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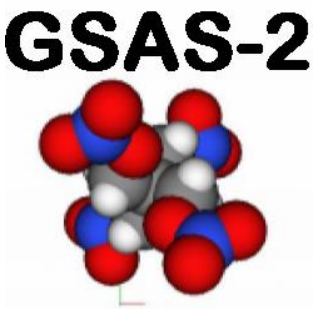
BEFORE GSAS TO GSAS-II & BEYOND



ROBERT VON DREELE
APS/ANL

ESS, Lund, Sweden
June, 2018

PLUTO REACTOR AERE HARWELL – 1970'S

PANDA Diffractometer

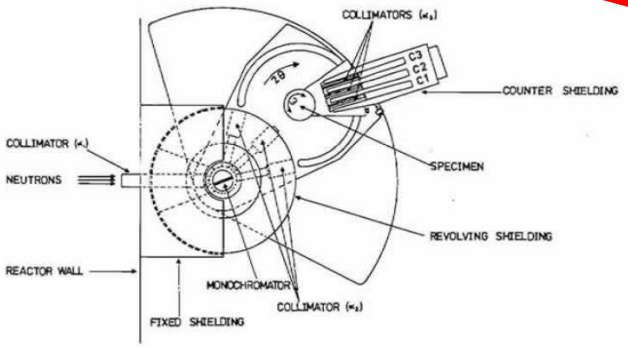
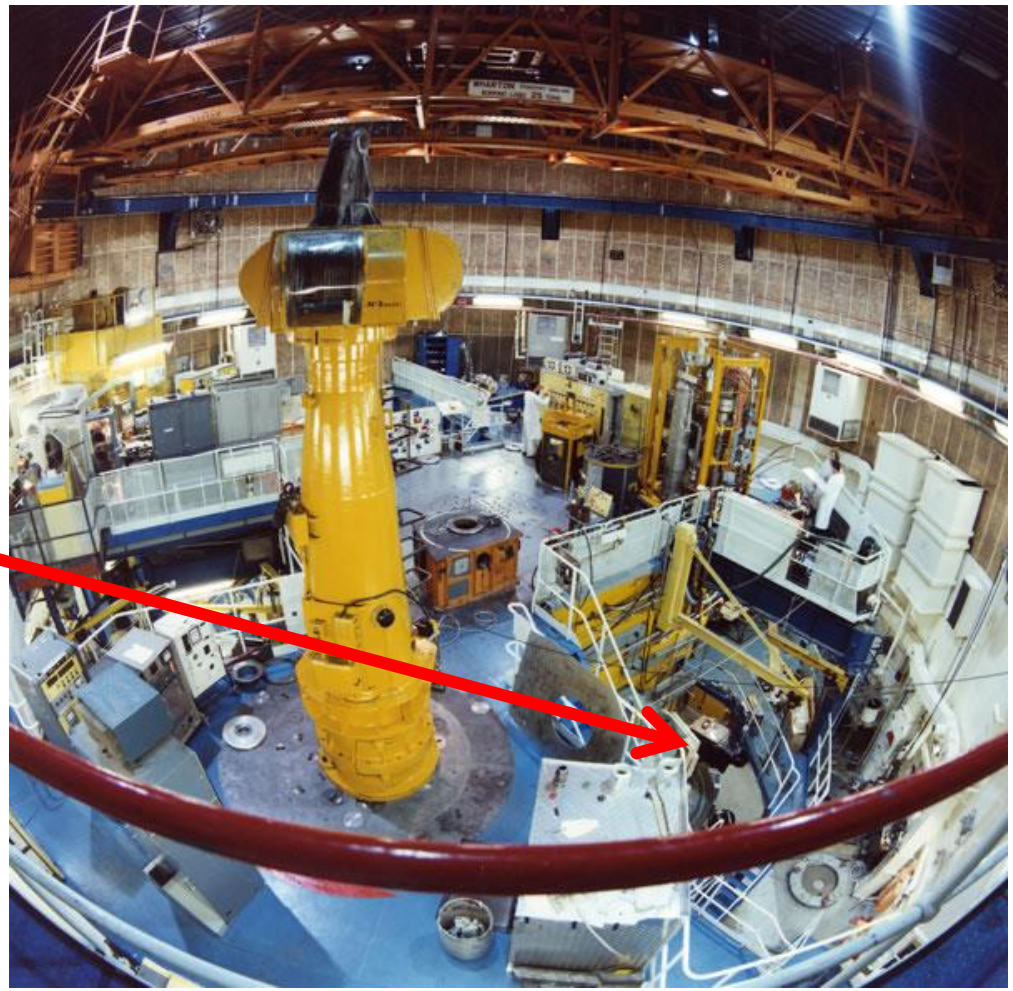


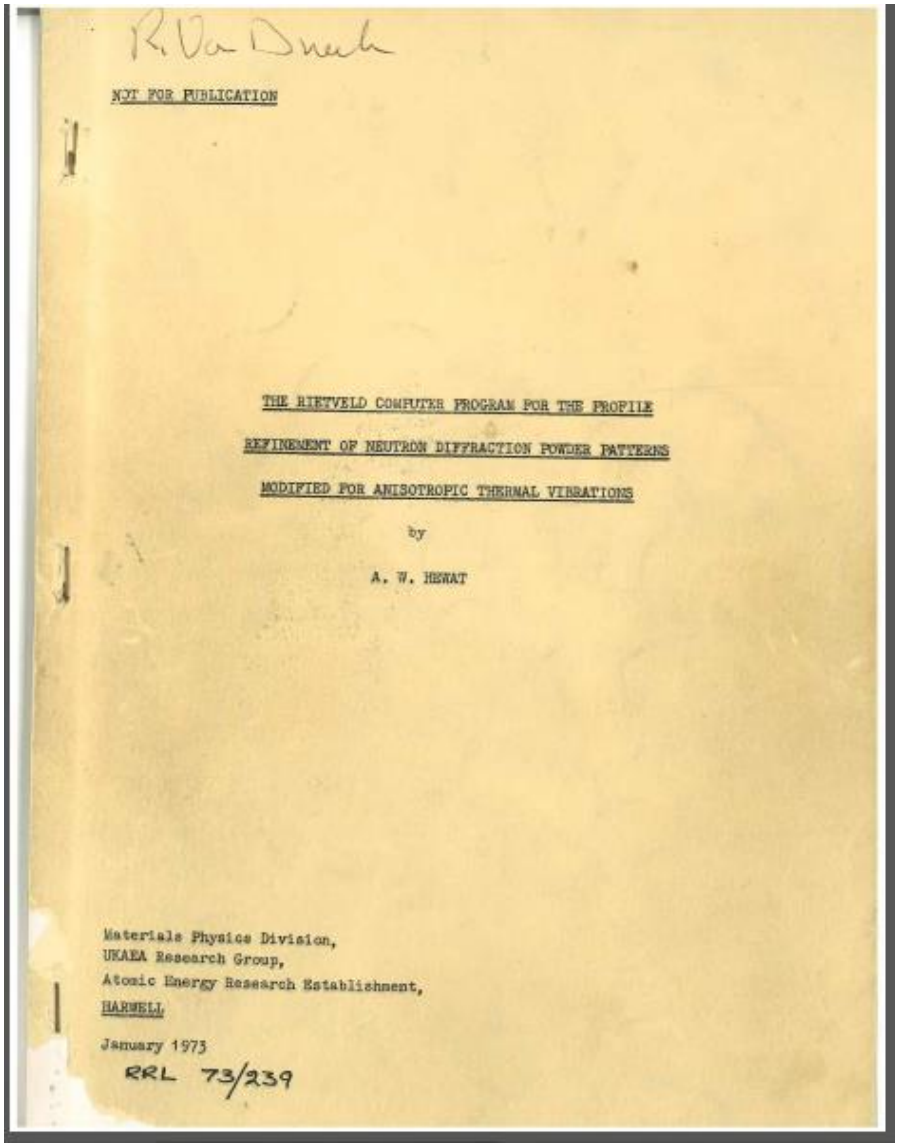
Fig. 2. A schematic diagram of a neutron powder diffractometer named PANDA which is installed at A.E.R.E. Harwell.

?



AKC & RBVD experiment: $2\Theta_m$ 92°,λ=1.57-1.61Å, 2-2.5x10^5 n/scm^2, scan @50m/deg

This is where it starts - Alan's Manual



R. Van Dreele

NOT FOR PUBLICATION

THE RIETVELD COMPUTER PROGRAM FOR THE PROFILE

REFINEMENT OF NEUTRON DIFFRACTION POWDER PATTERNS

MODIFIED FOR ANISOTROPIC THERMAL VIBRATIONS

by

A. W. HEWAT

Materials Physics Division,
UKAEA Research Group,
Atomic Energy Research Establishment,
HARWELL.

January 1973

RRL 73/239

Original with my annotations of additions to input file for my 1973 version

WHAT DID IT RUN ON?
CHILTON ICL1906A – AERE HARWELL, UK

256k 24bit words (~ 800kB)
OS: GeorgeIII & George4
Produced ~1MW of heat
About as much compute power as a old cell phone
Banbury Rd. Oxford
ICL1906a similar

WHAT DID WE DO WITH IT? – 3 DAY SCANS! LHe TEMPS.

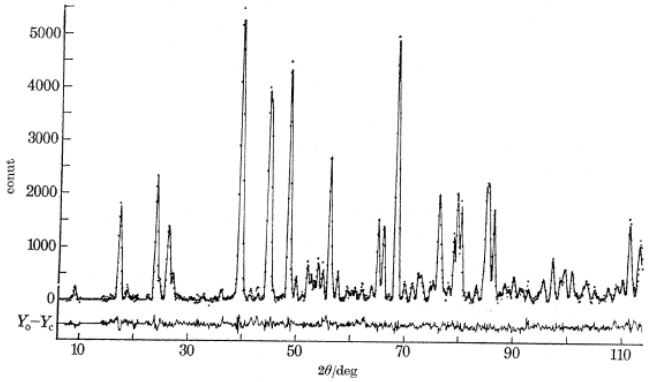
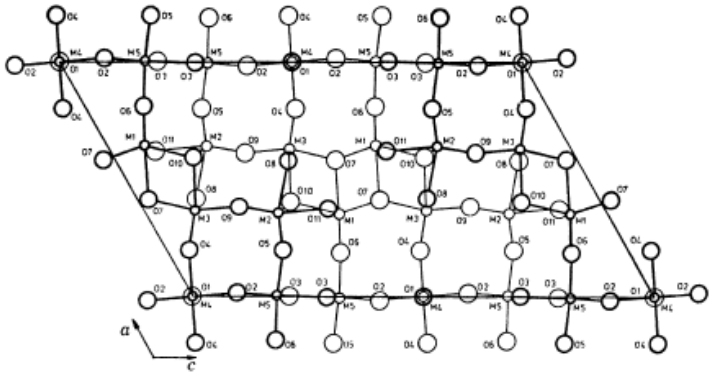


FIGURE 3. Neutron powder diffraction profile for $TiNb_2O_7$. Lines and points represent calculated and observed profiles, respectively. A difference curve is shown.



$TiNb_2O_7$;A2/m,a=11.89,b=3.80,c=20.37,β=120.2º
603 refl.,1077 data points

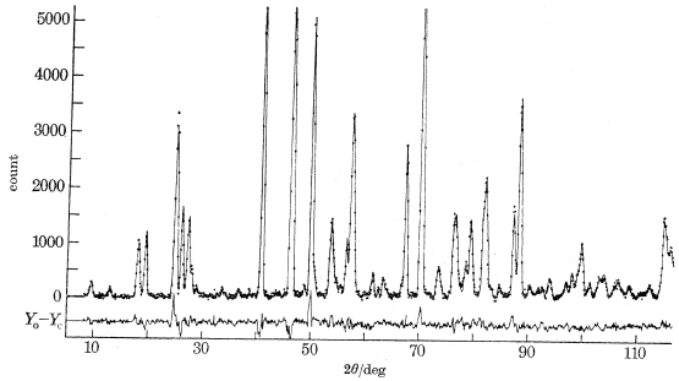
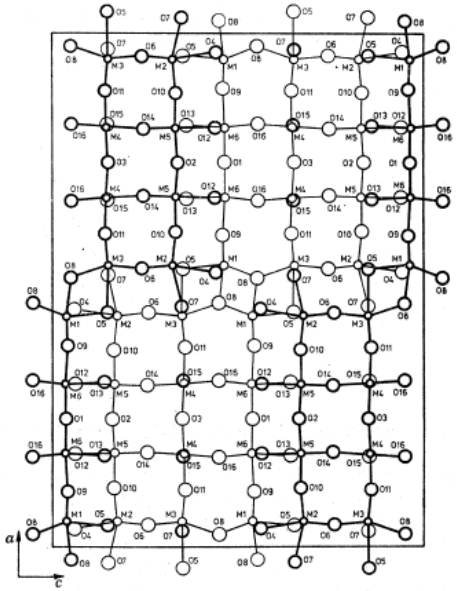


FIGURE 4. Neutron powder diffraction profile for ortho-$Ti_2Nb_{10}O_{29}$. Lines and points represent calculated and observed profiles, respectively. A difference curve is also shown.



o-$Ti_2Nb_{10}O_{29}$, Amma,
a=28.30,b=3.78,c=20.35
843 ref., 1116 data points

R. B. Von Dreele and A. K. Cheetham
Proc. R. Soc. Lond. A 1974 **338**, 311-326

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HUGO'S PROGRAM FAMILY TREE

pref & profls?
Hugo Rietveld – 1967, 1969 Petten

Algol & Fortran

pref & profls?
Alan Hewat – 1973 Harwell

add U_{ij} refinement
Chilton ICL 1906a

pref & profls?
Von Dreele – 1973 Oxford

Bigger structures & add X-rays (didn't work!)
Oxford ICL1906a

tofpref & tofls
Von Dreele – 1982 RAL

Neutron TOF, IPNS adopt.
by Rotella for VAX

DBW2.9 – 1981-94
DBWS-9006PC
Ga. Tech.
Young & Wiles

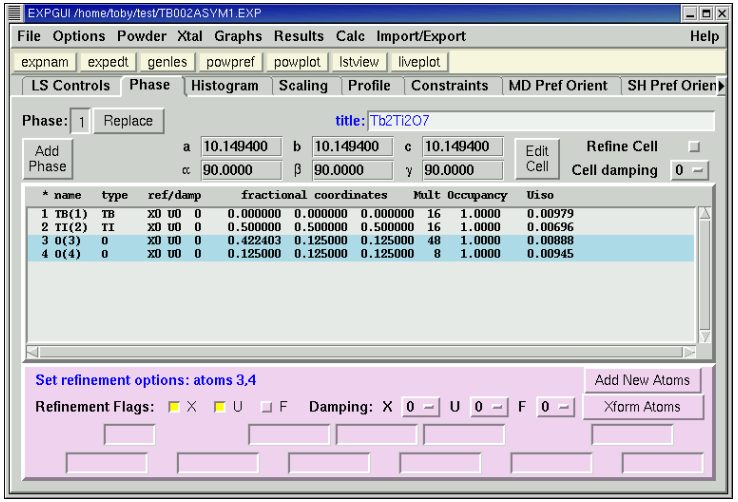
Original, x-ray profiles - Young &
Mackie Wiles rewrite – single pgm
Sakthivel revised; Run on IBM PC

LPHM – Hunter & Howard – Australia
FullProf – J. Rodriguez-Carvajal (now revised but same "pcr" file)
Phillips – instrument pkg.
– might be other descendants from DBW/DBWS

GENERAL STRUCTURE ANALYSIS SYSTEM GSAS

- 1982-1986 Initial development – for multidata TOF neutron powder & single crystal data – A.C. Larson & R.B. Von Dreele
- VAX Fortran; ISAM file structure; batch process calculations
- Multidata/multiphase – complex input file (experiment file)
- Menu-driven editor – EXPEDT - All about taming the control file
  - state of the art in 1980's
- Later EXPGUI (B.H. Toby) – more modern interface (1990's)
- Fundamental crystallographic calculations – refinement, Fourier maps, structure drawings & geometry (dist, angle, etc.) – no solution tools

```
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
EXPEDT data setup options:
 <?> - Type this help listing
 D   - Distance/angle calculation set up
 F   - Fourier calculation set up
 K n - Delete all but the last n history records
 L   - Least squares refinement set up
 P   - Powder data preparation
 R   - Review data in the experiment file
 S   - Single crystal data preparation
 X   - Exit from EXPEDT
```



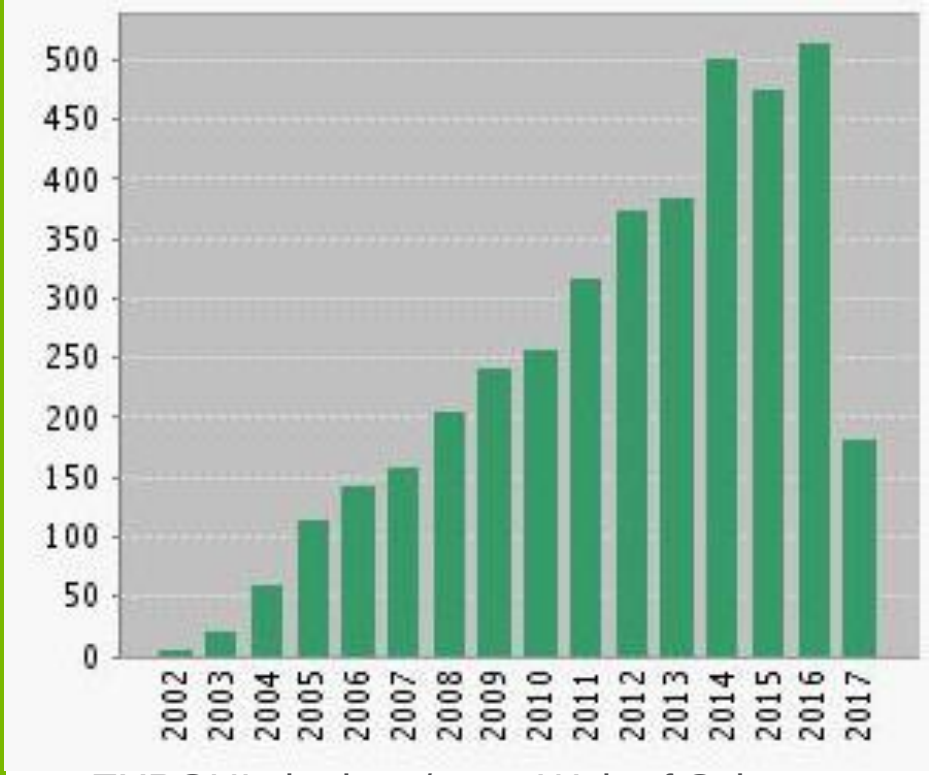
GSAS:

Extensions 1986-2004

- VAX → IRIX (ISAM emulator) → PC (→ OSX)
- CW neutron & X-ray (X-ray energy dispersive)
- New profile functions as developed (mustrain, size, strain, etc.)
- Texture – spherical harmonics
- Proteins (powders!)
- Easily scripted
- Documented – LAUR 86-748 “GSAS Manual”
- Widely accepted by community – by 2018 ~8000 citations to LAUR 86-748

- But: reached design limits on expansion (9 phases/99 histograms)
- Dated interface (both EXPEDT & EXPGUI) & steep learning curve
- Lacked powder indexing & structure solution tools
- Modern 2D detector data needed proper preprocessing
- Need new tool for modern crystallography→ GSAS-II

FOR DIFFRACTION ANALYSIS, GSAS & EXPGUI ARE WIDELY USED



EXPGUI citations/year; Web of Science

- **Need a new code, GSAS & EXPGUI**
  - **Hard to maintain**
  - **Impossible to expand**
  - **Didn't cover full scope**

Wide Range of Fields

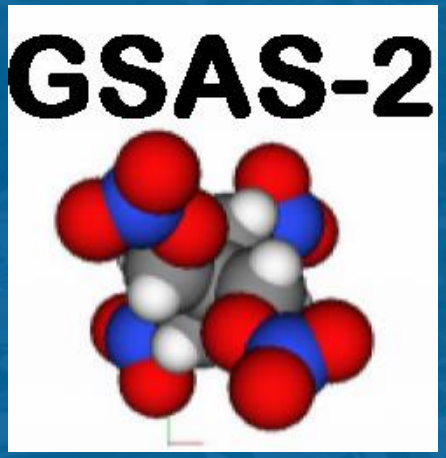
Web of Science Category	% of total
CHEMISTRY PHYSICAL	31.6
MATERIALS SCIENCE MULTIDISCIPLINARY	30.4
PHYSICS CONDENSED MATTER	15.7
CHEMISTRY INORGANIC NUCLEAR	14.2
CHEMISTRY MULTIDISCIPLINARY	12.1
PHYSICS APPLIED	8.6
NANOSCIENCE NANOTECHNOLOGY	7.7
CRYSTALLOGRAPHY	6.6
MINERALOGY	6.4
METALLURGY METALLURGICAL ENGINEERING	4.9
ELECTROCHEMISTRY	4.9
GEOCHEMISTRY GEOPHYSICS	4.7
ENERGY FUELS	4.5
MATERIALS SCIENCE CERAMICS	4.0
CHEMISTRY APPLIED	2.3
PHYSICS ATOMIC MOLECULAR CHEMICAL	2.0
PHYSICS MULTIDISCIPLINARY	2.0

Highly utilized in DOE/SUF

Argonne	DE-AC02-06CH11357	11.1%
Brookhaven	DE-AC02-98CH10886	3.5%
Lawrence Berkeley	DE-AC02-05CH11231	1.6%
HPCAT/DOE-NNSA	DE-NA0001974	1.5%
GSECARS/DOE-Geo	DE-AC52-06NA25396	1.4%
HPCAT/DOE-BES	DE-FG02-99ER45775	1.4%
National Basic Research Program of China	2011CB808200	1.3%

20%

GSAS-II



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

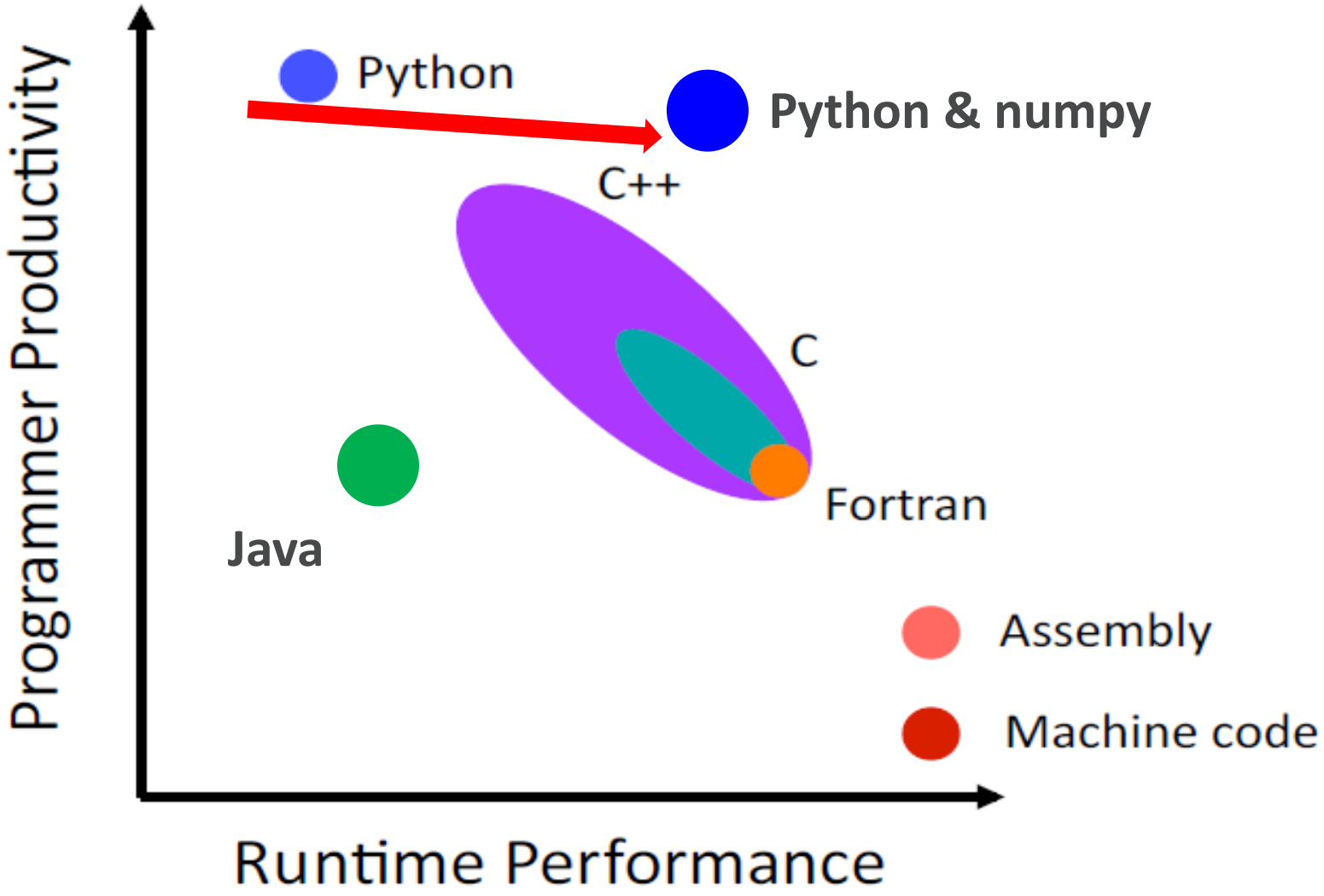
GSAS-II is intended to more than replace GSAS & EXPGUI with a new, modern, extensible, and *open-source* crystallographic analysis

- 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 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!)



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

ANOTHER EXAMPLE – OMIT MAP CALCULATIONS

OMIT map – a kind of Fourier map (T.N. Bhat, J. Appl. Cryst. 21, 29-281, 1988)

Usefulness:

- Least biased electron density map for rebuilding structure (mostly for macromolecular structures)

Algorithm:

- Compute density from structure factors & phases
- Unit cell divided into boxes
- In turn – flatten each box, do IFFT to make phases, compute new density & save box (toss the rest).
- Finally assemble all boxes into new “OMIT” map.

Coding:

- Old CCP4 code – covers 114 pages of printout, ~ 80 lines/page (~9000 lines of Fortran & some c)! Not readily available for nonmacro problems
- GSAS-II python – computed in 65 lines & there is another 80 lines to export it in CCP4 format. Universal for all crystal structures.

Which is easier to understand and maintain?

New Hessian LSQ - modified Levenberg/Marquardt-SVD Algorithm

Steps:

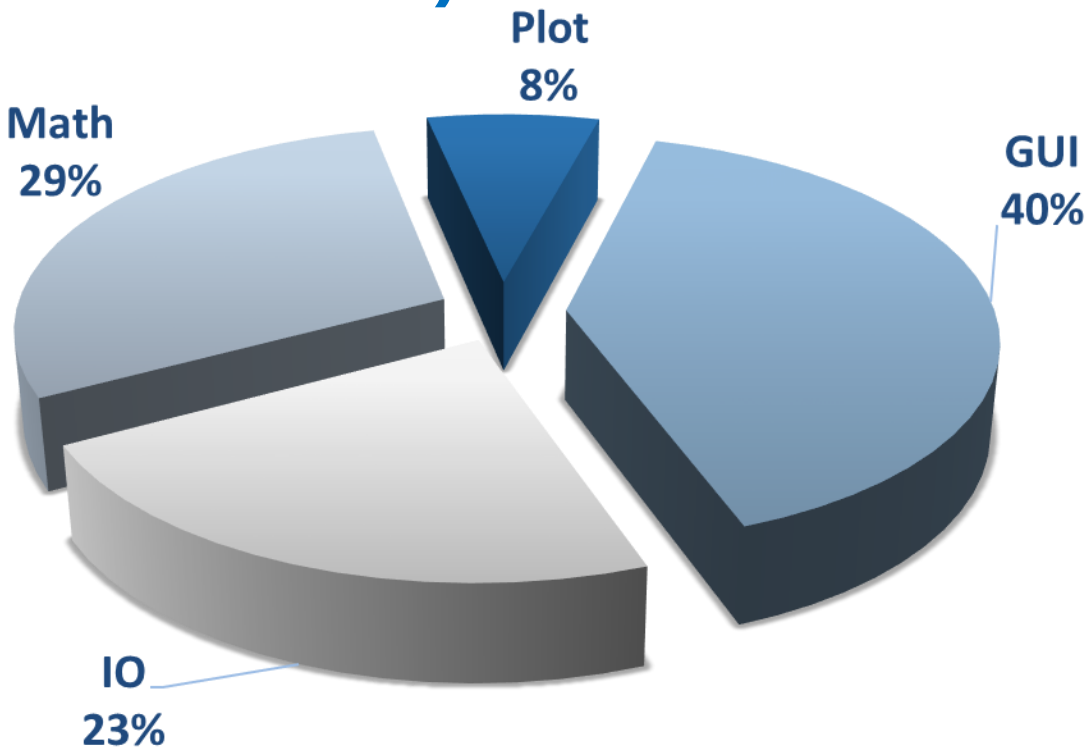
1. Compute $A_{ij} = \sum w \frac{\partial I_c}{\partial p_i} \frac{\partial I_c}{\partial p_j}$ **SLOW step**
2. Normalize $A'_{ij} = A_{ij} / \sqrt{A_{ii} A_{jj}}$
3. compute $\chi^2(p)$
4. Select λ (=0.001)
5. Modify $A''_{ii} = A'_{ii}(1+\lambda)$
6. Make SVD inversion of A"
7. Solve for δp (unnormalized!)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

FAST steps

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

NB^2: this thing is exceedingly robust

GSAS-II CODE DISTRIBUTION (LINES OF CODE & COMMENTS)

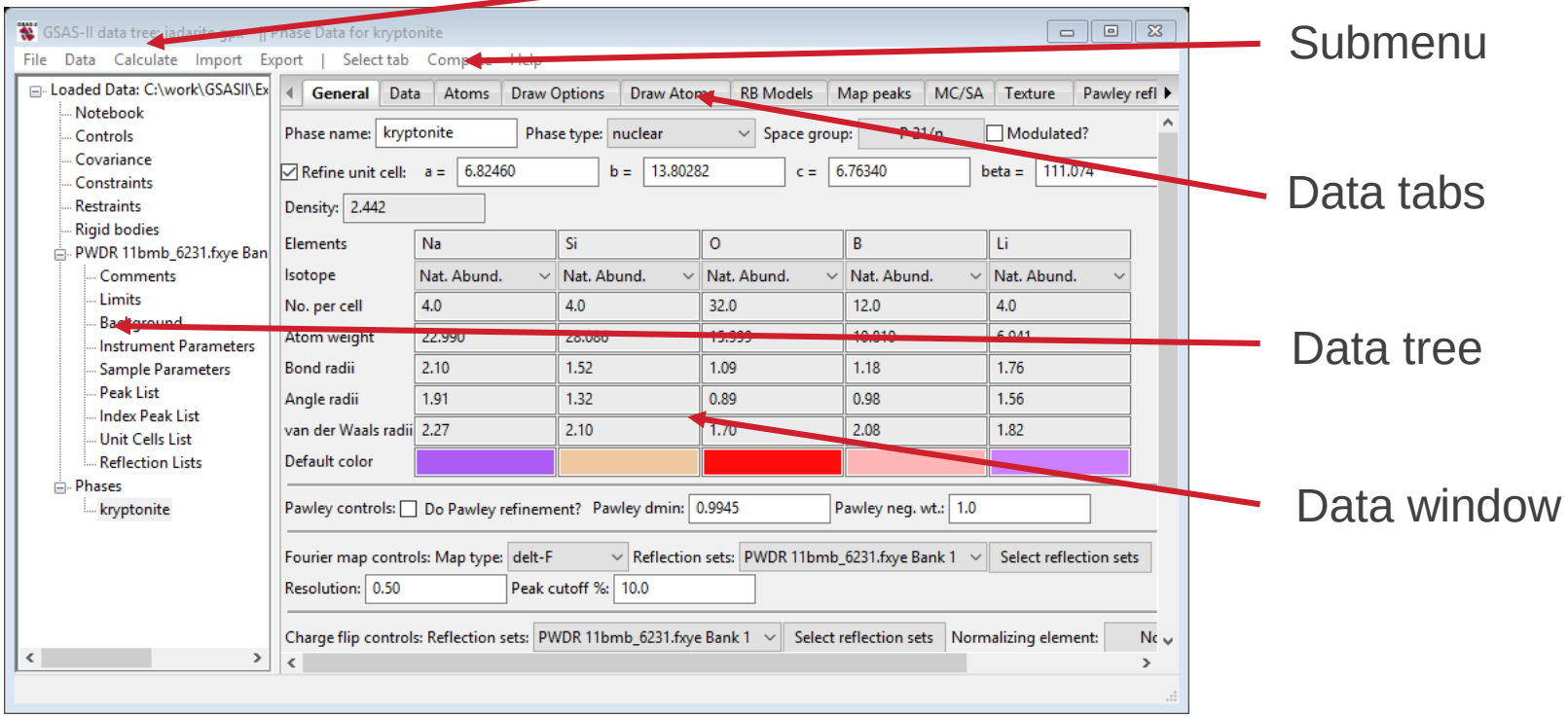


Approx. 100,000 lines of python in GSAS-II = 3.3Mb + 11Mb binaries
vs 125,000 lines of Fortran in GSAS (16Mb in gsaskit)
NB: 29 GSAS-II tutorials are ~0.6Gb!

GSAS-II DEVELOPMENT - PYTHON

Started Nov. 2008 – 1st usable version late 2011- early 2012

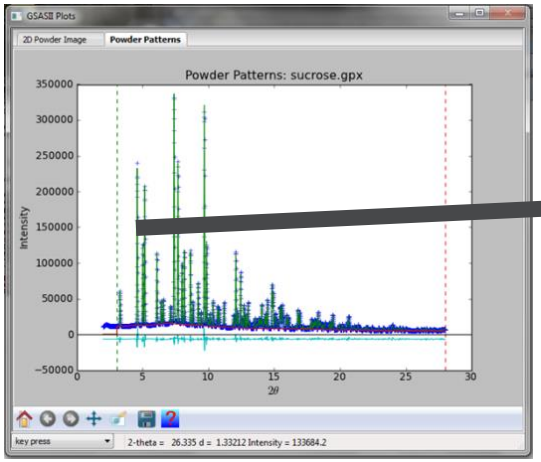
GSAS-II: modern GUI – 2 frames + console

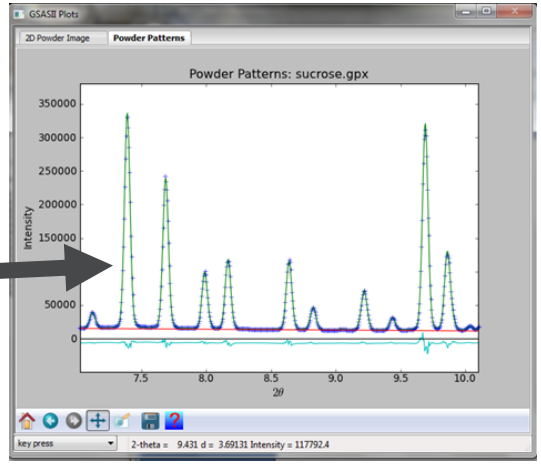


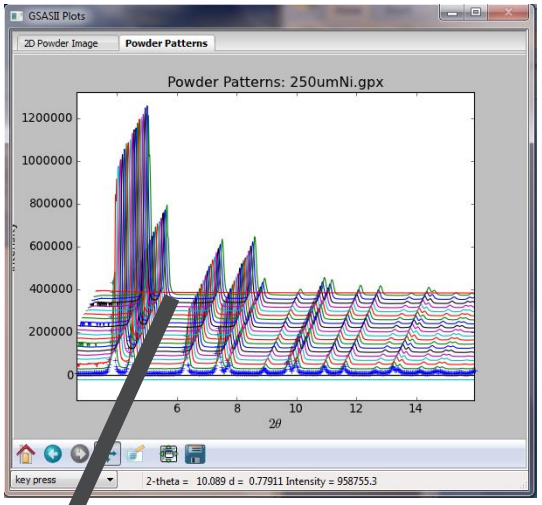
Plot & console in separate frames

THE PLOTS - ADVANCED VISUALIZATION

Powder profile – easy zoom

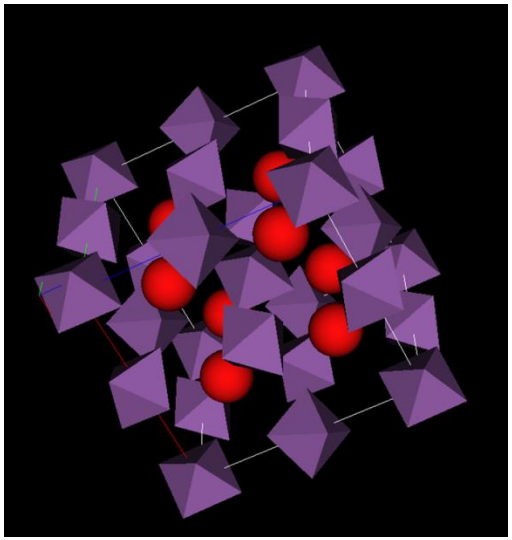




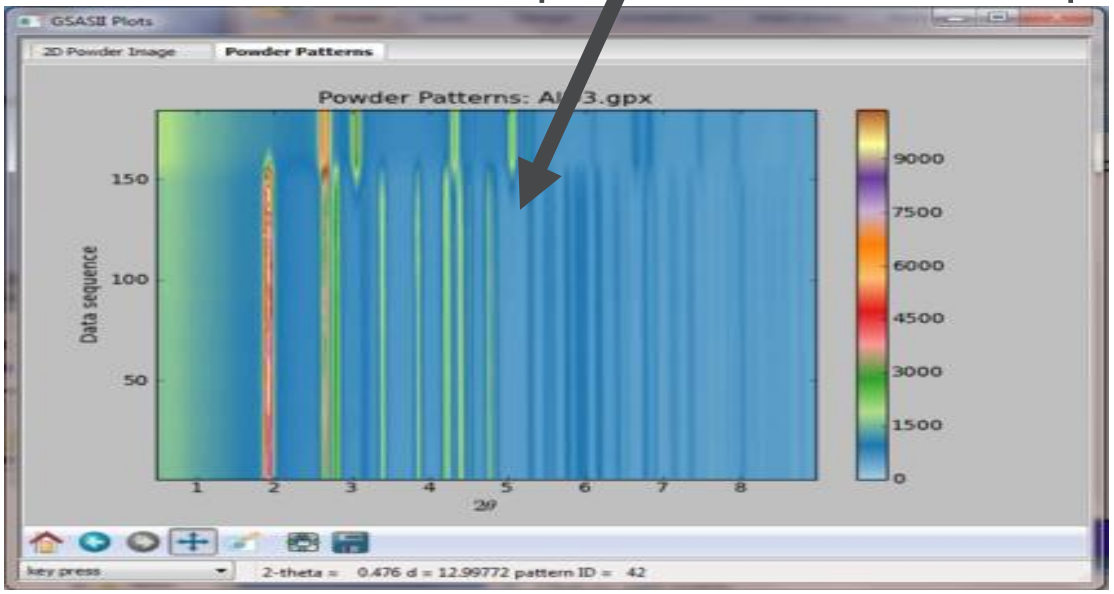


Contour plot

Waterfall plot

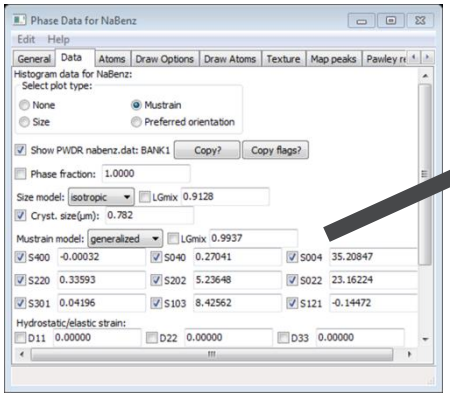


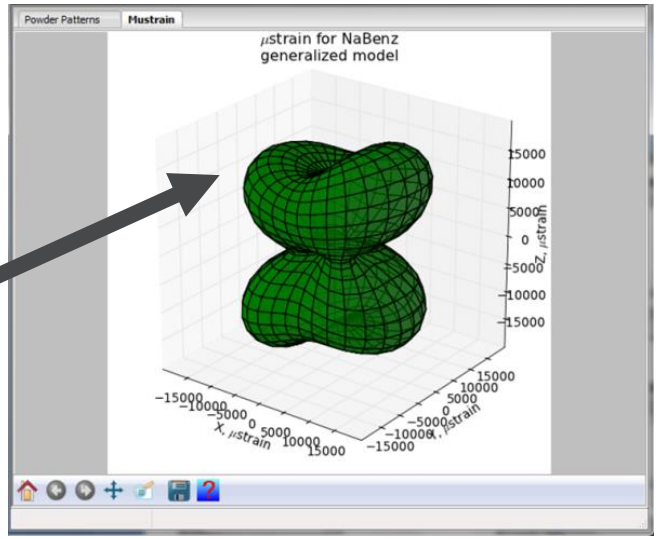
Structure drawing



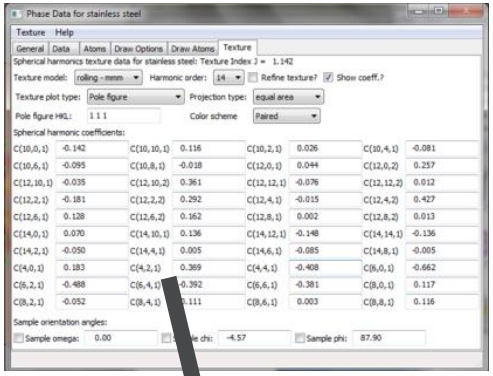
MORE PLOTS IN GSAS-II: NUMBERS AS PICTURES

μstrain surface

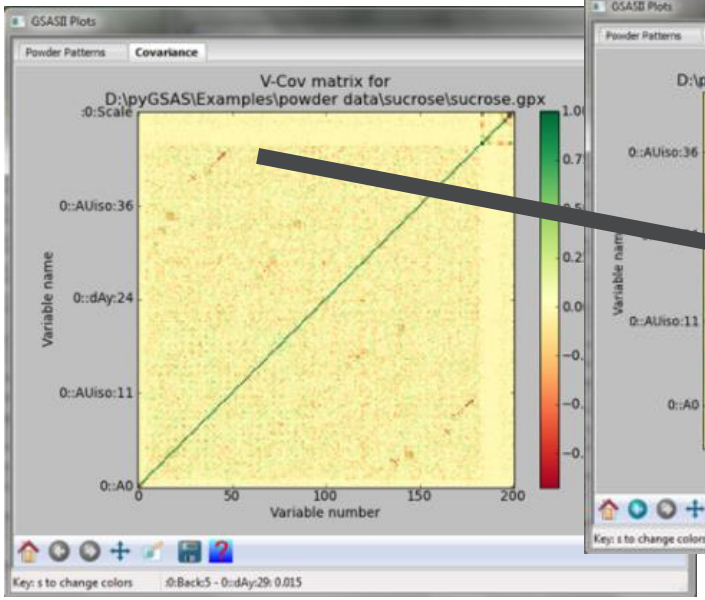


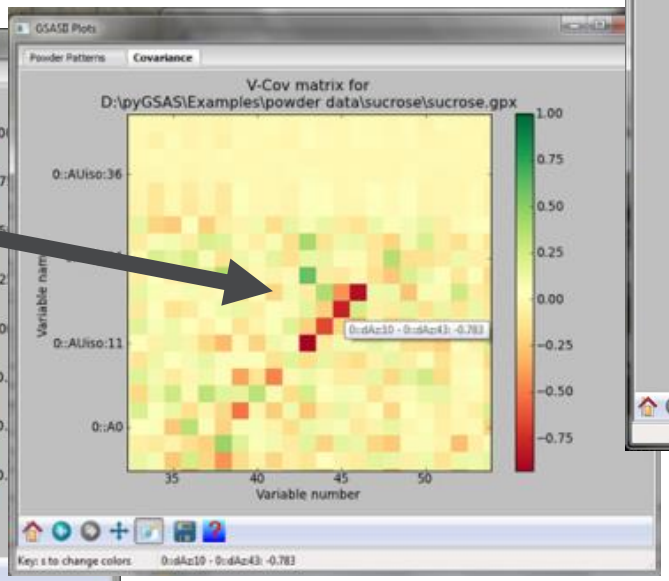


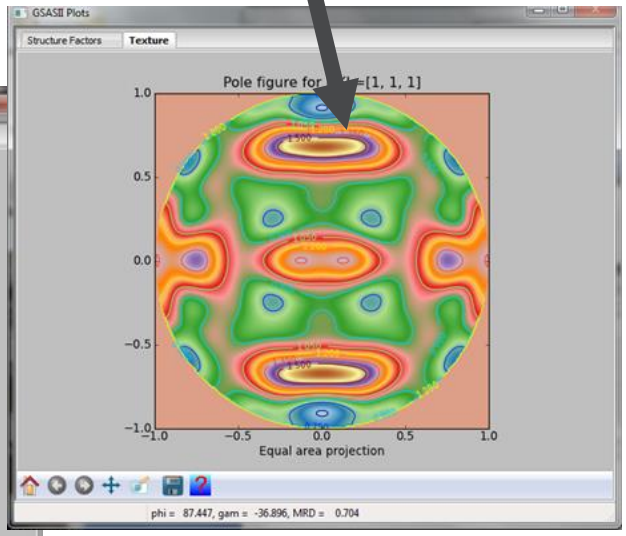
Texture – sph. harmonics



v-cov matrix



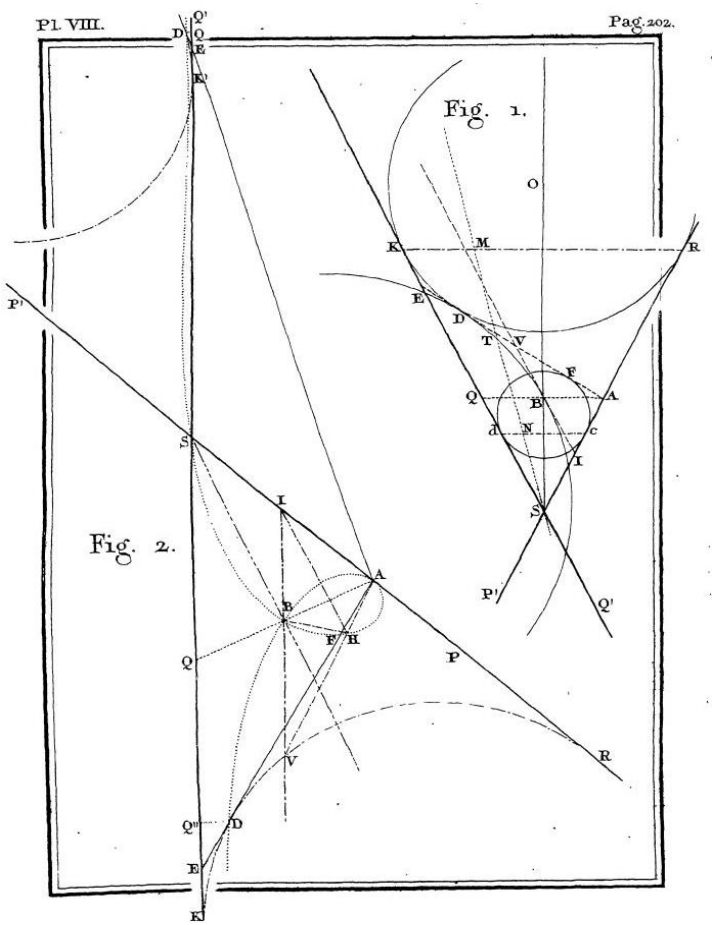




2D IMAGE CALIBRATION & INTEGRATION

Where is the incident beam on the detector?

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



Taken from Dandelin's original paper; p.202
Fig. 1: Shows the 2 spheres in contact with plane EA

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

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

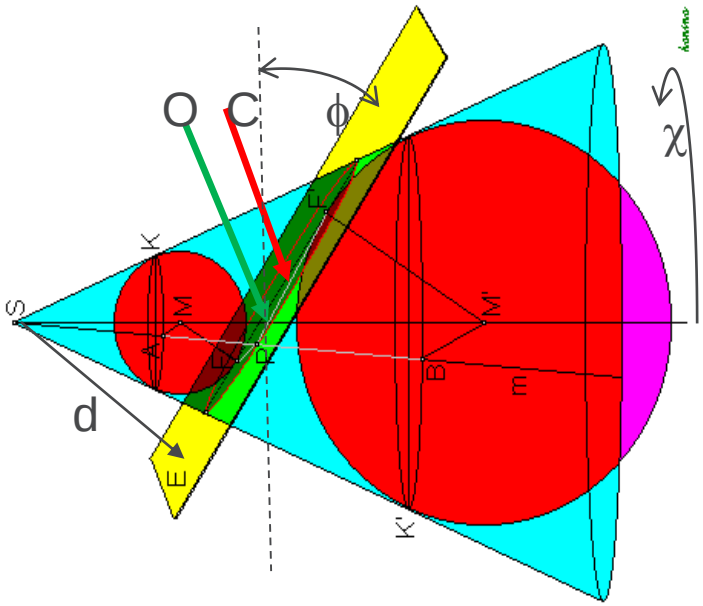
This is not something new!

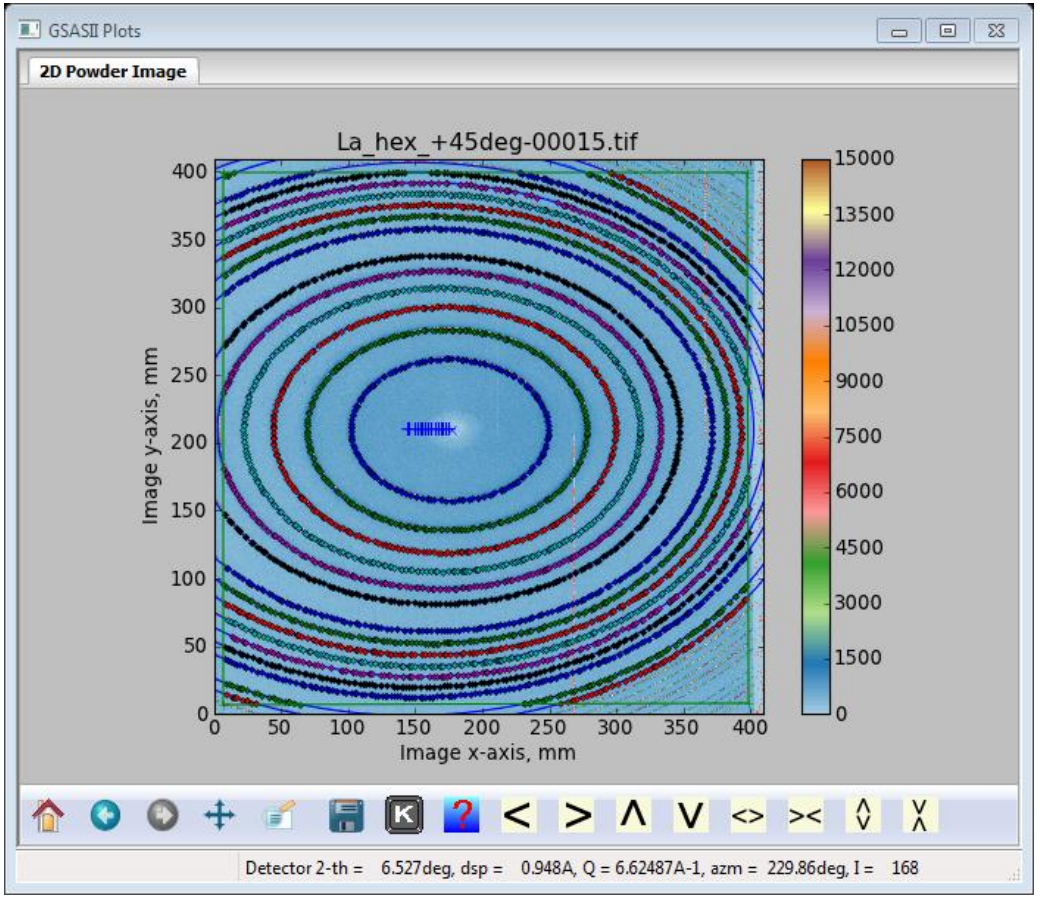
Dandelin sphere construction used in GSAS-II for image plate orientation calibration

2D IMAGE CALIBRATION (REPLACE FIT2D)

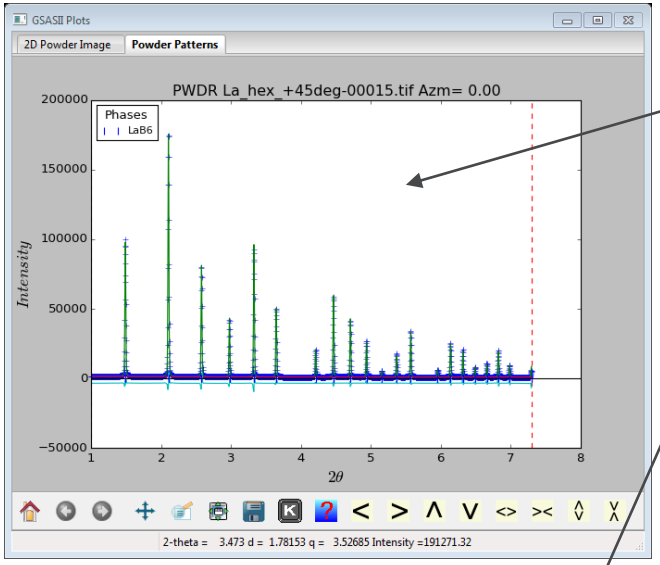
Correct calibration for tilt

- Dandelin sphere construction (1822)

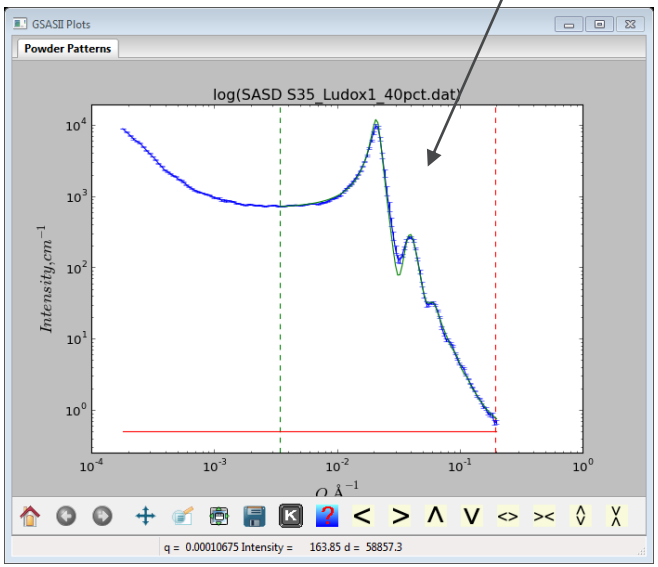


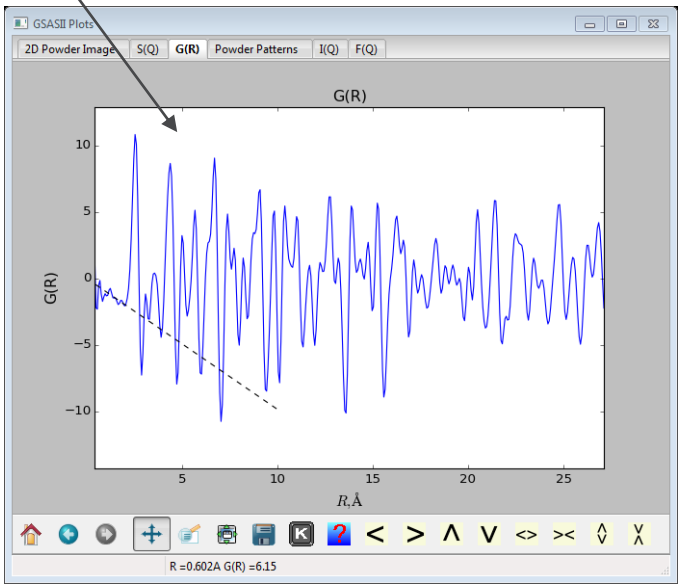


AFTER IMAGE PROCESSING IN GSAS-II – STAY IN PROJECT FILE



- Powder diffraction analysis
- Small angle data analysis
- PDF calculation – can be automatic with integration





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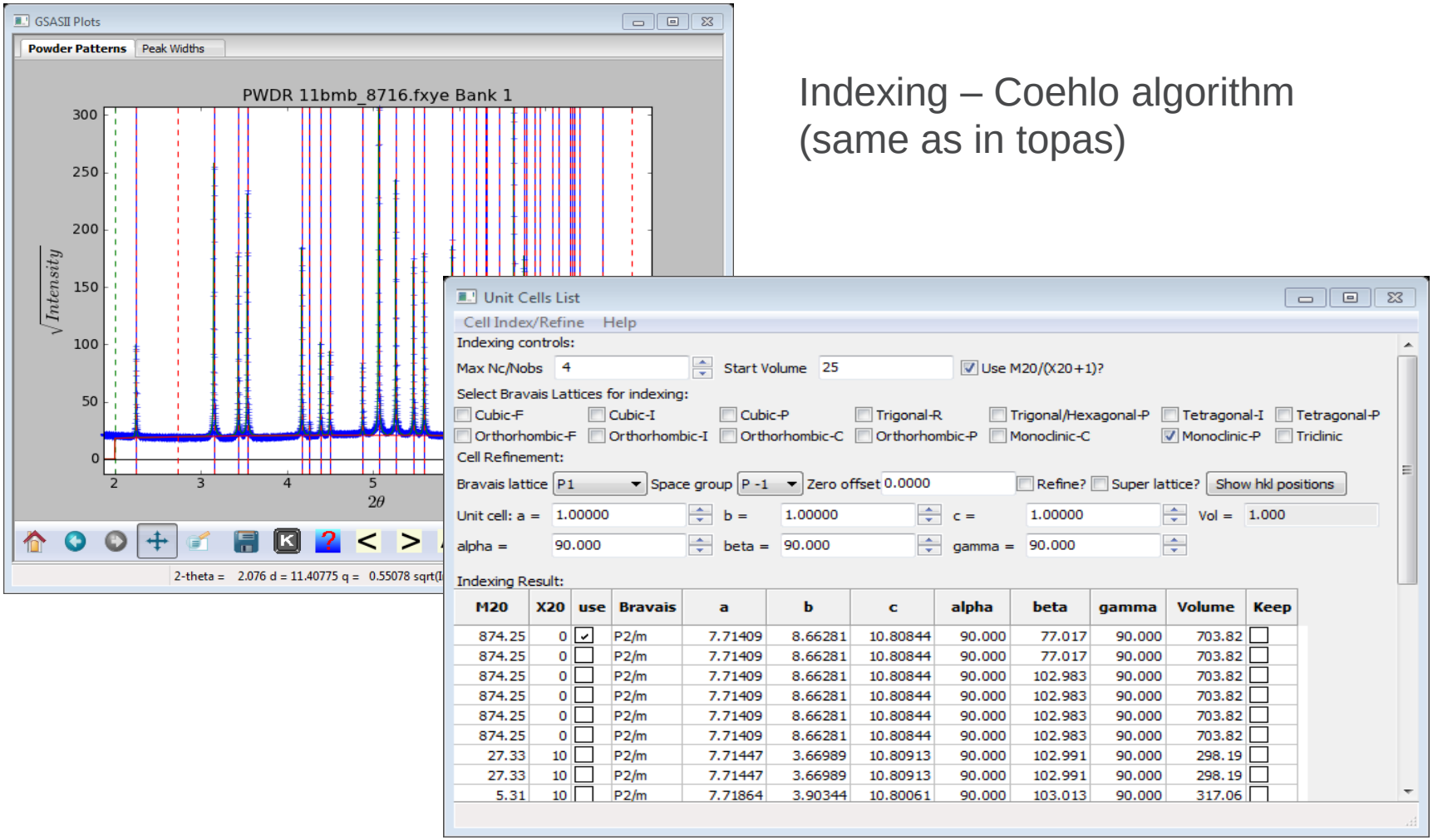
PEAK PICKING, FITTING & INDEXING

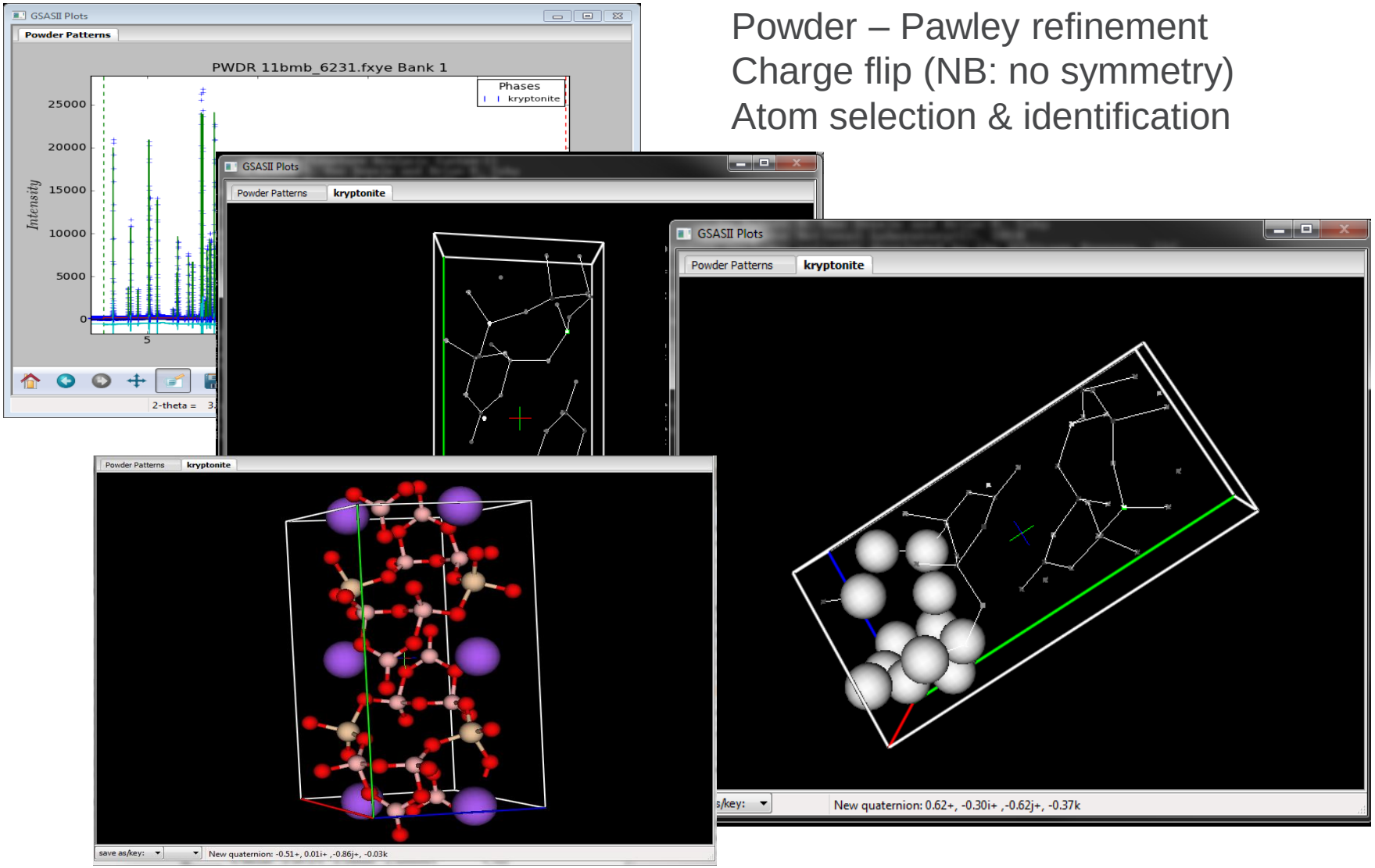


M20	X20	use	Bravais	a	b	c	alpha	beta	gamma	Volume	Keep
874.25	0	✓	P2/m	7.71409	8.66281	10.80844	90.000	77.017	90.000	703.82	
874.25	0		P2/m	7.71409	8.66281	10.80844	90.000	77.017	90.000	703.82	
874.25	0		P2/m	7.71409	8.66281	10.80844	90.000	102.983	90.000	703.82	
874.25	0		P2/m	7.71409	8.66281	10.80844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

Indexing – Coehlo algorithm (same as in topas)

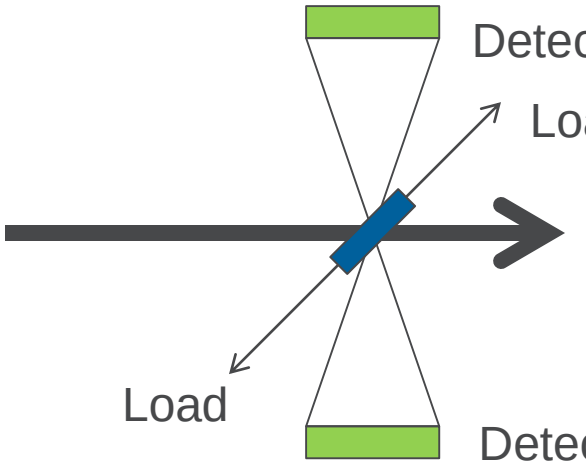
STRUCTURE SOLUTION

Charge Flipping 3D & 4D



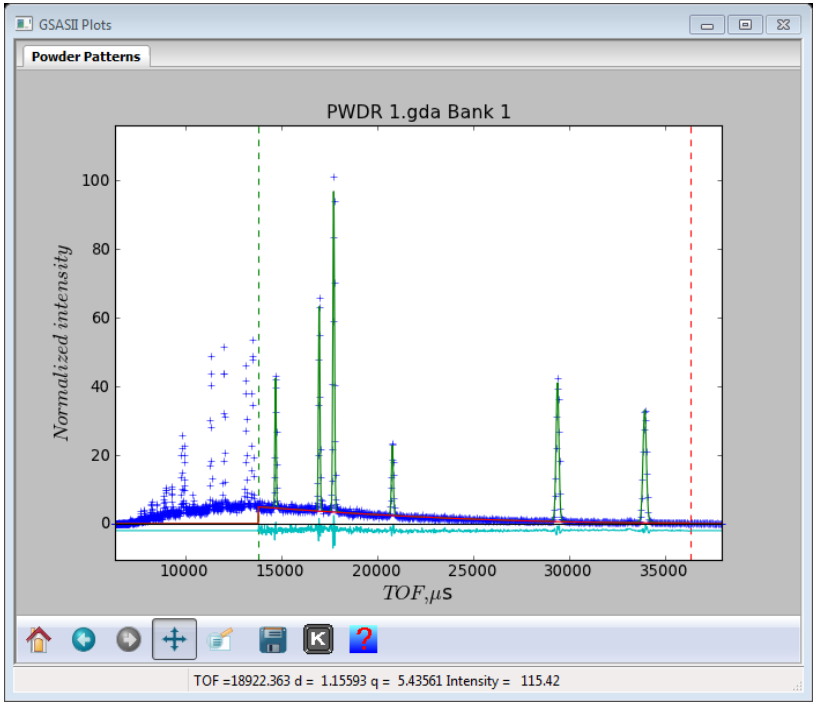
Powder – Pawley refinement
Charge flip (NB: no symmetry)
Atom selection & identification

SEQUENTIAL PEAK FITTING – OBSERVATION OF STRAIN – SNS VULCAN DIFFRACTOMETER



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

One pattern –
single peak fits: 6 lines
Follow vs time & loading



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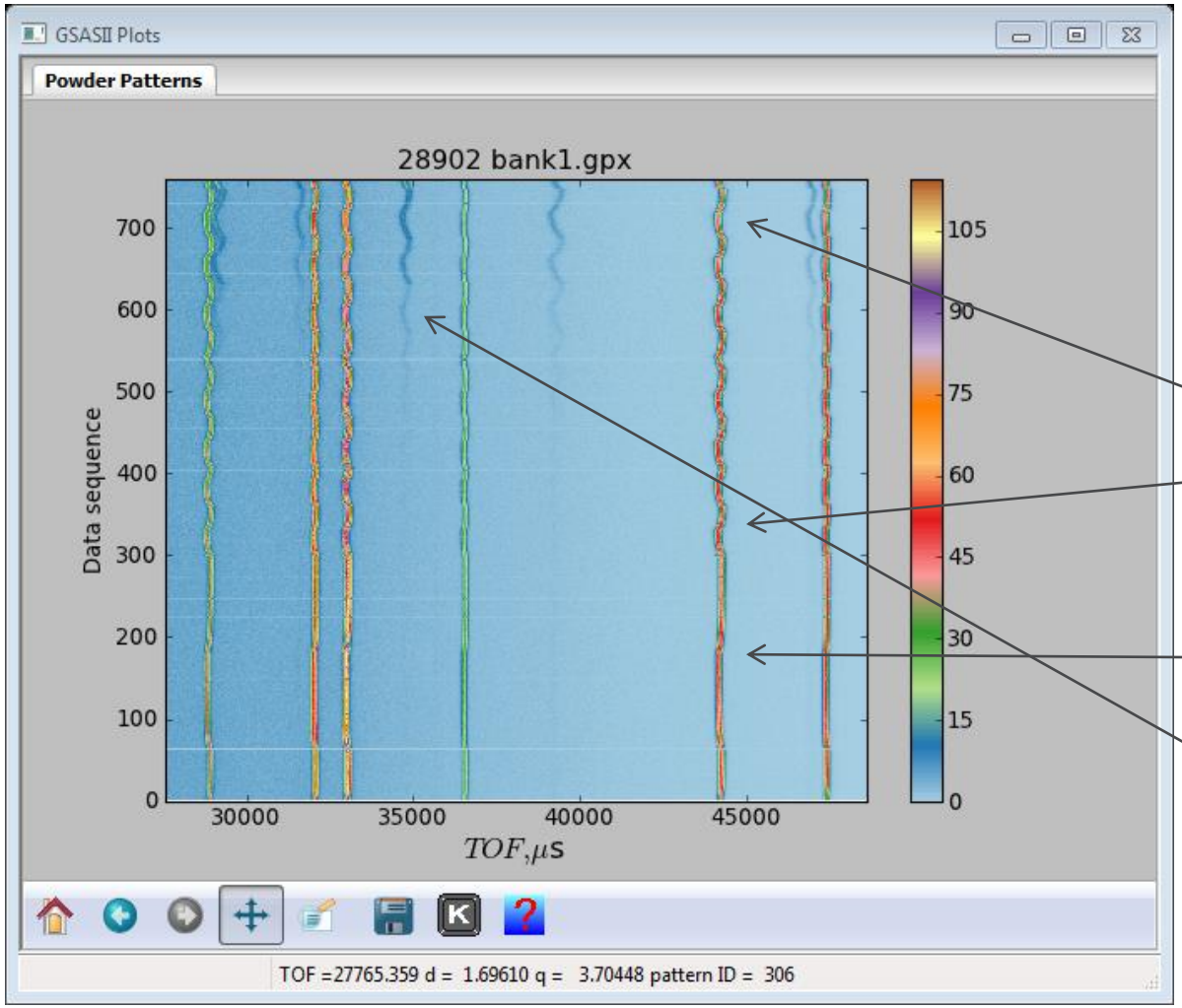
~800 TOF POWDER PATTERNS IN GSAS-II



8-9 fast load cycles

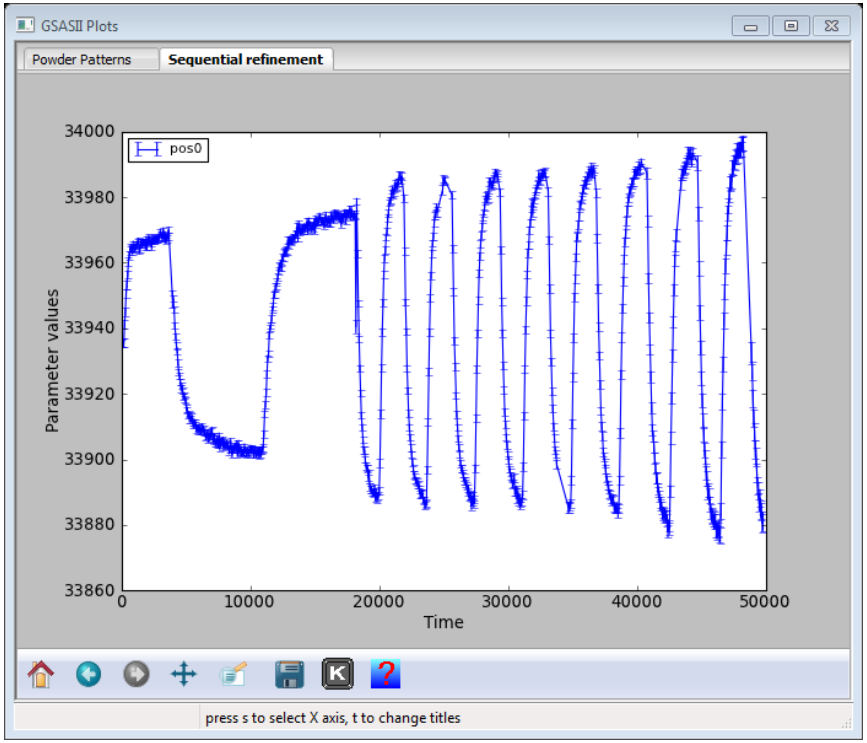
1 Slow load cycle

2nd phase appears (ferrite - BCC) Main peaks – austenite - FCC

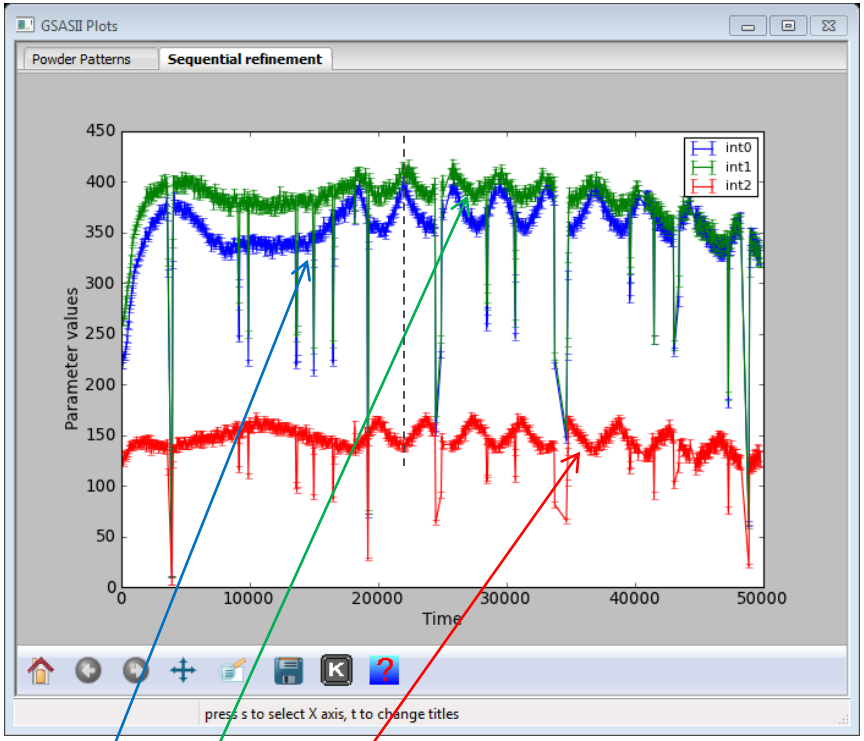
Do sequential peak fitting – 6 peaks + background
~1.5 min to complete!

SOME SEQUENTIAL PEAK FIT RESULTS

Lots to explore here – all within GSAS-II



Austenite 111 position



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

INCOMMENSURATE STRUCTURES IN GSAS-II

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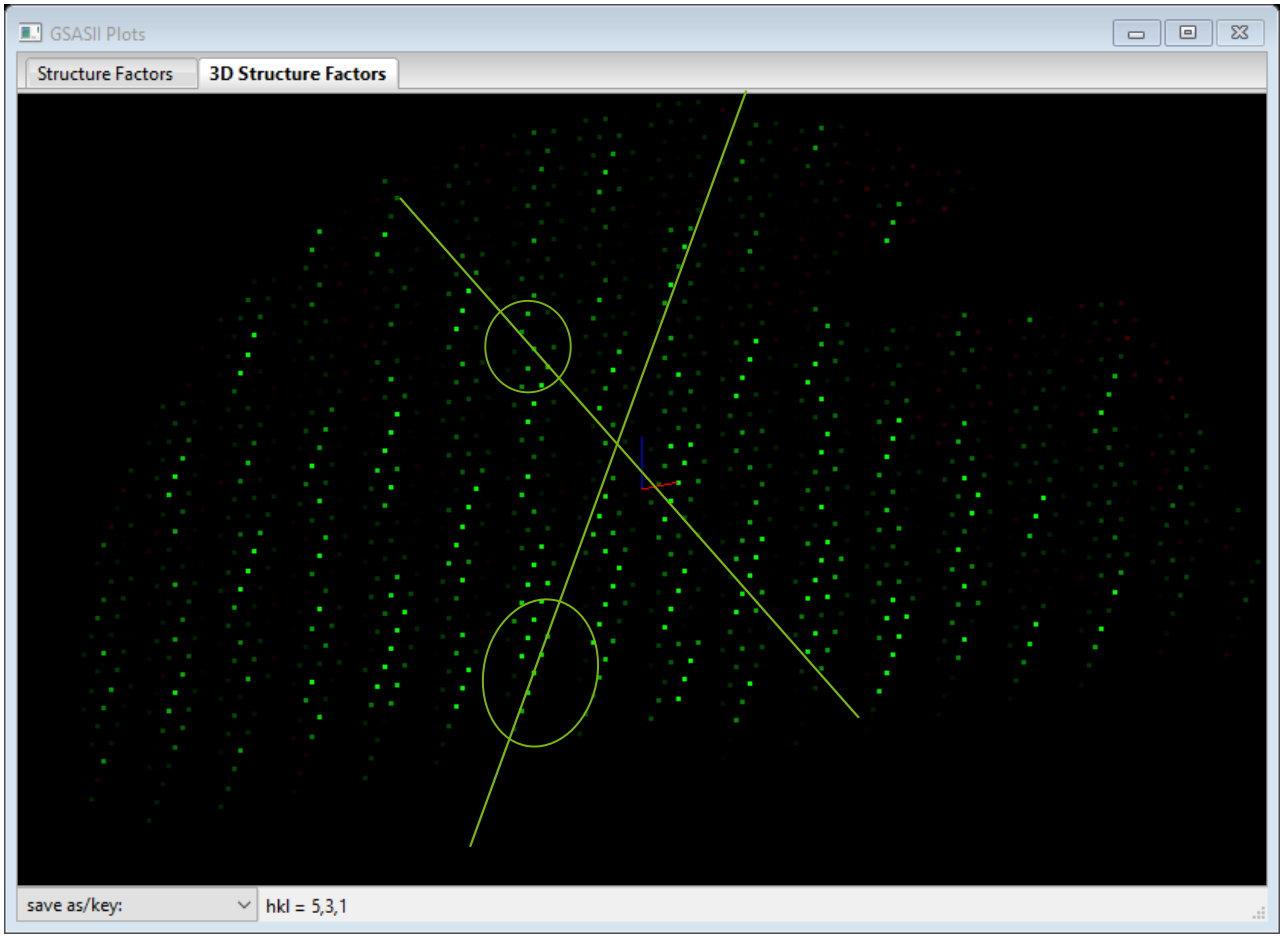
INCOMMENSURATE STRUCTURES N GSAS-II

Book: “Incommensurate Crystallography” S. van Smaalen



H=G+mq

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

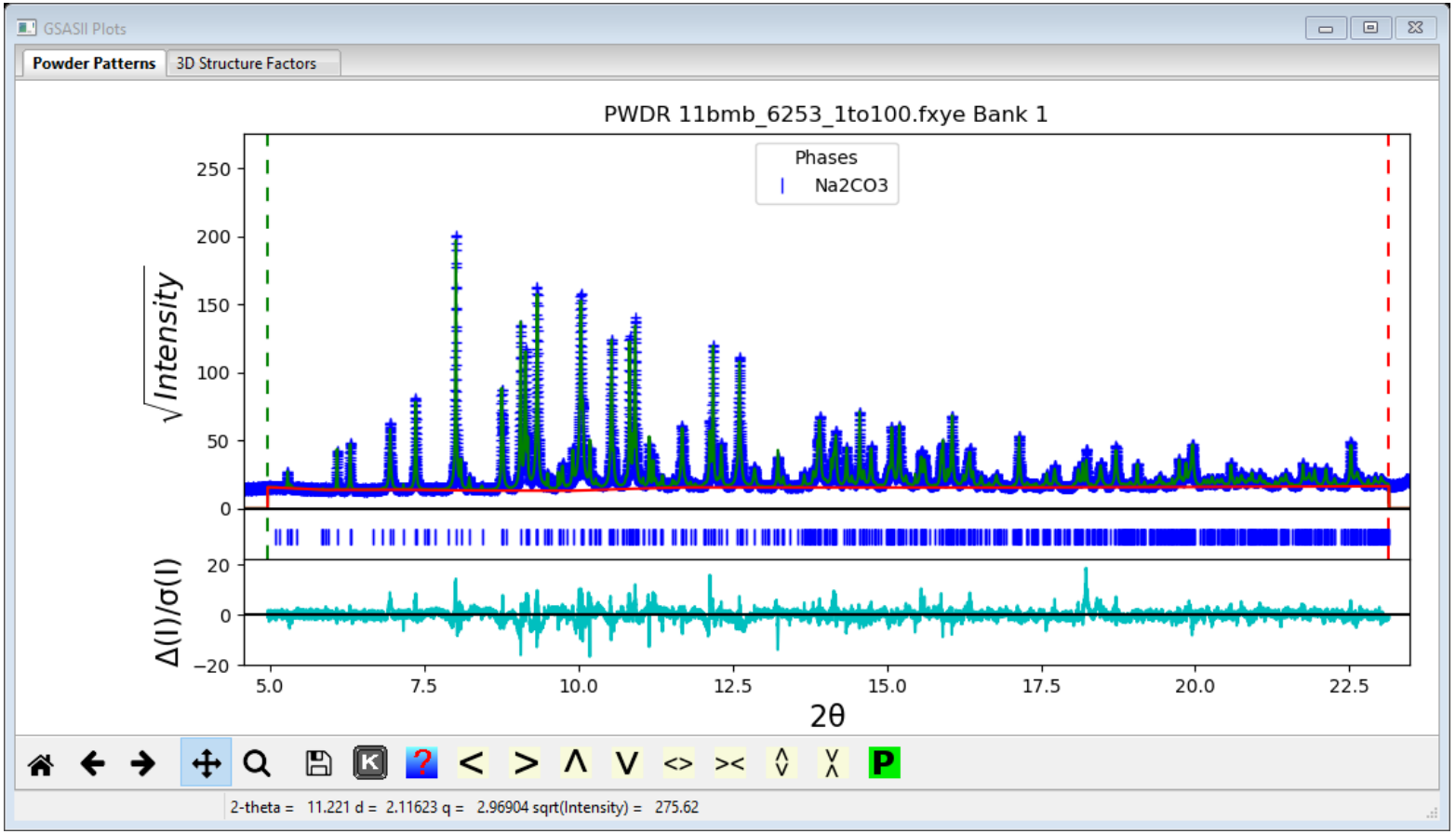
For Na_2CO_3
q= 0.183,0,.319

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

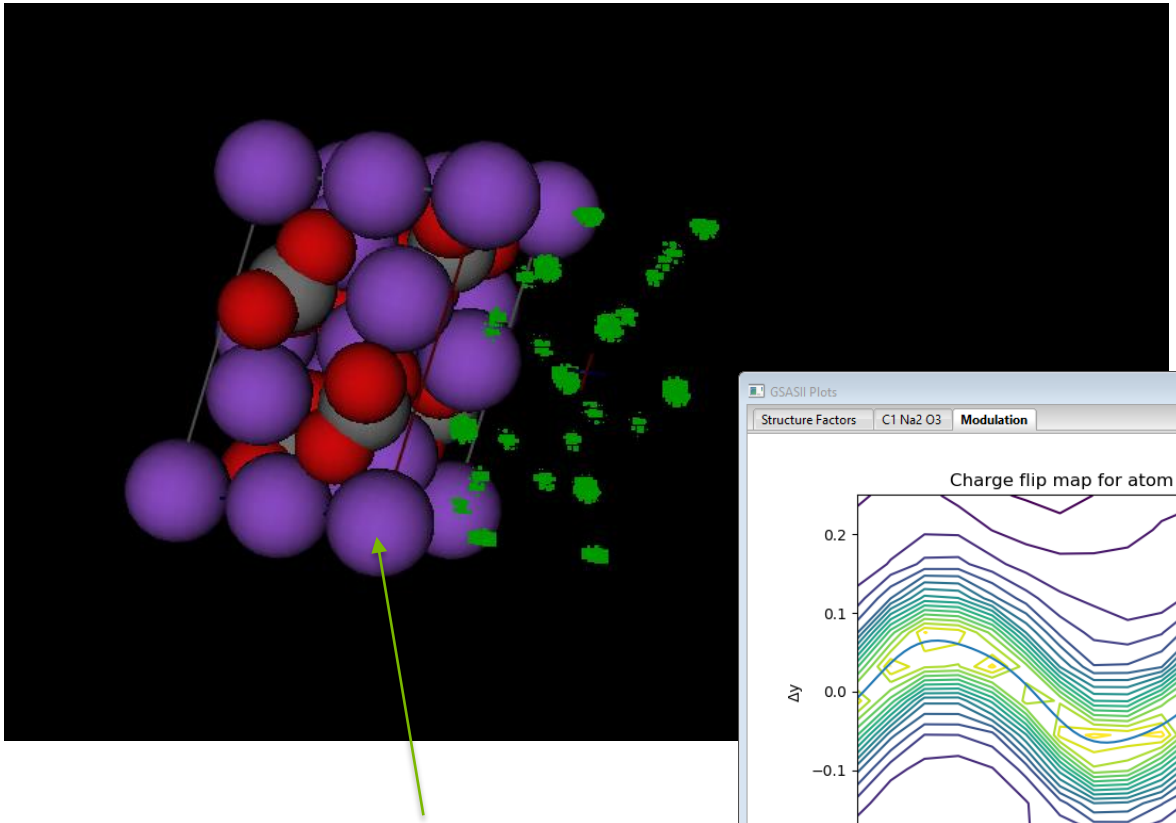
Na_2CO_3 – 11BM @ APS room temp.

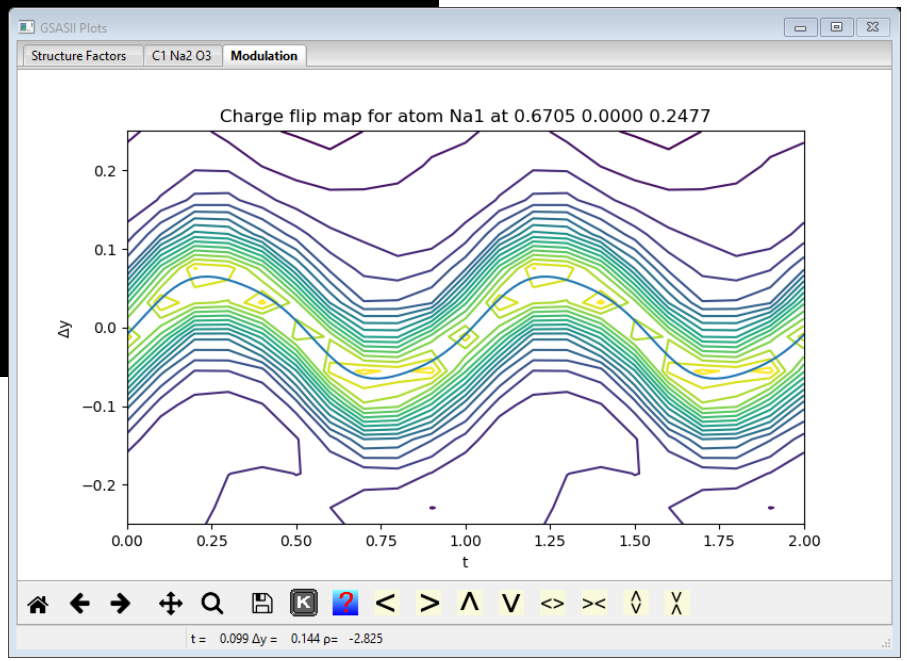


Includes m=-2,-1,1,2 superlattice reflections; Rietveld refinement includes 1st & 2nd order harmonics on position depending on atom

INCOMMENSURATE STRUCTURE SOLUTION

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

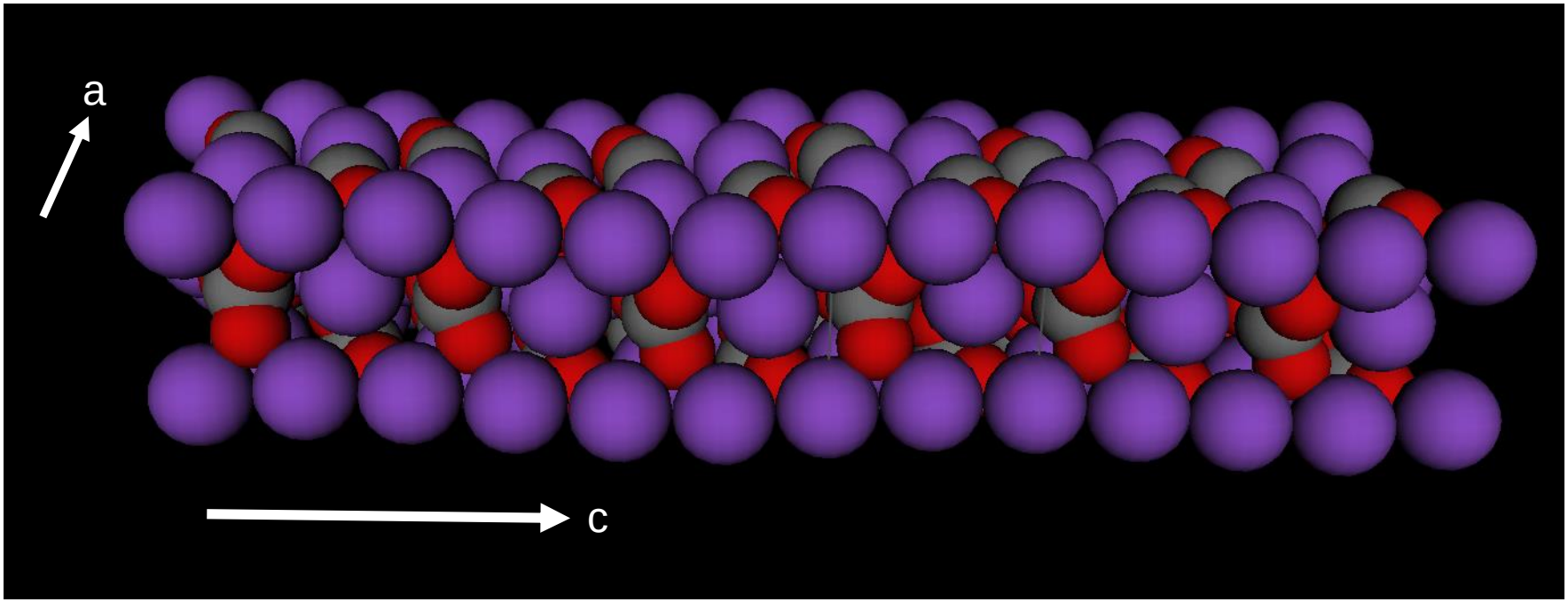




Modulation of atom positions (Na1-y)
Fit function – fourier series in tau

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

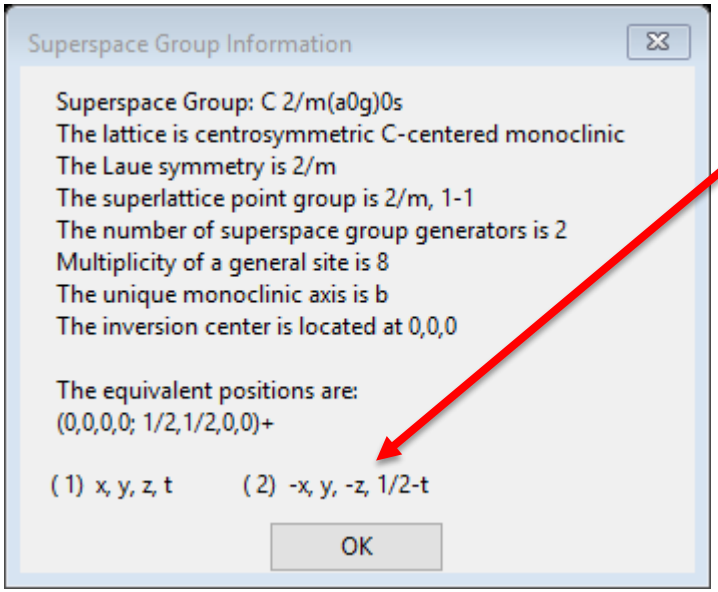
e.g. Na_2CO_3 – C2/m(α0γ)os

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 STRUCTURES IN GSAS-II

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MAGNETISM – SOME BASICS

Assumptions: unpolarized neutrons, ideal powder (no texture), elastic scattering – no cross term; sum intensities

Nuclear structure factor Magnetic structure factor

$$\left|F_{\mathbf{h}}\right|^2 = \left|\sum_n b_n \exp\left\{2\pi i\left(\mathbf{h}\cdot\mathbf{r}\right)\right\}\right|^2 + \left|\sum_m \mathbf{q}_m p_m \exp\left\{2\pi i\left(\mathbf{h}\cdot\mathbf{r}\right)\right\}\right|^2$$

All atoms Magnetic ions only

GSAS-II: 2 phases
1) “chemical” nuclear – all atoms
2) only magnetic ions

Need not be same lattice/space group, but describe same atomic arrangement for magnetic ions.

STRUCTURE FACTOR – POWDERS & NO POLARIZATION

The p's & q's? (after Bacon, 1975)

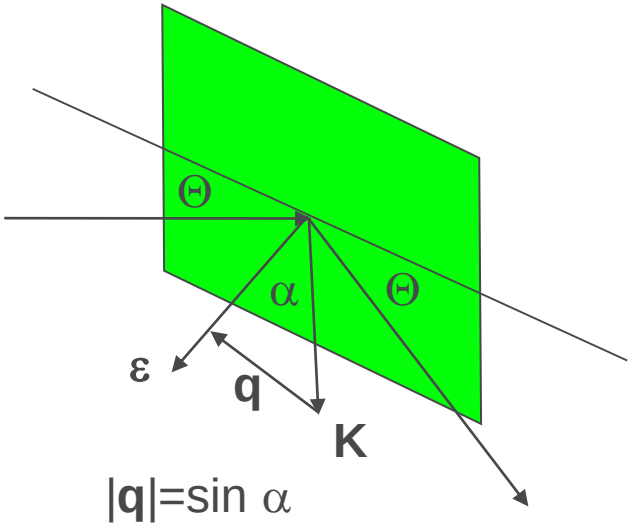
$$\mathbf{q}_m = \boldsymbol{\varepsilon}_\mathbf{h}(\boldsymbol{\varepsilon}_\mathbf{h} \cdot \mathbf{K}_m) - \mathbf{K}_m$$

$$p_m = \left(e^2\gamma / m_N c^2 \right) S_m f_m$$

$\boldsymbol{\varepsilon}_\mathbf{h}$ – *unit vector* || **h** – diffraction vector
$\mathbf{K}_m$ – *unit vector* || *magnetic moment on atom m*
$\therefore$ **q** *small for* **h** || ***K*** *& large for* **h** $\perp$ **K**

0.539×10^{-12}cm – similar to b_n
e – electron charge
γ *– neutron magnetic moment*
m_N *– neutron mass*
c – speed of light

S – magnetic moment (Bohr magnetons)
f – 1-electron magnetic form factor



|**q**|=sin α

MAGNETIC FORM FACTOR - f_m

Fourier transform of unpaired e$^-$ density:
valence e$^-$; outer shell
Sharp fall off with Q (small d, etc.)

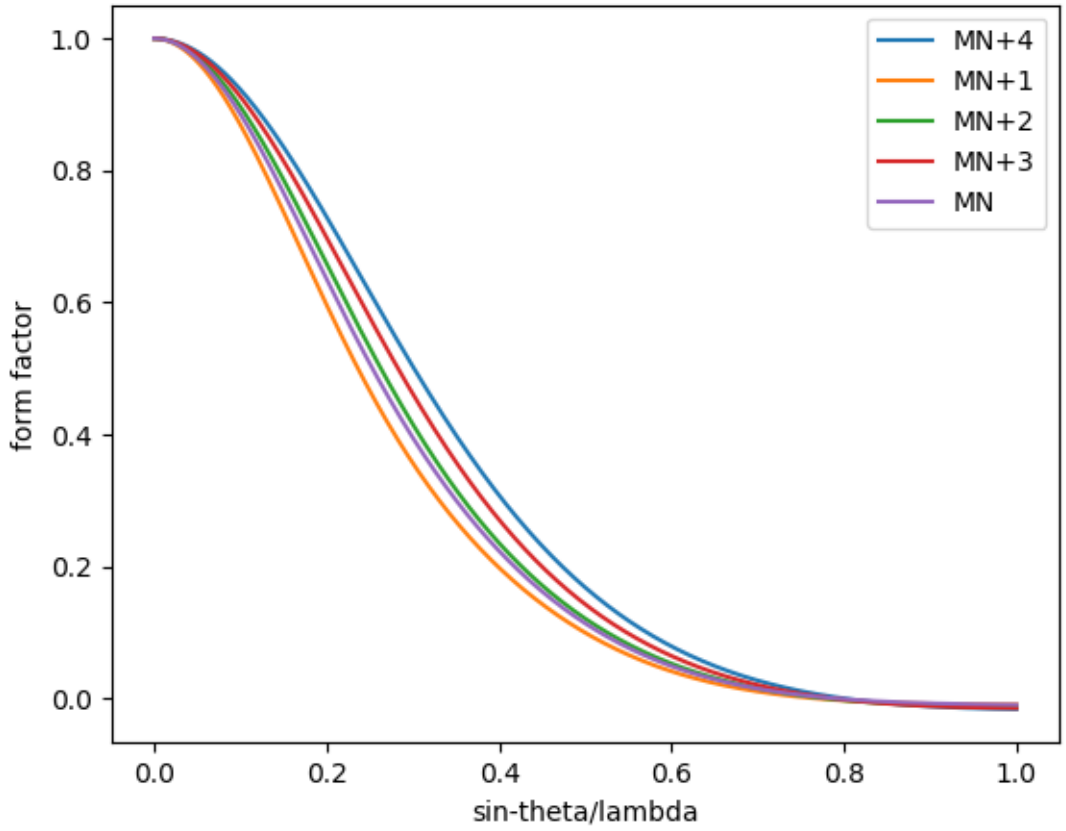
In GSAS-II:
Form factor coefficients <j_0> and <j_2> (higher terms ignored)

$$f_m = C + \sum_{i=1}^{4} A_i \exp\left(-B_i \sin^2\Theta/\lambda^2\right) + \left(\frac{2}{g} - 1\right)\left[C' + \sum_{i=1}^{4} A'_i \exp\left(-B'_i \sin^2\Theta/\lambda^2\right)\right]\sin^2\Theta/\lambda^2$$

Landé g factor = 2 for 1st row transition elements:
quenched orbital contribution
In general f_m → 0 for sinΘ/λ > 0.5; d<1.0
Tables from J. Brown (ITC-C) & Kobayashi K, Nagao T, Ito M. (Acta A67, 473-480, 2011)
(No input for user tables; might allow additions/substitutions in coeff. tables if there is interest)

MAGNETIC FORM FACTORS

E. g. for Mn & ions – some valence sensitivity



GSAS-II uses the high spin versions where there is a choice – 3rd row transition elements (W-Ir) given by Kobayashi, et al.

MAGNETIC SYMMETRY IN GSAS-II

Symbol driven; 2nd setting (if appropriate); BNS settings (not OG)

- Symbol based: allows nonstandard space groups – symbol interpretation yields operators (ITXC Vol I version! Thx to A. C. Larson's code)
- NB: does know that e.g. "F m -3 m" is really Fm3m
- Spin flip designation on generators (e.g. symbol components)
- Magnetic type IV – by transformation from chemical cell (with constraints) & selection of magnetic centering type
- Grey groups by adding 1' to symbol (incommensurate only)
- → all std & nonstd BNS designations reachable in GSAS-II
- Can be changed after input
- On the other hand:

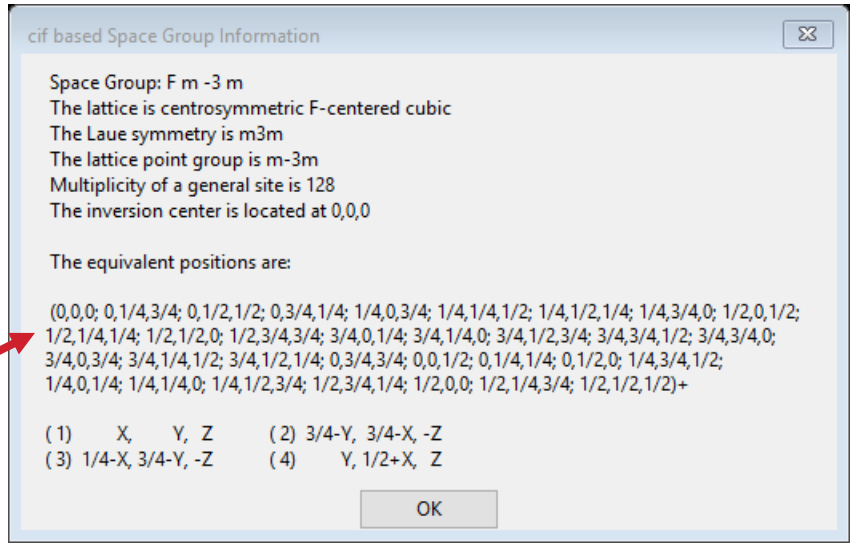
Import Bilbao magnetic cif files:

operators from mcif file

(fixed – can't change 'em)

Occasionally peculiar:

NiO mcif has 32 centering ops!



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BNS vs OG

GSAS-II choice: BNS

- OG – Opechowski-Guccione(1965): 1651 distinct magnetic space groups in book (Litvin, 2013 available on line from IUCr; NB: >11,000 pages!). For type IV magnetic structures the unit cell does not generate the lattice of magnetic moments & requires fractional hkls for reciprocal lattice.
- BNS – Belov-Neronova-Smirnova(1957): unit cell does generate complete magnetic lattice (e.g. type IV cell doubling with added lattice centering operations); hkl always integers. BNS set in Shubnikov, Belov, et al. book Colored Symmetry (1964).
- Stokes & Campbell compiled BNS/OG mag space group data – computer readable (but only std versions & 1st setting).
- GSAS-II allows non-std versions (that can be symbol interpreted, e.g. “F d” – a variant of Cc; something like “R 2/c” won’t work). NB: GSAS-II always uses 2nd setting (inversion @ origin).
- Spin flips → Pnma: Pn’m’a, Pnm’a’, etc. by choice; can be non-std
- Type IV – Transformation tool to new cell & add lattice centering; moves atoms

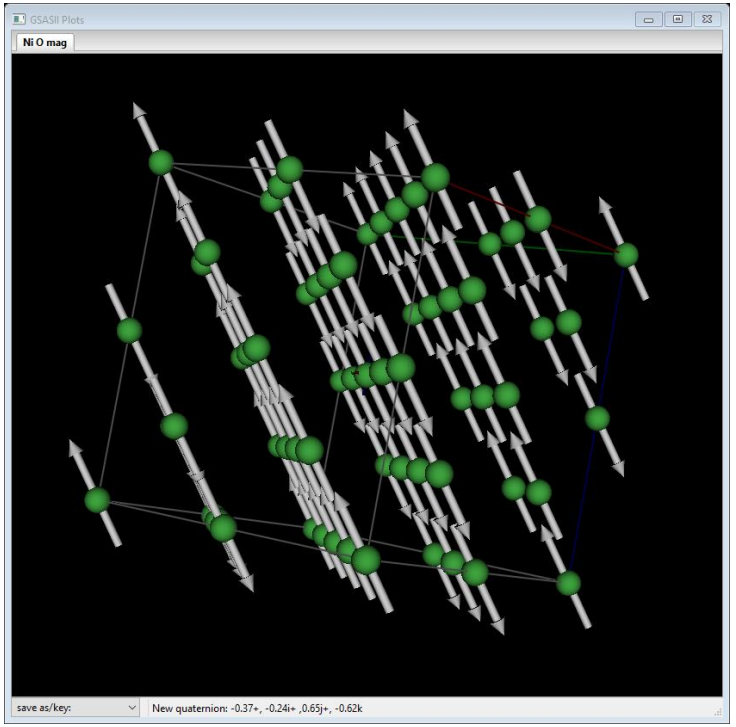
  Pnma: $P_a$nma, $P_b$nma, $P_C$nma, etc.

BILBAO MCIF FILES

~450 structures (Gallego, et al. JAC 49, 1750-1776, 2016)

- Tables: zero propagation vector, Type III, Type IV – 1, 2 & 3 propagation vectors, & incommensurate magnetic structures (more later)
- All single phase with Jmol viewer to visualize; full set sym. ops. & lattice centering ops all with “time reversal” (+/- 1) operator; uses BNS system
- Thus, chemical cell & magnetic cell coincident; nonstandard settings (occasionally quite odd, cf. NiO example)
- GSAS-II uses ops (overrides symbol Interpretation) → draw structures & compute powder patterns, etc.
- Magnetic moments – crystal axes components; Bohr magnetons. GSAS-II uses this convention.

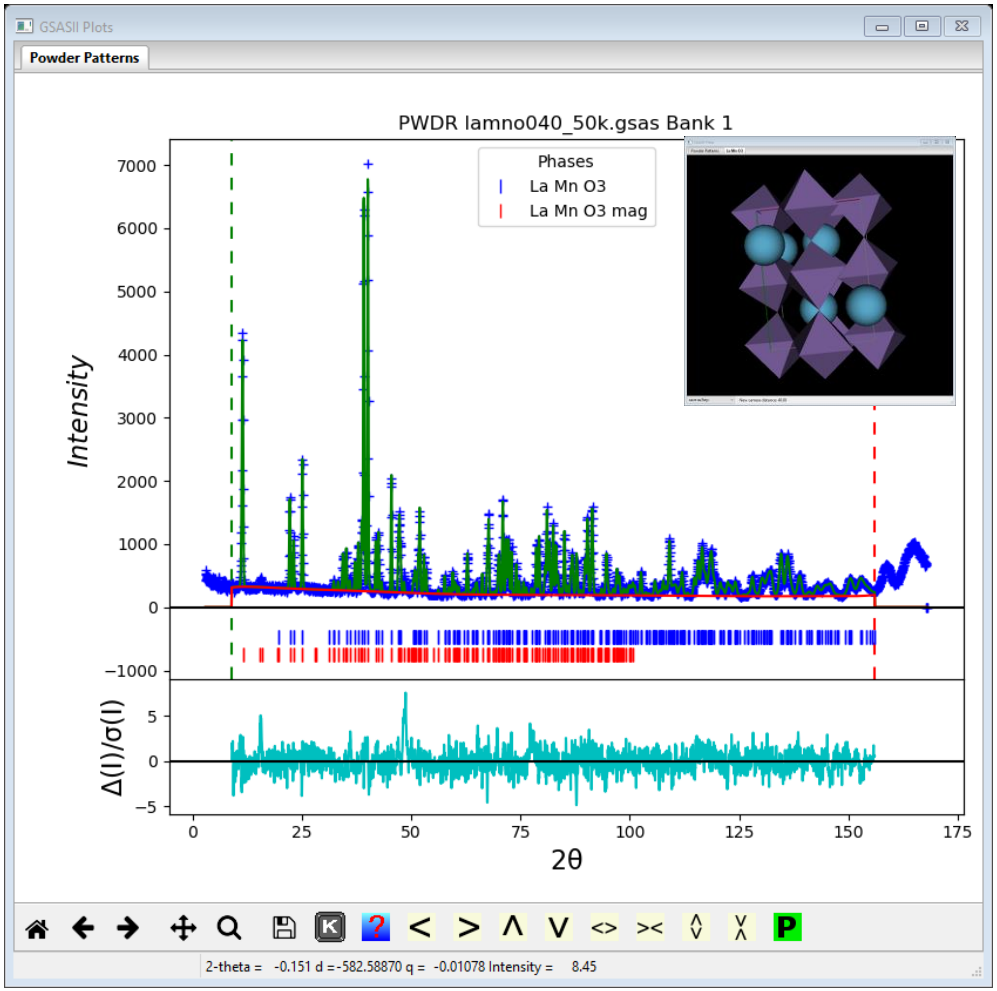
NB: old GSAS used Cartesian magnetic moment components



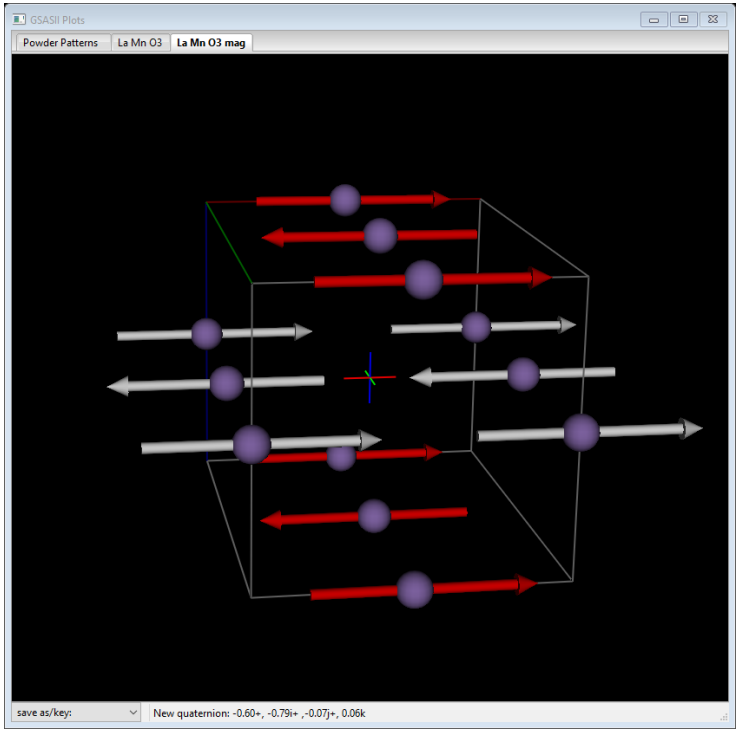
MAGNETIC STRUCTURE ANALYSIS IN GSAS-II

Magnetic Rietveld refinement – 2 phase

- Simple example – $LaMnO_3$ @50K (NIST- BT1)



Antiferromagnet Pn'ma'
Fe @ 0,0,1/2 Mx,My,Mz
allowed but only Mx >0
Mx=3.678(19)μ_B



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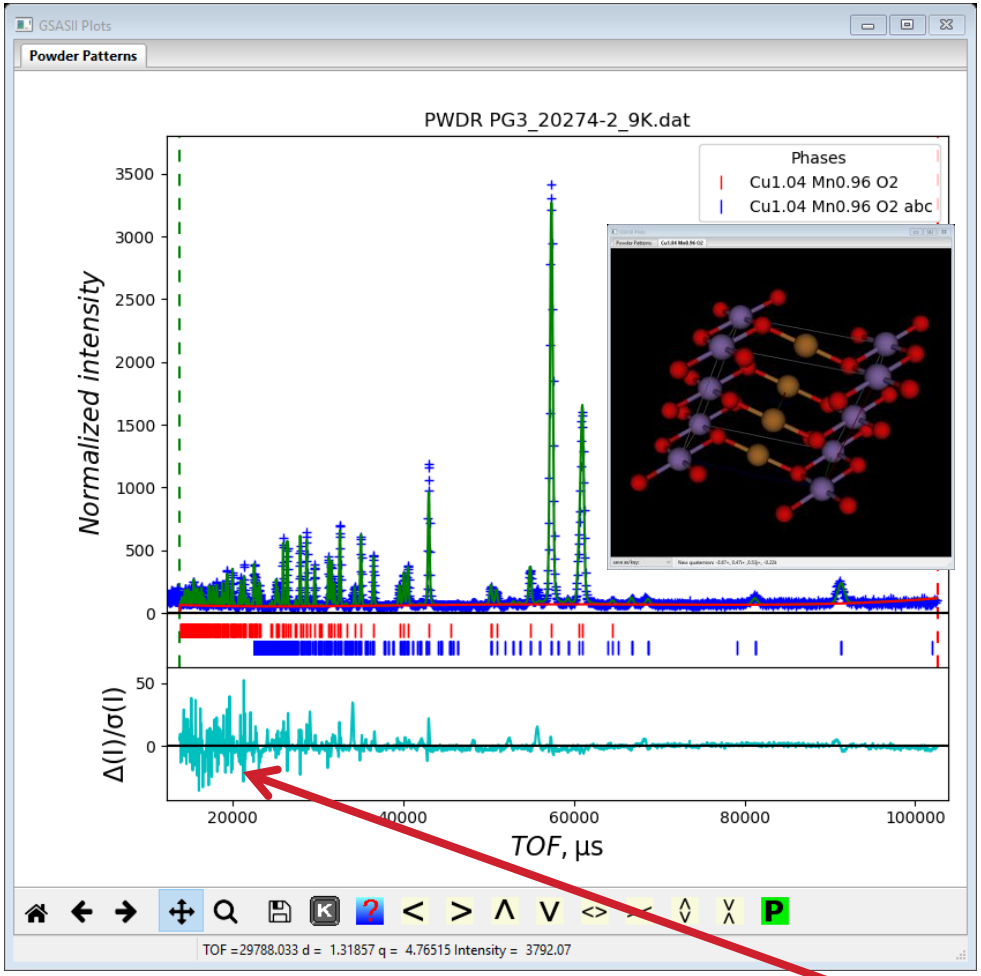
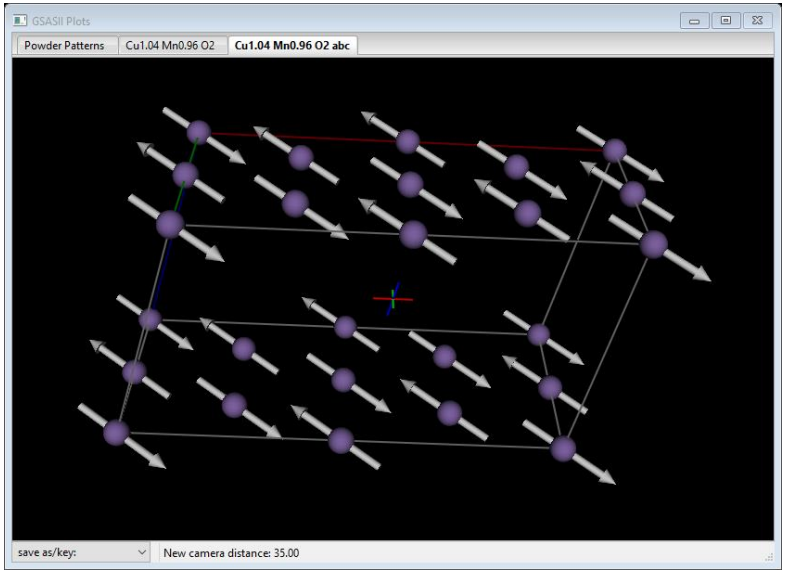
POWGEN DATA EXAMPLE

$Cu_{1.04}Mn_{0.96}O_2$ Type IV antiferromagnet (Bilbao 1.178 similar)



C2/m
5.554,2.885,5.902,104.354→
C-1
11.0866,5.7707,5.902, 90,104.354,90

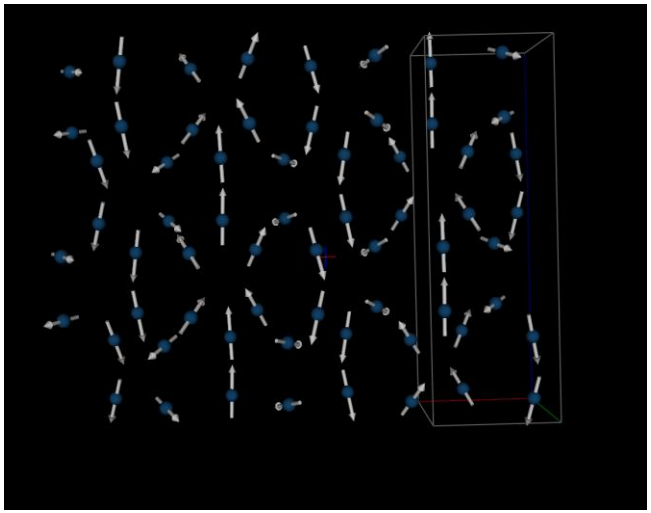


4 linked Mn atoms: @ 0,0,0:
Mx,My,Mz=1.70,0.65,0.67
Rest @ ¼, ¼,0; ½,0,0 & ¼,-¼,0

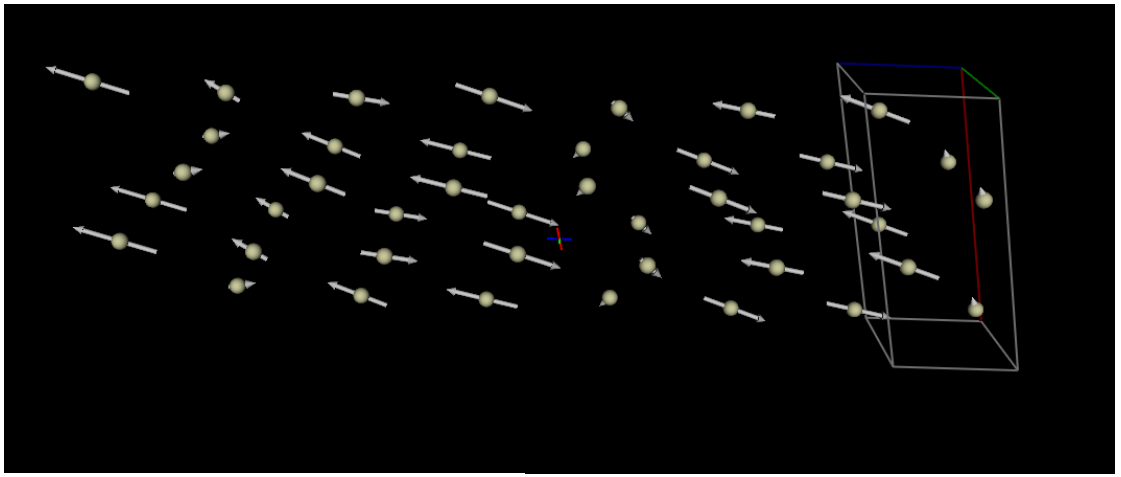
NB: something odd about POWGEN wts?
Similar in LaB_6 fit

MAGNETIC INCOMMENSURATE STRUCTURES

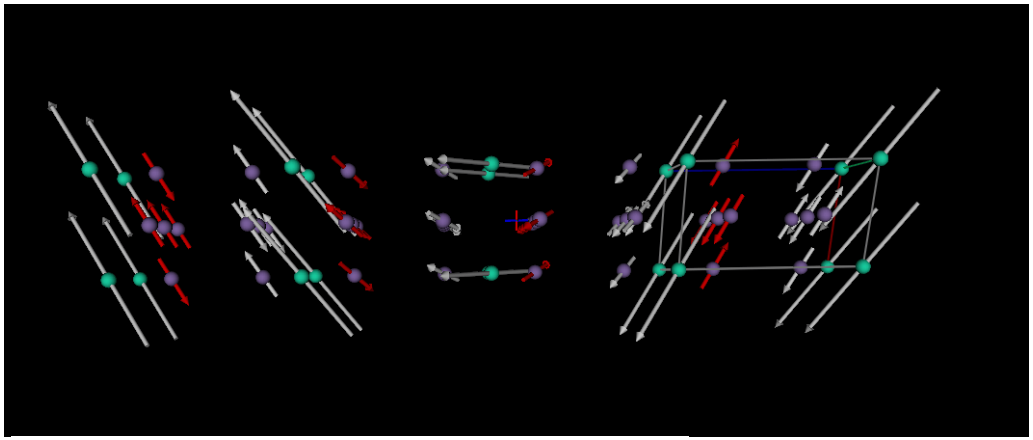
Some examples:



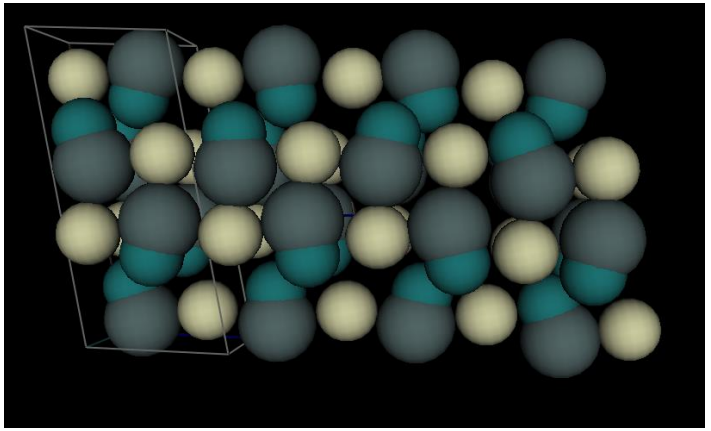
β-Li_2IrO_3



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)
- Magnetic structures
  - Structure solving aids i.e. selection of magnetic cell & space group from observed data

OTHER THINGS NEW IN GSAS-II

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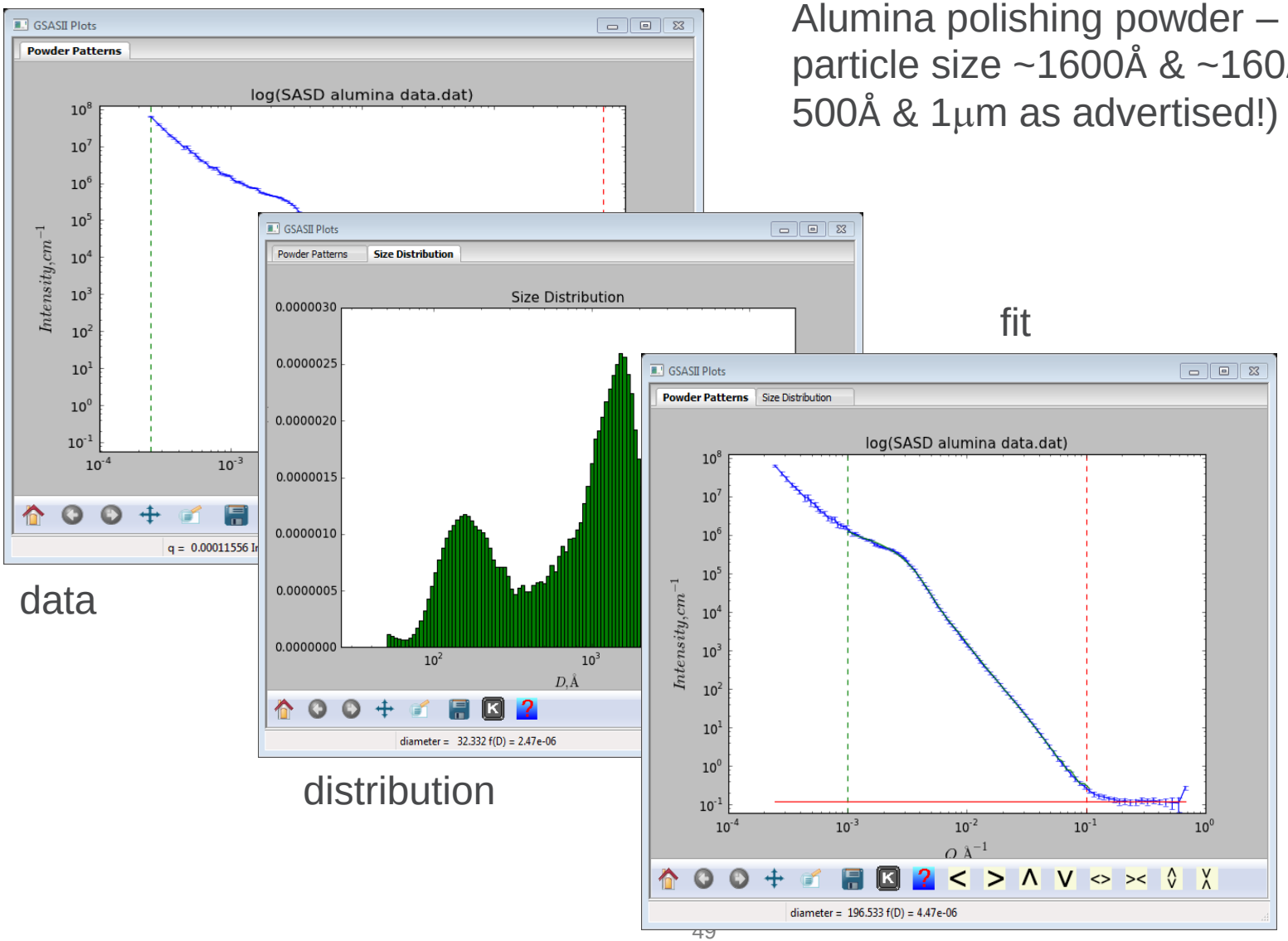
SMALL ANGLE SCATTERING – SIZE DISTRIBUTION

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



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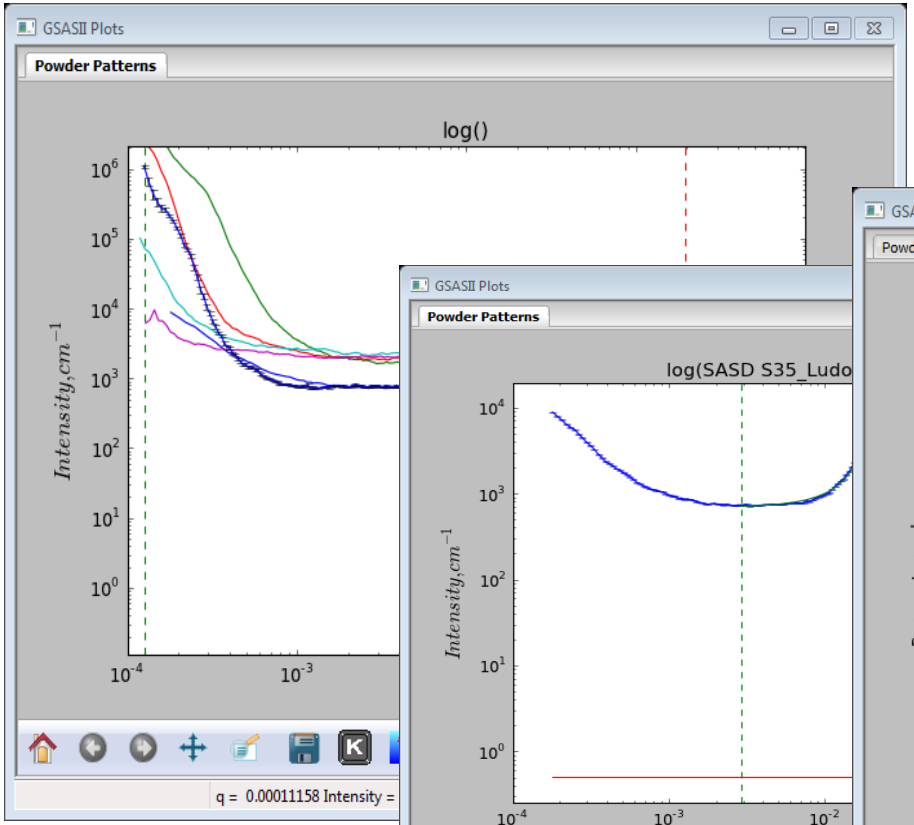
SMALL ANGLE SCATTERING – SEQUENTIAL DATA ANALYSIS

Ludox colloidal silica from Aldrich – dilution range

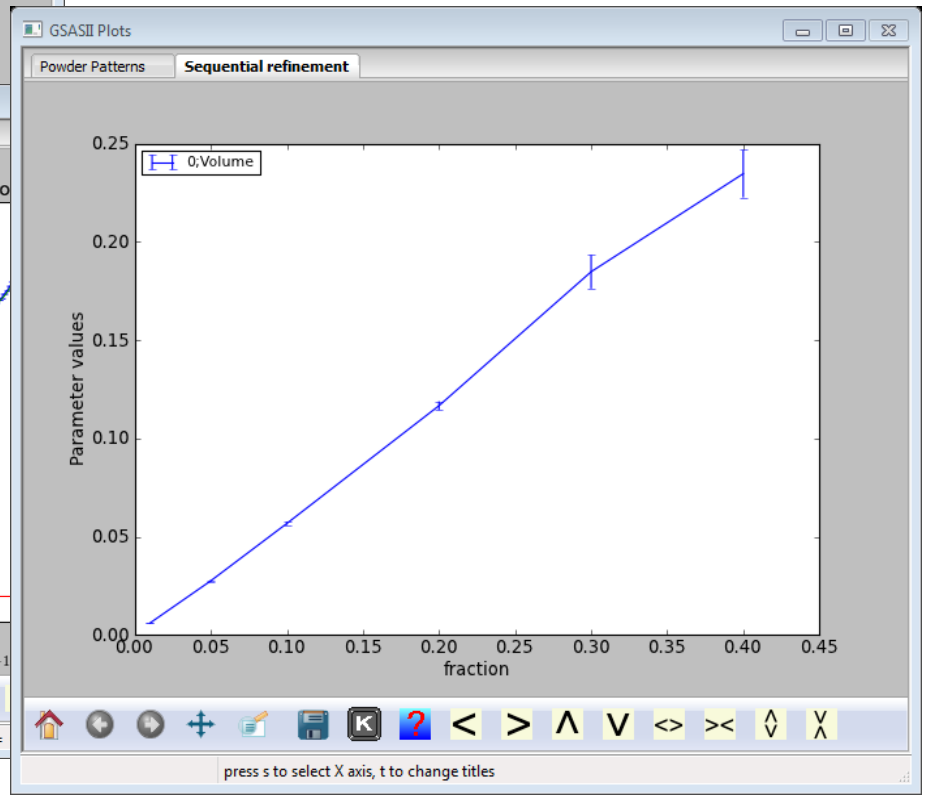


data

One fit

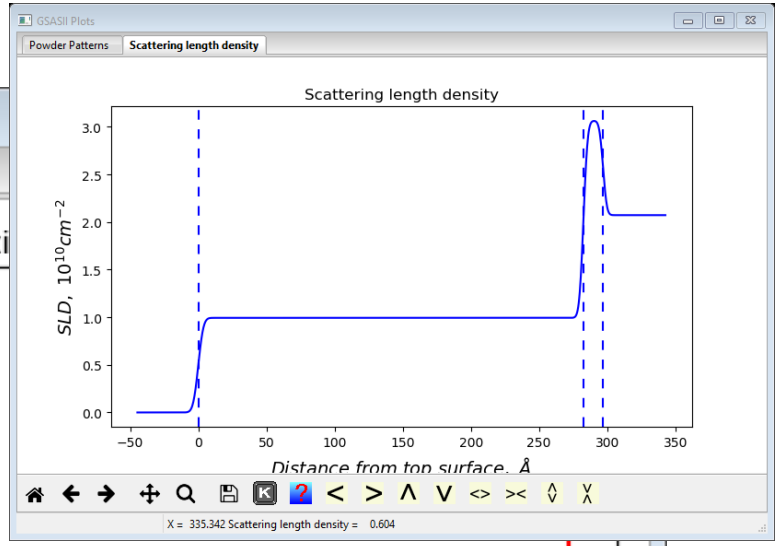
Fit – hard sphere; log normal distribution, size, mean, vol. fr.

Sequential result – find slope/intercept



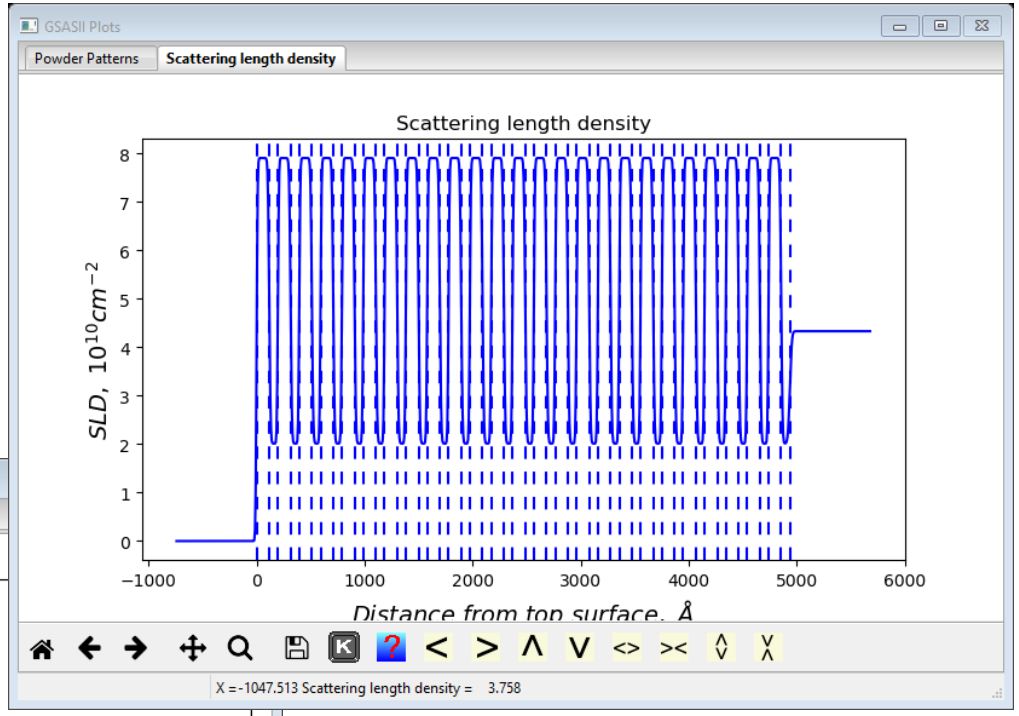
REFLECTIVITY

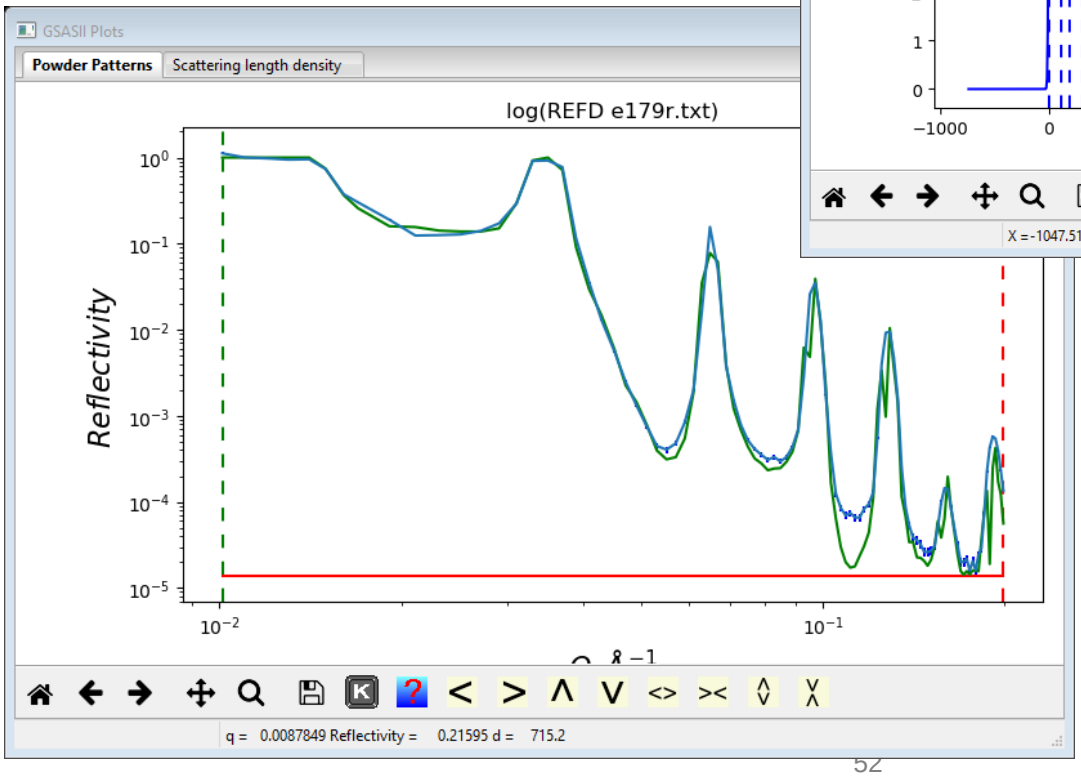
CW x-ray & neutron (no TOF yet)



MULTILAYER REFLECTIVITY

25 layers on a substrate
Common thickness & contrast





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THANK YOU