Surface and Interface Scattering

August 17, 2023

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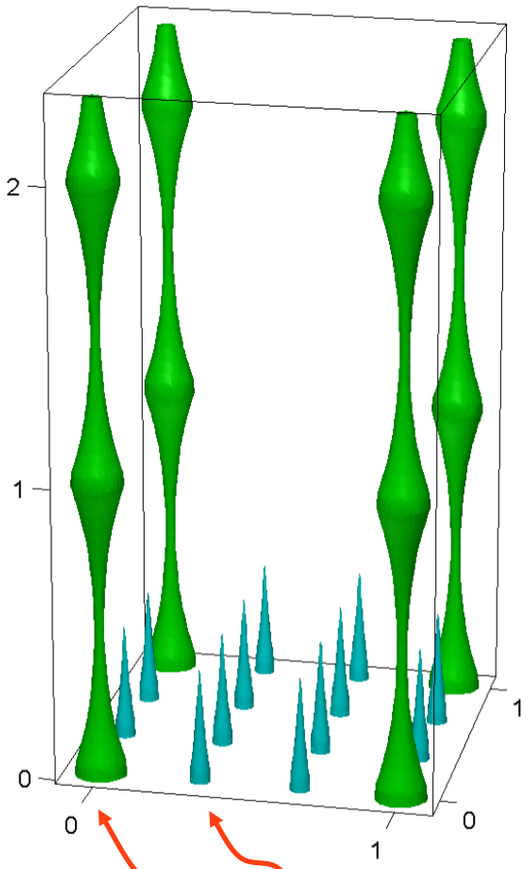
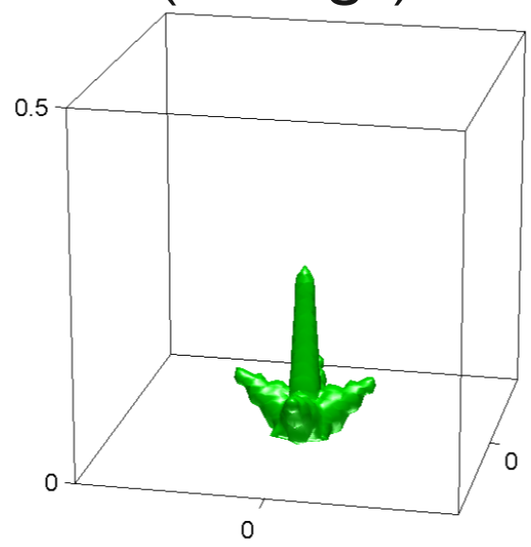
Surface x-ray diffraction (SXRD, SXS, GIXS, GIXD, ...)

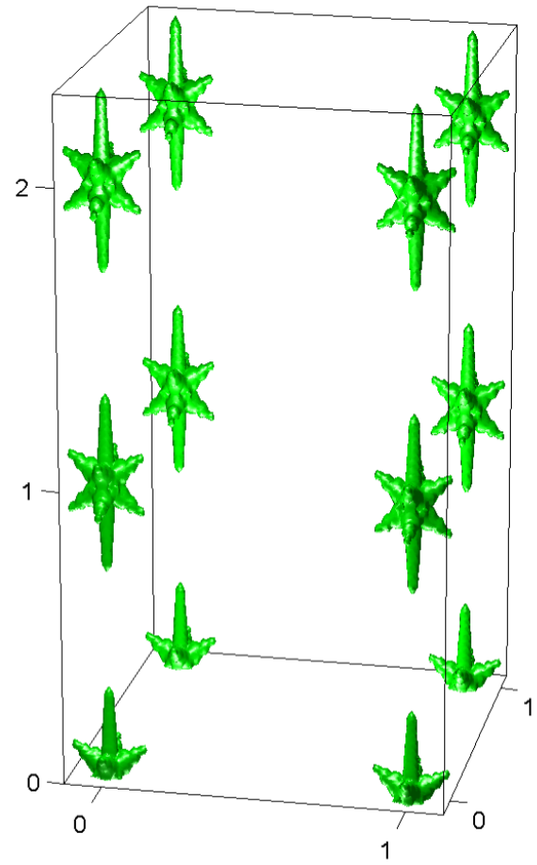
1D Fourier transform



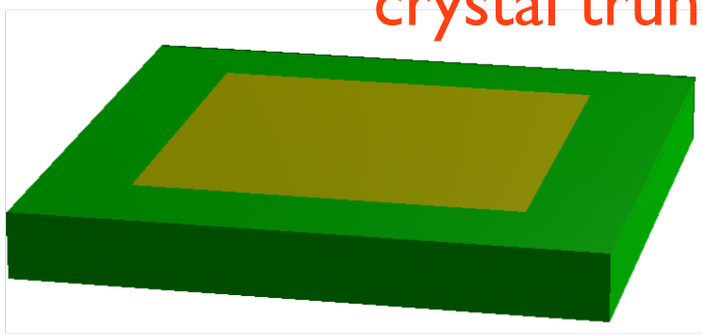
3D Fourier transform (average)



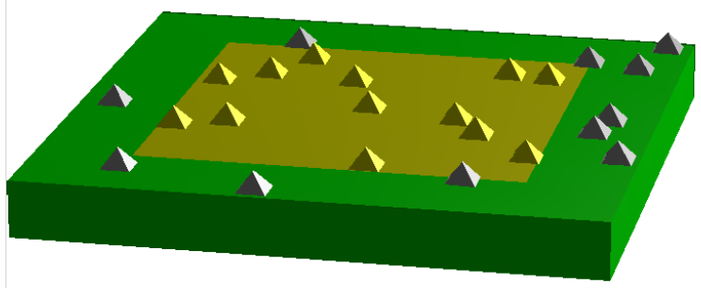
3D Fourier transform



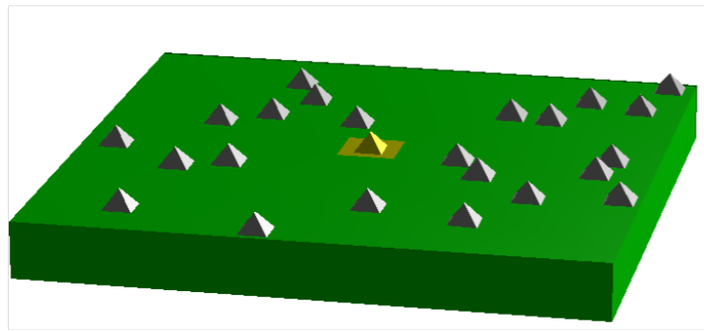
superstructure rods (SRs)
crystal truncation rods (CTRs)



SXRD



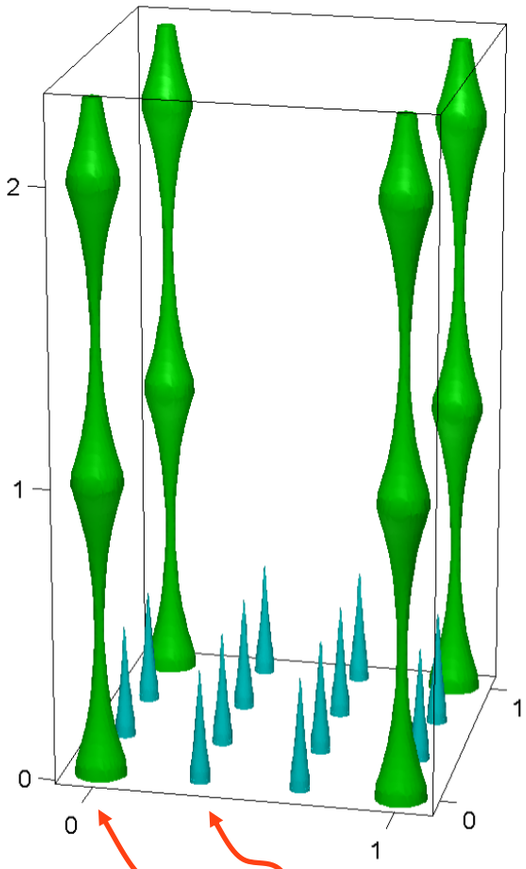
GISAXS

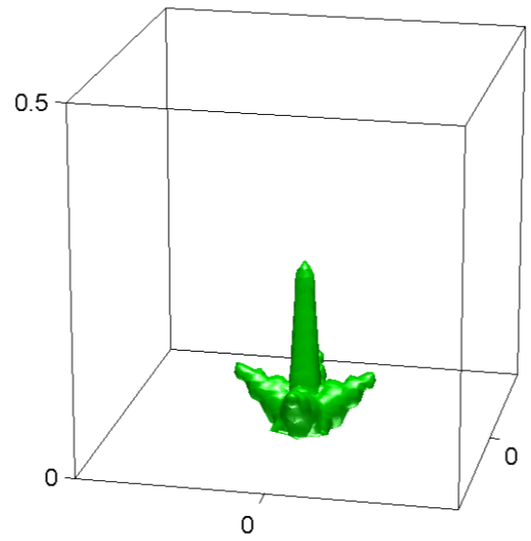


CDI

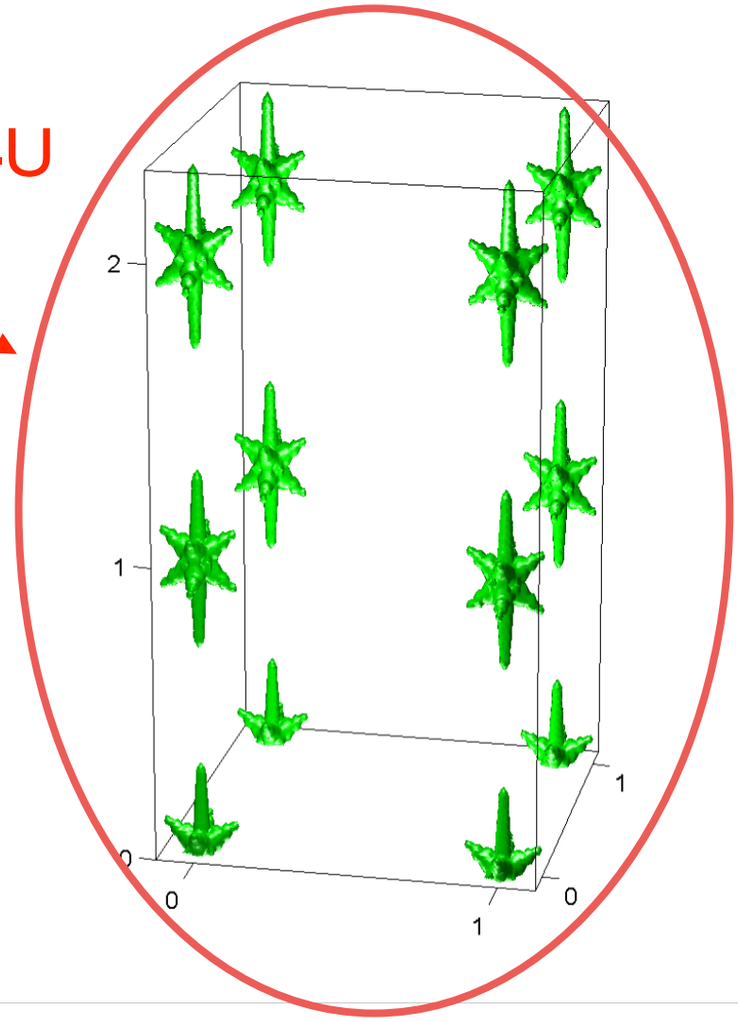
D. D. Fong *et al.* MRS Bulletin **35,** 504 (2010)

Surface x-ray diffraction (SXRD, SXS, GIXS, GIXD, ...)

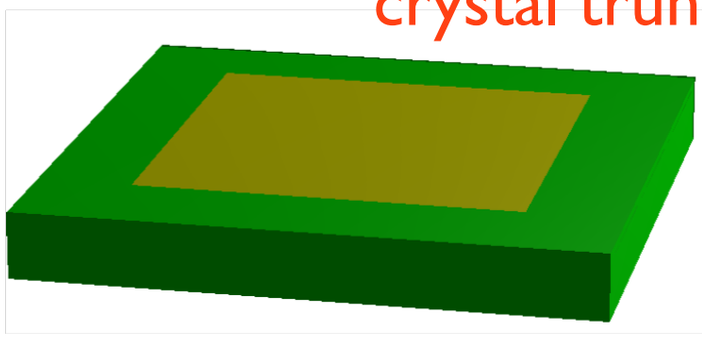




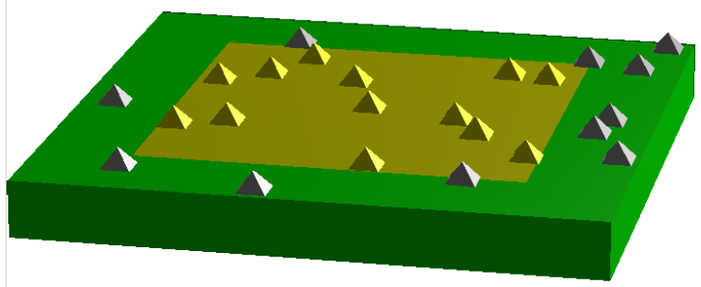
enhanced by APS-U



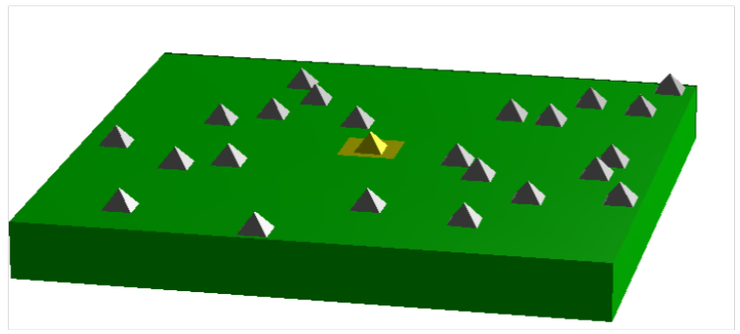
superstructure rods (SRs)
crystal truncation rods (CTRs)



SXRD



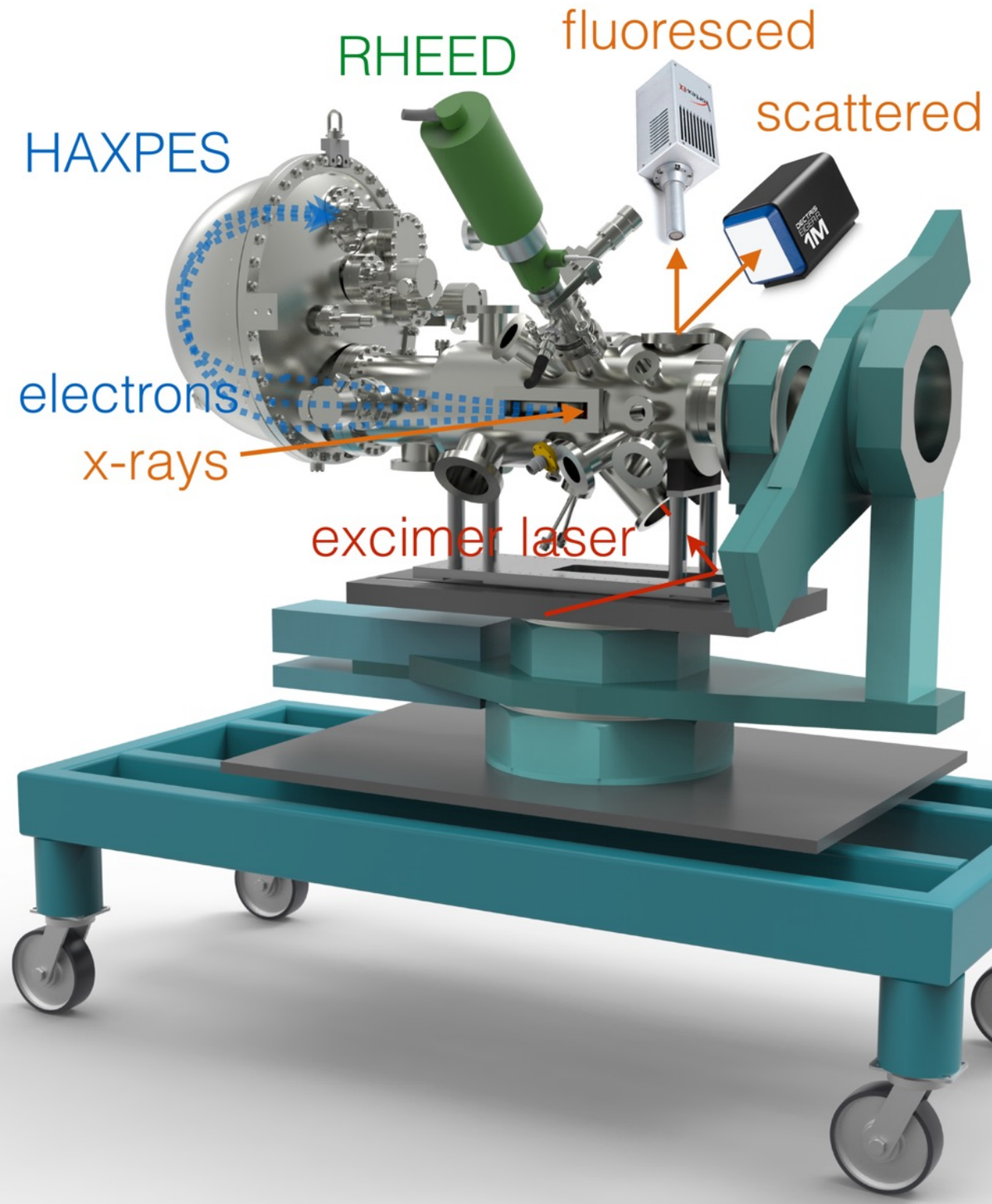
GISAXS



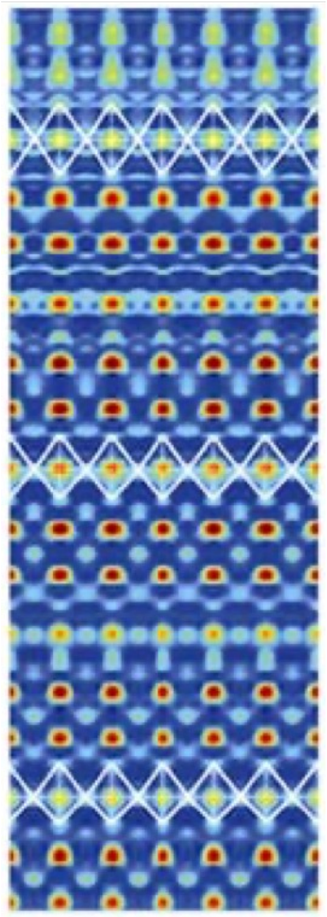
CDI

D. D. Fong *et al.* MRS Bulletin **35,** 504 (2010)

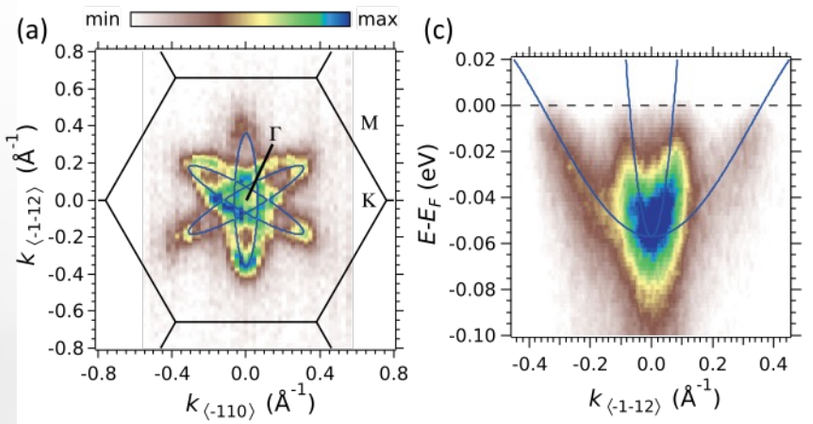
Motivation: Watch materials creation



- atomic structure (SXRD)
- occupied electronic levels (HAXPES)
- unoccupied electronic levels (XANES)
- band structure (HARPES)

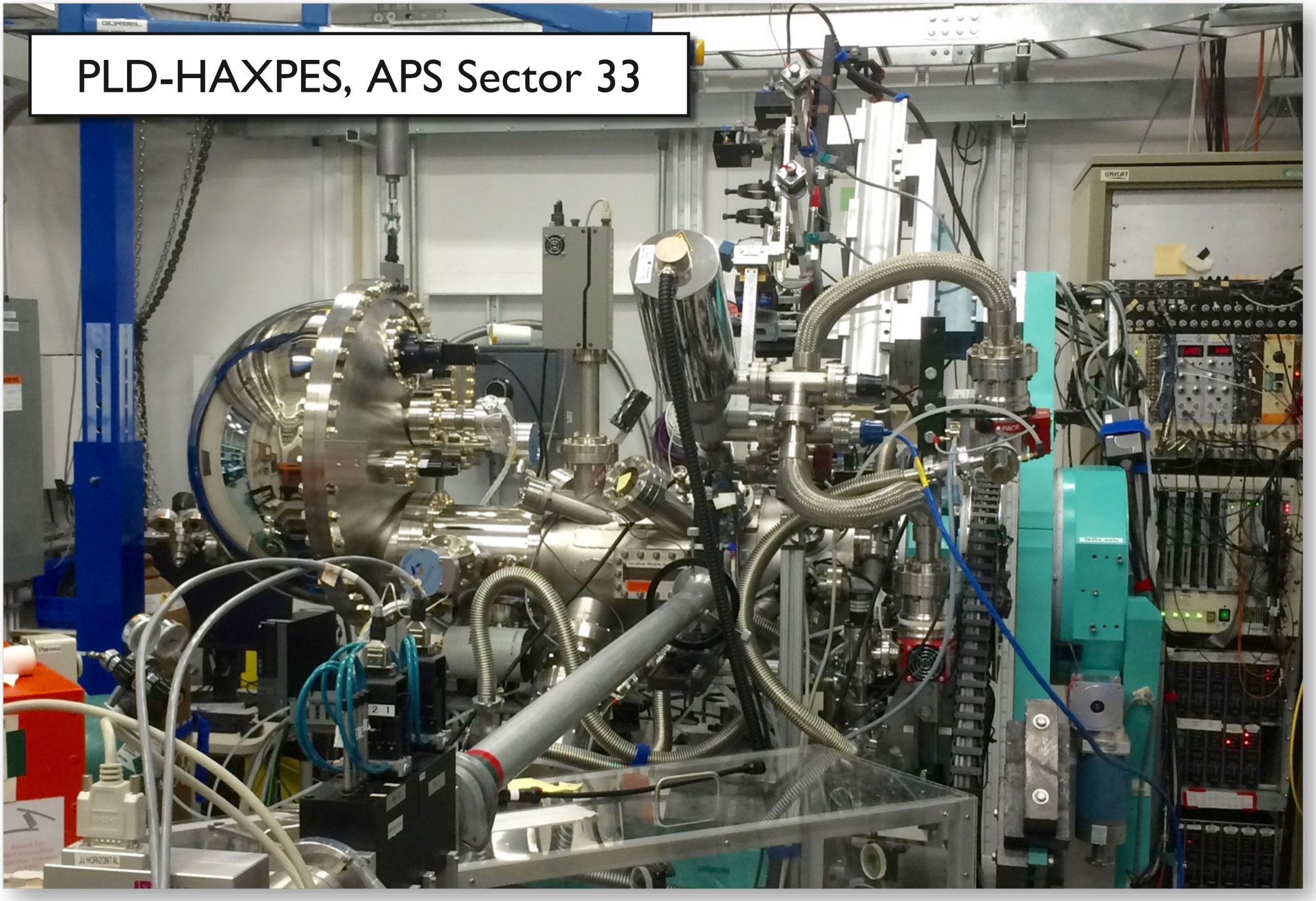


H. Zhou *et* al., PNAS **107**, 8103 (2010).

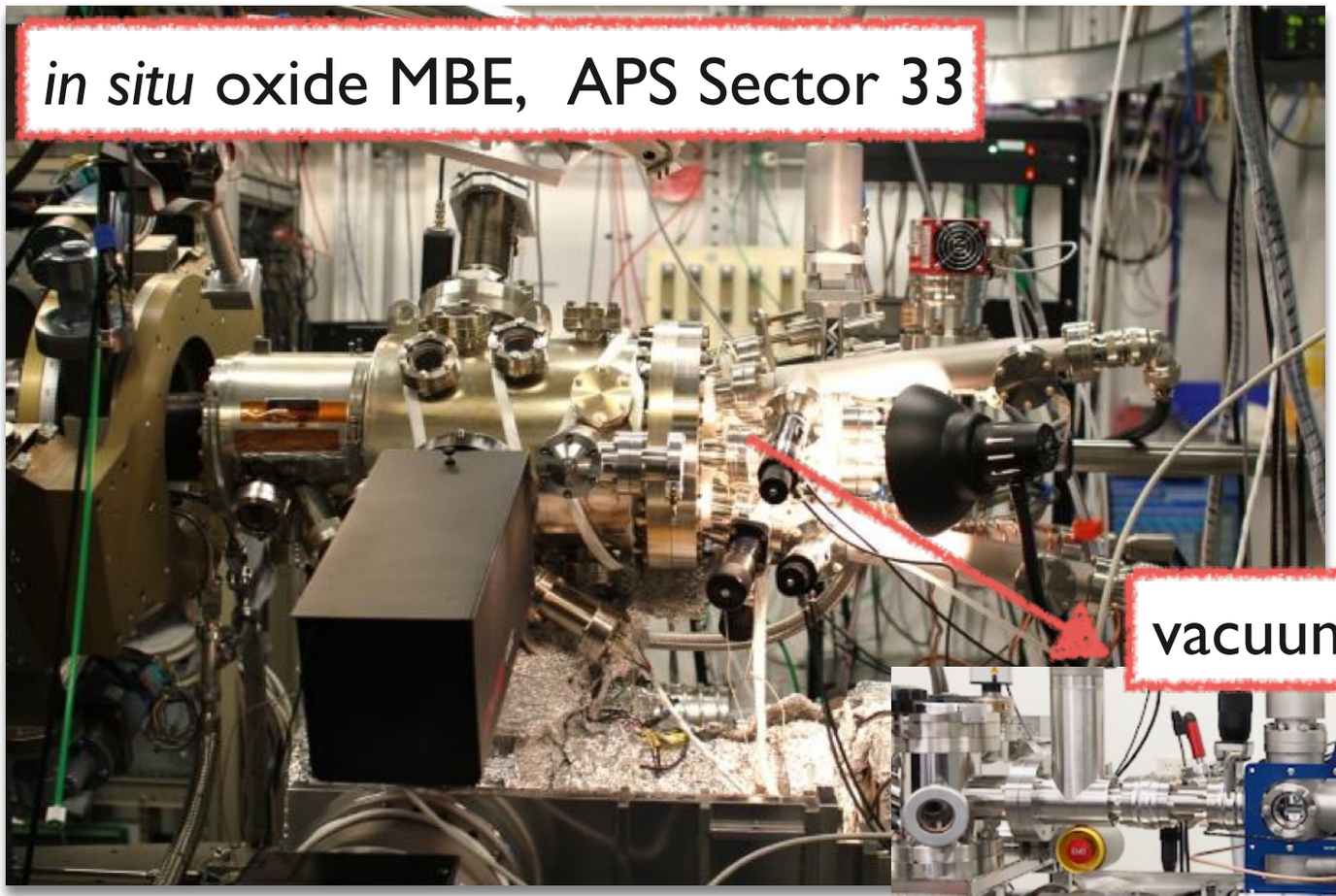


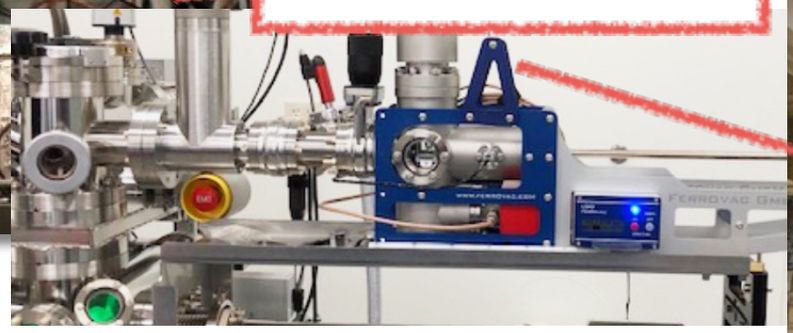
T.C. Rödel *et al.*, Phys. Rev. Appl. **1**, 051002 (2014).

Motivation: Watch materials creation & property evolution during creation

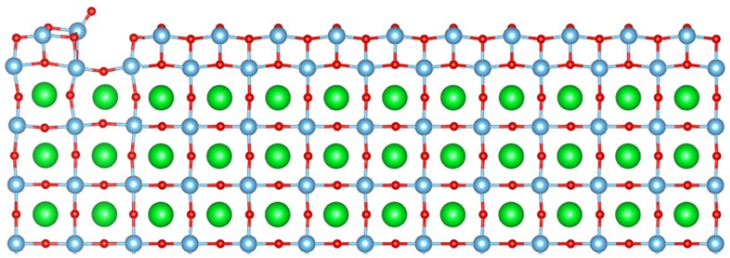


Motivation: Watch materials creation & property evolution during creation

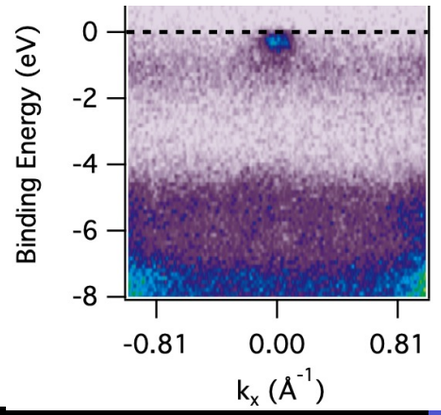




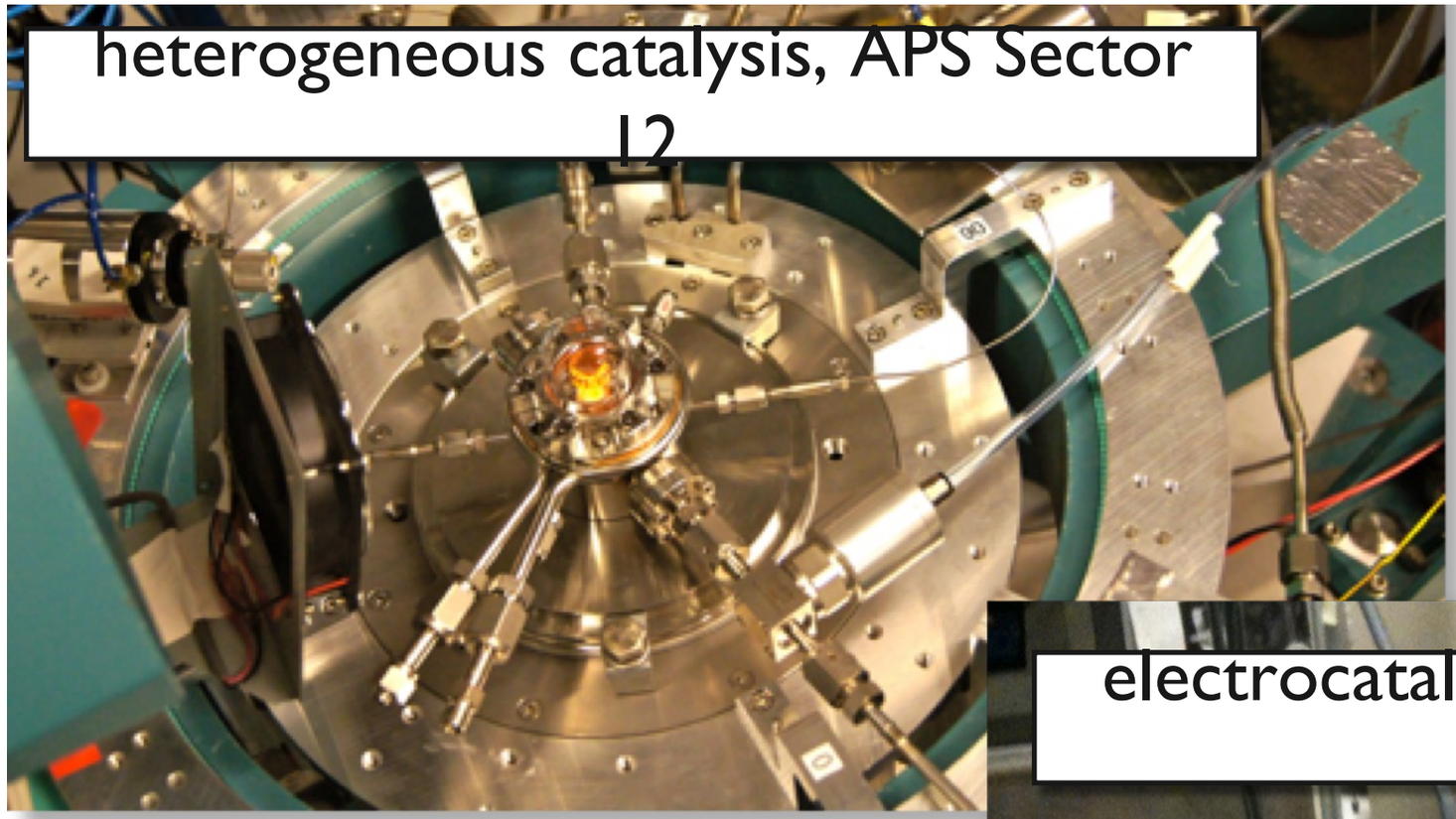
atomic structure

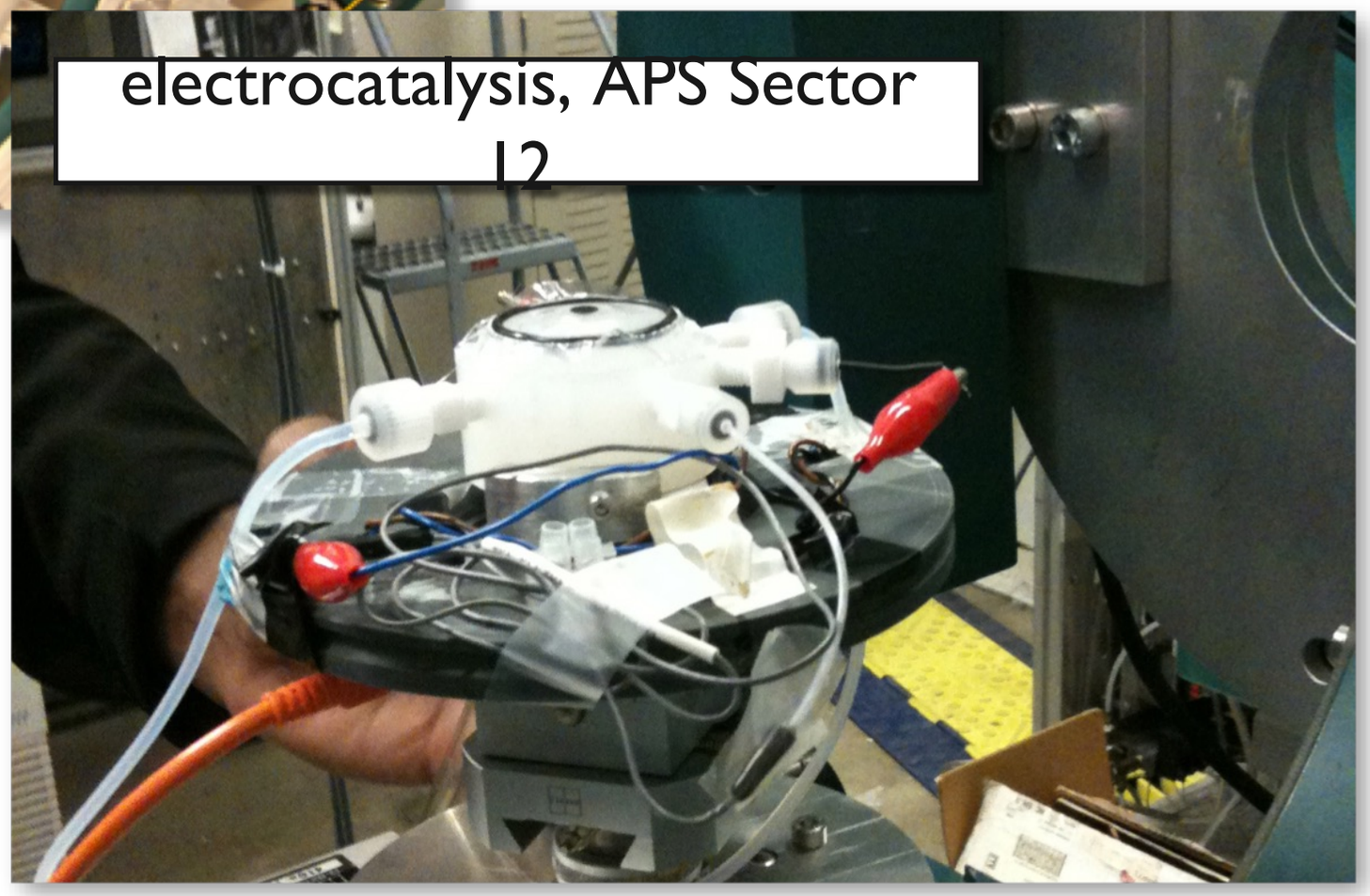


electronic structure



Motivation: Watch surfaces during reaction

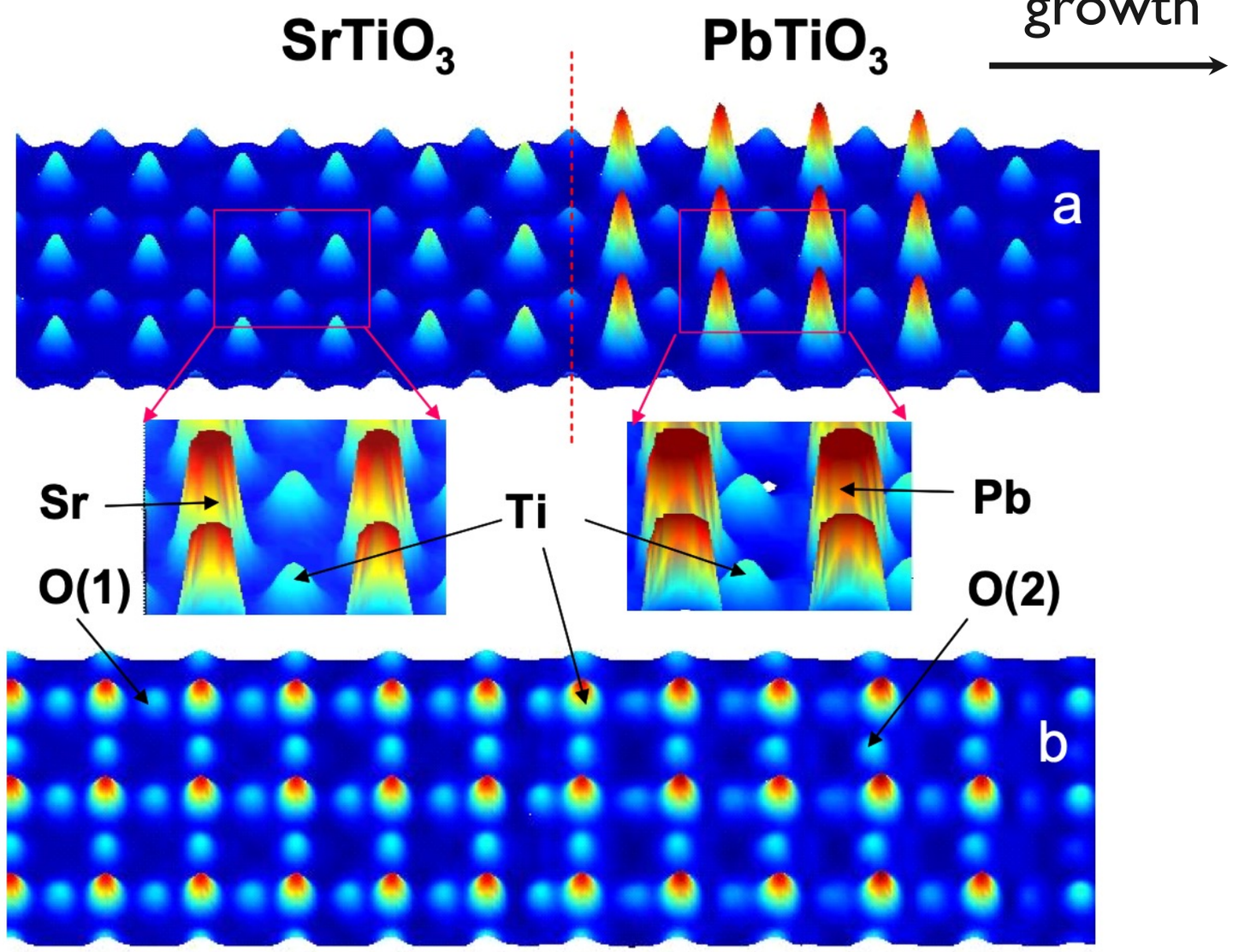


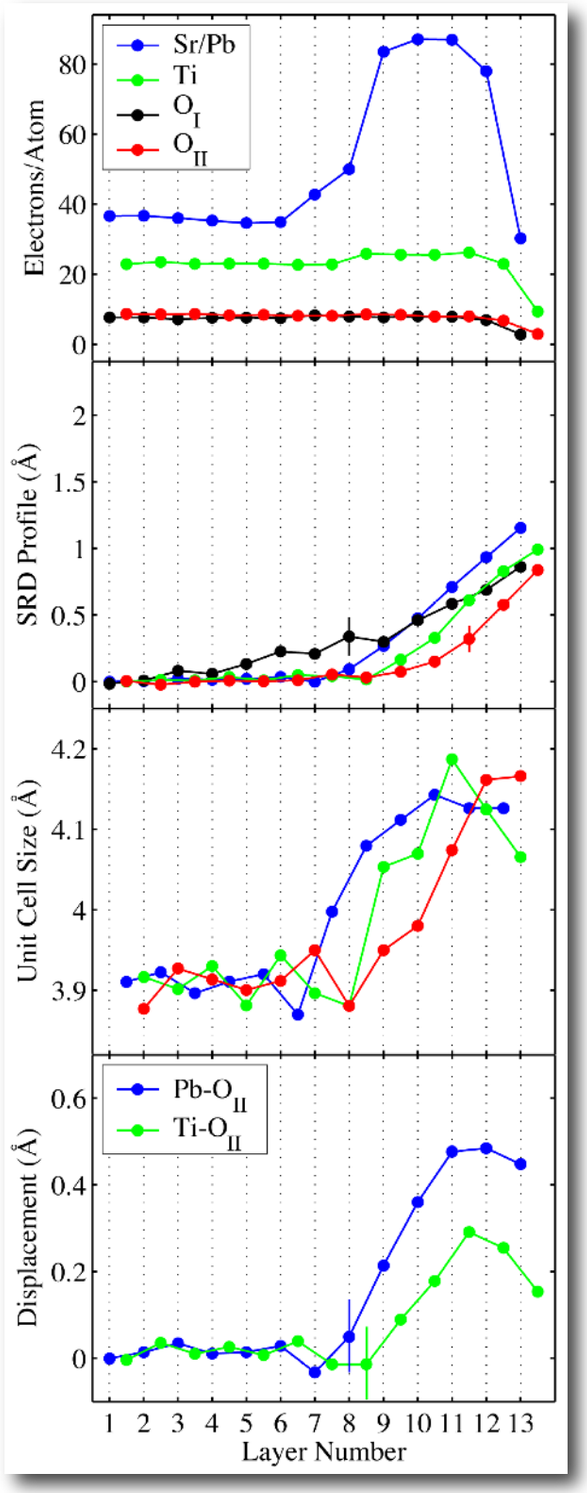


Example from APS Sector 12

$PbTiO_3/SrTiO_3$ (001)

- can look at 3D atomic resolution structure (like TEM)
- but can look at non-destructively





D. D. Fong *et al.* Phys. Rev. B **71,** 144112 (2005)

Outline

I. Surface X-ray Diffraction (SXRD)

- Modeling F(Q)
  - *Structure factor for a crystal*
  - *Structure for a film / substrate*
    - Effect of roughness
  - *Fitting examples*

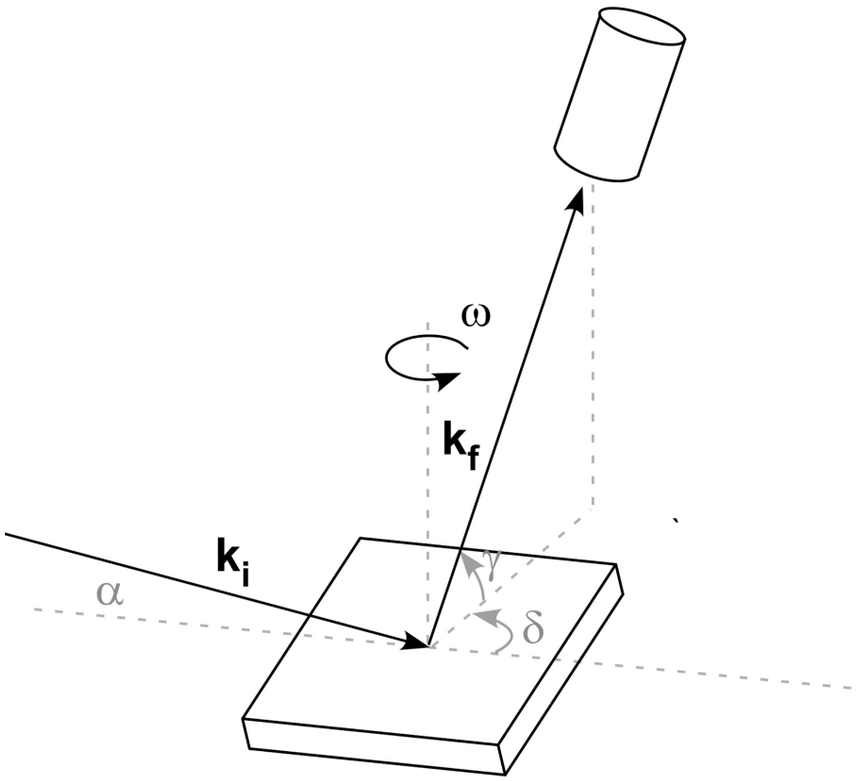
II. Direct methods

III. Example results

IV. Practicalities

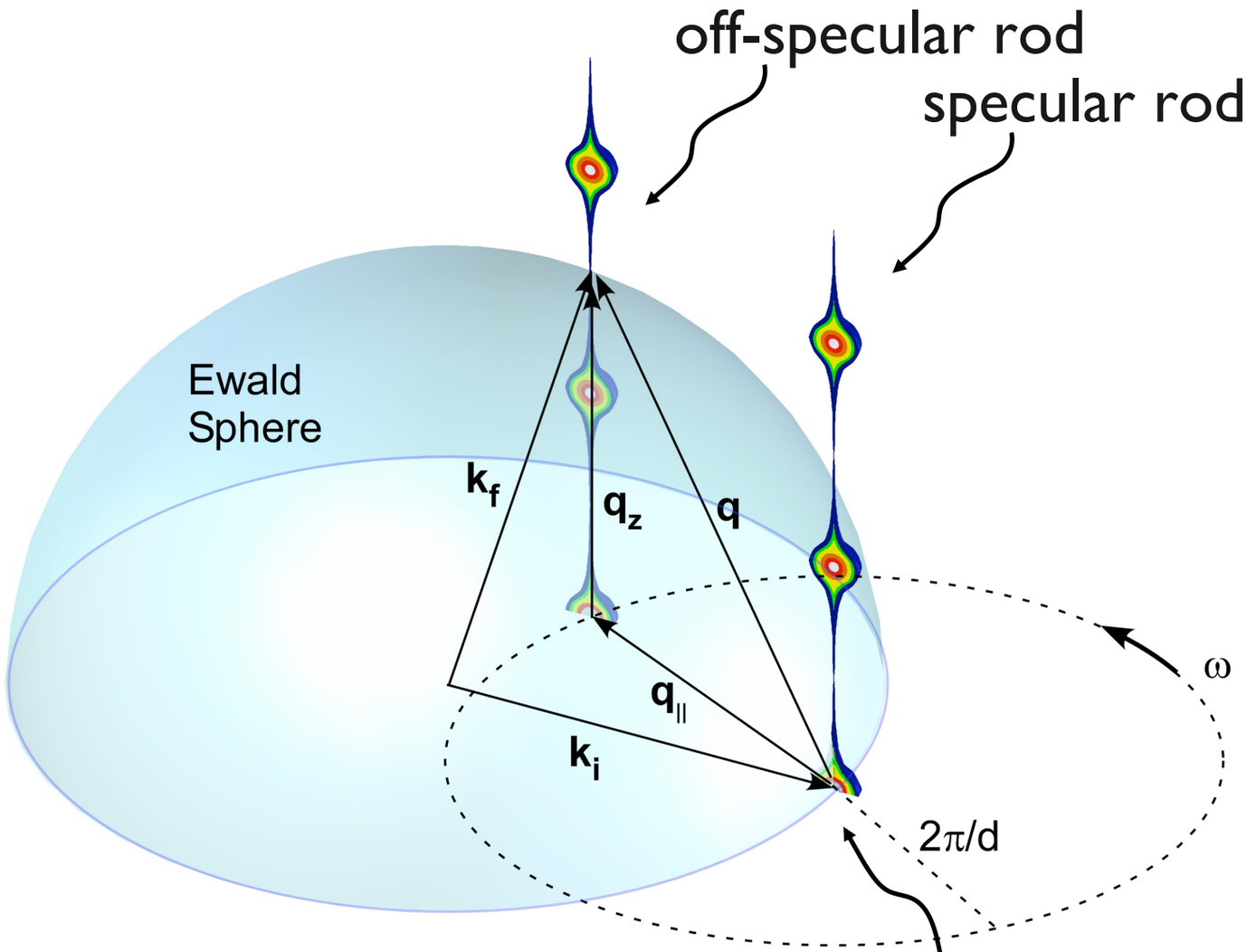
V. X-ray photon correlation spectroscopy (XPCS)

SXRD geometry



(a)

real space



(b)

reciprocal space

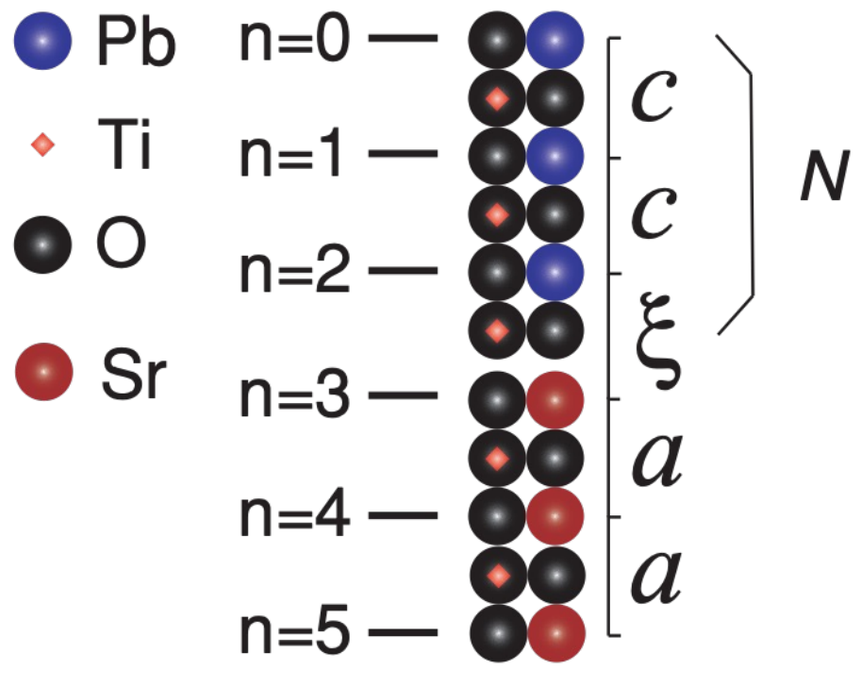
T. T. Fister & D. D. Fong *in Thin Film Metal-Oxides*, Springer (2010)

Modeling *F*(*Q*) for a CTR

Ex. $PbTiO_3$ / $SrTiO_3$ (001)

$$F_{\mathrm{CTR}}(\mathbf{Q}) = N_1 N_2 F_{\mathrm{column}}(\mathbf{Q})$$

$$F_{\mathrm{column}}(\mathbf{Q}) = \sum_{n=0}^{\infty} F_n^{\text{unit cell}}(\mathbf{Q}) e^{-n(iQ_z d_n + d_n/\zeta_n)}$$



Geometric series: {1, 1/2, 1/4, 1/8, 1/16, 1/32, …}

What is the sum over the first 6 terms?

a = 1 (first term)

r = 1/2 (common ratio)

N = 6 terms

$$\sum_{n=0}^{N-1} ar^n = a\left(\frac{1-r^N}{1-r}\right)$$

= 1.96875

for $|r| < 1$: series converges

$$\sum_{n=0}^{\infty} ar^n = a\left(\frac{1}{1-r}\right)$$

= 2

Modeling *F*(*Q*) for a CTR

Ex. $PbTiO_3$ / $SrTiO_3$ (001)

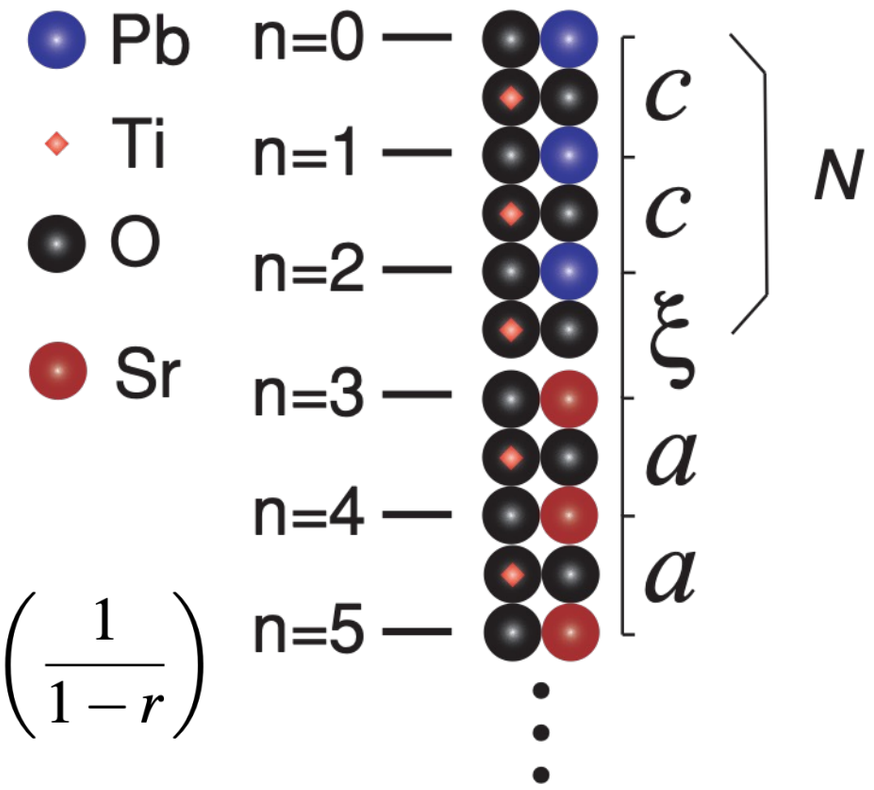
$$F_{\mathrm{CTR}}(\mathbf{Q}) = N_1 N_2 F_{\mathrm{column}}(\mathbf{Q})$$

$$F_{\mathrm{column}}(\mathbf{Q}) = \sum_{n=0}^{\infty} F_n^{\text{unit cell}}(\mathbf{Q}) e^{-n(iQ_z d_n + d_n/\zeta_n)}$$

for $r = e^{ix}$ in $\sum_{n=0}^{N-1} ar^n = a\left(\frac{1-r^N}{1-r}\right)$ or $\sum_{n=0}^{\infty} ar^n = a\left(\frac{1}{1-r}\right)$

$$\sum_{n=0}^{N-1} e^{ixn} = \frac{1-e^{ixN}}{1-e^{ix}}$$

$$\sum_{n=0}^{\infty} e^{-ixn} = \frac{1}{1-e^{-ix}}$$



Modeling *F*(*Q*) for a CTR

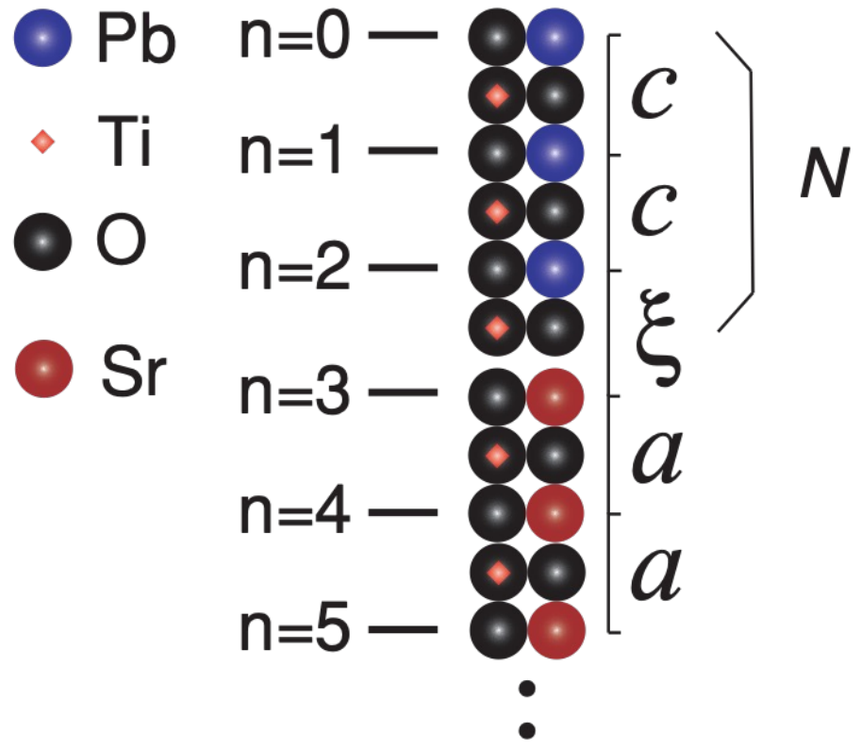
Ex. $PbTiO_3$ / $SrTiO_3$ (001)

$$F_{\mathrm{CTR}}(\mathbf{Q}) = N_1 N_2 F_{\mathrm{column}}(\mathbf{Q})$$

$$F_{\mathrm{column}}(\mathbf{Q}) = \sum_{n=0}^{\infty} F_n^{\text{unit cell}}(\mathbf{Q}) e^{-n(iQ_z d_n + d_n/\zeta_n)}$$

$$F_{\mathrm{column}}(\mathbf{Q}) = F_{\mathrm{PbTiO_3}}^{\text{unit cell}}(\mathbf{Q}) \left(\frac{1 - e^{-iNQ_z c}}{1 - e^{-iQ_z c}} \right)$$

$$+ e^{-iQ_z((N-1)c+\xi)} F_{\mathrm{SrTiO_3}}^{\text{unit cell}}(\mathbf{Q}) \frac{1}{1 - e^{-iQ_z a}}$$



or if *N* is not too big, and you can fit many parameters:

$$= f_{\mathrm{Pb}} \sum_{j=1}^{N_{\mathrm{Pb}}} e^{i\mathbf{Q}\cdot\mathbf{r}_j} + f_{\mathrm{Ti}} \sum_{j=1}^{N_{\mathrm{Ti}}} e^{i\mathbf{Q}\cdot\mathbf{r}_j} + f_{\mathrm{O}} \sum_{j=1}^{N_{\mathrm{O}}} e^{i\mathbf{Q}\cdot\mathbf{r}_j} + F_{\mathrm{SrTiO_3}}^{\text{unit cell}}(\mathbf{Q}) \frac{1}{1 - e^{-iQ_z a}}$$

Modeling *F*(*Q*) for a CTR

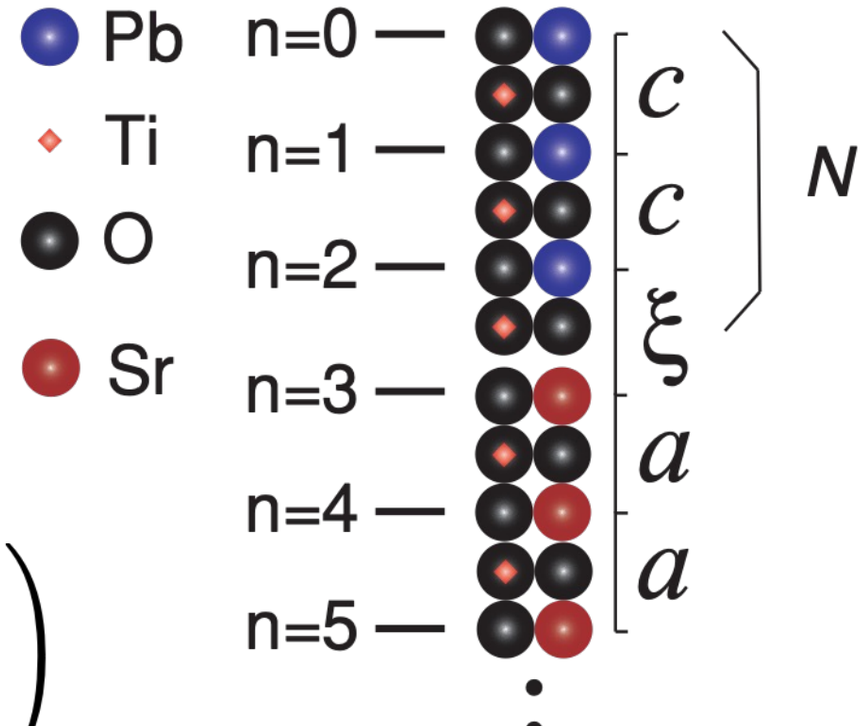
Ex. $PbTiO_3$ / $SrTiO_3$ (001)

$$F_{\mathrm{CTR}}(\mathbf{Q}) = N_1 N_2 F_{\mathrm{column}}(\mathbf{Q})$$

$$F_{\mathrm{column}}(\mathbf{Q}) = \sum_{n=0}^{\infty} F_n^{\text{unit cell}}(\mathbf{Q}) e^{-n(iQ_z d_n + d_n/\zeta_n)}$$

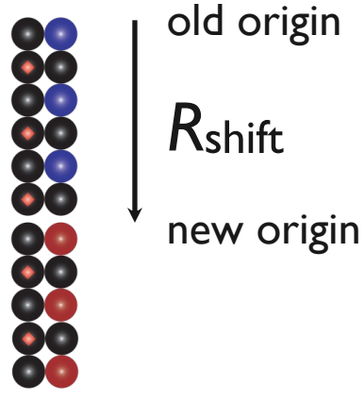
$$F_{\mathrm{column}}(\mathbf{Q}) = F_{\mathrm{PbTiO_3}}^{\text{unit cell}}(\mathbf{Q}) \left(\frac{1 - e^{-iNQ_z c} e^{-Nc/\zeta_{\mathrm{PbTiO_3}}}}{1 - e^{-iQ_z c} e^{-c/\zeta_{\mathrm{PbTiO_3}}}} \right)$$

$$+ e^{-iQ_z((N-1)c+\xi)} e^{-((N-1)c+\xi)/\zeta_{\mathrm{PbTiO_3}}} F_{\mathrm{SrTiO_3}}^{\text{unit cell}}(\mathbf{Q}) \frac{1}{1 - e^{-iQ_z a} e^{-a/\zeta_{\mathrm{SrTiO_3}}}}$$



$$F_{\mathrm{column}}(\mathbf{Q}) = S(\mathbf{Q}) + B(\mathbf{Q})$$

Note that you can move the origin by multiplying by $e^{iQ_z \cdot R_{\mathrm{shift}}}$



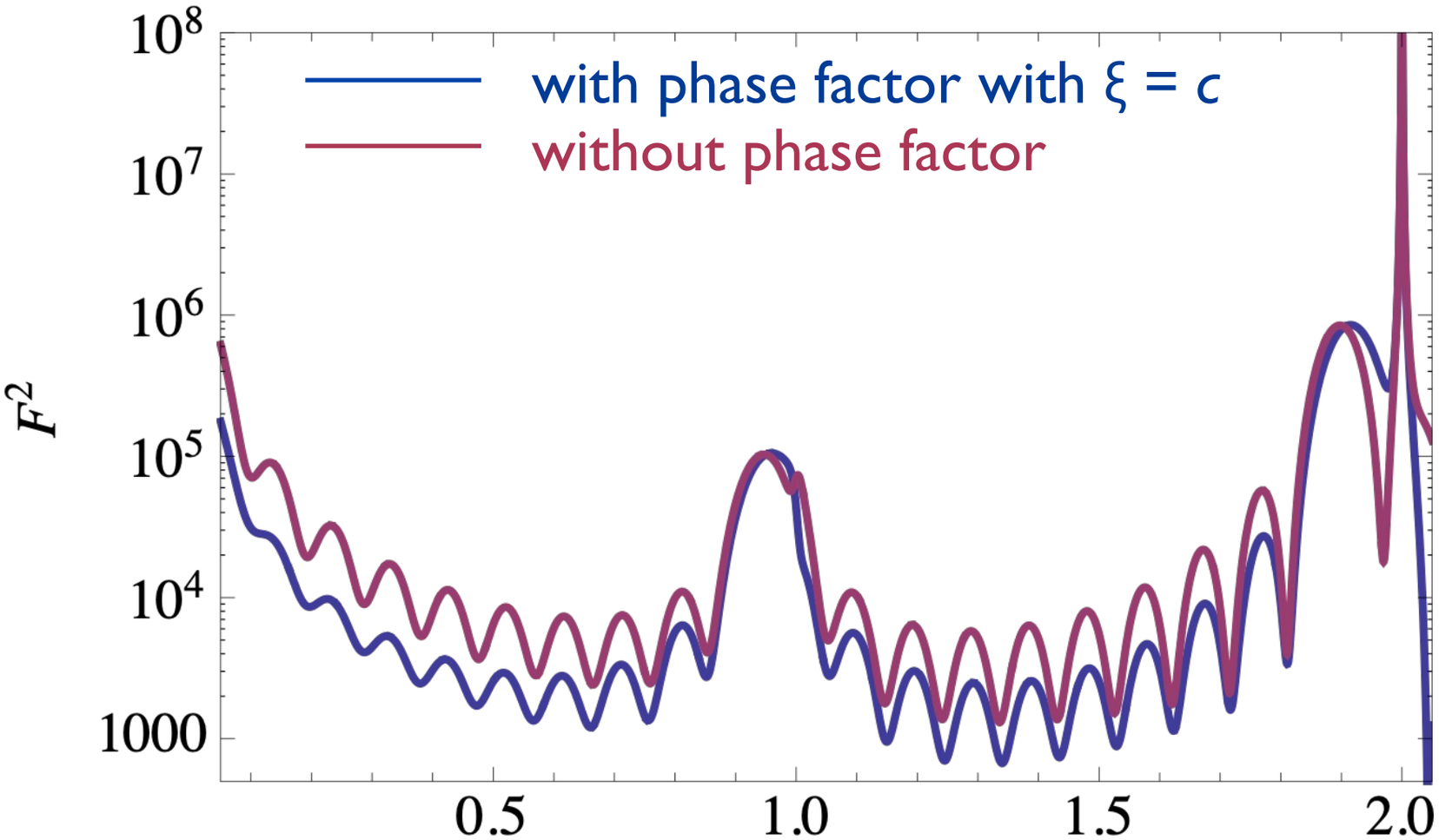
D. D. Fong and C. Thompson, Annu. Rev. Mater. Res. **36,** 431 (2006)

Modeling *F*(*Q*) for a CTR

Don't forget the phase factor

- Ex. $PbTiO_3$ / $SrTiO_3$ (001)

$$F_{\text{column}}(\mathbf{Q}) = F^{\text{unit cell}}_{PbTiO_3}(\mathbf{Q})\left(\frac{1-e^{-iNQ_zc}}{1-e^{-iQ_zc}}\right) + F^{\text{unit cell}}_{SrTiO_3}(\mathbf{Q})\frac{1}{1-e^{-iQ_za}}$$



$$\text{thickness} = \frac{a_{\text{ref}}}{\Delta_{\text{minima}}} \sim \frac{a_{\text{ref}}}{\text{FWHM}_{\text{Bragg}}}$$

Modeling *F*(*Q*) for a CTR

Unit cell structure factor:

$$F_{PbTiO_3}^{\text{unit cell}}(\mathbf{Q}) = \sum_{j=1}^{N_{uc}} f_j(Q) e^{-B_j(Q/4\pi)^2} e^{i\mathbf{Q}\cdot\mathbf{R}_j}$$

$$= f_{O(1)}(Q) e^{-B_{O(1)}(Q/4\pi)^2}$$

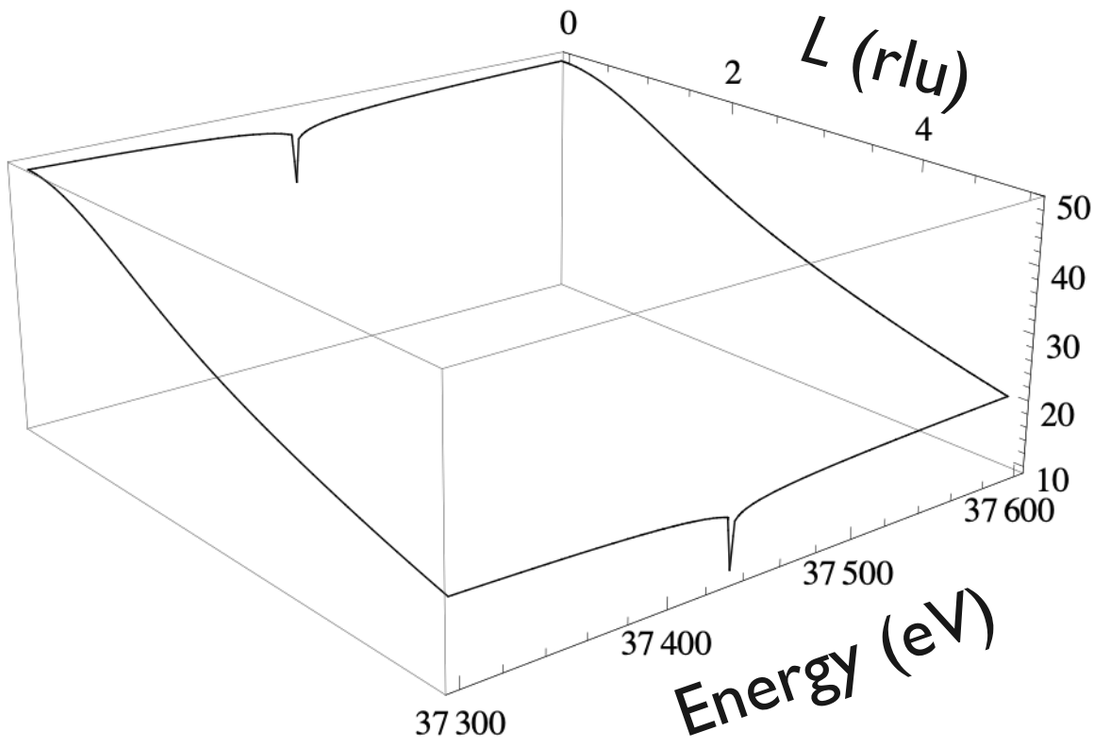
Atomic form factor:

$$+ f_{O(2)}(Q) e^{-B_{O(2)}(Q/4\pi)^2} e^{iQ_y a/2} e^{iQ_z(\pm\delta z_{O(2)} - c/2)}$$

$$+ f_{O(2)}(Q) e^{-B_{O(2)}(Q/4\pi)^2} e^{iQ_x a/2} e^{iQ_y a/2} e^{iQ_z(\pm\delta z_{O(2)} - c/2)}$$

$$+ f_{Ti}(Q) e^{-B_{Ti}(Q/4\pi)^2} e^{iQ_z(\pm\delta z_{Ti} - c/2)}$$

$$+ f_{Pb}(Q) e^{-B_{Pb}(Q/4\pi)^2} e^{iQ_x a/2} e^{iQ_y a/2} e^{iQ_z(\pm\delta z_{Pb})}$$



Re(f_{Ba})

$$f(Q,E) = f_0(Q) + f'(E) + if''(E)$$

see f0_WaasKirf.dat
- based on Waasmaier-Kirfel model:
D. Waasmaier & A. Kirfel, Acta Cryst. **A51,** 416-413 (1995).

see http://henke.lbl.gov/optical_constants/sf/sf.tar.gz, from D.T. Cromer & D. Liberman, Acta Cryst. **A37,** 267 (1981) or http://www.tagen.tohoku.ac.jp/general/building/iamp/database/scm/AXS/ from Y. Waseda, Novel Application of Anomalous (Resonance) X-ray Scattering for Structural Characterization of Disordered Materials. New York. Springer. 1984

Modeling *F*(*Q*) for a CTR

Debye-Waller factors

- need to look up in the literature
  - e.g., *isotropic Debye Waller factors*

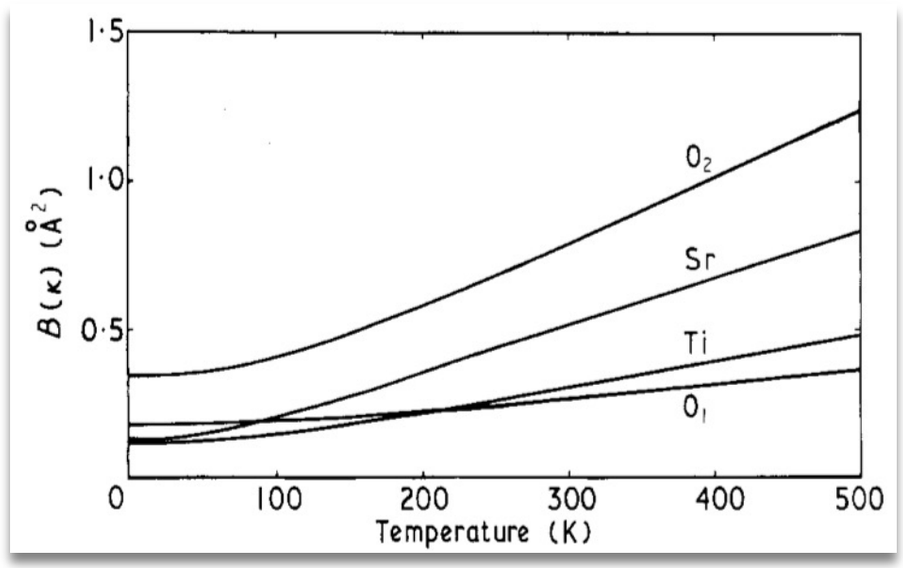


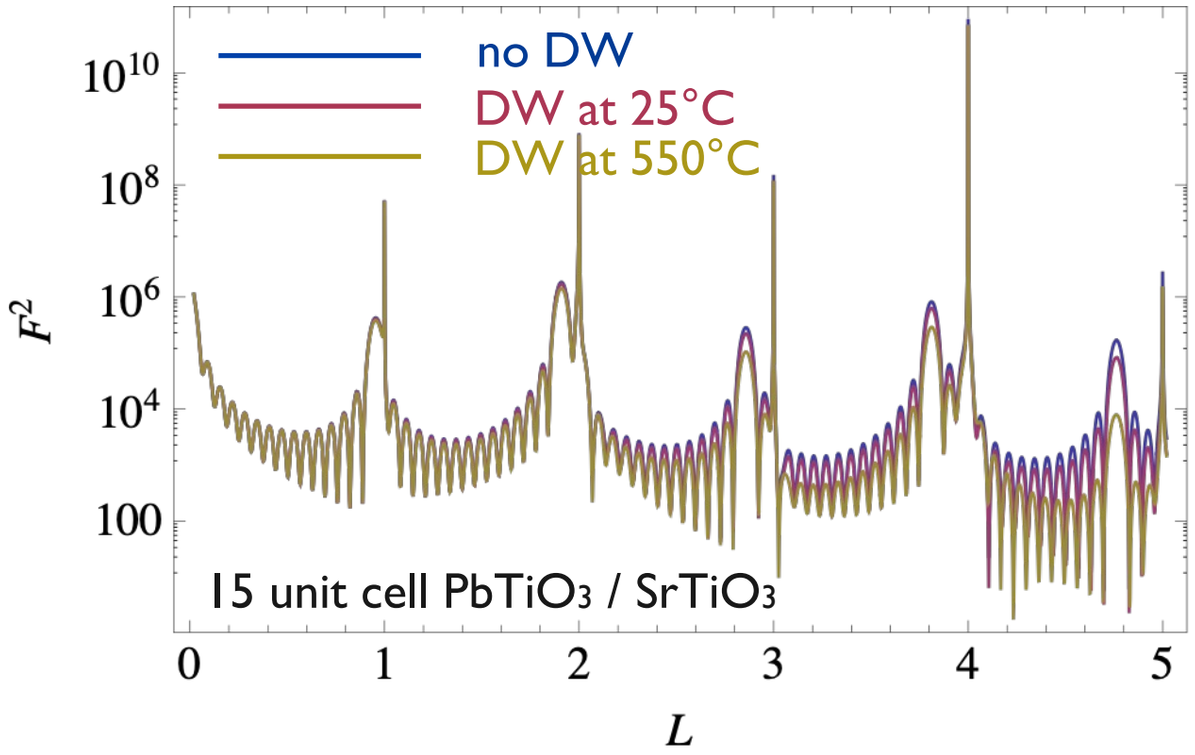
Table 5. Calculated temperature factors $B(\kappa)$, Å^2, for models 4, 5 and 6 compared with experimentally determined values for $BaTiO_3$.

Temperature (K)	Model	B(Sr)	B(Ti)	$B(O_1)$	$B(O_2)$
100	4 (90)	0·199	0·135	0·194	0·402
	5 (90)	0·208	0·155	0·185	0·397
	6 (90)	0·228	0·194	0·195	0·399
300	4 (297)	0·492	0·251	0·278	0·807
	5 (297)	0·511	0·303	0·258	0·790
	6 (297)	0·526	0·352	0·275	0·783

for $SrTiO_3$: W. G. Stirling, J. Phys. C **5,** 2711 (1972)

Table 2. *Summary of parameters refined at all temperatures* (Pb *at origin*)

	−183 °C	−115 °C	25 °C	550 °C
Isotropic temperature factor refinement				
δz_{Tl}(Å)	0·167	0·171	0·162	0
$\delta z_{O(1)}$(Å)	0·492	0·479	0·473	0
$\delta z_{O(2)}$(Å)	0·505	0·504	0·486	0
B(Pb)	0·378 (100)	0·757 (84)	0·706 (89)	2·711 (167)
B(Ti)	0·284 (215)	0·364 (187)	0·060 (170)	0·694 (225)
B[O(1)]	0·670 (140)	0·713 (123)	0·351 (117)	1·549 (102)
B[O(2)]	0·498 (98)	0·862 (85)	0·477 (75)	B[O(1)]
R_{nuc}	5·22	5·90	4·35	3·10
R_{prof}	12·47	12·21	10·19	12·07
R_w	15·20	15·87	12·83	16·57

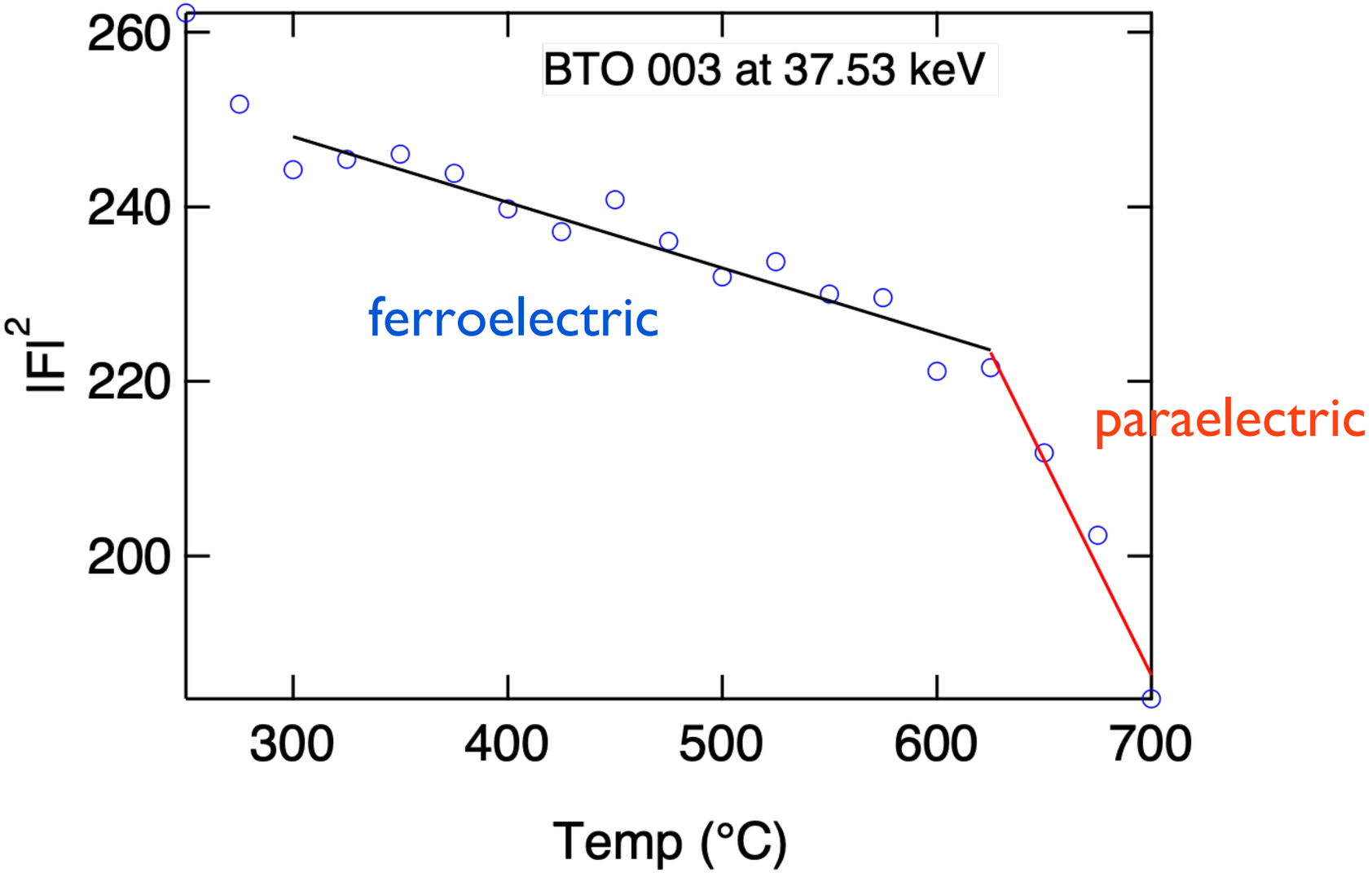


for $PbTiO_3$: A. M. Glazer & S. A. Mabud, Acta Cryst. B **34,** 1065 (1978)

Modeling *F*(*Q*) for a CTR

The Debye-Waller factors depend on phase

- can tell phase transitions by intensity changes
- e.g., for a 15 unit cell thick $BaTiO_3$ / $SrTiO_3$



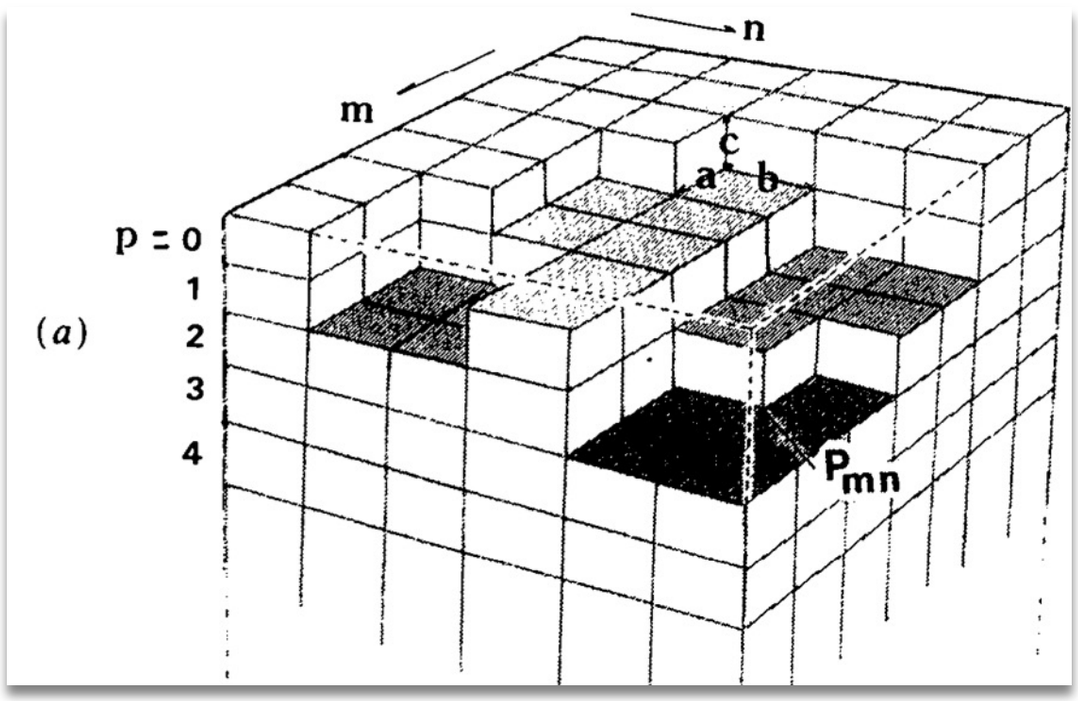
Modeling *F*(*Q*) for a CTR

Continuous roughness

- Gaussian distribution of step heights about a mean surface

$$R^2 = e^{-4\pi^2\langle\Delta p^2\rangle(Q_z - Q_B)^2}$$

σ^2 → mean square deviation of step heights in units of the lattice spacing



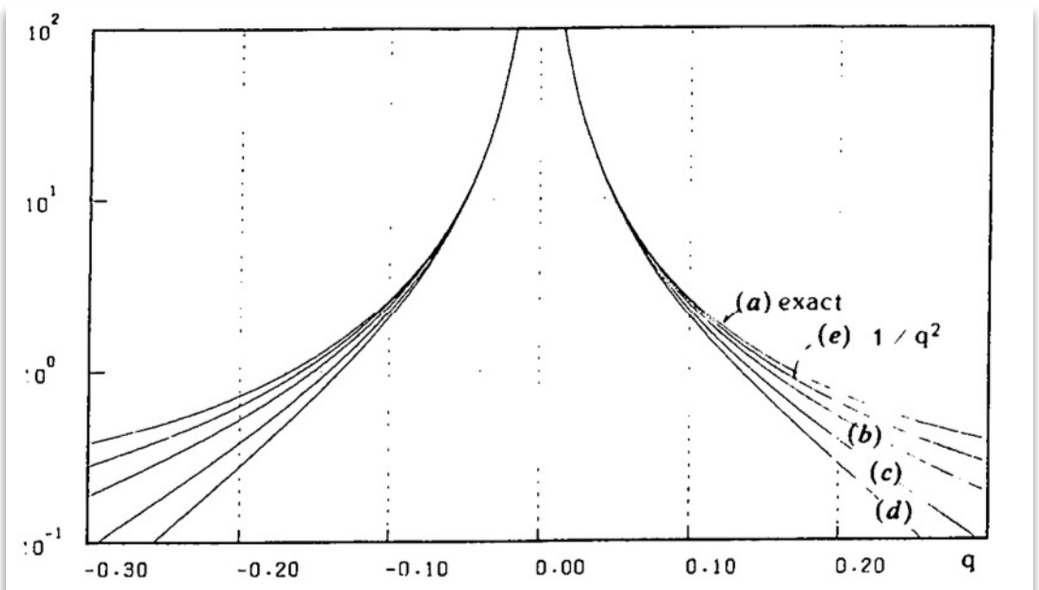


Fig. 6. Intensity change of the CTR scattering along the rod for several different degrees of surface roughness. (*a*) Ideal flat surface; (*b*), (*c*) and (*d*) rough surfaces with $\langle\Delta p^2\rangle = 0.2$, 0.4 and 0.6 in Debye–Waller-like factor, respectively; (*e*) the $1/q^2$ relation, showing its deviation from the exact calculation (*a*) for the ideally flat surface.

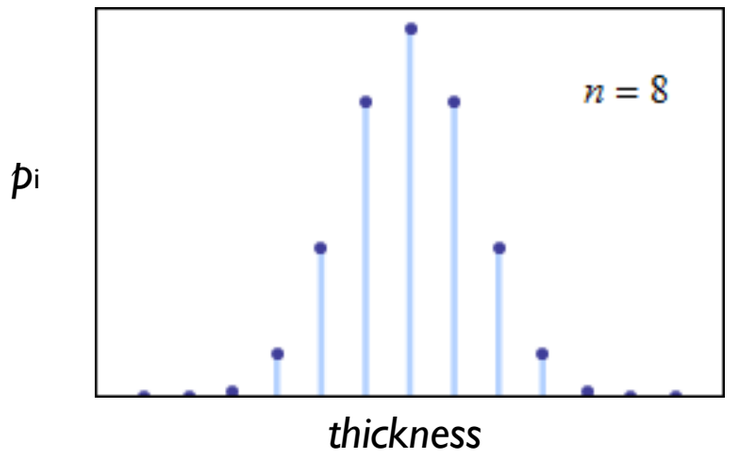
J. Harada, Acta Cryst. A **48,** 764 (1992)

Modeling *F*(*Q*) for a CTR

Discrete roughness - film thickness gradient

- On top of "continuous roughness", we may have thickness non-uniformity of the film
- If we have a Gaussian distribution of thicknesses about a mean thickness, we simply coherently add up contributions from each thickness

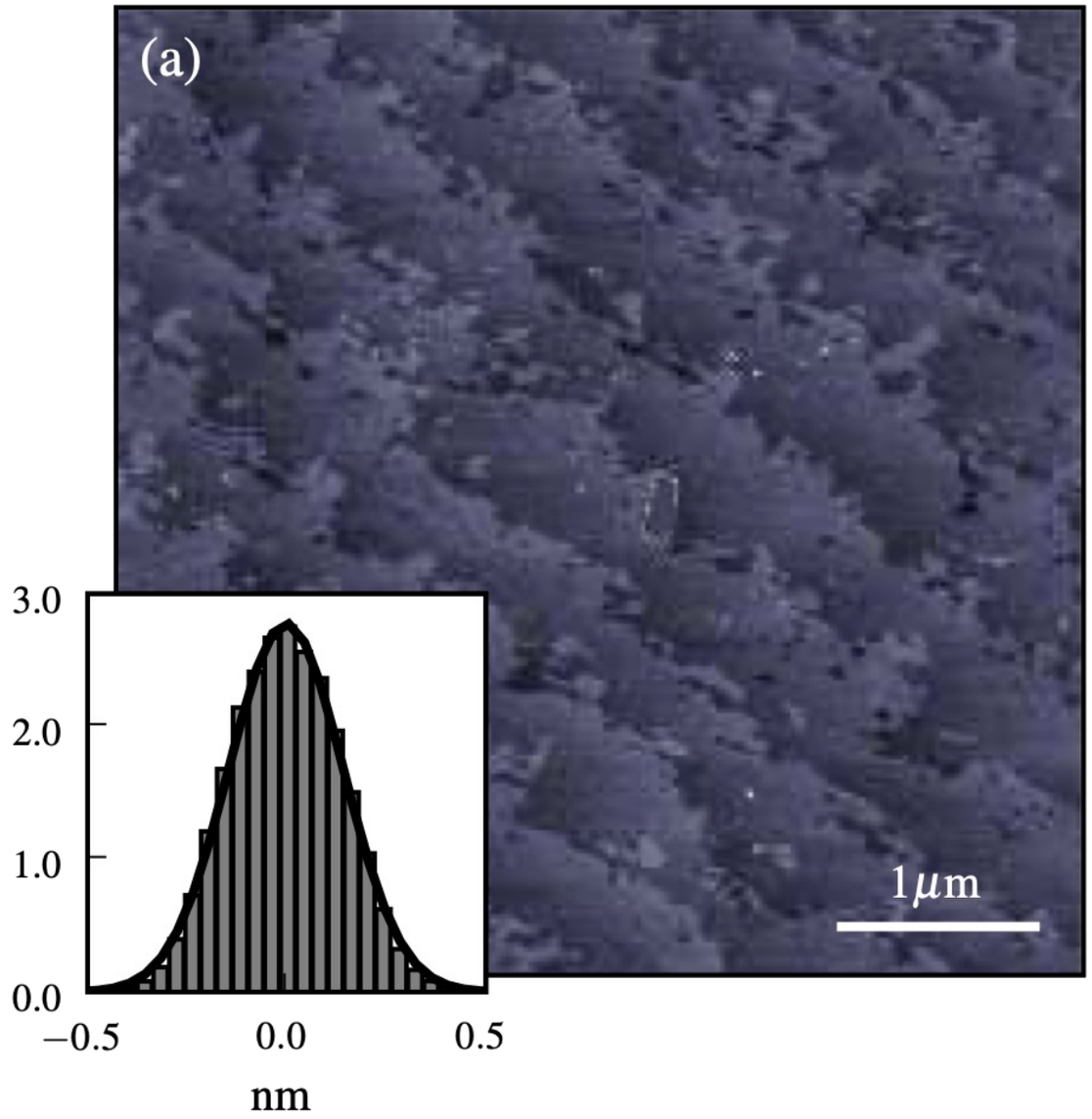
$$F_{\mathrm{CTR}}(\mathbf{Q}) = p_1 F_{\mathrm{thickness\ 1}}(\mathbf{Q}) + p_2 F_{\mathrm{thickness\ 2}}(\mathbf{Q}) + p_3 F_{\mathrm{thickness\ 3}}(\mathbf{Q}) + \ldots$$

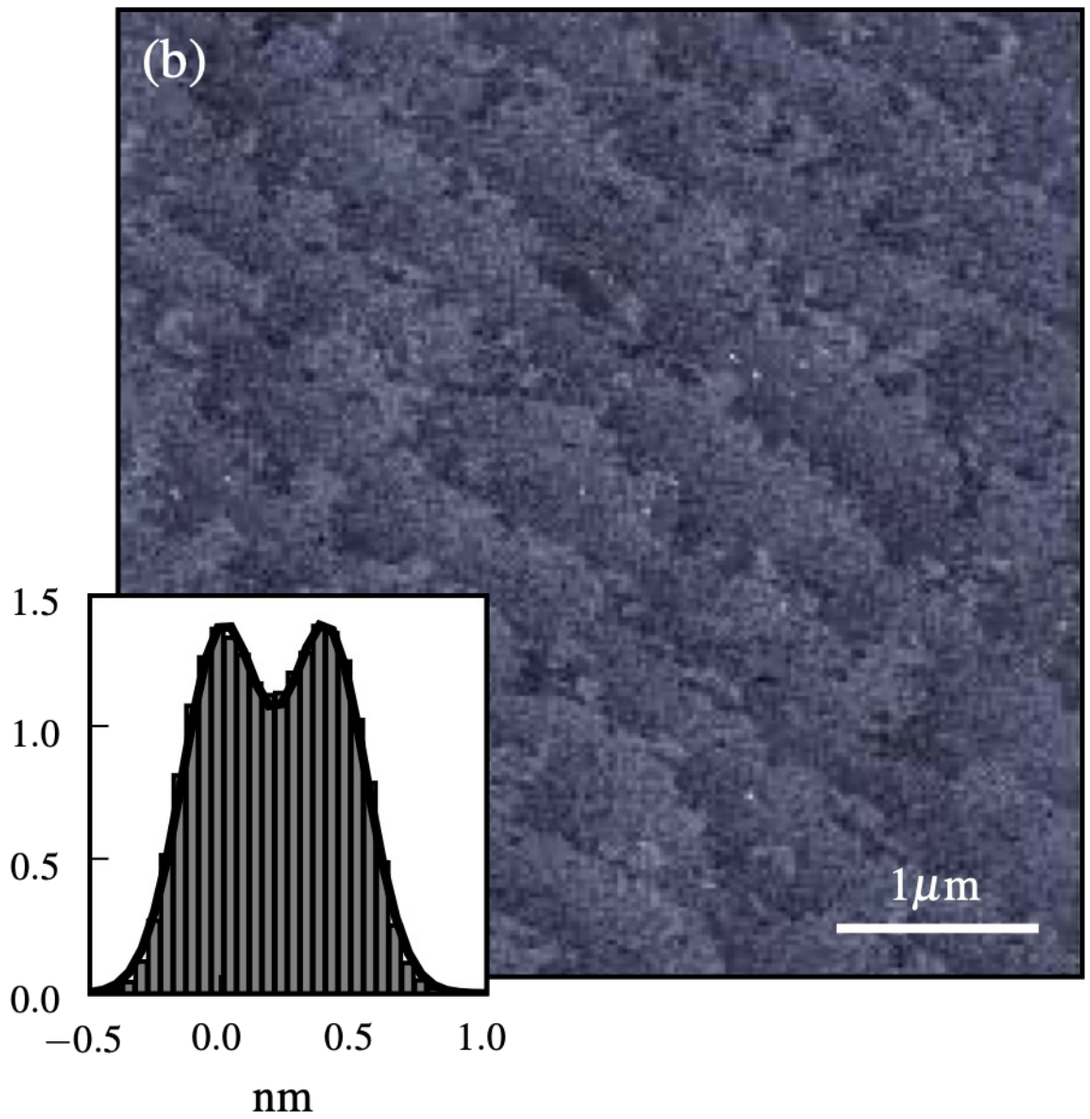


C. Thompson *et al.*, Appl. Phys. Lett. **71,** 3516 (1997)

Modeling *F*(*Q*) for a CTR

AFM of PLD film: bimodal thickness





D. Dale *et al.*, Phys. Rev. B **74,** 085419 (2006)

Modeling *F*(*Q*) for a CTR

Discrete roughness - more general

- can account for non-Gaussian thickness non-uniformity (e.g., bimodal distribution)
  - e.g., *in PLD, for n pulses of (random) growth*

Probability of getting exactly *k* layers to grow at unit cell position *x* after *n* pulses, with each pulse resulting in a coverage of *p* (i.e., binomial distribution)

$$P(X=k)=\binom{n}{k}p^k(1-p)^{(n-k)} \quad \text{where} \quad \binom{n}{k}=\frac{n!}{k!(n-k)!}$$

in our language
p = coverage, θ
$n = \sigma_d^2 / (c^2\,\theta(1-\theta))$

$$R^2=\left[1-4\theta(1-\theta)\sin^2(\pi L)\right]^{\frac{\sigma_d^2}{c^2\theta(1-\theta)}}$$

D. Dale *et al.*, Phys. Rev. B **74,** 085419 (2006)

More on roughness

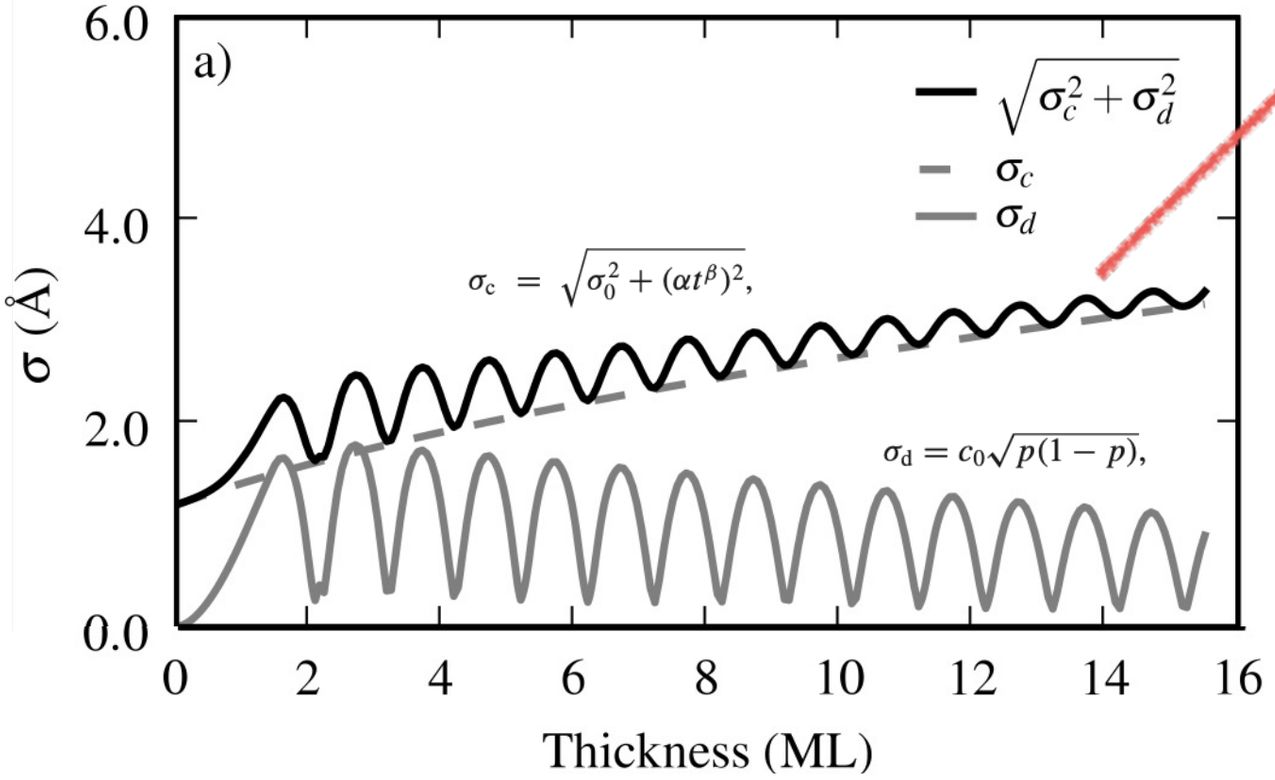
In situ growth & roughness evolution for LSMO/STO(001)

$$\sigma_{\text{total}} = \sqrt{\sigma^2_{\text{continous}} + \sigma^2_{\text{discrete}}}$$ becomes

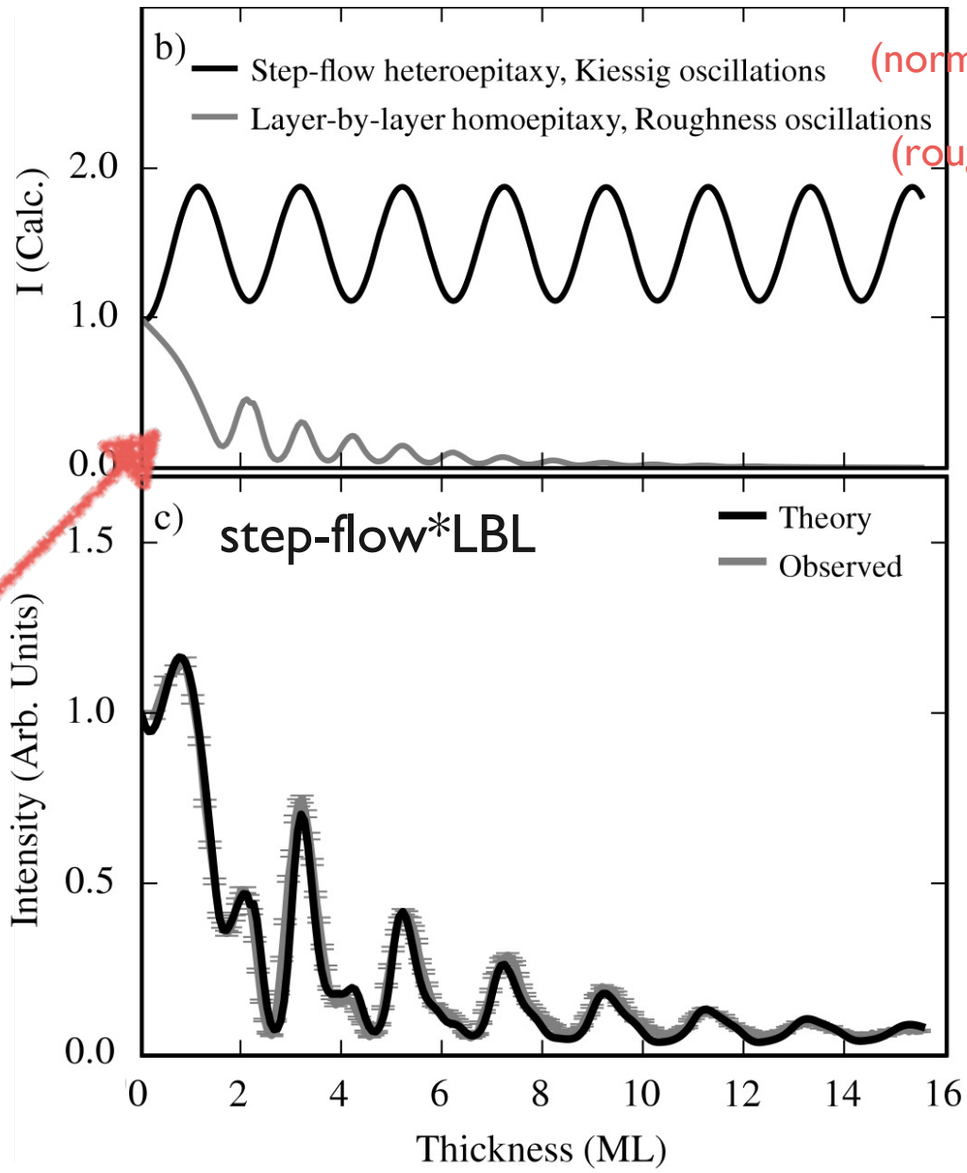
$$R(Q)^2 = e^{\frac{-4\sigma_c^2}{a^2}\sin^2(Q_z a/2)}\left[1 - 4\theta(1-\theta)\sin^2(\pi L)\right]^{\frac{\sigma_d^2}{c^2\theta(1-\theta)}}$$

$$I(Q) = R^2(Q) I_0(Q)$$

Growth of LSMO/STO(001) by PLD



@ 0 0 1/2



(normal osc of F)

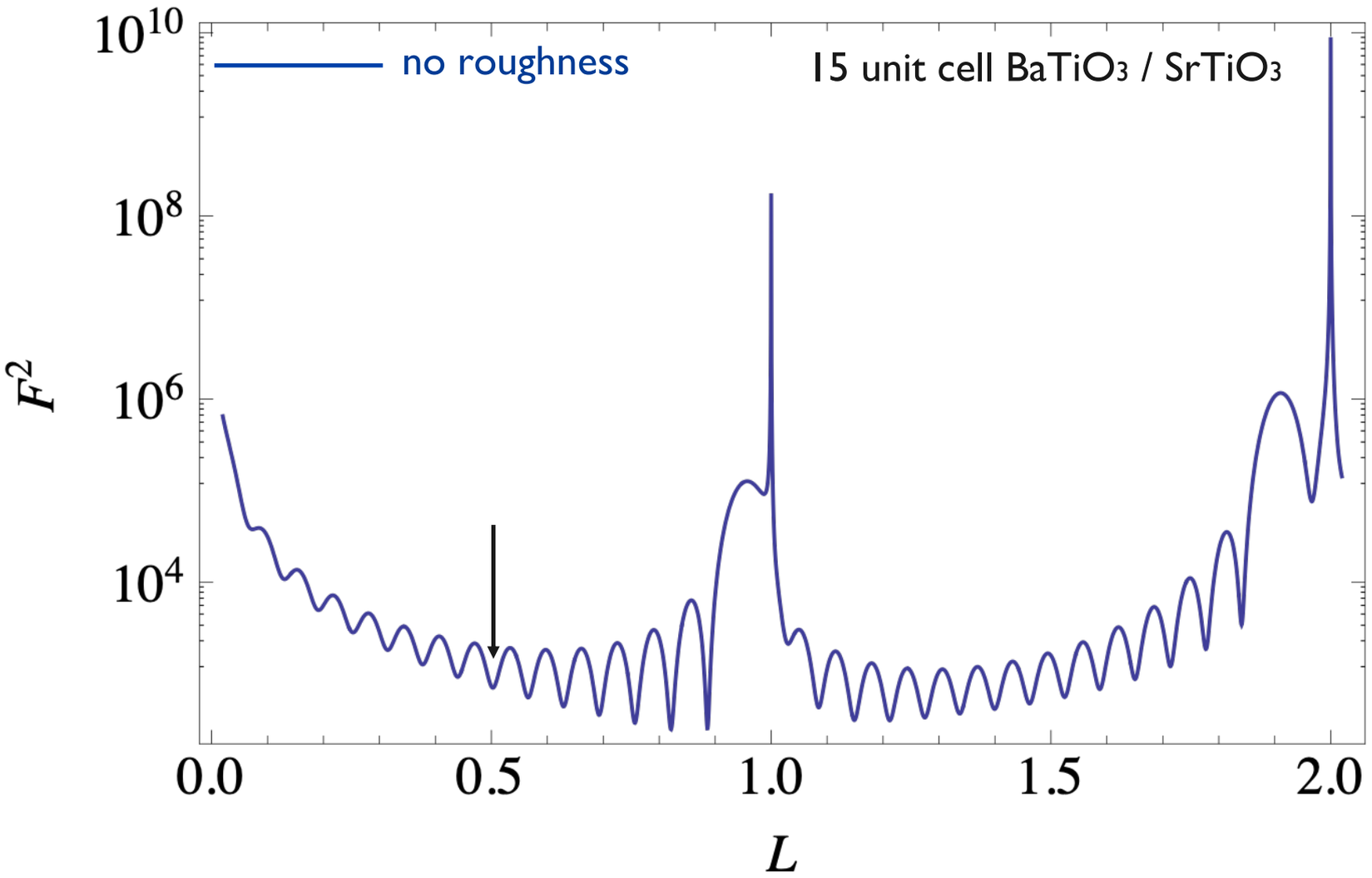
(rough/smooth)

D. Dale *et al.*, J. Phys: Condens. Matter **20,** 264008 (2008)

More on roughness

Dale model: Continuous roughness + discrete roughness

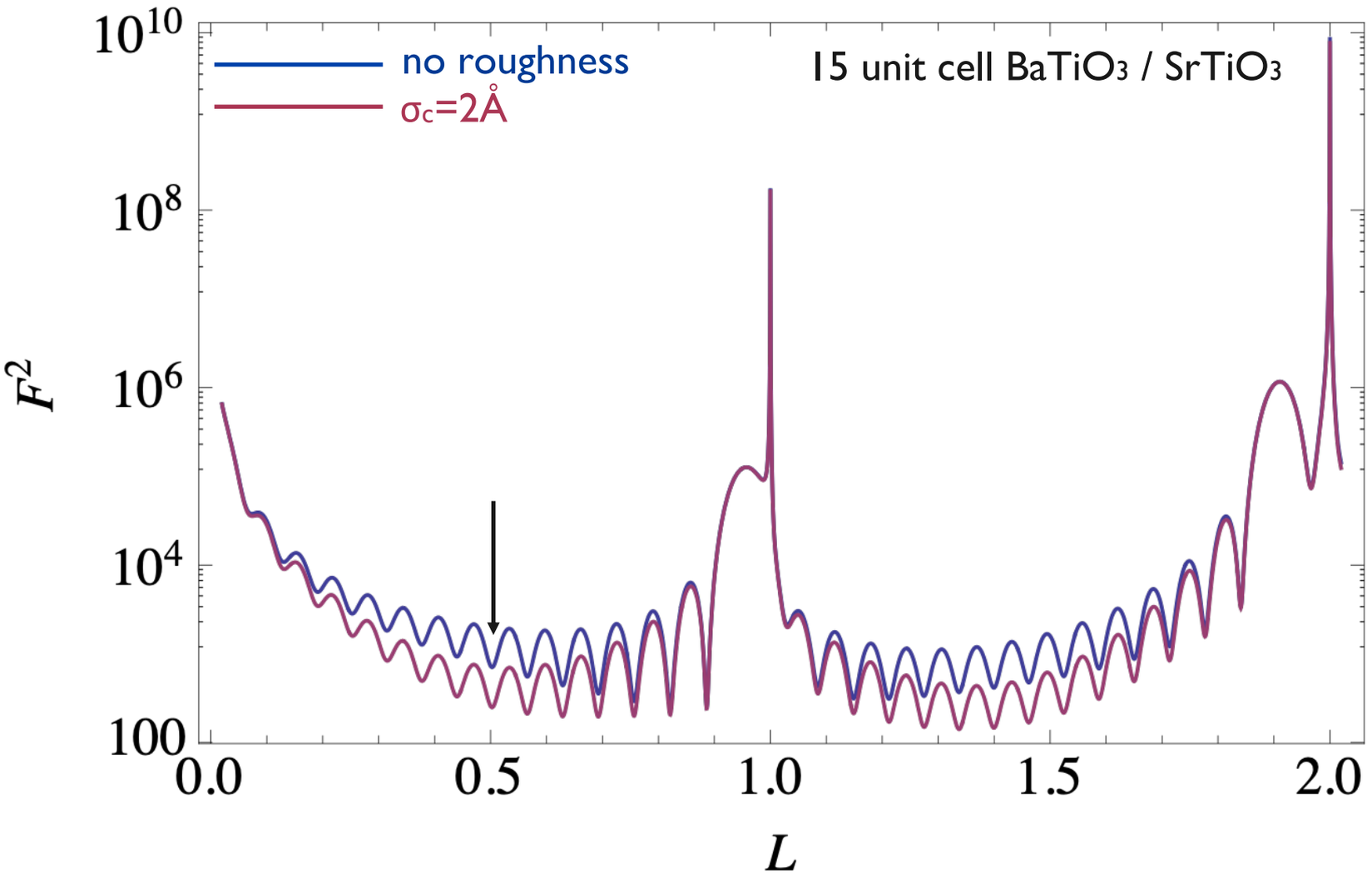
$$\sigma_{\text{total}} = \sqrt{\sigma^2_{\text{continous}} + \sigma^2_{\text{discrete}}}$$



More on roughness

Dale model: Continuous roughness + discrete roughness

$$\sigma_{\text{total}} = \sqrt{\sigma^2_{\text{continous}} + \sigma^2_{\text{discrete}}}$$

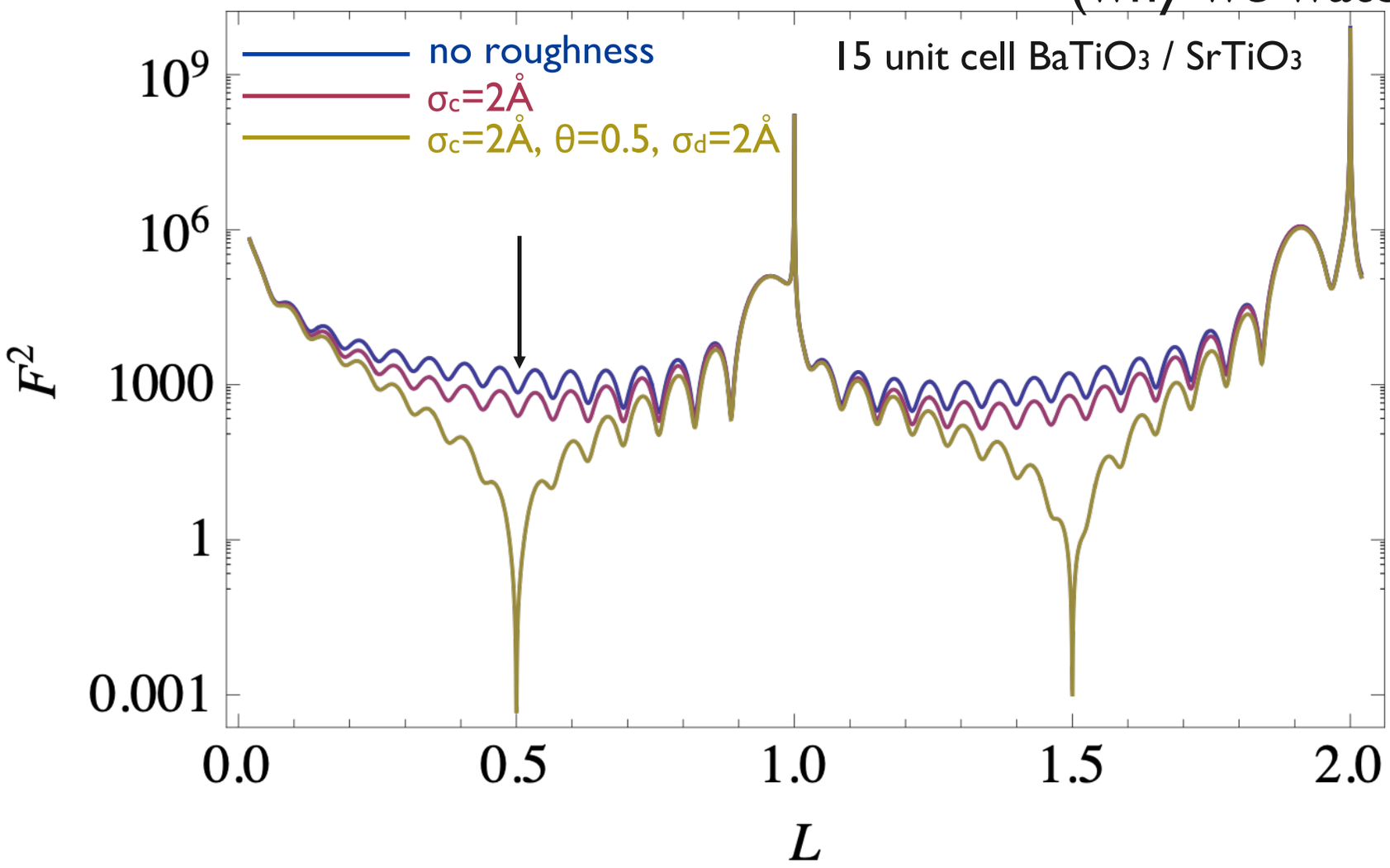


More on roughness

Dale model: Continuous roughness + discrete roughness

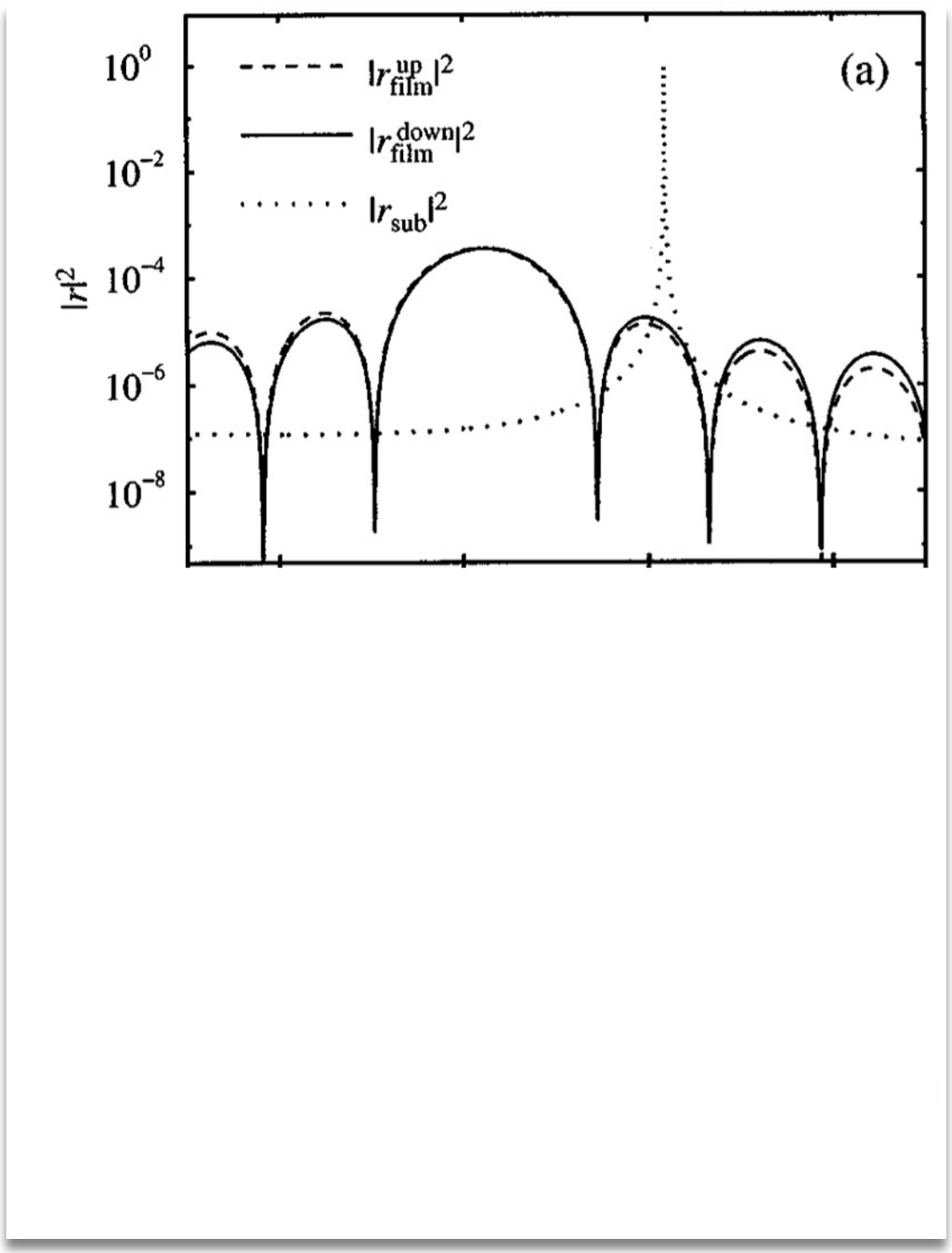
$$\sigma_{\text{total}} = \sqrt{\sigma^2_{\text{continous}} + \sigma^2_{\text{discrete}}}$$

really important at mid-zones
(why we watch during growth)



Fitting example: ferroelectric $PbTiO_3$ / $SrTiO_3$ (001)

Friedel's law: intensities appear the same at Bragg peaks (regardless of centrosymmetry)



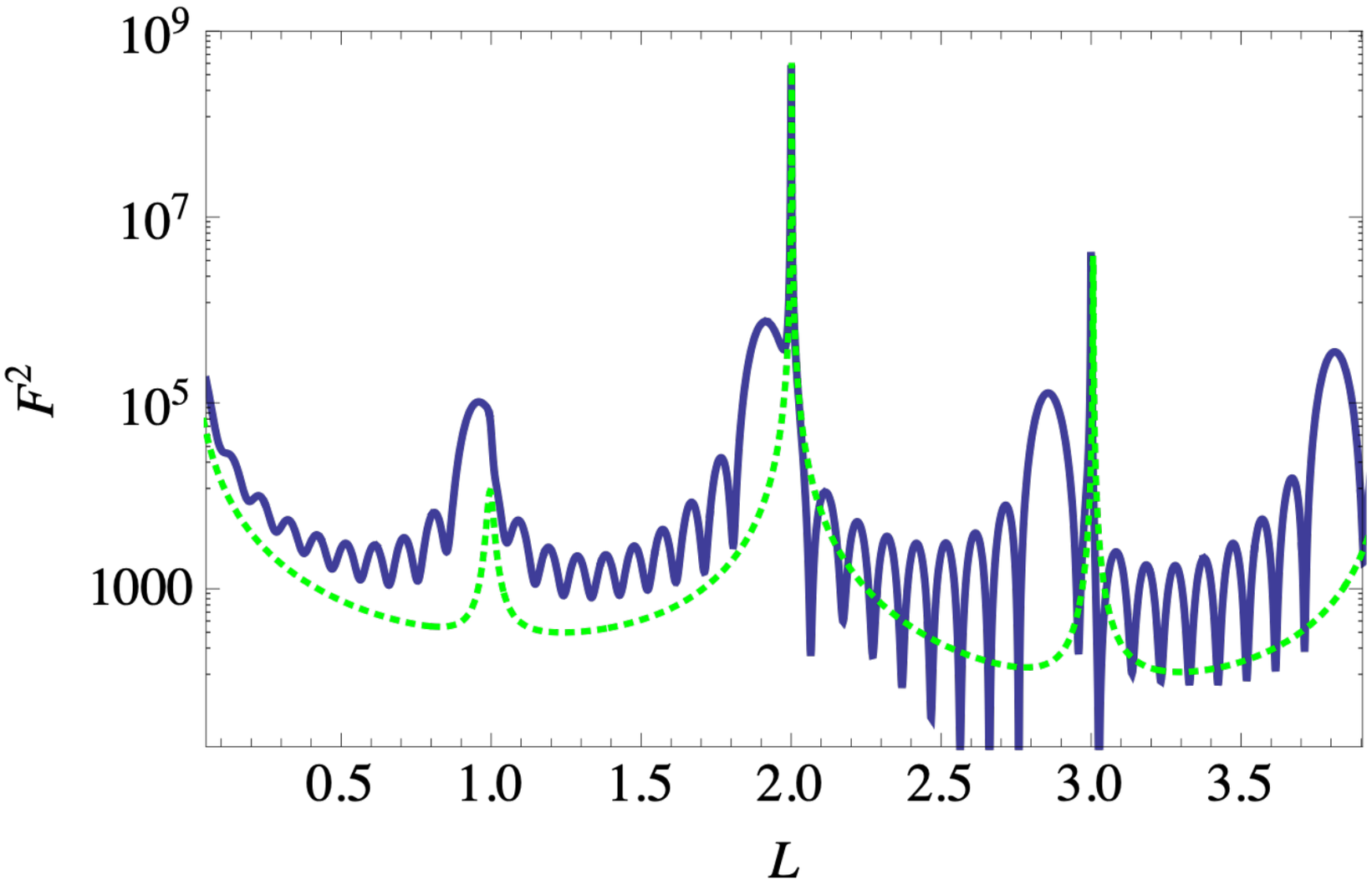
C. Thompson *et al.*, Appl. Phys. Lett. **71,** 3516 (1997)

Example calculations

Thickness fringes - compare to STO

- changes in electron density and/or lattice parameter
  - see *Mathematica file FPTO_STO_scattering_tests.nb*

10uc PTO/STO with c_{film}=4.1 Å, a_{sub}=3.905 Å, ξ = 3.905 Å (both ρ and c)



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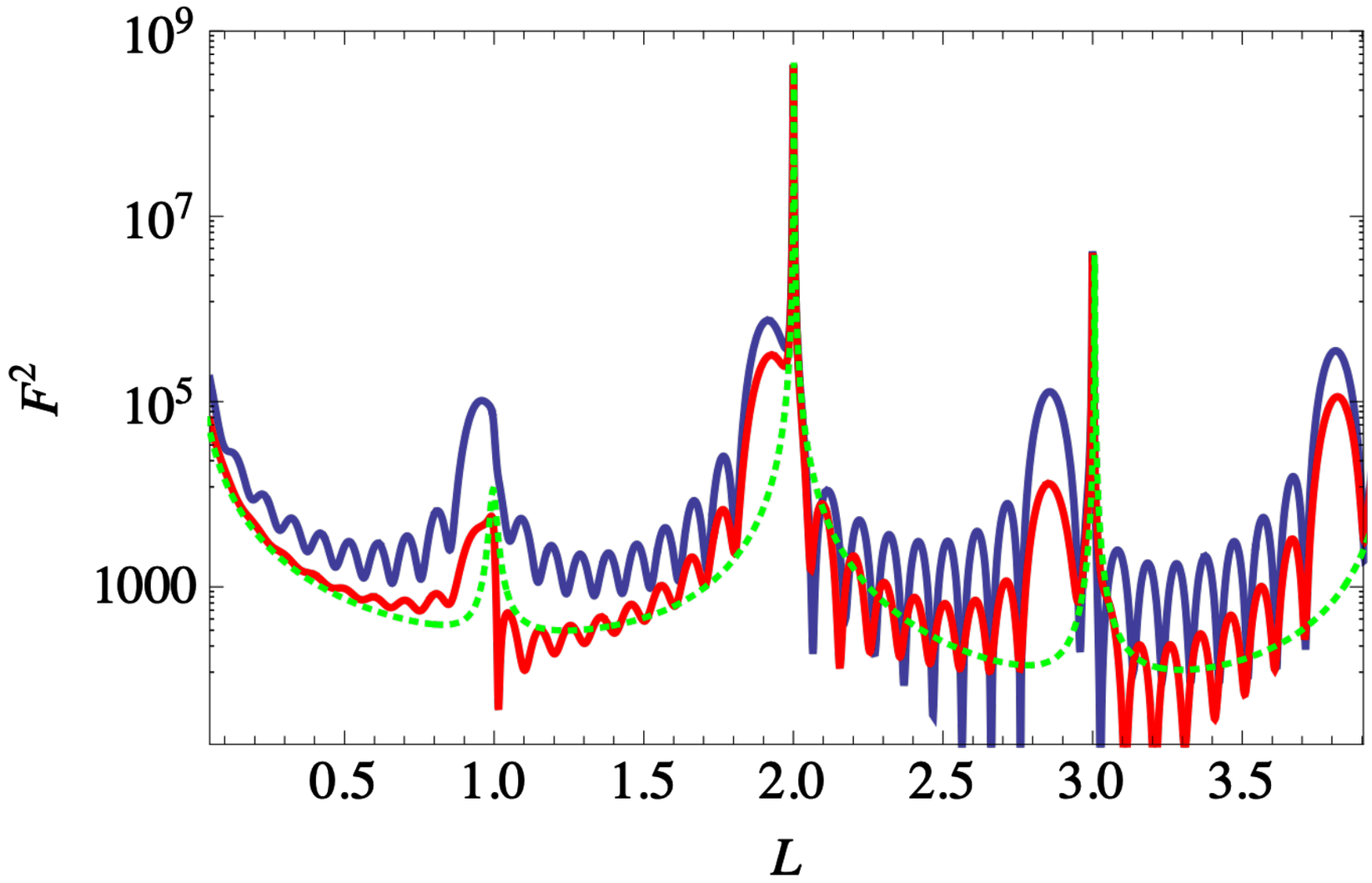
10uc PTO/STO with c_{film}=4.1 Å, a_{sub}=3.905 Å, ξ = 3.905 Å (both ρ and c)

10uc STO/STO with c_{film}=4.1 Å, a_{sub}=3.905 Å, ξ = 3.905 Å (just Δc)

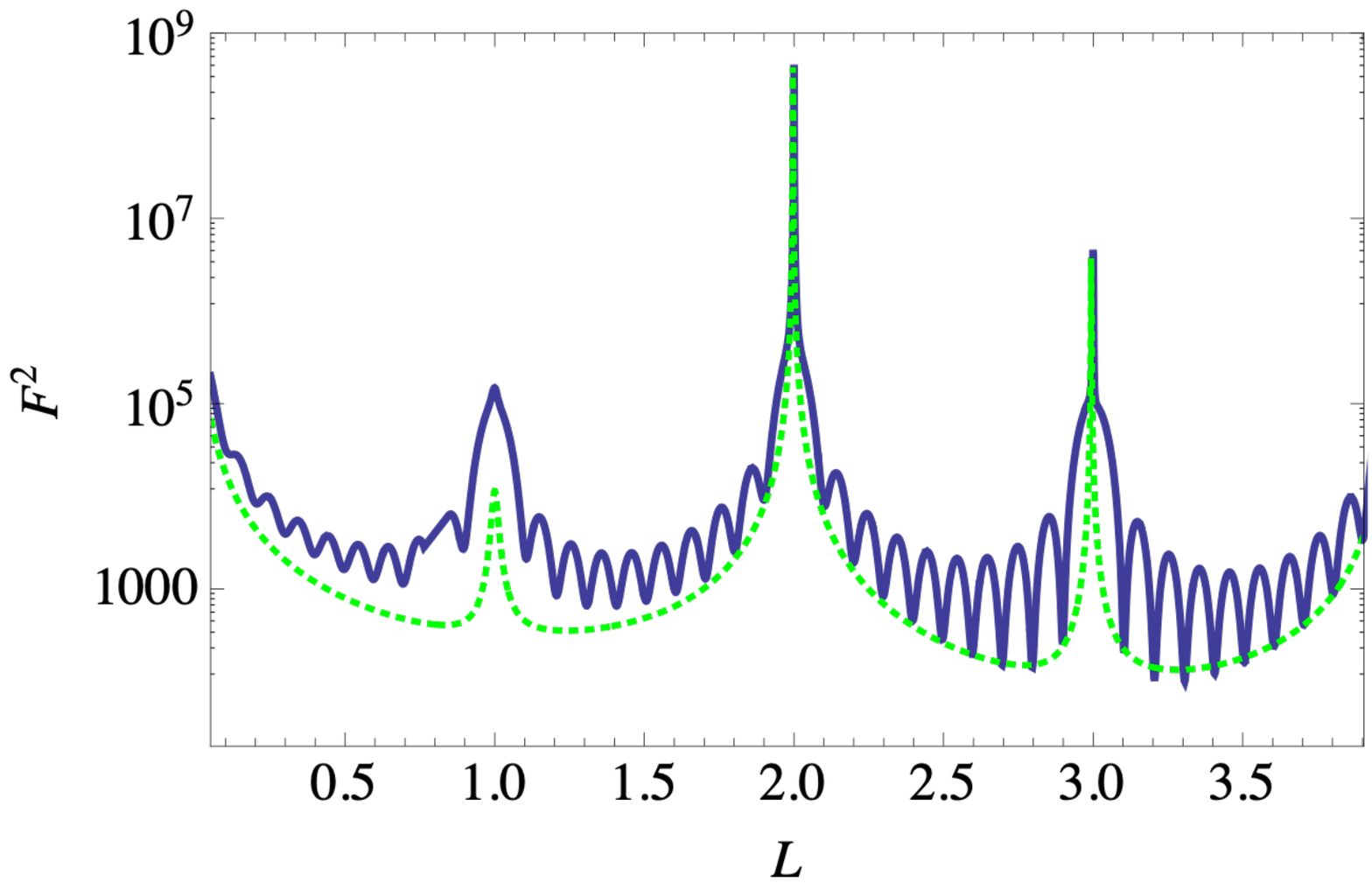


Example calculations

Thickness fringes - compare to STO

- changes in electron density and/or lattice parameter

10uc PTO/STO with c_{film}=3.905 Å, a_{sub}=3.905 Å, ξ = 3.905 Å (just Δρ)



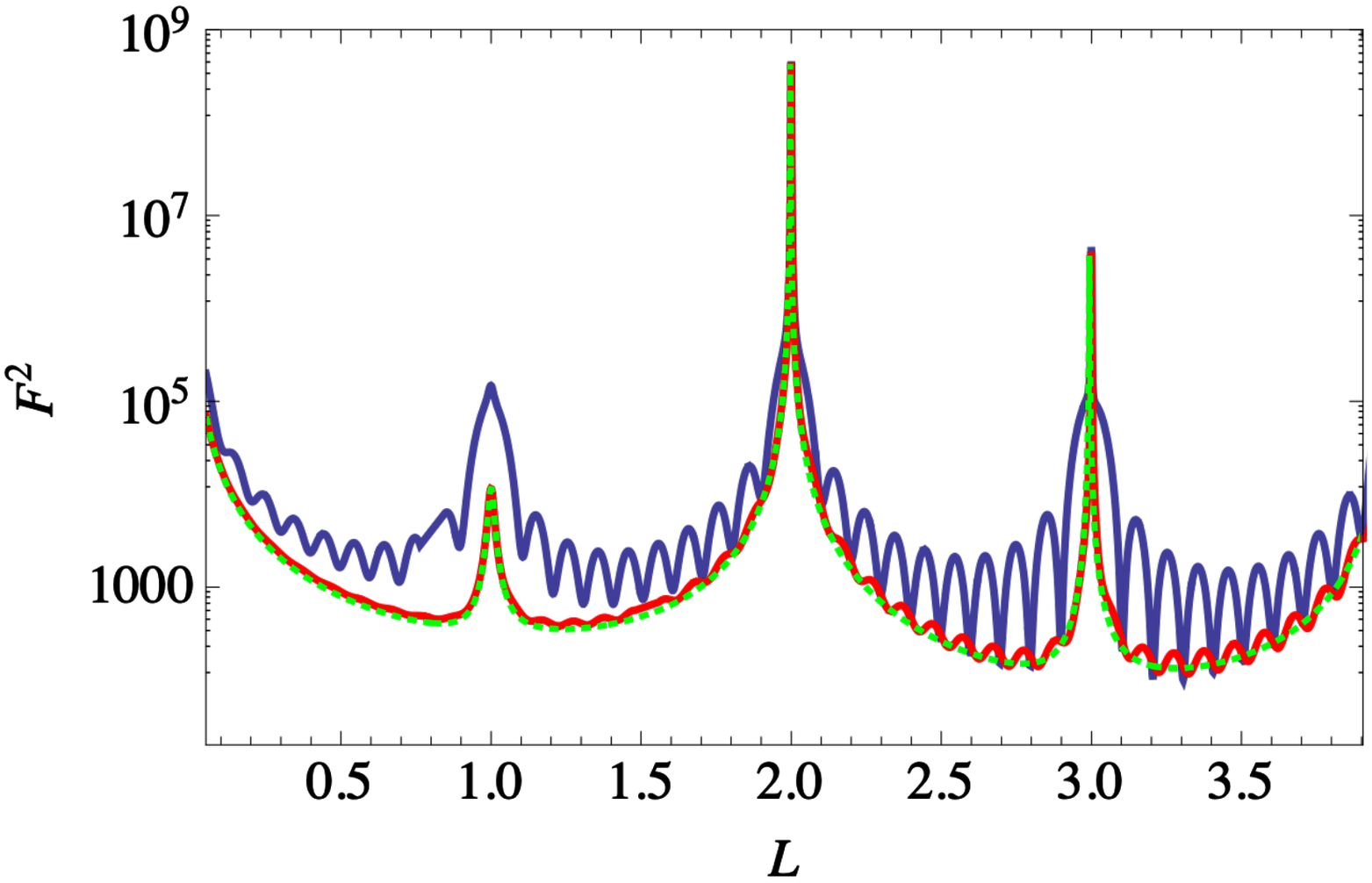
Example calculations

Thickness fringes - compare to STO

- changes in electron density and/or lattice parameter

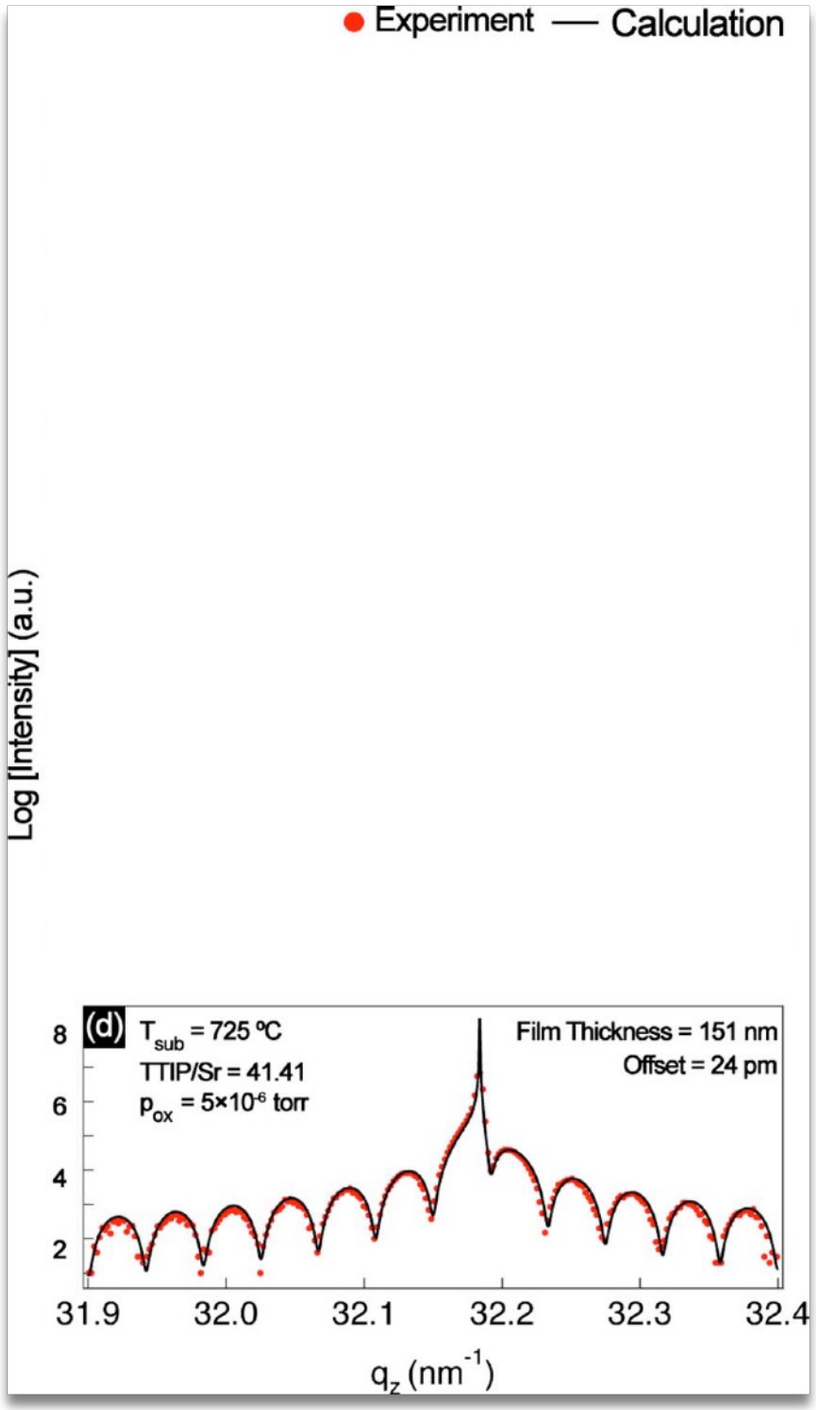
10uc PTO/STO with c_{film}=3.905 Å, a_{sub}=3.905 Å, ξ = 3.905 Å (just Δρ)

10uc STO/STO with c_{film}=3.905 Å, a_{sub}=3.905 Å, ξ = 3.93 Å (just ξ)



Experimental verification - hybrid MBE + MOCVD

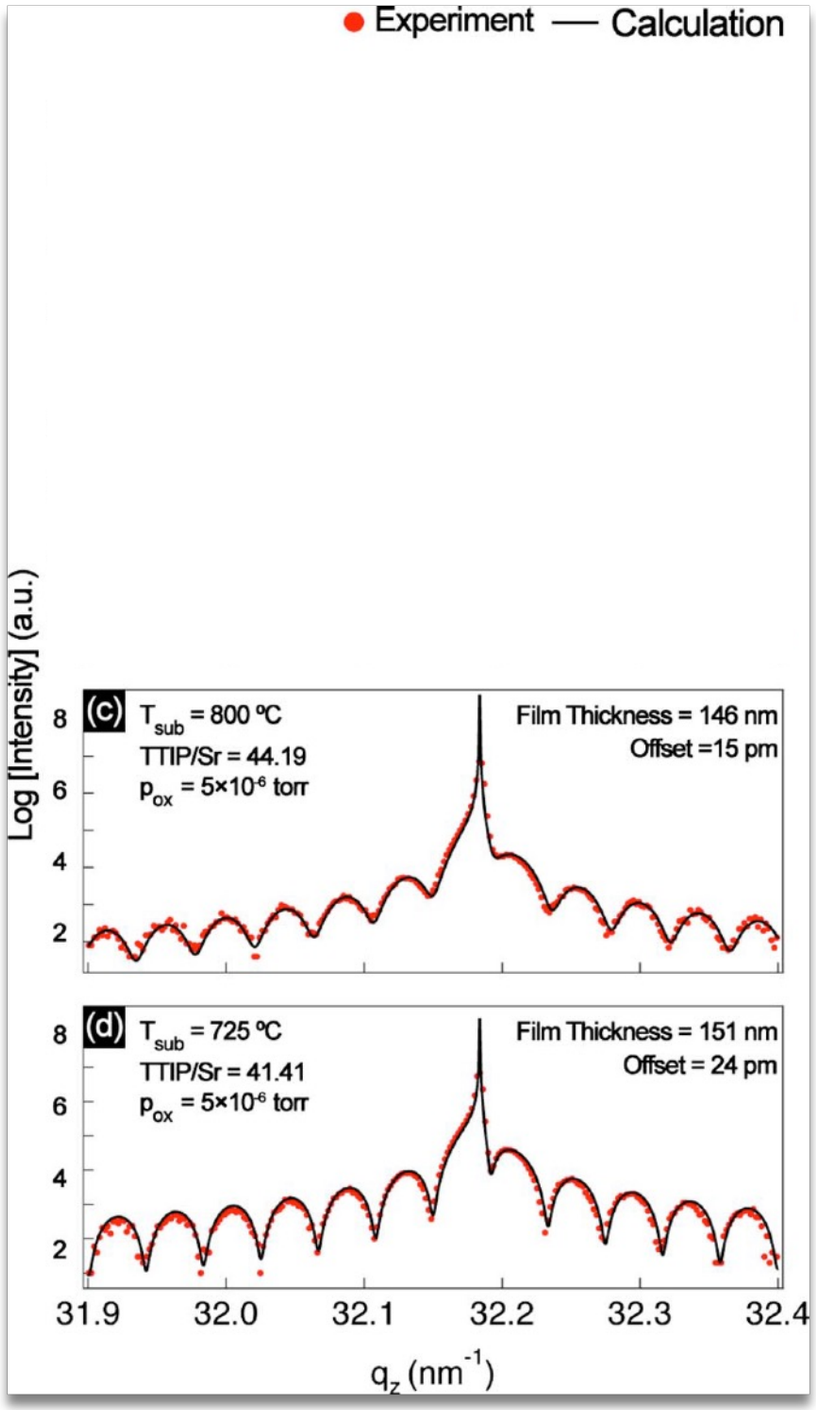
stoichiometric STO on STO



LeBeau *et al.*, Appl. Phys. Lett. **95,** 142905 (2009)

Experimental verification - hybrid MBE + MOCVD

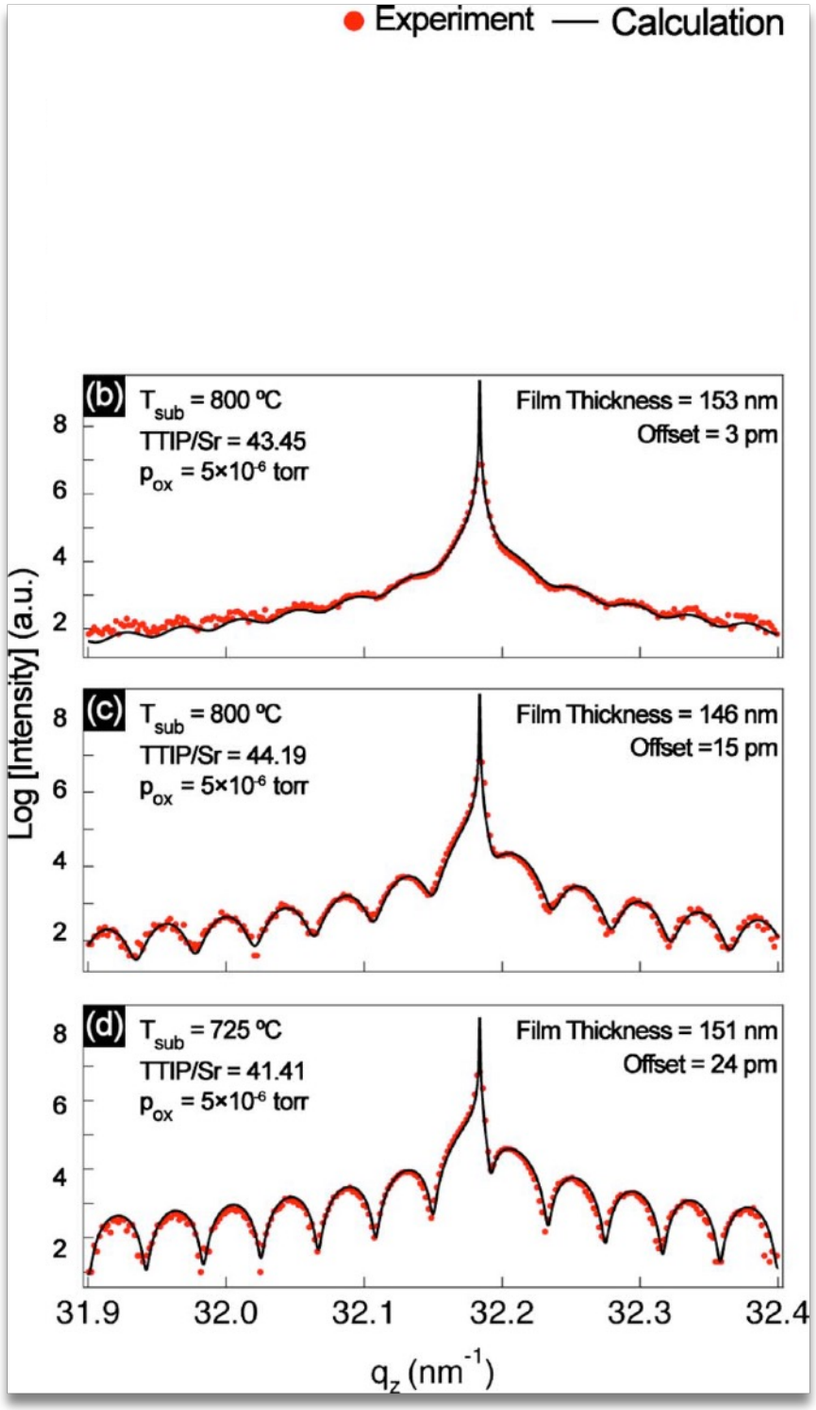
stoichiometric STO on STO



LeBeau *et al.*, Appl. Phys. Lett. **95,** 142905 (2009)

Experimental verification - hybrid MBE + MOCVD

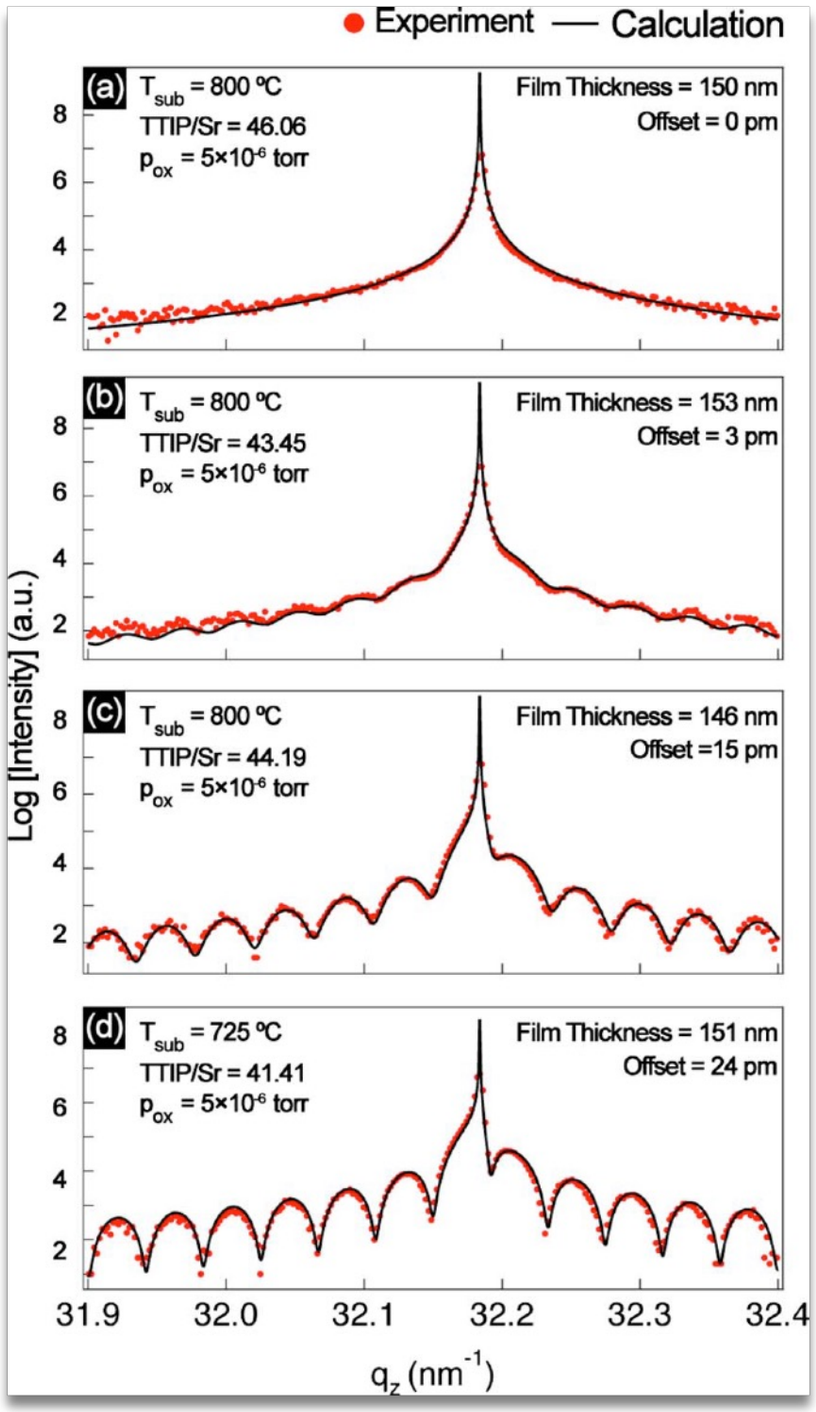
stoichiometric STO on STO



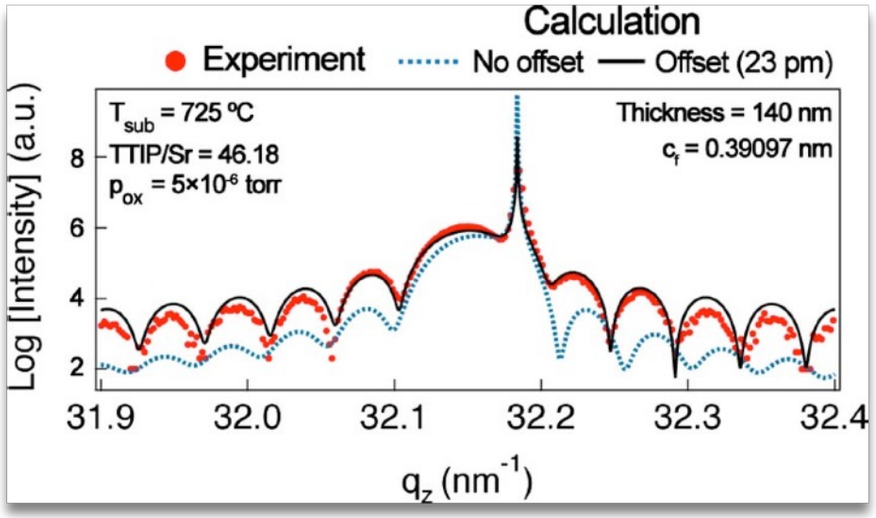
LeBeau *et al.*, Appl. Phys. Lett. **95,** 142905 (2009)

Experimental verification - hybrid MBE + MOCVD

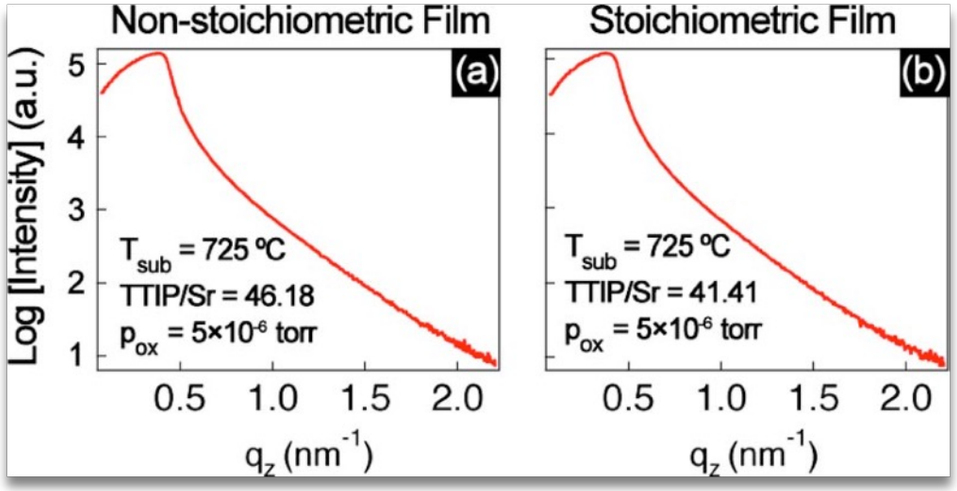
stoichiometric STO on STO



purposefully non-stoichiometric STO

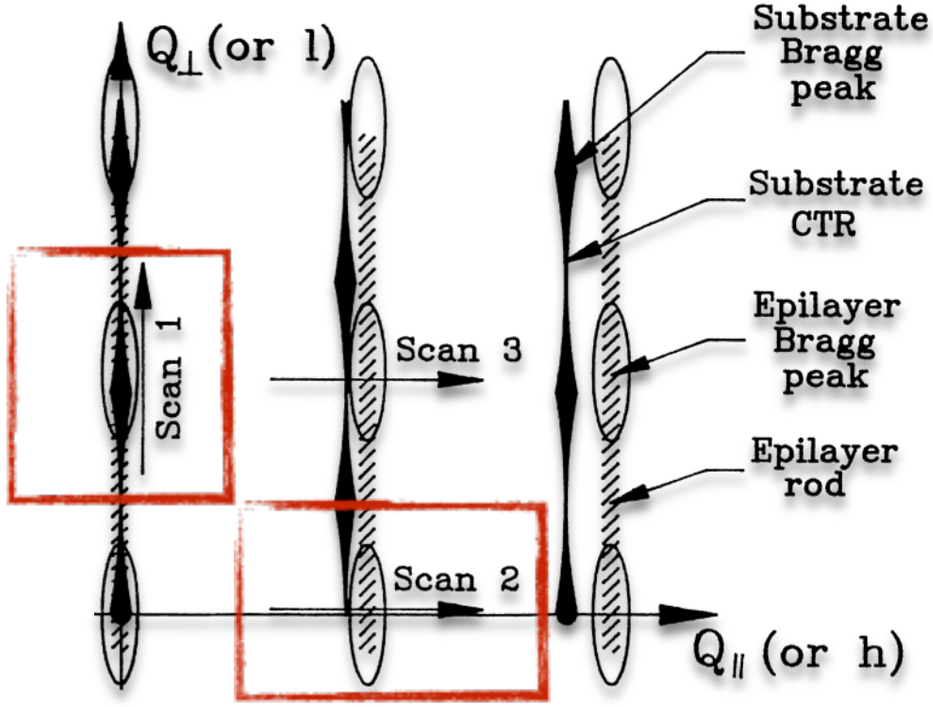


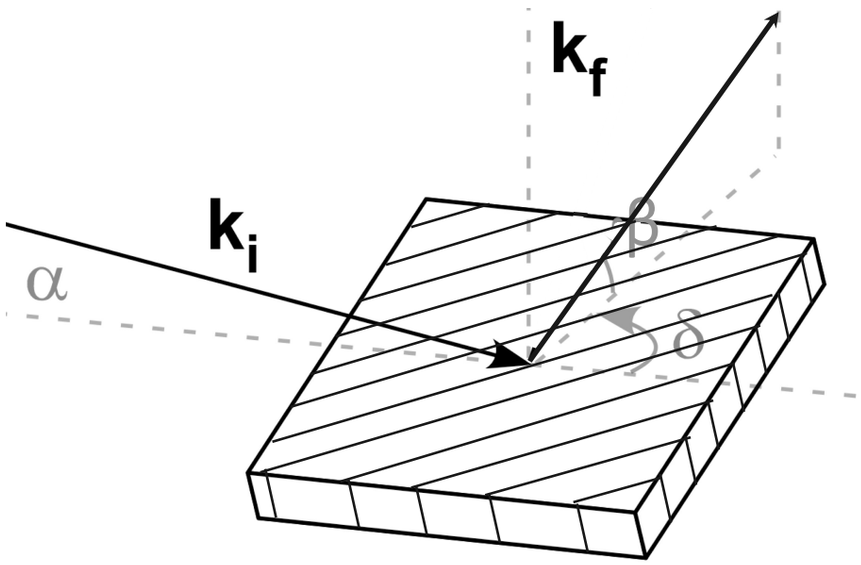
reflectivity is ~ insensitive to the stoichiometry



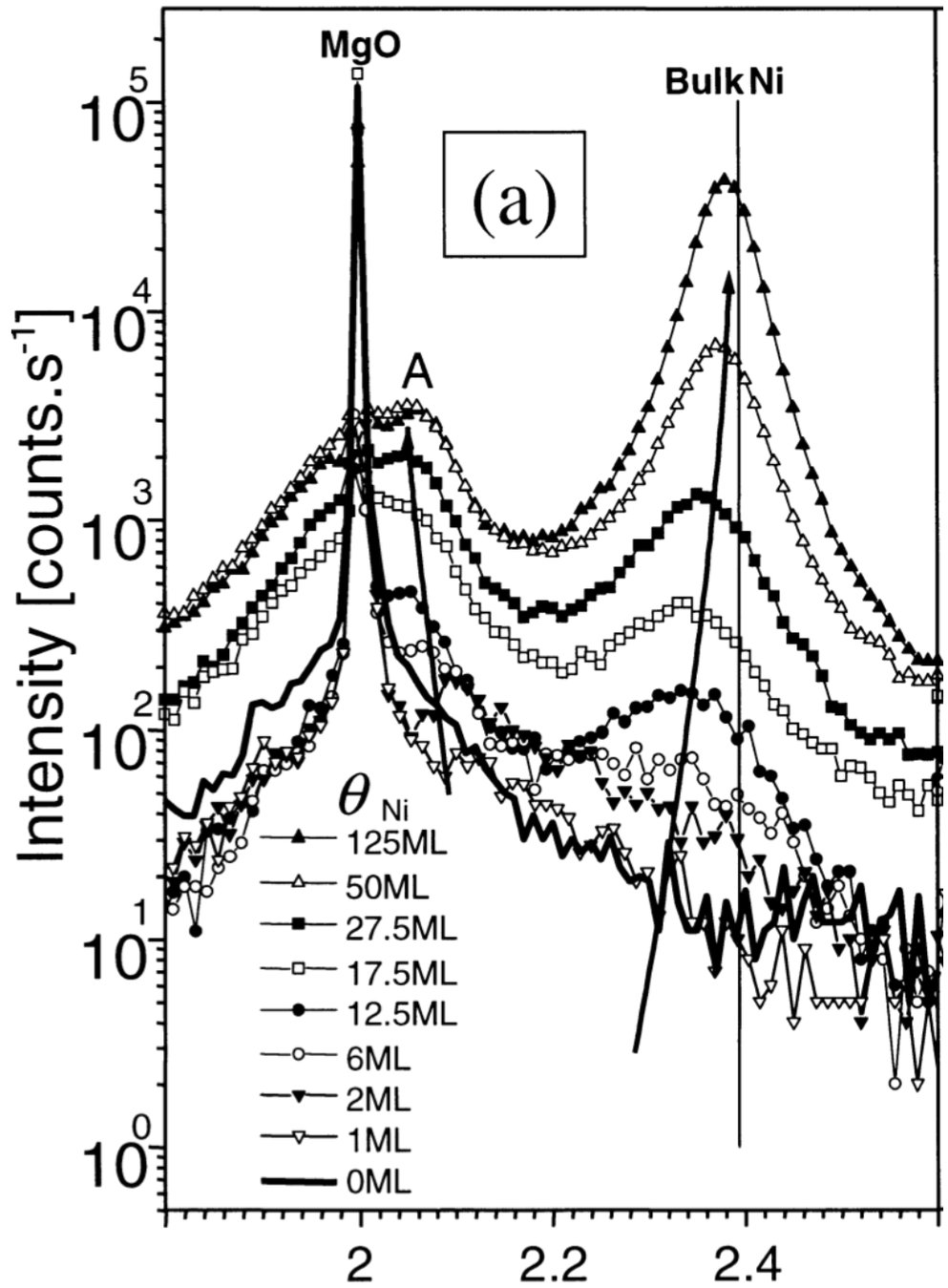
LeBeau *et al.*, Appl. Phys. Lett. **95,** 142905 (2009)

Aside: In-plane peaks ($L \sim 0$): grazing incidence diffraction





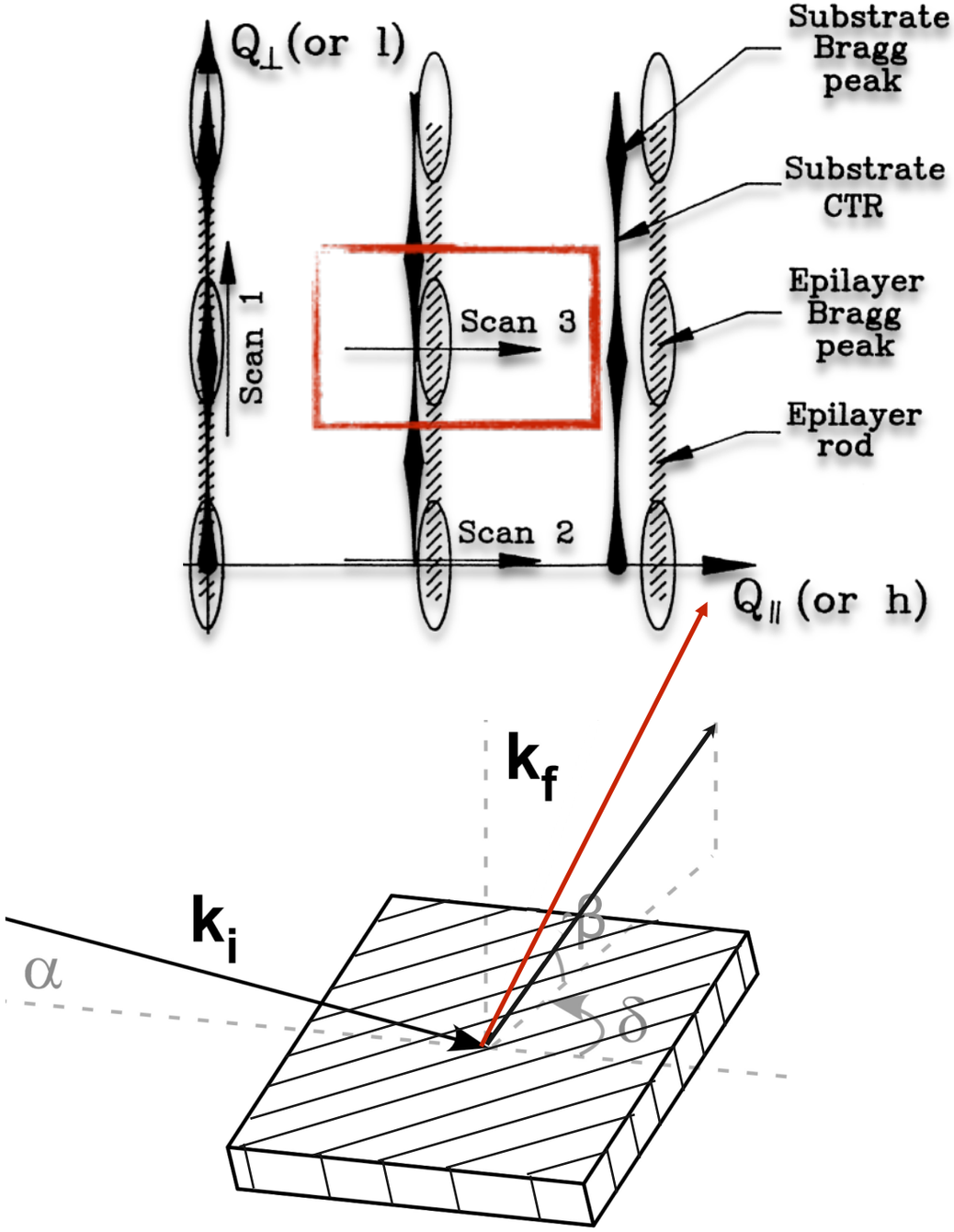
G. Renaud, Surf. Sci. Rep. **32,** 1 (1998)



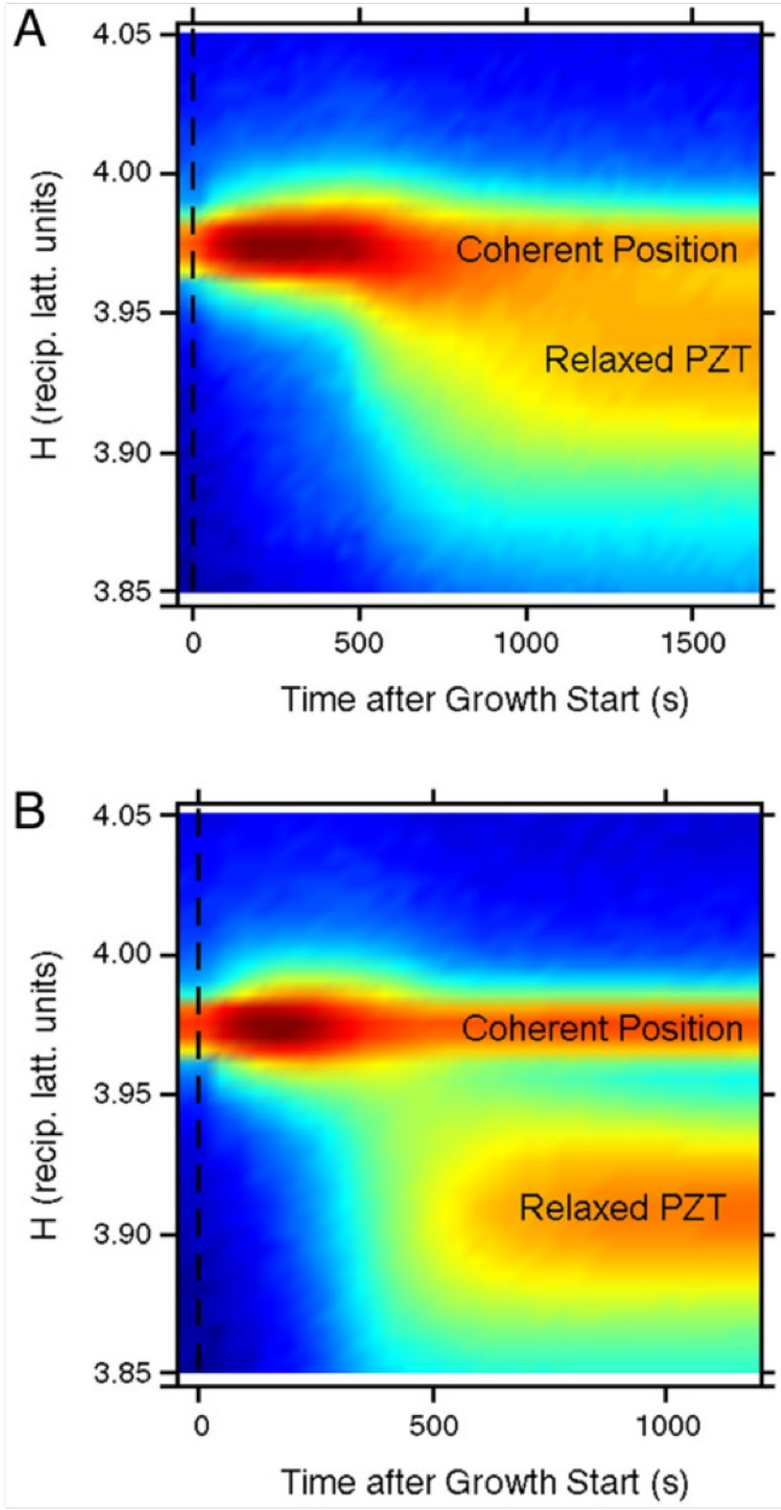
α ~ 0.1°

K=0, L=0.1

Aside: In-plane peaks ($L \neq 0$): grazing incidence diffraction



G. Renaud, Surf. Sci. Rep. **32,** 1 (1998)



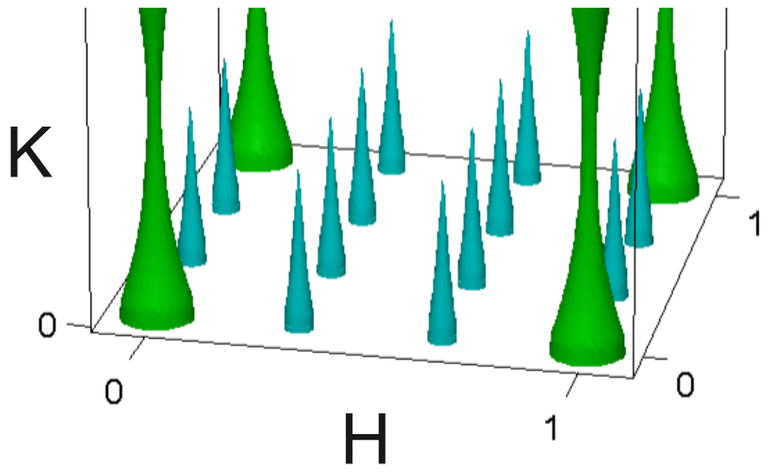
α=0.04°
at 402 peak

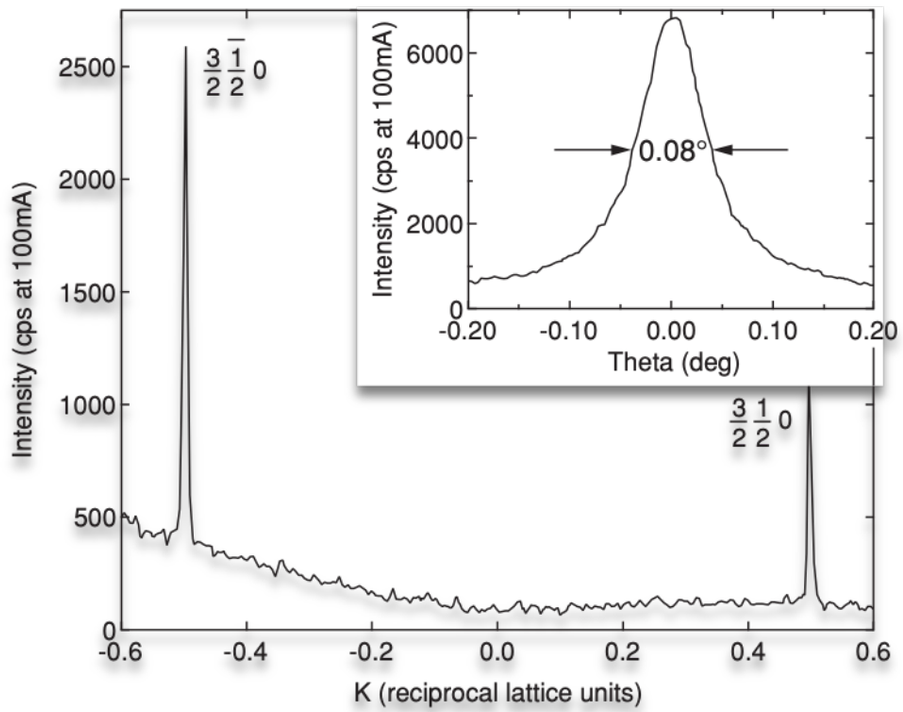
8.6% Zr in PZT

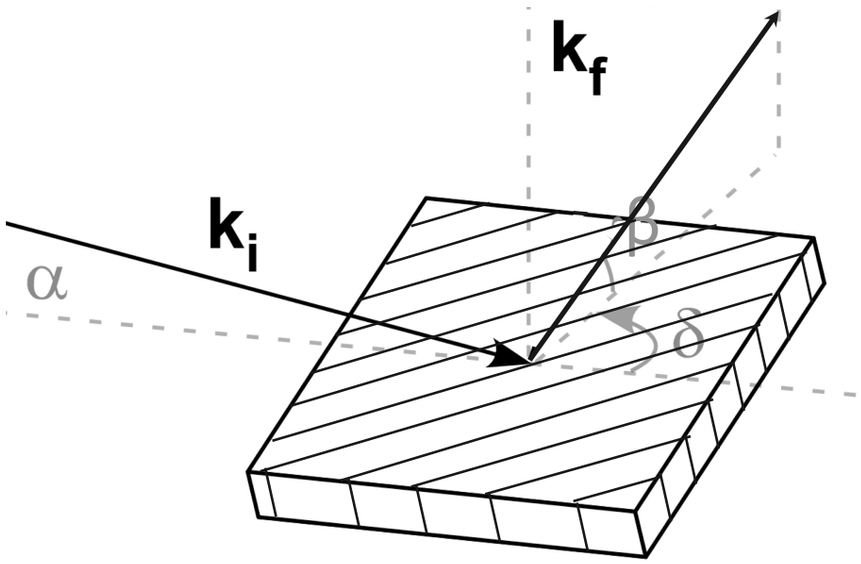
15.9% Zr in PZT

R.-V. Wang et al., Thin Solid Films **515,** 5593 (2007)

Aside: In-plane peaks ($L \sim 0$): surface reconstructions



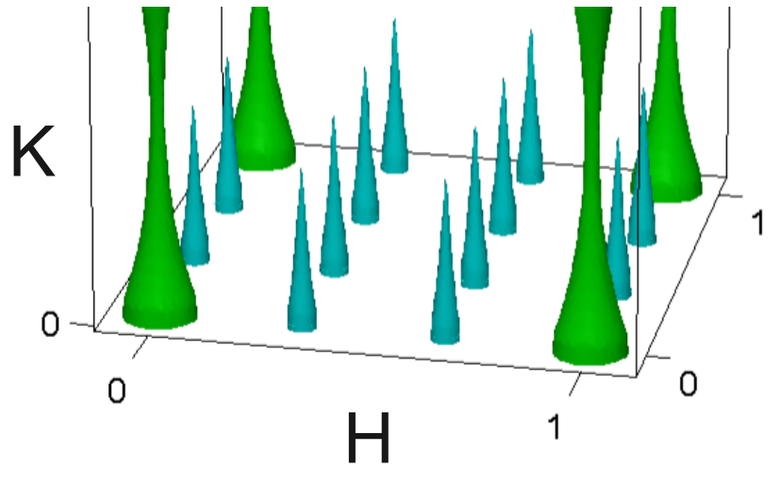


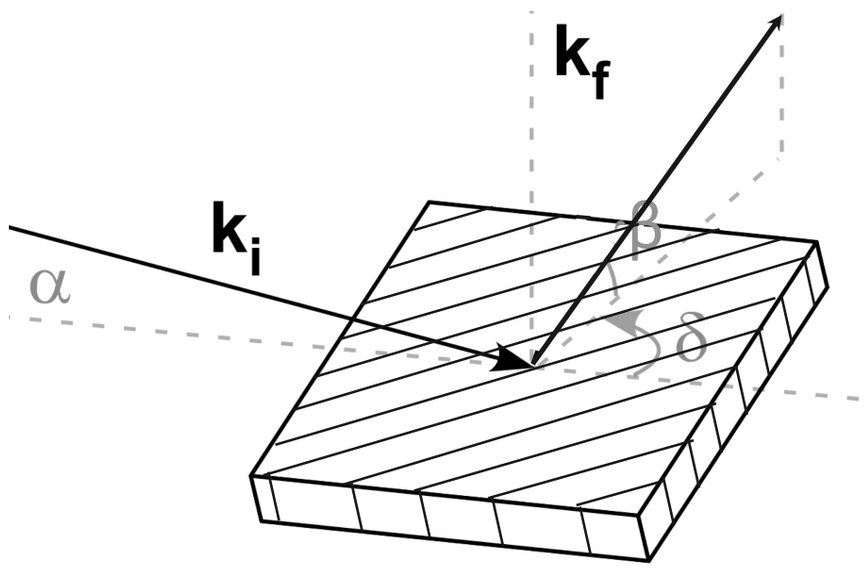


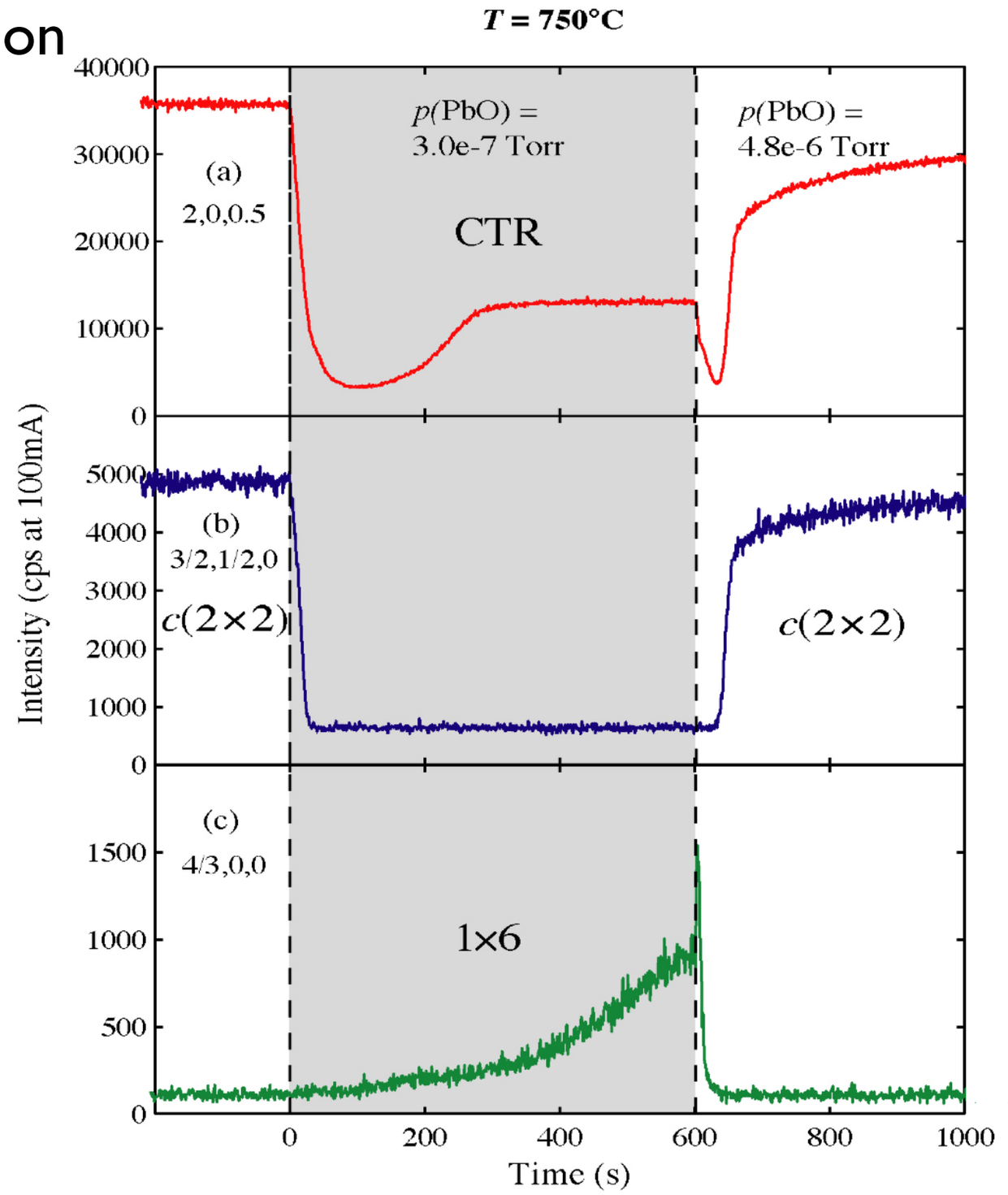
A. Munkholm *et al.*, Phys. Rev. Lett. **88,** 016101 (2001)

Aside: In-plane peaks ($L \sim 0$): surface reconstructions

$PbTiO_3$: PbO-induced reconstruction



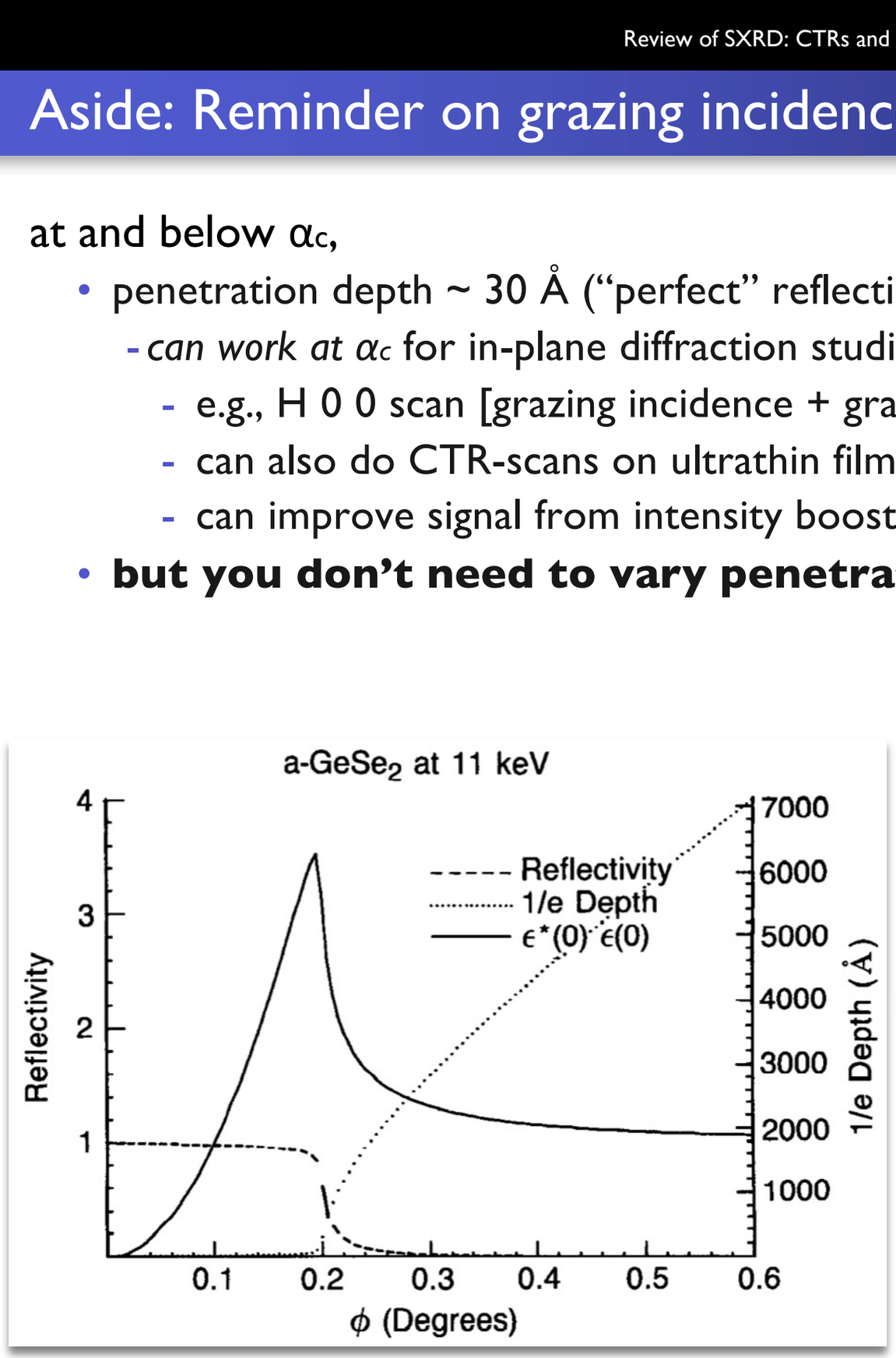




Aside: Reminder on grazing incidence

at and below α_c,

- penetration depth ~ 30 Å ("perfect" reflection below α_c)
  - *can work at* α_c for in-plane diffraction studies [some people do grazing exit scans]
    - e.g., H 0 0 scan [grazing incidence + grazing exit]
    - can also do CTR-scans on ultrathin films (e.g., 1-5 unit cells)
    - can improve signal from intensity boost at α_c ($\epsilon^*\epsilon$)+ large footprint
- **but you don't need to vary penetration depth to get depth dependent info!**

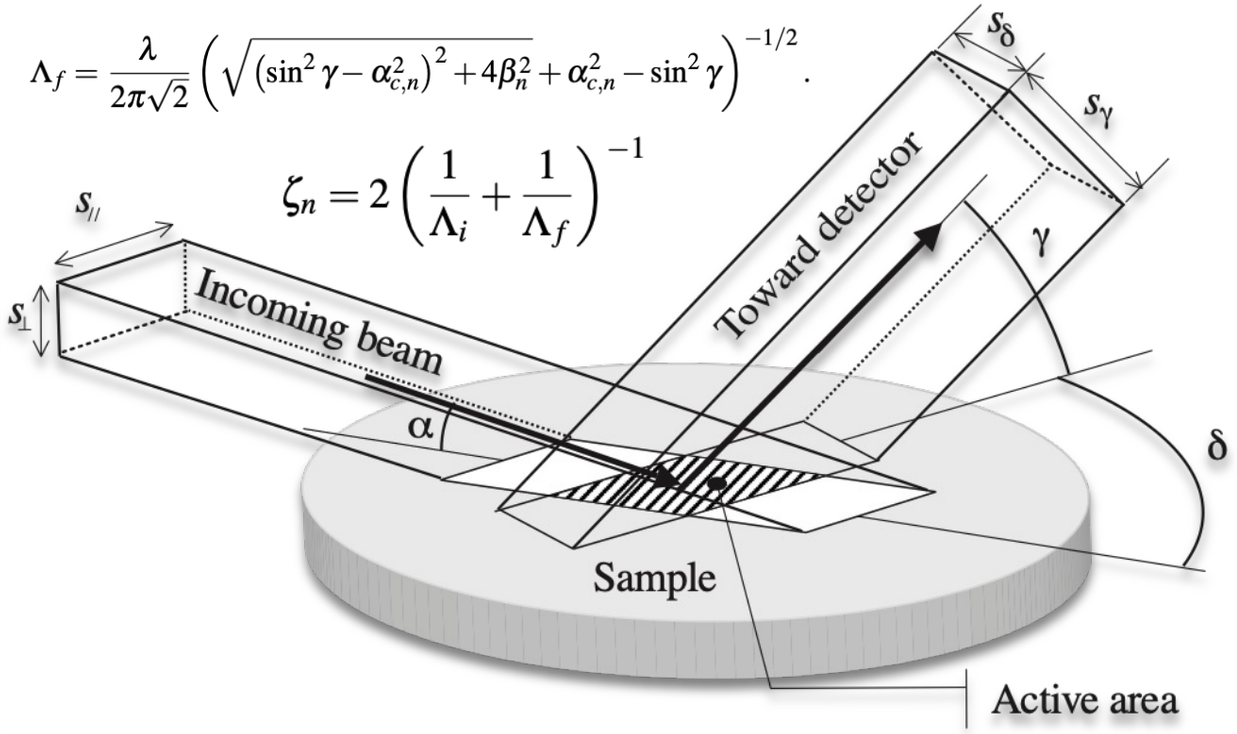


P. H. Fuoss and S. Brennan, Annu. Rev. Mater. Sci. 20, 365 (1990)

$$\Lambda_i = \frac{\lambda}{2\pi\sqrt{2}}\left(\sqrt{\left(\sin^2\alpha_i - \alpha_{c,n}^2\right)^2 + 4\beta_n^2} + \alpha_{c,n}^2 - \sin^2\alpha_i\right)^{-1/2}$$

$$\Lambda_f = \frac{\lambda}{2\pi\sqrt{2}}\left(\sqrt{\left(\sin^2\gamma - \alpha_{c,n}^2\right)^2 + 4\beta_n^2} + \alpha_{c,n}^2 - \sin^2\gamma\right)^{-1/2}.$$

$$\zeta_n = 2\left(\frac{1}{\Lambda_i} + \frac{1}{\Lambda_f}\right)^{-1}$$



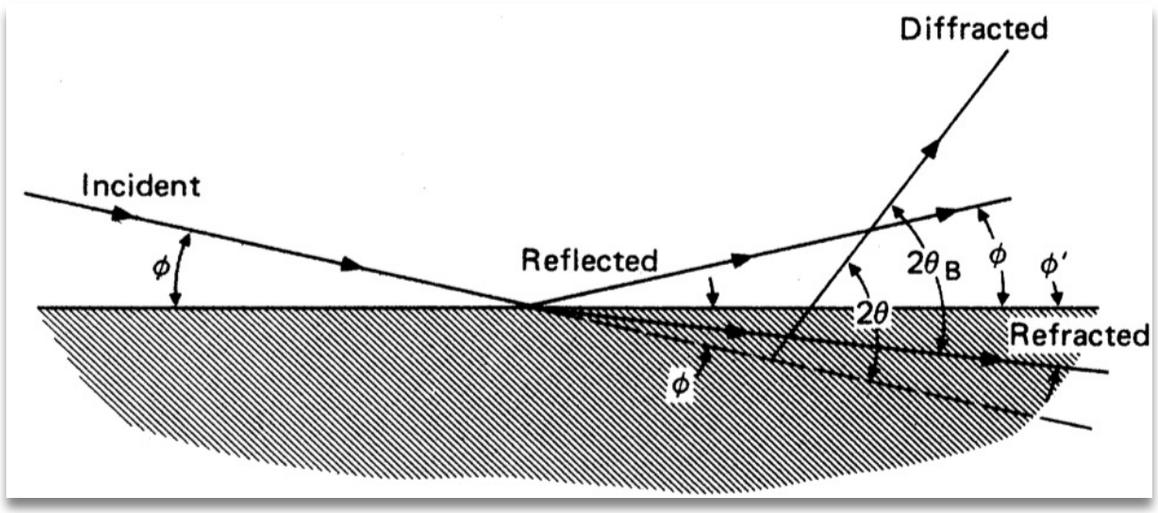
O. Robach *et al.*, J. Appl. Cryst. **33,** 1006 (2000)

Aside: Grazing incidence: effects of refraction

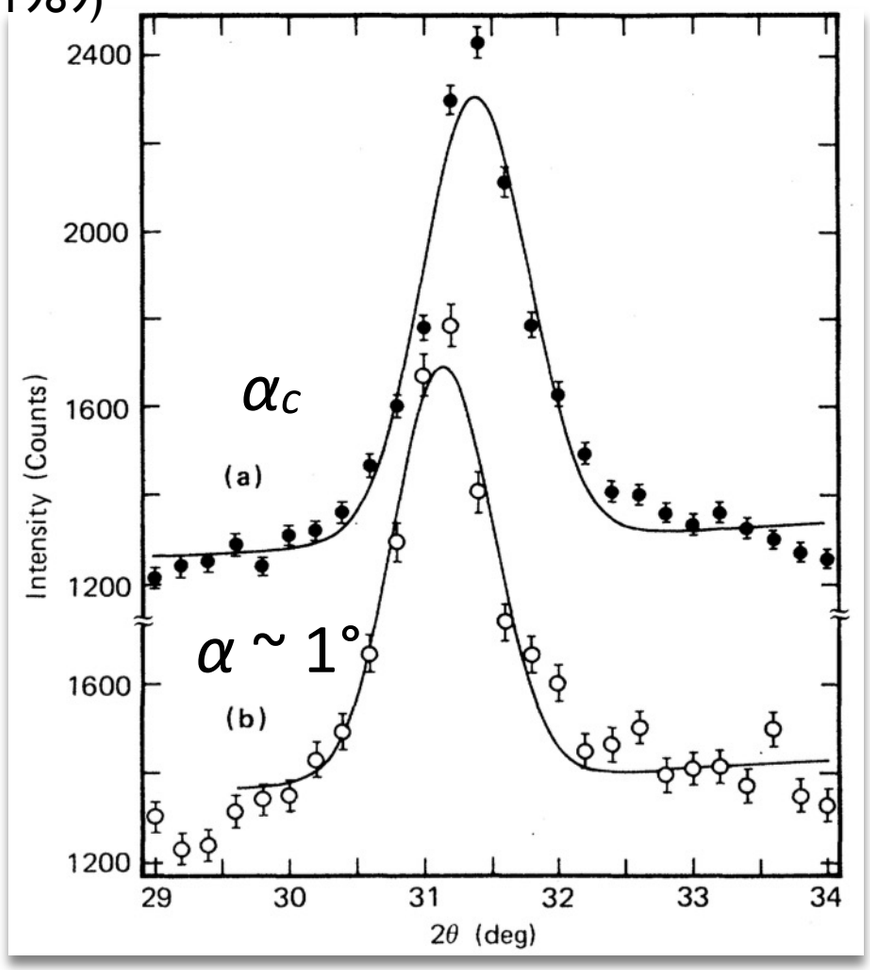
In-plane diffraction (L ~ 0): no problem

But if you stay at α_c to run up a CTR or SR:

- diffracted beam appears at altered L-position



M. F. Toney and S. Brennan, Phys. Rev. B **39,** 7963 (1989)



Angular shift in out-of-plane direction:

$$2\Delta\theta = 2\theta - 2\theta_B$$
$$= \phi - \frac{(k_r')_z}{(k_r')_x}$$
$$\approx \phi - \frac{1}{\sqrt{2}}\{[(\phi^2-\phi_c^2)^2+4\beta^2]^{1/2}-\phi_c^2+\phi^2\}^{1/2}.$$

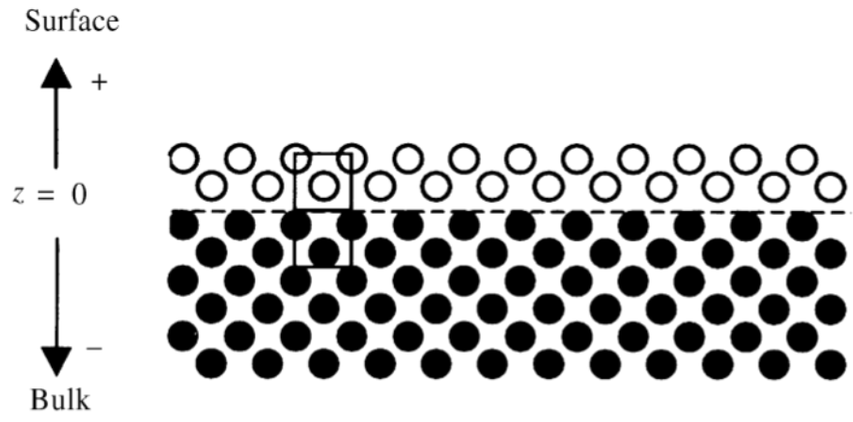
So in general, we like to keep α ~ 1°

A few more refinements on models for surface reconstructions (ANA-ROD)

Could add occupancies in form factor

$$F_{\text{surf}} = \sum_{j}^{\substack{\text{surface} \\ \text{unit cell}}} f_j \theta_j \exp[-B_j Q^2/(16\pi^2)] \exp[2\pi i(hx_j + ky_j + lz_j)],$$

could build a roughness model



Could add occupancies for surface domains

- e.g., for a surface reconstruction only covering portions

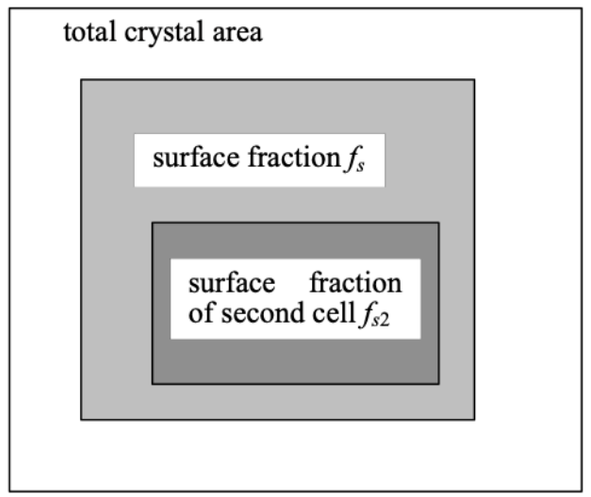
$$F_{\text{sum}} = SR\left[(1-f_s)\sum_{j}^{N_d} \alpha_j F_{b,j}^2 + f_s \sum_{j}^{N_d} \alpha_j (F_{s,j} + F_{b,j})^2\right]^{1/2}.$$

(incoherent addition of each domain)

$$F_{\text{sum,coh}} = SR\left\{(1-f_s)\left(\sum_{j}^{N_d} \alpha_j F_{b,j}\right)^2 + f_s\left[\sum_{j}^{N_d} \alpha_j (F_{s,j} + F_{b,j})\right]^2\right\}^{1/2}.$$

(coherent addition of each domain)

- S = scale factor S,
- R = roughness factor R
- f_s = fractional surface coverage f
- Fb = structure factor for bulk
- Fs = structure factor for surface
- N_d = number of symmetry-related surface domains
- α_j = occupancy of domain j



People have been using ANA-ROD for relatively simple surface structures

- http://www.esrf.eu/computing/scientific/joint_projects/ANA-ROD/

E. Vlieg, J. Appl. Cryst. 33, 401 (2000)

A word on coherent vs incoherent addition

Intensity is given by incoherent sum of all "coherent regions" *N*

$$I(\mathbf{Q}) = \sum_{N} C(\mathbf{Q}) \left| \sum_{\{\mathbf{s}_{||}\}} \frac{F_{sub}(\mathbf{Q}) e^{-i\mathbf{Q}\cdot\mathbf{R}(\mathbf{s}_{||})}}{1 - e^{iQ_z c_0}} \right|^2$$

- *C*(Q) is a geometrical prefactor (discussed later)
- R($s_{||}$) is a vector pointing to the "column"

Coherent region depends on coherence length of x-ray source and correlation length of sample

- synchrotron coherence length ~ 1 μm
- lab source coherence length ~ 1 nm
- correlation length of perfect single crystal ~ size of sample
- correlation length of amorphous material ~ very small

For coherent scattering, the goal is the make sure the $\sum_{\{\mathbf{s}_{||}\}}$ sum dominates over $\sum_{N}$

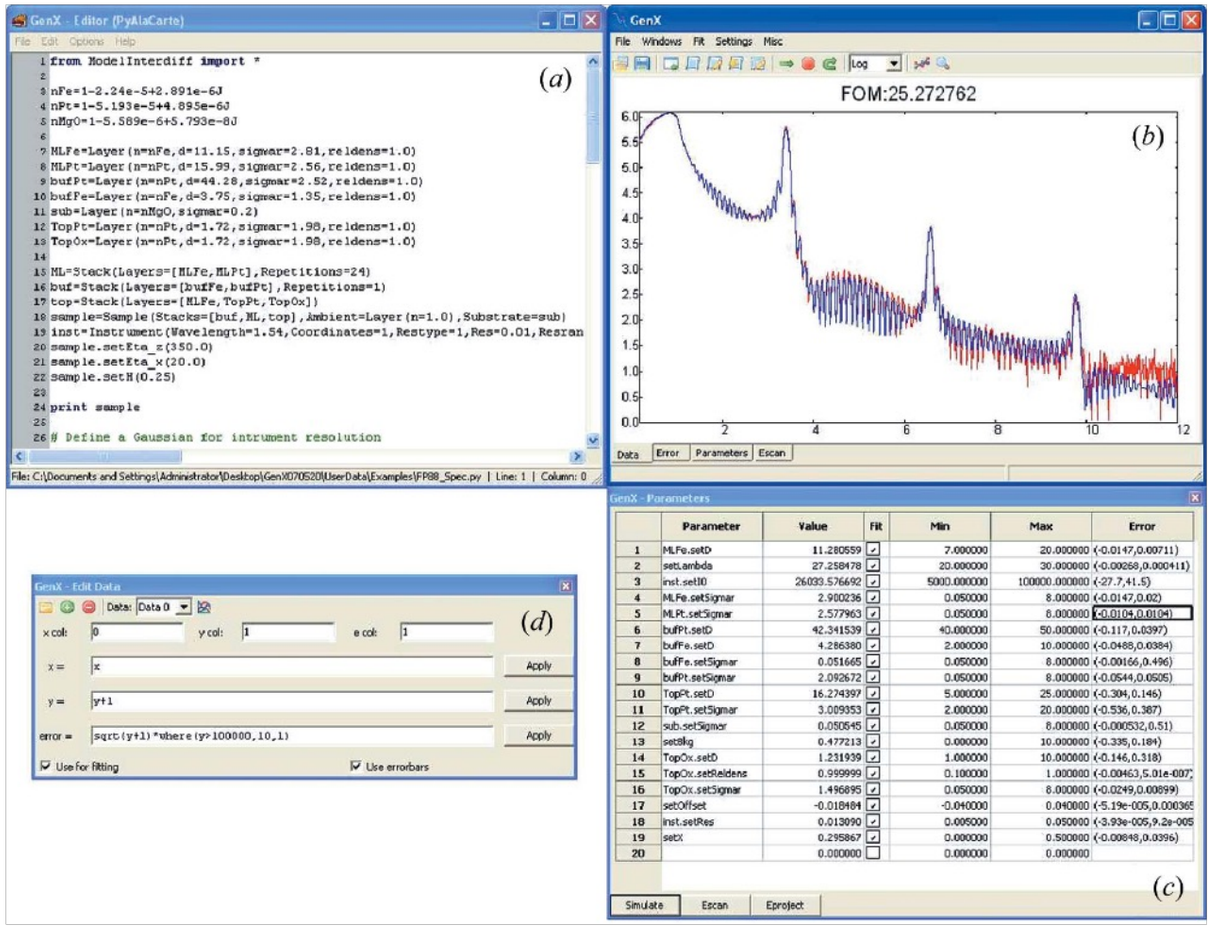
- But sometimes you can't avoid incoherent components: $I = I_1 + I_2 + I_3 + I_4 + \ldots$ where each I_j comes from different domains (e.g., surface domains, grains, variants (including octahedral rotations))
- However -- you can limit the size of your synchrotron beam to ~ synchrotron coherence length; then scattered intensity will be mostly coherent; then you could reconstruct an amorphous region or look at surfaces

D. Dale *et al.*, Phys. Rev. B **74,** 085419 (2006))

Fitting complex structures & the problem with fitting

Lots of parameters

- Lot of coupled parameters: e.g., occupancy factors vs Debye-Waller factors
- need a large range in Q to tell the difference (need huge data set for better uniqueness)
- genetic algorithm (GenX) - http://genx.sourceforge.net



M. Björck and G. Andersson, J. Appl. Cryst. **40,** 1174 (2007).

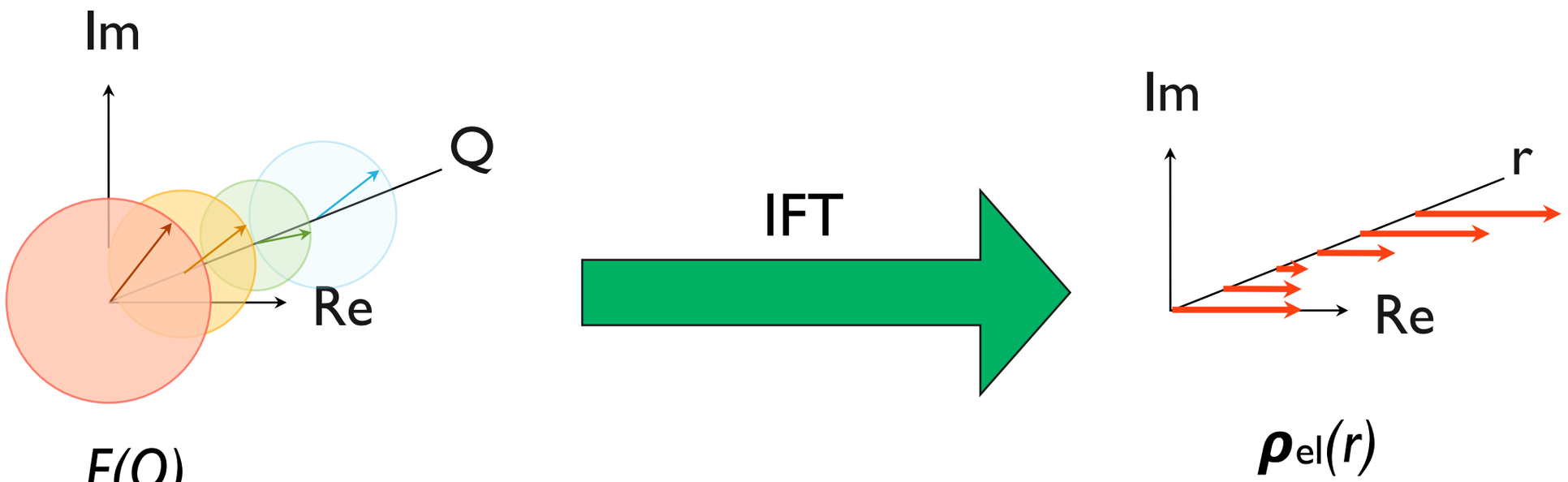
Direct Methods

- Trying to avoid fitting
- Assumes coherent scattering

Fourier cycling

Need to assign some phases (imaginary parts) to *F(Q)* to start

Ideally:

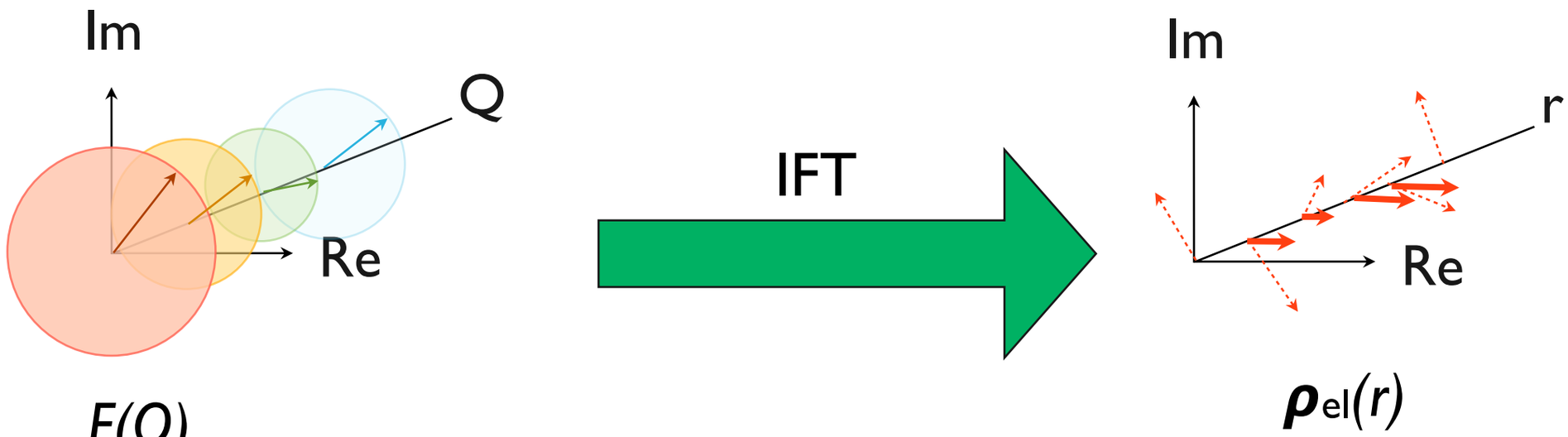


F(Q)

$\rho_{el}(r)$

Fourier cycling

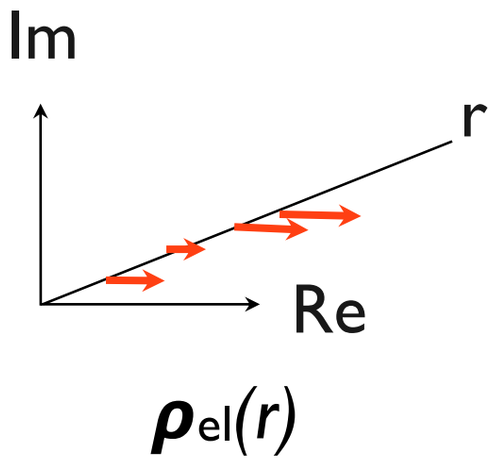
So force it to be real & positive (zero the imaginary & negative parts)



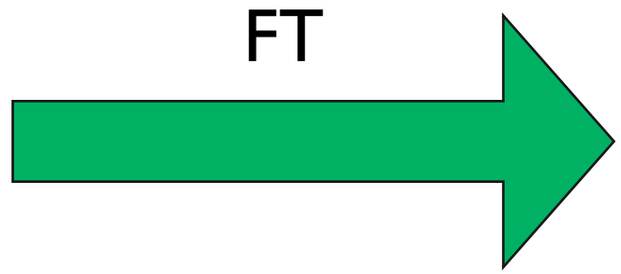
$F(Q)$

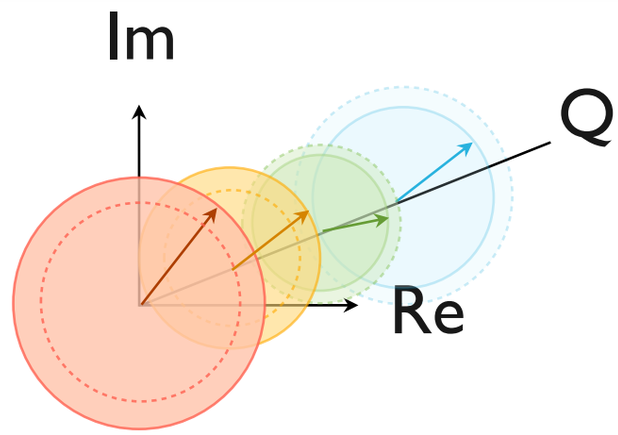
$\rho_{el}(r)$

Fourier cycling — now FT

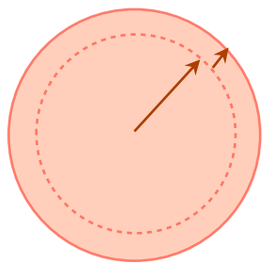


$\rho_{el}(r)$





$F(Q)$



Fix the amplitude of $F(Q)$ to match the data

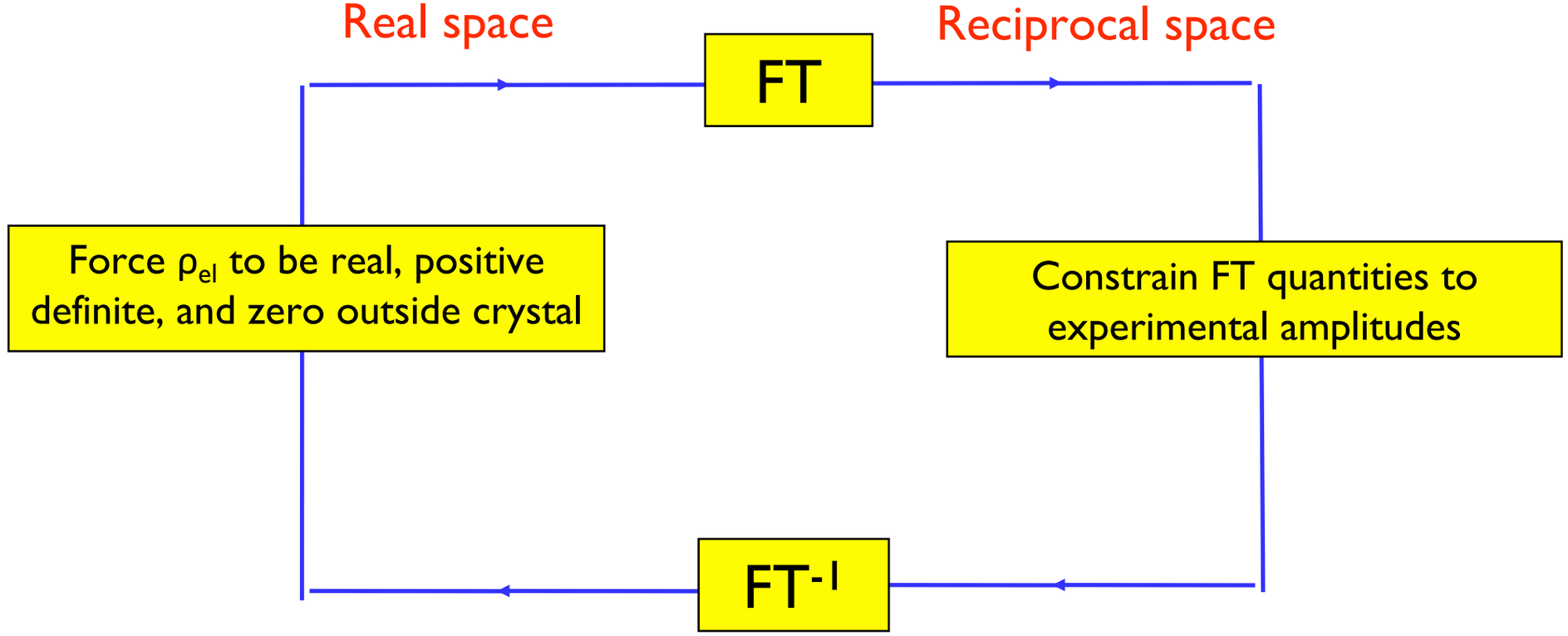
This corresponds to error corrections in reciprocal space: $\Delta F(Q)$

Can be shown that these are "minimum-change" operations such that the sum of the squared errors can be minimized through an iterative algorithm (Fourier cycling)

Fourier cycling

R. W. Gerchberg and W. O. Saxton, "A practical algorithm for the determination of the phase from image and diffraction plane pictures," Optik **35**, 237 (1972)

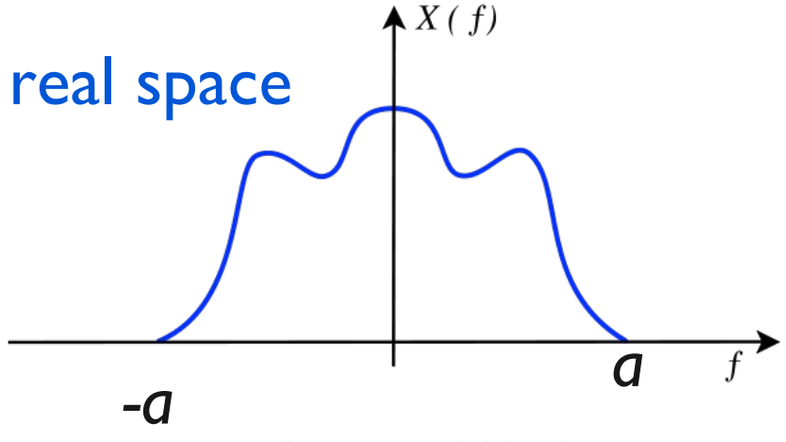
J. R. Fienup, Opt. Letters **3**, 27 (1978); Appl. Opt. **21**, 2758 (1982)



Oversampling

How much data do you need to take to reconstruct ρ_{el}?

sample in real space



Need to sample by at least $\Delta Q = 1/(2a)$, but this assumes we can access the complex structure factor

- since we can only sample the structure factor amplitude, we need to sample by $\Delta Q = 1/(4a)$
- for a thin film, this is $\Delta Q = 1/(2t)$, so for a 2 unit cell film, we need to sample at a spacing of $\Delta L \sim 0.25$
- Not a problem for CTRs (continuous): we typically usually sample at least twice this (~ 7 points per thickness fringe) - **oversampling** (can only be done along *L* for thin films)

D. Sayre, Struct. Chem. **13,** 81 (2002)

Other methods to directly solve for phase

Use of a reference wave [holography - D. Gabor, Nature **161**, 777 (1948)]

- applied to SXRD with

$$F(Q) = S(Q) + B(Q)$$

$B(Q)$: reference wave

- $F_{surf}(Q)$ determined by IFT (but crude - fitting needed afterwards)

T. Takahashi et al., *Surf. Sci.* **493**, 36 (2001)
K. Sumitani et al., *Jpn. J. Appl. Phys.* **42**, L189 (2003)

- can also use the COBRA assumption that $\frac{dS(Q)}{dQ} \ll \frac{dB(Q)}{dQ}$

  - *then*

$$\left|F\left(Q-\frac{\Delta Q}{2}\right)\right| = \left|S(Q)+B\left(Q-\frac{\Delta Q}{2}\right)\right|$$

$$\left|F\left(Q+\frac{\Delta Q}{2}\right)\right| = \left|S(Q)+B\left(Q+\frac{\Delta Q}{2}\right)\right|$$

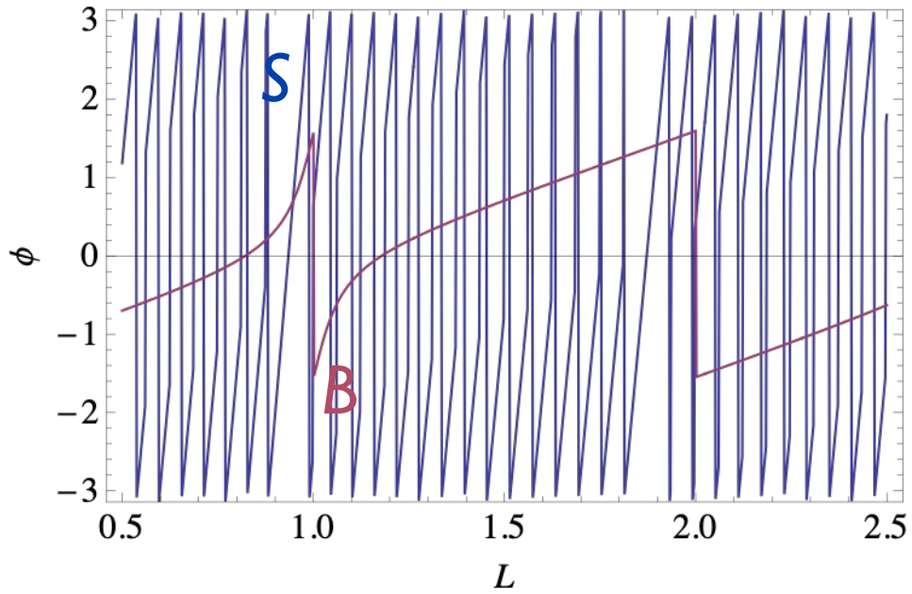
- and you have 2 equations and 2 unknowns (complex $S(Q)$)

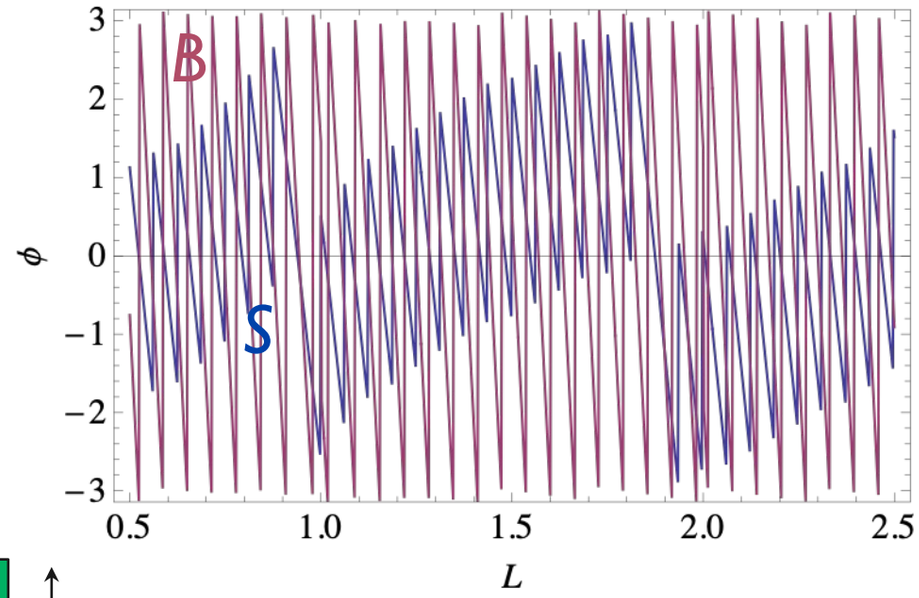
M. Sowwan, Y. Yacoby, *et al.*, Phys. Rev. B **66**, 205311 (200

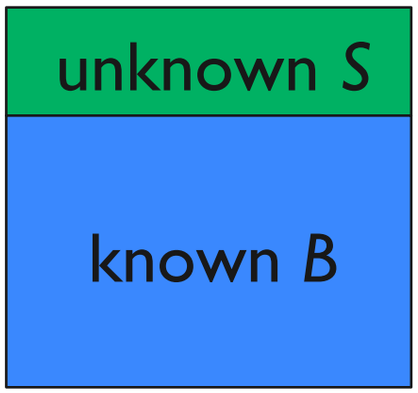
Other methods to directly solve for phase

How can this assumption be true? $\frac{dS(Q)}{dQ} \ll \frac{dB(Q)}{dQ}$

Can make it closer to being true by moving the origin of reciprocal space to near the top of the film (works better for thinner films)







origin

so “tricks” can be played….

Folded structures

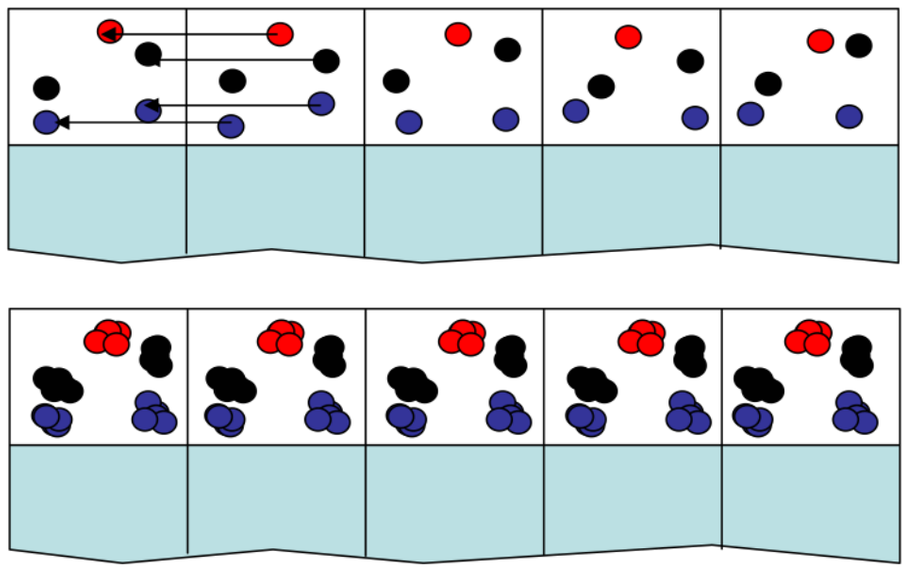
COBRA only examines the CTRs (not SRs)

- still some information on SRs can be retrieved

$$F(Q) = \sum_{n}^{N_{N_{\text{basis}}}} e^{iQ\cdot R_n} \sum_{j}^{N_{\text{basis}}} f_j(Q) e^{iQ\cdot r_j}$$

R_n is a vector going to each repeat unit
r_j is a vector describing the basis of each repeat unit

$$F(Q) = \sum_{n}^{N_{N_{\text{basis}}}} e^{iQ\cdot R_n} \left(\underbrace{\sum_{j}^{N_{uc,\text{basis}}} f_j(Q) e^{iQ\cdot r_j}}_{\text{normal unit cell structure factor}} + \underbrace{\sum_{d}^{N_d} f_d(Q) e^{iQ\cdot r'_d}}_{\text{deviants}} \right)$$



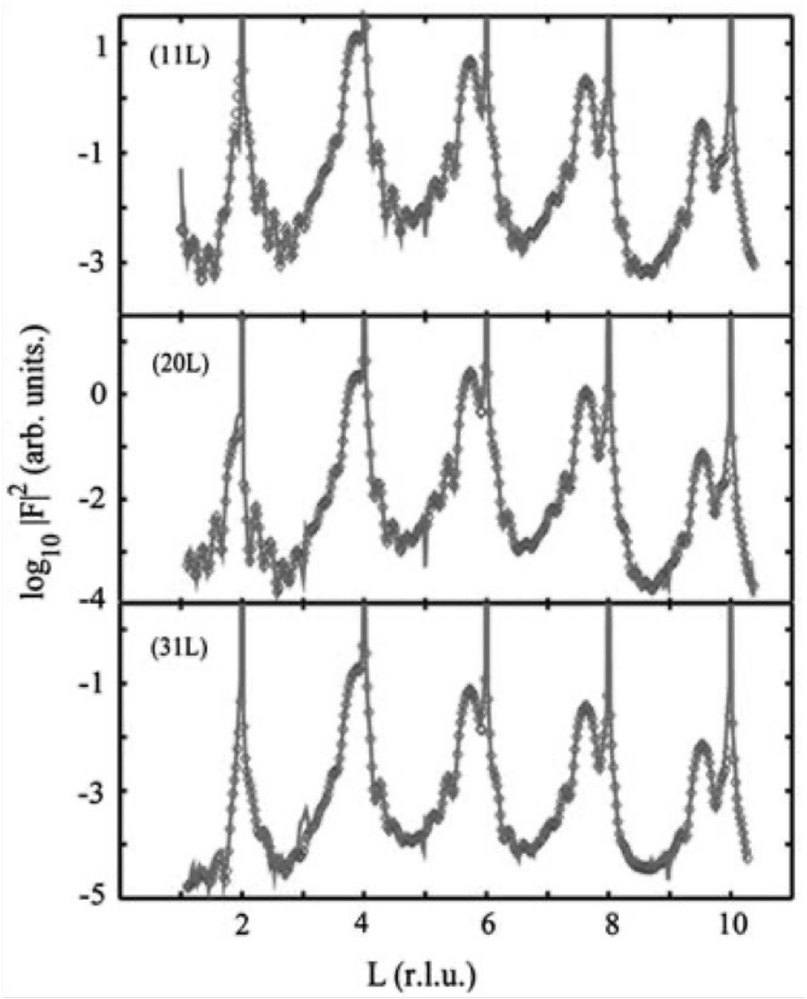
atoms “fold” into substrate-defined unit cell

Folded structures

Measure all independent rods $F_{HK}(L)$

$$F(\mathbf{q}) = \sum_{j=1}^{N_{uc}} f_j(q) e^{i\mathbf{q}\cdot\mathbf{r}_j}$$

$$F_{HKL} = f_A e^{\pi i(H+K)} + f_B e^{\pi i(L)} + f_O\left[1 + e^{\pi i(K+L)} + e^{\pi i(H+K+L)}\right]$$



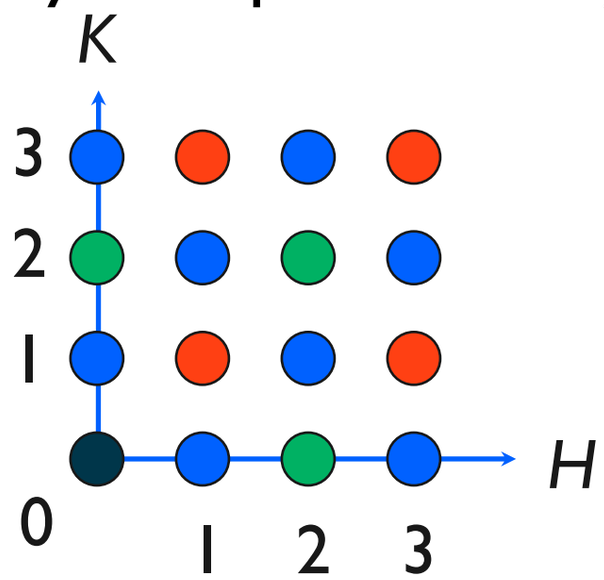
E.g., for 4mm perovskite symmetry:

3 independent rods

- (even, even, *L*)
- (odd, odd, *L*)
- (odd, even, *L*)

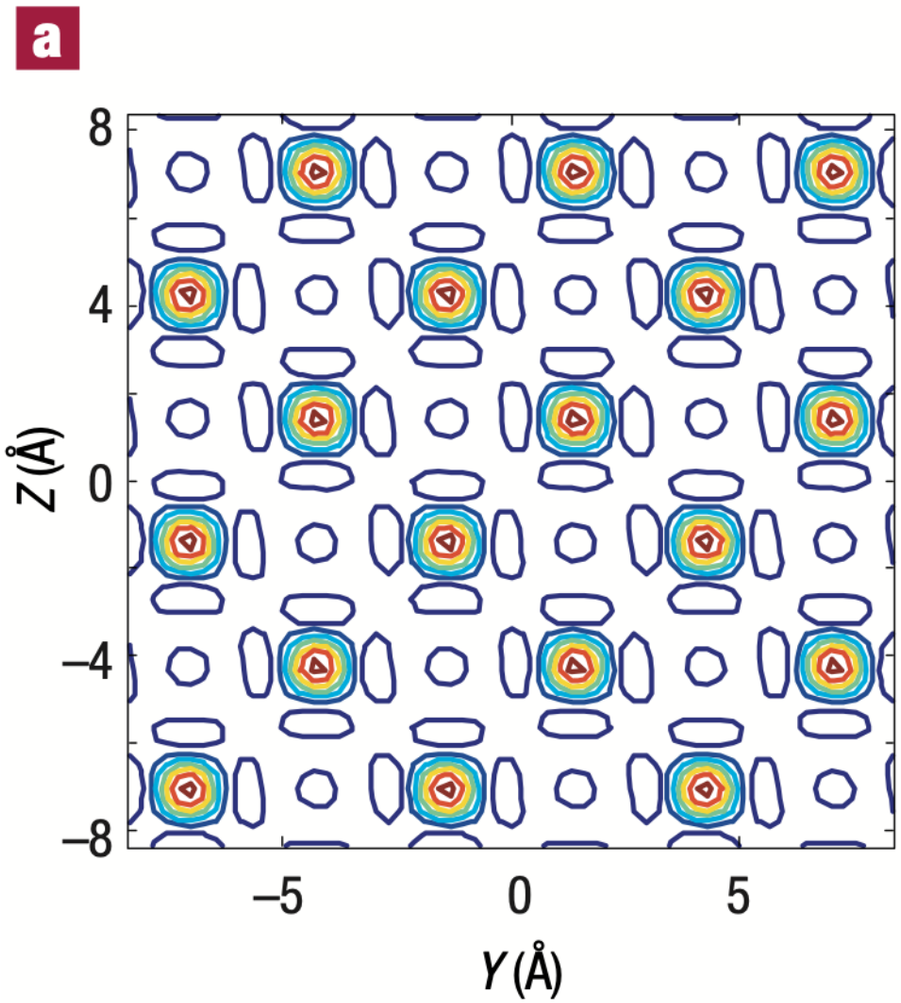
Typically more rods are measured for reduced error (at least 6 off-specular + specular)

- specular is often different (non-registered surface layers can modify the specular rod)

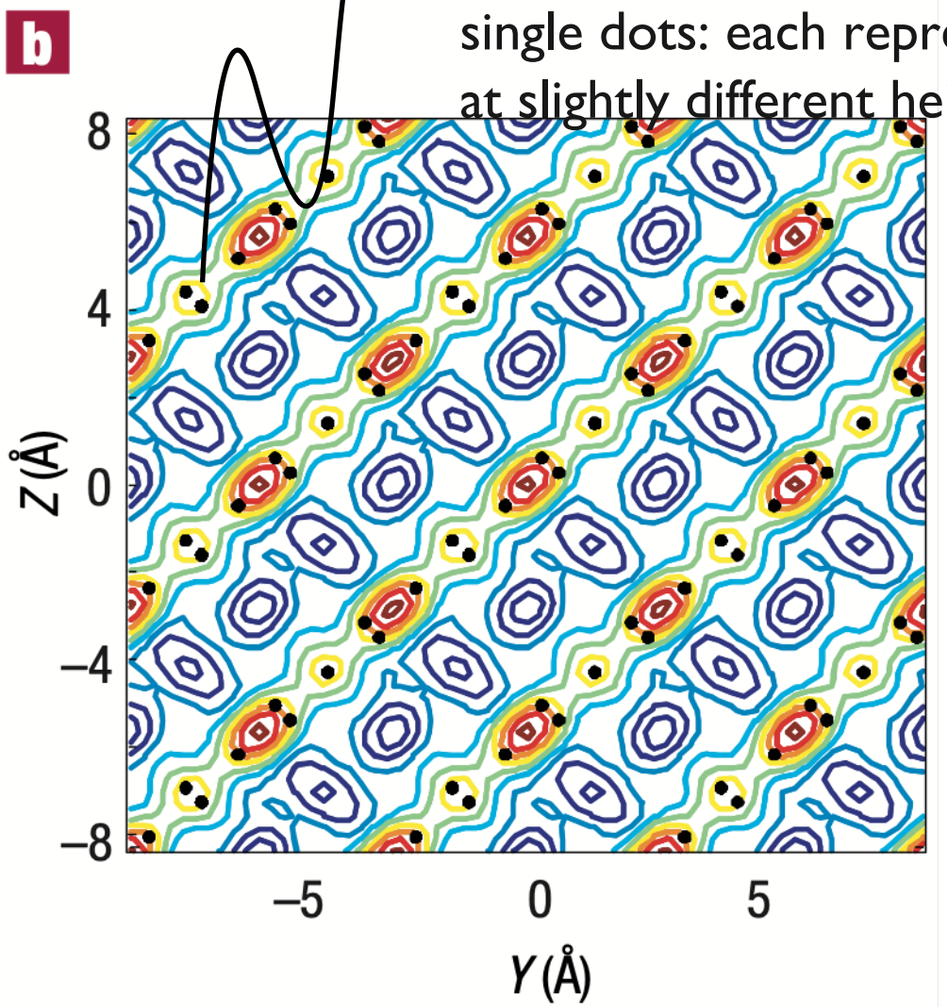


Folded structures

Gd_2O_3 on GaAs(001)



in GaAs(001) substrate

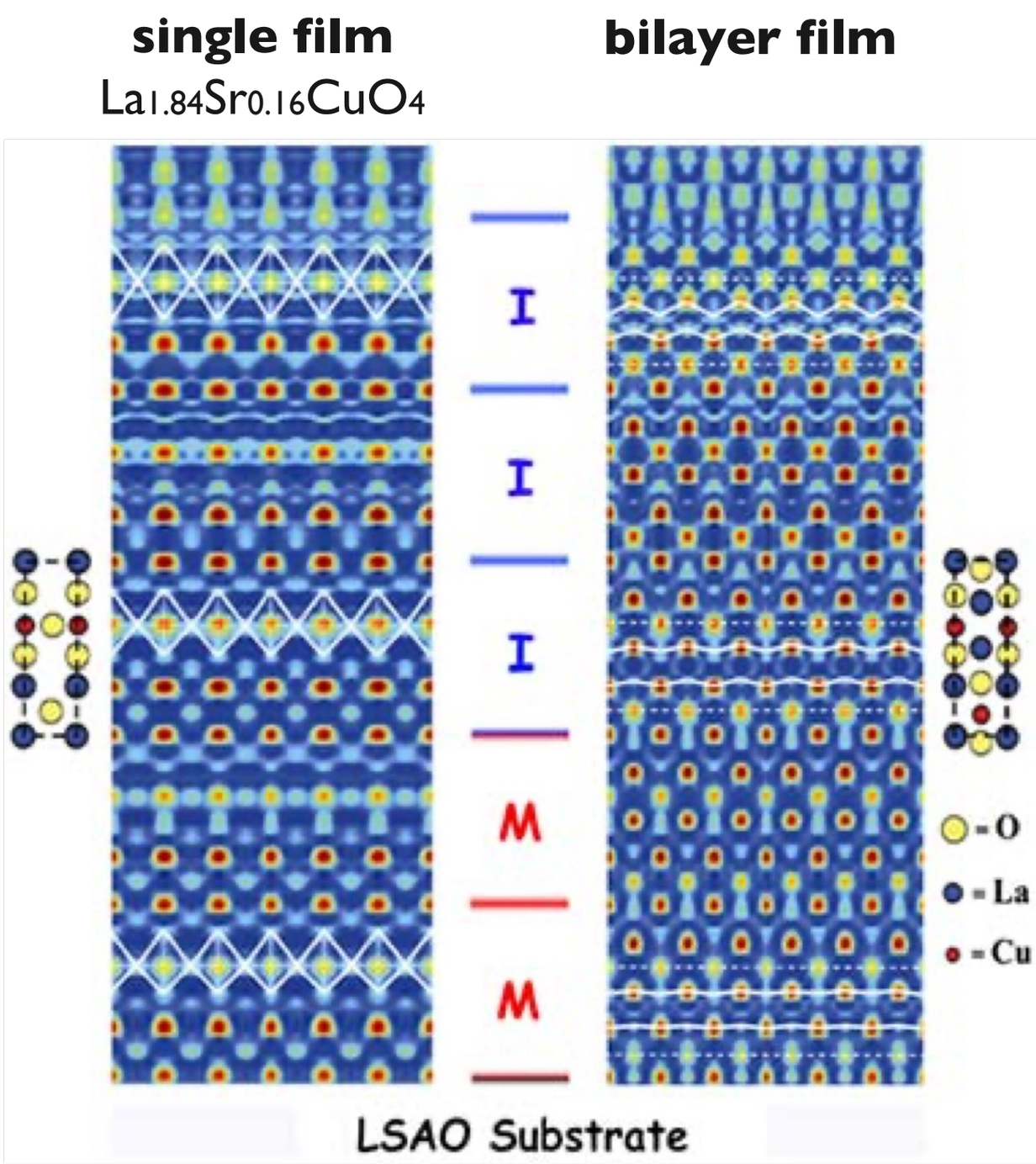


9th layer of Gd_2O_3 film above interface

Y. Yacoby *et al.*, Nature Mater. **1**, 99 (2002)

Folded structures

$La_{2-x}Sr_xCuO_4$ on $LaSrAlO_4(001)$



Zhou *et al.*, PNAS**10**, 8103 (2010)

More on algorithms

COBRA: Y. Yacoby et al. Phys. Rev. B **87,** 014108 (2013) & references therein

1. lots of data massage
2. fit *F* in reciprocal space (*F* = *S*+*B*): this applies constraints in reciprocal space
3. apply COBRA assumption and solve for amplitude and phase of *S*
4. IFT[*F*] -- look at this real space solution
   - *could use this to make a new fitting model & start over*
   - *could apply real space constraints (real, positive, support); if so, then return to step 2*
5. once you get a ρ that makes sense, do Fourier cycling, which refines atomic positions

Difference map - modification to Fourier cycling

- avoids getting trapped in local minima (sort of like genetic algorithm)

PARADIGM: Fung *et al.*, Acta Cryst. A **63,** 239 (2007)

DCAF: M Björck *et al.* J. Phys.: Condens. Matter **20,** 445006 (2008)

- uses Fourier cycling + difference map
- can start with random phases

Problem -- not unique (better with more data; 1D data is not unique)

S. Marchesini, Rev. Sci. Instrum. **78,** 011301 (2007)

Another way: DFT + fitting

To account for disorder, defects, and non-equilibrium processes, we combine insights from theory and experiment into one fitting procedure

$$R^2 = \chi^2 + \chi^2_{res} + \frac{1}{2}\frac{\kappa}{kT}\sum_I (\zeta_I - Z_I)^2$$

Experiment

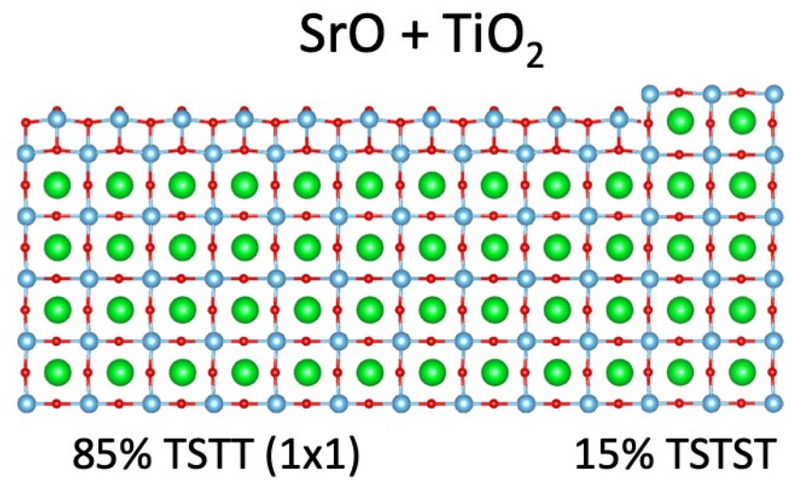
DFT

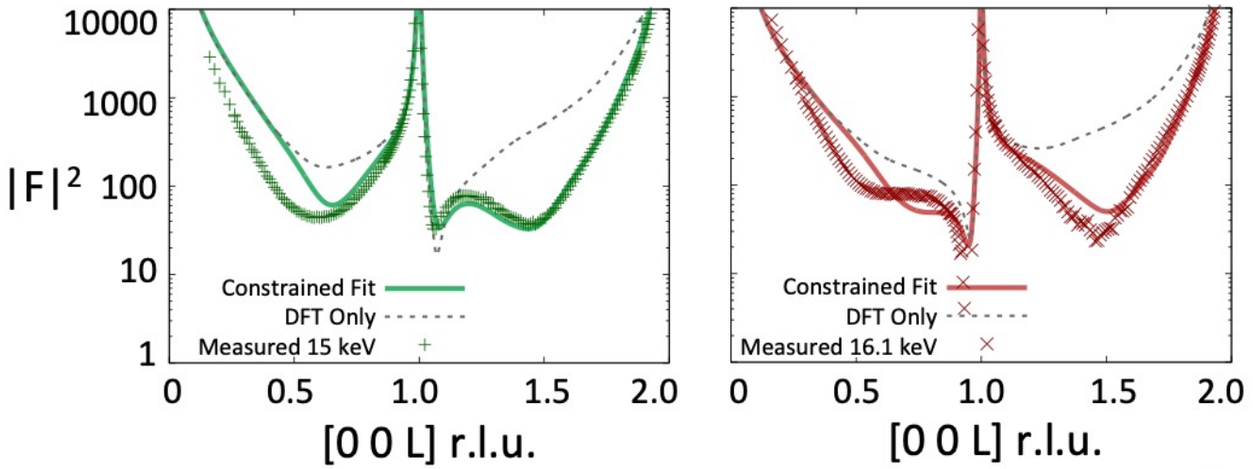
Fit residual R^2 for non-linear least squares fitting of atomic positions $\{\zeta_I\}$, Debye-Waller factors $\{\sigma_I\}$, and occupancies $\{\theta_I\}$ of each atom.

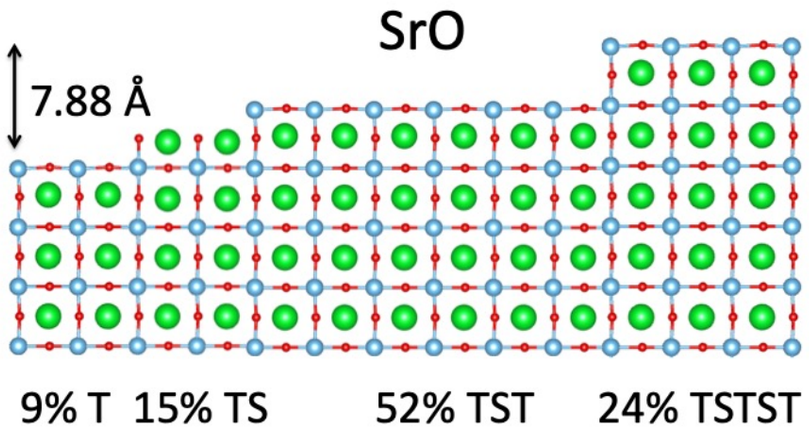
- Experimental chi-squared χ^2 constrains predicted structure factor $|F(\zeta,\sigma,\theta)|^2$ to measured structure factor $|F_{exp}|^2$.
- Resonant (χ^2_{res}) and non-resonant (χ^2) data may both be included in residual.
- Penalty function prevents atomic positions $\{\zeta_I\}$ from varying significantly from the DFT predicted positions $\{Z_I\}$.
- κ/kT determines weight of the penalty function compared to $\chi 2$ with effective spring constant κ and temperature dependent energy scale kT.
- measures deviation from DFT structure.

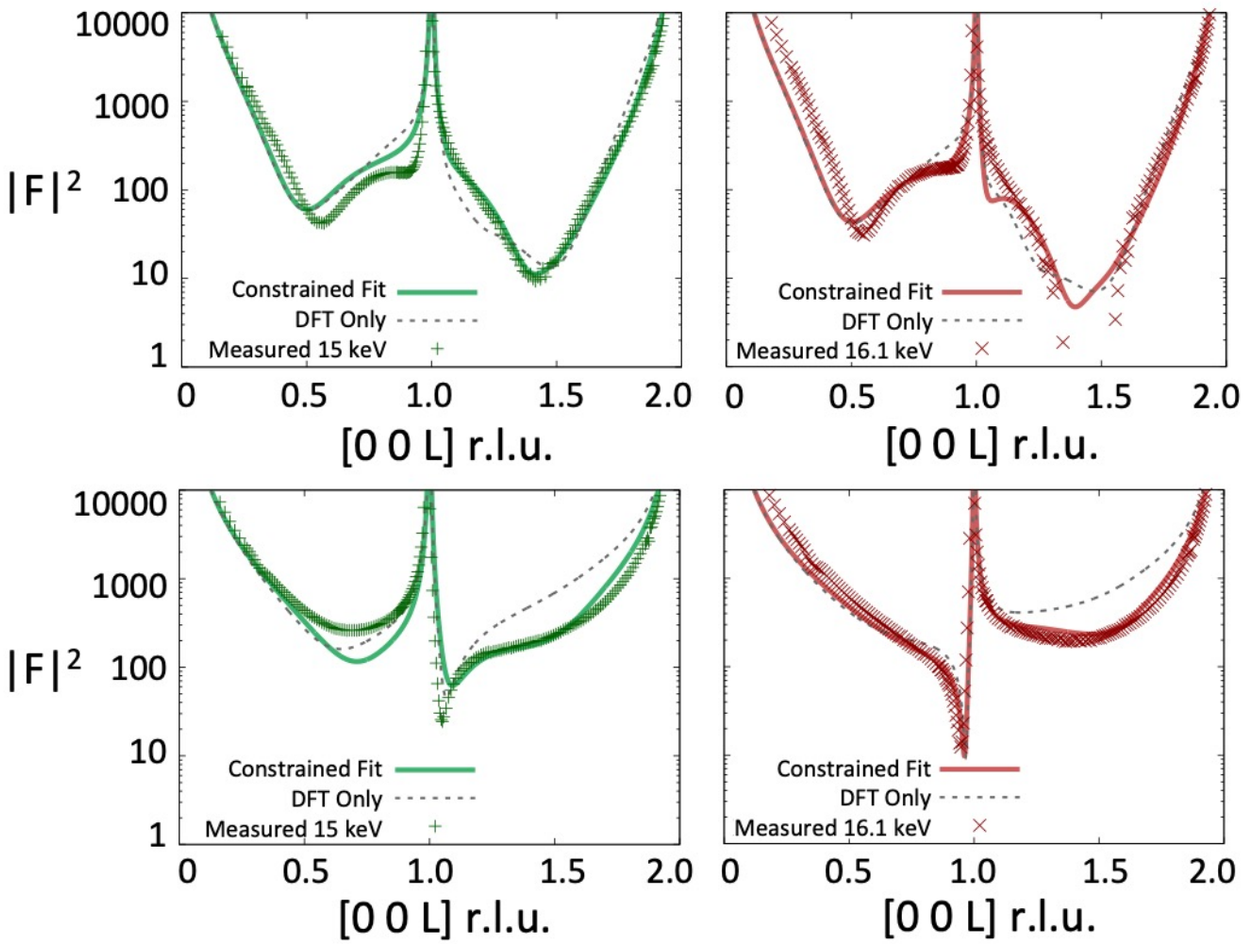
M. Plaza, K. Letchworth-Weaver, et al, *JACS* **138** (25), 7816-7819 (2016)

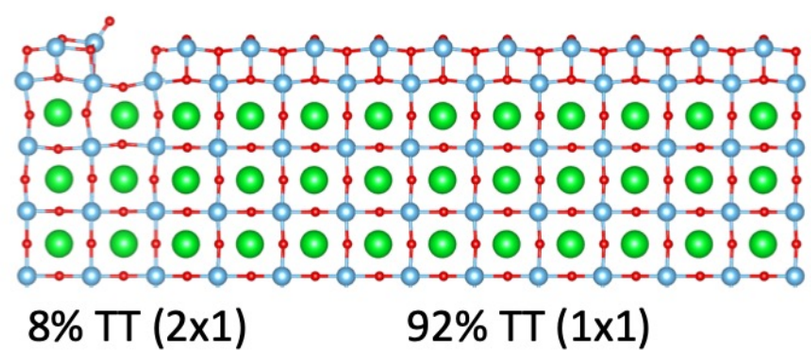
Another way: DFT + fitting











After the synchrotron upgrades (e.g., APS upgrade, ESRF upgrade, ...)

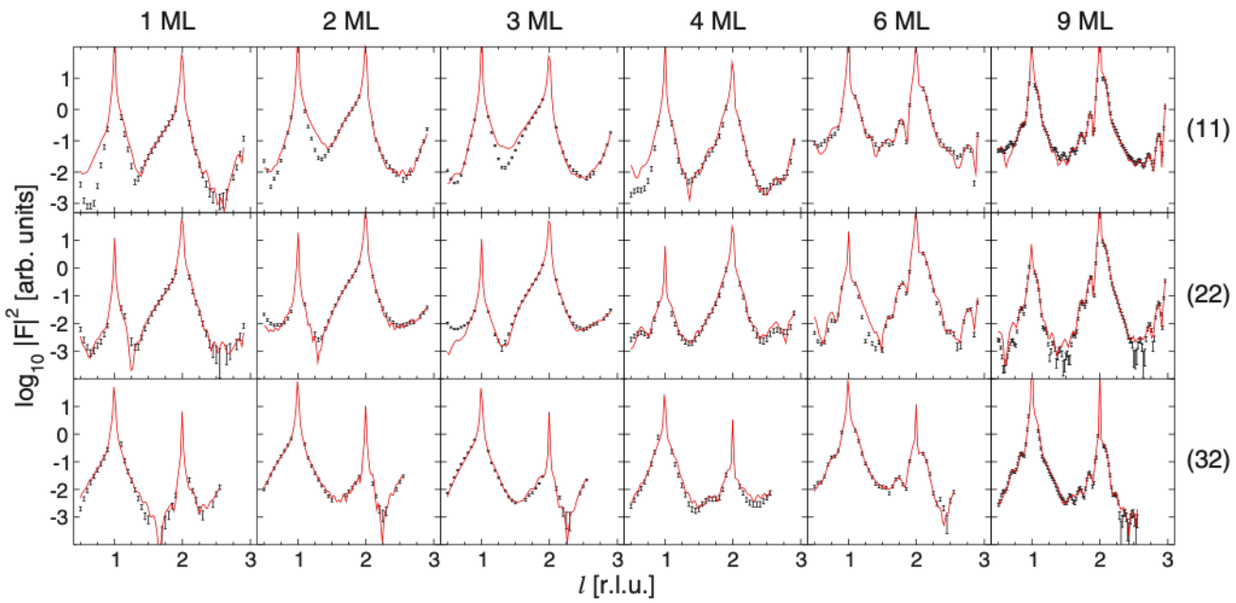
Much more coherent flux (at least 100x)

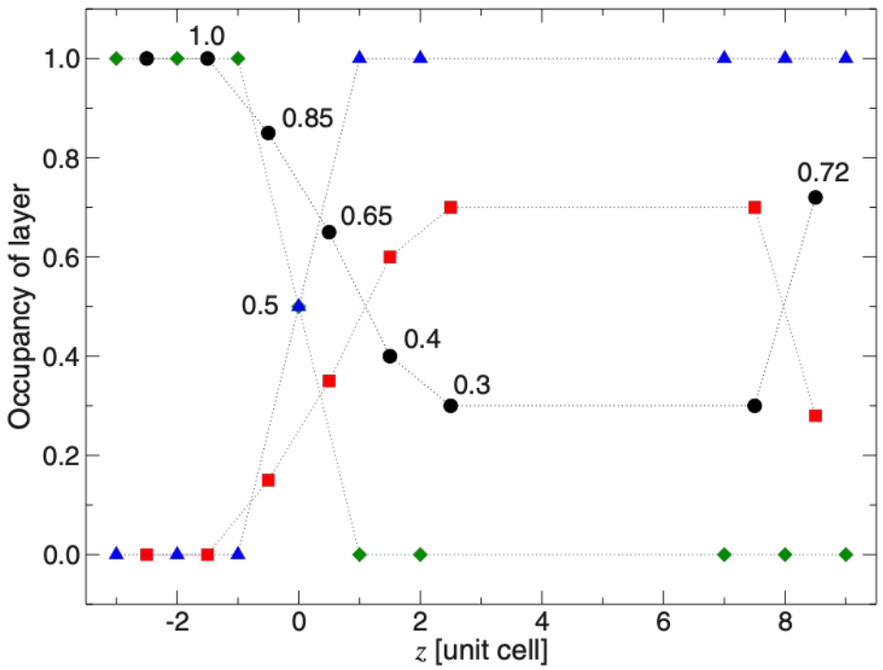
1. COBRA & other analysis techniques: still will be necessary at least in the short term if using a large beam (~ 1 mm or more)
2. if using a small beam (~1 μm), direct IFT should be possible, but you still need to capture a large amount of reciprocal space
3. could potentially raster scan ~1 μm beam across ~1 mm and build a large real space image

Example results

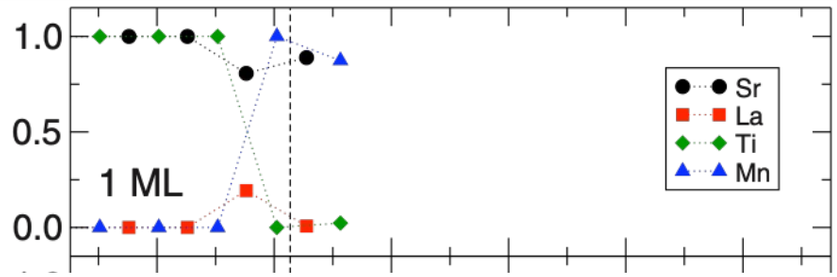
Growth of $La_{0.65}Sr_{0.35}MnO_3$ / $SrTiO_3$ (001) - COBRA

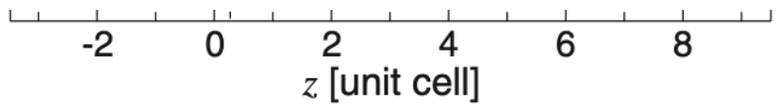
Observe that Sr likes to "float" during PLD





R. Herger *et al.*, Phys. Rev. B **77,** 085401 (2007)





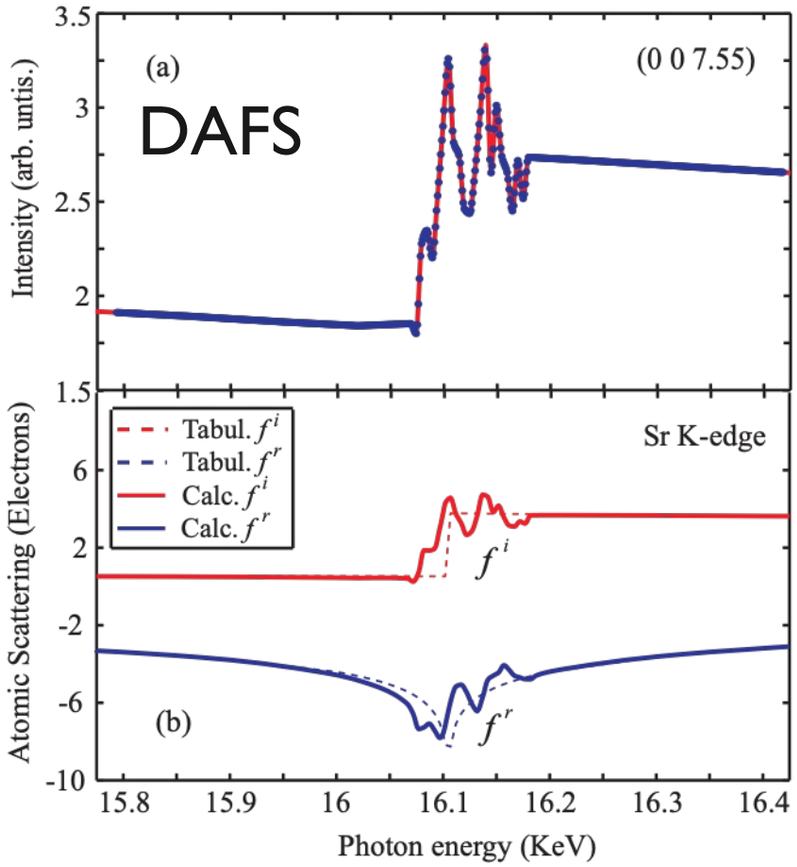
Growth of La_2CuO_4 / $La_{1.55}Sr_{0.45}CuO_4$ / $LaSrAlO_4$ (001) - resonant

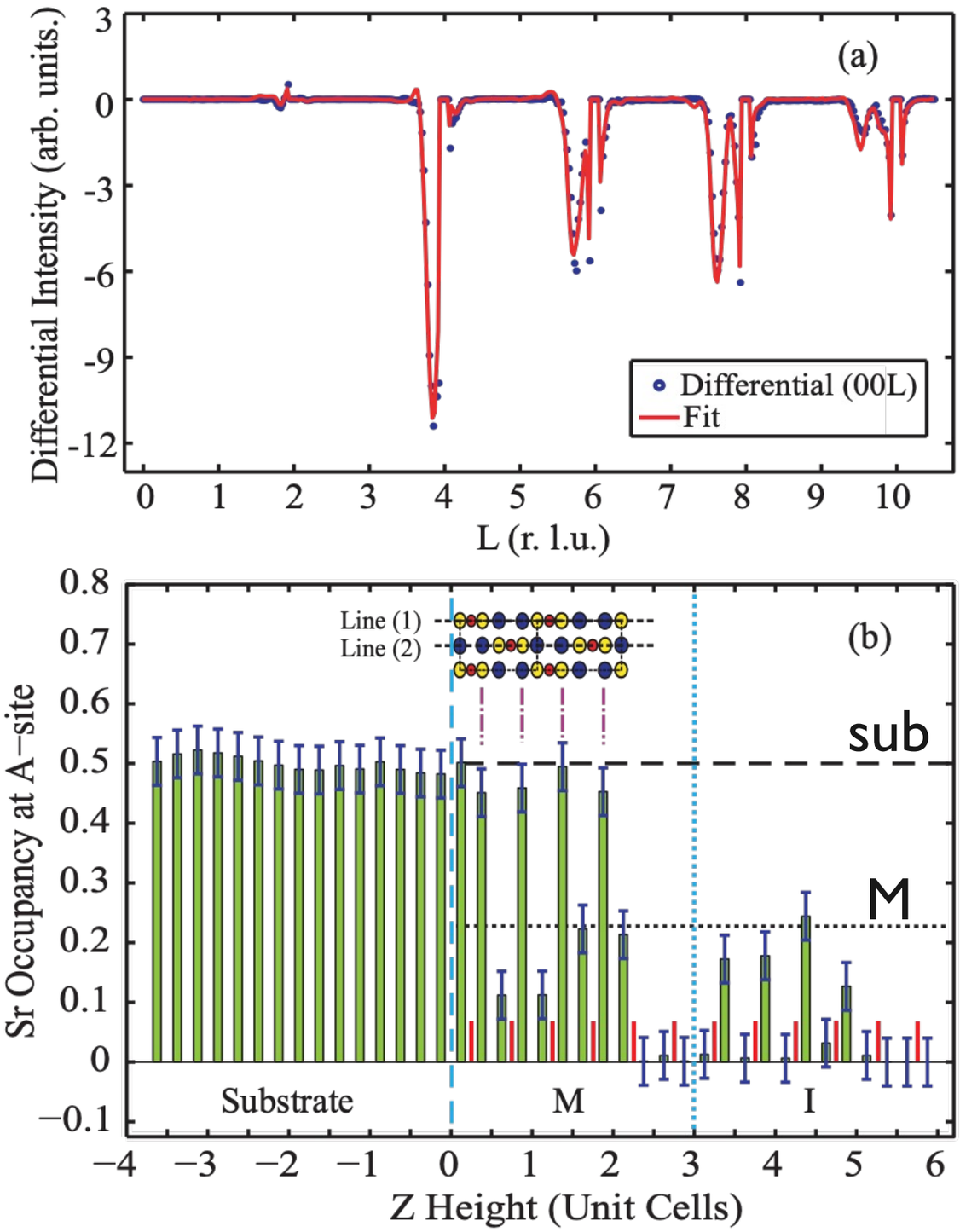
Differential COBRA

- first solve structure at non-resonant energy

$$\rho_H = \rho_L + \sum_i \rho_{i1}^A(\vec{r} - \vec{r}_i)c_{i1}\Delta f_{A1}.$$

- measure 00L at an energy ~ Sr K-edge
- fit the intensity difference
- observe that Sr likes to "float" during oxide MBE above the CuO_2 planes

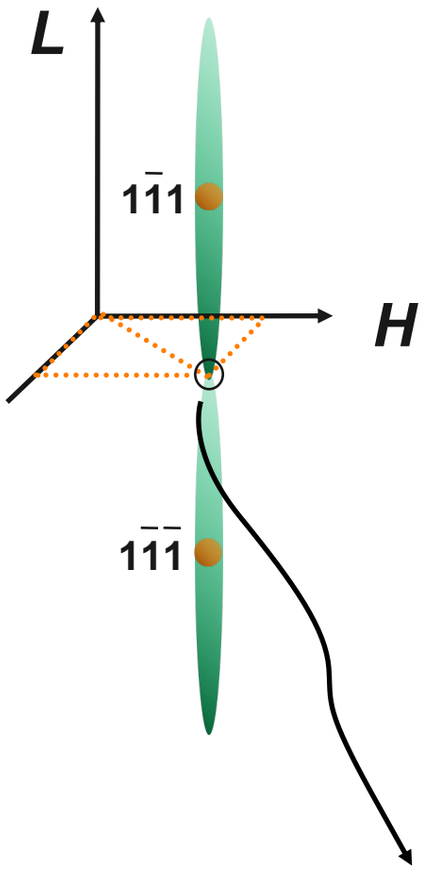


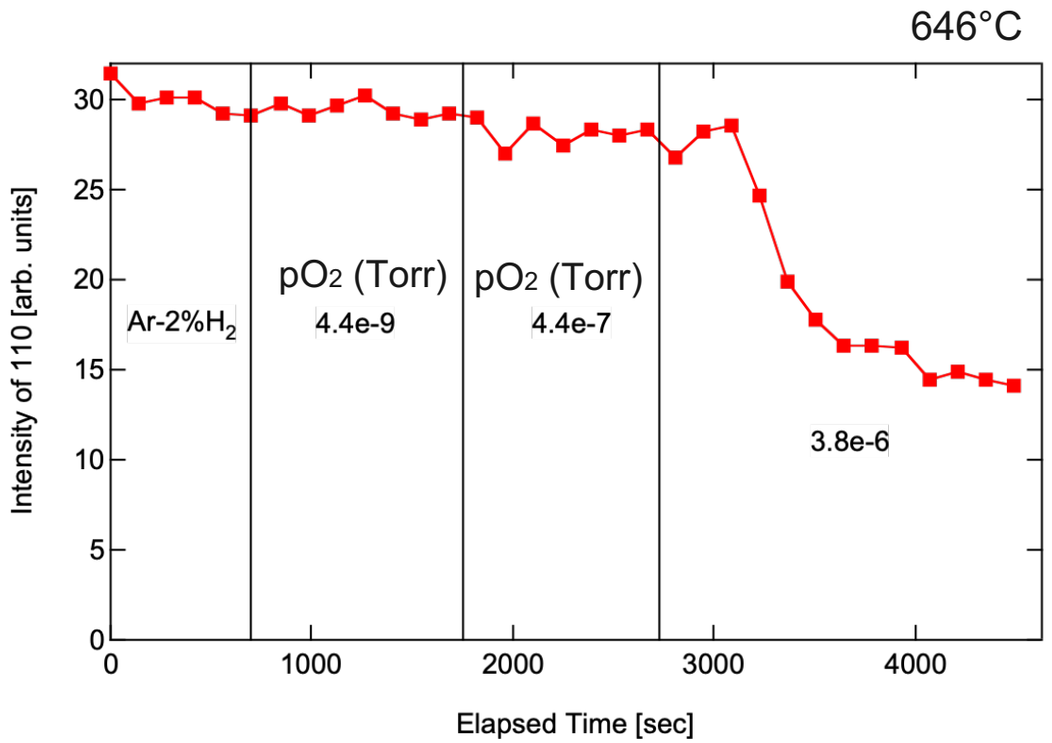


Y. Yacoby *et al.* PRB **87**, 014108 (2013)

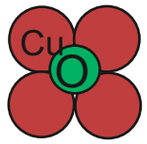
Single monolayers: oxygen adsorption onto Cu (001)

Watch 110 during pO_2 increase





Assuming adsorption onto hollow sites

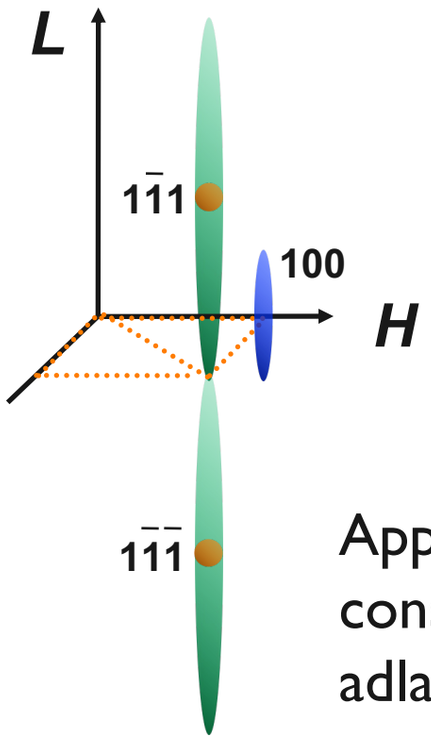


$$I_{1\bar{1}0} \approx \left(\frac{f_{\mathrm{Cu}}}{2} - \theta f_{\mathrm{O}} \right)^2$$

θ: oxygen coverage in ML (normalized by # of Cu surface atoms)

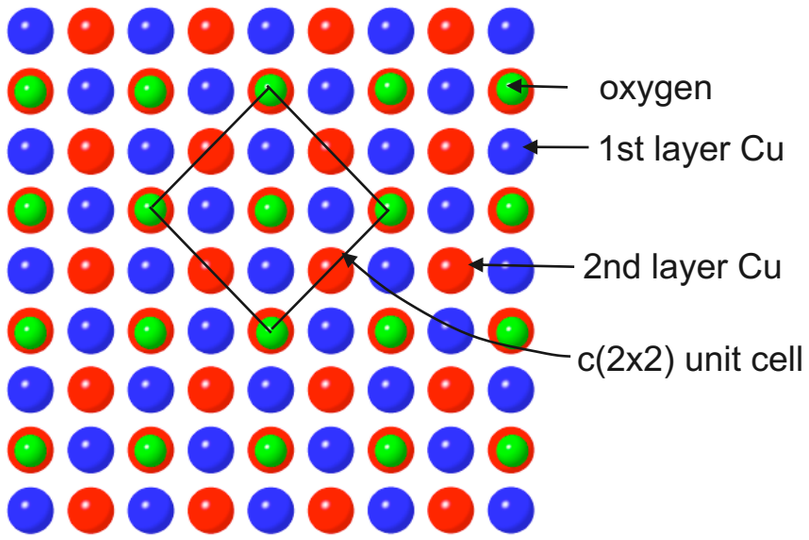
Single monolayers: oxygen adsorption onto Cu (001)

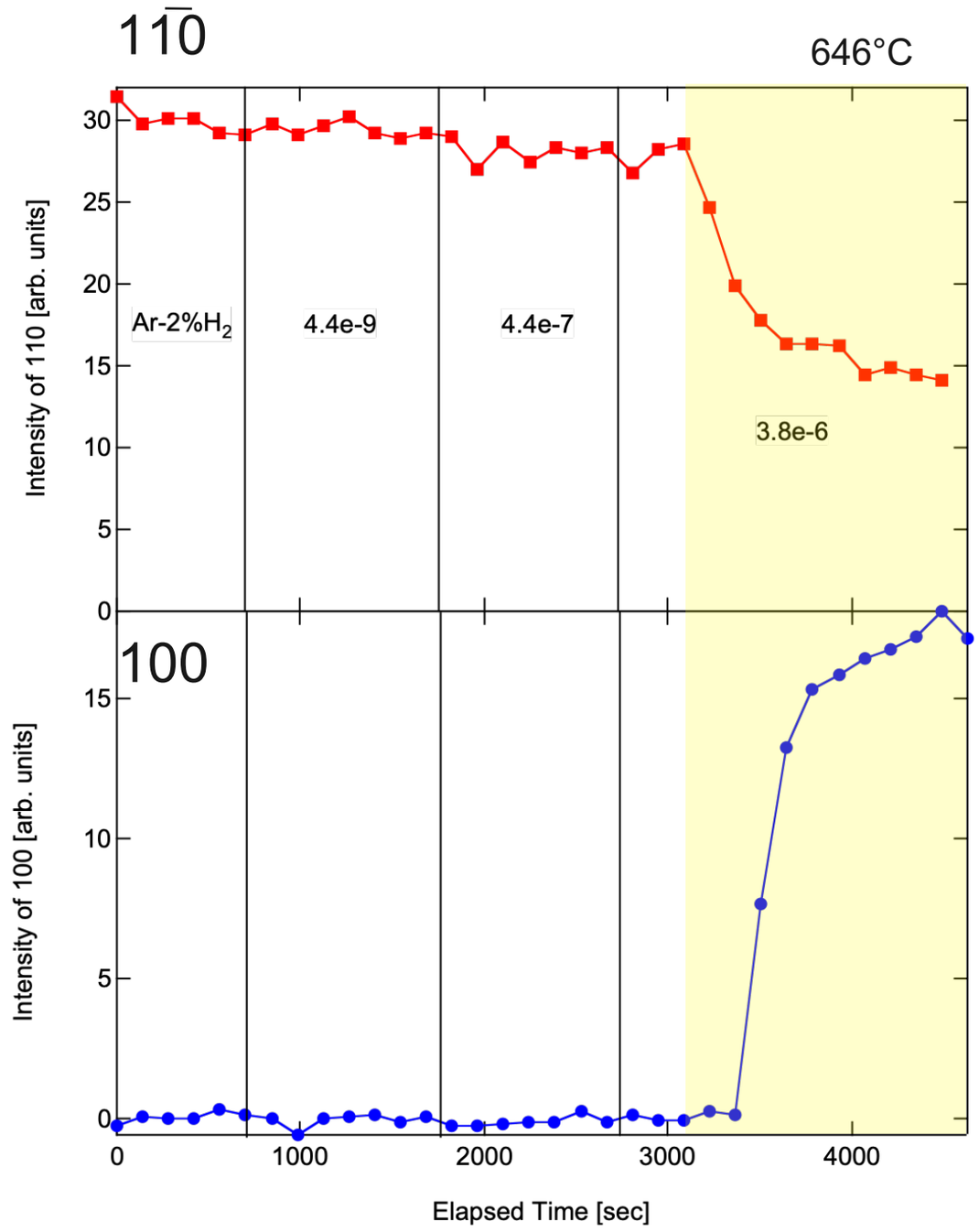
As θ → 0.5 ML, 100 superstructure rod appears



Appearance of 100 is consistent with oxygen adlayer with c(2x2) symmetry

$$I_{100} \approx \left(\frac{f_O}{2}\right)^2$$

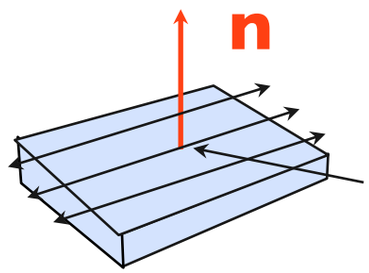




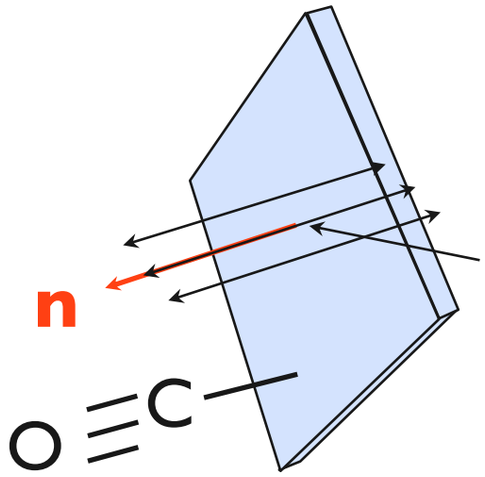
Single monolayers: CO adsorption onto Pt (111) - DAFS on SR at L=0.2

Polarized SXRD sensitive to surface bond anisotropy (even at Pt L_{III})

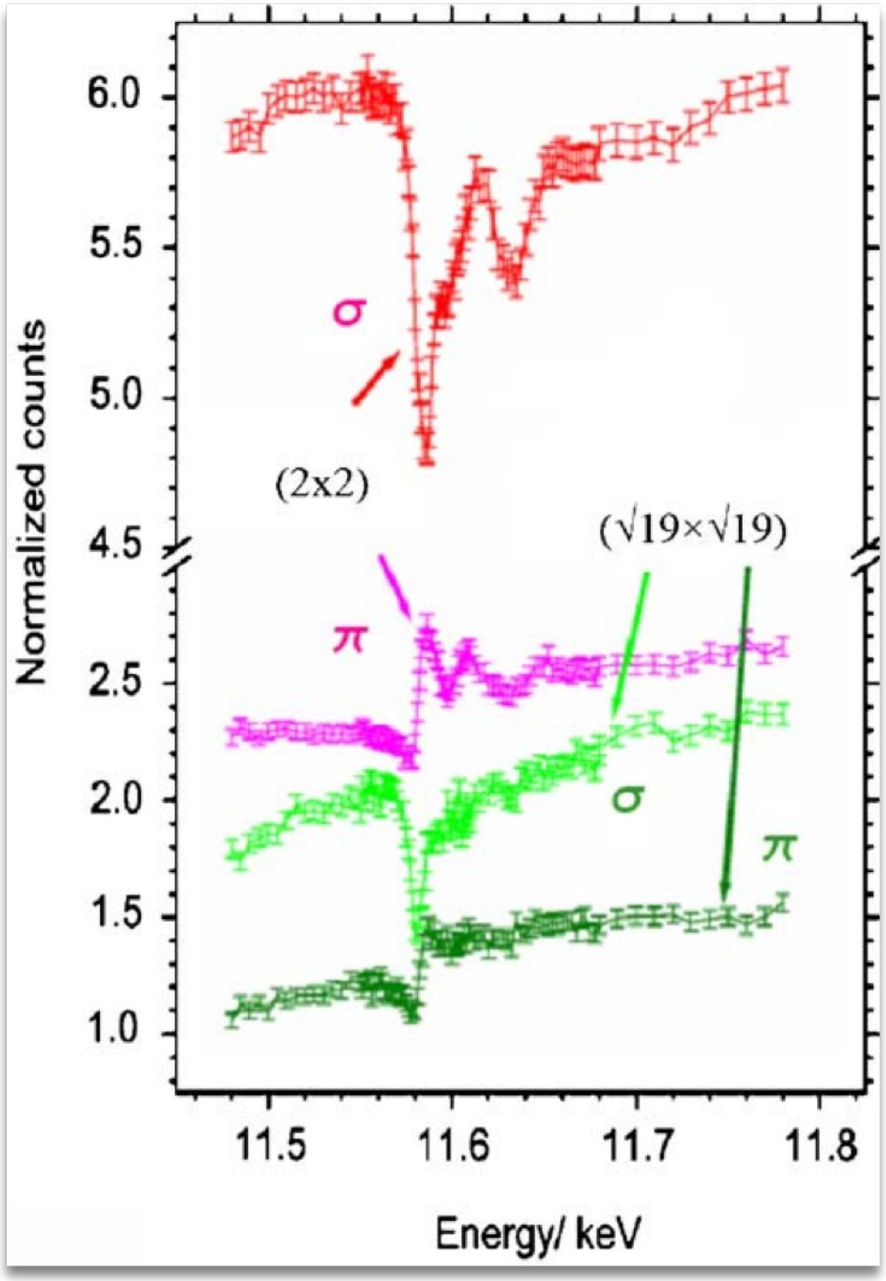
- provides 2D short-range structure



incoming x-rays
σ-polarized



incoming x-rays
π-polarized



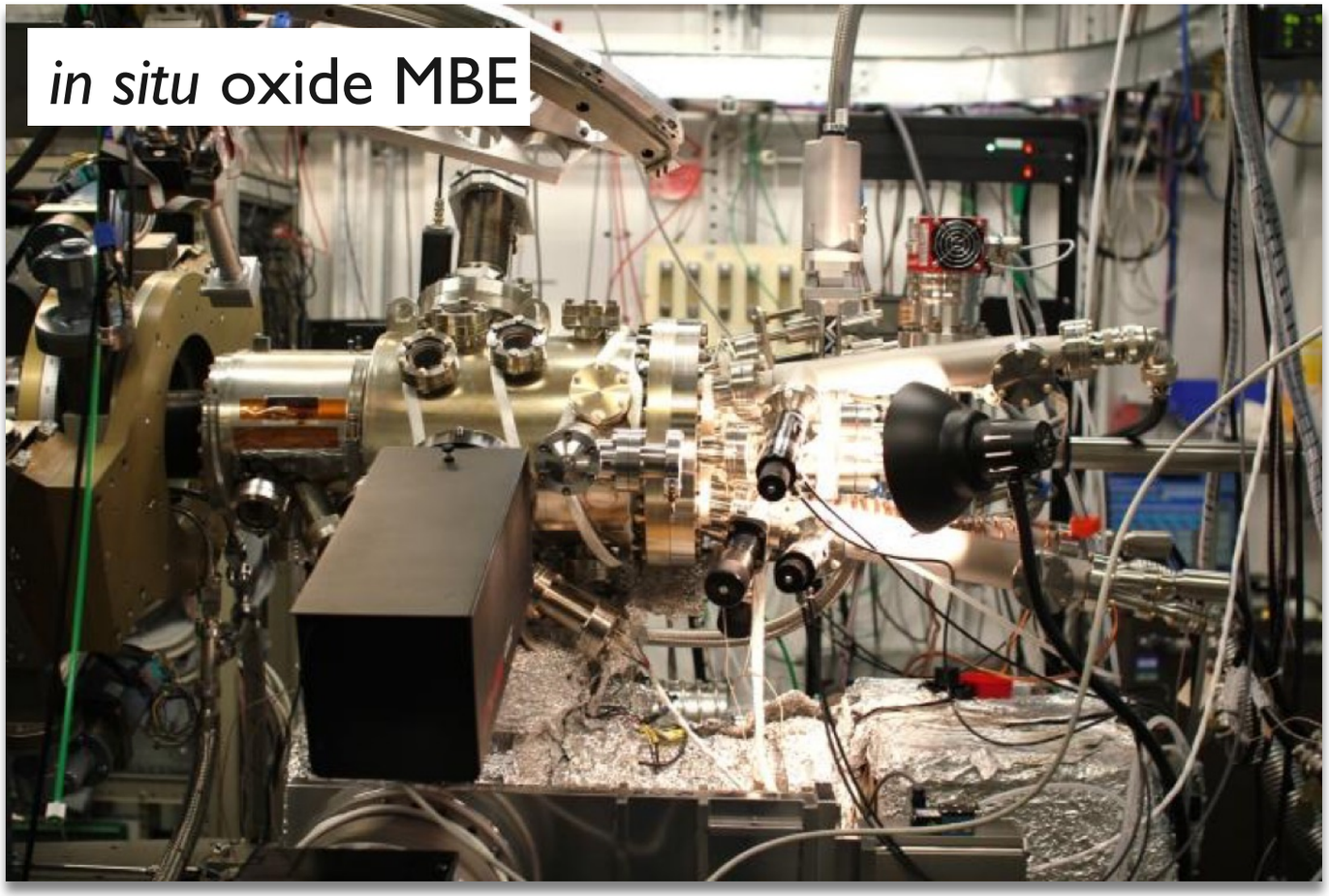
A. Menzel *et al.*, Europhys. Lett. **74,** 1032 (2006)

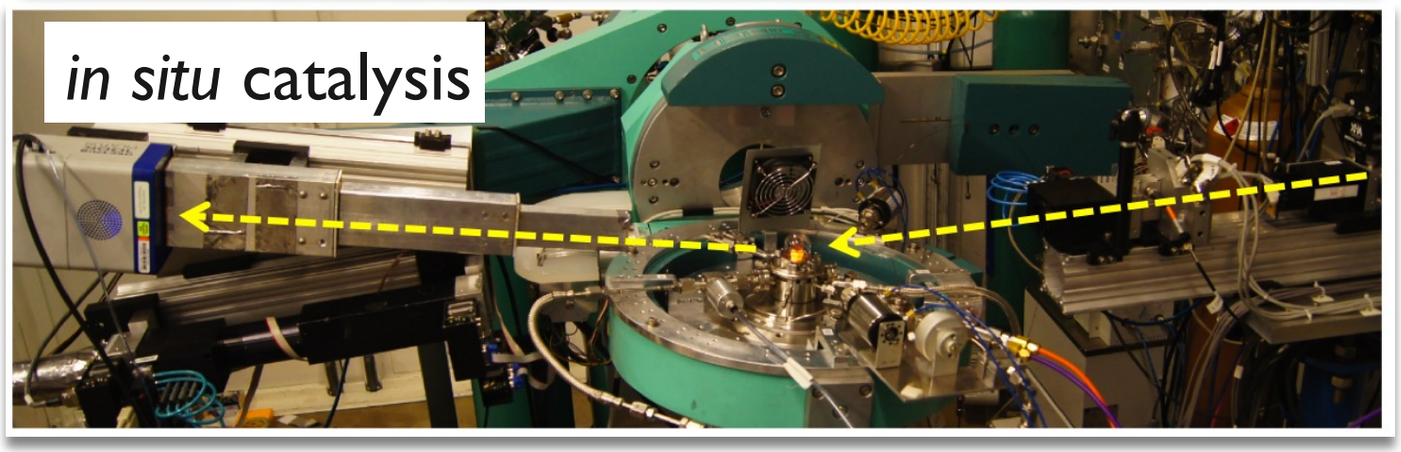
provides info on local chemical environment of CO adsorbate

A. Menzel *et al.*, Rad. Phys. Chem. **75,** 1651 (2006)

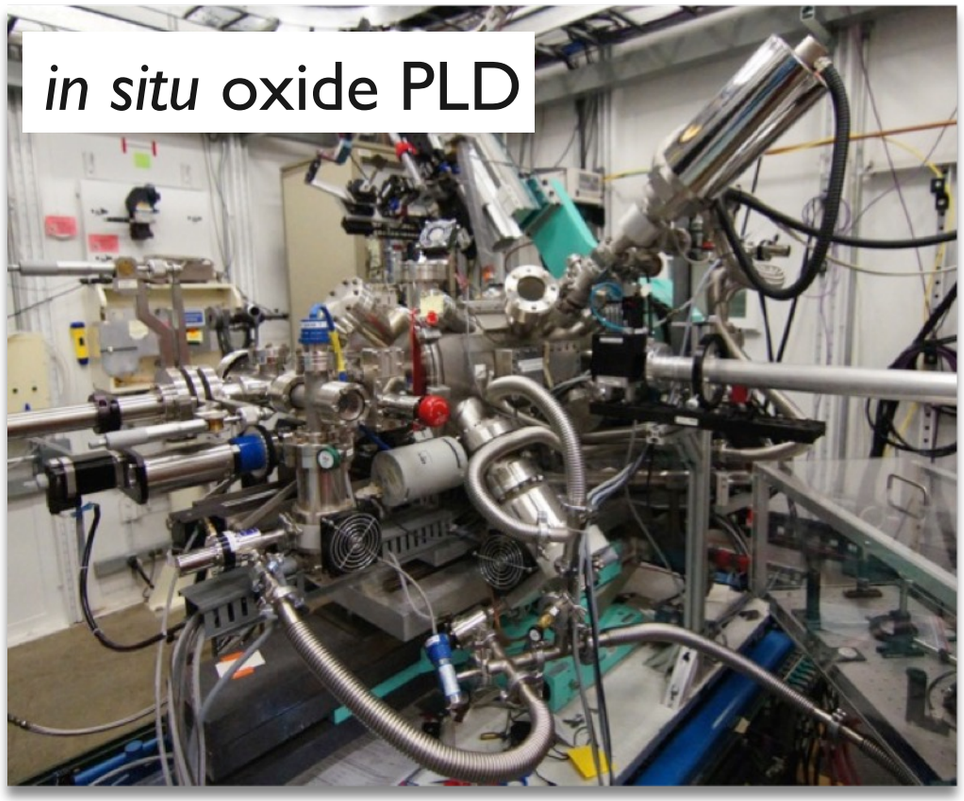
Practicalities

SXRD geometry + a lot of equipment



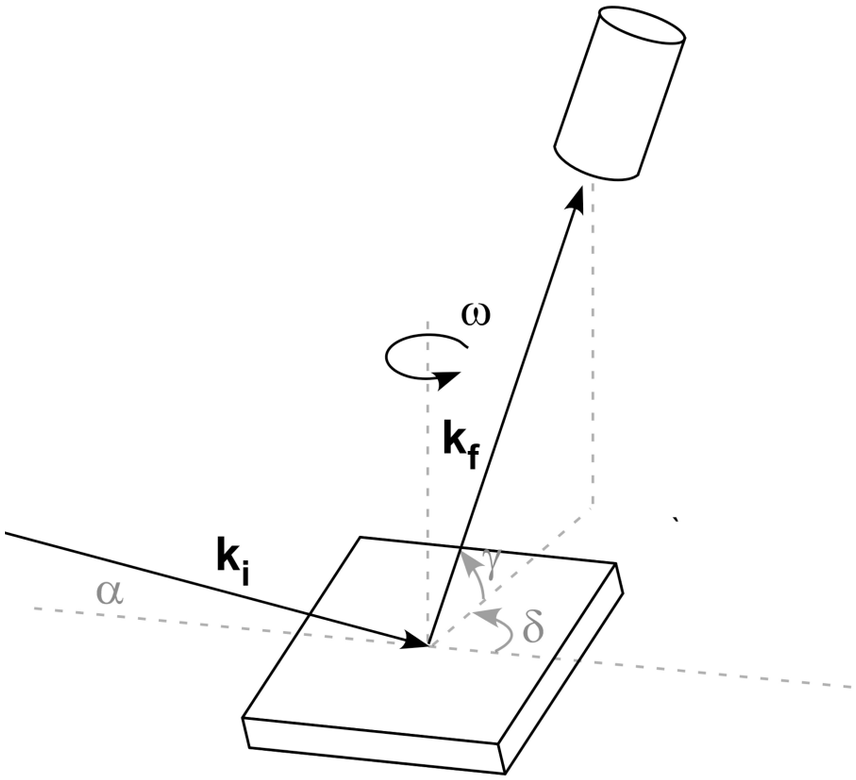


in situ oxide sputtering



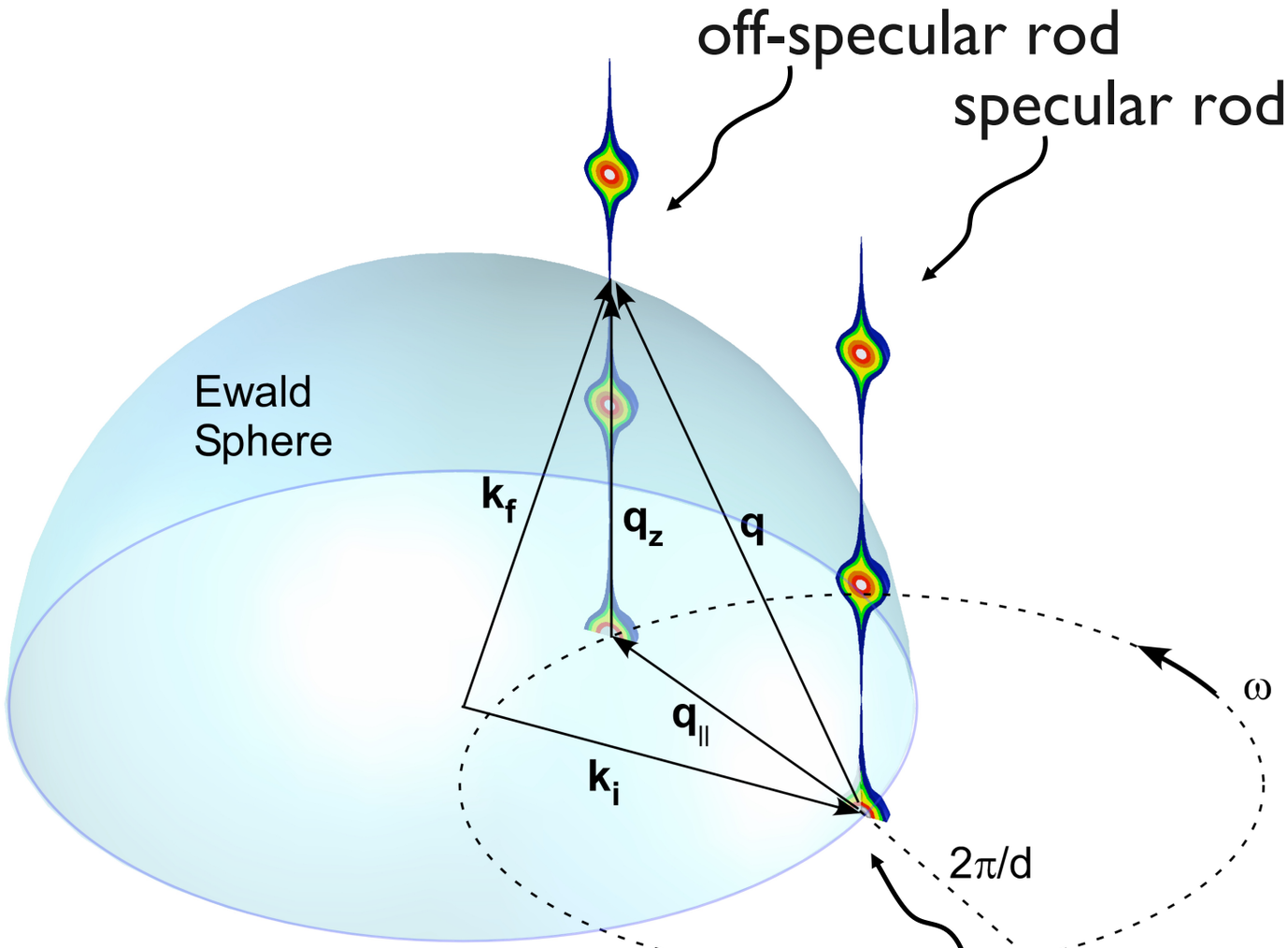
- Can do a lot by combining SXRD + *in situ*
- Need to have the proper geometry

SXRD geometry



(a)

real space



(b)

reciprocal space

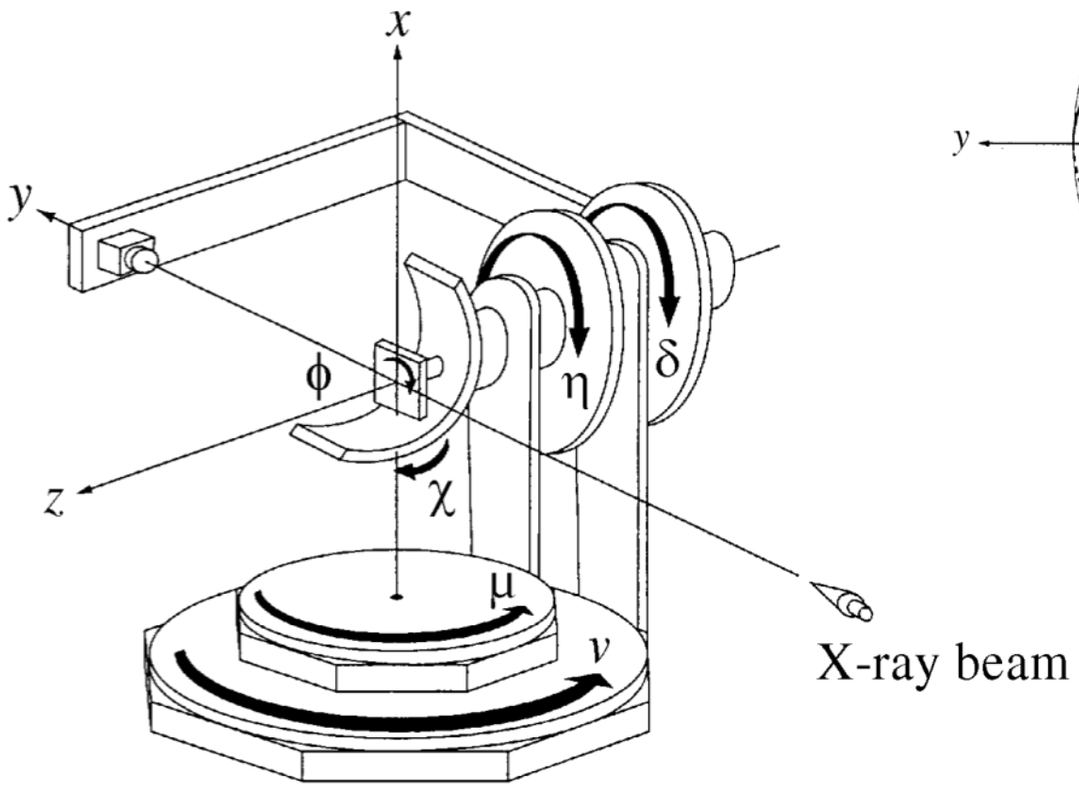
T. T. Fister & D. D. Fong *in Thin Film Metal-Oxides*, Springer (2010)

Six-circle geometry (4S+2D)

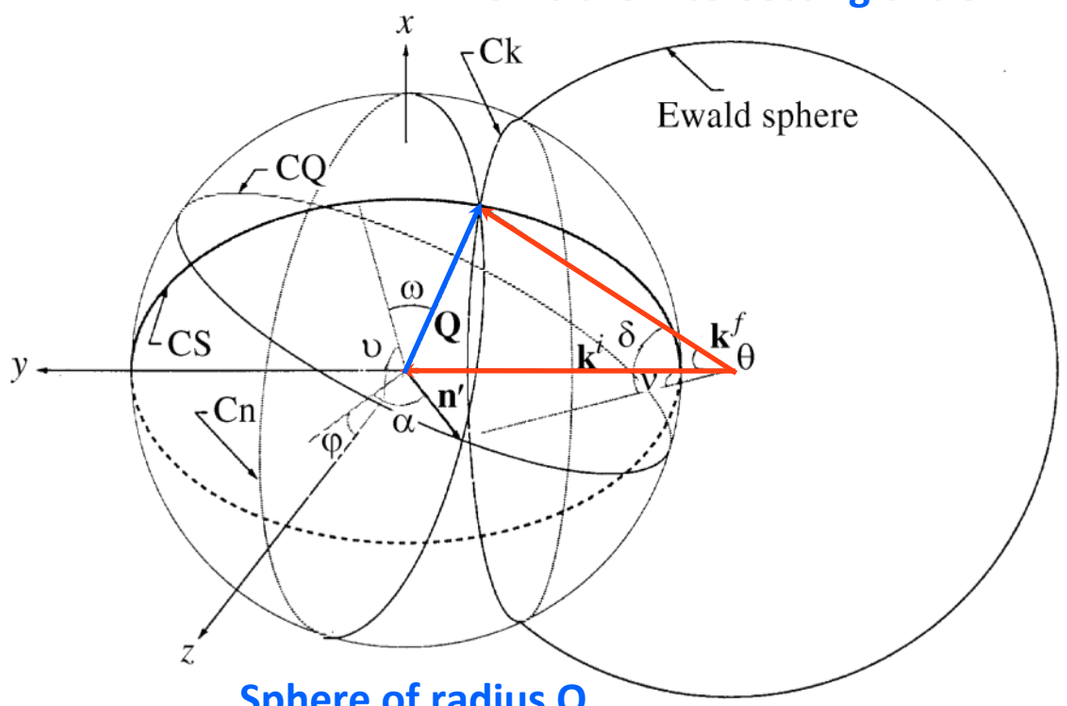
Note the laboratory coordinate system (x,y,z)

Q is defined by

- θ = ω = Bragg angle of Q (=4π**sin(**θ)/λ) (longitudinal angle from xz-plane toward y)
- ν = qaz = azimuthal angle for Q (from z-axis)
- n (sample reference vector - often assumed equal to the sample normal)
- α = incident angle (longitudinal angle from xz-plane toward y)
- ϕ = naz = azimuthal angle for n (from z-axis)
- typically, n = sample normal
- naz = 0: sample normal along z
- naz = 90°: sample normal along x



Ck is the intersecting circle



Sphere of radius Q

H. You, J. Appl. Cryst. **32,** 614 (1999)

T. T. Fister *et al.*, J. Appl. Cryst. **46** (2013)

Six-circle geometry

First, relate **h** (i.e., Q) to (x, y, z) [4S]

Next, relate $\mathbf{k_f}$ to (x, y, z) [2D]

Next, by definition: at diffraction condition: $\mathbf{h} = \mathbf{k_f} - \mathbf{k_i}$

4S

$$\mathbf{h} \xrightarrow{\mathbf{B}} \mathbf{h}_c \xrightarrow{\mathbf{U}} \mathbf{h}_\phi \xrightarrow{\mathbf{\Phi}} \mathbf{h}_\chi \xrightarrow{\mathbf{X}} \mathbf{h}_\eta \xrightarrow{\mathbf{H}} \mathbf{h}_\mu \xrightarrow{\mathbf{M}} \mathbf{h}_M,$$

$$\mathbf{\Phi} = \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\mathbf{X} = \begin{pmatrix} \cos\chi & 0 & \sin\chi \\ 0 & 1 & 0 \\ -\sin\chi & 0 & \cos\chi \end{pmatrix},$$

$$\mathbf{H} = \begin{pmatrix} \cos\eta & \sin\eta & 0 \\ -\sin\eta & \cos\eta & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\mathbf{M} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\mu & -\sin\mu \\ 0 & \sin\mu & \cos\mu \end{pmatrix}.$$

$$\mathbf{h}_M = \mathbf{MHX\Phi UBh}$$

2D

$$\mathbf{k}_0^f \xrightarrow{\mathbf{\Delta}} \mathbf{k}_\delta^f \xrightarrow{\mathbf{\Pi}} \mathbf{k}_\nu^f$$

$$\mathbf{\Delta} = \begin{pmatrix} \cos\delta & \sin\delta & 0 \\ -\sin\delta & \cos\delta & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\mathbf{\Pi} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\nu & -\sin\nu \\ 0 & \sin\nu & \cos\nu \end{pmatrix}.$$

$$\mathbf{k}_\nu^f = k\mathbf{\Pi\Delta}\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = k\begin{pmatrix} \sin\delta \\ \cos\nu\cos\delta \\ \sin\nu\cos\delta \end{pmatrix}$$

at diffraction condition:

$$\mathbf{h}_M = \mathbf{Q}_L,$$

where $\mathbf{h}_M = \mathbf{MHX\Phi UBh}$

and $$\mathbf{Q}_L = \mathbf{k}_\nu^f - \mathbf{k}_L^i = (\mathbf{\Pi\Delta} - \mathbf{I})\begin{pmatrix} 0 \\ k \\ 0 \end{pmatrix} = k\begin{pmatrix} \sin\delta \\ \cos\delta\cos\nu - 1 \\ \cos\delta\sin\nu \end{pmatrix},$$

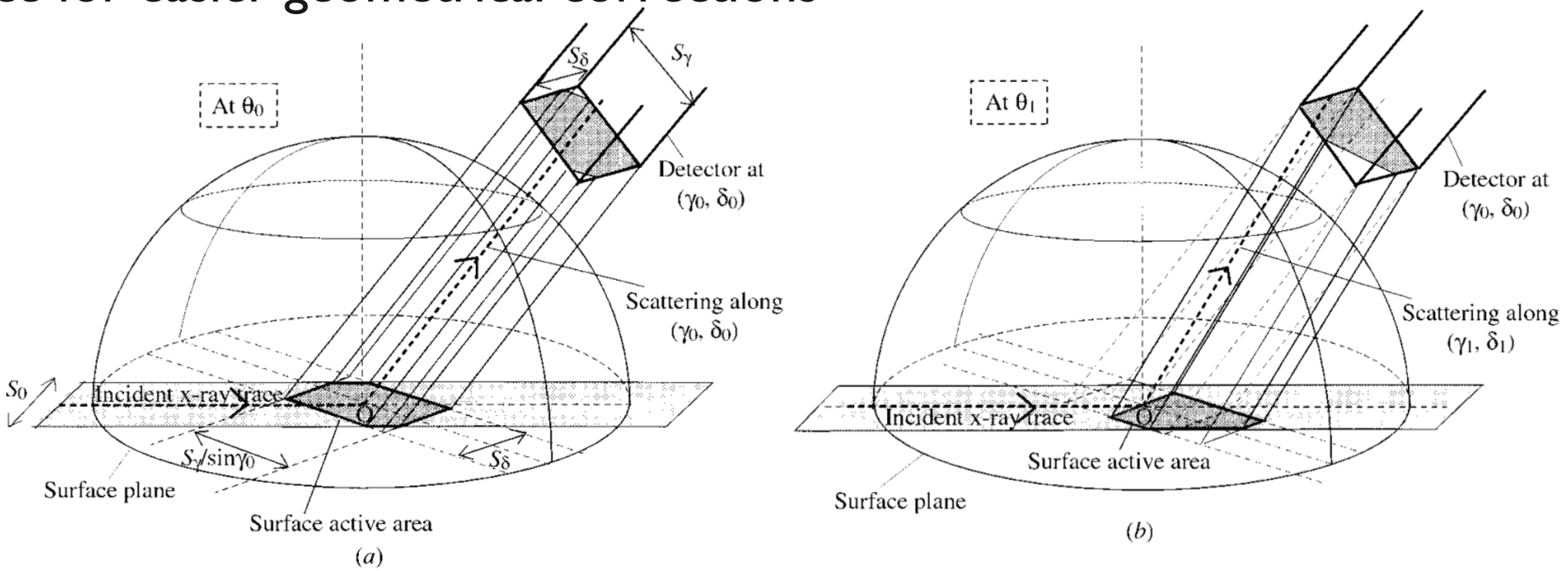
Six-circle geometry

Put everything into software

- spec -- http://www.certif.com
- modes for six-circle, four-circle, etc.
- then you can type (effectively) "go to 202; scan along 20L"

Why do you need a six-circle?

- you can keep a constant x-ray footprint on the sample
- nice for $L \sim 0$ work
- nice for easier geometrical corrections



N. Jedrecy, J. Appl. Cryst. **33,** 1365 (2000)

Geometrical corrections

Integrated intensity often came from a φ-scan+point detector

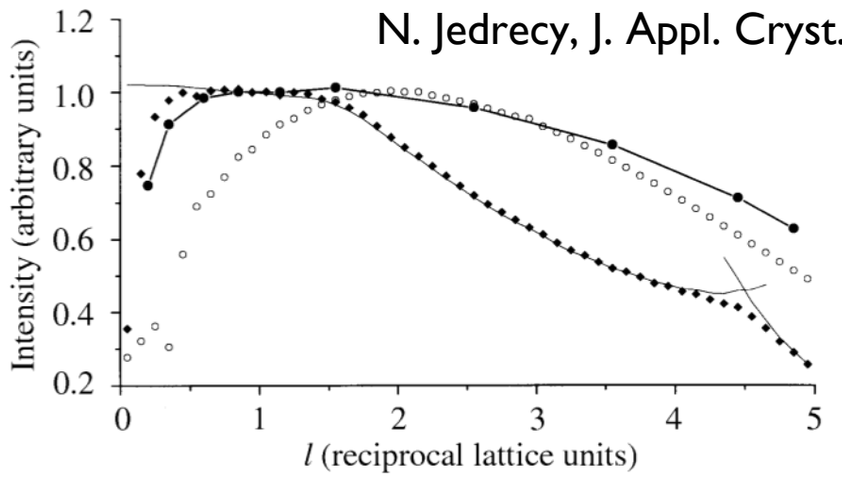
- Corrected integrated intensity

$$I_{\text{int},\varphi} = (\Phi_0/\omega_0)\int (\mathrm{d}\sigma/\mathrm{d}\Omega)\,\mathrm{d}\gamma\,\mathrm{d}\psi\,\mathrm{d}\varphi,$$

$$I_{\text{int},\varphi} = (\Phi_0 r_e^2 A_0 \lambda^2 \Delta\gamma/\omega_0 A_u^2)|F_{hkl}|^2 C_{\text{tot}},$$

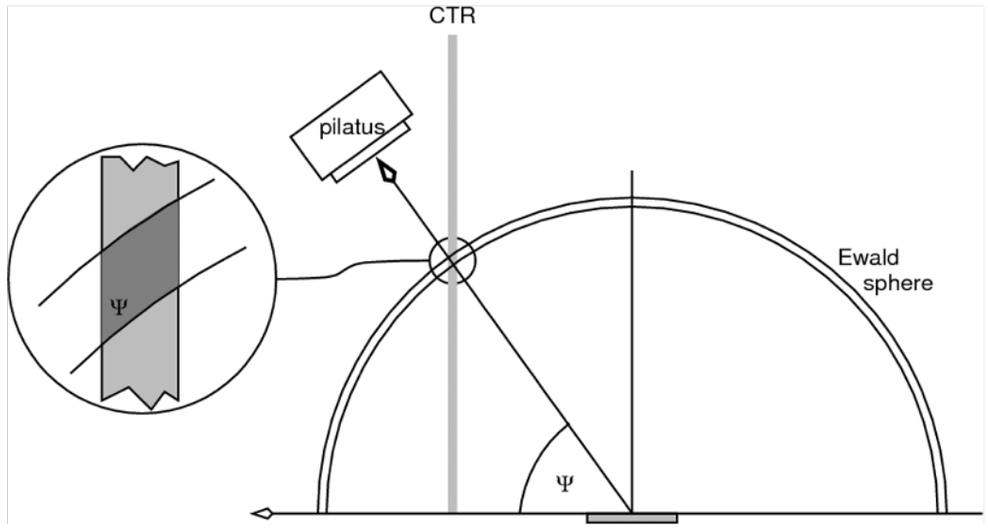
$$C_{\text{tot}} = P L_\varphi C_{\text{rod}} C_{\text{area}} C_{\text{det}} C_{\text{beam}}.$$

E. Vlieg, J. Appl. Cryst. 30, 532 (1997)



N. Jedrecy, J. Appl. Cryst. **33,** 1365 (2000)

- With 2D detectors (like Pilatus), it is easier, since we don't rock sample



still have polarization corrections:

horizontal sample

$$P_{\mathbf{n}_{\text{up,down}}} = 1 - \sin^2\delta\cos^2\gamma$$

vertical sample

$$P_{\mathbf{n}_{\text{in,out}}} = 1 - (\sin\alpha\cos\delta\cos\gamma + \cos\alpha\sin\gamma)^2$$

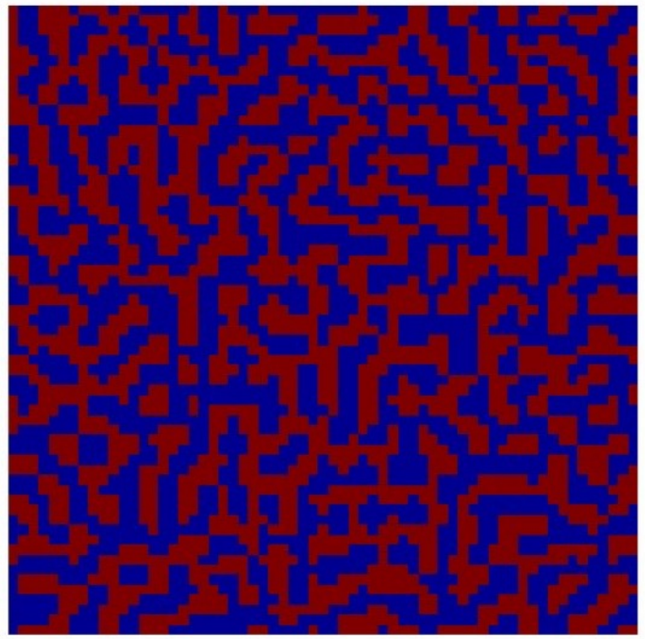
$$C_{\text{tot, spec}} = P\left[\frac{A_{\text{num}}}{\sin\alpha}\right] \qquad C_{\text{tot, non-spec}} = P\left[\frac{1}{\cos\delta\sin(\nu-\alpha)}\right]$$

C. M. Schlepütz *et al.*, Acta Cryst. A **61,** 418 (2005)

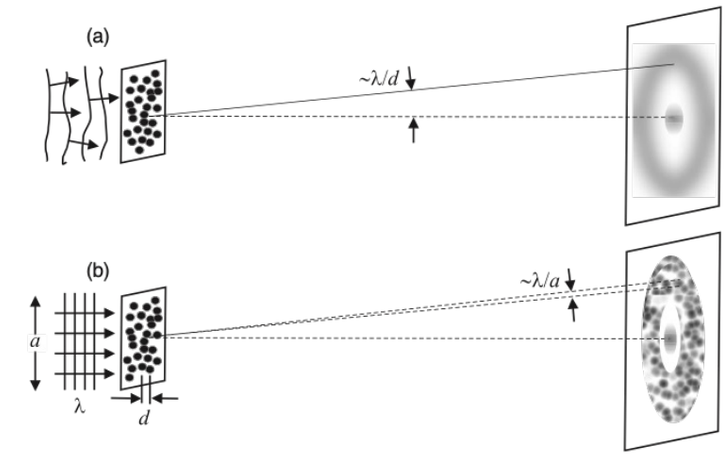
X-ray photon correlation spectroscopy

With coherent x-rays, x-ray photon correlation spectroscopy (XPCS)

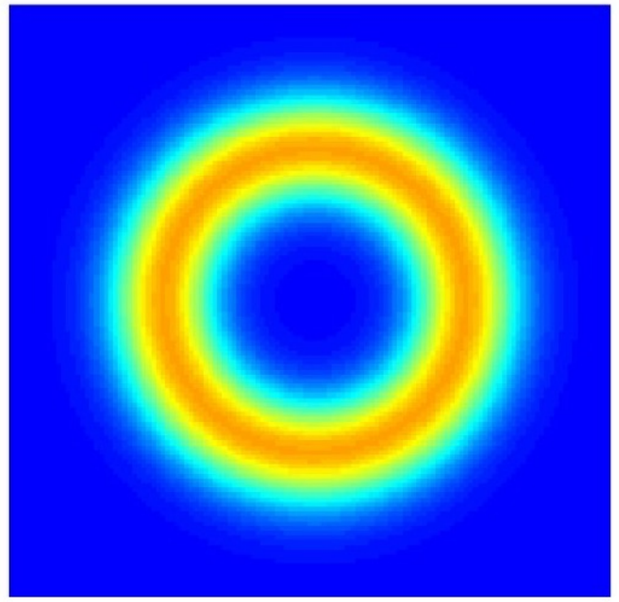
sample with disorder
(e.g. domains)

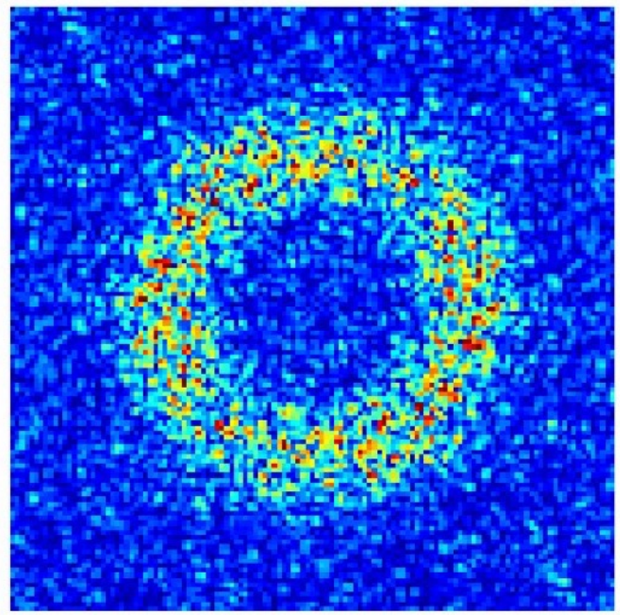


- ***Incoherent Beam: Diffuse Scattering***
  - **Measures averages, e.g. size, correlations**
- ***Coherent Beam: Speckle***
  - **Speckle depends on exact arrangement**



scattering



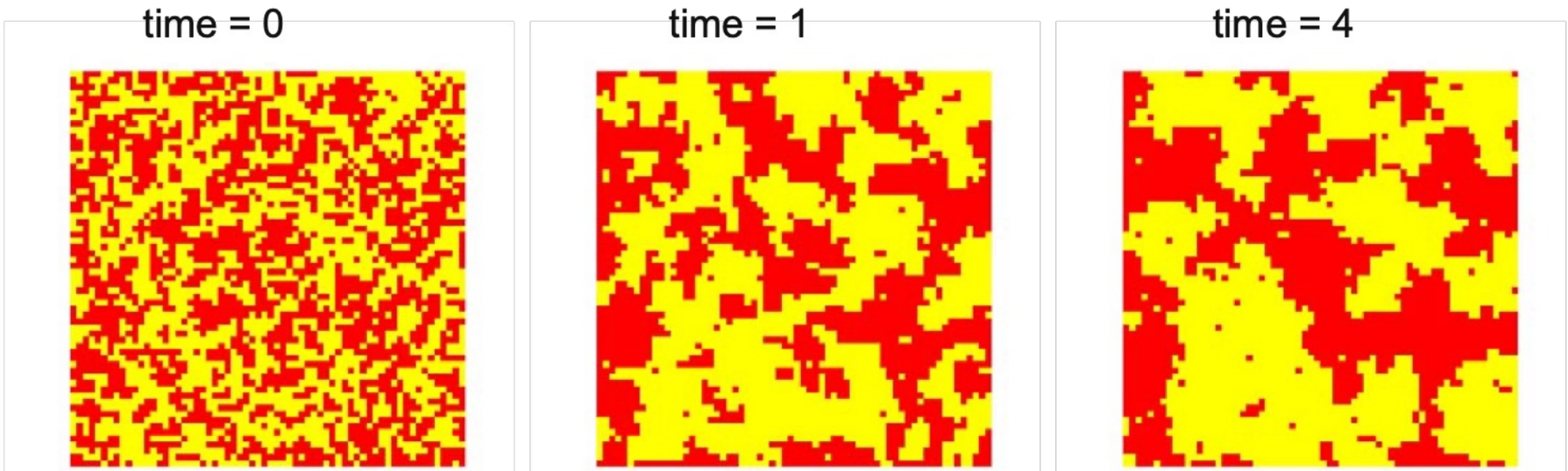


from G B Stephenson

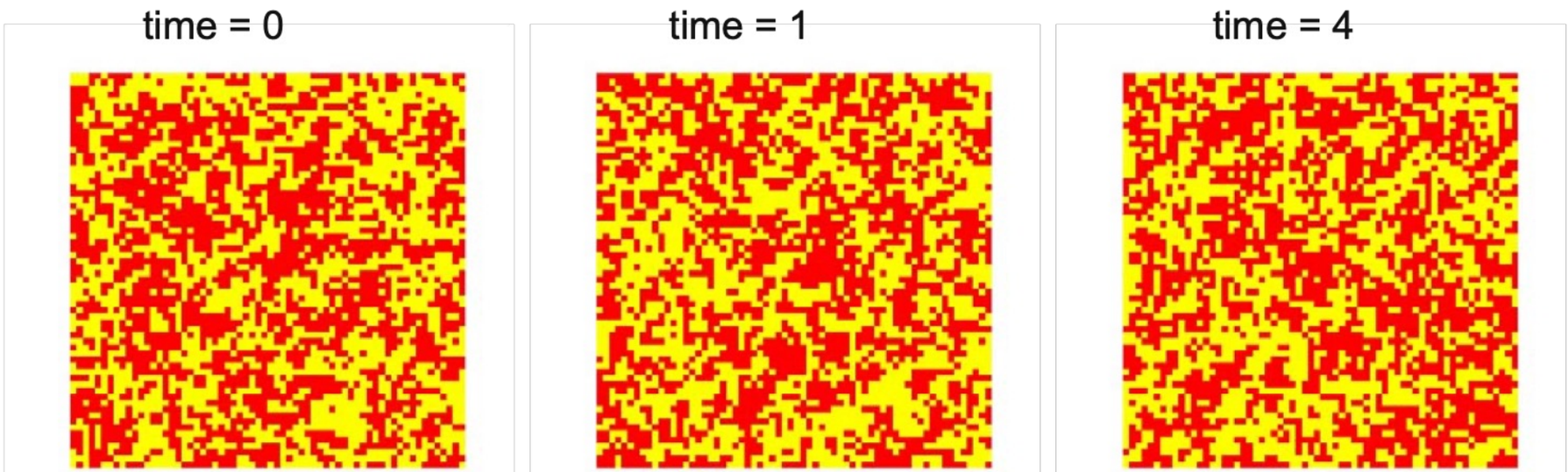
J. F. van der Veen & F. Pfeiffer, J. Phys. Condens. Matter **16,** 5003 2004

Speckle reveals equilibrium dynamics

A. Non-equilibrium dynamics: average structure changes



B. Equilibrium dynamics: average structure is static

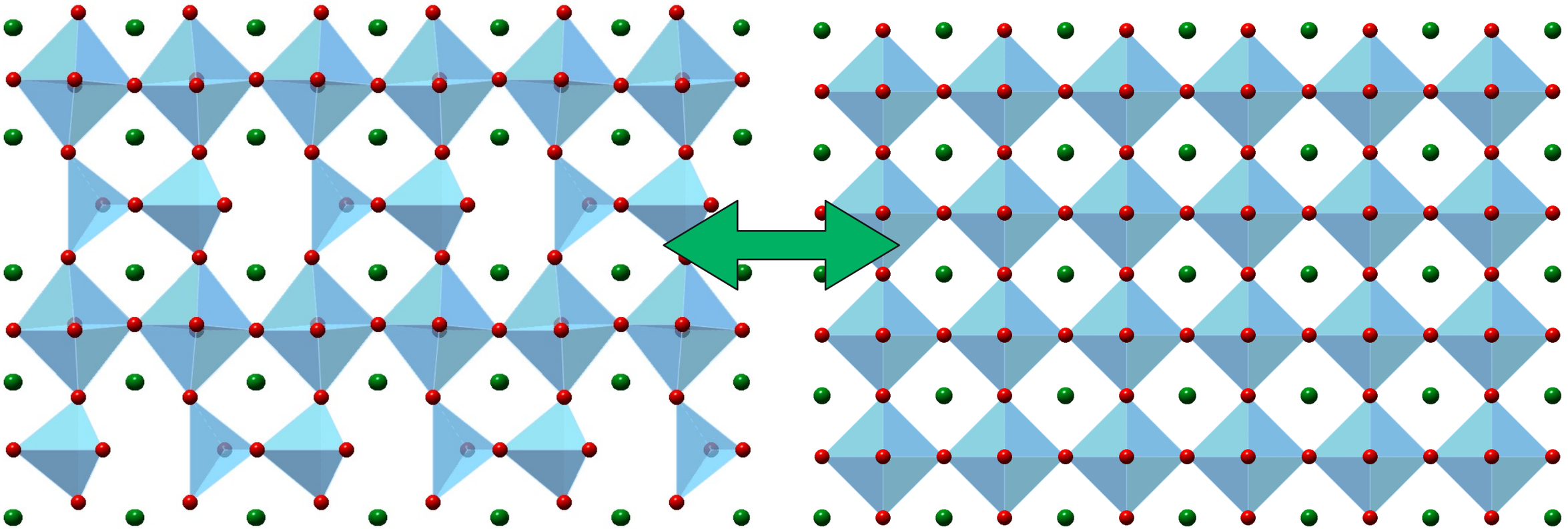


*G.B. Stephenson, A. Robert, G. Grübel, Nature Mater. **8**, 702 (2009)*

Non-equilibrium dynamics: phase transitions

$SrCoO_{2.5}$

$SrCoO_3$



antiferromagnetic insulator

ferromagnetic metal

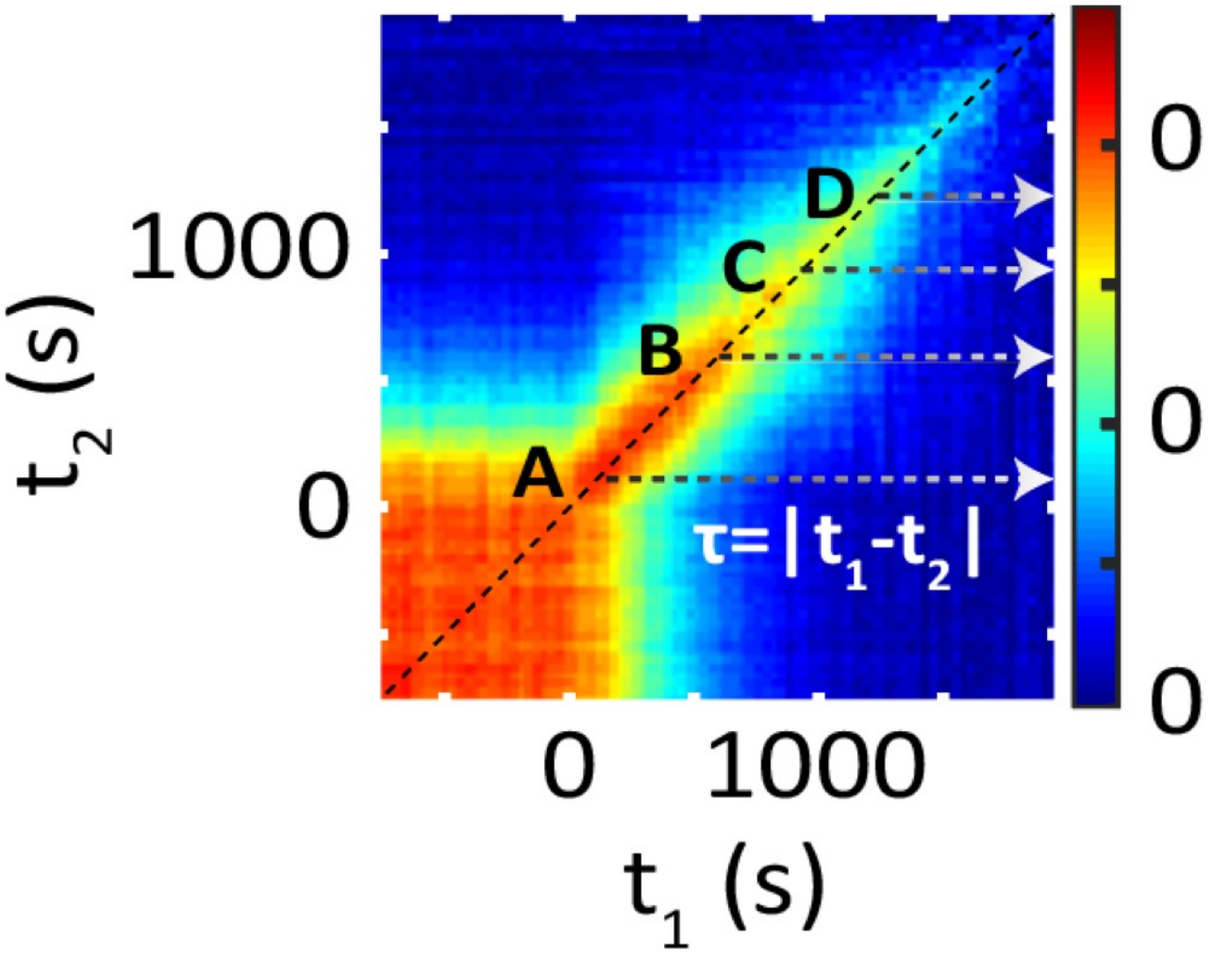
Non-equilibrium dynamics: phase transitions

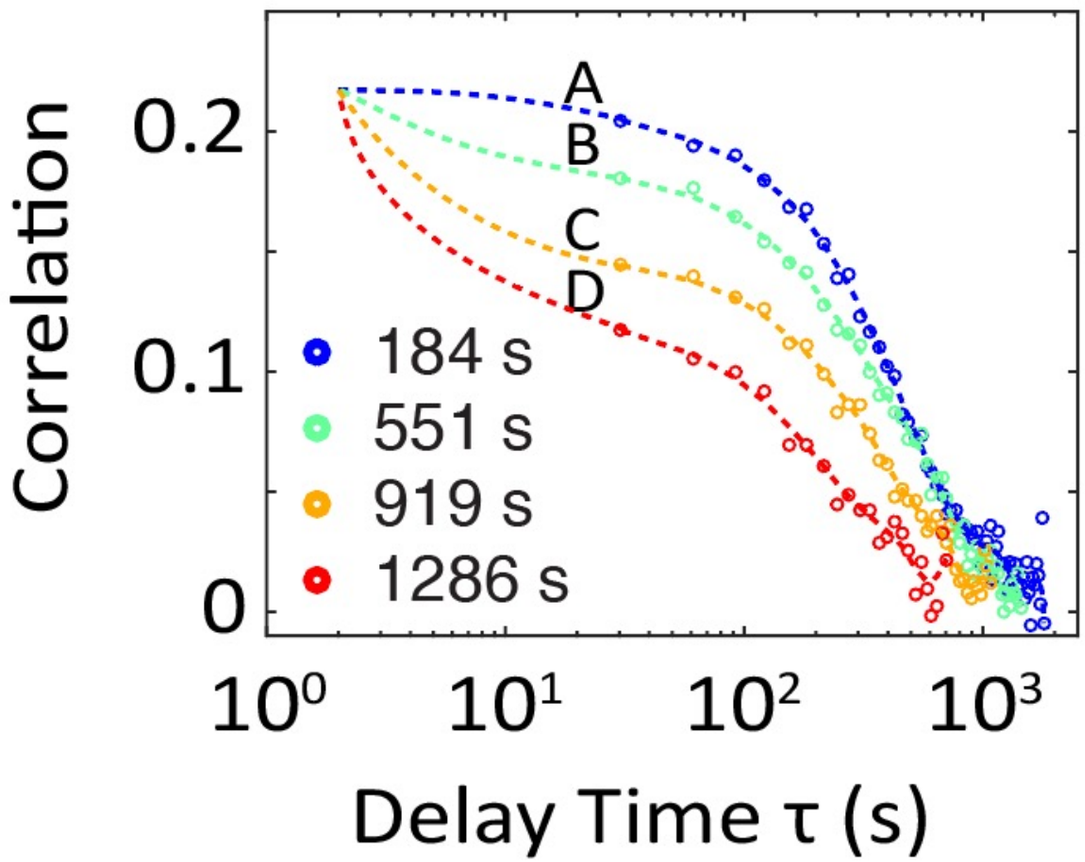
$$C(q, t_1, t_2) = \frac{\langle I(t_1)I(t_2)\rangle - \langle I(t_1)\rangle\langle I(t_2)\rangle}{[\langle I^2(t_1)\rangle - \langle I(t_1)\rangle^2]^{1/2}[\langle I^2(t_2)\rangle - \langle I(t_2)\rangle^2]^{1/2}}$$

(two-time correlation function for non-equilibrium dynamics)

$SrCoO_{2.5}$ / $SrTiO_3$ (001)

330°C, $N_2 \rightarrow O_2$



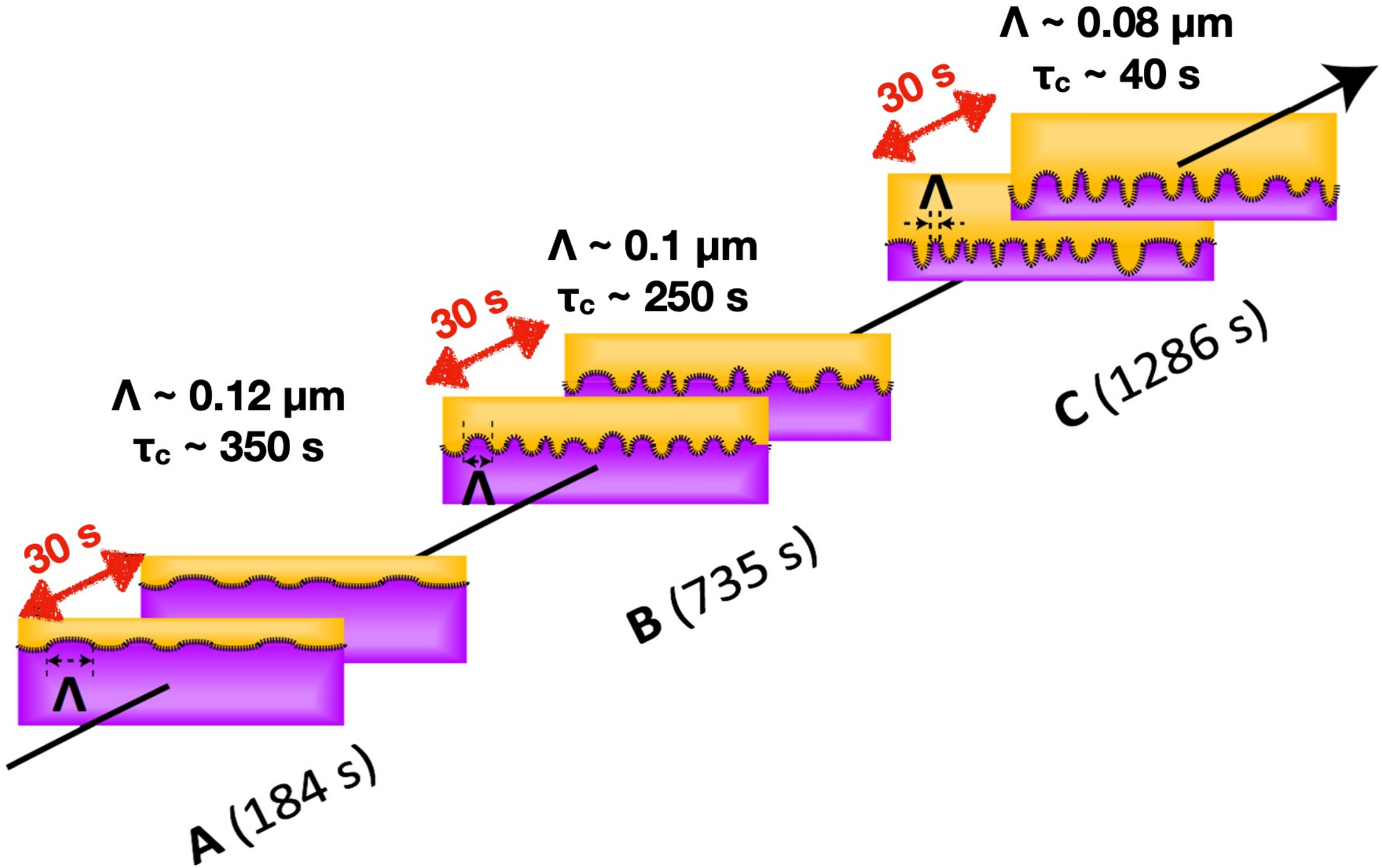


fluctuations speed up with time

Q. Zhang et al., PRL 129, 235701 (2022)

Non-equilibrium dynamics: phase transitions

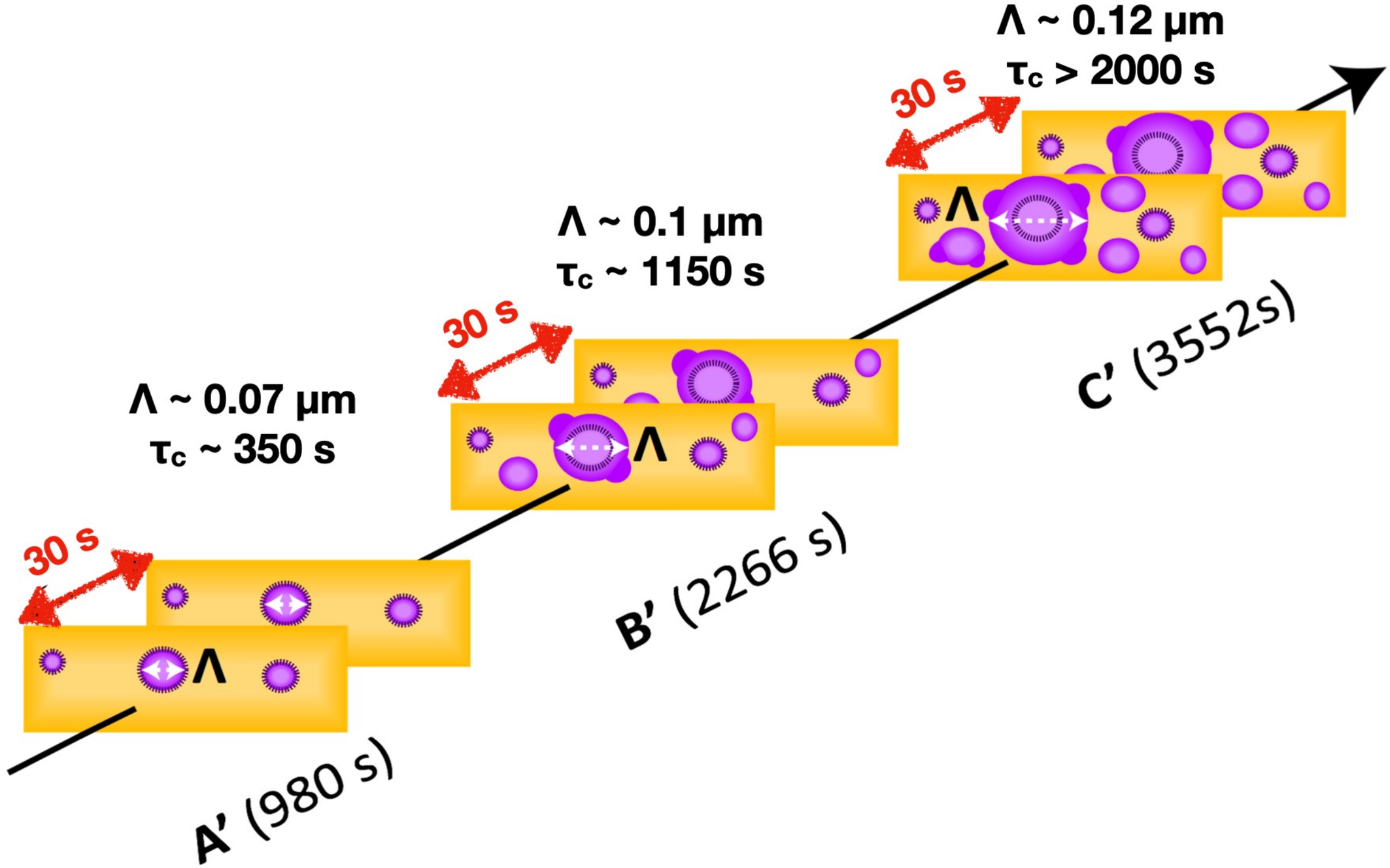
Dynamics during reduction (PV→BM)



Q. Zhang et al., PRL 129, 235701 (2022)

Non-equilibrium dynamics: phase transitions

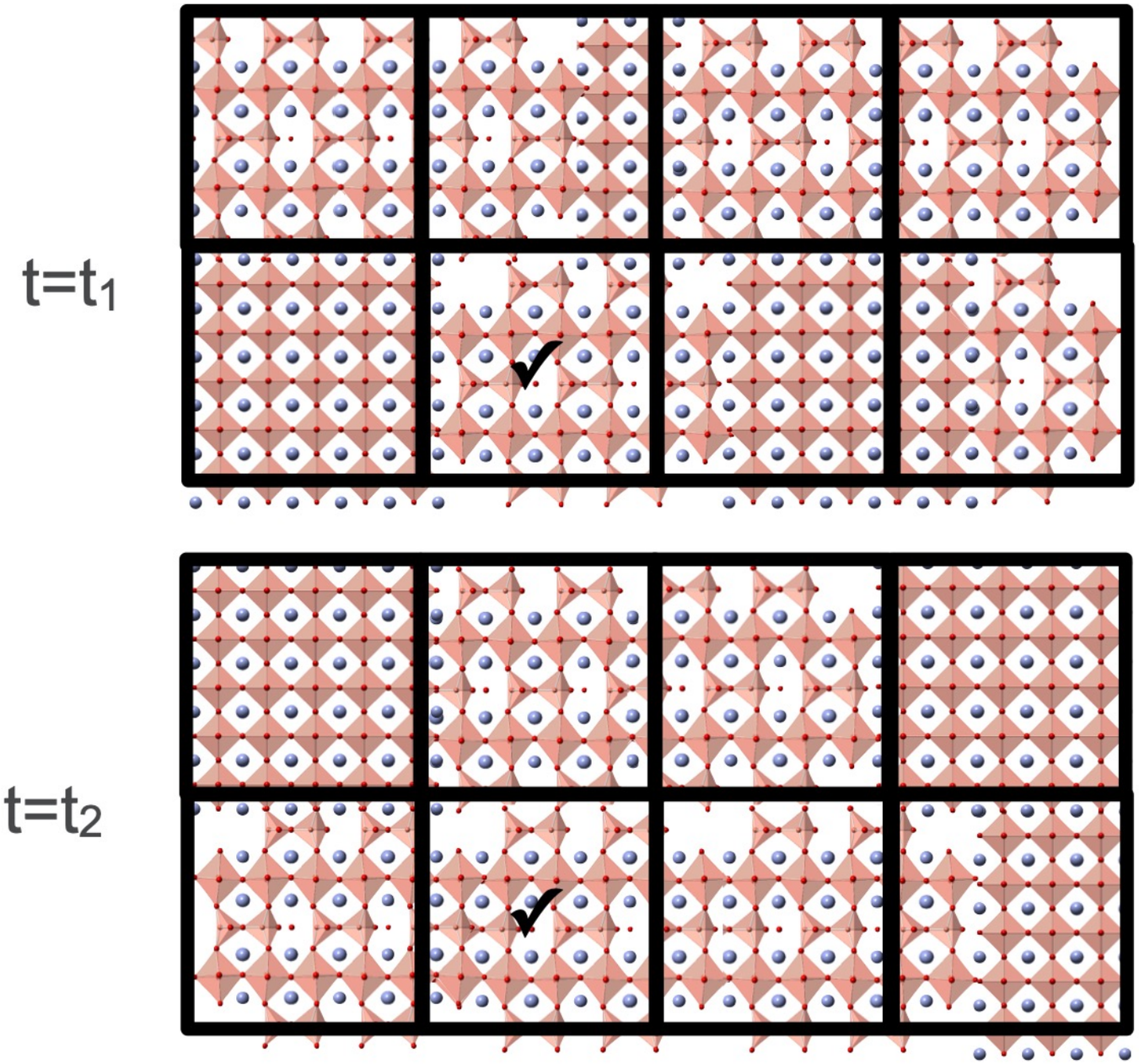
Dynamics during oxidation (BM→PV)



Q. Zhang et al., PRL 129, 235701 (2022)

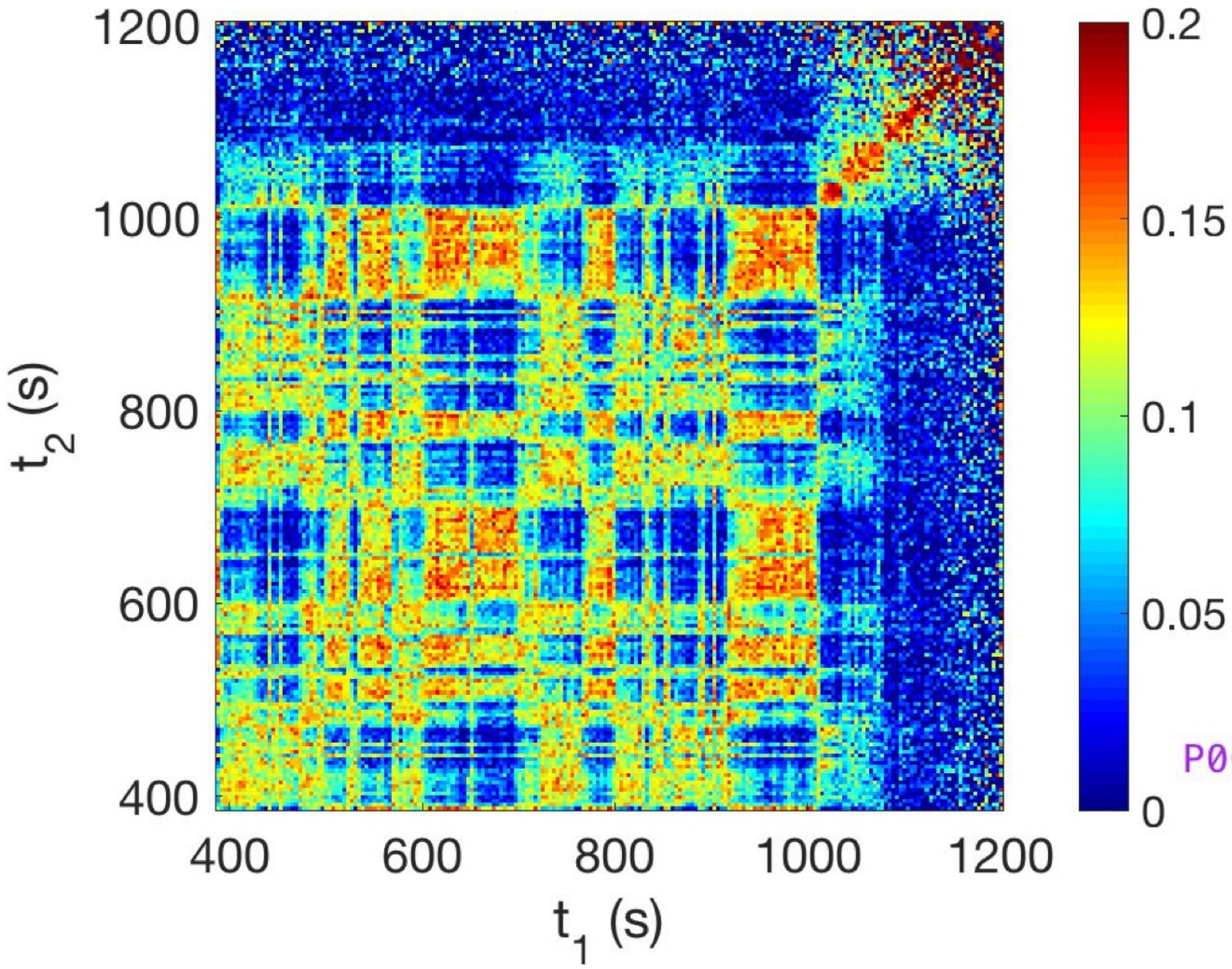
Equilibrium dynamics: phase transitions

$SrCoO_{2.5}$ at moderate temperatures (~ 350°C)



Equilibrium dynamics: phase transitions

$SrCoO_{2.5}$ / LSAT at moderate temperatures (~ 350°C)



Questions?