

Interfacial strains in nanocrystals revealed by coherent X-ray diffraction

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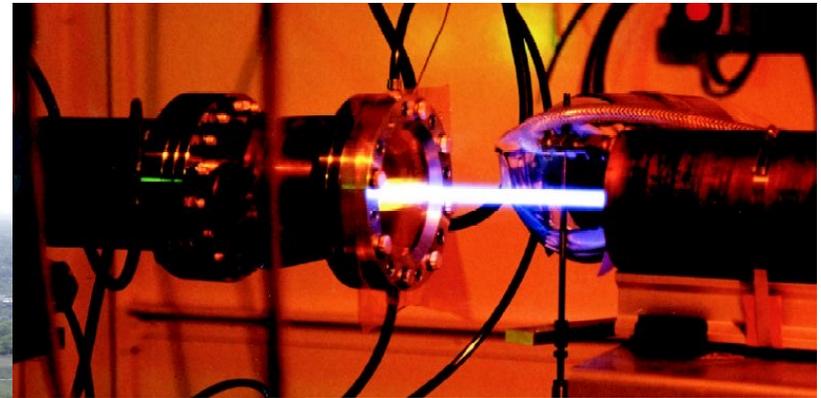
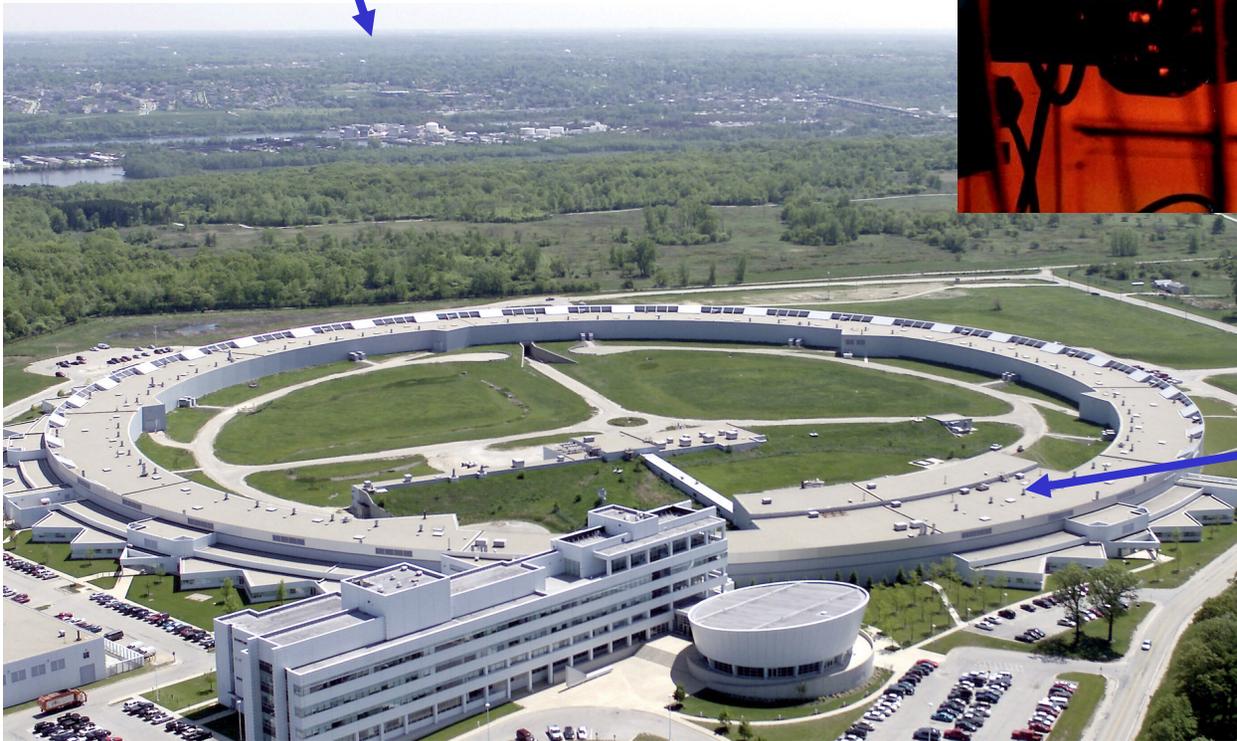
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Surface Structure and Morphology
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Outline

- Coherent X-ray Diffraction
- How to Solve the **Phase** Problem
- Nanocrystal Shapes
- Extension to **Phase** Objects
- Interfacial Contact Forces
- “Anomalous” Thermal Expansion

Synchrotron Radiation

Urbana

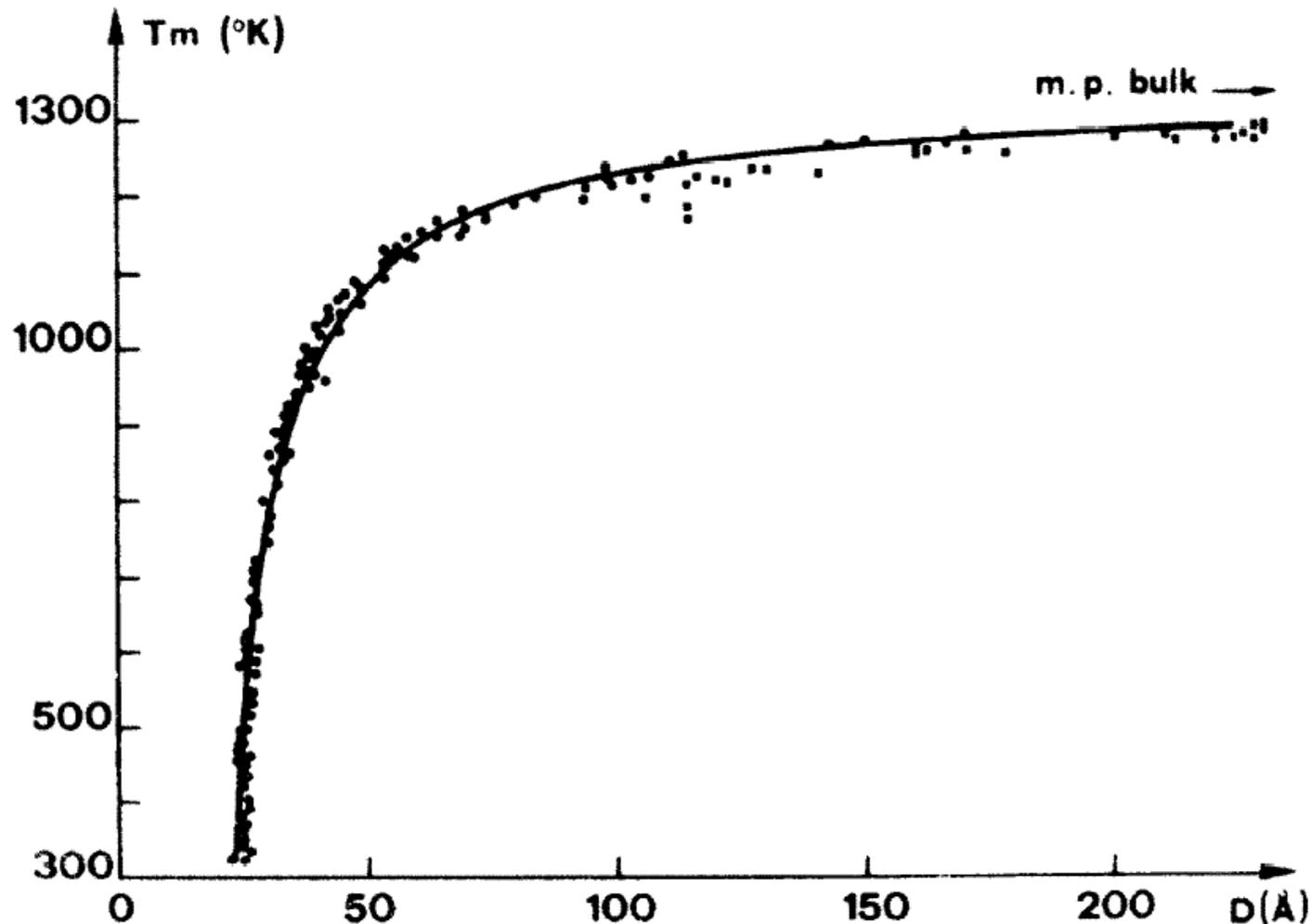


34-ID-C

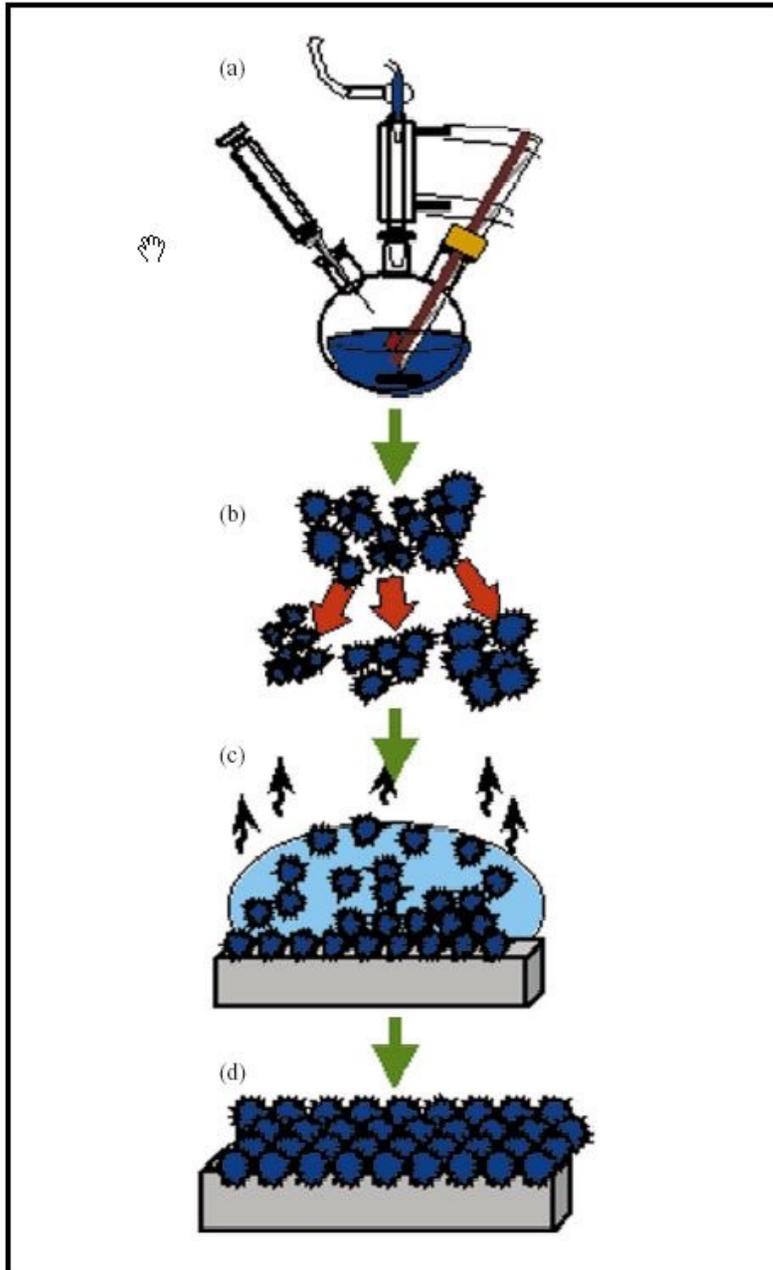


Size-dependent Melting of Au Particles

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

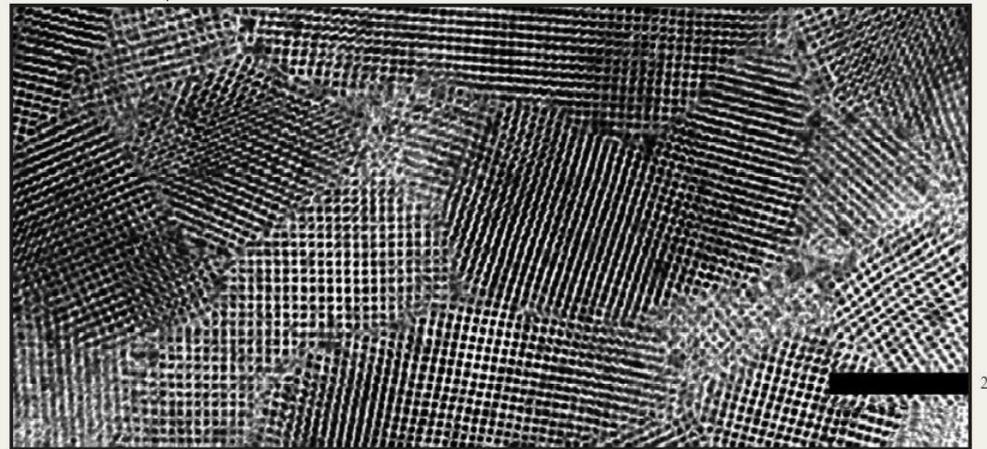


Chemical Synthesis of Nanocrystals

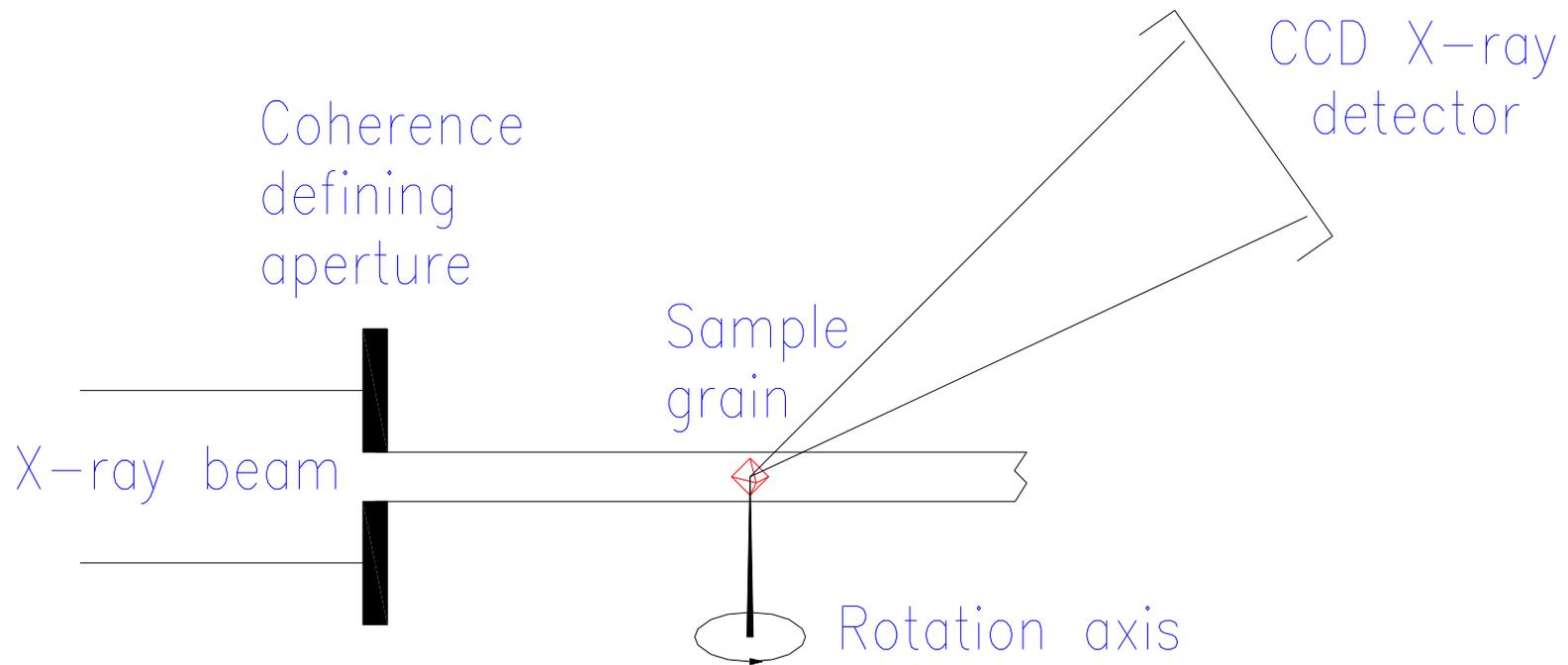


- Reactants introduced rapidly
- High temperature solvent
- Surfactant/organic capping agent
- Square superlattice (200nm scale)

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



Lensless X-ray Microscope

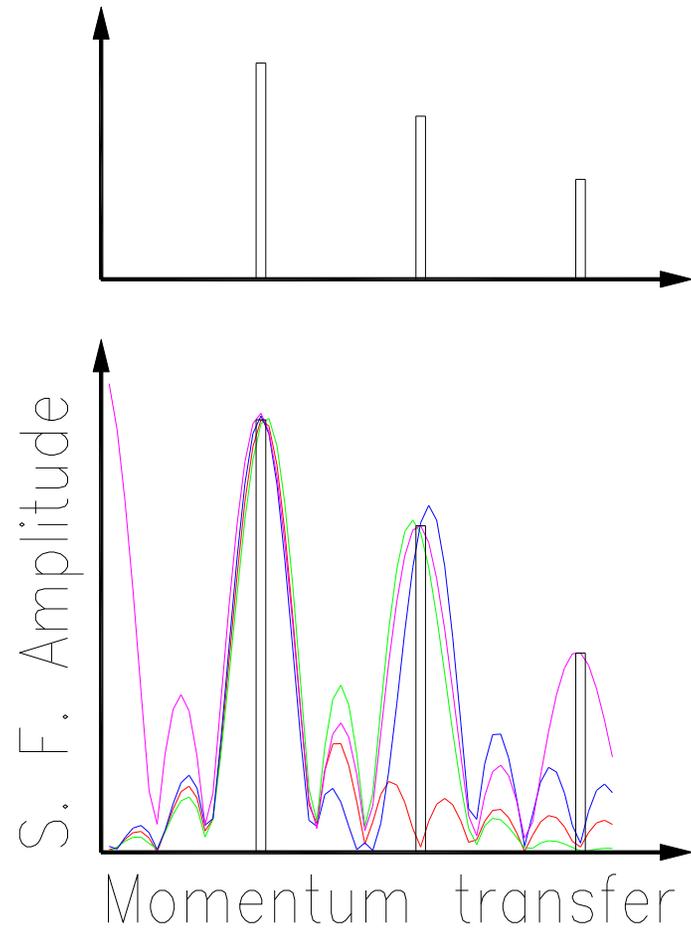
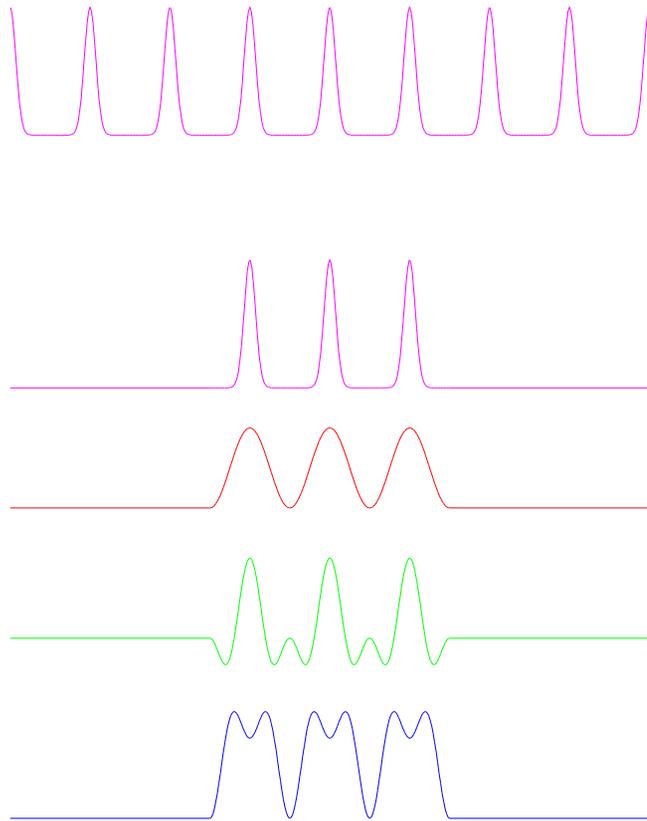


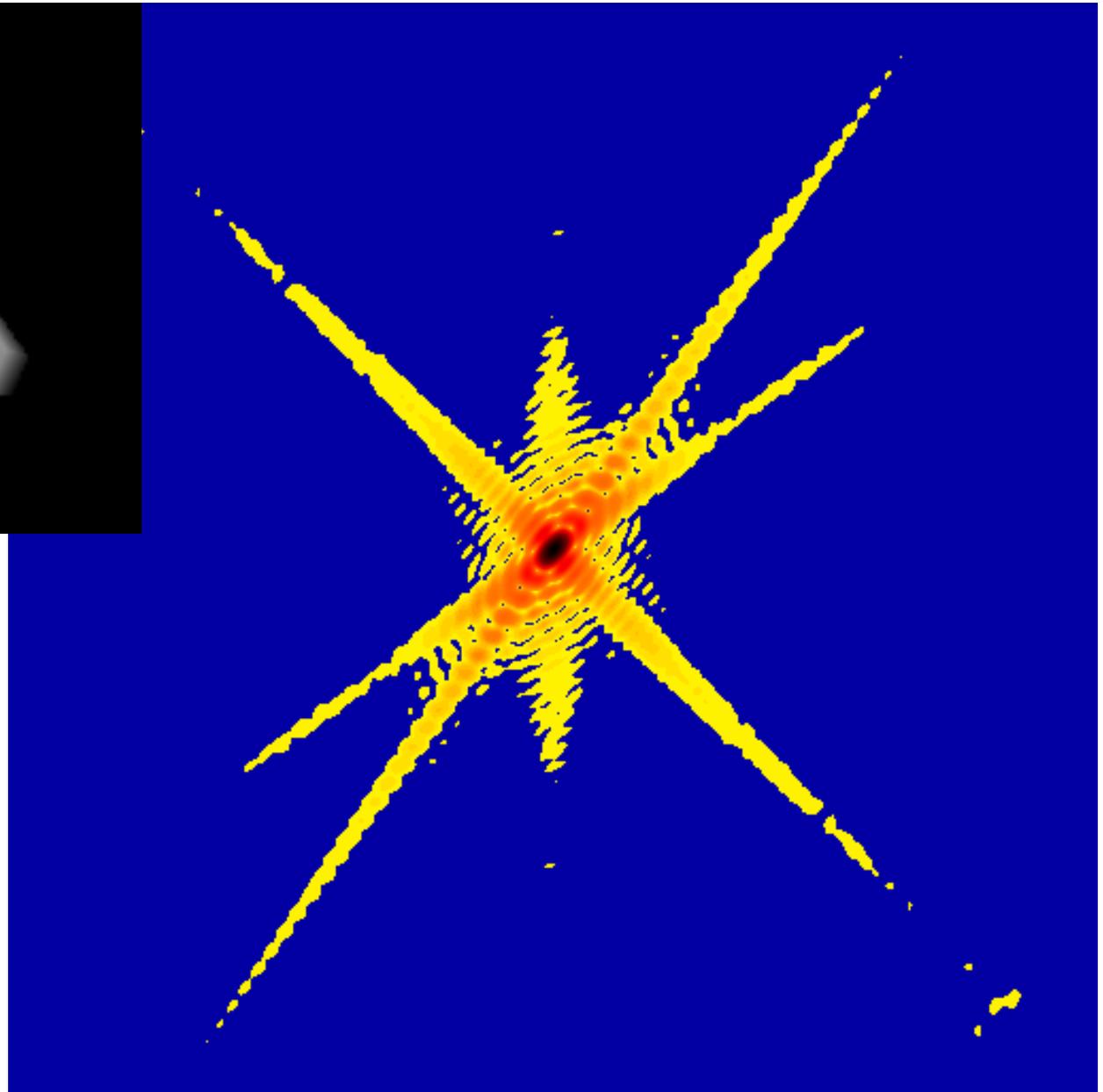
Real-space Constraints in Crystallography

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

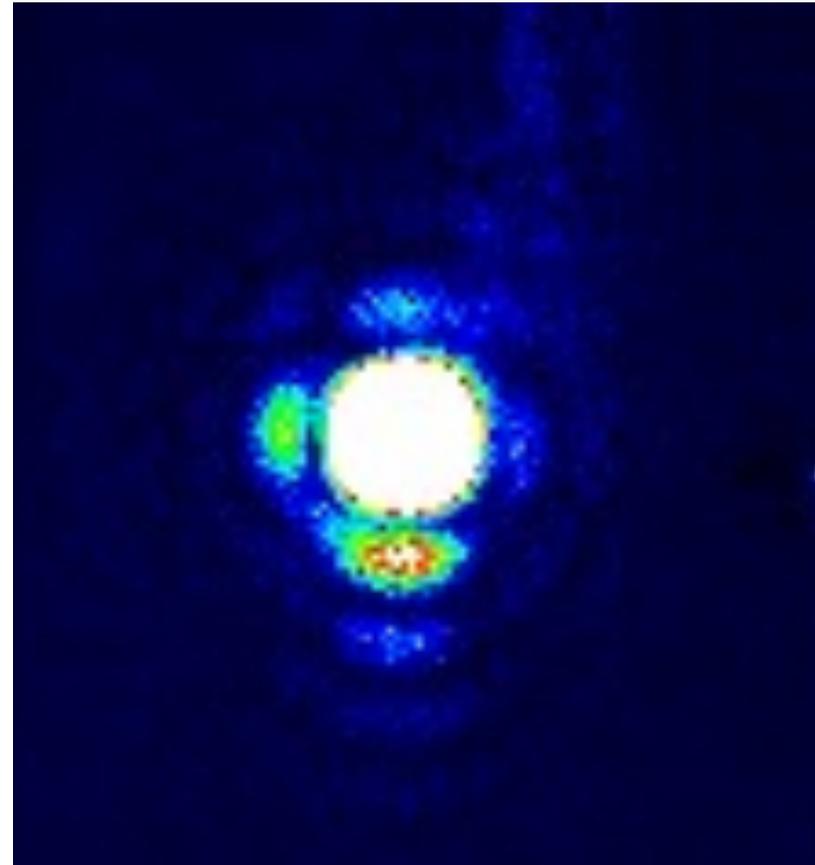
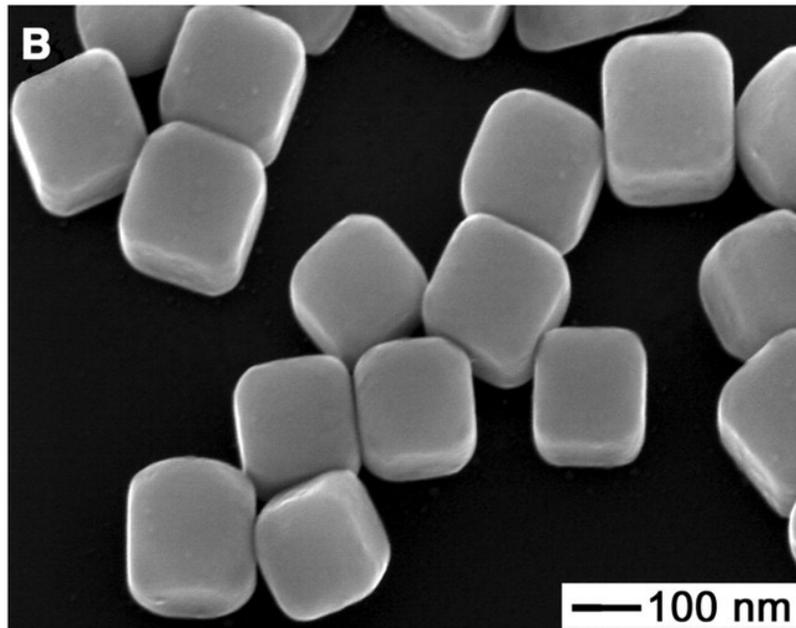
- ‘Positivity’ and ‘Atomicity’ constraints (Sayre)
- Finite **support**, molecular envelope
- Solvent flattening/Molecular replacement
- Non-crystallographic symmetry
- Non-uniqueness is ‘pathologically rare’ ($d > 1$)
- Uses memory to avoid stagnation (Fienup HIO)

Oversampling solves Phase Problem



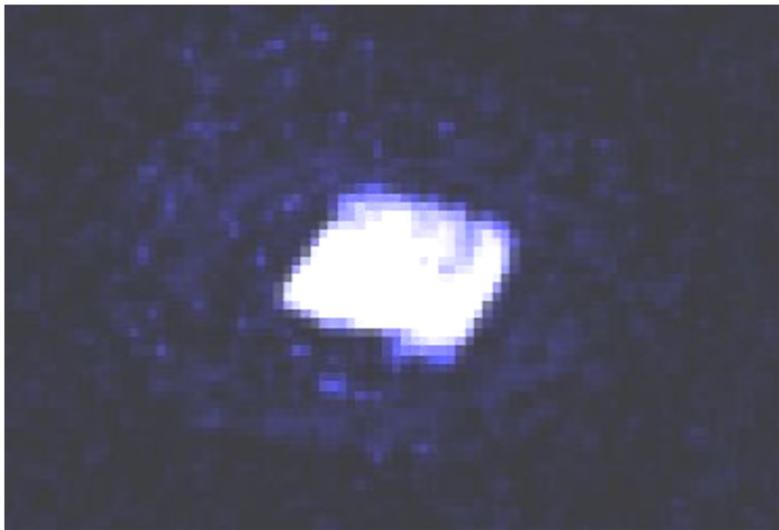


Chemically Synthesized Silver Nanocubes

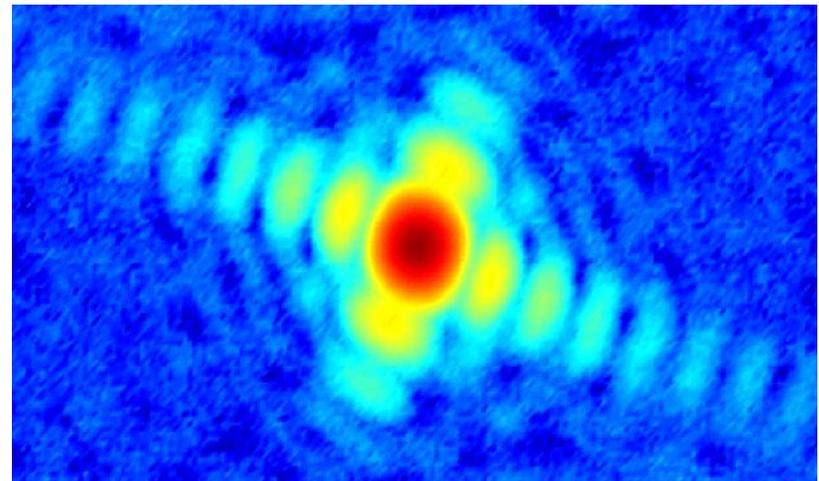
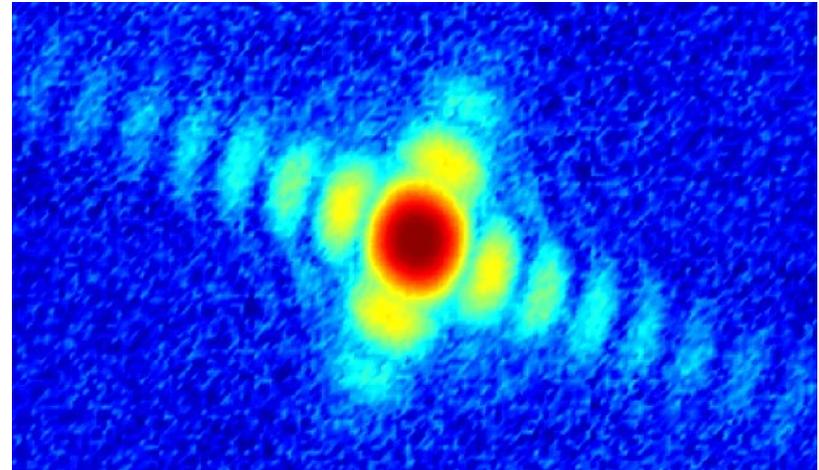


Yugang Sun and Younan Xia,
Science 298 2177 (2003)

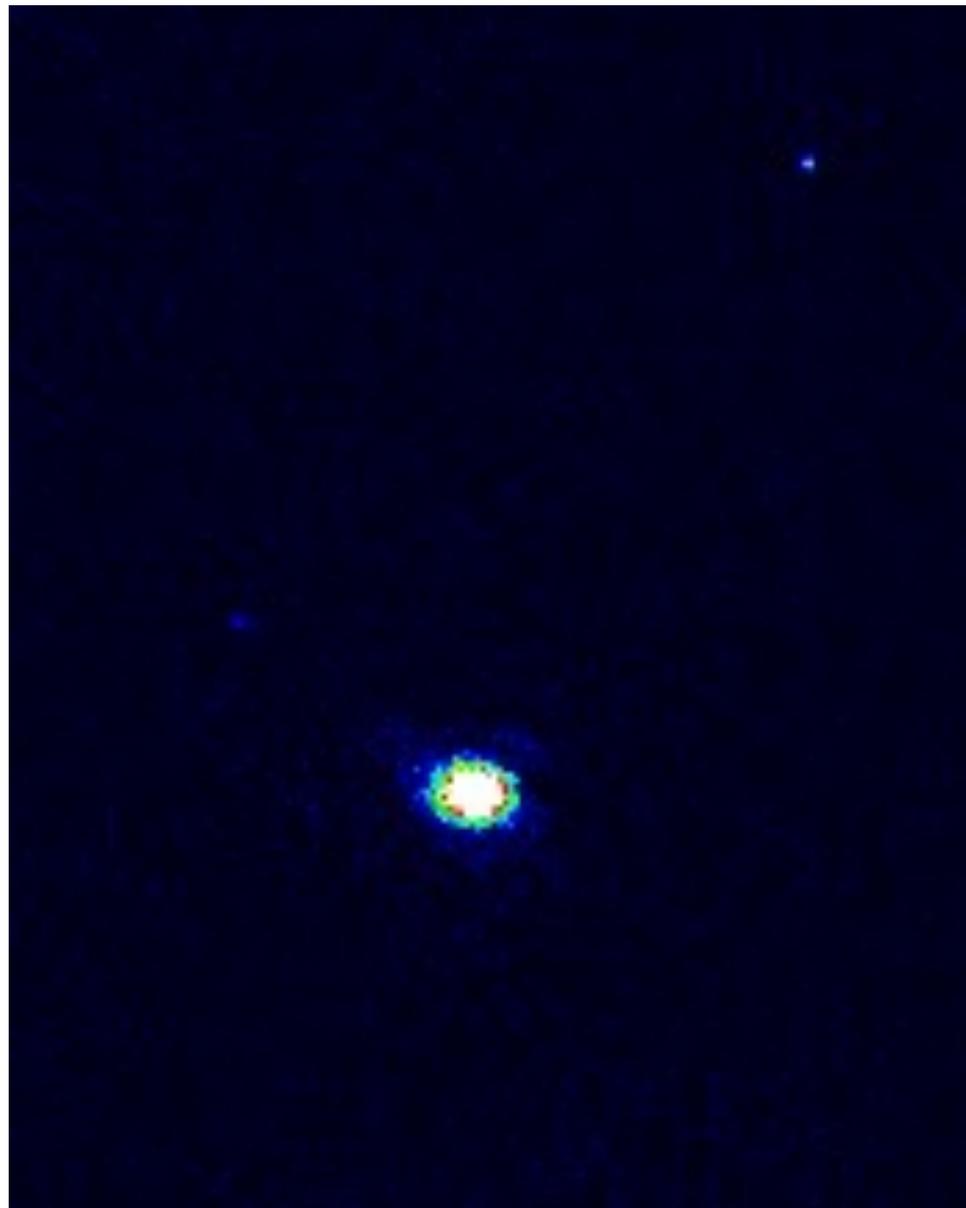
Reconstruction of Ag Nanocrystal

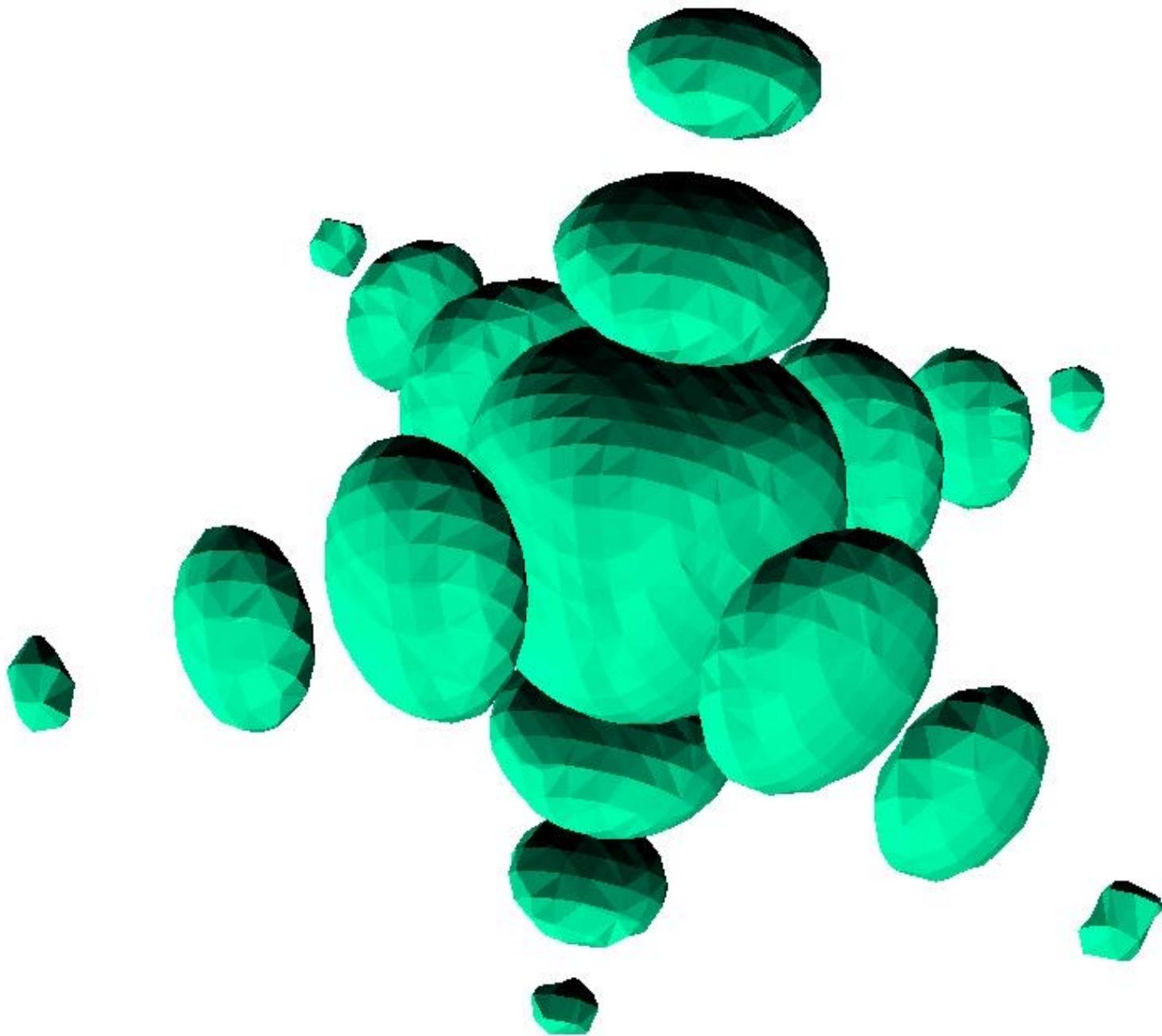


←→
200nm

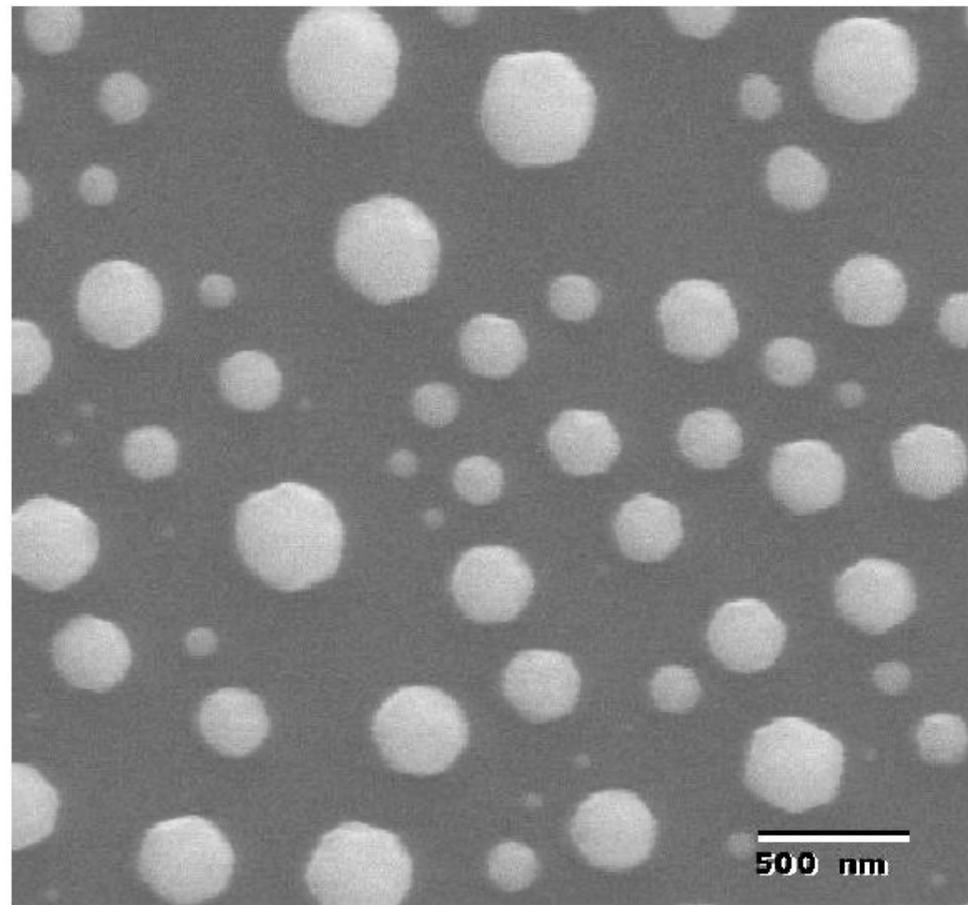


Rocking
scan of Ag
cubes with
 0.01° steps

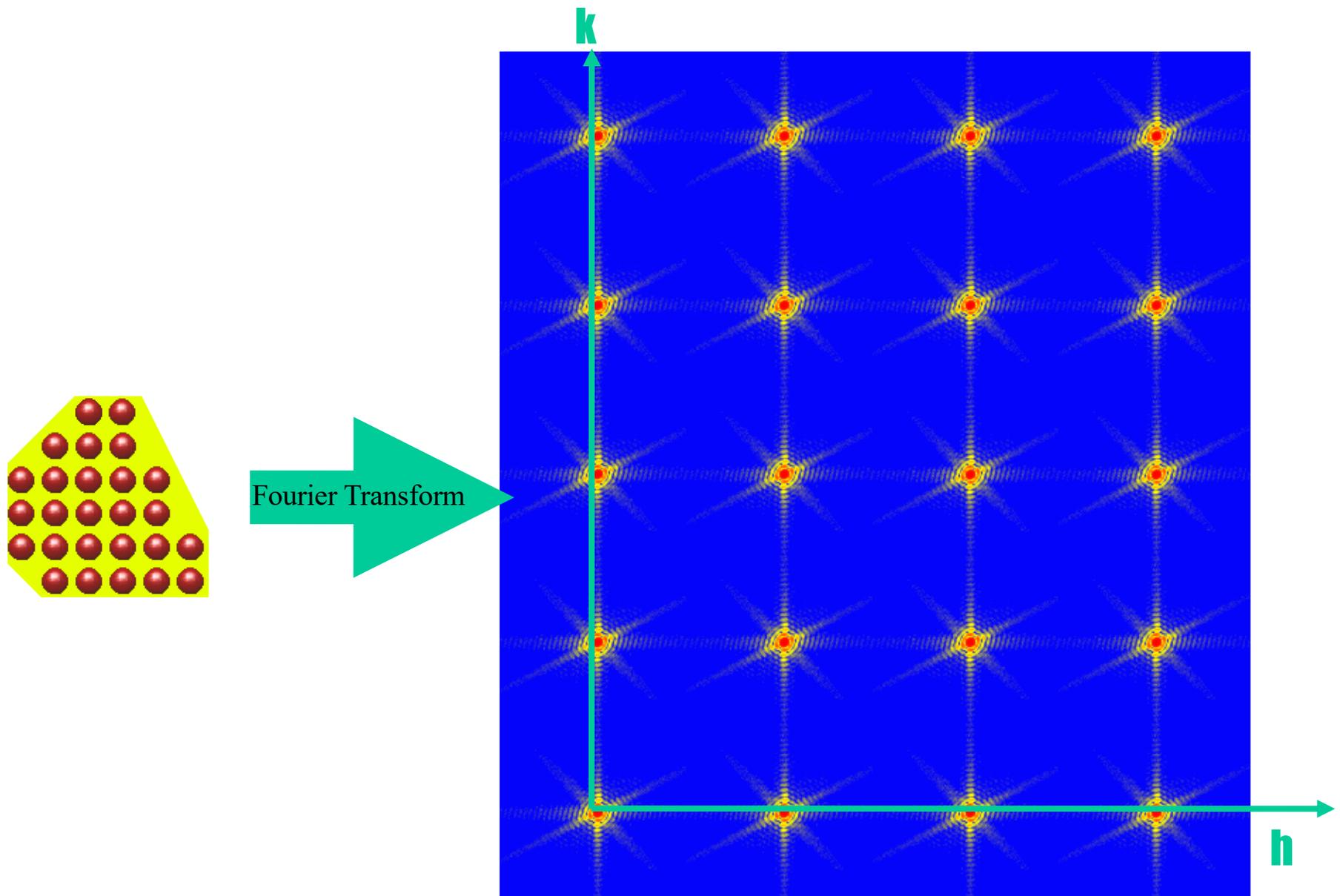




In situ growth of Pb crystals



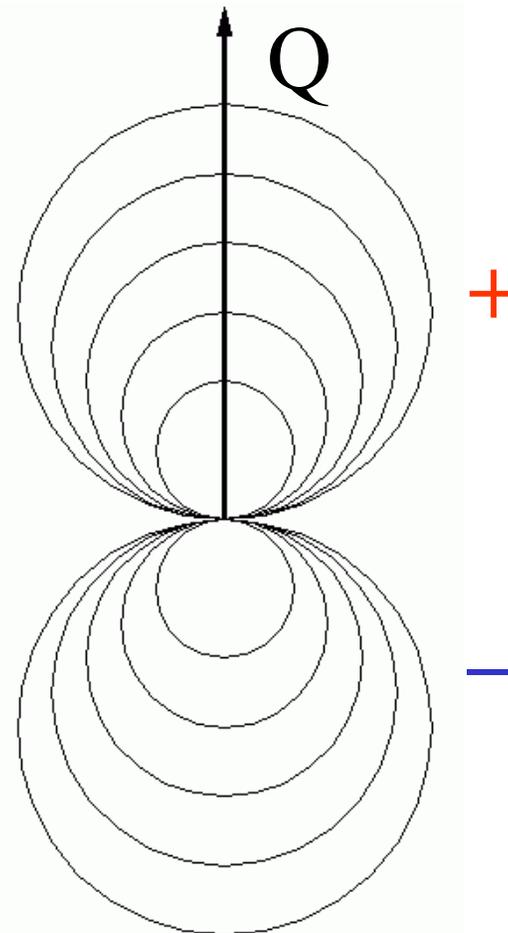
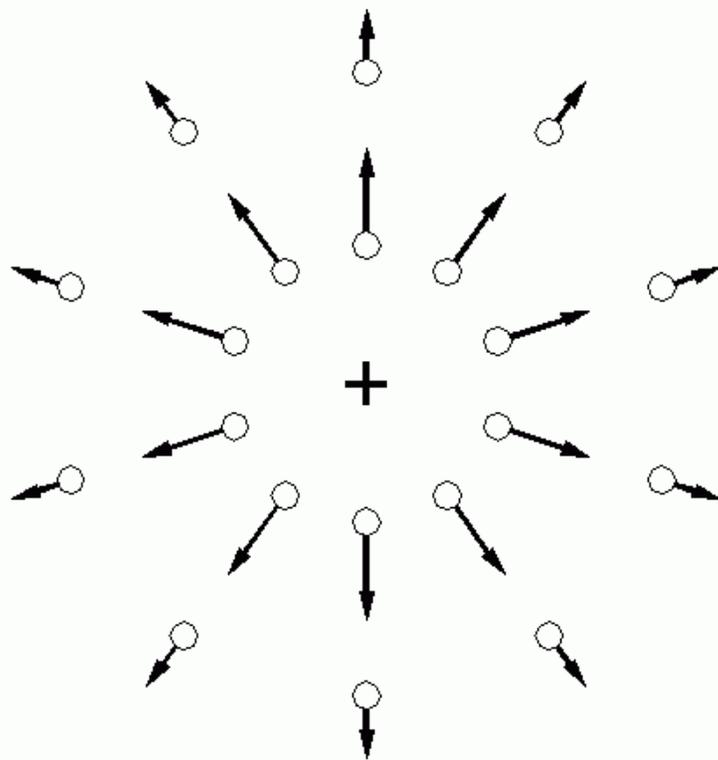
Coherent Diffraction from Crystals



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



Good statistics, 3D diffraction data

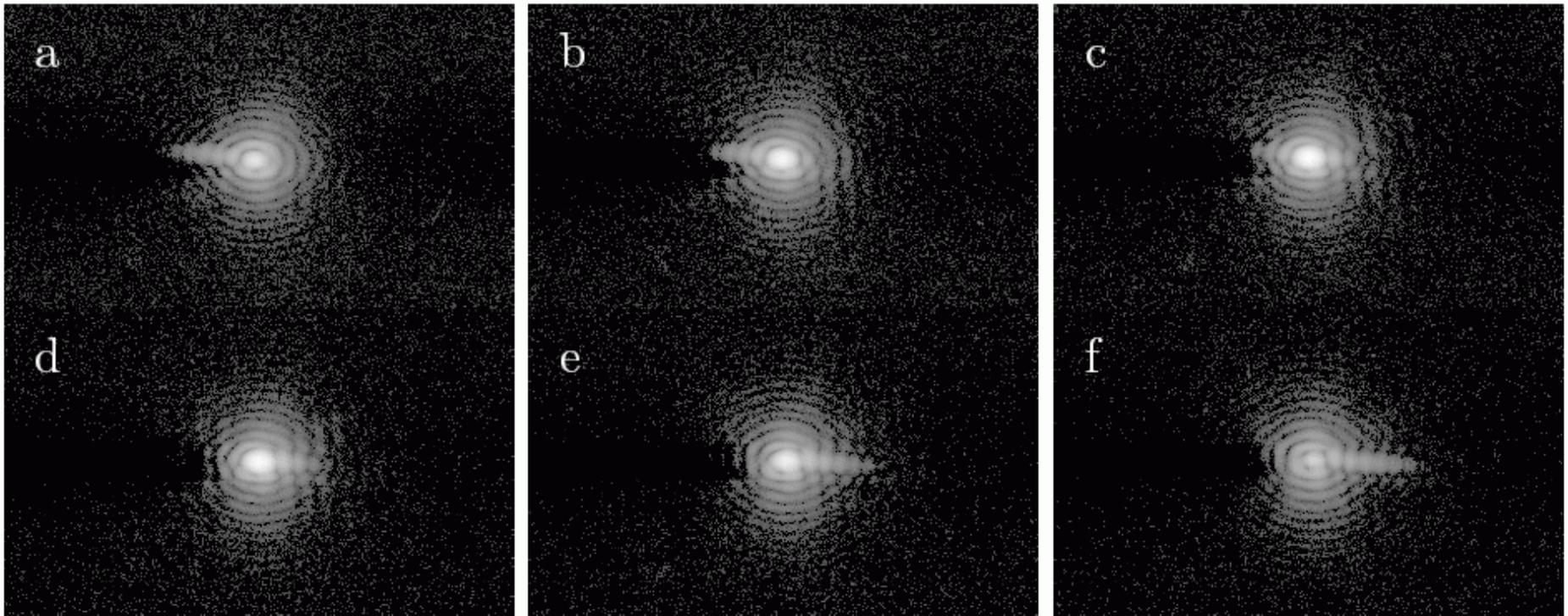
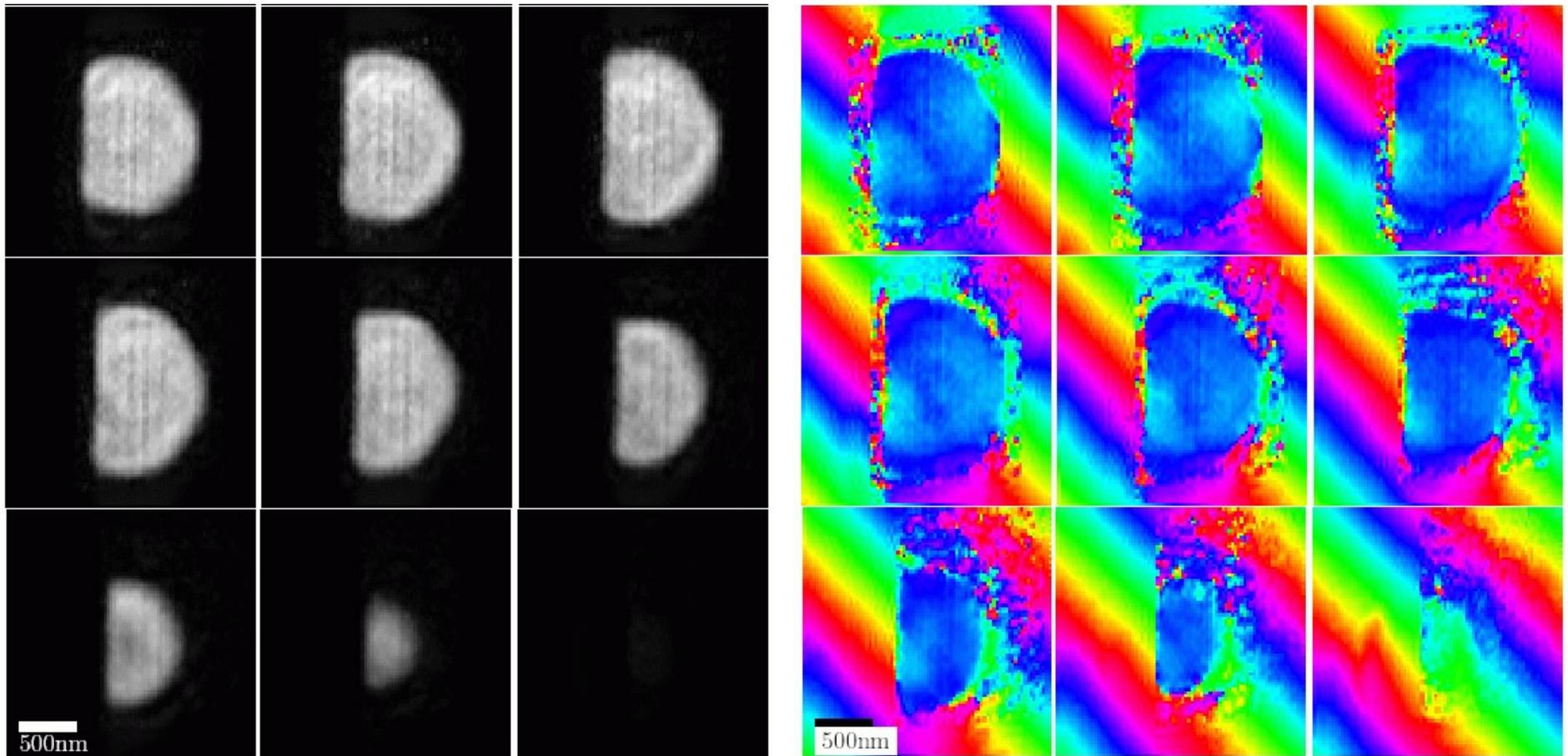
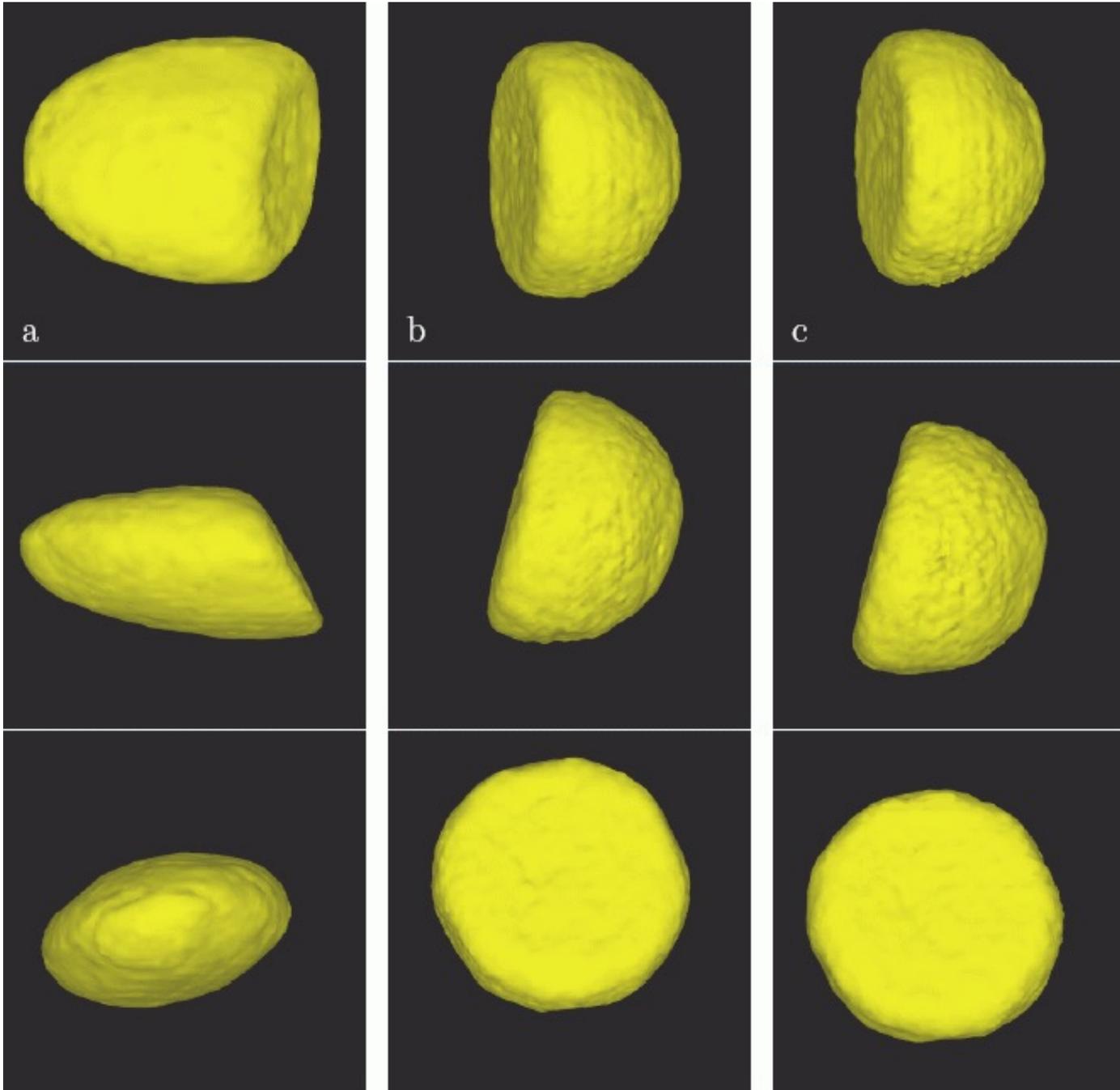


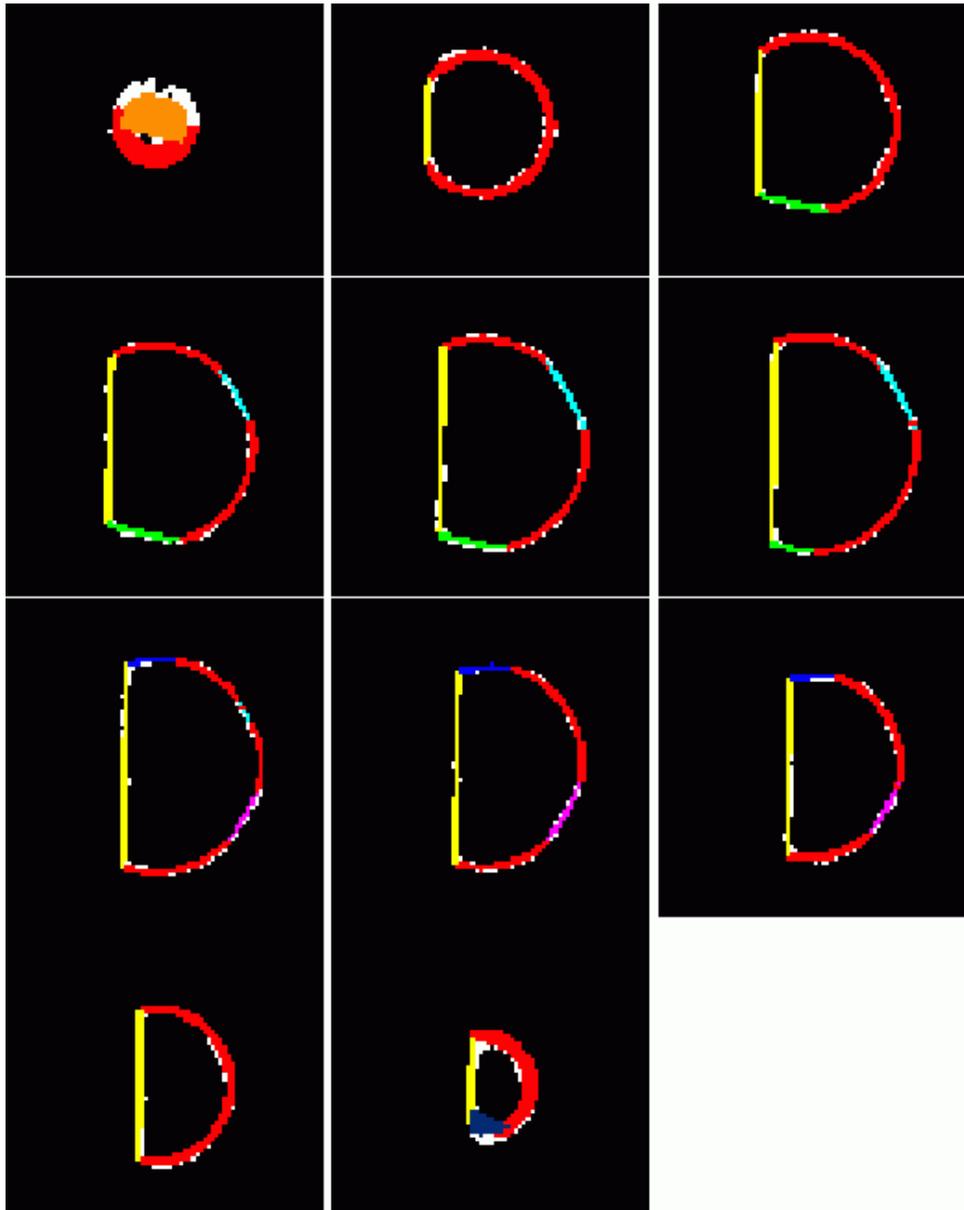
Figure 4.12: Center slices from 3D CXD pattern from Pb sample, on a log scale. Data file 296 from 10/03.

Complex Density (amplitude *and* phase)



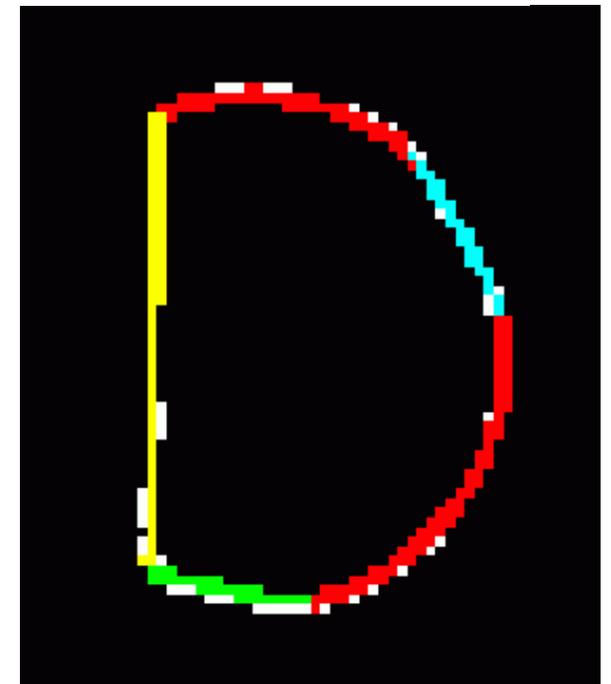


Fitting to faceted shape

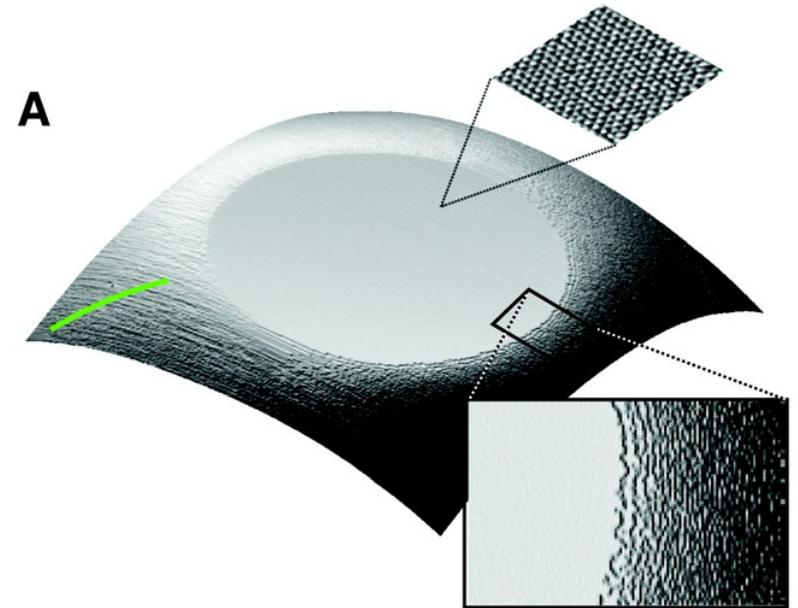


	$ R $		P0	P1	P2	P3	P4	P5	P6
	9.4	P0	0	85	149	79	134	106	71
	25.7	P1		0	123	164	83	76	102
	25.1	P2			0	72	67	74	110
	25.9	P3				0	111	106	76
	25.4	P4					0	113	68
	25.4	P5						0	176
	26.0	P6							0 0

Angles between facets

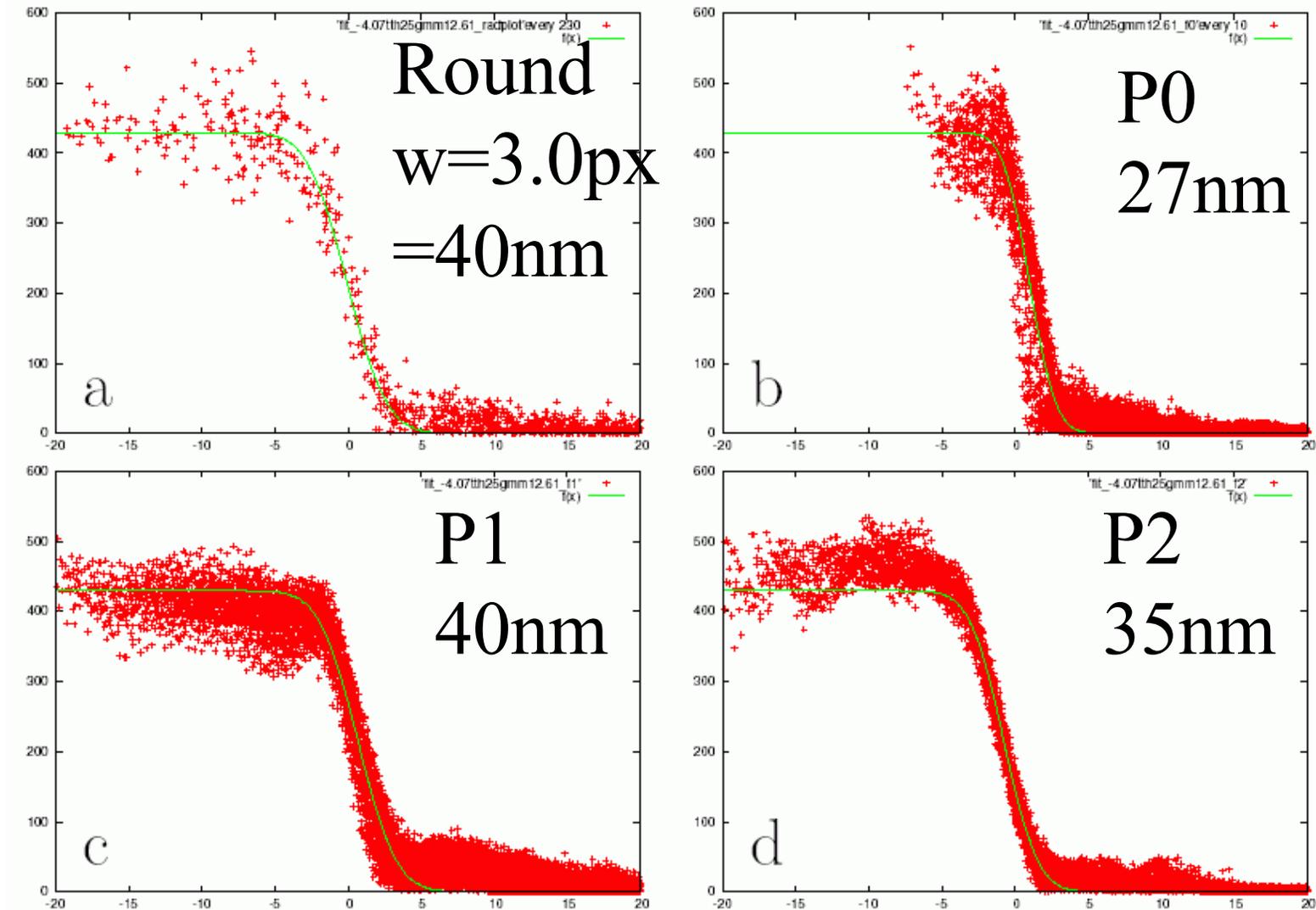


Facets of Equilibrium Crystal Shape

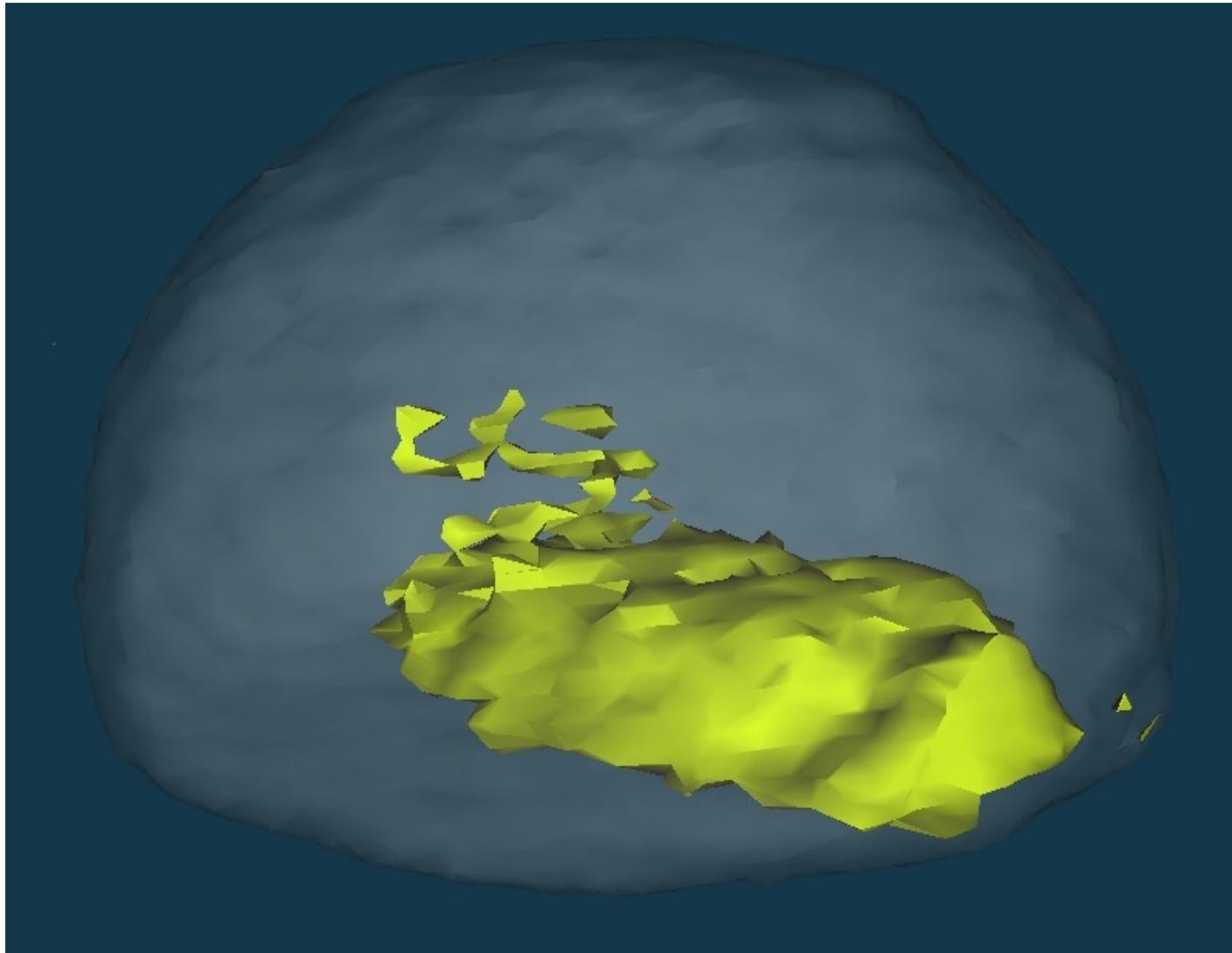


Thurmer K, Williams E, Reutt-Robey J
Science 297 2033 (2002)

Density distribution across surface

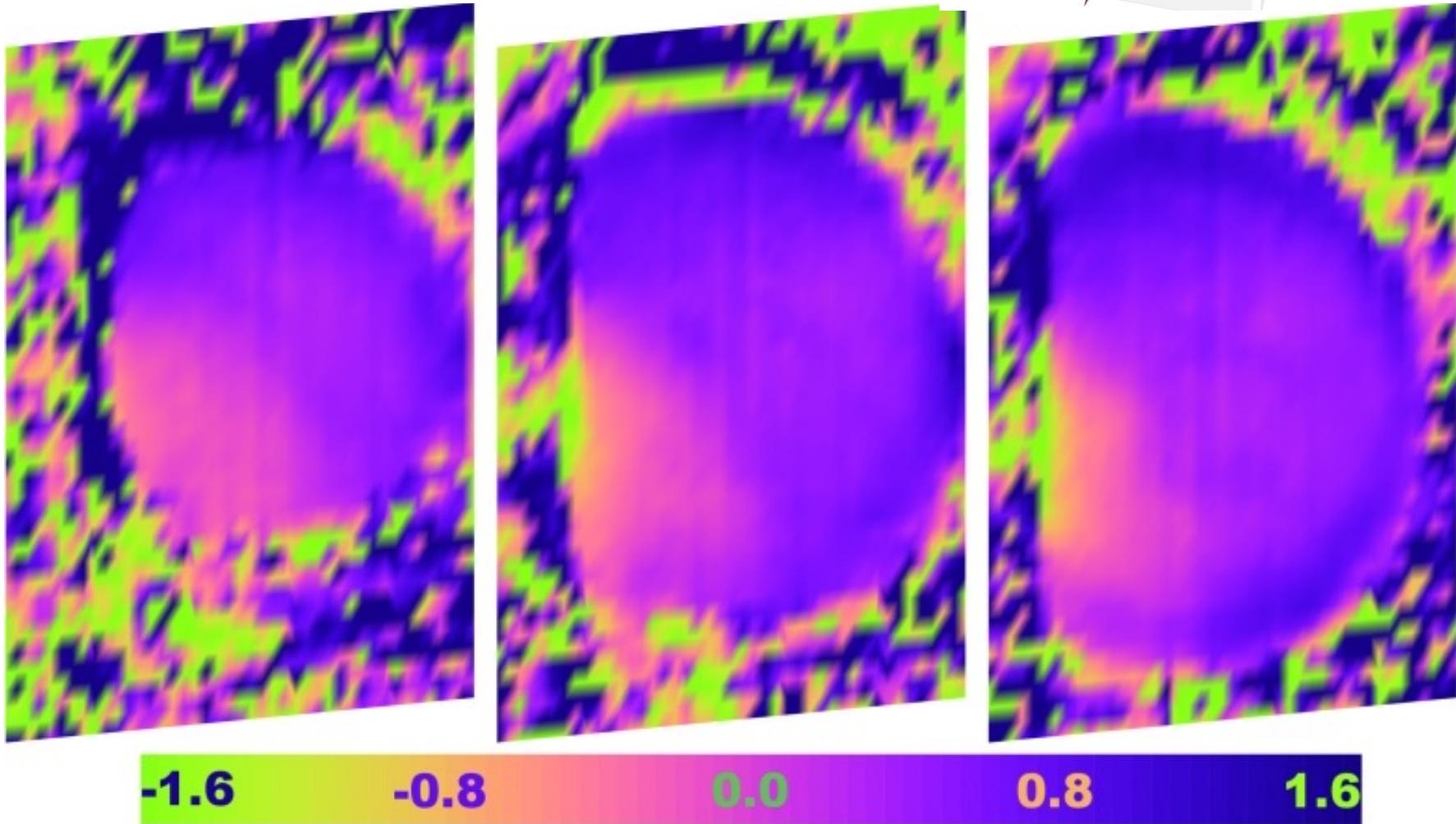
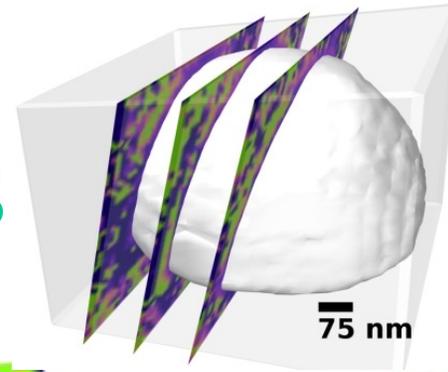


Modeling of 3D Phase Bump

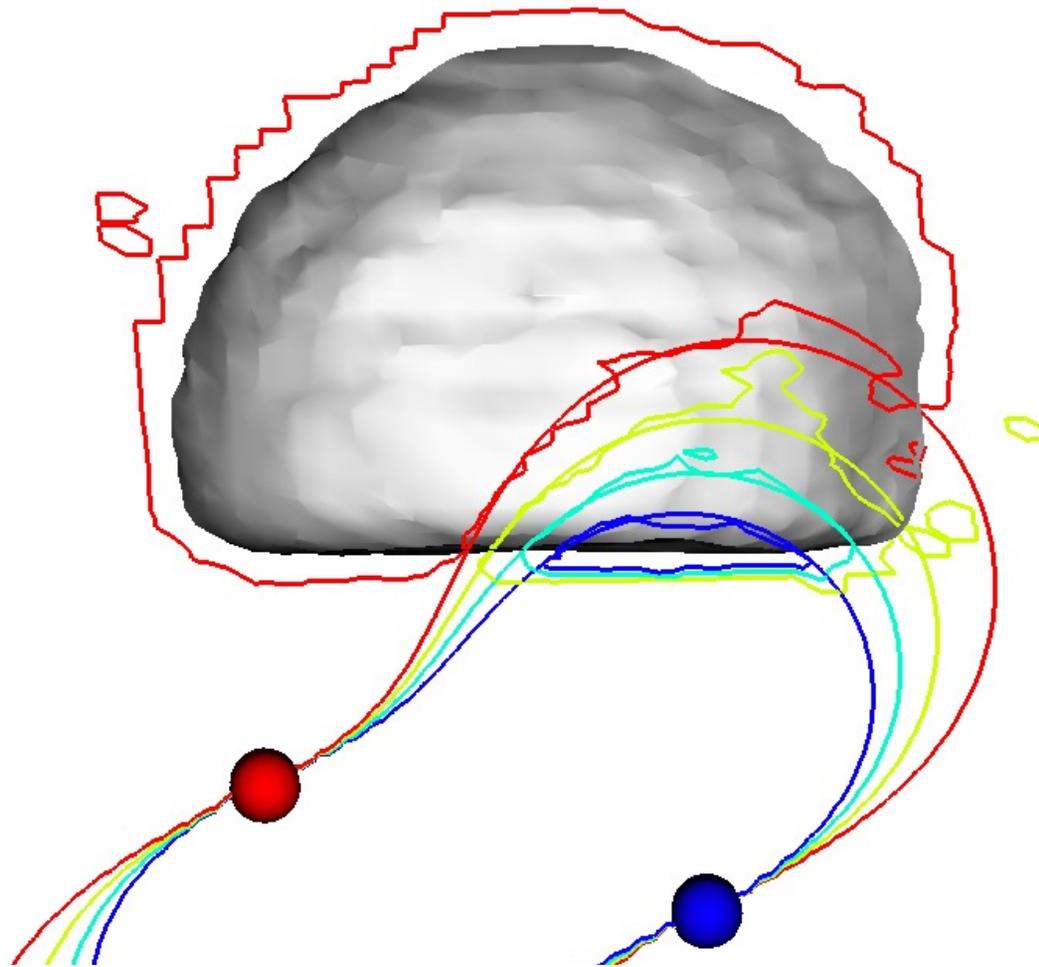


I. K. Robinson, AVS-53, Nov 2006

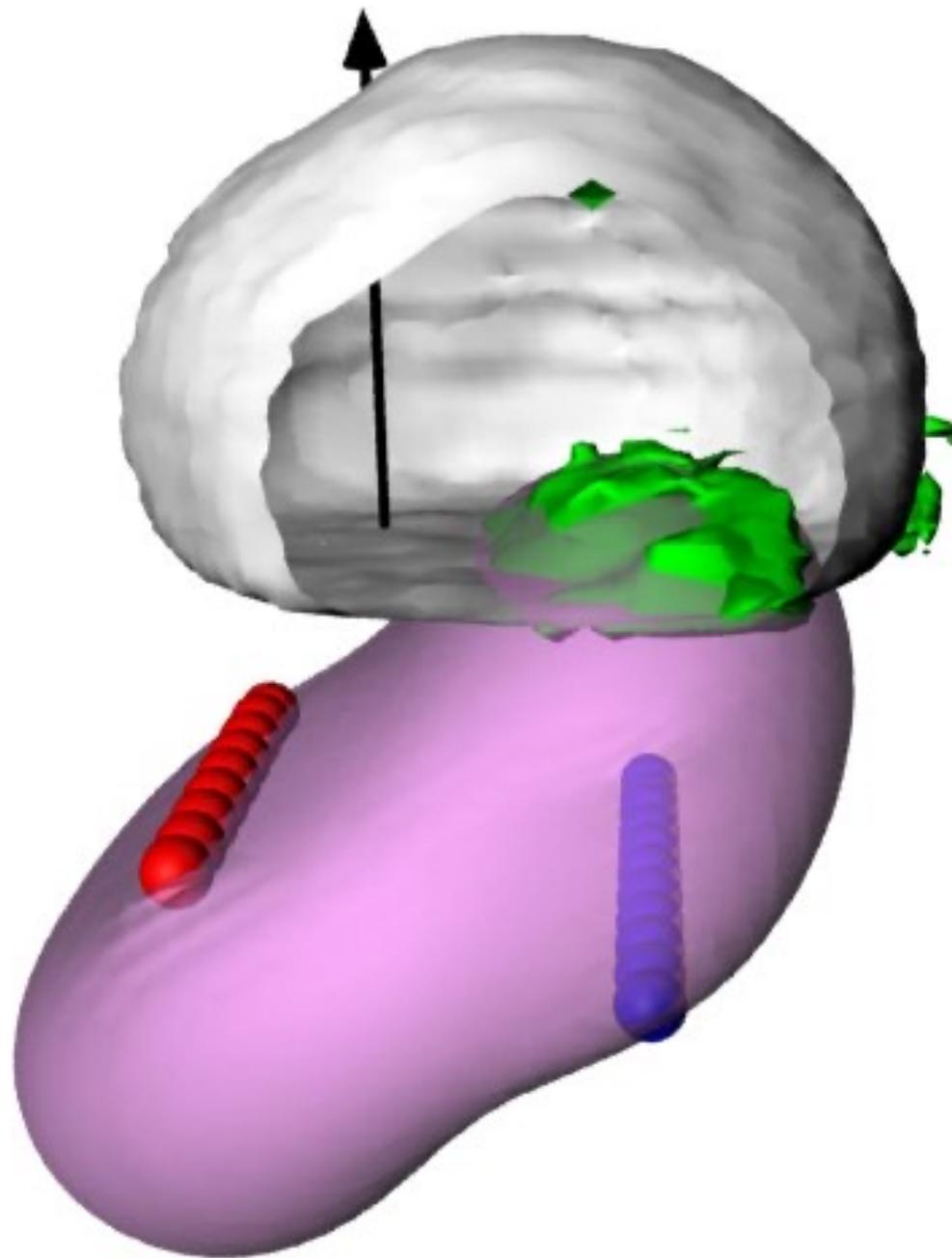
3D phase map sections



Field lines of Point Charges

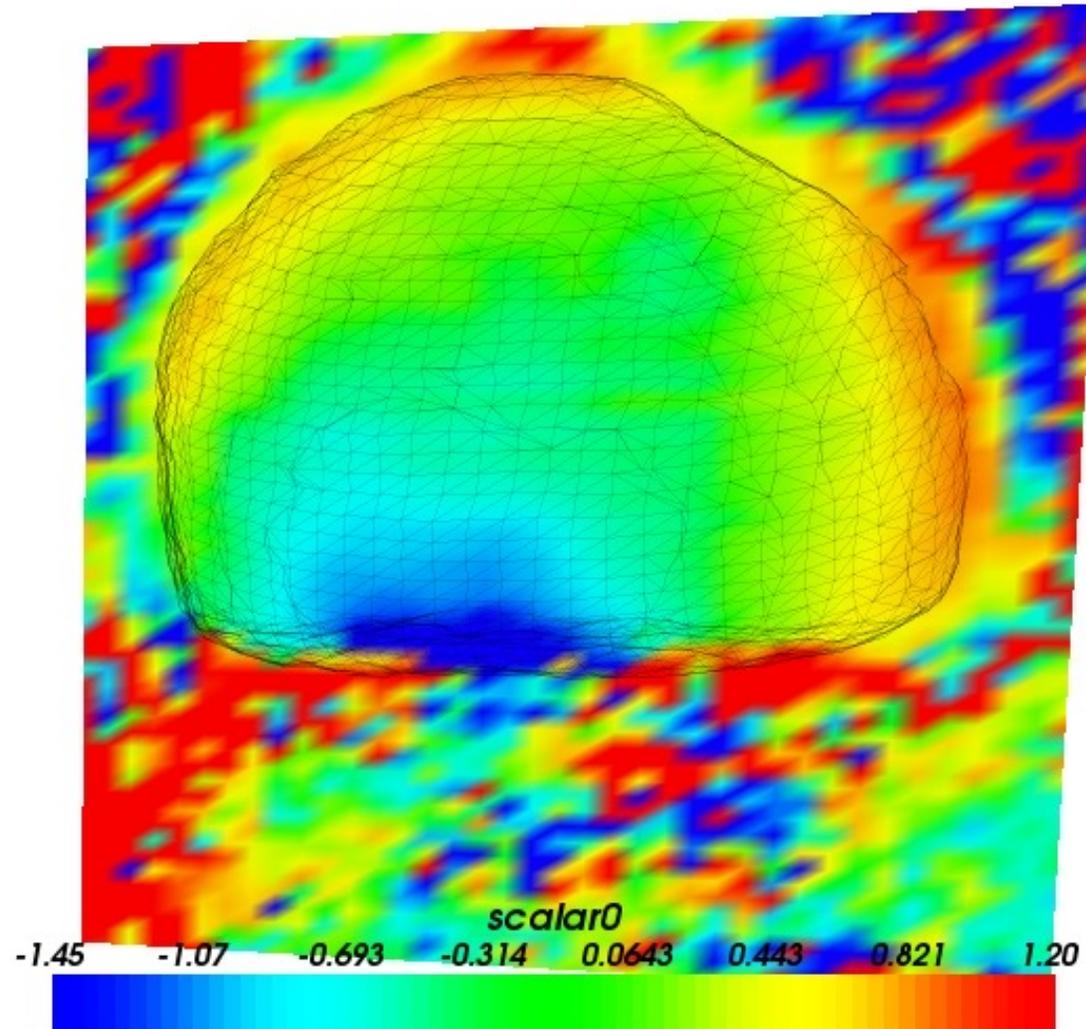


I. K. Robinson, AVS-53, Nov 2006

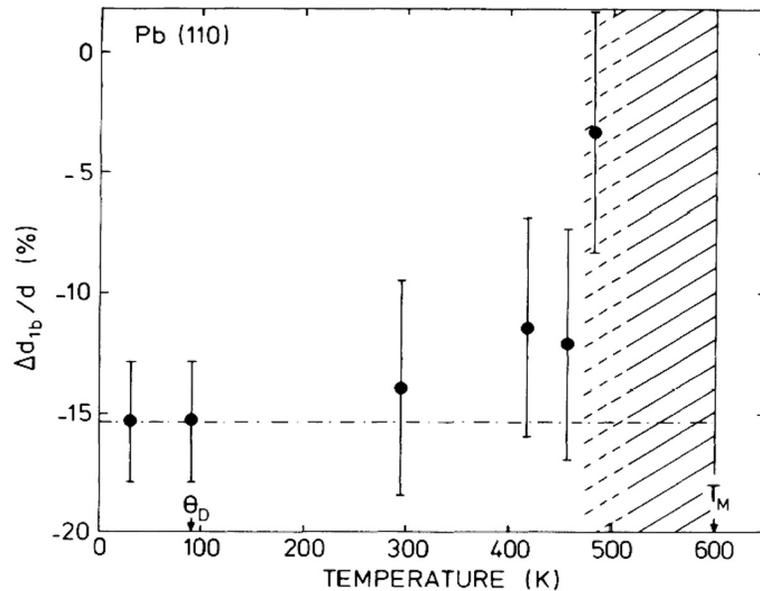


Contours showing Positive Phase

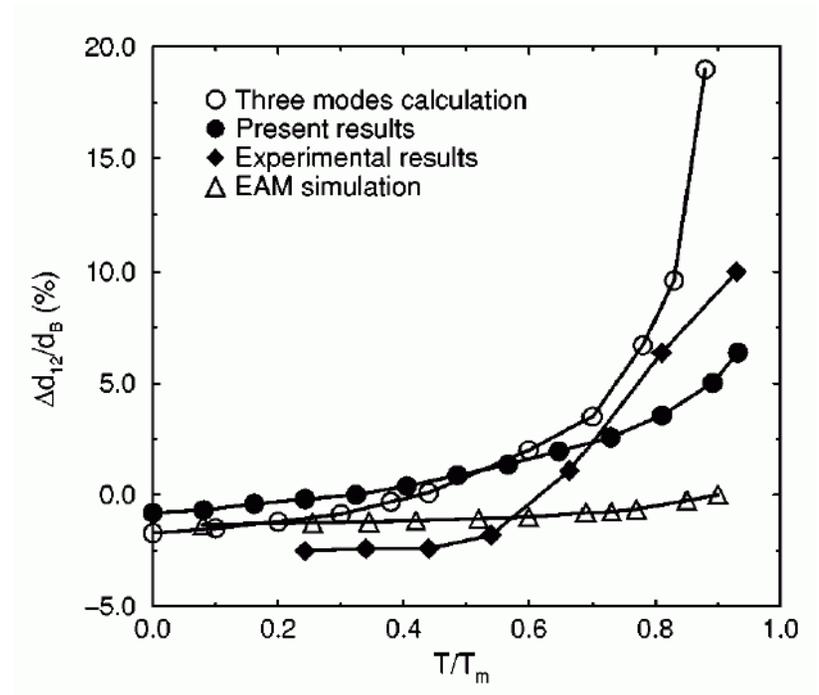
including correction for refraction by crystal



“Anomalous” Thermal Expansion of surfaces



Pb(110) experiment
J. Frenken, F. Huussen and
J.F.van der Veen, PRL 58 401 (1987)



Ag(111) theory
J. Xie (Scheffler group)
PRB 59 970 (1999)

Conclusions

- 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