In Situ and *Operando* Studies of Thin-Film Epitaxy using X Rays

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Outline

- CIGS Solar Cell
- Importance of structural properties
- How to measure
  1. Material properties
  2. Film thickness
  3. Growth mode
  4. Surface morphology
  5. Valence Band
  6. 3D structure

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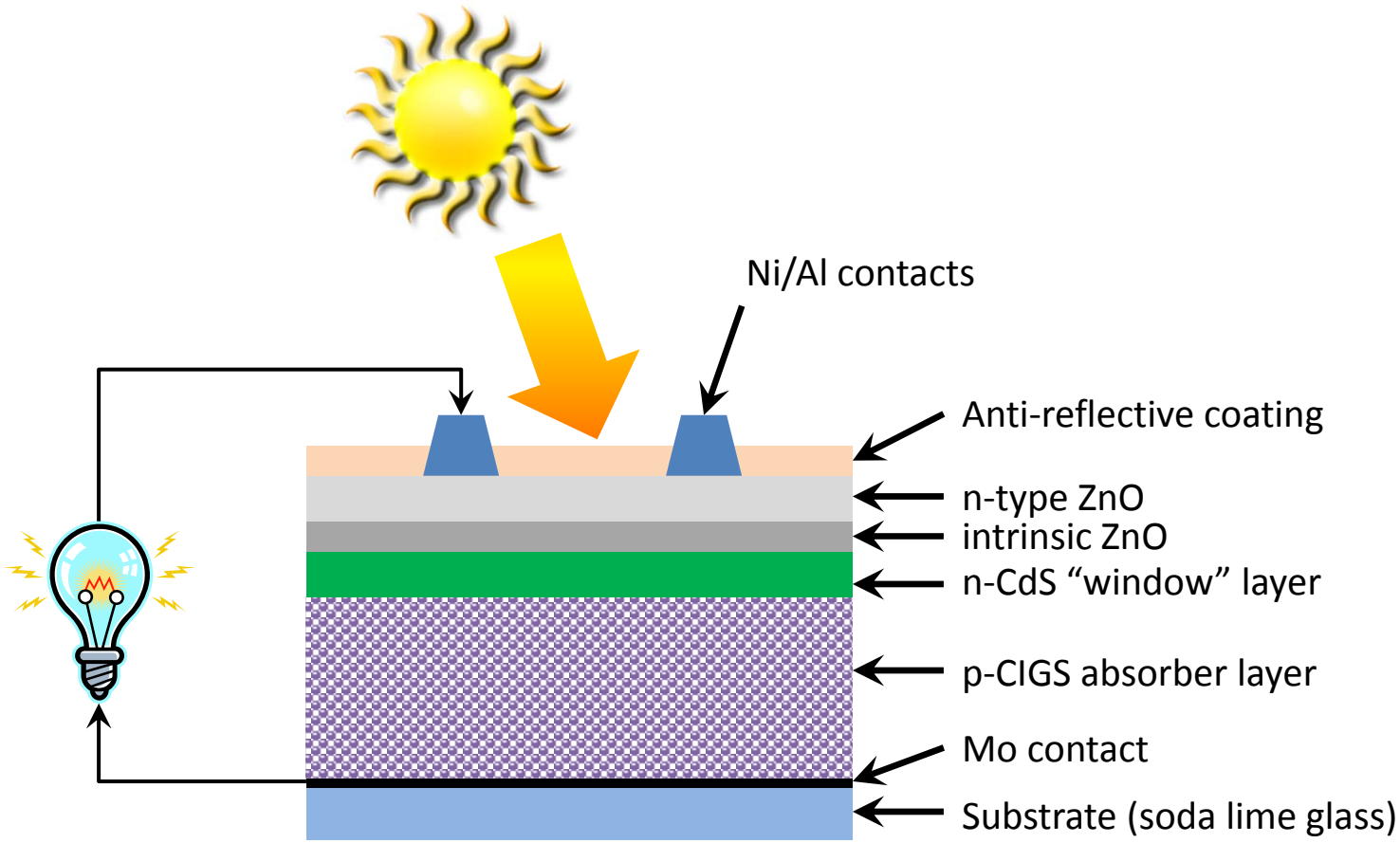
The $Cu(In,Ga)S_2$ Solar Cell



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It's Complicated

- Lots of layers
- Lots of interfaces
- Lots of structure

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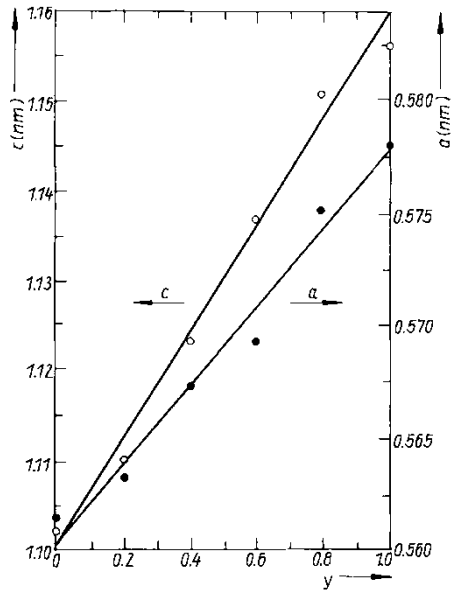
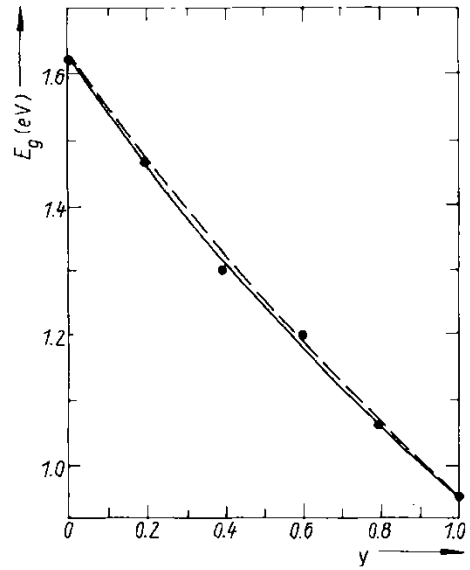
Variation of CIGS properties with composition



Variation of lattice constant as a function of composition for $CuIn_yGa_{1-y}Se_2$ alloys.

T. Tinoco, et al, Physica Status Solidi (a) **124** (2), 427-434 (1991).



Variation of the energy gap as a function of composition for $CuIn_yGa_{1-y}Se_2$ alloys.

T. Tinoco, et al, Physica Status Solidi (a) **124** (2), 427-434 (1991).

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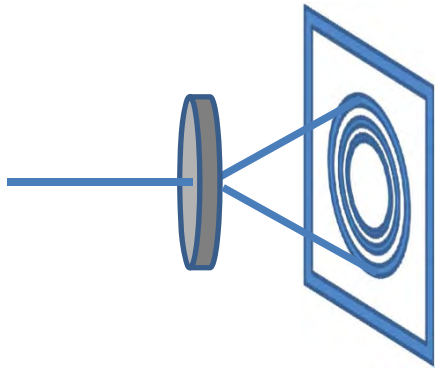
Powder Diffraction

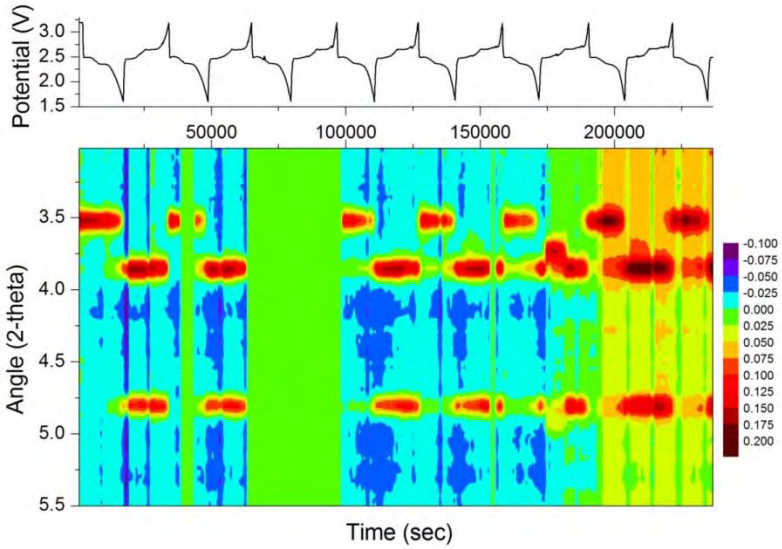
Energy Materials: Organic Electrodes for Batteries

Requires: High Energy, Small beams, Flux (Abruña)



- Organic anode material
  - Dicyanoanthraquinone
- Apply organic chemistry synthesis to a battery component
- Voltage-induced Phase Change

K. Silberstein



***Operando* x-ray powder diffraction**

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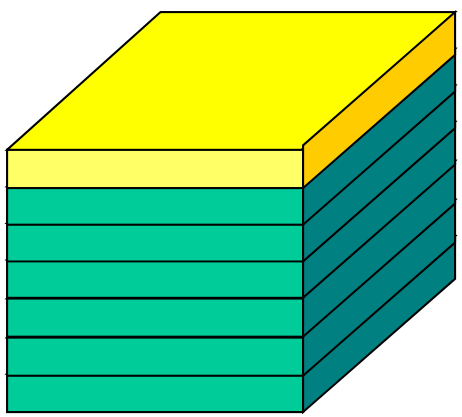
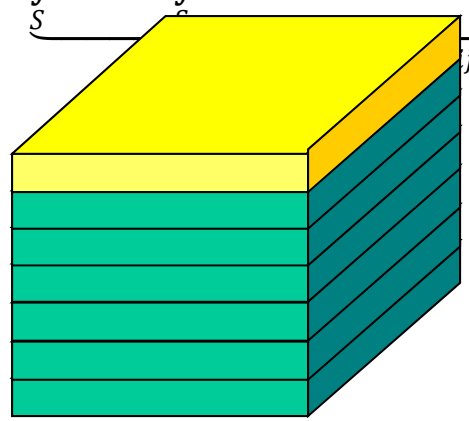
Kinematic Scattering Theory

$$\rho_s(\vec{r}) = \bar{\rho}_s + \delta\rho_s(\vec{r})$$

$$\frac{d\sigma}{d\Omega} = r_e^2 \left\{ \underbrace{\left| F_{substr}(\vec{q}) \frac{2}{1-e^{-i(\vec{q}\cdot\hat{n})d}} \int_S d^3\vec{r}_\parallel \int_{S_{\infty}} d^3\vec{r}_\perp \, \rho_m(\vec{r}_1)\rho(\vec{r}_2) \right|^2}_{Specular\ \ Reflectivity\ \ \&\ CTRs} + \underbrace{\int_S d^2\vec{r}_{\parallel_1} \int_S d^2\vec{r}_{\parallel_2} \, e^{i\vec{q}\cdot(\vec{r}_{\parallel_1}-\vec{r}_{\parallel_2})} \langle \delta\rho_s(\vec{r}_{\parallel_1})\delta\rho_s(\vec{r}_{\parallel_2})\rangle}_{Diffuse} \right\}$$





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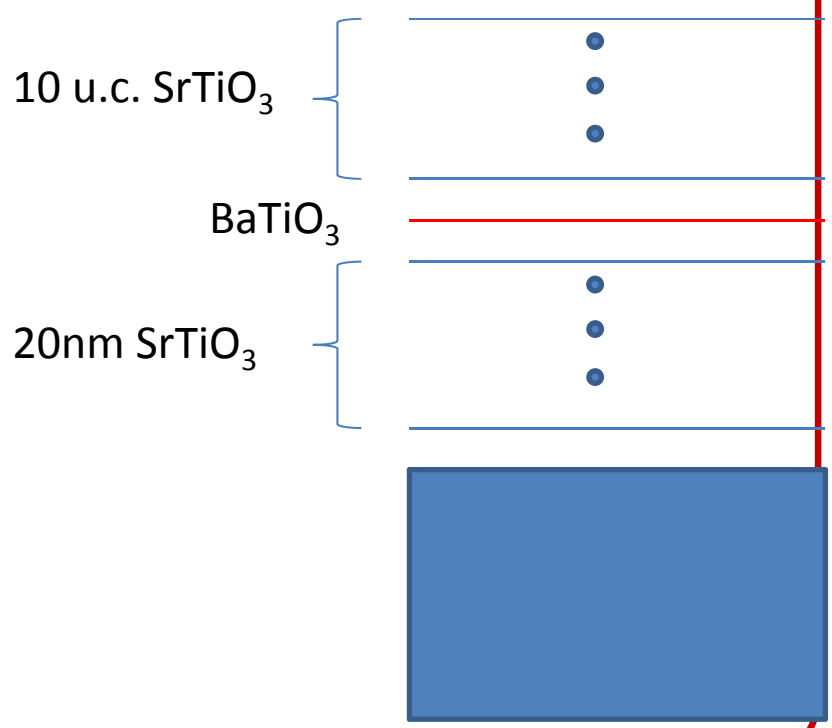
Compared with experimental result

- Sample used in 2013 December beamrun

1. Co-deposition
2. After the growth, we have HF etching and oxygen annealing and vacuum annealing, in order to get the double layer TiO2 termination

The structure of sample:



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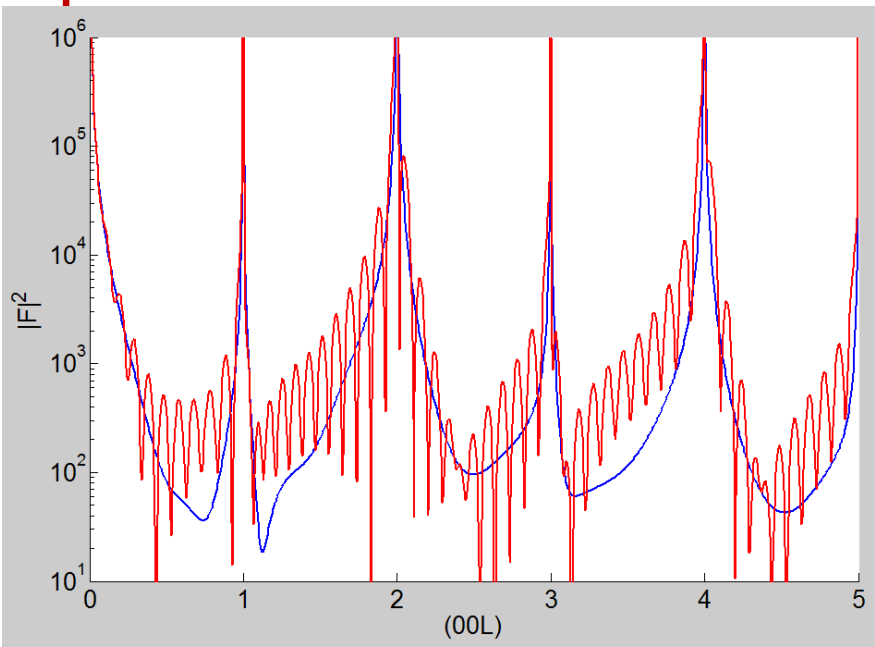
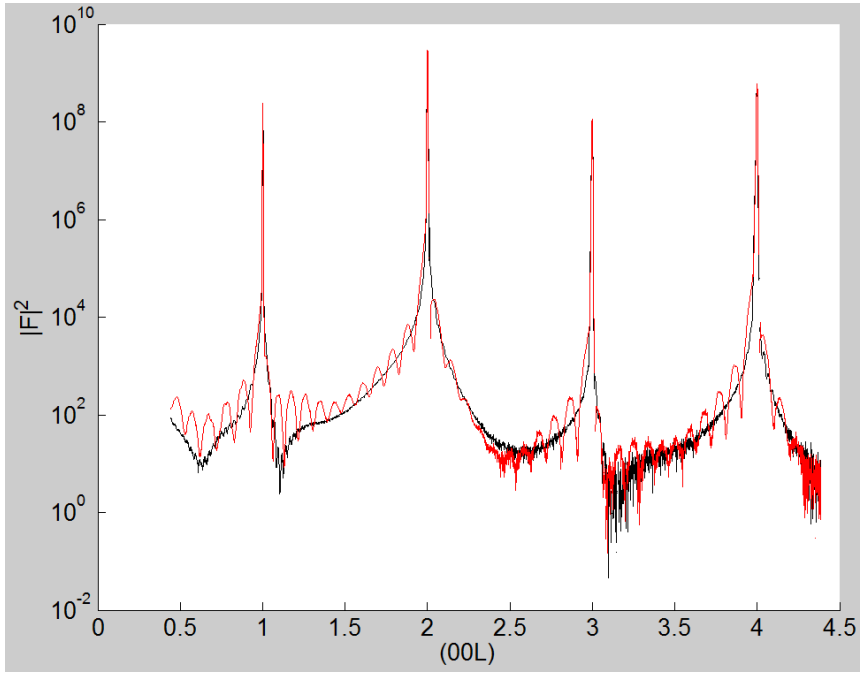
Compared with experimental result

- Data from 2013 December





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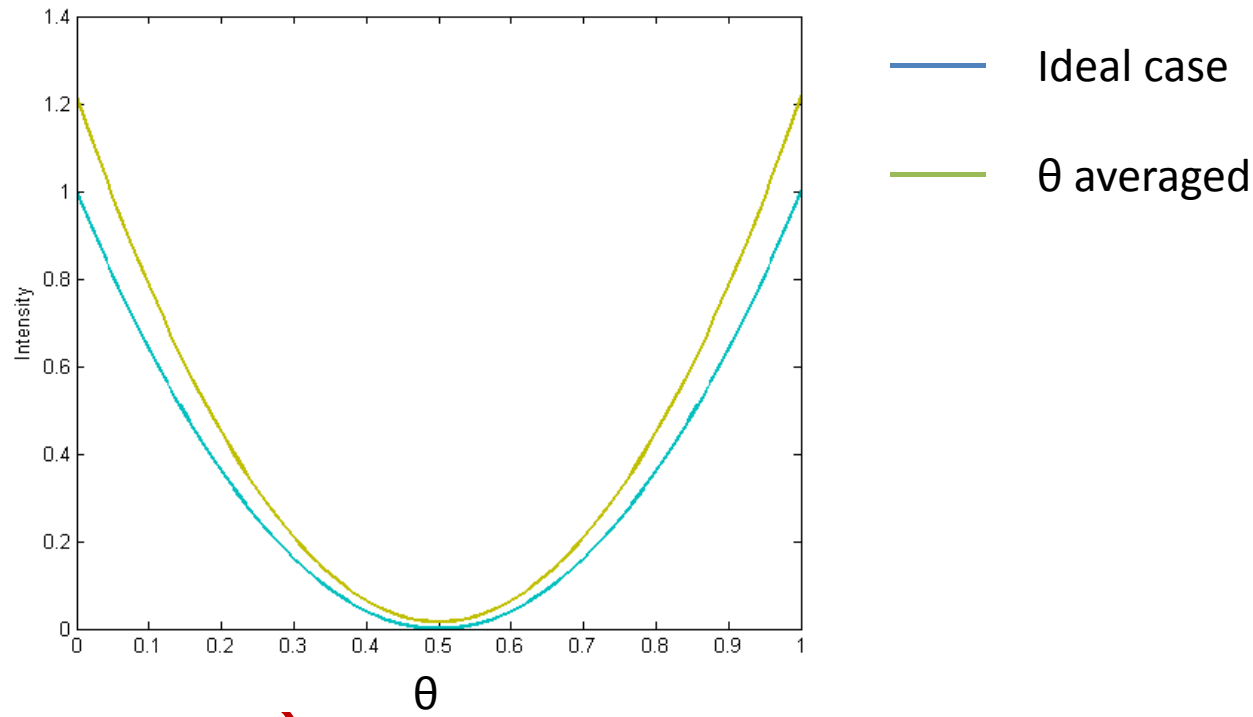
Simple Layer-by-layer XRR

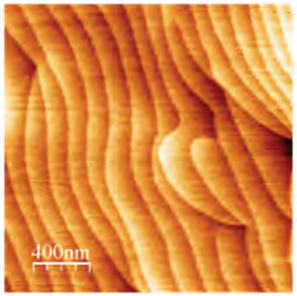
$$A(q) = \sum_{n=-\infty}^{0} e^{-inqd} + \theta e^{-iqd} \rightarrow I\left(\theta: q = \frac{1}{2}\left(\frac{2\pi}{d}\right)\right) \propto (1-2\theta)^2$$

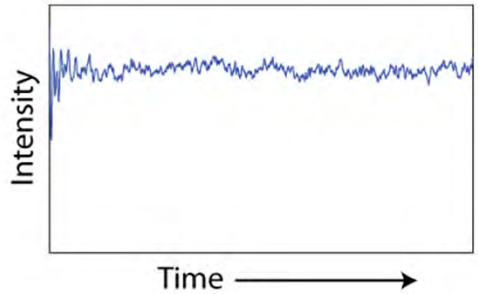
Add some averaging due to θ(x).



Thin Film Growth Modes

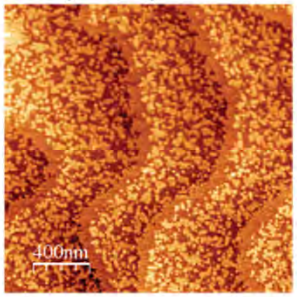
Step Flow Growth

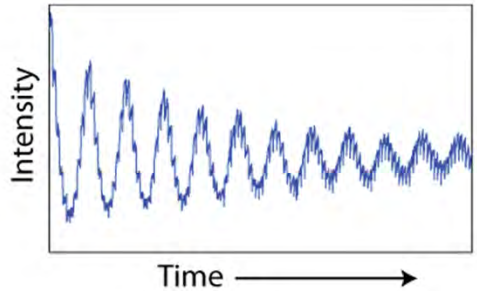




- Adatoms land on Surface and diffuse directly to a step edge.
- Constant Surface Roughness

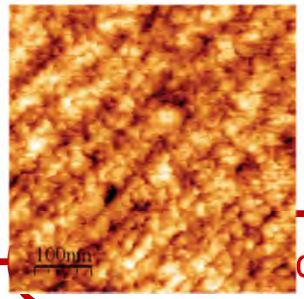
Layer By Layer Growth

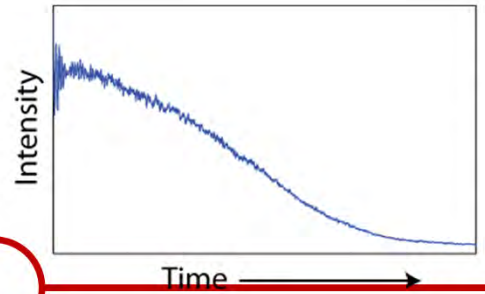




- Islands nucleate on the surface, coarsen, and coalelece, followed by monolayer completion.
- Roughenss oscillates with a period of 1 monolayer.

3D Island Growth





- Islands nucleate on top of existing islands.
- Surface roughens with every laser pulse.

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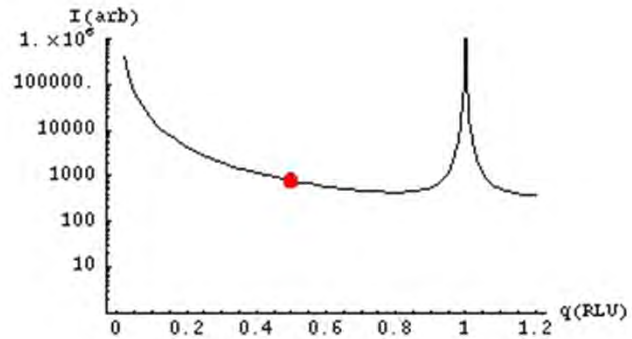
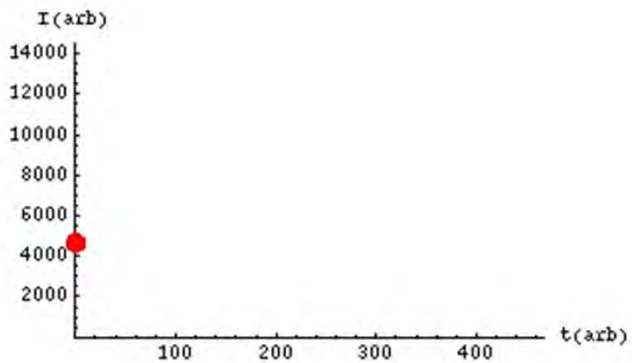
Time-Dependent Specular Reflectivity

Layer-by-layer growth of $La_{0.7}Sr_{0.3}MnO_3$ on $SrTiO_3$

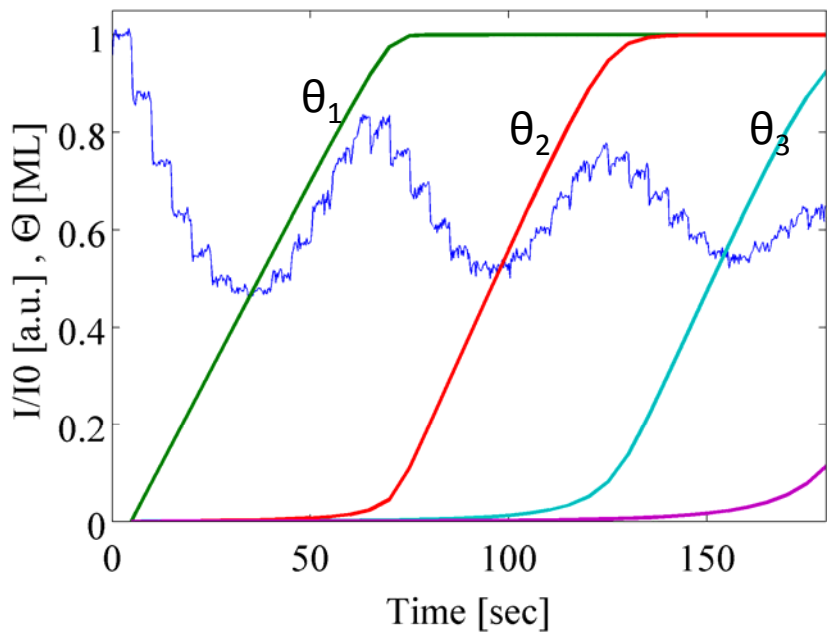
- Periodic changes in step-edge density
- Electron density contrast between film and substrate results in Keissig fringes
- Oscillations in anti-Bragg intensity due to roughness and Keissig fringes
- M monolayers yield M maxima in the anti-Bragg I vs. t data





Layer by Layer Growth: X-Ray Reflectivity

$$I(\vec{q}) = \left| F_{sub}(\vec{q}) \frac{1}{1 - e^{i(\vec{q}\cdot\hat{n})d}} + F_{film}(\vec{q}) \sum_{m=1}^{\infty} \theta_m(t) e^{-i(\vec{q}\cdot\hat{n})md} \right|^2$$



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(Time-resolved) X-Ray Reflectivity

- Measures average electron density as a function of height
- Very sensitive to single unit cell high step roughness at “anti-Bragg” position.
- Able to measure inter-plane transport.
- No information about in-plane structure or transport.

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While specular reflectivity and crystal truncation rod scattering is very powerful and has been successfully used to solve a variety of surface and interface crystal structures, it is subtly related to the surface morphology.

To gain access to in-plane structure of surfaces and interfaces, we can utilize the surface diffuse scattering.

(time-resolved) Diffuse Scattering

$$\frac{d\sigma}{d\Omega} = r_e^2 \left\{ \underbrace{\left| F_{substr}(\vec{q}) \frac{1}{1 - e^{-i(\vec{q}\cdot\hat{n})d}} + F_{film}(\vec{q}) \sum_{m=1}^{\infty} \theta_m(t) e^{i(\vec{q}\cdot\hat{n})md} \right|^2}_{Specular\ \ Reflectivity\ \ \&\ CTRs} + \underbrace{\int_S d^2\vec{r}_{\parallel_1} \int_S d^2\vec{r}_{\parallel_2}\, e^{i\vec{q}\cdot(\vec{r}_{\parallel_1} - \vec{r}_{\parallel_2})} \langle \delta\rho_s(\vec{r}_{\parallel_1}) \delta\rho_s(\vec{r}_{\parallel_2}) \rangle}_{Surface\ \ Diffuse} \right\}$$

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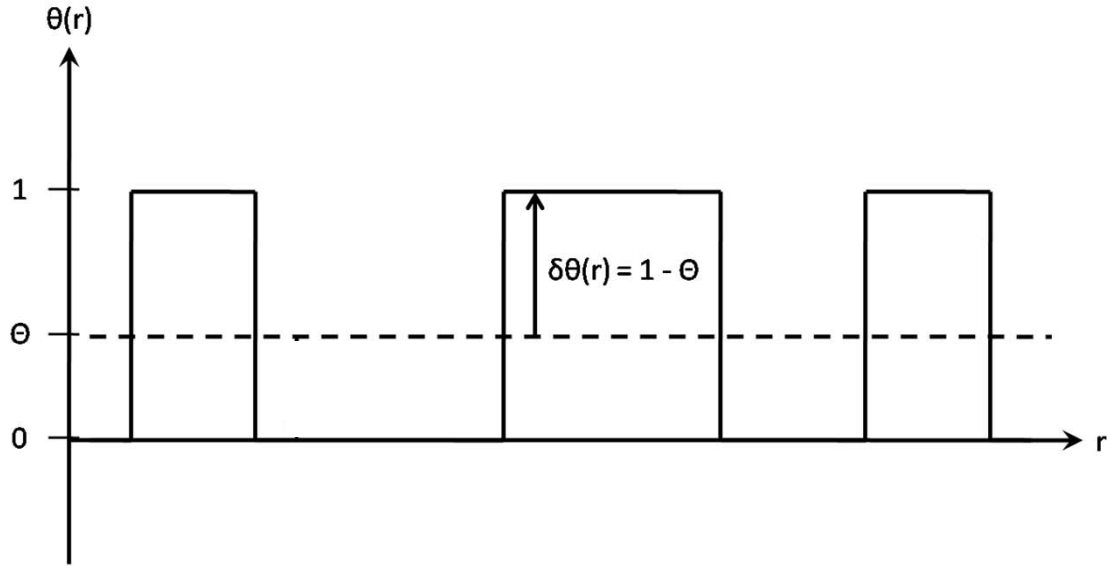
Note: Surface scattering is from fluctuations about average surface density.



As deposition occurs, amplitude of fluctuations varies as (1-θ).

Therefore, structure factor of the average island $\langle f \rangle^2$ has a $(1-\theta)^2$ dependence.

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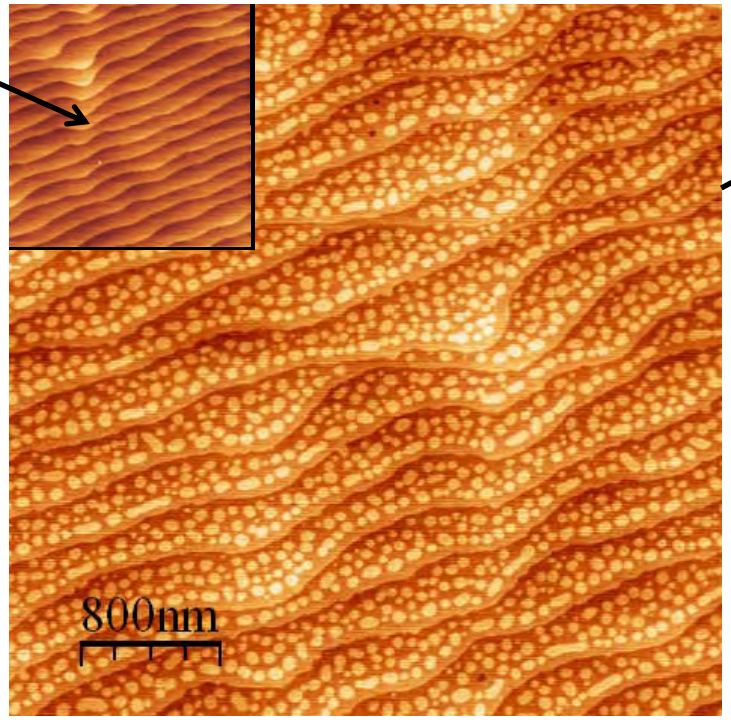
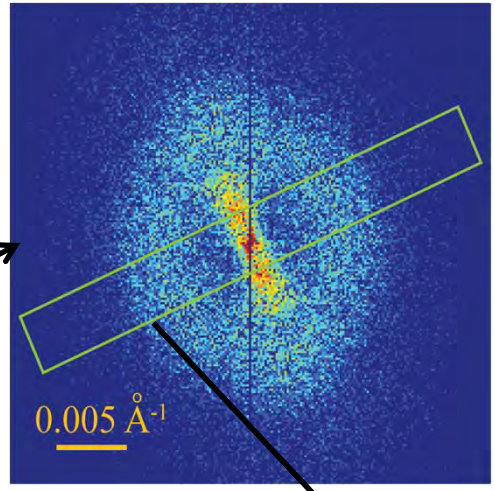
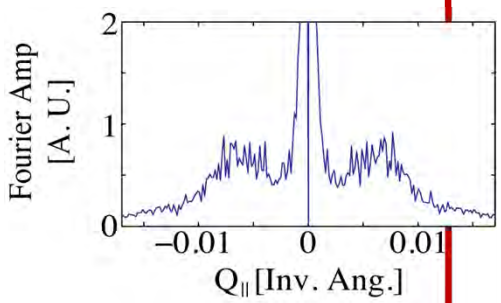
Atomic Force Microscopy

11.3 Monolayers of $SrTiO_3$

Starting Surface







Excellent real space images of small number of stationary islands.

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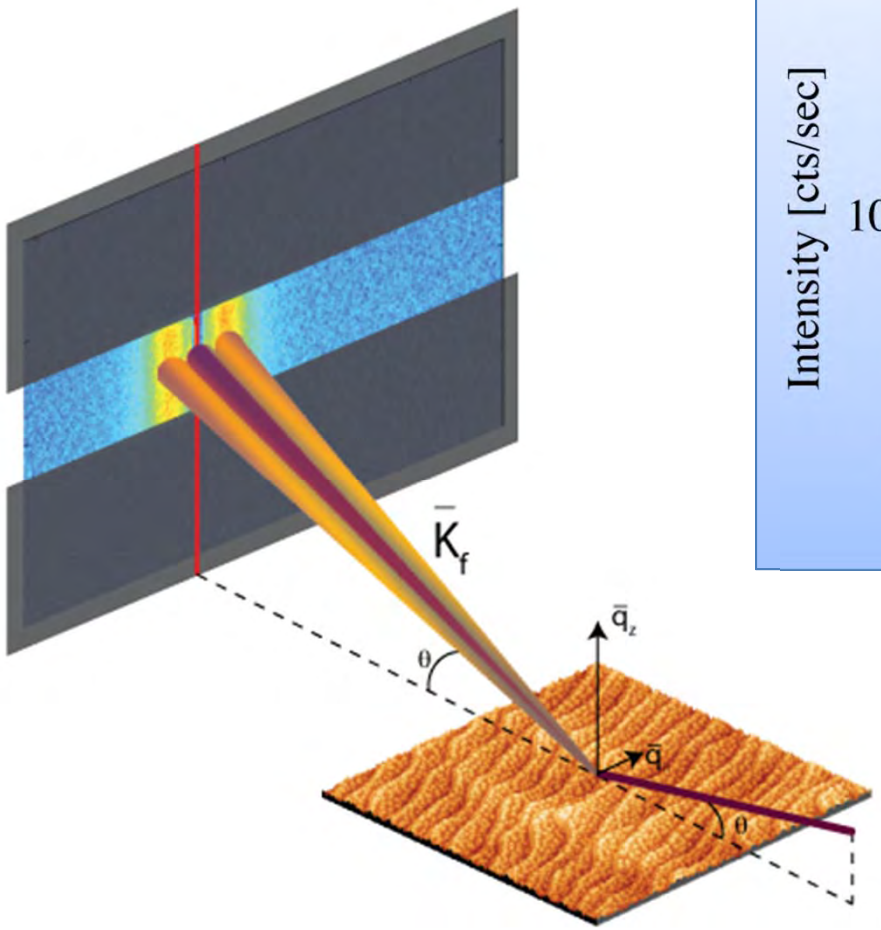
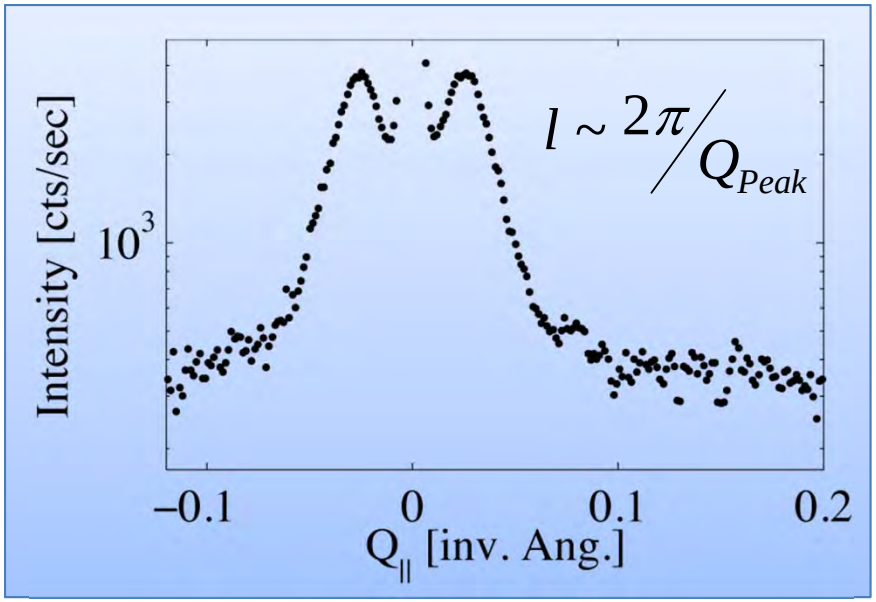
Scattering Geometry





200 ms Time Resolution

- Optimum between diffuse signal and thermal background

$$q_z = 0.275 \text{ r.l.u.}$$

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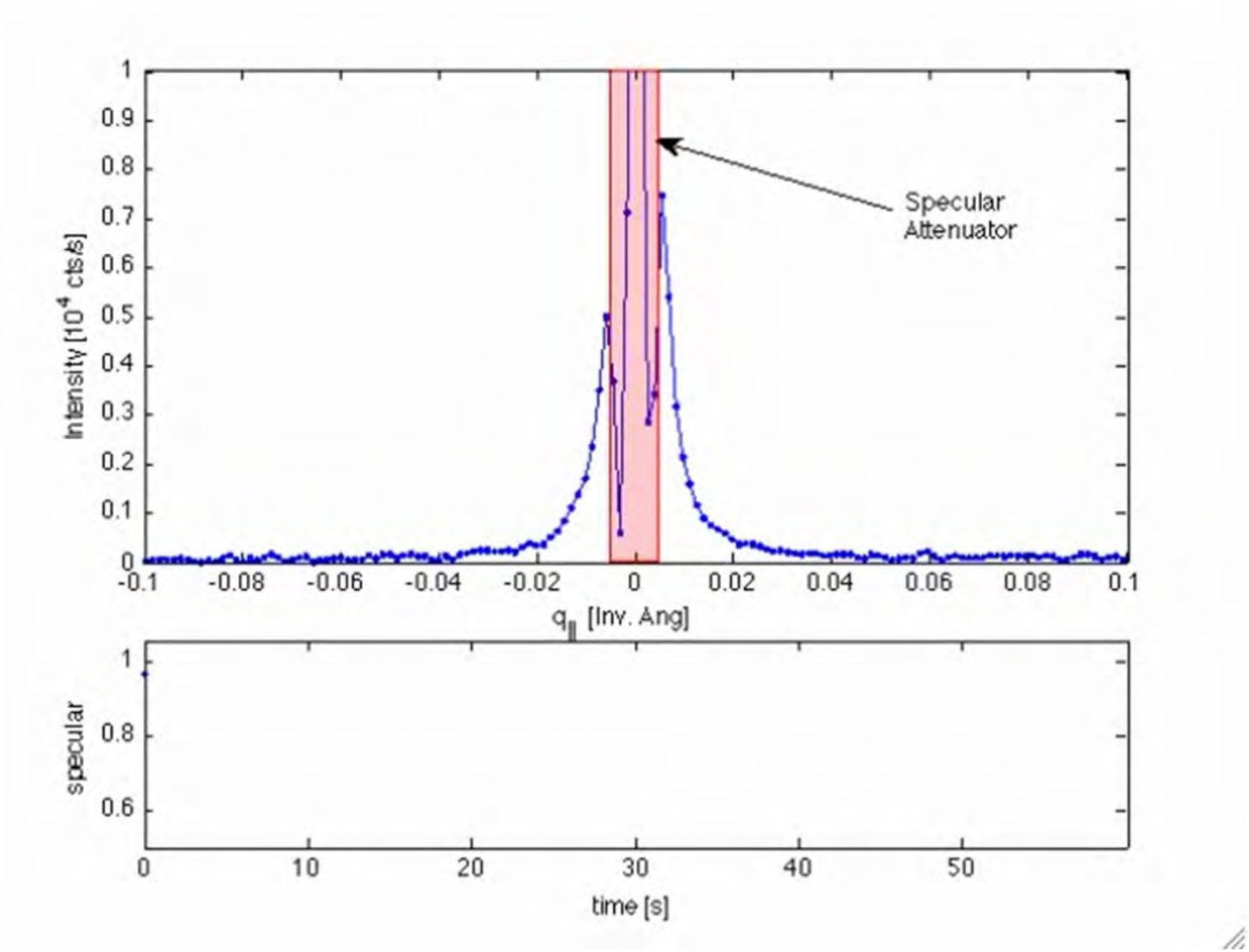
Show Movie



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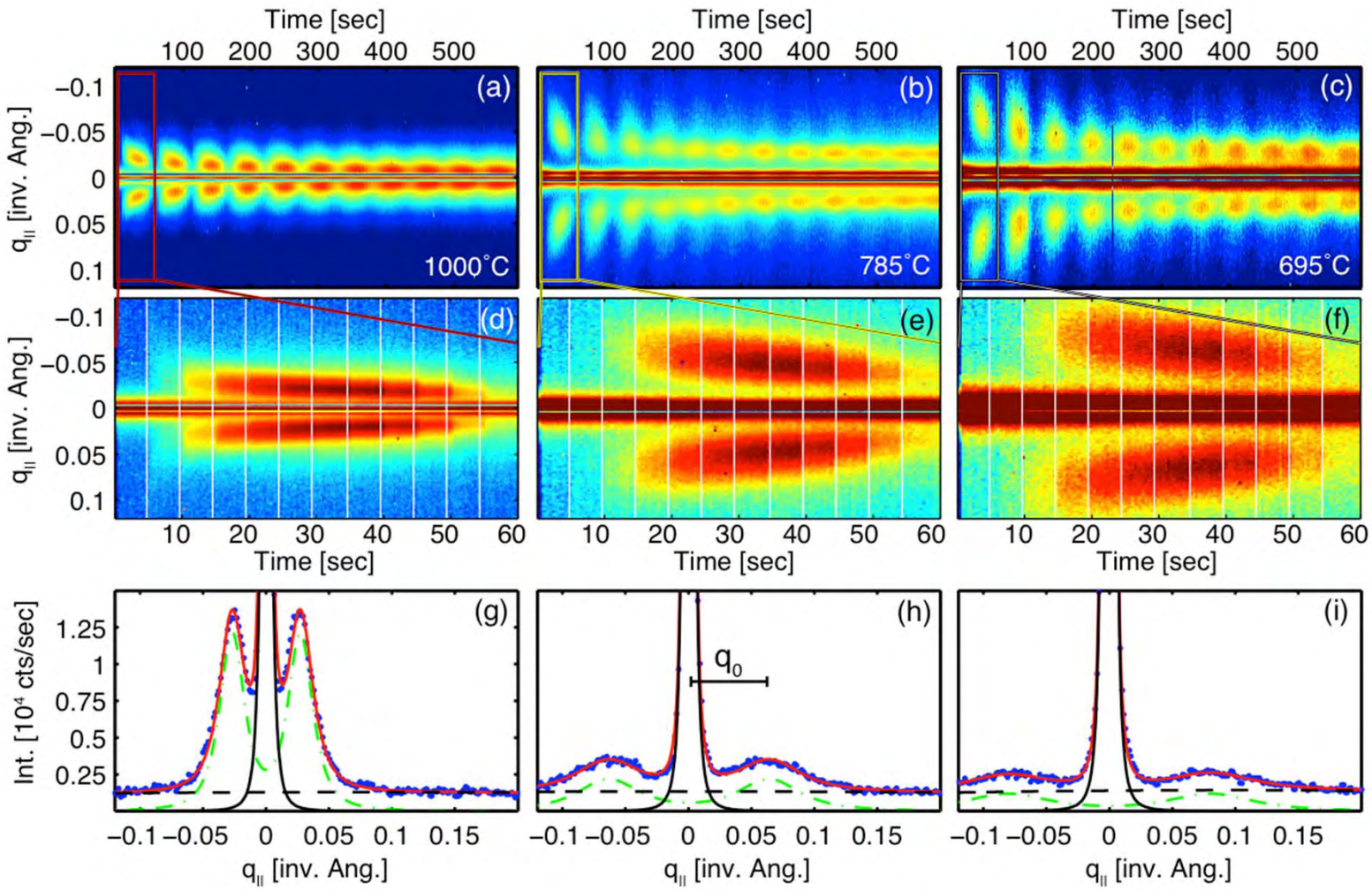
Temperature Dependence



Ferguson, J.D., et. al. *Physical Review Letters* **103**, 256103 (2009).

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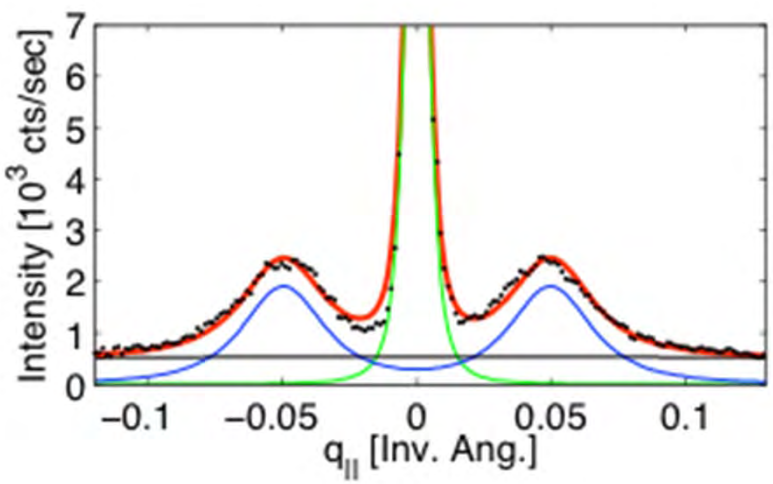
Modeling the Diffuse Scattering

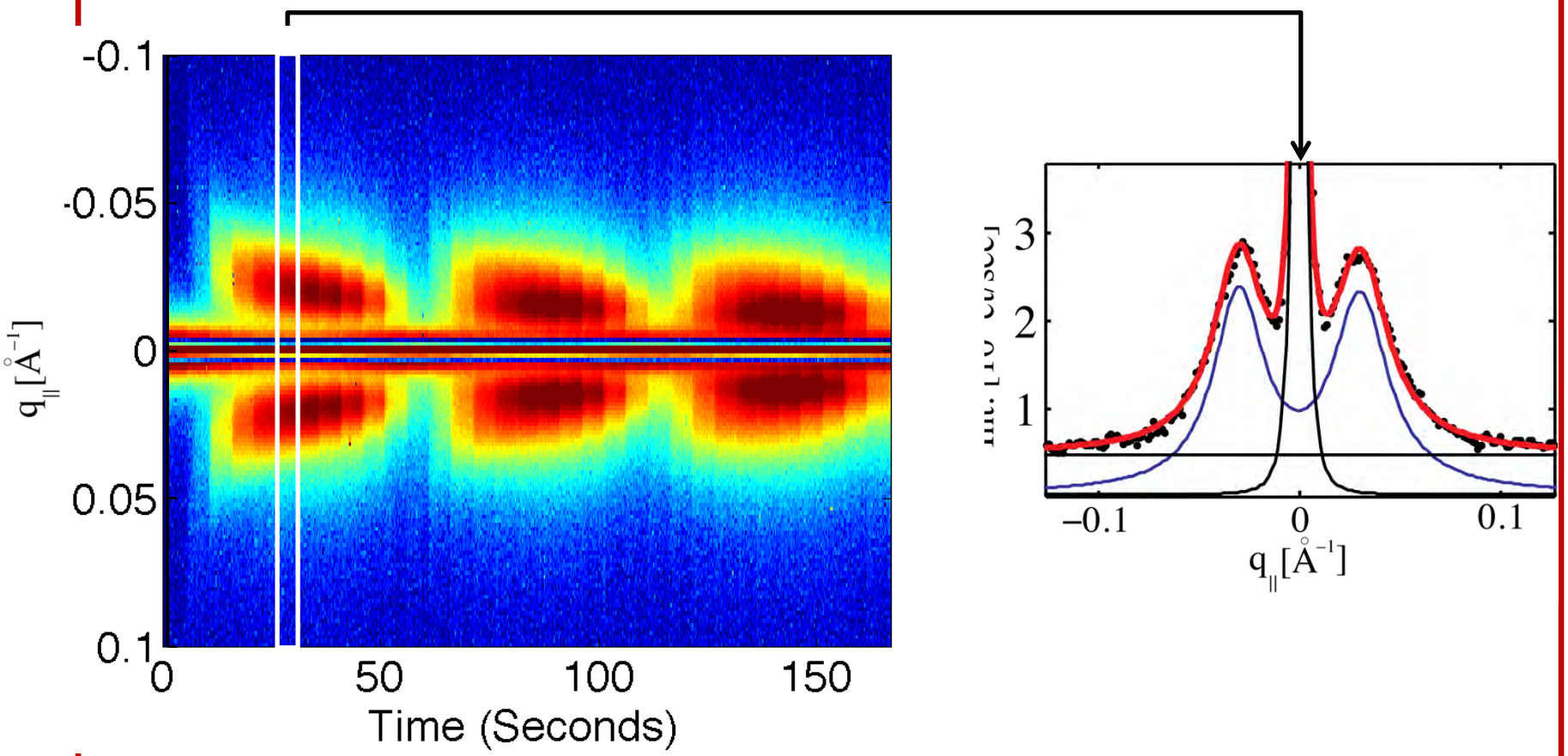


$$I(q) \propto \frac{1}{(1+\xi^2(q-q_0)^2)^{\frac{3}{2}}}$$

Key Points:

- **Peak Position** – Distance between island centers
- **Integrated Intensity** – Amount of material in all islands
- **Full Width Half Max** – Island-Island correlation length

Time Resolved Diffuse Scattering



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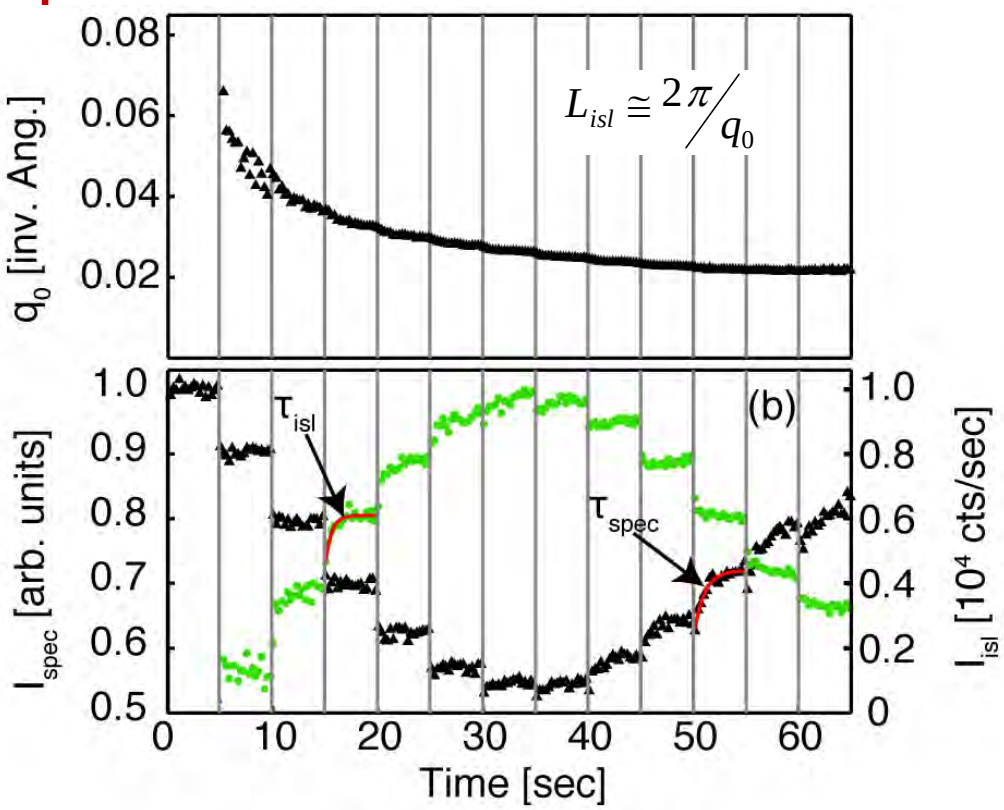
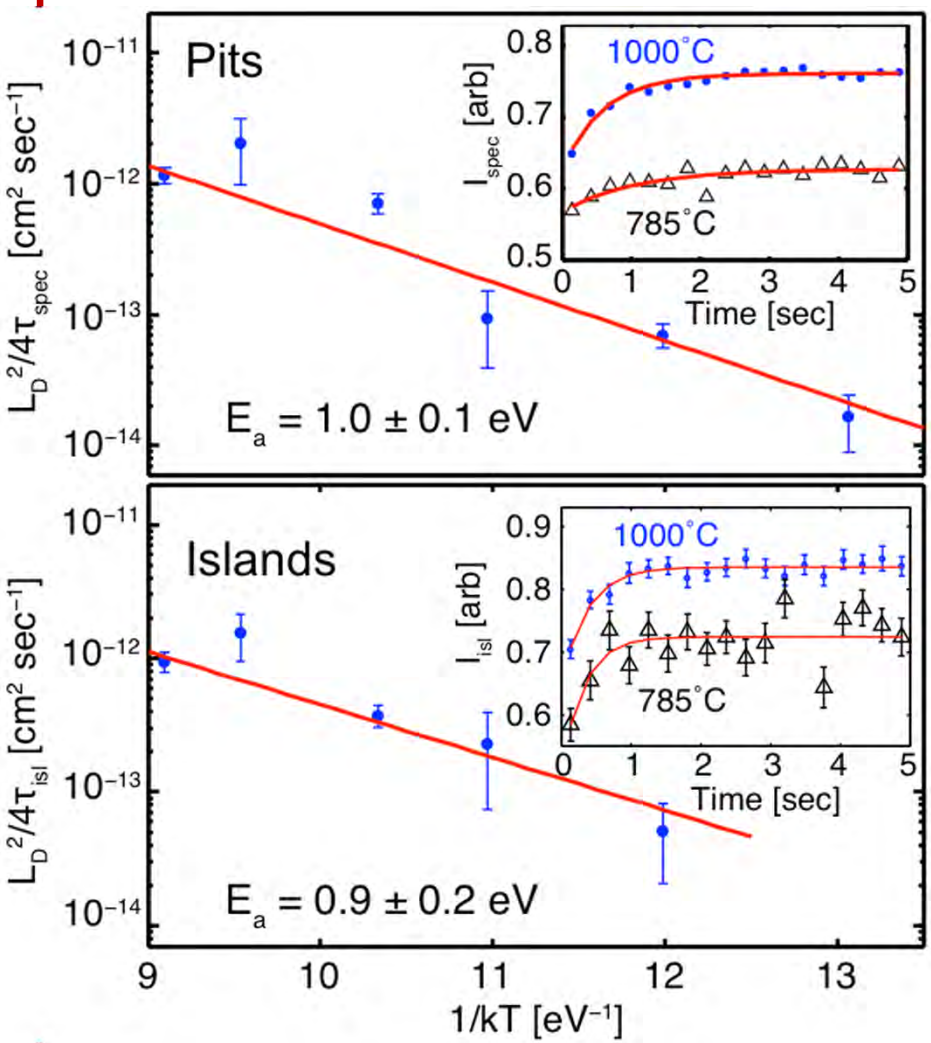
Best Fit Results to Model



- Island coarsening is significant and occurring on timescale of seconds.
- No additional nucleation of islands after 1st pulse
- Specular and diffuse both show time dependent behavior.
- $I_{tot} = I_{spec} + I_{isl} + I_{sm}$
- Time dependent I_{isl} ➔ mass transfer from smaller to larger islands

Ferguson, J.D., et. al. *Physical Review Letters* **103**, 256103 (2009).

Diffusivity: Islands vs. Pits



Ferguson, J.D., et. al. *Physical Review Letters* **103**, 256103 (2009).

- The diffusivity for the island and the pit morphology are the same.

- By measuring the length scale and the characteristic diffusion time, we can determine D_0 and E_a:

$$D = D_0 e^{-E_a/kT}$$

- The prefactor $D_0 = 10^{-8\pm1}$ $cm^2 sec^{-1}$ is 10^5 times smaller than compared to semiconductor or metal epitaxy.
- Attributed to correlated motion of multiple atoms.

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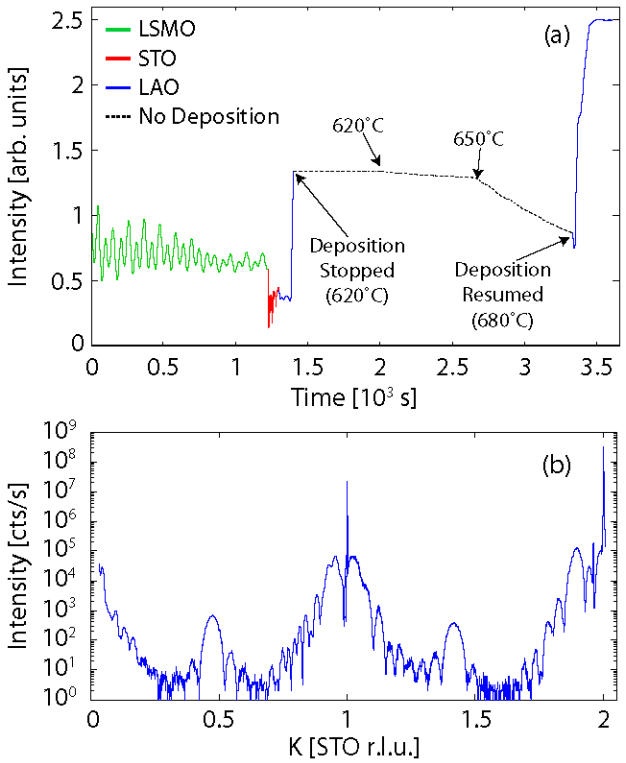
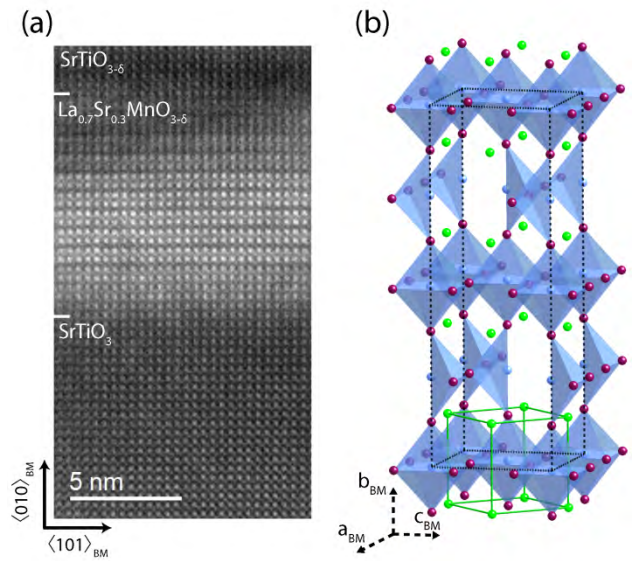
A surprise in LSMO heterostructures: the formation of epitaxial brownmillerite phases





J.D. Ferguson, Y. Kim, L. F. Kourkoutis, A. Vodnick, A.R. Woll, D.A. Muller, and J.D. Brock, "Epitaxial Oxygen Getter for a Perovskite to Brownmillerite Phase Transformation," Accepted for Publication by Advanced Materials (2010).

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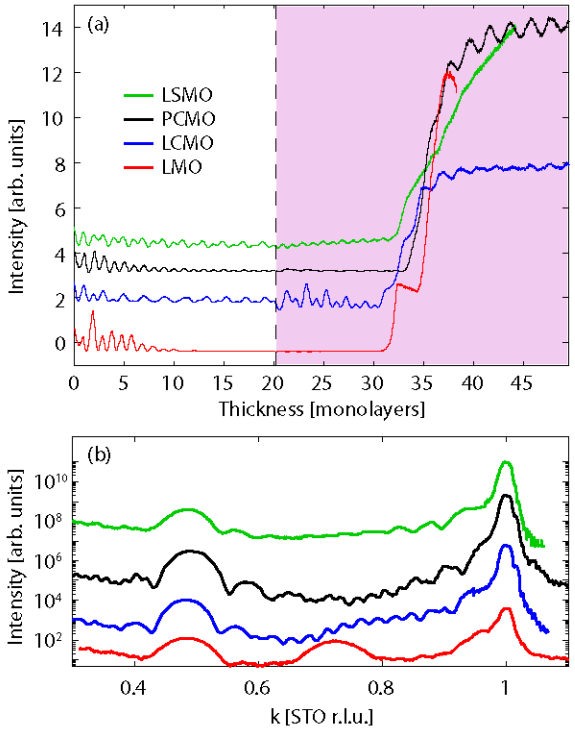
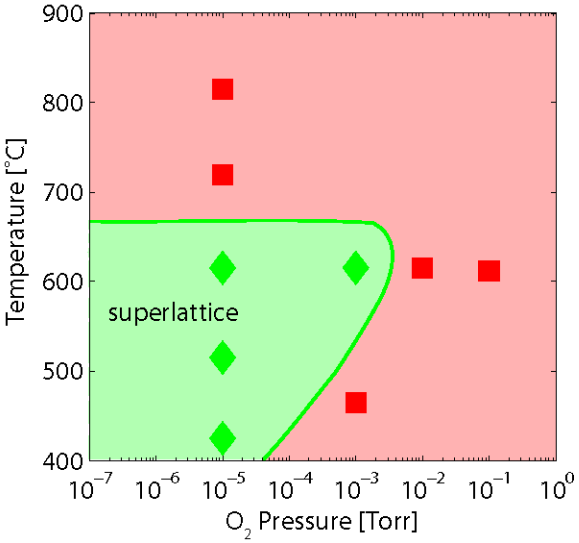
Method works for all the manganates we studied.





In situ x-ray studies were the key to this discovery.

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Next Steps: Going beyond line-shape analysis

$$I_{diff}(q_{\parallel}, t) = 2\pi|f|^2 \int_0^{\infty} \rho d\rho \, J_0(q_{\parallel}\rho) \, \langle \delta n(0,t) \delta n(\rho,t) \rangle$$

$$G(r,t) \equiv \langle \delta n(0,t) \, \delta n(r,t) \rangle$$

G(r,t) is maximum amount of information available in a scattering experiment

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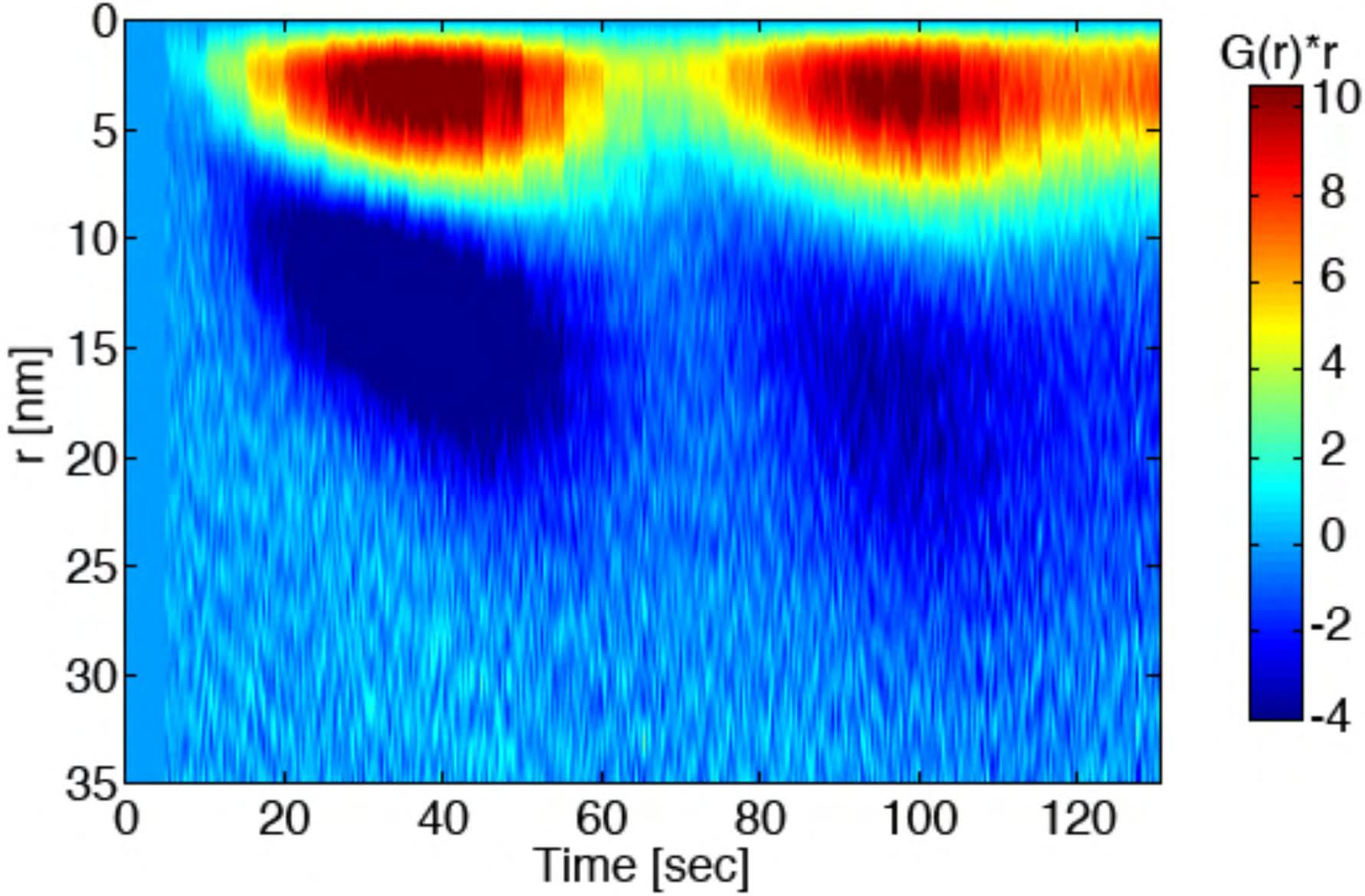
G(r,t)*r


0
5
10
15
20
25
30
35
r [nm]
0
20
40
60
80
100
120
Time [sec]
G(r)*r
10
8
6
4
2
0
-2
-4

Next Steps

Clearly, a "PDF"-type of analysis to extract g(r) from the scattering data would be very interesting.

Such an analysis is challenging due to the island structure factor, $\langle f(q) \rangle^2$, changing at the same time as g(r).

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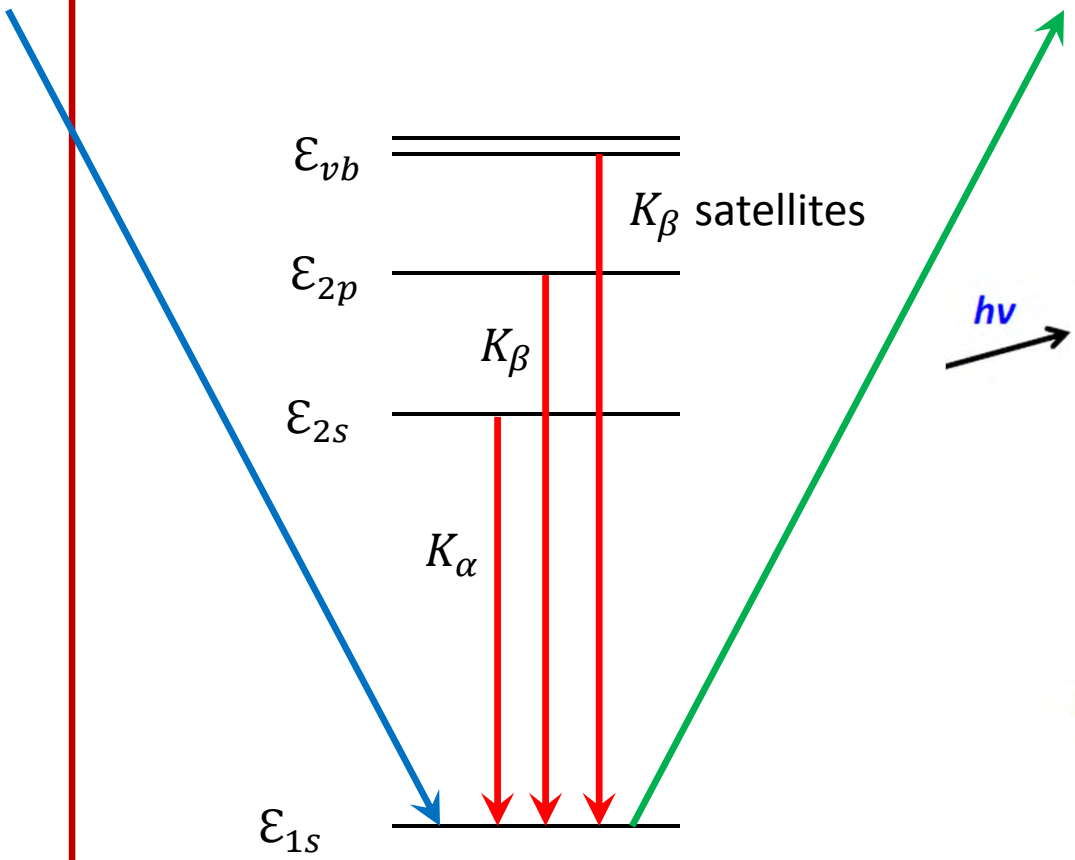
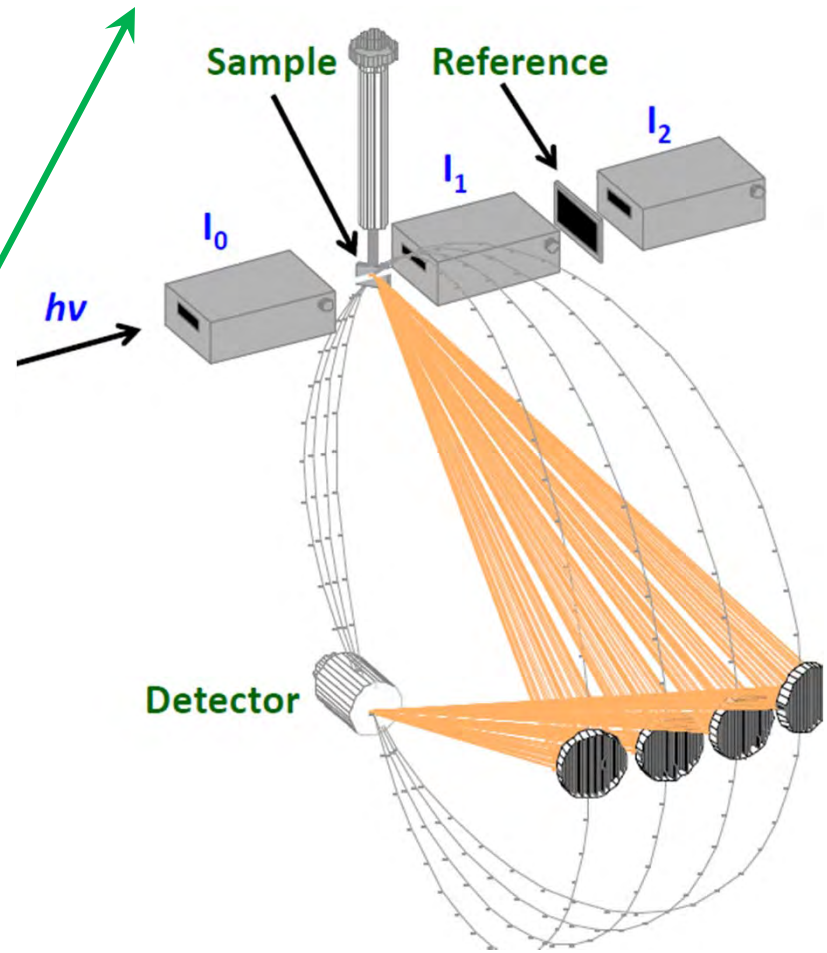
X-Ray Emission Spectroscopy (Valence to core transitions)





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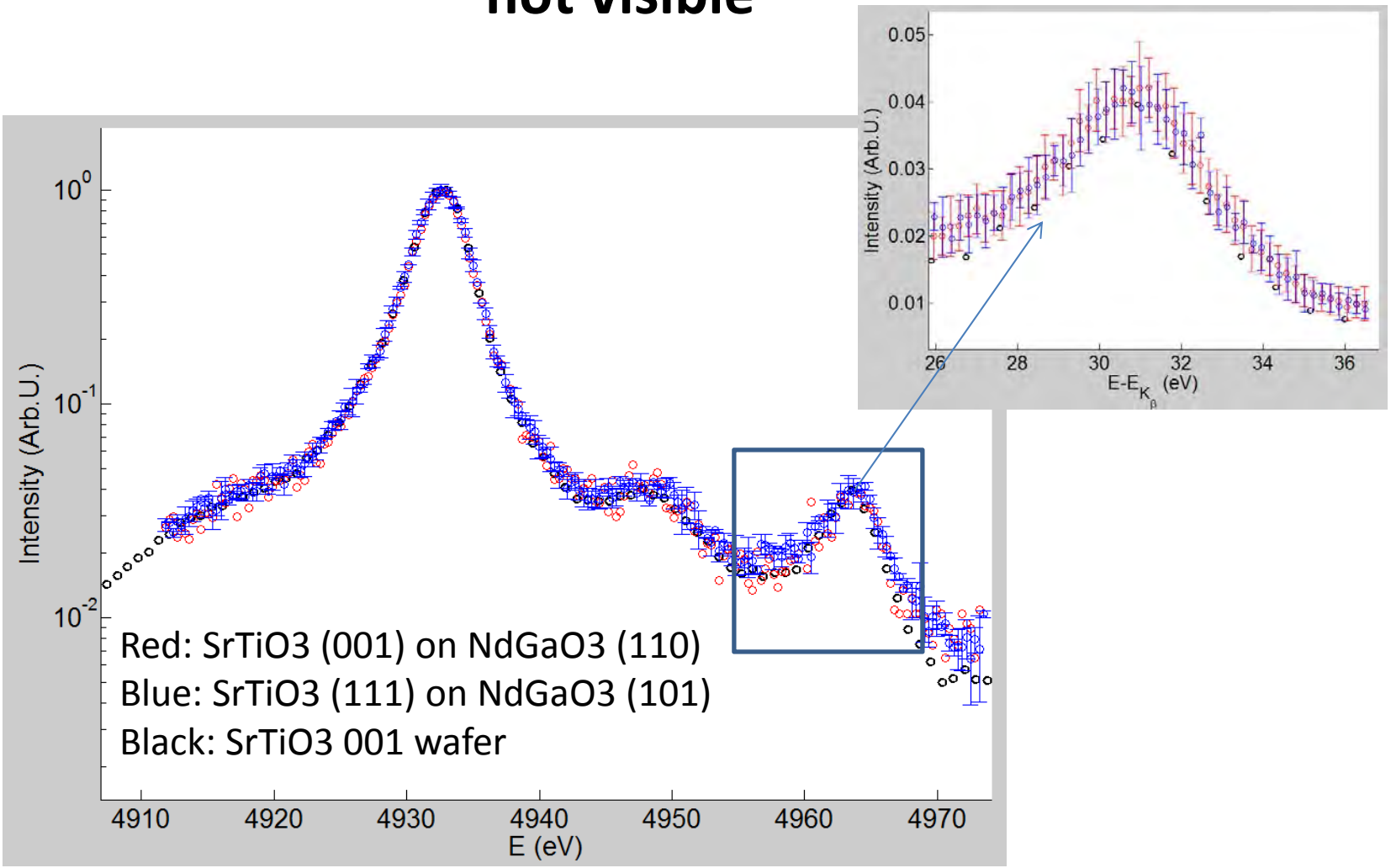
Lattice strain induced shift of Valence Band is not visible



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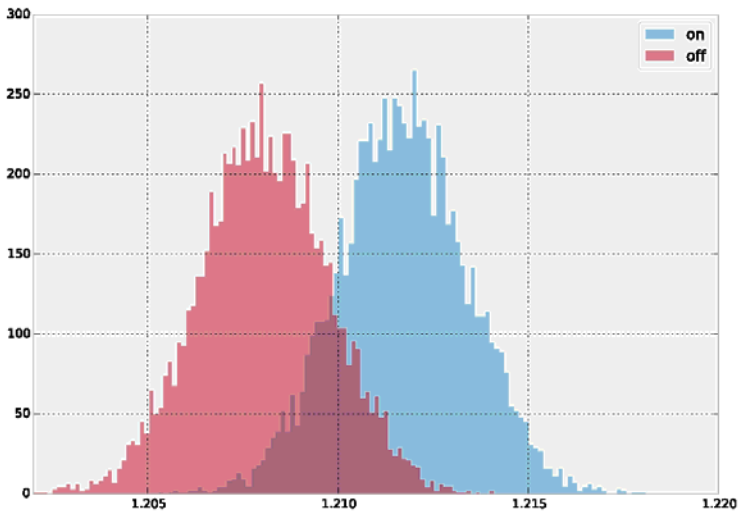
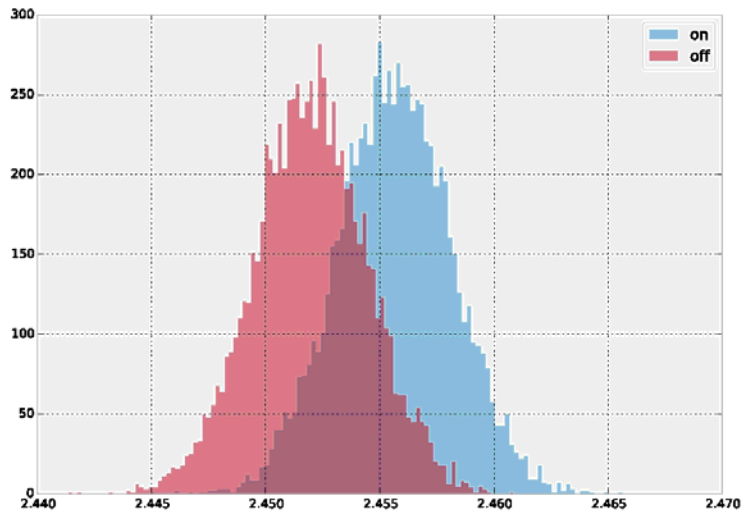
UV induced Valence Band Shift is Visible

$\mathcal{E}_{Ti\ 2p} + 32.0$



α

$\mathcal{E}_{Ti\ 2p} + 32.5$



α

$$I(\mathcal{E}) \sim \mathcal{P}(\alpha \cdot I_{CESR})$$

Intensity increases when UV is on → must be peak shift not amplitude change

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The Future

- Real-time, 3D imaging of
  - Density
  - Elemental composition
  - Crystal orientation
  - Strain state

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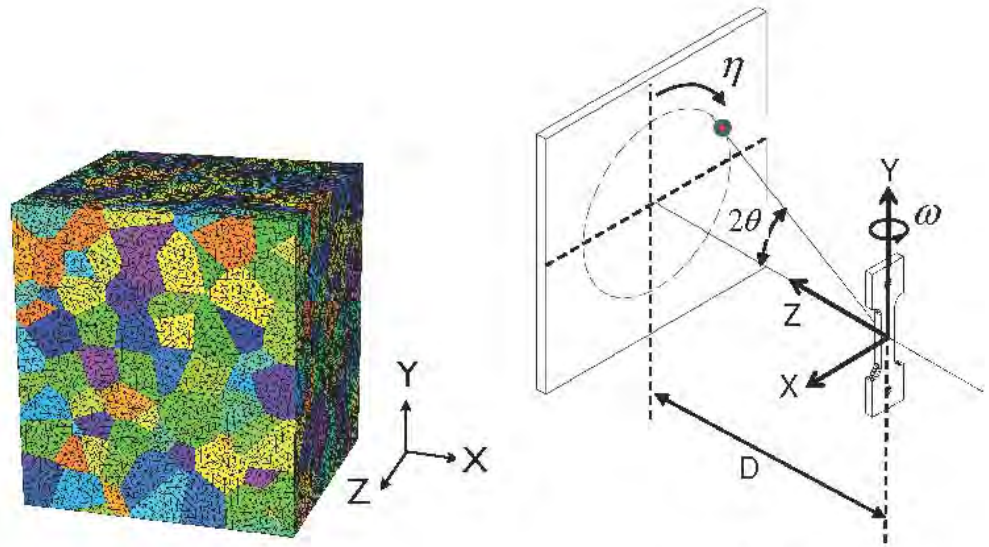

(a) Virtual Polycrystal (b) HEXD Experiment

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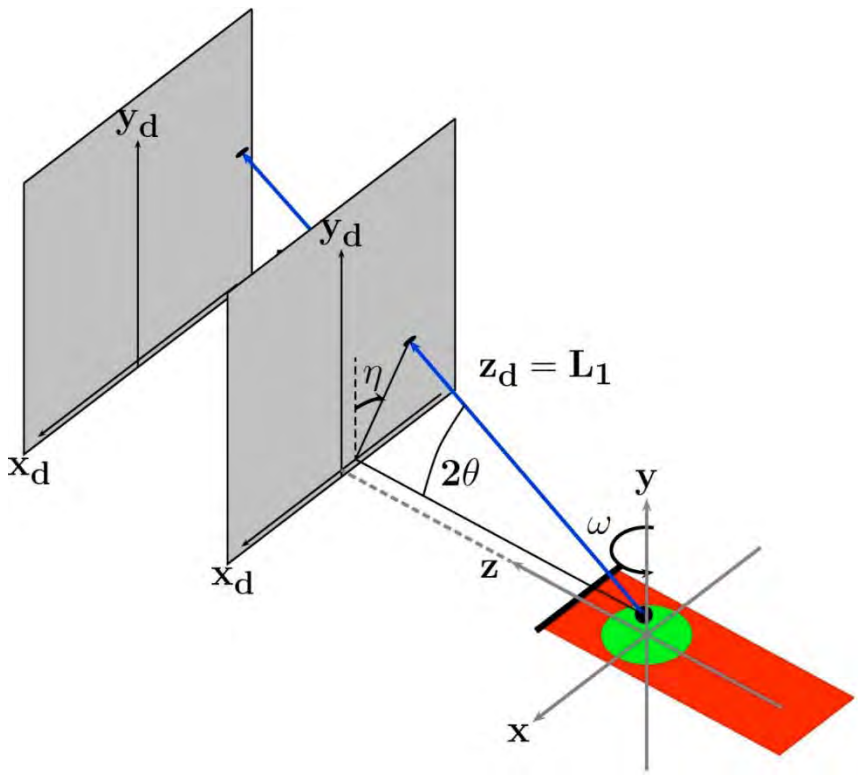

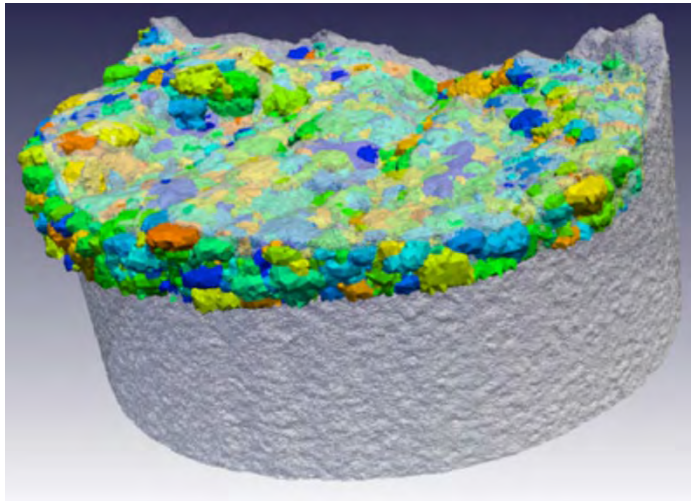

Figure courtesy Bob Sutter

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What do we need?

- We have x-ray beam lines, etc.
- We need compatible environmental chambers.
- Randy Headrick's rail system works quite well…