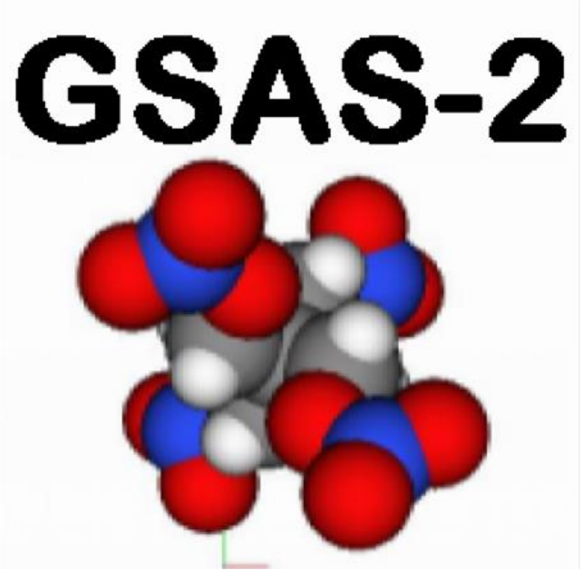
GSAS-II OVERVIEW

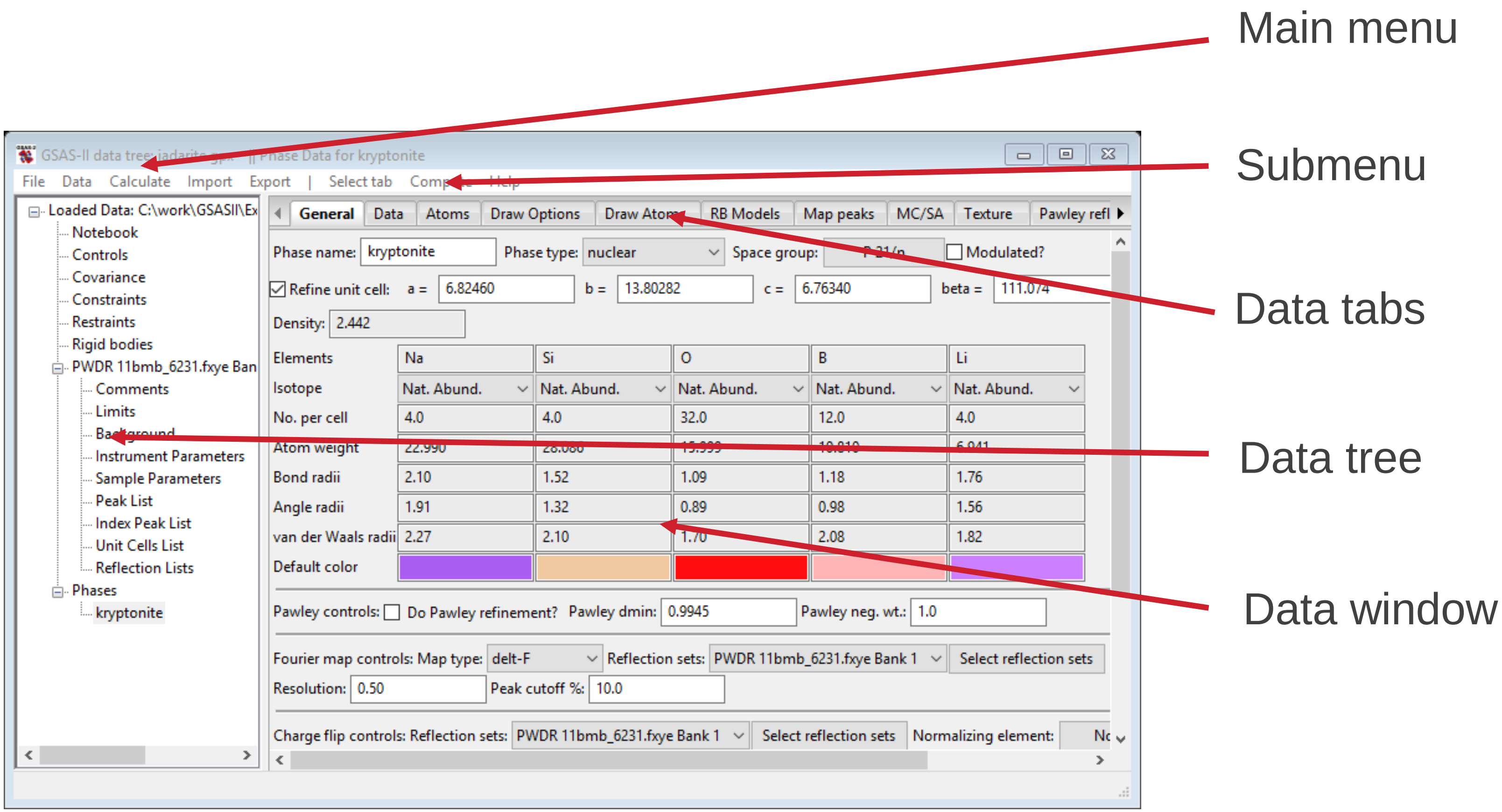


ROBERT VON DREELE
APS, ANL
vondreele@anl.gov

Canadian Powder Diffraction Workshop

GSAS-II – MODERN GUI APPLICATION FOR CRYSTALLOGRAPHY (IN PYTHON)

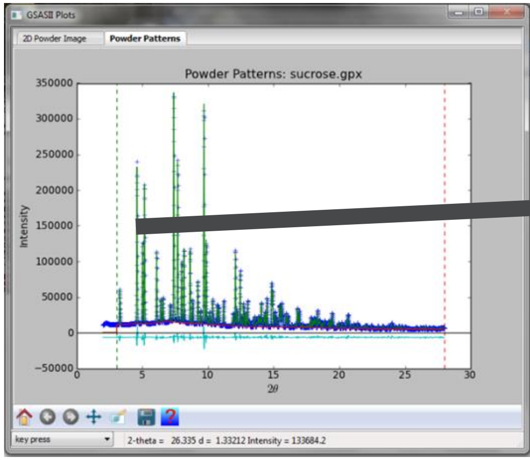
GSAS-II: MODERN GUI
– 2 FRAME LAYOUT + CONSOLE

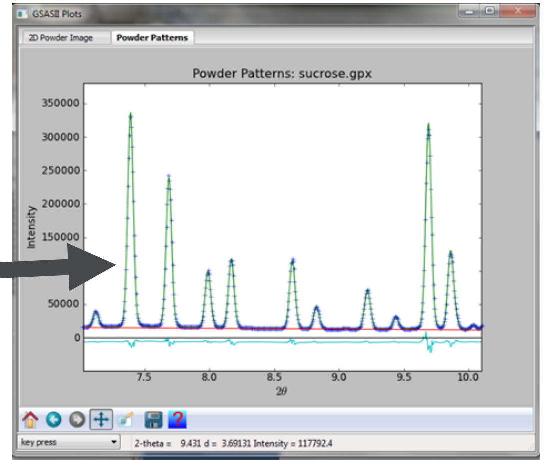


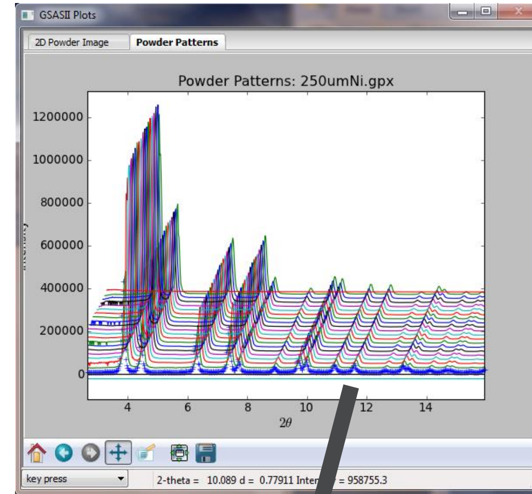
Plot & console in separate frames

THE PLOTS - ADVANCED VISUALIZATION

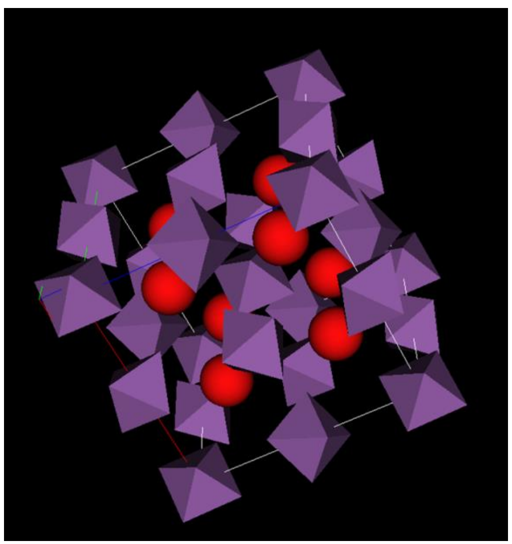
Powder profile – easy zoom



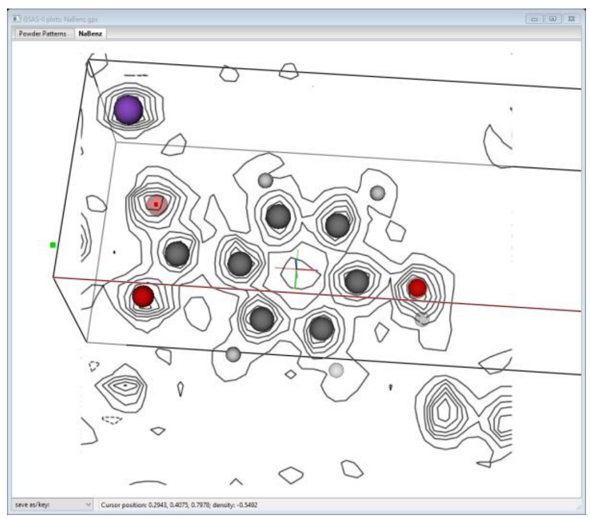




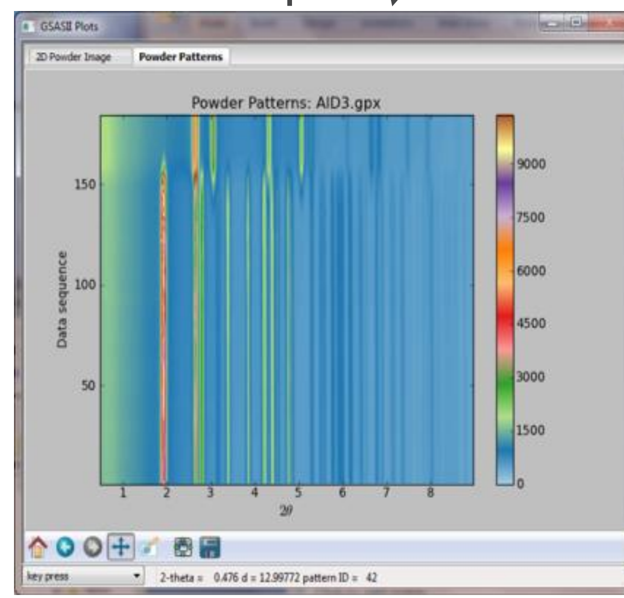
Waterfall plot



Structure drawing



Contoured density thru any plane



Contour plot

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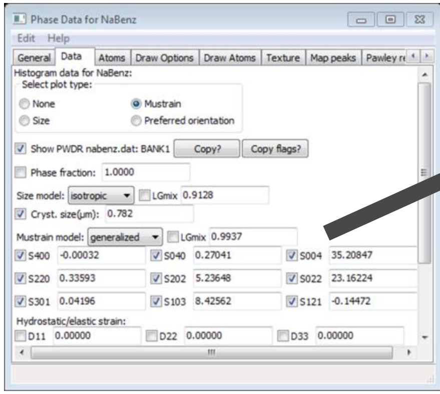
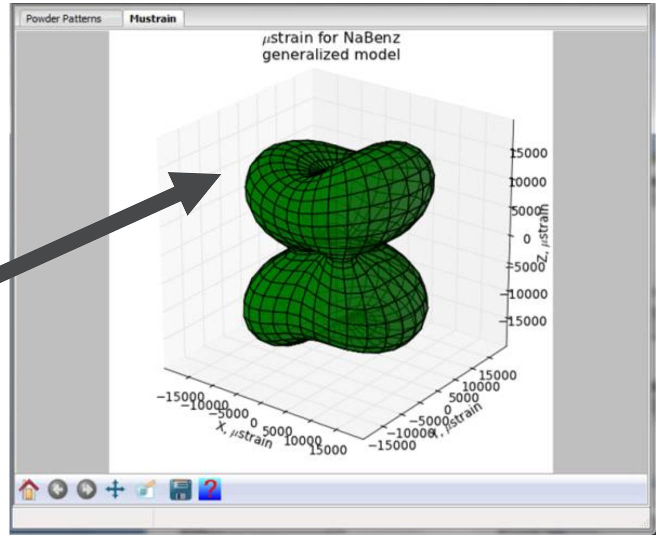
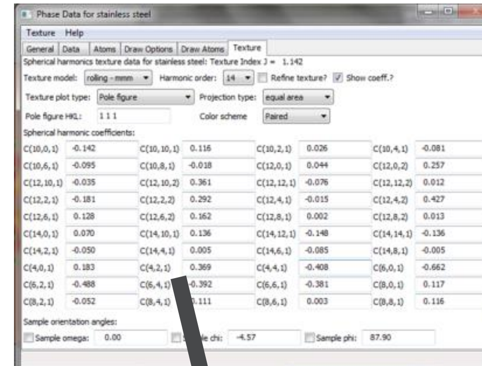
ADVANCED VISUALIZATION IN GSAS-II: NUMBERS AS PICTURES

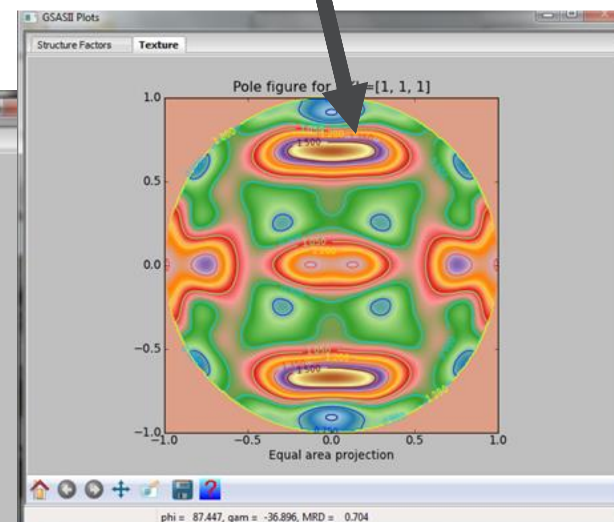
μstrain surface



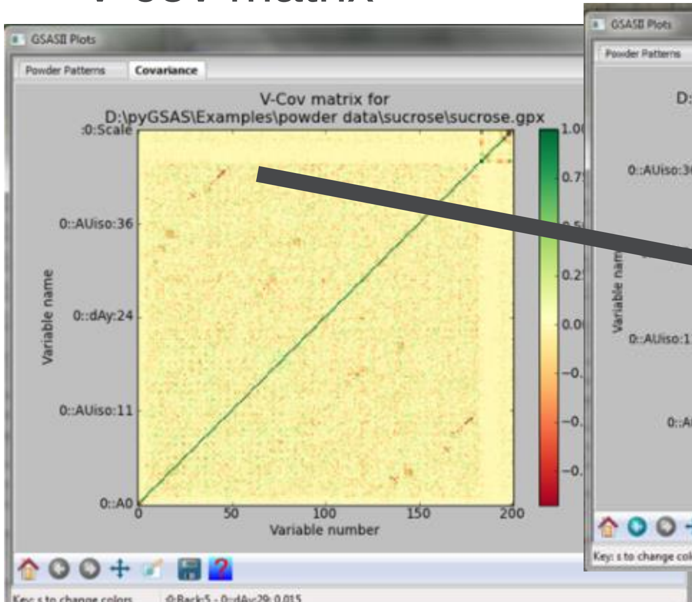


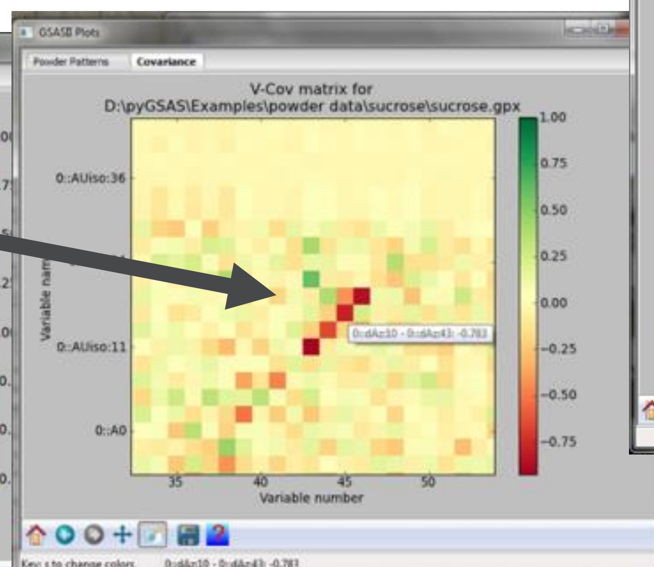
Texture – sph. harmonics





v-cov matrix

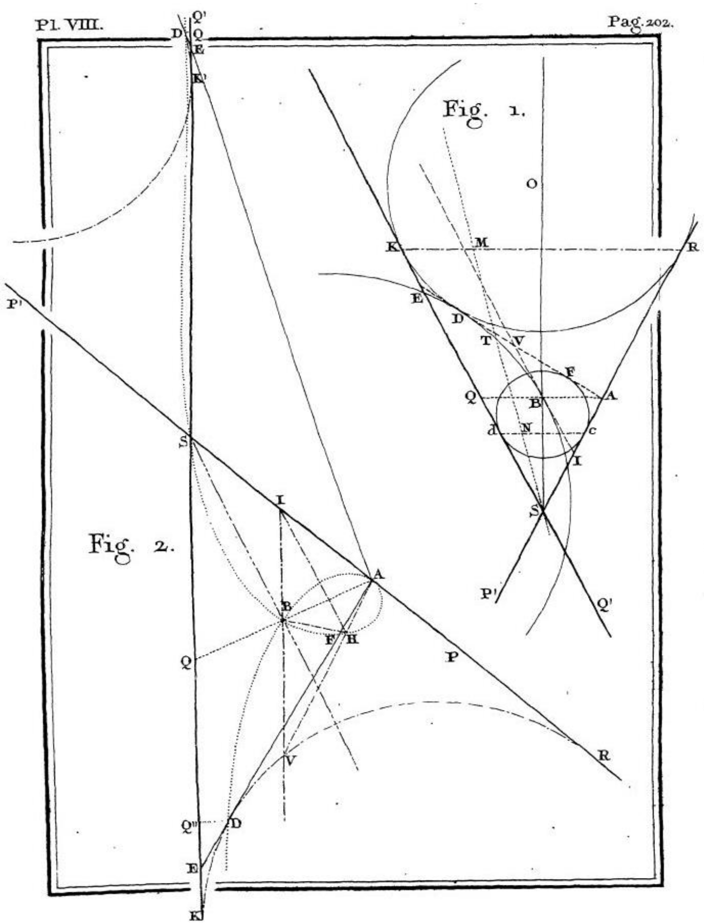




CONIC SECTIONS

Where is the incident beam on the detector?

Fit2D (& DataSqueeze) – assumes center of the diffraction ellipse - False
Analysis – G.P. Dandelin,
Noveaux memories de l'Academie royal de Bruxelles, 2, 171-202 (1822)
Drawing by Dandelin p.202



Taken from Dandelin's original paper
Fig. 1: Shows the 2 spheres in contact with plane EA

- line SO is cone axis
- F&D are the ellipse foci on the plane

He refers to a work by M. Quetlet as having previously made this construction - source?

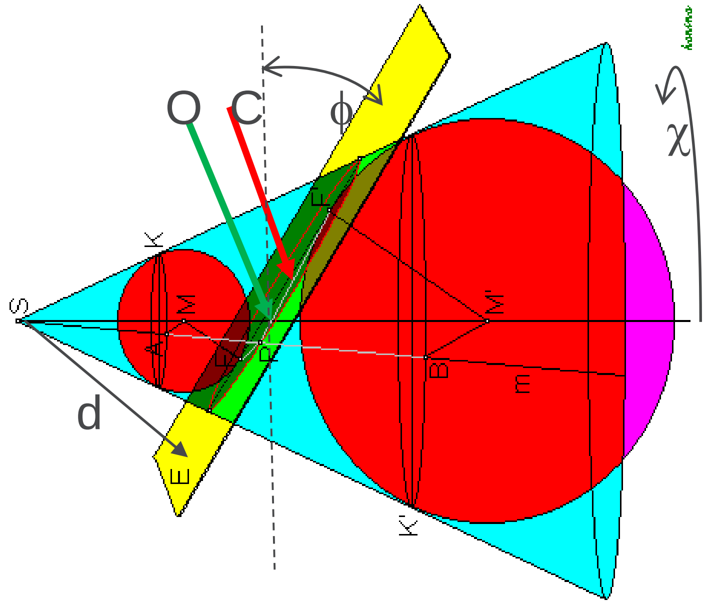
This is not something new!

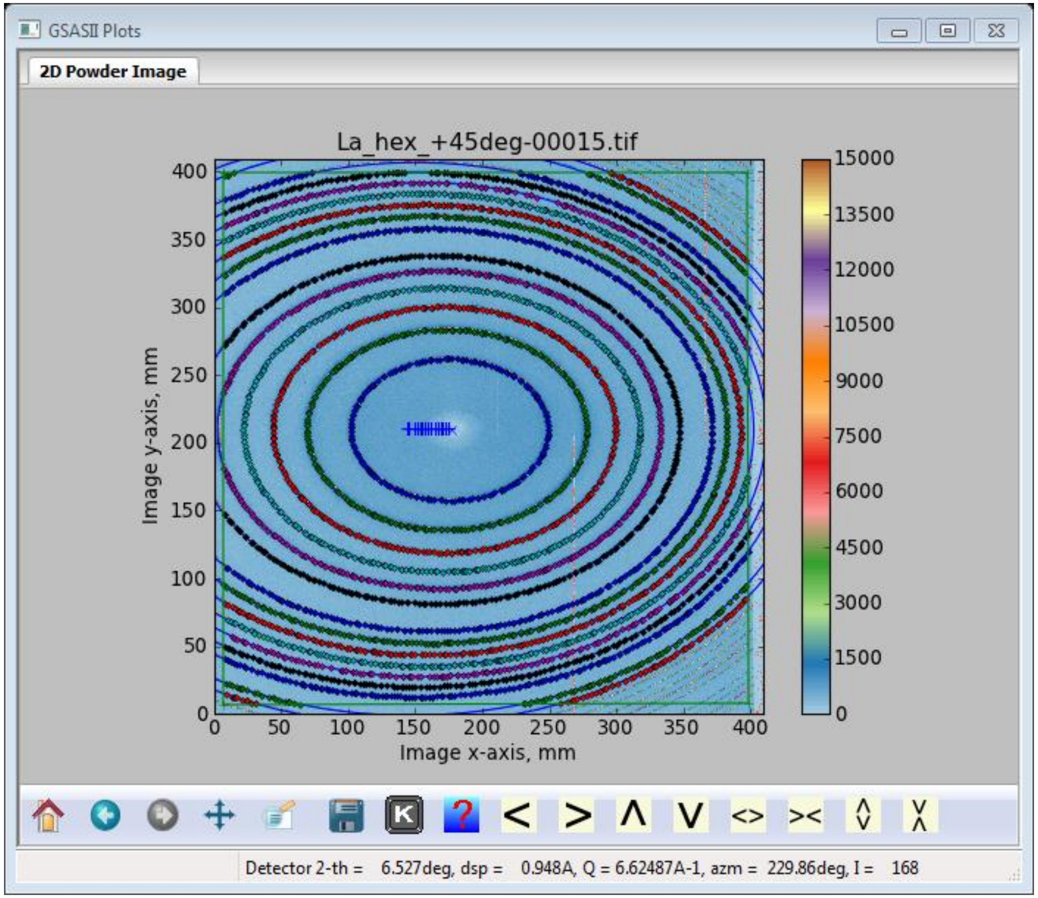
Dandelin sphere construction used in GSAS-II for image plate orientation calibration

2D IMAGE CALIBRATION (REPLACE FIT2D)

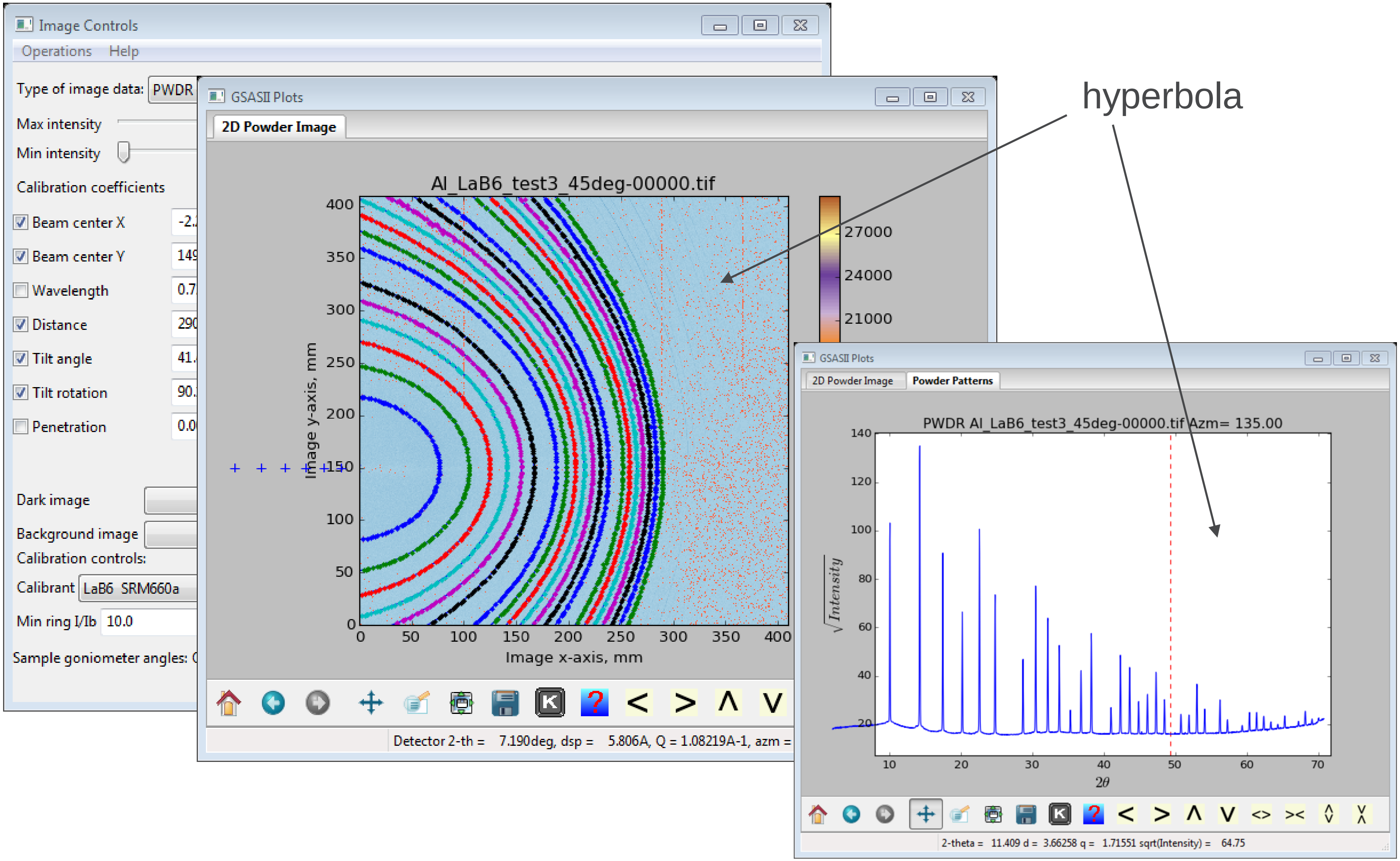
Correct calibration for tilt

- Dandelin sphere construction (1822)



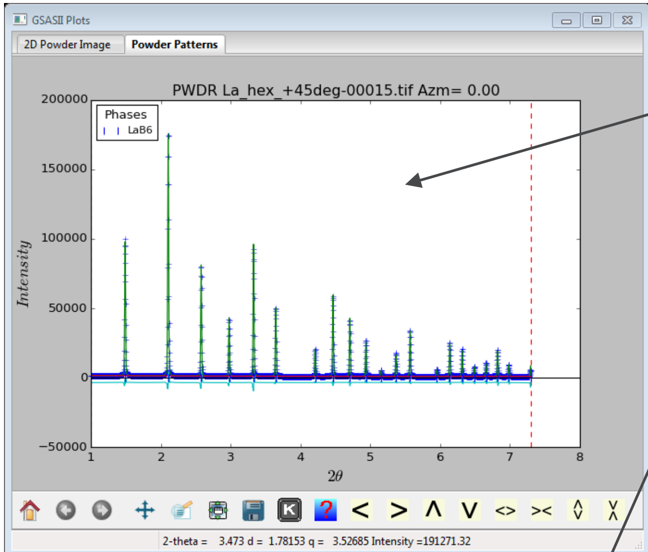


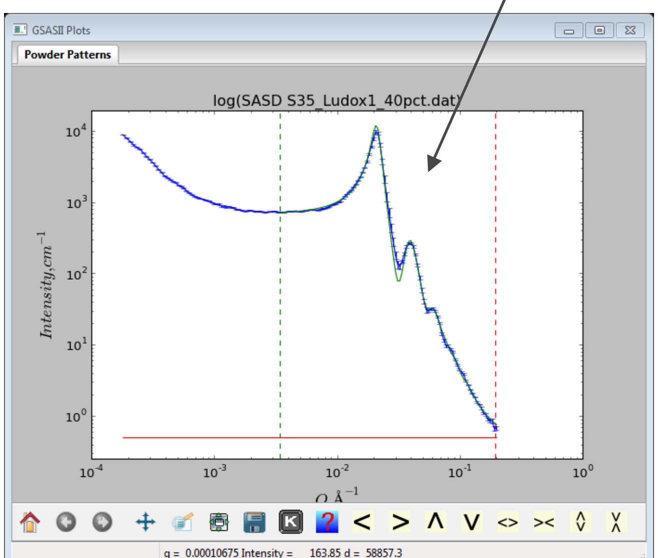
OFFSET & TILTED DETECTORS – AN EXAMPLE

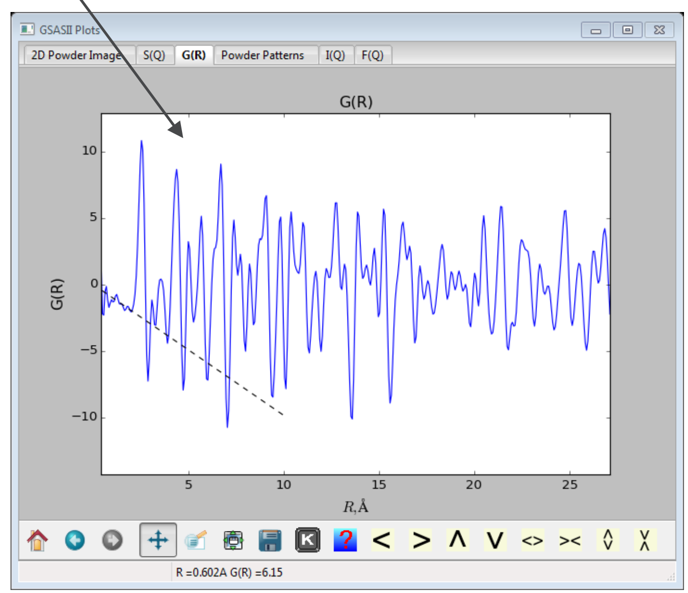


AFTER IMAGE PROCESSING IN GSAS-II – STAY IN PROJECT FILE

- Powder diffraction analysis
- Small angle data analysis
- PDF calculation (needs some development & enthusiastic users)







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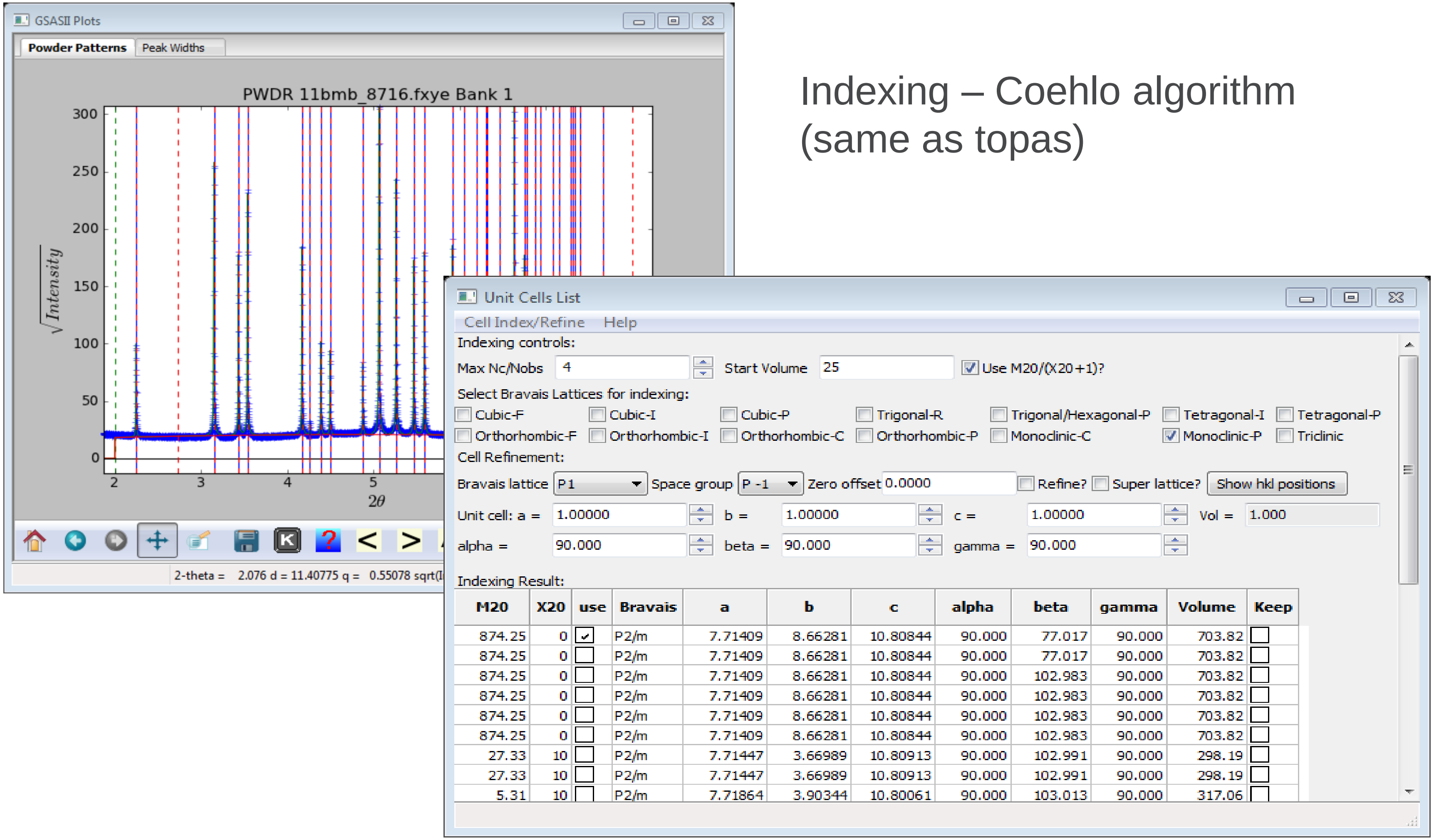
PEAK PICKING, FITTING & INDEXING



M20	X20	use	Bravais	a	b	c	alpha	beta	gamma	Volume	Keep
874.25	0	✓	P2/m	7.71409	8.66281	10.80844	90.000	77.017	90.000	703.82	
874.25	0		P2/m	7.71409	8.66281	10.80844	90.000	77.017	90.000	703.82	
874.25	0		P2/m	7.71409	8.66281	10.80844	90.000	102.983	90.000	703.82	
874.25	0		P2/m	7.71409	8.66281	10.80844	90.000	102.983	90.000	703.82	
874.25	0		P2/m	7.71409	8.66281	10.80844	90.000	102.983	90.000	703.82	
874.25	0		P2/m	7.71409	8.66281	10.80844	90.000	102.983	90.000	703.82	
27.33	10		P2/m	7.71447	3.66989	10.80913	90.000	102.991	90.000	298.19	
27.33	10		P2/m	7.71447	3.66989	10.80913	90.000	102.991	90.000	298.19	
5.31	10		P2/m	7.71864	3.90344	10.80061	90.000	103.013	90.000	317.06	

Indexing – Coehlo algorithm (same as topas)

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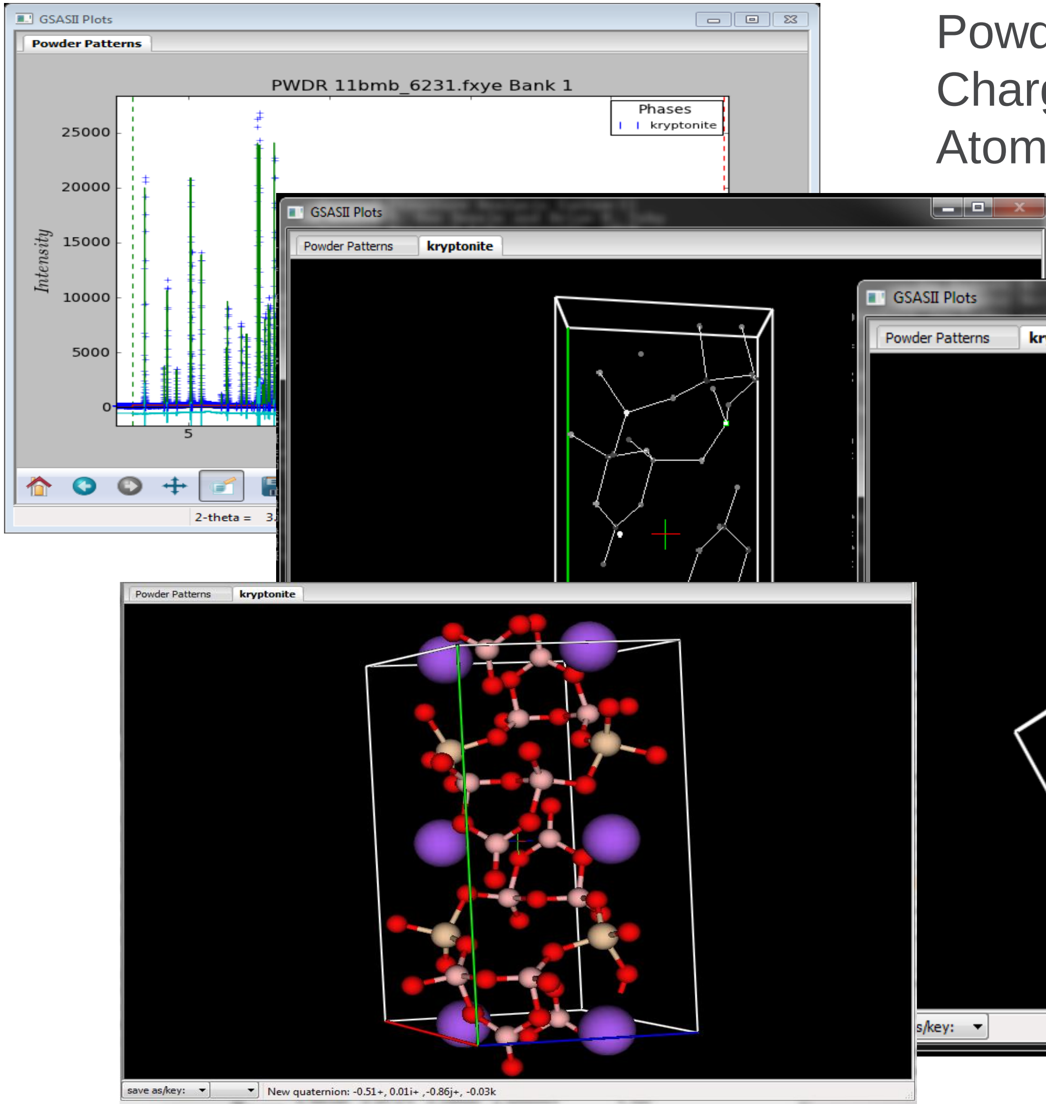
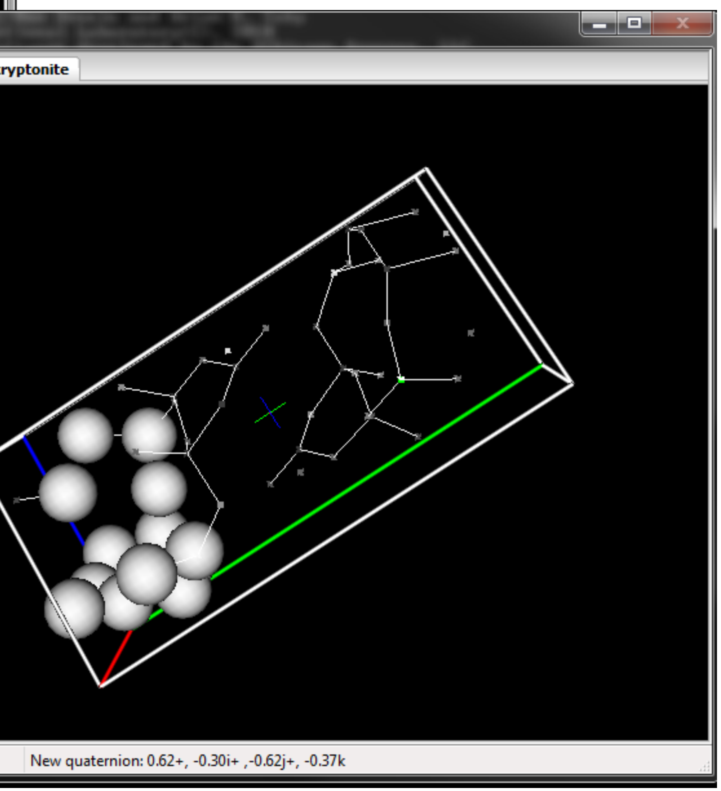
STRUCTURE SOLUTION

Charge Flipping 3D & 4D



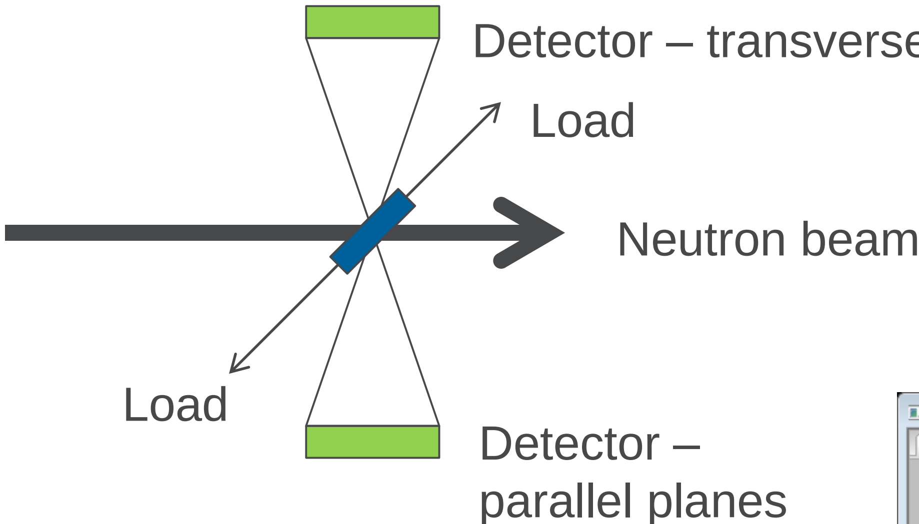


Powder – Pawley refinement

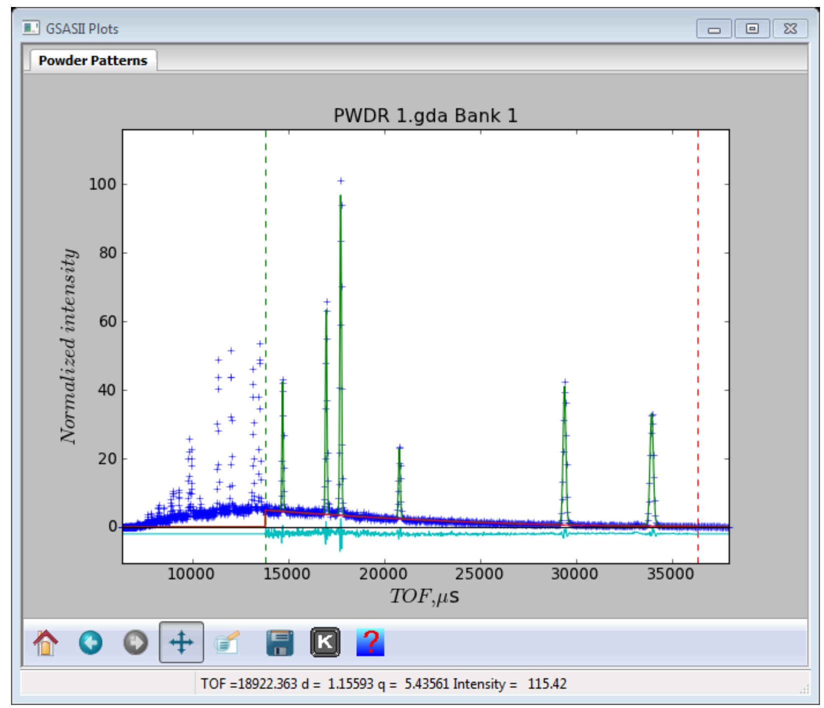
Charge flip (NB: no symmetry)

Atom selection & identification

SEQUENTIAL PEAK FITTING – OBSERVATION OF STRAIN – SNS VULCAN DIFFRACTOMETER



Sample: ¼” stainless steel rod, 1 min exposures over 13+ hrs
~800 patterns
Cycle tension – compression loading

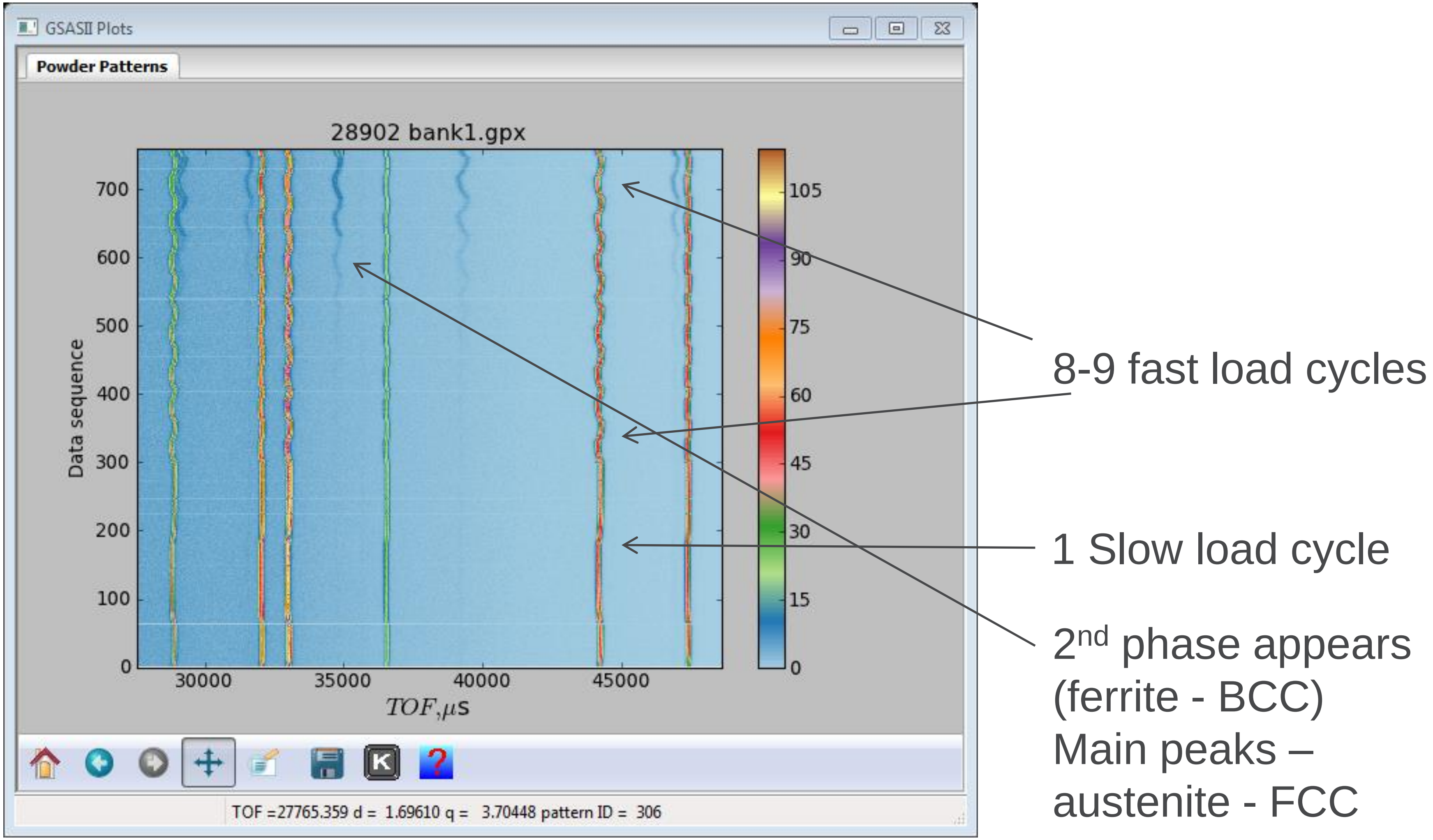


One pattern –

single peak fits: 6 lines

Follow vs time & loading

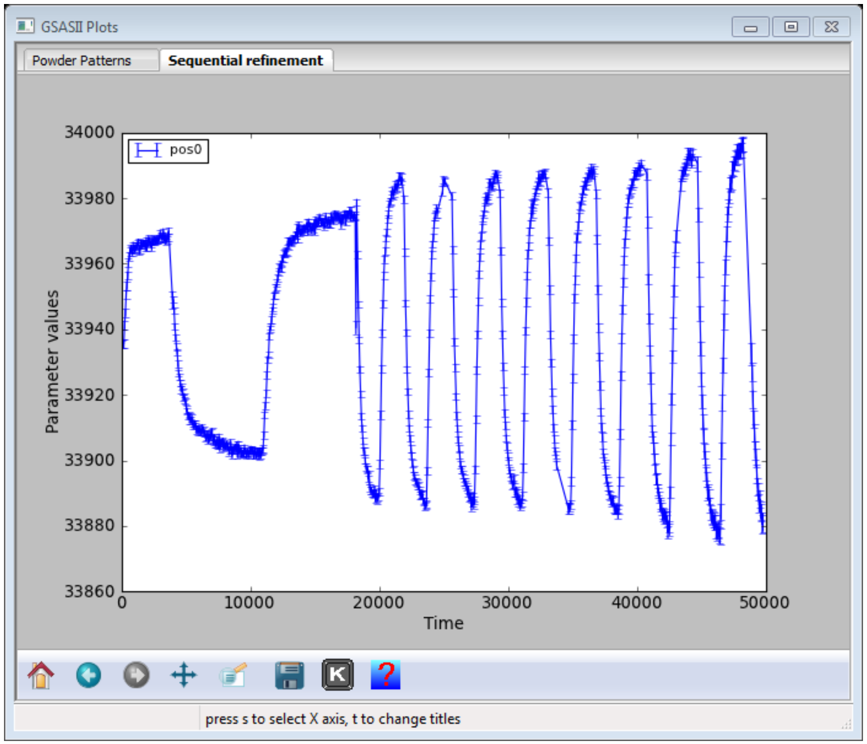
~800 TOF POWDER PATTERNS IN GSAS-II



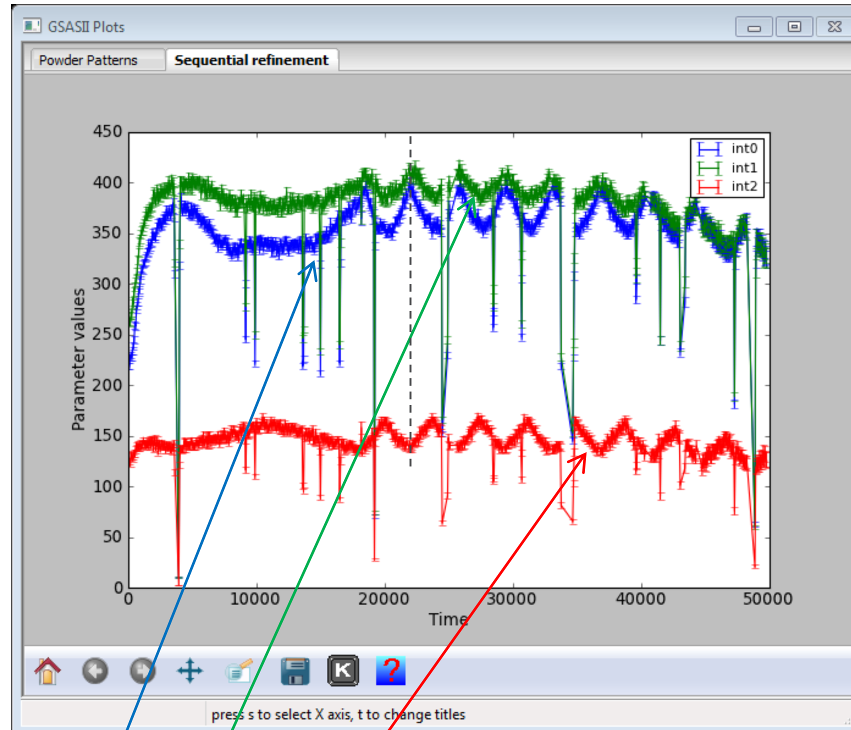
Do sequential peak fitting – 6 peaks + background
~1.5 min to complete!

SOME SEQUENTIAL PEAK FIT RESULTS

Lots to explore here – all within GSAS-II



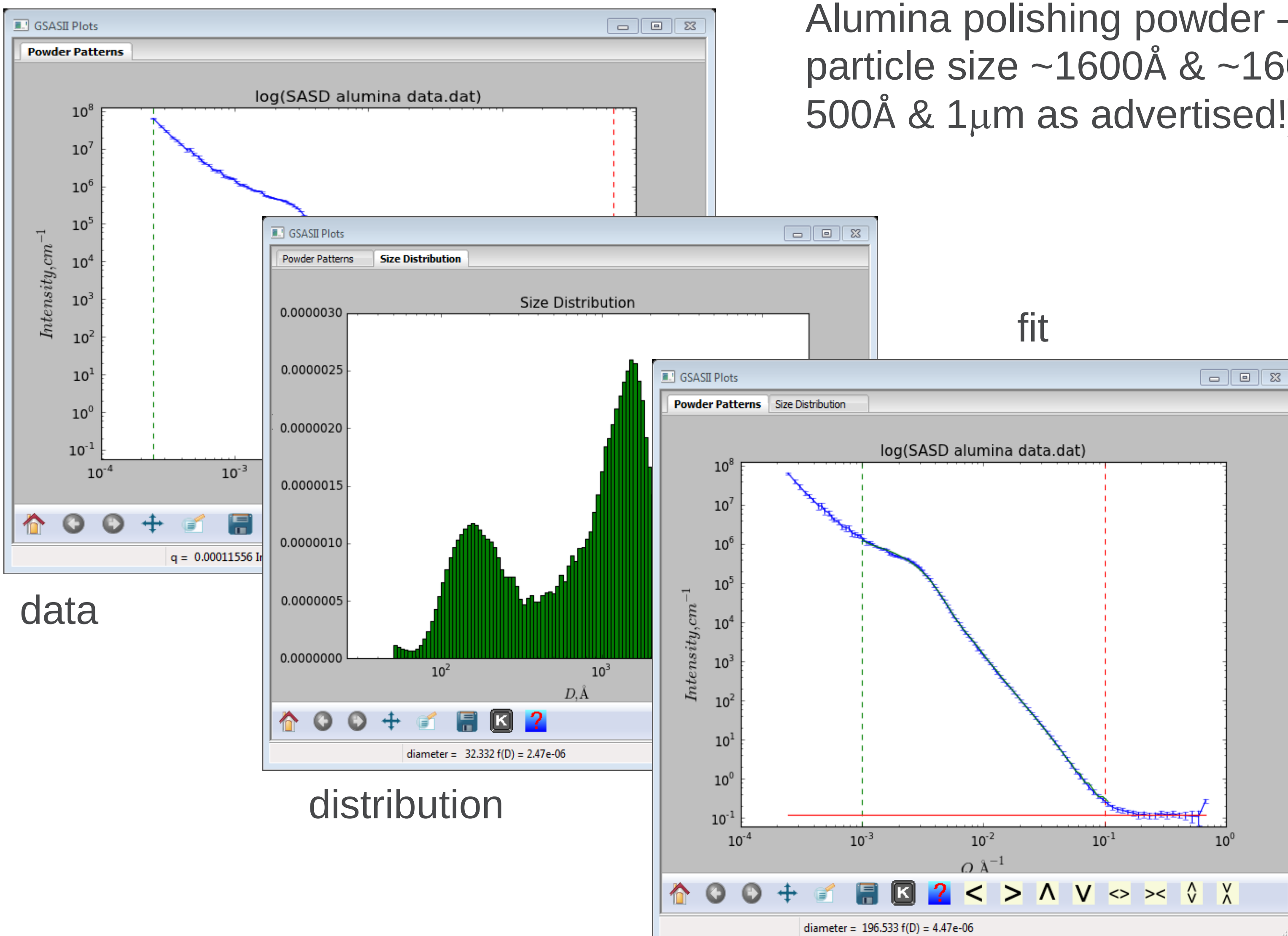
Austenite 111 position



Austenite 111, 200 & 210 intensity
NB: note misalignment of 111, 200 vs 210
Crystallite reorientation under load
Spikes (down) – beam dropouts

SMALL ANGLE SCATTERING – SIZE DISTRIBUTION

Alumina polishing powder – bimodal particle size ~1600Å & ~160Å (not 500Å & 1μm as advertised!)



data

distribution

fit

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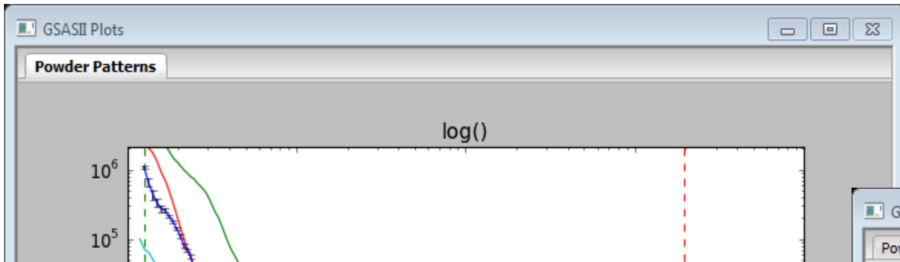
SMALL ANGLE SCATTERING – SEQUENTIAL DATA ANALYSIS

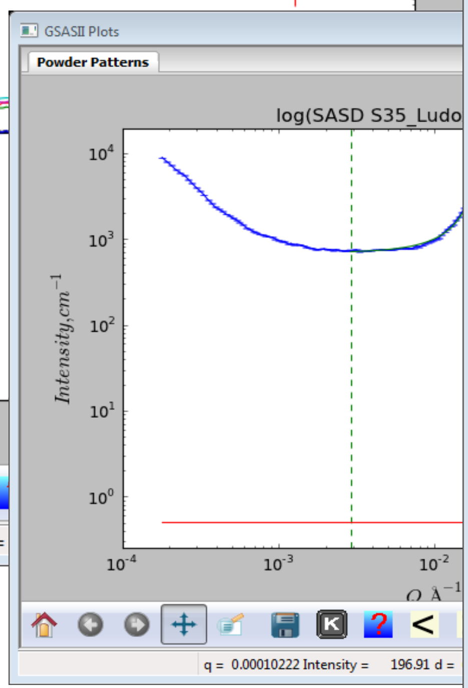
Ludox colloidal silica from Aldrich – dilution range

Fit – hard sphere; log normal distribution, size, mean, vol. fr.

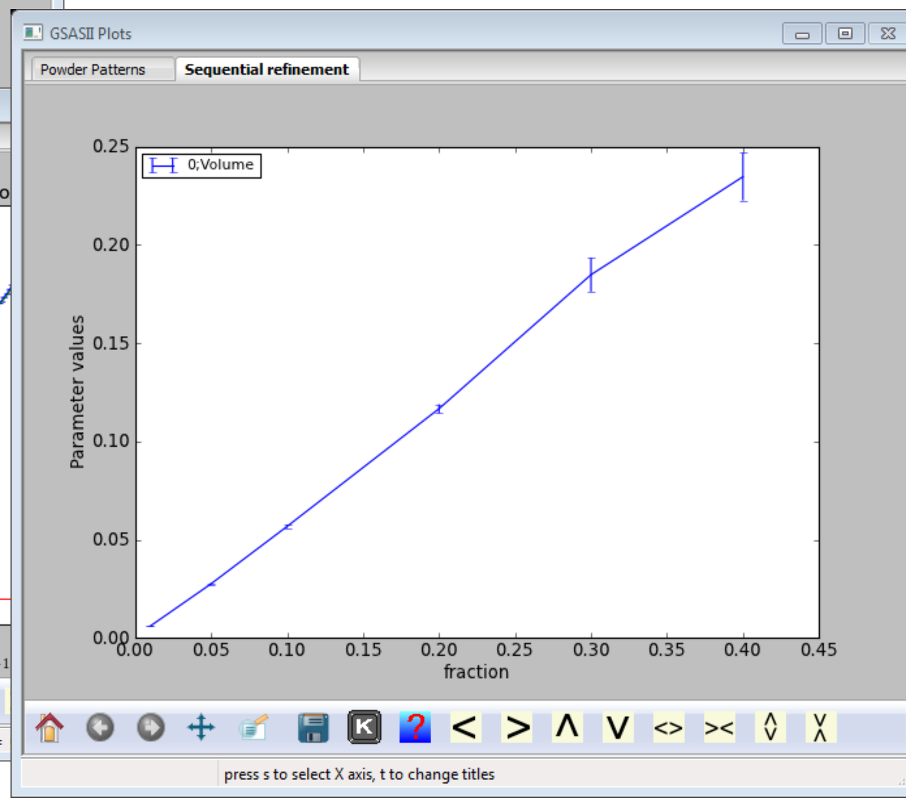
Sequential result – find slope/intercept



data

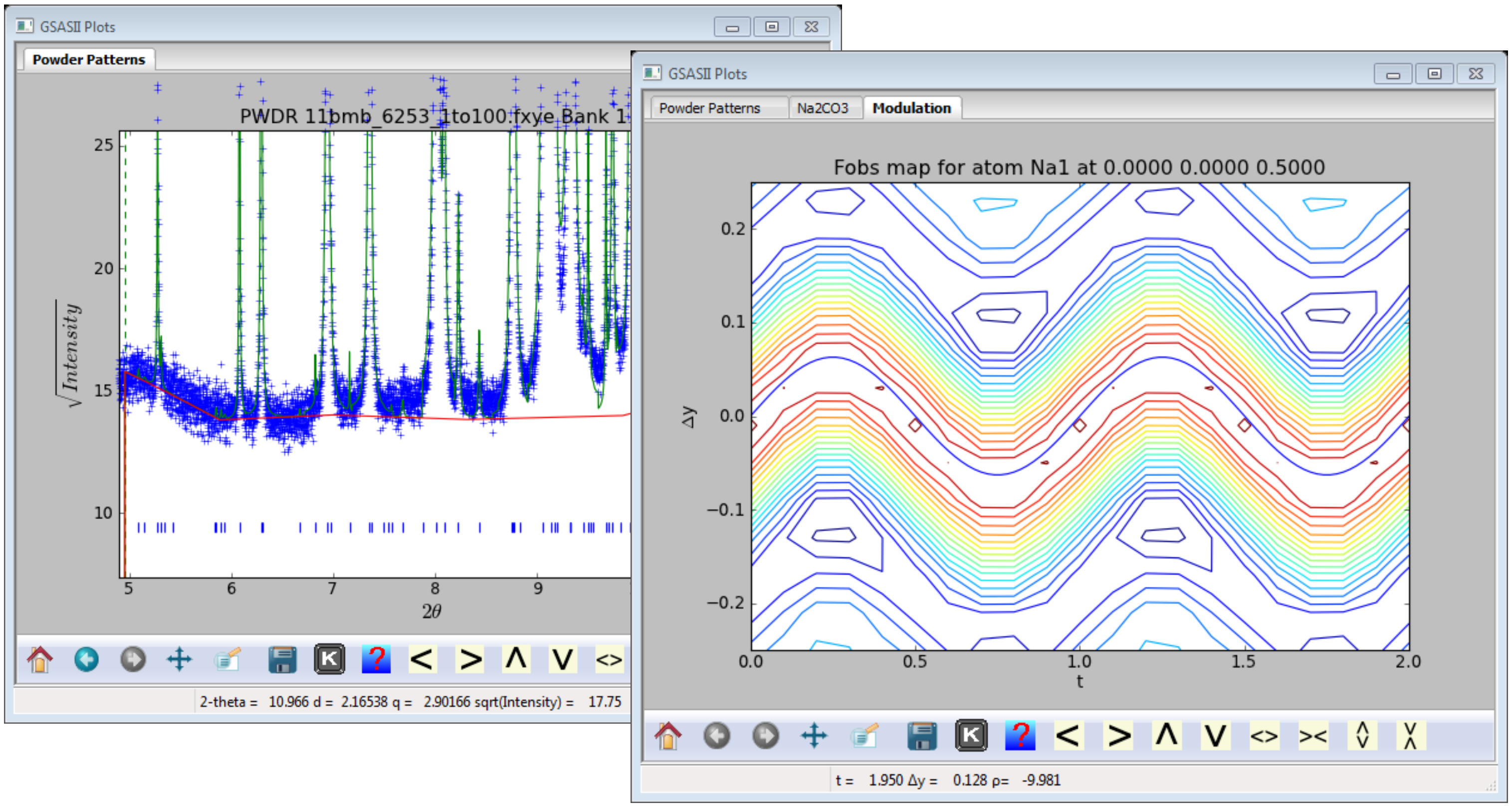


One fit



INCOMMENSURATE STRUCTURES

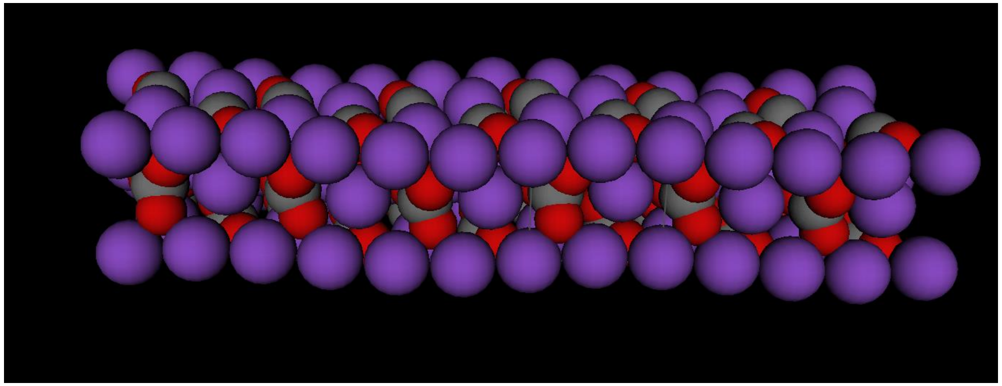
Simple materials – ex. Na_2CO_3 C 2/m (a0g)0s super space group M = (0.1833,0,0.3191)



INCOMMENSURATE STRUCTURES IN GSAS-II

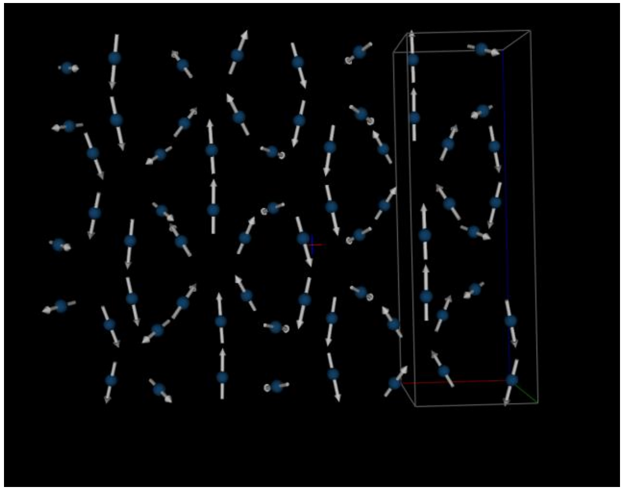
Chemical & magnetic – object: full structure analysis

- Import incommensurate cif & mcif files & draw them – example: Na_2CO_3



SC & powder data collected at APS
Structure solution test both with GSAS-II

- Incommensurate magnetic mcif file & draw them – example: β-Li_2IrO_3



Determined from SC x-ray resonant diffraction (Diamond) & neutron powder data (ISIS)

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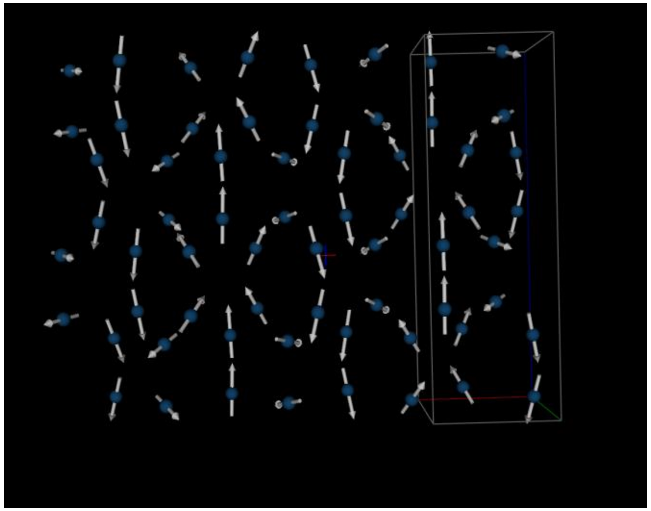
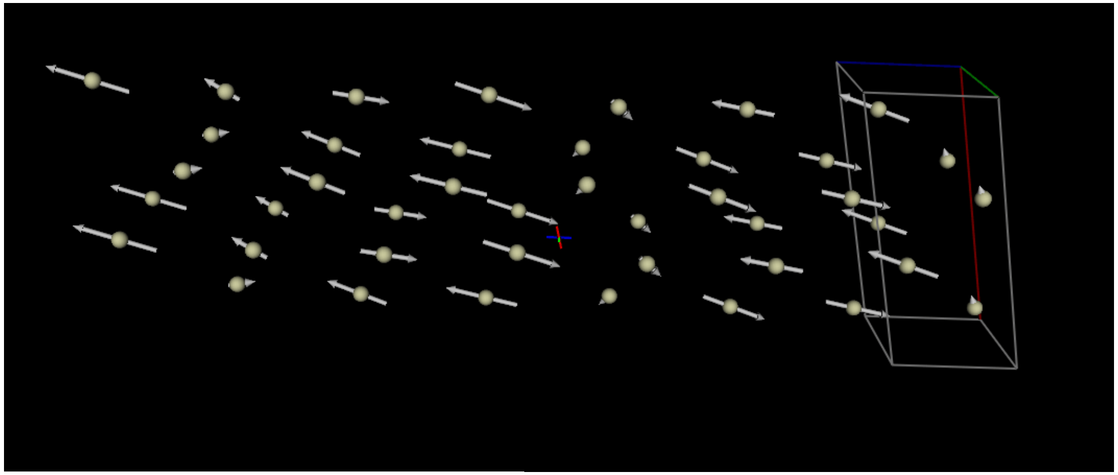
MAGNETIC INCOMMENSURATE STRUCTURES

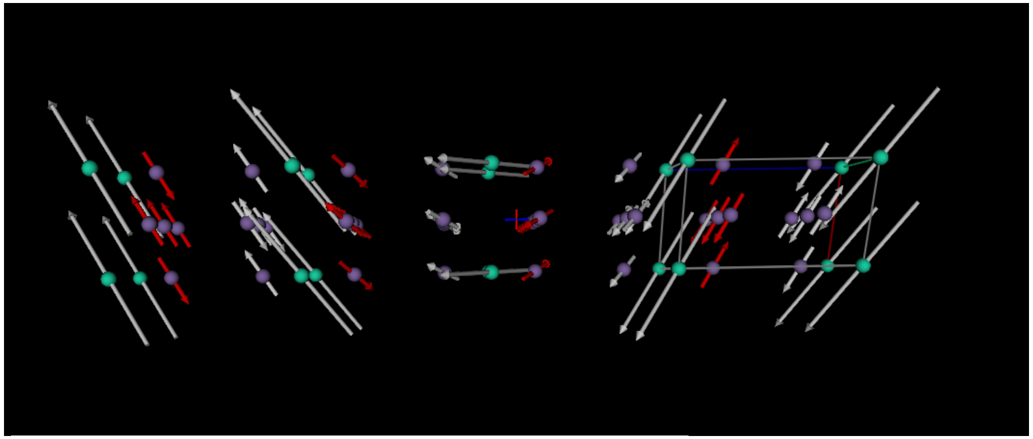
Some examples:



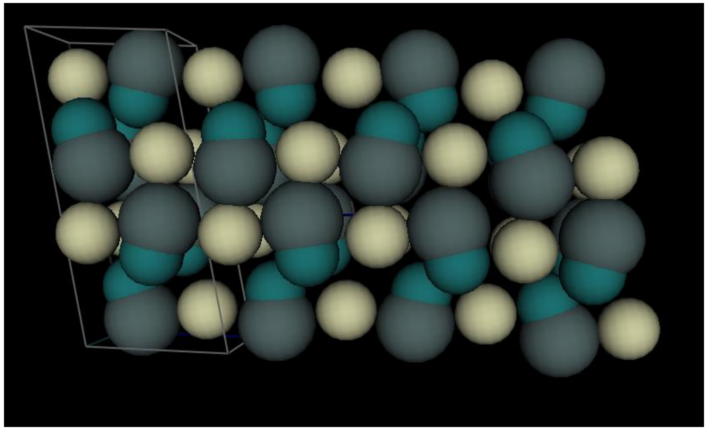
β-Li_2IrO_3



CeRuSn – Ce moment



$DyMn_6Ge_6$ – residual moment



CeRuSn – structure modulation

GSAS-II INSTALLATION

GSAS-II INSTALLATION

Search web for “GSAS-II” → only thing out there:

See GSAS-II “home page” https://subversion.xray.aps.anl.gov/trac/pyGSAS.

- Includes
  - Installation instructions – includes a 1-step for python/GSAS-II
  - Tutorials - ~50 of these

GSAS-II CAPABILITIES

GSAS-II CAPABILITIES & EXAMPLES

Powder data

- 2D Images:
  - calibration & integration → 1D patterns
  - Direct strain fitting → 3 strain tensor elements*
- 1D patterns
  - Peak picking & fitting*
  - Indexing & space group selection → make new phase
- Multidata X-ray/neutron, CW/TOF → all combinations possible
- Structure solution
  - Stochastic – Monte Carlo/Simulated Annealing
  - Deterministic – Charge Flipping (3D & 4D)
- Structure Refinement – Rietveld Method*
  - Pawley refinement (needed for Structure Solution)
  - (3+1) Incommensurate structures
  - Constraints & restraints
  - Rigid bodies (2 kinds)
  - Texture Analysis → spherical harmonics*
- Stacking Faults → DIFFaX simulations (NB: no refinement)
- Pair Distribution Function → data transformation (e.g. make PDF)

* Can use Sequential Analysis

GSAS-II CAPABILITIES & EXAMPLES

Single Crystal Data

- Multidata X-ray/neutron → all combinations possible
- Structure solution
  - Stochastic – Monte Carlo/Simulated Annealing
  - Deterministic – Charge Flipping (3D & 4D)
- Structure Refinement –Levenberg-Marquardt least squares*
  - (3+1) Incommensurate structures
  - Constraints & restraints
  - Rigid bodies (2 kinds)
  - Merohedral & pseudomerohedral twinning
  - Extinction (Gaussian/Lorentzian Primary & Secondary I & II)
- Stacking Faults → DIFFaX simulations (NB: no refinement)

* Can use Sequential Analysis

GSAS-II CAPABILITIES & EXAMPLES

Small Angle Diffraction Data

- 2D Images:
  - calibration & integration → 1D patterns
- 1D Small Angle Data
  - Scaling to glassy carbon standard
  - Size Analysis
    - Maximum Entropy Analysis
    - Total Non-negative Least Squares
  - Model fitting – components*
    - Particle shapes – e.g. spheres, disks, hollow spheres,…
    - Porod scattering
    - Bragg peaks

* Can use Sequential Analysis

SEQUENTIAL DATA ANALYSIS

Multiple data sets – no maximum number

- 2D Images:
  - Direct strain fitting → 3 strain tensor elements
- 1D patterns
  - Peak picking & fitting
  - Structure Refinement – Rietveld Method
  - Small angle data – model fitting
- Results table
  - Parameter plotting vs experiment variable (e.g.. Temperature)
  - Parametric equation modeling & fitting

GSAS-II TUTORIALS

BEST WAY TO LEARN GSAS-II IS BY RUNNING SELECTED TUTORIALS

Most major sections of the program are demonstrated by tutorial examples – best for today is to pick one/two for now

Basic GSAS-II tutorials

- Starting GSAS-II describes how the user interface works

- Fitting laboratory X-ray powder data for fluoroapatite
- CW Neutron Powder fit for Yttrium-Iron Garnet
- Combined X-ray/CW-neutron refinement of PbSO4
- Combined X-ray/TOF-neutron Rietveld refinement

MORE ADVANCED TUTORIALS

Parametric Rietveld fitting

- Sequential refinement of multiple datasets (prerequisite for next)
  - Parametric Fitting and Pseudo Variables for Sequential Fits

Structure solution

- Fitting individual peaks & autoindexing (prerequisite for next two)
  - Charge Flipping structure solution for jadarite
  - Charge Flipping structure solution for sucrose
- Charge Flipping structure solution with Xray single crystal data
- Charge flipping with neutron TOF single crystal data
- Monte-Carlo simulated annealing structure determination

MORE ADVANCED TUTORIALS (II)

Stacking Fault Modeling

- Stacking fault simulations for diamond
- Stacking fault simulations for Keokuk kaolinite
- Stacking fault simulations for Georgia kaolinite

Image Calibration/Integration

- Calibration of an area detector
- Integration of area detector data
- Calibration of a Neutron TOF diffractometer

MORE ADVANCED TUTORIALS (III)

Small-Angle Scattering

- Small angle x-ray data size distribution (alumina powder)
- Fitting small angle x-ray data (alumina powder)
- Image Processing of small angle x-ray data
- Sequential refinement with small angle scattering data

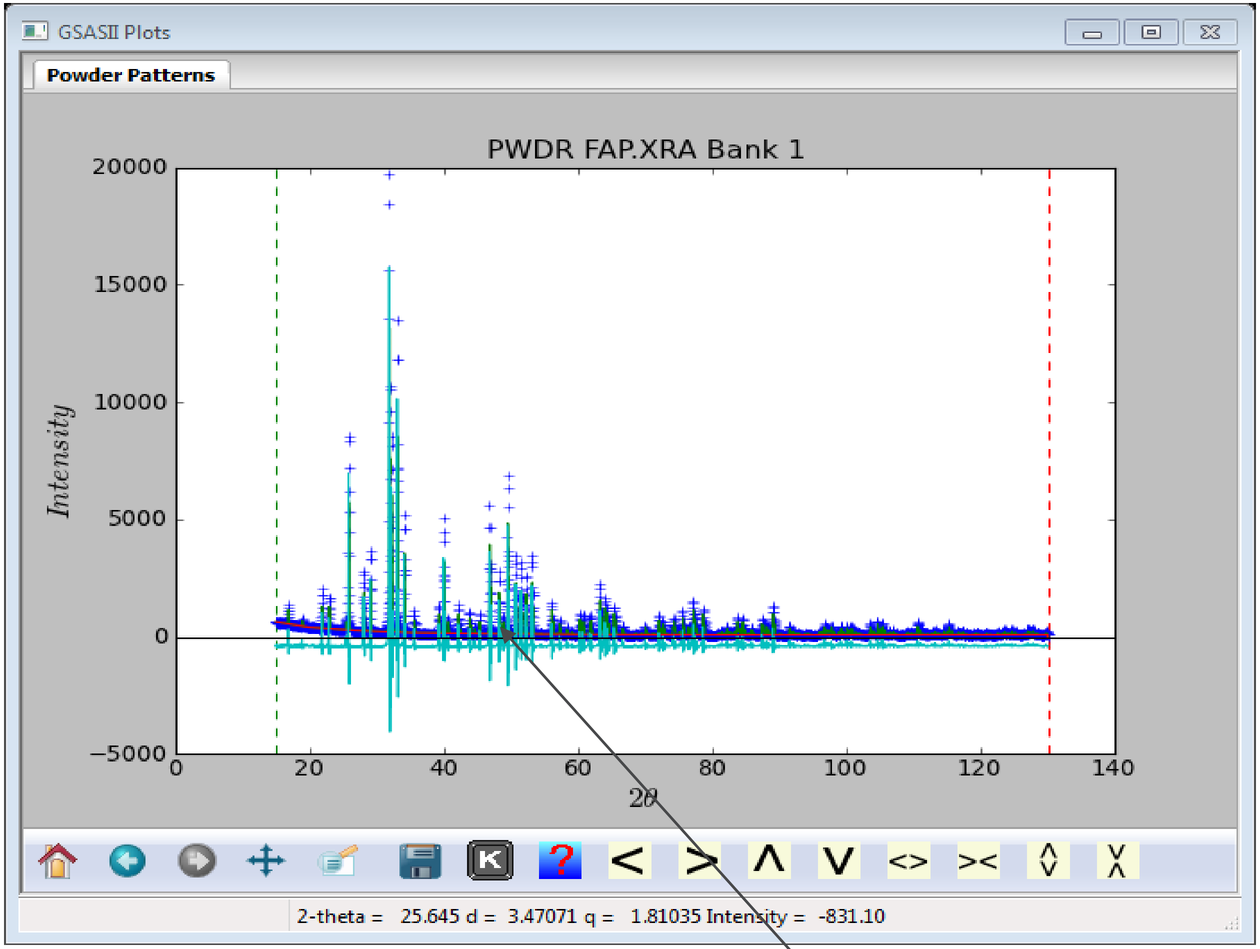
Other

- Texture analysis of 2D data
- Rietveld Refinement detail:
  - Fitting the Starting Background using Fixed Points
- Merohedral twin refinements
- Single crystal refinement from TOF data
- Scripting a GSAS-II Refinement from Python
- Strain fitting of 2D data

RIETVELD REFINEMENT – A SIMPLE EXAMPLE

AN EXAMPLE: FLUROAPATITE

Add atoms & do default initial refinement – scale & background

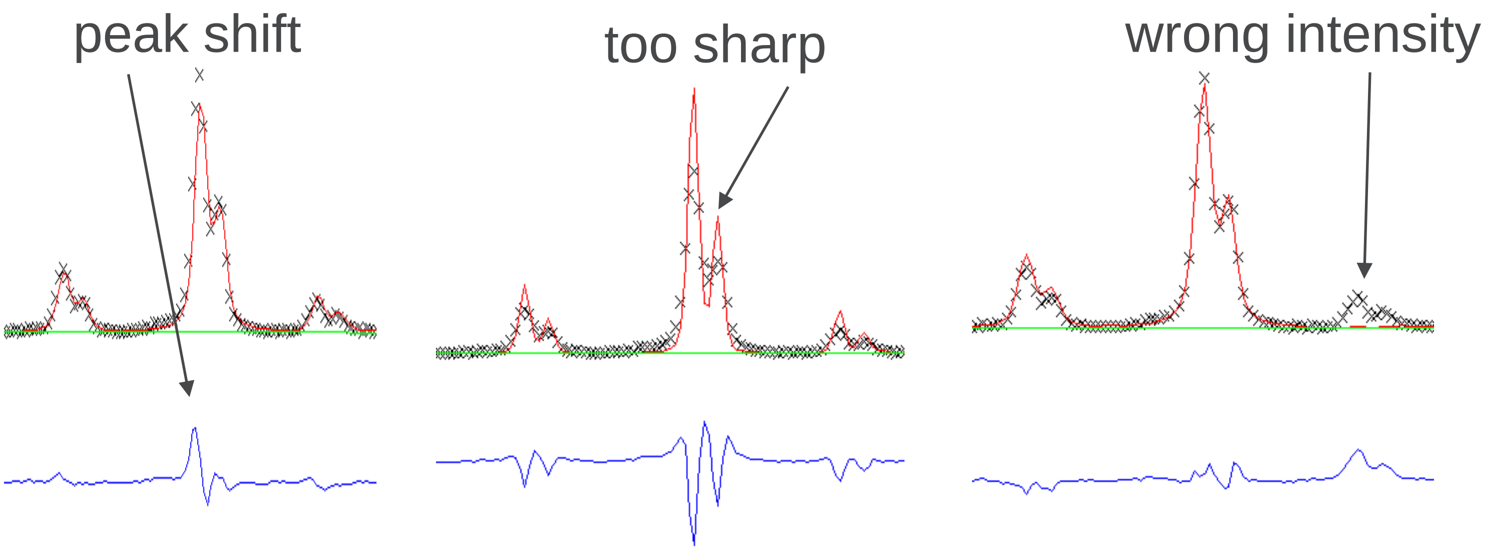


- Notice shape of difference curve – position/shape/intensity errors

ERRORS & PARAMETERS?

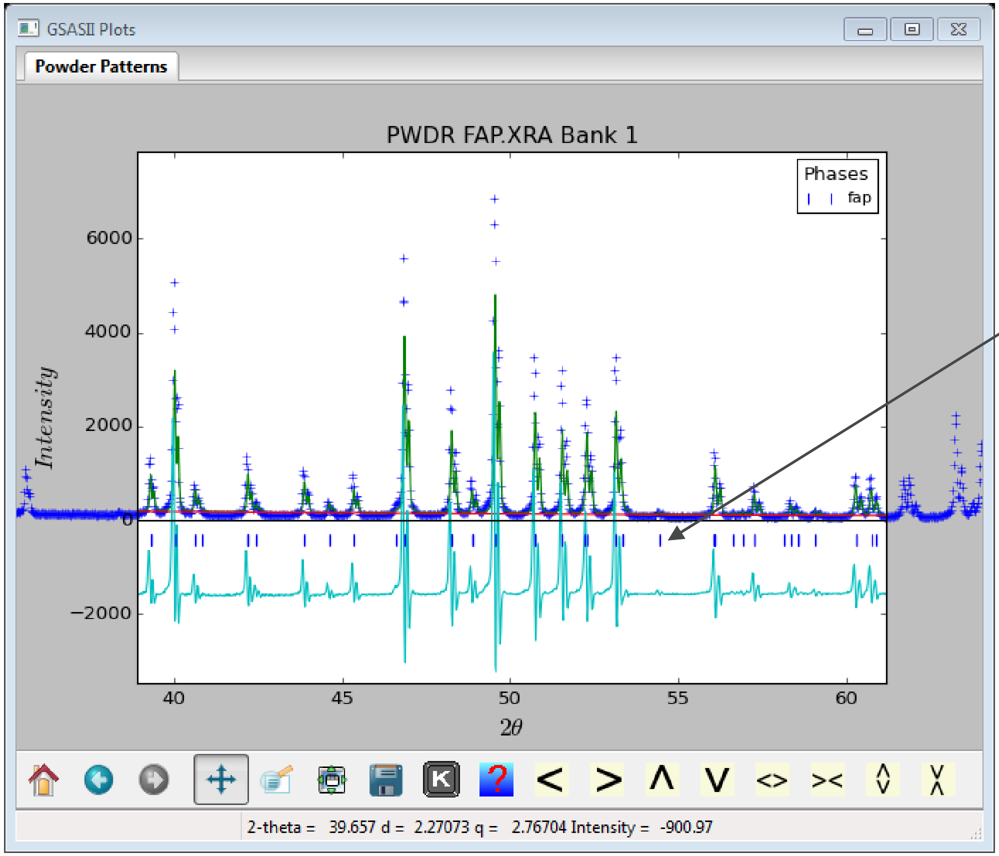
- position – lattice parameters, zero point (not common)
  - other systematic effects – sample shift/offset
- shape – profile coefficients – sample size/μstrain
  (U, V, W, X, Y, etc. in GSAS-II are instrument parms.)
- intensity – crystal structure (atom positions & thermal parameters)
  - other systematic effects (absorption/extinction/preferred orientation)

NB – get linear combination of all the above
NB^2 – trend with 2Θ (or TOF) important



a – too small   size - too large   Ca2(x) – too small

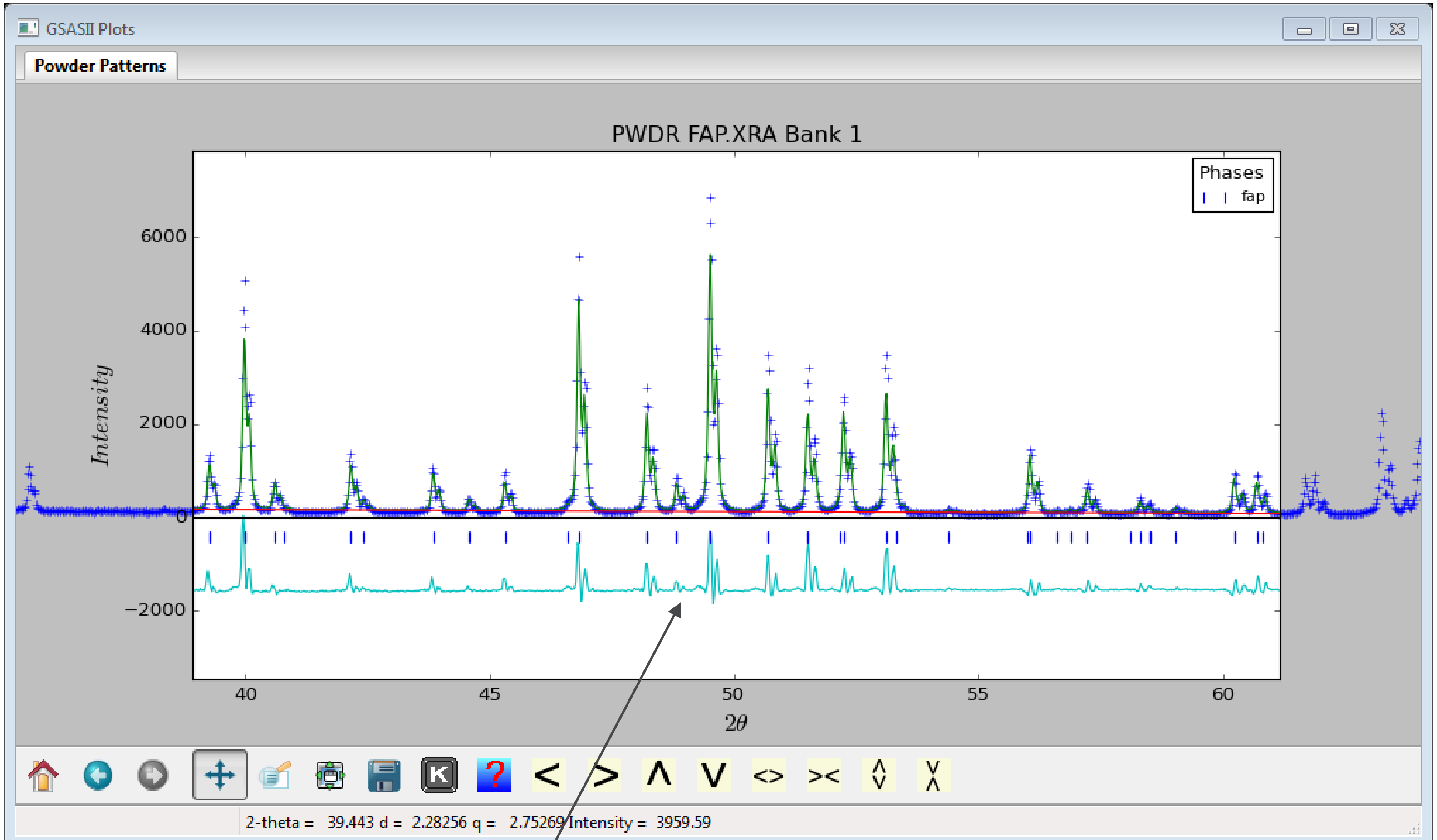
DIFFERENCE CURVE – WHAT TO DO NEXT?



Characteristic "up-down-up" →profile error
NB – can be "down-up-down" for too "fat" profile

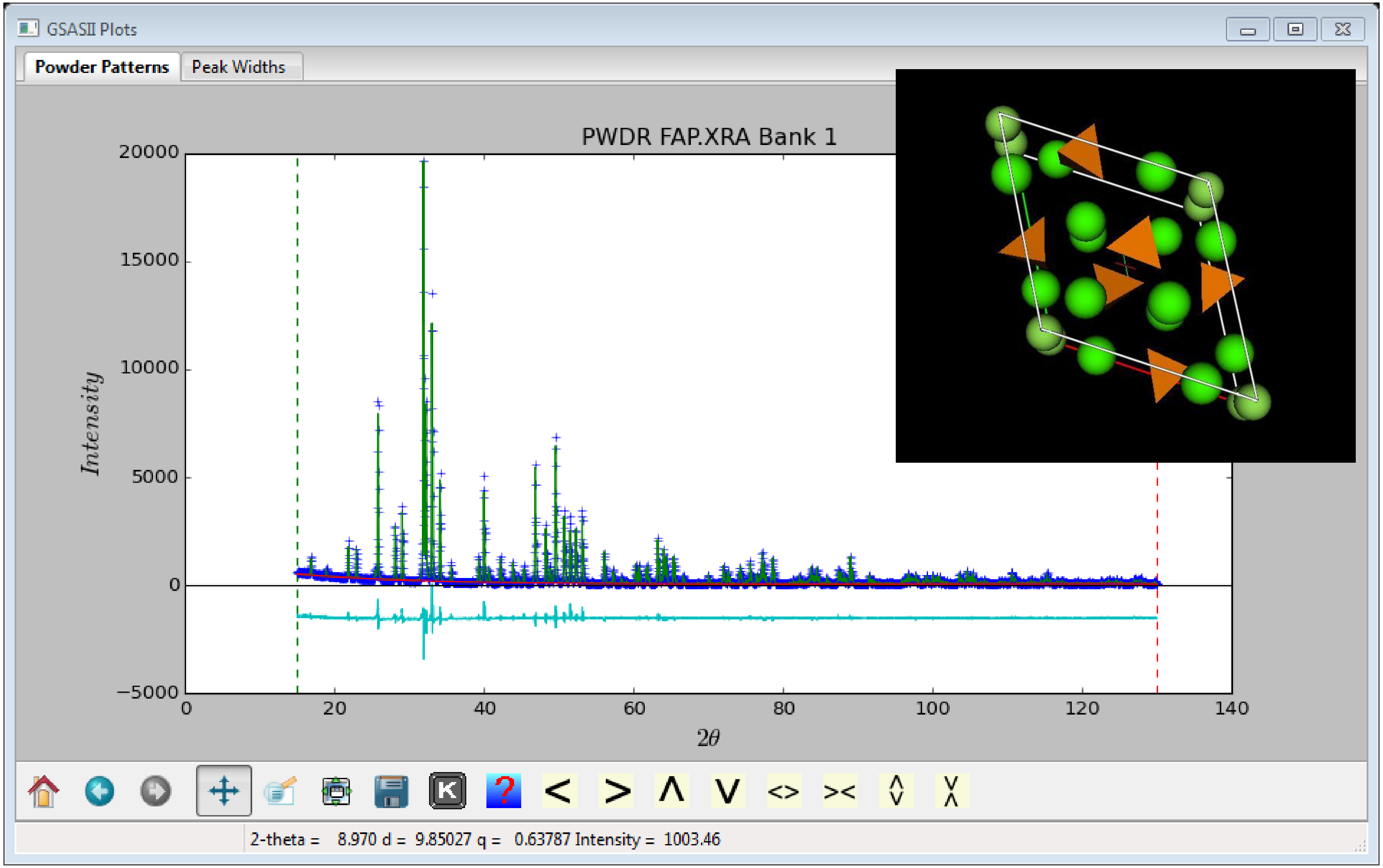
- Dominant error – peak positions? peak shapes - too sharp?
- Refine sample μstrain parameter next & include lattice parameters
- **<u>NB - EACH CASE IS DIFFERENT – no magic recipe</u>**

RESULT – MUCH IMPROVED!



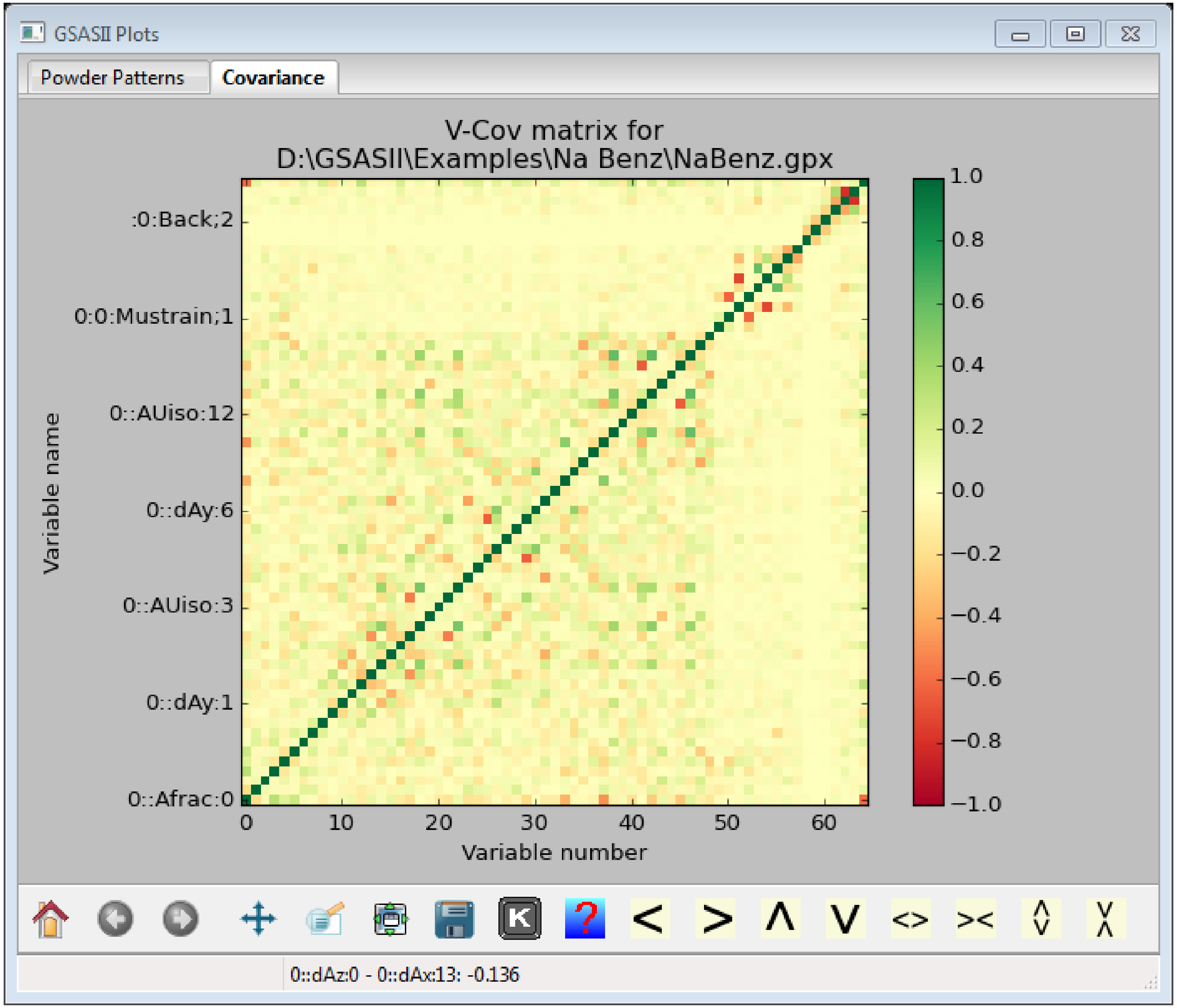
- **maybe intensity differences remain**
  - **– refine coordinates & thermal parms.**

RESULT – ESSENTIALLY UNCHANGED



- Thus, major error in the initial model –
  peak shapes & sample displacement/lattice parameters

A USEFUL PLOT – COVARIANCE MATRIX



Green: cov>0
Red: cov<0
Yellow: cov~0
Cursor reports:
Cov or value(esd) on diagonal
Can be zoomed!

Beware white bands & nan: Singularities!

A FEW FINAL WORDS

“A Rietveld refinement is never perfected, merely abandoned” (P. Stephens, 2000)

“Rietveld refinement is one of those few fields of intellectual endeavor wherein the more one does it, the less one understands.” (Sue Kesson)

“A Rietveld refinement is done when you run out of parameters” (R. Von Dreele)

Books:

Modern Powder Diffraction, Eds. J. Post & D. Bish (1989)

The Rietveld Method, Ed. R.A. Young (1993)

Powder Diffraction: Theory & Practice, Eds. R. Dinnebier & S. Billinge (2008)