Version 2.0
04.12.2024

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:

2θ calculator for LaB6 using two detectors

Enter approximate 2θ (°)

Detector 1 (Ch1): 3

Detector 2 (Ch0): 5

Enter peak detection parameters

Minimum background level (counts): 80

Minimum peak to peak distance (eV): 20

Exclude incorrectly starred (*) peaks from left to right; count from zero (comma delimited)

Detector 1 (Ch1): ,10,12,14,15,16

Detector 2 (Ch0): ,13,16,18,24,26

Assign hkl to the starred peaks (comma delimited)

Detector 1 (no entries means ignore detector)

100,110,210,211

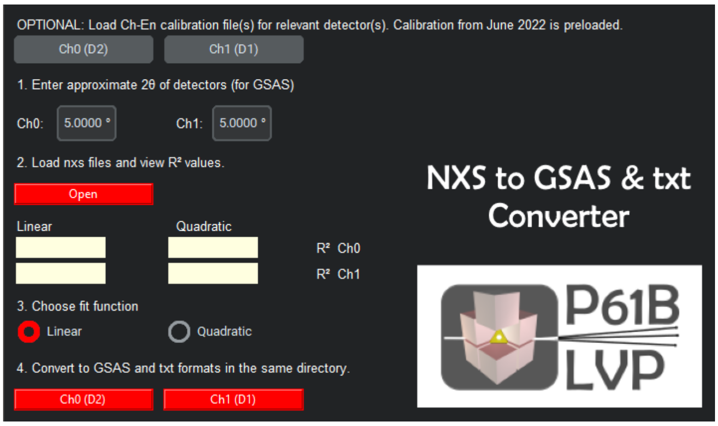
Detector 2 (no entries means ignore detector)

110,111,200,210,211,220,221,310,311,320,321,410,411,421

Detector 1 (°): 3.03385, 0.00368

Detector 2 (°): 4.99576, 0.00577

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



OPTIONAL: Load Ch-En calibration file(s) for relevant detector(s). Calibration from June 2022 is preloaded.

1. Enter approximate 2θ of detectors (for GSAS)

Ch0: 5.0000 °   Ch1: 5.0000 °

2. Load nxs files and view R^2 values.

3. Choose fit function

● Linear   ○ Quadratic

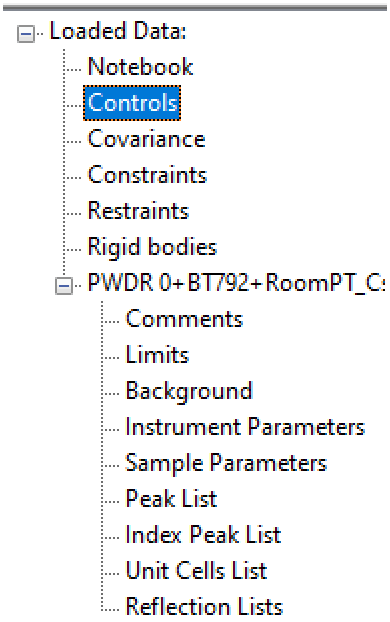
4. Convert to GSAS and txt formats in the same directory.

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

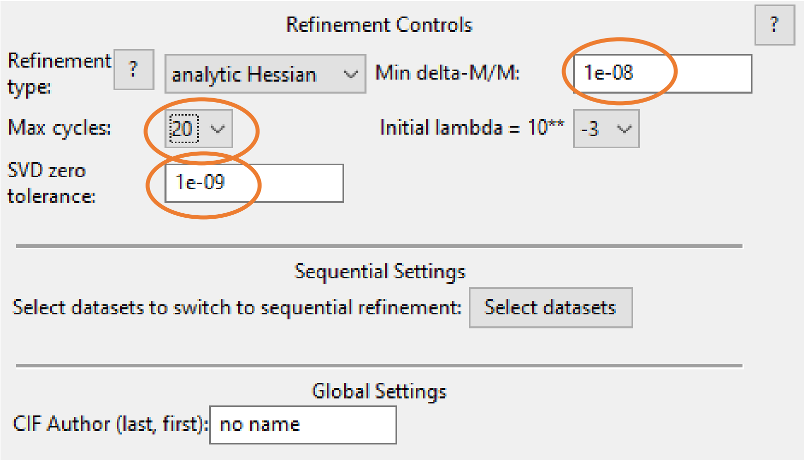
Start-up GSAS-II. You will be presented with two blank windows.

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 **instrument parameter file**. To open your first powder data file, please use the **dummy file** provided on the beamline website (software page) or ask the beamline staff.
3. The data is then loaded in the list, showing the file name. There are a number of entries for each data file you import:



- Loaded Data:
  - 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

4. Go to ‘Control’ first and change the default values to the following, because refinements converge very slowly:



Refinement Controls

Refinement type: analytic Hessian

Min delta-M/M: 1e-08

Max cycles: 20

Initial lambda = 10** -3

SVD zero tolerance: 1e-09

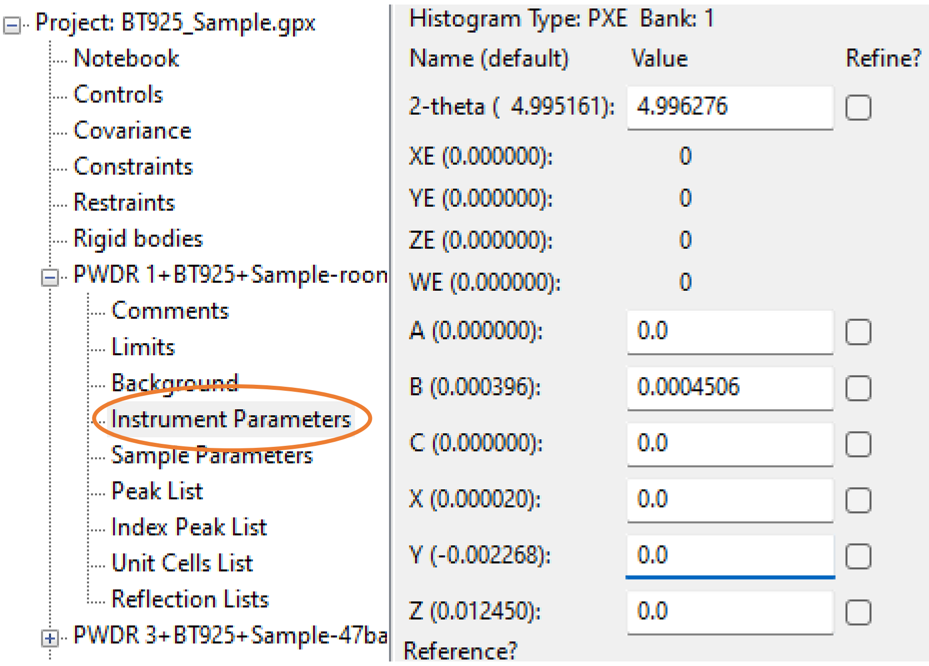
Sequential Settings

Select datasets to switch to sequential refinement: Select datasets

Global Settings

CIF Author (last, first): no name

5. Inspect the Instrument Parameters section. It should look like this in the latest version of GSAS (v. 3e6d4c, #5801 at the time of writing):



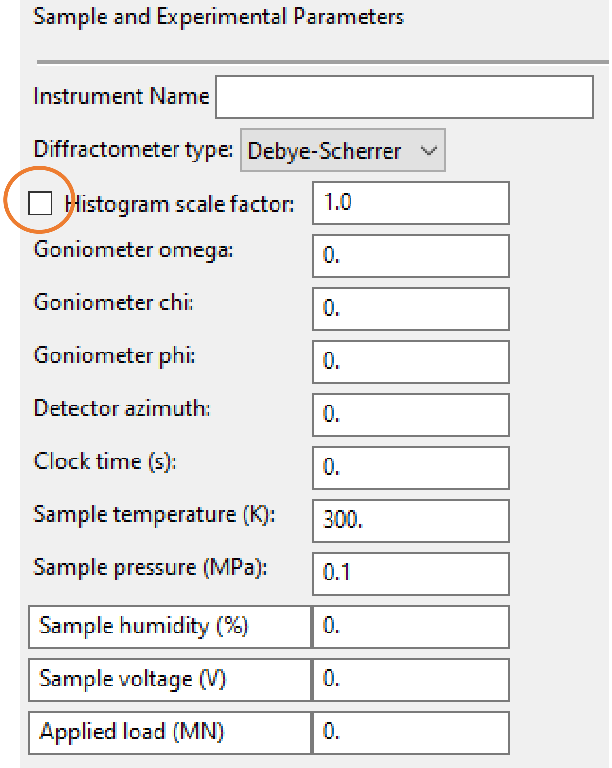
Histogram Type: PXE Bank: 1

Name (default)	Value	Refine?
2-theta (4.995161):	4.996276	☐
XE (0.000000):	0	
YE (0.000000):	0	
ZE (0.000000):	0	
WE (0.000000):	0	
A (0.000000):	0.0	☐
B (0.000396):	0.0004506	☐
C (0.000000):	0.0	☐
X (0.000020):	0.0	☐
Y (-0.002268):	0.0	☐
Z (0.012450):	0.0	☐

Reference?

- **a.** **Enter the 2θ value from the LaB62theta app**, or refine the diffraction pattern for LaB6 here to try to optimize the detector angle.
- b. Note: The parameters **XE, YE, ZE, and WE can be ignored** and are not used in the refinement. They relate to other data types that are imported in channel format and still need to be converted to energy. You can force them to be zero if you reload the instrument parameter file (from the BL website).
- c. The parameters A, B, and C are the Gaussian peak shape terms. **Typically, only B is used, and highly recommended.**
- **d.** The parameters X, Y, and Z are the Lorentzian peak shape terms. Typically, they are not used (or only Y in some cases). That’s because as you will learn later on, we want to include micro-strain for each phase in the refinement, which uses the Lorentzian component. **You should not use Y (X, Z) and micro-strain at the same time!**

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.



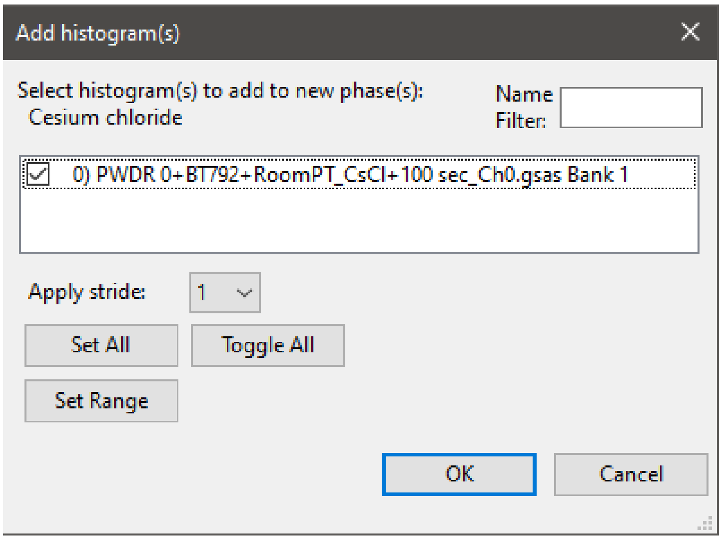
Sample and Experimental Parameters

Instrument Name:
Diffractometer type: Debye-Scherrer
☐ Histogram scale factor: 1.0
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.

7. Add the phases you want to include in the fit.

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 histogram(s)

Select histogram(s) to add to new phase(s):
Cesium chloride

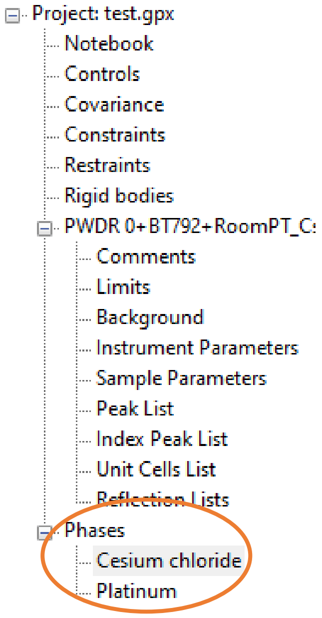
Name Filter:

☑ 0) PWDR 0+BT792+RoomPT_CsCl+100 sec_Ch0.gsas Bank 1

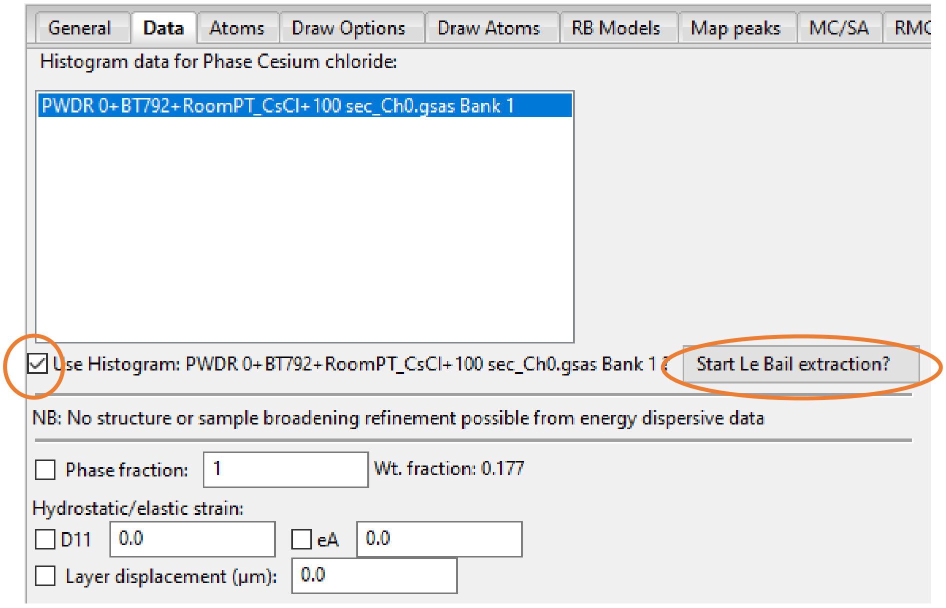
Apply stride: 1

Add the phase to the appropriate data file.

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



9. For **all imported data files**, in each Phase entry (Data tab) first **disable** the Histogram checkbox **for each imported pattern**, then **enable** the use of the histogram **for the file you want to refine** **AND** **start the Le Bail extraction**.



Histogram data for Phase Cesium chloride:

PWDR 0+BT792+RoomPT_CsCl+100 sec_Ch0.gsas Bank 1

☑ Use Histogram: PWDR 0+BT792+RoomPT_CsCl+100 sec_Ch0.gsas Bank 1

NB: No structure or sample broadening refinement possible from energy dispersive data

☐ Phase fraction: 1 Wt. fraction: 0.177

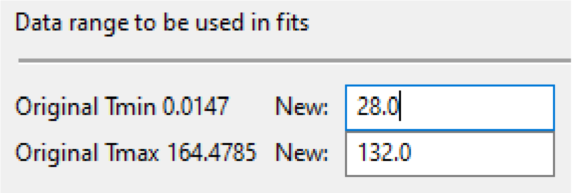
Hydrostatic/elastic strain:

☐ D11 0.0 ☐ eA 0.0

☐ Layer displacement (μm): 0.0

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

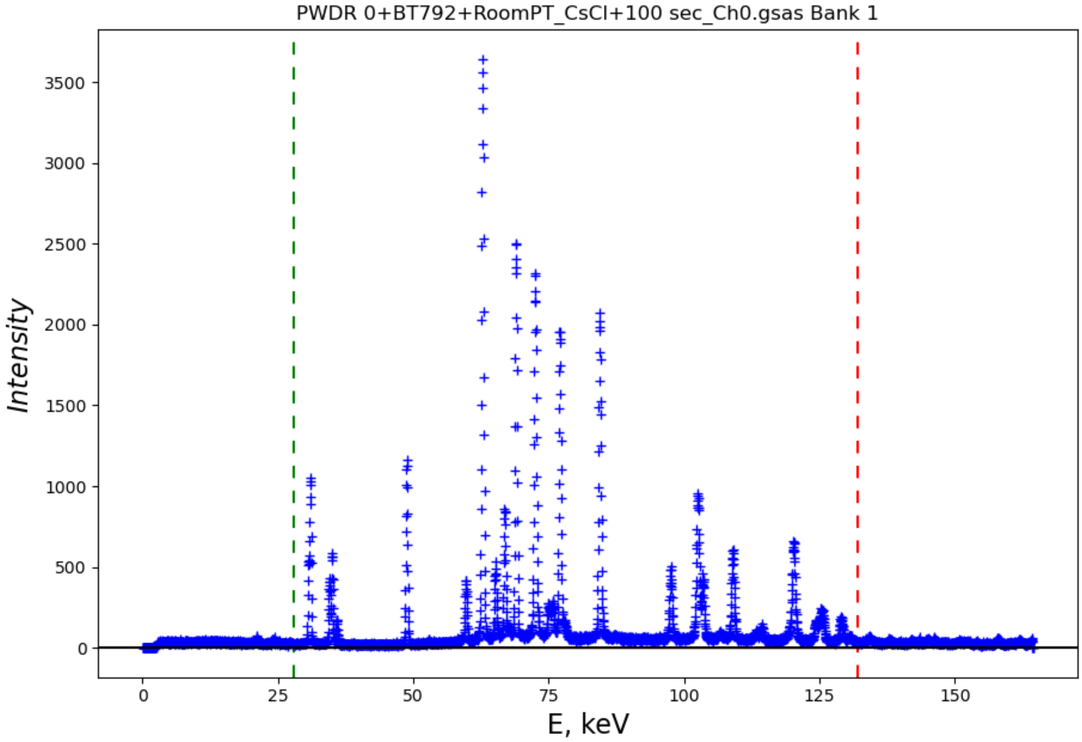
10. Next, go to ‘Limits’ and **set the appropriate global range** (in keV) where the sample peaks are visible. Do not try to include very weak peaks that are just above the noise, e.g. in the highest energy range.



Data range to be used in fits

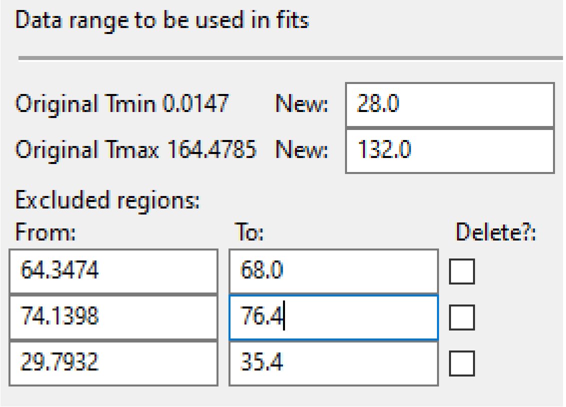
Original Tmin 0.0147 New: 28.0

Original Tmax 164.4785 New: 132.0



11. 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 excluded region



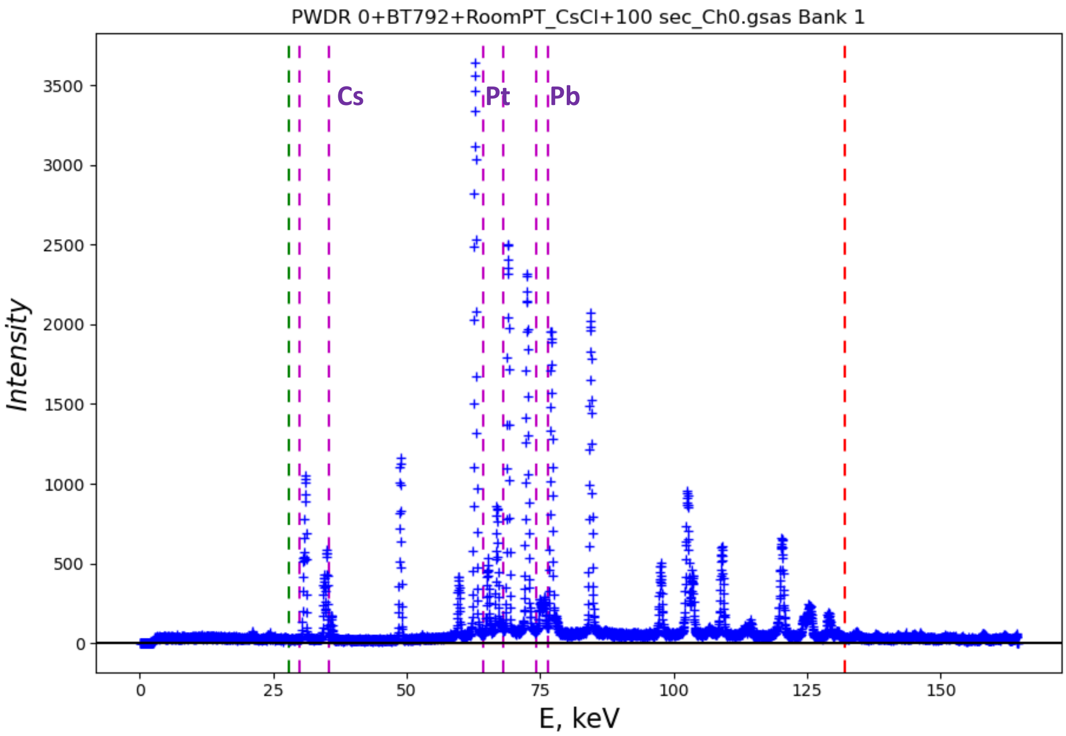
Data range to be used in fits

Original Tmin 0.0147 New: 28.0

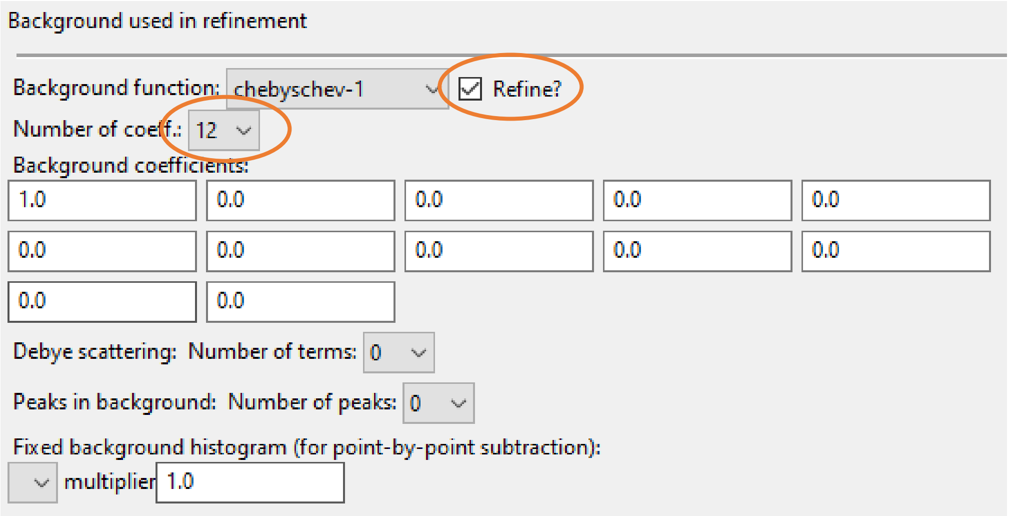
Original Tmax 164.4785 New: 132.0

Excluded regions:

From:	To:	Delete?:
64.3474	68.0	☐
74.1398	76.4	☐
29.7932	35.4	☐



12. Finally, add refinable background parameters to the profile. It may be desirable to manually add points on the profile to force a good fit, but this is **not recommended**. Use the built-in function, for as many as **12 coefficients** for good results.



Background used in refinement

Background function: chebyschev-1 ☑ Refine?

Number of coeff.: 12

Background coefficients:

1.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0
0.0	0.0			

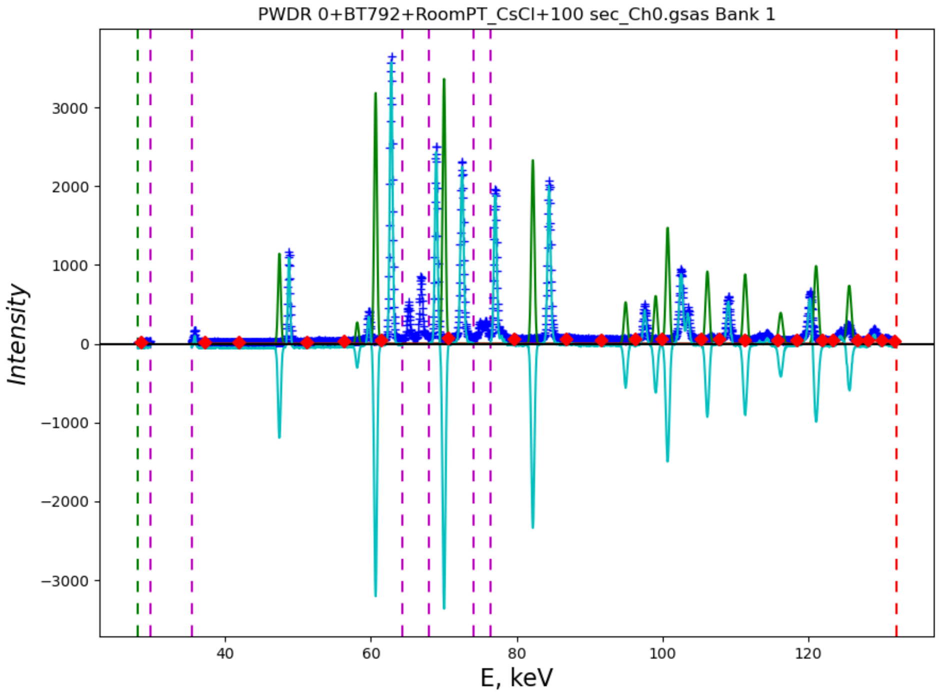
Debye scattering: Number of terms: 0

Peaks in background: Number of peaks: 0

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

multiplier 1.0

a. Adding points (not recommended!):



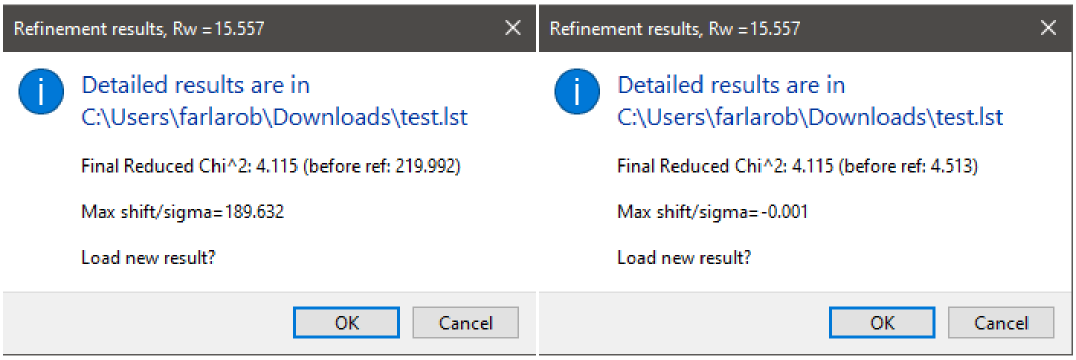
Background refinement

1. The first thing you need is a good background fit. Do **not** yet enable refinement of the B parameter (set a fixed value of e.g. 0.0005). Otherwise, especially if the unit cell parameters of the phases are not 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** (i.e. start) a Le Bail extraction for the phases. Keep extraction for all other files (if more than 1 are imported) **off**.
    b. **Enable** 'Refine unit cell' for all phases, and if known, enter the expected unit cell parameters/volumes in advance. Set the min and max limits carefully.
    c. **Add excluded regions** where unknown/unwanted peaks show:
        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!
    d. **Enable** 'Background refinement' for a number of coefficients (e.g. 12).
    e. **Make sure all parameters in 'Instrument Parameters' are disabled!** These parameters affect the way the background is fitted.
    f. **[After a successful background fit**: **Enable the 'B' peak shape parameter** in 'Instrument Parameters'. You can also do this in later refinement cycles]
2. Hit 'Ctrl + R' and start a refinement. You might repeat it until the shift is near zero.
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 parameters from future refinements.

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 until you see no more shift (0.000, or < 0.010). That means the refinement should have found a global minimum.


Refinement results, Rw = 15.557

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

Final Reduced Chi^2: 4.115 (before ref: 219.992)

Max shift/sigma= 189.632

Load new result?

Refinement results, Rw = 15.557

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

Final Reduced Chi^2: 4.115 (before ref: 4.513)

Max shift/sigma= -0.001

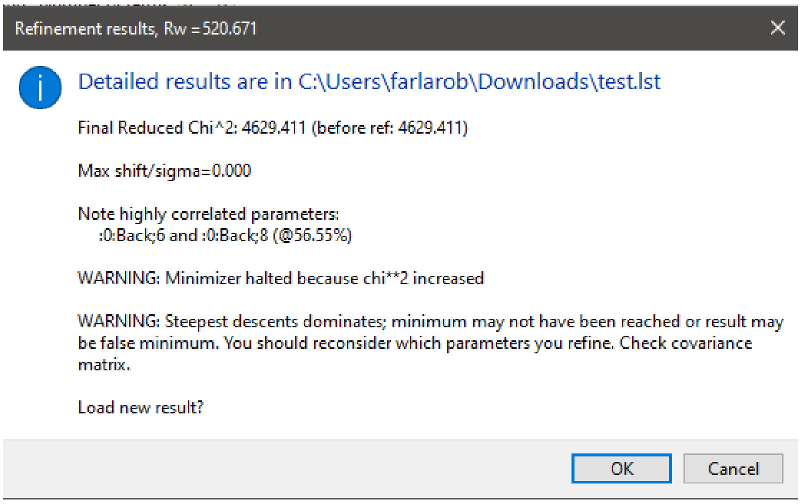
Load new result?

b. **IMPORTANT!** Sometimes the pop up shows no shift, but many **warnings** (see below). It could be the refinement is stuck in a local minimum, cannot approach a minimum and/or parameters are dropped. Try to fix this. There are some options:

   i. **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.

   ii. Try to **refine only the unit cells of the phases**, or 1 phase at a time.

   iii. **Temporarily, reinclude the background** into the refinement and repeat the steps above.



Refinement results, Rw =520.671

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

Final Reduced Chi^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%)

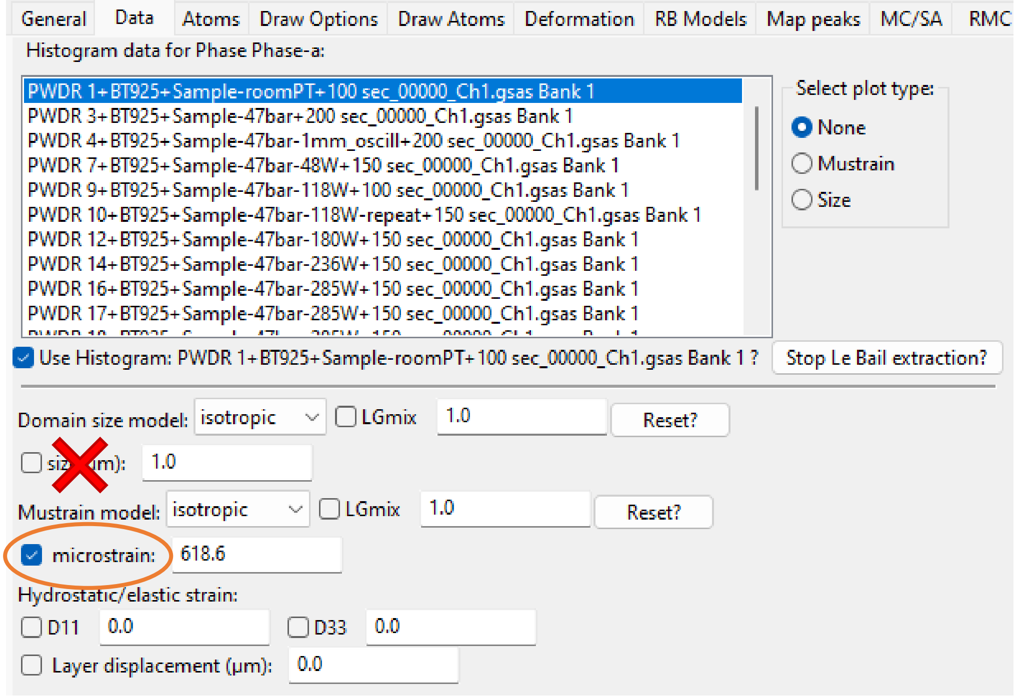
WARNING: Minimizer halted because chi**2 increased

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?

   iv. Other times, if you're sure you already have the best possible refinement, then just ignore the above warnings.

2. Next, **enable** the **micro-strain parameter** in the **Data tab** for each phase:
(note that you should also keep using "**Refine unit cell**" in the General tab, and **histogram** and **Le Bail extraction** in the Data tab)



Histogram data for Phase Phase-a:

PWDR 1+BT925+Sample-roomPT+100 sec_00000_Ch1.gsas Bank 1
PWDR 3+BT925+Sample-47bar+200 sec_00000_Ch1.gsas Bank 1
PWDR 4+BT925+Sample-47bar-1mm_oscill+200 sec_00000_Ch1.gsas Bank 1
PWDR 7+BT925+Sample-47bar-48W+150 sec_00000_Ch1.gsas Bank 1
PWDR 9+BT925+Sample-47bar-118W+100 sec_00000_Ch1.gsas Bank 1
PWDR 10+BT925+Sample-47bar-118W-repeat+150 sec_00000_Ch1.gsas Bank 1
PWDR 12+BT925+Sample-47bar-180W+150 sec_00000_Ch1.gsas Bank 1
PWDR 14+BT925+Sample-47bar-236W+150 sec_00000_Ch1.gsas Bank 1
PWDR 16+BT925+Sample-47bar-285W+150 sec_00000_Ch1.gsas Bank 1
PWDR 17+BT925+Sample-47bar-285W+150 sec_00000_Ch1.gsas Bank 1

Select plot type:
● None
○ Mustrain
○ Size

☑ Use Histogram: PWDR 1+BT925+Sample-roomPT+100 sec_00000_Ch1.gsas Bank 1 ?

Domain size model: isotropic ☐ LGmix 1.0

☐ size (μm): 1.0

Mustrain model: isotropic ☐ LGmix 1.0

☑ microstrain: 618.6

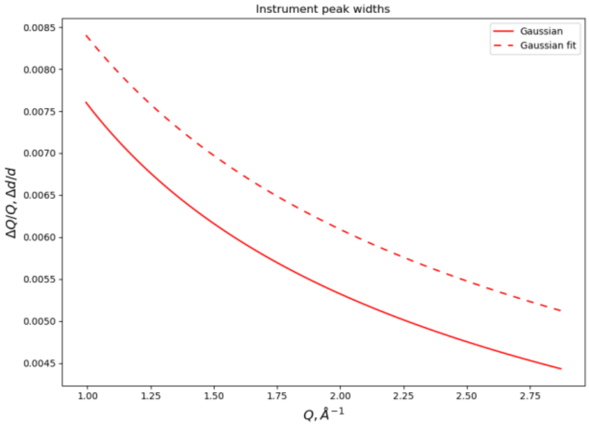
Hydrostatic/elastic strain:
☐ D11 0.0 ☐ D33 0.0
☐ Layer displacement (μm): 0.0

2. cont… When refining the micro-strain (as the last step), make sure the value is always **positive**! If it turns **negative** after a refinement, reset it to 1000 and do not use it.

Note, **never** include the **crystallite size parameter** in the refinement. ED-XRD data is **not** of high-quality that this can be used reliably to extract the grain size of the sample/phase!

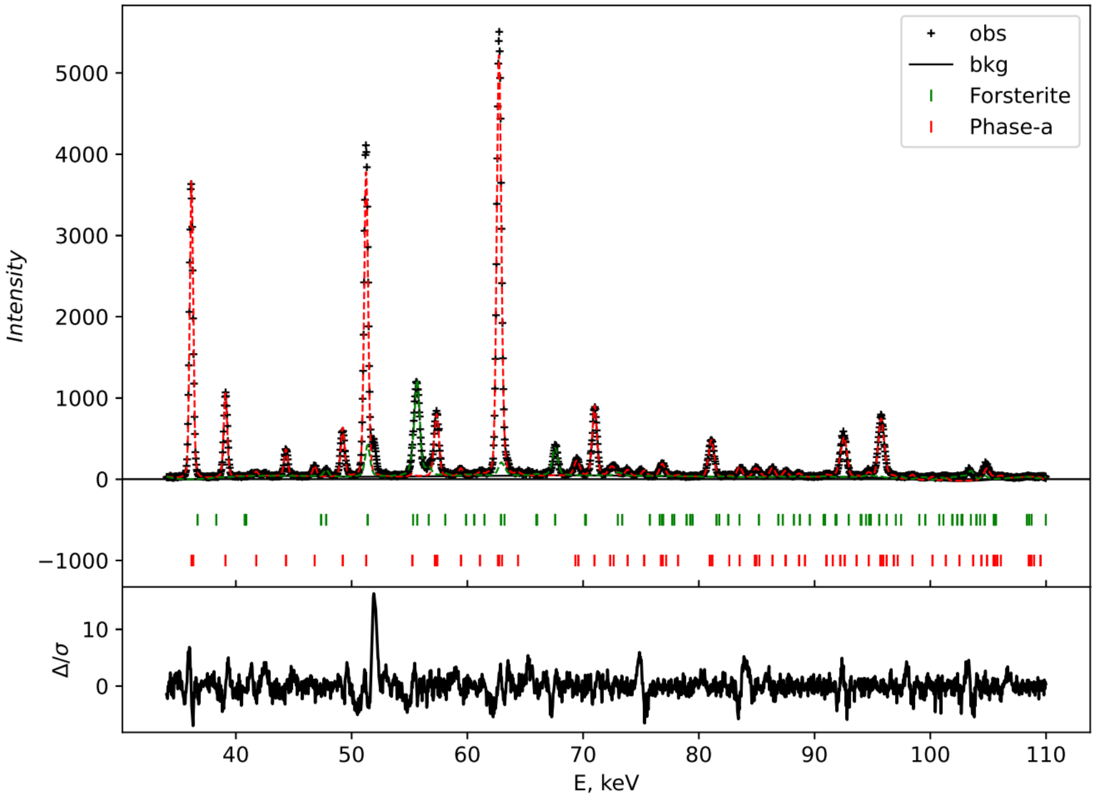
Note, never refine the global Lorentzian parameters (X,Y,Z) with micro-strain. They conflict!

3. FYI. The plot below shows the initial (imported) instrument parameters in parenthesis (solid line) and the user refined parameters (dashed line). This is not very informative otherwise.



The final result

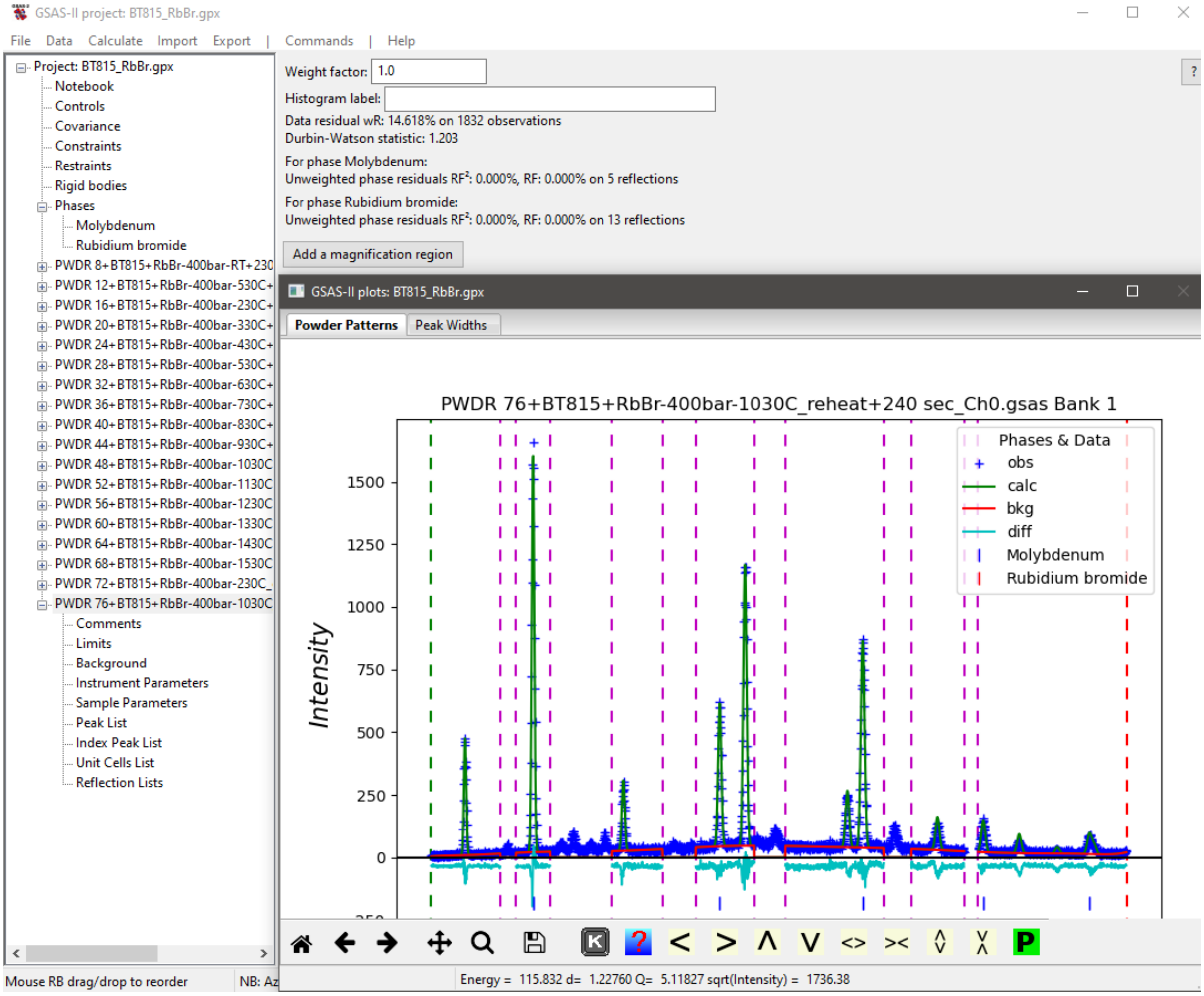
Finally, the results are displayed in the graph (Tab: Powder patterns) and can be exported for your manuscript (green P button). You can also show the phase deconvolution profiles. Click on the data entry in the list starting with PWDR. Then in the menu “Commands” click on **Phase partial config**. Allow the calculation and result is shown in the graph. See example below for phase A and forsterite:



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:

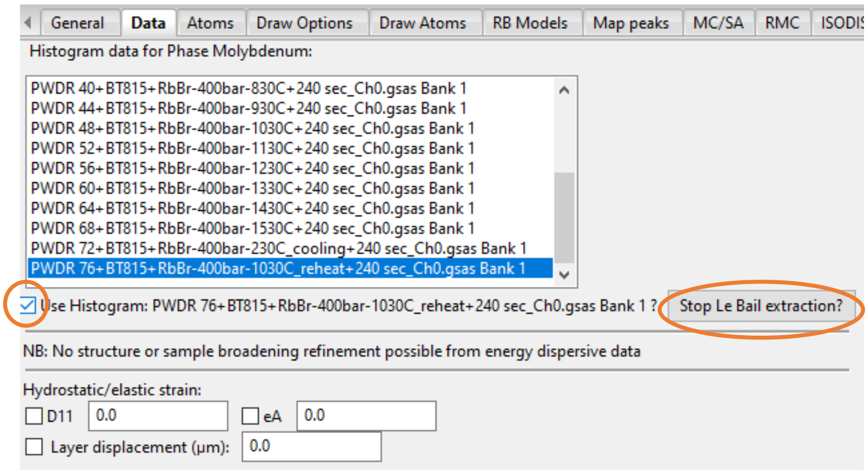


Weight factor: 1.0
Histogram label:
Data residual wR: 14.618% on 1832 observations
Durbin-Watson statistic: 1.203
For phase Molybdenum:
Unweighted phase residuals RF^2: 0.000%, RF: 0.000% on 5 reflections
For phase Rubidium bromide:
Unweighted phase residuals RF^2: 0.000%, RF: 0.000% on 13 reflections

Energy = 115.832 d= 1.22760 Q= 5.11827 sqrt(Intensity) = 1736.38

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.



Histogram data for Phase Molybdenum:

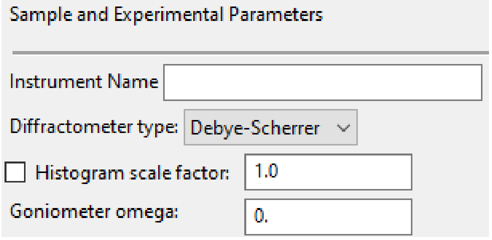
PWDR 40+BT815+RbBr-400bar-830C+240 sec_Ch0.gsas Bank 1
PWDR 44+BT815+RbBr-400bar-930C+240 sec_Ch0.gsas Bank 1
PWDR 48+BT815+RbBr-400bar-1030C+240 sec_Ch0.gsas Bank 1
PWDR 52+BT815+RbBr-400bar-1130C+240 sec_Ch0.gsas Bank 1
PWDR 56+BT815+RbBr-400bar-1230C+240 sec_Ch0.gsas Bank 1
PWDR 60+BT815+RbBr-400bar-1330C+240 sec_Ch0.gsas Bank 1
PWDR 64+BT815+RbBr-400bar-1430C+240 sec_Ch0.gsas Bank 1
PWDR 68+BT815+RbBr-400bar-1530C+240 sec_Ch0.gsas Bank 1
PWDR 72+BT815+RbBr-400bar-230C_cooling+240 sec_Ch0.gsas Bank 1
PWDR 76+BT815+RbBr-400bar-1030C_reheat+240 sec_Ch0.gsas Bank 1

☑ Use Histogram: PWDR 76+BT815+RbBr-400bar-1030C_reheat+240 sec_Ch0.gsas Bank 1 ? Stop Le Bail extraction?

NB: No structure or sample broadening refinement possible from energy dispersive data

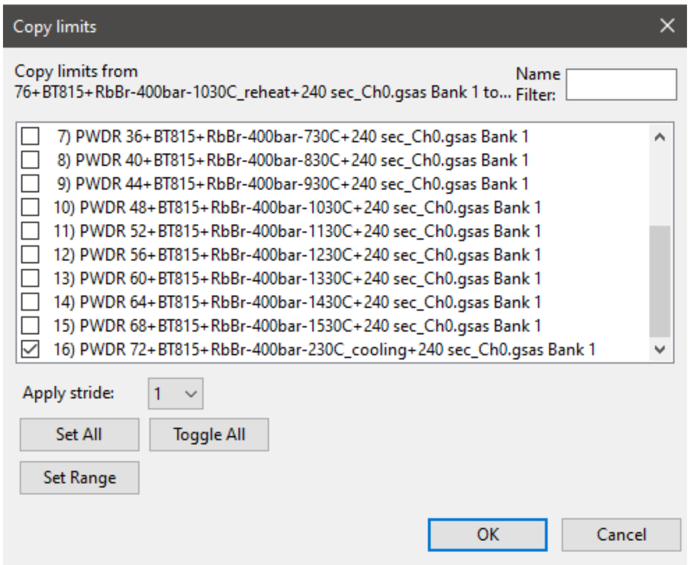
Hydrostatic/elastic strain:
☐ D11 0.0 ☐ eA 0.0
☐ Layer displacement (μm): 0.0

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


Sample and Experimental Parameters

Instrument Name
Diffractometer type: Debye-Scherrer
☐ Histogram scale factor: 1.0
Goniometer omega: 0.

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


Copy limits

Copy limits from 76+BT815+RbBr-400bar-1030C_reheat+240 sec_Ch0.gsas Bank 1 to...
Name Filter:

☐ 7) PWDR 36+BT815+RbBr-400bar-730C+240 sec_Ch0.gsas Bank 1
☐ 8) PWDR 40+BT815+RbBr-400bar-830C+240 sec_Ch0.gsas Bank 1
☐ 9) PWDR 44+BT815+RbBr-400bar-930C+240 sec_Ch0.gsas Bank 1
☐ 10) PWDR 48+BT815+RbBr-400bar-1030C+240 sec_Ch0.gsas Bank 1
☐ 11) PWDR 52+BT815+RbBr-400bar-1130C+240 sec_Ch0.gsas Bank 1
☐ 12) PWDR 56+BT815+RbBr-400bar-1230C+240 sec_Ch0.gsas Bank 1
☐ 13) PWDR 60+BT815+RbBr-400bar-1330C+240 sec_Ch0.gsas Bank 1
☐ 14) PWDR 64+BT815+RbBr-400bar-1430C+240 sec_Ch0.gsas Bank 1
☐ 15) PWDR 68+BT815+RbBr-400bar-1530C+240 sec_Ch0.gsas Bank 1
☑ 16) PWDR 72+BT815+RbBr-400bar-230C_cooling+240 sec_Ch0.gsas Bank 1

Apply stride: 1

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. 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.

8. Disable the Background and finish refinement with the cell params, ‘B’ and optionally micro-strain, 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.

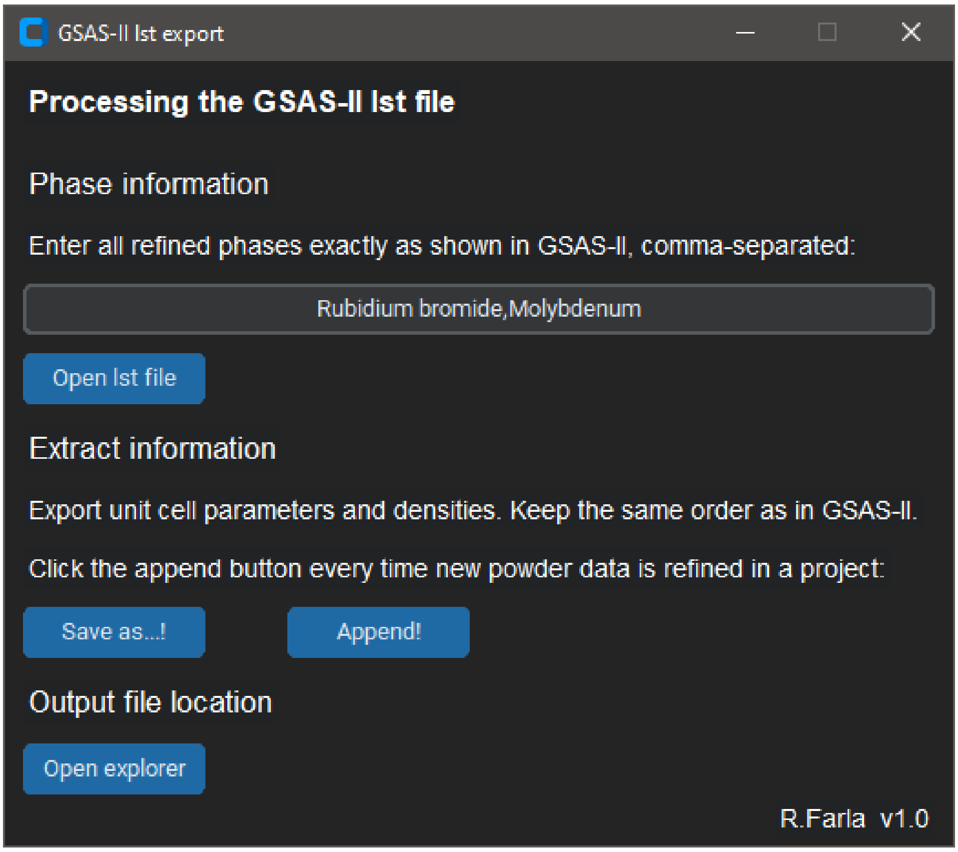
Before you repeat these steps for the next imported powder data file, you should know this:

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:



Processing the GSAS-II lst file

Phase information

Enter all refined phases exactly as shown in GSAS-II, comma-separated:

Rubidium bromide,Molybdenum

Extract information

Export unit cell parameters and densities. Keep the same order as in GSAS-II.

Click the append button every time new powder data is refined in a project:

Output file location

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/cm**3
```

```
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/cm**3
```

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