Structural Principles of Nanoparticles from Coherent X-ray Diffraction

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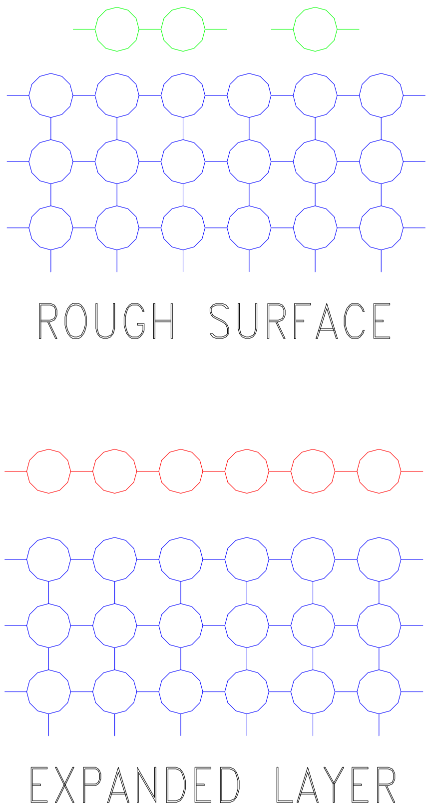
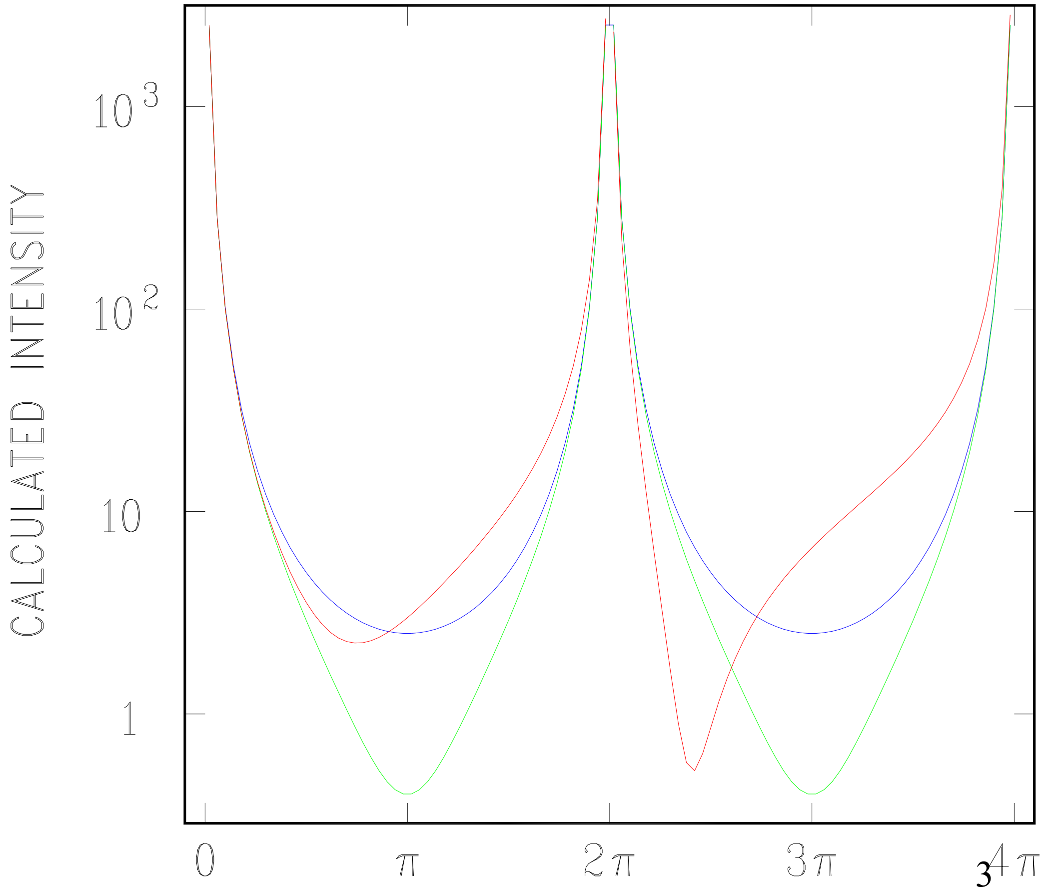
Outline

- Surface X-ray diffraction
- Nanocrystal structures
- Coherent X-ray diffraction
- Crystal strain as complex density
- Strain induced by surface reactions
- Partial coherence correction

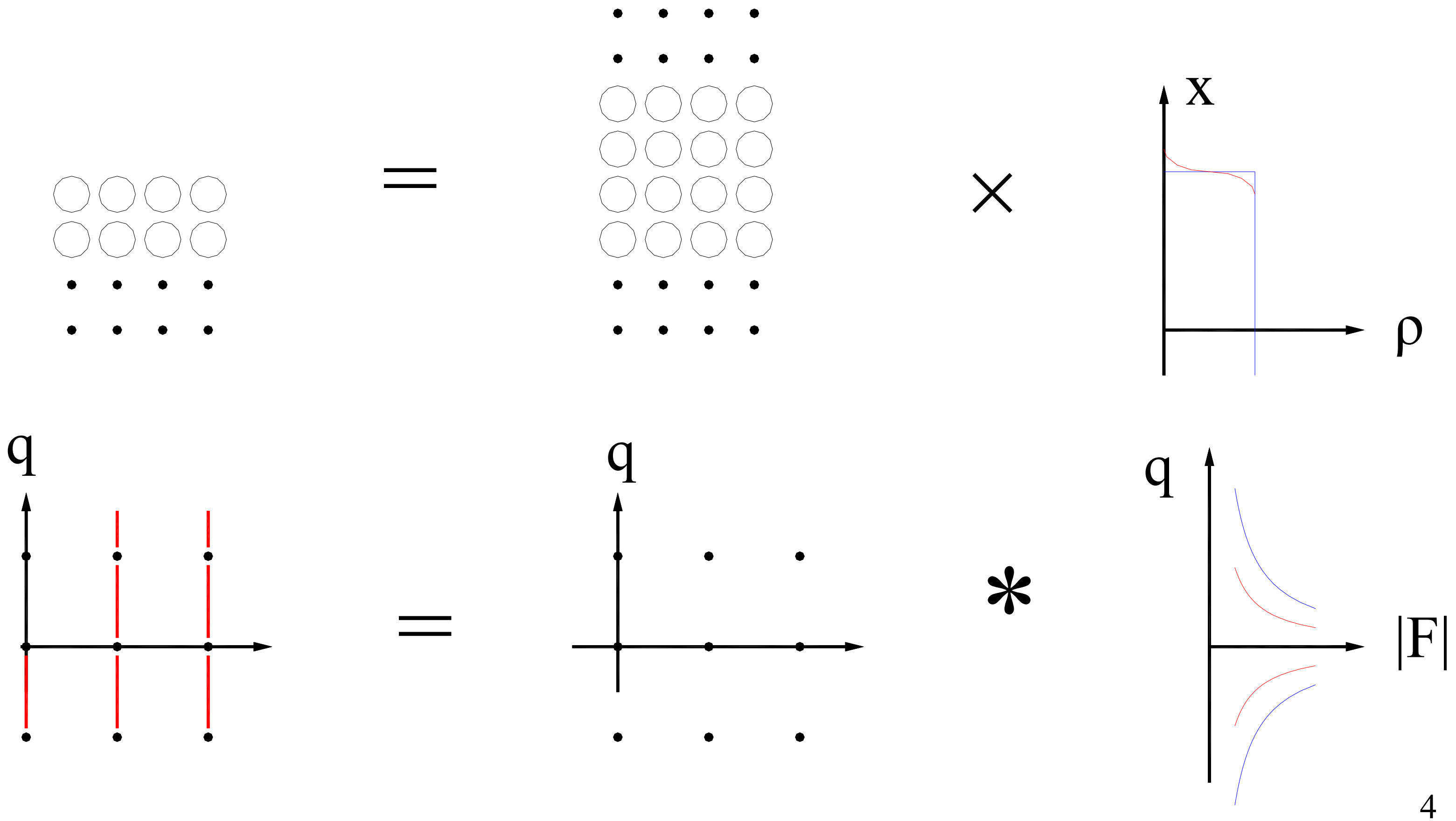
CTR is Sensitive to Surface Structure



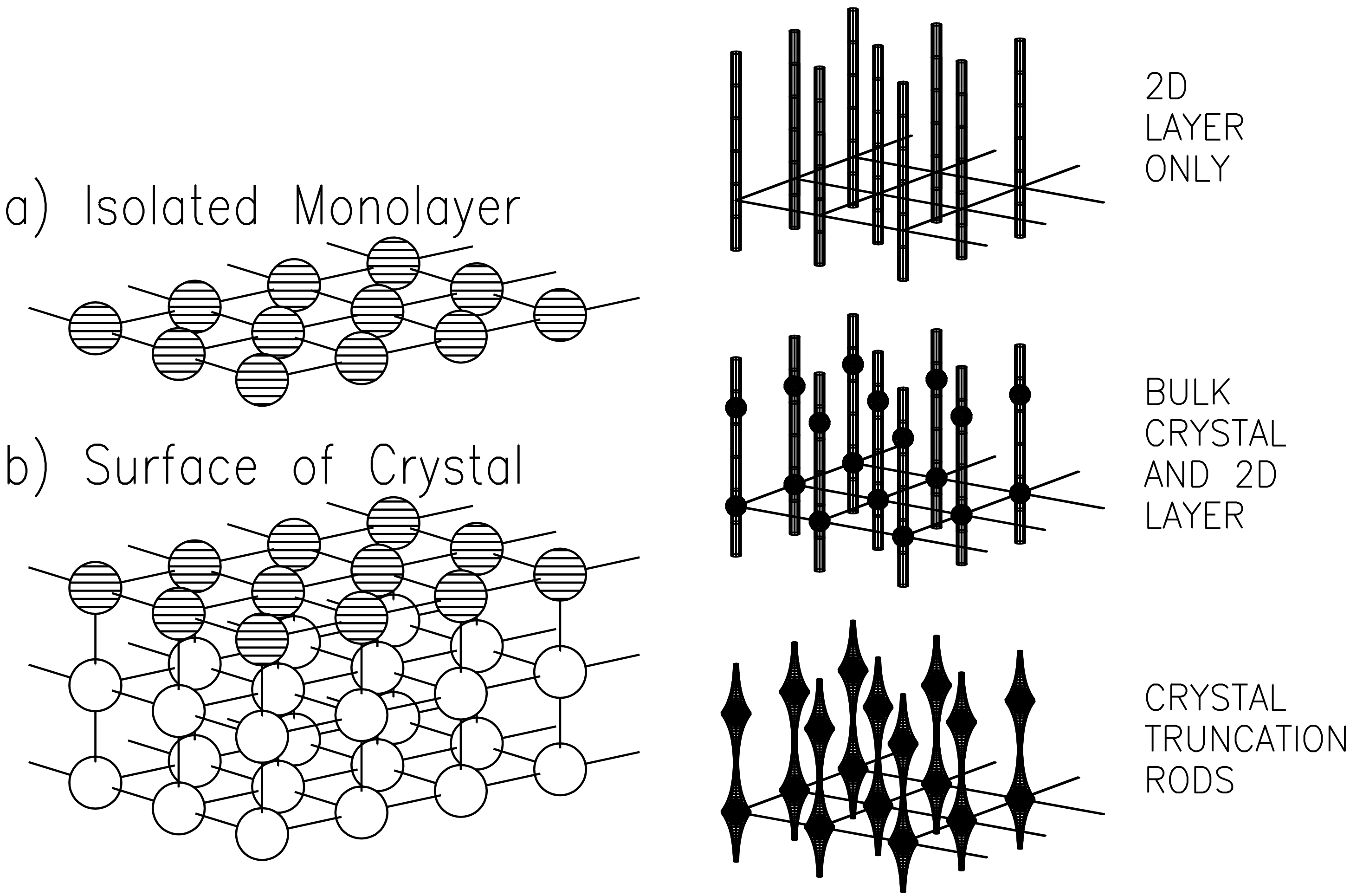


I. K.

CTR as Convolution



Crystal Truncation Rods (1986)



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)

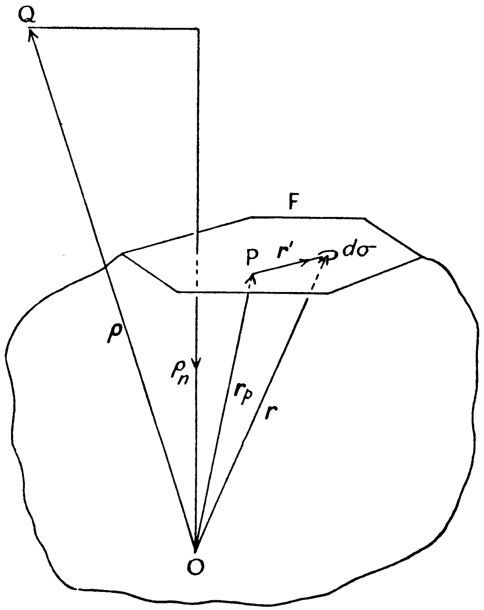
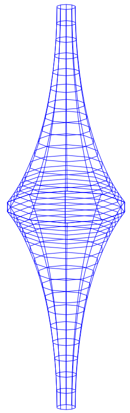
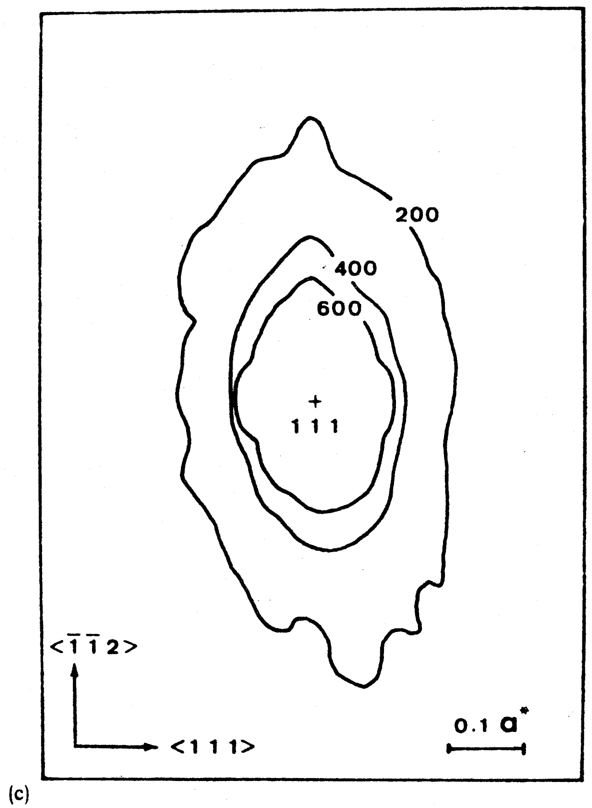


Fig. 200

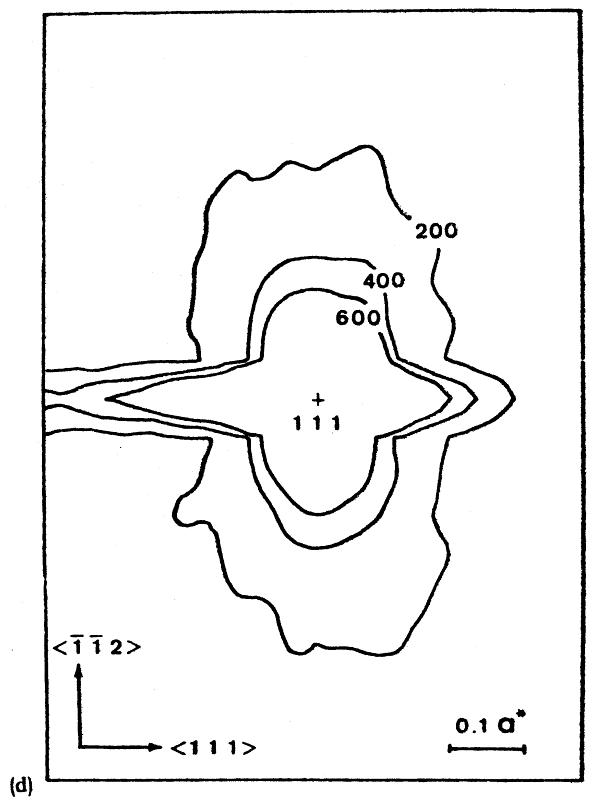


"Stacheln"

Diffuse Scattering from Si Wafer



Unpolished wafer

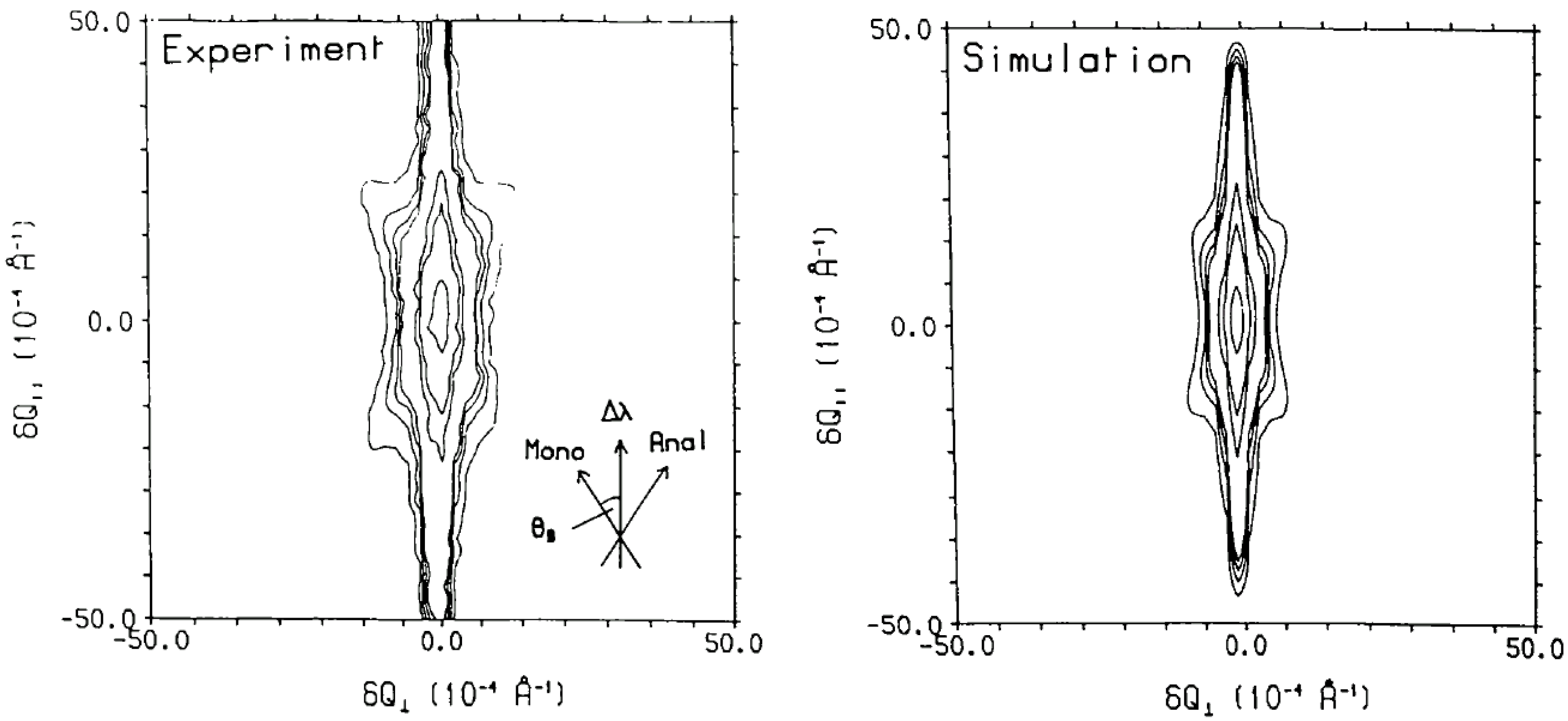


40 microns removed

N. Kashiwagara, J. Harada and M. Ogino, J. Appl. Phys <u>54</u> 2706 (1983)

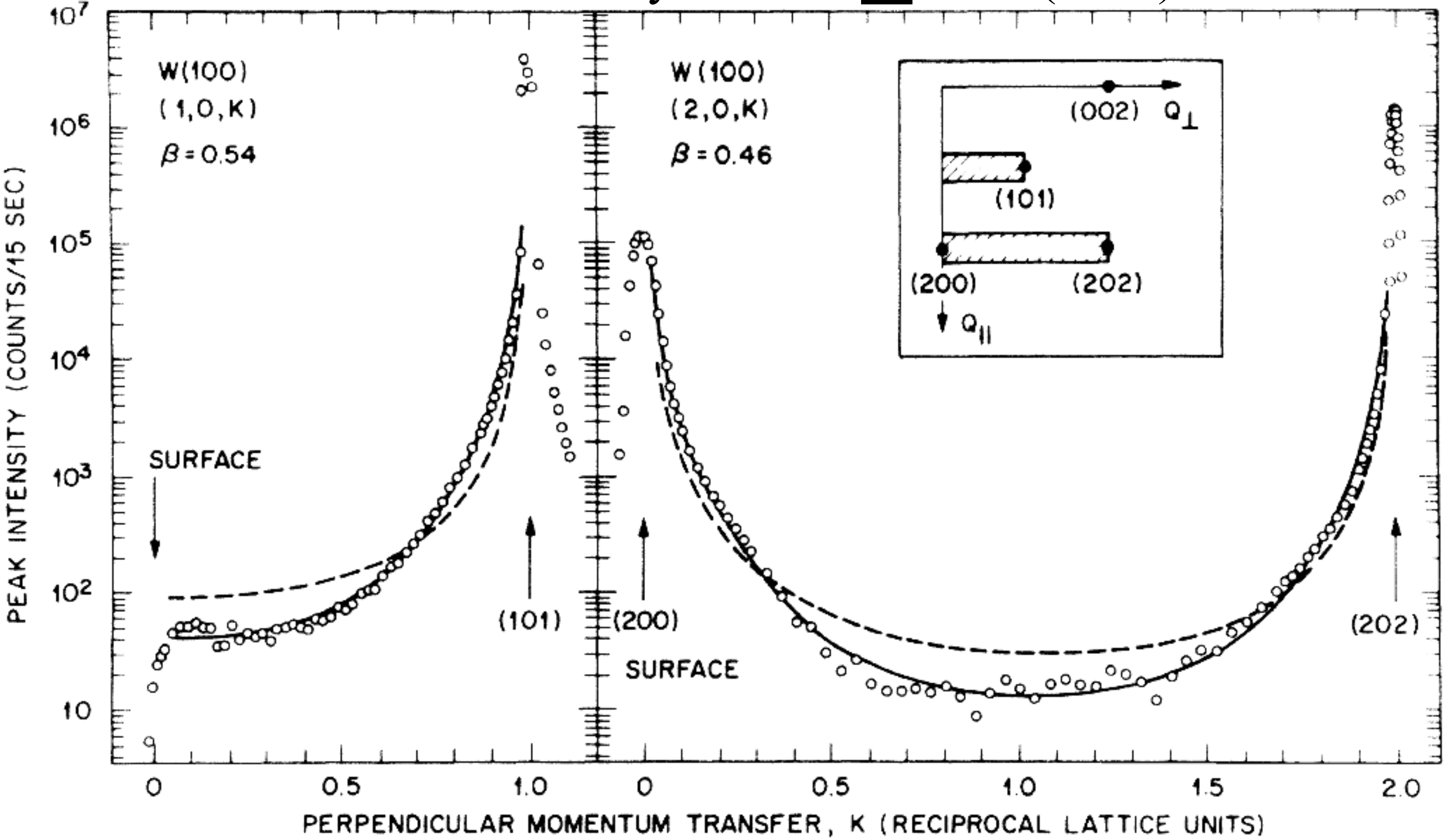
Resolution Function of the Triple-Axis Spectrometer

R. A. Cowley *et. al.*, Acta Cryst **A45** 415 (1989)



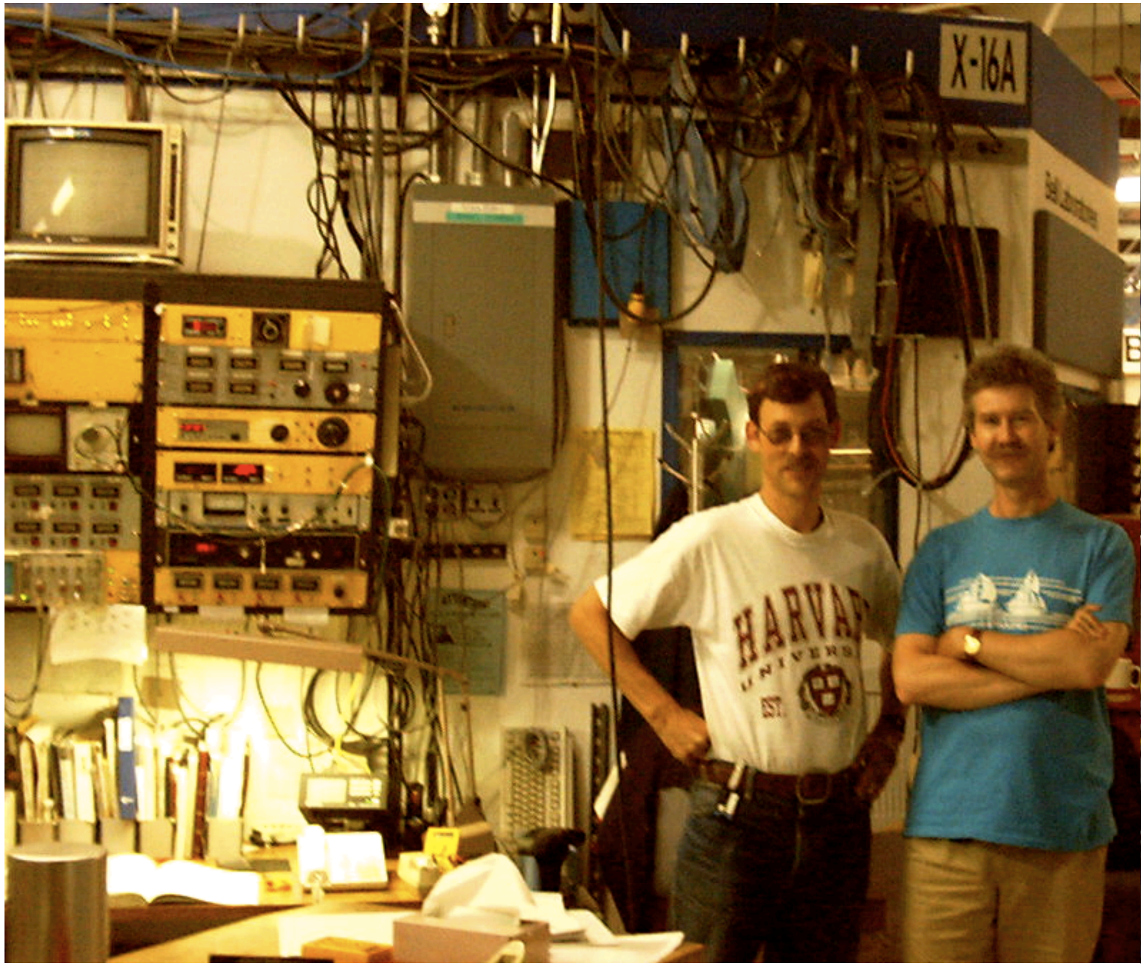
CRYSTAL TRUNCATION RODS AND SURFACE ROUGHNESS

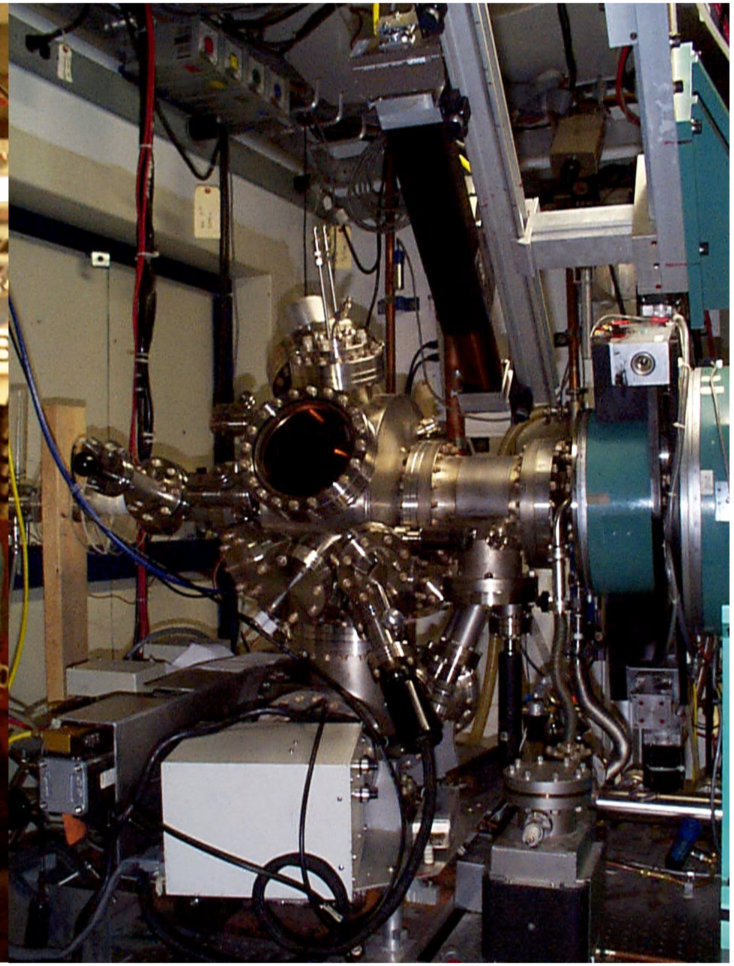
I.K.Robinson Phys Rev B 33 3830 (1986)



X16A Surface X-ray Diffraction

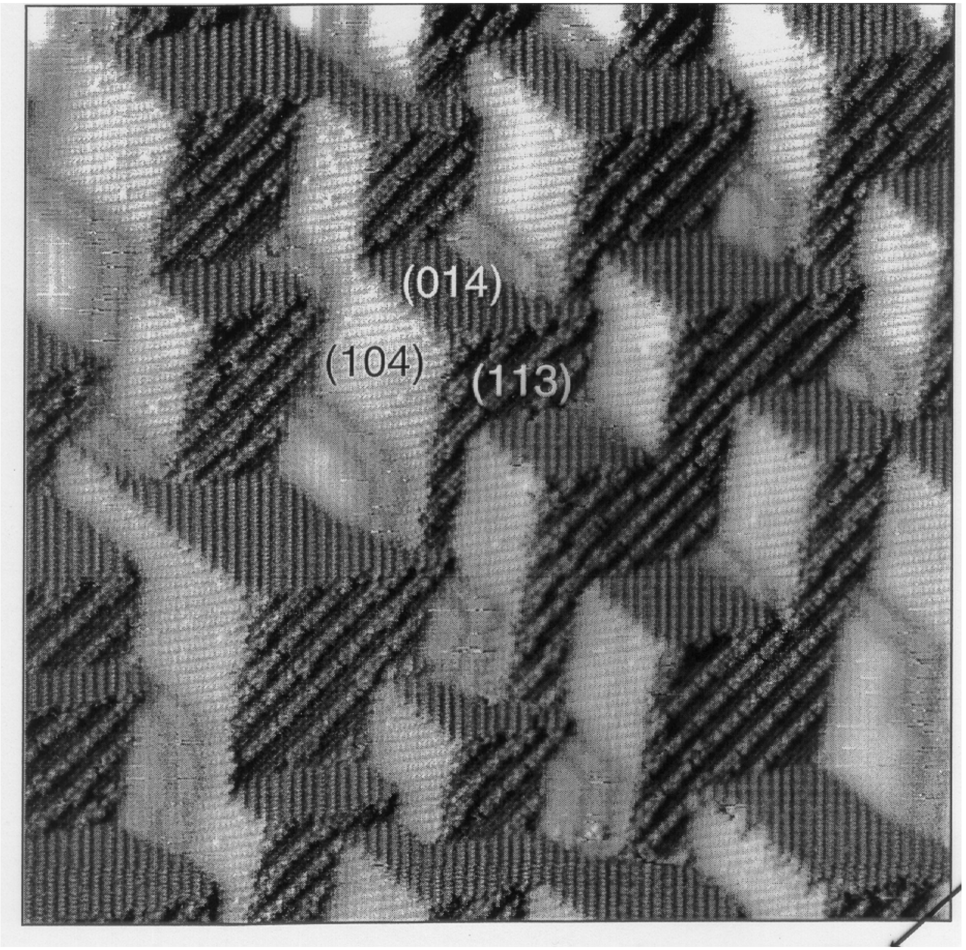
Brookhaven National Lab (1987 – 2004)

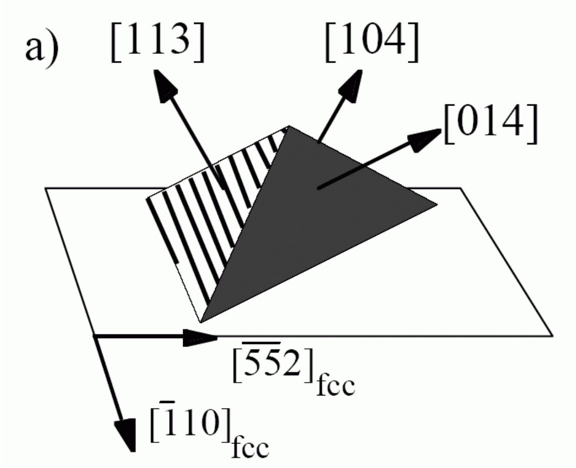


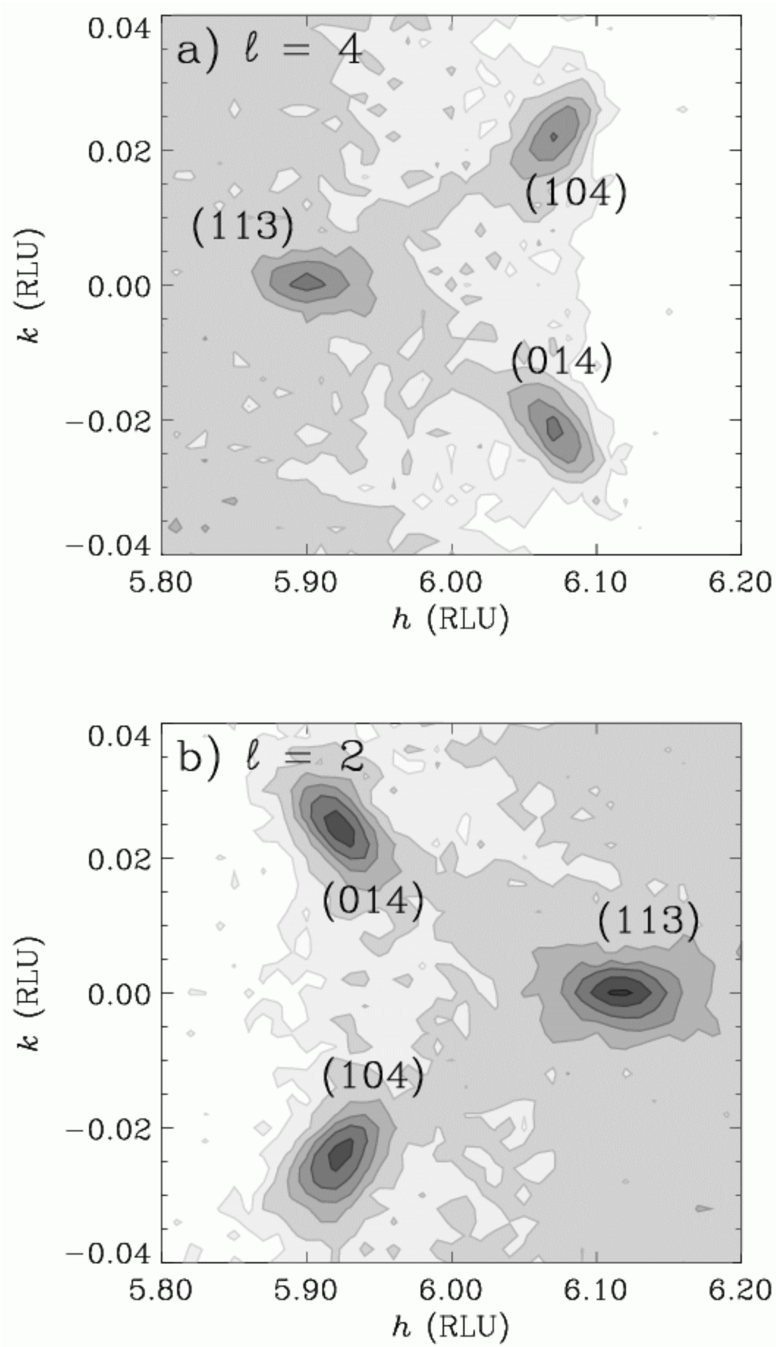


Cu(115) after Oxidation: STM

S. Reiter and E. Taglauer, Surf. Sci. **367** 33 (1996)







Cu(115) after Oxidation: X16A

Don Walko, UIUC PhD Dissertation (2000)

Outlook for Surface X-ray Diffraction

- Nanocrystals
- New physical properties
- Alloys
- Semiconductors
- Oxides
- Catalysts
- Interfaces

Outlook for Surface X-ray Diffraction

- Nanocrystals
- New physical properties
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- Nano Oxides
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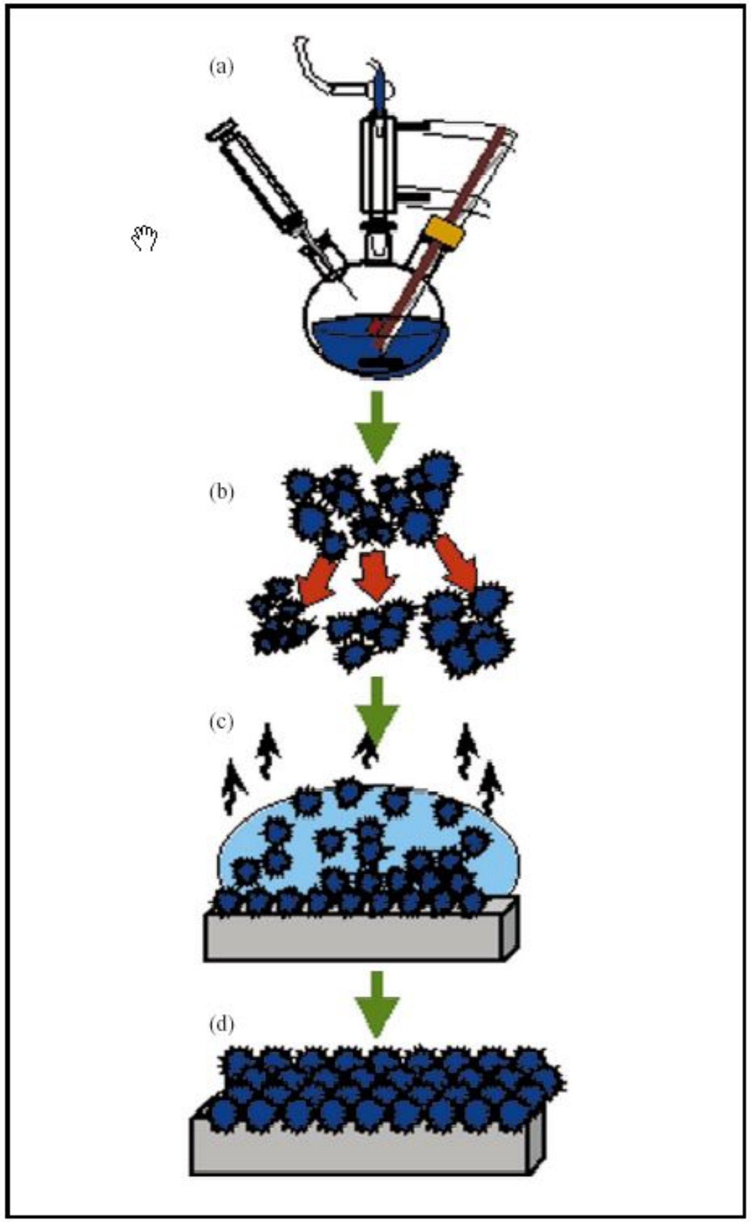
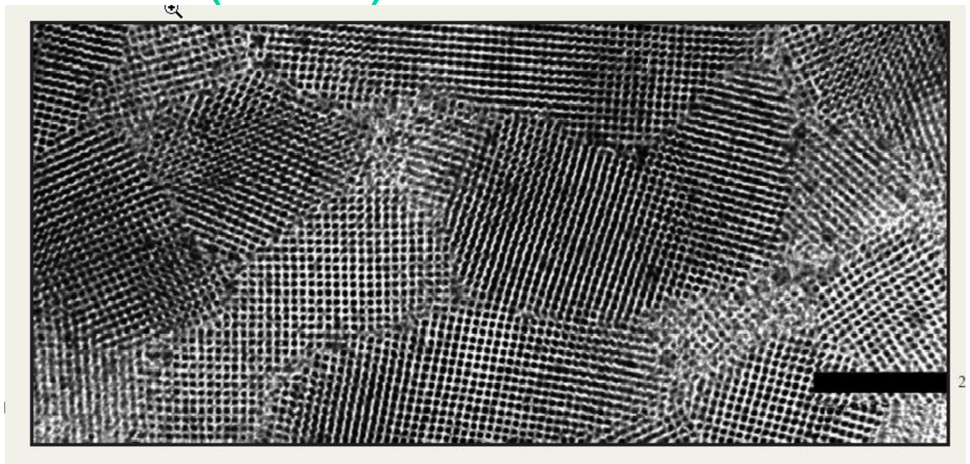
Chemical Synthesis of Nanocrystals



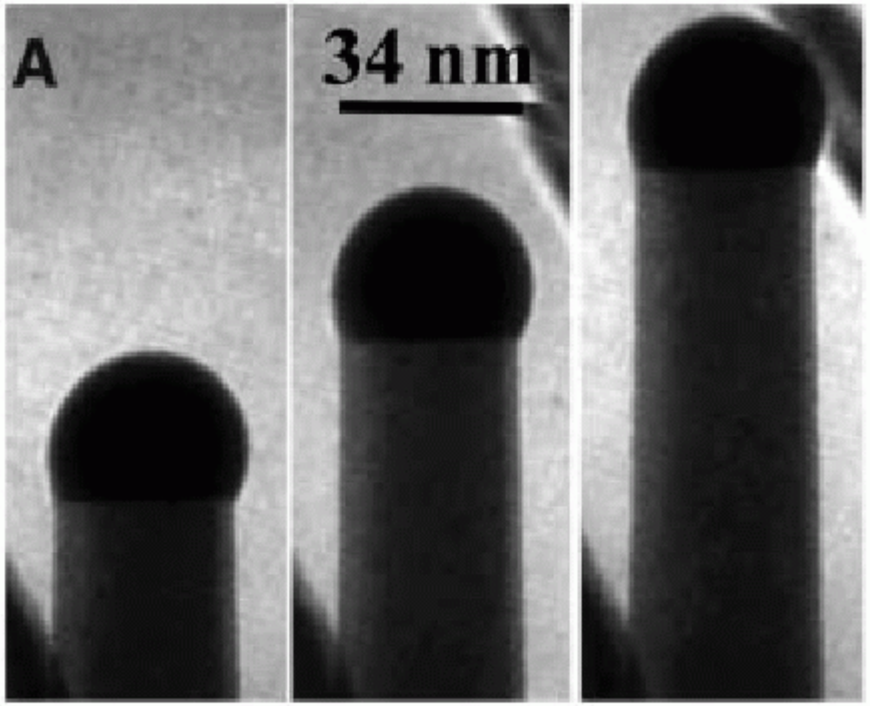
- Reactants introduced rapidly
- High temperature solvent
- Surfactant/organic capping agent
- Square superlattice (200nm scale)

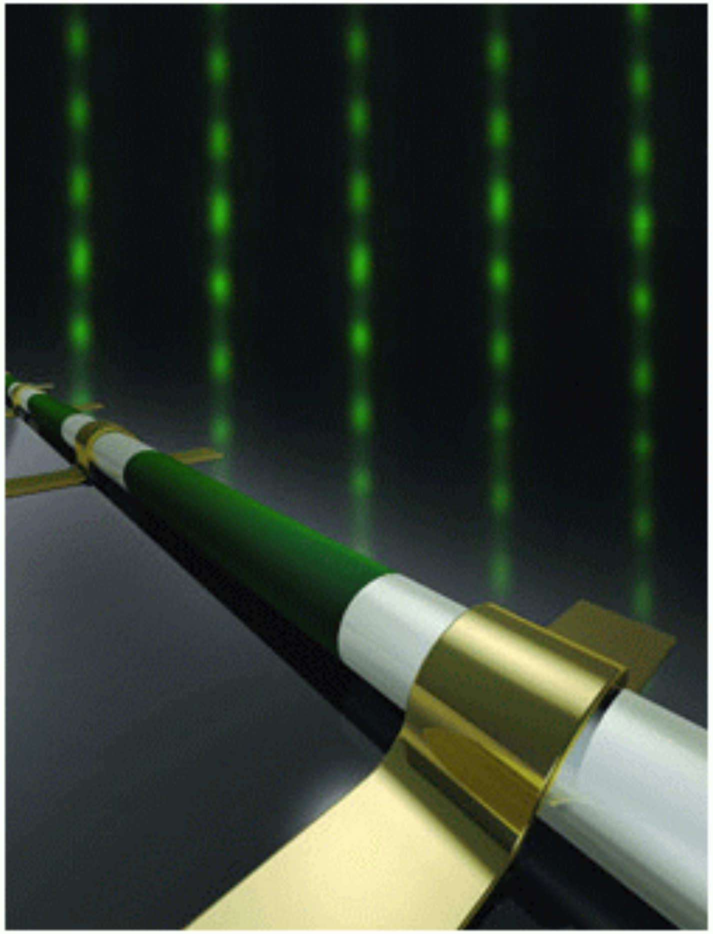
C. B. Murray, IBM J. Res. & Dev. **45** 47 (2001)



VLS growth of nanowires

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

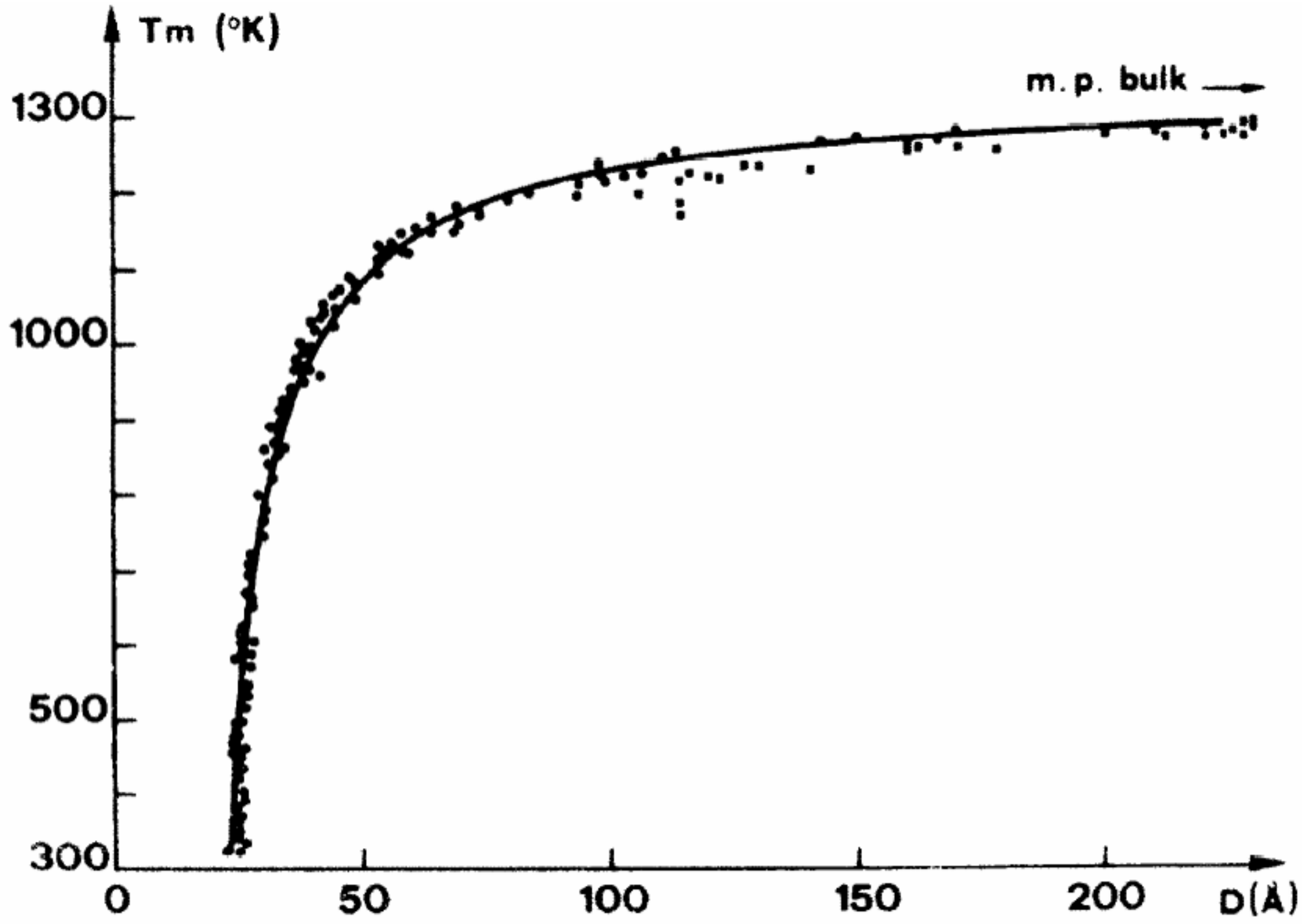




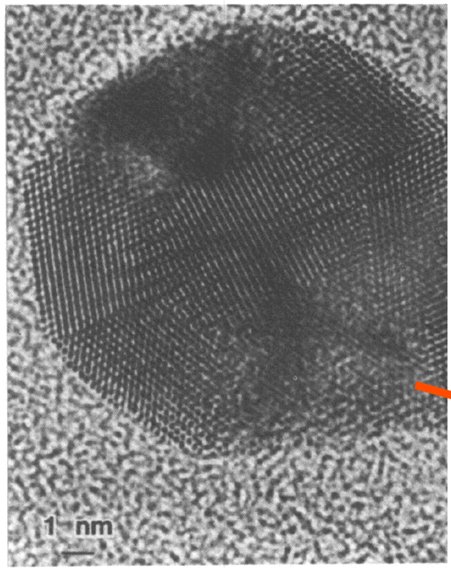
NiSi/Si nanowire heterostructure devices. *Nature* **430**, 61 (2004).

Size-dependent Melting of Au Particles

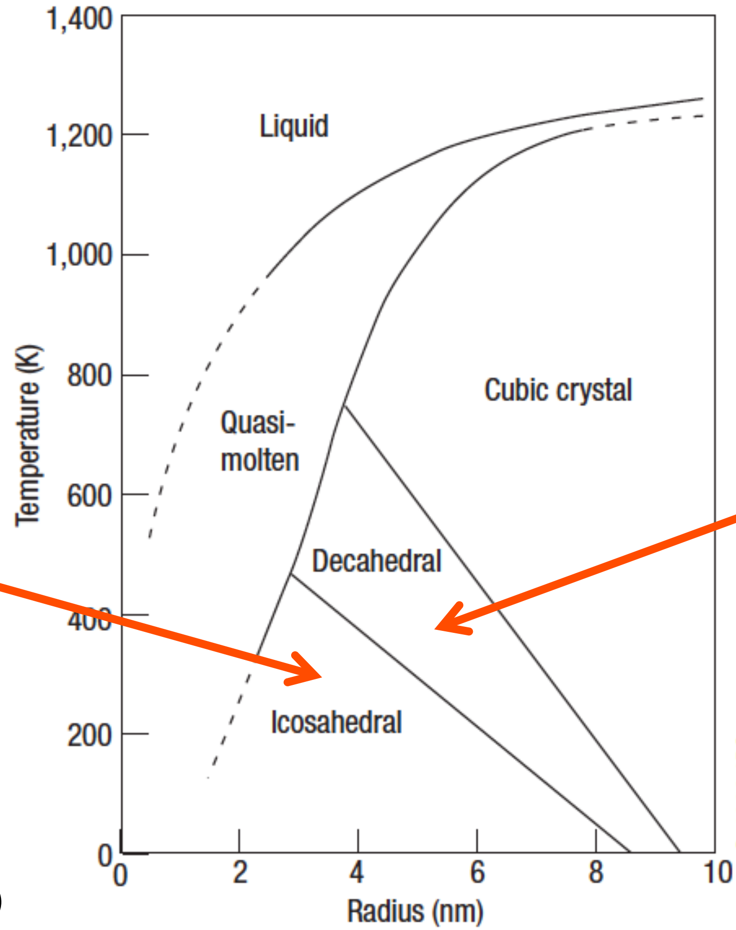
P. Buffat and J-P. Borel, Phys. Rev. A 2287-97 (1975)

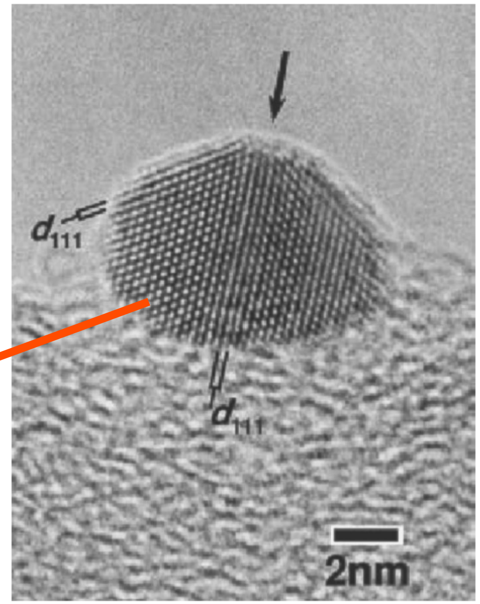


Structure of Gold vs Size



L. D. Marks, RPP (1994)





Koga and Sugawara (2003)

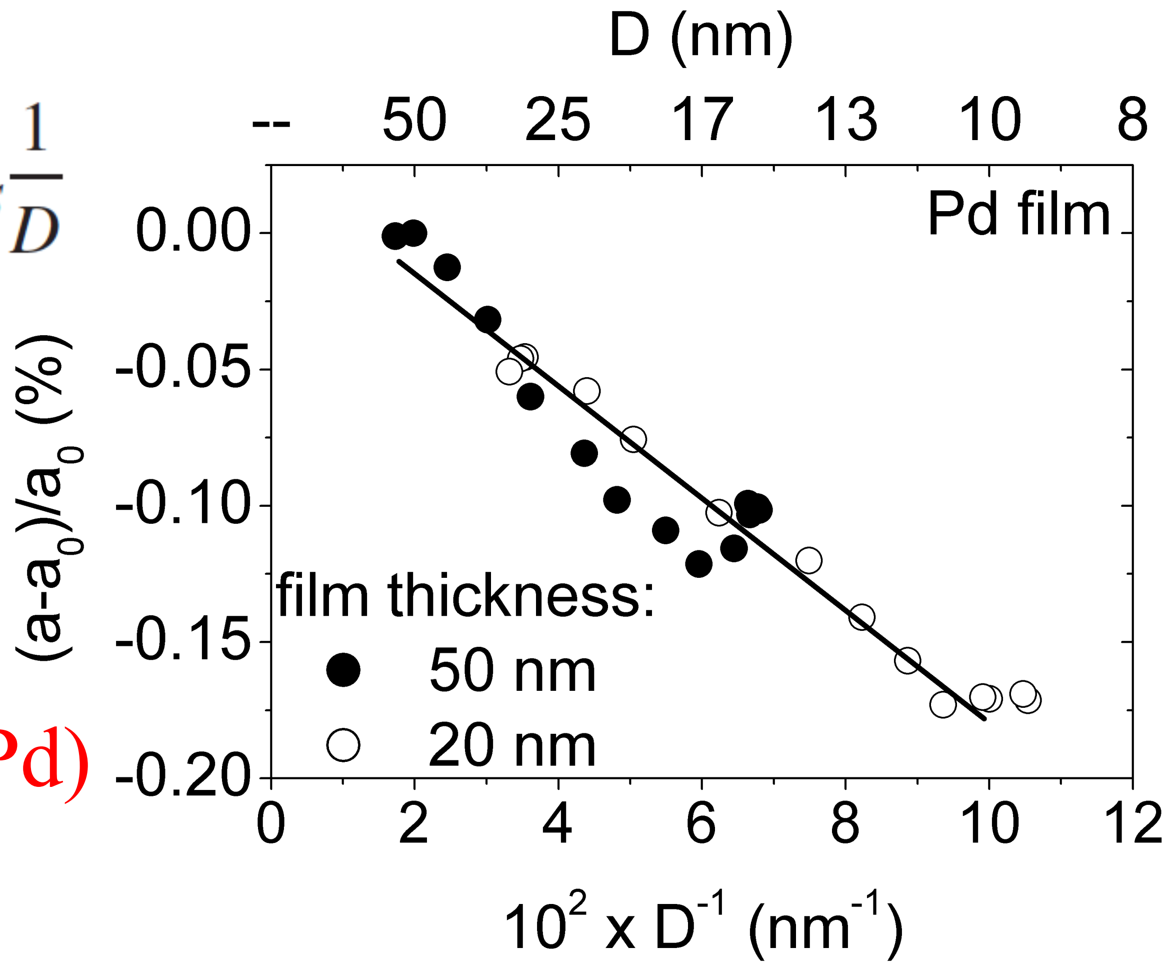
Contraction of Small Particles

Gibbs Thomson pressure + Bulk modulus

Sheng, Welzel & Mittemeijer, APL 97 153109 (2010)

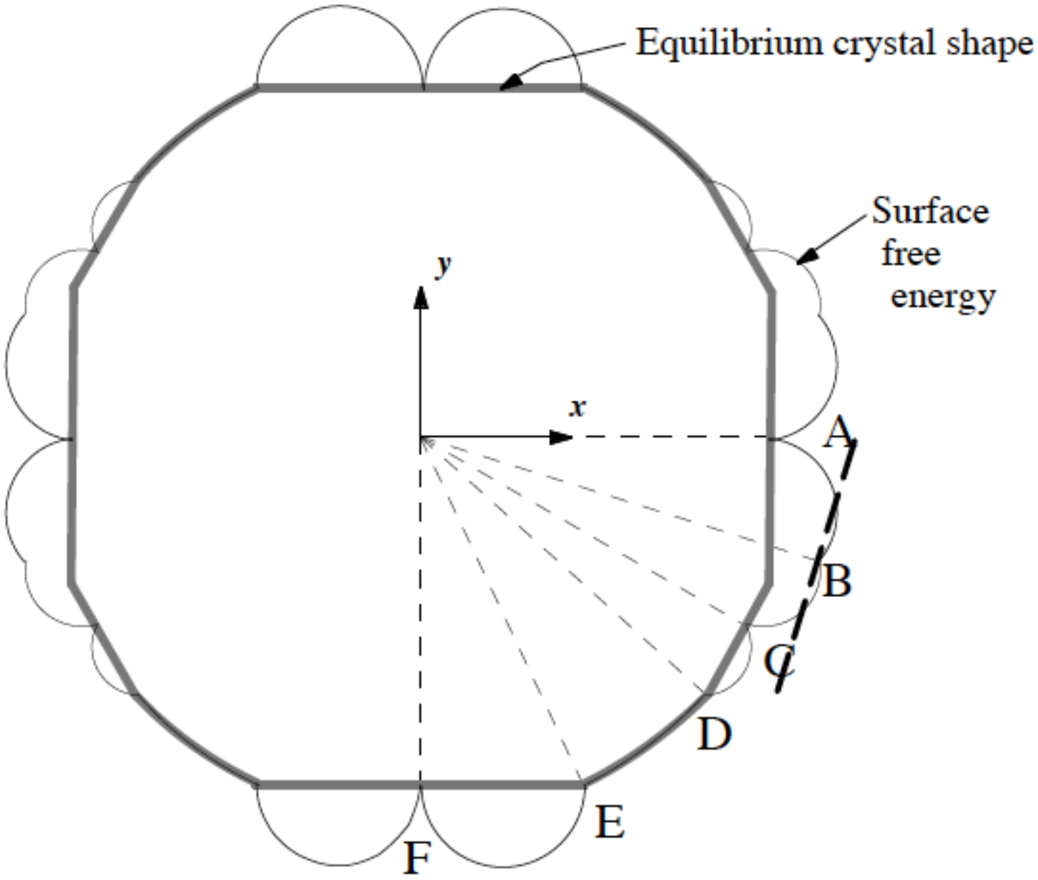
$$\frac{a - a_0}{a_0} = -\frac{4}{3K}\sigma_S\frac{1}{D}$$

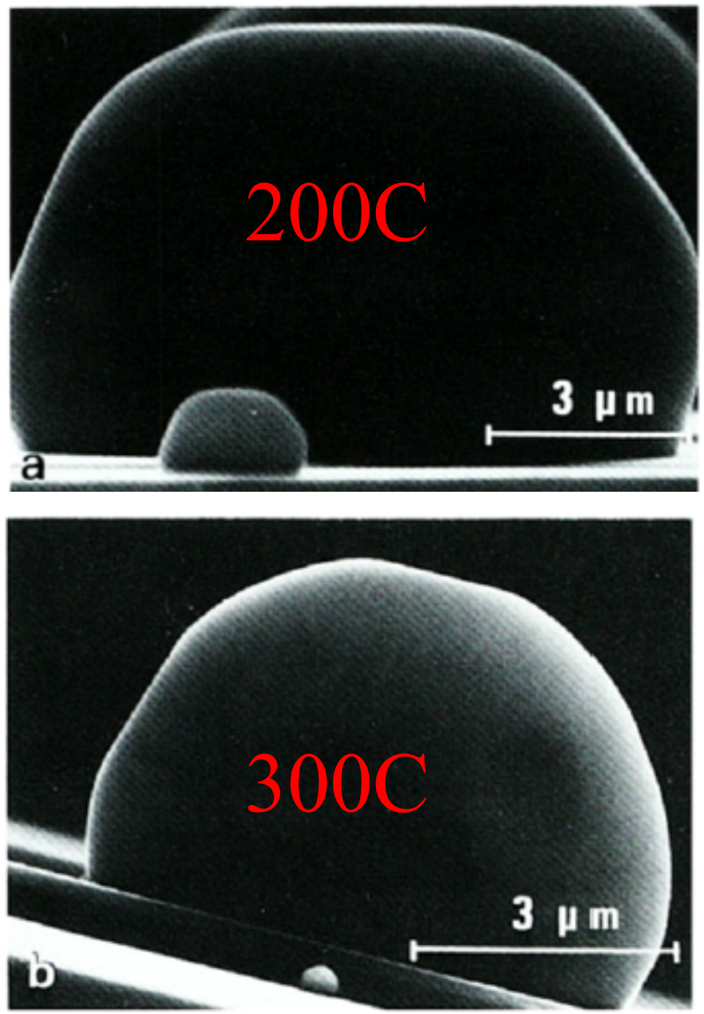
$\sigma_S = 2\text{N/m}$ (Pd)



Equilibrium crystal shape

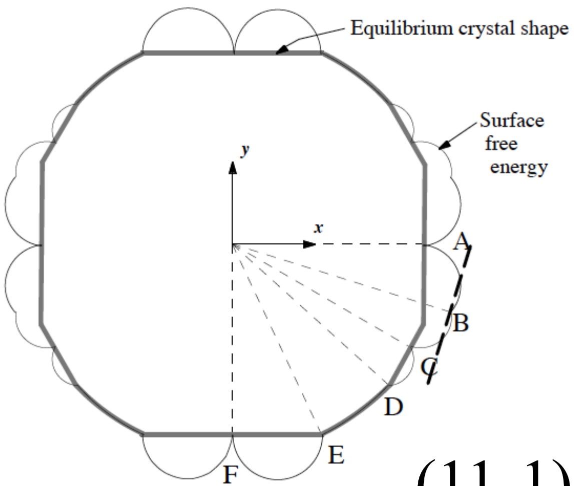
Wulff construction; Heyraud & Metois, Surf Sci 128 334 (1983)





Equilibrium crystal shape

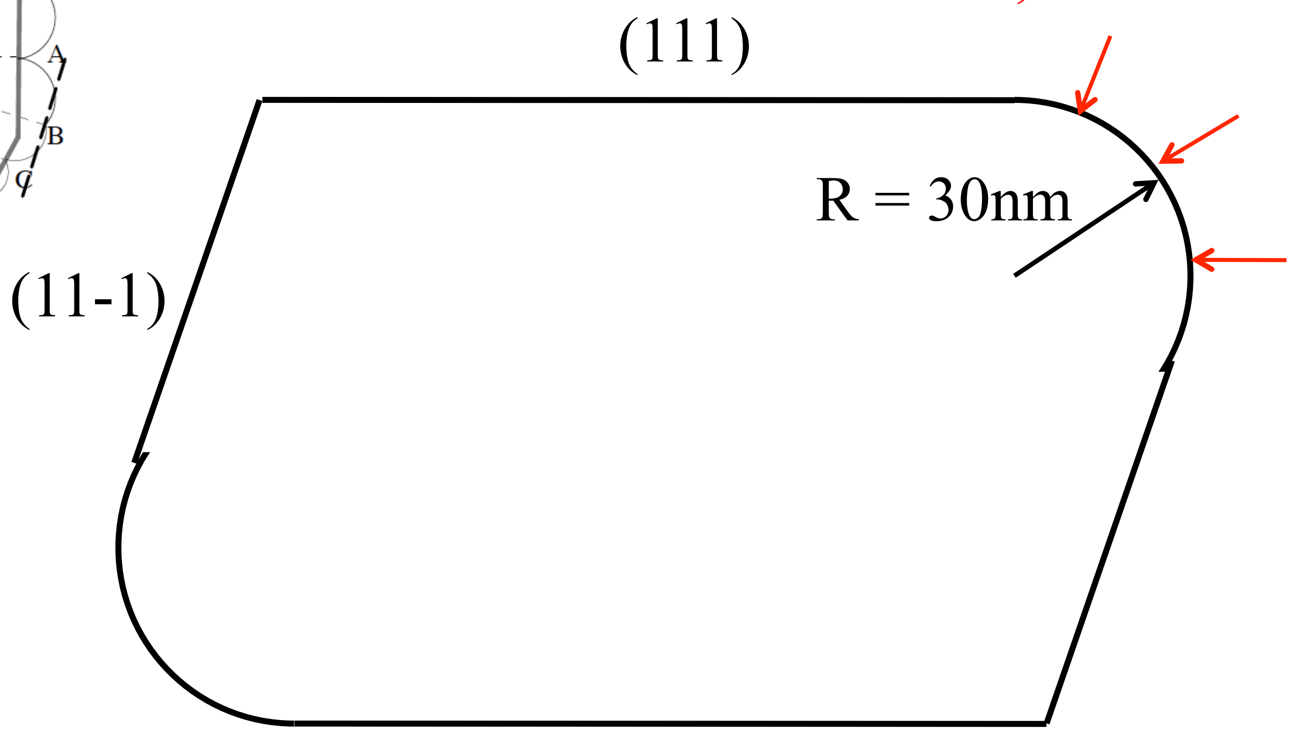
Wulff construction + Gibbs Thomson (Young-Laplace) pressure



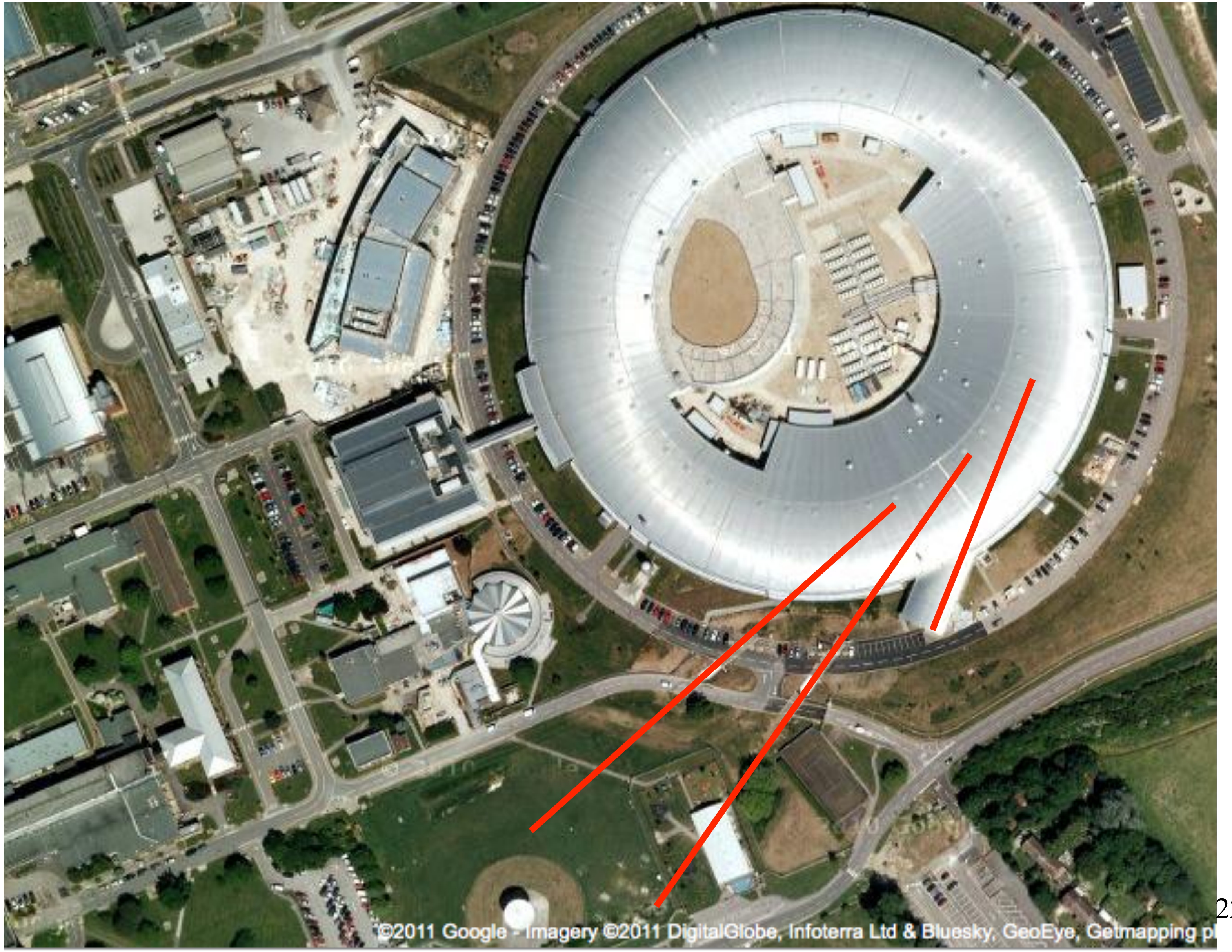
$\gamma = 2\text{N/m}$

$P = 2\gamma/R = 70\text{MPa}$

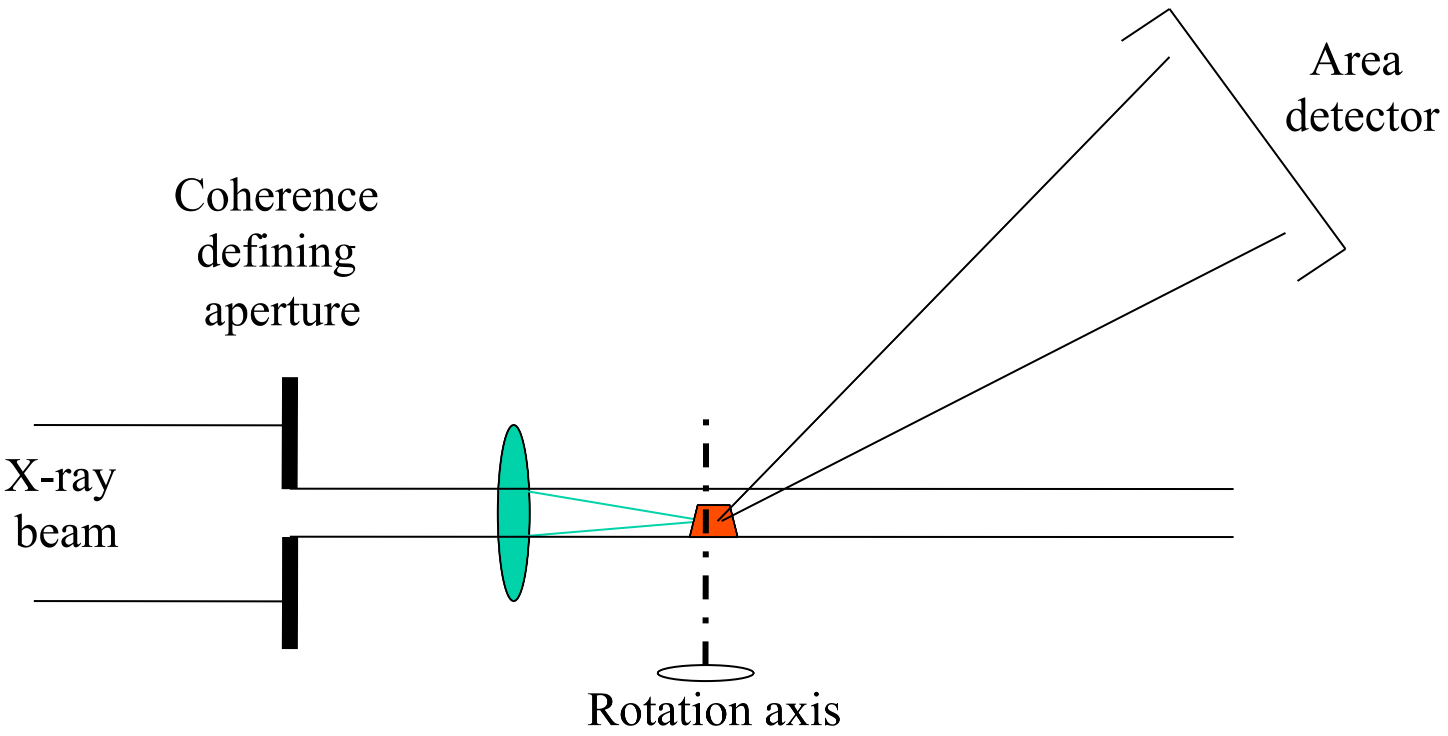
$\varepsilon = 0.1\%, \ \Phi = 0.6 \text{ rad}$

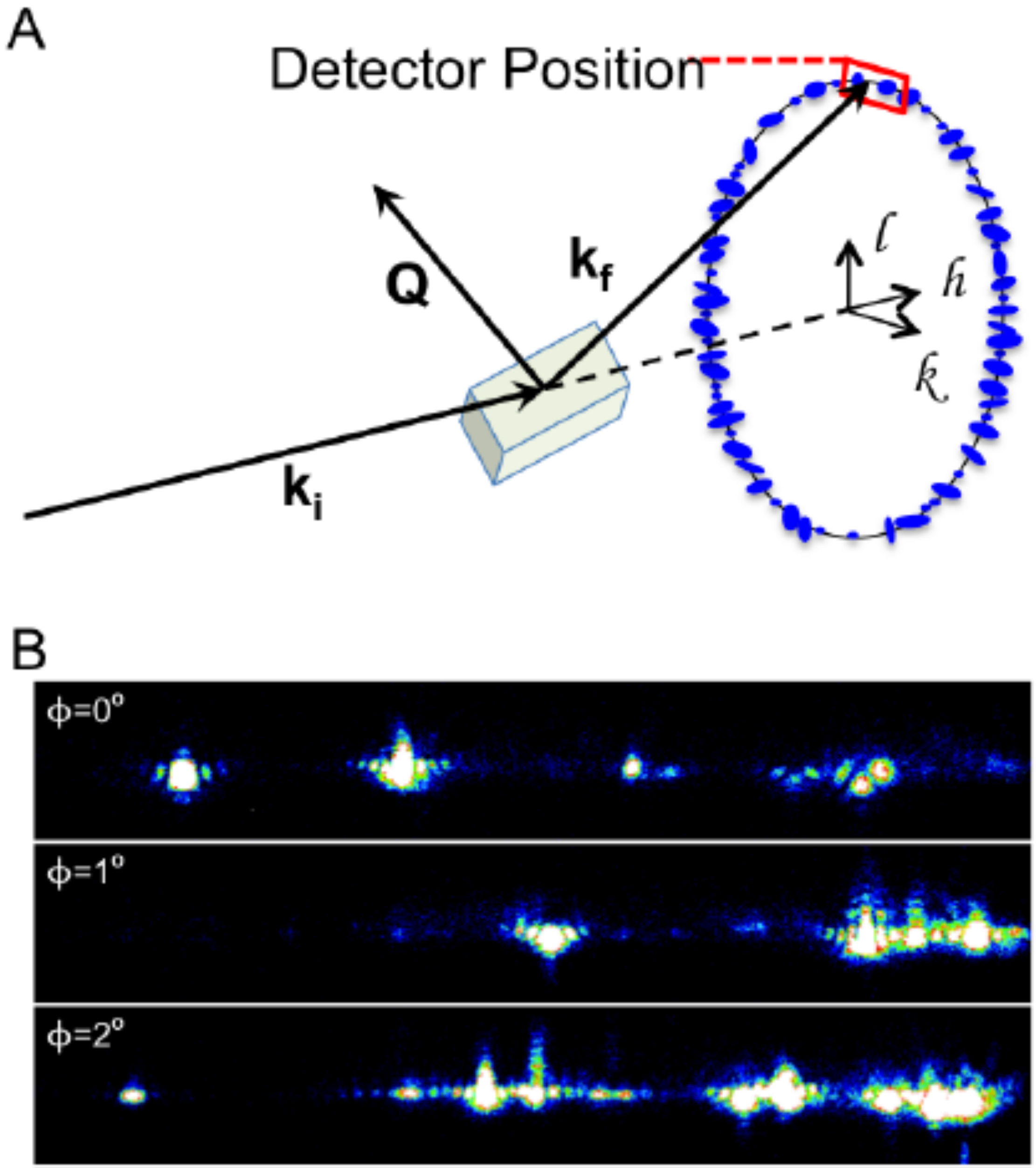


Diamond Light Source, 2009

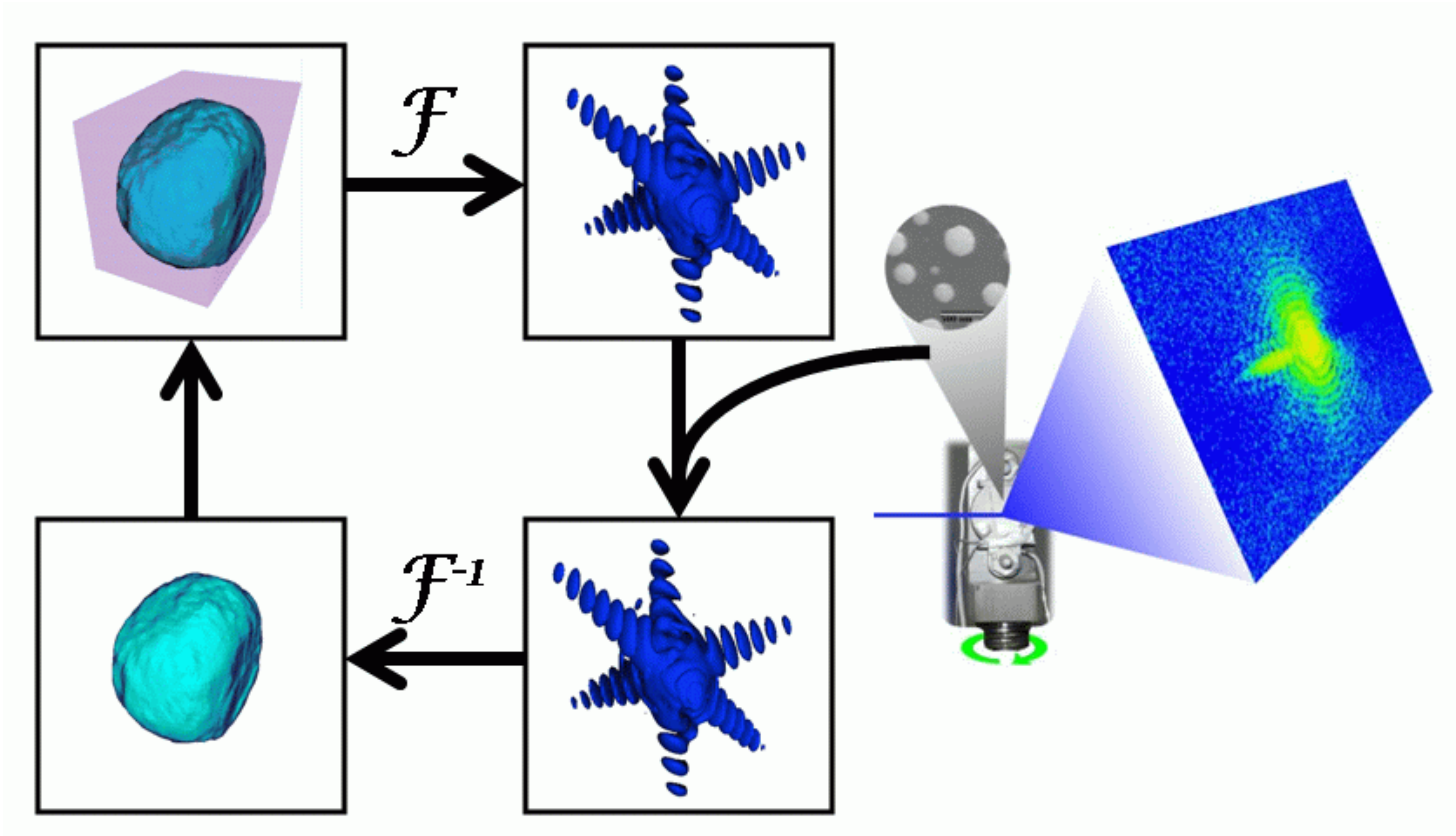


Lensless X-ray Microscope, 2003

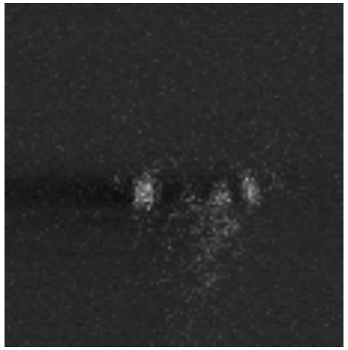


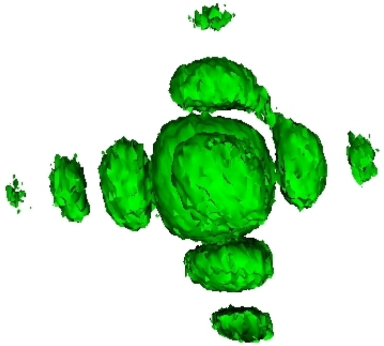

A
Detector Position
Q
$\mathbf{k_f}$
$\mathbf{k_i}$
l
h
k
B
ϕ=0°
ϕ=1°
ϕ=2°

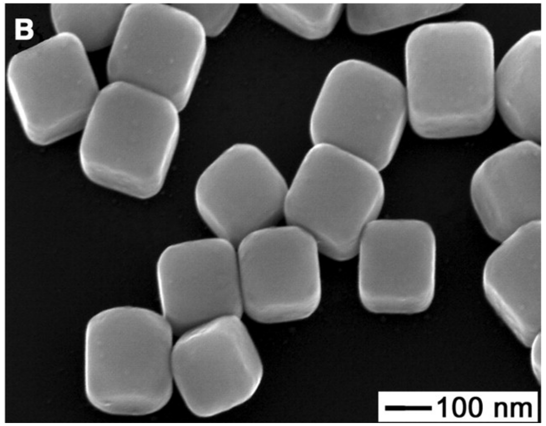
Generic "Error Reduction" method

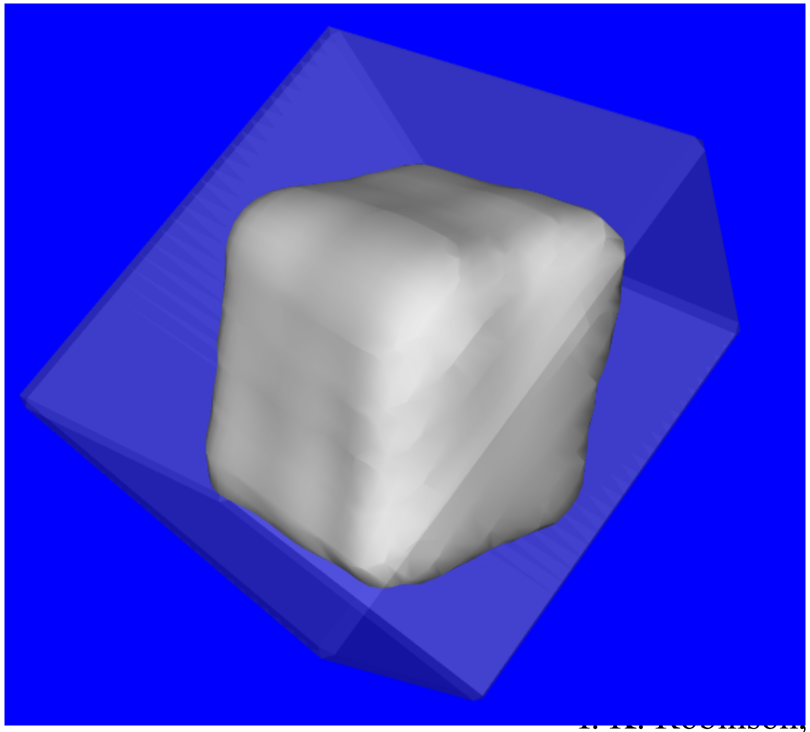


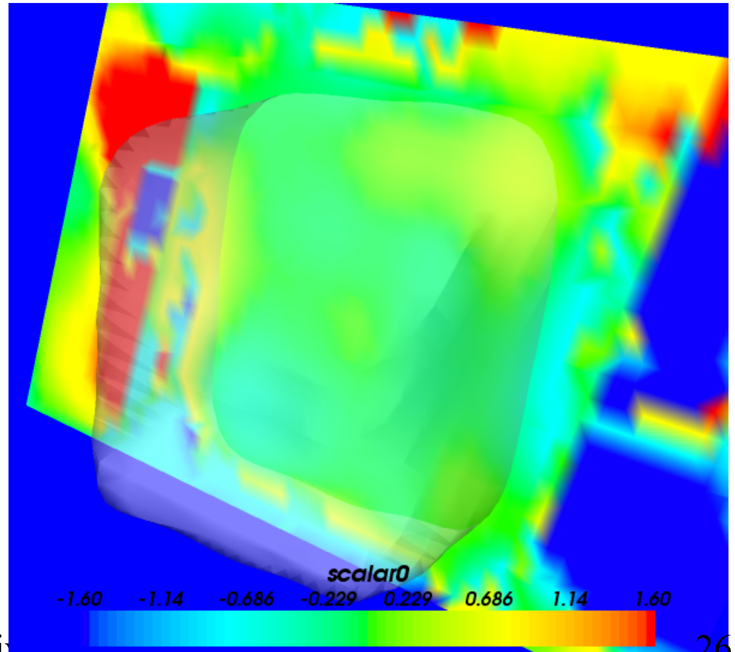
J. R. Fienup Appl. Opt. 21 2758 (1982)
R. W. Gerchberg and W. O. Saxton Optik 35 237 (1972)





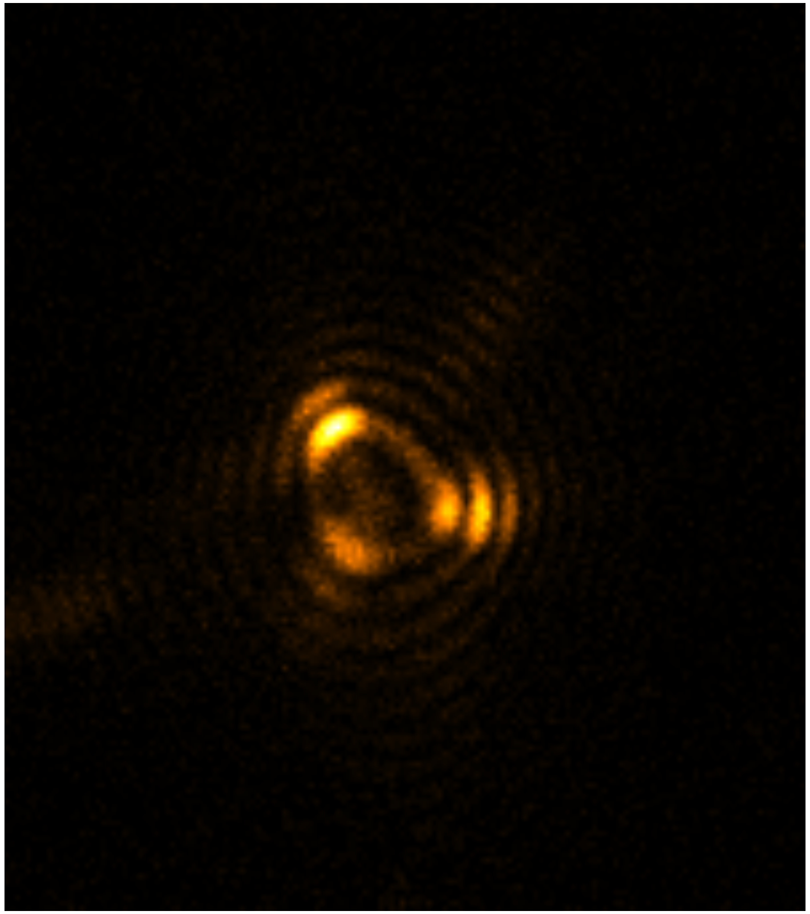

B
100 nm

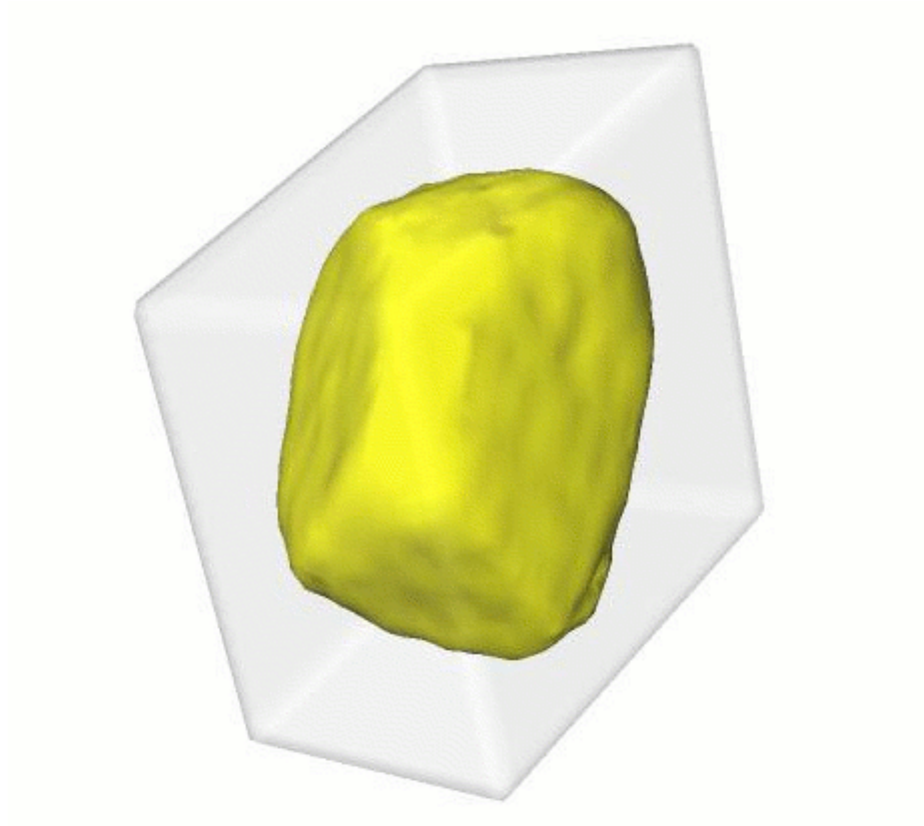



scalar0
-1.60 -1.14 -0.686 -0.229 0.229 0.686 1.14 1.60

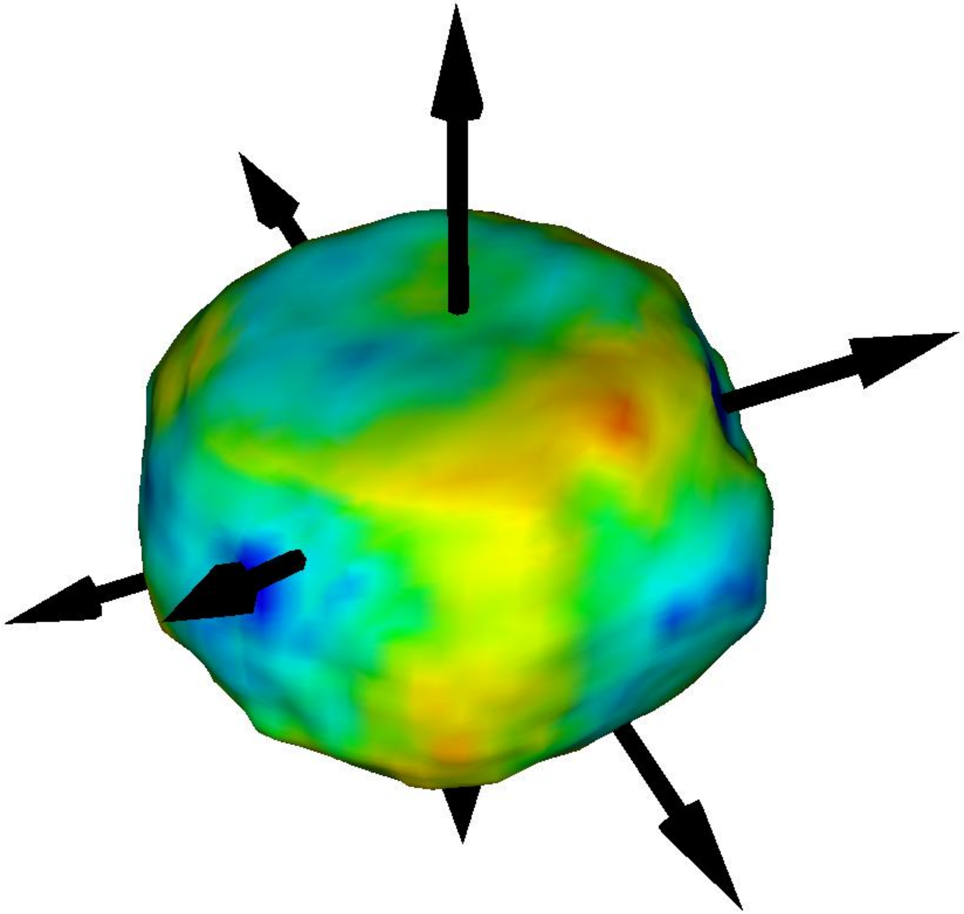
Gold nanocrystal reconstruction

showing support used for 20 HIO followed by 10 ER

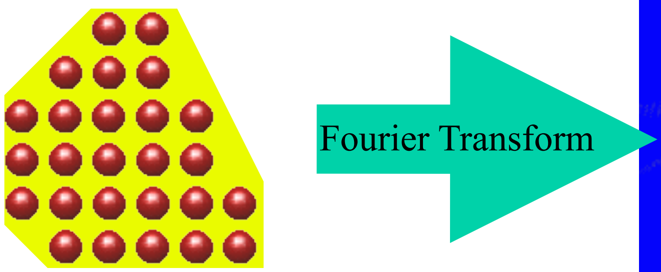


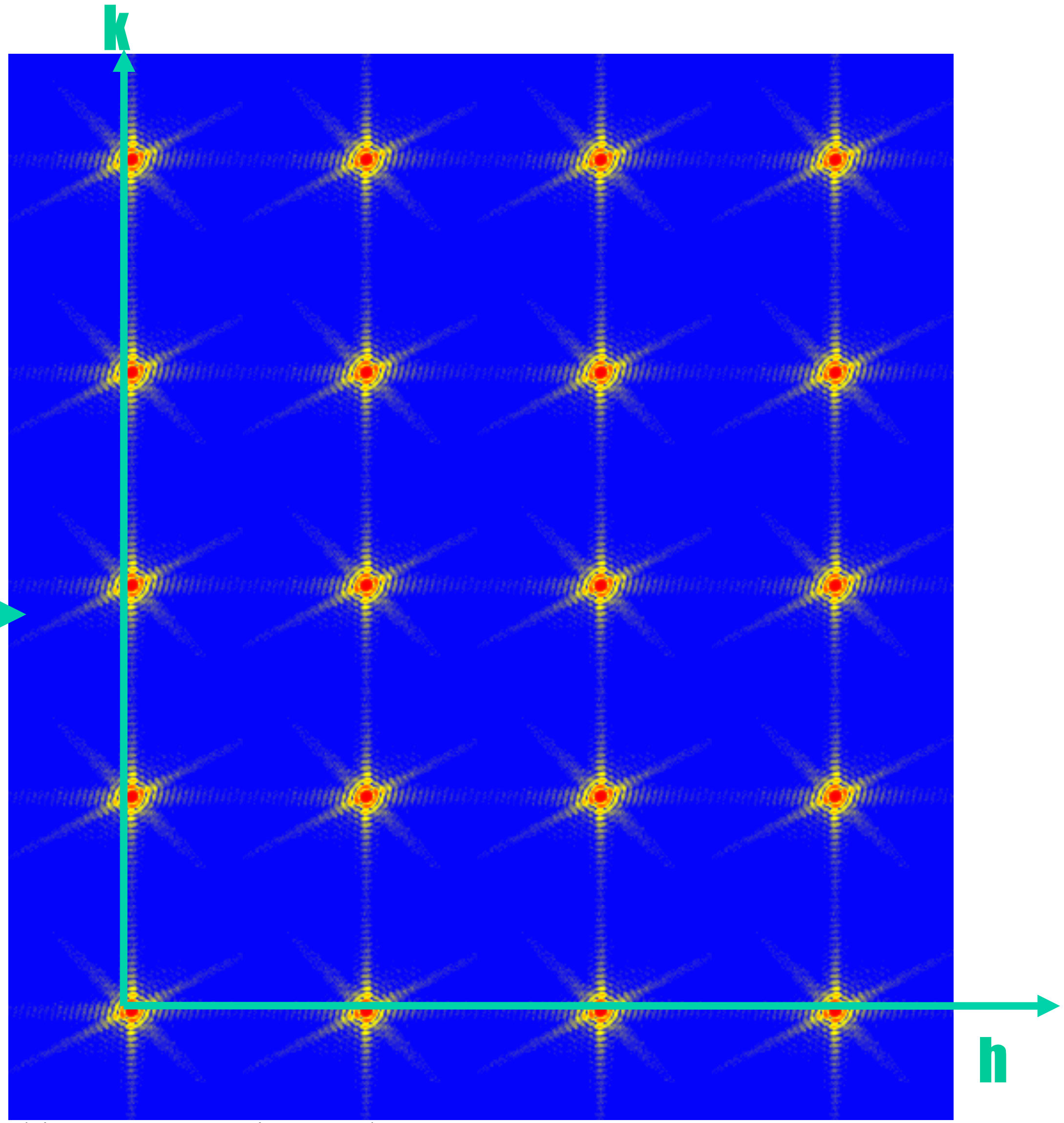


Phase isosurface of residual strain



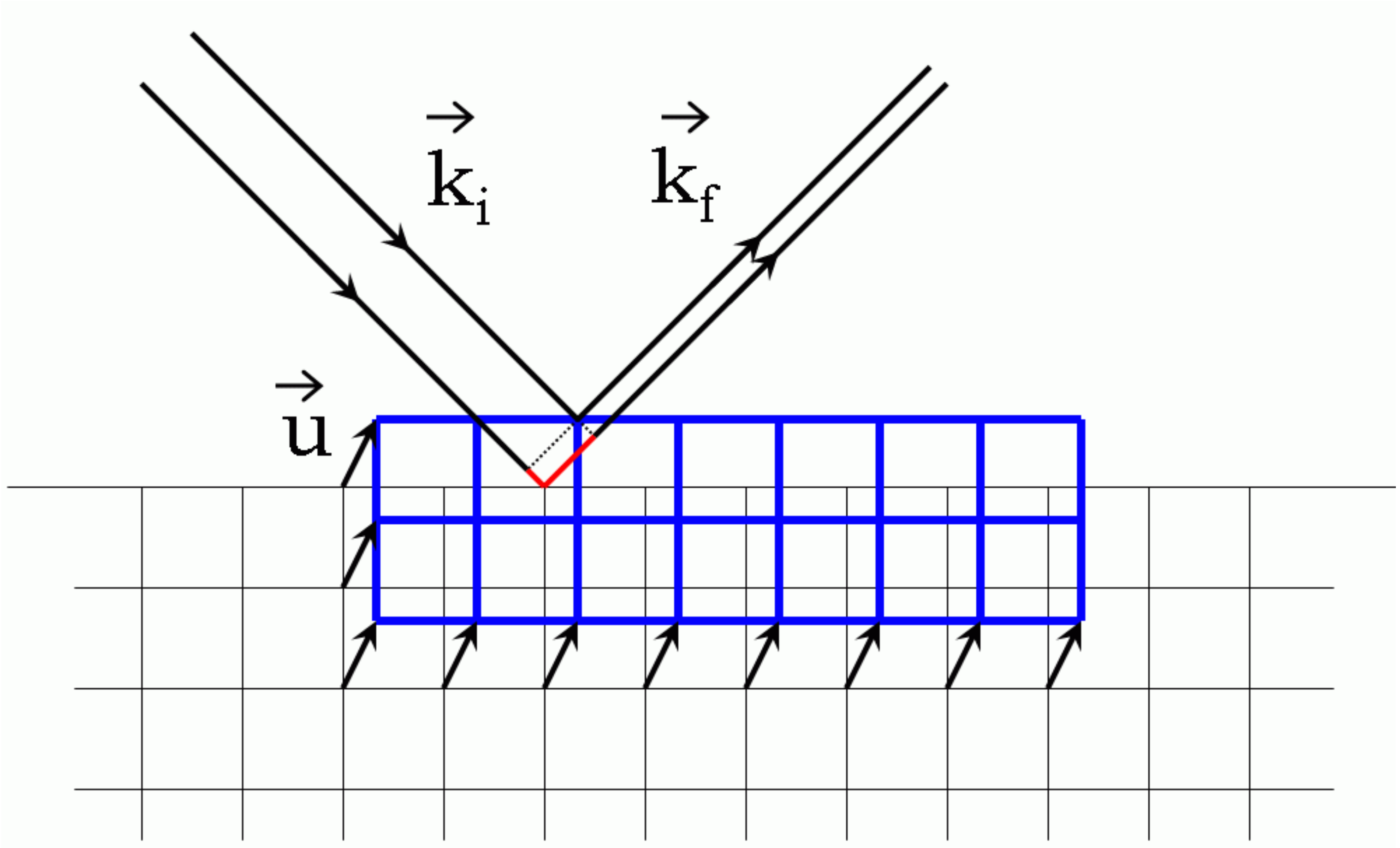
Coherent Diffraction from Crystals





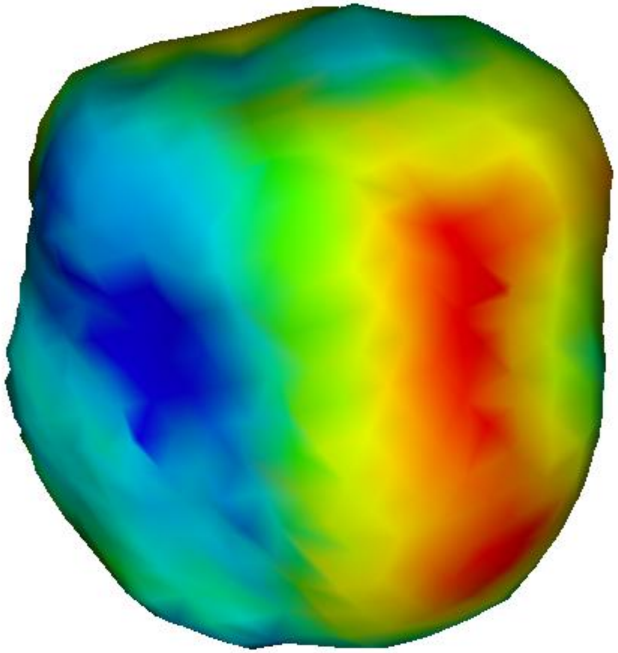
Sensitivity to strain

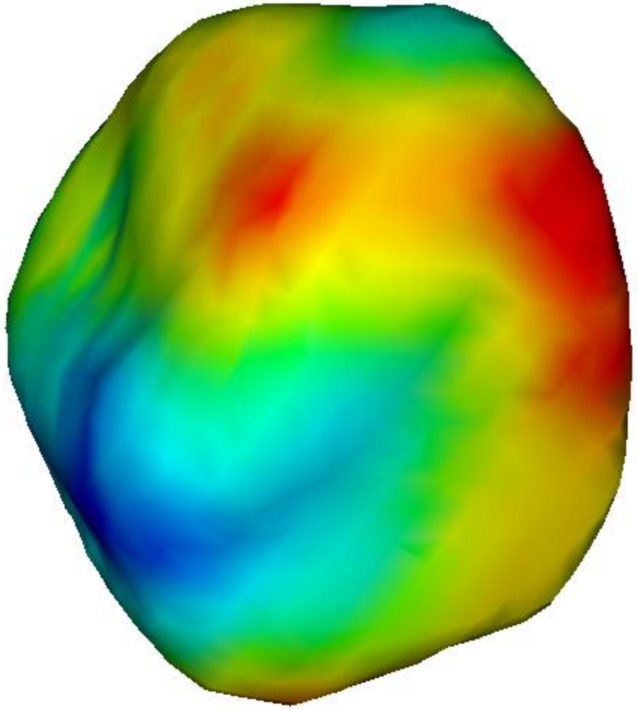
$$\Delta\varphi = \mathbf{k_f \cdot u - k_i \cdot u = Q \cdot u}$$



Phase isosurface of residual strain

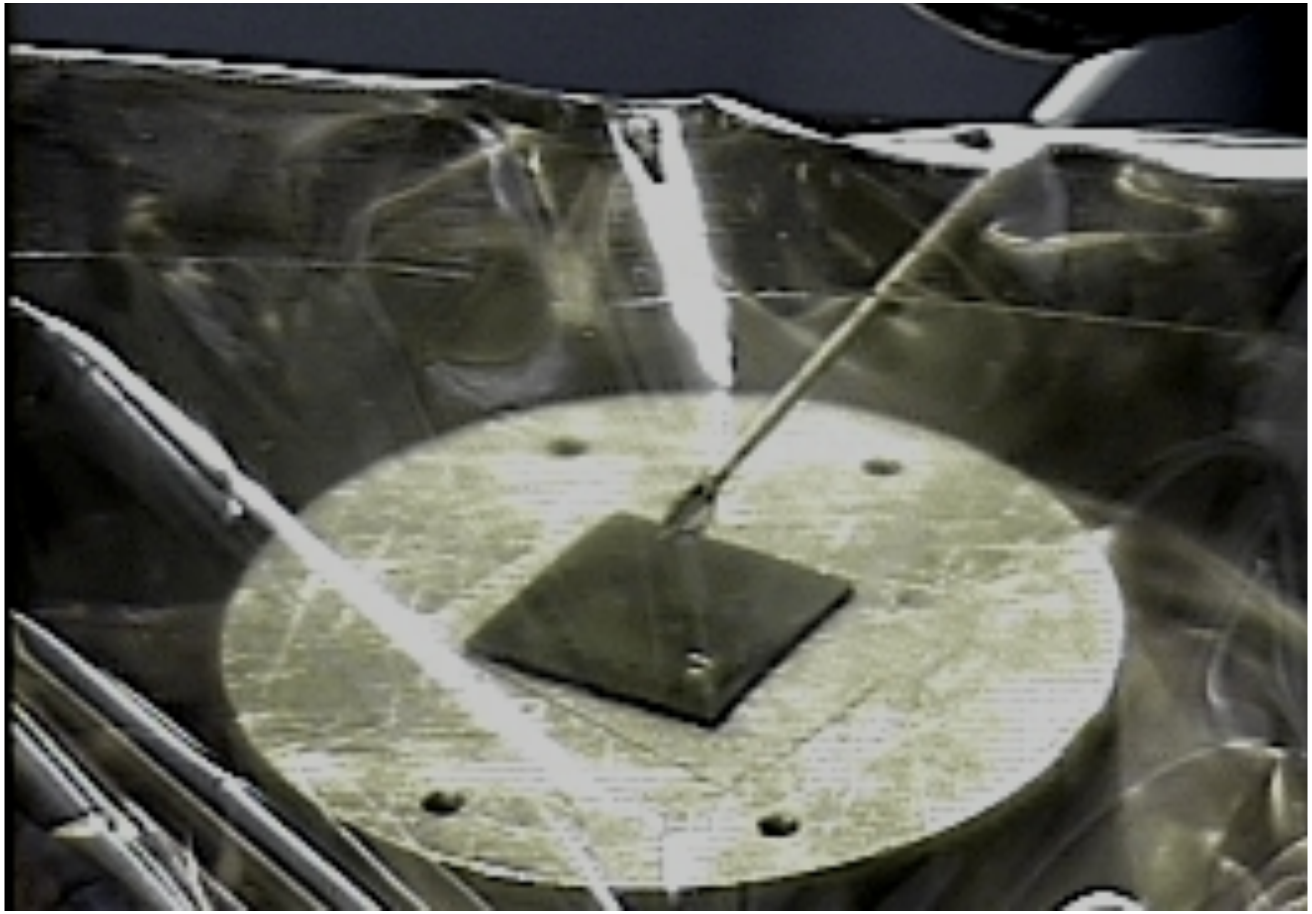
200nm Barium Titanate (BTO) crystals





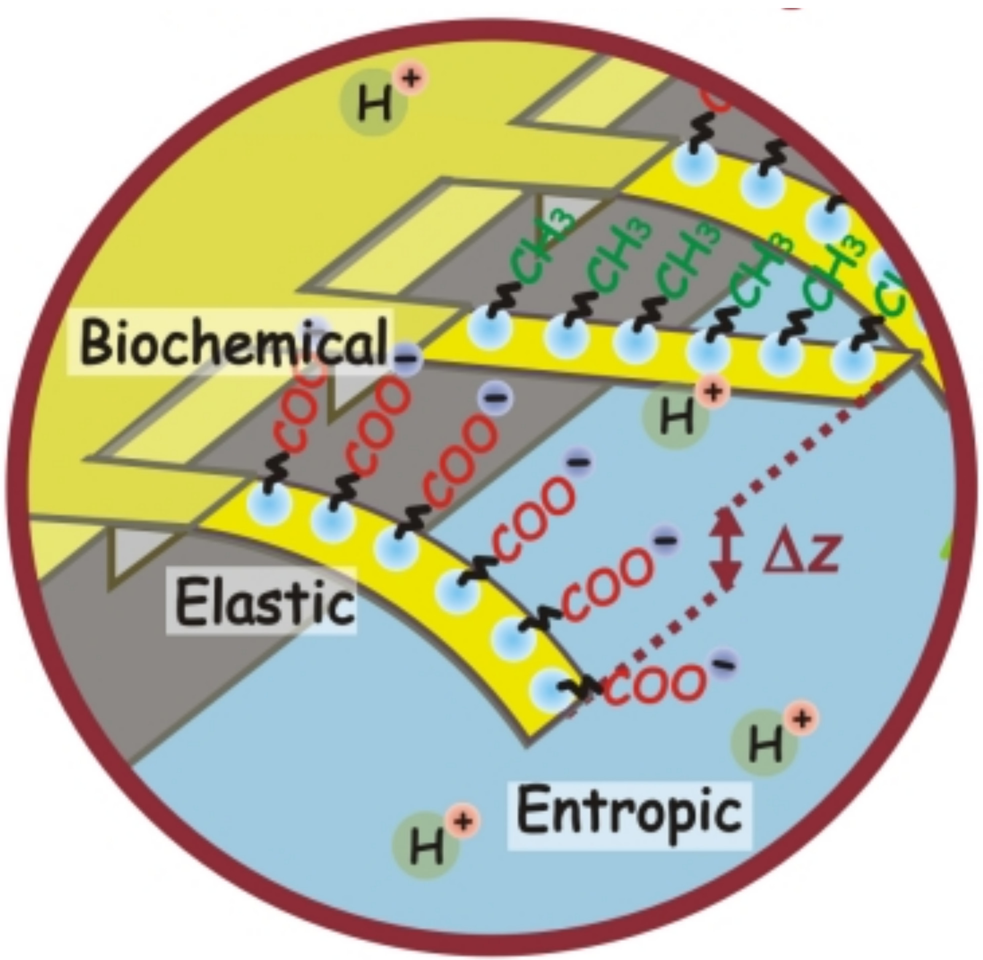
Dosing with C_3H_7SH in ethanol

Moyu Watari, Rachel McKendry, Manuel Voegtli, Gabriel Aeppli, Yeong- Ah Soh, Xiaowen Shi, Gang Xiong, Xiaojing Huang, Ross Harder and Ian Robinson, Nature Materials (2011)



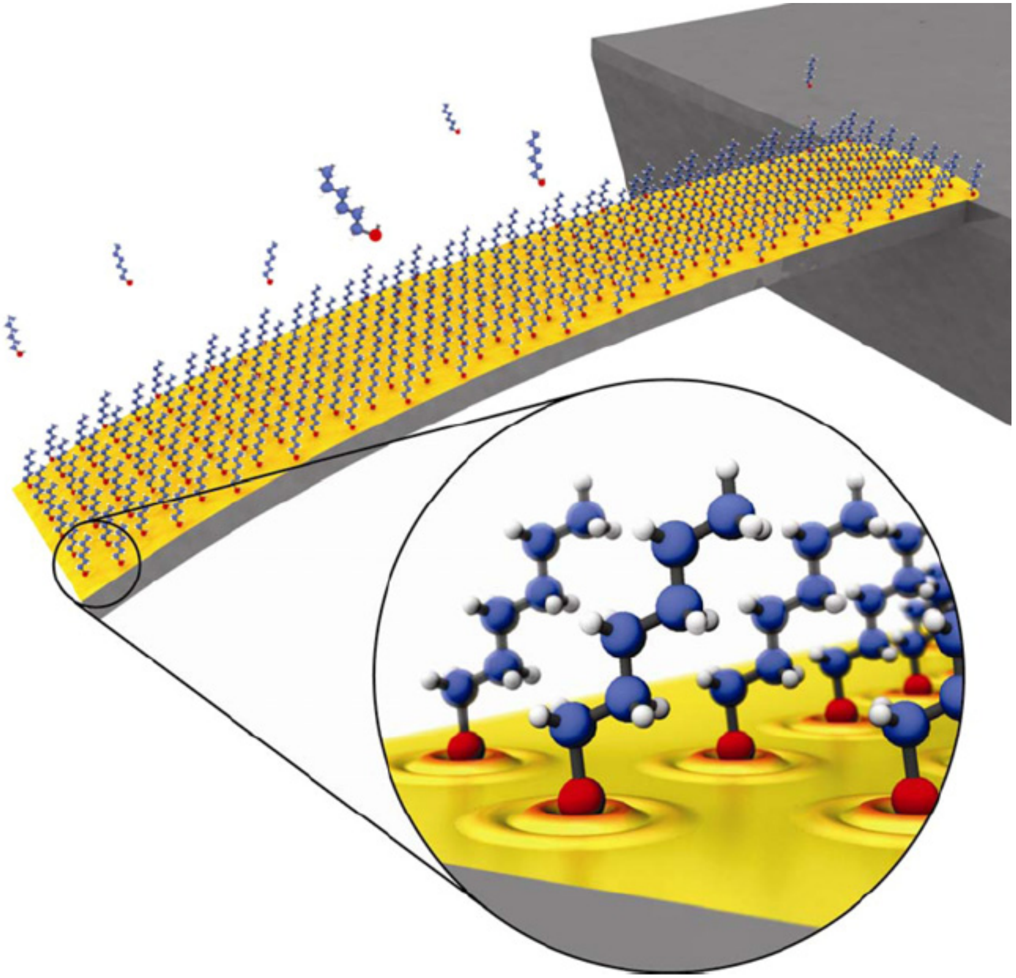
Nanocantilevers

Dr Rachel McKendrie



Formation of SAM on cantilever

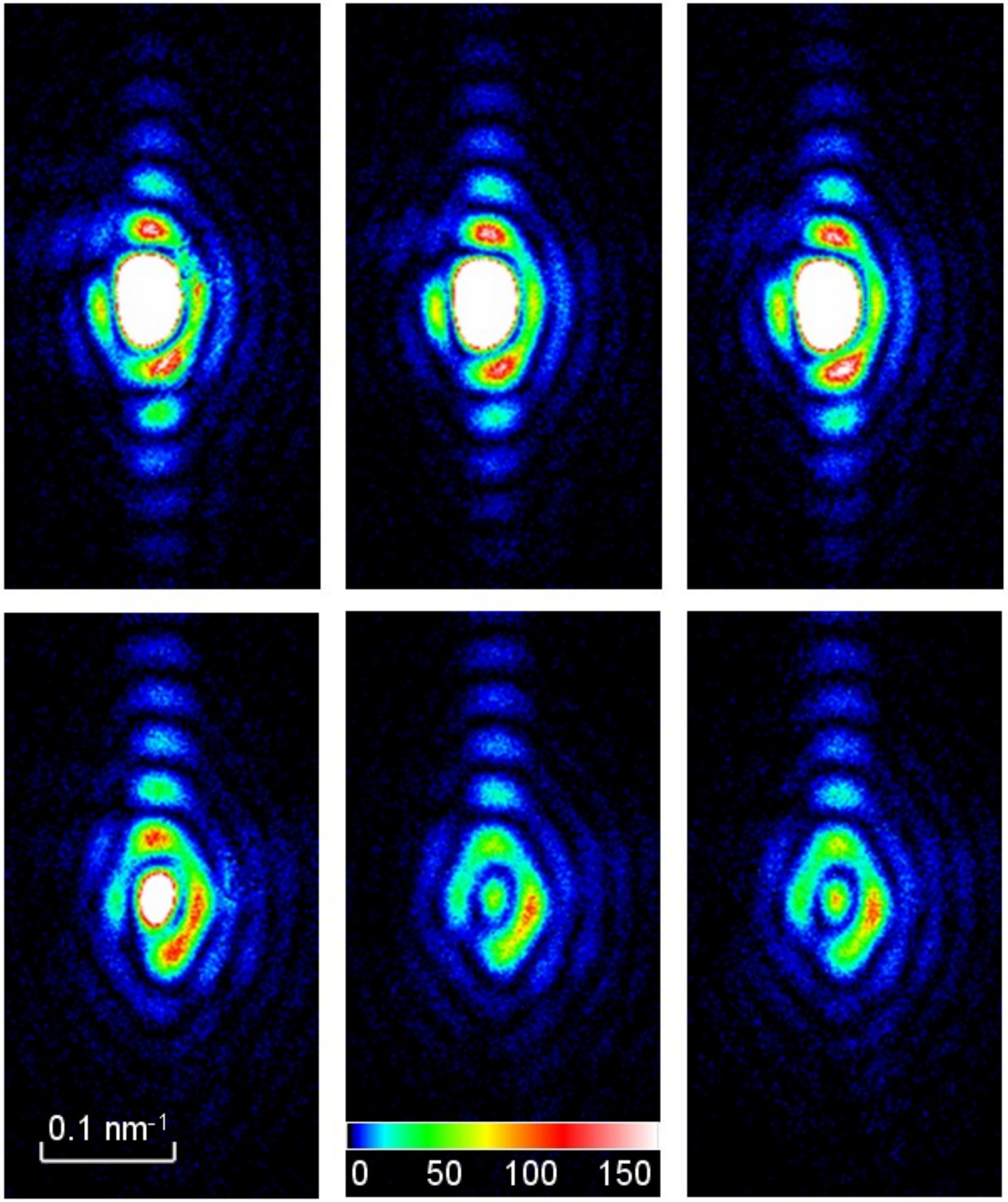
M. Godin et al, Nanotechnology 21 (2010) 075501



Rocking curve of Au crystal

Before dosing / dose 1 / dose 2

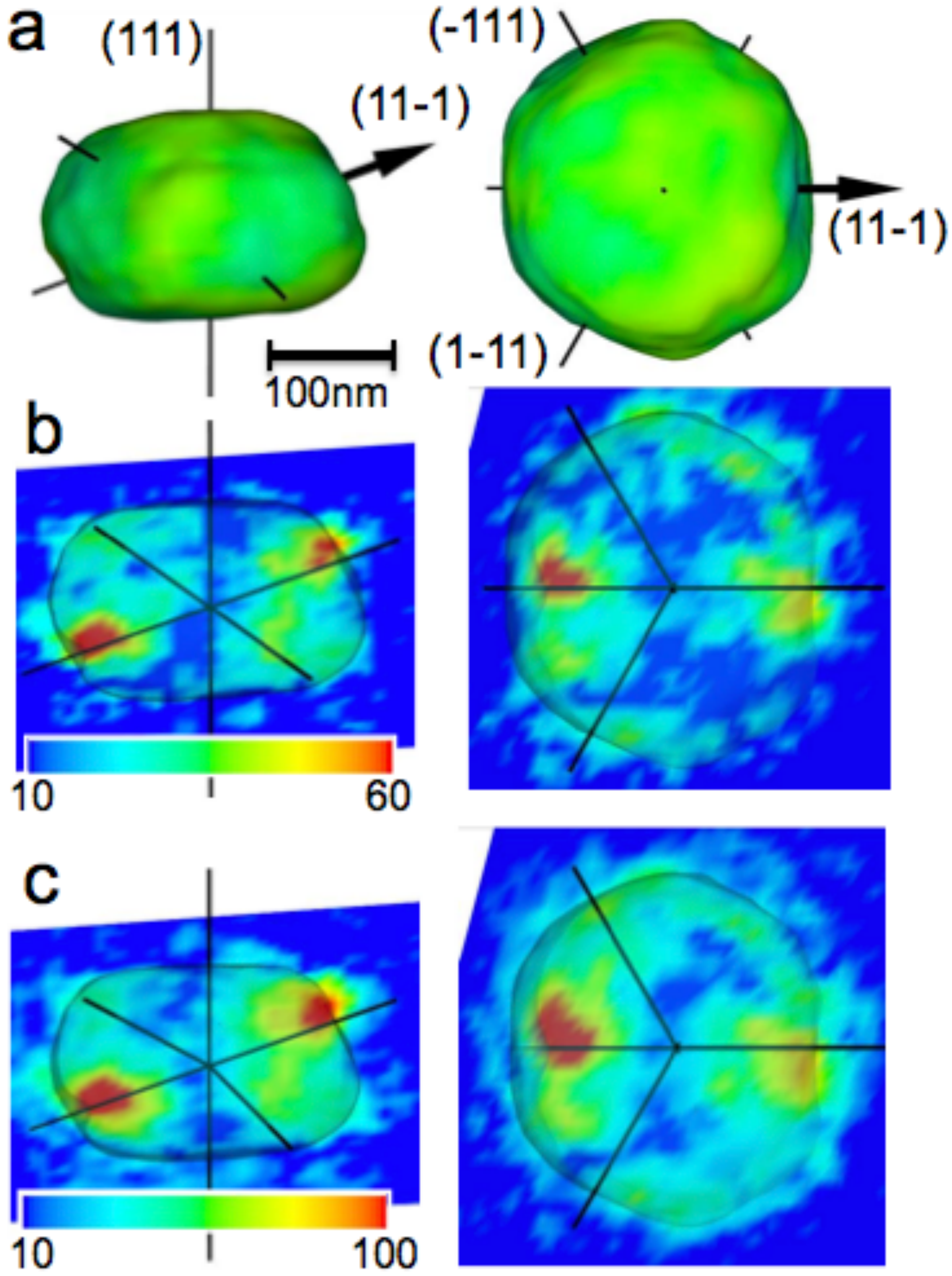
I. K



Difference Fourier:

Magnitude of phase change caused by dosing

Moyu Watari et al, Nature Materials (2011)

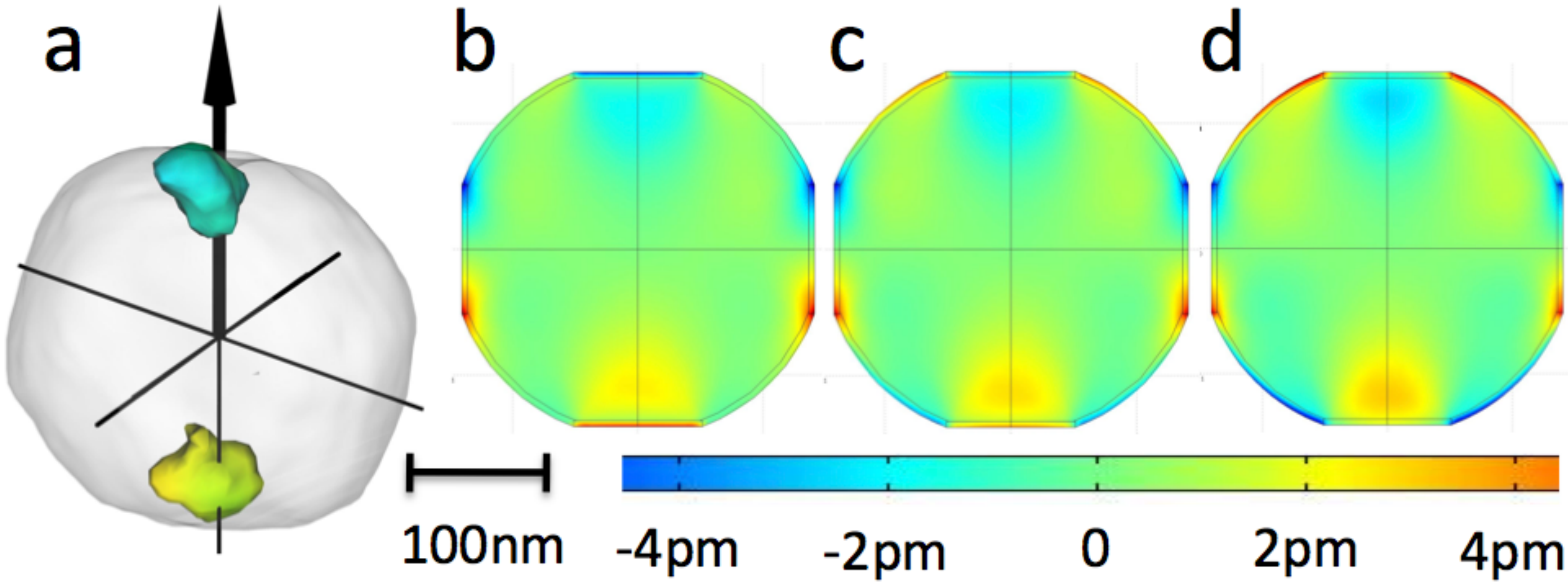


I. K. Robinso

Finite-element Analysis

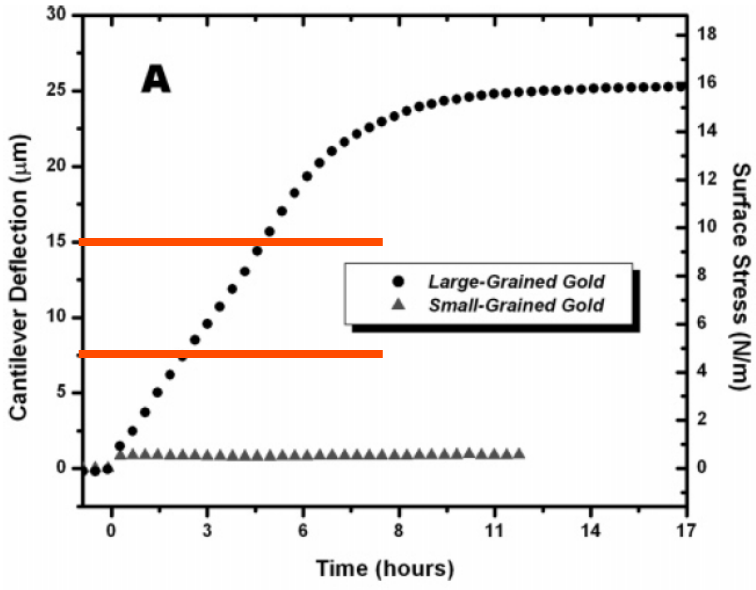
Differential stress introduced in "skin"

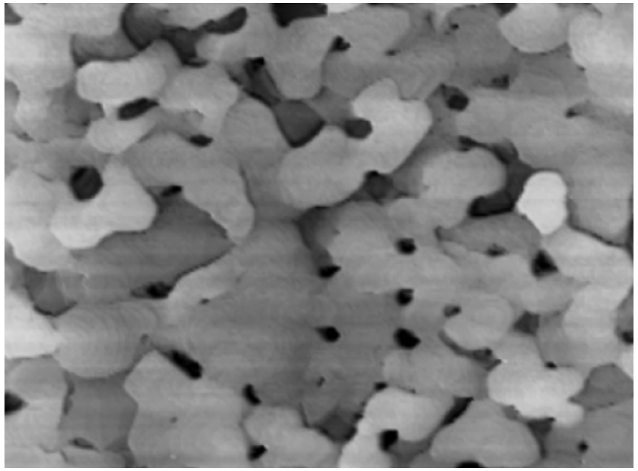
+/- 3×10^8 Pa in 5nm thickness = 1.5N/m



Cantilever strain experiment

M. Godin et al Langmuir **20** 7090 (2004)

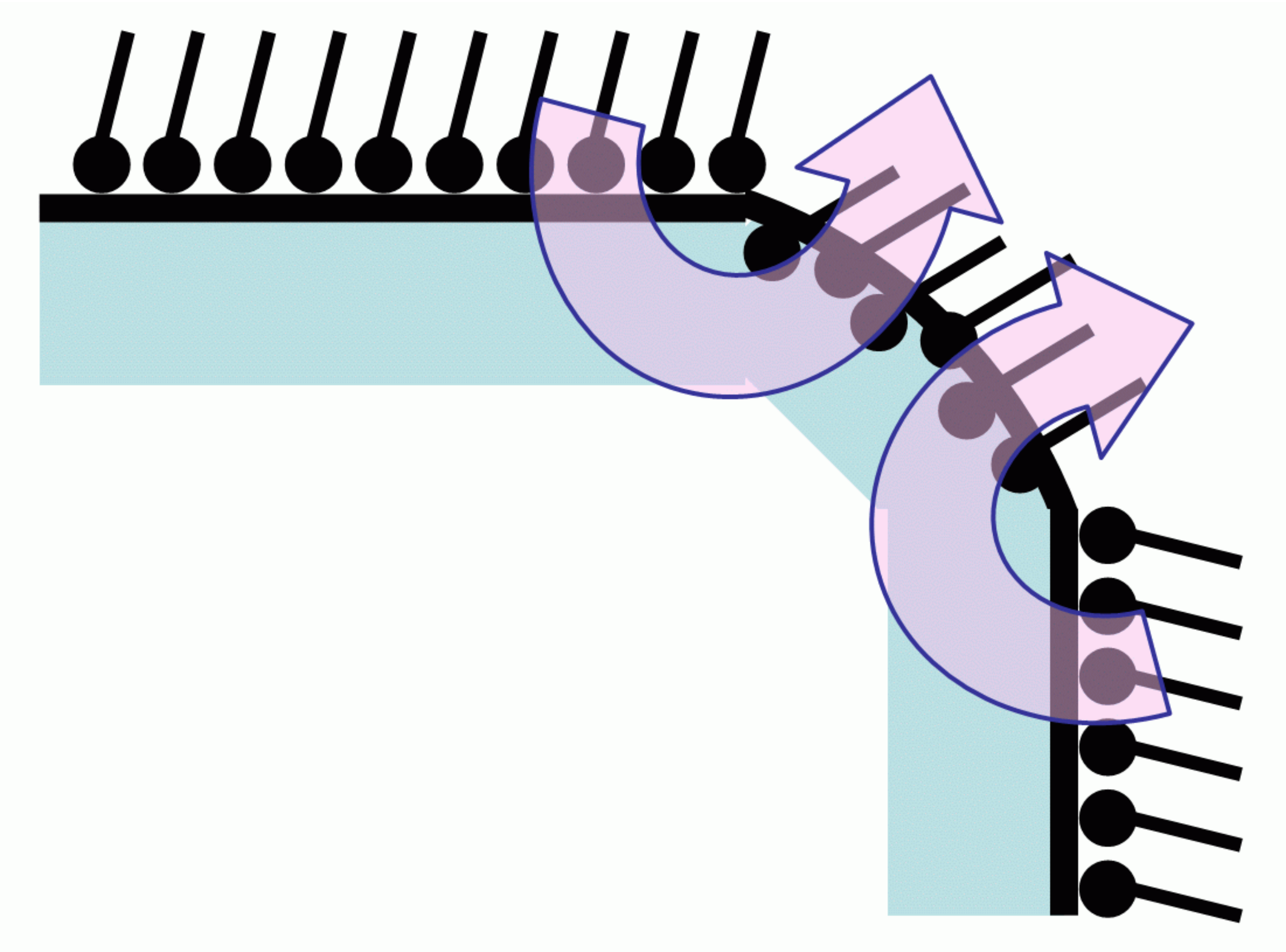




3×2μm STM image

Calculated surface stress from FEA analysis:
4.5±2N/m after 1hr, 9.5±3N/m after 2hrs

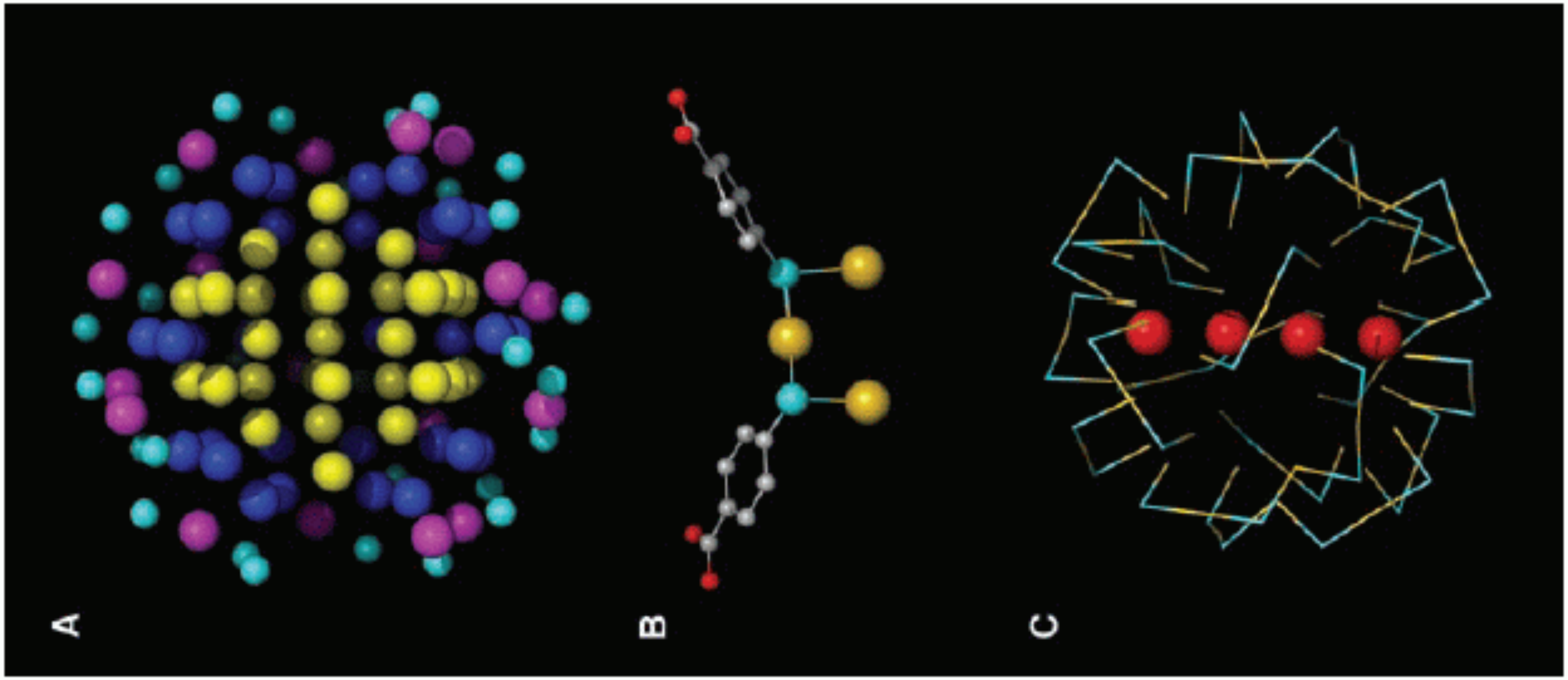
Differential adsorption, thiol/Au

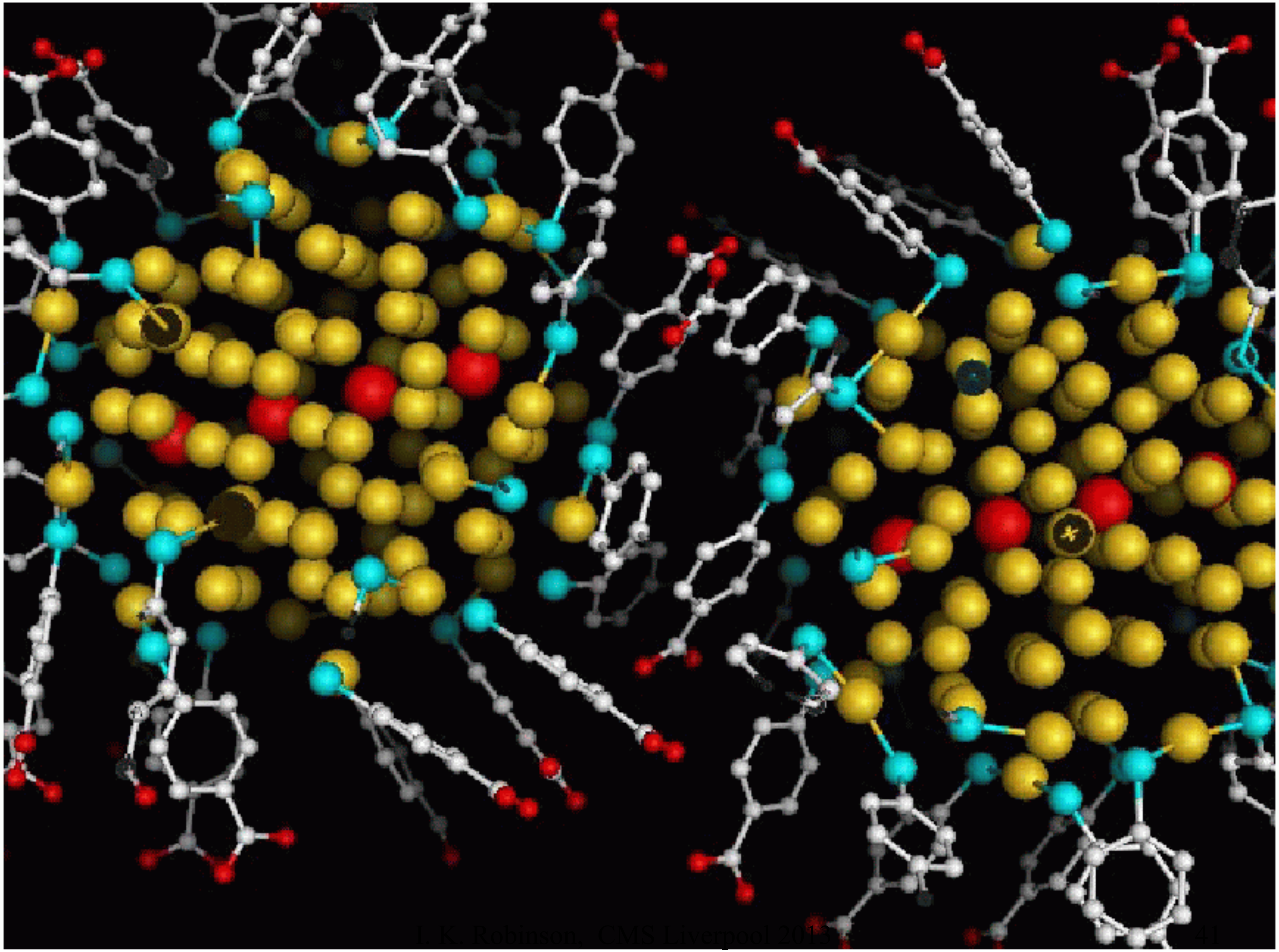


Gold-sulphur network in 1.6nm NC

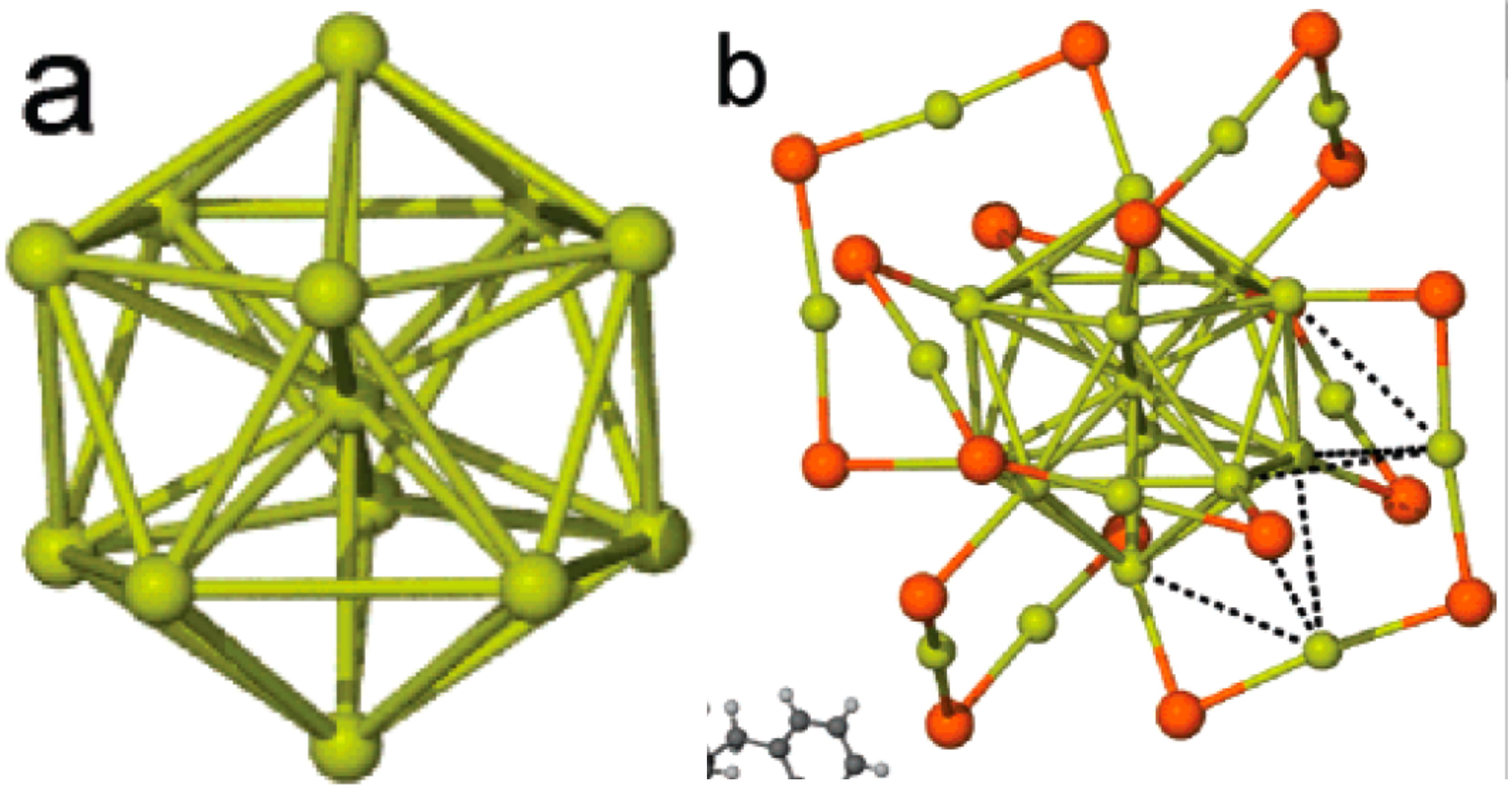
p-mercaptobenzoic acid (p-MBA)

P. D. Jadzinsky et al, Science 318, 430 (2007)



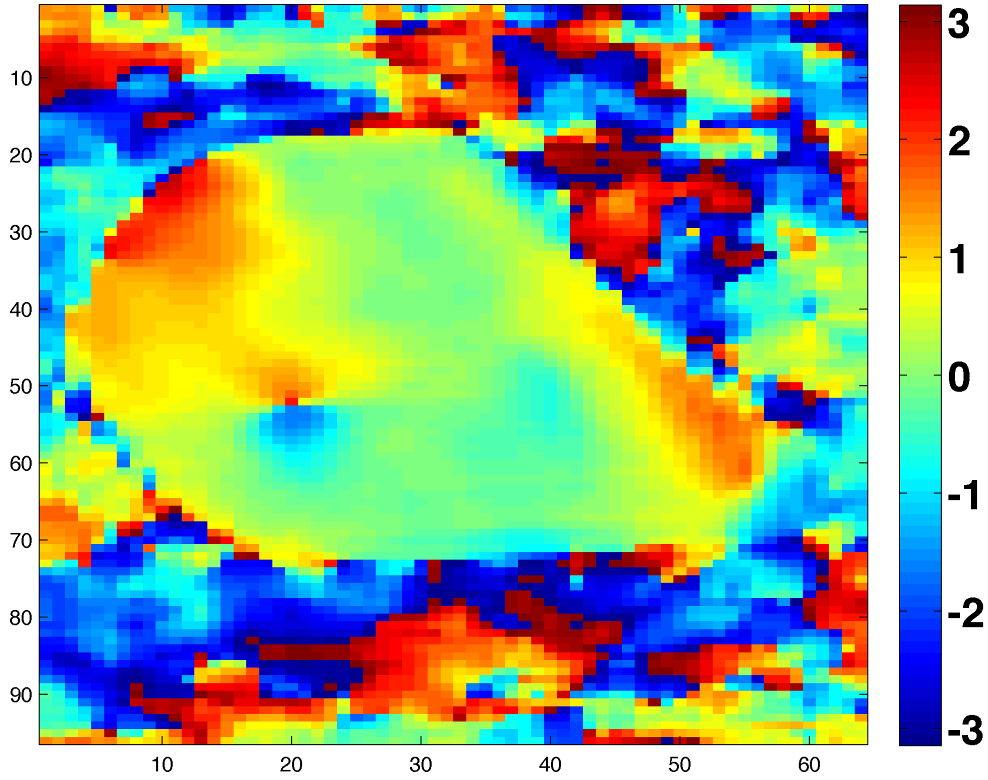


Gold-sulphur structure $Au_{13}(Au_2RS_3)_6$ $=Au_{25}RS_{18}$ Heaven et al, JACS 130 3755 (2008)



Strain around Dislocation in Au

Jesse Clark, August 2012

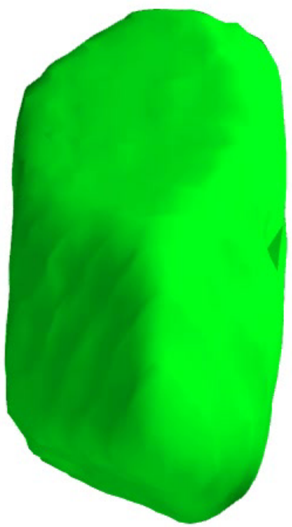


Vary transverse coherence

using horizontal entrance slit settings

$12\mu m$

High coherence



Assuming perfect coherence

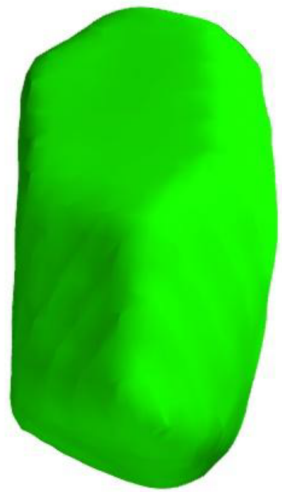
$50\mu m$

Low coherence

Assuming perfect coherence

$50\mu m$

Low coherence



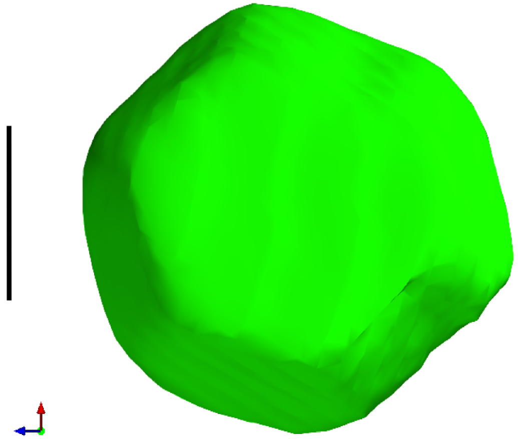
Correcting for partial coherence

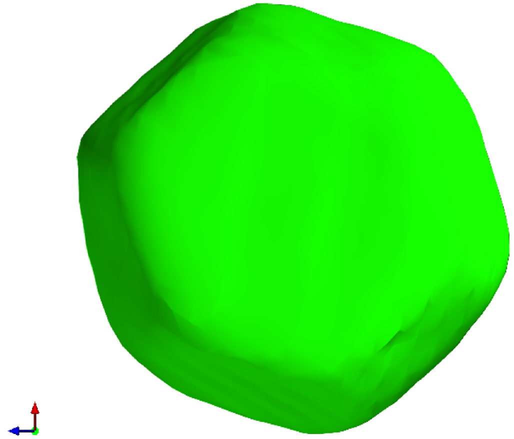
Top view of crystal

Jesse Clark et al, Nature Comms, 3 993 (2012)

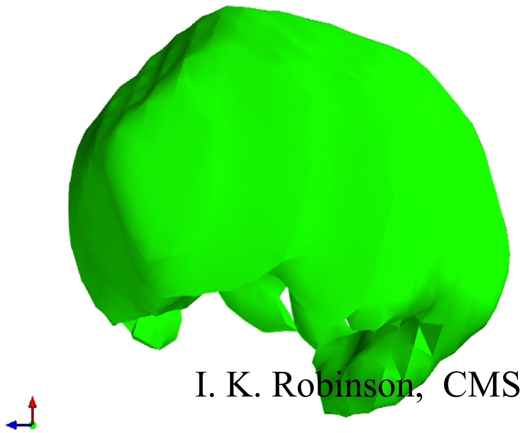
Assuming full coherence | Correcting for partial coherence

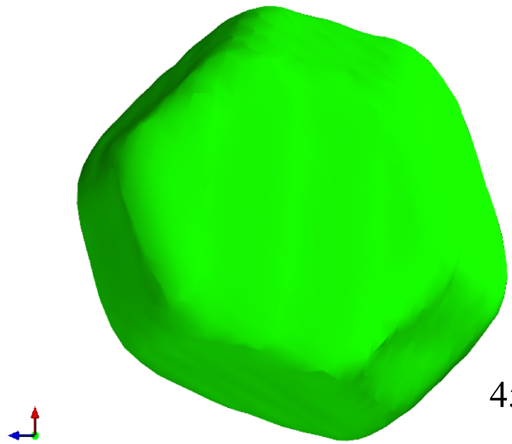
‘High’ coherence





‘Low’ coherence





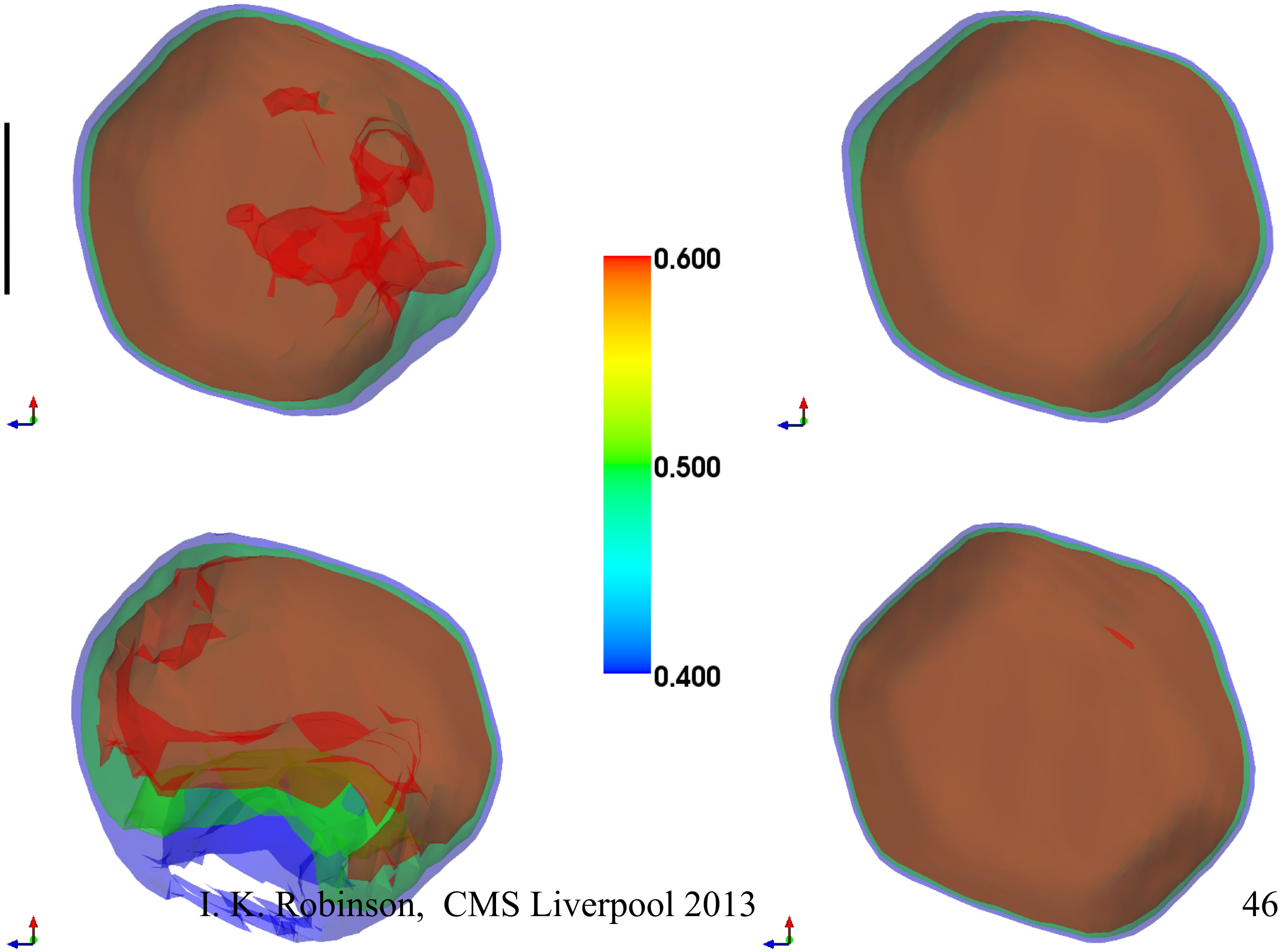
Top view of crystal

Jesse Clark et al, Nature Comms, 3 993 (2012

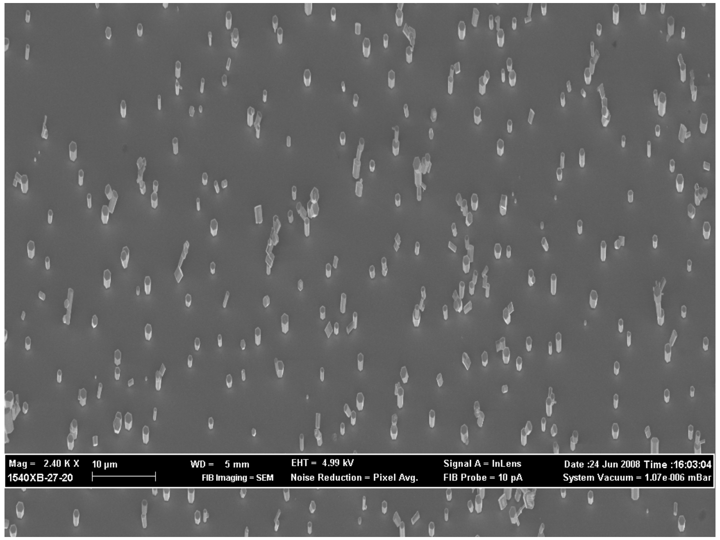
Assuming full coherence | Correcting for partial coherence

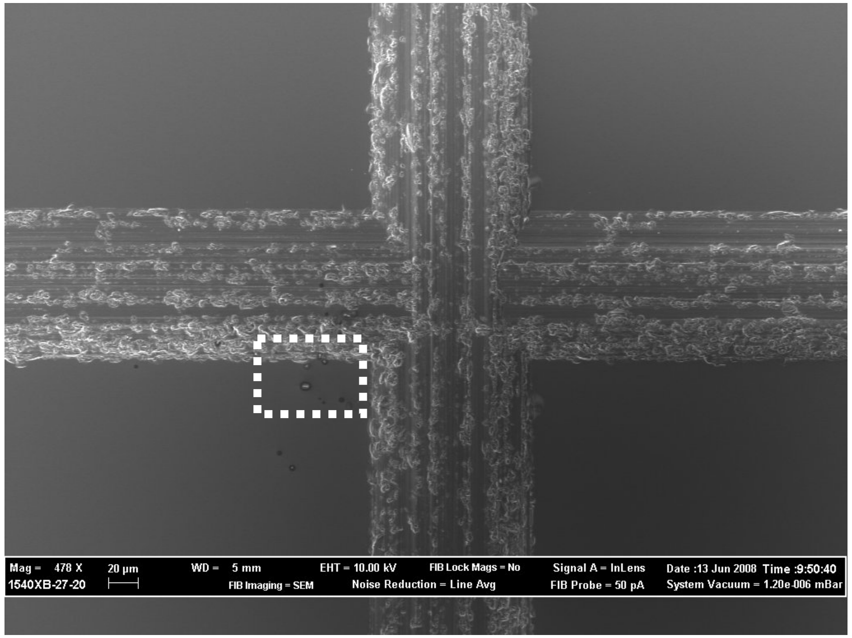
'High' coherence

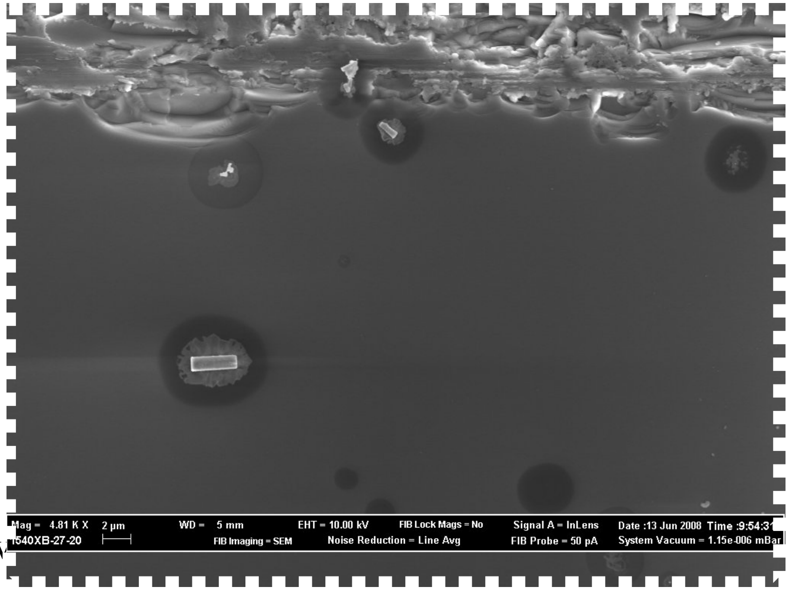
'Low' coherence



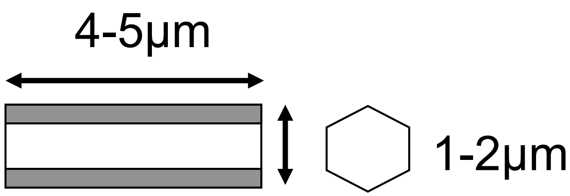
ZnO Sample Preparation



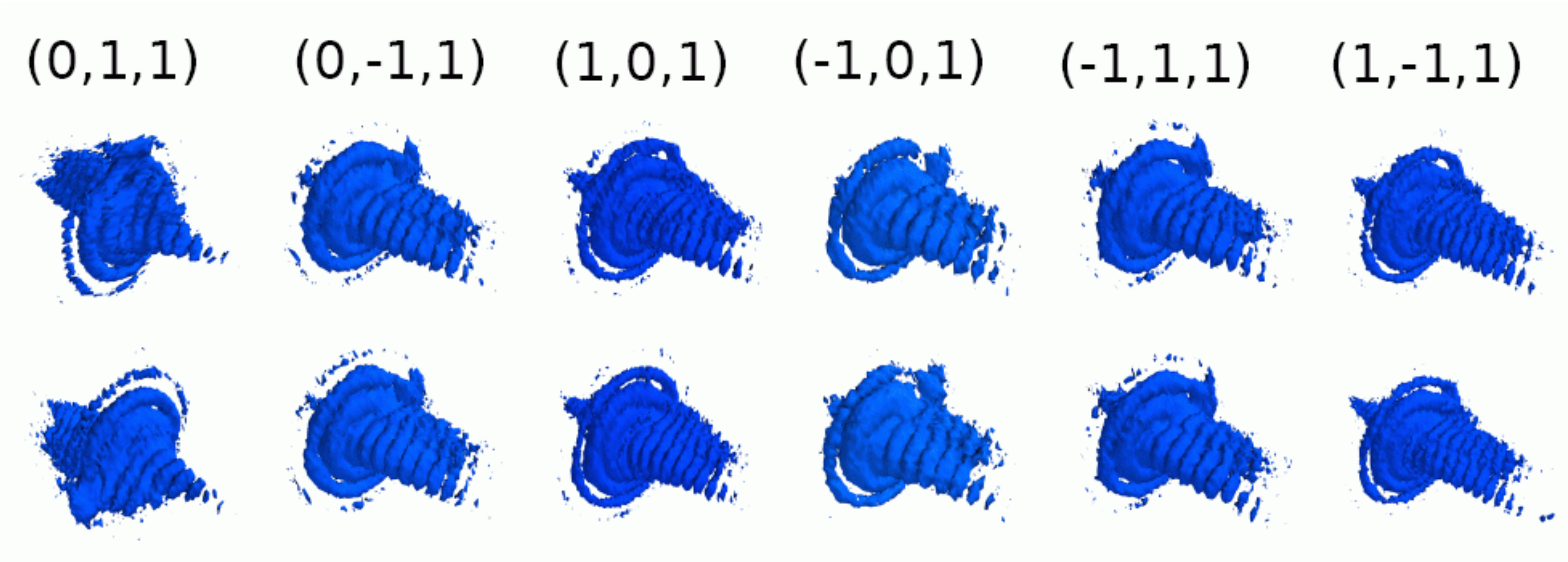




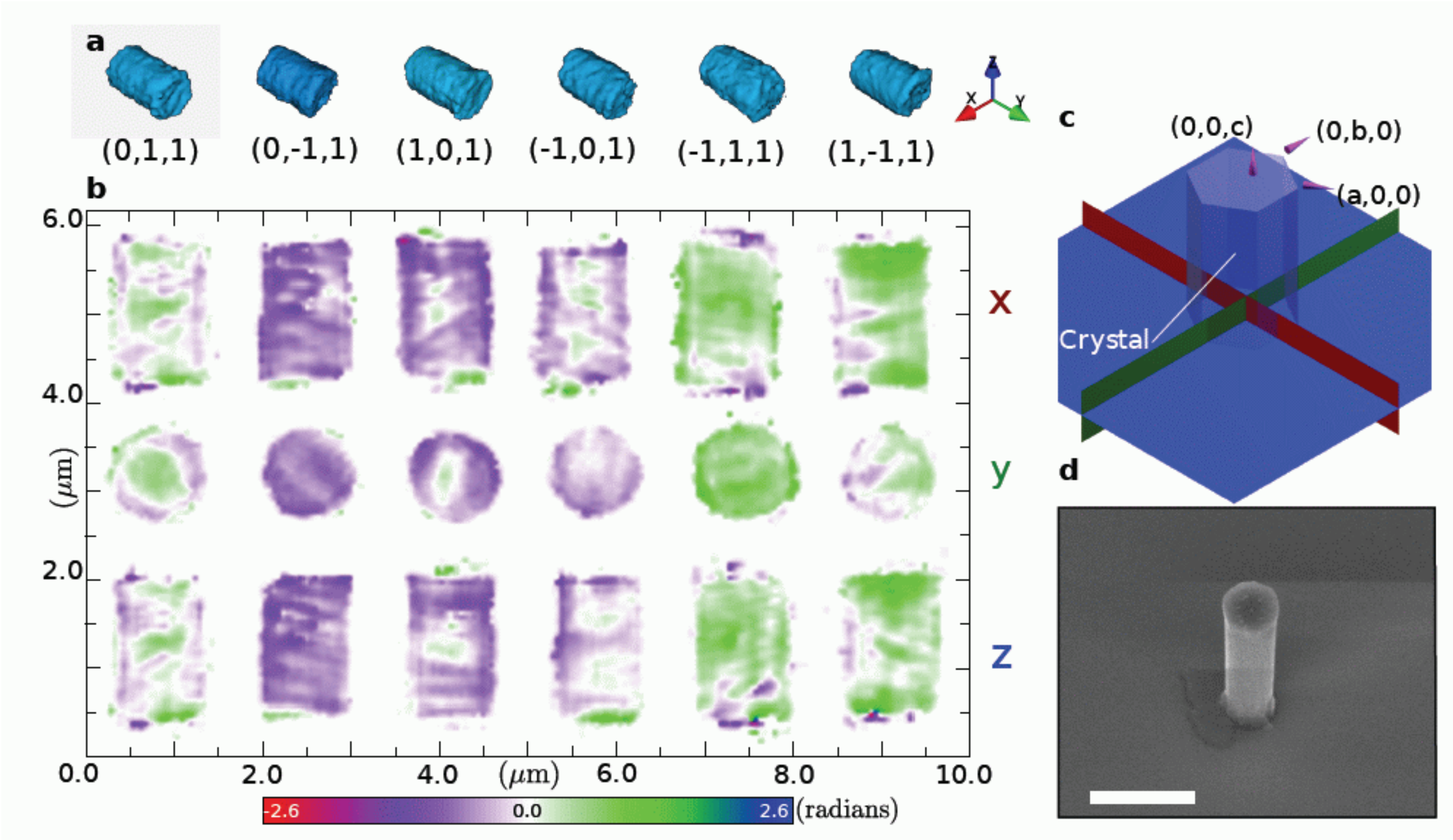
Dimensions:



Extension to 6 Bragg Peaks

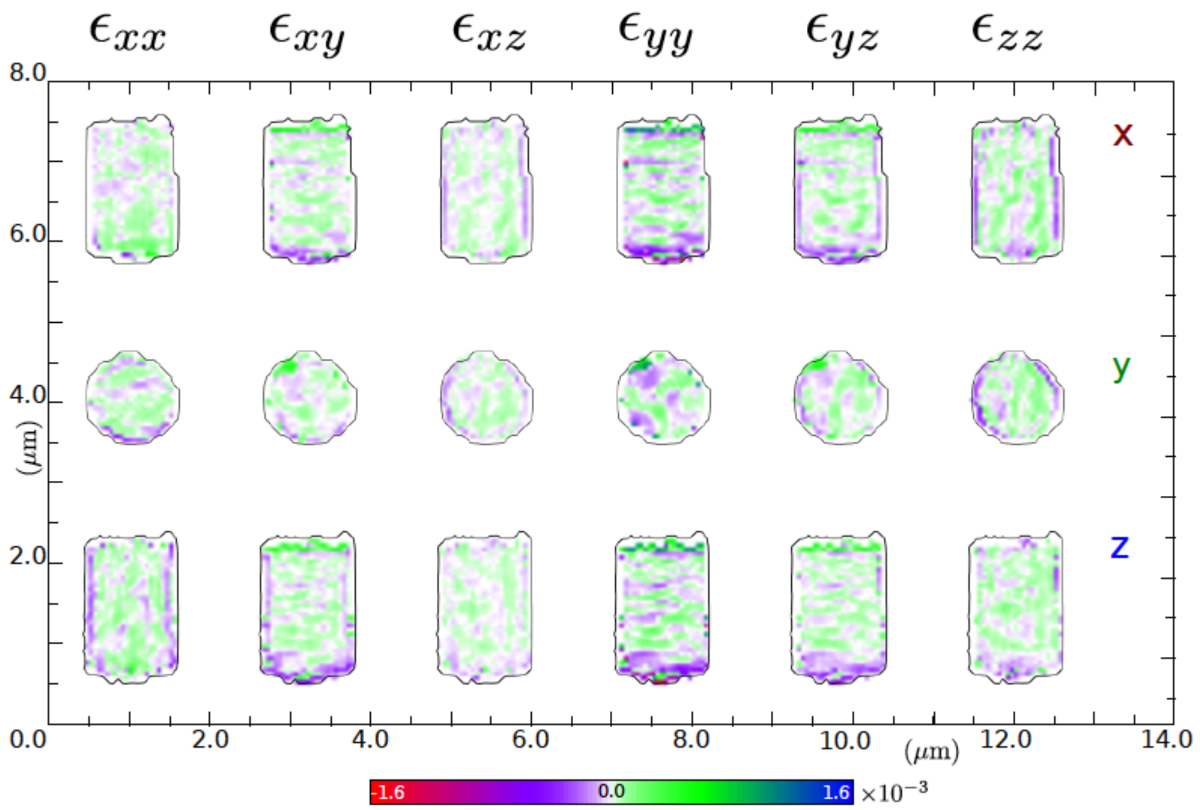


Extension to 6 Bragg Peaks



Full Strain Tensor

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j}\right) \quad , \quad \tau_{ij} = \left(\frac{\partial u_j}{\partial x_i} - \frac{\partial u_i}{\partial x_j}\right)$$



Coherent x-ray diffraction (CXD)

- Surface has become Nano
- Complex density can image strain
- Strain associated with nano-shape
- Differential strain with thiol chemistry
- Partial coherence correction
- Full strain tensor