Static Surface Structure

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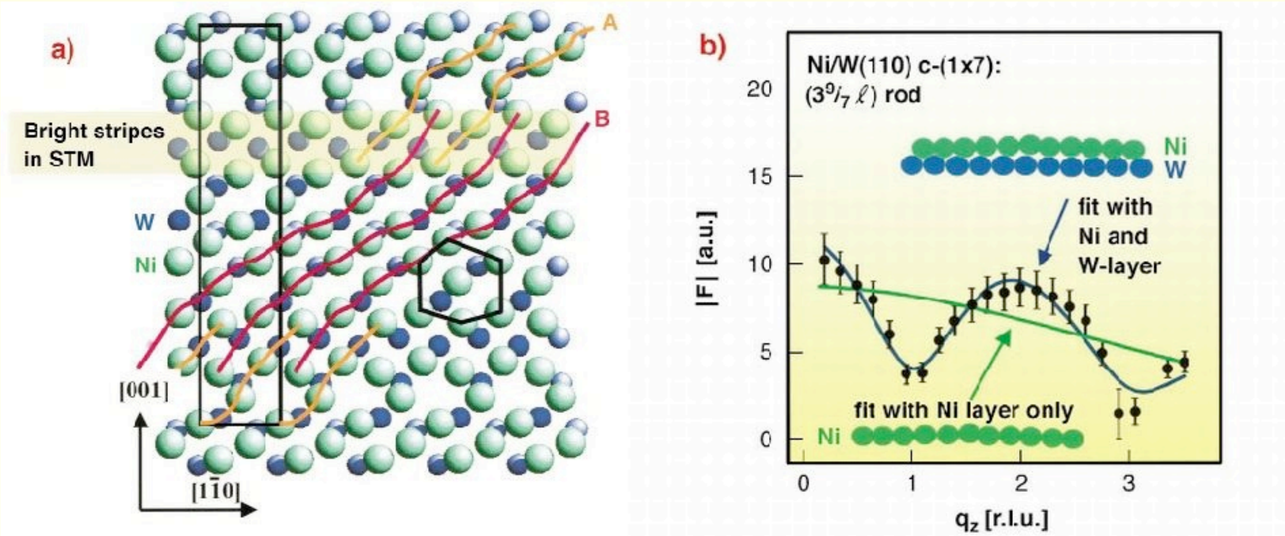
- Science on “static” structures
- Data acquisition/reduction/analysis needs for complex surfaces

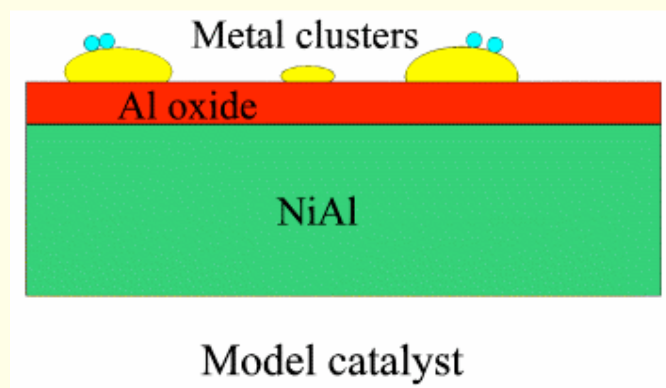


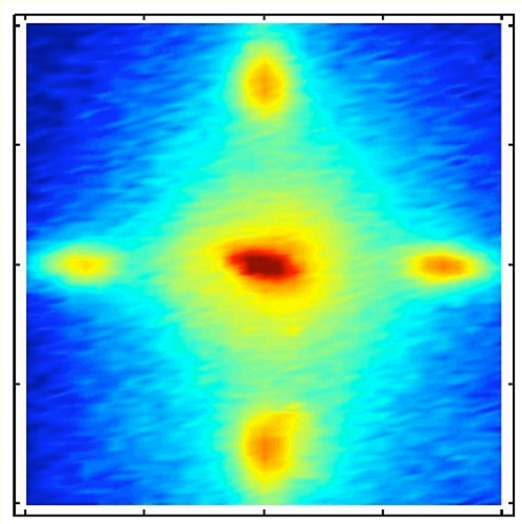
Meyerheim (MPI-Halle)

Surface magnetic systems

Stierle (MPI-Stuttgart)

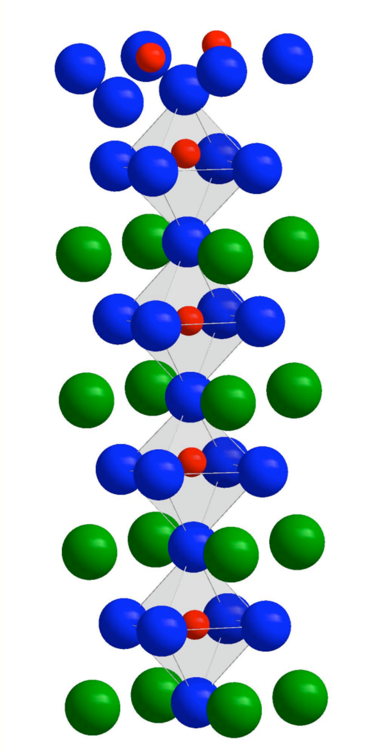
Oxide Catalysts





Stephenson et al. (APS)

Striped domain in ultrathin ferroelectrics ($PbTiO_3$)

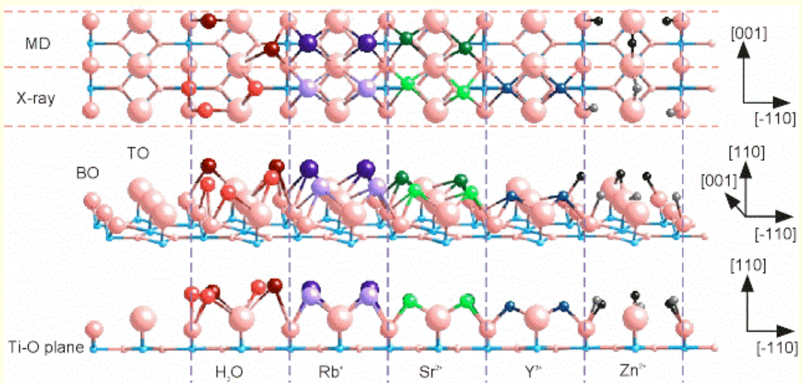


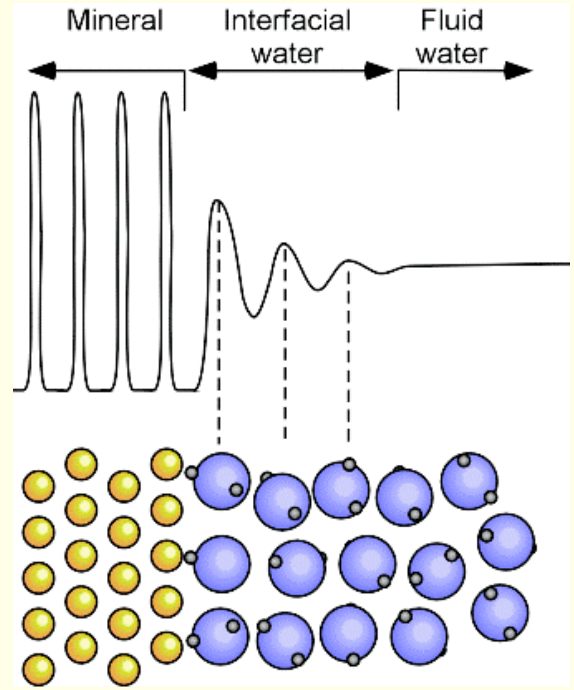
Willmott et al. (SLS)

Complex surfaces of perovskites ($SrTiO_3$)

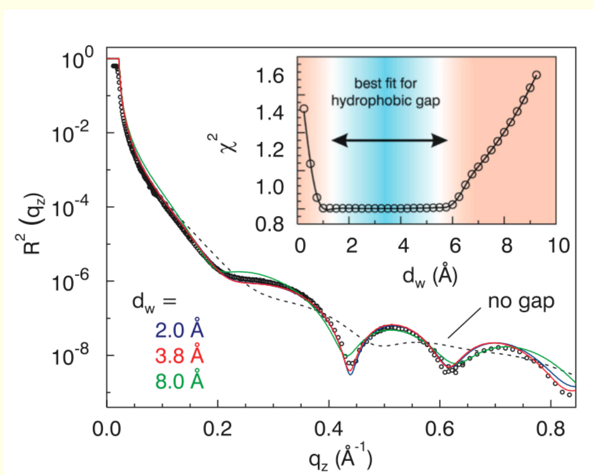
Fenter (ANL) water/mineral interface;

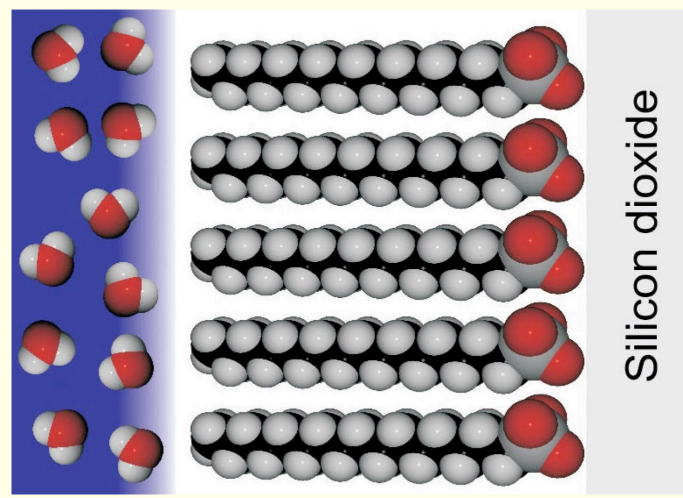
Ordering in water; Electrical double layer

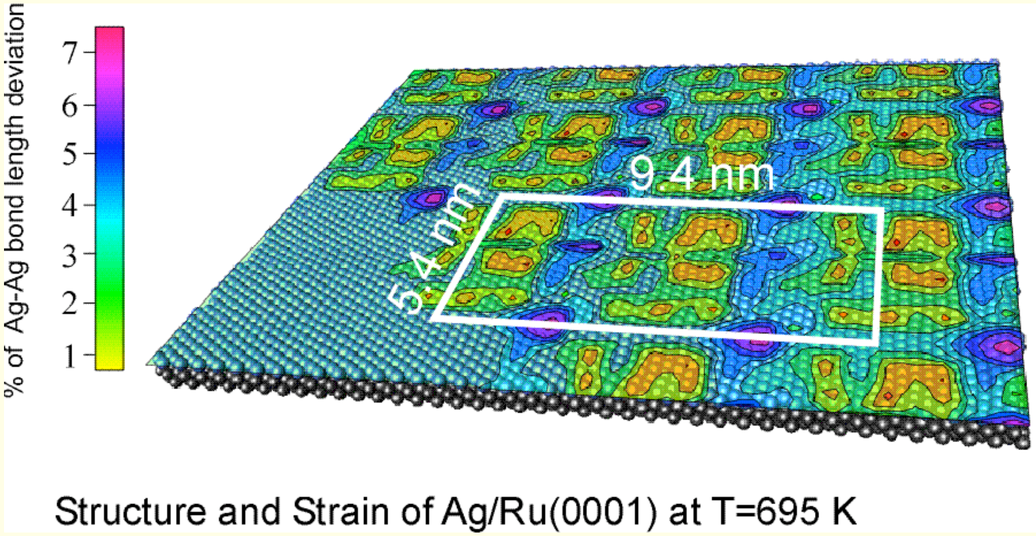




Reichert (MPI-Stuttgart) oil/wate interface (hydrophobicity)



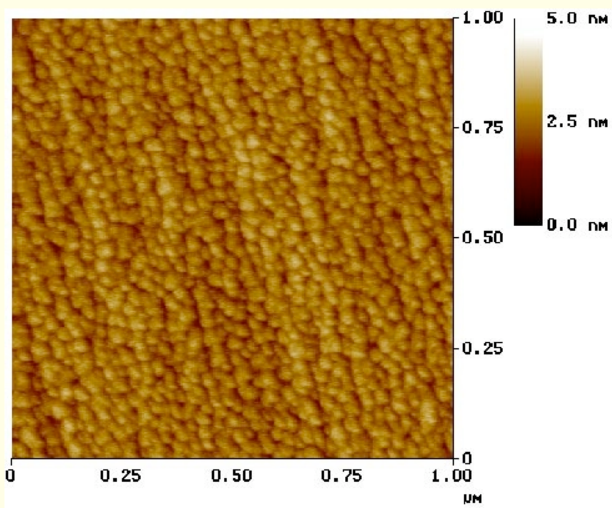


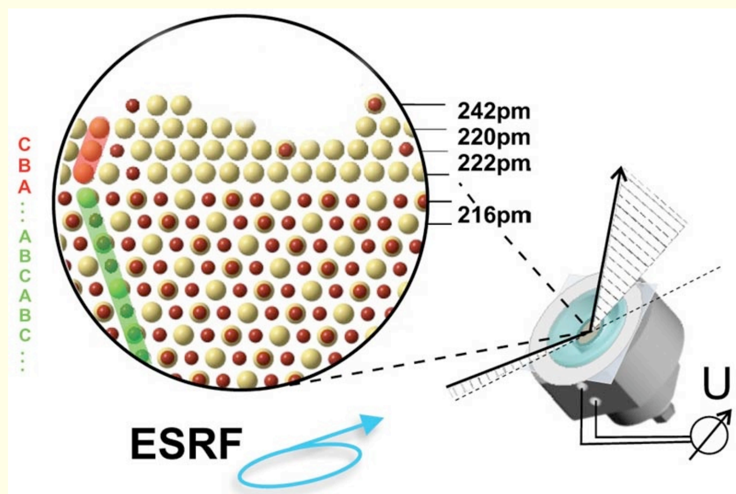


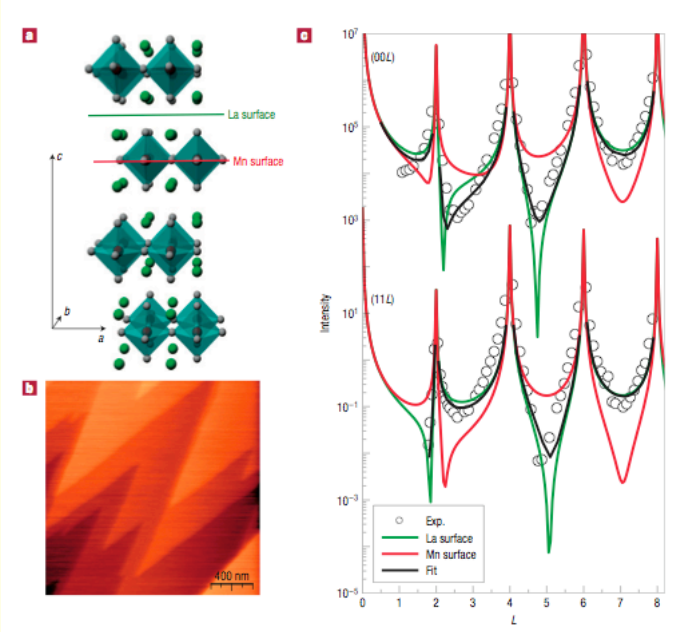
Keller (né Zajonz) (MPI-Stuttgart)

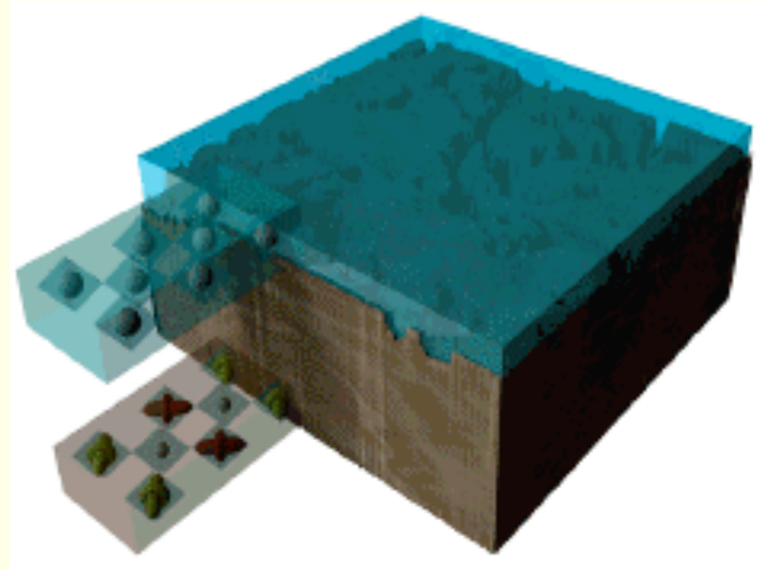
strain in nanostructured layers

Renner (ESRF/MPI-Stuttgart)
Corrosion-induced nanostructures



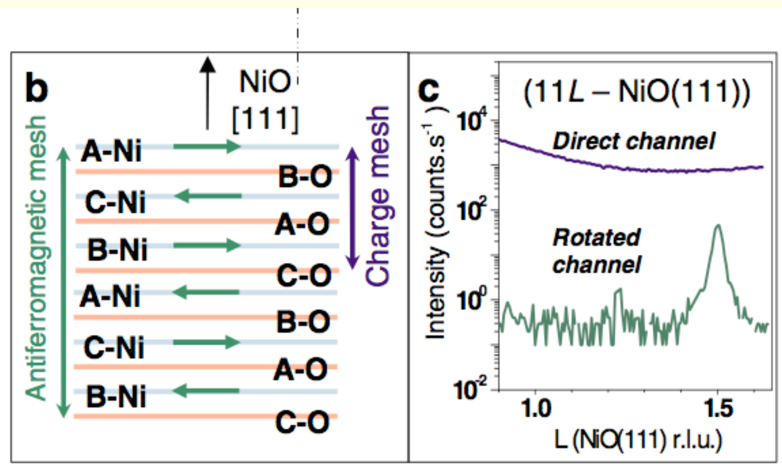




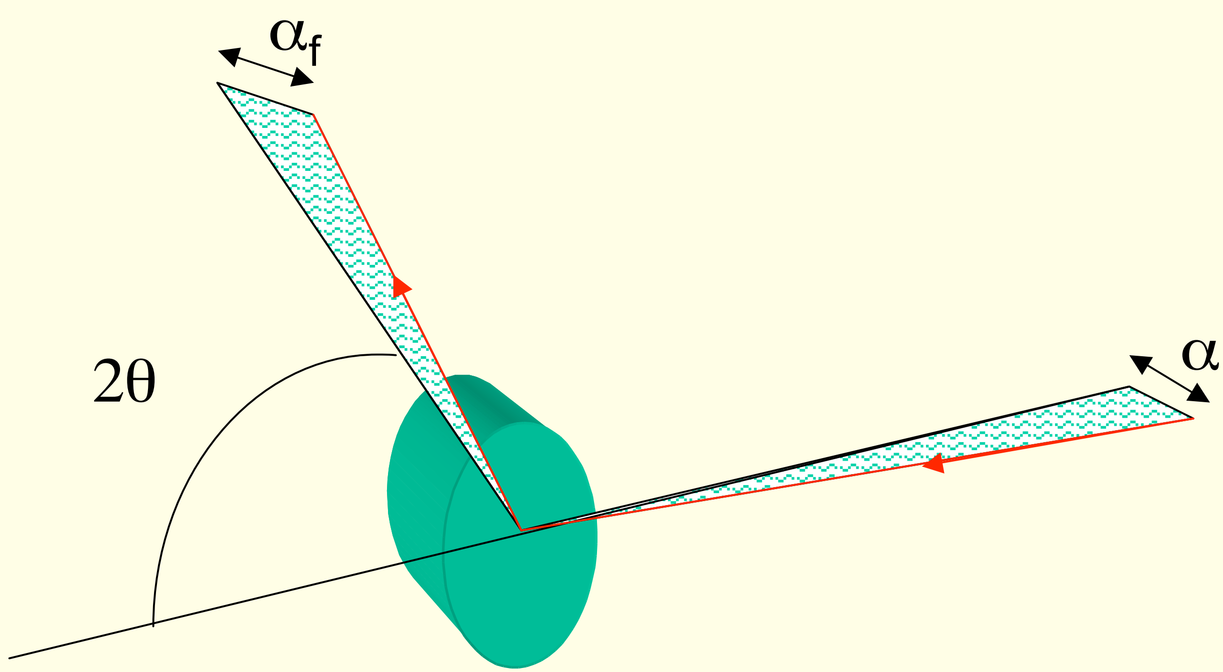


Hill et al. (NSLS-II)
Surface effects on orbital ordering

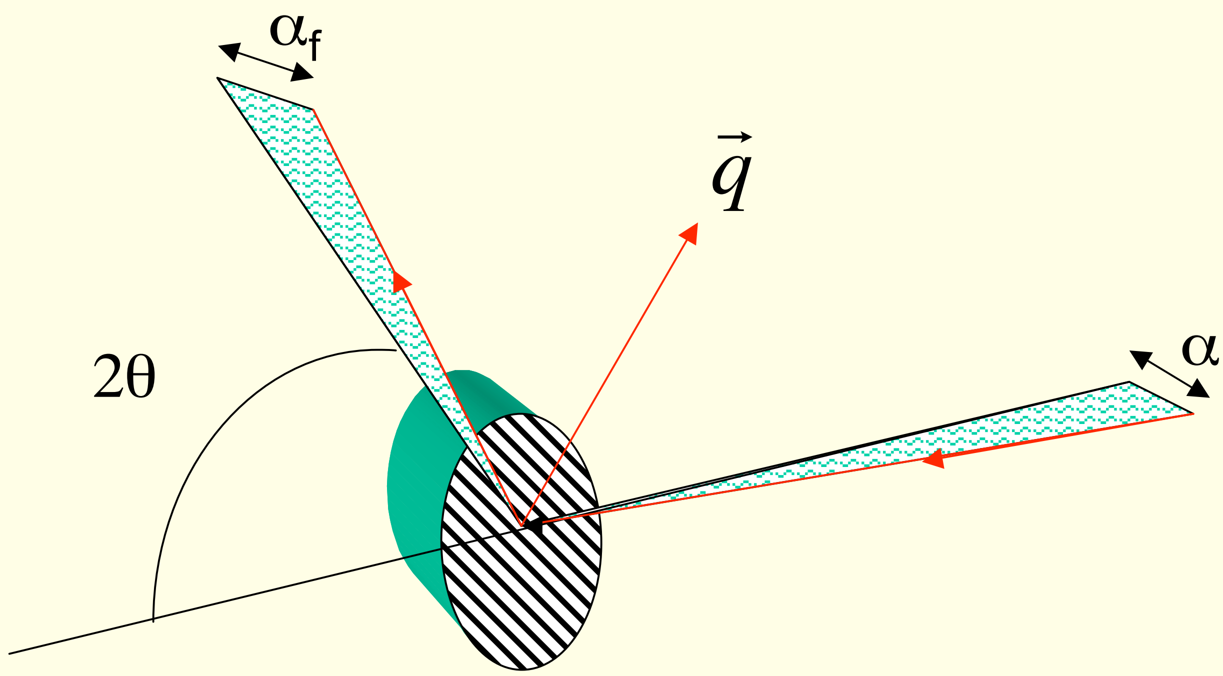
Barbier et al. (ESRF)
Surface magnetism in NiO



SXRD geometry

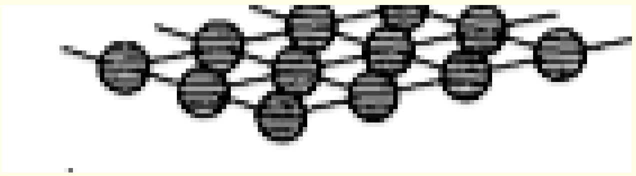


SXRD geometry

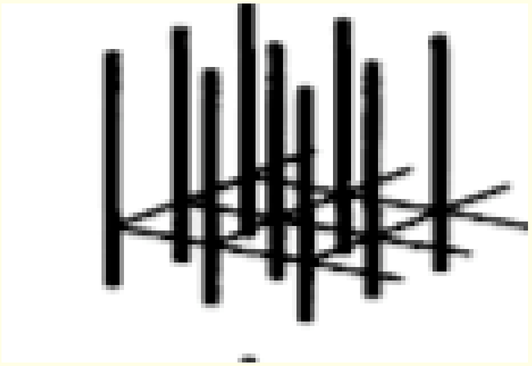


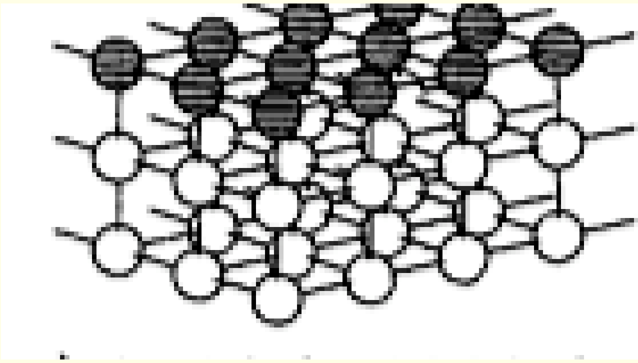
ML and Surface Diffraction

Real Space | Reciprocal Space



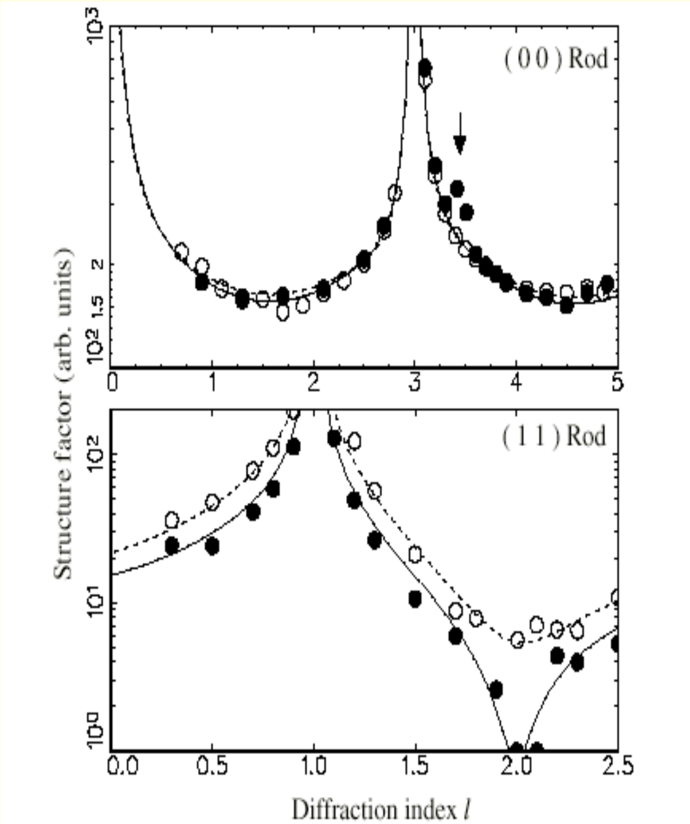
Isolated Monolayer





Surface of Crystal

Typical SXRD Study:



- Acquire *F*'s (in-plane and/or CTR)
- Make intelligent guesses about surface geometry (Patterson map, chemical intuition, other studies.)
- Refine atomic positions (*R*-factor, χ^2)

What is needed for real progress?

Complex surfaces

Consider an (S×T) reconstruction:

- *n*ST atoms (where *n* is # of atoms/bulk unit cell)
- >3*n*ST free parameters
- (Recent study of $SrTiO_3$(001)-(2×2)+(2×1) used 394 free parameters.)
- Want at least ~10*n*ST structure factors

Complex surfaces

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Need speed-up in:

- DATA ACQUISITION and
- ANALYSIS

Data Acquisition

- Source: bright, high-flux, yada yada (NSLS-II)
- Diffractometer: fast motors, stable, settles quickly….
- Detector!!! Large speed-up is possible.

Data Reduction

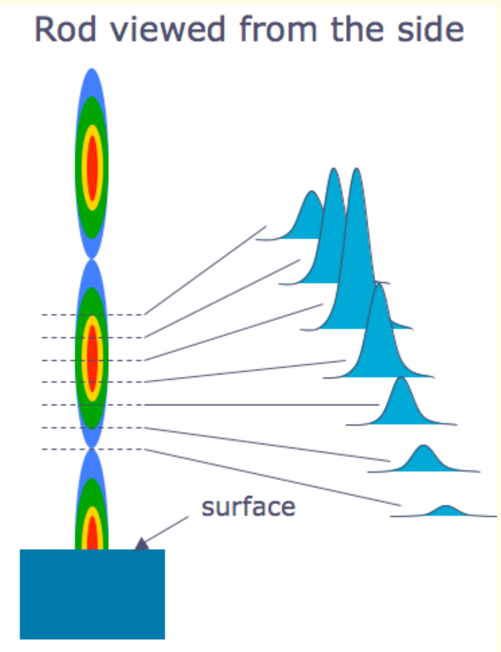
- Better software
- standardization (2-edged sword?)
- on-the-fly

Data Analysis
Complex surfaces

Consider an (SxT) reconstruction:

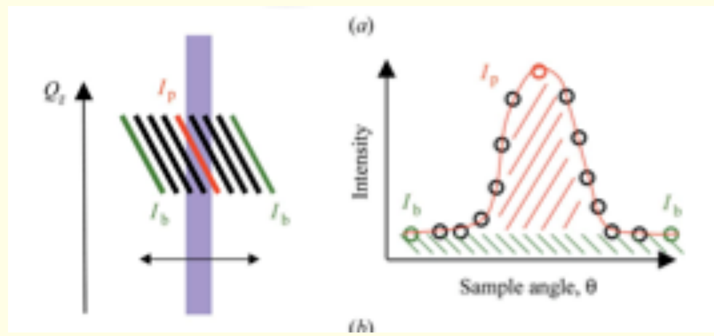
- *n*ST atoms (where *n* is # of atoms/bulk unit cell)
- >3*n*ST free parameters
- (Recent study of $SrTiO_3$(001)-(2x2) used 394 free parameters.)
- Want at least ~10*n*ST structure factors
- Chem. intuition, Patterson fcn. not sufficient
- Grid search: P^{3nST} configurations to be evaluated (where *P* is number of positions/u.c.)
- Even for high-symmetry sites, this gets out of hand.
- Need: direct methods to generate starting models

Data Acquisition



Courtesy of C. Schlepütz (Swiss Light Source)

Scan Mode: φ-scan



Fenter et al., J. Synch. Rad. (2006).

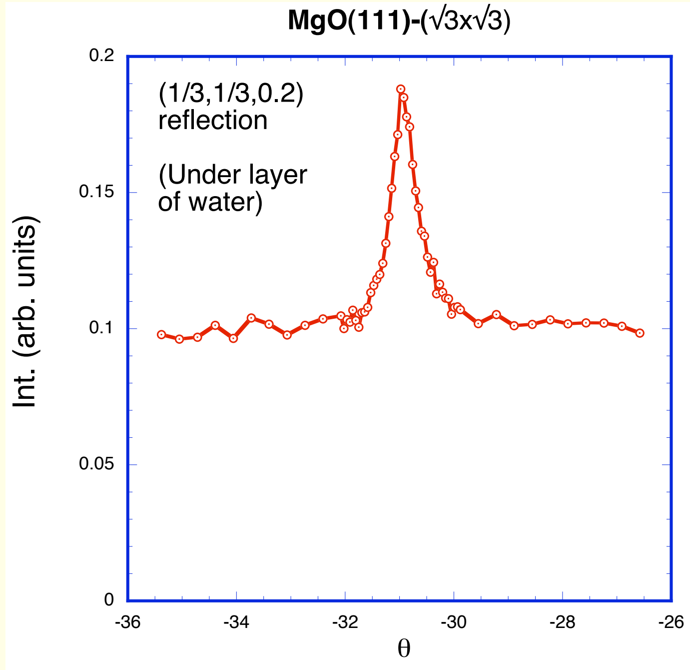
- Record intensity across the rod ("rocking curve") using a "point" detector
- Intensity = ∫ rocking curve

Data Acquisition

Scan Mode: "open slit"

- Specht and Walker
  (J. Appl. Cryst., 1993)
- Record entire diffracted intensity intersecting Ewald sphere
- Envisioned using a "point" detector
- MUCH faster than ϕ-scan (30x)

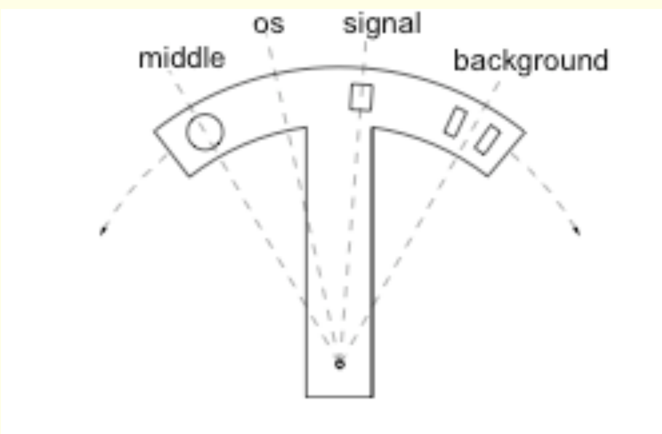
Problem: Background!



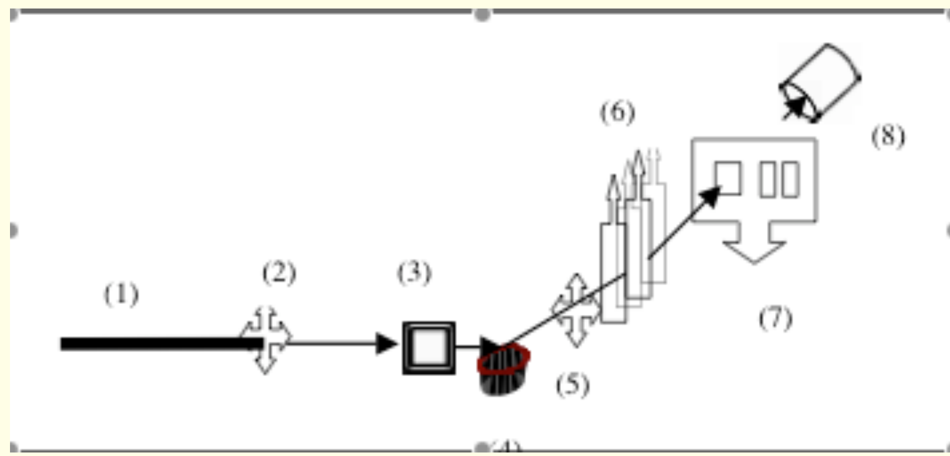
Data Acquisition

Scan Mode: “ridge” or “paddle”

- Record either peak or entire diffracted intensity, and then subtract a measure of the background
- “paddle” implemented at MHATT (APS)



Codrin Cionca (Univ. of Michigan thesis)

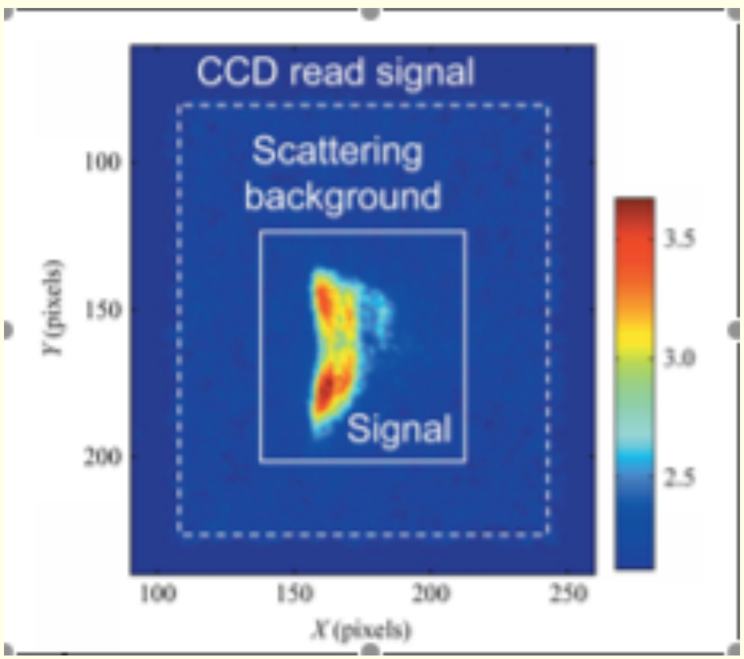


Mukhles Sowwan (Hebrew Univ. thesis)

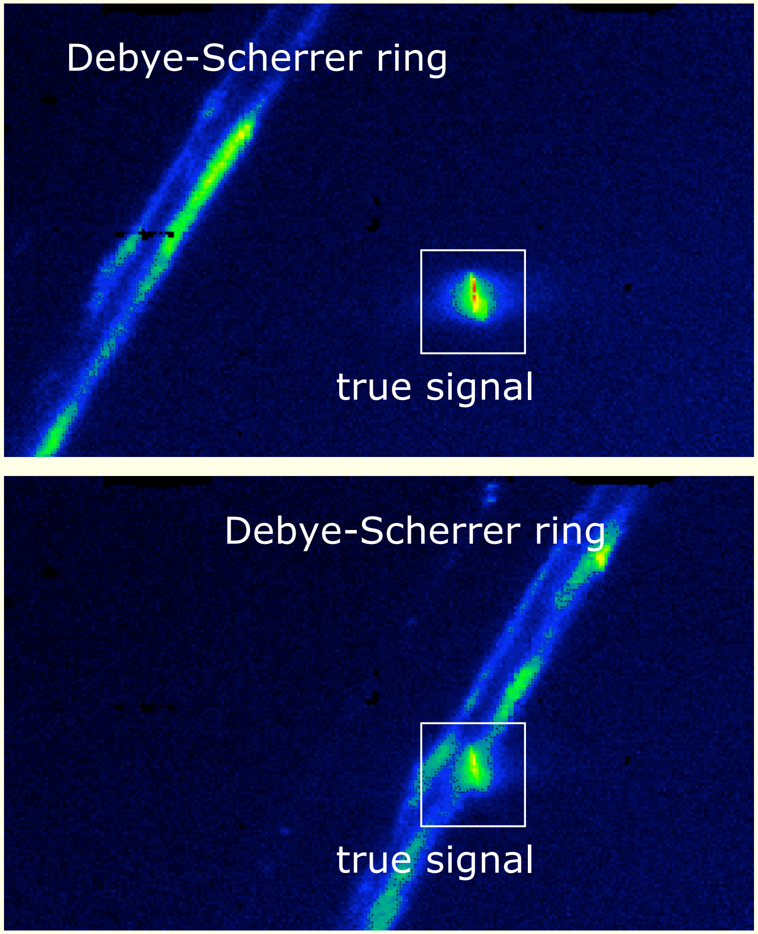
Data Acquisition

Use an area detector: “open slit” properly implemented!

- Can use “electronic slits”
- subtract background after the fact



Fenter et al., J. Synch. Rad. (2006).



Courtesy of C. Schlepütz and Phil Willmott
(Swiss Light Source)

Data Acquisition

Area detectors: CCD or pixel. Both work well.

CCD: -available in large formats (165 mm dia., MAR)
(But size is typically not that useful for SXRD.)
-integrating, so not sensitive to count rate.
-modest dynamic range (well depth); some dark current

Pixel: -photon-counting, with modest E-resolution
-max ct. rate: 2.7 MHz/pixel; non-linear at high ct. rate
-no dark current (as in 0 cts)
-fast readout (3 ms); 20 bits => 1 Mcount full register
-avail. 487x195 pixels, 172x172 μm^2 each (Pilatus)

Both: need better software integration!

Data Acquisition

Comparison of traditional and CCD open slit:

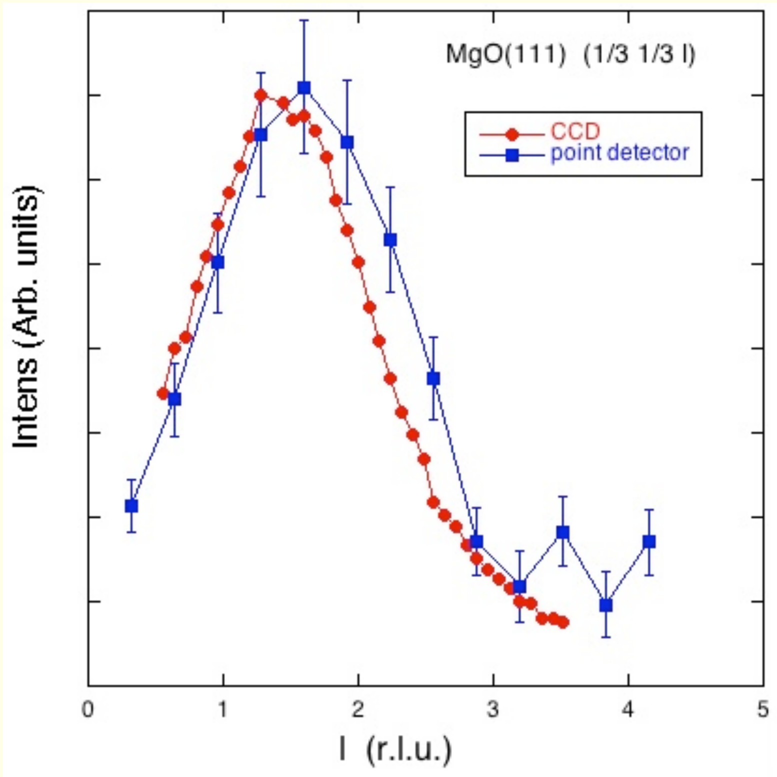
- MgO(111)-(√ 3 x√ 3)
- φ-scan: ESRF, dual undulators
- CCD: APS Undulator A

- φ-scan: 30 min.
- CCD: 4.5 min. (readout!)

Speedup: 20x just from scanning

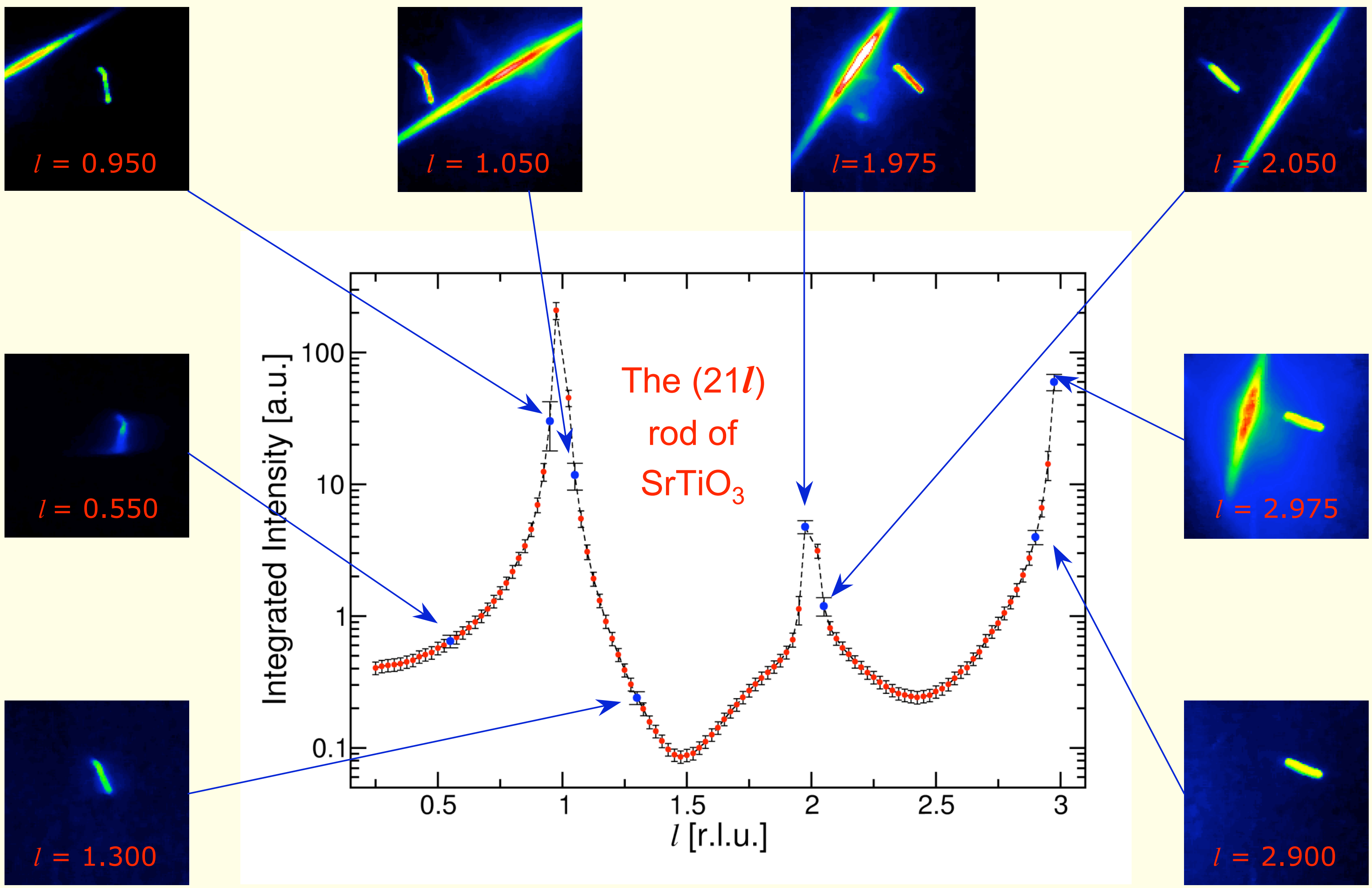
Also allows trajectory scans

=> HUGE potential speedup



Lyman et al.

Recording CTRs with PILATUS



Courtesy of C. Schlepütz and Phil Wllmott (Swiss Light Source)

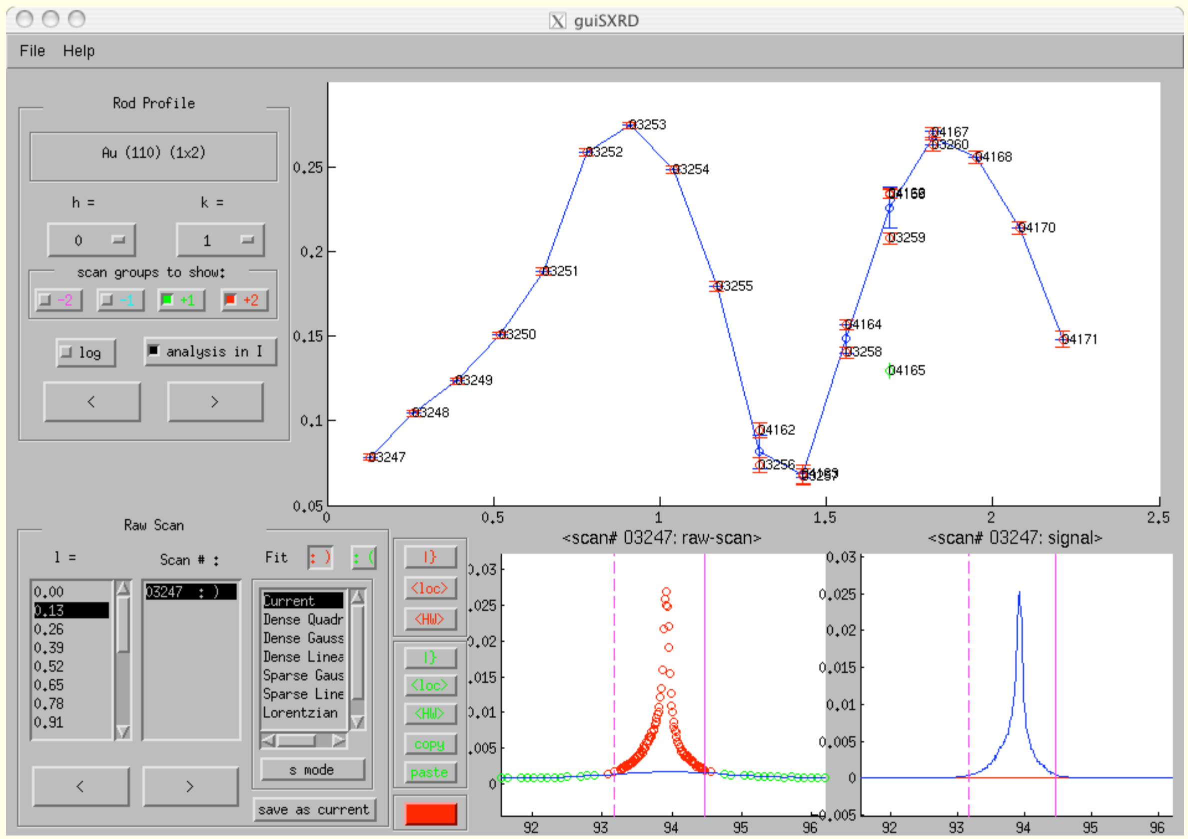
Data Reduction

- ANA from Vlieg
  Supported by ESRF; real programmers!

- guiSXRD from Fung (UWM) (Freely avail.)
  MATLAB-based

  Platform-independent

  Home-brew



Direct Methods

Non-periodic Objects

- Miao, Chapman, Sayre (oversampled 2D diffr. pattern)
- Robinson et al. (coherent scattering)

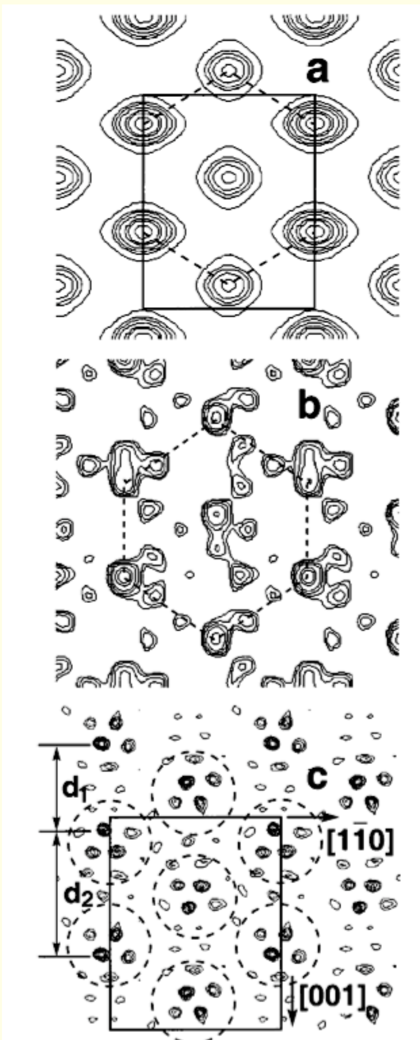
Surfaces/Superstructures

- Rius, Torrelles, et al. (2D diff. structure, atomicity)
- Marks et al. (Oversampling, atomicity)
- Yacoby, Pindak, Clarke, et al. (COBRA, $F^{surf}\left(\vec{q}+\Delta\vec{q}\right) \approx F^{surf}\left(\vec{q}\right)$)
- Saldin, Lyman (PARADIGM) oversampled CTR/SSR dataset
- Fenter (oversampled reflectivity)

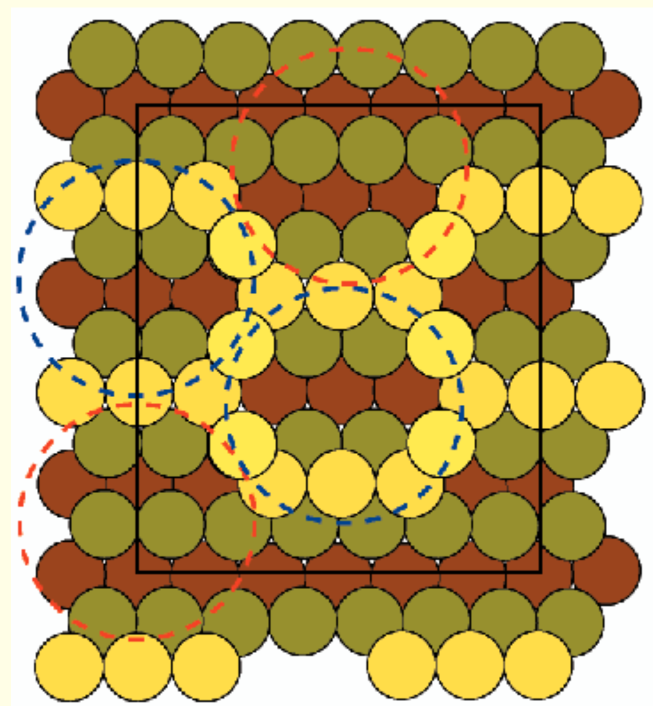
Rius/Torrelles: difference sum function

<u>Pro</u>: uses SSR => can recover full u.c.
<u>Con</u>: uses *only* SSR => only gets difference

Comment: only demonstrated to date on in-plane data, which renders 2D projection



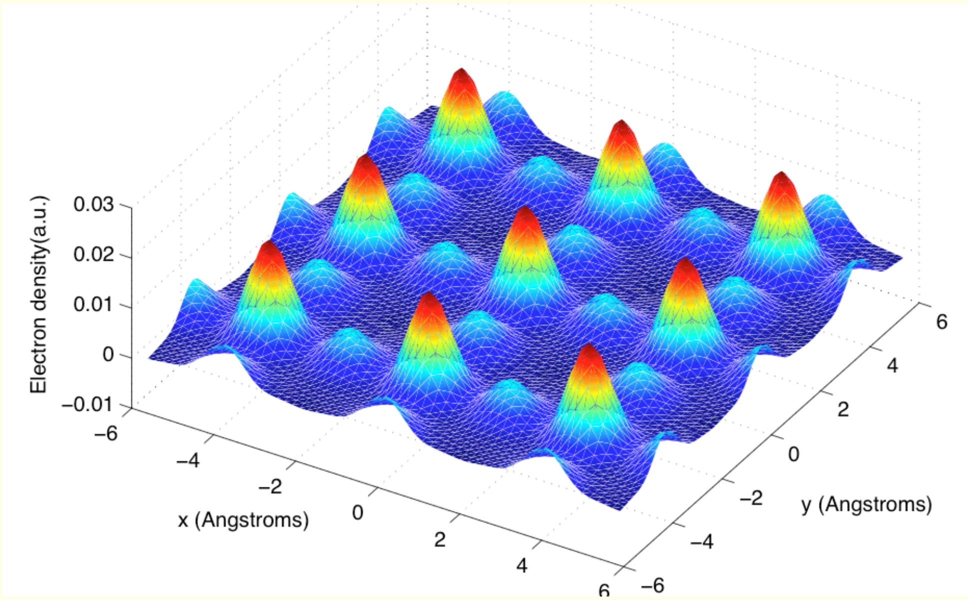
C_{60}/Au(110)-p(5x6)



COBRA

TiO_2 plane in $PbTiO_3$

3D representation of 2D cut through e-density



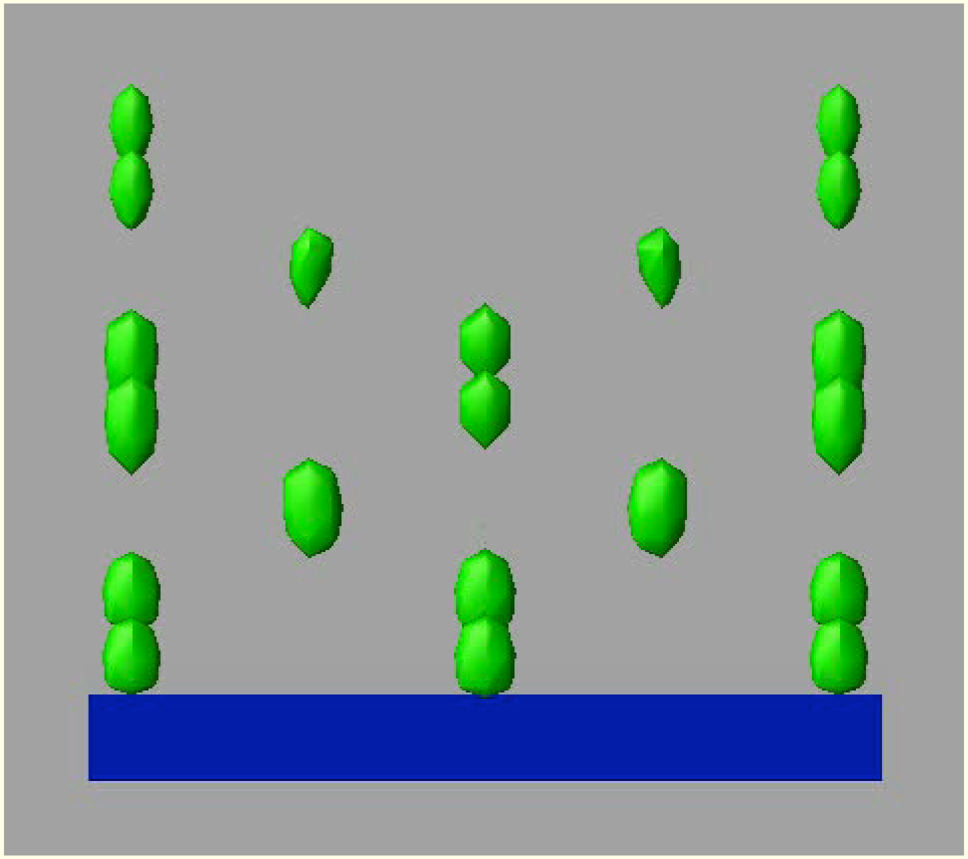
Codrin Cionca (Univ. of Michigan thesis)

Pro: uses CTR => can recover 3D structure
Con: uses *only* CTR => only gets surface u.c. folded into (1x1) bulk u.c.
Requires closely spaced surface structure factors.

Comment: can often use other information to "unfold"

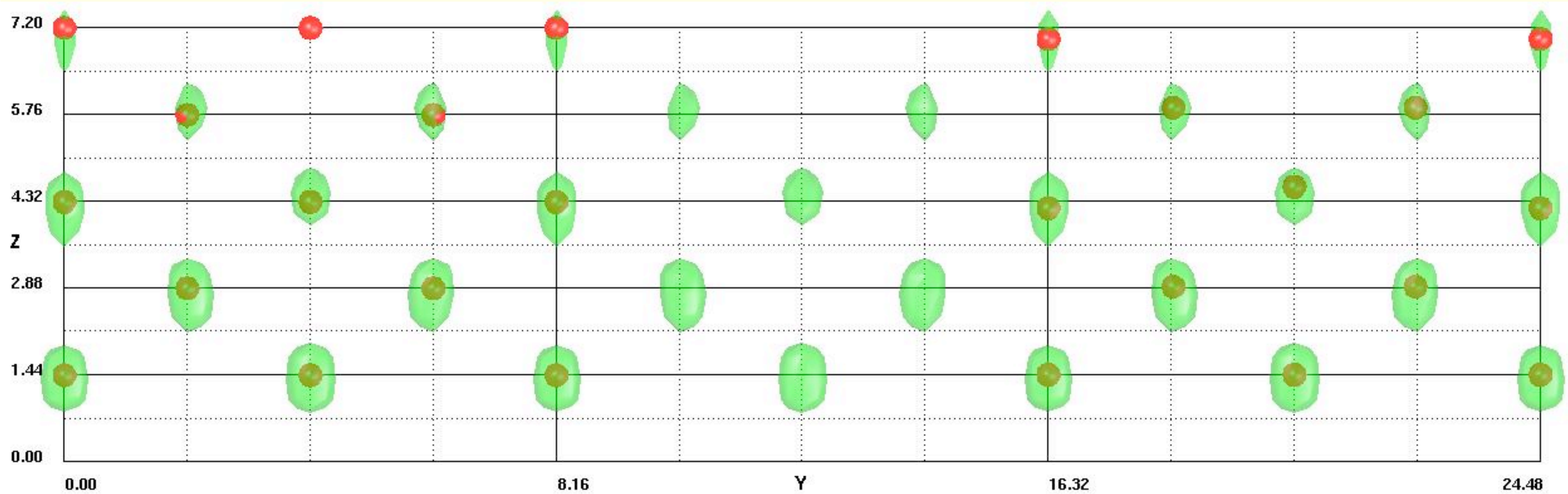
PARADIGM: 3D Reconstruction of e-density

Au(110)-(2x1)

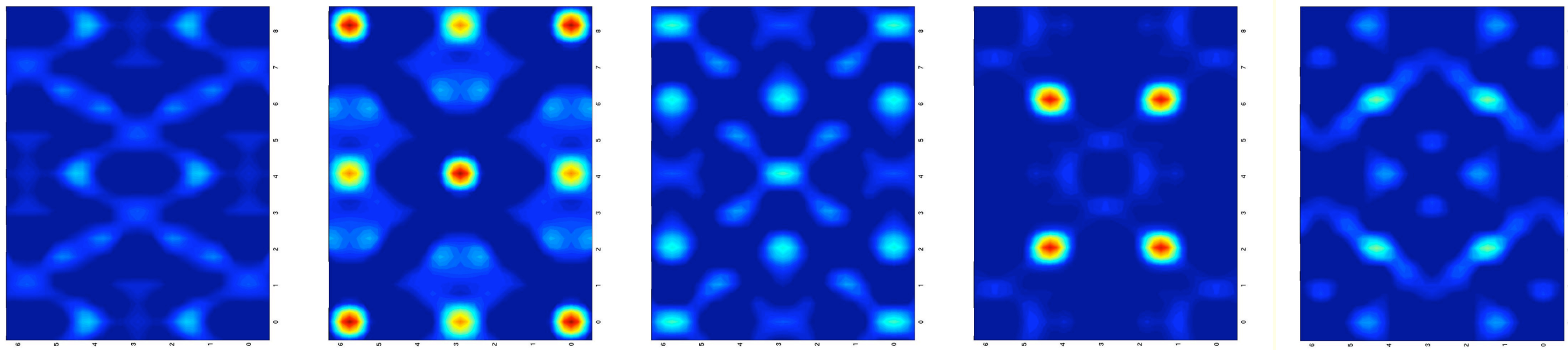


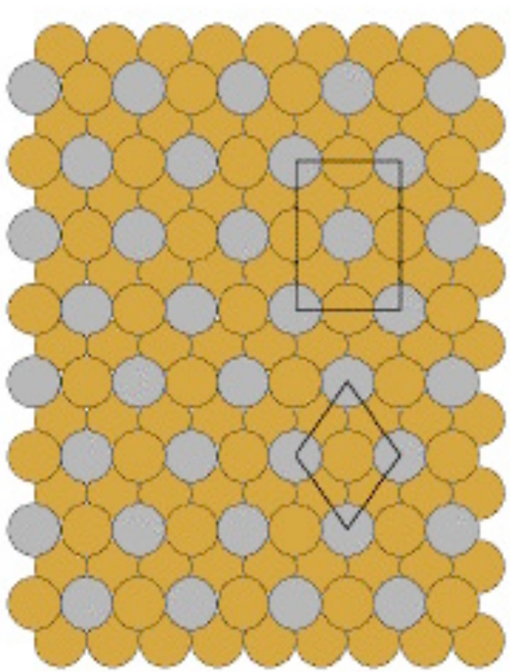
Pro: uses CTR and SSR => can recover 3D structure of full surface u.c.
Con: Requires extensive dataset (CTR and SSR) (though need not be closely spaced.)

Paradigm: Recovered electron density of Au(110)-(2x1)



PARADIGM: 2D cuts through e-density





All hollow sites occupied,
but by dissimilar atoms

Sb/Au(110)-c(2x2)

Conventional Refinement

Available fitting software:

- ROD by E. Vlieg (U. Nijmegen; ESRF-supported)
  - -uses non-linear fitting: Fast, but can get stuck in false minima
  - -supported by professional programmers.
- FIT by O. Bunk (Swiss Light Source)
  - -uses grid search: Robust, but slow.
  - -no support
- Others????

Thanks for your attention!