

# Coherent X-ray Diffraction for Phasing in Crystallography

- Ian Robinson
- Ivan Vartanyants      Department of Physics  
University of Illinois
- Franz Pfeiffer
- Mark Pfeifer
- Garth Williams      AsCA'03 Conference,  
Broome, August 2003
- Curtis Benson

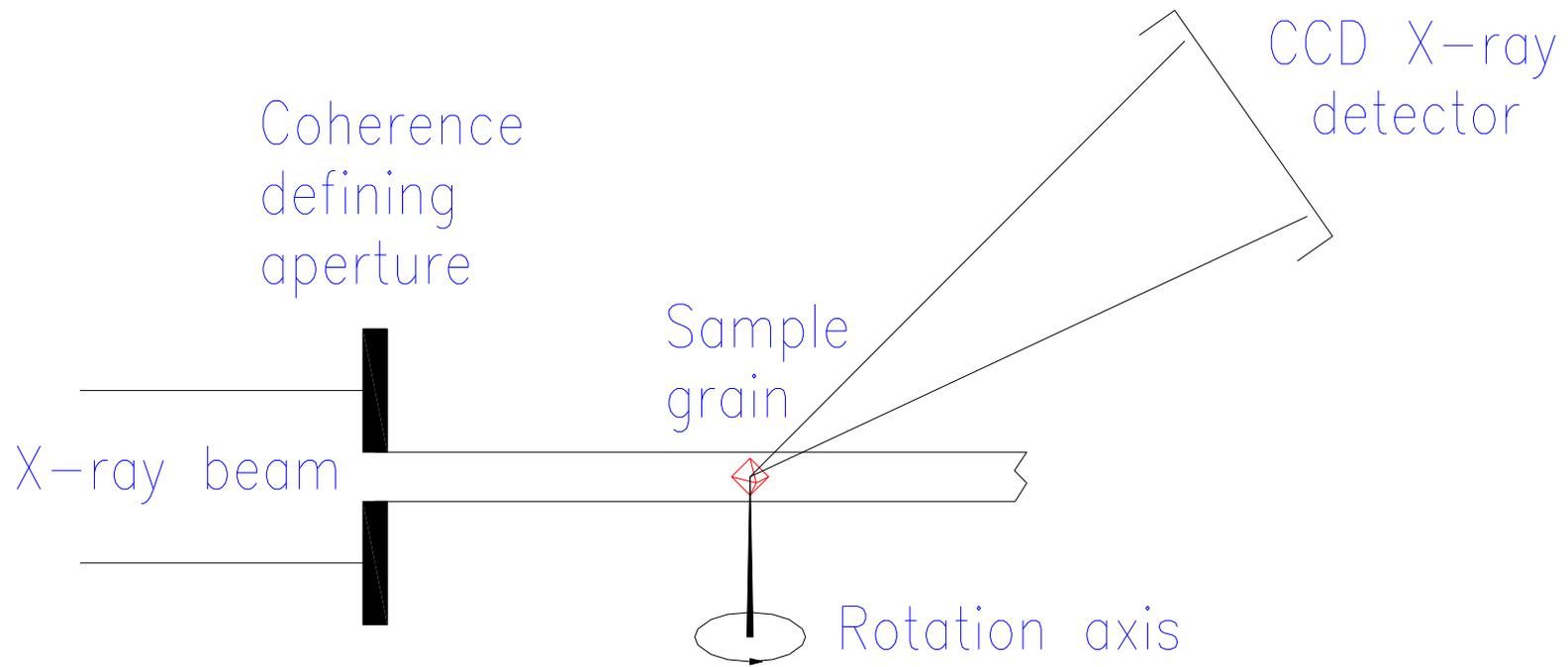
# Outline

- Coherence in Diffraction
- The **Phase** Problem
- Coherent Diffraction from Surfaces
- Nanocrystal Shapes
- How small can we go?
- Future Applications of CXD

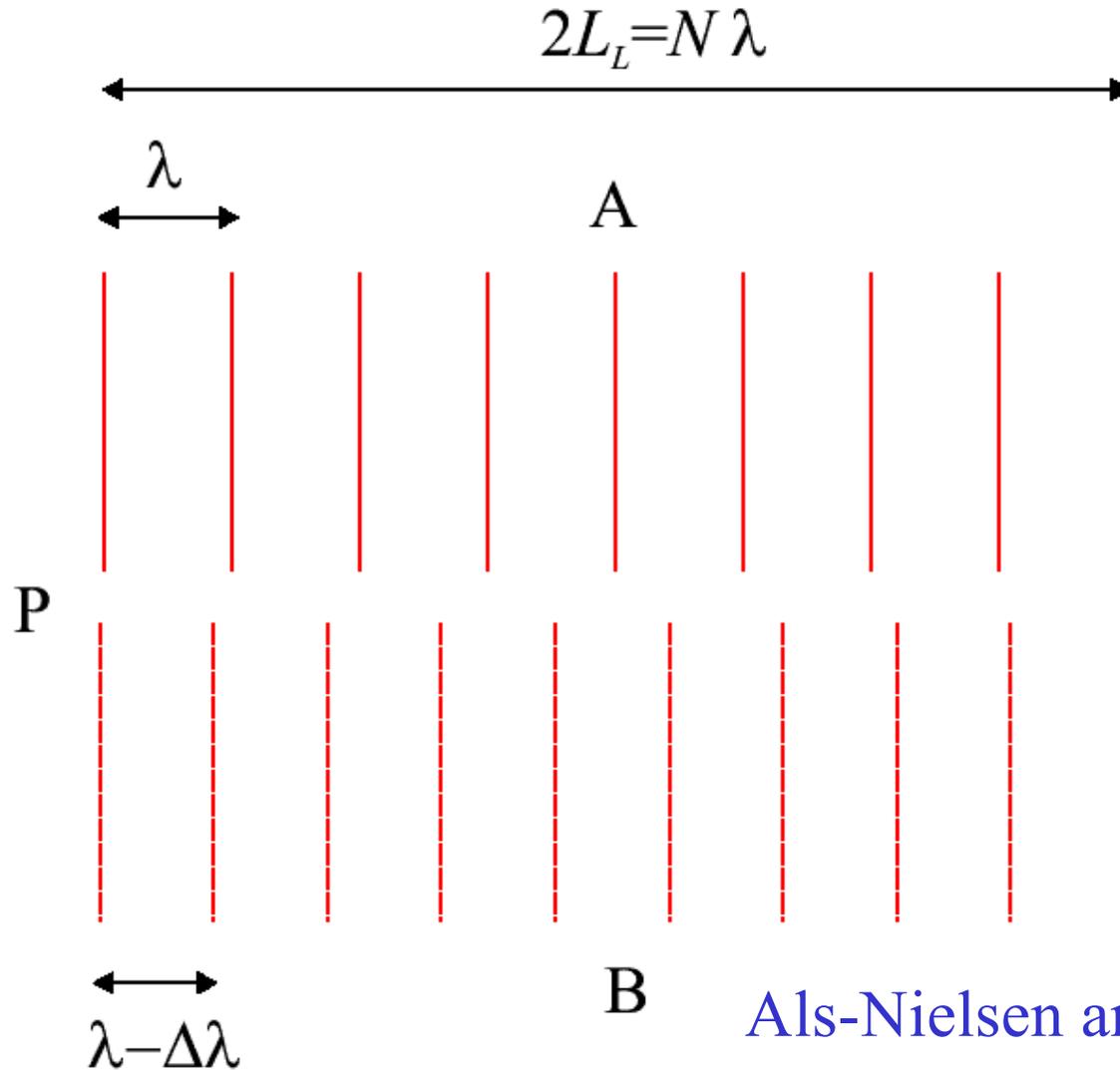
# Uses of Coherence in Diffraction

- 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

# Lensless X-ray Microscope



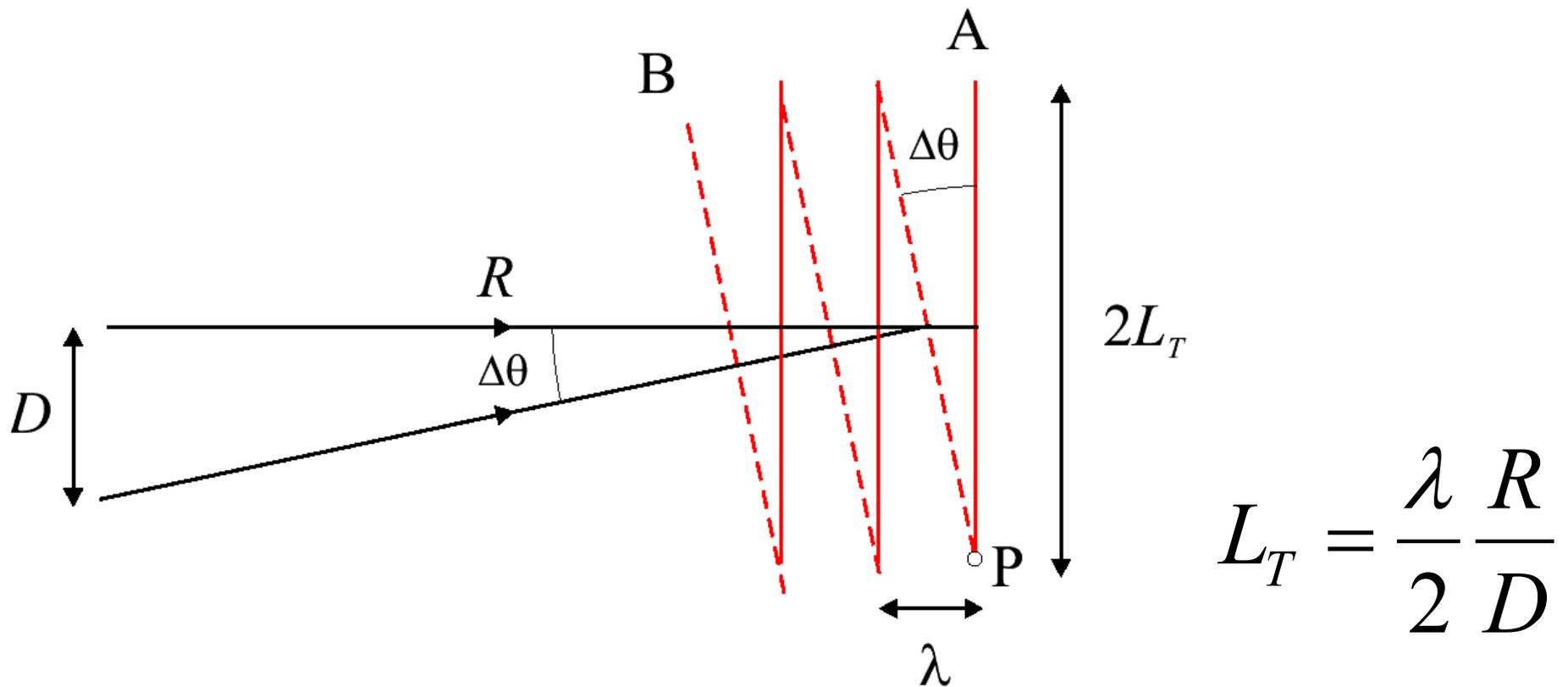
# Longitudinal Coherence



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

Als-Nielsen and McMorro (2001)

# Lateral (Transverse) Coherence



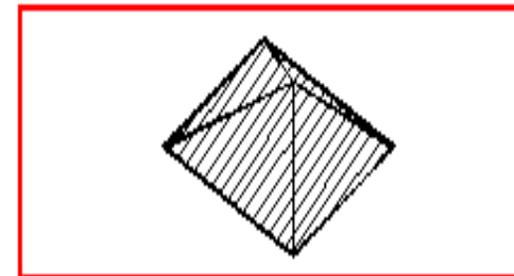
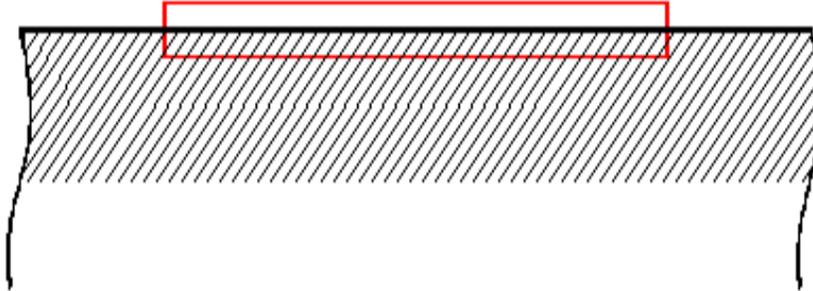
Als-Nielsen and McMorrow (2001)

# Coherence at the APS

Typical of Undulator-based Synchrotron Source  
eg Future Australian Synchrotron Project

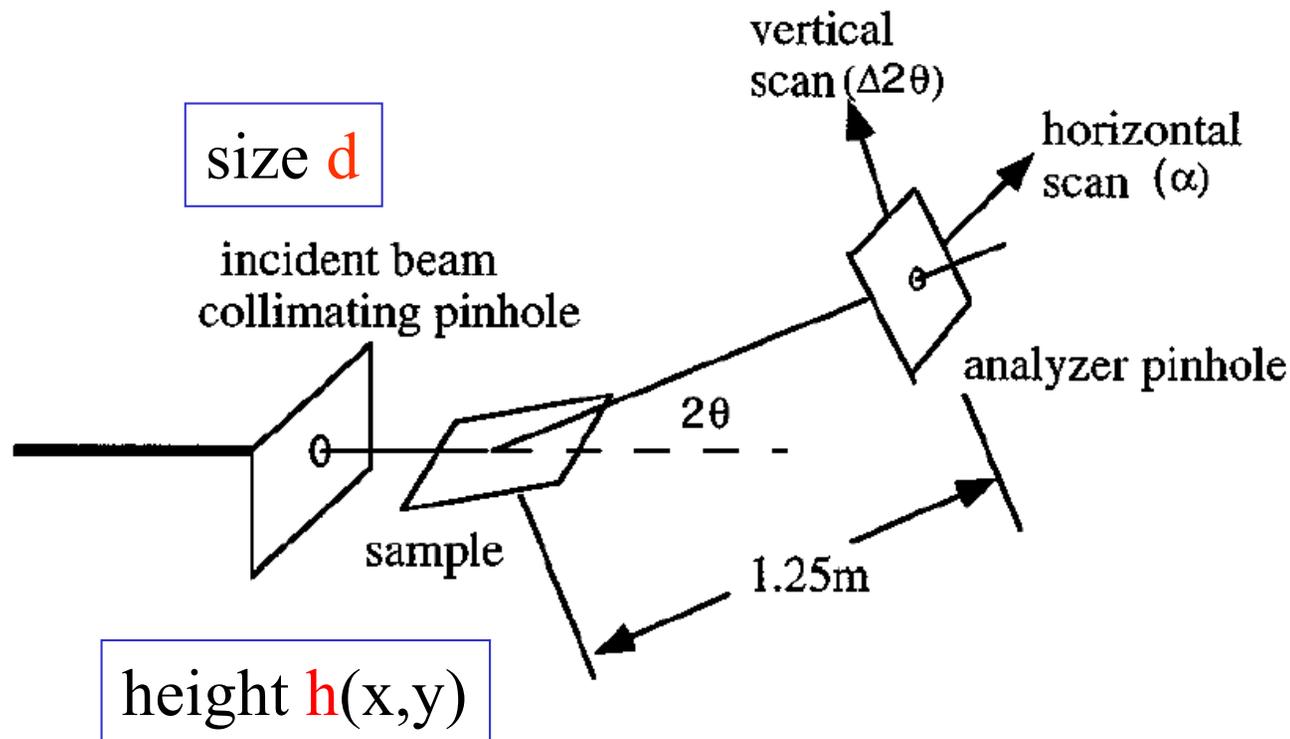
Coherence of	$\xi_{\text{VER}}$	$\xi_{\text{HORIZ}}$	$\xi_{\text{LONG}}$	Flux
Raw Undulator	35 $\mu\text{m}$	9 $\mu\text{m}$	0.004 $\mu\text{m}$	$2 \times 10^{12}$
Si(111) Monochromator	35 $\mu\text{m}$	9 $\mu\text{m}$	1 $\mu\text{m}$	$1 \times 10^{10}$
C(111) Monochromator	35 $\mu\text{m}$	9 $\mu\text{m}$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

Coherent region defined by slits



# Surface Coherent X-ray Diffraction

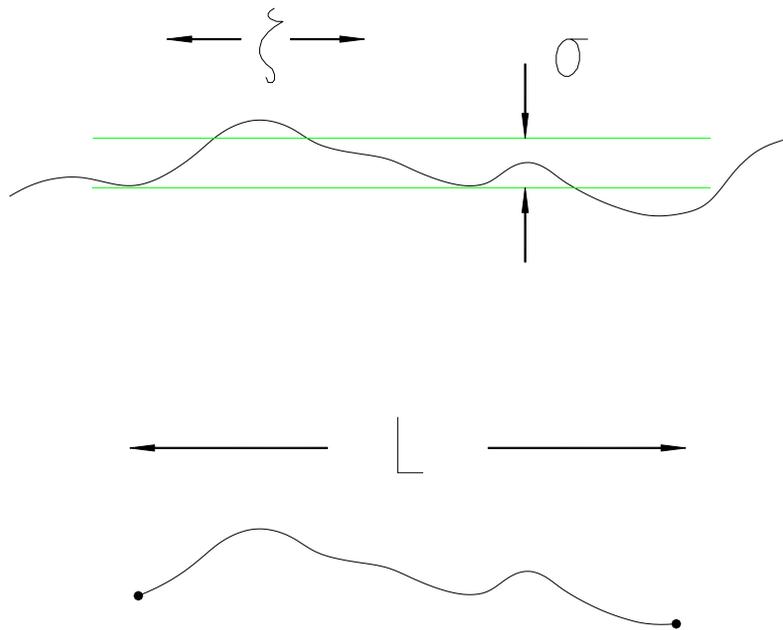
$$A(q_x, q_y) = \int_{-d/2}^{d/2} dx dy e^{iq_z h(x,y)} e^{iq_x x} e^{iq_y y}.$$



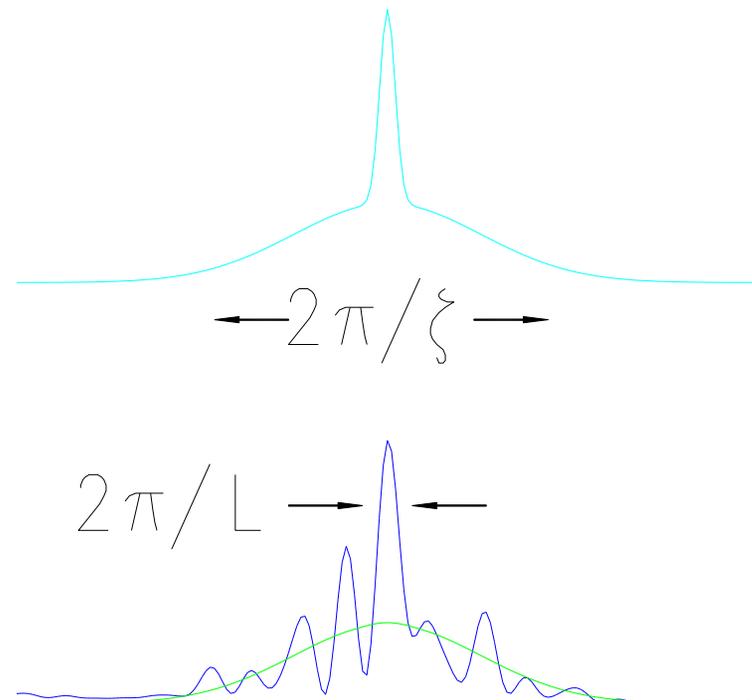


# Diffuse Scattering acquires Structure using CXD

Real Space

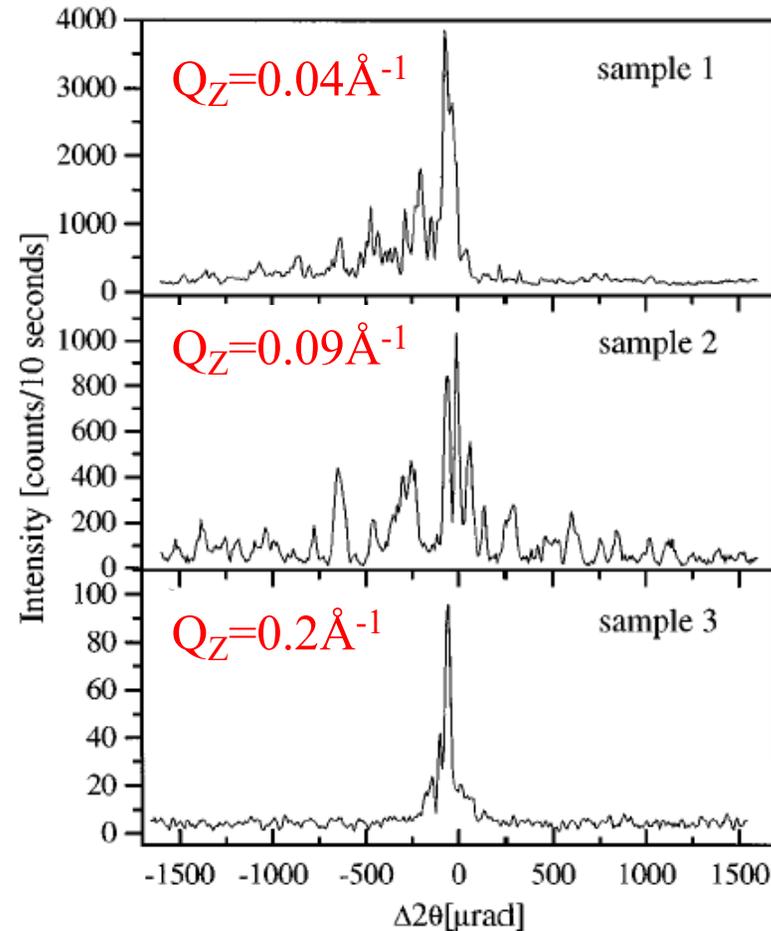
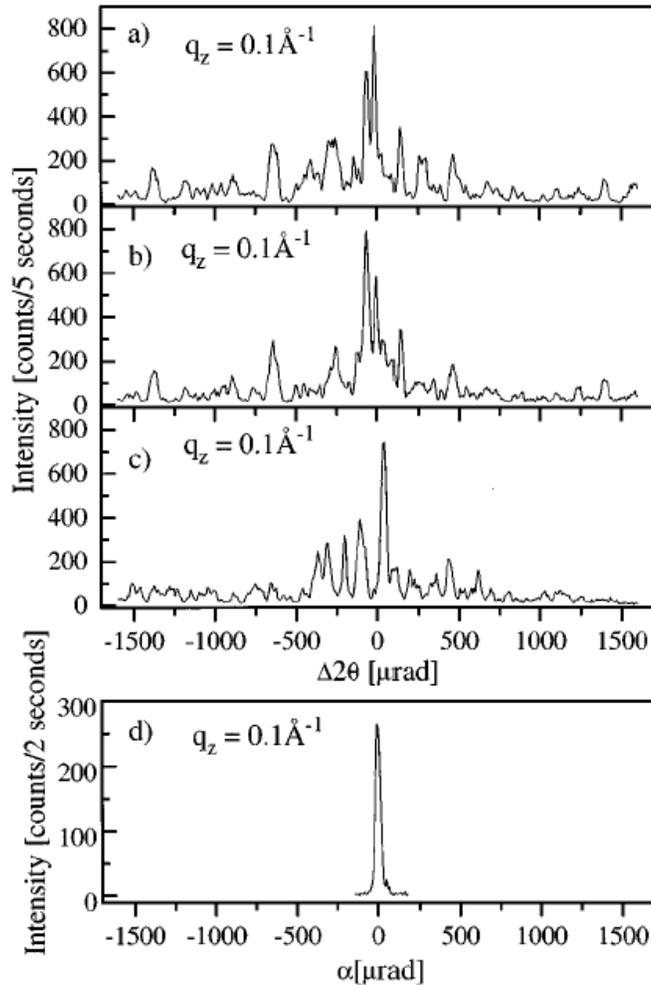


Reciprocal Space

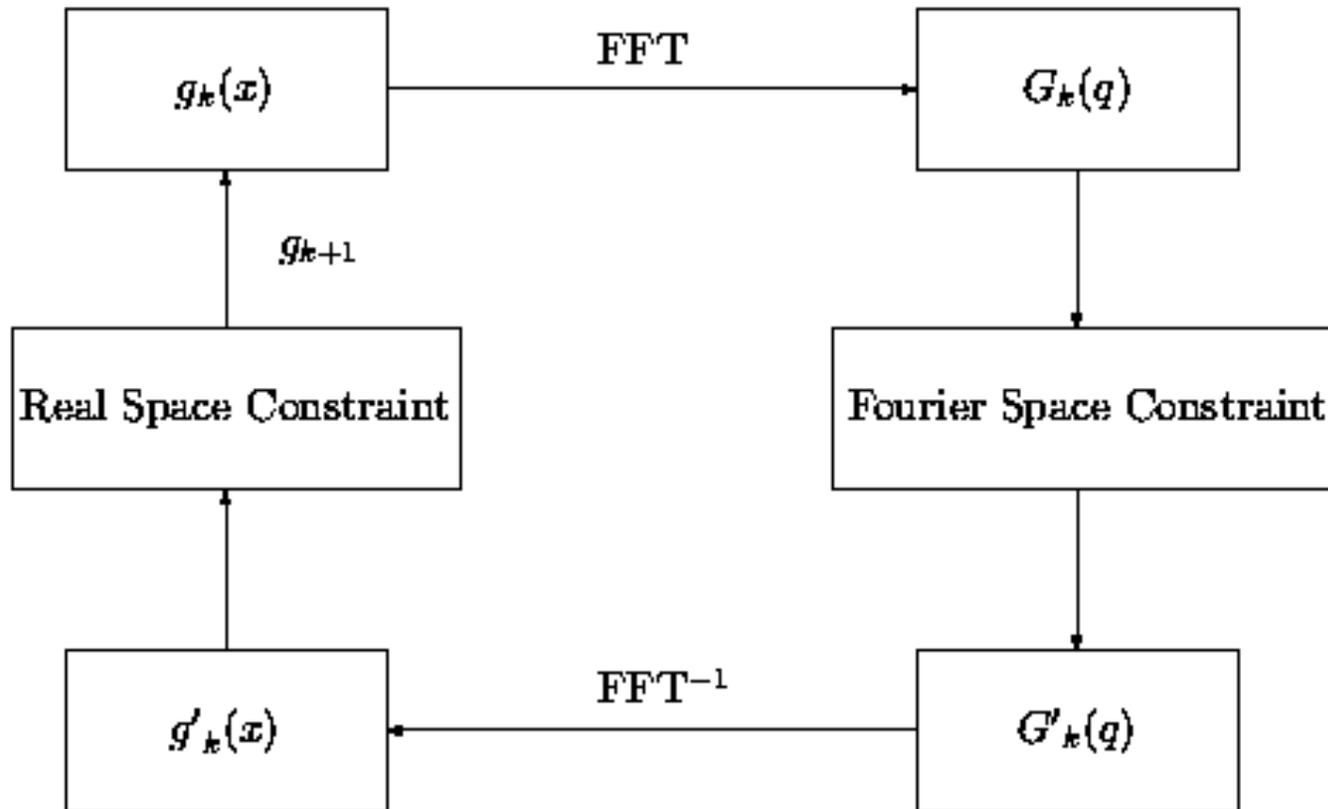


# Si Samples of Different Roughness

J. L. Libbert *et al* Phys. Rev. B **56** 6454 (1997)



# Generic “Error Reduction” method



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

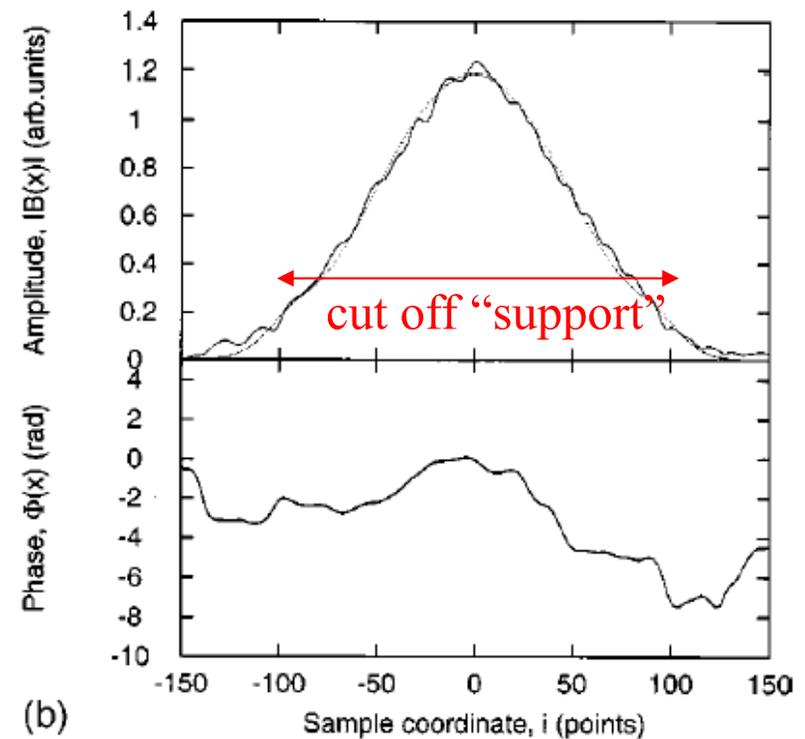
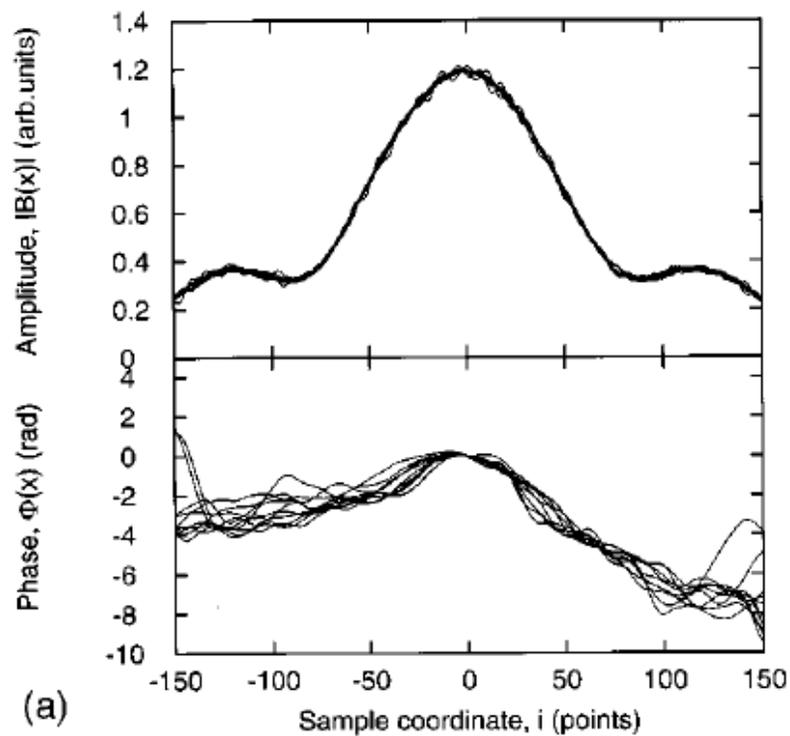
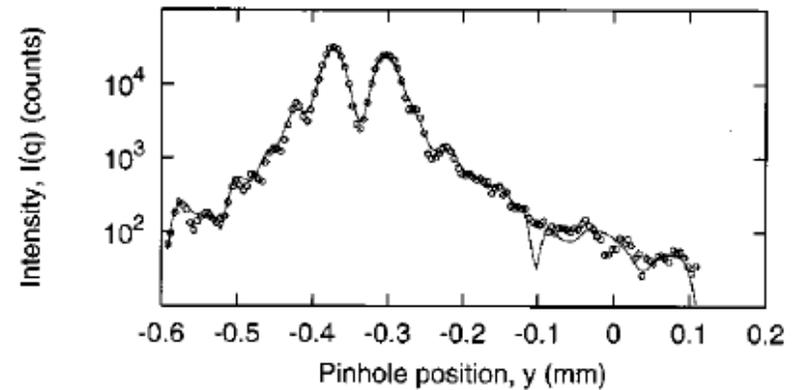
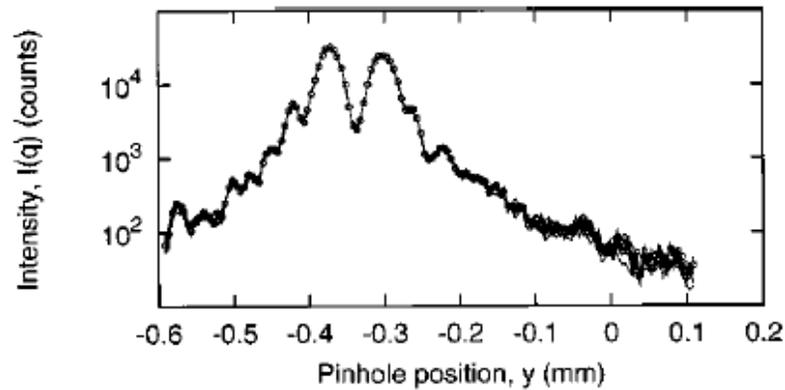
R. W. Gerchberg and W. O. Saxton *Optik* 35 237 (1972)

# Real-space Constraints in Crystallography

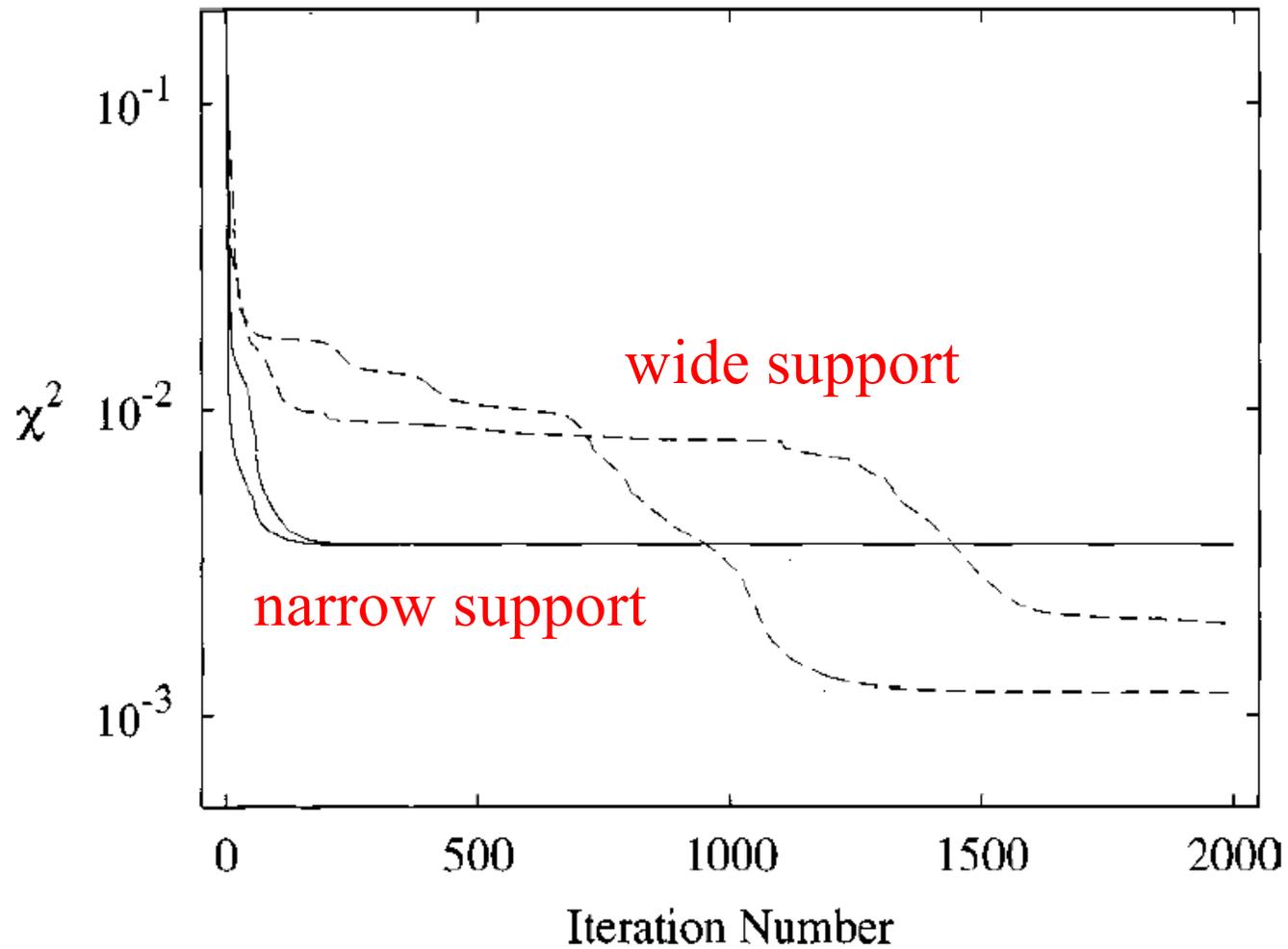
R. P. Millane, J. Opt. Soc Am. A **13** 725 (1996)

- ‘Positivity’, ‘Atomicity’ constraints (Sayre)
- Solvent flattening
- Non-crystallographic symmetry
- Molecular replacement
- Finite **support** = molecular envelope
- Non-uniqueness is ‘pathologically rare’ ( $d > 1$ )

# Phasing using G-S Algorithm



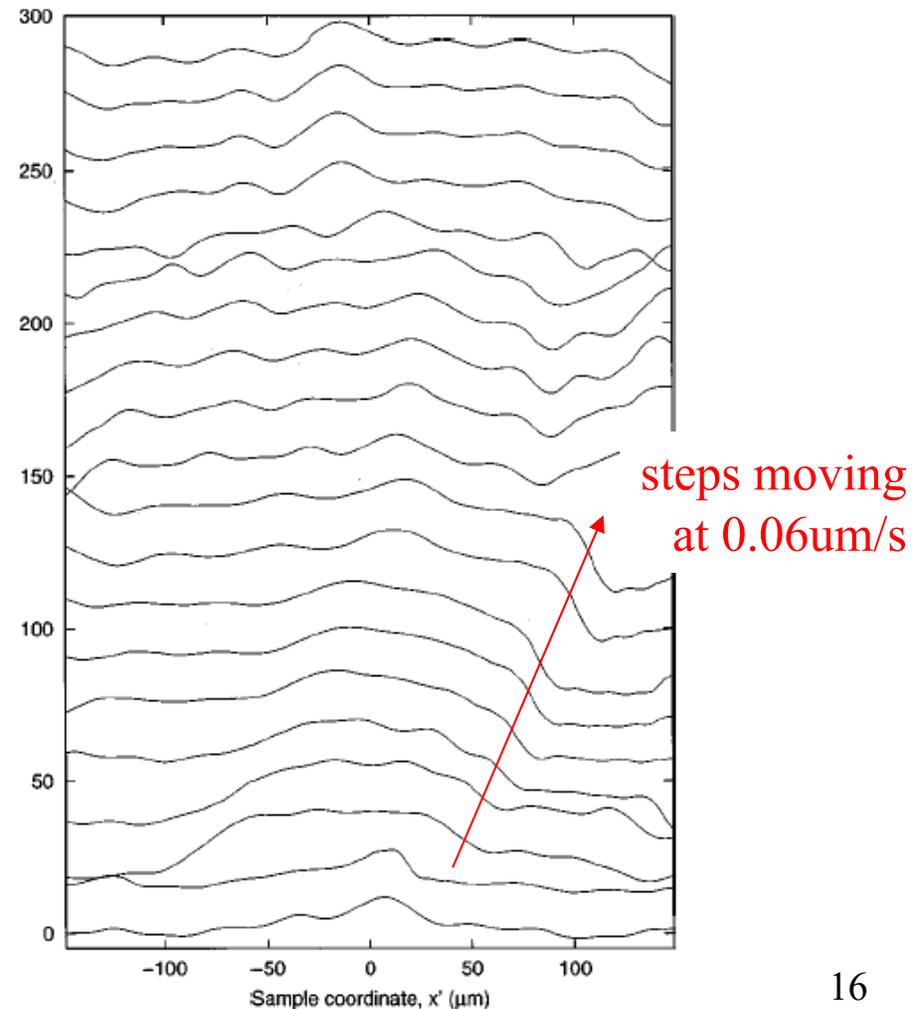
# Convergence Trajectory



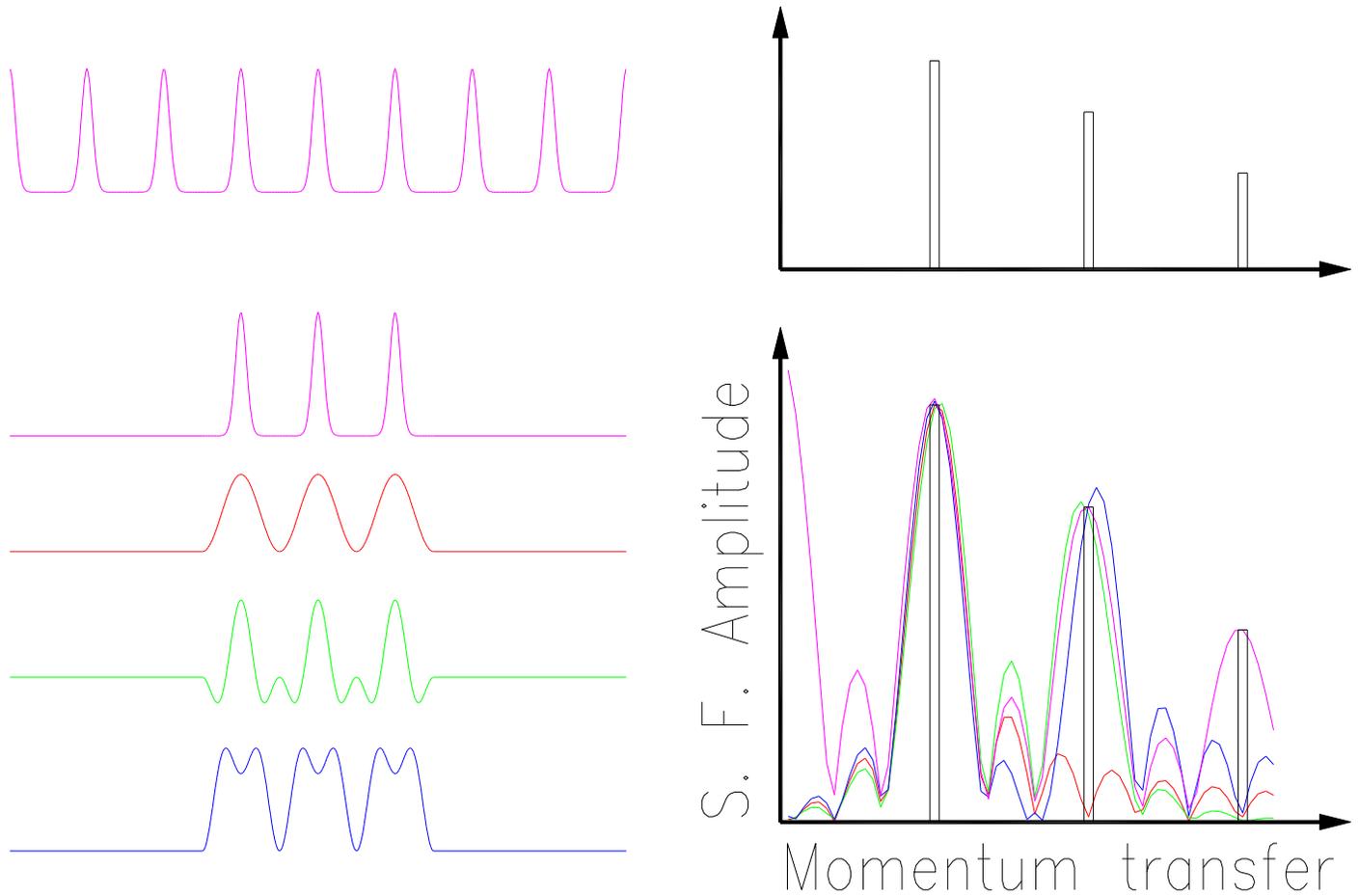
# *In-situ* Regrowth of Oxide on Si

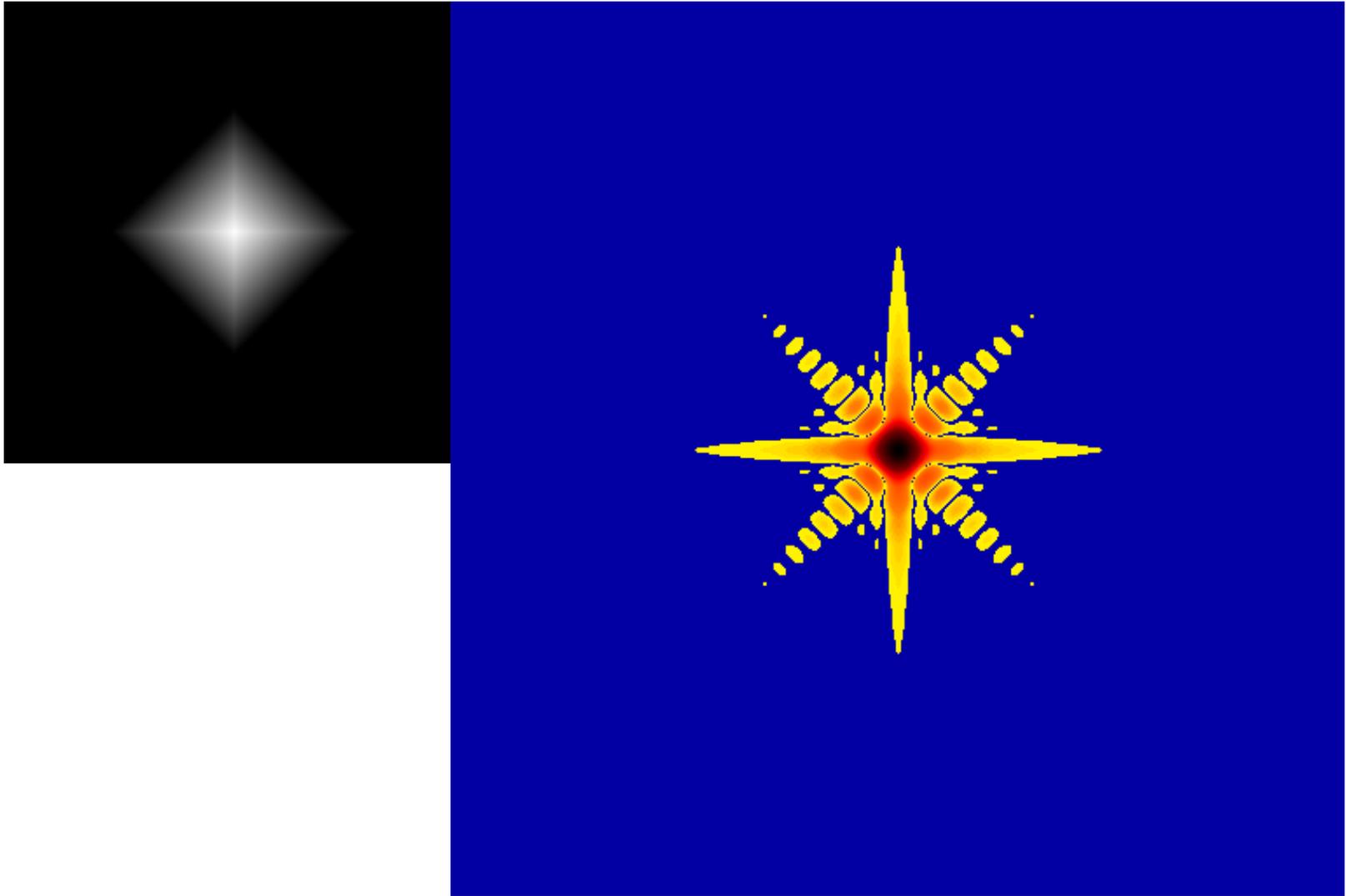
Phys. Rev. B **60** 9965 (1999)

- Wafer stripped with HF at  $t=0$
- CXD pattern measured every 180 sec
- Each profile reconstructed independently
- Random starting phase each time



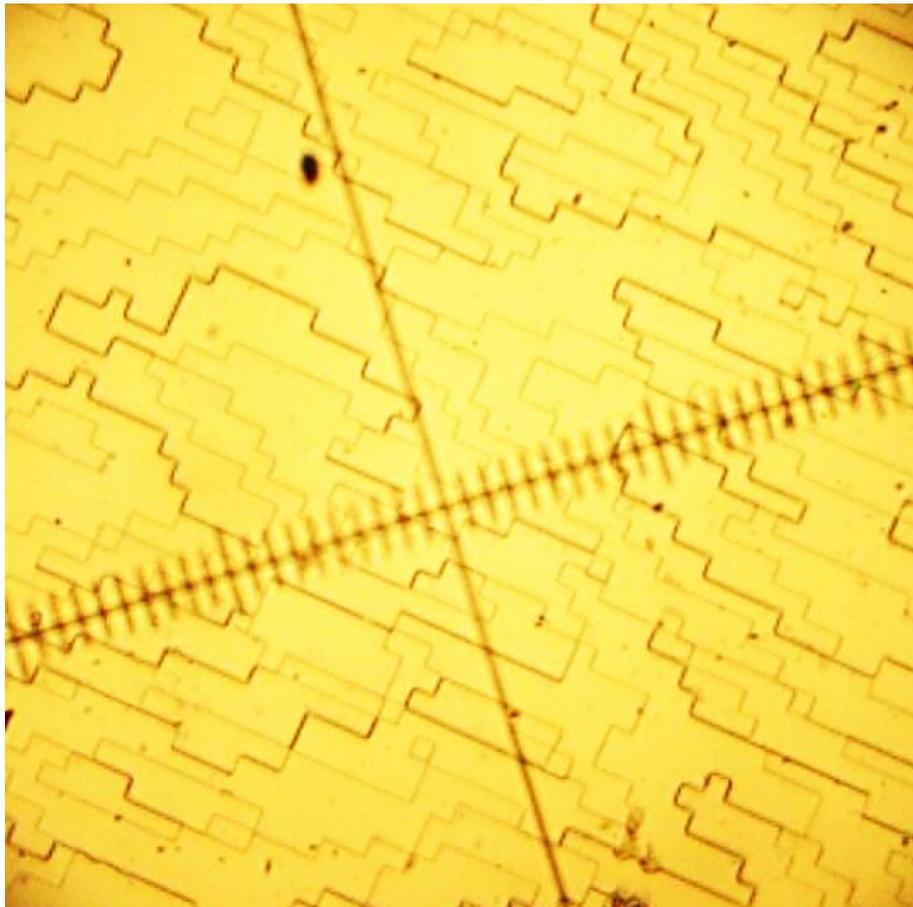
# Phase Problem: Finite-size Effect



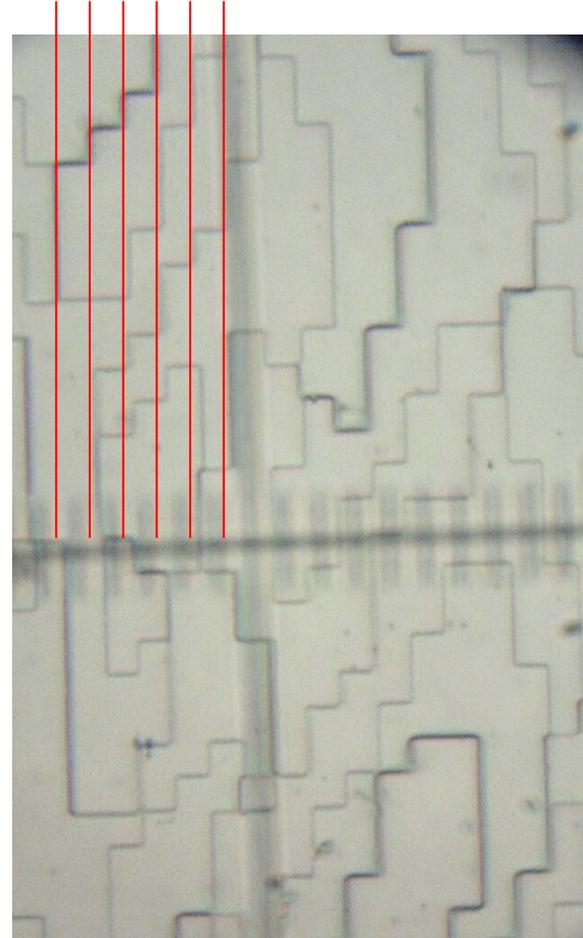


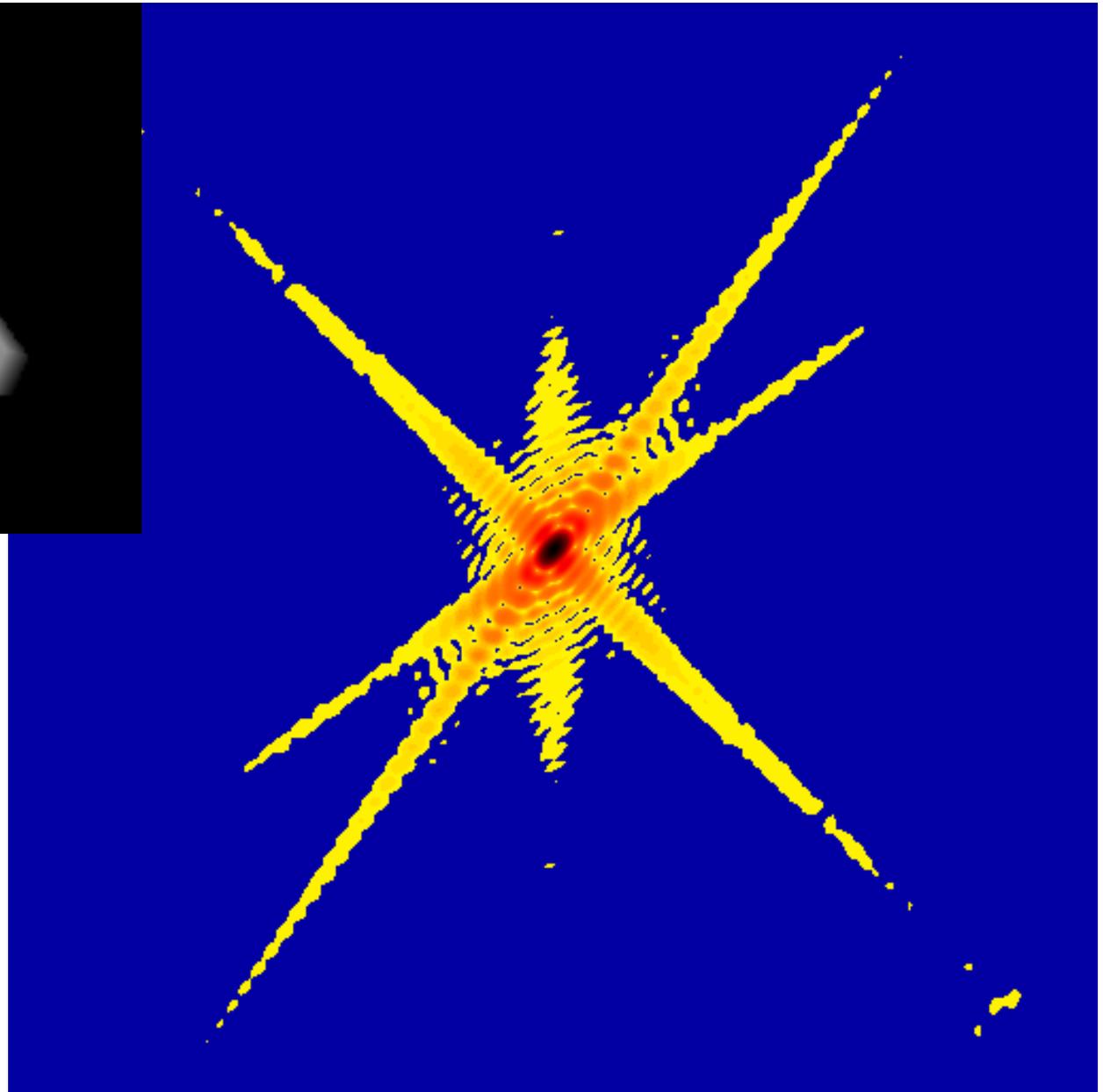
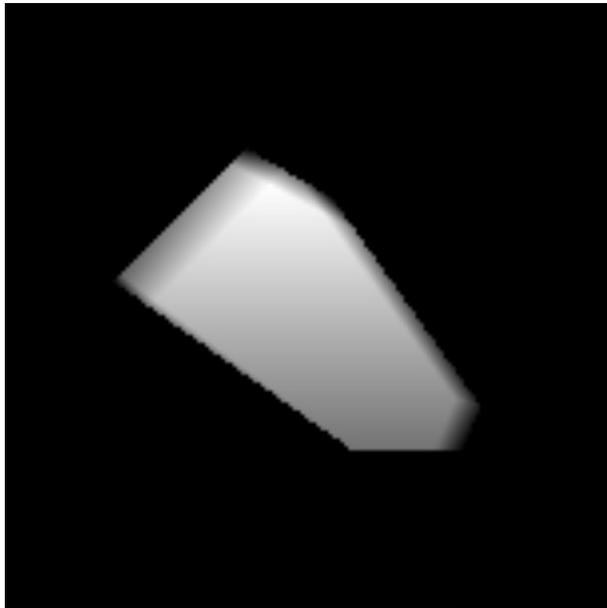


# Microscope Images of Gratings



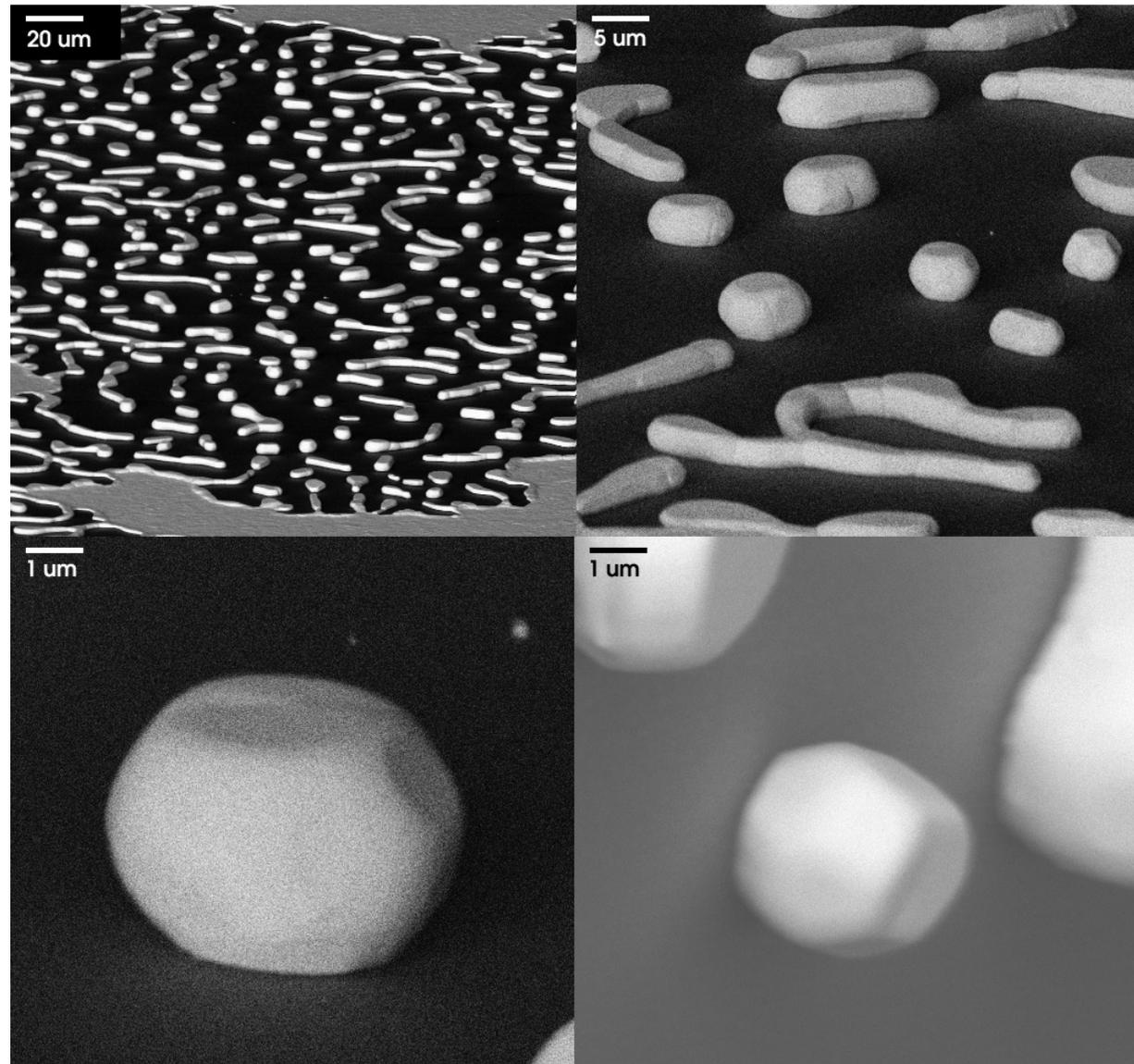
5 $\mu$ m grid lines



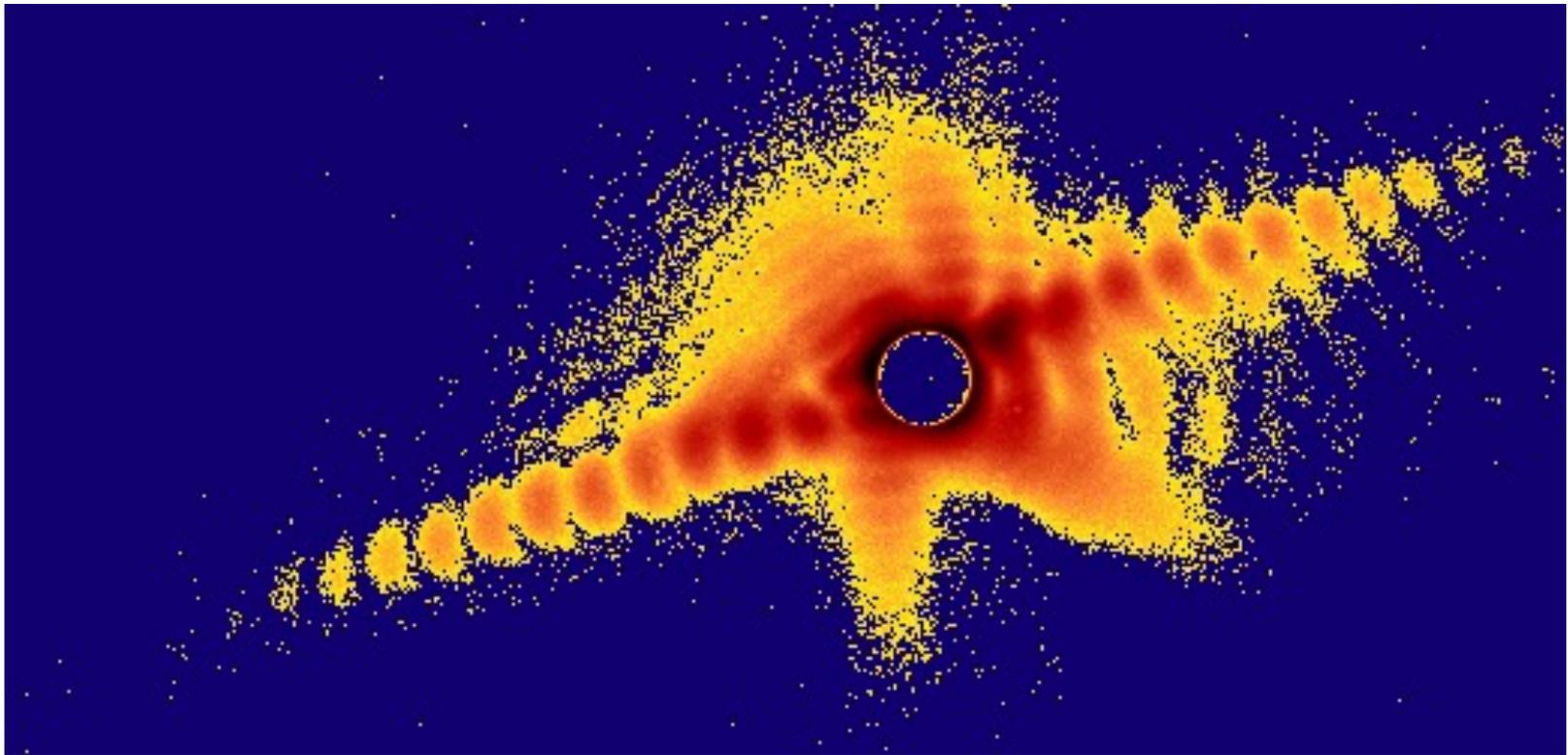


# SEMS

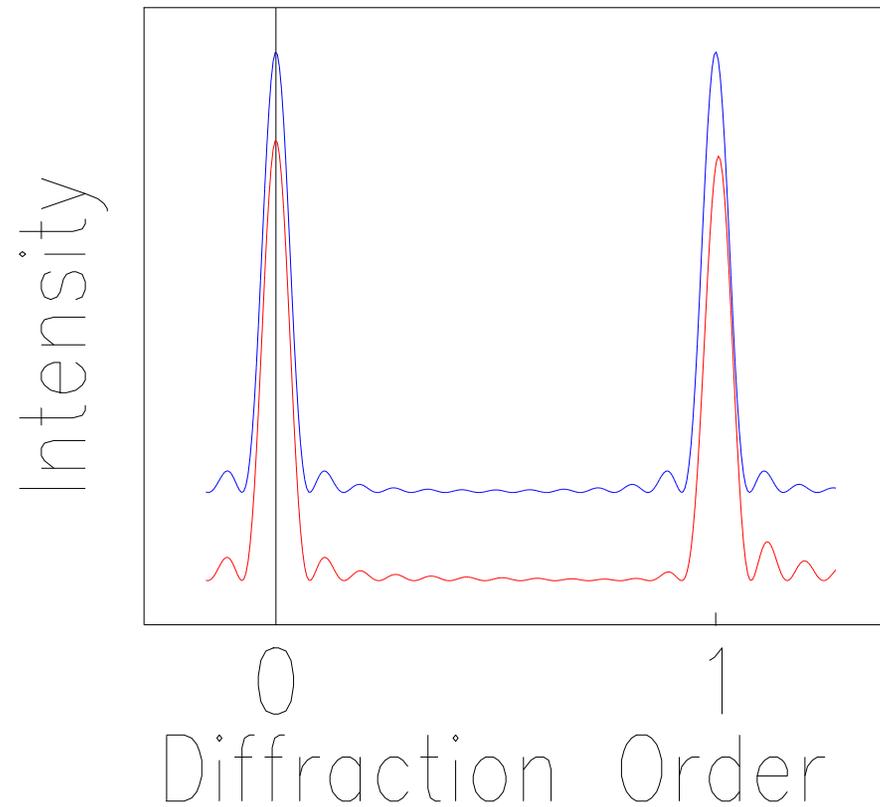
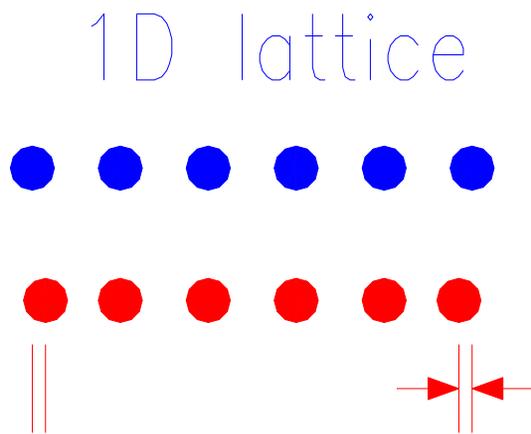
- Au blanket film
- Quartz substrate
- Annealed at 950°C for 70 hrs.



# Micron-sized gold crystal: (111) Bragg reflection

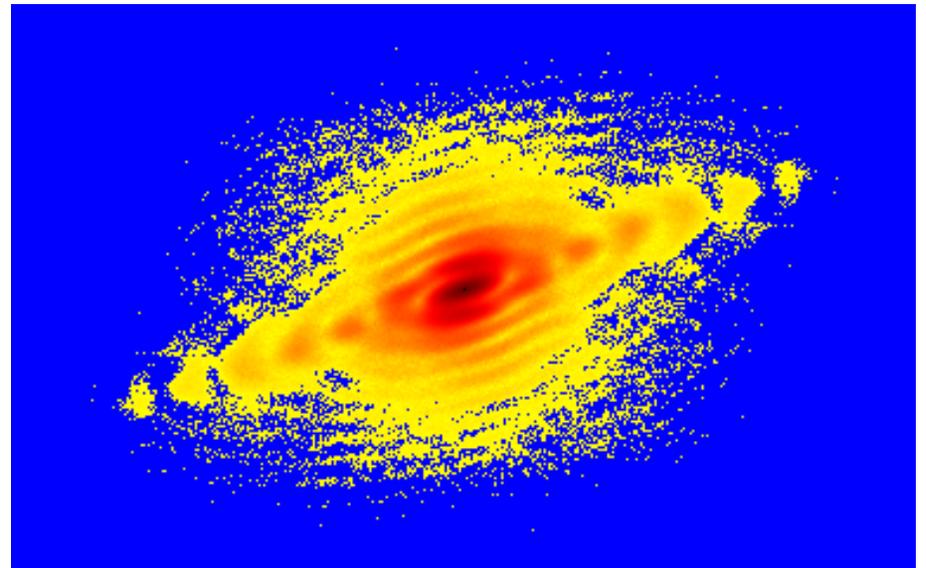
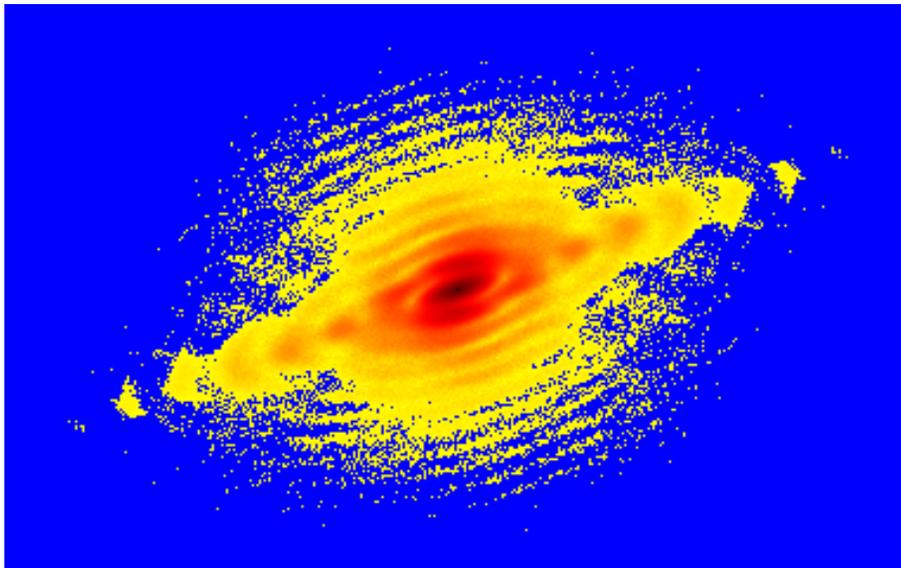
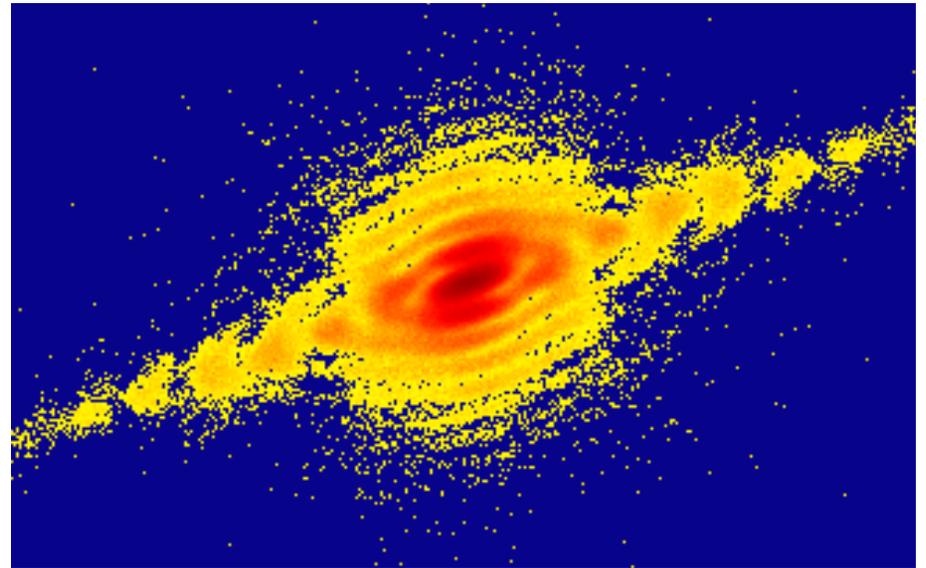


# Imaging of Lattice Strains



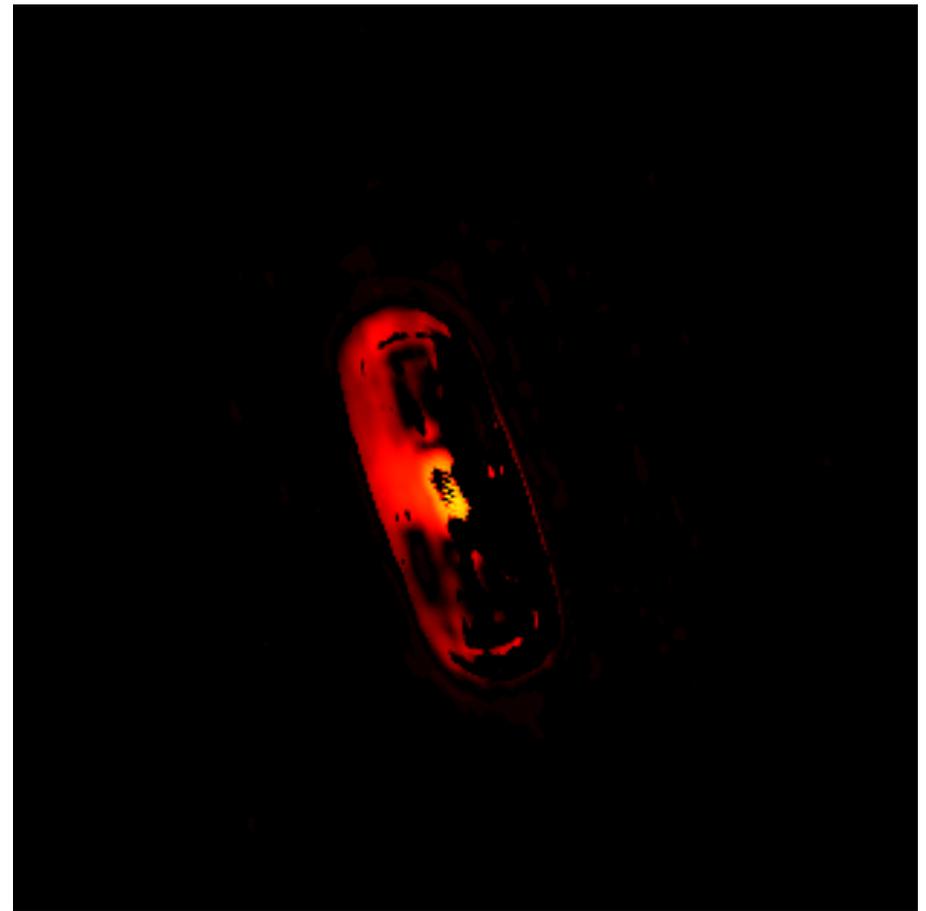
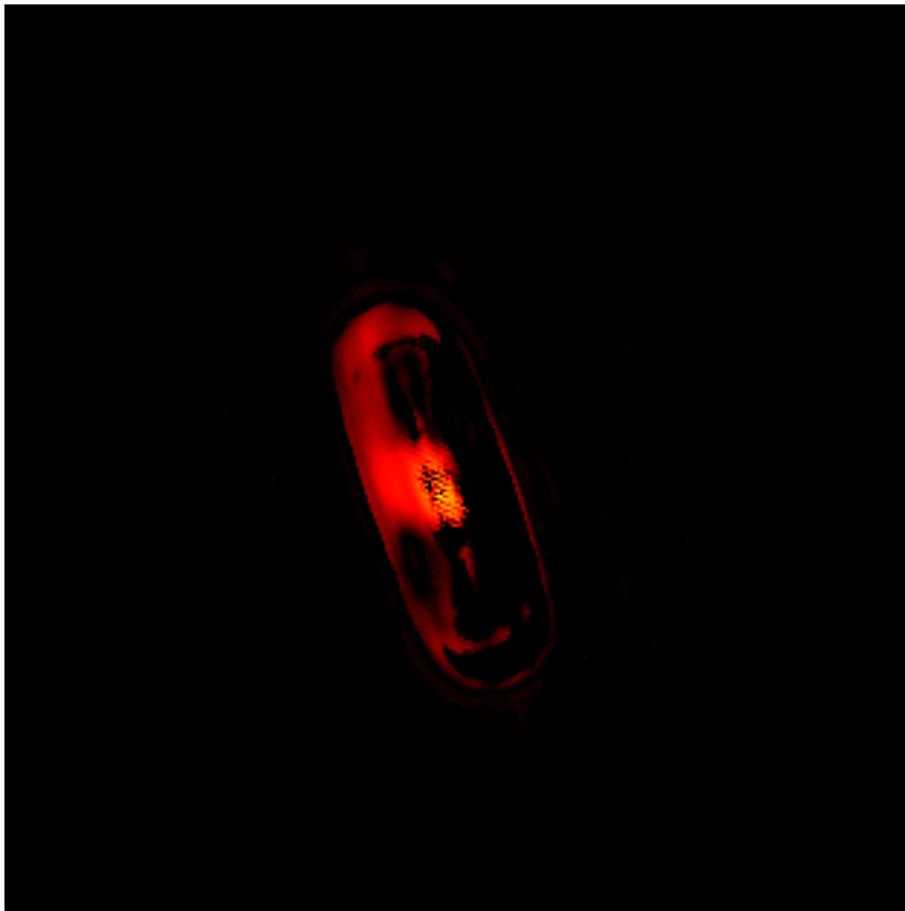
# Symmetrized Data and two best fits

$\text{Chisq}=0.0005$

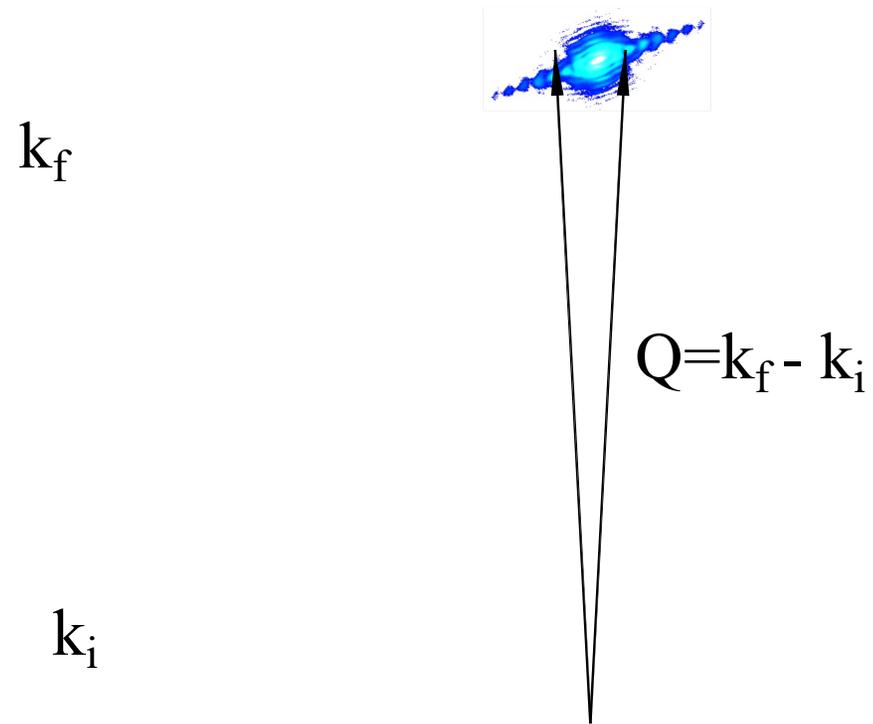


# 2D Reconstructions

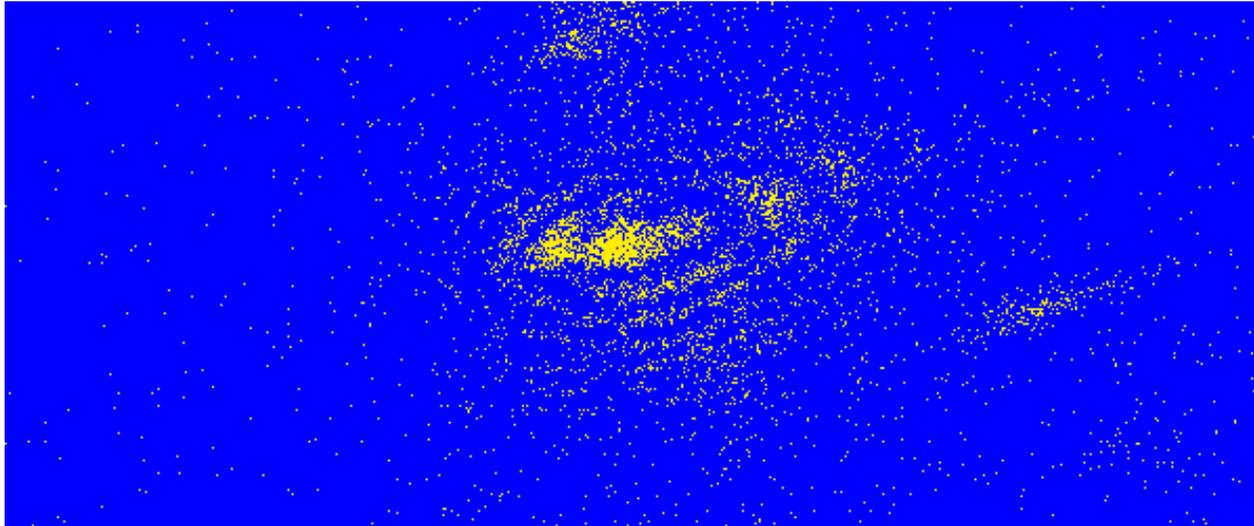
chisquare = 0.0005



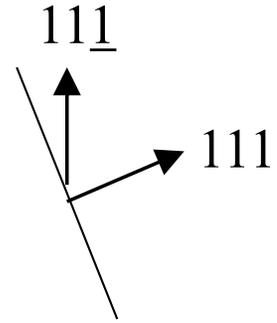
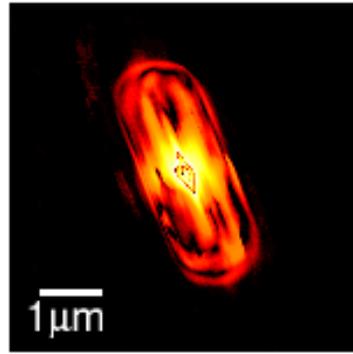
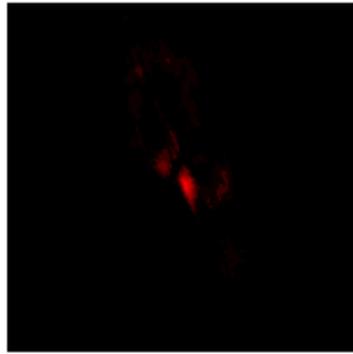
# 3D Diffraction Method



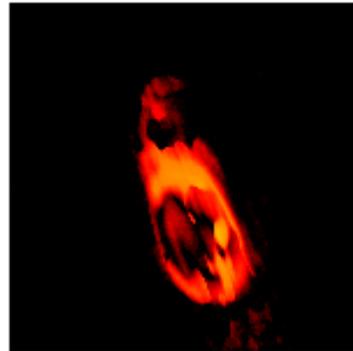
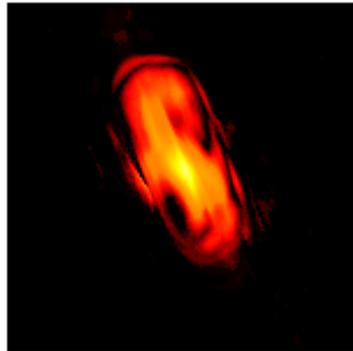
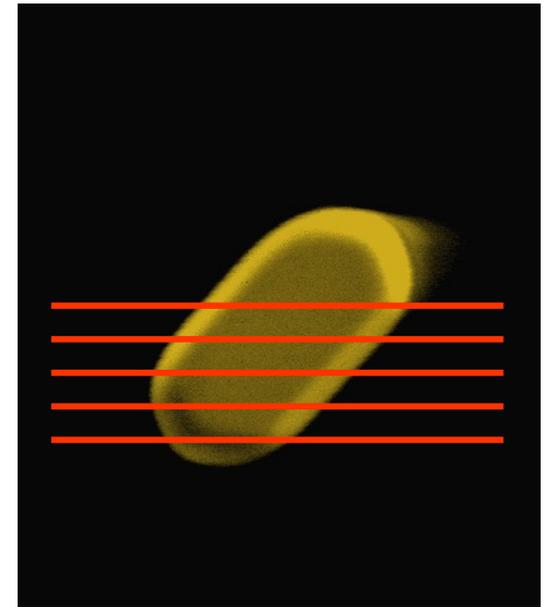
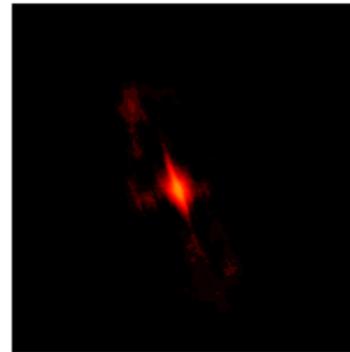
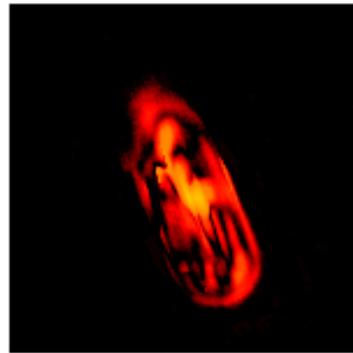
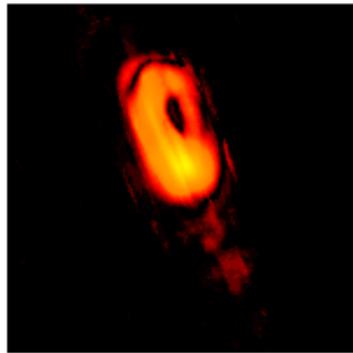
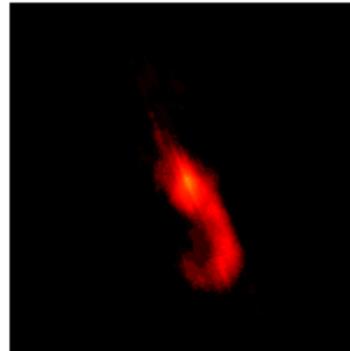
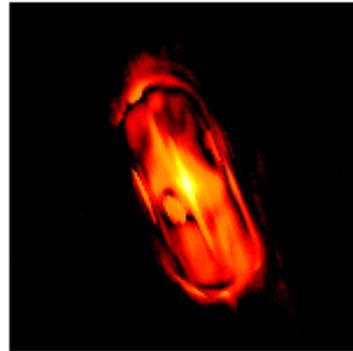
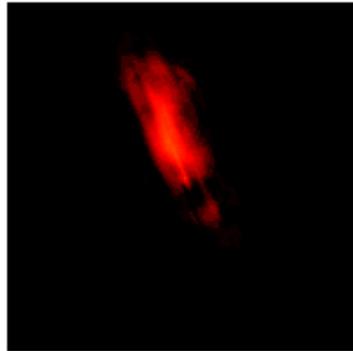
# 3D Diffraction Data 1 micron Au crystal



\* Center is Symmetric \*

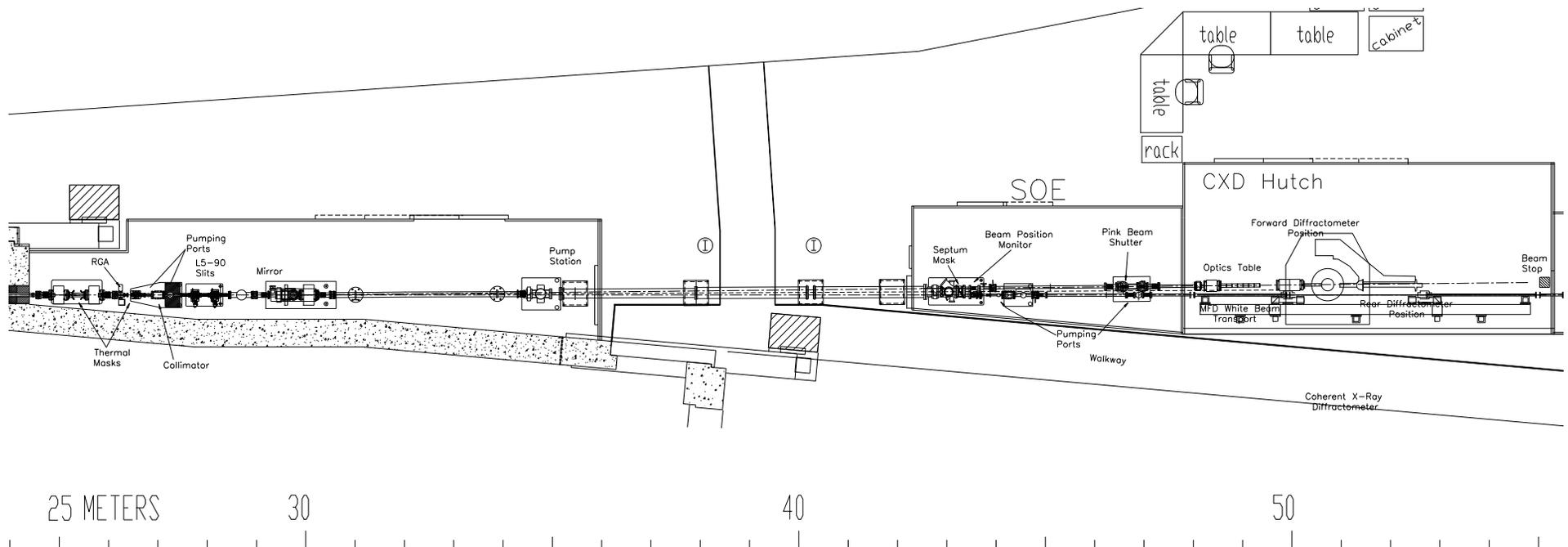


Slices through  
plan view SEM:



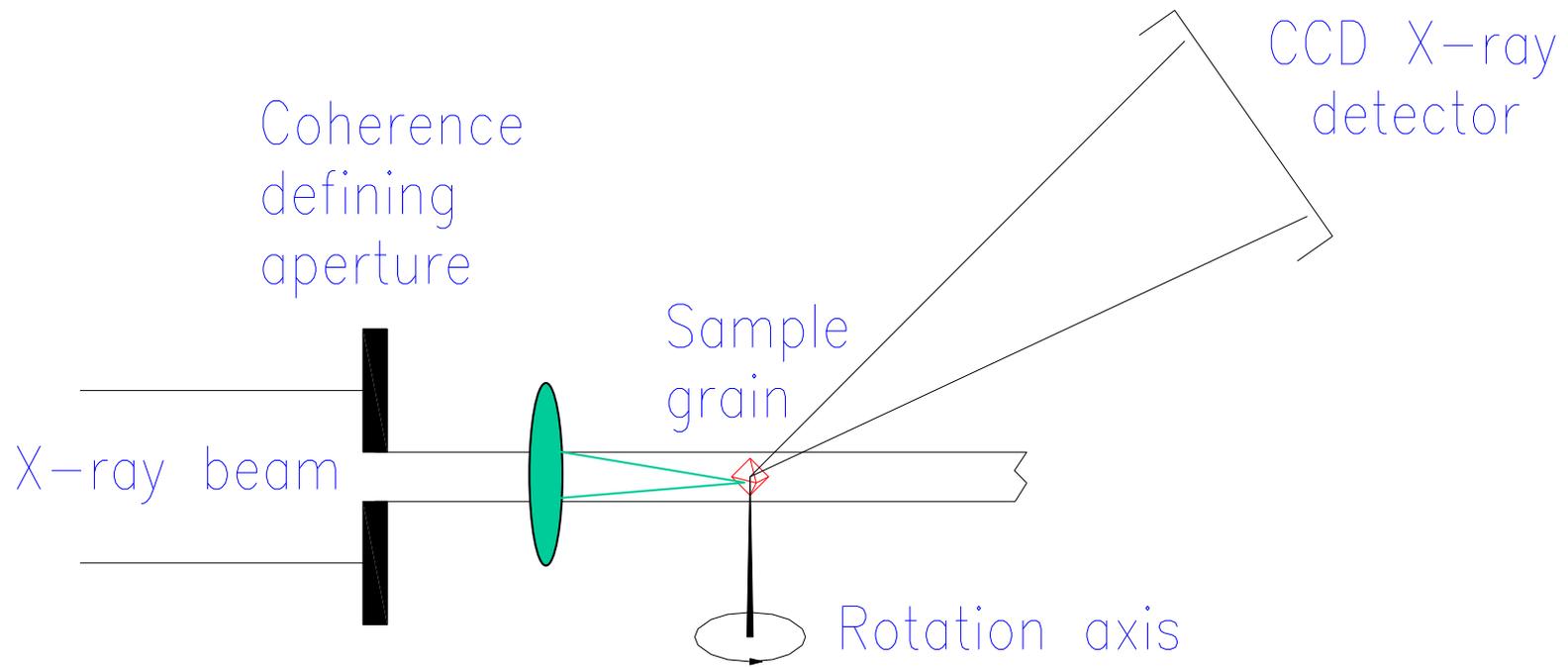
# CXD Beamline at APS Sector 34

## Prototype for Australian Synchrotron Project?

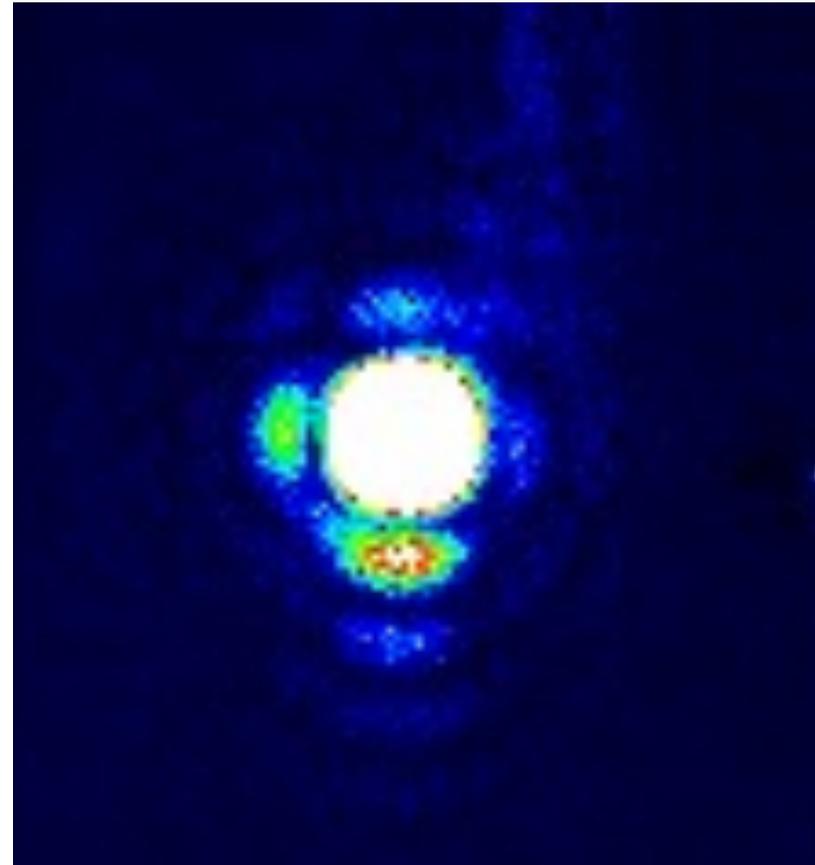
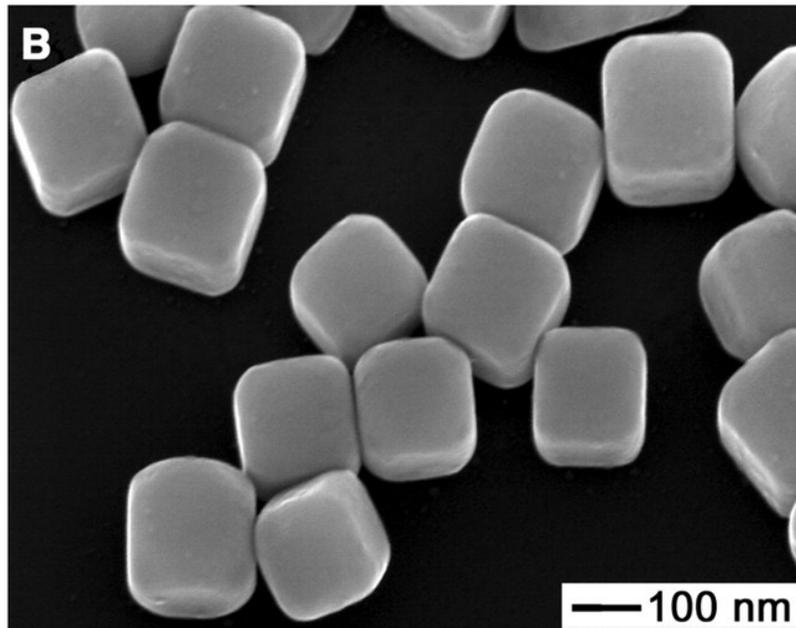




# Lensless X-ray Microscope

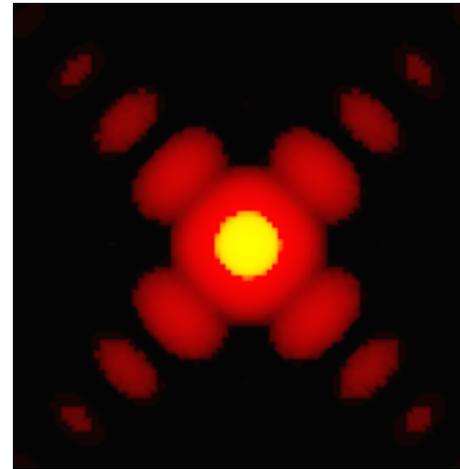
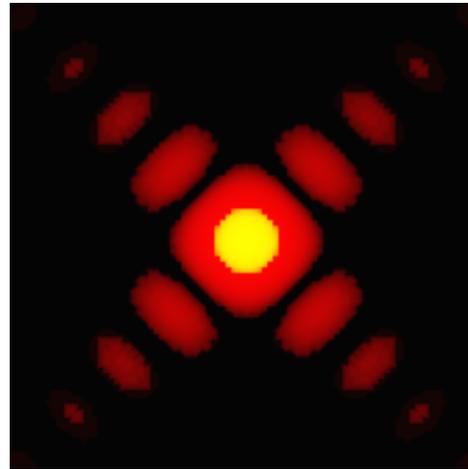


# CXD from Silver Nanocubes

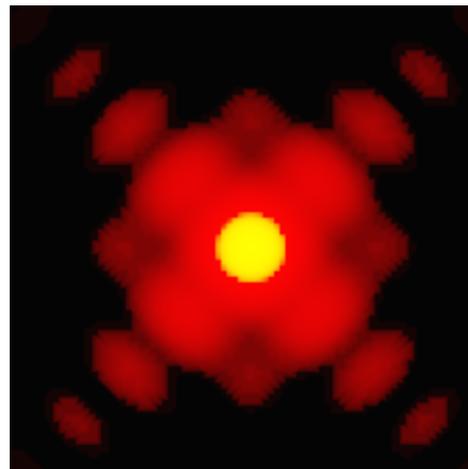


Yugang Sun and Younan Xia,  
*Science* 298 2177 (2003)

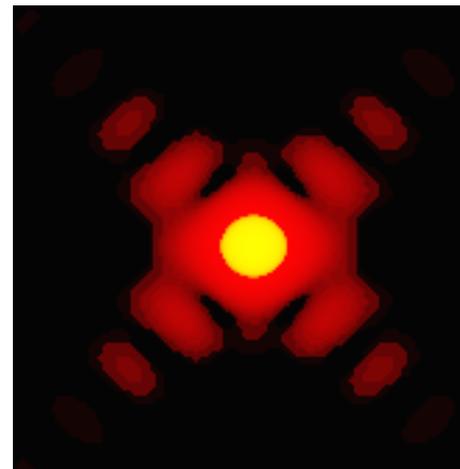
# Spherical and cylindrical waves



$\pi/4$



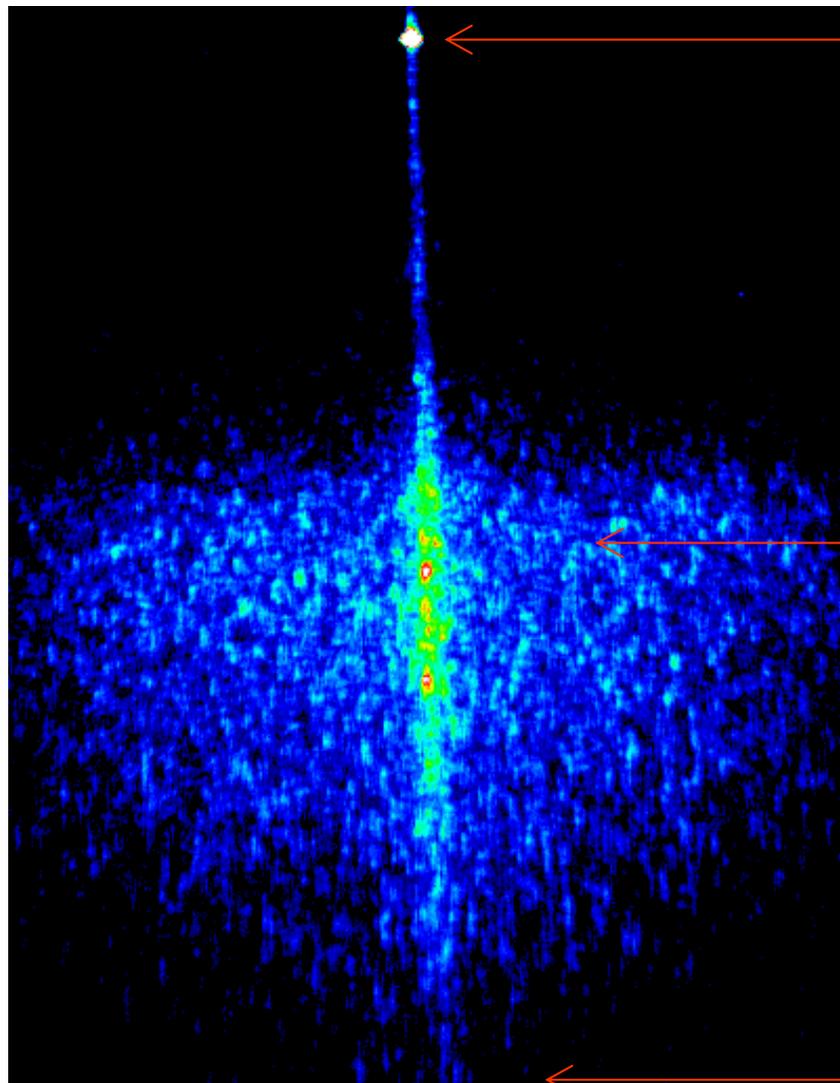
$\pi/2$



$\pi/4$  (x)

# Structure in “Yoneda” Peak

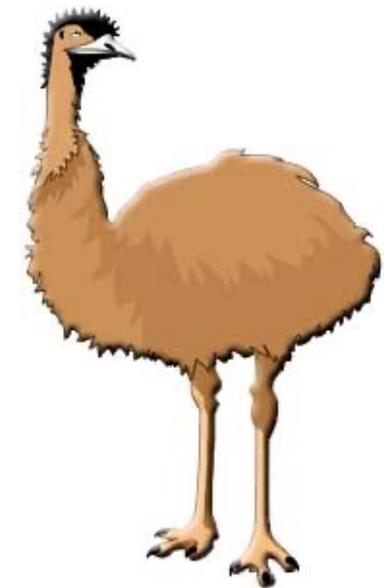
Grazing-exit diffraction from a 1000Å Au polycrystalline film



Specular ( $\alpha_f \sim \alpha_i$ )

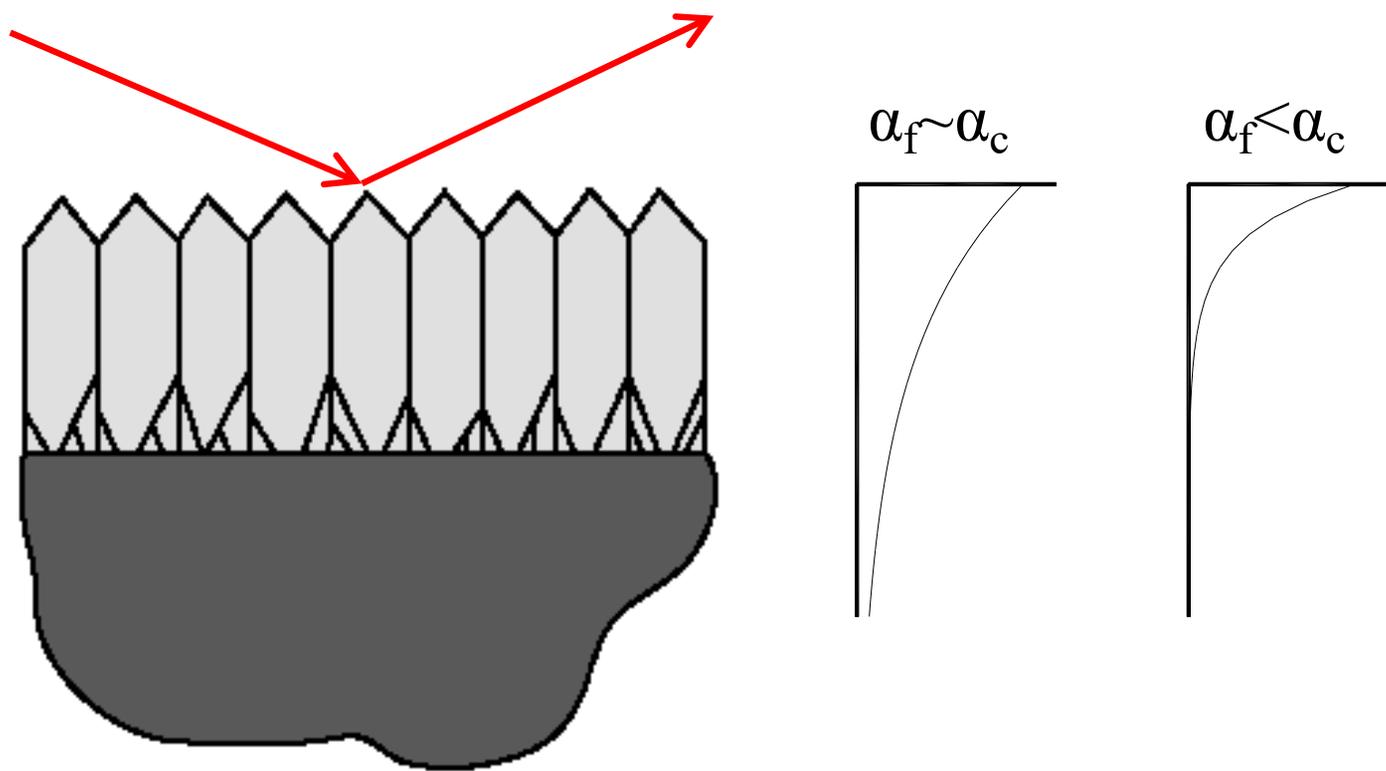
$\alpha_f \sim \alpha_c$

$\alpha_f \sim 0$

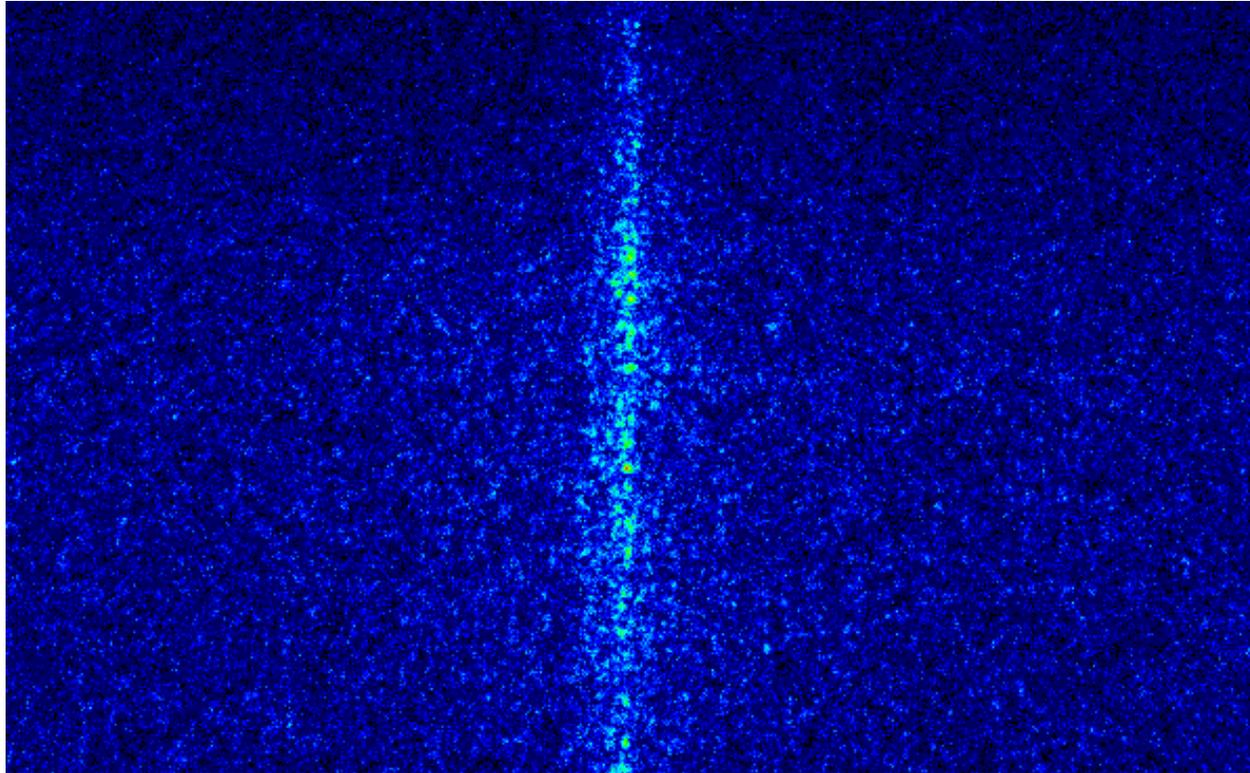


# Competitive Grain Growth

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



# Angle series, $0.01^\circ$ steps

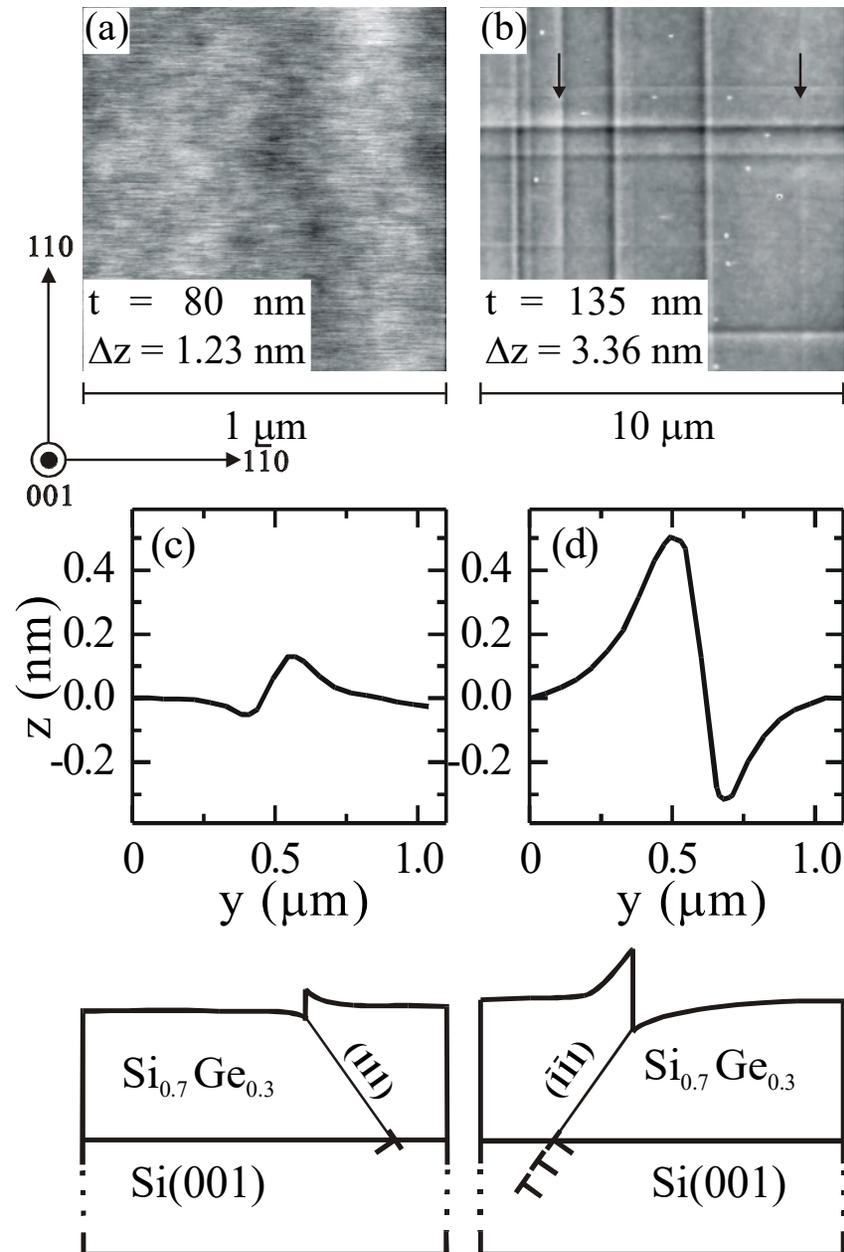


Low dislocation density GeSi films

Thickness close to critical thickness

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

T. Spila, UIUC Thesis

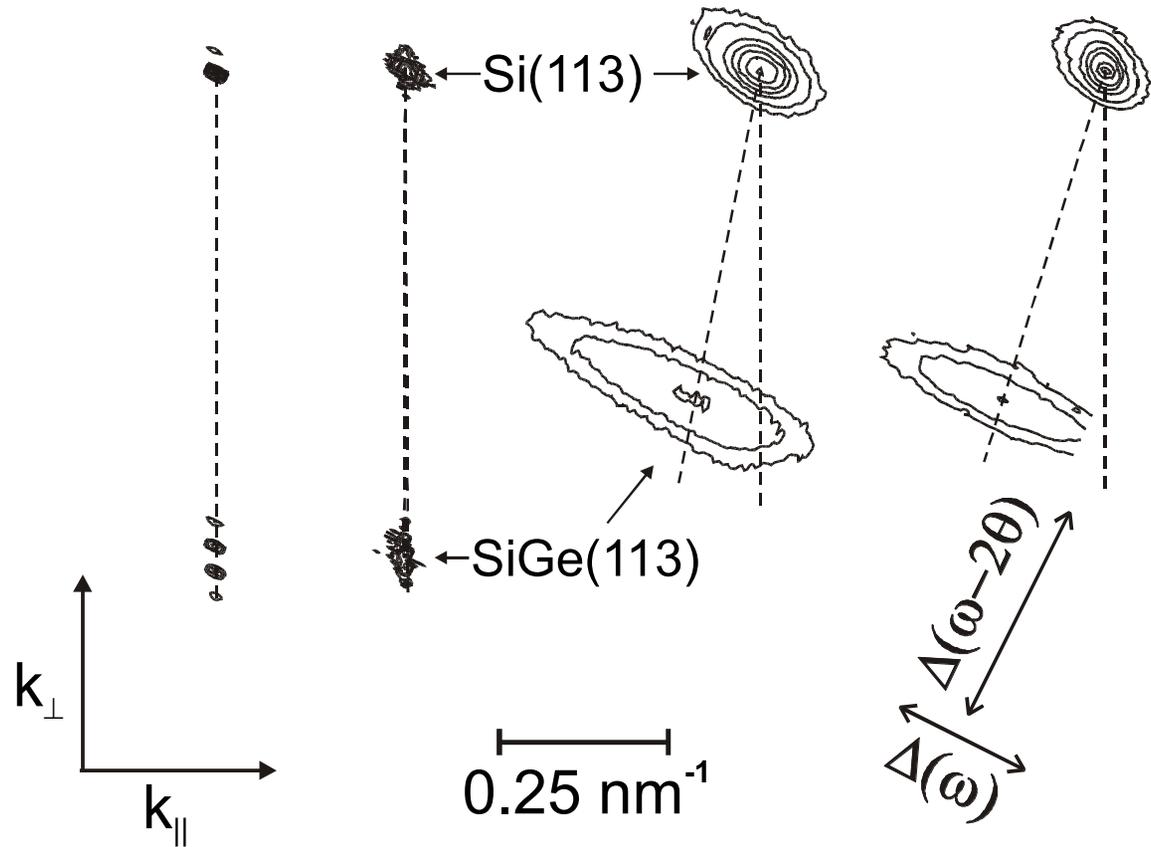


# $\text{Si}_{0.7}\text{Ge}_{0.3}/\text{Si}(001)$

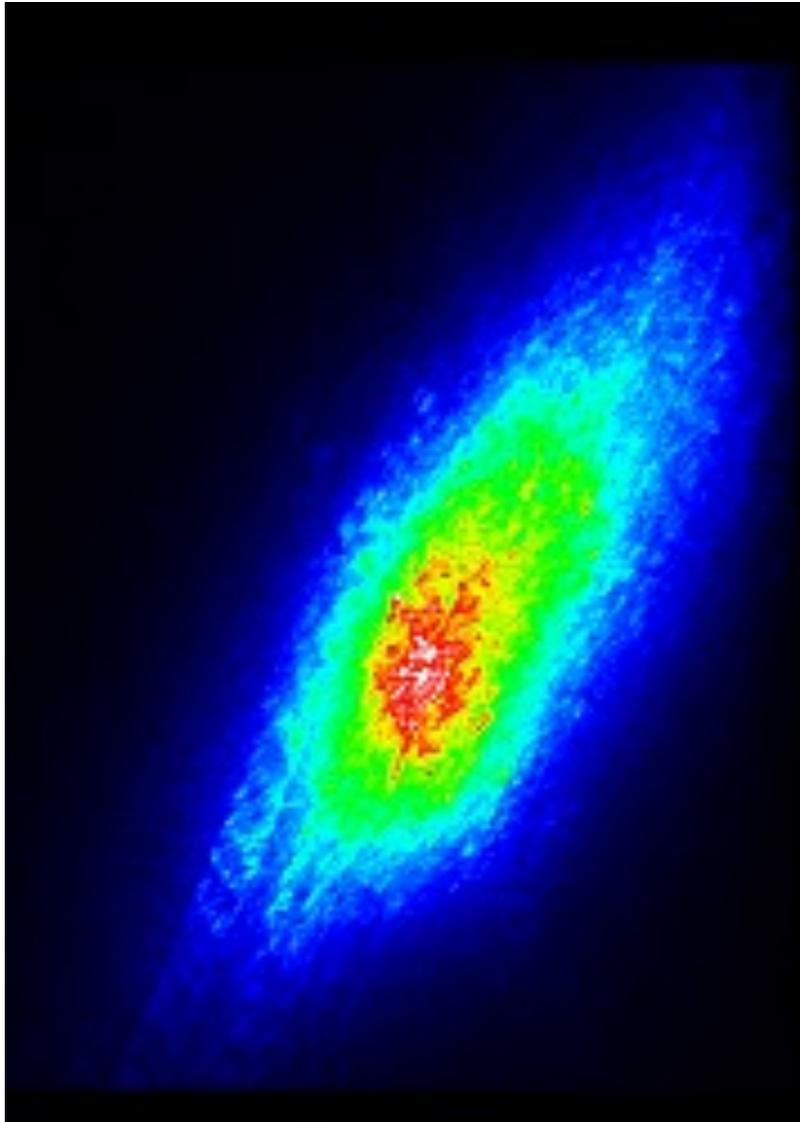
$T_s = 450\text{ }^\circ\text{C}$

$t =$  80      135      350      440 nm

$R =$  0      1      51      78 %

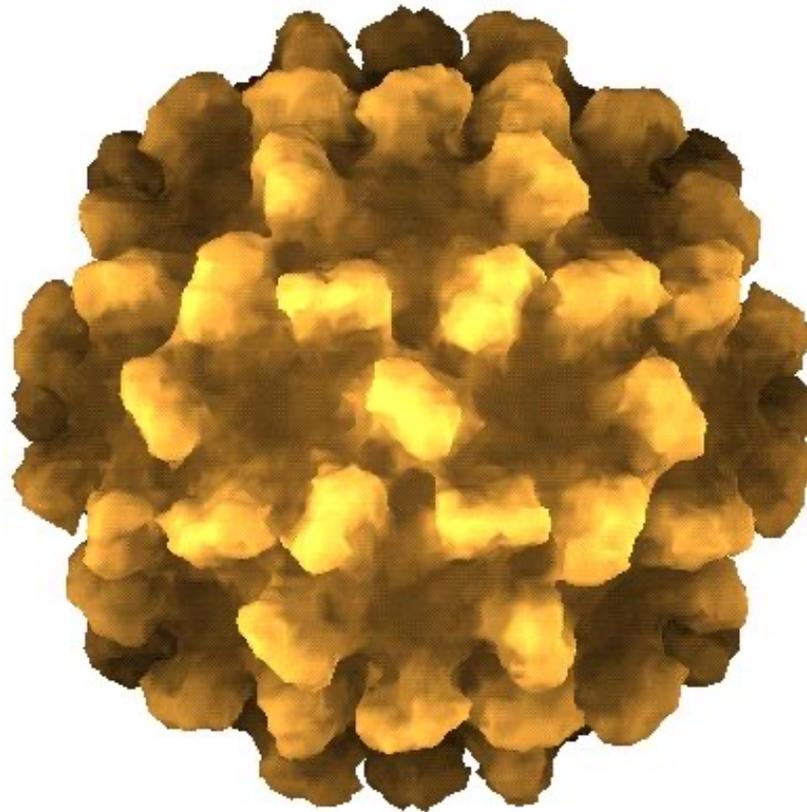


# $\text{Ge}_x\text{Si}_{1-x}$ Film Diffraction



- 202 Bragg Peak
- 2800Å film
- 2° incidence angle
- 8.5 keV
- 20 $\mu\text{m}$   $\times$  40 $\mu\text{m}$  beam  
onto KB mirror
- 1 $\mu\text{m}$   $\times$  1 $\mu\text{m}$  focus
- 0.5 $\mu\text{m}$  sample steps
- APS 34-ID-C

# Tomato Bushy Stunt Virus 1980



# Conclusions and Outlook

- Inversion of CXD demonstrated
- Internal structure of Au Nanocrystals
- Preservation of coherence upon focussing
- Single dislocations possible now
- Single molecules one day with XFELs