

GSAS-2 ED-XRD refinement guide

Full pattern fit using the Le Bail extraction method

Reason for use: necessary for obtaining accurate unit cell volumes and errors thereof for materials at high HPHT. Hand-picking peaks in PDIndexer may lead to biased results and may not constrain the unit cell correctly (especially if the fitting range is not set adequately for each peak). PDIndexer also does not deconvolve overlapping peaks (of multiple materials), which limits the number of peaks that can be included in the fit. Having said that, if too many peaks of multiple phases overlap, GSAS-II will also have trouble refining the cell parameters correctly.

Preliminary requirements

Before using GSAS-II for pattern refinement, you need two things:

- Channel-Energy calibration of detectors used.
- Calibrated 2θ diffraction angle of detectors used.

The beamline station P61B offers **software tools** to obtain this information from the raw data files acquired during the calibrations.

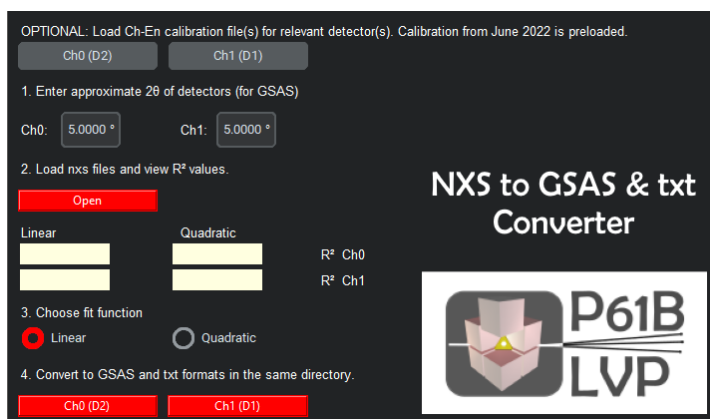
1. Ch2En

- Offers the channel-energy calibration parameters for **PDIndexer**, in the files:
 - Ch#_Ch-En_linearcalibration.txt
 - Ch#_Ch-En_quadraticcalibration.txt
- Offers the complete information (channel # for each peak energy) for the data conversion tool **NXS2GSAS**, in the file:
 - Ch#_for_NXS2GSAS_detcalib.txt

2. LaB62theta offers the calibration of 2θ for one or both detectors using an interactive GUI:



3. **NXS2GSAS** is used to convert the acquired EDXRD data files to readable format for GSAS-II:

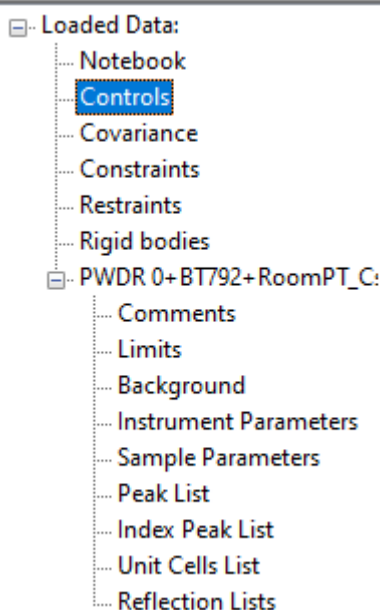


4. **LaB6 refinement in GSAS-II** to obtain a specific **Instrument Parameters file** (*.instprm) for the current beam time. To calibrate the Instrument Parameters file for your beam time, you first need to load a generic parameters file. Older versions of GSAS-II require a different one than the latest version of GSAS-II. Both versions are provided on the beamline computers. You may ask the beamline staff for this important calibration, if you have no experience yet.

Setting up the GSAS-II environment

Start-up GSAS-II. You will be presented with two blank windows.

1. Import the ED-XRD GSAS data file (use the NXS to GSAS conversion app provided at the beamline): Import → Powder data → from GSAS powder data file.
 - a. Note, you can only import data from 1 detector (channel) at a time!
2. A new dialog window asks for the **LaB₆-calibrated instrument parameter file specific for your beam time**.
3. The data is loaded in the list, showing the file name. There are a number of entries for each data file you import:



4. Go to 'Control' first and change the default values to the following:

Refinement Controls

Refinement type: ? analytic Hessian Min delta-M/M: 1e-08

Max cycles: 20 Initial lambda = 10** -3

SVD zero tolerance: 1e-09

Sequential Settings

Select datasets to switch to sequential refinement: Select datasets

Global Settings

CIF Author (last, first): no name

5. We can inspect the Instrument Parameters after the LaB6 calibration:

Project: E:\DESY Beamline\Users

Histogram Type: PXE Bank: 1

Name (default)	Value	Refine?
2-theta): (4.996479)	4.996479	
XE (-0.062393):	-0.0623925	
YE (0.284198):	0.284198	
ZE (-0.267852):	-0.267852	
A (0.000000):	0.0	
B (0.000455):	0.00045549	
C (0.000619):	0.00061894	

Tree view items: Notebook, Controls, Covariance, Constraints, Restraints, Rigid bodies, PWDR 0+BT792+RoomPT_C, Comments, Limits, Background, Instrument Parameters, Sample Parameters, Peak List, Index Peak List, Unit Cells List, Reflection Lists, Phases, Cesium chloride, Platinum.

- The 2-theta value and other instrument parameters should be already calibrated beforehand using LaB6 (using the beamline app and GSAS-II). This information is provided by the instrument parameter file you loaded.
→ **NEVER include 2-theta or XE, YE, ZE in your EDXRD data refinements!**
- The parameters A, B, and C relate to the peak shape (e.g. widths). A and C are closely correlated, and standard practice is to keep A at zero ('0').
- At the moment, do NOT make any changes or add any parameters to be refined.

6. Next, in 'Sample Parameters' disable the checkbox for 'Histogram scale factor'. This is very important or the Le Bail fit routine for ED-XRD will fail.

Sample and Experimental Parameters

Instrument Name

Diffractometer type: Debye-Scherrer

Histogram scale factor:

Goniometer omega:

Goniometer chi:

Goniometer phi:

Detector azimuth:

Clock time (s):

Sample temperature (K):

Sample pressure (MPa):

Sample humidity (%)

Sample voltage (V)

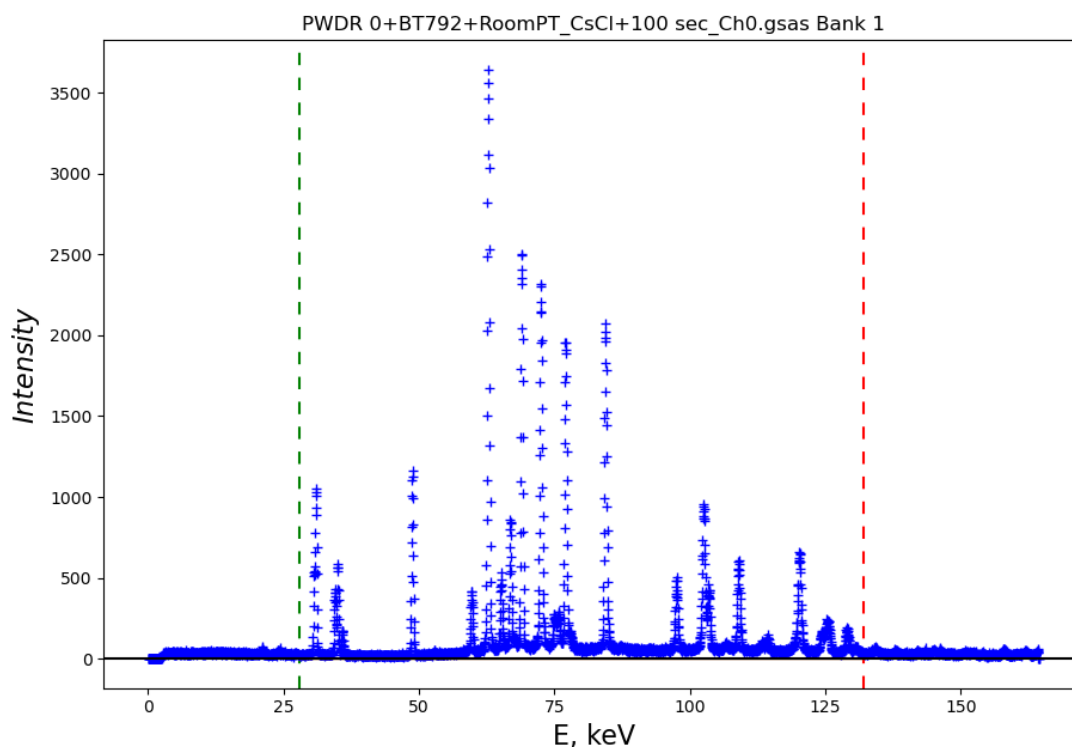
Applied load (MN)

7. Then, go to 'Limits' and set the appropriate range (in keV) where the sample peaks are most prominent. Do not try to include very weak peaks that are just above the noise, e.g. in the highest energy range.

Data range to be used in fits

Original Tmin 0.0147 New:

Original Tmax 164.4785 New:



8. It's best to exclude additional ranges, e.g. where x-ray fluorescence lines of Pb and other metals exist. Also remove any phase peaks that do not have a symmetric 'gaussian' shape, or are too weak in intensity (e.g. less than 50 counts). Go the menu: Edit Limits → Add exclude

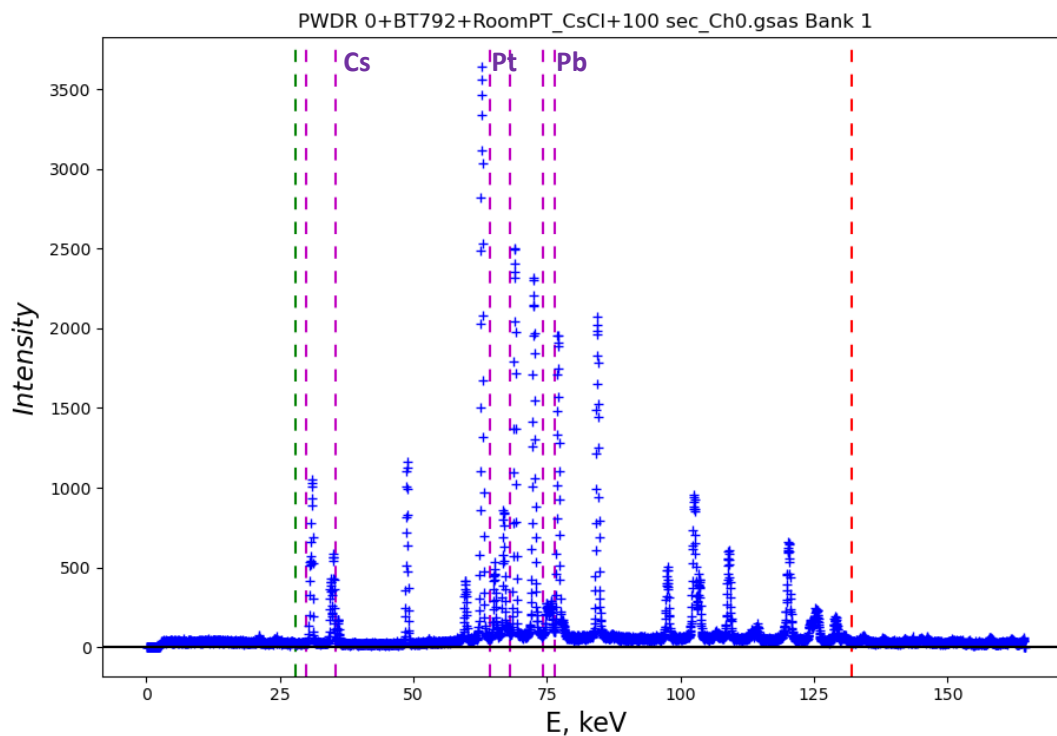
Data range to be used in fits

Original Tmin 0.0147 New:

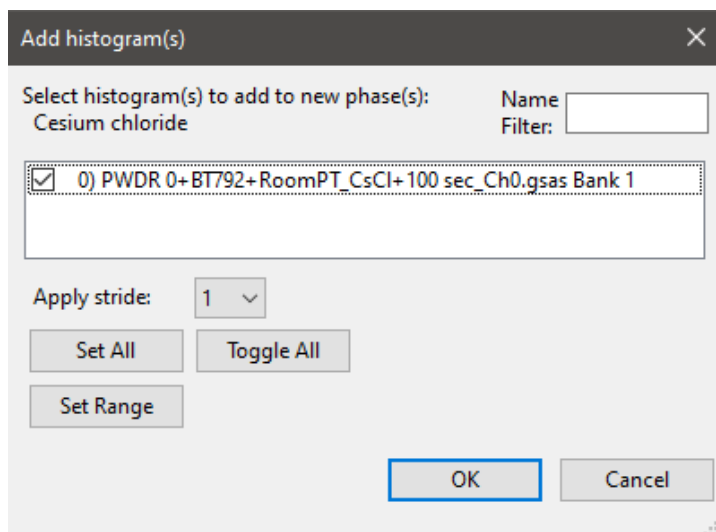
Original Tmax 164.4785 New:

Excluded regions:

From:	To:	Delete?:
<input type="text" value="64.3474"/>	<input type="text" value="68.0"/>	<input type="checkbox"/>
<input type="text" value="74.1398"/>	<input type="text" value="76.4"/>	<input type="checkbox"/>
<input type="text" value="29.7932"/>	<input type="text" value="35.4"/>	<input type="checkbox"/>

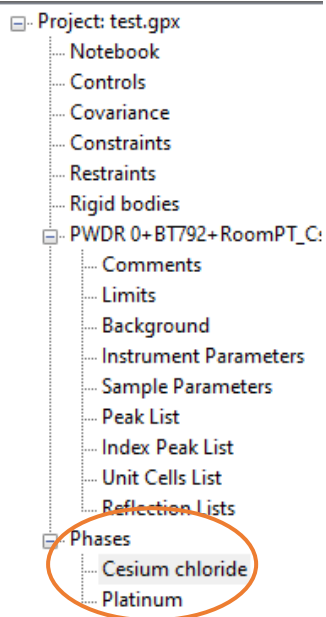


9. Now we add the phases we want to fit in the pattern. Go to menu: Import → Phase → from CIF file. Do this for all phases one-by-one. You will be asked to add the phase any and all data file which are currently loaded in GSAS-II.

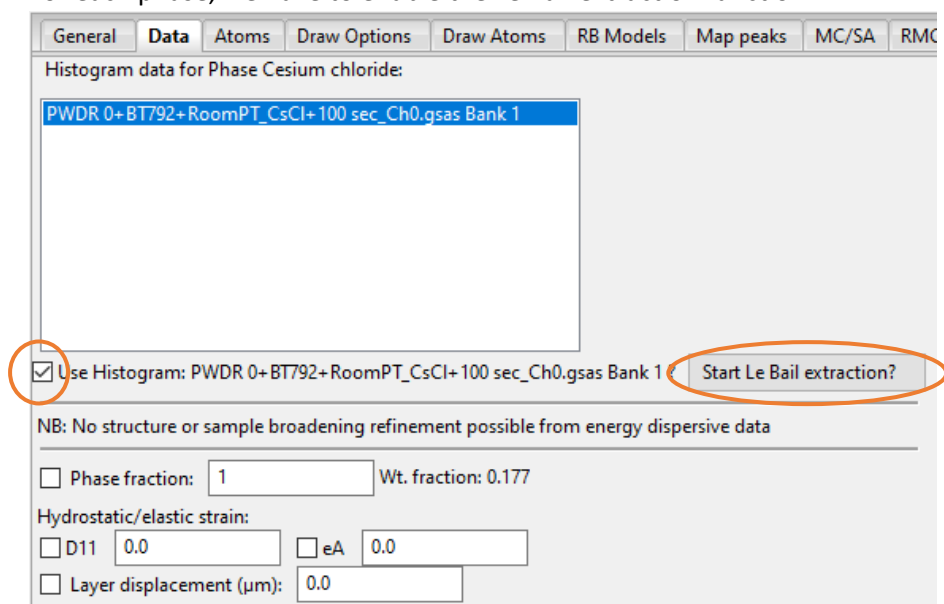


Add the phase to the appropriate data file.

10. The phases are located in a separate list menu:



11. For each phase, we have to enable the Le Bail extraction function.



WARNING! When adding additional data files to a project, you must **turn off histograms and Le Bail extraction** for all entries except for the pattern you want to refine!!

12. Next, add a background fit to the profile. It may be desirable to manually add points on the profile. Use the built-in function, for as many as 12 coefficients for good results.

Background used in refinement

Background function: Refine?

Number of coef.:

Background coefficients:

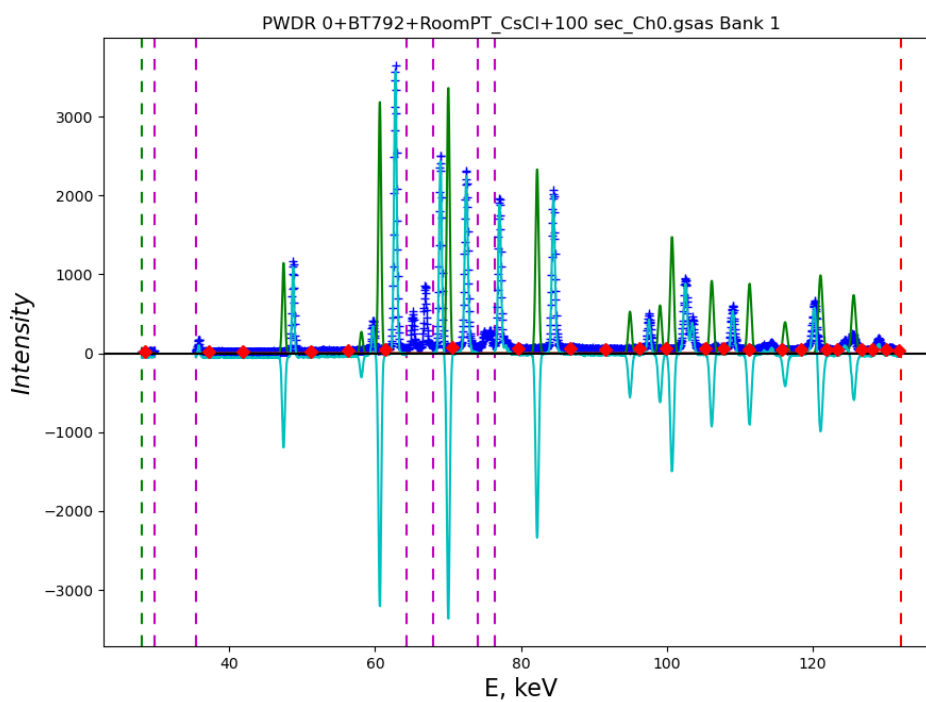
<input type="text" value="1.0"/>	<input type="text" value="0.0"/>	<input type="text" value="0.0"/>	<input type="text" value="0.0"/>	<input type="text" value="0.0"/>
<input type="text" value="0.0"/>	<input type="text" value="0.0"/>	<input type="text" value="0.0"/>	<input type="text" value="0.0"/>	<input type="text" value="0.0"/>
<input type="text" value="0.0"/>	<input type="text" value="0.0"/>			

Debye scattering: Number of terms:

Peaks in background: Number of peaks:

Fixed background histogram (for point-by-point subtraction):

- a. Adding points (if desired):

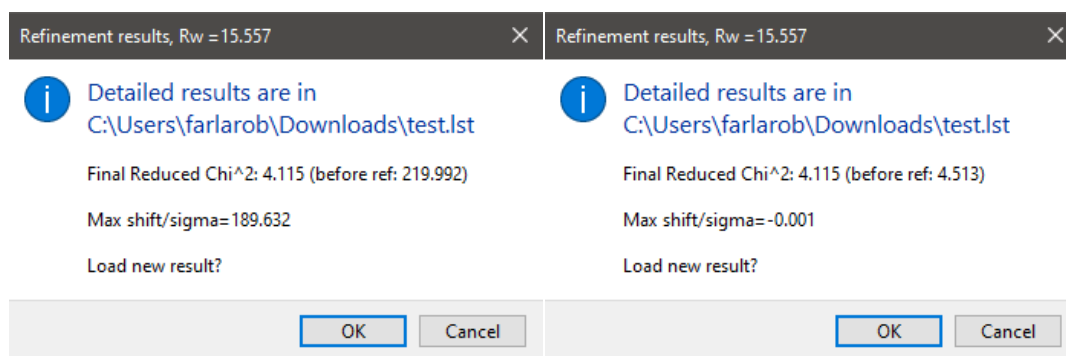


Background refinement

1. The first thing you need is a good background fit. Only refining the background might not give you the desired result, however. Le Bail extraction appears to be a requirement and so this should be enabled for all included phases. As a result, if the unit cell volumes of the phases are not already approximately correct, the background polynomial will become very wavy and not find a global minimum. Here are some tips to ensure a successful background refinement:
 - a. Enable 'Refine unit cell' for all phases, and if known, enter the expected unit cell parameters/volumes in advance. Enable Le Bail extraction for the given powder datafile, if not already done so. Stop extraction for all other files if more than 1 are imported.
 - b. Set the min and max limits carefully. Then **add excluded regions** where peaks might be that are not the sample:
 - i. Known fluorescence peaks (e.g. for Pb)
 - ii. Overlapping peaks
 - iii. Peaks that appear too asymmetric.This step is very important to a successful background fit!
 - c. Enable 'Background refinement' for some number of coefficients (e.g. 12).
 - d. **Make sure the 'C' parameter in 'Instrument Parameters' is 0.0 and disabled!** This parameter affects the way the background is fitted.
 - e. Optionally: Enable the 'B' peak shape parameter in 'Instrument Parameters'. You can also do this in a later refinement cycle.
2. Hit 'Ctrl + R' and start a refinement. You might repeat it twice.
3. Inspect the background fit. If you guessed the unit cell parameters wrong, you can now make a new, better initial guess. Then refine again until the peaks line up.
4. After a few cycles, the background should be very good and you can disable the Background.

Improving the unit cell volume and peak shape

1. Continue refinement of the peak shapes and unit cell of the phases.
 - a. Enable the 'B' parameter for gaussian peak shape refinement and keep the unit cell of the phases enabled. Disable the background. Refine a few cycles.
 - b. Optional: enable the 'C' parameter and continue refinement a few cycles.
 - c. Finally, disable the 'C' parameter and repeat step 'a' above until you see no more shift (0.000, or < 0.010). That means the refinement should have found the global minimum.



- d. **WARNING!** Sometimes the pop up shows no shift, but many warnings (see below). It could be the refinement is stuck in a local minimum or cannot approach a minimum. You need to fix this and there are some options:
- Inspect the profile fit and be very sure that no unknown peak, or false peak is located near an expected sample peak. If this is the case, add an excluded region for this unwanted peak. This solves most problems concerning refinements not able to converge to a global minimum.
 - Try to refine only the unit cells of the phases, or 1 phase at a time.
 - Add the background back into the refinement and repeat the steps above.

Refinement results, $R_w = 520.671$ ✕

i Detailed results are in <C:\Users\farlarob\Downloads\test.lst>

Final Reduced χ^2 : 4629.411 (before ref: 4629.411)

Max shift/sigma=0.000

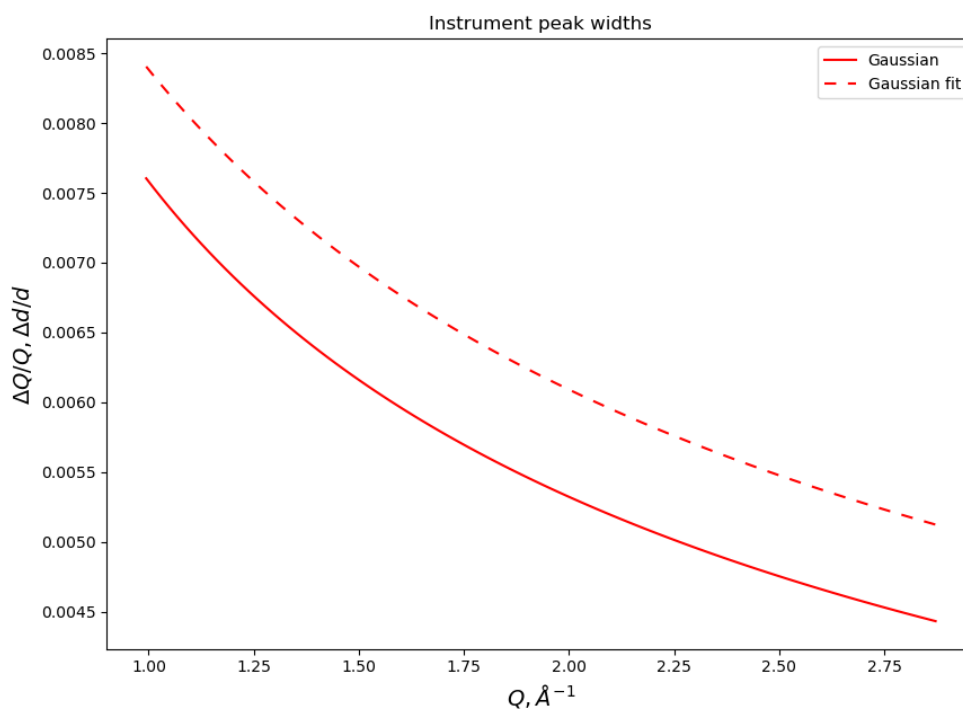
Note highly correlated parameters:
:0:Back;6 and :0:Back;8 (@56.55%)

WARNING: Minimizer halted because χ^2 increased

WARNING: Steepest descents dominates; minimum may not have been reached or result may be false minimum. You should reconsider which parameters you refine. Check covariance matrix.

Load new result?

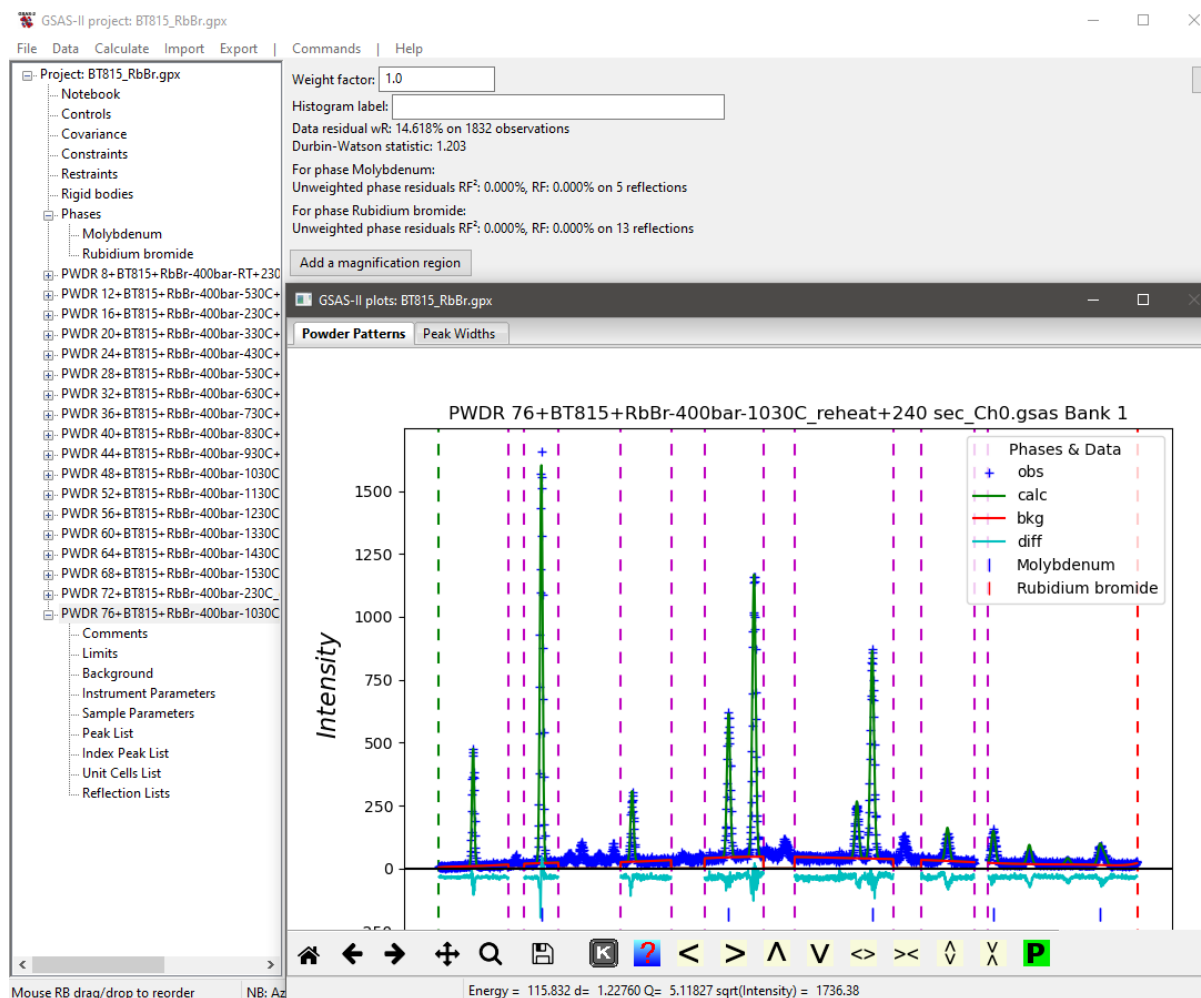
The plot below shows the initial (imported) instrument parameters in parenthesis (solid line) and the user refined parameters (dashed line).



Continuing with the next diffraction pattern

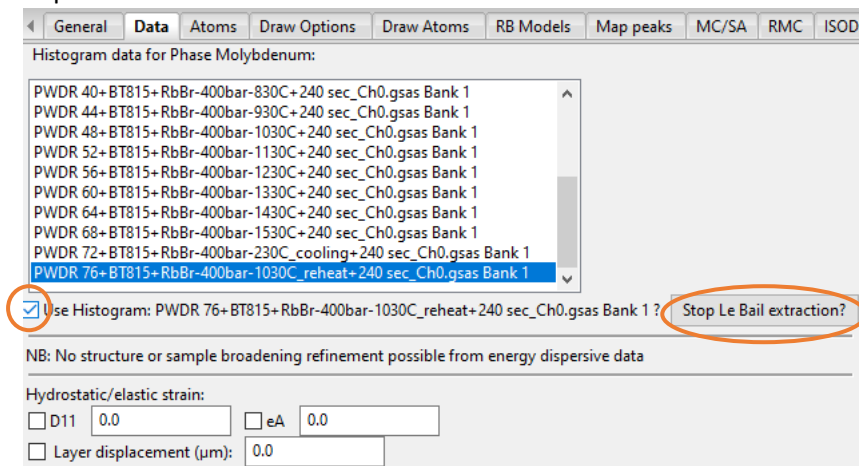
Most of the time, you will have collected diffraction patterns of the sample over a pressure and temperature range. It does not make sense to start each refinement from scratch in a new project file. That is why GSAS-II allows you to import additional data files into the same project (e.g. saved with the experiment run number and sample in the filename).

Here is an example:

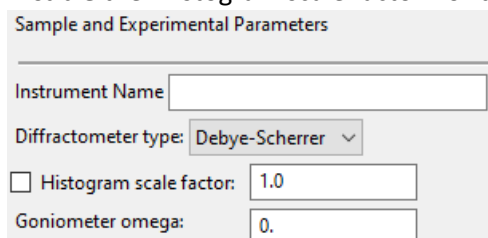


Steps for quick refinement of multiple files:

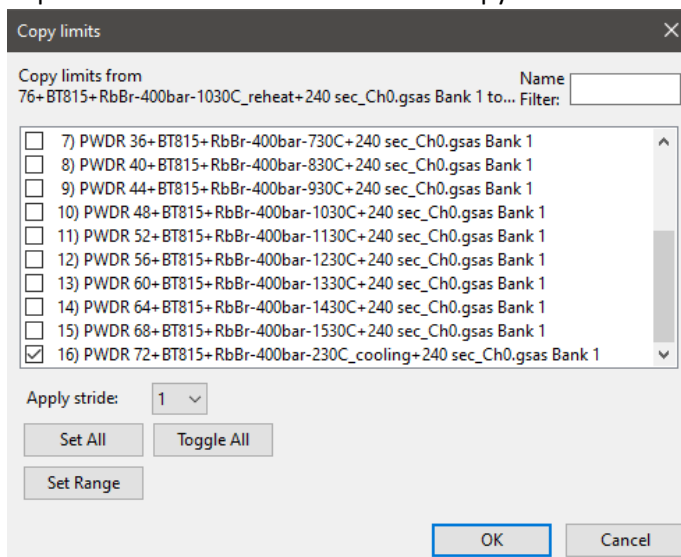
1. Import a new powder data file as described earlier.
2. For **each phase**, **disable** Le Bail extraction for the previous file, and **enable** it for the newly imported file.



3. **Disable** the 'Histogram scale factor' for the new data entry



4. Go to the previous successful refined entry and click on 'Limits'. Copy the limits to the newly imported data file via 'Edit Limits' → Copy



Check the profile to see if no peaks have shifted (partially) in the excluded regions. Update the limits of the excluded regions, if necessary.

5. Also **copy** the 'Background' and 'Instrument Parameters' (optionally) to the new data entry.
6. **Make sure nothing is left to refine in the old data entries.**
7. Set the 'C' parameter to zero (0.0), if previously refined.
8. For the new data entry, now enable 'Background' and 'B' parameter. The unit cell parameters should also remain enabled in the first refinement.
→ Start refinement until the shift is small.

9. Disable the Background, and optionally enable the 'C' parameter. ('B' and unit cell params remain enabled). → Refine again.
10. Disable 'C' and finish refinement with the cell params and 'B' until the shift is zero (0.000). The fit should be excellent at this point.

These appear to be a lot of steps, but in fact they only take a few minutes and the new refinement of a diffraction pattern at slightly different pressure and/or temperature will converge quickly to a new global minimum.

Before you repeat these steps for the next imported powder data file, you should know this:

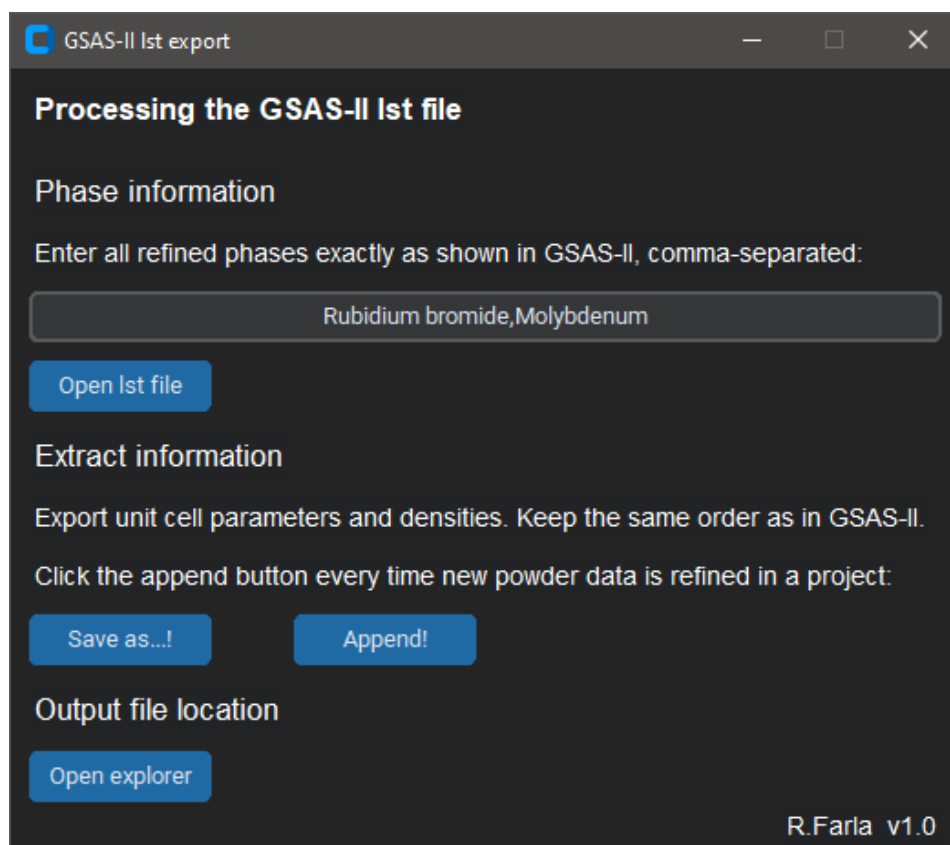
Final steps

The useful data are exported into a *.lst file (as you may have noticed in the many dialogue windows already). There, for each phase, you can find the resulting lattice parameter, unit cell volume and the standard errors, as well as the calculated densities. See page 14.

WARNING: The lst file will be overwritten each time, because it takes the name of the project.

To solve this particular issue, I have developed a python software tool to extract the information from the lst file, carried out after each refinement of a powder pattern. The software is called **GSASlstExtract**, and can be downloaded from the beamline website software page.

The app looks like this:



Example of refinement results in the lst file:

Number of function calls: 28 No. of observations: 1880 No. of parameters: 2 User rejected: 0 Sp. gp. extinct: 0
Refinement time = 1.677s, 0.152s/cycle, for 11 cycles
wR = 31.16%, chi**2 = 34714.5, GOF = 4.30

Parameters generated by constraints

name : 0::A0 1::A0
value : 0.05871 0.06491
sig : 0.00000 0.00001

Phases:

Result for phase: **Cesium chloride**

=====

Reciprocal metric tensor:

names : A11 A22 A33 A12 A13 A23
values: 0.058712030 0.058712030 0.058712030 0.000000000 0.000000000 0.000000000
esds : 0.000004691

New unit cell:

names : a b c alpha beta gamma Volume
values: **4.127019** 4.127019 4.127019 90.0000 90.0000 90.0000 **70.293**
esds : **0.000165** **0.008**

Atoms:

name x y z frac Uiso U11 U22 U33 U12 U13 U23

Cs1 Cs+1:

values: 0.00000 0.00000 0.00000 1.000 0.01000

sig :

Cl1 Cl-1:

values: 0.50000 0.50000 0.50000 1.000 0.01000

sig :

Density: 3.9772 g/cm3**

Result for phase: **Platinum**

Reciprocal metric tensor:

names : A11 A22 A33 A12 A13 A23
 values: 0.064907749 0.064907749 0.064907749 0.000000000 0.000000000 0.000000000
 esds : 0.000007198

New unit cell:

names : a b c alpha beta gamma Volume
 values: **3.925109** 3.925109 3.925109 90.0000 90.0000 90.0000 **60.472**
 esds : **0.000218** **0.010**

Atoms:

name x y z frac Uiso U11 U22 U33 U12 U13 U23

Pt1 Pt:
 values: 0.00000 0.00000 0.00000 1.000 0.01000
 sig :

Density: 21.4284 g/cm3**

Example of GSASlstExtract output file:

a	a_eds	volume	volume_eds	density	of_all_phases					
4.17407	0.000384	72.724	0.02	4.8492	3.134156	0.000174	30.787	0.005	10.3494	
4.235674	0.000197	75.992	0.011	4.6407	3.142147	9.80E-05	31.023	0.003	10.2707	
4.235604	0.000212	75.988	0.011	4.6409	3.142827	0.000102	31.043	0.003	10.264	