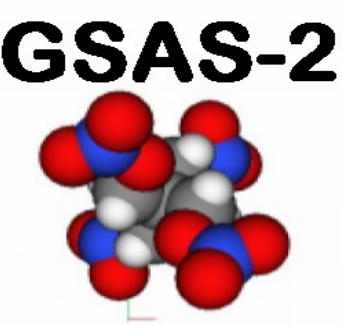
A VERY BRIEF INTRODUCTION TO GSAS-II.



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Advanced Photon Source
Argonne National Laboratory
USA

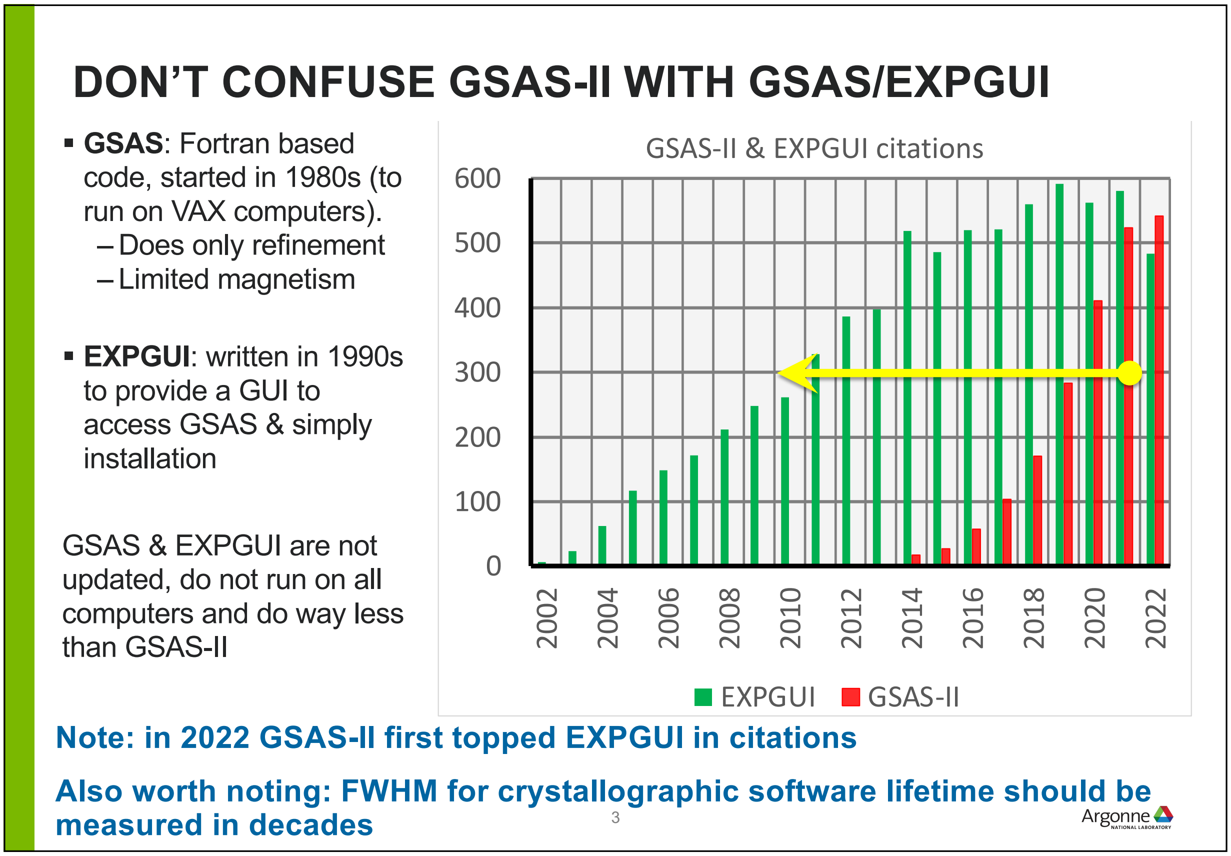
OUTLINE

WHAT I WILL COVER

- A bit of History: GSAS/EXPGUI
- Why GSAS-II & about it
- GSAS-II GUI organization
- Key GSAS-II concepts
- Sequential refinement
- Magnetism in GSAS-II
- Magnetic Structure Determination
- Magnetic Space Group Identification

WHAT I WILL NOT COVER (SOME SLIDES PROVIDED)

- GSAS-II details & settings
  - Section by section details
  - Texture
  - Constraints & restraints
- Profile treatment
- Rigid Bodies
- Incommensurate structures
- Other GSAS-II capabilities
  - Scripting
  - Small angle; reflectivity
- Refinement recipes (for novices)



DON’T CONFUSE GSAS-II WITH GSAS/EXPGUI

- **GSAS**: Fortran based code, started in 1980s (to run on VAX computers).
  - Does only refinement
  - Limited magnetism

- **EXPGUI**: written in 1990s to provide a GUI to access GSAS & simply installation

GSAS & EXPGUI are not updated, do not run on all computers and do way less than GSAS-II

Note: in 2022 GSAS-II first topped EXPGUI in citations

Also worth noting: FWHM for crystallographic software lifetime should be measured in decades

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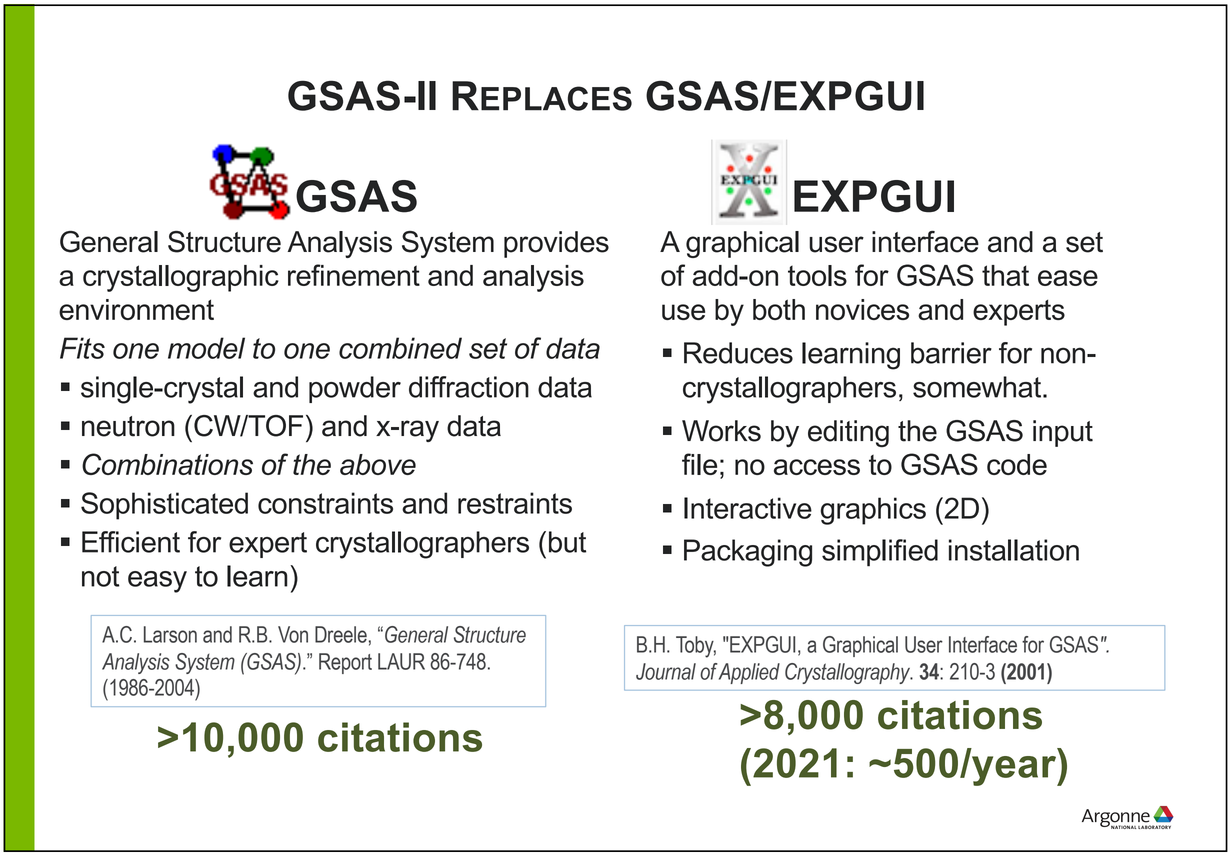


GSAS-II REPLACES GSAS/EXPGUI

GSAS

General Structure Analysis System provides a crystallographic refinement and analysis environment

Fits one model to one combined set of data

- single-crystal and powder diffraction data
- neutron (CW/TOF) and x-ray data
- *Combinations of the above*
- Sophisticated constraints and restraints
- Efficient for expert crystallographers (but not easy to learn)

A.C. Larson and R.B. Von Dreele, “*General Structure Analysis System (GSAS).*” Report LAUR 86-748. (1986-2004)

>10,000 citations

EXPGUI

A graphical user interface and a set of add-on tools for GSAS that ease use by both novices and experts

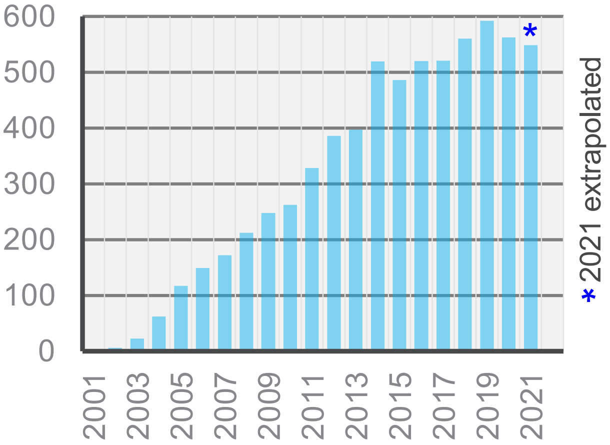
- Reduces learning barrier for non-crystallographers, somewhat.
- Works by editing the GSAS input file; no access to GSAS code
- Interactive graphics (2D)
- Packaging simplified installation

B.H. Toby, "EXPGUI, a Graphical User Interface for GSAS". *Journal of Applied Crystallography*. **34**: 210-3 **(2001)**

>8,000 citations (2021: ~500/year)

GSAS/EXPGUI IS STILL WIDELY USED

(BUT WE WISH YOU WOULD NOT)



Funding agency	Cite %
United States Department of Energy DOE (US)	18.4
National Natural Science Foundation of China NSFC	15.8
National Science Foundation NSF (US)	11.1
Eng. Physical Sciences Research Council EPSRC (UK)	5.2
National Council for Scientific and Technological Development CNPq (Brazil)	3.7
National Basic Research Program of China	3.2
European Union EU	2.6
Natural Sciences and Eng. Research Council of Canada	2.4
CAPES (Brazil)	2.2
Australian Research Council	2.0

Wide Range of Fields

Web of Science Categories	% of total
Materials Science Multidisciplinary	40.0
Chemistry Physical	31.2
Physics Applied	14.5
Physics Condensed Matter	14.5
Chemistry Inorganic Nuclear	13.1
Chemistry Multidisciplinary	11.6
Nanoscience Nanotechnology	8.0
Metallurgy Metallurgical Engineering	6.1
Crystallography	5.6
Materials Science Ceramics	5.5
Energy Fuels	5.2
Mineralogy	5.2
Electrochemistry	5.1
Geochemistry Geophysics	3.6
Physics Atomic Molecular Chemical	2.1
Physics Multidisciplinary	2.1
Engineering Chemical	2.0
Chemistry Applied	1.9
Multidisciplinary Sciences	1.8
Materials Science Characterization Testing	1.8
Engineering Electrical Electronic	1.3
Materials Science Coatings Films	1.2
Environmental Sciences	1.1
Optics	1.0

(Web of Science data 9/2020)

MOVING FROM GSAS/EXPGUI TO GSAS-II

WHY REINVENT THE WHEEL?

- GSAS issues
  - Basic code developed in 1980's (for VAX, then ported to Unix, then Windows, then Linux then Mac)
  - Not easily extensible; very hard to reuse code
  - GSAS does not provide data reduction, indexing or structure solution tools
  - Limited to 99 datasets & 9 phases (= ∞ in 1985; too few in 2010)
  - GSAS compiles only as 32-bit executable (G77 compiler & PGPLOT obsolete)
- EXPGUI issues
  - EXPGUI requires a version of Tcl/Tk that is >15 years out of date
  - Graphics requires BLT package – no longer maintained

GSAS-II: DESIGN PRINCIPLES

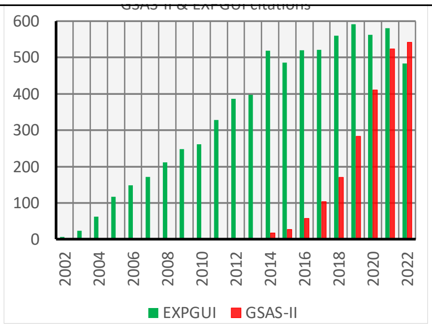
Project started in ~2008 to replace GSAS & EXPGUI with a new, modern, extensible, and open-source crystallographic analysis

- Don't require user to input anything that can be derived or looked up; enter information only once (same as GSAS)
- Lead beginners through processes without compromising flexibility needed for advanced work
- Support analysis of all types of data for problems from pyrochlores to proteins
- Provides all aspects of data analysis (from raw data to publication), including capabilities not in GSAS/EXPGUI:
  - Area detector data reduction
  - Indexing, structure solution and PDF computations
  - Small-angle scattering analysis
  - Parametric fitting
- Modern coding (Python) with a bit of Fortran for speed/reuse
- Extensive visualization & GUI for all features; partial scripting support

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)**.

WHERE ARE WE WITH GSAS-II?

Reads most powder diffraction images including from the Curiosity Rover on Mars!



GSAS-II use by lab:
ANL: 11%
ORNL: 8%
BNL: 6%

GSAS-II use by funding source:
38% DOE
23% NSF

- GSAS-II is being actively developed
- No limits on phases and datasets
- Almost all initial planned features done
  - Many requests for new features
- Bugs are fixed; often within hours
  - Please report bugs so we can fix them
- GSAS-II capabilities are being expanded
  - (as we do this we make new bugs, of course)
- GSAS-II questions (e-mail preferred) are answered as time permits; this sometimes results in features; please use mailing list (see `http://bit.ly/GSASIIemail`)

Note: GSAS & EXPGUI are no longer supported

- We will not take them away, but they may not continue to run; ***no new versions***

`http://bit.ly/GSASII`
(or `https://subversion.xray.aps.anl.gov/trac/pyGSAS`)

MAJOR CAPABILITIES IN GSAS-II

- Any number of datasets: single crystal & powder data of all types (new: pink-beam)
- Any number of phases (standard, protein or magnetic)
- Small angle scattering & reflectometry
- Image integration & PDF computation (w/optional beamline automation)
- Extensive visualization: 2- & 3-D graphics to make sense of just about all numbers
- Sequential and parametric fitting: for 10^1 to 10^4 related datasets
- API for scripting (fairly extensive, but not complete)
- ~50 worked through tutorials provide examples for different aspects of GSAS-II
- Fundamental parameters ➔ profile terms

Other

- Simple installation kits (Windows, Mac, Linux). Also supported on Raspberry Pi and ARM-Mac (“Apple Silicon”)
- Open source: all code distributed; code developer’s manual is nearly 300 pages

WHAT CAN YOU DO WITH GSAS-II?

GSAS-II has extensive capabilities, some available otherwise only in very specialized programs

- Data reduction/initial processing
  - Image calibration & integration
  - Peak fitting/position determination
  - PDF computation (x-rays)
  - TOF calibration
- Structure solution
  - Indexing
  - Pawley & LeBail intensity extraction
  - Charge flipping
  - Rigid body simulated annealing
  - Fourier maps
- Crystallographic analysis
  - Powder diffraction
  - Single-crystal diffraction
  - Neutron and x-ray diffraction
  - Fitting of any of the above, combined
- Comprehensive constraint & restraints
- Magnetic scattering (soon incommensurate)
- Fitting of modulated (3+1) structural models (neutron or x-ray)
- Multiple-wavelength single crystal
- Fitting of twinned single-crystal datasets
- Parametric structural analysis
  - Parametric equation fitting
- 2D dataset fitting:
  - Strain fitting
  - Texture fitting
- Stacking fault modeling (DIFFaX)
- Small-angle scattering analysis
- Reflectometry (CW)

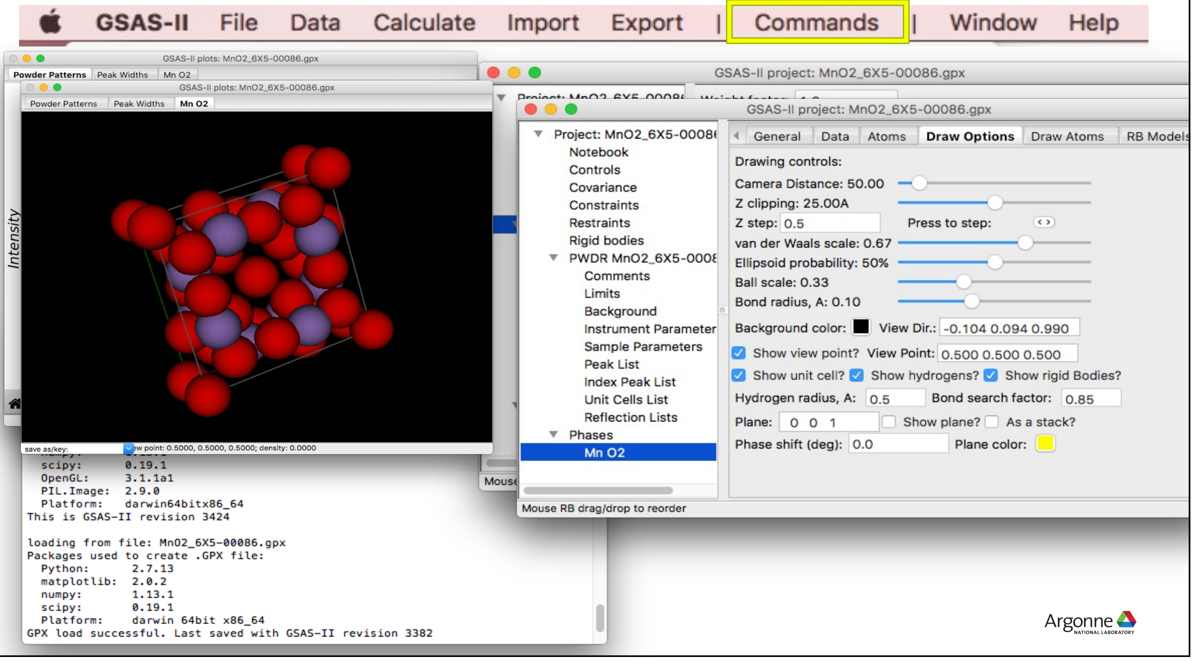
WHY USE GSAS-II FOR MAGNETISM?

- GSAS-II is the most modern and powerful package for structural analysis powder and single crystal data
  - Comprehensive; Easy to learn
  - Facile for parametric studies
  - Handles almost all types of diffraction studies – in combination
  - Simple transition to magnetism based on chemical crystallography (aka “nuclear structure”)
  - Straight-forward implementation of color space groups (via BNS)
  - Integrated into Bilboa and BYU Isotropy web software suites
  - In Python, open source
  - Actively developed: please send ideas (or even better code)
- Why not GSAS-II:
  - Does not support representational analysis (directly)
  - Does not yet handle incommensurate magnetism
  - No polarized neutron scattering support
  - Actively developed: new code means new bugs

GSAS-II GUI ORGANIZATION

GRAPHICAL USER INTERFACE

GUI has three windows: Data Window, Plot Window & Console



view point: 0.5000, 0.5000, 0.5000; density: 0.0000

Drawing controls:

Camera Distance: 50.00

Z clipping: 25.00A

Z step: 0.5 Press to step:

van der Waals scale: 0.67

Ellipsoid probability: 50%

Ball scale: 0.33

Bond radius, A: 0.10

Background color: ■ View Dir.: -0.104 0.094 0.990

☑ Show view point? View Point: 0.500 0.500 0.500

☑ Show unit cell? ☑ Show hydrogens? ☑ Show rigid Bodies?

Hydrogen radius, A: 0.5 Bond search factor: 0.85

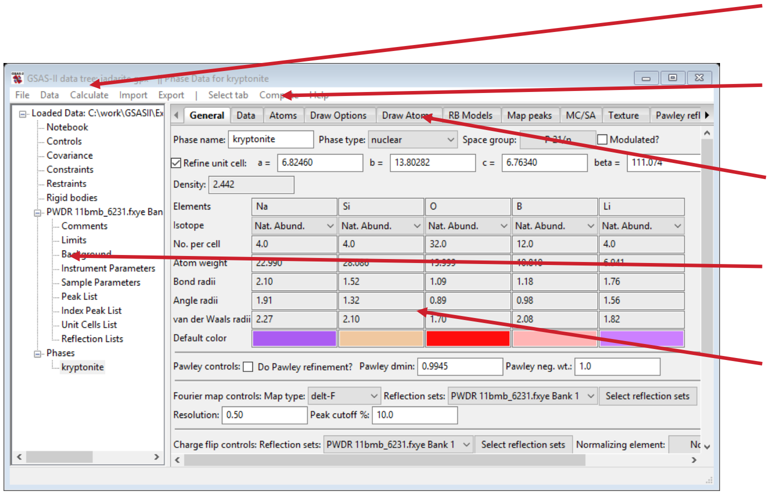
Plane: 0 0 1 ☐ Show plane? ☐ As a stack?

Phase shift (deg): 0.0 Plane color: 🟨

```
  scipy:      0.19.1
  OpenGL:     3.1.1a1
  PIL.Image:  2.9.0
  Platform:   darwin64bitx86_64
This is GSAS-II revision 3424

loading from file: MnO2_6X5-00086.gpx
Packages used to create .GPX file:
  Python:      2.7.13
  matplotlib:  2.0.2
  numpy:       1.13.1
  scipy:       0.19.1
  Platform:    darwin 64bit x86_64
GPX load successful. Last saved with GSAS-II revision 3382
```

GSAS-II MAIN WINDOW



Phase name: kryptonite Phase type: nuclear Space group: P 21/n ☐ Modulated?

☑ Refine unit cell: a = 6.82460 b = 13.80282 c = 6.76340 beta = 111.074

Density: 2.442

Elements	Na	Si	O	B	Li
Isotope	Nat. Abund.	Nat. Abund.	Nat. Abund.	Nat. Abund.	Nat. Abund.
No. per cell	4.0	4.0	32.0	12.0	4.0
Atom weight	22.990	28.086	15.999	10.810	6.941
Bond radii	2.10	1.52	1.09	1.18	1.76
Angle radii	1.91	1.32	0.89	0.98	1.56
van der Waals radii	2.27	2.10	1.70	2.08	1.82
Default color	🟪	🟧	🟥	🟥	🟪

Pawley controls: ☐ Do Pawley refinement? Pawley dmin: 0.9945 Pawley neg. wt.: 1.0

Fourier map controls: Map type: delt-F Reflection sets: PWDR 11bmb_6231.fxye Bank 1 Select reflection sets

Resolution: 0.50 Peak cutoff %: 10.0

Charge flip controls: Reflection sets: PWDR 11bmb_6231.fxye Bank 1 Select reflection sets Normalizing element: Na

Main menu

Submenu

Data tabs

Data tree

Data window

For Mac menu is in system-determined location (default, top of screen)

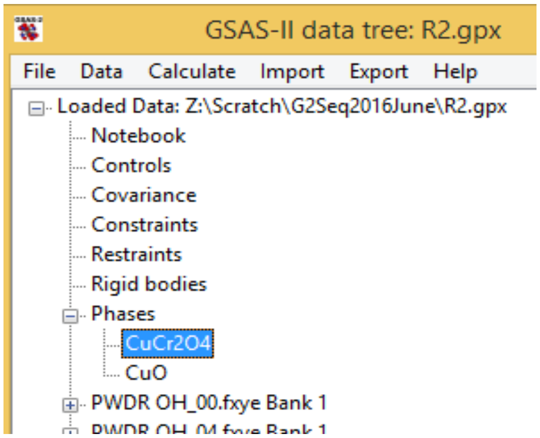
THE MAIN GSAS-II DATA WINDOW: DATA TREE

This provides a hierarchical view of the project.

Used *for item selection.* Menu contents and data window contents change with selection

Items can be (order optional):

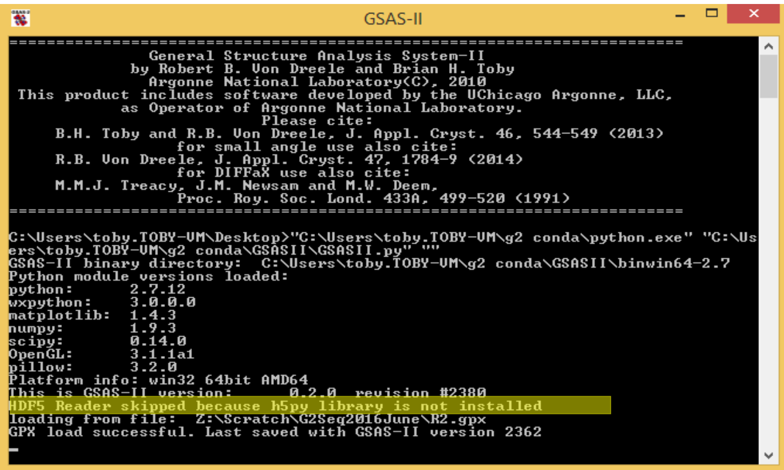
- Overall options/results (Controls/Covariance,…)
- Phases
  - No limit on number of phases
- Dataset (Histogram) items
  - Each type of data has a unique prefix
    - PWDR: powder data
    - IMG: images
    - HKLF: Single xtal
    - SASD: small angle
    - PDF: Pair distribution fxn
- Clicking on item opens it for viewing/editing and may create graphics
- Children of items can be hidden



Number of data items is limited only by available memory

OUTPUT WINDOW

- Status information and error messages are displayed in the “DOS” (terminal) window.
  - Look here when things are not working
  - The information here is essential for debugging: please send readable copy
  - Output only: not possible to type any input here



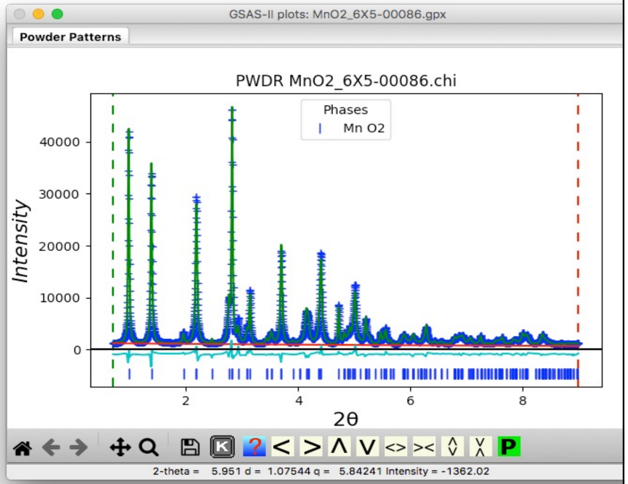
```
========================================================================
               General Structure Analysis System-II
             by Robert B. Von Dreele and Brian H. Toby
               Argonne National Laboratory(C), 2010
 This product includes software developed by the UChicago Argonne, LLC,
            as Operator of Argonne National Laboratory.
                           Please cite:
     B.H. Toby and R.B. Von Dreele, J. Appl. Cryst. 46, 544-549 (2013)
                  for small angle use also cite:
     R.B. Von Dreele, J. Appl. Cryst. 47, 1784-9 (2014)
                  for DIFFaX use also cite:
     M.M.J. Treacy, J.M. Newsam and M.W. Deem,
                  Proc. Roy. Soc. Lond. 433A, 499-520 (1991)
========================================================================

C:\Users\toby.TOBY-VM\Desktop>"C:\Users\toby.TOBY-VM\g2 conda\python.exe" "C:\Us
ers\toby.TOBY-VM\g2 conda\GSASII\GSASII.py" ""
GSAS-II binary directory:  C:\Users\toby.TOBY-VM\g2 conda\GSASII\binwin64-2.7
Python module versions loaded:
python:      2.7.12
wxpython:    3.0.0.0
matplotlib:  1.4.3
numpy:       1.9.3
scipy:       0.14.0
OpenGL:      3.1.1a1
pillow:      3.2.0
Platform info: win32 64bit AMD64
This is GSAS-II version:      0.2.0  revision #2380
HDF5 Reader skipped because h5py library is not installed
loading from file:  Z:\Scratch\G2Seq2016June\R2.gpx
GPX load successful. Last saved with GSAS-II version 2362
_
```

WORKING WITH THE PLOT WINDOW

Plot window has toolbar at bottom

- Position/Zoom plot
  - Select & unselect
  - When selected mouse "locked"
- Control "zoom" Stack
  - Home button useful for resize
- Save hard copy
- Provides list of defined keys for plot
- Help page
- Position/zoom without mouse "lock"
- Publication Rietveld plot; color/sym. selection, etc.



2-theta = 5.951 d = 1.07544 q = 5.84241 Intensity = -1362.02

Note that many plot elements can be dragged (limits, ticks) when appropriate tree item is selected

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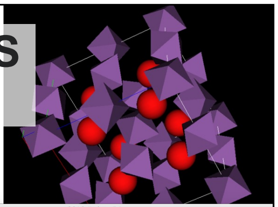
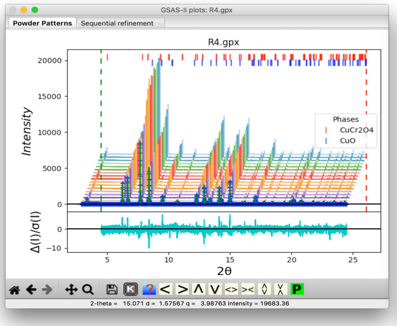
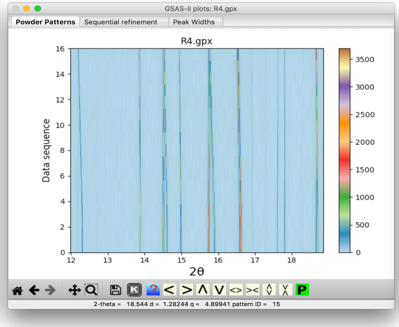
GSAS-II OFFERS MANY DIFFERENT TYPES OF GRAPHICS AND GRAPHICS MODES



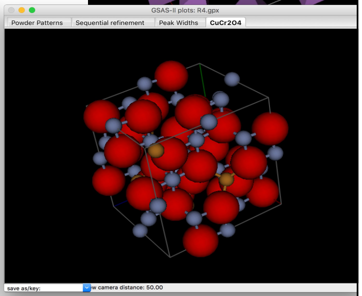
Many different graphics modes offered



2-theta = 15.071 d = 1.57567 q = 3.98763 Intensity = 19683.36

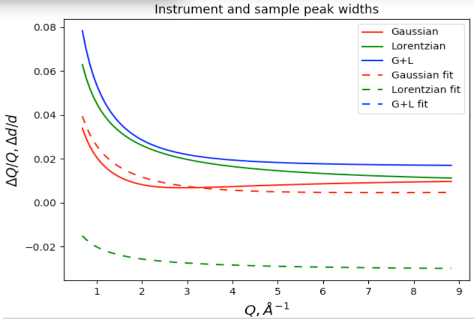


2-theta = 18.544 d = 1.28244 q = 4.89941 pattern ID = 15



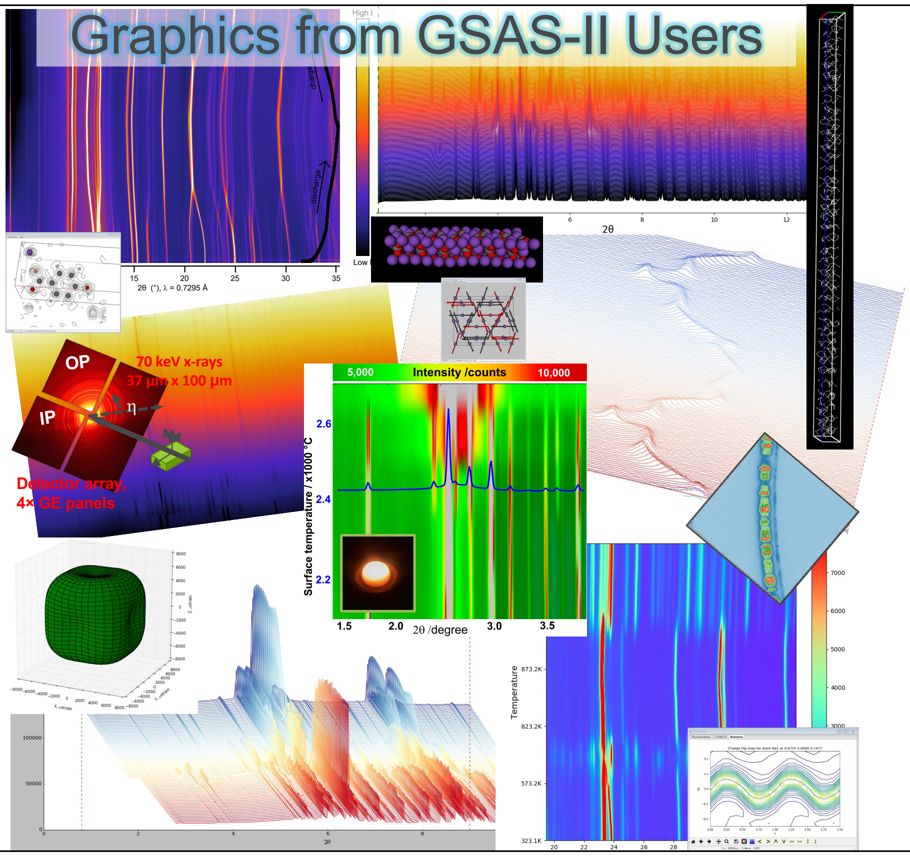
save as/key:

camera distance: 50.00



- Most displays of any complex data have associated graphics

Graphics from GSAS-II Users

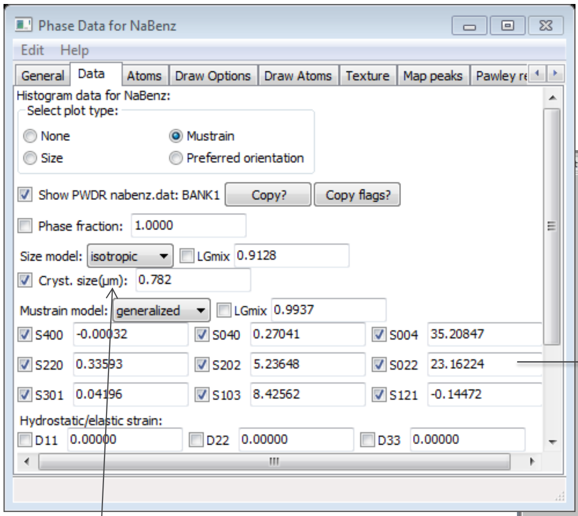


Cover from Summer 2019 issue of Reflexions (American Crystallographic Association Newsletter)

GSAS-II: VISUALIZATION & REAL UNITS BRINGS MEANING TO NUMBERS.

GSAS-2

Valuable for experts. Vital for novices!



Phase Data for NaBenz

Histogram data for NaBenz:

Select plot type:

○ None ● Mustrain
○ Size ○ Preferred orientation

☑ Show PWDR nabenz.dat: BANK1 Copy? Copy flags?

☐ Phase fraction: 1.0000

Size model: isotropic ☐ LGmix 0.9128

☑ Cryst. size(µm): 0.782

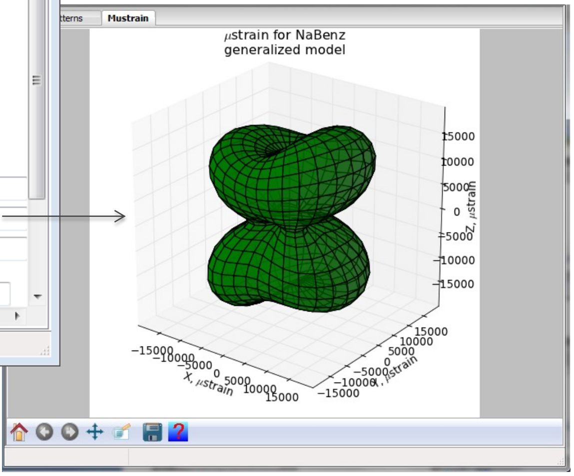
Mustrain model: generalized ☐ LGmix 0.9937

☑ S400 -0.00032	☑ S040 0.27041	☑ S004 35.20847
☑ S220 0.33593	☑ S202 5.23648	☑ S022 23.16224
☑ S301 0.04196	☑ S103 8.42562	☑ S121 -0.14472

Hydrostatic/elastic strain:

☐ D11 0.00000 ☐ D22 0.00000 ☐ D33 0.00000

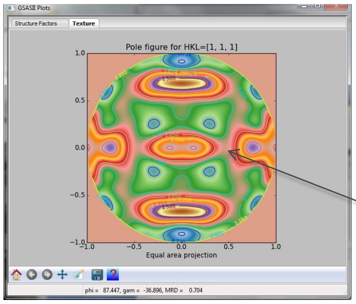
µ-Strain surface



NB: size in µm size

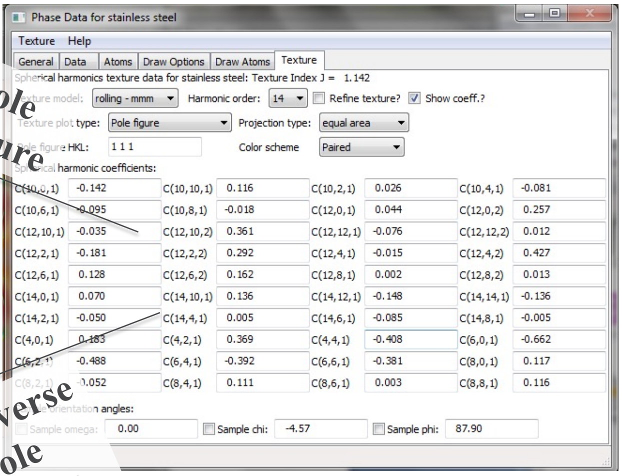
GSAS-II: TEXTURE FROM SPHERICAL HARMONICS

GSAS-2



phi = 87.447, gam = -36.896, MRD = 0.704

Pole figure



Spherical harmonics texture data for stainless steel: Texture Index J = 1.142

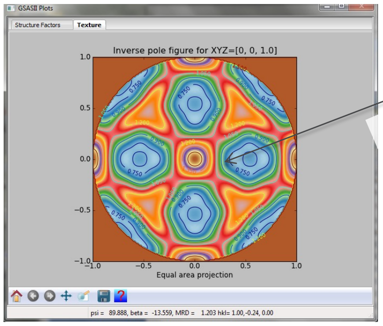
Texture model: rolling - mmm
Harmonic order: 14
☐ Refine texture?
☑ Show coeff.?
Texture plot type: Pole figure
Projection type: equal area
Pole figure HKL: 1 1 1
Color scheme: Paired

Spherical harmonic coefficients:

C(10,0,1)	-0.142	C(10,10,1)	0.116	C(10,2,1)	0.026	C(10,4,1)	-0.081
C(10,6,1)	-0.095	C(10,8,1)	-0.018	C(12,0,1)	0.044	C(12,0,2)	0.257
C(12,10,1)	-0.035	C(12,10,2)	0.361	C(12,12,1)	-0.076	C(12,12,2)	0.012
C(12,2,1)	-0.181	C(12,2,2)	0.292	C(12,4,1)	-0.015	C(12,4,2)	0.427
C(12,6,1)	0.128	C(12,6,2)	0.162	C(12,8,1)	0.002	C(12,8,2)	0.013
C(14,0,1)	0.070	C(14,10,1)	0.136	C(14,12,1)	-0.148	C(14,14,1)	-0.136
C(14,2,1)	-0.050	C(14,4,1)	0.005	C(14,6,1)	-0.085	C(14,8,1)	-0.005
C(4,0,1)	0.183	C(4,2,1)	0.369	C(4,4,1)	-0.408	C(6,0,1)	-0.662
C(6,2,1)	-0.488	C(6,4,1)	-0.392	C(6,6,1)	-0.381	C(8,0,1)	0.117
C(8,2,1)	-0.052	C(8,4,1)	0.111	C(8,6,1)	0.003	C(8,8,1)	0.116

Sample orientation angles:

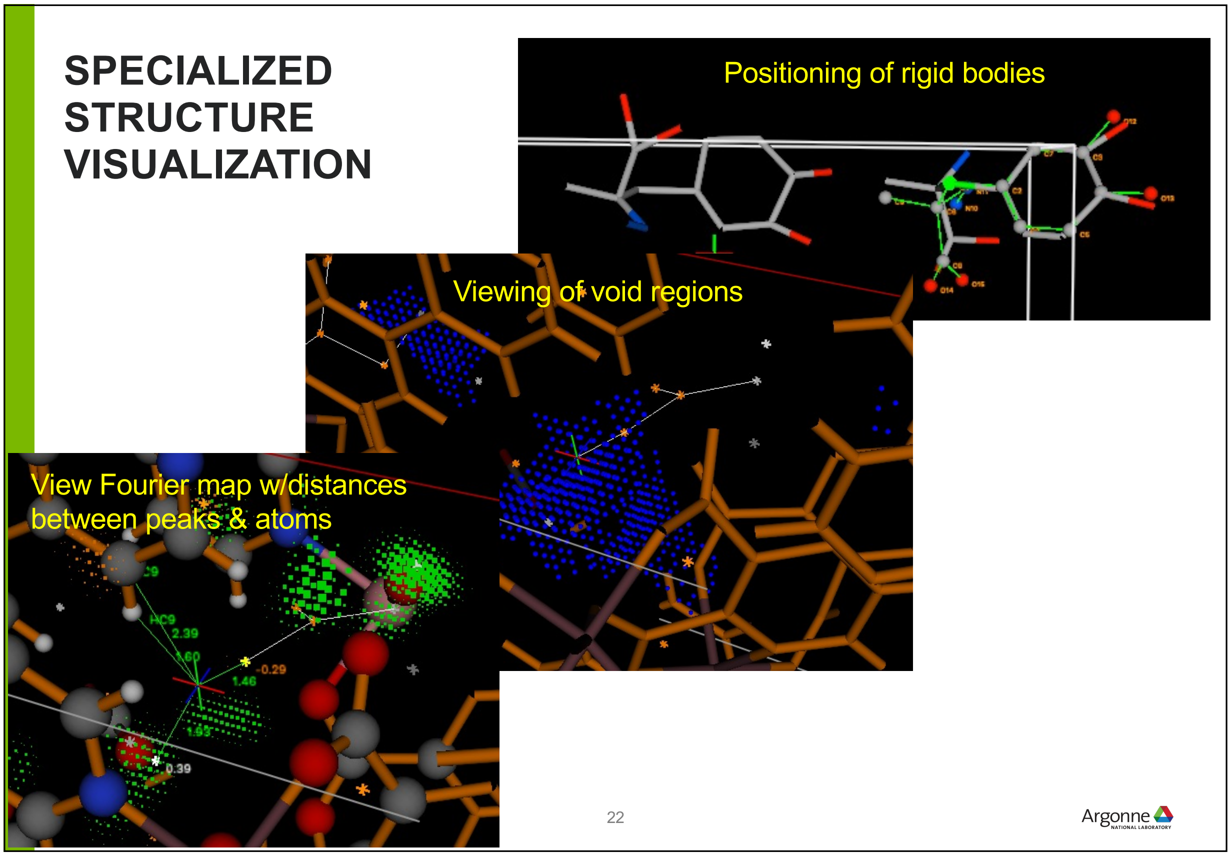
☐ Sample omega: 0.00
☐ Sample chi: -4.57
☐ Sample phi: 87.90



psi = 89.888, beta = -13.559, MRD = 1.203 hkl= 1.00,-0.24, 0.00

Inverse pole figure

SPECIALIZED STRUCTURE VISUALIZATION

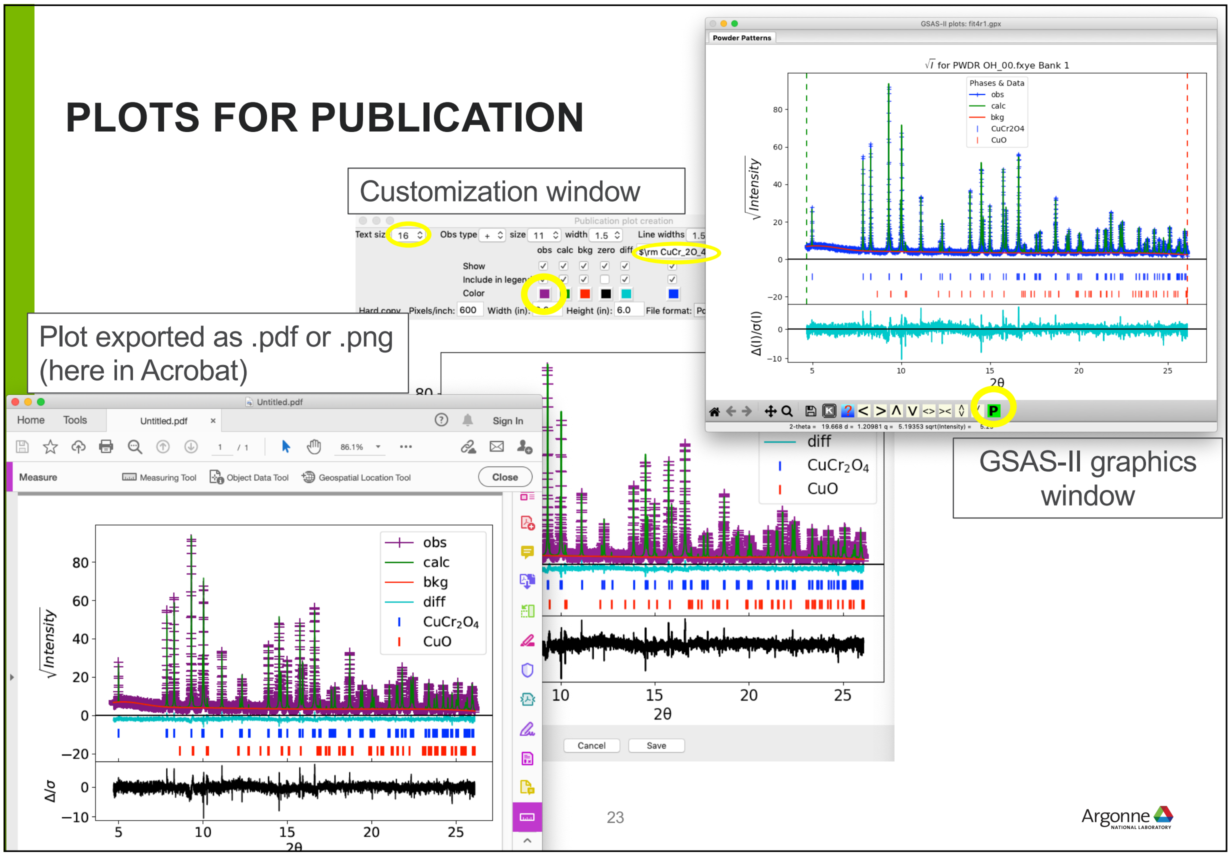


Positioning of rigid bodies

Viewing of void regions

View Fourier map w/distances between peaks & atoms

PLOTS FOR PUBLICATION



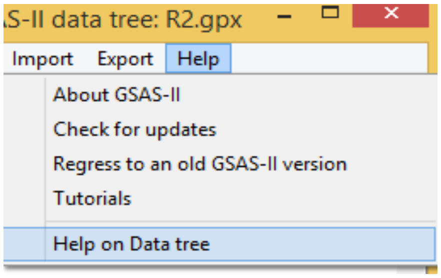
Customization window

Plot exported as .pdf or .png (here in Acrobat)

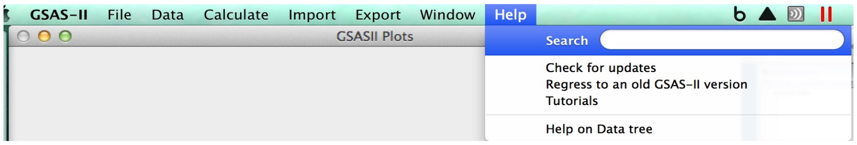
GSAS-II graphics window

HELP MENU HAS LOTS OF GOOD STUFF

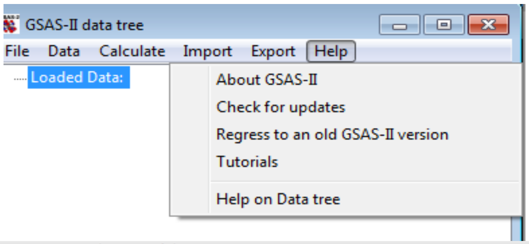
- The help menu will allow you to
  - – see what version of GSAS-II you have
  - – Update to a new (or older) version
  - – Access a single “help” web page
    - Help on current data tree item
  - – Access ~50 tutorials (as web pages) showcasing different aspects of GSAS-II

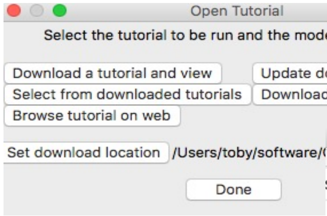


ACCESS TUTORIALS FROM HELP MENU

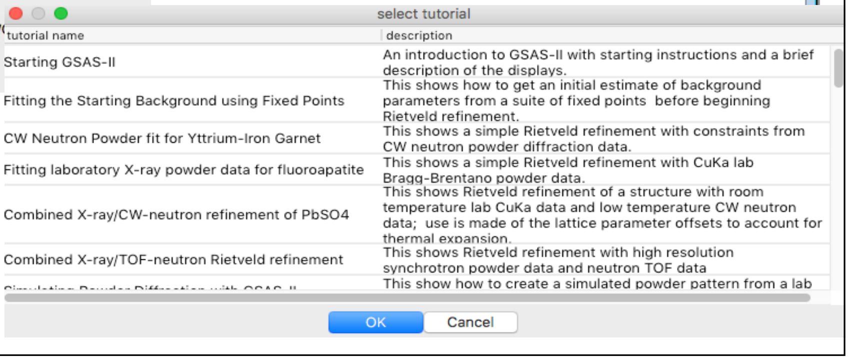


Load the files you want to have, where you want to place them. Example data files are loaded too.





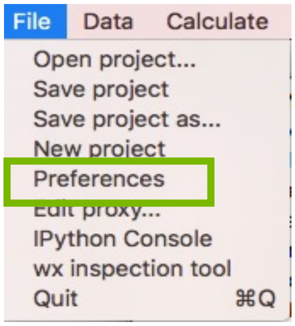
/Users/toby/software/(

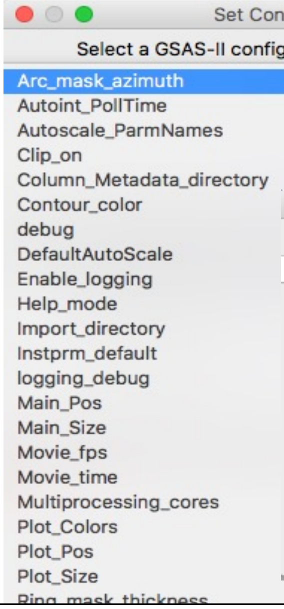


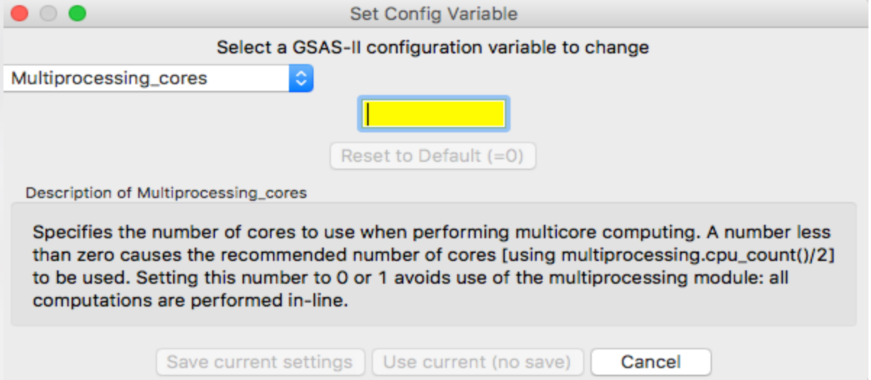
tutorial name	description
Starting GSAS-II	An introduction to GSAS-II with starting instructions and a brief description of the displays.
Fitting the Starting Background using Fixed Points	This shows how to get an initial estimate of background parameters from a suite of fixed points before beginning Rietveld refinement.
CW Neutron Powder fit for Yttrium-Iron Garnet	This shows a simple Rietveld refinement with constraints from CW neutron powder diffraction data.
Fitting laboratory X-ray powder data for fluoroapatite	This shows a simple Rietveld refinement with CuKa lab Bragg-Brentano powder data.
Combined X-ray/CW-neutron refinement of PbSO4	This shows Rietveld refinement of a structure with room temperature lab CuKa data and low temperature CW neutron data; use is made of the lattice parameter offsets to account for thermal expansion.
Combined X-ray/TOF-neutron Rietveld refinement	This shows Rietveld refinement with high resolution synchrotron powder data and neutron TOF data
Simulating Powder Diffraction with GSAS-II	This show how to create a simulated powder pattern from a lab

WORTH KNOWING ABOUT: FILE/PREFERENCES MENU COMMAND

- This is where we provide options for controlling details on how GSAS-II operates







Select a GSAS-II configuration variable to change

Multiprocessing_cores

Description of Multiprocessing_cores

Specifies the number of cores to use when performing multicore computing. A number less than zero causes the recommended number of cores [using multiprocessing.cpu_count()/2] to be used. Setting this number to 0 or 1 avoids use of the multiprocessing module: all computations are performed in-line.

KEY GSAS-II CONCEPTS

GSAS-II TERMS & CONCEPTS

- **Controls**: affect operation of program (e.g. number of cycles run)
- **Parameters**: values that affect diffraction computation
  - **Fitted parameters (Variables)**: parameters that GSAS-II will optimize

- **Constraints**: fix or group parameters to reduce model complexity. In effect, reduces number of fitted parameters
- **Restraints**: introduce external “observations” (prejudice) to push refinement away from non-physical results

Note that both are adding the crystallographer’s prejudices into the model. With a constraint, there will be no direct evidence if this prejudice is wrong (but the fit will be worse). The effect of the restraint will depend on how strongly it is weighted.

- **Combined fit**: where a model is fit to multiple datasets simultaneously
- **Sequential fit**: a refinement for a set of related datasets where the model is fit to each dataset one-at-a-time

TERMS (CONTINUED)

- **Histogram**: a set of data (powder, single-crystal, pink beam,…)
  - "**Dummy Histogram**" specifies a type of dataset to be simulated
  - Note that GSAS-II reads most common data files, but is easily extensible for more

- **Instrument Parameters:** a file that defines the data type and instrument settings
  - GSAS-II accepts old GSAS .prm files but also has a new more sensible file format

Alternate intensity fitting methods:

- **Pawley fitting** [G. Stewart] – each reflection intensity for phase is treated as an independent Least-squares variable (same for all histograms)
  - Selected by phase: reflection intensities same for all histograms

- **LeBail fitting** [Armel…] – fits reflection intensities using Rietveld intensity extraction (steepest descents)
  - selected by phase & histogram
  - Initial F_{hkl} values set to unity
  - Is a bit easier to use than Pawley

SPACE GROUP TREATMENT IN GSAS-II

Very flexible space group treatment

- GSAS-II Space group treatment is symbol based:
  - Allows nonstandard space groups – symbol interpretation yields operators (Interpretation follows Inter. Tables Vol I, using code by A. C. Larson)
  - NB: does know that e.g. "`F m -3 m`" is really *Fm*3*m*, etc.

- GSAS-II allows non-std space group versions (where is symbol interpreted),
  - e.g. "`F d`" – a variant of *Cc*
  - Incompatible usage not allowed (something like "`R 2/c`" won't work).

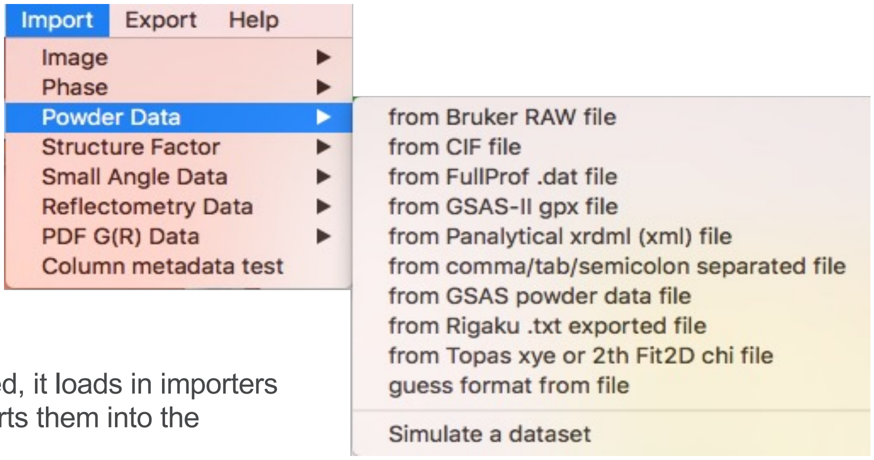
- Why support non-standard space groups?
  - If phase in *Fmmm* transforms to triclinic, "best" description keeps original cell and would be $F\bar{1}$

- GSAS-II always uses 2nd origin setting (because placing inversion operator @ origin gives simplest computation)
  - Menu command to transform Origin 1 --> Origin 2
- BNS color space groups & (3+1) Superspace groups supported

TO GET HISTOGRAMS & PHASES INTO GSAS-II, USE IMPORT MENU ITEMS

These are “user customizable”

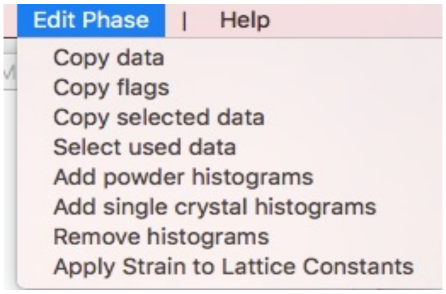
- Import menu is way to get “stuff” into GSAS-II
  - Phases can also be created using Data/Add Phase & enter structure info manually



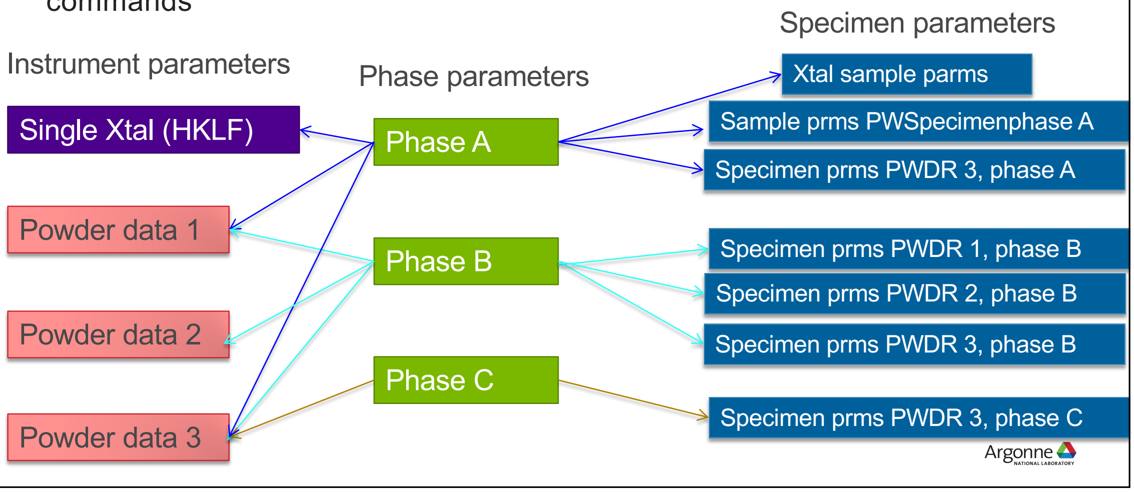
When GSAS-II is started, it loads in importers and exporters and inserts them into the menus.

These are relatively short & simple routines and instructions are provided on how to create them.

PHASES & HISTOGRAMS MUST BE “LINKED” TOGETHER



- For each data set: which phase(s) are present?
  - Can be set as phases or data are read into GSAS-II
  - Can also be set from Phase/Data tab with “Add powder…” or “Add single crystal…” commands



Instrument parameters

Single Xtal (HKLF)

Powder data 1

Powder data 2

Powder data 3

Phase parameters

Phase A

Phase B

Phase C

Specimen parameters

Xtal sample parms

Sample prms PWSpecimenphase A

Specimen prms PWDR 3, phase A

Specimen prms PWDR 1, phase B

Specimen prms PWDR 2, phase B

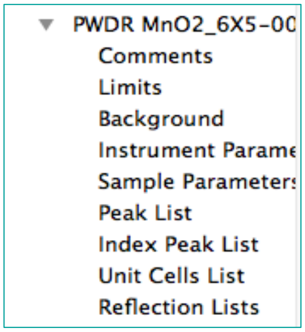
Specimen prms PWDR 3, phase B

Specimen prms PWDR 3, phase C

GSAS-II PARAMETER TYPES

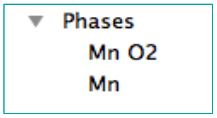
We classify parameters/controls in one of four ways

- Overall controls (one set per project)



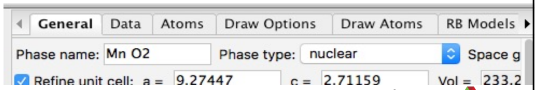
PWDR MnO2_6X5-00
- Comments
- Limits
- Background
- Instrument Parame
- Sample Parameters
- Peak List
- Index Peak List
- Unit Cells List
- Reflection Lists

- Histogram parameters (`:h:<name>`)
  - One set for every histogram (set of data)
  - Parameter set varies with data type
  - Separated into different tree items



Phases
- Mn O2
- Mn

- Phase parameters (`p::<name>`)
  - One set for every phase
  - Separated by type with tabs on window
- Phase*Data parameters (Specimen or HAP terms, `p:h:<name>`)
  - One set for every phase in every histogram; Found under <Phase>/Data tab
  - Specimen-specific things such as size/microstrain broadening, preferred orientation
  - Customization option (Separate HistPhaseTreeItem) to make take these out of Phase and promote to top level in tree



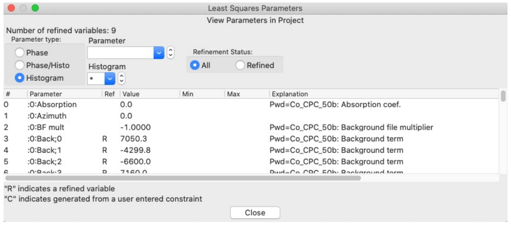
Phase name: Mn O2 Phase type: nuclear Space g

☑ Refine unit cell: a = 9.27447 c = 2.71159 Vol = 233.2

GSAS-II PARAMETER NAMING

- **Every parameter in GSAS-II that can be varied has a unique name of form:**

  <ph>:<hist>:<Name>:<atom#>



Number of refined variables: 9

Parameter type: ○ Phase ○ Phase/Histo ● Histogram

Parameter

Histogram *

Refinement Status: ● All ○ Refined

#	Parameter	Ref	Value	Min	Max	Explanation
0	:0:Absorption		0.0			Pwd=Co_CPC_50b: Absorption coef.
1	:0:Azimuth		0.0			
2	:0:BF mult		-1.0000			Pwd=Co_CPC_50b: Background file multiplier
3	:0:Back;0	R	7050.3			Pwd=Co_CPC_50b: Background term
4	:0:Back;1	R	-4299.8			Pwd=Co_CPC_50b: Background term
5	:0:Back;2	R	-6600.0			Pwd=Co_CPC_50b: Background term
6	:0:Back;3	R	7160.0			Pwd=Co_CPC_50b: Background term

"R" indicates a refined variable
"C" indicates generated from a user entered constraint

- Histogram parameters are named `:h:<name>`

  Example: `:1:Scale` (Scale factor for 2nd histogram)

- Phase parameters are named `p::<name>`

  Example: `0::Vol` (Unit cell volume for 1st phase, N.B. computed from reciprocal cell tensor)

  - Atom parameters are named `p::<name>:n`

    Example: `0::AUiso:0` (Uiso for 1st atom in 1st phase)

- Phase*Data parameters are named `p:h:<name>`
  - Example: `1:0:Scale` (Phase fraction for 2nd phase in 1st histogram)

- To see the parameters listed and explained, use Calculate/"View LS Parameters"

GSAS-II PROFILE MODEL

Isolate sample effects from instrument

Design: instrument parameters (one set for every histogram) are determined once (with a standard) and are never varied for user samples

- Ideal: beamline scientist provides an instrument parameter file
- DIY: fit profile terms to a standard (see tutorial)
- Worst case: fit for histogram, but limited size/microstrain characterization
- When a file is not available, use “Cancel” to get access to default parameter sets
- CW: generate instrument parameter from ”Fundamental Parameters”

Why: When instrumental terms are determined microstrain & crystallite broadening can be varied directly

- microstrain & crystallite broadening terms for each dataset in each phase with choice of varying levels of complexity

- Can you use the old-fashioned approach of refining instrumental terms for each dataset?
  - Yes, but we wish you would not

GSAS-II CW PROFILE TERMS

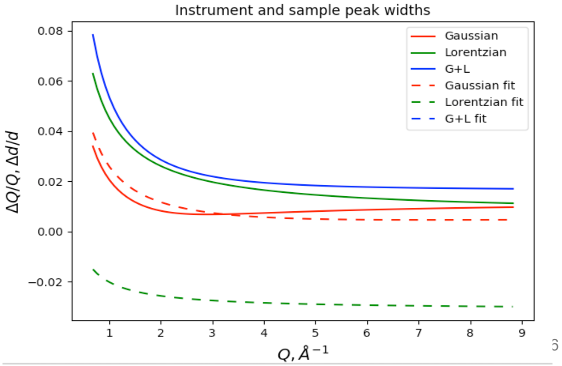
Profile terms are found in <Histogram>/Instrument Parameters

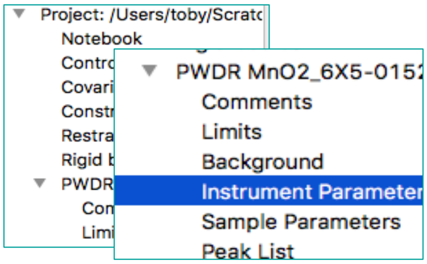
Gaussian: $\sigma^2 = U \tan^2\theta + V \tan\theta + W$

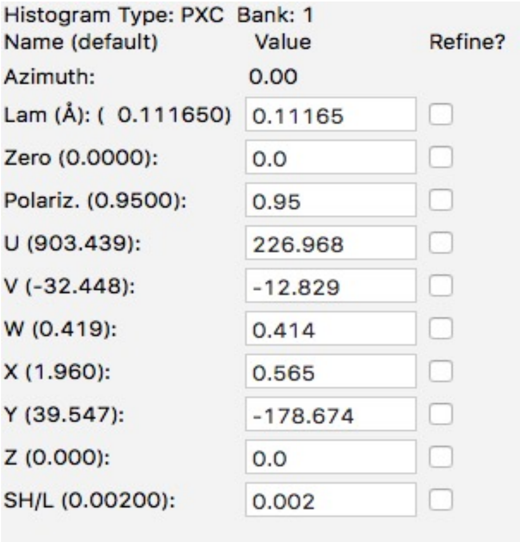
FWHM = $\sigma * (8 \ln 2)^{0.5}$

Lorentzian: FWHM = $X / \cos\theta + Y \tan\theta + Z$

- N.B.: Lam, Z, Zero, Polariz, are rarely refined







Histogram Type: PXC Bank: 1

Name (default)	Value	Refine?
Azimuth:	0.00	
Lam (Å): (0.111650)	0.11165	☐
Zero (0.0000):	0.0	☐
Polariz. (0.9500):	0.95	☐
U (903.439):	226.968	☐
V (-32.448):	-12.829	☐
W (0.419):	0.414	☐
X (1.960):	0.565	☐
Y (39.547):	-178.674	☐
Z (0.000):	0.0	☐
SH/L (0.00200):	0.002	☐

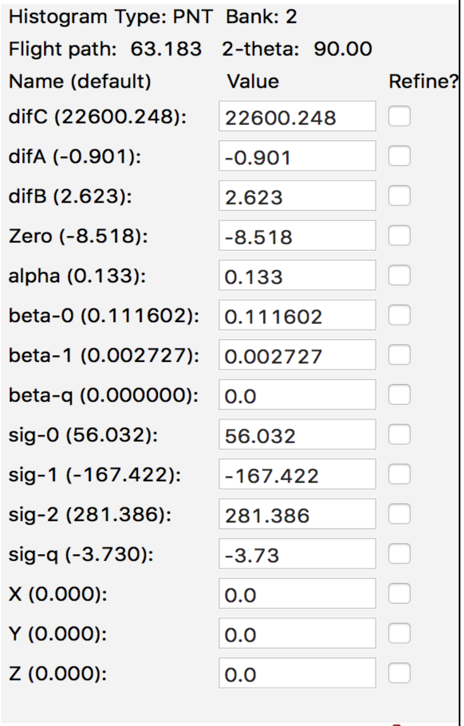
GSAS-II TOF PROFILE TERMS

- TOF (microsec) = Zero + difC*d + difA*d^2 + difB/d

Peak shapes are generated by convolution of double exponential and pseudo-Voigt

- Rise side (alpha): α/d
- Decay side (beta): $\beta_0 + \beta_1{*}d^{-4} + \beta_q{*}d^{-2}$
- Gaussian broadening, sigma,
  - $\sigma = \sigma_0 + \sigma_1{*}d^2 + \sigma_2{*}d^4 + \sigma_q{*}d$
  - FWHM = σ * sqrt (8 ln 2)
- Lorentzian broadening, gamma,
  - $\gamma = Z + X{*}d + Y{*}d^2$

    = FWHM



Histogram Type: PNT Bank: 2
Flight path: 63.183 2-theta: 90.00

Name (default)	Value	Refine?
difC (22600.248):	22600.248	☐
difA (-0.901):	-0.901	☐
difB (2.623):	2.623	☐
Zero (-8.518):	-8.518	☐
alpha (0.133):	0.133	☐
beta-0 (0.111602):	0.111602	☐
beta-1 (0.002727):	0.002727	☐
beta-q (0.000000):	0.0	☐
sig-0 (56.032):	56.032	☐
sig-1 (-167.422):	-167.422	☐
sig-2 (281.386):	281.386	☐
sig-q (-3.730):	-3.73	☐
X (0.000):	0.0	☐
Y (0.000):	0.0	☐
Z (0.000):	0.0	☐

SAMPLE-DEPENDENT BROADENING IS ON DATA TAB OF PHASE ENTRY

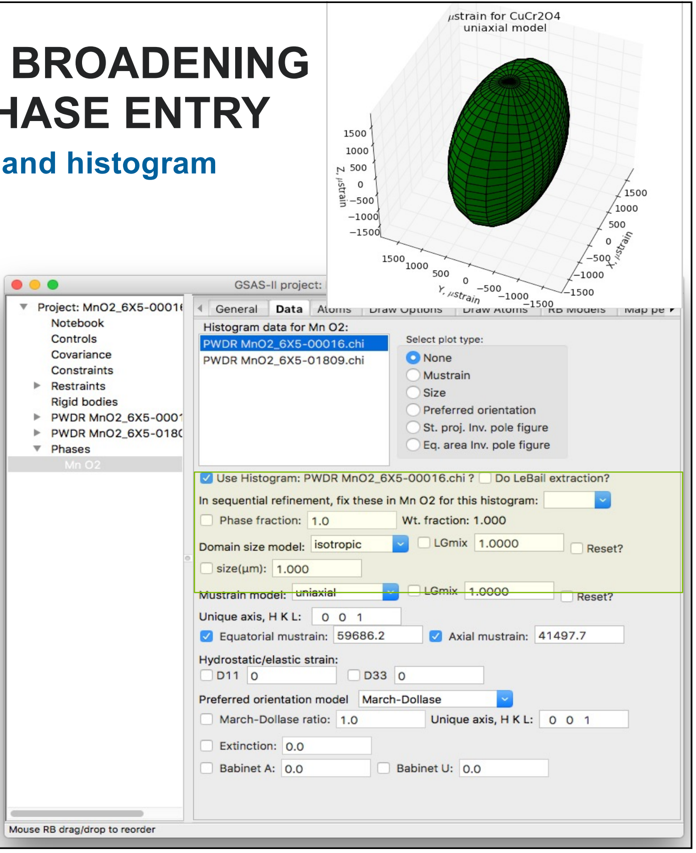
N.B. values vary by both phase and histogram

- Select histogram at top

- Size (in microns) can be
  - Isotropic (single value)
  - Axial (two values and an axis)
  - Ellipsoidal (6 values -- like U_{ij})

- Microstrain ($\Delta Q/Q \times 10^6$)
  - Isotropic (single value)
  - Axial (two values and an axis)
  - General (Stephens model; # of terms depend on Laue class)

N.B. LGmix is amount of Lorentzian vs. Gaussian (usual 1 is best)



Histogram data for Mn O2:
PWDR MnO2_6X5-00016.chi
PWDR MnO2_6X5-01809.chi

Select plot type:
● None
○ Mustrain
○ Size
○ Preferred orientation
○ St. proj. Inv. pole figure
○ Eq. area Inv. pole figure

☑ Use Histogram: PWDR MnO2_6X5-00016.chi ? ☐ Do LeBail extraction?
In sequential refinement, fix these in Mn O2 for this histogram:
☐ Phase fraction: 1.0 Wt. fraction: 1.000
Domain size model: isotropic ☐ LGmix 1.0000 ☐ Reset?
☐ size(μm): 1.000
Mustrain model: uniaxial ☐ LGmix 1.0000 ☐ Reset?
Unique axis, H K L: 0 0 1
☑ Equatorial mustrain: 59686.2 ☑ Axial mustrain: 41497.7
Hydrostatic/elastic strain:
☐ D11 0 ☐ D33 0
Preferred orientation model March-Dollase
☐ March-Dollase ratio: 1.0 Unique axis, H K L: 0 0 1
☐ Extinction: 0.0
☐ Babinet A: 0.0 ☐ Babinet U: 0.0

SEQUENTIAL REFINEMENT IN GSAS-II

GSAS-II offers three modes for fitting to a set of datasets.

- **Combined refinement**: All phases and parameters are adjusted to best fit all the datasets.
  - Any number of phases, any number of datasets; phase parameters will be the same for all datasets (but note use of D_{ij} allows lattice parameters to differ by dataset)
  - Good for multiple measurements under a single set of conditions (or very similar conditions)
- **Sequential refinement:** Each dataset is fit, one-at-a-time, to any number of phases.
  - All parameters are allowed to vary to best-fit each dataset in turn (use of D_{ij} required).
  - Good where there are wide changes in atom positions, phase transformations, etc.

  Sequential Refinement allows for treatment of a large number of datasets in a single project file and with automation.
- **Scripting (new):** allows for algorithmic adaptation; parallelization,… See tutorial or paper.

O'Donnell, J. H., Dreele, R. B. V., Chan, M. K. Y., and Toby, B. H. (**2018**). "A Scripting Interface for GSAS-II," Journal of Applied Crystallography **51**, 1244-1250.

SEQUENTIAL REFINEMENT

SEQUENTIAL REFINEMENT CONCEPT

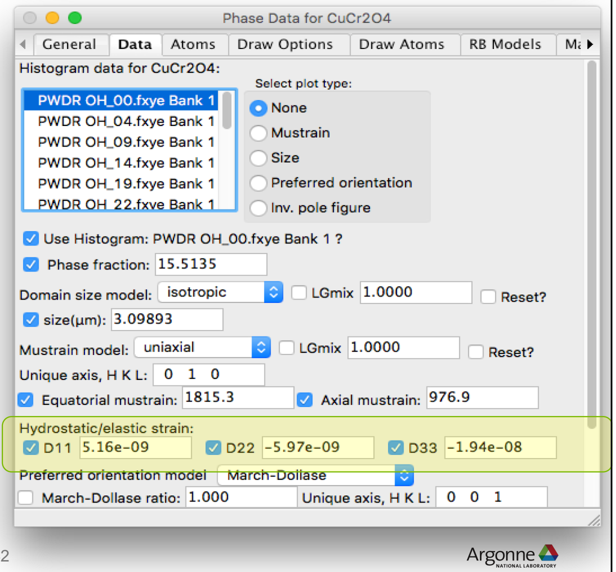
Concept: set up a refinement on the first dataset.

- Repeat that refinement on subsequent datasets varying the same parameters
- When there are changes in the sample that require extra parameters (one example, appearance of a new phase), one can add new parameters for subsequent refinements
- Optional: copy the results from fitting each dataset as the starting point for fitting next (usually a good idea).
  - Only possible when parameters are the same for all datasets in the series
- It is possible to do initial fitting with a subset of patterns in the project file and then go on to a different subset of patterns,…
  - In the end, conduct a sequential fit over all subsets
- Sequential refinements produce a convenient table of results that can be used for plotting of secondary fitting.

Note: ***automation does not lift the requirement that you must think about what you are doing and carefully review results from your fits.***

NOTES ON LATTICE CONSTANTS

- Cell lengths are associated with phases, but are expected to change in a parametric study
  - For each histogram, there are a set of hydrostatic strain tensors; these modify the cell parameters
  - These D_{ij} values must be refined in a sequential fit
- This means one can do a combined fit with lattice constants differing by dataset (histogram) (but all coordinates, Uiso values etc. will be the same)
- One cannot refine unit cell parameters and D_{ij} values for a phase at the same time.



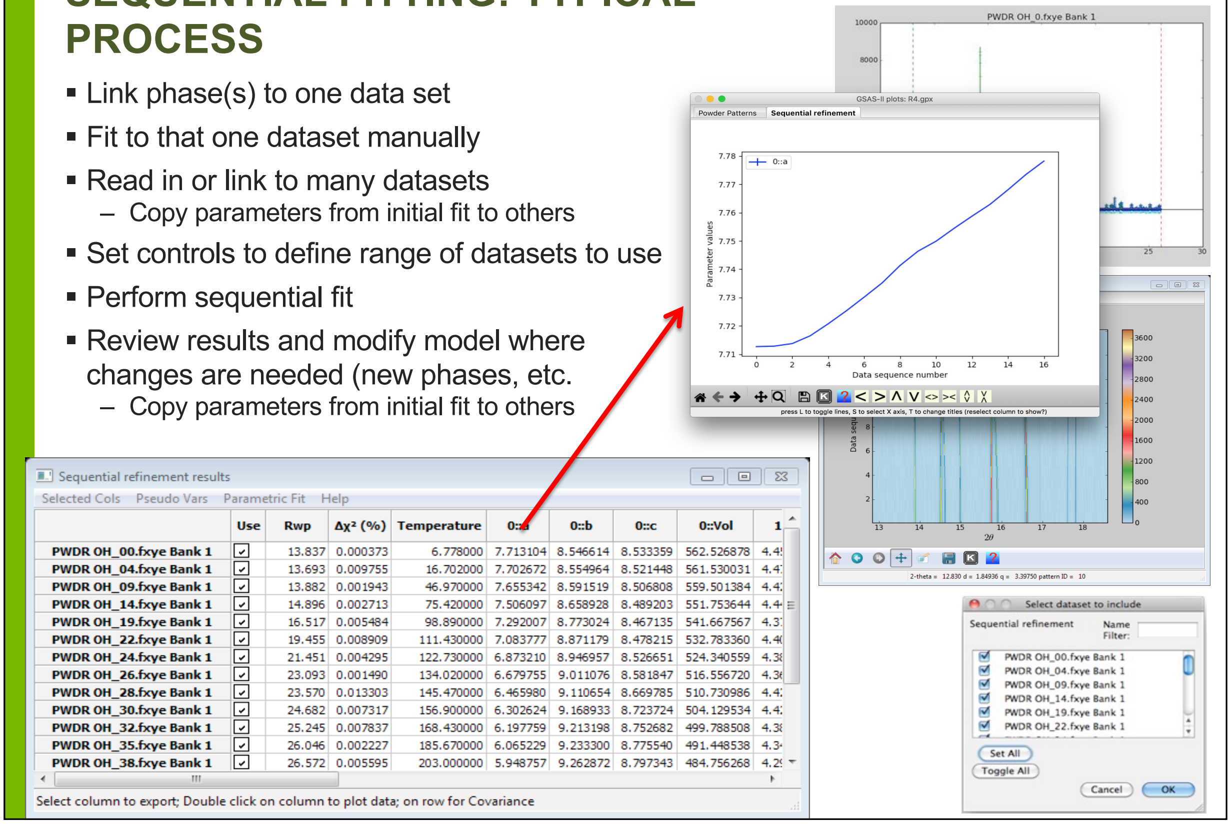
Histogram data for CuCr2O4:

PWDR OH_00.fxye Bank 1
PWDR OH_04.fxye Bank 1
PWDR OH_09.fxye Bank 1
PWDR OH_14.fxye Bank 1
PWDR OH_19.fxye Bank 1
PWDR OH_22.fxye Bank 1

☑ Use Histogram: PWDR OH_00.fxye Bank 1 ?
☑ Phase fraction: 15.5135
Domain size model: isotropic ☐ LGmix 1.0000 ☐ Reset?
☑ size(µm): 3.09893
Mustrain model: uniaxial ☐ LGmix 1.0000 ☐ Reset?
Unique axis, H K L: 0 1 0
☑ Equatorial mustrain: 1815.3 ☑ Axial mustrain: 976.9
Hydrostatic/elastic strain:
☑ D11 5.16e-09 ☑ D22 -5.97e-09 ☑ D33 -1.94e-08
Preferred orientation model March-Dollase
☐ March-Dollase ratio: 1.000 Unique axis, H K L: 0 0 1

SEQUENTIAL FITTING: TYPICAL PROCESS

- Link phase(s) to one data set
- Fit to that one dataset manually
- Read in or link to many datasets
  - Copy parameters from initial fit to others
- Set controls to define range of datasets to use
- Perform sequential fit
- Review results and modify model where changes are needed (new phases, etc.
  - Copy parameters from initial fit to others



press L to toggle lines, S to select X axis, T to change titles (reselect column to show?)

2-theta = 12.830 d = 1.84936 q = 3.39750 pattern ID = 10

	Use	Rwp	Δχ² (%)	Temperature	0::a	0::b	0::c	0::Vol	1
PWDR OH_00.fxye Bank 1	☑	13.837	0.000373	6.778000	7.713104	8.546614	8.533359	562.526878	4.4
PWDR OH_04.fxye Bank 1	☑	13.693	0.009755	16.702000	7.702672	8.554964	8.521448	561.530031	4.4
PWDR OH_09.fxye Bank 1	☑	13.882	0.001943	46.970000	7.655342	8.591519	8.506808	559.501384	4.4
PWDR OH_14.fxye Bank 1	☑	14.896	0.002713	75.420000	7.506097	8.658928	8.489203	551.753644	4.4
PWDR OH_19.fxye Bank 1	☑	16.517	0.005484	98.890000	7.292007	8.773024	8.467135	541.667567	4.3
PWDR OH_22.fxye Bank 1	☑	19.455	0.008909	111.430000	7.083777	8.871179	8.478215	532.783360	4.4
PWDR OH_24.fxye Bank 1	☑	21.451	0.004295	122.730000	6.873210	8.946957	8.526651	524.340559	4.3
PWDR OH_26.fxye Bank 1	☑	23.093	0.001490	134.020000	6.679755	9.011076	8.581847	516.556720	4.3
PWDR OH_28.fxye Bank 1	☑	23.570	0.013303	145.470000	6.465980	9.110654	8.669785	510.730986	4.4
PWDR OH_30.fxye Bank 1	☑	24.682	0.007317	156.900000	6.302624	9.168933	8.723724	504.129534	4.4
PWDR OH_32.fxye Bank 1	☑	25.245	0.007837	168.430000	6.197759	9.213198	8.752682	499.788508	4.3
PWDR OH_35.fxye Bank 1	☑	26.046	0.002227	185.670000	6.065229	9.233300	8.775540	491.448538	4.3
PWDR OH_38.fxye Bank 1	☑	26.572	0.005595	203.000000	5.948757	9.262872	8.797343	484.756268	4.2

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

Select dataset to include

Sequential refinement

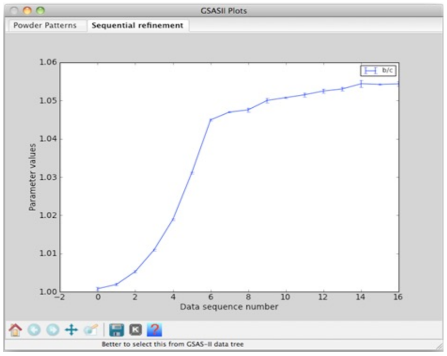
Name Filter:

- ☑ PWDR OH_00.fxye Bank 1
- ☑ PWDR OH_04.fxye Bank 1
- ☑ PWDR OH_09.fxye Bank 1
- ☑ PWDR OH_14.fxye Bank 1
- ☑ PWDR OH_19.fxye Bank 1
- ☑ PWDR OH_22.fxye Bank 1

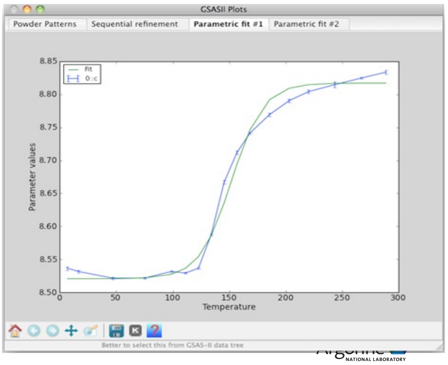
Set All · Toggle All · Cancel · OK

EQUATION OF STATE (PARAMETRIC) FITTING

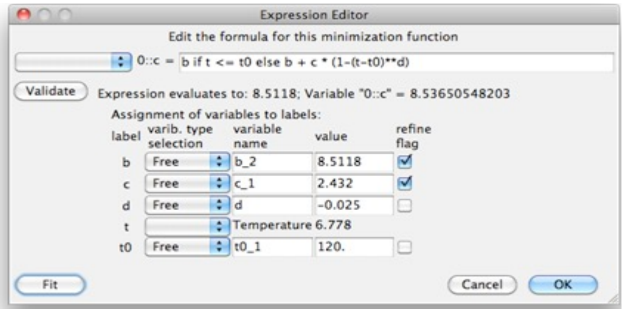
- New parameters may be described as functions of existing variables and values (Pseudo Vars)
  - Function is defined in Python allowing completely arbitrary, non-linear expressions
  - Covariance is properly used to estimate uncertainties on pseudo vars
- Variables and pseudo vars may be plotted
- Arbitrary parametric functions may be fit to variables and pseudo vars
  - Uncertainties properly used in weighting
  - Fit values may be shared across multiple parametric functions



Better to select this from GSAS-II data tree



Better to select this from GSAS-II data tree



Edit the formula for this minimization function

0::c = b if t <= t0 else b + c * (1-(t-t0)**d)

Expression evaluates to: 8.5118; Variable "0::c" = 8.53650548203

Assignment of variables to labels:

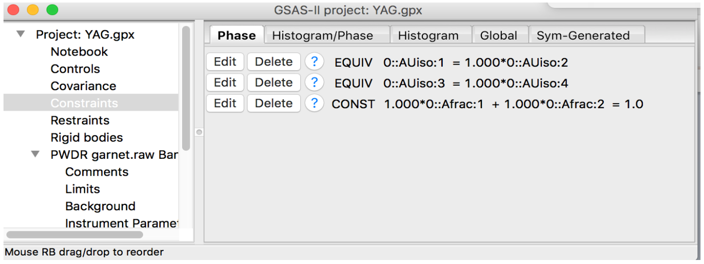
label	varib. type selection	variable name	value	refine flag
b	Free	b_2	8.5118	☑
c	Free	c_1	2.432	☑
d	Free	d	-0.025	☐
t		Temperature 6.778		
t0	Free	t0_1	120.	☐

OTHER UNIQUE CAPABILITIES

GSAS-II CONSTRAINT CLASSES

GSAS-II has many types of constraints:

- Phase (interrelating atom parameters, sample values,…)
- Histogram (interrelating instrumental profile, scale factor…)
- Specimen (Histogram*Phase) (interrelating microstrain, crystallite size…)
- Global (parameters independent of phase or histogram)
- Symmetry-Generated (on cell and atom parameters, read-only)



```
EQUIV  0::AUiso:1  = 1.000*0::AUiso:2
EQUIV  0::AUiso:3  = 1.000*0::AUiso:4
CONST  1.000*0::Afrac:1  + 1.000*0::Afrac:2  = 1.0
```

Rigid body constraints are implemented with a comprehensive GUI for defining them (see tutorial)

GSAS-II CONSTRAINT TYPES

Constraints come in four flavors

- Holds: This prevents a named parameter from changing, for example to keep the z value for an atom from shifting even though the coordinates are varied.
  - Hold dAz for O5, phase 0
- Equivalence: This “chains together” multiple parameters so that one variable determines several parameters
  - Uiso for atom 1 = Uiso for atom 2 = 0.5 * Uiso for atom 3…
- Constraint: This defines that a set of parameters must add up to a constant
  - Frac(atom 1) + Frac(atom 2) + Frac(atom 3) = 1.0

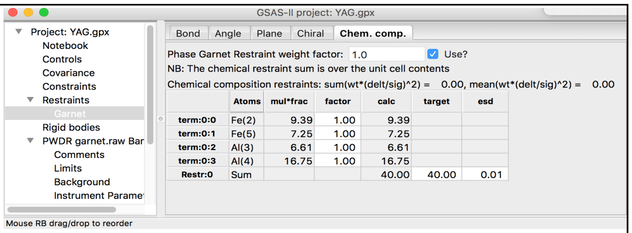
    In this example, three degrees of freedom have been lowered to two via this constraint
- New Variable:
  - Frac for atom 1 + Frac for atom 2 + Frac for atom 3 = new variable

    This will allow definition of distortion mode(s), based on representational analysis

These constraints can be combined and mixed as long as the equations are internally consistent. Example:

- Frac(atom 1) + Frac(atom 2) + Frac(atom 3) = 1.0
- Frac(atom 1) = Frac(atom 2)
  - This leaves a single degree of freedom

GSAS-II RESTRAINTS



Phase Garnet Restraint weight factor: 1.0 ☑ Use?

NB: The chemical restraint sum is over the unit cell contents

Chemical composition restraints: sum(wt*(delt/sig)^2) = 0.00, mean(wt*(delt/sig)^2) = 0.00

	Atoms	mul*frac	factor	calc	target	esd
term:0:0	Fe(2)	9.39	1.00	9.39		
term:0:1	Fe(5)	7.25	1.00	7.25		
term:0:2	Al(3)	6.61	1.00	6.61		
term:0:3	Al(4)	16.75	1.00	16.75		
Restr:0	Sum			40.00	40.00	0.01

GSAS-II allows restraints to be placed on interatomic distances and angles, most commonly used for bonded atoms.

- A target value and uncertainty is supplied for each noted distance/angle
- An overall weight is supplied for all distance and all angle restraints
- The goodness of fit gets worse as the distance or angle deviates from the target value supplied in the restraint
- Note that since there may be only a handful of restraints and 10^5 powder data points, a very large weight may be needed in the initial stages of a refinement so that the restraints count for a significant part of the GOF

Chemical compositional restraints can be used to “push” a refinement to match a chemical analysis result (for example an overall composition) or charge balance,…

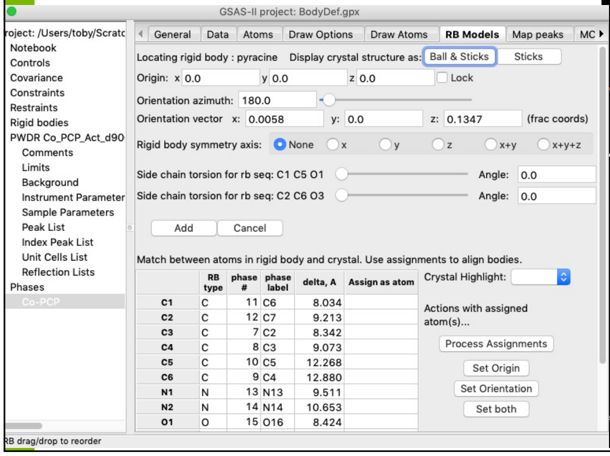
Other types of restraints (plane and chiral) are most commonly used for biomolecules.

Generalized (DIY) allows any arbitrary function of parameters to be defined

RIGID BODIES IN GSAS-II

Allow simplification of structural models
Enhanced with extensive graphics

- Rigid bodies fix relative positions of atoms, but torsion refinement is possible
- RB's have a single origin quaternion for positioning (max 6 params)
  - have grouped ADP (simple or TLS) & occupancy fitting



GSAS-II project: BodyDef.gpx

Locating rigid body : pyracine Display crystal structure as: Ball & Sticks

Origin: x 0.0 y 0.0 z 0.0 ☐ Lock

Orientation azimuth: 180.0

Orientation vector x: 0.0058 y: 0.0 z: 0.1347 (frac coords)

Rigid body symmetry axis: ● None ○ x ○ y ○ z ○ x+y ○ x+y+z

Side chain torsion for rb seq: C1 C5 O1 Angle: 0.0

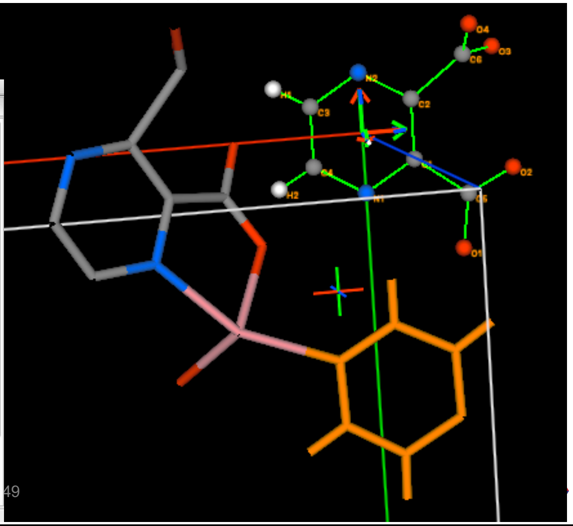
Side chain torsion for rb seq: C2 C6 O3 Angle: 0.0

Match between atoms in rigid body and crystal. Use assignments to align bodies.

	RB type	phase #	phase label	delta, A	Assign as atom
C1	C	11	C6	8.034	
C2	C	12	C7	9.213	
C3	C	7	C2	8.342	
C4	C	8	C3	9.073	
C5	C	10	C5	12.268	
C6	C	9	C4	12.880	
N1	N	13	N13	9.511	
N2	N	14	N14	10.653	
O1	O	15	O16	8.424	

Crystal Highlight:

Actions with assigned atom(s)...



MUCH OF GSAS-II CAN BE ACCESSED FROM PYTHON SCRIPTS

All features in GSAS-II are available from the GUI; increasing amounts of the capabilities are designed to be used from Python scripts

The GSASIIscriptable module provides access to key parts of the GSAS-II code

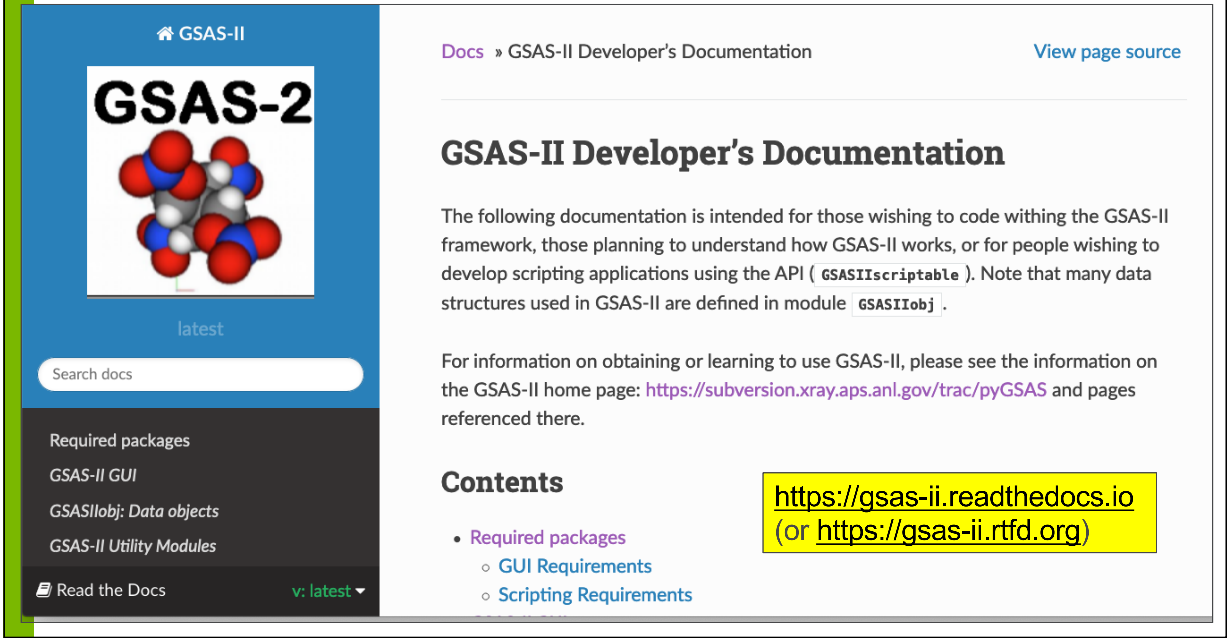
Example:

- Script to simulate a diffraction pattern

```
import os,sys
sys.path.insert(0,'/Users/toby/software/G2/GSASII')
import GSASIIscriptable as G2sc
datadir = "/Users/toby/software/G2/Tutorials/PythonScript/data"
PathWrap = lambda fil: os.path.join(datadir,fil)
gpx = G2sc.G2Project(filename='PbSO4sim.gpx') # create a project
phase0 = gpx.add_phase(PathWrap("PbSO4-Wyckoff.cif"),
         phasename="PbSO4",fmthint='CIF') # add a phase to the project
# add a simulated histogram and link it to the previous phase(s)
hist1 = gpx.add_simulated_powder_histogram("PbSO4 simulation",
            PathWrap("inst_d1a.prm"),5.,120.,Npoints=1000,
            phases=gpx.phases(),scale=500000.)
gpx.do_refinements()   # calculate pattern
gpx.save()
# save results
gpx.histogram(0).Export('PbSO4data','.csv','hist') # data
gpx.histogram(0).Export('PbSO4refl','.csv','refl') # reflections
```

EXTENSIVE CODE DOCUMENTATION

Currently the documentation is ~400 pages (in PDF), including extensive indices



GSAS-II Developer's Documentation

The following documentation is intended for those wishing to code withing the GSAS-II framework, those planning to understand how GSAS-II works, or for people wishing to develop scripting applications using the API (`GSASIIscriptable`). Note that many data structures used in GSAS-II are defined in module `GSASIIobj` .

For information on obtaining or learning to use GSAS-II, please see the information on the GSAS-II home page: https://subversion.xray.aps.anl.gov/trac/pyGSAS and pages referenced there.

Contents

- Required packages
  - GUI Requirements
  - Scripting Requirements

https://gsas-ii.readthedocs.io
(or https://gsas-ii.rtfd.org)

SPACE GROUP TRANSFORMATIONS IN GSAS-II, INCLUDING MAGNETISM

GSAS-II USES BNS COLOR SPACE GROUPS TO DESCRIBE MAGNETIC STRUCTURES

- OG – Opechowski-Guccione(1965): 1651 unique magnetic space groups in book (Litvin, 2013 available on line from IUCr; NB: >11,000 pages!). 1651 = 1191magnetic+230 gray+230 nonmagnetic groups. 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 uses group theory to interpret space group symbols, which allows for interpretation of non-standard settings (e.g. “F d” – a variant of Cc; inconsistent symbols 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.

MAGNETIC SYMMETRY IN GSAS-II

BNS Symbol driven; Always 2nd Origin setting (if appropriate)

- For magnetism:
  - 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)

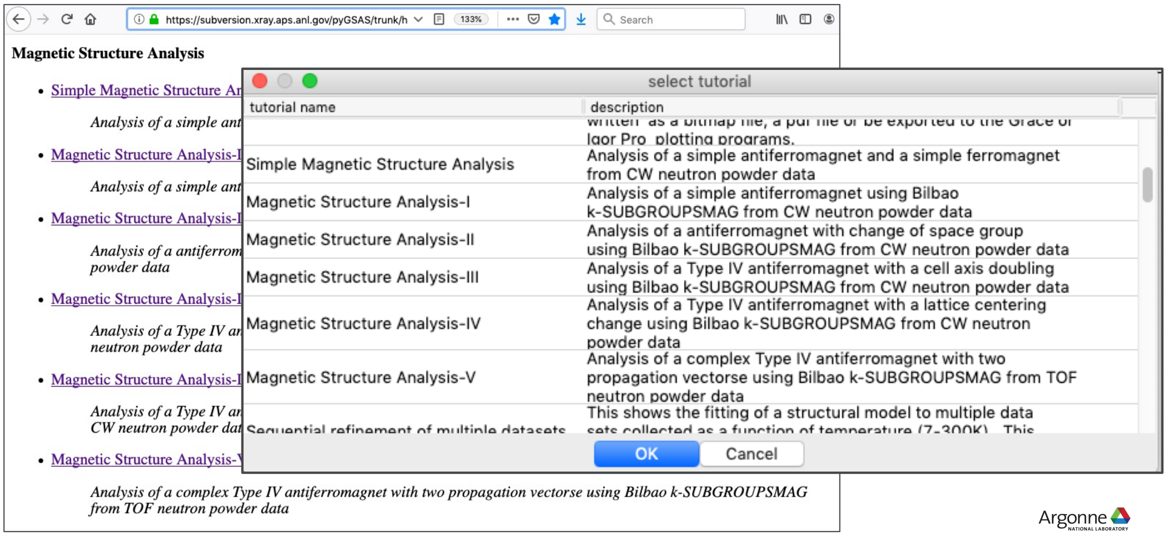
- When BNS space group is generated by transform from chemical cell, it can be changed after input
  - Generates BNS symbol for standard and non-standard space group settings

- GSAS-II Magnetic moments: components along crystal axes
  - Units: Bohr magnetons.
  - (NB: old GSAS used Cartesian magnetic moment components)

TO LEARN HOW TO PERFORM MAGNETIC REFINEMENTS, SEE TUTORIALS

6 tutorials cover different

- See tutorials in Help menu
- or http://bit.ly/GSASIItutorials (https://subversion.xray.aps.anl.gov/pyGSAS/trunk/help/Tutorials.html)



Magnetic Structure Analysis

- Simple Magnetic Structure An

  Analysis of a simple ant
- Magnetic Structure Analysis-I

  Analysis of a simple ant
- Magnetic Structure Analysis-I

  Analysis of a antiferrom powder data
- Magnetic Structure Analysis-I

  Analysis of a Type IV an neutron powder data
- Magnetic Structure Analysis-I

  Analysis of a Type IV an CW neutron powder dat
- Magnetic Structure Analysis-V

  Analysis of a complex Type IV antiferromagnet with two propagation vectorse using Bilbao k-SUBGROUPSMAG from TOF neutron powder data

tutorial name	description
	written as a bitmap file, a pdf file or be exported to the Grace or Igor Pro plotting programs.
Simple Magnetic Structure Analysis	Analysis of a simple antiferromagnet and a simple ferromagnet from CW neutron powder data
Magnetic Structure Analysis-I	Analysis of a simple antiferromagnet using Bilbao k-SUBGROUPSMAG from CW neutron powder data
Magnetic Structure Analysis-II	Analysis of a antiferromagnet with change of space group using Bilbao k-SUBGROUPSMAG from CW neutron powder data
Magnetic Structure Analysis-III	Analysis of a Type IV antiferromagnet with a cell axis doubling using Bilbao k-SUBGROUPSMAG from CW neutron powder data
Magnetic Structure Analysis-IV	Analysis of a Type IV antiferromagnet with a lattice centering change using Bilbao k-SUBGROUPSMAG from CW neutron powder data
Magnetic Structure Analysis-V	Analysis of a complex Type IV antiferromagnet with two propagation vectorse using Bilbao k-SUBGROUPSMAG from TOF neutron powder data
Sequential refinement of multiple datasets	This shows the fitting of a structural model to multiple data sets collected as a function of temperature (7-300K). This

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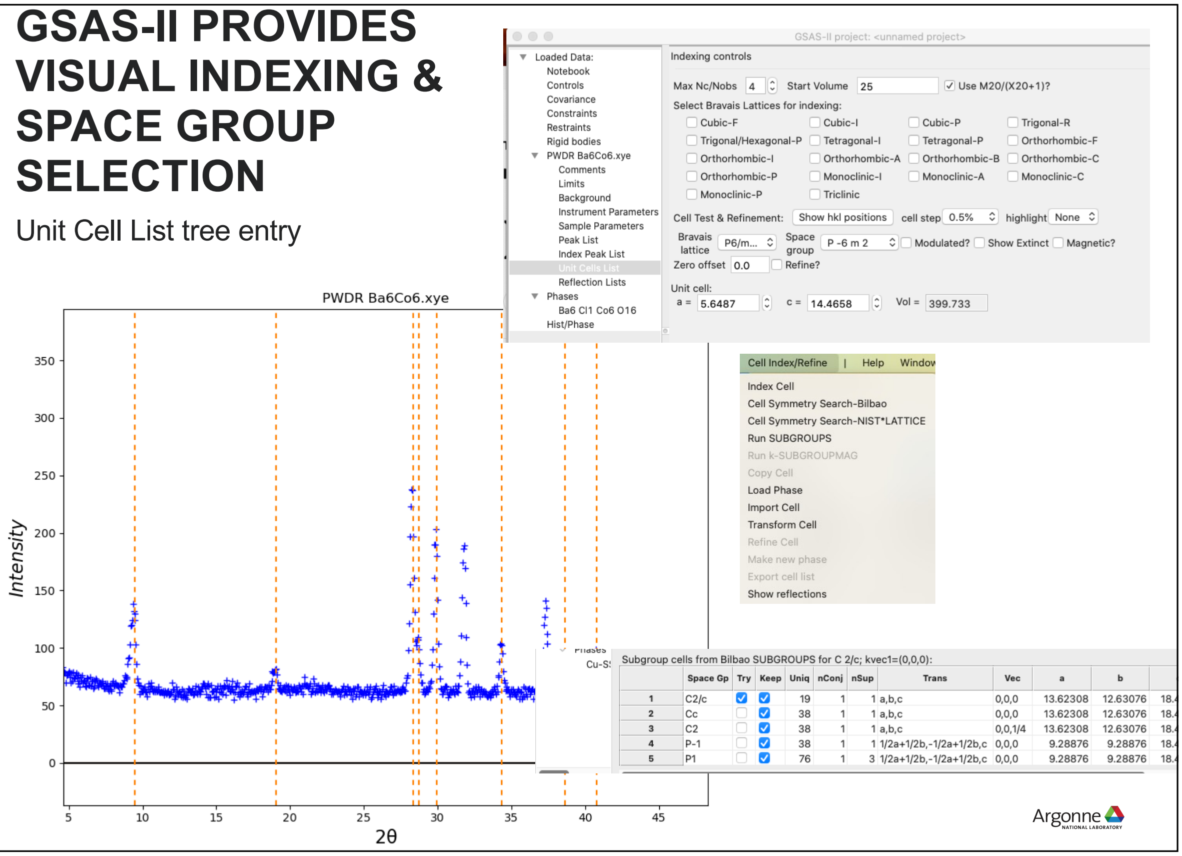
GSAS-II PROVIDES VISUAL INDEXING & SPACE GROUP SELECTION

Unit Cell List tree entry



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/Hexagonal-P ☐ Tetragonal-I ☐ Tetragonal-P ☐ Orthorhombic-F
☐ Orthorhombic-I ☐ Orthorhombic-A ☐ Orthorhombic-B ☐ Orthorhombic-C
☐ Orthorhombic-P ☐ Monoclinic-I ☐ Monoclinic-A ☐ Monoclinic-C
☐ Monoclinic-P ☐ Triclinic

Cell Test & Refinement: Show hkl positions cell step 0.5% highlight None

Bravais lattice P6/m... Space group P -6 m 2 ☐ Modulated? ☐ Show Extinct ☐ Magnetic?

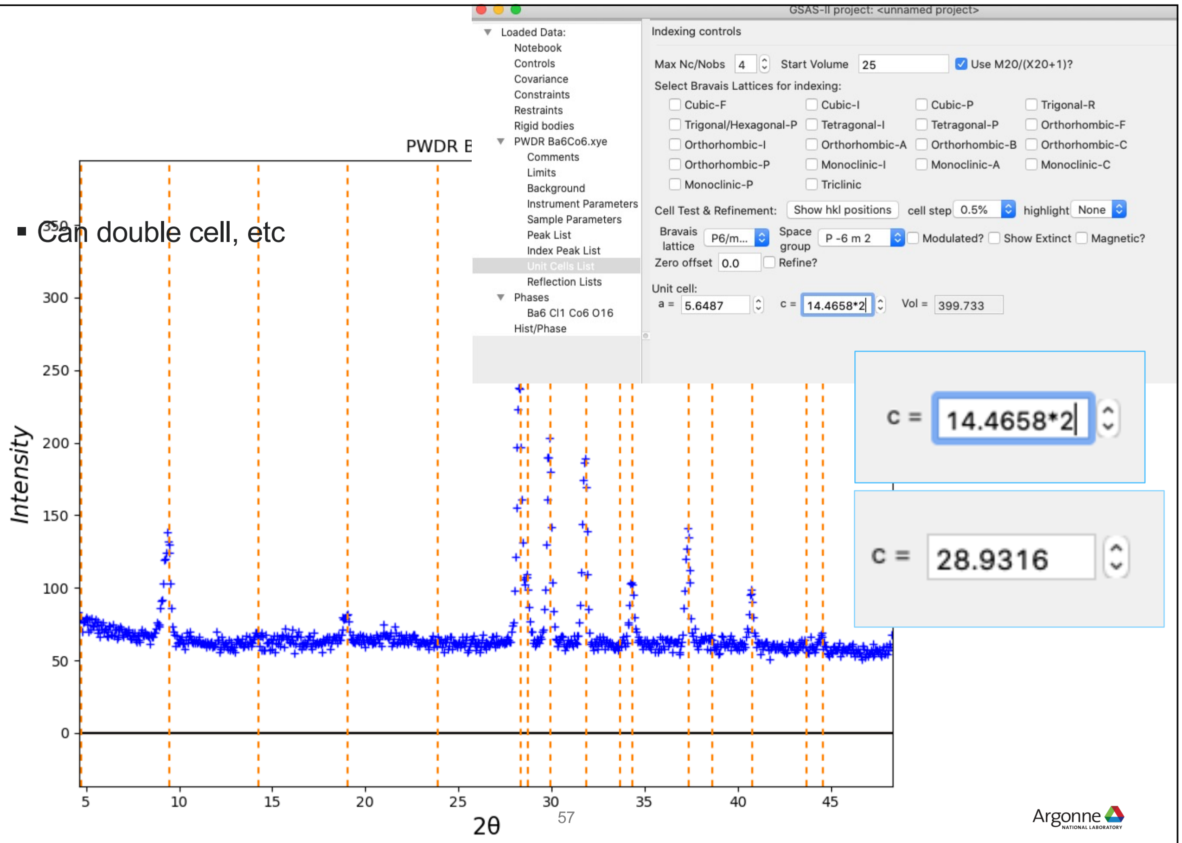
Zero offset 0.0 ☐ Refine?

Unit cell:
a = 5.6487 c = 14.4658 Vol = 399.733

Subgroup cells from Bilbao SUBGROUPS for C 2/c; kvec1=(0,0,0):

	Space Gp	Try	Keep	Uniq	nConj	nSup	Trans	Vec	a	b	
1	C2/c	☑	☑	19	1	1	a,b,c	0,0,0	13.62308	12.63076	18.4
2	Cc	☐	☑	38	1	1	a,b,c	0,0,0	13.62308	12.63076	18.4
3	C2	☐	☑	38	1	1	a,b,c	0,0,1/4	13.62308	12.63076	18.4
4	P-1	☐	☑	38	1	1	1/2a+1/2b,-1/2a+1/2b,c	0,0,0	9.28876	9.28876	18.4
5	P1	☐	☑	76	1	3	1/2a+1/2b,-1/2a+1/2b,c	0,0,0	9.28876	9.28876	18.4

- Can double cell, etc



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/Hexagonal-P ☐ Tetragonal-I ☐ Tetragonal-P ☐ Orthorhombic-F
☐ Orthorhombic-I ☐ Orthorhombic-A ☐ Orthorhombic-B ☐ Orthorhombic-C
☐ Orthorhombic-P ☐ Monoclinic-I ☐ Monoclinic-A ☐ Monoclinic-C
☐ Monoclinic-P ☐ Triclinic

Cell Test & Refinement: Show hkl positions cell step 0.5% highlight None

Bravais lattice P6/m... Space group P -6 m 2 ☐ Modulated? ☐ Show Extinct ☐ Magnetic?

Zero offset 0.0 ☐ Refine?

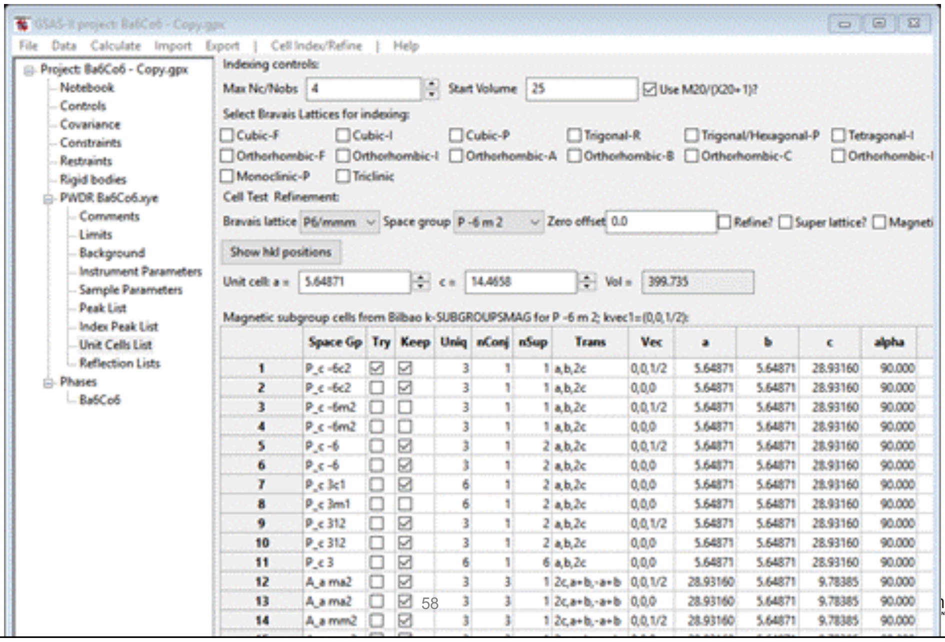
Unit cell:
a = 5.6487 c = 14.4658*2 Vol = 399.733

c = 14.4658*2

c = 28.9316

CAN VIEW EXTINCTIONS FOR SELECTED BNS SPACE GROUP

After calling Bilboa k-SUBGROUPMAG to generate list



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/Hexagonal-P ☐ Tetragonal-I
☐ Orthorhombic-F ☐ Orthorhombic-I ☐ Orthorhombic-A ☐ Orthorhombic-B ☐ Orthorhombic-C ☐ Orthorhombic-I
☐ Monoclinic-P ☐ Triclinic

Cell Test Refinement:

Bravais lattice P6/mmm Space group P -6 m 2 Zero offset 0.0 ☐ Refine? ☐ Super lattice? ☐ Magneti

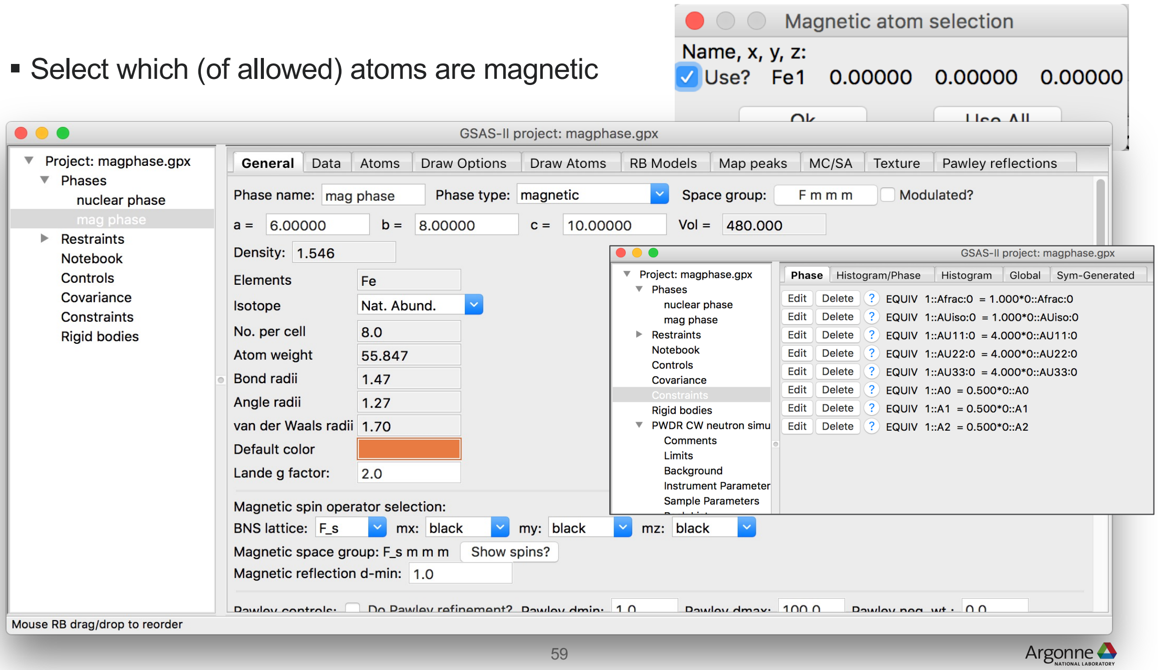
Unit cell: a = 5.64871 c = 14.4658 Vol = 399.735

Magnetic subgroup cells from Bilbao k-SUBGROUPSMAG for P -6 m 2; kvec1=(0,0,1/2):

	Space Gp	Try	Keep	Uniq	nConj	nSup	Trans	Vec	a	b	c	alpha
1	P_c -6c2	☑	☑	3	1	1	a,b,2c	0,0,1/2	5.64871	5.64871	28.93160	90.000
2	P_c -6c2	☐	☑	3	1	1	a,b,2c	0,0,0	5.64871	5.64871	28.93160	90.000
3	P_c -6m2	☐	☐	3	1	1	a,b,2c	0,0,1/2	5.64871	5.64871	28.93160	90.000
4	P_c -6m2	☐	☐	3	1	1	a,b,2c	0,0,0	5.64871	5.64871	28.93160	90.000
5	P_c -6	☐	☑	3	1	2	a,b,2c	0,0,1/2	5.64871	5.64871	28.93160	90.000
6	P_c -6	☐	☑	3	1	2	a,b,2c	0,0,0	5.64871	5.64871	28.93160	90.000
7	P_c 3c1	☐	☑	6	1	2	a,b,2c	0,0,0	5.64871	5.64871	28.93160	90.000
8	P_c 3m1	☐	☐	6	1	2	a,b,2c	0,0,0	5.64871	5.64871	28.93160	90.000
9	P_c 312	☐	☑	3	1	2	a,b,2c	0,0,1/2	5.64871	5.64871	28.93160	90.000
10	P_c 312	☐	☑	3	1	2	a,b,2c	0,0,0	5.64871	5.64871	28.93160	90.000
11	P_c 3	☐	☑	6	1	6	a,b,2c	0,0,0	5.64871	5.64871	28.93160	90.000
12	A_a ma2	☐	☑	3	3	1	2c,a+b,-a+b	0,0,1/2	28.93160	5.64871	9.78385	90.000
13	A_a ma2	☐	☑	3	3	1	2c,a+b,-a+b	0,0,0	28.93160	5.64871	9.78385	90.000
14	A_a mm2	☐	☑	3	3	1	2c,a+b,-a+b	0,0,1/2	28.93160	5.64871	9.78385	90.000

TRANSFORM CREATES A 2ND (MAGNETIC) PHASE

- Select which (of allowed) atoms are magnetic



Magnetic atom selection

Name, x, y, z:

☑ Use? Fe1 0.00000 0.00000 0.00000

GSAS-II project: magphase.gpx

Phase name: mag phase
Phase type: magnetic
Space group: F m m m
☐ Modulated?
a = 6.00000 b = 8.00000 c = 10.00000 Vol = 480.000
Density: 1.546

Elements	Fe
Isotope	Nat. Abund.
No. per cell	8.0
Atom weight	55.847
Bond radii	1.47
Angle radii	1.27
van der Waals radii	1.70
Default color	🟧
Lande g factor:	2.0

Magnetic spin operator selection:
BNS lattice: F_s mx: black my: black mz: black
Magnetic space group: F_s m m m
Magnetic reflection d-min: 1.0

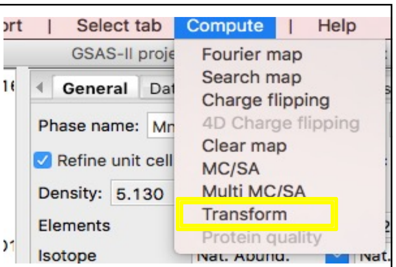
GSAS-II project: magphase.gpx

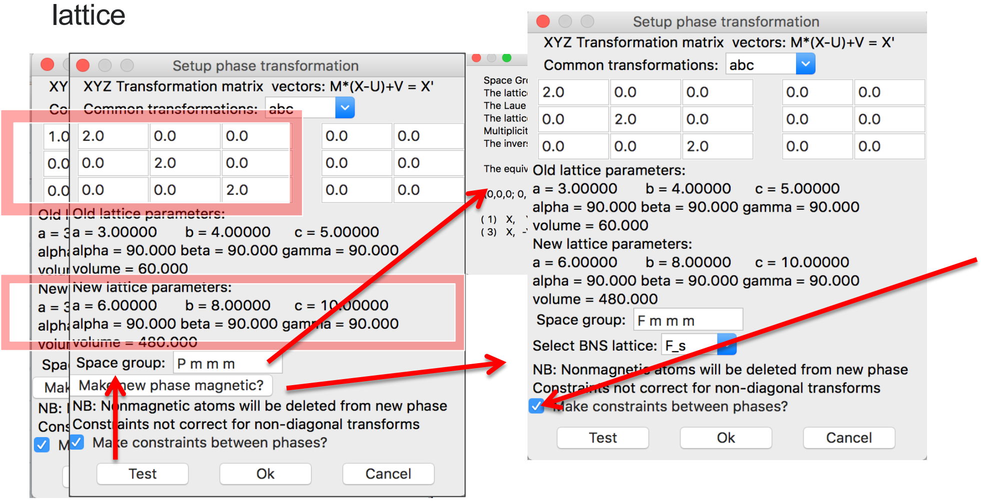
EQUIV 1::Afrac:0 = 1.000*0::Afrac:0
EQUIV 1::AUiso:0 = 1.000*0::AUiso:0
EQUIV 1::AU11:0 = 4.000*0::AU11:0
EQUIV 1::AU22:0 = 4.000*0::AU22:0
EQUIV 1::AU33:0 = 4.000*0::AU33:0
EQUIV 1::A0 = 0.500*0::A0
EQUIV 1::A1 = 0.500*0::A1
EQUIV 1::A2 = 0.500*0::A2

TRANSFORM PHASE

Transform phase is a general purpose tool with specific magnetic capabilities

- Phase/General tab: Compute/Transform provides mechanism for converting chemical structure to magnetic lattice





Setup phase transformation

XYZ Transformation matrix vectors: M*(X-U)+V = X'
Common transformations: abc

2.0	0.0	0.0	0.0	0.0
0.0	2.0	0.0	0.0	0.0
0.0	0.0	2.0	0.0	0.0

Old lattice parameters:
a = 3.00000 b = 4.00000 c = 5.00000
alpha = 90.000 beta = 90.000 gamma = 90.000
volume = 60.000
New lattice parameters:
a = 6.00000 b = 8.00000 c = 10.00000
alpha = 90.000 beta = 90.000 gamma = 90.000
volume = 480.000
Space group: P m m m
☐ Make new phase magnetic?
NB: Nonmagnetic atoms will be deleted from new phase
Constraints not correct for non-diagonal transforms
☑ Make constraints between phases?

Setup phase transformation

XYZ Transformation matrix vectors: M*(X-U)+V = X'
Common transformations: abc

2.0	0.0	0.0	0.0	0.0
0.0	2.0	0.0	0.0	0.0
0.0	0.0	2.0	0.0	0.0

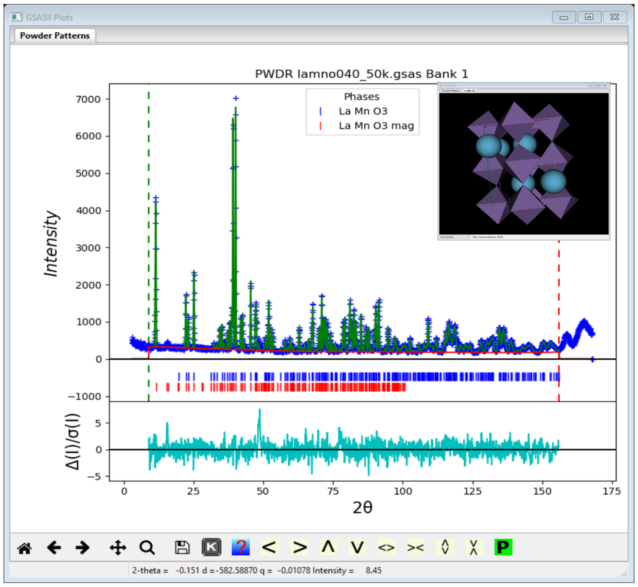
Old lattice parameters:
a = 3.00000 b = 4.00000 c = 5.00000
alpha = 90.000 beta = 90.000 gamma = 90.000
volume = 60.000
New lattice parameters:
a = 6.00000 b = 8.00000 c = 10.00000
alpha = 90.000 beta = 90.000 gamma = 90.000
volume = 480.000
Space group: F m m m
Select BNS lattice: F_s
NB: Nonmagnetic atoms will be deleted from new phase
Constraints not correct for non-diagonal transforms
☑ Make constraints between phases?

Ensures lattice constants and magnetic atoms stay "locked"

MAGNETIC STRUCTURE ANALYSIS IN GSAS-II

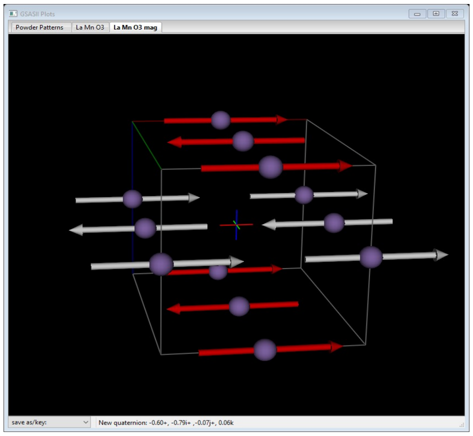
Magnetic Rietveld refinement – 2 phase

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



```
2-theta =   -0.151 d =-582.58870 q =  -0.01078 Intensity =    8.45
```

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



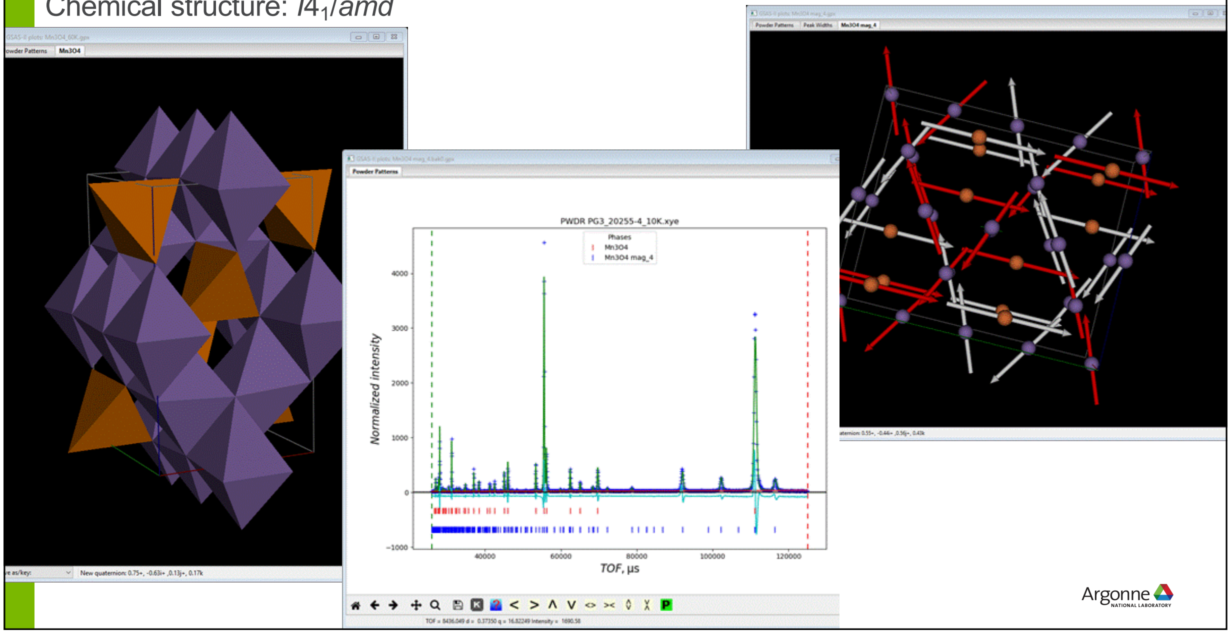
```
New quaternion: -0.60+, -0.79i+ ,-0.07j+, 0.06k
```

POWGEN DATA EXAMPLE

Magnetic Structures in GSAS-II - Tutorial V
Mn_3O_4 (hausmannite)

Chemical structure: *I*4$_1$/*amd*

10 K: *Pbn’a’*



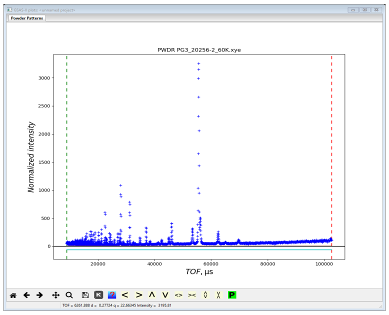
```
New quaternion: 0.75+, -0.63i+ ,0.13j+, 0.17k
```

MAGNETIC STRUCTURE DETERMINATION IN GSAS-II: PRELIMINARIES

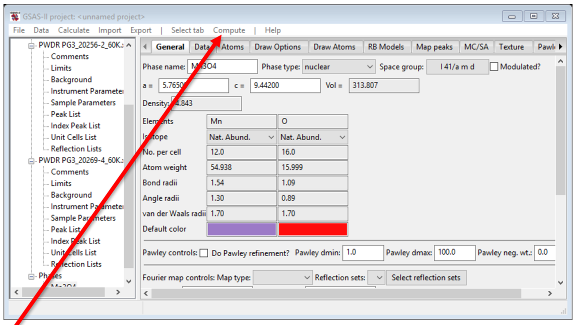
START: DATA & CHEMICAL STRUCTURE

Tutorial: Magnetic Structures in GSAS-II – V (most complex case) Mn_3O_4 – hausmannite – POWGEN data

Import data (as topas file; x,y,e table @60K) & import chemical structure (cif file)



TOF = 6261.888 d = 0.27724 q = 22.66345 Intensity = 3195.81



Phase name: Mn3O4 Phase type: nuclear Space group: I 41/a m d ☐ Modulated?

a = 5.7650 c = 9.44200 Vol = 313.807

Density: 4.843

Elements	Mn	O
Isotope	Nat. Abund.	Nat. Abund.
No. per cell	12.0	16.0
Atom weight	54.938	15.999
Bond radii	1.54	1.09
Angle radii	1.30	0.89
van der Waals radii	1.70	1.70
Default color	🟪	🟥

Pawley controls: ☐ Do Pawley refinement? Pawley dmin: 1.0 Pawley dmax: 100.0 Pawley neg. wt.: 0.0

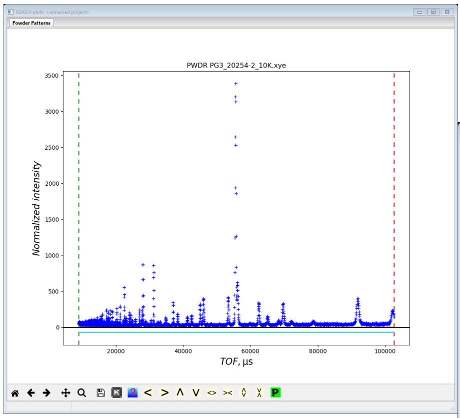
Fourier map controls: Map type: Reflection sets:

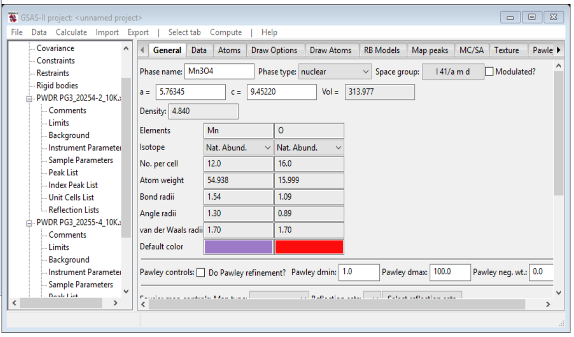
not magnetic – do structure refinement 1st → Low T chemical structure
NB: cif files sometimes in 1st setting; GSAS-II wants 2nd setting
Transformation tool: in menu
Result: in GSAS-II project file *.gpx – use for input to magnetic structure determination

MAGNETIC STRUCTURE OF Mn_3O_4 AT 10K

New GSAS-II project: read in data & chemical structure

POWGEN data & phase from 60K result





Phase name: Mn3O4 Phase type: nuclear Space group: I 41/a m d ☐ Modulated?

a = 5.76345 c = 9.45220 Vol = 313.977

Density: 4.840

Elements	Mn	O
Isotope	Nat. Abund.	Nat. Abund.
No. per cell	12.0	16.0
Atom weight	54.938	15.999
Bond radii	1.54	1.09
Angle radii	1.30	0.89
van der Waals radii	1.70	1.70

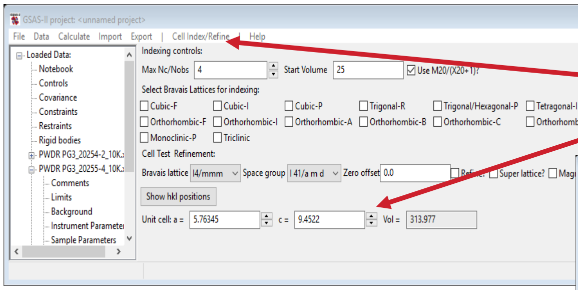
Pawley controls: ☐ Do Pawley refinement? Pawley dmin: 1.0 Pawley dmax: 100.0 Pawley neg. wt.: 0.0

NB: this is the chemical phase; magnetic phase added later (with Mn only)

MAGNETIC STRUCTURE PRELIMINARIES

Magnetic lattice & propagation vectors – indexing pattern

Unit Cells List (for the PWDR data set)



Indexing controls:

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

Select Bravais Lattices for indexing:

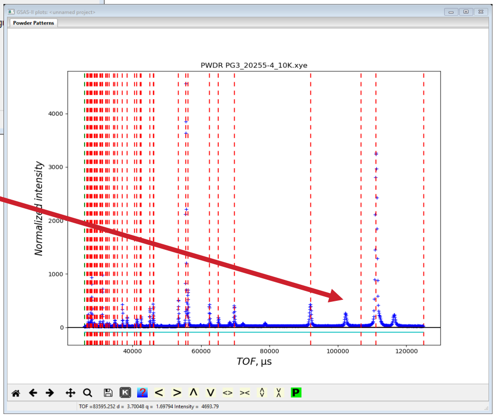
☐ Cubic-F ☐ Cubic-I ☐ Cubic-P ☐ Trigonal-R ☐ Trigonal/Hexagonal-P ☐ Tetragonal-I ☐ Tetragonal-P
☐ Orthorhombic-F ☐ Orthorhombic-I ☐ Orthorhombic-A ☐ Orthorhombic-B ☐ Orthorhombic-C ☐ Orthorhombic-P ☐ Monoclinic-C
☐ Monoclinic-P ☐ Triclinic

Cell Test Refinement:

Bravais lattice I4/mmm Space group I 41/a m d Zero offset 0.0 ☐ Refine? ☐ Super lattice? ☐ Mag

Unit cell: a = 5.76345 c = 9.4522 Vol = 313.977

Menu:
Load unit cell from phase
& index pattern (I 4/m m m)



Unindexed lines: cell doubling needed
Easily explored here:
Set P4/mmm & double a or b →
Every line indexed
→ 2 propagation vectors suggested
by 2 phase changes from 60K to 10K:
I chose (0,½,0) & (0,0,1) –
double b & remove centering

MAGNETIC SPACE GROUP IDENTIFICATION

MAGNETIC SPACE GROUP SELECTION

Need exhaustive list that are subgroups of parent grey group

Magnetic space group is from loss of symmetry
Parent: I 4_1/amd1' → 128 operations!

x,y,z
-y+1/4,x+3/4,z+1/4
-x+1/2,-y,z+1/2
y+1/4,-x+1/4,z+3/4
-x,y,z
-y+1/4,-x+3/4,z+1/4
x+1/2,-y,z+1/2
y+1/4,x+1/4,z+3/4
-x,-y,-z
y+3/4,-x+1/4,-z+3/4
x+1/2,y,-z+1/2
-y+3/4,x+3/4,-z+1/4
x,-y,-z
y+3/4,x+1/4,-z+3/4
-x+1/2,y,-z+1/2
-y+3/4,-x+3/4,-z+1/4
-x,-y,-z
y+3/4,-x+1/4,-z+3/4
x+1/2,y,-z+1/2
-y+3/4,x+3/4,-z+1/4
x,-y,-z
y+3/4,x+1/4,-z+3/4
-x+1/2,y,-z+1/2
-y+3/4,-x+3/4,-z+1/4
x,y,z
-y+1/4,x+3/4,z+1/4
-x+1/2,-y,z+1/2
y+1/4,-x+1/4,z+3/4
-x,y,z
-y+1/4,-x+3/4,z+1/4
x+1/2,-y,z+1/2
y+1/4,x+1/4,z+3/4

x+1/2,y+1/2,z+1/2
-y+3/4,x+1/4,z+3/4
-x,-y+1/2,z
y+3/4,-x+3/4,z+1/4
-x+1/2,y+1/2,z+1/2
-y+3/4,-x+1/4,z+3/4
x,-y+1/2,z
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y+3/4,-x+3/4,z+1/4
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x,y,z
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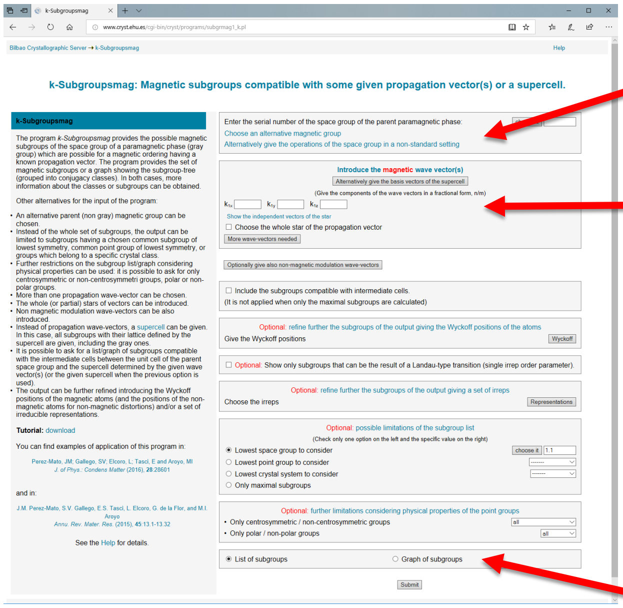
-y+3/4,x+1/4,z+3/4
-x,-y+1/2,z
y+3/4,-x+3/4,z+1/4
-x+1/2,y+1/2,z+1/2
-y+3/4,-x+1/4,z+3/4
x,-y+1/2,z
y+3/4,x+3/4,z+1/4
-x+1/2,-y+1/2,-z+1/2
y+1/4,-x+3/4,-z+1/4
x,y+1/2,-z
-y+1/4,x+1/4,-z+3/4
x+1/2,-y+1/2,-z+1/2
y+1/4,x+3/4,-z+1/4
-x,y+1/2,-z
-y+1/4,-x+1/4,-z+3/4
-x+1/2,-y+1/2,-z+1/2
y+1/4,-x+3/4,-z+1/4
x,y+1/2,-z
-y+1/4,x+1/4,-z+3/4
x+1/2,-y+1/2,-z+1/2
y+1/4,x+3/4,-z+1/4
-x,y+1/2,-z
-y+1/4,-x+1/4,-z+3/4
x+1/2,y+1/2,z+1/2
-y+3/4,x+1/4,z+3/4
-x,-y+1/2,z
y+3/4,-x+3/4,z+1/4
-x+1/2,y+1/2,z+1/2
-y+3/4,-x+1/4,z+3/4
x,-y+1/2,z
y+3/4,x+3/4,z+1/4

Actually twice as many with 0,½,0 prop. vector!
Now start removing cycles of operations to give new space group (subgroup of parent)
NB: new origin might be different to match standard setting
Horrible job by hand!
Use Bilbao tools: k-SUBGROUPSMAG

MAGNETIC SPACE GROUP IDENTIFICATION

Bilbao Crystallographic Server – k-SUBGROUPSMAG

A subgroup of the parent chemical space group as a gray group



k-Subgroupsmag: Magnetic subgroups compatible with some given propagation vector(s) or a supercell.

k-Subgroupsmag

The program *k-Subgroupsmag* provides the possible magnetic subgroups of the space group of a paramagnetic phase (gray group) which are possible for a magnetic ordering having a known propagation vector. The program provides the set of magnetic subgroups or a graph showing the subgroup-tree (grouped into conjugacy classes). In both cases, more information about the classes or subgroups can be obtained.

Other alternatives for the input of the program:

- An alternative parent (non gray) magnetic group can be chosen.
- Instead of the whole set of subgroups, the output can be limited to subgroups having a chosen common subgroup of lowest symmetry, common point group of lowest symmetry, or groups which belong to a specific crystal class.
- Further restrictions on the subgroup list/graph considering physical properties can be used: it is possible to ask for only centrosymmetric or non-centrosymmetri groups, polar or non-polar groups.
- More than one propagation wave-vector can be chosen.
- The whole (or partial) stars of vectors can be introduced.
- Non magnetic modulation wave-vectors can be also introduced.
- Instead of propagation wave-vectors, a supercell can be given. In this case, all subgroups with their lattice defined by the supercell are given, including the gray ones.
- It is possible to ask for a list/graph of subgroups compatible with the intermediate cells between the unit cell of the parent space group and the supercell determined by the given wave vector(s) (or the given supercell when the previous option is used).
- The output can be further refined introducing the Wyckoff positions of the magnetic atoms (and the positions of the non-magnetic atoms for non-magnetic distortions) and/or a set of irreducible representations.

Tutorial: download

You can find examples of application of this program in:

Perez-Mato, JM; Gallego, SV; Elcoro, L; Tasci, E and Aroyo, MI
J. of Phys.: Condens Matter (2016), **28**:28601

and in:

J.M. Perez-Mato, S.V. Gallego, E.S. Tasci, L. Elcoro, G. de la Flor, and M.I. Aroyo
Annu. Rev. Mater. Res. (2015), **45**:13.1-13.32

See the Help for details.

Enter the serial number of the space group of the parent paramagnetic phase:

Choose an alternative magnetic group

Alternatively give the operations of the space group in a non-standard setting

Introduce the magnetic wave vector(s)

Alternatively give the basis vectors of the supercell

(Give the components of the wave vectors in a fractional form, n/m)

k_{1x} ___ k_{1y} ___ k_{1z} ___

Show the independent vectors of the star

☐ Choose the whole star of the propagation vector

More wave-vectors needed

Optionally give also non-magnetic modulation wave-vectors

☐ Include the subgroups compatible with intermediate cells.
(It is not applied when only the maximal subgroups are calculated)

Optional: refine further the subgroups of the output giving the Wyckoff positions of the atoms
Give the Wyckoff positions — Wyckoff

☐ Optional: Show only subgroups that can be the result of a Landau-type transition (single irrep order parameter).

Optional: refine further the subgroups of the output giving a set of irreps
Choose the irreps — Representations

Optional: possible limitations of the subgroup list
(Check only one option on the left and the specific value on the right)

● Lowest space group to consider — choose it 1.1
○ Lowest point group to consider — -------
○ Lowest crystal system to consider — -------
○ Only maximal subgroups

Optional: further limitations considering physical properties of the point groups

- Only centrosymmetric / non-centrosymmetric groups — all
- Only polar / non-polar groups — all

● List of subgroups ○ Graph of subgroups

Submit

Space group number
Alternatively – input operators
Allows non-std space groups.

Propagation vector(s)

Optional controls –
Limit results

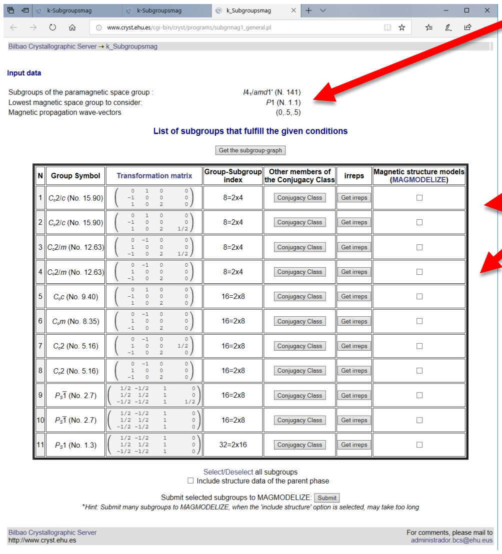
Result as list (or graph)

---

k-SUBGROUPSMAG RESULT

Full list of possible magnetic space groups – by elimination of operators from parent gray group

E.g. start: **$I4_1$/amd1'**; k=(0,½, ½)



Input data

Subgroups of the paramagnetic space group :	$I4_1/amd1'$ (N. 141)
Lowest magnetic space group to consider:	$P1$ (N. 1.1)
Magnetic propagation wave-vectors	(0,.5,.5)

List of subgroups that fulfill the given conditions

Get the subgroup-graph

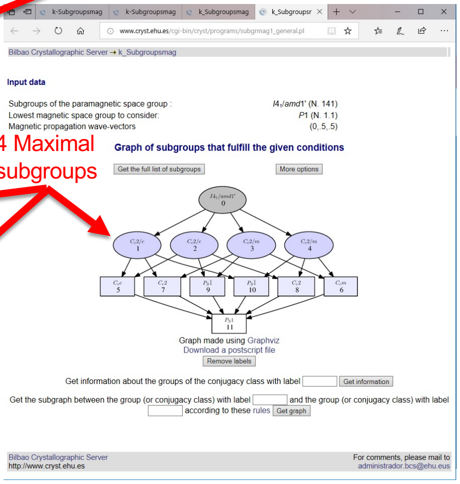
N	Group Symbol	Transformation matrix	Group-Subgroup index	Other members of the Conjugacy Class	irreps	Magnetic structure models (MAGMODELIZE)
1	C_c2/c (No. 15.90)	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 1 & 0 & 2 & 0 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	☐
2	C_c2/c (No. 15.90)	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 1 & 0 & 2 & 1/2 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	☐
3	C_c2/m (No. 12.63)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 1/2 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	☐
4	C_c2/m (No. 12.63)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 0 \end{pmatrix}$	8=2x4	Conjugacy Class	Get irreps	☐
5	C_cc (No. 9.40)	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 1 & 0 & 2 & 0 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
6	C_cm (No. 8.35)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 0 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
7	C_c2 (No. 5.16)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 1/2 \\ -1 & 0 & 2 & 0 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
8	C_c2 (No. 5.16)	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ -1 & 0 & 2 & 0 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
9	$P_S\bar{1}$ (No. 2.7)	$\begin{pmatrix} 1/2 & -1/2 & 1 & 0 \\ 1/2 & 1/2 & 1 & 0 \\ -1/2 & -1/2 & 1 & 1/2 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
10	$P_S\bar{1}$ (No. 2.7)	$\begin{pmatrix} 1/2 & -1/2 & 1 & 0 \\ 1/2 & 1/2 & 1 & 0 \\ -1/2 & -1/2 & 1 & 0 \end{pmatrix}$	16=2x8	Conjugacy Class	Get irreps	☐
11	P_S1 (No. 1.3)	$\begin{pmatrix} 1/2 & -1/2 & 1 & 0 \\ 1/2 & 1/2 & 1 & 0 \\ -1/2 & -1/2 & 1 & 0 \end{pmatrix}$	32=2x16	Conjugacy Class	Get irreps	☐

Select/Deselect all subgroups
☐ Include structure data of the parent phase

Submit selected subgroups to MAGMODELIZE: Submit
**Hint: Submit many subgroups to MAGMODELIZE, when the 'include structure' option is selected, may take too long*

Bilbao Crystallographic Server
http://www.cryst.ehu.es

For comments, please mail to
administrador.bcs@ehu.eus



Input data

Subgroups of the paramagnetic space group :	$I4_1/amd1'$ (N. 141)
Lowest magnetic space group to consider:	$P1$ (N. 1.1)
Magnetic propagation wave-vectors	(0,.5,.5)

Graph of subgroups that fulfill the given conditions

Get the full list of subgroups — More options

Graph made using Graphviz
Download a postscript file
Remove labels

Get information about the groups of the conjugacy class with label ___ Get information

Get the subgraph between the group (or conjugacy class) with label ___ and the group (or conjugacy class) with label ___ according to these rules Get graph

Bilbao Crystallographic Server
http://www.cryst.ehu.es

For comments, please mail to
administrador.bcs@ehu.eus

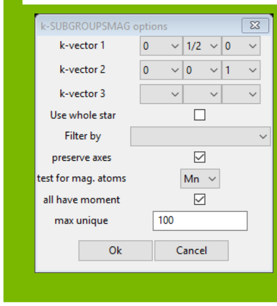
4 Maximal subgroups

Intended process: use symbol (or operators) & transformation matrix/vector & try against data. Tools for structure input → test for allowed mag. moments

GSAS-II ← → k-SUBGROUPSMAG

Direct call & data retrieval from web page table in Python
Example: Mn_3O_4 “hausmannite” at 10K – Type IV magnetic structure

GSAS-II + $I4_1/amd$



k-vector 1: 0 | 1/2 | 0

k-vector 2: 0 | 0 | 1

k-vector 3:

Use whole star ☐

Filter by

preserve axes ☑

test for mag. atoms: Mn

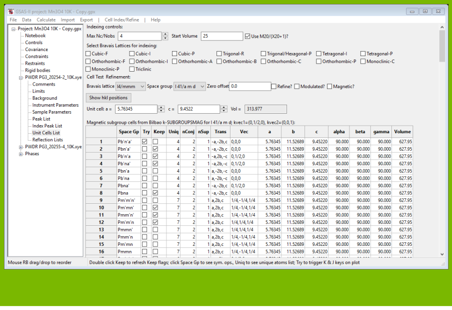
all have moment ☑

max unique: 100

Send request

Bilbao site
www.cryst.ehu.es/cgi-bin/programs/subgrmag1_general_GSAS.pl

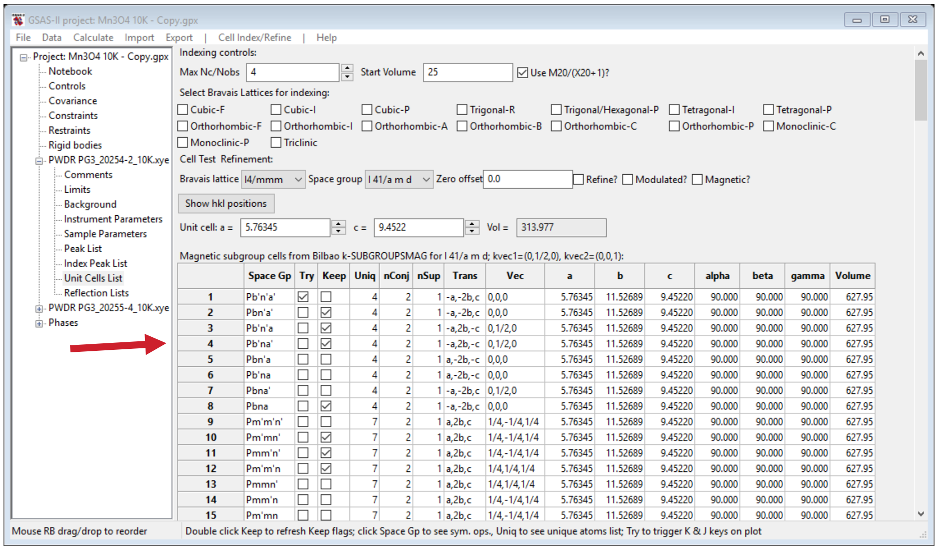
Makes html table of magnetic space subgroups, etc.



Return result
205 subgroups!
64 maximal subgroups!

RESULT FROM k-SUBGROUPSMAG (GSAS)

205 possible magnetic space subgroups (64 maximal) for $I4_1/amd$ & k=(0,½,0) +(0,0,0)



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/Hexagonal-P ☐ Tetragonal-I ☐ Tetragonal-P
☐ Orthorhombic-F ☐ Orthorhombic-I ☐ Orthorhombic-A ☐ Orthorhombic-B ☐ Orthorhombic-C ☐ Orthorhombic-P ☐ Monoclinic-C
☐ Monoclinic-P ☐ Triclinic

Cell Test Refinement:

Bravais lattice: I4/mmm | Space group: I 41/a m d | Zero offset: 0.0 | ☐ Refine? ☐ Modulated? ☐ Magnetic?

Unit cell: a = 5.76345 | c = 9.4522 | Vol = 313.977

Magnetic subgroup cells from Bilbao k-SUBGROUPSMAG for I 41/a m d; kvec1=(0,1/2,0), kvec2=(0,0,1):

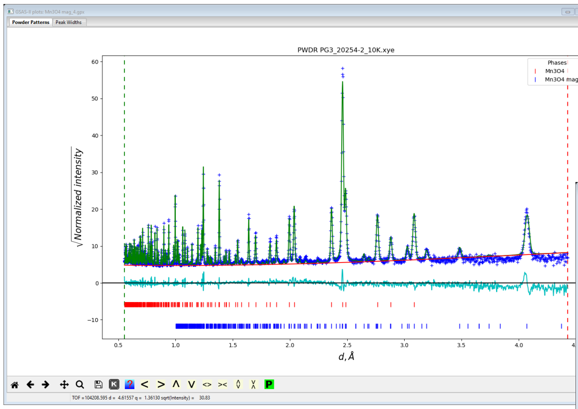
	Space Gp	Try	Keep	Uniq	nConj	nSup	Trans	Vec	a	b	c	alpha	beta	gamma	Volume
1	Pb'n'a'	☑	☐	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
2	Pbn'a'	☐	☑	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
3	Pb'n'a	☐	☑	4	2	1	-a,2b,-c	0,1/2,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
4	Pb'na'	☐	☑	4	2	1	-a,2b,-c	0,1/2,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
5	Pbn'a	☐	☐	4	2	1	a,-2b,-c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
6	Pb'na	☐	☐	4	2	1	a,-2b,-c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
7	Pbna'	☐	☐	4	2	1	-a,-2b,c	0,1/2,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
8	Pbna	☐	☑	4	2	1	-a,-2b,c	0,0,0	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
9	Pm'm'n'	☐	☐	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
10	Pm'mn'	☐	☑	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
11	Pmm'n'	☐	☑	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
12	Pm'm'n	☐	☑	7	2	1	a,2b,c	1/4,1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
13	Pmmn'	☐	☐	7	2	1	a,2b,c	1/4,1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
14	Pmm'n	☐	☐	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95
15	Pm'mn	☐	☐	7	2	1	a,2b,c	1/4,-1/4,1/4	5.76345	11.52689	9.45220	90.000	90.000	90.000	627.95

Double click Keep to refresh Keep flags; click Space Gp to see sym. ops., Uniq to see unique atoms list; Try to trigger K & J keys on plot

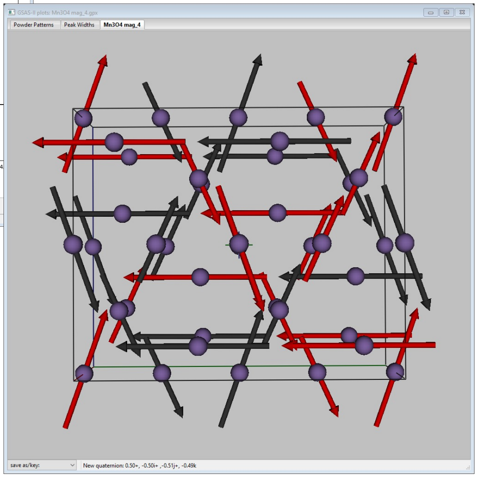
Only 4 have all Mn with moment & minimal no. of Mn sites(4) – try each one
Selection creates magnetic phase; refine moments: best is Pb’na’ (#4)

MAGNETIC STRUCTURE OF Mn_3O_4 AT 4K

Data from SNS/POWGEN – 2 frames; R_{wp} ~15%



TOF = 104208.595 d = 4.61557 q = 1.36130 sqrt(Intensity) = 30.83



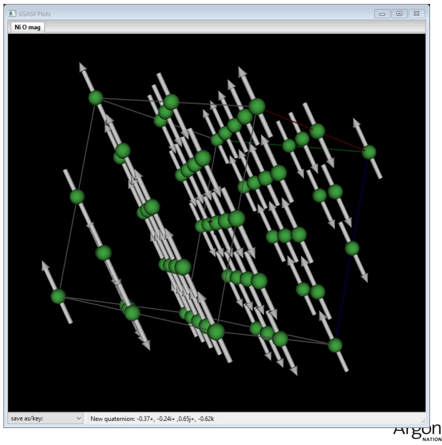
New quaternion: 0.50+, -0.50i+ ,-0.51j+, -0.49k

3 intersecting ferromagnetically coupled sets of moments – overall antiferromagnet
Agrees with Jensen, J.B. & Nielsen, O.V. J. Phys. C: Solid State Phys. (1974), 7, 409-424 except that mag space group is now identified as Pb'na' .

BILBAO MCIF FILES

~1,850 structures (Gallego, et al. JAC 49, 1750-1776, 2016.)

- Tables: zero propagation vector, Type III, Type IV, 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 sym ops (overrides symbol Interpretation) → draw structures & compute powder patterns, etc.
- Magnetic moments – crystal axes components; Bohr magnetons. GSAS-II uses this convention.



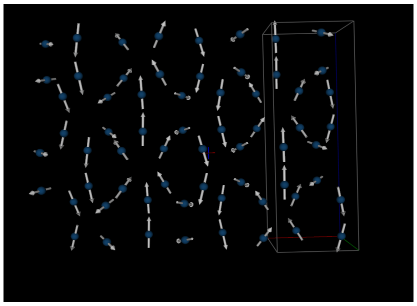
New quaternion: -0.37+, -0.24i+ ,0.65j+, -0.62k

GSAS-II AND INCOMMENSURATE MAGNETISM

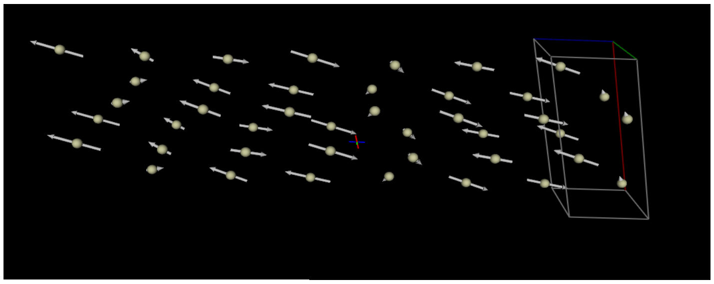
- GSAS-II can read and plot magCIFs, even if incommensurate
- Incommensurate structures: Make movies with spins or atoms as a function of τ
- There is a bug in the incommensurate magnetic structure factor computation that Bob has not been able to find

---

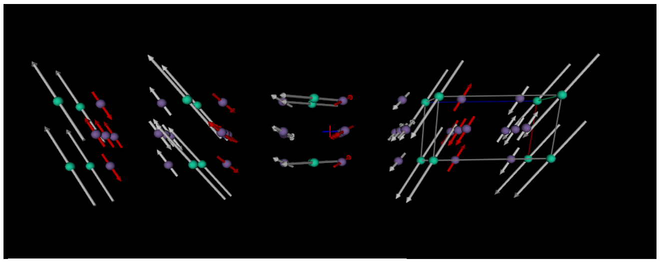
PLOTTING MAGNETIC INCOMMENSURATE STRUCTURES: EXAMPLES



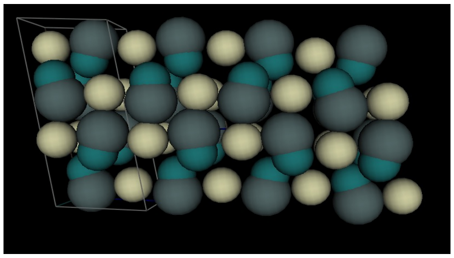
β-Li_2IrO_3



CeRuSn – Ce moment



$DyMn_6Ge_6$ – residual moment



CeRuSn –
structure modulation

CONCLUSIONS:

GSAS-II is a comprehensive system for all types of crystallographic analysis

GSAS-II uses a crystallographic approach to magnetic structures

Try out the tutorials (http://bit.ly/GSASIItutorials)

Home page: http://bit.ly/GSASII

PLEASE JOIN THE GSAS-II MAILING LIST

So that we can get information to you, please subscribe to the GSAS-II mailing list, (or monitor the archives to look for announcements)

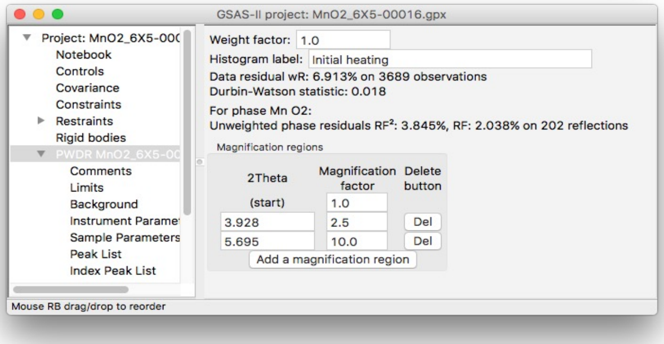
- To subscribe:
  - use https://mailman.aps.anl.gov/mailman/listinfo/GSAS-II for the Web interface
  - or send an e-mail to GSAS-II-request@mailman.aps.anl.gov
    - Use subject “subscribe” (or subscribe <password> where <password> is your preference for a mailing list login password).
- To see archives: https://mailman.aps.anl.gov/pipermail/gsas-ii/

OTHER SLIDE DECK SECTIONS

1. Other GSAS-II settings and parameters
2. GSAS-II treatment of profiles
3. Sequential refinement
4. Scripting with GSAS-II
5. Rigid bodies in GSAS-II
6. Incommensurate atomic structures
7. Other stuff: Small angle & reflectivity scattering
8. Refinement Recipes

HISTOGRAM SECTIONS TOP LEVEL

- Provides histogram fit statistics
- Label is used to show in plot (optional)
- Magnification regions used to show detail in Rietveld plot
  - Lines can be dragged when this tree item is selected
- Tick mark location can be dragged to change
- Difference plot location can be dragged



Weight factor: 1.0

Histogram label: Initial heating

Data residual wR: 6.913% on 3689 observations

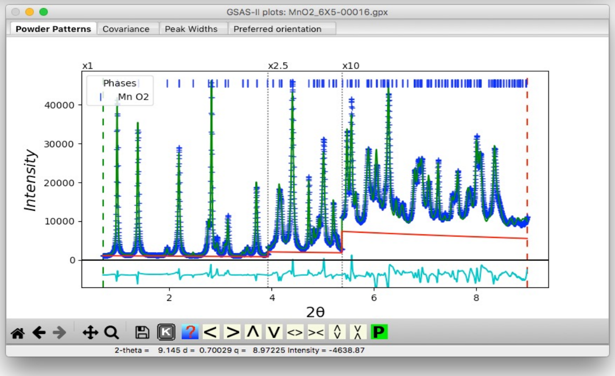
Durbin-Watson statistic: 0.018

For phase Mn O2:

Unweighted phase residuals RF^2: 3.845%, RF: 2.038% on 202 reflections

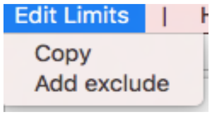
Magnification regions

2Theta	Magnification factor	Delete button
(start)	1.0	
3.928	2.5	Del
5.695	10.0	Del



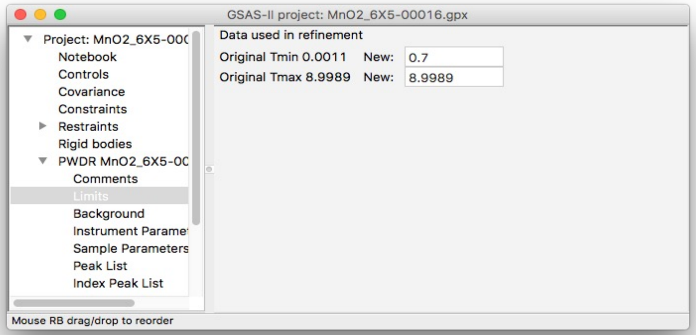
2-theta = 9.145 d = 0.70029 q = 8.97225 Intensity = -4638.87

HISTOGRAM: LIMITS



- Changes range of data to be used
- Lines can be dragged on plot from here

- Menu allows
  - Creation of excluded regions
  - Limits/regions to be copied to other histograms

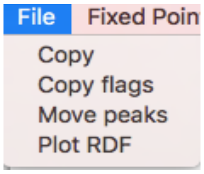


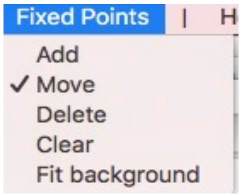
Data used in refinement

Original Tmin 0.0011 New: 0.7

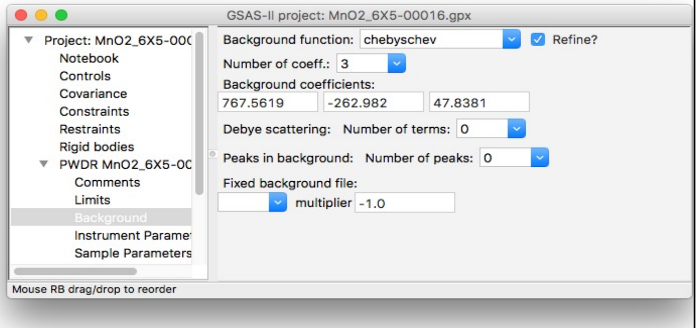
Original Tmax 8.9989 New: 8.9989

HISTOGRAM: BACKGROUND





- Defines background equation and number of terms
- Debye scattering allows creation of a complex background
- Background peaks treat wide features
- Can subtract another histogram here



Background function: chebyschev ☑ Refine?

Number of coeff.: 3

Background coefficients:

767.5619 -262.982 47.8381

Debye scattering: Number of terms: 0

Peaks in background: Number of peaks: 0

Fixed background file:

multiplier -1.0

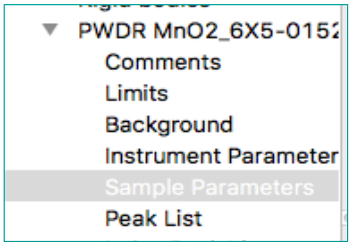
When starting to fit a complex background, it can be useful to define fixed points and then fit a function to it.

- Fix the coefficients initially, but refine them later
- See tutorial “Fitting background using fixed points”

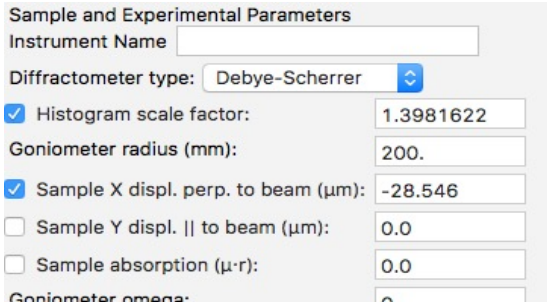
HISTOGRAM: SAMPLE PARAMETERS

These often should be varied

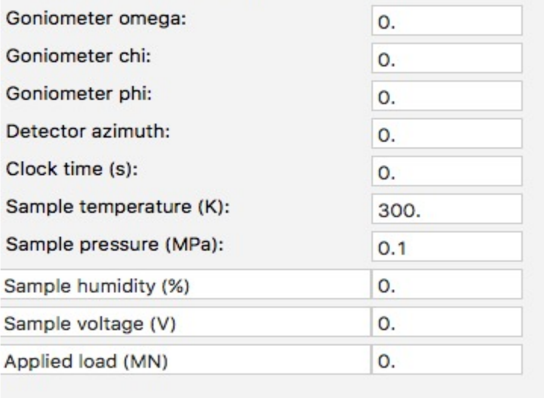
- What we used to refine as a zero correction is usually sample displacement
  - Sample Y can only be refined when data extend >>120 degrees 2θ
- Absorption correlates with Uiso values
  - better set than refined
  - For TOF value is at 1Å (adjusted as needed)



Metadata settings are here
(N.B. last 3 have user-defined labels)



Sample and Experimental Parameters
Instrument Name
Diffractometer type: Debye-Scherrer
☑ Histogram scale factor: 1.3981622
Goniometer radius (mm): 200.
☑ Sample X displ. perp. to beam (μm): -28.546
☐ Sample Y displ. || to beam (μm): 0.0
☐ Sample absorption (μ·r): 0.0
Goniometer omega:



Goniometer omega: 0.
Goniometer chi: 0.
Goniometer phi: 0.
Detector azimuth: 0.
Clock time (s): 0.
Sample temperature (K): 300.
Sample pressure (MPa): 0.1
Sample humidity (%) 0.
Sample voltage (V) 0.
Applied load (MN) 0.

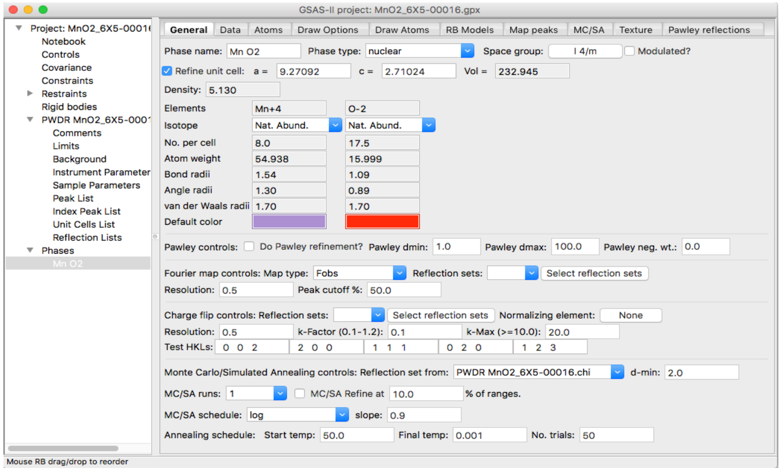
OTHER HISTOGRAM SECTIONS

- Peak List: used for fitting peaks without lattice constants
  - See tutorial “Fitting individual peaks & autoindexing”
  - Can be used to get starting profile terms (see tutorial “Determining Starting Profile Parameters from a Standard”)
- Index Peak List: used to hold peaks to be used in indexing patterns
- Unit Cells List:
  - Search for units cells (autoindexing)
  - Show reflection positions generated from a unit cell and space group (or 3+1 superspace group)
- Reflection Lists:
  - Note that each phase has a separate tab
  - Menu items allow reflection plotting

PHASE/GENERAL TAB

Used to define some overall phase info and control structure determination parameters

- Unit cell
- Space group
- Isotopic composition (note types from atom list)



Phase name: Mn O2 Phase type: nuclear Space group: I 4/m ☐ Modulated?

☑ Refine unit cell: a = 9.27092 c = 2.71024 Vol = 232.945

Density: 5.130

Elements	Mn+4	O-2
Isotope	Nat. Abund.	Nat. Abund.
No. per cell	8.0	17.5
Atom weight	54.938	15.999
Bond radii	1.54	1.09
Angle radii	1.30	0.89
van der Waals radii	1.70	1.70
Default color	🟪	🟥

Pawley controls: ☐ Do Pawley refinement? Pawley dmin: 1.0 Pawley dmax: 100.0 Pawley neg. wt.: 0.0

Fourier map controls: Map type: Fobs Reflection sets:
Resolution: 0.5 Peak cutoff %: 50.0

Charge flip controls: Reflection sets: Normalizing element: None
Resolution: 0.5 k-Factor (0.1-1.2): 0.1 k-Max (>=10.0): 20.0
Test HKLs: 0 0 2 | 2 0 0 | 1 1 1 | 0 2 0 | 1 2 3

Monte Carlo/Simulated Annealing controls: Reflection set from: PWDR MnO2_6X5-00016.chi d-min: 2.0
MC/SA runs: 1 ☐ MC/SA Refine at 10.0 % of ranges.
MC/SA schedule: log slope: 0.9
Annealing schedule: Start temp: 50.0 Final temp: 0.001 No. trials: 50

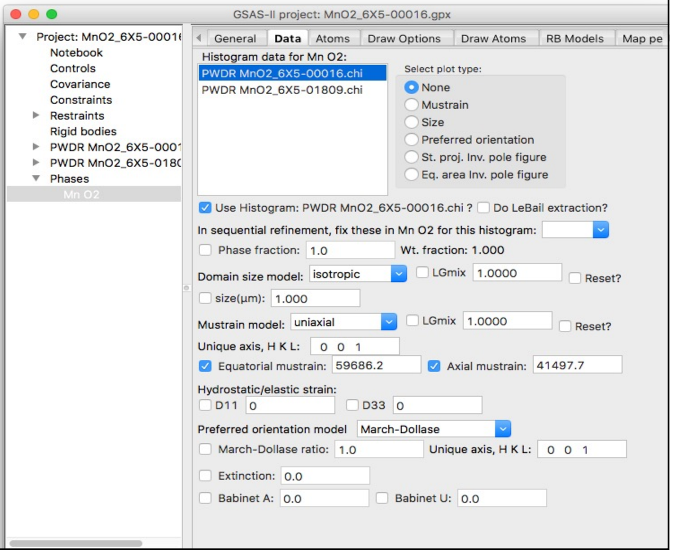
PHASE/DATA TAB

Contains all parameters that vary by both phase and histogram

- Select histogram at top;
- Plot different parameter sets
- Use flag includes phase into histogram (unused histograms are ignored)
- Sequential Fix: overrides atom flags
- Phase fraction: determines mass fraction in mixtures
- Size/microstrain broadening

To be discussed:

- Hydrostatic/elastic strain
  - Changes to lattice constants
- Preferred orientation



Histogram data for Mn O2:
PWDR MnO2_6X5-00016.chi
PWDR MnO2_6X5-01809.chi

Select plot type:
● None
○ Mustrain
○ Size
○ Preferred orientation
○ St. proj. Inv. pole figure
○ Eq. area Inv. pole figure

☑ Use Histogram: PWDR MnO2_6X5-00016.chi ? ☐ Do LeBail extraction?

In sequential refinement, fix these in Mn O2 for this histogram:

☐ Phase fraction: 1.0 Wt. fraction: 1.000

Domain size model: isotropic ☐ LGmix 1.0000 ☐ Reset?
☐ size(µm): 1.000

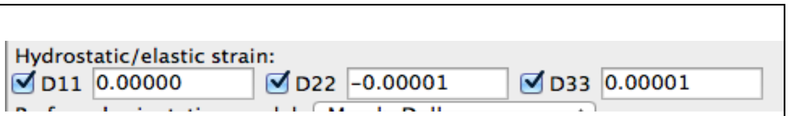
Mustrain model: uniaxial ☐ LGmix 1.0000 ☐ Reset?
Unique axis, H K L: 0 0 1
☑ Equatorial mustrain: 59686.2 ☑ Axial mustrain: 41497.7

Hydrostatic/elastic strain:
☐ D11 0 ☐ D33 0

Preferred orientation model March-Dollase
☐ March-Dollase ratio: 1.0 Unique axis, H K L: 0 0 1

☐ Extinction: 0.0
☐ Babinet A: 0.0 ☐ Babinet U: 0.0

HYDROSTATIC STRAIN (LATTICE CONSTANT SHIFTS)



Hydrostatic/elastic strain:

☑ D11 0.00000 ☑ D22 -0.00001 ☑ D33 0.00001

GSAS-II also offers terms for hydrostatic strain, D_{ij} which add to the reciprocal tensor terms, A_{ij}

(For a formal definition see the lattice module documentation or the GSAS manual, profile type 5)

- The number of terms matches the number of independent lattice parameters (1 for cubic, 4 for monoclinic,…).

Uses:

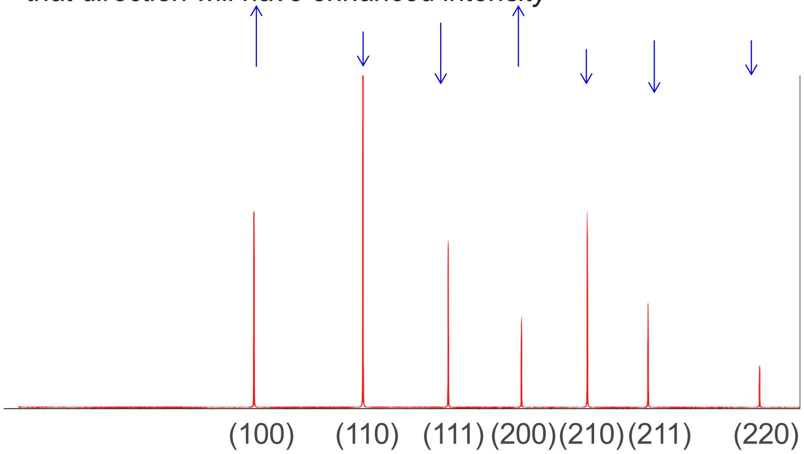
- Deviations in lattice due to pressure or temperature
- Combined refinements where lattice parameters differ due to calibration, temperature
- Sequential fitting

UNDERSTANDING TEXTURE

Non-random crystal arrangement affects reflection intensities

- Crystallite orientation will increase the intensity of reflections in orientations that are over-represented and will decrease other reflections

If we have an overabundance of crystals aligned in along the (100) face, the reflections in that direction will have enhanced intensity



Texture can be measured directly in a specialized measurement (pole figure)

To model texture we use two approaches: March-Dollase model or Orientation Distribution Function (spherical harmonics)

TEXTURE (PREFERRED ORIENTATION) IN GSAS-II

Three different approaches

- When characterizing texture, multiple sample settings are needed (typically a TOF measurement)
  - Use the Phase/Texture tab which provides texture symmetry, plotting info,…
  - Single model used for the phase across all histograms
  - Make sure histograms have correct orientation information

- When trying to correct for [unwanted] texture in structure determination, use either March-Dollase or Spherical Harmonics in the Phase/Data section
  - March-Dollase as a single refined term, but requires an identified preferred axis

  - ***Advice***: turning on spherical harmonic refinement with a small number of terms (low order) will show improvement in fit if there is significant texture. Add terms until no further significant improvement is noted.

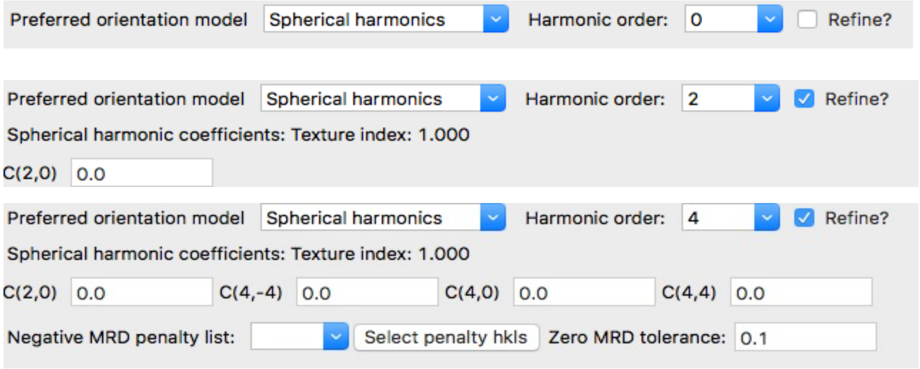
PREFERRED ORIENTATION CORRECTIONS

In Phase/Data tab

- March-Dollase

Preferred orientation model: March-Dollase
☑ March-Dollase ratio: 1.0 Unique axis, H K L: 0 0 1

- Spherical Harmonics
  - Number of terms determined by Laue class & order selection



Preferred orientation model: Spherical harmonics Harmonic order: 0 ☐ Refine?

Preferred orientation model: Spherical harmonics Harmonic order: 2 ☑ Refine?
Spherical harmonic coefficients: Texture index: 1.000
C(2,0) 0.0

Preferred orientation model: Spherical harmonics Harmonic order: 4 ☑ Refine?
Spherical harmonic coefficients: Texture index: 1.000
C(2,0) 0.0 C(4,-4) 0.0 C(4,0) 0.0 C(4,4) 0.0
Negative MRD penalty list: Zero MRD tolerance: 0.1

RESTRAINTS AND CONSTRAINTS: WHAT IS THE DIFFERENCE?

- A **constraint** reduces the number of parameters that are refined in a model by introducing relationships between variable parameters
  - Example: if we have two atoms sharing a site *and assume* that there are no vacancies , rather than having two occupancy parameters, o(A) and O(b) we can simplify the refinement because O(b) = 1 – O(a)
  - Example: if we have a phenyl group (C_6H_5) rather than treating it as 6 independent C atoms (with 18 variable parameters), we can describe it as a set of atoms that move as a unit (a rigid body). This requires only 6 parameters (3 rotations and 3 positions).
- A **restraint** adds a cost function to the refinement that “pushes” the refinement towards a result computed from the variable parameters. This adds “data” to the refinement
  - Example: we can make the fit worse if the atoms in phenyl group (C_6H_5) deviate from a plane

Note that both are adding the crystallographer’s prejudices into the model. With a constraint, there will be no direct evidence if this prejudice is wrong (but the fit will be worse)

The effect of the restraint will depend on how strongly it is weighted.

Sometimes “soft constraint” is used to refer to a restraint – a poor terminology choice.

GSAS-II CONSTRAINT CLASSES

GSAS-II Shows five groupings of constraints:

- Phase (interrelating atom parameters, sample values,…)
- Histogram (interrelating instrumental profile, scale factor…)
- Specimen (Histogram*Phase) (interrelating microstrain, crystallite size…)
- Global (parameters independent of phase or histogram)
- Symmetry-Generated (on cell and atom parameters, read-only)

Rigid body constraints are implemented, but the GUI for defining them could probably be improved.

GSAS-II CONSTRAINT TYPES

Constraints come in four flavors

- Holds: This prevents a named parameter from changing, for example to keep the z value for an atom from shifting even though the coordinates are varied.
  - Hold dAz for O5, phase 0
- Equivalence: This “chains together” multiple parameters so that one variable determines several parameters
  - Uiso for atom 1 = Uiso for atom 2 = 0.5 * Uiso for atom 3…
- Constraint: This defines that a set of parameters must add up to a constant
  - Frac(atom 1) + Frac(atom 2) + Frac(atom 3) = 1.0

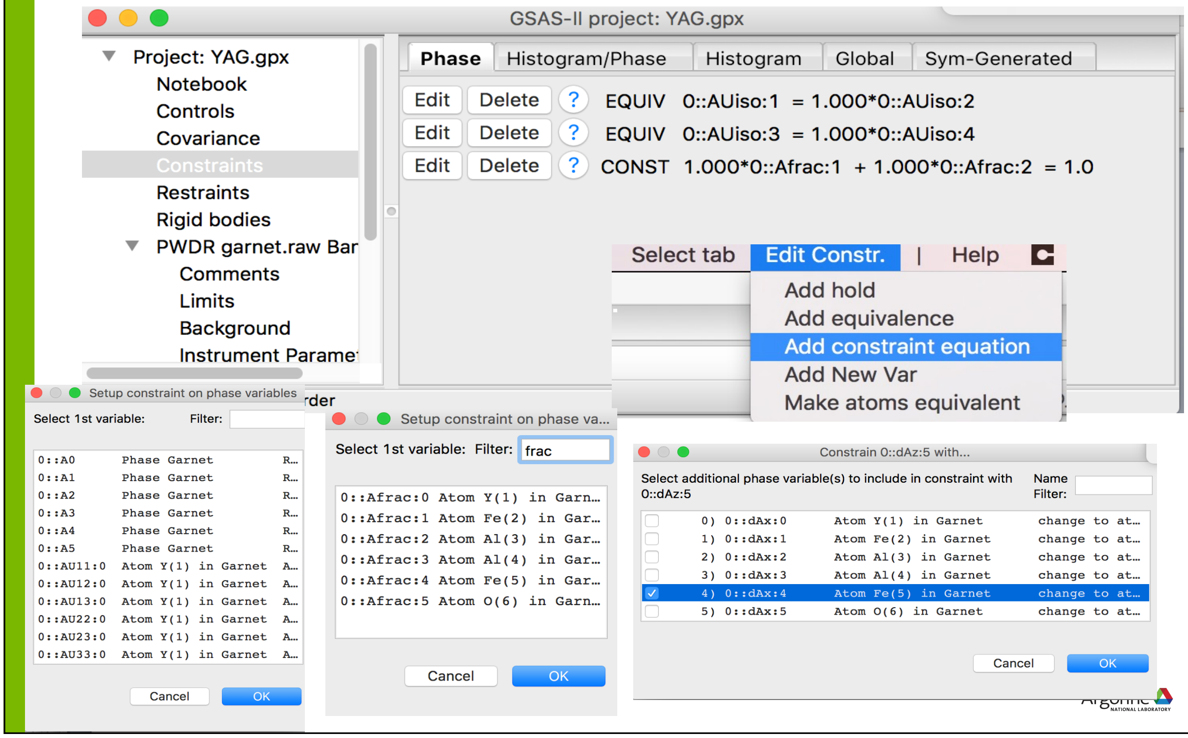
    In this example, three degrees of freedom have been lowered to two via this constraint
- New Variable:
  - Frac for atom 1 + Frac for atom 2 + Frac for atom 3 = new variable

    This will allow definition of distortion mode(s), based on representational analysis

These constraints can be combined and mixed as long as the equations are internally consistent. Example:

- Frac(atom 1) + Frac(atom 2) + Frac(atom 3) = 1.0
- Frac(atom 1) = Frac(atom 2)
  - This leaves a single degree of freedom

CREATING A CONSTRAINT



```
EQUIV  0::AUiso:1  = 1.000*0::AUiso:2
EQUIV  0::AUiso:3  = 1.000*0::AUiso:4
CONST  1.000*0::Afrac:1  + 1.000*0::Afrac:2  = 1.0
```

Setup constraint on phase variables

Select 1st variable: Filter:

```
0::A0      Phase Garnet        R…
0::A1      Phase Garnet        R…
0::A2      Phase Garnet        R…
0::A3      Phase Garnet        R…
0::A4      Phase Garnet        R…
0::A5      Phase Garnet        R…
0::AU11:0  Atom Y(1) in Garnet A…
0::AU12:0  Atom Y(1) in Garnet A…
0::AU13:0  Atom Y(1) in Garnet A…
0::AU22:0  Atom Y(1) in Garnet A…
0::AU23:0  Atom Y(1) in Garnet A…
0::AU33:0  Atom Y(1) in Garnet A…
```

Cancel OK

Setup constraint on phase va…

Select 1st variable: Filter: frac

```
0::Afrac:0 Atom Y(1) in Garn…
0::Afrac:1 Atom Fe(2) in Gar…
0::Afrac:2 Atom Al(3) in Gar…
0::Afrac:3 Atom Al(4) in Gar…
0::Afrac:4 Atom Fe(5) in Gar…
0::Afrac:5 Atom O(6) in Garn…
```

Cancel OK

Constrain 0::dAz:5 with...

Select additional phase variable(s) to include in constraint with 0::dAz:5

Name Filter:

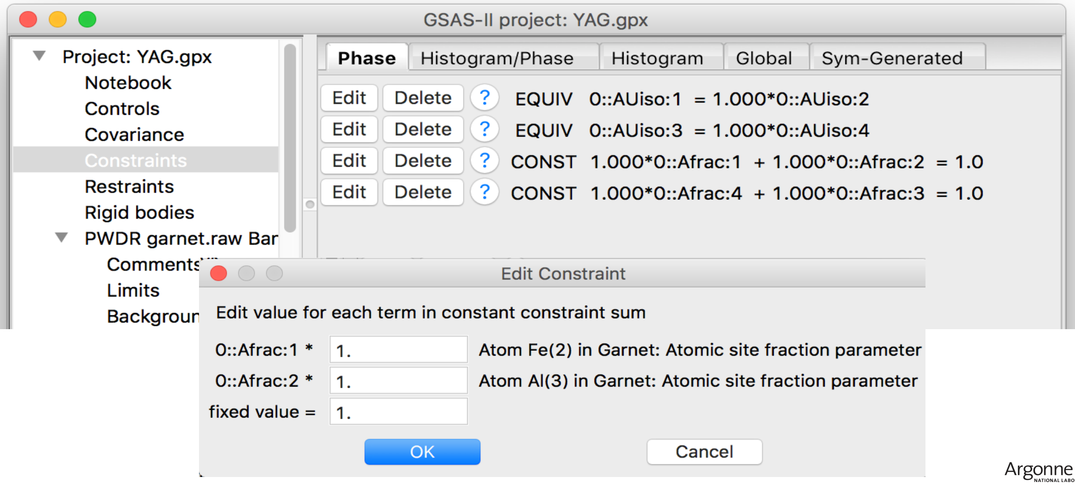
```
☐  0) 0::dAx:0   Atom Y(1) in Garnet    change to at…
☐  1) 0::dAx:1   Atom Fe(2) in Garnet   change to at…
☐  2) 0::dAx:2   Atom Al(3) in Garnet   change to at…
☐  3) 0::dAx:3   Atom Al(4) in Garnet   change to at…
☑  4) 0::dAx:4   Atom Fe(5) in Garnet   change to at…
☐  5) 0::dAx:5   Atom O(6) in Garnet    change to at…
```

Cancel OK

EDITING CONSTRAINT

After constraint is created

- Use Edit button to change multipliers or total



EQUIV 0::AUiso:1 = 1.000*0::AUiso:2

EQUIV 0::AUiso:3 = 1.000*0::AUiso:4

CONST 1.000*0::Afrac:1 + 1.000*0::Afrac:2 = 1.0

CONST 1.000*0::Afrac:4 + 1.000*0::Afrac:3 = 1.0

Edit value for each term in constant constraint sum

0::Afrac:1 * 1. Atom Fe(2) in Garnet: Atomic site fraction parameter

0::Afrac:2 * 1. Atom Al(3) in Garnet: Atomic site fraction parameter

fixed value = 1.

GSAS-II RESTRAINTS

GSAS-II allows restraints to be placed on interatomic distances and angles, most commonly used for bonded atoms.

- A target value and uncertainty is supplied for each noted distance/angle
- An overall weight is supplied for all distance and all angle restraints
- The goodness of fit gets worse as the distance or angle deviates from the target value supplied in the restraint
- Note that since there may be only a handful of restraints and 10^5 powder data points, a very large weight may be needed in the initial stages of a refinement so that the restraints count for a significant part of the GOF

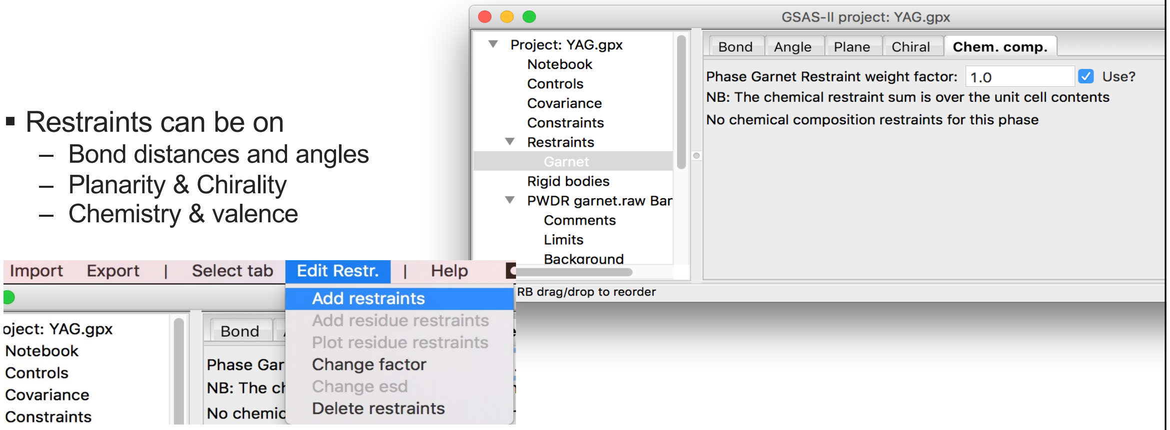
Chemical compositional restraints can be used to “push” a refinement to match a chemical analysis result (for example an overall composition) or charge balance,…

Other types of restraints (plane and chiral) are most commonly used for biomolecules.

Generalized (DIY) allows any arbitrary function of parameters to be defined

SETTING UP A RESTRAINT: EXAMPLE

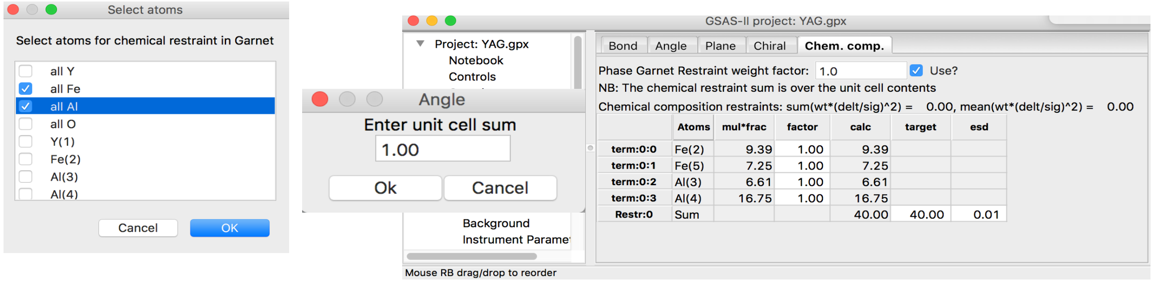
- Restraints can be on
  - Bond distances and angles
  - Planarity & Chirality
  - Chemistry & valence



Phase Garnet Restraint weight factor: 1.0 ☑ Use?

NB: The chemical restraint sum is over the unit cell contents

No chemical composition restraints for this phase



Select atoms for chemical restraint in Garnet

☐ all Y
☑ all Fe
☑ all Al
☐ all O
☐ Y(1)
☐ Fe(2)
☐ Al(3)
☐ Al(4)

Enter unit cell sum: 1.00

Phase Garnet Restraint weight factor: 1.0 ☑ Use?

NB: The chemical restraint sum is over the unit cell contents

Chemical composition restraints: sum(wt*(delt/sig)^2) = 0.00, mean(wt*(delt/sig)^2) = 0.00

	Atoms	mul*frac	factor	calc	target	esd
term:0:0	Fe(2)	9.39	1.00	9.39		
term:0:1	Fe(5)	7.25	1.00	7.25		
term:0:2	Al(3)	6.61	1.00	6.61		
term:0:3	Al(4)	16.75	1.00	16.75		
Restr:0	Sum			40.00	40.00	0.01

GSAS-II TREATMENT OF PROFILES

Argonne NATIONAL LABORATORY

PEAK BROADENING: INSTRUMENTAL CONTRIBUTIONS

Background

- Resolution of a CW neutron instrument (Cagliotti via Rietveld) is:

$$\mathrm{FWHM}^2 = U \tan^2\theta + V \tan\theta + W.$$

  - Cagliotti, G., Paoletti, A., and Ricci, F. P. (**1958**). "Choice of collimators for a crystal spectrometer for neutron diffraction," *Nucl.Instrum.* 3, 223.

- Note that a better choice would have been

$$\mathrm{FWHM}^2 = U \tan^2(\theta-\theta_m) + V \tan(\theta-\theta_m) + W$$

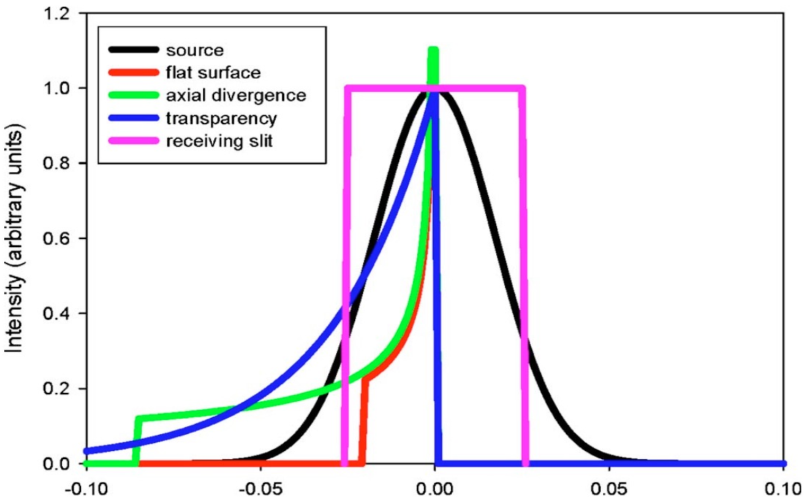
Where θ_m is the monochromator setting angle (E. Prince)

In x-ray instruments there is usually some Cauchy (Lorentzian) broadening

$$\mathrm{FWHM} = X / \cos\theta + Y \tan\theta$$

ALTERNATE INSTRUMENTAL PROFILE APPROACH: FUNDAMENTAL PARAMETERS

Convolute broadening effect of each beamline component

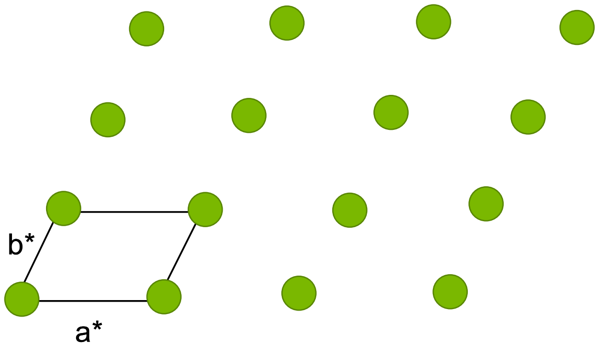


From Kaduk, J. A., and Reid, J. (2011). "Typical values of Rietveld instrument profile coefficients," *Powder Diffraction* 26, 88-93.

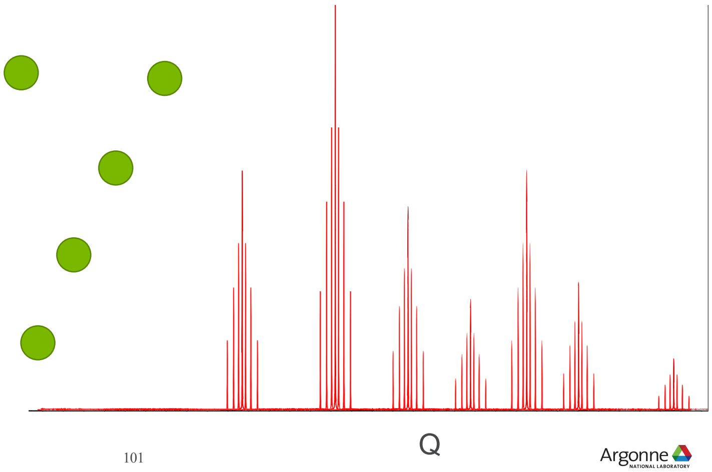
UNDERSTANDING SAMPLE EFFECTS (I): CRYSTALLITE (SIZE) BROADENING

The Fourier transform (FT) from an *infinite* array of regularly spaced objects is an array of delta functions.

The FT from a *finite* length array is broadened; all maxima are broadened equally in Q (or d).



Reciprocal Space

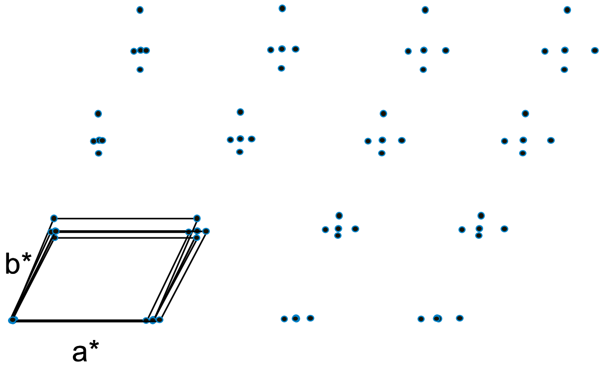


UNDERSTANDING SAMPLE EFFECTS (II): MICROSTRAIN (RESIDUAL STRESS) BROADENING

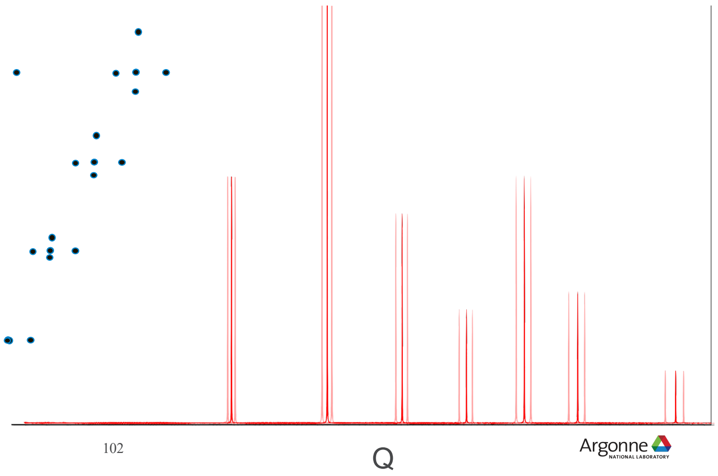
Strain & stress changes the lattice constants of a material

- In a material with residual stress
  - some crystallites are under tension (real space larger lattice, reciprocal space smaller),
  - others are compressed

Shift of peak ≈ Q, broadening increases linearly with Q ($\Delta Q/Q$ or $\Delta d/d$ constant)



Reciprocal Space



COMPARISON OF MICROSTRAIN AND CRYSTALLITE BROADENING

Crystallite broadening

- $\Delta Q \approx \Delta d^* = \text{constant}$

$$\Delta d^* = \frac{\Delta d}{d^2} = \frac{\Delta\Theta \cot\Theta}{d}$$

$$= \frac{\Delta 2\Theta \cot\Theta \sin\Theta}{\lambda}$$

$$\Delta 2\Theta = \frac{\lambda \Delta d}{d^2 \cos\Theta} = \frac{k}{\cos\Theta}$$

Microstrain broadening

- $\Delta Q/Q \approx \Delta d^*/d^* = \text{constant}$

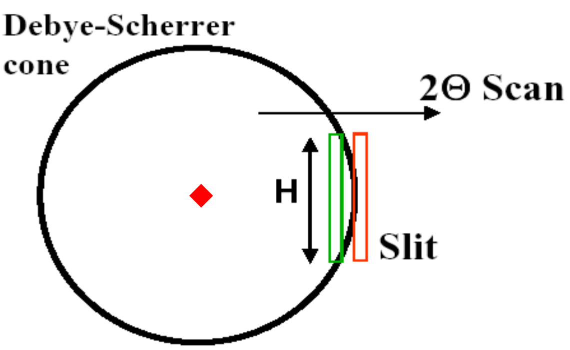
$$\frac{\Delta d}{d} = \frac{\Delta d^*}{d^*} = \Delta\Theta \cot\Theta$$

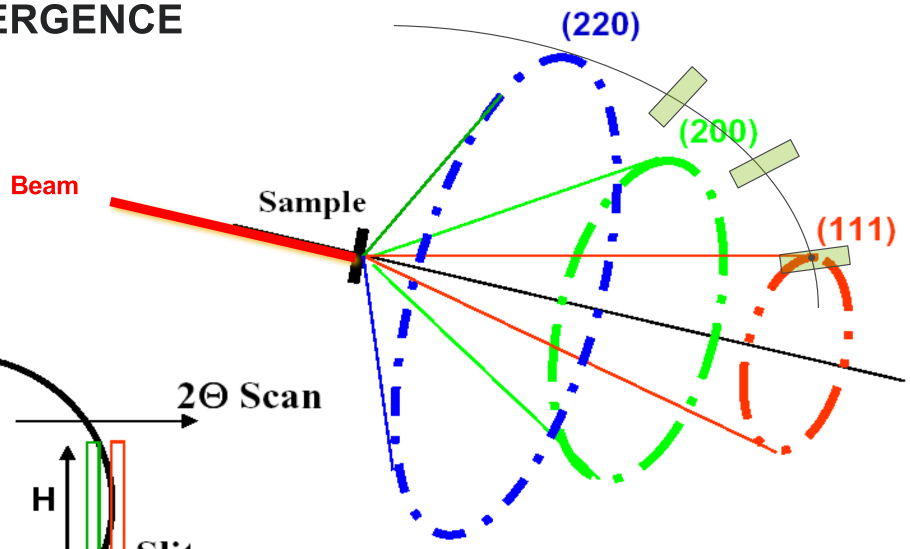
$$\Delta 2\Theta = \frac{2\Delta d}{d} \tan\Theta$$

$$\Delta 2\Theta = k \tan\Theta$$

See GSAS Manual, pp 158-167.

LOW ANGLE ASYMMETRY (CW) AXIAL DIVERGENCE

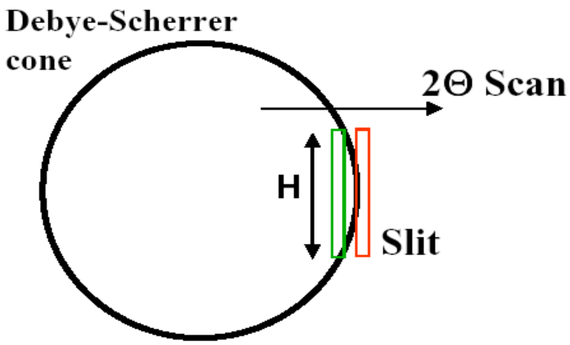


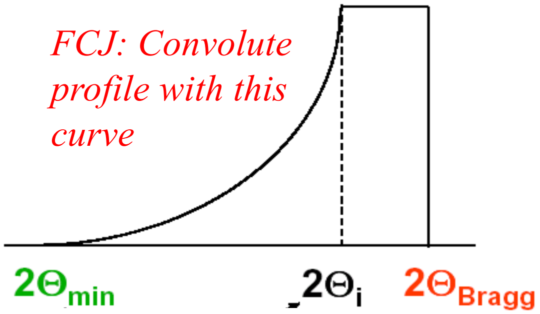


Bragg cones in powder diffraction

AXIAL DIVERGENCE IN GSAS-II

Work of Finger, Cox & Jephcoat, based on derivations by van Laar & Yelon





FCJ: Convolute profile with this curve

Axial divergence depends on three parameters, the sample height 2S, the slit height 2H and the diffractometer radius. Only the ratios matter. Diffractometers are typically designed with S/L ≅ H/L = 0.005 to 0.020

S/L & H/L can't be refined together, so GSAS-II uses an average, SH/L

GSAS-II PROFILE MODEL

Isolate sample effects from instrument

Design: instrument parameters (one set for every histogram) are determined once (with a standard) and are never varied for user samples

- Ideal: beamline scientist provides an instrument parameter file
- DIY: fit profile terms to a standard (see tutorial)
- Worst case: fit for histogram, but limited size/microstrain characterization
- When a file is not available, use "Cancel" to get access to default parameter sets

Why: When instrumental terms are determined microstrain & crystallite broadening can be varied directly

- microstrain & crystallite broadening terms for each dataset in each phase with choice of varying levels of complexity

- Can you use the old-fashioned approach of refining instrumental terms for each dataset?
  - Yes, but we wish you would not

GSAS-II CW PROFILE TERMS

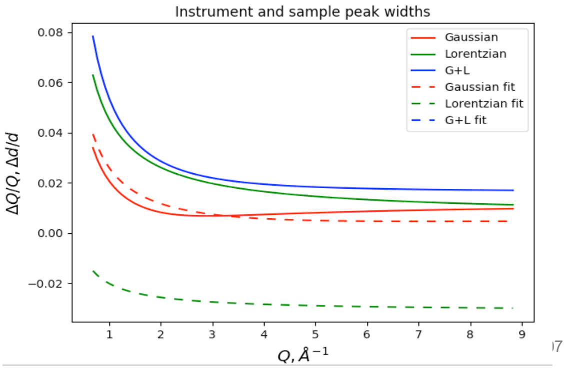
Profile terms are found in <Histogram>/Instrument Parameters

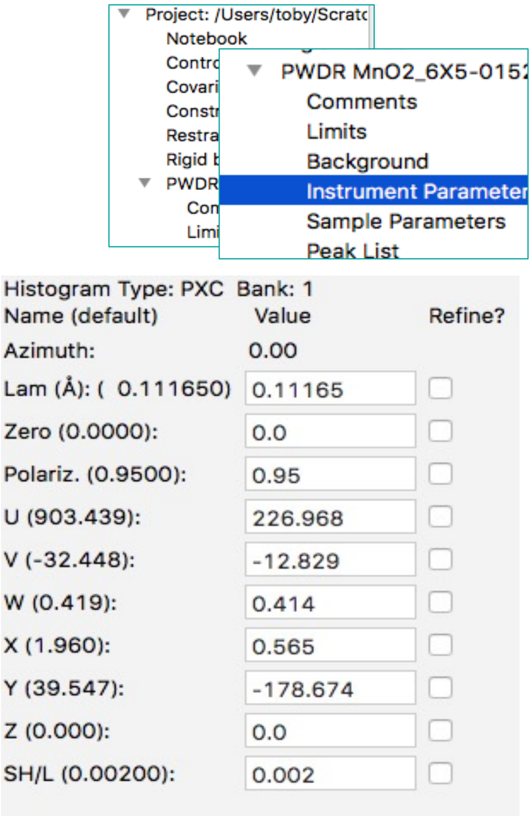
Gaussian: $\sigma^2 = U \tan^2\theta + V \tan\theta + W$

$\mathrm{FWHM} = \sigma * (8 \ln 2)^{0.5}$

Lorentzian: $\mathrm{FWHM} = X / \cos\theta + Y \tan\theta + Z$

- N.B.: Lam, Z, Zero, Polariz, are rarely refined


Instrument and sample peak widths



Histogram Type: PXC Bank: 1

Name (default)	Value	Refine?
Azimuth:	0.00	
Lam (Å): (0.111650)	0.11165	☐
Zero (0.0000):	0.0	☐
Polariz. (0.9500):	0.95	☐
U (903.439):	226.968	☐
V (-32.448):	-12.829	☐
W (0.419):	0.414	☐
X (1.960):	0.565	☐
Y (39.547):	-178.674	☐
Z (0.000):	0.0	☐
SH/L (0.00200):	0.002	☐

RELATIONS BETWEEN GSAS(-II) AND FULLPROF CW PROFILE TERMS

From **Kaduk, J. A., and Reid, J. (2011**). "Typical values of Rietveld instrument profile coefficients," *Powder Diffraction* **26**, 88-93.

$$GU(\mathrm{GSAS}) = 1803.4U(\mathrm{FULLPROF}), \qquad (13)$$

$$GV(\mathrm{GSAS}) = 1803.4V(\mathrm{FULLPROF}), \qquad (14)$$

$$GW(\mathrm{GSAS}) = 1803.4W(\mathrm{FULLPROF}), \qquad (15)$$

$$GP(\mathrm{GSAS}) = 1803.4IG(\mathrm{FULLPROF}), \qquad (16)$$

$$LX(\mathrm{GSAS}) = 100Y(\mathrm{FULLPROF}), \qquad (17)$$

$$LY(\mathrm{GSAS}) = 100X(\mathrm{FULLPROF}), \qquad (18)$$

$$S/L(\mathrm{GSAS}) = S\_L(\mathrm{FULLPROF}), \qquad (19)$$

$$H/L(\mathrm{GSAS}) = D\_L(\mathrm{FULLPROF}). \qquad (20)$$

SAMPLE BROADENING TREATMENT IN GSAS-II

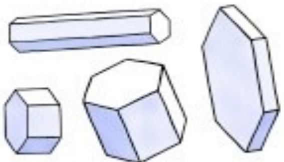
Samples broaden diffraction peaks in two possible ways, microstrain (aka residual stress) and crystallite size broadening. For each of these GSAS-II offers 3 levels of complexity

- Isotropic broadening: one value (+LGmix)
- Uniaxial broadening: two values (+LGmix) and a reciprocal space direction (set intelligently based on cell type)
- Generalized:
  - Size is always 6 terms describing an ellipsoid (constraints may be needed)
  - Microstrain: 2 to 15 terms depending on cell

LGmix is usually 1, for Lorentzian crystallite size (& µstrain) broadening (unusual case) can be 0 for Gaussian or a value between 0 & 1 for a mix of the two.

ANISOTROPIC BROADENING: BROADENING CAN BE DIRECTION-DEPENDENT

Crystallite broadening will vary with *hkl* when crystallites have smaller average dimensions in certain crystallographic directions, broadening reflections by class



www.its.caltech.edu/~atomic/snowcrystals

Microstrain broadening will vary with *hkl* if a material is more stiff (harder) in some crystallographic directions than others, again broadening reflections by class

$$\sigma^2(M_{hkl}) = \sum_{HKL} S_{HKL} h^H k^K l^L \ , H + K + L = 4$$

Cubic – m3m – 2 terms

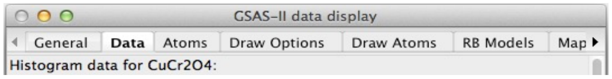
$$\sigma^2(M_{hkl}) = S_{400}(h^4 + k^4 + l^4) + 3S_{220}(h^2k^2 + h^2l^2 + k^2l^2)$$

General expression – triclinic – 15 terms

$$\begin{aligned}\sigma^2(M_{hkl}) = {} & S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3(S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2) + \\ & 2(S_{310}h^3k + S_{103}hl^3 + S_{031}k^3l + S_{130}hk^3 + S_{301}h^3l + S_{013}kl^3) + \\ & 4(S_{211}h^2kl + S_{121}hk^2l + S_{112}hkl^2)\end{aligned}$$

CRYSTALLITE SIZE BROADENING IN GSAS-II

Found in phase/data tab



Histogram data for CuCr2O4:

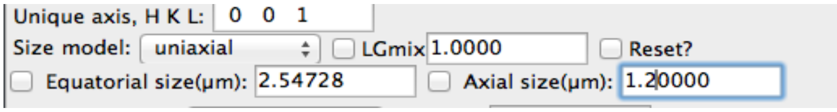
When instrumental parameters accurate (from standard) the size broadening can be read directly in microns:

Isotropic size

Size model: isotropic ☐ LGmix 1.0000 ☐ Reset?
☐ Cryst. size(μm): 2.54728

Uniaxial size broadening (in plane and out).

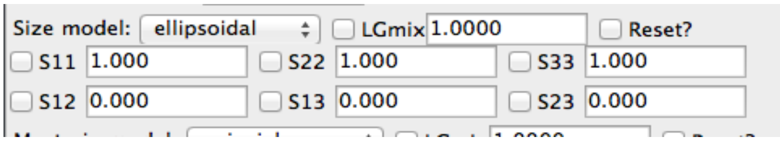
Note direction as *hkl*



Unique axis, H K L: 0 0 1
Size model: uniaxial ☐ LGmix 1.0000 ☐ Reset?
☐ Equatorial size(μm): 2.54728 ☐ Axial size(μm): 1.20000

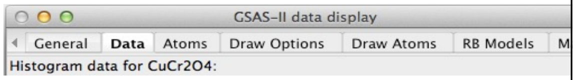
For Experts only:

Generalized size broadening, as six term tensor (complex, see plot)



Size model: ellipsoidal ☐ LGmix 1.0000 ☐ Reset?
☐ S11 1.000 ☐ S22 1.000 ☐ S33 1.000
☐ S12 0.000 ☐ S13 0.000 ☐ S23 0.000

MICROSTRAIN BROADENING IN GSAS-II

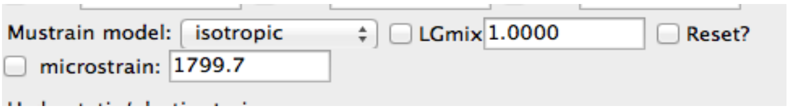


Histogram data for CuCr2O4:

When instrumental parameters are accurate (fit from standard) the strain broadening can be read directly. Values are Δd/d x 10^6 (= ΔQ/Q x 10^6) (no units)

N.B. If elastic strain constant is known, microstrain can be converted to a force

Isotropic microstrain

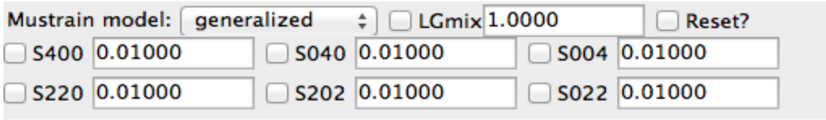


Mustrain model: isotropic ☐ LGmix 1.0000 ☐ Reset?
☐ microstrain: 1799.7

Uniaxial microstrain broadening (in plane and out).

Mustrain model: uniaxial ☐ LGmix 1.0000 ☐ Reset?
Unique axis, H K L: 0 1 0
☐ Equatorial mustrain: 1799.7 ☐ Axial mustrain: 964.6

Microstrain broadening can also be treated with the Stephens model (# of terms depends on symmetry)



Mustrain model: generalized ☐ LGmix 1.0000 ☐ Reset?
☐ S400 0.01000 ☐ S040 0.01000 ☐ S004 0.01000
☐ S220 0.01000 ☐ S202 0.01000 ☐ S022 0.01000

Anisotropic microstrain: Stephens, P. W. (**1999**). "Phenomenonological Model of Anisotropic Peak Broadening in Powder Diffraction." *Journal of Applied Crystallography* **32**(2): 281

USING BROADENING IN GSAS-II

How to use:

- Always start with isotropic. Do not vary both size and microstrain if the data range is small.
- Which one is most significant? Can the other be removed without degrading the fit?
  - Small microstrain or big small size values are insignificant
- If you suspect more terms are needed, try uniaxial.
  - Does fit improve significantly?
  - For higher symmetry crystal systems the direction is fixed (e.g. 001 for c-unique)
- Generalized (Stephens) microstrain usually refines well and when needed produces significant improvement in fit
- Generalized (ellipsoidal) size broadening is rare and is not recommended for high-symmetry materials

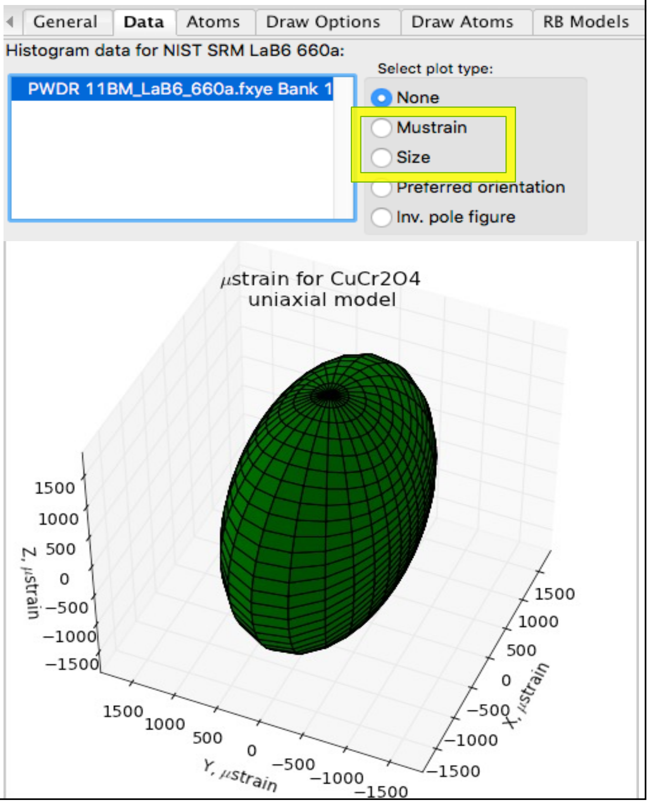
---

VISUALIZING BROADENING

GSAS-II can plot anisotropic strain or crystallite broadening as a three dimensional surface

- Select plot type on Data tab near histogram selection

When using generalized size/microstrain models, look at the plot to see if the values make sense



SEQUENTIAL REFINEMENT

POWDER DIFFRACTION MEASUREMENTS CAN BE QUICK AND EASY (OR HARD)

- With synchrotrons and area detectors, full patterns can be collected in a small fraction of a second.
- Neutron and high resolution synchrotron patterns can be collected in minutes
- This allows for **parametric** (+ *in situ* and *operando*) diffraction studies, where large numbers of diffraction patterns are collected as a function of:
  - Temperature
  - Pressure
  - Chemical composition
  - Electrochemical potential
  - Chemical reaction
  - Cycling (e.g. electrochemical)
- Manual analysis of such data in serial fashion is very time consuming

SEQUENTIAL REFINEMENT IN GSAS-II

GSAS-II offers three modes for fitting to a set of datasets.

- **Combined refinement**: All phases and parameters are adjusted to best fit all the datasets.
  - Any number of phases, any number of datasets; phase parameters will be the same for all datasets (but note use of D_{ij} allows lattice parameters to differ by dataset)
  - Good for multiple measurements under a single set of conditions (or very similar conditions)
- **Sequential refinement:** Each dataset is fit, one-at-a-time, to any number of phases.
  - All parameters are allowed to vary to best-fit each dataset in turn (use of D_{ij} required).
  - Good where there are wide changes in atom positions, phase transformations, etc.

  Sequential Refinement allows for treatment of a large number of datasets in a single project file and with automation.
- **Scripting (new):** allows for algorithmic adaptation; parallelization,… See tutorial or paper.

O'Donnell, J. H., Dreele, R. B. V., Chan, M. K. Y., and Toby, B. H. (**2018**). "A Scripting Interface for GSAS-II," Journal of Applied Crystallography **51**, 1244-1250.

SEQUENTIAL REFINEMENT CONCEPT

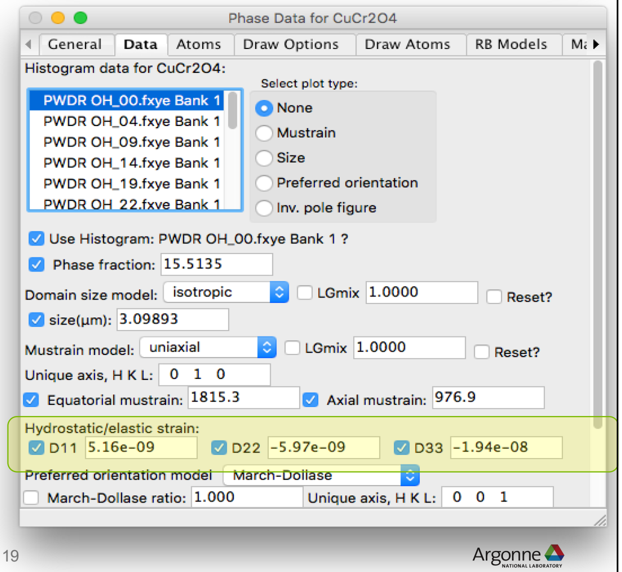
Concept: set up a refinement on the first dataset.

- Repeat that refinement on subsequent datasets varying the same parameters
- When there are changes in the sample that require extra parameters (one example, appearance of a new phase), one can add new parameters for subsequent refinements
- Optional: copy the results from fitting each dataset as the starting point for fitting next (usually a good idea).
  - Only possible when parameters are the same for all datasets in the series
- It is possible to do initial fitting with a subset of patterns in the project file and then go on to a different subset of patterns,…
  - In the end, conduct a sequential fit over all subsets
- Sequential refinements produce a convenient table of results that can be used for plotting of secondary fitting.

Note: ***automation does not lift the requirement that you must think about what you are doing and carefully review results from your fits.***

NOTES ON LATTICE CONSTANTS

- Cell lengths are associated with phases, but are expected to change in a parametric study
  - For each histogram, there are a set of hydrostatic strain tensors; these modify the cell parameters
  - These D_{ij} values must be refined in a sequential fit
- This means one can do a combined fit with lattice constants differing by dataset (histogram) (but all coordinates, Uiso values etc. will be the same)
- One cannot refine unit cell parameters and D_{ij} values for a phase at the same time.



Histogram data for CuCr2O4:

PWDR OH_00.fxye Bank 1
PWDR OH_04.fxye Bank 1
PWDR OH_09.fxye Bank 1
PWDR OH_14.fxye Bank 1
PWDR OH_19.fxye Bank 1
PWDR OH_22.fxye Bank 1

Select plot type:
● None
○ Mustrain
○ Size
○ Preferred orientation
○ Inv. pole figure

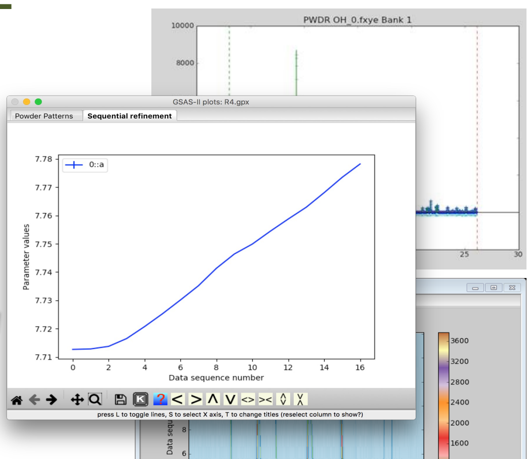
☑ Use Histogram: PWDR OH_00.fxye Bank 1 ?
☑ Phase fraction: 15.5135
Domain size model: isotropic ☐ LGmix 1.0000 ☐ Reset?
☑ size(µm): 3.09893
Mustrain model: uniaxial ☐ LGmix 1.0000 ☐ Reset?
Unique axis, H K L: 0 1 0
☑ Equatorial mustrain: 1815.3 ☑ Axial mustrain: 976.9
Hydrostatic/elastic strain:
☑ D11 5.16e-09 ☑ D22 -5.97e-09 ☑ D33 -1.94e-08
Preferred orientation model March-Dollase
☐ March-Dollase ratio: 1.000 Unique axis, H K L: 0 0 1

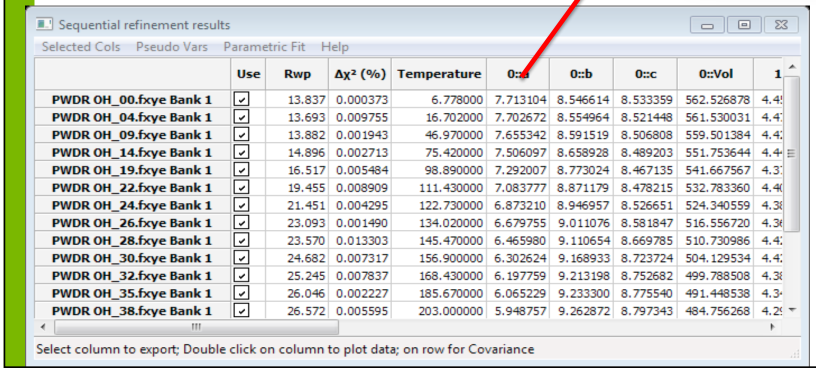
A FEW WAYS TO PERFORM A SEQUENTIAL FIT

- Fit a data set in a project as a normal refinement, then add more datasets and switch to a sequential refinement.
- Start with all datasets in a project, select only one dataset to fit sequentially, then add more (all?) datasets to range sequential fit.
- Use a separate project to fit selected dataset(s) then set up a sequential refinement

SEQUENTIAL FITTING: TYPICAL PROCESS

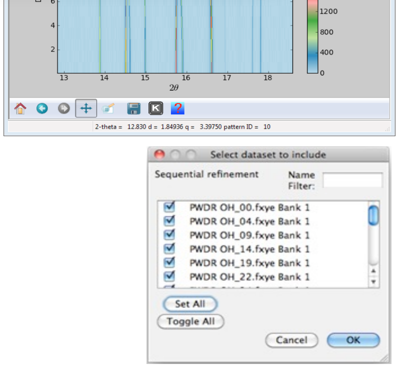
- Link phase(s) to one data set
- Fit to that one dataset manually
- Read in or link to many datasets
  - Copy parameters from initial fit to others
- Set controls to define range of datasets to use
- Perform sequential fit
- Review results and modify model where changes are needed (new phases, etc.
  - Copy parameters from initial fit to others





	Use	Rwp	Δχ² (%)	Temperature	0::a	0::b	0::c	0::Vol	1
PWDR OH_00.fxye Bank 1	☑	13.837	0.000373	6.778000	7.713104	8.546614	8.533359	562.526878	4.4
PWDR OH_04.fxye Bank 1	☑	13.693	0.009755	16.702000	7.702672	8.554964	8.521448	561.530031	4.4
PWDR OH_09.fxye Bank 1	☑	13.882	0.001943	46.970000	7.655342	8.591519	8.506808	559.501384	4.4
PWDR OH_14.fxye Bank 1	☑	14.896	0.002713	75.420000	7.506097	8.658928	8.489203	551.753644	4.4
PWDR OH_19.fxye Bank 1	☑	16.517	0.005484	98.890000	7.292007	8.773024	8.467135	541.667567	4.3
PWDR OH_22.fxye Bank 1	☑	19.455	0.008909	111.430000	7.083777	8.871179	8.478215	532.783360	4.4
PWDR OH_24.fxye Bank 1	☑	21.451	0.004295	122.730000	6.873210	8.946957	8.526651	524.340559	4.3
PWDR OH_26.fxye Bank 1	☑	23.093	0.001490	134.020000	6.679755	9.011076	8.581847	516.556720	4.3
PWDR OH_28.fxye Bank 1	☑	23.570	0.013303	145.470000	6.465980	9.110654	8.669785	510.730986	4.4
PWDR OH_30.fxye Bank 1	☑	24.682	0.007317	156.900000	6.302624	9.168933	8.723724	504.129534	4.4
PWDR OH_32.fxye Bank 1	☑	25.245	0.007837	168.430000	6.197759	9.213198	8.752682	499.788508	4.3
PWDR OH_35.fxye Bank 1	☑	26.046	0.002227	185.670000	6.065229	9.233300	8.775540	491.448538	4.3
PWDR OH_38.fxye Bank 1	☑	26.572	0.005595	203.000000	5.948757	9.262872	8.797343	484.756268	4.2

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



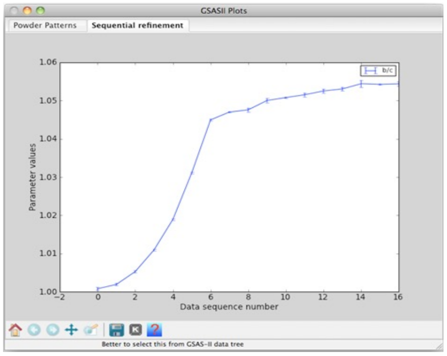
Sequential refinement

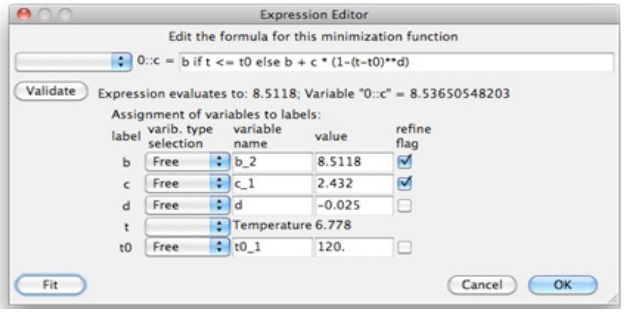
Name Filter:

- ☑ PWDR OH_00.fxye Bank 1
- ☑ PWDR OH_04.fxye Bank 1
- ☑ PWDR OH_09.fxye Bank 1
- ☑ PWDR OH_14.fxye Bank 1
- ☑ PWDR OH_19.fxye Bank 1
- ☑ PWDR OH_22.fxye Bank 1

EQUATION OF STATE (PARAMETRIC) FITTING

- New parameters may be described as functions of existing variables and values (Pseudo Vars)
  - Function is defined in Python allowing completely arbitrary, non-linear expressions
  - Covariance is properly used to estimate uncertainties on pseudo vars
- Variables and pseudo vars may be plotted
- Arbitrary parametric functions may be fit to variables and pseudo vars
  - Uncertainties properly used in weighting
  - Fit values may be shared across multiple parametric functions





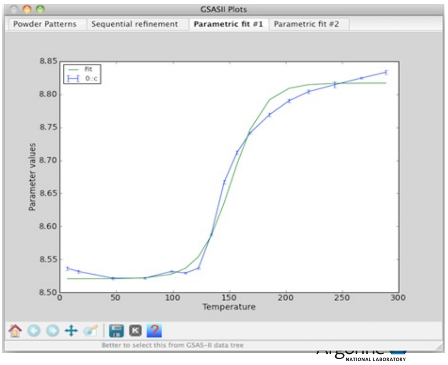
Edit the formula for this minimization function

0::c = `b if t <= t0 else b + c * (1-(t-t0)**d)`

Expression evaluates to: 8.5118; Variable "0::c" = 8.53650548203

Assignment of variables to labels:

label	varib. type selection	variable name	value	refine flag
b	Free	b_2	8.5118	☑
c	Free	c_1	2.432	☑
d	Free	d	-0.025	☐
t		Temperature	6.778	
t0	Free	t0_1	120.	☐



SCRIPTING WITH GSAS-II

MUCH OF GSAS-II CAN BE ACCESSED FROM PYTHON SCRIPTS

All features in GSAS-II are available from the GUI; increasing amounts of the capabilities are designed to be used from Python scripts

The GSASIIscriptable module provides access to key parts of the GSAS-II code

Example:

- Script to simulate a diffraction pattern

```
import os,sys
sys.path.insert(0,'/Users/toby/software/G2/GSASII')
import GSASIIscriptable as G2sc
datadir = "/Users/toby/software/G2/Tutorials/PythonScript/data"
PathWrap = lambda fil: os.path.join(datadir,fil)
gpx = G2sc.G2Project(filename='PbSO4sim.gpx') # create a project
phase0 = gpx.add_phase(PathWrap("PbSO4-Wyckoff.cif"),
         phasename="PbSO4",fmthint='CIF') # add a phase to the project
# add a simulated histogram and link it to the previous phase(s)
hist1 = gpx.add_simulated_powder_histogram("PbSO4 simulation",
            PathWrap("inst_d1a.prm"),5.,120.,Npoints=1000,
            phases=gpx.phases(),scale=500000.)
gpx.do_refinements()   # calculate pattern
gpx.save()
# save results
gpx.histogram(0).Export('PbSO4data','.csv','hist') # data
gpx.histogram(0).Export('PbSO4refl','.csv','refl') # reflections
```

SCRIPTING CAPABILITIES

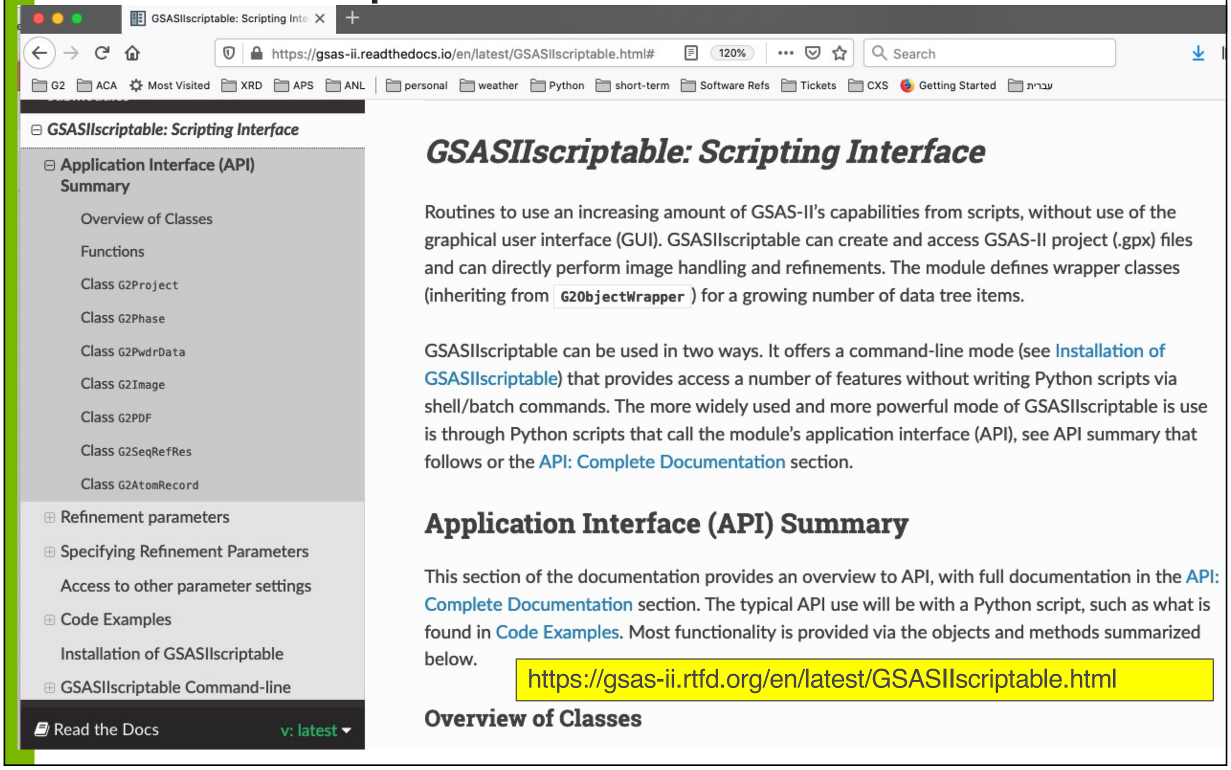
Current capabilities

- Refinements & sequential fits
- Pattern simulation
- Peak fitting
- Image integration & PDF computation
- Image calibration

Other routines are designed to be incorporated into other programs (GSASIIlattice and GSASIIspc for lattice and space group computations).

Argonne NATIONAL LABORATORY

SEE GSASIIscriptable FOR SCRIPTING DOCUMENTATION



GSASIIscriptable: Scripting Interface

Routines to use an increasing amount of GSAS-II's capabilities from scripts, without use of the graphical user interface (GUI). GSASIIscriptable can create and access GSAS-II project (.gpx) files and can directly perform image handling and refinements. The module defines wrapper classes (inheriting from `G2ObjectWrapper`) for a growing number of data tree items.

GSASIIscriptable can be used in two ways. It offers a command-line mode (see Installation of GSASIIscriptable) that provides access a number of features without writing Python scripts via shell/batch commands. The more widely used and more powerful mode of GSASIIscriptable is use is through Python scripts that call the module's application interface (API), see API summary that follows or the API: Complete Documentation section.

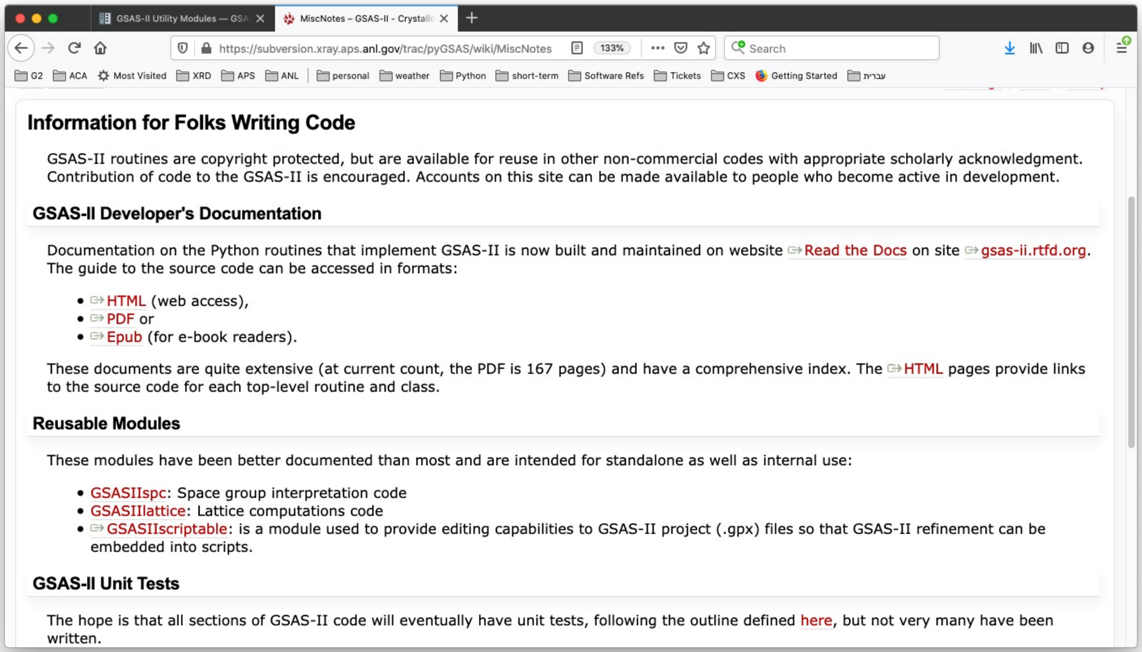
Application Interface (API) Summary

This section of the documentation provides an overview to API, with full documentation in the API: Complete Documentation section. The typical API use will be with a Python script, such as what is found in Code Examples. Most functionality is provided via the objects and methods summarized below.

https://gsas-ii.rtfd.org/en/latest/GSASIIscriptable.html

Overview of Classes

FOR CODE DEVELOPERS



Information for Folks Writing Code

GSAS-II routines are copyright protected, but are available for reuse in other non-commercial codes with appropriate scholarly acknowledgment. Contribution of code to the GSAS-II is encouraged. Accounts on this site can be made available to people who become active in development.

GSAS-II Developer's Documentation

Documentation on the Python routines that implement GSAS-II is now built and maintained on website Read the Docs on site gsas-ii.rtfd.org. The guide to the source code can be accessed in formats:

- HTML (web access),
- PDF or
- Epub (for e-book readers).

These documents are quite extensive (at current count, the PDF is 167 pages) and have a comprehensive index. The HTML pages provide links to the source code for each top-level routine and class.

Reusable Modules

These modules have been better documented than most and are intended for standalone as well as internal use:

- GSASIIspc: Space group interpretation code
- GSASIIlattice: Lattice computations code
- GSASIIscriptable: is a module used to provide editing capabilities to GSAS-II project (.gpx) files so that GSAS-II refinement can be embedded into scripts.

GSAS-II Unit Tests

The hope is that all sections of GSAS-II code will eventually have unit tests, following the outline defined here, but not very many have been written.

https://subversion.xray.aps.anl.gov/trac/pyGSAS/wiki/MiscNotes

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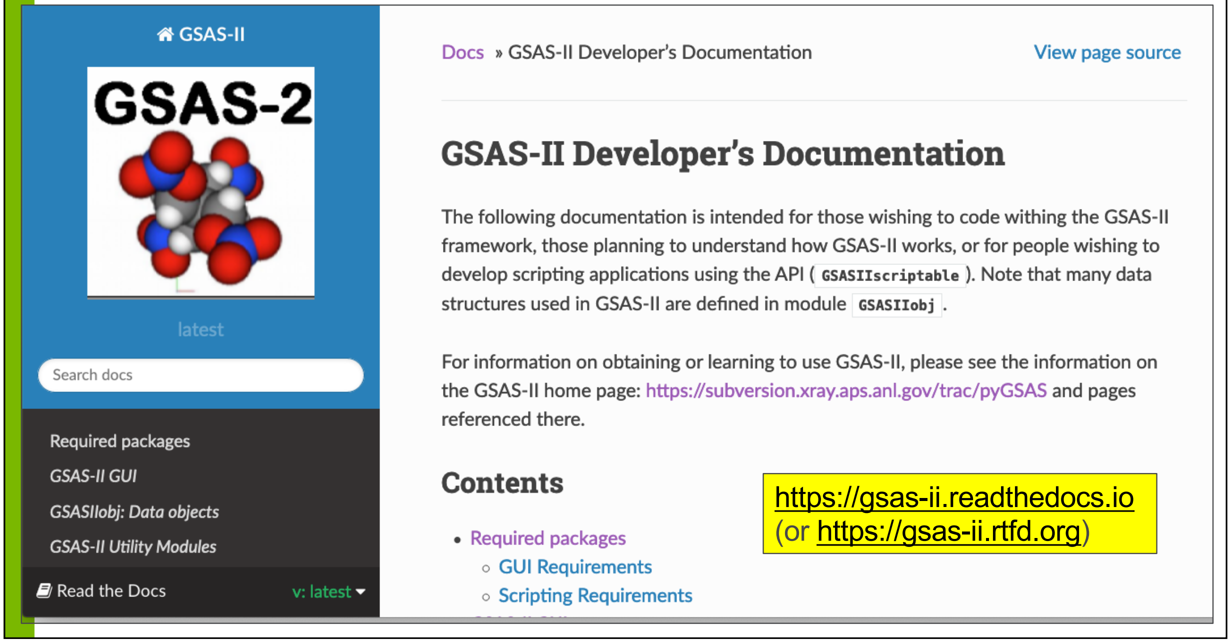
EXTENSIVE CODE DOCUMENTATION

Currently the documentation is ~300 pages (in PDF), including extensive indicies



Docs » GSAS-II Developer's Documentation

GSAS-II Developer's Documentation

The following documentation is intended for those wishing to code withing the GSAS-II framework, those planning to understand how GSAS-II works, or for people wishing to develop scripting applications using the API (`GSASIIscriptable`). Note that many data structures used in GSAS-II are defined in module `GSASIIobj` .

For information on obtaining or learning to use GSAS-II, please see the information on the GSAS-II home page: https://subversion.xray.aps.anl.gov/trac/pyGSAS and pages referenced there.

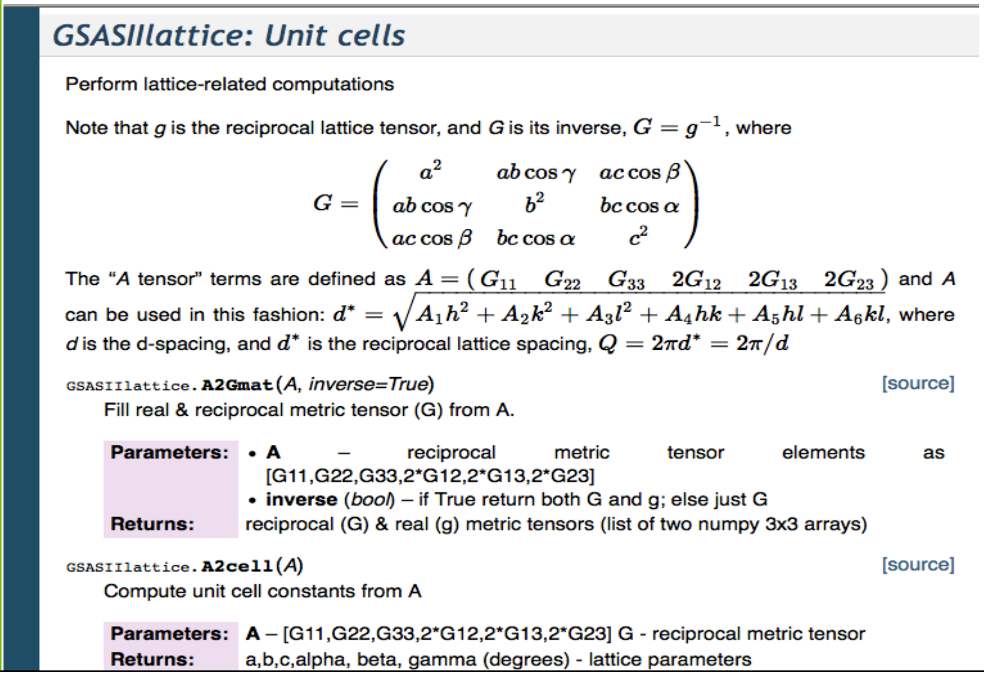
Contents

- Required packages
  - GUI Requirements
  - Scripting Requirements

https://gsas-ii.readthedocs.io
(or https://gsas-ii.rtfd.org)

DOCUMENTATION LISTS ALL TOP-LEVEL ROUTINES

Level of detail varies



GSASIIlattice: Unit cells

Perform lattice-related computations

Note that *g* is the reciprocal lattice tensor, and *G* is its inverse, $G = g^{-1}$, where

$$G = \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix}$$

The "*A* tensor" terms are defined as $A = (\,G_{11} \quad G_{22} \quad G_{33} \quad 2G_{12} \quad 2G_{13} \quad 2G_{23}\,)$ and *A* can be used in this fashion: $d^* = \sqrt{A_1h^2 + A_2k^2 + A_3l^2 + A_4hk + A_5hl + A_6kl}$, where *d* is the d-spacing, and d^* is the reciprocal lattice spacing, $Q = 2\pi d^* = 2\pi/d$

`GSASIIlattice.`**`A2Gmat`**(*A*, *inverse=True*) [source]

Fill real & reciprocal metric tensor (G) from A.

Parameters:
- **A** – reciprocal metric tensor elements as [G11,G22,G33,2*G12,2*G13,2*G23]
- **inverse** (*bool*) – if True return both G and g; else just G

Returns: reciprocal (G) & real (g) metric tensors (list of two numpy 3x3 arrays)

`GSASIIlattice.`**`A2cell`**(*A*) [source]

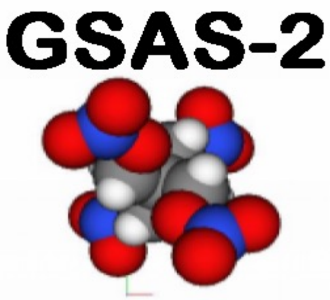
Compute unit cell constants from A

Parameters: **A** – [G11,G22,G33,2*G12,2*G13,2*G23] G - reciprocal metric tensor

Returns: a,b,c,alpha, beta, gamma (degrees) - lattice parameters

---

RIGID BODIES IN GSAS-II: WHY, WHAT AND HOW



BRIAN TOBY
Senior Scientist

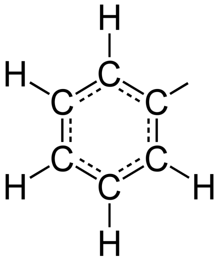
WHY USE CONSTRAINTS?

Reason #1. Structure refinement

Frequently, particularly with powder diffraction, one does not have enough data to independently determine the position of every non-hydrogen atom at the expected level of accuracy.

Use of constraints allows a crystallographic model to be simplified to be consistent with what has been measured.

Example: the 6 C atoms in a phenyl group (C_6H_5) offer 18 degrees of freedom, but if the group's internal geometry is fixed, only 6 (or less) degrees need to be treated, plus the fit structure will be more reasonable since the internal geometry of a phenyl group is well-known and does not change.



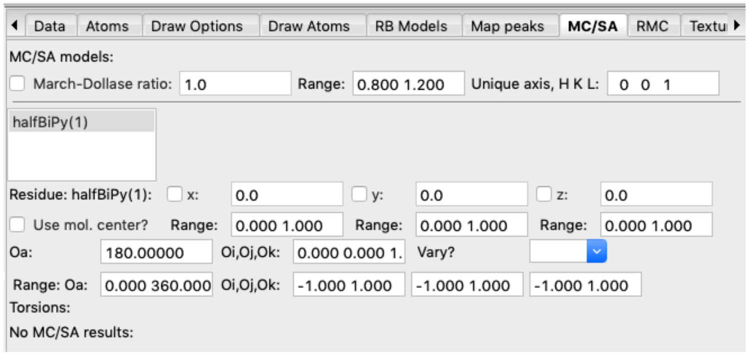
https://commons.wikimedia.org/wiki/File:Phenyl-group-2D-flat.png#/media/File:Phenyl-group-2D-flat.png

Note: when too many parameters are varied, the model will be "overfit." Unreasonable results are obtained because the data are not sufficient to independently determine all the terms that are being fit. *"Fitting to noise."*

WHY USE RIGID BODIES?

Reason #2. Structure solution

- When a structure must be solved, the complexity of that problem can be huge if every atom is considered as an independent entity. However, often large portions of the structure have known internal geometries and can be treated as groups where the group has only an unknown location and/or orientation. Sometimes a few torsional parameters may unknown and can also be included.
- Rigid bodies can be used with the Monte-Carlo/Simulated Annealing structure solution module (see the MC/SA tab in the Phase panel.)



MC/SA models:

☐ March-Dollase ratio: 1.0 Range: 0.800 1.200 Unique axis, H K L: 0 0 1

halfBiPy(1)

Residue: halfBiPy(1): ☐ x: 0.0 ☐ y: 0.0 ☐ z: 0.0

☐ Use mol. center? Range: 0.000 1.000 Range: 0.000 1.000 Range: 0.000 1.000

Oa: 180.00000 Oi,Oj,Ok: 0.000 0.000 1. Vary?

Range: Oa: 0.000 360.000 Oi,Oj,Ok: -1.000 1.000 -1.000 1.000 -1.000 1.000

Torsions:

No MC/SA results:

WHAT ARE RIGID BODIES?

Rigid bodies require two sets of axes.

1. ***the usual set of crystallographic coordinates (along a, b & c) and***
2. ***Cartesian axes, internal to the body***

Rigid body parameters set the relation of these coordinate systems.

- Atom positions inside rigid bodies are specified in Cartesian coordinates, relative to an origin.
- Rigid bodies will be placed inside a crystal structure with *at most* 6 degrees of freedom externally: 3 coordinates for the origin location and 3 orientation parameters. Symmetry may fix some of these.
- Group motion (TLS) terms for rigid bodies can be used generate to treat atomic displacement parameters (“thermal motion”) for the atoms in the group.
- GSAS-II allows additional internal degrees of freedom in rigid bodies:
  1. **Vector rigid bodies:** offers grouped bond lengths
  2. **Residue rigid bodies:** offers torsion angles

HOW DOES GSAS-II IMPLEMENT RIGID BODIES?

Use of rigid bodies in GSAS-II is a two-step process.

- First the rigid body is defined
  - Note that GSAS-II offers two types of rigid bodies (vector and residue)
  - Any number of bodies of either type may be defined

- Second, the rigid body is inserted into a structure
  - This creates a mapping from atoms in the structure and those in the body
  - Atoms may be added to the structure as the body is inserted
  - The atoms in the structure need not be in the same order as in the rigid body
  - A rigid body may be inserted multiple times in one or more phases

Once a body is inserted, its position, orientation, overall displacement factors (aka thermal motion) and occupancy factor may be refined. Residue bodies have optional torsions that can be refined; vector bodies have optional length parameters that can be refined.

GSAS-II VECTOR RIGID BODIES

Option 1: Named from the concept of adding vectors

- Vector rigid bodies have fixed geometries, but optionally allow for one or more scaling parameters
  - The scaling parameters can be refined (but can be fixed).
- The scaling parameters determine size factors for the rigid body and typically define bond lengths.
- In vector rigid body a set of atom positions (r_j) are generated from coordinates $v_{j,k}$

$$r_j = t_1 \cdot v_{j,1} + t_2 \cdot v_{j,2} + \ldots$$

or equivalently

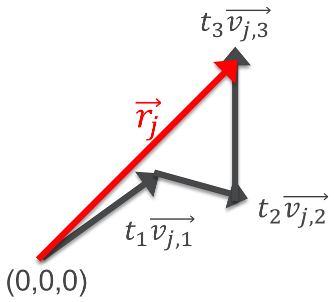
$$\begin{bmatrix} \bar{r}_1 \\ \bar{r}_2 \\ \bar{r}_3 \\ . \\ . \\ . \\ \bar{r}_n \end{bmatrix} = t_1 \begin{bmatrix} \bar{v}1,1 \\ \bar{v}2,1 \\ \bar{v}3,1 \\ . \\ . \\ . \\ \bar{v}n,1 \end{bmatrix} + t_2 \begin{bmatrix} \bar{v}1,2 \\ \bar{v}2,2 \\ \bar{v}3,2 \\ . \\ . \\ . \\ \bar{v}n,2 \end{bmatrix} + \ldots$$

VECTOR RIGID BODIES: CONCEPT

A sum of vectors provides the position of each atom

- A concept that explains both the name and reasoning that helps understand how vector bodies work is to consider that each atom position is generated relative to the origin from the sum of a scaled set of vectors:

$$\overrightarrow{r_j} = t_1\overrightarrow{v_{j,1}} + t_2\overrightarrow{v_{j,2}} + t_3\overrightarrow{v_{j,3}} + \ \ldots$$



$$\begin{bmatrix} \bar{r}_1 \\ \bar{r}_2 \\ \bar{r}_3 \\ . \\ . \\ . \\ \bar{r}_n \end{bmatrix} = t_1 \begin{bmatrix} \bar{v}1,1 \\ \bar{v}2,1 \\ \bar{v}3,1 \\ . \\ . \\ . \\ \bar{v}n,1 \end{bmatrix} + t_2 \begin{bmatrix} \bar{v}1,2 \\ \bar{v}2,2 \\ \bar{v}3,2 \\ . \\ . \\ . \\ \bar{v}n,2 \end{bmatrix} + \ldots$$

FICTITIOUS VECTOR RB EXAMPLE

Vector example: option 1 part A

- Imagine a square rigid body with 8 atoms
  - for simplicity z (=0 for all atoms) is omitted here.

Coordinates for A:

(0.5,0.5), (0.5,-0.5), (-0.5,-0.5), (-0.5,0.5)

- A-A distance is 1

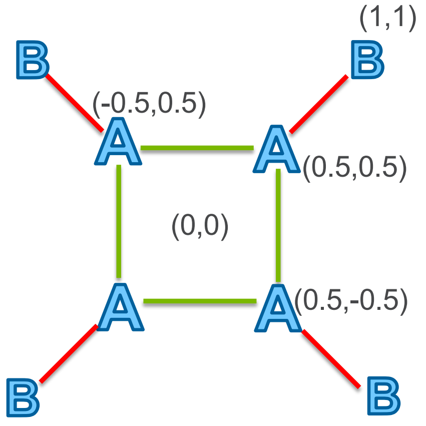
Coordinates for B:

(1,1), (1,-1), (-1,-1), (-1,1)

- A-B distance is $1/\sqrt{2}$

This can be expressed as a single matrix:

$$\begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_8 \end{pmatrix} = \begin{pmatrix} 0.5 & 0.5 \\ -0.5 & 0.5 \\ -0.5 & -0.5 \\ 0.5 & -0.5 \\ 1 & 1 \\ -1 & 1 \\ -1 & -1 \\ 1 & -1 \end{pmatrix}$$

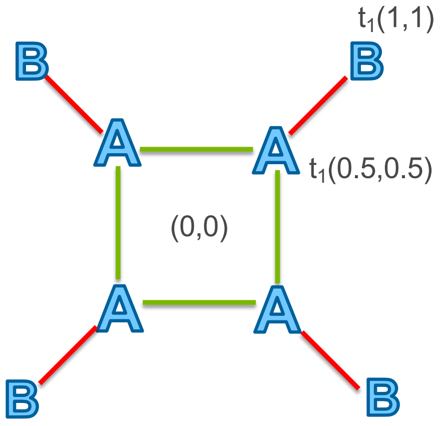


FICTITIOUS VECTOR RB EXAMPLE

Vector example: option 1 part B

- Single matrix with scaling factor :

$$\begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_8 \end{pmatrix} = t_1 \begin{pmatrix} 0.5 & 0.5 \\ -0.5 & 0.5 \\ -0.5 & -0.5 \\ 0.5 & -0.5 \\ 1 & 1 \\ -1 & 1 \\ -1 & -1 \\ 1 & -1 \end{pmatrix}$$



Note that t_1 scales the entire rigid body

- A-A bonds are length t_1
- A-B bonds are length $t_1/\sqrt{2}$

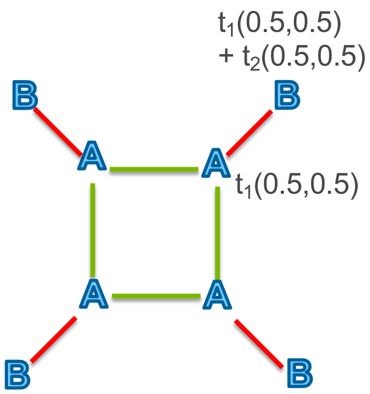
Arbitrary units can be used for coordinates since t_1 scales them to Ångstroms.

FICTITIOUS VECTOR RB EXAMPLE

Vector example: option 2

- With two matrices we can make A-A and A-B lengths into separate variables:

$$\begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_8 \end{pmatrix} = t_1 \begin{pmatrix} 0.5 & 0.5 \\ -0.5 & 0.5 \\ -0.5 & -0.5 \\ 0.5 & -0.5 \\ 0.5 & 0.5 \\ -0.5 & 0.5 \\ -0.5 & -0.5 \\ 0.5 & -0.5 \end{pmatrix} + t_2 \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0.5 & 0.5 \\ -0.5 & 0.5 \\ -0.5 & -0.5 \\ 0.5 & -0.5 \end{pmatrix}$$



Note that t_1 scales the entire rigid body; A & B atoms all move with t_1

Note that only B atoms move with t_2

- A-A bonds are length t_1
- A-B bonds are length $t_2 /\sqrt{2}$

GSAS-II RESIDUE RIGID BODIES

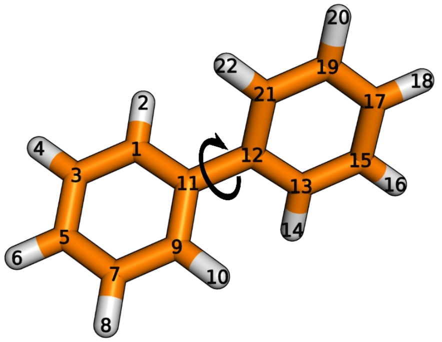
Type 2. Name from use of “residues” in protein crystallography

The dimensions of a residue rigid body cannot change, but there can be torsion angles defined, which allow sections of the molecule to reposition. There can be multiple torsions in a rigid body.

Example: this biphenyl [$(C_6H_5)_2$] molecule has one potential *internal* degree of freedom which is the torsional angle on the C-C bond joining the two rings (atoms 11 & 12 in diagram)

Residue coordinates must be in Ångstroms

When defining torsions, GSAS-II needs two atoms to be defined: an origin and a pivot atom. Other atoms bonded to the pivot are called riders.



Torsion origin: 11, pivot 12, riders 13 & 21 (*or equivalently, origin: 12, pivot: 11, riders: 1 & 9*)

http://erg.biophys.msu.ru/tiki/tiki-index.php?page=Ab+initio+energy+scan

METHODS TO GENERATE RIGID BODY COORDINATES

There are several approaches for generating rigid body coordinates.

1. For simple 2-D bodies, the object can sketched out on paper and the coordinates can be derived from simple geometry.
2. A molecular editor, force-field or quantum code* can be used to build and minimize the approximate (gas phase) structure for a molecule or fragment. Cartesian coordinates are then exported.
   - The open source Avogadro program is a good choice (https://sourceforge.net/projects/avogadro/); write XYZ output.
3. If you have a crystal structure (for example, from CSD) containing the rigid body you wish to use, those atoms can be extracted into a GSAS-II rigid body.
   - You can extract atoms from a structure and then optimize in Avogadro

* Note that GSAS-II will not read a Z-matrix file (which is commonly used for simulations) but OpenBabel (http://openbabel.org) will convert this to XYZ output format.

SYMMETRY AND RIGID BODIES

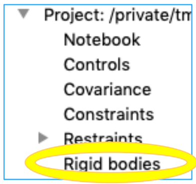
Before defining a rigid body, it is important to consider how those atoms will appear in the model. Symmetry can place constraints on the rigid body origin and axial orientation *in Cartesian space* and dictate how the RB is constructed.

- Is there internal symmetry to the rigid body? If so, is that symmetry enforced by the space group symmetry in the lattice?
  - For the example that follows, we will have a rigid body on a center of symmetry (-1) site. This means that the Cartesian origin must be placed at the crystallographic site where the -1 is located.
  - More details on symmetry and rigid bodies will be covered later
- Note that a single rigid body may be inserted in multiple locations in a single structure, but if the moiety is found in different symmetry environments, the body might need to be defined with more than one description.

If TLS parameters will be refined, it is best to put the origin at the center of mass

HOW ARE RIGID BODIES USED IN GSAS-II?

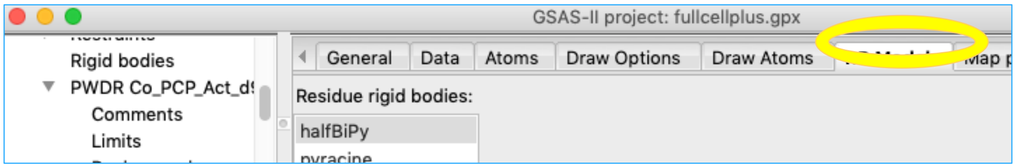
Two steps are needed for rigid bodies



Create: Bodies are first defined for a project

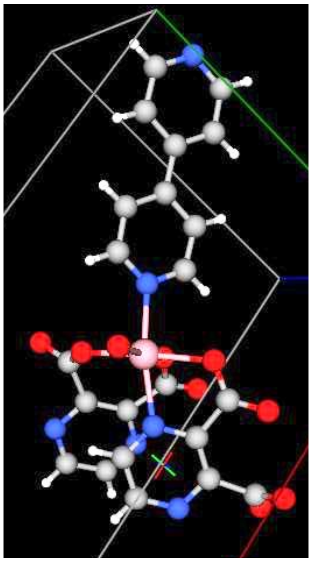
- Define atom positions, Cartesian origin & axes. This is done in the "Rigid bodies" tree item

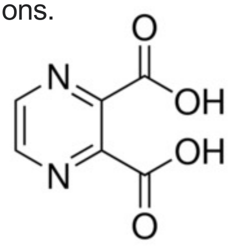
Insert: The defined rigid body is placed into a crystal structure, defining the position of the group and its orientation. Inserting a body also defines which atoms in the structure will have their coordinates generated from the body. This is done in the "RB Models" phase tab.



TWO RB EXAMPLES IN ONE MOF STRUCTURE

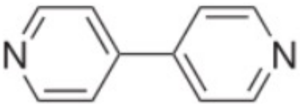
- The pictured structure is built from a metal ion, 4-4'-bipyridine molecules, and 2,3-pyrazinedicarboxylic acid ions.





2,3-pyrazinedicarboxylic acid

https://www.sigmaaldrich.com/catalog/product/aldrich/p56208?lang=en&region=US



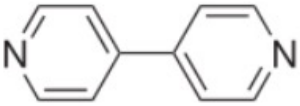
4-4'-bipyridine

The asymmetric unit contains

- a half 4-4'-bipyridine (bipyridine)
- a single complete 2,3-pyrazinedicarboxylic acid ion (pyrazine)

The symmetry of each needs to be considered separately

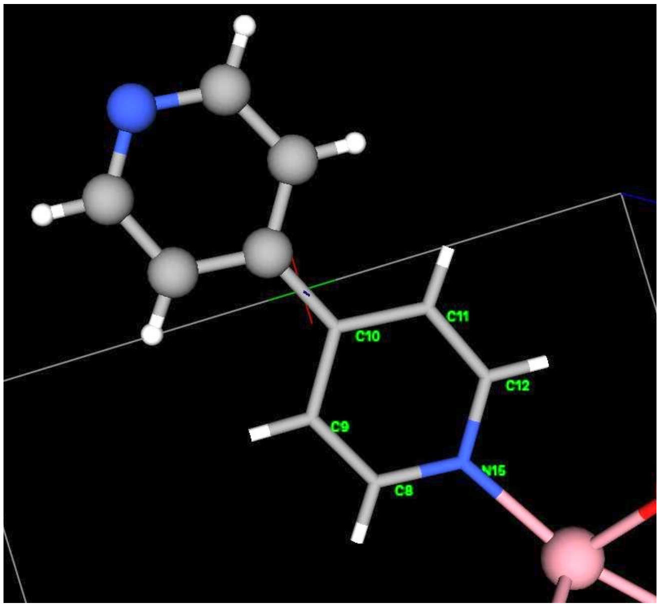
4-4’-BIPYRIDINE (BIPYRIDINE)



Care required: this is on a special position

- The asymmetric unit is drawn as stick figure & labeled (symmetry-generated atoms are ball-and-stick)
- Note that there is a center of symmetry ($\bar{1}$) between C10 and its symmetry-twin.
- Examination of plot or coordinates identifies the $\bar{1}$ location as (0,$\frac{1}{2}$,1)

To preserve the symmetry, the origin for the rigid body must be at the midpoint between C10 and C10’. That will be placed at (0,$\frac{1}{2}$,1) in crystal coordinates.

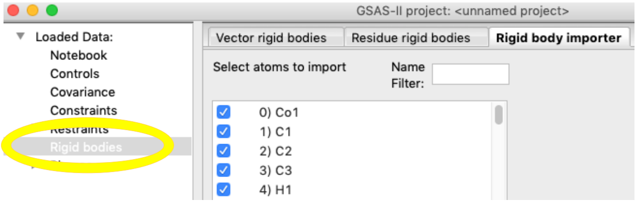


CREATE THE BIPYRIDINE RIGID BODY (1)

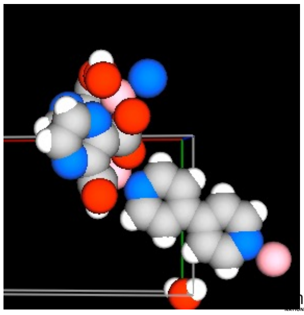
Work can be done in a new project, but a phase is needed to create the “Rigid Bodies” tree entry

In this example we will use a publication as the source of coordinates for the rigid body.

- Note that because we will need both C10 and C10’ to establish the origin, the structure must be expanded to provide both atoms before it is read in.
- From either “Vector rigid bodies” or “Residue rigid bodies” use the Edit Vector Body/Extract from file menu command
- Select a file format, in this case CIF and then find the CIF file and select it
  - All atoms are brought into the ”Rigid body importer” selector and are plotted.



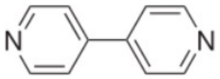
☑ 0) Co1
☑ 1) C1
☑ 2) C2
☑ 3) C3
☑ 4) H1

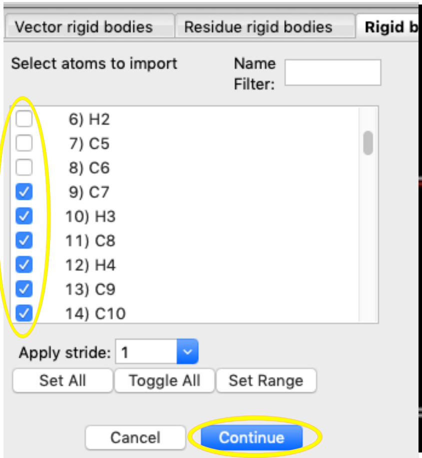


CREATE THE BIPYRIDINE RIGID BODY (2)

Select the atoms needed to build the rigid body

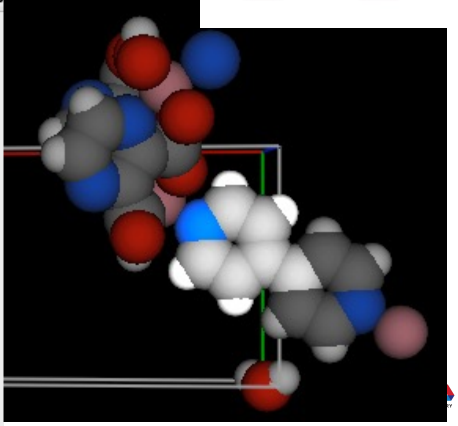
- In the Atom selector, unselect all atoms, and select only the atoms from one ring plus one atom on the other ring.
  - Note that selected atoms are brightly colored while unselected atoms appear much darker.
- Press continue





☐ 6) H2
☐ 7) C5
☐ 8) C6
☑ 9) C7
☑ 10) H3
☑ 11) C8
☑ 12) H4
☑ 13) C9
☑ 14) C10

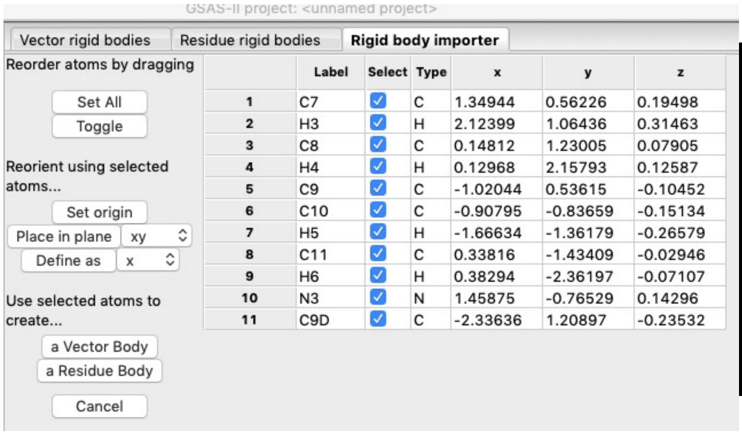
Apply stride: 1



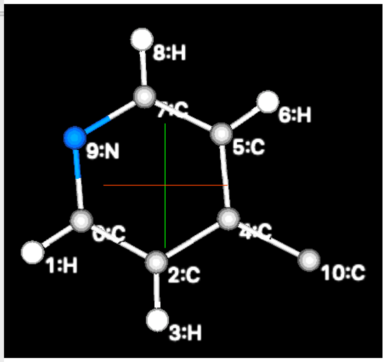
CREATE THE BIPYRIDINE RIGID BODY (3)

For convenience (but not required) we will define the axes orientation

Once the atoms are selected, a new table with Cartesian coordinates and a plot of the atoms is shown.



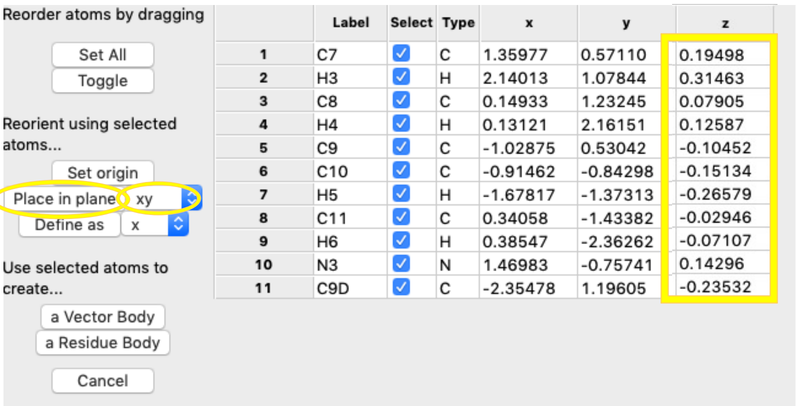
	Label	Select	Type	x	y	z
1	C7	☑	C	1.34944	0.56226	0.19498
2	H3	☑	H	2.12399	1.06436	0.31463
3	C8	☑	C	0.14812	1.23005	0.07905
4	H4	☑	H	0.12968	2.15793	0.12587
5	C9	☑	C	-1.02044	0.53615	-0.10452
6	C10	☑	C	-0.90795	-0.83659	-0.15134
7	H5	☑	H	-1.66634	-1.36179	-0.26579
8	C11	☑	C	0.33816	-1.43409	-0.02946
9	H6	☑	H	0.38294	-2.36197	-0.07107
10	N3	☑	N	1.45875	-0.76529	0.14296
11	C9D	☑	C	-2.33636	1.20897	-0.23532



CREATE THE BIPYRIDINE RIGID BODY (4)

Put atoms in plane (optional)

With all atoms selected, click on the place in plane, with “xy” selected adjacent. Note that the z values are nearly zero. There is no visible change in the plot except that the cross hairs rotate, showing the different axes directions.

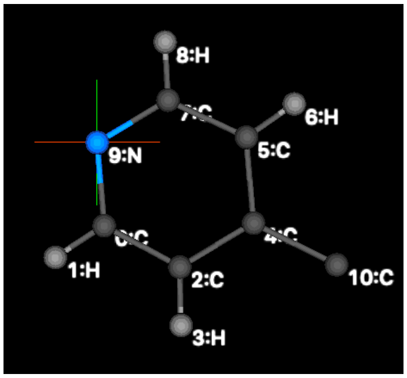


	Label	Select	Type	x	y	z
1	C7	☑	C	1.35977	0.57110	0.19498
2	H3	☑	H	2.14013	1.07844	0.31463
3	C8	☑	C	0.14933	1.23245	0.07905
4	H4	☑	H	0.13121	2.16151	0.12587
5	C9	☑	C	-1.02875	0.53042	-0.10452
6	C10	☑	C	-0.91462	-0.84298	-0.15134
7	H5	☑	H	-1.67817	-1.37313	-0.26579
8	C11	☑	C	0.34058	-1.43382	-0.02946
9	H6	☑	H	0.38547	-2.36262	-0.07107
10	N3	☑	N	1.46983	-0.75741	0.14296
11	C9D	☑	C	-2.35478	1.19605	-0.23532

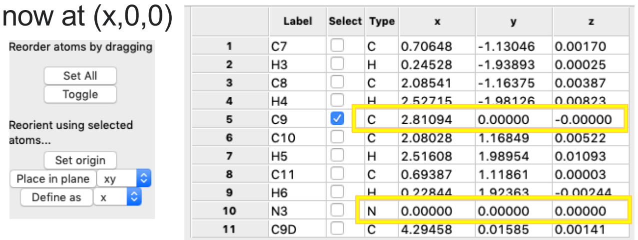
CREATE THE BIPYRIDINE RIGID BODY (5)

Set up the axes (optional)

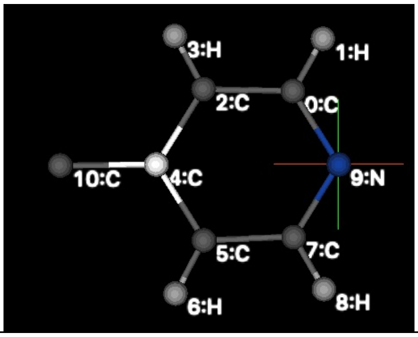
We will make the x-axis run from the N atom to one of the C atoms by unselecting the N atom and then toggle (so that it is the only selected atom). Temporarily make that atom the origin by pressing the “Set origin” button. Note that the cross hairs move to the N atom and its coordinates are now (0,0,0).



Then unselect the N atom and select the C atom and press ”define as” with “x” selected. The body rotates and the selected C atom is now at (x,0,0)

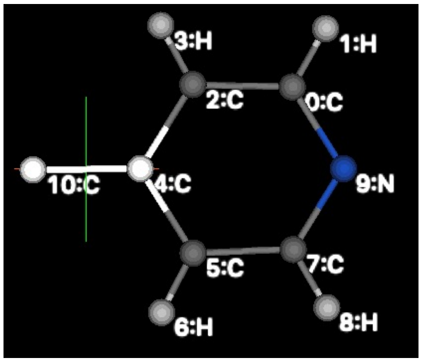


	Label	Select	Type	x	y	z
1	C7	☐	C	0.70648	-1.13046	0.00170
2	H3	☐	H	0.24528	-1.93893	0.00025
3	C8	☐	C	2.08541	-1.16375	0.00387
4	H4	☐	H	2.52715	-1.98126	0.00823
5	C9	☑	C	2.81094	0.00000	-0.00000
6	C10	☐	C	2.08028	1.16849	0.00522
7	H5	☐	H	2.51608	1.98954	0.01093
8	C11	☐	C	0.69387	1.11861	0.00003
9	H6	☐	H	0.22844	1.92363	-0.00244
10	N3	☐	N	0.00000	0.00000	0.00000
11	C9D	☐	C	4.29458	0.01585	0.00141



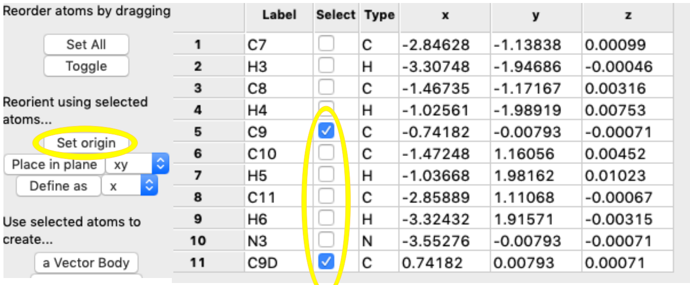
CREATE THE BIPYRIDINE RIGID BODY (6)

Required: place origin on center of symmetry



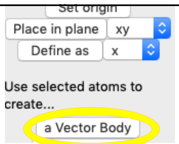
The midpoint between the two rings *must* be the location of the center of symmetry.

Select the two C atoms that join the two rings. Then press the “Set origin” button to put the origin at the average of the two selected positions.

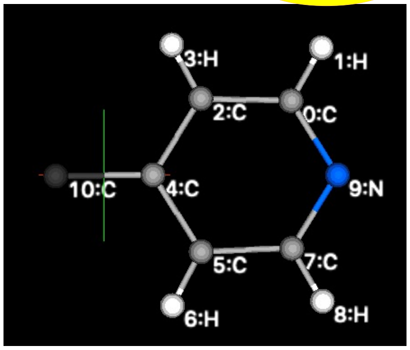


	Label	Select	Type	x	y	z
1	C7	☐	C	-2.84628	-1.13838	0.00099
2	H3	☐	H	-3.30748	-1.94686	-0.00046
3	C8	☐	C	-1.46735	-1.17167	0.00316
4	H4	☐	H	-1.02561	-1.98919	0.00753
5	C9	☑	C	-0.74182	-0.00793	-0.00071
6	C10	☐	C	-1.47248	1.16056	0.00452
7	H5	☐	H	-1.03668	1.98162	0.01023
8	C11	☐	C	-2.85889	1.11068	-0.00067
9	H6	☐	H	-3.32432	1.91571	-0.00315
10	N3	☐	N	-3.55276	-0.00793	-0.00071
11	C9D	☑	C	0.74182	0.00793	0.00071

CREATE THE BIPYRIDINE RIGID BODY (7)



Export all atoms in the ring, but not the “extra” atom



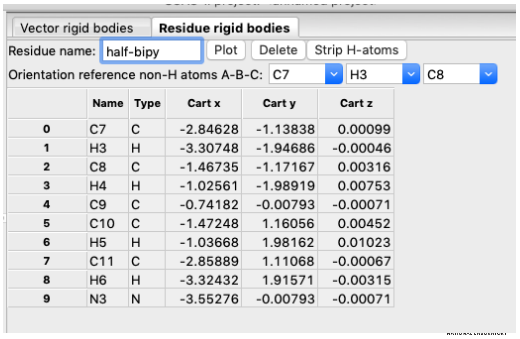
We want to export all but the last C atom (C11). (This can be done simply by unselect the 4th atom and press toggle, highlighting all atoms in the one ring.)

Then create a residue rigid body by pressing the “a Residue Body” button.

Change the name of the body

If you will use the body in a different project, use “Edit Rigid Body”/“Save rigid body” to write a file.

Note: while we will use a residue body here, since there are no torsions for this body, a vector rigid body would work just as well.



Residue name: half-bipy

Orientation reference non-H atoms A-B-C: C7 H3 C8

	Name	Type	Cart x	Cart y	Cart z
0	C7	C	-2.84628	-1.13838	0.00099
1	H3	H	-3.30748	-1.94686	-0.00046
2	C8	C	-1.46735	-1.17167	0.00316
3	H4	H	-1.02561	-1.98919	0.00753
4	C9	C	-0.74182	-0.00793	-0.00071
5	C10	C	-1.47248	1.16056	0.00452
6	H5	H	-1.03668	1.98162	0.01023
7	C11	C	-2.85889	1.11068	-0.00067
8	H6	H	-3.32432	1.91571	-0.00315
9	N3	N	-3.55276	-0.00793	-0.00071

INSERT THE 2,3-PYRAZINEDICARBOXYLIC ACID (PYRAZINE)

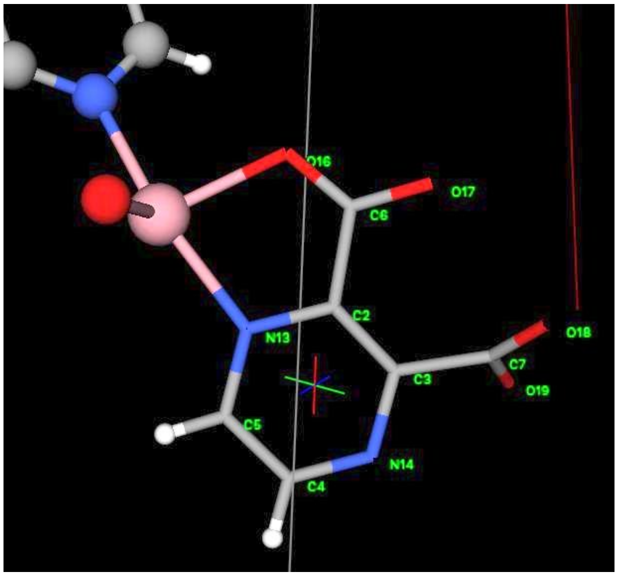
Note: not on a special position

The asymmetric unit structure has been drawn here

  - Pyrazine asymmetric unit drawn as stick figure & labeled

- Note that the ion is planar with the exception of the 4 oxygens
  - The O atoms will need torsions to position them

There is no internal symmetry here so the origin of the body can be arbitrary

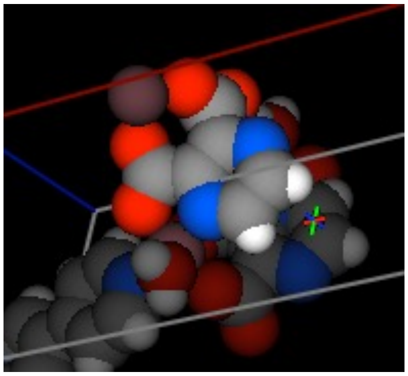


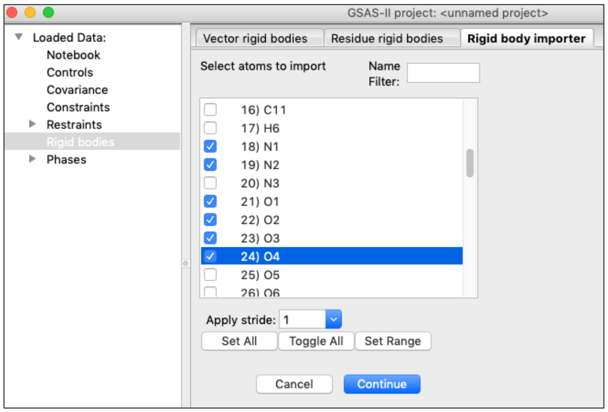
CREATE THE PYRAZINE RIGID BODY (1)

Import the CIF file again, but select different atoms

Repeating the previous process: use “Edit Vector Body”/“Extract from file” menu command again

- Select a file format (in this case CIF) and then find the CIF file and select it. Then select the 6 C atoms, 2 N and 2 H atoms and 4 O atoms in the pyrazine ion.
  - To see, it will help to reorient the 3D display by dragging with the mouse left and right buttons





Select atoms to import

Name Filter:

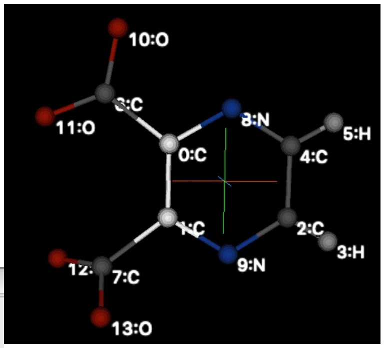
☐ 16) C11
☐ 17) H6
☑ 18) N1
☑ 19) N2
☐ 20) N3
☑ 21) O1
☑ 22) O2
☑ 23) O3
☑ 24) O4
☐ 25) O5
☐ 26) O6

Apply stride: 1

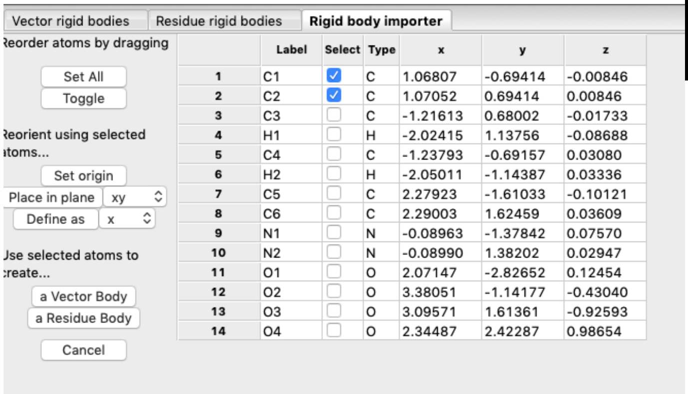
CREATE THE PYRAZINE RIGID BODY (2)

Place atoms in a plane and redefine the origin

Unselect the O atoms, since they are not planar and press “Set origin” and “Place in plane” buttons (with “xy” selected)



Select the two C atoms and press “Define as” (with “x” selected) to place the x-axis between the selected atoms



	Label	Select	Type	x	y	z
1	C1	☑	C	1.06807	-0.69414	-0.00846
2	C2	☑	C	1.07052	0.69414	0.00846
3	C3	☐	C	-1.21613	0.68002	-0.01733
4	H1	☐	H	-2.02415	1.13756	-0.08688
5	C4	☐	C	-1.23793	-0.69157	0.03080
6	H2	☐	H	-2.05011	-1.14387	0.03336
7	C5	☐	C	2.27923	-1.61033	-0.10121
8	C6	☐	C	2.29003	1.62459	0.03609
9	N1	☐	N	-0.08963	-1.37842	0.07570
10	N2	☐	N	-0.08990	1.38202	0.02947
11	O1	☐	O	2.07147	-2.82652	0.12454
12	O2	☐	O	3.38051	-1.14177	-0.43040
13	O3	☐	O	3.09571	1.61361	-0.92593
14	O4	☐	O	2.34487	2.42287	0.98654

Note that these origin & axes settings are for convenience in viewing and understanding the body, but are not required.

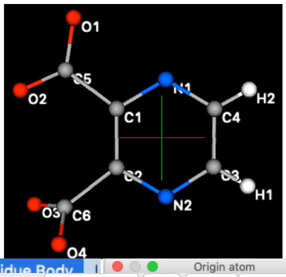
CREATE THE PYRAZINE RIGID BODY (3)

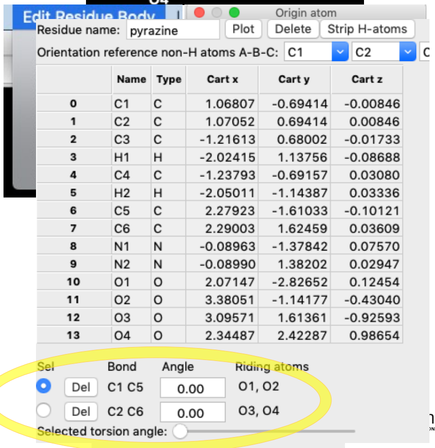
Create body & define carboxylic torsions

Since this ion needs torsional rotation for the carboxylic groups, a residue rigid body is required.

- Select all atoms and then press “a Rigid Body” to create it.
- Select the new body and rename it.
- Define two torsional degrees of freedom: (It helps to press the “Plot” button to identify the atoms.) Use Edit Rigid Body/Define torsion menu item.
  - Origin C1; Pivot C5 (riding O1 & O2)
  - Origin C2; Pivot C6 (riding O3 & O4)

Save the rigid body, if will be needed in a different project.





Residue name: pyrazine

Orientation reference non-H atoms A-B-C: C1 C2

	Name	Type	Cart x	Cart y	Cart z
0	C1	C	1.06807	-0.69414	-0.00846
1	C2	C	1.07052	0.69414	0.00846
2	C3	C	-1.21613	0.68002	-0.01733
3	H1	H	-2.02415	1.13756	-0.08688
4	C4	C	-1.23793	-0.69157	0.03080
5	H2	H	-2.05011	-1.14387	0.03336
6	C5	C	2.27923	-1.61033	-0.10121
7	C6	C	2.29003	1.62459	0.03609
8	N1	N	-0.08963	-1.37842	0.07570
9	N2	N	-0.08990	1.38202	0.02947
10	O1	O	2.07147	-2.82652	0.12454
11	O2	O	3.38051	-1.14177	-0.43040
12	O3	O	3.09571	1.61361	-0.92593
13	O4	O	2.34487	2.42287	0.98654

Sel		Bond	Angle	Riding atoms
●	Del	C1 C5	0.00	O1, O2
○	Del	C2 C6	0.00	O3, O4

Selected torsion angle:

PREPARE TO INSERT RIGID BODIES

In this case we have a rough idea where the rigid bodies are located, so we will place them to match approximate of atoms in the structure.

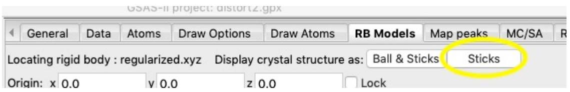
Notes

- The rigid bodies have H atoms, but the atoms list does not; any rigid body atoms not in the atoms list can be added to the atoms list when the body is inserted
- There are some distortions in groups that will be corrected when atom positions are generated by from the rigid bodies.
- Note the atom list need not be ordered to match the rigid body, but that can make things more convenient.

VIEWING STRUCTURES & RIGID BODIES

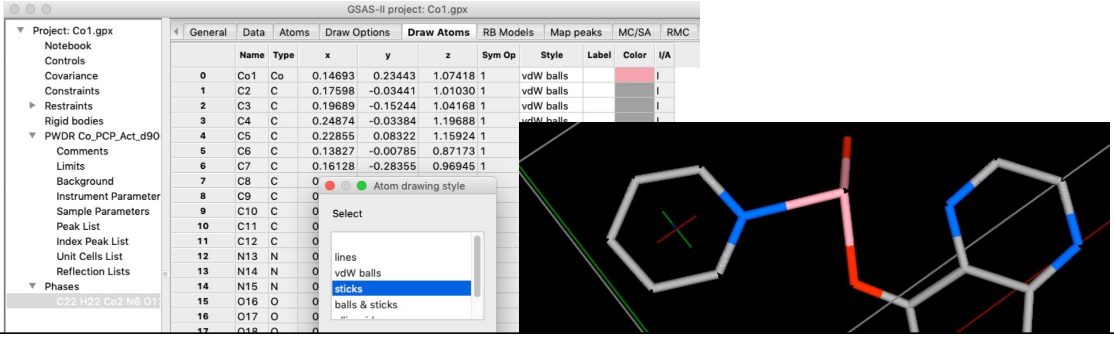
The view of the structure is determined by the atoms copied from the asymmetric cell into the Draw Atoms array and their settings.

- To best view the structure and rigid body use “Stick” or “Balls & Stick” modes.
  - Select using the buttons on the RB Models tab or by double-clicking on the column labeled ”style” in the “Draw Atoms” tab



Locating rigid body : regularized.xyz Display crystal structure as: Ball & Sticks Sticks

Origin: x 0.0 y 0.0 z 0.0 ☐ Lock



	Name	Type	x	y	z	Sym Op	Style	Label	Color	I/A
0	Co1	Co	0.14693	0.23443	1.07418	1	vdW balls		🟥	I
1	C2	C	0.17598	-0.03441	1.01030	1	vdW balls		▨	I
2	C3	C	0.19689	-0.15244	1.04168	1	vdW balls		▨	I
3	C4	C	0.24874	-0.03384	1.19688	1	vdW balls		▨	I
4	C5	C	0.22855	0.08322	1.15924	1				
5	C6	C	0.13827	-0.00785	0.87173	1				
6	C7	C	0.16128	-0.28355	0.96945	1				
7	C8	C	0							
8	C9	C	0							
9	C10	C	0							
10	C11	C	0							
11	C12	C	0							
12	N13	N	0							
13	N14	N	0							
14	N15	N	0							
15	O16	O	0							
16	O17	O	0							

ORIENTING STRUCTURES IN WINDOW

Mouse movements change view of structure

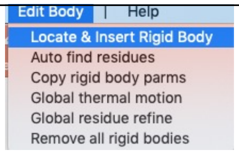
When the structure is viewed, use of the mouse buttons changes the view of the crystal structure:

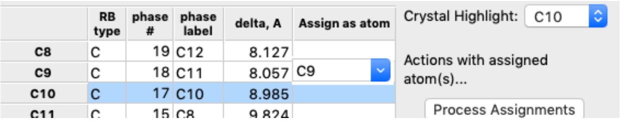
- Holding down left button (left drag): rotates axes around screen x & y
- Holding down right button (right drag): Moves the viewpoint, which is kept at the center of the screen (effectively translating the structure)
- Holding down center button (center drag): rotates axes around screen z
- Rotating the scroll wheel: changes "camera position" (zoom in/out)

When the Rigid Body and structure are shown together, holding the Alt button while dragging the mouse causes the same movements, but only to the rigid body

- Pressing the "c" key sets the viewpoint to (½,½,½) [value can also be edited in Draw Options tab]

HIGHLIGHTING ATOMS





	RB type	phase #	phase label	delta, A	Assign as atom
C8	C	19	C12	8.127	
C9	C	18	C11	8.057	C9
C10	C	17	C10	8.985	
C11	C	15	C8	9.824	

Crystal Highlight: C10

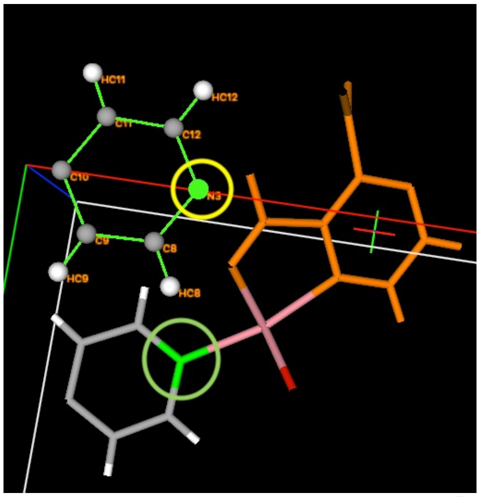
Actions with assigned atom(s)...

The "Locate and Insert Rigid Body" command creates table with rigid body atoms and matching atoms in crystal structure (with the distance between them).

Atoms can be paired.

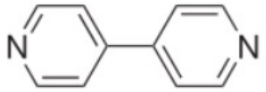
To help determine which atoms should be paired, specific atoms can be highlighted.

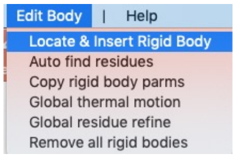
- Selecting a row causes the rigid body atom and the matching crystal structure atom to be highlighted
- To highlight a different atom in the crystal, use the "Crystal Highlight" pulldown, or press Tab to select crystal atoms
- Pressing Alt+Tab cycles through the rigid body atoms.



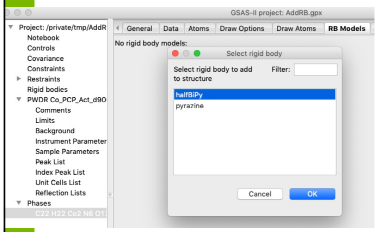
INSERT THE BIPYRIDINE INTO THE STRUCTURE (1)

Assumes rigid body is already defined (or read in)





- Go to RB Models phase tab; use “Edit Body”/“Locate and Insert Rigid Body”; select the bipyridine fragment.



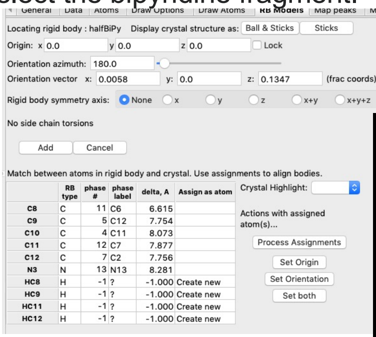
No rigid body models:

Select rigid body to add to structure

Filter:

halfBiPy

pyrazine



Locating rigid body : halfBiPy

Display crystal structure as:

Origin: x 0.0 y 0.0 z 0.0 ☐ Lock

Orientation azimuth: 180.0

Orientation vector x: 0.0058 y: 0.0 z: 0.1347 (frac coords)

Rigid body symmetry axis: ● None ○ x ○ y ○ z ○ x+y ○ x+y+z

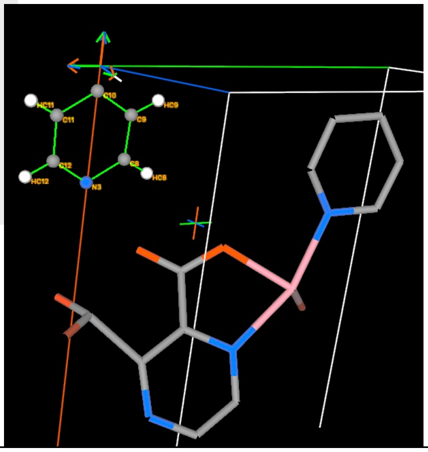
No side chain torsions

Match between atoms in rigid body and crystal. Use assignments to align bodies.

	RB type	phase #	phase label	delta, A	Assign as atom
C8	C	11	C6	6.615	
C9	C	5	C12	7.754	
C10	C	4	C11	8.073	
C11	C	12	C7	7.877	
C12	C	7	C2	7.756	
N3	N	13	N13	8.281	
HC8	H	-1	?	-1.000	Create new
HC9	H	-1	?	-1.000	Create new
HC11	H	-1	?	-1.000	Create new
HC12	H	-1	?	-1.000	Create new

Crystal Highlight:

Actions with assigned atom(s)...



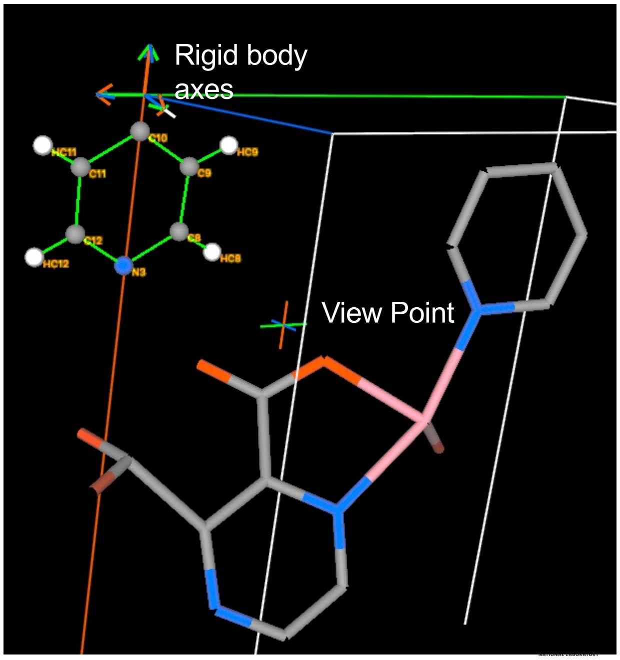
Note that the crystal structure is shown as the stick diagram; the rigid body is shown as balls & green sticks

Also, the rigid body has H atoms, the crystal structure does not; H atoms will be added to structure (noted as “Create new” in table) since they can’t be matched

---

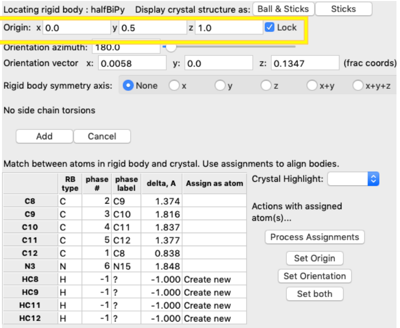
WHAT IS SHOWN IN STRUCTURE PLOT

- The View Point (six-line star) shows the cell axes. Move with right mouse; reset to (½,½,½) with “c”
- The triplet with arrows shows the Cartesian axes with the origin placed the rigid body position
- Axes & cell edges are colored red, green & blue for x, y & z, respectively
- The white line in the triplet is the vector direction for the rigid body orientation. The azimuth angle rotates the rigid body around this axis.



INSERT THE BIPYRIDINE INTO THE STRUCTURE (2)

Position RB close to location in structure



Locating rigid body : halfBiPy Display crystal structure as: Ball & Sticks Sticks

Origin: x 0.0 y 0.5 z 1.0 ☑ Lock

Orientation azimuth: 180.0

Orientation vector x: 0.0058 y: 0.0 z: 0.1347 (frac coords)

Rigid body symmetry axis: ● None ○ x ○ y ○ z ○ x+y ○ x+y+z

No side chain torsions

Add Cancel

Match between atoms in rigid body and crystal. Use assignments to align bodies.

	RB type	phase #	phase label	delta, A	Assign as atom
C8	C	2	C9	1.374	
C9	C	3	C10	1.816	
C10	C	4	C11	1.837	
C11	C	5	C12	1.377	
C12	C	1	C8	0.838	
N3	N	6	N15	1.848	
HC8	H	-1	?	-1.000	Create new
HC9	H	-1	?	-1.000	Create new
HC11	H	-1	?	-1.000	Create new
HC12	H	-1	?	-1.000	Create new

Crystal Highlight:

Actions with assigned atom(s)...

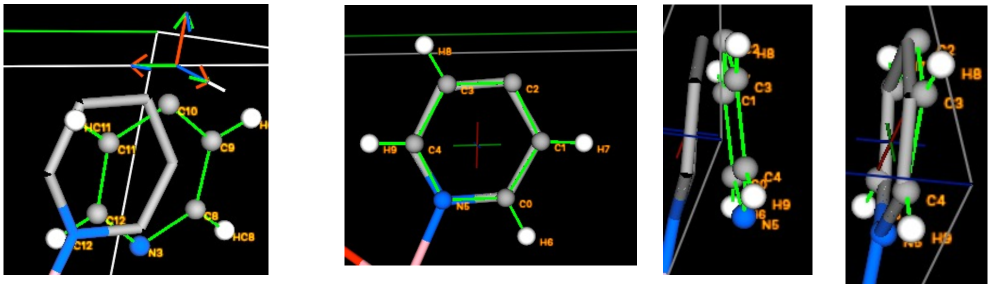
Process Assignments

Set Origin

Set Orientation

Set both

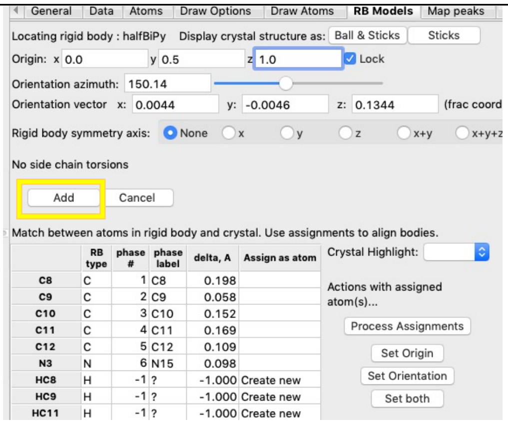
- Use mouse to reorient view of structure
- Holding Alt down & use of Left/Middle/Right repositions the rigid body.
- As noted before: bipyradine origin must be at $\bar{1}$
- Edit origin to enter (0,$\frac{1}{2}$,1) (N.B. RB is now close as shown below)
  - Press lock to prevent changing this by accident with Alt+right mouse
- Use Alt+Left & Alt+Middle to get bodies close; rotating plot for multiple views



Note that as the atoms are moved, the table is updated with the closest matches between atoms and the distances between them.

INSERT THE BIPYRIDINE INTO THE STRUCTURE (3)

RB has been located close to site in structure



General | Data | Atoms | Draw Options | Draw Atoms | RB Models | Map peaks

Locating rigid body : halfBiPy Display crystal structure as: Ball & Sticks Sticks

Origin: x 0.0 y 0.5 z 1.0 ☑ Lock

Orientation azimuth: 150.14

Orientation vector x: 0.0044 y: -0.0046 z: 0.1344 (frac coord

Rigid body symmetry axis: ● None ○ x ○ y ○ z ○ x+y ○ x+y+z

No side chain torsions

Add Cancel

Match between atoms in rigid body and crystal. Use assignments to align bodies.

	RB type	phase #	phase label	delta, A	Assign as atom
C8	C	1	C8	0.198	
C9	C	2	C9	0.058	
C10	C	3	C10	0.152	
C11	C	4	C11	0.169	
C12	C	5	C12	0.109	
N3	N	6	N15	0.098	
HC8	H	-1	?	-1.000	Create new
HC9	H	-1	?	-1.000	Create new
HC11	H	-1	?	-1.000	Create new

Crystal Highlight:

Actions with assigned atom(s)...

Process Assignments

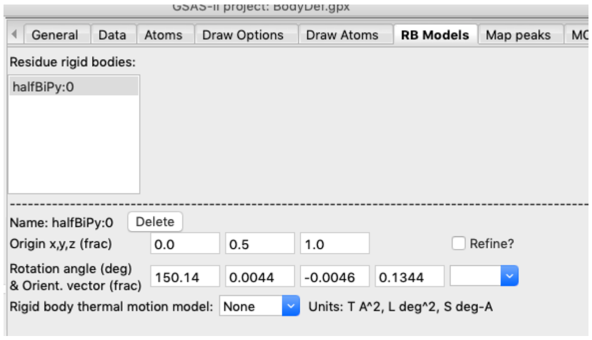
Set Origin

Set Orientation

Set both

- Adjust until all non-H atoms match within ~0.2Å
- Press "Add" to use use this origin and orientation.

The window changes to show the rigid body parameters. Rigid body bonds are shown in Orange (by default)



GSAS-II project: BodyDef.gpx

General | Data | Atoms | Draw Options | Draw Atoms | RB Models | Map peaks | MC

Residue rigid bodies:

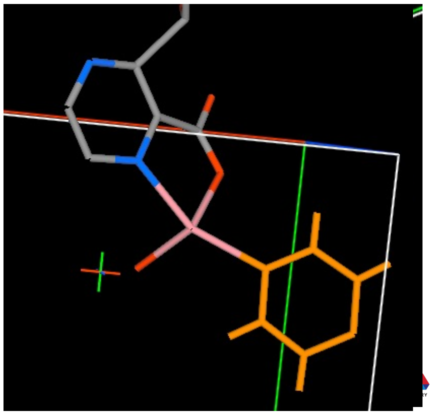
halfBiPy:0

Name: halfBiPy:0 Delete

Origin x,y,z (frac) 0.0 0.5 1.0 ☐ Refine?

Rotation angle (deg) & Orient. vector (frac) 150.14 0.0044 -0.0046 0.1344

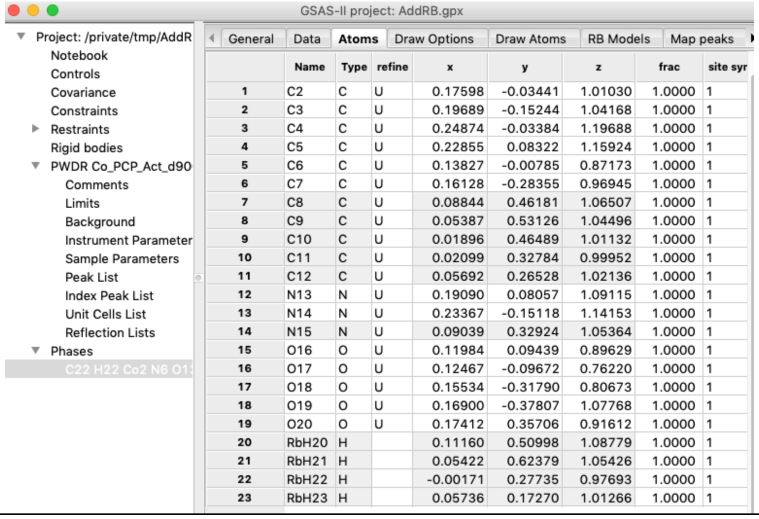
Rigid body thermal motion model: None Units: T A^2, L deg^2, S deg-A



CHANGE IN THE ATOMS TABLE

Atoms in the rigid body are displayed in gray

- After the rigid body is added, atoms in rigid bodies are highlighted in gray in the atoms display.
  - Note that atoms added to the list when the RB was included are name “Rb…” and are placed at the end of the list.


GSAS-II project: AddRB.gpx

Project: /private/tmp/AddR
Notebook
Controls
Covariance
Constraints
Restraints
Rigid bodies
PWDR Co_PCP_Act_d90
  Comments
  Limits
  Background
  Instrument Parameter
  Sample Parameters
  Peak List
  Index Peak List
  Unit Cells List
  Reflection Lists
Phases
  C22 H22 Co2 N6 O1

	Name	Type	refine	x	y	z	frac	site syr
1	C2	C	U	0.17598	-0.03441	1.01030	1.0000	1
2	C3	C	U	0.19689	-0.15244	1.04168	1.0000	1
3	C4	C	U	0.24874	-0.03384	1.19688	1.0000	1
4	C5	C	U	0.22855	0.08322	1.15924	1.0000	1
5	C6	C	U	0.13827	-0.00785	0.87173	1.0000	1
6	C7	C	U	0.16128	-0.28355	0.96945	1.0000	1
7	C8	C	U	0.08844	0.46181	1.06507	1.0000	1
8	C9	C	U	0.05387	0.53126	1.04496	1.0000	1
9	C10	C	U	0.01896	0.46489	1.01132	1.0000	1
10	C11	C	U	0.02099	0.32784	0.99952	1.0000	1
11	C12	C	U	0.05692	0.26528	1.02136	1.0000	1
12	N13	N	U	0.19090	0.08057	1.09115	1.0000	1
13	N14	N	U	0.23367	-0.15118	1.14153	1.0000	1
14	N15	N	U	0.09039	0.32924	1.05364	1.0000	1
15	O16	O	U	0.11984	0.09439	0.89629	1.0000	1
16	O17	O	U	0.12467	-0.09672	0.76220	1.0000	1
17	O18	O	U	0.15534	-0.31790	0.80673	1.0000	1
18	O19	O	U	0.16900	-0.37807	1.07768	1.0000	1
19	O20	O	U	0.17412	0.35706	0.91612	1.0000	1
20	RbH20	H		0.11160	0.50998	1.08779	1.0000	1
21	RbH21	H		0.05422	0.62379	1.05426	1.0000	1
22	RbH22	H		-0.00171	0.27735	0.97693	1.0000	1
23	RbH23	H		0.05736	0.17270	1.01266	1.0000	1

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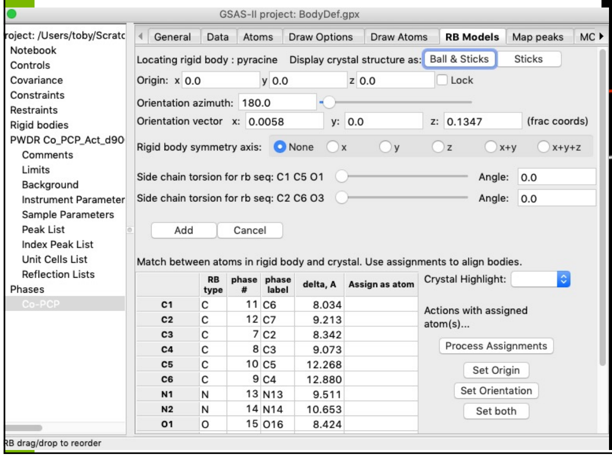
INSERT THE PYRAZINE INTO THE STRUCTURE (1)

Identify the body

- Go to RB Models phase tab; use “Edit Body”/“Locate and Insert Rigid Body”; select the pyrazine fragment
- Note that for this body, both the origin and orientation must be determined.


GSAS-II project: BodyDef.gpx

roject: /Users/toby/Scratc
Notebook
Controls
Covariance
Constraints
Restraints
Rigid bodies
PWDR Co_PCP_Act_d90
  Comments
  Limits
  Background
  Instrument Parameter
  Sample Parameters
  Peak List
  Index Peak List
  Unit Cells List
  Reflection Lists
Phases
  Co-PCP

Locating rigid body : pyracine
Display crystal structure as: Ball & Sticks | Sticks
Origin: x 0.0 y 0.0 z 0.0 ☐ Lock
Orientation azimuth: 180.0
Orientation vector x: 0.0058 y: 0.0 z: 0.1347 (frac coords)
Rigid body symmetry axis: ● None ○ x ○ y ○ z ○ x+y ○ x+y+z
Side chain torsion for rb seq: C1 C5 O1 Angle: 0.0
Side chain torsion for rb seq: C2 C6 O3 Angle: 0.0

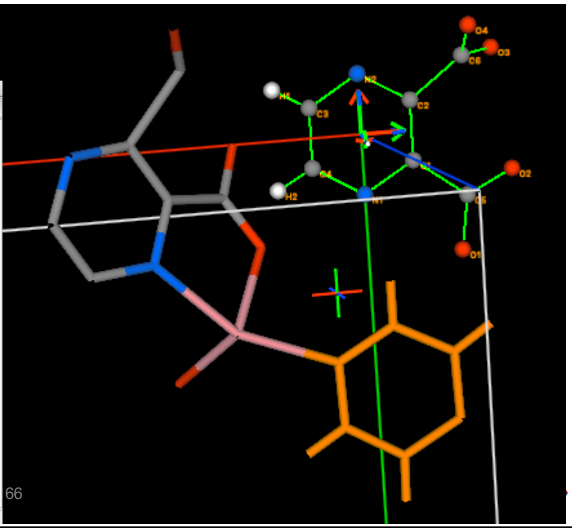
Match between atoms in rigid body and crystal. Use assignments to align bodies.

	RB type	phase #	phase label	delta, A	Assign as atom
C1	C	11	C6	8.034	
C2	C	12	C7	9.213	
C3	C	7	C2	8.342	
C4	C	8	C3	9.073	
C5	C	10	C5	12.268	
C6	C	9	C4	12.880	
N1	N	13	N13	9.511	
N2	N	14	N14	10.653	
O1	O	15	O16	8.424	

Crystal Highlight:

Actions with assigned atom(s)...

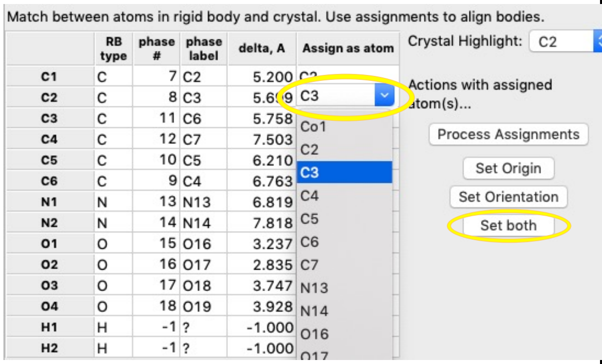
RB drag/drop to reorder



INSERT THE PYRAZINE INTO THE STRUCTURE (2)

Define pairs of atoms

- This time we will identify rigid atoms that should be paired with specific atoms in the structure. We will use the 1st two C and 1st two N atoms. Then press the “Set both” button for a best-fit.

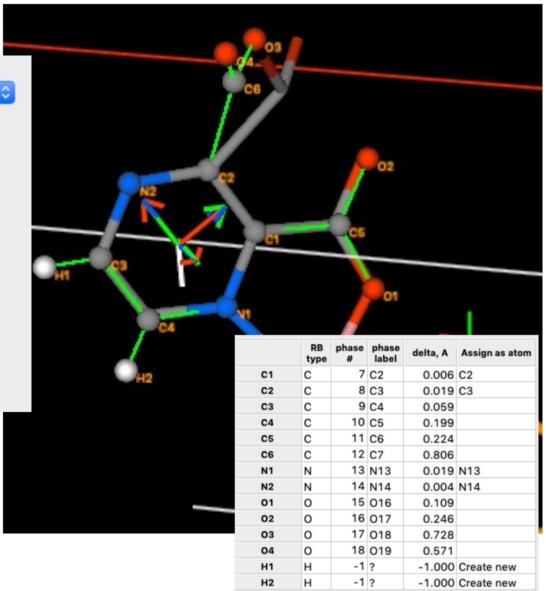


Match between atoms in rigid body and crystal. Use assignments to align bodies.

	RB type	phase #	phase label	delta, A	Assign as atom
C1	C	7	C2	5.200	C2
C2	C	8	C3	5.6?9	C3
C3	C	11	C6	5.758	
C4	C	12	C7	7.503	
C5	C	10	C5	6.210	
C6	C	9	C4	6.763	
N1	N	13	N13	6.819	
N2	N	14	N14	7.818	
O1	O	15	O16	3.237	
O2	O	16	O17	2.835	
O3	O	17	O18	3.747	
O4	O	18	O19	3.928	
H1	H	-1	?	-1.000	
H2	H	-1	?	-1.000	

Crystal Highlight: C2

Actions with assigned atom(s)...



	RB type	phase #	phase label	delta, A	Assign as atom
C1	C	7	C2	0.006	C2
C2	C	8	C3	0.019	C3
C3	C	9	C4	0.059	
C4	C	10	C5	0.199	
C5	C	11	C6	0.224	
C6	C	12	C7	0.806	
N1	N	13	N13	0.019	N13
N2	N	14	N14	0.004	N14
O1	O	15	O16	0.109	
O2	O	16	O17	0.246	
O3	O	17	O18	0.728	
O4	O	18	O19	0.571	
H1	H	-1	?	-1.000	Create new
H2	H	-1	?	-1.000	Create new

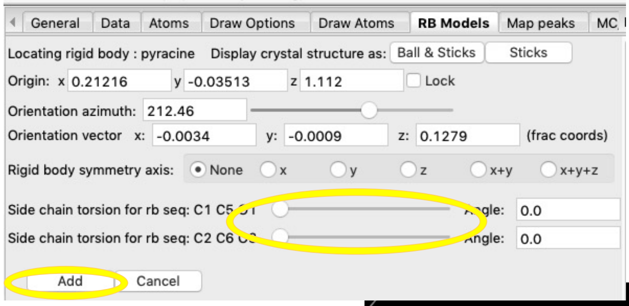
With 4 sets of atoms paired an excellent alignment is obtained

---

INSERT THE PYRAZINE INTO THE STRUCTURE (3)

Adjust torsions

- The torsions set at 0 degrees reproduces the initial structure well, but moving the sliders shows different options.
- Press the “Add” button to insert this body.



Locating rigid body : pyracine   Display crystal structure as: Ball & Sticks   Sticks

Origin: x 0.21216 y -0.03513 z 1.112 ☐ Lock

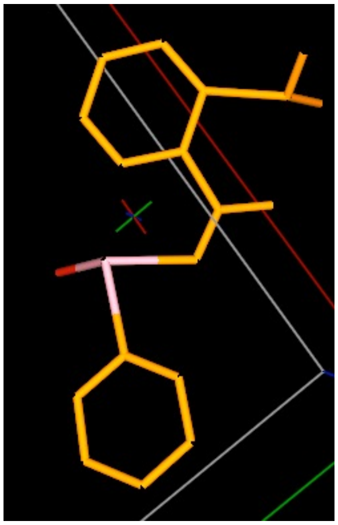
Orientation azimuth: 212.46

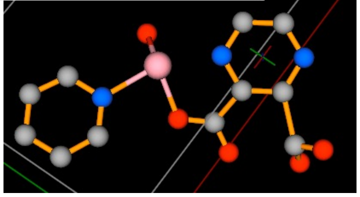
Orientation vector x: -0.0034 y: -0.0009 z: 0.1279 (frac coords)

Rigid body symmetry axis: ● None ○ x ○ y ○ z ○ x+y ○ x+y+z

Side chain torsion for rb seq: C1 C5 O1   Angle: 0.0

Side chain torsion for rb seq: C2 C6 C   Angle: 0.0





Bonds in rigid bodies are shown as orange lines in stick or ball-and-stick plots

REFINEMENT WITH RIGID BODIES

Orientation and Origin can be refined

Origin: The rigid body origin can be refined or not. (In special cases it may be necessary to use a “Hold” constraint on one or two origin parameters – see following slides.)

Orientation: orientation is defined by a quaternion, reorganized as a unit vector (V) and azimuthal rotation around that vector (A). Orientation can be refined in one of three modes: “A”, “AV” or “V”.

- In “AV” mode, both the vector and azimuth are refined
- In “A” mode, only azimuthal rotation is refined. This is used when symmetry requires a particular orientation for the vector.
- In “V” mode, only the vector is refined. This is used for linear molecules where the linear axis is aligned with the RB vector.

☑ Refine?

AV

Example: For bipyridine discussed earlier, the origin cannot be refined, but for pyrazine it should be. For both, the orientation can be refined as “AV”

RIGID BODIES WITH INTERNAL CRYSTALLOGRAPHIC SYMMETRY

It is fairly common that a rigid body will have internal symmetry, such as the 6/m symmetry of the C atoms in a phenyl group; it is somewhat less common for the crystal symmetry to enforce some or all of the symmetry of the rigid body. When this does occur, the rigid body must be placed at a special location (point, axis or plane) with higher crystallographic symmetry. Placement and refinement will require special attention.

When a rigid body is placed on a crystallographic symmetry location, several changes may be needed:

- The RB must be defined to align the Cartesian axes/origin to the symmetry:

  The Cartesian RB symmetry axis must be defined along x, y or z (or x+y or x+y+z). The Cartesian origin must be defined to match symmetry points or planes in the body

- The body must be inserted into the structure to retain symmetry:

  The RB must be inserted into the crystal structure to place the quaternion rotation vector along the selected Cartesian axis. The origin will be a high-symmetry Wyckoff site

- Which rigid body parameters may be refined:

  It will not be possible to refine all six degrees of freedom; symmetry will determine what parameters can be refined.

  The origin in crystal space must be constrained to stay on the axis or plane; if on a symmetry point, it cannot be refined.

RIGID BODIES ON SPECIAL POSITIONS

Setting constraints on the body position

Usually the x,y & z components for the rigid body positions are all refined, but symmetry may require a constraint such as x=0 or x=y, while for individual atoms, these constraints are created automatically, for rigid bodies constraints must be generated manually.

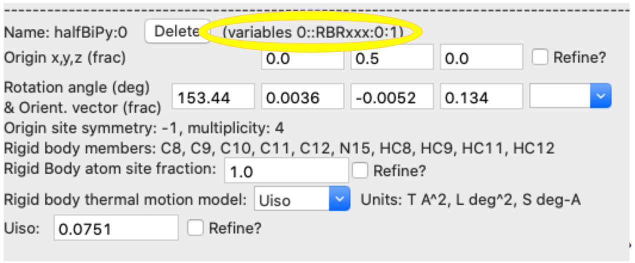
Do this by creating holds or equivalences on the appropriate parameters in the Constraints/Phase tree section

- Note naming of rigid body origin parameters:

Residue bodies:
RBRPx:n:m: for x (…Py for y, ...Pz for z), where n is the rigid body number and m is the insertion number.

Vector bodies: RBVPx:n:m etc.

The variable name is shown for each body in the RB Models tab



Name: halfBiPy:0 (variables 0::RBRxxx:0:1)
Origin x,y,z (frac) 0.0 0.5 0.0 ☐ Refine?
Rotation angle (deg) & Orient. vector (frac) 153.44 0.0036 -0.0052 0.134
Origin site symmetry: -1, multiplicity: 4
Rigid body members: C8, C9, C10, C11, C12, N15, HC8, HC9, HC11, HC12
Rigid Body atom site fraction: 1.0 ☐ Refine?
Rigid body thermal motion model: Uiso Units: T A^2, L deg^2, S deg-A
Uiso: 0.0751 ☐ Refine?

SPECIAL CASES: SYMMETRY INTERNAL TO RIGID BODIES (1)

Classified by symmetry class

Here are the different cases for rigid body symmetry:

- **Center of symmetry**: The Cartesian origin will need to be the $\bar{1}$ position. This will always be either on an atom or at the midpoint between two (or, unlikely, more) atoms. Usually only one from each symmetry-related pair of atoms will be included in the body (or occupancies must be set to 0.5 due to atom duplication). There are no requirements on orientation of axes.
  - Crystal coordinates: The rigid body origin will be defined as the $\bar{1}$ site and will not be refined. The body orientation can be refined in “AV” mode (no constraints).
  - Occupancies: Consider if atoms are duplicated by the $\bar{1}$ and if so lower frac relative to any atom at the origin
- **Mirror plane**: The rigid body must be defined so that the normal to the mirror plane must be along a fixed Cartesian axis* for the body and the Cartesian origin must be defined so that it lies in the mirror plane. (i.e., if z will be the normal direction then the plane must be at z=0).
  - Crystal coordinates: One coordinate in the rigid body origin will need to be fixed on the mirror plane (typically place a hold on variable p::RBRPξ:#:# ξ=*x, y or z*; diagonal mirror planes may require equivalences between x, y and/or z) so that the origin may be refined. The RB orientation vector will need to be fixed along the mirror plane normal. Only the RB azimuth angle can be refined (mode “A”).
  - Occupancies: Consider if atoms are duplicated, if so lower frac relative to atoms on the plane

* Possible Cartesian axes that can be used for the symmetry direction are *x, y, z, x+y* or *x+y+z*

SPECIAL CASES: SYMMETRY INTERNAL TO RIGID BODIES (2)

Additional symmetry classes

- **Rotation axis**: The Cartesian origin must be defined on the axis, which will be at a midpoint between a group of atoms or on an atom. Align the axis along a fixed Cartesian axis* .
  - Crystal coordinates: coordinates for the rigid body origin will need to be constrained to stay on the axis by placing holds and/or constraints on two origin parameters (*p*::RBRPξ:#:# ξ=*x, y or z*) to leave one free parameter. The RB orientation vector will need to be fixed along the axis. For orientation only the RB azimuth angle can be refined (mode “A”).
  - Occupancies: Consider if atoms are duplicated by the axis and if so lower frac relative to any atoms on the axis
- **Improper rotation axes** define both an axis and a perpendicular plane. The Cartesian origin must be fixed on the point where the axis meets the plane and the symmetry axis for the RB must be aligned with the quaternion axis. In crystal coordinates the origin is fixed and for orientation only the RB azimuth angle can be refined (mode “A”).
- **Glide planes** and **screw axes** could require constraints similar to the previous examples, but this would occur only in the unlikely event that a molecular fragment has such internal symmetry.

* Possible Cartesian axes that can be used for the symmetry direction are *x, y, z, x+y* or *x+y+z*

SPECIAL CASES: SYMMETRY INTERNAL TO RIGID BODIES (3)

Constraints on Linear Rigid Bodies

A **Linear rigid body** has two orientational degrees of freedom rather than three, since a rotation of the object along the linear axis leaves it unchanged. The RB should be defined so that the linear axis falls on one of the allowed Cartesian axes*. How it will be treated depends on the symmetry for the location where it will be placed.

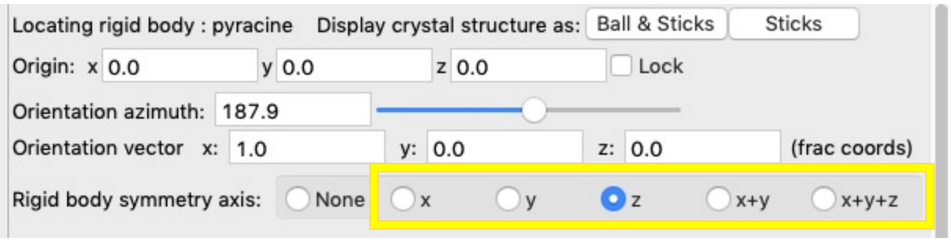
- **General position**: when a linear rigid body is placed in a location with no symmetry, there are no restrictions on the origin location or the orientation. The origin can be refined freely and the orientation can be refined in “V” mode (two degrees of freedom).
- **Symmetry axis**: when a linear body is placed on a symmetry axis, orientation must be engineered to lie on that axis. Such a body has only one degree of freedom, the position along that axis (use appropriate constraints on the origin). The orientation cannot be refined.
- **Symmetry plane**: the most common case is a linear RB lying in a mirror plane. When inserting, the rigid body symmetry axis must be defined along the normal to that plane. The origin for the RB will have two degrees of freedom (use appropriate constraints) and there will be one orientational degree of freedom, to rotate the body around the azimuthal angle (“A” mode).

* Possible Cartesian axes that can be used for the symmetry direction are *x, y, z, x+y* or *x+y+z*

INSERTING THE RIGID BODY: SYMMETRY SETTINGS

For bodies on mirror planes or rotation axes

- When inserting a body with azimuthal symmetry constraints, the axis previously defined as the symmetry axis must be designated



Locating rigid body : pyracine Display crystal structure as: Ball & Sticks Sticks

Origin: x 0.0 y 0.0 z 0.0 ☐ Lock

Orientation azimuth: 187.9

Orientation vector x: 1.0 y: 0.0 z: 0.0 (frac coords)

Rigid body symmetry axis: ○ None ○ x ○ y ● z ○ x+y ○ x+y+z

- The orientation vector will need to be specified as well as the origin.

- The effect of rigid body angular rotation can be viewed with the azimuth slider

---

ADP FITTING FOR RIGID BODIES

ADP = Atomic Displacement Parameters (~ thermal parameters)

Motion of atoms in rigid bodies can be refined with individual displacement parameters (DP: Uiso or Uaniso) but this is usually not a good thing to do. Simpler models treat all atoms in the body with grouped terms.

The simplest model has a single Uiso value for all atoms in the rigid body

It is also possible to describe group motion using “TLS terms”.

- The T terms describe translational motion, which will be the same for all atoms in the group, but can differ by direction like anisotropic DPs.
- The L terms describe libration, which can be thought of as frustrated rotations around the origin of the body. The further the atom is located from the body origin, the larger L will make the DP.
- The S terms describe “screw” motion, which combines T & L motion, and is not needed if the group motion is unhindered and origin is at the center of mass.

Start fitting using a single Uiso value. The next most complex model is to define constraints to have a single T ($T_{11}=T_{22}=T_{33}$) & single L term ($L_{11}=L_{22}=L_{33}$). I sometimes use a few T & L terms, but with powder data, never more than a few.

OCCUPANCIES FOR RIGID BODIES

Rigid bodies have a single term for the occupancy for all atoms in the body. This can be refined where appropriate.

- When a rigid body has lower internal symmetry than the site where it is placed, the body will be disordered; a fractional occupancy value of 0.5 (or lower) will be needed.
- When a rigid body has internal symmetry and is placed at a site consistent with that symmetry, there will be duplication of atoms. GSAS-II will determine when atoms are duplicated and will set duplicates to have Frac=0 so that the “extra” atom(s) are ignored.

Example:

  – In a previous example, a rigid body was defined for bipyridine using only one half of the atoms, this was inserted at a $\bar{1}$ position where no atoms are duplicated. Note this body definition could not be used at a lower symmetry site because atoms would be missing.

  – The rigid body could have been defined with both rings. If then inserted at the $\bar{1}$ site, one half of the atoms would have an initial occupancy of 1 (which could be refined). The other half of the atoms would have their occupancy fixed at 0.

OTHER RIGID BODY TRICKS

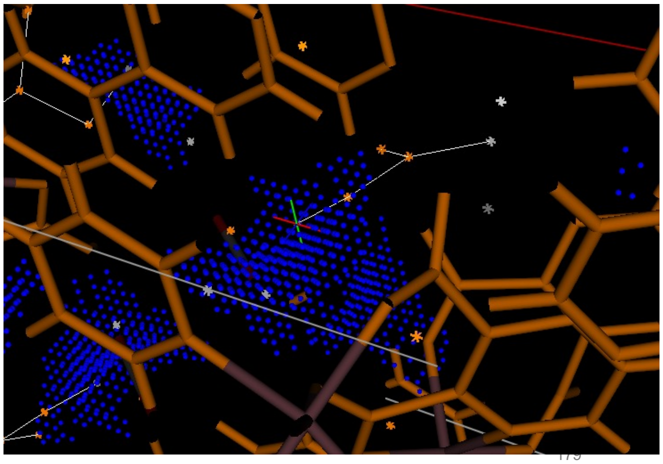
- It can be useful to combine restraints with rigid body constraints. For the example structure, restraints can be placed on the Co-O and Co-N bond distances, which places further restrictions to prevent the refinement from overfitting.
- Rigid Body torsions will not move H atoms as riders. If H atoms are needed, use Edit Atoms/”on selected atoms…”/“Calc H atoms” to generate H atoms on riders.
- On occasion I have needed to have two rigid bodies that have a fixed connection with each other, but still have degrees of freedom. To do that in GSAS/EXPGUI, I define the bodies so that they share an origin at the point which joins them. I then constrain the origin of the two groups to refine together. This is probably not needed in GSAS-II, since both groups of atoms can be placed in a single body with a torsion between them.

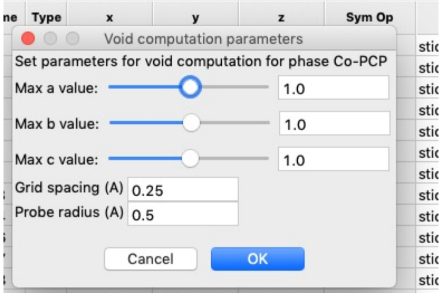
OTHER NICE TOOLS FOR GUEST/SOLVENT MOLECULE STRUCTURES

Understanding the spatial environment in crystal space

Void space visualizer: “Edit Figure”/”Create Void Map” (in Draw Atoms)

- Resulting map shows regions of space without atoms





GSAS-II project: 50bar_new.gpx

Void computation parameters

Set parameters for void computation for phase Co-PCP

Max a value: 1.0

Max b value: 1.0

Max c value: 1.0

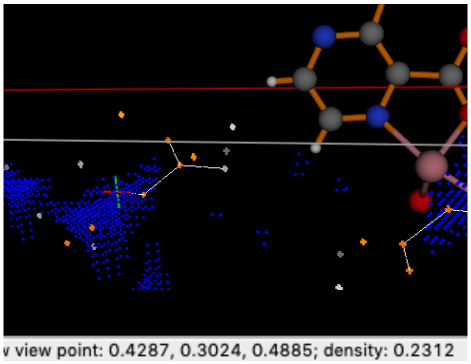
Grid spacing (A) 0.25

Probe radius (A) 0.5

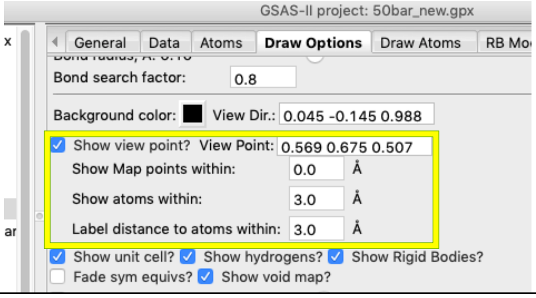
OTHER NICE TOOLS FOR GUEST/SOLVENT MOLECULE STRUCTURES

Using the View Point

- By default, the view point is set to (½,½,½)
- Move the view point using right mouse button
  - Movement is in screen x-y
  - Rotate drawing (left mouse) for 3rd dimension
  - Position is shown in bottom frame
  - Reset to (½,½,½) by pressing “c” key
  - Type in coordinates on Draw Options
- Optionally, highlight distances around view point; shows symmetry-related atoms



v view point: 0.4287, 0.3024, 0.4885; density: 0.2312



GSAS-II project: 50bar_new.gpx

Bond search factor: 0.8

Background color: ■ View Dir.: 0.045 -0.145 0.988

☑ Show view point? View Point: 0.569 0.675 0.507

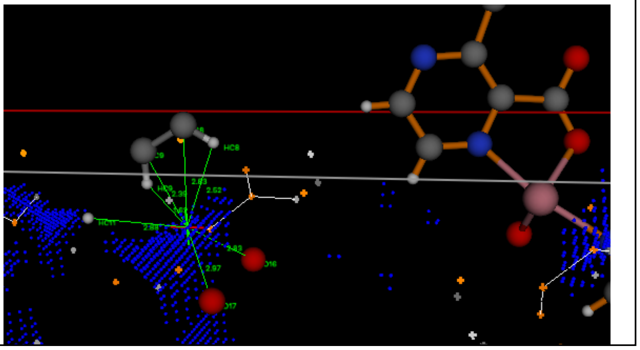
Show Map points within: 0.0 Å

Show atoms within: 3.0 Å

Label distance to atoms within: 3.0 Å

☑ Show unit cell? ☑ Show hydrogens? ☑ Show Rigid Bodies?

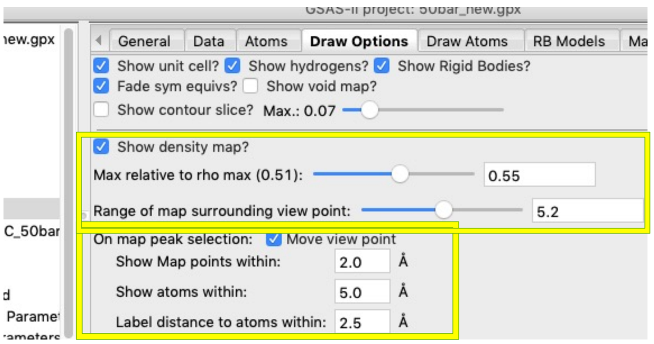
☐ Fade sym equivs? ☑ Show void map?



OTHER NICE TOOLS FOR GUEST/SOLVENT MOLECULE STRUCTURES

New feature: understand Fourier map peaks

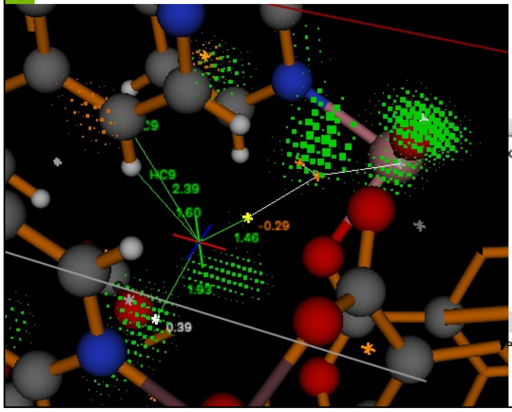
- Highlight distances around a selected Fourier map peak
- Note distances are labeled as set in Draw Options
- Also, optionally show map

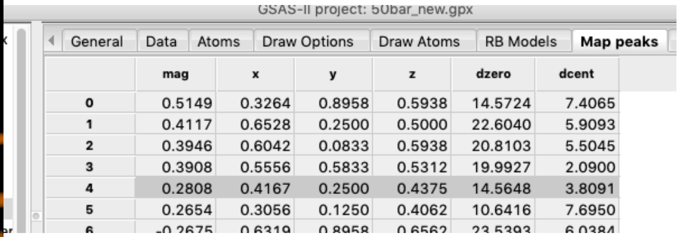

GSAS-II project: 50bar_new.gpx

☑ Show unit cell? ☑ Show hydrogens? ☑ Show Rigid Bodies?
☑ Fade sym equivs? ☐ Show void map?
☐ Show contour slice? Max.: 0.07

☑ Show density map?
Max relative to rho max (0.51): 0.55
Range of map surrounding view point: 5.2

On map peak selection: ☑ Move view point
Show Map points within: 2.0 Å
Show atoms within: 5.0 Å
Label distance to atoms within: 2.5 Å

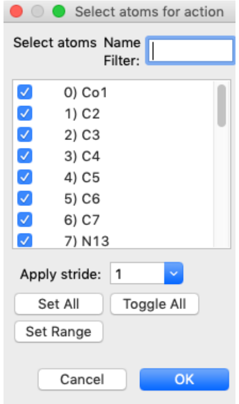



GSAS-II project: 50bar_new.gpx

	mag	x	y	z	dzero	dcent
0	0.5149	0.3264	0.8958	0.5938	14.5724	7.4065
1	0.4117	0.6528	0.2500	0.5000	22.6040	5.9093
2	0.3946	0.6042	0.0833	0.5938	20.8103	5.5045
3	0.3908	0.5556	0.5833	0.5312	19.9927	2.0900
4	0.2808	0.4167	0.2500	0.4375	14.5648	3.8091
5	0.2654	0.3056	0.1250	0.4062	10.6416	7.6950
6	-0.2675	0.6319	0.8958	0.6562	23.5393	6.0384

A FEW OTHER NEW VISUALIZATION/MAP FEATURES

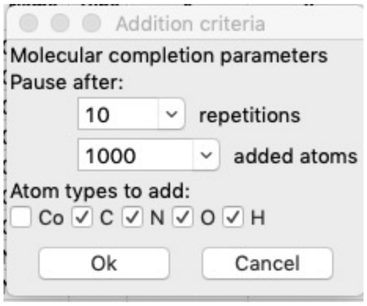
- Map peaks (Map peaks menu)
  - Equivalent peaks: finds peaks related by symmetry to a selected peak
  - Unique Peaks: brings one symmetry-unique peak to top of list
- Draw Atoms (Edit Figure menu)
  - Complete Molecule: Adds atoms bonded to selected atoms already in draw list


Select atoms for action

Select atoms Name Filter:

☑ 0) Co1
☑ 1) C2
☑ 2) C3
☑ 3) C4
☑ 4) C5
☑ 5) C6
☑ 6) C7
☑ 7) N13

Apply stride: 1


Addition criteria

Molecular completion parameters
Pause after:
10 repetitions
1000 added atoms
Atom types to add:
☐ Co ☑ C ☑ N ☑ O ☑ H

CONCLUSIONS

Rigid bodies are fun, perhaps not easy, but very useful

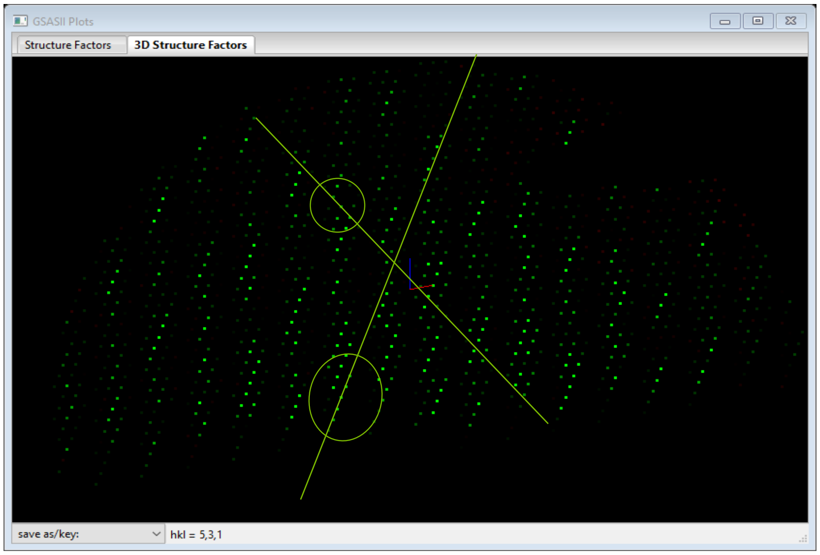
GSAS-II has two very powerful rigid body implementations

New GSAS-II tools make them much easier to create and use

INCOMMENSURATE ATOMIC STRUCTURES

INCOMMENSURATE STRUCTURES IN GSAS-II

Book: “Incommensurate Crystallography” S. van Smaalen



hkl = 5,3,1

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

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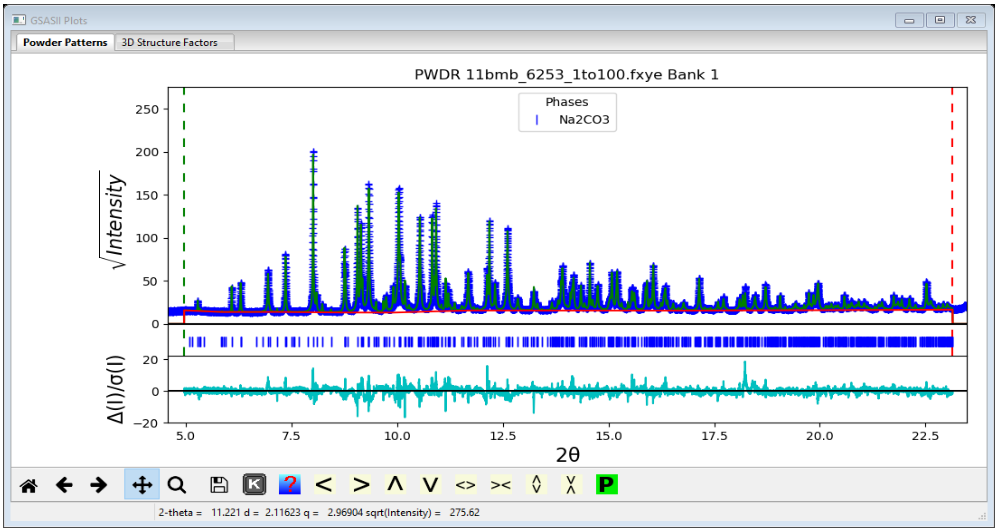
POWDER DIFFRACTION

Na_2CO_3 – 11BM @ APS room temp.

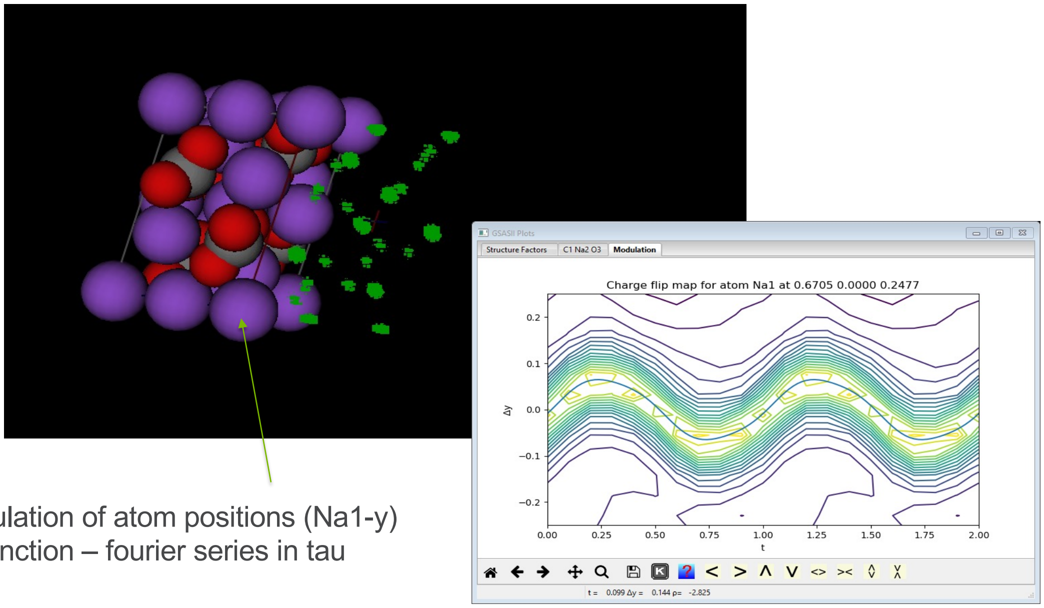


2-theta = 11.221 d = 2.11623 q = 2.96904 sqrt(Intensity) = 275.62

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

INCOMMENSURATE STRUCTURE SOLUTION

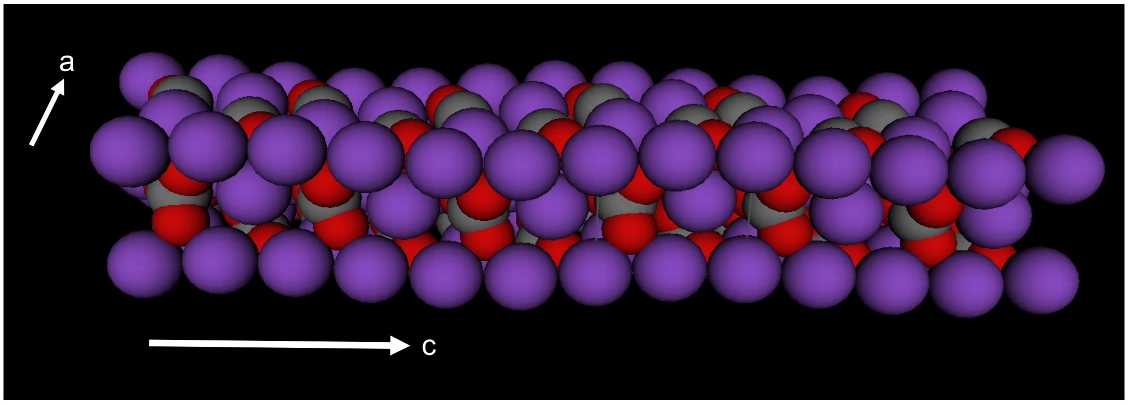
4D charge flipping; single crystal & powders (e.g. Pawley refinement)



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

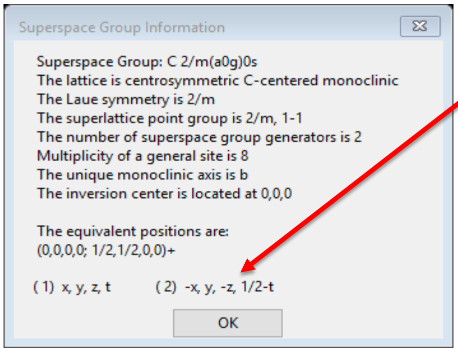
e.g. Na_2CO_3 – C2/m(α0γ)os

Space group

Modulation vector

Translation component

Operators: conventional space group & 4th dimensional component



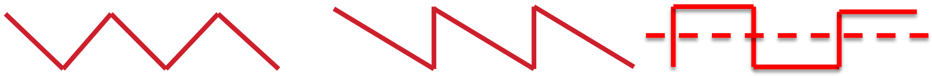
```
Superspace Group: C 2/m(a0g)0s
The lattice is centrosymmetric C-centered monoclinic
The Laue symmetry is 2/m
The superlattice point group is 2/m, 1-1
The number of superspace group generators is 2
Multiplicity of a general site is 8
The unique monoclinic axis is b
The inversion center is located at 0,0,0

The equivalent positions are:
(0,0,0,0; 1/2,1/2,0,0)+

( 1)  x, y, z, t          ( 2)  -x, y, -z, 1/2-t
```

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

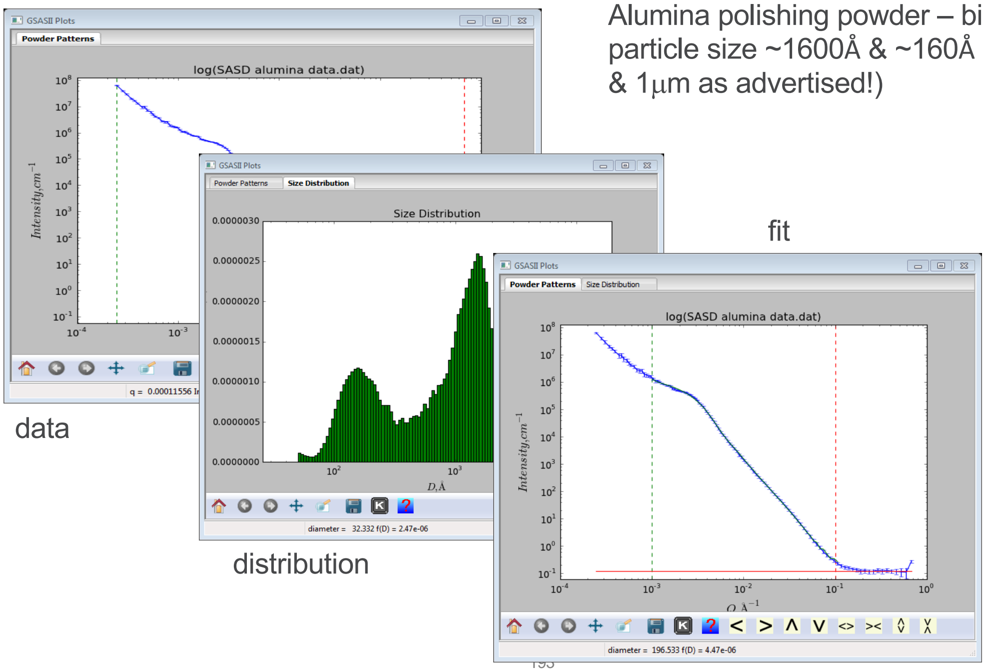
Cases not allowed in GSAS-II

- 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

OTHER STUFF IN GSAS-II

SMALL ANGLE SCATTERING – SIZE DISTRIBUTION

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



q = 0.00011556 I

diameter = 32.332 f(D) = 2.47e-06

diameter = 196.533 f(D) = 4.47e-06

data

distribution

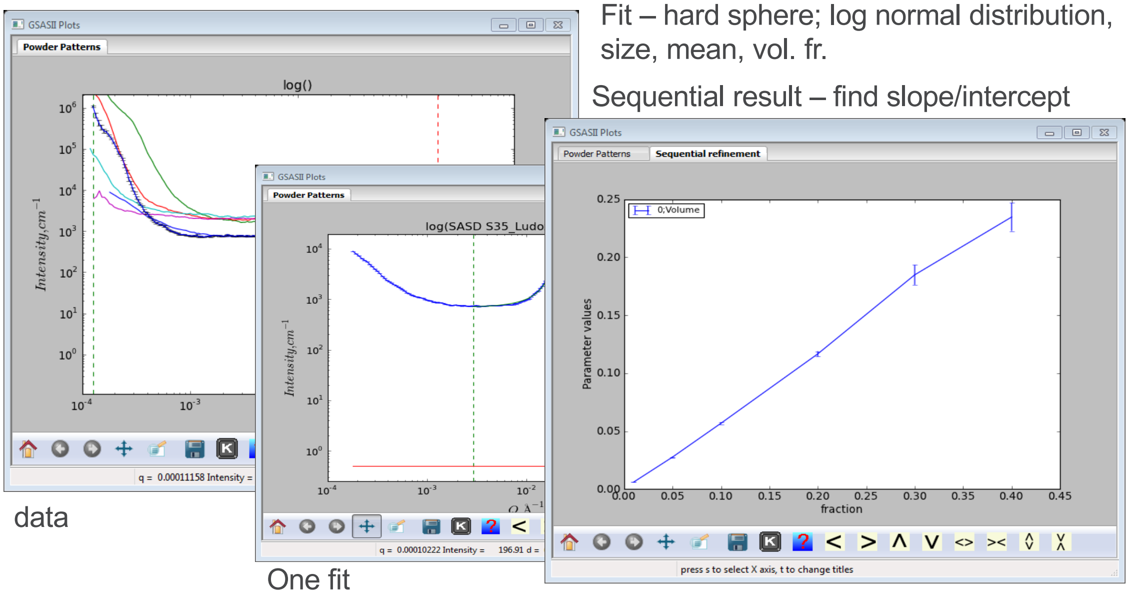
fit

SMALL ANGLE SCATTERING – SEQUENTIAL DATA ANALYSIS

Ludox colloidal silica from Aldrich – dilution range

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

Sequential result – find slope/intercept



q = 0.00011158 Intensity =

q = 0.00010222 Intensity = 196.91 d =

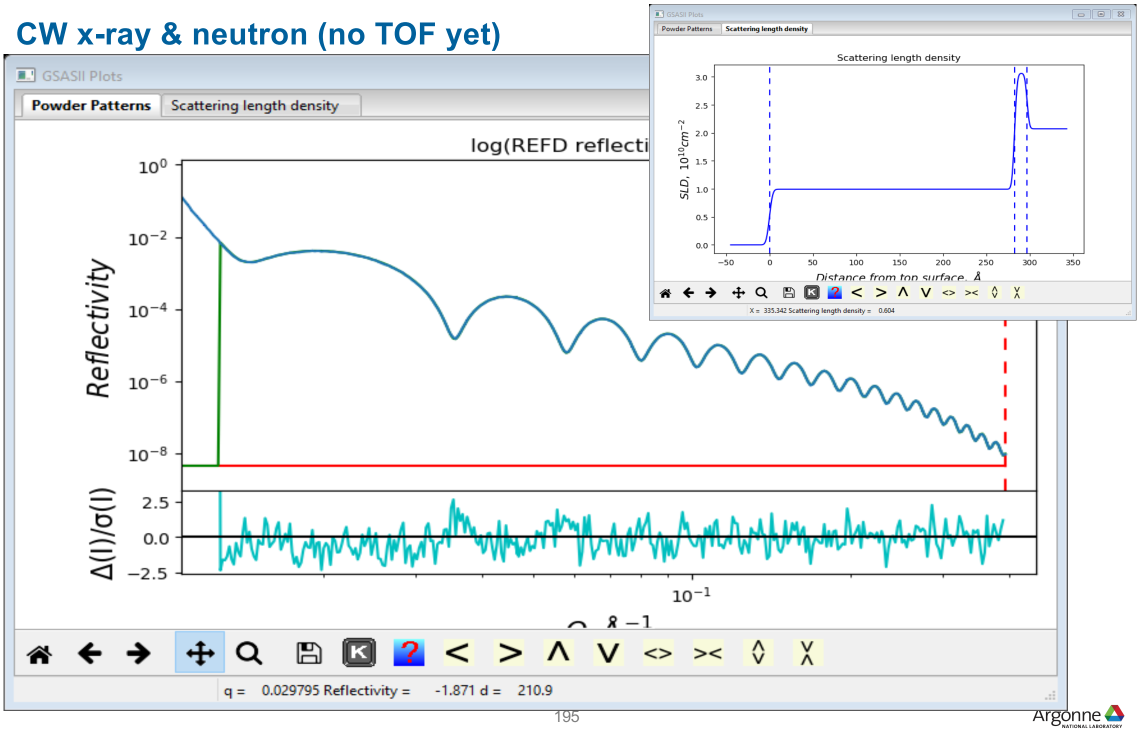
press s to select X axis, t to change titles

data

One fit

REFLECTIVITY

CW x-ray & neutron (no TOF yet)

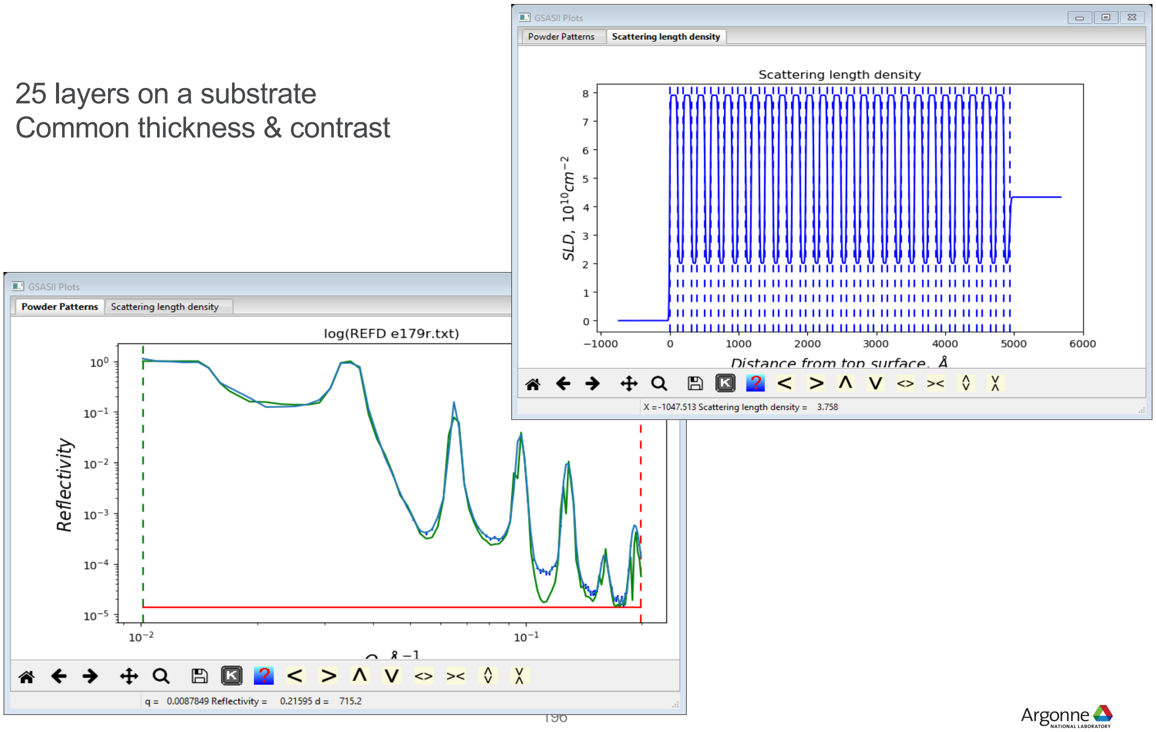


q = 0.029795 Reflectivity = -1.871 d = 210.9

X = 335.342 Scattering length density = 0.604

MULTILAYER REFLECTIVITY

25 layers on a substrate
Common thickness & contrast



X =-1047.513 Scattering length density = 3.758

q = 0.0087849 Reflectivity = 0.21595 d = 715.2

REFINEMENT RECIPES

WHAT TO REFINE AND WHEN?

If all parameters in a refinement were close to the true minima and correlation is minimal, then it would fine to start by optimizing all everything.

Who is that lucky?

In practice parameters must be relaxed slowly, with the order dictated by which parameters are farthest from the correct values

BASIC STRATEGY

Need reasonable values for unit cell, scale factor, background and profile before refining structural parameters, locating missing atoms…
  - Le Bail fit allows fit of cell, background and profile

- Always use a standard to determine the true instrumental profile (or get beamline scientist to do it!)
  - With accurate profile terms you only need to worry about sample broadening
  - Postpone asymmetric broadening treatment until late in the refinement
- When you can't determine the instrumental profile, follow CW or TOF tutorial to get approximate values before starting
- Having reasonable profile terms can save you from heartache
  - With this, you only need to fit sample broadening

REFINEMENT RECIPE (PART 1)

No single strategy works in all cases

- Fit unit cell with small # of background terms

  Think: Are reflections in ~ the correct places?
- Fit sample displacement (CW neutron/synchrotron)

  Think: Are all peaks indexed?
  - If not: check cell & rethink space group
  - impurity phases?
- Is Background reasonable?
  - Add more terms
  - Use fit to fixed background points & don't refine background to get started with difficult problems (see tutorial)

REFINEMENT RECIPE (PART 2)

- Is peak shape in the right ball park?
  - If possible, postpone profile refinement to later stages
  - If profile is way off due to sample broadening, (you do have reasonable instrumental terms!) refine only sample terms (see if either microstrain or size alone can take care of most broadening)

- Fit atom coordinates
  - release "big" atoms first
    - big = high multiplicity*b or *f(Q)

REFINEMENT RECIPE (PART 3)

- Refine displacement parameters (U_{iso})
  - for complex structures, group Uiso terms

  Think: Is the structure reasonable in terms of distances & angles?
  - missing atoms? Examine Fourier map
  - Refine occupancies? (x-rays: beware!)

- Add more complex sample broadening terms (microstrain + size together, see if uniaxial treatment on more significant term produces a large Rwp improvement)

- Usually not necessary to refine Instrumental profile terms

REFINEMENT RECIPE (PART 4)

Think: Are all lines indexed & reasonably fit?

If not, are some peaks wider than others?
- Consider anisotropic broadening

Are groups of reflections all computing high or low?
- Consider preferred orientation

Think: Is refinement stable and are values chemically plausible?

Wrong space group?

Too few reflections?
- Get better (or more) data, add hard/soft constraints

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REFINEMENT RECIPE (PART 5): FINISH UP

- Refine background, if fixed from LeBail. Add more background terms, if needed.
- Ungroup U_{iso}’s if data allow.
- Attempt anisotropic refinement of “big” atoms, when data quality permits.

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REFINEMENT RECIPE (PART 6)

Common problem: At high Q, peaks run together so that background cannot be determined.

- Choice of Background determines average U_{iso}. Refining Background and U_{iso} together results in good fits but unreasonable average U_{iso}(<0.001 or >0.025 Å^2) values.

Solution: Need to fix the average U_{iso}.

- set all U_{iso} = to something reasonable (say 0.01 to 0.03)
- refine background
- fix background, & refine U_{iso}’ s
- Document in your paper that background and displacement parameters had too much correlation for independent refinement & say what was done.

WRAP UP

Rietveld fits are almost never perfect since materials and instruments are not perfect. There is almost always something more to try.

Complex problems may stretch the limits of what can be learned from the data. Getting better data is always best, but more frequently one must reduce the complexity of the model (restraints and constraints)

GSAS-II offers many options to address this.

SCALE FACTOR

- There is a scale factor for each histogram
- There is a phase fraction for every phase in every histogram.
  - Phase fraction multiplies scale factor
  - Phase fraction × Z × Molecular Weight (asym unit) ∝ weight fraction of phase (GSAS-II computes)

Redundant parameters: Don't refine scale and all phase fractions together, unless a constraint is placed on the total phase fractions

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USE RESTRAINTS EARLY WHEN FITTING RECALCITRANT MODELS

Builds *a priori* knowledge into refinement

- Weighted "cost" function added to total $\chi2$
  - bond distances & angles
  - unit cell contents
  - misc. geometrical (mostly for macromolecular)
- Can be used to guide a balky refinement
  - relax weight at end to 0 (if possible)
- Not always possible to remove Restraint weight
  - be sure to separate derived vs. "driven" results in your paper!