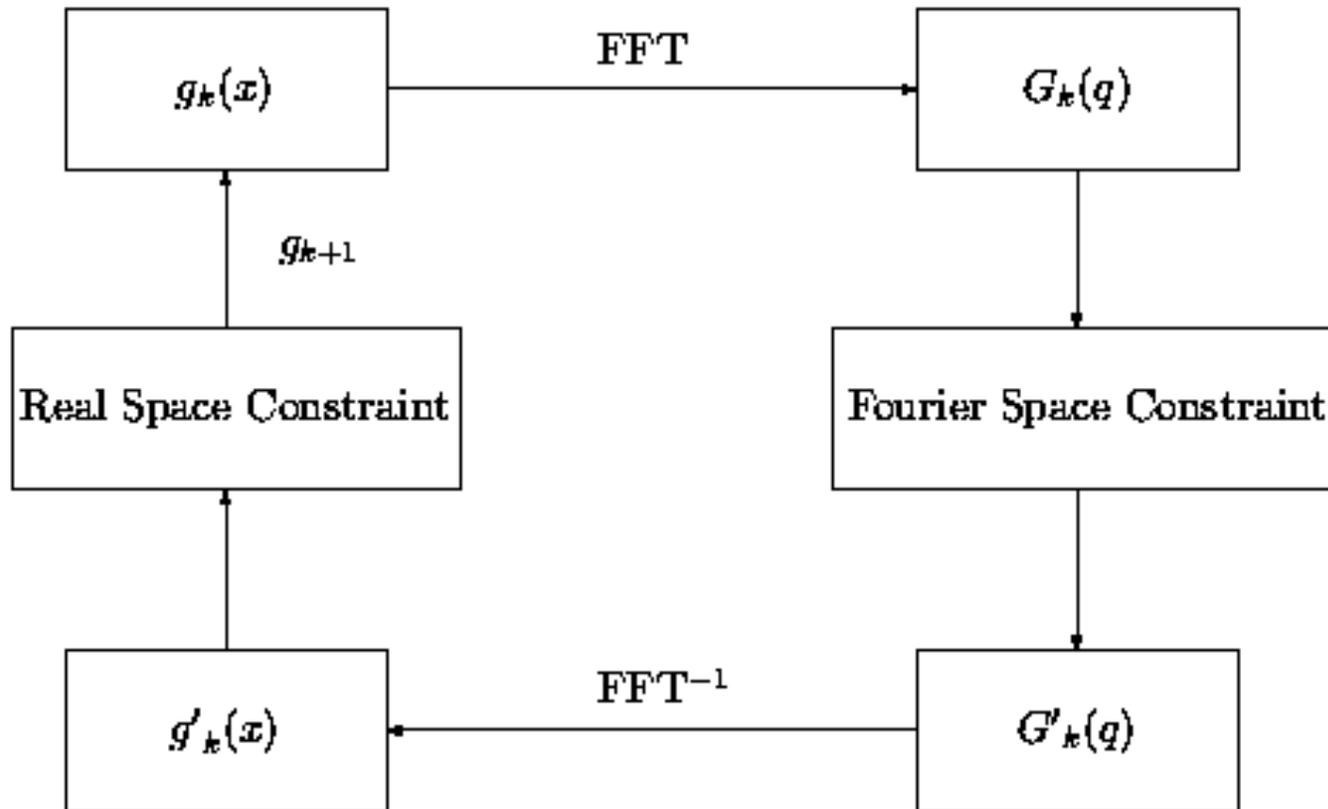
Reciprocal Space



Lensless X-ray Microscope



Generic “Error Reduction” method



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

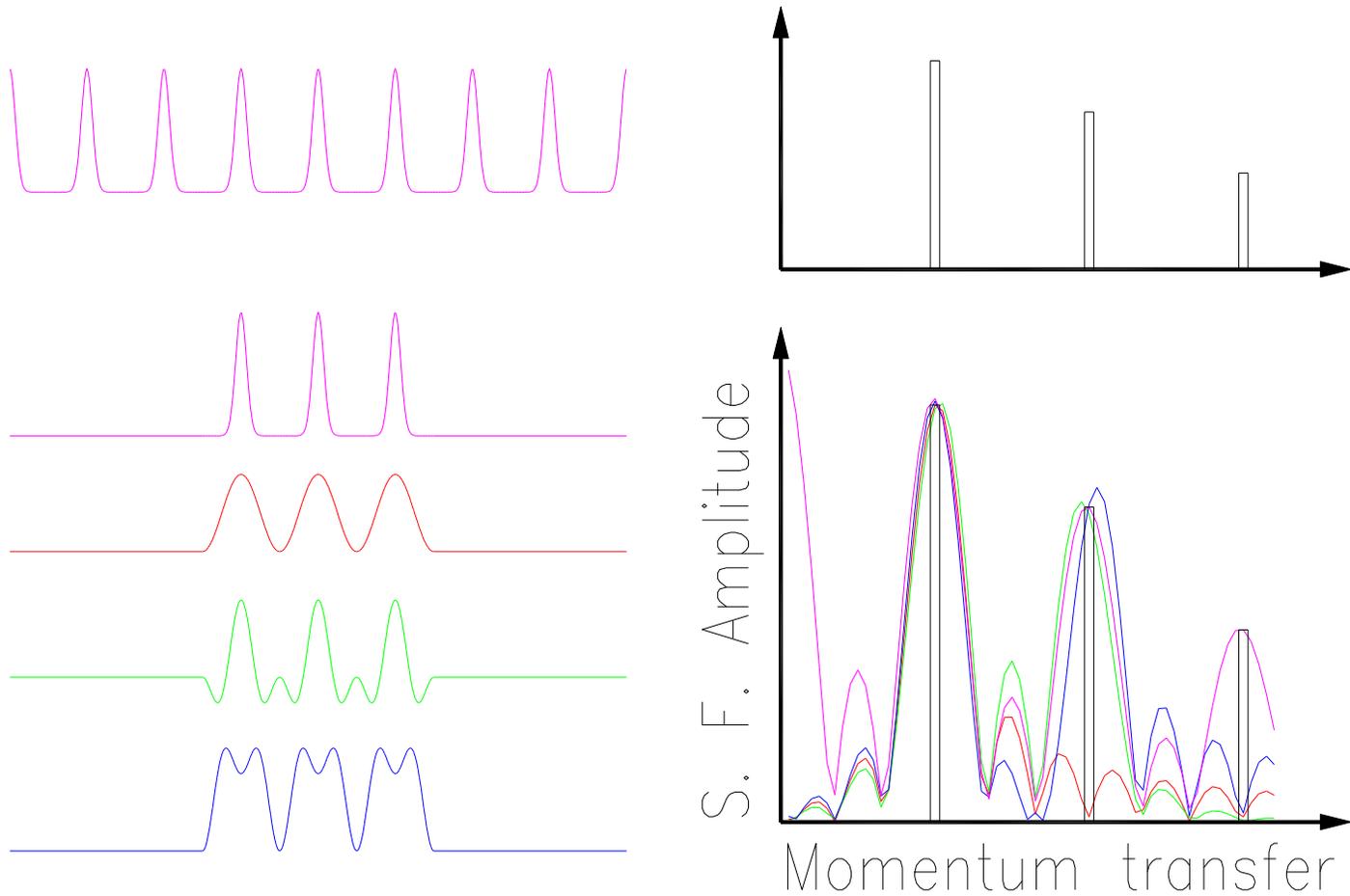
R. W. Gerchberg and W. O. Saxton *Optik* 35 237 (1972)

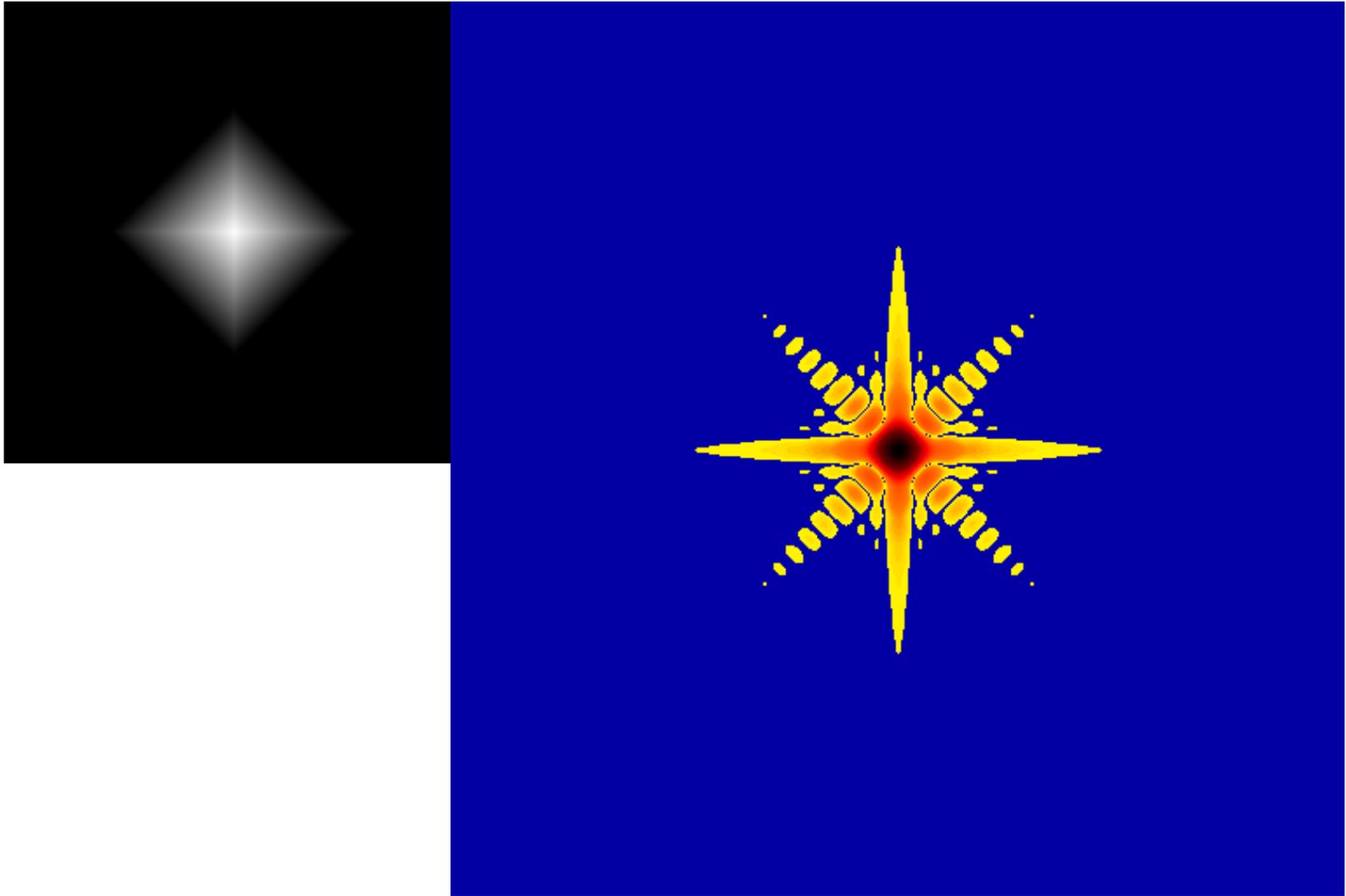
Real-space Constraints in Crystallography

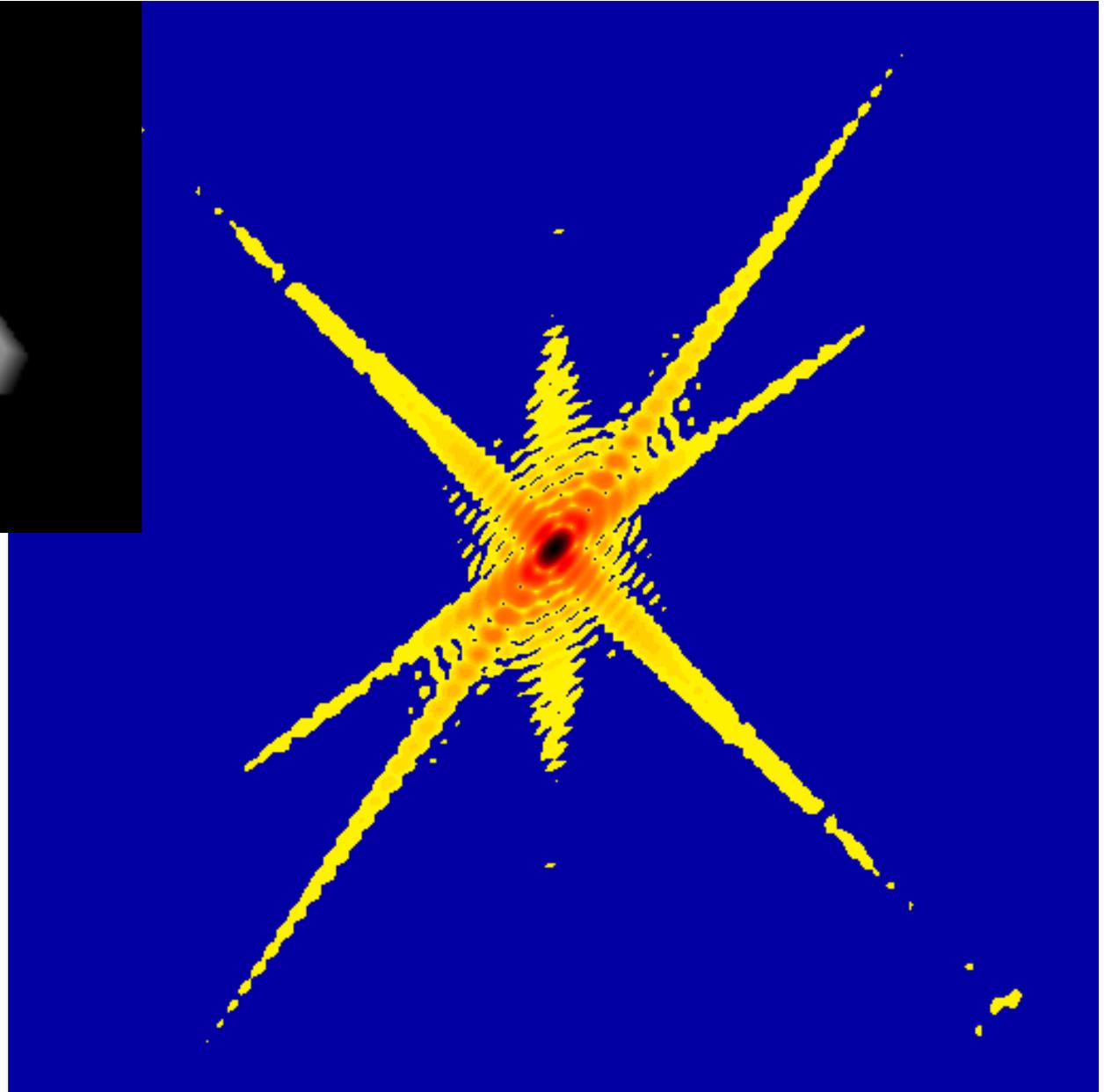
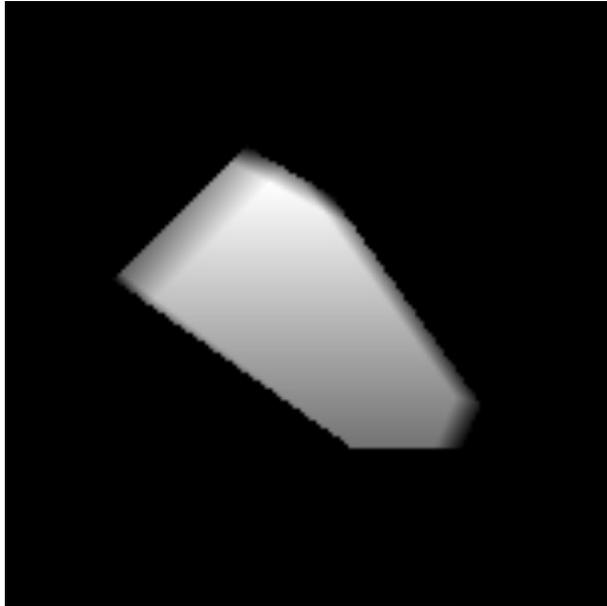
R. P. Millane, J. Opt. Soc Am. A **13** 725 (1996)

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

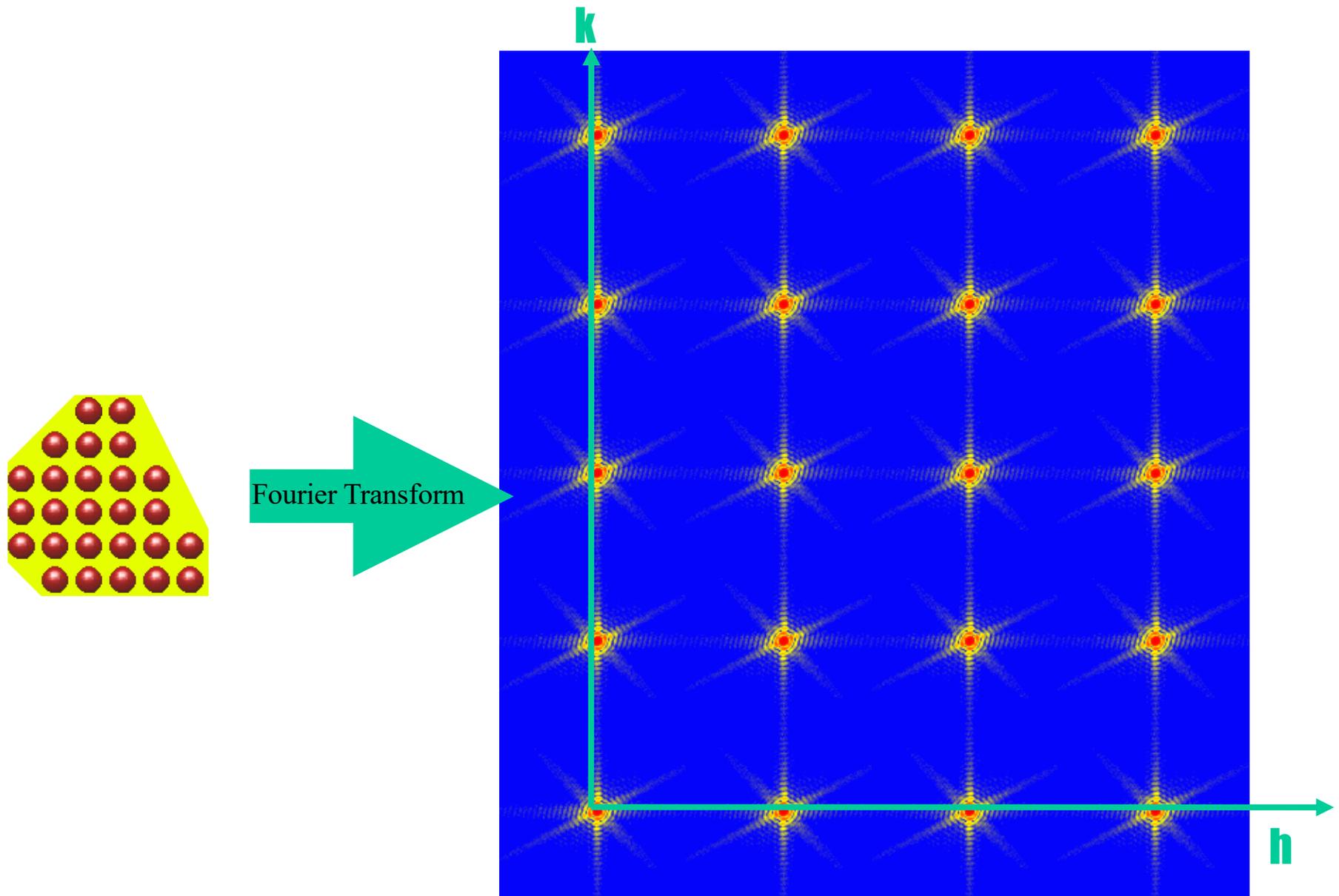
Phase Problem: Finite-size Effect

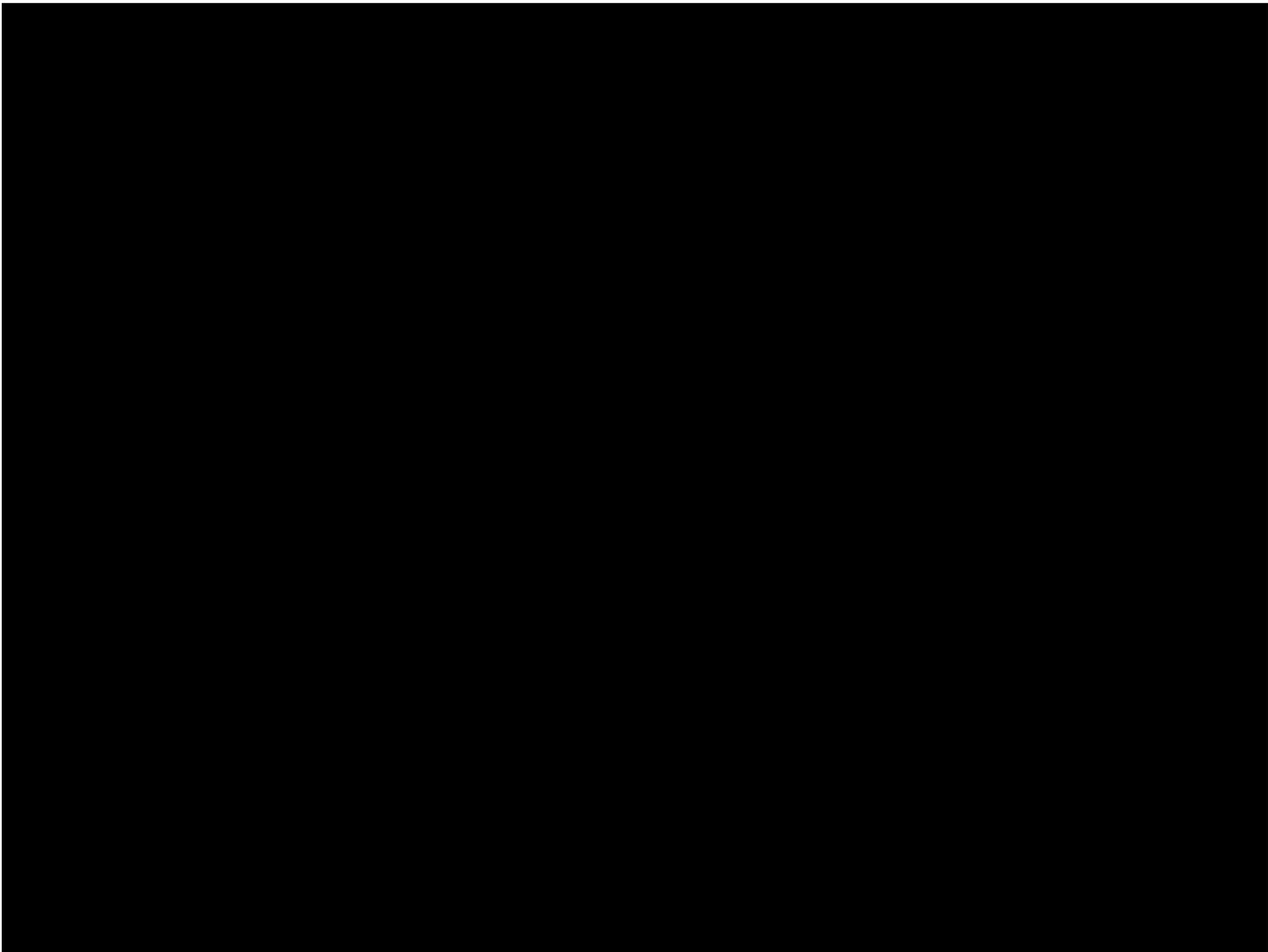




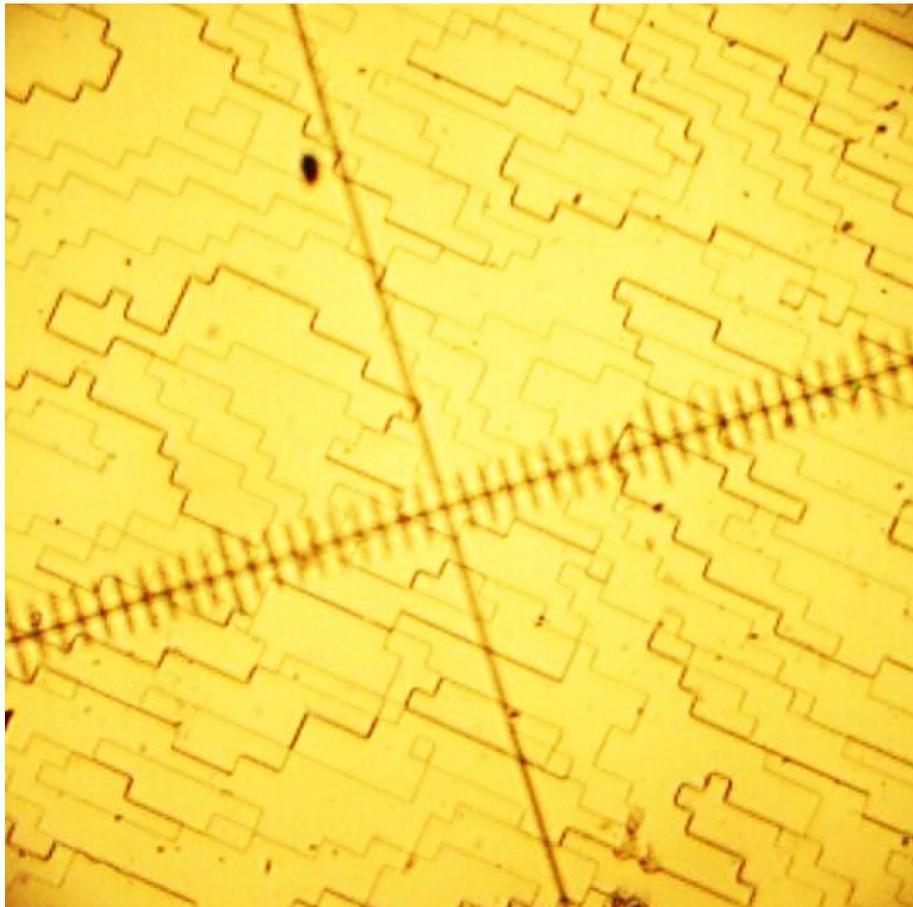


Coherent Diffraction from Crystals

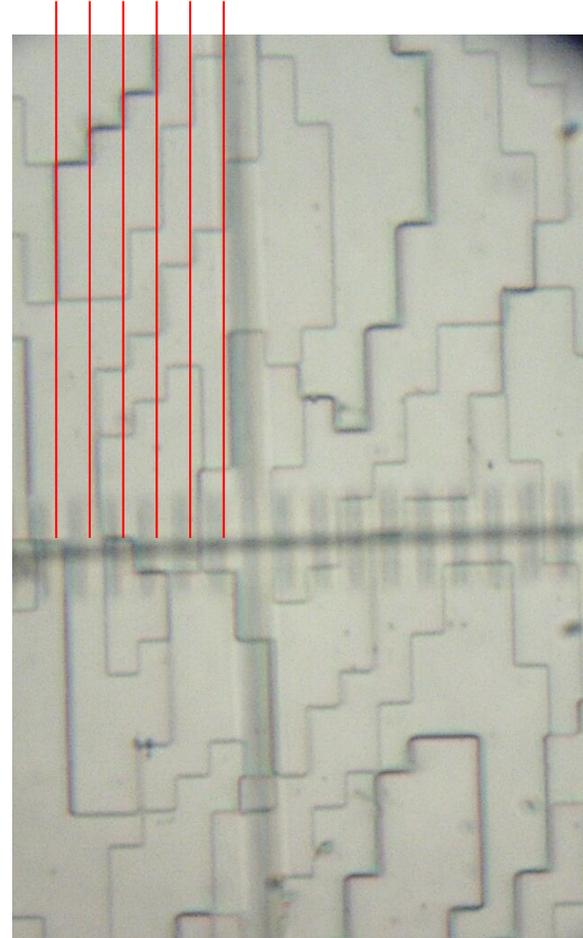




Microscope Images of Gratings

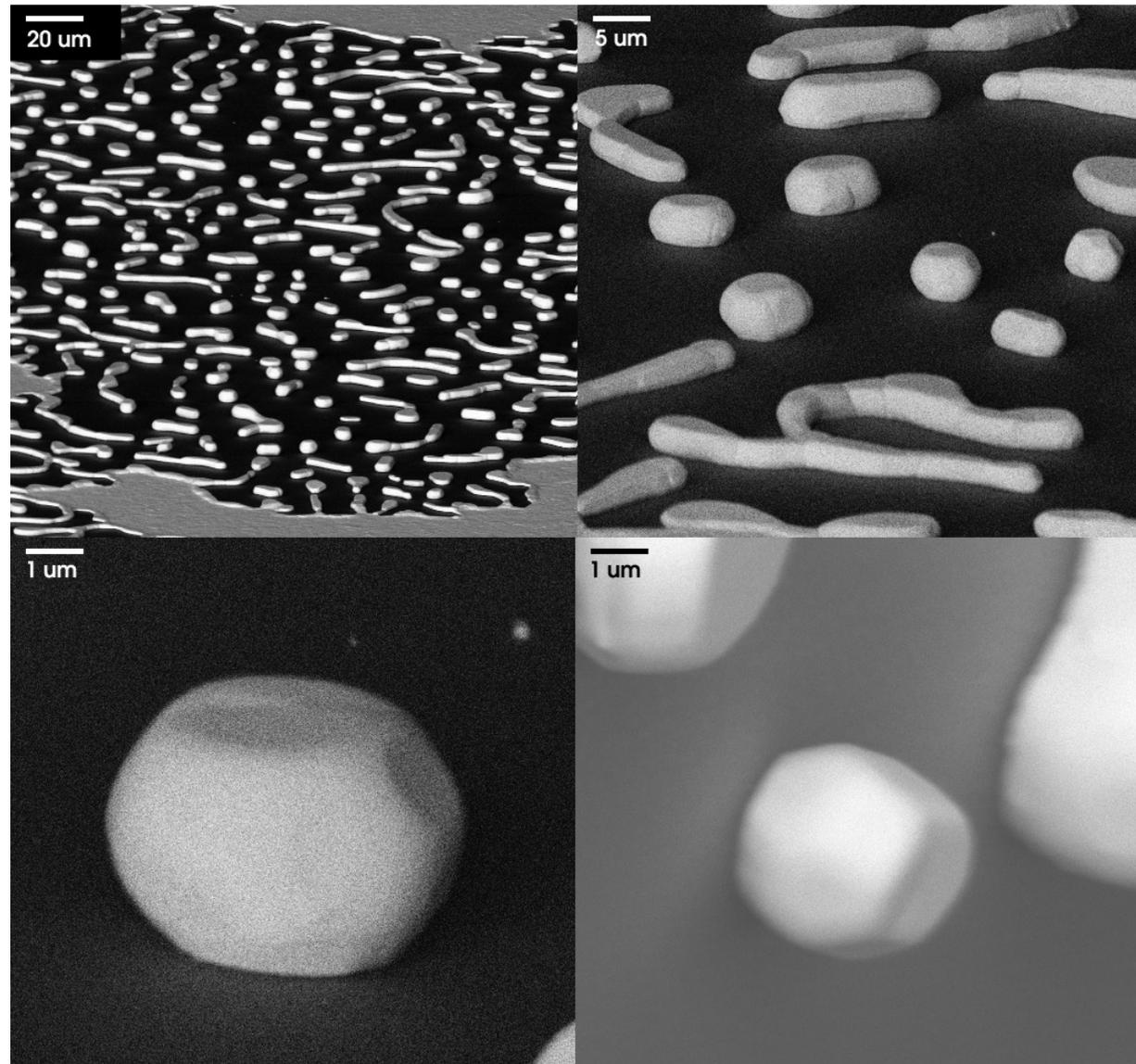


5 μ m grid lines



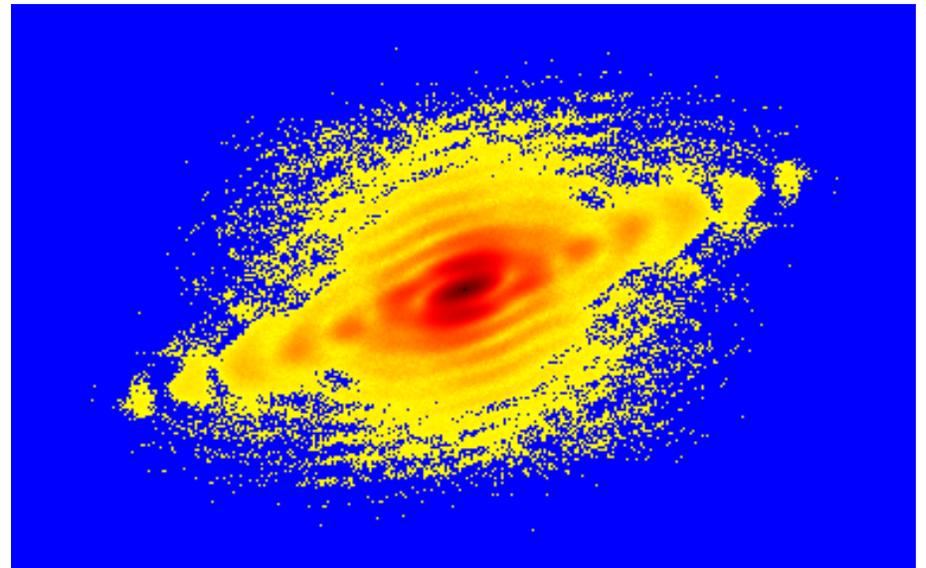
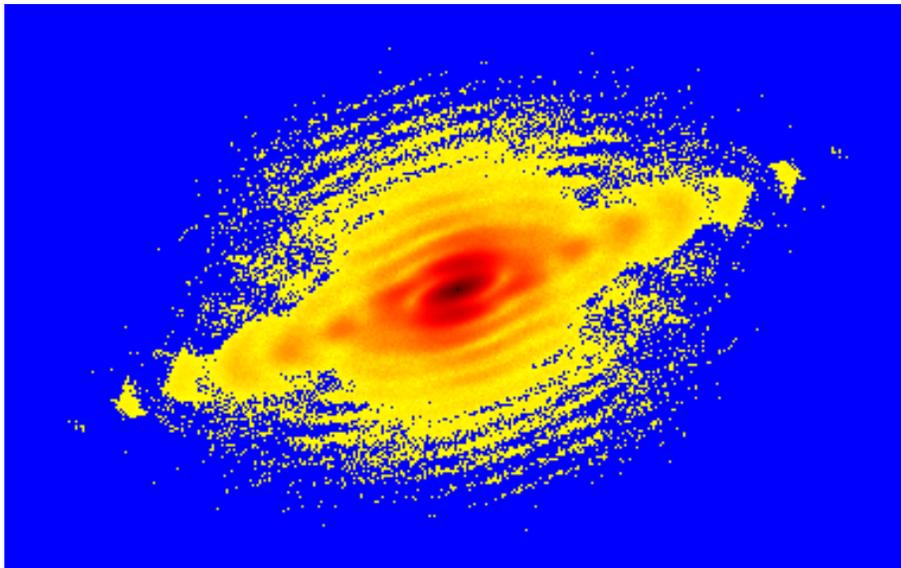
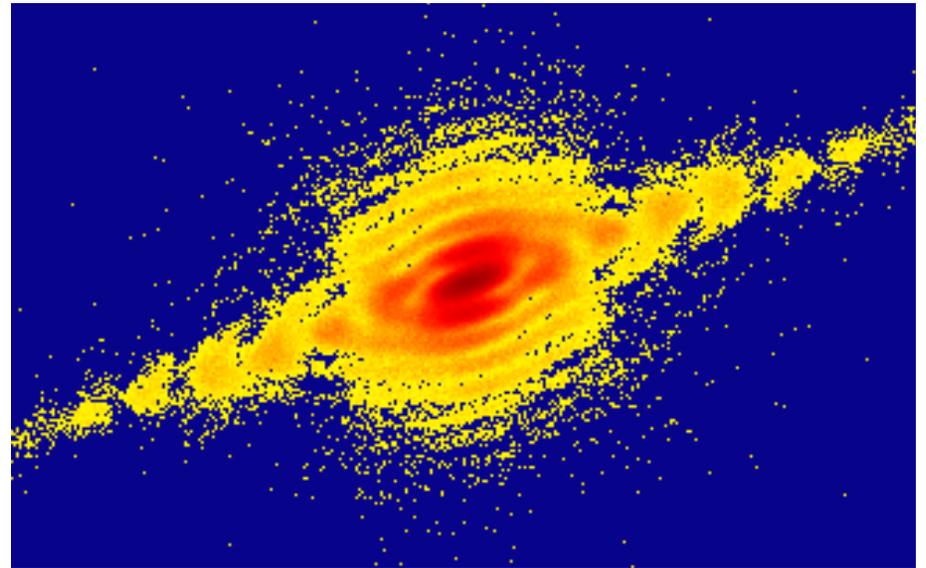
SEMS

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



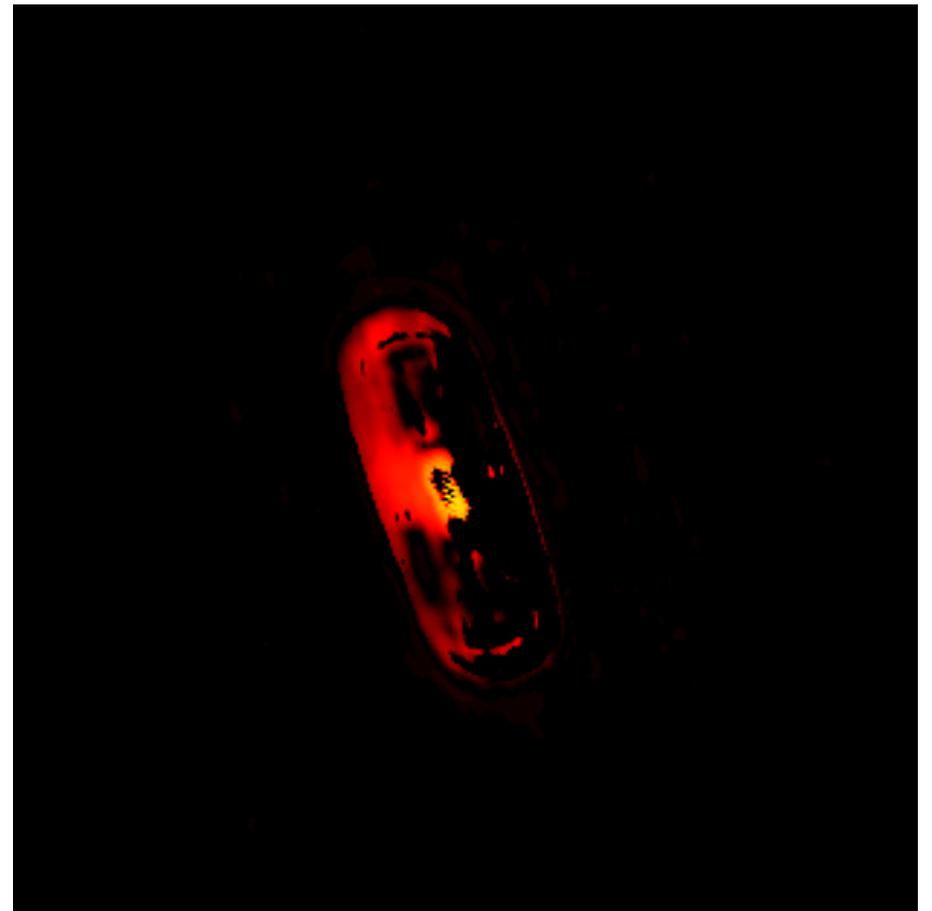
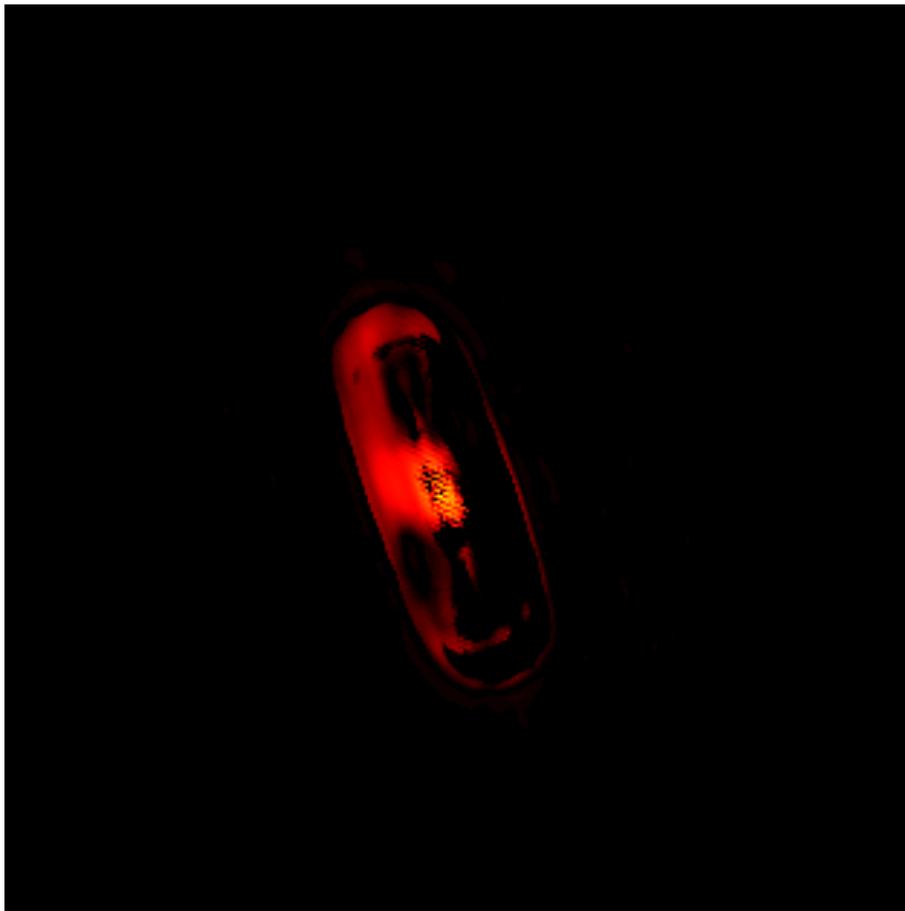
Symmetrized Data and two best fits

$\text{Chisq}=0.0005$

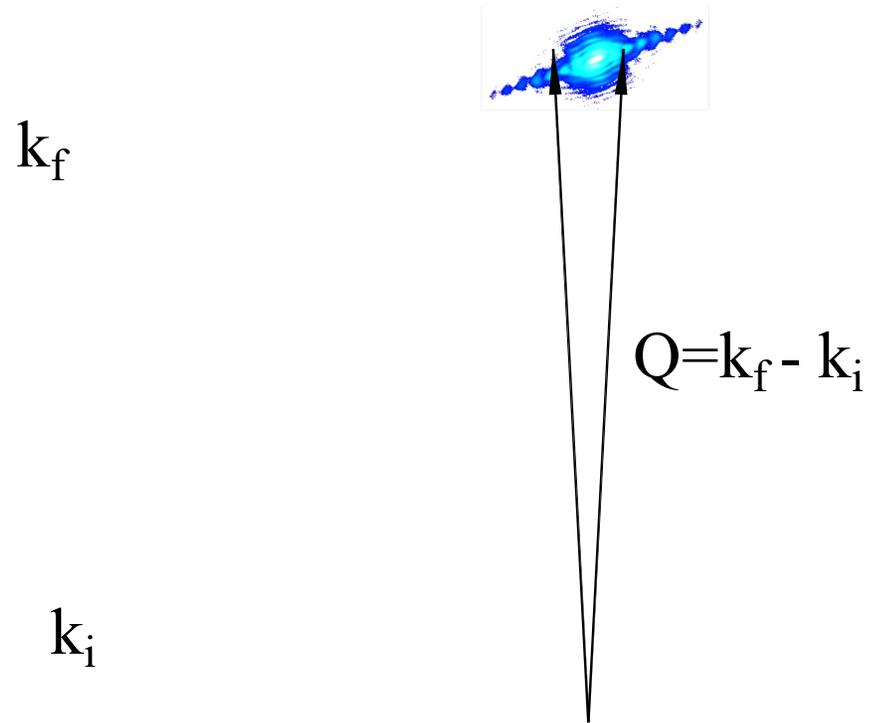


2D Reconstructions

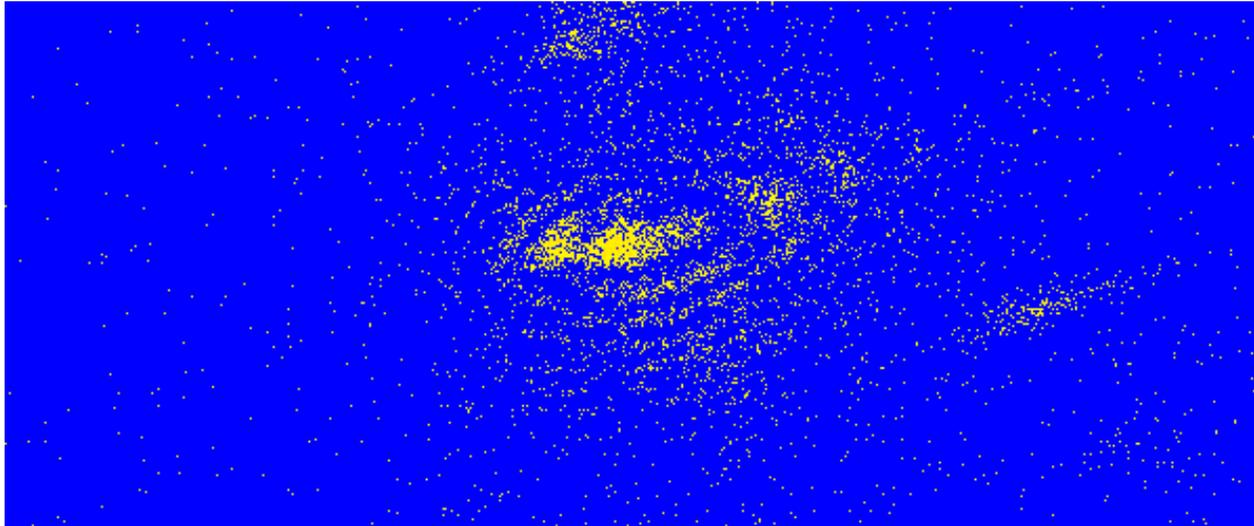
chisquare = 0.0005



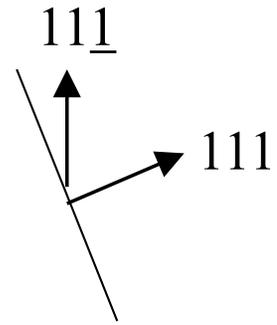
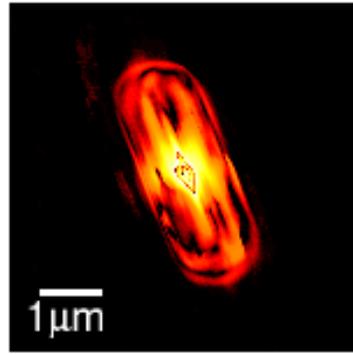
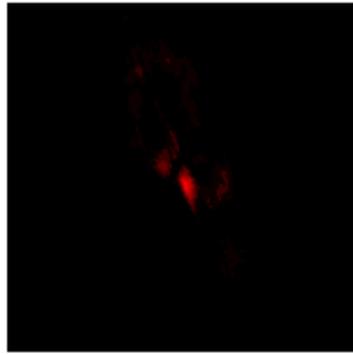
3D Diffraction Method



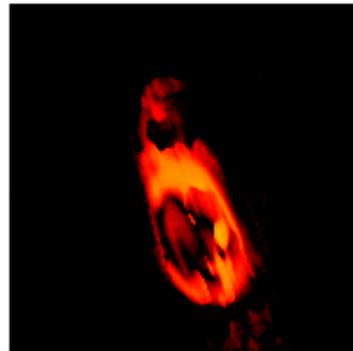
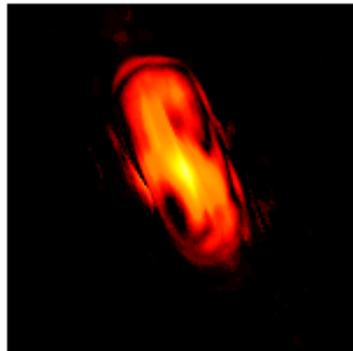
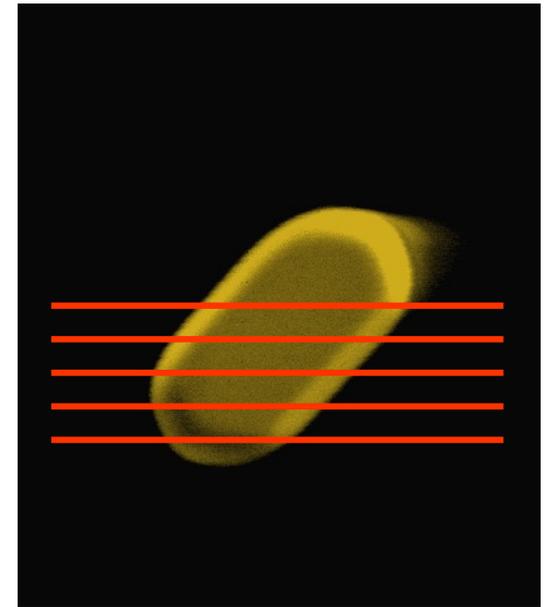
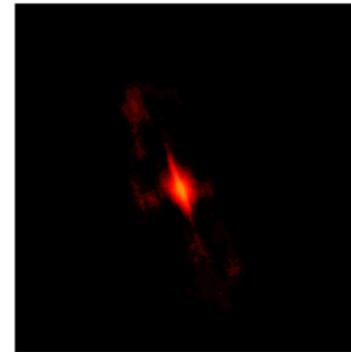
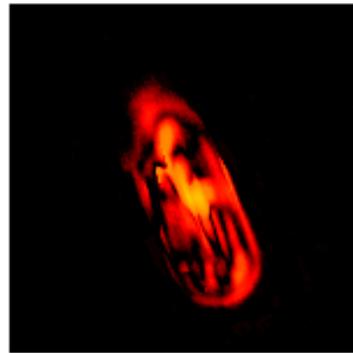
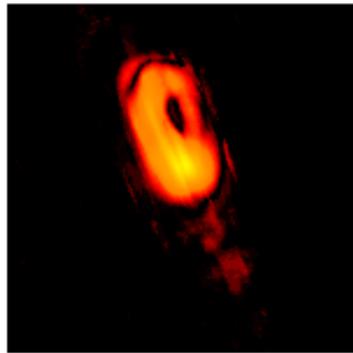
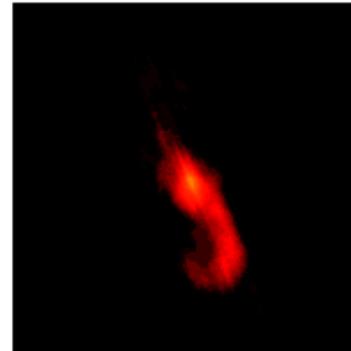
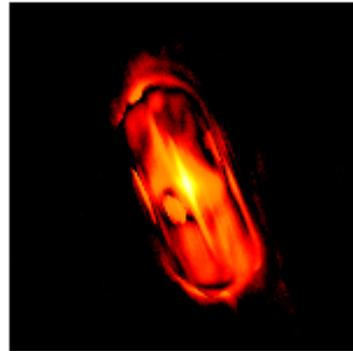
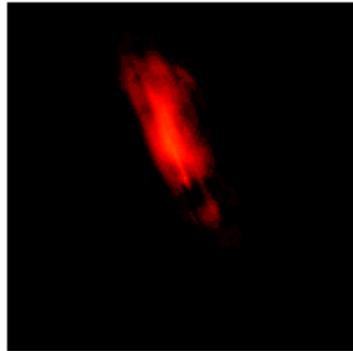
3D Diffraction Data 1 micron Au crystal



* Center is Symmetric *

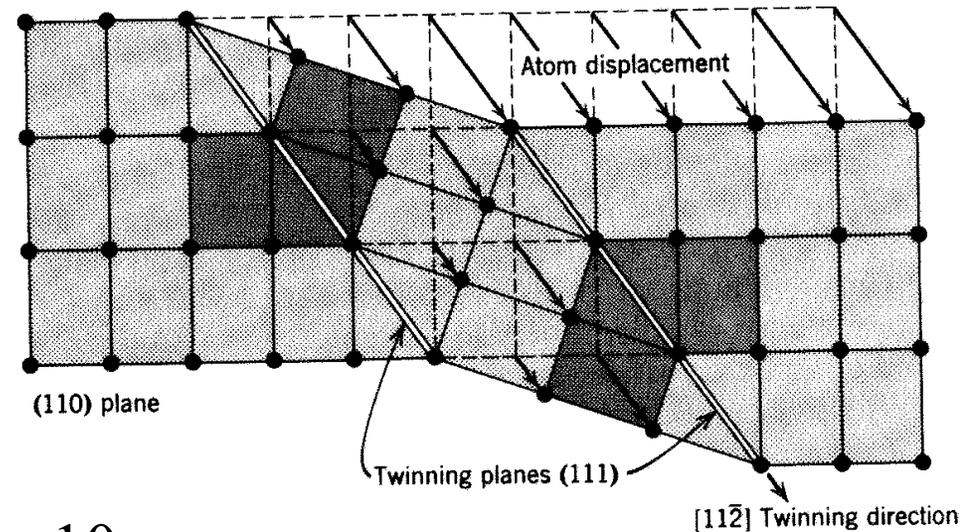


Slices through
plan view SEM:

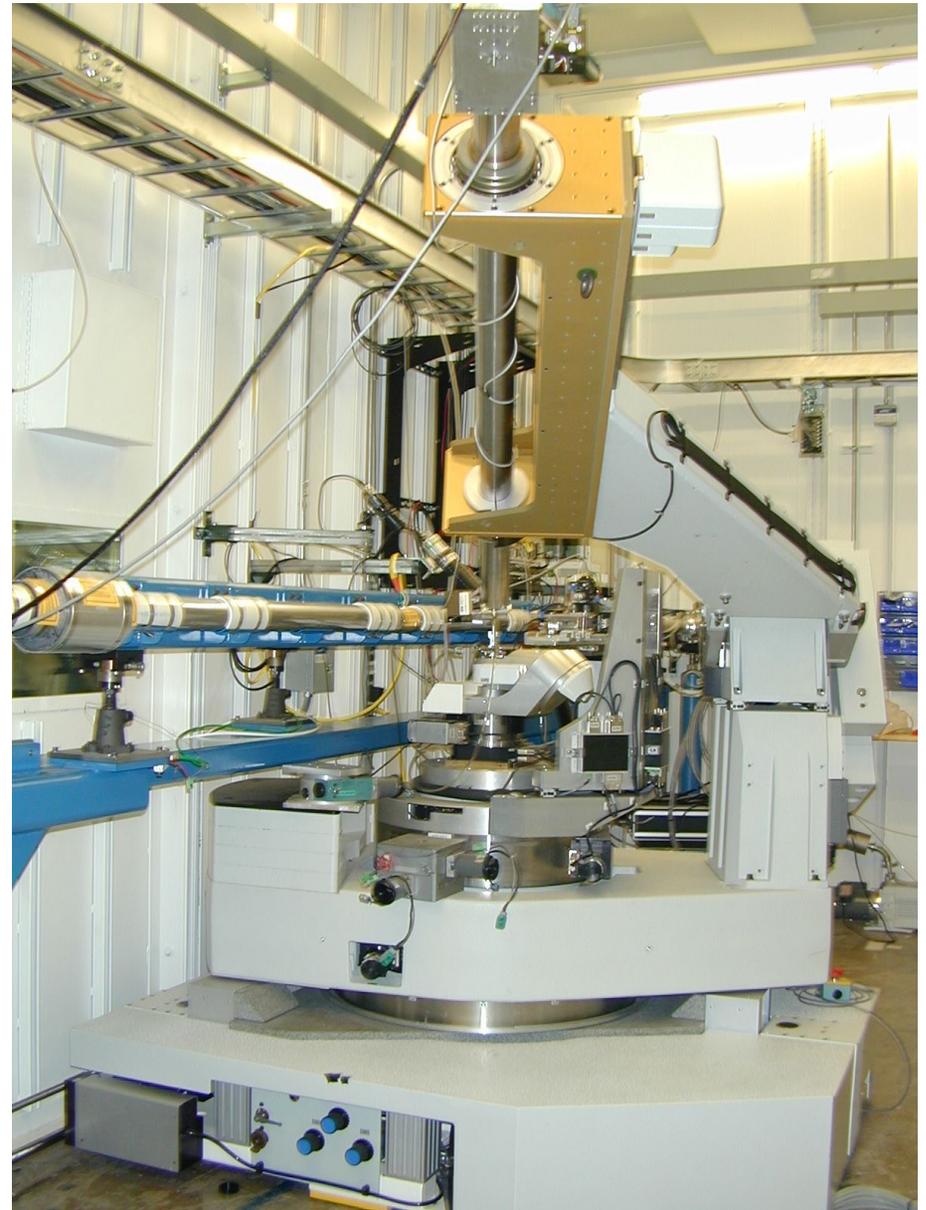
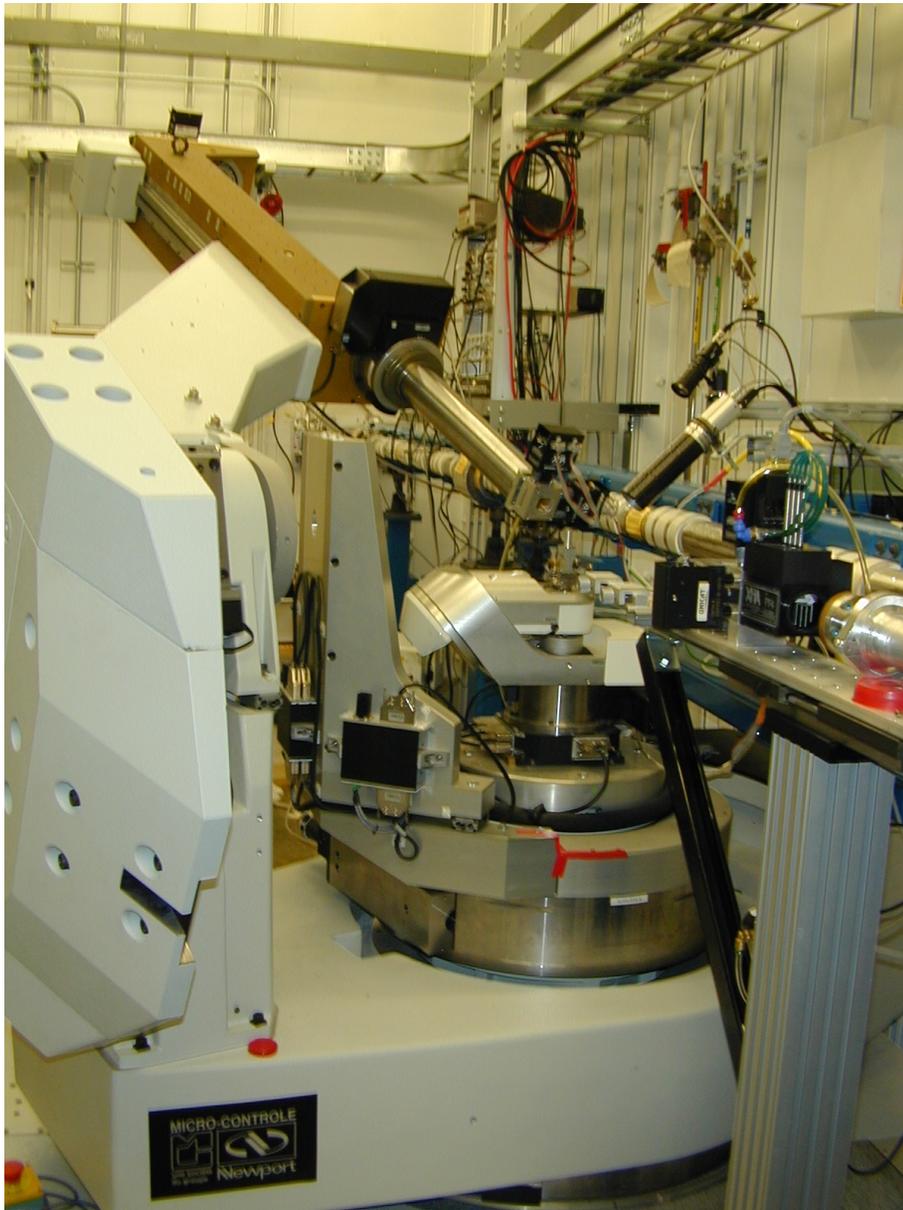


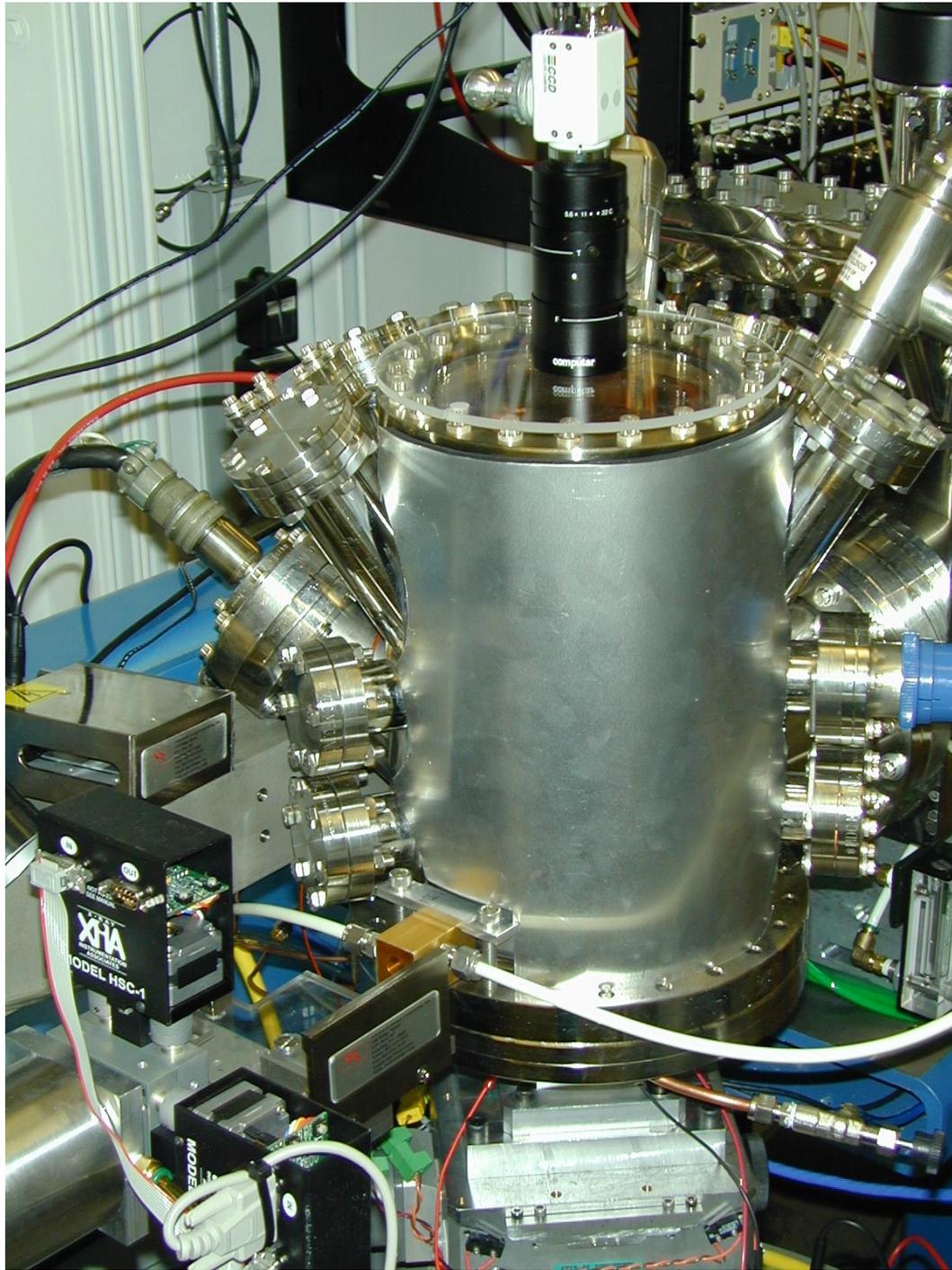
Twinning in deformed FCC metals

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

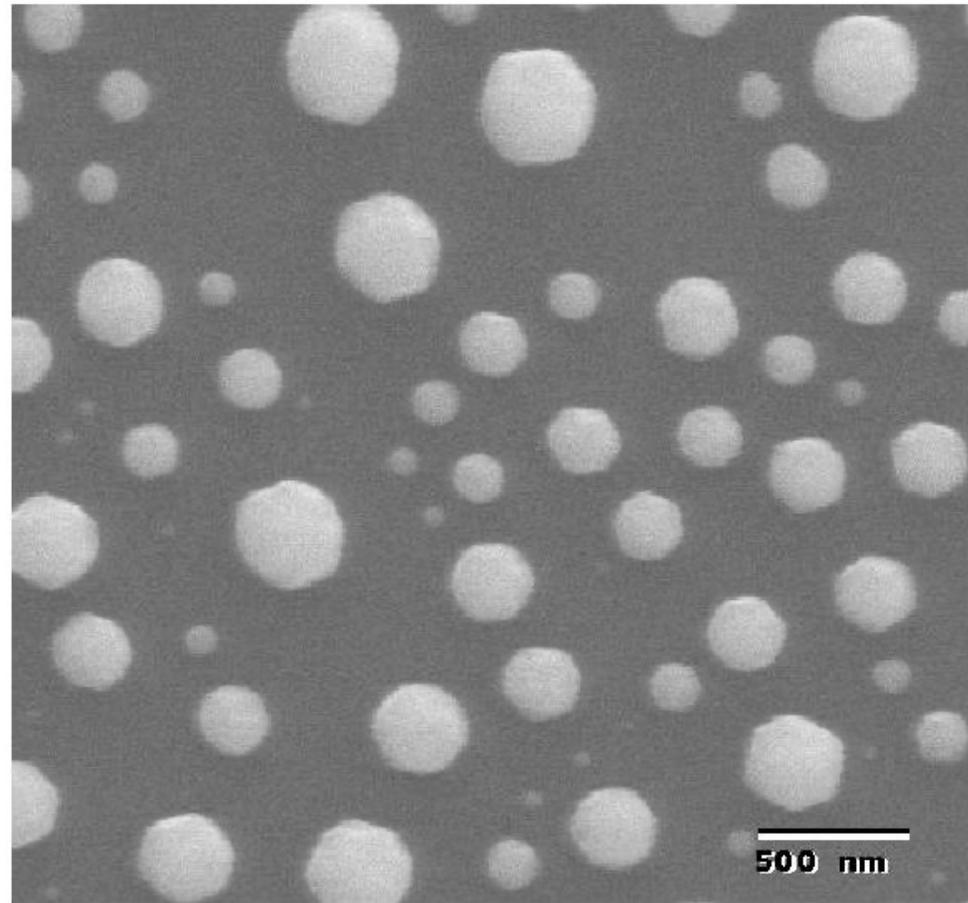
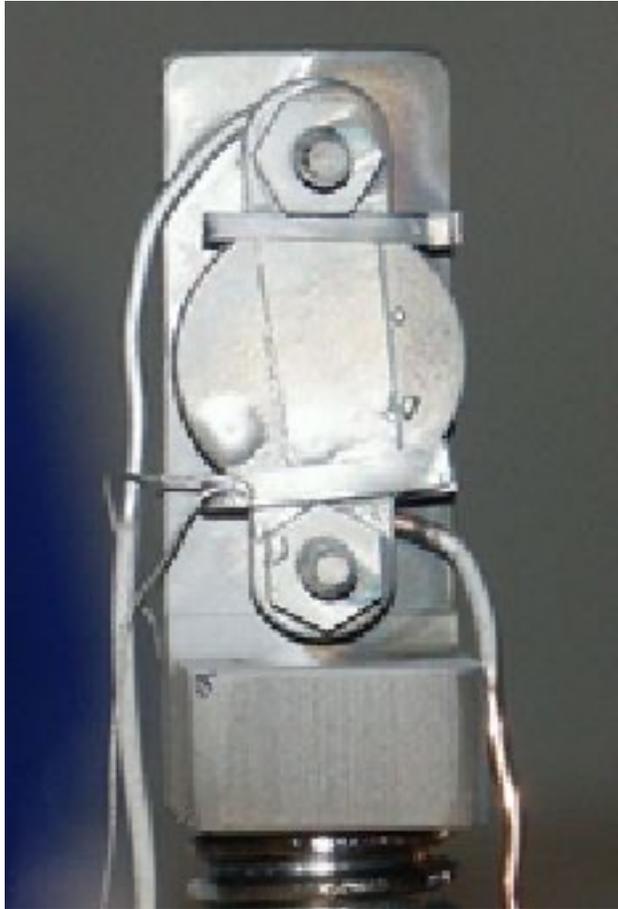


■ $\sim 10\mu\text{m}$
Cu





In situ growth of Pb crystals



Good statistics, 3D diffraction data

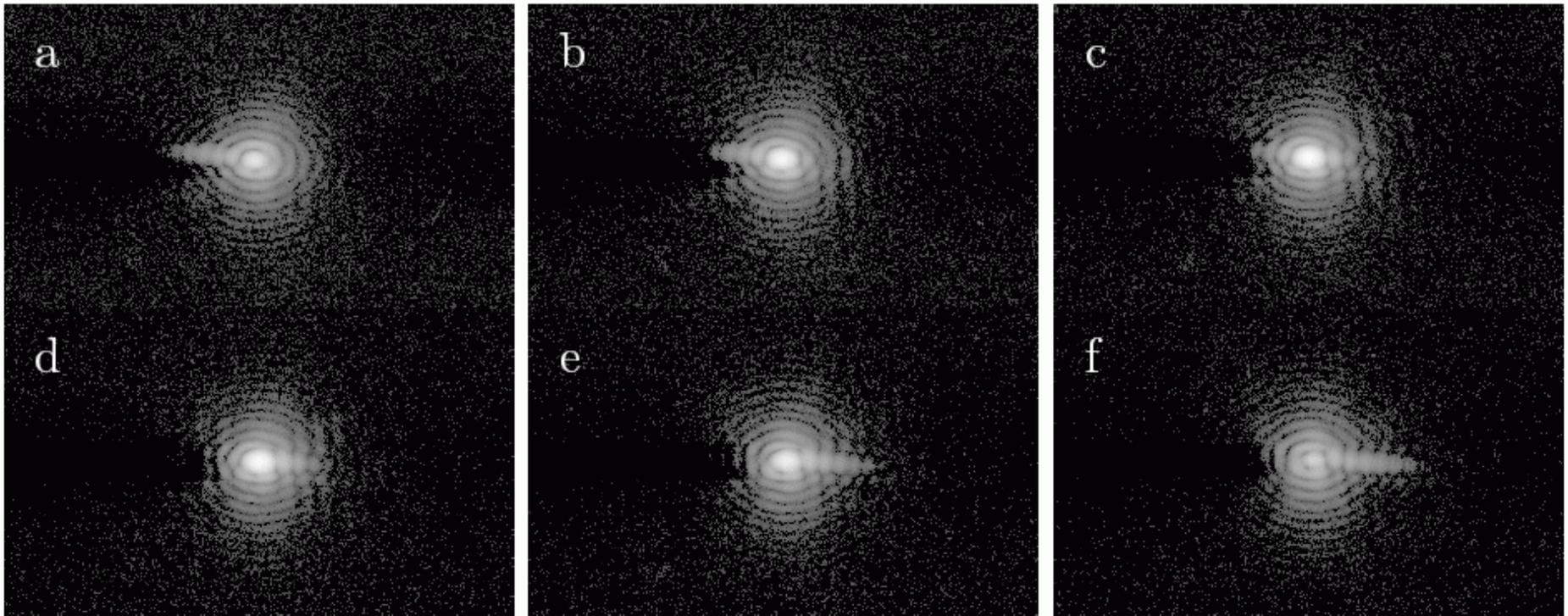
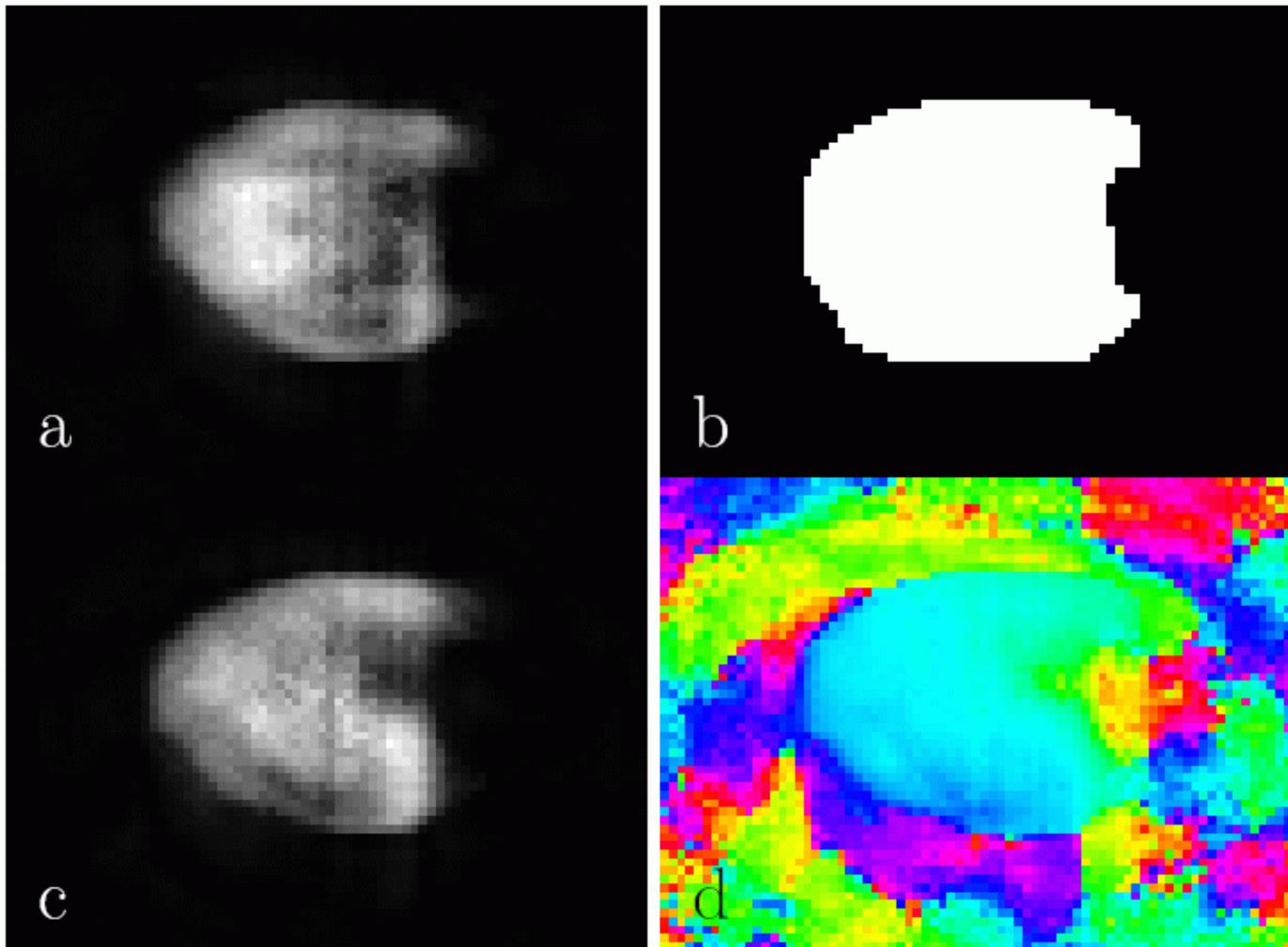
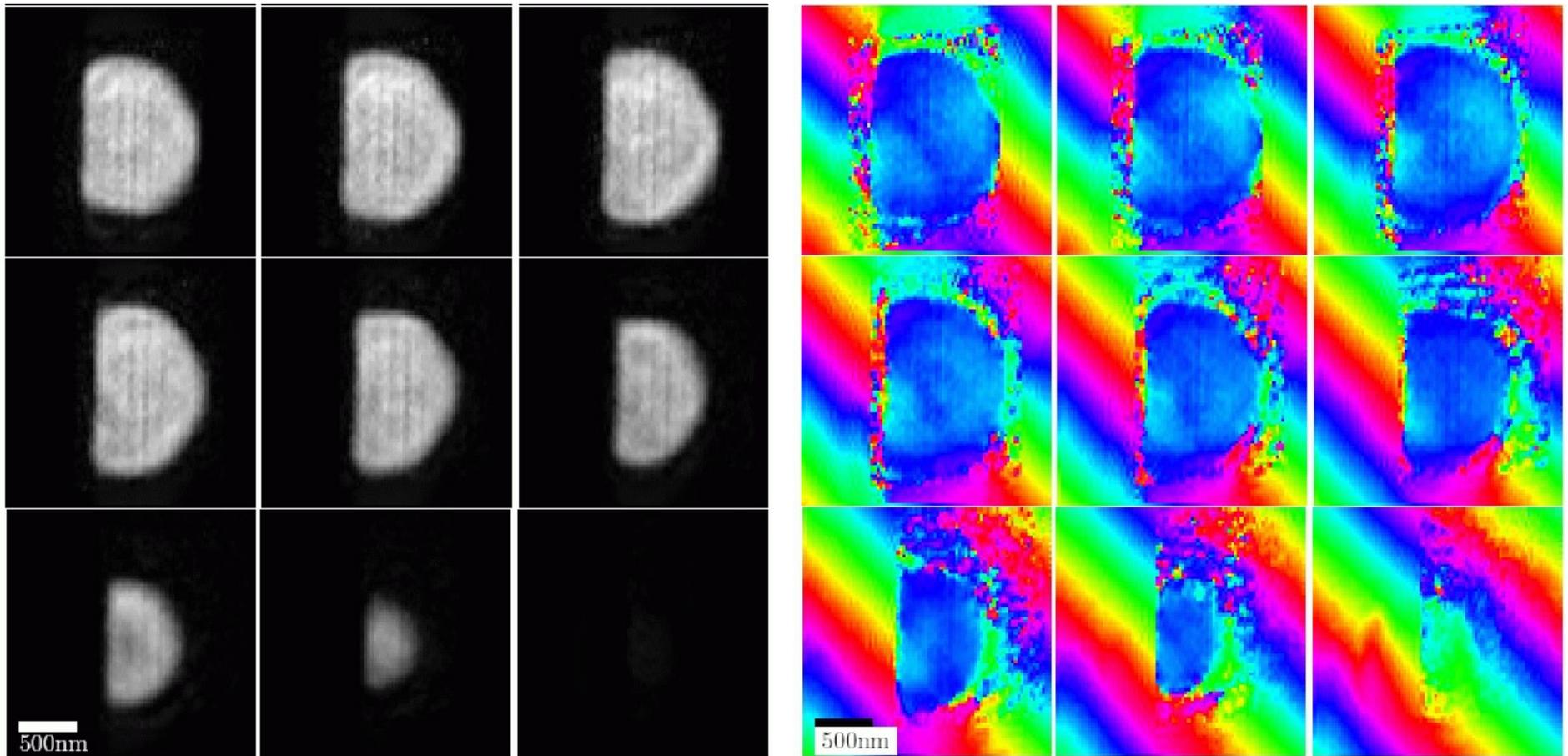


Figure 4.12: Center slices from 3D CXD pattern from Pb sample, on a log scale. Data file 296 from 10/03.

Learn shape of “tight” support

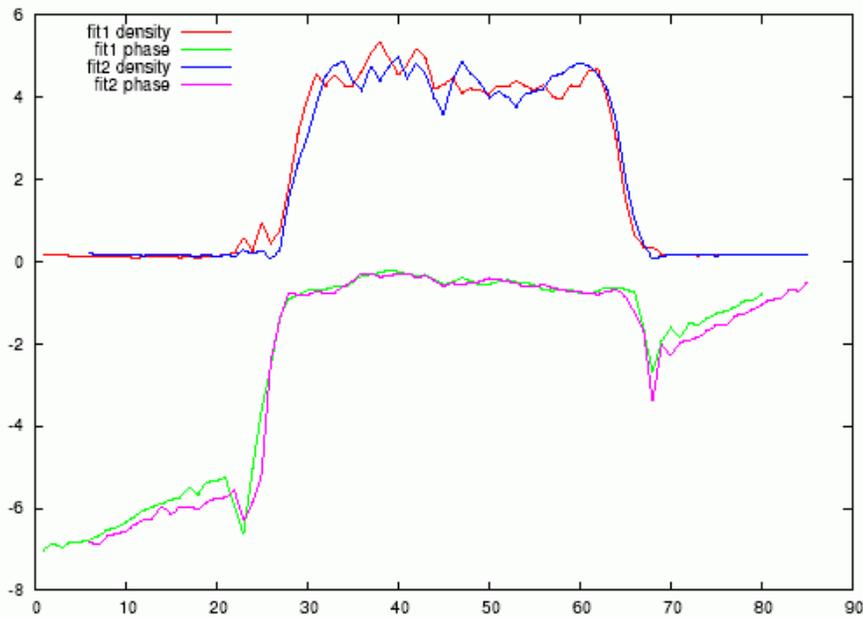


Then refine amplitude *and* phase

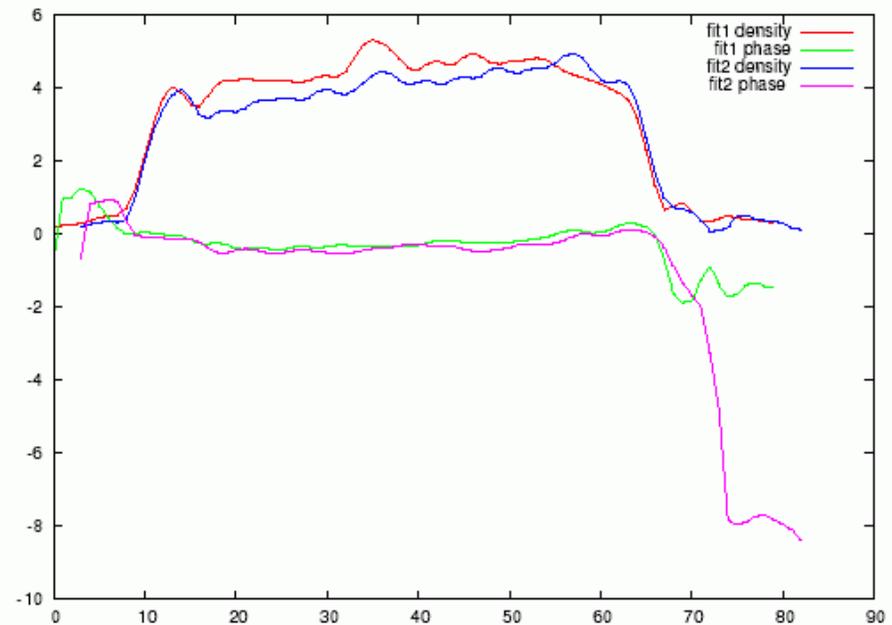


Amplitude/phase cross sections

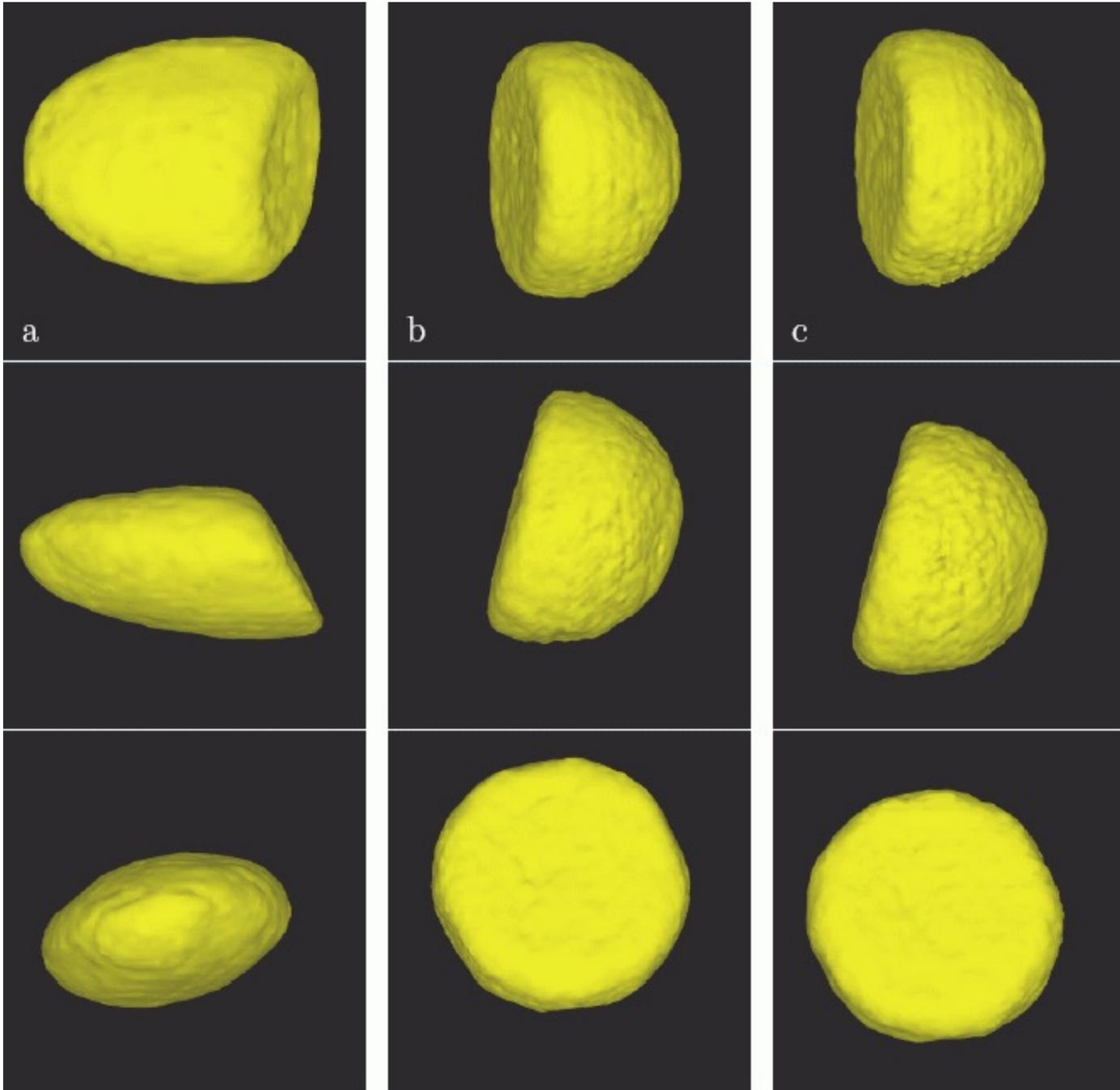
x-striations do not reproduce



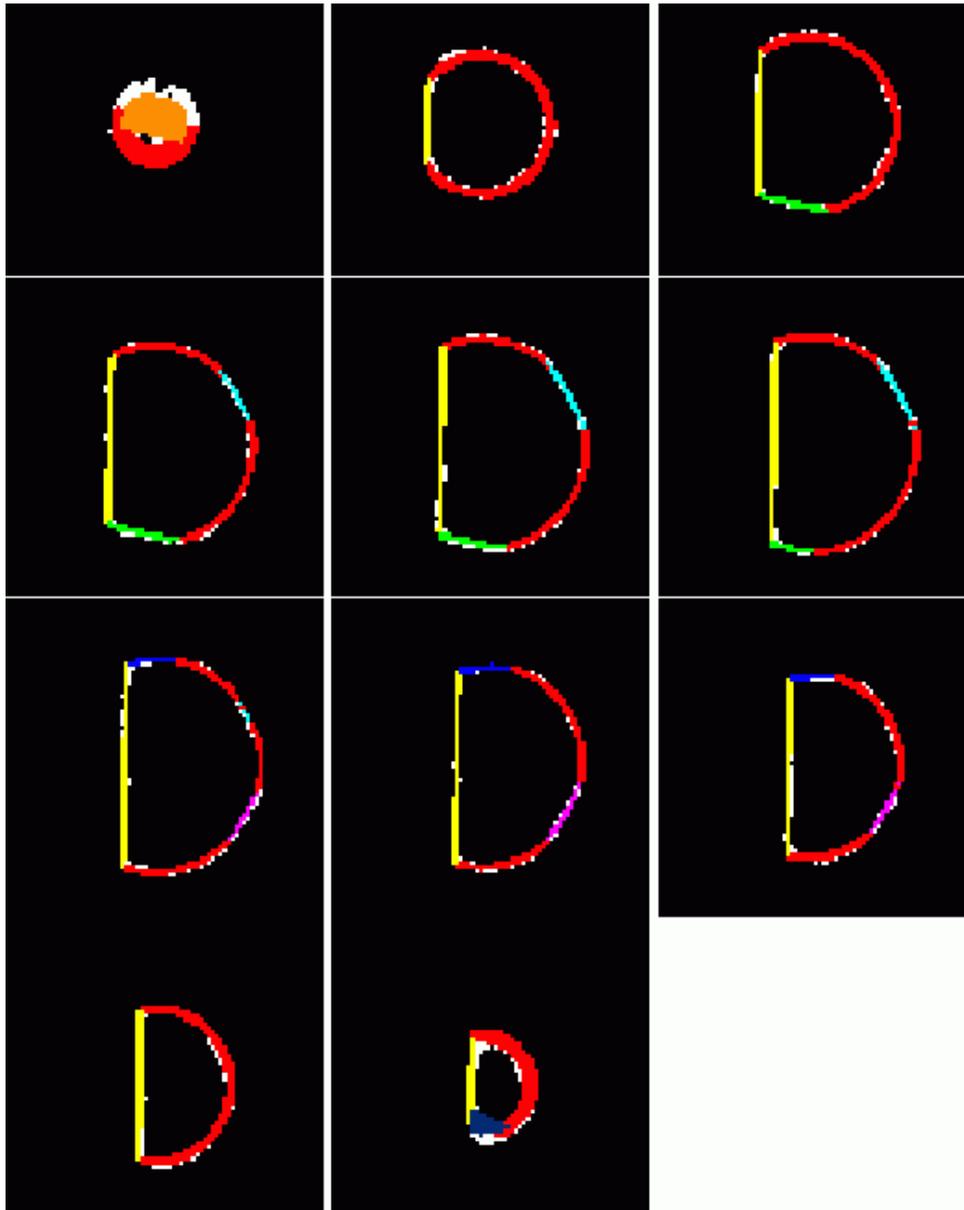
x-coordinate



y-coordinate

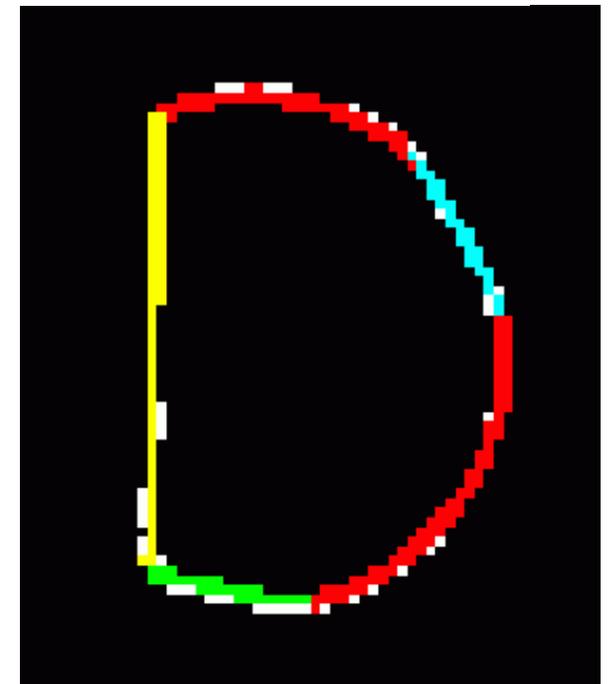


Fitting to faceted shape



	$ 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

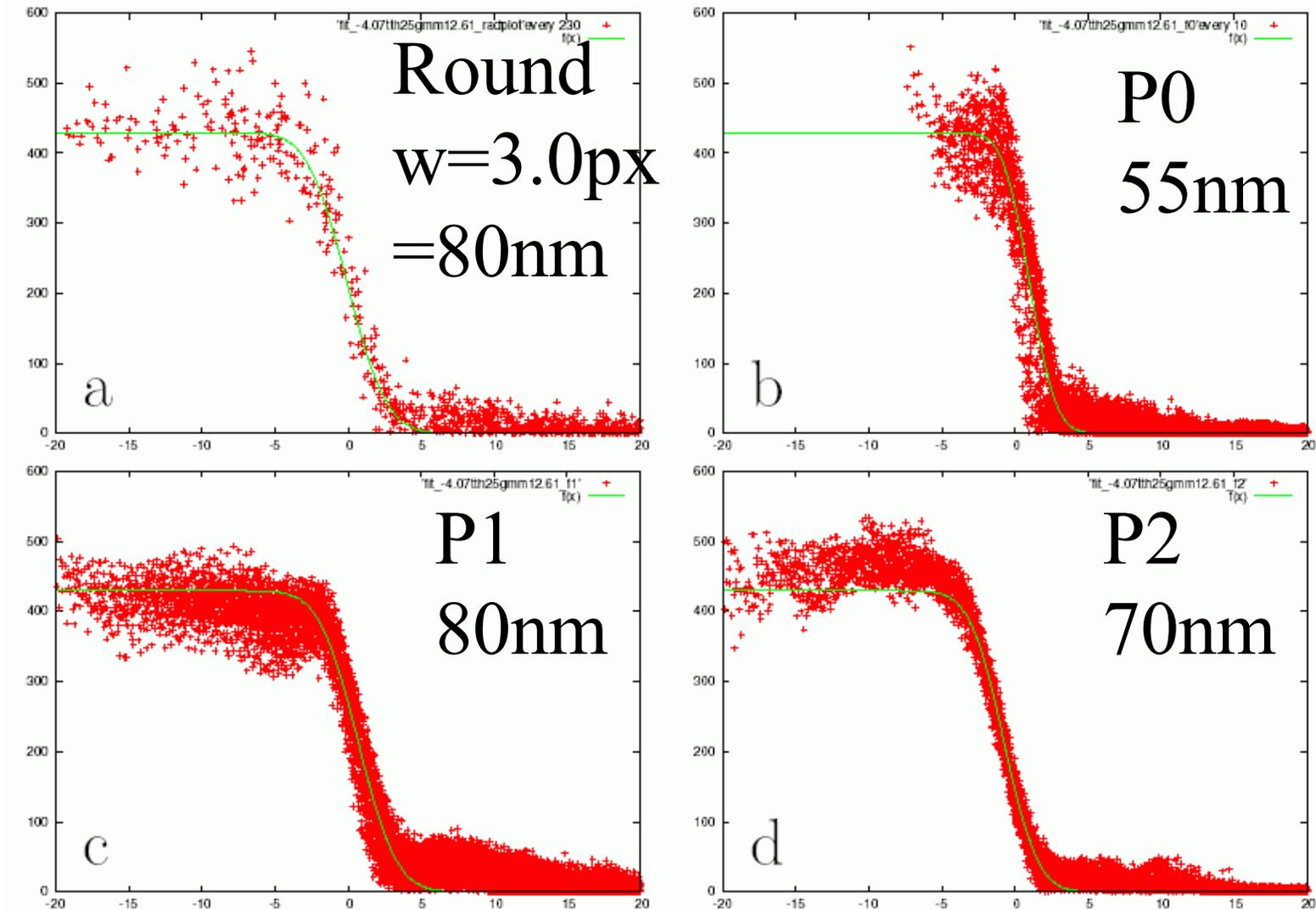
Angles between facets



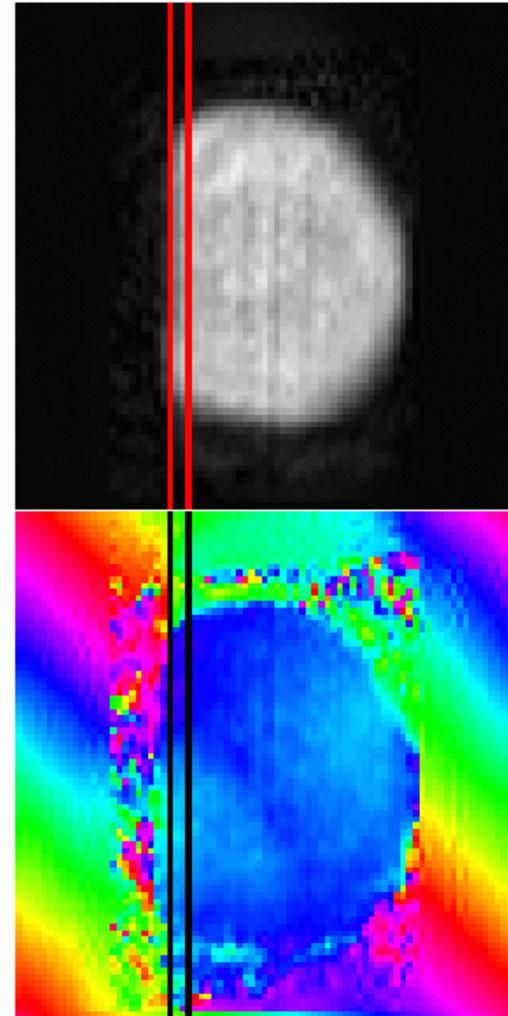
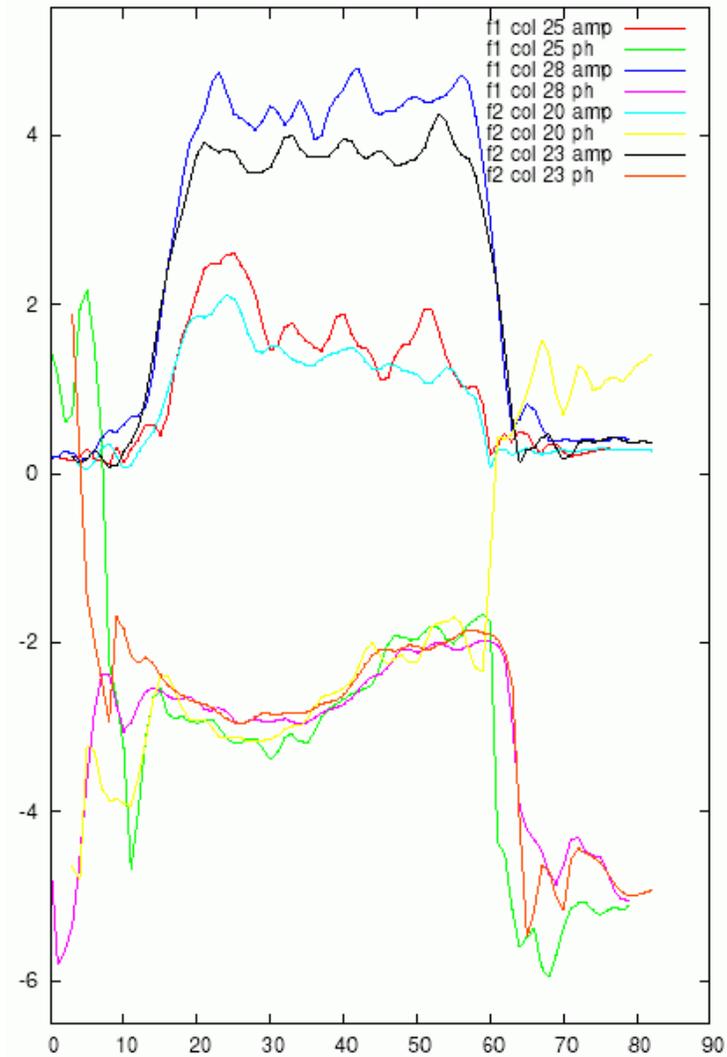
Facets of Equilibrium Crystal Shape



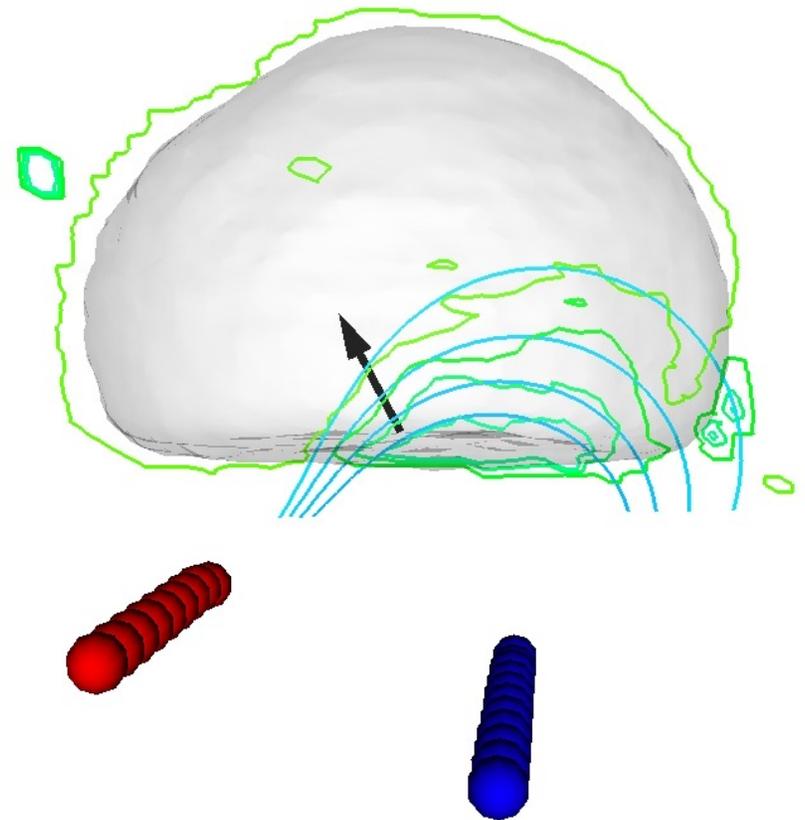
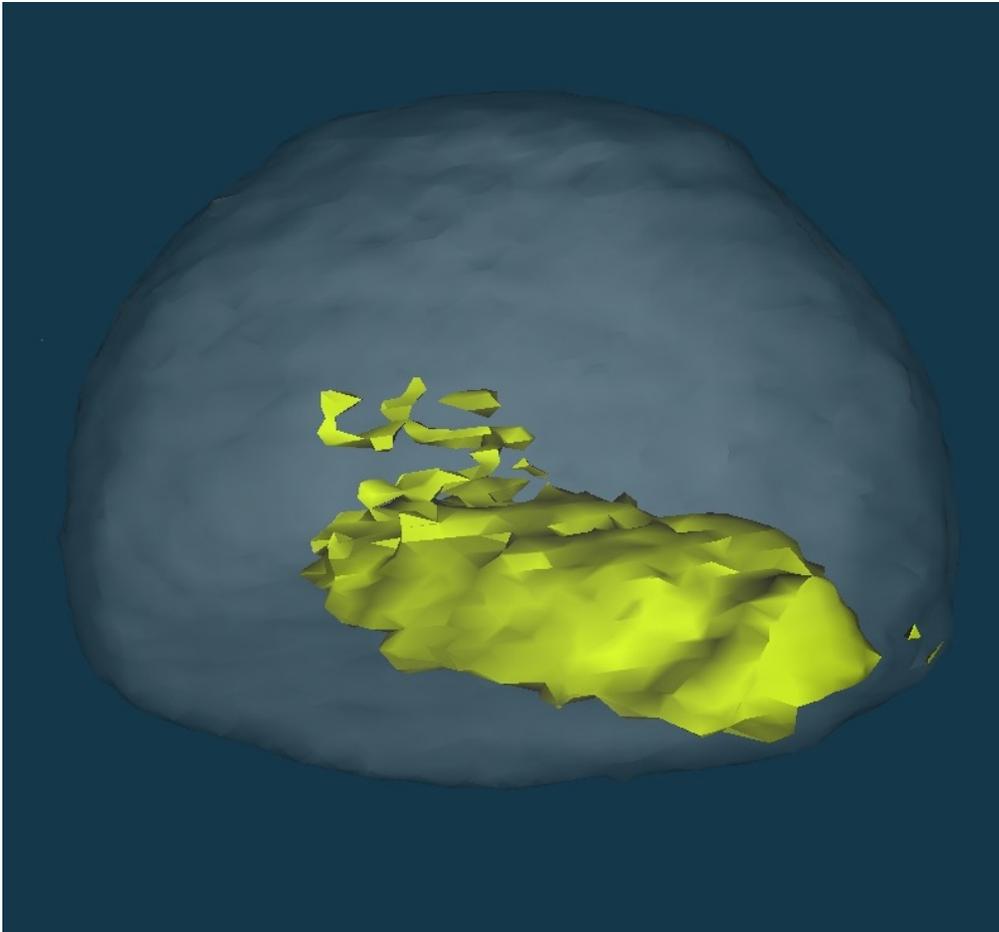
Density distribution across surface



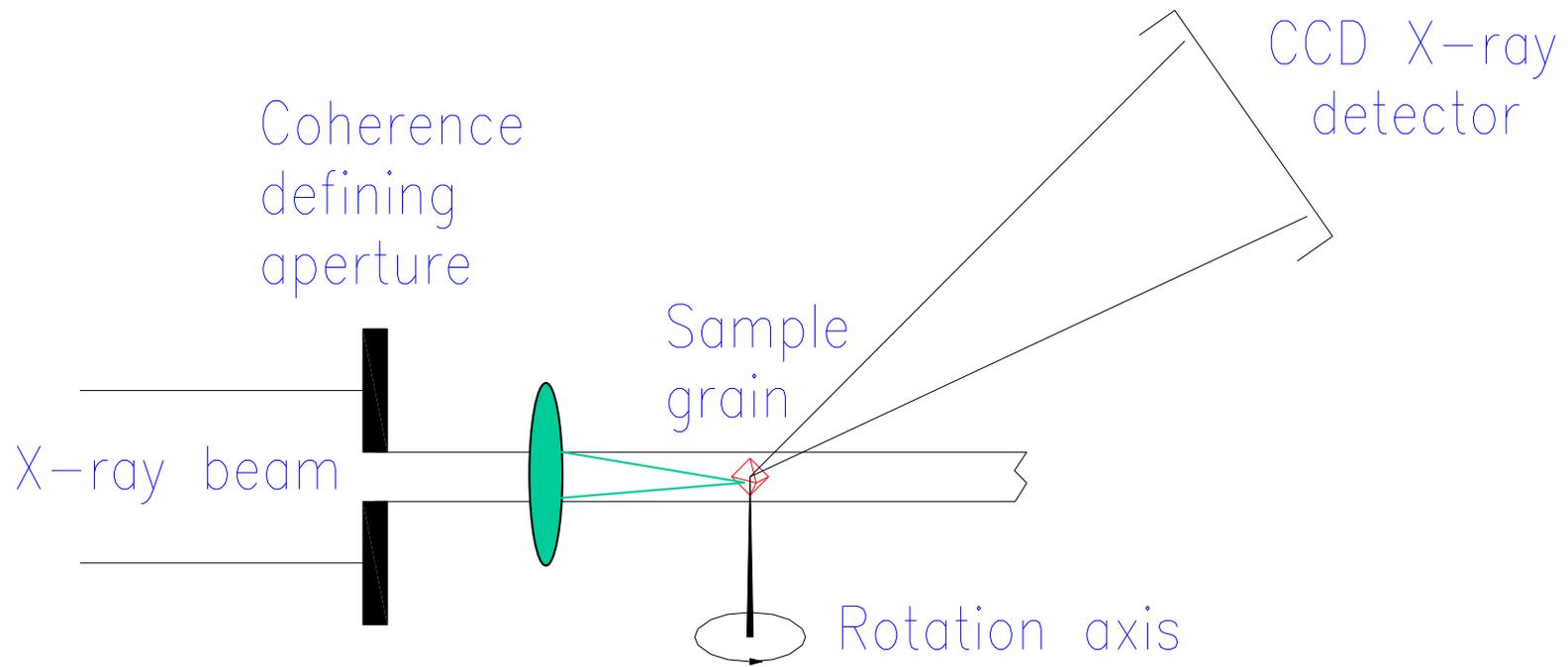
Phase structure near substrate interface



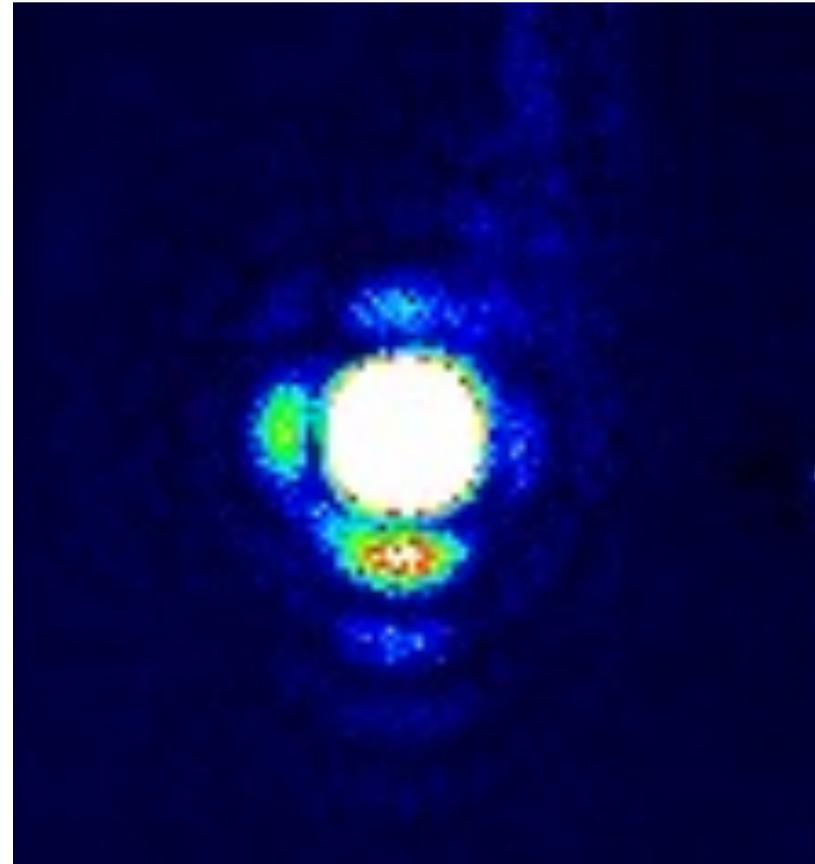
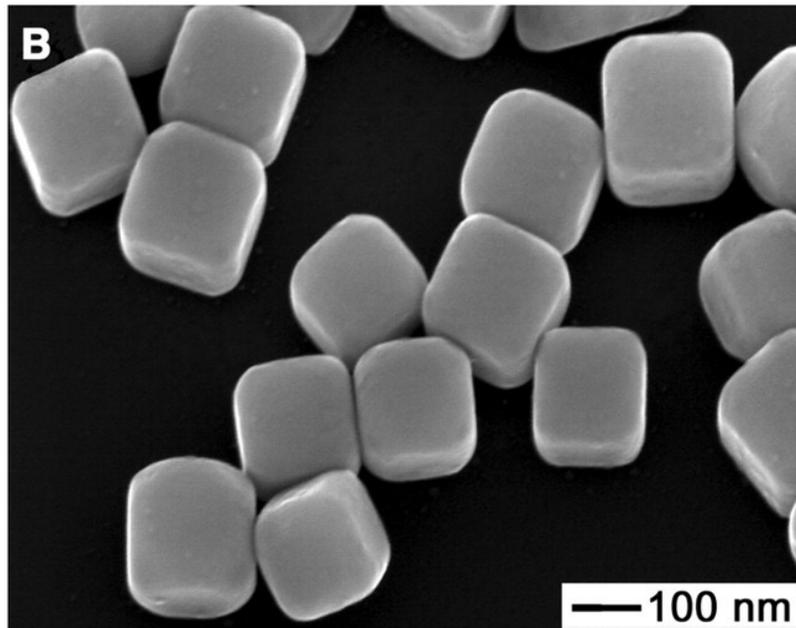
Modeling of 3D Phase Bump



Lensless X-ray Microscope

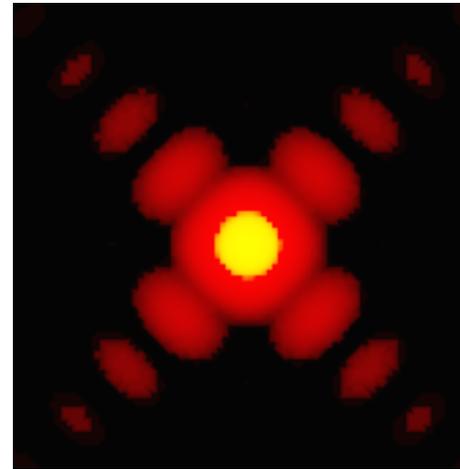
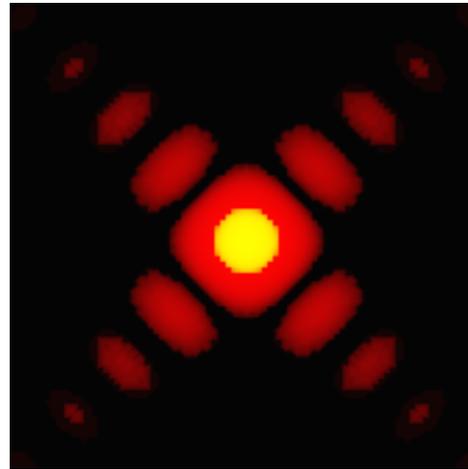


CXD from Silver Nanocubes



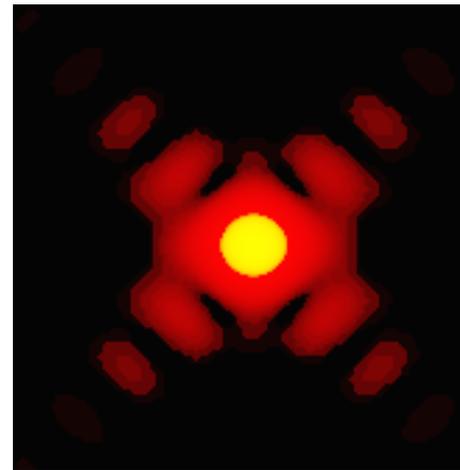
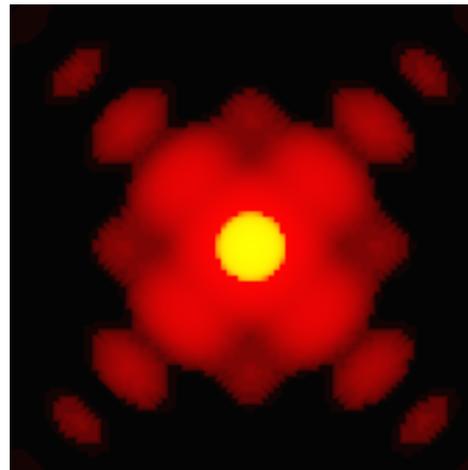
Yugang Sun and Younan Xia,
Science 298 2177 (2003)

Spherical and cylindrical waves



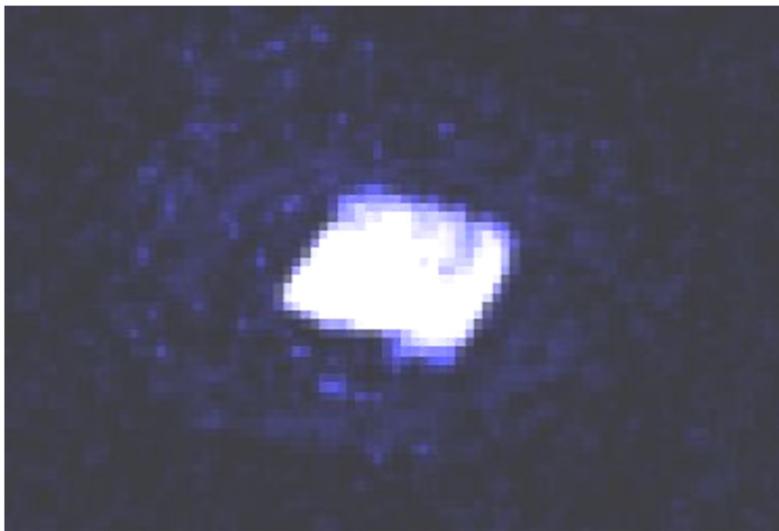
$\pi/4$

$\pi/2$

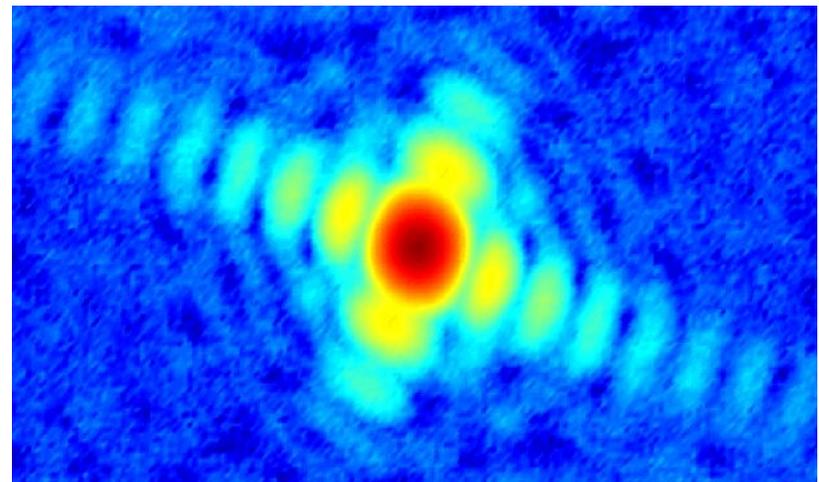
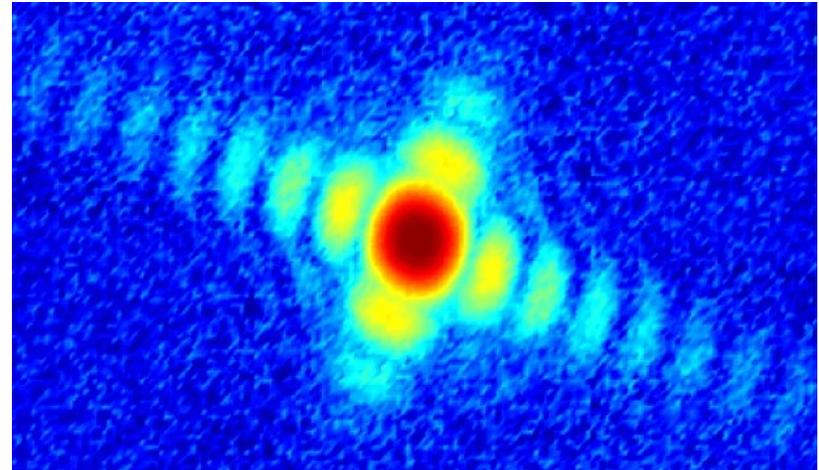


$\pi/4$ (x)

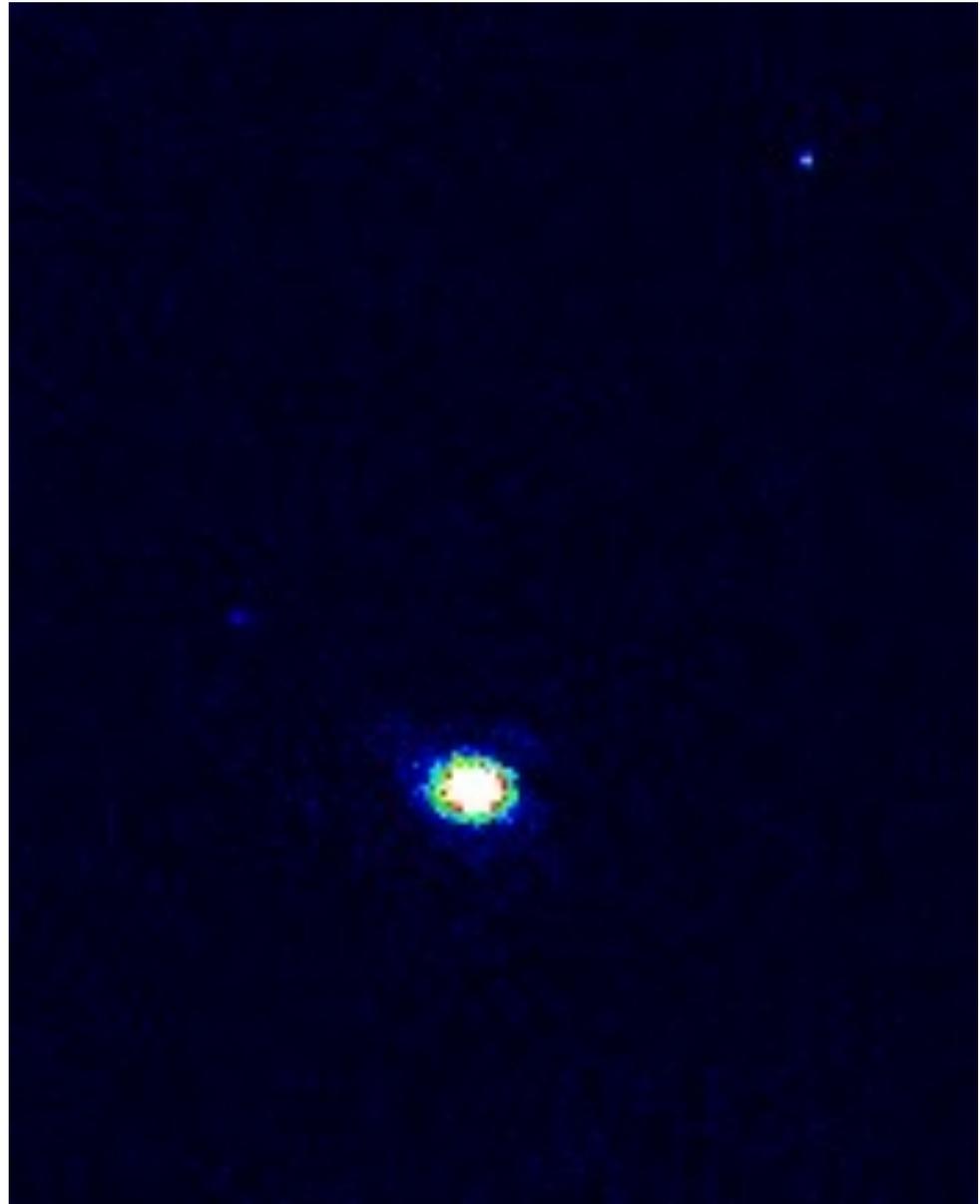
Reconstruction of Ag Nanocrystal



←→
200nm



Rocking
scan of Ag
cubes with
 0.01° steps



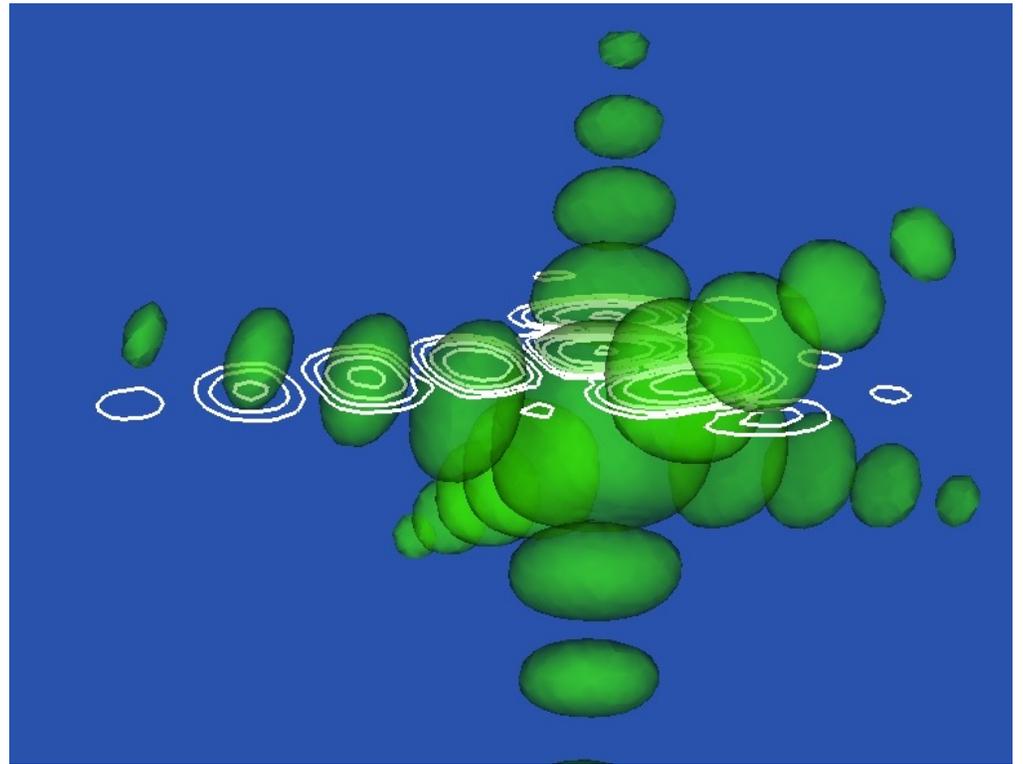
Miscentered Non-Centrosymmetric Reciprocal Space Slice



$$A_q \neq A_{\bar{q}}^*$$

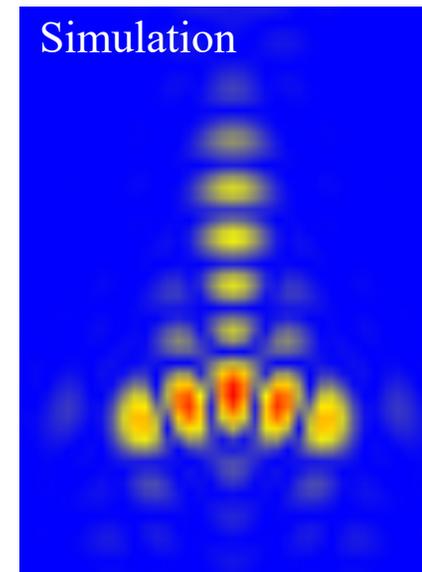
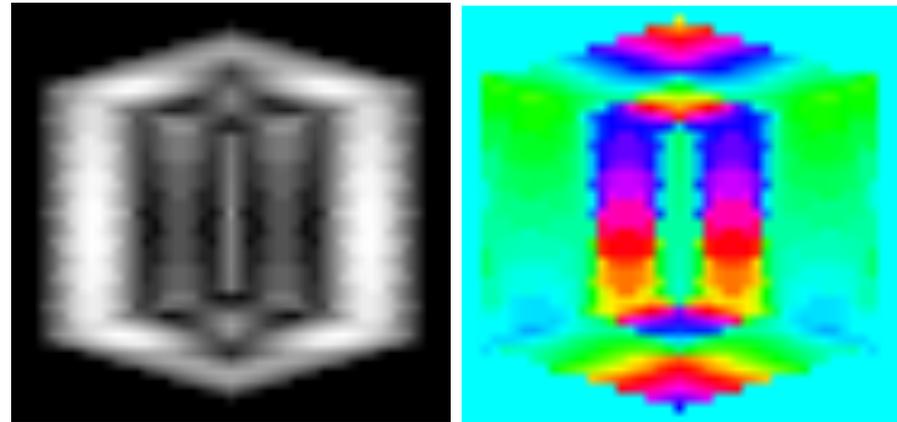
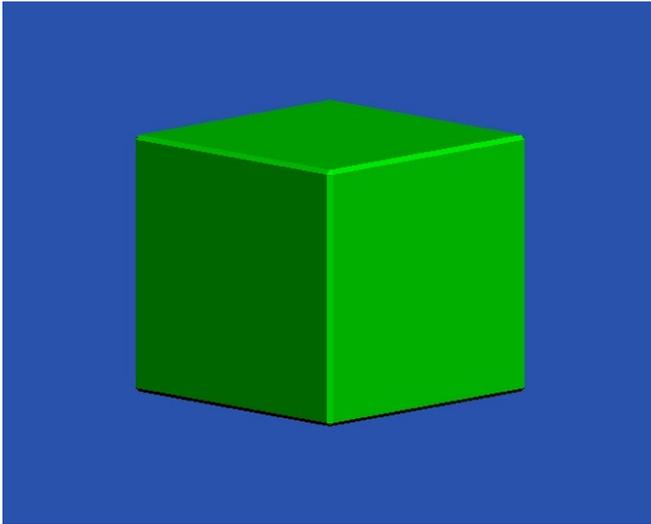


Real-space phase.

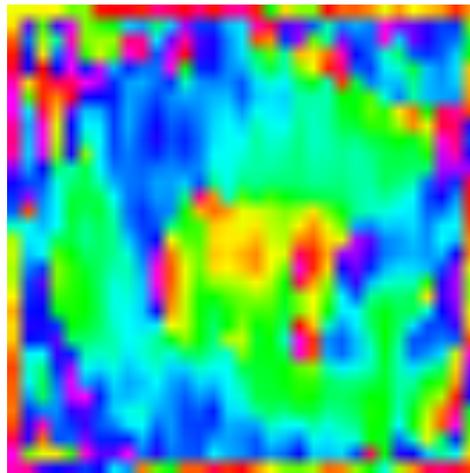
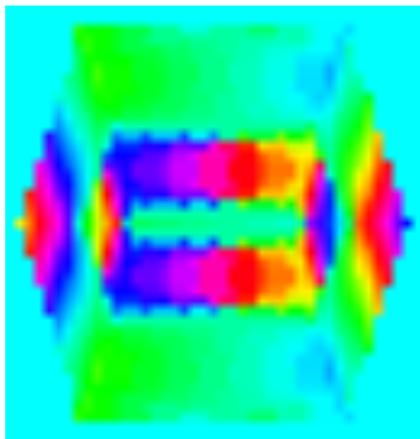
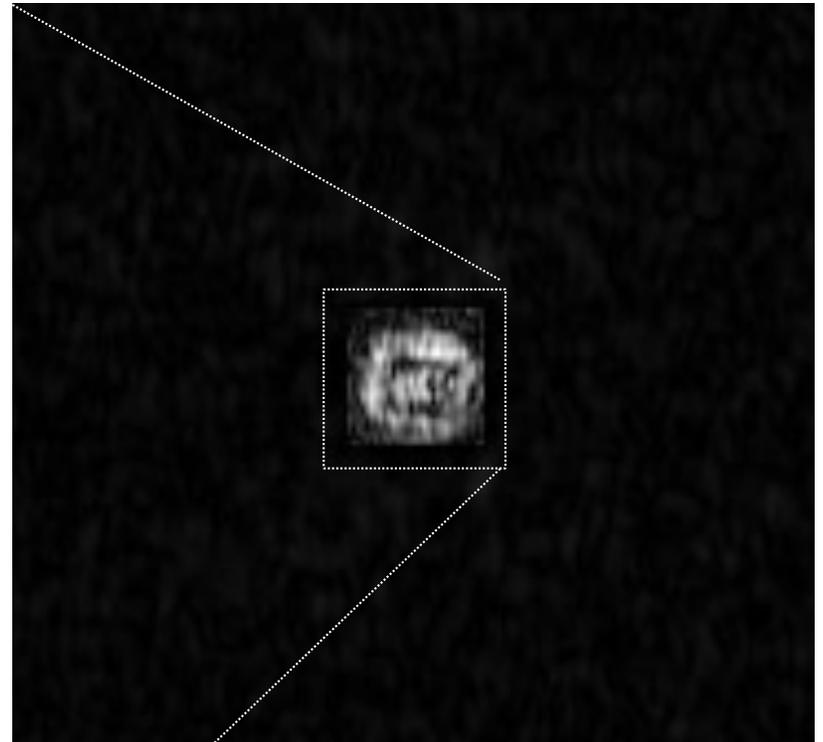
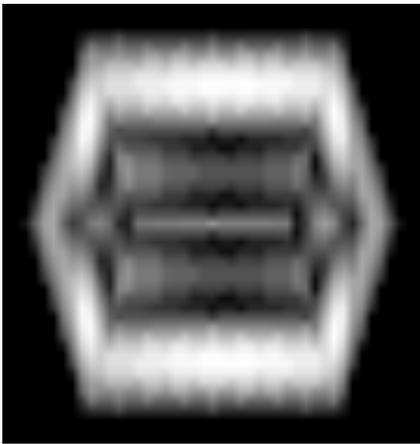


What can we expect to see?

$$A(\bar{q}_o + \bar{q}_z) = \sum_i \underbrace{\sum_z \rho(x, y, z)}_{u_i(x, y)} e^{2\pi i \bar{q}_z \cdot \bar{z}_i} e^{2\pi i (\bar{q}_o) \cdot \bar{r}_i}$$

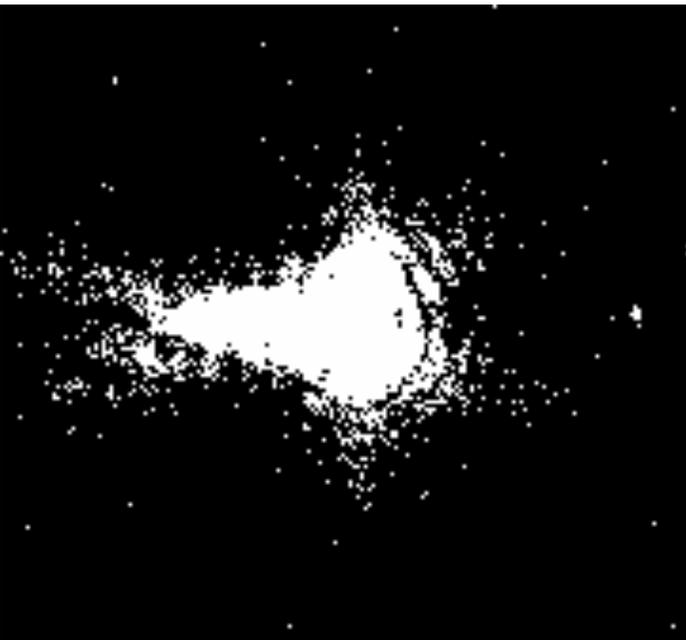
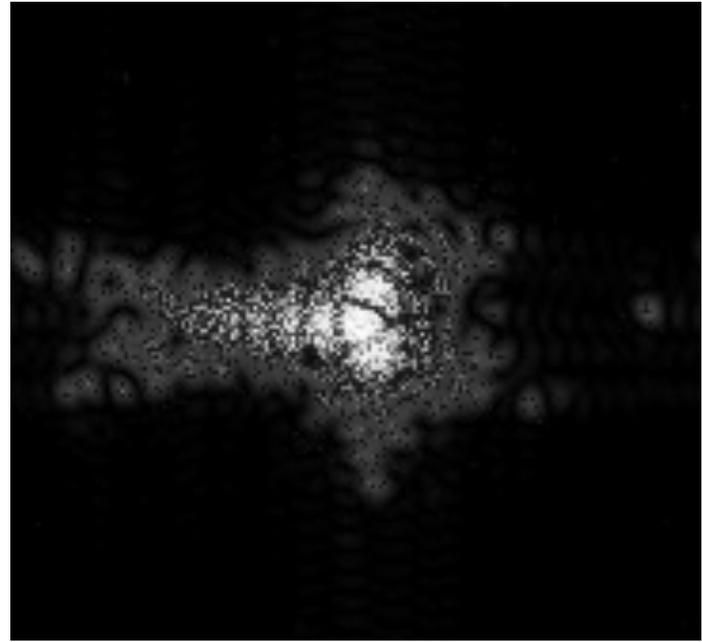
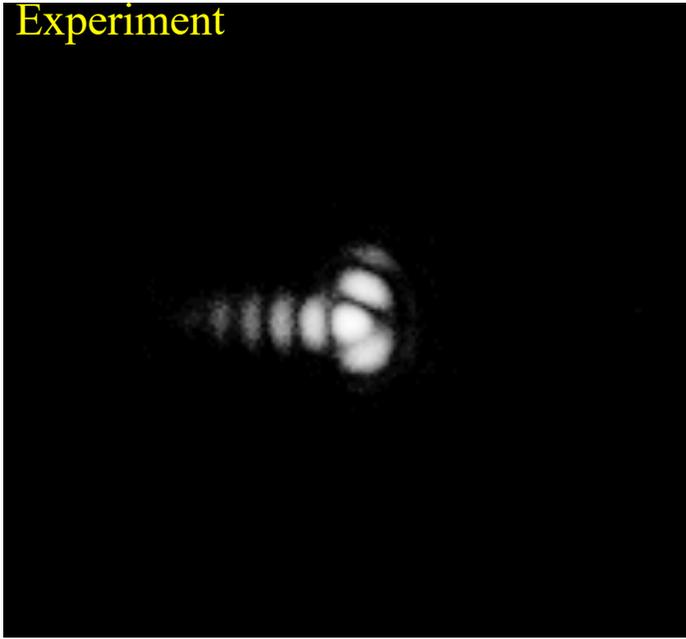


Direct Space Result (1000 Iterations)



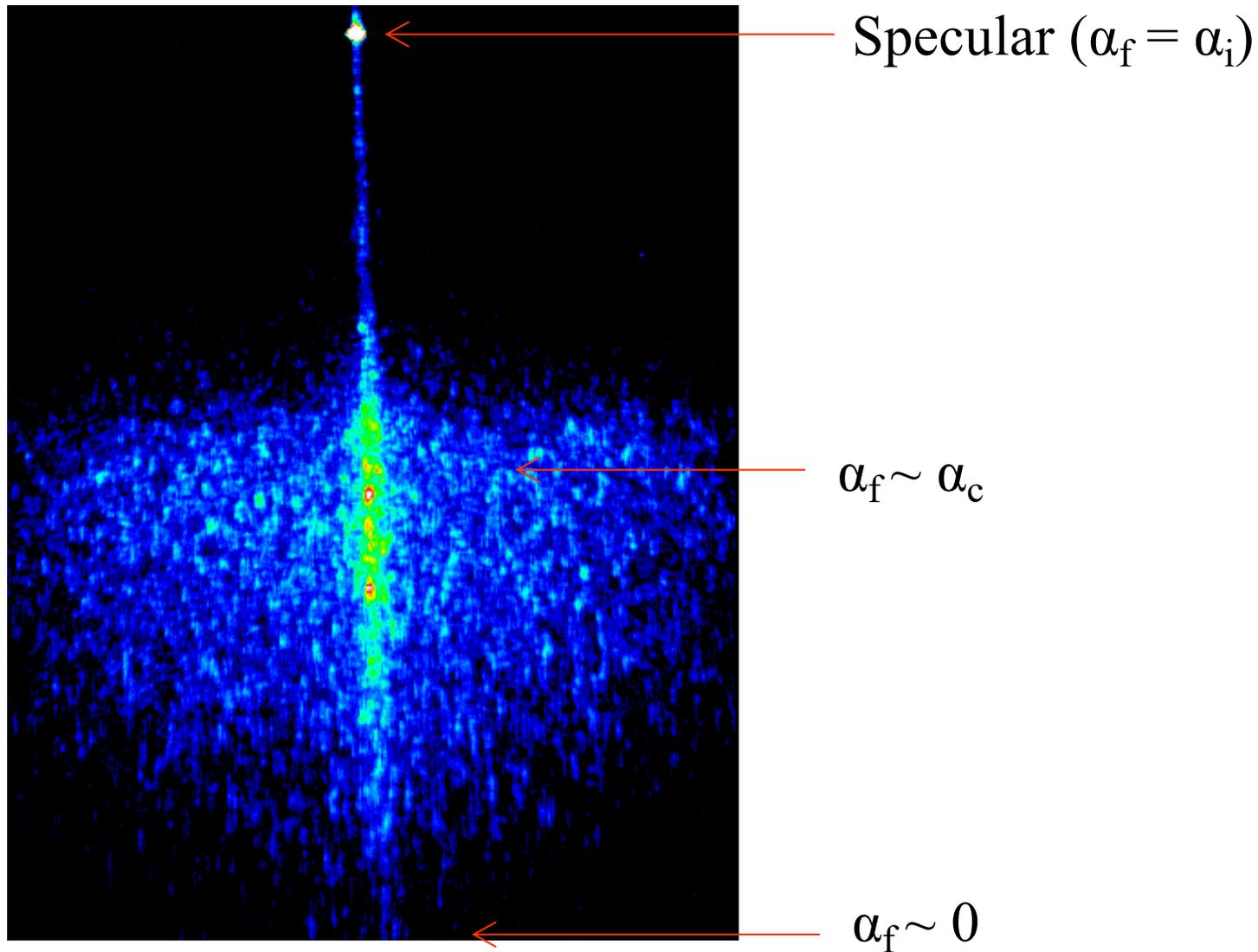
Reciprocal Space Result (1000 iterations)

Experiment



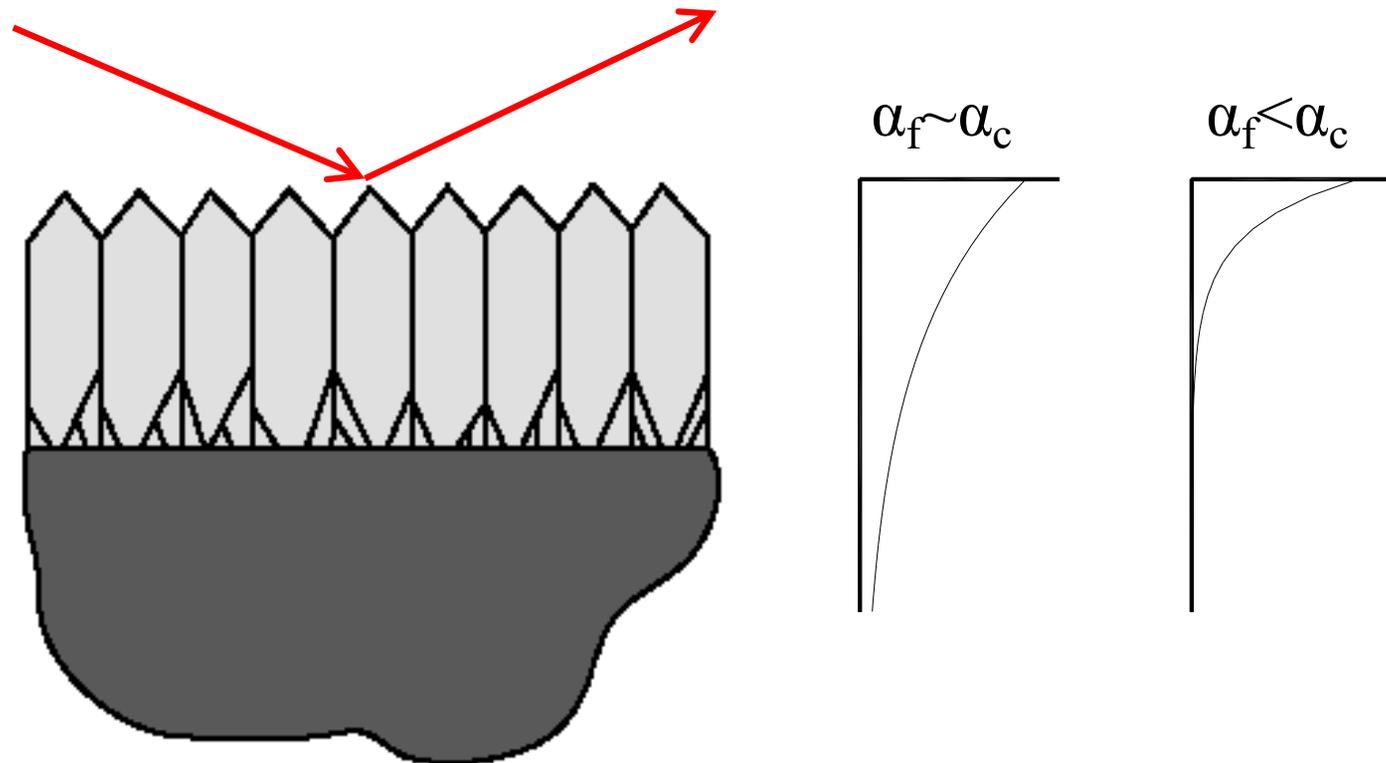
Fine Structure in “Yoneda” Peak

Grazing-exit diffraction from a 1000Å Au polycrystalline film

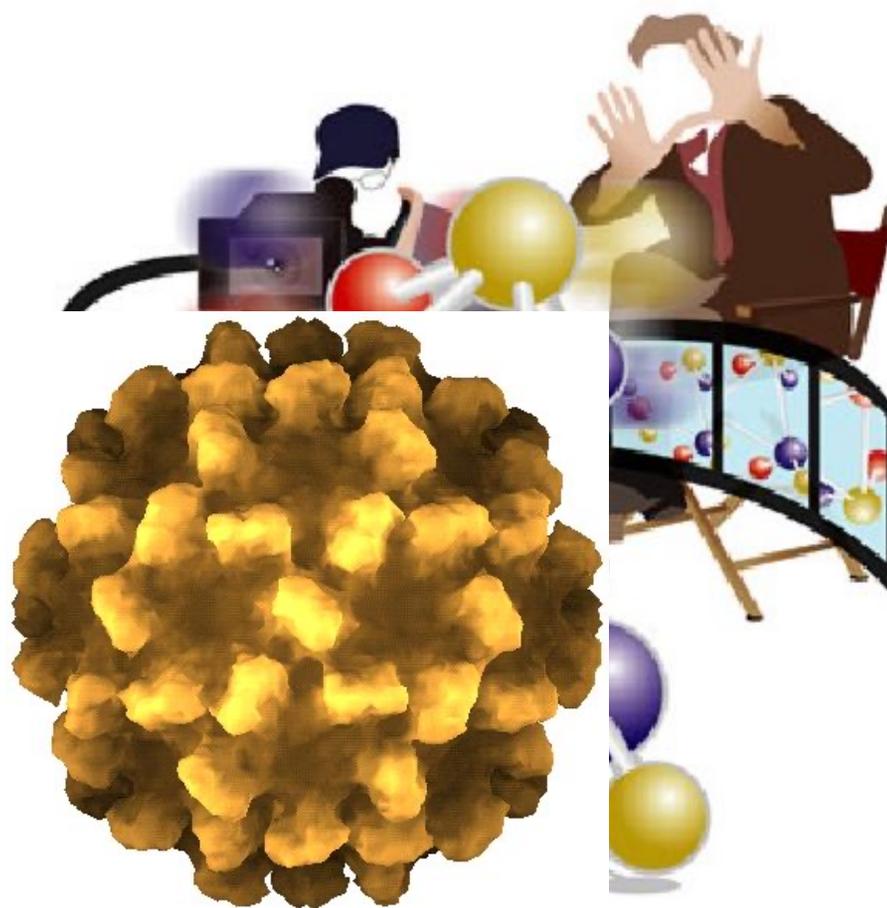


Competitive Grain Growth

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



Molecular Movies using XFEL



Conclusions and Outlook

- Inversion of CXD demonstrated
- Internal structure of Au Nanocrystals
- Preservation of coherence upon focussing
- Complex density represents strain
- Single molecules one day