# GSAS/EXPGUI Alumina example (Intro)

## What's this all about?

The goal of Rietveld analysis is to fit a structural model ("crystal structure") to powder diffraction data. To do this requires determining the structural parameters [unit cell, atom positions and displacement (thermal) parameters, etc.] for all crystalline phases present, as well as a variety of instrumental and sample parameters that describe the experimental and sample conditions: scale factors, peak broadening, the background, preferred orientation, etc. In most cases Rietveld analysis is performed to determine the structural parameters, but increasingly, the method is also used to determine relative amounts of the crystallographic phases, the amount and type of peak broadening, the preferred orientation, or similar types of sample characterization.

This exercise provides a tutorial example of how to use the GSAS software package with the EXPGUI interface to perform Rietveld analysis. The material chosen for this exercise, corundum (aka alumina, sapphire or ruby), has a simple structure, so the starting coordinates have been distorted so that there is an improvement obtained by performing the fit. Likewise, this sample exhibited virtually no sample-related broadening, so the instrumental peak profile was altered so that the peak profile terms would not agree with the data, again so that the exercise would demonstrate the sorts of steps needed for typical Rietveld refinements. The tutorial consists of 11 web pages, each has a series of related steps. There are also editorial comments, that explain a point further or explain how these steps might be applied differently in another case. *These comments are in specified in italic type*.

Rietveld analysis works using non-linear least-squares fitting to optimize (refine) parameters. This means that we must start with approximate values for all parameters that will be fit. We then allow the software to optimize a small subset of the parameters -- a minimal number of parameters that must be fit before any progress can be made. Slowly, additional parameters are selected to be refined, until all parameters in the model (if the data support that) are refined. Despite the simplicity of the material, this exercise demonstrates many of the procedures needed for more complex materials.

EXPGUI and GSAS run on Windows, Linux and IRIX (Silicon Graphics computers). The example figures show in this tutorial were generated in Unix, but virtually all GSAS and EXPGUI operation is identical between Unix and Windows. Note also that the appearance of EXPGUI changes slightly as new features are added. The screen images do not exactly match the current version of EXPGUI.

## Getting Started

To perform this tutorial on your own computer, you will need to have GSAS and EXPGUI loaded on your computer (see installation links on the EXPGUI home page). You will also need three files that are referenced in the following web pages:

- The Raw data: al2o3001.gsa
- The instrument parameter file: bt1demo.ins
- A CIF file with unit cell and atomic parameters: alumina.cif

These three files can be downloaded as a single .ZIP file, or accessed via anonymous ftp from site ftp.ncnr.nist.gov in directory `/pub/cryst/gsas/tutorials`

> **Note:** *While it is possible to have your working GSAS files (i.e. the .EXP file, etc.) in a separate directory from the raw data file(s), I discourage this practice, as it then becomes quite difficult to later copy or move the .EXP file from one directory or computer to another. For this reason, I suggest copying these files into the directory where you will keep your GSAS files.*

## Tutorial Outline



## Sample files

- al2o3001.gsa -- the alumina neutron diffraction data
- bt1demo.ins -- the instrument parameter file
- alumina.cif -- a CIF file with unit cell and atomic parameters:

## Acknowledgments

GSAS is written by Allen C. Larson and Robert B. Von Dreele, MS-H805, Los Alamos National Laboratory, Los Alamos, NM 87545. Problems, questions or kudos concerning GSAS should be sent to Robert B. Von Dreele at vondreele@anl.gov



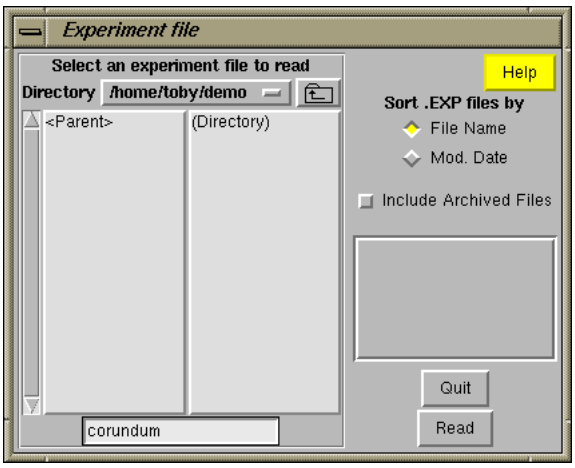
EXPGUI is written by Brian H. Toby of the NIST Center for Neutron Research, Brian.Toby@NIST.GOV



# GSAS/EXPGUI Alumina tutorial (part 1)
# Creating an Experiment File

For this exercise we will use the EXPGUI interface to access the features of GSAS. The method used to start EXPGUI depends on what type of computer you are using. On Windows, EXPGUI is typically started by clicking on the appropriate desktop icon, or by selecting an entry in the START menu. In Unix, it is typically started by typing the command expgui in a Unix terminal window (it is also possible to create icons & menu entries in some versions of Unix).

In all platforms, once EXPGUI has been started, a GSAS Experiment (.EXP) file must be selected. The window shown to the right is opened when EXPGUI is started, where file to be used is selected. The .EXP file is the heart of a GSAS project. While other files are used by GSAS programs, all structural information and control parameters are contained within this file.




The first step in this tutorial is to select the directory where the al2o3001.gsa, bt1demo.ins and alumina.cif files were placed. Do this by clicking on the "Directory" button at the top of the window, or by navigating up and down the directory tree by clicking on the "<Parent>" or individual directory names. Clicking on the folder icon with an arrow on it (to the right of the directory button) has the same effect as the "<Parent>" entry.

Once the correct directory has been located, the next step is to create a new, empty, .EXP file. To do this, the file name we wish to use (corundum) is typed into the bottom box of the file selection window. Note that the capitalization you use here does not matter and .EXP is added by default. After the name has been entered press the "Read" button or press the keyboard "Enter" key.

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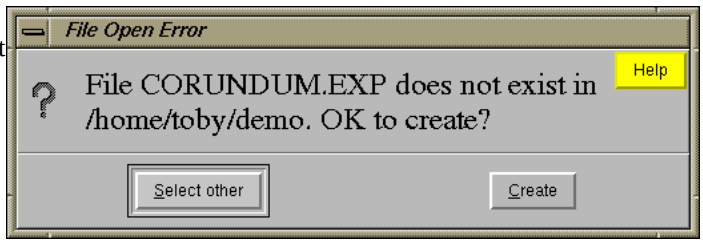
To make sure that you really intend to create a new Experiment file, rather than the more common task of opening a previous file, the warning message to the right is displayed and you must click on the "Create" button to continue.

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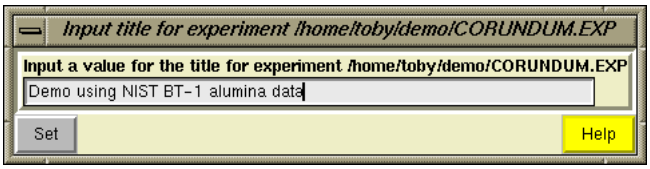
At this point, you are prompted to provide an overall title for the experiment file. Enter anything you would like (preferably something that will remind you what you were doing a year from now, when you try to figure out what this strange file was for. When you have finished entering information, press the "Set" button.

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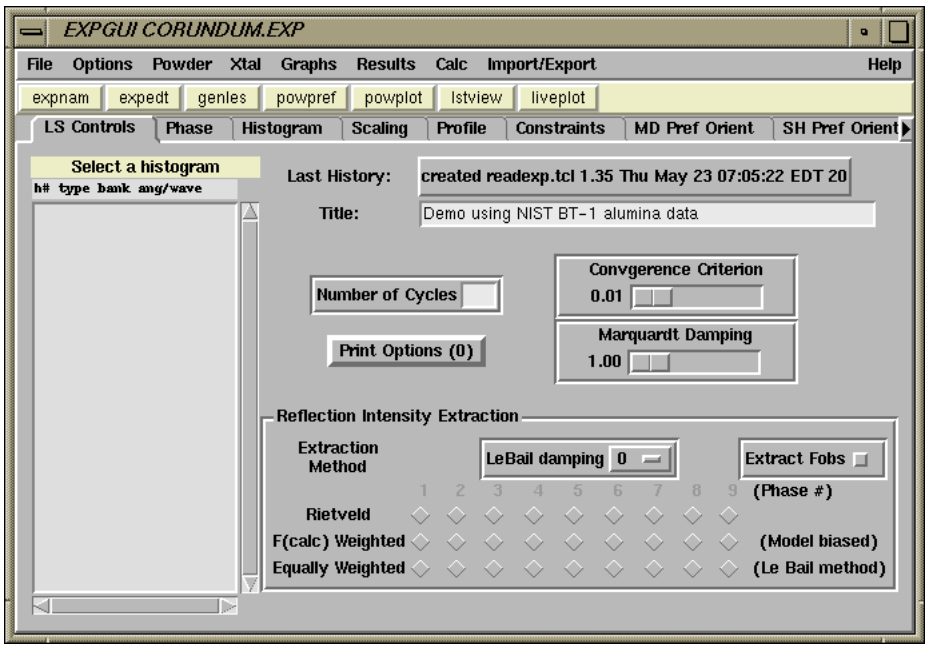
At this point, the Experiment file, CORUNDUM.EXP, has been created and EXPGUI displays what (little) information can be found in this file, as is seen below:




Note that the title is displayed near the top of the window in a "edit" box -- this title can be changed simply by typing into the box. Above the title

is the last "history record." GSAS records a history record each time a program is run that modifies the .EXP file and this information is displayed here. In the next step we will start adding information to this experiment file.

# GSAS/EXPGUI Alumina tutorial (part 2)
# Adding a phase

*When a GSAS experiment file is first created, a fair amount of information must be supplied before the refinement of parameters can be started. At a minimum, a crystallographic phase must be defined, a set of diffraction data must be loaded and a starting values for experimental parameters must be defined. Fortunately, this can be a fairly simple operation with GSAS and EXPGUI.*

This page shows how a crystallographic phase is specified in EXPGUI. For a mixture, this step would be repeated for each crystallographic phase. If an impurity is identified in a later stage of the refinement, this step can be run at that point to define this additional crystallographic phase. GSAS allows up to nine crystallographic phases to be included in a model.

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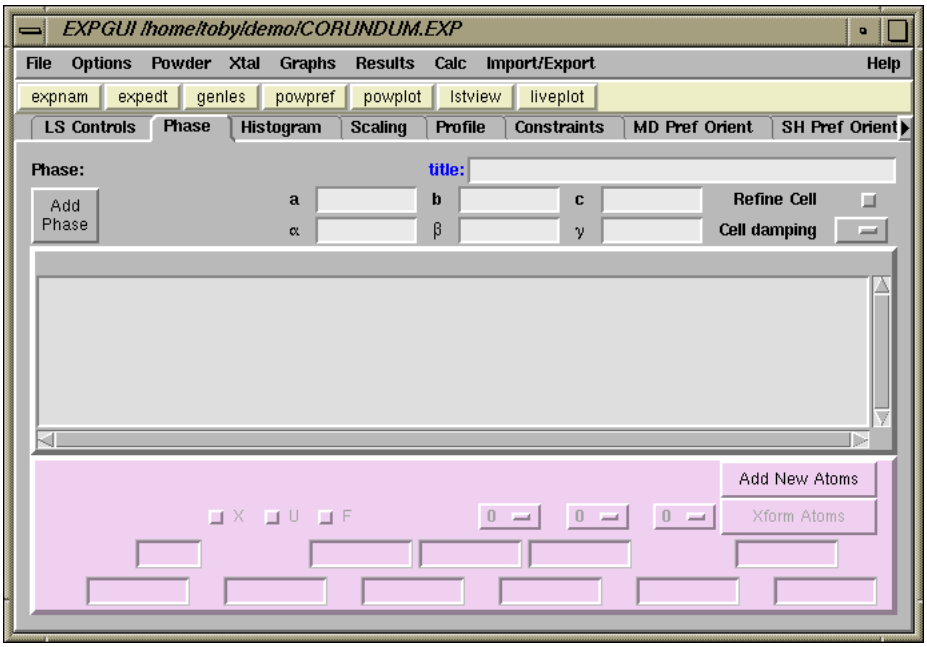
To enter information about a crystallographic phase, modify crystallographic parameters, or select crystallographic parameters to be optimized the "Phase" panel must be selected by clicking on the "Phase" tab in the upper left of the EXPGUI window. The window then appears as shown just below this text.




*It should be noted that the Phase panel will have a slightly different appearance after one or more phases have been entered, (see below).*

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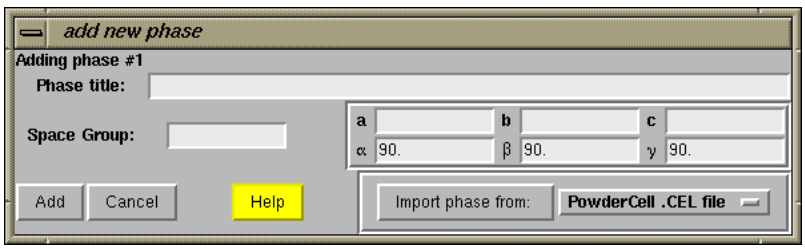
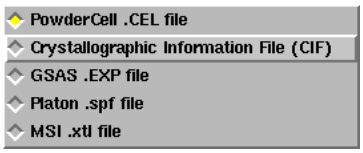
The next step is to press the "Add Phase" button in the upper left. The "Add New Phase" window, shown immediately below, is then generated.



Information about the phase can be added directly into the boxes, or phase information can be read from a file. For this exercise, we will read unit cell parameters, the space group and atom parameters from a CIF file. This means that we need to select the "Crystallographic Information File (CIF)" format from the options by pressing the file format button in the lower right-hand corner.

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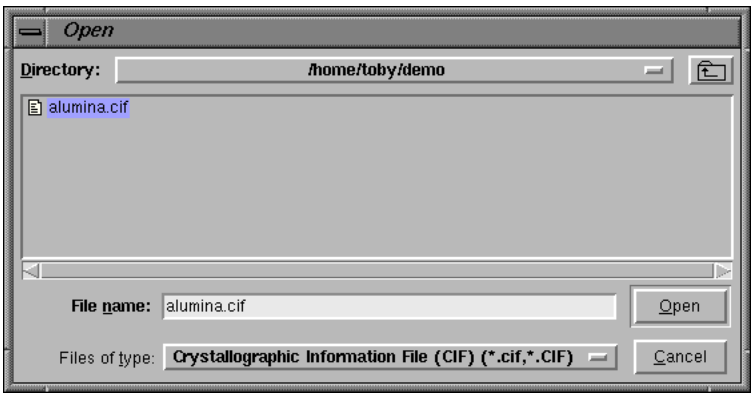
When the "Import Phase from" button is pressed, an "open file" window is created (this window has a slightly different appearance, but the same function in Windows). On this window, the file to be read is selected, and then the "Read" button is pressed.

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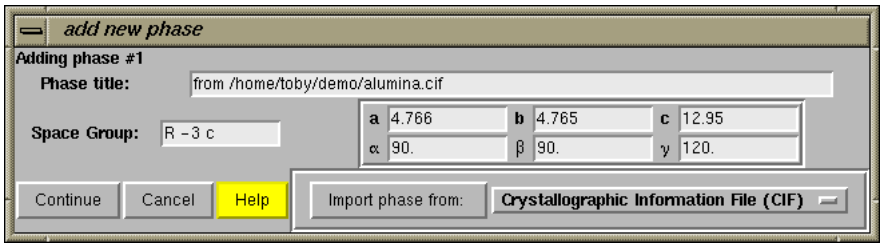
The CIF is then read and the unit cell information is included in the appropriate entry boxes, as shown below. If this input is acceptable, press "Continue".

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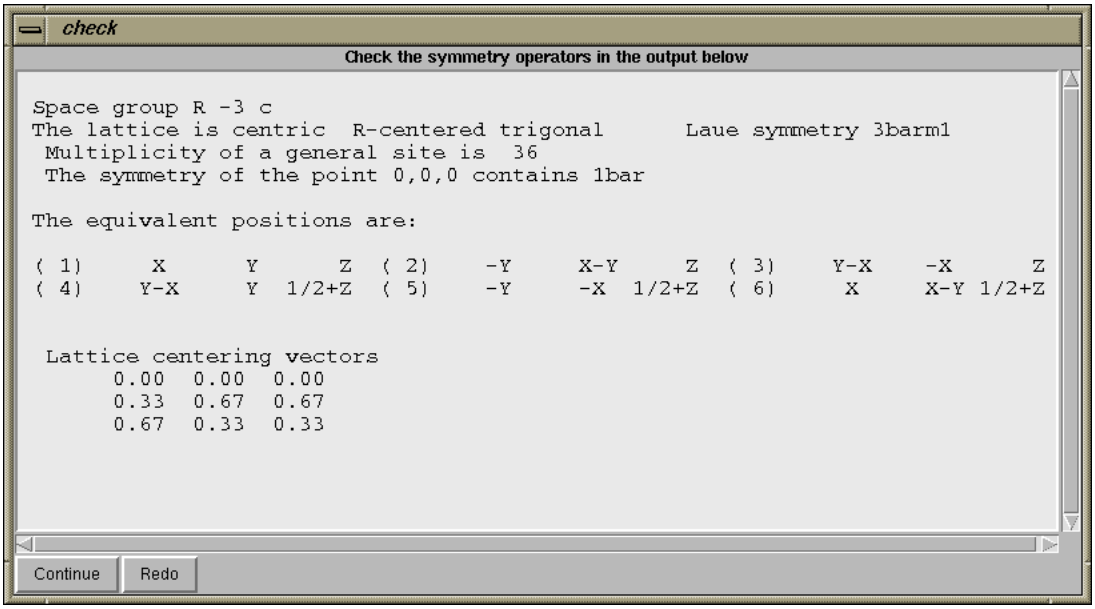
One of the places where errors occur in the preparation of GSAS input is in the entering of space group symbols. For this reason, after the "Continue" button is pressed, a window such as the one below, is created to help you confirm that the correct space group has been entered.



*It is recommended that you read through this information to check that this is correct. As an example of a possible error, if one entered the corundum example in the rhombohedral setting, rather than the hexagonal setting, then the space group should be entered as "R -3 c R" (where the final R indicates the rhombohedral setting). The listing of lattice centering vectors is only appropriate for the hexagonal (centered) cell.*

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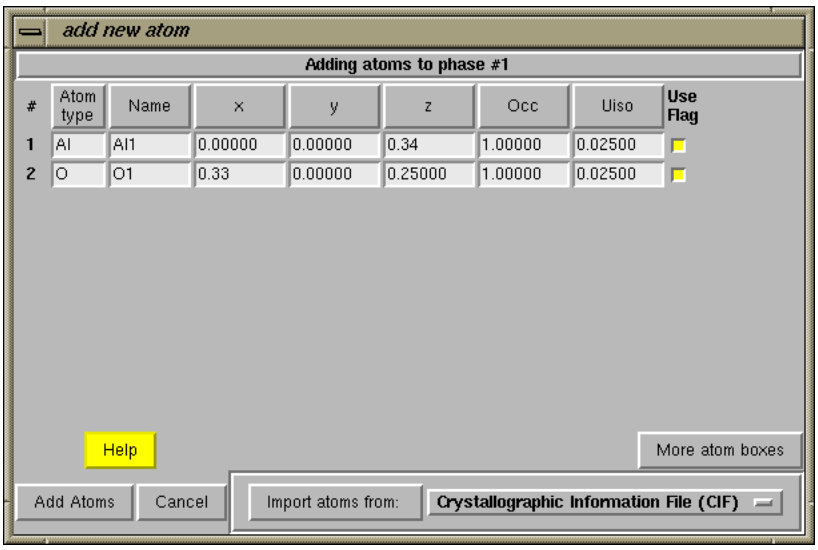
Since the symmetry information is correct in this example, press the "Continue" button on the "check symmetry" window. At this point, since atom coordinates were read from the CIF file, the "add new atoms" window is opened and the atom coordinates are entered into the appropriate boxes, as seen below. Press the "Add Atoms" button at the lower left to continue.




*Note that if atoms were not being read in from a file, it would now be necessary to press the "Add New Atoms" button to input atoms to the phase. In this case, there would be no atoms entered into the window.*

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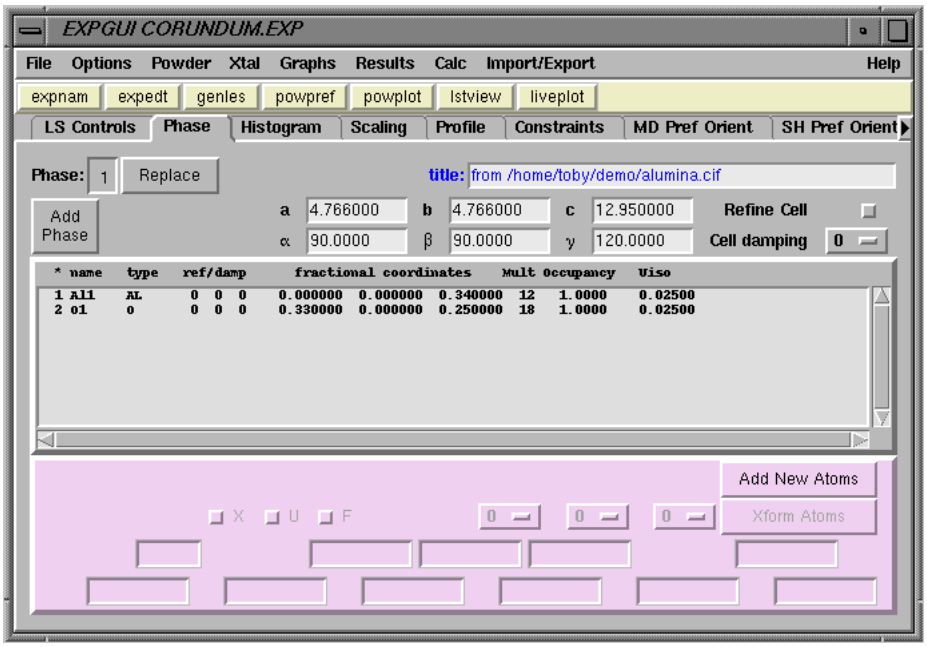
After pressing the "Add Atoms" button, the two atoms are added to the experiment and the phase panel appears, as below.




# GSAS/EXPGUI Alumina tutorial (part 3)
# Specifying Powder Diffraction Data (Adding a Histogram)

*GSAS uses the term "histogram" to refer to a diffraction data set. A histogram can also be a set of "soft constraints," e.g. a set of target parameters, such as bond distances, that the model will also try to fit. GSAS can fit a model to up to 99 histograms simultaneously, although the majority of refinements done in GSAS use a single histogram or at most only a few histograms. GSAS can use single crystal or powder diffraction data, either neutron or x-ray. For neutron powder diffraction data, the data can be obtained from either time-of-flight (TOF) or constant wavelength (CW) instruments. GSAS can use x-ray data from synchrotron, laboratory alpha-1,2, and even energy-dispersive x-ray instruments.*

*Two files are needed to load a powder diffraction histogram. The first is a file containing the powder diffraction data, often called a GSAS raw data file (often using the extension .RAW, .GSA or .GSAS) and the second file is an instrument parameter file (.INS or .INST) that defines what type of data is included in the raw file (x-ray/neutron, CW/TOF/ED, etc.) as well as starting values for the diffractometer constants and peak shape parameters. There are a number of available formats for the raw data files and types of records in the instrument parameter file; this information is defined in the GSAS documentation. Note that raw data files can contain more than one set of data and that an instrument parameter file can contain more than one set of parameters. This feature is rarely used, with the exception of TOF instrumentation, where detectors are grouped into banks and the results for each bank are included in a single file. Software for translating diffraction data into a format accepted by GSAS is available at most user facilities or can be found at the CCP14 web site Appropriate instrument parameter files can usually be provided by the instrument scientist at a user facility or prototypes can be found in the GSAS distribution files.*

This web page demonstrates how the alumina powder diffraction data are now added to the experiment file. For this tutorial exercise, a special instrument parameter file that has peak shape values narrower than the actual instrument is provided. The tutorial would be less challenging if the appropriate instrument parameter file is used.

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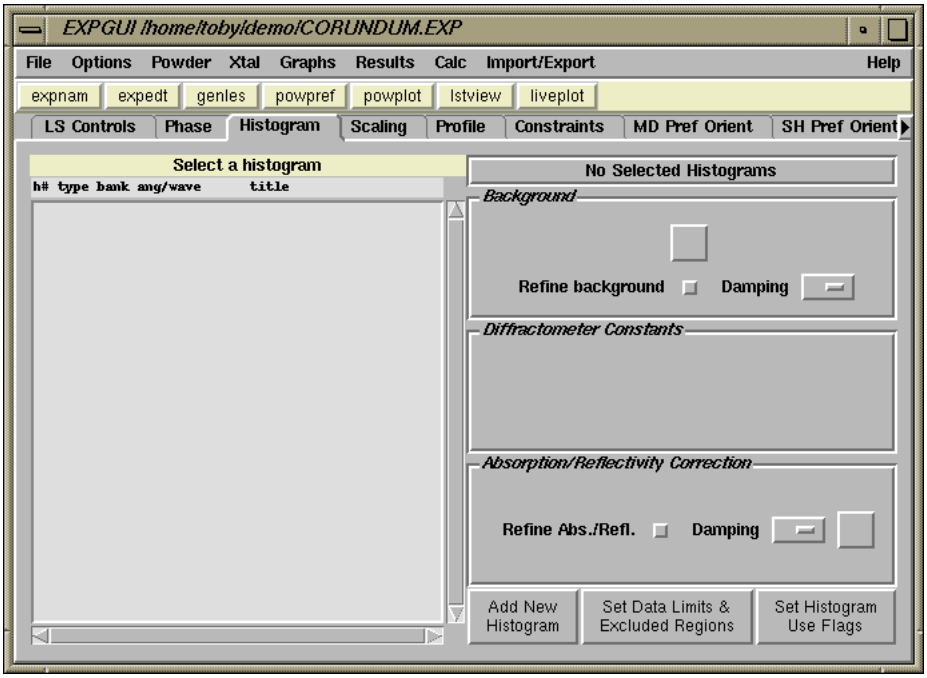
The Histogram panel is selected by clicking on the Histogram tab, as is shown below. In this case, no data has been defined, as can be determined by the absence of entries in the histogram selection box, in the upper left. The "Add New Histogram" button, at the lower right, is used to add [additional] powder diffraction data sets to the refinement, as will be demonstrated in this page. The histogram panel is used to modify various parameters associated with each set of diffraction data, for example the diffractometer constants (such as wavelength), the background function and terms.

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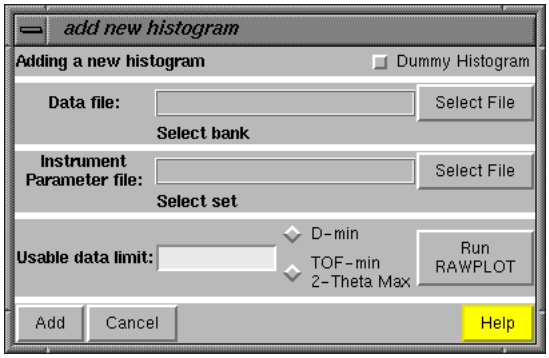
Pressing the "Add New Histogram" button causes the "add new histogram" window, shown to the right, to be displayed. The entries on this window are usually considered from top to bottom. The "Dummy Histogram" option is used to simulate powder diffraction data, and is not used in this tutorial example. So the next item of interest is to select a data file. This is done by pressing the upper of the two "Select File" buttons.

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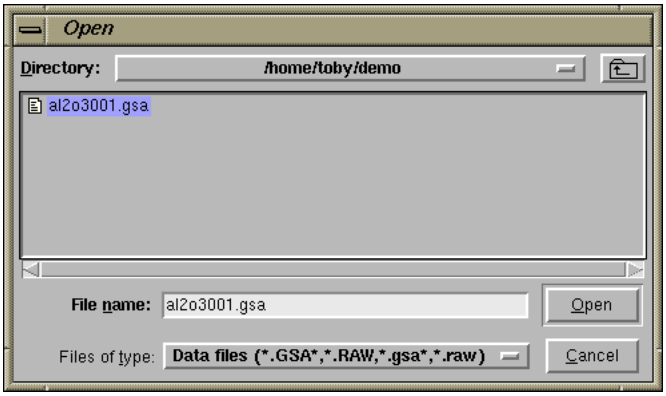
Pressing the "Select File" button creates a file open window, such as the one to the right (or slightly different in appearance in windows). Select the input file for this exercise, the file you downloaded earlier, al2o3001.gsa. Double-click on the entry, or select is and press the "Open" button. This open window will then close.

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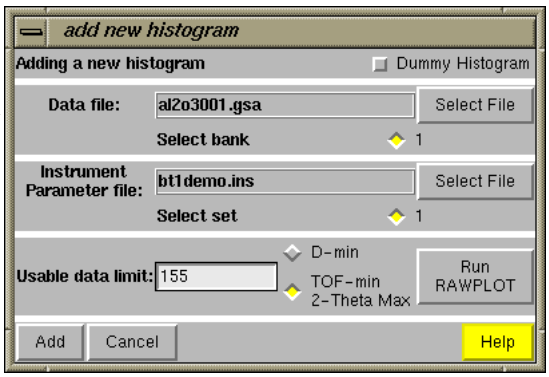
Selecting the raw data file in the open window causes the al2o3001.gsa file to be loaded into the upper box on the "add new histogram" window. This file is scanned to and check mark entries are created for each bank in the file. The al2o3001.gsa file also defines a default instrument parameter file, which is the bt1demo.ins that was downloaded earlier, so this file name is entered into the "Instrument Parameter File" section.

The "Usable data limit" sets the maximum range of data to be used in fitting. This is usually determined by plotting the data to see where no further peaks are present. This can be done here with the GSAS RAWPLOT program. For this exercise, change the defaulted value (the entire data range) to 155 degrees, to exclude a single very broad high-angle peak. The press the "Add" button in the lower left.

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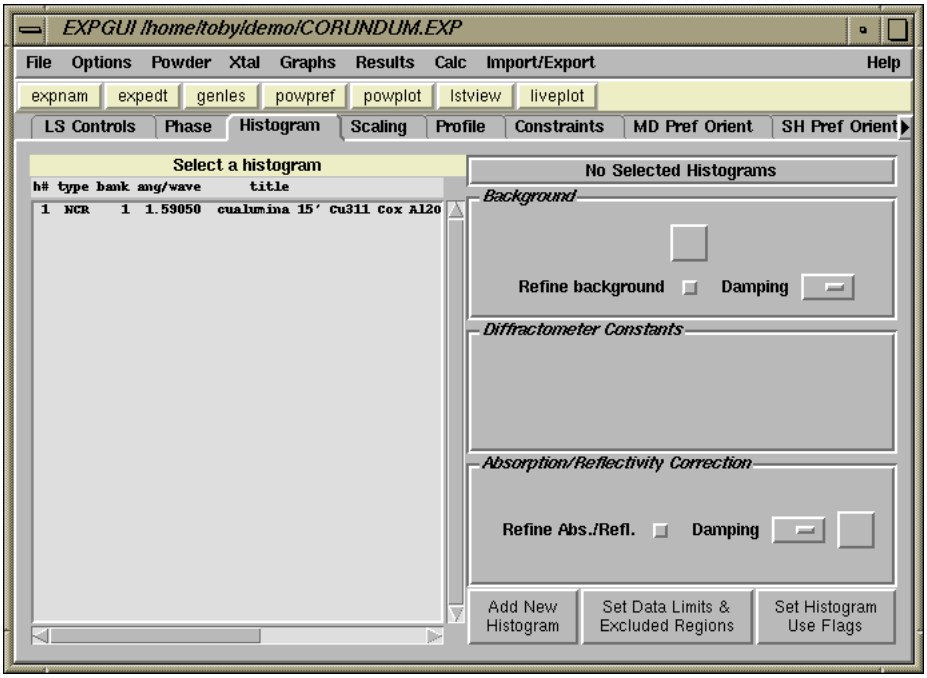
After the "Add" button is pressed, the EXPGUI program runs a GSAS program, EXPTOOL, that actually adds the data reference to the experiment. If an error occurs, this result is shown. If no error occurs, the histogram panel is redisplayed, but this time a histogram appears in the upper left, as seen below.




# GSAS/EXPGUI Alumina tutorial (part 4)
# Changing the Background Function

*GSAS offers approximately 10 different background functions (not all are implemented in EXPGUI). For each of these functions, the number of terms to be used is adjustable. The more terms the more complex the shape that can be fit. Each of these background functions has different shapes, and in theory, each function will have advantages under different circumstances. However, this author finds that the Shifted Chebyschev (type #1) is preferable to the others for the vast majority of Rietveld refinements and almost never uses any other function.*

When a histogram is first added in GSAS, the background function is set to the Cosine Fourier series option (type #2) with two adjustable terms. In this section of the tutorial, we change the background function and the number of terms.

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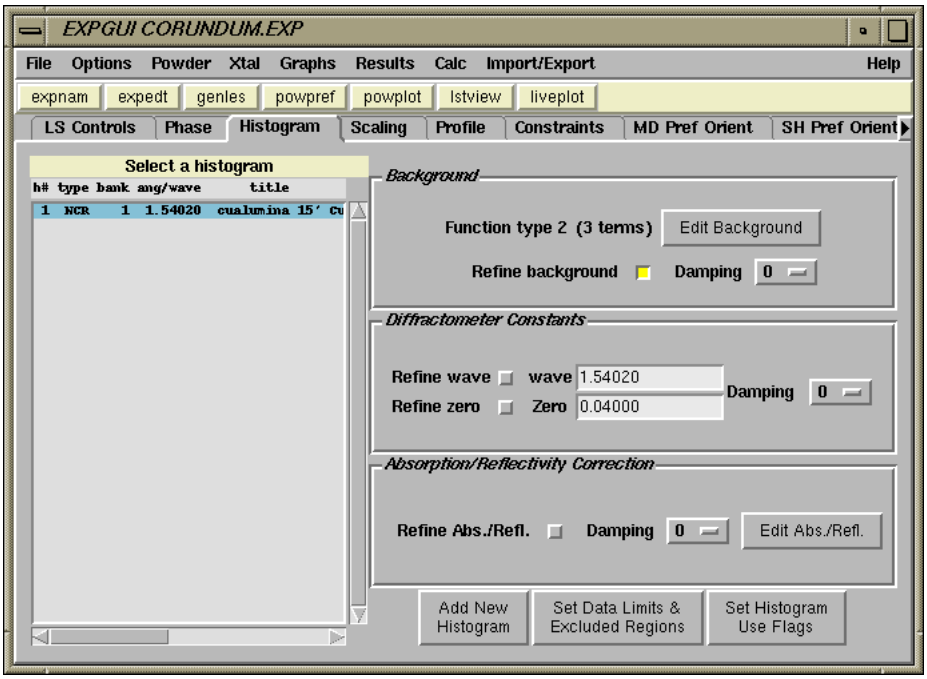
To change the background function, press the "Edit Background" button on the histogram panel.



*Note the "Refine background" check box has been selected -- this means that the background parameters will be refined (optimized) when GENLES is run. The damping parameter to the immediate left is set to 0 -- this means that the full computed shift will be applied. In cases where a refinement has trouble reaching a minimum, it may be advantageous to increase damping (a setting of 1 implies 90% of the computed shift will be applied and a damping setting of 9 yields a shift of 10%.)*

*Every refinable parameter in GSAS has a refinement flag (either for the group, as in this case, or for each individual parameter) and a damping parameter. The appearance of the check box is slightly different in windows: a "x" appears in the box when the parameter is selected.*

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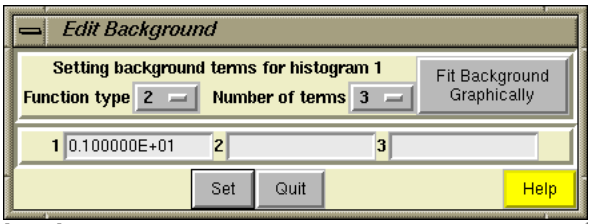
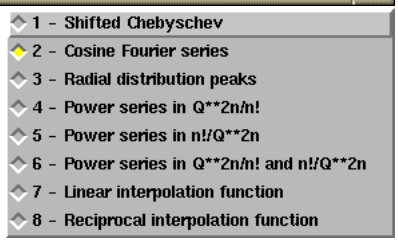
After the "Edit Background" button is pressed, The "Edit Background" window opens, as is shown to the right. In this window both the function type and the number of terms can be changed.




Clicking on the "Function type" menu offers a choice of function types, as is shown to the right. Choose function type #1, the Shifted Chebyschev function.




*Note that the "Fit Background Graphically" invokes the EXPGUI BKGEDIT program, which is used to fit a background function directly to user-supplied points. This is a very useful initial way to fit the background in difficult cases.*

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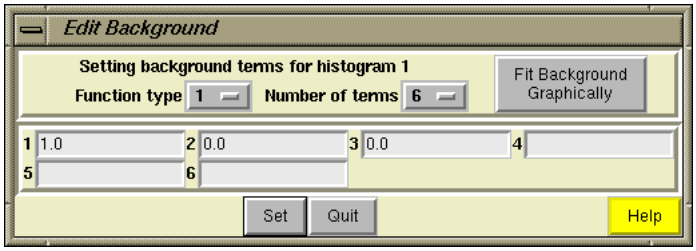
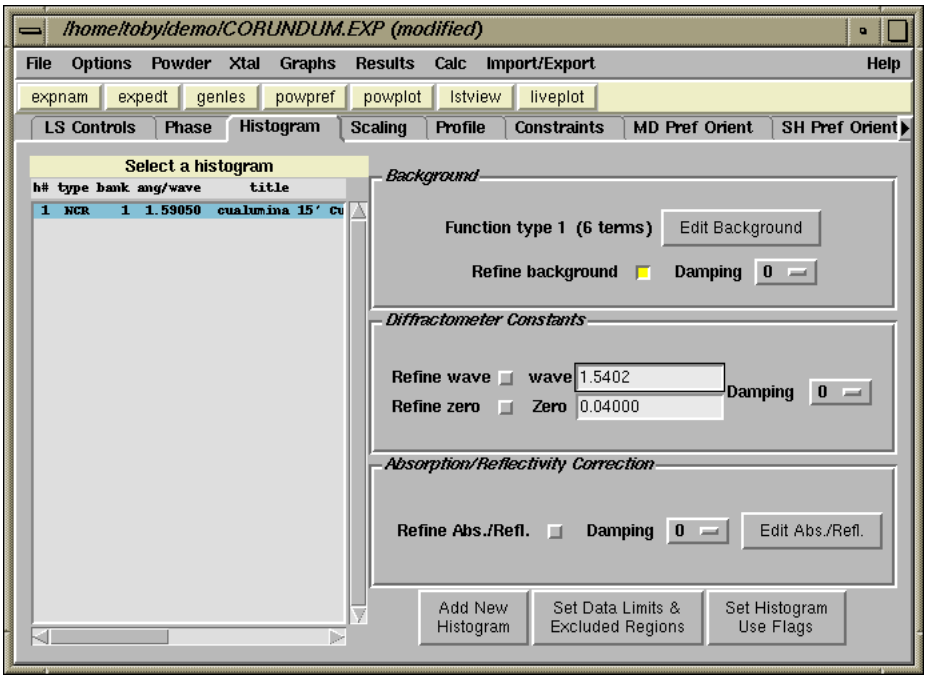
Also in the "Edit Background" window, press on the "Number of terms" button and change this number to 6, as is shown to the right. Note that with the Chebyschev polynomial arbitrary (including zero) starting values for the background terms is acceptable.




After the "Set" button is pressed, the changes are then seen on the histogram panel, as shown below. Note that by default, the refine background flag is set, allowing these parameters to be optimized.



# GSAS/EXPGUI Alumina tutorial (part 5)
# Initial Fitting: Refine Scale Factor and Background

*At this point we are almost ready to start fitting parameters, but before we do that the POWPREF program must be run. In GSAS, each data point has a list of reflections that contribute to that data point. This assignment must be made in POWPREF before the least squares fit can be performed in the GSAS program GENLES. The program must also be rerun if a new phase or histogram is added to the refinement. POWPREF should also be rerun if the lattice constants or profile terms change significantly.*

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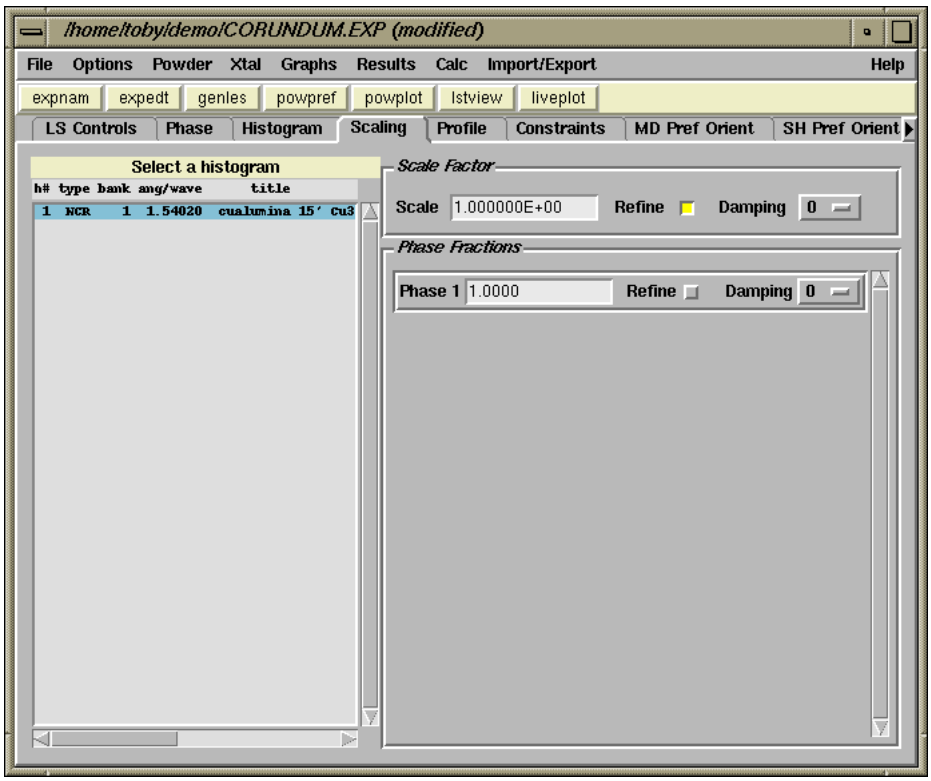
We want to refine the background and the scale factor to get started. The scaling parameters are shown on the Scaling panel, shown below. GSAS offers us an overall scale factor for each histogram, plus a phase fraction scale factor for each phase. These two factors have exactly the same effect for a single-phase refinement, so only one can be used. By default, the scale factor refinement flag is turned on and the phase fraction is off. This is what we will use.

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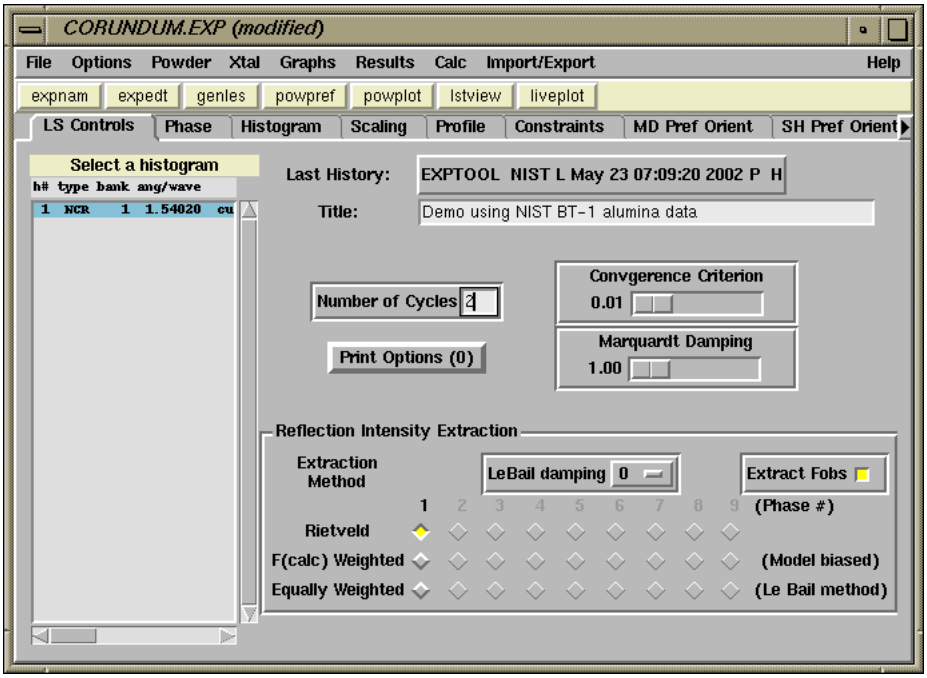
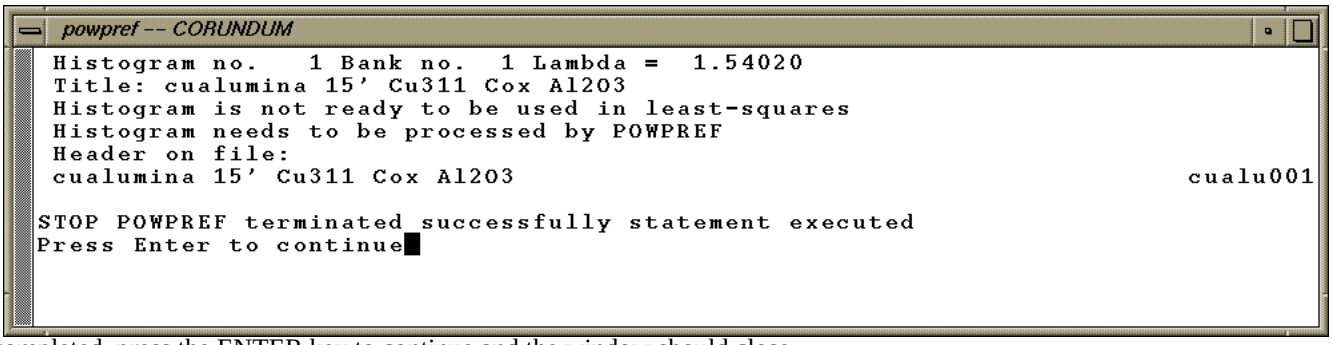
The other change that we will make in the default refinement options is to lower the number of refinement cycles to 2. Also, make sure the "Extract $F_{obs}$" check box on the least-squares pane is selected.

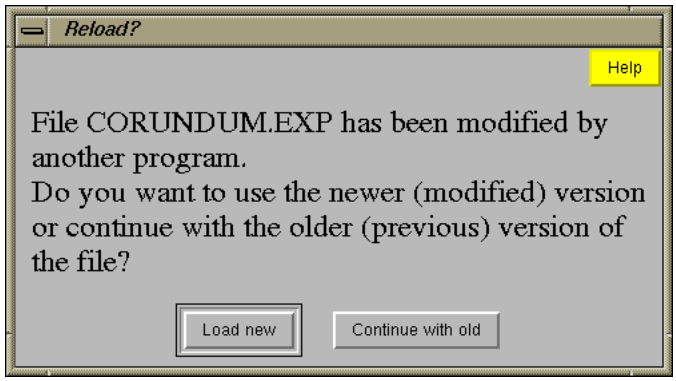



We are now ready to start running programs. First run POWPREF by pressing the POWPREF button on the beige tool bar (or selecting the POWPREF option in the Powder menu list.) That causes a window, such as the one below to open as POWPREF runs.



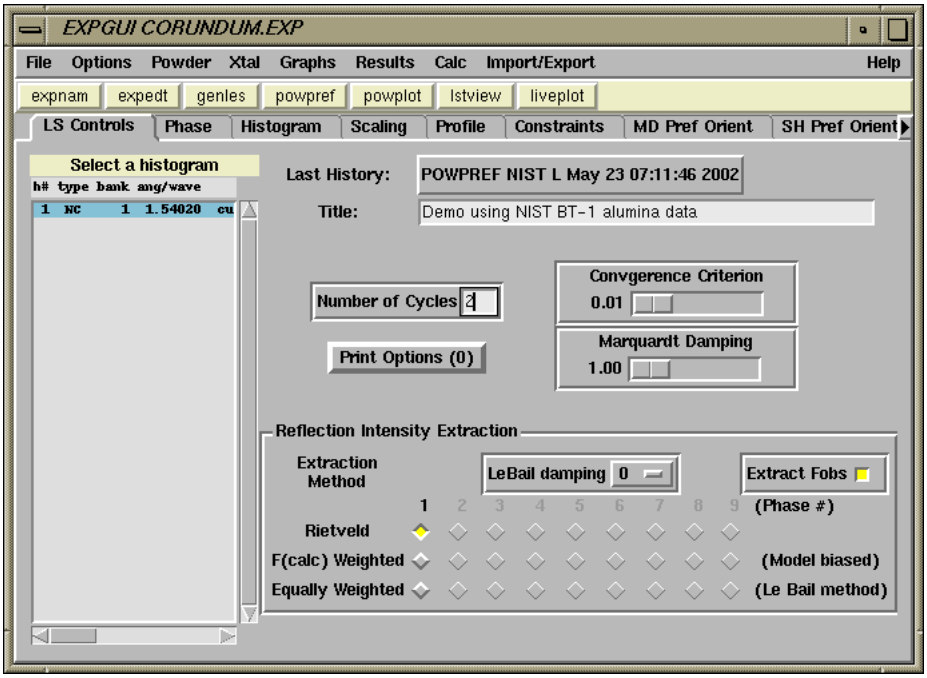

When POWPREF has completed, press the ENTER key to continue and the window should close.

The POWPREF program makes changes to the experiment (.EXP) file and this is noted by EXPGUI by the display of the warning message to the right. At this point you do want to accept the changes made by POWPREF, so click "Load New" and EXPGUI will reread the revised file.

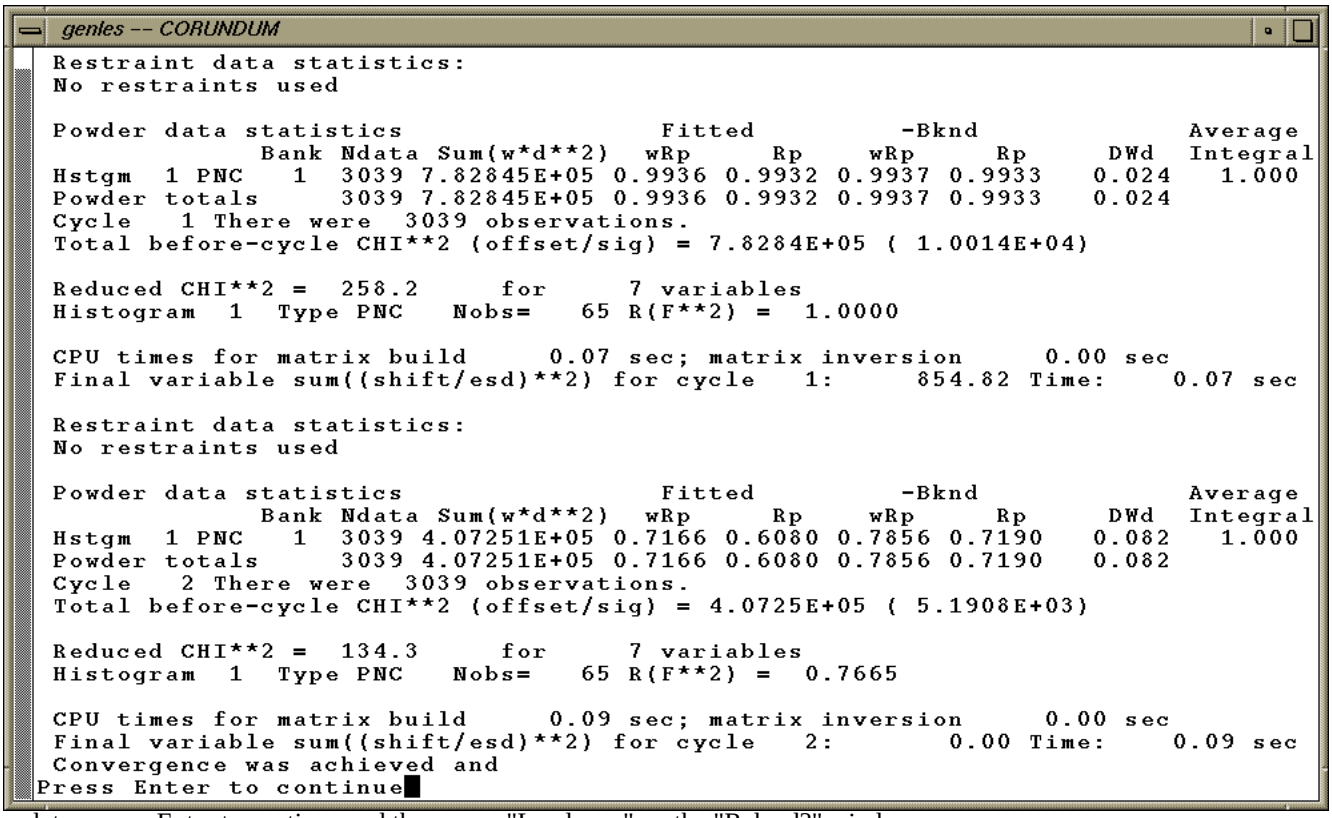



*By default, this window is shown every time the experiment file is modified by any GSAS program. This allows the file to be "rolled back" to the previous version, in case of a disastrous refinement run, by pressing "Continue with old." However, some EXPGUI users find it annoying to be asked this question all the time. In the EXPGUI Options menu, there is a menu item called "Autoload EXP". If the "Autoload EXP" option is checked, the experiment file will always be read automatically, but then it is no longer possible to roll back erroneous steps so easily.*

Note that the displayed history record has been updated to reflect the running of POWPREF.




We can now initiate the refinement, by launching the GENLES program to optimize the scale factor and background parameters. The output from this run is shown below.




After the refinement completes, press Enter to continue and then press "Load new" on the "Reload?" window.

*The output from the GENLES run shows several points worth noting. First note that the number of variables (varied parameters) is 7, from the scale factor plus the 6 background terms. Note that the initial weighted R-factor (wRp or Rwp) and Chi-squared values are 99% and 258, respectively but drop to 72% and 134, respectively after a cycle of refinement. In the first cycle of refinement, there are very large shifts in the parameters, but the parameters converge in the second cycle. This is noted by the sum[(shift/esd)**2] term which is 855 in the first cycle, but 0 in the second cycle. Note that shifts become insignificant when they are small with respect to the esd (standard uncertainty), so a value of 855 means that at least some of the parameters made very large shifts in the first cycle. Note that GSAS does not compute the R-factor or Chi-squared terms after the second refinement cycle.*

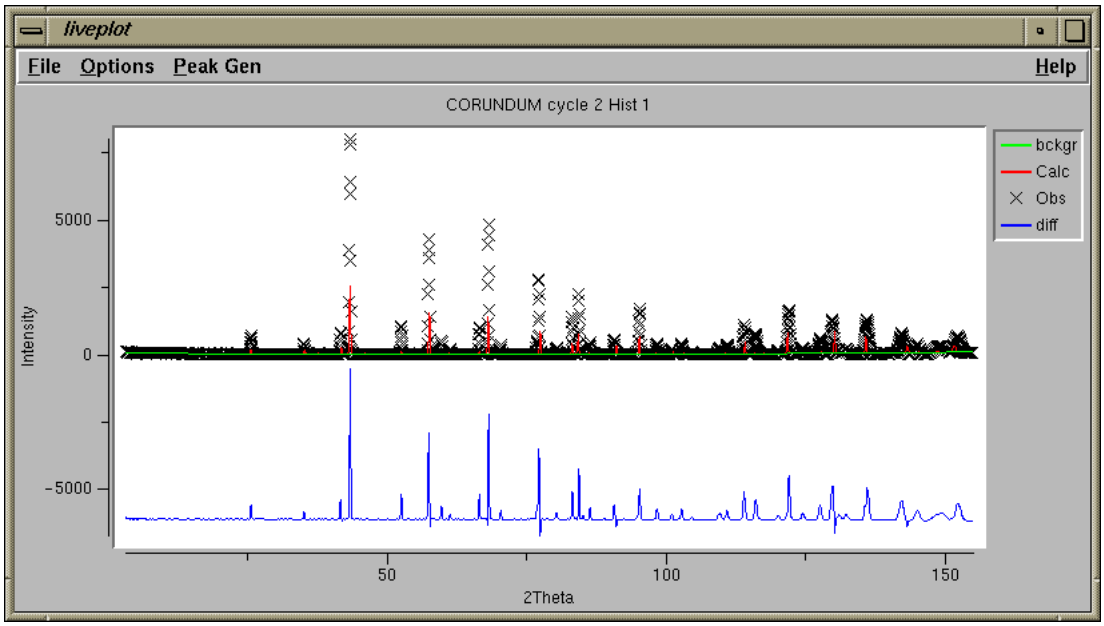
# GSAS/EXPGUI Alumina tutorial (part 6)
# Plotting the Initial Fit

*While Chi-squared and R-values provide some measure of how a fit is progressing, the only way to actually understand the quality of the fit and what problems need to be corrected, is to look at agreement between the observed diffraction data and the corresponding values computed from the fit. This is sometimes called a Rietveld plot.*

The GSAS program POWPLOT and the EXPGUI program LIVEPLOT allow the fit to be examined graphically. In this tutorial step, LIVEPLOT is used to examine the results.

---

Press the LIVEPLOT button on the button bar (or use a menu command) to start LIVEPLOT. You should then see a plot like the one below.

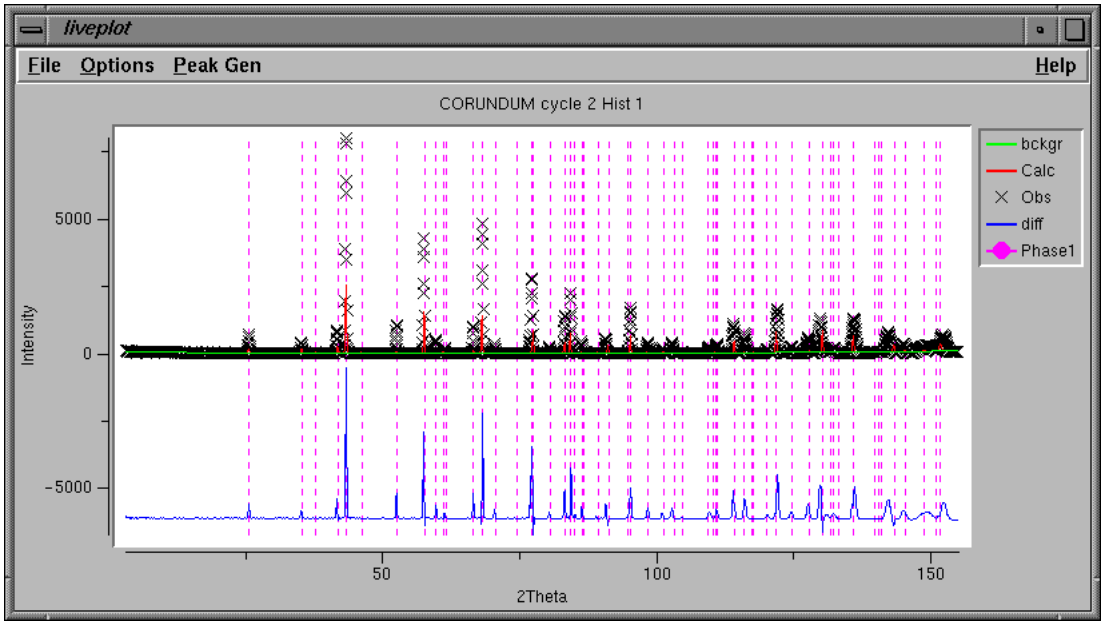



*In this plot, the data are "X" characters, the calculated values are a red line. The fitted background is shown as a green line. Offset below, the observed pattern minus the computed pattern is shown in blue. The observed and computed values do not agree very well, but seem to follow the same trends. In the subsequent plots we will see in more detail what some of the discrepancies are.*

*Note that the size of the plot can be changed by changing the size of the window.*

---

It will help to see the actual positions of the reflections. This display can be turned on by pressing the "1" key (1 for phase 1, 2 for phase 2...) in the LIVEPLOT window. (This can also be done using the Tickmarks submenu in the File menu.)

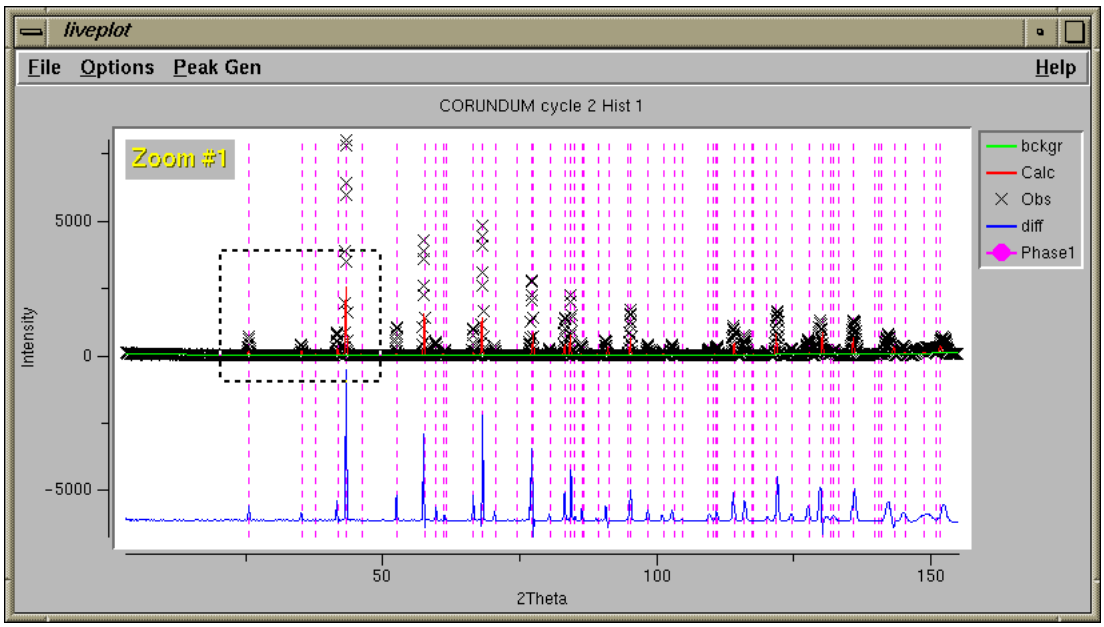



*Note that the color, length, style, placement of the tick mark lines can be changed in the Options menu.*

*Note also that the reflection indices for a tick mark can be displayed by pressing the "h" key when the cursor is positioned over a tick mark.*

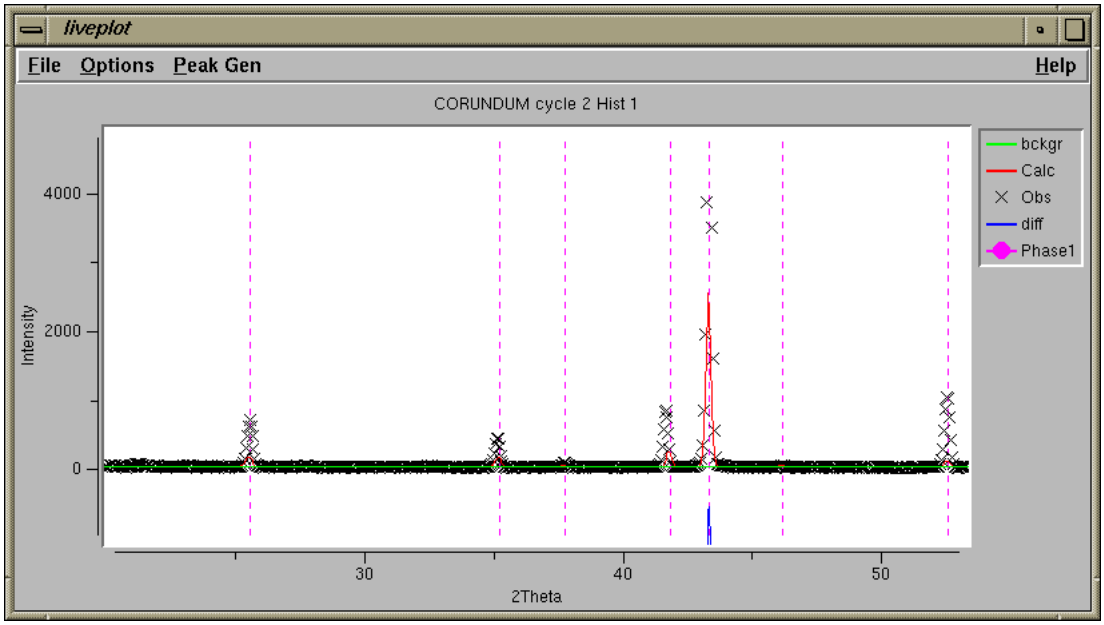
---

With all the data displayed, at appears that the tick marks are in the right places at lower angles, but are not well placed at 140 degrees and higher. It would be good to see the plot at high magnification to see more detail, however. "Zooming in" is accomplished by clicking the mouse in the lower left and upper right corners of the region to be viewed (lower right & upper left also works). A box is displayed, as below, after the first mouse click. After the second the plot is redrawn.

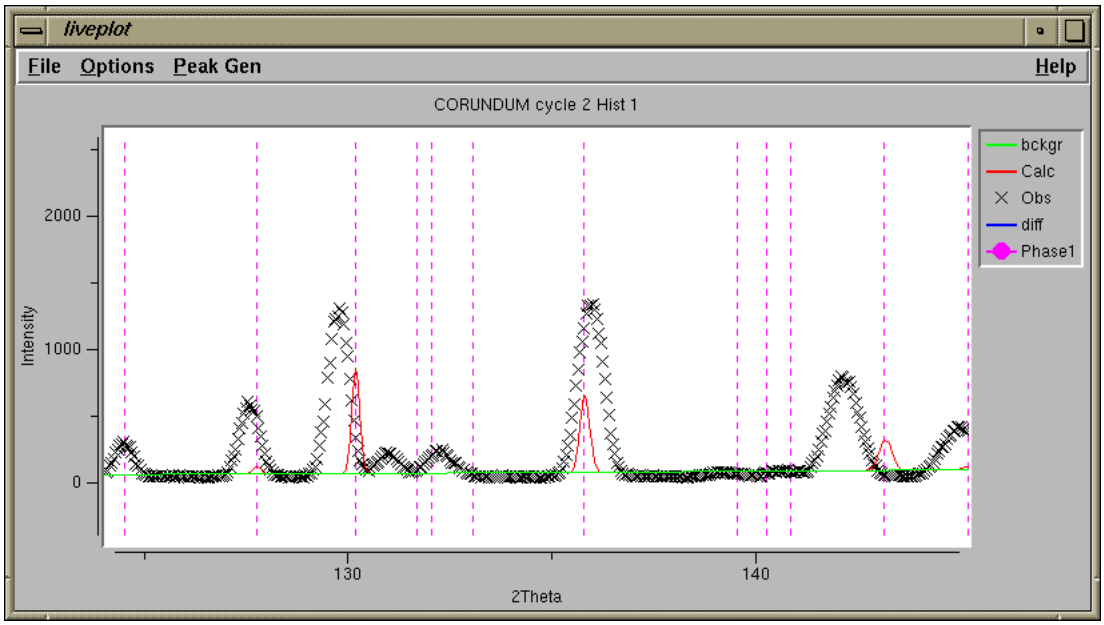



---

Note with the plot zoomed in, it can now be seen that the lattice parameters do not index the peak 42 degrees very well. The computed peak widths agree reasonably well with the observed.



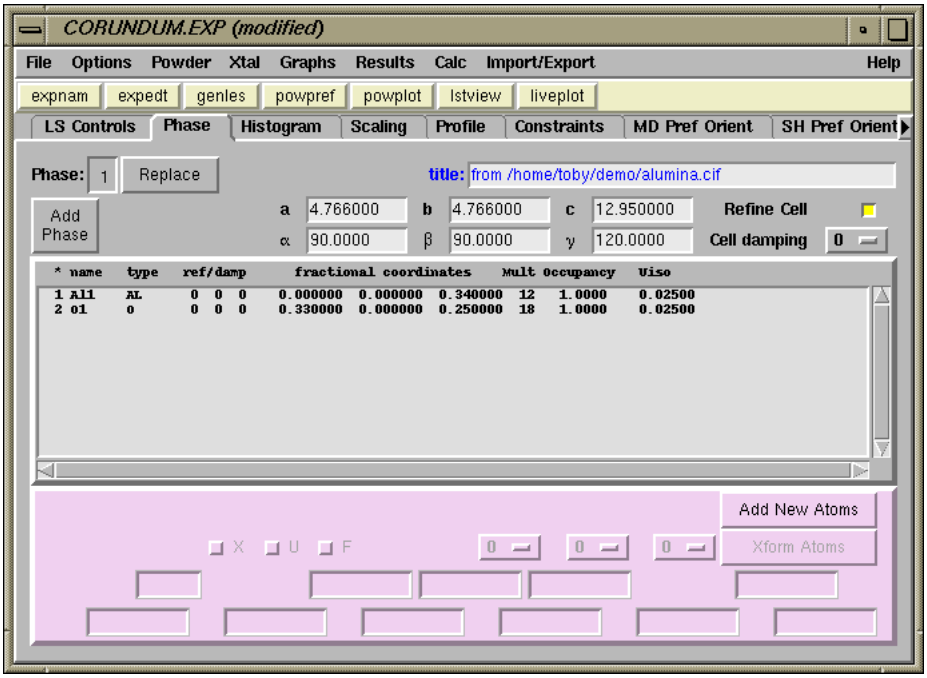

The fit is even worse at high angle. Also, the computed peak widths are much narrower than the observed.



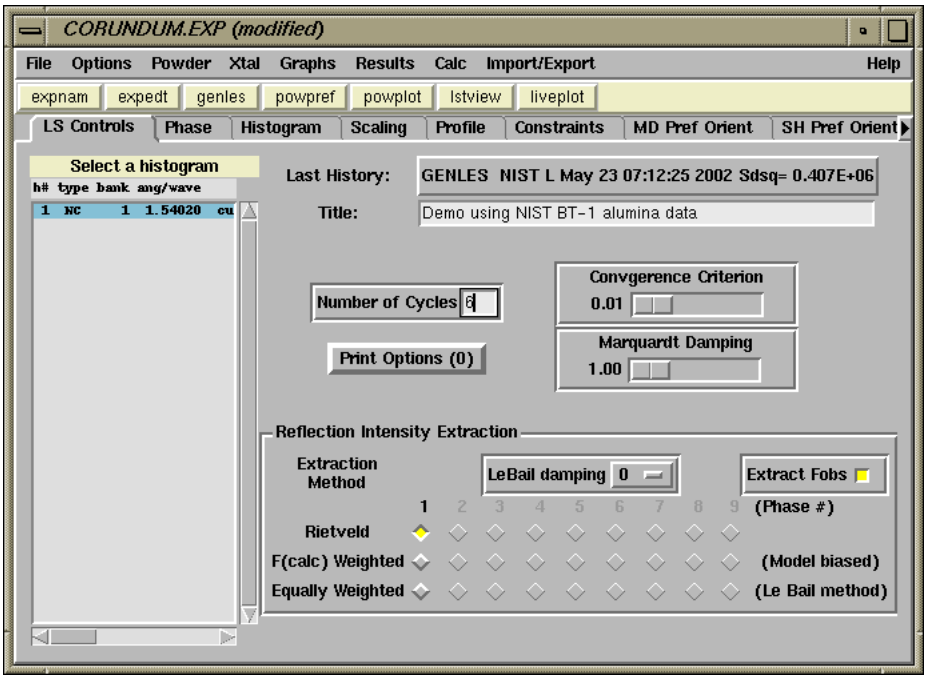

# GSAS/EXPGUI Alumina tutorial (part 7)
# Fitting the Unit Cell

In the previous tutorial, we saw that the unit cell was not doing a very good job of indexing the diffraction peaks. Since a large number of peaks did have computed reflections at least partly overlapping the observed peaks, we are close enough to fit the unit cell parameters using a refinement. If that were not true -- the tick marks did not fall in the range of the peaks, refinement would not be possible.

One the Phase panel, turn on the flag to refine the unit cell parameters (upper right), as shown below.




Also, increase the number of cycles to 6.



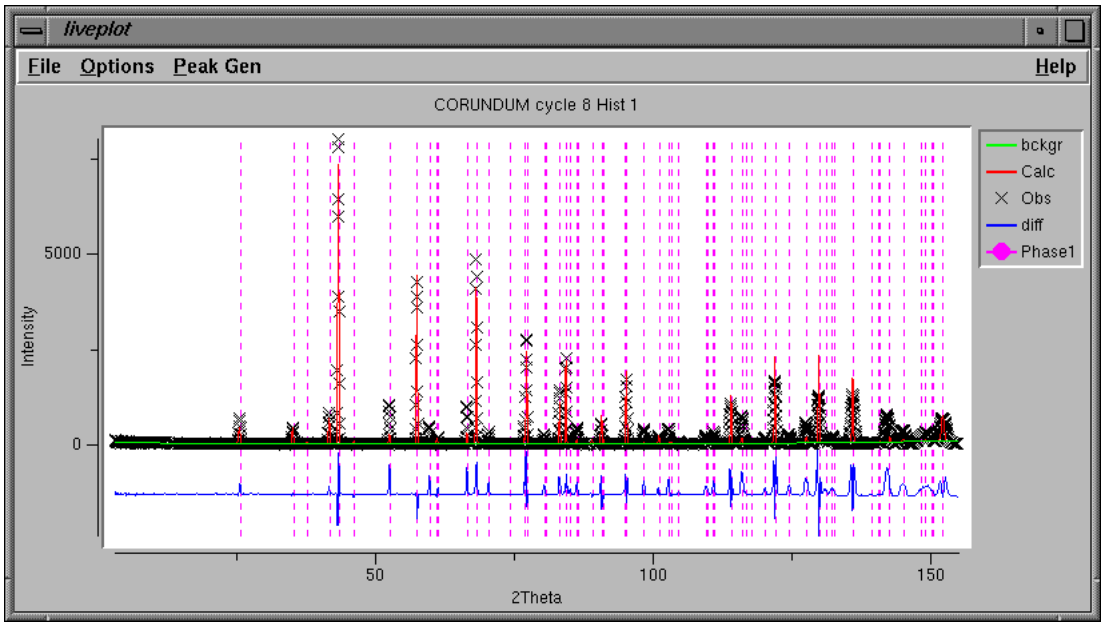

Run GENLES (as before). Note there are now 9 parameters (scale, 6 background, + 2 cell) and that the fit significantly improves, as seen below.

```
genles -- CORUNDUM
 Total before-cycle CHI**2 (offset/sig) = 2.1905E+05 ( 2.7750E+03)

 Reduced CHI**2 =  72.29     for     9 variables
 Histogram  1  Type PNC   Nobs=   65 R(F**2) =  0.4523

 CPU times for matrix build     0.08 sec; matrix inversion     0.00 sec
 Final variable sum((shift/esd)**2) for cycle   7:      78.29 Time:    0.08 sec

 Restraint data statistics:
 No restraints used

 Powder data statistics                  Fitted         -Bknd              Average
              Bank Ndata Sum(w*d**2)  wRp     Rp     wRp     Rp     DWd  Integral
 Hstgm  1 PNC   1  3039 2.12335E+05 0.5174 0.3873 0.5450 0.4262   0.125    0.898
 Powder totals     3039 2.12335E+05 0.5174 0.3873 0.5450 0.4262   0.125
 Cycle   8 There were  3039 observations.
 Total before-cycle CHI**2 (offset/sig) = 2.1233E+05 ( 2.6887E+03)

 Reduced CHI**2 =  70.08     for     9 variables
 Histogram  1  Type PNC   Nobs=   65 R(F**2) =  0.4385

 CPU times for matrix build     0.08 sec; matrix inversion     0.01 sec
 Final variable sum((shift/esd)**2) for cycle   8:      24.36 Time:    0.09 sec
Press Enter to continue
```

(As before, press Enter & load the modified experiment file into EXPGUI.)

---

The peak positions are fit much better than before, as seen in the LIVEPLOT output below.



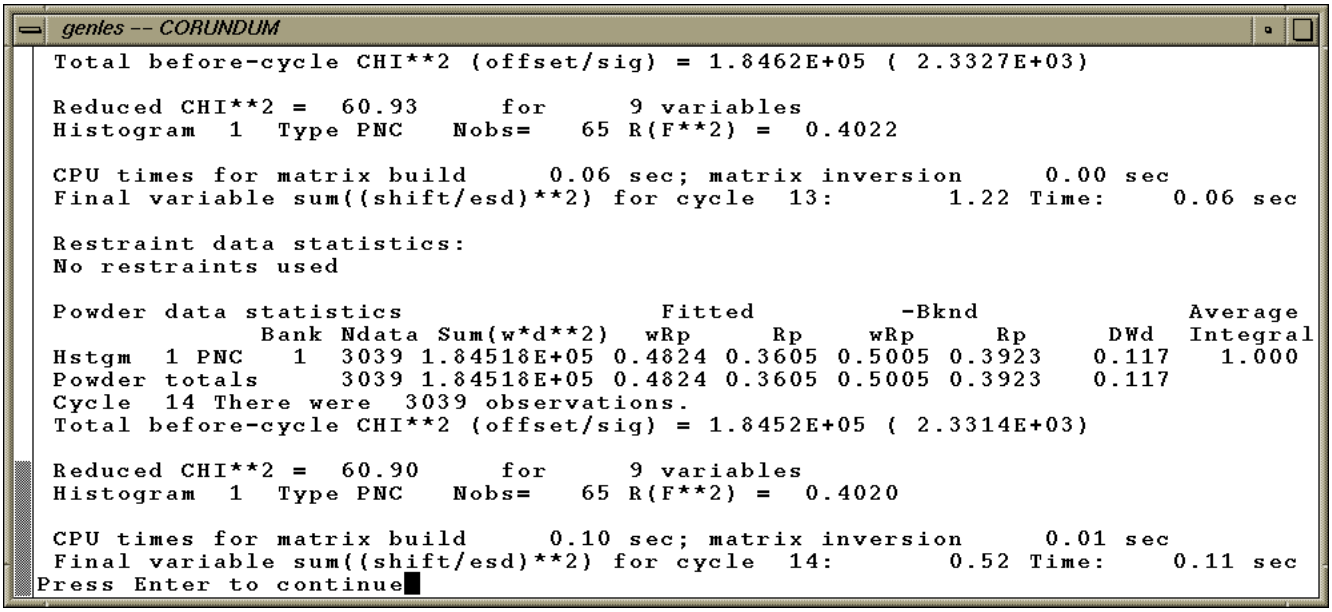

---

Since the peak positions have changed significantly, we now need to rerun POWPREF and use the new peak positions to decide which data points need to be indexed with each reflection.

```
powpref -- CORUNDUM
 Histogram no.    1 Bank no.   1 Lambda =  1.54020
 Title: cualumina 15' Cu311 Cox Al203
 **** Histogram will be used in least-squares
 Header on file:
 cualumina 15' Cu311 Cox Al203                                        cualu001

STOP POWPREF terminated successfully statement executed
Press Enter to continue
```

---

It is not strictly necessary to run GENLES again, but note that CHI-squared improves from 70 to 60 just from the better indexing.

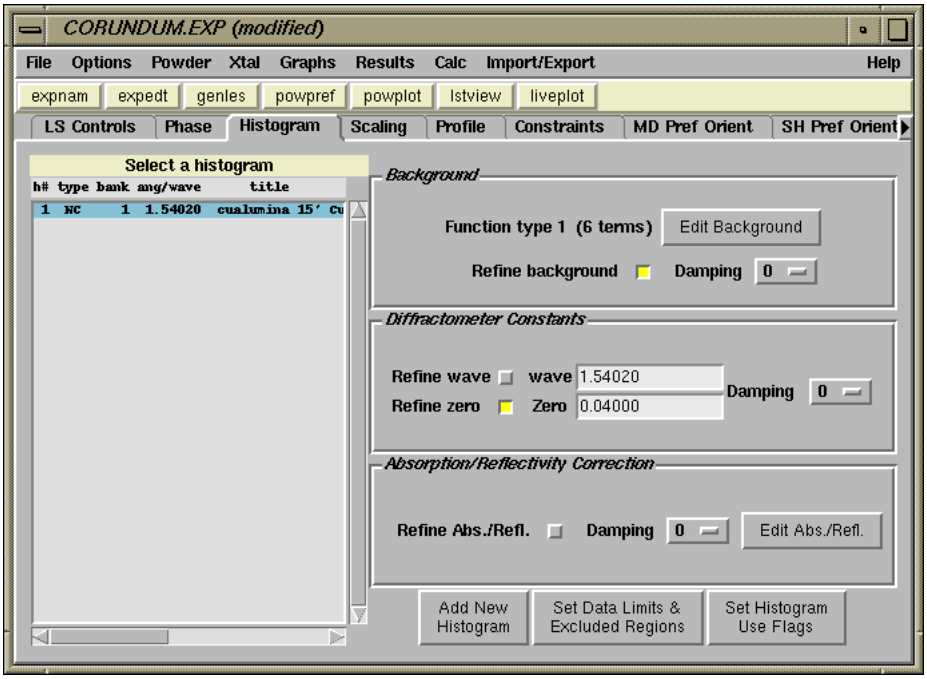



# GSAS/EXPGUI Alumina tutorial (part 8)
# Fitting the Diffractometer Zero Correction

Now that the unit cell parameters have been fit, it is now a good idea to also refine the diffractometer zero correction.

---

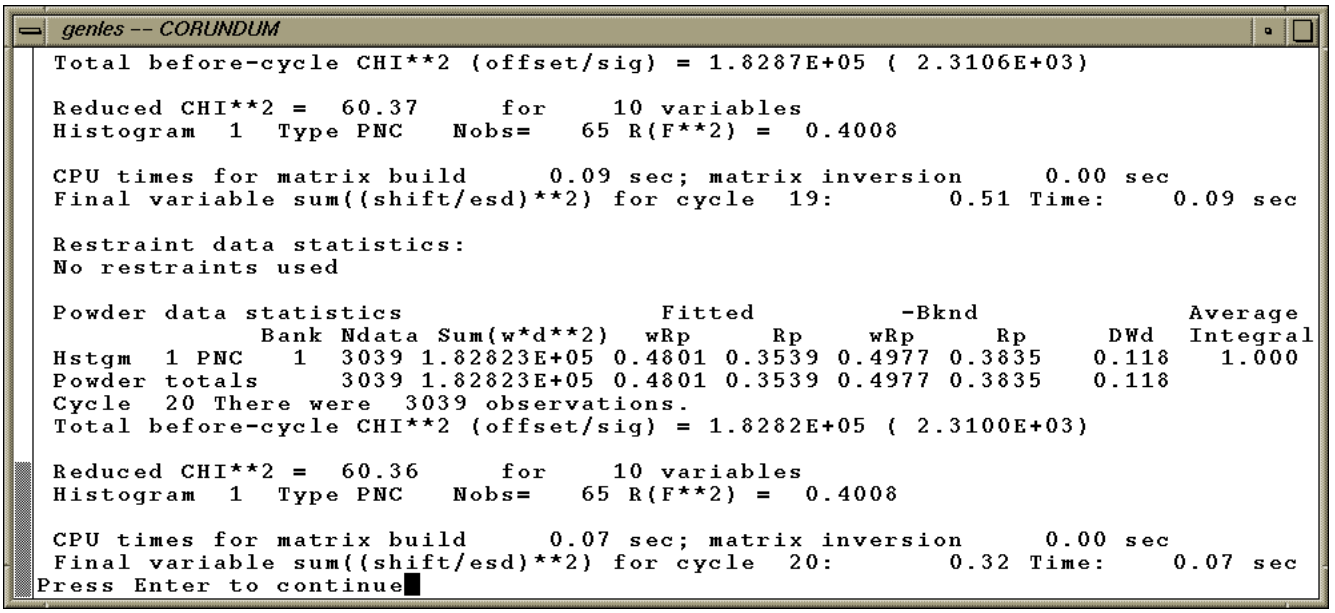
The diffractometer zero correction refinement flag is found on the histogram panel, as seen below. Click on the check box for the zero correction near the middle of the window to refine the parameter.



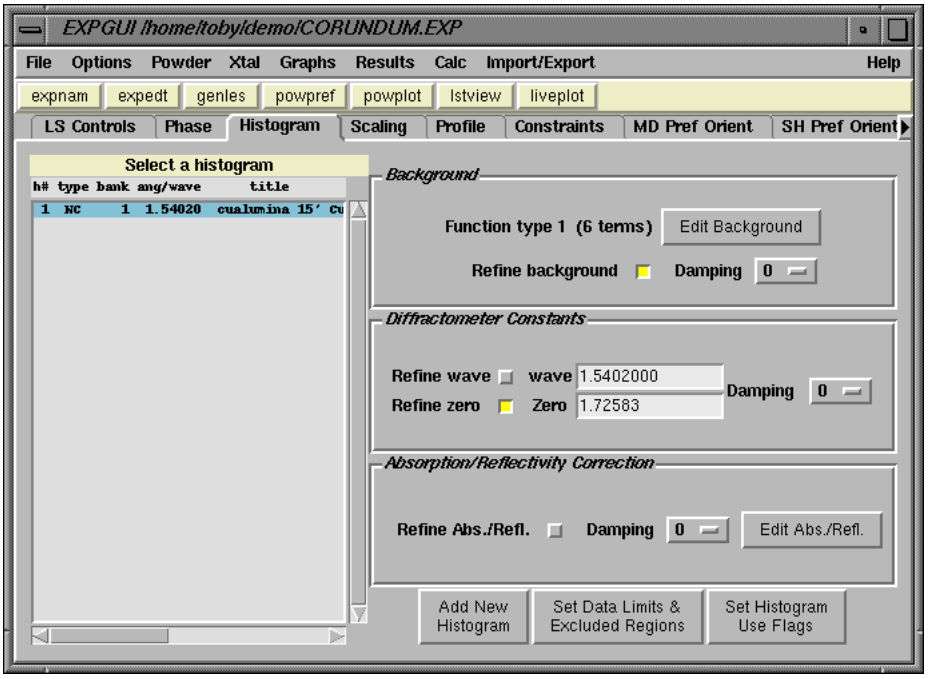

*Note that the diffractometer zero correction is refined for parallel beam instruments, such as neutron and synchrotron diffractometers. It should not be used for Bragg-Brentano instruments (laboratory flat-plate parafocussing instruments). For Bragg-Brentano instruments, instead the sample displacement parameter (shft) should be refined instead. When needed, for Bragg-Brentano instruments, the sample transparency correction (trns) may also be refined.*

---

When GENLES is run, as shown below, a small but significant improvement is seen in the agreement factors.

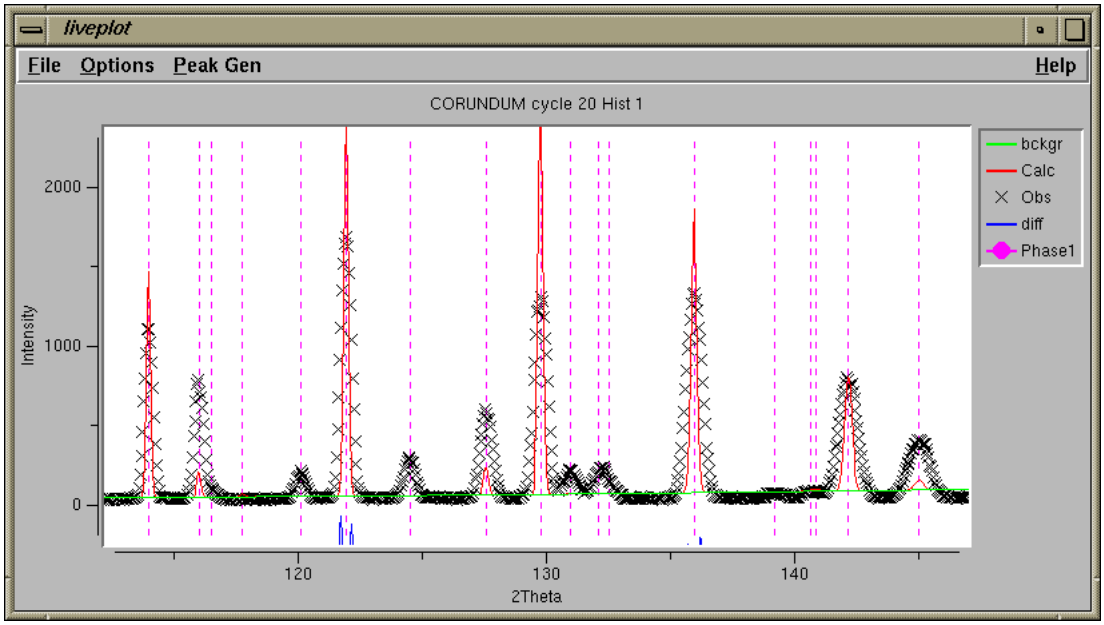



Note that the zero correction has refined from the starting value of 0.04 (0.0004 degrees two-theta) to 1.73 (0.0173 degrees two-theta). This small correction is needed to obtain a good fit and accurate lattice parameters.




# GSAS/EXPGUI Alumina tutorial (part 9)
# Initial Fitting of Profile Parameters

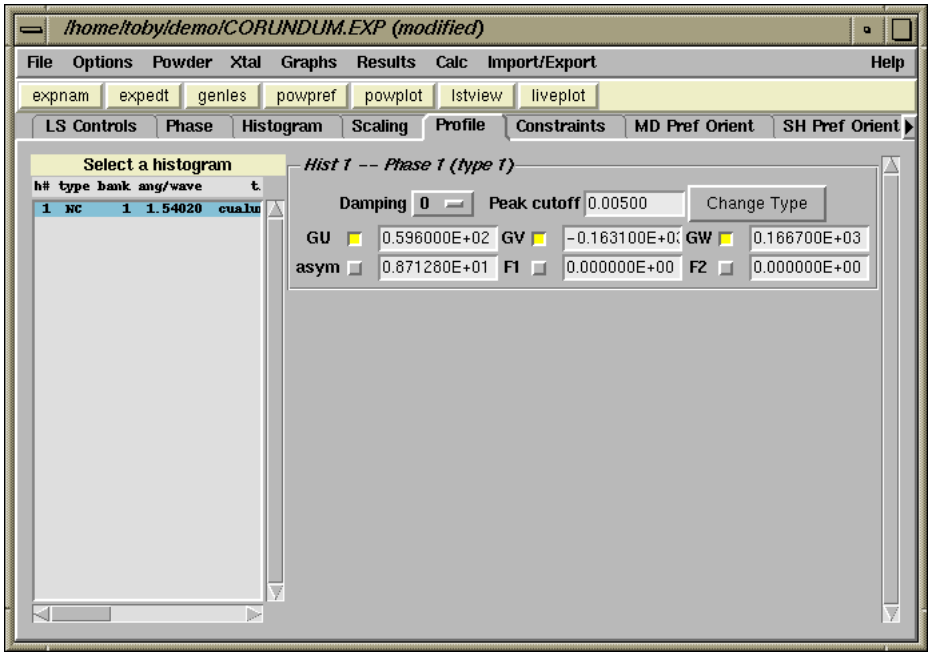
After the unit cell is fit, the next step is typically to improve the crystallographic model if the profile is well-fit. In this case, however, we cannot do that since the high-angle peaks are much broader than the calculated pattern. This is demonstrated clearly in the LIVEPLOT output shown below.




*The plot above shows several problems that need to be addressed by refining parameters. As noted before, the observed peaks are significantly broader than the calculated, this is addressed by optimizing the peak shape parameters. Also, the relative intensities in the calculated pattern does not match the observed intensities, this can potentially be addressed by refinement of coordinates and, to a lesser extent, individual displacement (temperature) parameters. It is also worth noting that the computed background is too high at higher two-theta values. This may be improved by refinement of the background when the peak intensities are better fit or may require the addition of more background parameters. In any case, neither the coordinates or the background can be effectively optimized until a reasonable fit is obtained for the peak shape.*

---

In the Profile panel shown below, the three Gaussian peak width terms (GU, GV & GW, also known as the Cagilloti terms U, V & W), are added to the refinement.



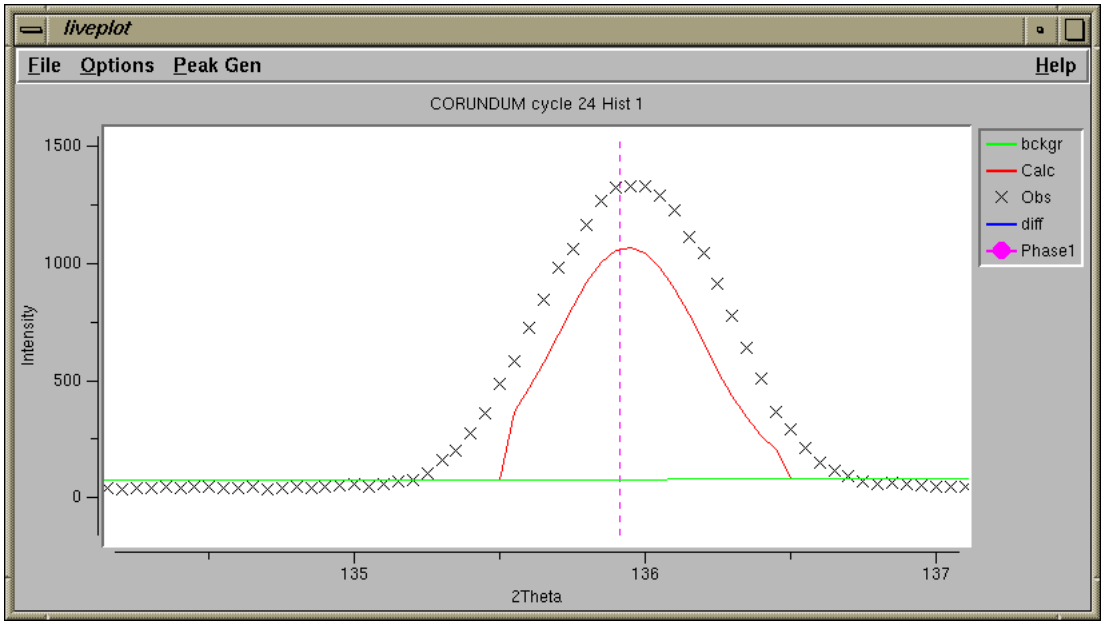

---

After the flags are set for the profile terms, the GENLES program is rerun. At this point, the fit improves considerably.

```
genles -- CORUNDUM
 Total before-cycle CHI**2 (offset/sig) = 1.3222E+05 ( 1.6607E+03)

 Reduced CHI**2 =   43.69      for     13 variables
 Histogram   1   Type PNC    Nobs=    65 R(F**2) =  0.3707

 CPU times for matrix build      0.08 sec; matrix inversion      0.00 sec
 Final variable sum((shift/esd)**2) for cycle  25:        0.17 Time:     0.08 sec

 Restraint data statistics:
 No restraints used

 Powder data statistics                    Fitted          -Bknd              Average
              Bank Ndata Sum(w*d**2)   wRp      Rp     wRp      Rp      DWd  Integral
 Hstgm  1 PNC    1  3039 1.32216E+05 0.4083 0.3080 0.4107 0.3297    0.080    0.971
 Powder totals      3039 1.32216E+05 0.4083 0.3080 0.4107 0.3297    0.080
 Cycle  26 There were  3039 observations.
 Total before-cycle CHI**2 (offset/sig) = 1.3222E+05 ( 1.6607E+03)

 Reduced CHI**2 =   43.69      for     13 variables
 Histogram   1   Type PNC    Nobs=    65 R(F**2) =  0.3714

 CPU times for matrix build      0.09 sec; matrix inversion      0.00 sec
 Final variable sum((shift/esd)**2) for cycle  26:        0.03 Time:     0.09 sec
Press Enter to continue
```

---

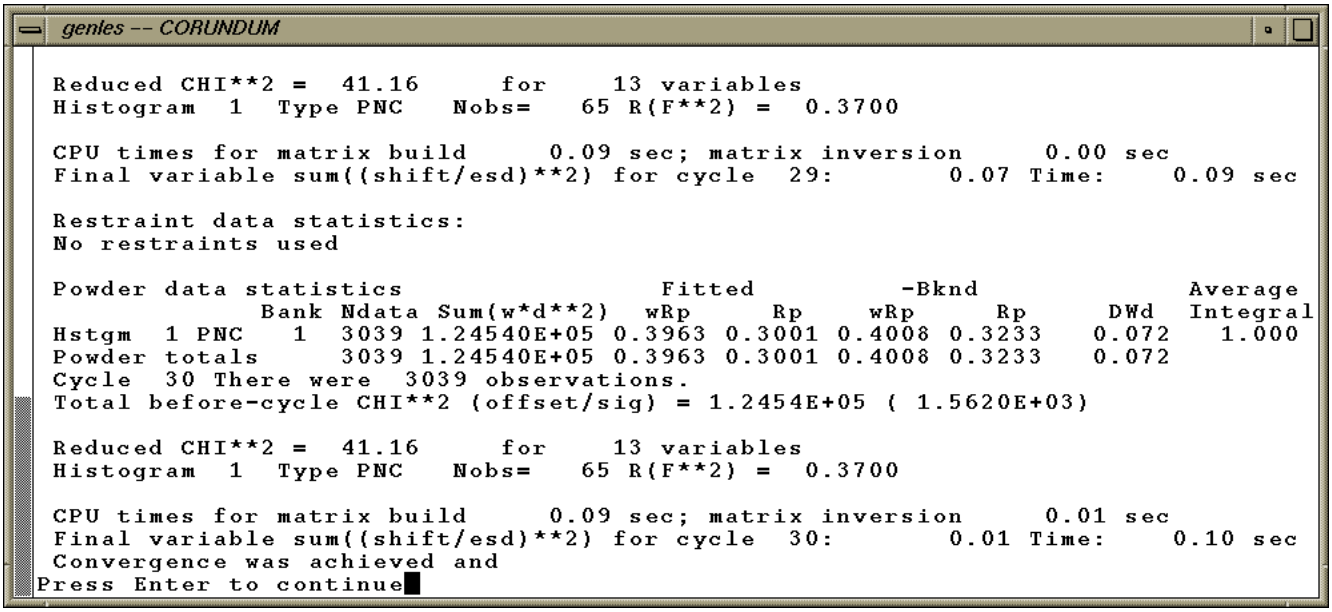
If the fit is examined closely at this stage with LIVEPLOT (as shown below), it can be seen that the peaks at high angle appear to be trucated on each side. This is due to the fact that the peak profiles have gotten much broader, but POWPREF has not yet been rerun, so not enough data points are included in the computation.



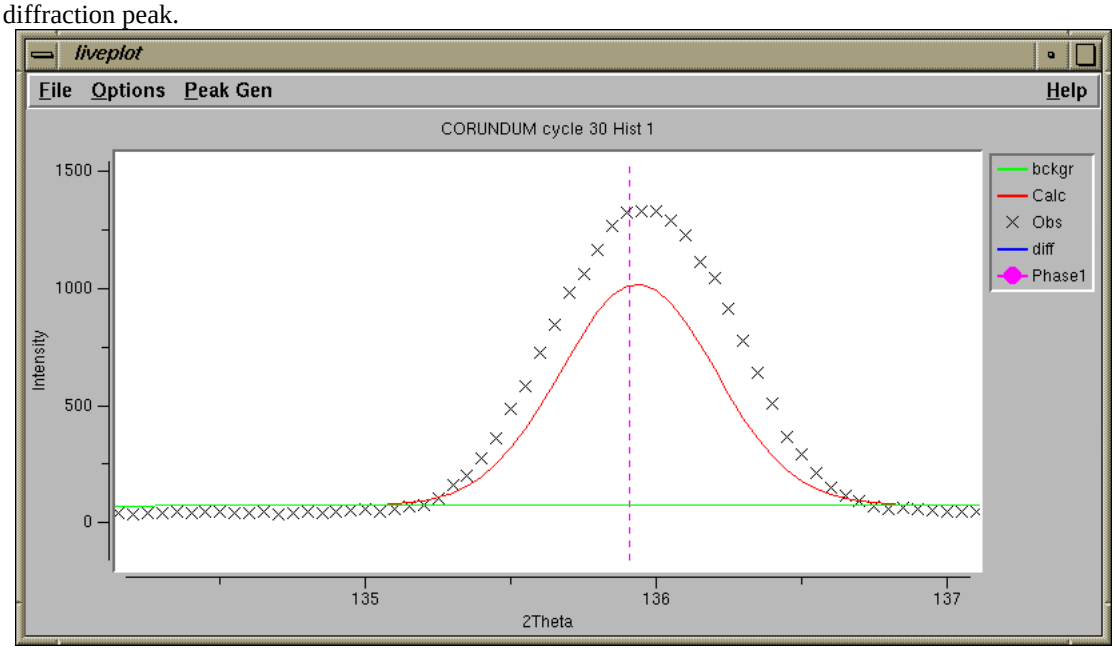

*This sort of problem occurs fairly commonly for neophyte GSAS users. The way to avoid this is to remember to rerun POWPREF after any significant change in the lattice parameters, zero correction or peak profile terms. Also be sure to run POWPREF after adding phases, histograms or changing the excluded regions.*

---

Run POWPREF and then GENLES again. Note that still more improvement is seen in the Chi-squared and R-factors.



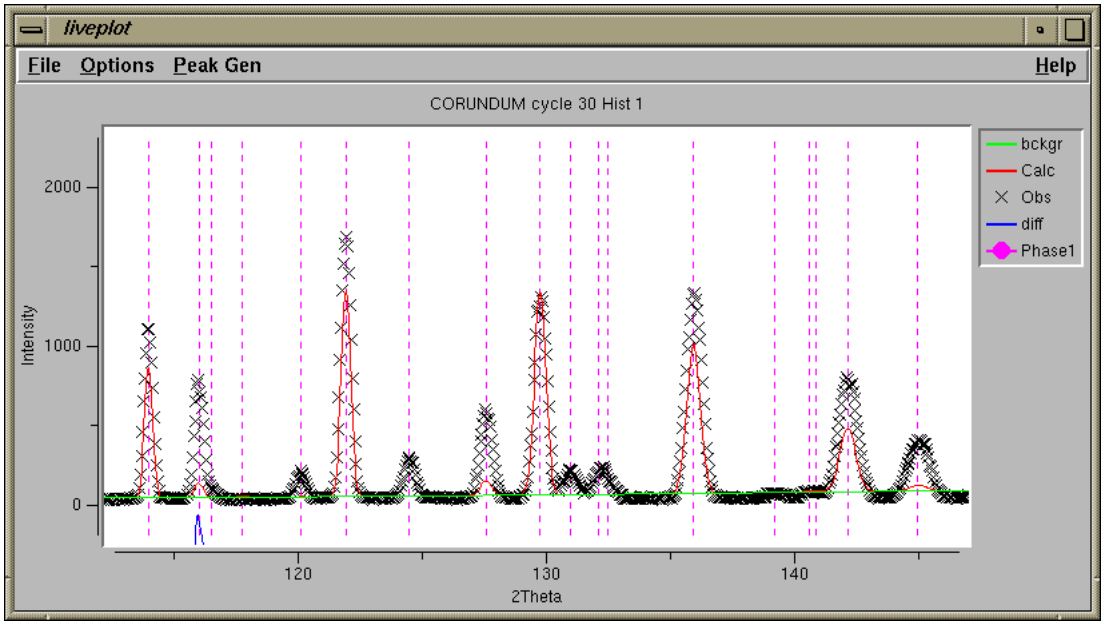

Now LIVEPLOT shows a normally-shaped diffraction peak.



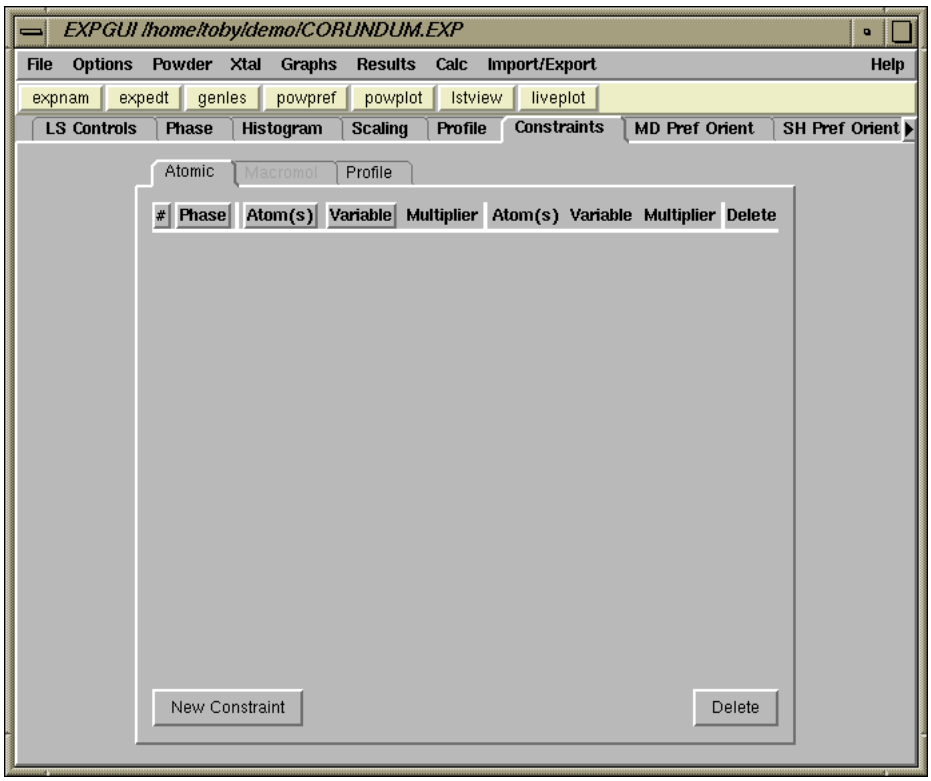

# GSAS/EXPGUI Alumina tutorial (part 10)
# Group $U_{iso}$ parameters & Refine coordinates and Overall $U_{iso}$.

At this stage in the refinement we have a good fit for the experimental parameters, but need to improve the crystallographic model. To reduce the number of parameters needed in the initial stages of this part of the process, we will define a constraint that requires a single overall $U_{iso}$ value for all atoms.

Note that at this stage in the refinement, the peak shape agrees well, but there are significant differences between the observed and computed intensities. This implies that the crystallographic model is in some way inadequate.



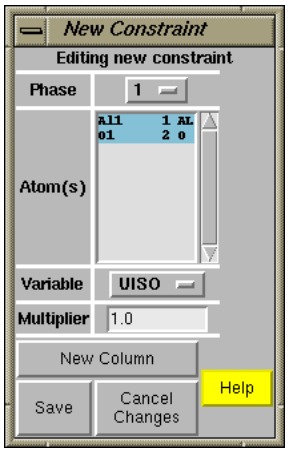

To group atoms so that they share a single atomic displacement parameter (displacement parameter is the preferred name for "temperature factor"), the parameters need to be constrained together. The Constraints panel allows constraints to be defined to link parameters together. At present EXPGUI allows constraints to be created for atomic parameters and for profile terms. GSAS implements many other types of constraints, but they must be accessed via the GSAS EXPEDT program. Press the "New Constraint" button at the bottom of the window to create a new constraint on atomic parameters.




*While it is not needed in this case, in many projects it is best to refine an overall displacement parameter in the initial refinements for this parameter. In many refinements, there simply are not sufficient data to allow every atom to have an independently refined displacement parameter, in these circumstances, it is useful to group atoms together so that chemically similar atoms are constrained to have the same displacement parameter values.*

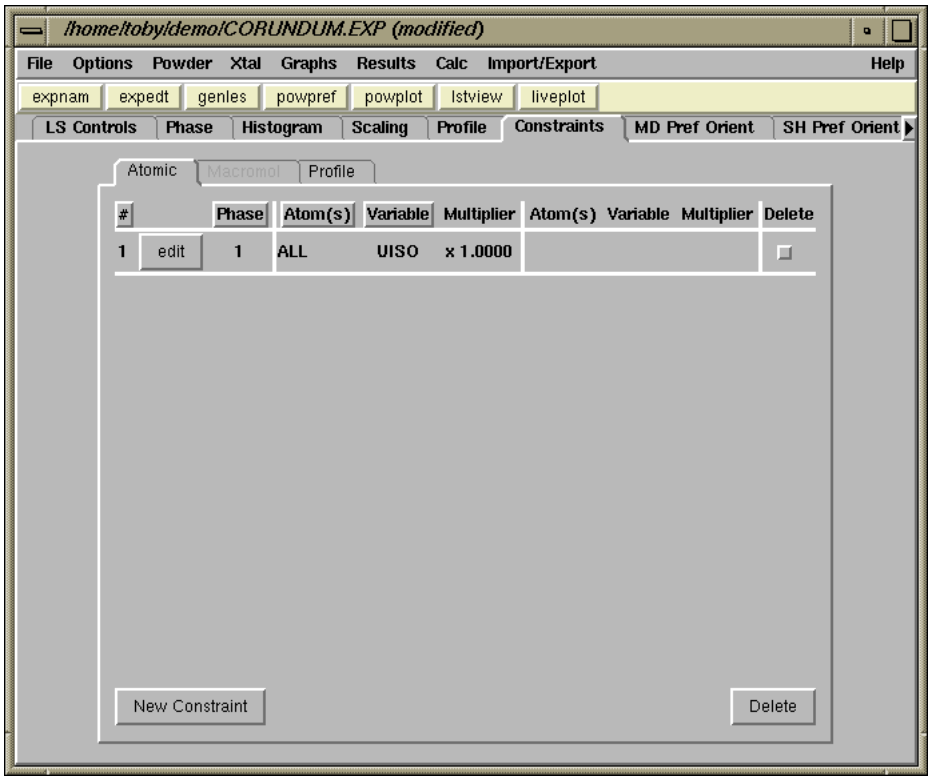
*It should be noted that these constraints do not actually require that the parameters have the same value. In fact, the constraints require that the shifts that applied in future refinement cycles have their ratios defined by the constraint values. Thus, for parameters to be contrained to be equal, the parameters must start at the same value as well as have the constraint ratio set to 1.*

After pressing the "New Constraint" button, the window to the right is created. From top to bottom, the phase is selected as phase 1 (there is no other choice in this example), both atoms are selected (to select a range of atoms use a mouse "drag" or hold the control key while clicking the [left] mouse button; selecting all atoms can also be done by press the right mouse button. Finally select UISO for the parameter, leave the multiplier as 1 and press "Save"



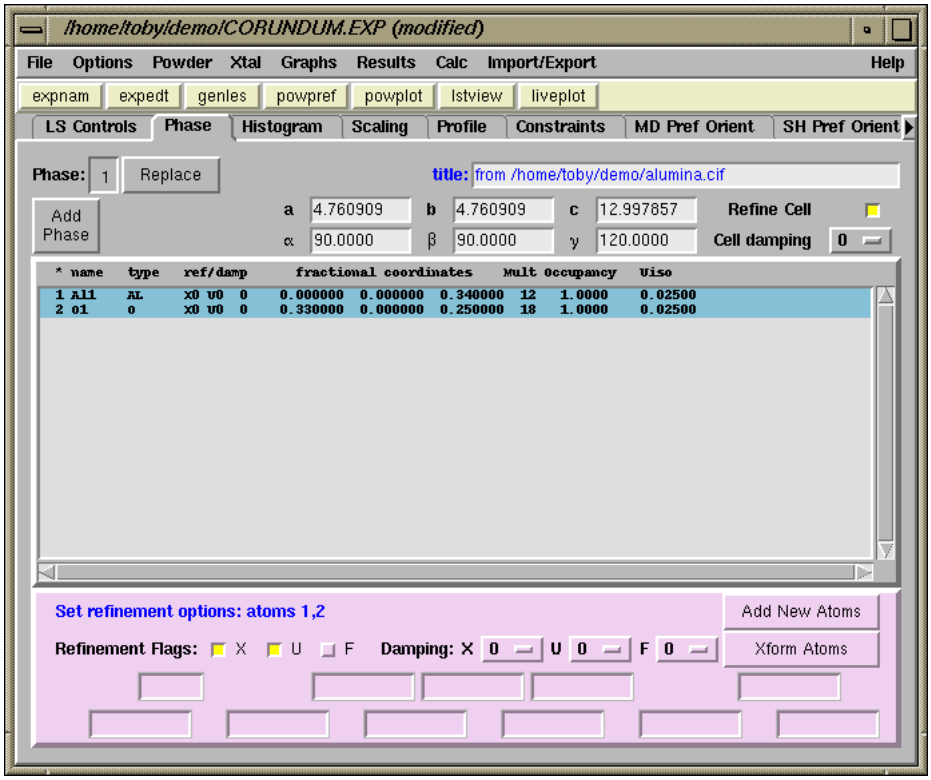

---

The Constraints panel now shows the constraint created in the previous step, as seen below.

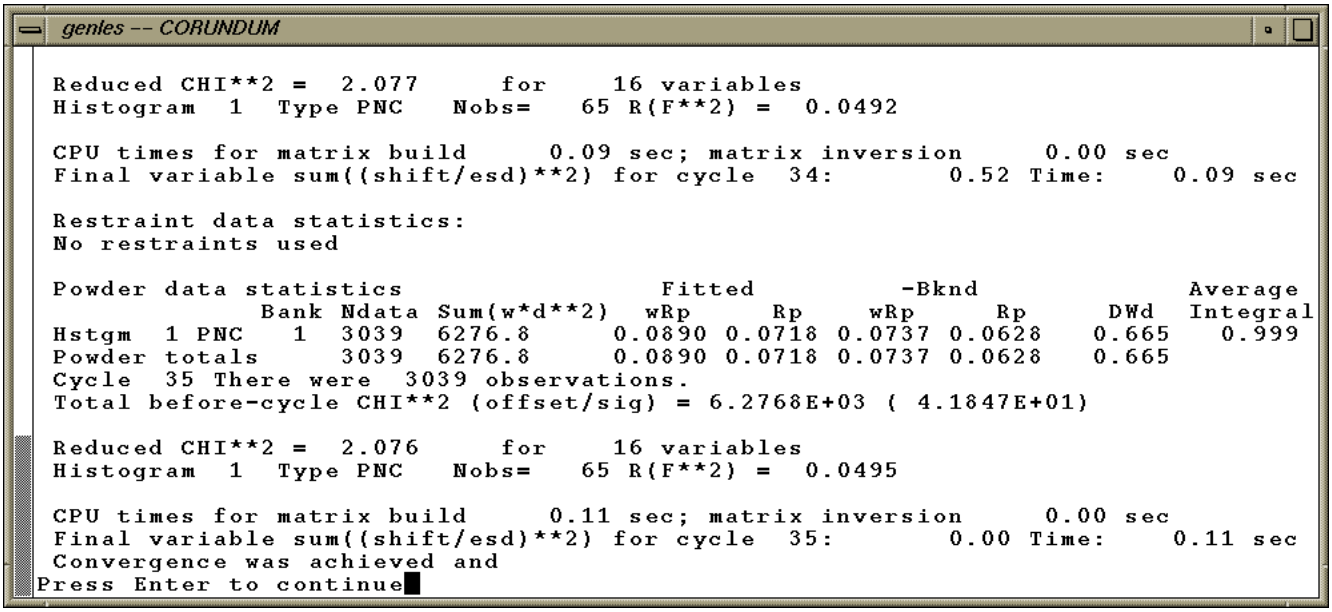



---

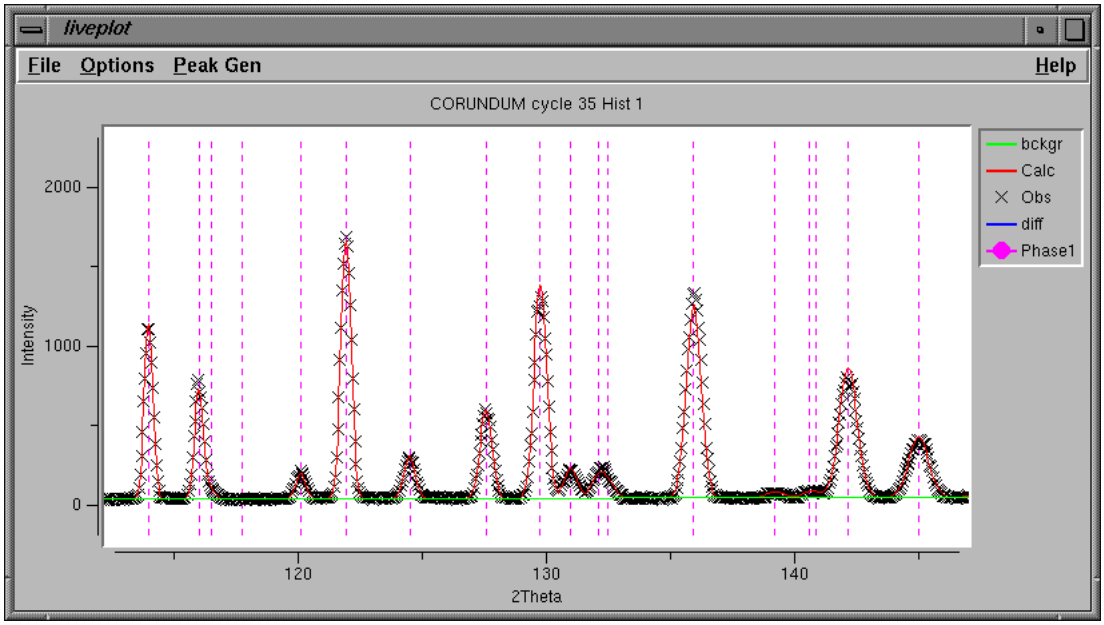
Now we are ready to set the refinement flags for the atoms on the Phase panel. Select both atoms in the list using the mouse. Select the X flag (near the bottom of the panel), this means refine x, y and z, as allowed by symmetry. Since the Al atom is on a special position, (0,0,z), only the z coordinate will be changed. Likewise the O atom is at a (x,0,1/4) position and only the x coordinate will be changed. Also select the U flag to refine the displacement (temperature) parameter for the two atoms. The previously defined constraint will be applied automatically.




Refinement of these three atomic parameters has a enormous impact on the quality of the fit, as seen by the improvement in the agreement seen in the GENLES run below.




The LIVEPLOT output shows a tremendous improvement in the agreement as well.



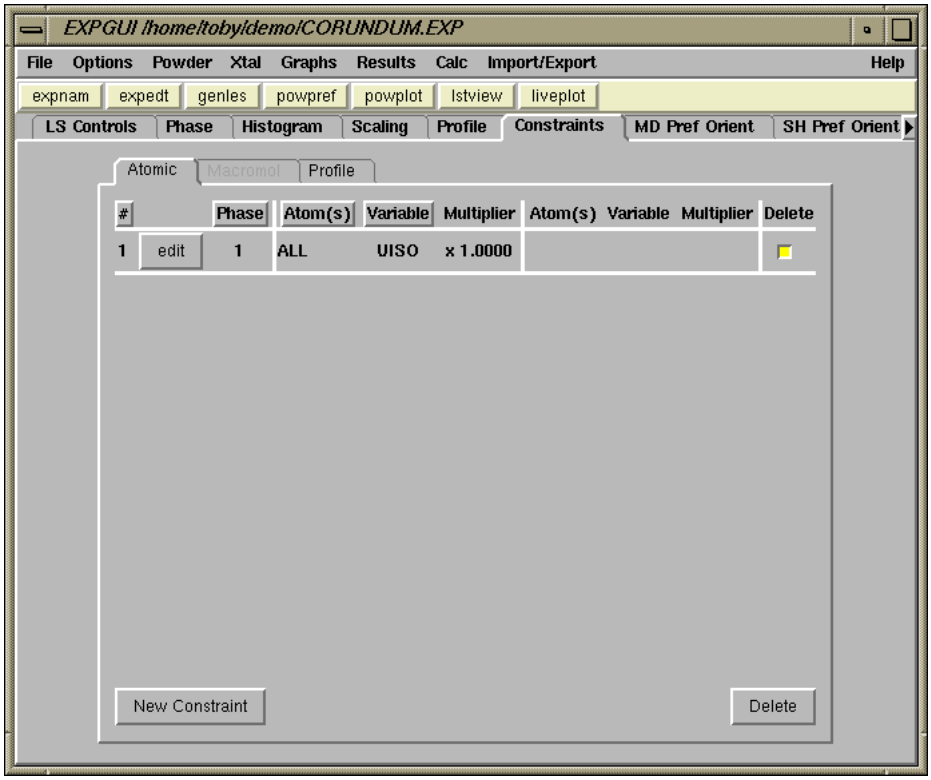

# GSAS/EXPGUI Alumina tutorial (part 11)
# Finishing Up

In the previous refinement steps we obtained quite good agreement between the computed pattern and the observed diffraction data, with a $Chi^2$ value of 2. CW neutron data have very regular peaks shapes and can often provide significantly better fits. Improving the fit allows perhaps slightly better values for the derived parameters, but more importantly offers smaller error estimates (standard uncertainties).

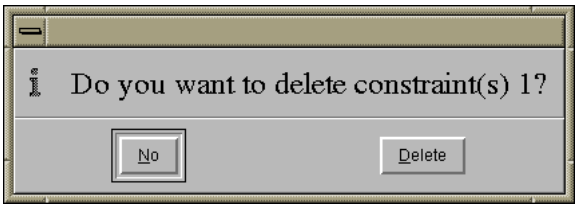
In this final step we will allow each atom to have independent $U_{iso}$ parameter, we will add more background terms, and we will switch the profile function to use the Finger-Cox-Jephcoat asymmetry parameter, which does a better job of modeling low-angle asymmetry.

---

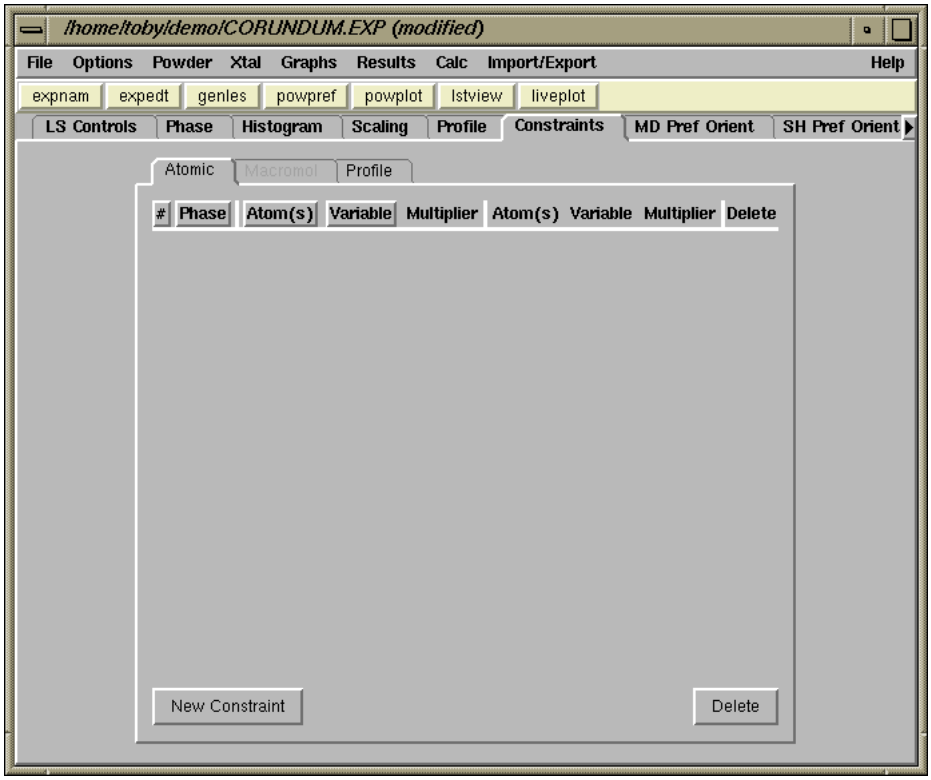
To delete the displacement factor constraint, go to the Constraints panel, and select the Delete check button to the right of the constraint, as shown below. Then press the "Delete" button below it, near the bottom of the window.




The program then prompts, as shown to the right, to confirm deleting the constraint.

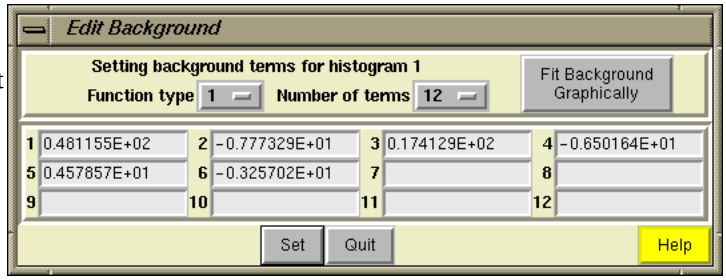



The constraint no longer appears in the panel, as shown below.



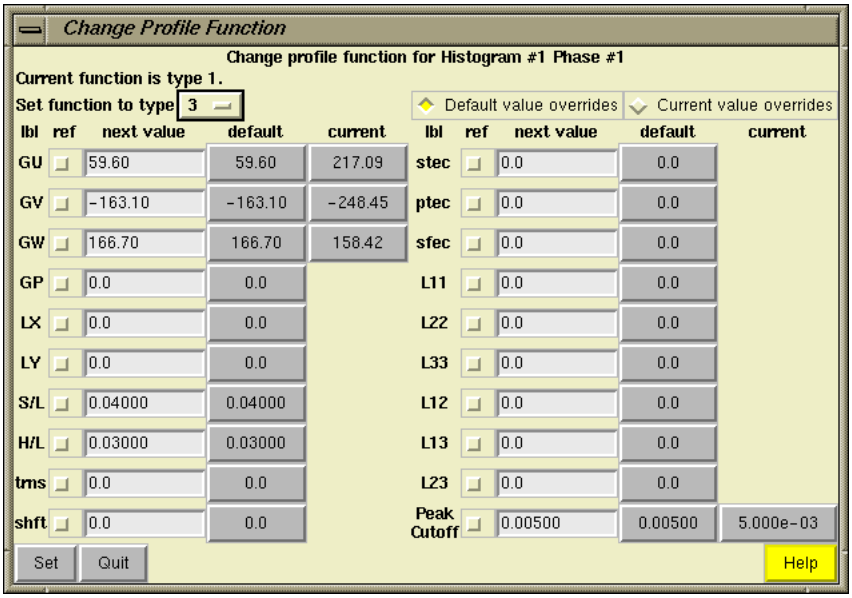

---

To increase the number of background terms, select the Histogram panel, and press the "Edit Background" button, as was done in part #4. The window to the right is then created. Click on the "Number of terms" pull-down menu and select 12 terms.




---

To change the profile function, go to the Profile panel and press the "Change Type" button. This opens a window where the function can be selected and where the starting value for each profile parameter can be set. Set the function type to 3 and see how the number of terms expands to what is seen below.




*Note that the instrument parameter file usually contains default values for the various profile terms. The values constitute the*

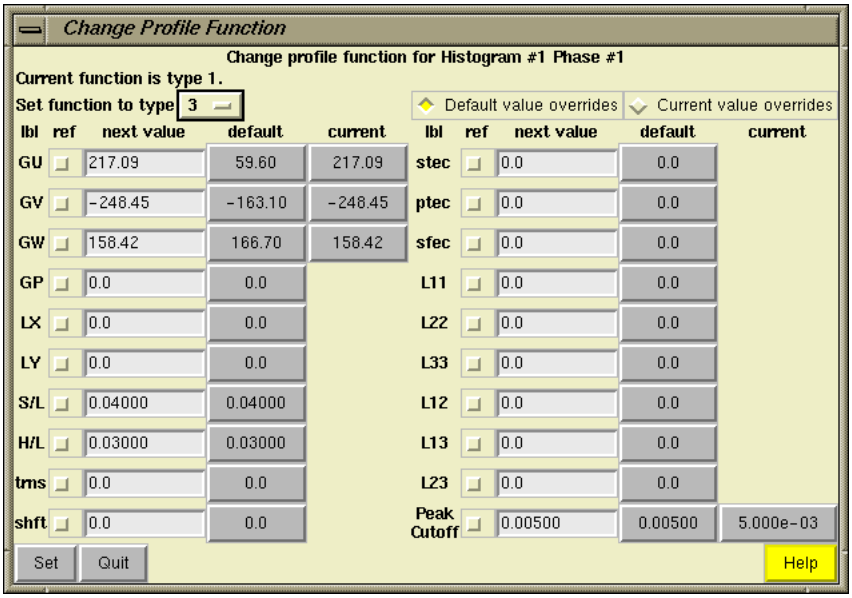
*left-hand columns of buttons. Where two terms are used the same way in different profile functions, the previous value is shown in the right-hand column.*

*The profile functions are described in detail in the GSAS documentation. For the CW neutron and x-ray functions, the functions can be summarized as follows:*

- *Type 1: Simple Gaussian peak shapes, poor asymmetry correction; appropriate for CW neutrons only.*
- *Type 2: Pseudo-Voight function, poor asymmetry correction; good for refinements where low-angle peaks are not significant*
- *Type 3: Similar to type 2, except this includes the Finger-Cox-Jephcoat asymmetry correction. Good even with significant low angle peaks.*
- *Type 4: Similar to type 3, except this includes the Stephens model for anisotropic strain broadening (where different classes of reflections have different widths).*

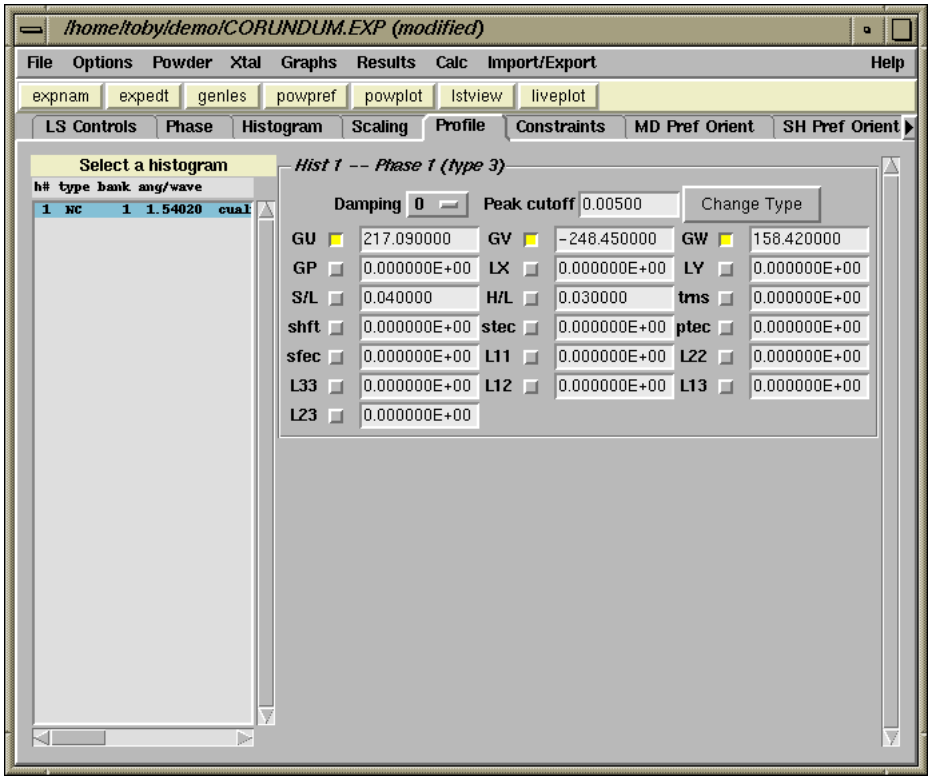
---

As is shown below, press on the "Current" button for GU, GV and GW, to change the starting values for those parameters to what was obtained previously, rather than the values in the instrument parameter file.

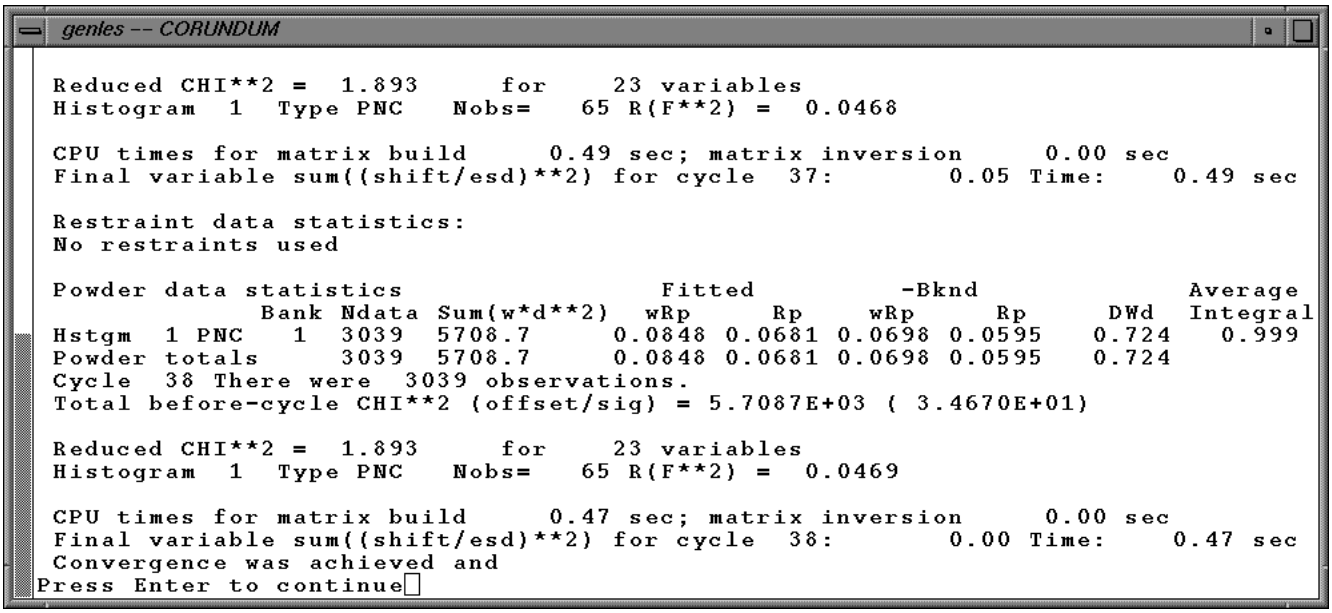



---

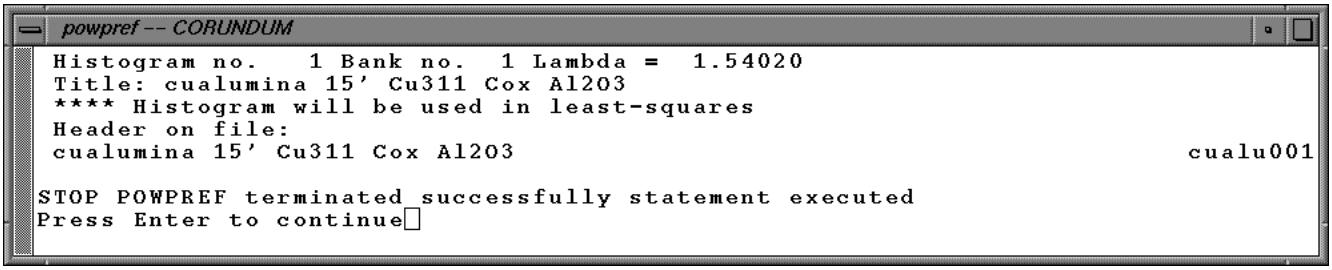
Again select GU, GV and GW for refinement in the Profile panel, as below.




With these extra parameters, the refinement converges with still better values for the agreement factors, as seen below.



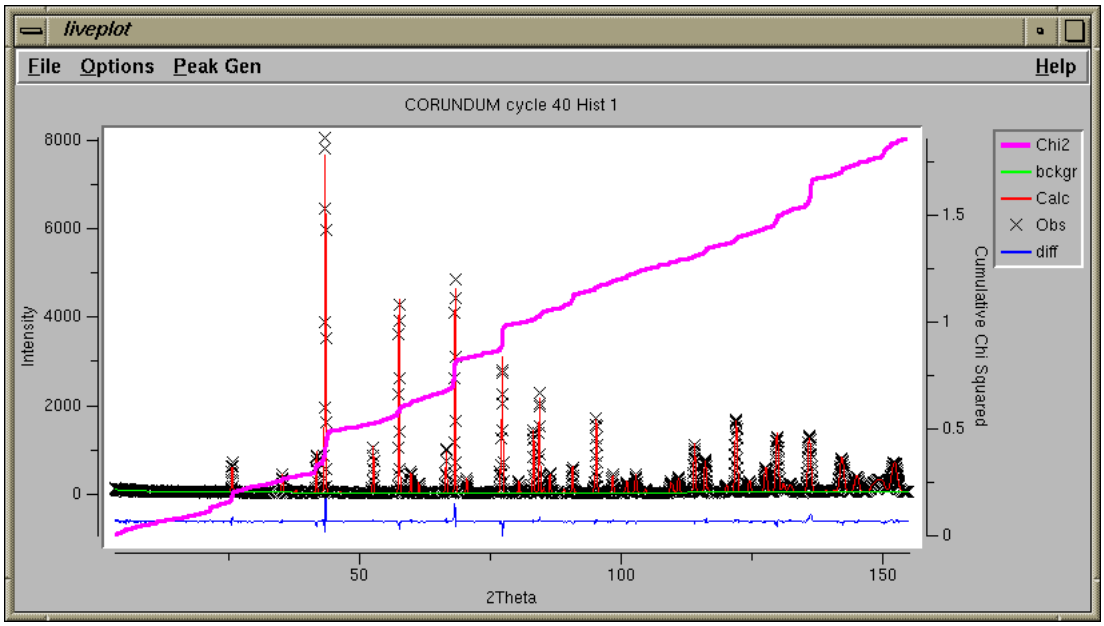

Since the diffractometer constants and profile terms have been changed, POWPREF should be run again.



The Chi$^2$ and Rwp improve even more when GENLES is run, indicating that the previous run of POWPREF was needed.

```
genles -- CORUNDUM

 Reduced CHI**2 =  1.876      for     23 variables
 Histogram  1  Type PNC   Nobs=   65 R(F**2) =  0.0470

 CPU times for matrix build     0.51 sec; matrix inversion     0.01 sec
 Final variable sum((shift/esd)**2) for cycle  39:       1.06 Time:    0.52 sec

 Restraint data statistics:
 No restraints used

 Powder data statistics                  Fitted          -Bknd              Average
              Bank Ndata Sum(w*d**2)  wRp     Rp     wRp     Rp      DWd  Integral
 Hstgm  1 PNC   1  3039  5659.0     0.0845 0.0678 0.0697 0.0594   0.726    1.000
 Powder totals     3039  5659.0     0.0845 0.0678 0.0697 0.0594   0.726
 Cycle  40 There were  3039 observations.
 Total before-cycle CHI**2 (offset/sig) = 5.6590E+03 ( 3.4030E+01)

 Reduced CHI**2 =  1.876      for     23 variables
 Histogram  1  Type PNC   Nobs=   65 R(F**2) =  0.0471

 CPU times for matrix build     0.55 sec; matrix inversion     0.00 sec
 Final variable sum((shift/esd)**2) for cycle  40:       0.00 Time:    0.55 sec
 Convergence was achieved and
Press Enter to continue
```

The resulting fit is quite good. By turning on "Cumulative Chi-squared" in the Options menu, the purple line diagonal line is shown. This highlights the worst fit areas of the pattern in terms of their impact on the weighted profile r-factor (Rwp) or in Chi$^2$.




*The Cumulative Chi-squared plot was first demonstrated by W. I. F. David at the Accuracy in Powder Diffraction Meeting-III (2001) (See the LIVEPLOT documentation for more information. The line would have a constant slope (slope=1), if all regions of the data are fit at the statistically expected level. The areas where the Cumulative Chi-squared has a much greater slope are regions that have poorer fits.*

This concludes this tutorial exercise. This has been a simple problem, in that the coordinates have few degrees of freedom and the refinement is quite stable, but it should illustrate many of the steps to be followed in most Rietveld fits.

Comments, corrections or questions: crystal@NIST.gov
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