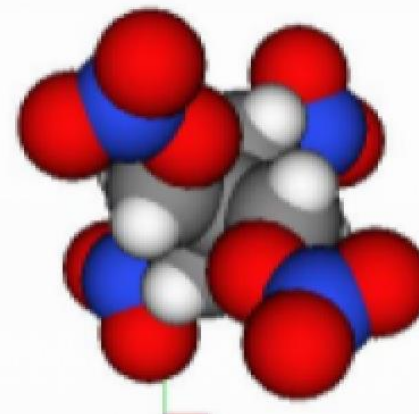


WHAT ELSE DOES GSAS-II DO?

GSAS-2



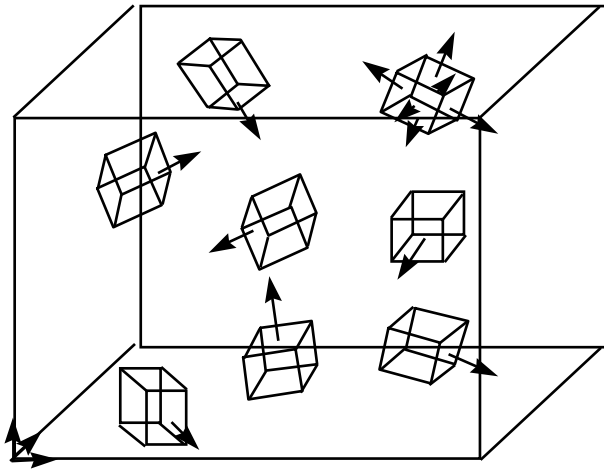
R. B. VON DREELE
ANL/APS (retired)
vondreele@anl.gov

Acknowledgements: DOE/SC

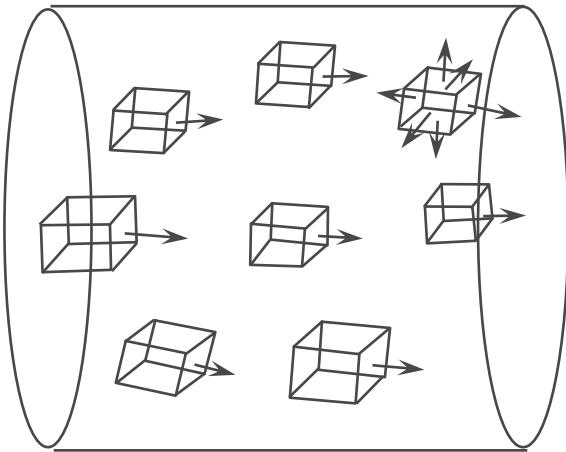
TEXTURE ANALYSIS

What is texture?

Nonrandom crystallite grain orientations



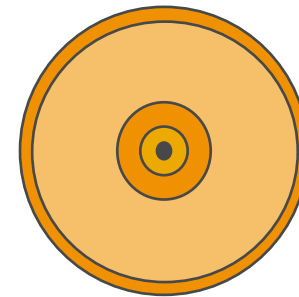
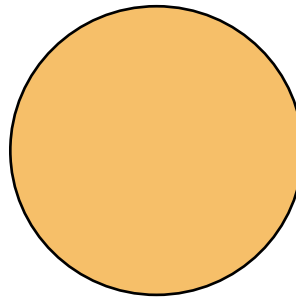
Loose powder



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

Incident beam
x-rays or neutrons

Sample

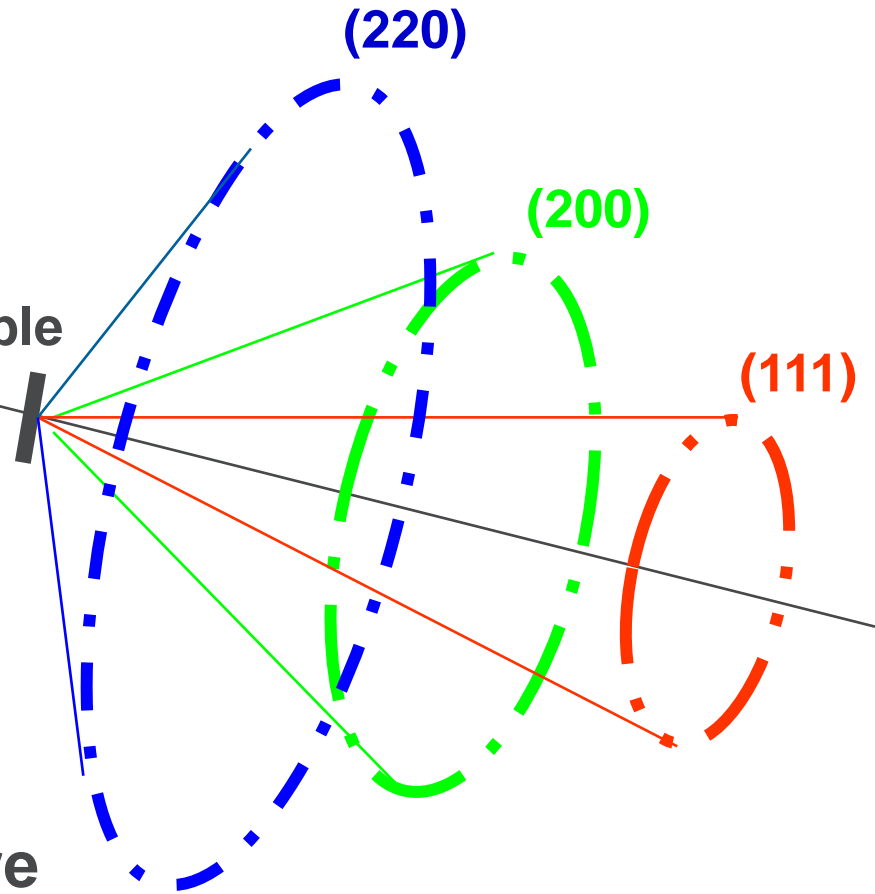
(220)

(200)

(111)

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

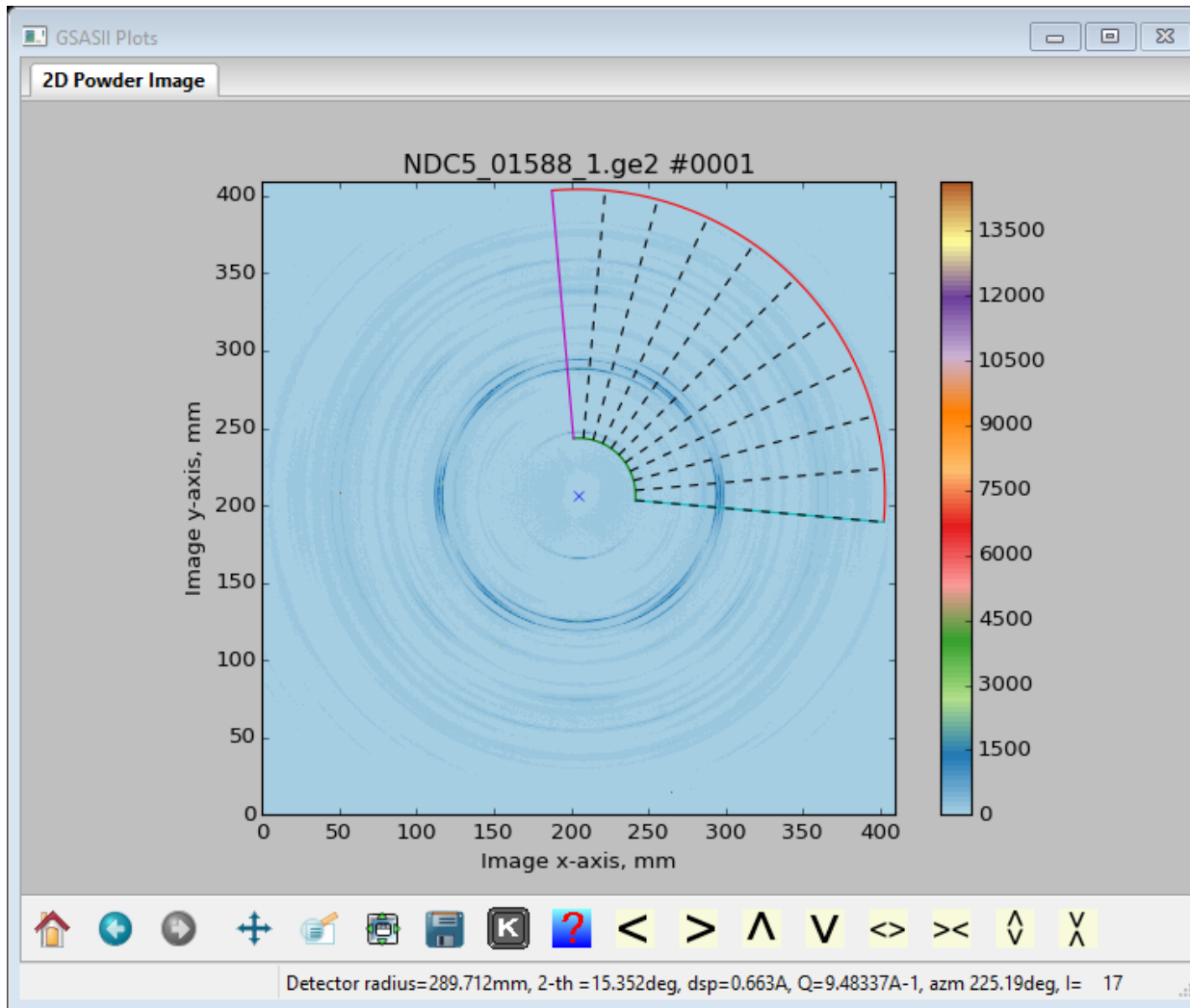
$$A(h, y) = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^l \sum_{n=-l}^l C_l^{mn} K_l^m(h) K_l^n(y)$$

- **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

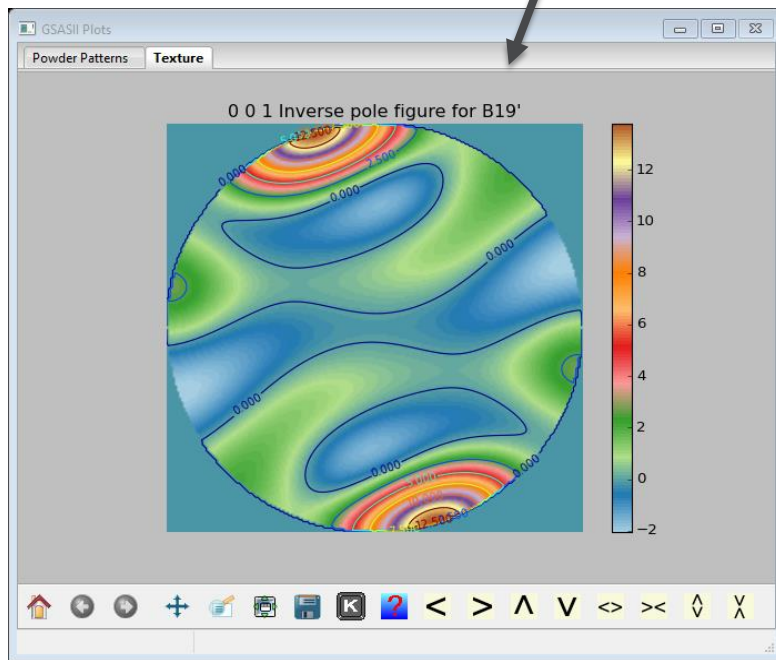
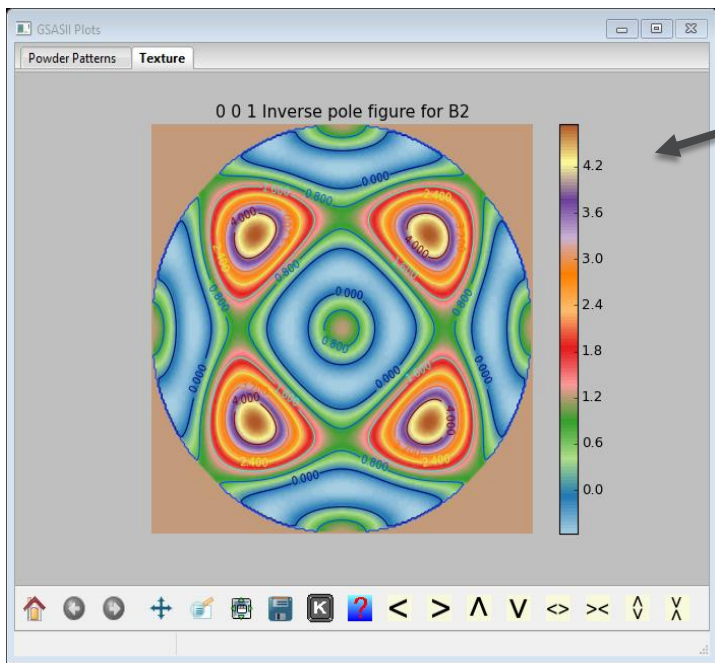
NiTi shape memory alloy wire: B2 & B19' phases



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

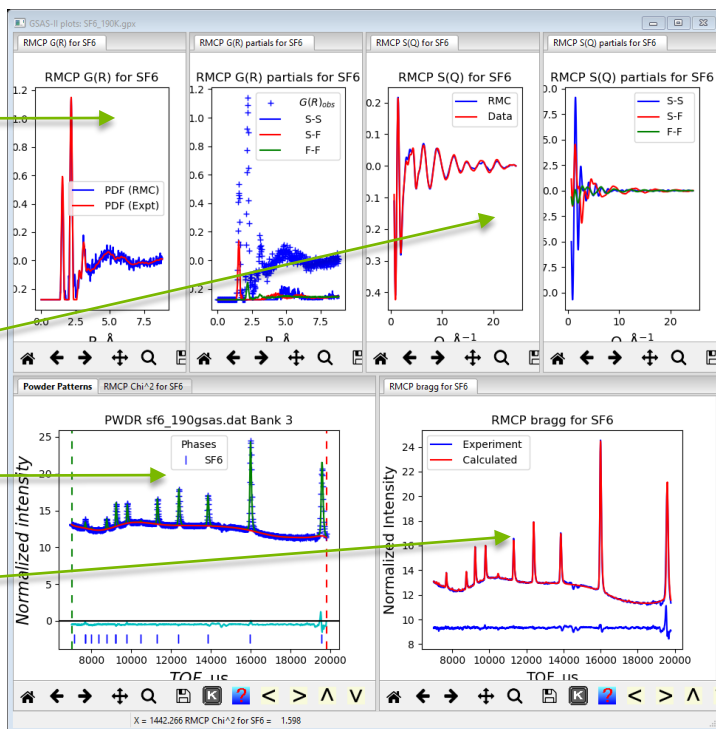
- Provide GUI interface to setup of RMCPProfile - save setup controls for reuse
- Initiate independent RMCPProfile execution – may run for hours
- Allow graphical display on intermediate results

G(R) & partials

S(Q) & partials

RR result

PWDR simulation



Project: SF6_190K.gpx

General Data Atoms Draw Options Draw Atoms RB Models Map peaks MC/SA RI

Metadata item: phase BCC
 Metadata item: comment test
 Metadata item: source GEM ISIS

Total running time (min): 10. Save interval time (min): 1.
 Lattice multipliers, if changed will force reset of atom positions:
 X-axis: 3 Y-axis: 3 Z-axis: 3
 NB: be sure to set cations first & anions last in atom ordering
 Set atom ordering: S F
 Set max shift: 0.05 0.1

Add Atom swap probabilities:

Enter constraints & restraints:
 Set minimum & maximum distances for:
 S-S S-F F-F
 Hard min: 4. 1.37 2.
 Search from: 0. 1.37 2.
 to: 0. 1.8 2.5

Use bond valence sum restraints for (set to 0 for non-bonded ones):

Add Fixed coordination number restraint:
 Add Average coordination number restraint:

Potential temperature (K): 190.
 Add A-B stretch potential restraints, search range (%): 30.
 Atom-A Atom-B AB dist potential
 Delete S F 1.564 2.
 Delete F F 2.2 2.
 Add A-B-C angle potential restraints, search range (%): 10.

Select data:
 Select one histogram for Bragg processing:
 PWDR sf6_190gsas.dat Bank 3 Weight 0.1
 Use size broadening? Use mustrain broadening?
 Select data for processing:

Format	Weight	Name
Select RMC	0.05	Neutron real space data; G(r): sf6_190k_gr.dat
Select RMC	0.01	Neutron reciprocal space data; F(Q): sf6_190k_fq.dat
Select		Neutron reciprocal space data; S(Q):
Select		X-ray real space data; G(r):

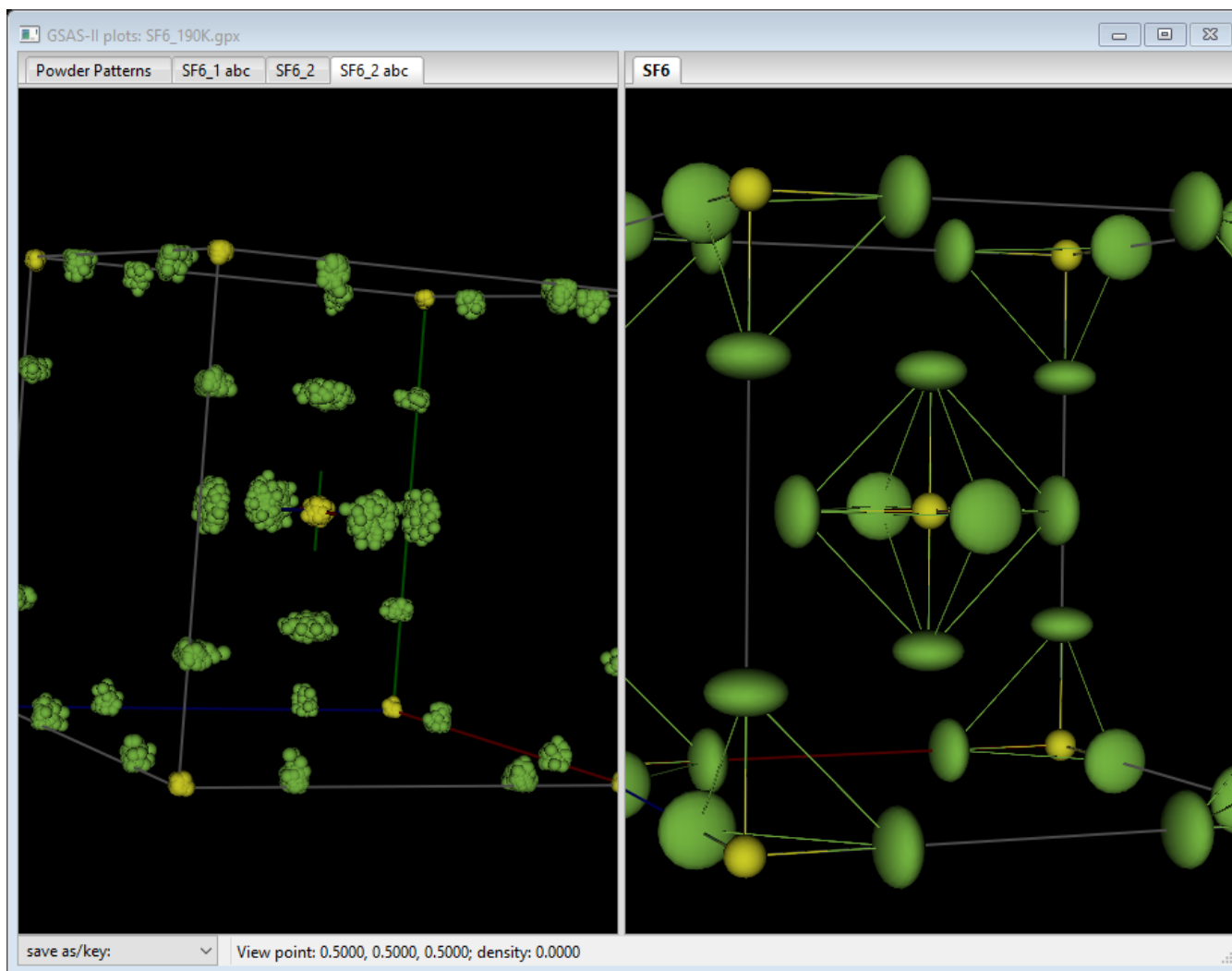
Mouse RB drag/drop to reorder

RMCPROFILE RESULT FOR SF₆

10x10x10 unit cell box – transform back to original

See disordered atom distribution

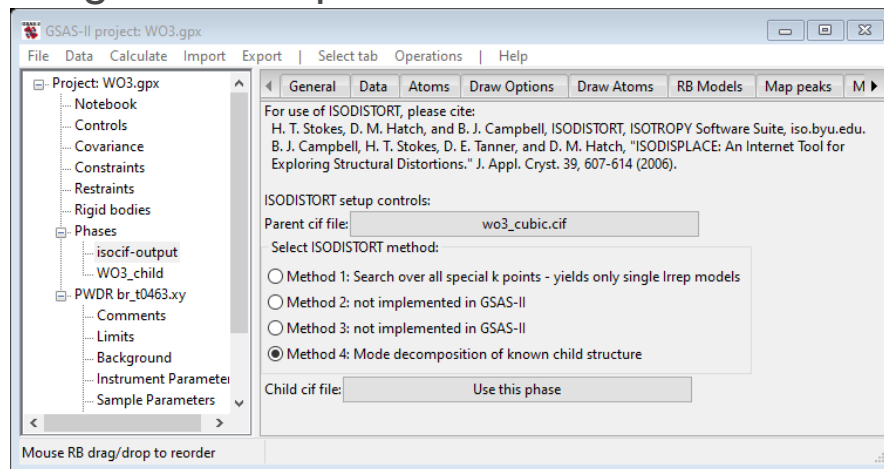
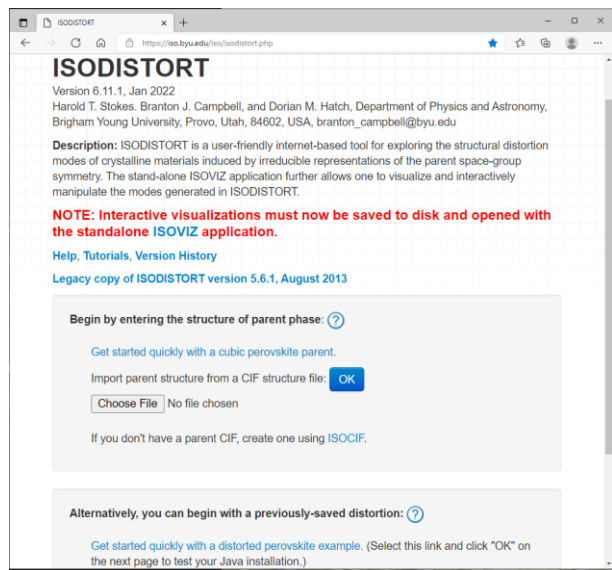
– compare to Rietveld U_{aniso} for F atom



ISODISTORT

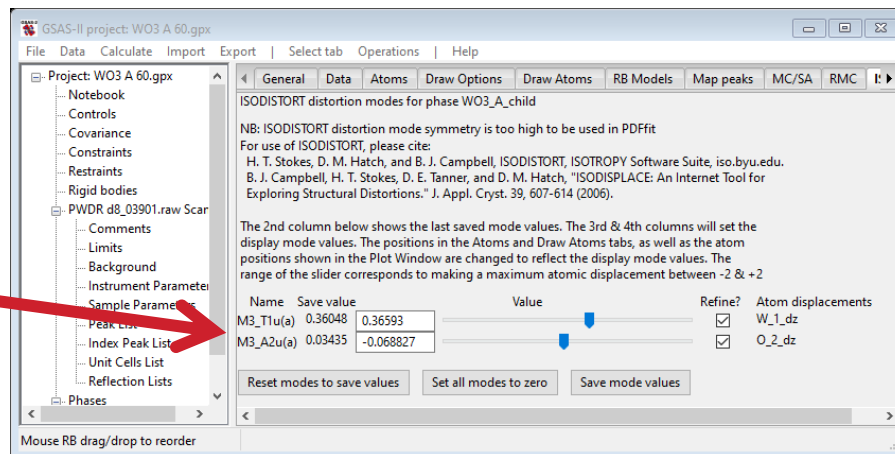
Implementation in GSAS-II

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

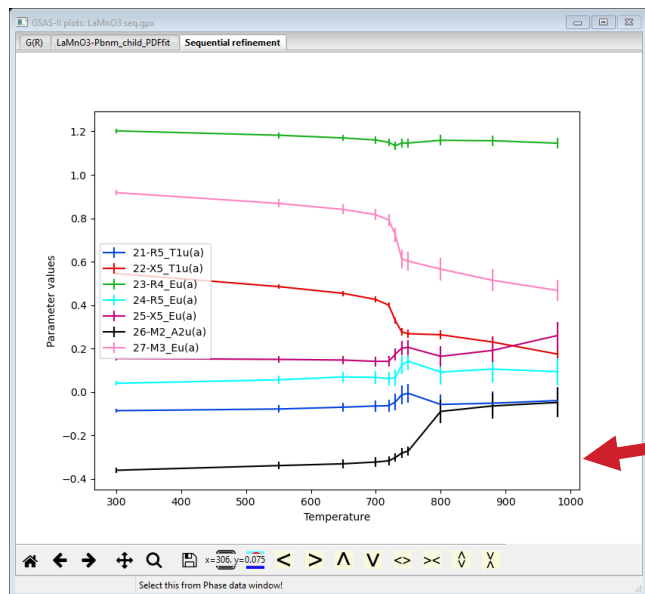
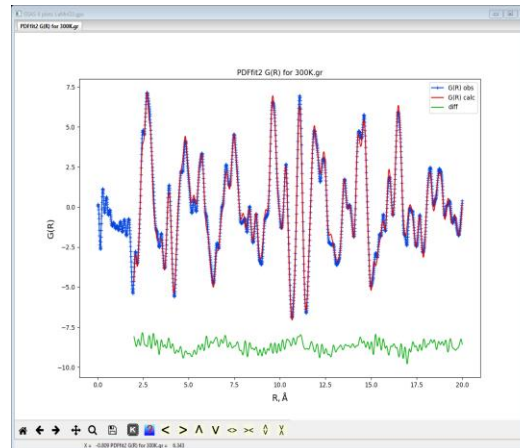
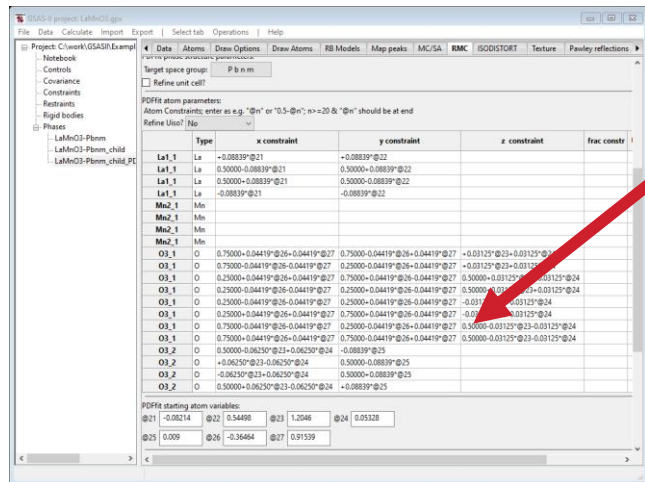
- To use: a multistep process → a cif file with modes; can be imported into GSAS-II with new variables for the modes.



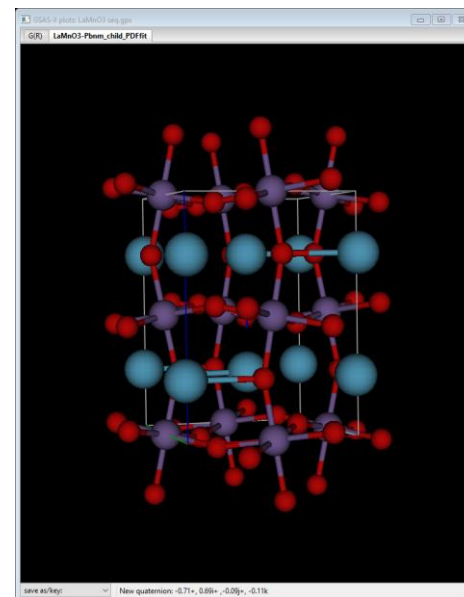
PDFFIT2 = "PDFfit" IN GSAS-II

"Small Box" modelling of pair distribution functions

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



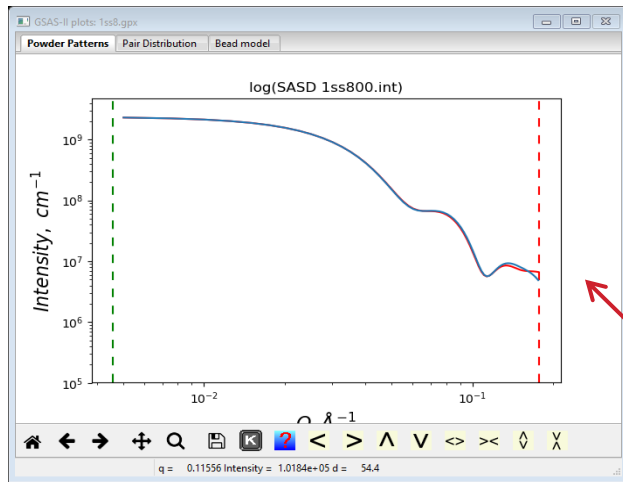
Parameters: mode displacements (\AA)
Can be fit for sequence of T



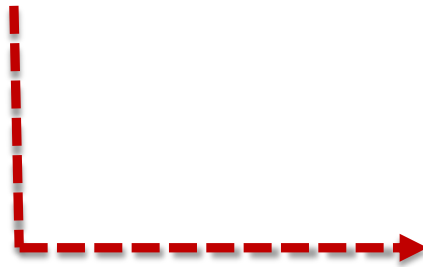
PROTEIN SHAPE ANALYSIS

PROTEIN SMALL ANGLE MODELING IN GSAS-II

Bead models via SHAPES (alternative to DAMMIN in python)

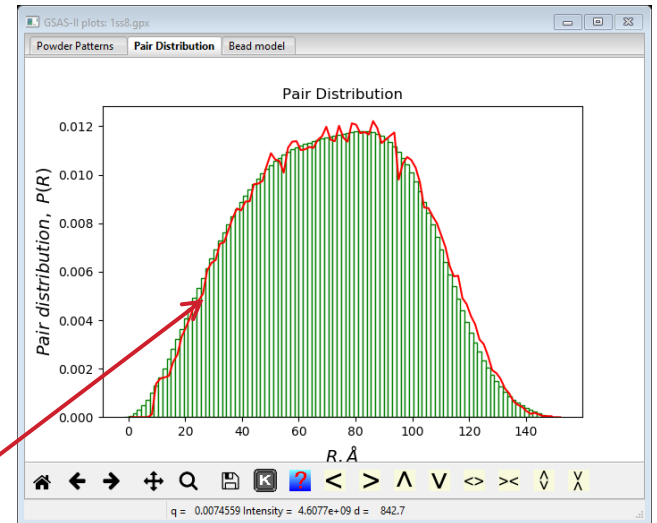


Data (simulated) from PDB 1ss8
3668 AA, 7-fold rot. symm.
E. Coli chaperonin GroEL

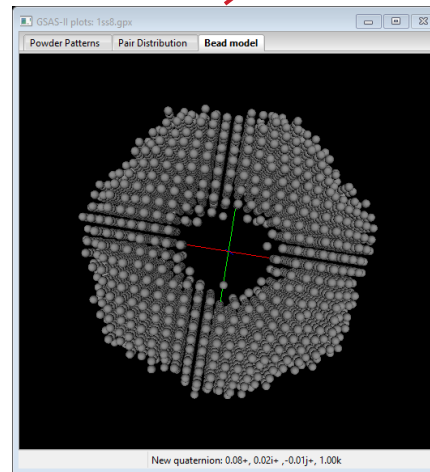


Direct fit?
(In development)

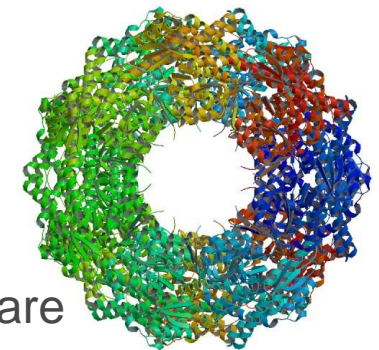
Make P(R)



calc



Run SHAPES
Make bead model



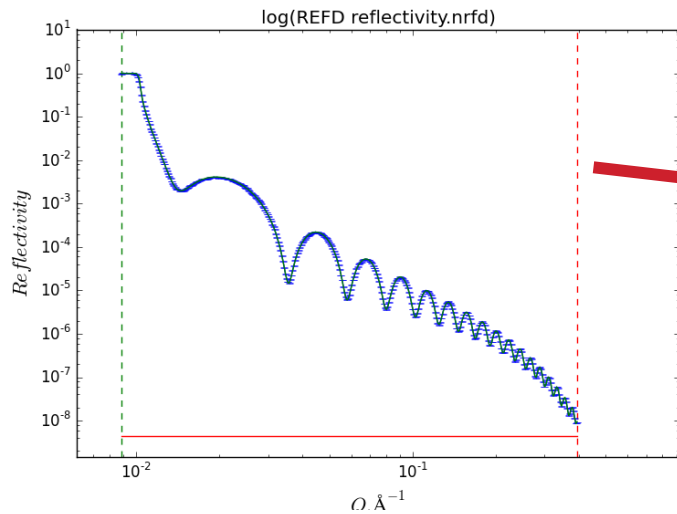
compare

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

REFLECTOMETRY

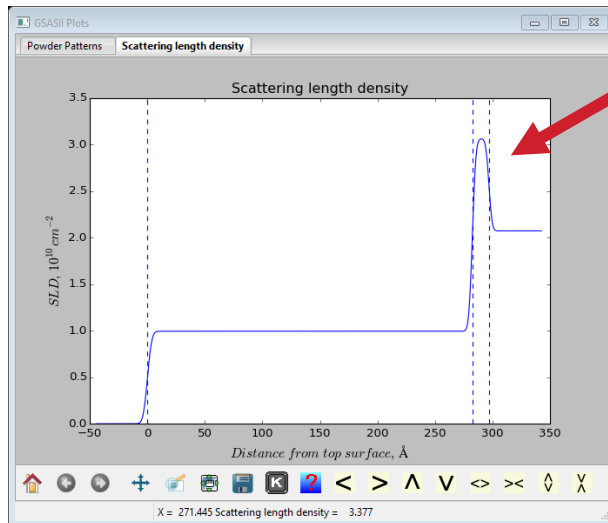
REFLECTOMETRY ANALYSIS IN GSAS-II

X-rays & Neutrons (CW at least)



Multilayer model
Scattering density

Modelling
Models Help
Reflectometry fitting for: REFD reflectivity.nrfd
Controls:
Instrument resolution type:
 None const $\Delta Q/Q$ (FWHM %): 3.0
Minimizer: LMLS Bounds factor: 0.85 Use 2% sig. weights
Plot controls: Plot SLD? Zero position location: Top
Global parameters:
Scale: 1.0 Refine? Flat bkg.: 4.4e-09 Refine?
Layer sequence: 1 2
Use sequence nos. from: 1: Alumina 2: Alumina
NB: Repeat sequence by e.g. 6*(1 2)
Layers: scatt. densities are $10^{10} \text{ cm}^{-2} = 10^{-4} \text{ \AA}^{-2}$
Top layer (superphase):
Substance: vacuum air or gas
Insert Delete
Layer no. 1
Substance: Alumina Den. Mult.: 0.1737 Refine? Real scat. den.: 0.9943 Imag scat. den.: 0
Magnetic SLD: 0.0 Refine? Real+mag scat. den.: 0.9943
Upper surface Roughness, \AA : 3.0 Refine? Layer Thickness, \AA : 282.63 Refine?
Insert Delete
Layer no. 2
Substance: Alumina Den. Mult.: 0.5352 Refine? Real scat. den.: 3.063 Imag scat. den.: 0
Magnetic SLD: 0.0 Refine? Real+mag scat. den.: 3.063
Upper surface Roughness, \AA : 2.4 Refine? Layer Thickness, \AA : 14.41 Refine?
Insert Delete
Bottom layer (substrate):
Substance: Silicon Den. Mult.: 1.0 Refine? Real scat. den.: 2.073 Imag scat. den.: 0
Magnetic SLD: 0.0 Refine? Real+mag scat. den.: 2.073
Upper surface Roughness, \AA : 2.2 Refine?



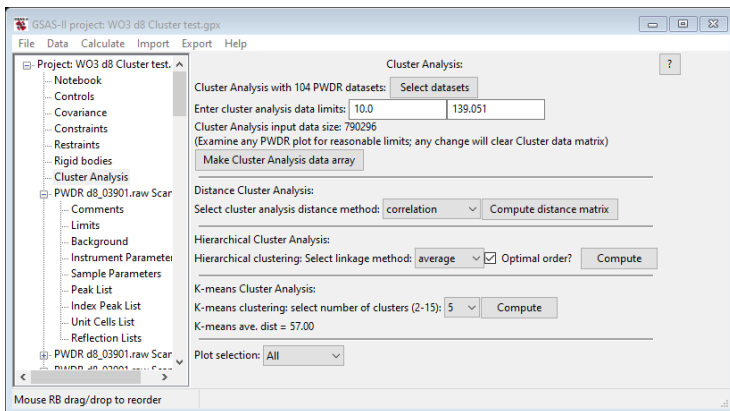
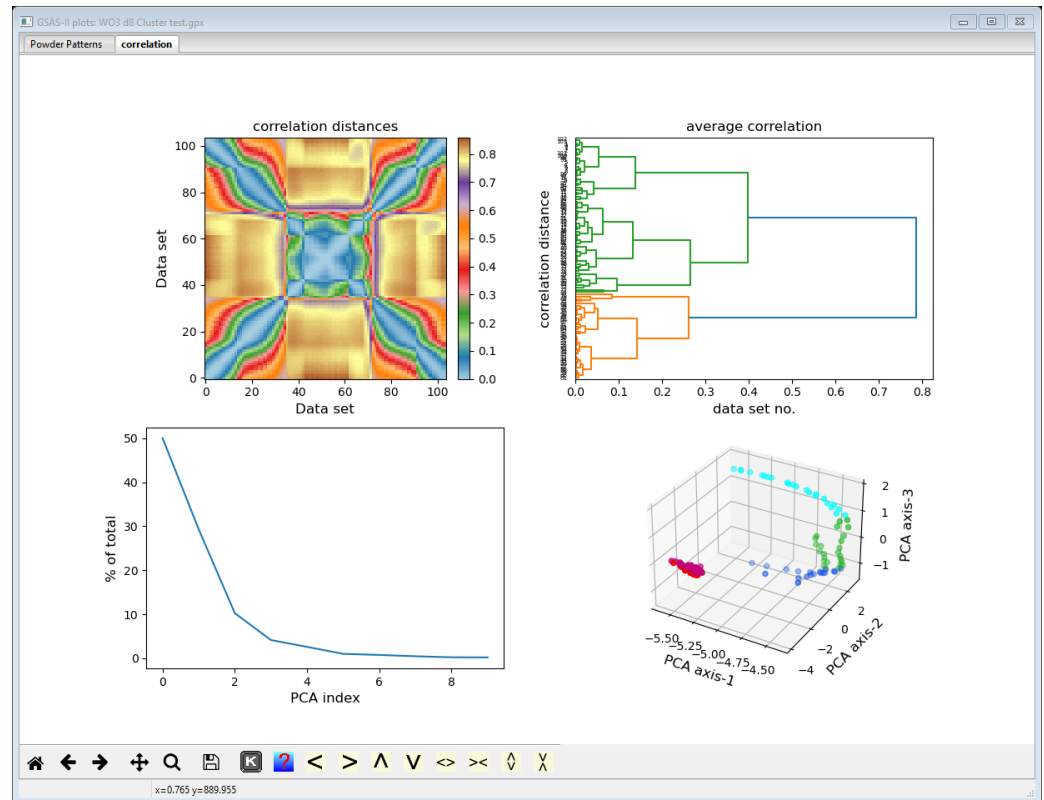
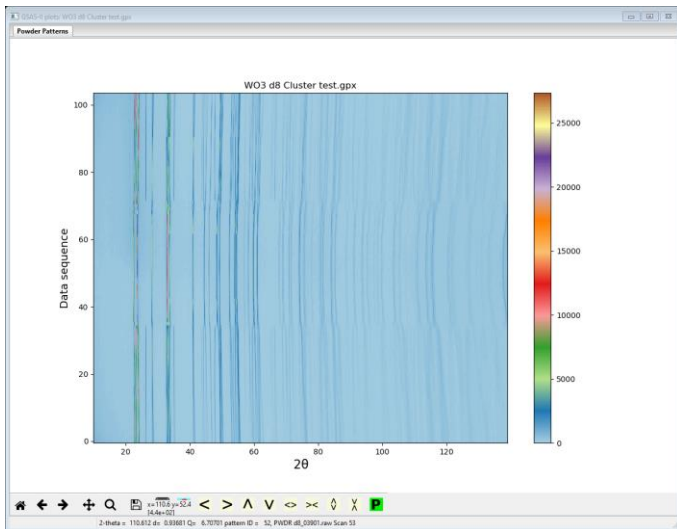
Define components, stacking sequence
(can be repeated), thickness & “roughness”
Fit by LSQ, MC/SA & “basinhopping”
(under development)

CLUSTER ANALYSIS

CLUSTER ANALYSIS

Another way of examining data – look for similar patterns

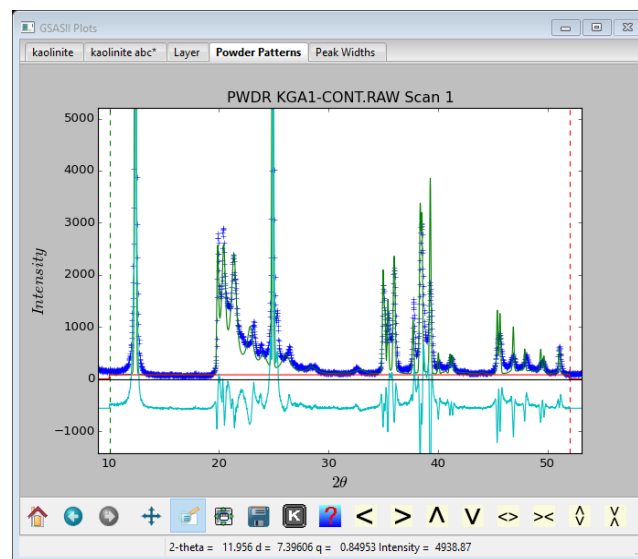
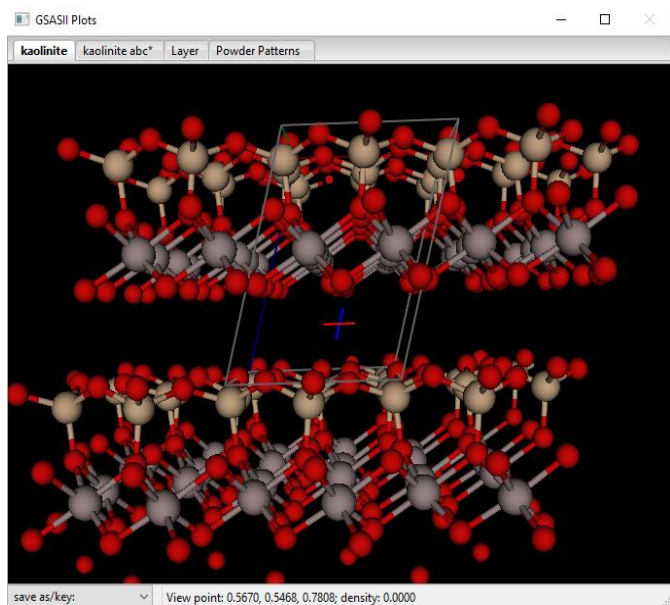
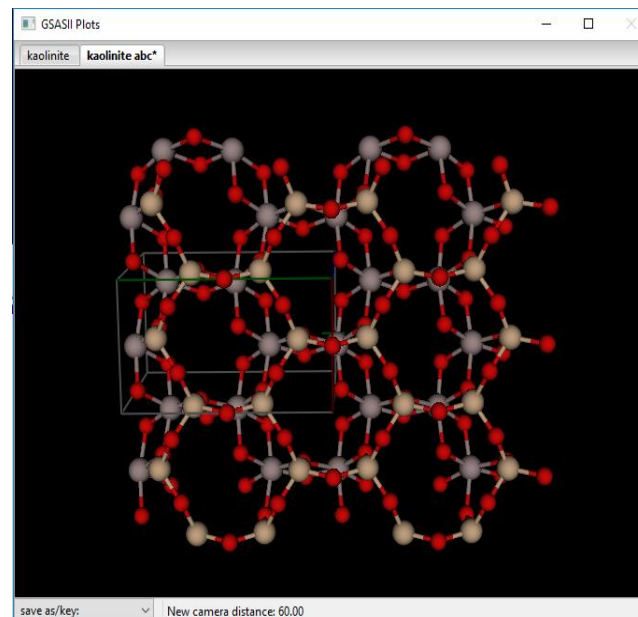
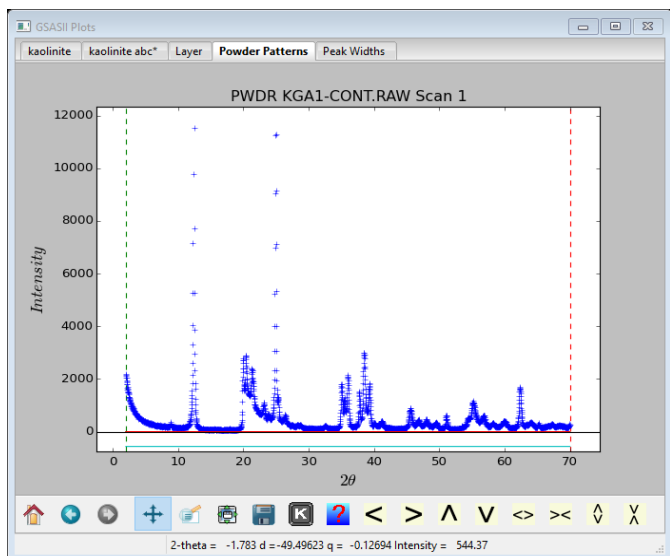
- Example – WO_3 x-ray data 300-1200K & back; 100 patterns. Multiple phase changes



Still under development & no help or tutorials yet.

STACKING FAULTS – DIFFAX IN GSAS-II

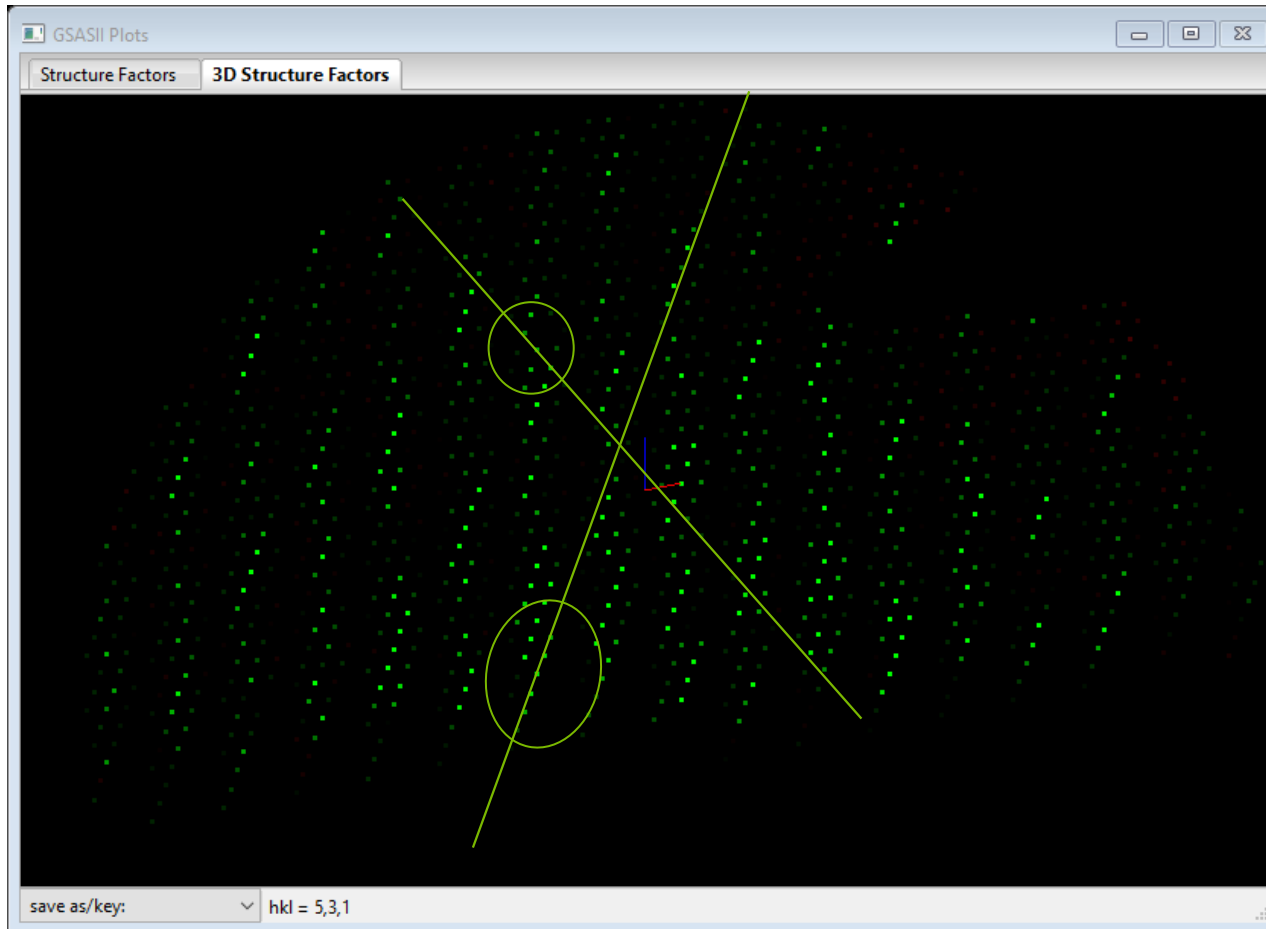
STACKING FAULTS IN KAOLINITE $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$



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

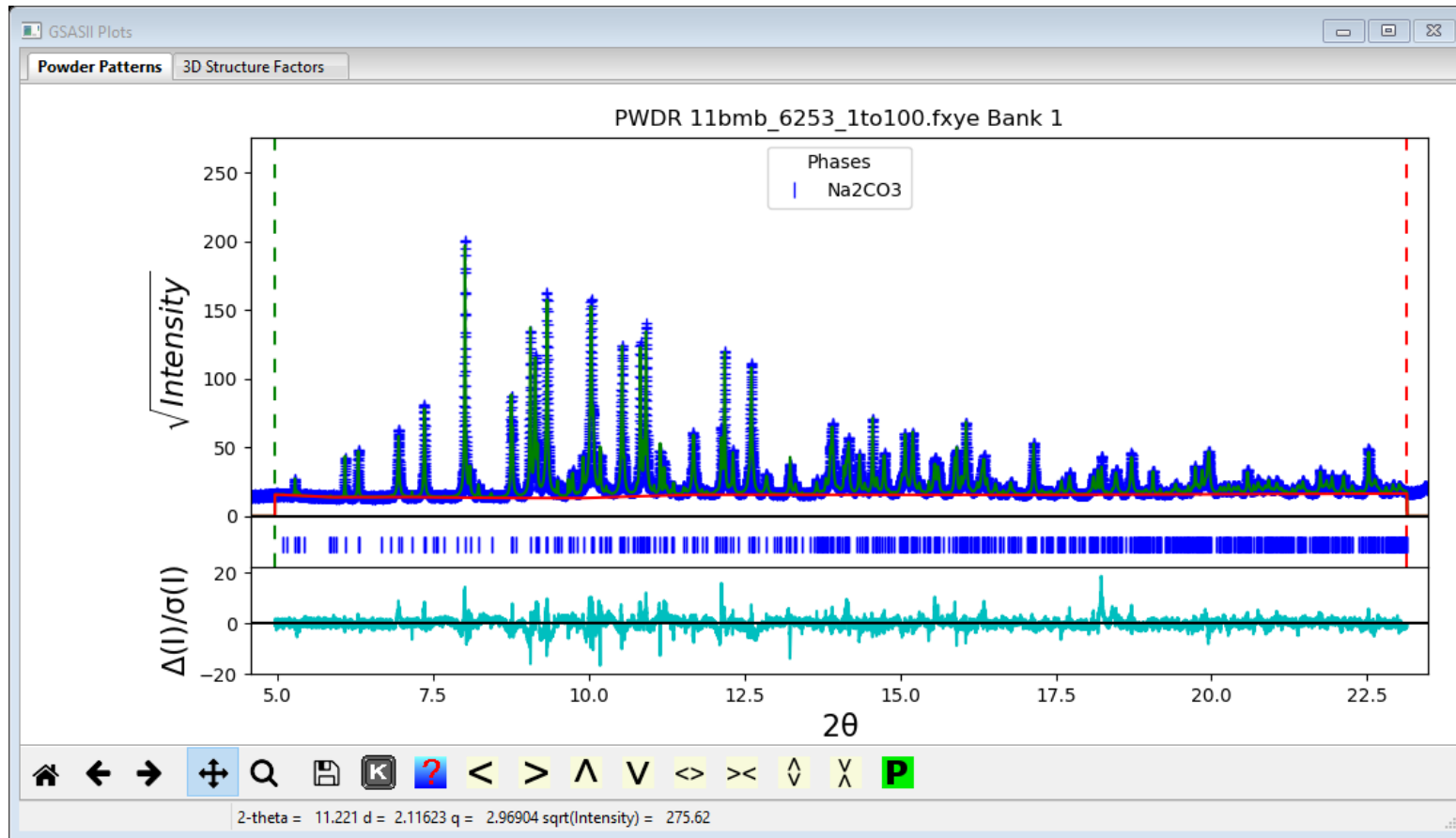
For Na₂CO₃
q= 0.183,0,.319

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

Na₂CO₃ – single crystal X-ray data – h0l zone → rows of spots don't line up

POWDER DIFFRACTION

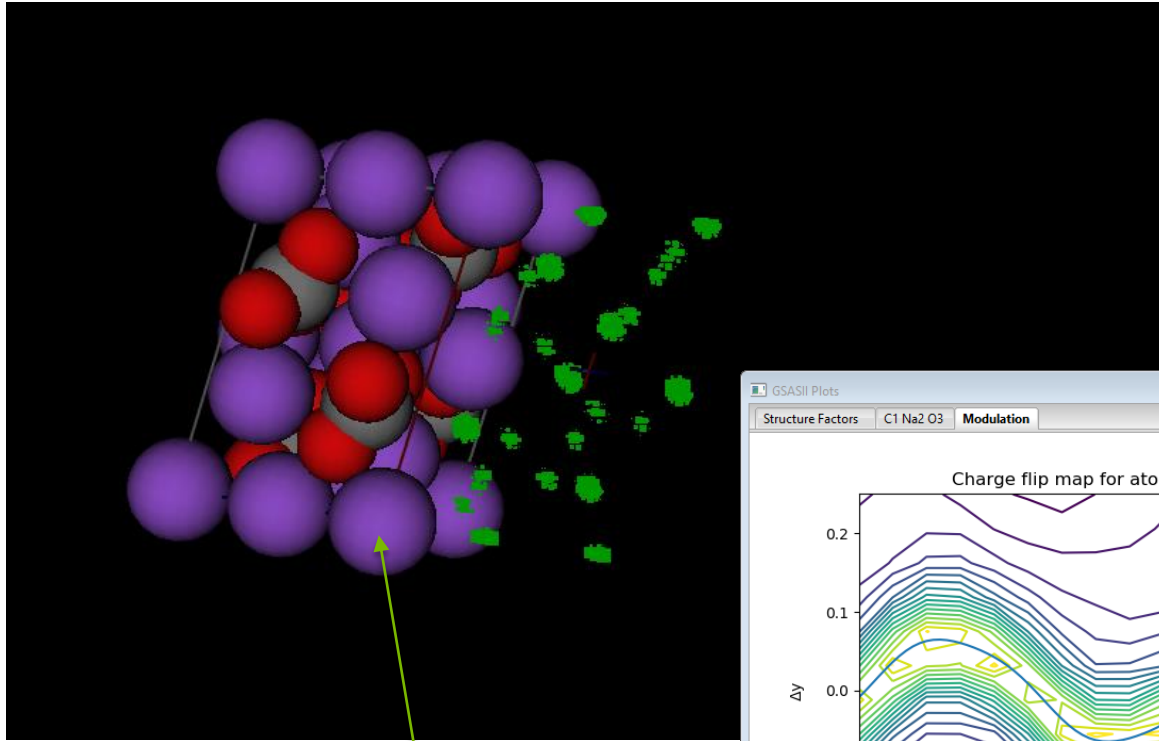
Na_2CO_3 – 11BM @ APS room temp.



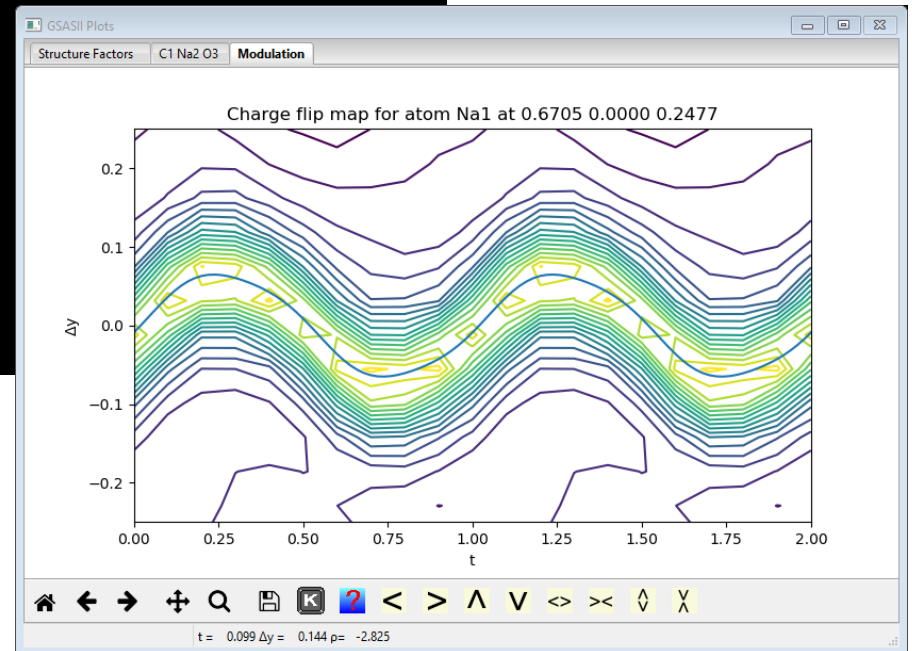
Includes $m=-2,-1,1,2$ superlattice reflections; Rietveld refinement includes 1st & 2nd order harmonics on position depending on atom

INCOMMENSURATE STRUCTURE SOLUTION

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

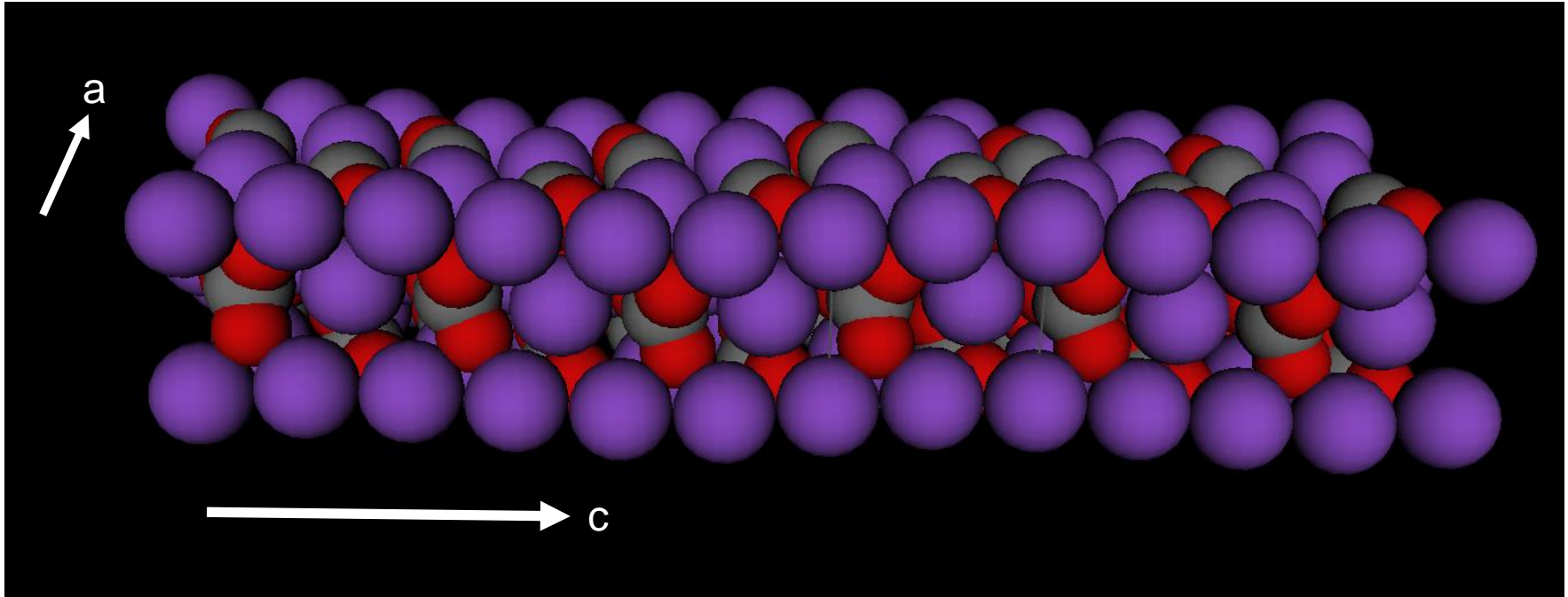


Modulation of atom positions (Na1-y)
Fit function – fourier series in tau



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 $\sim 6-7$ 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

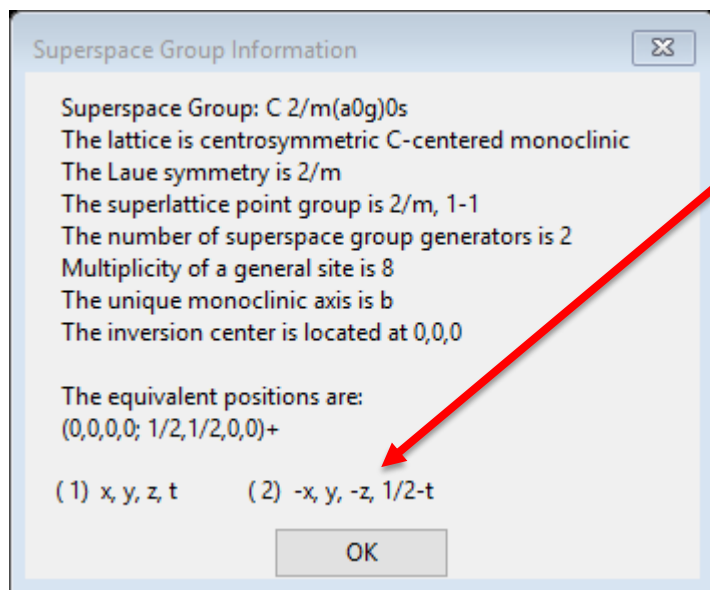
e.g. $\text{Na}_2\text{CO}_3 - \text{C}2/m(\alpha 0\gamma)0s$

Space group

Modulation vector

Translation component

Operators: conventional space group & 4th dim component



Possible modulation vectors:
e.g. $\alpha\beta\gamma$, $\alpha 0\gamma$, $0\beta 0$, $\alpha^{1/2}\gamma$, $1/2\beta 0$
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)

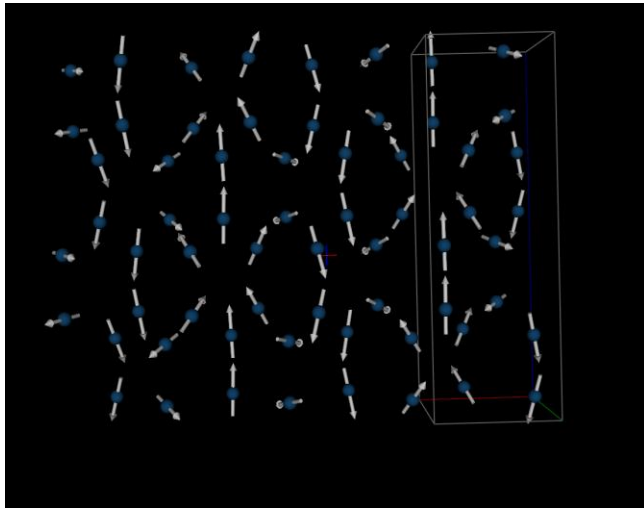
INCOMMENSURATE STRUCTURES

Cases not allowed in GSAS-II

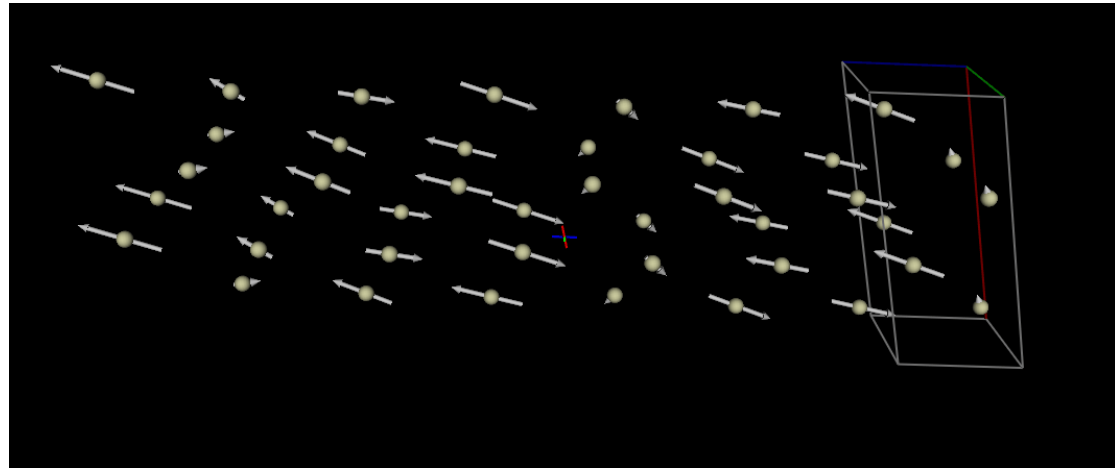
- 3+2 & 3+3 not allowed in GSAS-II
 - Too complex to deal with easily
 - 3-D 230 SG
 - For 3+1: 4,783 possible SG
 - For 3+2: 222,018 possible SG
 - For 3+3: 28,927,922 possible SG
 - But only a handful found – not worth the hassle
- Ad hoc centering not allowed
 - ‘X’ space groups – all have equivalent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

MAGNETIC INCOMMENSURATE STRUCTURES

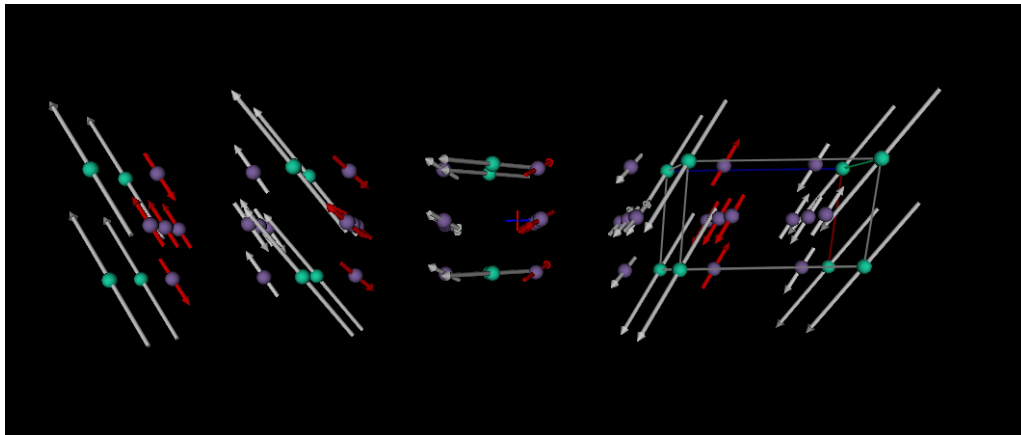
Some examples:



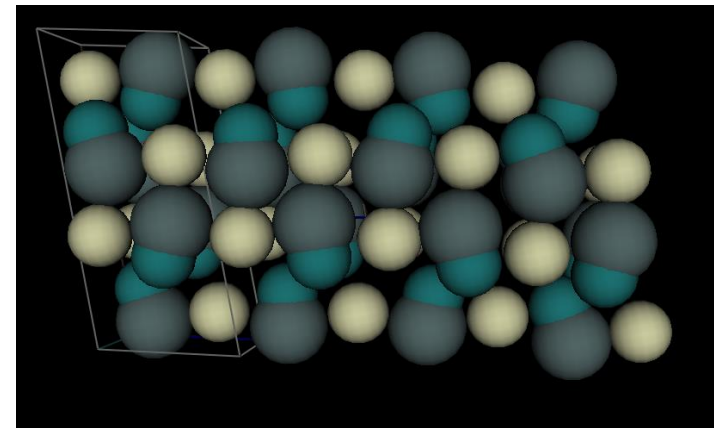
β -Li₂IrO₃



CeRuSn – Ce moment



DyMn₆Ge₆ – residual moment



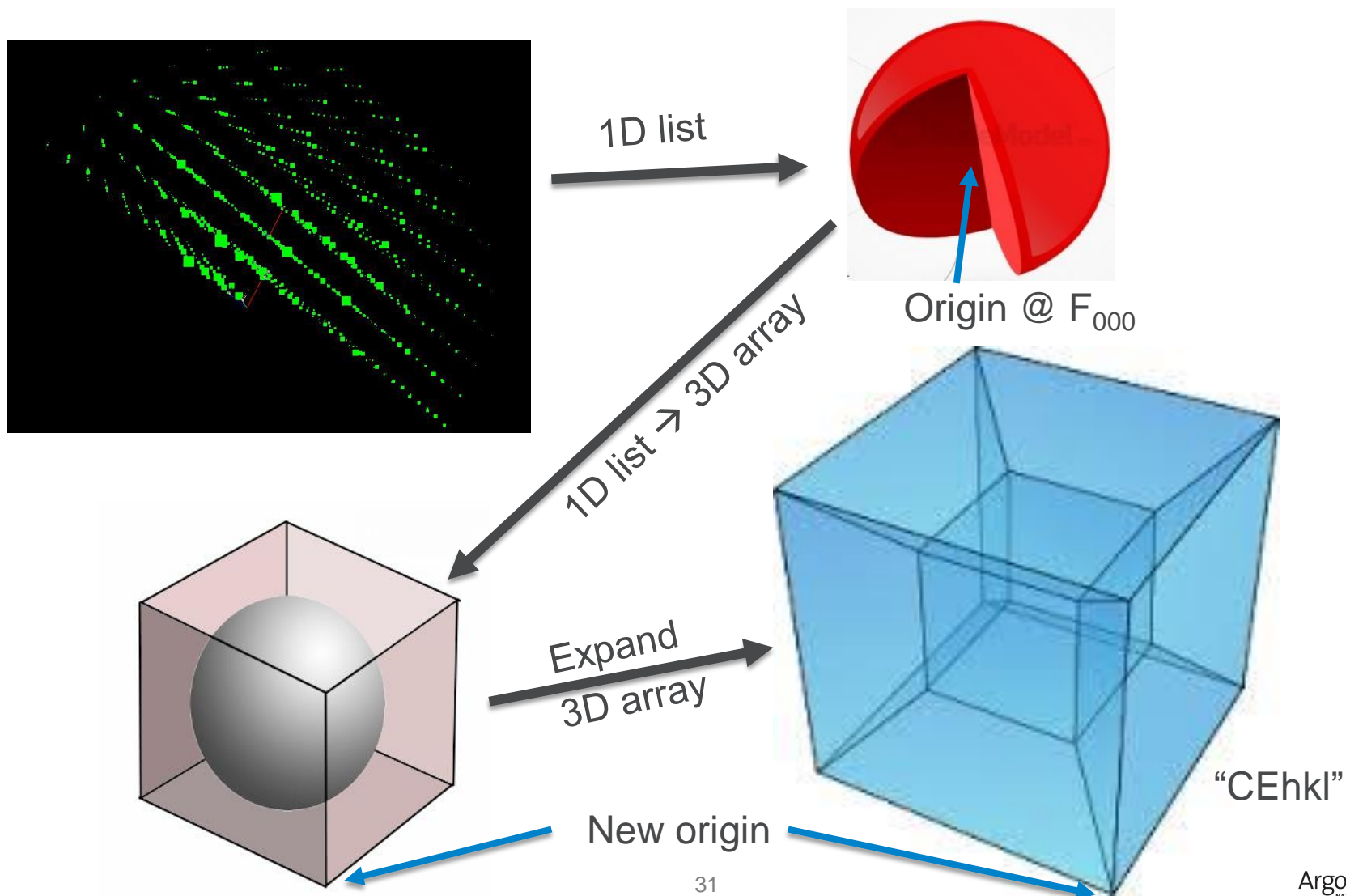
CeRuSn –
structure modulation

CHARGE FLIPPING

CHARGE FLIPPING

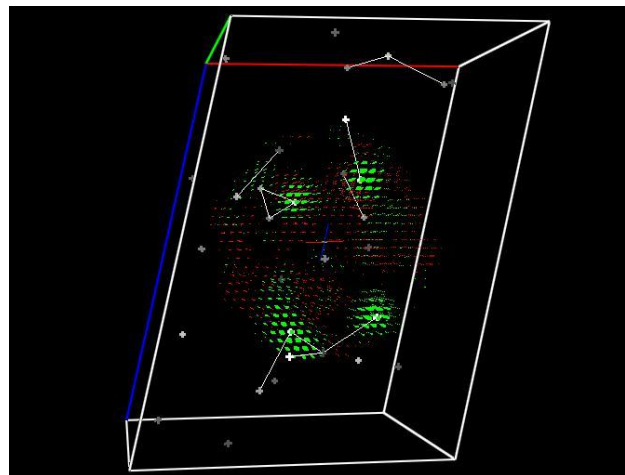
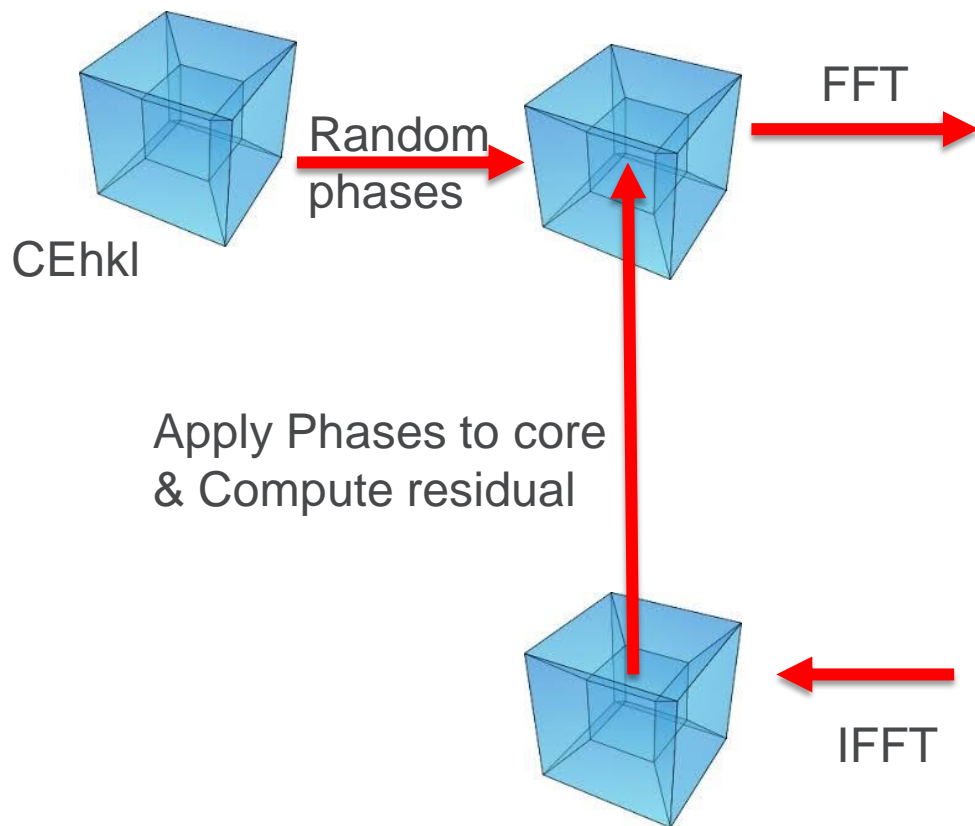
The algorithm set up:

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

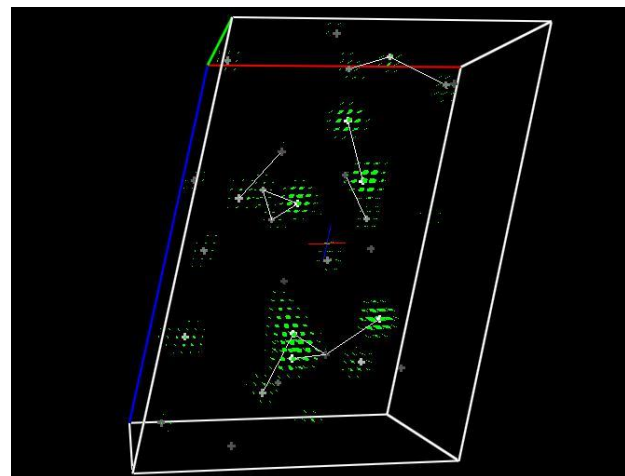


CHARGE FLIPPING

The Algorithm



Charge Flip



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
```

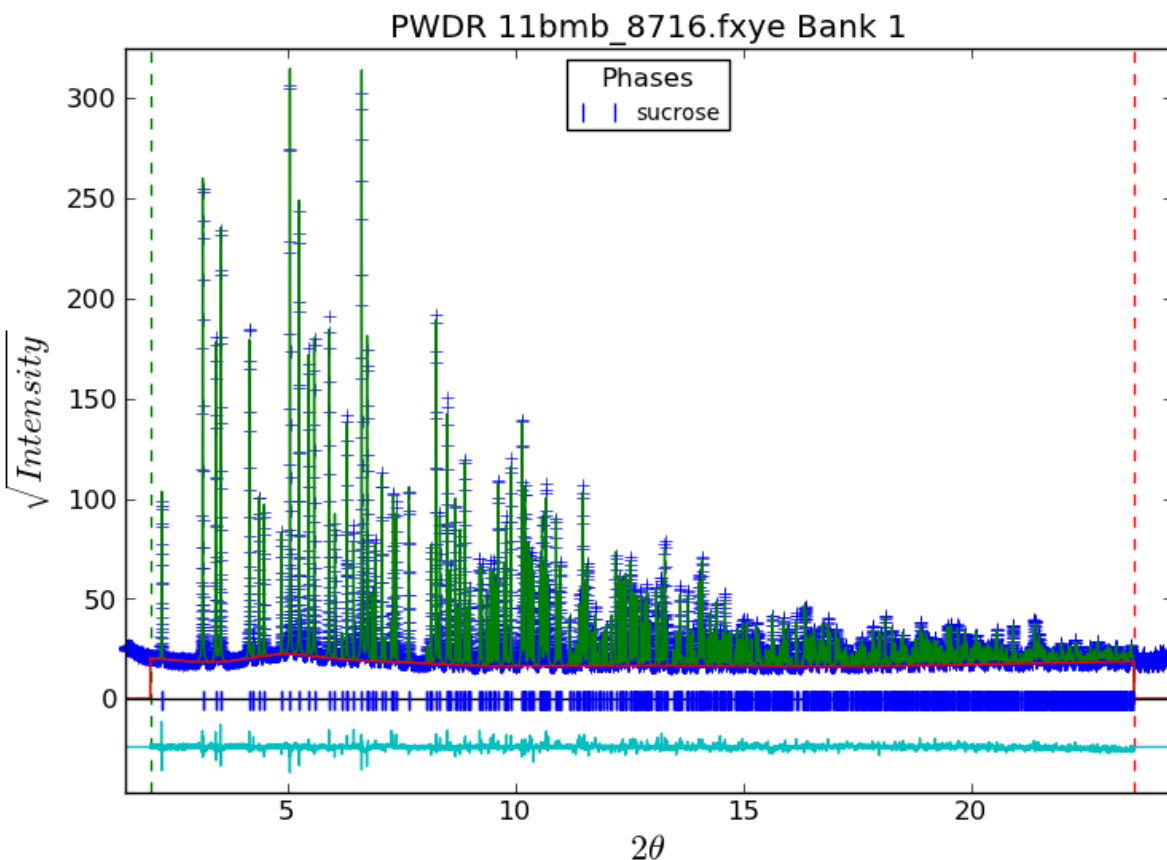
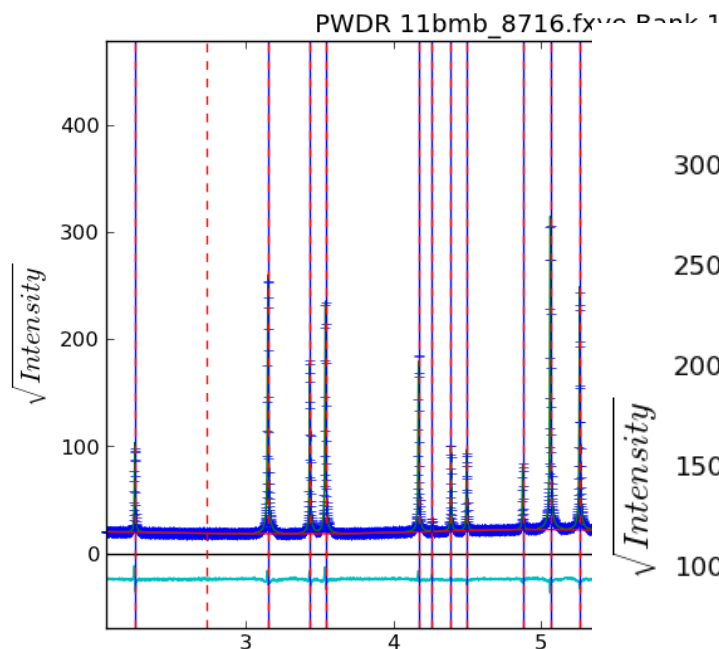
After user break:

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



Unit Cells List

Cell Index/Refine Help

Indexing controls:

Max Nc/Nobs 4 Start Volume 25 Use M20/(X20+1)?

Select Bravais Lattices for indexing:

Cubic-F Cubic-I Cubic-P Trigonal-R Trigonal/Hexago

Orthorhombic-F Orthorhombic-I Orthorhombic-C Orthorhombic-P Monoclinic-C

Cell Test Refinement:

Bravais lattice **P2/m** Space group **P.21** Zero offset 0.0007 Refine?

Unit cell: a = 7.71525 b = 8.66389 c = 10.80965

Indexing Result:

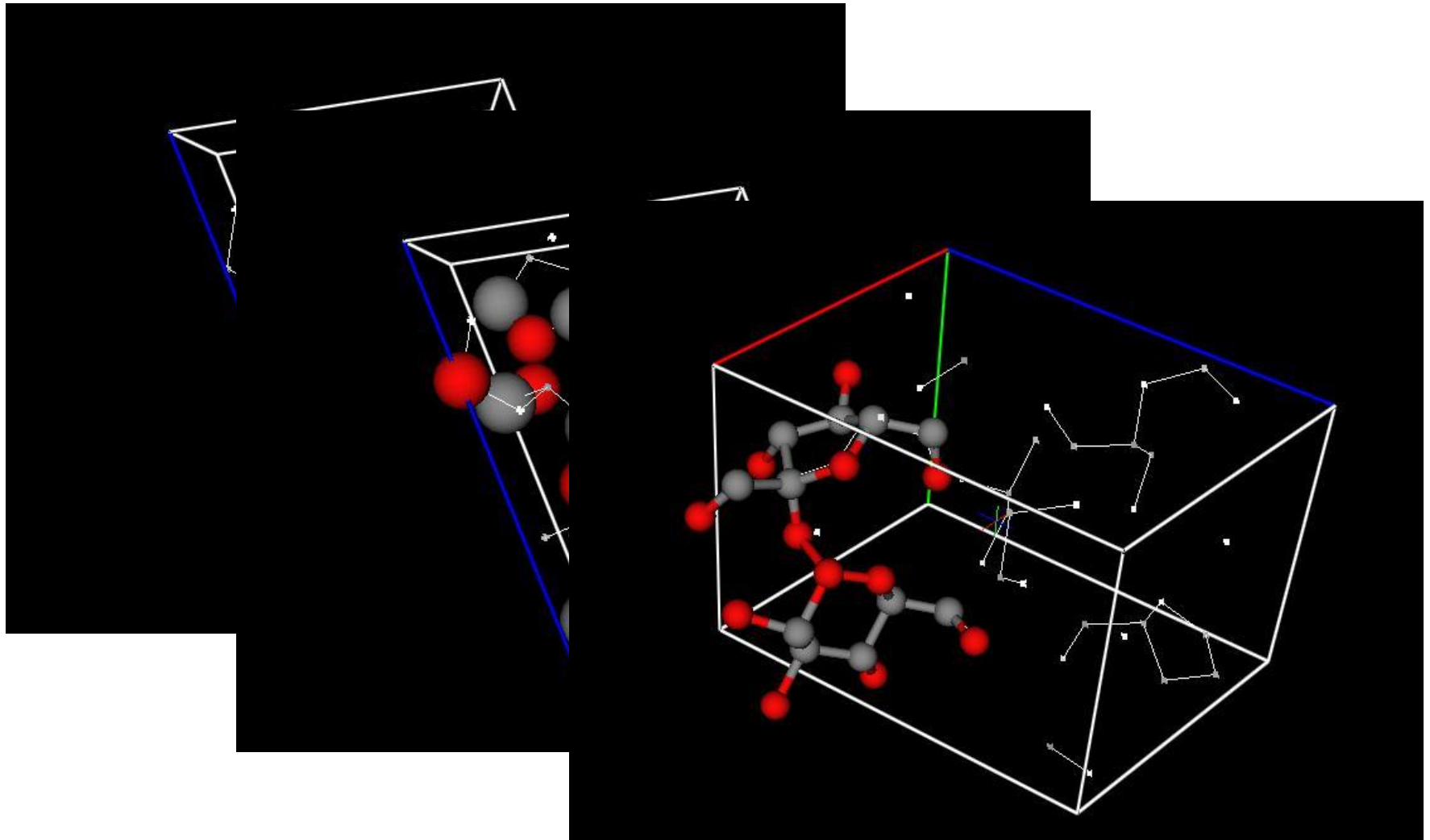
M20	X20	use	Bravais	a	b	c	alpha	beta	gamma	Volume	Keep
1312.84	0	<input checked="" type="checkbox"/>	P2/m	7.71525	8.66389	10.80965	90.000	102.983	90.000	704.09	<input type="checkbox"/>
907.76	0	<input type="checkbox"/>	P2/m	7.71412	8.66281	10.80843	90.000	102.982	90.000	703.82	<input type="checkbox"/>
15.05	0	<input type="checkbox"/>	P2/m	7.69200	8.66511	10.79433	90.000	102.664	90.000	701.96	<input type="checkbox"/>
2.38	1	<input type="checkbox"/>	P2/m	6.78185	10.56374	15.20797	90.000	98.621	90.000	1077.21	<input type="checkbox"/>
2.38	1	<input type="checkbox"/>	P2/m	6.78185	10.56374	15.20797	90.000	98.621	90.000	1077.21	<input type="checkbox"/>



781 unique hkl's
CF with 61440

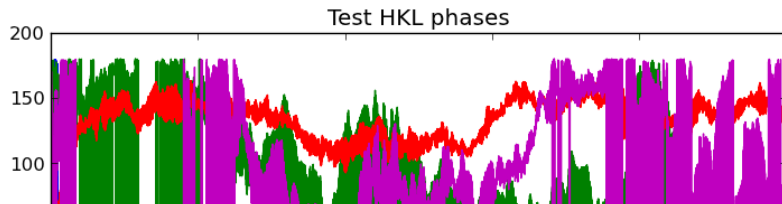
CHARGE FLIPPING SOLUTION

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

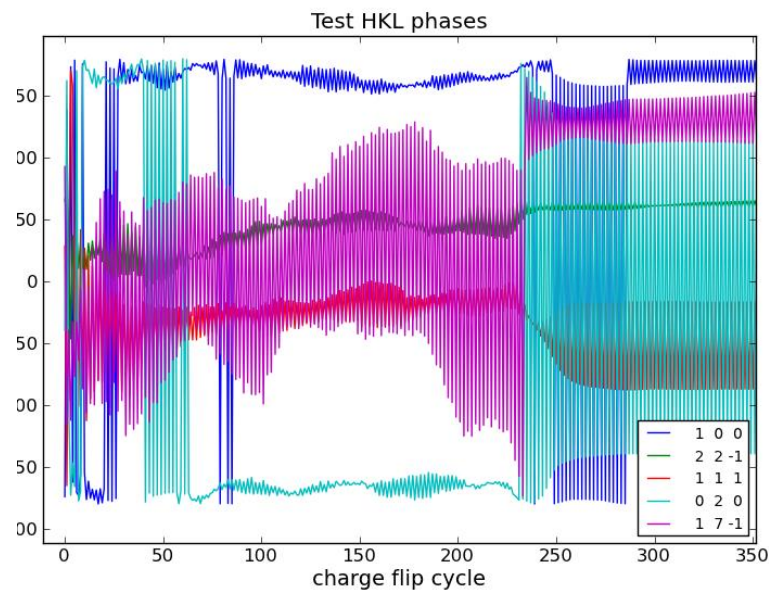
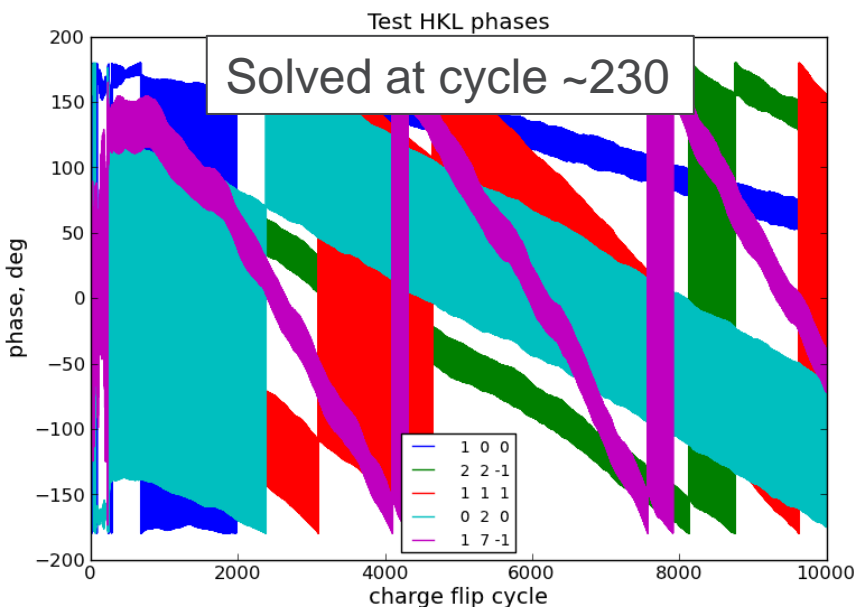
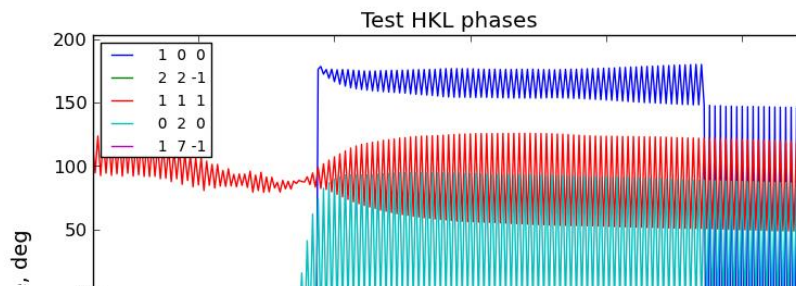
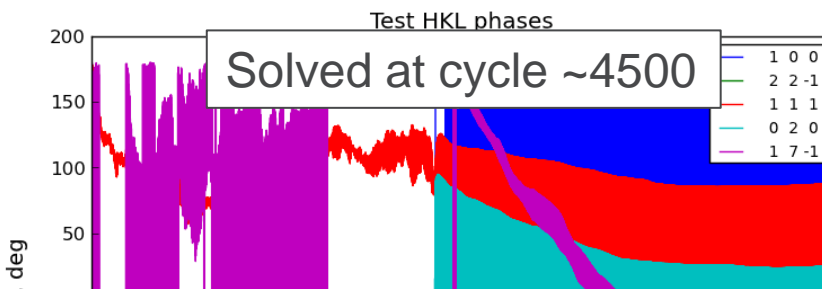


CHARGE FLIPPING – PHASES?

Track phases of 5 reflections – 10000 CF cycles



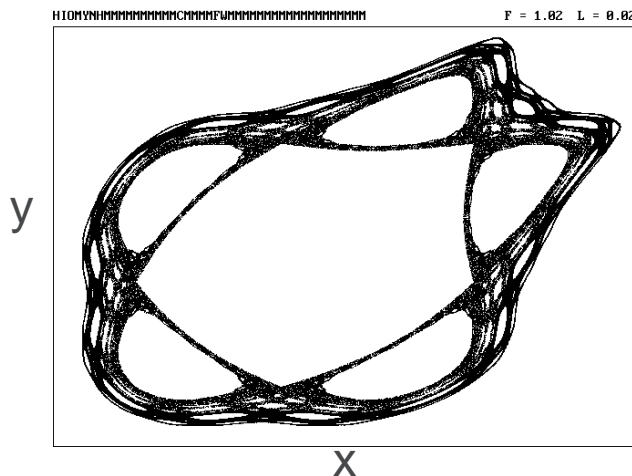
Not solved in 10000 cycles



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)

THANK YOU