Coherent X-ray diffraction for strain mapping in nanocrystals

Ian Robinson
Sébastien Boutet
Garth Williams
Mark Pfeifer
Ivan Vartaniants
Ross Harder
Steven Leake

University College London
London Centre for Nanotechnology
Diamond Light Source
University of Illinois

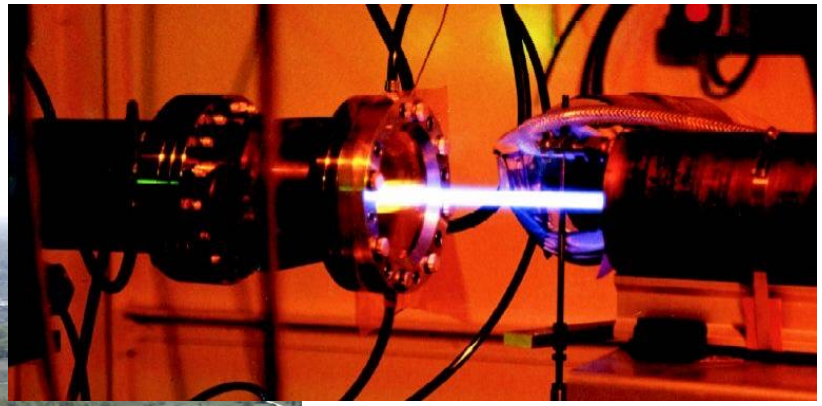
EPFL, Lausanne
October 25, 2007

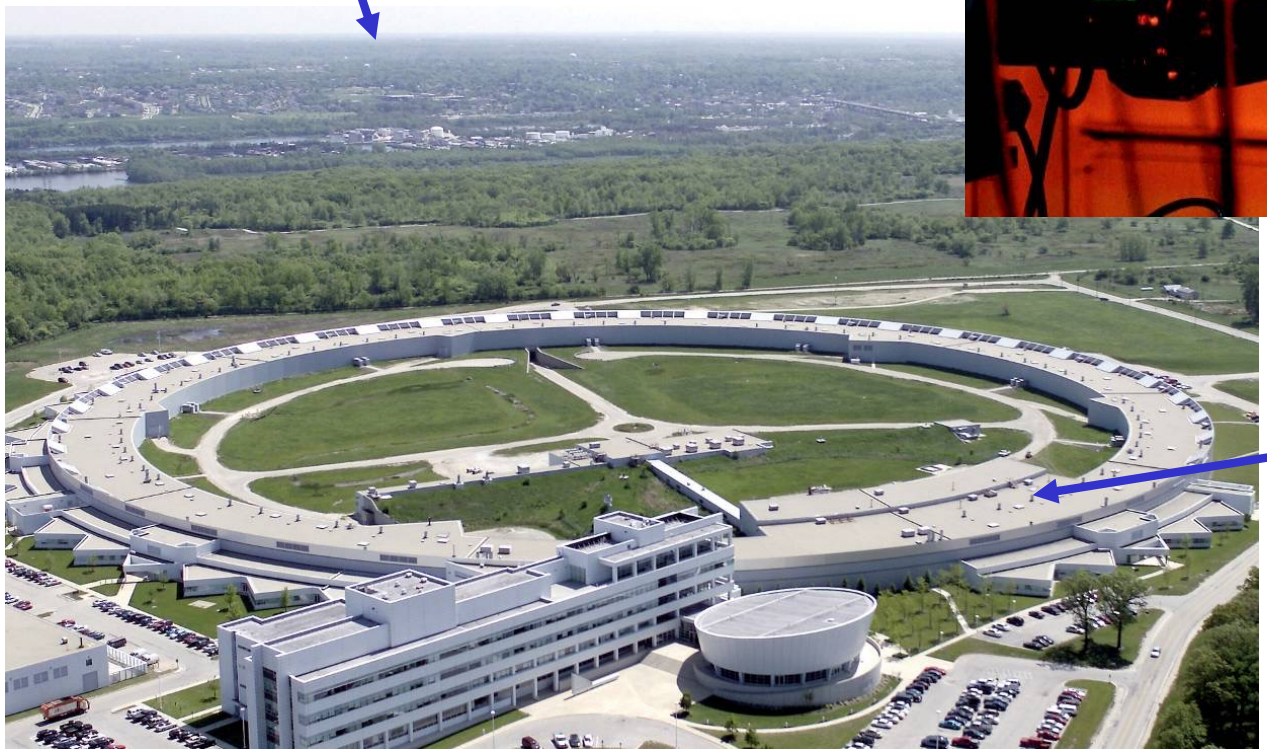
Outline

- Protein crystallisation study
- Coherent x-ray diffraction
- CXD can solve the phase problem
- Extension to phase objects
- Nanocrystal structures
- Nanowire structures

Synchrotron Radiation

Urbana

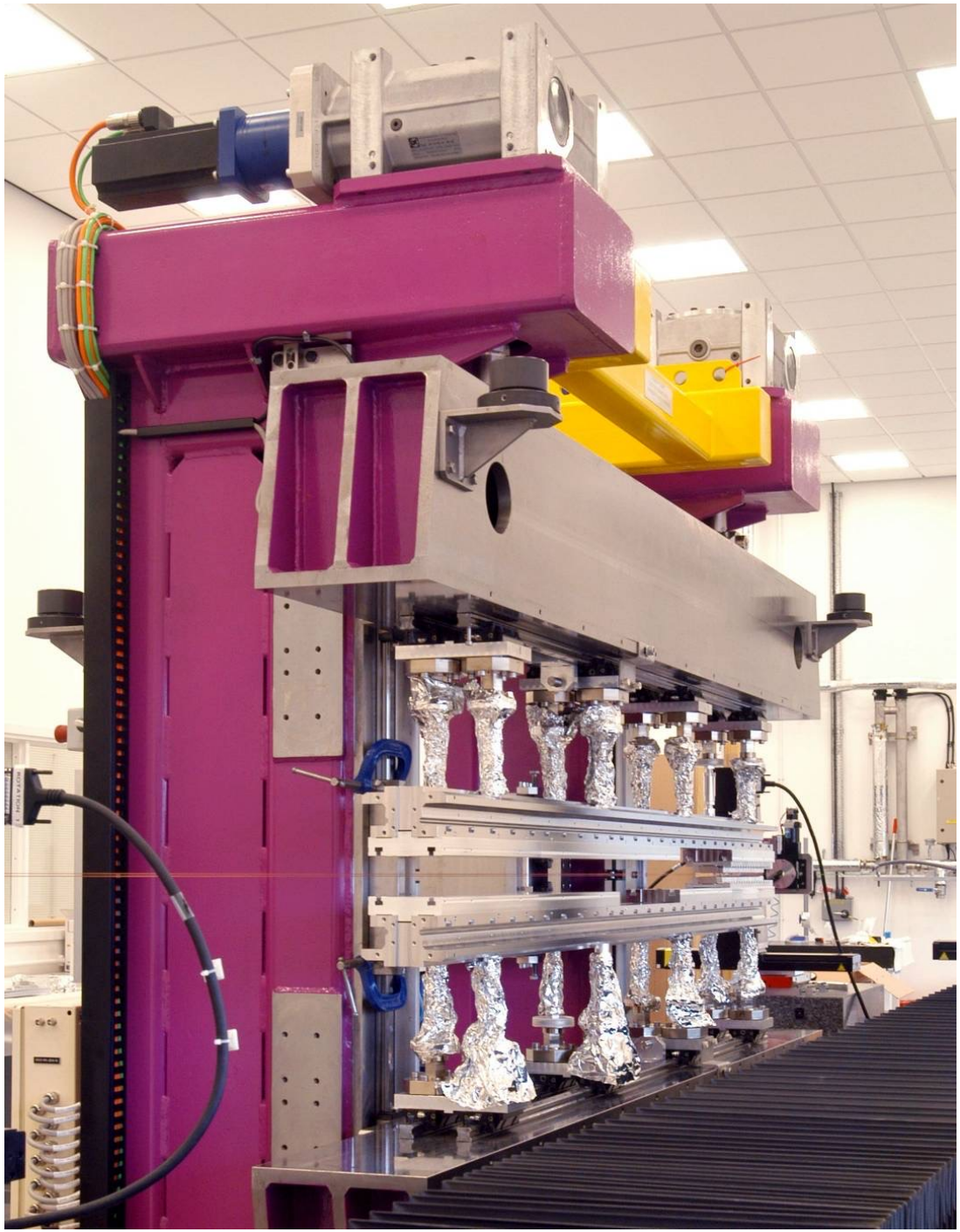




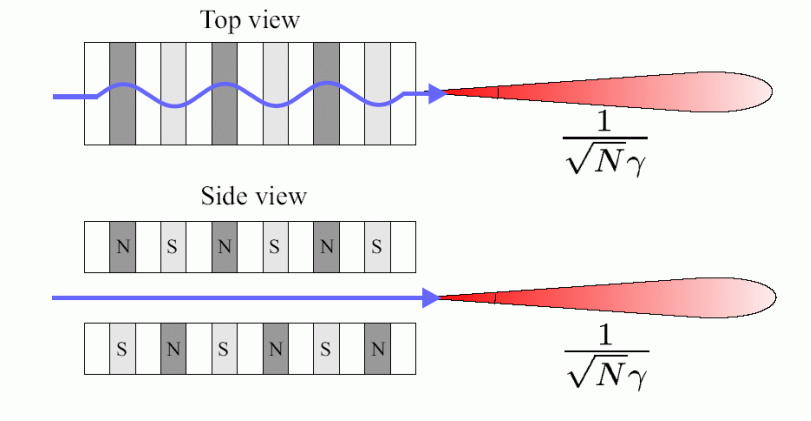
34-ID-C

Diamond Light Source (RAL)

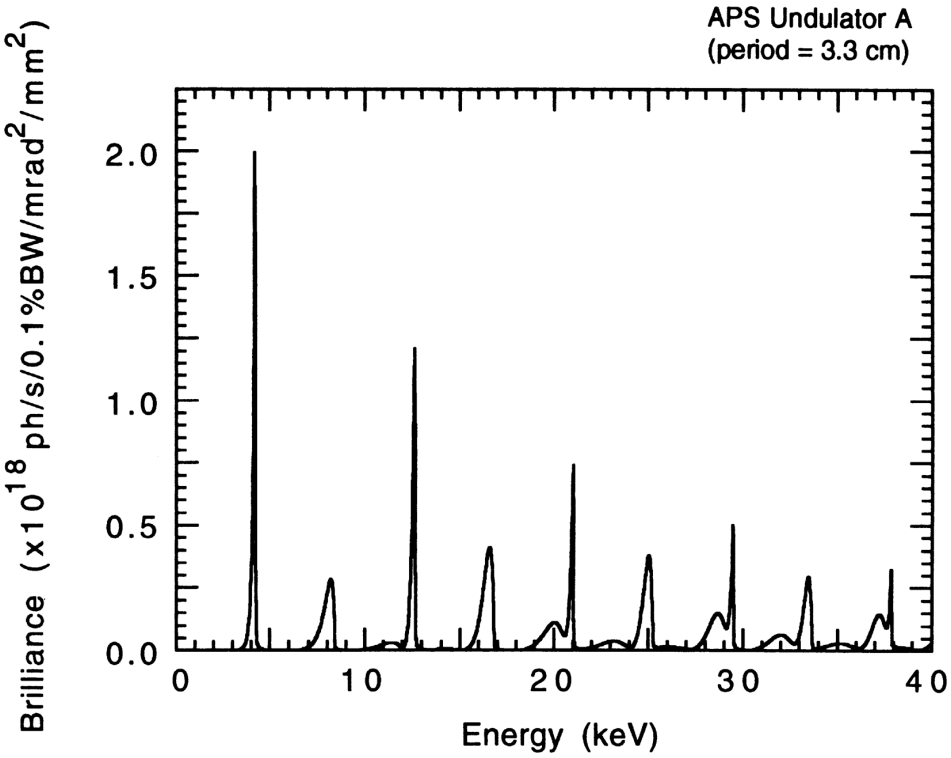
Diamond in-vacuum X-ray Undulator



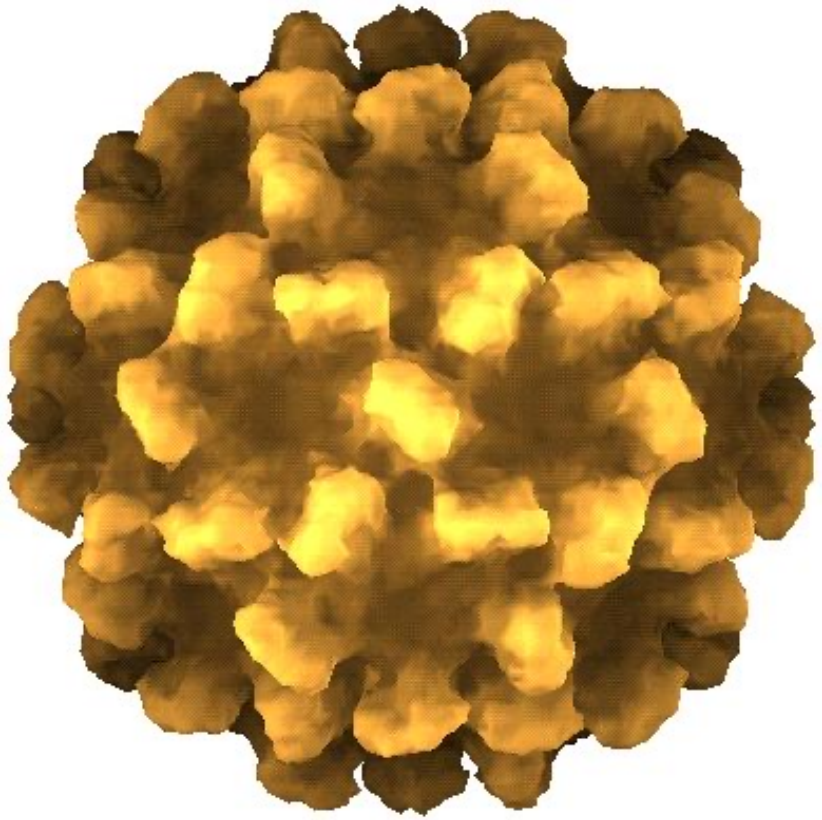
X-ray Undulator Principle



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

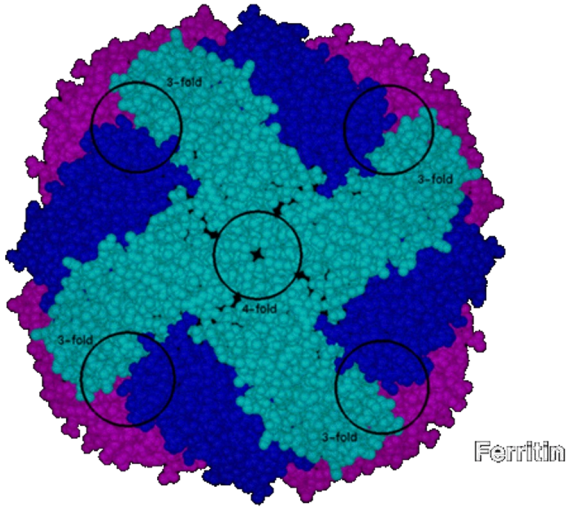


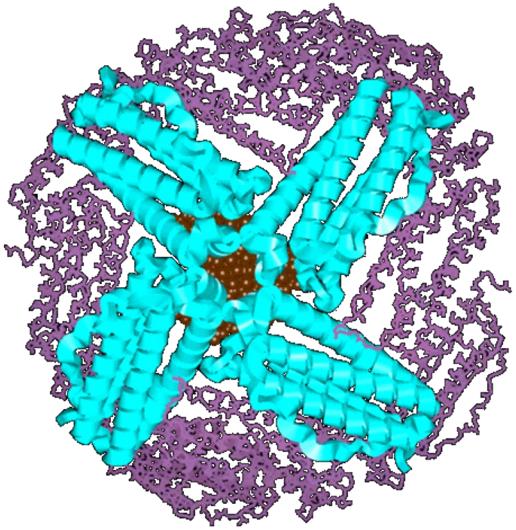
Tomato Bushy Stunt Virus
1980



Horse Spleen Ferritin

- Ferritin used in almost all living things for Iron Storage
- Made of 24 identical protein subunits arranged in 432 symmetry
- Crystallizes as FCC (I23)
- Inner shell diameter 80Å
- Outer shell diameter 130Å
- Iron core: ferrihydrite form
- With Iron : Holoferritin
- Empty Shell : Apoferritin





Critical Nucleation

Yau S.-T. and Vekilov P.G., *J. Am. Chem. Soc. (***2001),** *123,* 1080-1089

- a) Nucleation via planar 2D clustering
- b) Nucleation via compact close-packed 3D clustering
- Possible also via non-crystalline (eg icosahedral) nuclei.

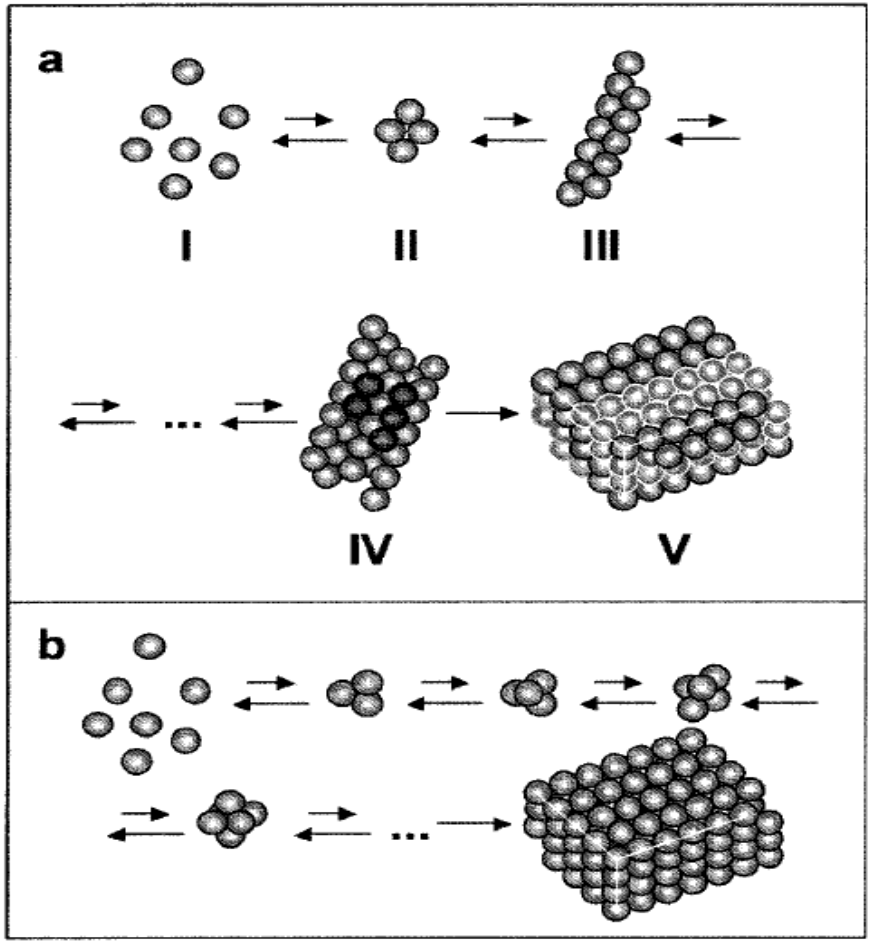
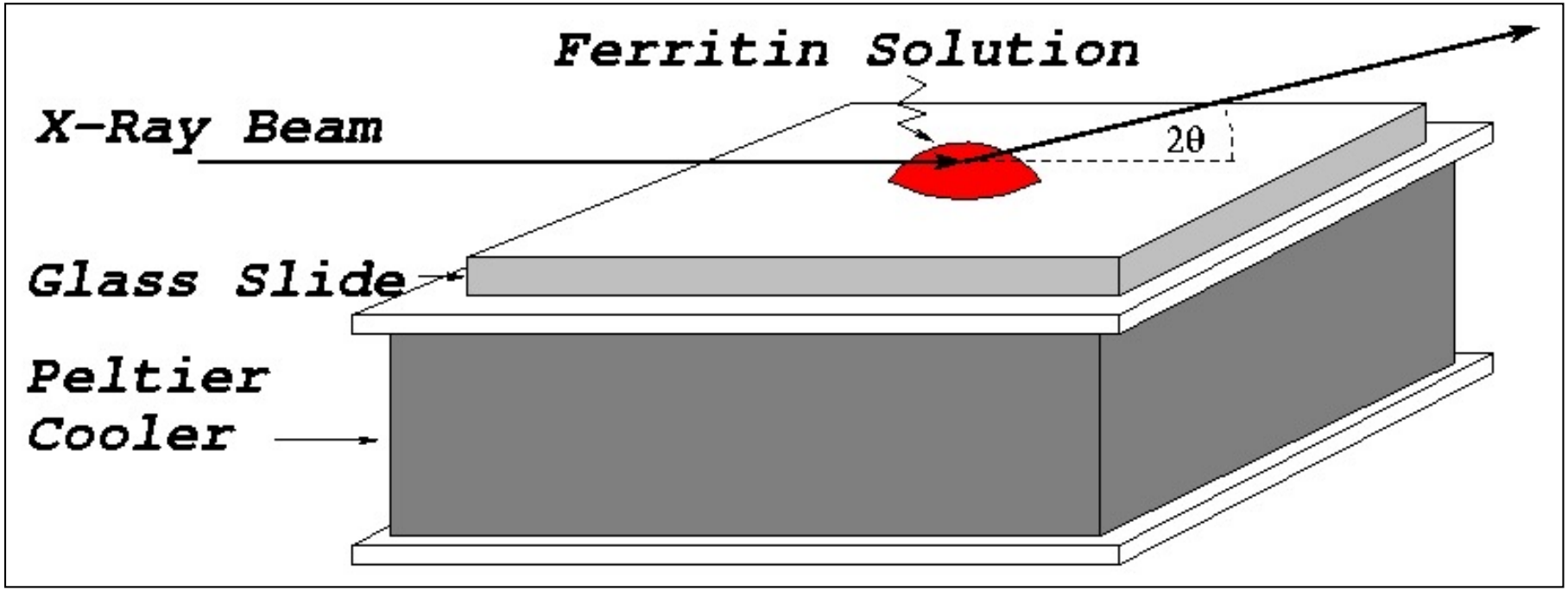
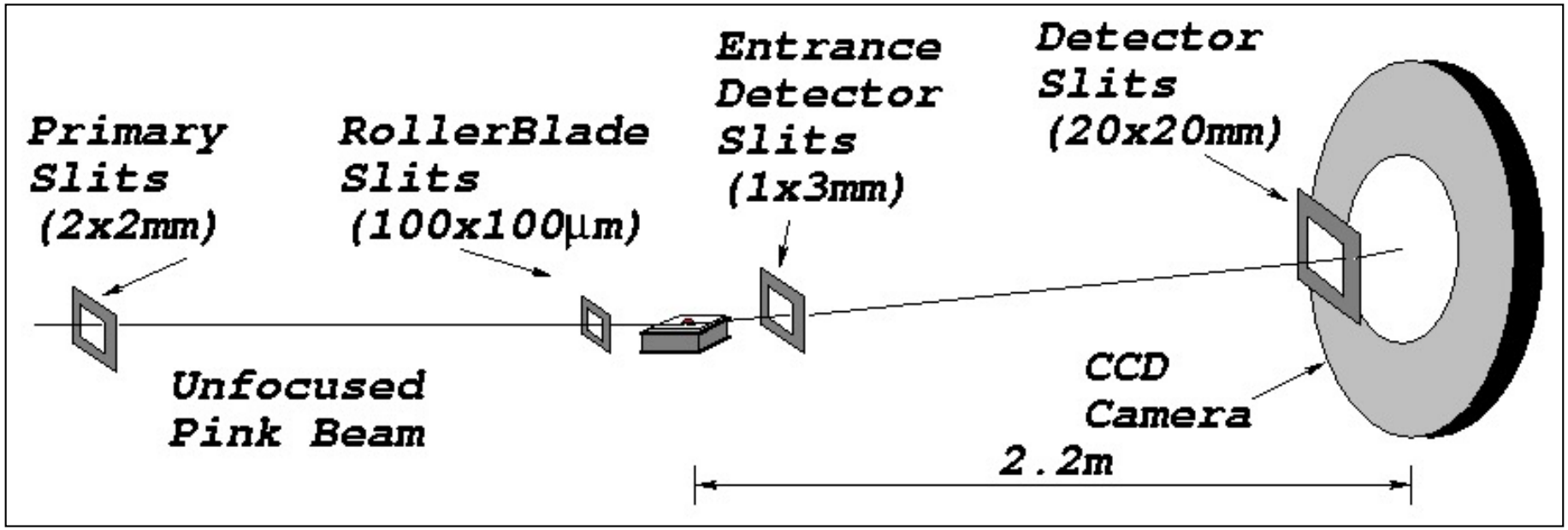


Figure 10. Schematic illustration of two nucleation pathways: (a) via a planar critical cluster (in IV molecules belonging to the second layer are shown in a lighter shade; in V the (110) layers that stack up to form this crystal are delineated by lighter and darker contours) and (b) via compact critical cluster.[5,6]

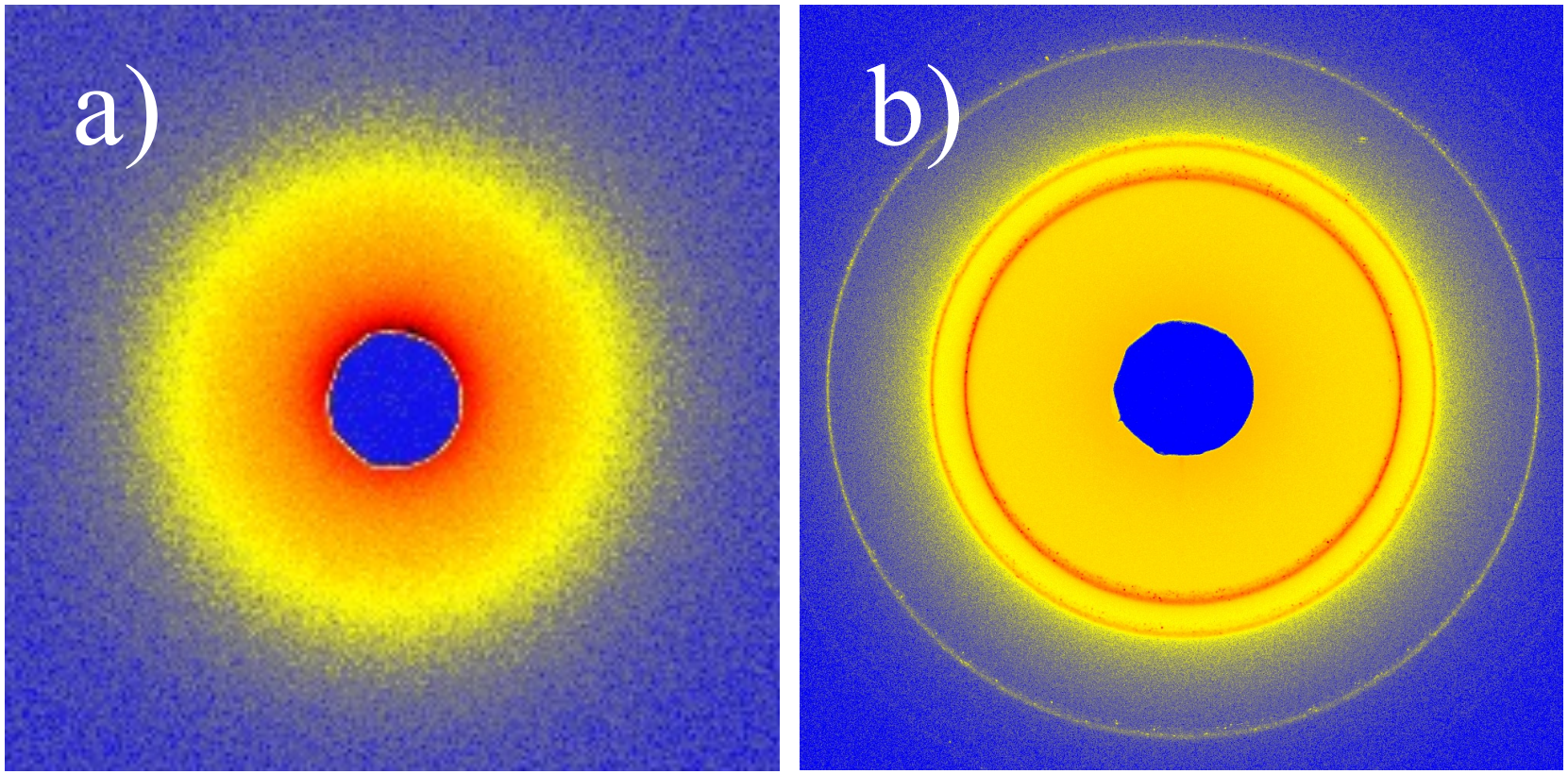
In-situ Study of Crystallization



Experiment at APS Sector 34



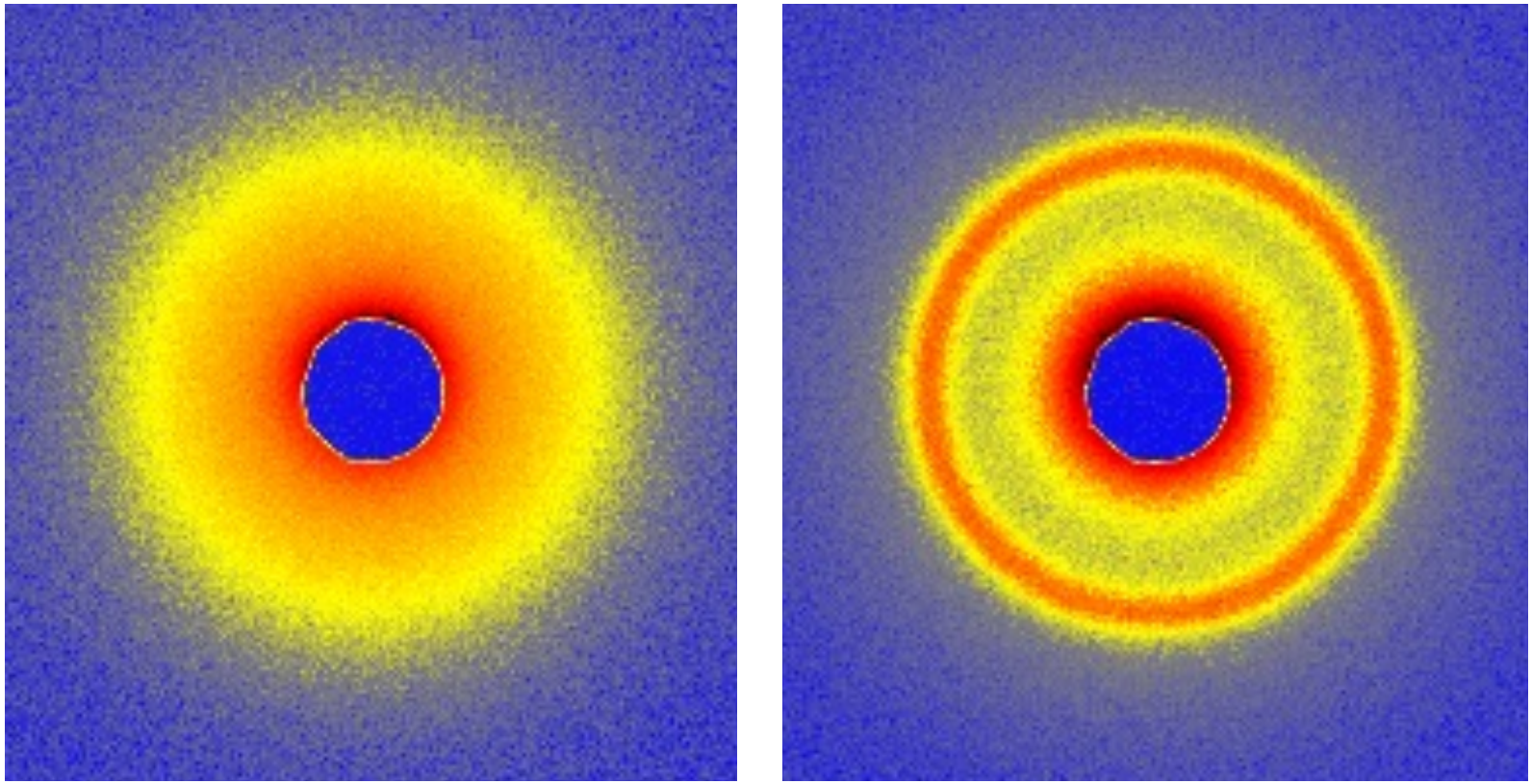
Crystallization of Holoferritin: SAXS



a) SAXS pattern of holoferritin at 10°C.

b) SAXS pattern after adding Cadmium salt

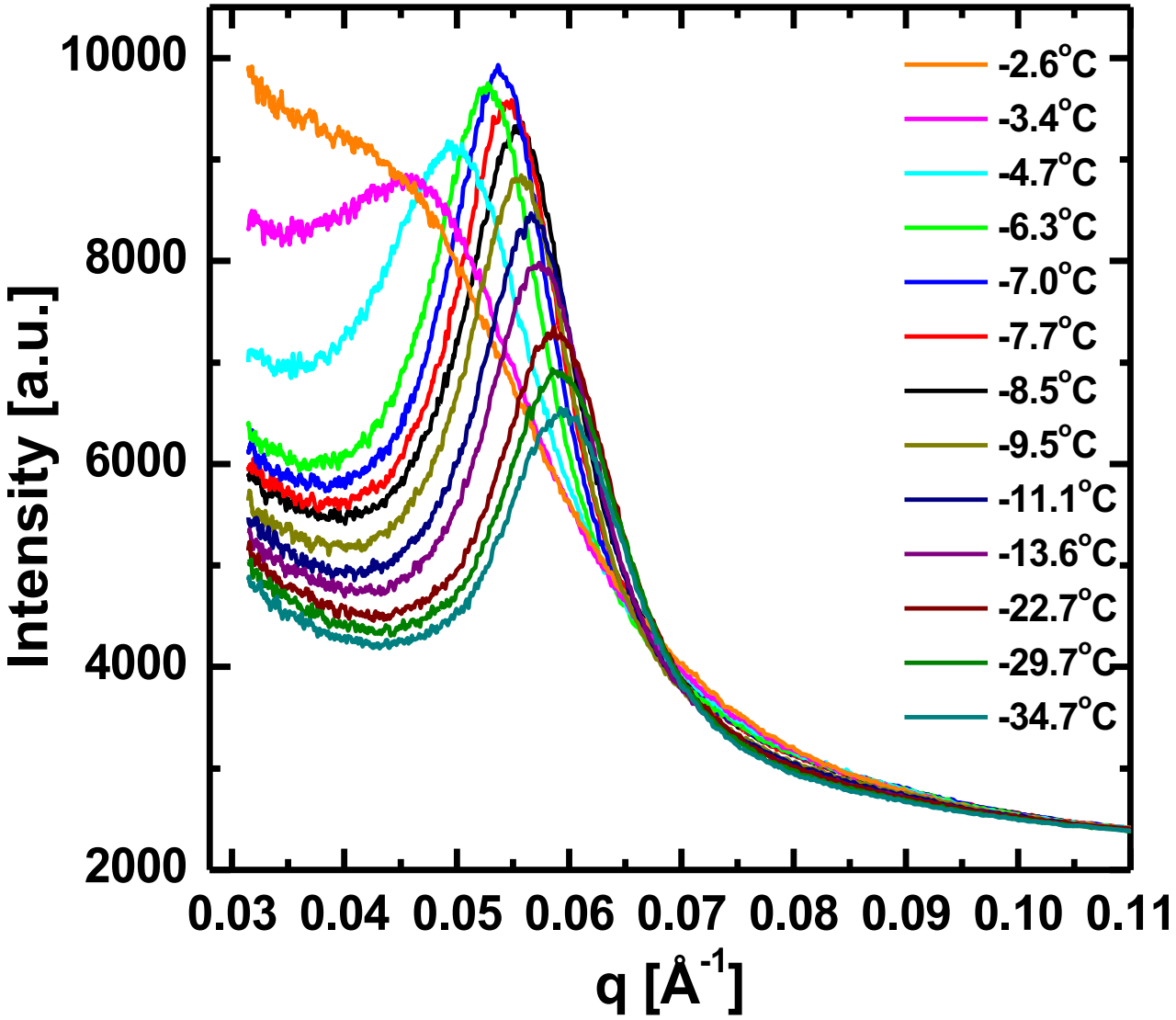
Effect of Temperature



SAXS pattern at T=+10°C and -10°C.

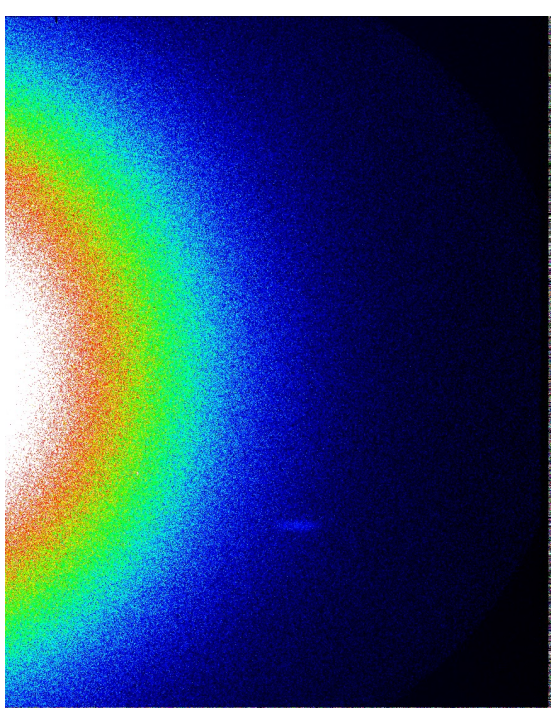
Holoferritin in dilute (10mg/ml) NaCl only.

Integrated SAXS Data

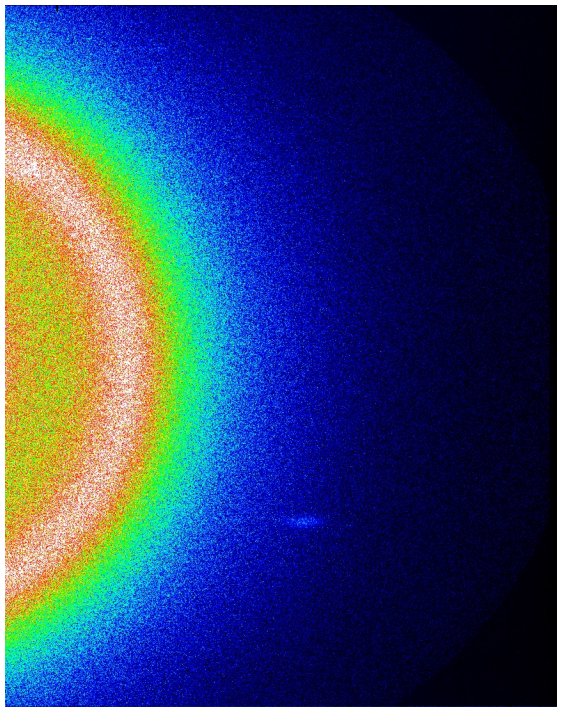


- The SAXS pattern shows a broad peak which shifts in position and changes in width as a function of temperature

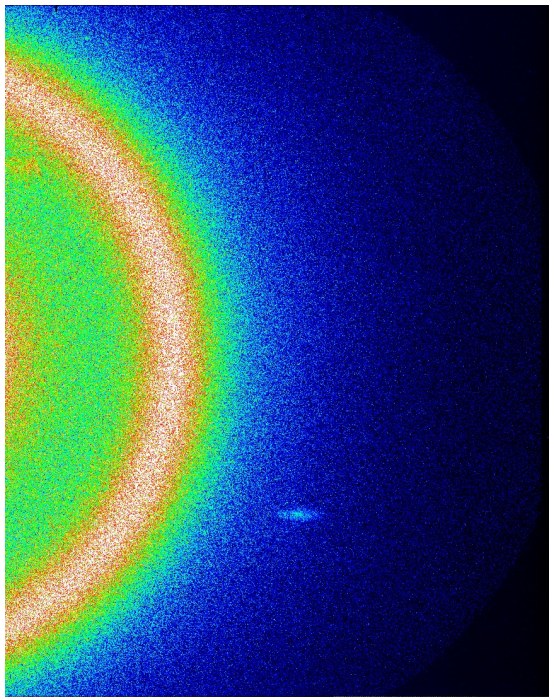
Ferritin Solution upon Freezing



T=13.3

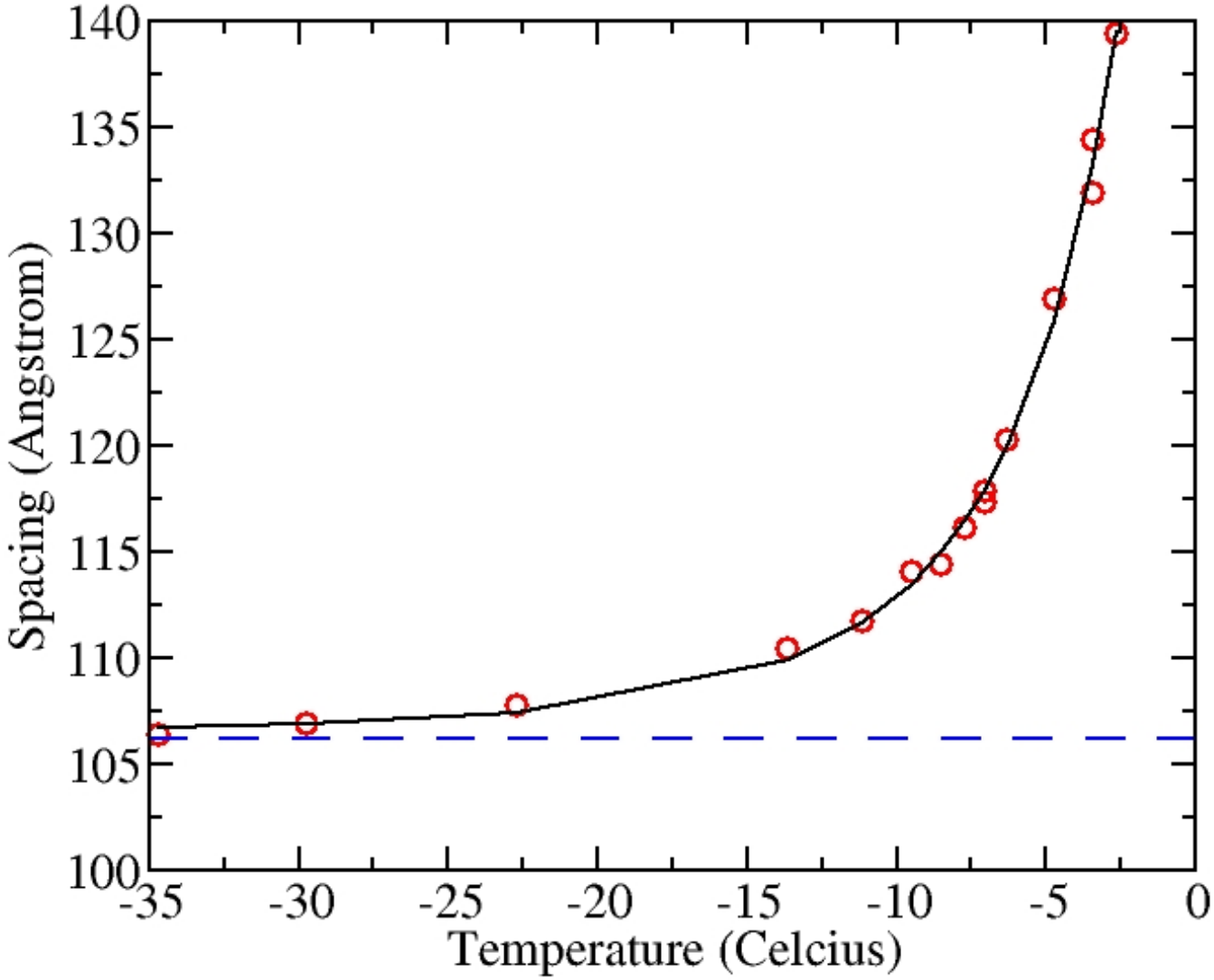


T=-4.7

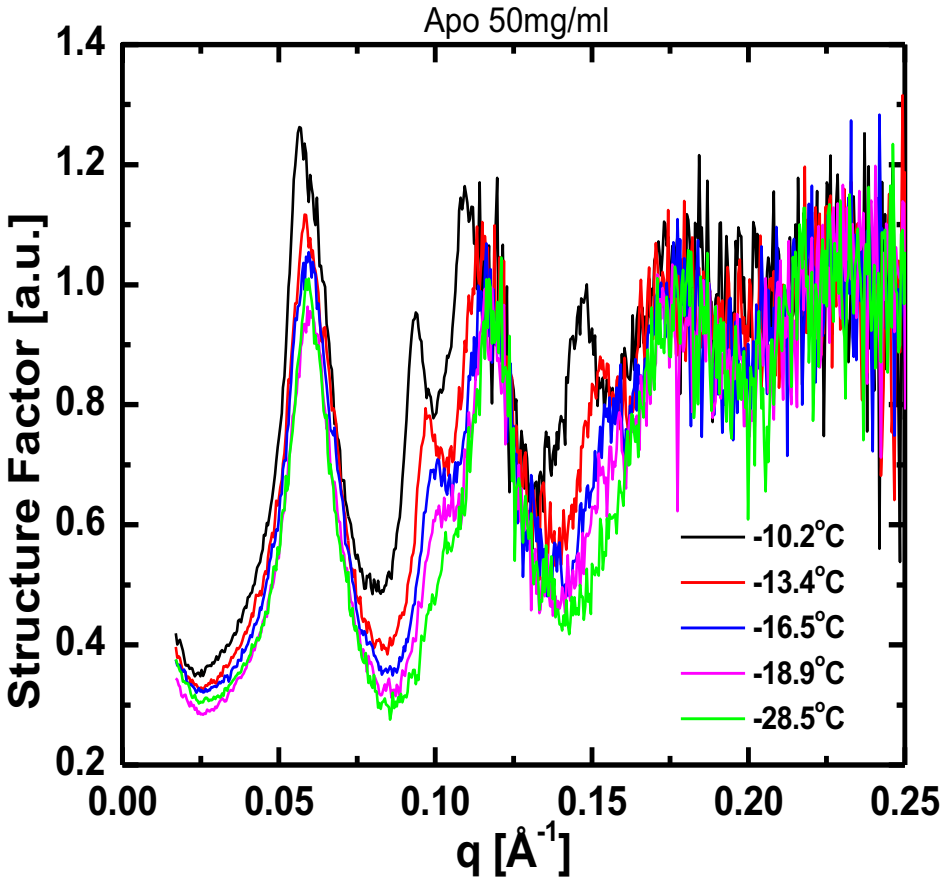


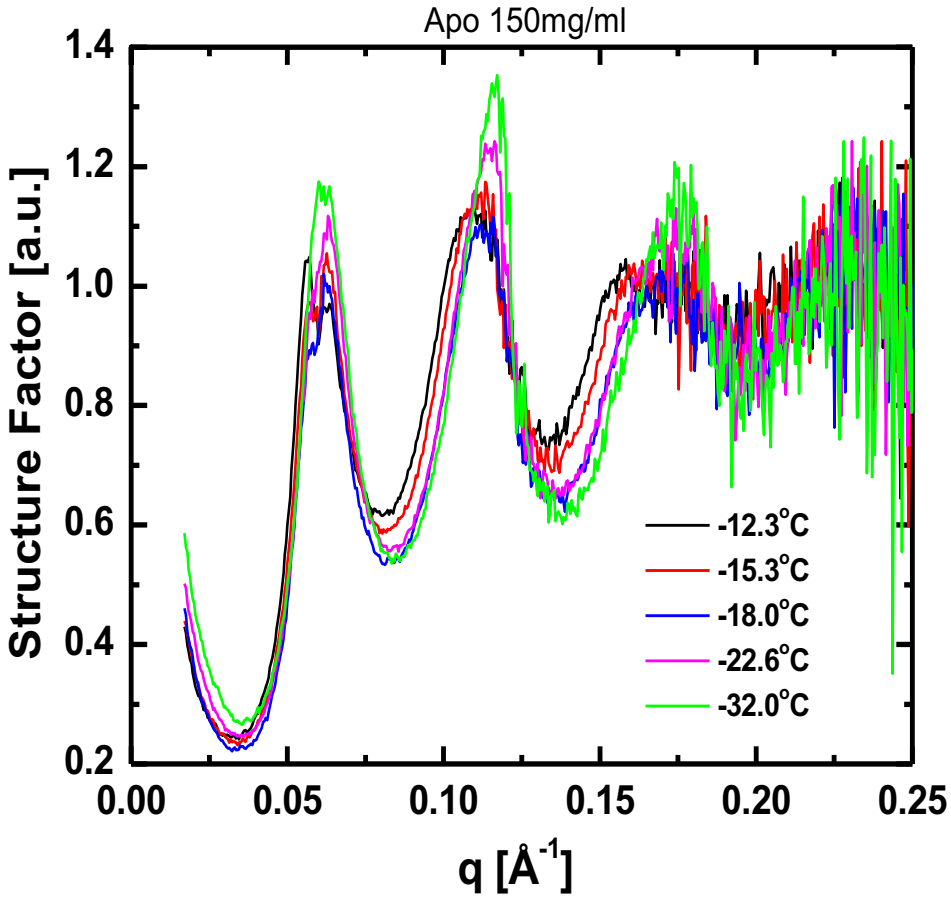
T=-34.7

Temperature Variation of Peak Position

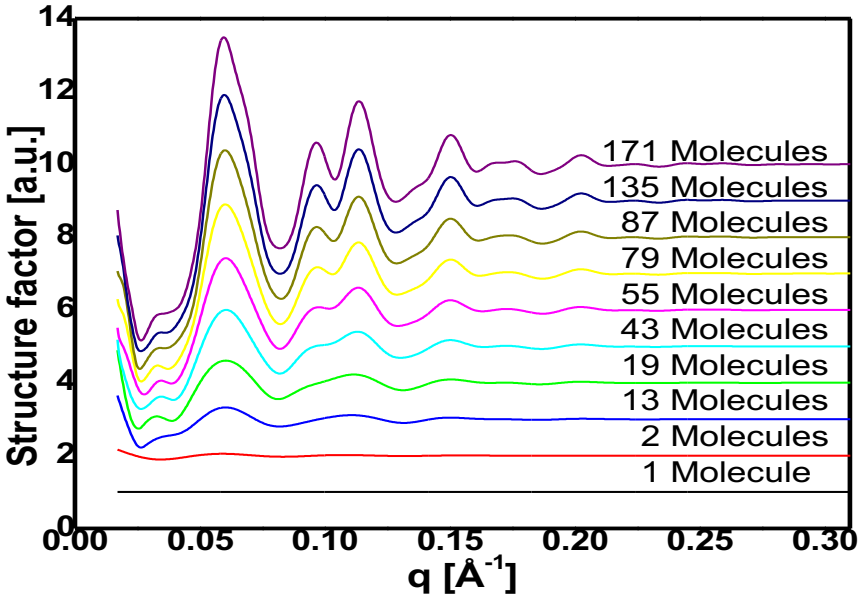


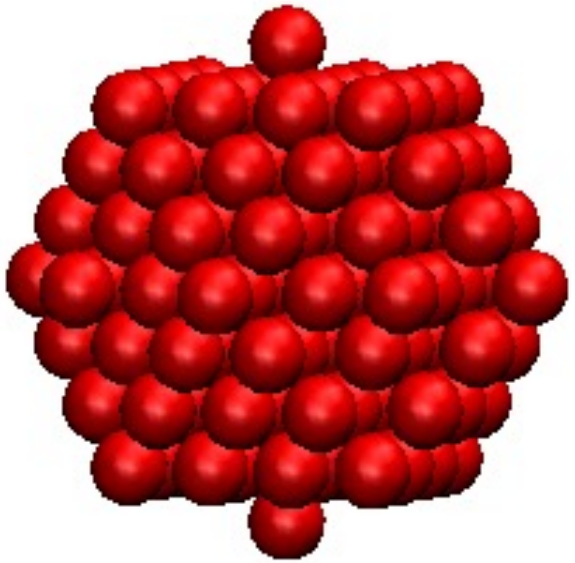
Structure Factors of Apoferritin

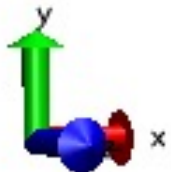




FCC Spherical Clusters

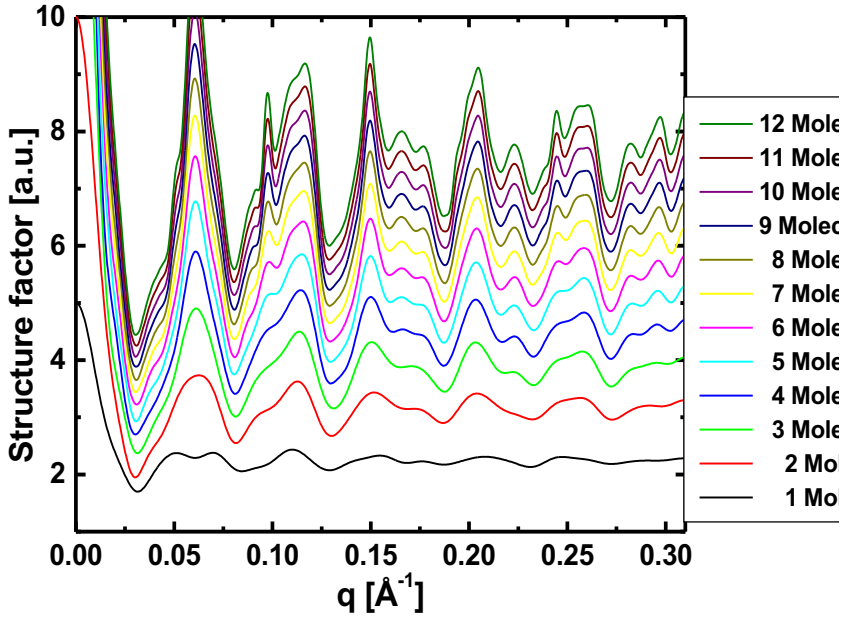


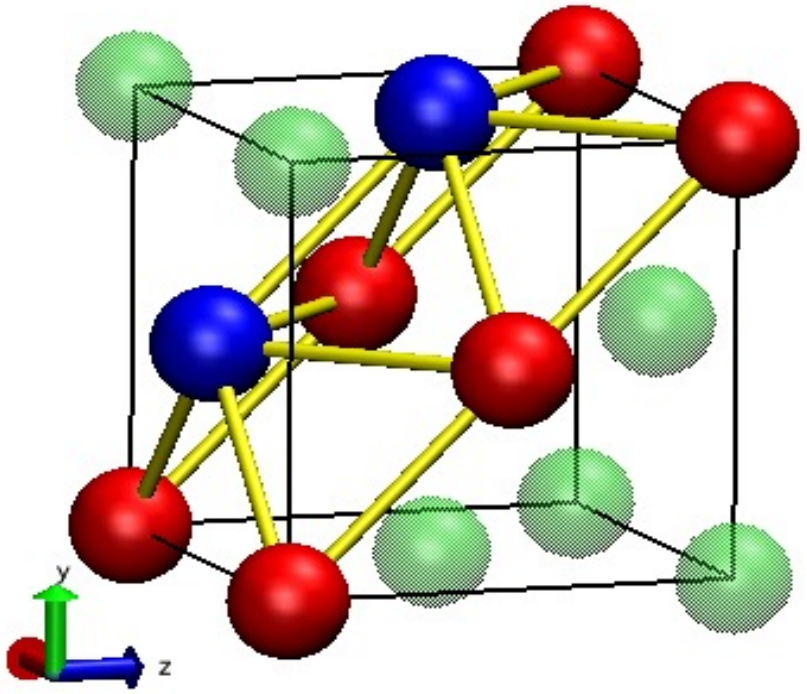




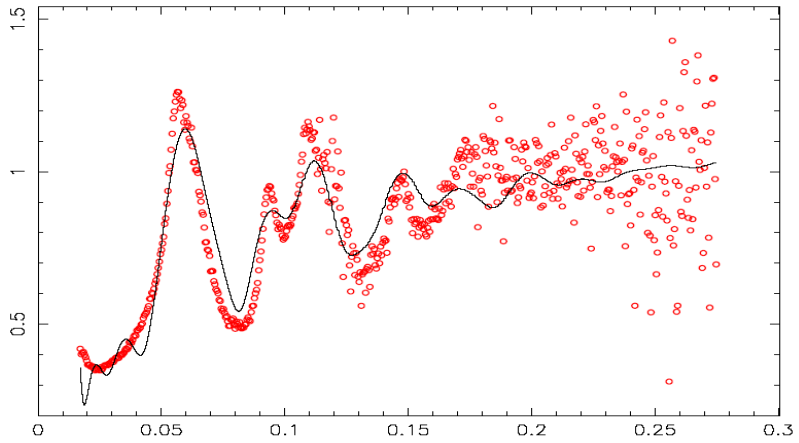
Planar Clusters of 110 Rods

Structure factor simulation as 5 <110> rods with 1 to 12 molecules per rod

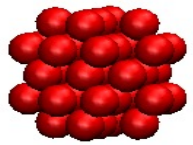


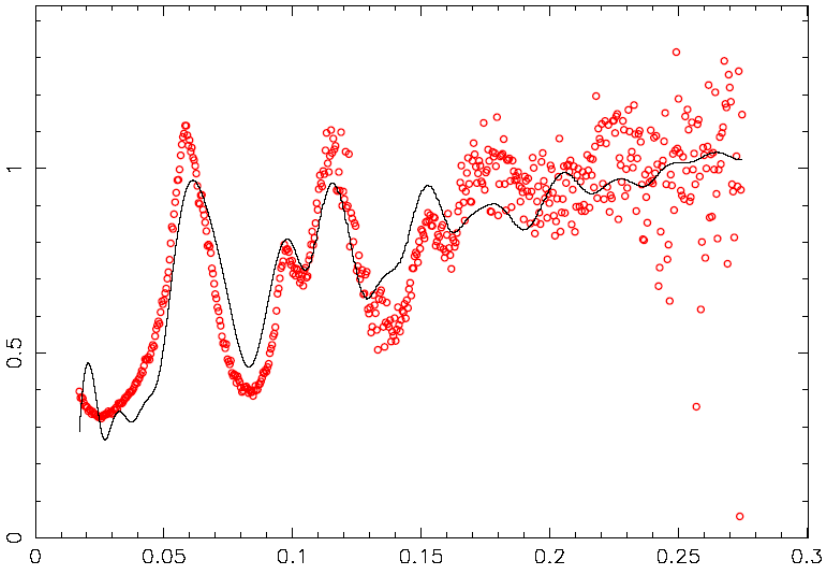


Best Fits

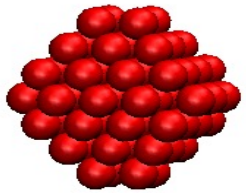


T=–10ºC
Cluster Size = 36



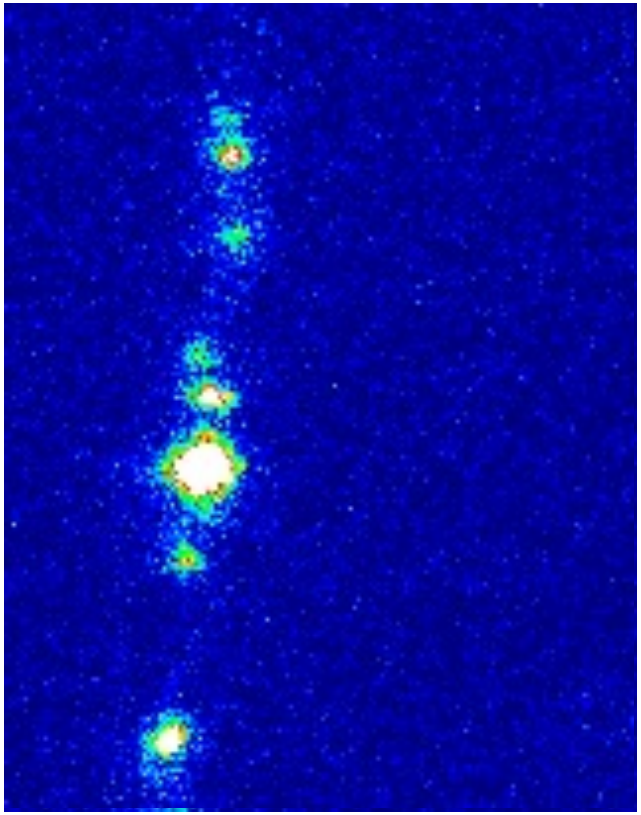


T=–13ºC
Cluster Size = 63

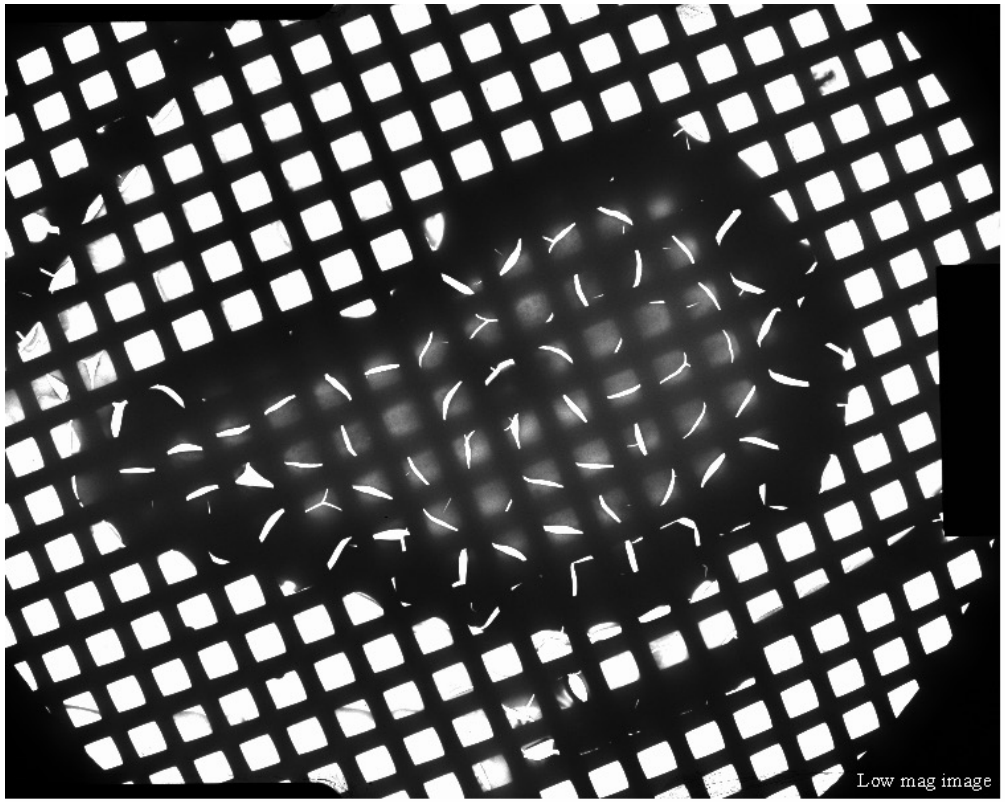


Ferritin (111) Powder Ring

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

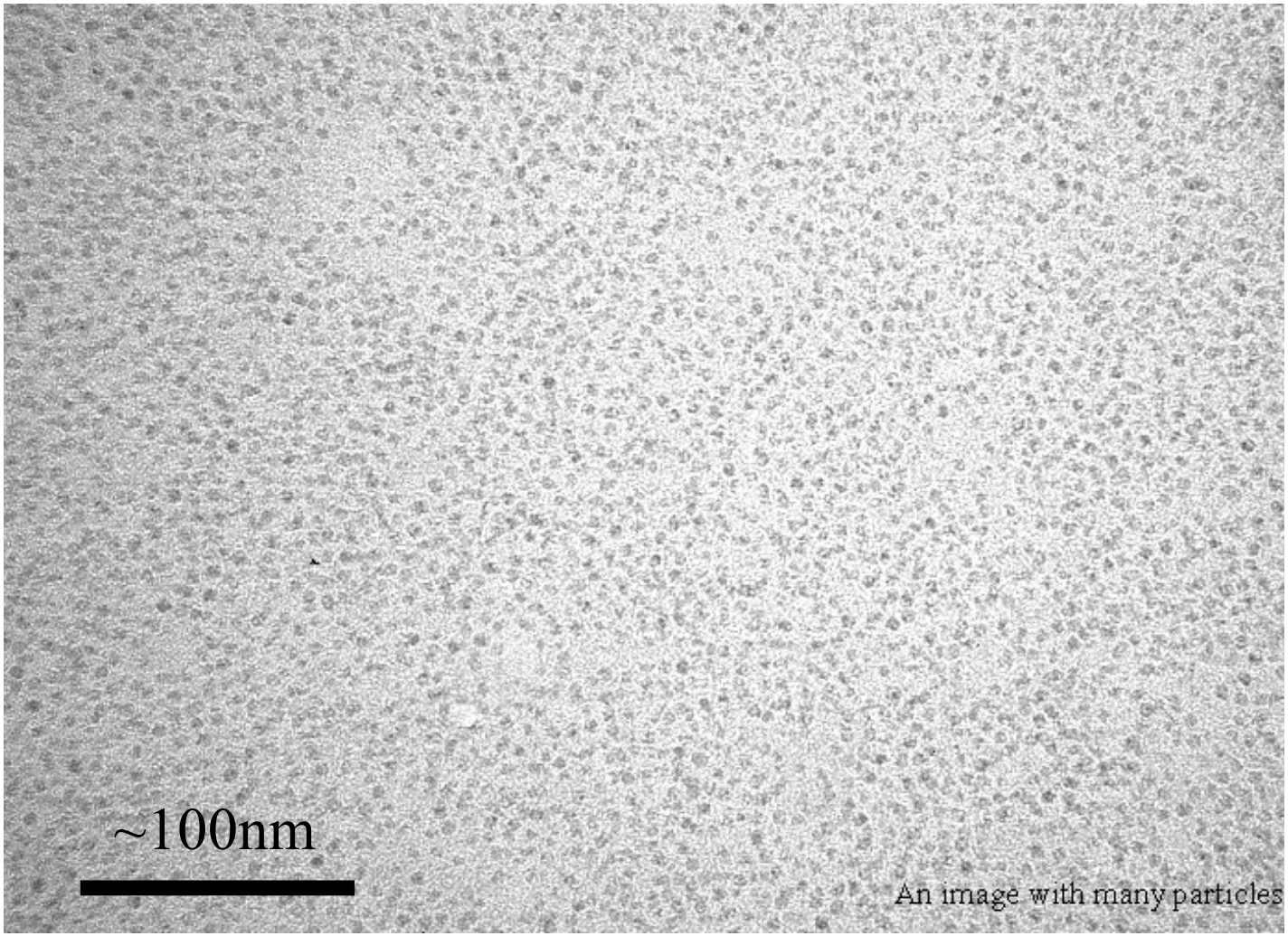


Overview of EM grid

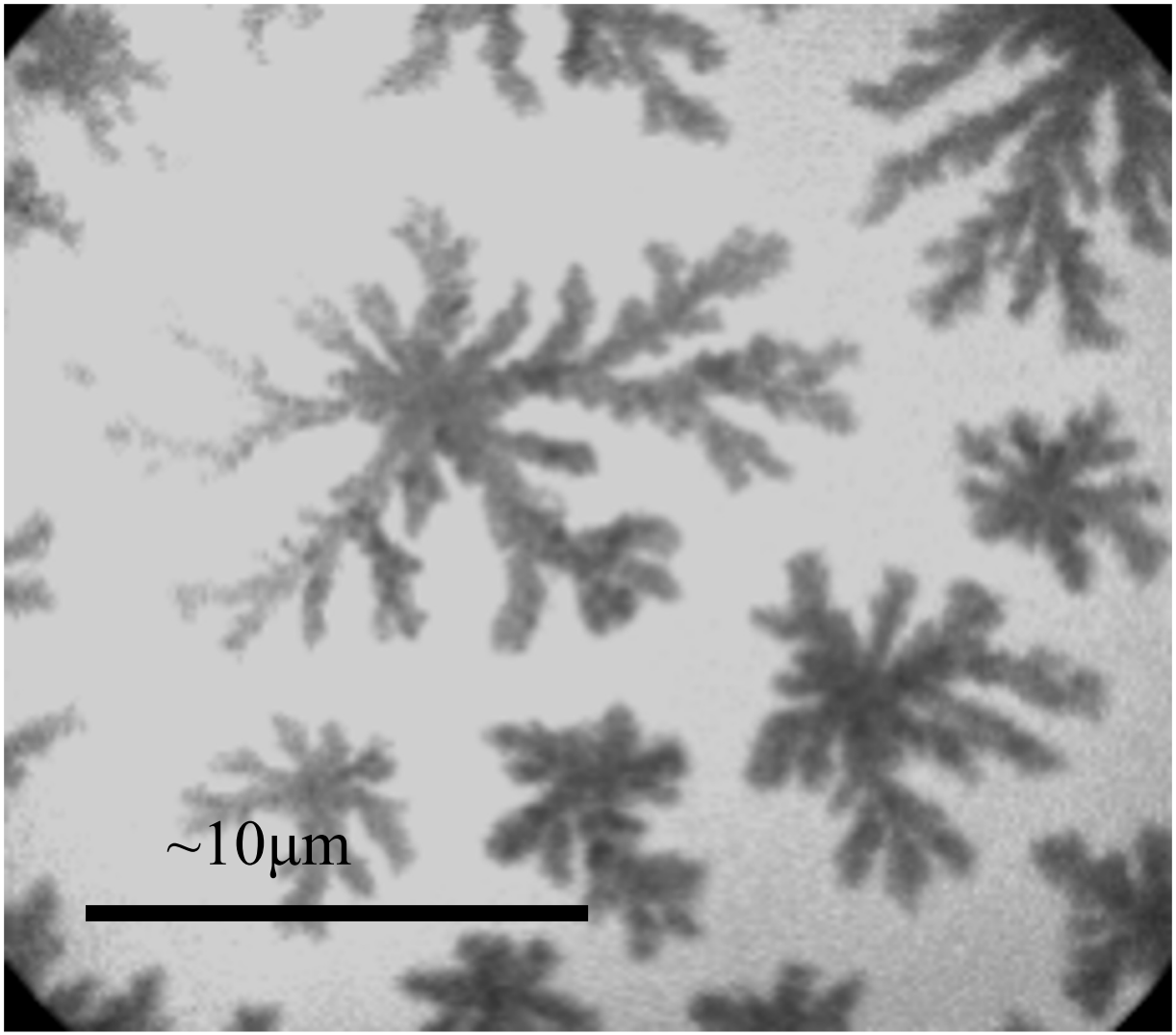


- 3mm diam grid
- a-carbon + "Formvar"
- 10mg/ml Ferritin
- 10mg/ml NaCl
- dipped grid
- dried in air
- no cryo-cooling
  - ▷three regions of different density

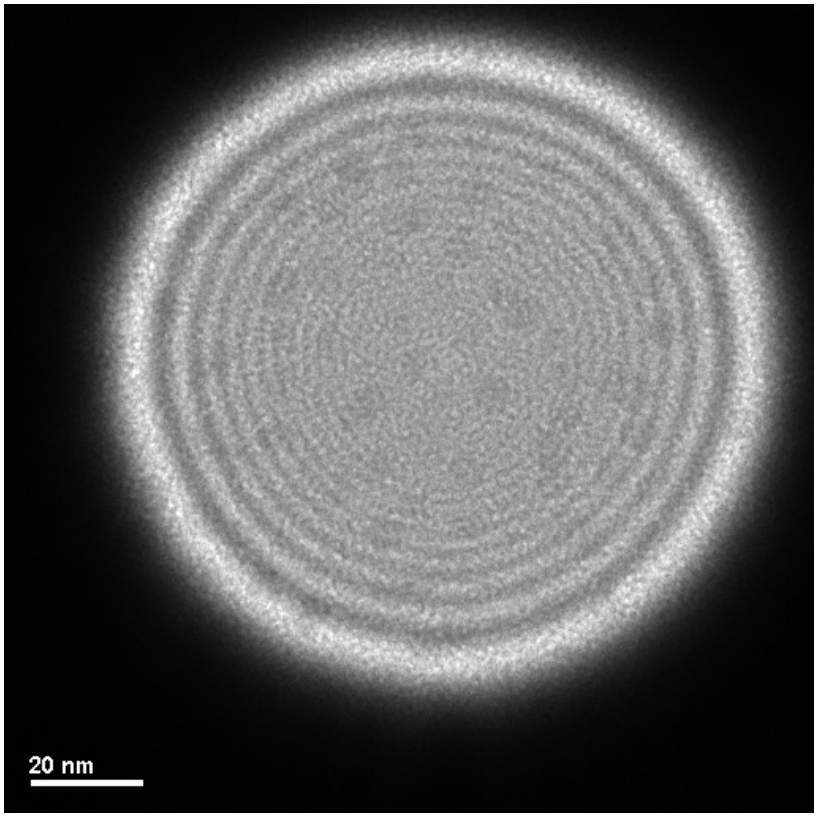
Border Region (low density)

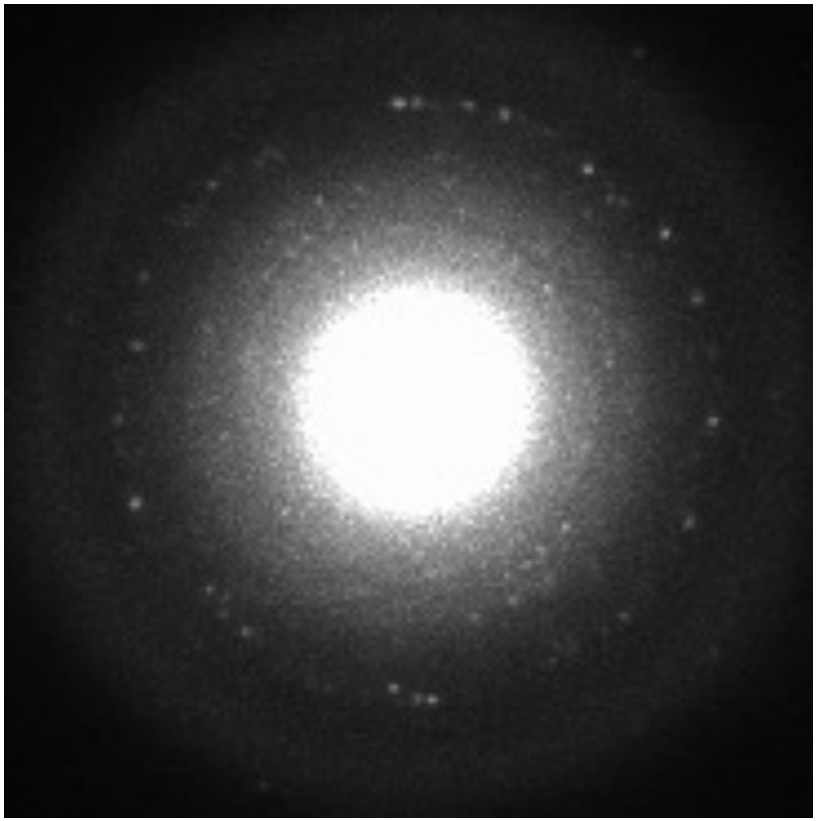


High Density Ring

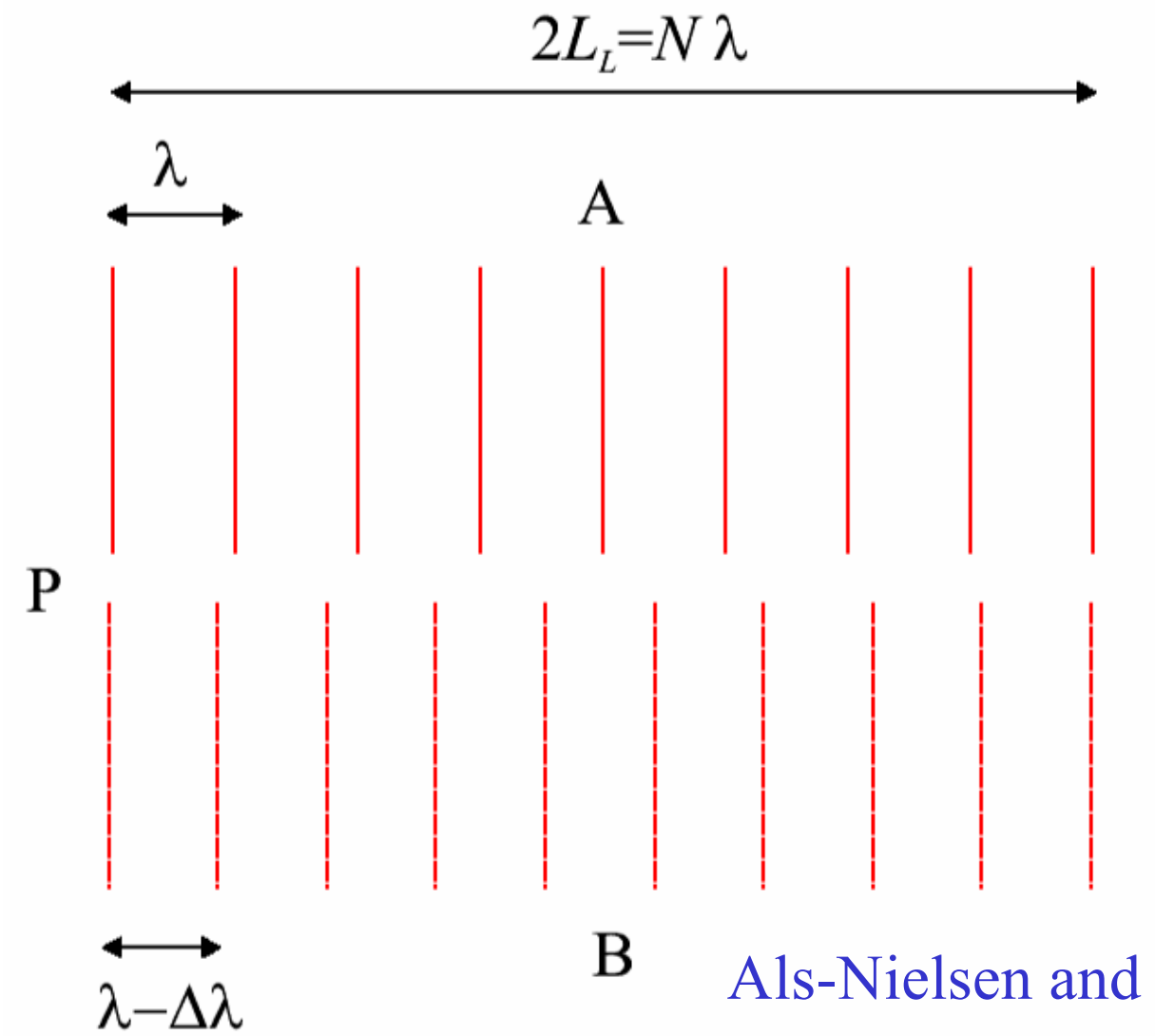


Diffraction from Border Region





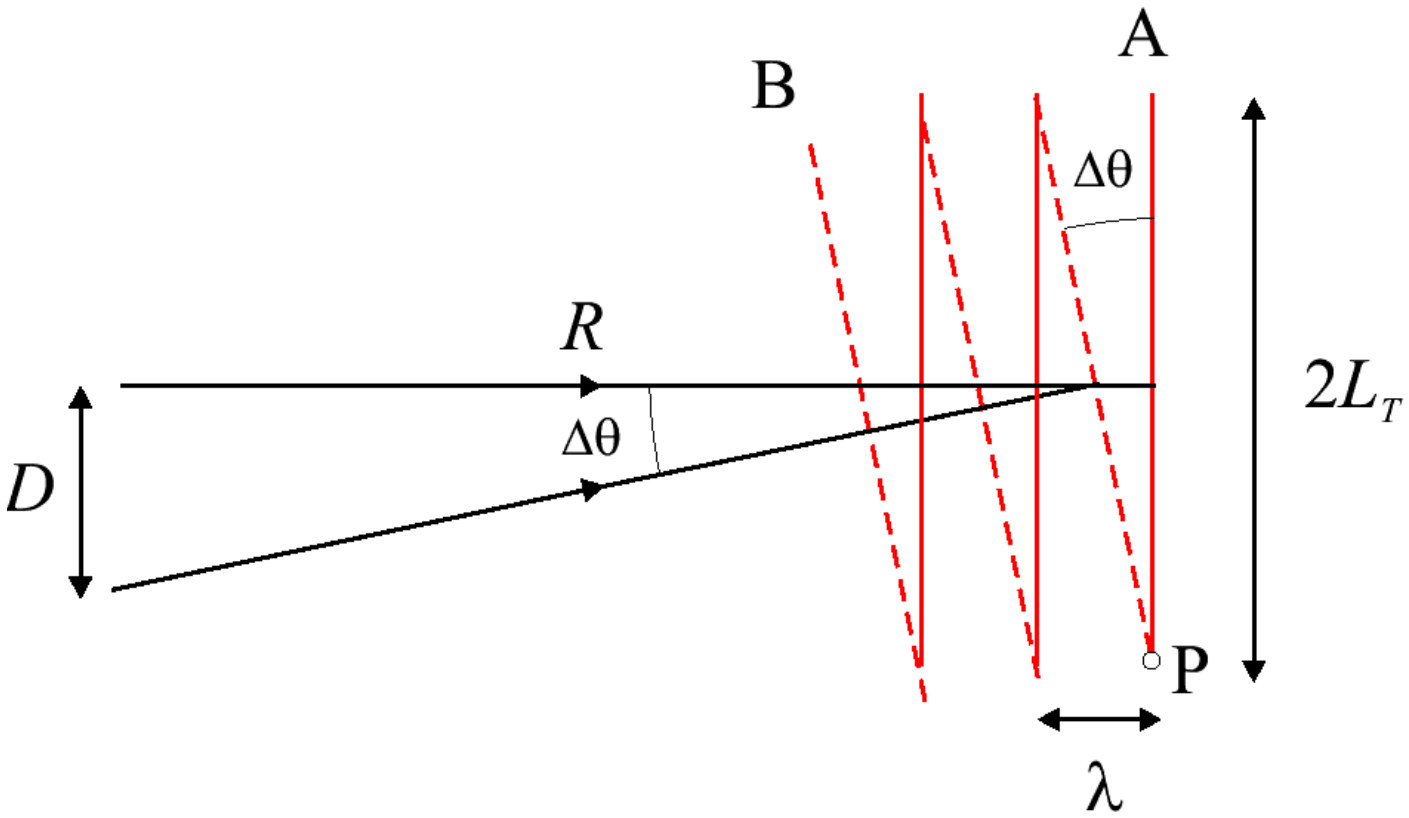
Longitudinal Coherence



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

Als-Nielsen and McMorrow (2001)

Lateral (Transverse) Coherence

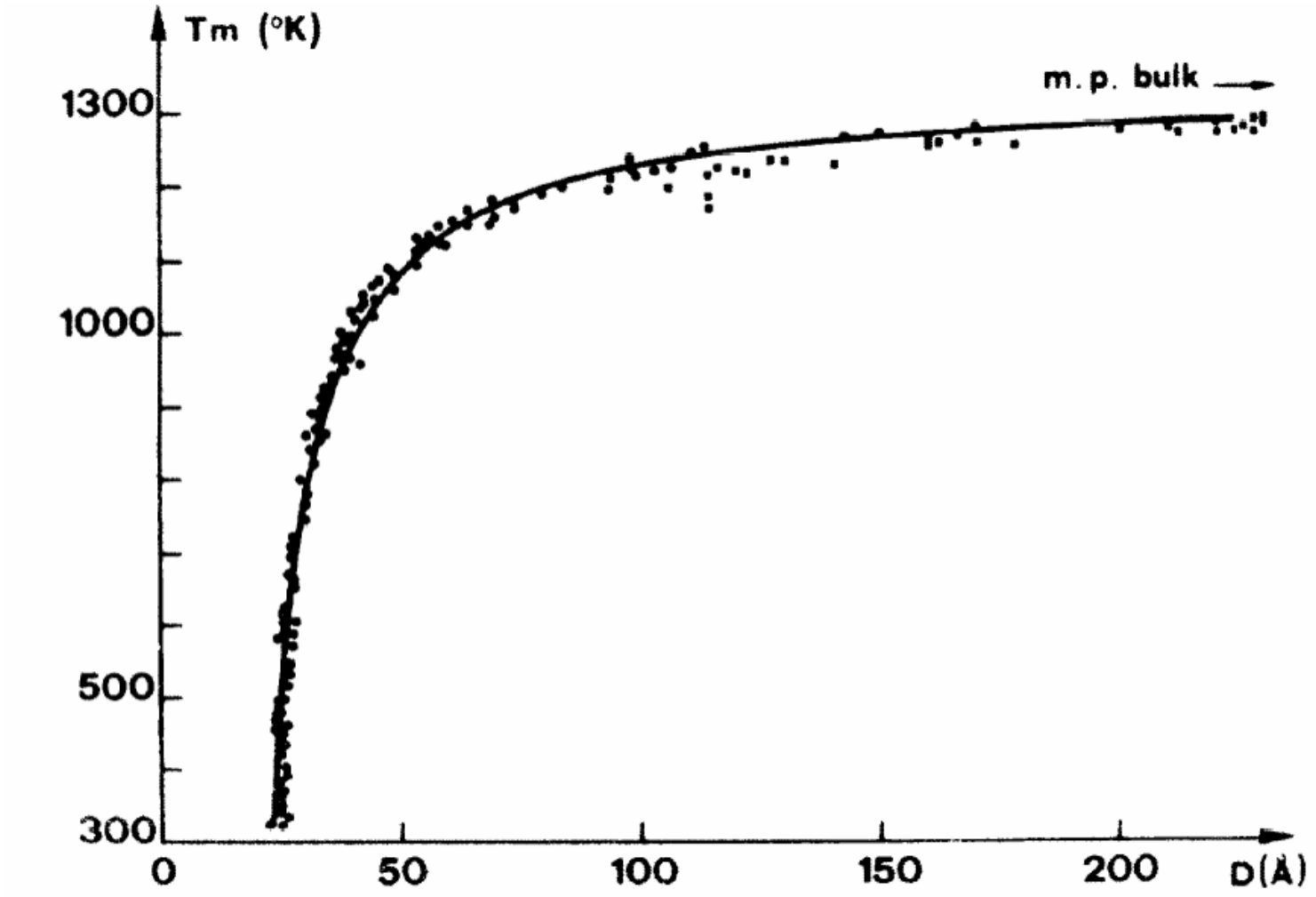


$$L_T = \frac{\lambda}{2}\frac{R}{D}$$

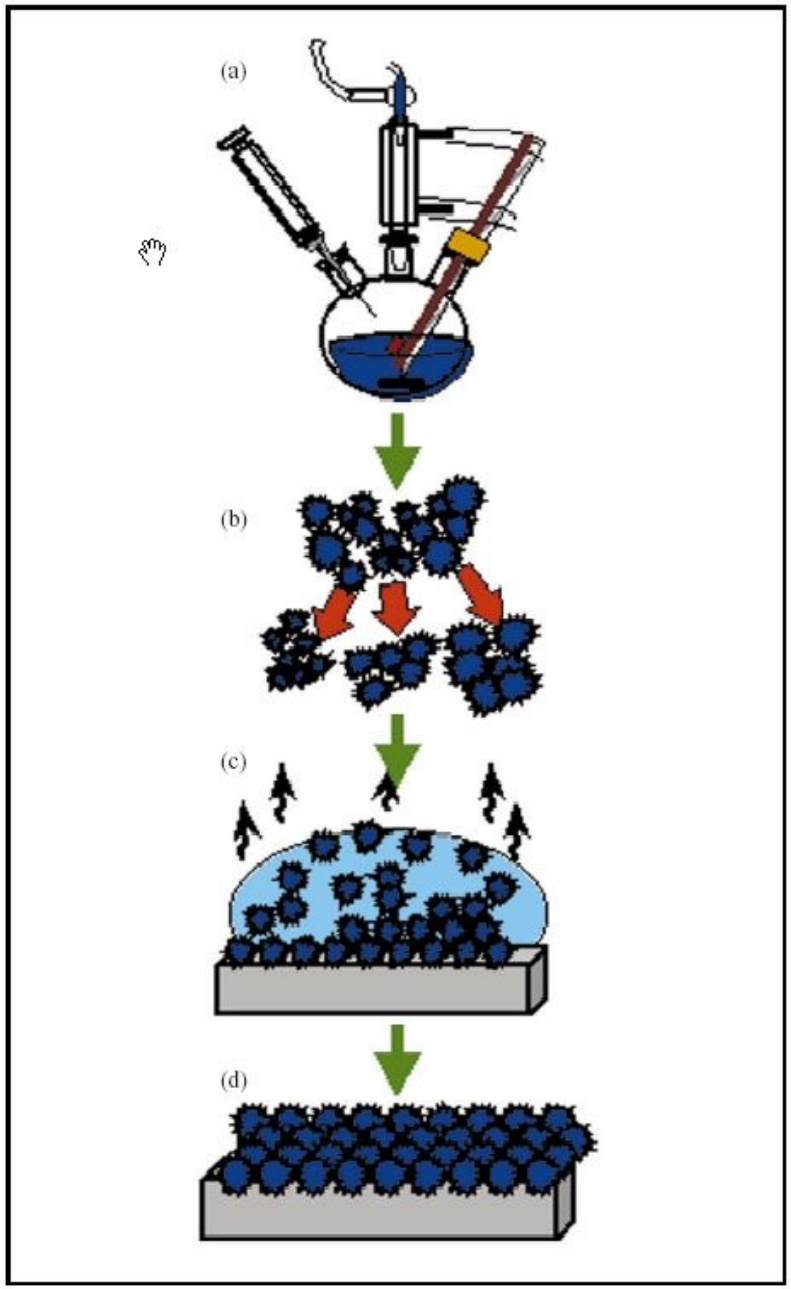
Als-Nielsen and McMorrow (2001)

Size-dependent Melting of Au Particles

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

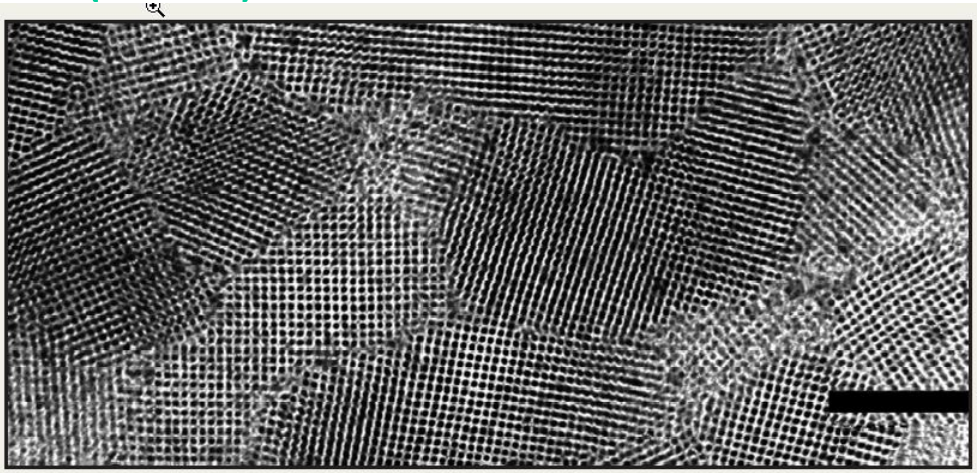


Chemical Synthesis of Nanocrystals

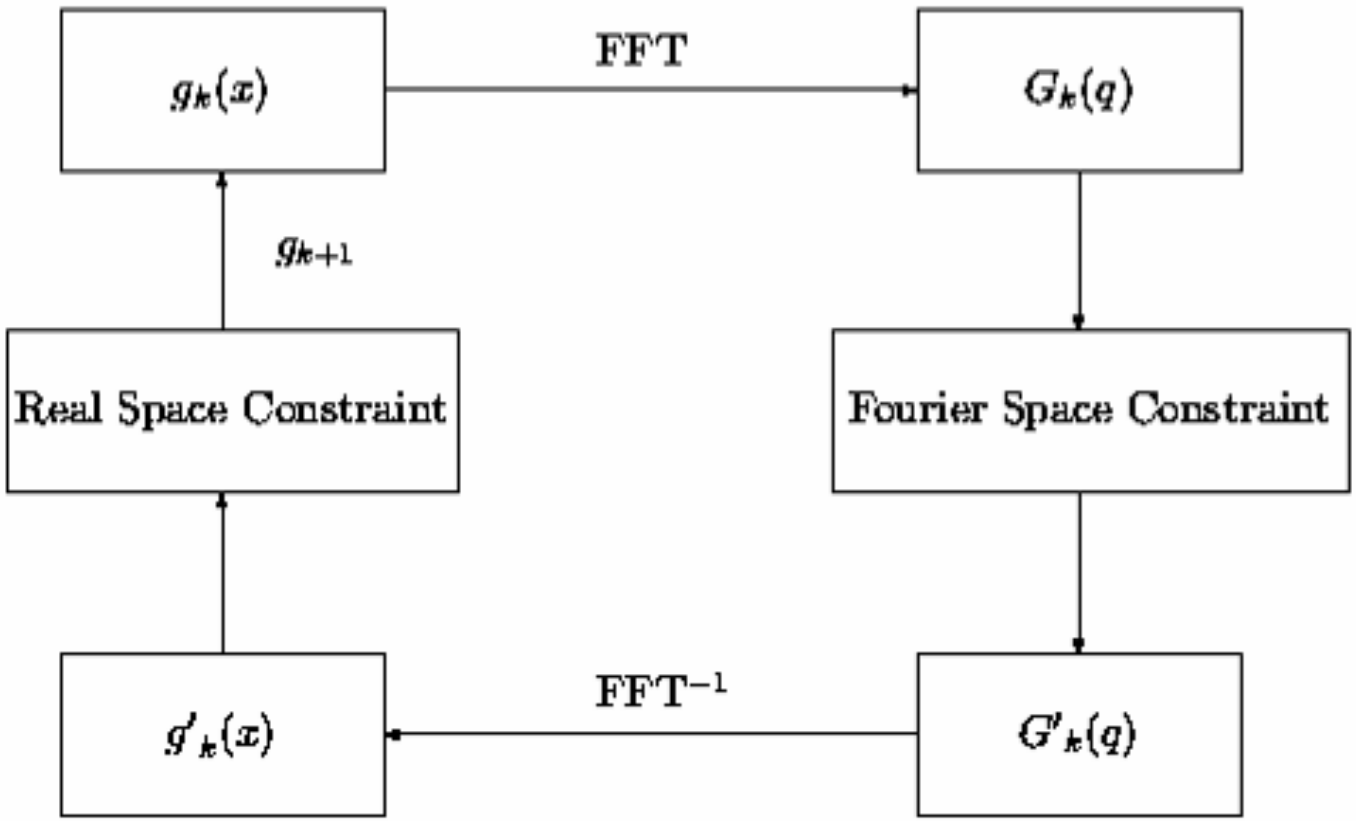


- Reactants introduced rapidly
- High temperature solvent
- Surfactant/organic capping agent
- Square superlattice (200nm scale)

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



Generic "Error Reduction" method



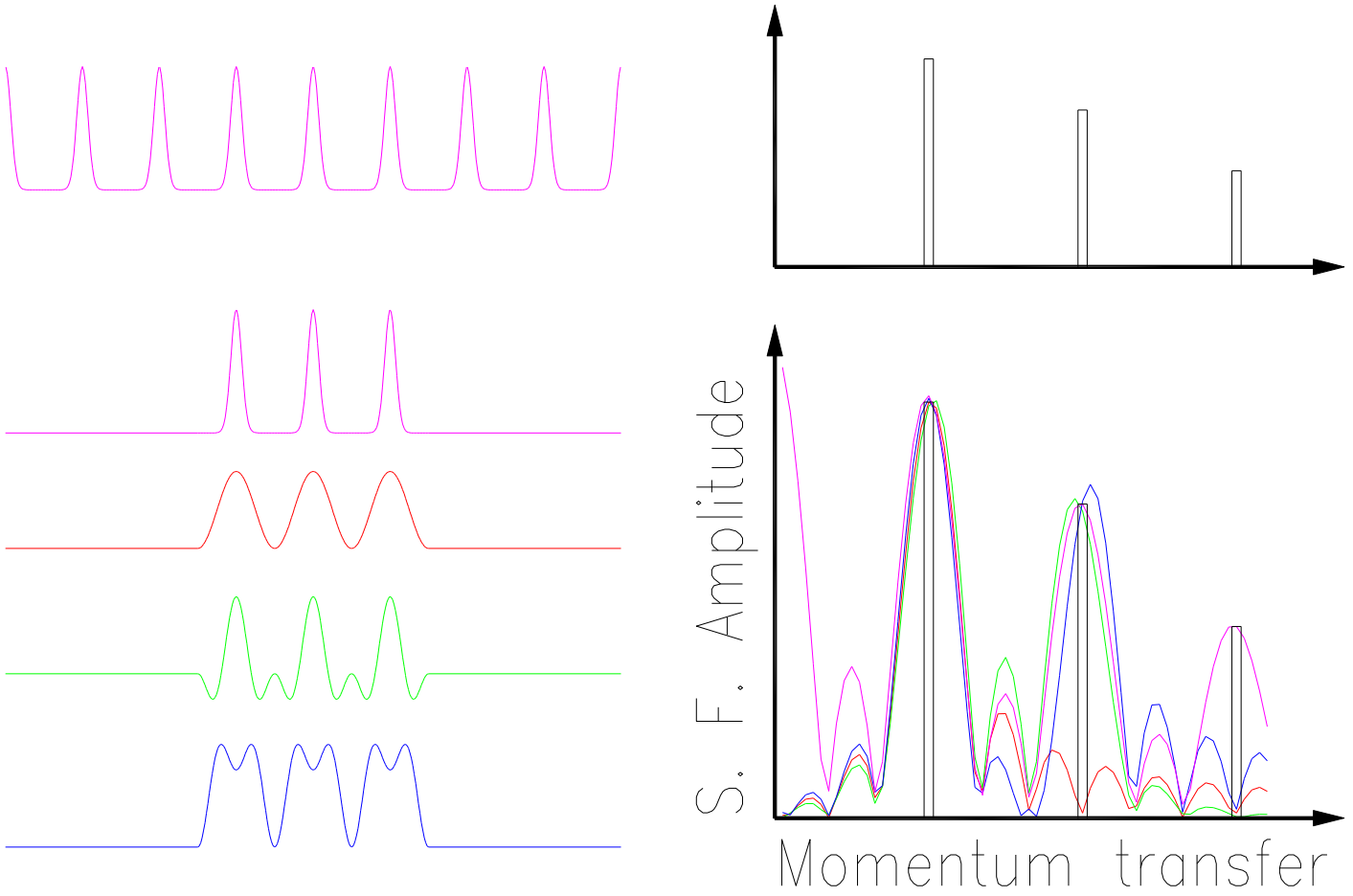
J. R. Fienup Appl. Opt. 21 2758 (1982)
R. W. Gerchberg and W. O. Saxton Optik 35 237 (1972)

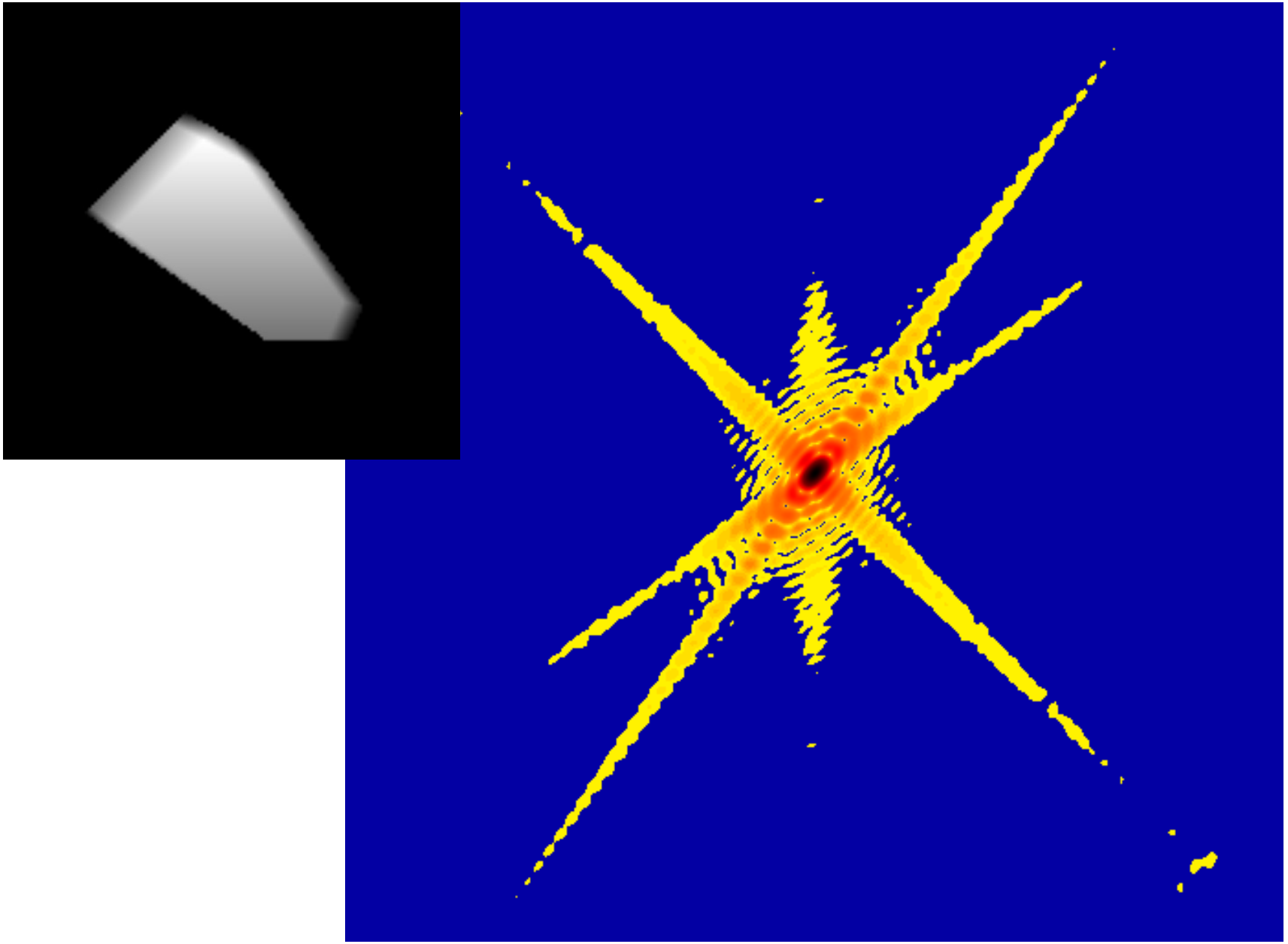
Real-space Constraints in Crystallograhy

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

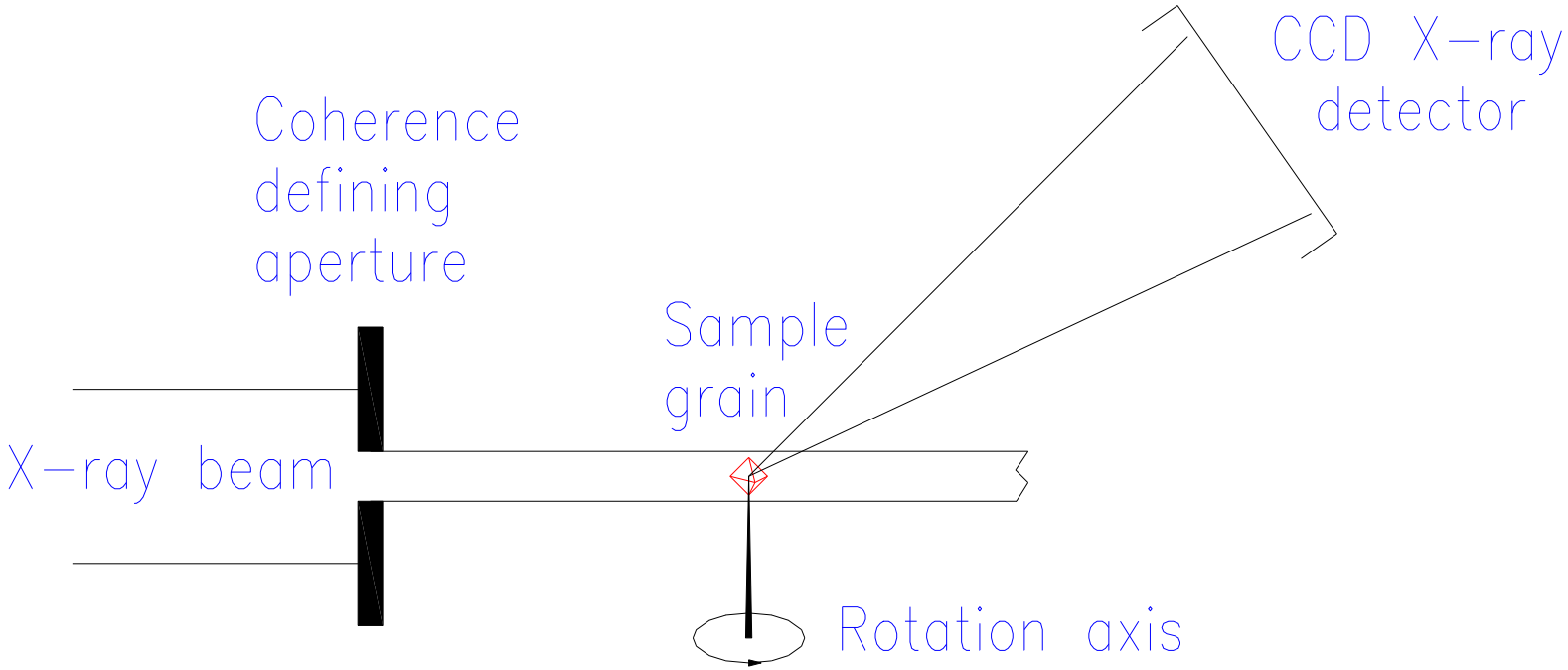
- 'Positivity' and 'Atomicity' constraints (Sayre)
- Finite support, molecular envelope
- Solvent flattening/Molecular replacement
- Non-crystallographic symmetry
- Non-uniqueness is 'pathologically rare' (d>1)
- Uses memory to avoid stagnation (Fienup HIO)

Oversampling solves Phase Problem

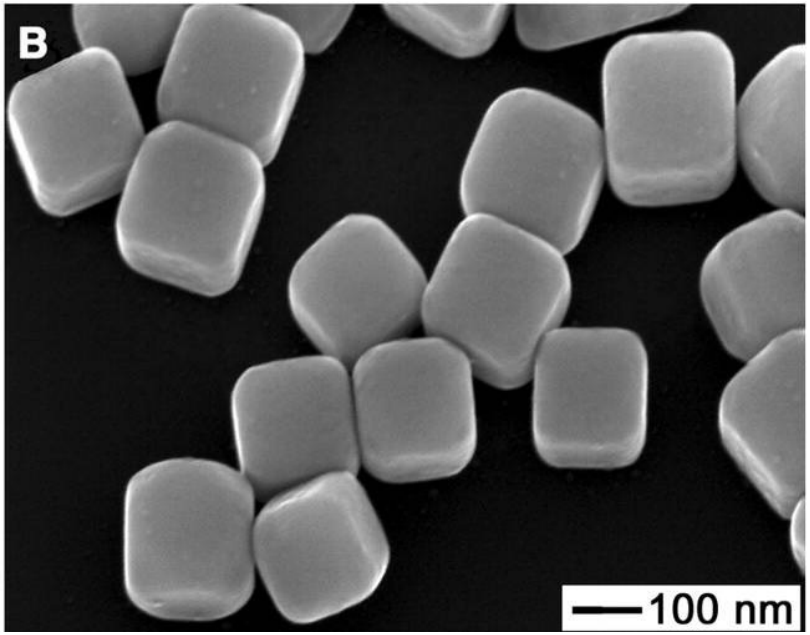


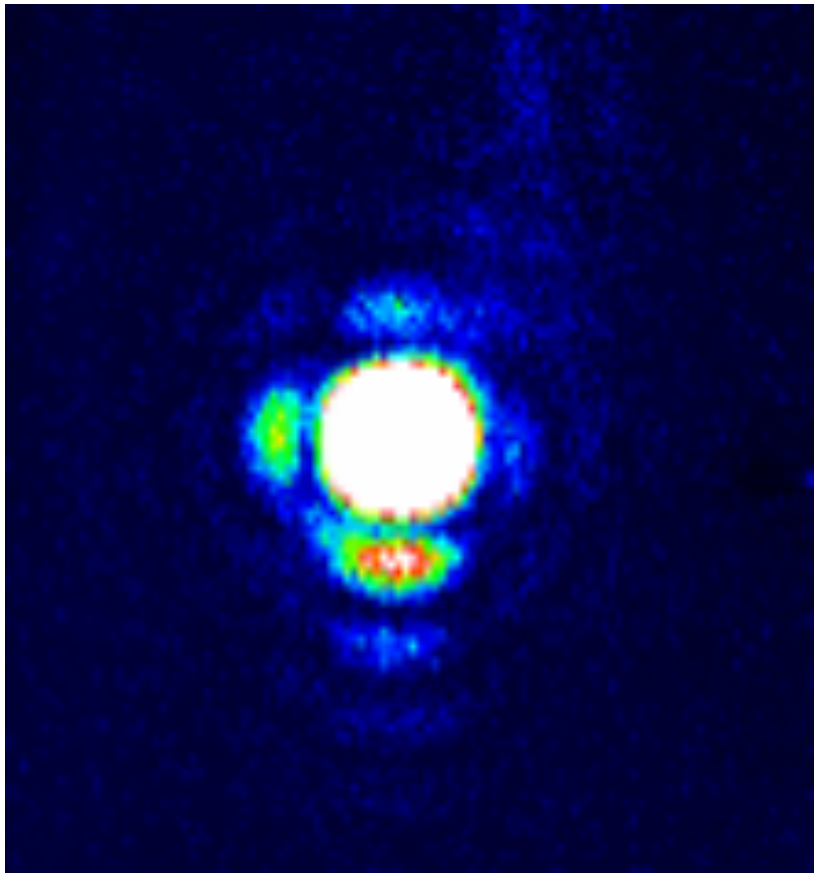


Lensless X-ray Microscope

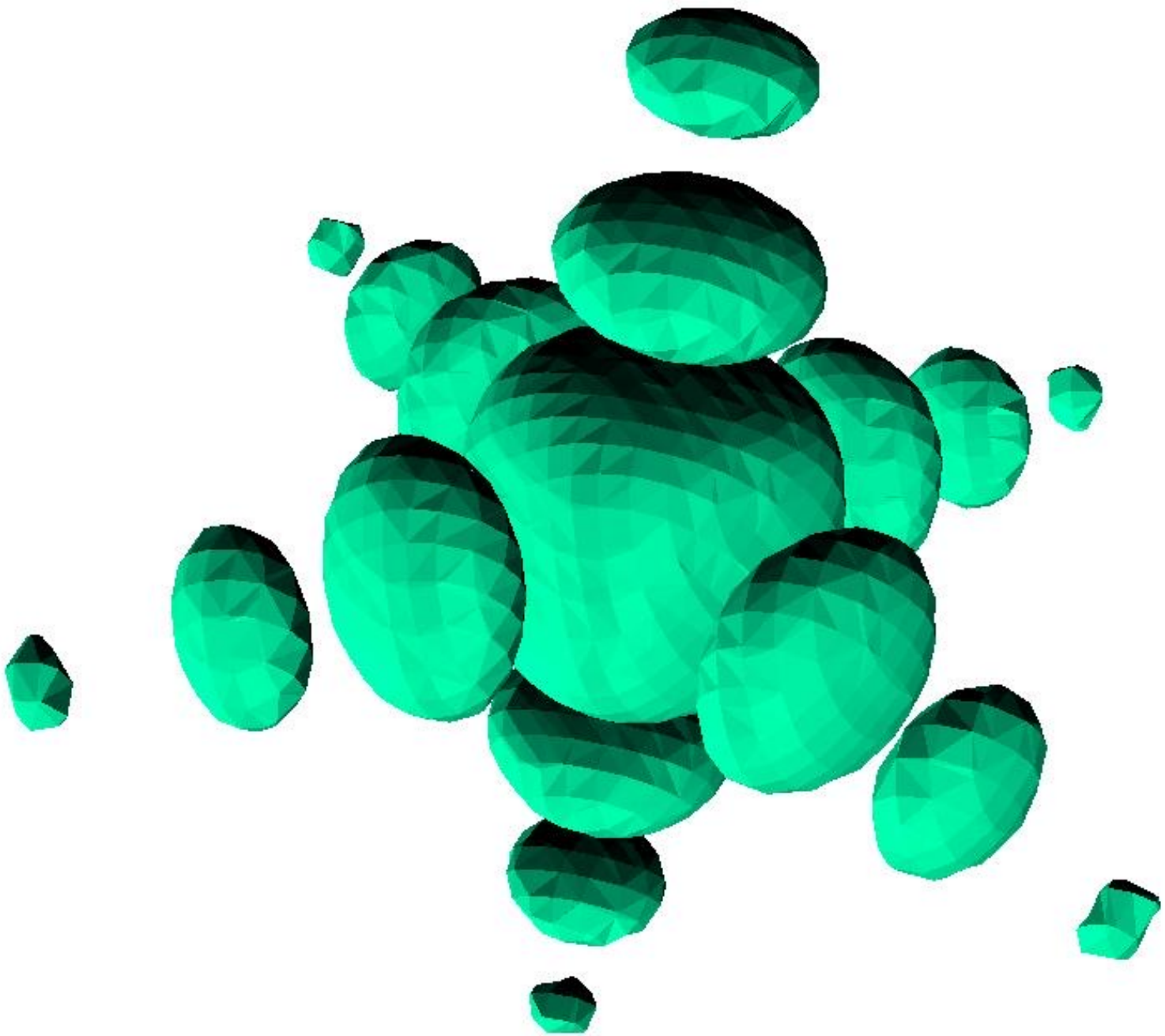


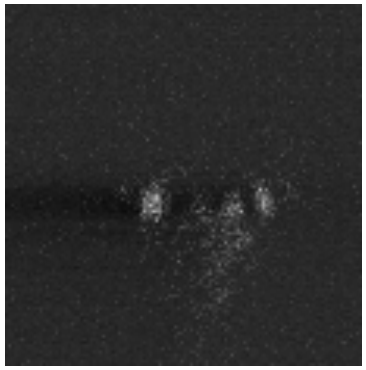
Chemically Synthesized Silver Nanocubes

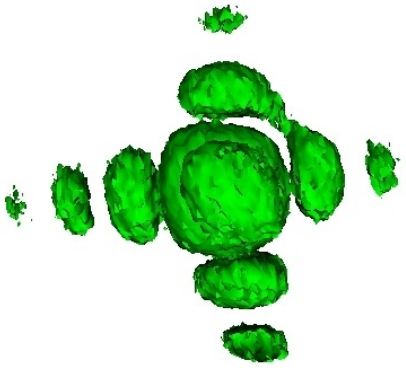


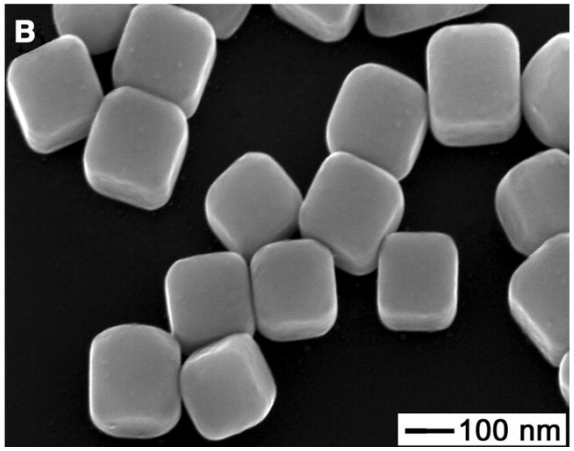


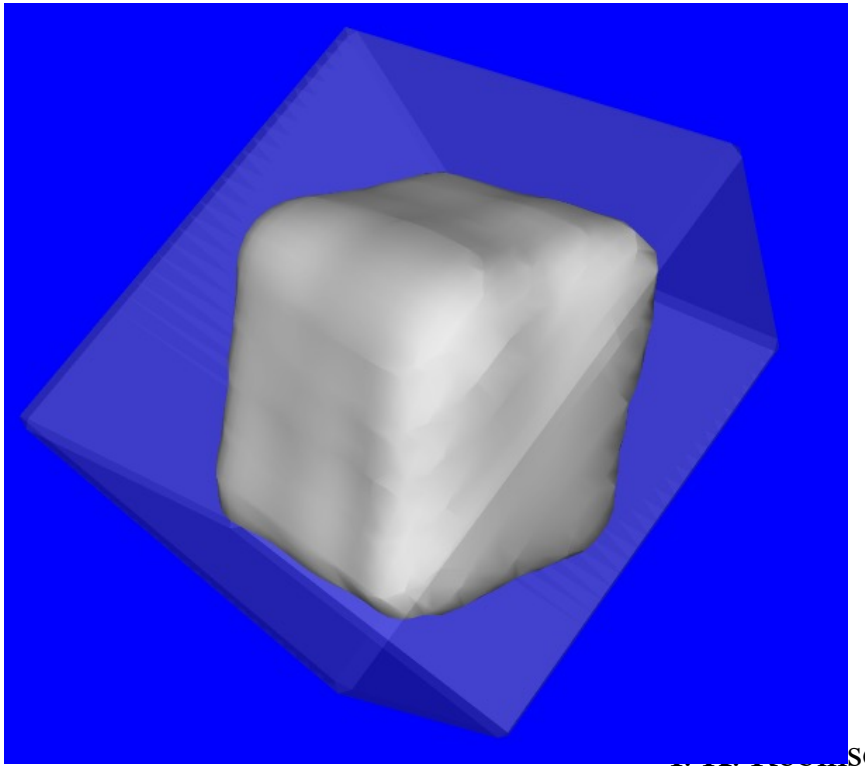
Yugang Sun and Younan Xia,
Science 298 2177 (2003)

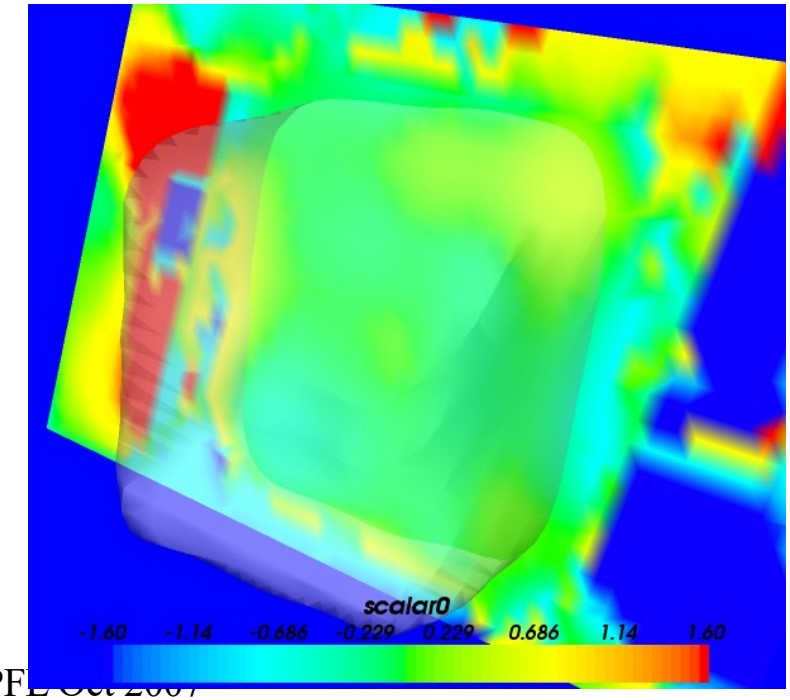




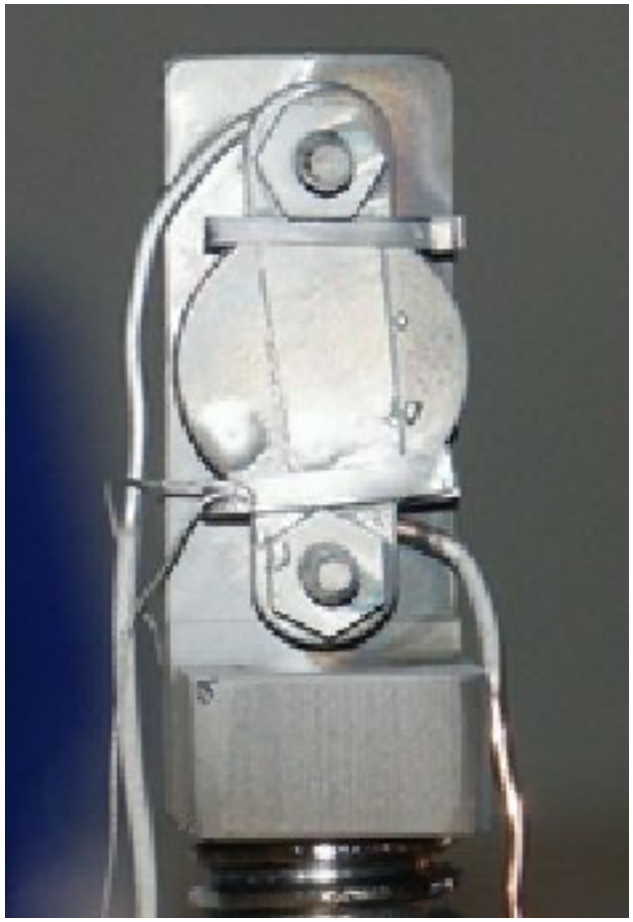


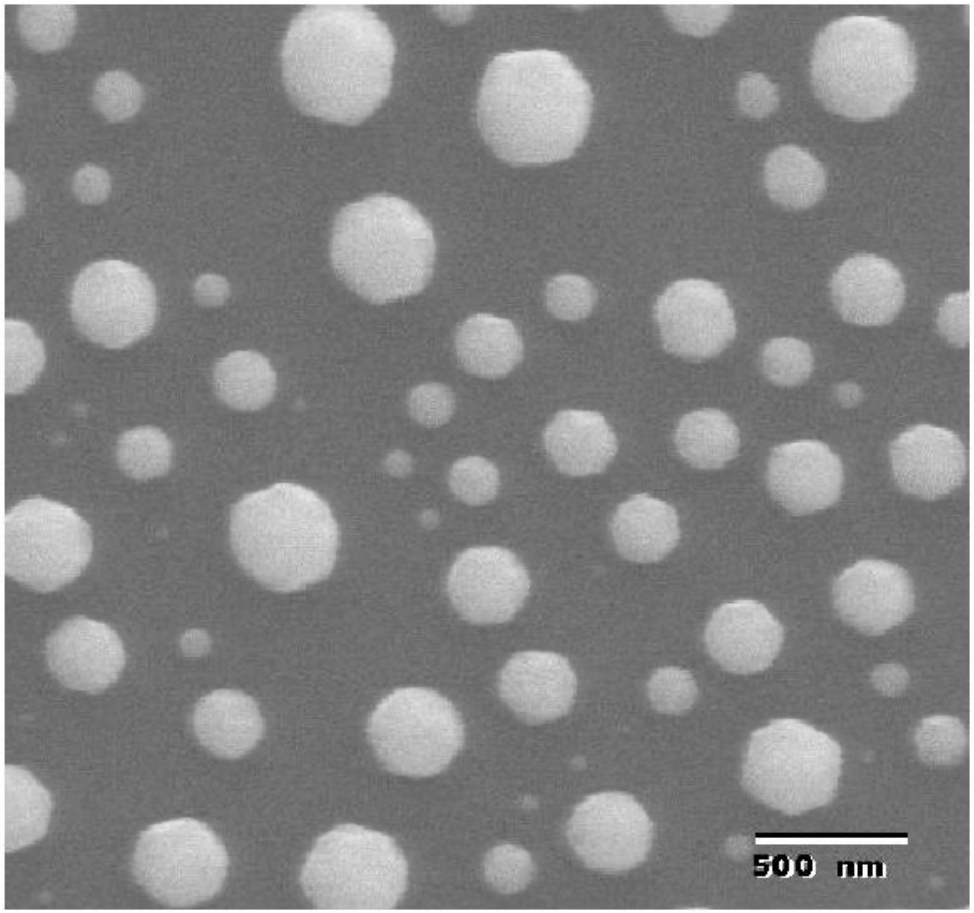

B
100 nm



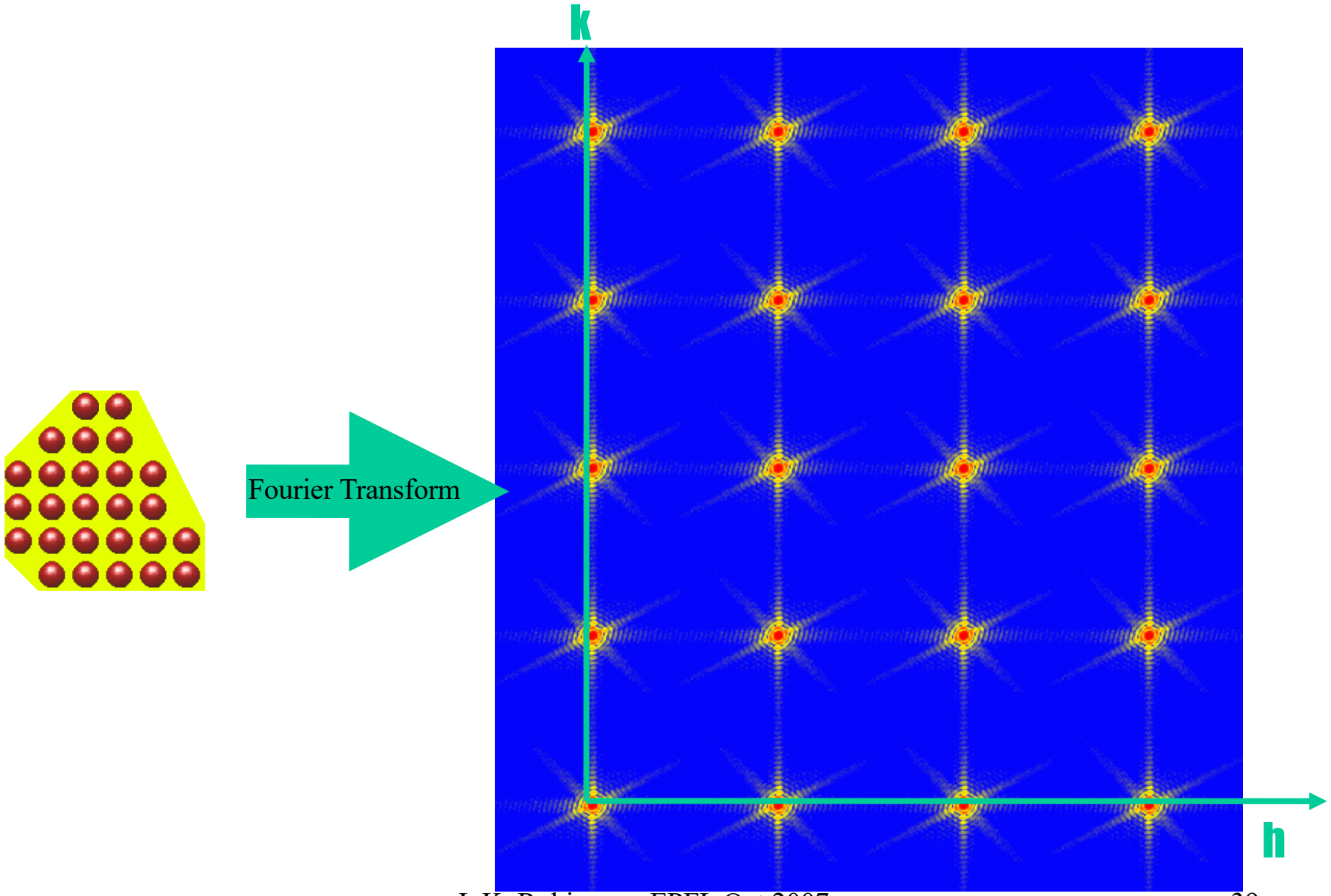

scalar0
-1.60 -1.14 -0.686 -0.229 0.229 0.686 1.14 1.60

In situ growth of Pb crystals





Coherent Diffraction from Crystals



Good statistics, 3D diffraction data

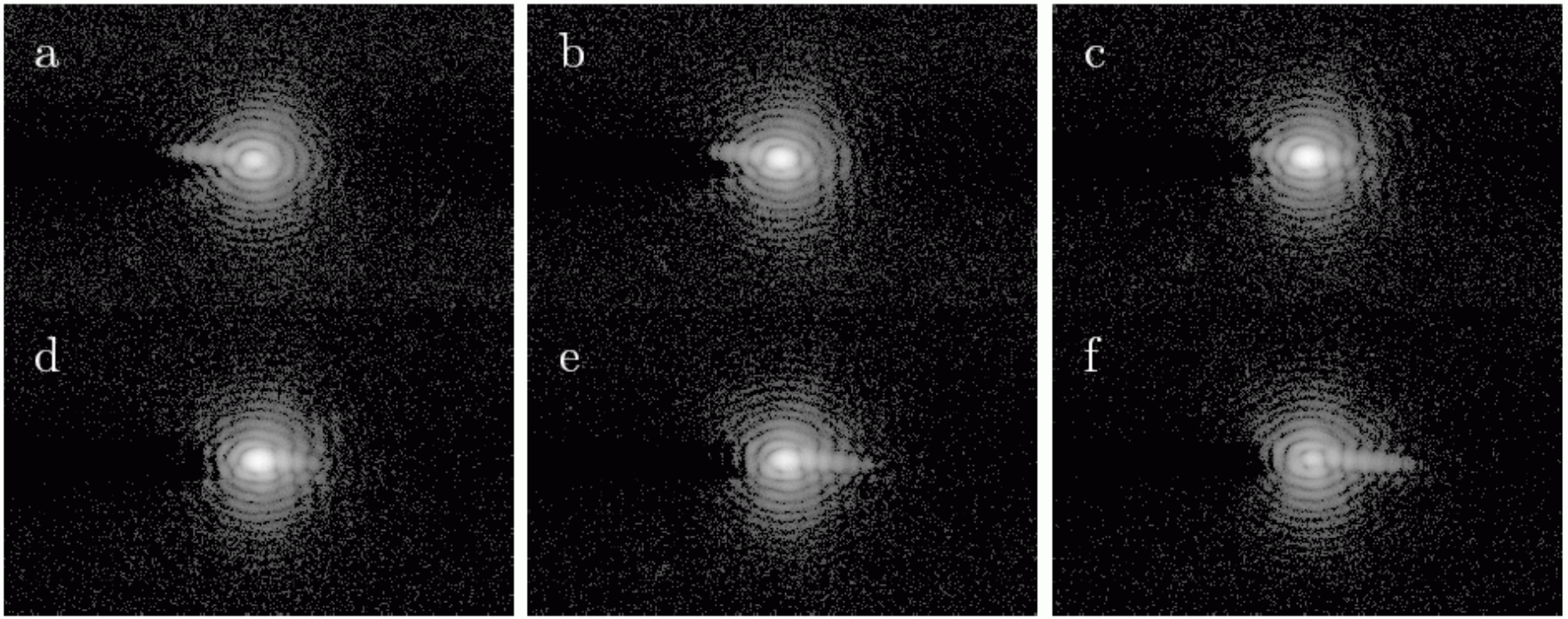
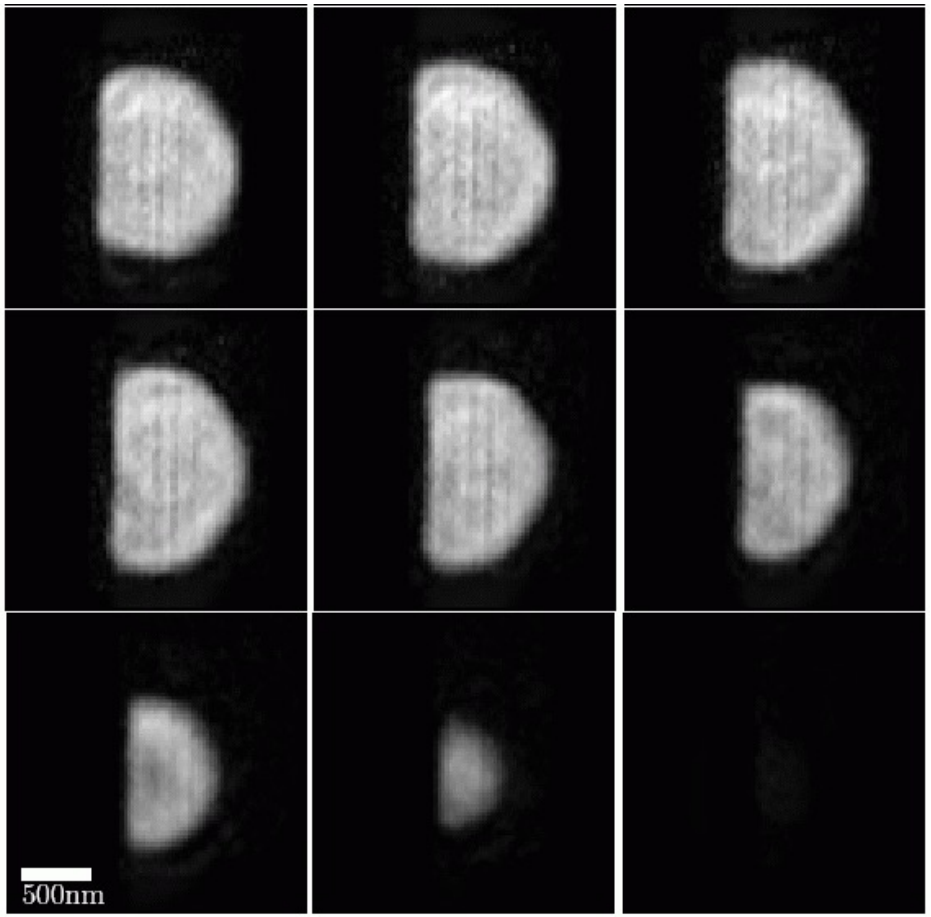
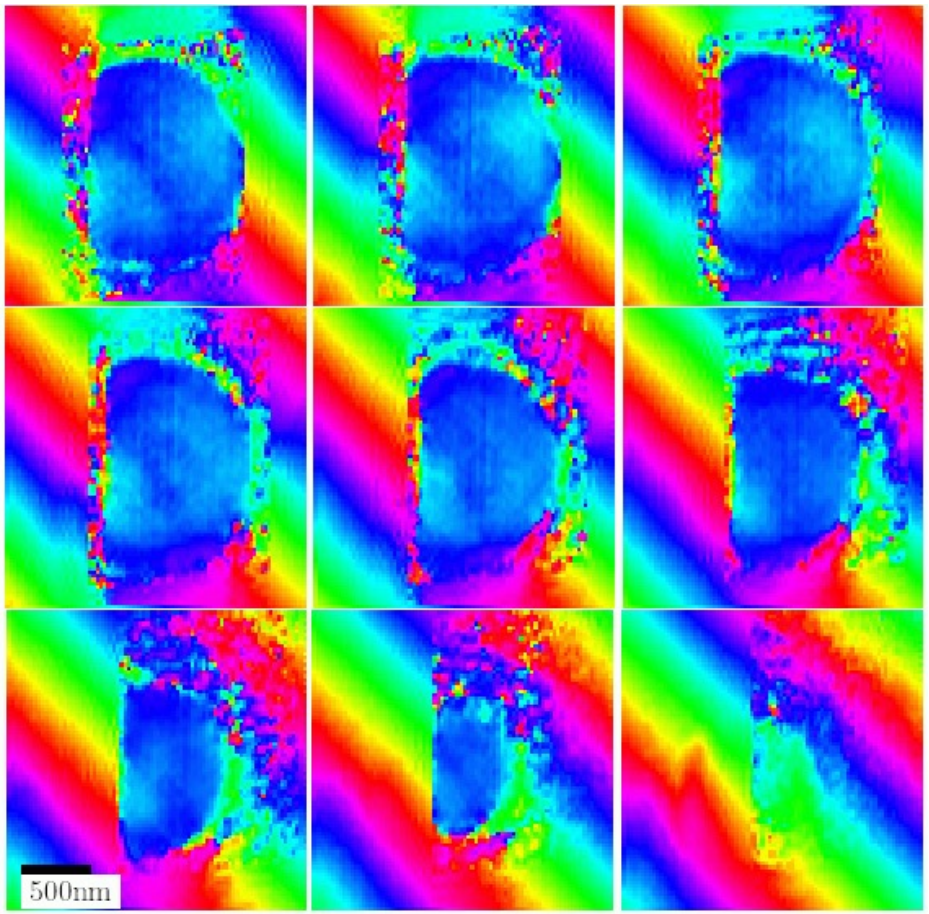


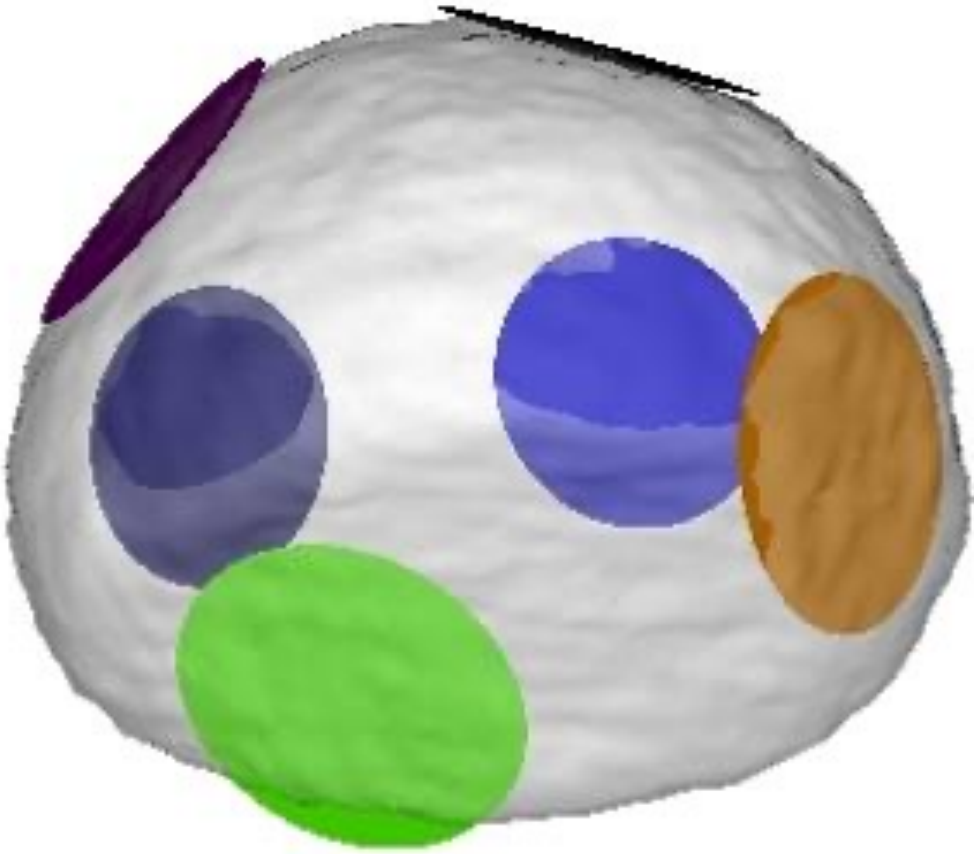
Figure 4.12: Center slices from 3D CXD pattern from Pb sample, on a log scale. Data file 296 from 10/03.

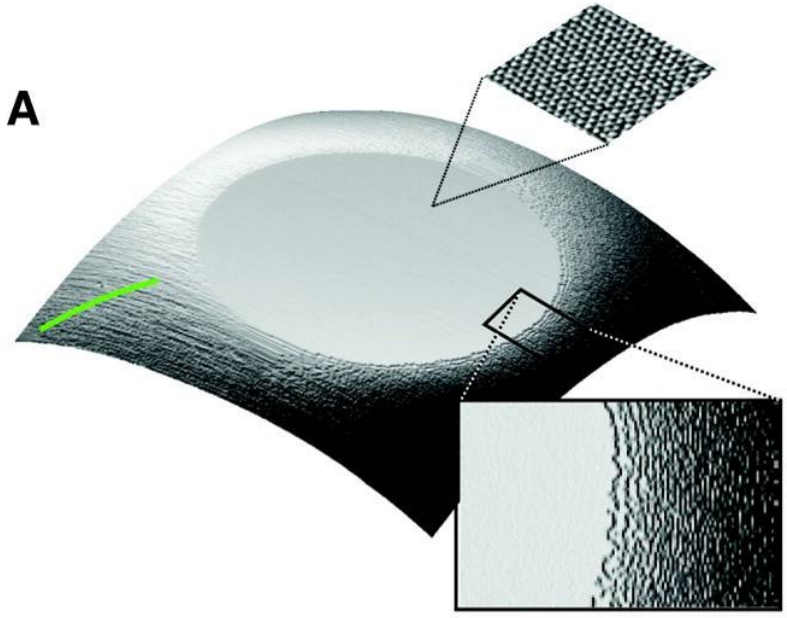
Complex Density (amplitude *and* phase)





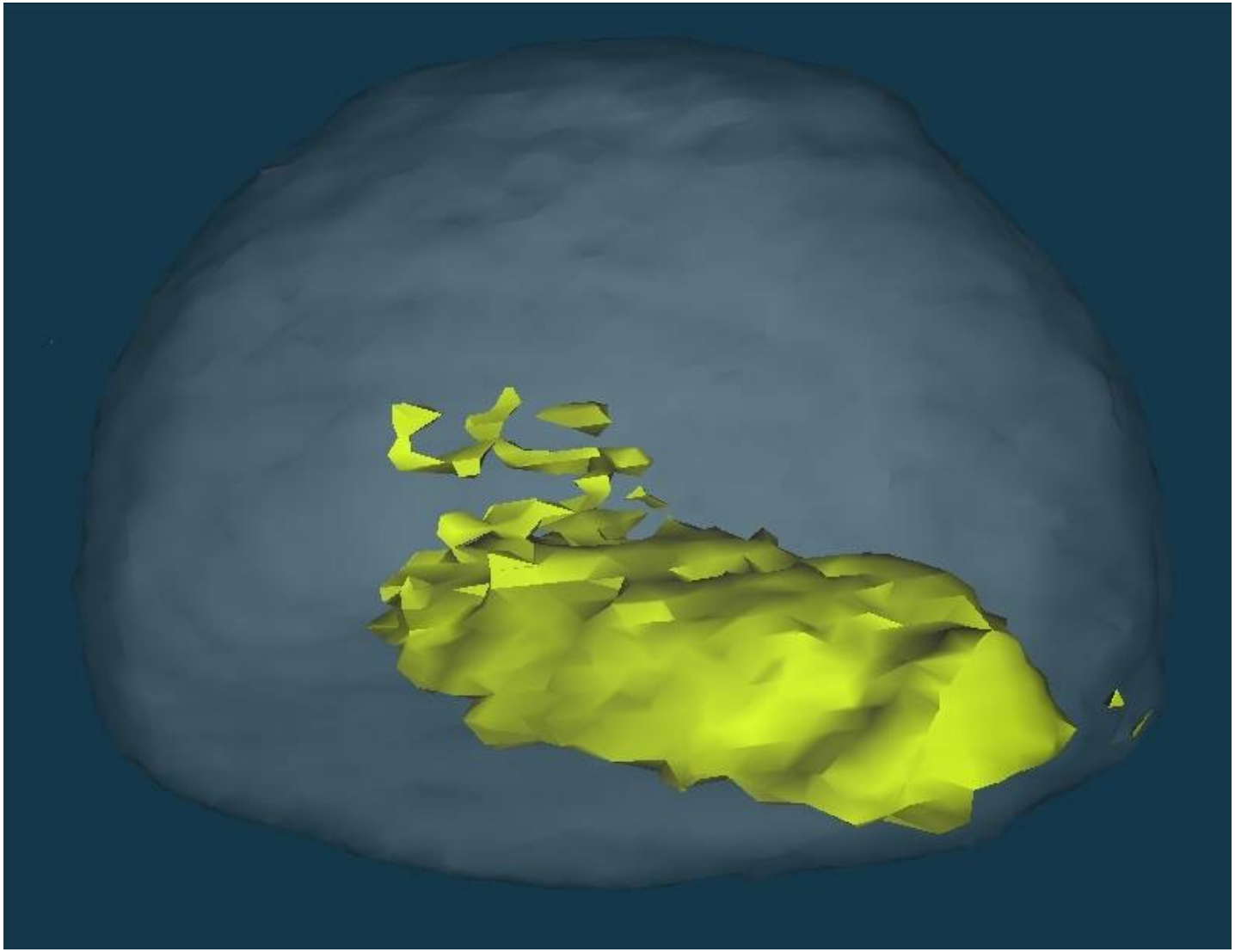
Facets of Equilibrium Crystal Shape



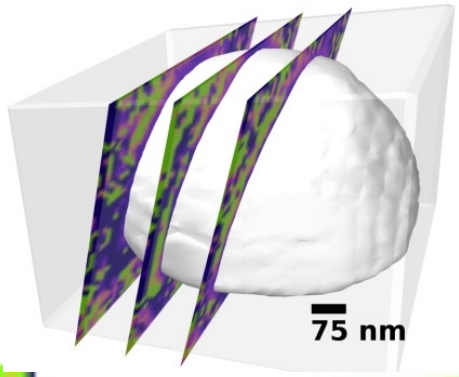


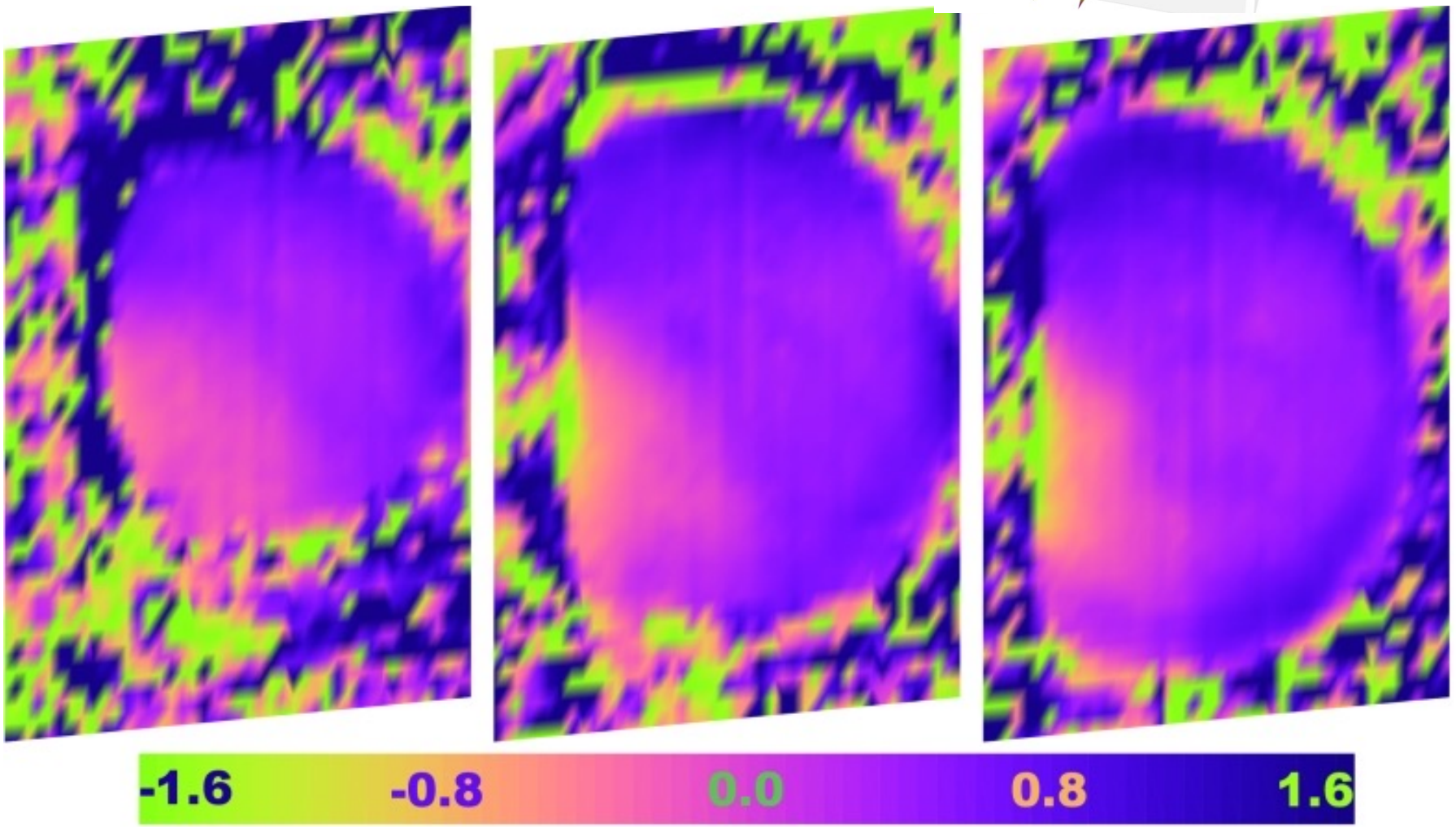
Thurmer K, Williams E, Reutt-Robey J
Science **297** 2033 (2002)

Modeling of 3D Phase Bump



3D phase map sections

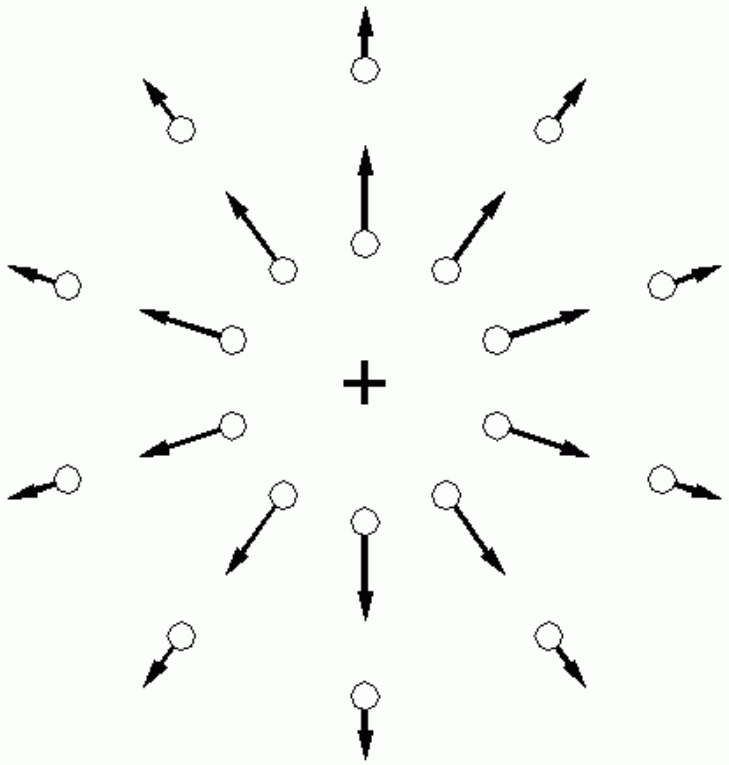


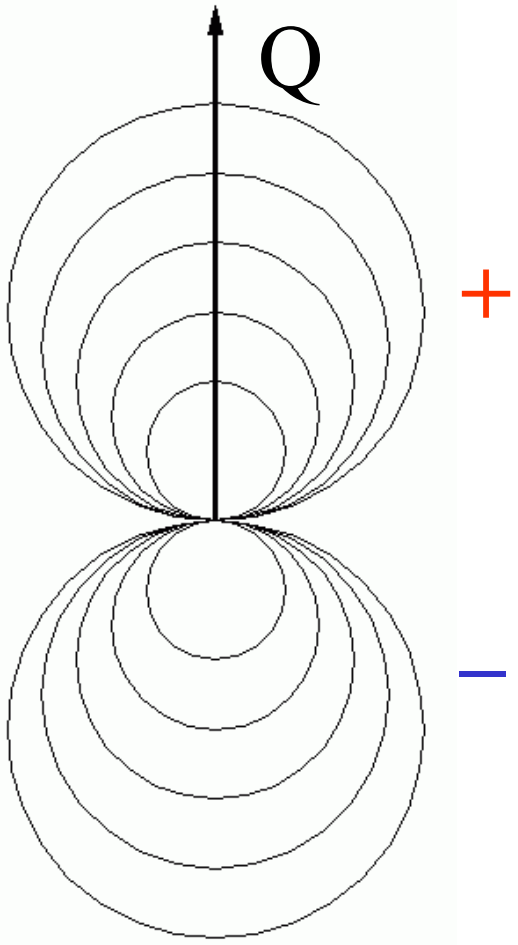


Diffraction by Strain of Point Defect

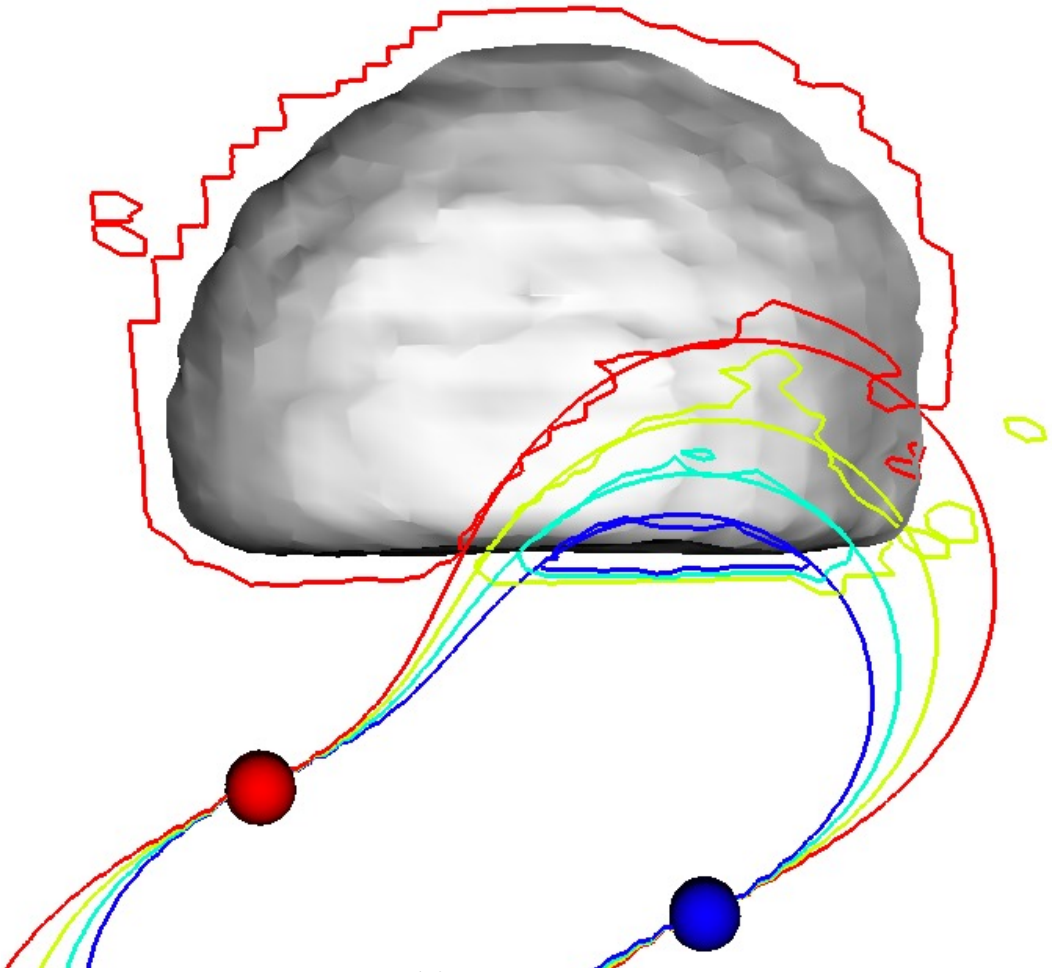
$$A \sim \sum e^{i\mathbf{Q}\cdot(\mathbf{R}_j+\mathbf{u}_j)}$$
$$\approx \sum e^{i\mathbf{Q}\cdot\mathbf{R}_j}(1+i\mathbf{Q}\cdot\mathbf{u}_j)$$

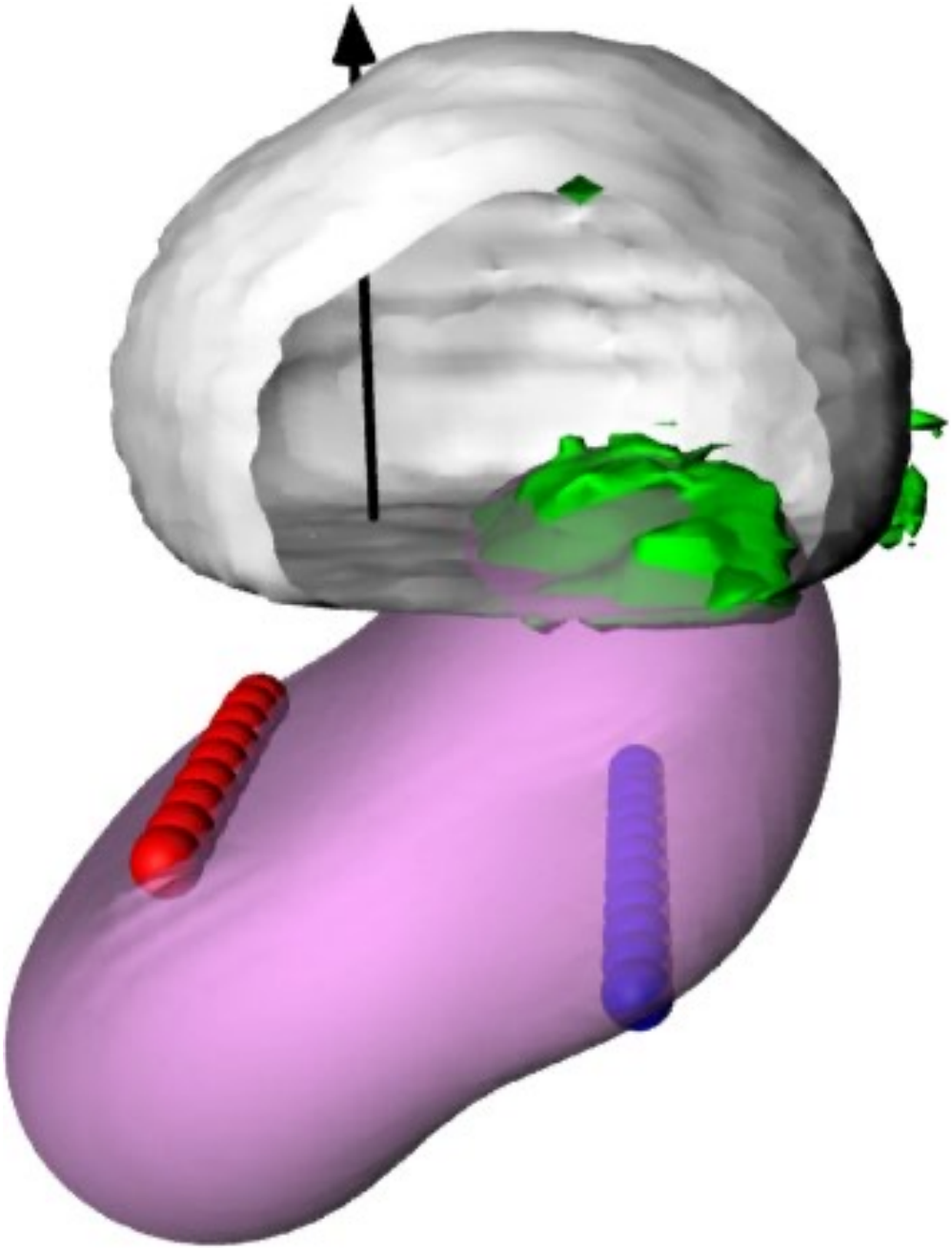
Imaginary density





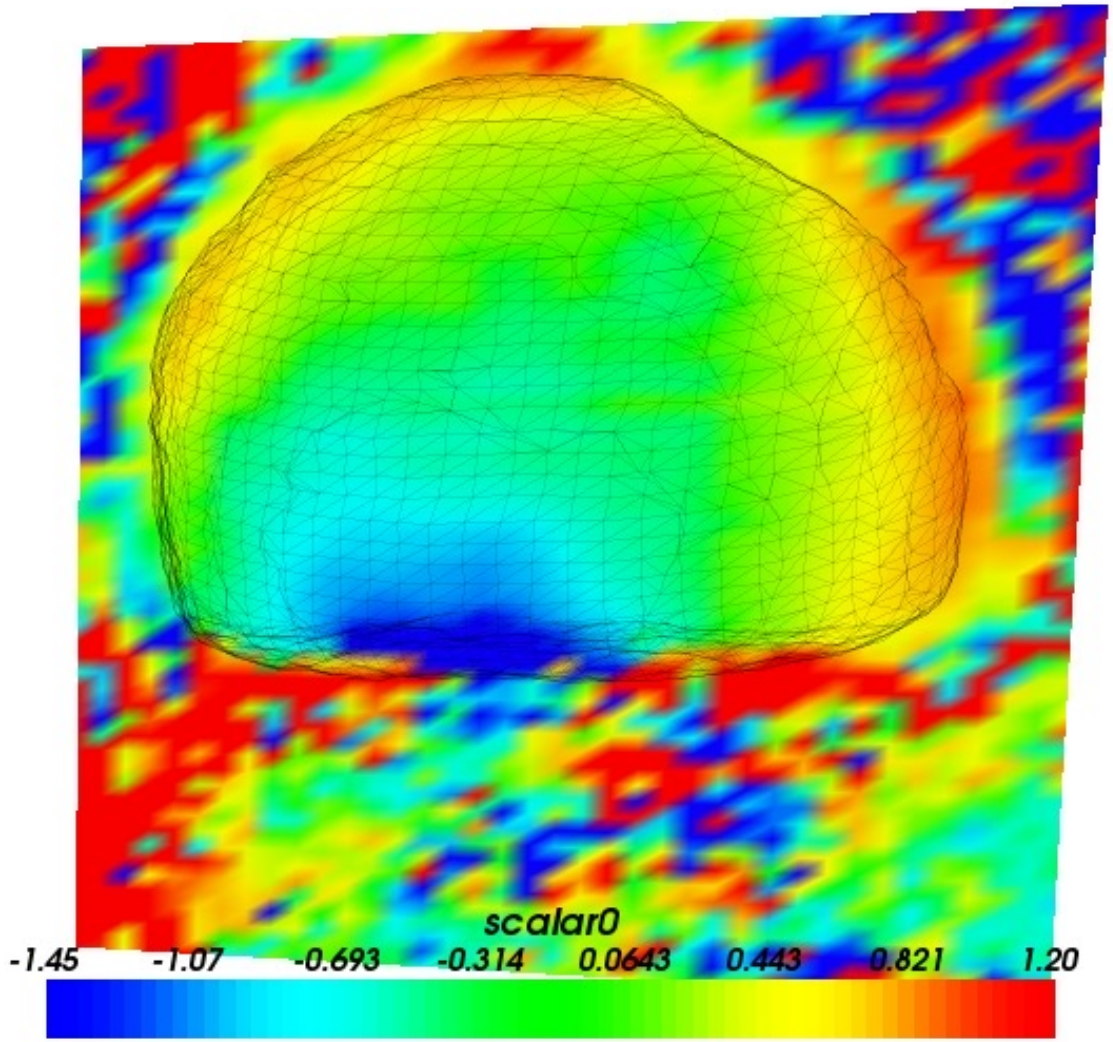
Field lines of Point Charges





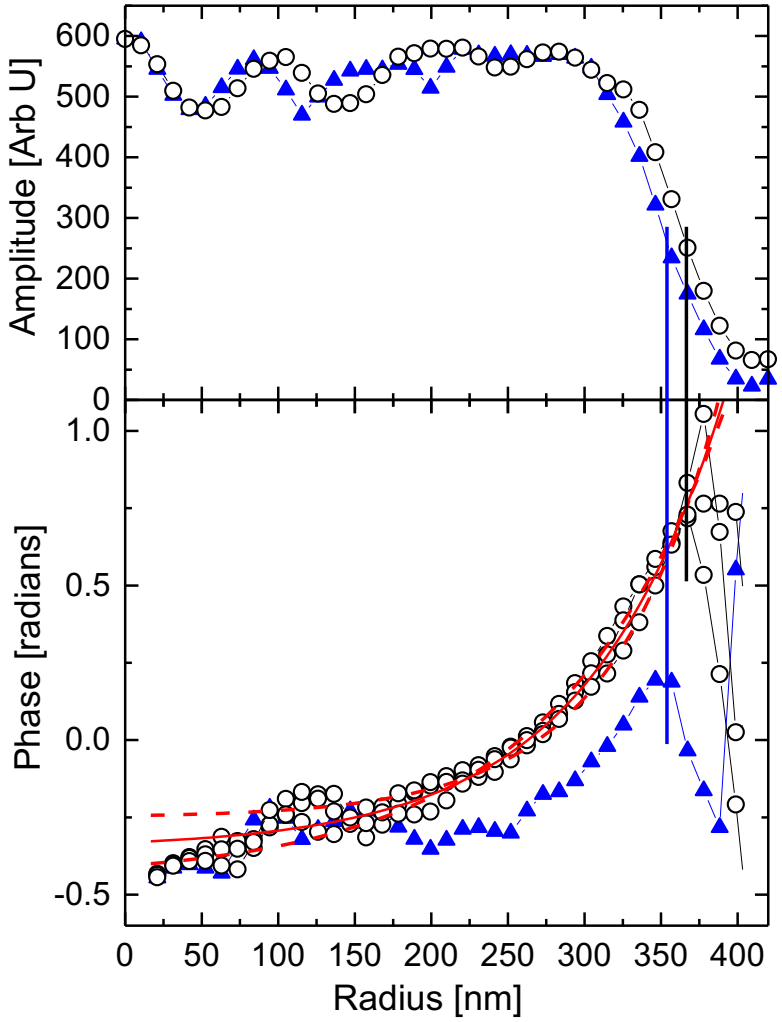
Contours showing Positive Phase

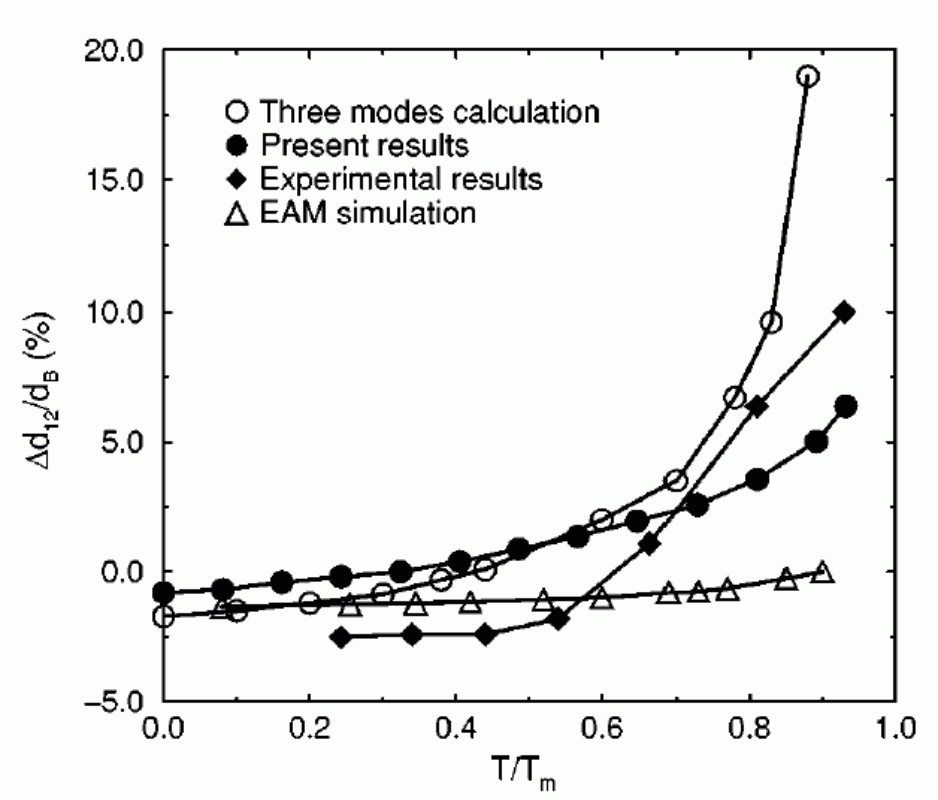
including correction for refraction by crystal



Surface Thermal Expansion

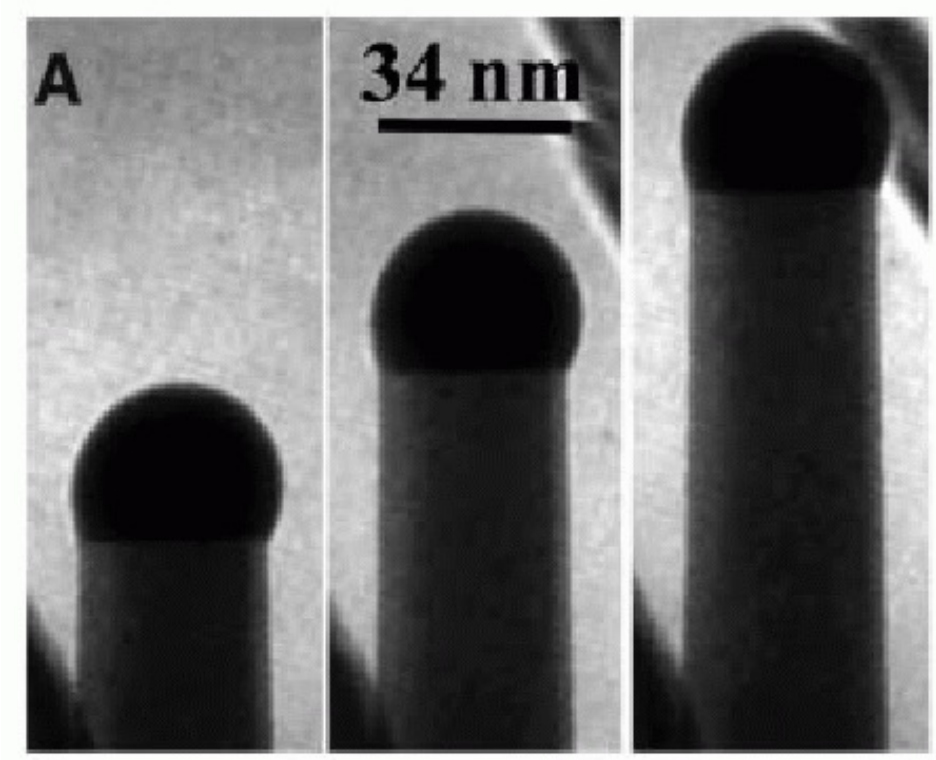
Ag(111): Scheffler et al PRB 59 970 (1999)

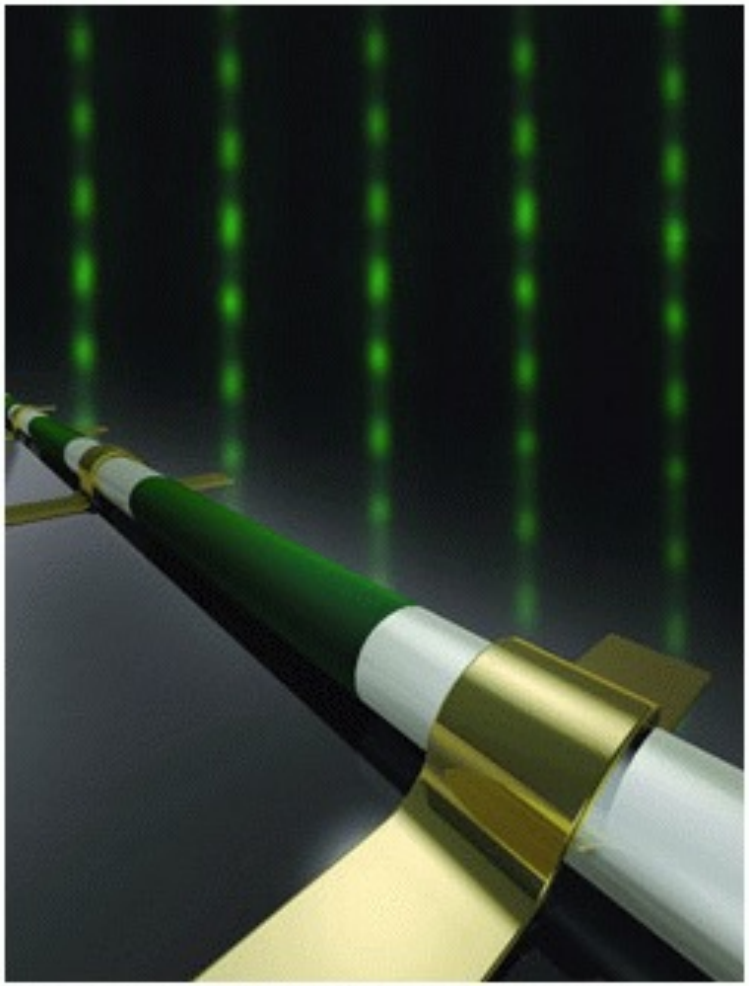




VLS growth of nanowires

S. Kodambaka et al., Science 316 729 (2007)



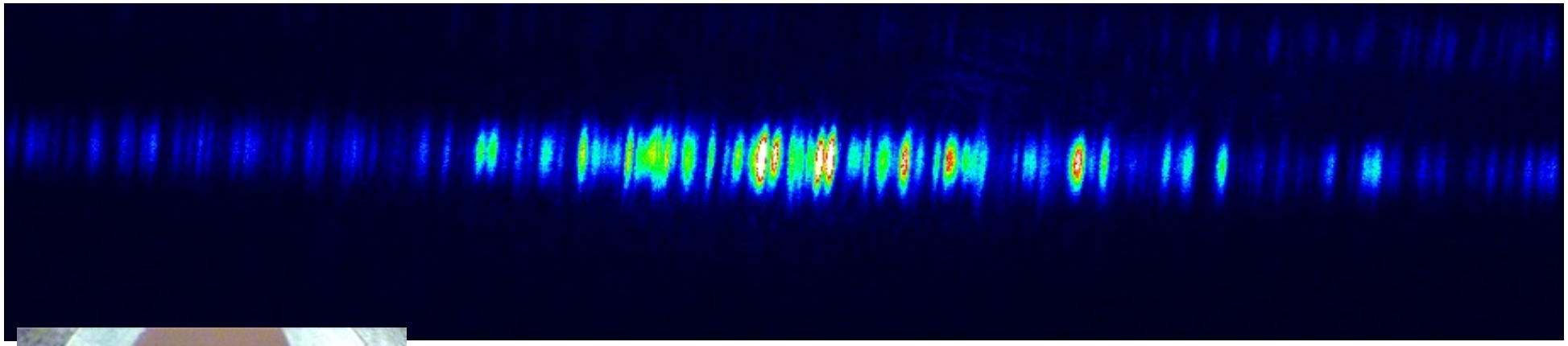


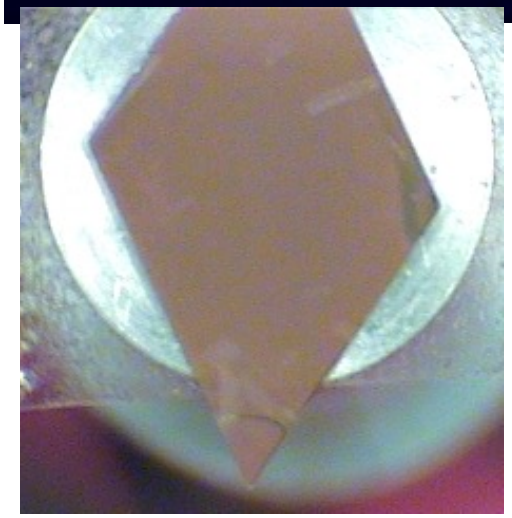
NiSi/Si nanowire heterostructure devices. *Nature* **430**, 61 (2004).

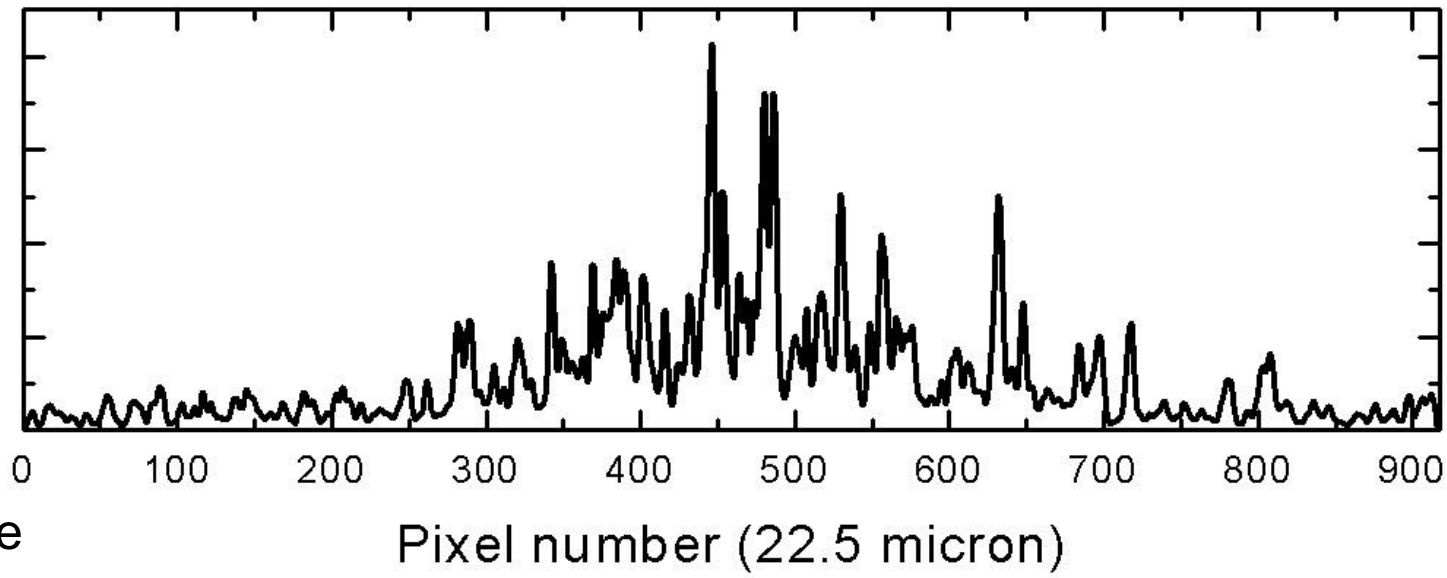
I. K. Robinson, EPFL

GaAs Nanowire "Barcode"

Vincent Favre-Nicolin, Joel Eymery (CEA),
Rienk Algra (Philips), Ross Harder



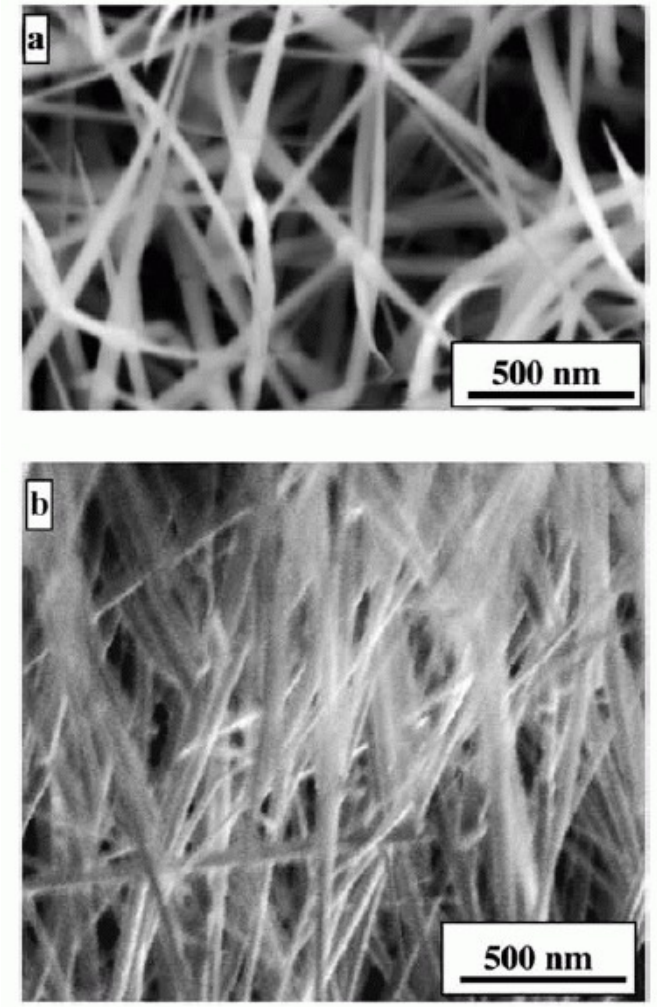


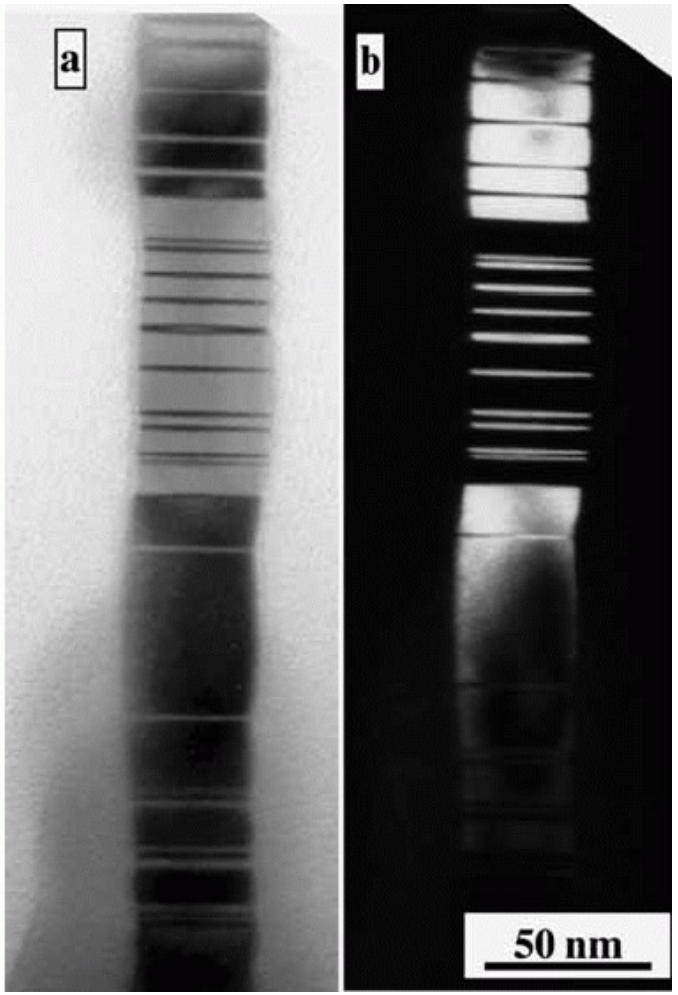


GaAsNW1106-22.spe
B9348 from Philips

Dark Field TEM of GaAs Nanowires

R. Banerjee et al, Phil. Mag. Lett. 86 807 (2006)

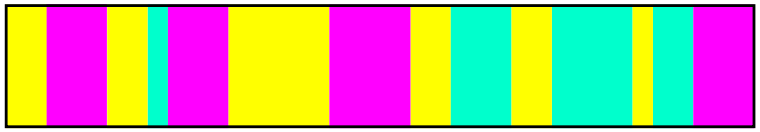




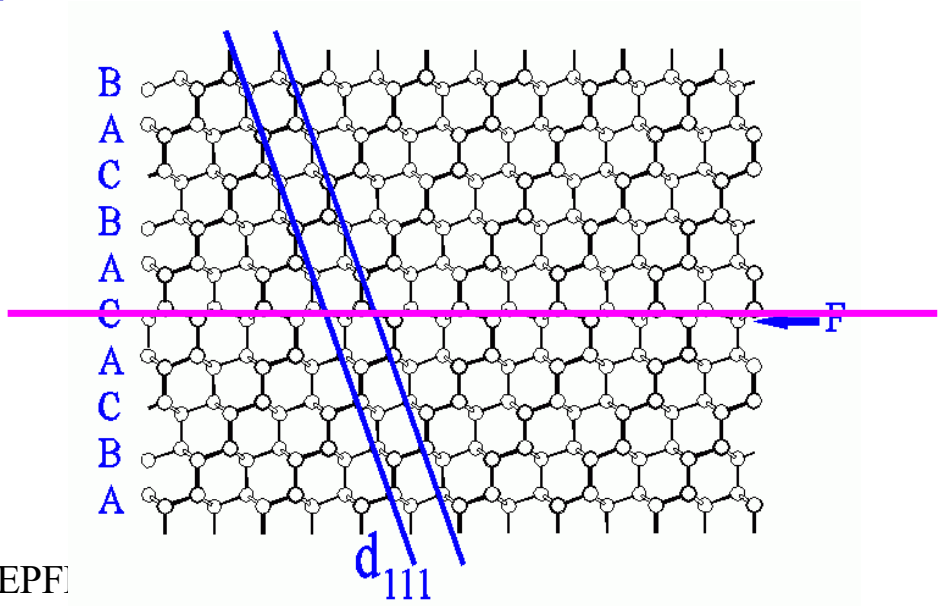
Models of Barcode Diffraction

(111) wires at (11-1) reflection

- Twinned stacking sequence

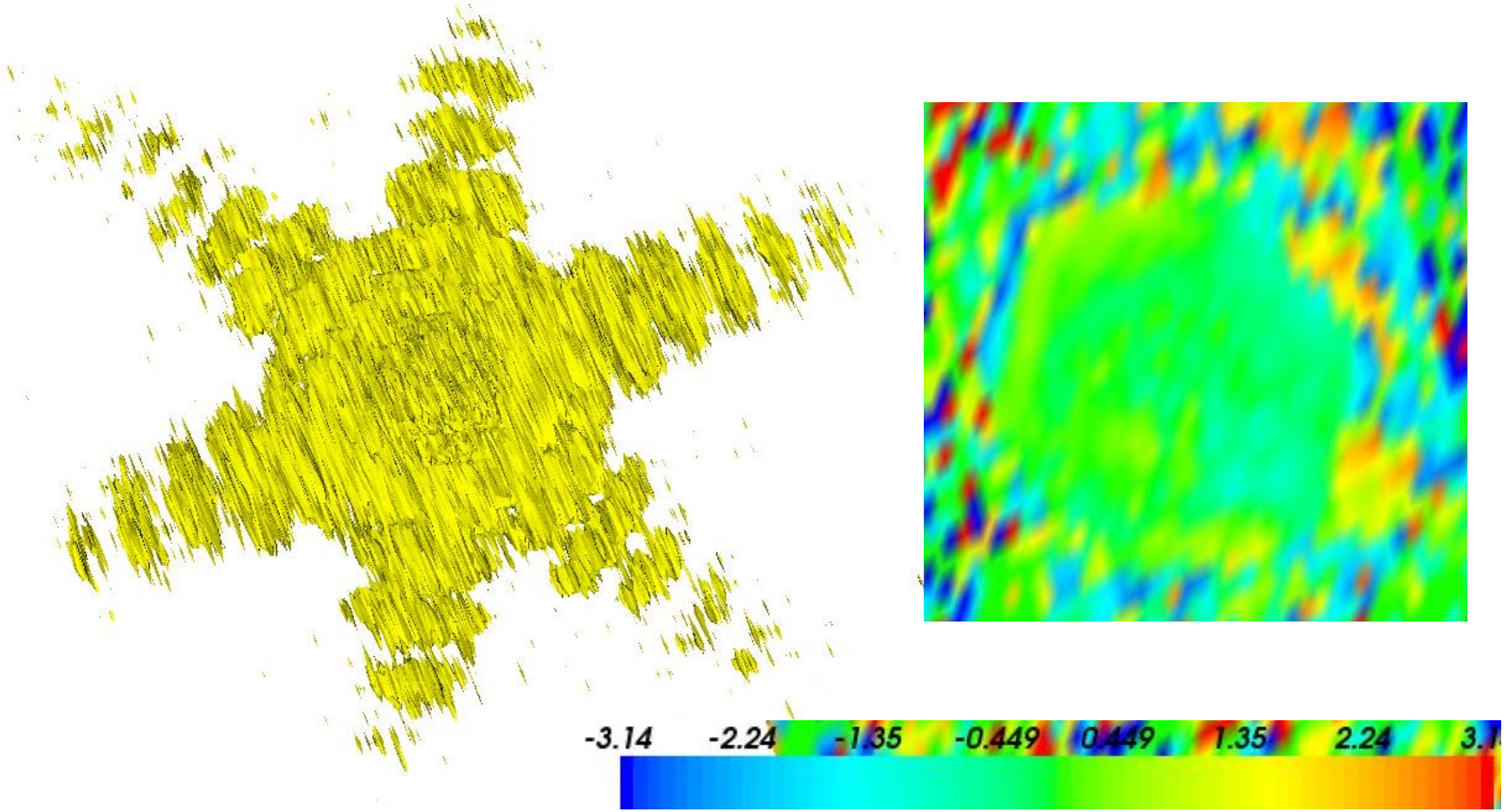


- Deformation faults



ZnO Nanowire Reconstruction

Ross Harder, Steven Leake, PhD project at UCL



Conclusions

- Clustering of ferritin before crystallisation
- Internal structure of Ag and Pb Nanocrystals
- 3D imaging practical for nanocrystals
- Phasing by computation instead of lens
- Strain fields imaged from asymmetric patterns
- Contact Forces cause strain inside crystal
- Surface strain has orientation dependence