

# Bragg Coherent X-ray Diffraction for Microstructure and Dynamics of Crystals

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I-16 Diamond  
34-ID-C APS  
I-07 Diamond  
XPP LCLS

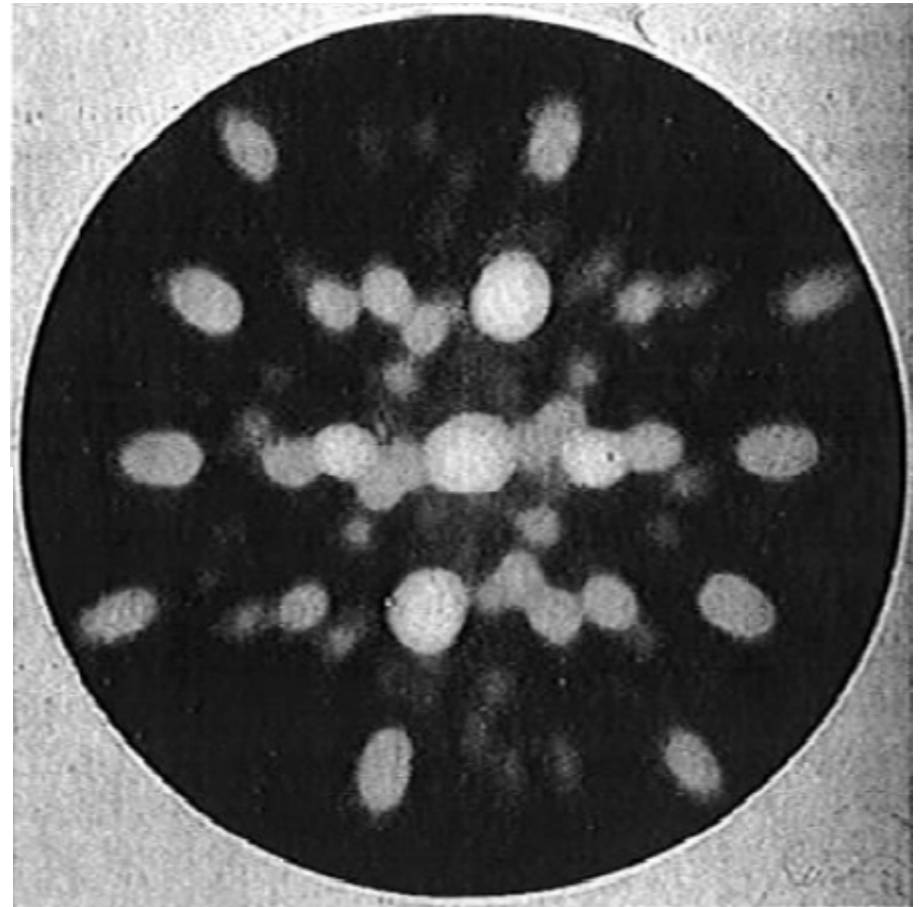
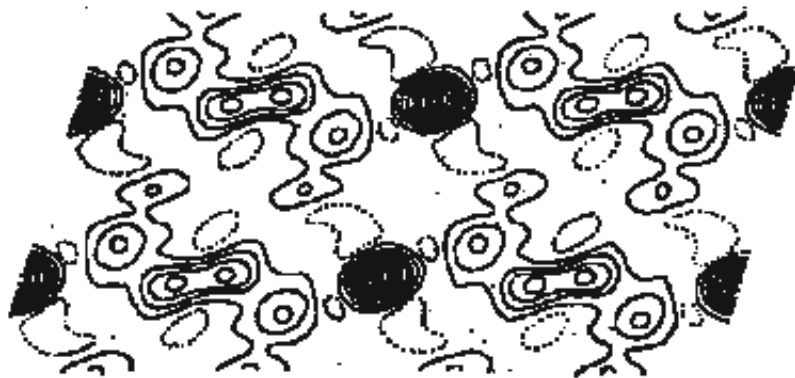
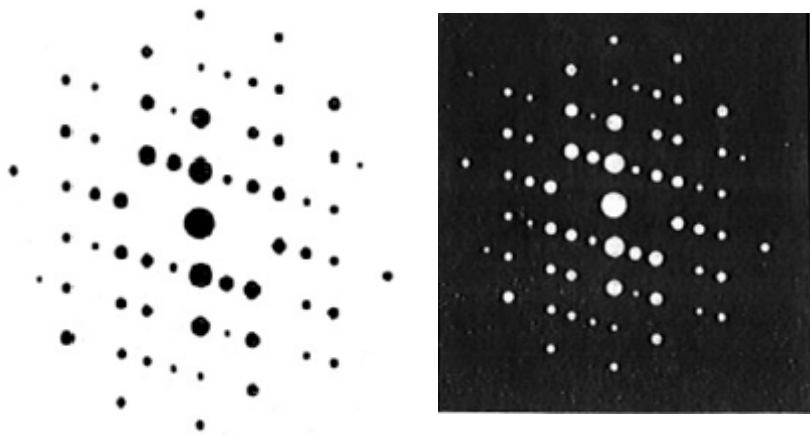
Condensed Matter Physics and  
Materials Science Department  
Brookhaven National Lab  
London Centre for Nanotechnology  
Materials Science and Technology  
Division Seminar, ORNL  
March 2017

# Outline

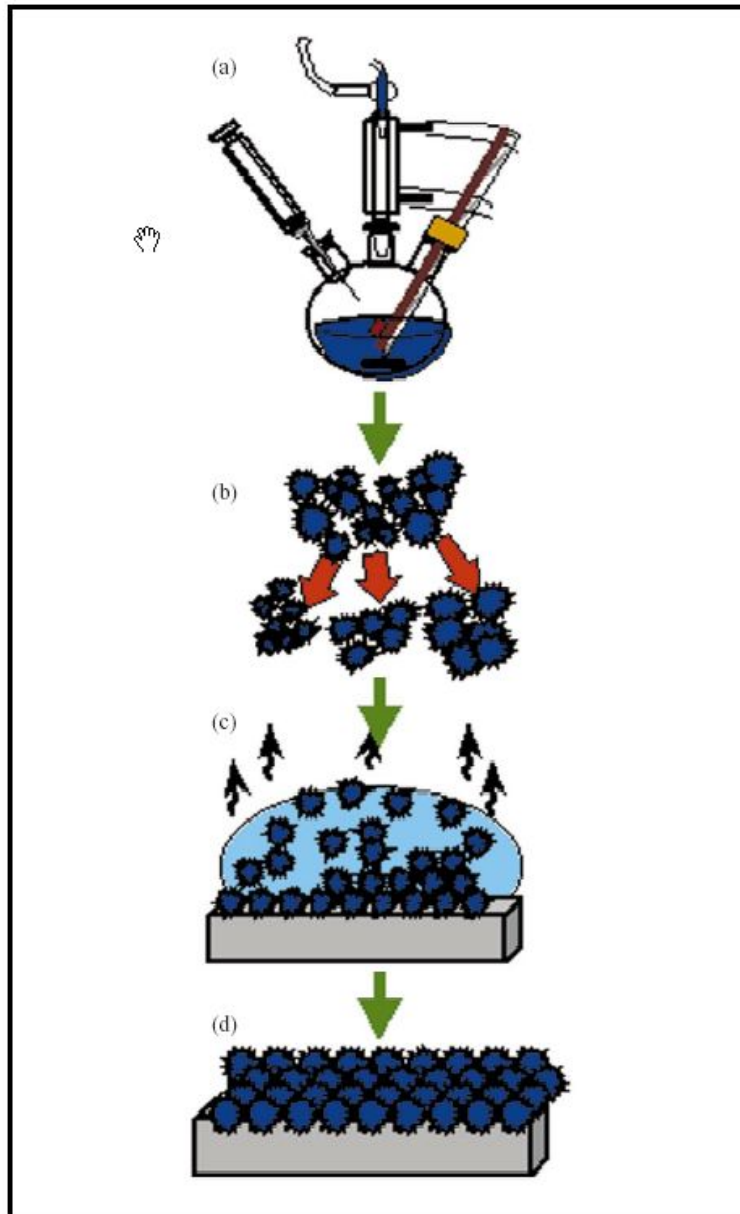
- Nanocrystal structures
- Coherent X-ray diffraction
- Crystal strain as complex density
- Dislocations during crystal growth
- Nanoscale alloying
- Ultrafast snapshots of moving matter
- Future BCDI Beamline at NSLS-II

# Bragg's "X-ray Microscope"

W.L.Bragg Nature 143 678 (1939): diopside,  $\text{CaMg}(\text{SiO}_3)_2$

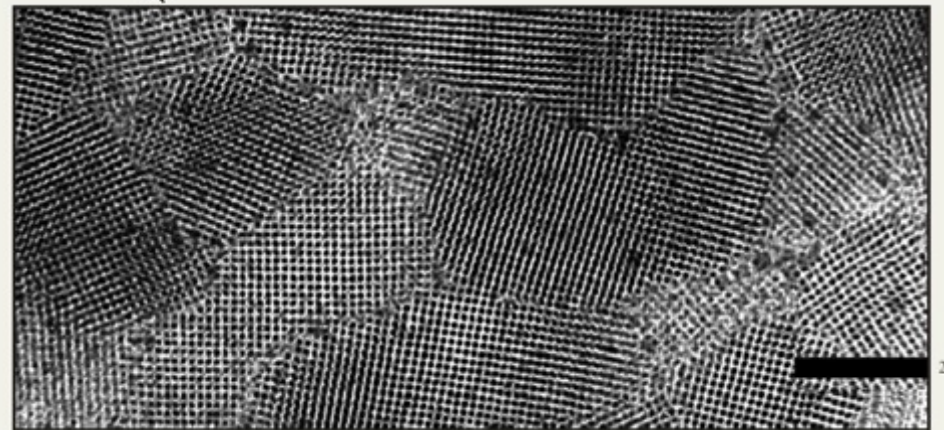


# Chemical Synthesis of Nanocrystals

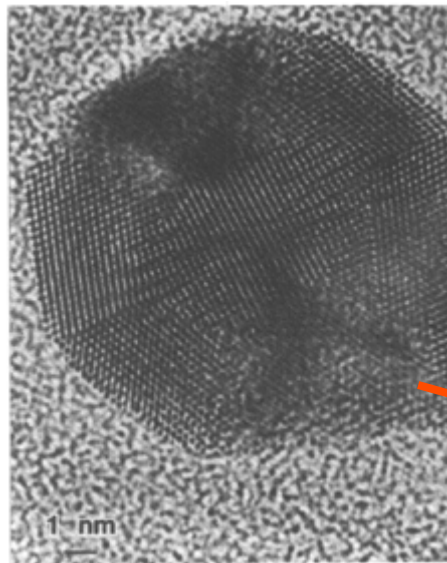


- Reactants introduced rapidly
- High temperature solvent
- Surfactant/organic capping agent
- Square superlattice (200nm scale)

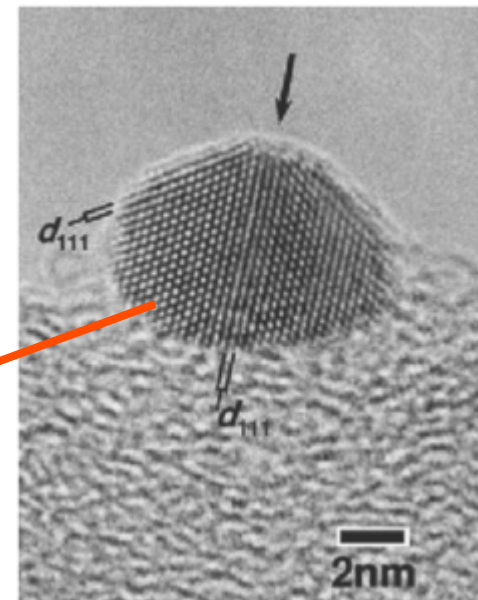
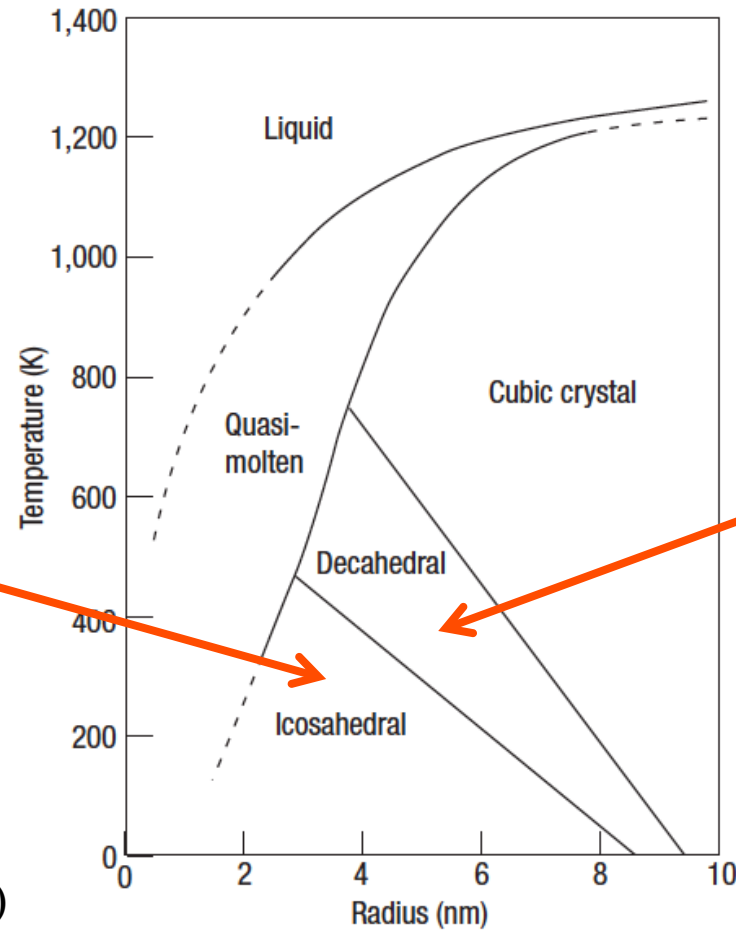
C. B. Murray, IBM J. Res. & Dev.  
45 47 (2001)



# Phase Diagram of Gold vs Size



L. D. Marks, RPP (1994)

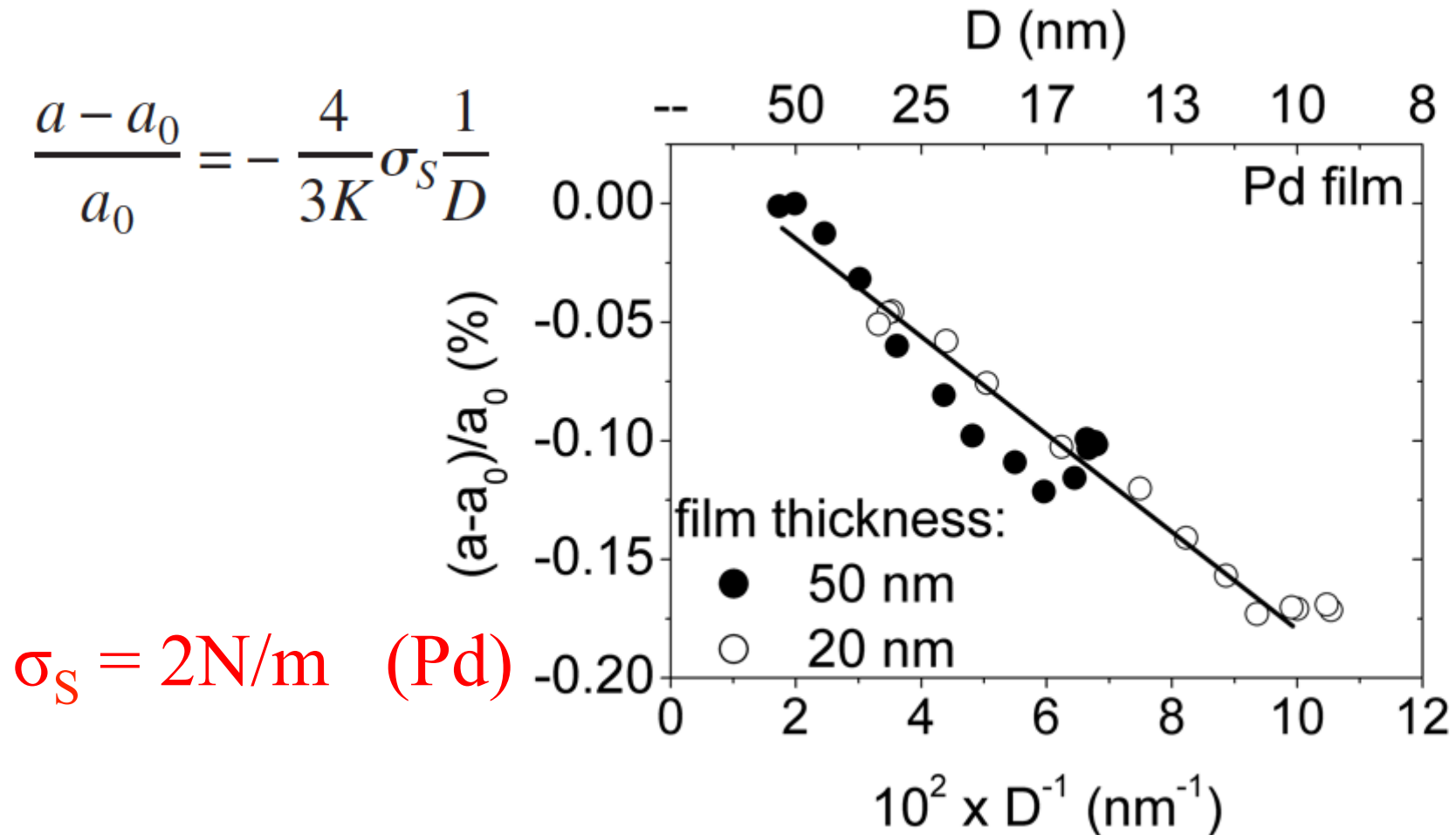


Koga and Sugawara (2003)

# Contraction of Small Particles

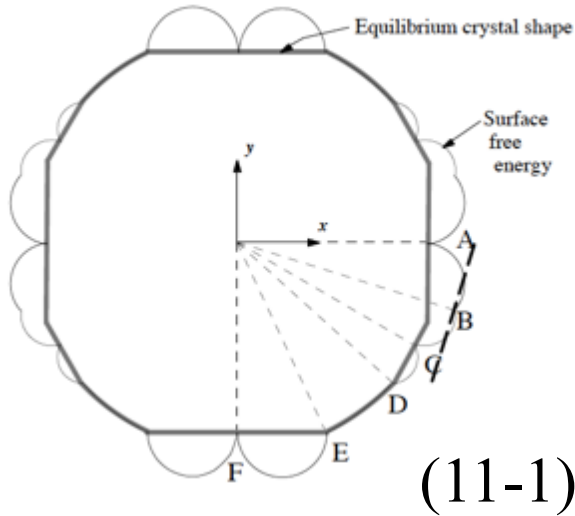
Gibbs Thomson pressure + Bulk modulus

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

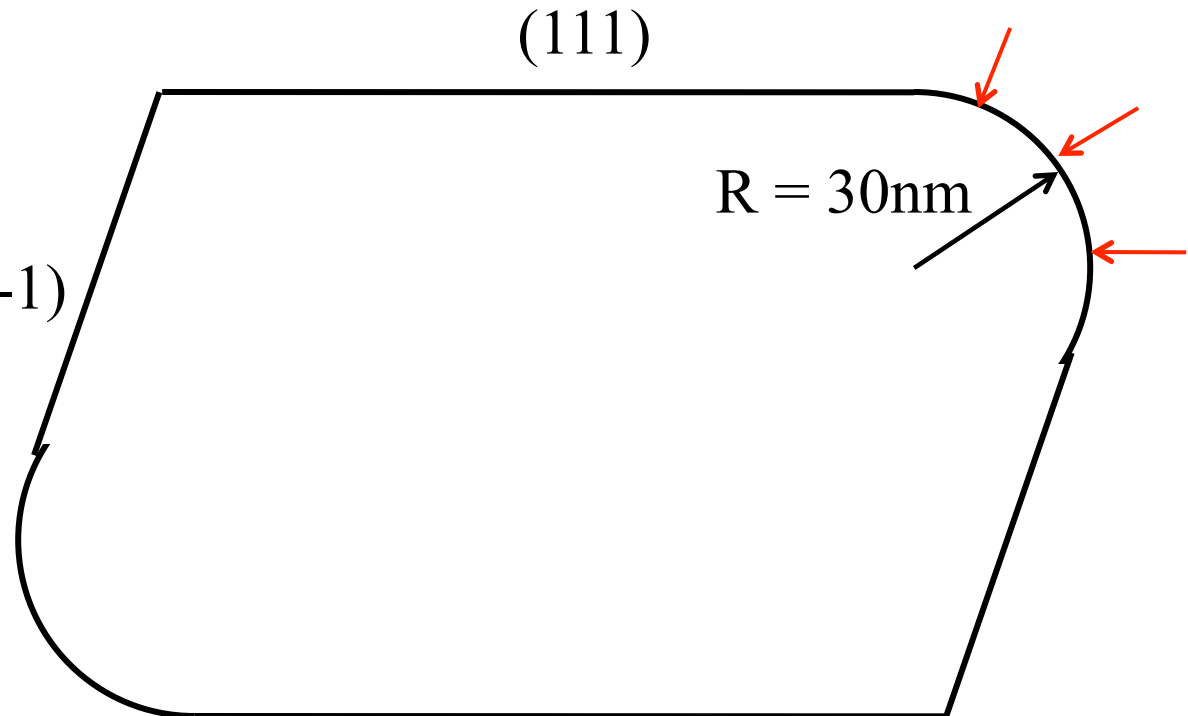


# Equilibrium crystal shape

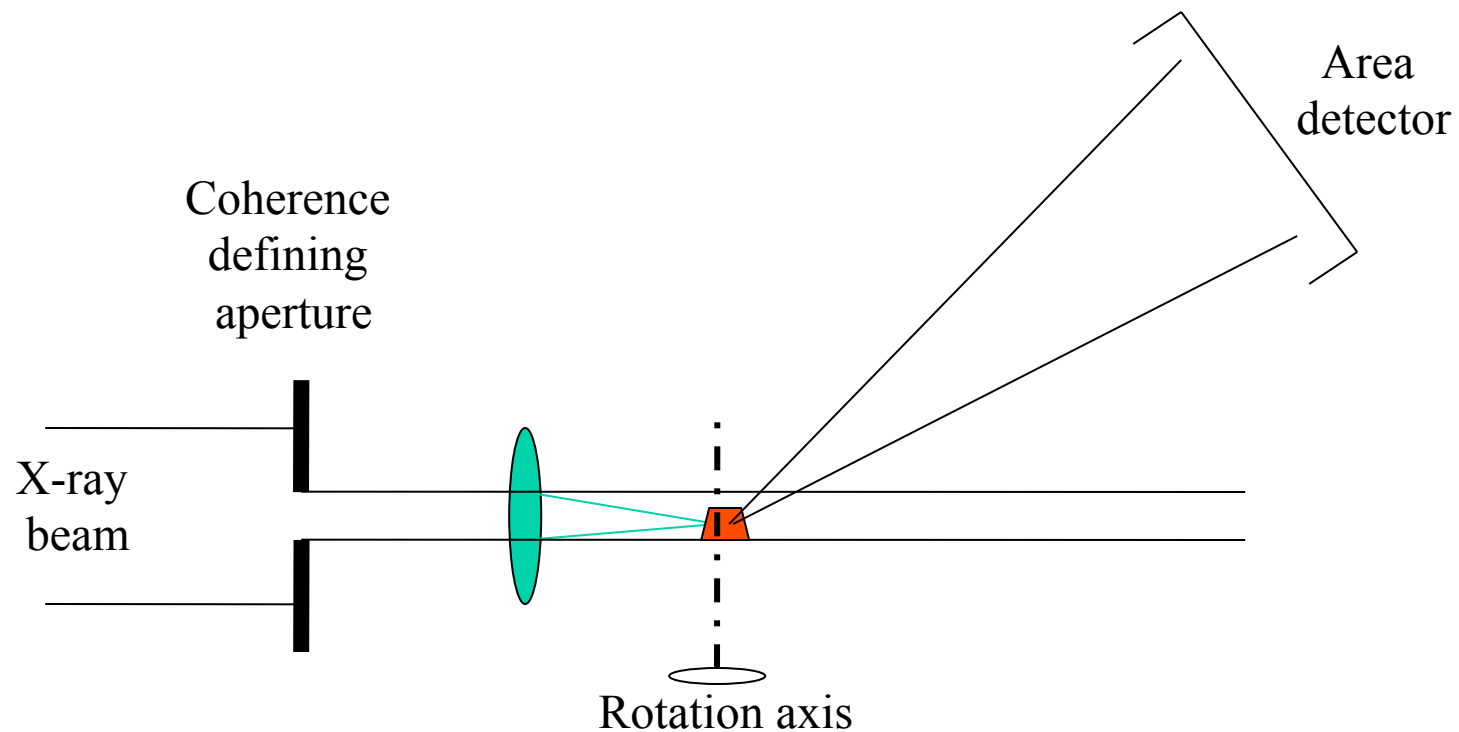
Wulff construction + Gibbs Thomson (Young-Laplace) pressure

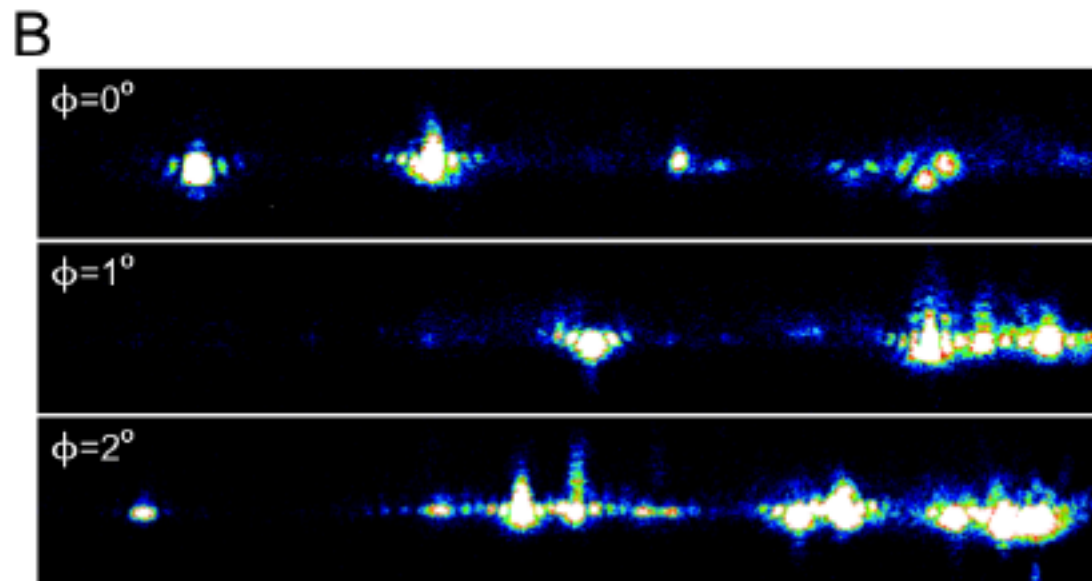
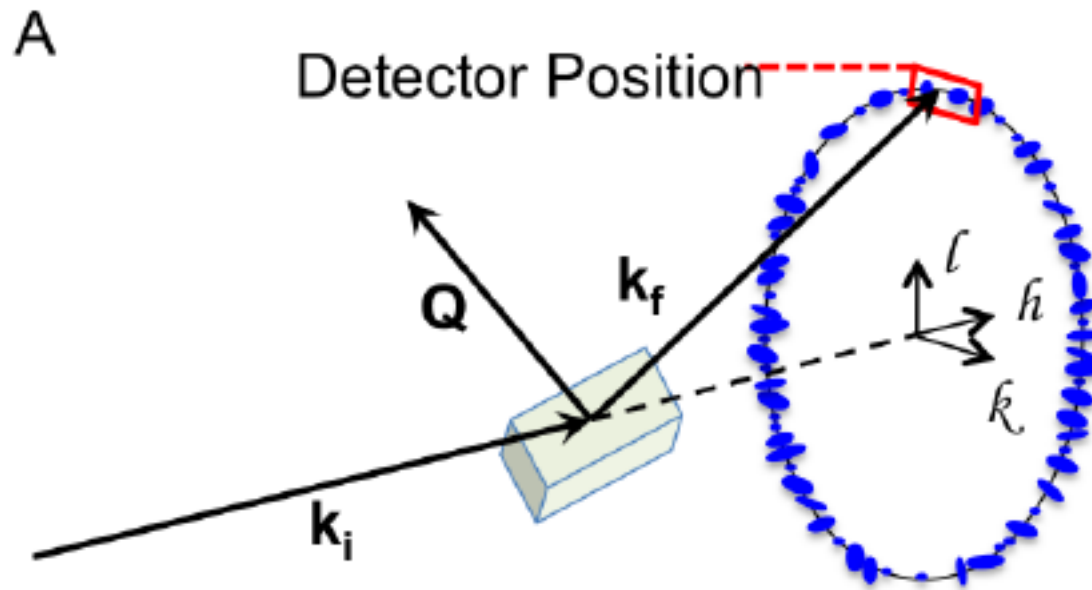


$$\gamma = 2\text{N/m}$$
$$P = 2\gamma/R = 70\text{MPa}$$
$$\varepsilon = 0.1\%, \quad \Phi = 0.6 \text{ rad}$$

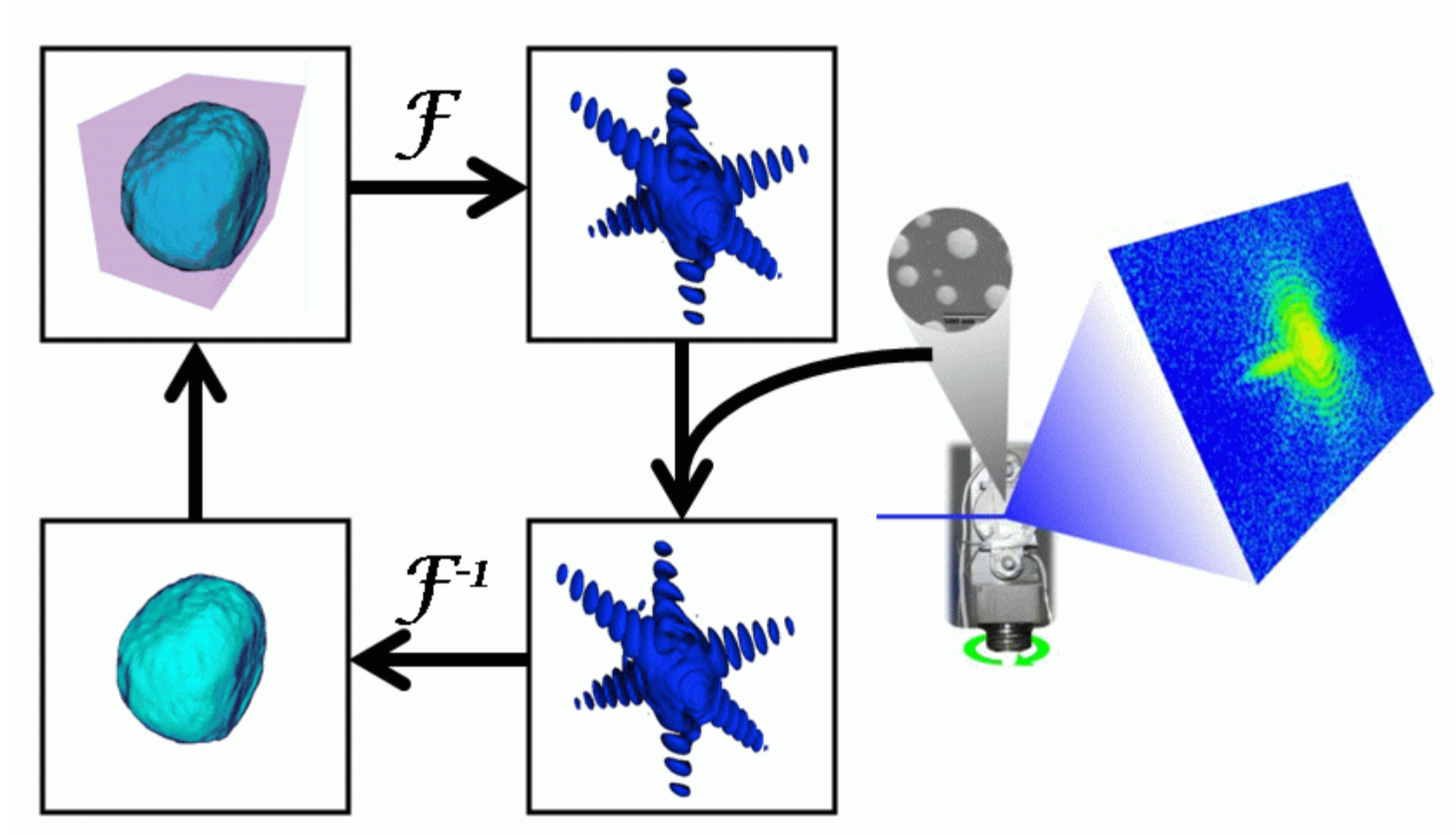


# Bragg Coherent Diffraction Imaging “Lensless” X-ray Microscope, 2003





# Generic “Error Reduction” method



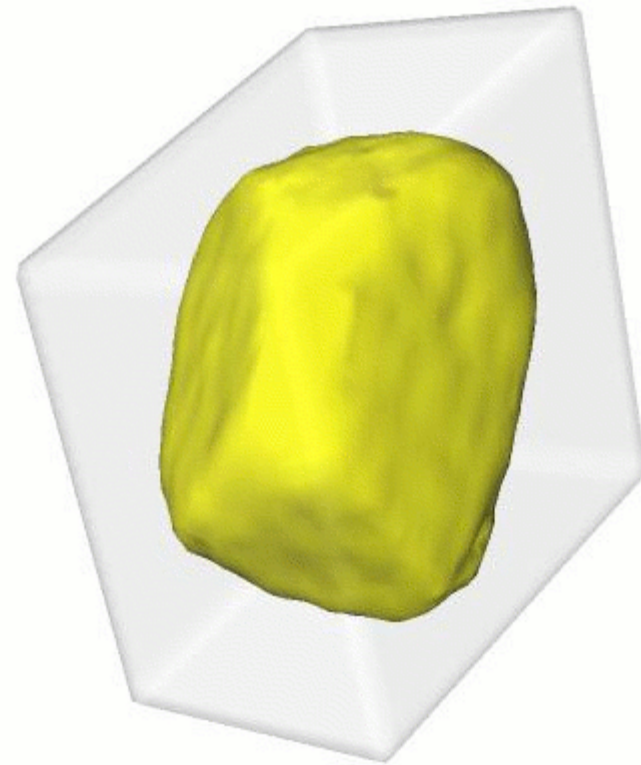
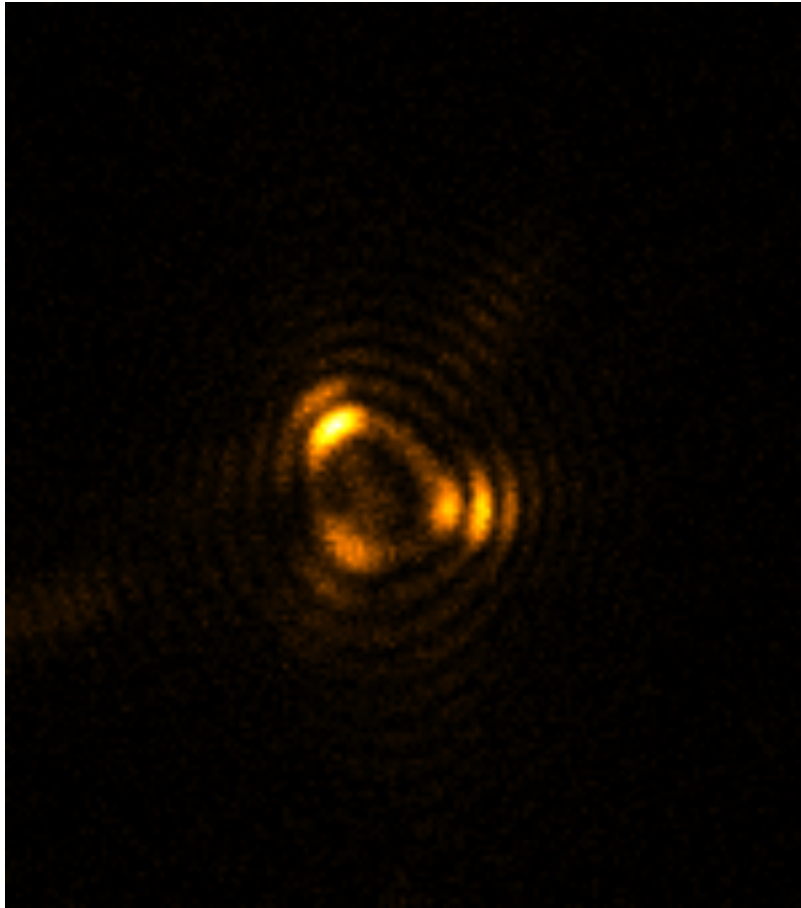
J. R. Fienup Appl. Opt. 21 2758 (1982)

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

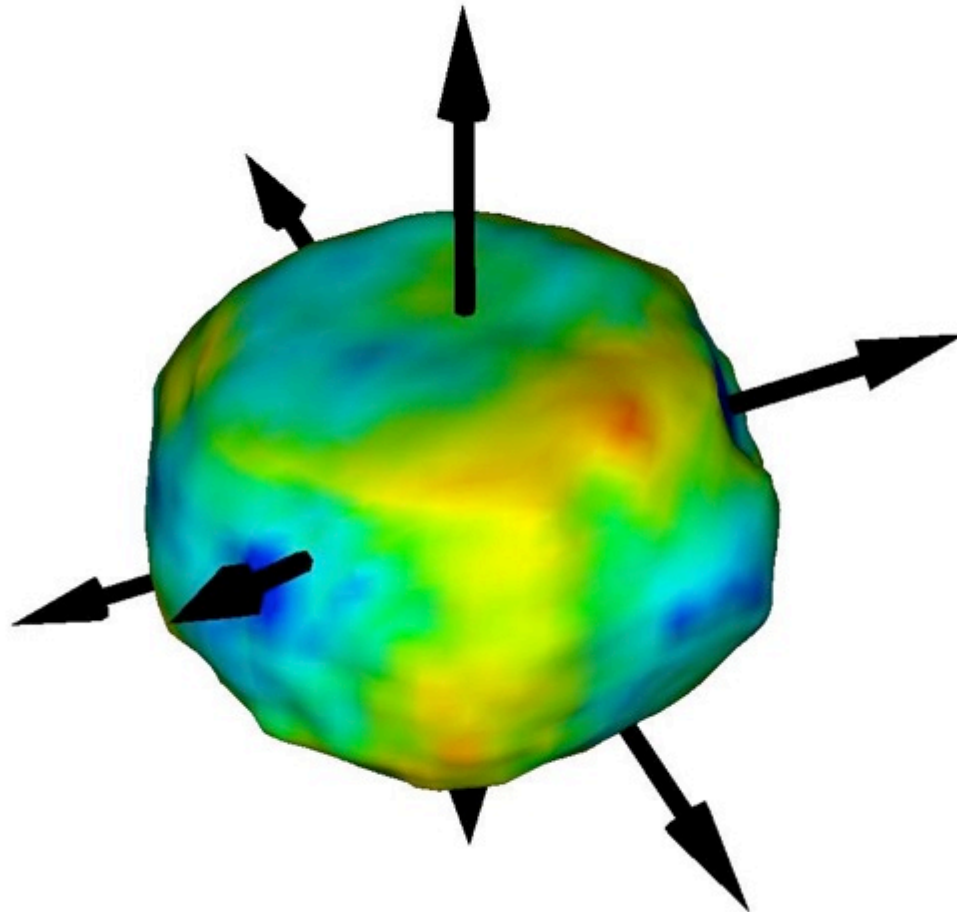
I. K. Robinson, ORNL 2017

# Gold nanocrystal reconstruction

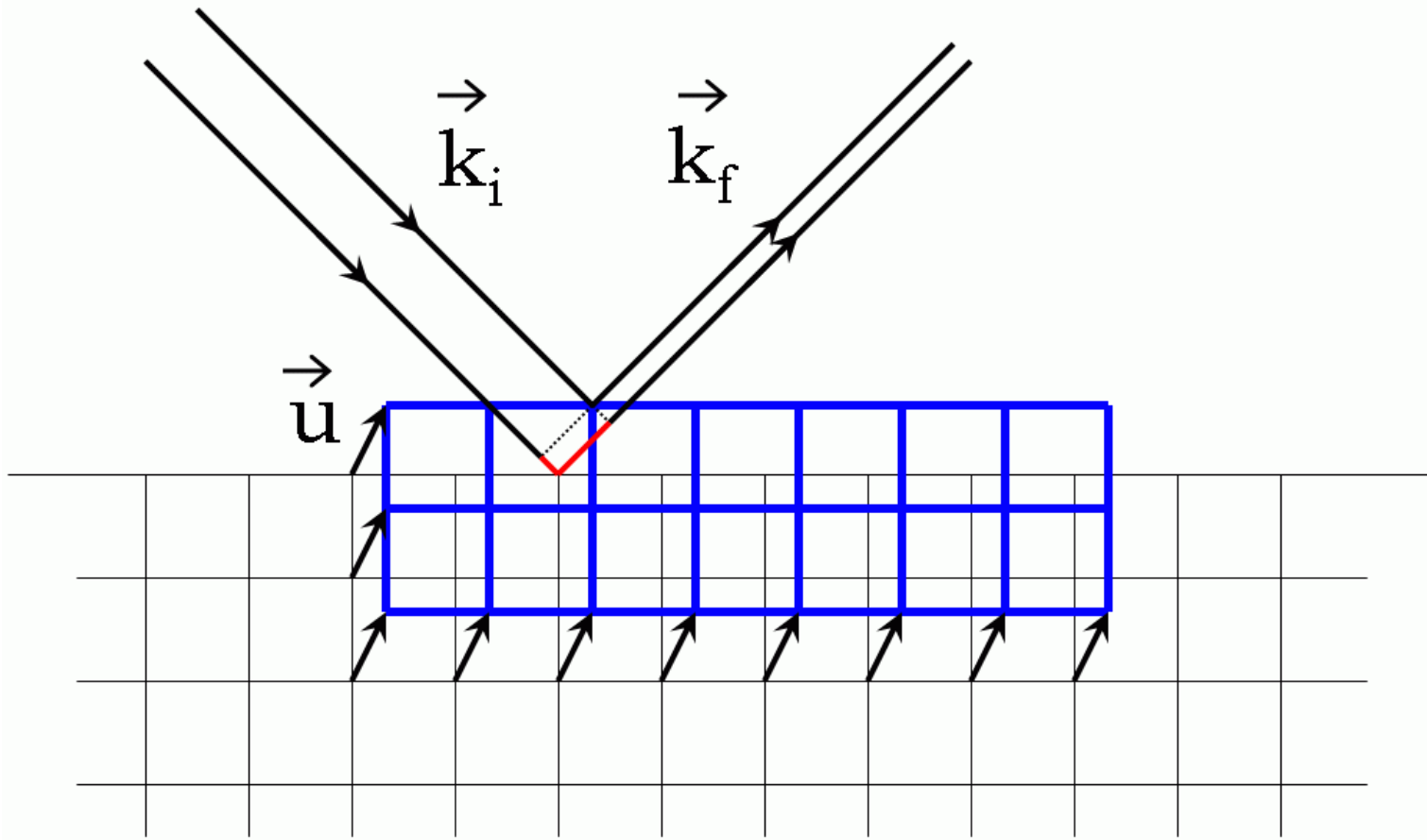
showing support used for 20 HIO followed by 10 ER



# Phase isosurface of residual strain

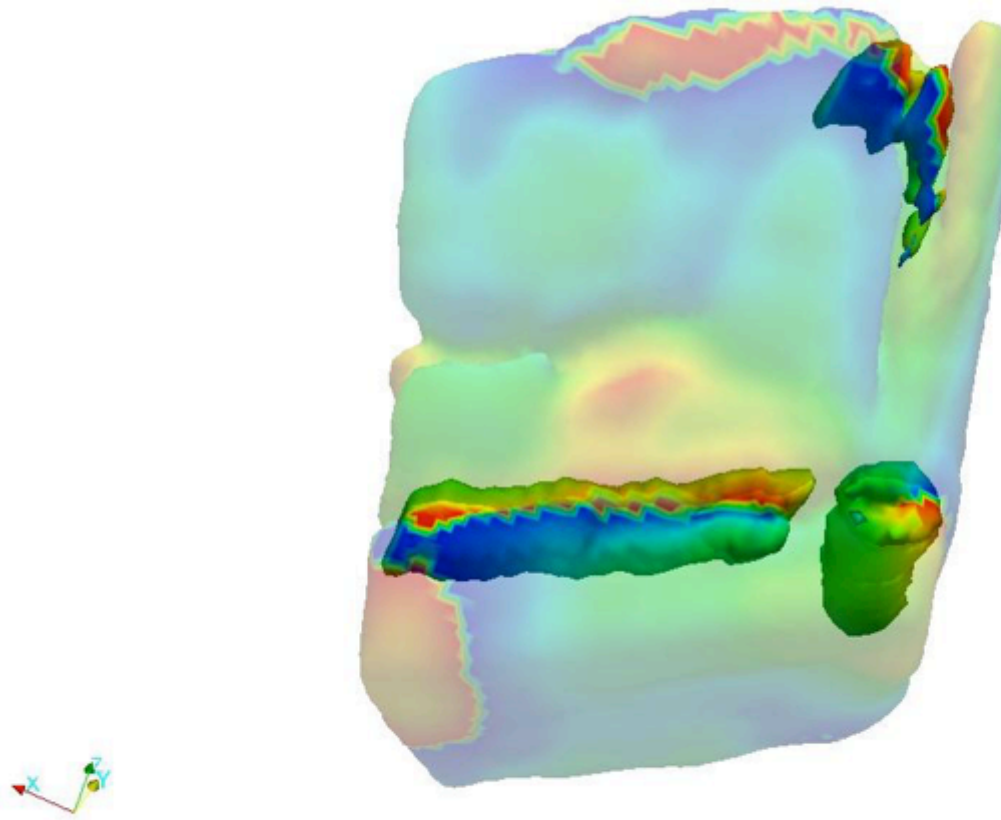


# Sensitivity to strain

$$\Delta\varphi = \mathbf{k}_f \cdot \mathbf{u} - \mathbf{k}_i \cdot \mathbf{u} = \mathbf{Q} \cdot \mathbf{u}$$


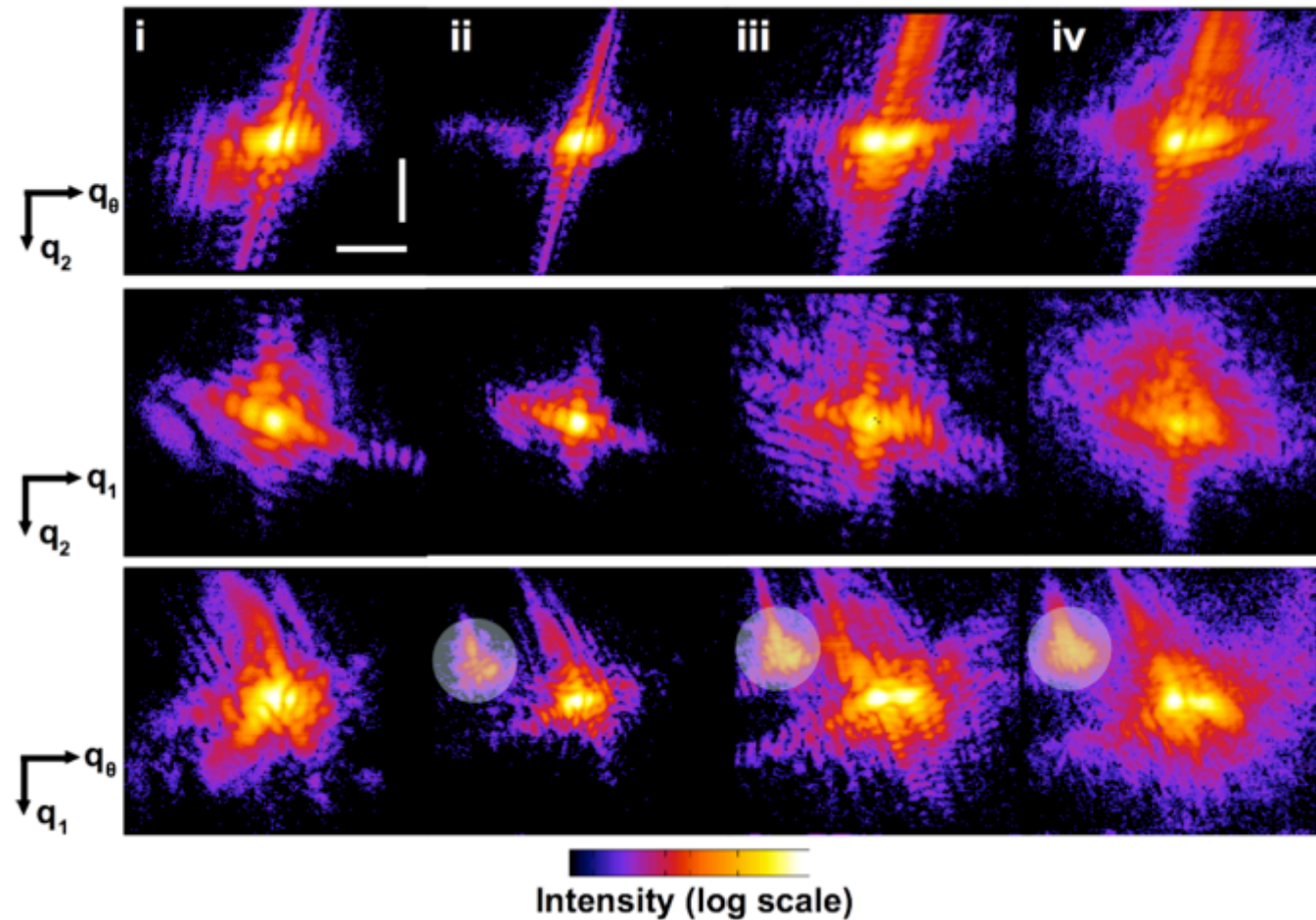
# Screw dislocations in Calcite

Jesse Clark, Johannes Ihli et al, Nat. Matls **14** 780 (2015)



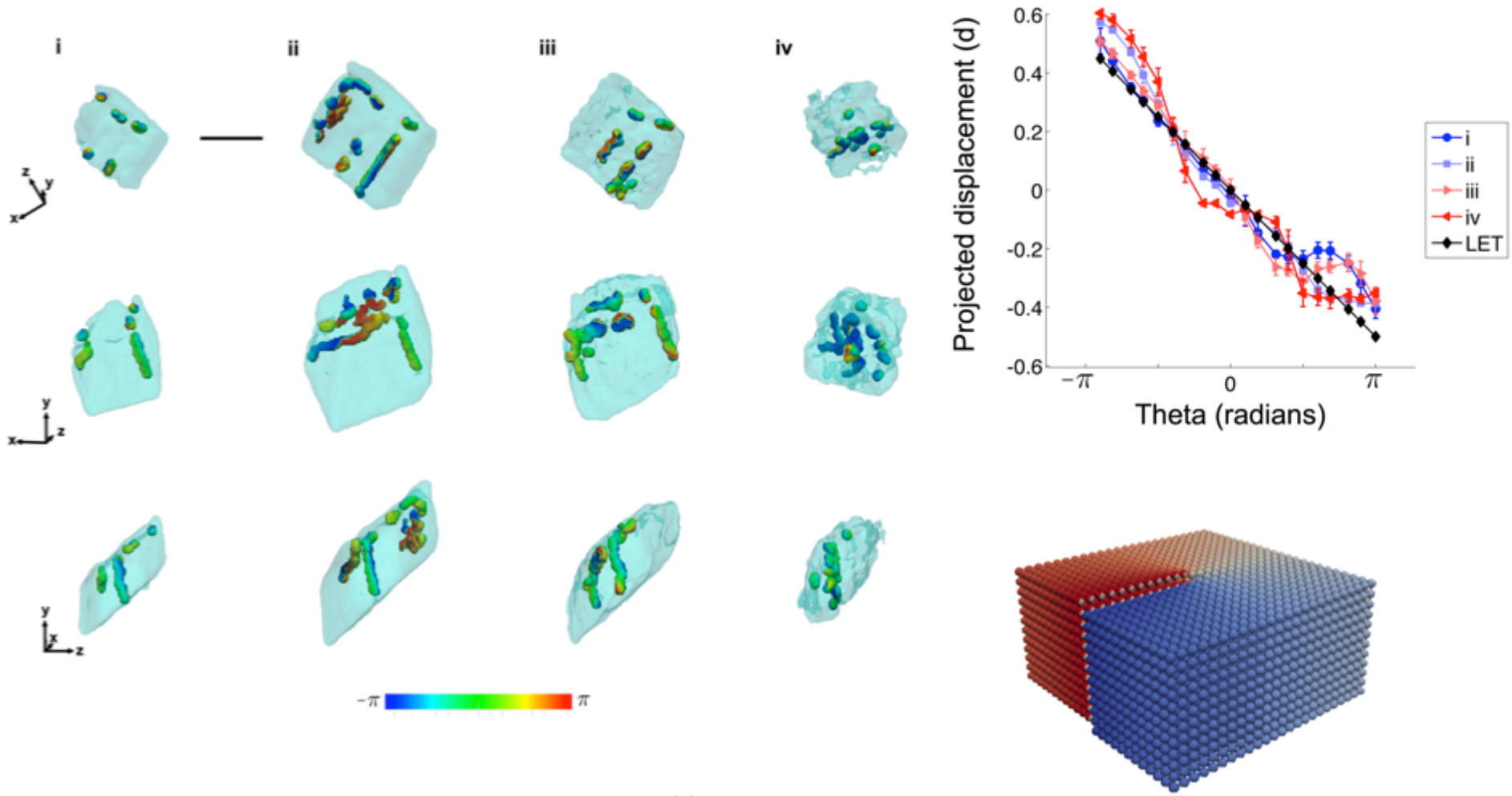
# Dissolution and Growth

J. Clark, J. Ihli, A. Schenk, Y. Kim, A. Kulak, J. Campbell, G. Nisbet, F. Meldrum, I. Robinson, Nat Mats **14** 780 (2015)



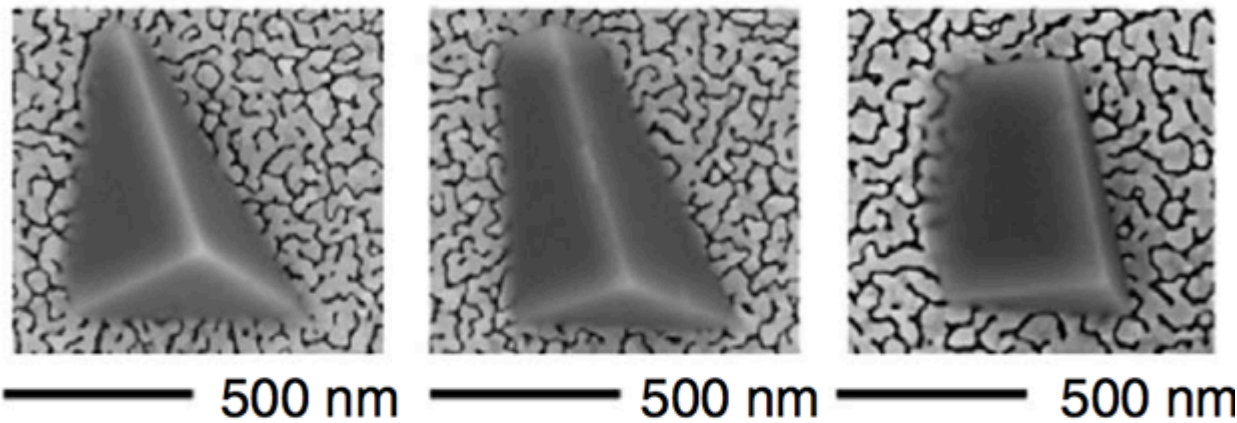
# Dissolution and Growth

J. Clark, J. Ihli, A. Schenk, Y. Kim, A. Kulak, J. Campbell, G. Nisbet, F. Meldrum, I. Robinson, Nat Mats **14** 780 (2015)



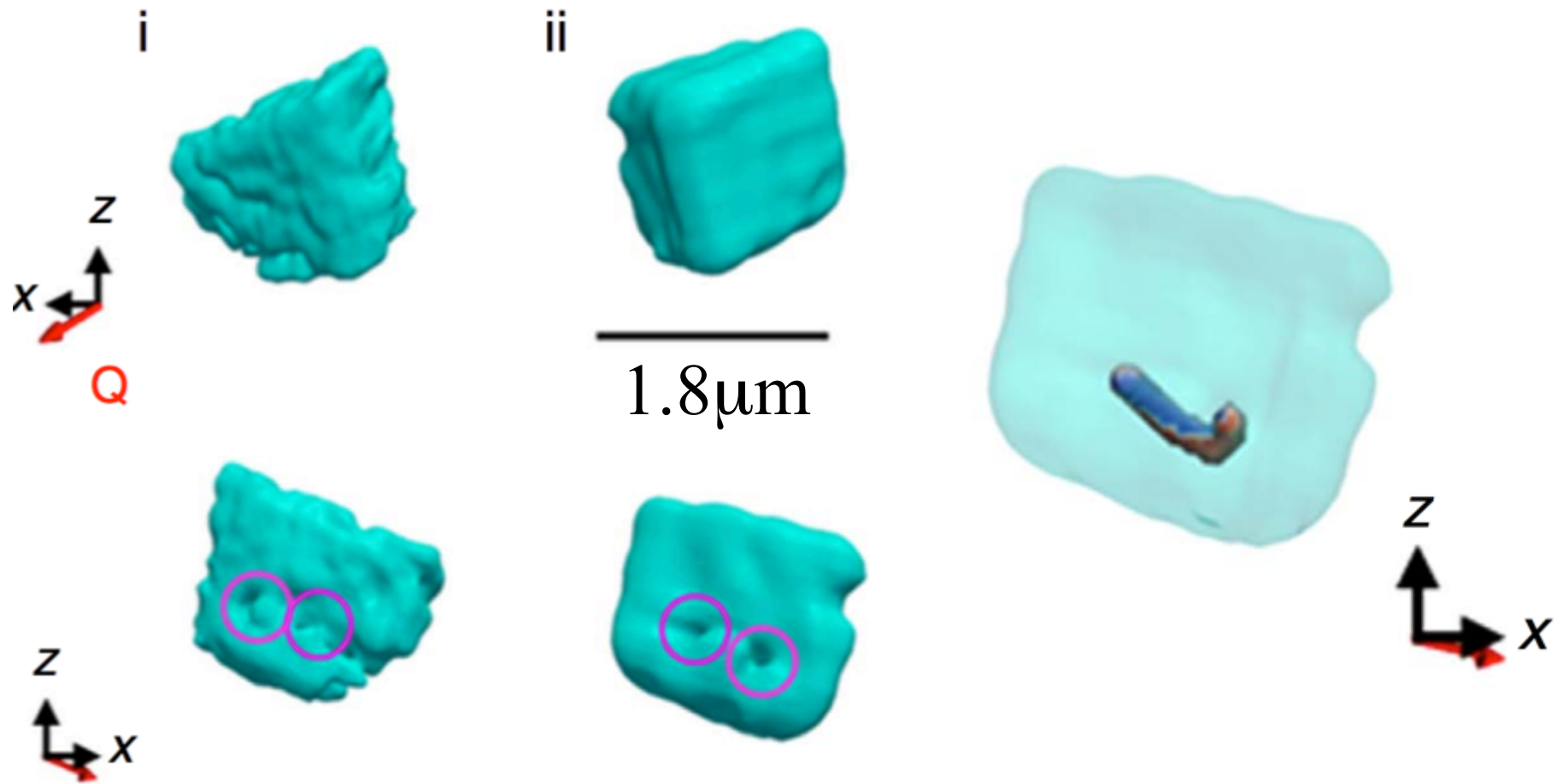
# Calcite growth on SAM/Au(111)

J. Ihli, J. N. Clark, et al, N. Comms 7 11878 (2016)



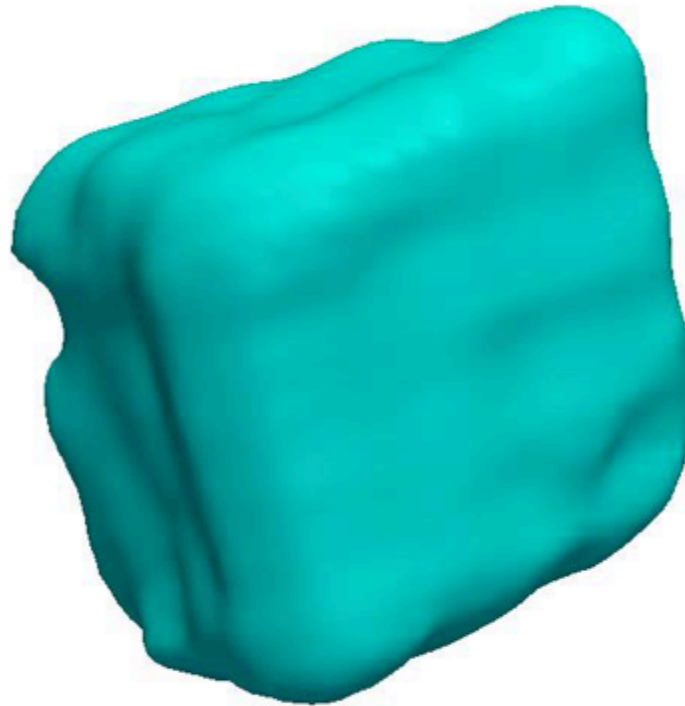
# Calcite growth on SAM/Au(111)

J. Ihli, J. N. Clark, et al, N. Comms 7 11878 (2016)

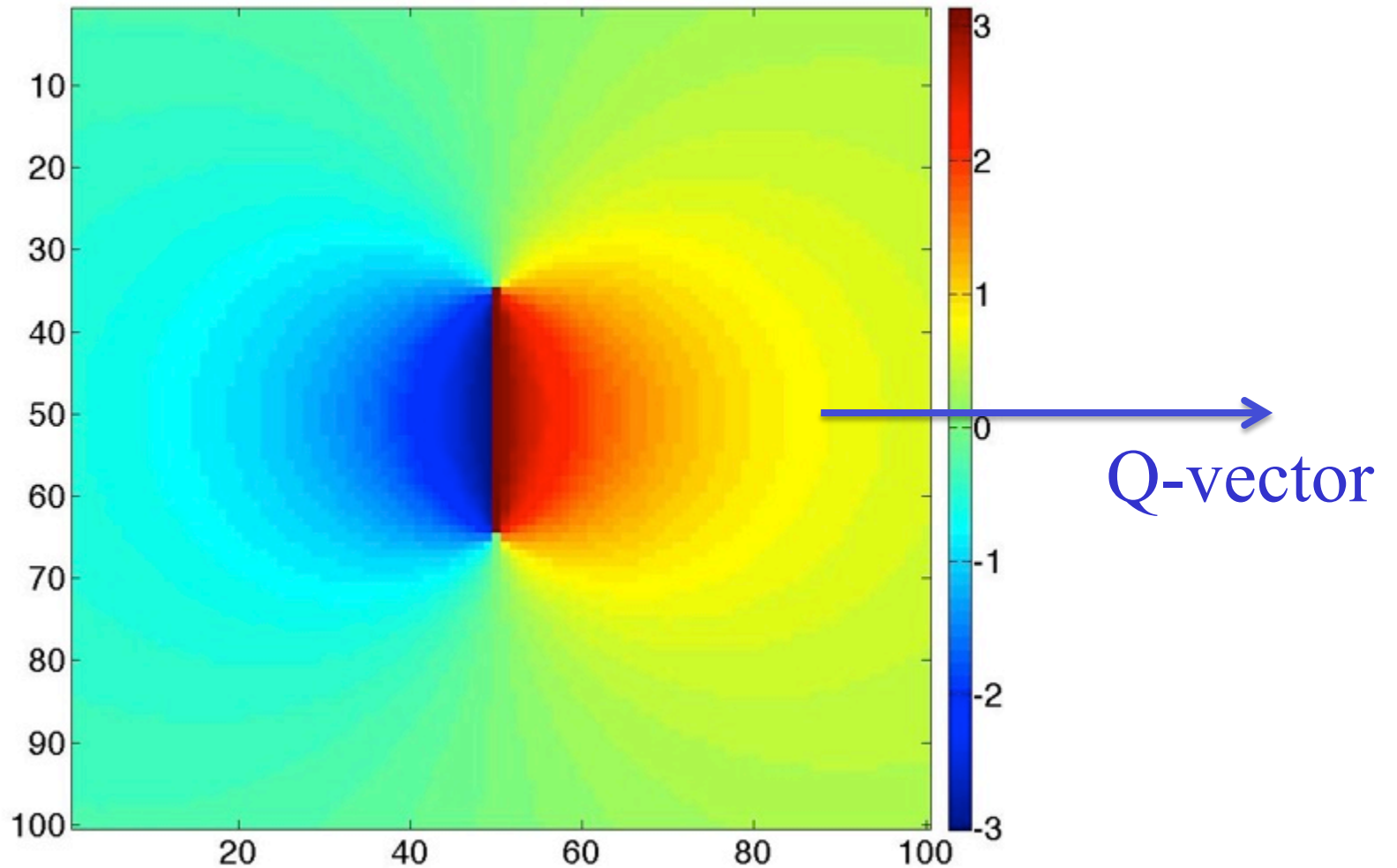


# Calcite growth on SAM/Au(111)

J. Ihli, J. N. Clark, et al, N. Comms 7 11878 (2016)

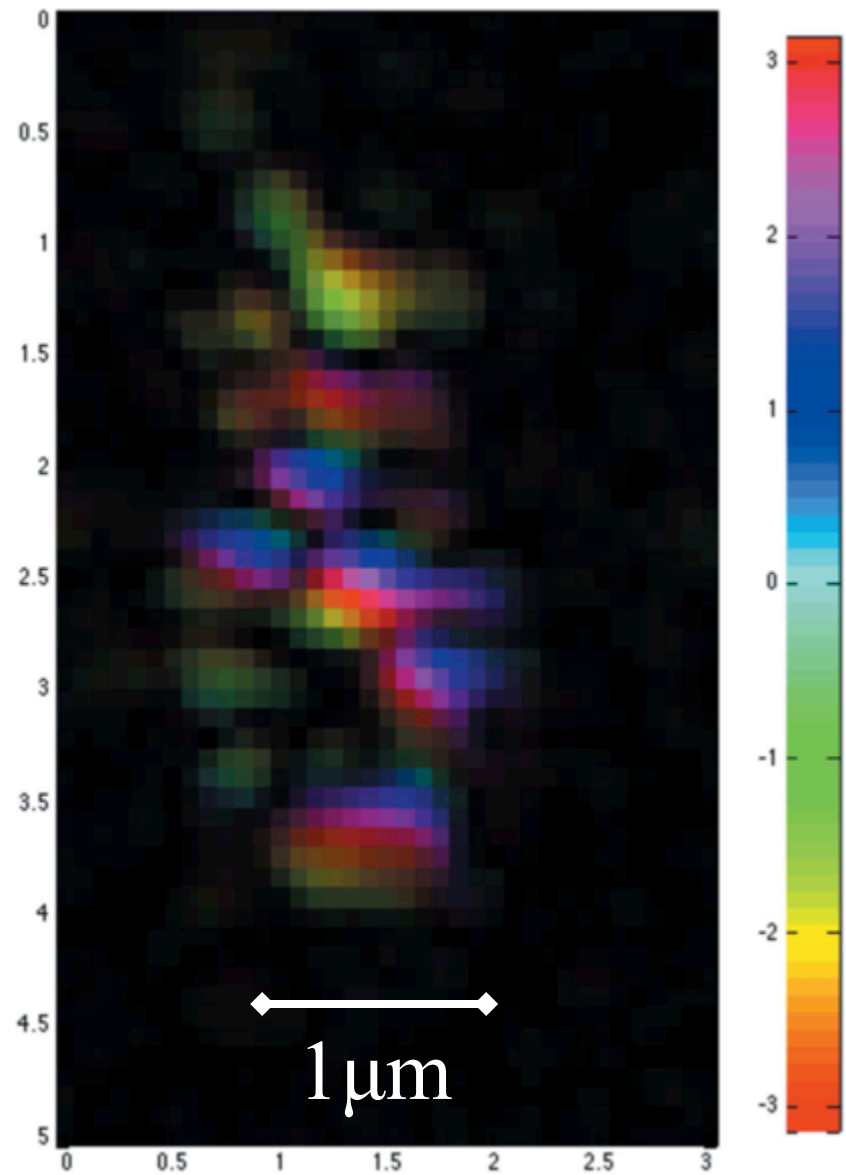
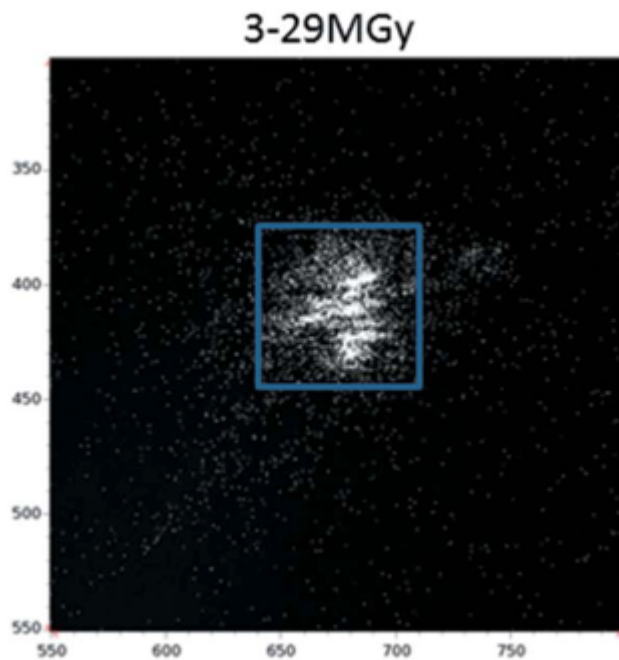


# Strain field of Edge Dislocation Loop



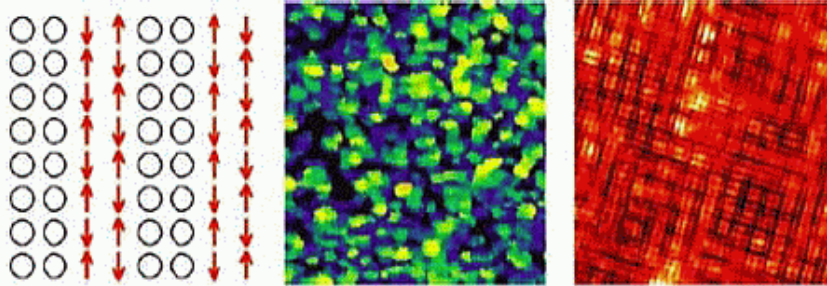
# Insect Virus BCDI

C. Nave et al J. Sync.  
Rad. 23, 228 (2016)



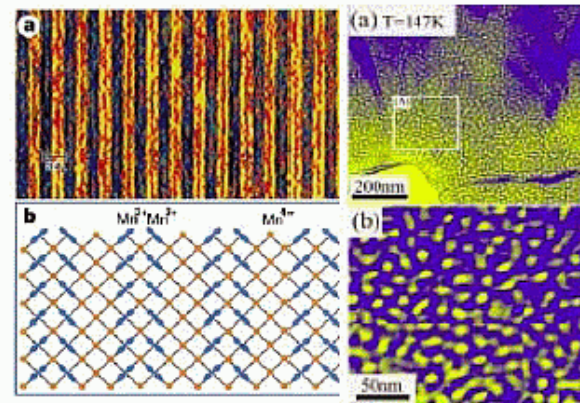
# Stripes, checkerboards and zig-zags

## High-Tc cuprates



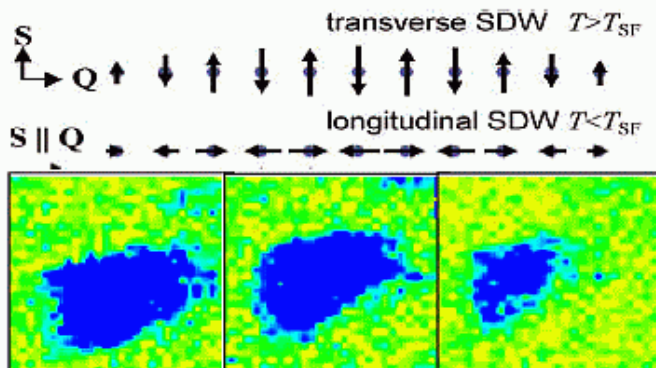
E. Dagotto, T. M. Rice, *Science* **271**, 618 (1996).  
T. Hanaguri et al., *Nature* **430**, 1001 (2004).

## CMR manganites

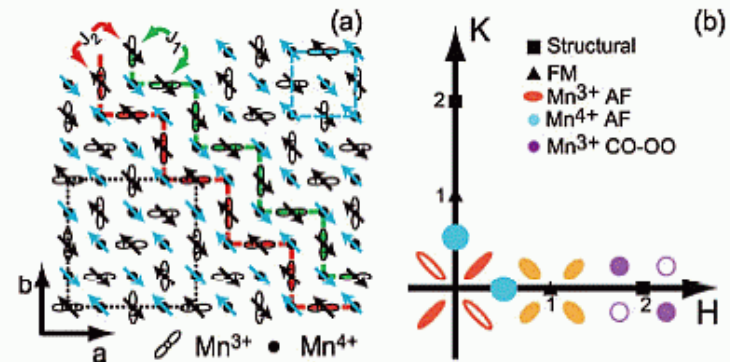


S. Mori et al., *Nature* **392**, 473 (1998)  
M. Uehara et al., *Nature* **399**, 560 (1999)

## AFM chromium

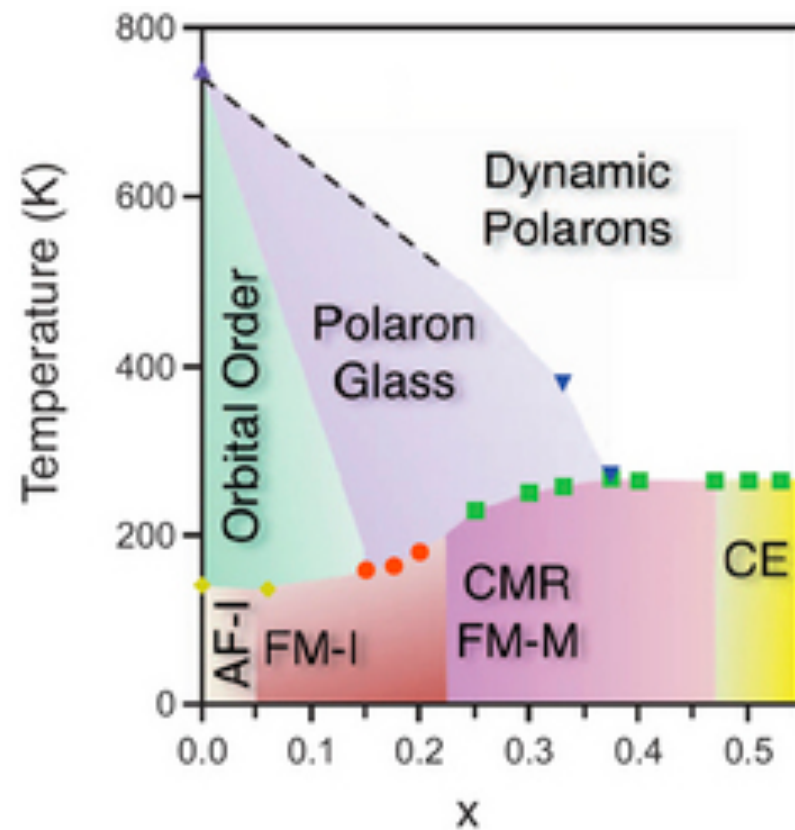
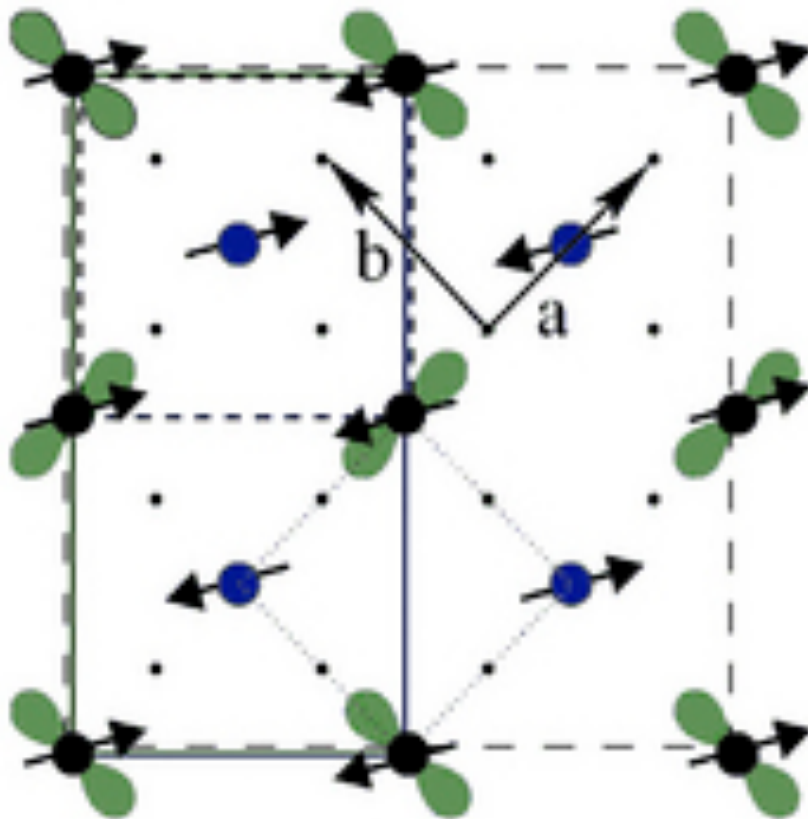


P. G. Evans et al., *Science* (2002)



# LCMO $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

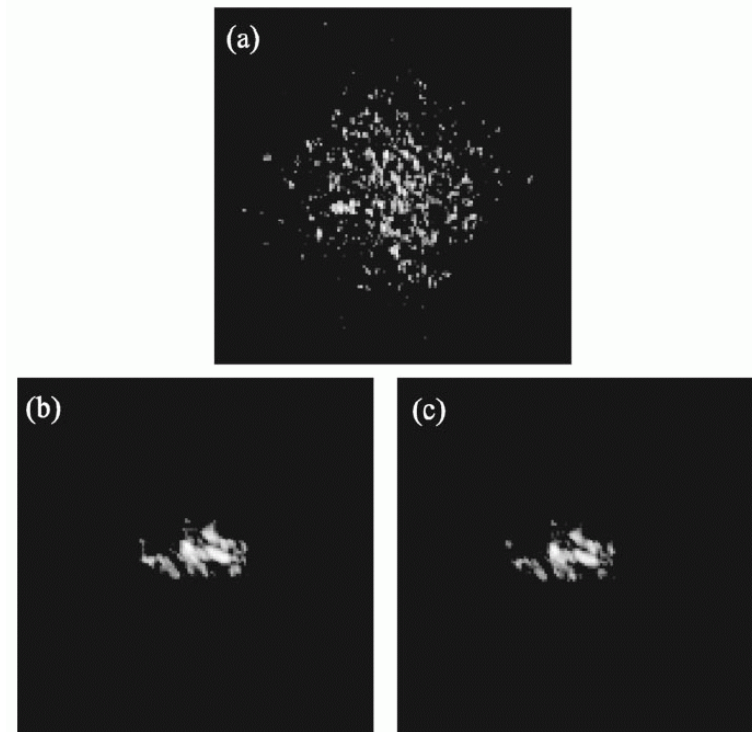
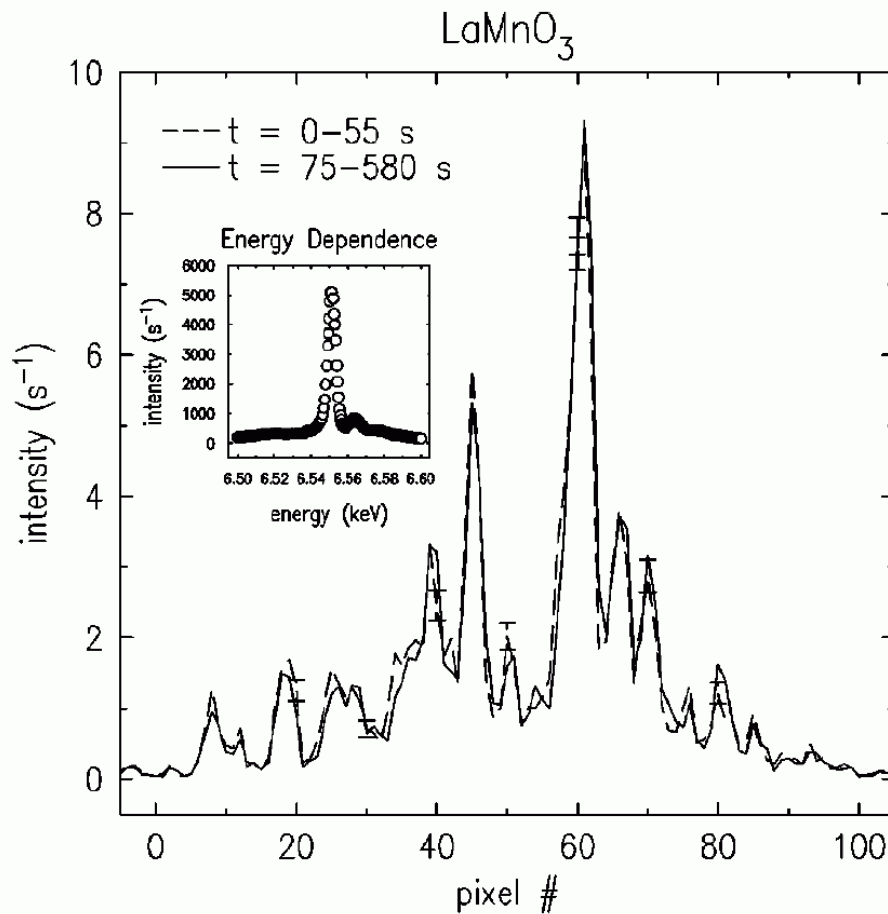
<http://www.psi.ch/swissfel/correlated-electron-phases>



# LaMnO<sub>3</sub> and Pr<sub>0.6</sub>Ca<sub>0.4</sub>MnO<sub>3</sub> speckle

C. S. Nelson, J. P. Hill, Doon Gibbs, F. Yakhou, F. Livet, Y. Tomioka, T. Kimura and Y. Tokura, PRB 66 134412 (2002)

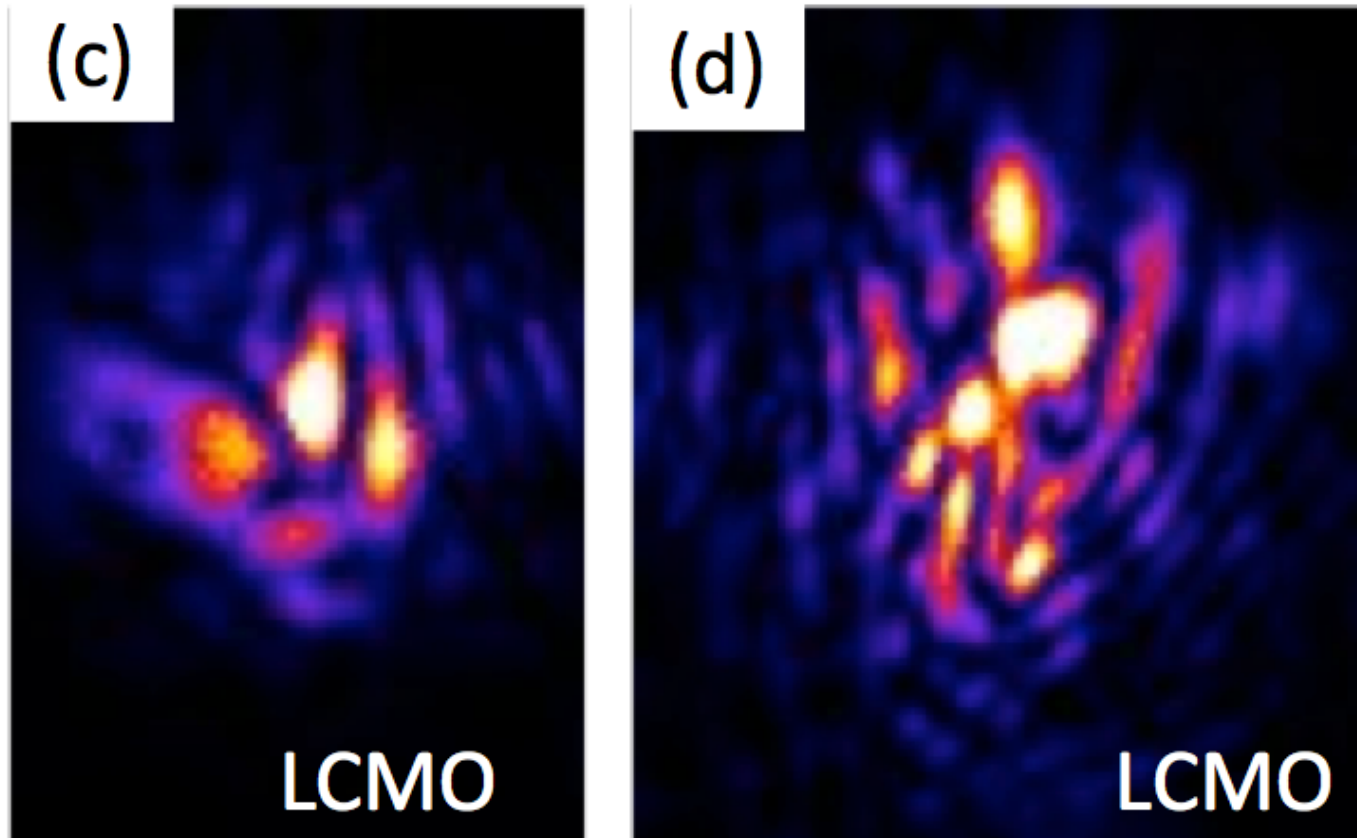
Pr<sub>0.6</sub>Ca<sub>0.4</sub>MnO<sub>3</sub>, T = 150 K



. Images of orbital (a) and charge (b), (c) order

# BCDI from $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

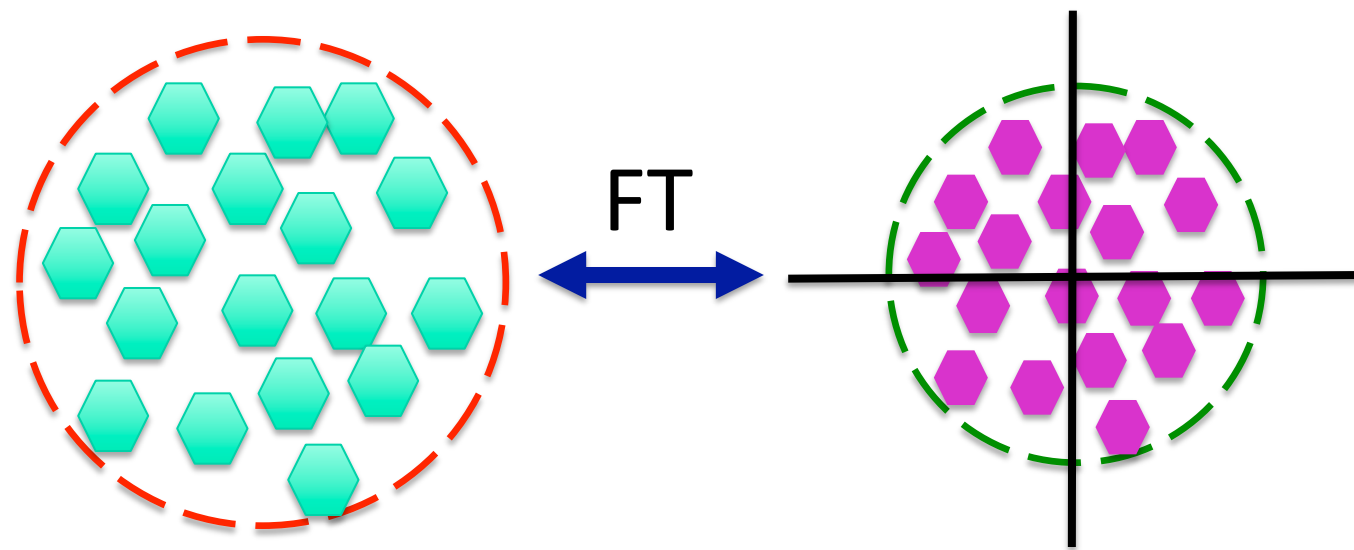
LCMO-500, Ian McNulty and Jon Logan, 34-ID-C Argonne



# Domain structures give speckled diffraction

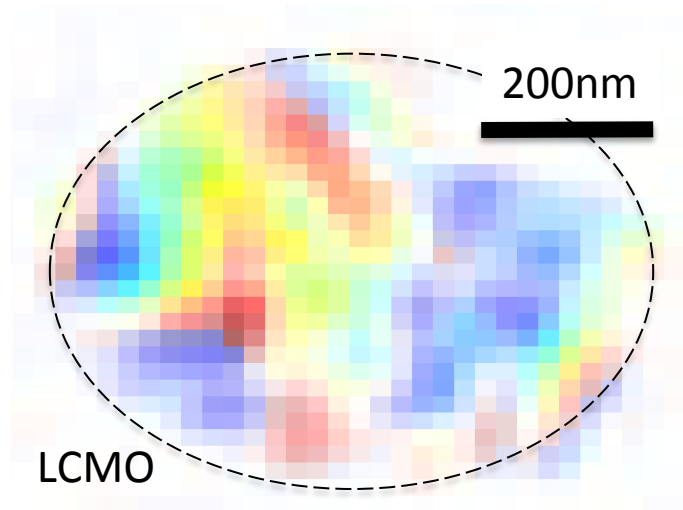
Real Space

Reciprocal Space



# BCDI from $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

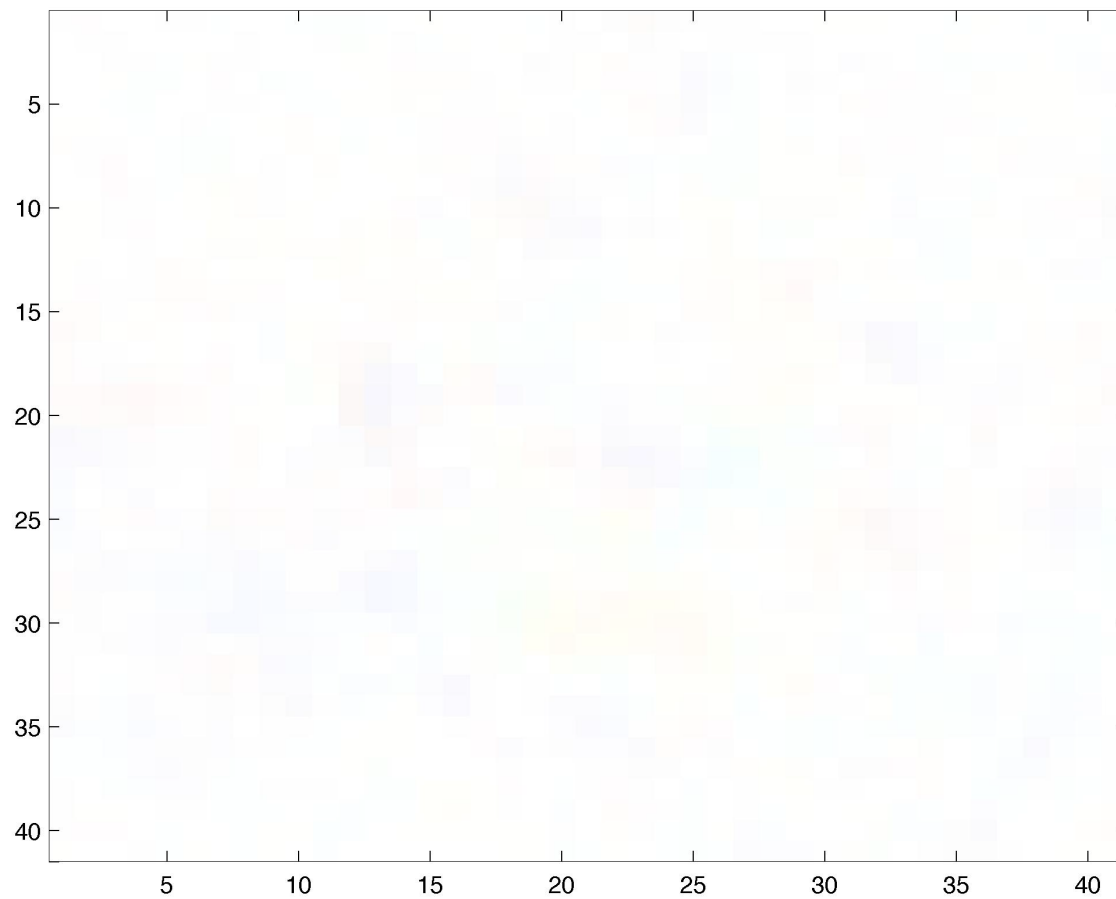
Ian McNulty and Jon Logan, 34-ID-C Argonne



LCMO\_500\_test31.png

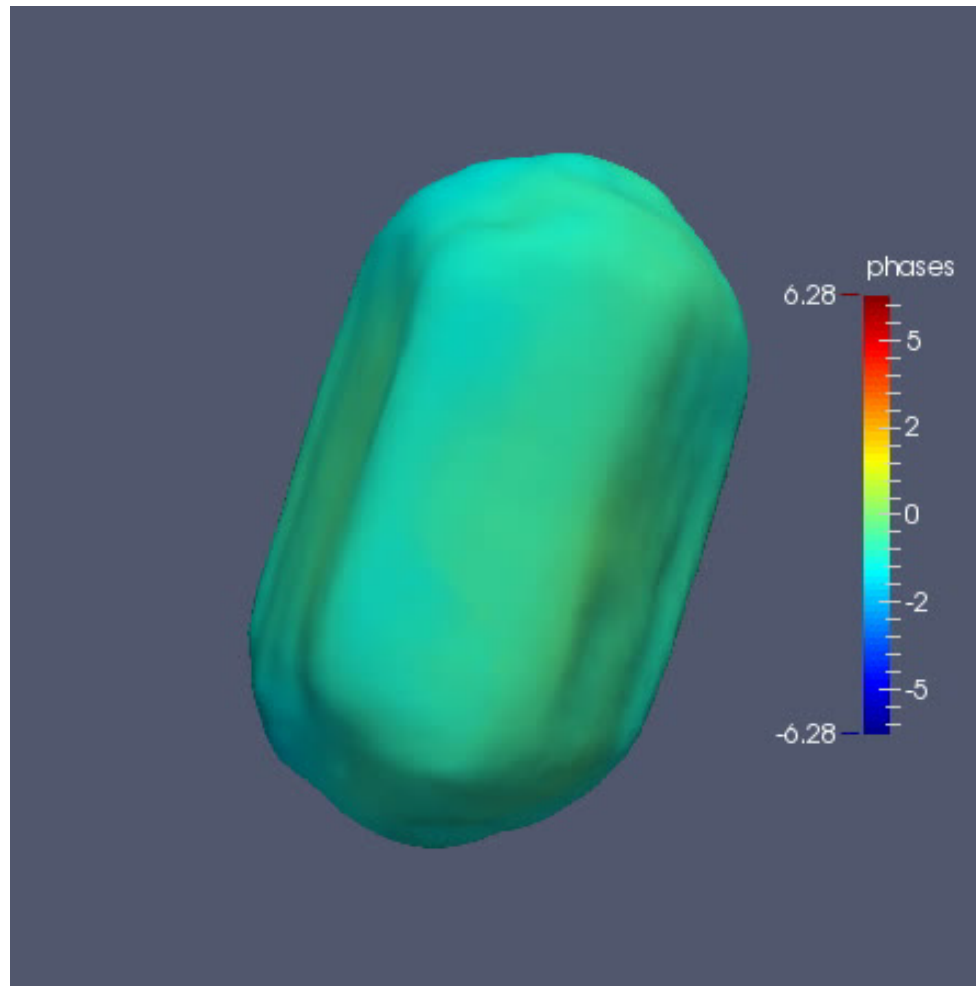
# BCDI from $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

LCMO-500, Ian McNulty and Jon Logan, 34-ID-C Argonne



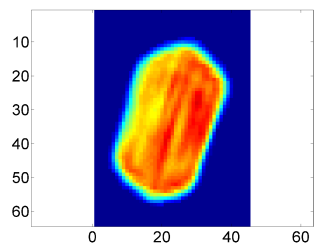
# Au NC before Fe deposition

Ana Estandarte, to be published



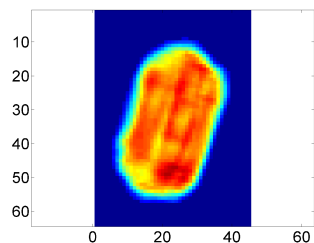
# Amplitude: xz-cut plane, $T=400^{\circ}\text{C}$

Before Fe dose

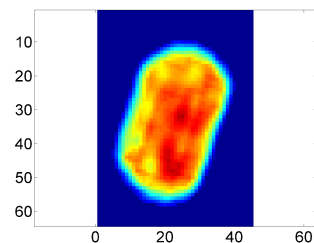


After 1<sup>st</sup> Fe dose,

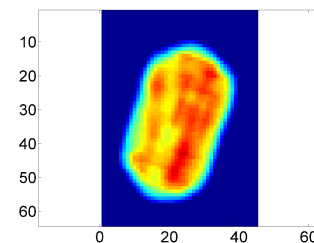
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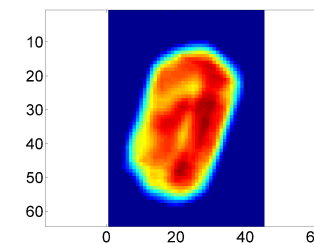
t=1hr



t=2hrs

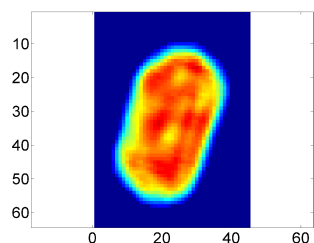


t=3hrs

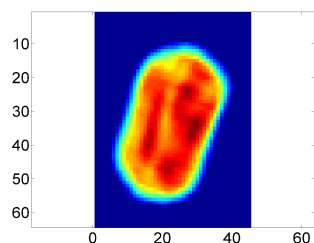


After 2<sup>nd</sup> Fe dose,

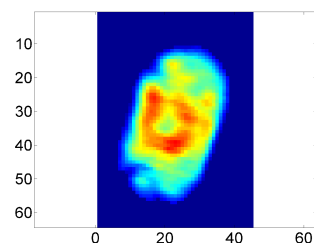
t=4hrs



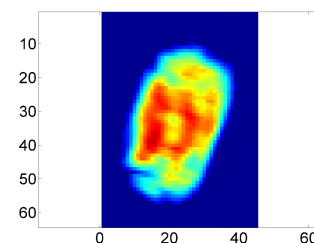
t=5hrs



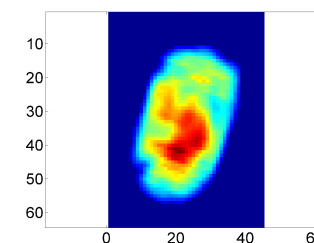
t=10min



t=1hr

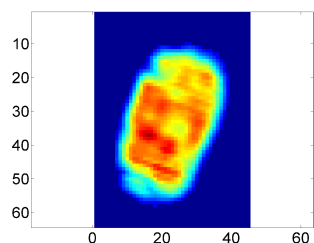


t=2hrs

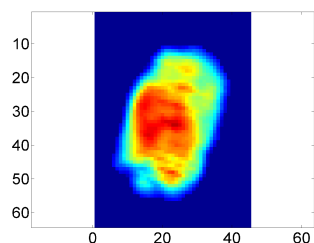


After 3<sup>rd</sup> Fe dose,

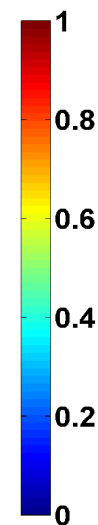
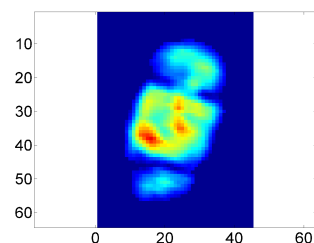
t=3hrs



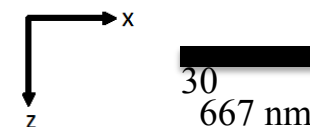
t=6hrs



t=20min

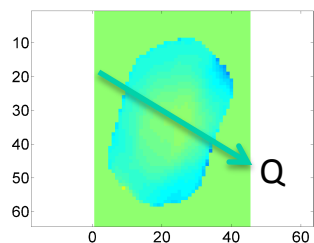


I. K. Robinson, ORNL 2017



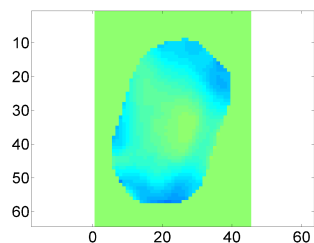
# Phase: xz-cut plane, $T=400^{\circ}\text{C}$

Before Fe dose

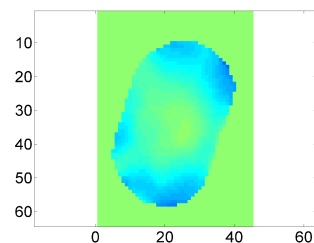


After 1<sup>st</sup> Fe dose,

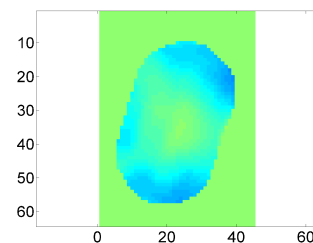
t=10min



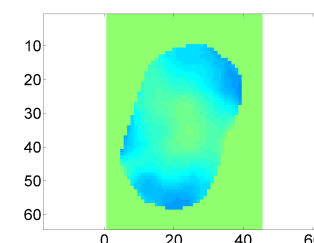
t=1hr



t=2hrs

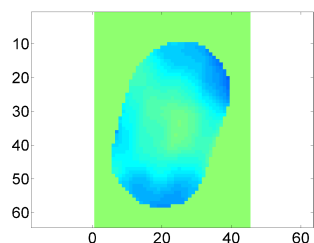


t=3hrs

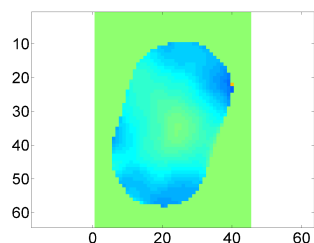


After 2<sup>nd</sup> Fe dose,

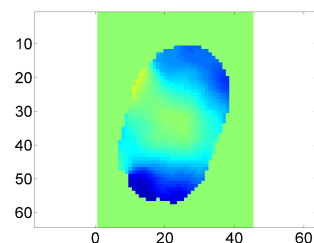
t=4hrs



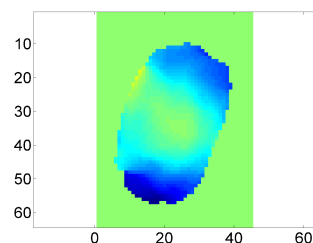
t=5hrs



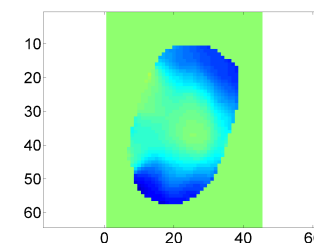
t=10min



t=1hr

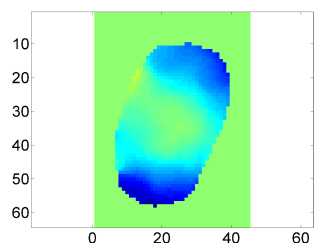


t=2hrs

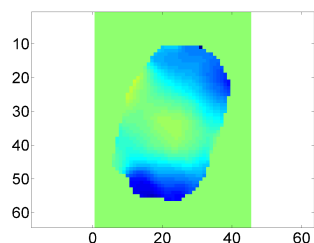


After 3<sup>rd</sup> Fe dose,

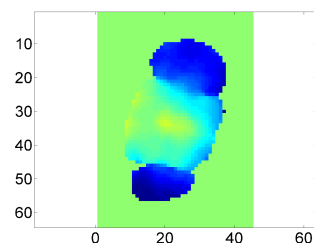
t=3hrs



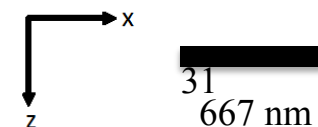
t=6hrs



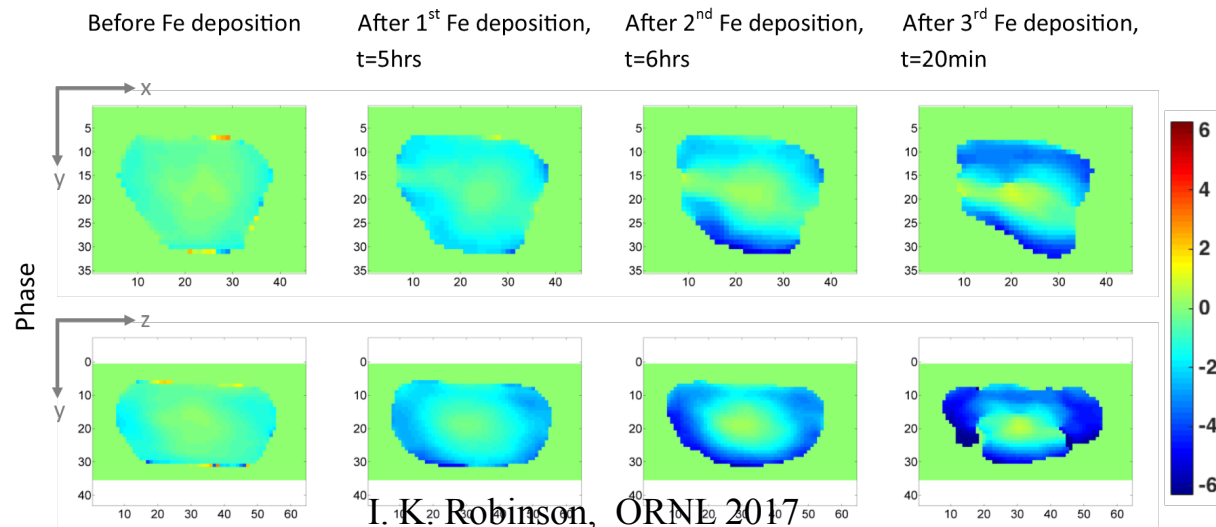
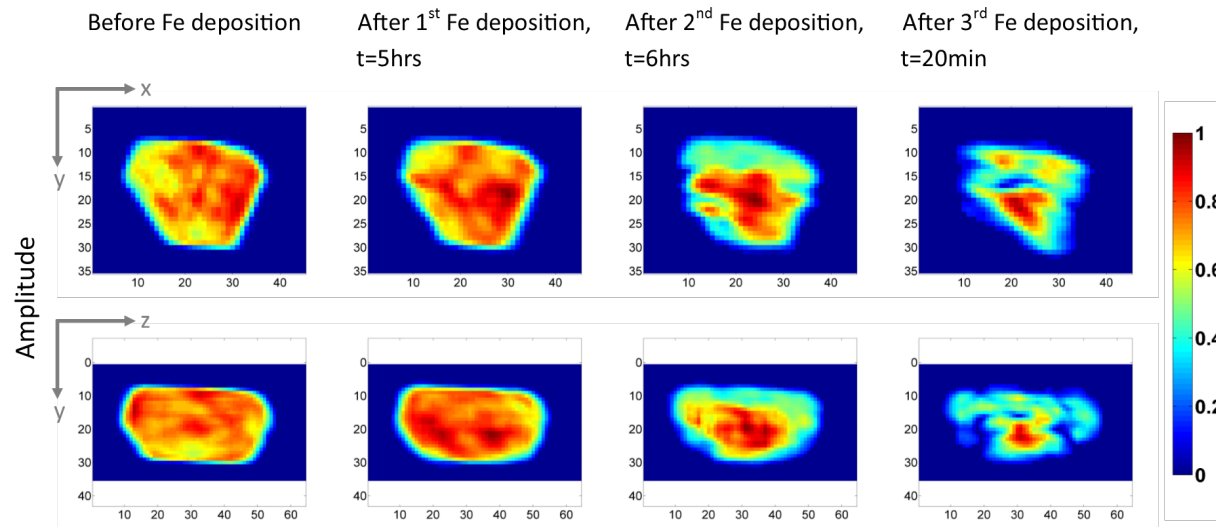
t=20min



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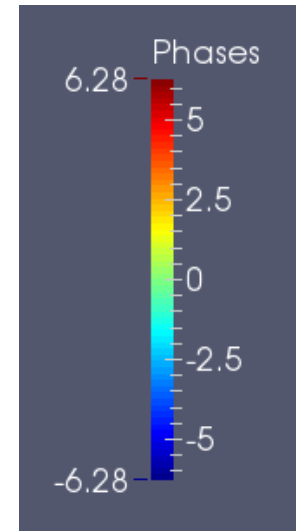
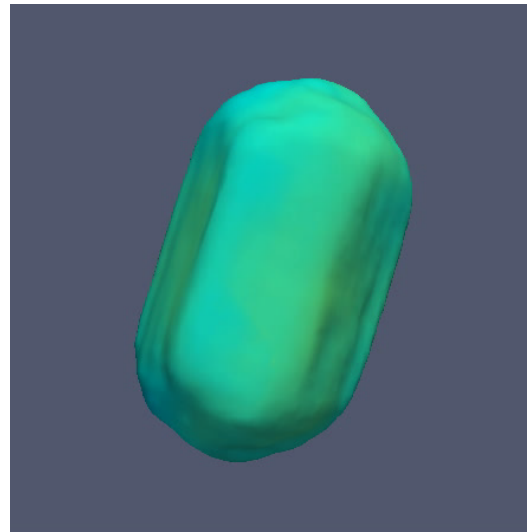
# xy- and zy-cut planes, $T=400^{\circ}\text{C}$



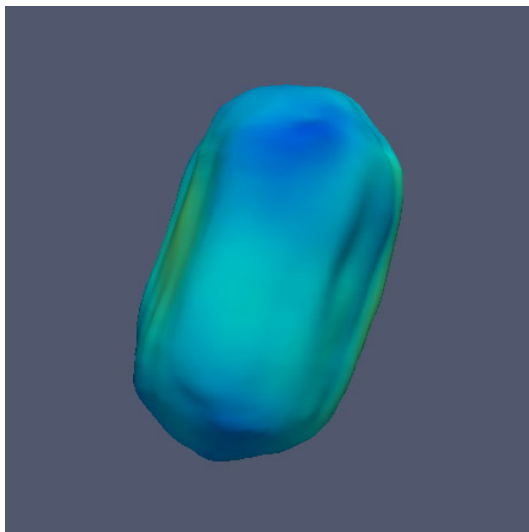
I. K. Robinson, ORNL 2017

# Phase Isosurface Images

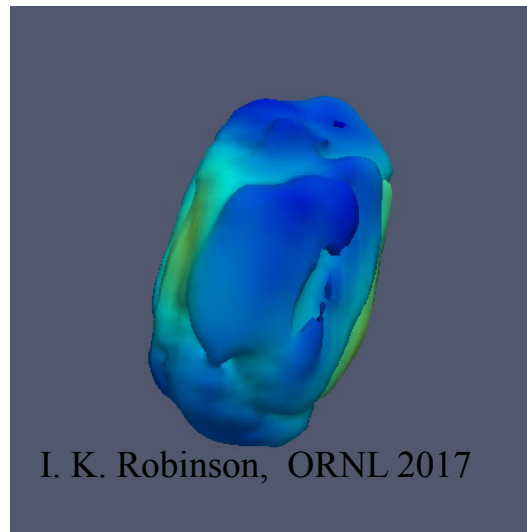
Control



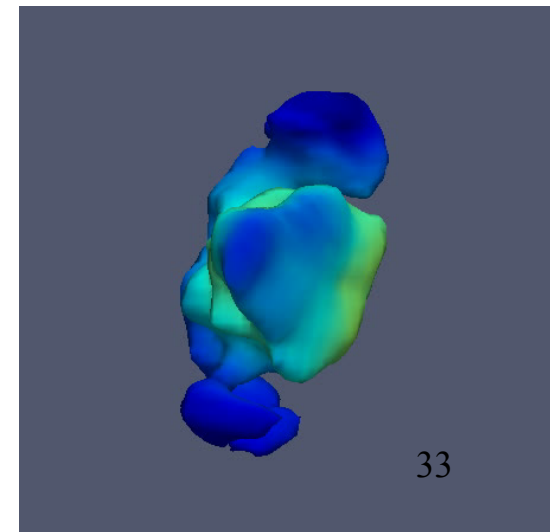
After 1<sup>st</sup> Fe dose



After 2<sup>nd</sup> Fe dose



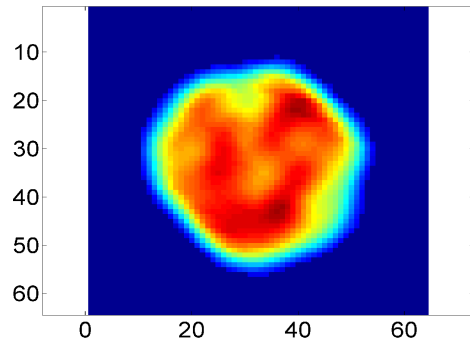
After 3<sup>rd</sup> Fe dose



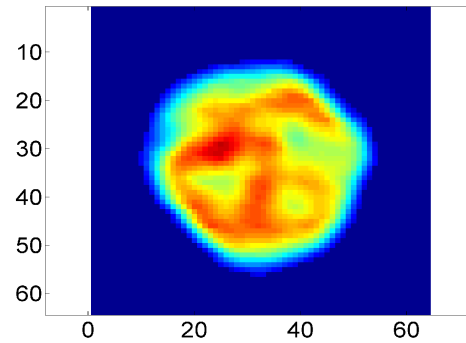
# Amplitude and Phase, $T=300^{\circ}\text{C}$

Ana Estandarte, to be published

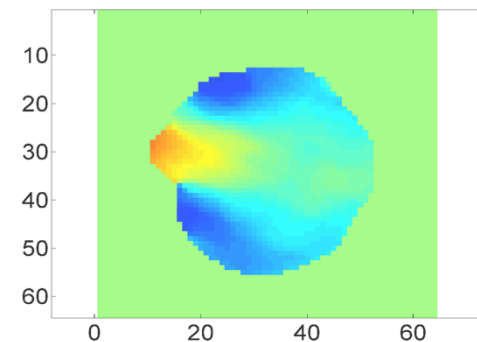
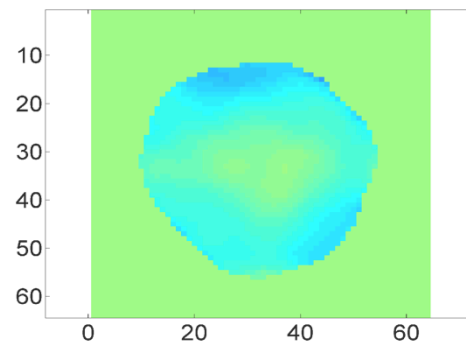
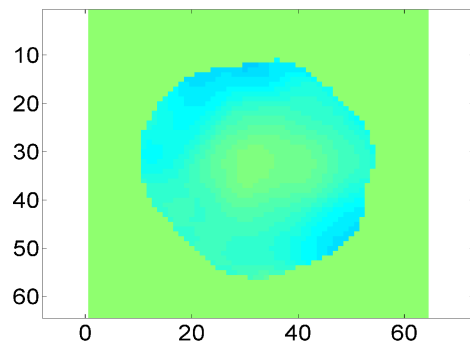
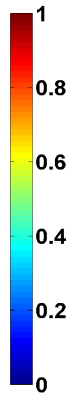
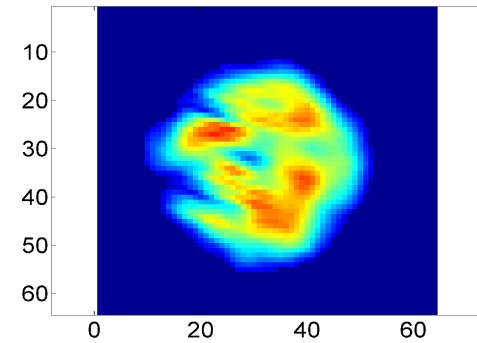
Before Fe dose



1<sup>st</sup> Fe dose, t=6hrs



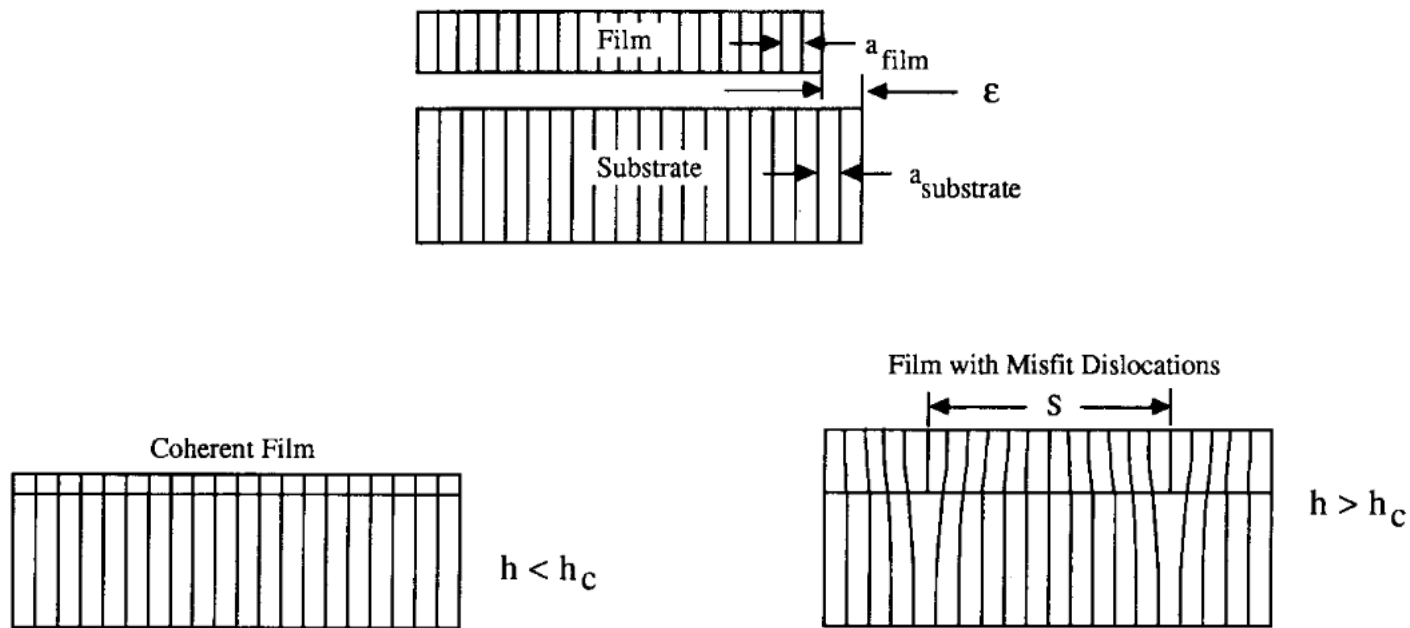
2<sup>nd</sup> Fe dose, t=8hrs



# Misfit Dislocations and Stacking Faults

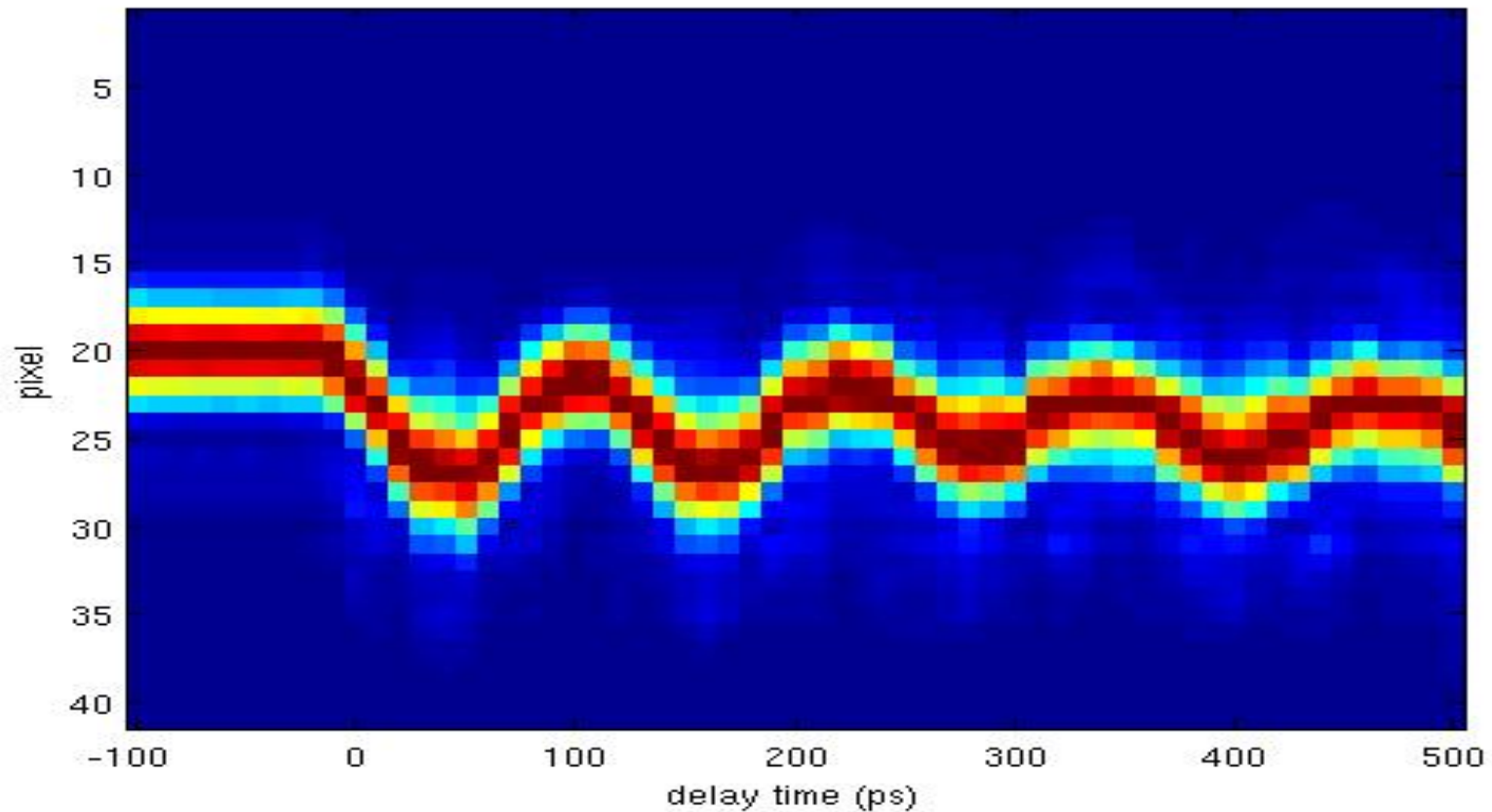
Ana Estandarte, to be published

- Alloying of Fe with Au  $\rightarrow$  contraction of the nanocrystal lattice
- Lattice misfit between AuFe shell and Au core  $\rightarrow$  formation of misfit dislocations



# Au Pump-probe at LCLS (XPP)

Justin Wark, Loren Beitra, Alexander Korsunsky, Ross Harder, David Fritz ,  
Sebastien Boutet, **Jesse Clark**, Garth Williams, Brian Abbey, Andy Higginbotham,  
Diling Zhu, Henrick Lemke, Mattieu Chollet, Marc Messerschmidt



# “Two-temperature” model

I.K. Robinson et al, Journal of Optics **18** 054007 (2016)

J.K. Chen et al, Int J. Heat Transfer **49** 307 (2006)

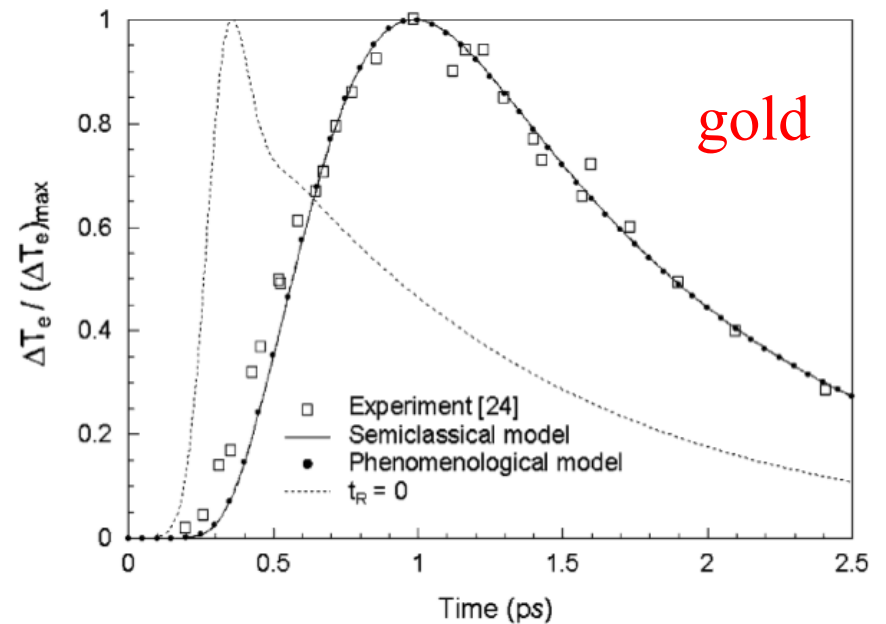
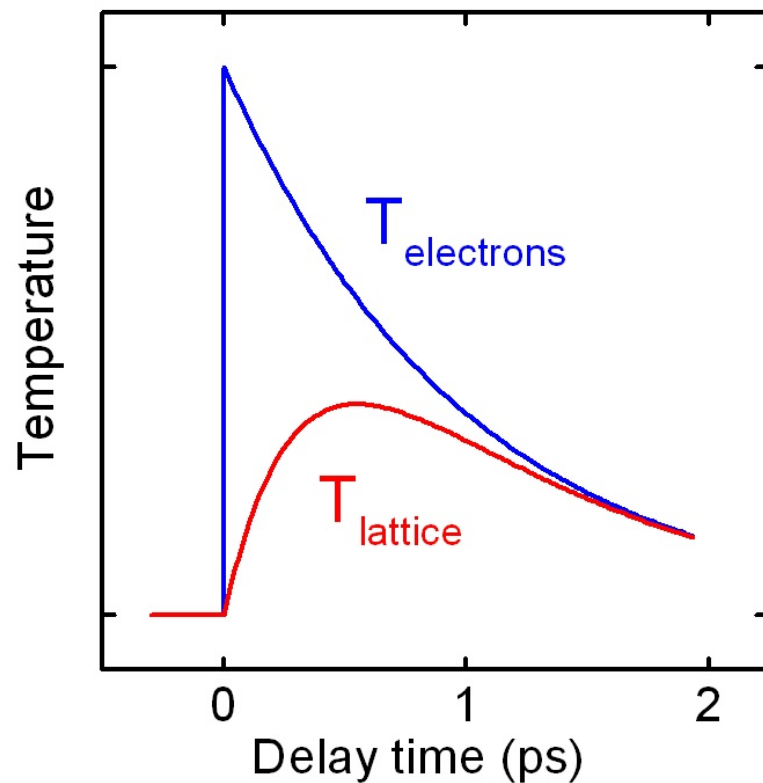
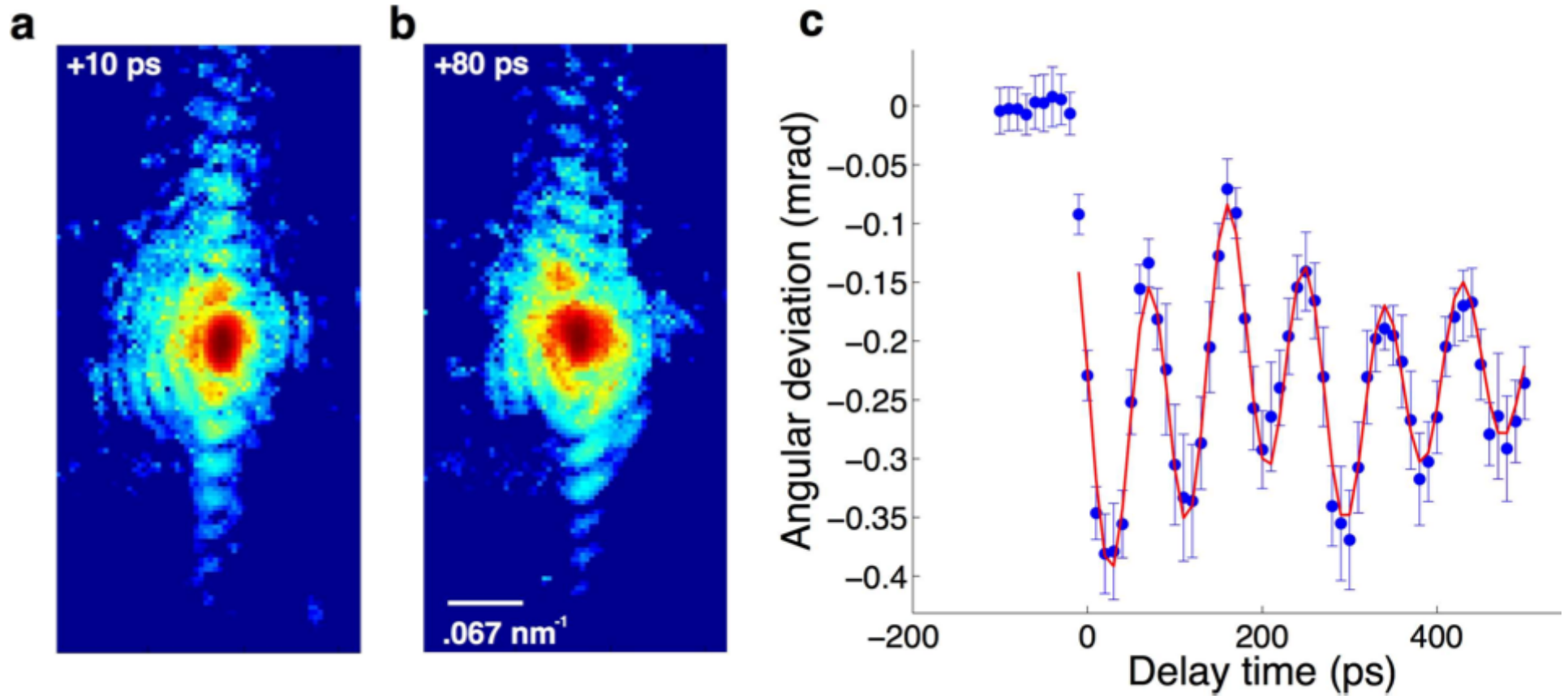


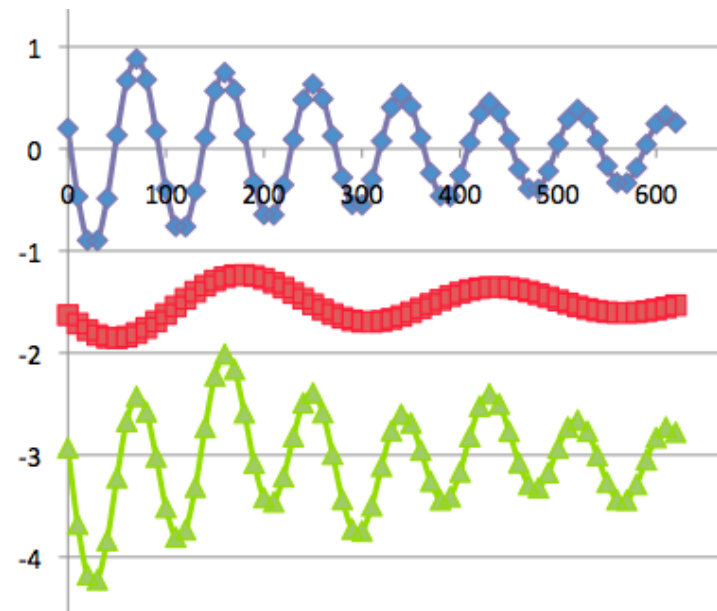
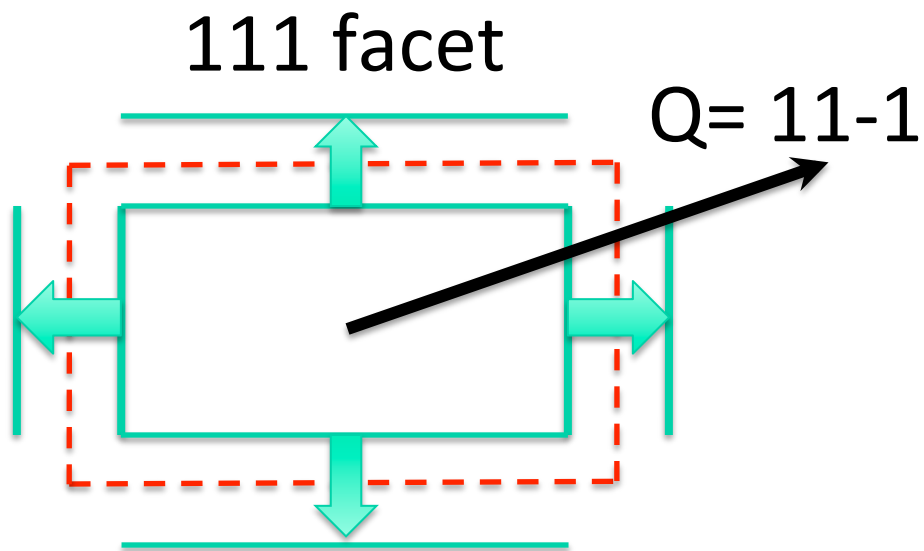
Fig. 2. Comparison of the change in electron temperature at the front surface of an 80-nm gold film irradiated by a 2.8 mJ/cm<sup>2</sup>, 800 nm, 150-fs laser pulse.

# Time resolved Bragg peak position



# Two Normal Modes of Vibration

$$S(\tau) = \sum_{n=1}^N A_n \exp[-(\tau/\tau_{d,n})^2] \cos(\omega_n \tau + \varphi_{0,n})$$

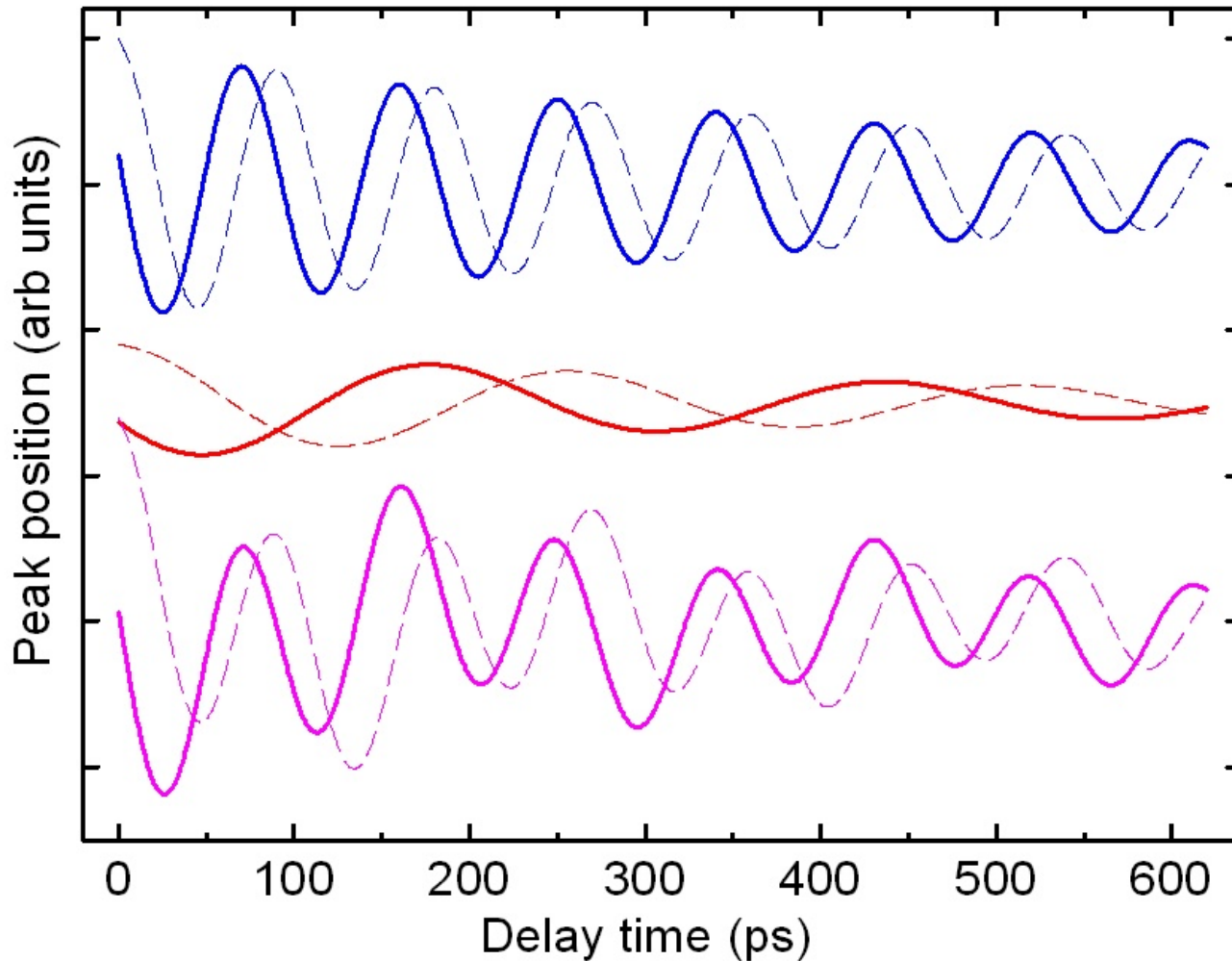


$$T_1 = 90\text{ps} \quad h_1 = 145\text{nm} \quad c_S = 3240\text{ m/s}$$

$$T_2 = 259\text{ps} \quad h_2 = 420\text{nm}$$

# Phase Origin of Vibrations

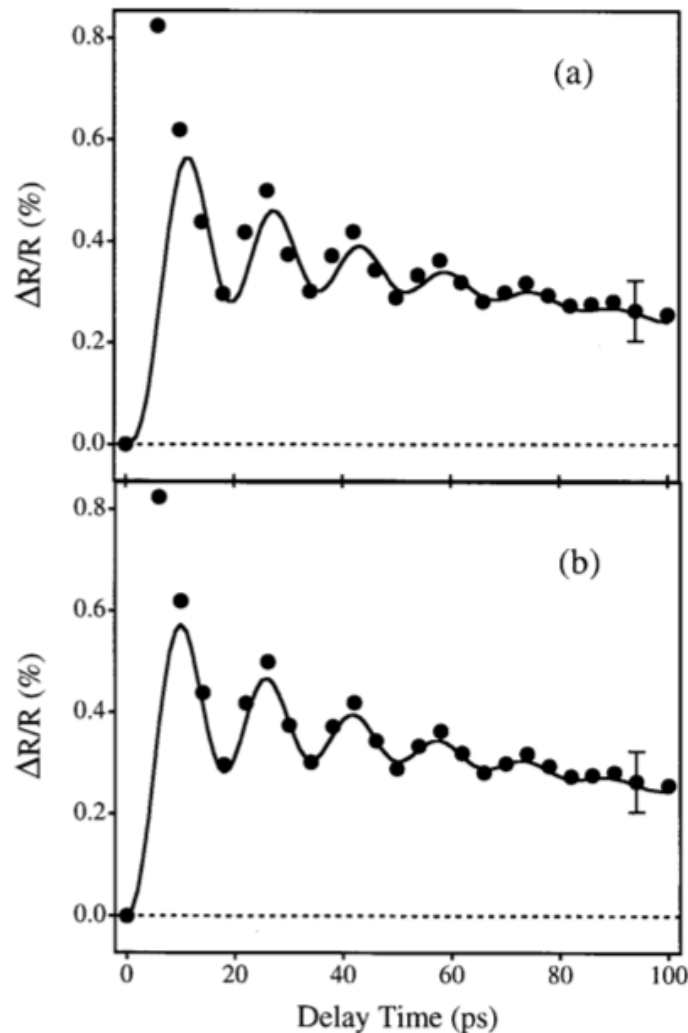
I.K. Robinson et al. Journal of Optics **18** 054007 (2016)



# Ultrafast Absorption Spectroscopy

24nm Au nanoparticles in H<sub>2</sub>O, converted to radius

G. V. Hartland, J. Chem. Phys. **116** 8048 (2002)

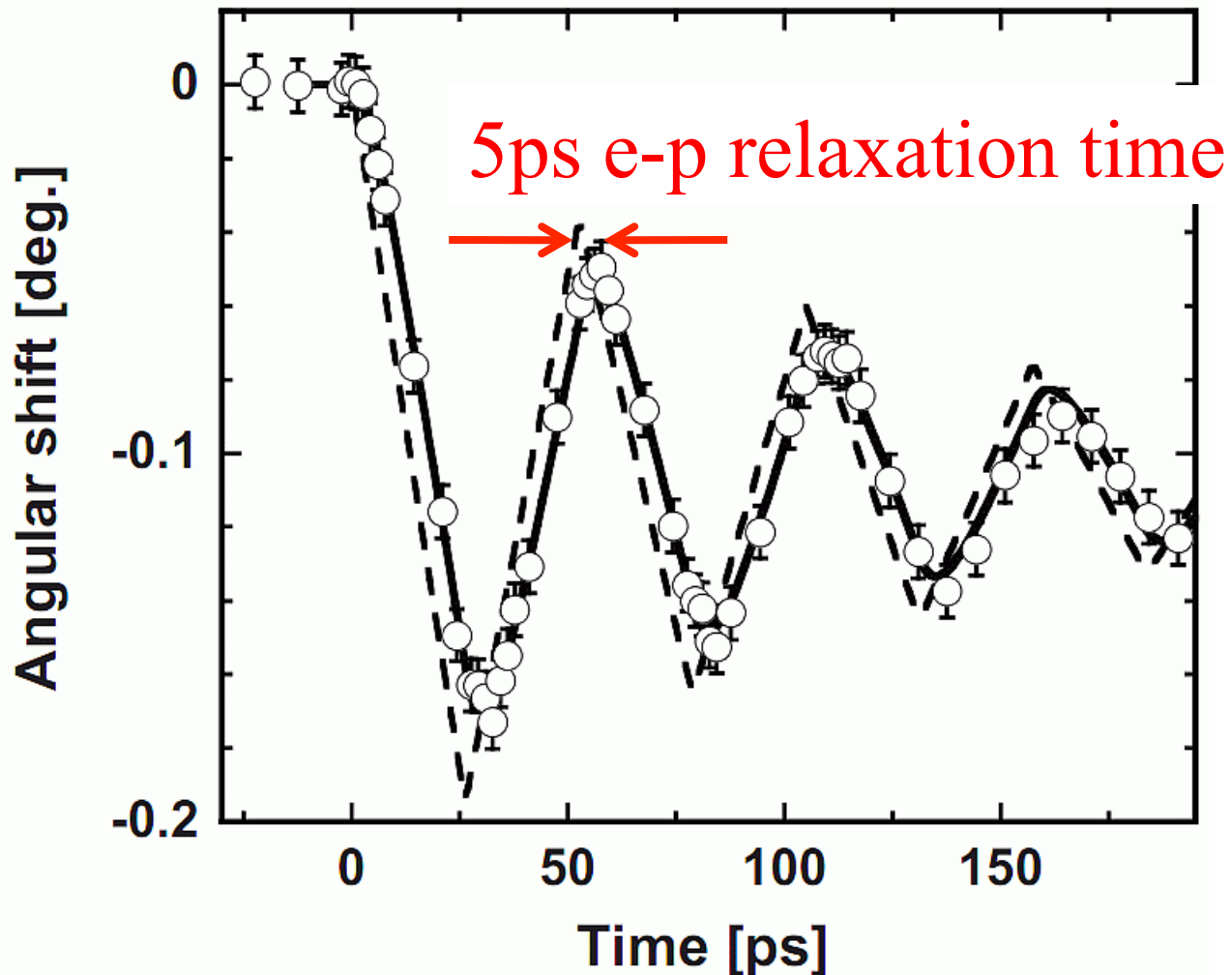


(a) Simple normal mode analysis with impulse heating.

(b) Corrected by adding 2T model and electronic contribution to thermal expansion coefficient.

# Plasma Source on 90nm Au film

M. Nicoul et al, APL 98 191902 (2011)

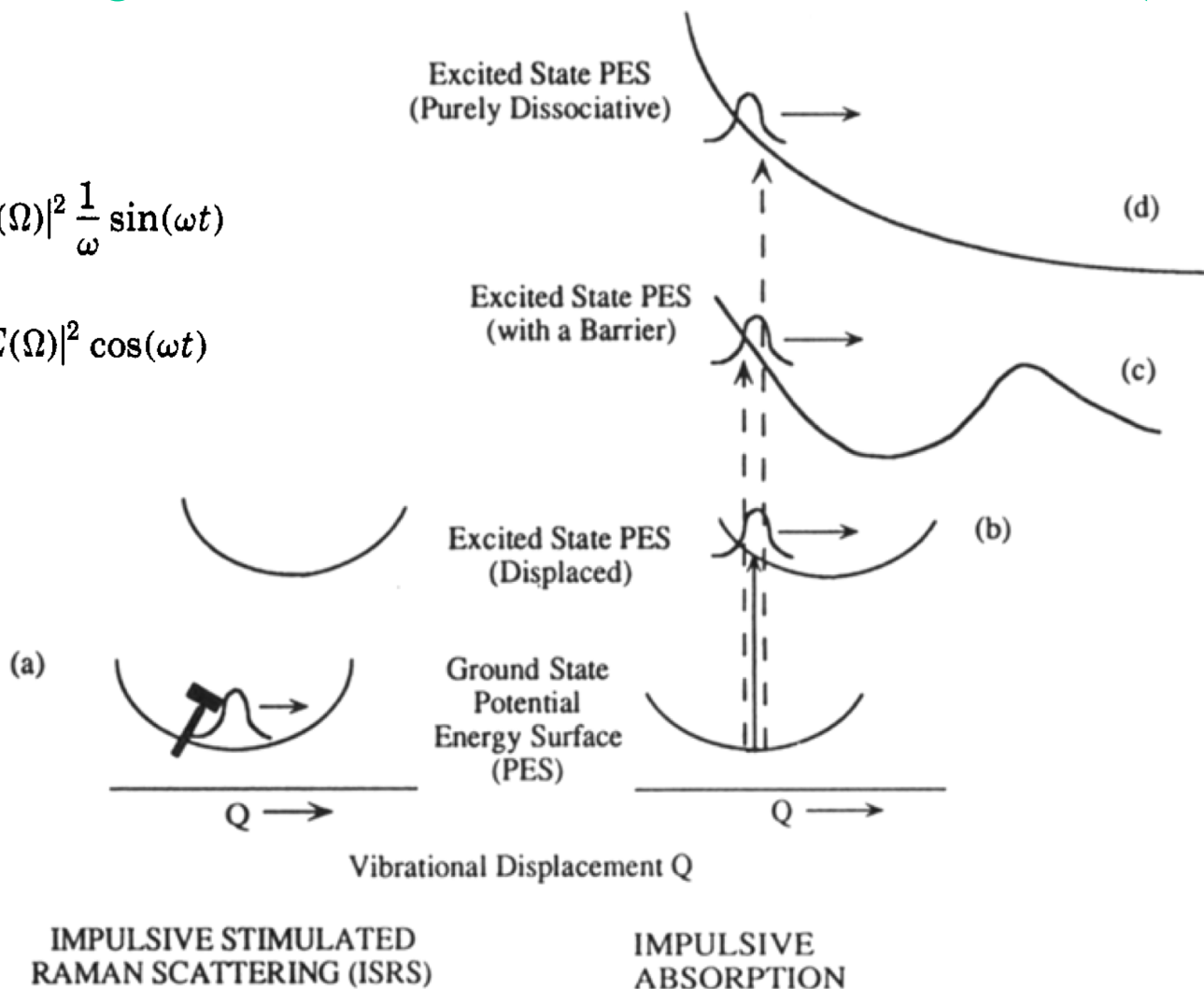


# Impulsive Stimulated Raman Scattering (ISRS)

L. Dhar, J. A. Rogers, and K. A. Nelson, Chem Rev 94 197 (1994)

$$\langle Q(t) \rangle_{\text{exact}} = T \left( \frac{\partial \alpha}{\partial q} \right) |E(\Omega)|^2 \frac{1}{\omega} \sin(\omega t)$$

$$\langle P(t) \rangle_{\text{exact}} = T \left( \frac{\partial \alpha}{\partial q} \right) |E(\Omega)|^2 \cos(\omega t)$$

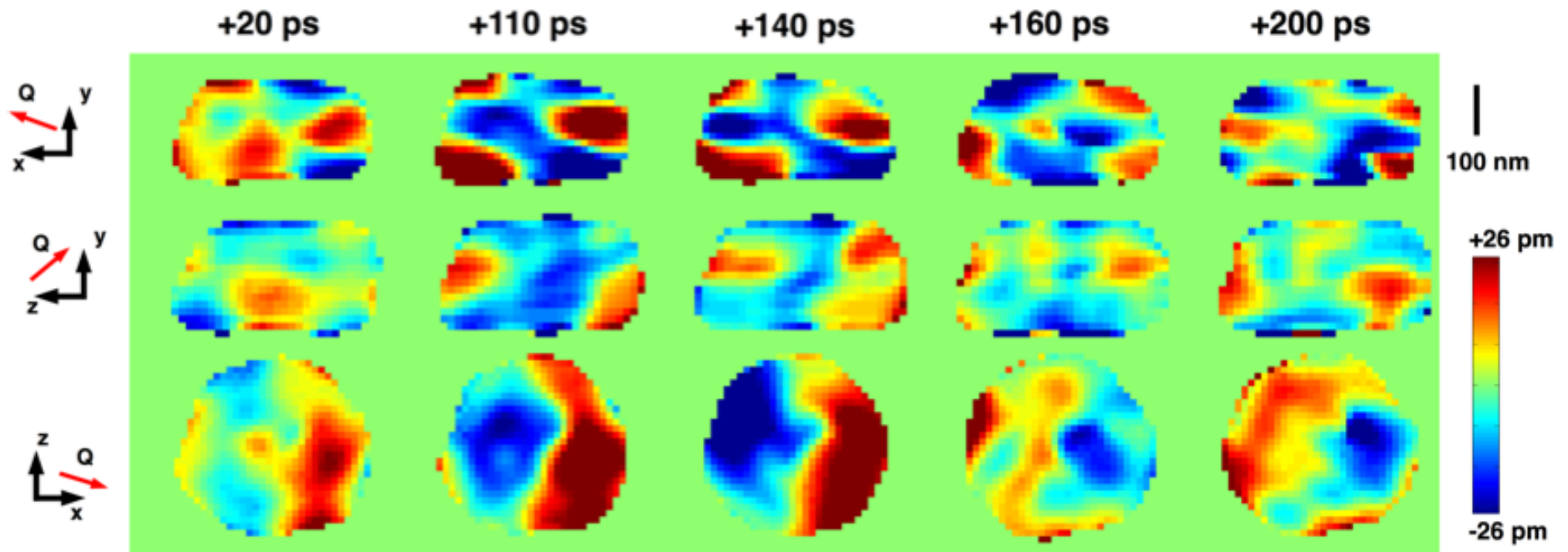


# Dynamic imaging of displacements

CDI inversion of 3D diffraction patterns

1000 frames averaged at each point of rocking curve

Jesse Clark et al, Science **341** 56 (2013)

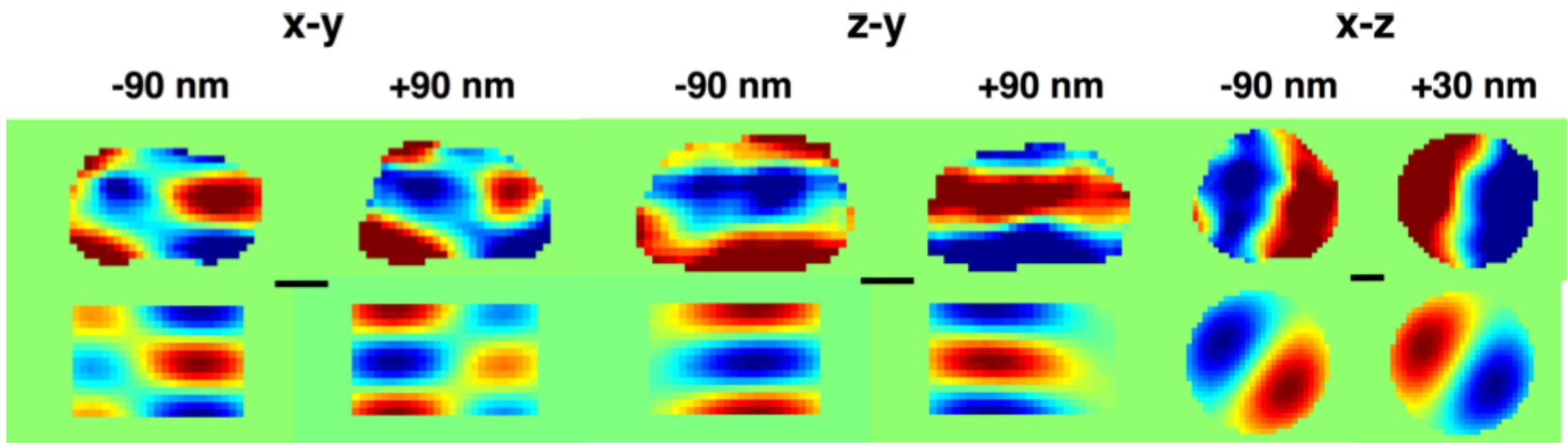


# Dynamic imaging of displacements

CDI inversion of 3D diffraction patterns

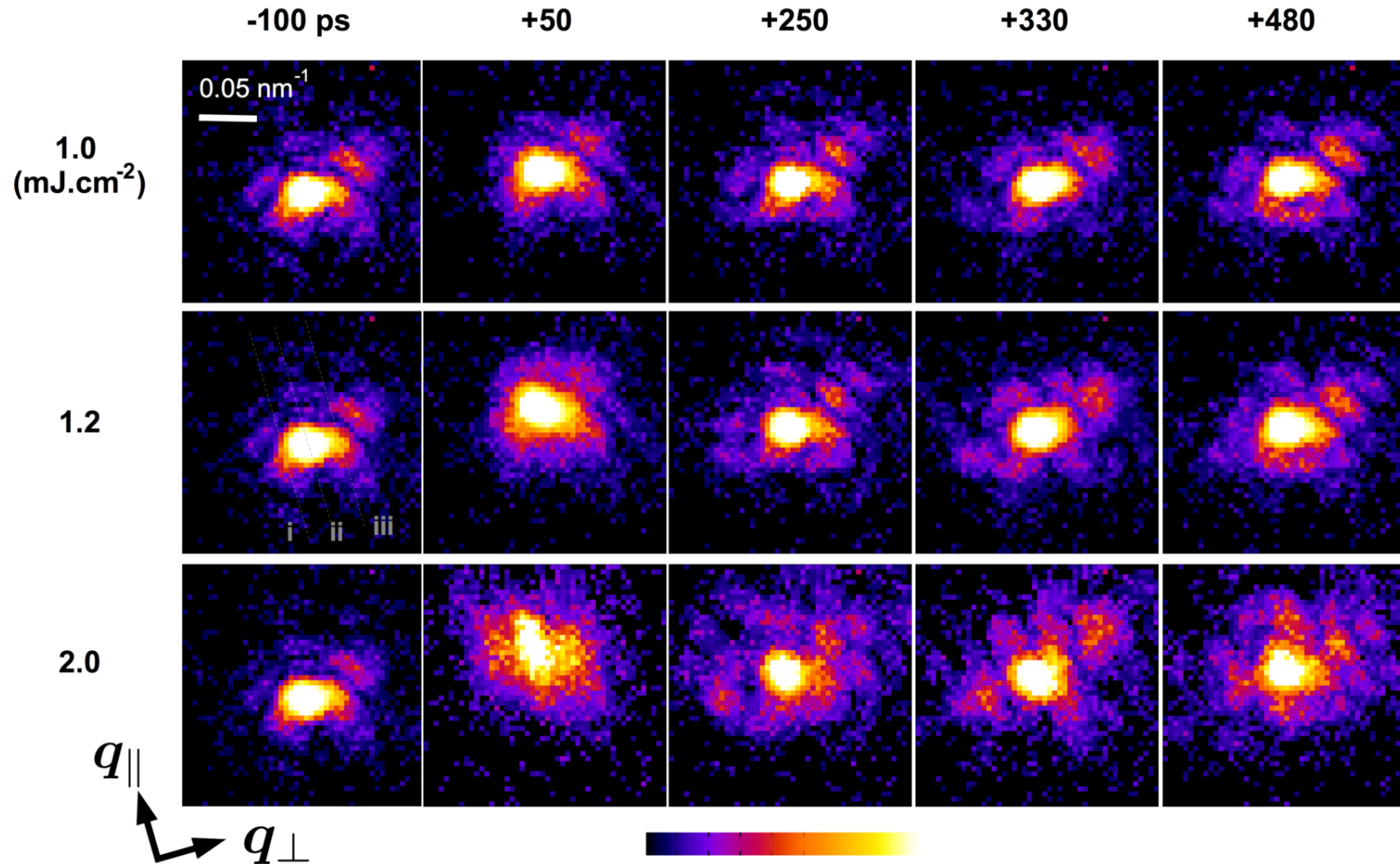
Comparison with (1,1) normal mode of cylinder

Jesse Clark et al, Science **341** 56 (2013)



# Dependence on Laser Fluence

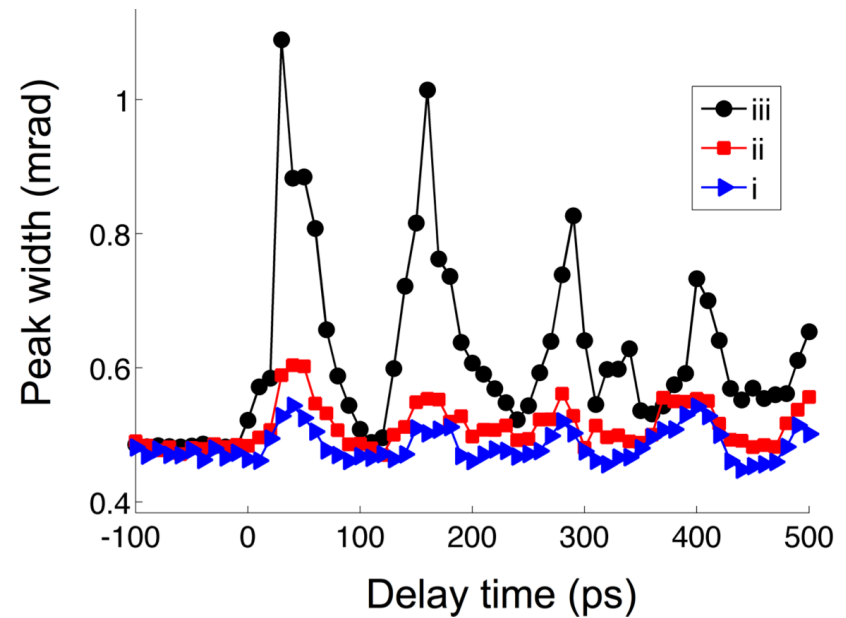
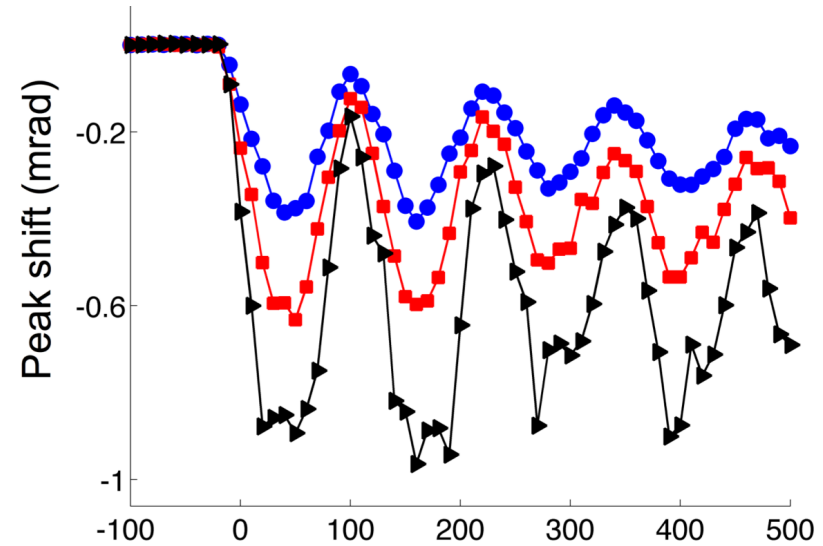
Jesse Clark et al, PNAS 112 7444 (2015)



# Dependence on Laser Fluence

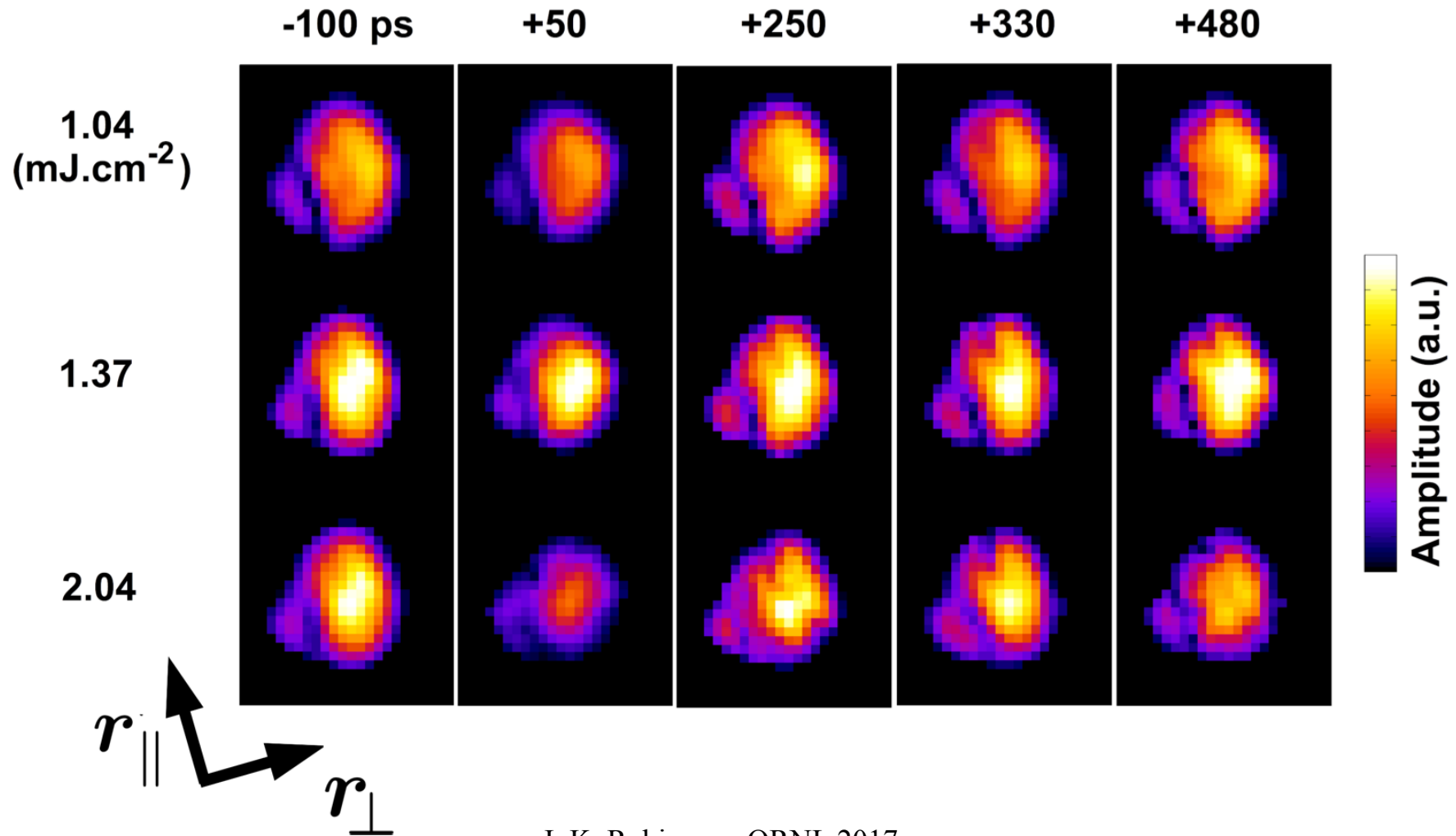
Jesse Clark et al, PNAS  
112 7444 (2015)

1.0 mJ cm<sup>-2</sup>  
1.4 mJ cm<sup>-2</sup>  
2.0 mJ cm<sup>-2</sup>



# Dependence on Laser Fluence

Jesse Clark et al, PNAS 112 7444 (2015)



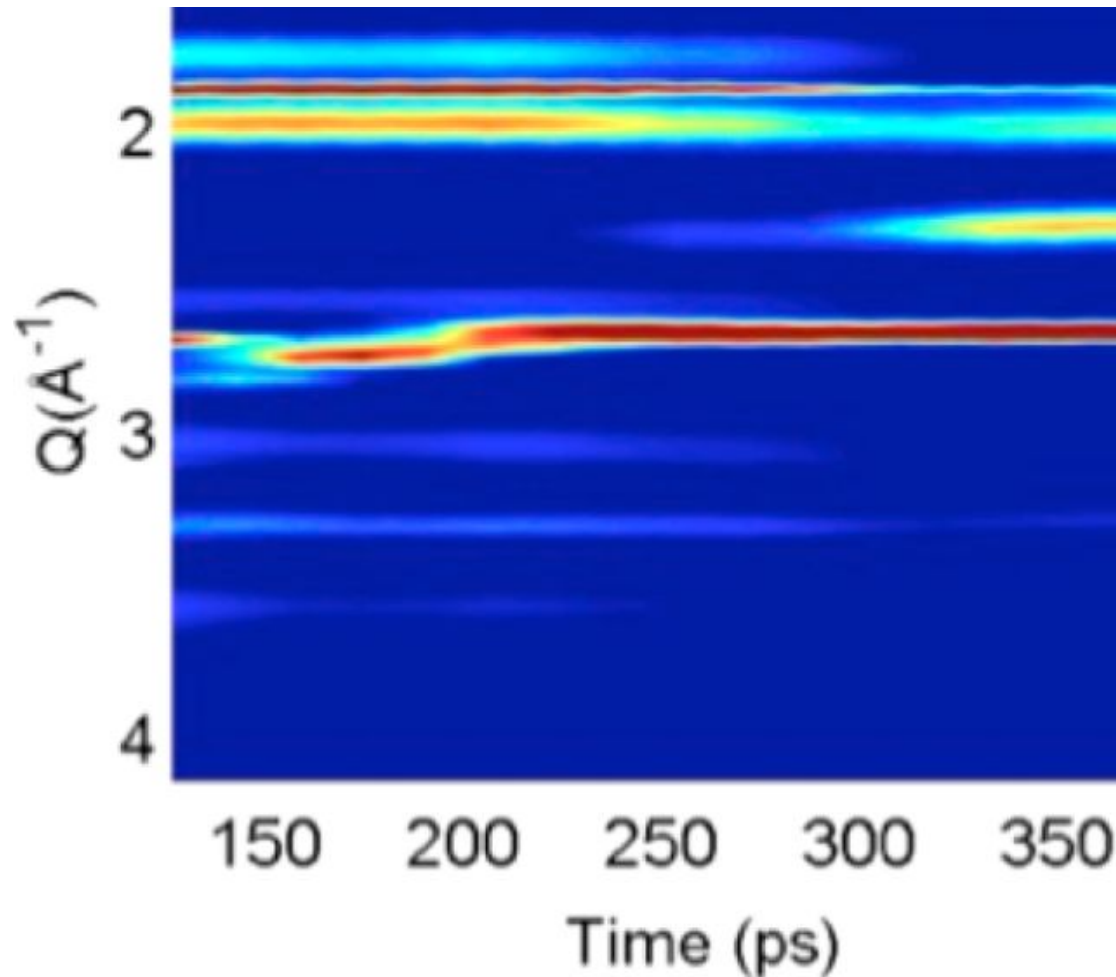
# Materials Science using XFELs

- Synthesize samples in nanoparticle format
- Nanoparticle array scanned through beam
- Pump-Probe has two state variables
  - Optical fluence = sample temperature
  - Delay time after ‘instantaneous’ heating
- Laser “pump” pulse to create new states
- Explore transient phase diagrams

# Laser induced transformation of CdS

Hexagonal-to-cubic phase transformation

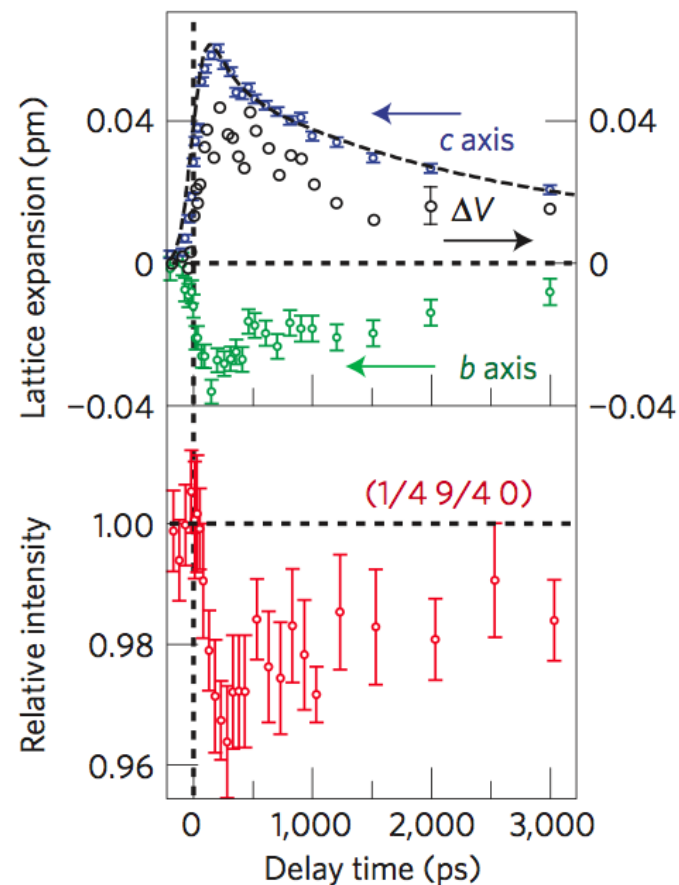
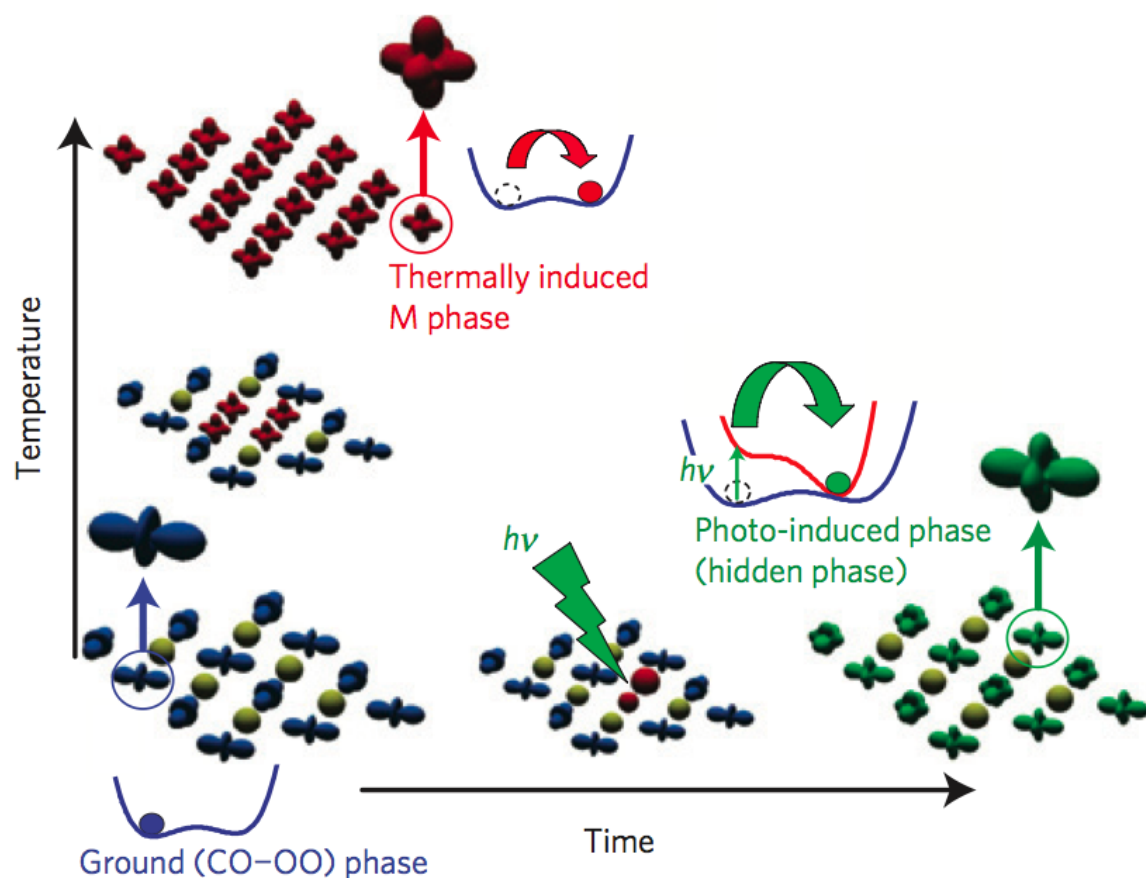
J. Wittenberg...A. Lindenberg, Nano Lett. 14 1995 (2014)



# Transient “Hidden” Phase in Manganite

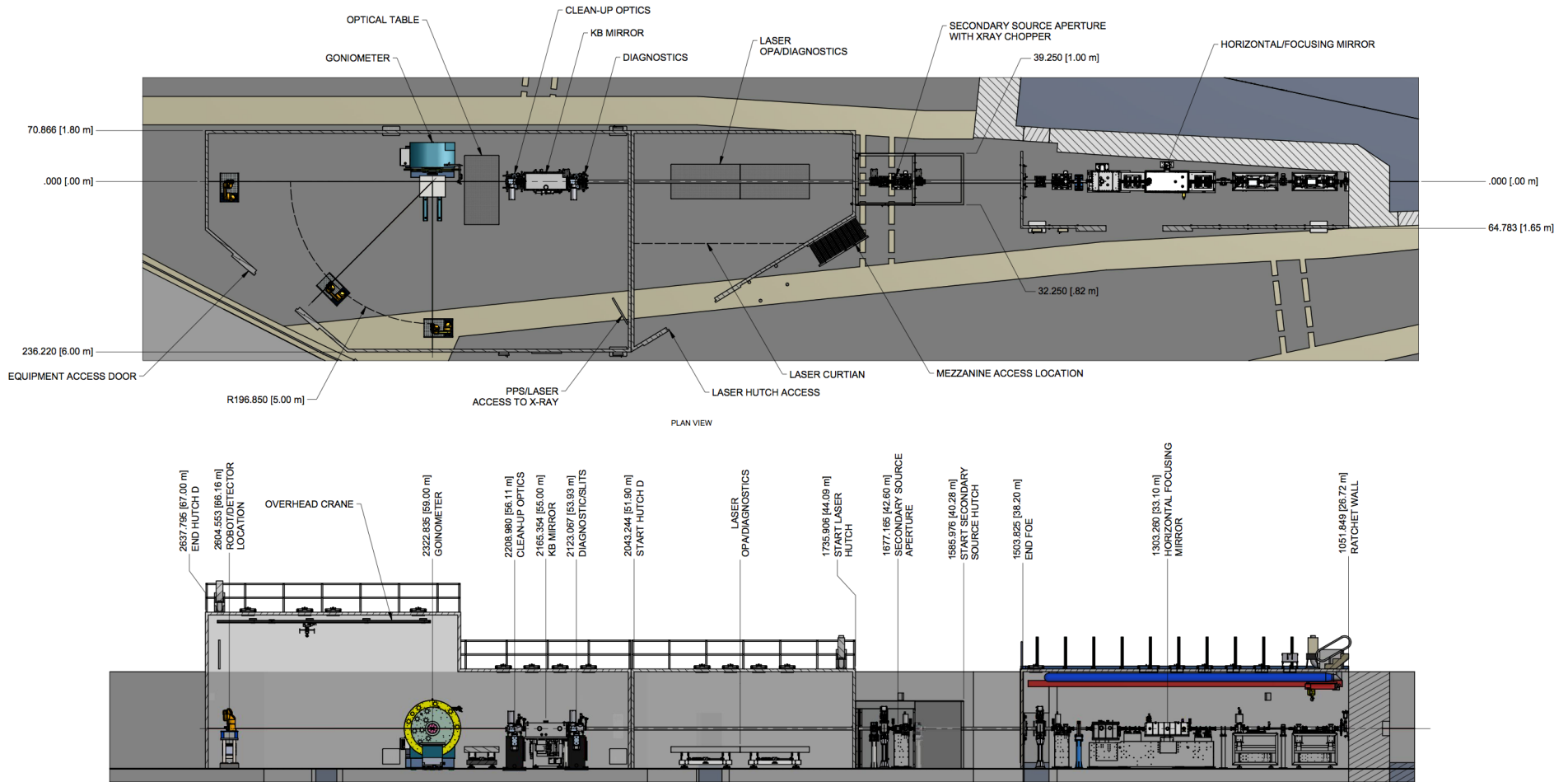
Hirohiko Ichikawa et al, Nature Materials **10** 101 (2011)

$\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  (NSMO) film on STO

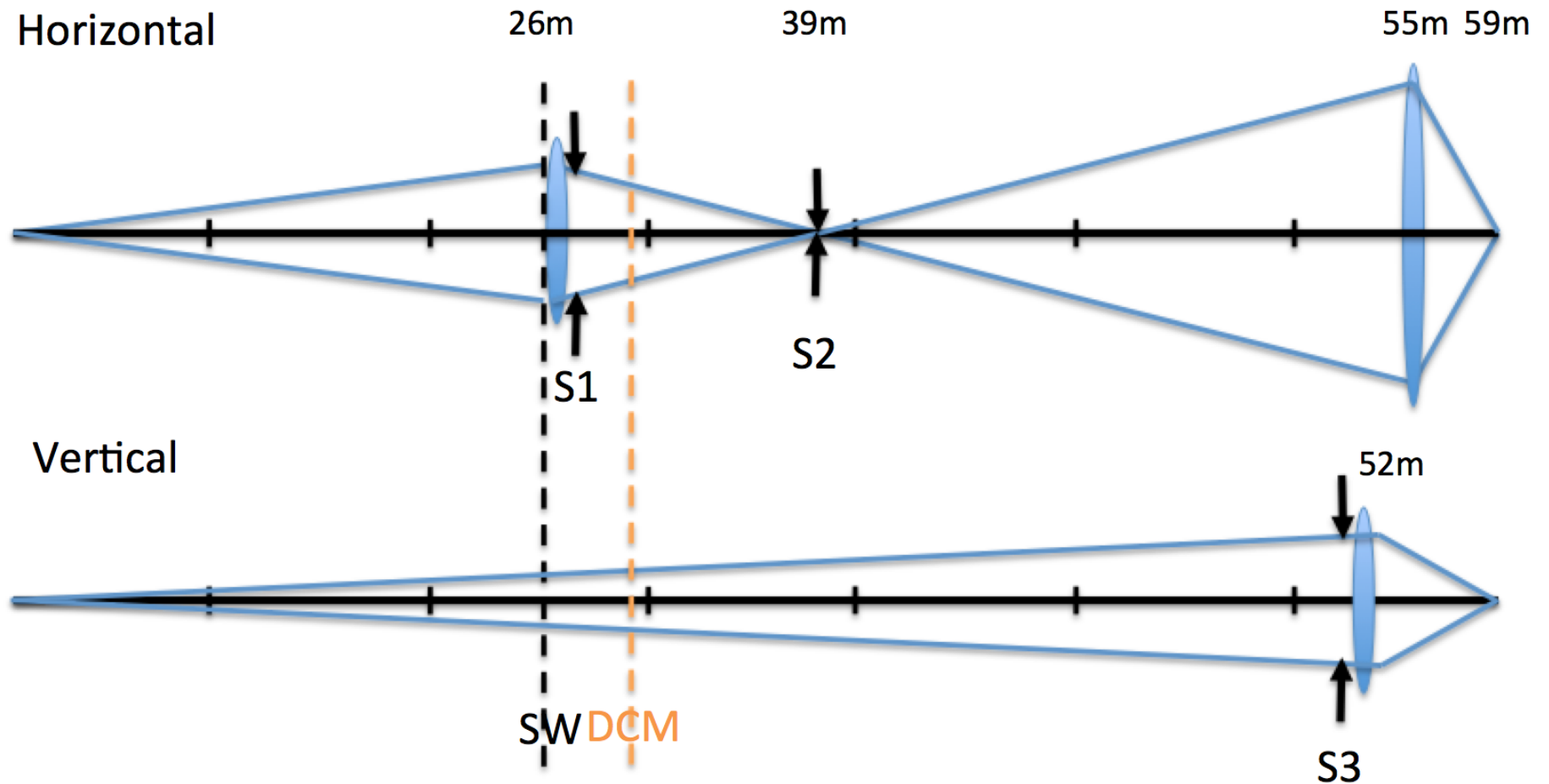


# BCDI beamline at NSLS-II

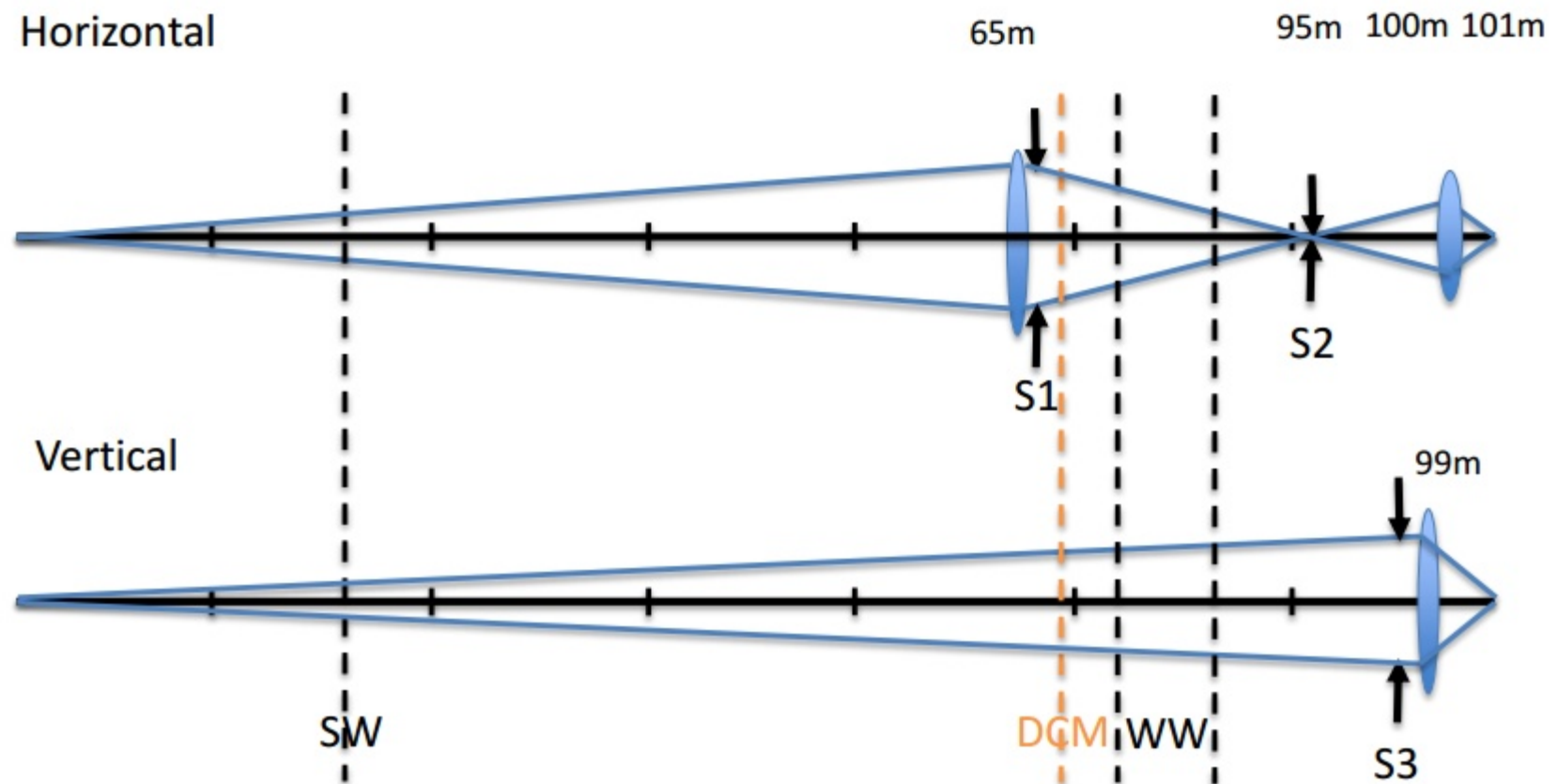
## Garth Williams and BDTeam



# “Short” optical layout

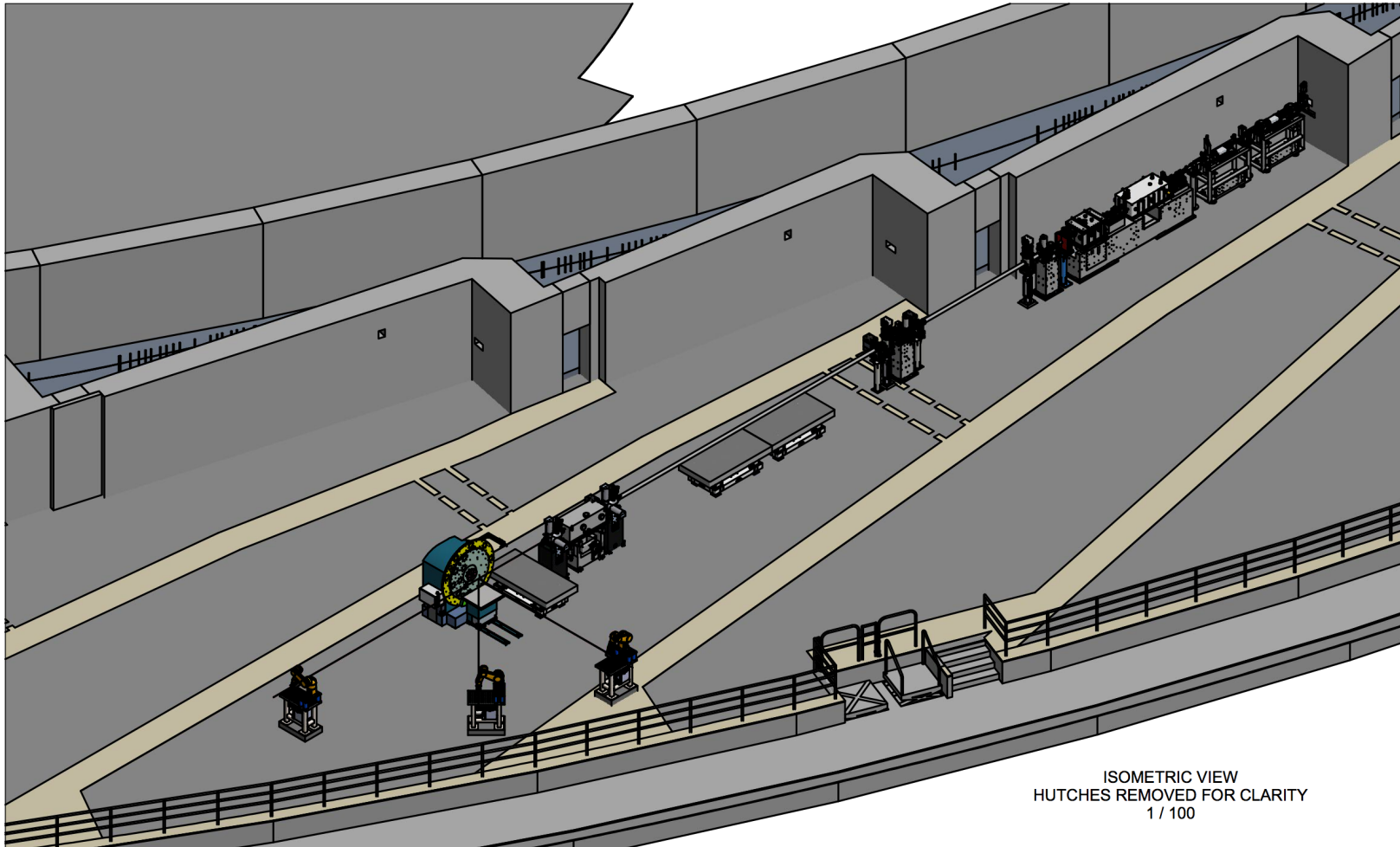


# “Long” optical layout



# BCDI beamline at NSLS-II

## Garth Williams and BDTeam



# Performance of BCDI beamline

- Full coherent flux of NSLS-II
- Si(111) monochromator ( $6 < E < 15 \text{ keV}$ )
- U20 in-vacuum undulator
- low-beta straight section, possibly long
- $1 \mu\text{m}$  to  $7 \mu\text{m}$  diameter coherent spot
- Separate laser hutch for co-localized focus
- Timing experiments as a “standard” option

# Bragg Coherent Diffraction Imaging

- Complex density can image strain
- Strain associated with nano-shape
- In-situ crystal growth of calcite
- Phase domains in  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$
- Ultrafast snapshots of vibrations
- Transient melting of nanoparticles
- New BCDI beamline at NSLS-II