# Phasing of Coherent X-ray Diffraction from Nanocrystals


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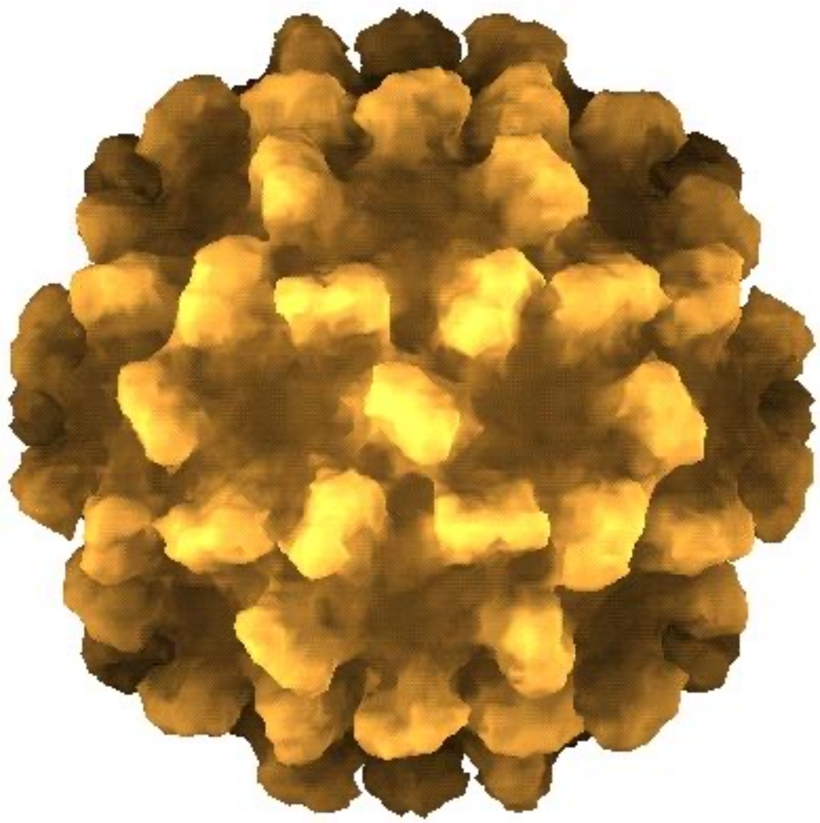
Condensed Matter Seminar
University of Illinois

# Outline

- Coherence in Diffraction
- The Phase Problem
- Coherent Diffraction from Surfaces
- Nanocrystal Shapes
- Crystallization of Proteins
- Future Applications

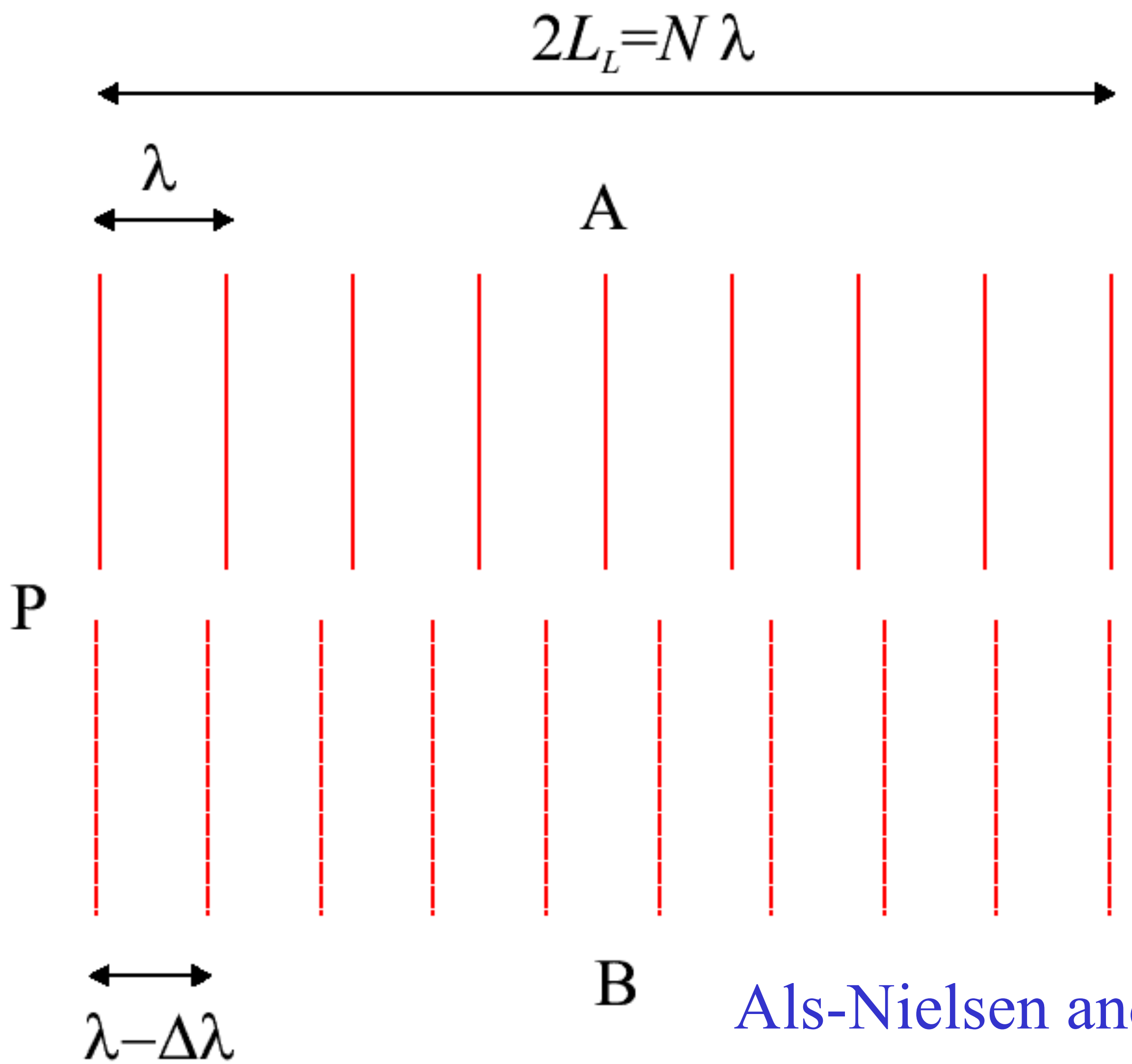
# Tomato Bushy Stunt Virus
# 1980



# 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

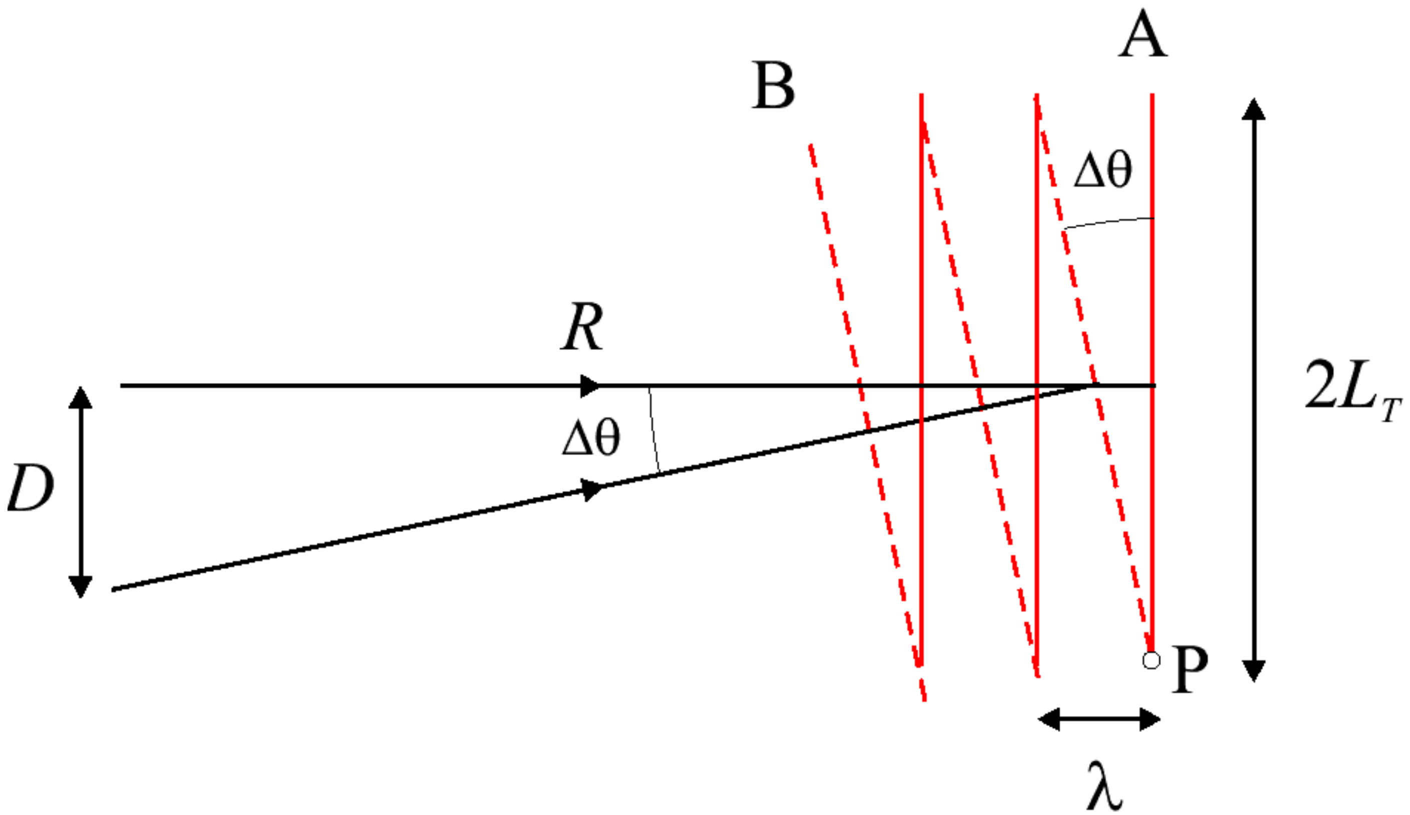
# Longitudinal Coherence




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

Als-Nielsen and McMorrow (2001)

# Lateral (Transverse) Coherence




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

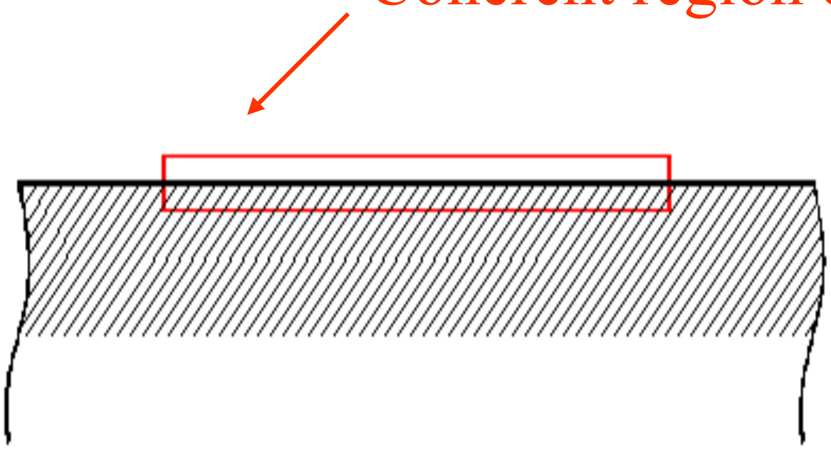
Als-Nielsen and McMorrow (2001)

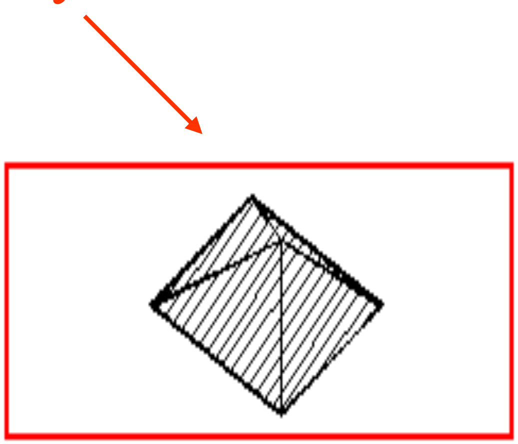
# Coherence at the APS

## Typical 3rd Generation (undulator) Synchrotron Source

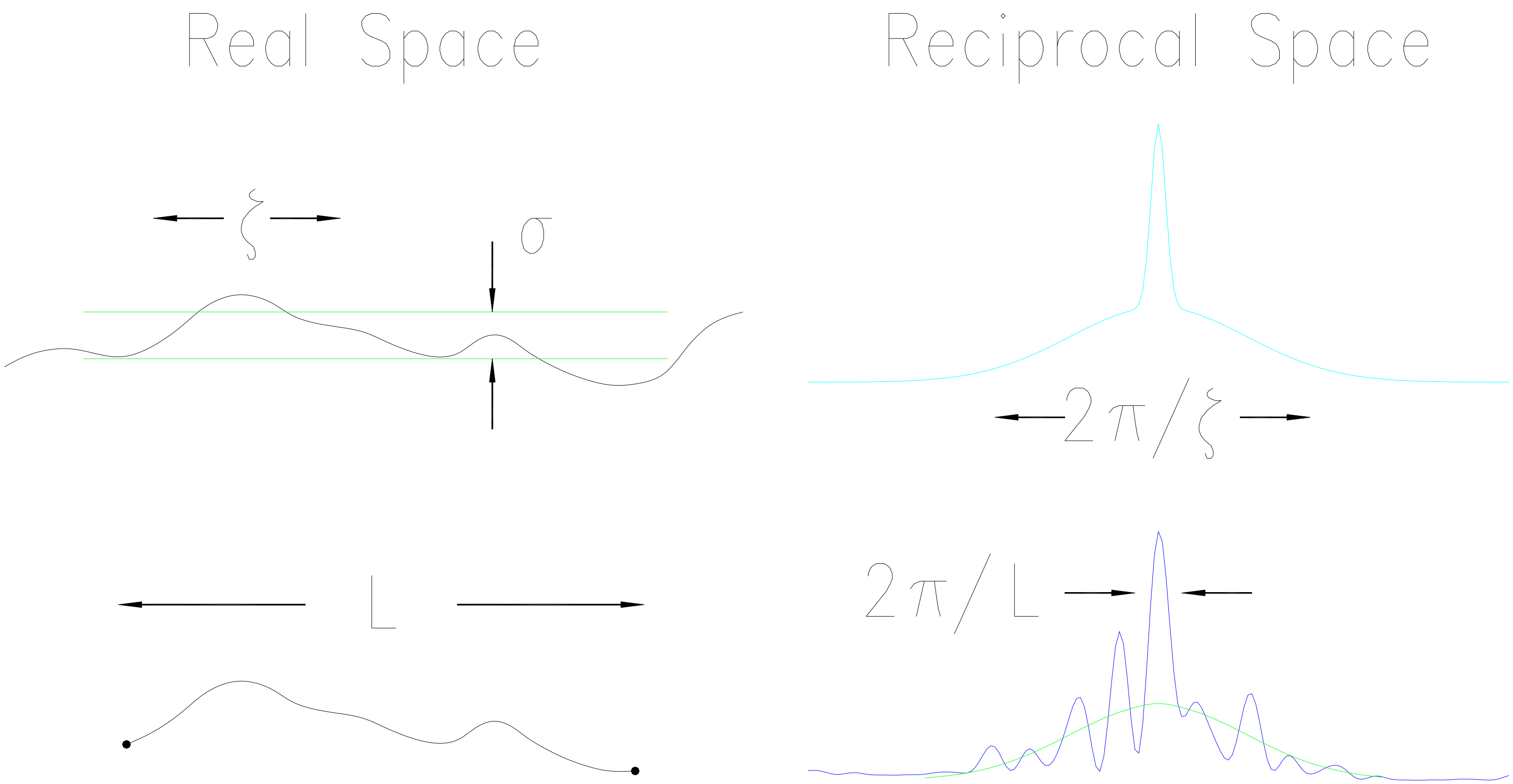
| Coherence of | $\xi_{VER}$ | $\xi_{HORIZ}$ | $\xi_{LONG}$ | Flux |
|---|---|---|---|---|
| Raw Undulator | 35μm | 9μm | 0.004μm | $2\times10^{12}$ |
| Si(111) Monochromator | 35μm | 9μm | 1μm | $1\times10^{10}$ |
| C(111) Monochromator | 35μm | 9μm | 3μm | $3\times10^{9}$ |

Coherent region defined by slits





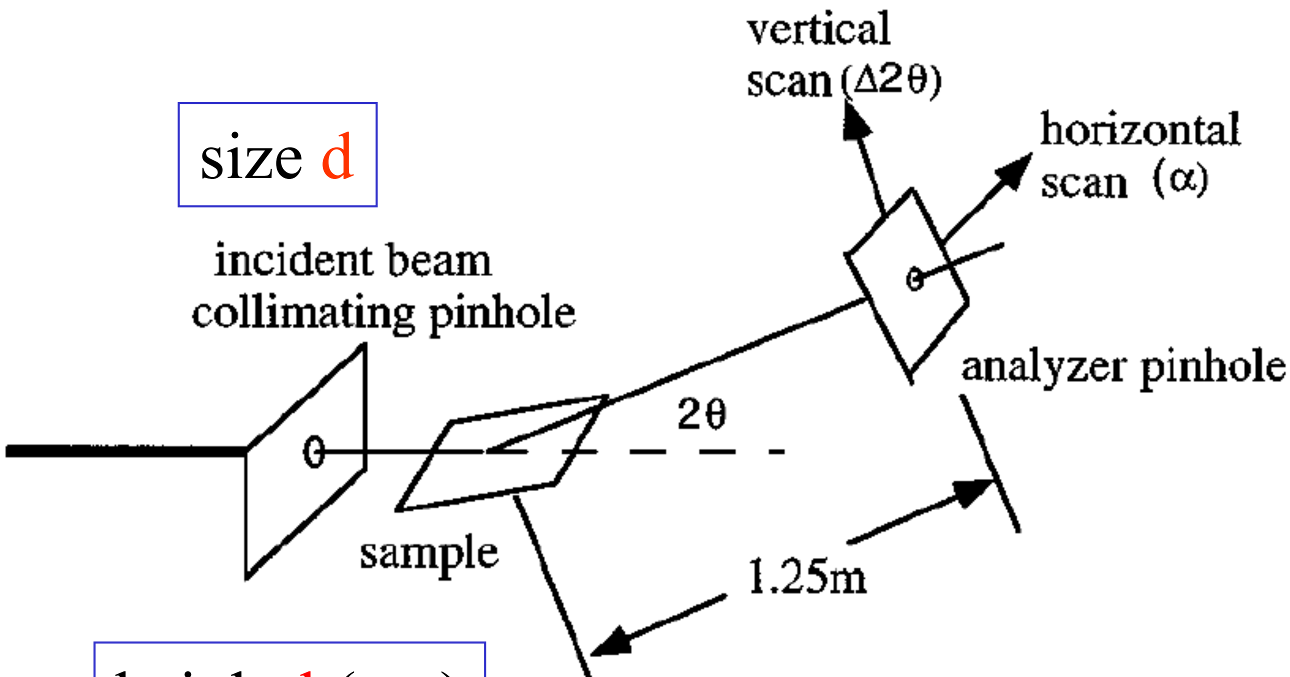
# Diffuse Scattering acquires Structure using CXD



# Surface Coherent X-ray Diffraction

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

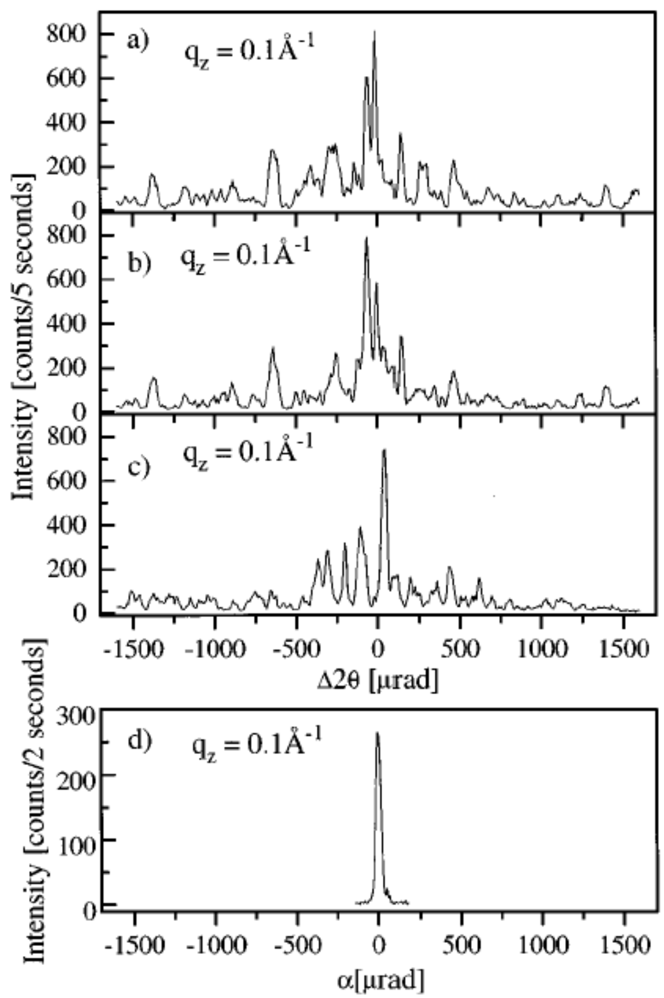
size d

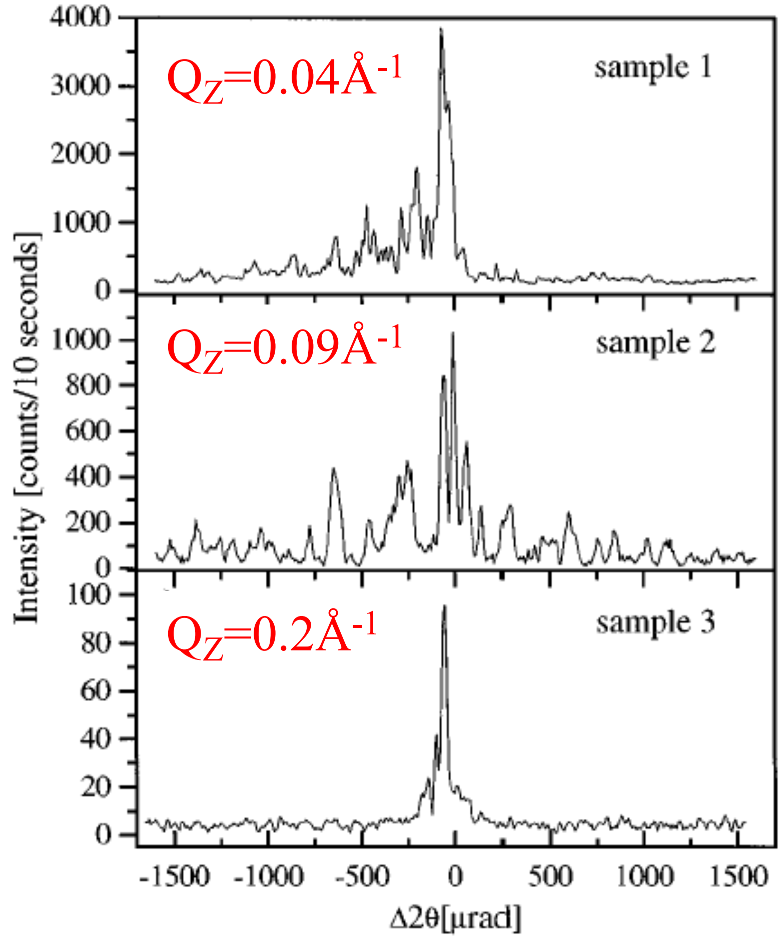



height h(x,y)

# Si Samples of Different Roughness

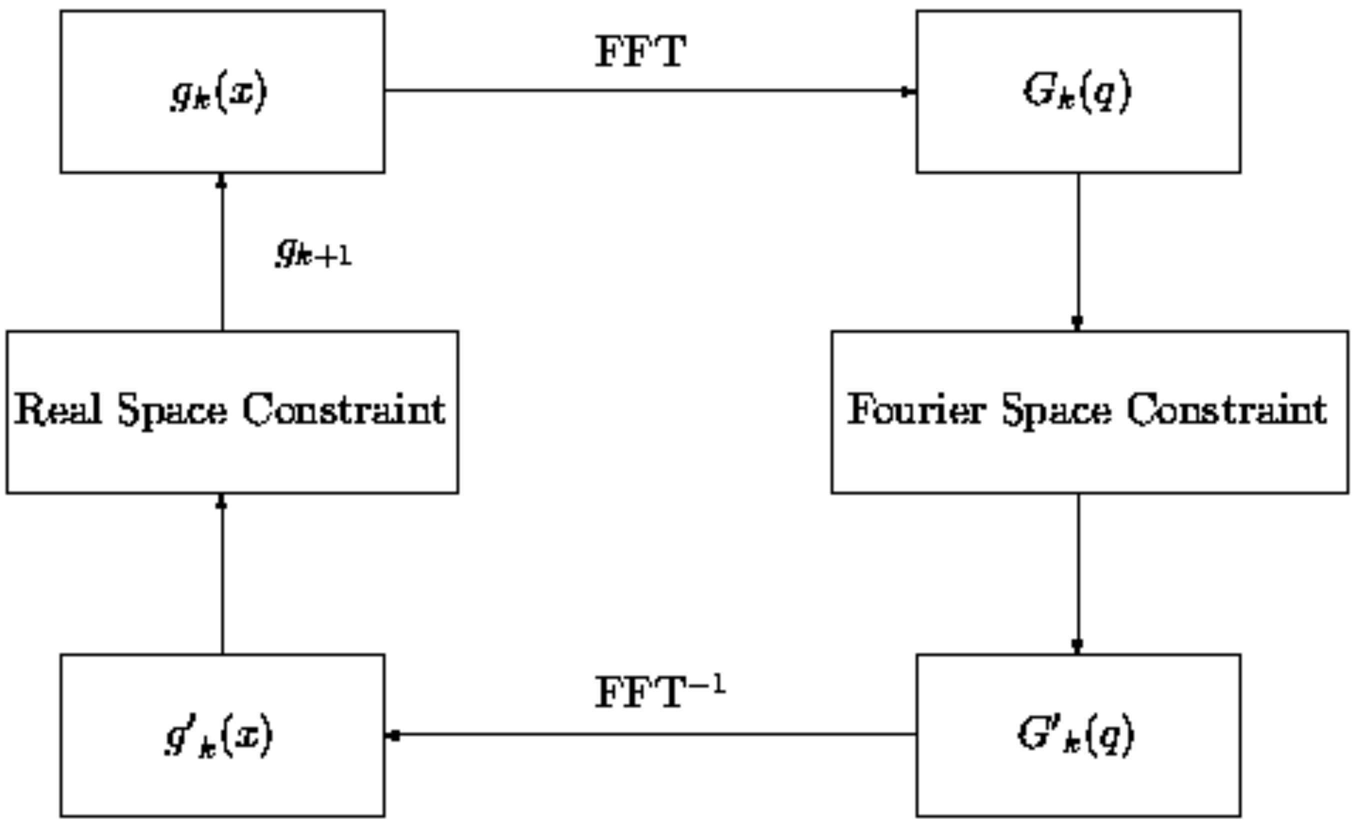
J. L. Libbert *et al* Phys. Rev. B **56** 6454 (1997)



[redacted]

# Generic “Error Reduction” method



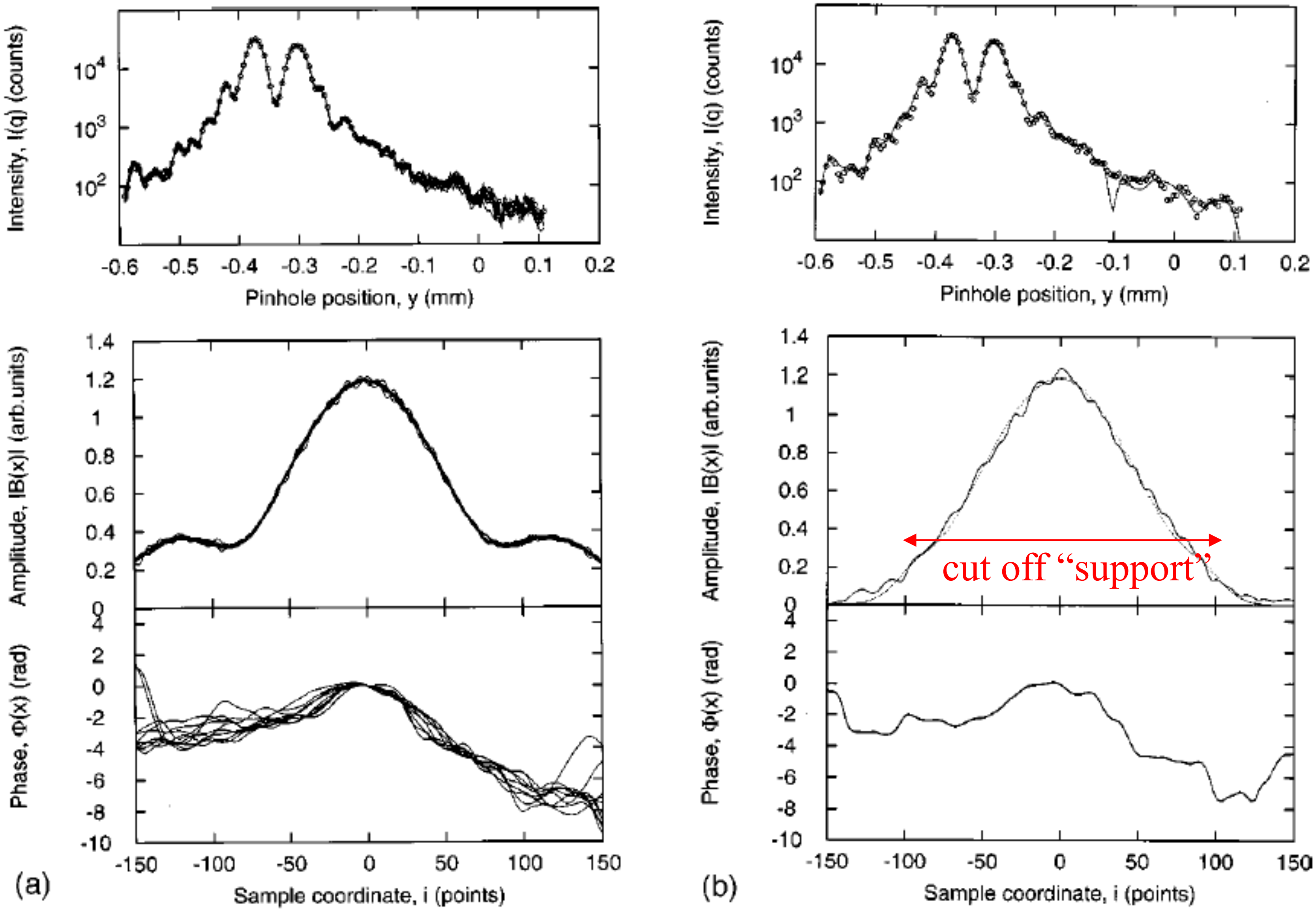

J. R. Fienup Appl. Opt. 21 2758 (1982)
R. W. Gerchberg and W. O. Saxton Optik 35 237 (1972)

# “ER” Methods in Crystallograhy

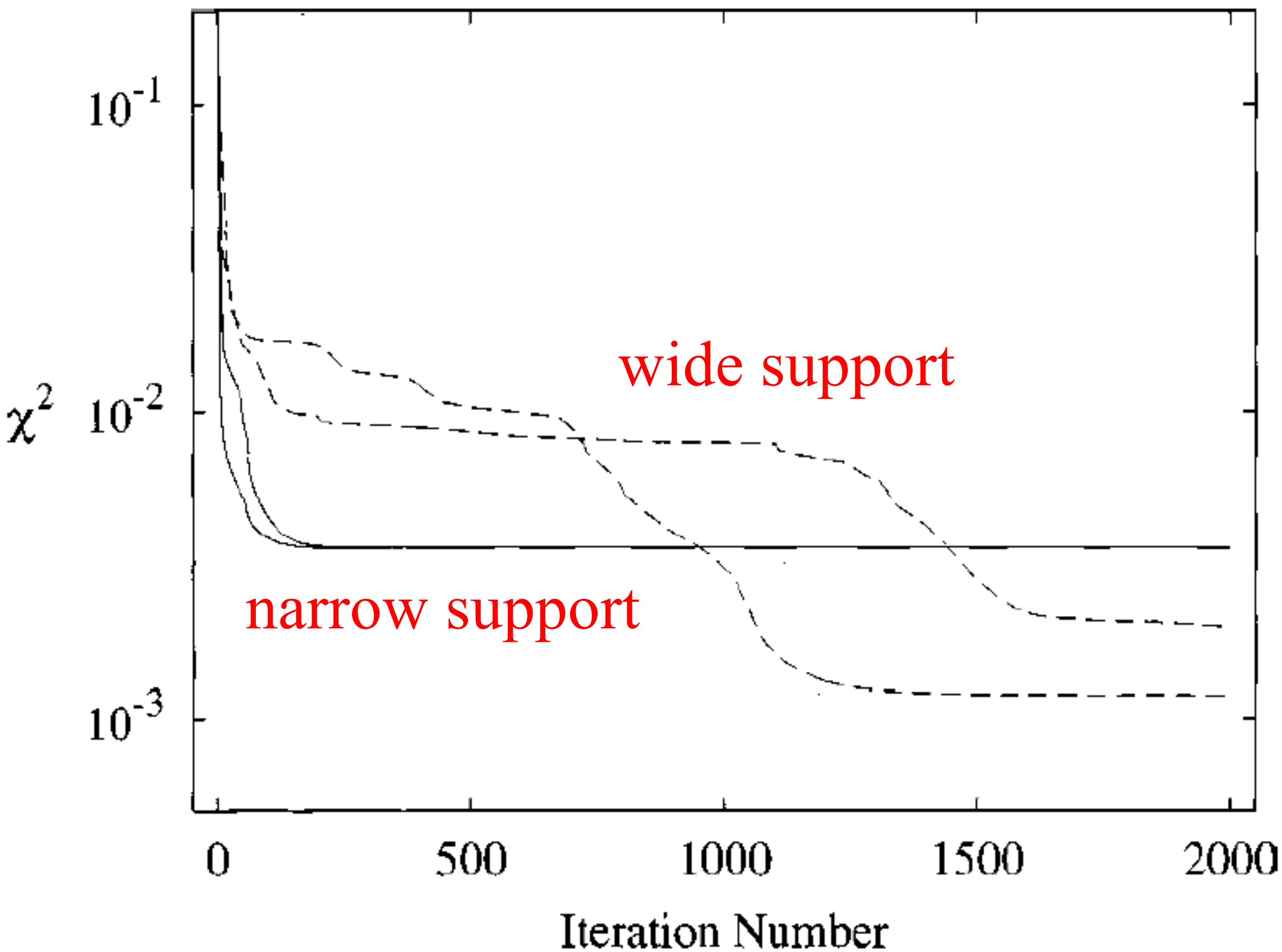
R. P. Millane, J. Opt. Soc Am. A **13** 725 (1996)

- ‘Positivity’ and ‘Atomicity’ constraints
- Finite support, molecular envelope
- Solvent flattening
- Molecular replacement
- Non-crystallographic symmetry
- Basis of ‘direct methods’ (Sayre, Bricogne)
- Non-uniqueness is ‘pathologically rare’ (d>1)

# Phasing using G-S Algorithm



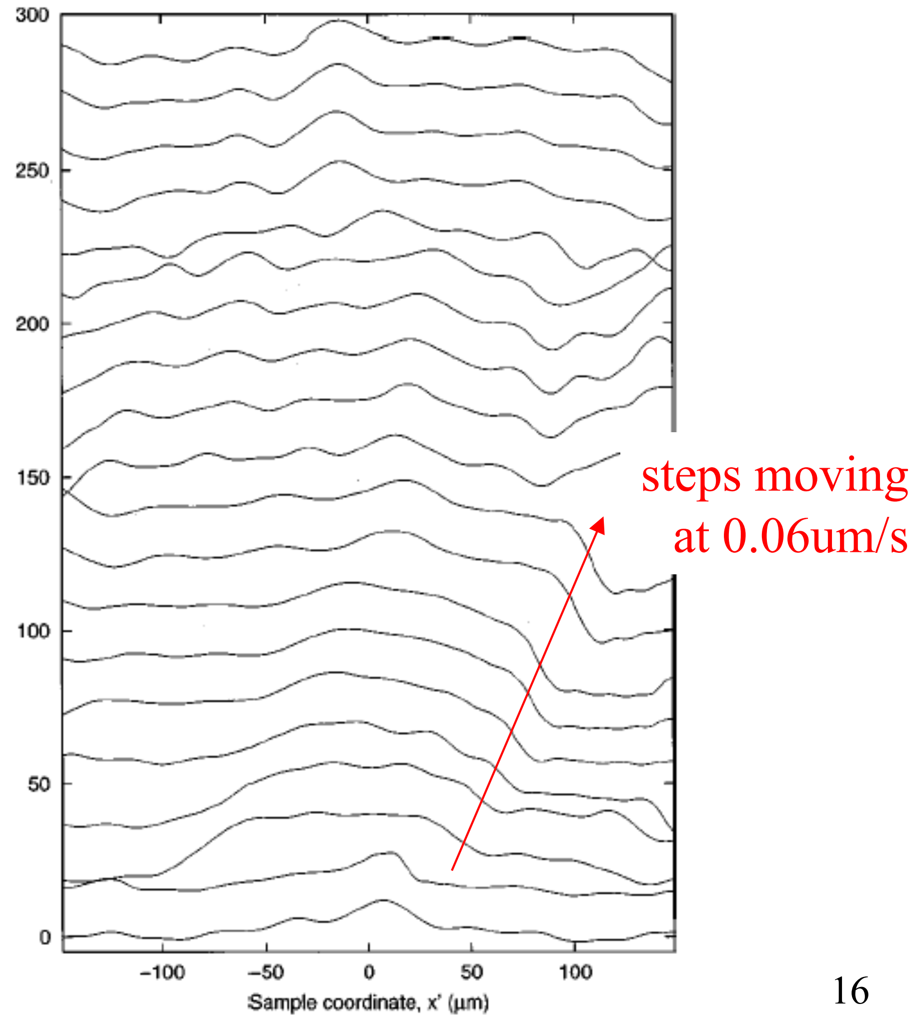
# Convergence Trajectory



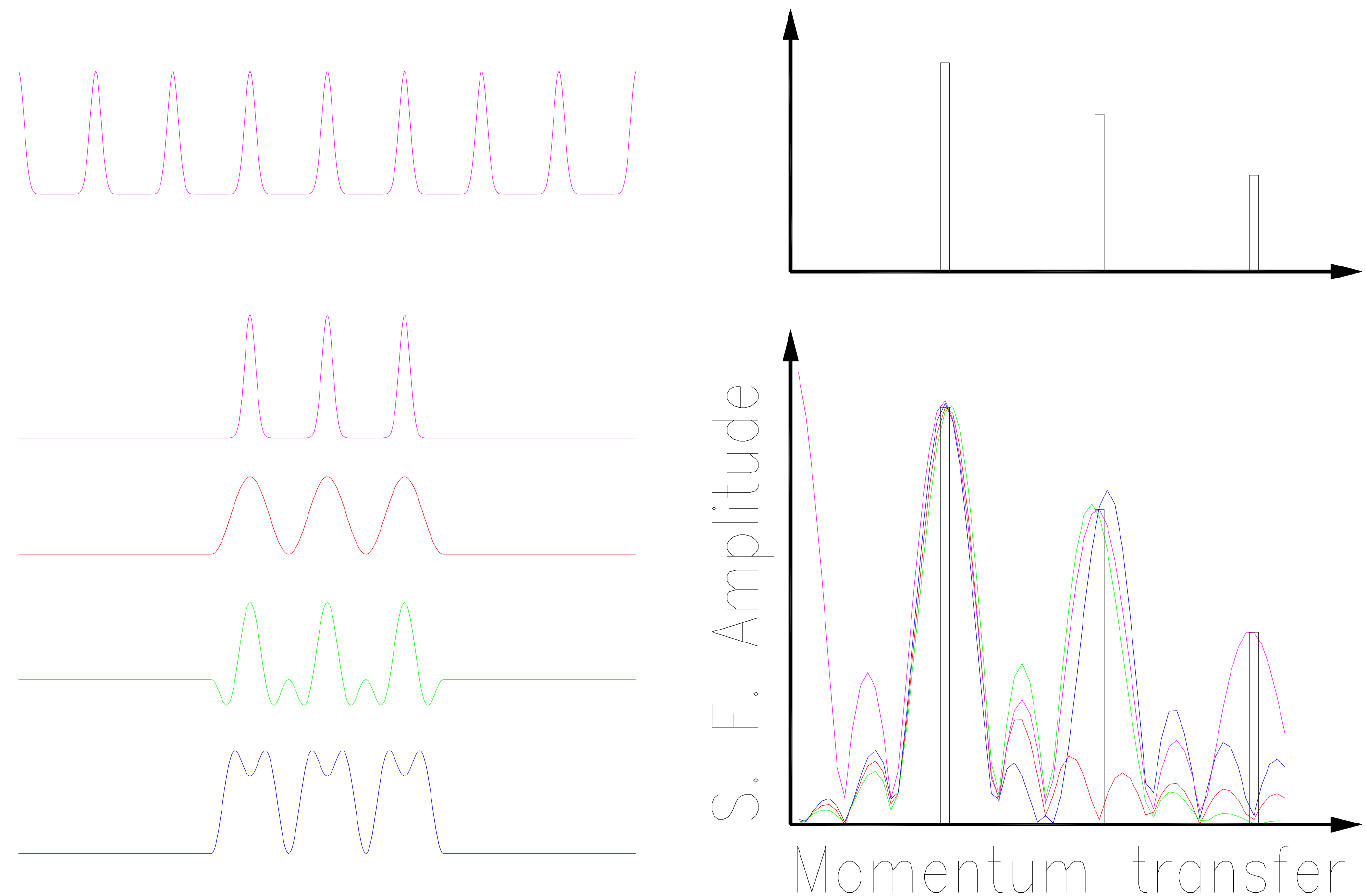
# *In-situ* Regrowth of Oxide on Si

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



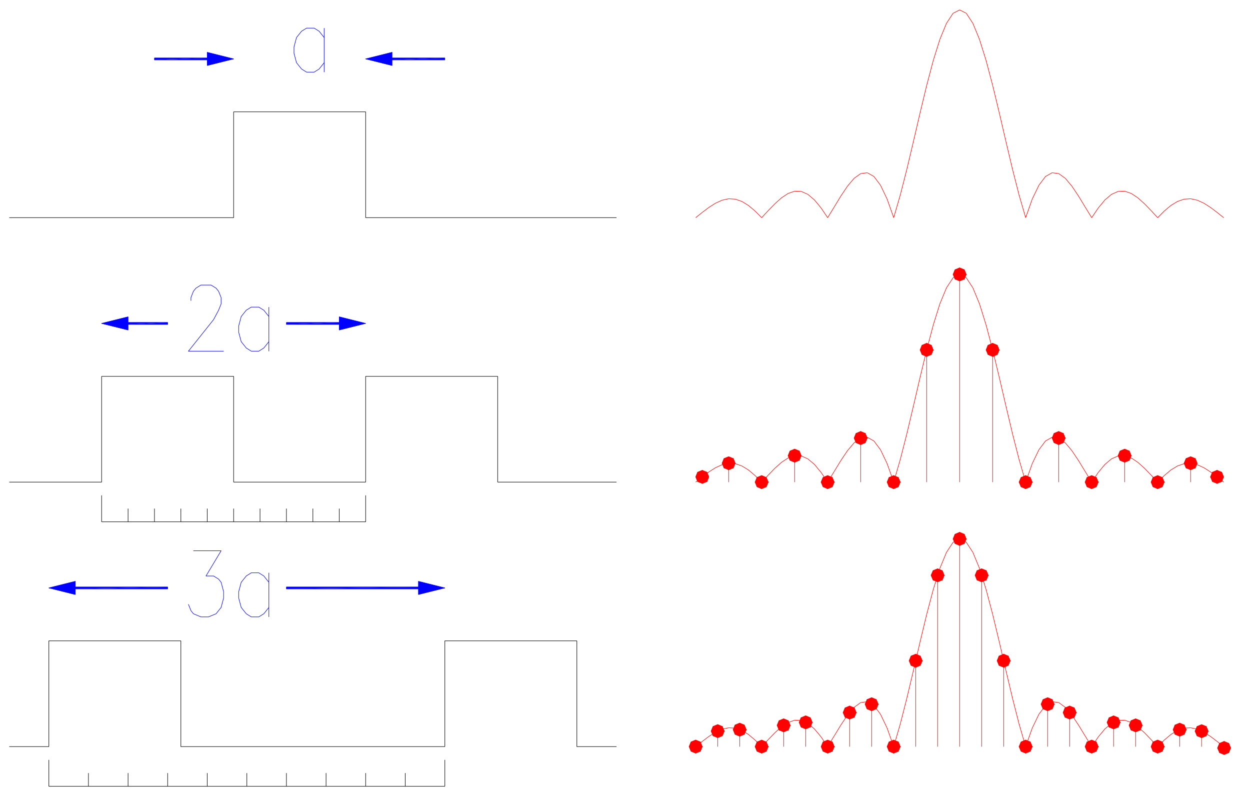
# Phase Problem: Finite-size Effect



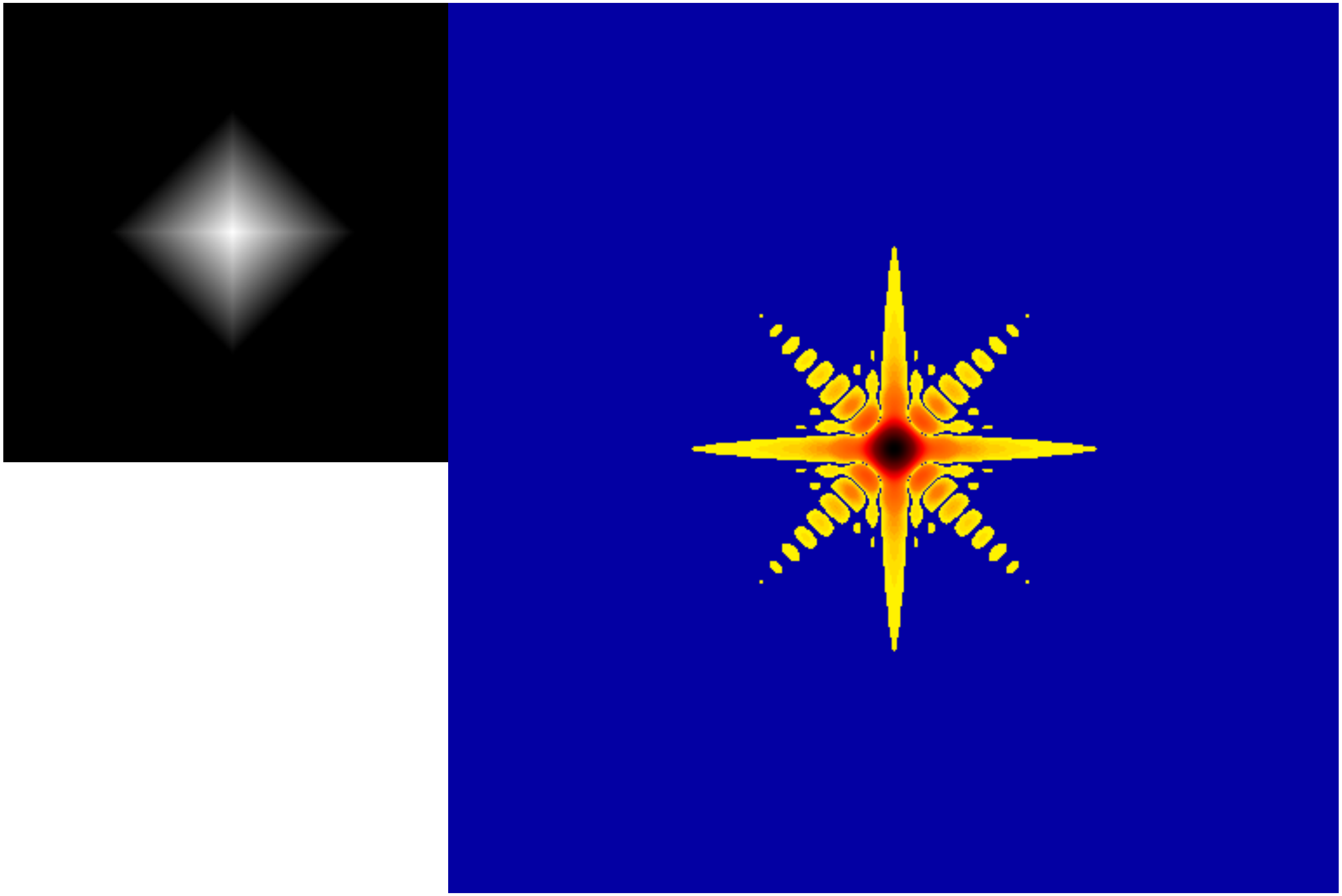
# Oversampling for Small Crystals

N points in 2a:
N/2 unknowns

N points in 3a:
N/3 unknowns




Always N/2 measurements



# Diffraction as a Surface Integral

**Die äußere Form der Kristalle in ihrem Einfluß auf die Interferenzerscheinungen an Raumgittern**

**Von M. v. Laue**

Annalen der Physik [5] 26 55 (1936)

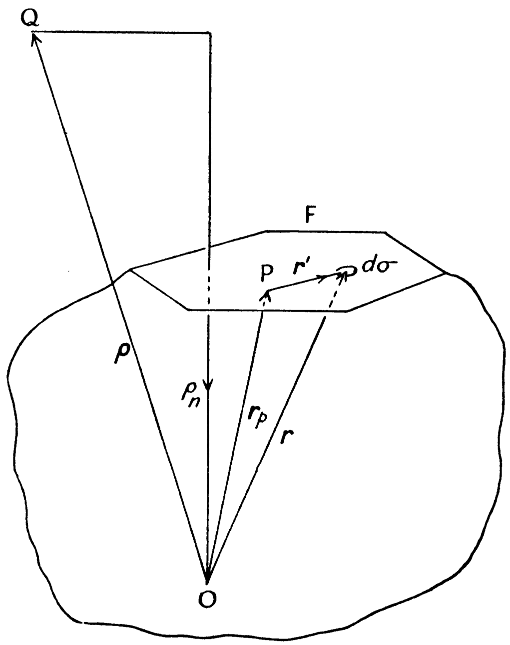
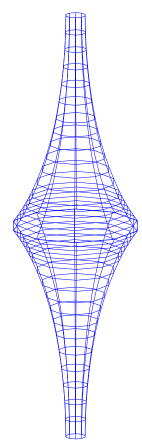
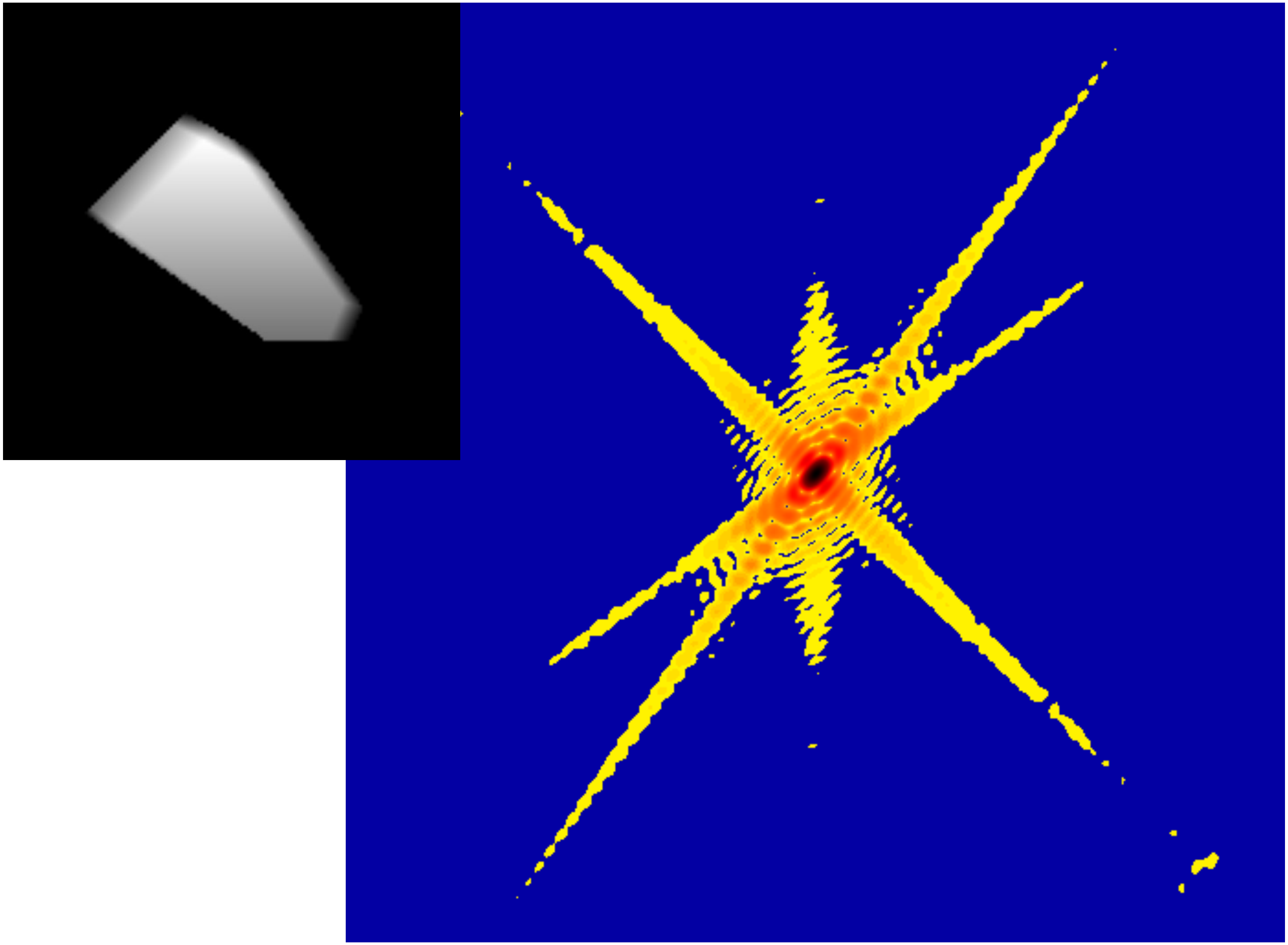



FIG. 200

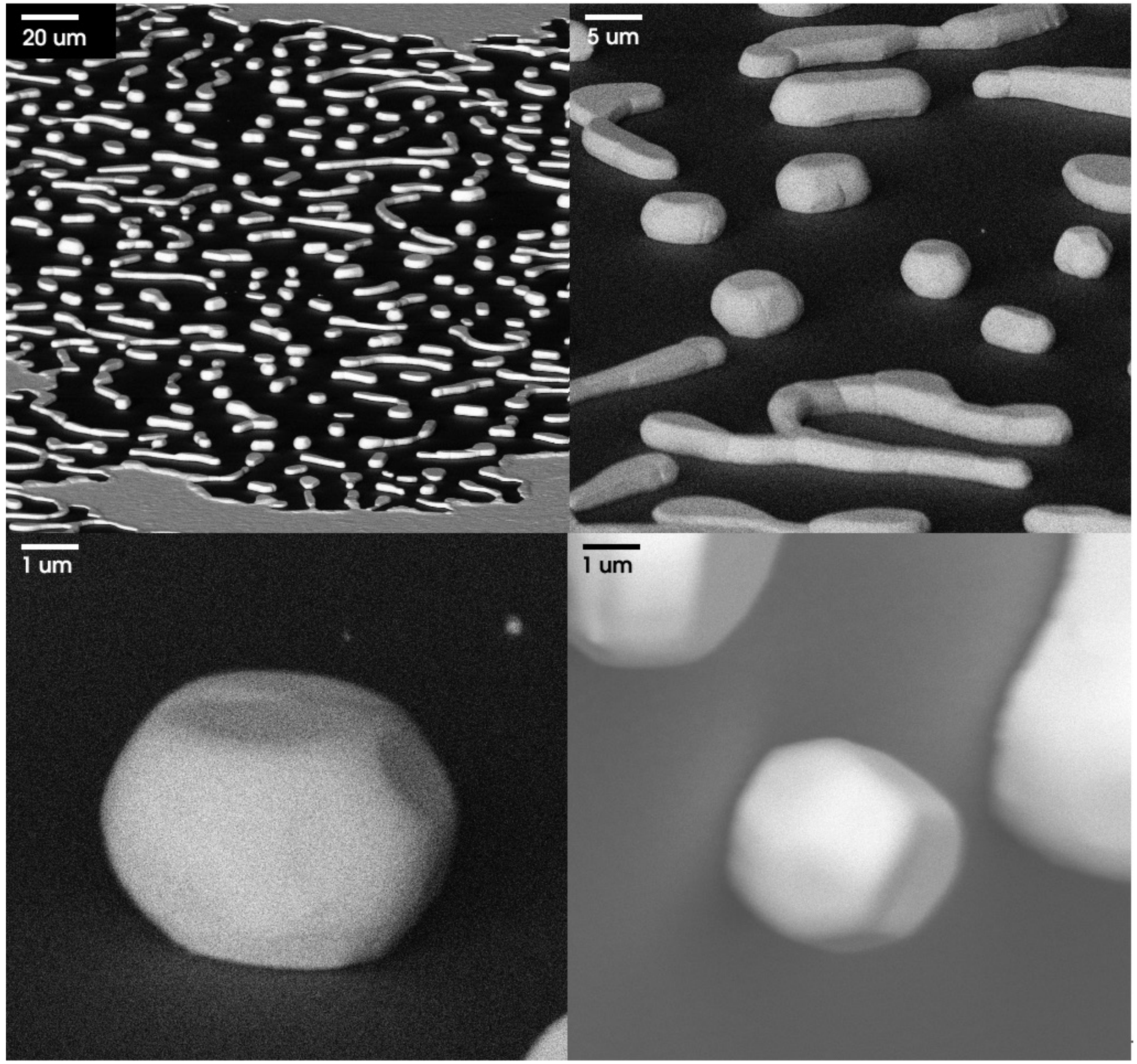


"Stacheln"

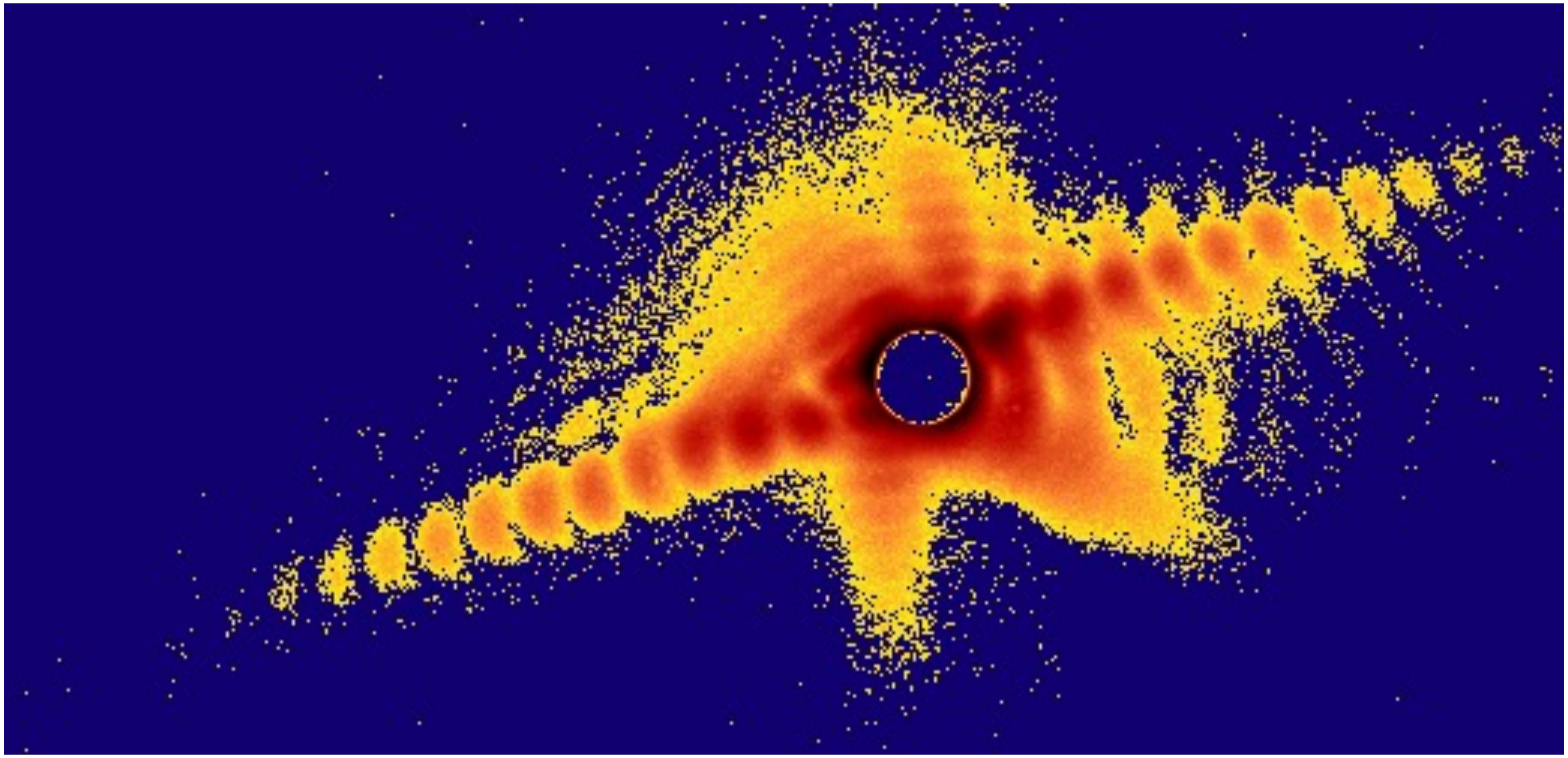


# SEMS

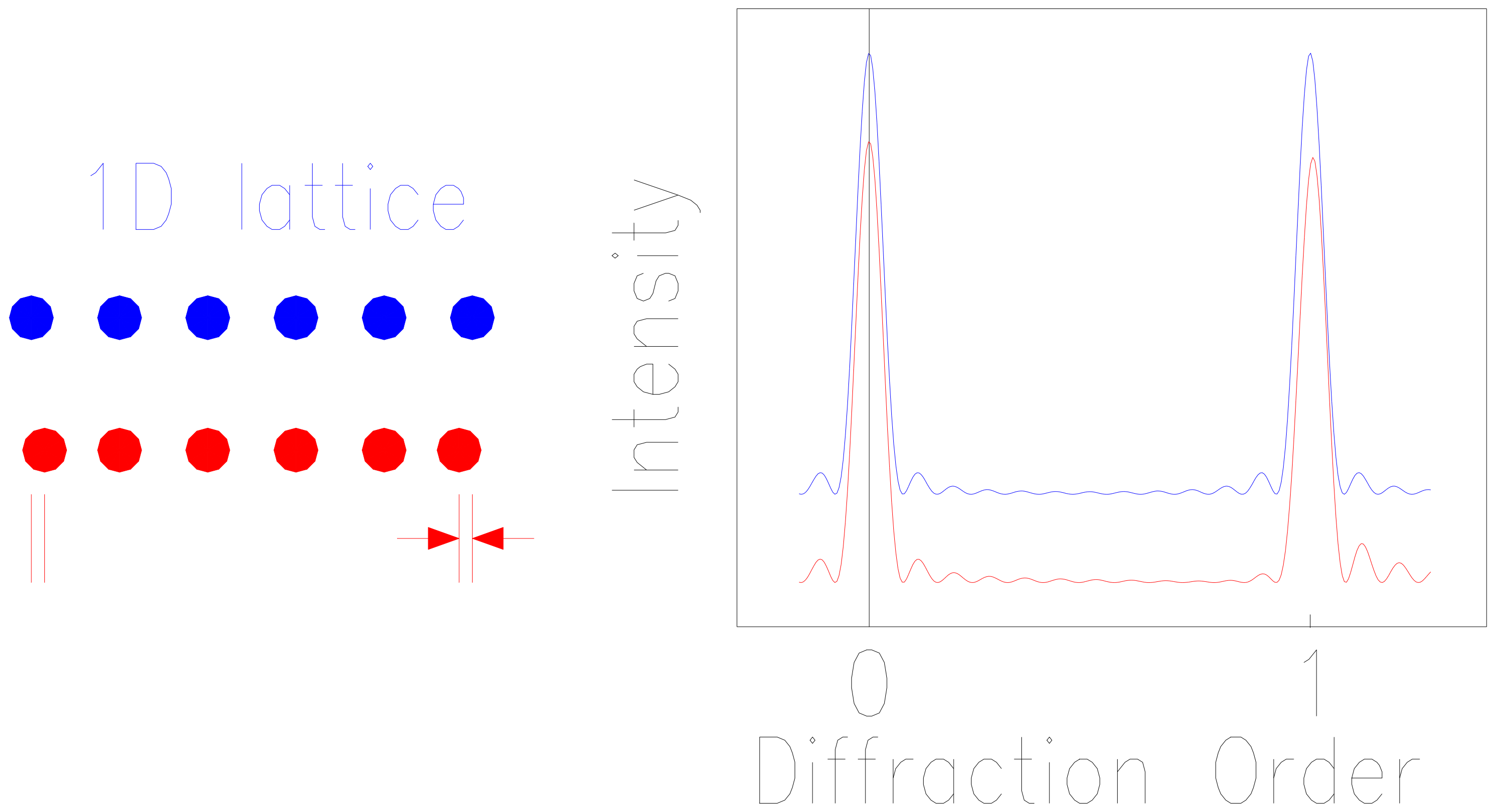
- Au blanket film
- Quartz substrate
- Annealed at 950°C for 70 hrs.

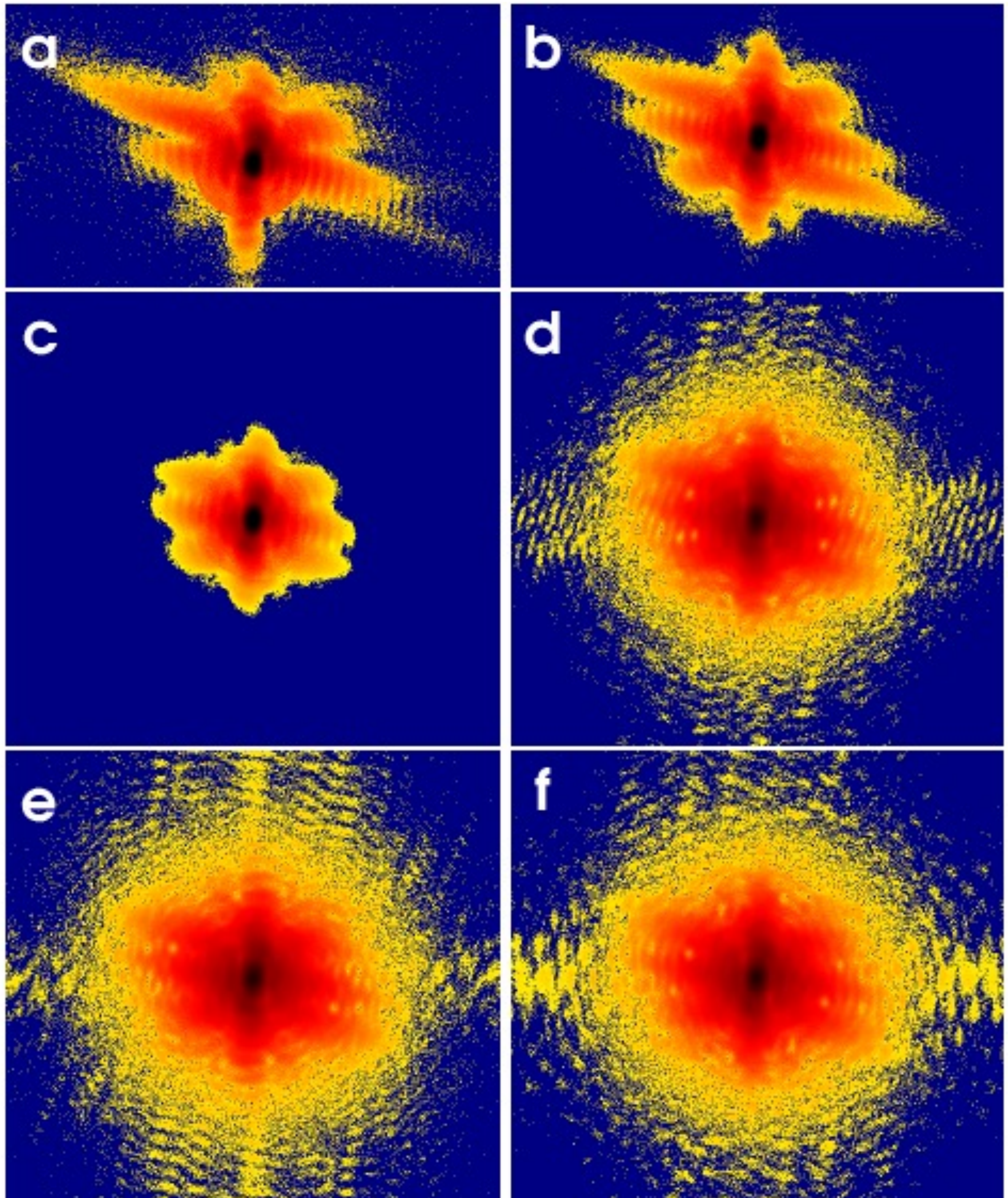


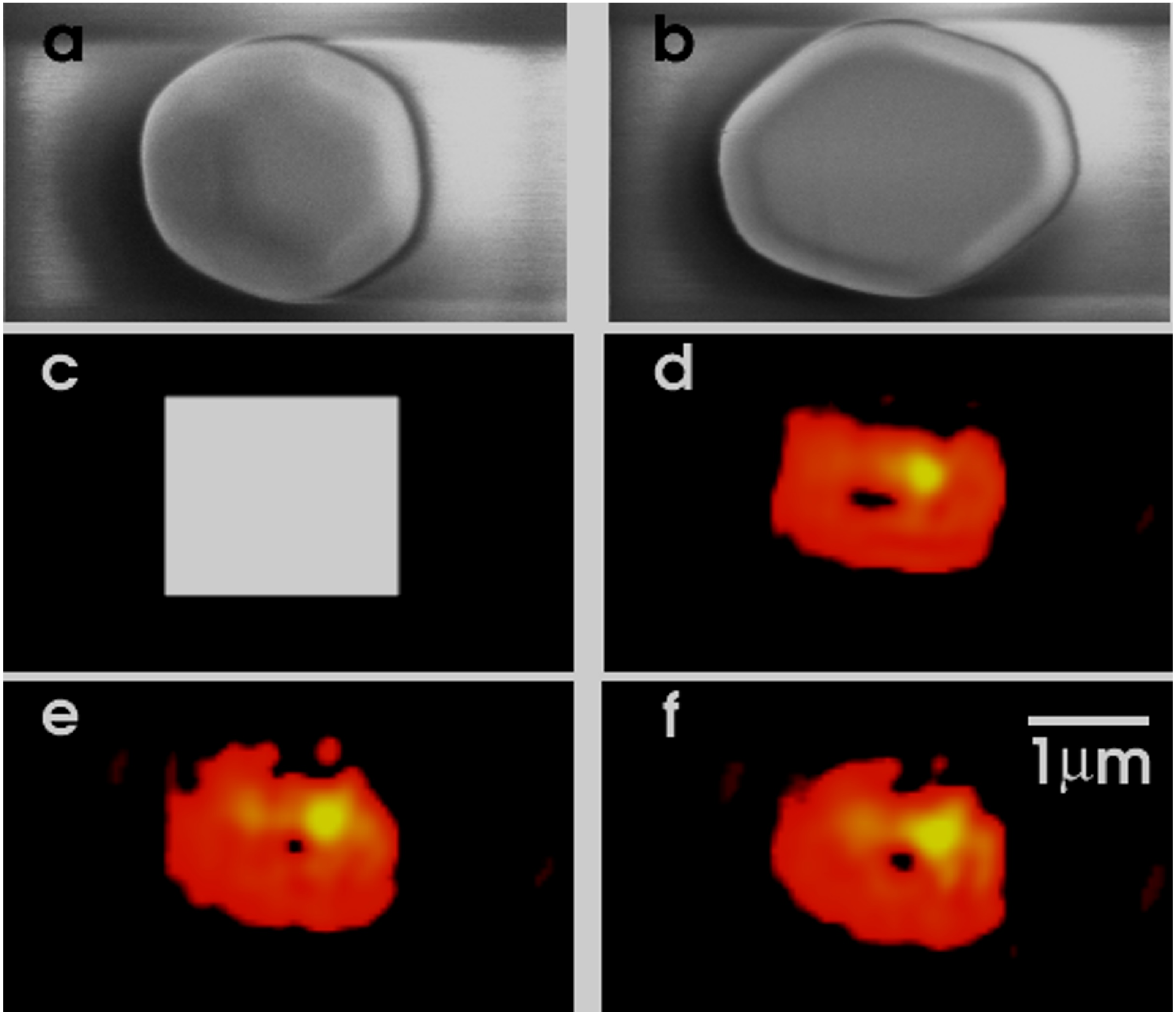
# Micron-sized gold crystal: (111) Bragg reflection



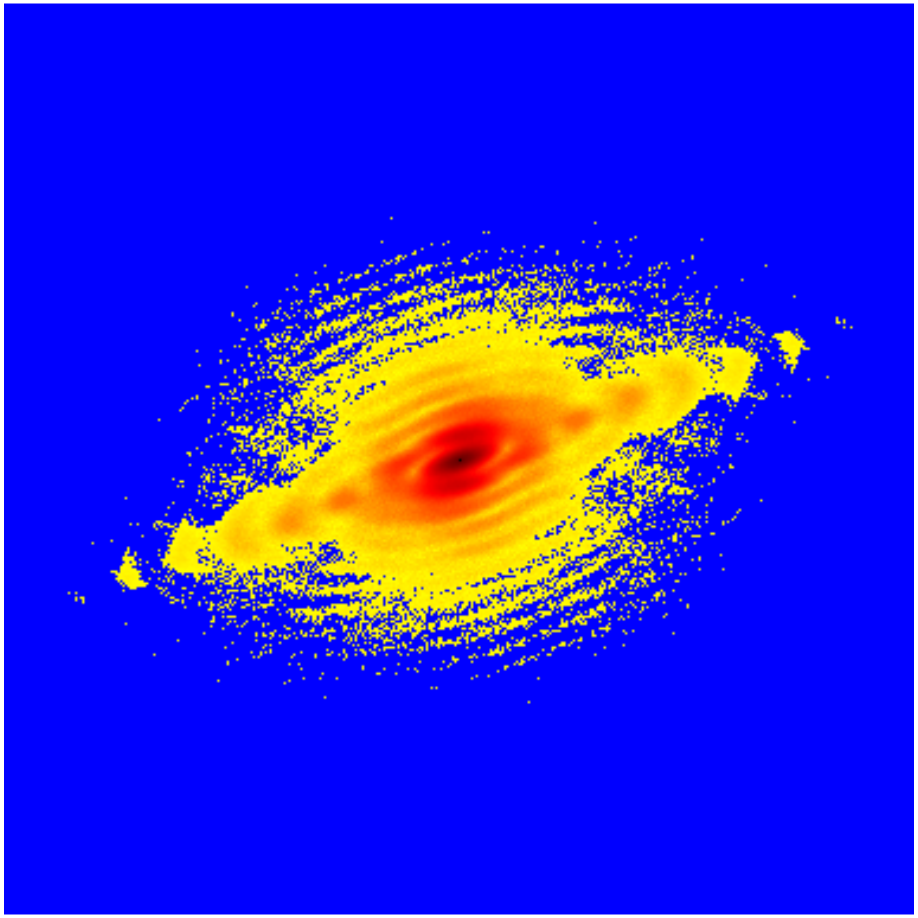
# Imaging of Lattice Strains

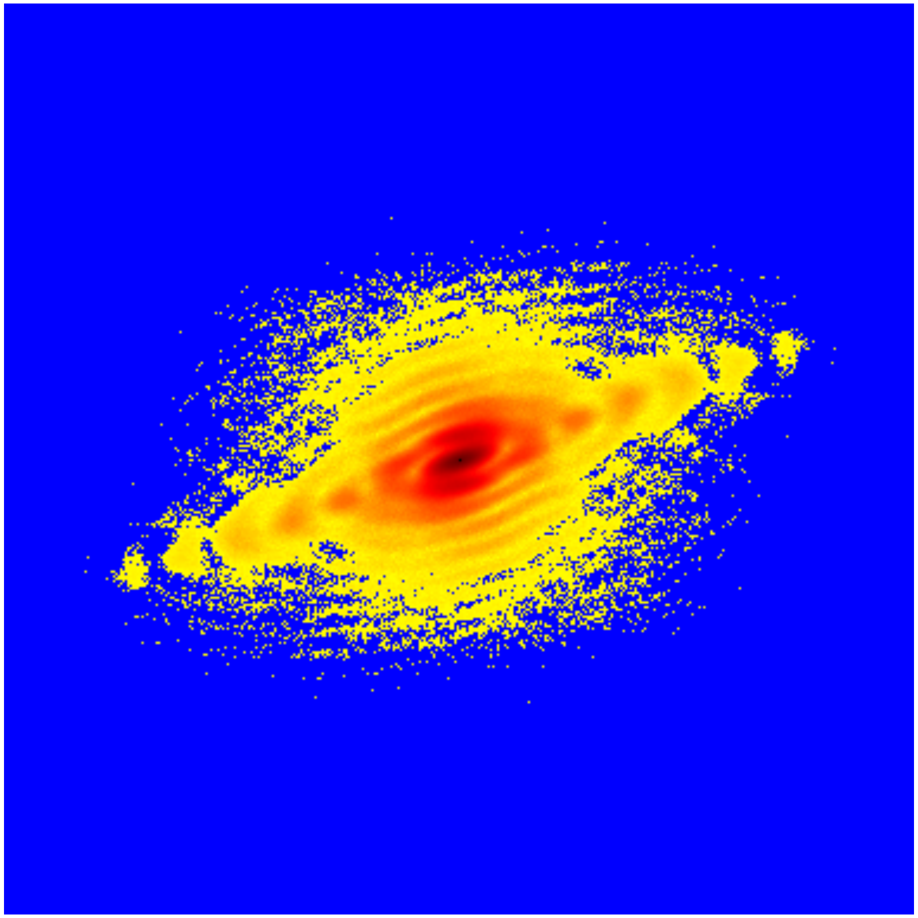



a
b
c
d
e
f

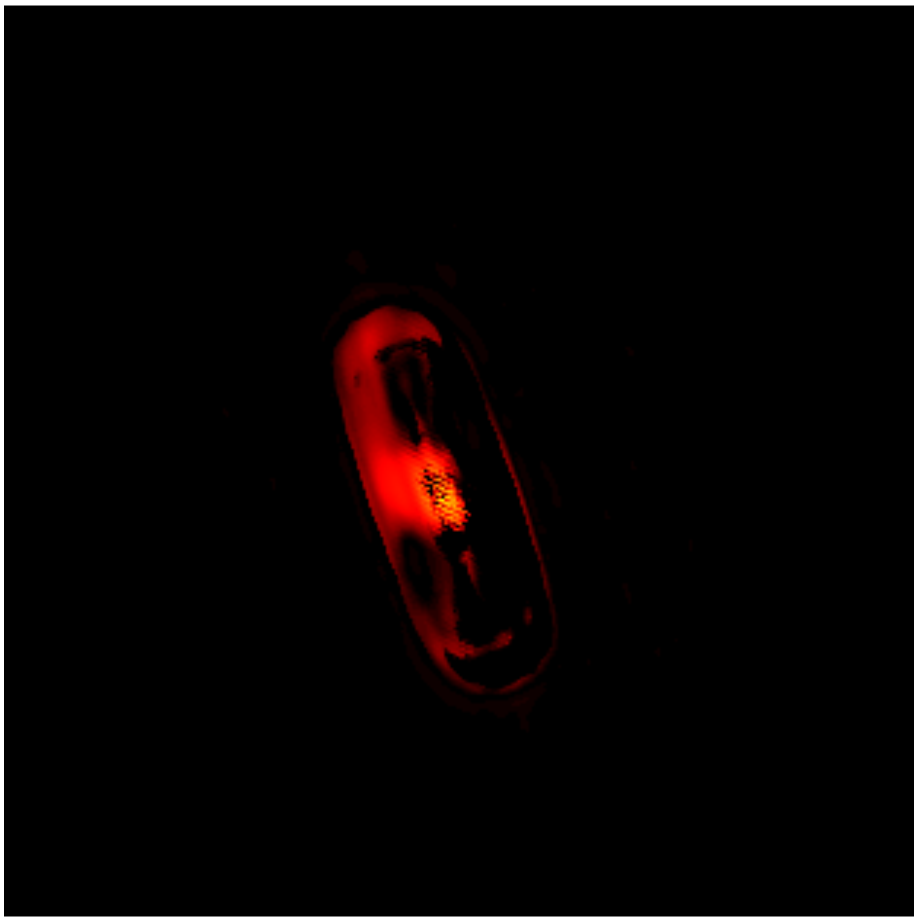

a
b
c
d
e
f
1μm

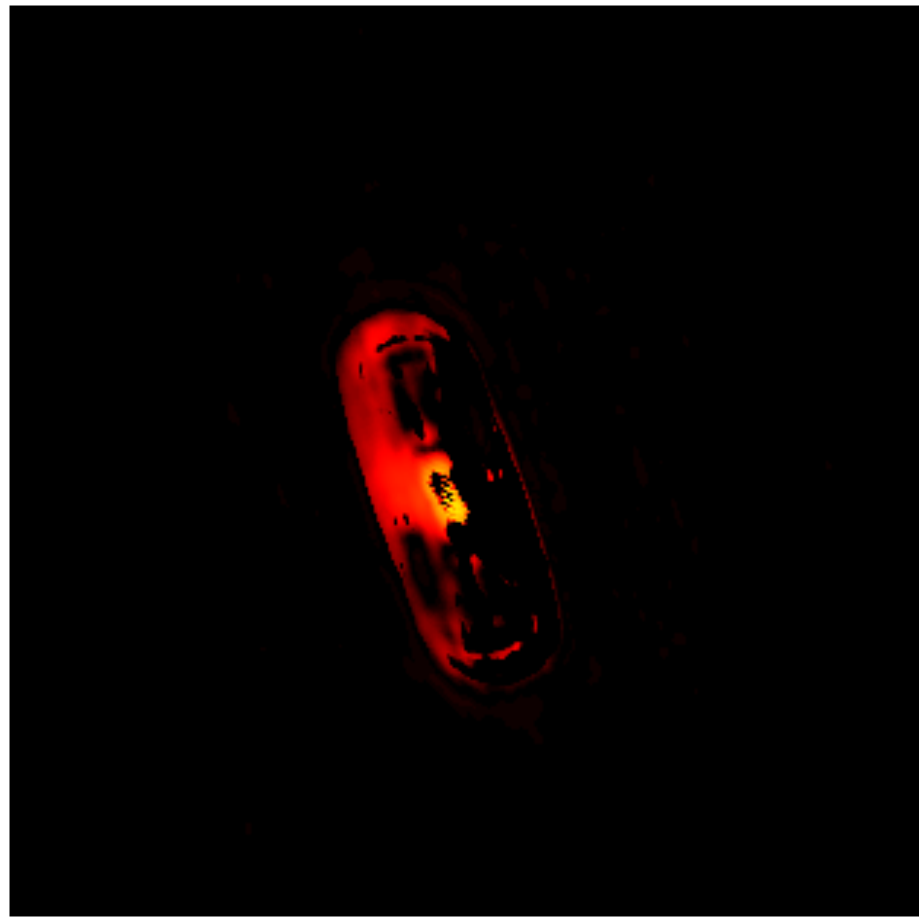
# 2D Diffraction Patterns





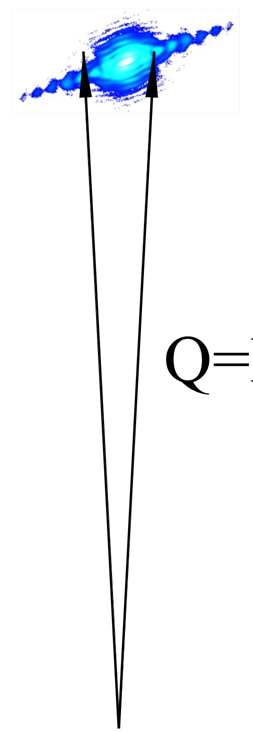
# 2D Reconstructions
## chisquare = 0.0005





# 3D Diffraction Method

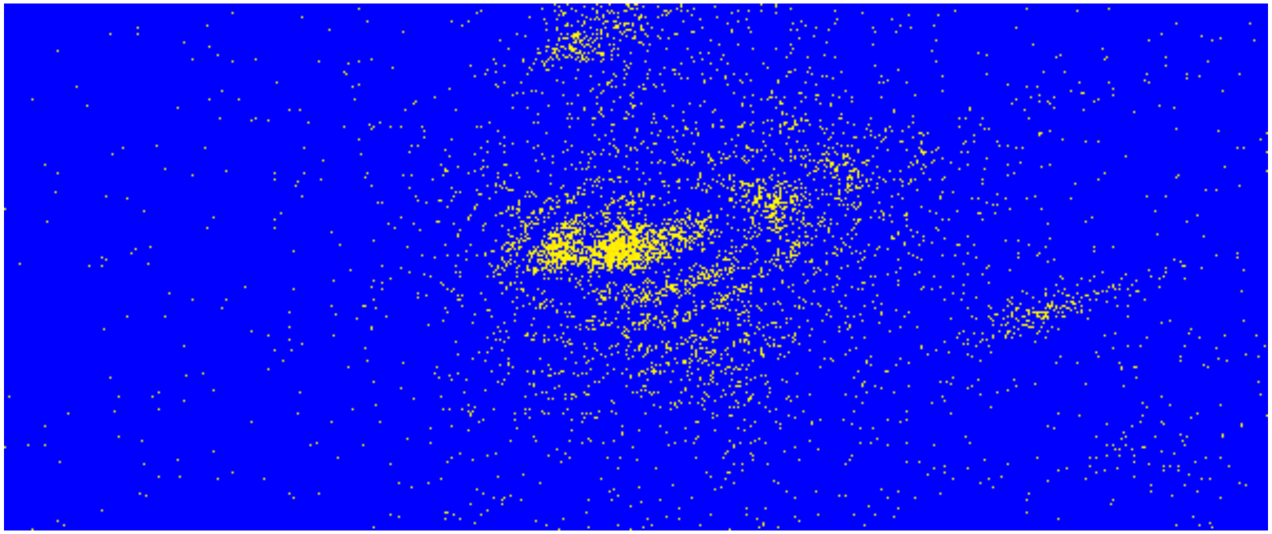
$k_f$



$Q = k_f - k_i$

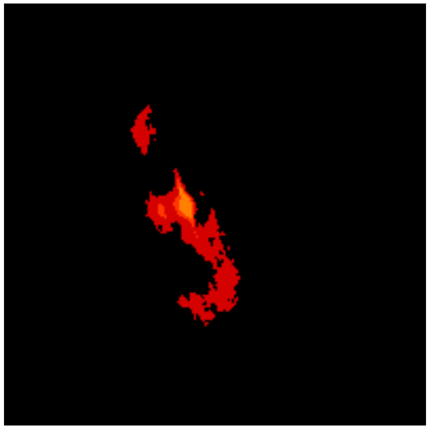
$k_i$

# 3D Diffraction Data
# 1 micron Au crystal

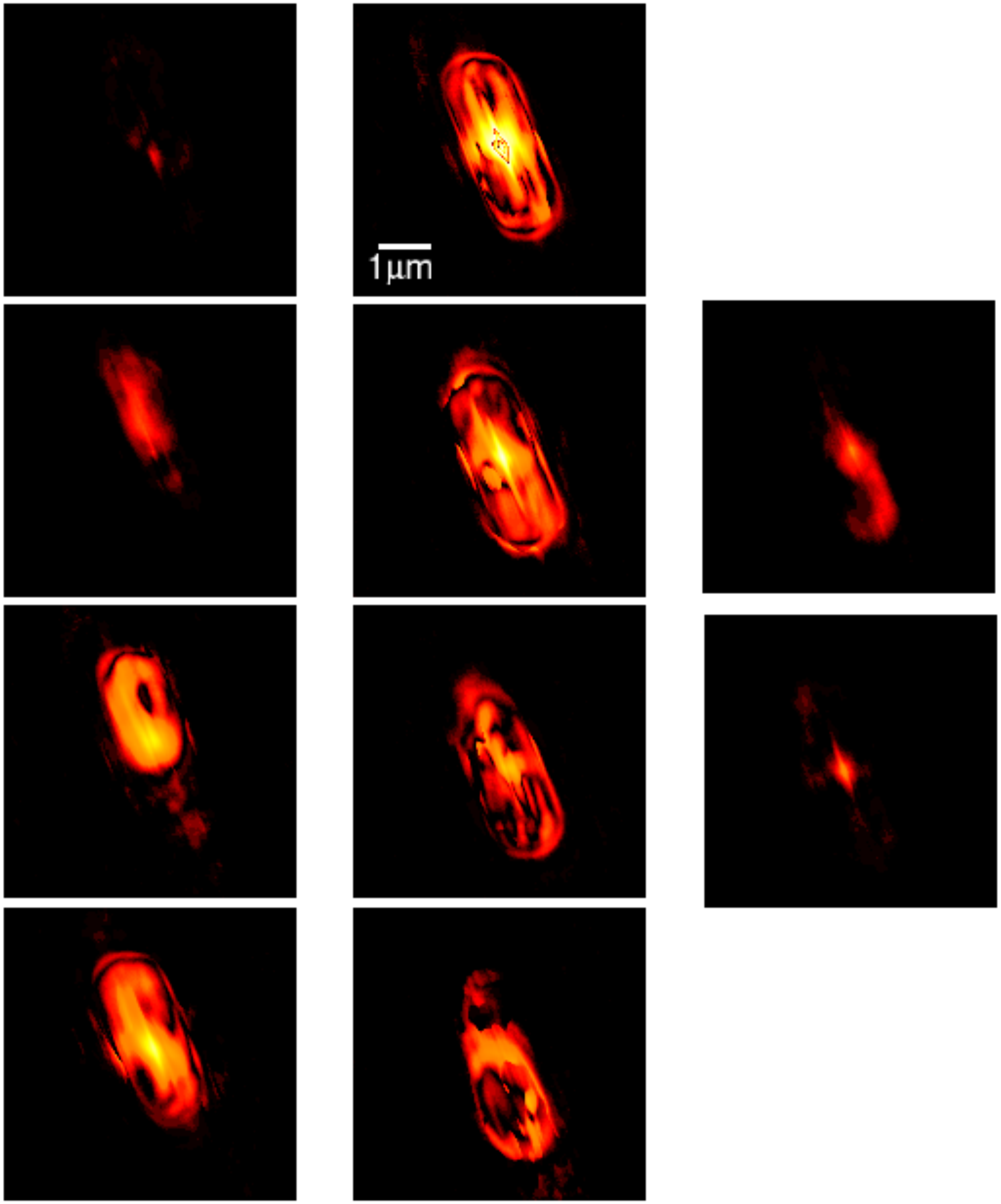


* Center is Symmetric *

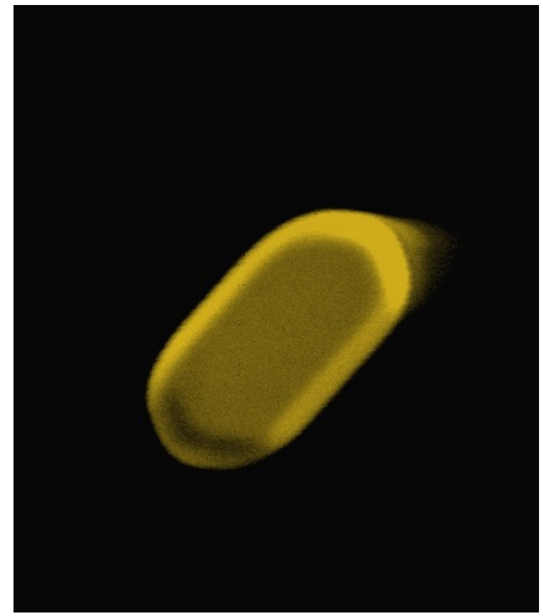
# 30 frames of 3D reconstruction 1 micron gold crystal



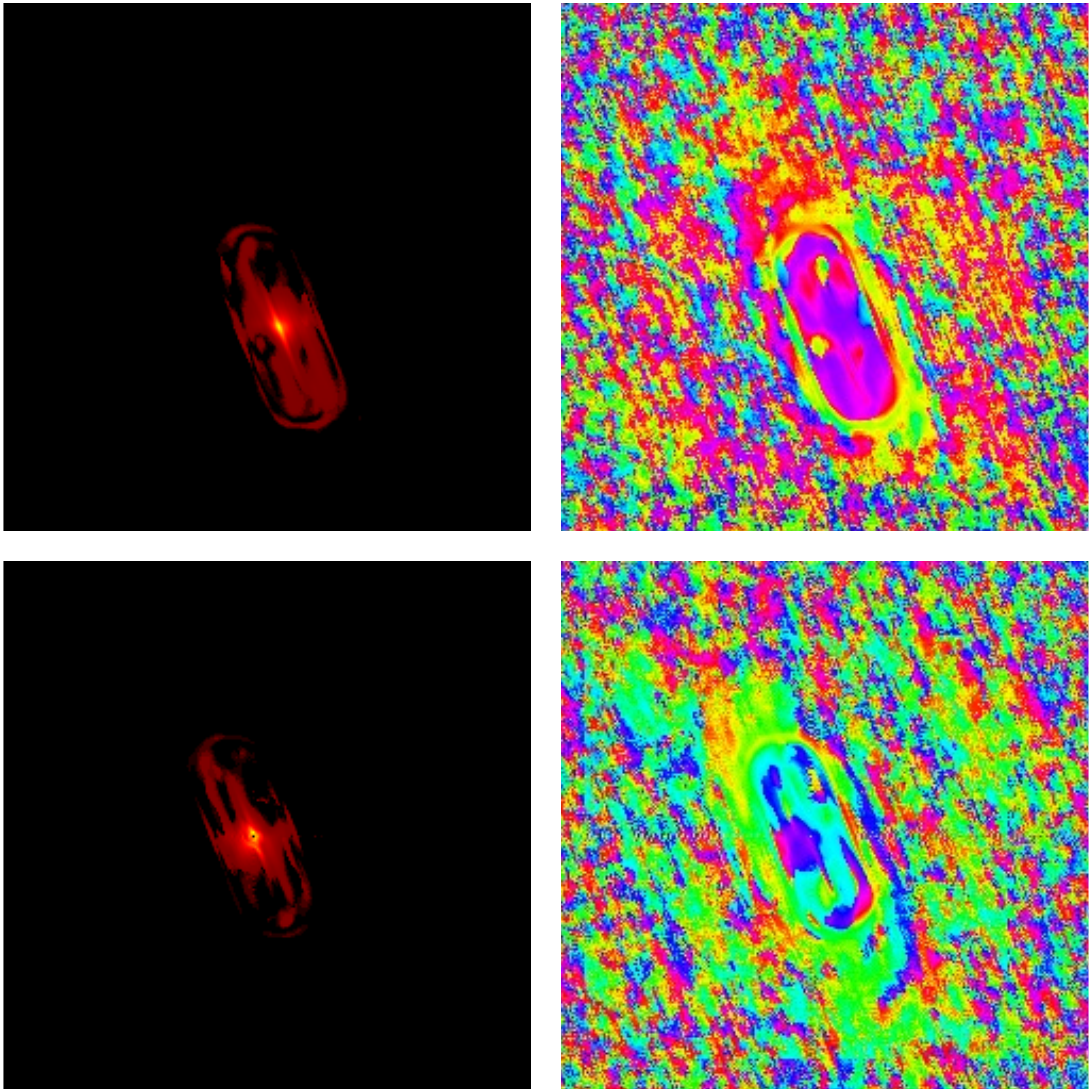
* CENTER *




Shape is
similar to plan
view SEM:

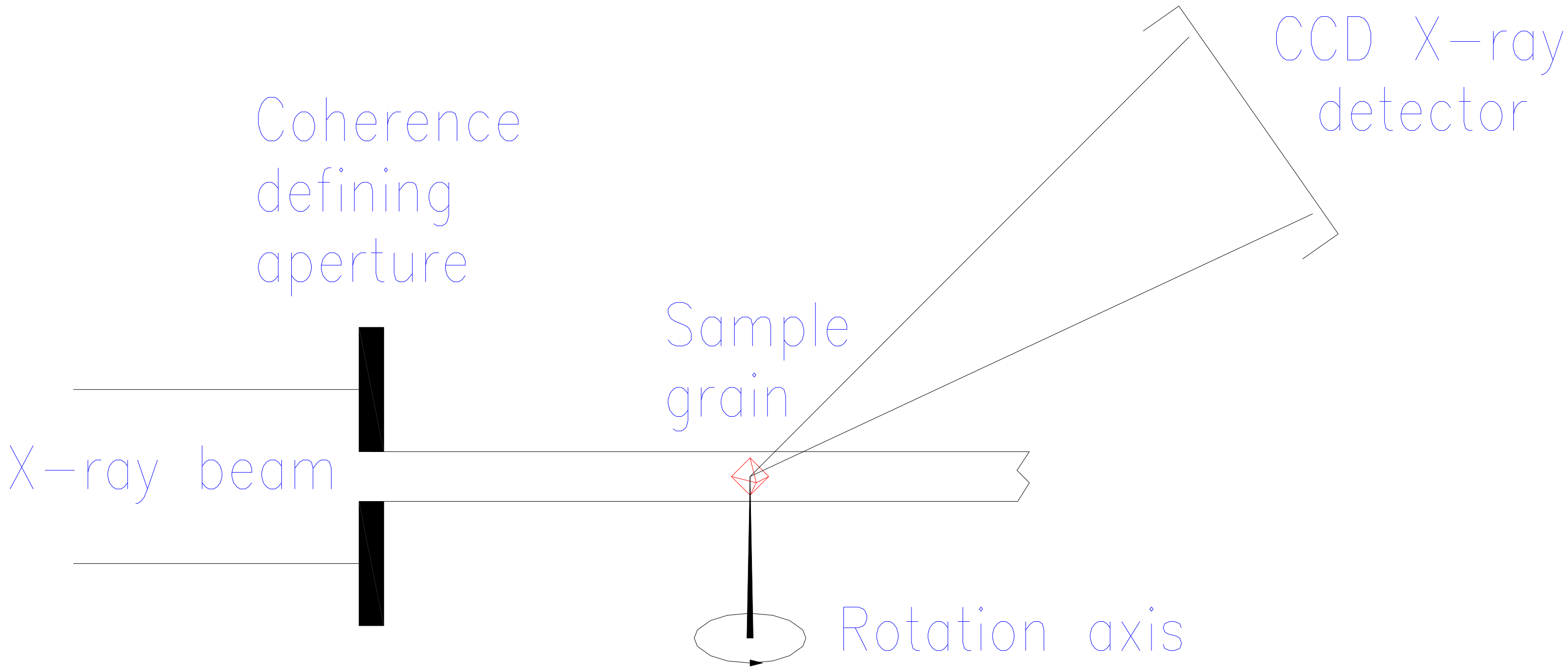


Amplitude



Phase

# Lensless X-ray Microscope



# UI research gets more crystal clear

## ■ X-ray beam gives close look at solids, liquids

By GREG KLINE
News-Gazette Staff Writer

Examine a sheet of steel, and you perceive a smooth surface. But down inside, near the atomic level, are multi-faceted crystalline structures, not unlike the much bigger crystals you can see with your eyes and turn into desk ornaments and chandeliers.

The nature of those microscopic structures is what makes metal strong.

Proteins, which have significant roles in biological processes, also can form crystals. Silicon, the base component of computer chips and other microelectronics, is full of them as well.

A greater understanding of how these tiny crystalline structures form and perform would be useful to everyone from structural biologists to steel makers.

Some University of Illinois scientists have developed a technique that should help. Their solution: Give the microscopic crystals an X-ray.

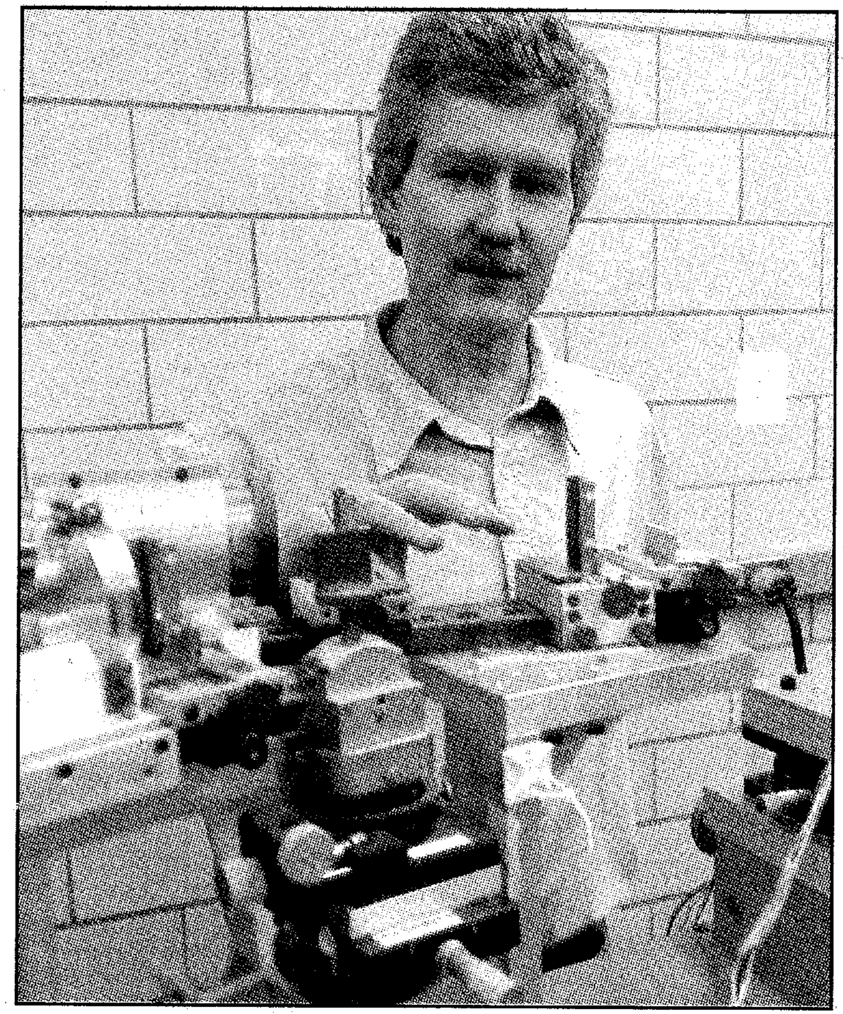
An X-ray microscope developed by UI researchers can make detailed, three-dimensional images of crystals formed inside both solids and liquids.

"You can find the positions of all the atoms inside," UI physics Professor Ian Robinson said recently. "We're getting additional measurements (than other methods). We're interpreting it more finely."

Robinson developed the microscope with graduate students Garth Williams, Mark Pfeifer and Sebastien Boutet and Ivan Vartanyants, a visiting scientist at the UI, using a high-powered X-ray beam generated at Argonne National Laboratory near Chicago. The National Science Foundation, U.S. Energy Department and state of Illinois funded the work.

The microscope isn't the kind where you peer through an eyepiece at something on a slide of glass below. It's lensless and it creates images on a computer screen using software routines developed by the UI researchers.

The images are formed by interpreting signals from the X-rays and collected with an electronic charge-coupled device similar to those used in digital cameras.



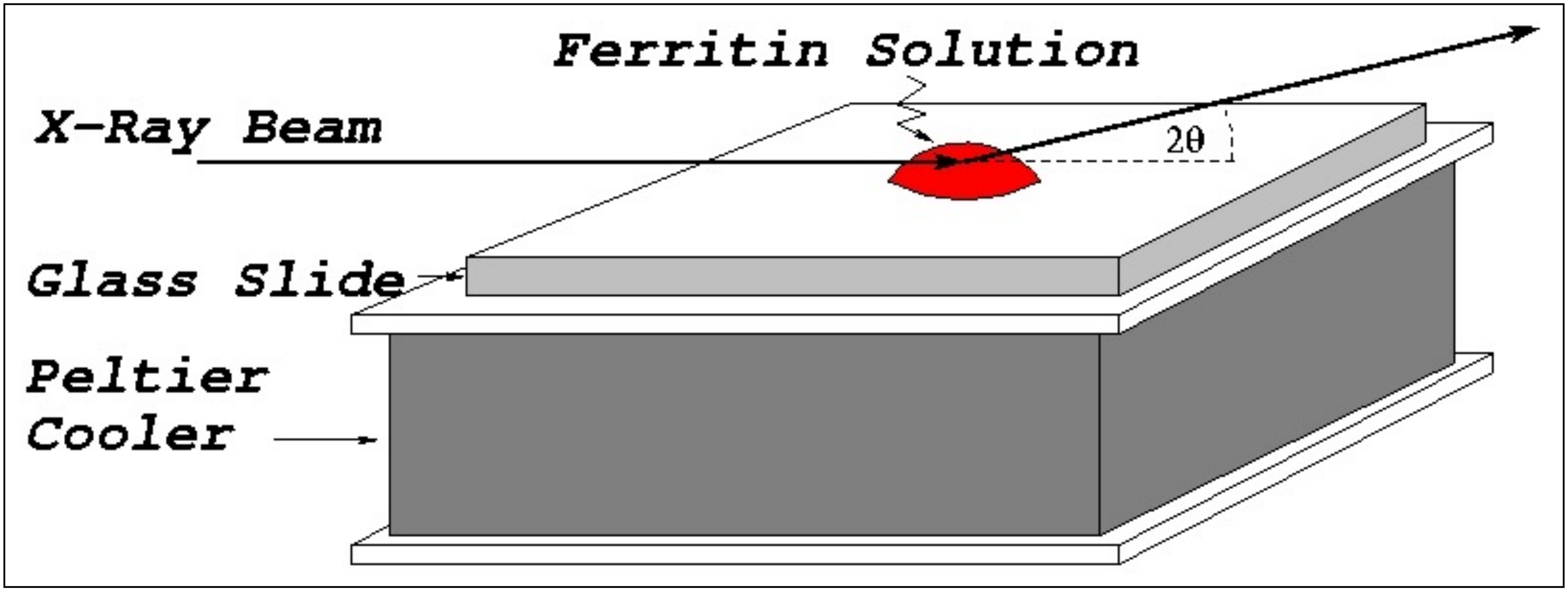
News-Gazette photo by Robert K. O'Daniell

**University of Illinois physics Professor Ian Robinson is using the X-ray microscope to study what happens when metals are cut and when they're ground together in low-temperature milling.**

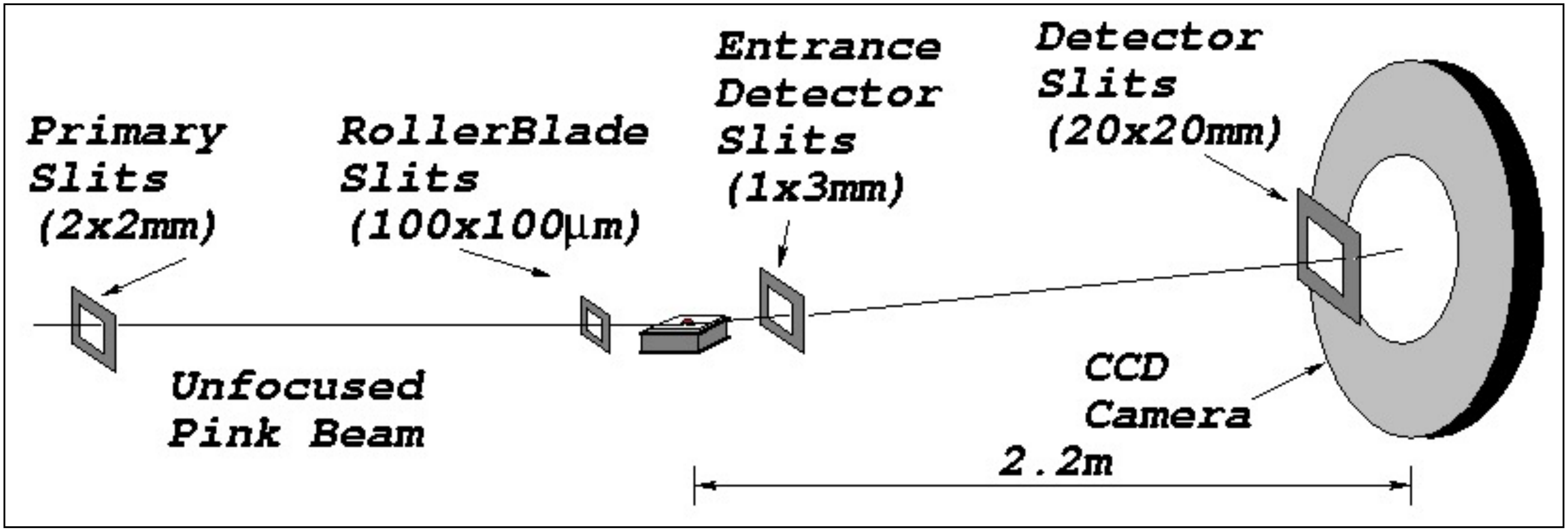
"You shine X-rays in a sample and you collect everything that is scattered, the light that is scattered by the sample,"

**Please see RESEARCH, B-2**

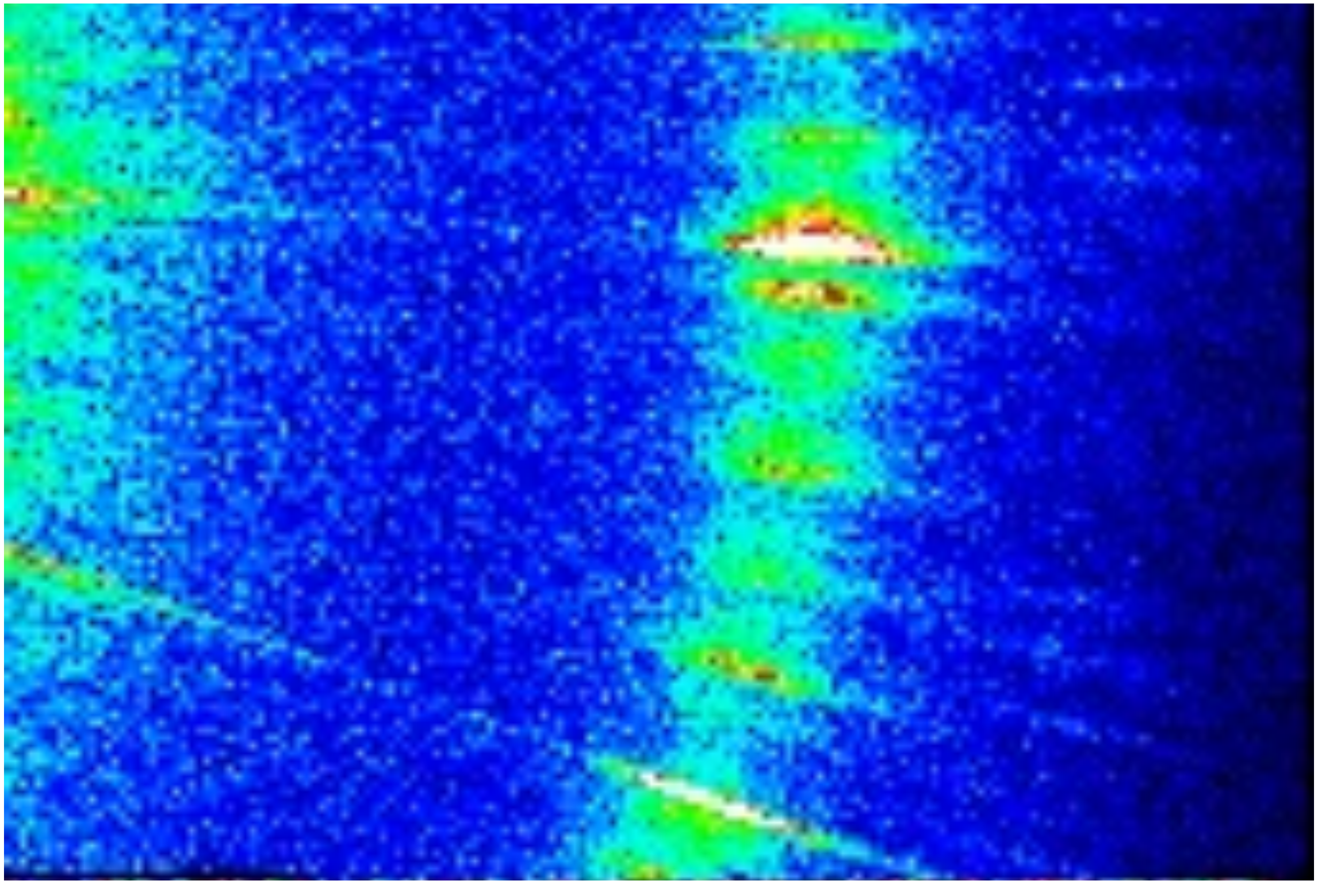
# In-situ Study of Crystallization



# Experiment at APS Sector 34

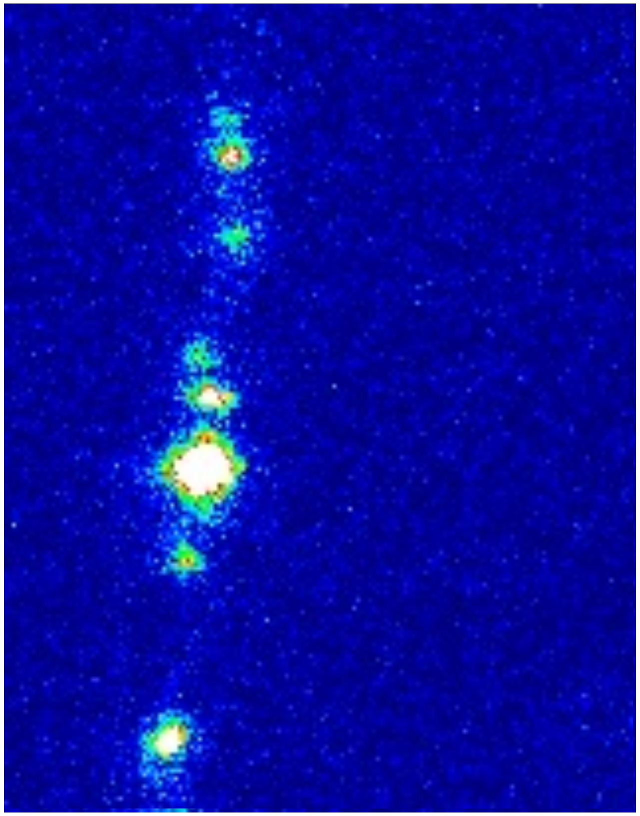


# “Pink beam” sees CTRs

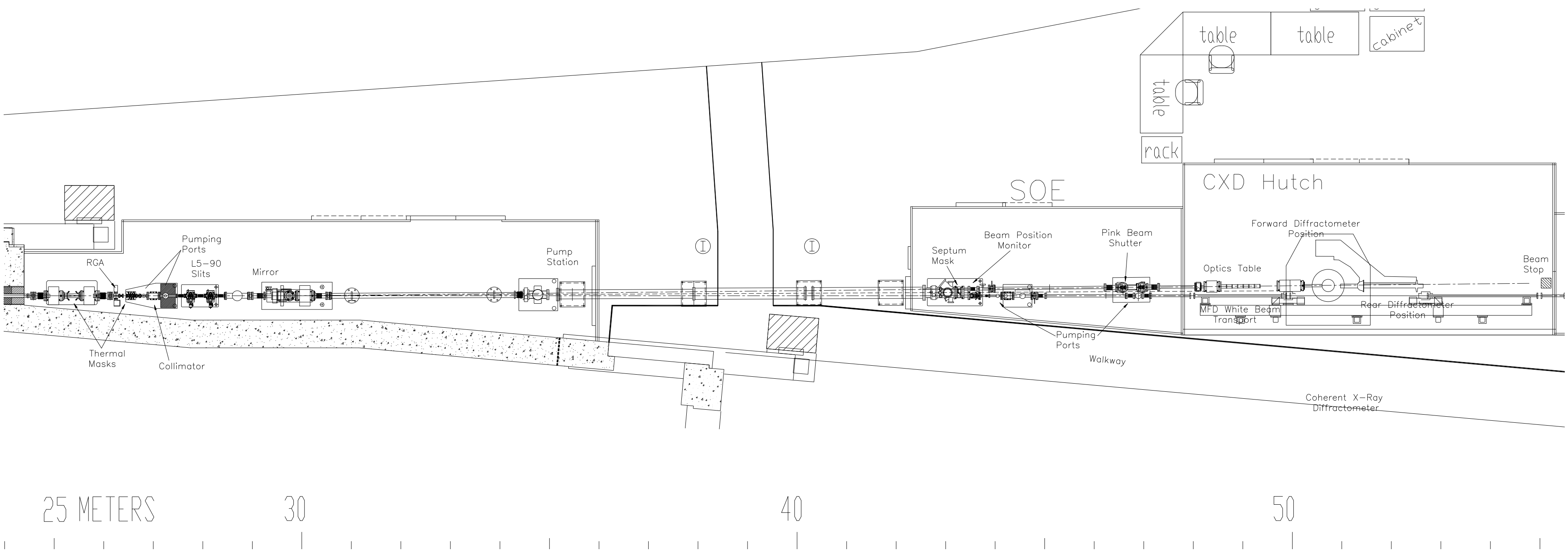


# Ferritin (111) Powder Ring

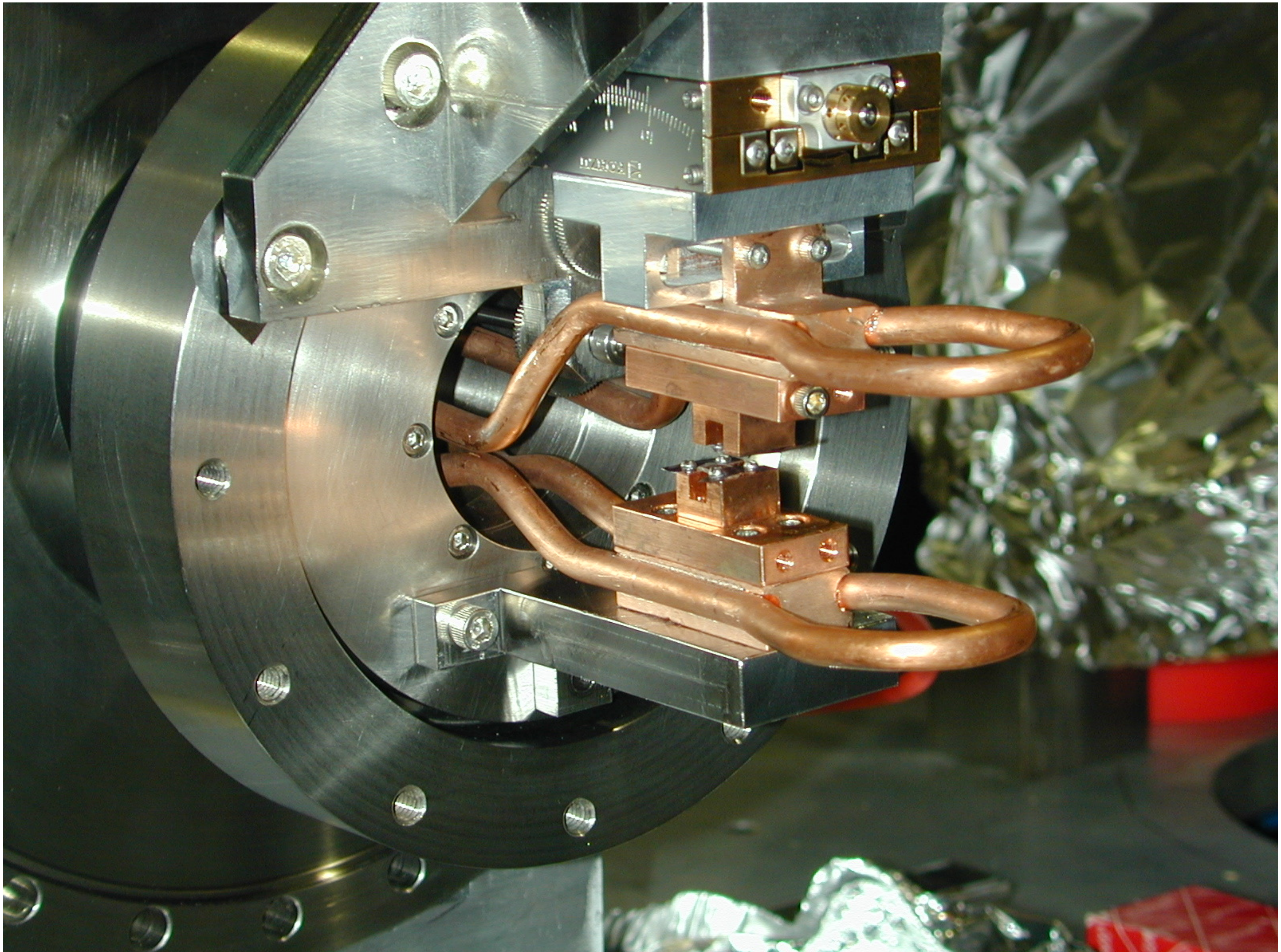
- 50 frames
- 30sec exposure
- 0.3sec playback
- 150x200 pixels of 22.5μm

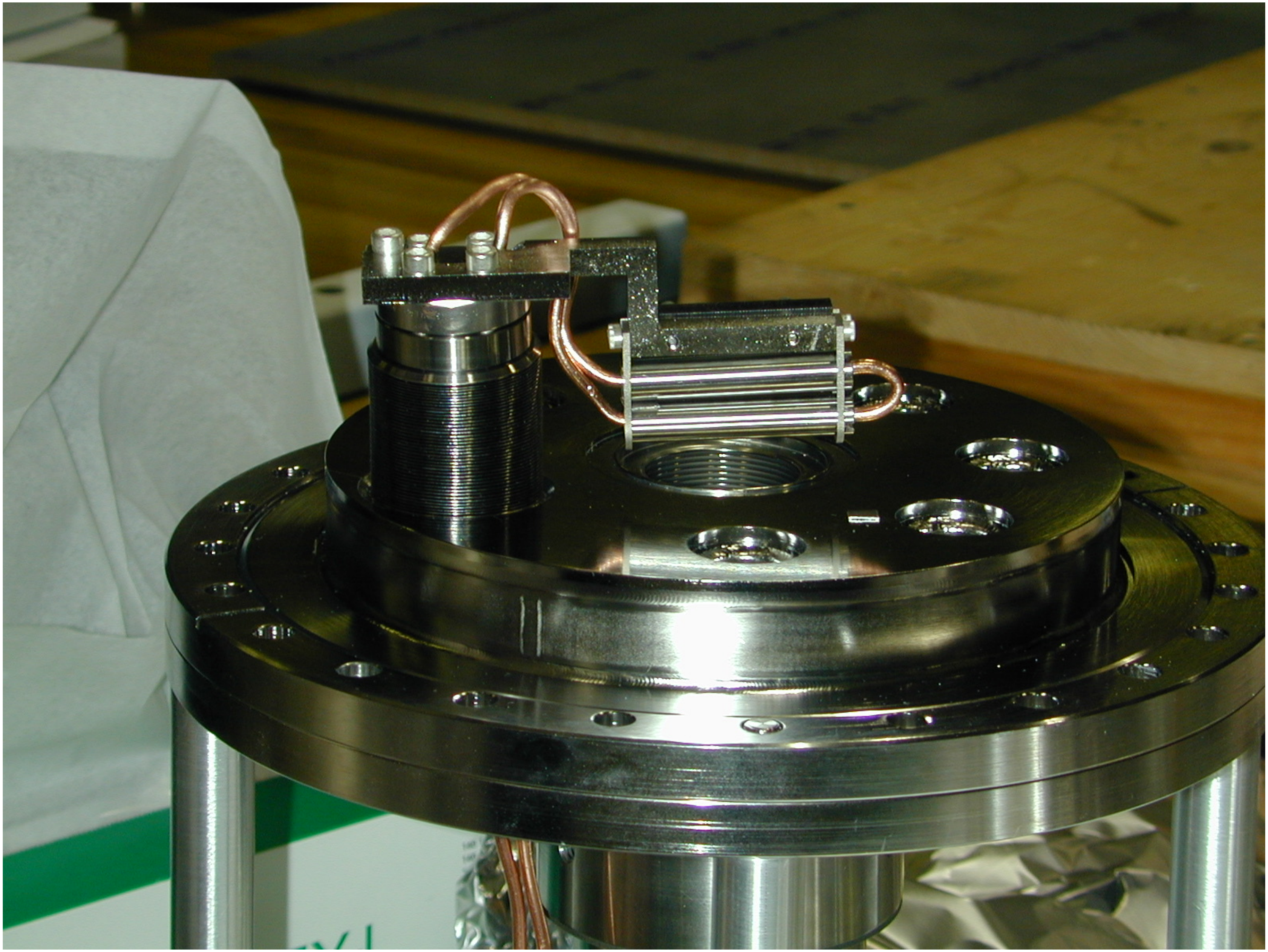


# CXD Beamline at APS Sector 34




MICRO-CONTROLE
Newport
MICRO-CONTROLE
Newport





# Conclusions

- "Diffuse" scattering acquires fine structure
- Surface/interface morphology
- Shapes of small particles
- CXD facility ready for experiments
- Future applications of CXD
  - Atomic-scale fluctuations
  - 3D Imaging of strain fields at the nm level