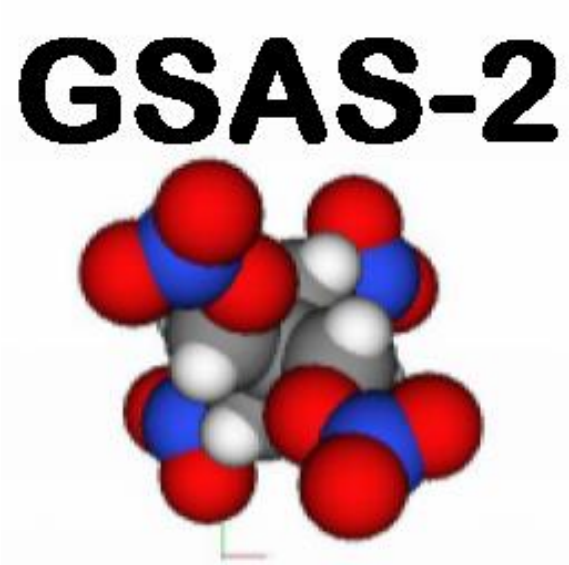
# GSAS-II SPECIAL TOPICS

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# CONSTRAINTS & RESTRAINTS

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

## Constraints – reduce no. of parameters

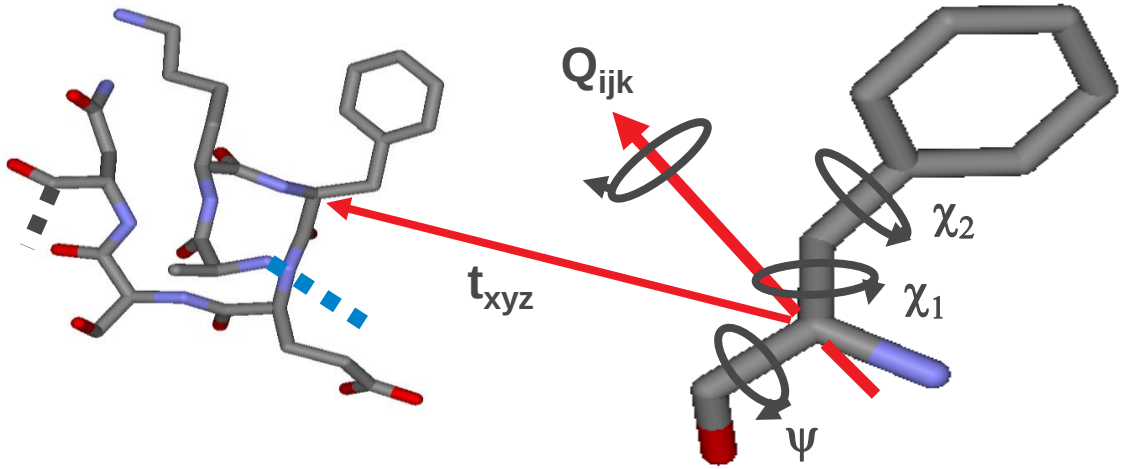
Derivative vector After constraints

$$\frac{\partial F}{\partial v_i} = R_{il} U_{lk} S_{kj} \frac{\partial F}{\partial p_j}$$

Derivative vector Before constraints

Rectangular matrices

Rigid body User Symmetry



# 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 gimbel lock as with Eulerian angles @ $\chi = 0$

# FULL MINIMIZATION FUNCTION + RESTRAINTS: ADDITIONAL "DATA"

## Least-squares – nonlinear; transcendental functions

$$M = f_Y \sum w_i \left(Y_{oi} - Y_{ci}\right)^2$$ **Powder profile (Rietveld)/Single crystal $F_{hkl}$**

$$+ f_a \sum w_i \left(a_{oi} - a_{ci}\right)^2$$ **Bond angles**

$$+ f_d \sum w_i \left(d_{oi} - d_{ci}\right)^2$$ **Bond distances**

$$+ f_t \sum w_i \left(-t_{ci}\right)^4$$ **Torsion angle pseudopotentials**

$$+ f_p \sum w_i \left(-p_{ci}\right)^2$$ **Plane RMS displacements**

$$+ f_v \sum w_i \left(v_{oi} - v_{ci}\right)^4$$ **van der Waals distances (if $v_{oi}<v_{ci}$)**

$$+ f_h \sum w_i \left(h_{oi} - h_{ci}\right)^2$$ **Hydrogen bonds**

$$+ f_x \sum w_i \left(x_{oi} - x_{ci}\right)^2$$ **Chiral volumes**

$$+ f_R \sum w_i \left(-R_{ci}\right)^4$$ **"ϕ/ψ" pseudopotential**

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

# RMCPROFILE IN GSAS-II

# RMCPROFILE “BIG BOX” SIMULATION

## GSAS-II interface development goals

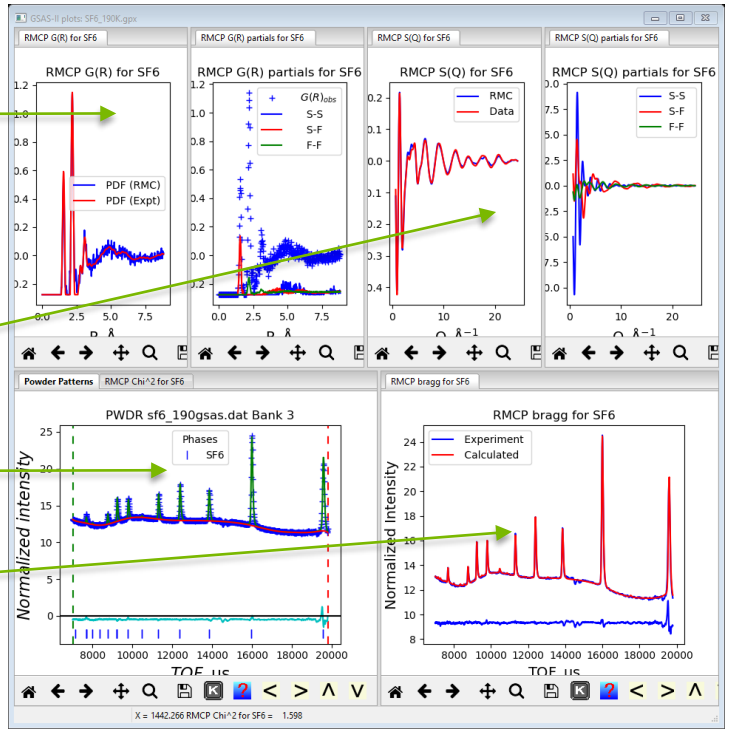
- Provide GUI interface to setup of RMCProfile - save setup controls for reuse
- Initiate independent RMCProfile execution – may run for hours
- Allow graphical display on intermediate results

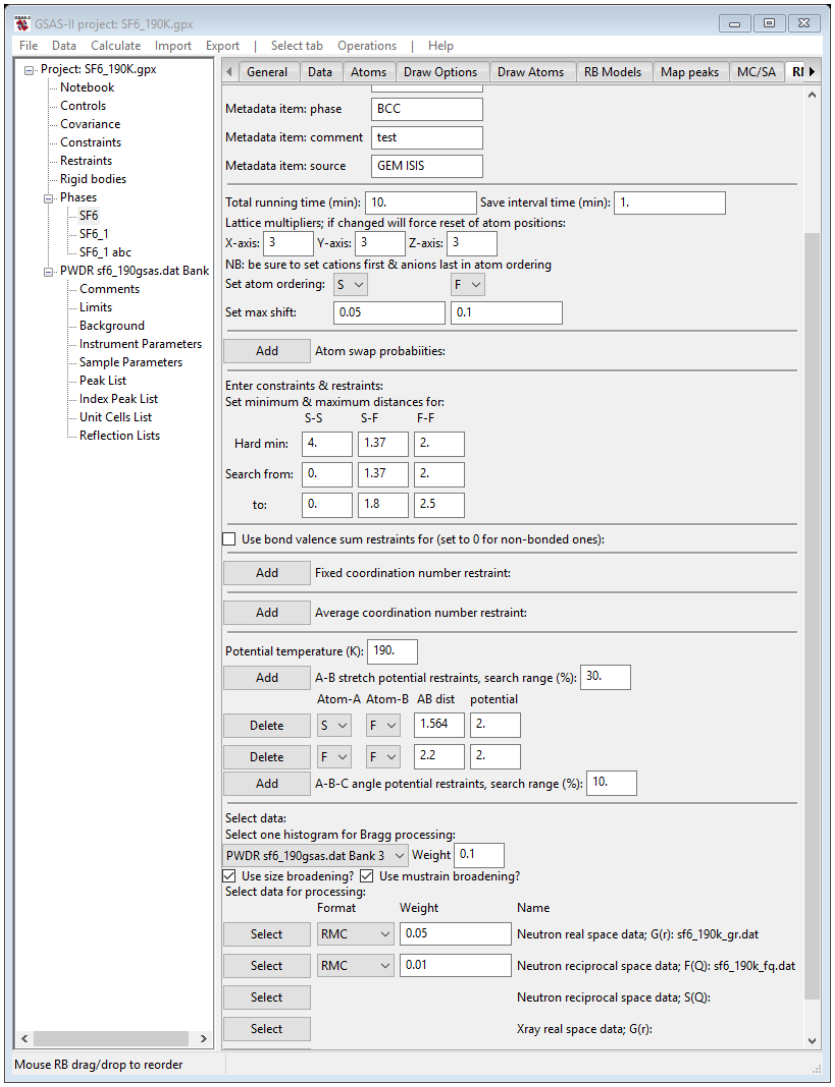
G(R) & partials

S(Q) & partials

RR result

PWDR simulation



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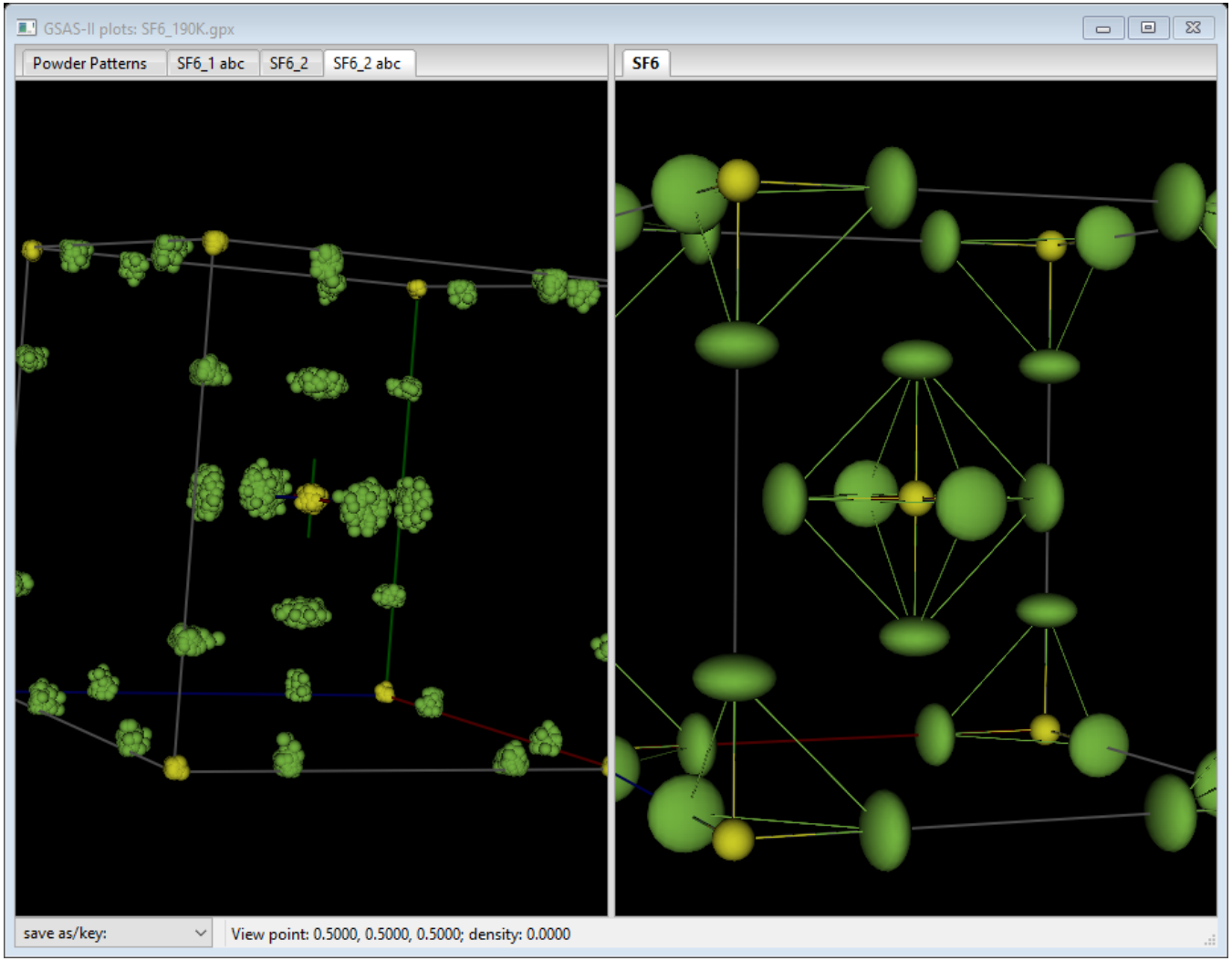
# RMCPROFILE RESULT FOR $SF_6$

## 10x10x10 unit cell box – transform back to original

## See disordered atom distribution

## – compare to Rietveld $U_{aniso}$ for F atom



# PDFFIT & ISODISTORT

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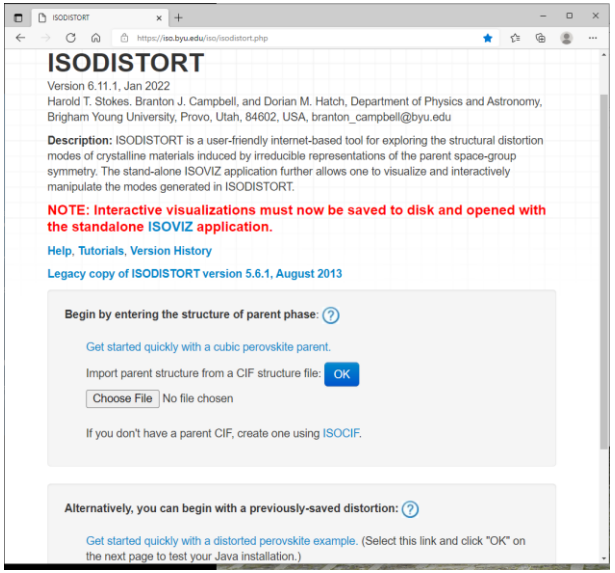
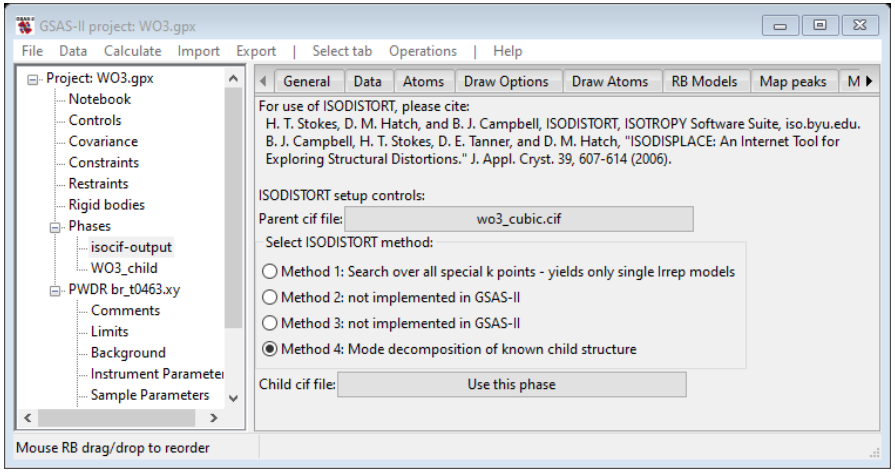
# ISODISTORT

## Implementation in GSAS-II

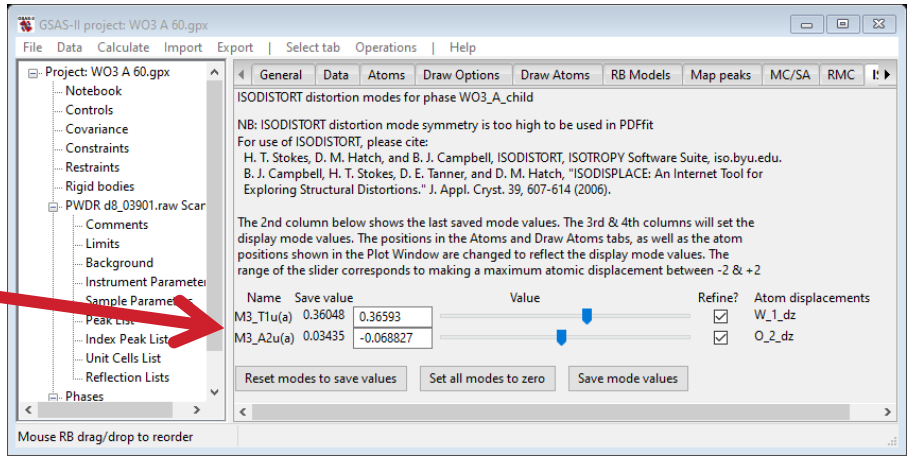
ISODISTORT: Web based tool for discerning mode displacements of atoms from an idealized parent structure




- 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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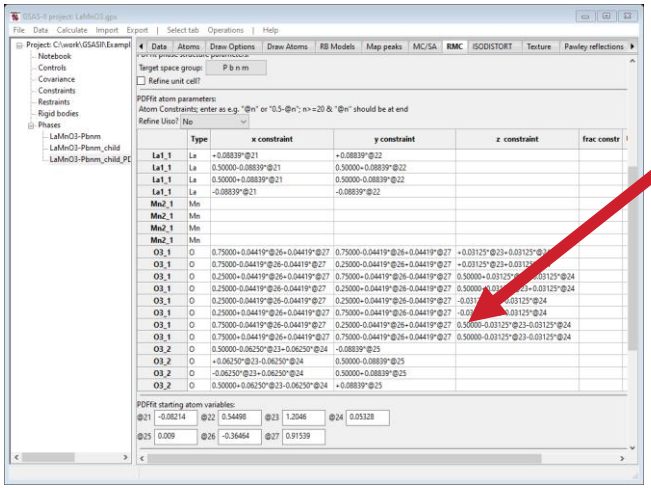
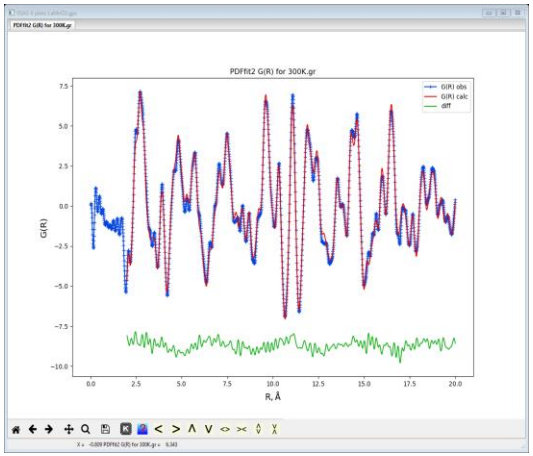
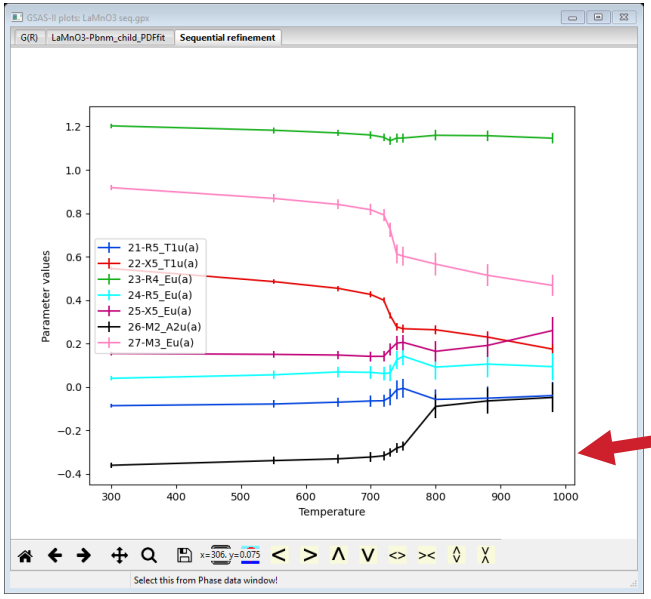
# PDFFIT2 = “PDFfit” IN GSAS-II

## “Small Box” modelling of pair distribution functions

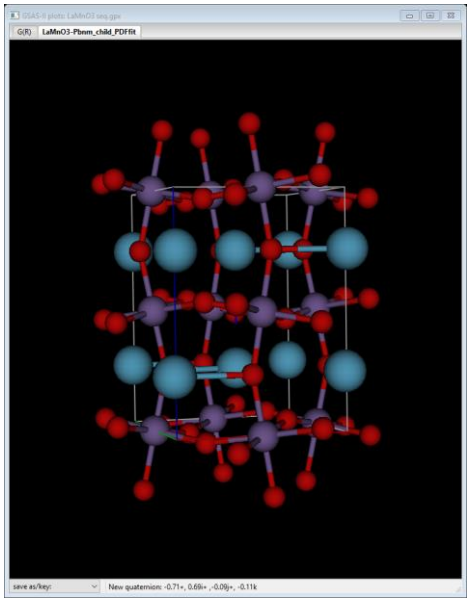
Use ISODISTORT – create the atom position constraints in new interface to PDFfit2






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



# INCOMMENSURATE STRUCTURES IN GSAS-II

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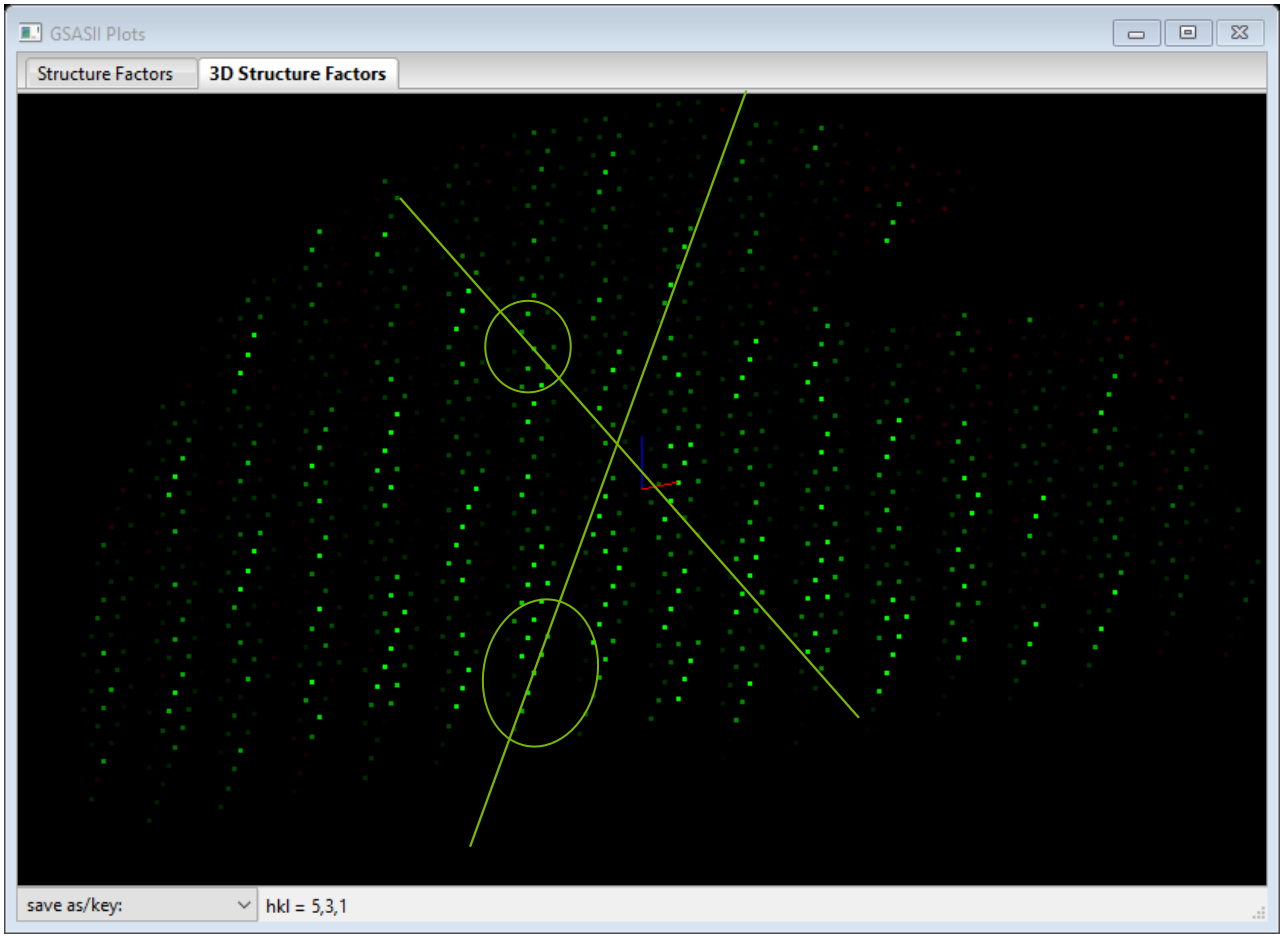
# INCOMMENSURATE STRUCTURES N GSAS-II

## Book: “Incommensurate Crystallography” S. van Smaalen




H=G+mq

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

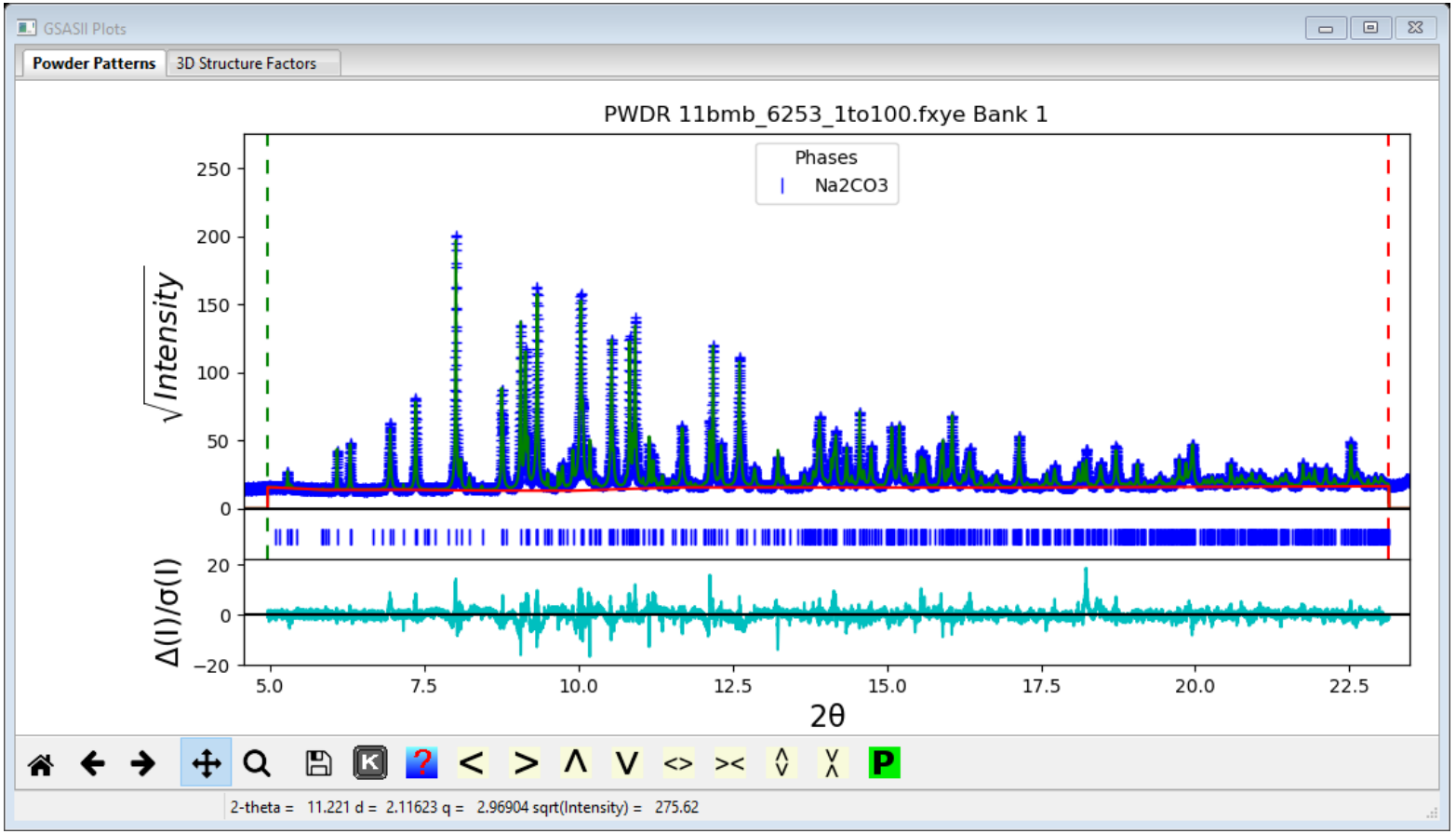
For $Na_2CO_3$
q= 0.183,0,.319

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

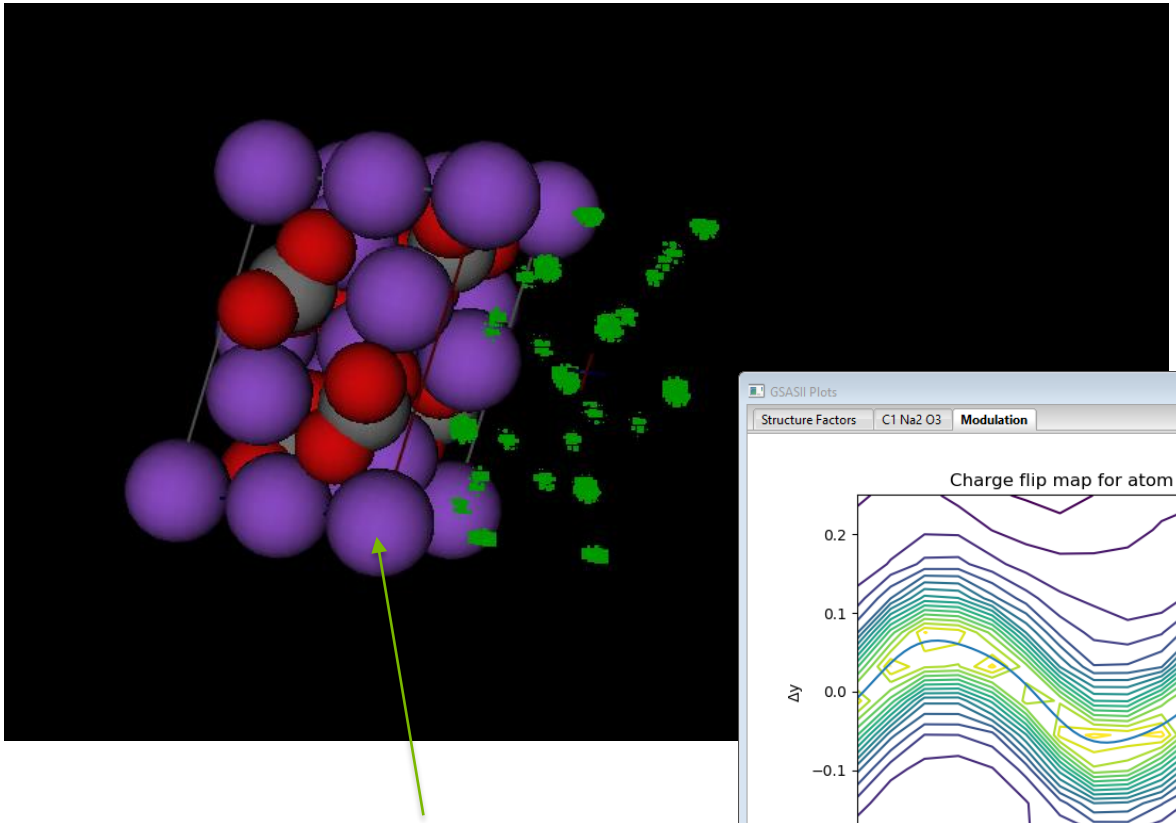
## $Na_2CO_3$ – 11BM @ APS room temp.

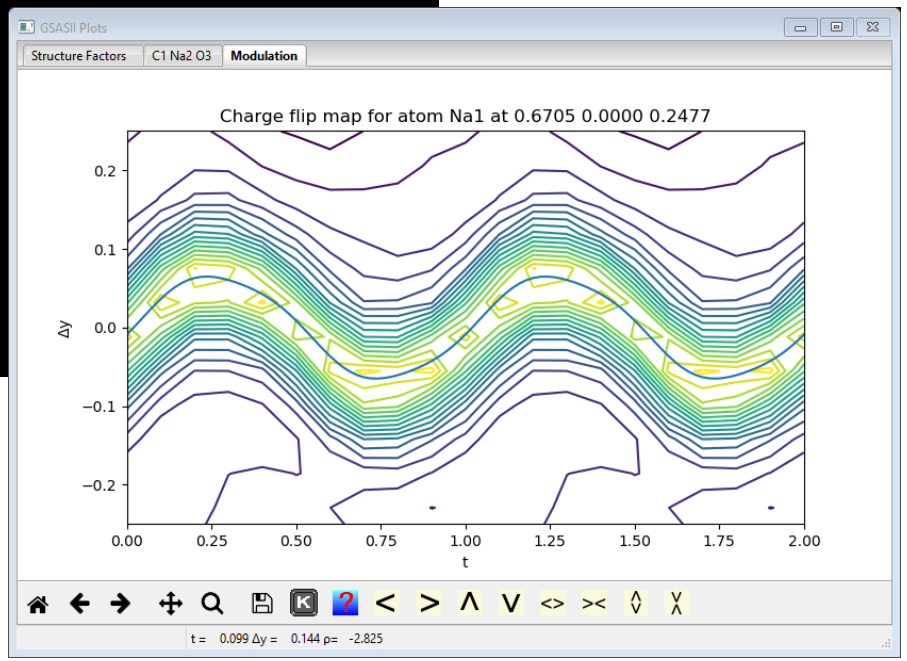



Includes m=-2,-1,1,2 superlattice reflections; Rietveld refinement includes 1st & 2nd order harmonics on position depending on atom

# INCOMMENSURATE STRUCTURE SOLUTION

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

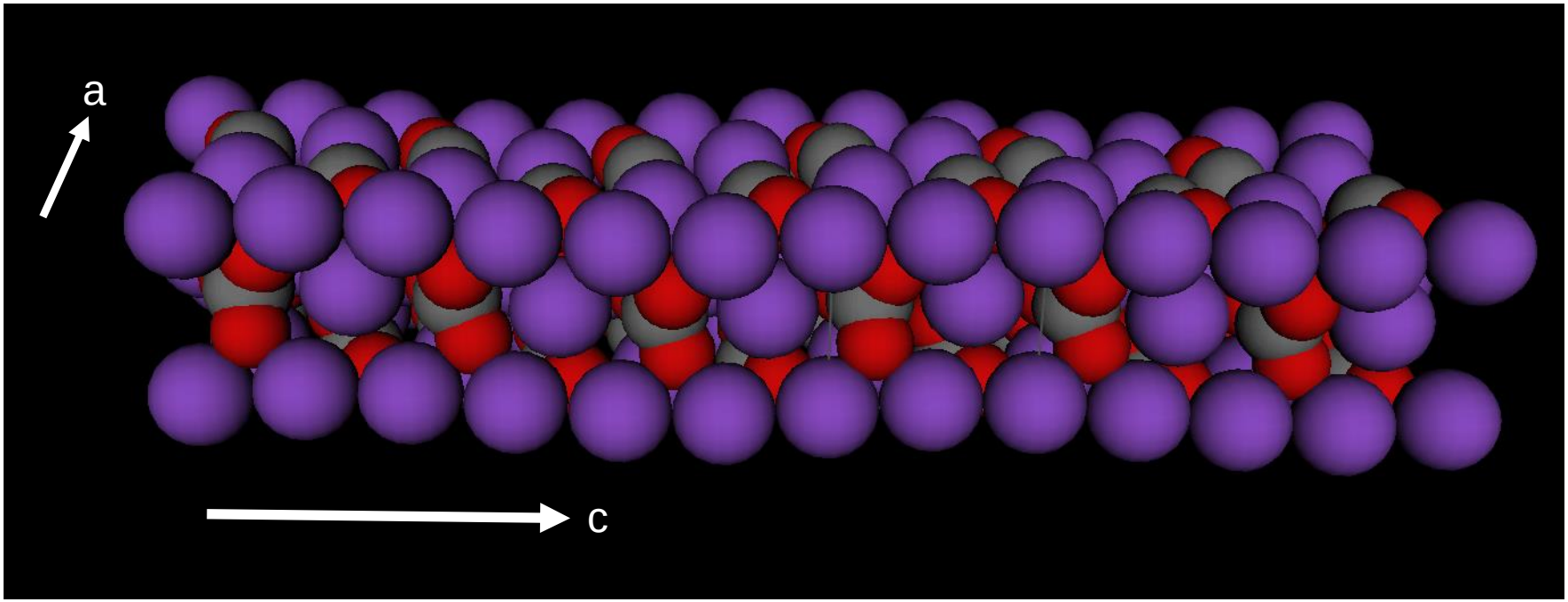





Modulation of atom positions (Na1-y)
Fit function – fourier series in tau

# 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

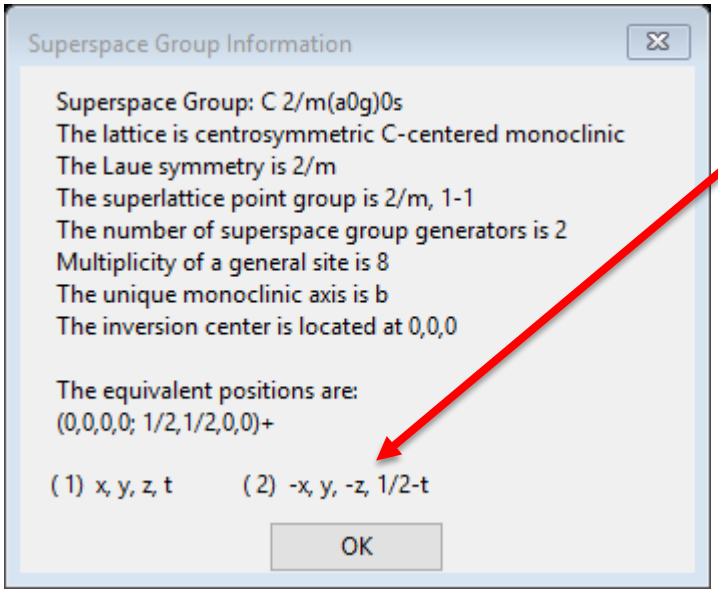
e.g. $Na_2CO_3$ – C2/m(α0γ)os

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)

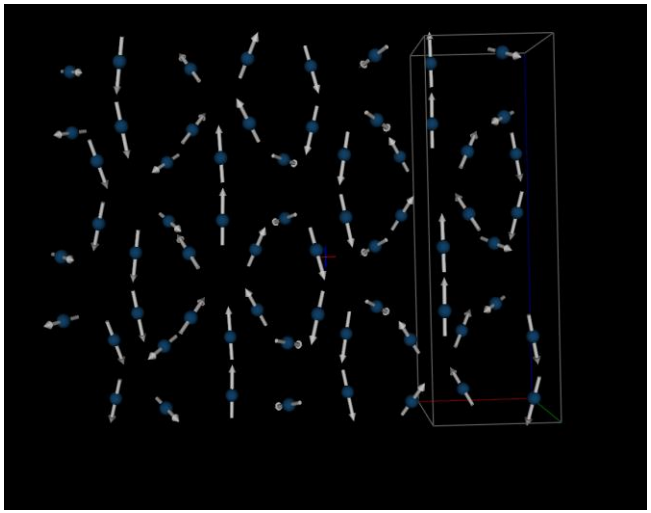
# INCOMMENSURATE STRUCTURES

## Cases not allowed in GSAS-II

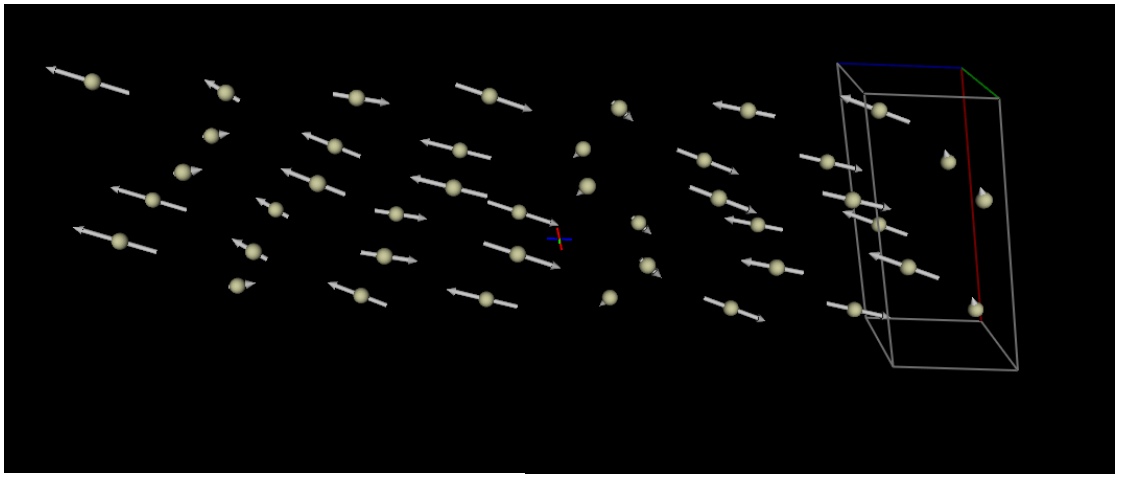
- 3+2 & 3+3 not allowed in GSAS-II
  - Too complex to deal with easily
  - 3-D 230 SG
  - For 3+1: 4,783 possible SG
  - For 3+2: 222,018 possible SG
  - For 3+3: 28,927,922 possible SG
  - But only a handful found – not worth the hassle
- Ad hoc centering not allowed
  - ‘X’ space groups – all have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

# MAGNETIC INCOMMENSURATE STRUCTURES

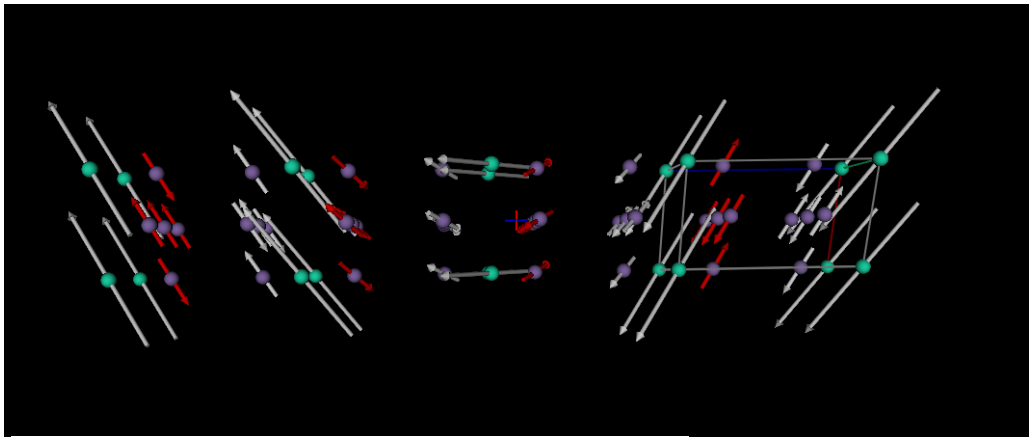
## Some examples:



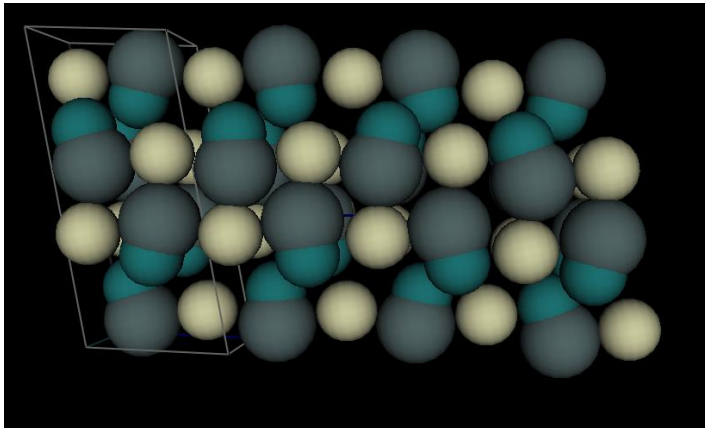
β-$Li_2IrO_3$



CeRuSn – Ce moment



$DyMn_6Ge_6$ – residual moment



CeRuSn –
structure modulation

# CURRENT STATUS

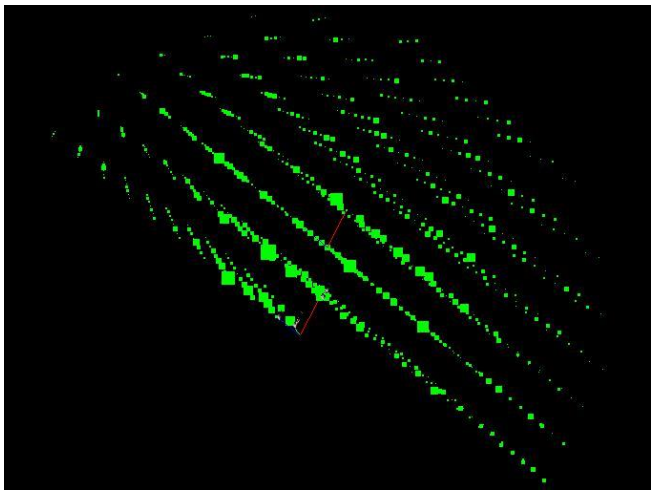
## GSAS-II & incommensurate/magnetic structures – still to be done!

- Incommensurate magnetic structures
  - Structure factor & derivatives math & refinement
  - Site symmetry rules for allowed Fourier coefficients
- Incommensurate structures
  - Certain high symmetry site symmetry rules (in tetragonal, trigonal & hexagonal)
  - Refinement of non Fourier functions (derivative issues)
  - Cif file output?
- Magnetic structures
  - Structure solving aids i.e. selection of magnetic cell & space group from observed data
  - Output mcif files TBD
  - 1st tutorial now available – Simple Magnetic Structures

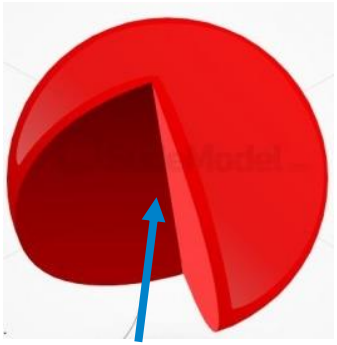
# CHARGE FLIPPING

# CHARGE FLIPPING

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

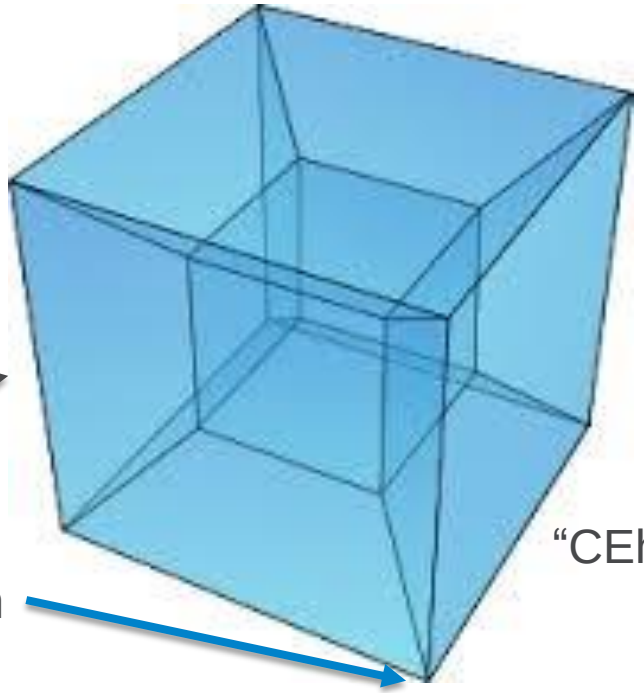


1D list

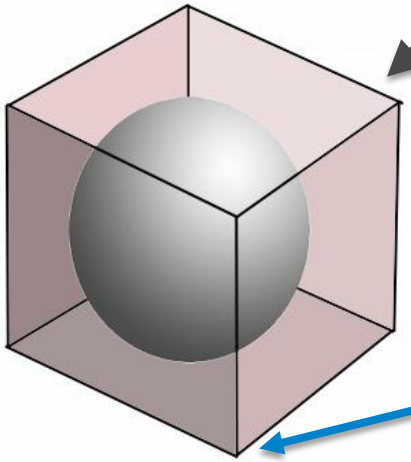


Origin @ $F_{000}$

1D list → 3D array



Expand 3D array

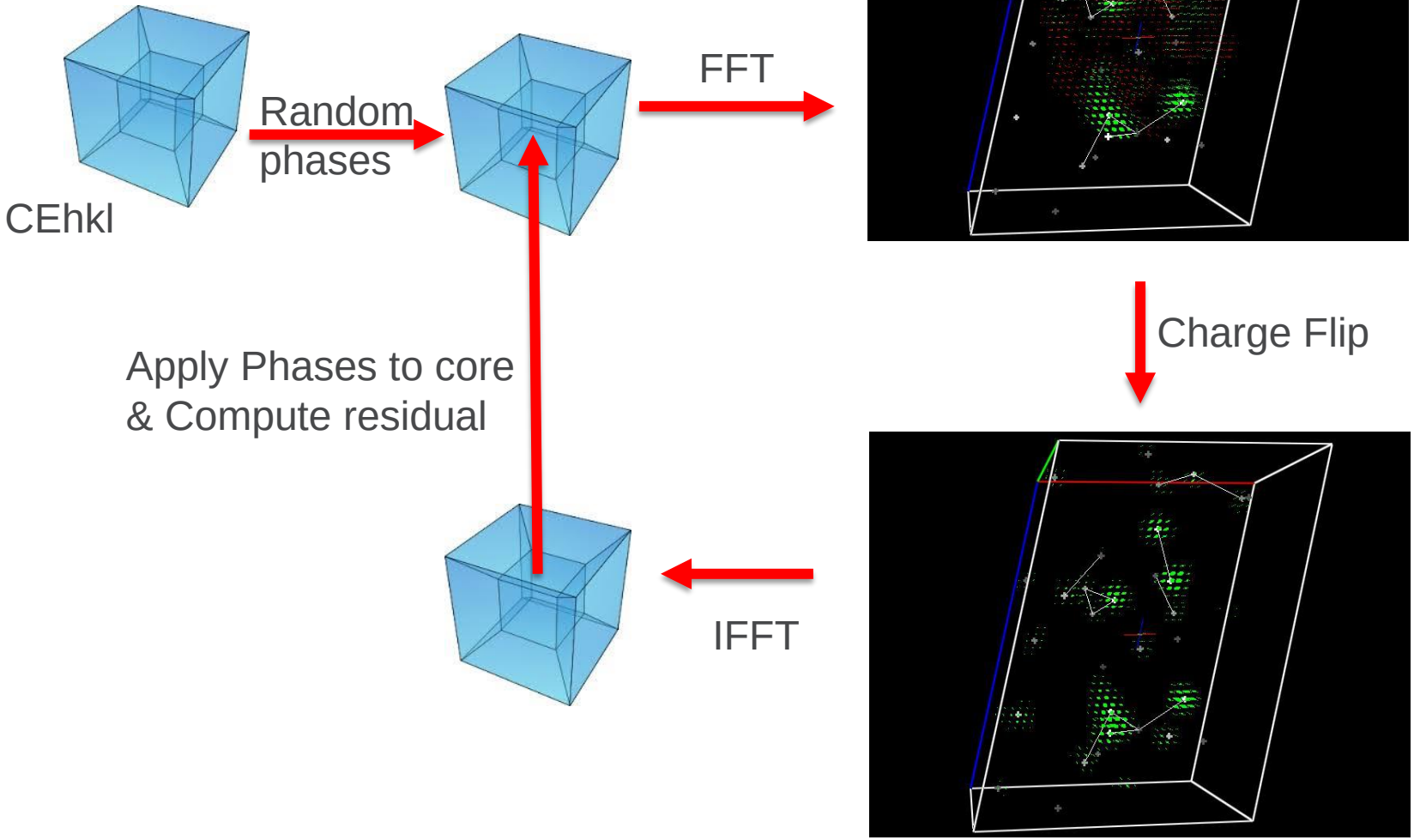


New origin

"CEhkl"

# 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
```

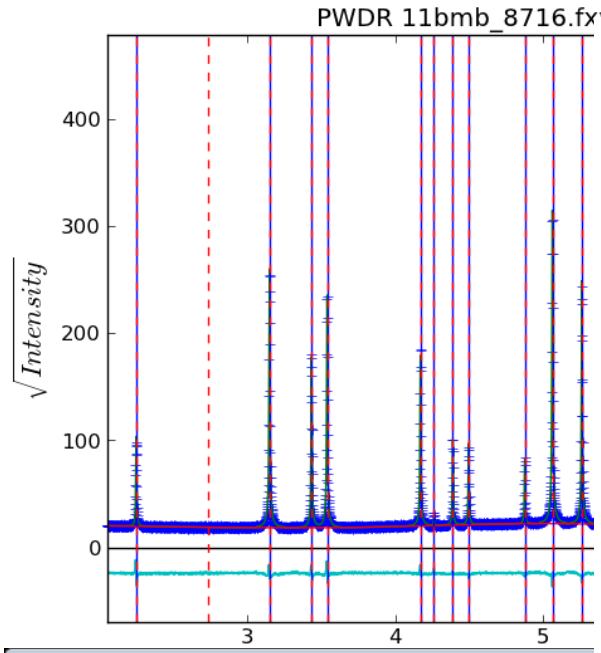
After user break:

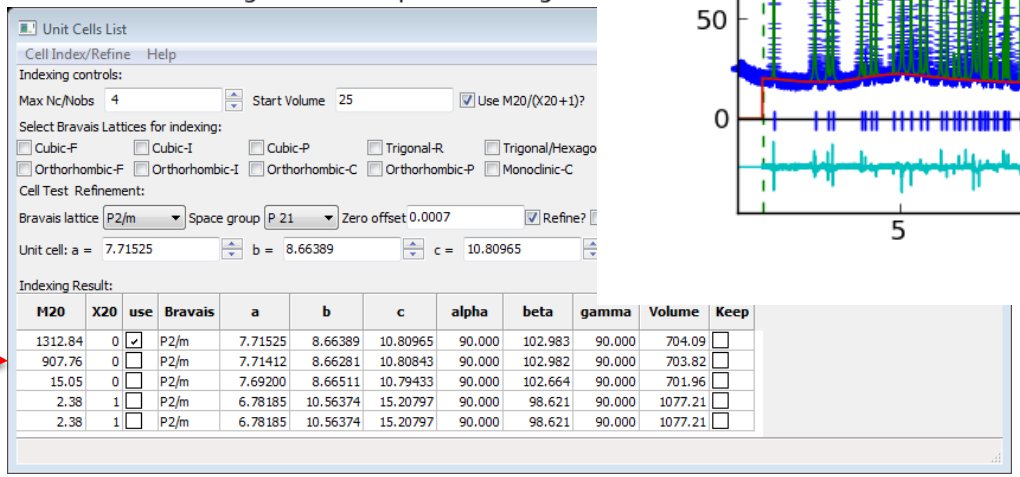
Repeat 1st line to get result map

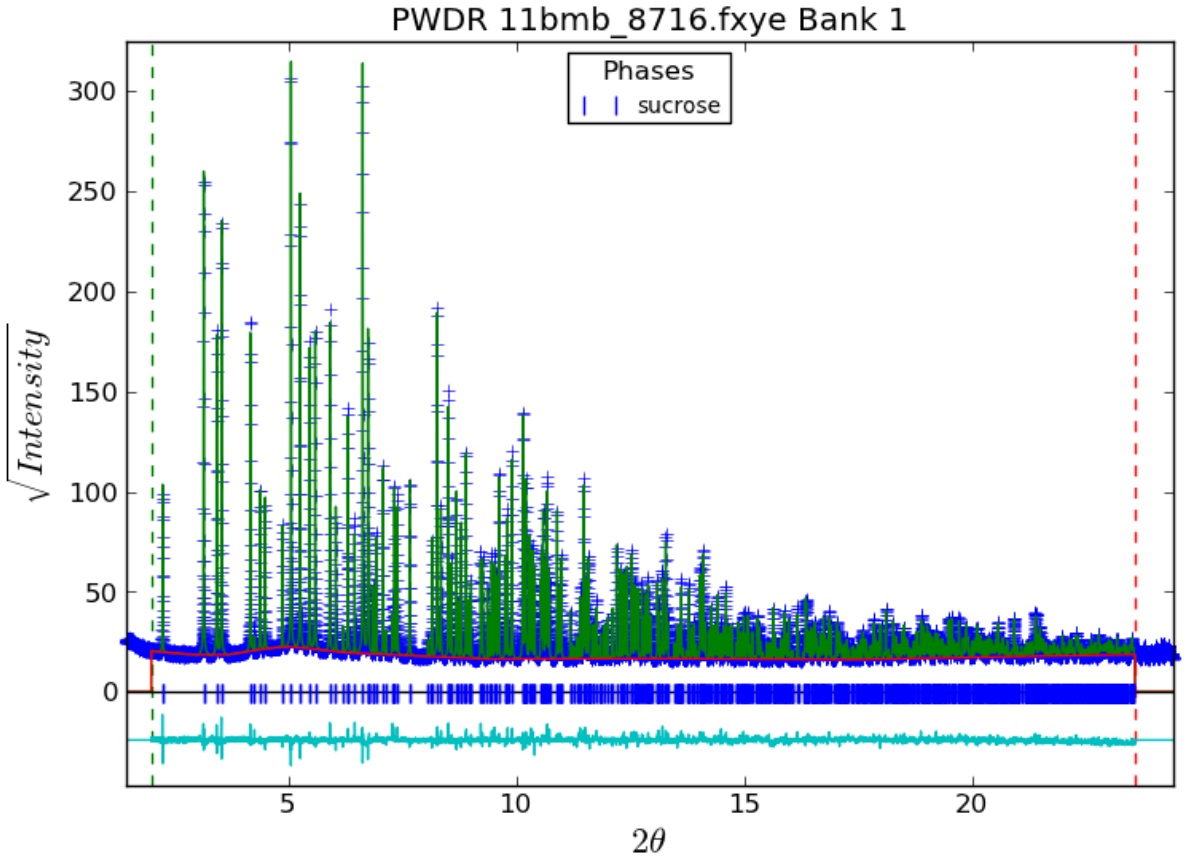
Find origin; search for peaks & display result

# EXAMPLE – SUCROSE POWDER

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




781 unique hkl's
CF with 61440

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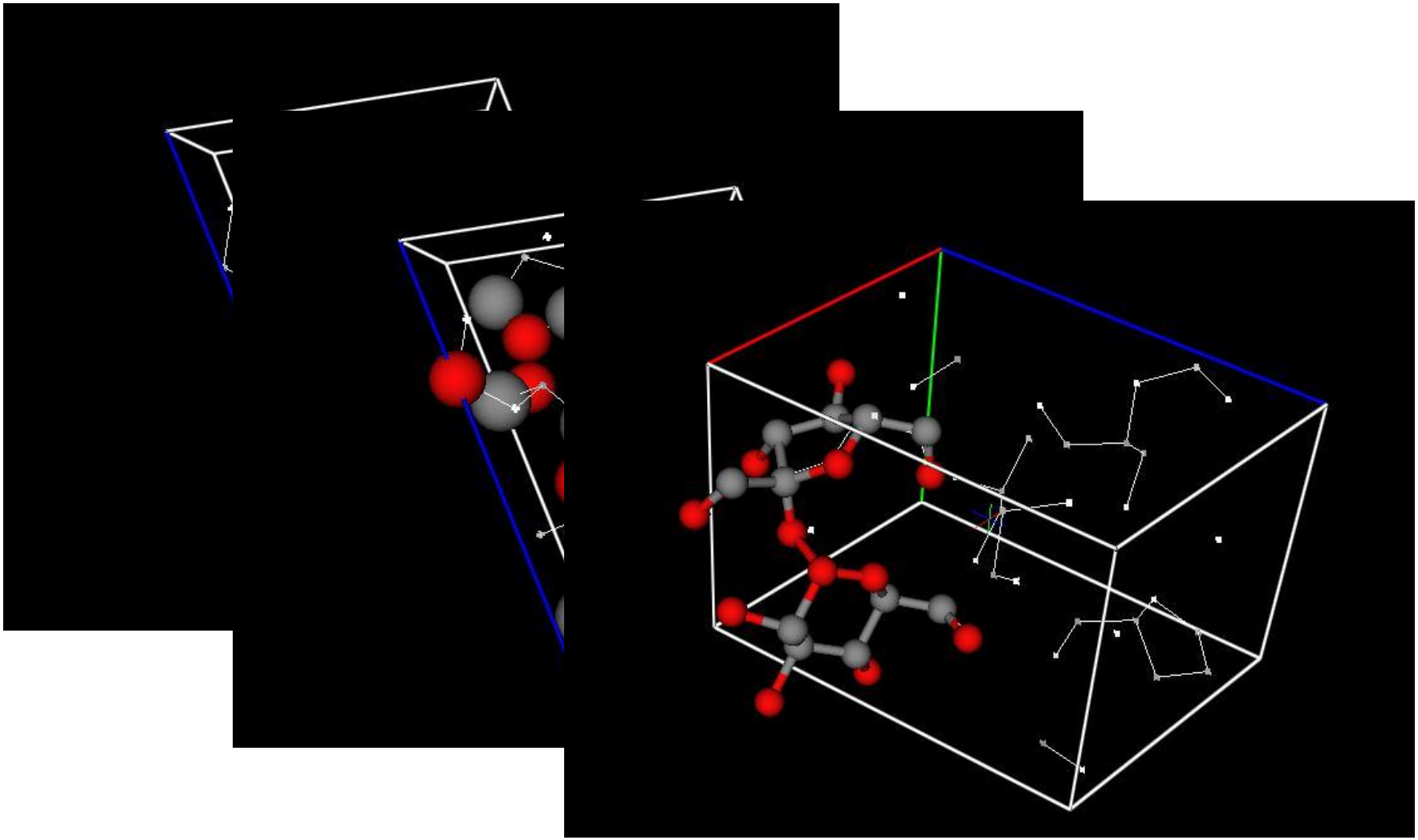
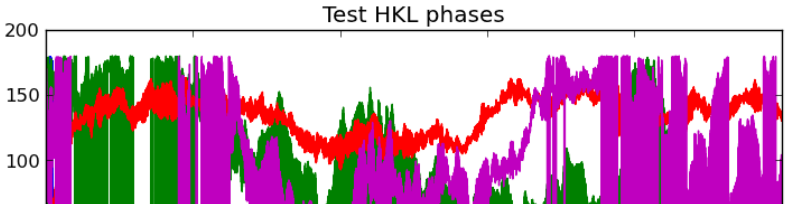
# CHARGE FLIPPING SOLUTION

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

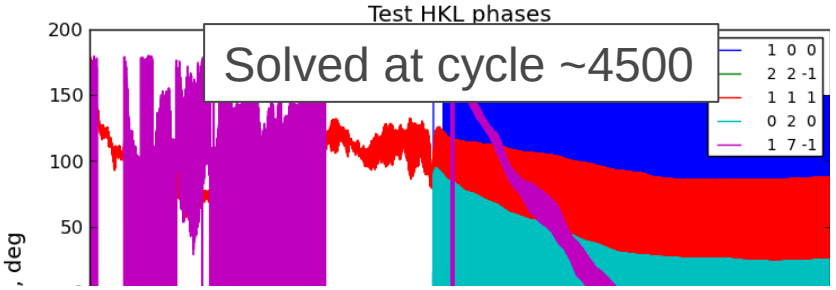


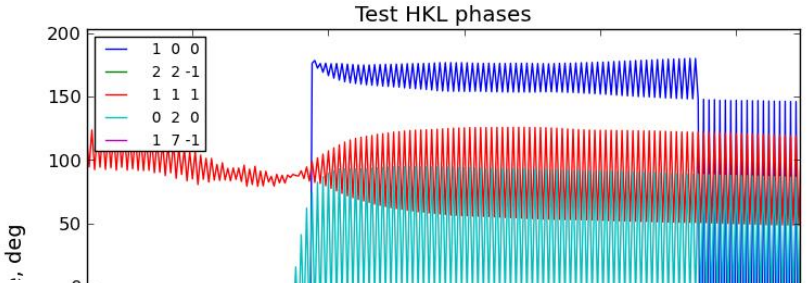
# CHARGE FLIPPING – PHASES?

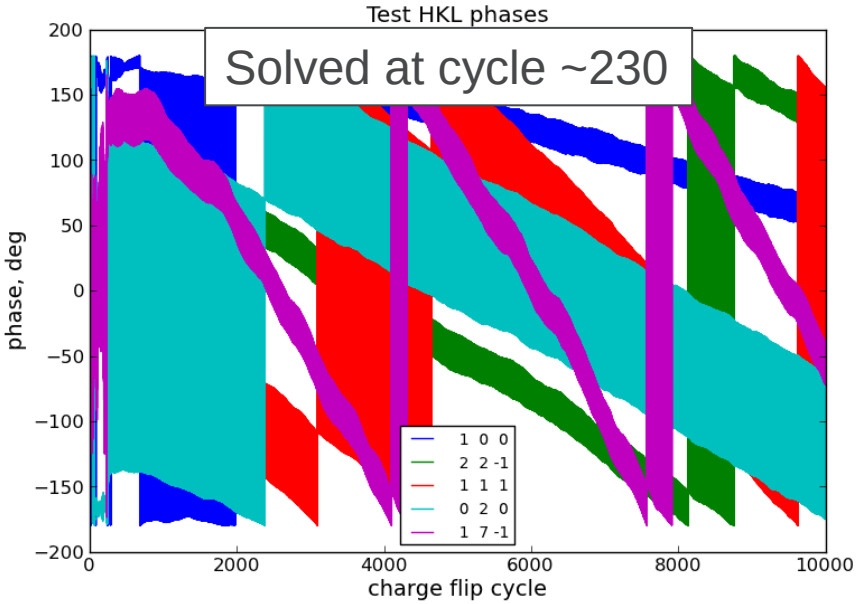
## Track phases of 5 reflections – 10000 CF cycles

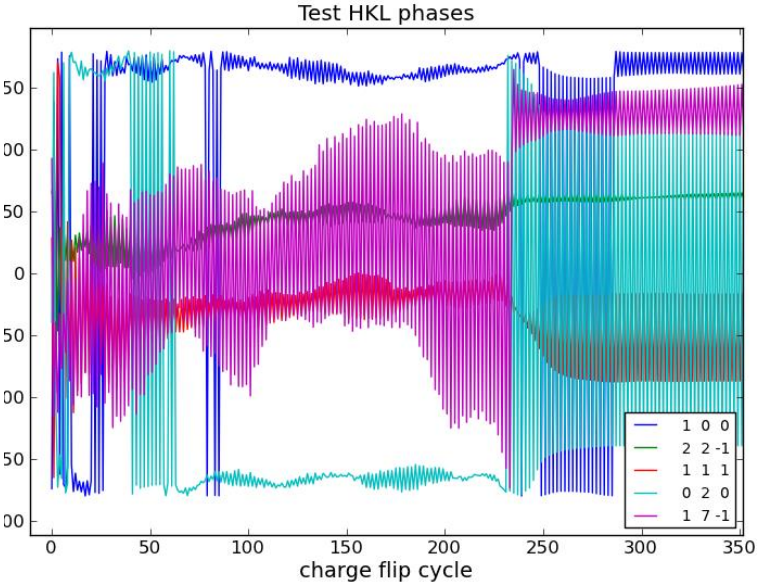



Not solved in 10000 cycles



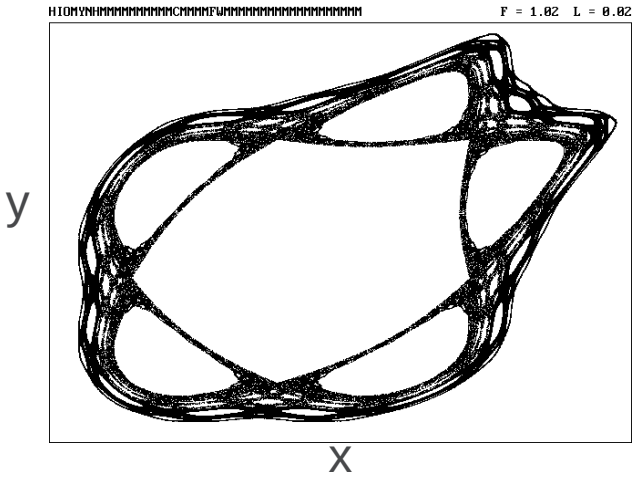



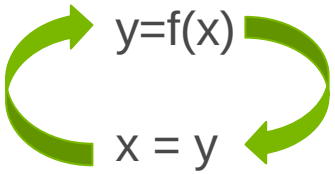



# CHARGE FLIPPING – CHAOS MATHEMATICS?

## 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