Coherent X-ray Diffraction as a probe of Nanocrystalline Materials

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Spring-8 Seminar
13 October 2004

Outline

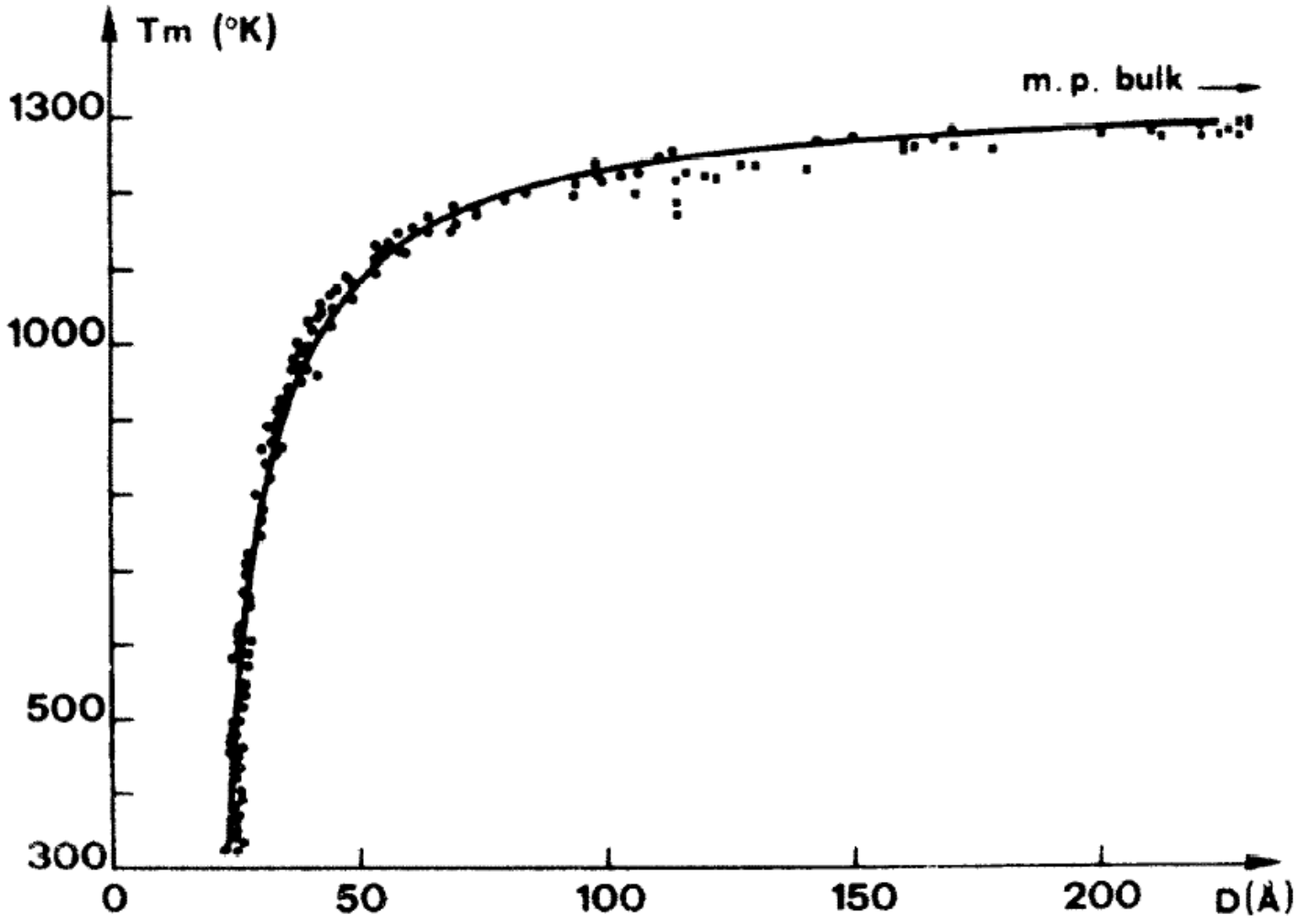
- Coherence in Diffraction
- The Phase Problem
- Nanocrystal Shapes
- Imaging of Phase Objects
- Quantum Dot structures
- How small can we go?

Goals of Coherent Diffraction

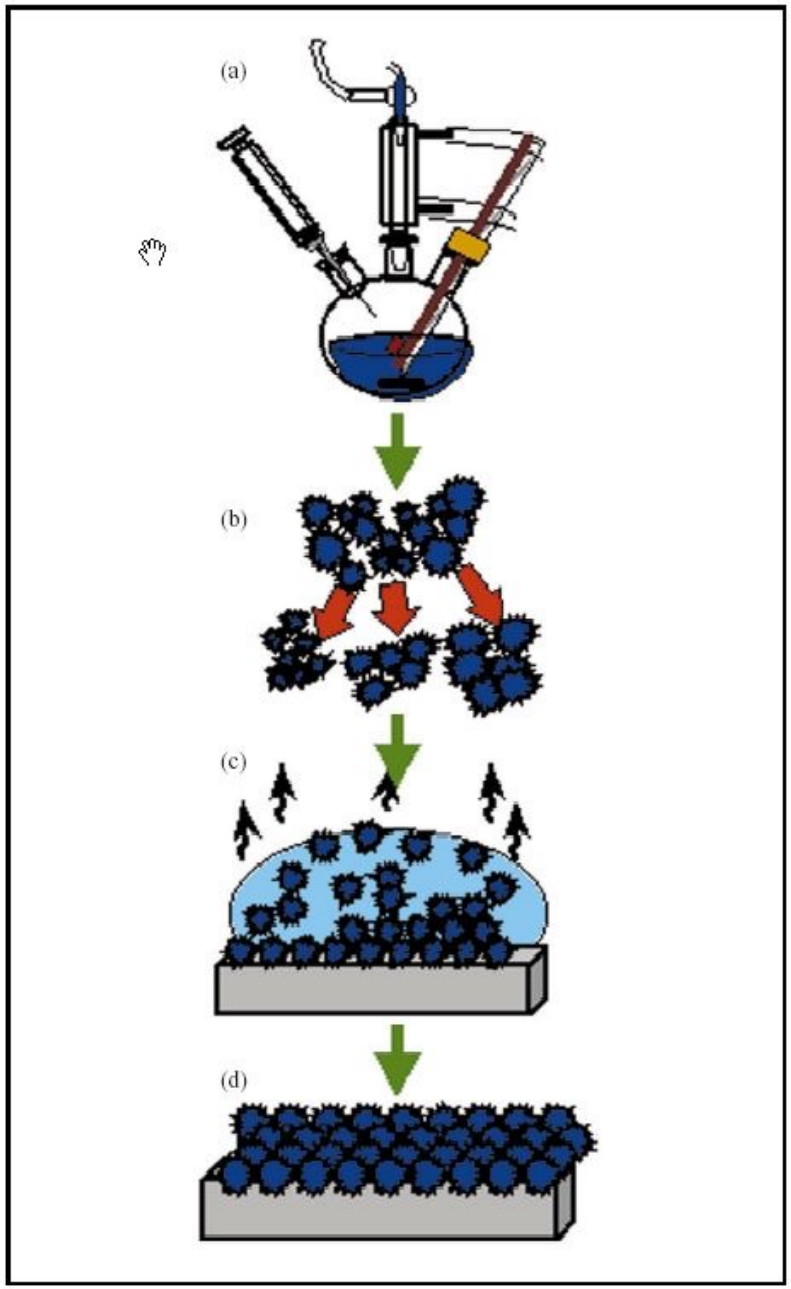
- Thermodynamic fluctuations
  - No ensemble average in CXD
- Probe of structure on nm scale
  - 1D, 2D and 3D
  - non-periodic object gives continuous F(**q**)
- Oversampling (in reciprocal space) permits solution of the phase problem

Size-dependent Melting of Au Particles

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

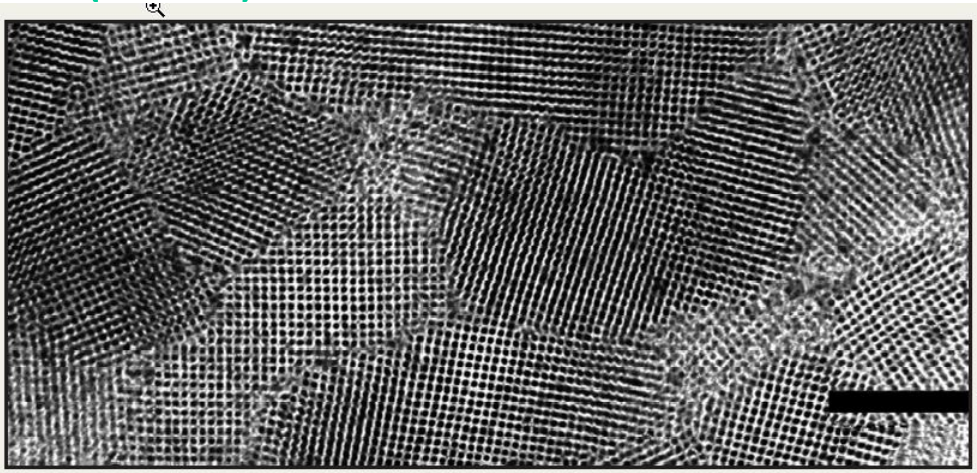


Chemical Synthesis of Nanocrystals

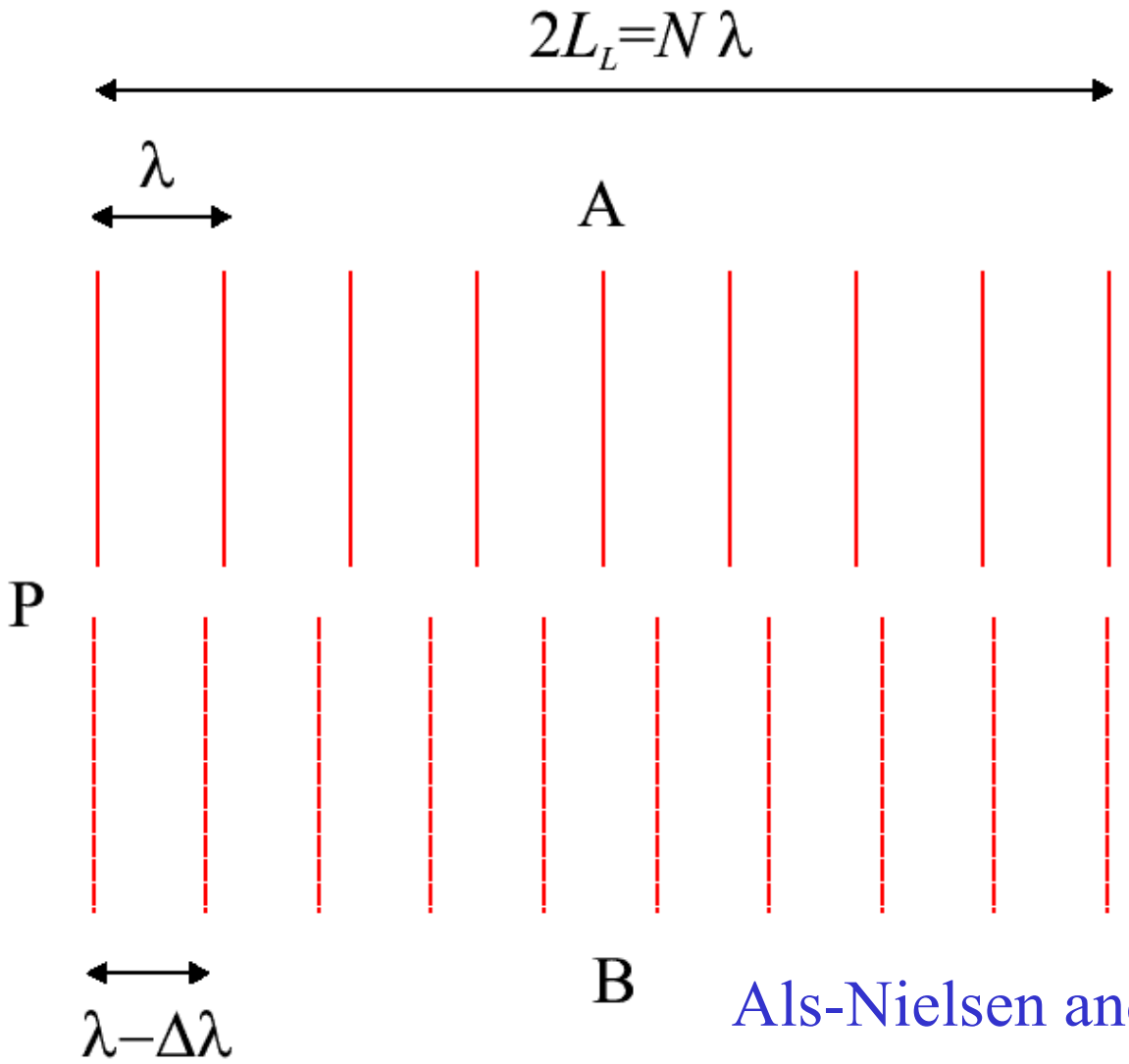


- Reactants introduced rapidly
- High temperature solvent
- Surfactant/organic capping agent
- Square superlattice (200nm scale)

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



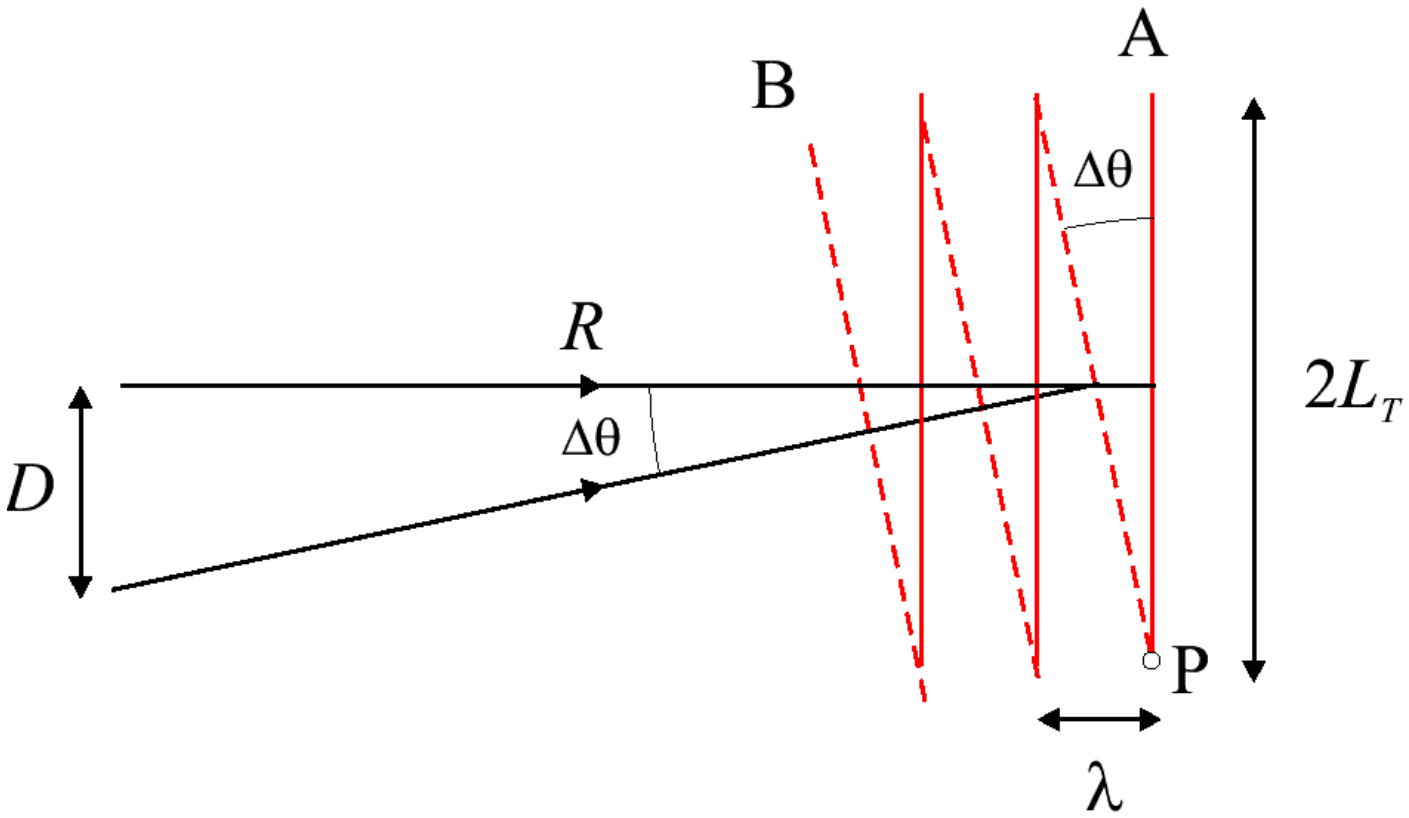
Longitudinal Coherence



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

Als-Nielsen and McMorrow (2001)

Lateral (Transverse) Coherence



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

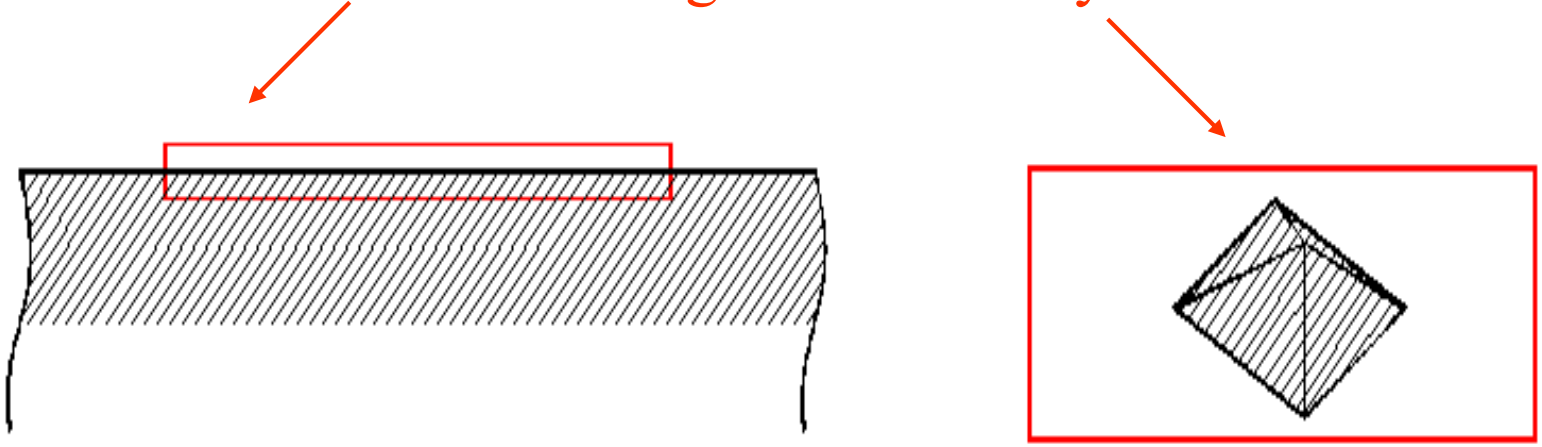
Als-Nielsen and McMorrow (2001)

Coherence at Spring8, APS or ESRF

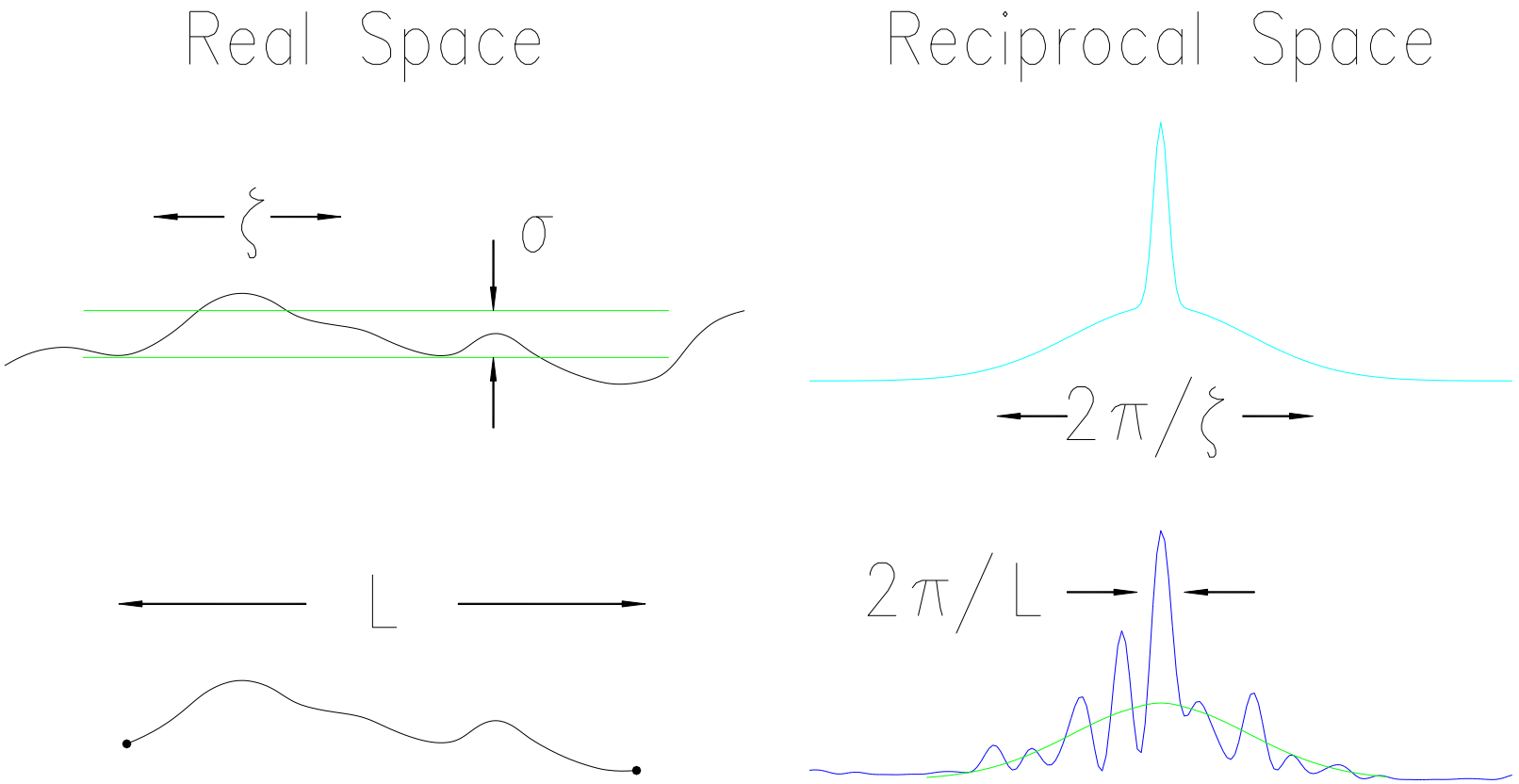
Typical of 3rd Generation (undulator) Synchrotron Source

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}

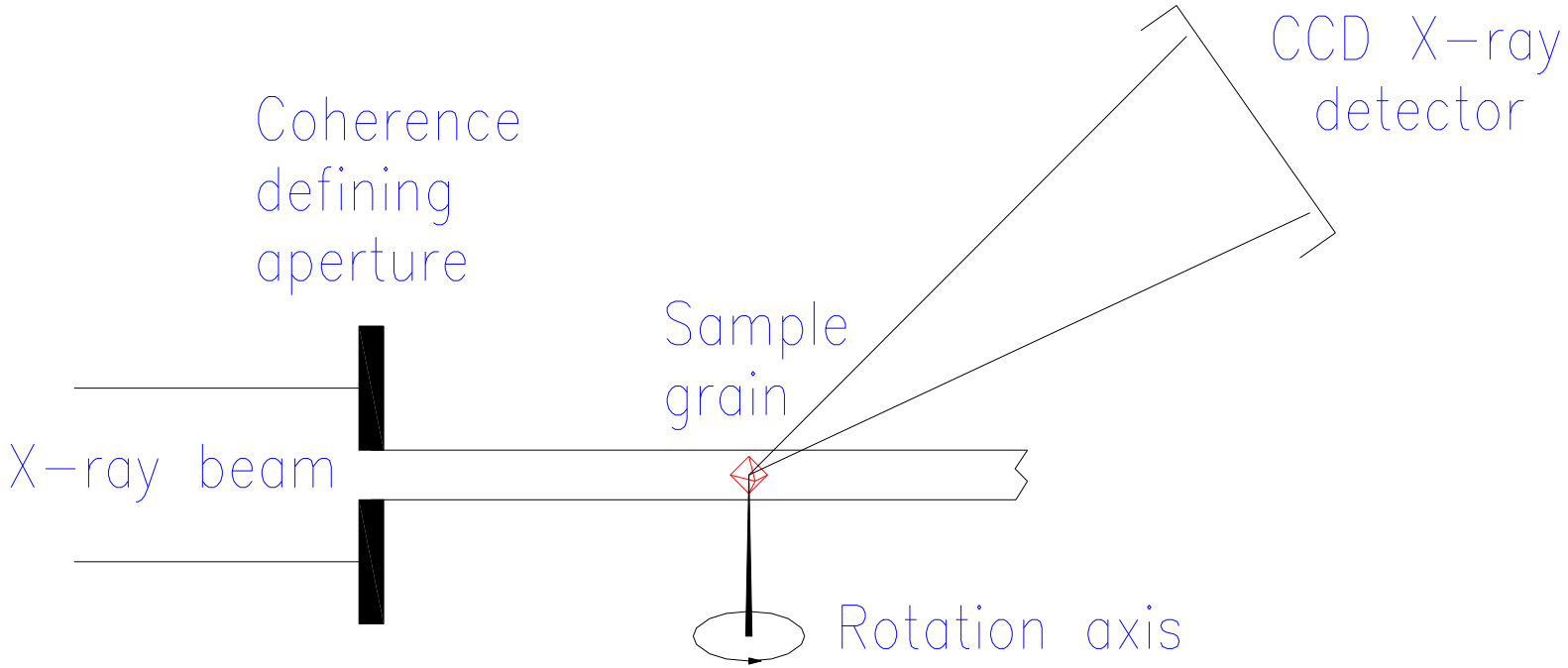
Coherent region defined by slits



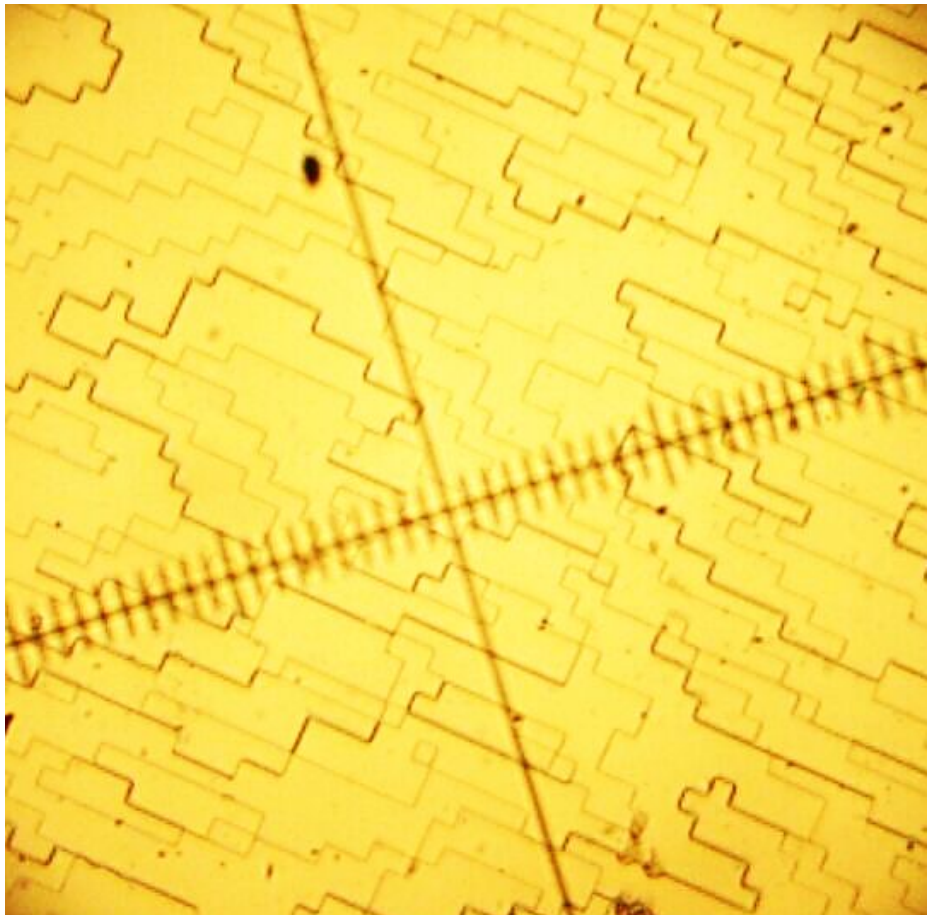
Diffuse Scattering acquires Structure using CXD



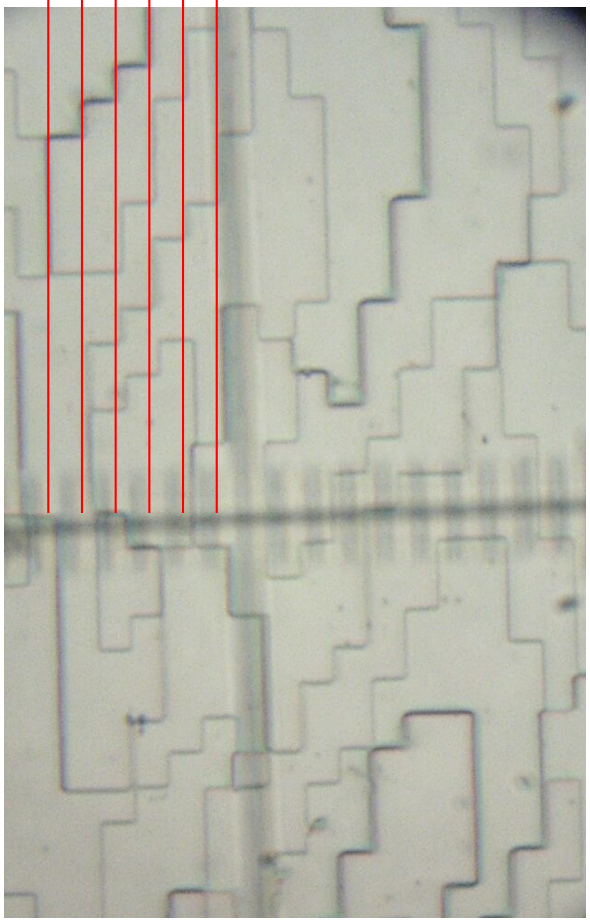
Lensless X-ray Microscope



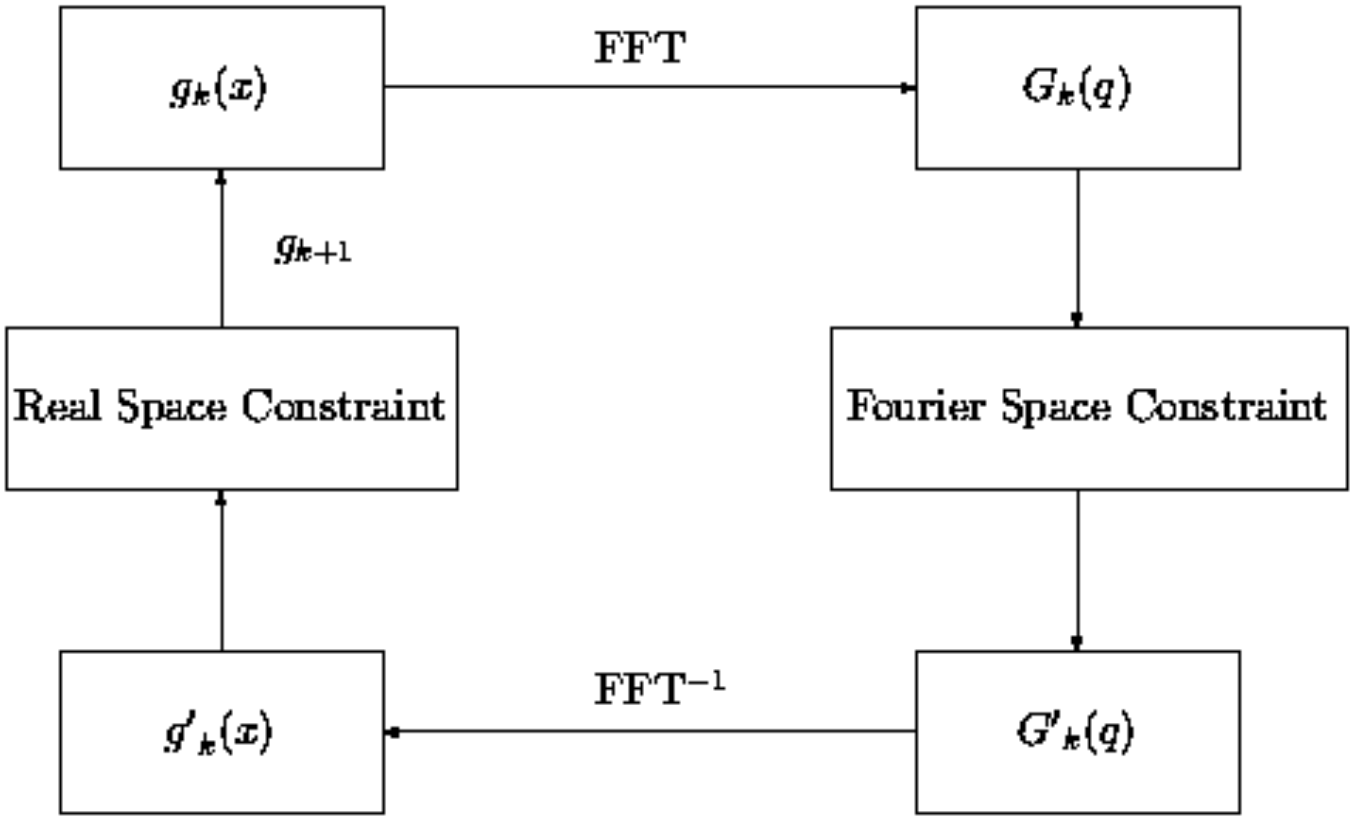
Microscope Images of Gratings



5μm grid lines



Generic "Error Reduction" method



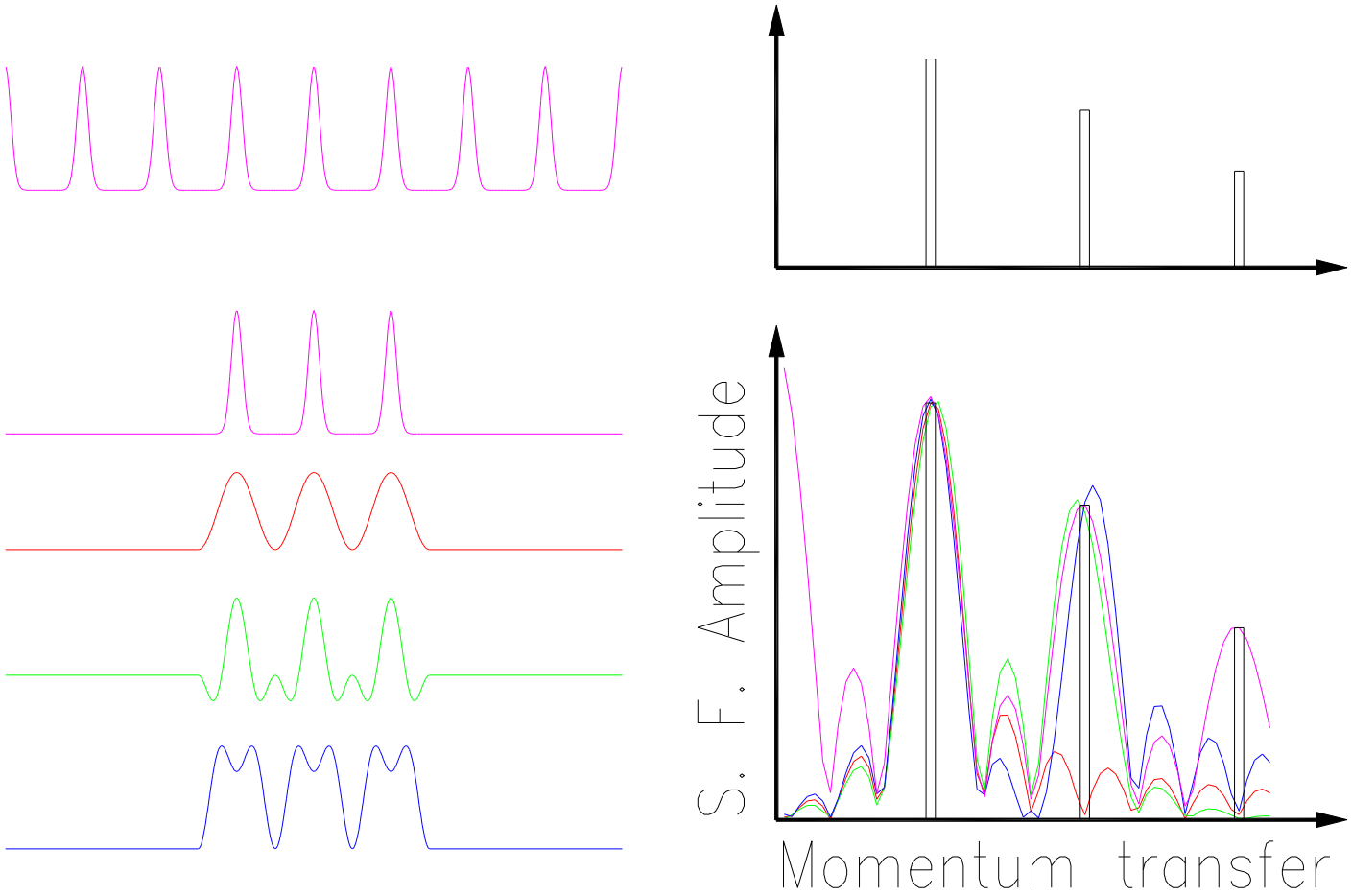
J. R. Fienup Appl. Opt. 21 2758 (1982)
R. W. Gerchberg and W. O. Saxton Optik 35 237 (1972)

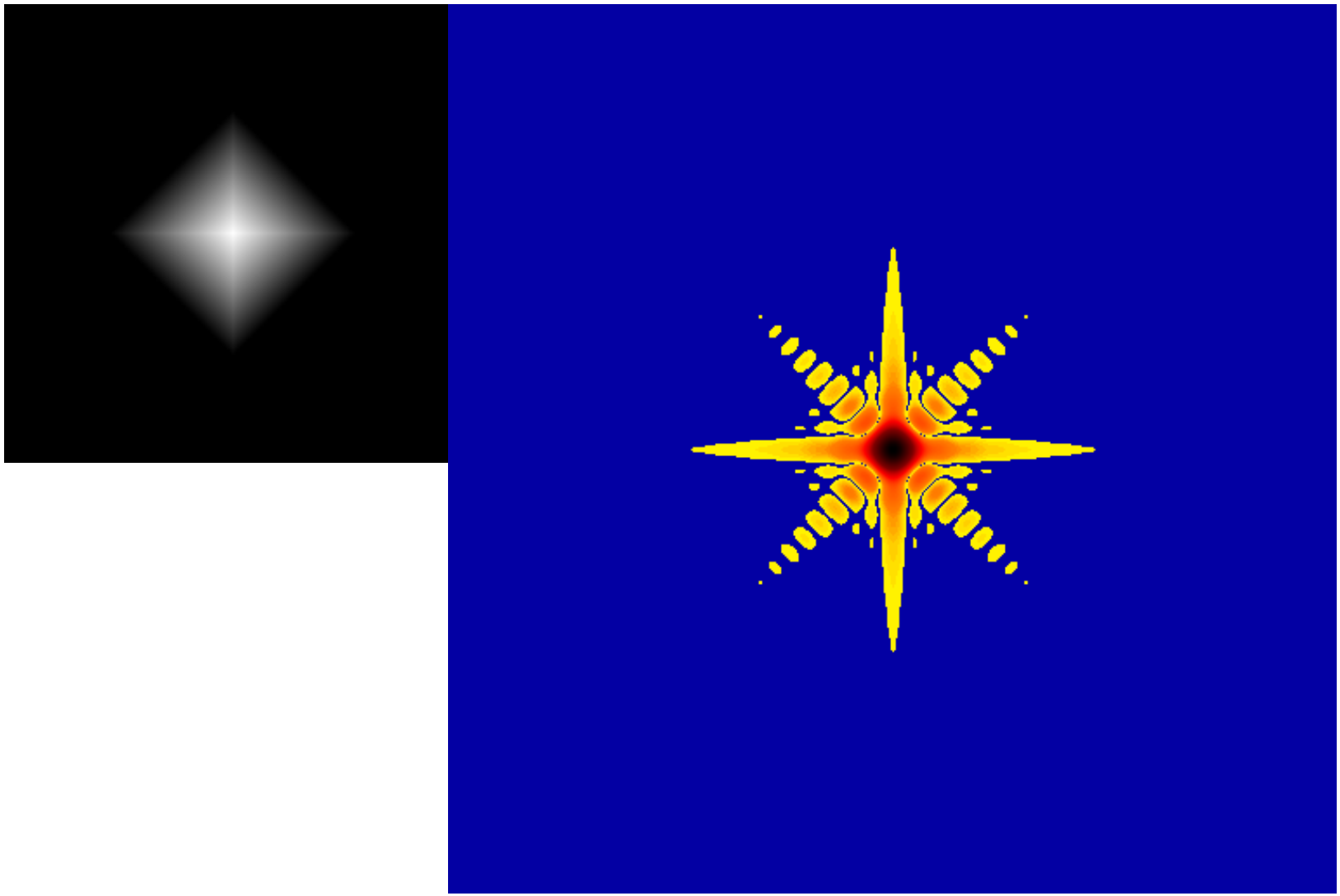
Real-space Constraints in Crystallograhy

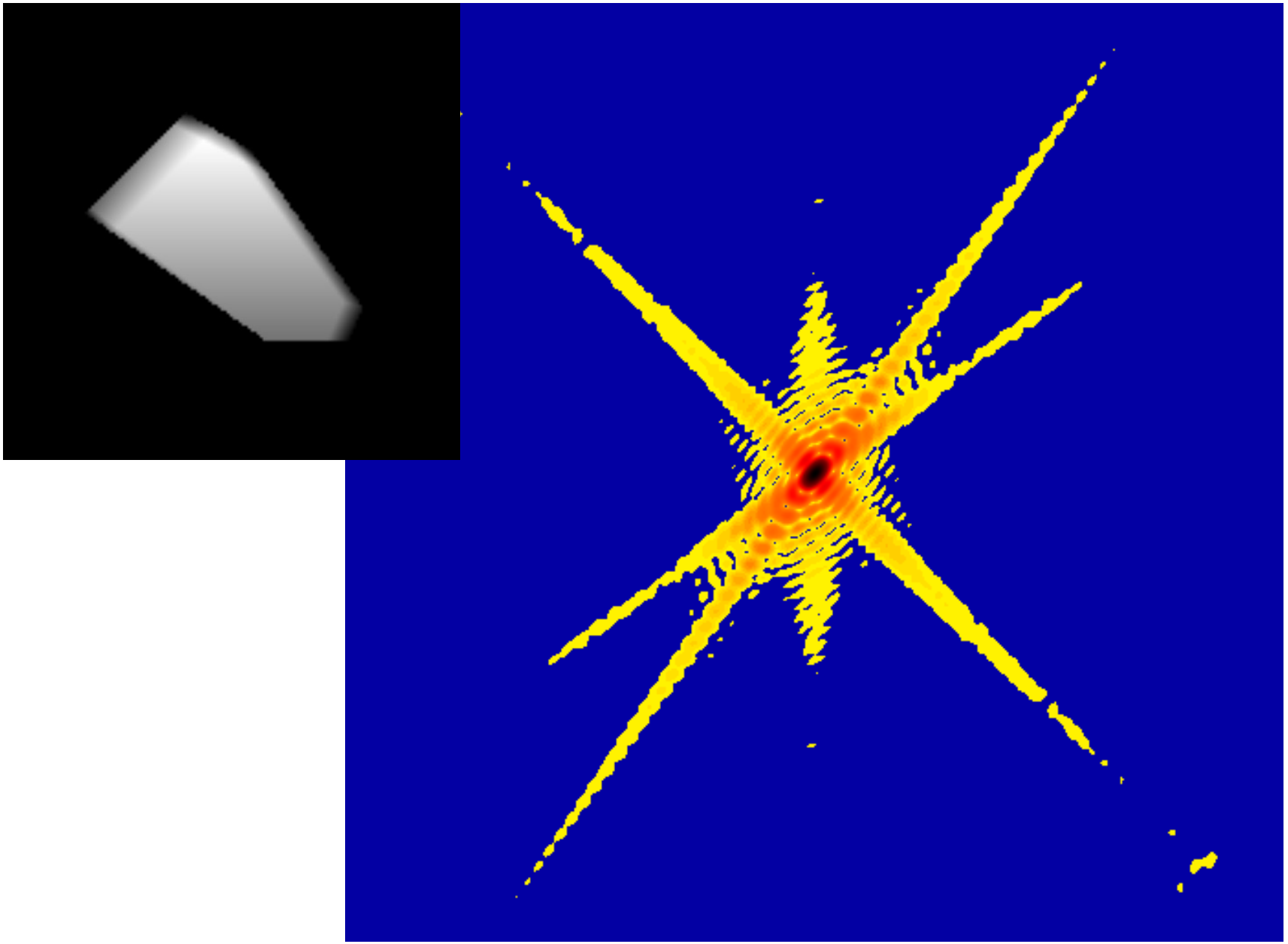
R. P. Millane, J. Opt. Soc Am. A **13** 725 (1996)

- '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)

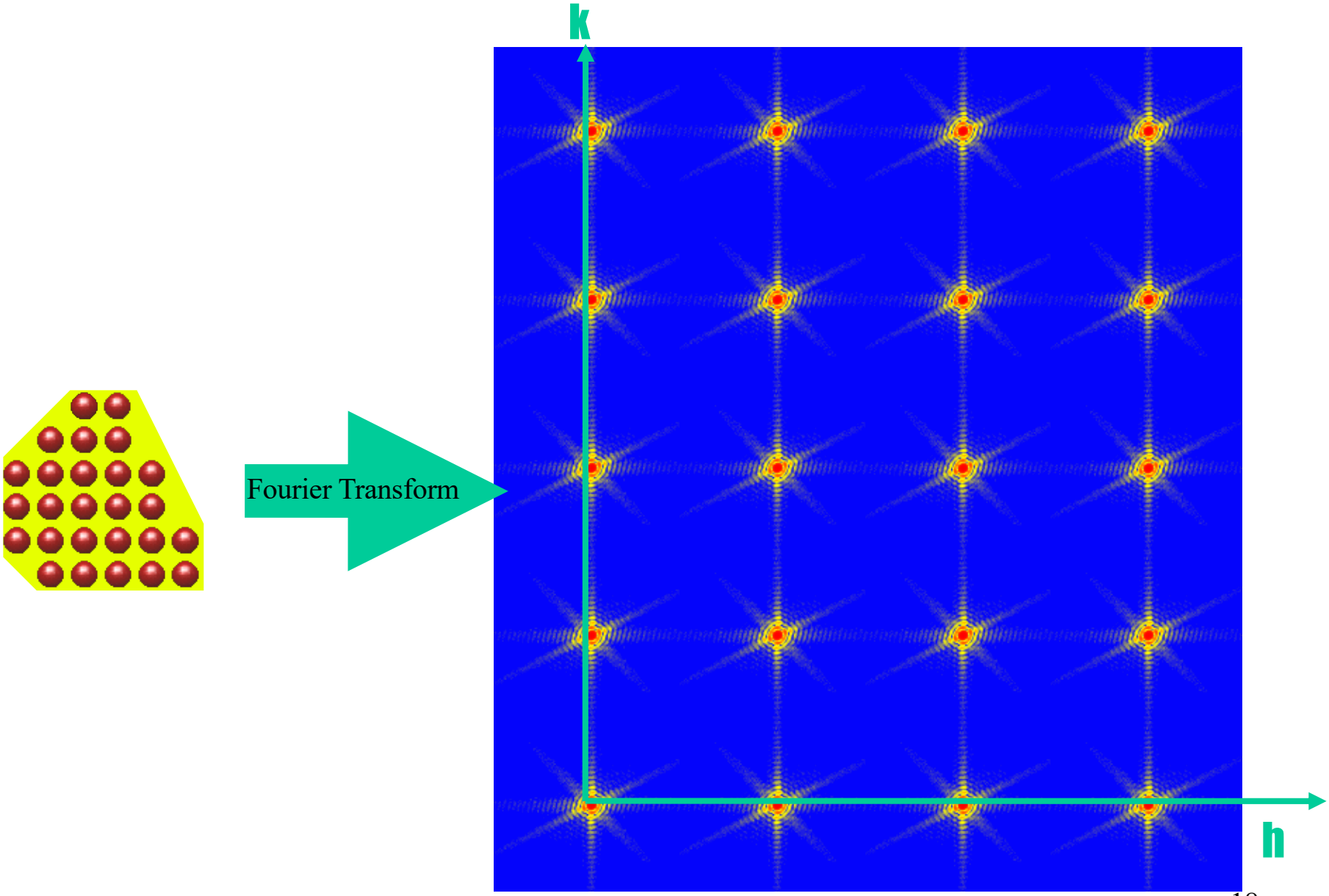
Phase Problem: Finite-size Effect





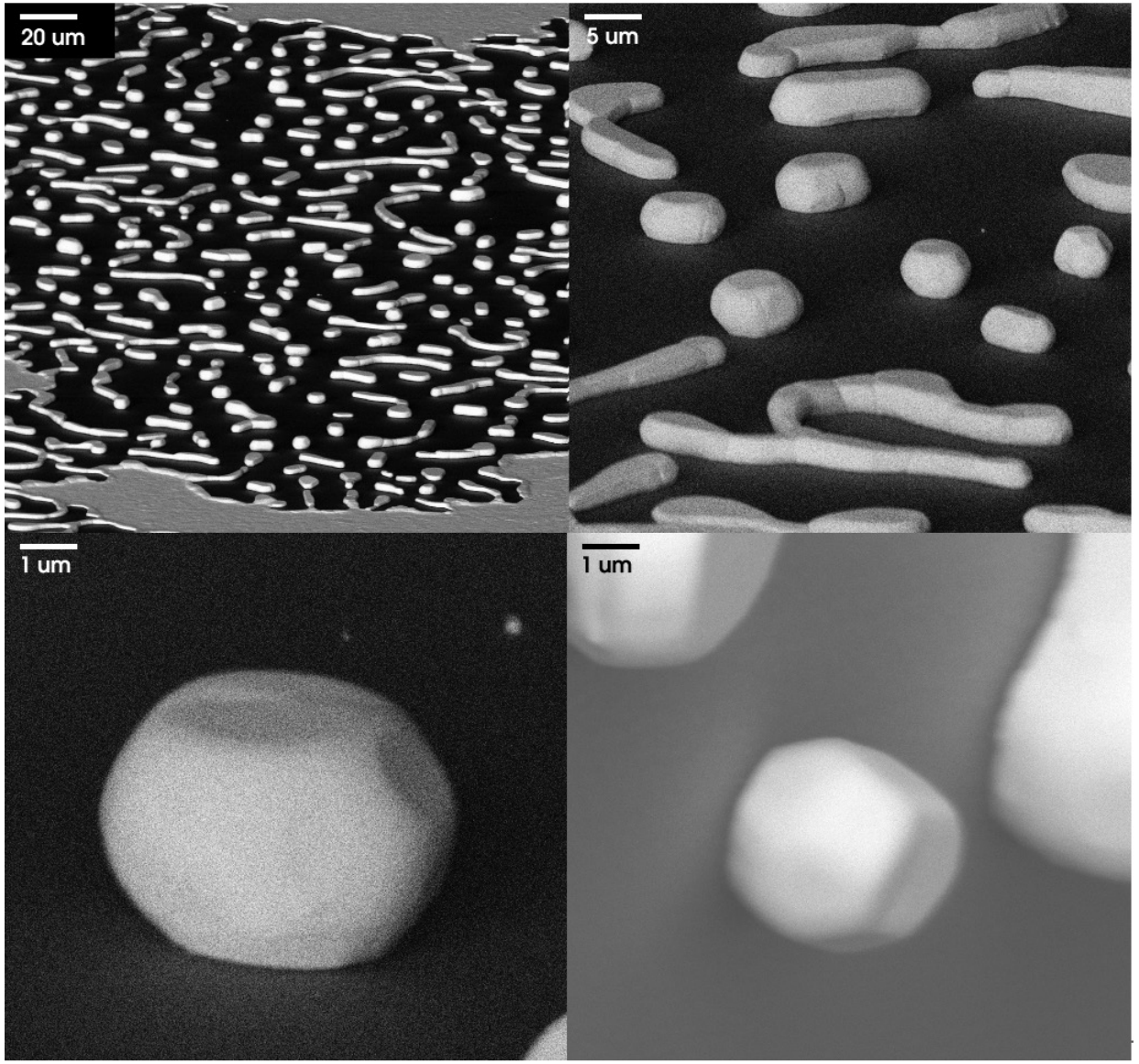


Coherent Diffraction from Crystals



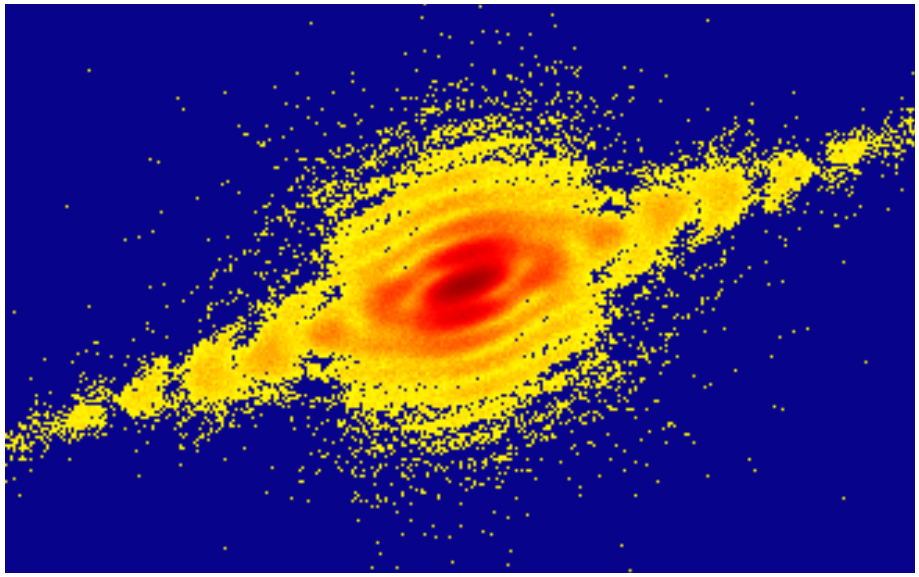
SEMS

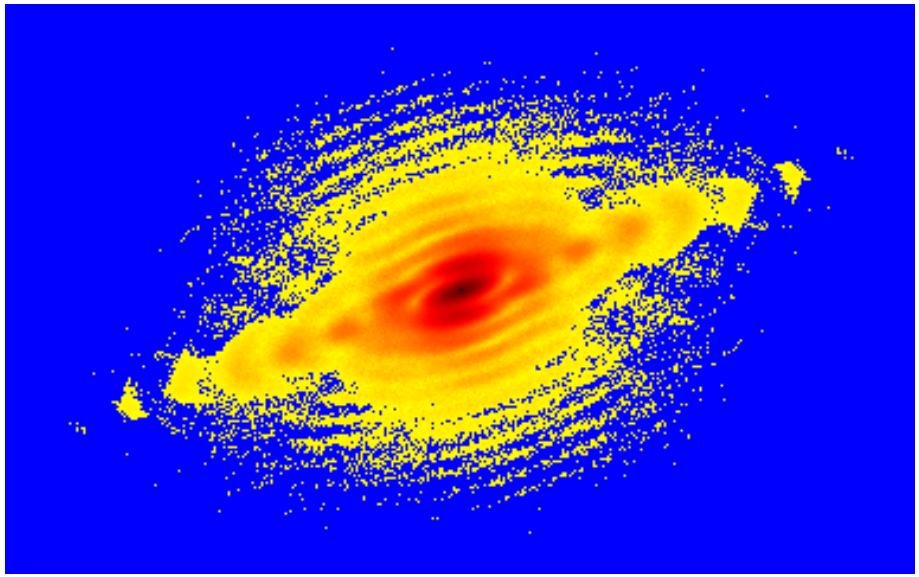
- Au blanket film
- Quartz substrate
- Annealed at 950°C for 70 hrs.

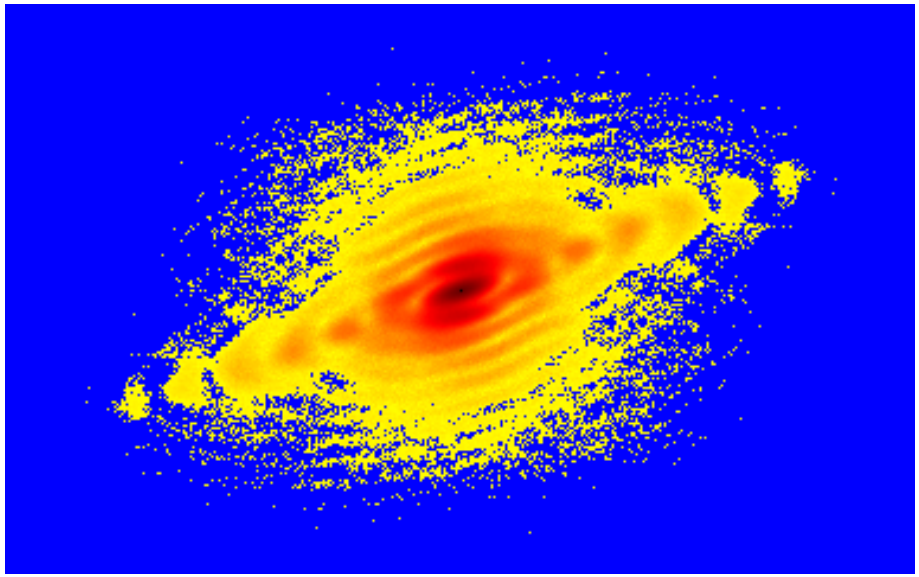


Symmetrized Data and two best fits

Chisq=0.0005

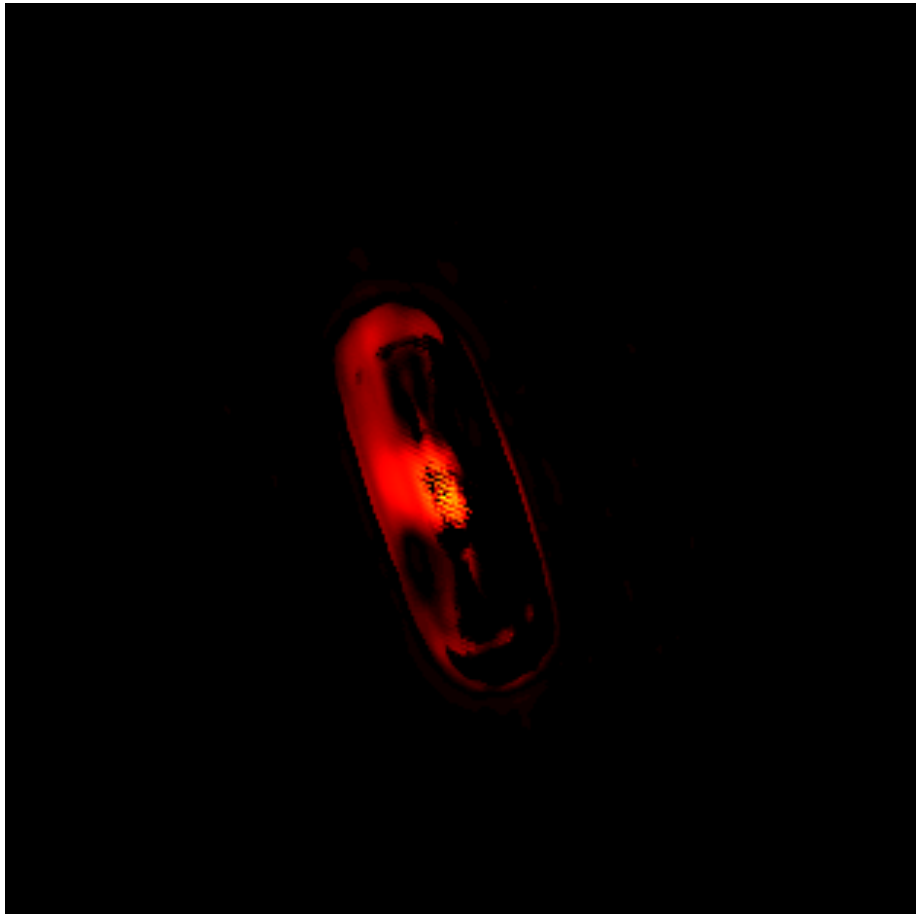


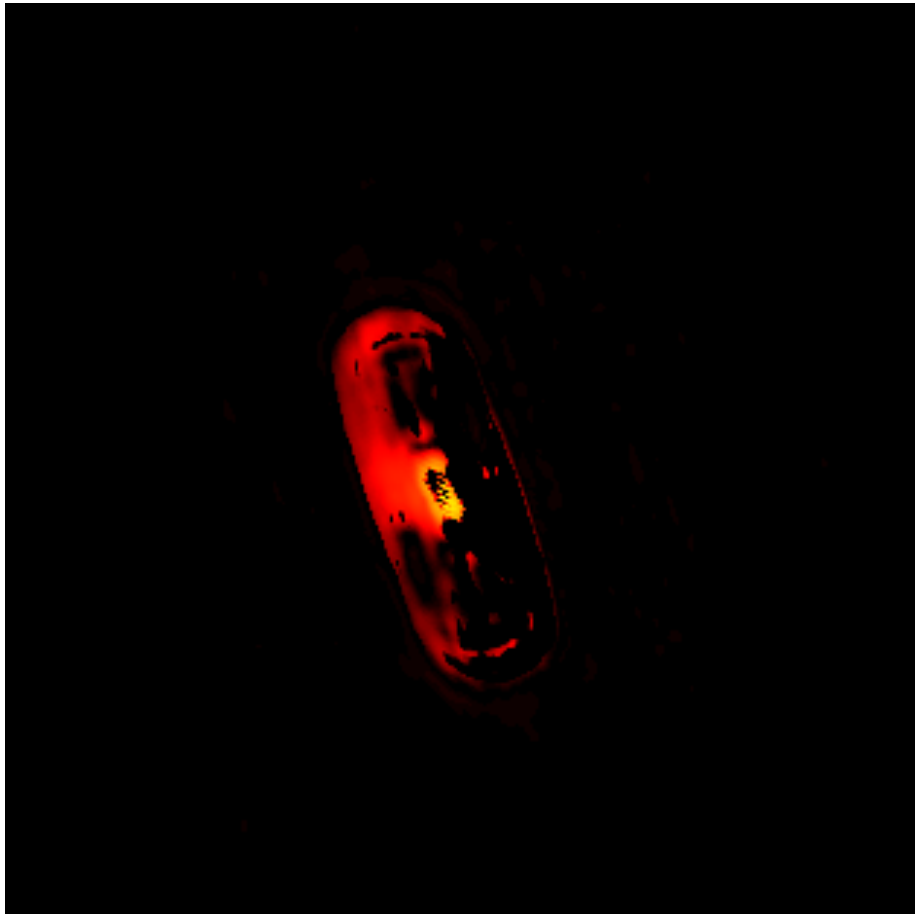




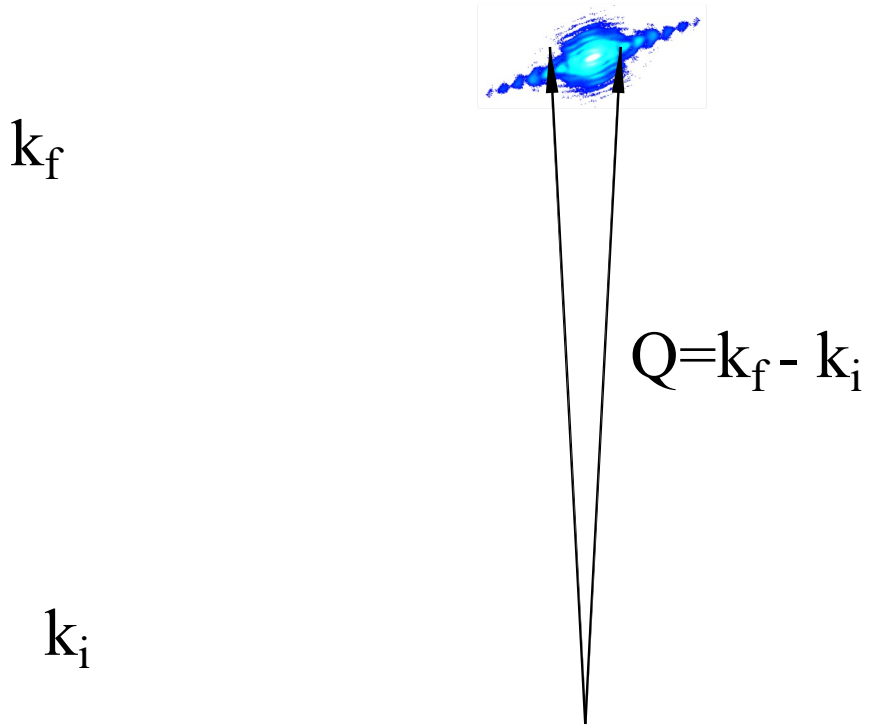
2D Reconstructions

chisquare = 0.0005

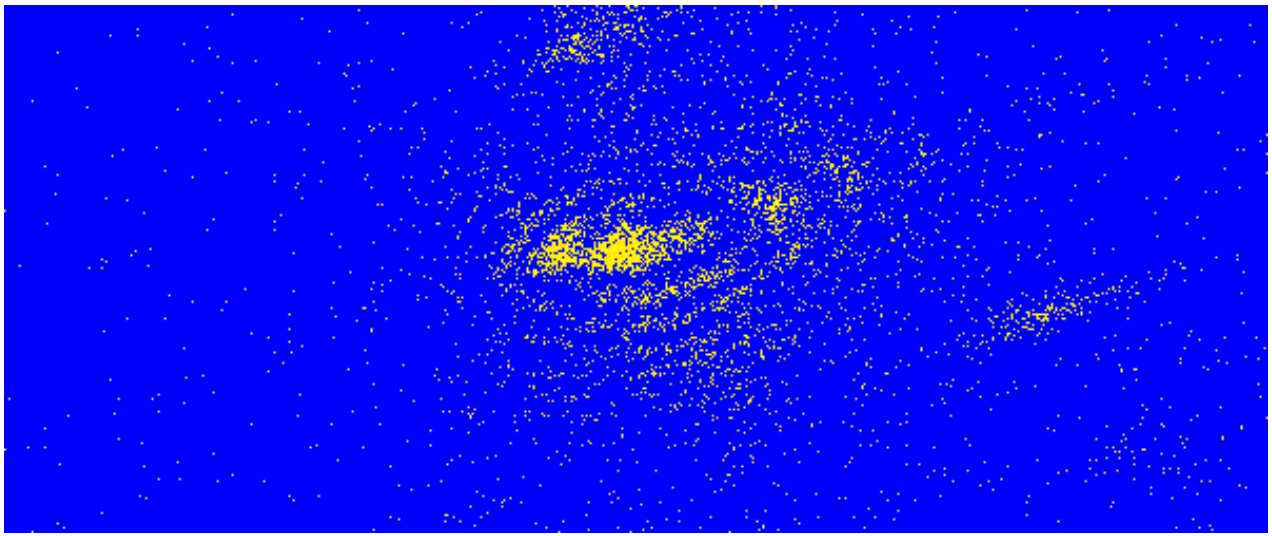




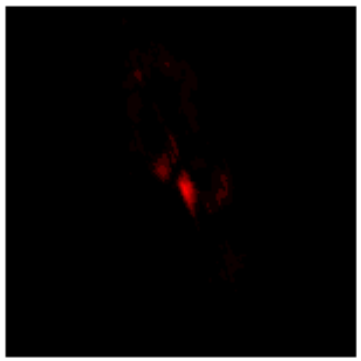
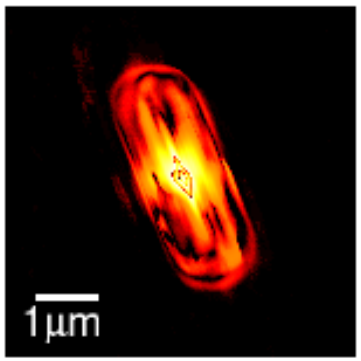
3D Diffraction Method

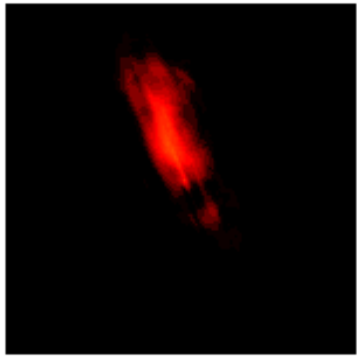
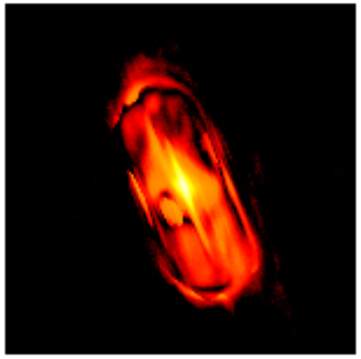
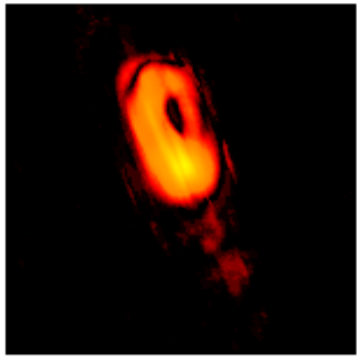
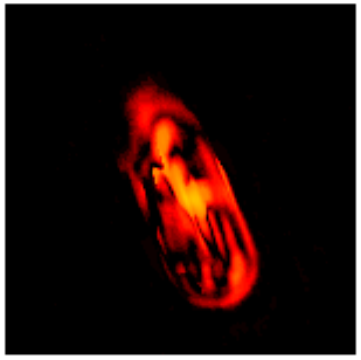
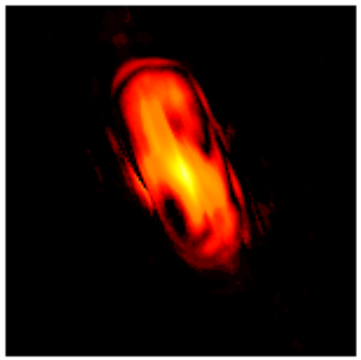
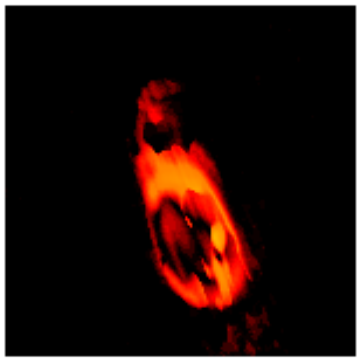
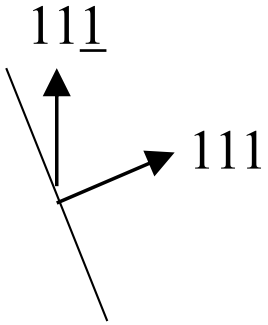


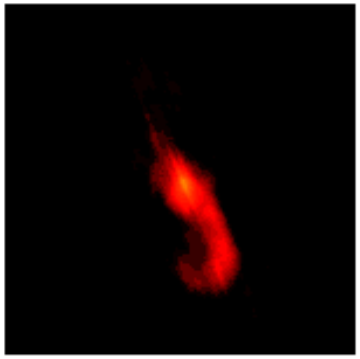
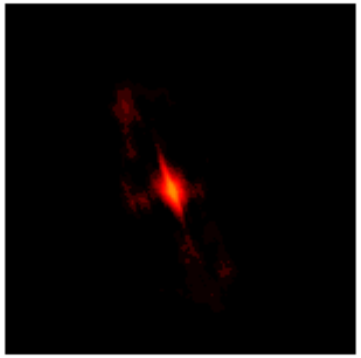
3D Diffraction Data
1 micron Au crystal



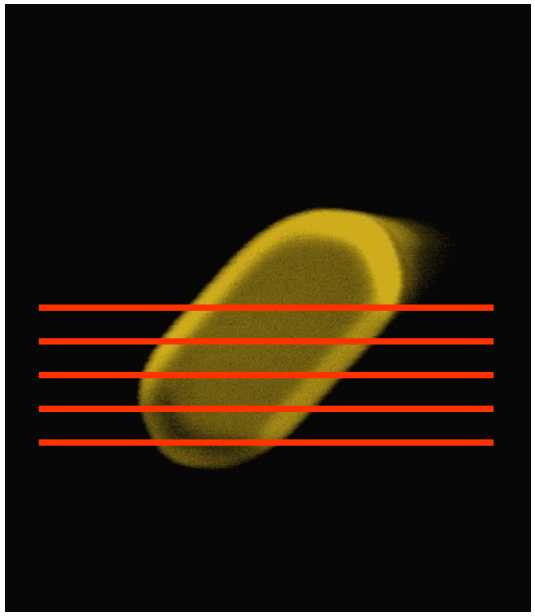
* Center is Symmetric *

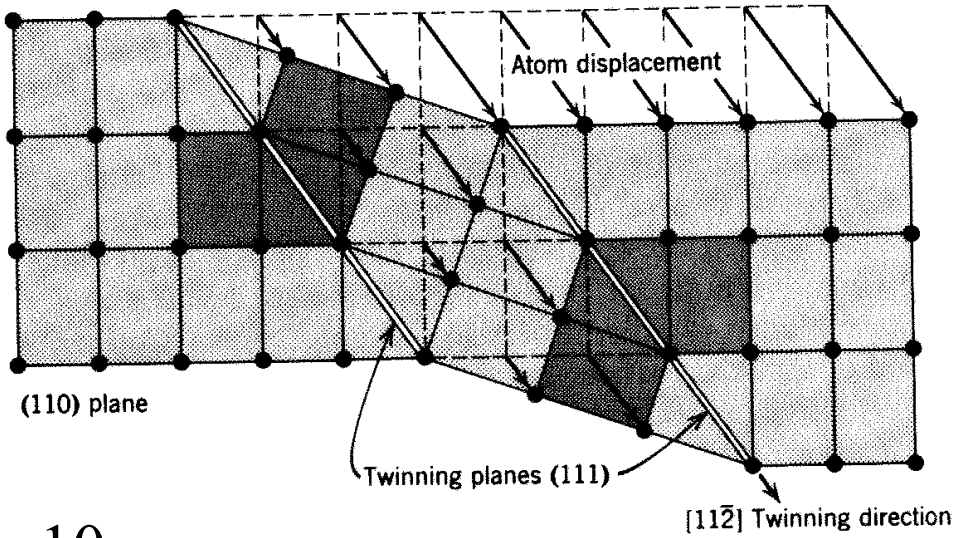



Slices through plan view SEM:



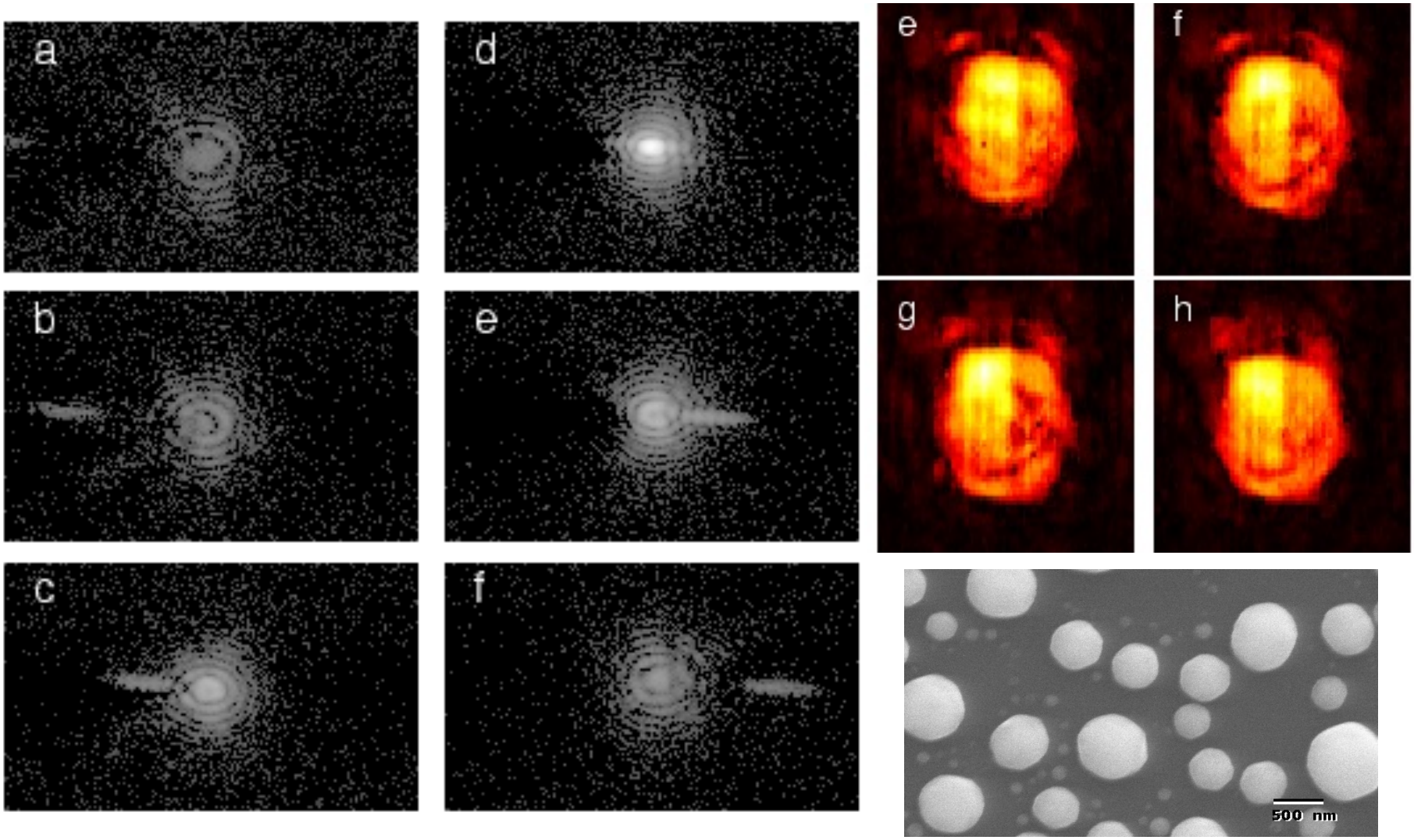
Twinning in deformed FCC metals

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

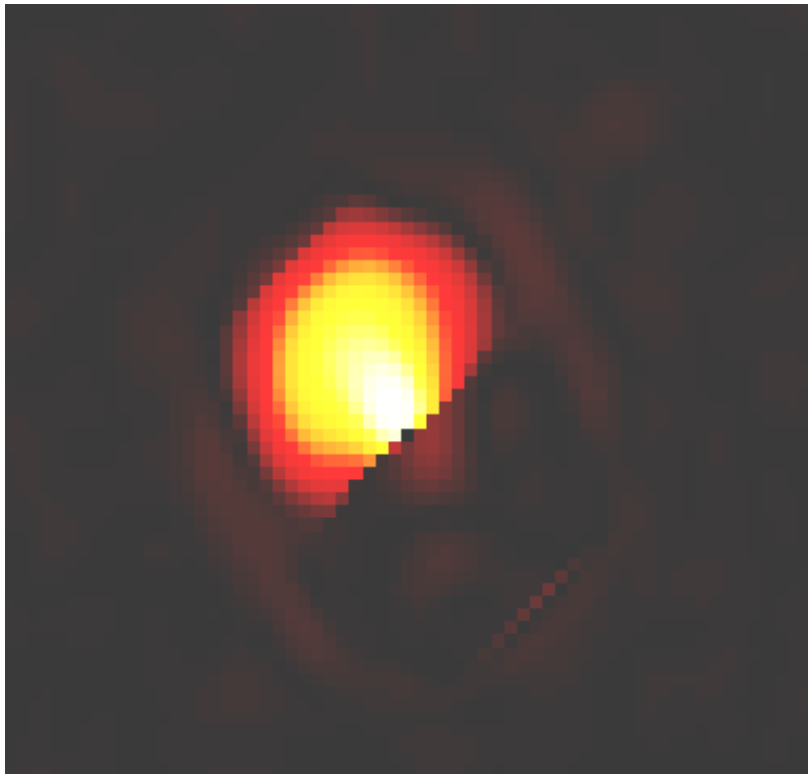


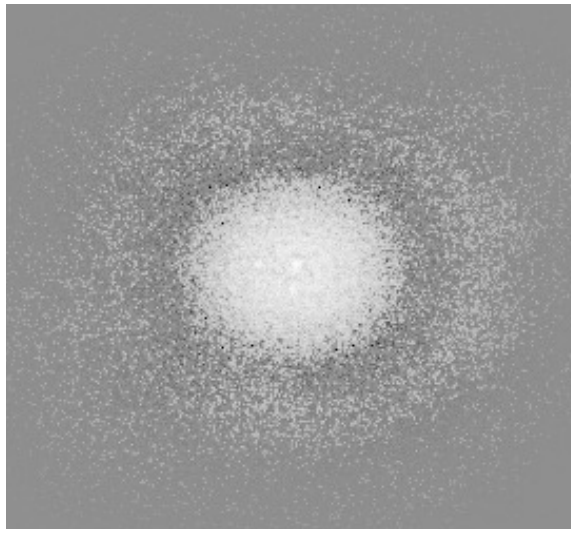
~10μm
Cu

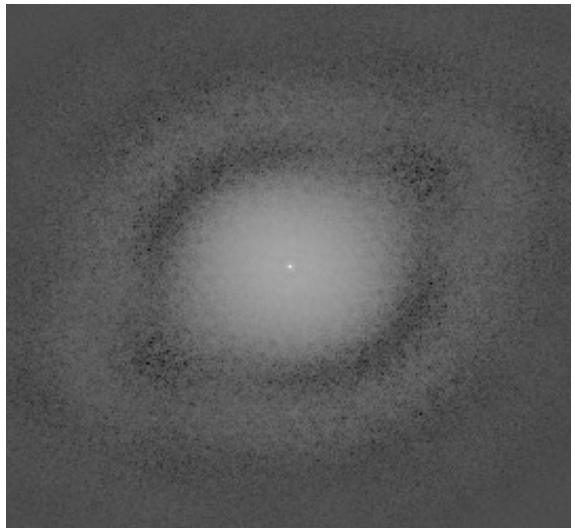
3D reconstruction of Pb nanocrystals



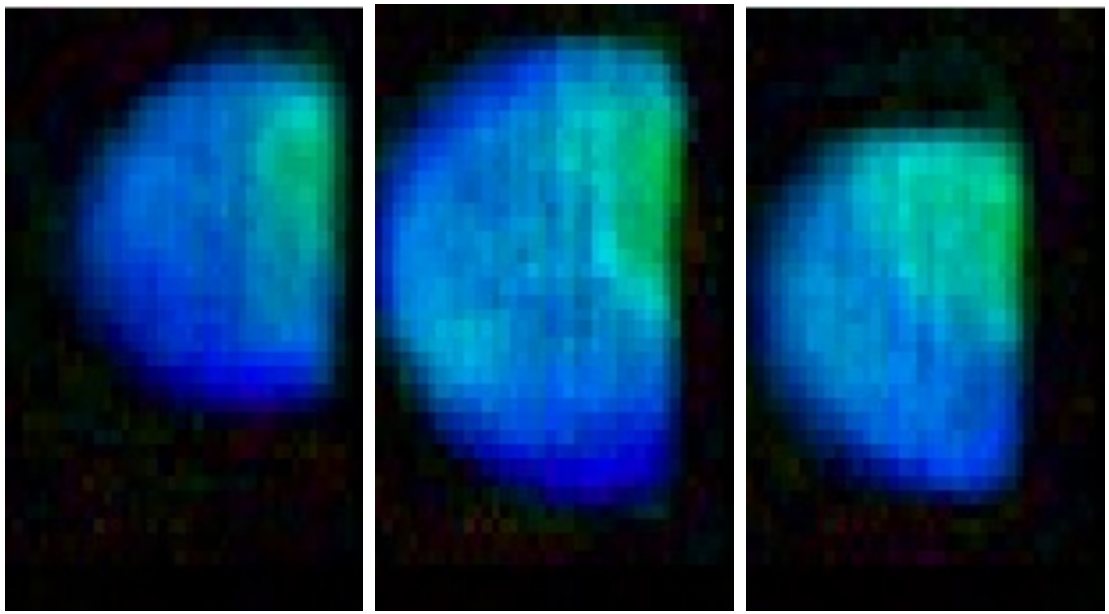
Reconstruction of Pb Nanocrystal



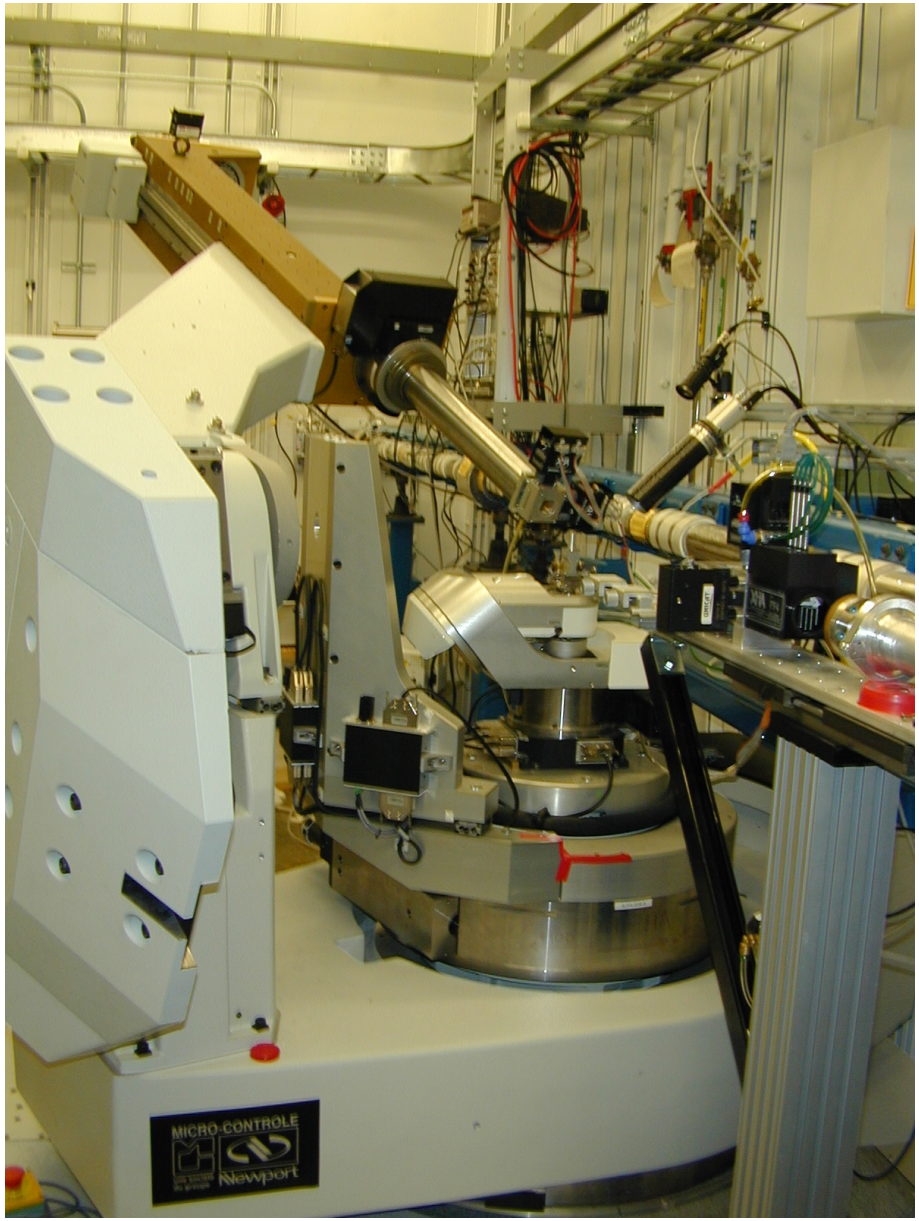


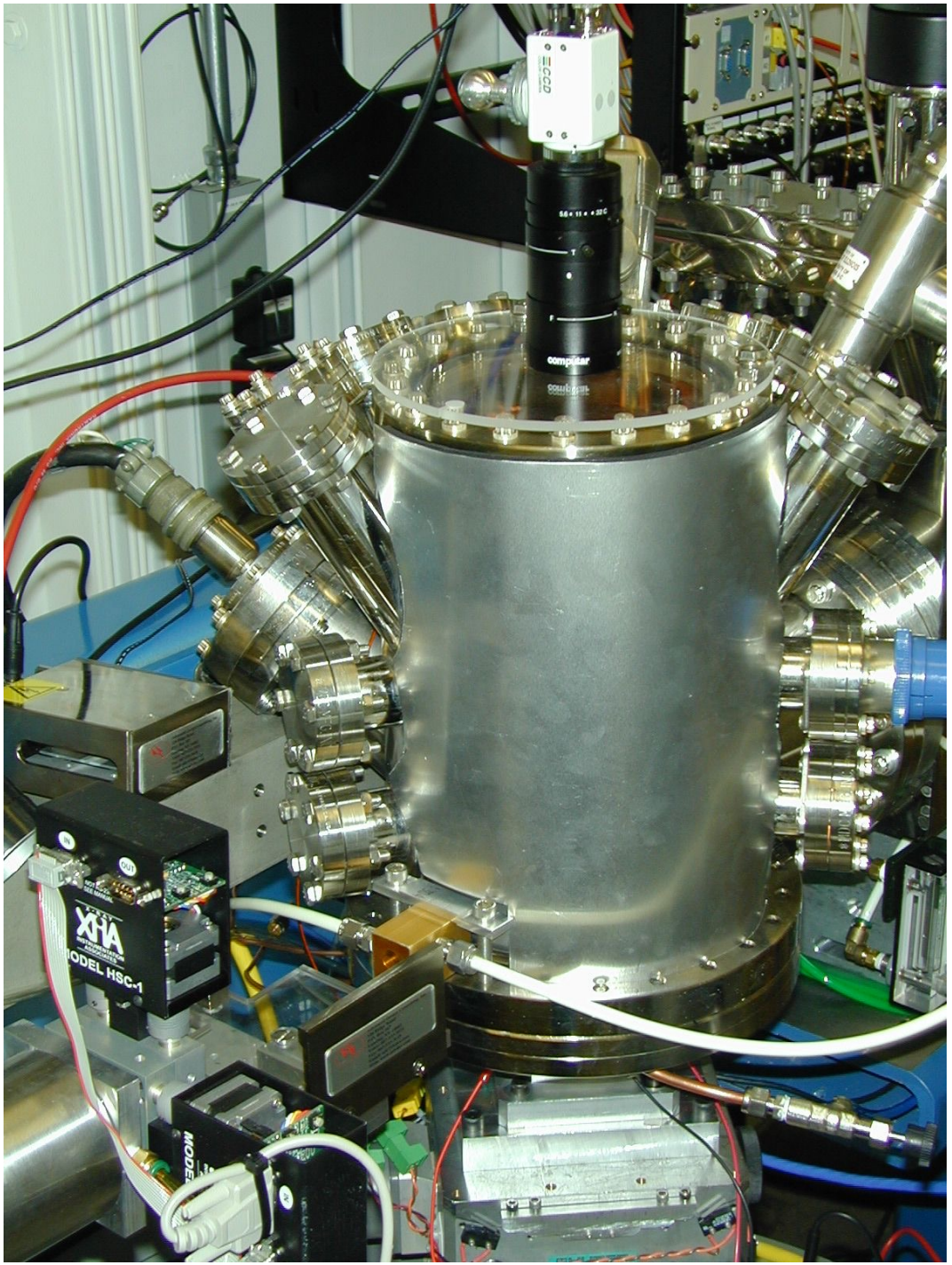


3D Phase Images of Lead Nanocrystals

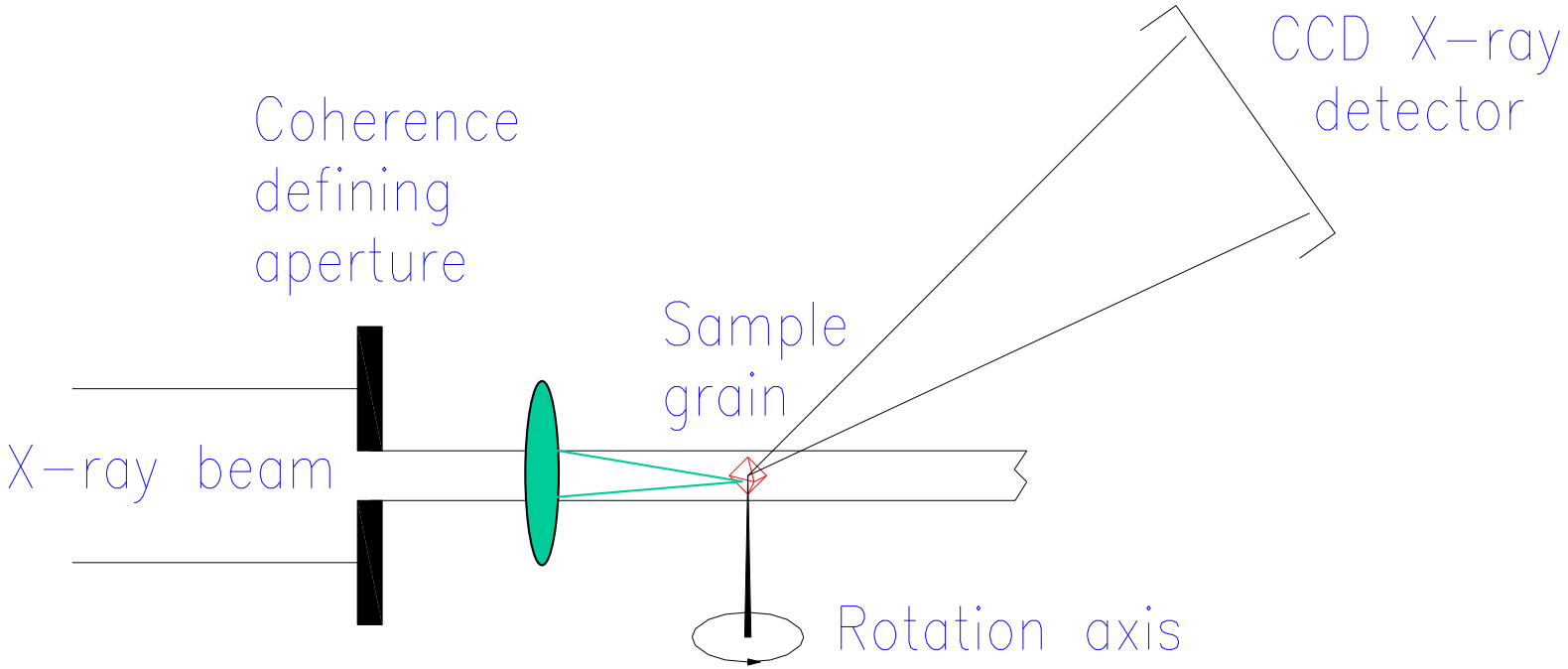


- 500nm Pb crystals grown in-situ in UHV system at APS (Argonne) on a SiO_2 support (vertical).
- 3D coherent X-ray diffraction data is inverted into hemi-spherical cross-sectional slices.
- These images are colored according to the phase of the density, which changes abruptly at an internal boundary.
- This plane is identified as a single deformation fault in the crystal.

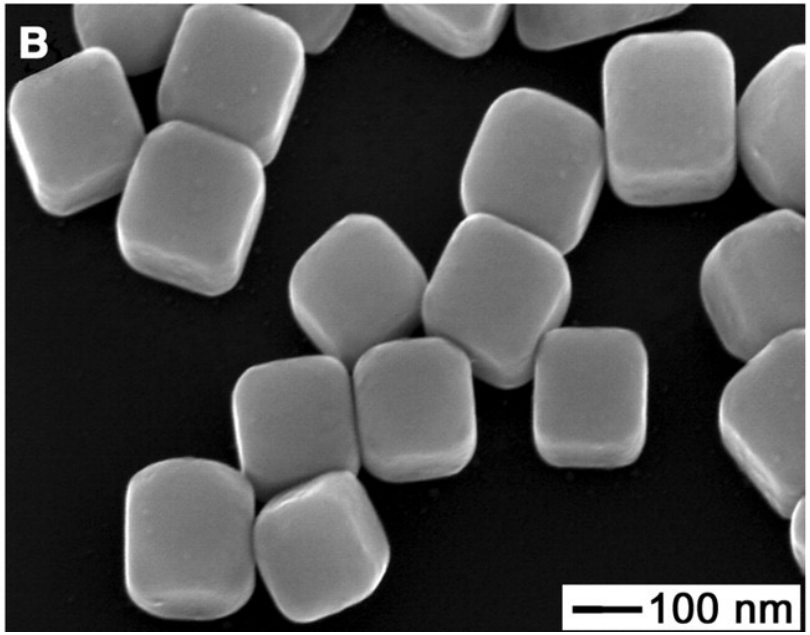

MICRO-CONTROLE
Newport

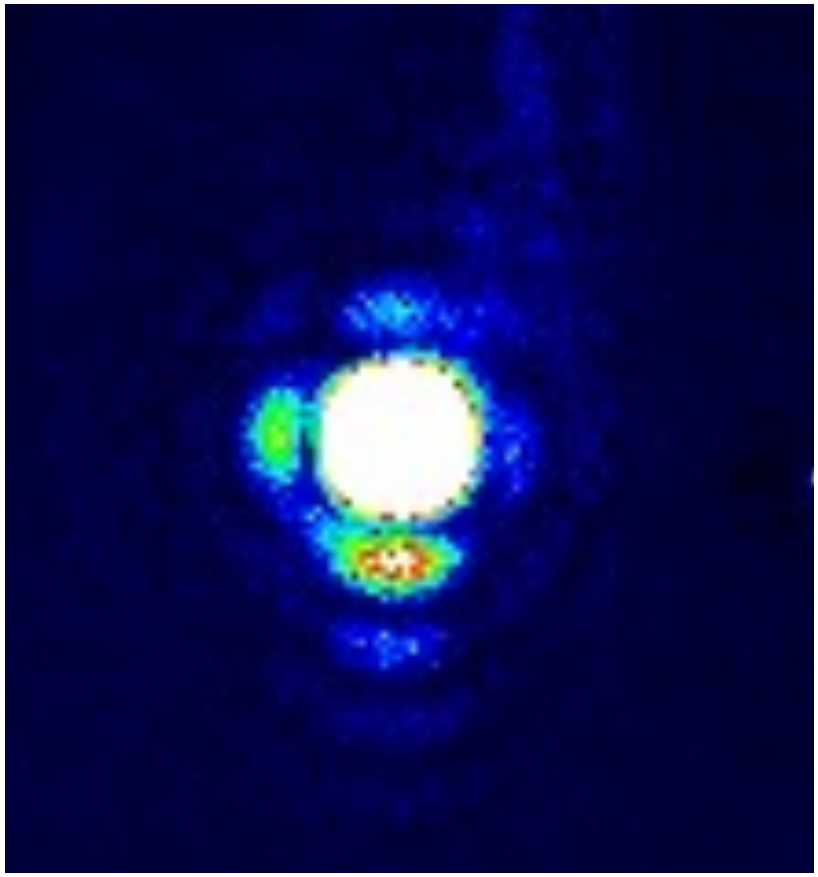

computar
MODEL HSC-1

Lensless X-ray Microscope



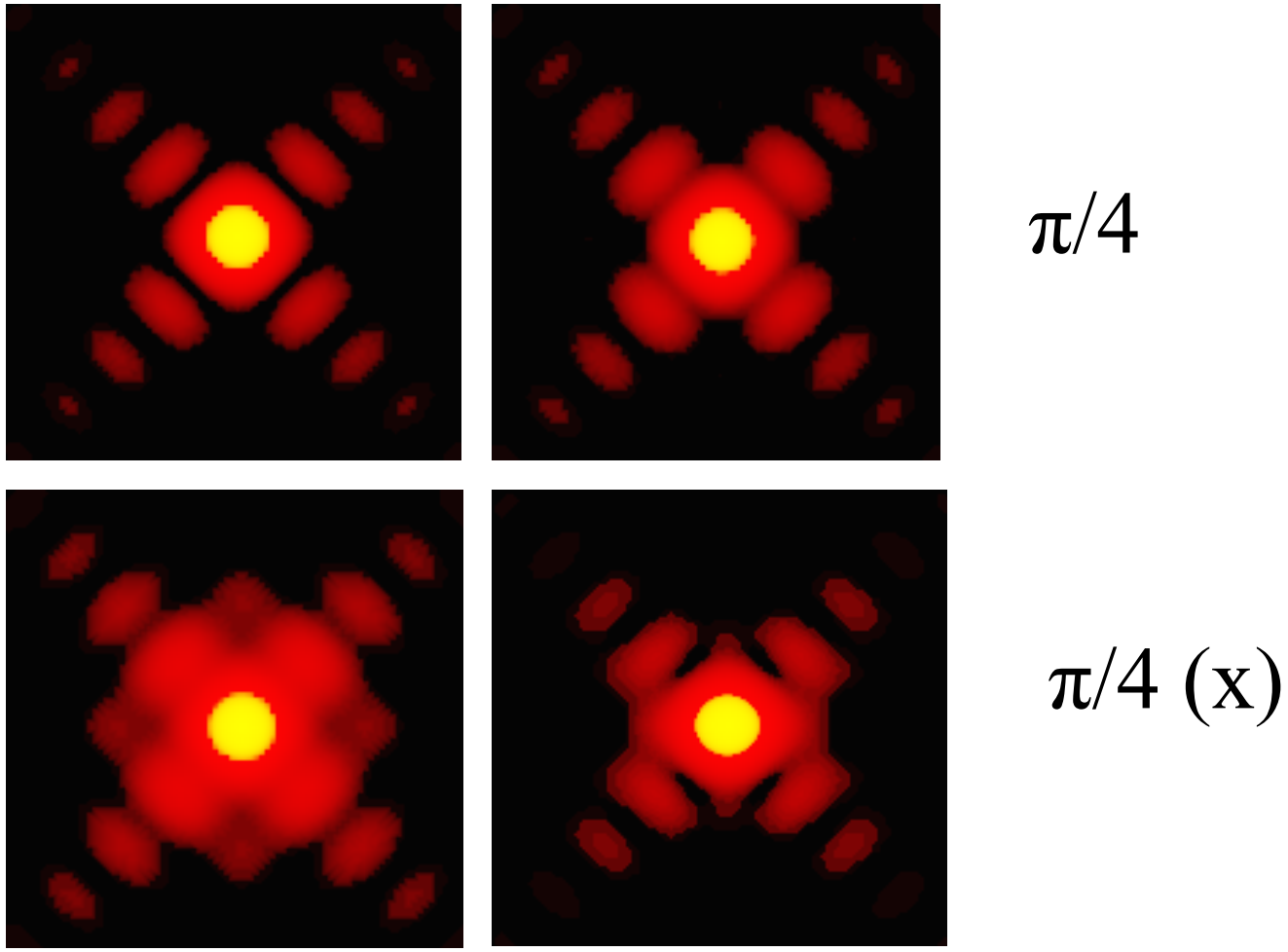
CXD from Silver Nanocubes





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

Spherical and cylindrical waves

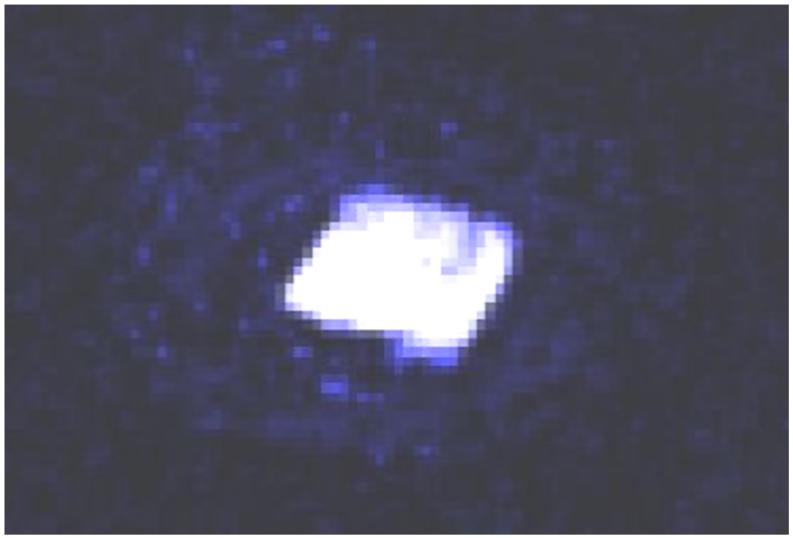


π/4

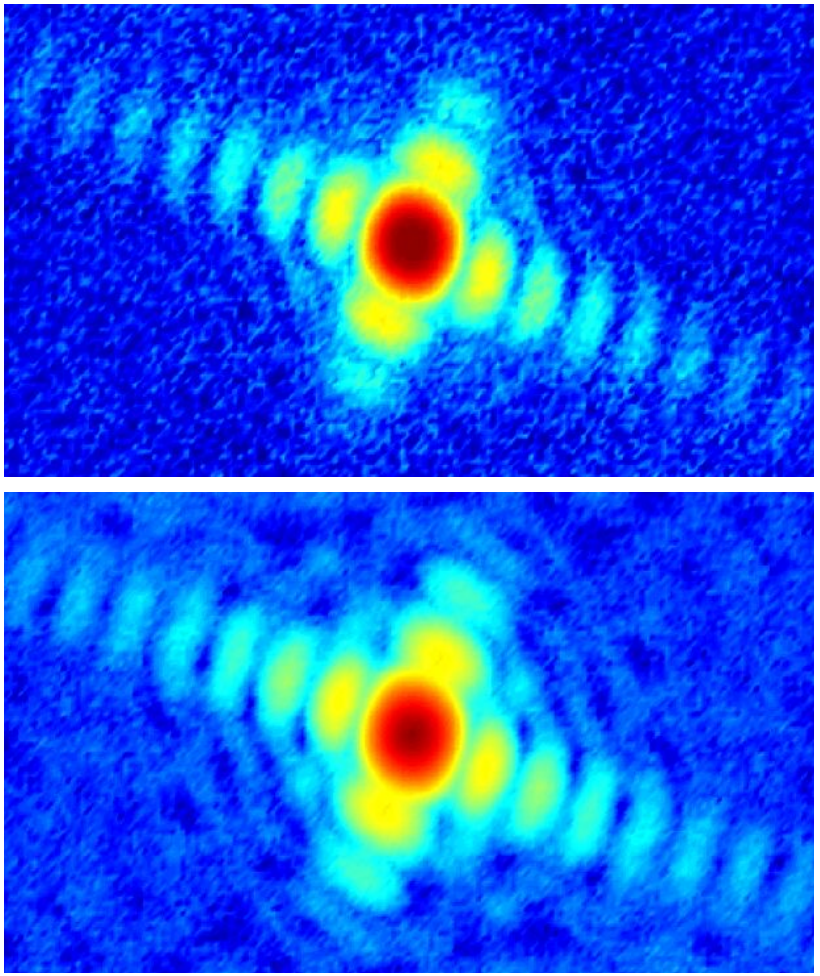
π/2

π/4 (x)

Reconstruction of Ag Nanocrystal

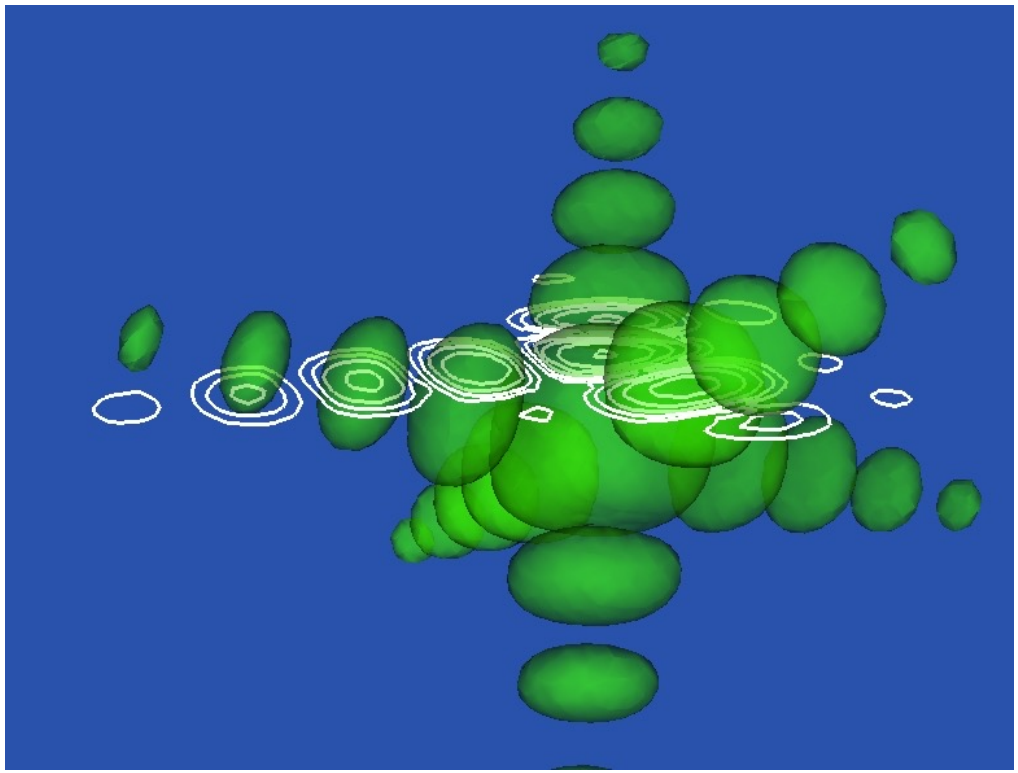


200nm



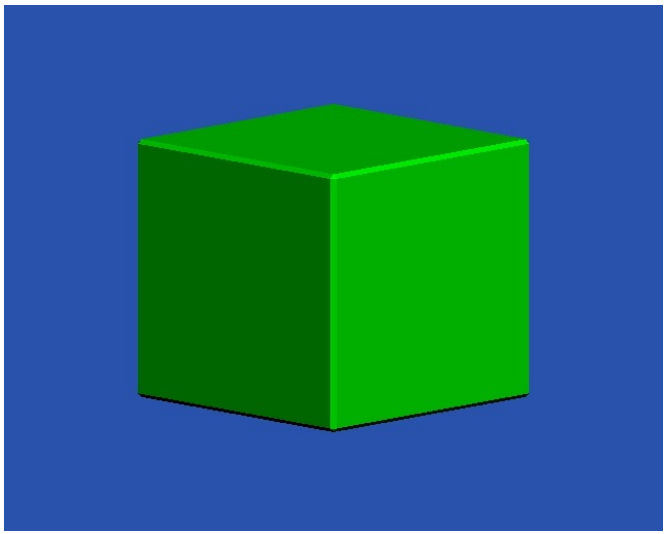
Miscentered Non-Centrosymmetric Reciprocal Space Slice

$$A_q \neq A^*_{\bar{q}}$$

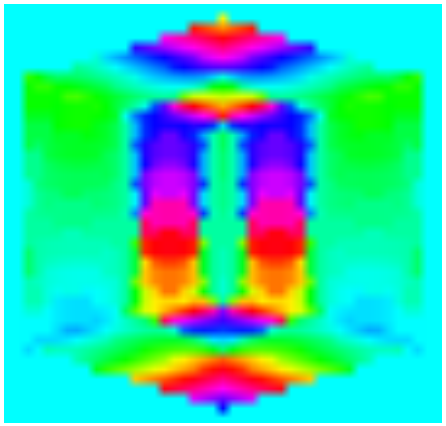


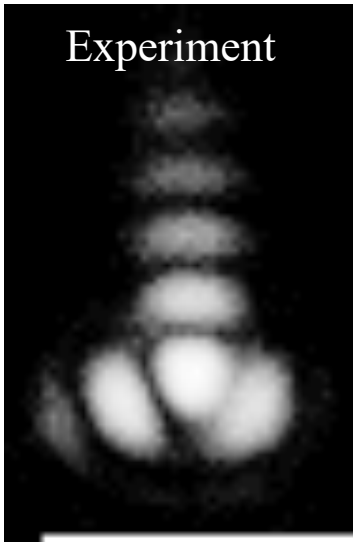
Real-space phase.

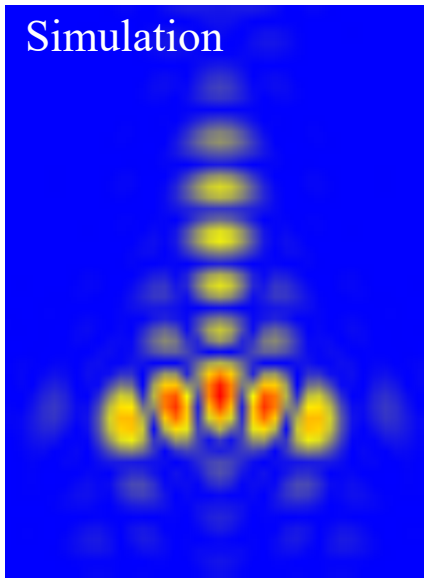
What can we expect to see?



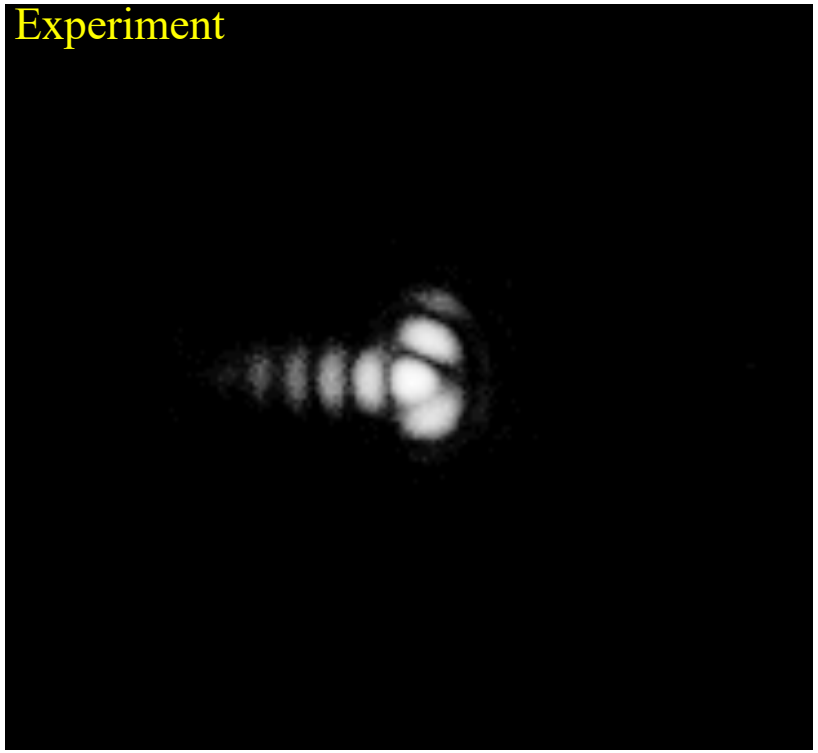
$$A(\bar{q}_o+\bar{q}_z)=\sum_i \sum_z \underbrace{\rho(x,y,z)}_{u_i(x,y)} e^{2\pi i \bar{q}_z\cdot\bar{z}_i} e^{2\pi i(\bar{q}_o)\cdot\bar{r}_i}$$

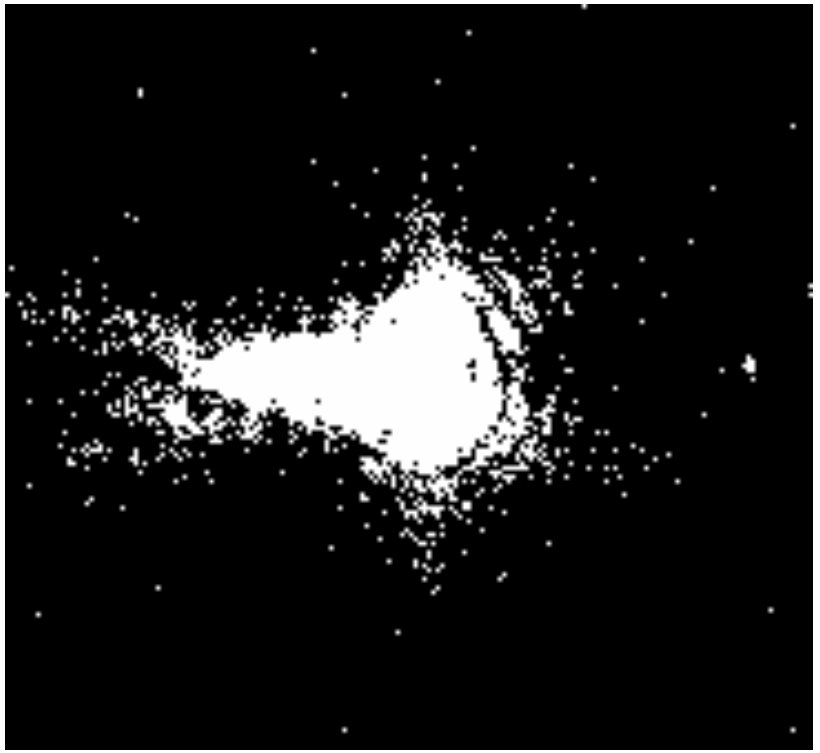




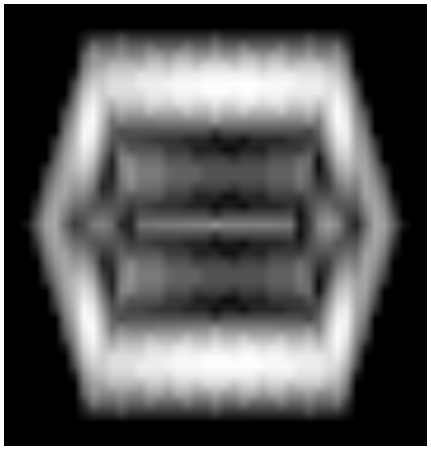


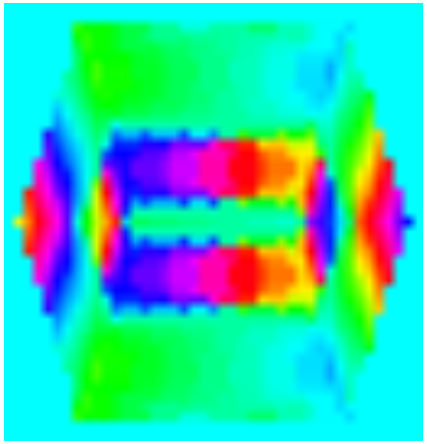
Data and Data Mask (>7% Max)

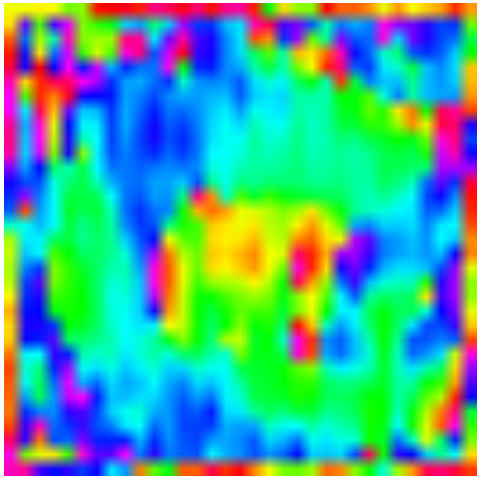


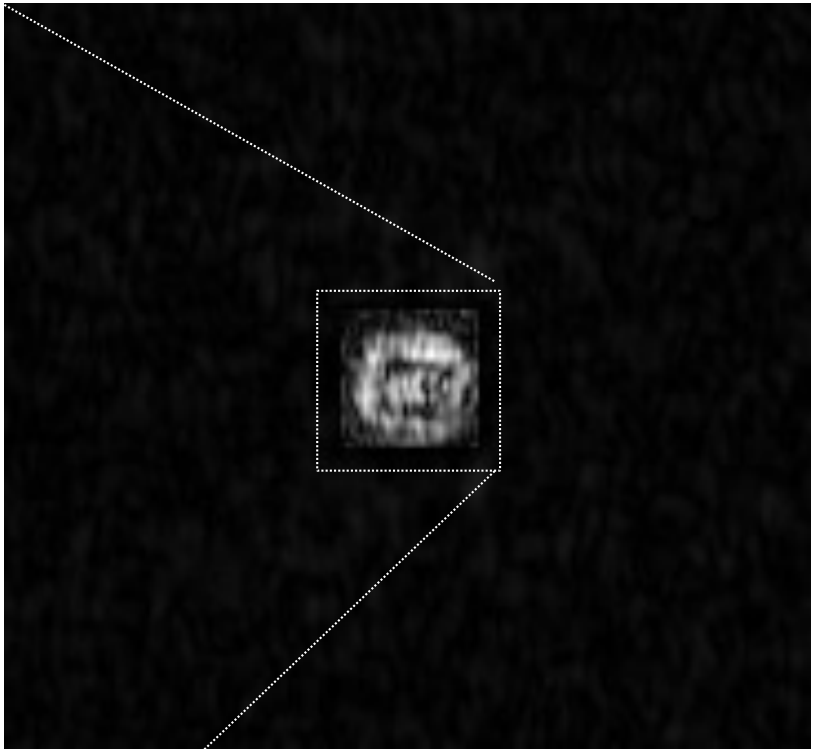


Direct Space Result (1000 Iterations)

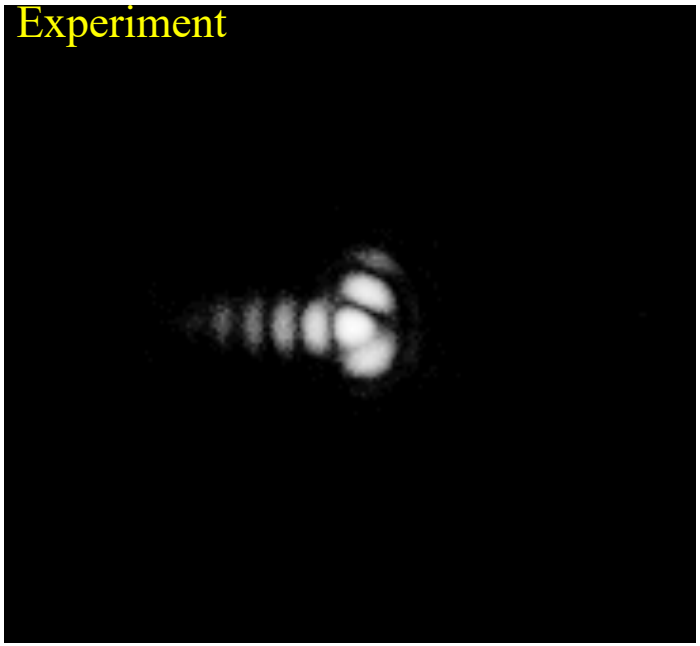


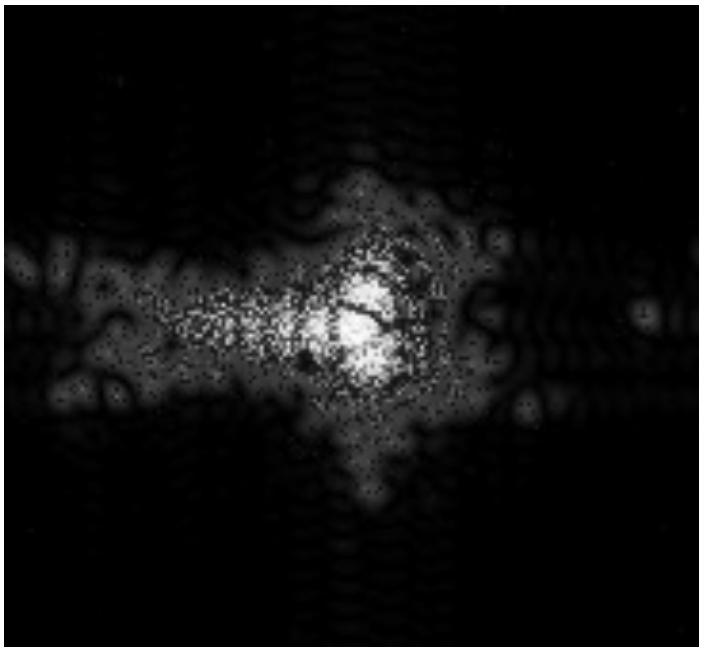


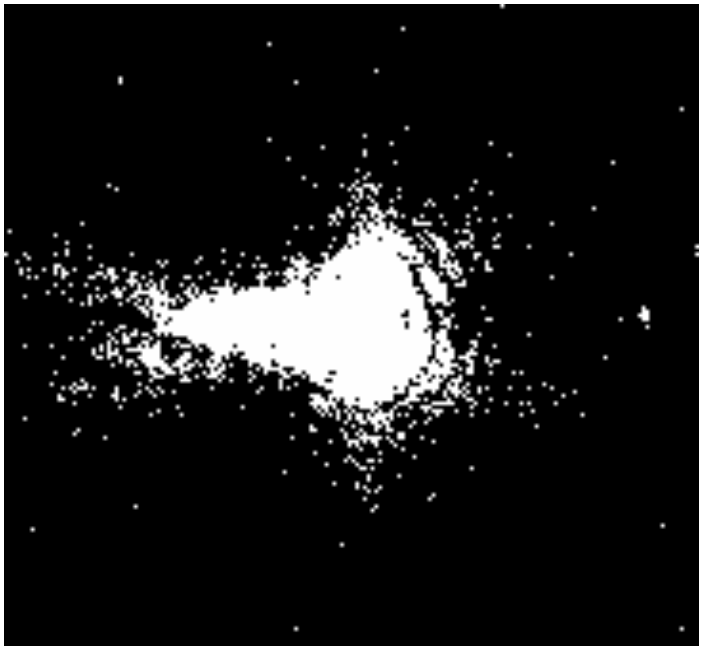


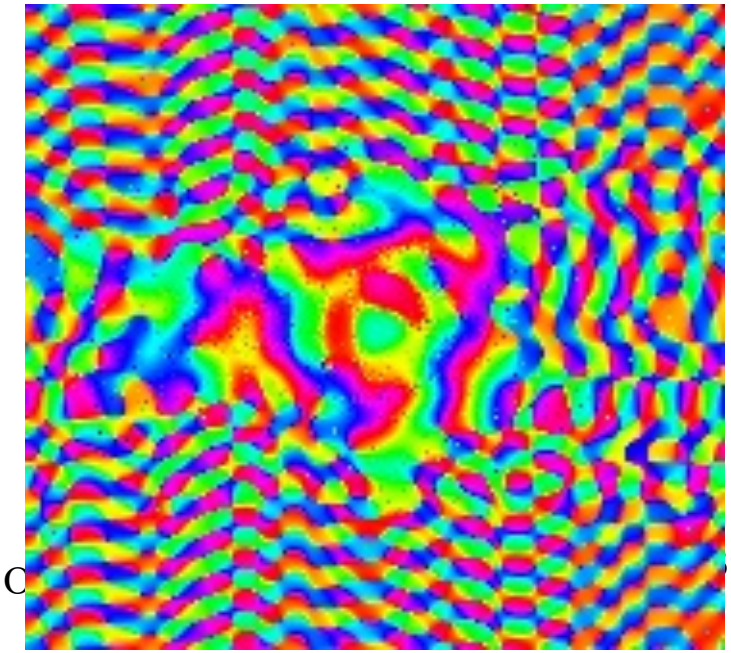


Reciprocal Space Result (1000 iterations)



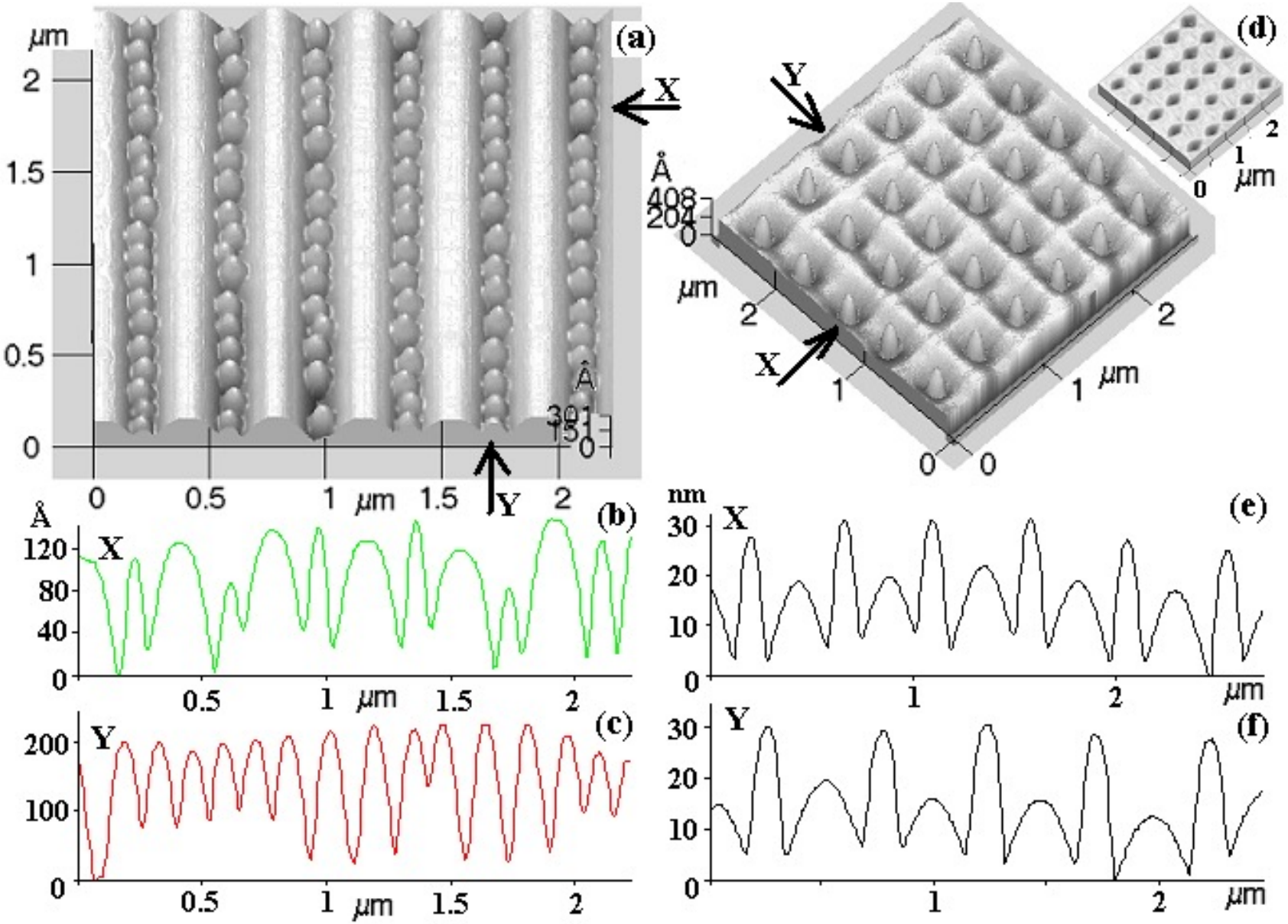






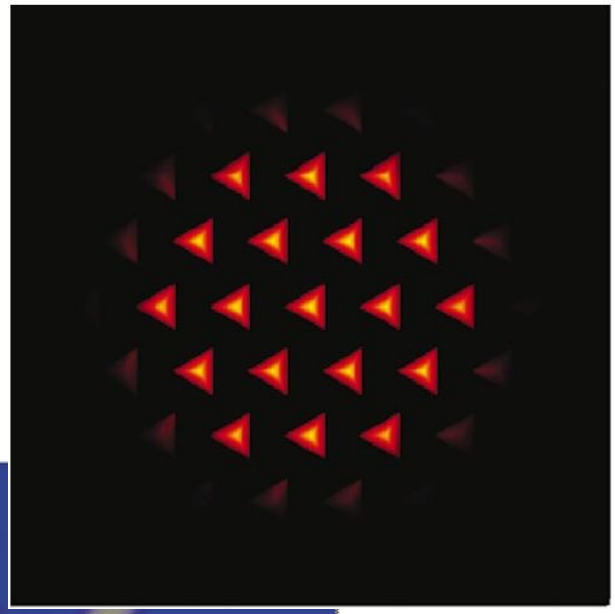
1D and 2D Quantum Dot Arrays

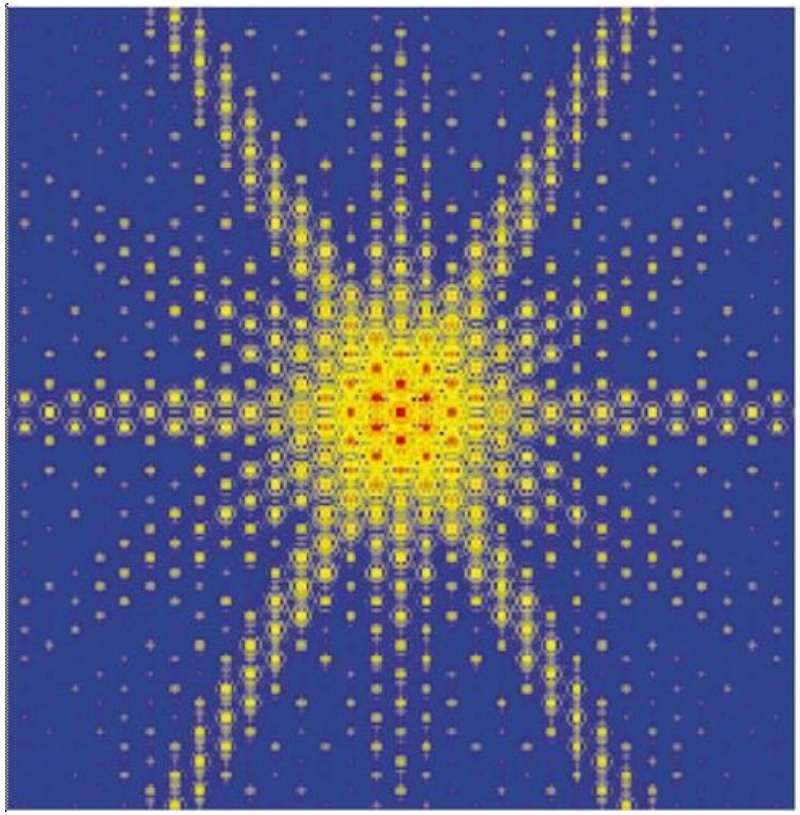
Zhenyang Zhong, G. Bauer, Johannes Kepler Universität Linz

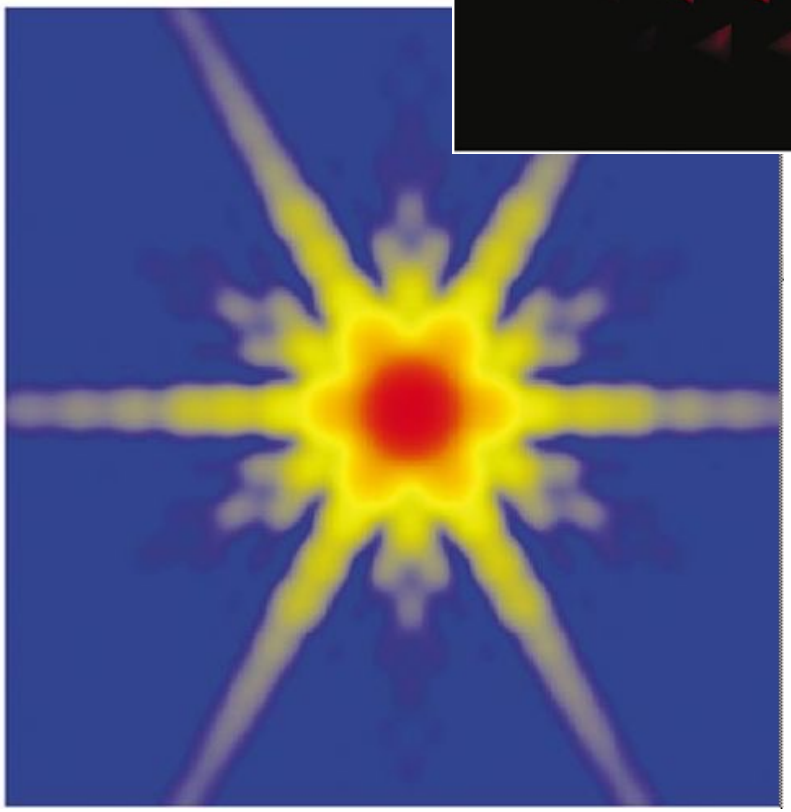


Vary Coherence (model)

I. A. Vartanyants and I. K. Robinson,
J. Sync. Rad. **10** 409 (2003)

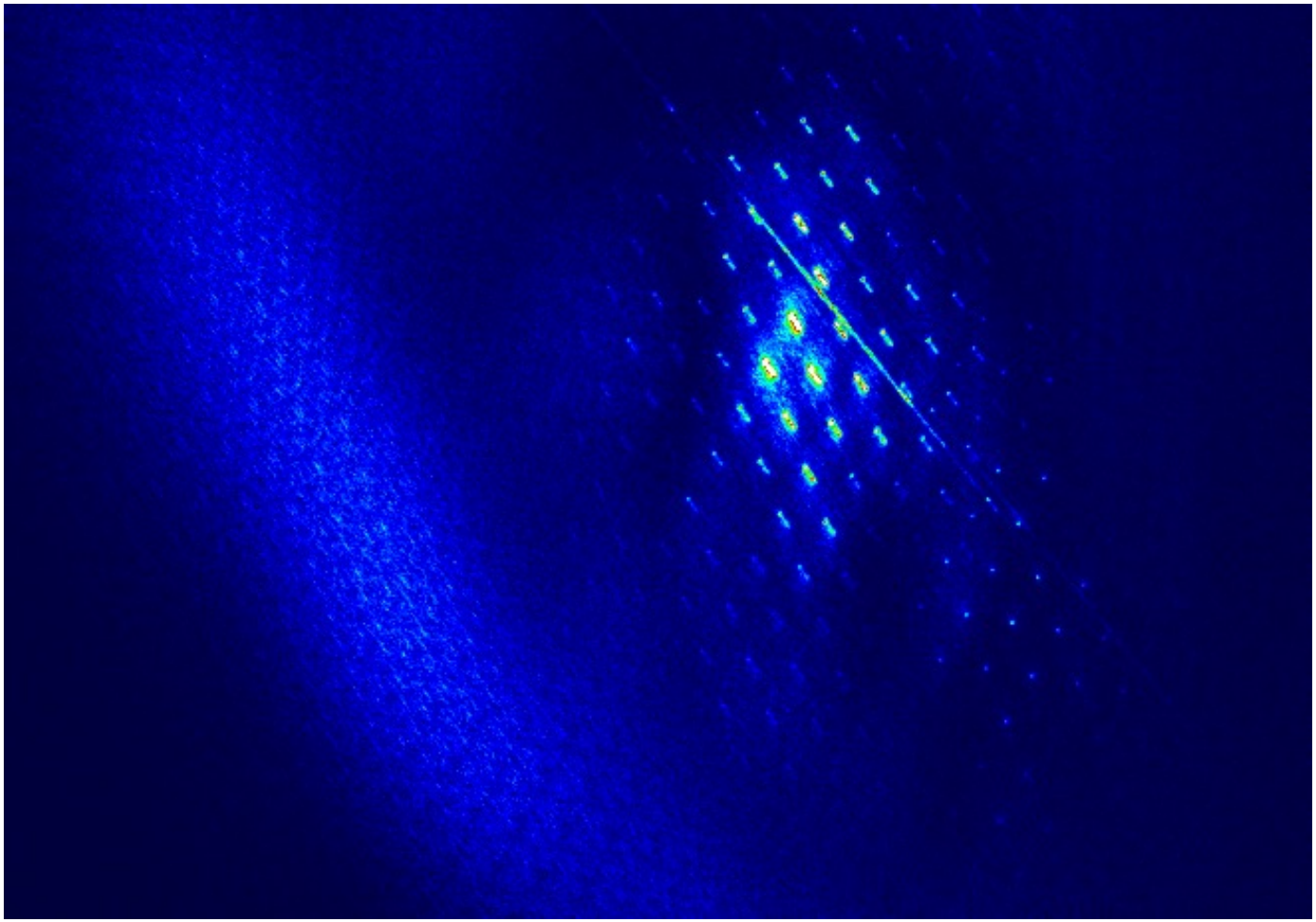




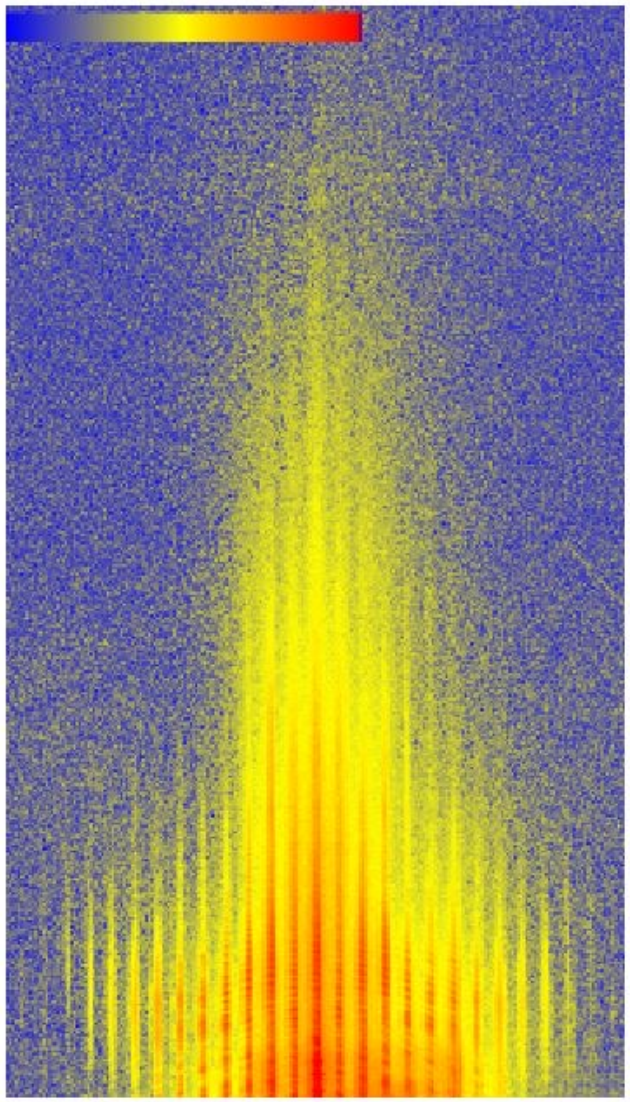


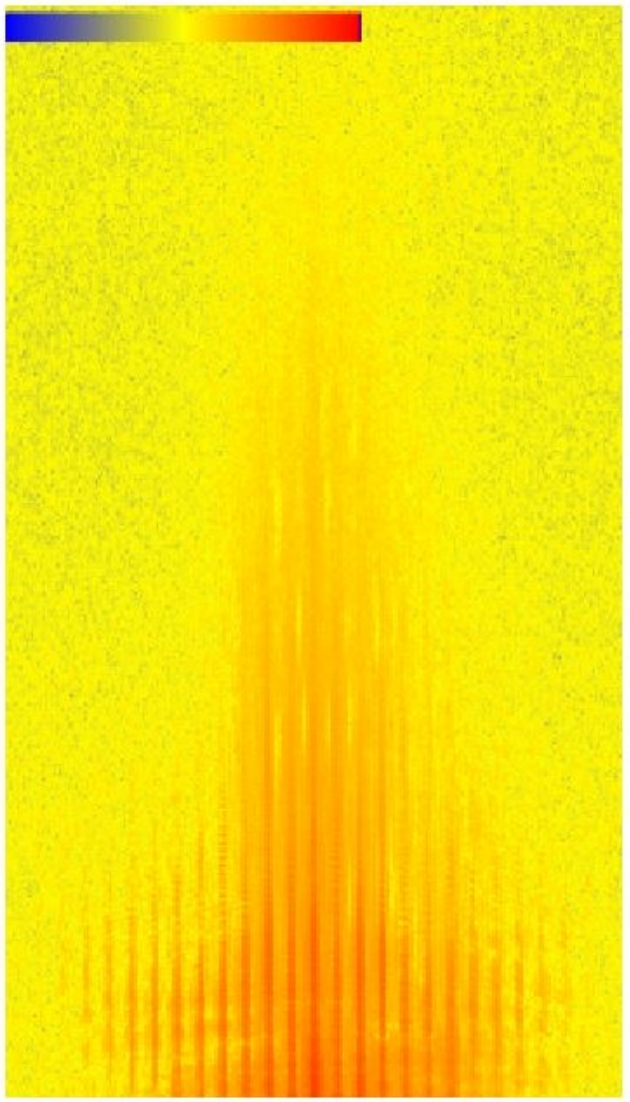
202 Diffraction from Ge QD array

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



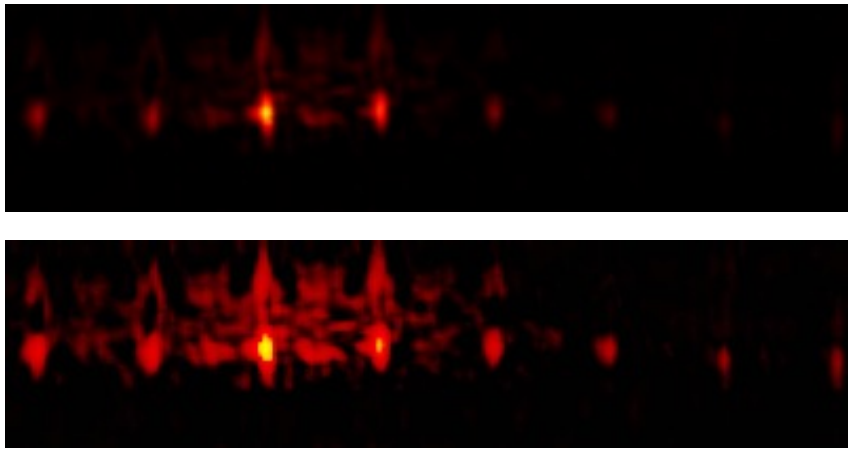
Result of fitting GISAXS data

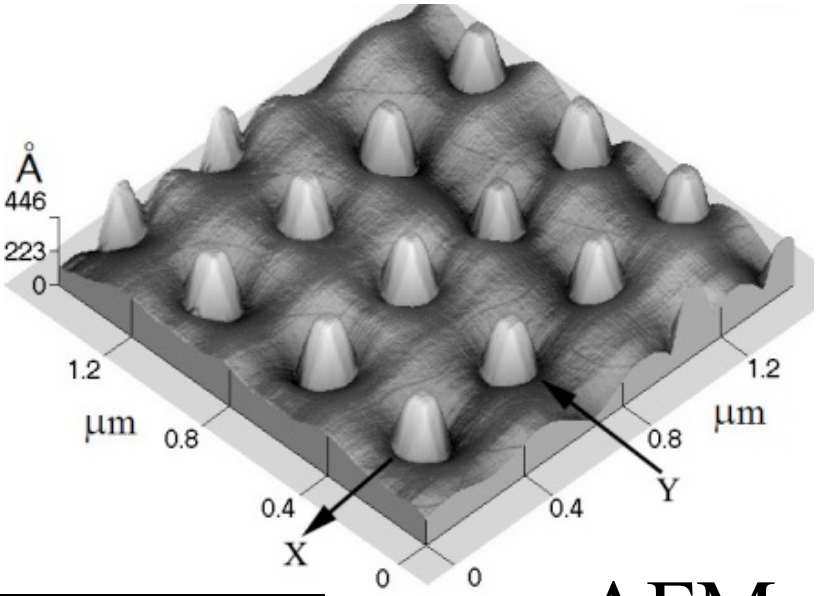




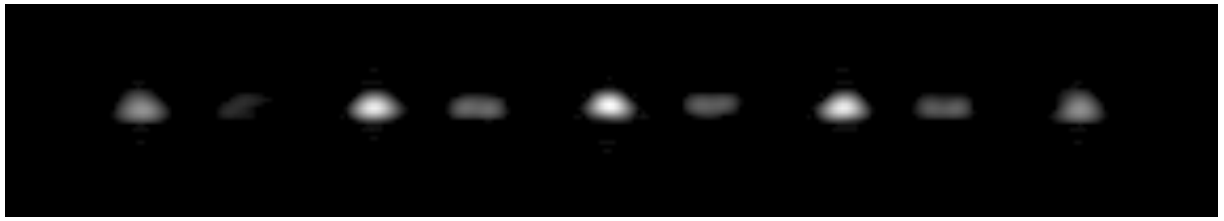
Images from Fitting GISAXS

with Jeff Onken



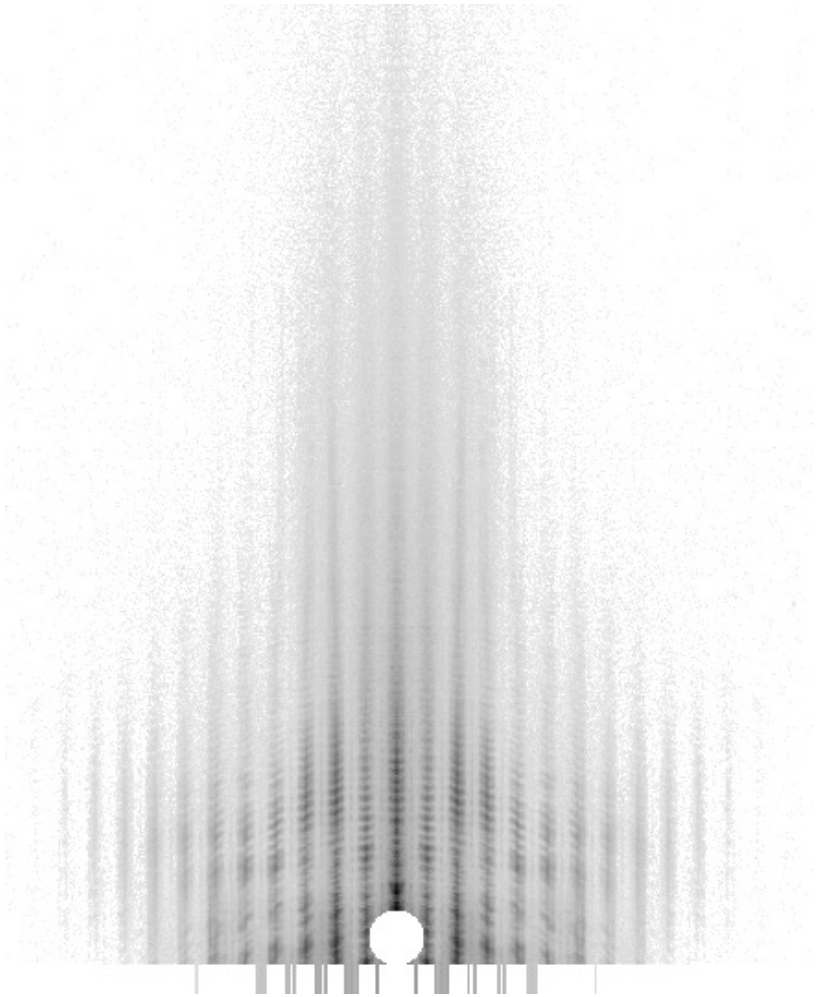


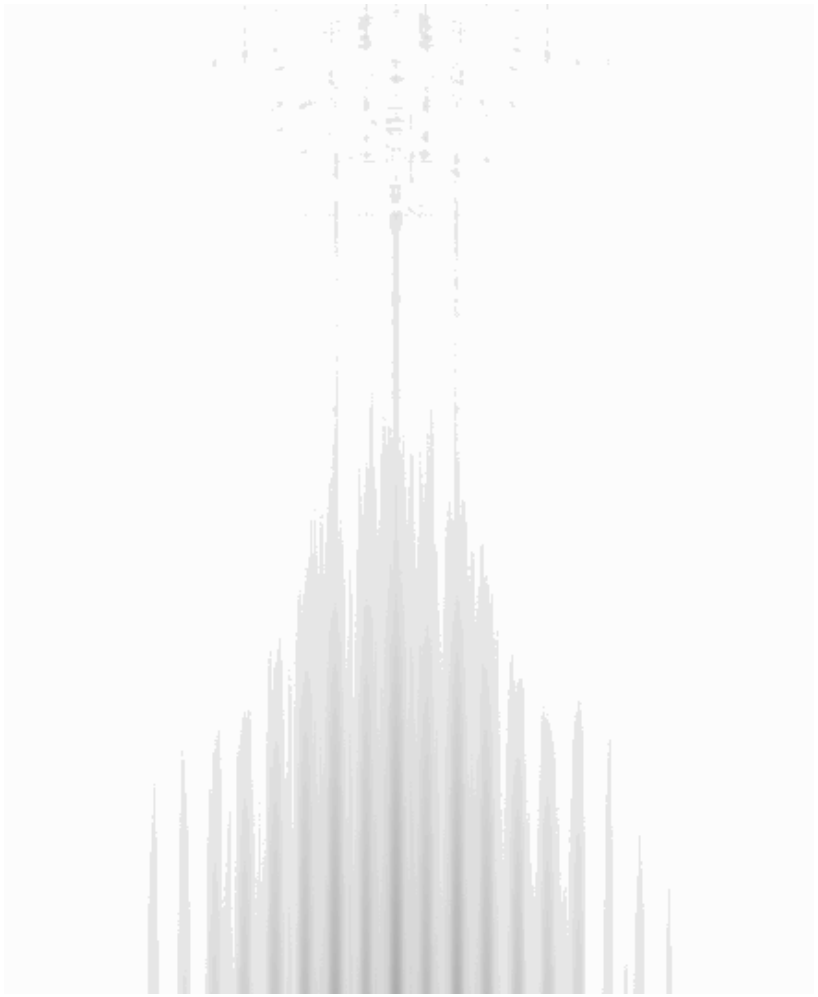
AFM



Mask used as support

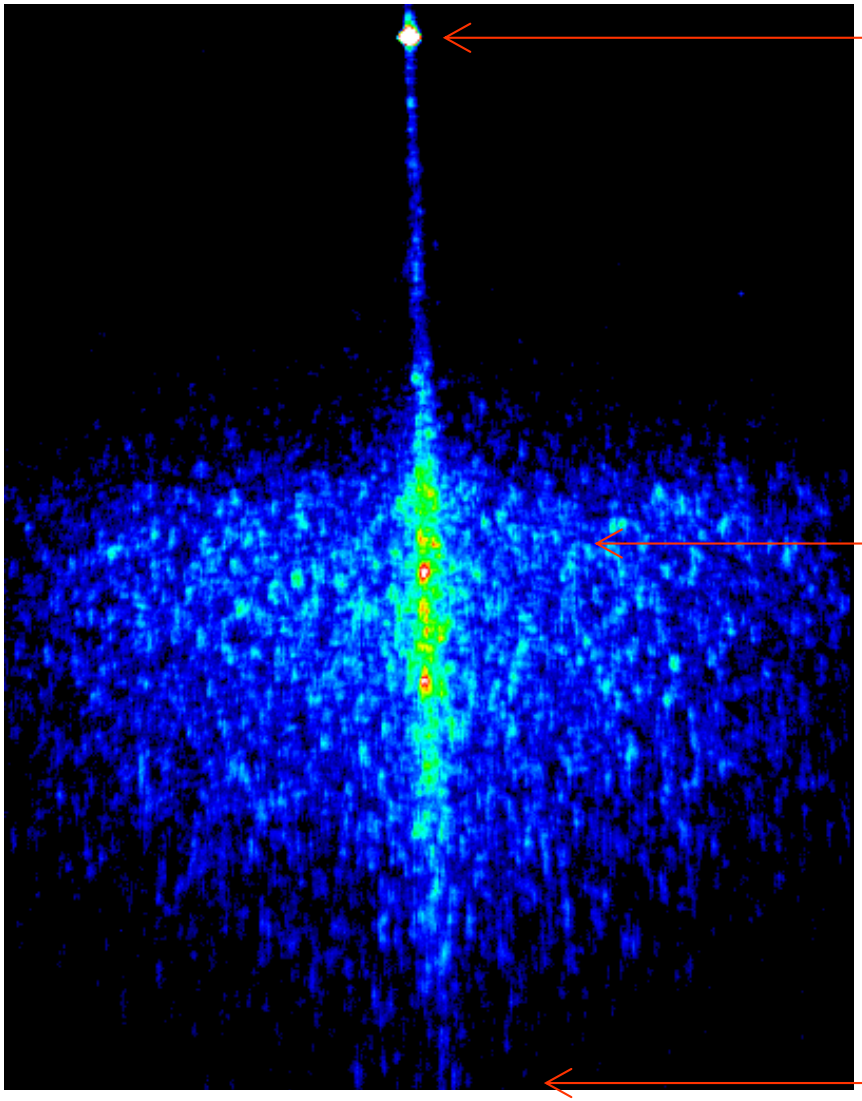
Diffraction pattern under constraint





Fine Structure in "Yoneda" Peak

Grazing-exit diffraction from a 1000A Au polycrystalline film



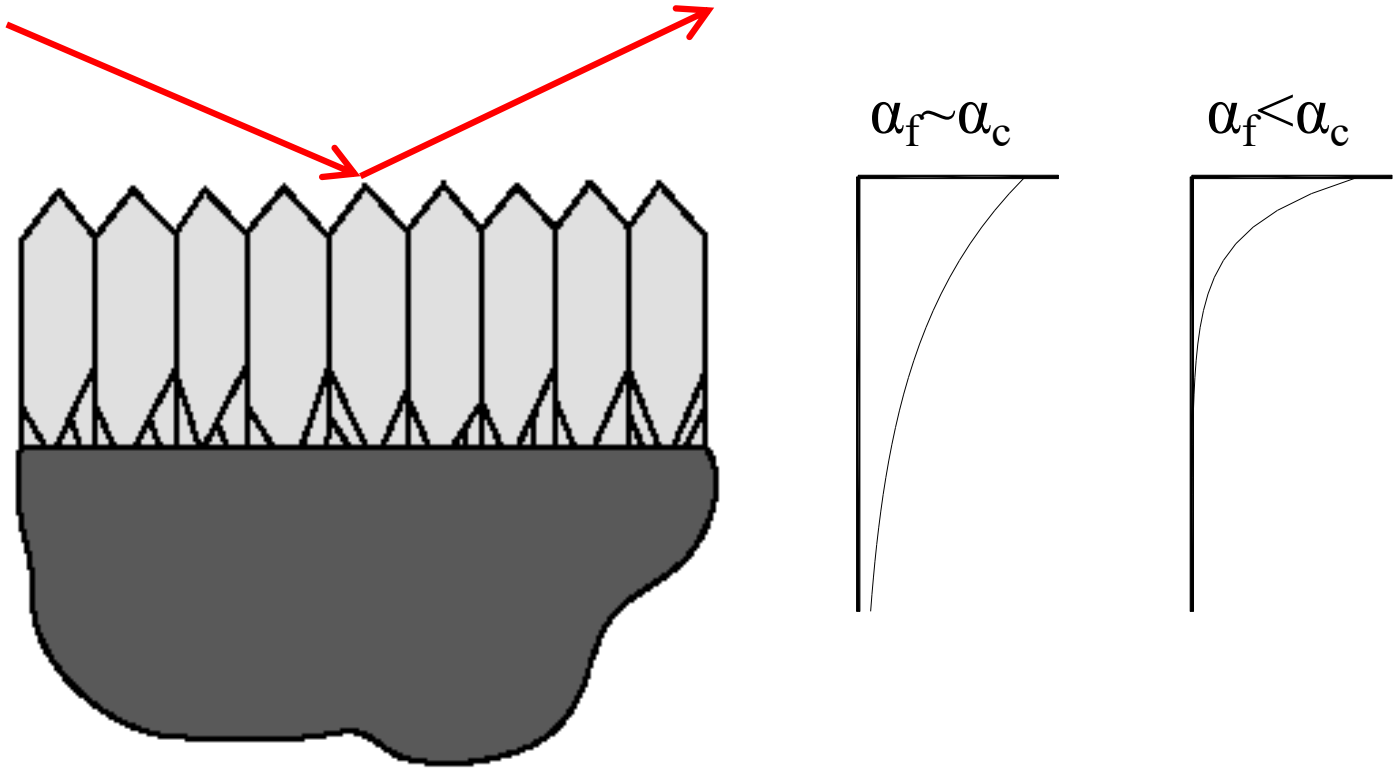
Specular ($\alpha_f = \alpha_i$)

$\alpha_f \sim \alpha_c$

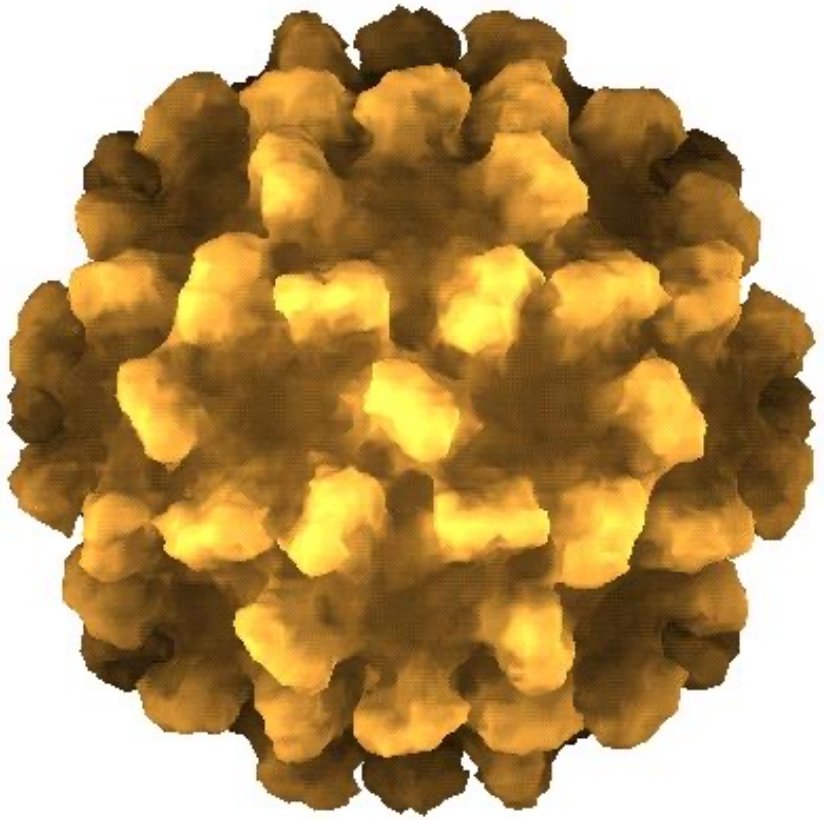
$\alpha_f \sim 0$

Competitive Grain Growth

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



Tomato Bushy Stunt Virus
1980



Conclusions and Outlook

- Inversion of CXD demonstrated
- Internal structure of Au Nanocrystals
- Preservation of coherence upon focussing
- Simple Quantum Dot stuctures possible now
- Single molecules one day