

Powder Neutron Diffraction Measurements of Selected Systems and Data Analysis

Summer School on the Fundamentals of Neutron Scattering
NIST Center for Neutron Research
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Necessary software packages for course

GSAS/EXPGUI: <https://drive.google.com/file/d/1gEGImIVPlgGaOgE8GDhpPFY1ft2EzGzz/view?usp=sharing>
VESTA: <https://jp-minerals.org/vesta/en/download.html>

Also useful but not necessary for this course: CMPR:
<https://www.ncnr.nist.gov/programs/crystallography/software/cmpr/>

Introduction

In this course, we will introduce the general concepts underlying elastic neutron scattering, also known as neutron diffraction. Specifically, we will focus on powder neutron diffraction. We start with a brief description of how powder neutron diffraction experiments are conducted, including some (but not too much) of the underlying physics and math that enable this technique. We describe when powder neutron diffraction measurements can be useful, and how they compare with powder X-ray diffraction measurements and single crystal diffraction. We briefly touch on using powder neutron diffraction measurements to determine magnetic properties. We give the practical aspects as we see them of obtaining these data, ranging from instrumental and sample considerations to obtaining and executing beam time at different user facilities. Finally, we will discuss the specifics of performing Rietveld refinements of powder diffraction patterns. After the lectures, we will walk through three examples of analyzing powder neutron diffraction data together. We expect that the students will follow along and perform the refinements themselves on their own machines as we go, and we will allot time for each step as we move through the examples.

On day one, after the introductory lecture, we will work through an example together to determine the structure of NiO. On day 2, we will begin the day with the second (and final) lecture and then work through a second example of analyzing powder neutron diffraction data together. Example 2 investigates ion conductivity in NASICON as a function of temperature. On day 3, we will start by answering any questions the students may have about data they have collected, or about experiments they are planning, etc. If you would like to ask us questions about diffraction measurements you have conducted or difficult data analysis, please bring the materials in question with you and we will have time for a discussion on the third day. Then we will move on to the final example, which probes hydrogen gas adsorption in a candidate storage material, $\text{Co}_2(m\text{-dobdc})$.

We will distribute the patterns to be analyzed together before the start of the course. We will use GSAS/EXPGUI for the refinements, which can be run on a Windows OS or on a suitable virtual emulator

(download link above). Please download and install GSAS/EXPGUI on your machine prior to the start of the school, and make sure you can open it up. If you have trouble downloading or installing GSAS, please contact Ben or Ryan (contact info above). During the lectures, we will mention tips and tricks for using other software packages for refinements, including TOPAS Academic, GSAS-II, and FullProf, but we will focus on and complete the examples using GSAS/EXPGUI. In addition, please download and install Vesta (download links above).

Below, please find details for each of the three examples.

Example 1: Refinement of NiO data for basic GSAS/EXPGUI use

While many graduate researchers have familiarity with lab X-ray and possible synchrotron powder data, it is likely that few on this course have experience with neutron powder diffraction. While this tutorial is designed for synchrotron X-ray data using the program GSAS, it introduces the basic steps for doing any refinement in GSAS/EXPGUI and does not rely on you knowing anything about neutron scattering. In the subsequent examples we will build on this platform and introduce neutron powder diffraction data and structural refinement.

This tutorial uses data from 11-BM. More information about that beamline and other tutorials can be found below. Files can be downloaded [here](#).

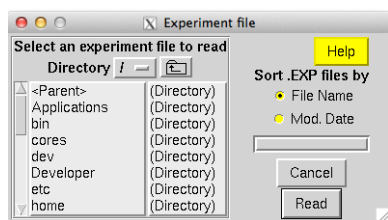
What is 11-BM?

<http://11bm.xor.aps.anl.gov/>

More tutorials:

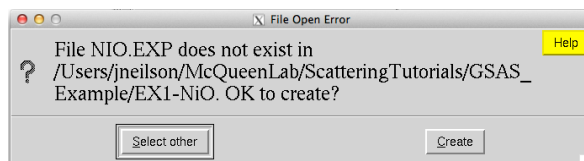
http://www.aps.anl.gov/Xray_Science_Division/Powder_Diffraction_Crystallography/

1. Making a GSAS file
 - a. Make a new directory for your refinement and copy your data and instrument parameter file into it (*.prm, *.iparm, etc). Make sure there are NO SPACES in your Folder extension or file names.
 - b. Start EXPGUI

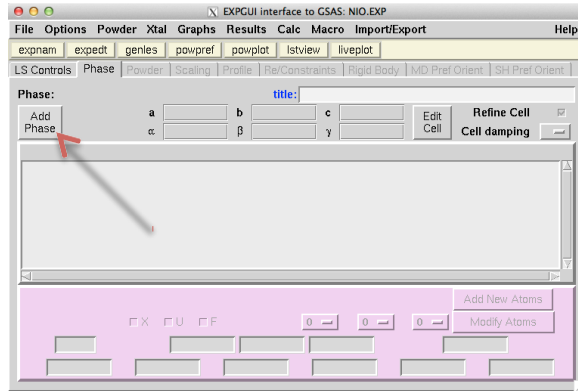


Enter in a file name for your experiment file (e.g., NiO.exp).

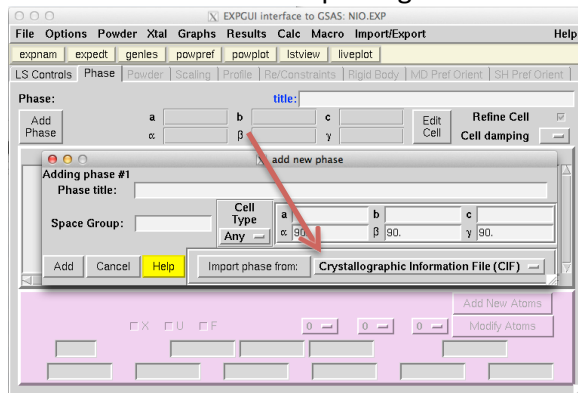
- c. Accept the “error” to create your GSAS file.



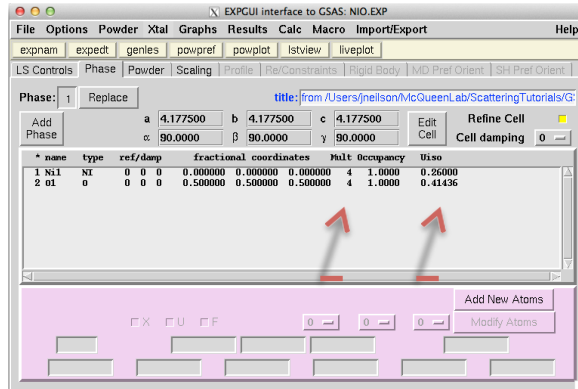
2. Add a phase



Use a *.cif file to make importing easier



a. Make sure that the starting structural model is reasonable:



Are the unit cell parameters right (i.e. cubic,

tetragonal, etc)? Are the Wyckoff multiplicities correct?

In hexagonal or rhombohedral cells, positions can sometimes be incorrect due to "rounding." For example: 0.3333 does not equal 1/3 (0.333333333).

Are the thermal parameters (U_{iso}) correct? Sometimes they are reported in a cif file as "B".

$$\text{To convert: } 8\pi^2 U_{iso} = B$$

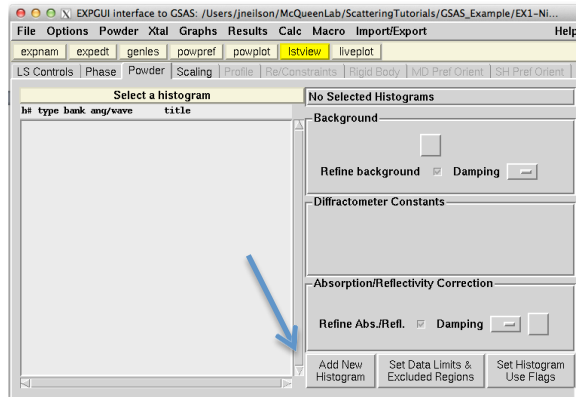
GSAS uses U_{iso} . Fullprof and TOPAS use B .

The thermal parameters generate the Debye-Waller factor, or the attenuation of high-angle Bragg reflections due to thermal motion (phonons).

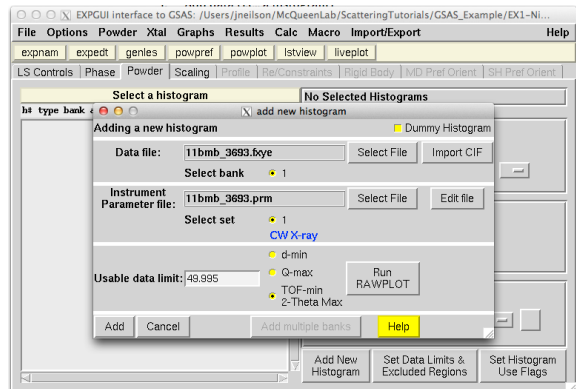
Reasonable thermal parameters for a transition metal center at 10 K should start

around, $U_{iso} = 0.005 - 0.01 \text{ \AA}^2$. Change the thermal parameters for both atoms now.

3. Add data (i.e., a histogram)



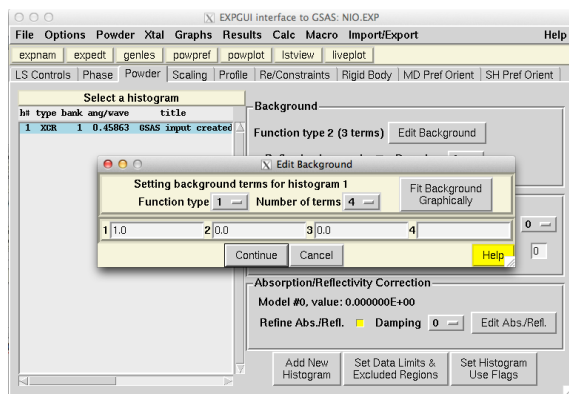
Select the appropriate data file (11bmb_3693.fxye) and instrument parameter file (11bmb_3693.prm).



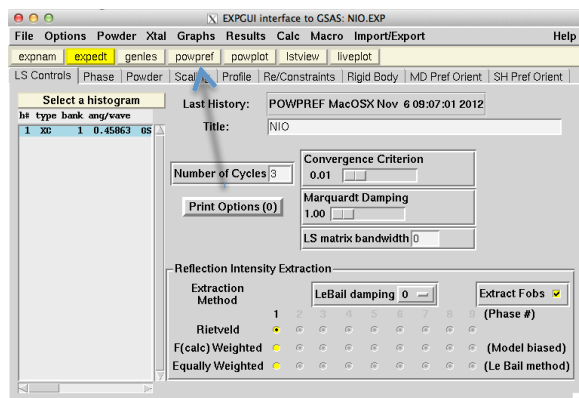
Add.

GSAS uses its own formatting for the data file (*.fxye, *.gsa, *.gsas). Use CMPR to convert different data formats.

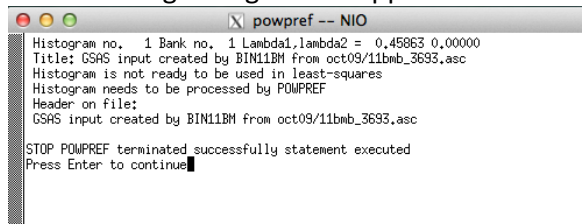
- a. Select the appropriate background function



b. Run POWPREF

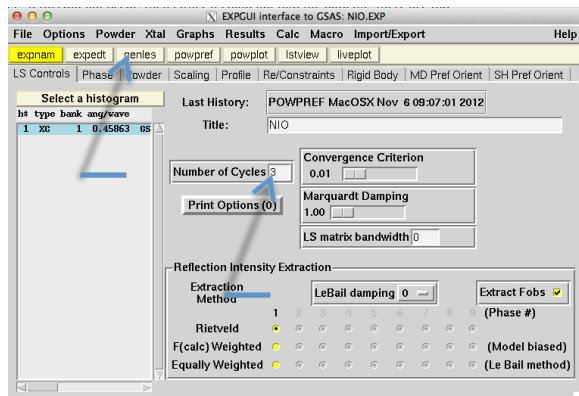


The following dialog should appear:



POWPREF generates the list of unique reflections from the lattice parameters and spacegroup. It prepares the data and model for subsequent least-squares analysis.

c. Run GENLES with a few least-squares cycles.



At this point, only the overall scale factor and background terms should be refining (the scalefactor comes on automatically).

```

genles -- NIO
Reduced CHI**2 = 9075.    for 5 variables
Histogram 1 Type PXC  Nobs = 25 R(F**2) = 2,7268

CPU times for matrix build 0,09 sec; matrix inversion 0,00 sec
Final variable sum((shift/esd)**2) for cycle 1: 48940,56 Time: 0,09 sec

Restraint data statistics:
No restraints used

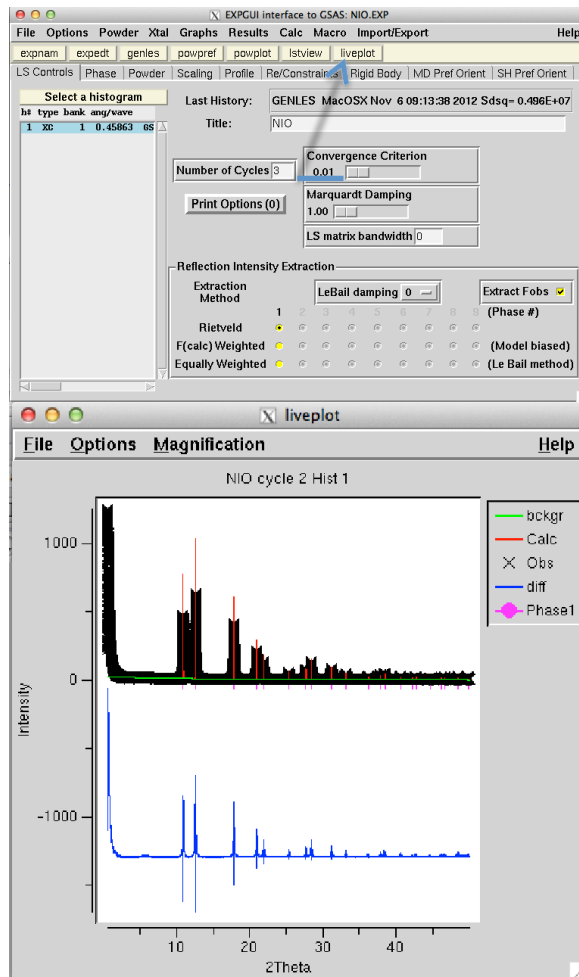
Powder data statistics
Bank Ndata Sum(w*d**2) wRp Rp wRp Rp IMod Integral
Hstgm 1 PXC 1 49496 4,96362E+06 0,7598 0,7047 0,8881 0,8426 0,014 0,991
Powder totals 49496 4,96362E+06 0,7598 0,7047 0,8881 0,8426 0,014
Cycle 2 There were 49496 observations.
Total before-cycle CHI**2 (offset/sig) = 4,9636E+06 ( 1,5620E+04)

Reduced CHI**2 = 100,3    for 5 variables
Histogram 1 Type PXC  Nobs = 25 R(F**2) = 0,8966

CPU times for matrix build 0,09 sec; matrix inversion 0,00 sec
Final variable sum((shift/esd)**2) for cycle 2: 0,00 Time: 0,09 sec
Convergence was achieved and
STOP GENLES terminated successfully statement executed
Press Enter to continue

```

d. Use liveplot to see the data and fit

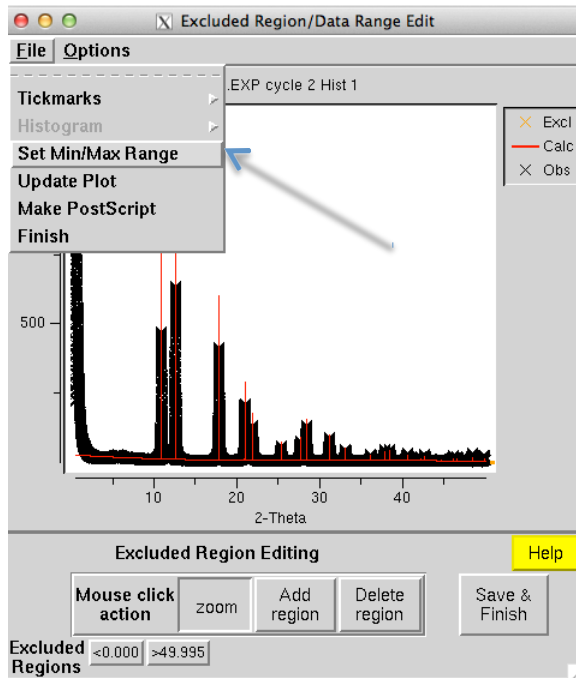
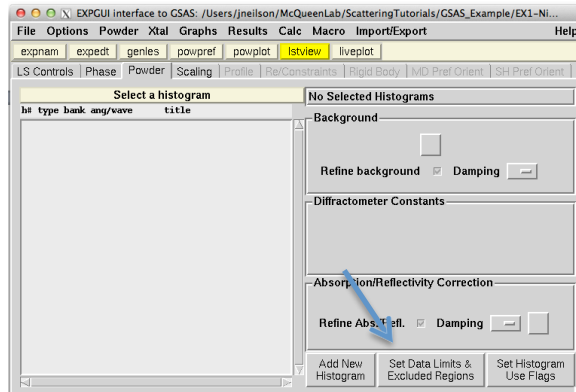


What is wrong here? To start with, the air-scattering at very low angles should be truncated, and the profile function is not quite right.

e. Excluding data regions

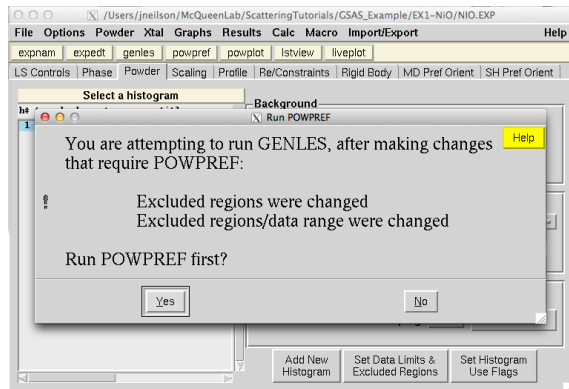
A note of caution: only exclude data if you are **positive** that the excluded region is spurious. This may require a control sample or consultation of the beamline scientist.

Possible spurious artifacts may arise from air scattering (low angles) or a weak, diffuse, broad hump from the sample capillary, etc.

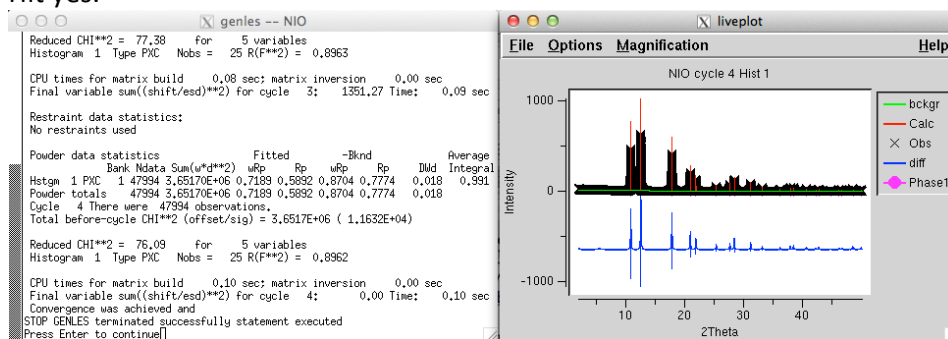


A new window should appear. Set the minimum 2θ to something like 2° . Then Save & Finish.

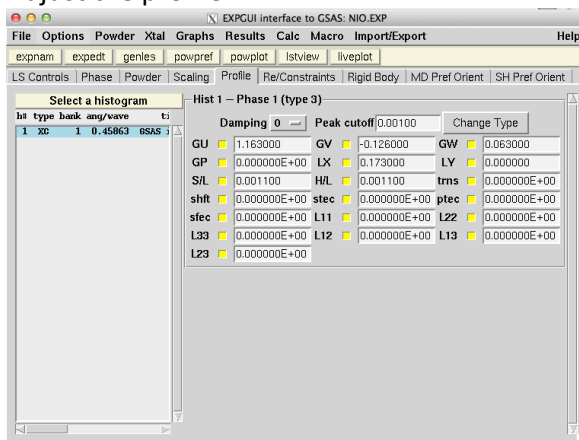
- f. Try running GENLES.
The following error should appear:



This is ok, as changes to the data file or space group require POWPREF to be re-run. Hit yes.



4. Adjust the profile.



The instrument parameter file should come with several default settings, which are dictated by the instrumental resolution (obtained by refinement to a known standard, such as LaB_6).

Profile 3 is often sufficient for most samples. There are several parameters that one can use. The GSAS manual describes in detail the exact definition and θ dependence of each parameter.

The Gaussian broadening parameters, GU, GV, and GW are typically set by the instrumental resolution. Depending on the sample contribution to the peak widths these may be refined, if you have good parameters from a standard reference data set, you can leave these fixed initially. Notice these are the Caglioti parameters U, V, and W.

Do not change S/L or H/L. These are set by the instrument geometry. These parameters deal with axial divergence.

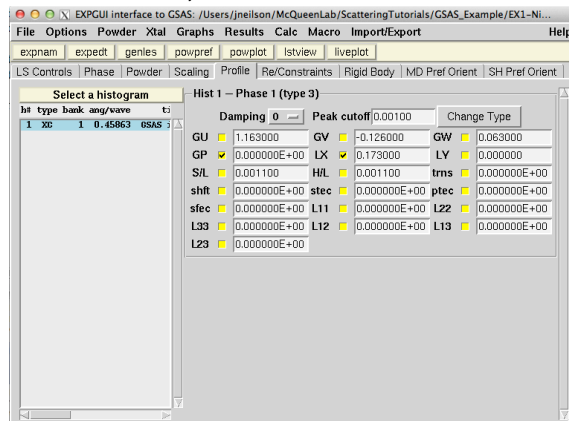
The first parameters to change are GP, LX, or LY.

GP: Scherrer coefficient for Gaussian broadening, $GP/\cos^2\theta$, often attributed to finite (nano)particle size.

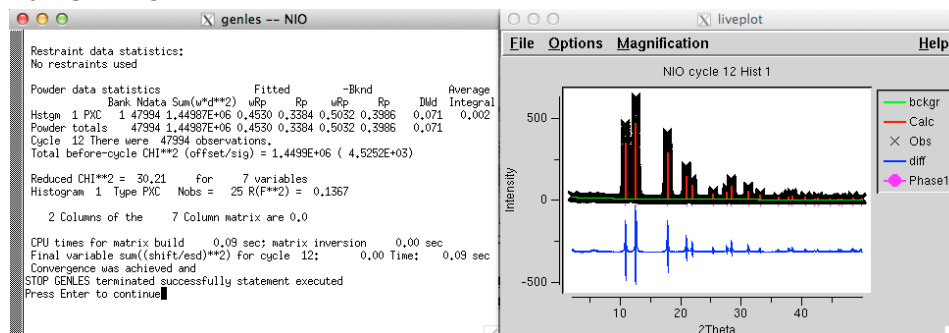
LX: Lorentzian coefficient, also Scherrer size broadening. Usual size broadening term, sometimes requires more than one though. Appears roughly as $\sim LX/\cos\theta$

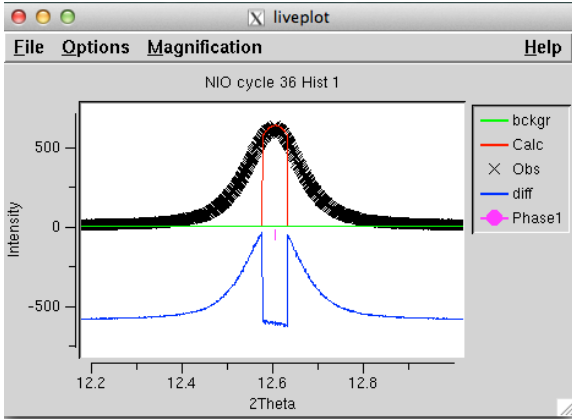
LY: Lorentzian coefficient, often from "microstrain". Appears roughly as $\sim LY*\tan\theta$

Typically, it is best to start with LX or GP; however, it is best practice to only refine one of them at a time, otherwise the refinement may diverge:



Run GENLES.





When re-running POWPREF, you may get the warning:

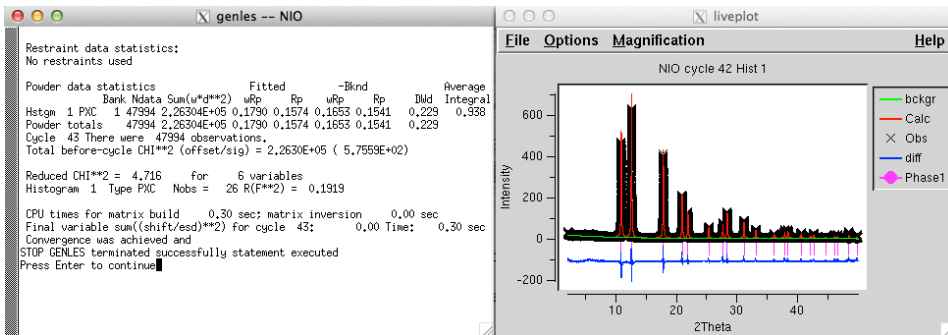
```

powpref -- NIO
Histogram no. 1 Bank no. 1 Lambda1,lambda2 = 0,45863 0,00000
Title: GSAS input created by BIN11BM from oct09/11bmb_3693.asc
**** Histogram will be used in least-squares
Header on file:
GSAS input created by BIN11BM from oct09/11bmb_3693.asc

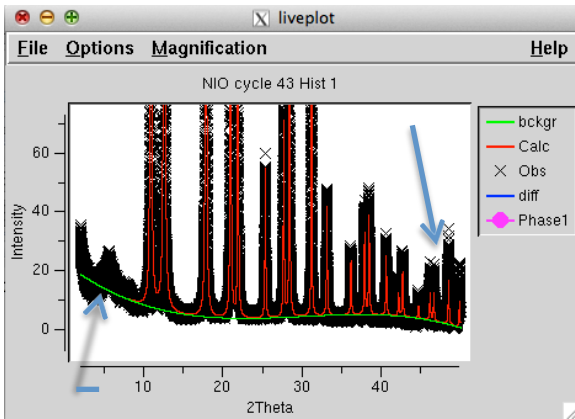
Some peaks are more than 500 profile points wide -
check your profile coefficients for histogram 1
STOP POWPREF terminated successfully statement executed
Press Enter to continue

```

For almost all data collected at 11-BM, your peaks will be more than 500 points wide.



Make sure that the “Final variable sum” is 0.00 or 0.01. This means that the least squares refinement has converged. If not, GENLES requires more cycles.

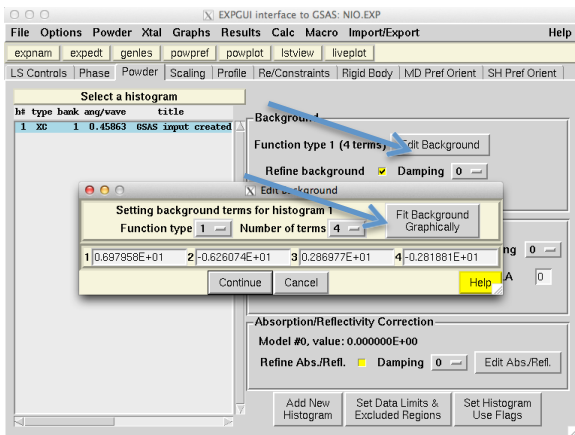


Here are two problems:

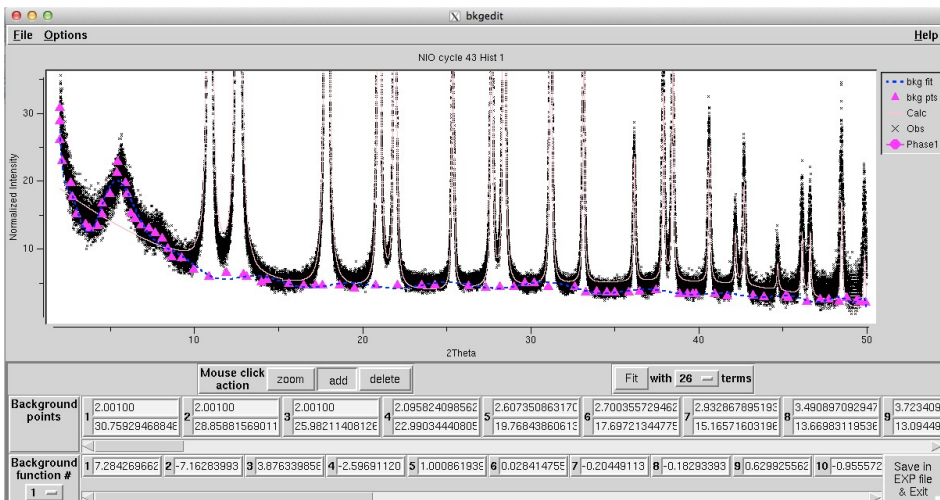
- a. Background from the sample capillary
- b. The high-angle peaks are overly attenuated. In this case, we can attribute that to incorrect $Uiso$'s.

5. Fix the background manually.

Edit background. Then “Fit Background Graphically”



Resize the new window. Zoom into the background (you can right click to unzoom).



Click the “add” button. Now, every time you click in the window, it should add a pink triangle. Add a lot of symbols to approximate the background profile. Then try to “fit” with several terms. For a sharp background function like this, you may need >20 terms. The background does not have to be perfect as you will refine it with least squares in the main program, but it should be relatively close to start with. “Save in EXP file & Exit.”

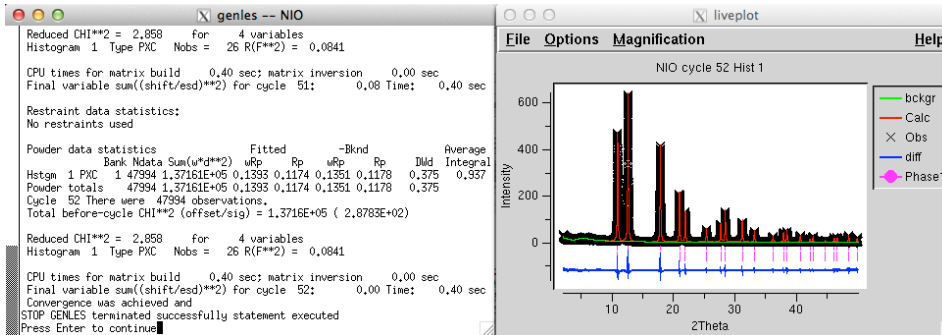
Run GENLES.

6. Refine the U_{iso} 's

Atom	name	type	ref/damp	fractional coordinates	Mult	Occupancy	Uiso
1	Ni1	Ni	0 0 0	0.000000 0.000000 0.000000	4	1.0000	0.01000
2	O1	O	0 0 0	0.500000 0.500000 0.500000	4	1.0000	0.01000

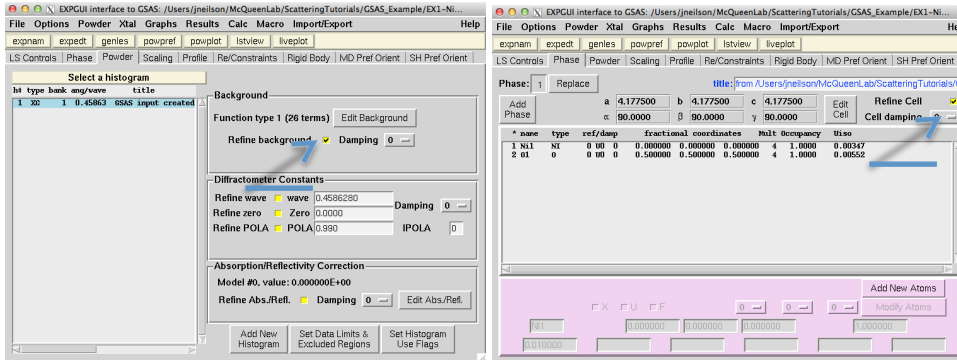
Select both atoms. Check the "U" box. A 'UO' should appear in each atom row, signifying that those refinement flags are on.

Run GENLES

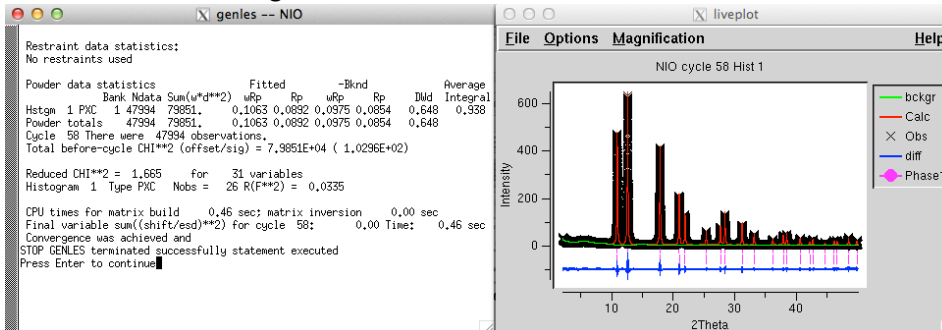


Ok, that is much better. Is it done?

Not yet. Try refining the cell (and the background).

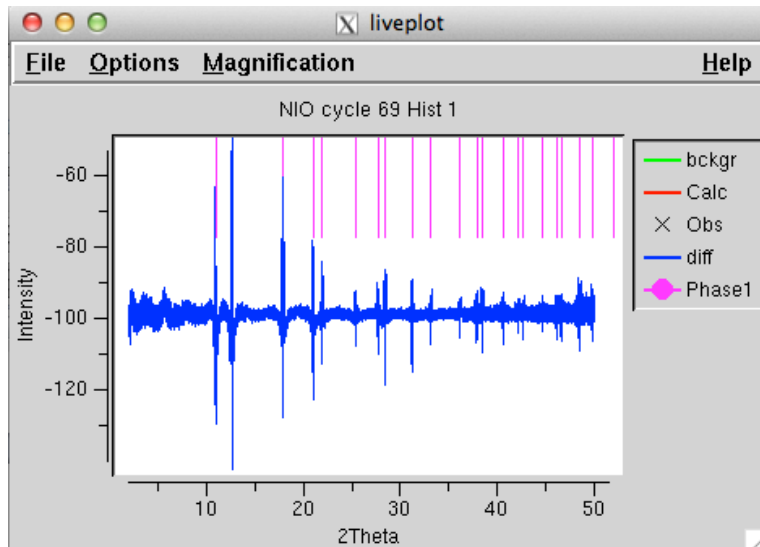


Run GENLES to convergence.



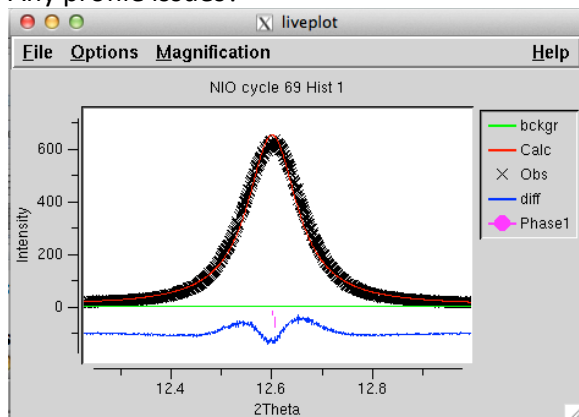
Done? Never!

a. Any systematic errors?



No. The errors in the difference pattern do not have any systematic hkl dependences. There are not any “form factor” errors (positive errors at low 2θ , negative errors at high 2θ , or viceversa).

b. Any profile issues?

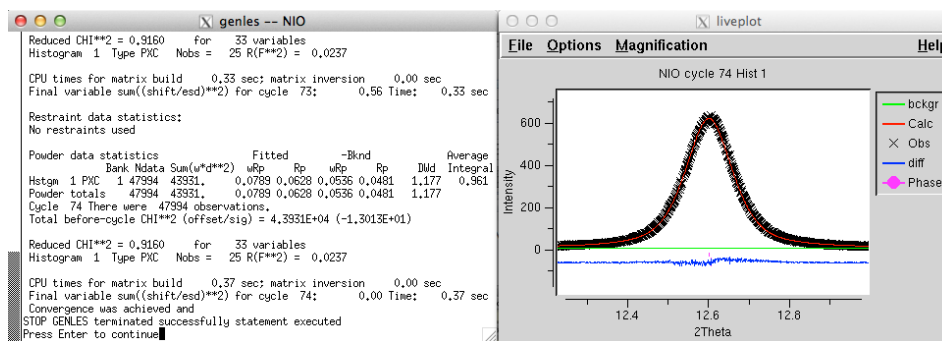


Yes. Not quite the right Gaussian/Lorentzian

weighting. Co-refine GP, LX, and LY:

Peak	Damping	Peak cutoff	Change Type
GU	0.116300E+01	-0.126000E+00	GW
GP	0.000000E+00	0.117672E+02	LY
SIL	0.110000E-02	0.110000E-02	trns
shift	0.000000E+00	0.000000E+00	ptec
spec	0.000000E+00	0.000000E+00	L22
L33	0.000000E+00	0.000000E+00	L13
L23	0.000000E+00		

Run GENLES until convergence:

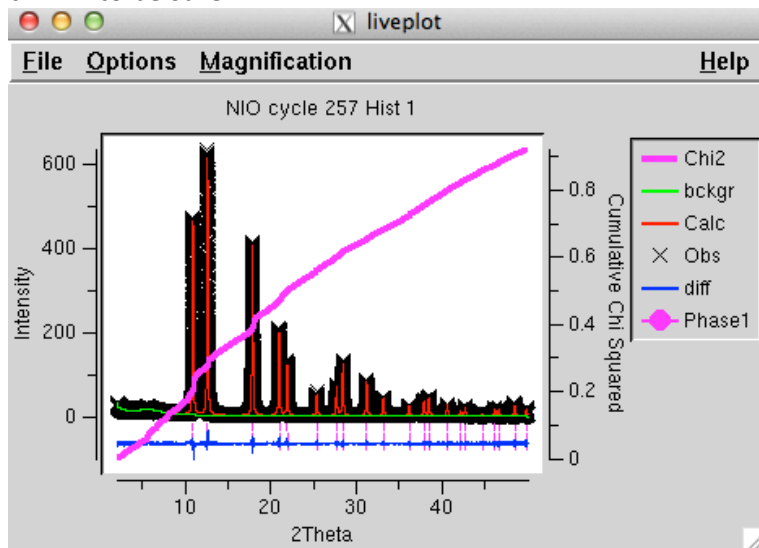


That fixed it!

Why is reduced $\chi^2 < 1$? I thought a “perfect” refinement has $\chi^2 = 1$?

This just means that the errors are not properly propagated (not surprising, since the errors are estimated from the sqrt of the intensity).

At this point, perhaps you would call the refinement done. Plot the cumulative χ^2 to be sure.



There are no real systematic errors.

For a simple structure such as NiO, there isn't much more that you can do.

7. Advanced topics to continue:
 - b. Hamilton R-Ration tests
 - c. Complex profile functions
 - d. Multi-phase refinements
 - e. Multi-histogram refinements

Example 2: Refinement of NASICON data over the 25 K – 400 K temperature range.

Motivation: The ion-conductor NASICON's performance is temperature dependent. Changes in the structure of the material are observable with neutron diffraction and can be used to explain why/how the NASICON material performs.

We will start with the 25. K data set, but this process will be repeated for the other data sets (100 K, 175 K, 250 K, 325 K, and 400 K). This data is from BT-1 at the NCNR, and some of the procedure below is specific to this instrument. Data can be found [here](#).

- 1) Launch EXPGUI
- 2) Navigate to the folder you want to save your data to and then save the file and project name in that folder. The .cif file and data that you want to work from for our refinement (NASICON.cif and *.gsas/*.inst files) should be placed in this folder.
- 3) **On phase tab, hit "Add phase"**: In the bottom right of the popup window, change the file to .cif. This will automatically pop up a window to navigate to the .cif of choice. Load in NASICON.cif. If the space group did not automatically populate, be sure to add the space group in. In this case, it is space group 167, R -3 c. (You can verify this from your .cif though for future refinements.). type in "R -3 c". Hit continue, and add atoms in the following popups, which are just confirming the symmetry rules for the space group.
- 4) **Load in data and .inst file.** On the powder tab, click "add new histogram." Find and load the data file for the 25K data set (NaZr1001.gsas) into GSAS. You should have the same named parameter file (.inst) in the same folder, which will automatically be found after selecting the data file. It will recognize it as neutron data and a maximum range. Make sure it is loaded in as TOF-min 2 theta data. If you encounter an error, try moving the .gsas and .inst files into the directory where you created and saved your GSAS file. We will trim the data later as we see fit. The data was taken with a wavelength of 1.54 Å. Check that this has been loaded in appropriately under "diffraction constants" on the powder tab.
- 5) **Profile:** navigate to the profile tab. Change the profile to type three by click on the "change type" box and changing the drop down number to 3. Hit continue.

At this stage of the refinement, the data has been added and profile set. From this point, we can deviate to either Le Bail or Rietveld fitting. However, it is always a good idea to do a Le Bail fit first for any refinement, as this allows you to obtain appropriate peak shapes for the data without complicating it with structural inputs. A Le Bail refinement ignores any information about atom types and positions, and instead fits intensity arbitrarily. The most important factors for this type of refinement is the unit cell and the peak shape.

- 6) **Setting the refinement to a Le Bail fit.** Navigate to the LS controls tab. In the "reflection intensity extraction" box, change the selection to "equally weighted". This selection makes the refinement a Le Bail fit. Whilst on the LS controls tab, change number of cycles to 0.

We will now officially load the data file so that we can view it.

- 7) **POWPREF** At the top of the EXPGUI window, click powpref. This will load up a cmd window. Press any key on the keyboard to accept. Now hit "load new" on the popup window. POWPREF can be

used to initialize any changes you make to your refinement. GSAS will usually alert you if you change something and that powpref needs to be run.

- 8) **GENLES** At the top of the EXPGUI window, click genles. This will begin a refinement, and run through as many cycles as you have set on the LS control tab. As we have 0 cycles set, it will simply just load in the data file. Do this twice. You will notice that on the first genles, the χ^2 is in the 200's, and on the second it is 80 something.

At this point if you hit the liveplot tab at the top of the EXPGUI window, you can view the data and fit. You can see that as we did not actually do a refinement, that the difference curve is basically the entire pattern.

- 9) **BACKGROUND** we will now graphically input the background. This is important for BT-1 data and allows us to capture a background close to what is there. Navigate to the powder tab, and at the bottom click "set data limits and excluded regions" If you zoom in on the low 2 theta region, you can see a large lead in on the data. This is from the instrument and can be excluded (chose 10 2theta). The same thing can be done at the end of the data, but we won't do that for this refinement. For this part, depending on your compound of interest, you need to make sure that you are not excluding any Bragg peaks of interest. For NASICON, there is nothing in these regions that needs to be fit. It is also worth noting, without belaboring any unnecessary details, that refine data further out in 2 theta, you gain more information about the thermal parameters. For our NASICON refinement, this is important. We recommend doing these refinements again after this using 10 – 150 2 theta and seeing how the refinement conclusions change.
- 10) **To make sure that the excluded regions are actually excluded, you need to run POWPREF, and then GENLES twice. Do that now.**
- 11) Now click "edit background." Go to "fit graphically." Zoom in on the black line (the data) by using the left click and creating a box around a region of interest. For this, do it so you are zoom in on the lowest intensity values of the data between 10 and 60 2 theta. Chose "add" then start clicking on parts of the data roughly every 7 2theta or so to build a background. Near 160, you will see that the data starts to curve upwards. This is an artifact of the instrument, but there is still important data contained here. Try and capture the baseline as best you can by following the line up. chose a 10 term polynomial, and hit fit. You will now have added a graphically fit baseline. Save and exit this window. Hit load new.

Starting the refinement

- 12) We will now start the refinement. On LS controls, set the cycle amount to 10. Hit powpref. Then GENLES to do a refinement. Hit Genles again. On the CMD window popup, you will see that this is producing refinement statistics. You should see that after running genles, that your reduced χ^2 should be somewhere around 20. Anything higher (like in the thousands) means something has gone wrong. This can happen sometimes when too many variables are turned on at once. As we have nothing refining at this point, this shouldn't be an issue.
- 13) On the phase tab, turn on refine unit cell. Hit genles. You will watch the refinement go through iterations, and the fit statistics get better. You can hit genles again as many times until this finds a comfortable minimum, which should be below 10 χ^2 . Make sure to uncheck this box when you are done. In general it is a good idea to know what parameters you are refining at all times, and to not refine the unit cell parameters after you have hit powpref to re-initialize the refinement, since this will lead to divergence of the refinement.

When you start changing peakshape numbers, especially outside of doing a refinement, it can throw GSAS off and it'll start spitting back enormous χ^2 values. If this ever happens, hit "continue with old" after you do the refinement. Change the cycles to 0 on the LS controls page. Then run powpref. Run GENLES a couple of times. This will stabilize the refinement, and you can continue again. This will work for most problems if GSAS starts to throw a tantrum during a refinement.

- 14) **PEAKSHAPE** We will now work on dealing with peakshape. This is a very important step and requires some knowledge (or educated guess) about your sample. The parameters which we will refine will be found on the profile tab. These parameters are GP, LX, and LY. The GP is for a gaussian size broadening, LX is for a Lorentzian broadening, and LY accounts for Lorentzian strain that exists within your sample. Most of the time, it is a good idea to refine these one at a time, starting with GP, then LX, then LY if need be.
- 15) **Change the profile cutoff** to 0.01000. Change the cycles to 0 on the ls tab, and then run powpref and genles a couple times. Sometimes, this cutoff needs to be adjusted mid refinement to help GSAS better capture the peakshape as it ends up in a local minimum that it can shake.
- 16) Change the cycles to 10, run powpref, and then genles.
- 17) Turn on the GP box to allow it to refine. Run genles. Do this a couple times if you see that the number is getting smaller each iteration. If it starts to swing back up, do "continue as old"
- 18) Turn on LY in the profile tab, and run genles.
- 19) Finally, turn on refine background and unit cell parameters and run genles a couple times. This should put the refinement near completion.

At this point, you will see that mostly every peak is captured, except for the strongest peak. This is not uncommon with refining powder patterns. The strongest peak is usually the hardest to get right. However, if you zoom in, you will see that every other peak is well captured so we know we've done the peakshape description correctly. This is reflected in the difference curve, which shows almost a flat line difference except near the strongest peak.

Rietveld refinement

At this stage we can move onto the Rietveld part of the refinement. To do this, resave your Le Bail fit as a new file with some notation that lets you know it's the Rietveld refinement.

- 1) On the LS controls tab, change the intensity extraction selection to Rietveld, and change the cycles to 0. Run powpref, then genles. You will need to close liveplot and reopen it, since the previous window was specific to the saved file we used for the Le Bail fit.
- 2) Turn off everything that is refining (unit cell, background, anything in the profile tab)
- 3) Change the cycles to 10, and run genles. This should stabilize the refinement near 12ish χ^2 .
- 4) We will now start to refine the positions of certain atoms. You will note that in GSAS, special positions are automatically recognized (e.g. zero, one-half, one-quarter, one-third, etc) and will not change unless you change the value. To refine positions, turn on Zr and turn on the "x" refinement flag. X is for position, U is for thermal parameter, and F is for occupancy. Run genles.
- 5) Do this for the remaining elements individually, then all together at once.

- 6) Do the same thing for thermal parameters one at a time for elements, hitting genes, then all together.
- 7) Once the thermal parameters and positions seem stable, refine unit cell and background individually, then all together. Make sure that the thermal parameters remain positive values. You will need to manually correct them to be positive small numbers (i.e. just copy/paste one of the other values of U for the negative terms). Negative thermal parameters are not real.
- 8) Once everything is turned on and refined, and the refinement seems stable, we are done. You will note that the Rietveld refinement will not be as good as the Le Bail fit. This is to be expected, as the Le Bail fit is as perfect of a refinement as you can get – because you’re completely ignoring the chemical model used to describe the data. You will also note that we never touched the profile tab during the Rietveld refinement. This is important, and it is not advised to do this.
- 9) To generate a .cif with error bars, make sure that that the last genes you do has all the parameters you’re refining turned on. You can set the number of iterations to 1 if you would like.

To export your data do the following things:

- 1) Click Results → DISAGL → Save and run Disagl. This will popup a text window, save the file (“close & Save as...”, then hit save) and continue. This step generates distances and angles for a final cif.
- 2) Click Import/Export → CIF Export → gsas2cif
- 3) Enter your name, and type yes
- 4) Hit load new.
- 5) In the folder that you’re working from, you now have a cif for the 25K refinement. Open the .cif in VESTA to visualize the structure. If anything looks off (i.e. atom positions, bond lengths/angles, thermal parameters, unit cell parameters, etc.), then these will need to be reassessed and corrected in your refinement.

Repeat the refinement for the 100 K – 400K data sets. You should use the cif from the previous refinement for each iterative refinement.

Comparing and observing the differences between temperature:

- 1) What do you notice about the refinements? Is the quality of the final refinement the same for each temperature?
- 2) What happens to the unit cell as you do your refinement? Make a graph of the unit cell parameters / volume as from your refinements. What do you notice? You should include estimated standard deviation (esd) values for these obtained values. Error bars will tell you if something is unstable from your refinement.
- 3) What happens to the thermal parameters of the elements as you go up in temperature? Do the thermal parameters change in the same way for each element in the structure? Make a graph with these values versus temperature for the elements to compare. Again, include error bars.

When you report .cifs for publication you should make sure your cif has error bars for everything that was refined during your work. This is important, as it helps you and any person who looks at the .cif understand how much to read into any given value.

As mentioned above, we would recommend repeating these refinements but making the refinable range of the data sets 10 – 150 2θ . If you do this, what do you notice about the values obtained, and the error bars that come with it? What does this tell you about what kind of data one needs to be able to say certain things about structures. Along those lines, how would wavelength and collection time affect these conclusions?

Congratulations, now you are ready to write your manuscript about how temperature effects ion conductivity in NASICON!

Example 3: High Resolution Neutron Data w/ Fourier Difference Maps

This is a tutorial to demonstrate basic use of Fourier Difference Maps in GSAS/EXPGUI. Depending on your material(s) some settings may need to be changed/adapted. Additionally Fourier maps are not absolutely always correct in determining missing aspects of your model, rather they hint at what your refinement might be missing. Always test by adding chemically reasonable information back in to the model and observing the Fourier difference. Data can be found [here](#).

1. Start similar to previous refinement. Use Le Bail extraction method, refining only parameters that are important to the profile peak shape and position. (Hint: Lattice parameter, zero error, size, strain, axial divergence, and background)
 - a. For the background - start with a manual background
 - b. Remember to never refine both axial divergence terms at the same time (H/L and S/L).
2. Get the profile as good as you can. Remember, this is the best fit you will ever get on this data!
3. Switch to Rietveld extraction method. Start by fixing all of the profile parameters and only refining scale.
 - a. You might notice that the fit seems somewhat poor. Several peaks are overfitting and some are underfitting. There is likely something missing from our refinement. Our next step is to try to use Fourier Difference maps to determine what is going on. Go to Graphs -> Fourier -> Setup Phase 1

7 EXPGUI interface to GSAS: GSAS_EX-3_RIET.EXP

File Options Powder Xtal Graphs Results Calc Macro Import/Export Help

expnam expedt genles

LS Controls Phase Powder

Phase: 1 Replace

Add Phase

a 25.84

α 90.00

* name	type	ref/damp
1 C1	C	0 0 0
2 C2	C	0 0 0
3 C6	C	0 0 0
4 C11	C	0 0 0
5 Co2	CO	0 0 0
6 H7	H	0 0 0
7 O9	O	0 0 0
8 O12	O	0 0 0
9 O15	O	0 0 0
10 C2m	C	0 0 0
11 H7m	H	0 0 0

Fourier
 forsrh
 forplot
 polfplot
 powplot
 ortep
 rawplot
 gsas2map
 liveplot
 vrstplot
 widpit
 absplt
 seqplot
 mustplot

Setup phase 1
 Setup phase 2
 Setup phase 3
 Setup phase 4
 Setup phase 5
 Setup phase 6
 Setup phase 7
 Setup phase 8
 Setup phase 9
 run fourier prog

3 Edit Refine Cell

0 Cell Cell damping 0

apancy Uiso

apancy	Uiso
0.0000	0.01000
0.0000	0.01000
0.0000	0.01400
0.0000	0.00760
0.0000	0.00200
0.0000	0.04500
0.0000	0.00500
0.0000	0.01800
0.0000	0.01000
0.0000	0.01200
0.0000	0.03500

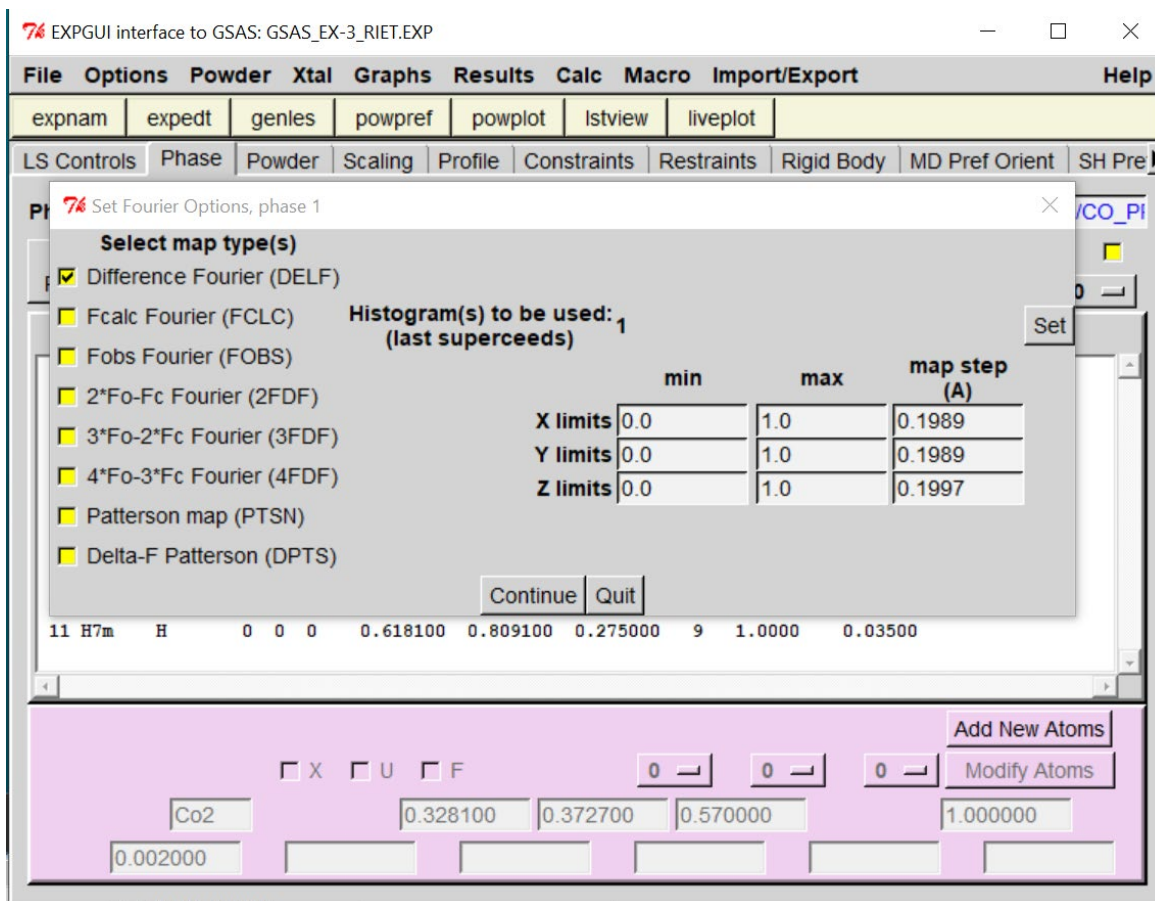
X U F

0 0 0

Co2 0.328100 0.372700 0.570000 1.000000

0.002000

Add New Atoms
Modify Atoms



- We will start by selecting the Difference Fourier (DELDF) option. This is a standard Fourier difference map of Fobs-Fcalc. Sometimes it is more beneficial to use others, such as 2FDF, but we will start simple here. In practice though, you can use more than one option. Additionally, you can sometimes limit your map due to symmetry (i.e. don't need to go from 0-1.0). Sometimes this is even necessary to limit the calculation size. We can use the full range here though.
- Next we will run our Fourier program. This is under Graph->Fourier->Run Fourier Program. A new window should pop up:

```

C:\WINDOWS\system32\cmd.exe - C:/GSAS/expgui/gasstd.bat C:\GSAS\exe\fourier.exe GSAS_EX-3_RIET
D:\Presentations\Workshop\High-res-neutron>REM a batch file to a DOS command and pause
D:\Presentations\Workshop\High-res-neutron>if "%GSAS%" == "" set gsas=c:\gsas
D:\Presentations\Workshop\High-res-neutron>set PGPLOT_FONT=C:\GSAS\pgl\grfont.dat
D:\Presentations\Workshop\High-res-neutron>set SYMOP=C:\GSAS\data\symop.dat
D:\Presentations\Workshop\High-res-neutron>C:\GSAS\exe\fourier.exe GSAS_EX-3_RIET
Calculation of a DELF map was requested.
CPU time for reading reflections was      0.00 sec.
CPU time for this FOURIER map was      0.16 sec.
STOP FOURIER completed successfully statement executed
D:\Presentations\Workshop\High-res-neutron>pause
Press any key to continue . . .

```

- d. Now we want to export our Fourier maps. We can go to Graph->forplot. This will once again open a new window. Here you can use ? to view the options, but we will be choosing a, n, e, and then q to quit. This should export a *.grd file.

```

-----
                Program FORPLOT Version Win32
                Crystal structure Fourier map drawing program
                Distributed on Fri Apr 18 08:12:00 2014
                -----

                Allen C. Larson and Robert B. Von Dreele
                Manuel Lujan, Jr. Neutron Scattering Center, MS-H805
                Los Alamos National Laboratory, Los Alamos, NM 87545

                Copyright, 2000, The Regents of the University of California.
                -----

Enter graphic screen option (<?>,A,B,C,D,Z) >a
Do you want to save graphics output (Y,<N>)? >n
A DELF file has been opened
Problem title:
Phase name: from D:/Presentations/Workshop/High-res-neutron/CO_PRIME_1P25D2_R.
Map parameters:
Map X axis divided into 130 steps, from 0 and covering 131 steps
Map Y axis divided into 130 steps, from 0 and covering 131 steps
Map Z axis divided into 34 steps, from 0 and covering 35 steps
Map scaling factor 1.E-02
Rescaled rho limits from -21.96 to 27.87
There were 600635 map elements stored
Selected maptype is DELF
The map values range from -21.96 to 27.87 with a scaling factor of 1.E-02
5 contours will be drawn between rho = 0.00 and 27.87
with an interval of 4.64
Contours will be drawn at:
4.64 9.29 13.93 18.58 23.22
The map center is at 0.00000 0.00000 0.00000
The map orientation vectors are:
U = 1.00000 0.00000 0.00000
V = 0.00000 1.00000 0.00000
Plot axes to crystal transformation matrix:
0.038693 0.022340 0.000000
0.000000 0.044679 0.000000
0.000000 0.000000 0.147332

Height of section above center is 0.000 A
The map size - center to edge is 5.00 A
The map grid interval is 0.300 A
Enter FORPLOT command (<?>,A,C,D,E,G,F,H,I,L,M,N,O,P,Q,R,S,T,V) >e
File GSAS_EX-3_RIET_DELF.grd written
Enter FORPLOT command (<?>,A,C,D,E,G,F,H,I,L,M,N,O,P,Q,R,S,T,V) >q

```

- e. Now we will want to export our CIF to compare to our Fourier map. Go to Import/Export->gsas2cif. Enter the relevant information then open up your CIF in VESTA. (For VESTA install go [here](#))

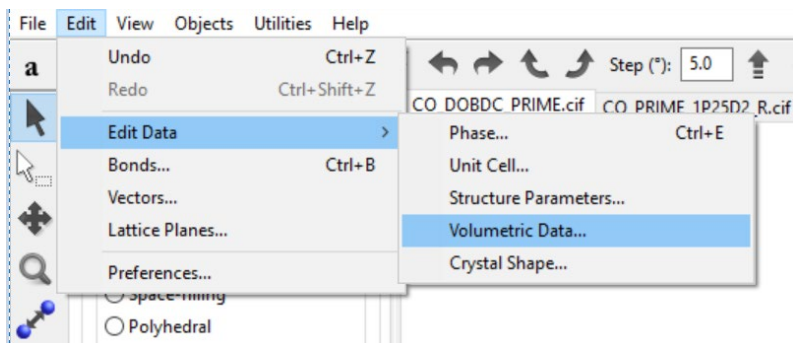
```
-----
Program GSAS2CIF Version Win32
Generate CIF files
Original design by Brian Toby, NIST
Distributed on Fri Apr 18 09:12:00 2014
-----

Allen C. Larson and Robert B. Von Dreele
Manuel Lujan, Jr. Neutron Scattering Center, MS-H805
Los Alamos National Laboratory, Los Alamos, NM 87545

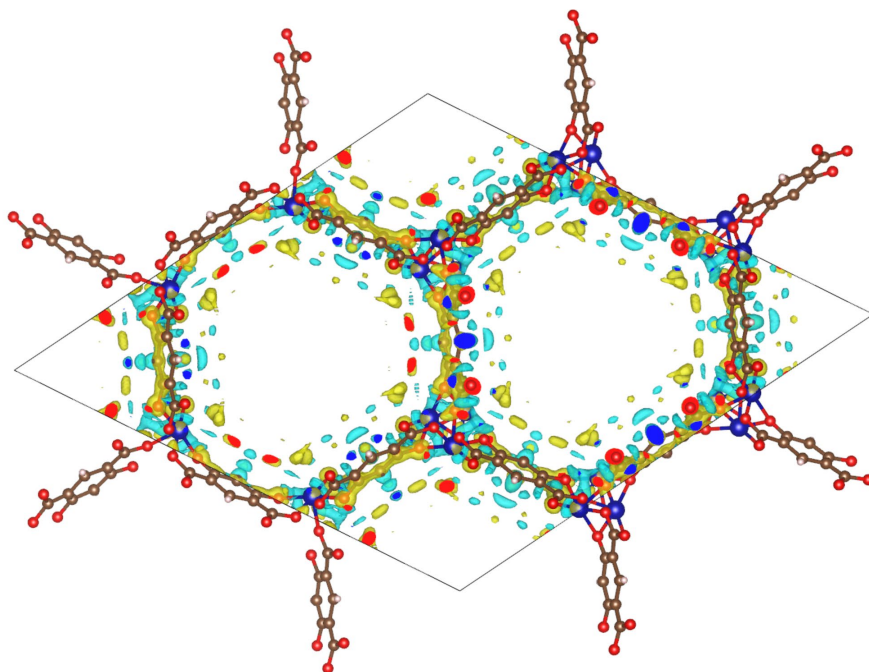
Copyright, 2000, The Regents of the University of California.

Enter your name: >Me
Do you want a short cif file with only atoms (Y/<N>)? >y
The Variance-covariance matrix (.CMT file) cannot be read.
Uncertainty estimates can not be reported.
Continue anyway? (Y,<N>) >y
The distance & angles (.DISAGL file) cannot be read. (Was DISAGL run?)
Distances and angles cannot be Reported.
Continue anyway? (Y,<N>) >y
Preparing publ section
Reading from GSAS data directory, file template_publ.cif
Creating file 1_publ.cif
Processing phase 1
```

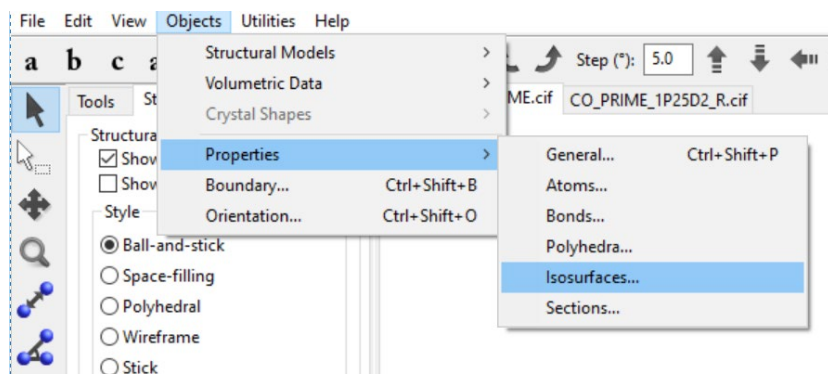
- f. Once you open your CIF in VESTA, go to Edit->Edit Data->Volumetric Data. Once there import your *.grd file, then hit Apply and/or OK.

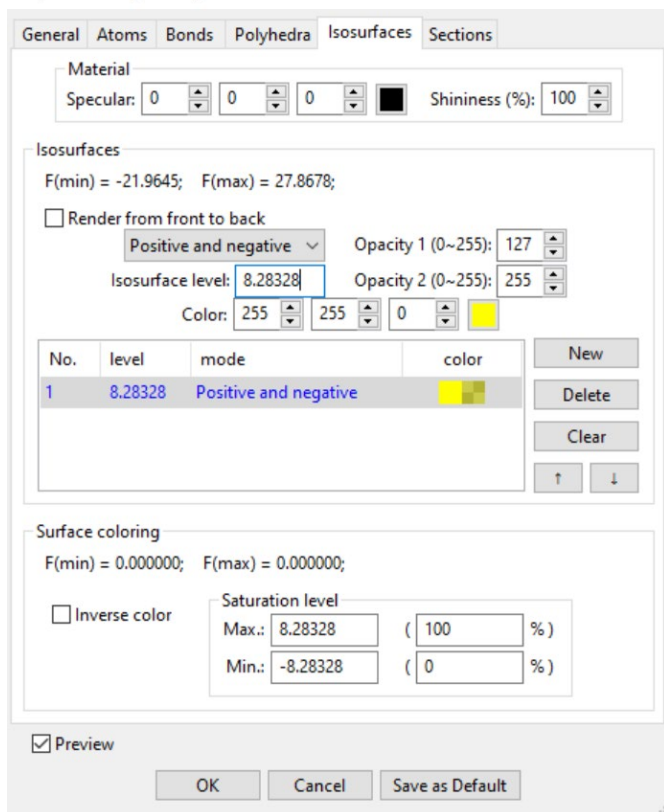


- g. The Fourier Map likely looks like a mess here (see below). Looking at the map this way is useless. We will have to scale it to see the largest effects.

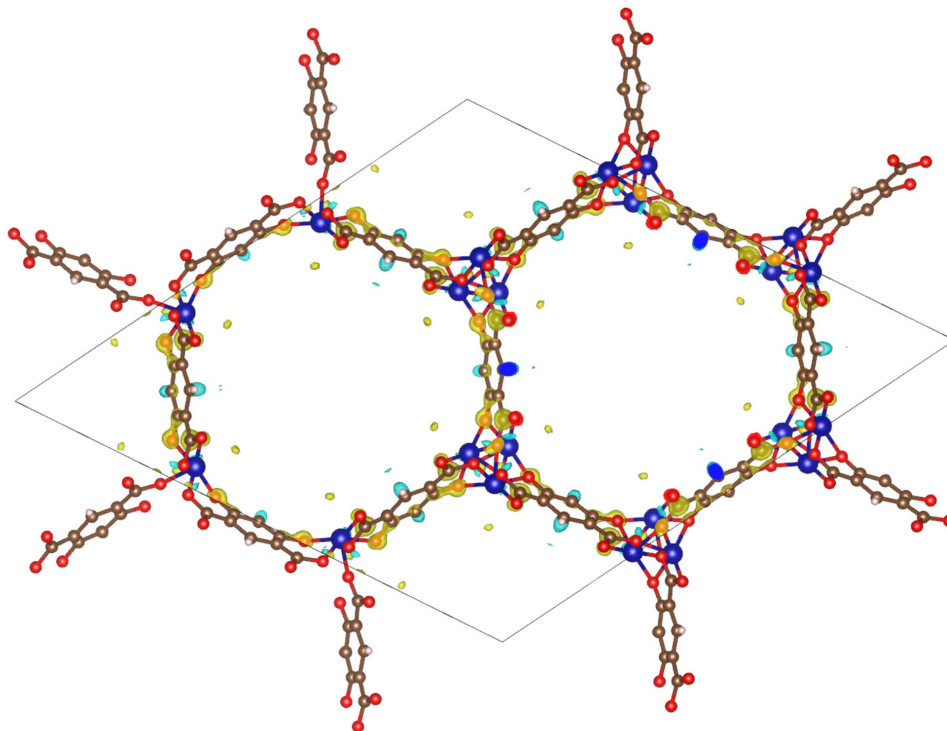


- h. Go to Object->Properties->Isosurfaces. The Isosurface level gives a cutoff to the observed Fourier difference map. Anything above (or below the negative value for negative difference) is observed. We want to increase this value to see the maximum differences.

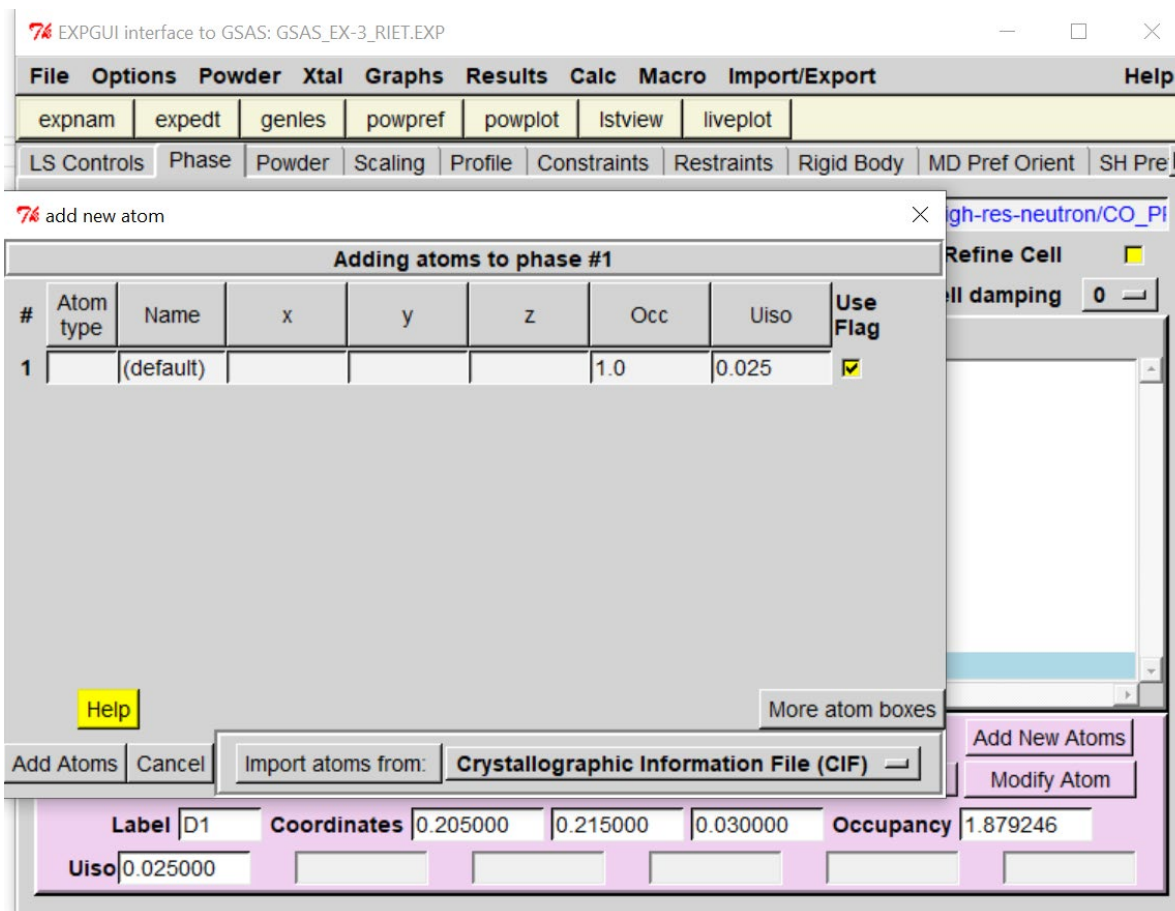




- i. We should start to see some discrete spots now where there are not atoms, but the Fourier map seems to indicate atoms should go.



4. Now we will add in the atoms we need to fit these positions. In our case these should be Deuterium atoms, as that is what our model is missing. Start by adding them into VESTA to get an idea where they should go. To do this in Vesta, go to edit→edit data→structure parameters and then click new. This will add a new dummy atom ('Xx') at the origin. Manually change the atom coordinates until the dummy atom sits inside or near the missing intensity in your Fourier map. This gives you the fractional coordinates of the missing atom. Then we can go back to GSAS and add them in there.



- a. We are someone certain of the position, so we can start by refining the occupancy. This should significantly improve the refinement. Note however that this occupancy refines larger than 1!!! This is typically a red flag. However, in this case the Deuterium atom is mimicking a D₂ molecule. Hence we instead expect a maximum occupancy of 2.
 - b. Once you are happy with the occupancy, you can refine the position. Feel free to export the CIF to verify the distance is not too close!
5. The fit should be looking pretty good at this point, however there is another atom missing. Try to export the Fourier map again and see if you can find it!