Surface and Interface Scattering

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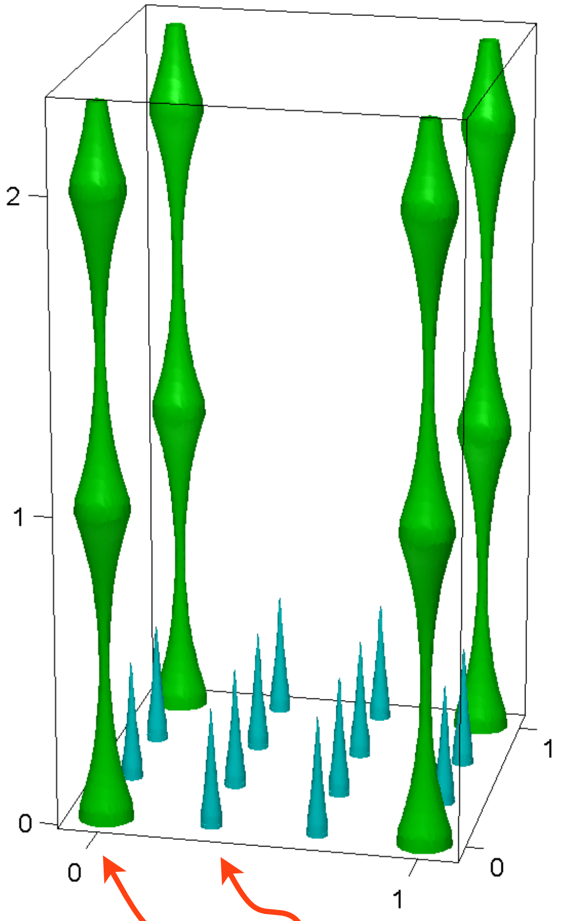
Surface x-ray diffraction (SXRD, SXS, GIXS, GIXD, ...)

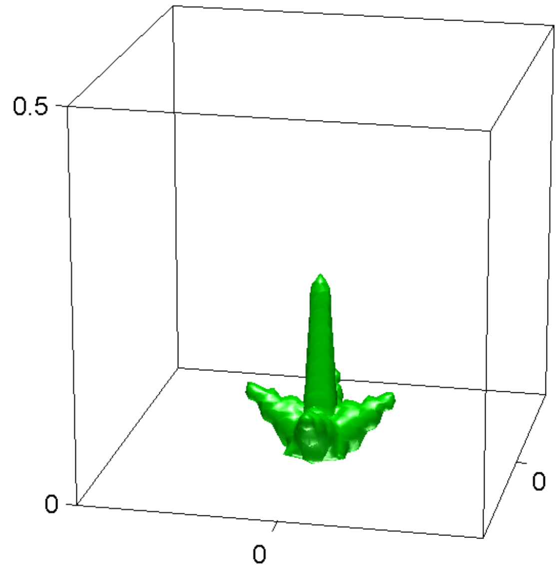
1D Fourier transform



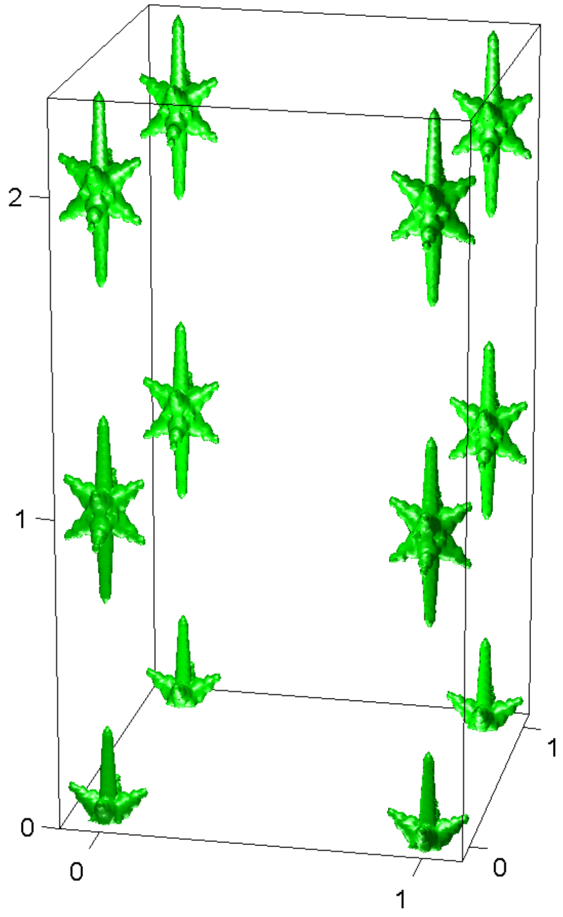
superstructure rods (SRs)

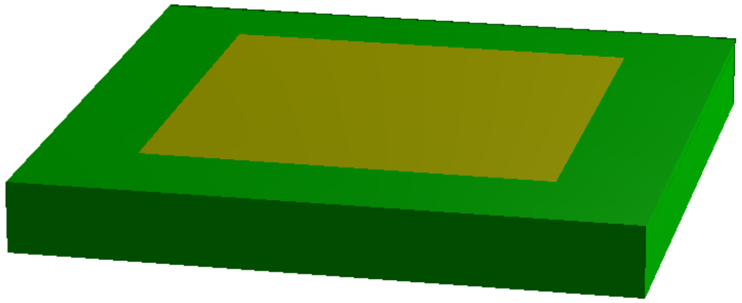
crystal truncation rods (CTRs)

3D Fourier transform (average)

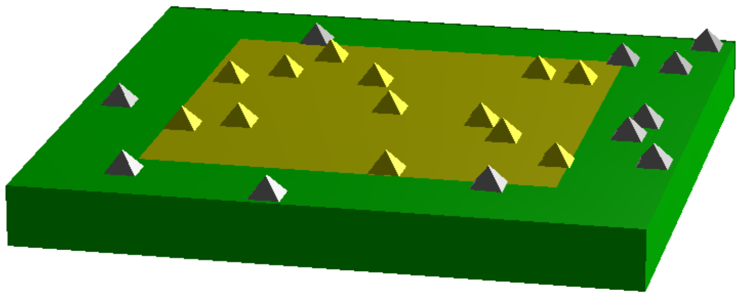


3D Fourier transform

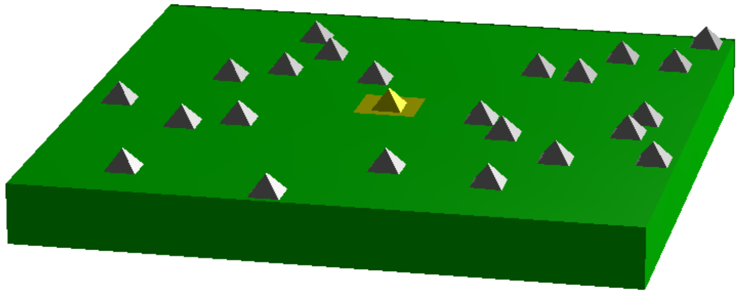




SXRD



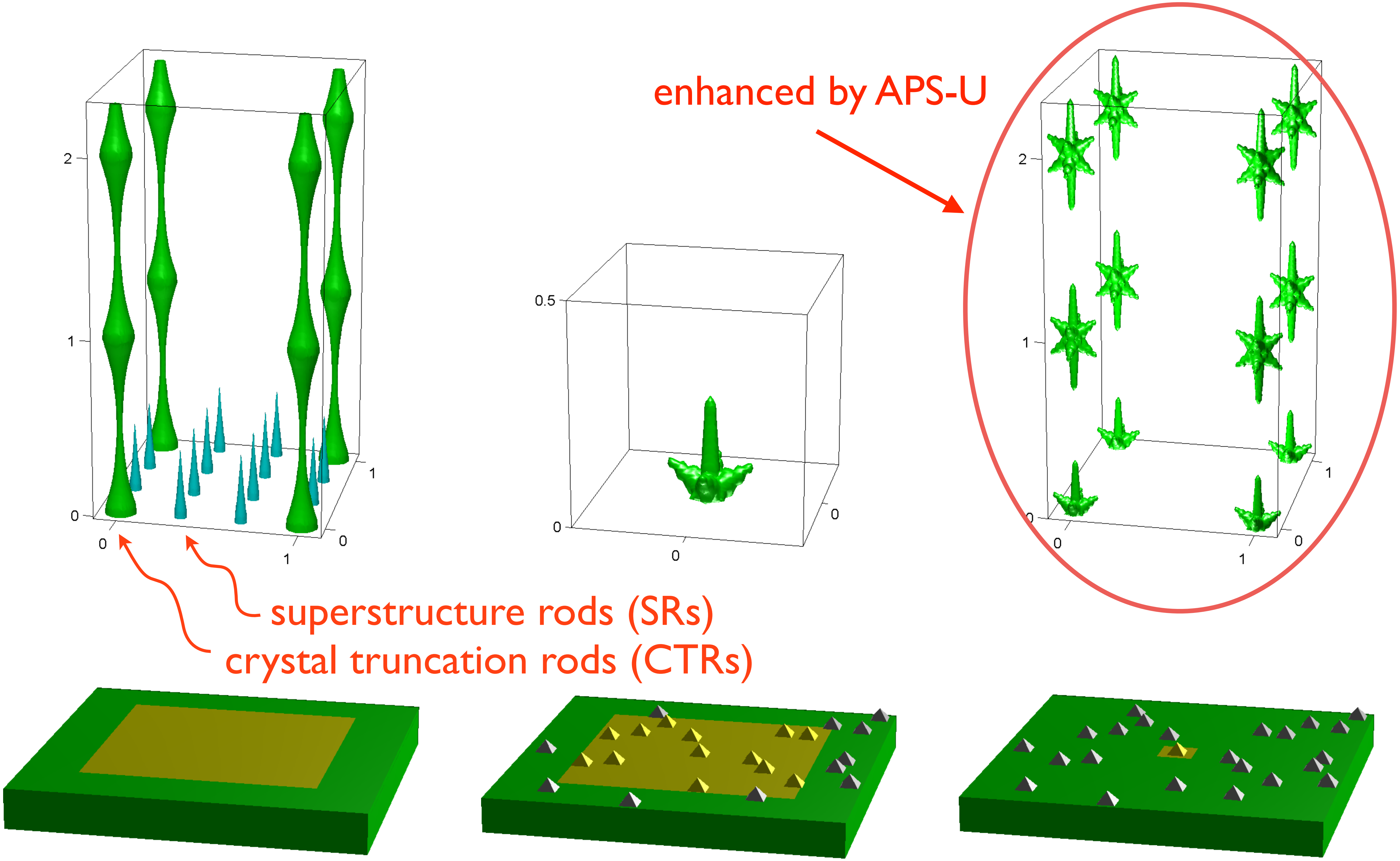
GISAXS



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)

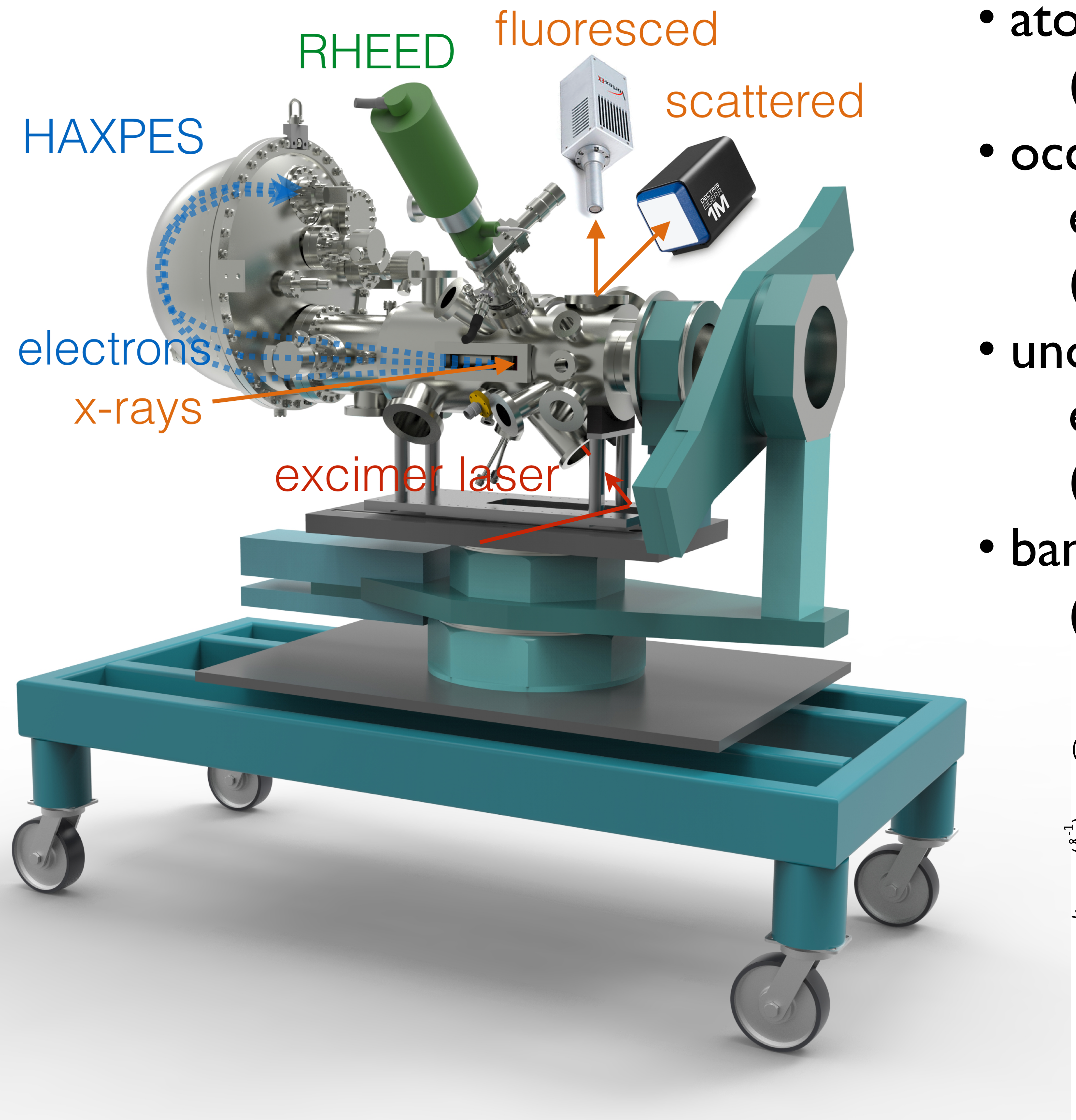
SXRD

GISAXS

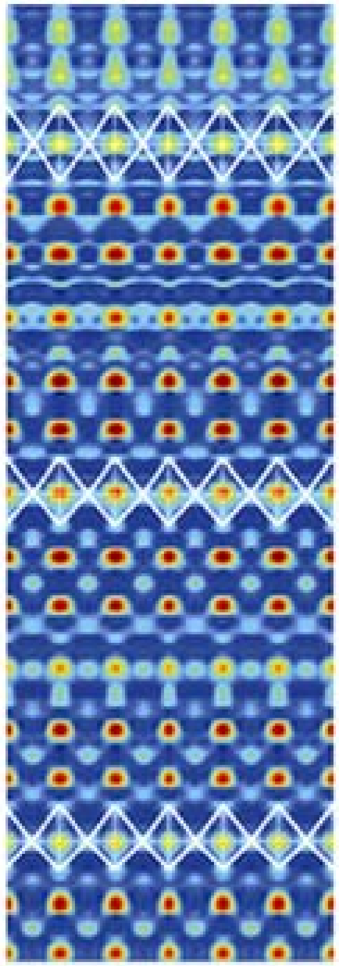
CDI

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

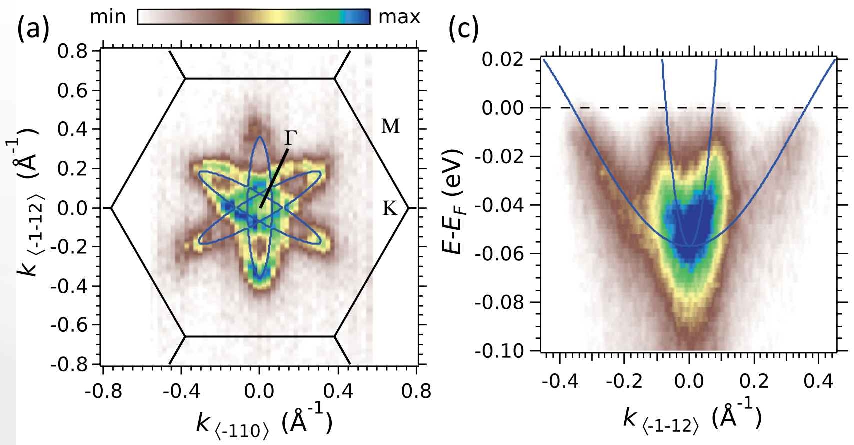
Motivation: Watch materials creation



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

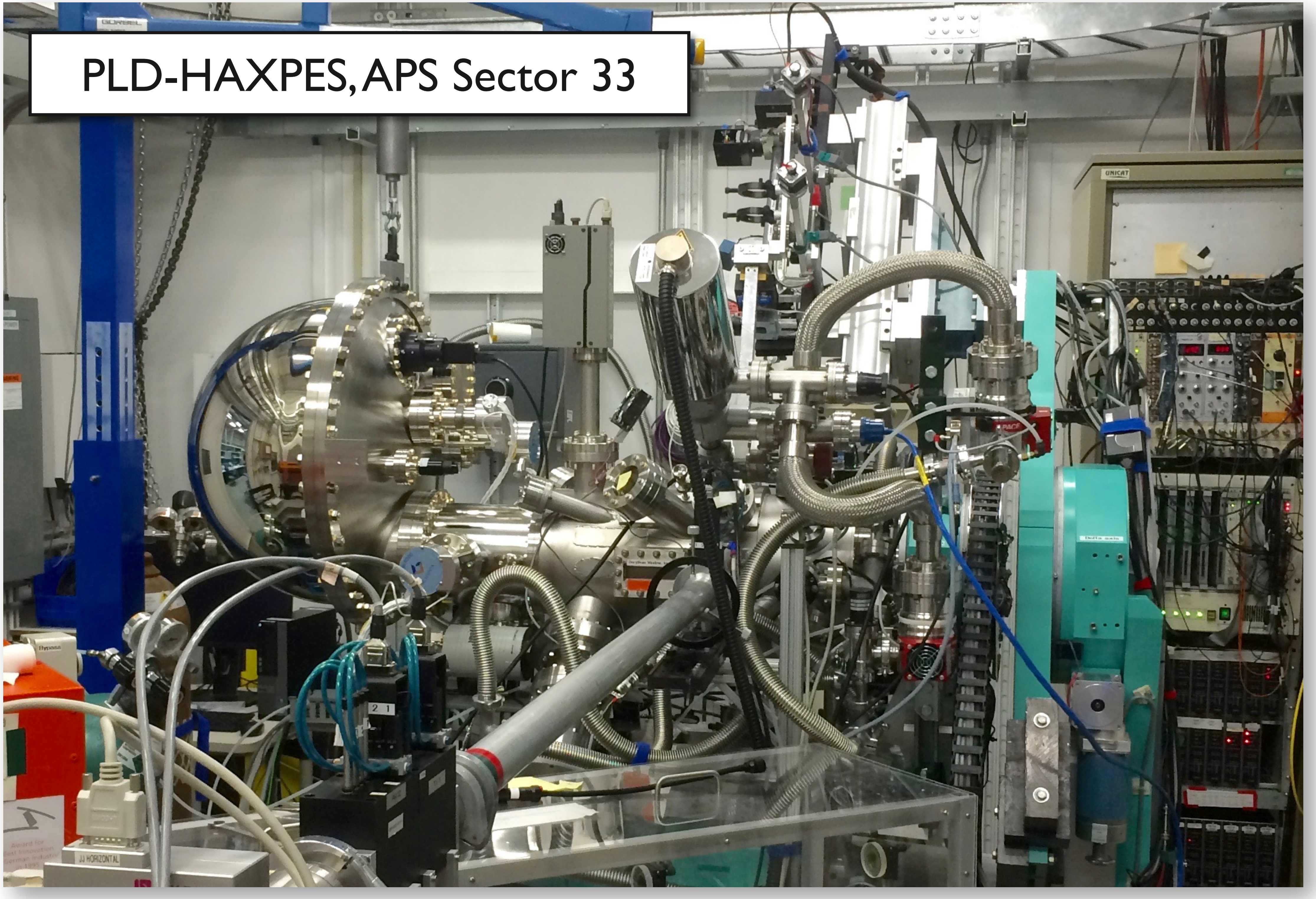


H. Zhou *et* al., PNAS **107**, 8103 (2010).



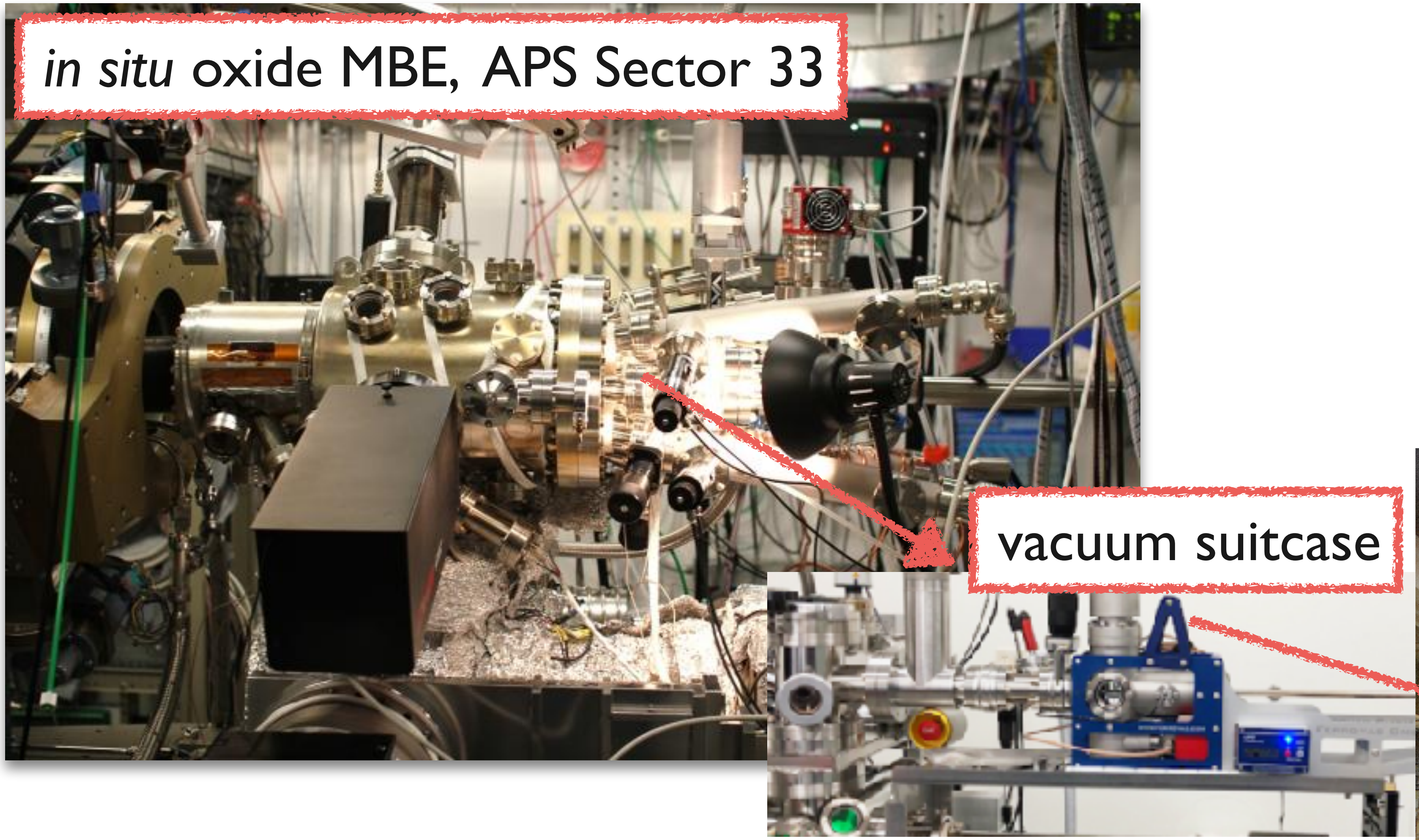
T.C. Rödel *et al.*, Phys. Rev. Appl. **1**, 051002 (2014).

Motivation: Watch materials creation & property evolution during creation



PLD-HAXPES, APS Sector 33

Motivation: Watch materials creation & property evolution during creation

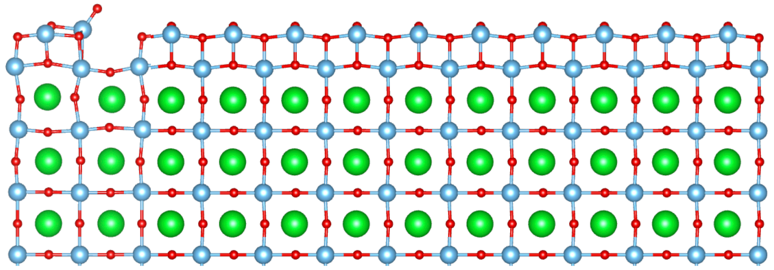


in situ oxide MBE, APS Sector 33

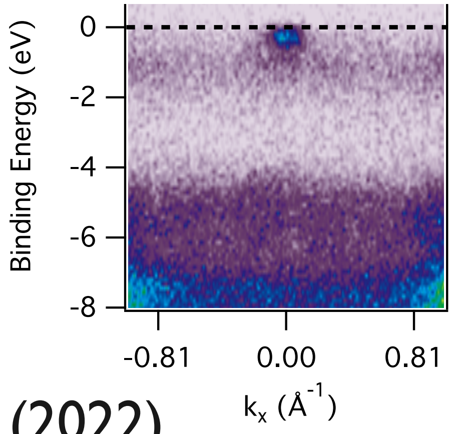
vacuum suitcase

ARPES at Sector 29

atomic structure

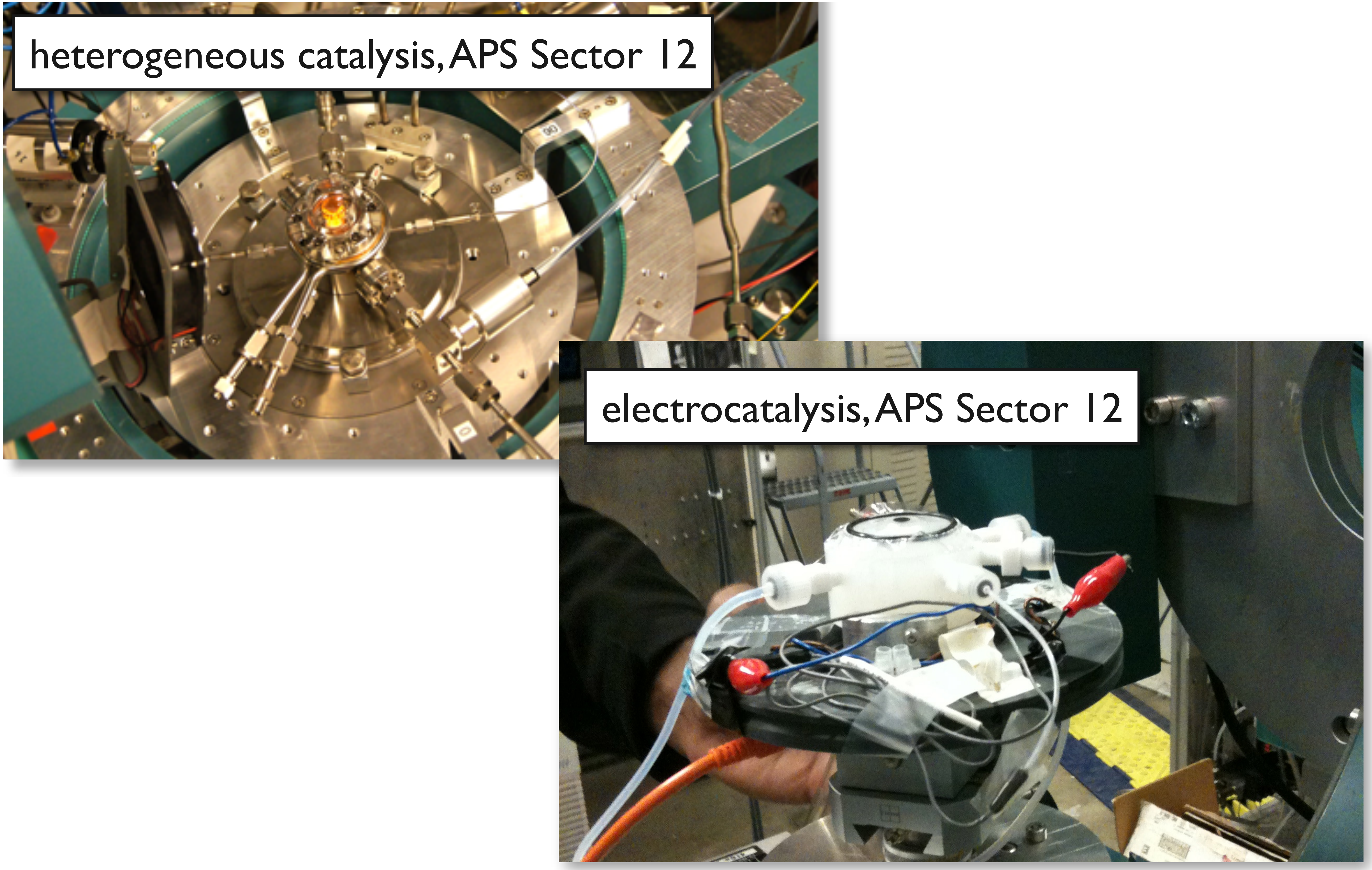


electronic structure



X. Yan et al. Adv. Mater. 34, 2200866 (2022)

Motivation: Watch surfaces during reaction



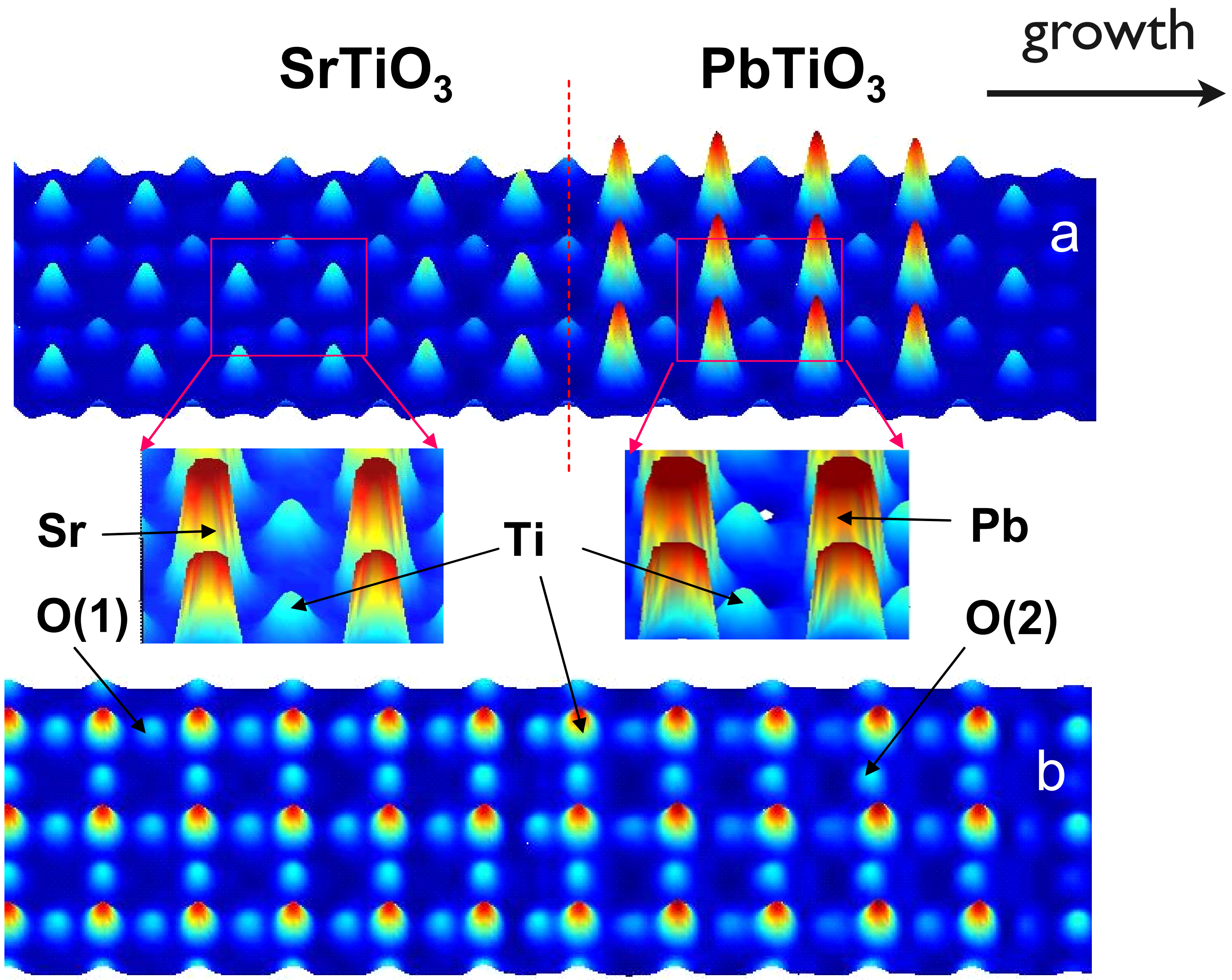
heterogeneous catalysis, APS Sector 12

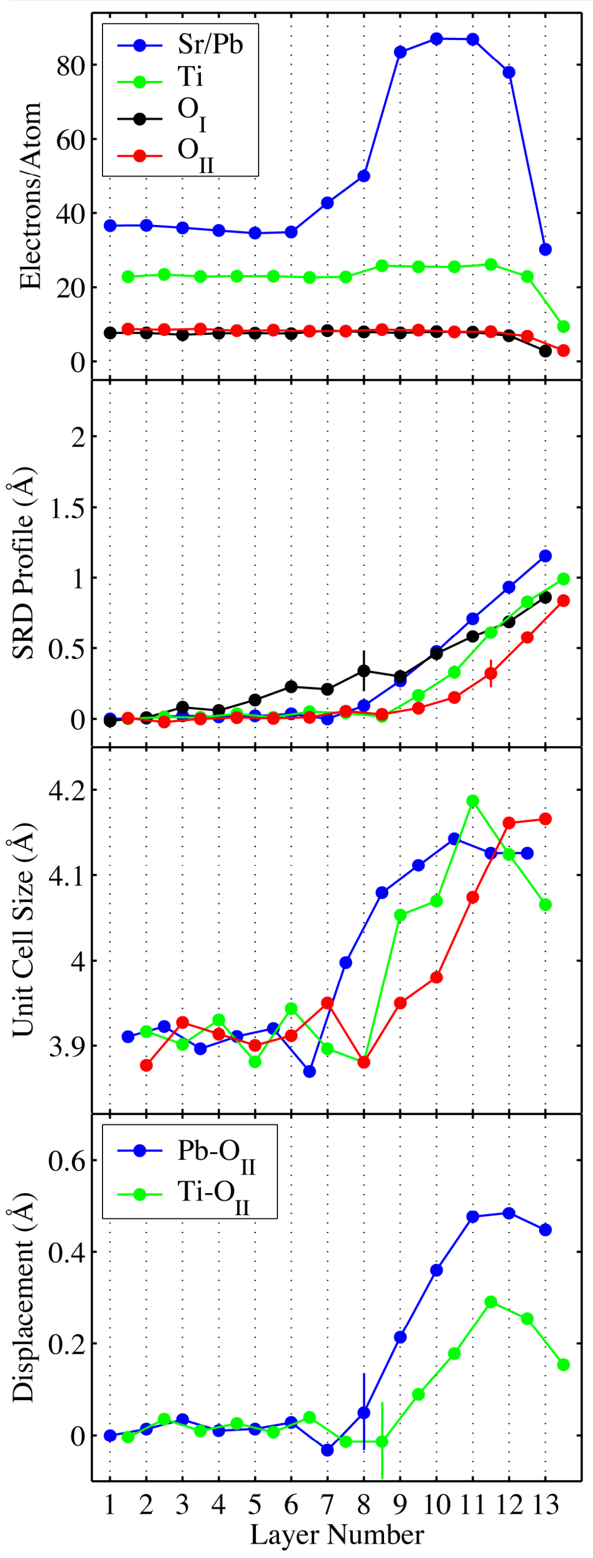
electrocatalysis, APS Sector 12

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*
- Why model? Can understand what SXRD is good for
- I will assume you are all working on epitaxial heterostructures...

II. Direct methods

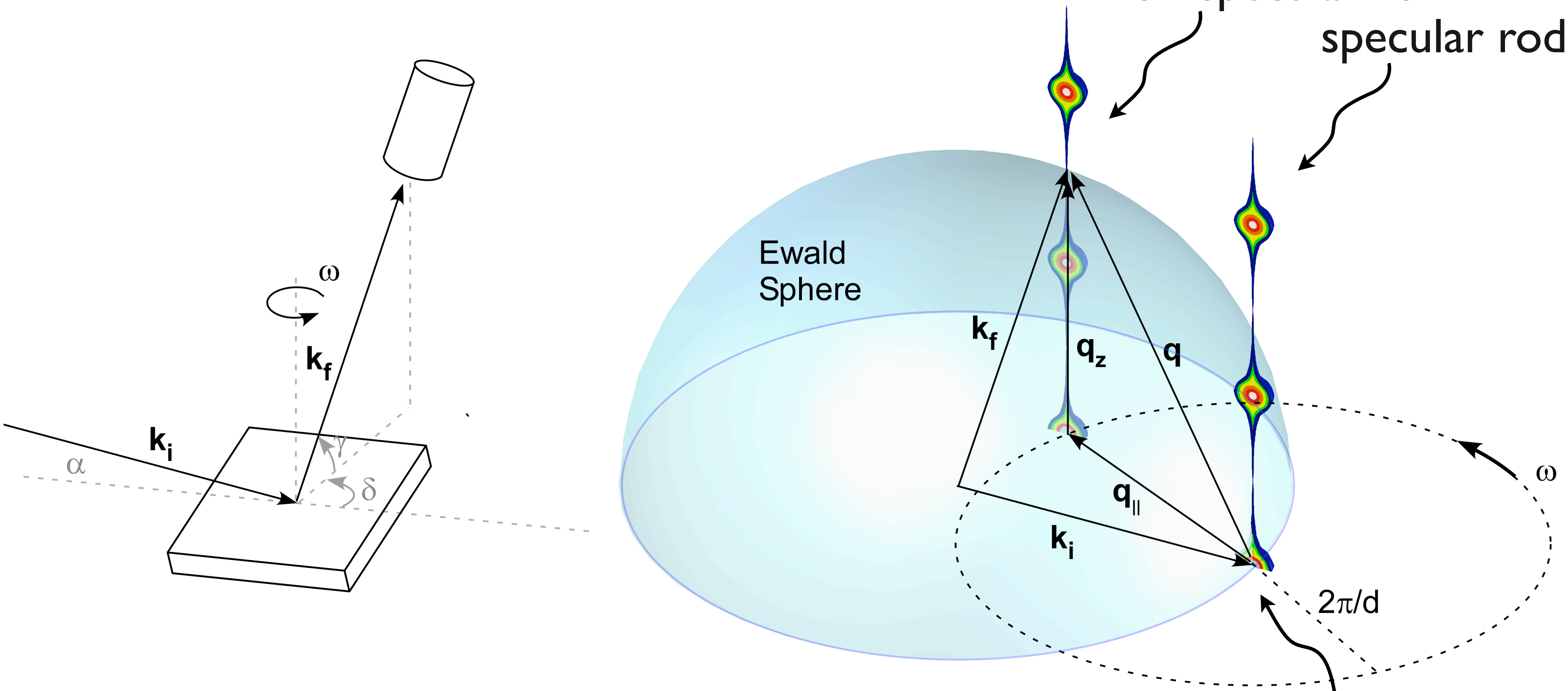
III. Example results

IV. Practicalities

V. X-ray photon correlation spectroscopy (XPCS)

SXRD geometry

I often work with (001) crystals



off-specular rod

specular rod

(a)

real space

(b)

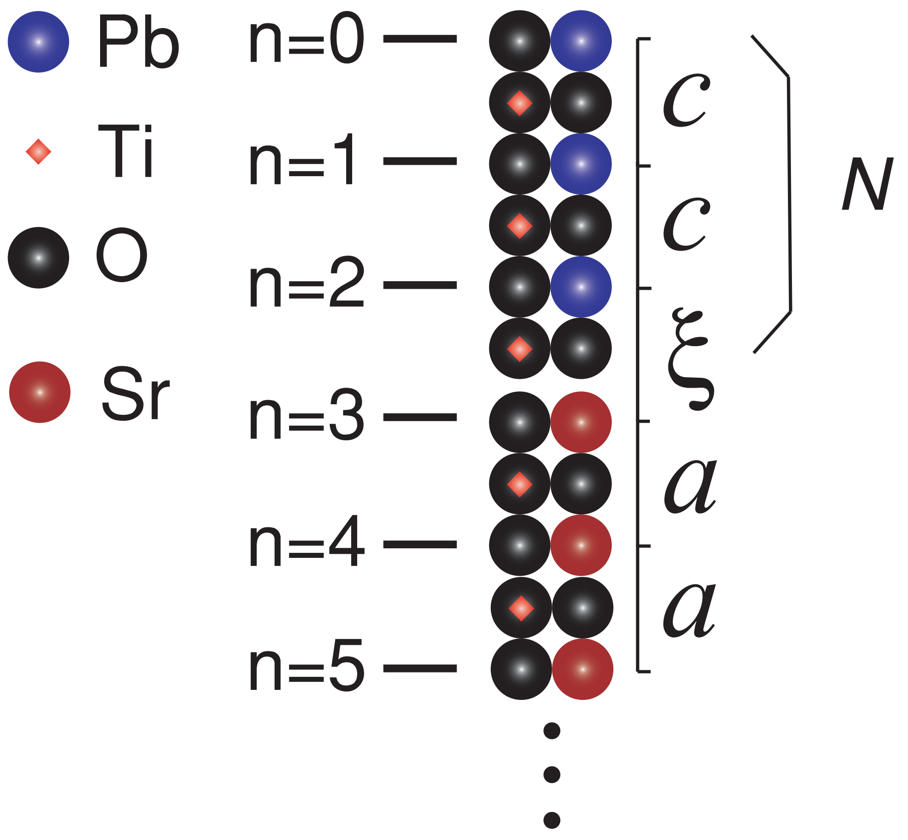
reciprocal space

origin of 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)



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

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

= geometric series: $a + ar + ar^2 + ar^3 + \ldots$

Example geom 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

Useful formulas for CTRs:

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

= 1.96875

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

= 2

We will use both of these expressions for film and substrate

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

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

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

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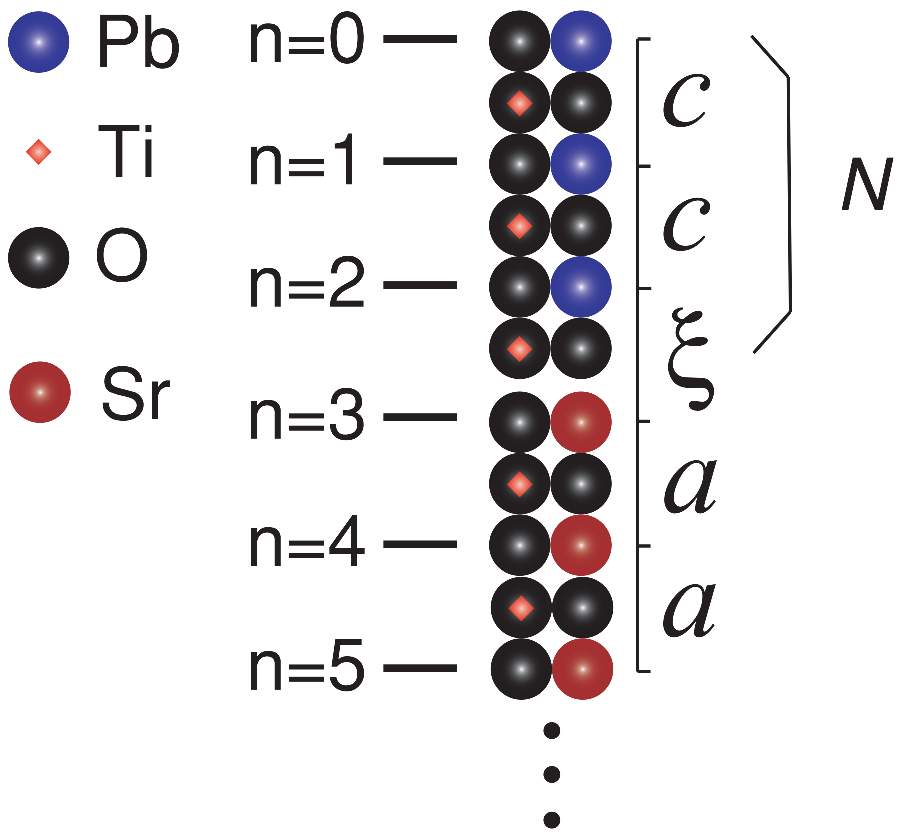
= geometric series: $a + ar + ar^2 + ar^3 + \ldots$



film

$$a = F_{\text{film}}^{\text{unit cell}}$$

$$r = e^{-iQ_z c}$$

$$N = \text{number of film unit cells}$$

substrate

$$a = F_{\text{sub}}^{\text{unit cell}}$$

$$r = e^{-iQ_z a}$$

$$N = \infty$$

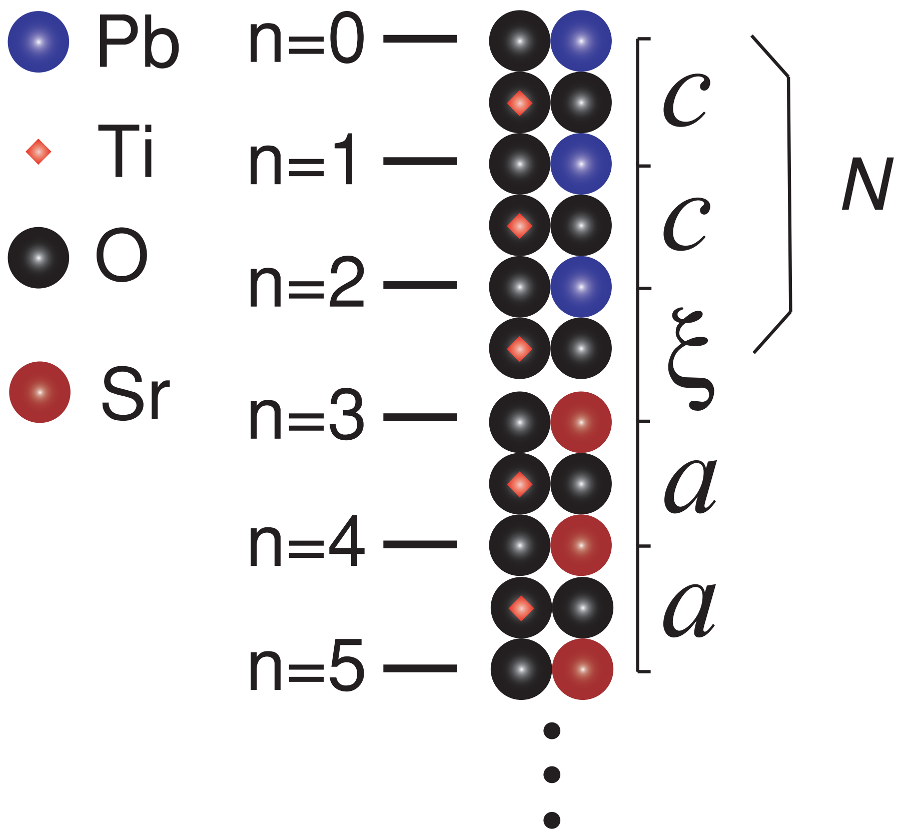
Modeling *F*(*Q*) for a CTR

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

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

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

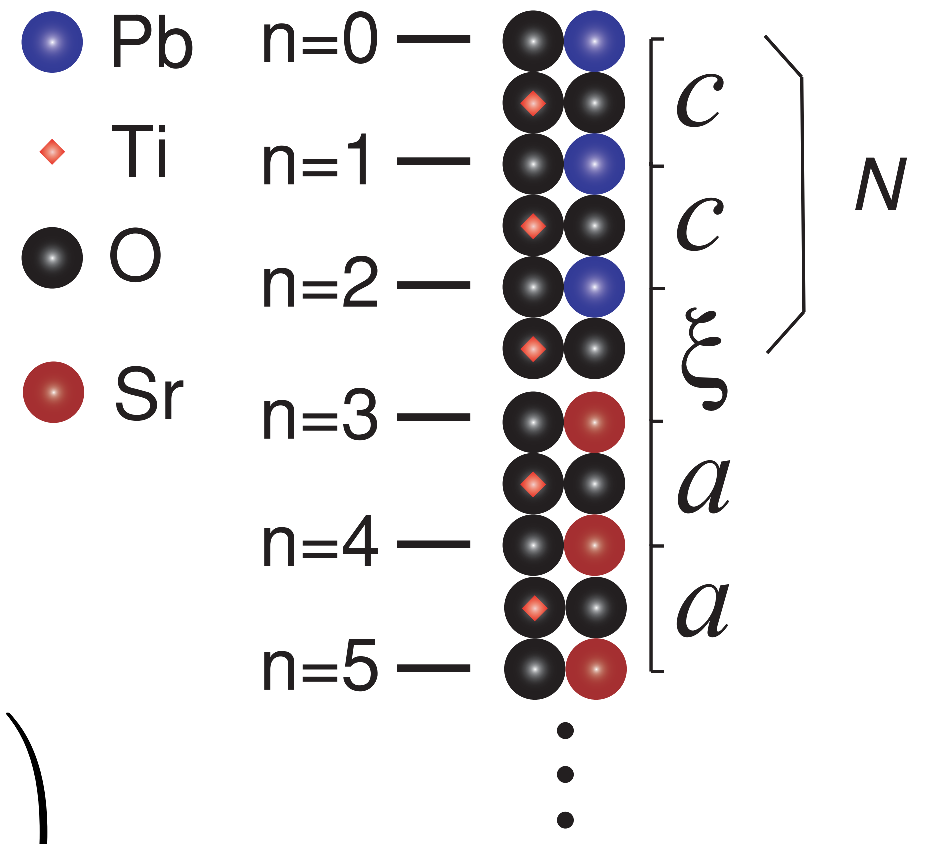
= geometric series: *a* + *ar* + ar^2 + ar^3 + …



$$\boxed{\begin{aligned} F_{\mathrm{column}}(\mathbf{Q}) &= F_{\mathrm{PbTiO_3}}^{\text{unit cell}}(\mathbf{Q})\left(\frac{1-e^{-iNQ_z c}}{1-e^{-iQ_z c}}\right) \\ &\quad \underbrace{+\,e^{-iQ_z((N-1)c+\boxed{\xi})}}_{\text{interface phase factor}} F_{\mathrm{SrTiO_3}}^{\text{unit cell}}(\mathbf{Q})\frac{1}{1-e^{-iQ_z a}} \end{aligned}}$$

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

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



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

absorption

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

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

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

where $\zeta_n = \lambda q_z / 4\pi \mu_n$

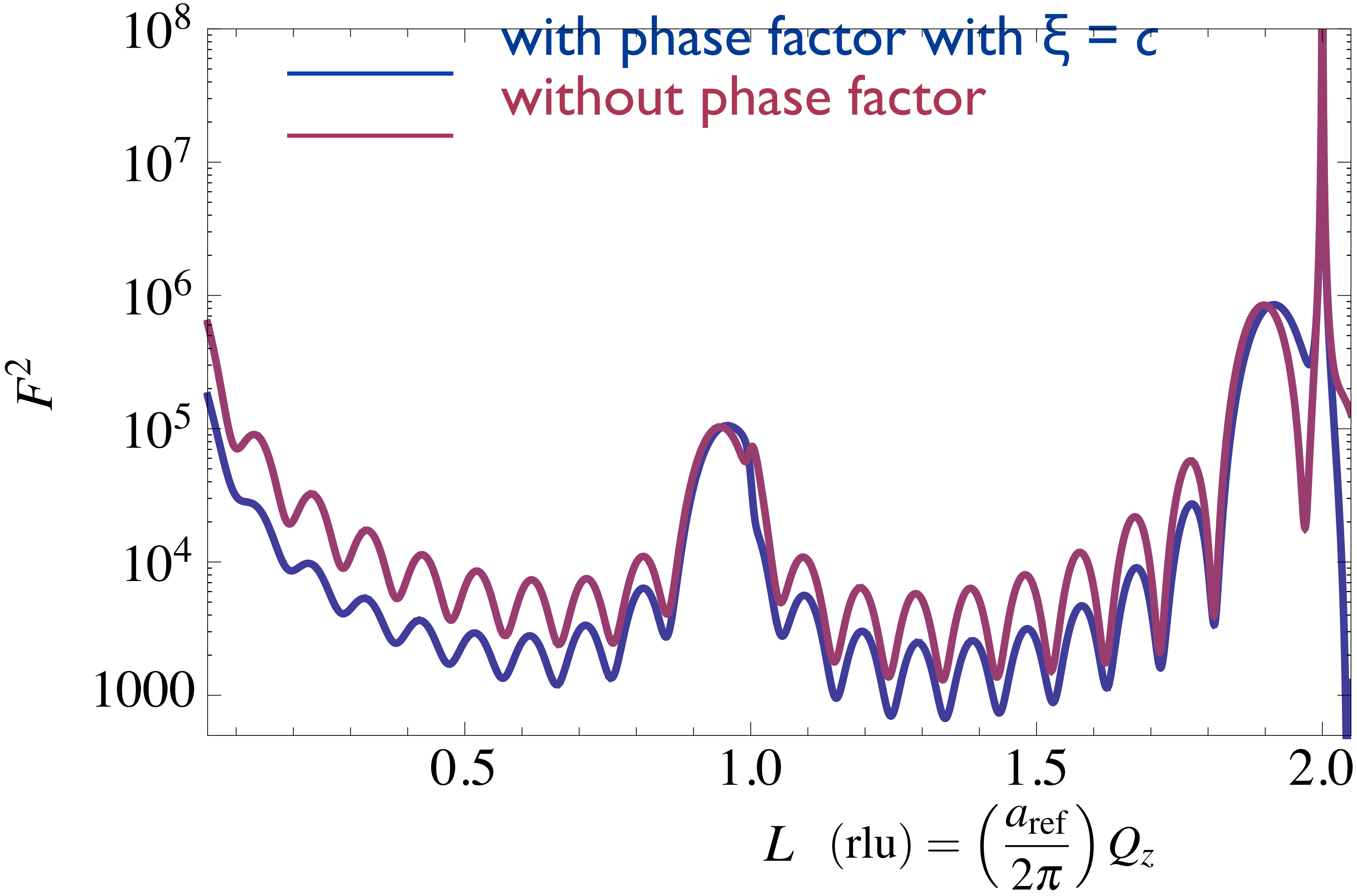
D. D. Fong and C. Thompson, Annu. Rev. Mater. Res. **36,** 431 (2006)

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

Don’t forget the interface phase factor

- Ex. PbTiO₃ / SrTiO₃ (001)

$$\xcancel{F_{\text{column}}(\mathbf{Q}) = F^{\text{unit cell}}_{\text{PbTiO}_3}(\mathbf{Q}) \left(\frac{1 - e^{-iNQ_z c}}{1 - e^{-iQ_z c}} \right)} \\ + F^{\text{unit cell}}_{\text{SrTiO}_3}(\mathbf{Q}) \frac{1}{1 - e^{-iQ_z a}}$$



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

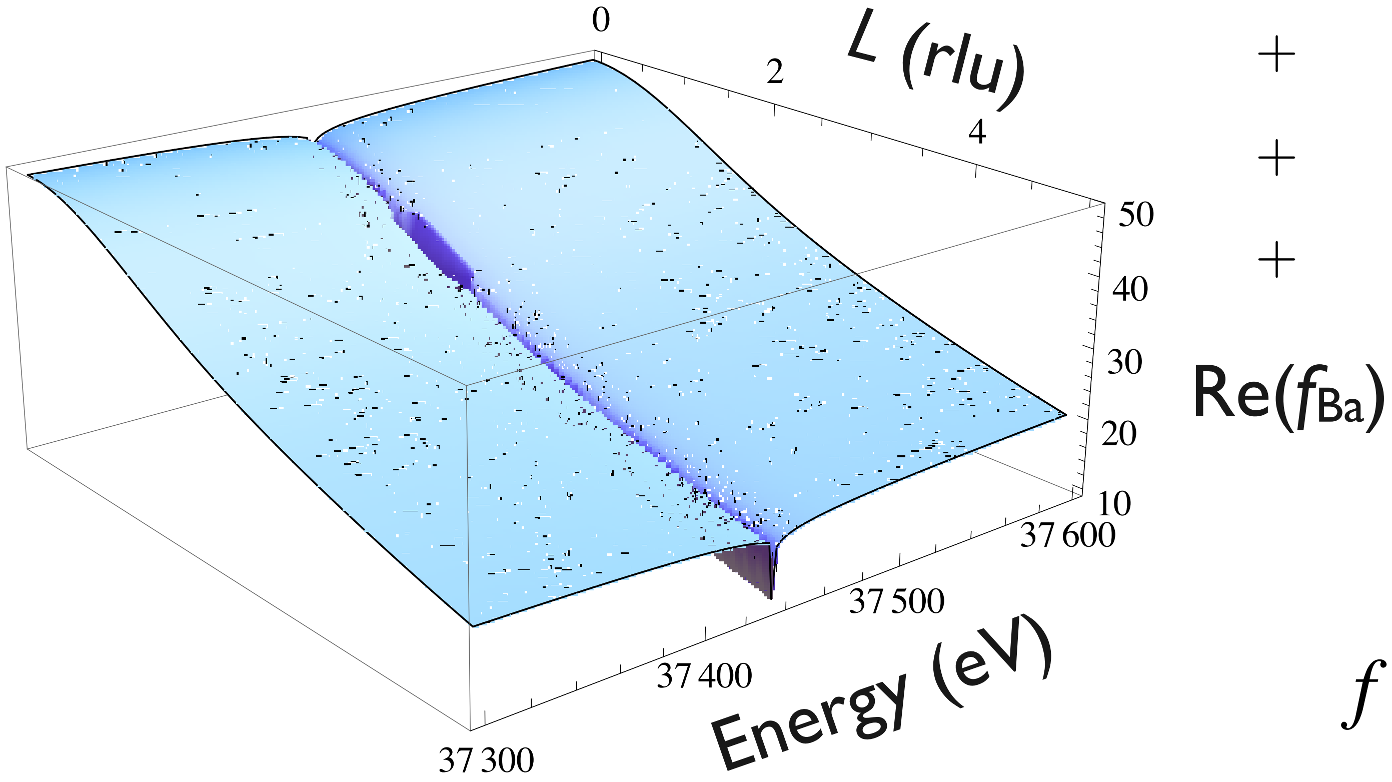
Modeling *F*(*Q*) for a CTR + temperature effects + X-ray energy effects

Unit cell structure factor:

DW factor

$$\begin{aligned}
F^{\text{unit cell}}_{\text{PbTiO}_3}(\mathbf{Q}) &= \sum_{j=1}^{N_{uc}} f_j(Q)\boxed{e^{-B_j(Q/4\pi)^2}}e^{i\mathbf{Q}\cdot\mathbf{R}_j} \\
&= f_{\text{O}(1)}(Q)\boxed{e^{-B_{\text{O}(1)}(Q/4\pi)^2}} \\
&+ f_{\text{O}(2)}(Q)\boxed{e^{-B_{\text{O}(2)}(Q/4\pi)^2}}e^{iQ_ya/2}e^{iQ_z(\pm\delta z_{\text{O}(2)}-c/2)} \\
&+ f_{\text{O}(2)}(Q)\boxed{e^{-B_{\text{O}(2)}(Q/4\pi)^2}}e^{iQ_xa/2}e^{iQ_ya/2}e^{iQ_z(\pm\delta z_{\text{O}(2)}-c/2)} \\
&+ f_{\text{Ti}}(Q)\boxed{e^{-B_{\text{Ti}}(Q/4\pi)^2}}e^{iQ_z(\pm\delta z_{\text{Ti}}-c/2)} \\
&+ f_{\text{Pb}}(Q)\boxed{e^{-B_{\text{Pb}}(Q/4\pi)^2}}e^{iQ_xa/2}e^{iQ_ya/2}e^{iQ_z(\pm\delta z_{\text{Pb}})}
\end{aligned}$$

Atomic form factor:



$$f(Q,E) = f_0(Q) + \underbrace{f'(E) + if''(E)}$$

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 + temperature effects

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)

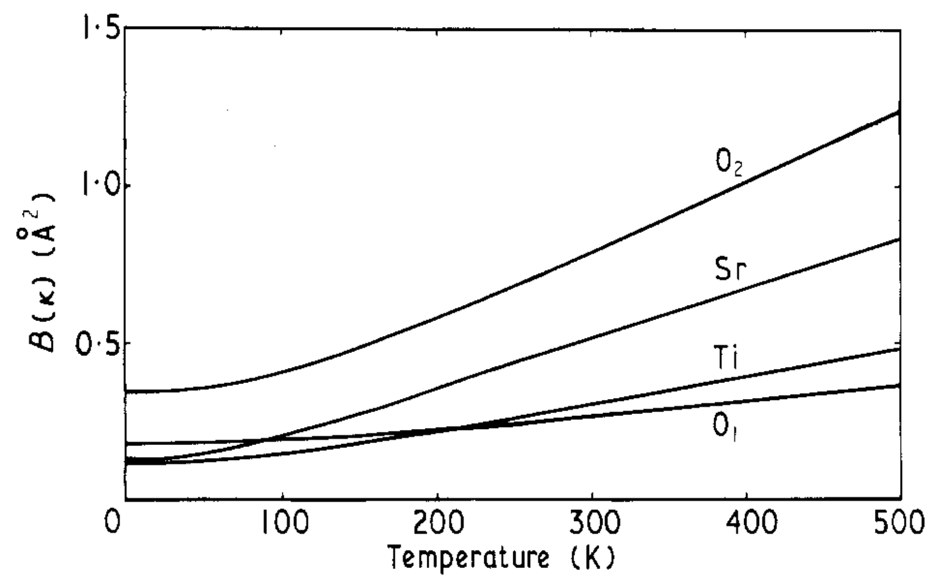
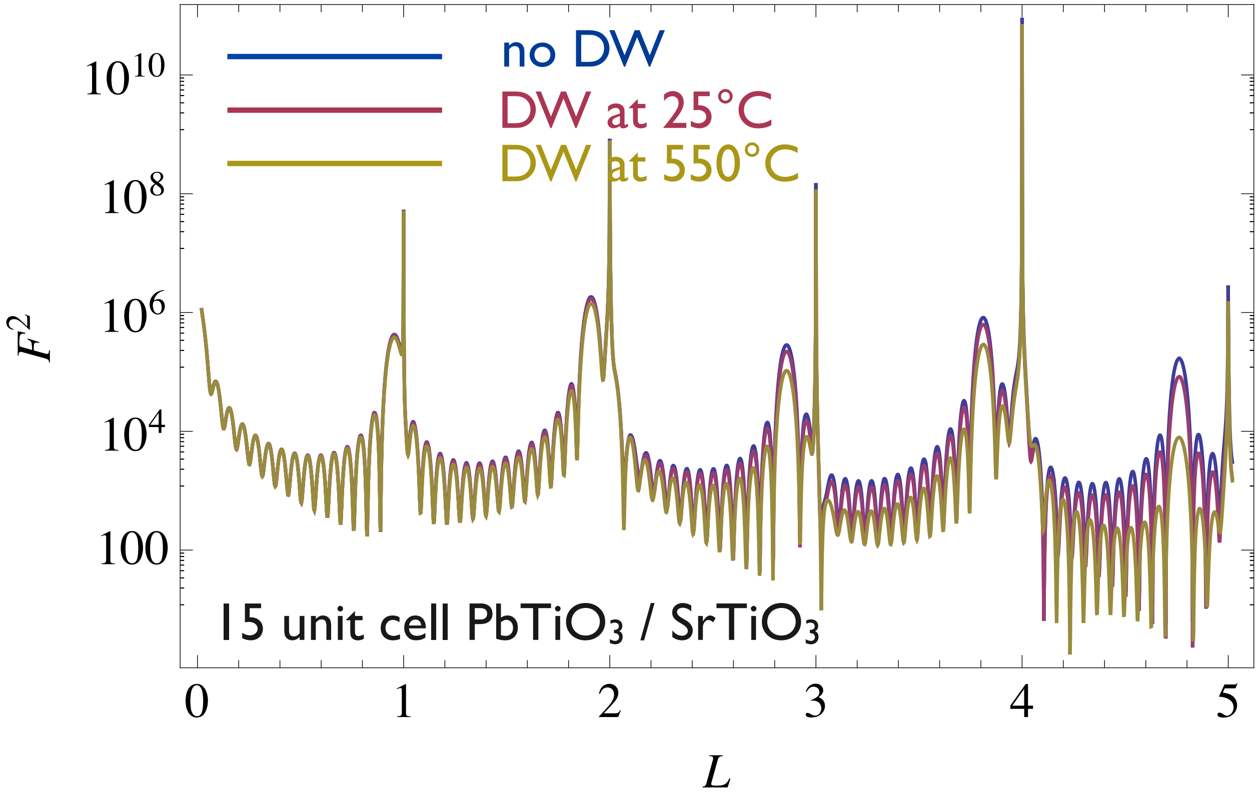


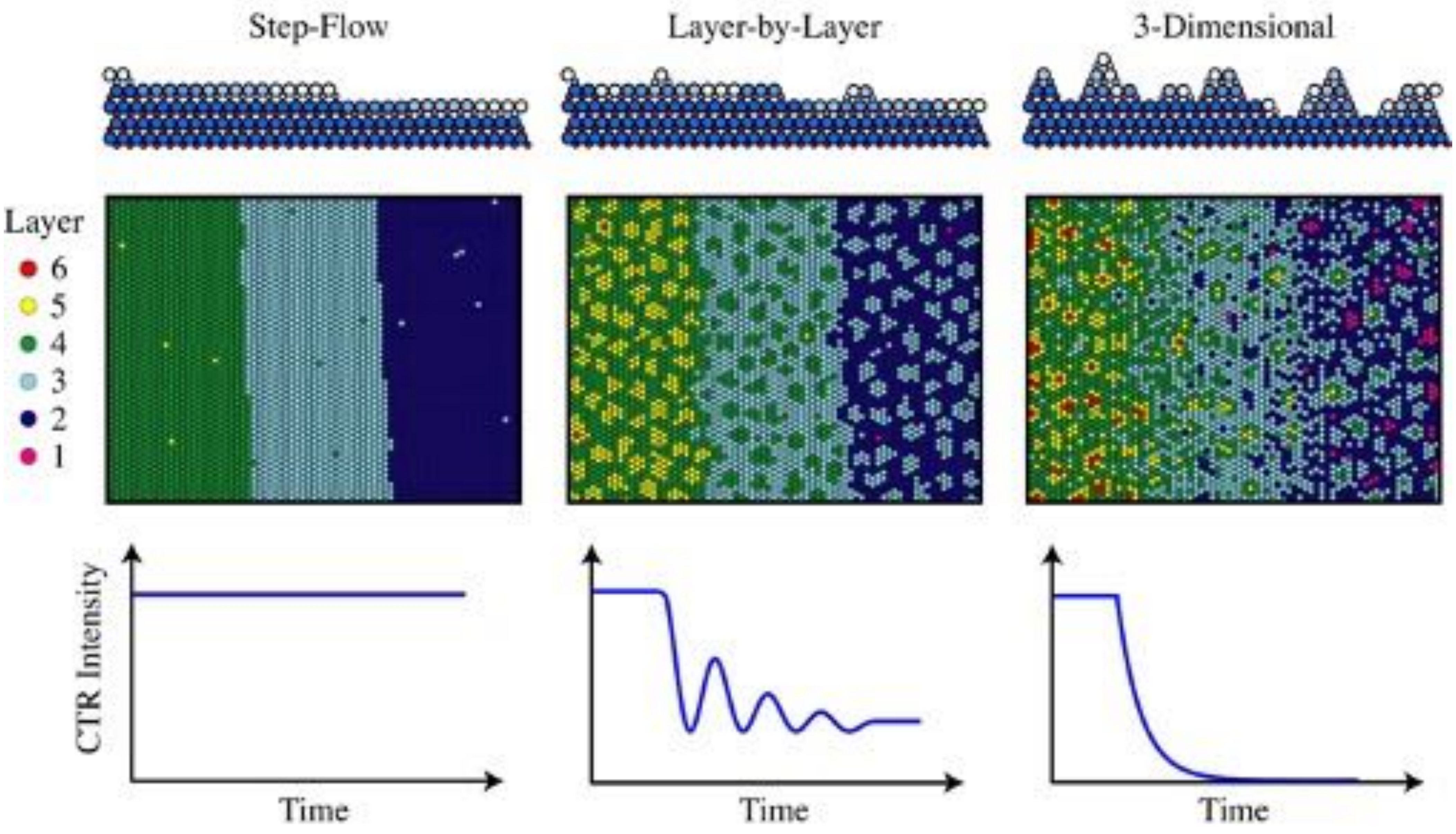
Table 2. *Summary of parameters refined at all temperatures* (Pb *at origin*)

	−183°C	−115°C	25°C	550°C
Isotropic temperature factor refinement				
δz_{Ti}(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



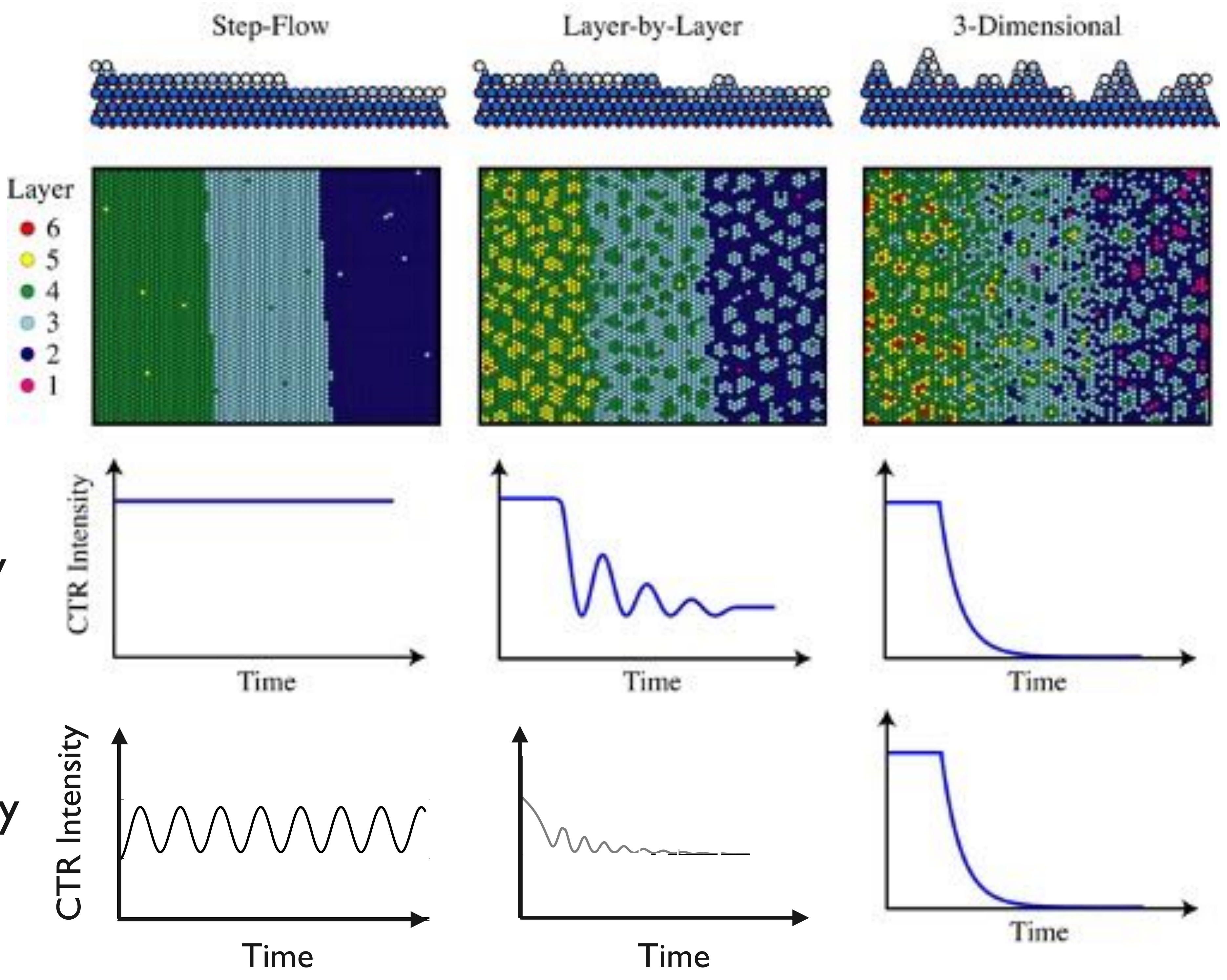
for $PbTiO_3$: A. M. Glazer & S. A. Mabud, Acta Cryst. B **34,** 1065 (1978)

Watching @ 0 0 1/2 during homoepitaxy



- ☆ Layer-by-layer growth: CTR intensity oscillates as individual monolayers nucleate and coalesce

Homoepitaxy vs heteroepitaxy



homoepitaxy

heteroepitaxy

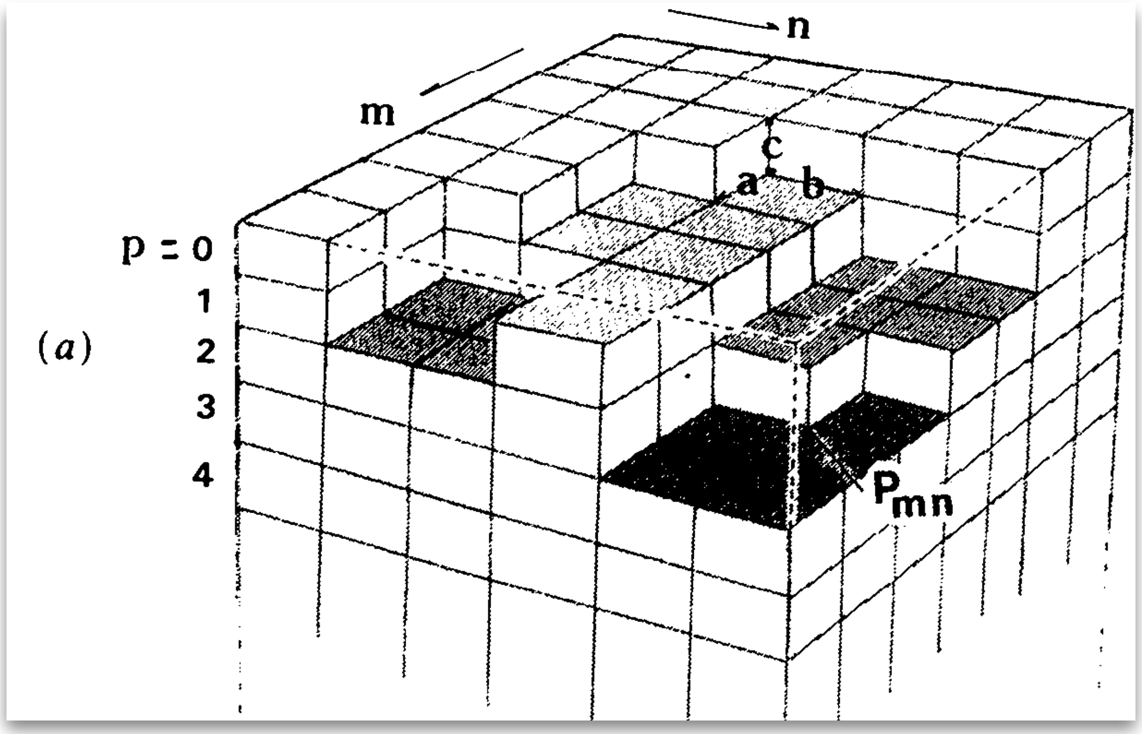
Modeling *F*(*Q*) for a CTR + continuous roughness

Continuous roughness

- Gaussian distribution of step heights about a mean surface

$$R^2 = e^{-4\pi^2 \underbrace{\langle \Delta p^2 \rangle}_{\sigma^2} (Q_z - Q_B)^2} \qquad I(Q) = R^2(Q) I_0(Q)$$

mean square deviation of step heights in units of the lattice spacing



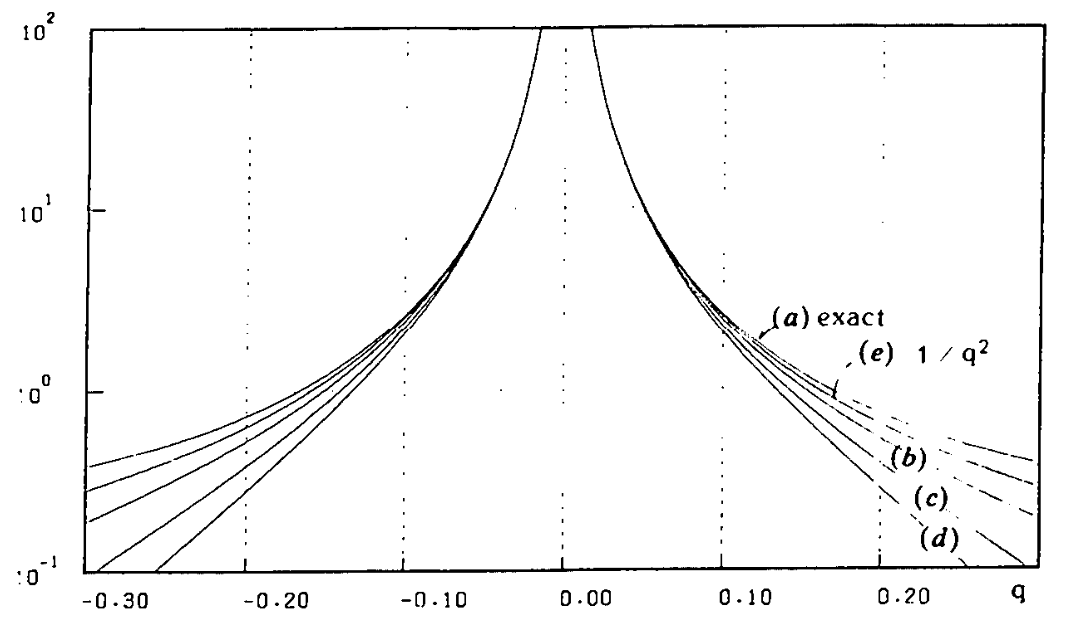


Fig. 6. Intensity change of the CTR scattering along the rod for several different degrees of surface roughness. (*a*) Ideal flat surface; (*b*), (*c*) and (*d*) rough surfaces with $\langle \Delta p^2 \rangle = 0.2, 0.4$ and 0.6 in Debye–Waller-like factor, respectively; (*e*) the $1/q^2$ relation,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

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)

Modeling roughness during heteroepitaxial growth

Good for modeling thin film growth & roughness evolution (θ=fraction covered)

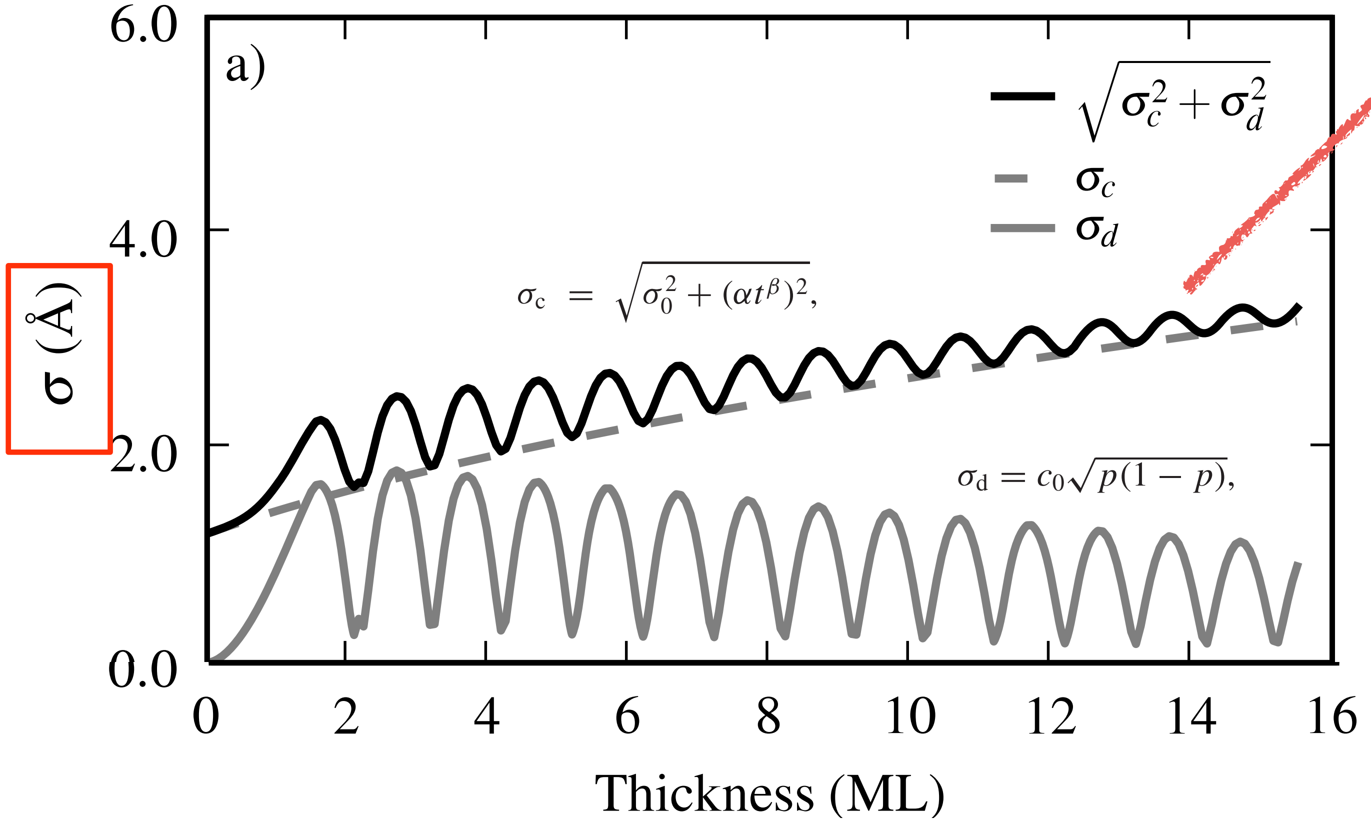
$$\sigma_{\text{total}} = \sqrt{\sigma^2_{\text{continous}} + \sigma^2_{\text{discrete}}}$$

becomes

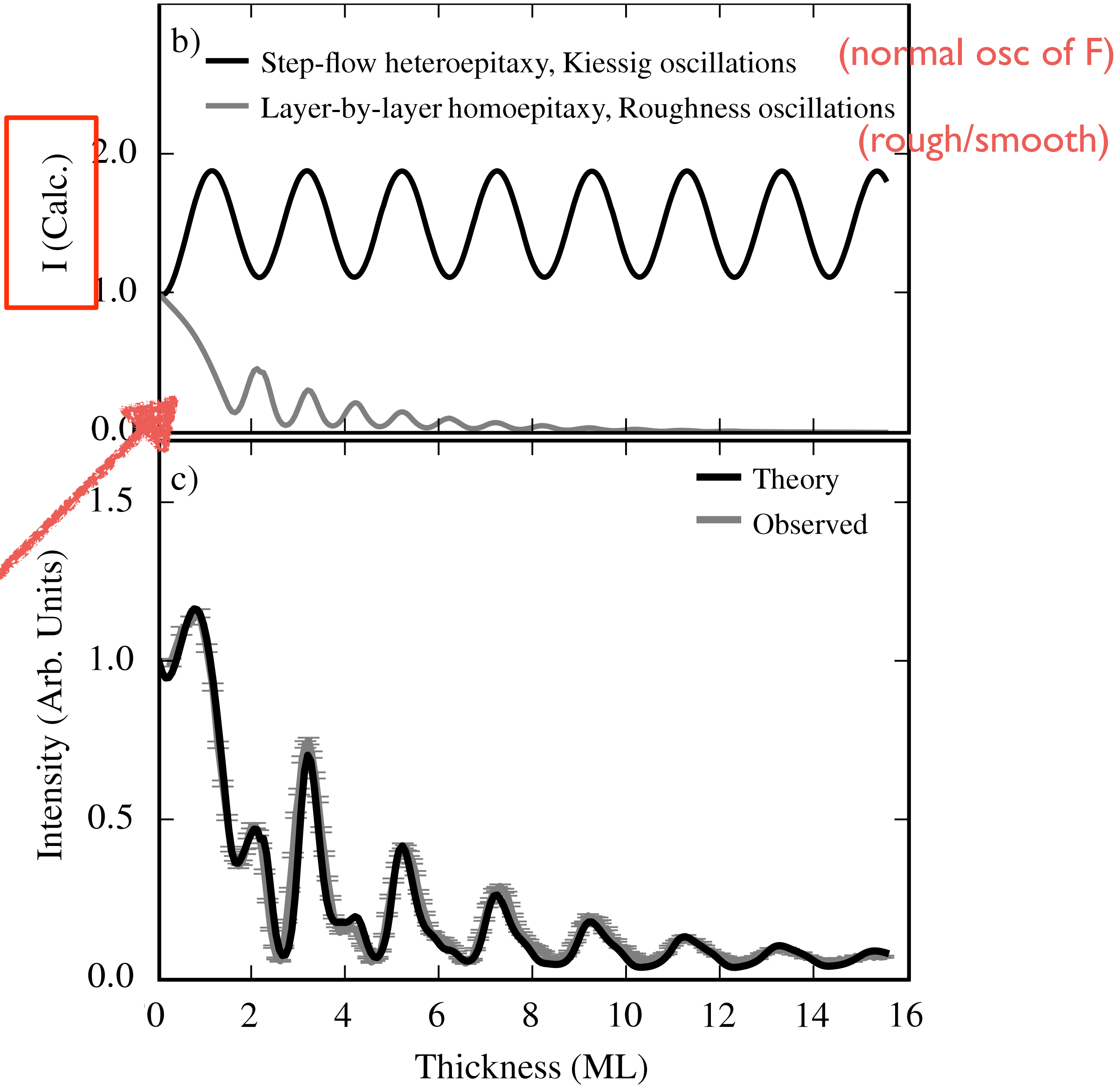
$$R(Q)^2 = e^{\frac{-4\sigma_c^2}{a^2}\sin^2(Q_z a/2)}\left[1-4\theta(1-\theta)\sin^2(\pi L)\right]^{\frac{\sigma_d^2}{c^2\theta(1-\theta)}}$$

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

Growth of LSMO/STO(001) by PLD



@ 0 0 1/2



You can separate continuous vs discrete roughness components

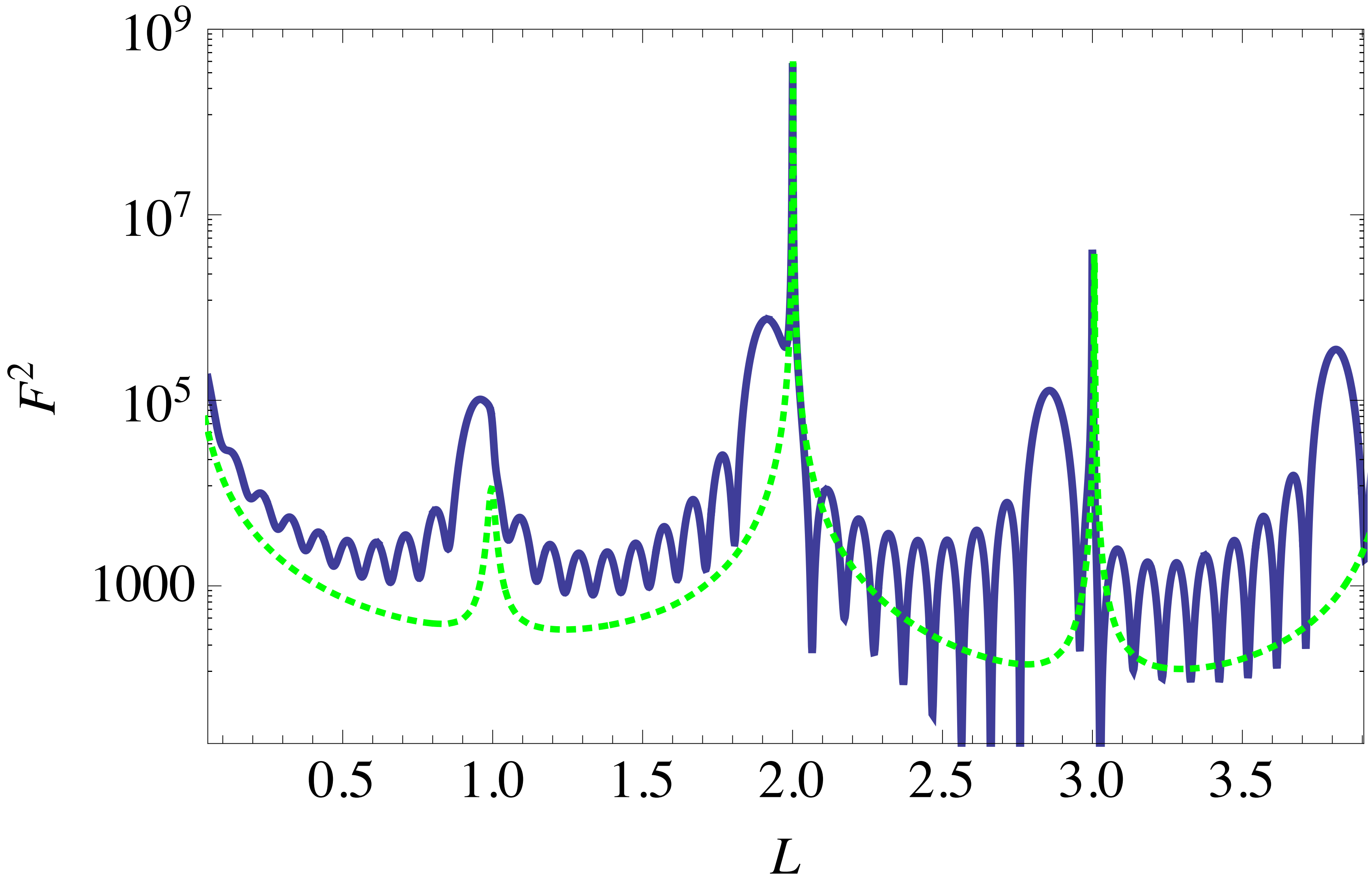
D. Dale *et al.*, J. Phys: Condens. Matter **20,** 264008 (2008)

Example calculations

Thickness fringes - compare to STO (green)

- changes in electron density and/or lattice parameter

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



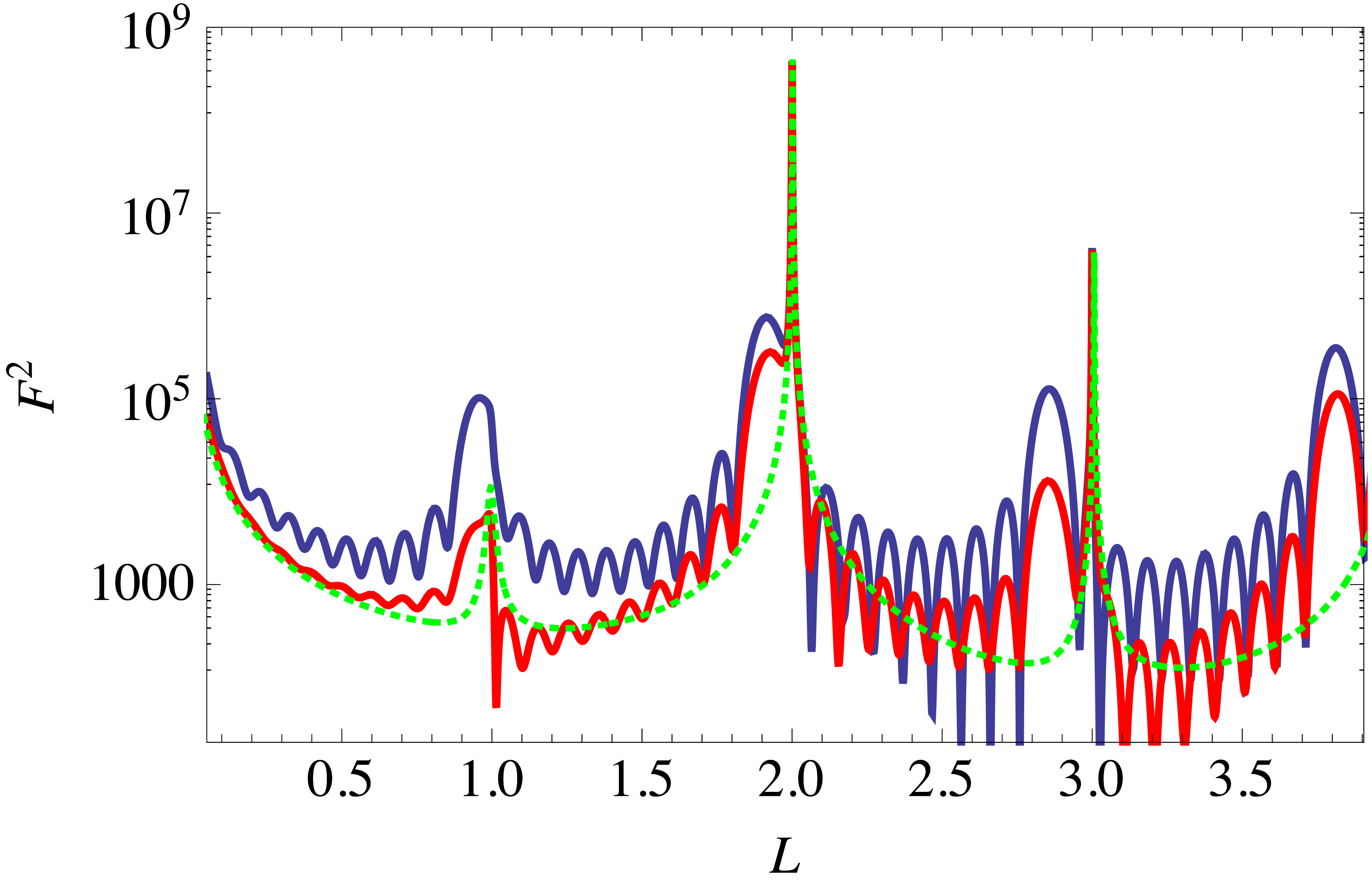
Example calculations

Thickness fringes - compare to STO (green)

- changes in electron density and/or lattice parameter

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

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

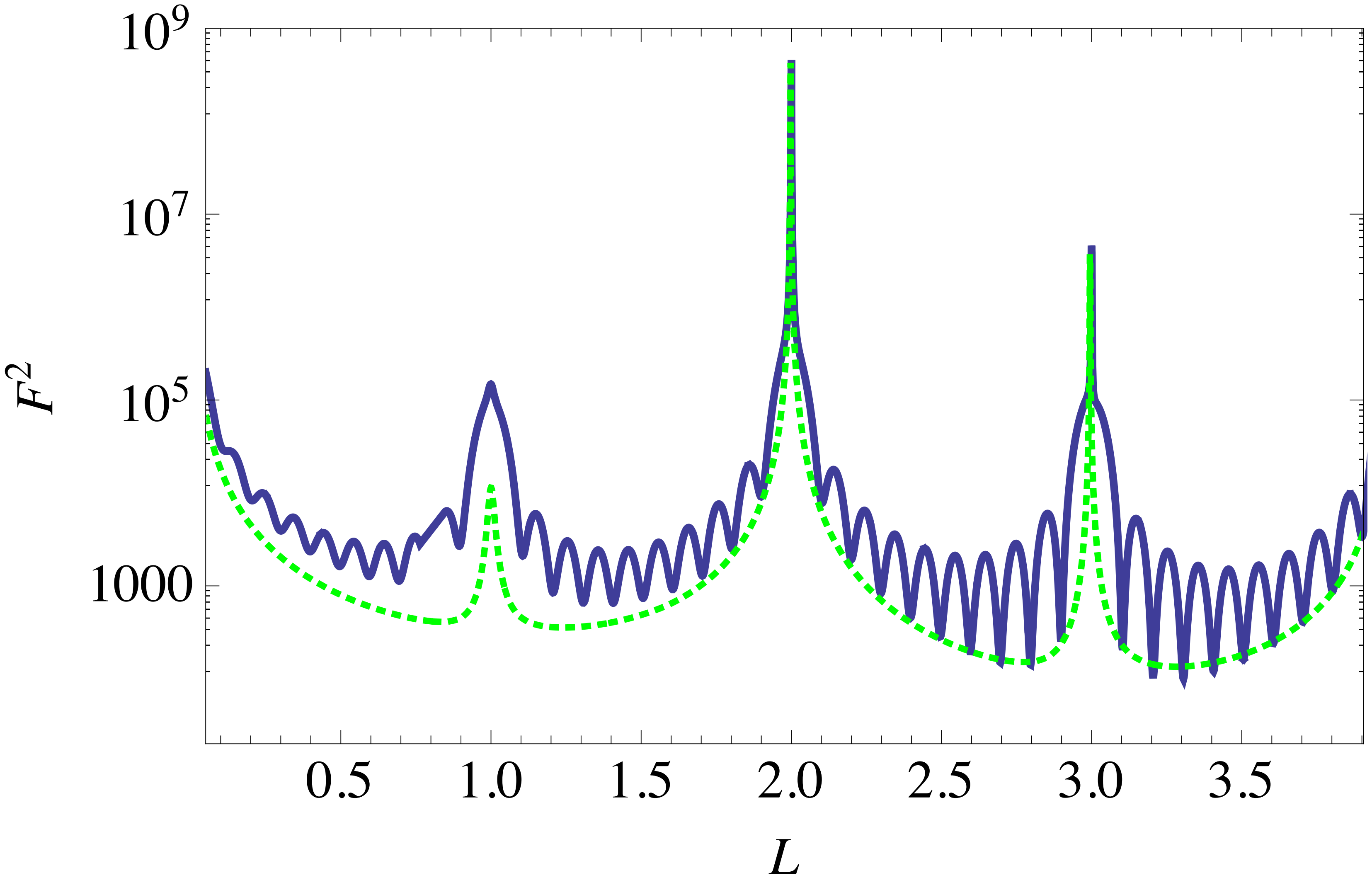


Example calculations

Thickness fringes - compare to STO (green)

- 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)



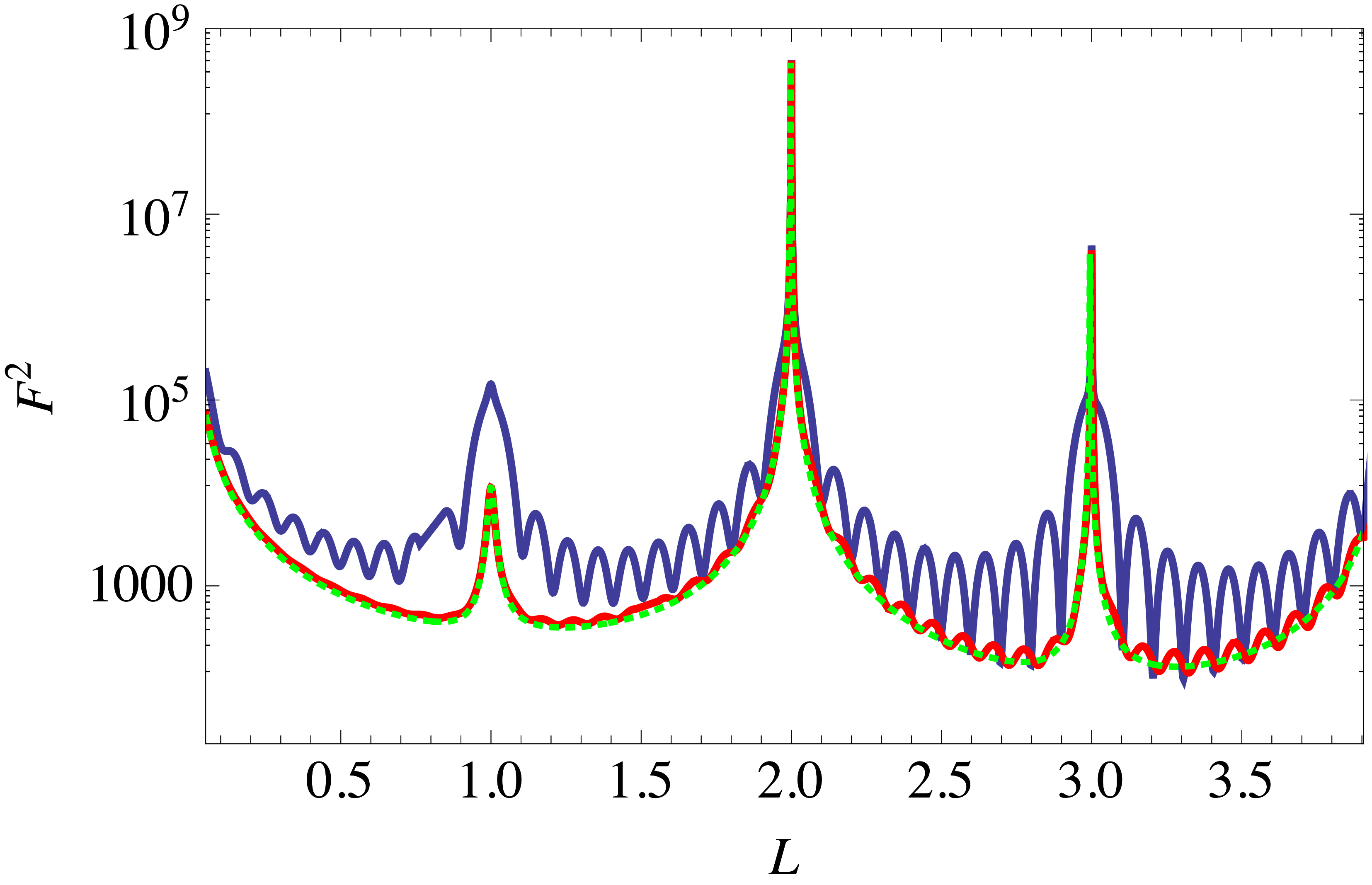
Example calculations

Thickness fringes - compare to STO (green)

- changes in electron density and/or lattice parameter

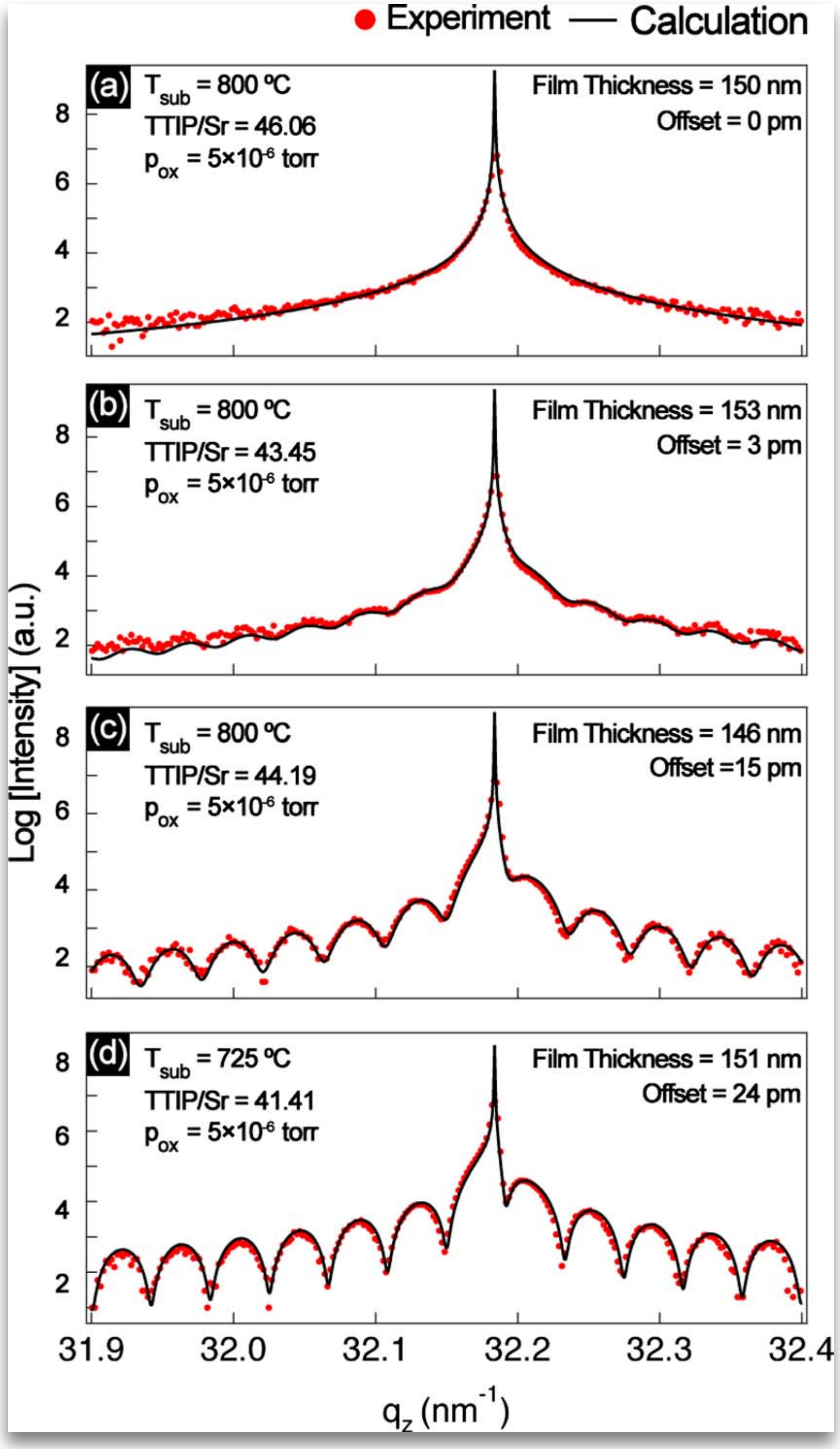
10uc PTO/STO with c_{film}=3.905 Å, a_{sub}=3.905 Å, ξ = 3.905 Å (just Δρ)

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

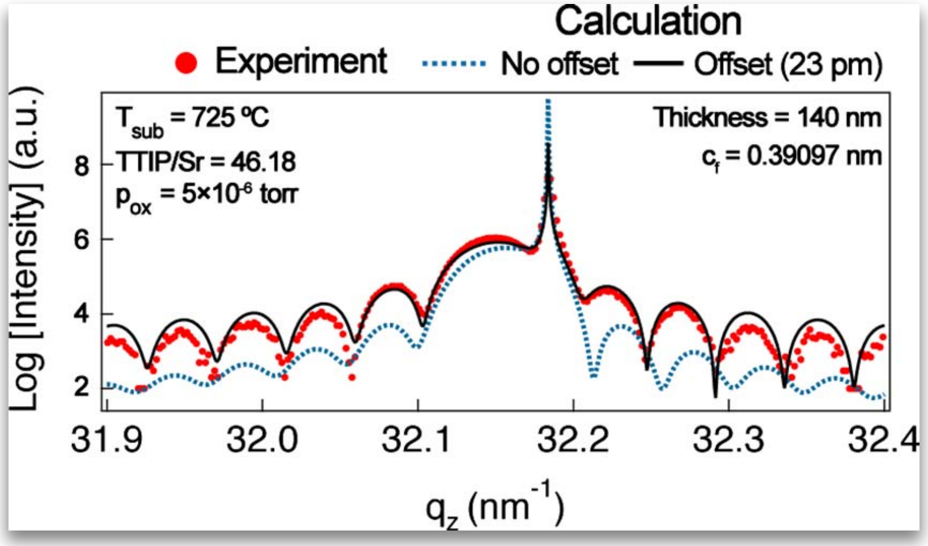


Experimental verification - hybrid MBE + MOCVD

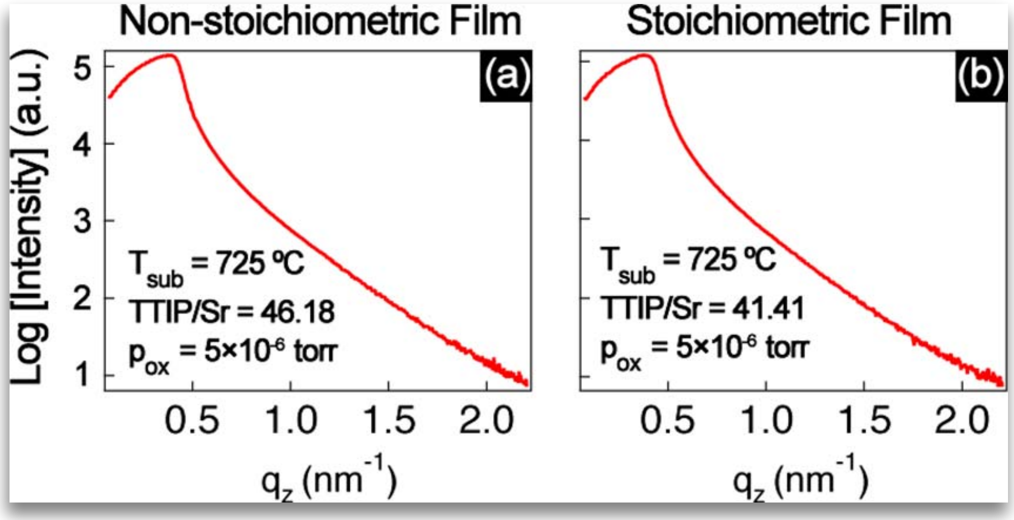
stoichiometric STO on STO with different ξ



purposefully non-stoichiometric STO



reflectivity is ~ insensitive to the stoichiometry



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

A few words on grazing incidence studies

Index of refraction

$n = 1 - \delta + i\beta$

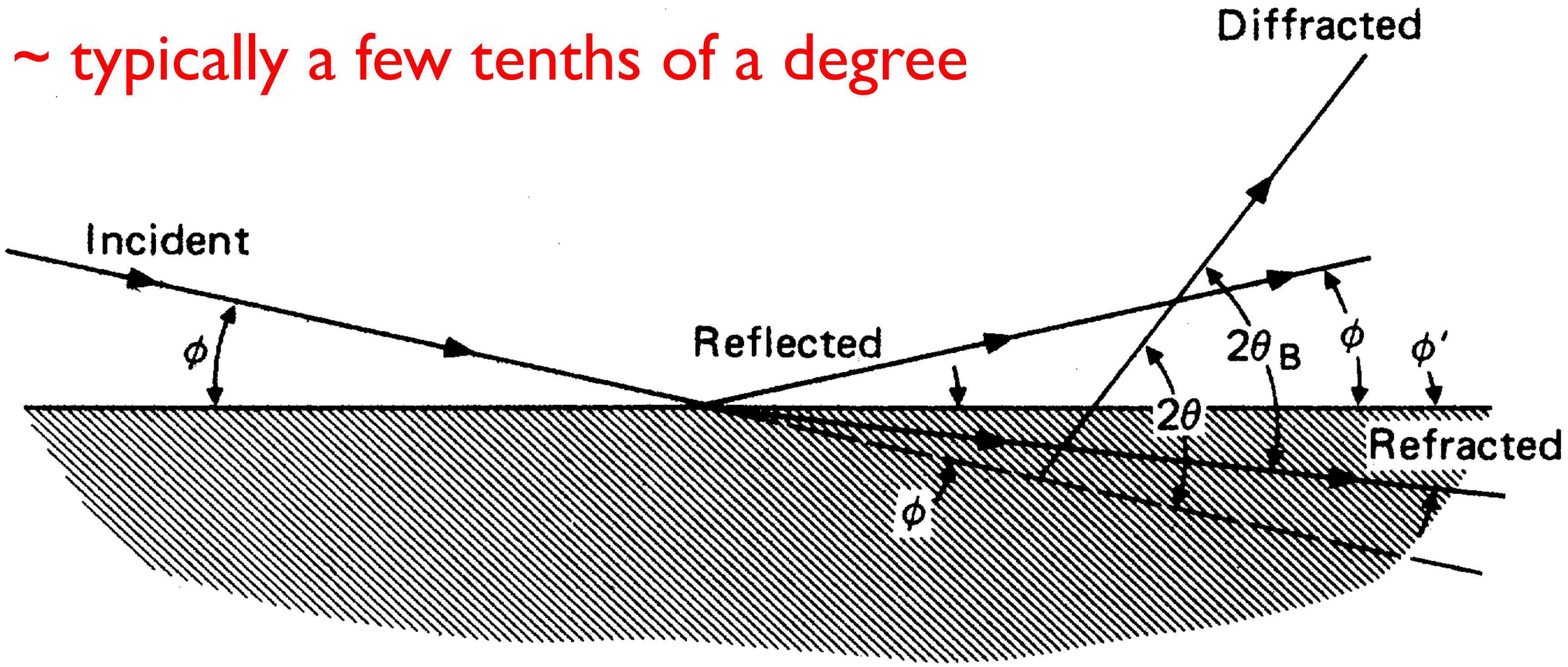
where δ related to mass density and $f'(Q)$

β related to absorption and $f''(Q)$

$$n \equiv 1 - \frac{2\pi \rho_{at} r_0}{k^2} \left\{ f^0(0) + f' + i f'' \right\}$$

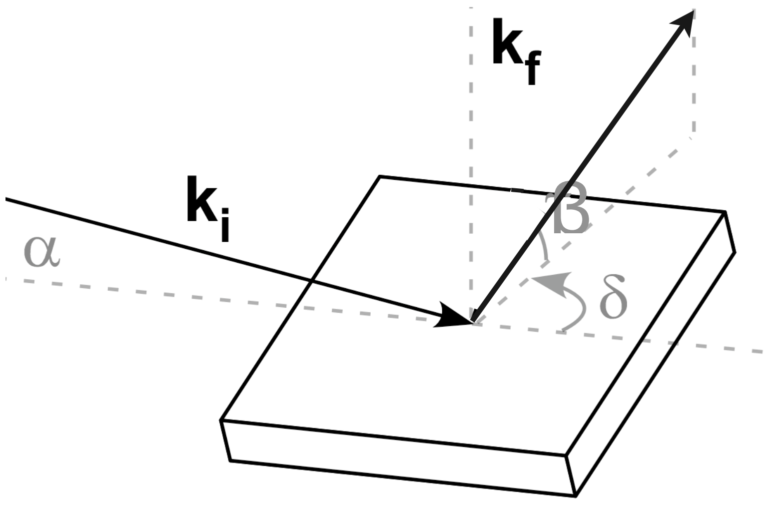
critical angle for total external reflection: $\alpha_c = (2\delta)^{1/2}$

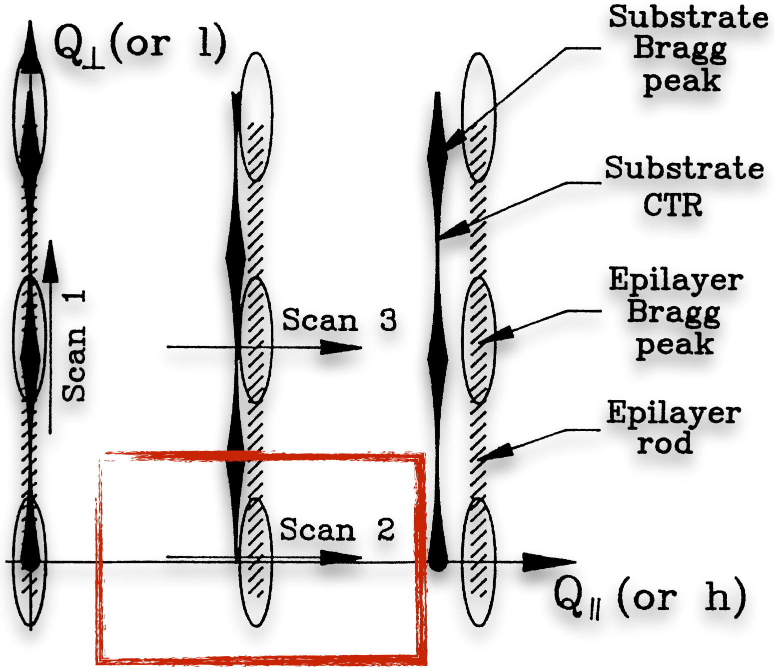
~ typically a few tenths of a degree



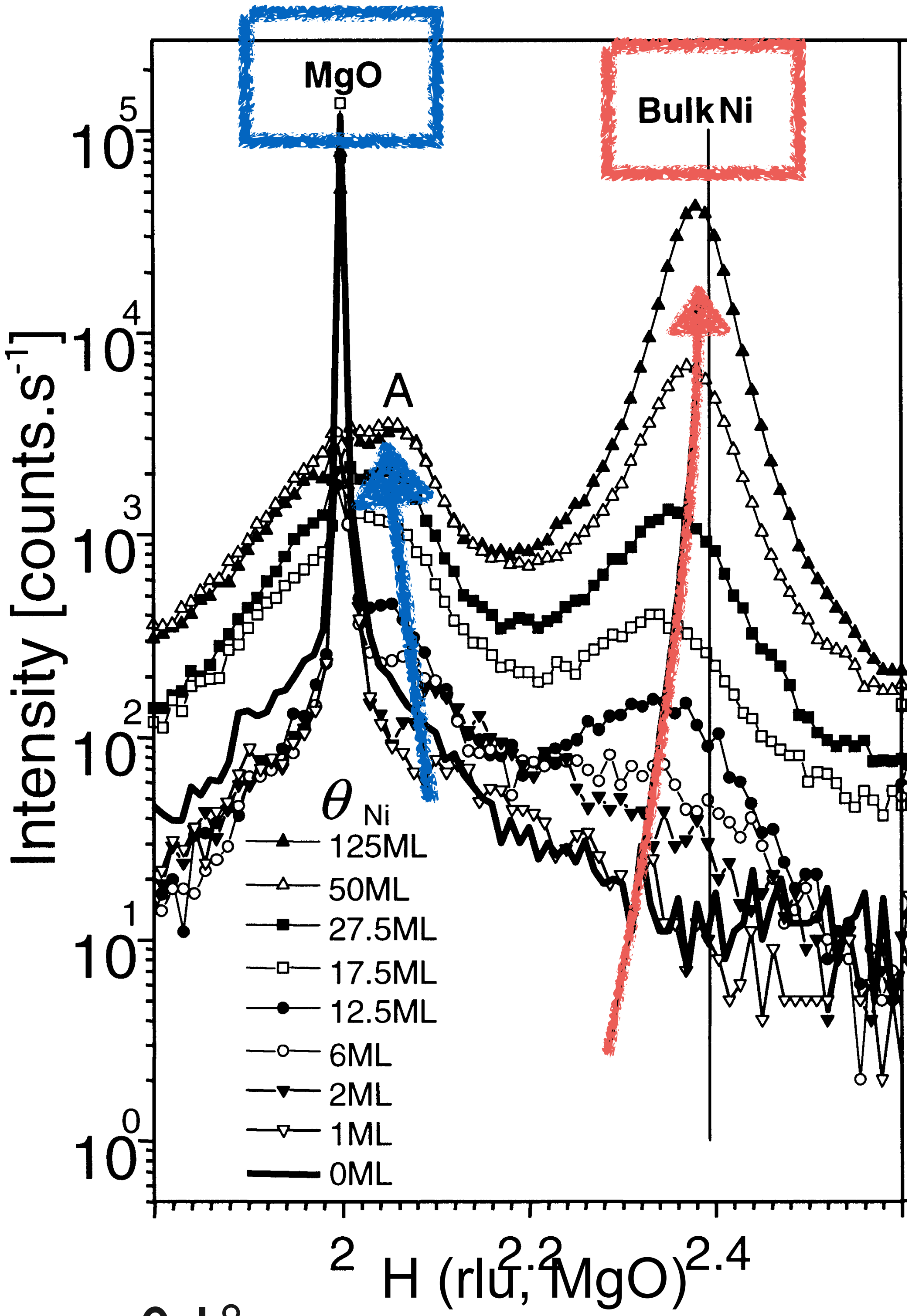
M. Toney and S. Brennan, Phys. Rev. B. **39,** 7963 (1989)

In-plane peaks (*L* ~ 0): grazing incidence diffraction





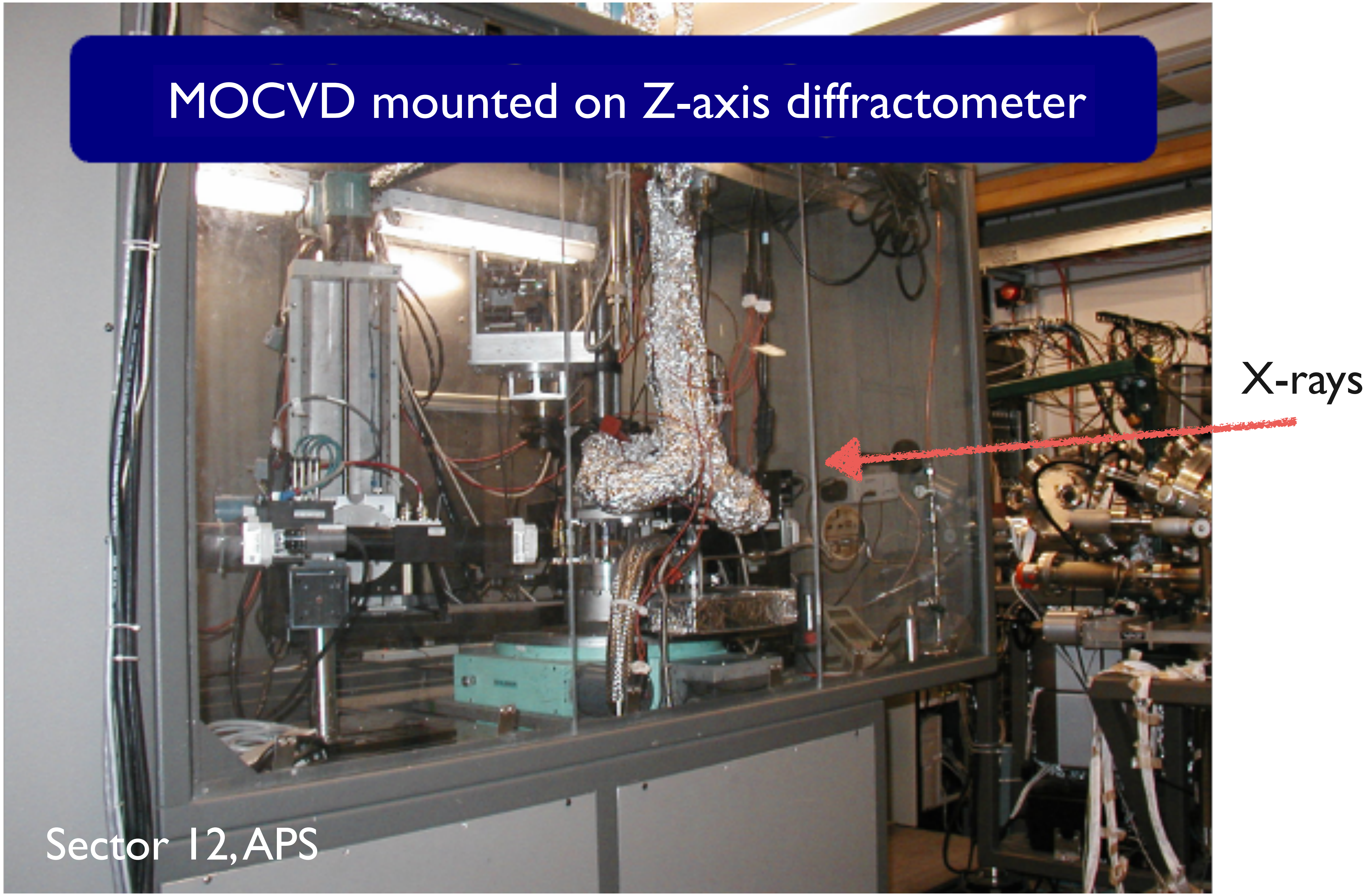
G. Renaud, Surf. Sci. Rep. **32,** 1 (1998)



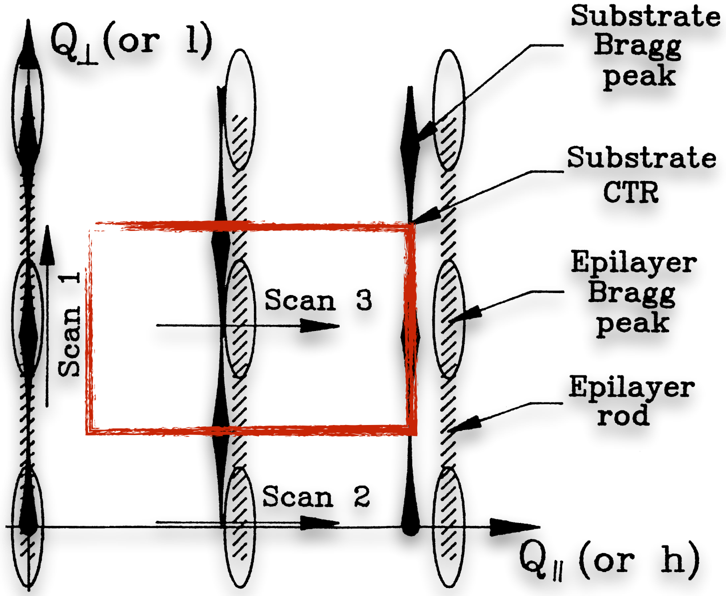
α ~ 0.1°

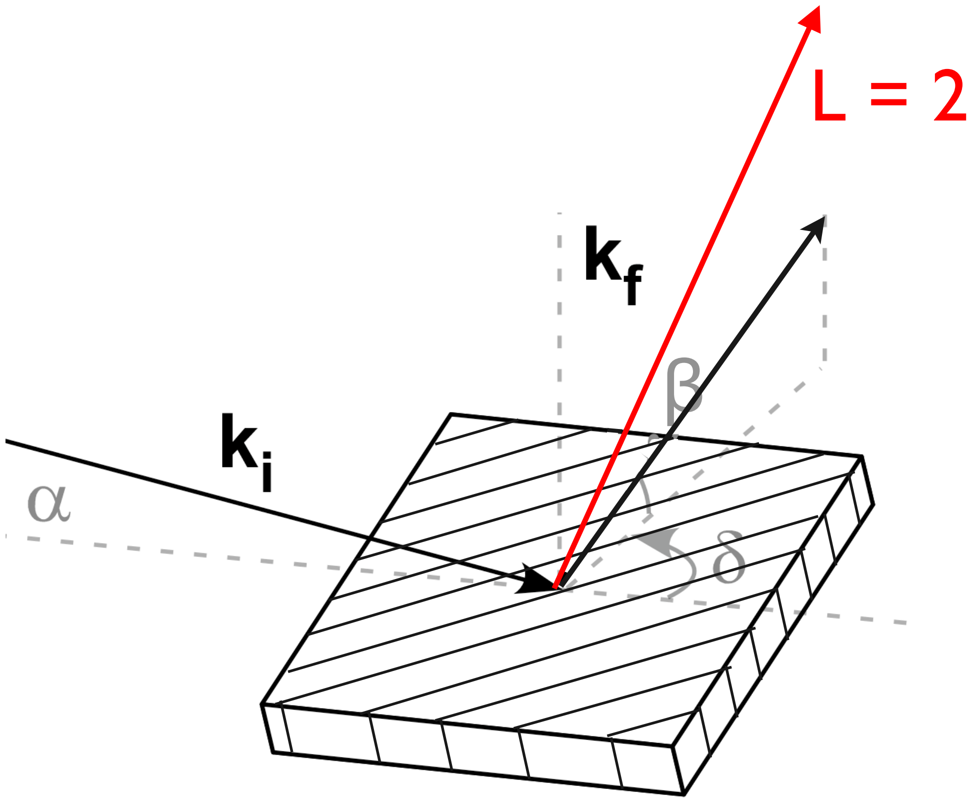
(L ~ 0.05: also near α_c but exiting the sample)

Growth of Pb(Zr,Ti)O_3 films on SrTiO_3 (001)

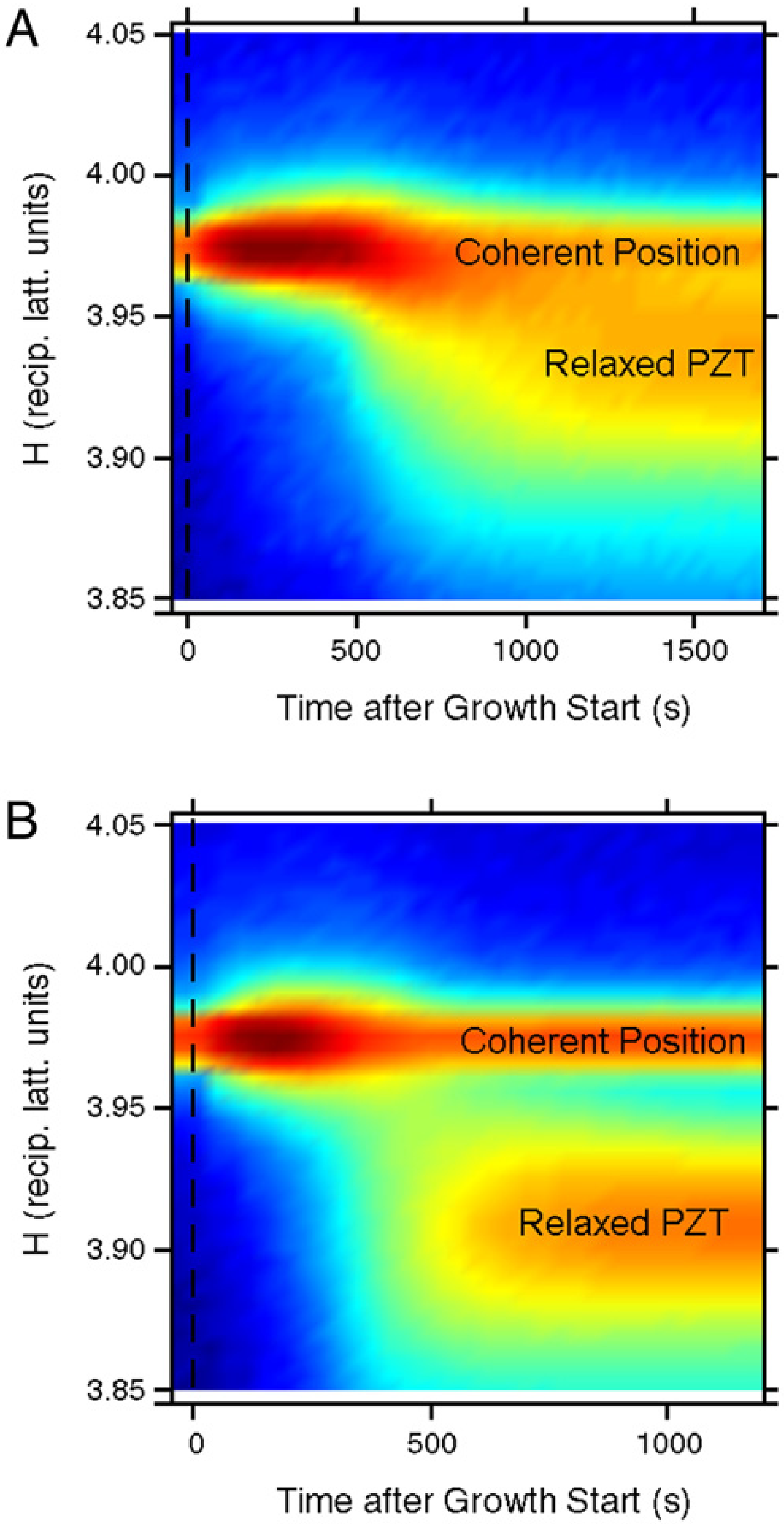


In-plane peaks ($L \neq 0$): grazing incidence diffraction





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



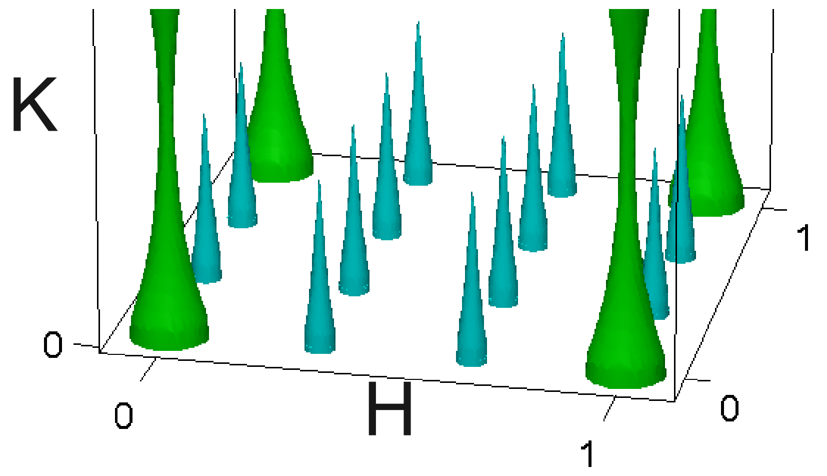
α=0.04°
at 402 peak

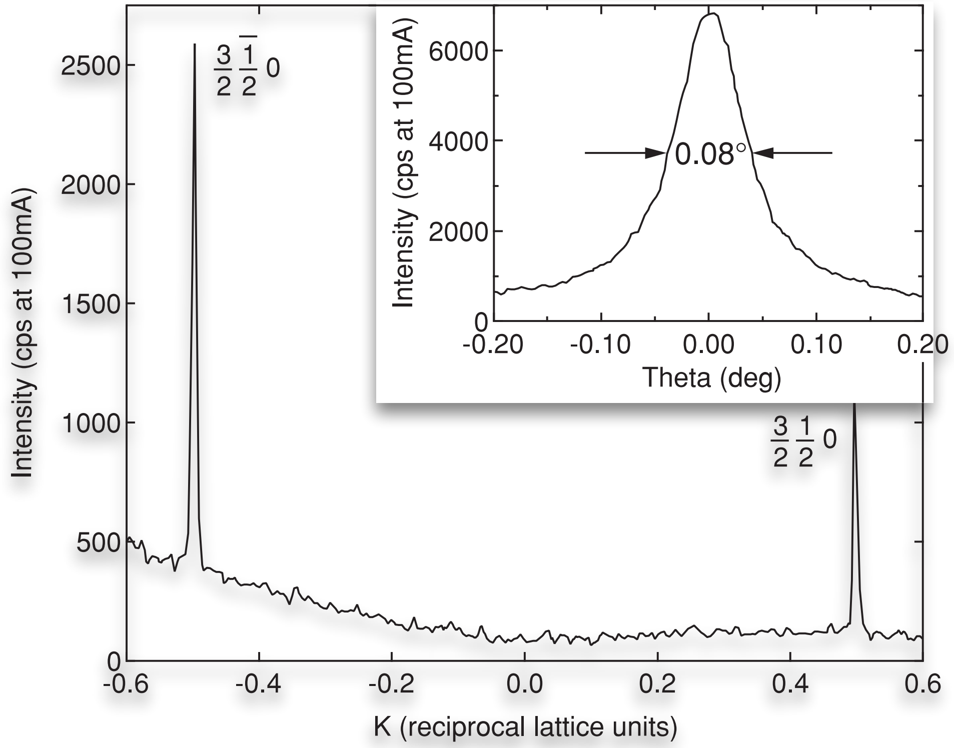
8.6% Zr in PZT

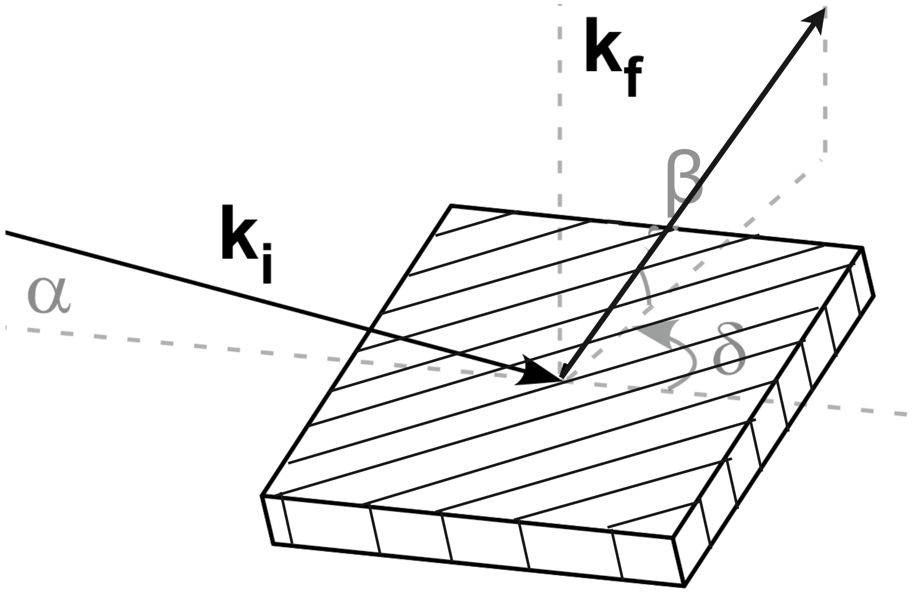
15.9% Zr in PZT

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

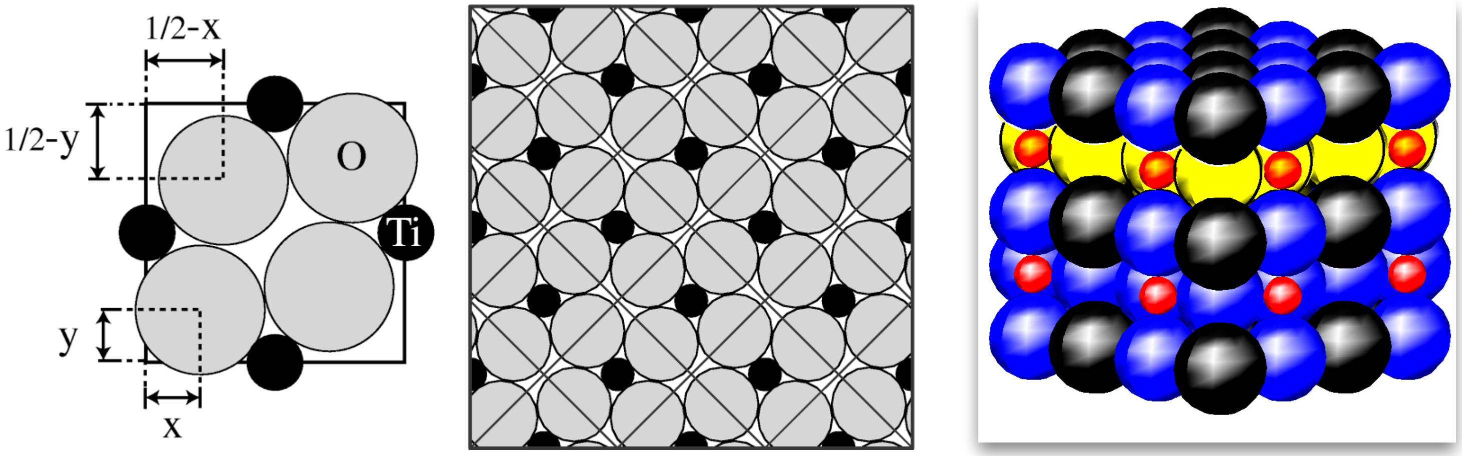
In-plane peaks (*L* ~ 0): surface reconstructions







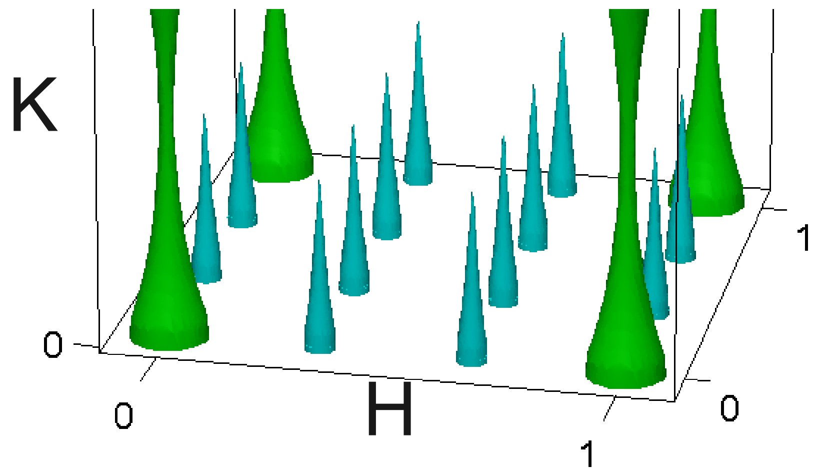
This is actually the layer under the PbO surface

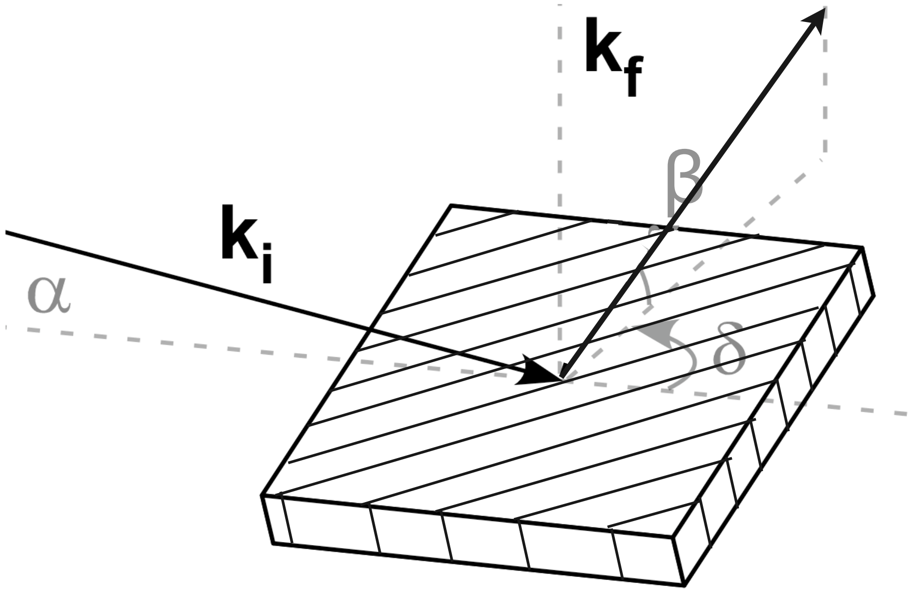


A. Munkholm *et al.*, Phys. Rev. Lett. **88,** 016101 (2001)

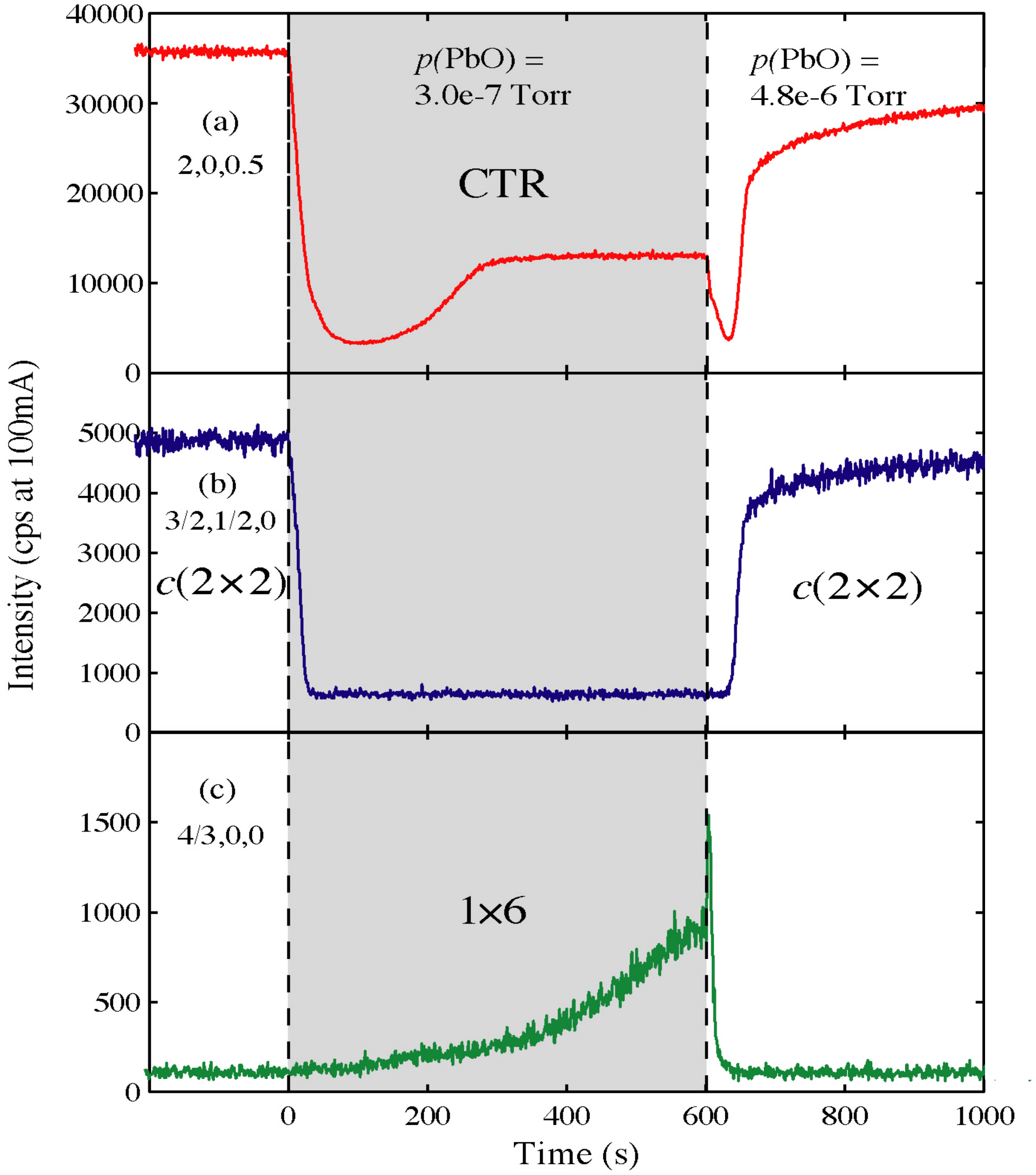
In-plane peaks (*L* ~ 0): surface reconstructions

$PbTiO_3$: PbO-induced reconstruction





750°C



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 [you get a relative intensity enhancement]
    - e.g., H 0 0 scan [grazing incidence + grazing exit] - often for studies of in-plane reconstruction peaks
    - can also do CTR-scans on ultrathin films (e.g., 1-5 unit cells) - but out-of-plane scans are shifted in *L*
    - can improve signal from intensity boost at α_c from total external reflection + large footprint
- **but you don’t need to vary penetration depth to get depth dependent info**
  - **from single crystals: modeling or solving phase problem also does it**

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

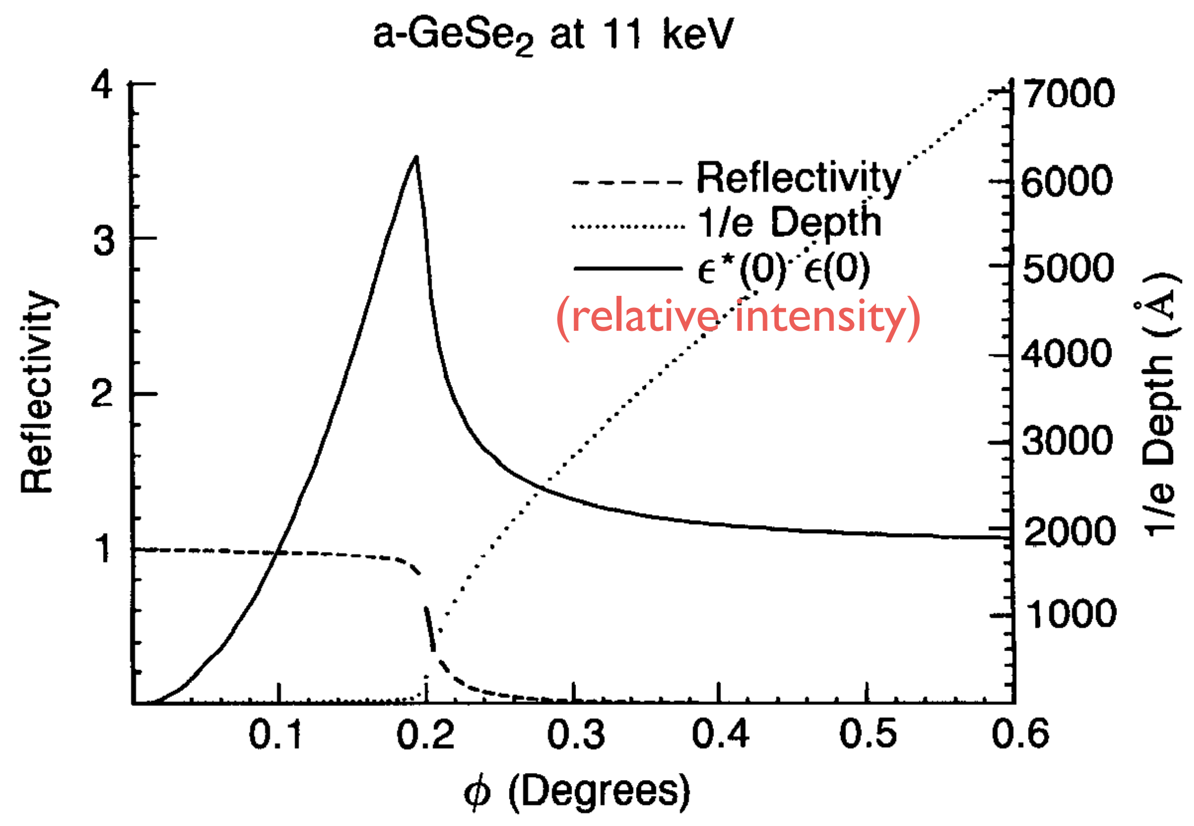
penetration depth

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

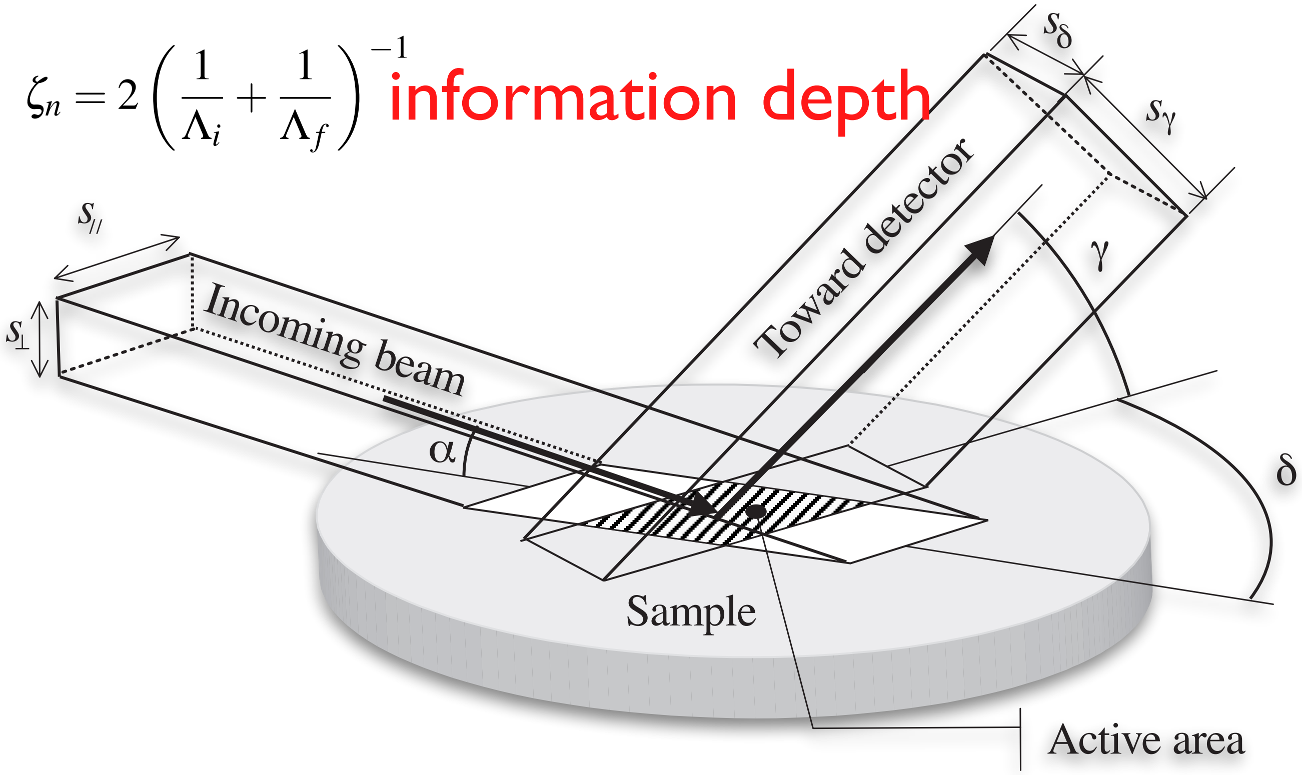
penetration depth

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

information depth



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



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

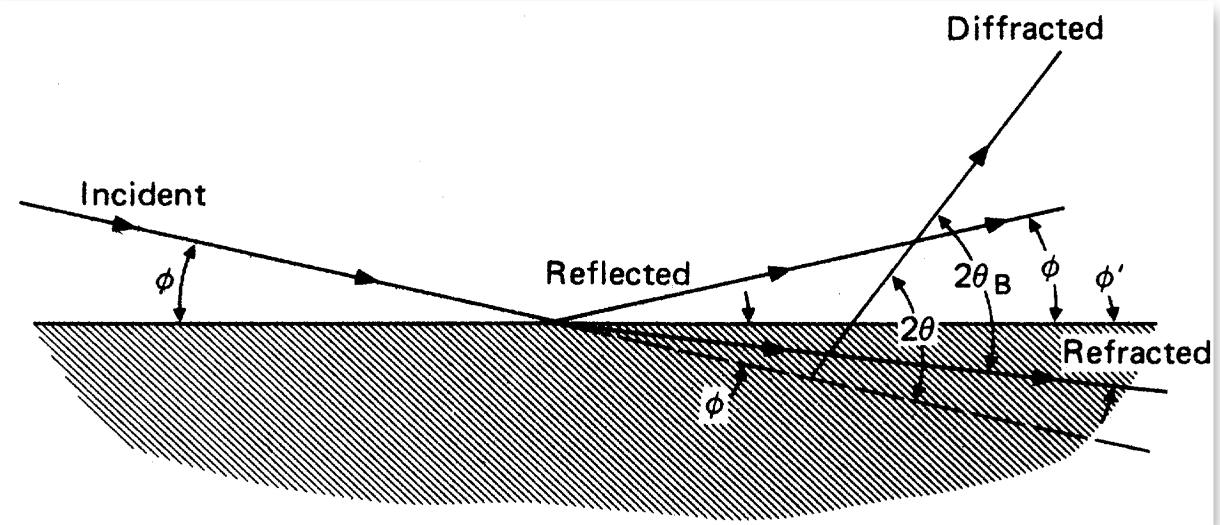
Grazing incidence: effects of refraction

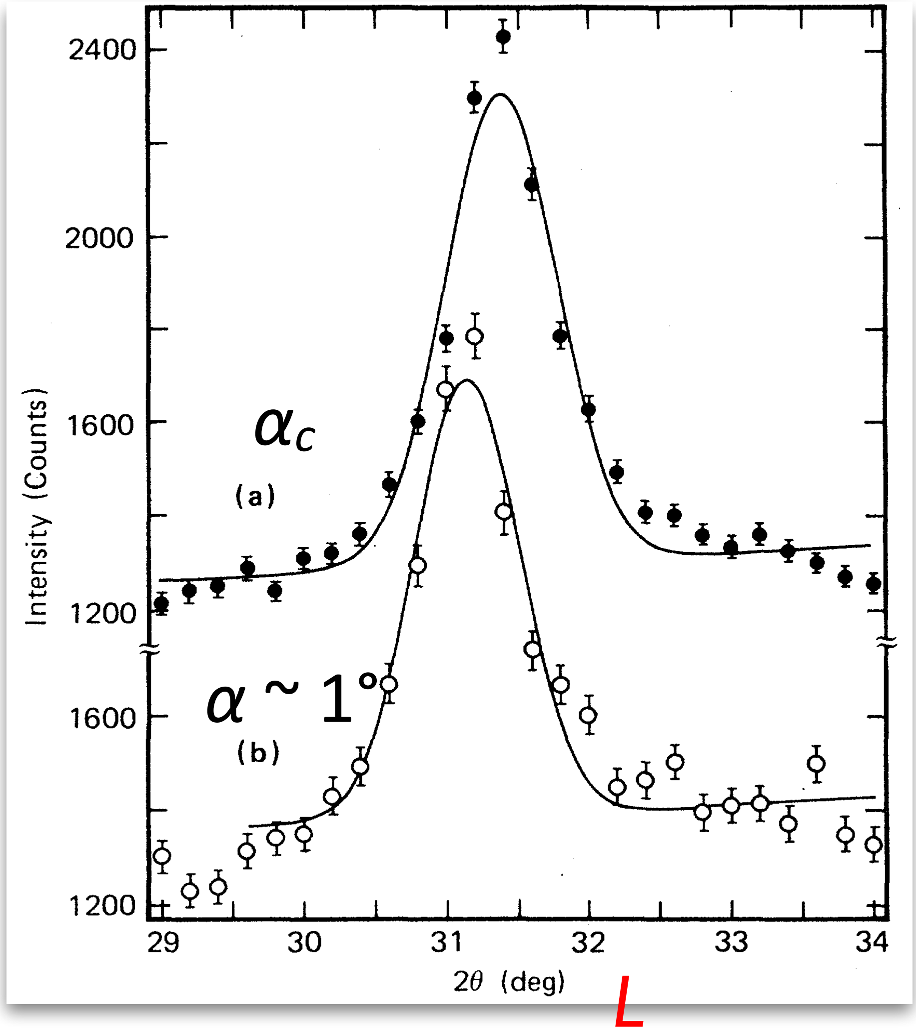
In-plane diffraction (L ~ 0): no problem

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

- diffracted beam appears at altered L-position due to refraction

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





Angular shift in out-of-plane direction:

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

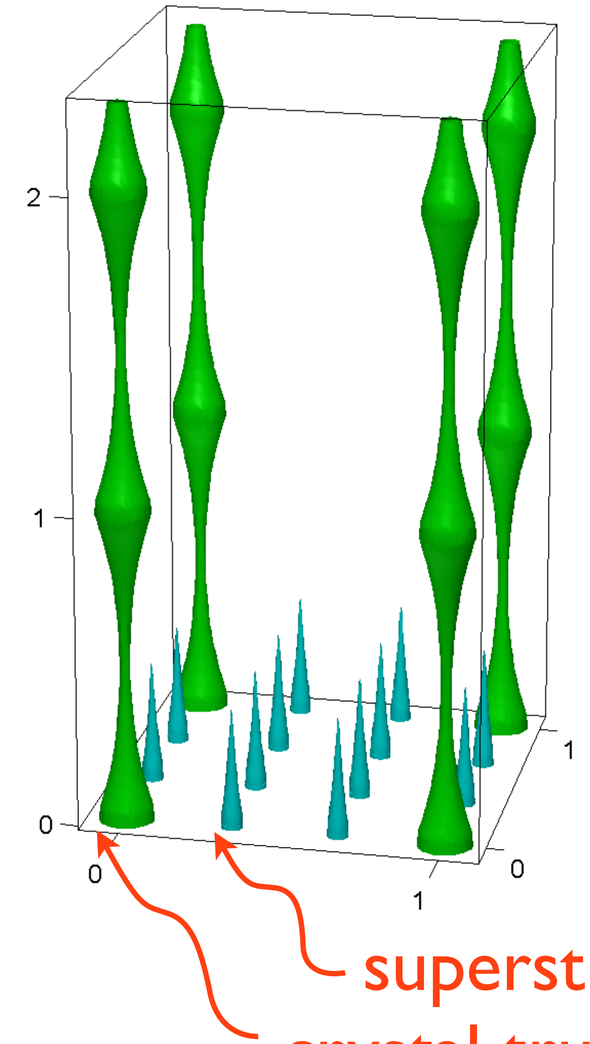
So in general, we like to keep α ~ 1°

Direct Methods

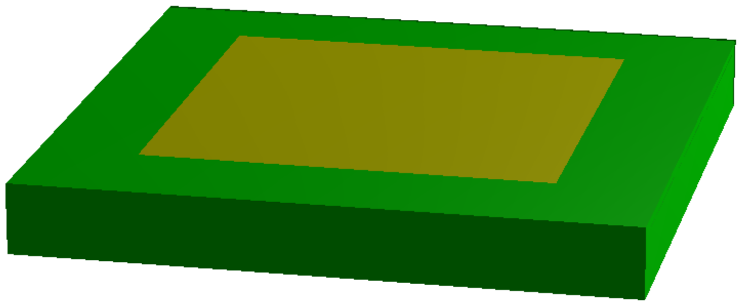
- Trying to avoid fitting
- Assumes coherent scattering (e.g., single crystal)
- if large single crystal -- doesn't need APS-U
- if small single crystal -- needs APS-U
- direct methods will become routine

Note: APS-U will make 3D Fourier transform easier

1D Fourier transform

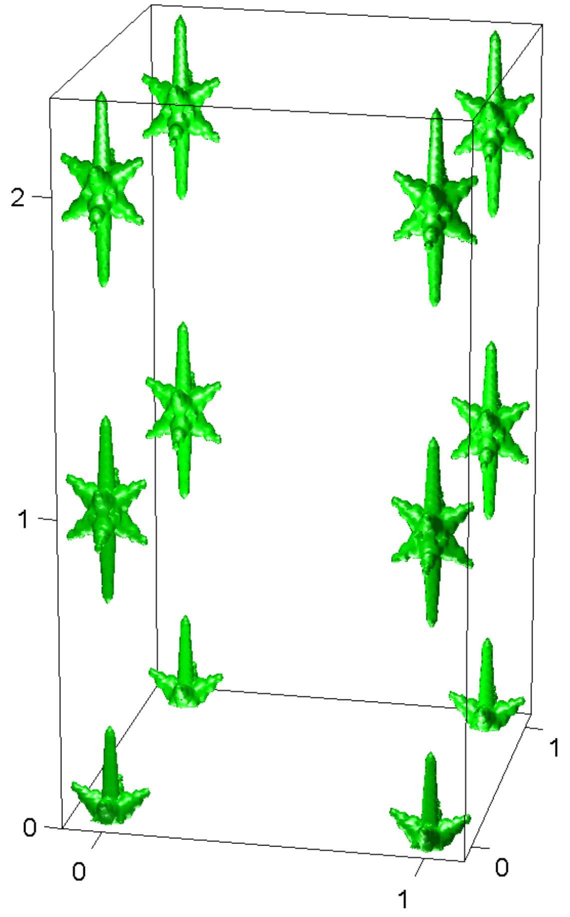


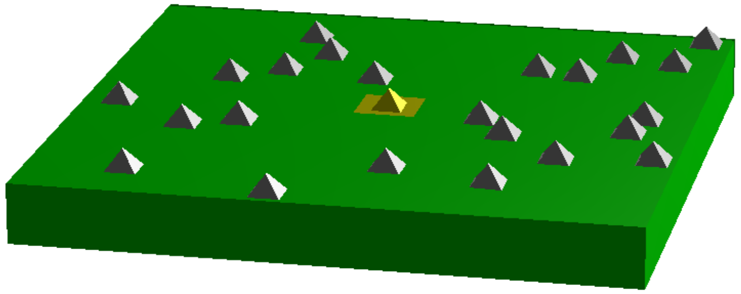
superstructure rods (SRs)
crystal truncation rods (CTRs)



SXRD

3D Fourier transform

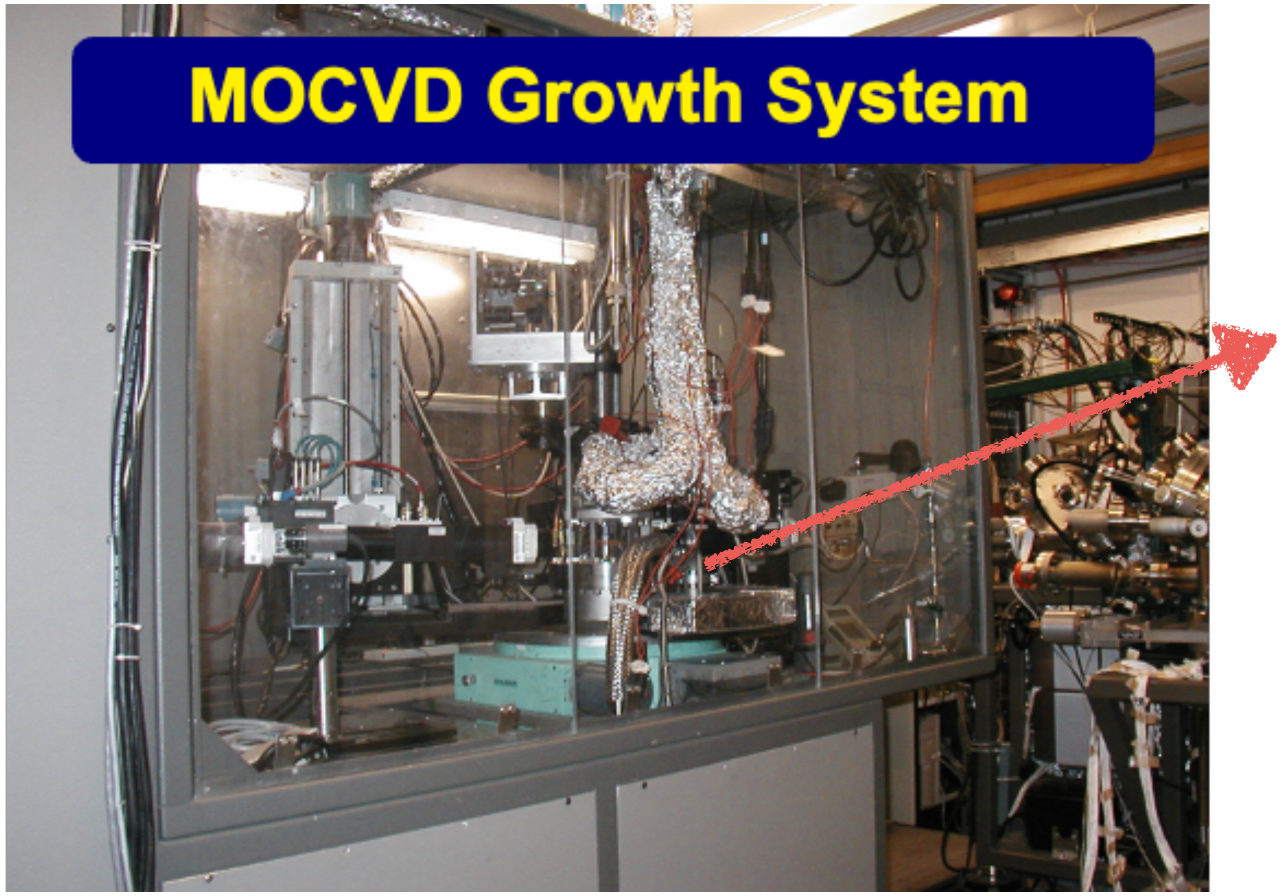




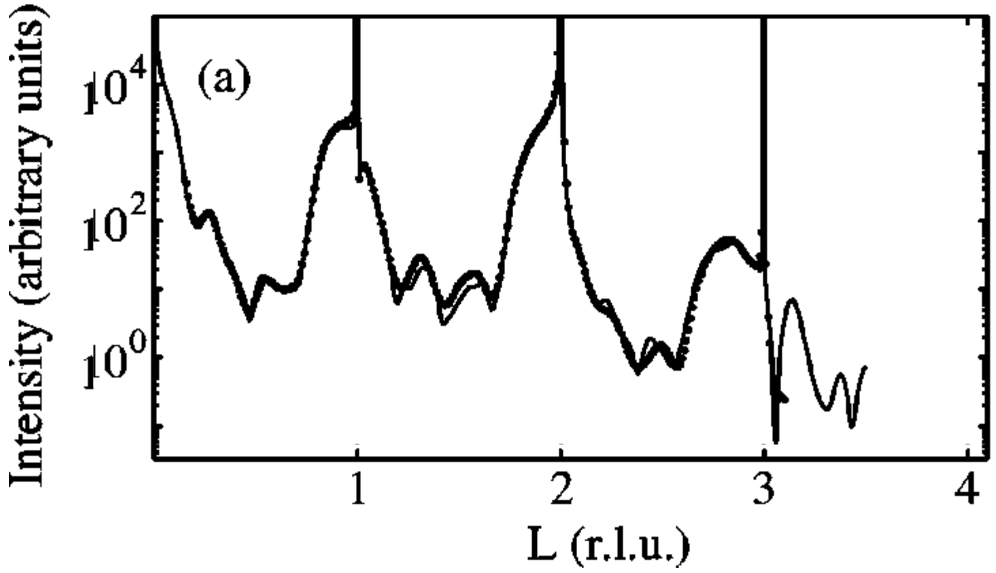
CDI

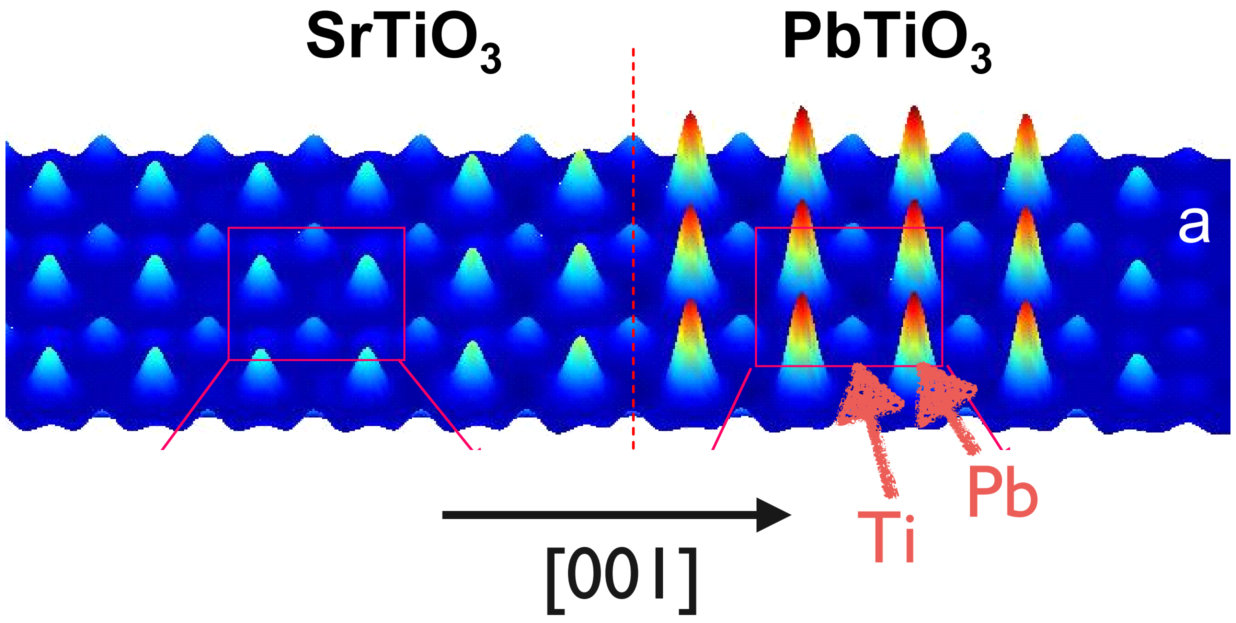
D. D. Fong *et al.* MRS Bulletin **35,** 504 (2010)

Example: 4-unit-cell $PbTiO_3$ / $SrTiO_3$ (001)



Growth of epitaxial ferroelectric $PbTiO_3$ by metal organic chemical vapor deposition (MOCVD)



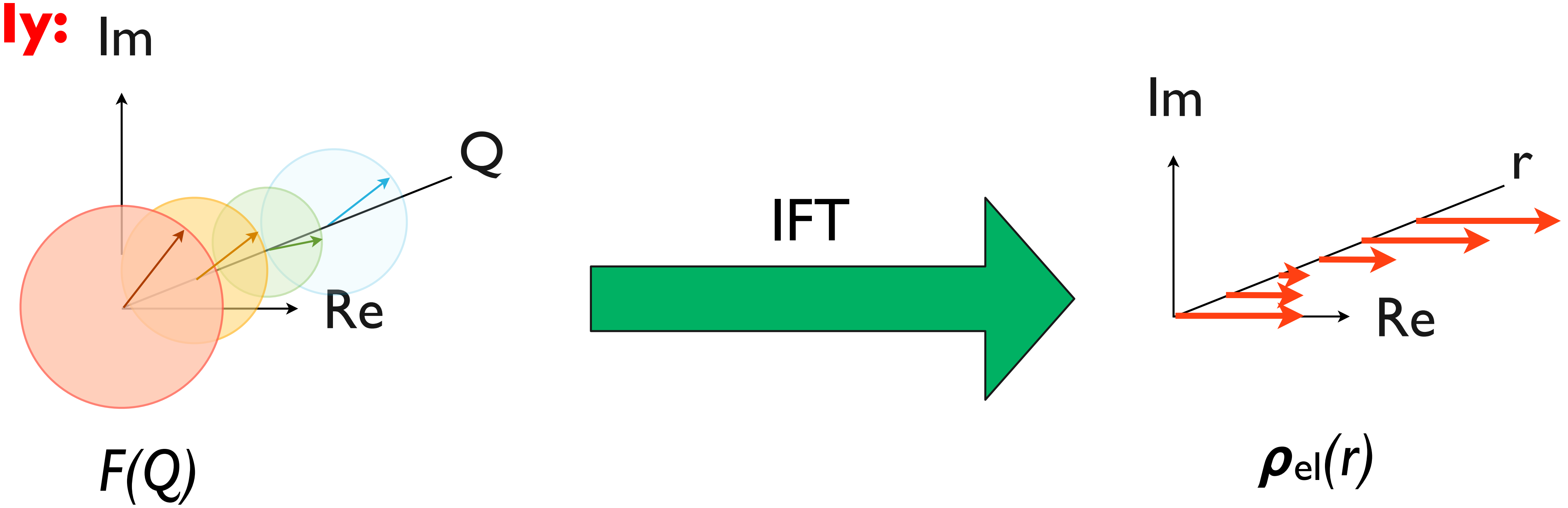


D. D. Fong, Y. Yacoby, et al., Phys. Rev. B, **71**, 144112 (2005)

Fourier cycling

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

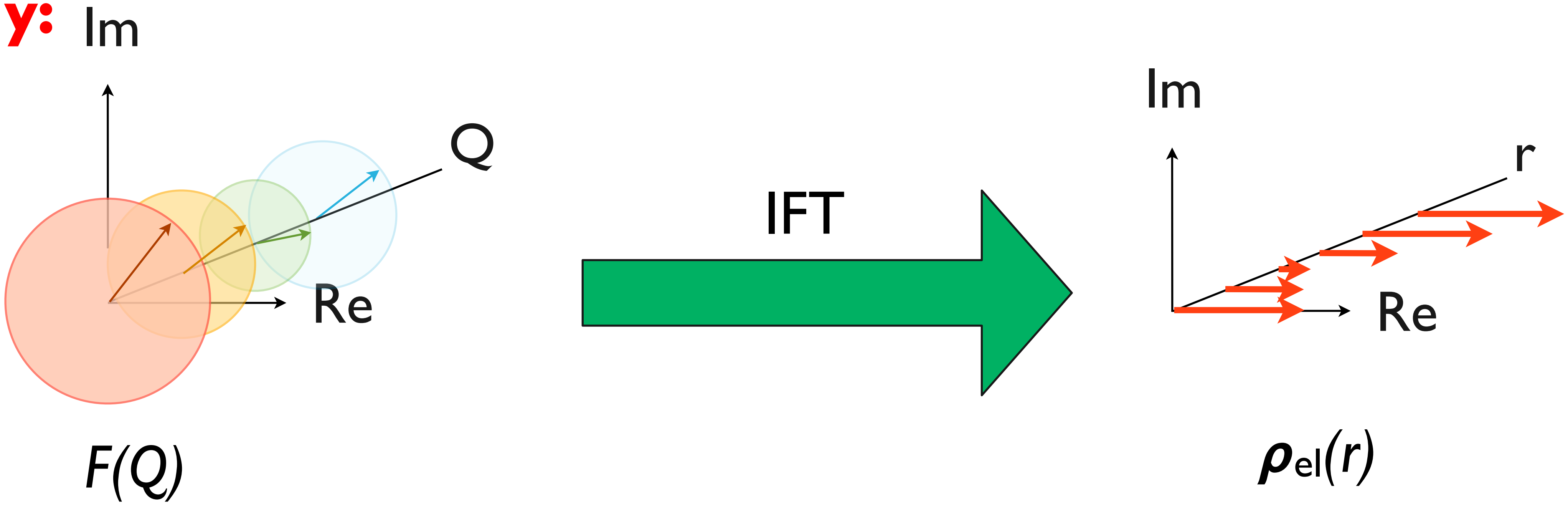
Ideally:



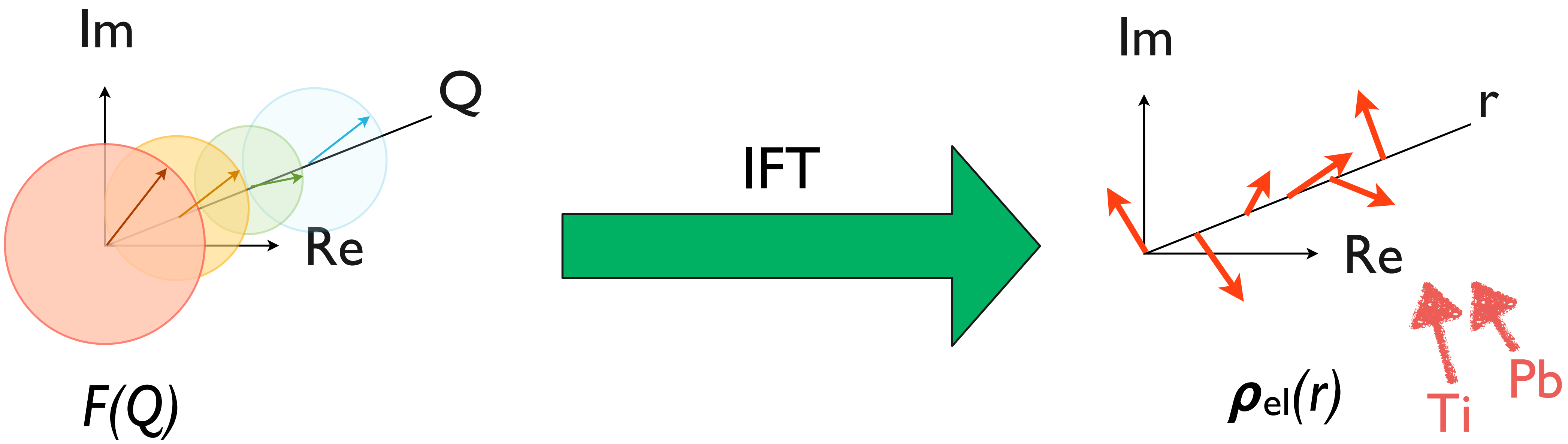
Fourier cycling

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

Ideally:

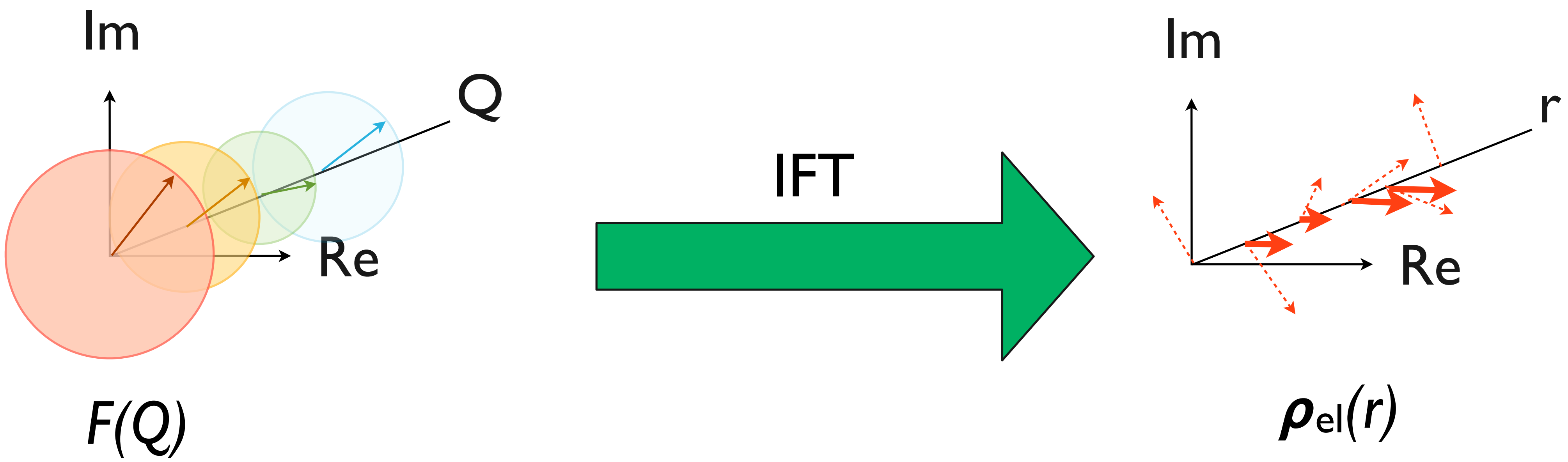


But usually:

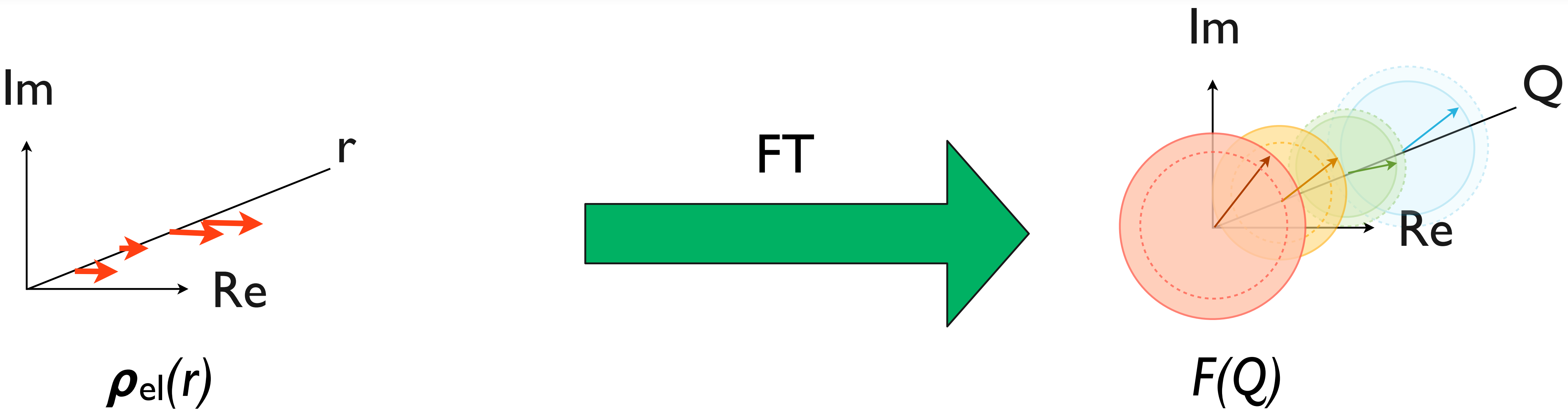


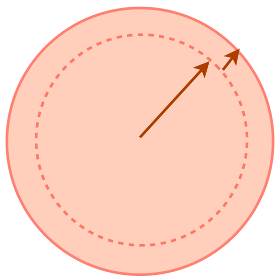
Fourier cycling

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



Fourier cycling — now FT





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

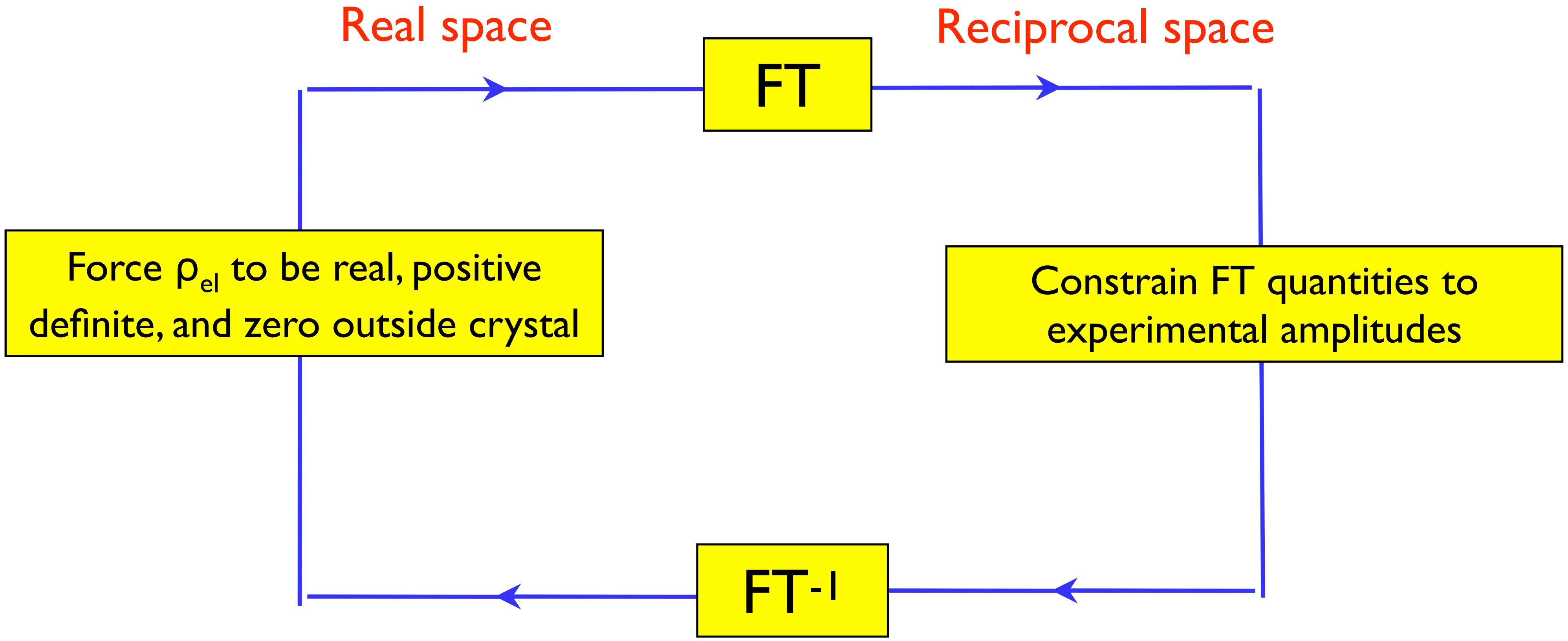
This corresponds to error corrections in reciprocal space: $\Delta F(Q)$

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)



Real space

Reciprocal space

FT

Force ρ_{el} to be real, positive definite, and zero outside crystal

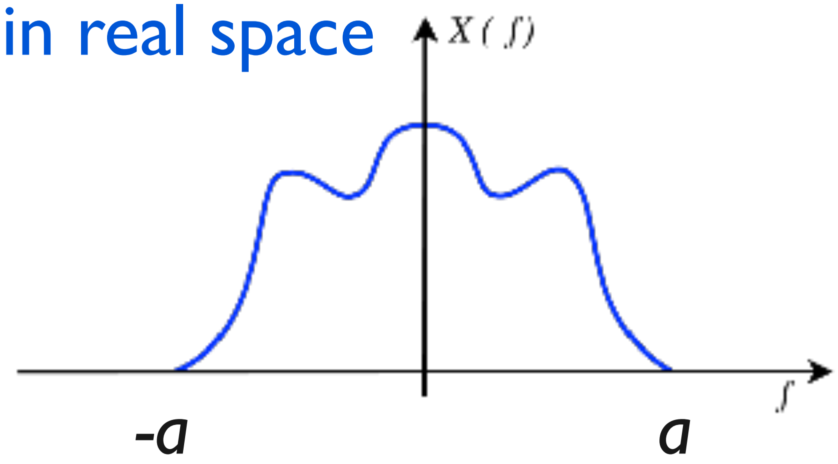
Constrain FT quantities to experimental amplitudes

FT^{-1}

Oversampling

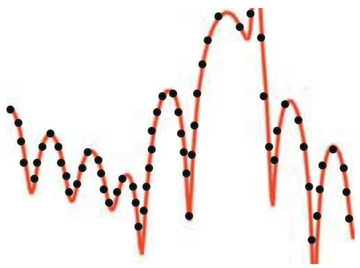
How much data do you need to take to reconstruct $\boldsymbol{\rho}_{\text{el}}$?

film thickness in real space



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

- 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 sample at least twice this (~ 7 points per thickness fringe) - **oversampling** (can only be done along *L* for thin films)
- We can do this for multiple CTRs



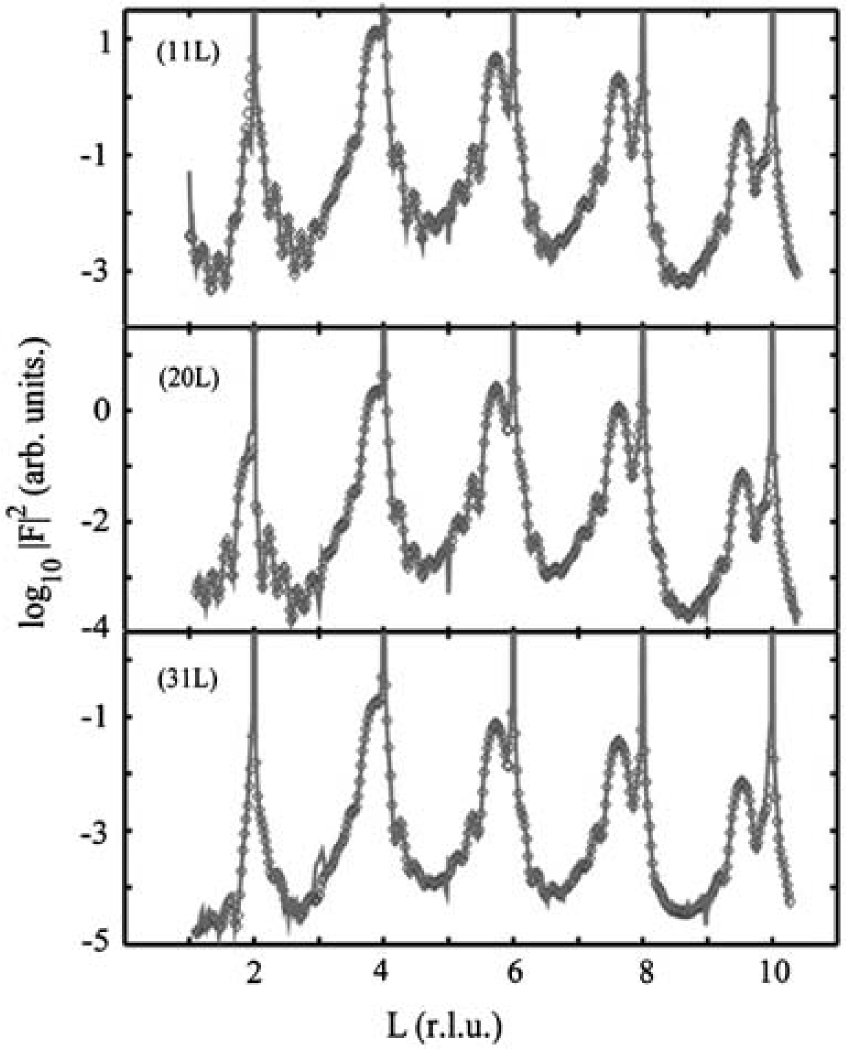
D. Sayre, Struct. Chem. **13,** 81 (2002)

COherent Bragg Rod Analysis (COBRA): Example $La_{2-x}Sr_xCuO_4$ / $LaSrAlO_4(001)$

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

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

$$\begin{aligned} F_{HKL} = {} & f_{\mathrm{A}} e^{\pi i(H+K)} + f_{\mathrm{B}} e^{\pi i(L)} \\ & + f_{\mathrm{O}}\left[1 + e^{\pi i(K+L)} + e^{\pi i(H+K+L)}\right] \end{aligned}$$

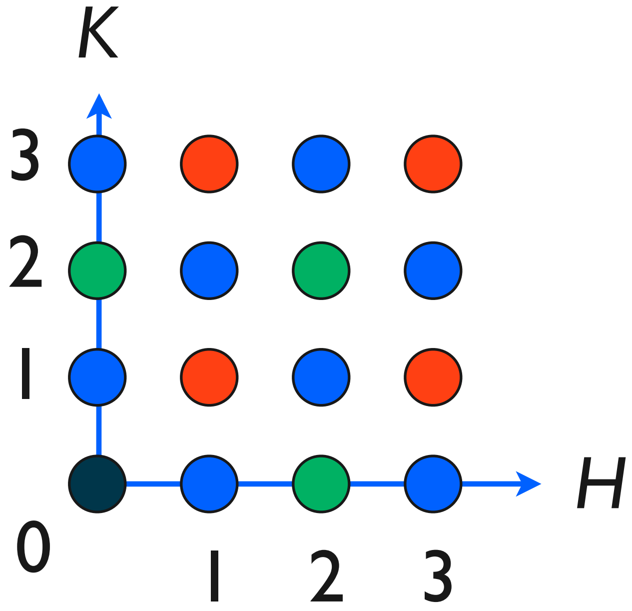


E.g., for 4mm perovskite symmetry: 3 independent rods

- (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)

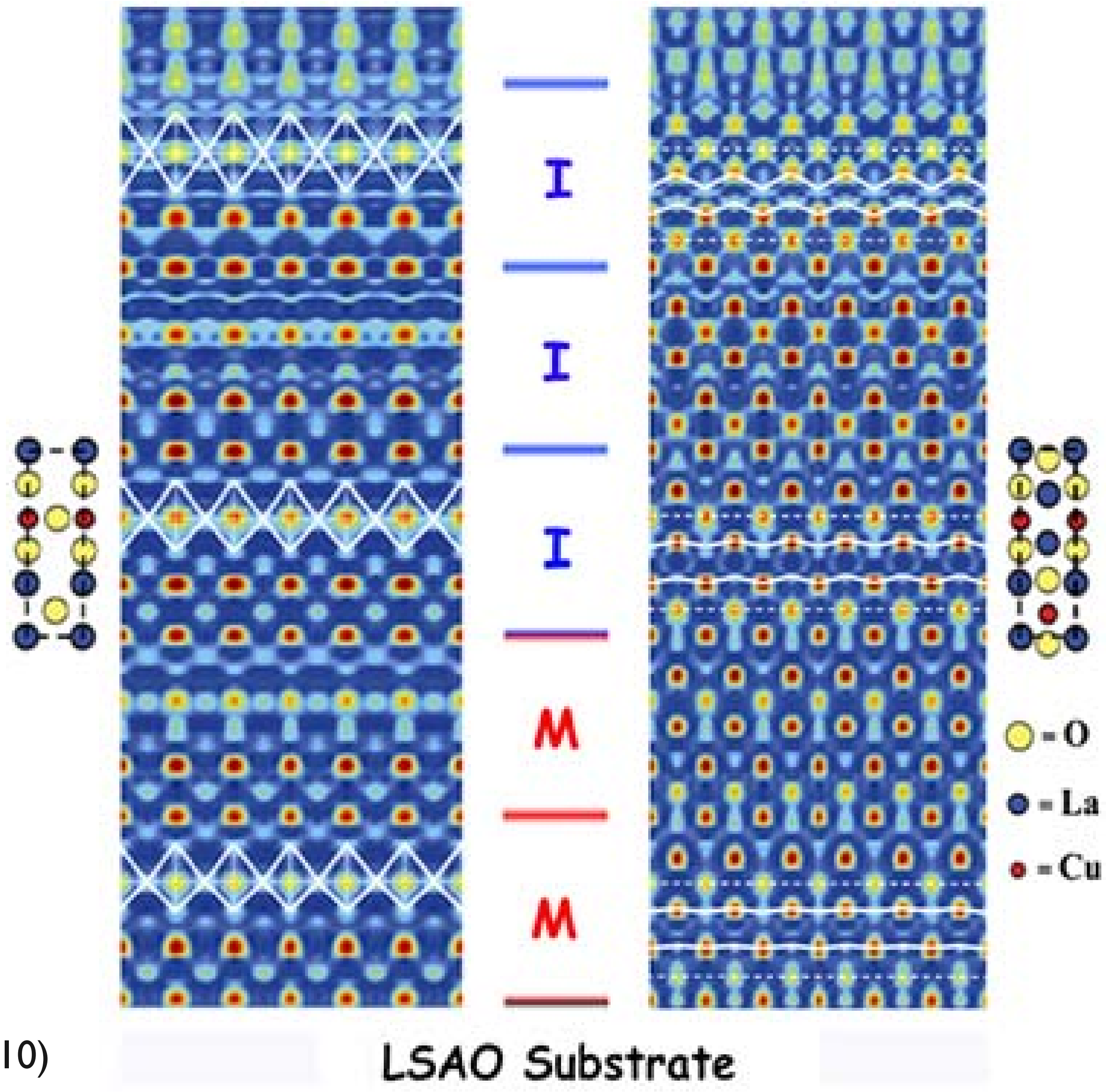


Real space structures for single and bilayer films

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

single film **bilayer film**

$La_{1.84}Sr_{0.16}CuO_4$



La_2CuO_4

La_2CuO_4

La_2CuO_4

$La_{1.55}Sr_{0.45}CuO_4$

$La_{1.55}Sr_{0.45}CuO_4$

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

Another way: DFT + fitting

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

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

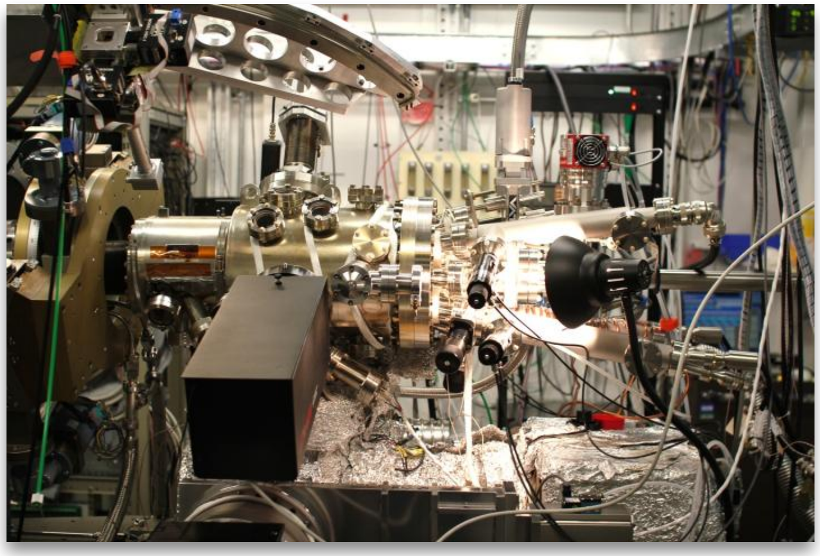
Experiment

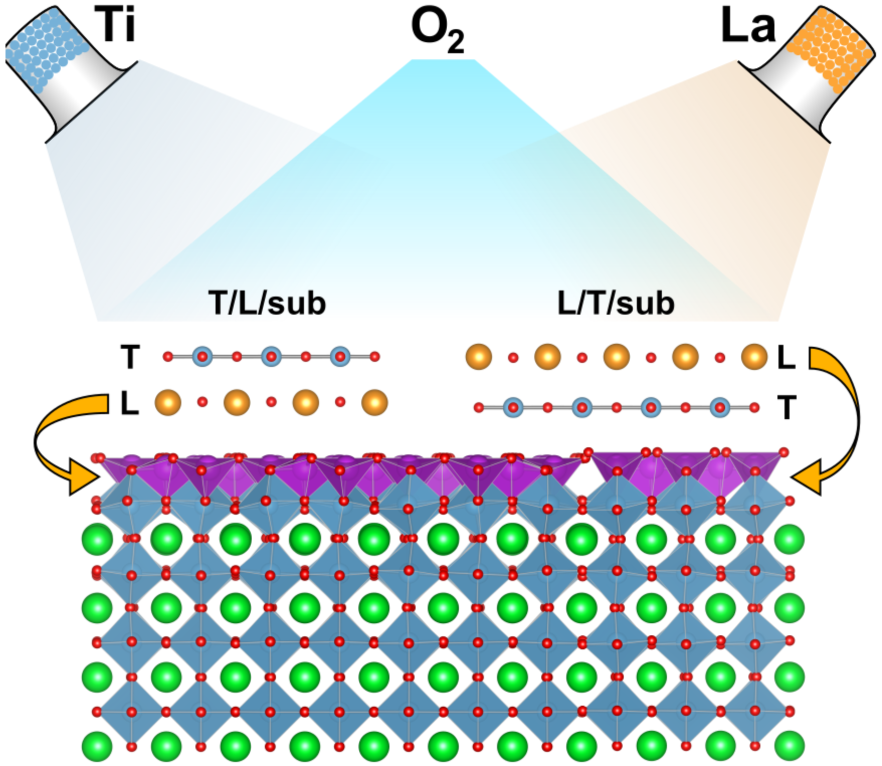
DFT

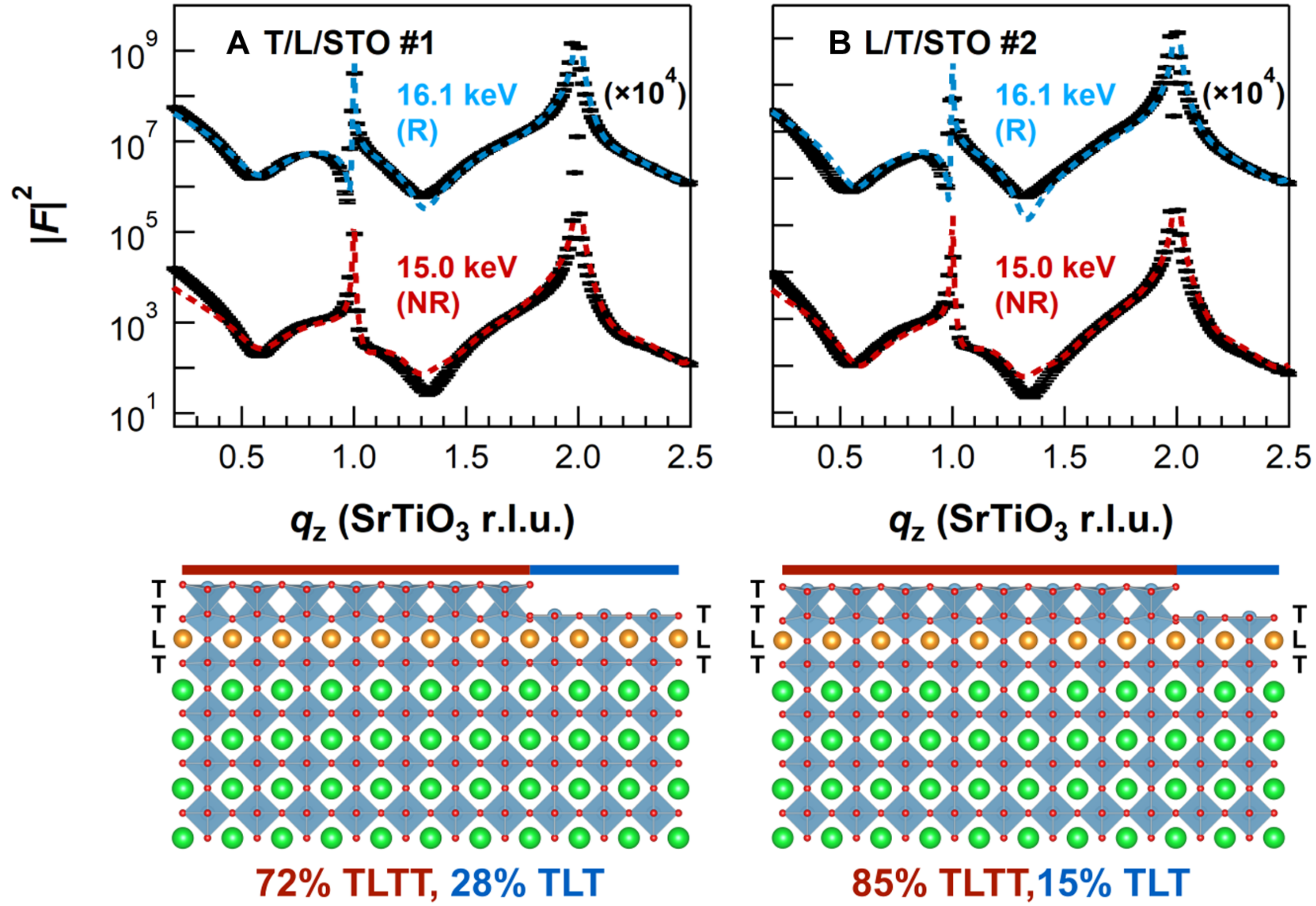
Fit residual R^2 for non-linear least squares fitting of atomic positions $\{\zeta_I\}$, Debye-Waller factors $\{\sigma_I\}$, and occupancies $\{\theta_I\}$ of each atom.

- Experimental chi-squared χ^2 constrains predicted structure factor $|F(\zeta,\sigma,\theta)|^2$ to measured structure factor $|F_{exp}|^2$.
- Resonant ($\chi^2{}_{res}$) 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.

Another way: DFT + fitting: here the $SrTiO_3$ (001) surface





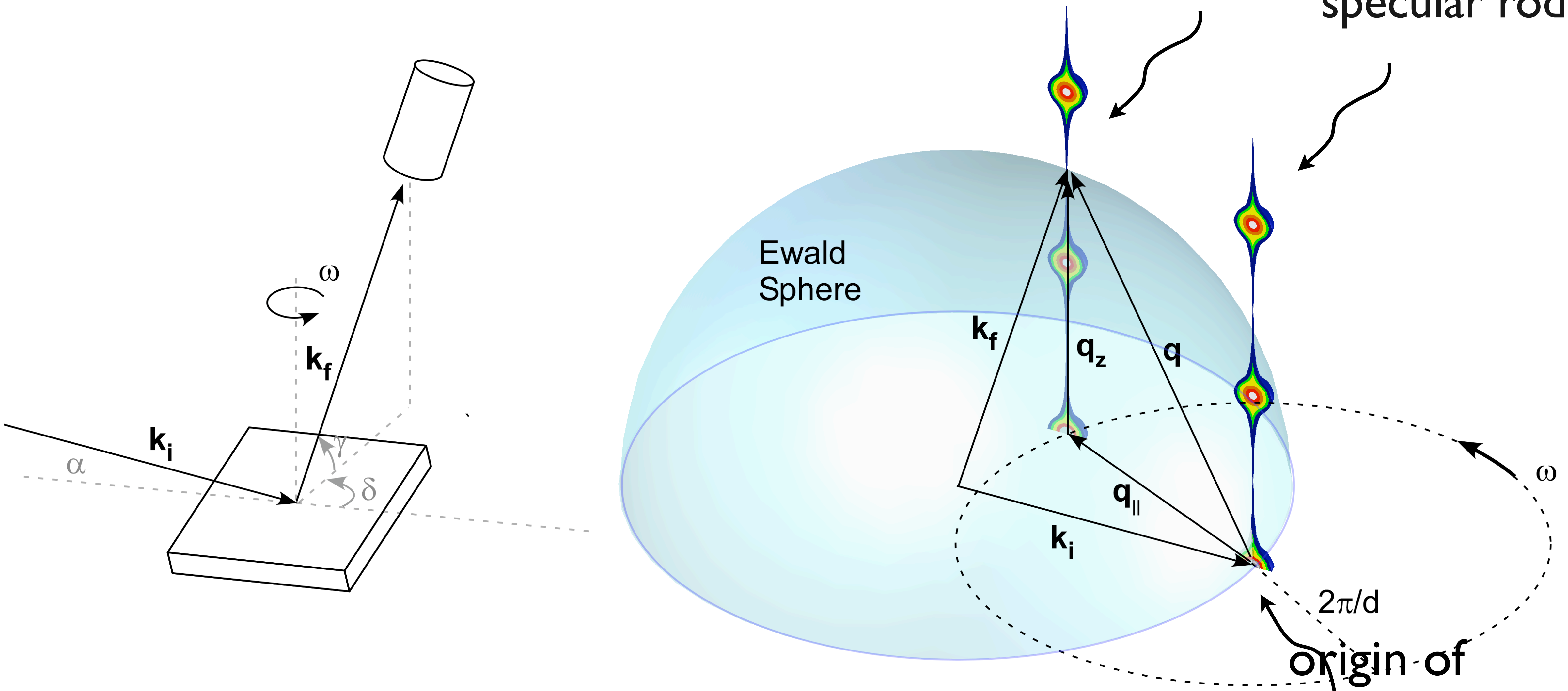


Chief advantage -- you get DFT-based information as well

- S.Y. Cook et al., Sci. Adv. **5,** eaav0764 (2019)

Practicalities

SXRD geometry



off-specular rod

specular rod

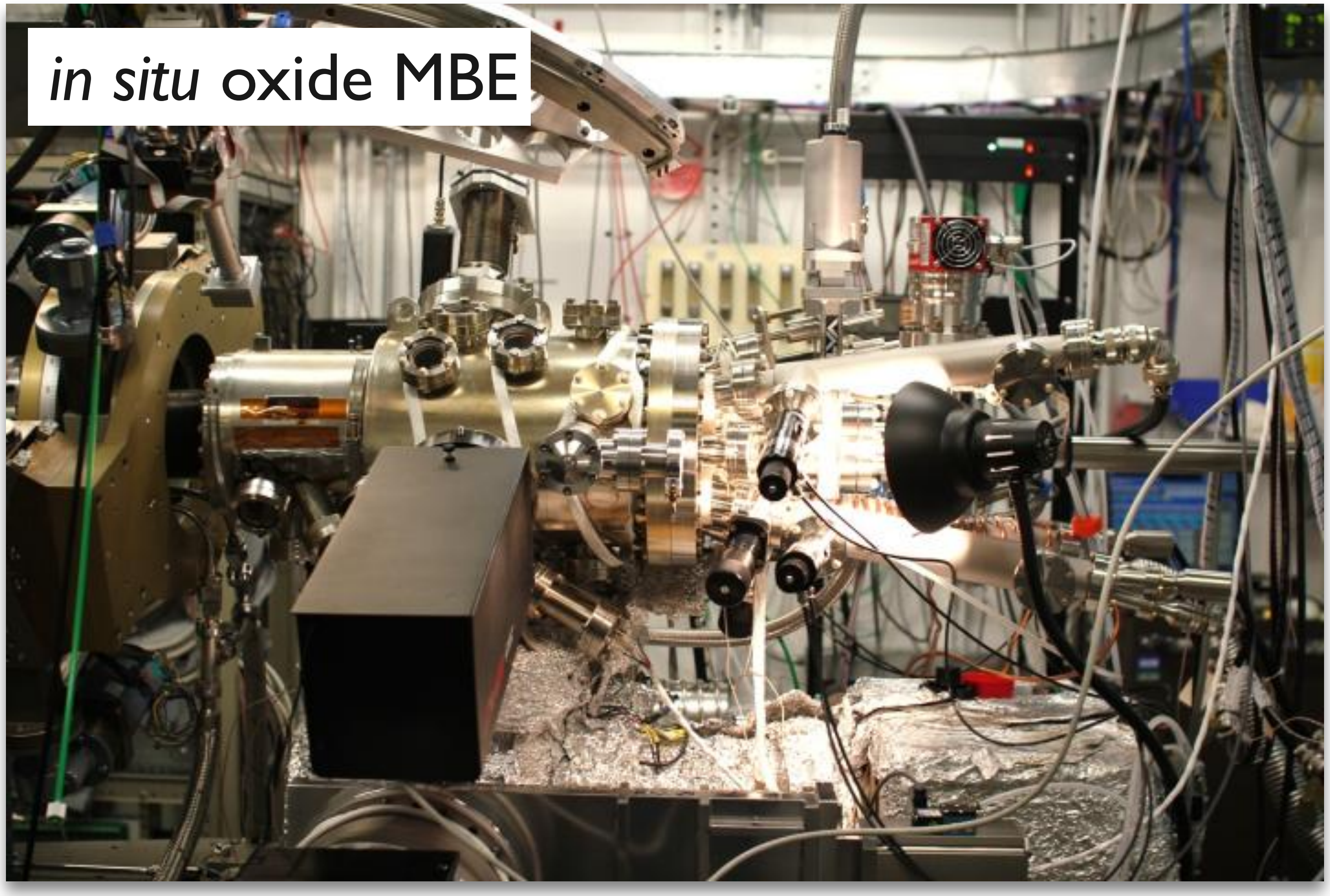
origin of reciprocal space

(a)
real space

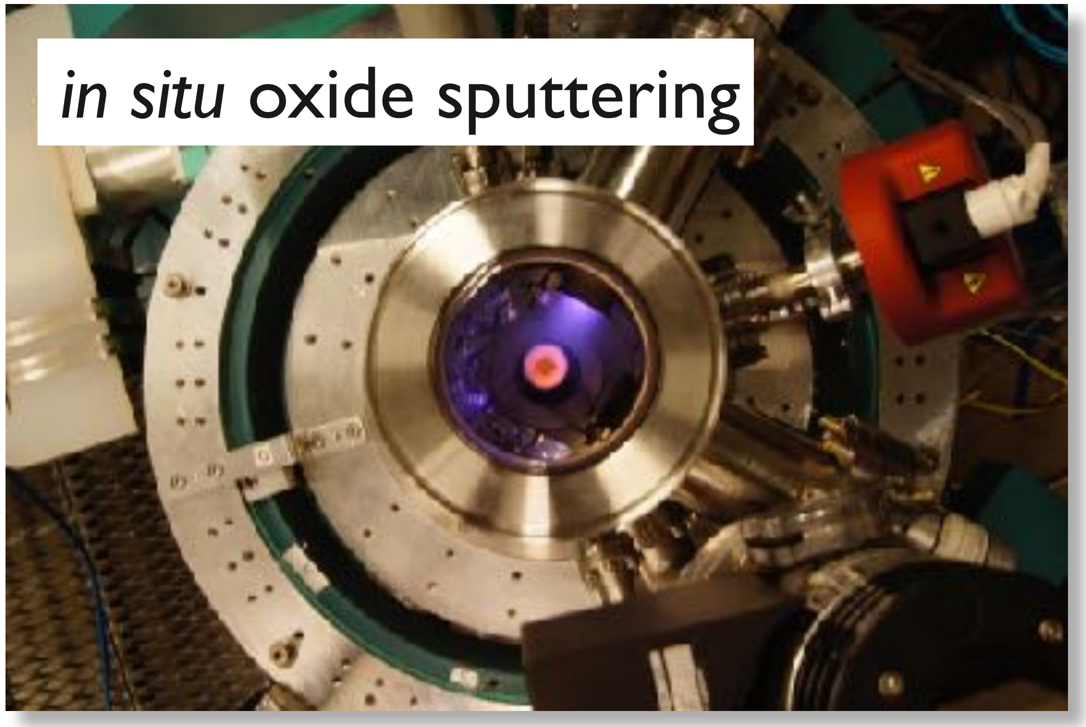
(b)
reciprocal space

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

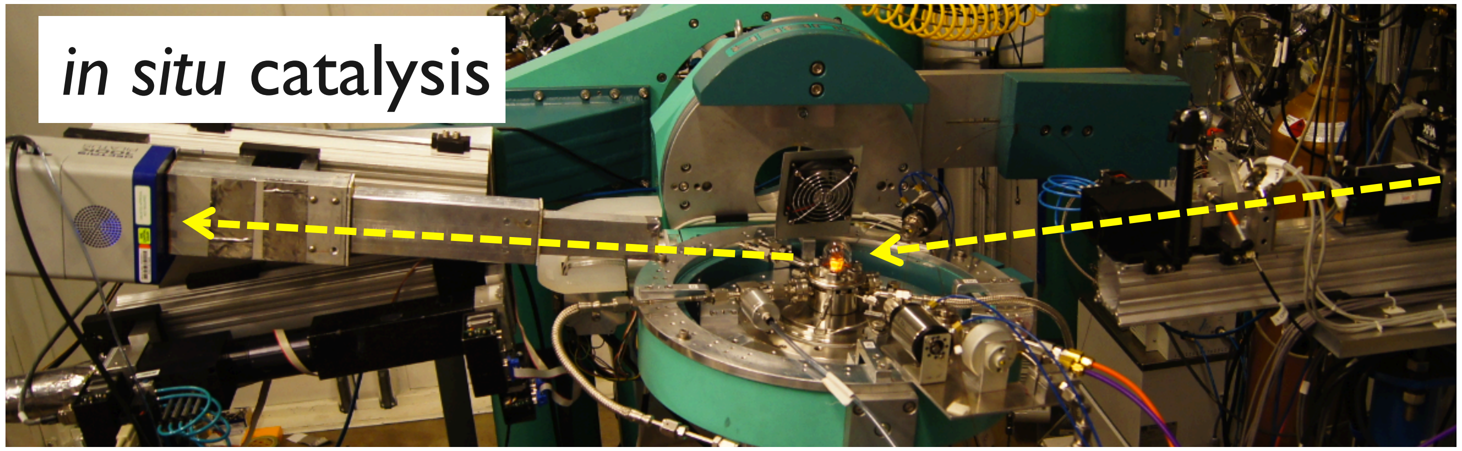
SXRD geometry + a lot of equipment



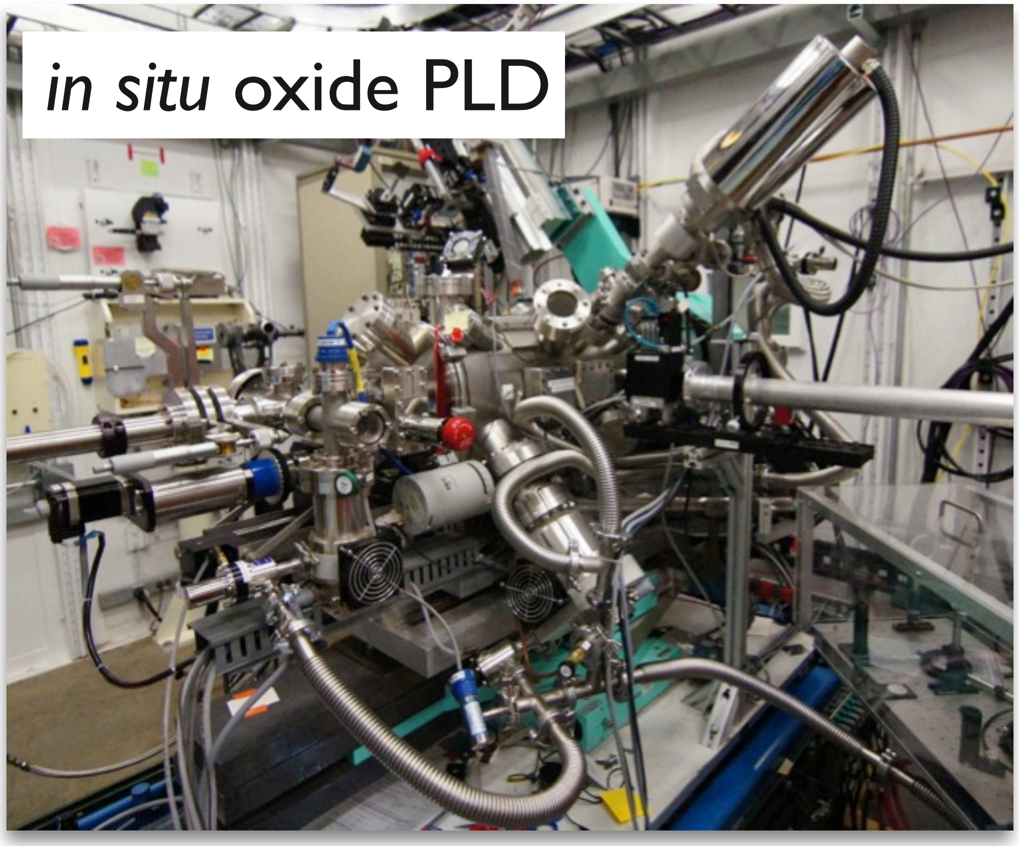
in situ oxide MBE



in situ oxide sputtering



in situ catalysis



in situ oxide PLD

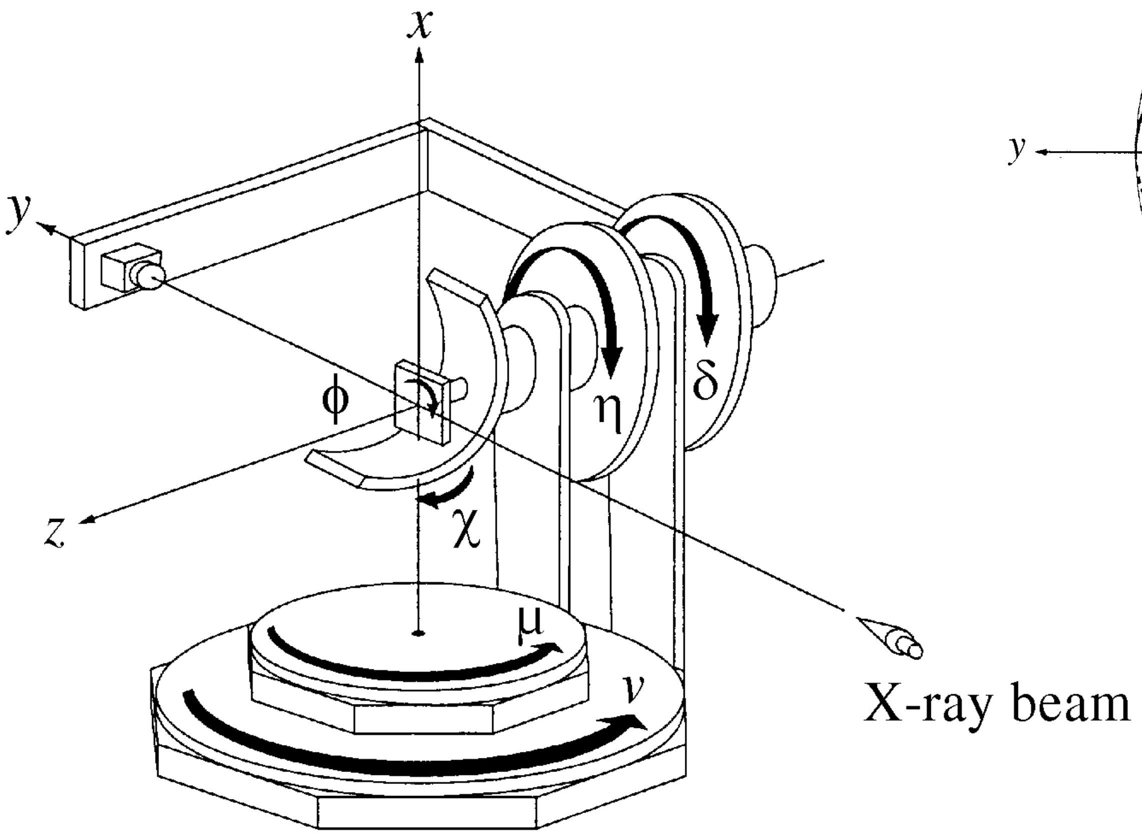
- Can do a lot by combining SXRD + *in situ*
- Need to have the proper geometry

Six-circle geometry (4S+2D)

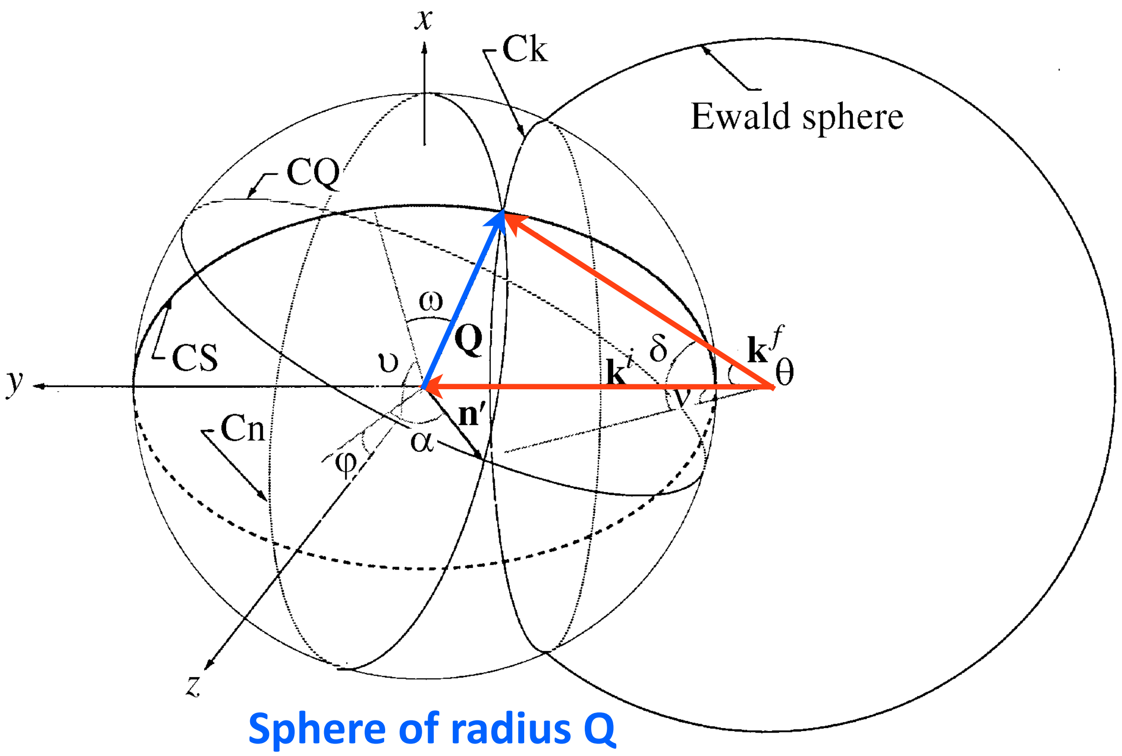
Note the laboratory coordinate system (x,y,z)

Q is defined by

- θ = ω = Bragg angle of Q (=4πsin(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 **k$_f$** to (x, y, z) [2D]

Next, by definition: at diffraction condition: **h** = **k$_f$** - **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 $\mathbf{Q}_L = \mathbf{k}_\nu^f - \mathbf{k}_L^i = (\mathbf{\Pi\Delta} - \mathbf{I})\begin{pmatrix} 0 \\ k \\ 0 \end{pmatrix} = k\begin{pmatrix} \sin\delta \\ \cos\delta\cos\nu - 1 \\ \cos\delta\sin\nu \end{pmatrix},$

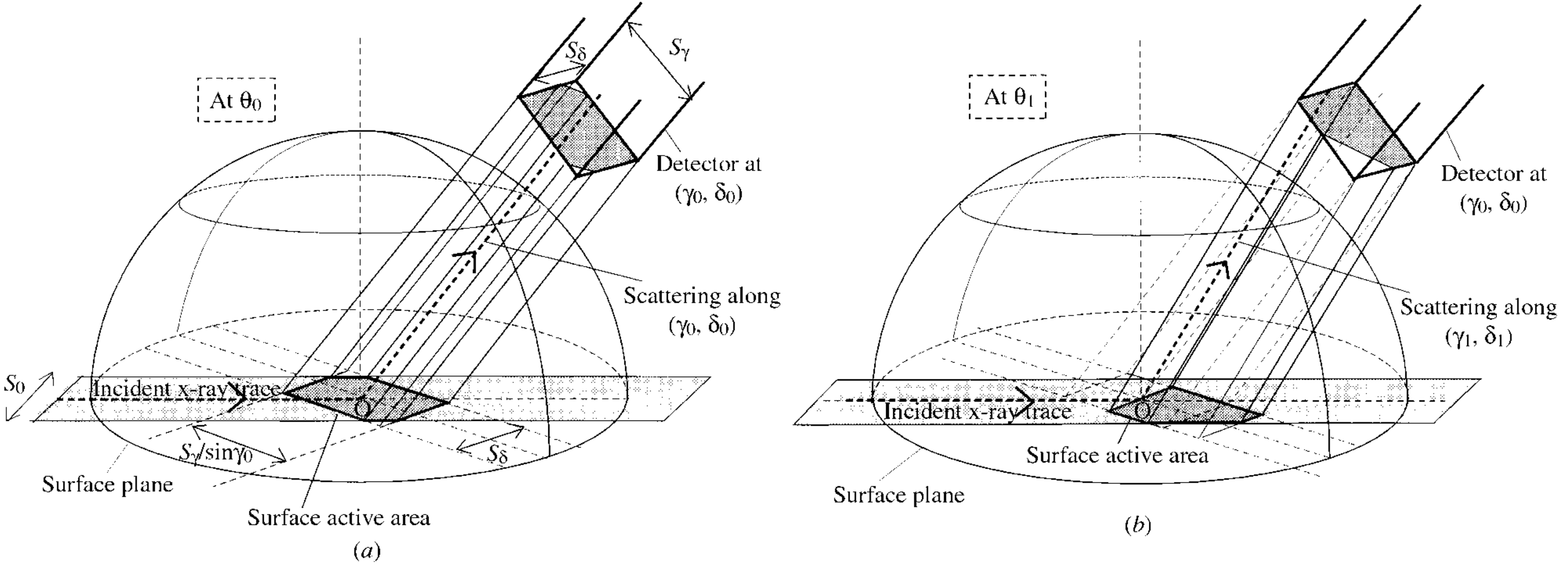
Six-circle geometry

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* ~ 0 work
- nice for easier geometrical corrections



(*a*) (*b*)

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

Geometrical corrections

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

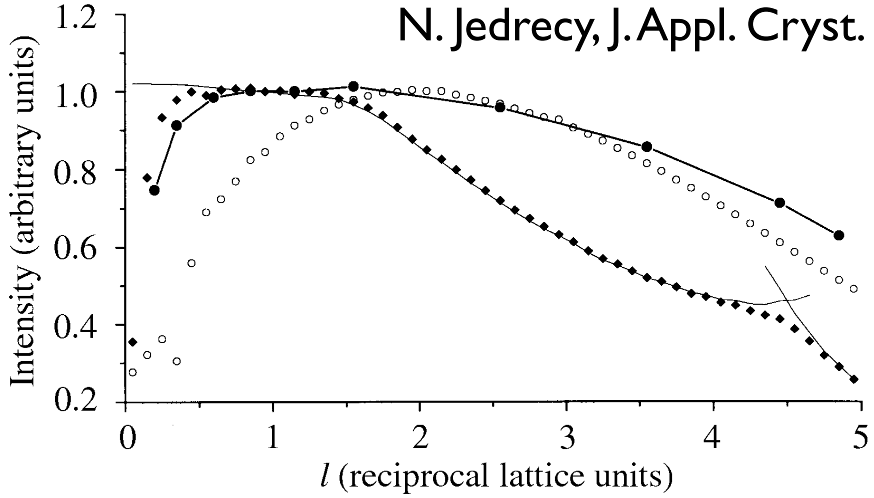
- Corrected integrated intensity

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

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

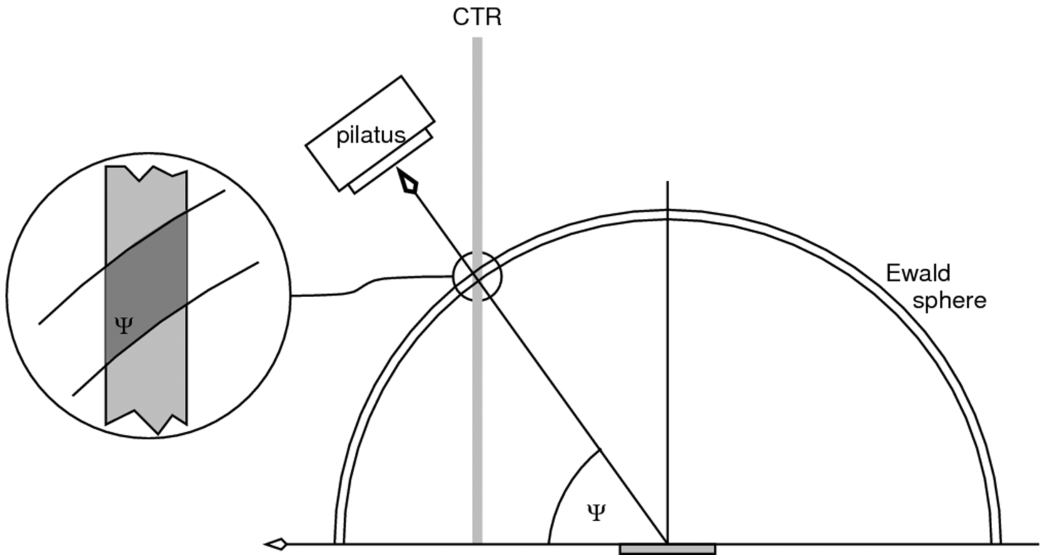
$$C_{\text{tot}} = P L_\varphi C_{\text{rod}} C_{\text{area}} C_{\text{det}} C_{\text{beam}}.$$

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

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

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

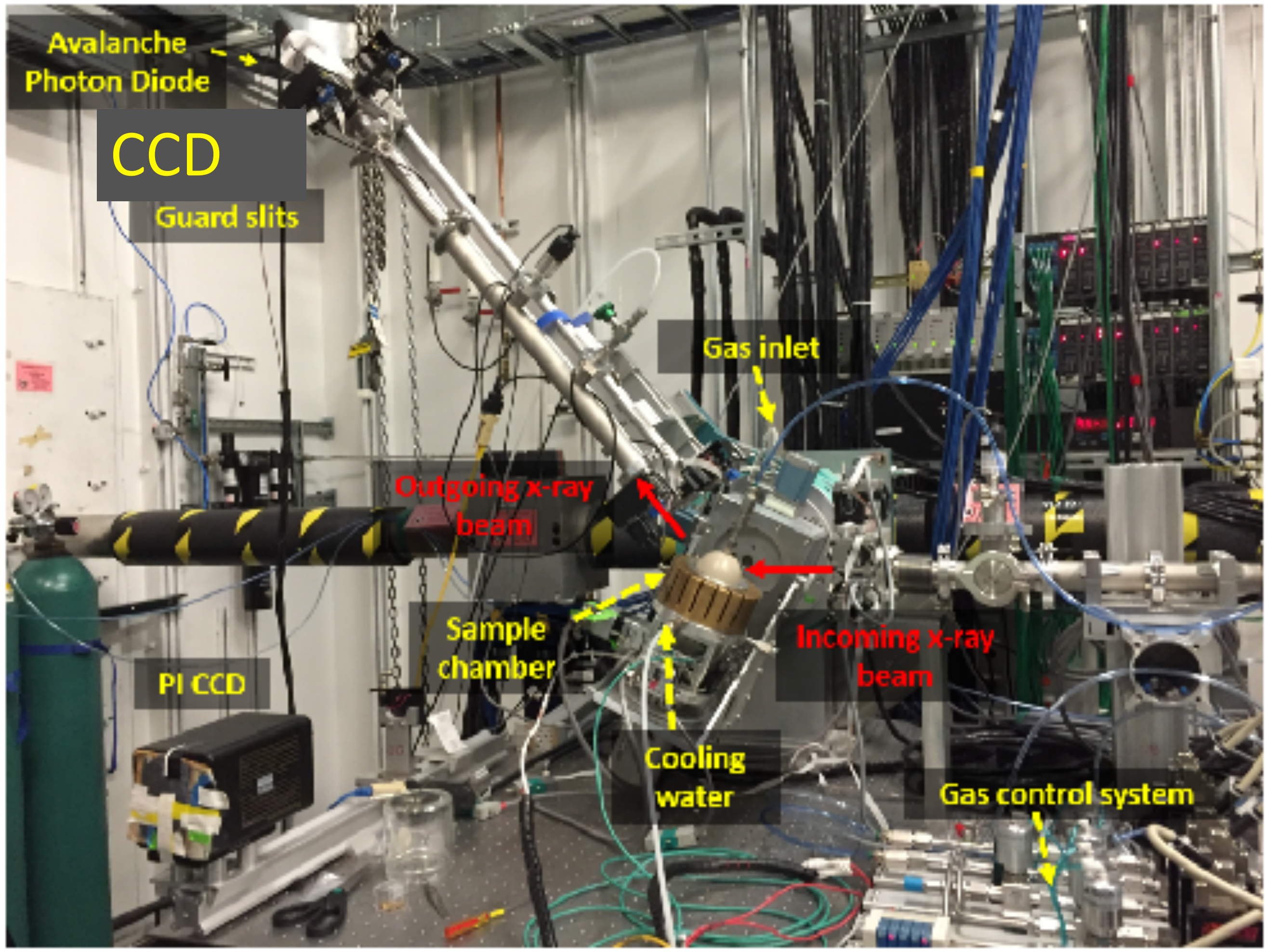
vertical sample

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

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

Example of SXRD + X-ray photon correlation spectroscopy

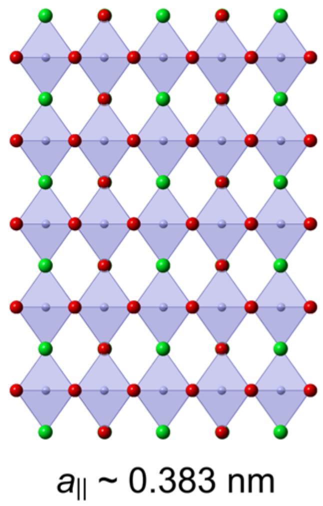
In situ SXRD with gas control system ($N_2 \leftrightarrow O_2$, *T*)



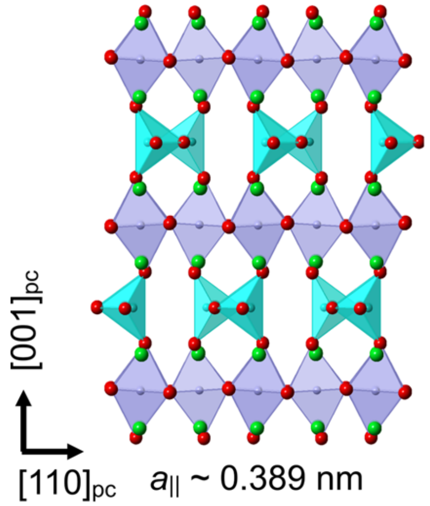
APS, Sector 8

$N_2 \leftrightarrow O_2$

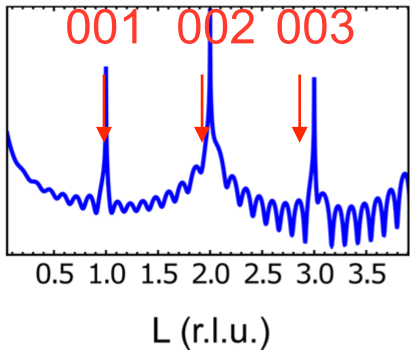
$SrCo^{4+}O_3$



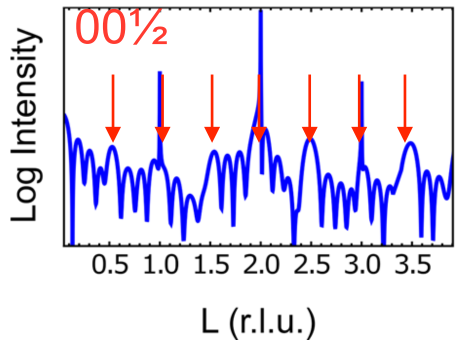
$SrCo^{3+}O_{2.5}$



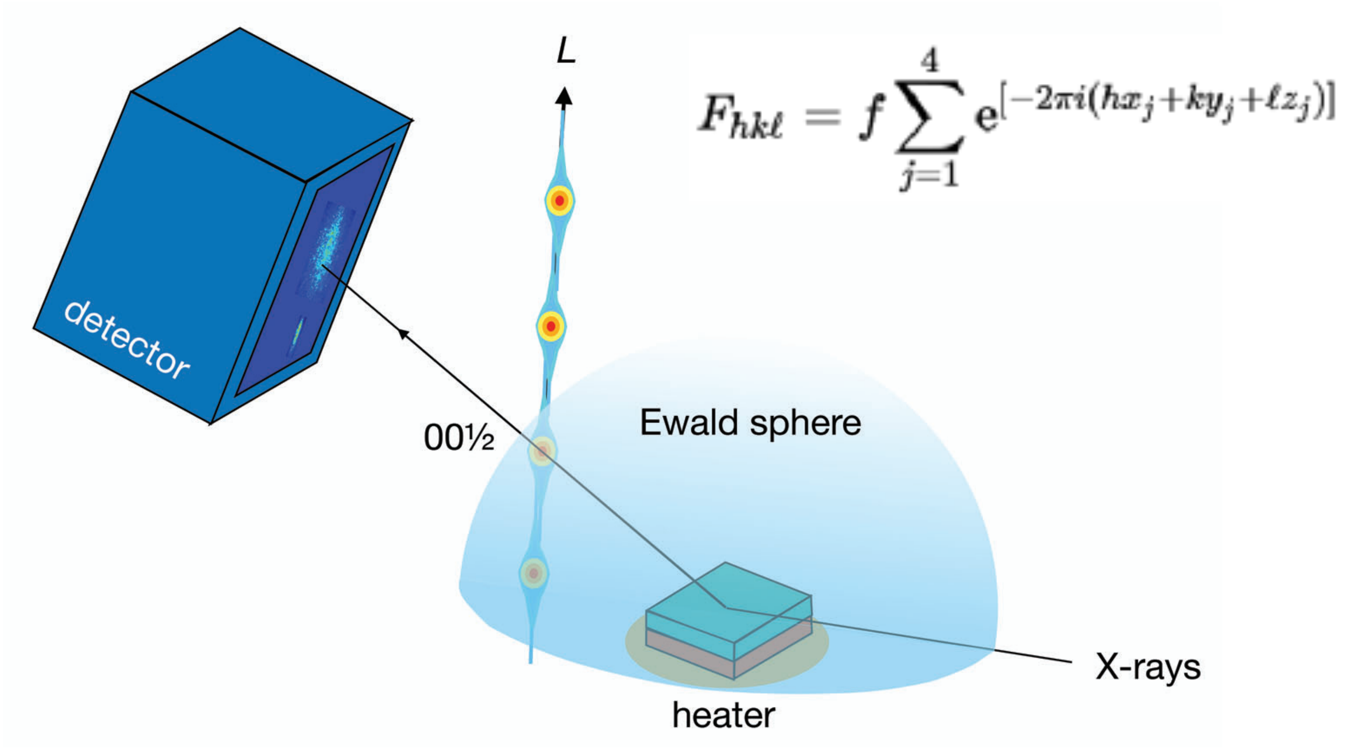
$SrCoO_3$



$SrCoO_{2.5}$

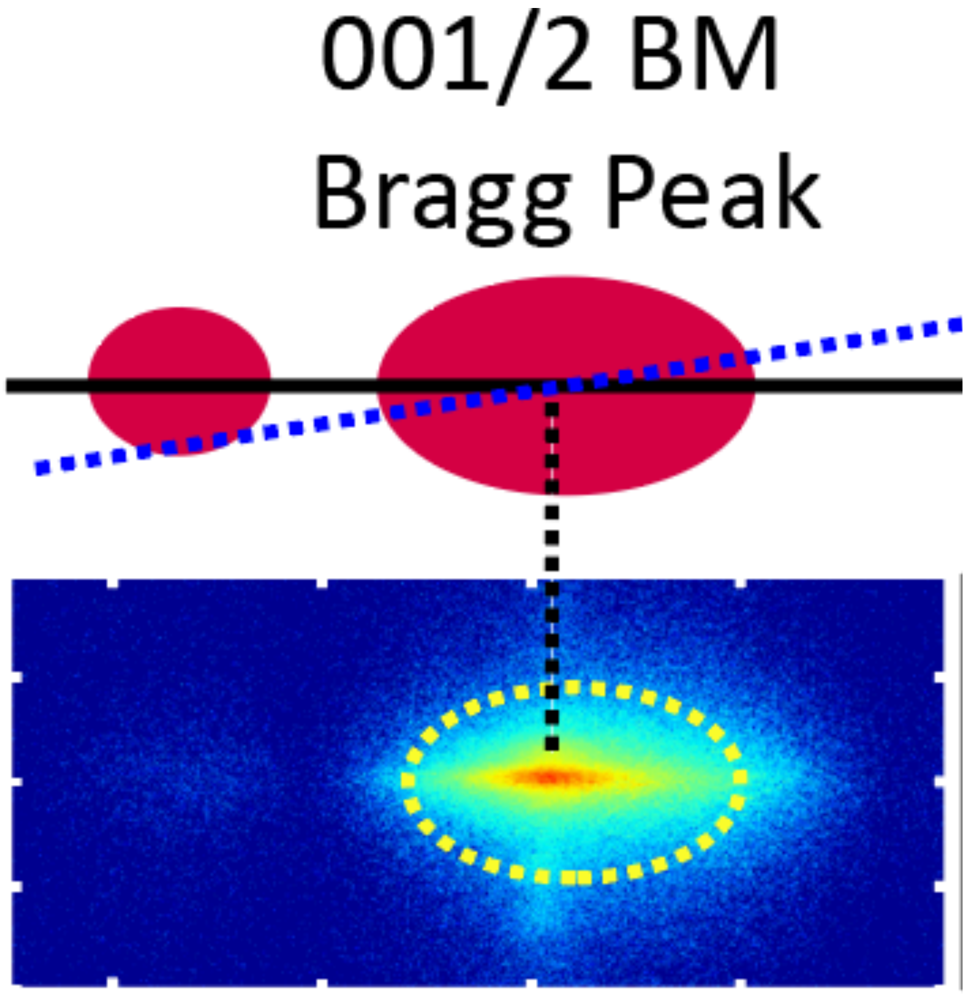


Time-dependent speckle reveals dynamics

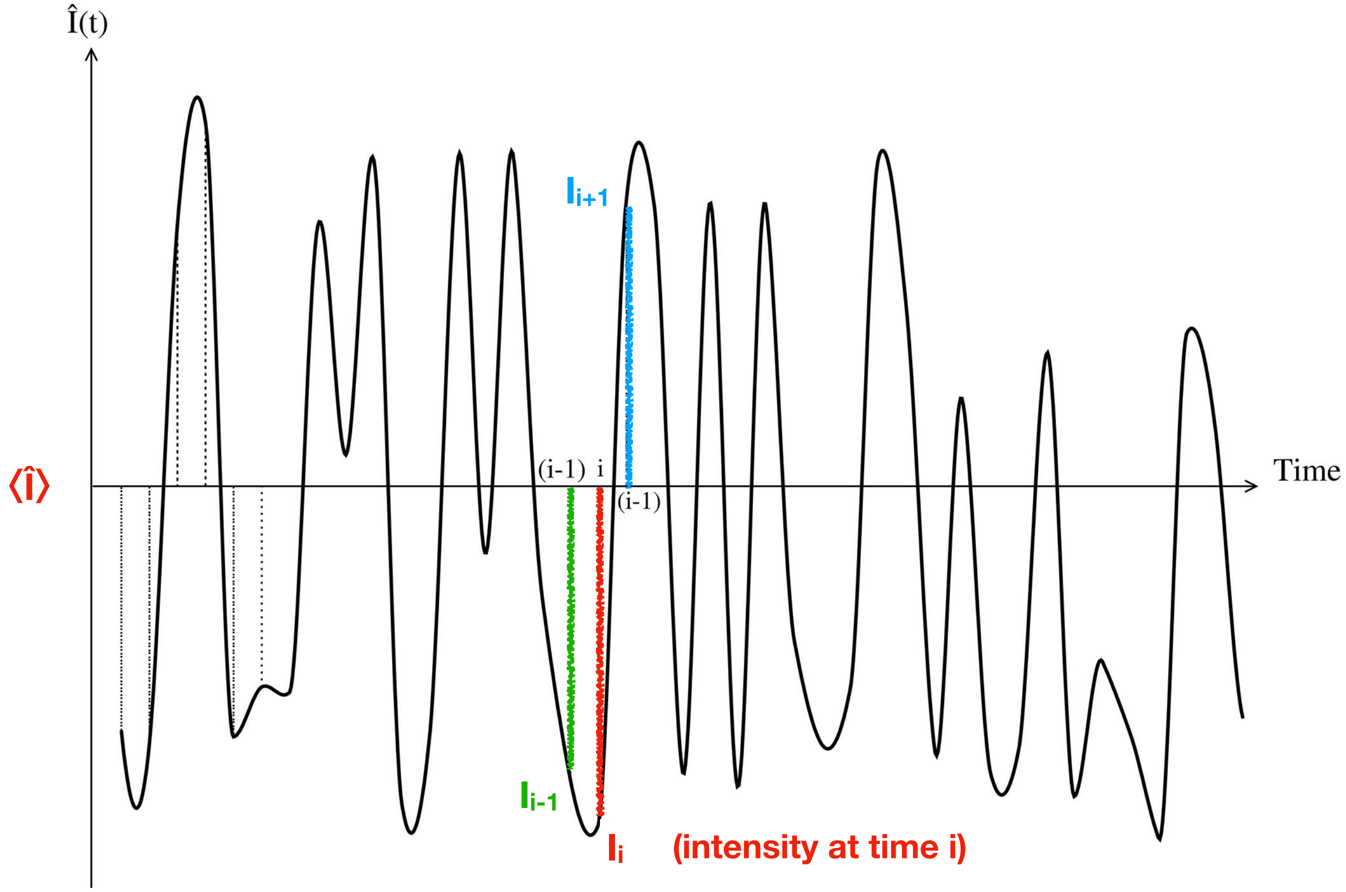


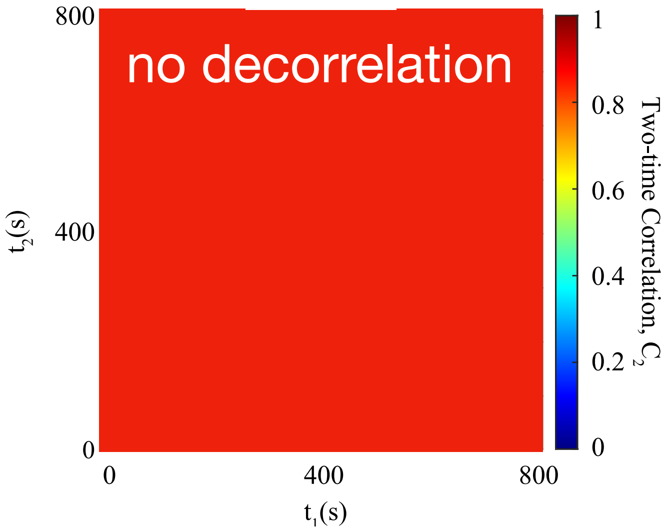
$$F_{hk\ell} = f\sum_{j=1}^{4} \mathrm{e}^{[-2\pi i(hx_j+ky_j+\ell z_j)]}$$

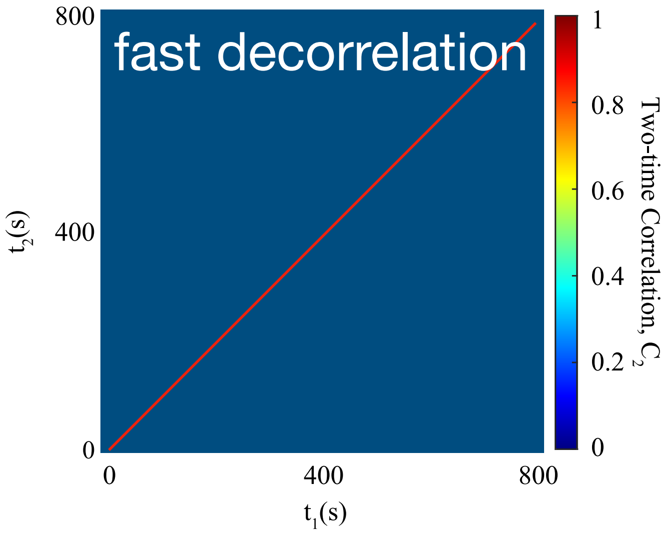
J. K. Wenderott et al. Adv. Mater. Int. 2300127 (2023)



Dynamics and time correlations (at any **Q**)





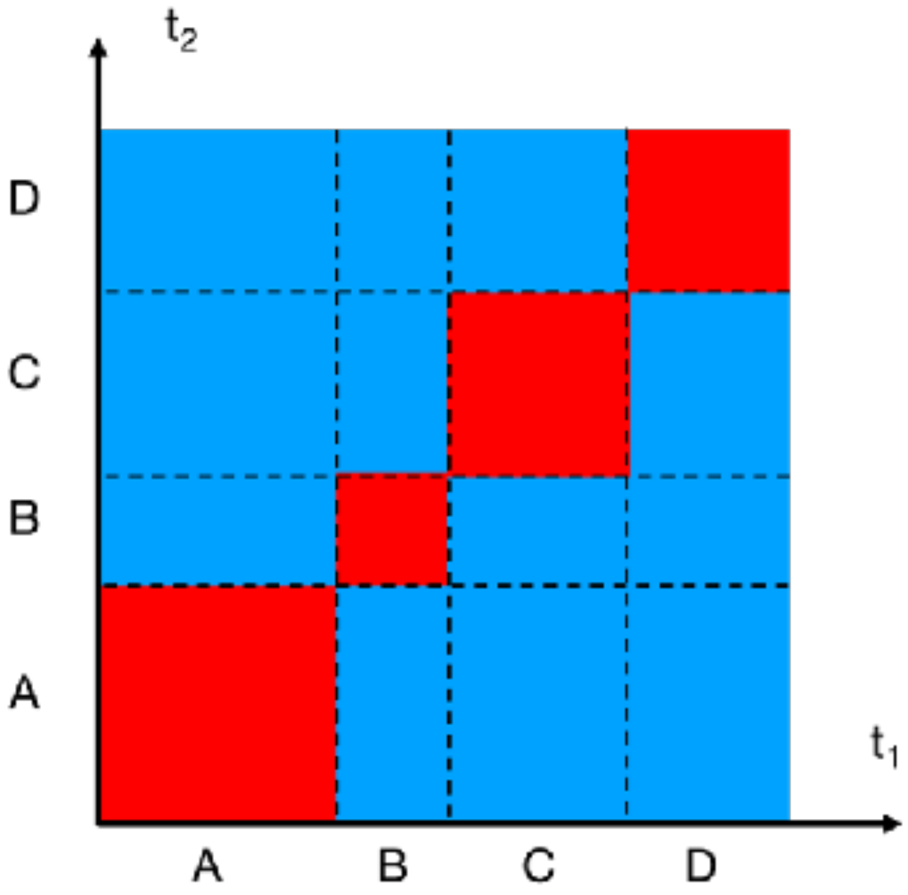


Two-time correlation function (C_2) at **Q**:

$$C_{m,n}(t_1, t_2)\left(\frac{I_{m,n}(t_1)-I^{inc}_{m,n}}{I^{inc}_{m,n}}\right)\left(\frac{I_{m,n}(t_2)-I^{inc}_{m,n}}{I^{inc}_{m,n}}\right)\rangle_q$$

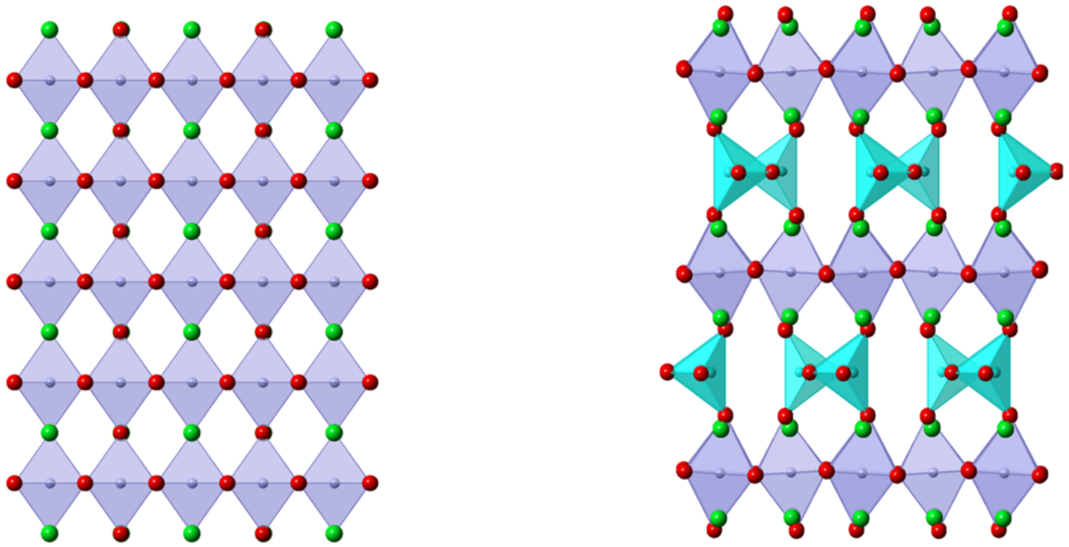
O. Bikondoa, J. Appl. Cryst. **50,** 357 (2017)

Dynamics and time correlations (at any **Q**)



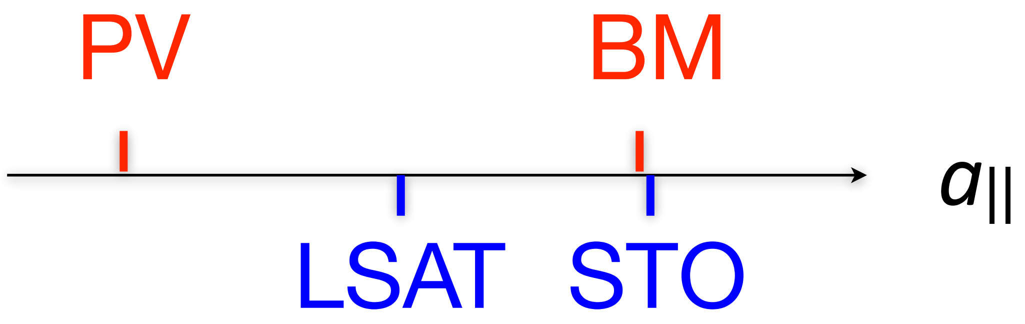
state of material varies from A to B to C to D

$SrCoO_x$/LSAT (001) phase equilibrium



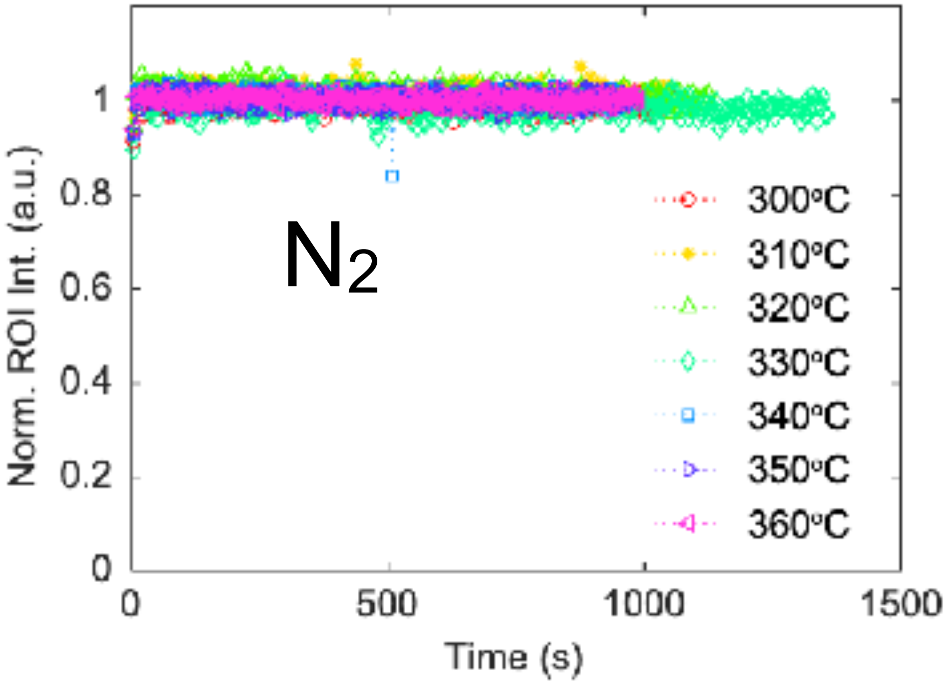
$SrCo^{4+}O_3$ — $a_{||}$ ~ 0.383 nm

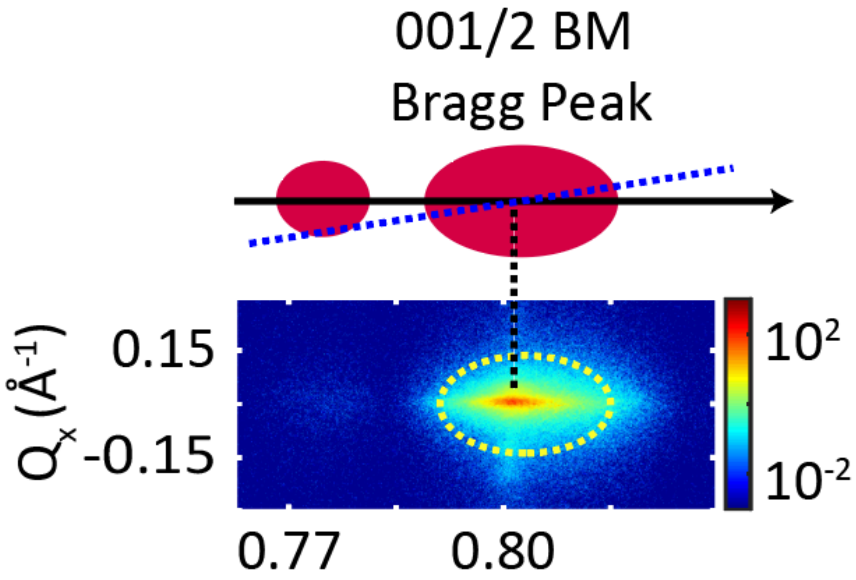
$SrCo^{3+}O_{2.5}$ — $a_{||}$ ~ 0.389 nm



$SrCoO_x$/LSAT (001): Kinetics in N_2

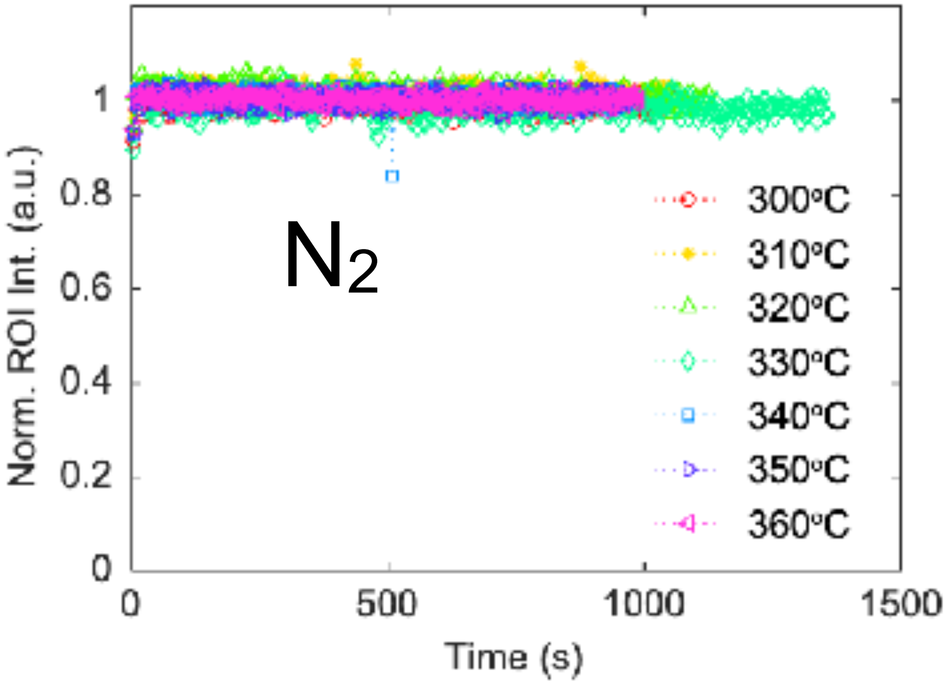
Intensity of 00½: stable with time



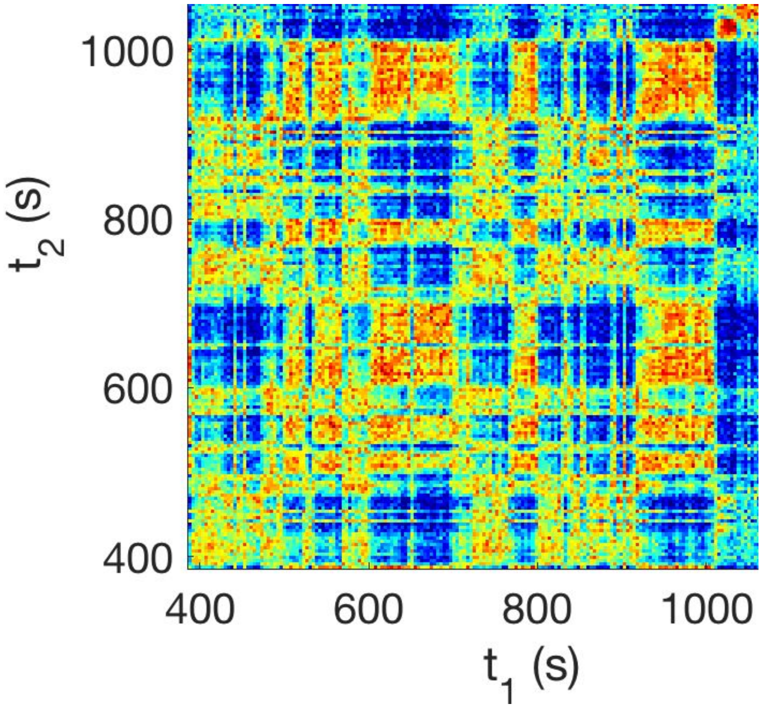


$SrCoO_x$/LSAT (001): Dynamics in N_2

Intensity of 00½: stable with time

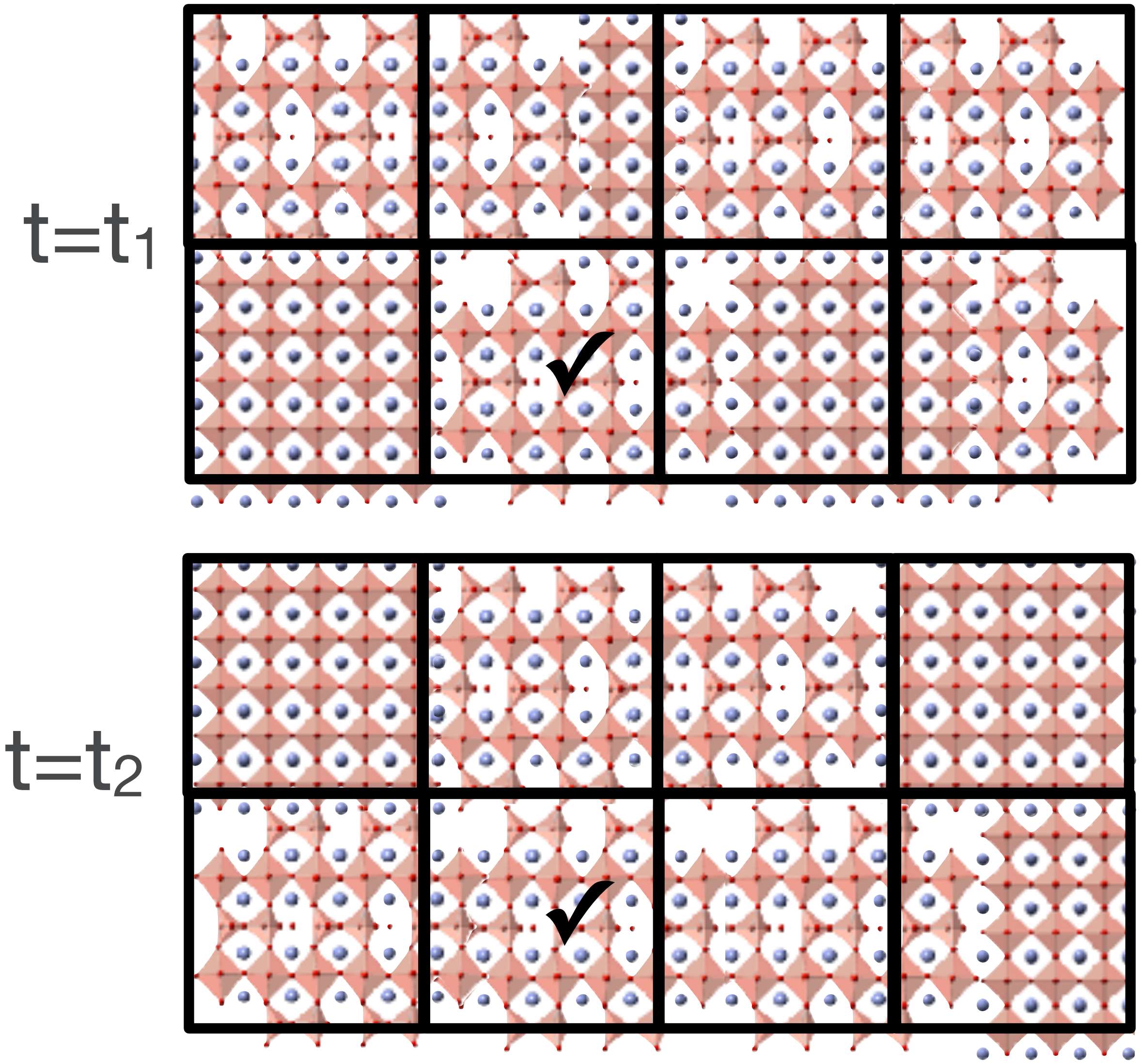


Dynamics of 00½: fluctuating with time



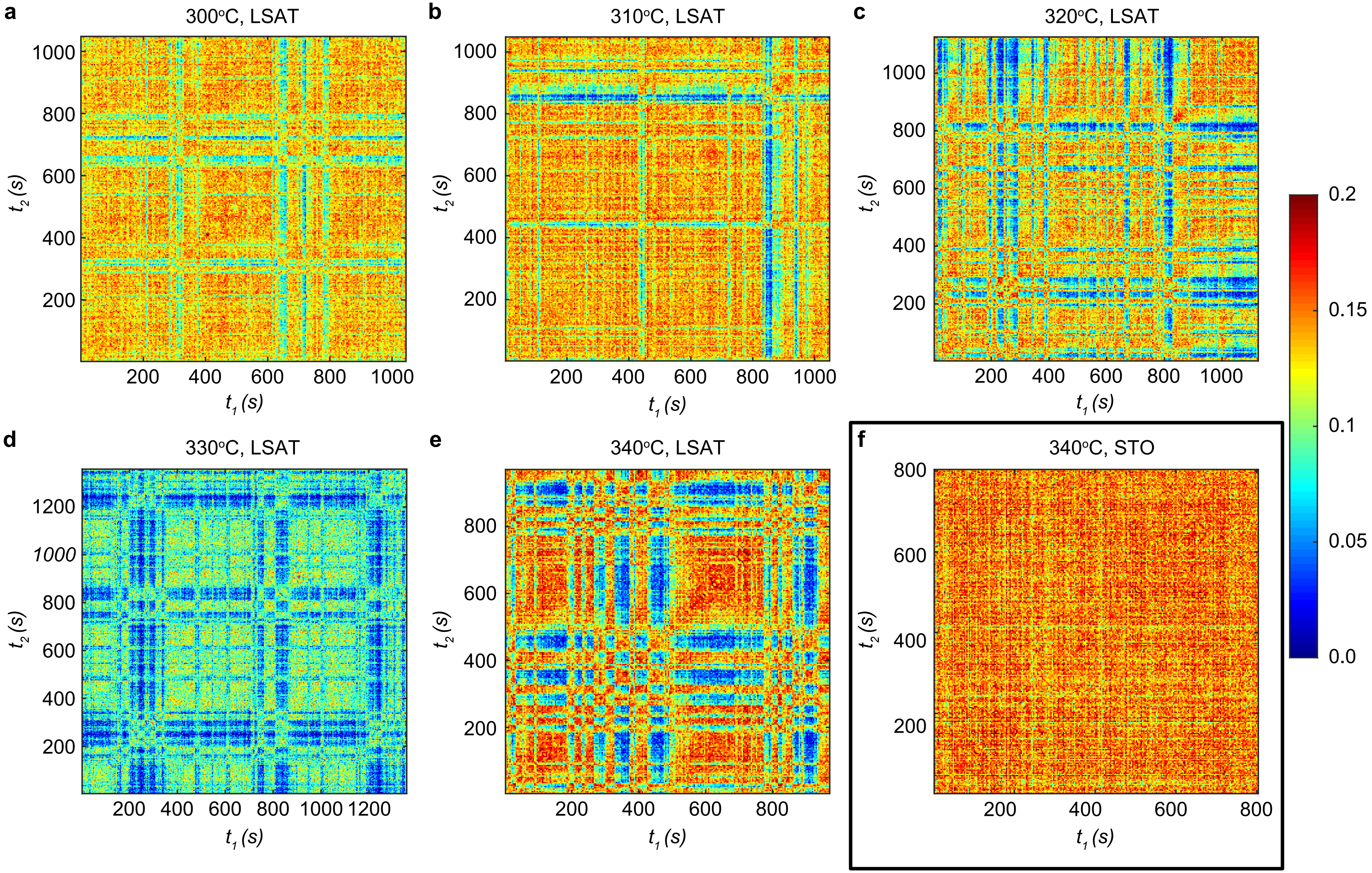
N_2 at 350°C

Real space: vacancy fluctuations at 350°C



partially correlated in time

Temperature dependence



Questions?

https://forms.office.com/g/MdYE7snFqs

NXS Lecture - Dillon Fong:
"Surface and Interface Scattering"

https://forms.office.com/g/MdYE7snFqs