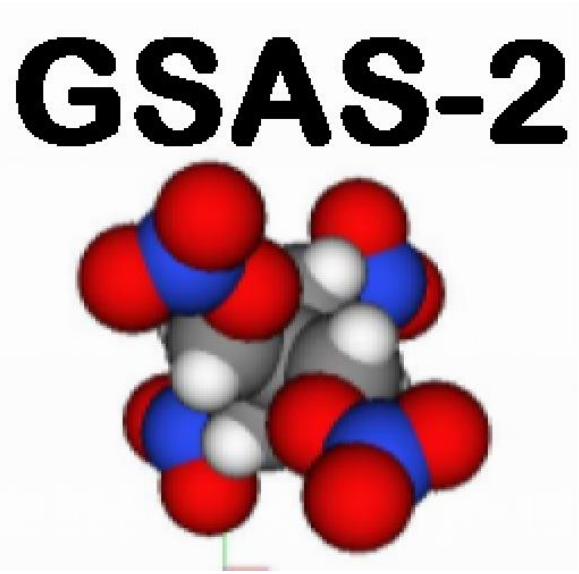
WHAT ELSE DOES GSAS-II DO?



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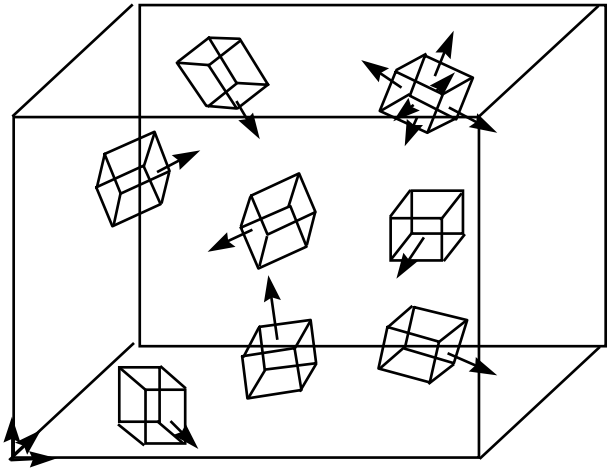
vondreele@anl.gov

Acknowledgements: DOE/SC

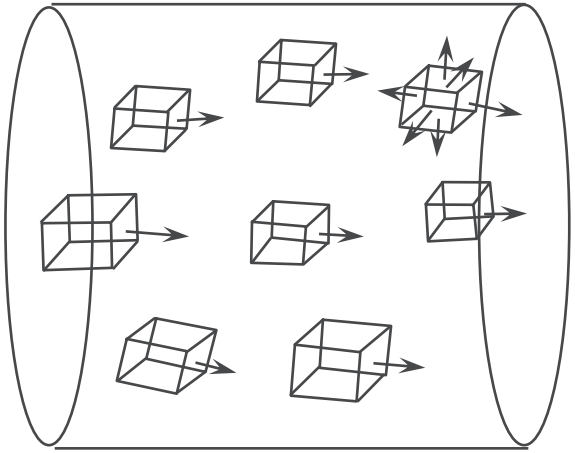
TEXTURE ANALYSIS

What is texture?

Nonrandom crystallite grain orientations



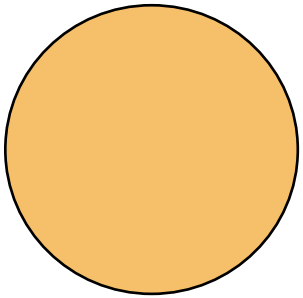
Loose powder



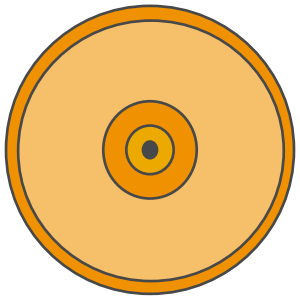
Metal wire

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



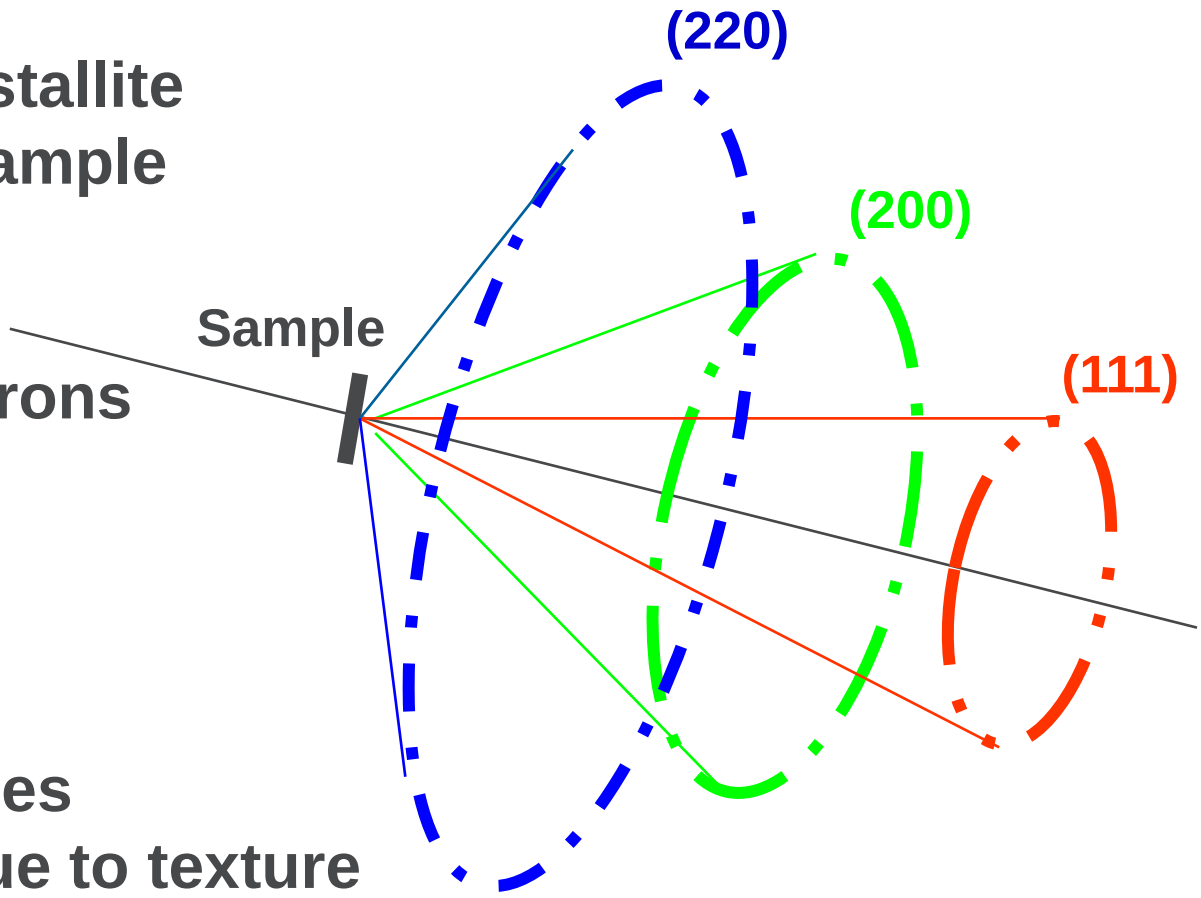
(100) wire texture

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

Orientation Distribution Function - probability function for texture

Texture - measurement by diffraction

Non-random crystallite orientations in sample



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

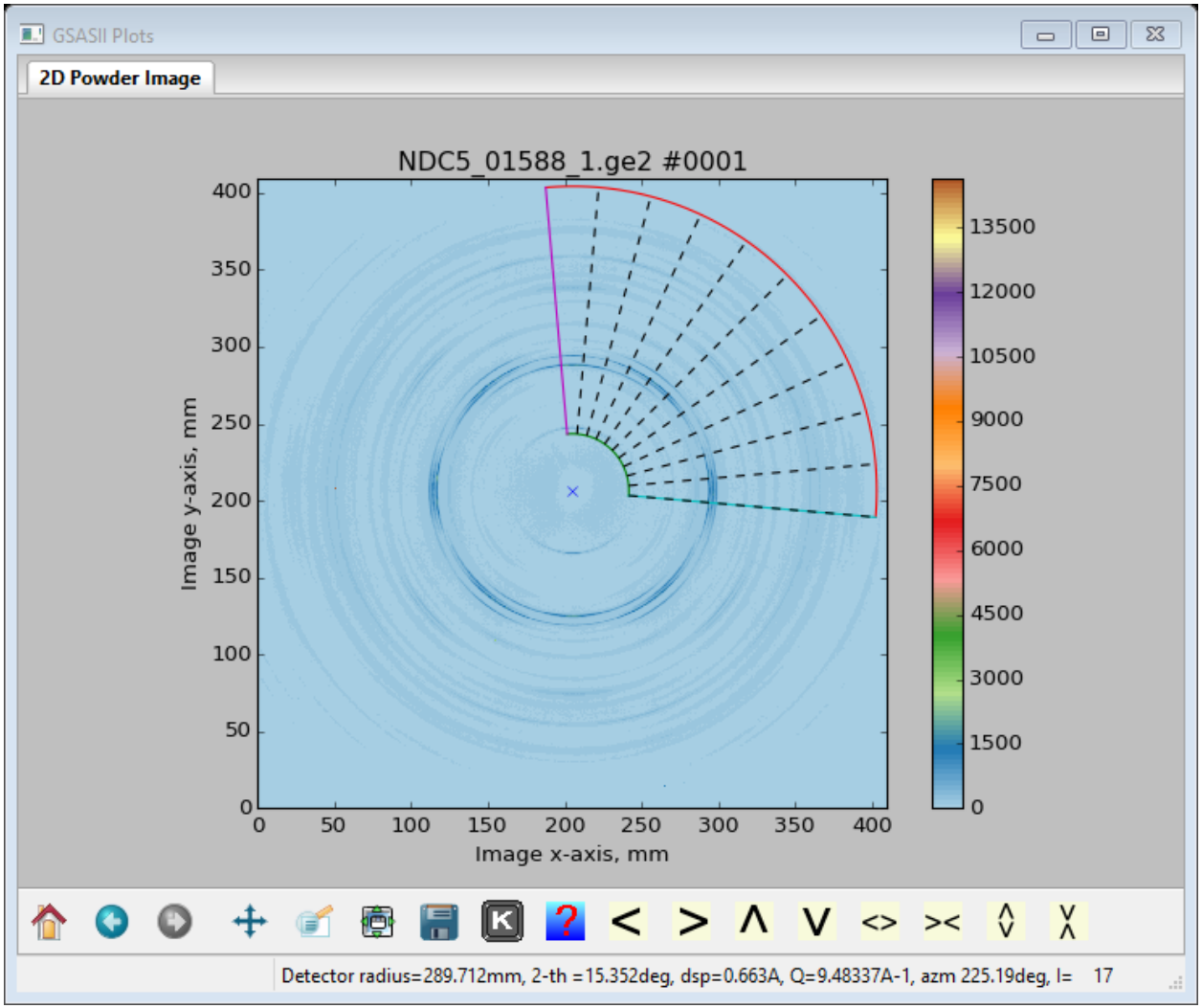
$$A(h,y)=\sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\sum_{m=-l}^{l}\sum_{n=-l}^{l}C_l^{mn}\,K_l^m(h)\,K_l^n(y)$$

- 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

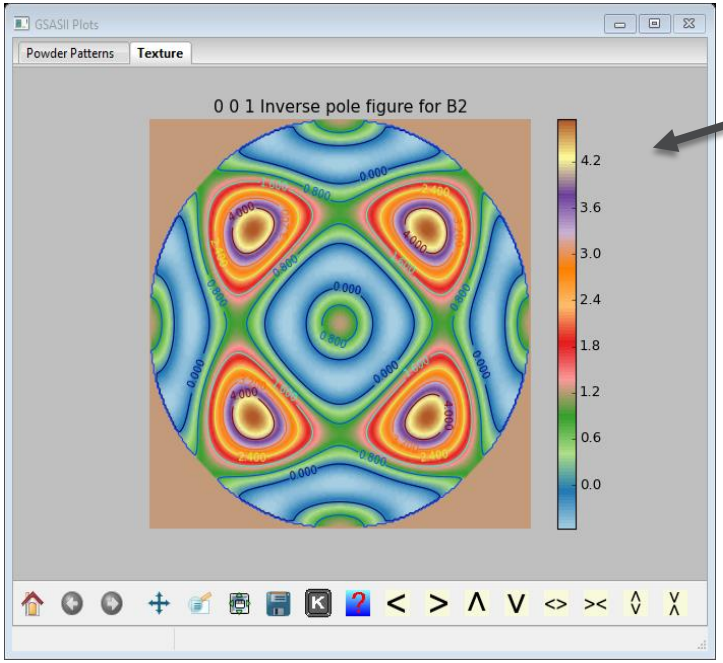
NiTi shape memory alloy wire: B2 & B19' phases

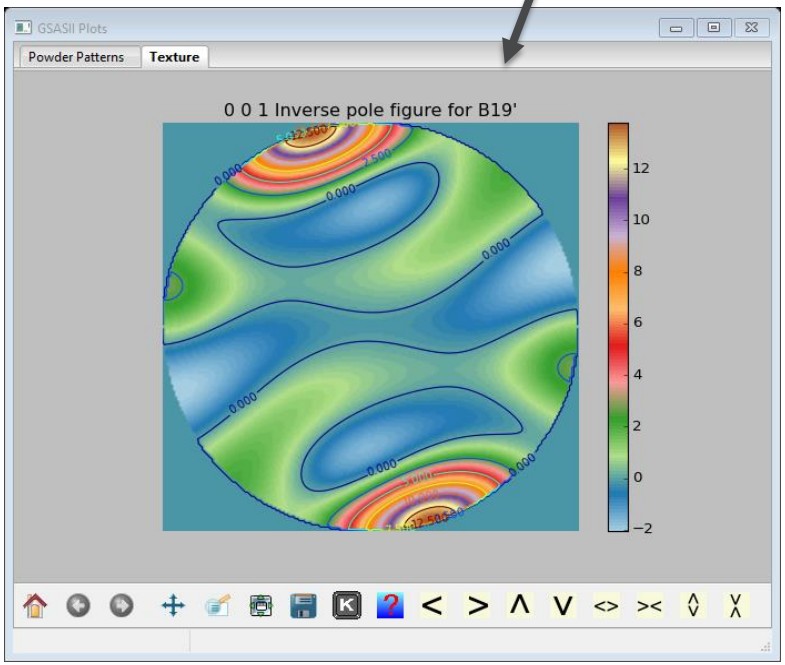


Sample – wire symmetry
Need only ¼ of image
Caked in 10° increments
Integration – PWDR patterns
Analyze for texture

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

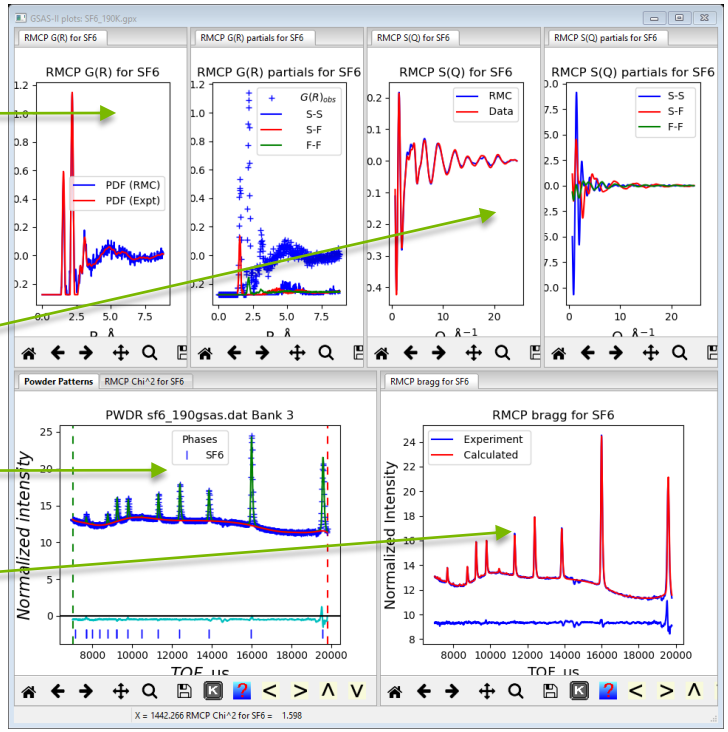
- Provide GUI interface to setup of RMCProfile - save setup controls for reuse
- Initiate independent RMCProfile execution – may run for hours
- Allow graphical display on intermediate results

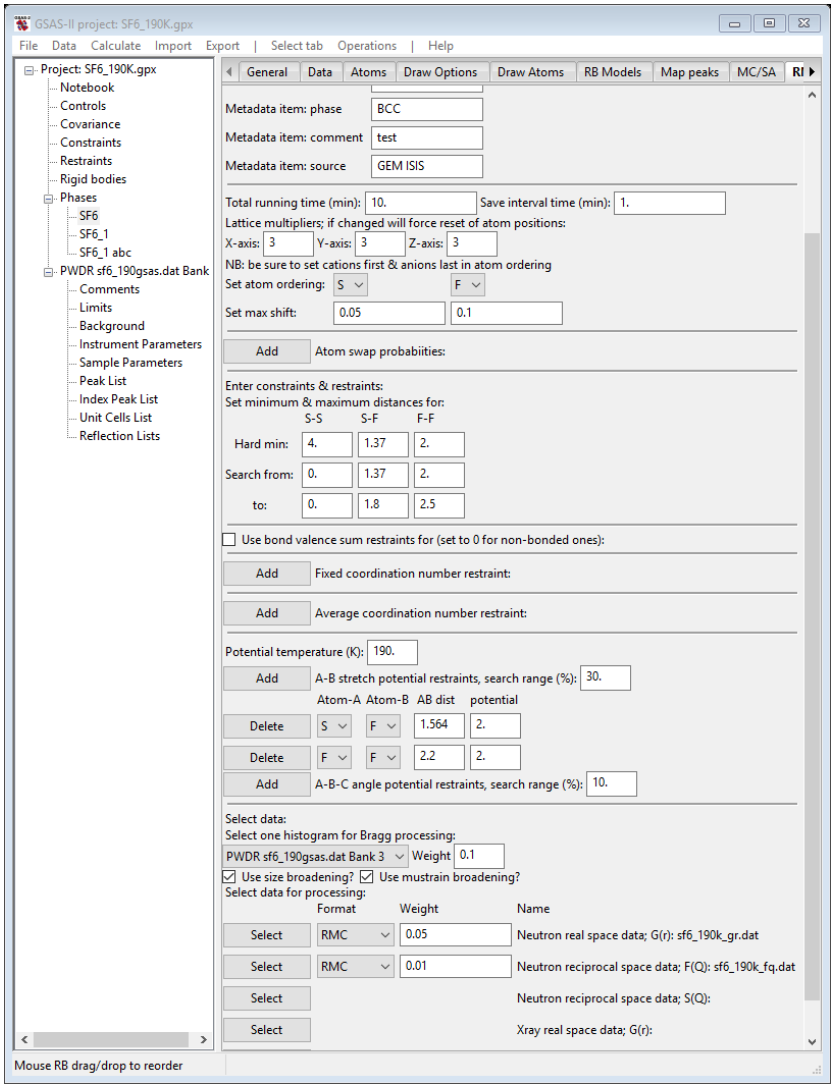
G(R) & partials

S(Q) & partials

RR result

PWDR simulation





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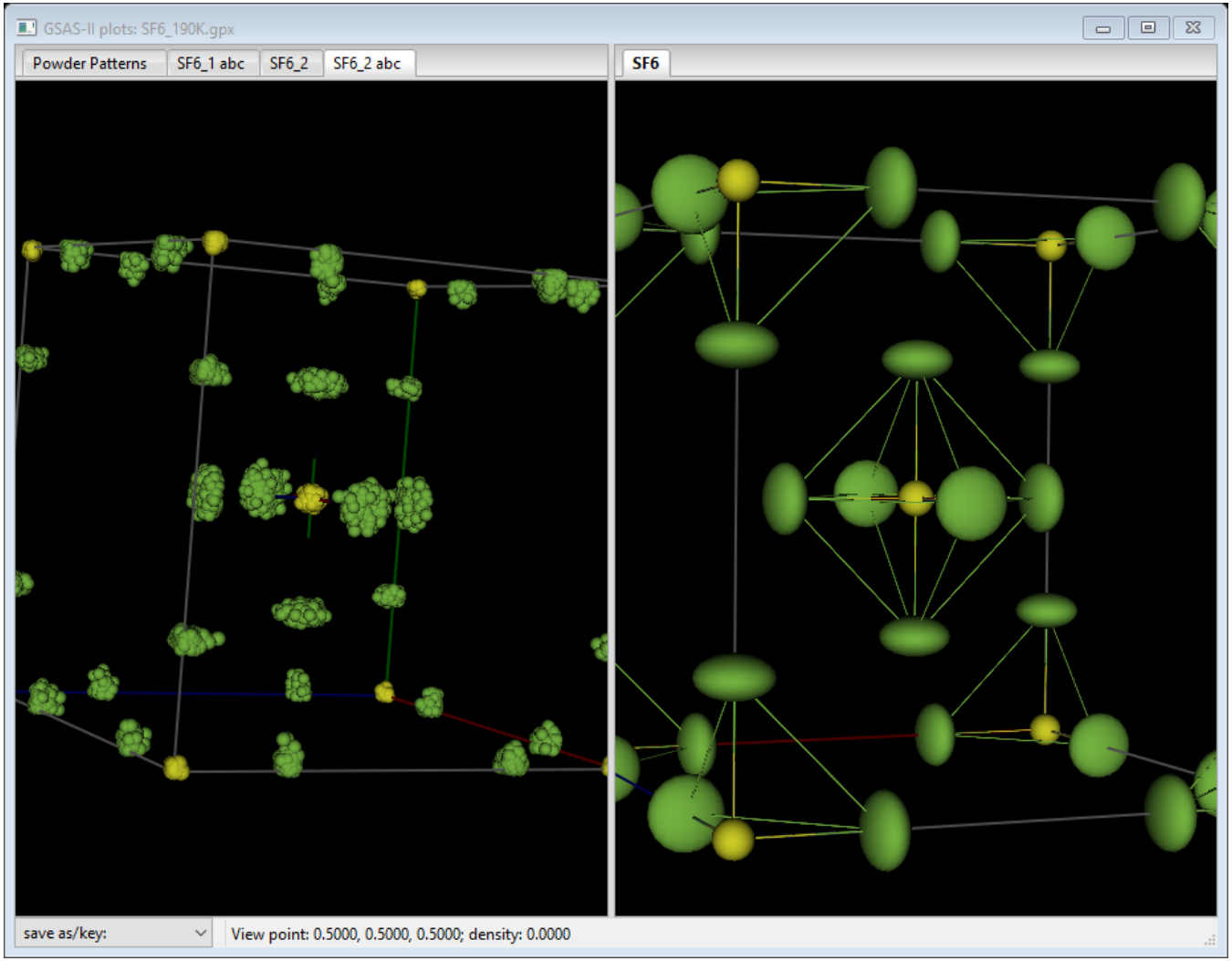
RMCPROFILE RESULT FOR SF_6

10x10x10 unit cell box – transform back to original

See disordered atom distribution

– compare to Rietveld U_{aniso} for F atom



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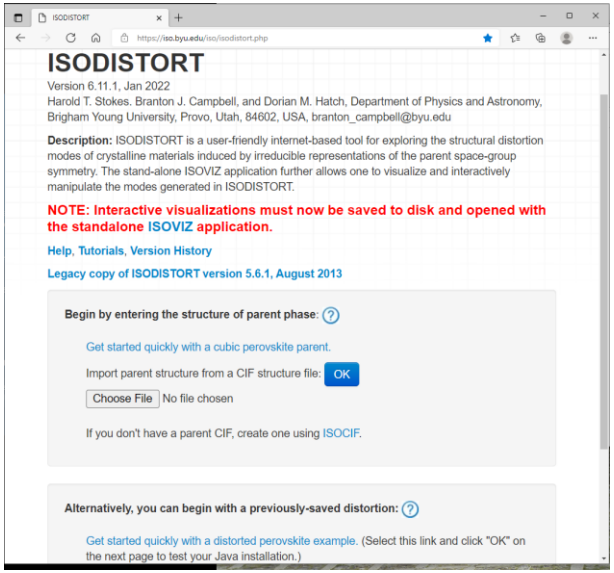
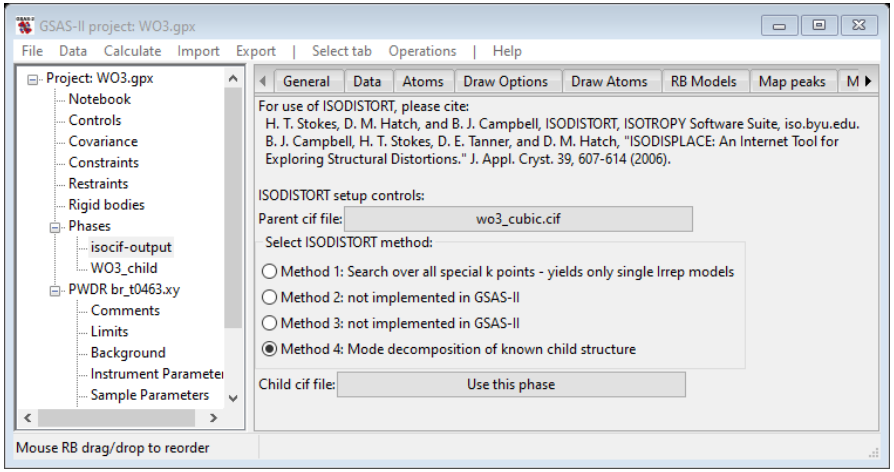
ISODISTORT

Implementation in GSAS-II

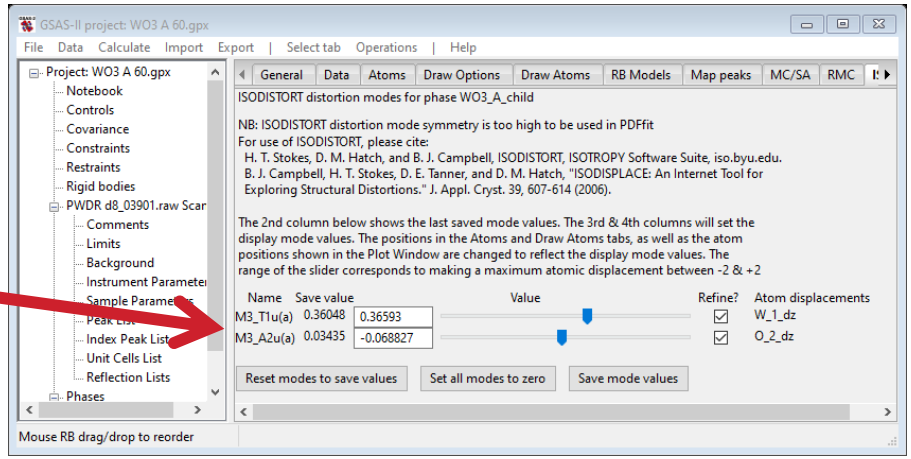
ISODISTORT: Web based tool for discerning mode displacements of atoms from an idealized parent structure





- 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.



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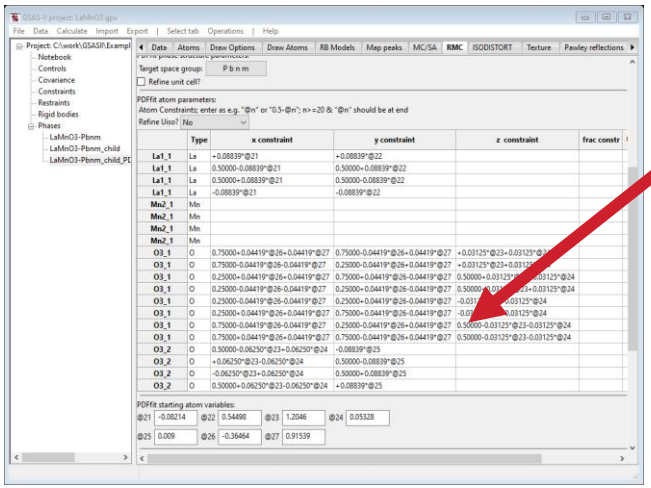
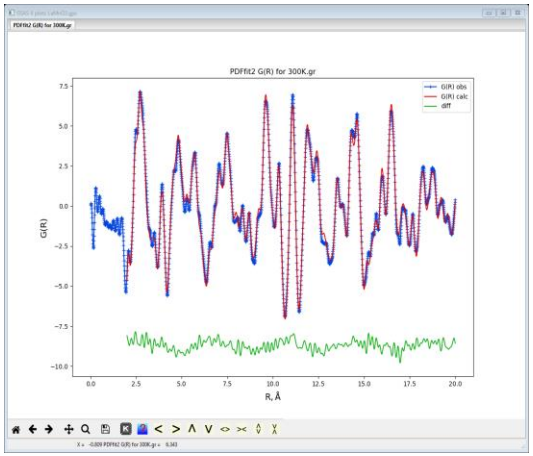
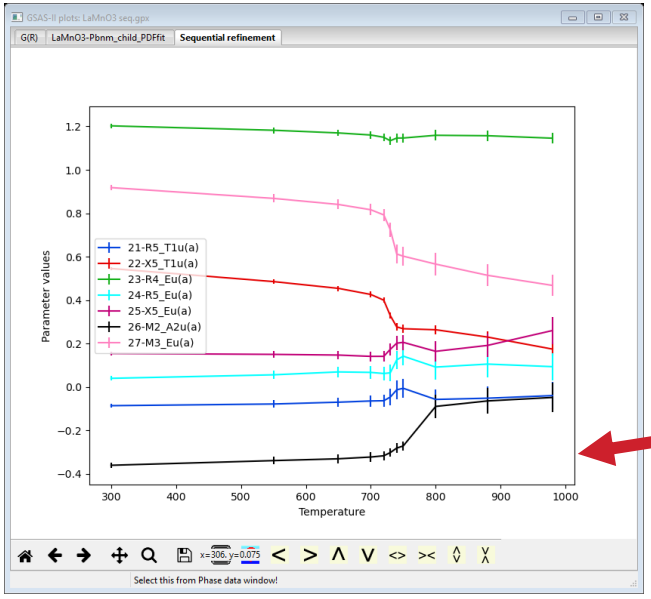
PDFFIT2 = “PDFfit” IN GSAS-II

“Small Box” modelling of pair distribution functions

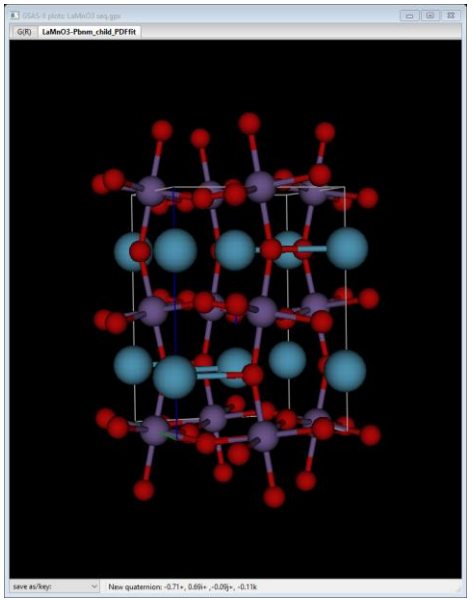
Use ISODISTORT – create the atom position constraints in new interface to PDFfit2







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



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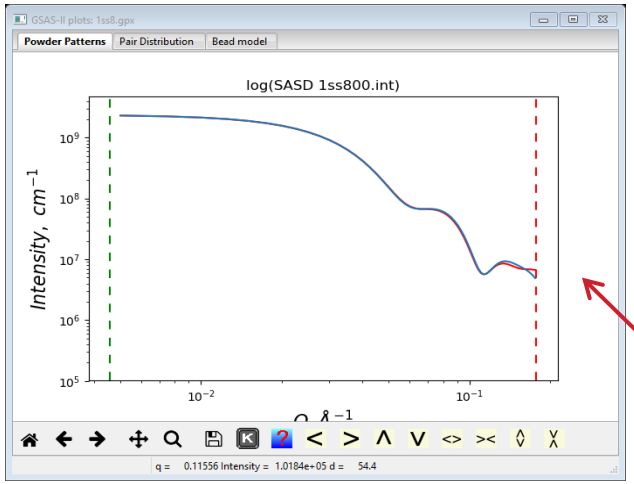
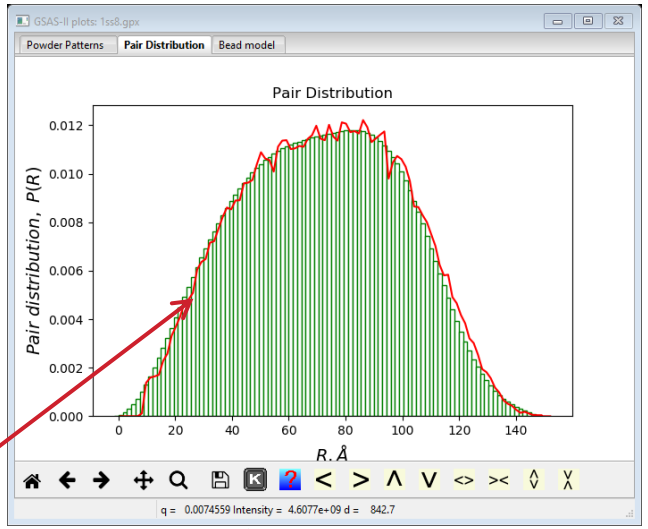
PROTEIN SHAPE ANALYSIS

PROTEIN SMALL ANGLE MODELING IN GSAS-II

Bead models via SHAPES (alternative to DAMMIN in python)

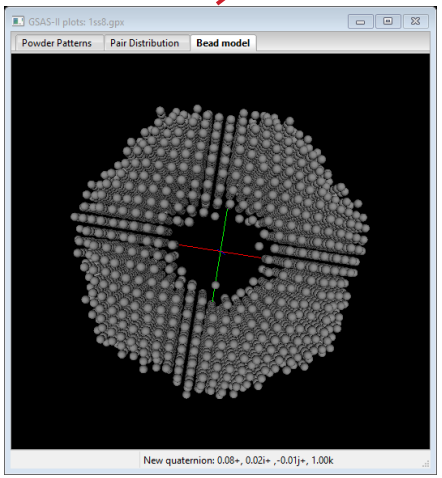


Make P(R)

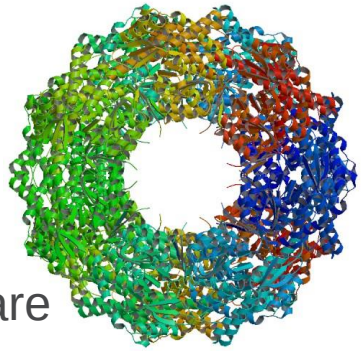


calc

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



Run SHAPES
Make bead model



compare

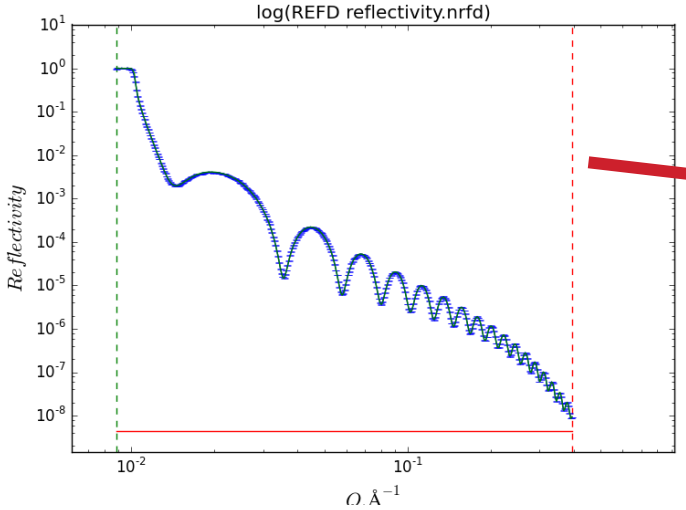
Direct fit?
(In development)

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

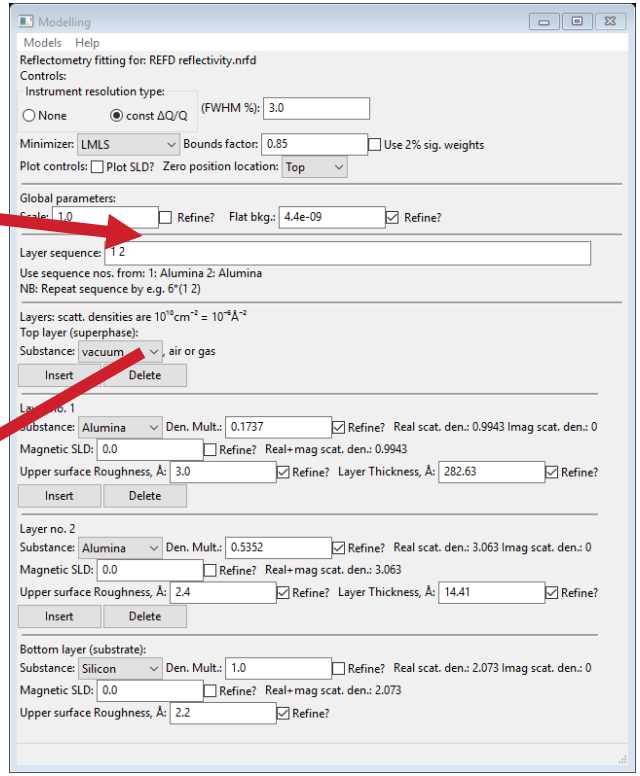
REFLECTOMETRY

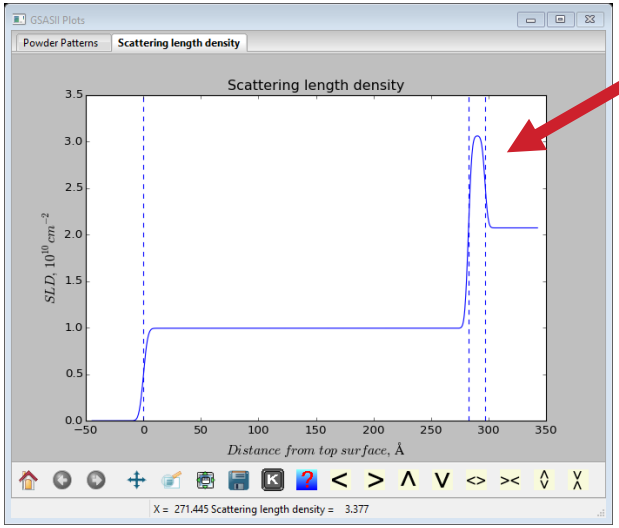
REFLECTOMETRY ANALYSIS IN GSAS-II

X-rays & Neutrons (CW at least)



Multilayer model
Scattering density





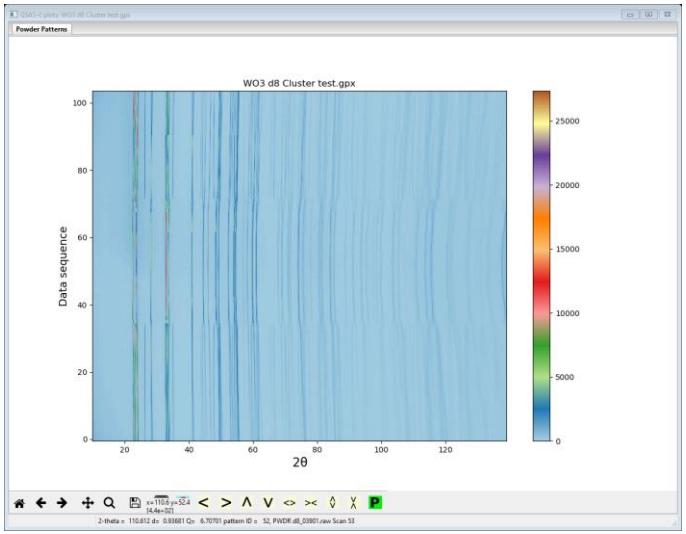
Define components, stacking sequence (can be repeated), thickness & “roughness”
Fit by LSQ, MC/SA & “basinhopping” (under development)

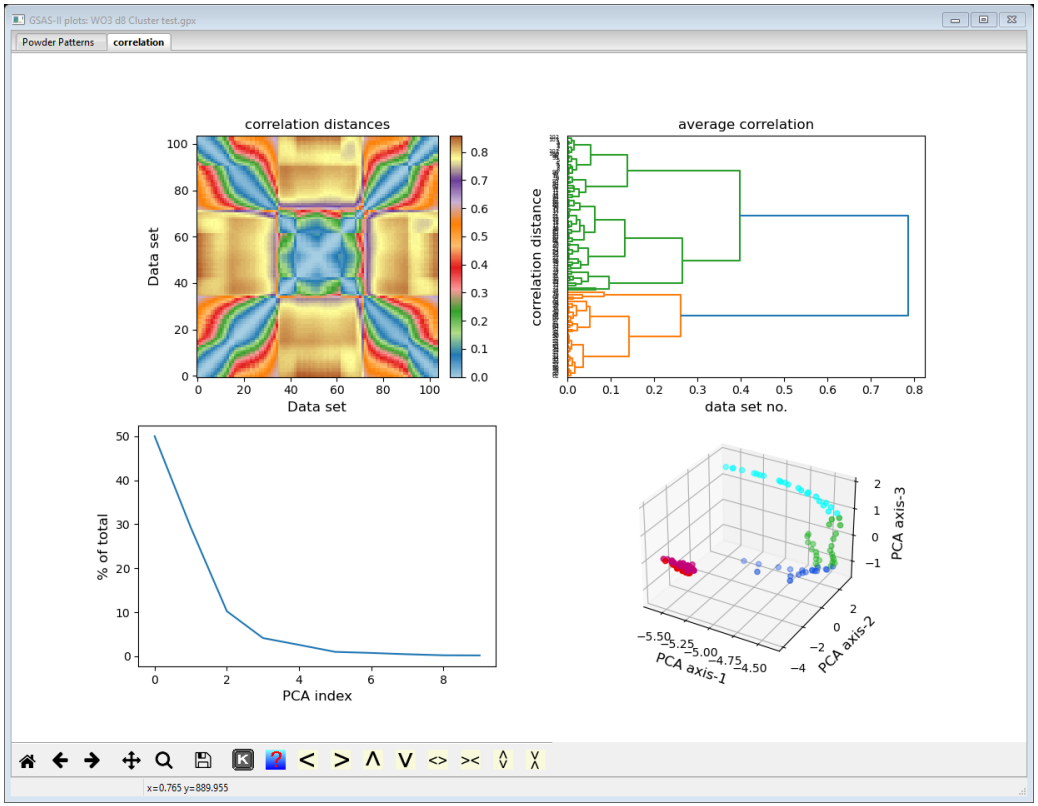
CLUSTER ANALYSIS

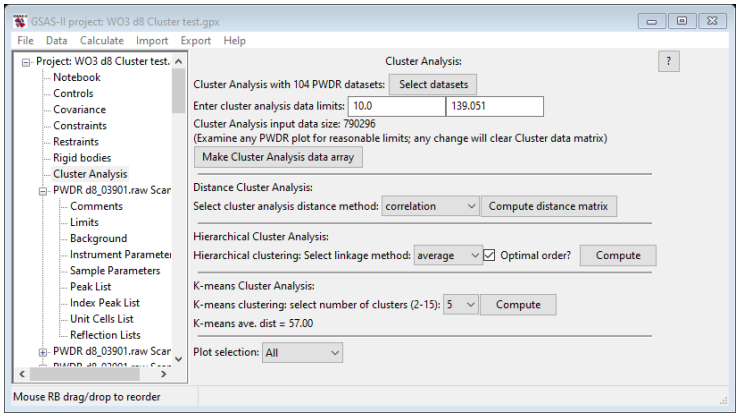
CLUSTER ANALYSIS

Another way of examining data – look for similar patterns

- Example – WO_3 x-ray data 300-1200K & back; 100 patterns. Multiple phase changes







Still under development & no help or tutorials yet.

STACKING FAULTS – DIFFAX IN GSAS-II

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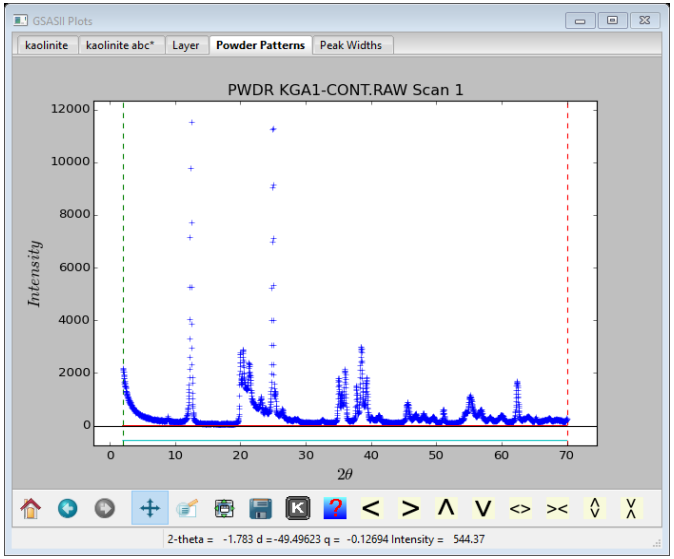
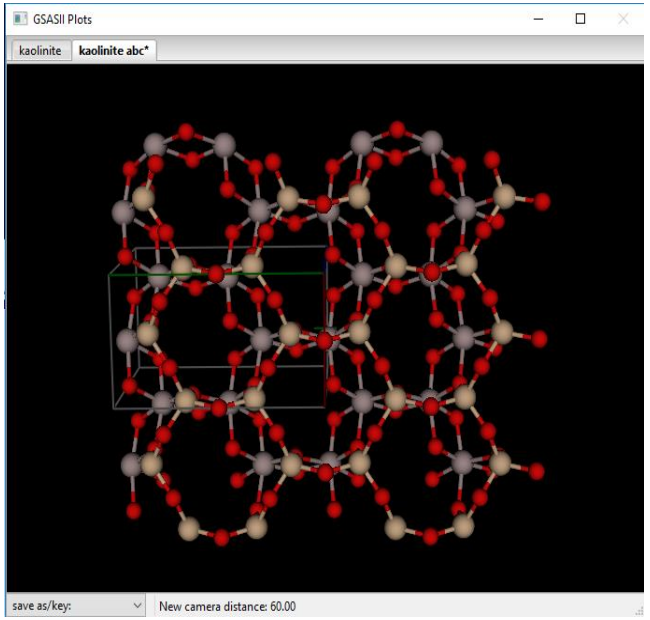
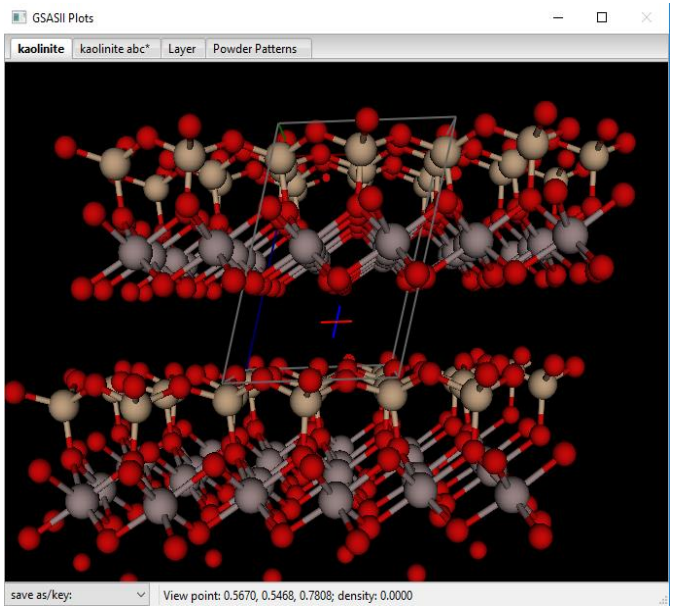
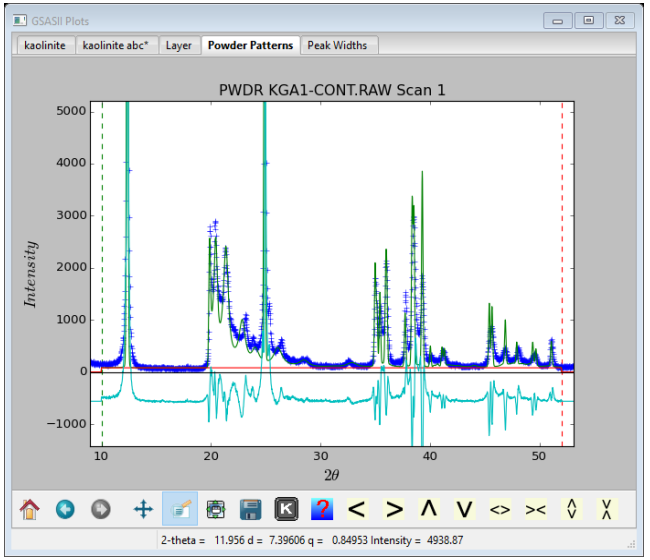
STACKING FAULTS IN KAOLINITE $Al_2Si_2O_5(OH)_4$









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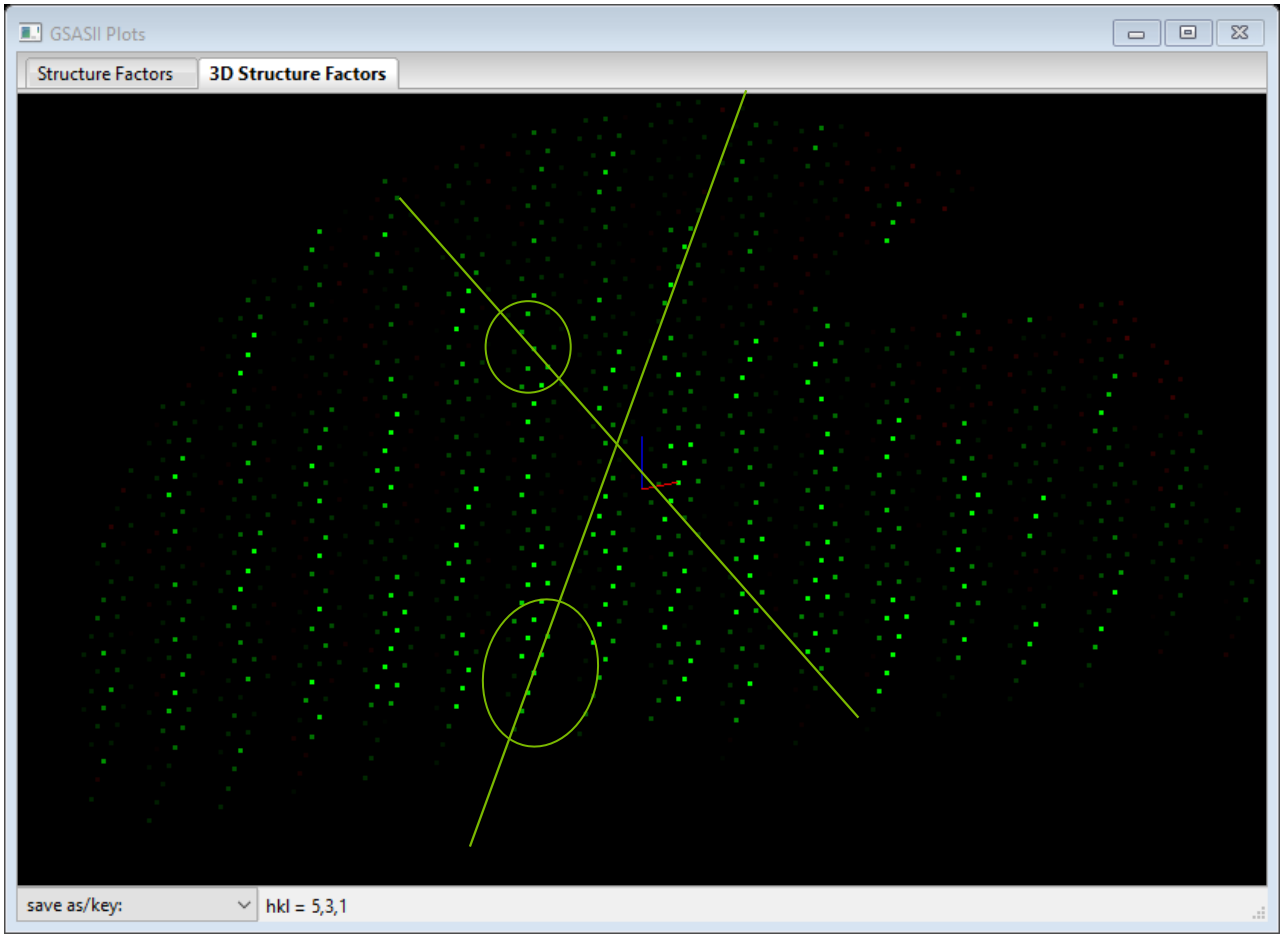
3+1 INCOMMENSURATE STRUCTURES

INCOMMENSURATE STRUCTURES N GSAS-II

Book: “Incommensurate Crystallography” S. van Smaalen



H=G+mq

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

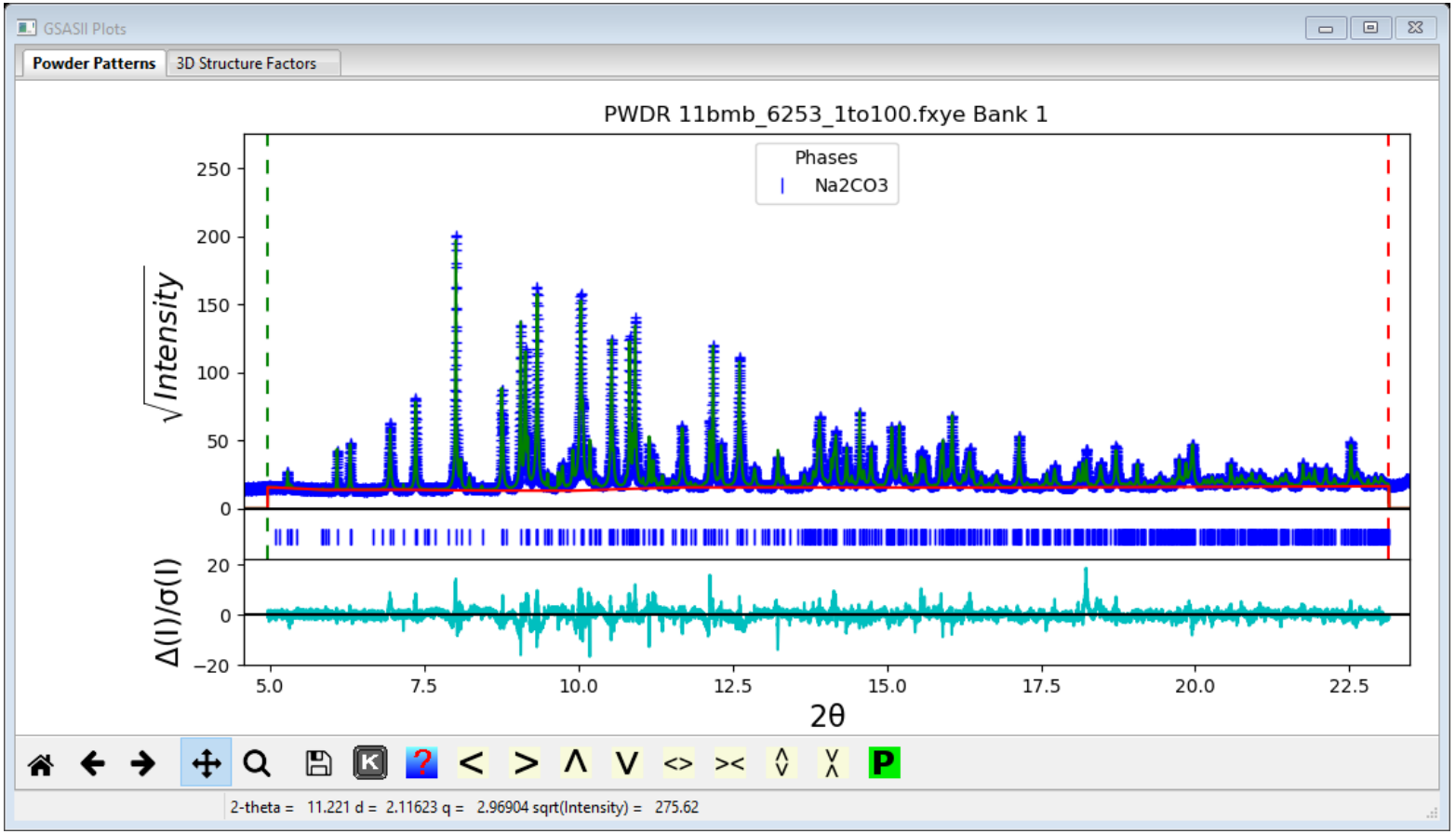
For Na_2CO_3
q= 0.183,0,.319

Each reflection: hklm
m=0 sublattice
m≠0 superlattice

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

POWDER DIFFRACTION

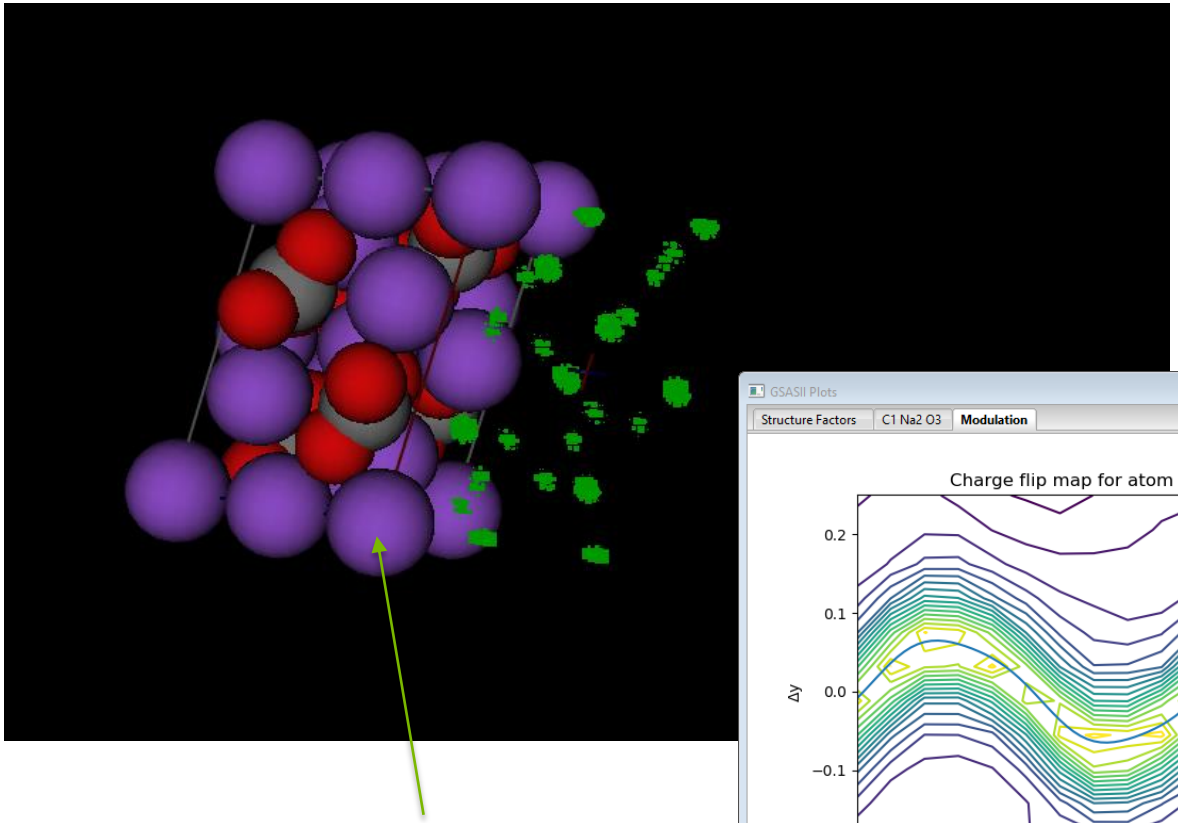
Na_2CO_3 – 11BM @ APS room temp.

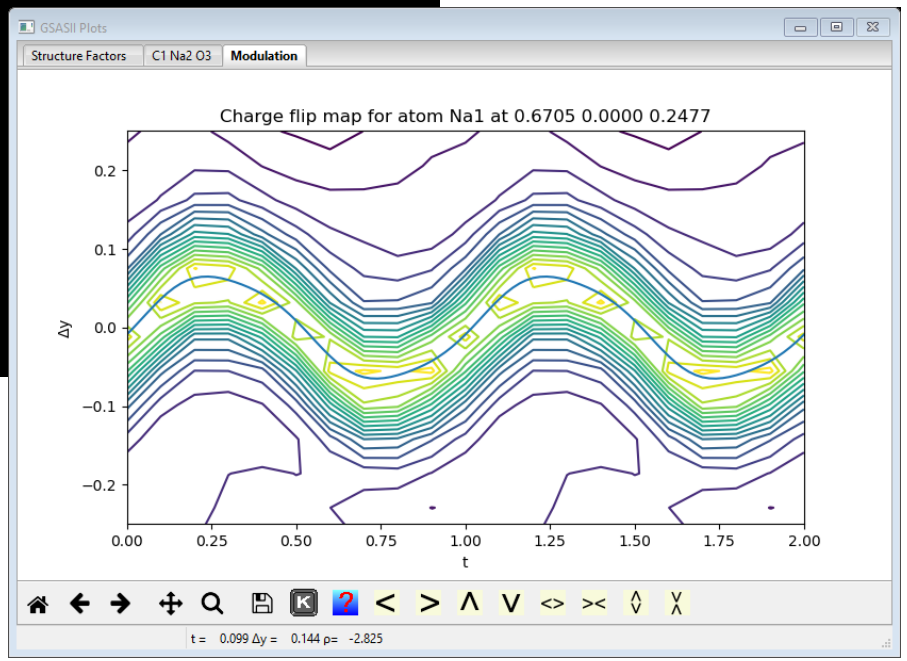


Includes m=-2,-1,1,2 superlattice reflections; Rietveld refinement includes 1st & 2nd order harmonics on position depending on atom

INCOMMENSURATE STRUCTURE SOLUTION

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

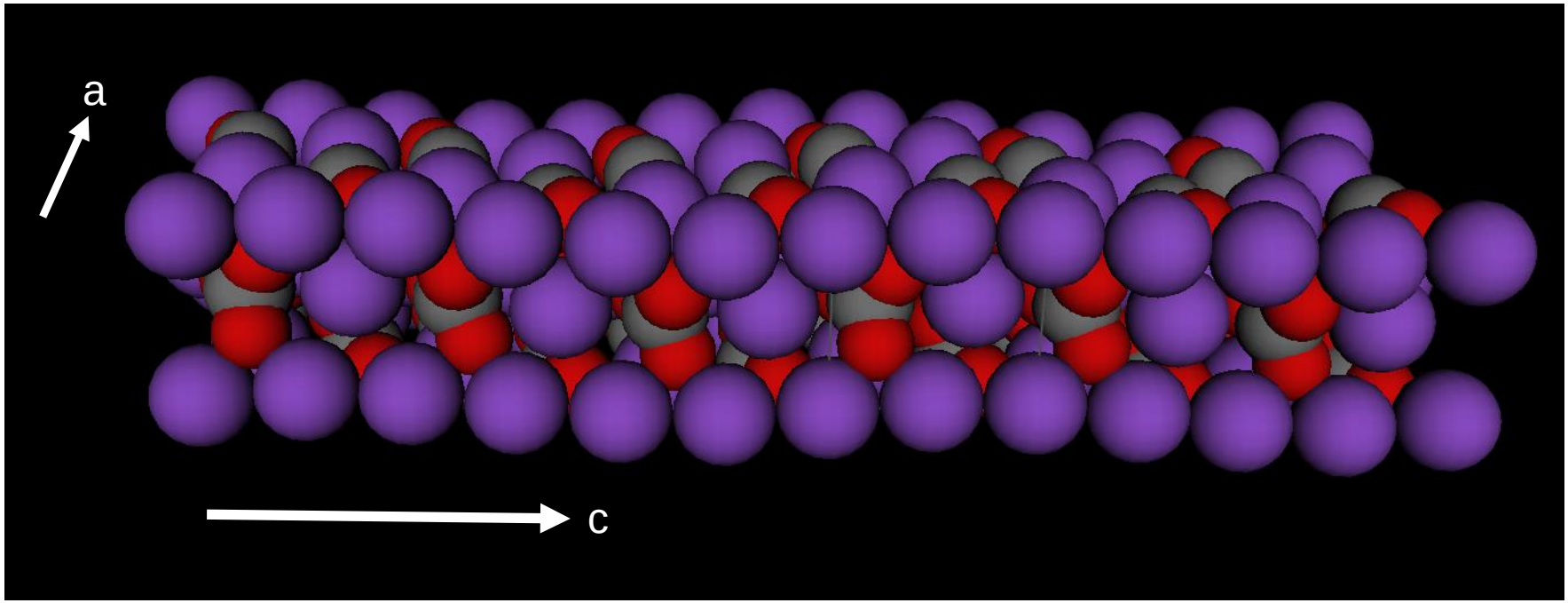




Modulation of atom positions (Na1-y)
Fit function – fourier series in tau

LATTICE MODULATION

Na_2CO_3 – single crystal data



Coordinated wave motion – Na lattice y motion/ CO_3 rocking motion
Recall q= 0.183,0,319 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

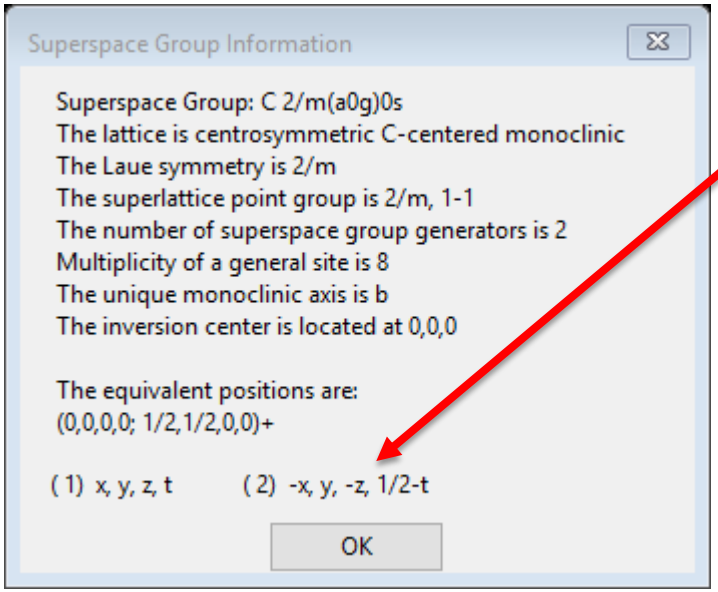
e.g. Na_2CO_3 – C2/m(α0γ)os

Space group

Modulation vector

Translation component

Operators: conventional space group & 4th dim component



Possible modulation vectors:
e.g. αβγ, α0γ, 0β0, α½γ, ½β0
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)

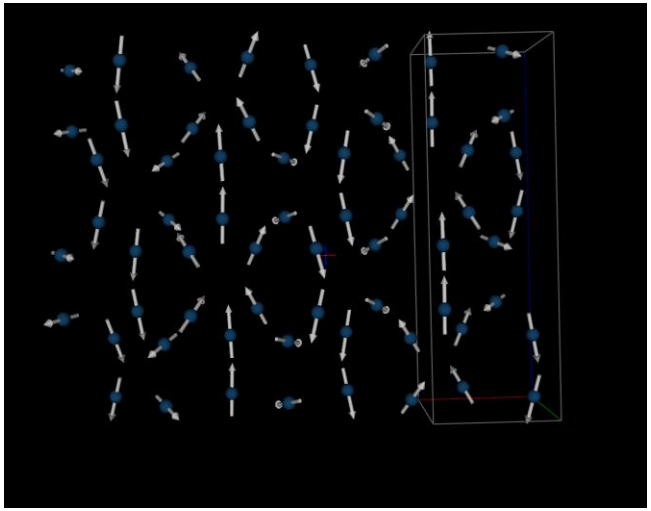
INCOMMENSURATE STRUCTURES

Cases not allowed in GSAS-II

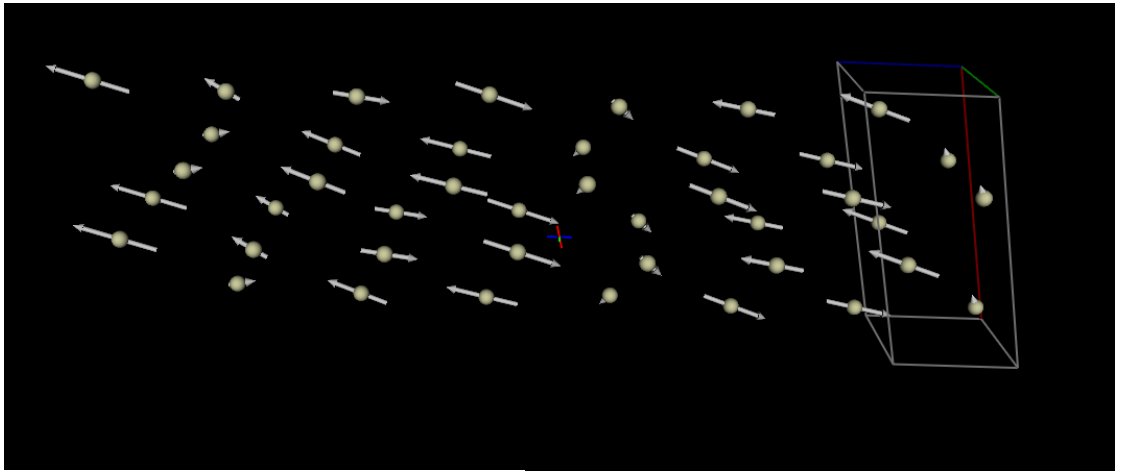
- 3+2 & 3+3 not allowed in GSAS-II
  - Too complex to deal with easily
  - 3-D 230 SG
  - For 3+1: 4,783 possible SG
  - For 3+2: 222,018 possible SG
  - For 3+3: 28,927,922 possible SG
  - But only a handful found – not worth the hassle
- Ad hoc centering not allowed
  - ‘X’ space groups – all have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

MAGNETIC INCOMMENSURATE STRUCTURES

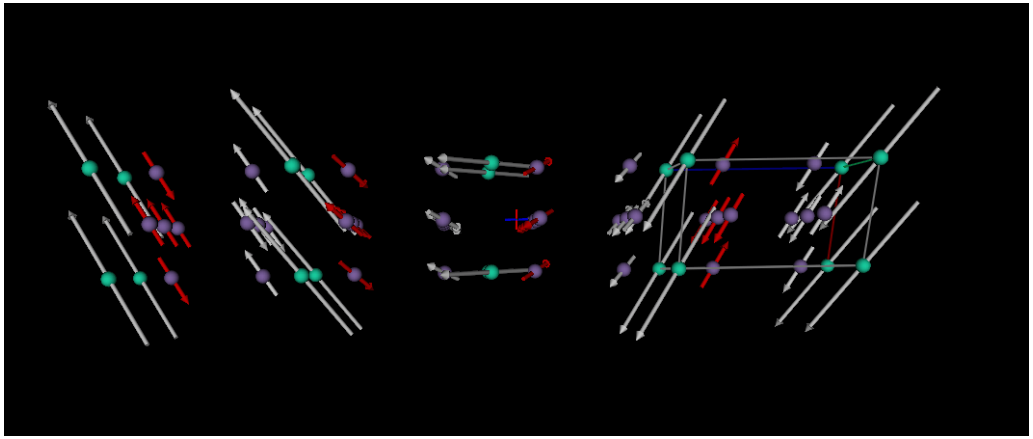
Some examples:



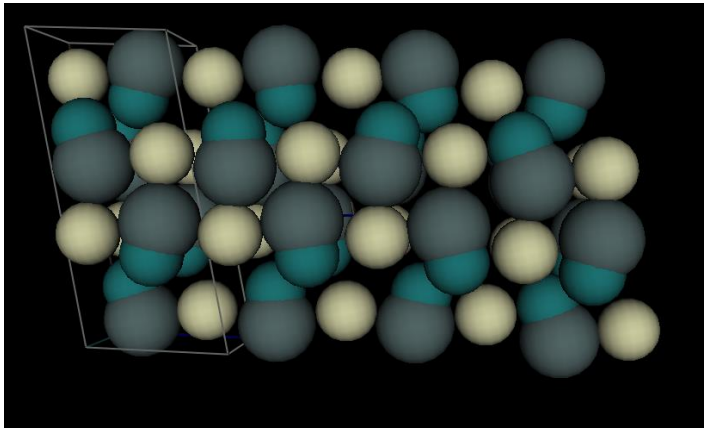
β-Li_2IrO_3



CeRuSn – Ce moment



$DyMn_6Ge_6$ – residual moment

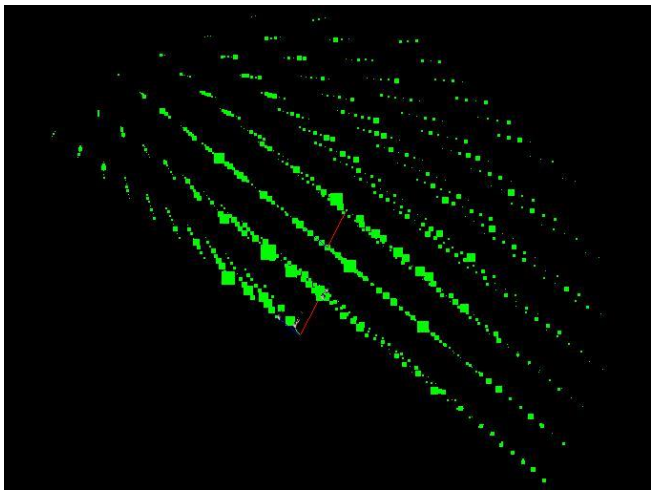


CeRuSn –
structure modulation

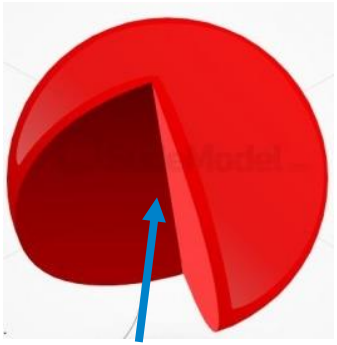
CHARGE FLIPPING

CHARGE FLIPPING

The algorithm set up:
~1Å unique reflections → sphere → box → 0.5Å box

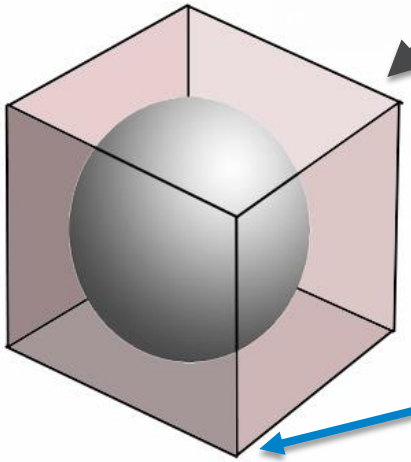


1D list

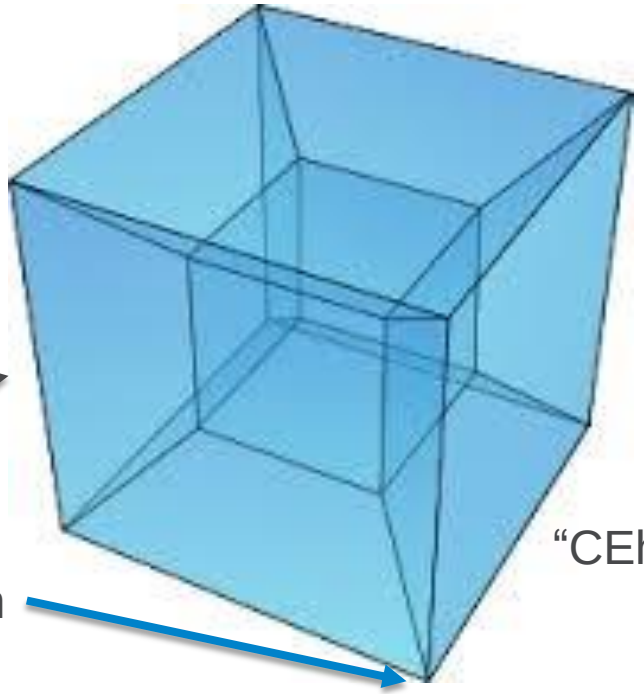


Origin @ F_{000}

1D list → 3D array



Expand 3D array

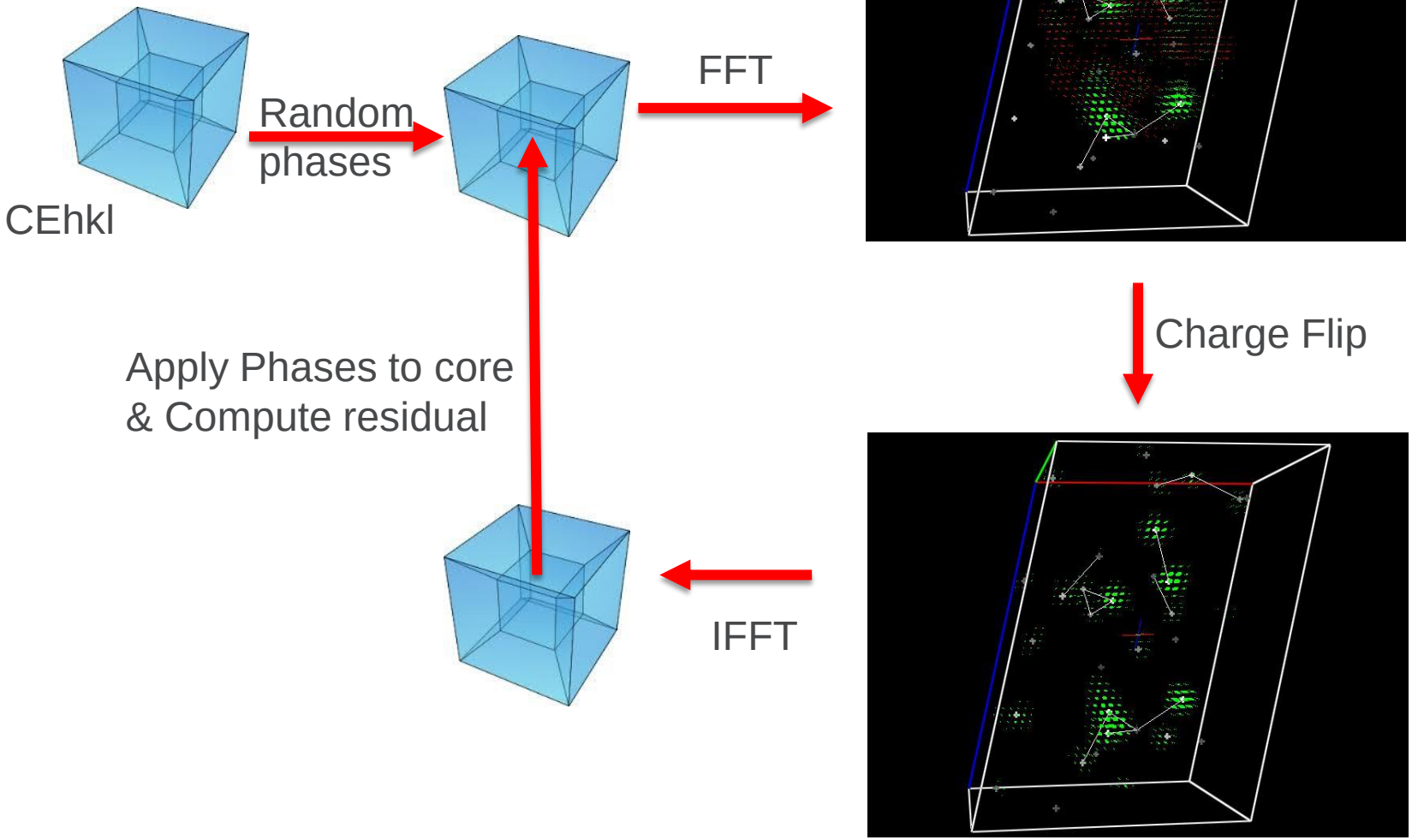


"CEhkl"

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
```

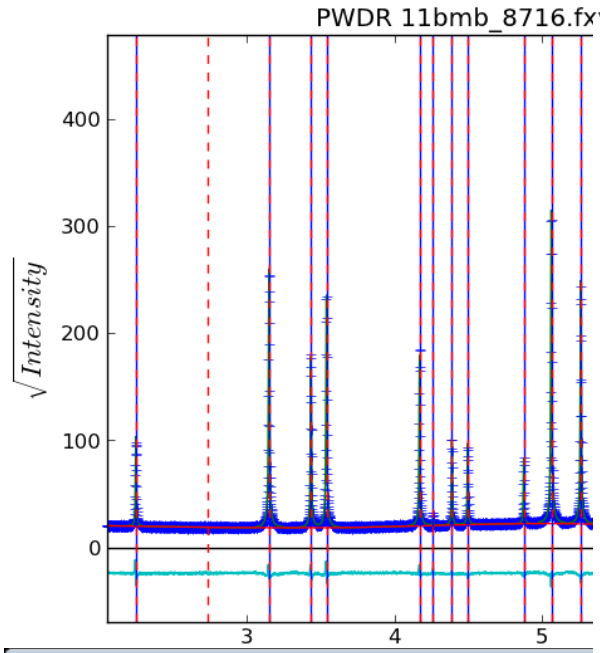
After user break:

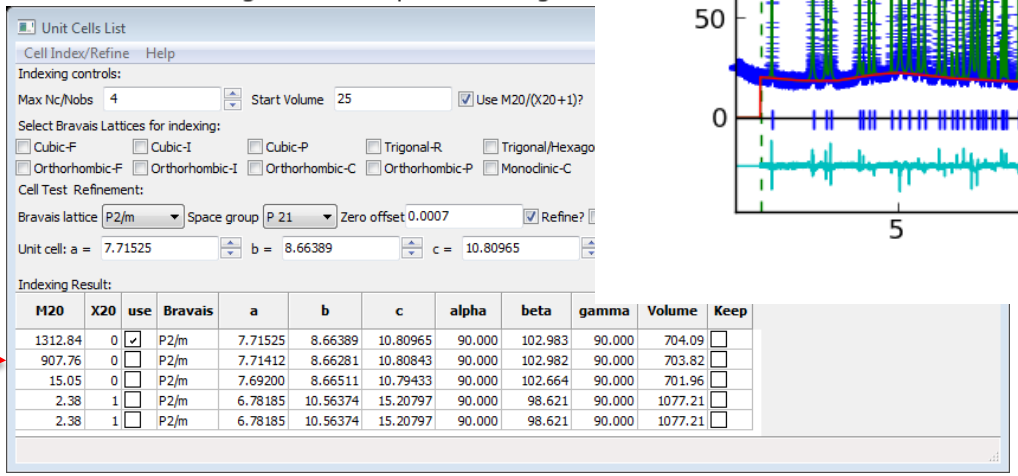
Repeat 1st line to get result map

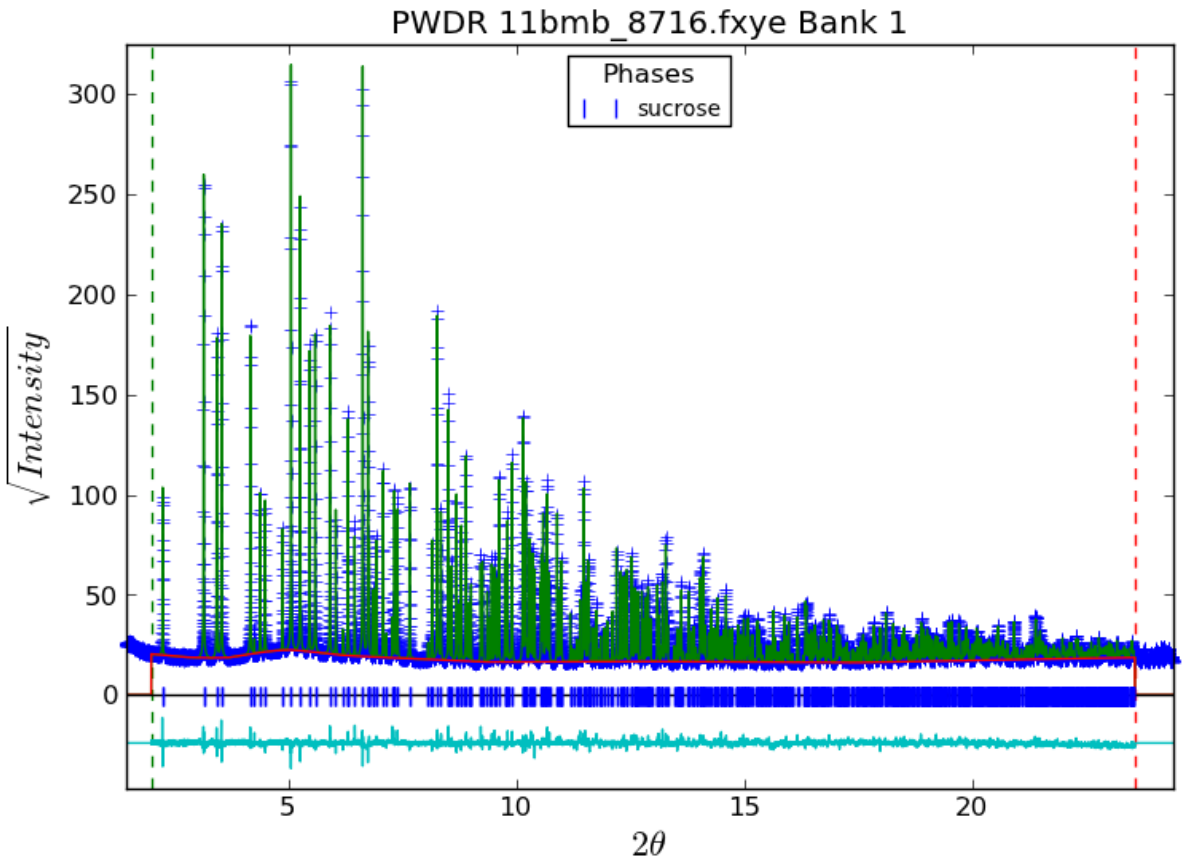
Find origin; search for peaks & display result

EXAMPLE – SUCROSE POWDER

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







781 unique hkl's
CF with 61440

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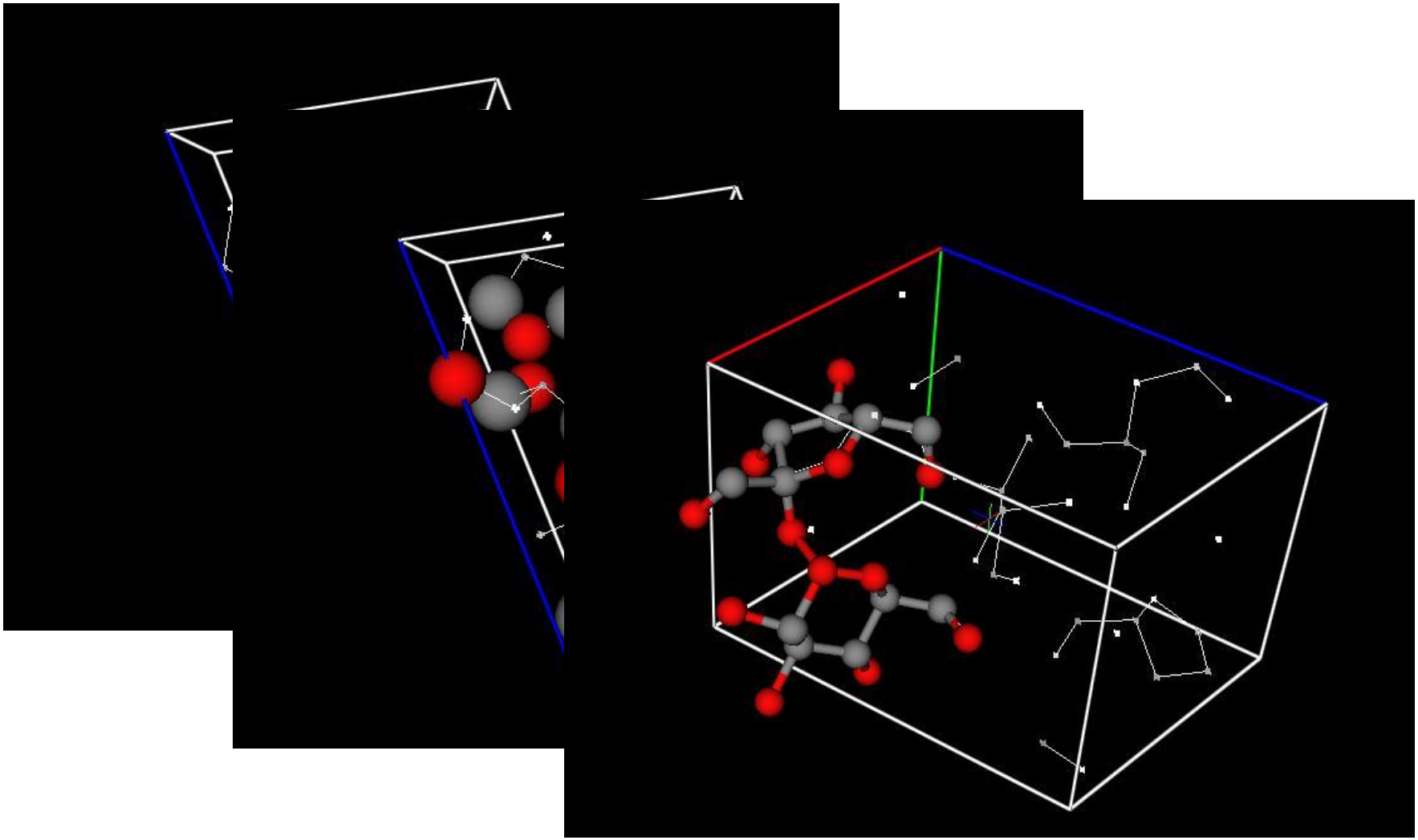
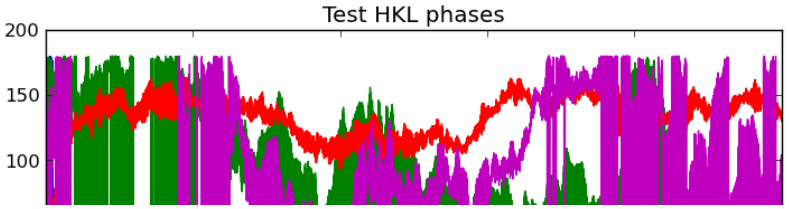
CHARGE FLIPPING SOLUTION

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

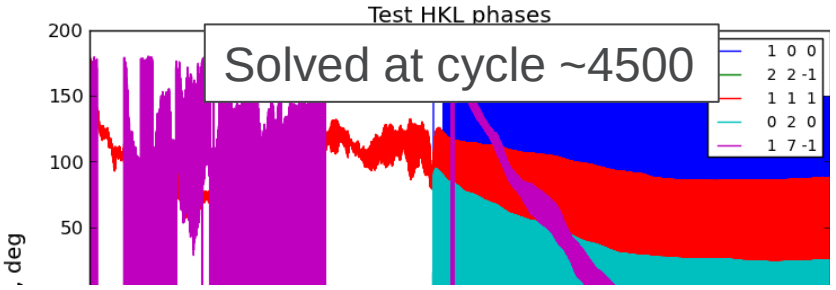


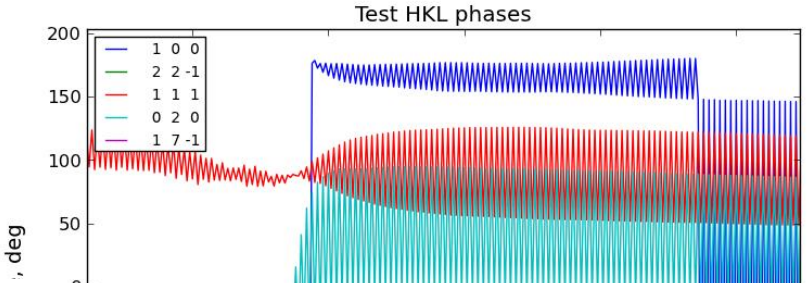
CHARGE FLIPPING – PHASES?

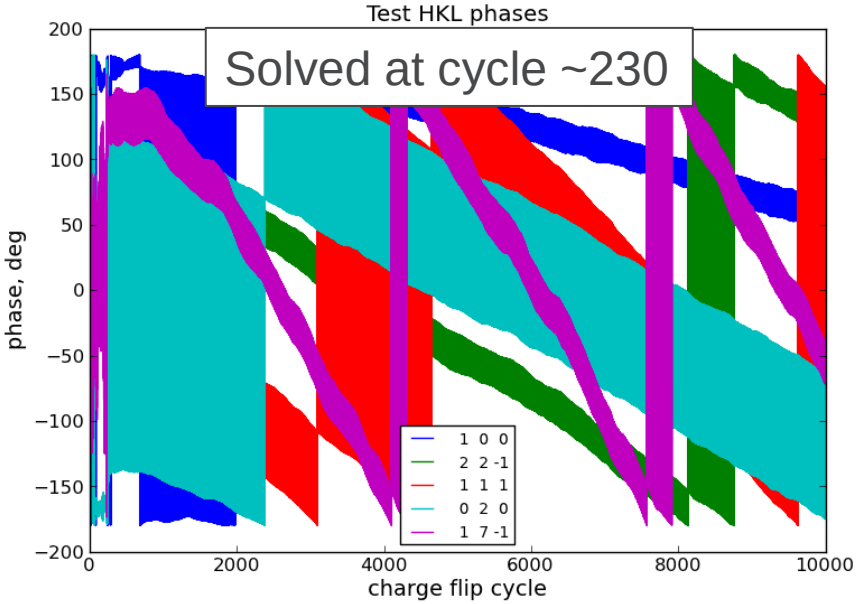
Track phases of 5 reflections – 10000 CF cycles

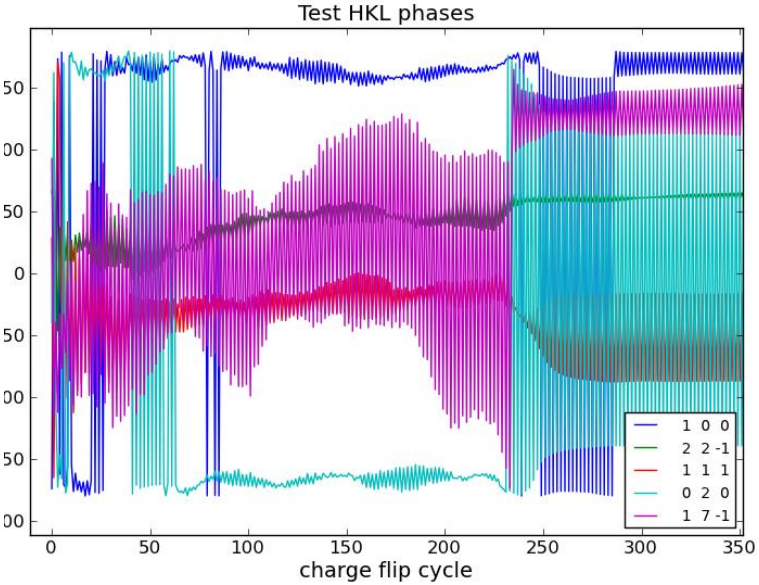


Not solved in 10000 cycles





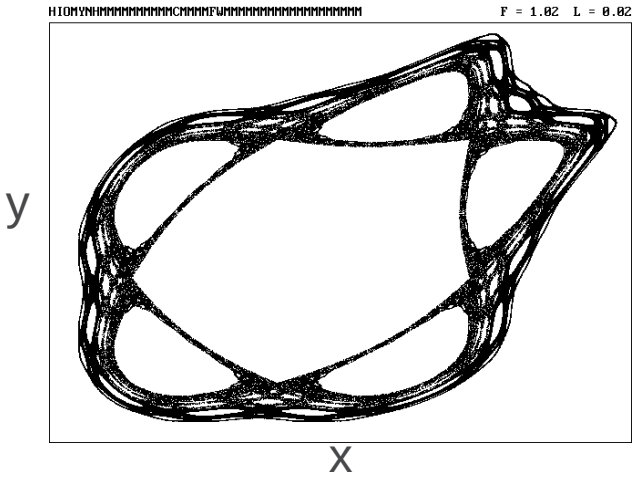


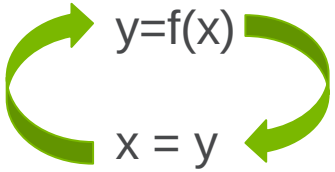


CHARGE FLIPPING – CHAOS MATHEMATICS?

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?)





f(x) - polynomial

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

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

THANK YOU

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