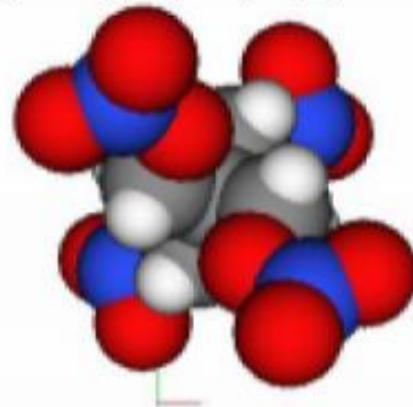


GSAS-II OVERVIEW (PARTS 1 & 2) GSAS-II TUTORIALS

GSAS-2



ROBERT VON DREELE
APS/ANL (retired)
vondreele@anl.gov

GSAS-II INSTALLATION

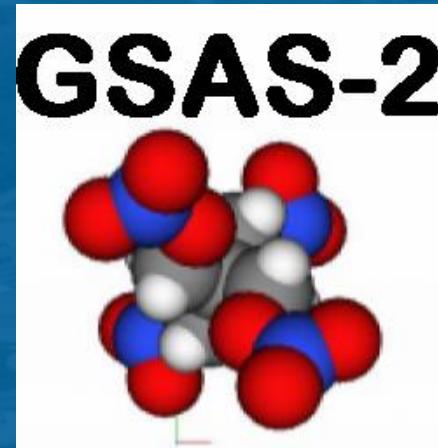
GSAS-II INSTALLATION

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; direct access via Help menu for GSAS-II.
 - **NB: Must have internet access!**
 - Usually installs in your personal space so no “authorizations” usually needed (unless your institution forbids it!)
 - Can be installed anywhere (even a memory stick – 5GB or more)
 - Don’t use the resulting GSAS-II directory for your project files; work elsewhere
 - **Update often!** Versions can change almost daily as we add/fix things. We work under the continuous software improvement model; not the fixed update schedule model commonly used by commercial software.

GSAS-II



GSAS-II: A MODERN ANALYSIS PACKAGE FOR ALL ASPECTS OF CRYSTALLOGRAPHY



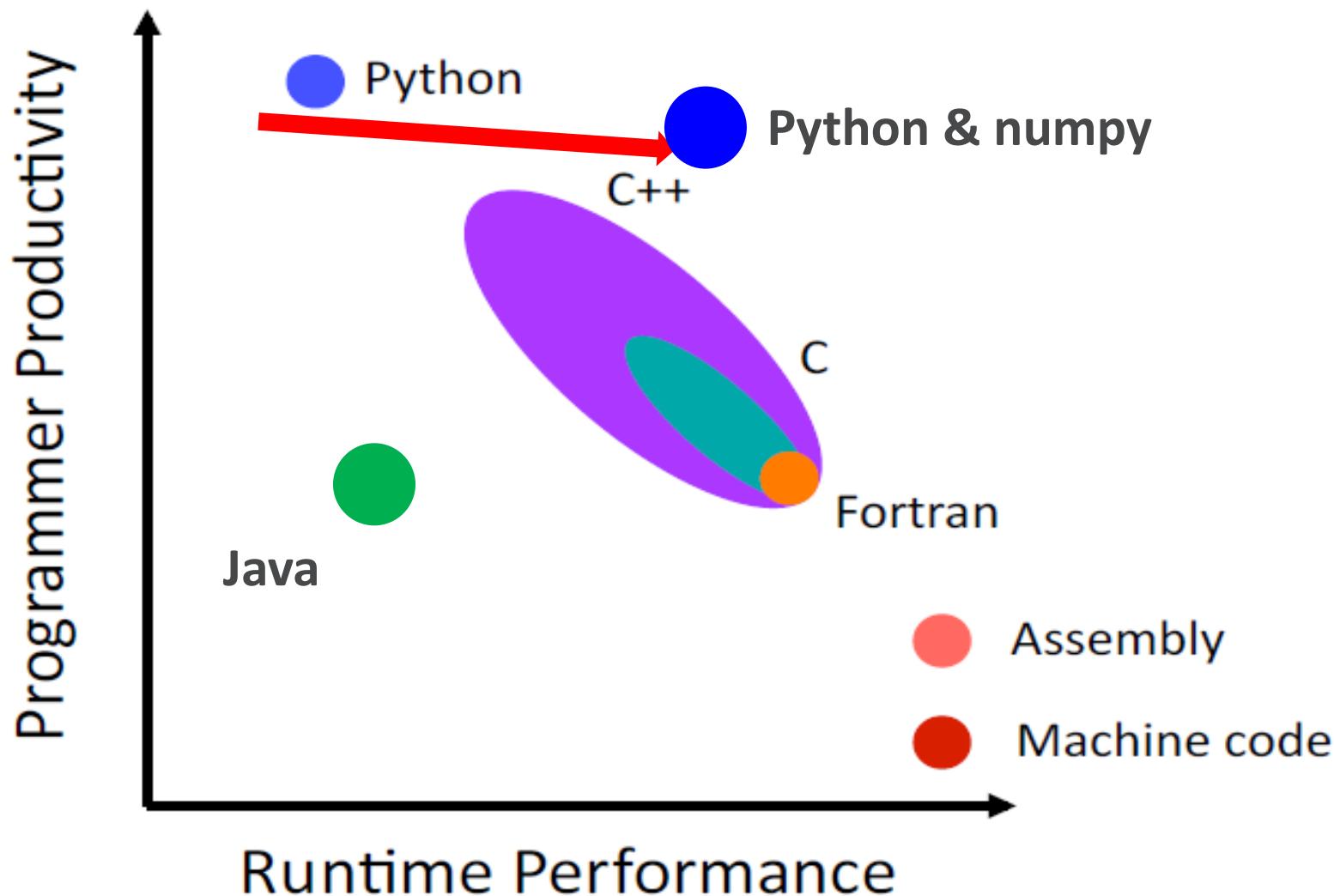
GSAS-II is intended to more than replace GSAS & EXPGUI with a new, modern, extensible, and open-source crystallographic analysis code

- Support all aspects of diffraction data analysis (from raw data to publication), including capabilities not in GSAS/EXPGUI
- Facile processing of large numbers of similar datasets
- Written with modern code (Python)
- Incorporates extensive visualization
- Use parameters that “make sense”
- Designed around GUI
- Design goal: Novice friendly, but expert efficient

GSAS-II reads powder diffraction images from all appropriate synchrotron & neutron beamlines, as well as the Curiosity Rover on Mars!

B.H. Toby and R.B. Von Dreele, "GSAS-II: The Genesis of a Modern Open-Source All-Purpose Crystallography Software Package". *Journal of Applied Crystallography*. **46**: p. 544-9 (2013).

WHY PYTHON – CHOICE OF LANGUAGES (~LOG SCALES?)



Based on: RW Grosse-Kunstleve, TC Terwilliger, NK Sauter & PD Adams,
Source Code for Biology and Medicine 2012, 7:5

WHY PYTHON?

Code snippet – charge flipping all inside a “while” loop

NB: CEhkl is F_{hkl} expanded over full sphere & zero filled out to 1/resolution limit as an array

Start with random phases for CEhkl

```

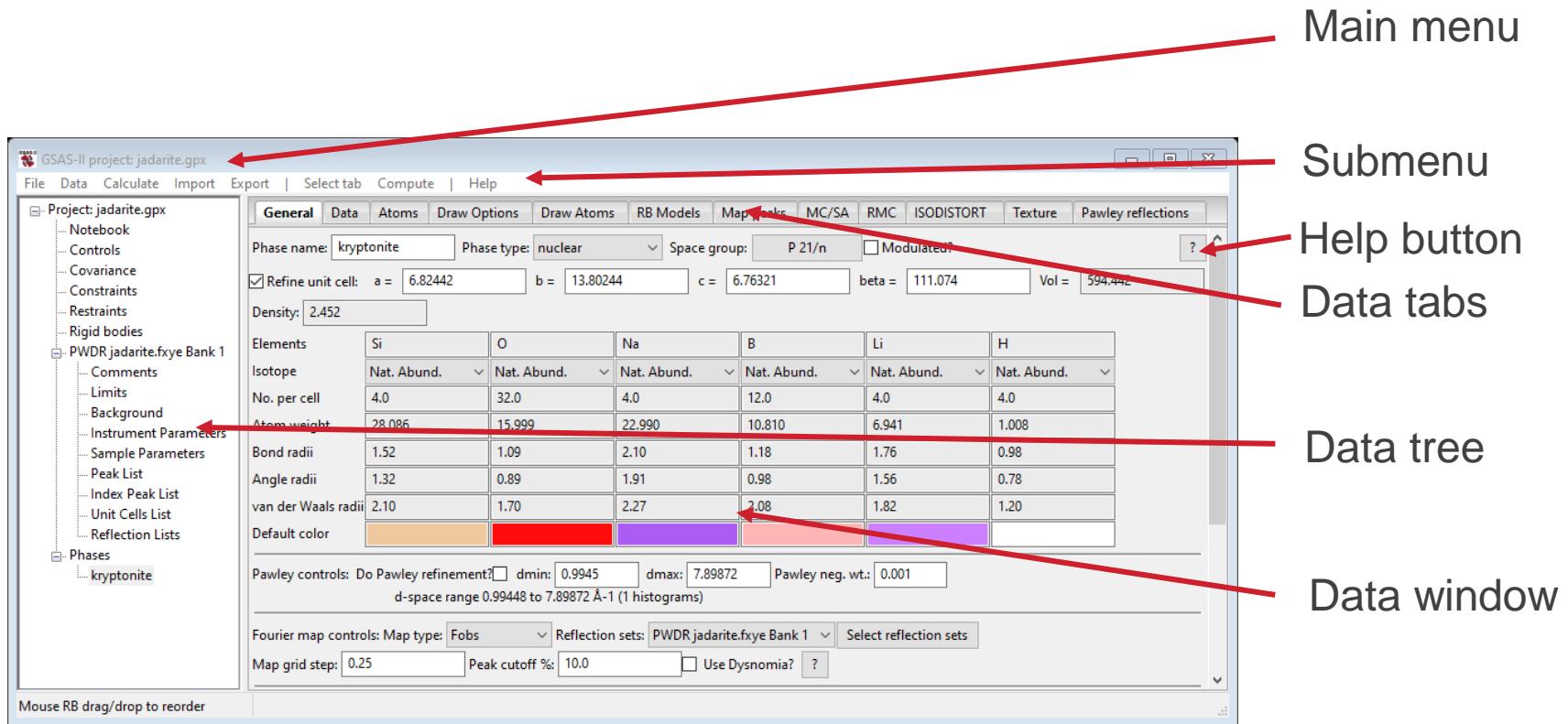
CErho = np.real(fft.fftn(fft.fftshift(CEhkl)))*(1.+0j)           #fft Fhkl → ρ(xyz)
CEsig = np.std(CErho)                                         #get σ(ρ)
CFrho = np.where(np.real(CErho) >= flipData['k-factor']*CEsig,CErho,-CErho) #CF ρ → ρ'
CFrho = np.where(np.real(CErho) <= flipData['k-Max']*CEsig,CFrho,-CFrho)   #U atom CF!
CFhkl = fft.ifftshift(fft.ifftn(CFrho))                      #fft ρ(xyz) → F'(hkl)
CFhkl = np.where(CFhkl,CFhkl,1.0)                            #avoid divide by zero
phase = CFhkl/np.absolute(CFhkl)                             # get φ(hkl) from F'
CEhkl = np.absolute(CEhkl)*phase                            #apply φ to F
Ncyc += 1                                                    #count tries
sumCF = np.sum(ma.array(np.absolute(CFhkl),mask=Emask))      #Σ F
DEhkl = np.absolute(np.absolute(Ehkl)/sumE-np.absolute(CFhkl)/sumCF) #ΣDF
Rcf = min(100.,np.sum(ma.array(DEhkl,mask=Emask)*100.))     #R-value for CF

```

NB: the 4D version is almost identical except that F_{hklm} is used

This stuff is fast! ~1s/cycle for 500K reflections/map points

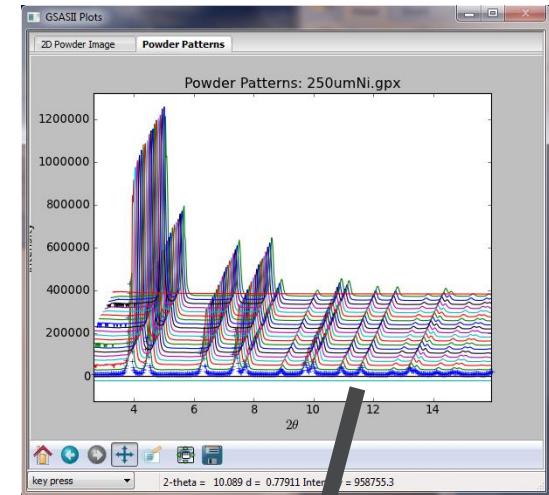
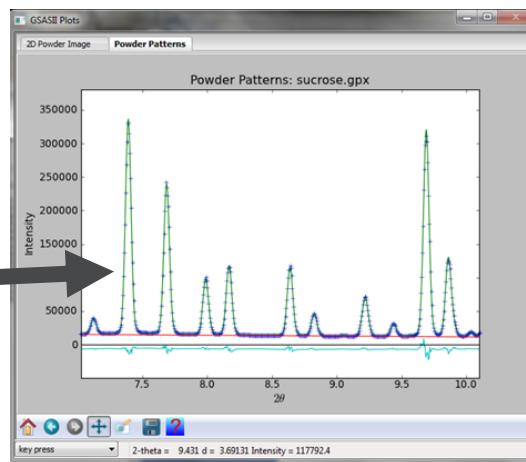
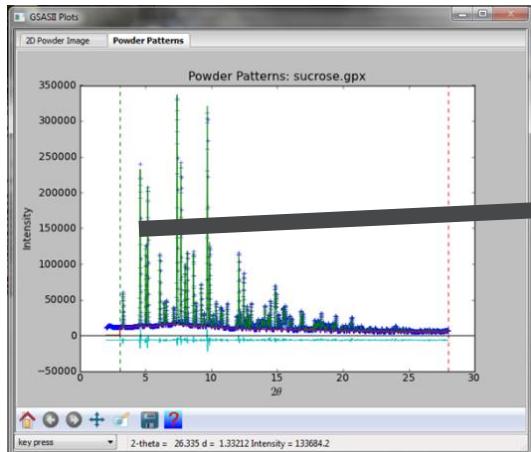
GSAS-II: MODERN GUI – 2 FRAME LAYOUT + CONSOLE



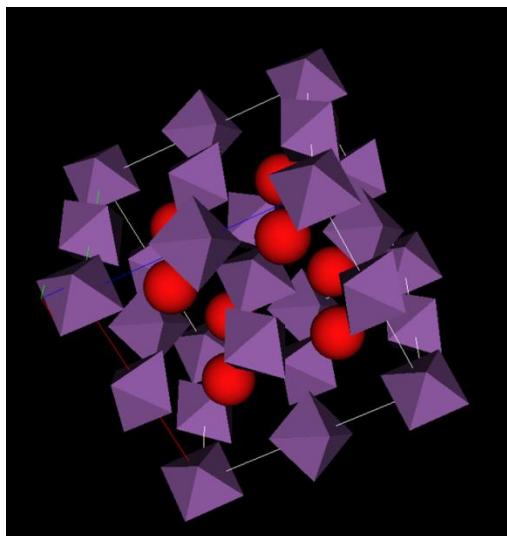
Plot & console in separate frames

THE PLOTS - ADVANCED VISUALIZATION

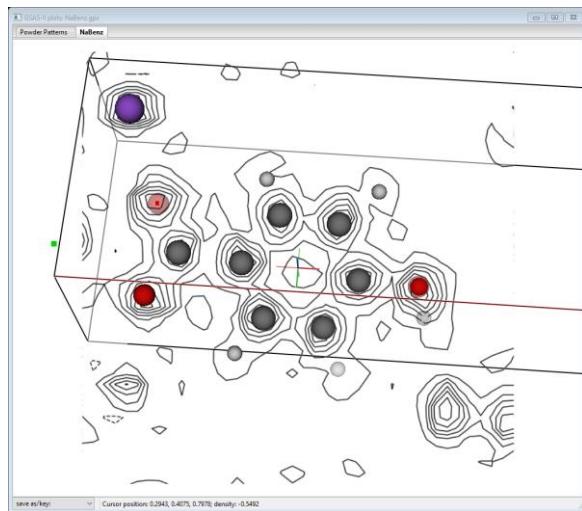
Powder profile – easy zoom



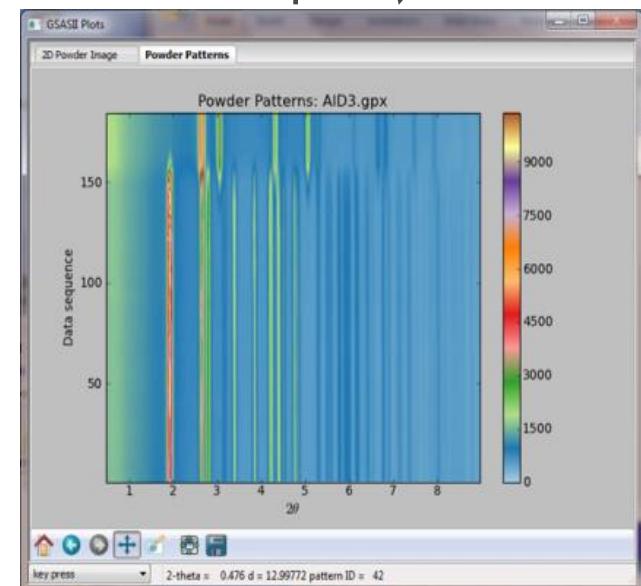
Waterfall plot



Structure drawing



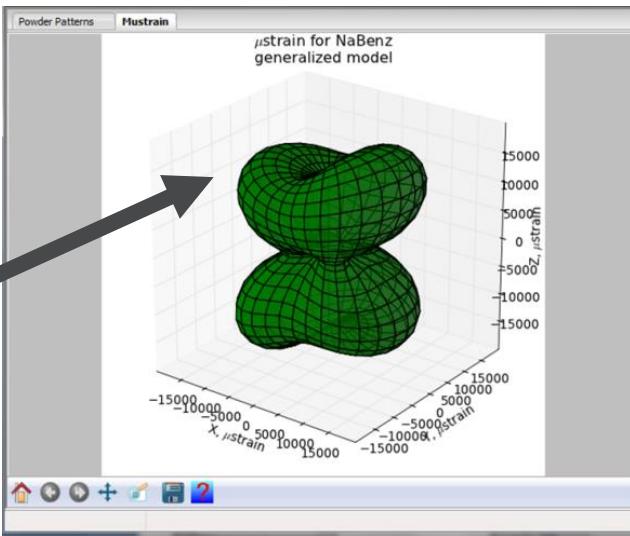
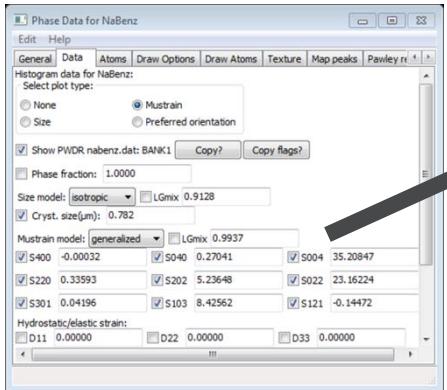
Contoured density thru
any plane



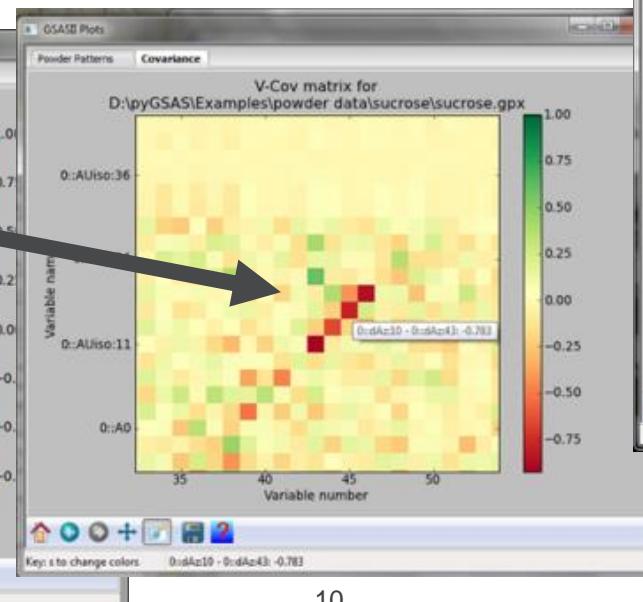
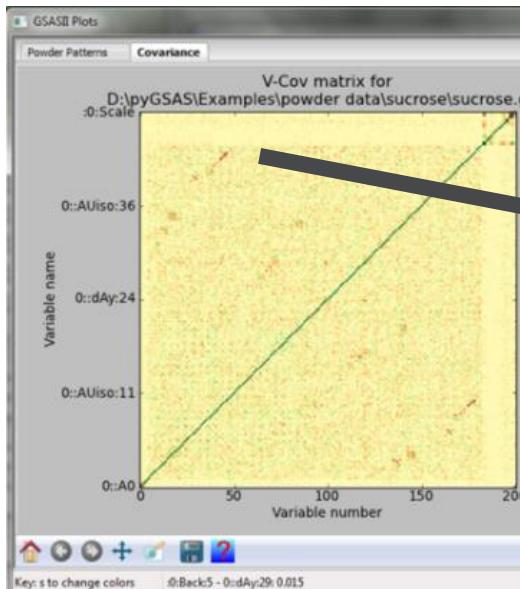
Contour plot

ADVANCED VISUALIZATION IN GSAS-II: NUMBERS AS PICTURES

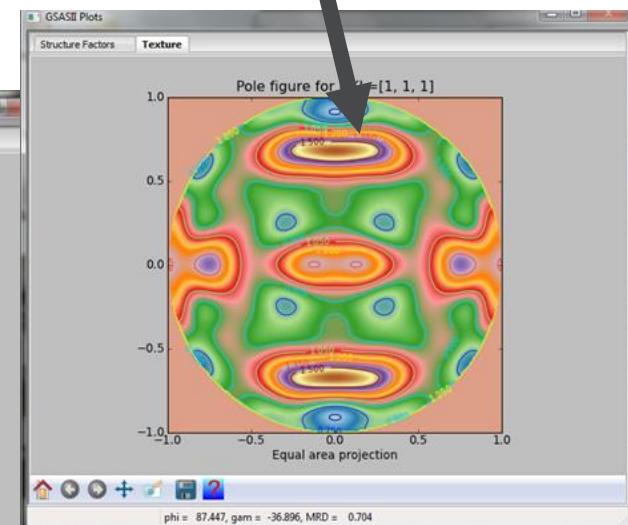
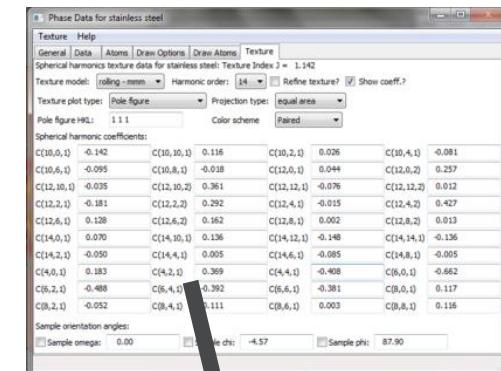
μ strain surface



v-cov matrix



Texture – sph. harmonics



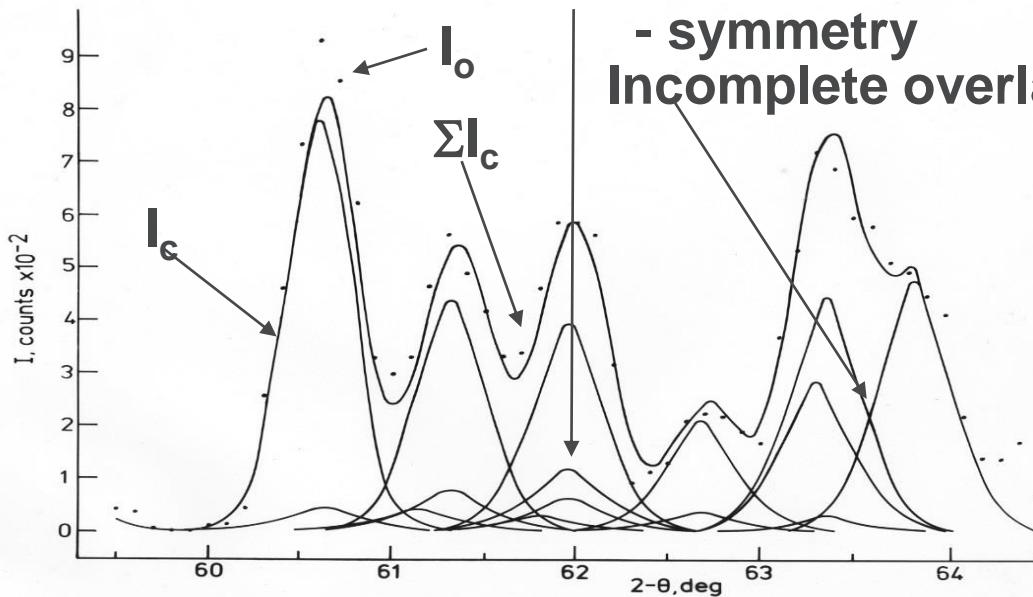
RIETVELD REFINEMENT IN GSAS-II

HISTORY – H.M. RIETVELD



Hugo Rietveld; neutron powder diffractometer, Petten, Netherlands
Papers: H.M. Rietveld, Acta Cryst. 22, 151-2(1967)
H.M. Rietveld, J. App. Cryst., 2, 65-71 (1969)

Multi-parameter, nonlinear LS curve
Exact overlaps



- symmetry
Incomplete overlaps

Residuals:

$$R_{wp} = \sqrt{\frac{\sum w(I_o - I_c)^2}{\sum wI_o^2}}$$

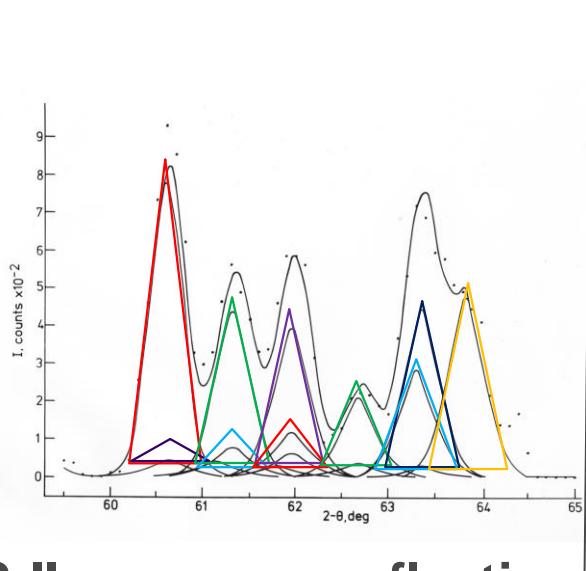
Rietveld Minimize

$$M_R = \sum w(I_o - I_c)^2$$

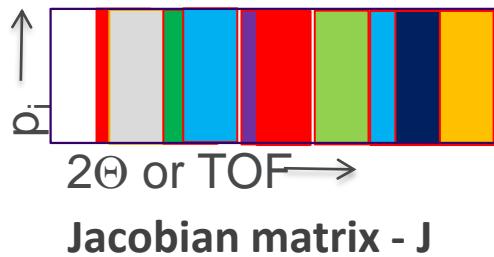
“chi-squared” or
“goodness-of-fit”

$$\chi^2 = M_R / (n-p)$$

GSAS-II ALGORITHM

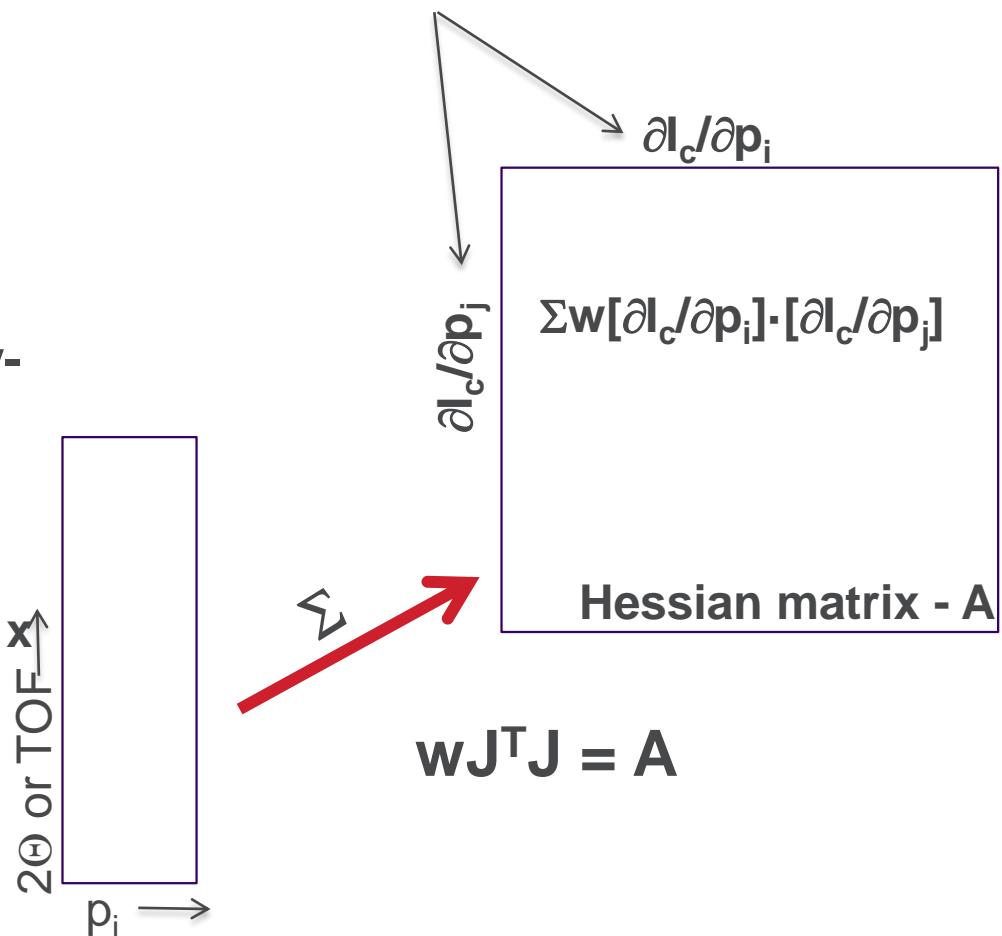


GSAS-II – process reflection-by-reflection to make \mathbf{I}_c (vector) & $\partial\mathbf{I}_c/\partial\mathbf{p}_i$ (Jacobian matrix)



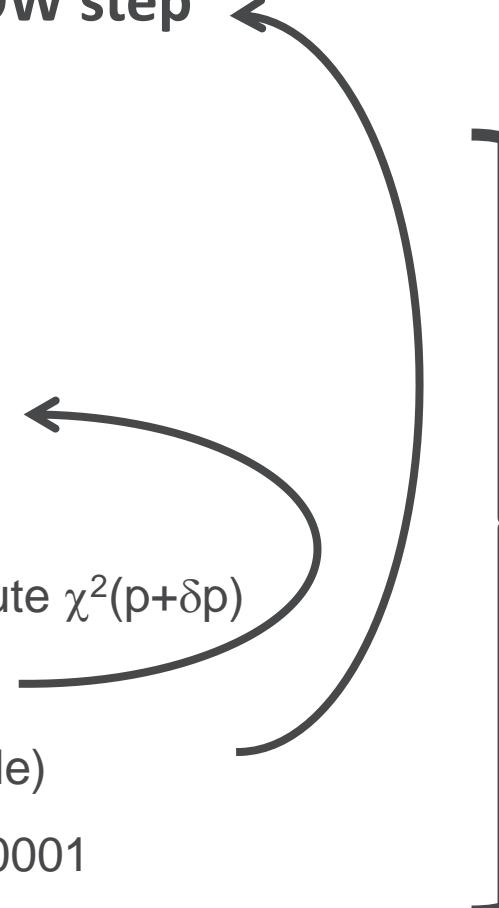
NB: GSAS-II – needs large memory!

GSAS & other software(?) – process point-by-point to make \mathbf{I}_c (value) & $\partial\mathbf{I}_c/\partial\mathbf{p}_i$ (vector)



REFINEMENT VIA MODIFIED LEVENBERG/MARQUARDT-SVD ALGORITHM

Steps:

1. Compute $A_{ij} = \sum w \frac{\partial I_c}{\partial p_i} \frac{\partial I_c}{\partial p_j}$ **SLOW step**
 2. Normalize $A'_{ij} = A_{ij} / \sqrt{A_{ii} A_{jj}}$
 3. compute $\chi^2(p)$
 4. Select $\lambda (=0.001, \text{"damping factor"})$
 5. Modify $A''_{ii} = A'_{ii}(1 + \lambda)$
 6. **Make SVD inversion of A"**
 7. Solve for δp (unnormalized!) & compute $\chi^2(p+\delta p)$
 8. If $\chi^2(p+\delta p) > \chi^2(p)$ then $\lambda * 10$ go to 5
 9. Else apply δp to p & go to 1 (new cycle)
 10. Quit when $\chi^2(p) - \chi^2(p+\delta p) / \chi^2(p) < 0.0001$
- 

NB: all in ~40 lines of python; all double precision

NB²: this thing is exceedingly robust – no user damping factors needed

SVD – SINGULAR VALUE DECOMPOSITION

Singularities & near singularities – see Mathematical Recipes 2.9

LS matrix: solve for x $Ax=b$ by $x=A^{-1}b$; x are the parameter shifts

SVD: replace $A = UwV$ where U & V are such that $U^{-1} = U^T$ & $V^{-1} = V^T$
& w – diagonal matrix; all same size as A

Then: $A^{-1} = V(1/w_{ii})U^T$

The trick: what to do if $w_{ii} \sim 0$? (singularity) → make $1/w_{ii} = 0!$ (instead of ∞)

Then: $x = V(1/w_{ii})U^Tb$ does away with ill-conditioned terms

Have to choose tolerance on $w_{ii} \sim 0$ (typically 10^{-6} but 10^{-3} for proteins works well)

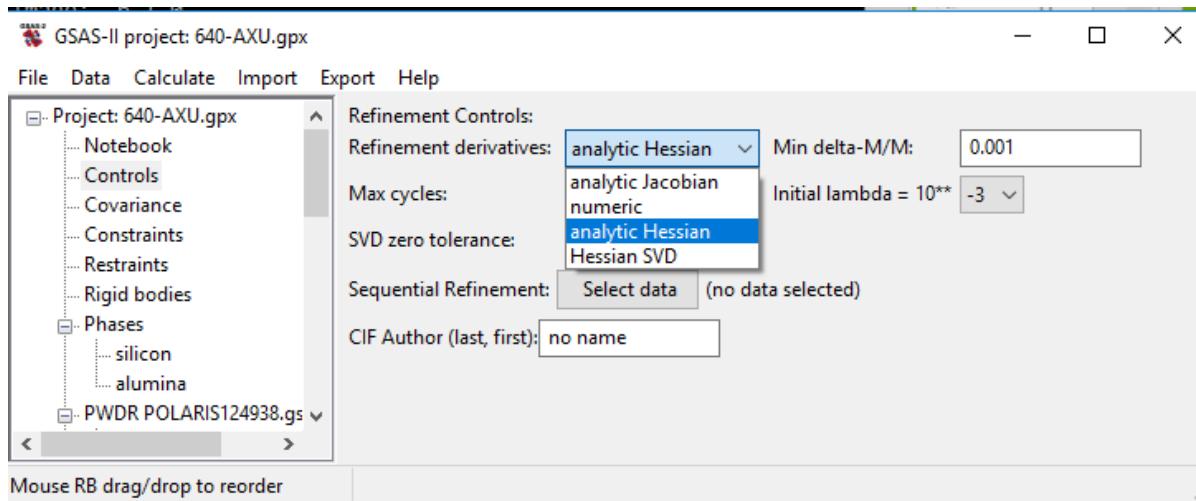
SVD is in python library as `numpy.linalg.svd`

& uses LAPACK _gesdd routine (fortran – code in MR 2.9)

NB: all double precision in python; downside is w_{ii} not 1:1 to parameters so id of failures difficult.

LEAST SQUARES ALGORITHMS IN GSAS-II

Useful choices – found in Controls



Analytic Hessian – default Levenberg-Marquardt SVD from Hessian & computed derivatives. Downside: hard singularities hard to find → “linear algebra errors” cause failures

Analytic Jacobian – uses Jacobian matrix (not Hessian) no SVD; identifies singularities & removes them from LS refinement; always runs to convergence

Hessian SVD – no Levenberg-Marquardt (might be better for single crystal data)
Same downside as Analytic Hessian

Numeric – no derivatives & slow – mostly for testing purposes.

LEAST SQUARES THEORY - CONTINUED

Error estimates (mostly from W.C. Hamilton)

Given observations $n > m$ parameters

with distributions that have finite 2nd moments

(no need to be “normal” although usually are for powders)

Then LS gives parameter estimates (shifts in our case)

with the minimum variance in any linear combination

The error estimates (“esd’s”) are

$$\sigma_i = \sqrt{\frac{b_{ii}}{\chi^2}} \quad \chi^2 = \frac{\sum w(I_o - I_c)^2}{n-m}$$

b_{ii} - diagonal elements of the inverted A matrix

Note: There is little justification for additional scaling of
the σ_i **NB: systematic errors will bias results beyond σ_i .**

$$\text{RIETVELD MODEL: } I_C = I_I \{ \sum K_p F_p^2 M_p L_p P(\Delta_p) + I_B \}$$

I_i - incident intensity - variable for fixed 2Θ (e.g. neutron TOF)

k_p - scale factor for particular phase

F_p^2 - structure factor for particular reflection

m_p - reflection multiplicity

L_p - correction factors on intensity - texture, etc.

$P(\Delta_p)$ - peak shape function - size & microstrain, etc.

Sum over all reflections under a profile point (multiple phases)

I_b – background function

More complex model than for single crystal diffraction

PROFILE FUNCTIONS $P(\Delta_p)$ – BASICS

$$\Delta_p = T_{\text{reflection}} - T_{\text{profile}} \quad (T = 2\Theta \text{ or TOF})$$

Gaussian profile - generally instrumental origin

$$G(\Delta T, \Gamma) = \sqrt{\frac{4 \ln 2}{\pi \Gamma^2}} \exp\left[\frac{-4 \ln 2 (\Delta T)^2}{\Gamma^2}\right]$$

Lorentzian profile - largely sample effect

$$L(\Delta T, \gamma) = \frac{2}{\pi \gamma} \frac{1}{1 + \left(\frac{2\Delta T}{\gamma}\right)^2}$$

Voigt – convolution = $\mathbf{G} \otimes \mathbf{L}$

Pseudo-Voigt – linear combination = $\eta \mathbf{L} + (1-\eta) \mathbf{G}$

η via Thompson, Cox & Hastings – pseudoVoigt = Voigt

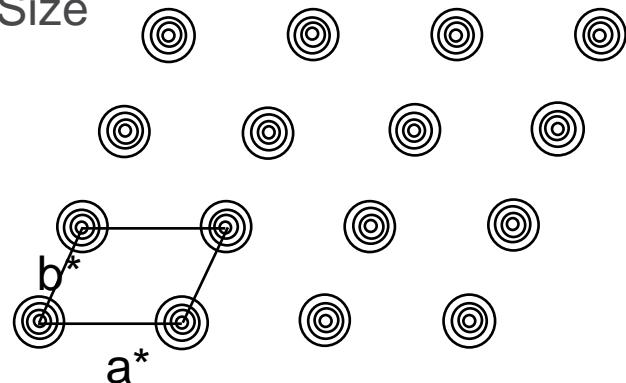
CW Asymmetry from axial divergence – Finger, Cox & Jephcoat

NB: in gsas & GSAS-II, T is 2Θ in centideg or TOF in μs

SAMPLE BROADENING

Isotropic Crystallite size & μ strain broadening

Size



Small ($<1\mu\text{m}$) crystals \rightarrow not δ -functions

Size distribution \rightarrow

superposition of sharp to broad spots

\rightarrow Shape \sim Lorentzian

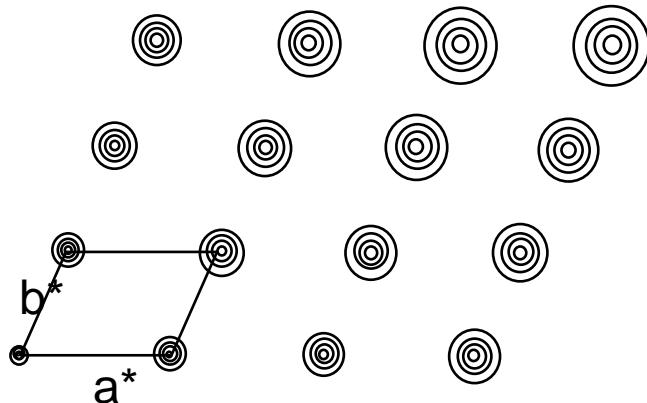
Width $\Delta d^* = \text{constant} = \Delta d/d^2 = \Delta\Theta \cot\Theta/d$

Bragg's Law: $\Delta 2\Theta = \lambda \Delta d/d^2 \cos\Theta$ ($= X/\cos\Theta$)

\rightarrow Scherrer equation

$$k=1, p = \text{size} \quad S = \frac{180k\lambda}{\pi p \cos \theta}$$

μ strain



Unit cell variation (defects??)

Lorentzian distribution \rightarrow shape

$\Delta d/d = \text{constant} = \Delta d^*/d^* = \Delta\Theta \cot\Theta$

Or: $\Delta 2\Theta = 2\Delta d \tan\Theta/d$ ($= Y \tan\Theta$)

$$M = 180\mu \tan \Theta / \pi$$

μ – μ strain ($\times 10^6$) parameter

CW PROFILE COEFFICIENTS

Lorentzian vs Gaussian sample broadening?

- Size:

$$S = \frac{180k\lambda}{\pi p \cos \theta} \quad \mu\text{strain:} \quad M = 180\mu \tan \Theta / \pi$$

- Need: S_Γ (Gauss) & S_γ (Lorentzian) sample broadening (2 slides back)

$$\Gamma_g^2 = 8\ln 2(U\tan^2\Theta + V\tan\Theta + W + S_\Gamma)$$

$$\gamma = \frac{X}{\cos\Theta} + Y\tan\Theta + Z + S_\gamma$$

- Mixing coeff for each; m_s & m_μ (NB: called 'mx' in GSAS-II; range 0-1)

$$S_\gamma = m_s S + m_\mu M$$

$$S_\Gamma = [(1 - m_s)^2 S^2 + (1 - m_\mu)^2 M^2] / 8\ln 2$$

- Normally m_s & $m_\mu = 1$ (all Lorentzian sample broadening) so:

$$S_\gamma = S + M$$

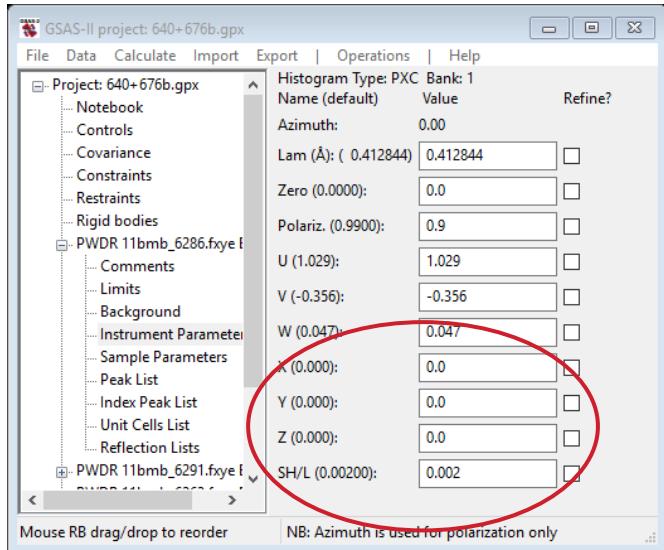
$$S_\Gamma = 0 \quad (\text{no Gaussian sample broadening})$$

- $X, Y, Z = 0$ (no Lorentzian instrument broadening)

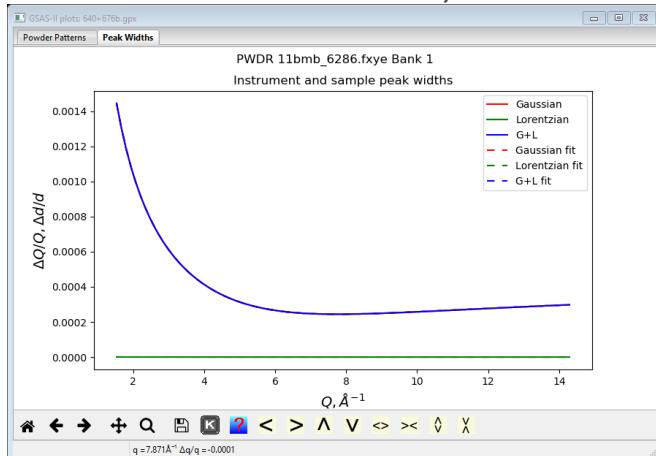
CW PROFILE PEAK BROADENING IN GSAS-II

The split of sample broadening from instrumental contribution

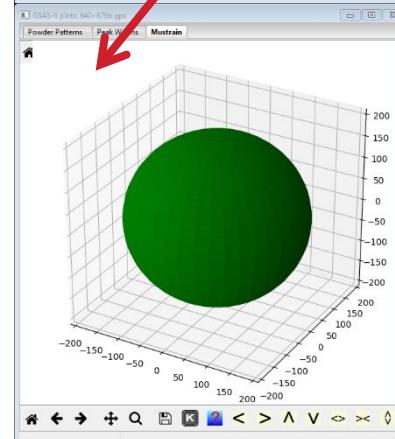
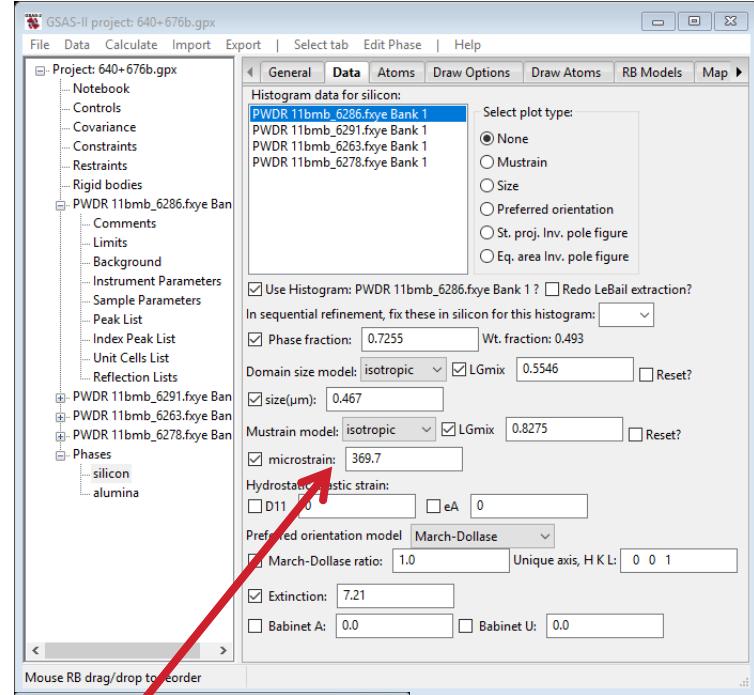
Instrument – fixed from calibration



NB: for APS 11BM X,Y & Z = 0



Sample – phase & histogram dependent
Refined & constrained as needed

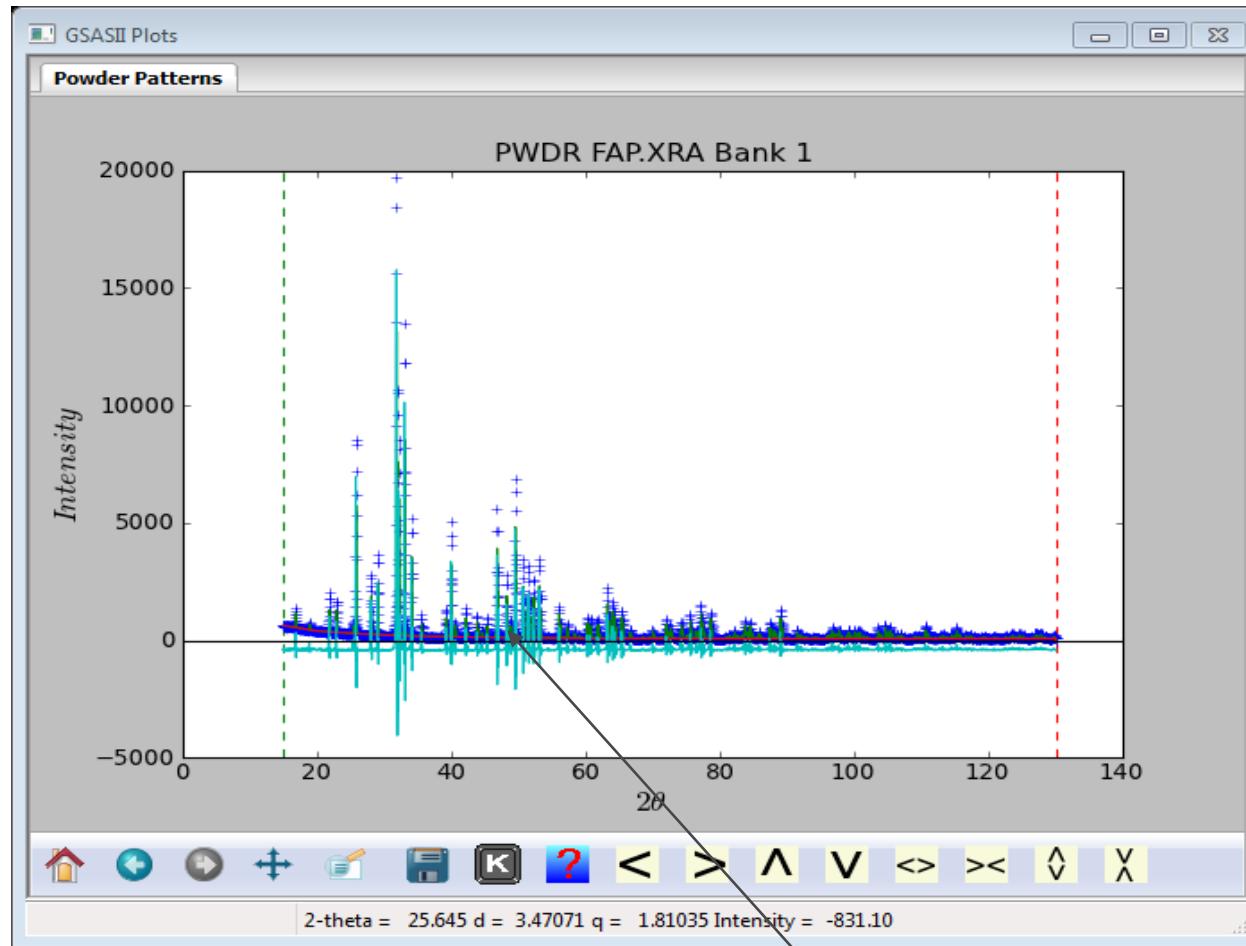


Sample:
New NIST SRMS
640f & 676b

RIETVELD REFINEMENT – A SIMPLE EXAMPLE

AN EXAMPLE: FLUROAPATITE

Add atoms & do default initial refinement
– scale & background



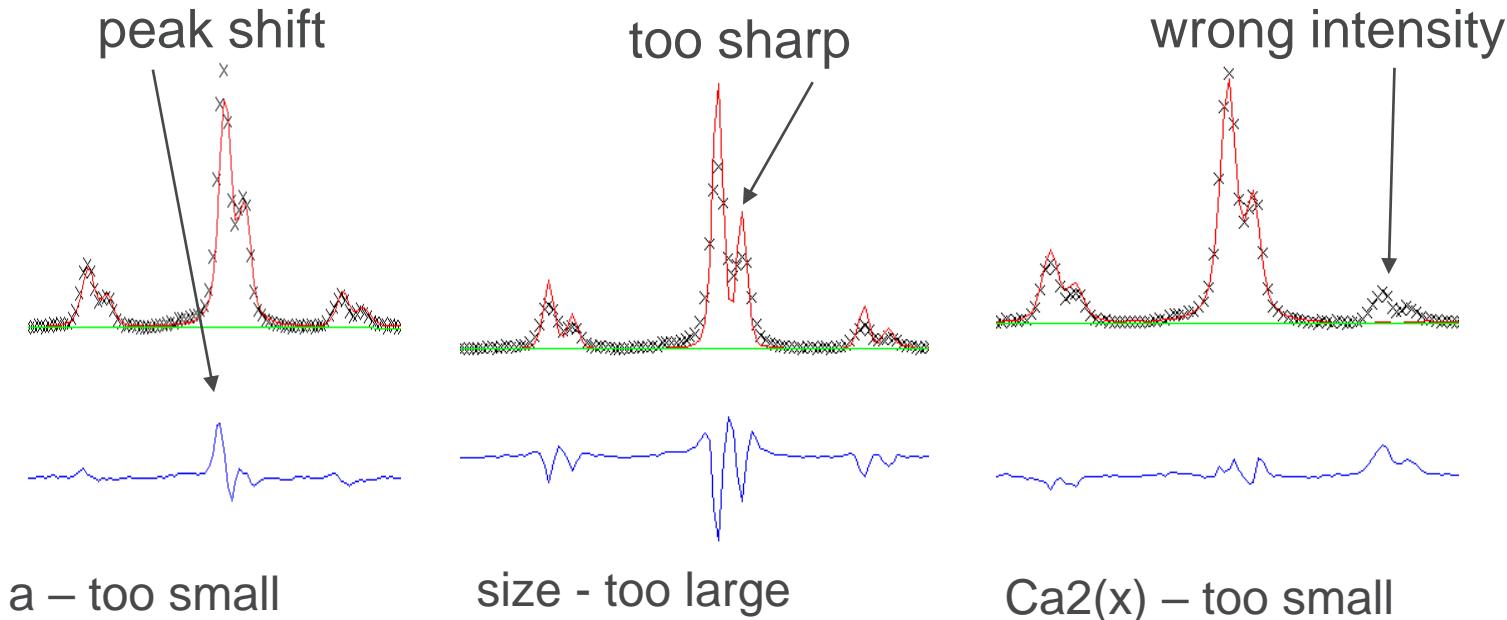
- Notice shape of difference curve – position/shape/intensity errors

ERRORS & PARAMETERS?

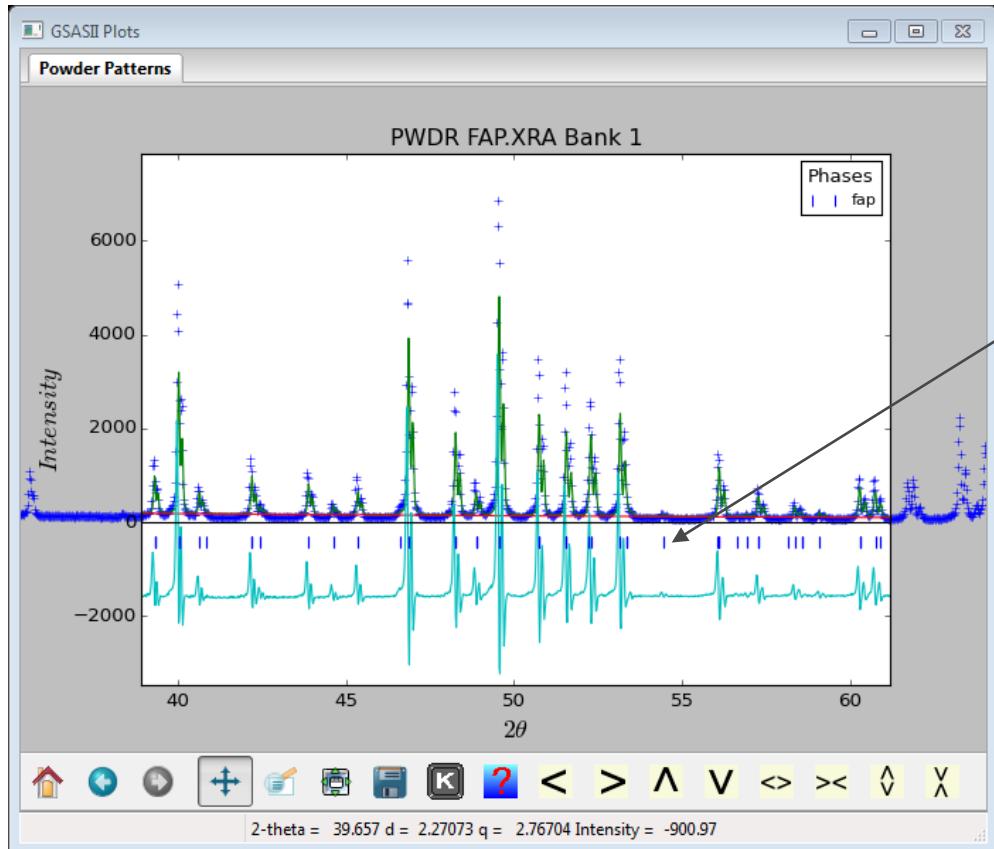
- position – lattice parameters, zero point (not common)
 - other systematic effects – sample shift/offset
- shape – profile coefficients – sample size/ μ strain
(U, V, W, X, Y, etc. in GSAS-II are instrument parms.)
- intensity – crystal structure (atom positions & thermal parameters)
 - other systematic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

NB – get linear combination of all the above

NB² – trend with 2Θ (or TOF) important



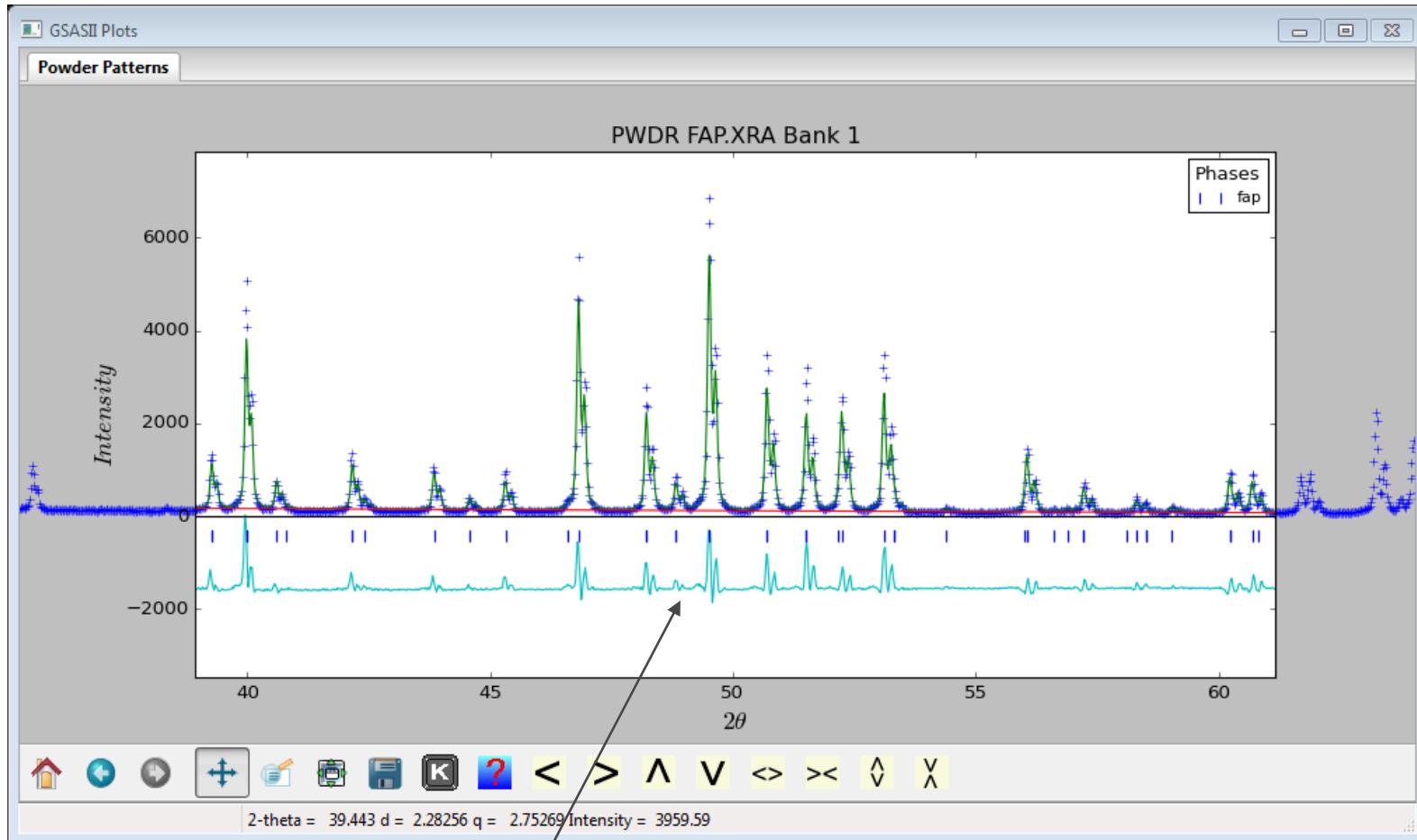
DIFFERENCE CURVE – WHAT TO DO NEXT?



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

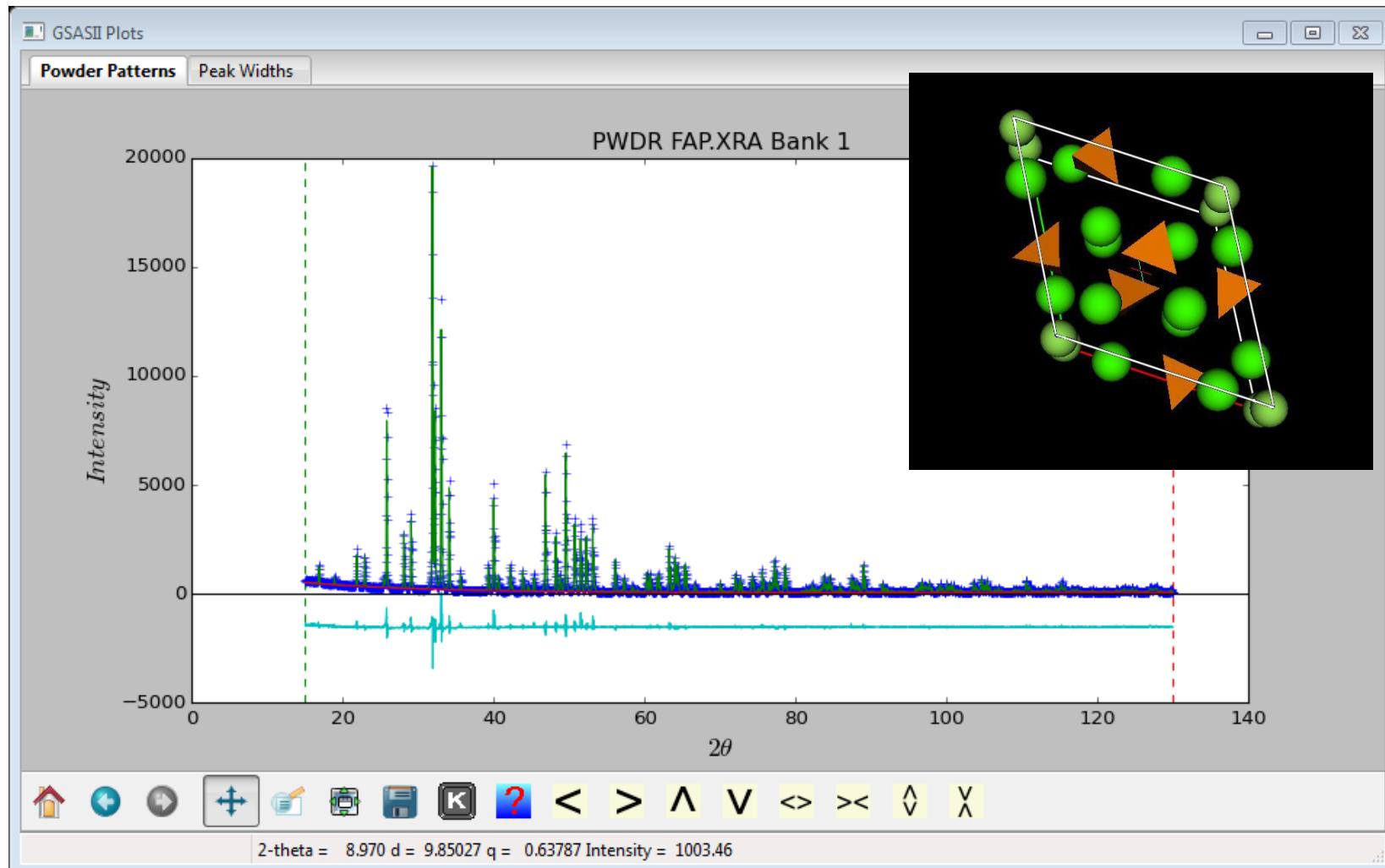
- Dominant error – peak positions? peak shapes - too sharp?
- Refine sample μ strain parameter next & include lattice parameters
- **NB - EACH CASE IS DIFFERENT – no magic recipe**

RESULT – MUCH IMPROVED!



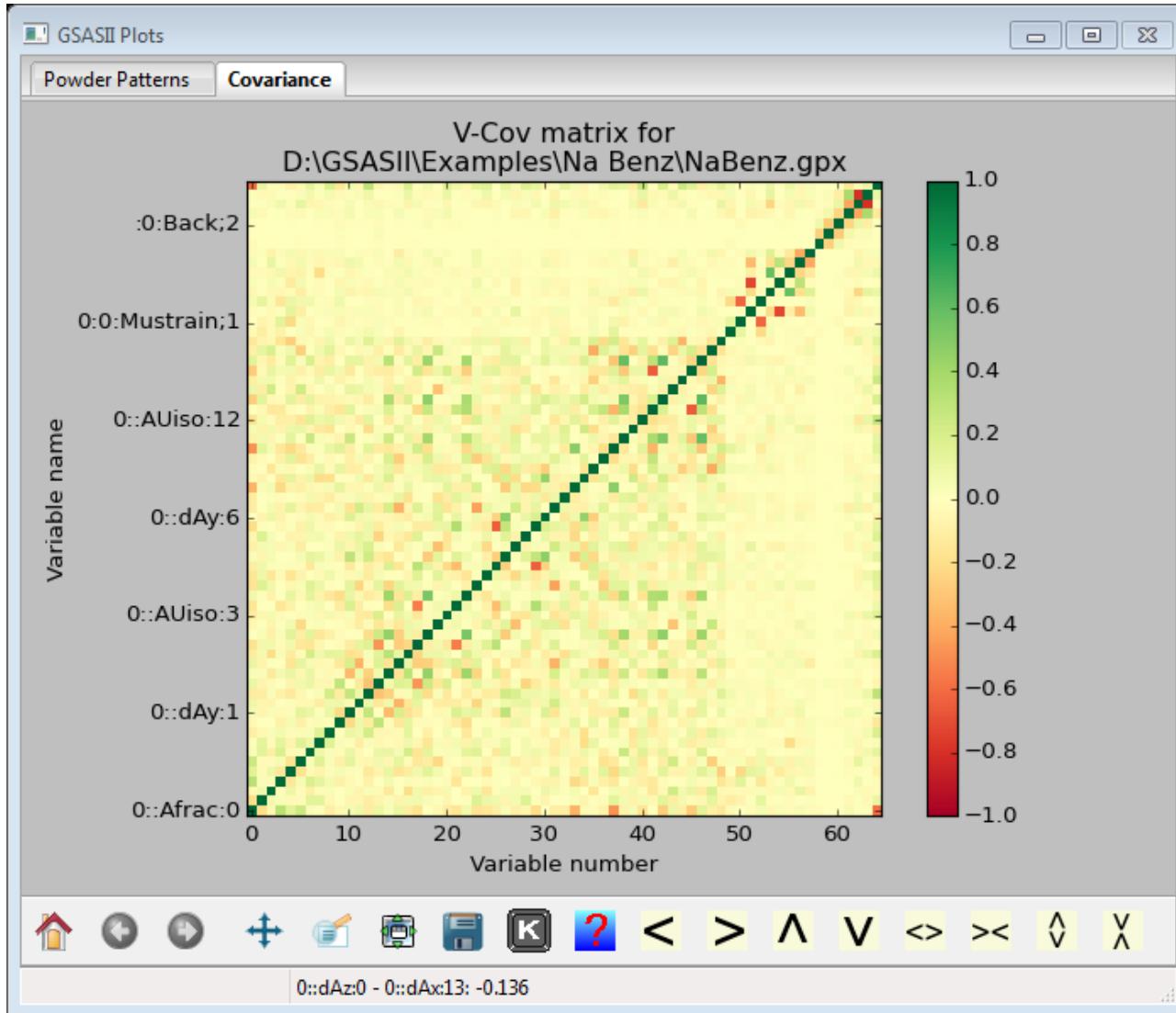
- maybe intensity differences remain
 - refine coordinates & thermal parms.

RESULT – ESSENTIALLY UNCHANGED



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

A USEFUL PLOT – COVARIANCE MATRIX



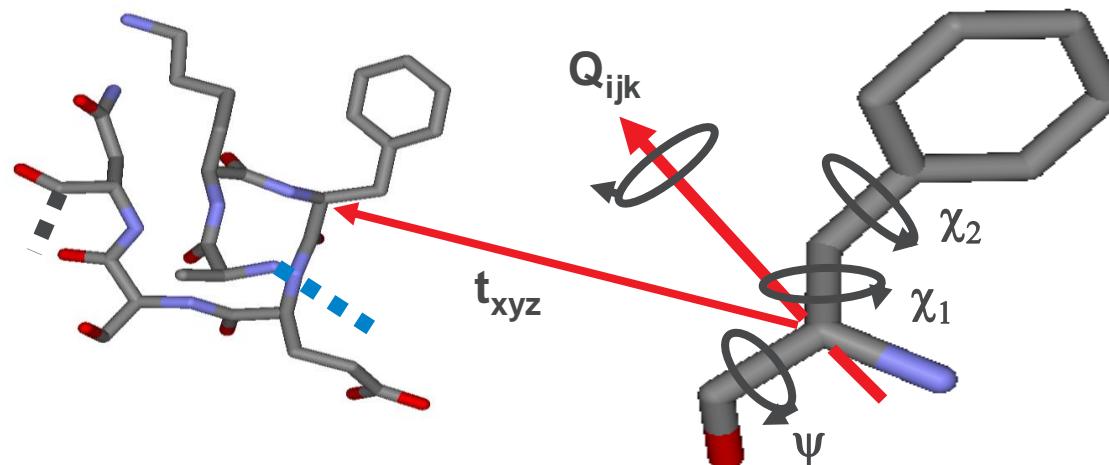
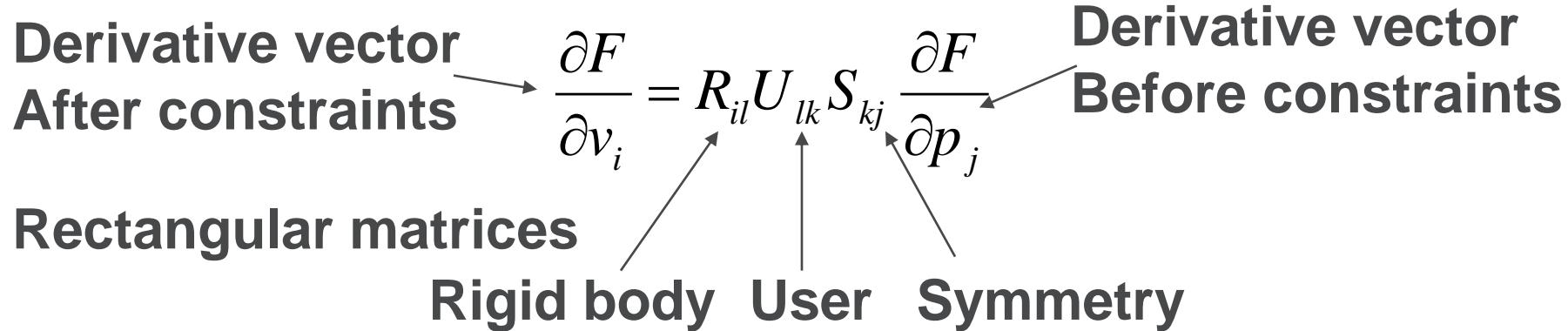
Green: $\text{cov} > 0$
Red: $\text{cov} < 0$
Yellow: $\text{cov} \sim 0$
Cursor reports:
Cov or
value(esd)
on diagonal
Can be
zoomed!

Beware white
bands & nan:
Singularities!

CONSTRAINTS & RESTRAINTS

CONSTRAINTS & RESTRAINTS - “WHAT TO DO WHEN YOU HAVE TOO MANY PARAMETERS & NOT ENOUGH DATA”

Constraints – reduce no. of parameters



QUATERNIONS – SIR WILLIAM ROWAN HAMILTON 1843



Broome Bridge, Dublin

Here as he walked by
on the 16th of October 1843
Sir William Rowan Hamilton
in a flash of genius discovered
the fundamental formula for
quaternion multiplication
 $i^2 = j^2 = k^2 = ijk = -1$
& cut it on a stone of this bridge.



"Quaternions came from Hamilton after his really good work had been done; and, though beautifully ingenious, have been an unmixed evil to those who have touched them in any way, including Clerk Maxwell. — Lord Kelvin, 1892.

NB: W.R. Hamilton is the H in $H\Psi = E\Psi$

Q_{ijk} – QUATERNION TO REPRESENT ROTATIONS IN GSAS-II

- In GSAS-II defined as: $Q_{ijk} = r + ai + bj + ck$ – 4D complex number – 1 real + 3 imaginary components
- Normalization: $r^2 + a^2 + b^2 + c^2 = 1$
- Rotation vector: $v = a_x + b_y + c_z$; $u = (a_x + b_y + c_z) / \sin(\alpha/2)$
- Rotation angle: $r^2 = \cos^2(\alpha/2)$; $a^2 + b^2 + c^2 = \sin^2(\alpha/2)$
- Quaternion product: $Q_{ab} = Q_a * Q_b \neq Q_b * Q_a$
- Quaternion vector transformation: $v' = QvQ^{-1}$
- Uses: RB rotations, structure drawings, etc.
- No gimbal lock as with Eulerian angles @ $\chi = 0$

FULL MINIMIZATION FUNCTION + RESTRAINTS: ADDITIONAL “DATA”

Least-squares – nonlinear; transcendental functions

$$M = f_Y \sum w_i (Y_{oi} - Y_{ci})^2 + f_a \sum w_i (a_{oi} - a_{ci})^2 + f_d \sum w_i (d_{oi} - d_{ci})^2 + f_t \sum w_i (-t_{ci})^4 + f_p \sum w_i (-p_{ci})^2 + f_v \sum w_i (v_{oi} - v_{ci})^4 + f_h \sum w_i (h_{oi} - h_{ci})^2 + f_x \sum w_i (x_{oi} - x_{ci})^2 + f_R \sum w_i (-R_{ci})^4$$

- Powder profile (Rietveld)/Single crystal F_{hkl}**
- Bond angles**
- Bond distances**
- Torsion angle pseudopotentials**
- Plane RMS displacements**
- van der Waals distances (if $v_{oi} < v_{ci}$)**
- Hydrogen bonds**
- Chiral volumes**
- “ ϕ/ψ ” pseudopotential**

NB: May be 1,000's of these terms for e.g. proteins

IMAGE PROCESSING IN GSAS-II

2D IMAGE DATA

Conic sections

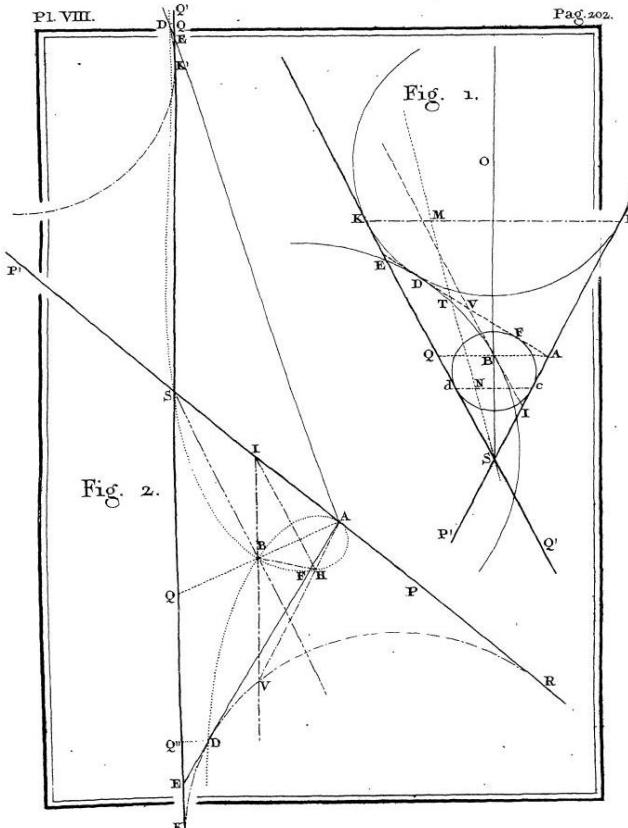
Where is the incident beam on the detector?

Fit2D (& DataSqueeze) – assumes center of the diffraction ellipse - **False**

Analysis – G.P. Dandelin,

Nouveaux 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

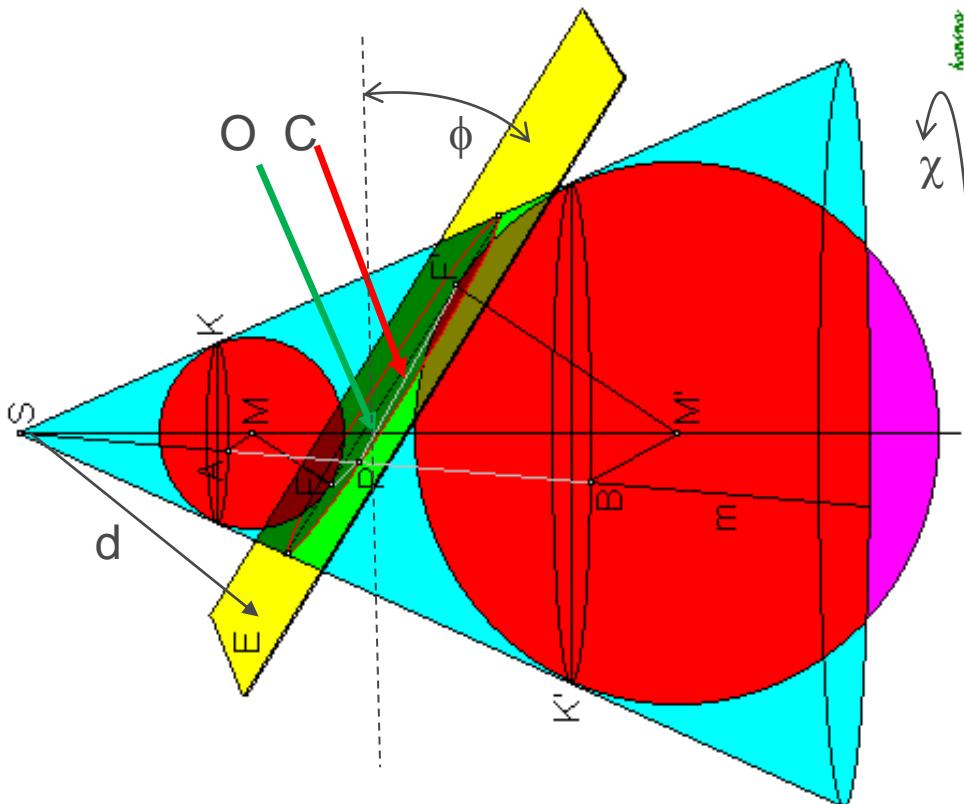
- line SO is cone axis
 - F&D are the ellipse foci on the plane
- He refers to a work by M. Quetlet as having previously made this construction
- source?

This is not something new!

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

NB: Irena get this right

GSAS-II IMAGE DETECTOR CALIBRATION VIA DANDELIN SPHERES

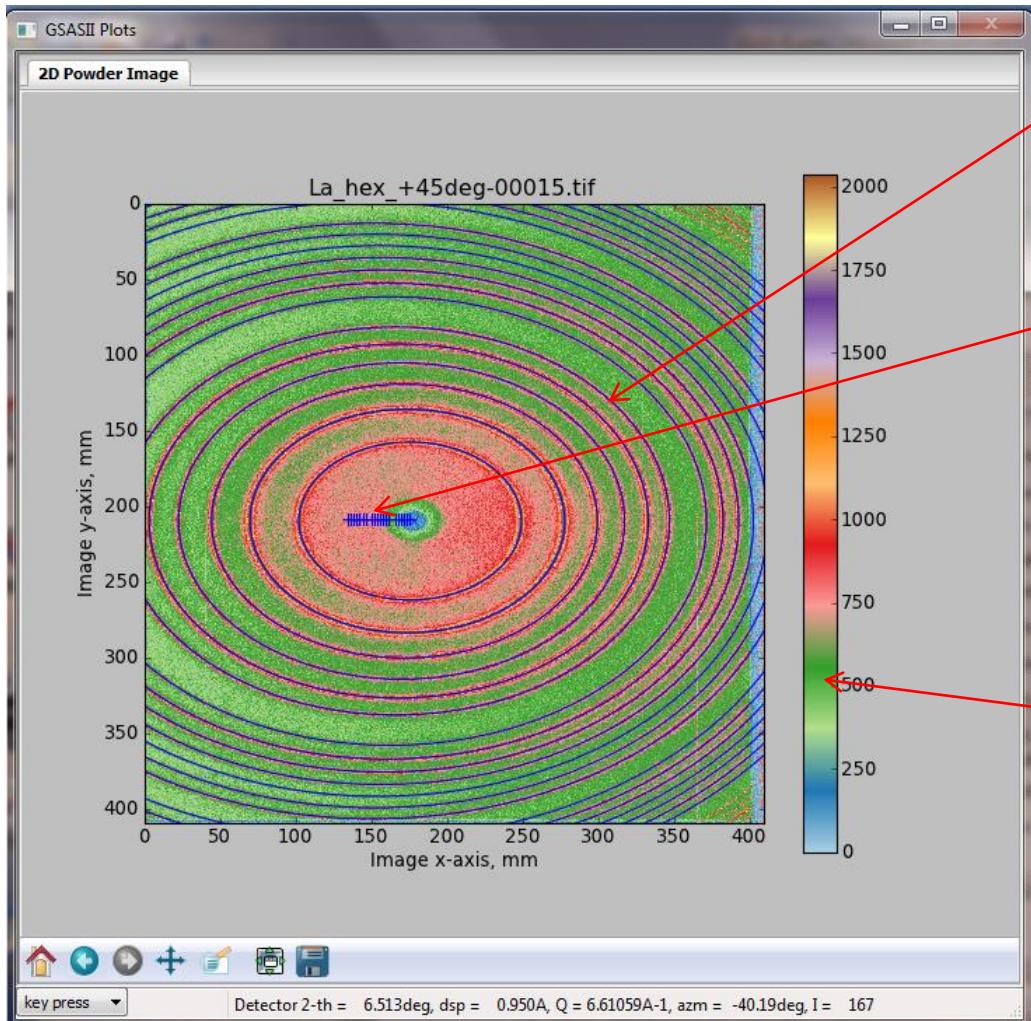


- Plane E is a tilted area detector
- The line SMM' is the Bragg cone axis – incident beam direction & passes through centers of both spheres
- Spheres touch plane at foci (F & F') of conic section (ellipse)
- Intersection of axis with plane (**O**) not at halfway point (**C**) between F & F' (ellipse center) – note similar triangles MFO & M'F'O of different sizes
- If plane is perpendicular to cone axis then conic section is a circle and O & C coincide
- GSAS-II parameters:
 - d – sample-detector plane distance
 - ϕ – detector tilt angle ($= 2\Theta_{\text{detector}}$)
 - χ – tilt azimuth angle
 - x_o, y_o – beam position @ **O** on detector

This is just geometry

2D IMAGES IN GSAS-II:

Calibration – tilted detector (e.g. 45° about vertical axis)



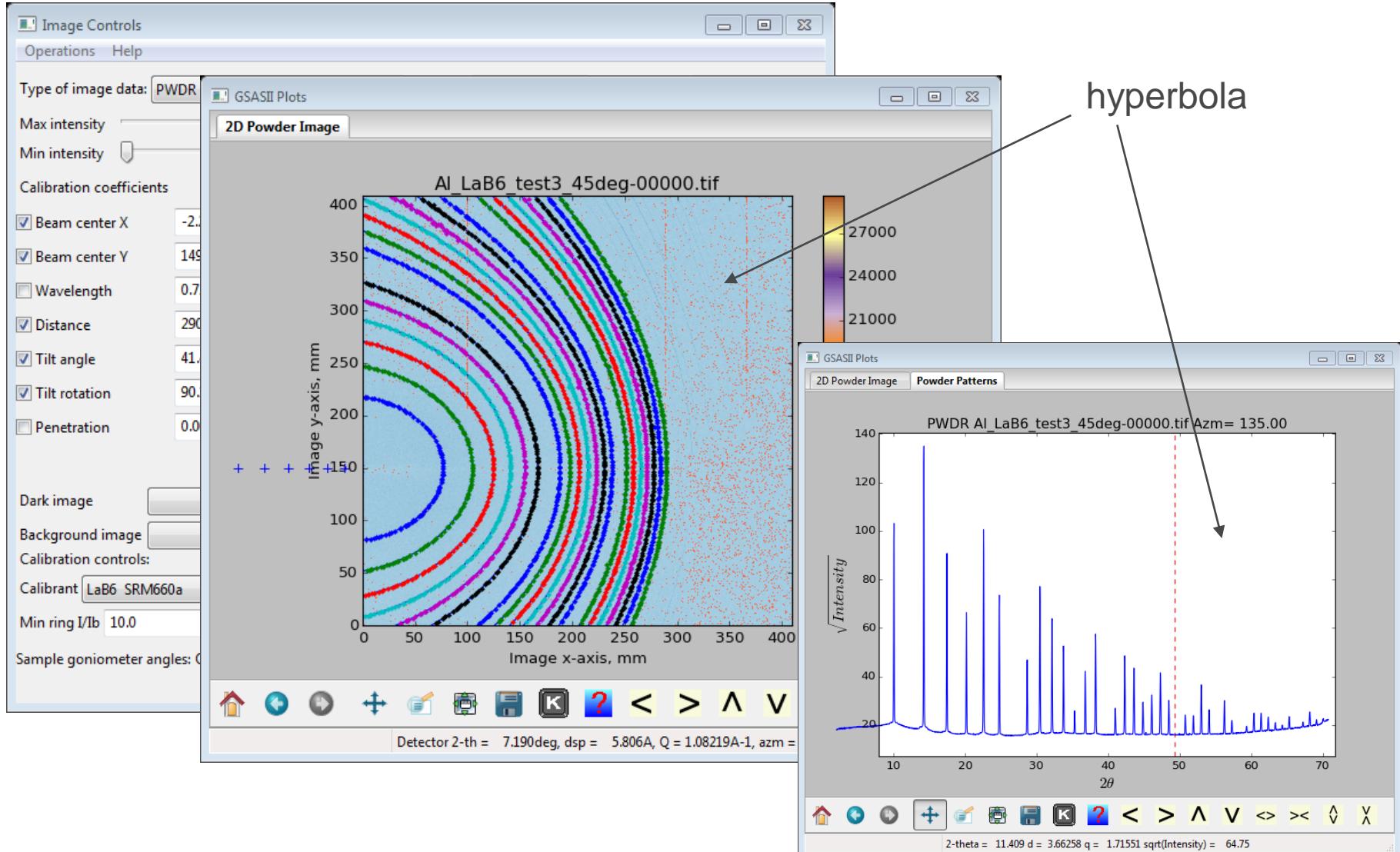
Ellipses – sections of Debye-Scherrer cones

Ellipse centers – not on beam center!

Fitting only requires material (LaB_6) and λ (e.g. don't need to know distance – get that from fit)

Choice of color scheme – “Paired” is shown

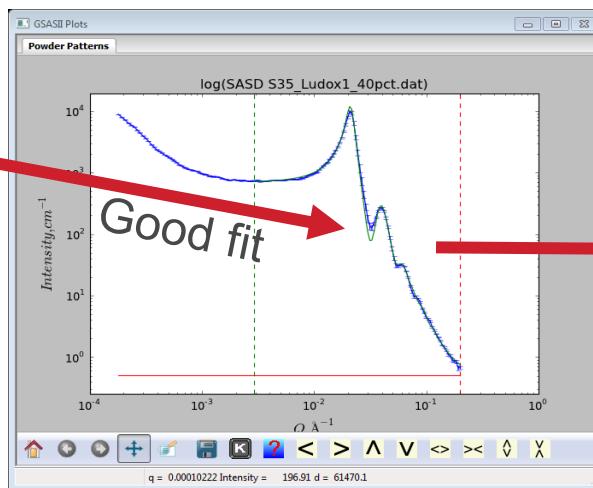
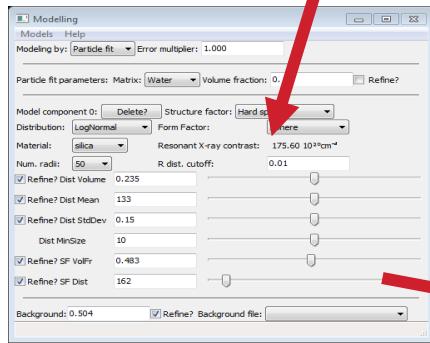
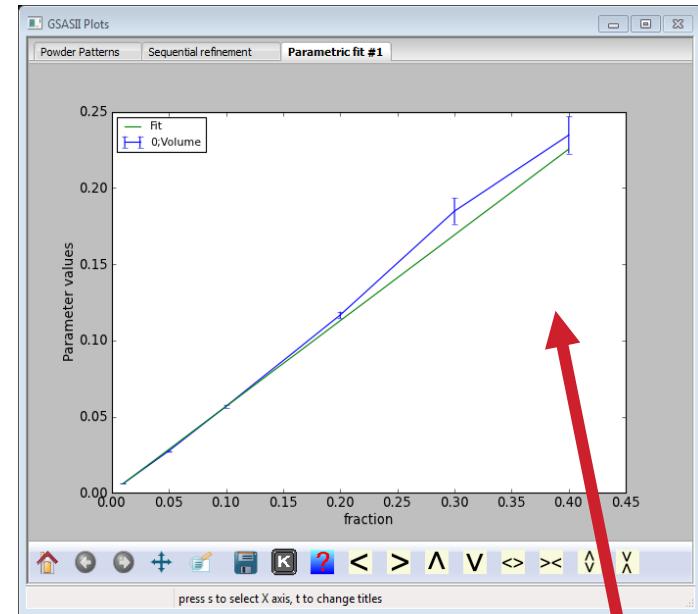
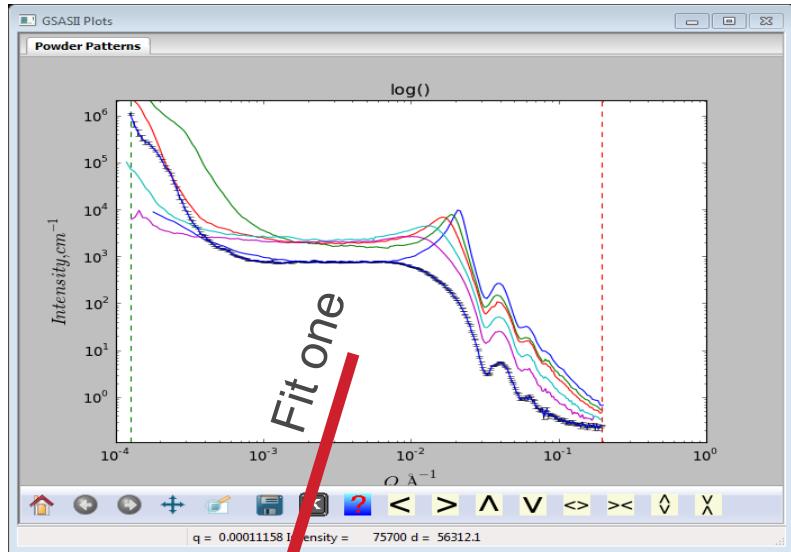
OFFSET & TILTED DETECTORS – AN EXAMPLE



SMALL ANGLE DATA ANALYSIS IN GSAS-II

SEQUENTIAL ANALYSIS

Series of experiments vs independent variable (e.g. composition)



Plot coeff. & fit to equation

GSAS-II Plots
Sequential refinement results

	User	Rwp	fraction	Back	0.Dist	0.VolFr	0.Volume	0.Means	0.Sigma
SASD S35_Ludox1_40pct.dat	3.553	0.400000	0.503530	162.350116	0.483169	0.234723	133.307516	0.149627	
SASD S40_Ludox2_30pct.dat	8.673	0.300000	0.403894	160.490330	0.369993	0.184833	136.794497	0.180324	
SASD S41_Ludox3_20pct.dat	3.626	0.200000	0.371692	173.47835	0.300004	0.116669	134.278946	0.152560	
SASD S42_Ludox4_10pct.dat	2.424	0.100000	0.305805	196.221060	0.190653	0.056749	134.199202	0.149174	
SASD S47_Ludox5_5pct.dat	2.142	0.050000	0.300112	223.312025	0.119394	0.027559	134.221218	0.152267	
SASD S49_Ludox6_1pct.dat	2.639	0.010000	0.240443	311.032692	0.030708	0.006053	134.205294	0.154655	

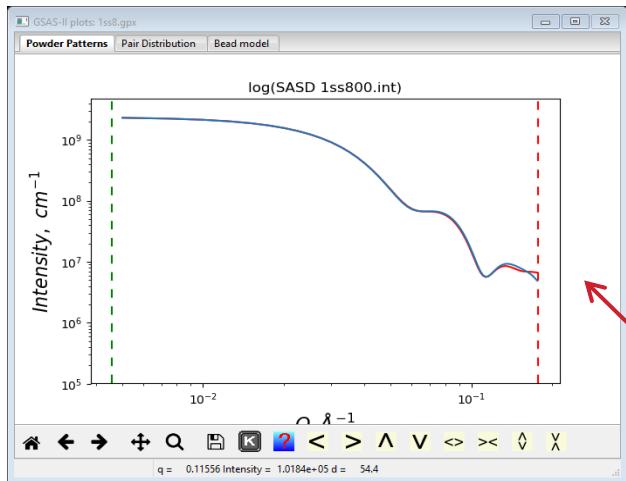
Select column to export; Double click on column to plot data; on row for Covariance

Do rest in sequence

All inside GSAS-II

PROTEIN SMALL ANGLE MODELING IN GSAS-II

Bead models via SHAPES (alternative to DAMMIN in python)

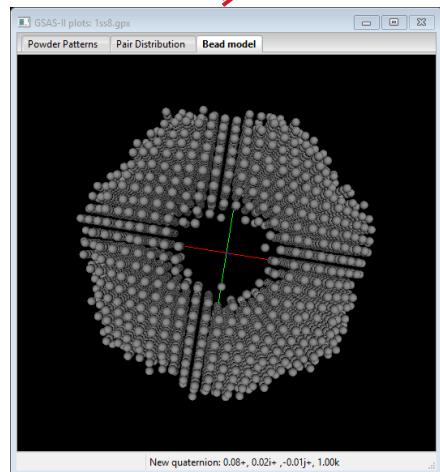
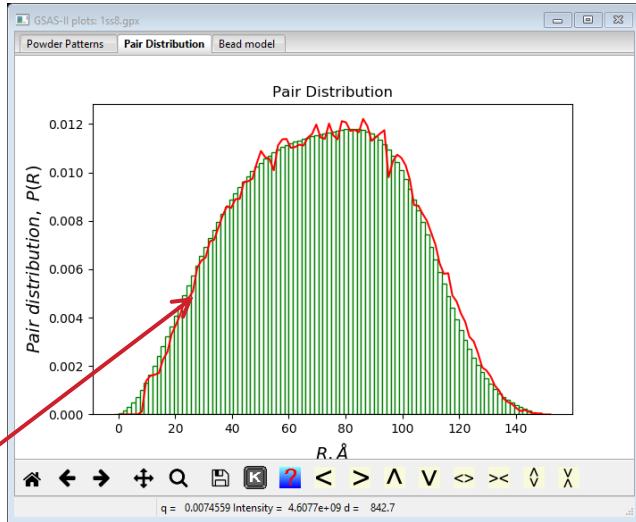


Data (simulated) from PDB 1ss8
3668 AA, 7-fold rot. symm.
E. Coli chaperonin GroEL

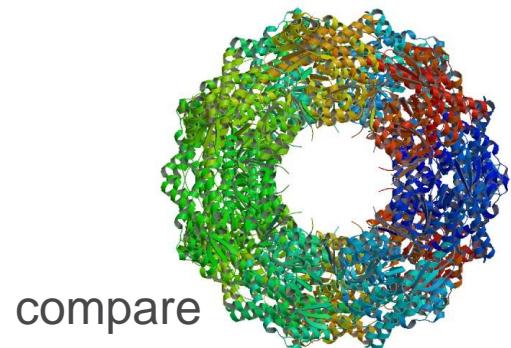


Direct fit?
(In development)

Make $P(R)$
calc



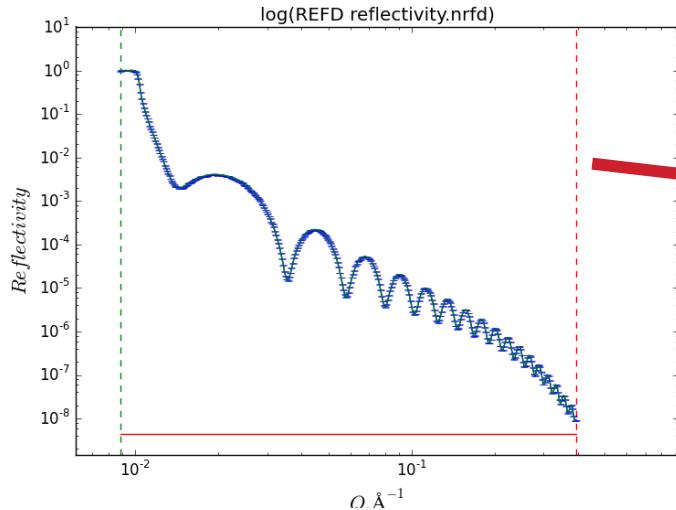
Run SHAPES
Make bead model



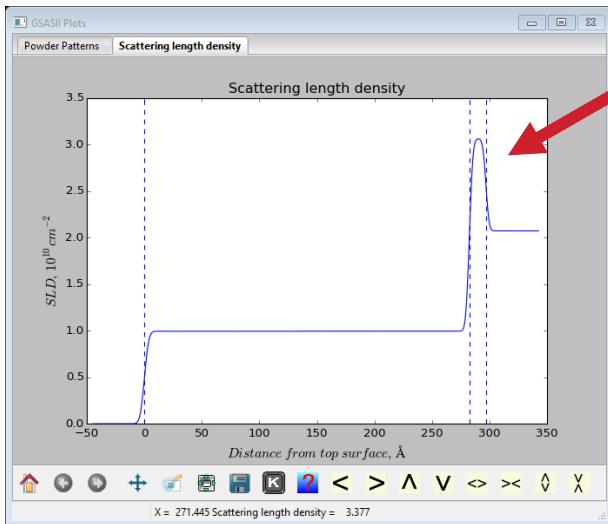
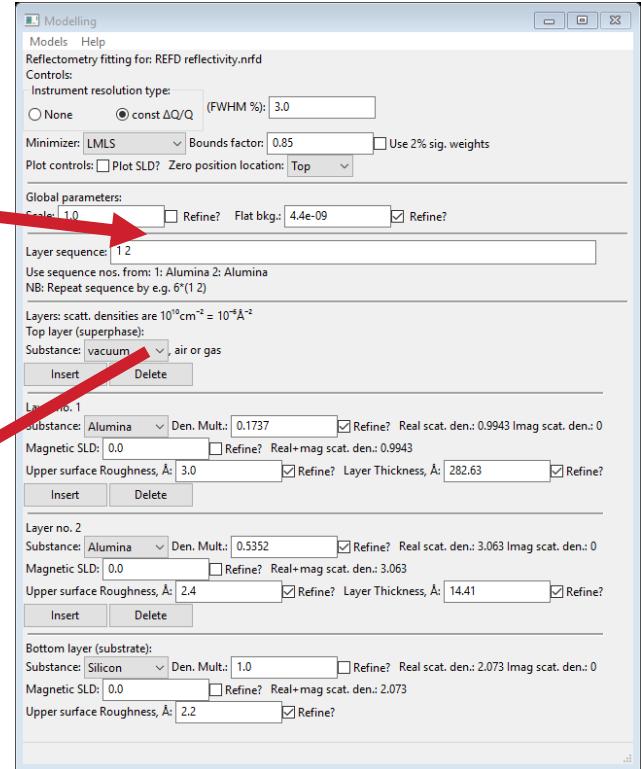
"SHAPES", J. Badger, J. Appl. Cryst 52, 937-944 (2019)

REFLECTOMETRY ANALYSIS IN GSAS-II

X-rays & Neutrons (CW at least)



Multilayer model
Scattering density



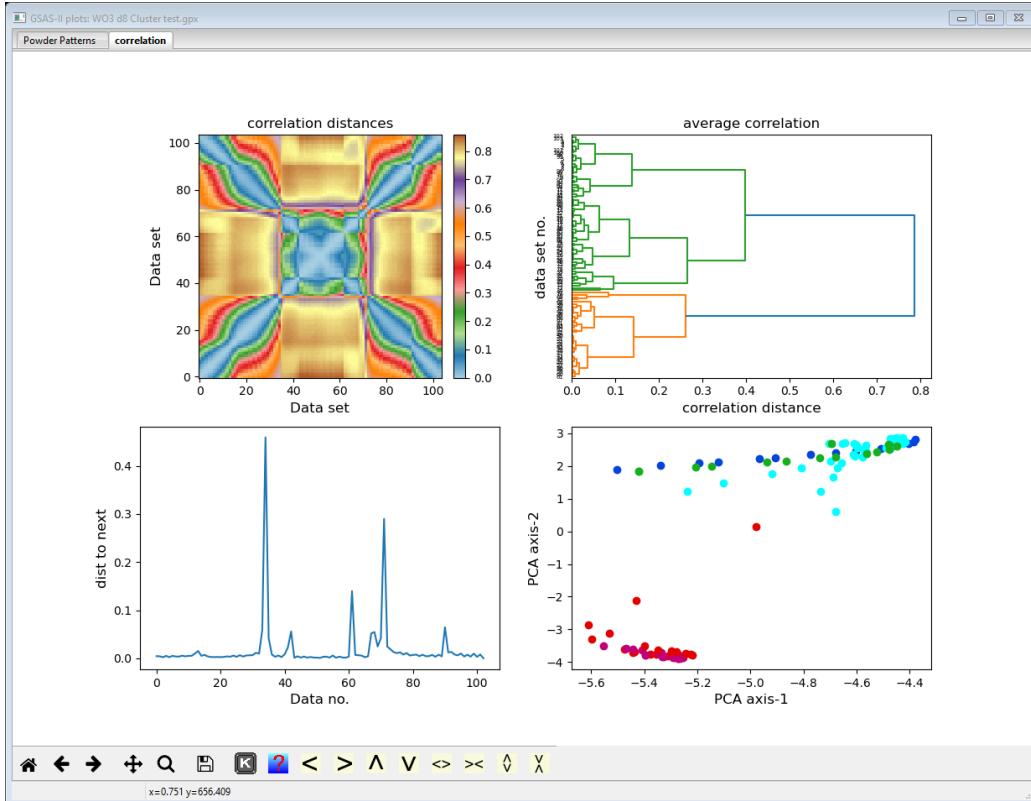
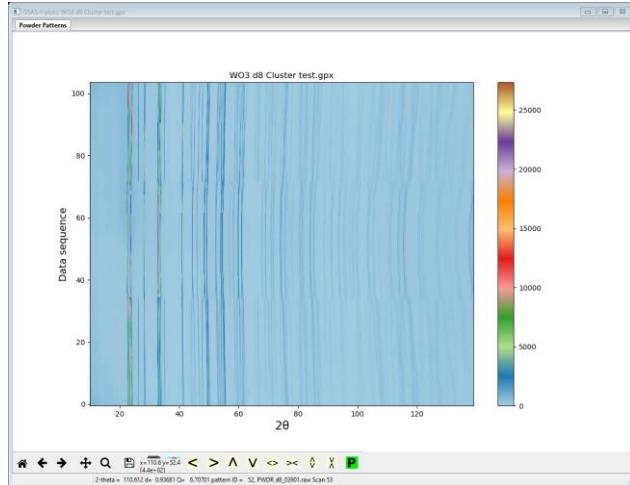
Define components, stacking sequence
(can be repeated), thickness & “roughness”
Fit by LSQ, MC/SA & “basinhopping”
(under development)

CLUSTER ANALYSIS

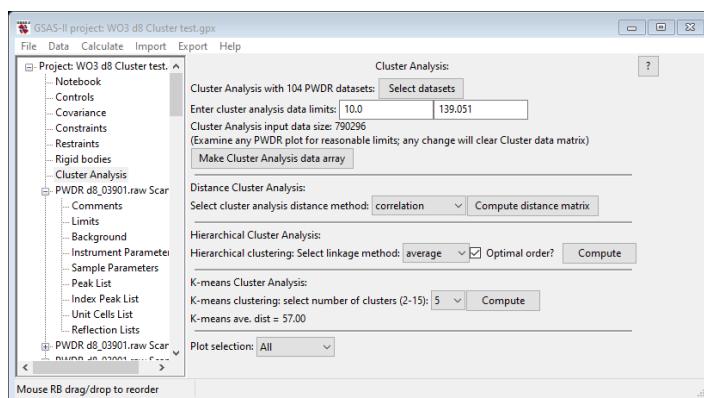
CLUSTER ANALYSIS IN GSAS-II

Another way of examining data – look for similar patterns

- Example – WO_3 x-ray data 300-1200K & back; 100 patterns. Multiple phase changes – consider each pattern as hyperdimensional vector & compare them



Distance matrix, dendogram,
serial distance changes & PCA
shown

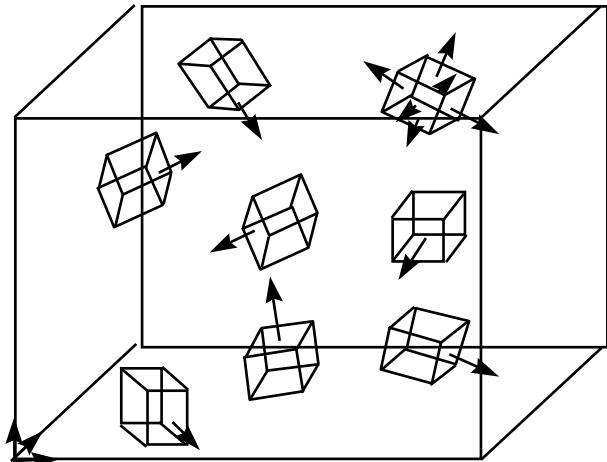


Uses scipy & Scikit-learn python libraries
– multiple choices of clustering algorithms
& outlier (bad data) analysis

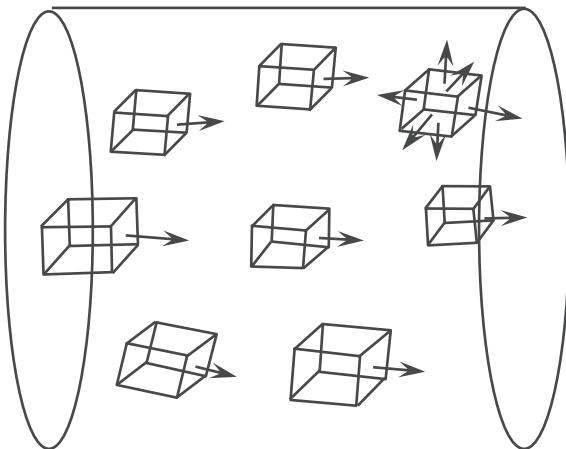
TEXTURE ANALYSIS

What is texture?

Nonrandom crystallite grain orientations



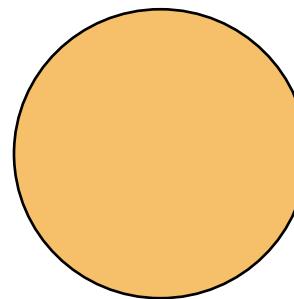
Loose powder



Metal wire

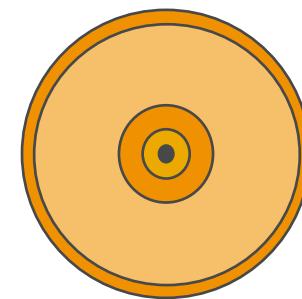
Random powder - all crystallite orientations equally probable - flat pole figure

Pole figure - stereographic projection of a crystal axis down some sample direction



(100) random texture

Crystallites oriented along wire axis - pole figure peaked in center and at the rim (100's are 90° apart)



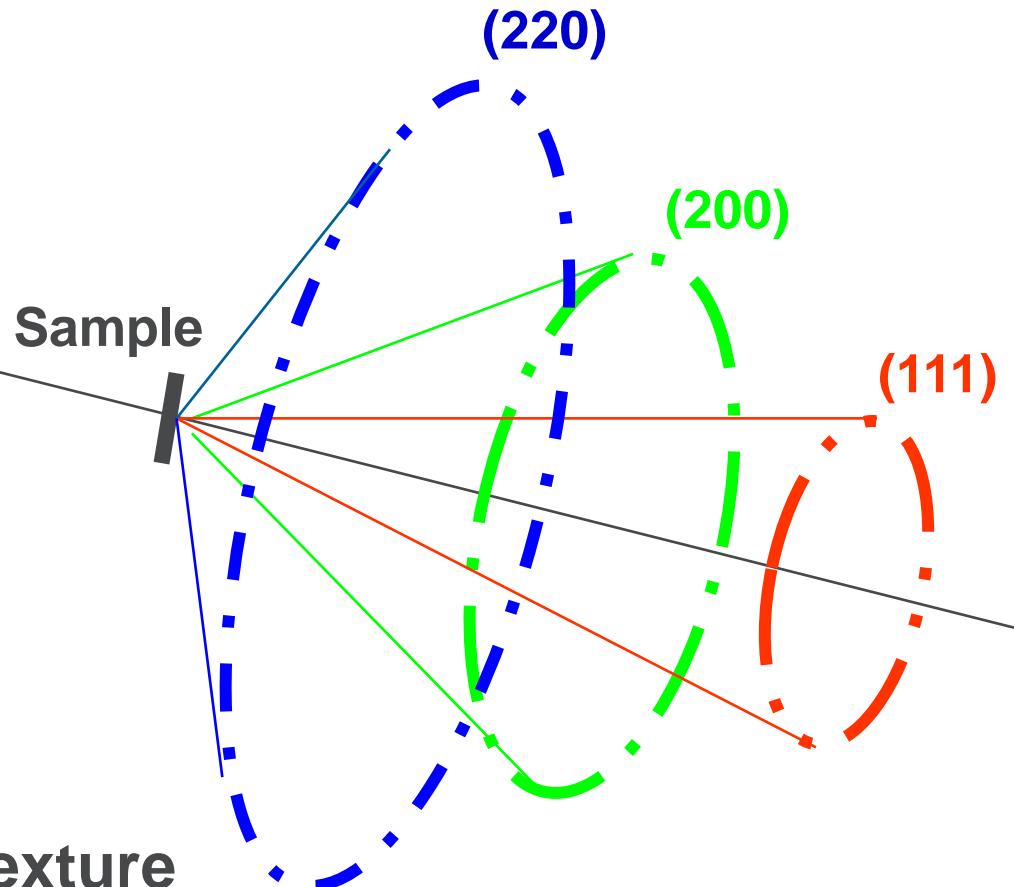
(100) wire texture

Orientation Distribution Function - probability function for texture

Texture - measurement by diffraction

Non-random crystallite orientations in sample

Incident beam
x-rays or neutrons



Debye-Scherrer cones

- uneven intensity due to texture
- also different pattern of unevenness for different hkl's
- Intensity pattern changes as sample is turned

Texture effect on reflection intensity – Sph. Harm. model

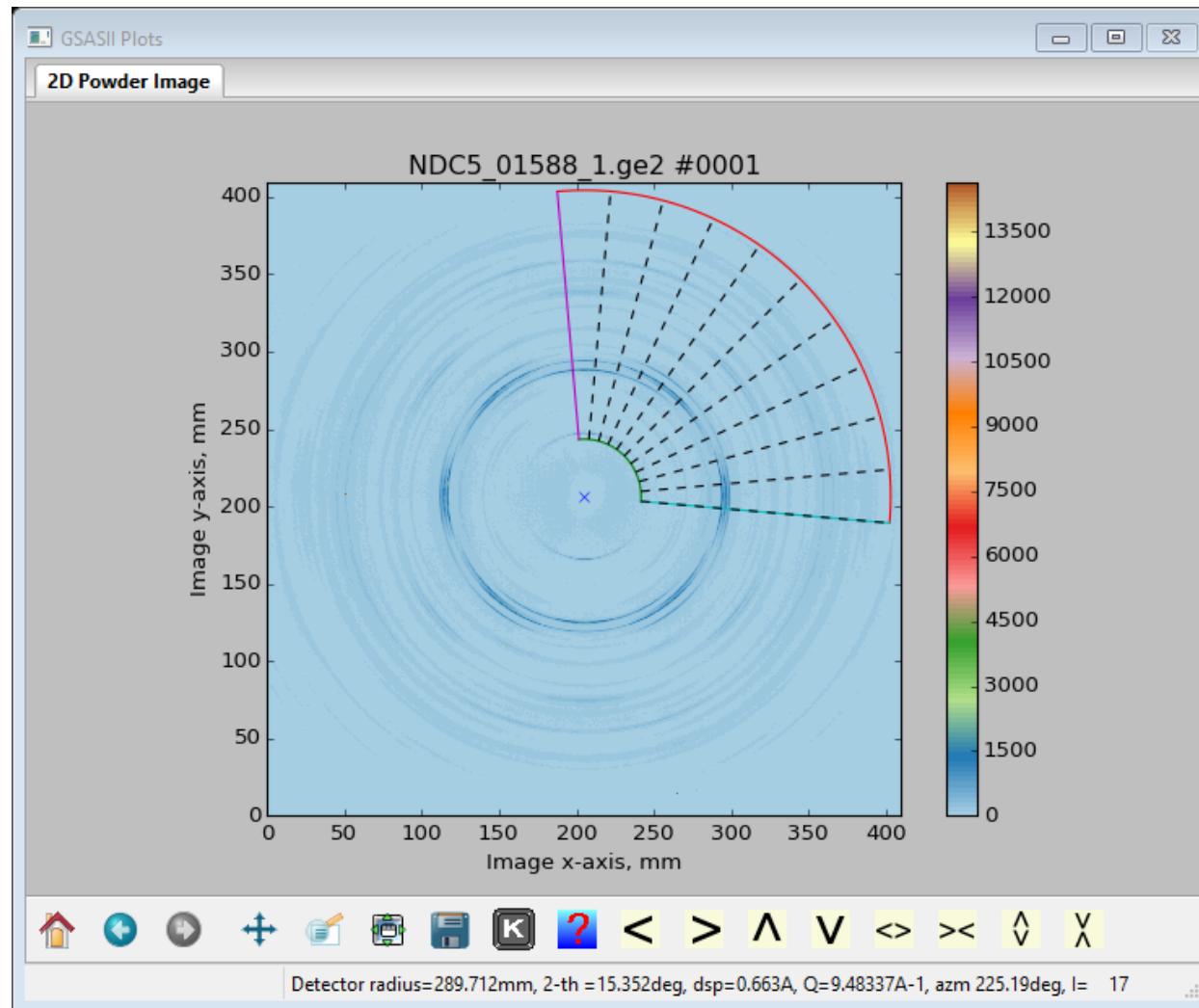
$$A(h, y) = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^l \sum_{n=-l}^l C_l^{mn} K_l^m(h) K_l^n(y)$$

- Projection of orientation distribution function for chosen reflection (h) and sample direction (y)
- K -symmetrized spherical harmonics - account for sample & crystal symmetry
- “Pole figure” - variation of single reflection intensity as fxn. of sample orientation - fixed h
- “Inverse pole figure” - modification of all reflection intensities by sample texture - fixed y - Ideally suited for neutron TOF diffraction
- Rietveld refinement of coefficients, C_l^{mn} , and 3 orientation angles - sample alignment

NB: In GSAS-II as correction & texture analysis

2D IMAGE

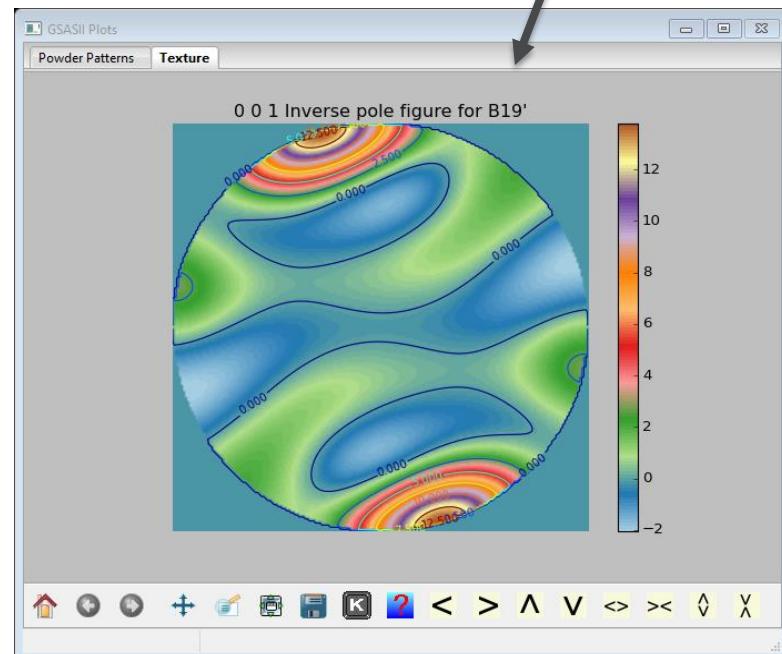
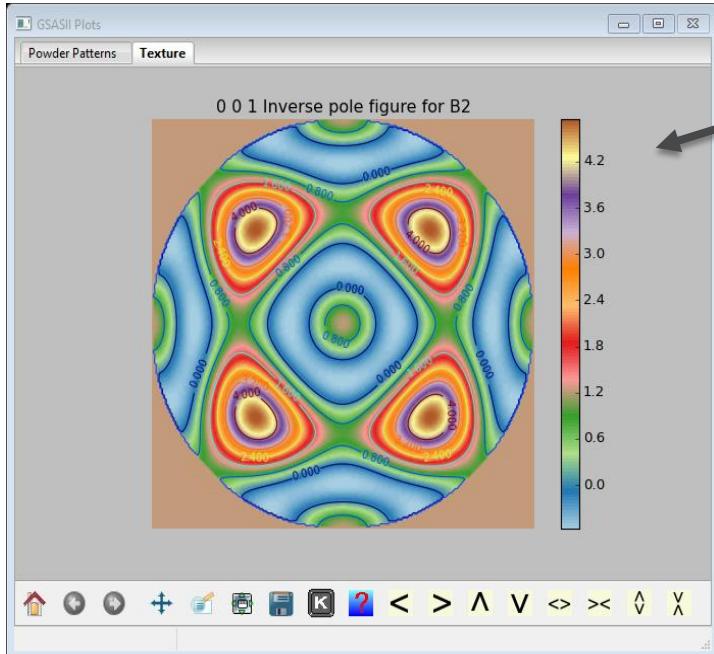
NiTi shape memory alloy wire: B2 & B19' phases



Sample – wire symmetry
Need only $\frac{1}{4}$ of image
Caked in 10° increments
Integration – PWDR patterns
Analyze for texture

GSAS-II TEXTURE ANALYSIS

Fit C_L^{mn} & crystal structure stuff – inverse pole figures B2 & B19'



Pole figures – bulls eyes (boring)
GSAS-II → 3 methods for texture

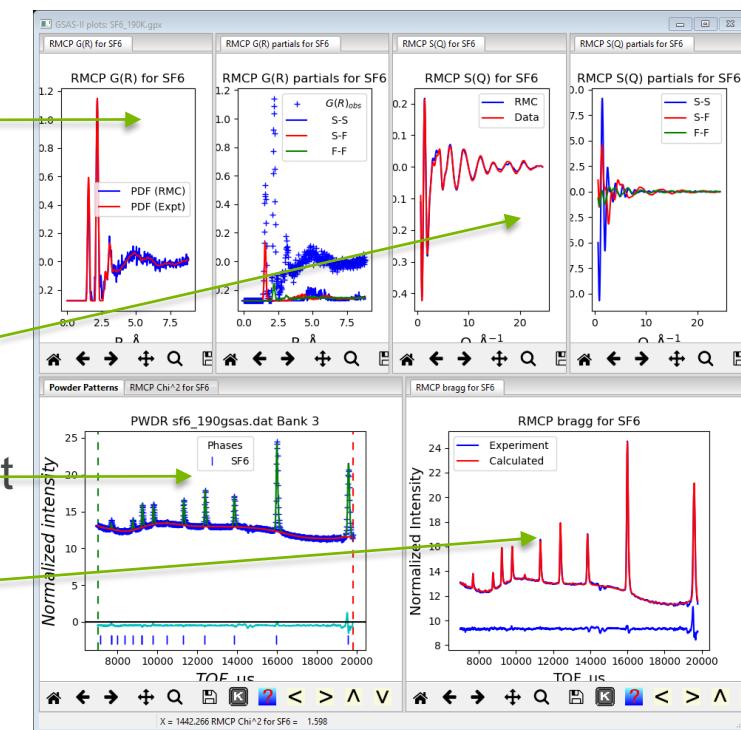
PDF FITTING

RMCprofile “BIG BOX” SIMULATION

GSAS-II interface

- Provide GUI interface to setup of RMCProfile - save setup controls for reuse
- Initiate independent RMCProfile execution – may run for hours
- Allow graphical display on intermediate results

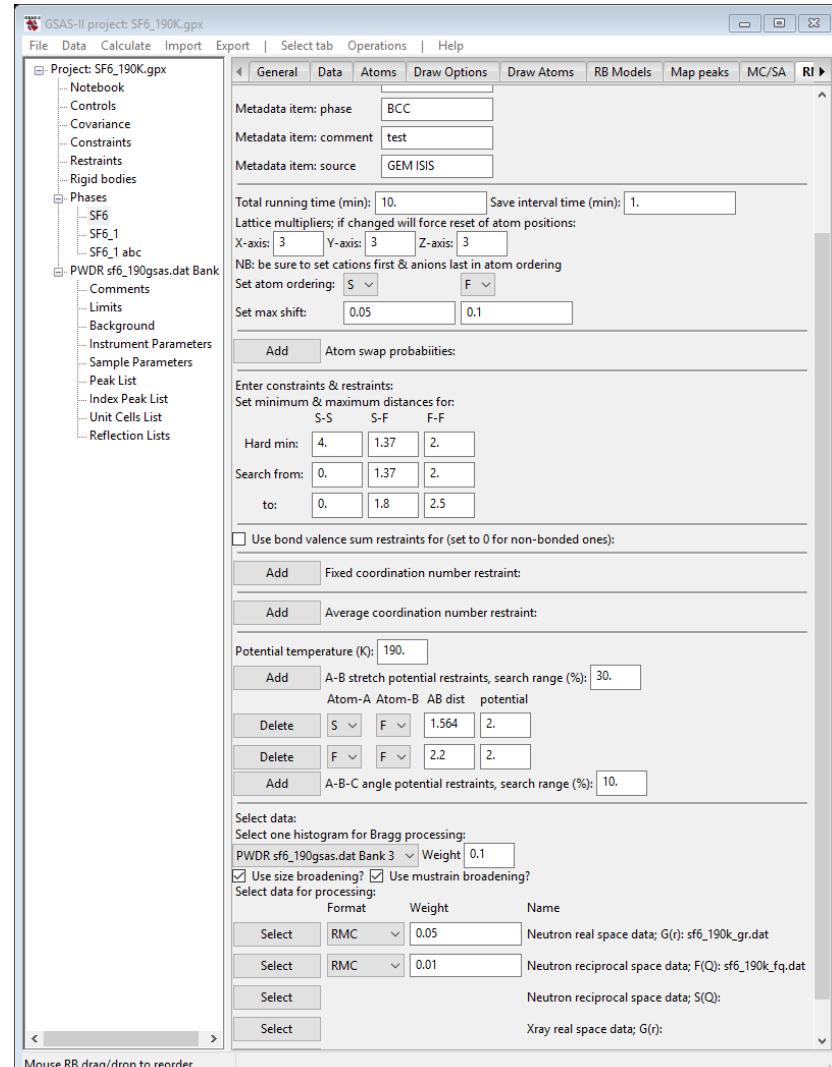
G(R) &
partials



S(Q) &
partials

RR result

PWDR
simulatio
n

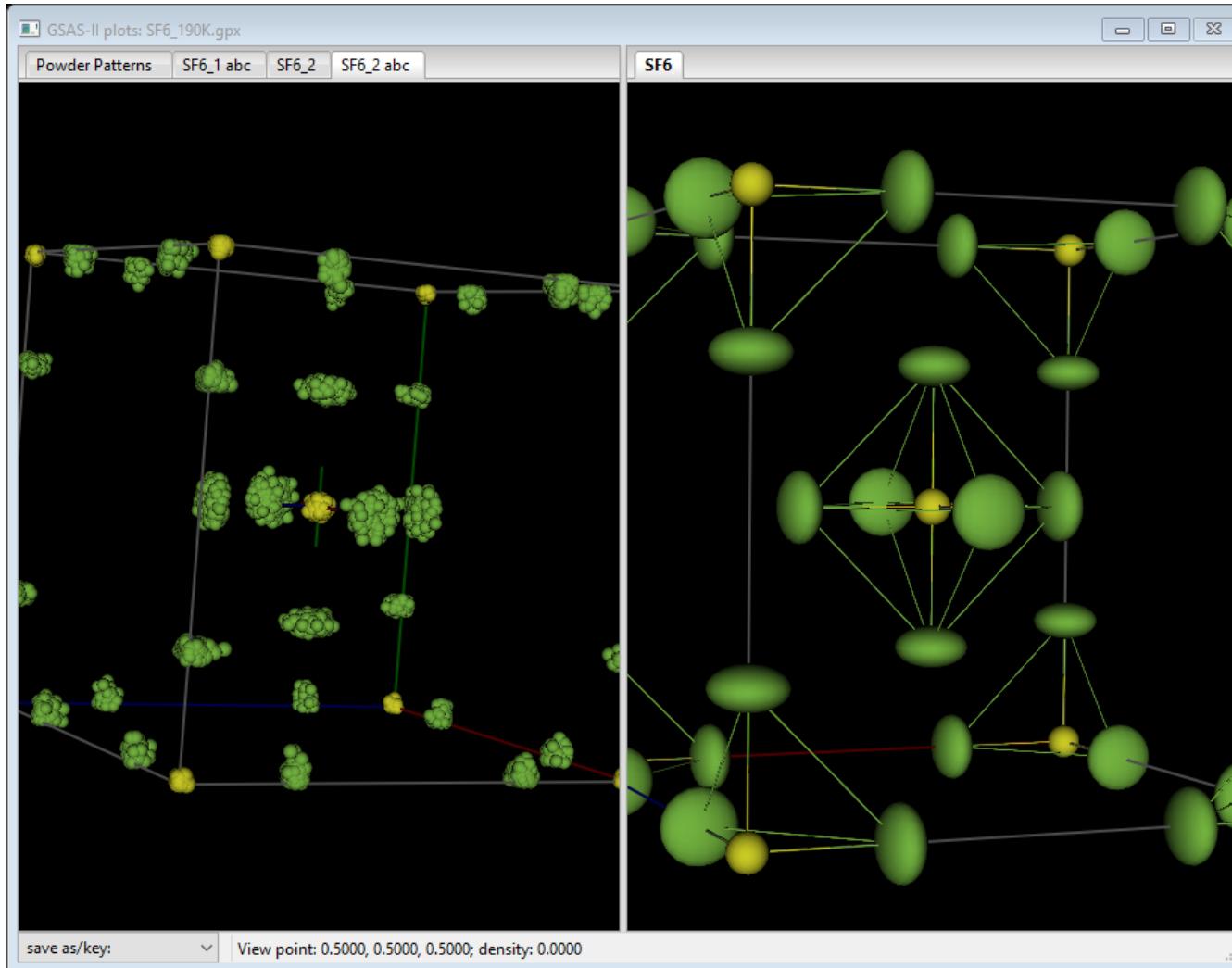


RMC PROFILE RESULT FOR SF₆

10x10x10 unit cell box – transform back to original

See disordered atom distribution

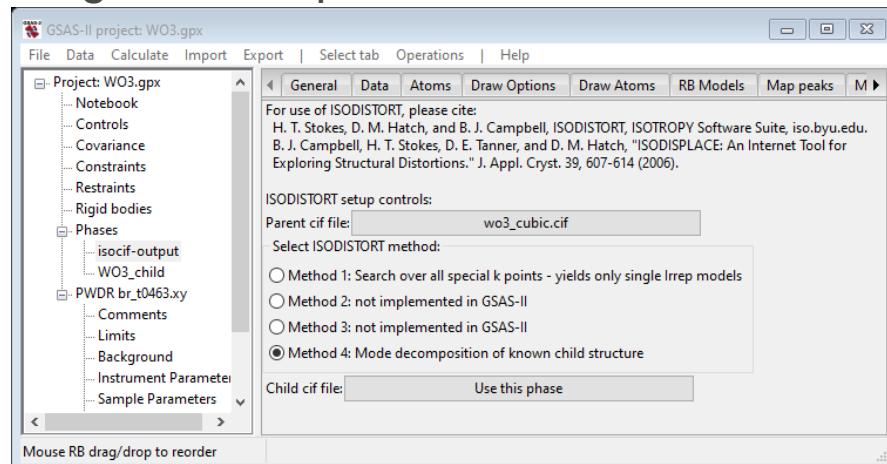
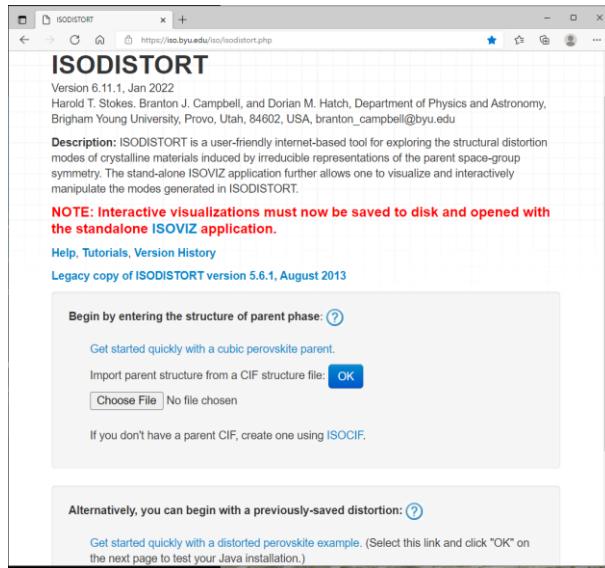
– compare to Rietveld U_{aniso} for F atom



ISODISTORT

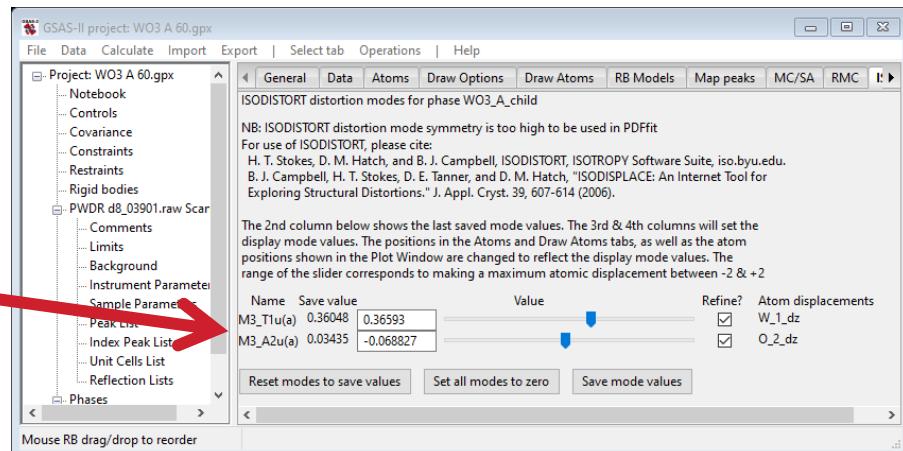
Implementation in GSAS-II

ISODISTORT: Web based tool for discerning mode displacements of atoms from an idealized parent structure



- New implementation – direct interaction between GSAS-II & ISODISTORT; simplified operation

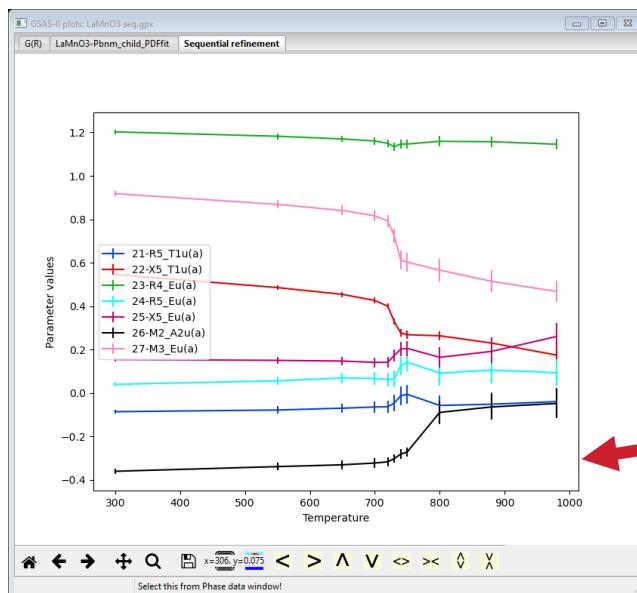
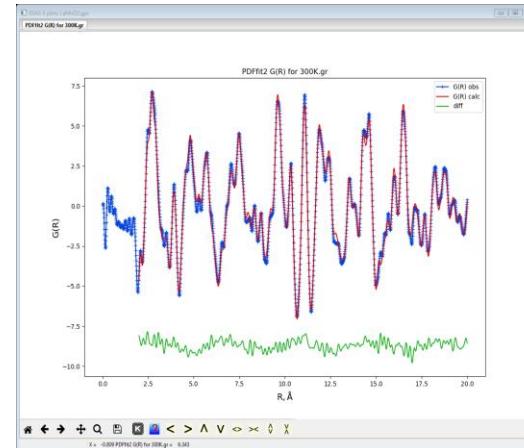
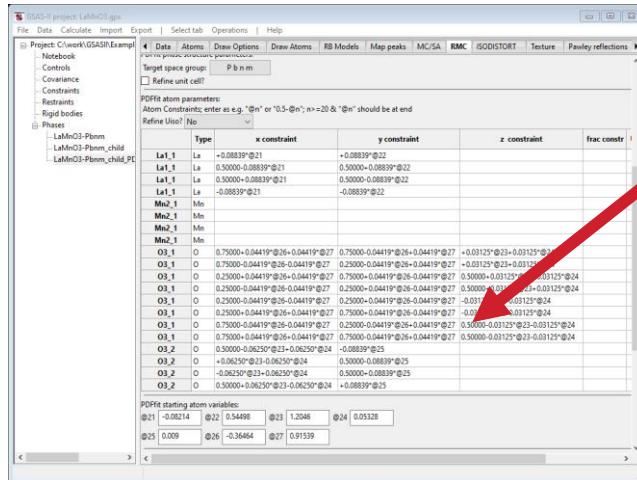
- To use: a multistep process → a cif file with modes; can be imported into GSAS-II with new variables for the modes.



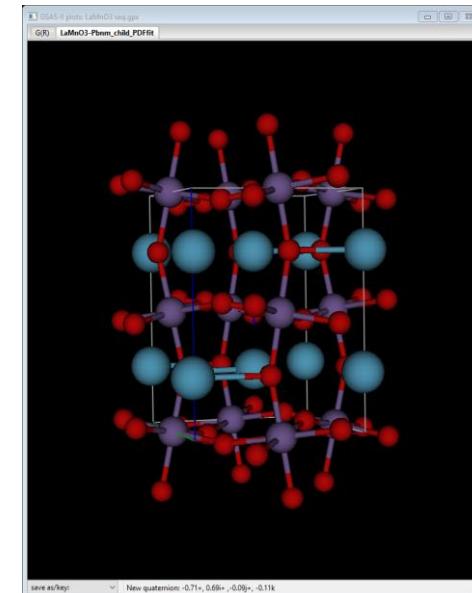
PDFFIT2 = “PDFfit” IN GSAS-II

“Small Box” modelling of pair distribution functions

Use ISODISTORT – create the atom position constraints in new interface to PDFfit2

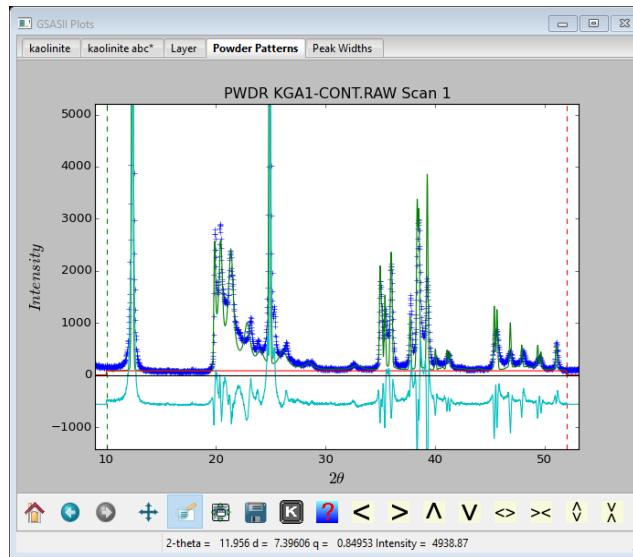
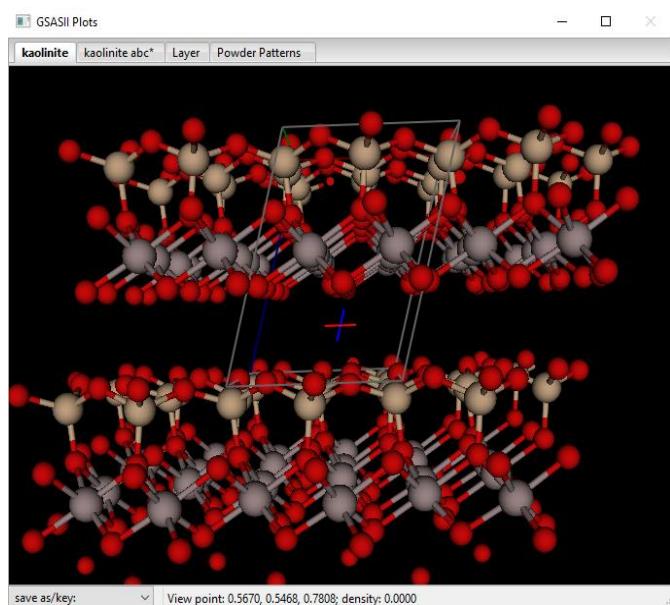
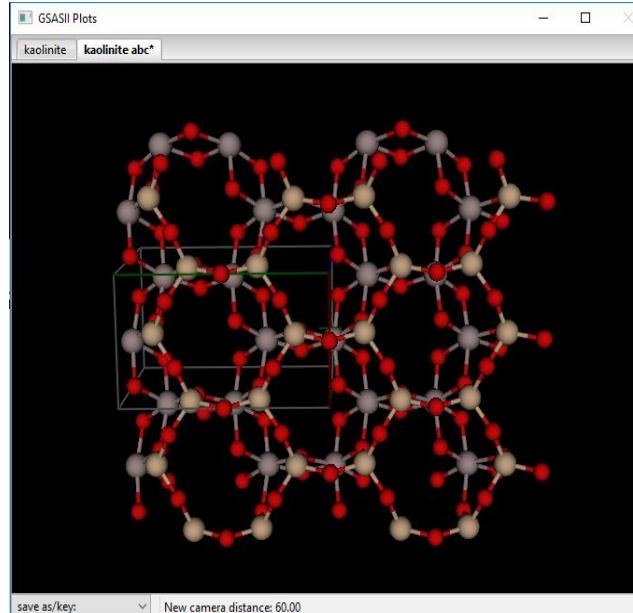
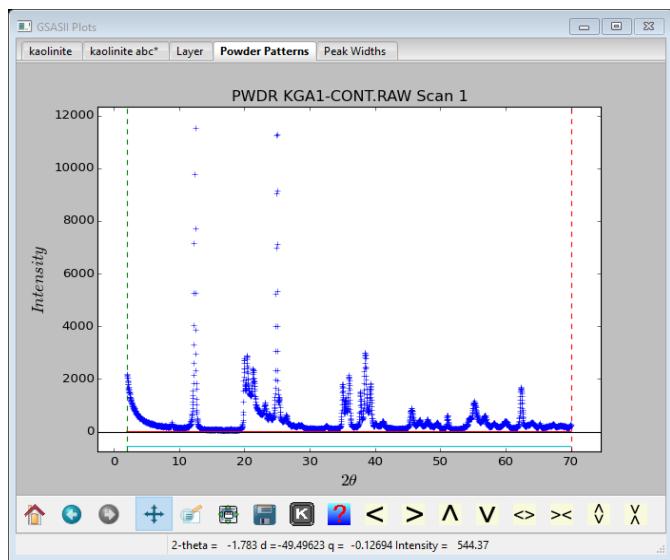


Parameters: mode displacements (\AA)
Can be fit for sequence of T



STACKING FAULTS – DIFFAX IN GSAS-II

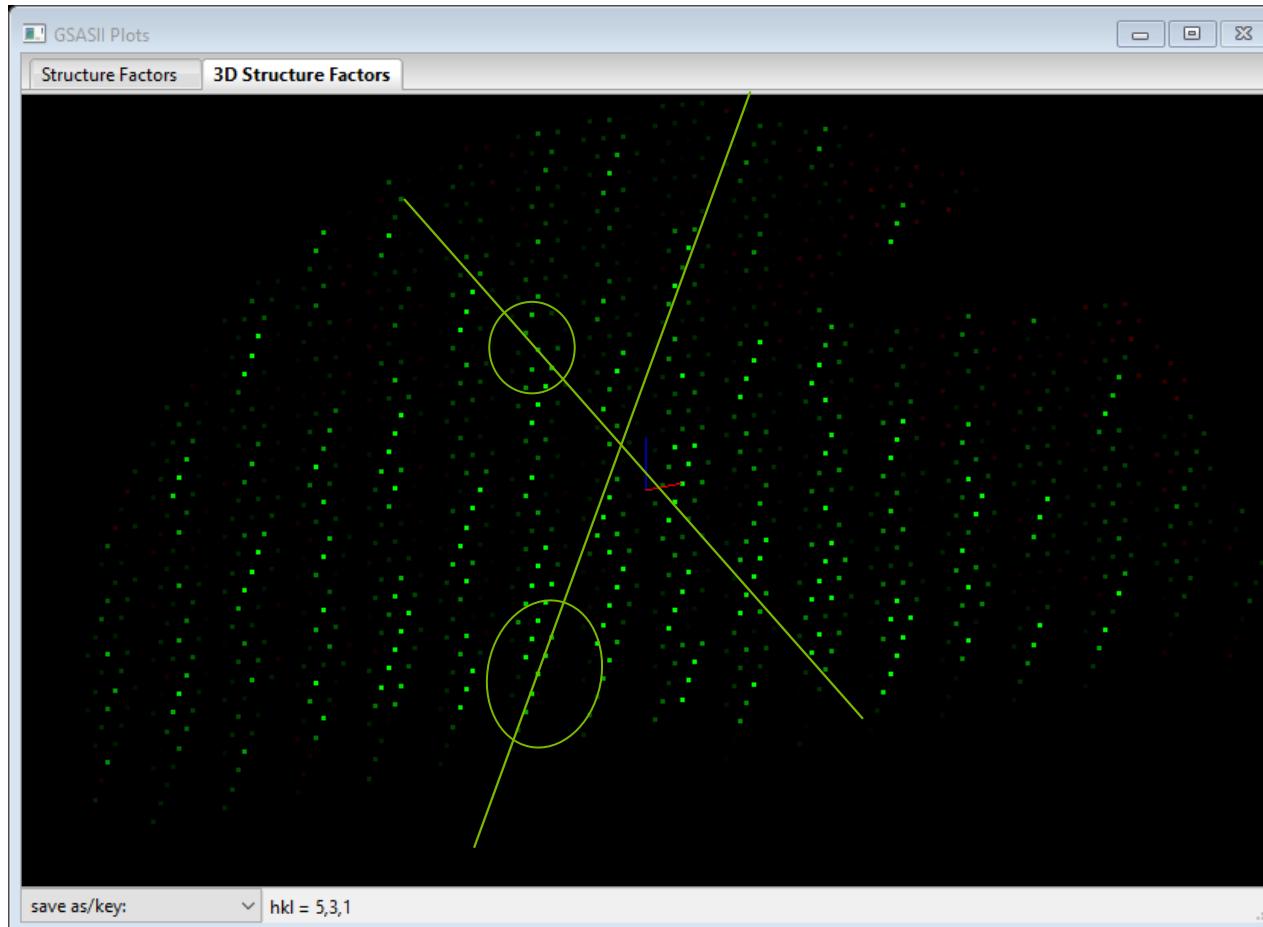
STACKING FAULTS IN KAOLINITE $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$



3+1 INCOMMENSURATE STRUCTURES

INCOMMENSURATE STRUCTURES N GSAS-II

Book: “Incommensurate Crystallography” S. van Smaalen



$$H = G + mq$$

G: substructure hkl
m: +/- small integers
q: modulation vector

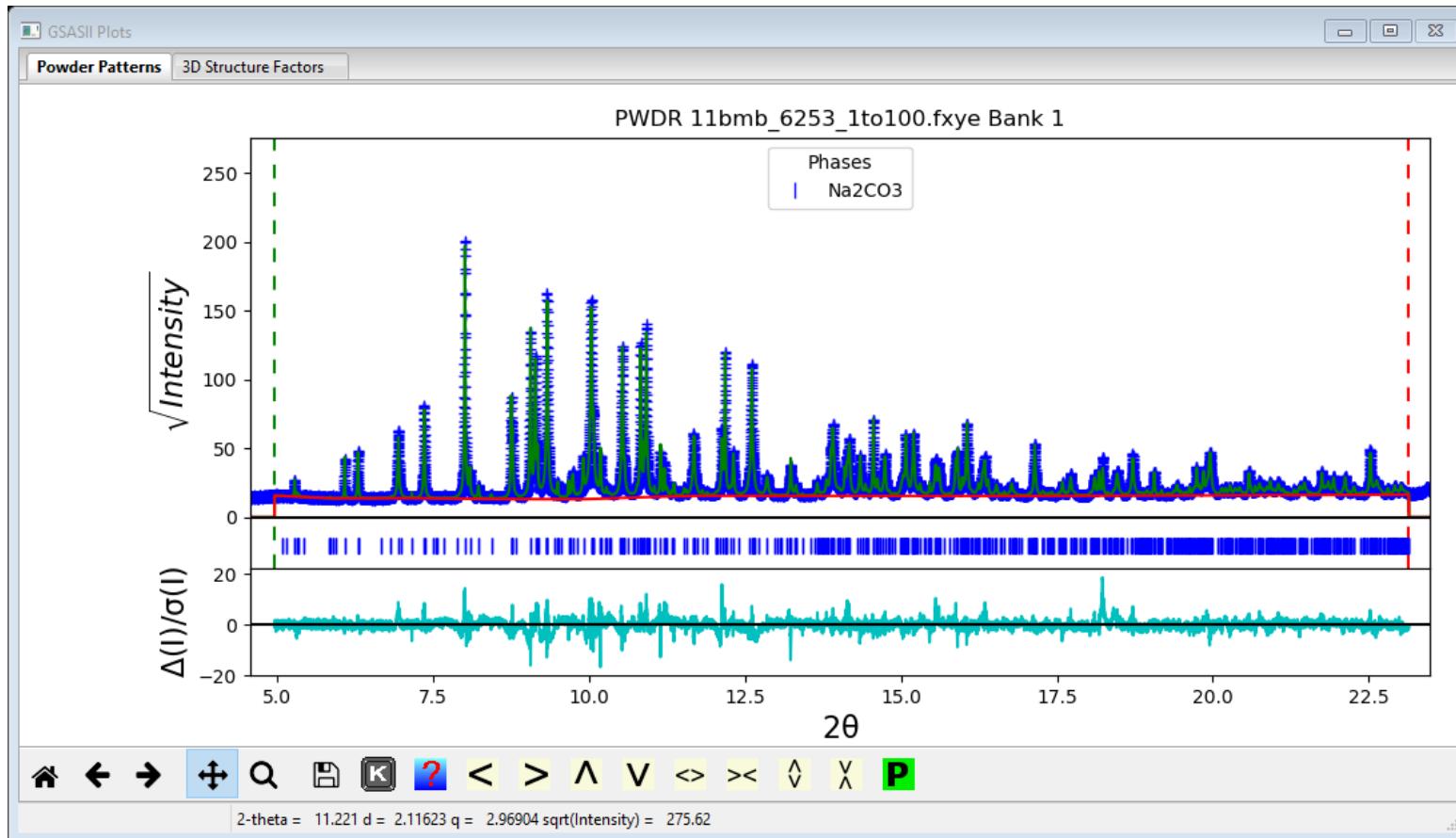
For Na_2CO_3
 $q = 0.183, 0, .319$

Each reflection: $hklm$
 $m=0$ sublattice
 $m \neq 0$ superlattice

Na_2CO_3 – single crystal X-ray data – $h0l$ zone → rows of spots don't line up

POWDER DIFFRACTION

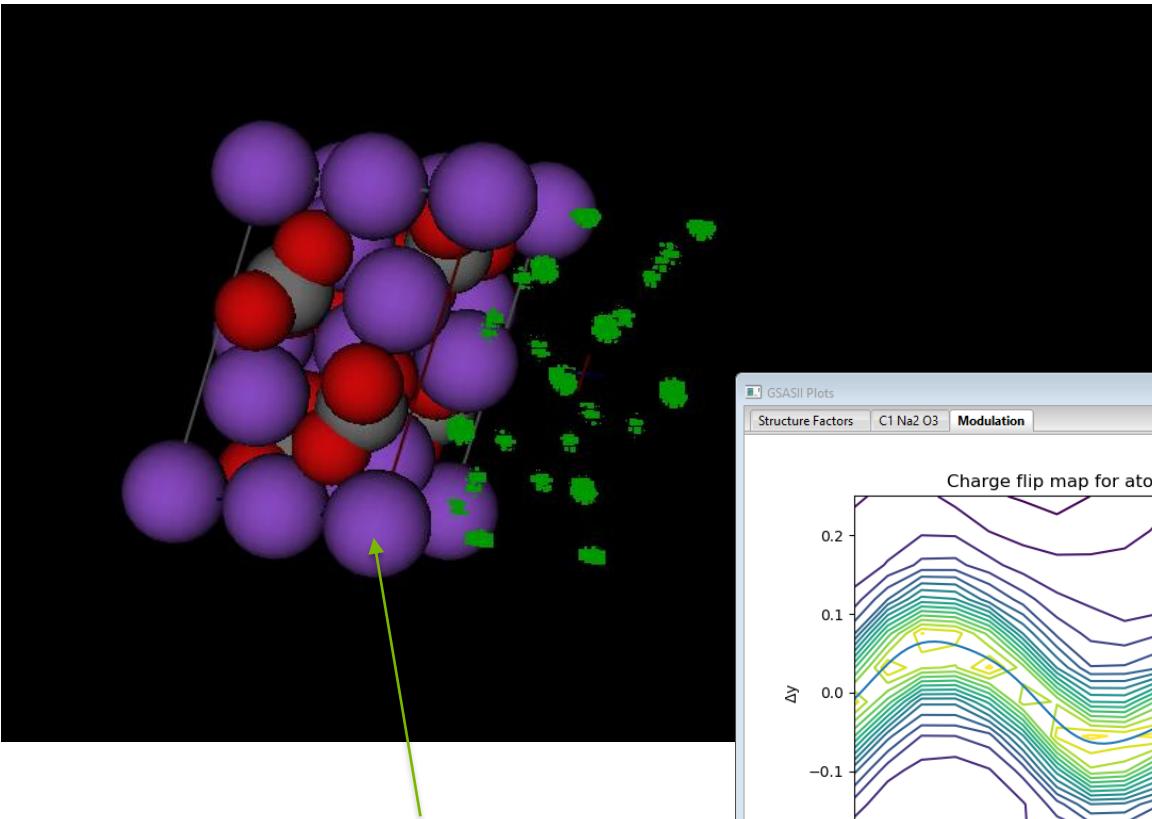
Na_2CO_3 – 11BM @ APS room temp.



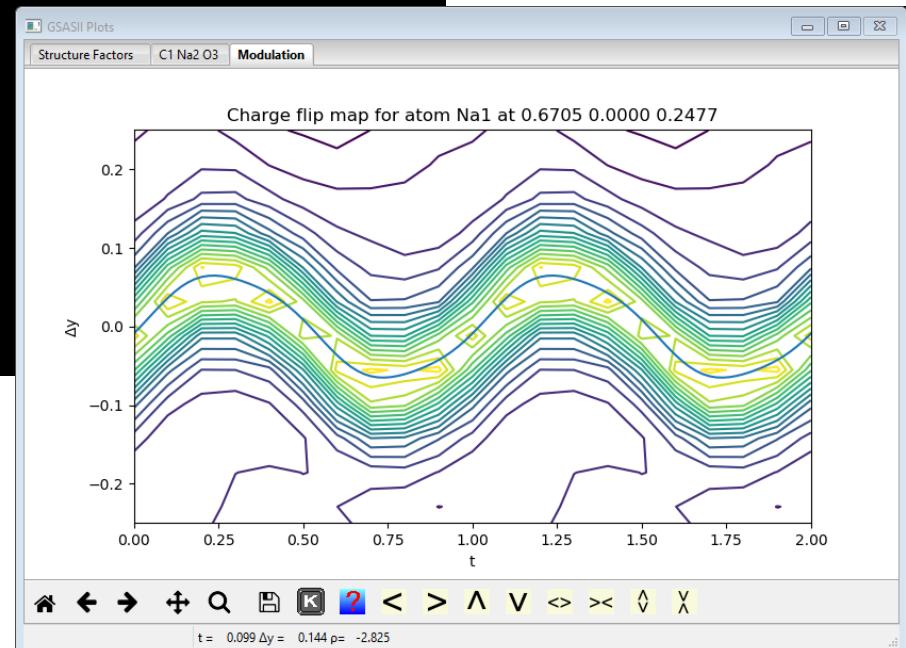
Includes $m=-2,-1,1,2$ superlattice reflections; Rietveld refinement includes 1st & 2nd order harmonics on position depending on atom

INCOMMENSURATE STRUCTURE SOLUTION

4D charge flipping; single crystal & powders (e.g. Pawley refinement)

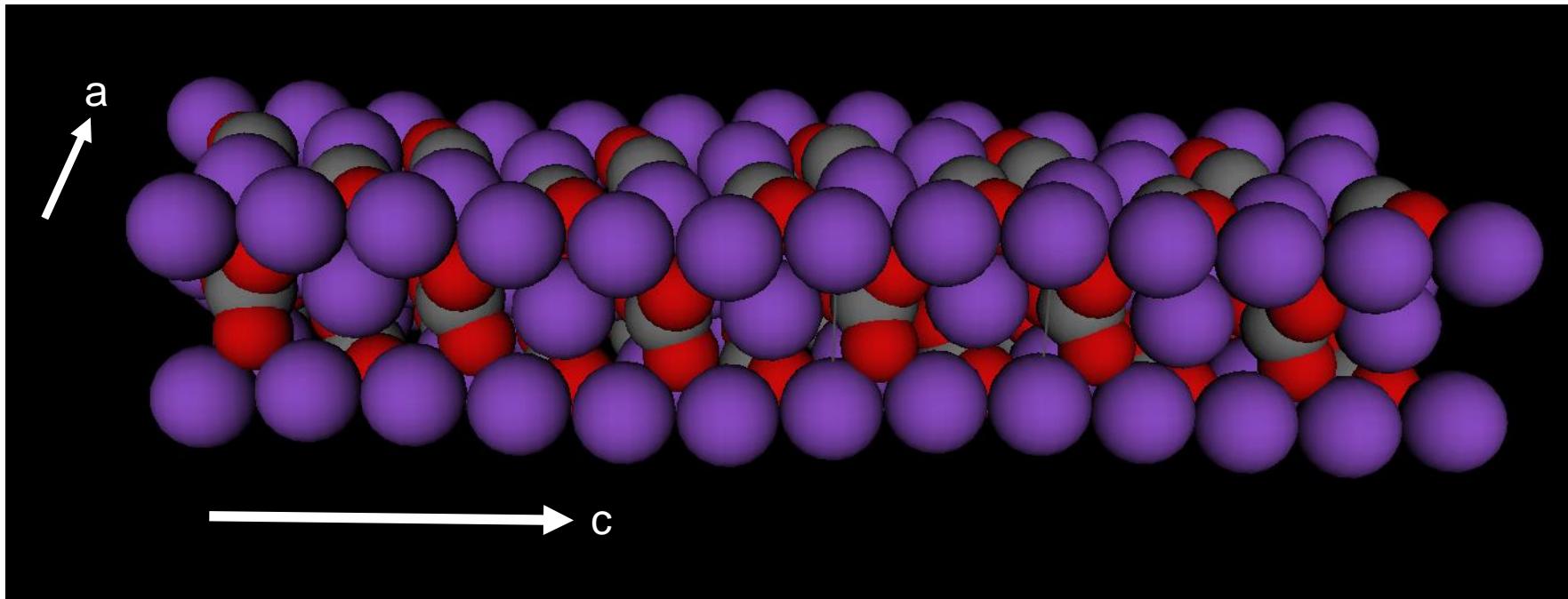


Modulation of atom positions (Na1-y)
Fit function – fourier series in tau



LATTICE MODULATION

Na_2CO_3 – single crystal data



Coordinated wave motion – Na lattice y motion/ CO_3 rocking motion
Recall $q = 0.183, 0, 0.319$ so period ~6-7 on x & ~3 on z
Possible modulations: positions, thermal parameters, site fractions
(& magnetic moments)

INCOMMENSURATE STRUCTURES

Symmetry symbols – interpreted by GSAS-II (not lookup)

- Space group + super symmetry symbol

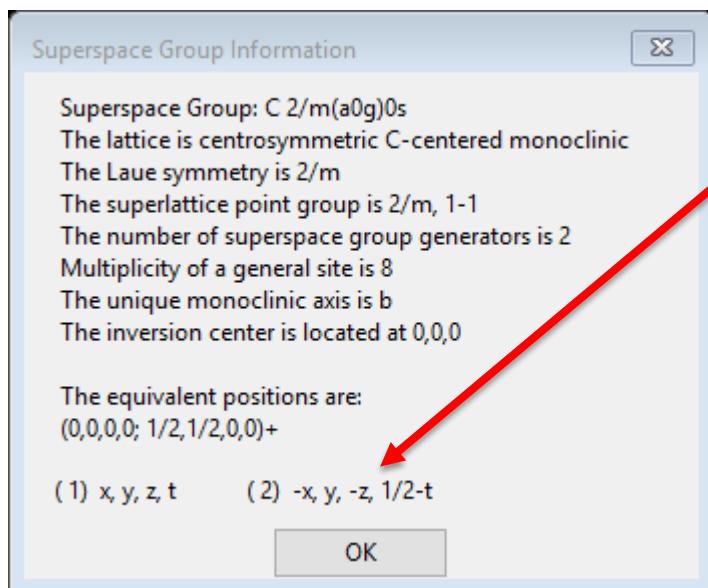
e.g. Na_2CO_3 – C2/m($a_0\gamma$)os

Space group

Translation component

Modulation vector

Operators: conventional space group & 4th dim component



Possible modulation vectors:
e.g. $\alpha\beta\gamma$, $\alpha_0\gamma$, $0\beta_0$, $\alpha\frac{1}{2}\gamma$, $\frac{1}{2}\beta_0$
Translations: 0,s,t,q,h
1-4 of these
Depend on space group
GSAS-II shows legal choices

MODULATION MODELS

Position, thermal motion, site fraction & magnetic moment

- Position: on x,y,z
 - Fourier series sin & cos – symmetry allowed choices
 - Zigzag, sawtooth & block – just 1, add Fourier for more terms



- Thermal motion:
 - Fourier series
- Site fraction:
 - Fourier series
 - Crenel – like block but 0/1 (not +/- x)
- Magnetic moment
 - Fourier (odd terms only – generally just 1)

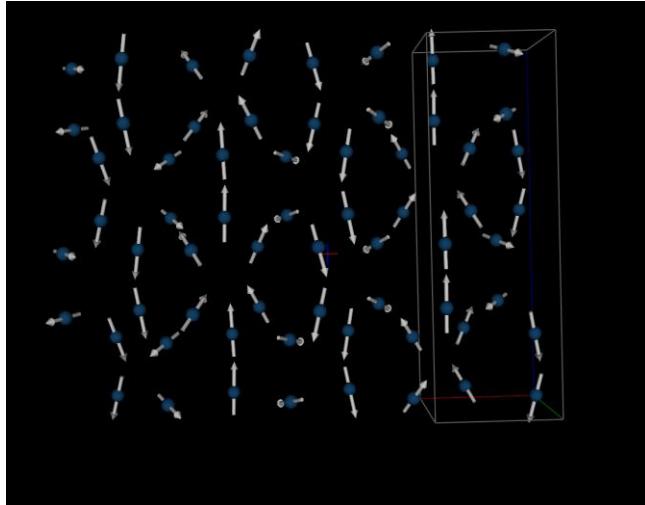
INCOMMENSURATE STRUCTURES

Cases not allowed in GSAS-II

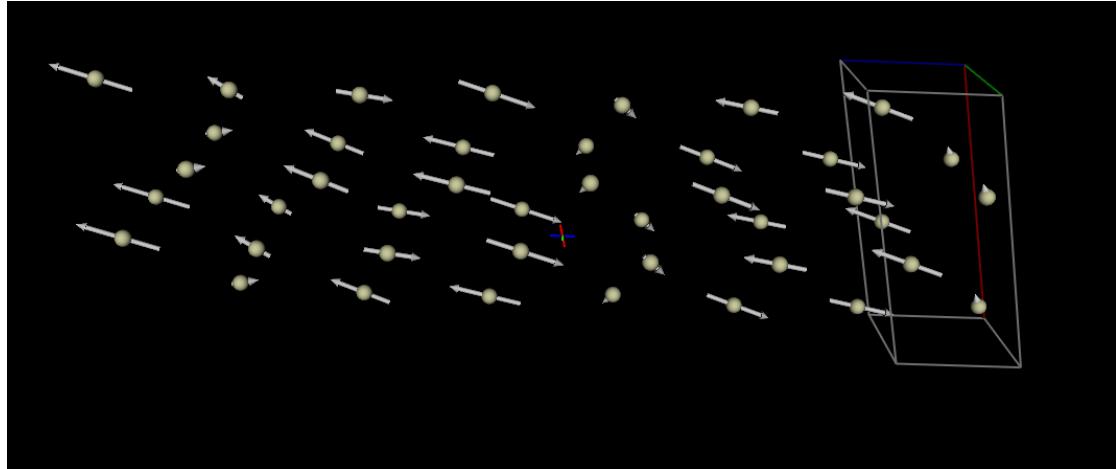
- 3+2 & 3+3 not allowed in GSAS-II
 - Too complex to deal with easily
 - 3-D 230 SG
 - For 3+1: 4,783 possible SG
 - For 3+2: 222,018 possible SG
 - For 3+3: 28,927,922 possible SG
 - But only a handful found – not worth the hassle
- Ad hoc centering not allowed
 - ‘X’ space groups – all have equivalent legal ones with transformation
- Other odd cases found in cif files not allowed
 - e.g. R-centered monoclinic

MAGNETIC INCOMMENSURATE STRUCTURES

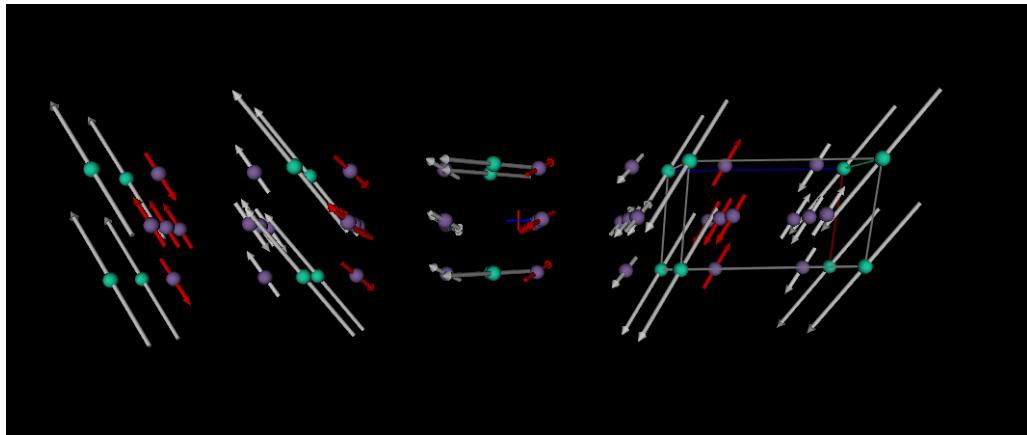
Some examples:



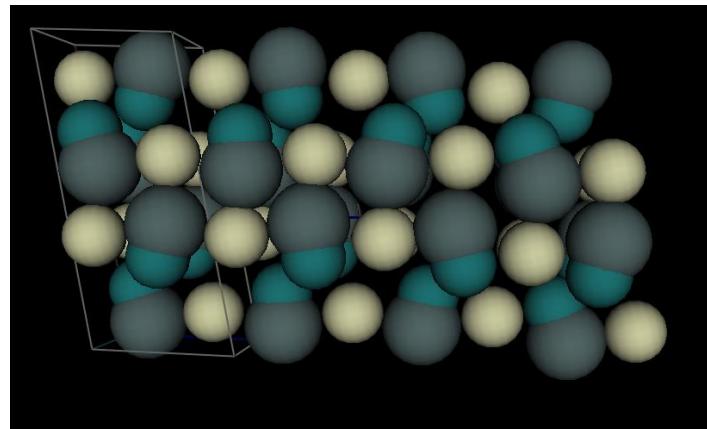
β -Li₂IrO₃



CeRuSn – Ce moment



DyMn₆Ge₆ – residual moment



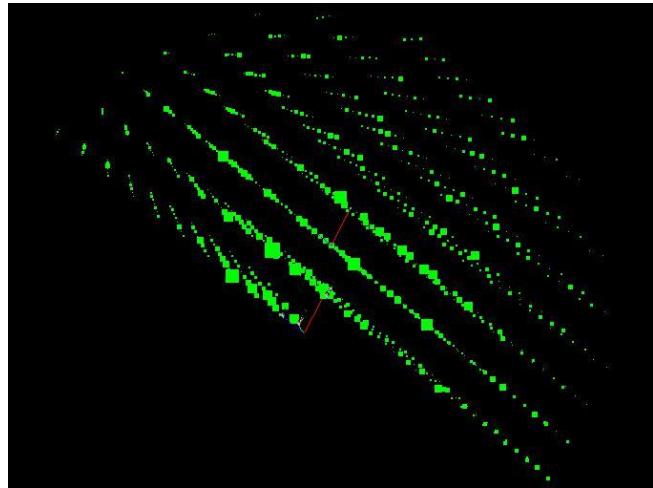
CeRuSn –
structure modulation

CHARGE FLIPPING

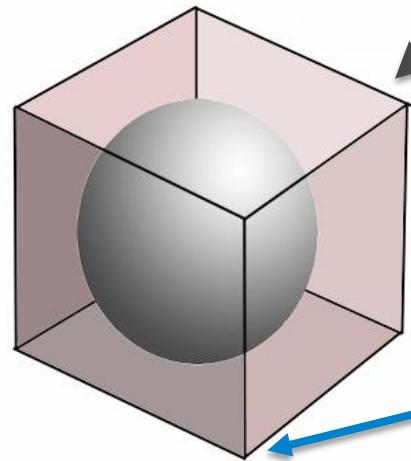
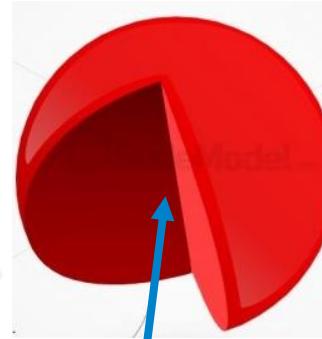
CHARGE FLIPPING

The algorithm set up:

~1Å unique reflections → sphere → box → 0.5Å box



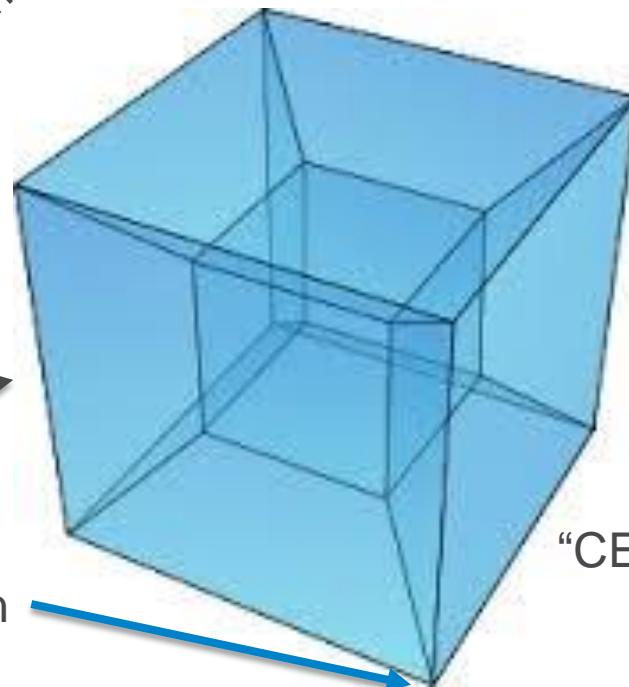
1D list



1D list → 3D array

Origin @ F_{000}

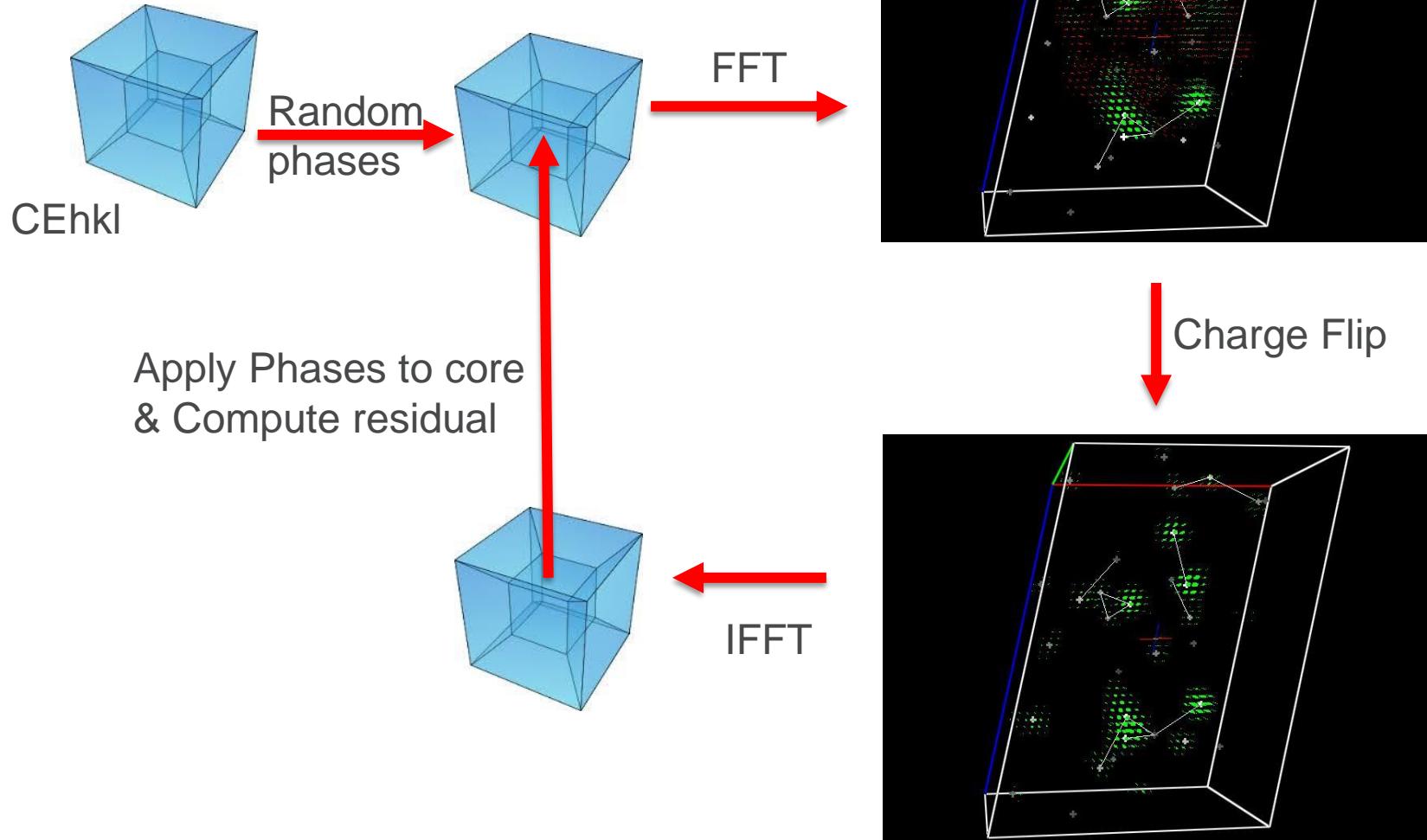
Expand
3D array



New origin

CHARGE FLIPPING

The Algorithm



CHARGE FLIPPING – 3D & 4D

Python loop – all double precision; start random phases for CEhkl

```
CErho = np.real(fft.fftn(fft.fftshift(CEhkl)))*(1.+0j)          #fft Fhkl → ρ(xyz)
CEsig = np.std(CErho)                                         #get σ(ρ)
CFrho = np.where(np.real(CErho) >= flipData['k-factor']*CEsig,CErho,-CErho) #CF ρ → ρ'
CFrho = np.where(np.real(CErho) <= flipData['k-Max']*CEsig,CFrho,-CFrho)   #U atom CF!
CFhkl = fft.ifftshift(fft.ifftn(CFrho))                      #fft ρ'(xyz) → F'(hkl)
CFhkl = np.where(CFhkl,CFhkl,1.0)                            #avoid divide by zero
phase = CFhkl/np.absolute(CFhkl)                             #get φ(hkl) from F'
CEhkl = np.absolute(CEhkl)*phase                            #apply φ to F
Ncyc += 1                                                    #count tries
sumCF = np.sum(ma.array(np.absolute(CFhkl),mask=Emask))      #Σ F
DEhkl = np.absolute(np.absolute(Ehkl)/sumE-np.absolute(CFhkl)/sumCF) #Σ |DF|
Rcf = min(100.,np.sum(ma.array(DEhkl,mask=Emask)*100.))    #residual
```

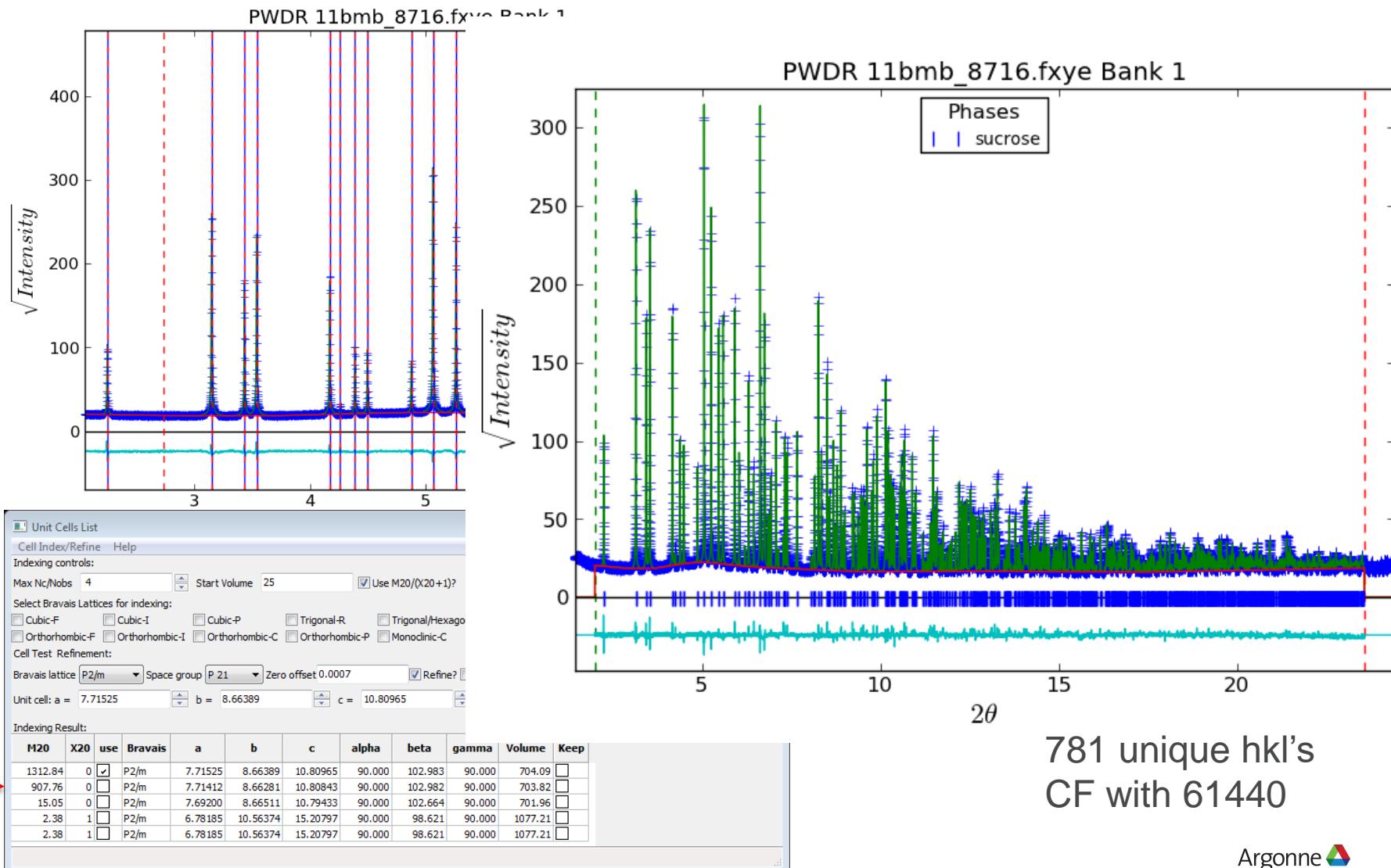
After user break:

Repeat 1st line to get result map

Find origin; search for peaks & display result

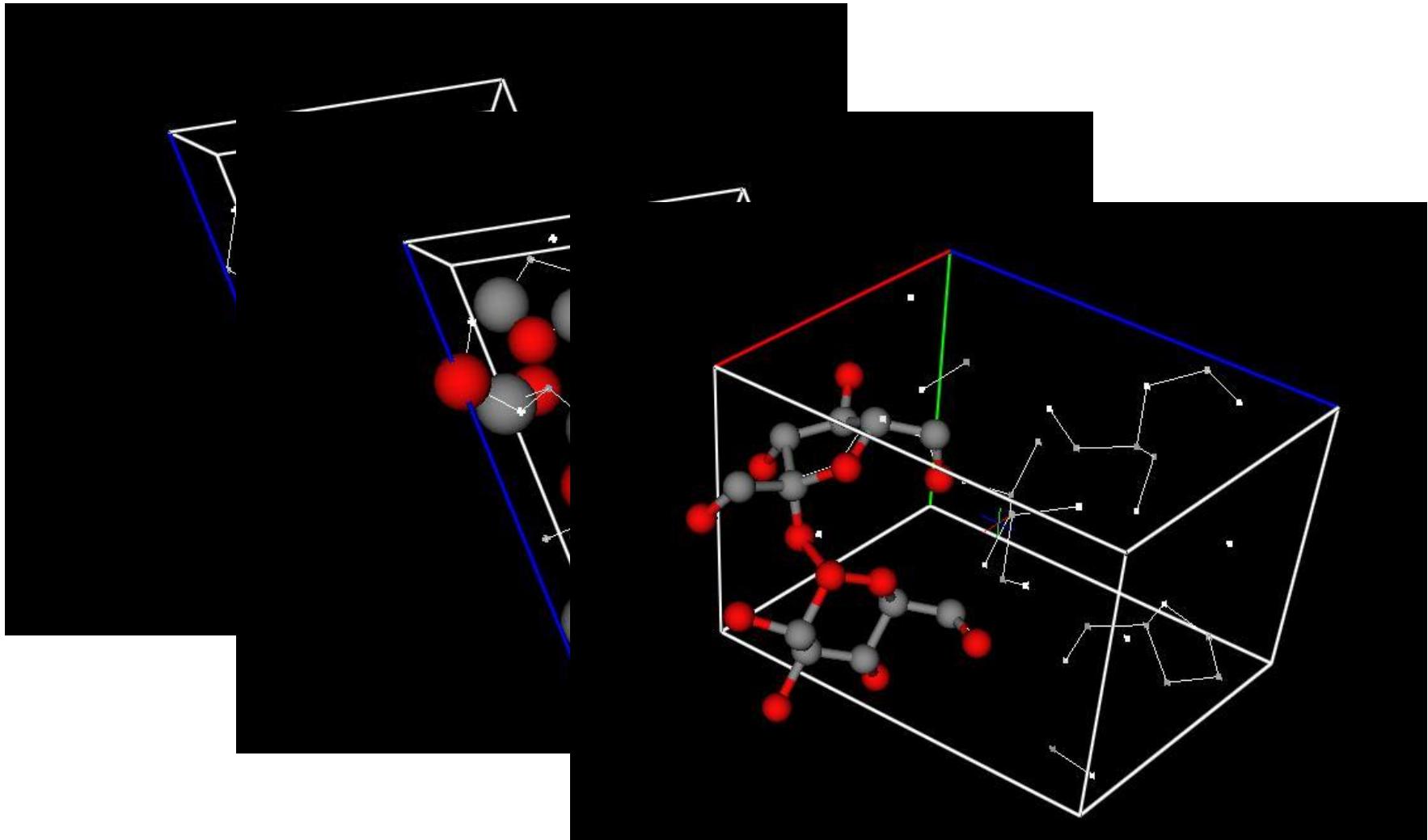
EXAMPLE – SUCROSE POWDER

11BM @ APS - 1st steps – peak fitting/indexing/Pawley refinement



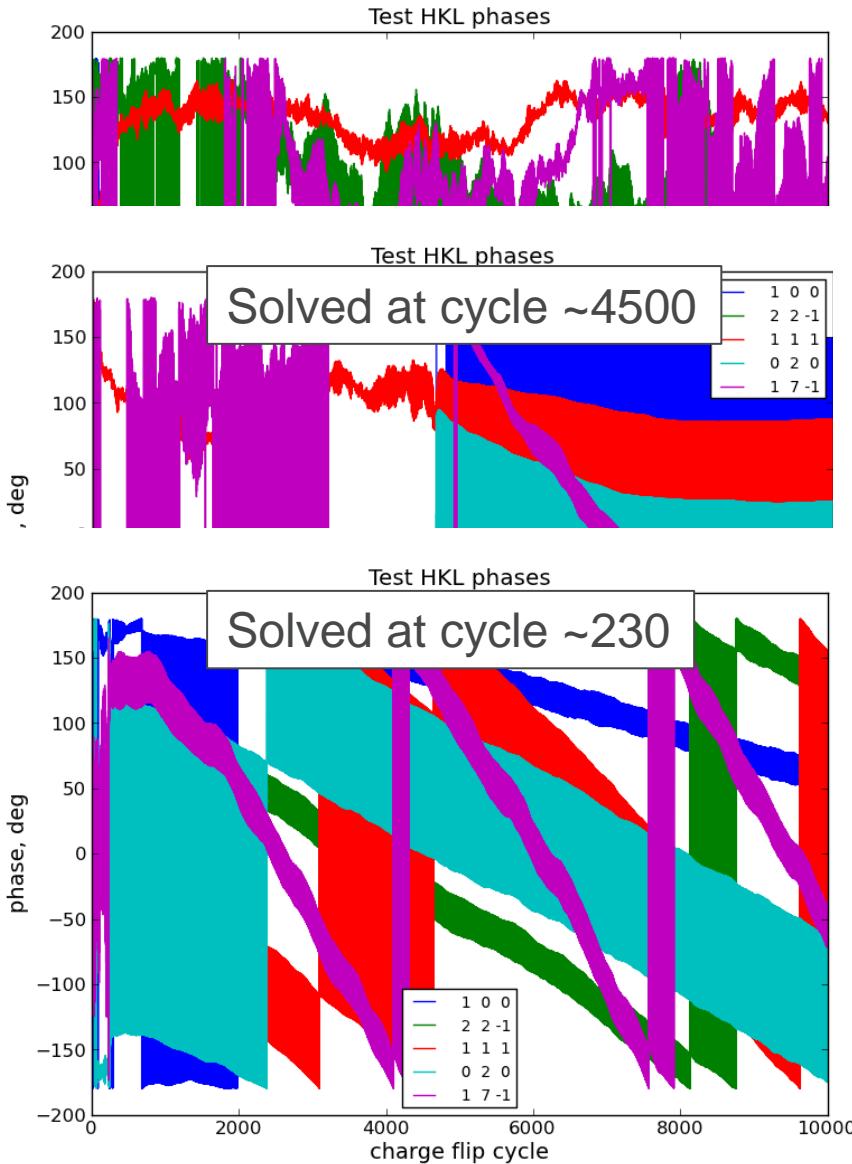
CHARGE FLIPPING SOLUTION

Residual ~45% → ~17% & 46 peaks in cell (NB: sucrose $C_{12}H_{22}O_{11}$)
Map peaks – unique set & select – identify atoms – make molecule

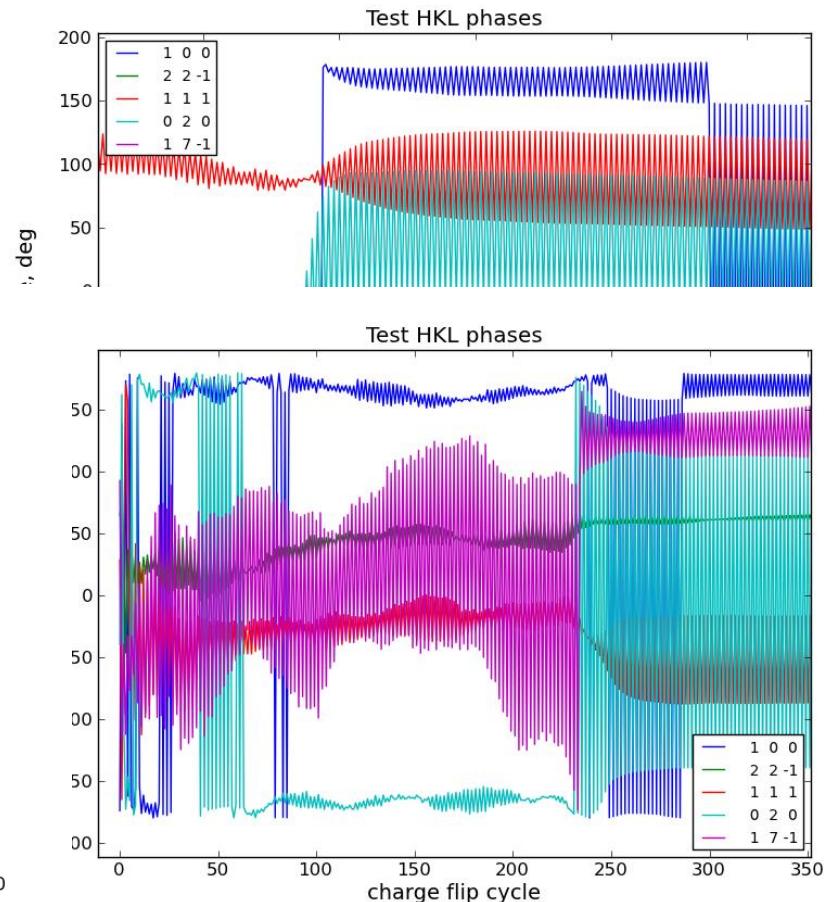


CHARGE FLIPPING – PHASES?

Track phases of 5 reflections – 10000 CF cycles



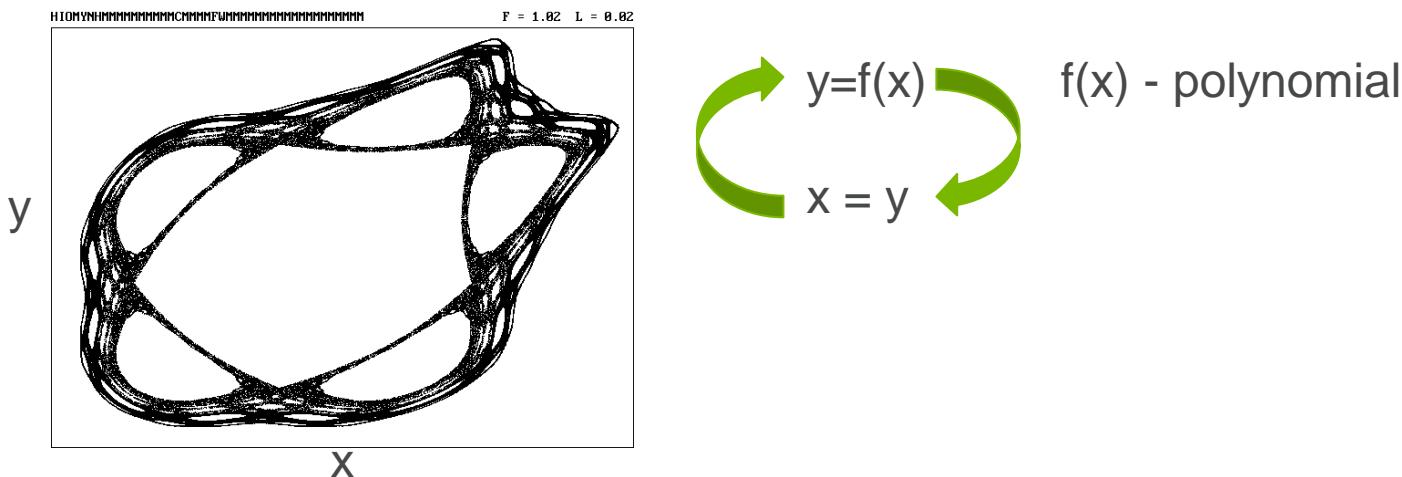
Not solved in 10000 cycles



CHARGE FLIPPING – CHAOS MATHEMATICS?

Strange attractors? Cantor dust? Butterfly effect? Basin of attraction?

- Cyclic algorithm – successive iteration – stable solution (apparently?)
- Chaotic phase behavior – but deterministic (Butterfly effect?)
- Hyper dimensionality ~7680-D for sucrose example (NB: no symmetry used)
- Infinite phase possibilities >> Infinite phase sets for recognizable atoms (Cantor dust?)



- Phase oscillation & drift – “symplectic” or “non-symplectic” strange attractors?
- Is there a “basin of attraction”?
- Does this really matter?

(picture from “Strange Attractors: Creating Patterns in Chaos” by J. C. Sprott)

The background of the slide is a grayscale aerial photograph of the Argonne National Laboratory complex. The image shows a dense network of buildings, roads, and green spaces, with a prominent circular structure in the center-left. The overall tone is blue.

THANK YOU

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
- Newest! (& bugs?) for python 3.6
<https://subversion.xray.aps.anl.gov/trac/pyGSAS/wiki/G2onPy3>

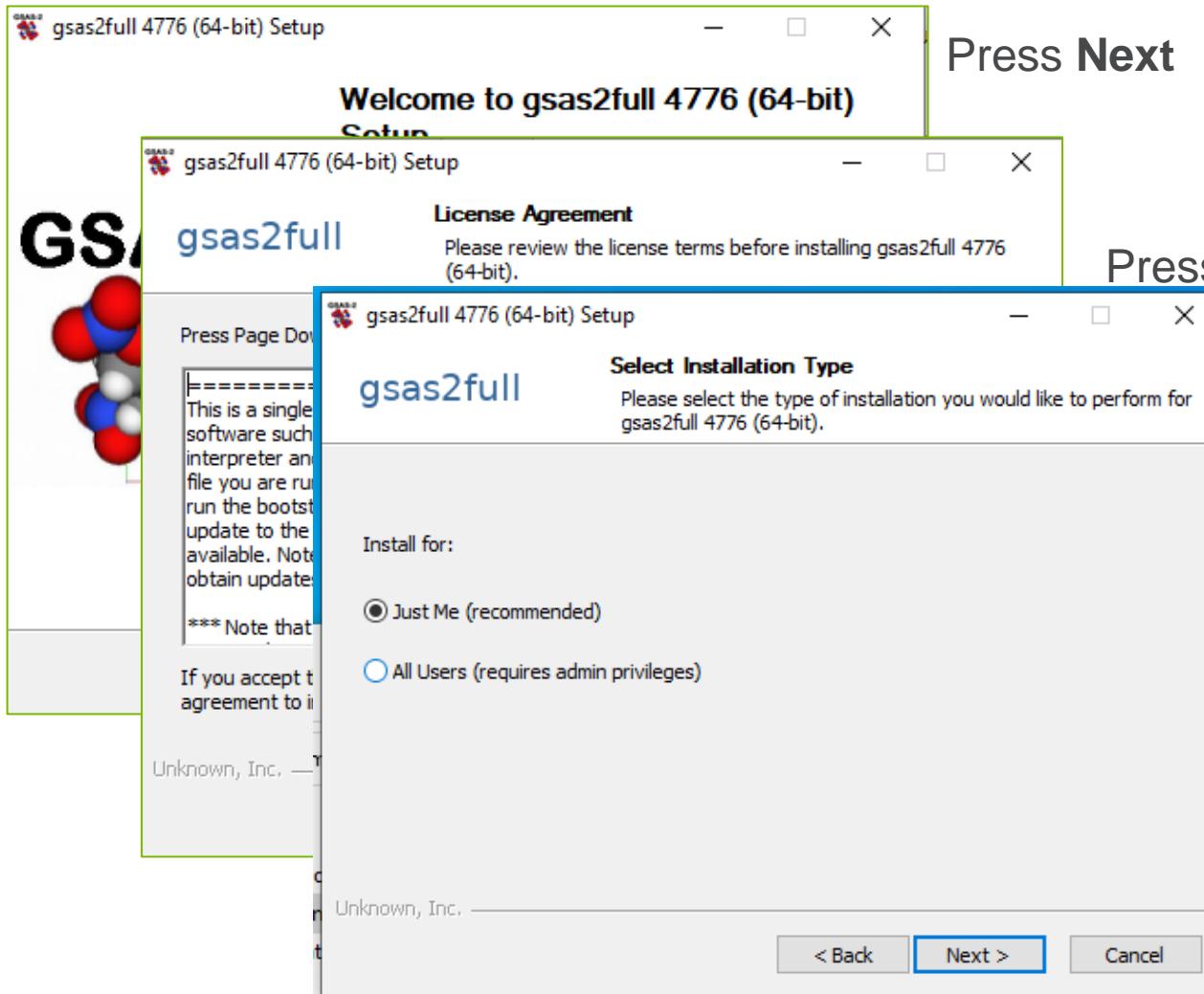
or

Find the download file (gsas2full-Latest-Windows-x86_64) in TLTDisk (S:) in “S:\xray\Gsas2full\Install Files” or download as

https://subversion.xray.aps.anl.gov/admin_pyGSAS/downloads/gsas2full-Latest-Windows-x86_64.exe

And run it

YOU SHOULD SEE:



gsas2full

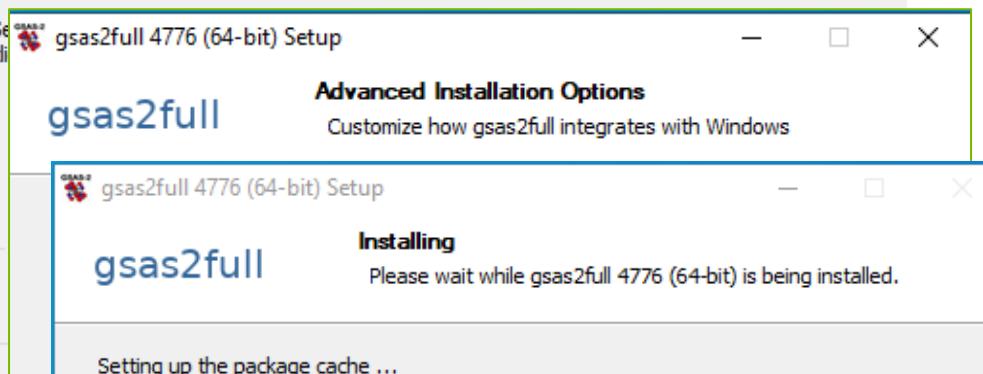
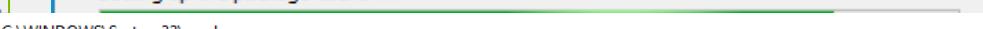
Choose Install Location

Choose the folder in which to install gsas2full 4776 (64-bit).

Can be anywhere you are allowed
(can be the ACA stick). Use default;
Press **Next>**

Don't select any of these
Press **Install**

Shows progress
Press **Next** when done

```
C:\Users\g1121530\gsas2\conda-meta>REM constructor fixups: missing empty directories & changed binary files -----
C:\Users\g1121530\gsas2\conda-meta>REM mkdir -p $PREFIX/GSASII/.svn/tmp
C:\Users\g1121530\gsas2\conda-meta>C:\Users\g1121530\gsas2\bin\svn revert -R C:\Users\g1121530\gsas2\GSASII\bindist
The system cannot find the path specified.

C:\Users\g1121530\gsas2\conda-meta>REM update the GSAS-II package if possible, create shortcuts & byte-compile...
C:\Users\g1121530\gsas2\conda-meta>call "C:\Users\g1121530\gsas2\Scripts\Activate"
(base) C:\Users\g1121530\gsas2\conda-meta>REM Now try to update to latest GSAS-II version (will fail if no network)
(base) C:\Users\g1121530\gsas2\conda-meta>"C:\Users\g1121530\gsas2\python.exe" "C:\Users\g1121530\gsas2\GSASII\bootstrap.py" --noinstall
Running bootstrap from C:\Users\g1121530\gsas2\GSASII at 2022-06-16 17:39:58.767896
    Id: $Id: bootstrap.py 4775 2021-01-16 18:52:00Z toby $
Python:      3.7.1
numpy:       1.19.1
*****
Preloading matplotlib to build fonts...
Checking python packages...

Checking for subversion...
  Found svn image: C:\Users\g1121530\gsas2\Library\bin\svn.exe
Ready to bootstrap GSAS-II from repository
      https://subversion.xray.aps.anl.gov/pyGSAS/
to C:\Users\g1121530\gsas2\GSASII
Enter your proxy address [none needed]:
```

Press Enter

Done!



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
- ... (there are more)

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