Tutorial: Crystal structure refinement of oxalic acid dihydrate using GSAS

The aim of this tutorial is to use GSAS to locate hydrogen in oxalic acid dihydrate and refine the crystal structure. By no means is it intended to provide a general receipe for structure refinement nor is it claimed the suggested route here is the best possible and only one to take. It serves as a mere example how it can be done. Oxalic acid dihydrate crystallises in the monoclinic space group P $2_1/n$ with lattice parameters a = 6.1143Å, b = 3.5870Å, c = 12.0109Å and β = 106.127°. The chemical composition is $(COOH)_2 \cdot 2H_2O$. GSAS originally is driven from a DOS prompt. However, a more modern version uses a graphical user interface EXPGUI to specify most of the input needed. Before starting EXPGUI and GSAS create a new folder called e.g. "Oxalic acid" on the C drive of your computer.

In order to get started double-click on the EXPGUI icon shown in Figure 1.

Fig. 1: EXPGUI icon – double click.

The following start-up screen appears (Fig. 2):

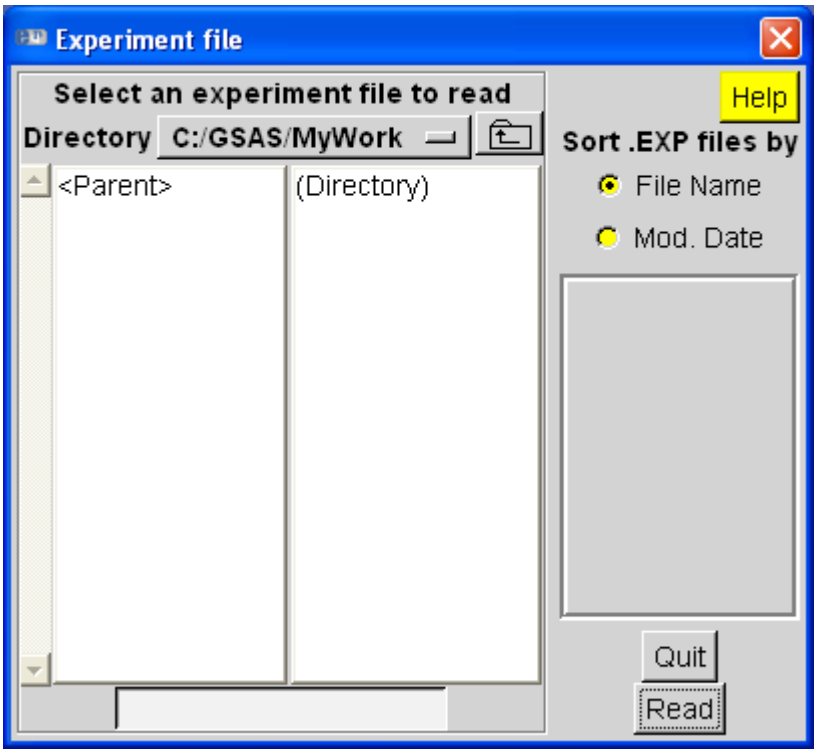

Figure 2: EXPGUI startup screen.

Select the directory you just created and type a job name in the text field at the bottom, e.g. 'Oxalic' (Figure 3) and press the 'Read' button.

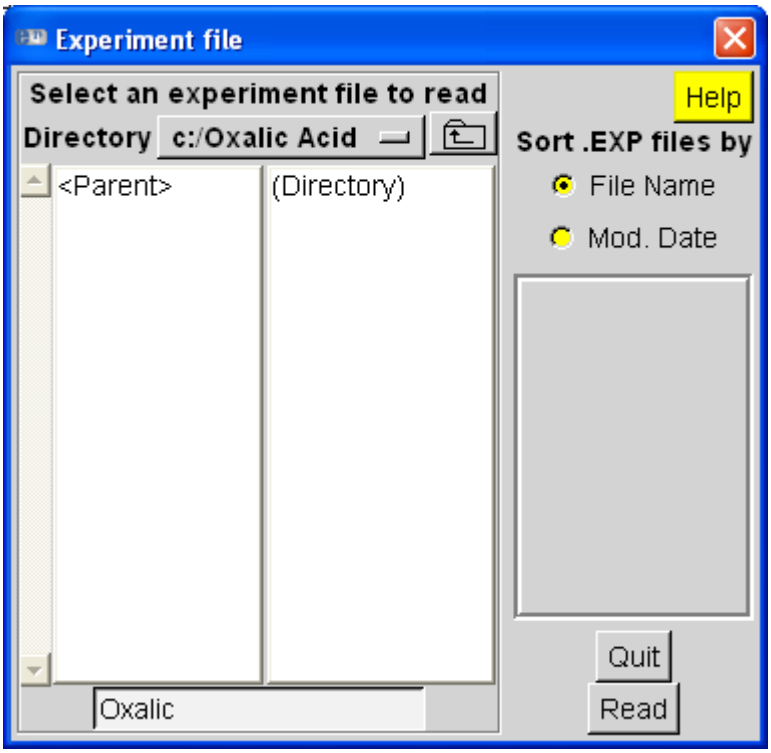

Figure 3: Select the 'C:/Oxalic Acid' folder and specify 'Oxalic' as the job name of this tutorial.

EXPGUI will next complain that it could not find a file with this name and offers the option to either select a different file or create a new file with this name. Since we would like to do the latter, press the 'Create' button (Fig. 4).

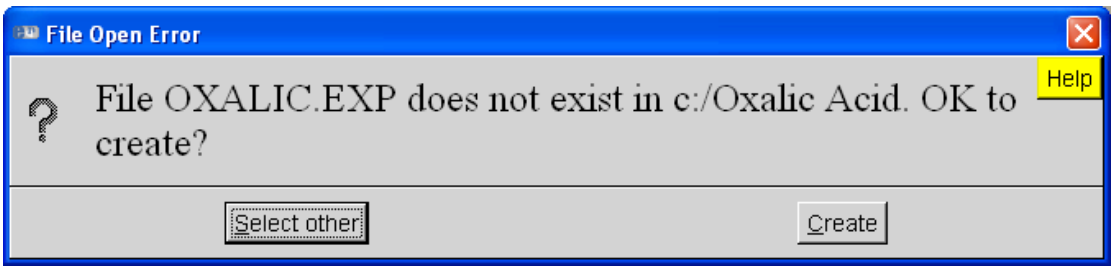

Figure 4: Select 'Create'.

Another window might pop up due to using a space in the file path. Simply ignore it and press 'Continue' (Fig. 5).

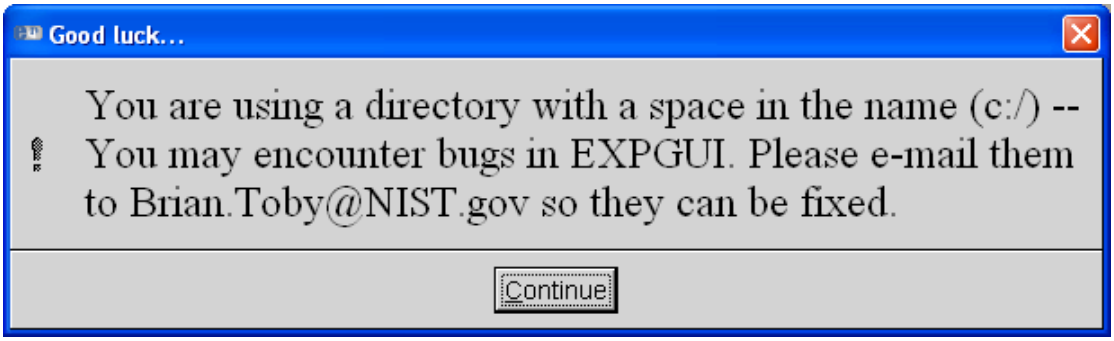

Figure 5: Press 'Continue'.

You are now to enter a title for this exercise. Any title is fine. As a suggestion you may type ‘Oxalic acid dihydrate at 300 K from SXD’ (Fig. 6).

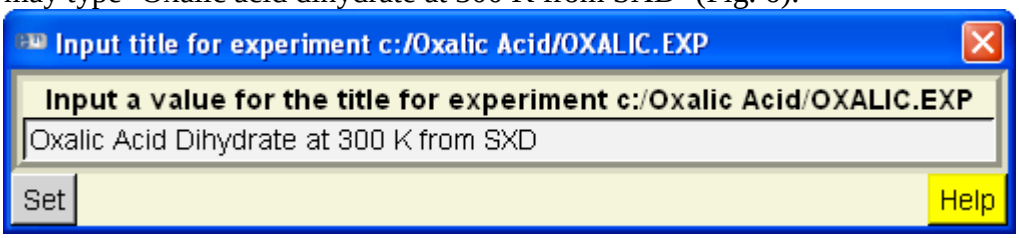

Figure 6: Specify a title and click ‘Set’.

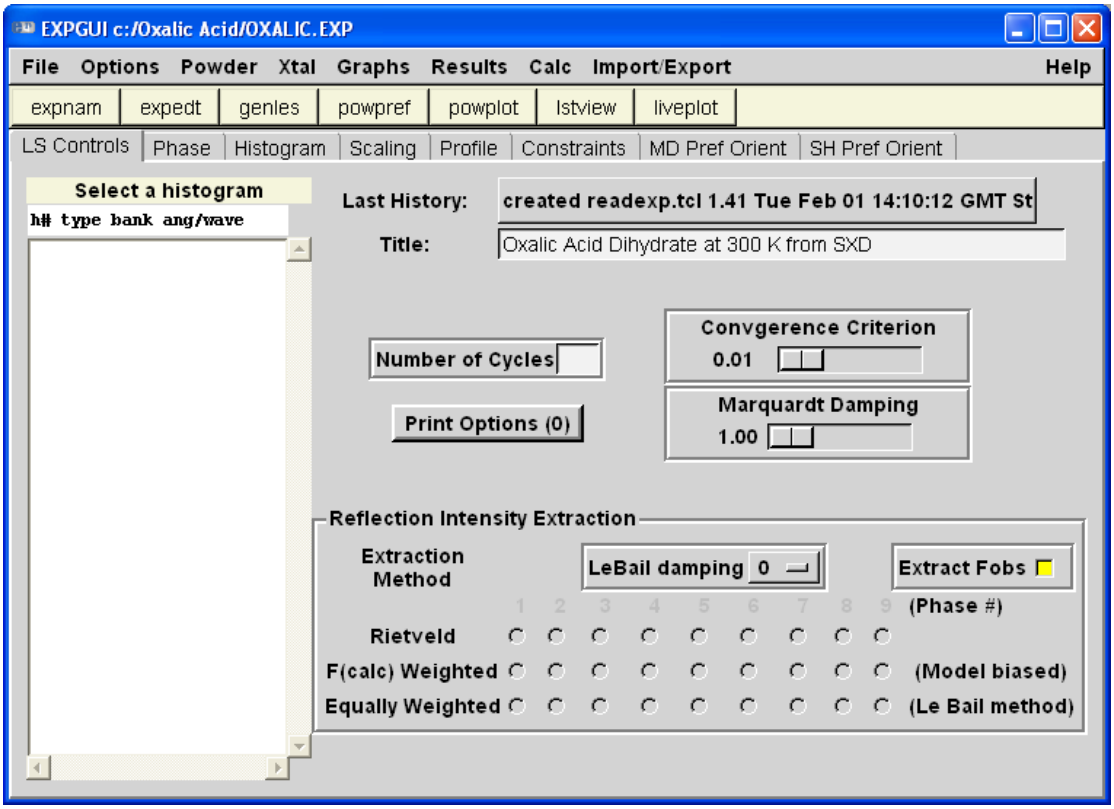

Figure 7: EXPGUI in its full glory.

The main EXPGUI should now appear on the screen (Figure 7). EXPGUI has mainly been made as an interface for inputting most of the parameters for powder diffraction data. However, internally it does have the option to also refine single-crystal data from X-rays, constant-wavelength and time-of-flight neutron data.

Parameters that cannot be accessed from within the GUI usually can be accessed from the command-line based EXPEDT. One such input is the specification of the space group and lattice parameters for a single-crystal refinement. We therefore start EXPEDT by pressing the corresponding button in EXPGUI. A screen similar to the one shown in Figure 8 should appear.

The first question posed to the user is ‘Is this the file you wish to use?’. The default answer to this question is the question mark ‘<?’>. Most menus inside EXPEDT are accessed by specifying a letter to go to the next submenu. In order to see what the options are accept the default selection and simply press the carriage return key <CR>. The question mark usually lists in detail what the options are (Fig. 9).

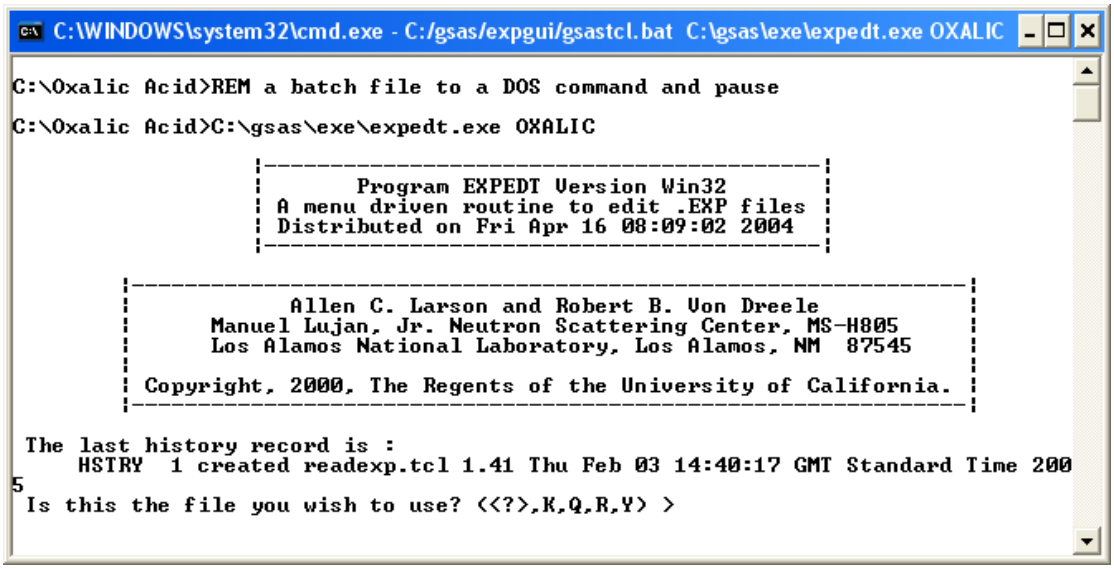

Figure 8: Start-up screen for EXPEDT.

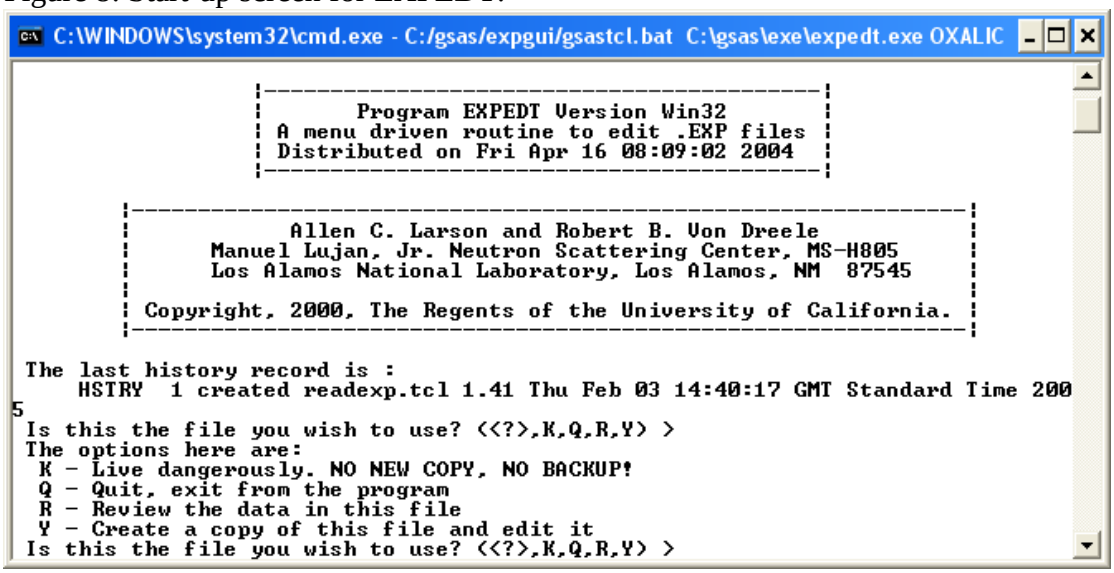

Figure 9: Detailed listing of options after initial start-up of EXPEDT.

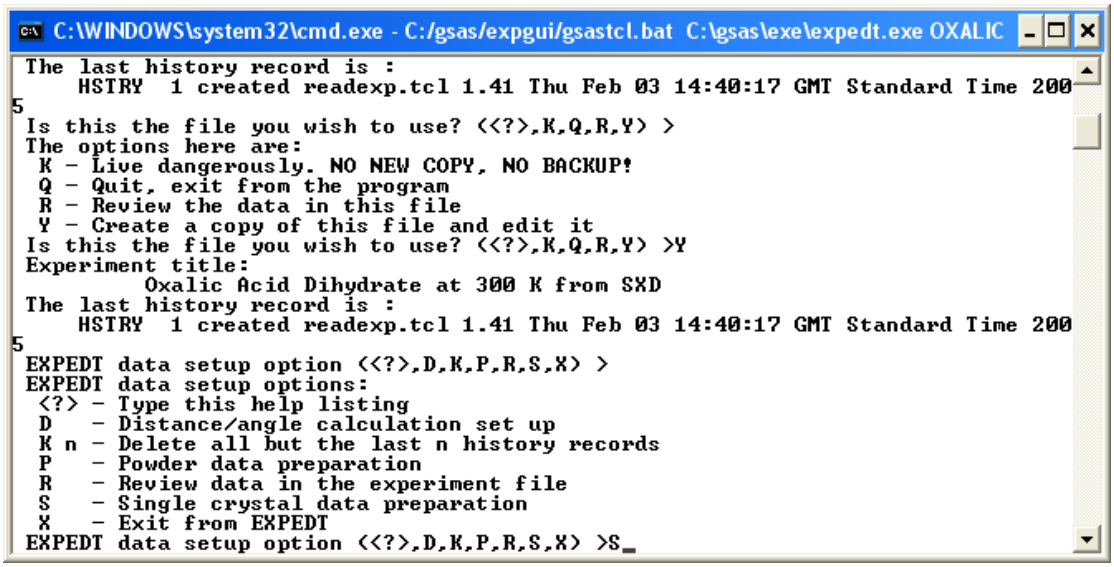

Figure 10: Options in the data setup level of EXPEDT.

Here, we would like to create a copy of this file and edit it. Enter ‘Y’ at the prompt and press <CR>. We are now on the data setup level. Press <CR> to see the options on this level (Fig. 10).

Since, we would like to treat single-crystal data choose ‘S’ for ‘Single crystal data preparation’ and press <CR>.

EXPEDT tells us that there is no phase information as of yet. We are about to change this. Select ‘I’ to insert a new phase (Fig. 11).

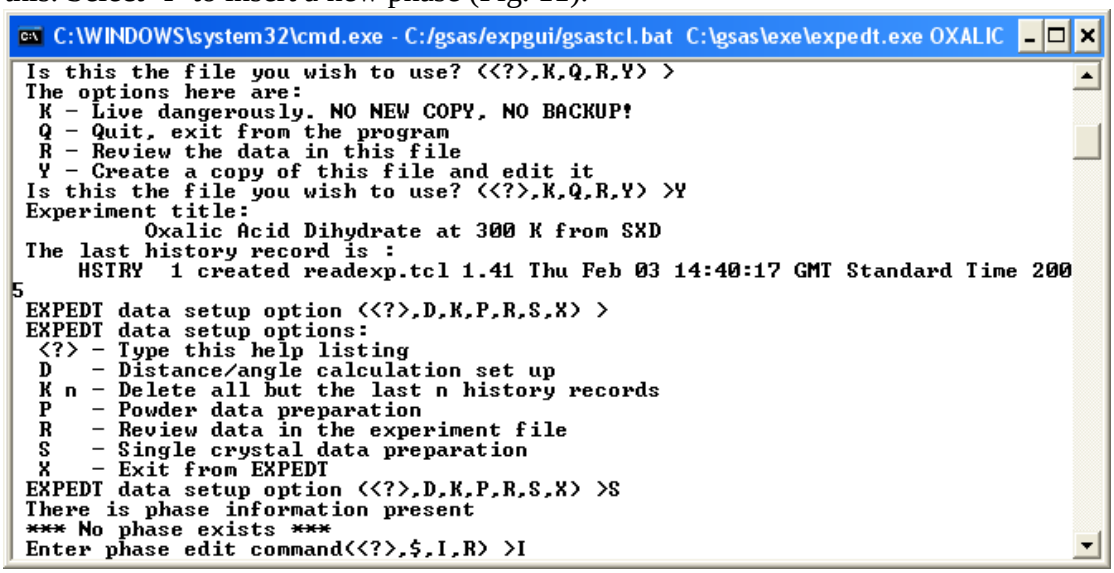

Figure 11: Select ‘I’ to enter a new phase.

First, insert a new title. Something like ‘Oxalic acid dehydrate at 300 K from SXD’ would be appropriate (Fig. 12). Don’t forget to finish with a <CR>.

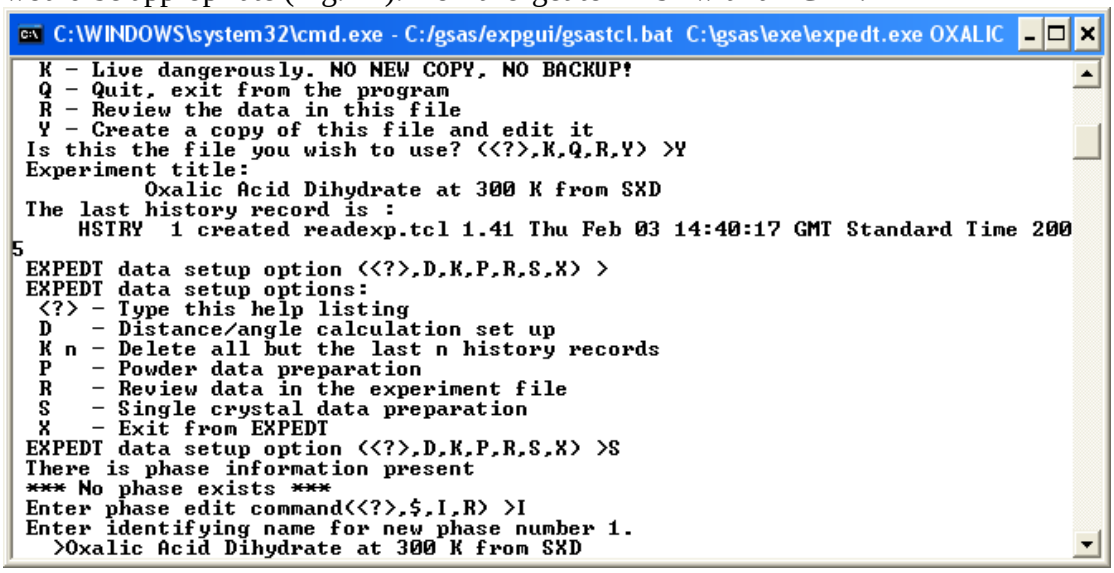

Figure 12: Enter a title and press <CR>.

The space group needs now to be specified. As mentioned in the beginning, oxalic acid dihydrate crystallises in the monoclinic space group P $2_1/n$ (Fig. 13). Be careful when specifying the space group. Omission of spaces may result in the wrong space group being used.

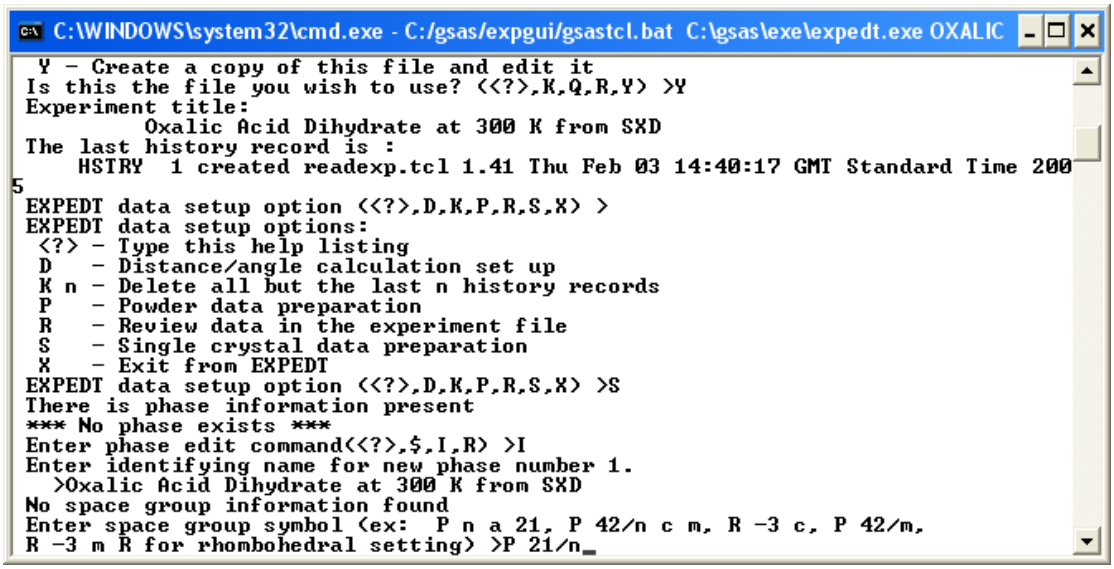

Figure 13: Specification of space group.

EXPEDT recognises the space group as being monoclinic and therefore only asks for a, b, c, and the angle β of the unit cell. Just as a reminder, these values are a = 6.1143Å, b = 3.5870Å, c = 12.0109Å and β = 106.127˚ (Fig. 14).

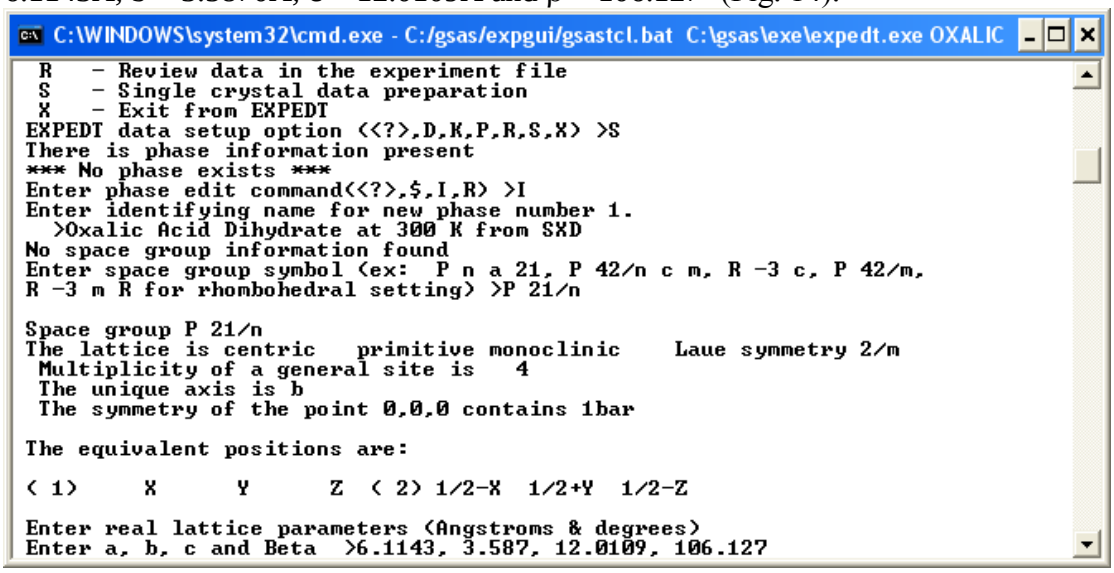

Figure 14: Input of lattice parameters.

EXPEDT computes the unit cell volume. If we knew the error estimates on the lattice parameters this information could be inserted using the ‘S’ submenu to enter the standard deviation on the lattice parameters. For now, we will leave this option. This concludes the specification of the lattice parameters and the unit cell and thus, we will quit EXPEDT. This can be done by entering ‘X’ for Exit followed by <CR>. Entering ‘X’ generally takes the user back to the previous level and so to completely exit EXPEDT ‘X’ needs to be entered on every level until the DOS window says ‘Press any key to continue’ (Fig. 15). Do exactly as suggested. The main EXPGUI window should now reappear (Fig. 16). By using EXPEDT to enter the space group and lattice parameters a file called ‘Oxalic.exp’ has been edited invisible to the user. This ‘.EXP’ file is the master file for the crystal structure refinement and care should be taken not to accidentally delete it as this may mean to start again from the beginning. EXPGUI notices that the content of the file ‘Oxalic.exp’ has been altered and thus asks whether

we would like to use the new version or restore the previous. Select ‘Load new’ as indicated in Fig. 16.

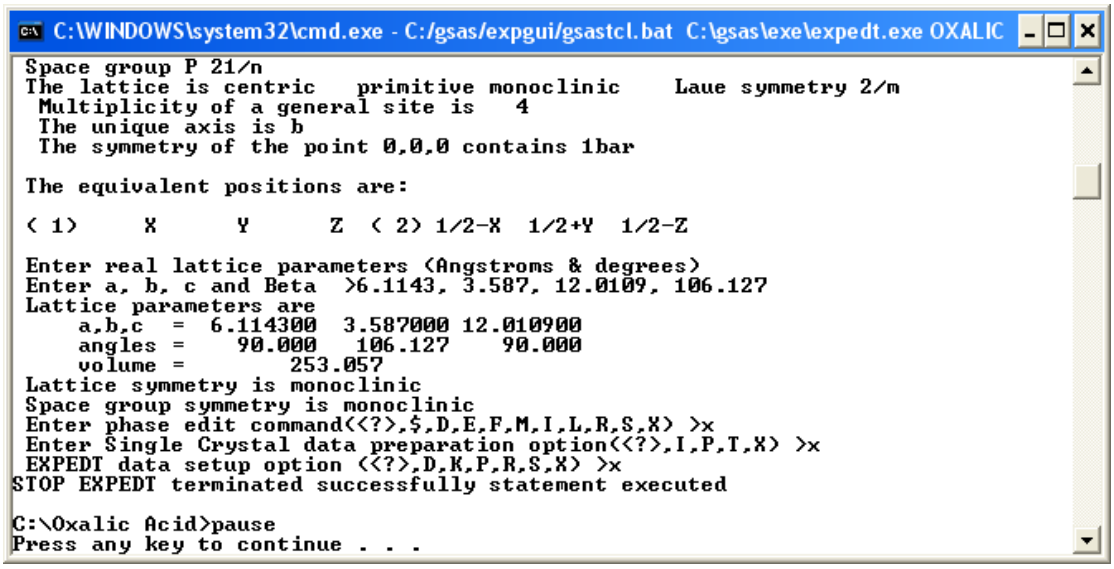

Figure 15: Just about to exit EXPEDT.

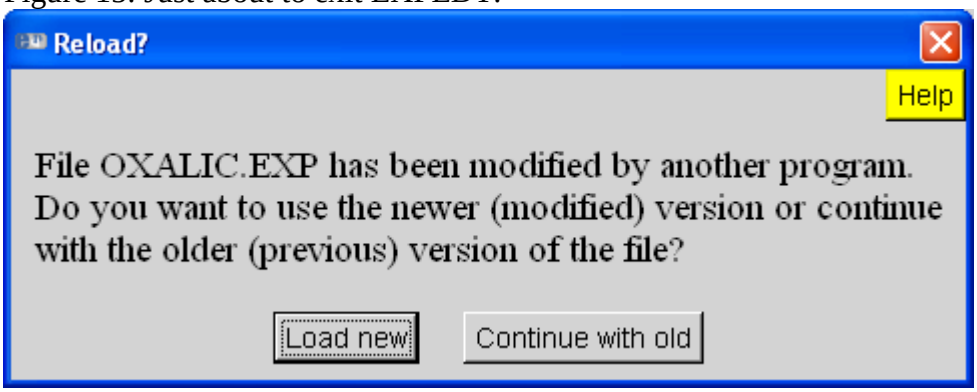

Figure 16: Select ‘Load new’.

To view the lattice parameter information click on the ‘Phase’ tab of EXPGUI. The lattice parameters appear as shown in Figure 17.

Before continuing with EXPGUI and GSAS, we need to prepare the SXD data. The crystal has been measured at five different omega settings (orientations) for about 1 hour at each setting. The temperature was close to 300 K. The raw data have been indexed and integrated using SXD2001. However, we still need to calculate the absorption correction and convert the files to GSAS histograms. To perform the absorption correction start SXD2001, load the ‘SXDII.instr’ file and click the ‘Calc. corrections’ button (Fig. 18).

A GUI similar to the one shown in Figure 19 should appear. The quantities to be specified by the user are the scattering and absorption cross section *per atom* and the number density in units of $Å^{-3}$. Information about the cross sections can be found on the internet at http://www.ncnr.nist.gov/resources/n-lengths/. They are summarised in table I.

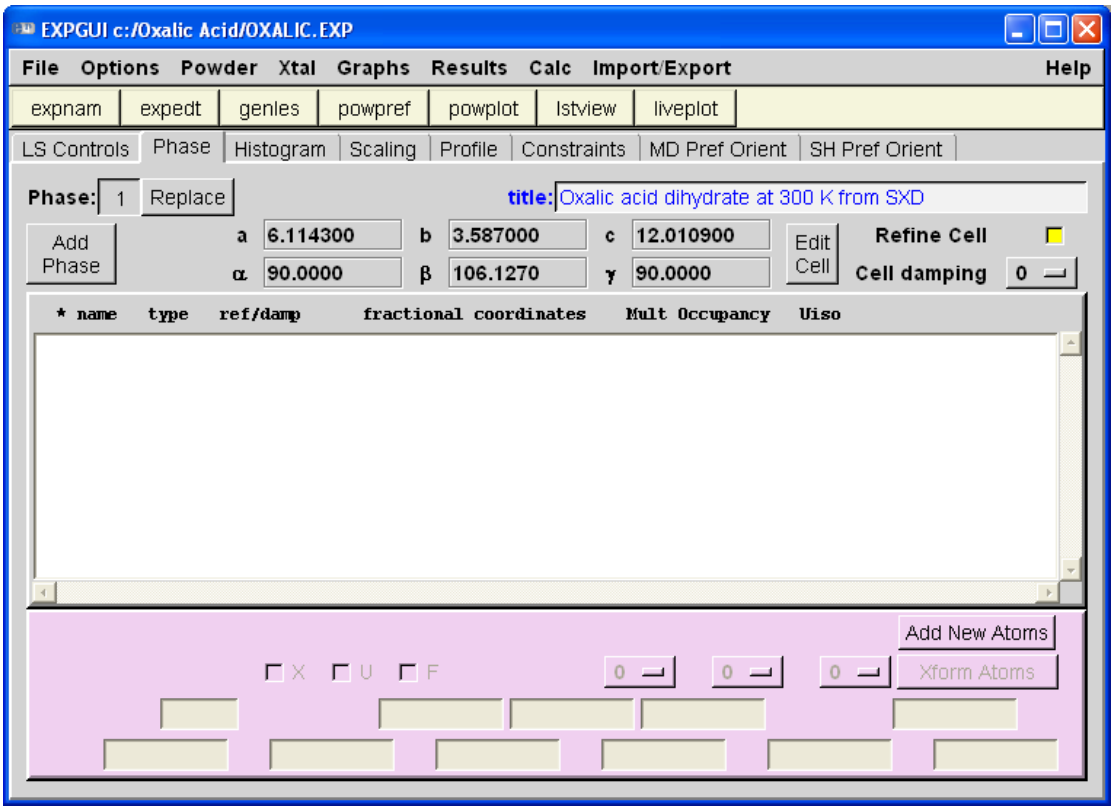

Figure 17: Appearance of the 'Phase' information after completing EXPEDT.

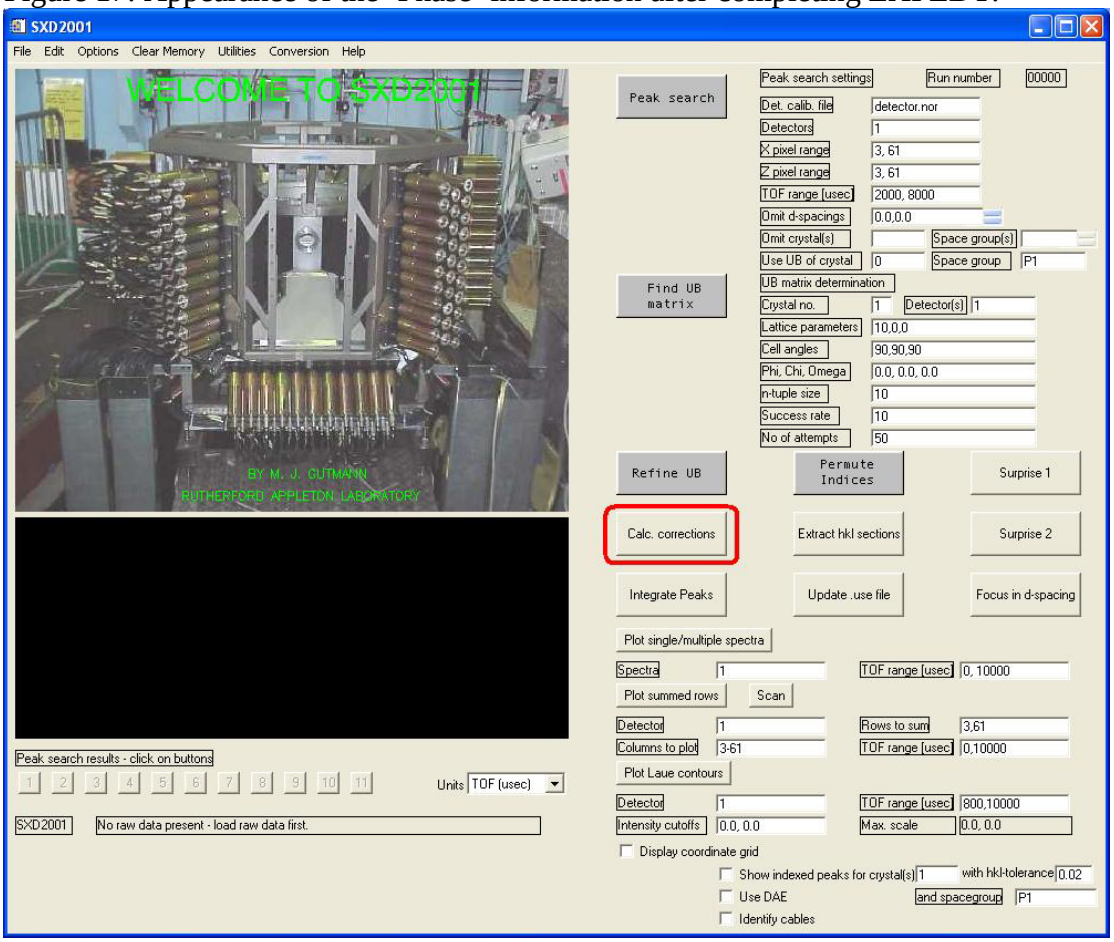

Figure 18: SXD2001 main GUI. The location of the 'Calc. corrections' button is indicated.

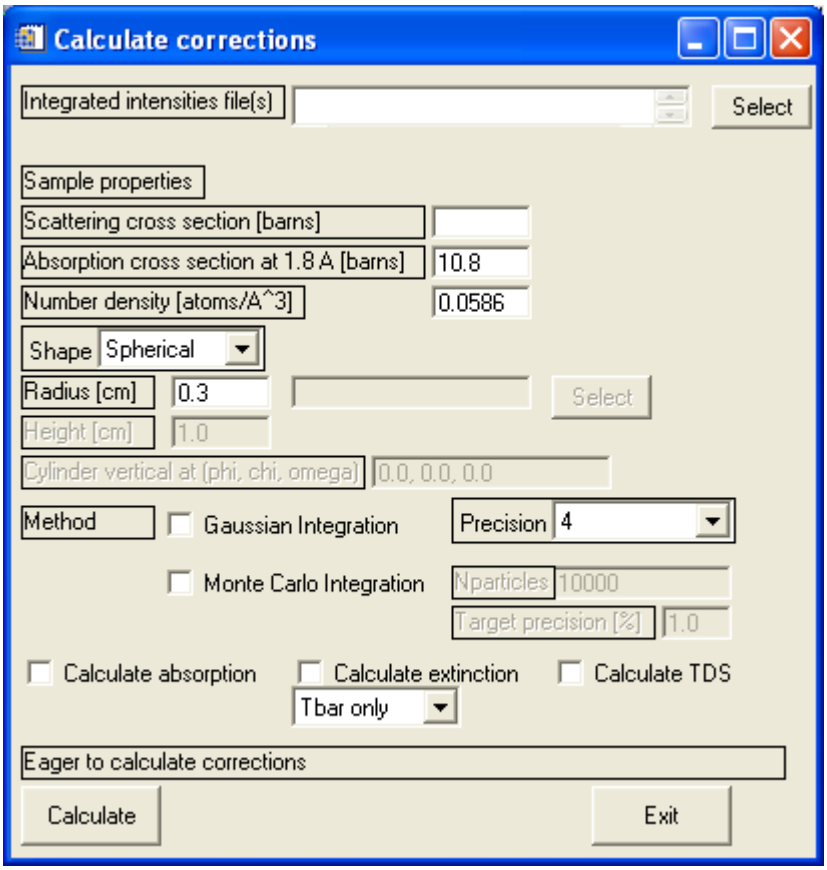

Figure 19: Initial appearance of the calculate corrections GUI.

Table I: Scattering and absorption cross sections of C, O and H (values taken from http://www.ncnr.nist.gov/resources/n-lengths/).

Element	Scattering cross section [barns]	Absorption cross section at 1.8 Å [barns]
H	82.02	0.3326
C	5.551	0.0035
O	4.232	0.00019

As can be seen from table I, the scattering cross section, which is the sum of the coherent and incoherent cross sections is very large for hydrogen. This is mainly due to the large incoherent cross section of hydrogen. This large cross section of hydrogen is often causing a large slowly varying background in the diffraction pattern. A way around this would be to replace deuterium for hydrogen. The scattering cross section is nearly independent of the energy, while the absorption cross section varies linearly with wavelength. Thus, this value is usually quoted for neutrons having a wavelength of 1.8Å corresponding to a neutron speed of 2200m/s or a thermal energy of 293 K.

As mentioned in the introduction, the chemical composition of Oxalic Acid Dihydrate is $(COOH)_2 \cdot 2H_2O$. The scattering and absorption cross section per atom are calculated as follows:

$$\sigma_{abs} = \frac{1}{n}\sum_{i=1}^{n}\sigma_{abs}^{i} \qquad (1)$$

$$\sigma_{scat} = \frac{1}{n}\sum_{i=1}^{n}\sigma_{scat}^{i} \qquad (2)$$

where n is the number of atoms in the formula and σ_{abs}^{i}, σ_{scat}^{i} is the absorption and scattering cross section, respectively, for atom i in the chemical formula.

Using the values in Table I compute the absorption and scattering cross section and enter them in the corresponding field in the 'Calc. corrections' GUI. If you need a calculator, Window XP usually supplies one in the 'Start' → 'All programs' → 'Accessories' menu.

Next, we calculate the number density. This number is defined as the number of atoms divided by the unit cell volume. This should be straightforward…(Hint: there are Z = 4 formula units per unit cell). Insert the result in the corresponding text field in the 'Calc. corrections' GUI. The number density can also be derived from the mass density. This is left as an exercise to the reader (Hint: Use Avogadro's number).

Select the intensity files 'sxd17210_1sb.int', 'sxd17211_1sb.int', 'sxd17212_1sb.int', 'sxd17213_1sb.int' and 'sxd17214_1sb.int' using the 'Browse' button in the 'Calc. corrections' GUI (Fig. 20). These files contain the results of the peak integration for the runs sxd17210 – sxd17214 corresponding to the runs for the present compound. For convenience, these files are located on the desktop.

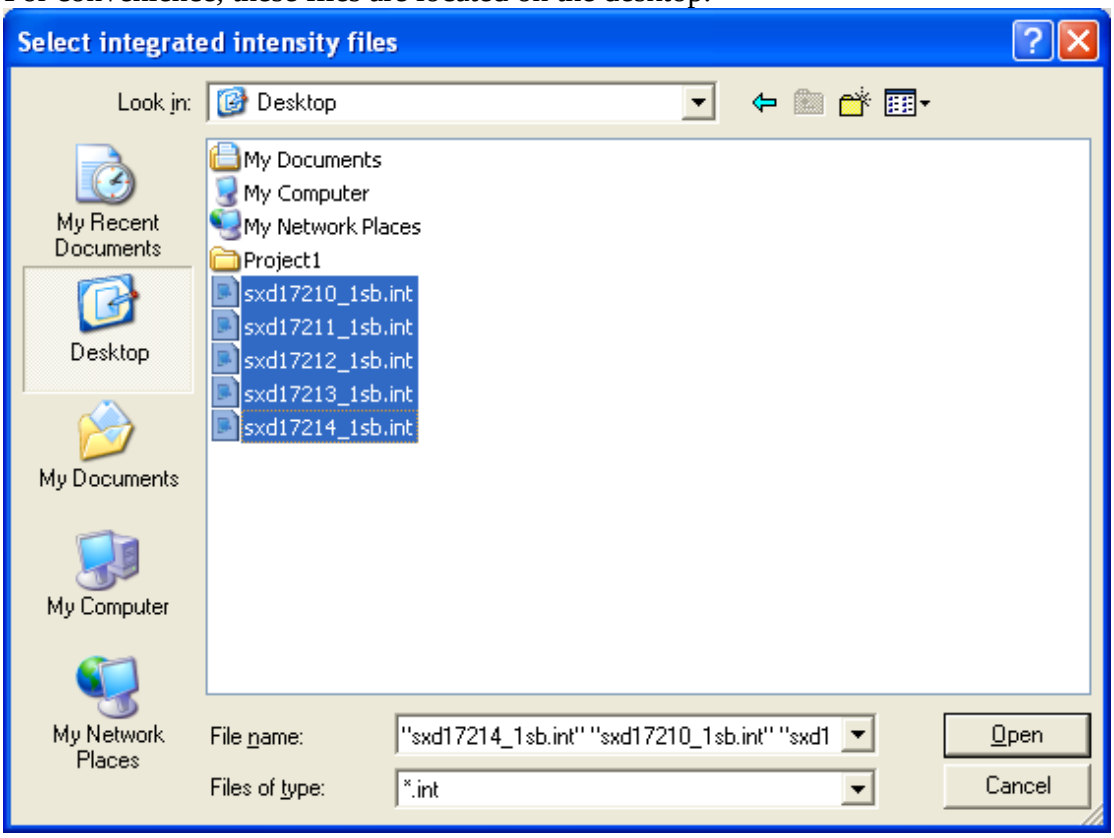

Figure 20: Select the reflection files for use in GSAS.

Finally, we need to know the sample shape. In our case, a cylindrical shape will be good enough. Specify a radius of 0.2 cm and a height of 0.4 cm. Select 'Gaussian Integration' with a precision of 32 points. The latter parameter corresponds to the

number of grid points used in the numerical integration – the higher, the more precise but also the slower the calculation will be.

Select ‘Calculate absorption’ and ‘Calculate extinction’ but leave the selection at ‘Tbar only’. This is the absorption weighted path length through the crystal and is needed for the Becker-Coppens type extinction correction (see later). The GUI should now appear similar to the one shown in Figure 21. Note, that the absorption and scattering cross section as well as the number density have been omitted and are left to the user to be calculated as an exercise. They are needed, so don’t omit them!

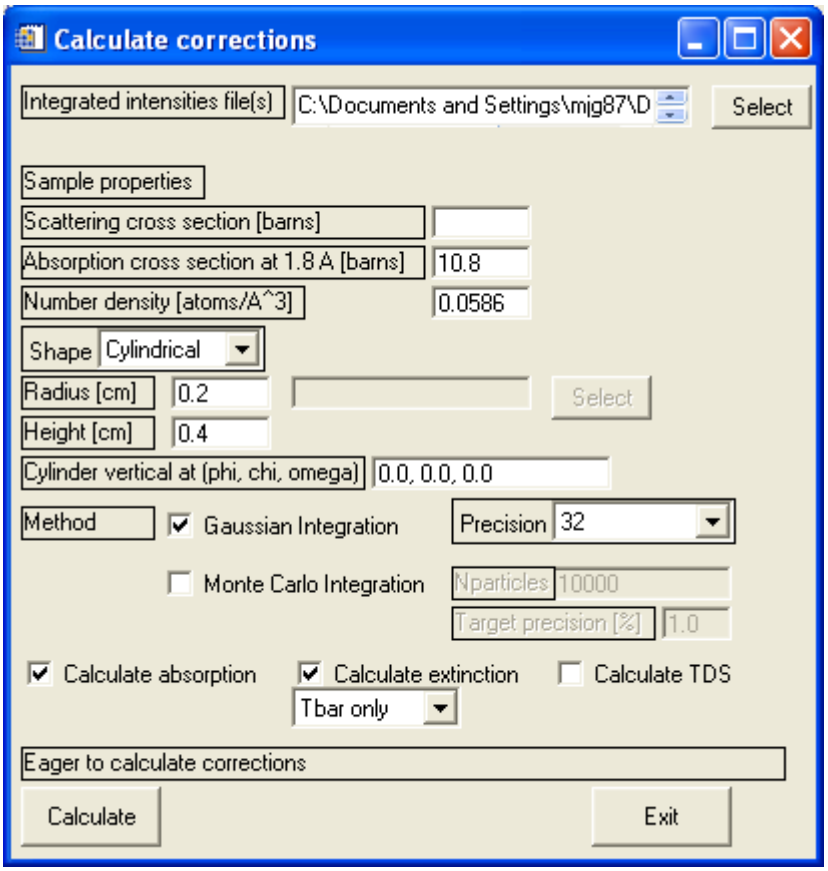

Figure 21: Specify the scattering and absorption cross section as well as the number density.

To calculate the corrections press the ‘Calculate button’ and wait until the text window just above says that it is done. Then exit.

The reflection files are now ready for importing into GSAS. This step must also be done from SXD2001 as GSAS does not provide a standard way to import SXD data. To facilitate this select in the ‘File’ menu in SXD2001 the ‘Generate GSAS reflection file’ option. Click into ‘OK’ in the first window that appears. This will pop up a dialog asking for a GSAS .EXP file. Point to the directory of your .EXP file and select it (Fig. 22). Click into ‘Open’.

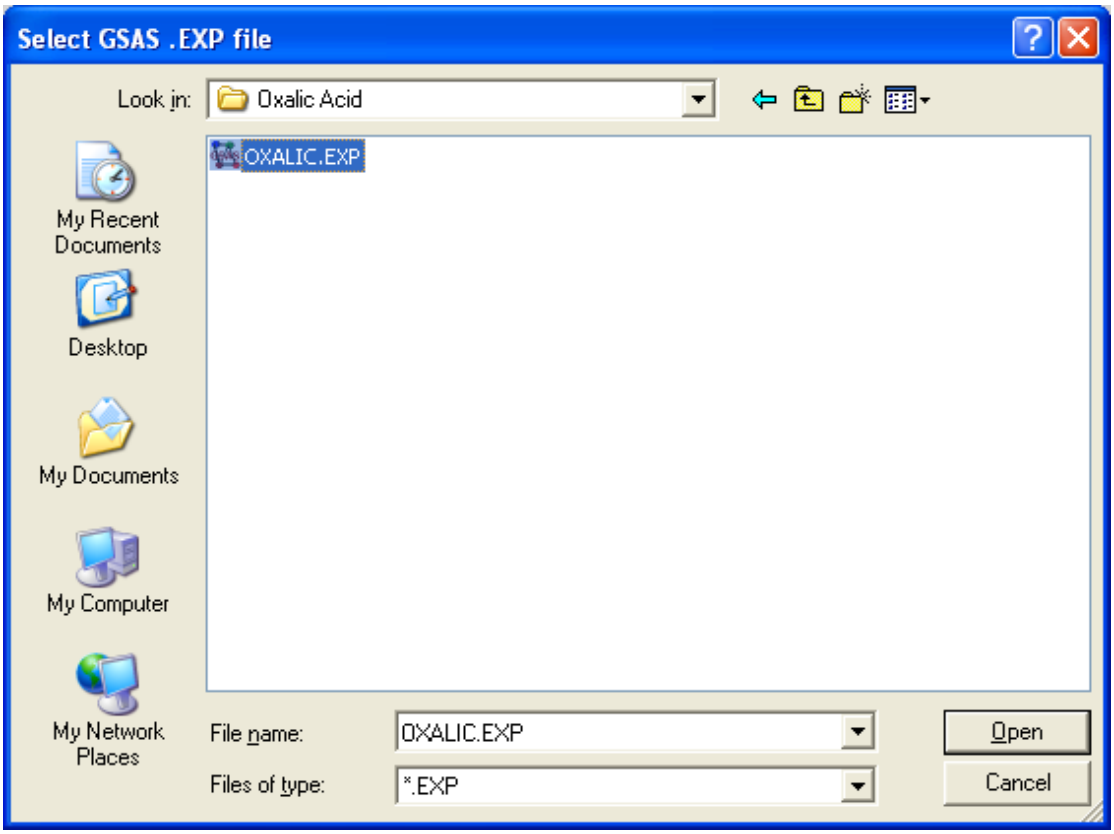

Figure 22: Select ‘Oxalic.exp’.

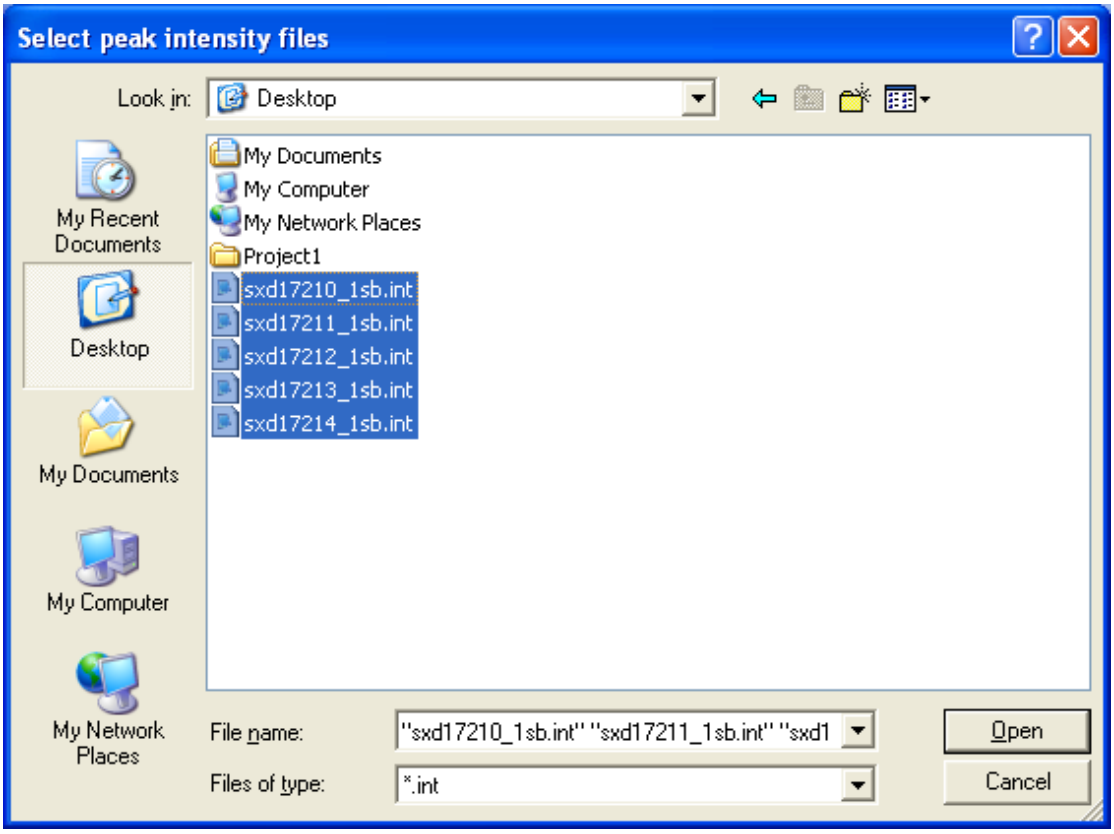

Figure 23: Select the reflection files.

Another dialog pops up asking for the reflection files. Point the directory path to your desktop and select simultaneously sxd17210_1sb.int – sxd17214_1sb.int as shown in Figure 23. Click again into 'Open'. A GUI similar to the one shown in Figure 24 will appear.

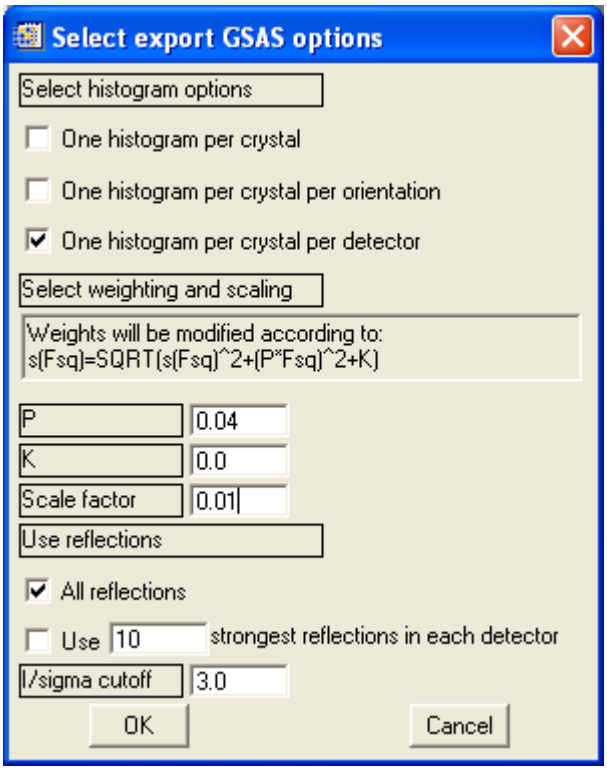

Figure 24: GSAS export options. Select 'One histogram per crystal per detector'.

Change the default selection of 'One histogram per crystal' to 'One histogram per crystal per detector', the scale to 0.01 and leave the other options as they are. The weighting options allow to change the weights used in the refinement. The default values result in a more linear weighting scheme for the reflections in the least-squares refinement. The scale factor (here to be set to 0.01) can be used in case problems are encountered with exporting strong reflections into the GSAS file format. Click into 'OK' and wait until EXPGUI starts to flash. It asks whether a newer version of the exp file should be loaded. The conversion process has written information about the histograms to the .EXP file and thus modified it. Select 'Load new'.

Starting positions for the oxygen and carbon atoms are given in table II. Don't forget that one should always be well prepared and use a well-characterised sample before doing a neutron experiment. These positions can be entered in the 'Phase section of EXPGUI. Click on the 'Add New Atoms' button and insert the atoms in the text box that appears as shown in Figure 25.

Table II: Positions of carbon and oxygen

Atom	x	y	z
C(1)	-0.045	0.054	0.052
O(1)	0.084	-0.059	0.149
O(2)	-0.220	0.231	0.037
O(3)	-0.049	0.112	0.319

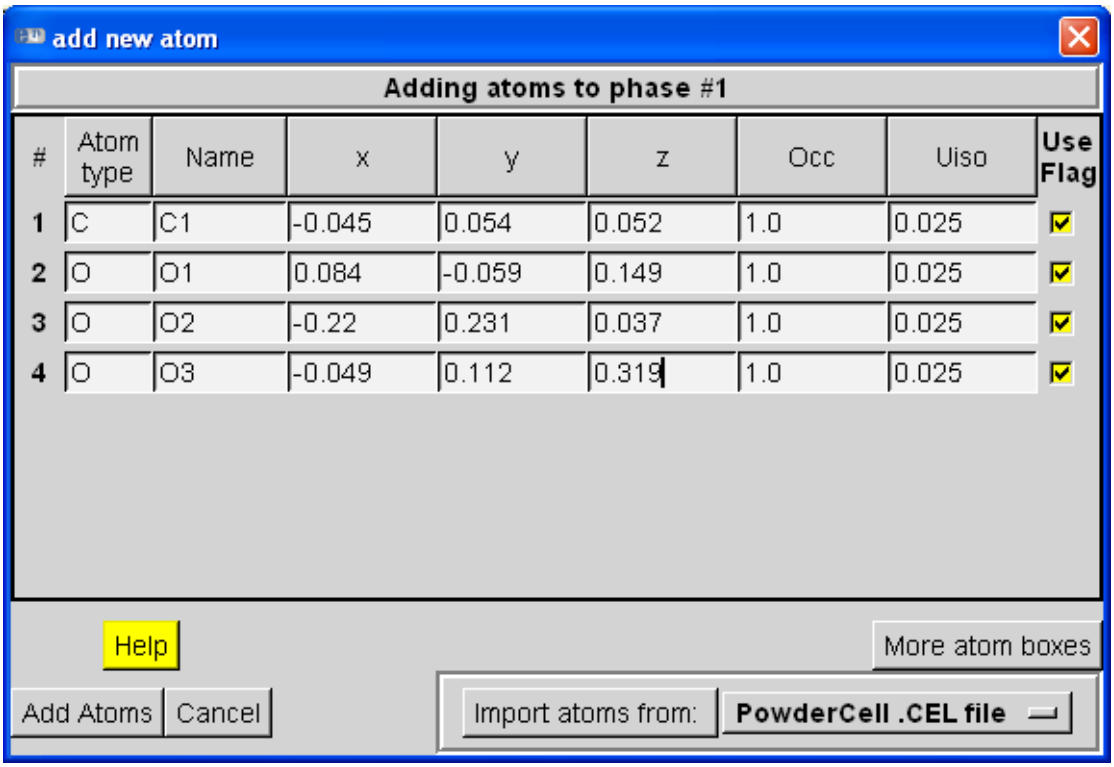

Figure 25: Add new atoms dialog. Click in 'Add Atoms' to finish.

Hopefully, the atoms have been added and the 'Phase' section of EXPGUI should now contain the information as shown in Fig. 26.

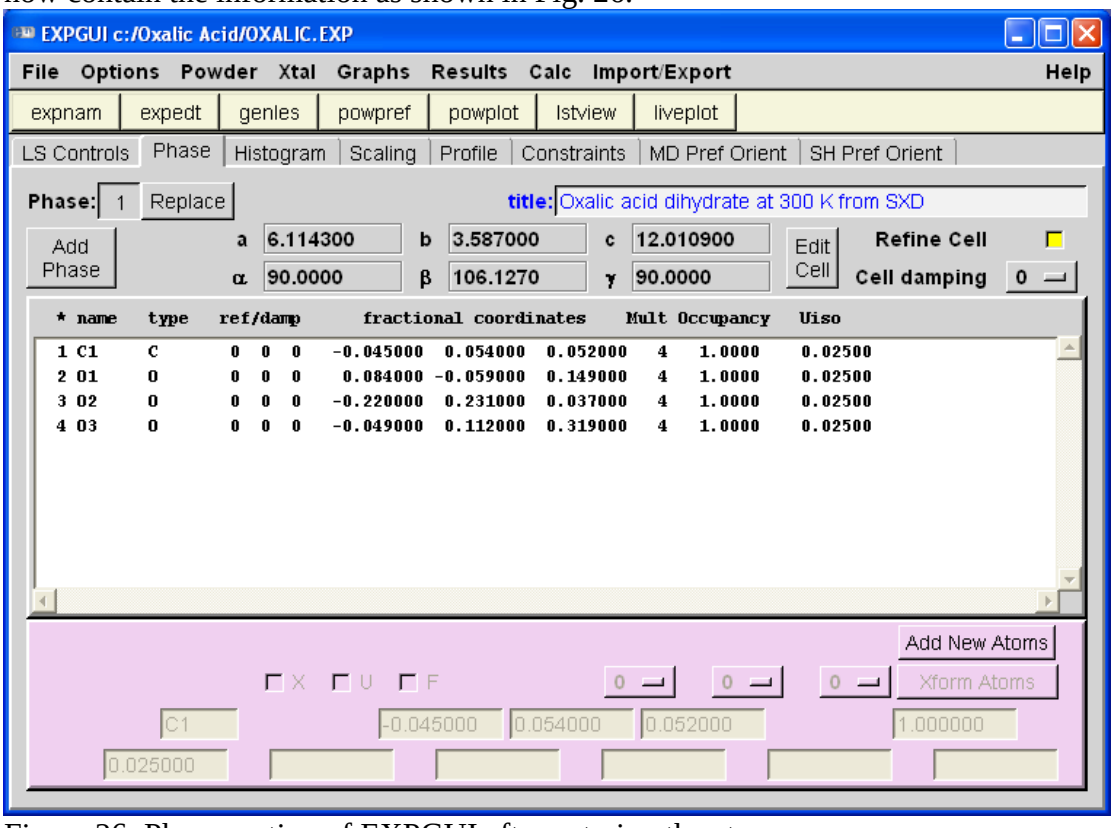

Figure 26: Phase section of EXPGUI after entering the atoms.

We are now ready to start some initial refinements. Do this by pressing the 'GENLES' button. Initially, the histogram scale factors are being refined. These are set by default for refinement. Apply GENLES a few times until the DOS window says 'Converged' (Fig. 27). GSAS can now and then diverge. Just try GENLES again, it often finds its way into the correct minimum.

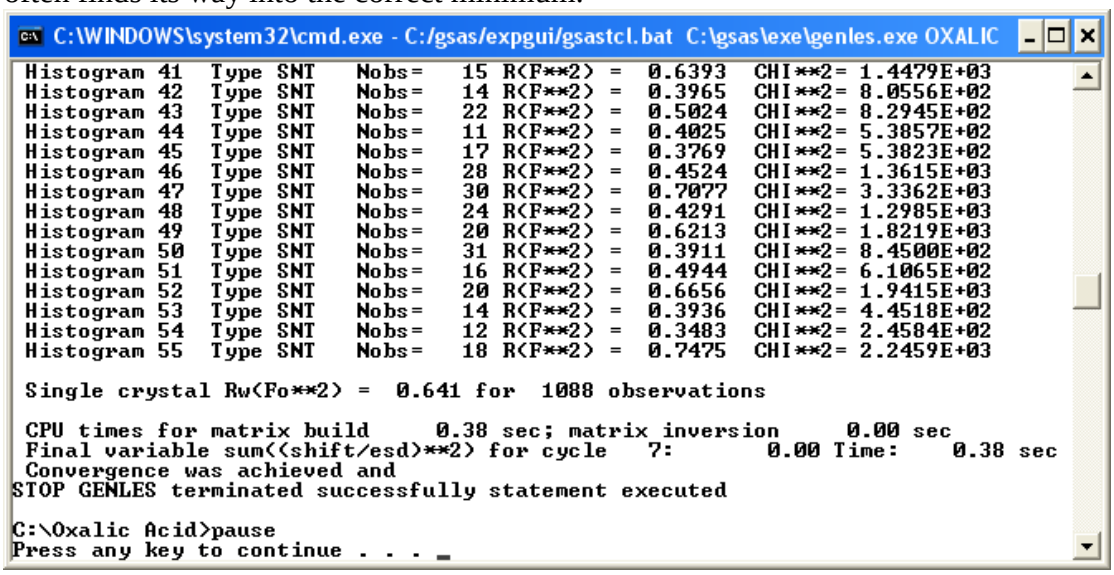

Figure 27: Initial refinement.

Note, that by default, the refinement is performed on F^2 with the weights according to $1/\sigma^2$. The number to observe during refinement is the 'Single crystal Rw(F0**2) (see Fig. 27). In addition, the unweighted R(F**2) for each individual histogram are output in the DOS window. After the first refinement cycle Rw(Fo**2) is 0.641, which is very high. This is not really surprising, since the H atoms are still missing and no structural parameters have been refined as of yet.

After pressing any key to continue, EXPGUI asks whether the new file should be loaded or the older version should be restored. Choose 'Load new file'.

Try to refine the atomic positions next. This can be done by selecting all atoms simultaneously using the mouse as you would do to select text in an ordinary text editor. The refinement flag for the atomic positions is set by checking the box labelled 'X' in EXPGUI. A 'X' should appear on each line specifying the atom position (Fig. 28).

Refine now again using GENLES. GSAS quickly converges and the Rw(Fo**2) slightly decreases to about 0.626. This is still not overwhelming.

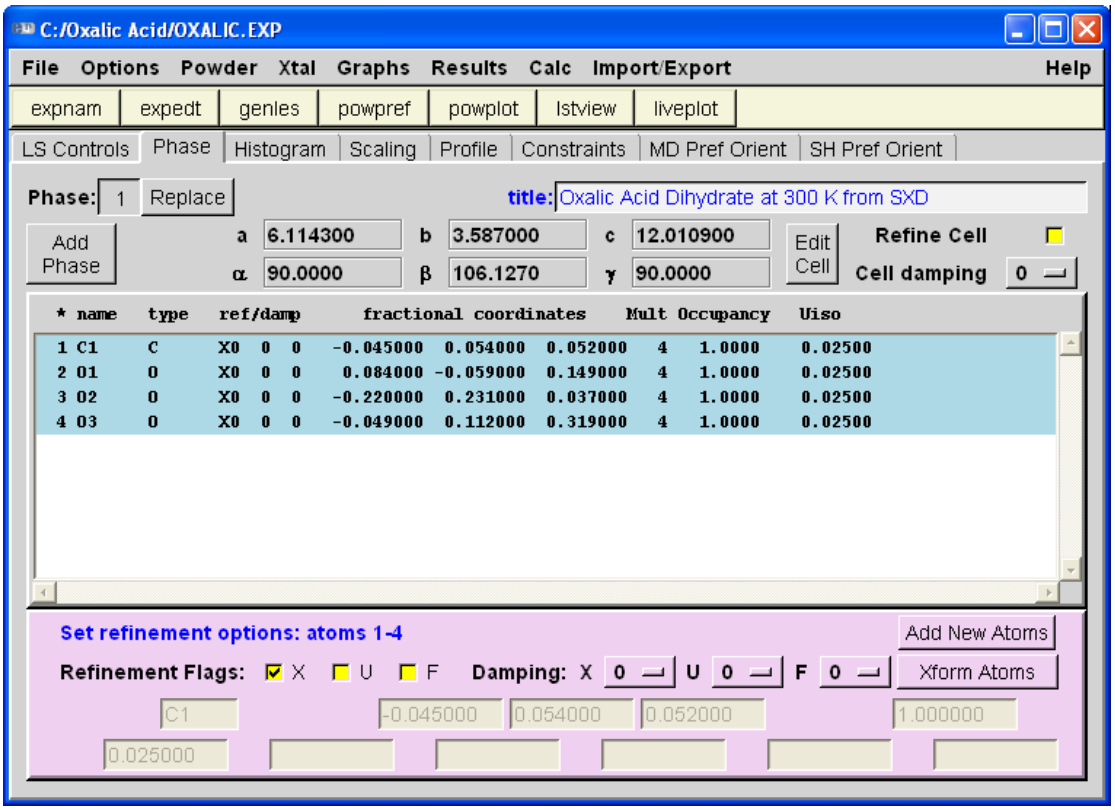

Figure 28: Setting the refinement flag to refine the atomic positions.

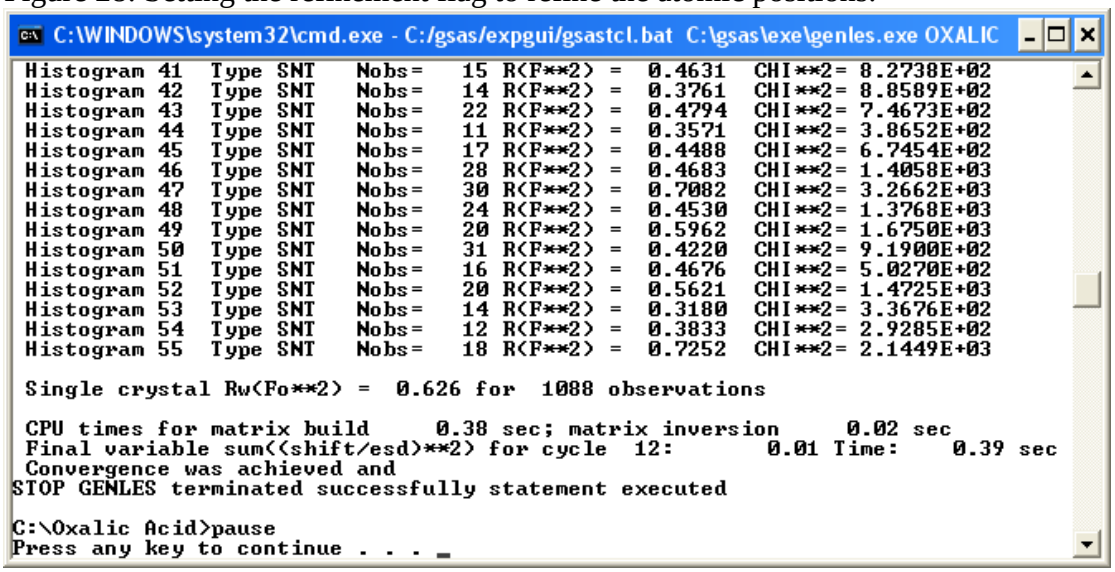

Figure 29: Refinement result after using GENLES.

A very important correction in neutron single-crystal diffraction is extinction. Compared to X-ray diffraction, crystals for neutron diffraction are quite large. Even in the absence of absorption effects, extinction often still is important. In order to access the extinction parameter start EXPEDT again. The now familiar screen shown in Figure 30 appears and the user should enter 'Y' to use the current EXP file.

All information relating to least-squares refinement can be found in the 'Least squares refinement set up' submenu of GSAS. Select 'L' as shown in Figure 31. By pressing <CR> the options are listed in detail. The extinction models can be found in the 'Edit overall parameters' section and therefore, we select 'O' (Fig. 32).

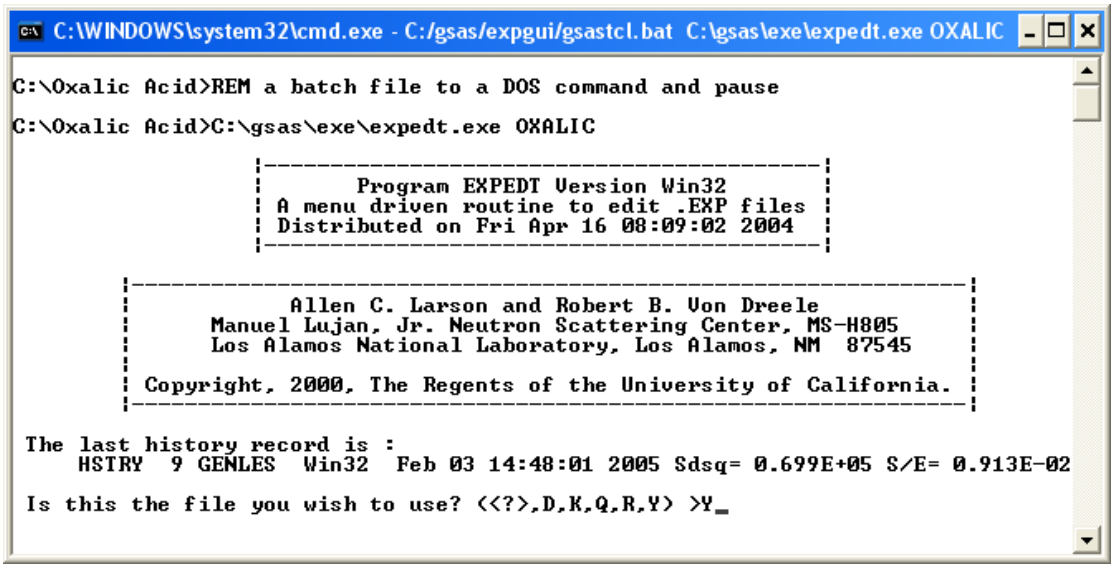

Figure 30: Select ‘Y’ to use the current file.

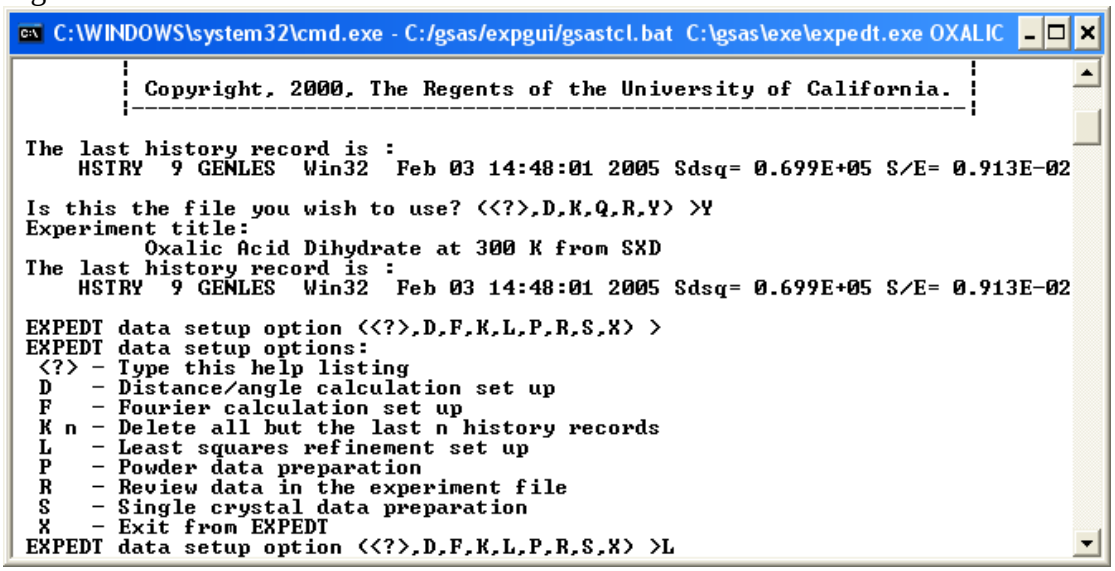

Figure 31: Select ‘L’ to access the least-squares submenu.

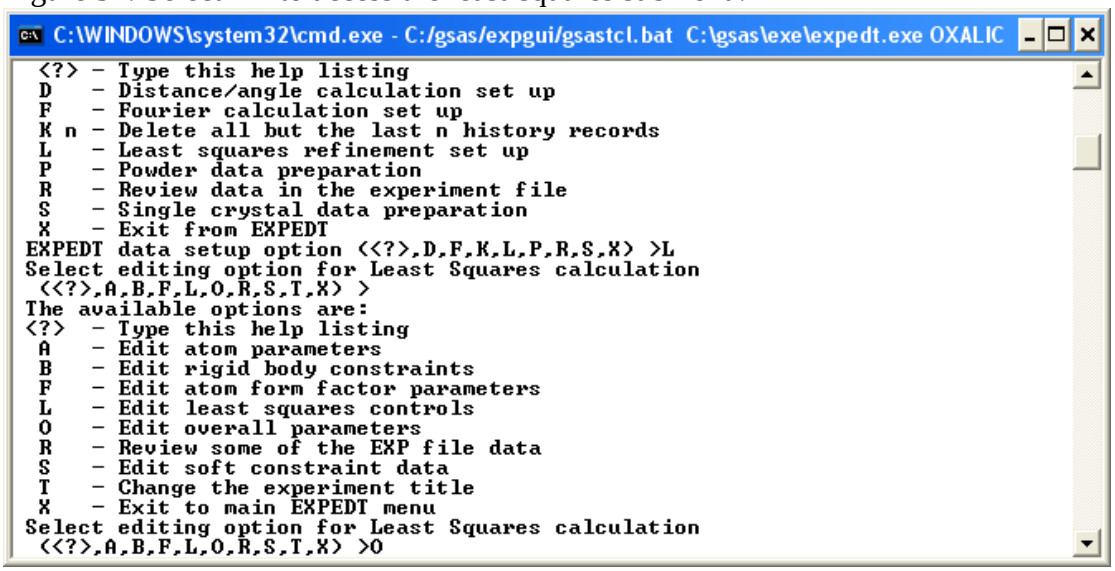

Figure 32: Select ‘O’ to access the overall parameters.

Finally, we can access the extinction models by selecting ‘E’ (Fig. 33).

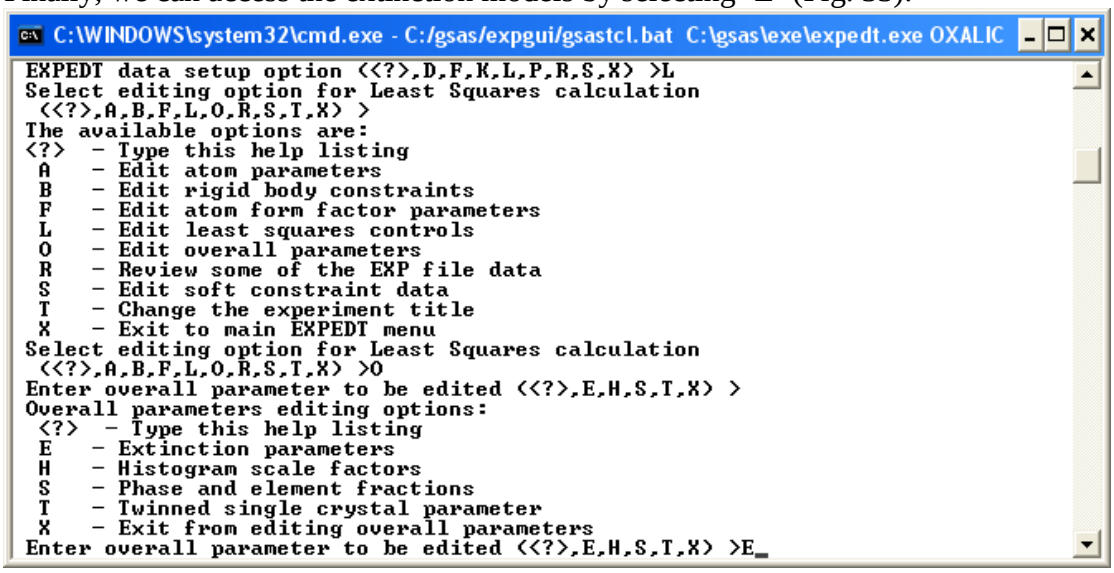

Figure 33: Select ‘E’ for ‘Extinction parameters’.

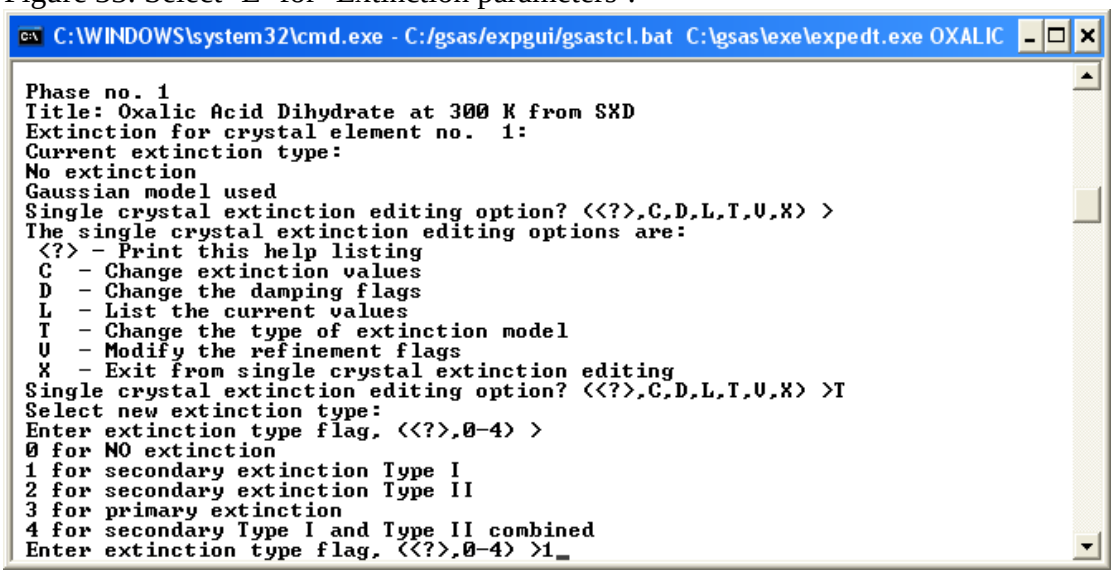

Figure 34: Select ‘T’ to access the different extinction models.

The extinction parameters submenu is under the letter ‘E’ (Fig. 33). By default, no extinction correction is applied. However, this will be necessary for our large crystal of oxalic acid dihydrate. Type ‘T’ and then <CR> to see a listing of the various models (Fig. 34). The models are numbered from 0 to 4. It is not necessarily clear which model should be used and one might have to try different models. In our case we select model number 1 which is secondary extinction of type I. GSAS asks whether a Lorentzian distribution model should be used. Select ‘Y’ as shown in Fig. 35.

Although an extinction model has been selected, the parameter is still 0.0 and the refinement flag is switched to ‘N’ for no refinement. Switch this flag to ‘Y’ by entering ‘V’ as shown in Fig. 36. Since we don’t know a good value for the extinction parameter we leave it to GENLES to refine it. Exit now EXPEDT by entering ‘X’ followed by <CR> as many times as is necessary. Remember, that each ‘X’ will take you to the previous menu. Run now GENLES again until it converges (Fig. 37).

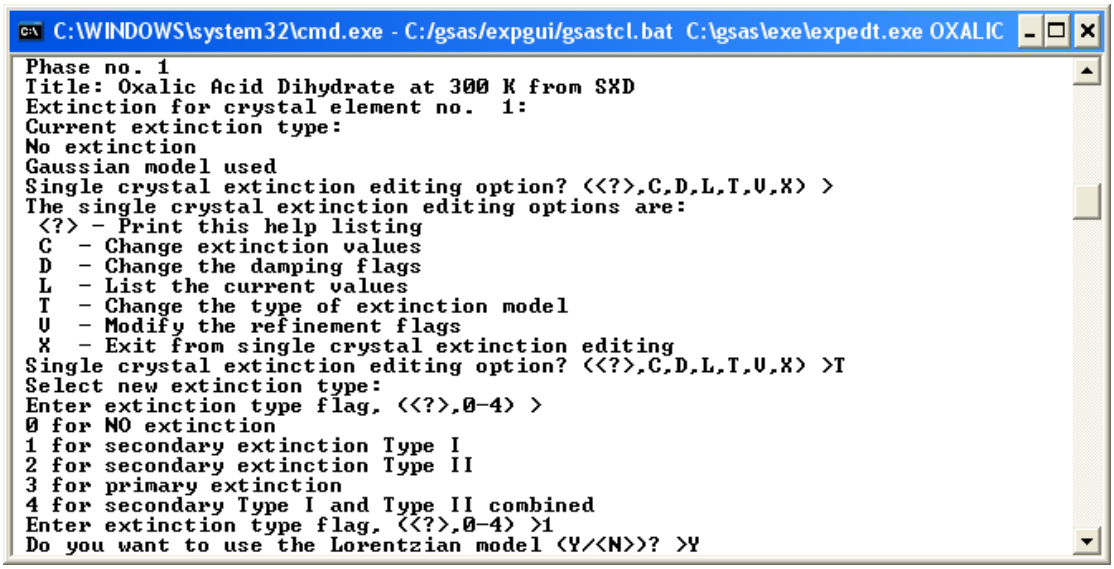

Figure 35: 'Y' selects a Lorentzian distribution.

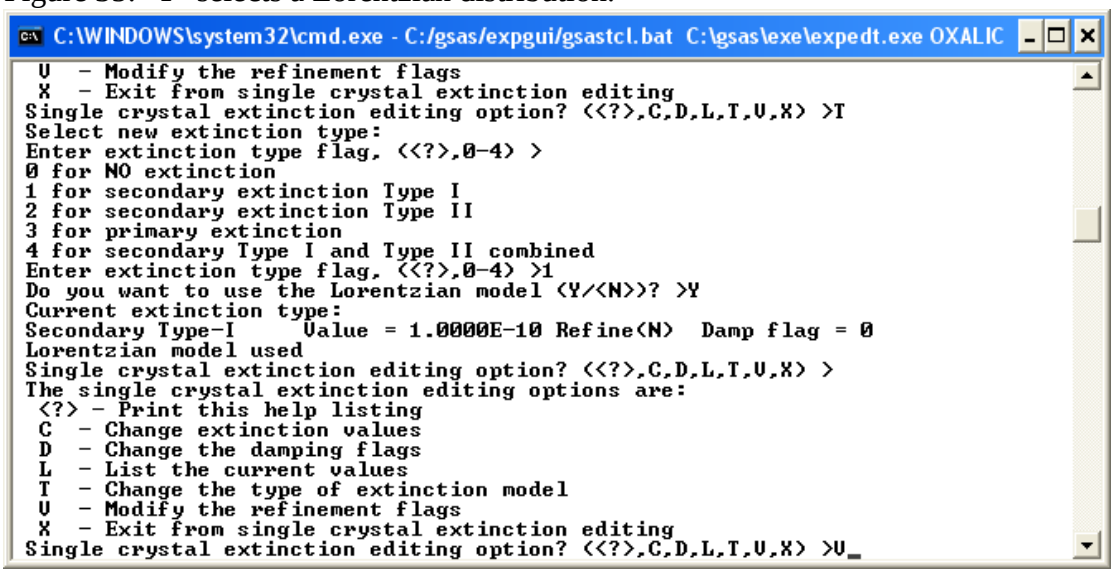

Figure 36: Switch the refinement flag on by entering 'V'.

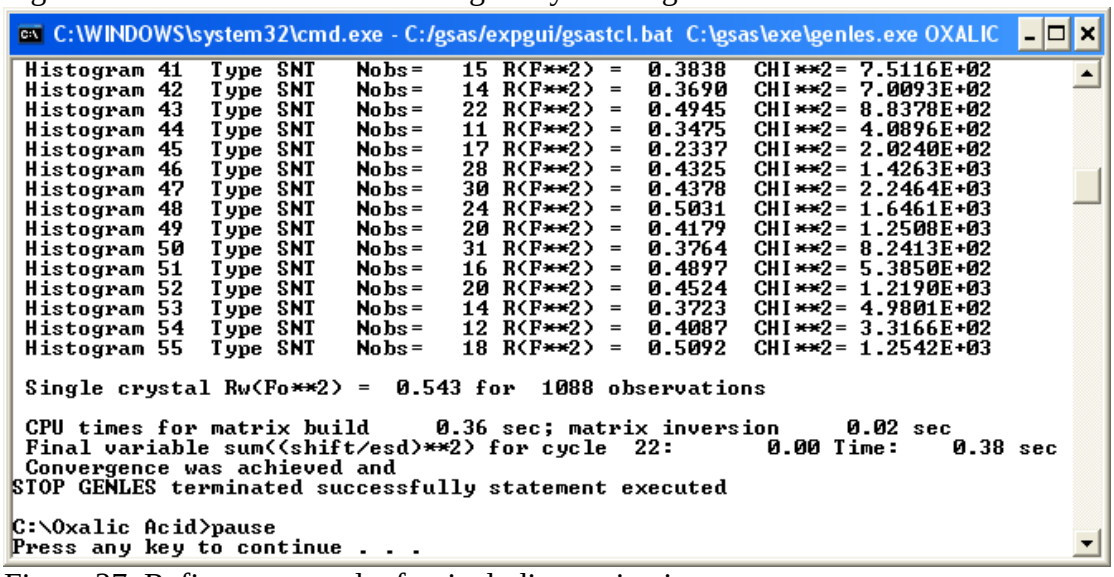

Figure 37: Refinement result after including extinction.

The refinement has improved significantly with Rw(Fo**2) being around 0.543. Next, try to refine the isotropic thermal parameters by selecting all atoms and checking the box labelled ‘U’ (Fig. 38). The letter ‘U’ should appear next to ‘X’ on each line specifying the atomic coordinates. Run again GENLES until it converges.

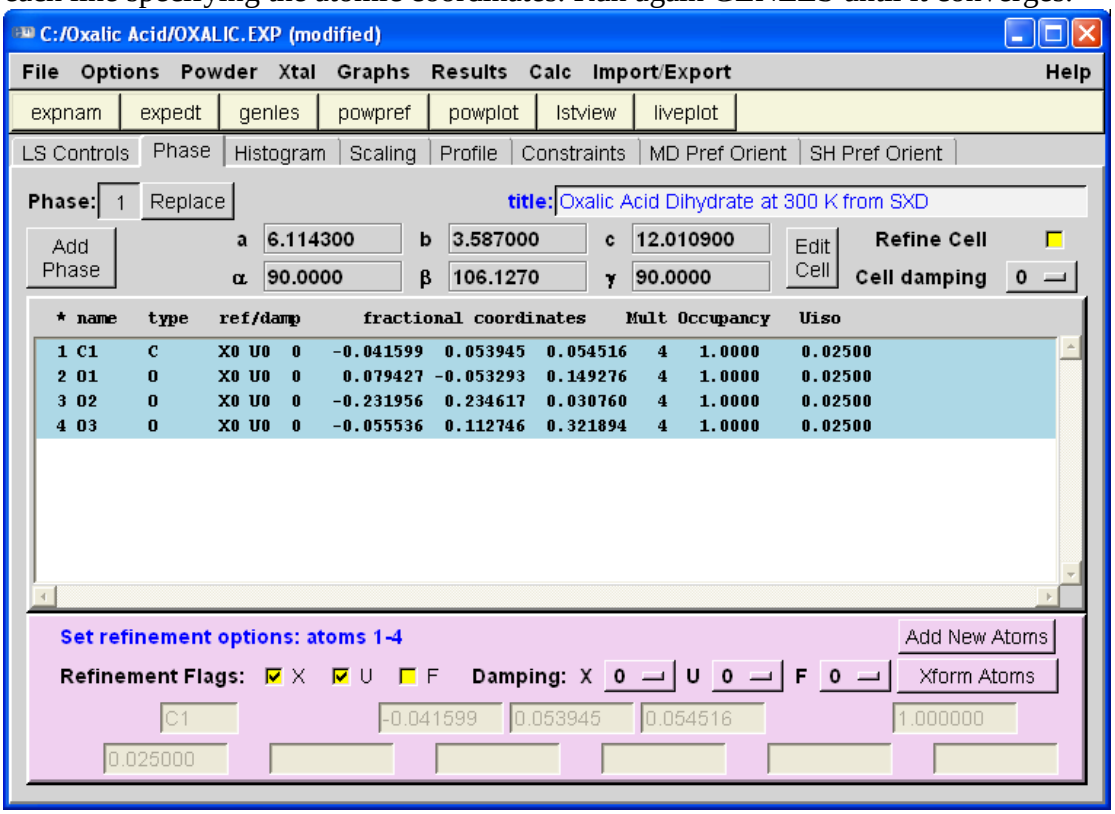

Figure 38: Switching the refinement flag for including isotropic thermal parameters.

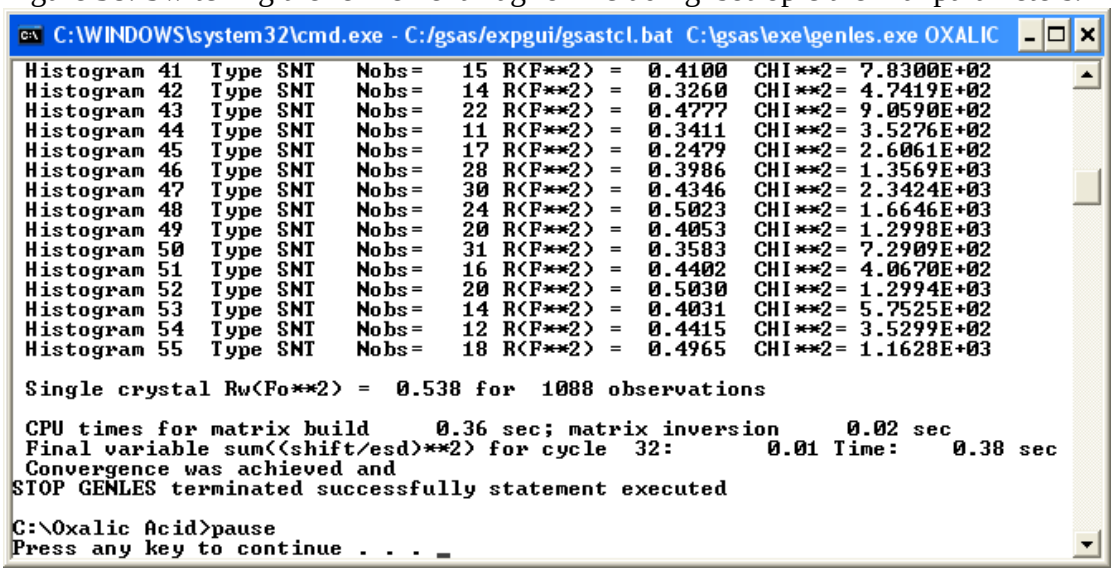

Figure 39: Refinement result after including isotropic thermal parameters.

Rw(F0**2) only slightly decreases to 0.538. It is now time to try to locate the hydrogen by plotting some Fourier maps. Open EXPEDT, select ‘Y’ as usual to use the current .EXP file and then ‘F’ for Fourier set up (Fig. 40). Entering a <CR> shows again the options (Fig. 41). To show the locations of all the atoms we select to calculate and Fobs map from the measured reflections. This can be selected by entering ‘FOBS’ as shown in Fig. 41.

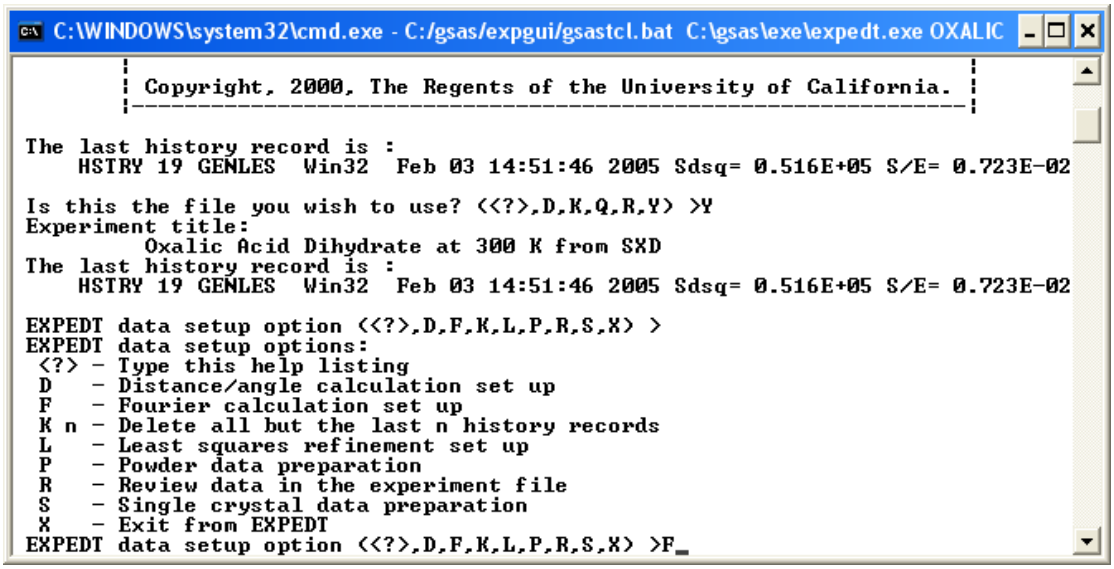

Figure 40: Select ‘F’ for Fourier setup.

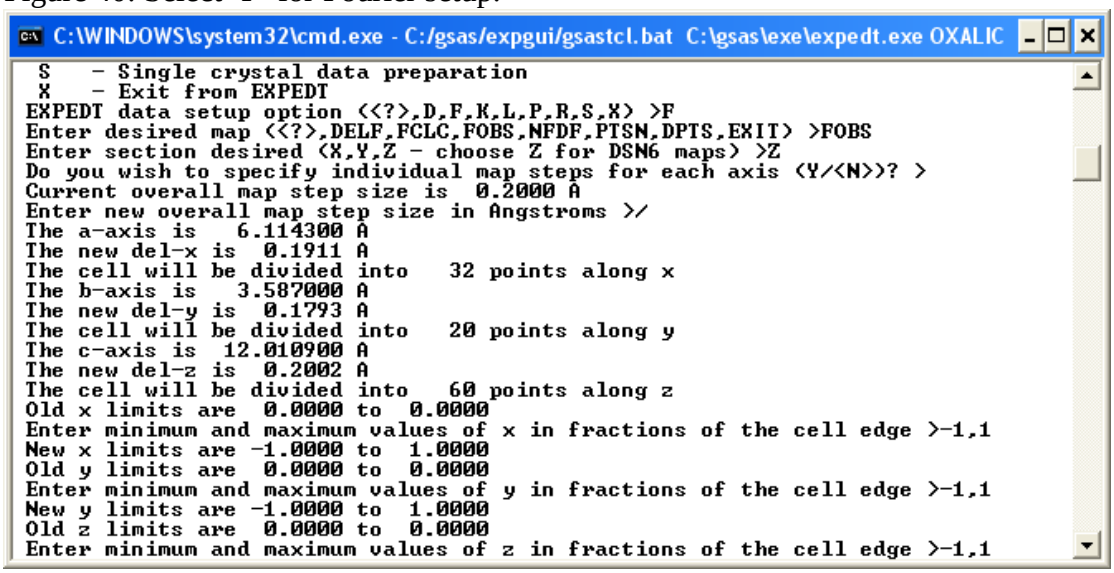

Figure 41: Select an FOBS map, enter ‘Z’ projection, accept the parameters for grid step size using a ‘/’, and set the calculation range along x, y, and z from -1 to +1.

Choose ‘Z’ as a map projection. Answer the next question with ‘N’. Accept the default of 0.2Å for the grid size in all three directions (Fig. 42). Default values are usually accepted by entering a ‘/’ followed by <CR>. Enter the minimum and maximum values for x, y, and z as -1.0 and 1.0, respectively. This is more than needed but is also on the safe side.

Next the histograms to be included need to be specified. There are 55 histograms in total, so enter them as shown, e.g. in Fig. 42. The input for the Patterson calculation is now completed. Exit EXPEDT by entering ‘X’ followed by <CR> as many times as necessary.

To calculate the Fobs map select ‘fourier’ from the ‘Graphs’ menu in the main EXPGUI menu. This will take a short time (Fig. 43).

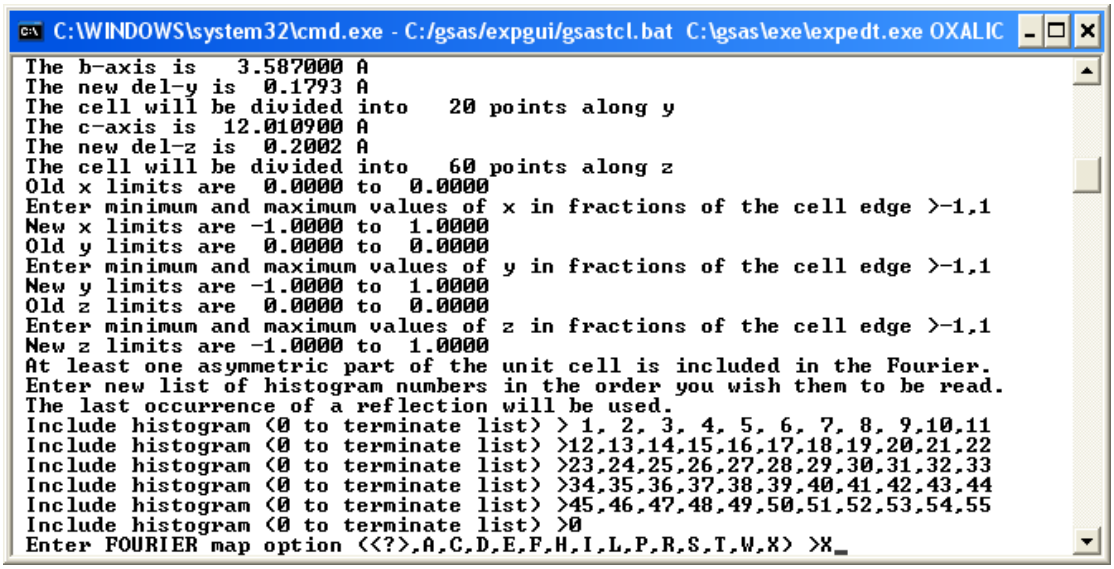

Figure 42: Specification of parameters for Fourier calculation.

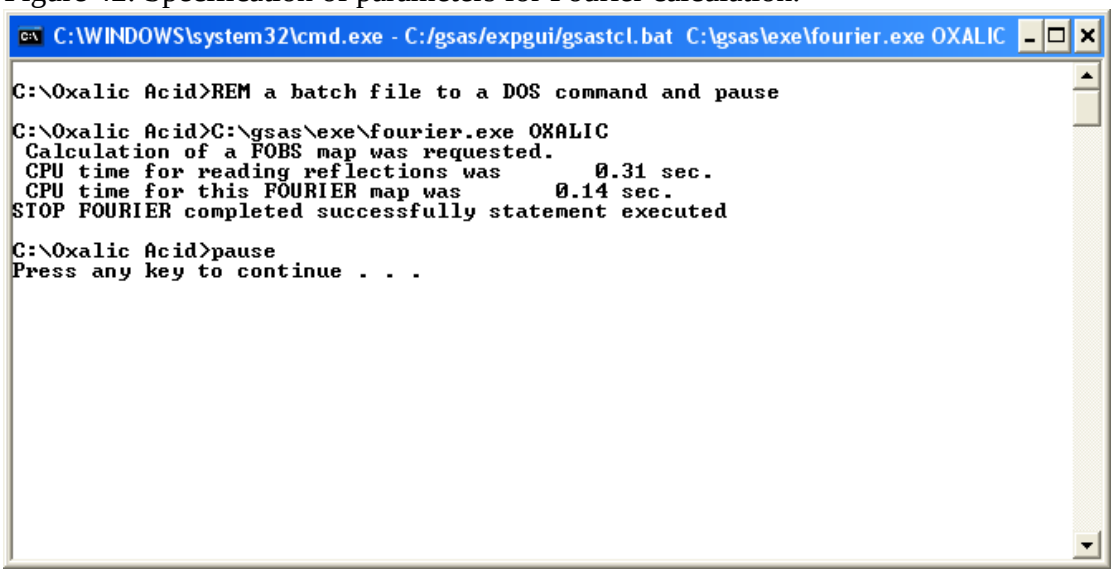

Figure 43: Successful completion of Fourier calculation.

A convenient means to locate the hydrogen is to perform a peak search on the Fobs map just calculated. This can be done using the program ‘forsrh’ under the ‘Graphs’ menu in the main EXPGUI window. The user is asked to specify an intensity cut-off and the maximum number of peaks to be stored in the list. Hydrogen corresponds to negative intensity holes in a Fobs map due to its negative coherent scattering length and thus we select -0.8. This value usually needs a bit of trial and error as sometimes too many, sometimes too few peaks are found. Enter a maximum of 50 peaks to be found and accept the default to not write an output file.

The peaks located are displayed in Fig. 45. As expected, 7 peaks were located as suggested by the chemical formula. Four of the peaks have a positive amplitude. Comparing them with the atom positions given in EXPGUI easily allows to identify them as being carbon and three oxygens, respectively. The remaining three peaks have a negative amplitude very close to the minimum value of the Fobs map and thus they must be the missing hydrogens.

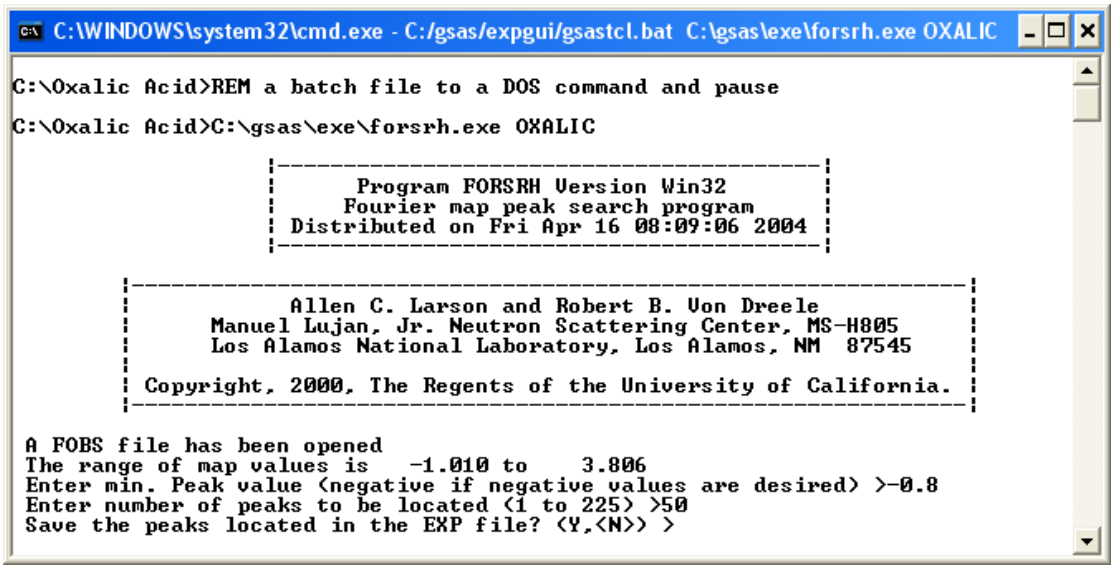

Figure 44: Input for forsrh.

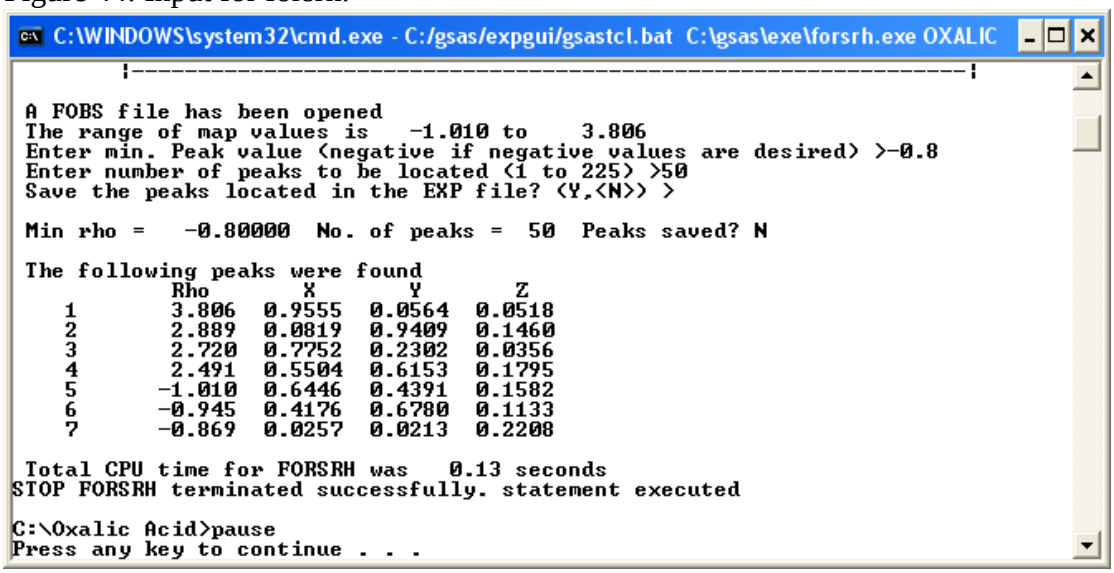

Figure 45: Peak search results.

Alternatively, it is also possible to draw Fourier maps. Just for completeness let us do this before continuing with the crystal structure refinement. To prepare the drawing of Fourier maps, select the program ‘forplot’ under the ‘Graphs’ menu. A screen similar to the one shown in Fig. 46 appears. Entering <CR> as usual shows the options. We choose ‘C’ and accept the default for not saving graphics output. The resulting screen provides some information about the available data and plotting options (Fig. 47).

For instance, the data have been rescaled to span a range between -1.01 and 3.81. By default 5 contours will be drawn at 0.63, 1.27, 1.90, 2.54, and 3.17. The map size from center to edge will be 5Å and the map grid interval 0.3Å. Since we are interested in seeing negative intensity from the hydrogen, the contour levels need to be modified such as to include negative contours as well. Let’s set 13 intervals at the values -1.0, -0.8, -0.6, -0.4, -0.2, 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4. In order to see which option will allow this press <CR>, select ‘N 13’ and enter the values as suggested (Fig. 47).

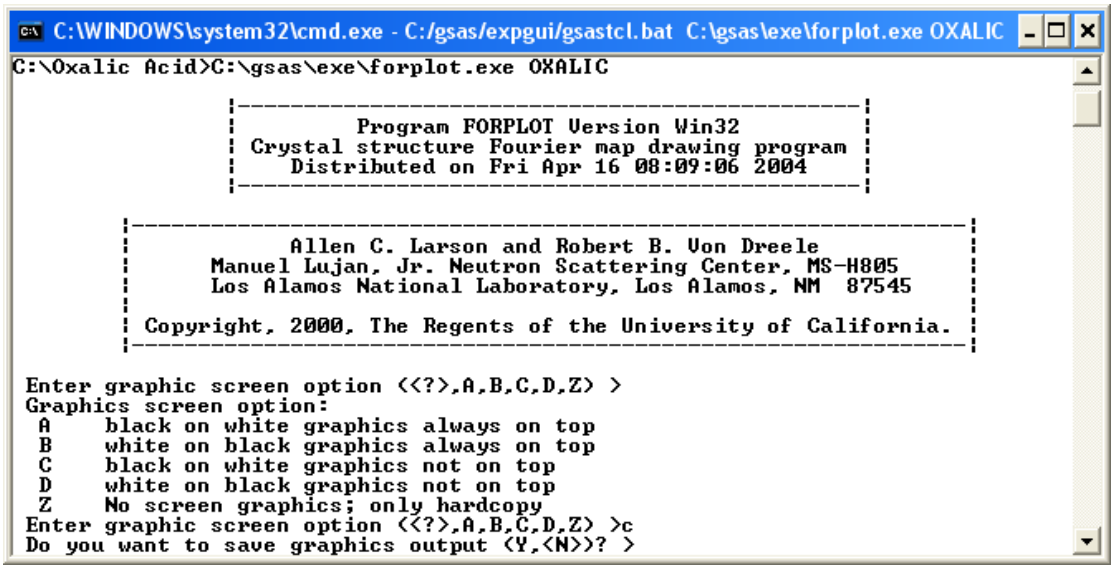

Figure 46: Initial screen of ‘forplot’. Select ‘C’ and accept the default for not saving graphics output.

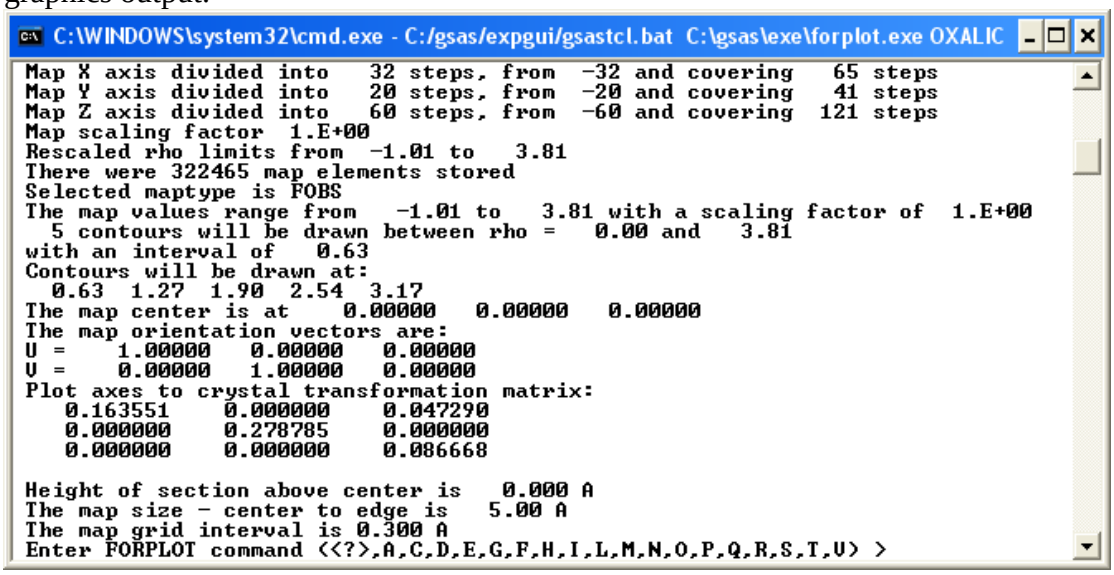

Figure 47: Default settings for drawing Fourier maps.

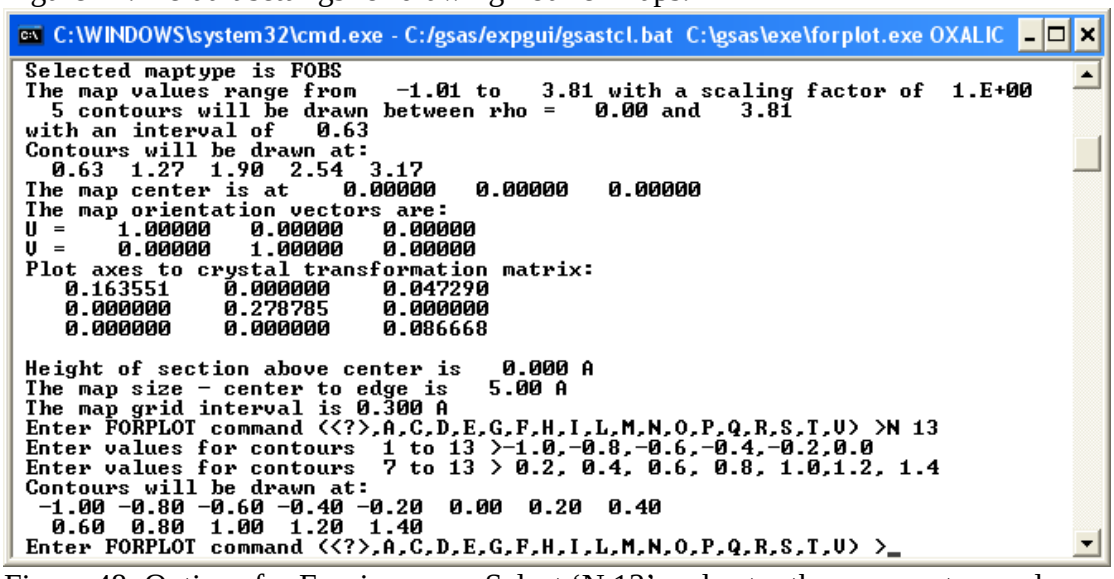

Figure 48: Options for Fourier maps. Select ‘N 13’ and enter the new contour values.

We would also like to enter a somewhat finer grid size and label the atoms. Enter ‘G 0.1’ for the former and ‘D’ followed by a ‘/’ for the latter (Fig. 49).

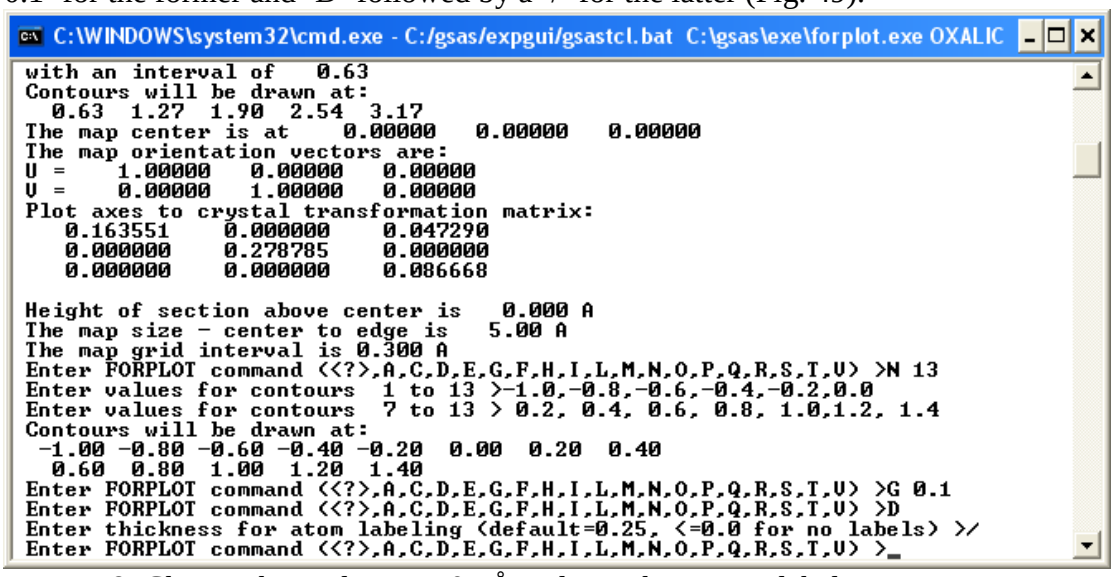

Figure 49: Change the grid step to 0.1Å and switch on atom labels.

To select a map at a particular level enter ‘H <value>’ where <value> is the z component in Å. To plot the map, enter ‘P’. These commands can all be specified in one line. For the sake of brevity here are some suggestions for drawing Fourier maps:

‘H 0.4 P’ shows the positions of C(1) at (-0.05, 0.046, 0.035) and O(2) at (-0.226, 0.236, 0.026) – very close to the refined value (Fig. 50).

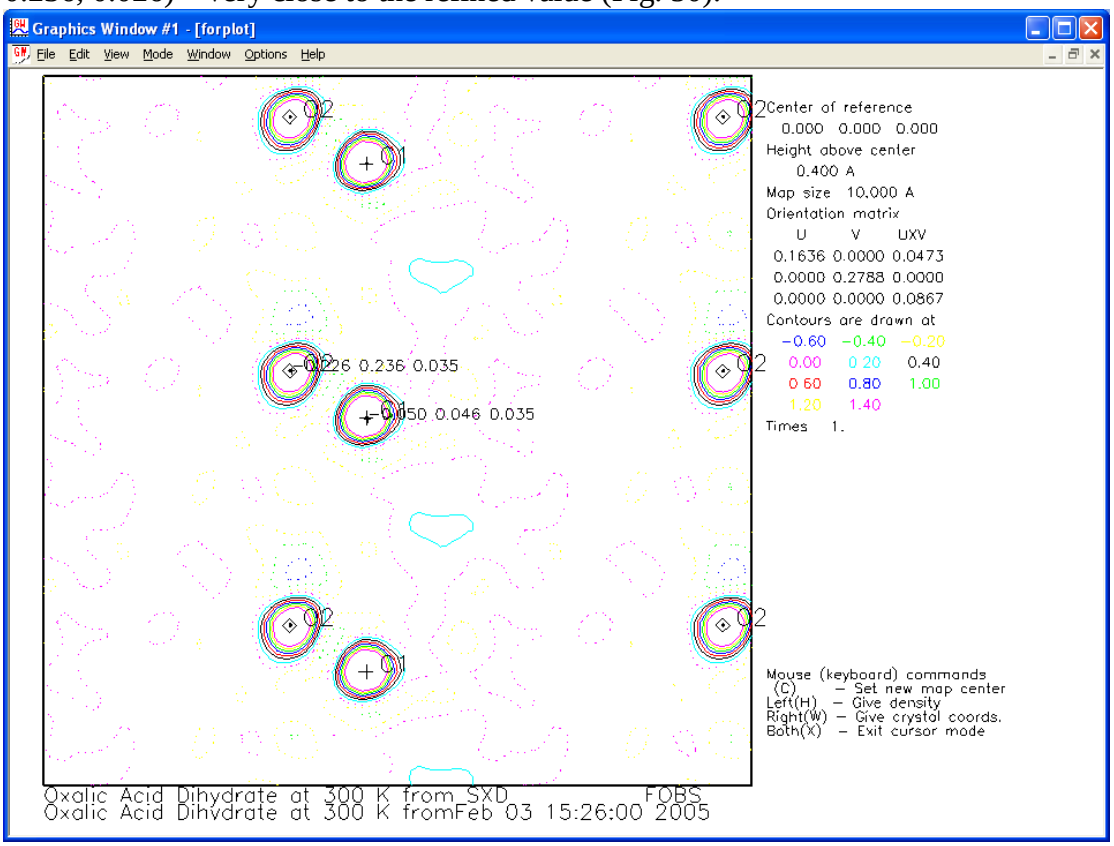

Figure 50: Location of C(1) and O(2) in the Fourier map. Click simultaneously with the left and right mouse button to gain back control over the DOS input window.

'H 1.7 P' shows the location of O(1). The selected atom is at (0.077, -0.054, 0.147) (Fig. 51).

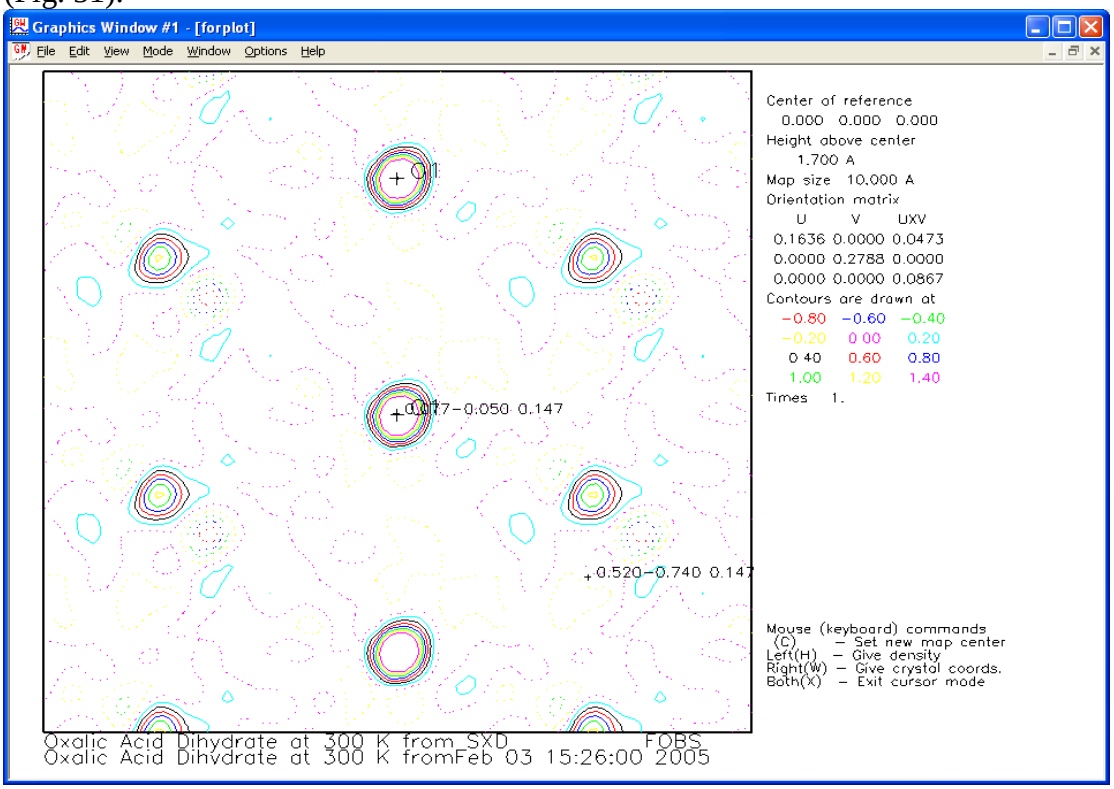

Figure 51: Location of O(1).

'H 2.6 P' shows the location of H(1) at (0.025, 0.02, 0.225). Note, that this corresponds to a negative hole in the Fourier map.

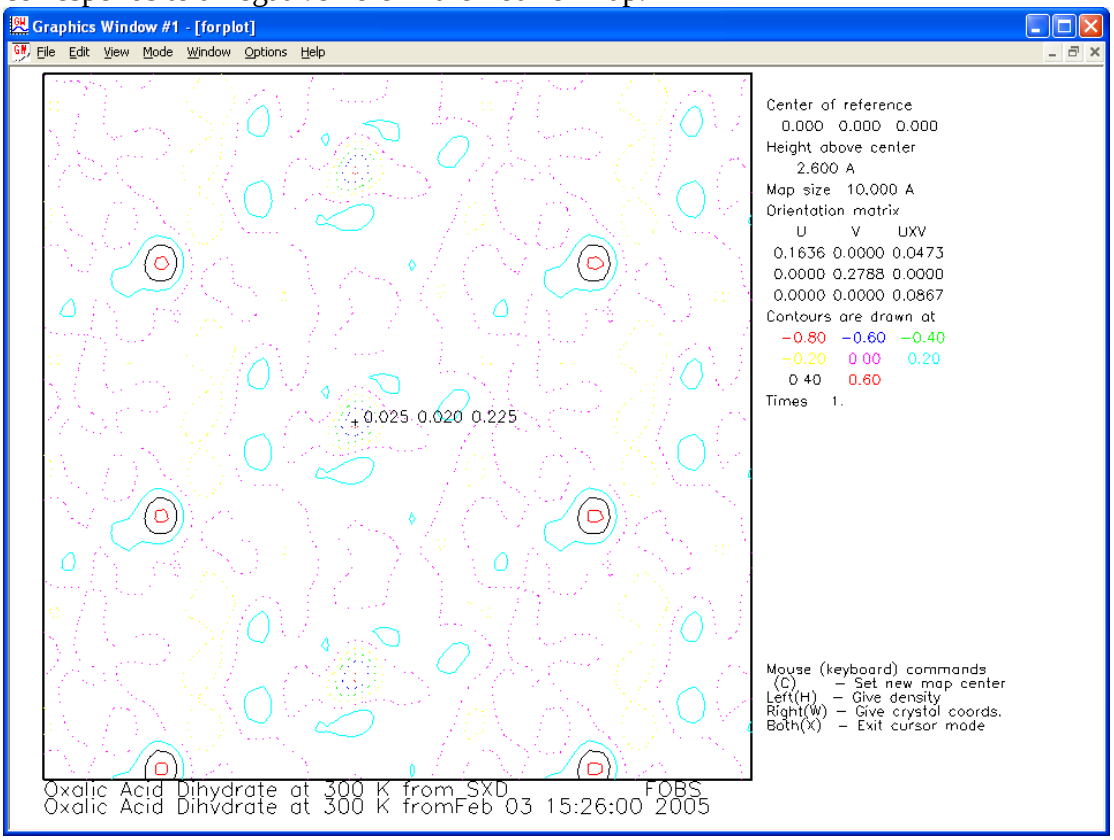

Figure 52: Location of H(2). The residual positive density comes from a nearby O(3).

‘H 3.6 P’ shows the location of O(3) at (-0.059, 0.118, 0.312) (Fig. 53).

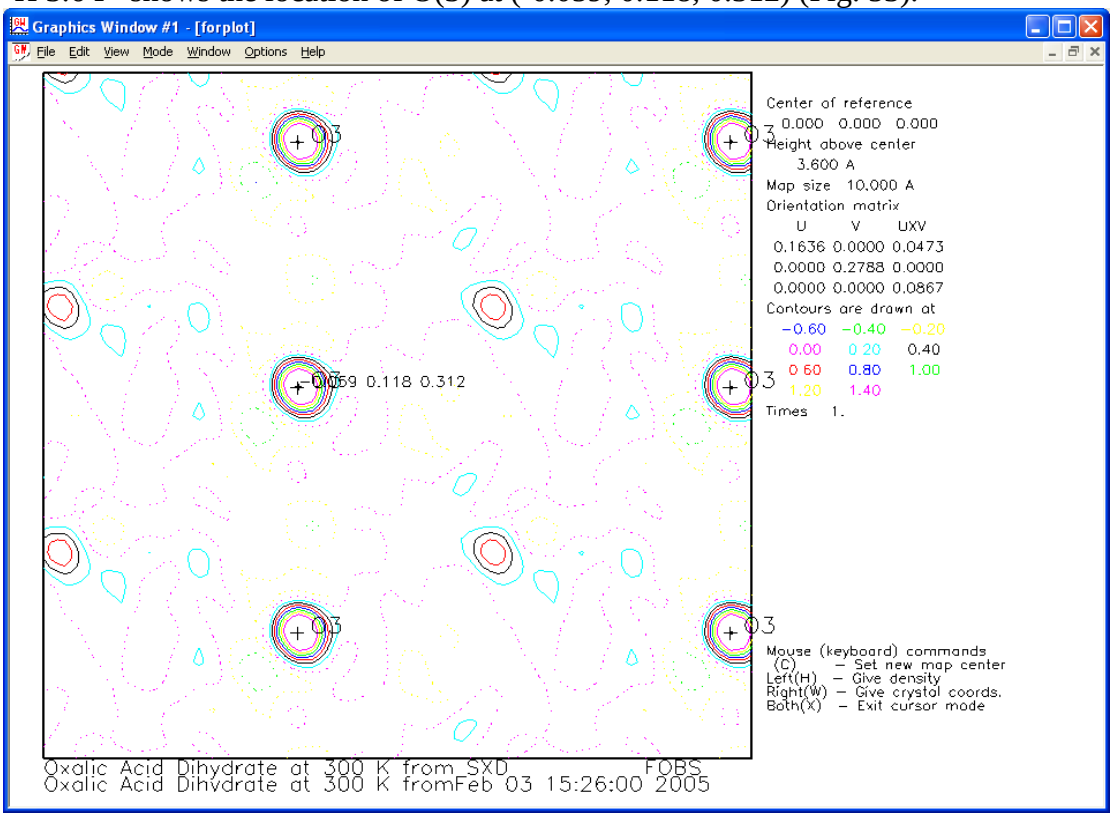

Figure 53: Location of O(3).

‘H 4.0 P’ shows H(3) at (-0.146, -0.046, 0.347) close to the strong positive peak corresponding to O(3). Also visible is O(1) (Fig. 54).

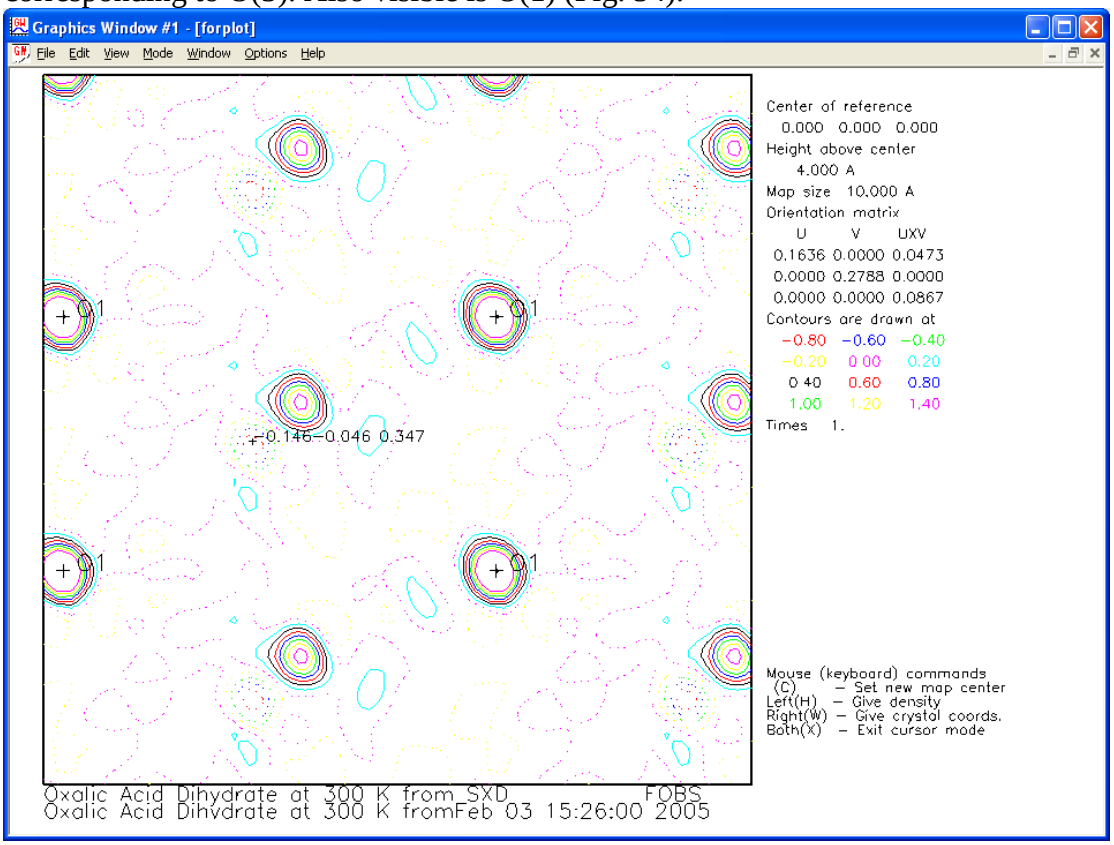

Figure 54: Location of a negative pocket corresponding to H close to O(3).

'H 4.4 P' finally locates H(2) at (0.081, 0.173, 0.381). Again, there is some positive density corresponding to O(1) (Fig. 55).

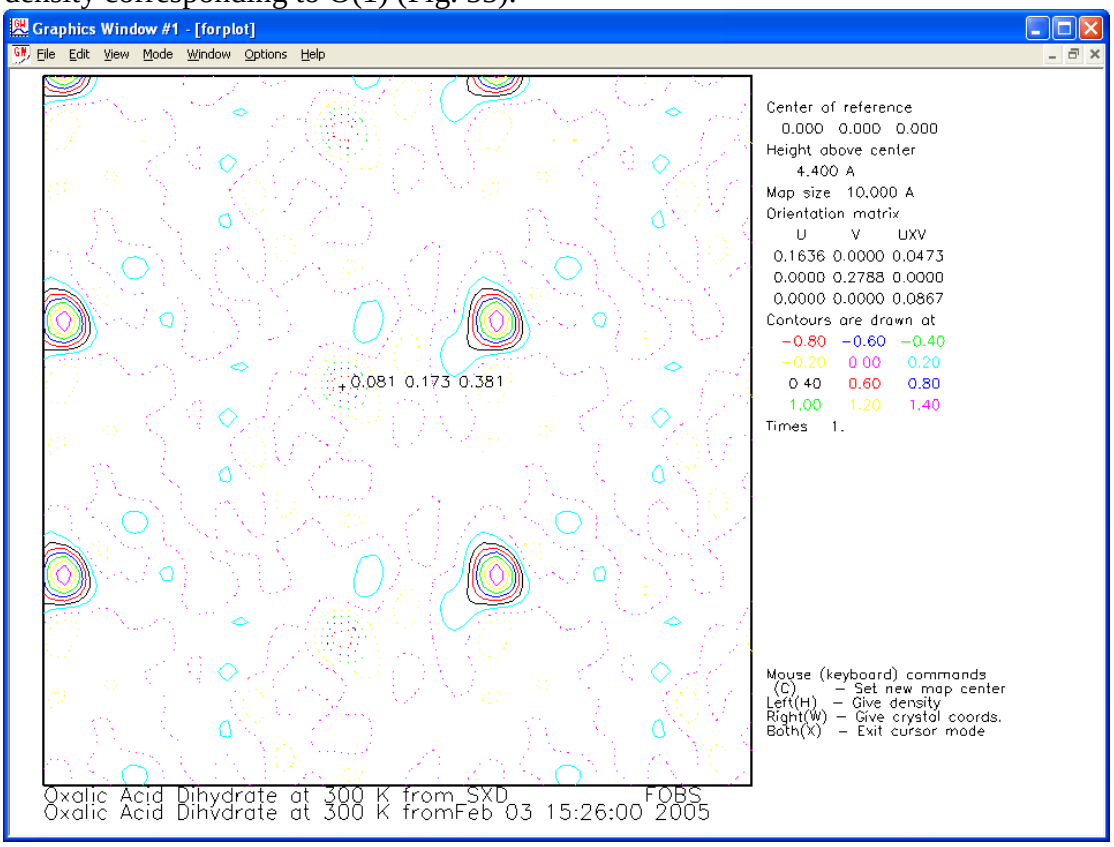

Figure 55: Location of the third hydrogen at a negative pocket.

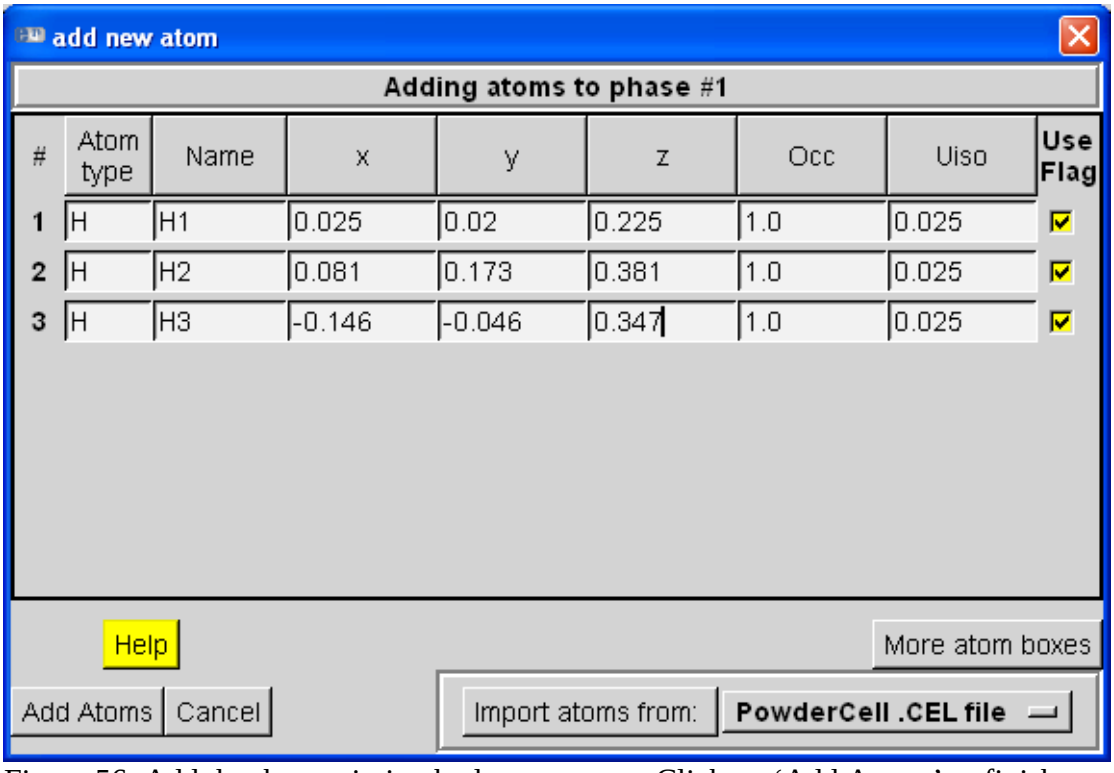

Figure 56: Add the three missing hydrogen atoms. Click on 'Add Atoms' to finish.

This concludes our search for the missing hydrogen. The coordinates found can now be entered into EXPGUI. Close the plot window and 'forplot' (note there is no 'X' option to exit, just click with the left mouse into the closing symbol of the window). Enter the coordinates for the three missing hydrogens by selecting the 'Add New Atoms' button in the 'Phase' section of EXPGUI. For convenience, we use the coordinates as derived from the Fourier maps (Fig. 56).

A new refinement using GENLES leads now to a dramatic reduction in Rw(Fo**2) to 0.276 (Fig. 57). Refine now the atomic positions of hydrogen including the isotropic thermal parameters (Fig. 59). The result is shown in Fig. 60.

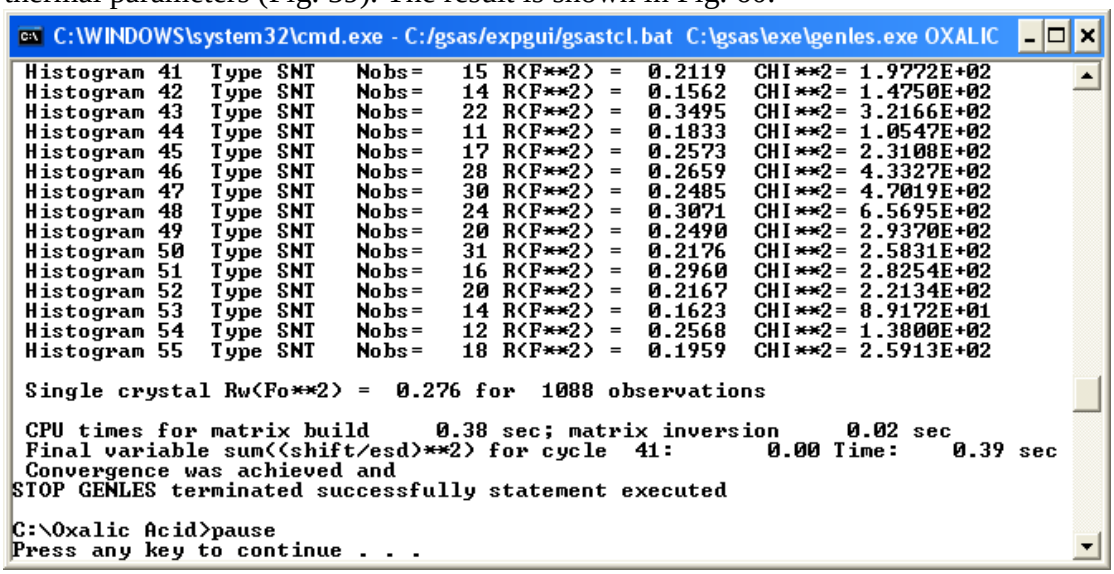

Figure 57: Refinement after including hydrogen.

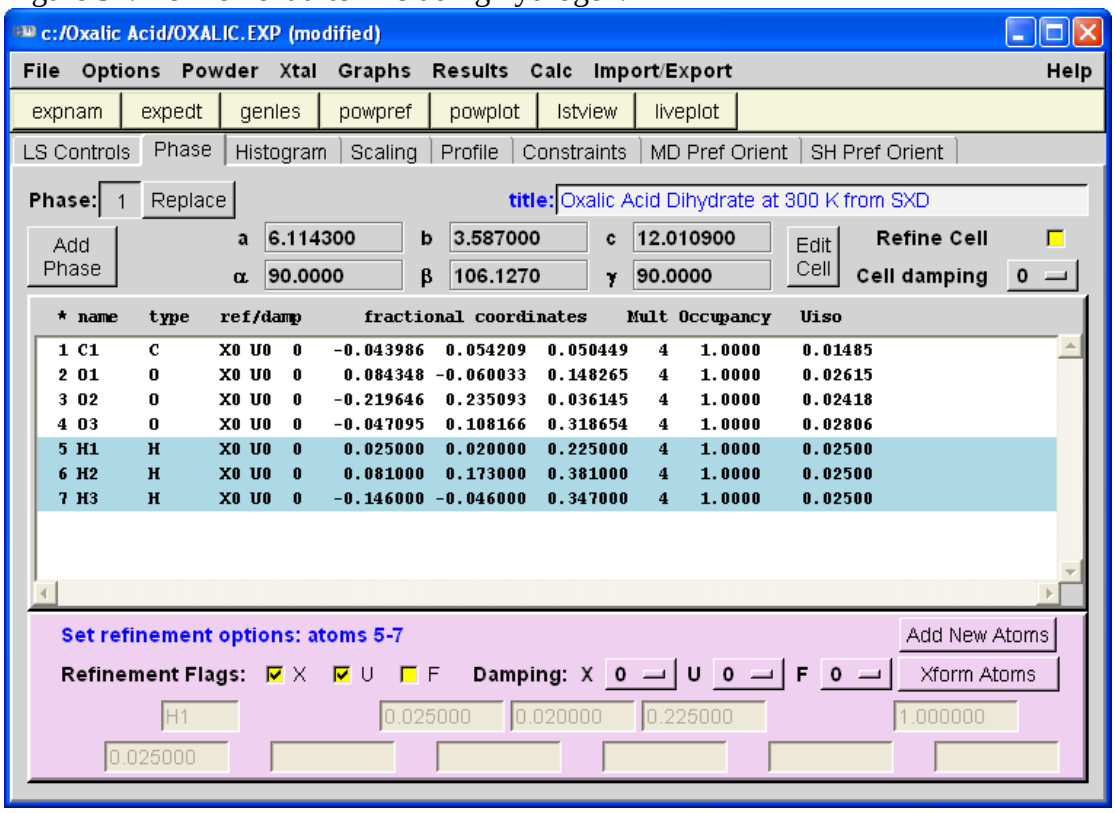

Figure 58: Select the three hydrogens and set the flags 'X' and 'U' by checking the appropriate boxes near 'Refinement Flags'.

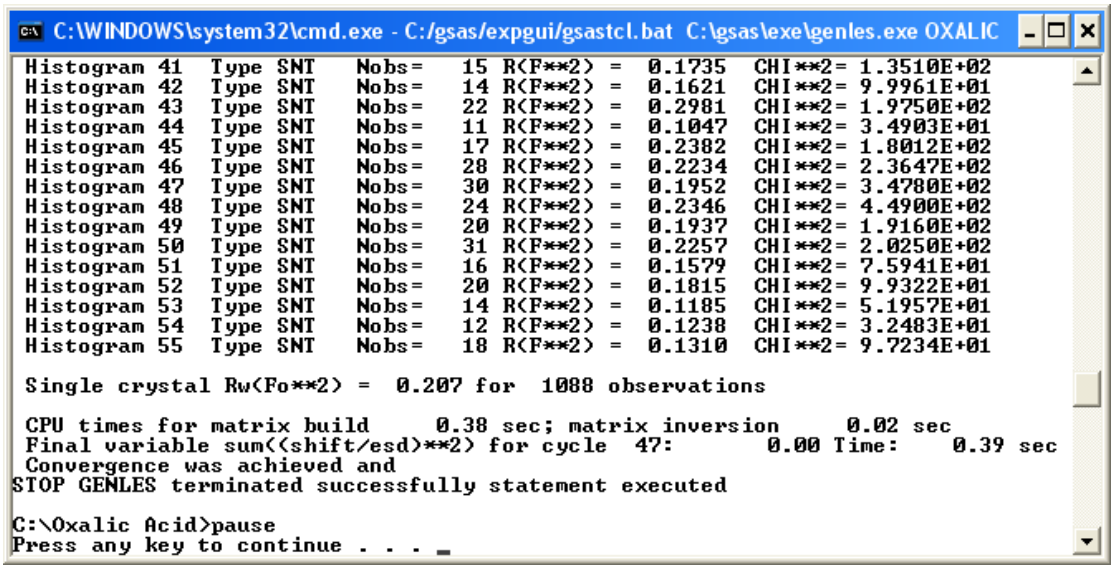

Figure 59: Refinement including hydrogen position and isotropic thermal parameter.

As a final step, we would like to change the isotropic thermal parameters to being anisotropic in order to get proper thermal ellipsoids. To do so, start again ‘EXPEDT’ and select ‘Y’ for using the current .EXP file. Enter the least-squares submenu by entering ‘L’ (Fig. 60).

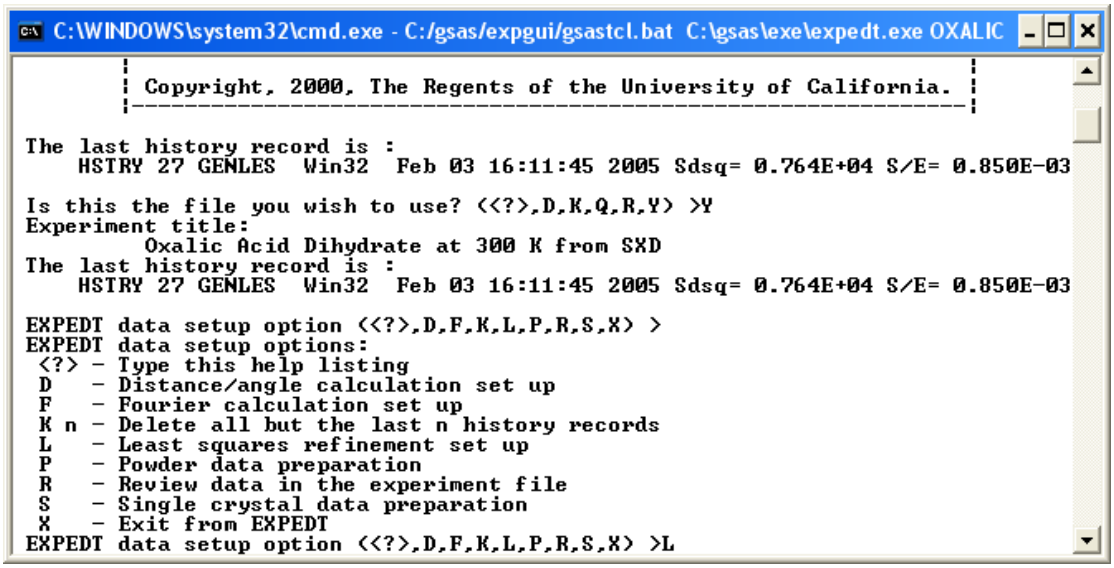

Figure 60: Enter the Least squares refinement set up.

In order to see what the options are, press <CR>. Select ‘A’ for ‘Edit atom parameters’ (Fig. 61).

Again, we get quite a selection of actions to choose from (Fig. 62). Typing ‘L’ gives a list of the atoms and their current parameters (Fig. 63). It looks very similar to the ‘Phase’ information in EXPGUI. The command we are interested in is ‘U’ to convert atom thermal factors. Type ‘U 1:7’ followed by <CR>. This will convert the thermal parameters for all atoms in the unit cell. EXPEDT asks whether the new thermal parameters should be isotropic (‘I’) or anisotropic (‘A’). We would like the latter, so enter ‘A’. The conversion is now being performed. Exit now EXPEDT using ‘X’ followed by <CR> as many times as is necessary until you arrive back at EXPGUI.

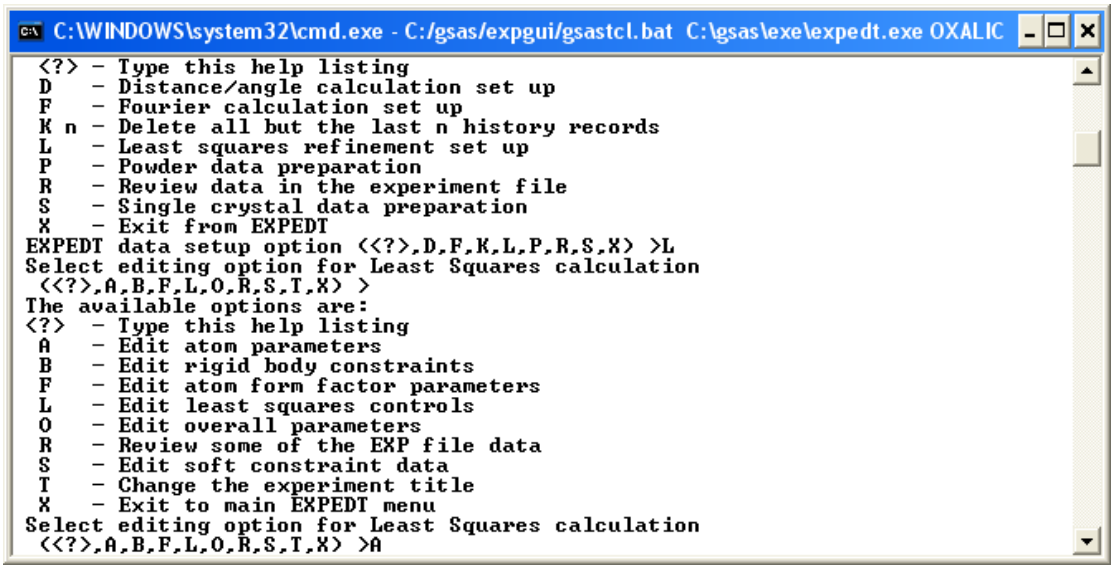

Figure 61: Select ‘A’ to access the atom parameters.

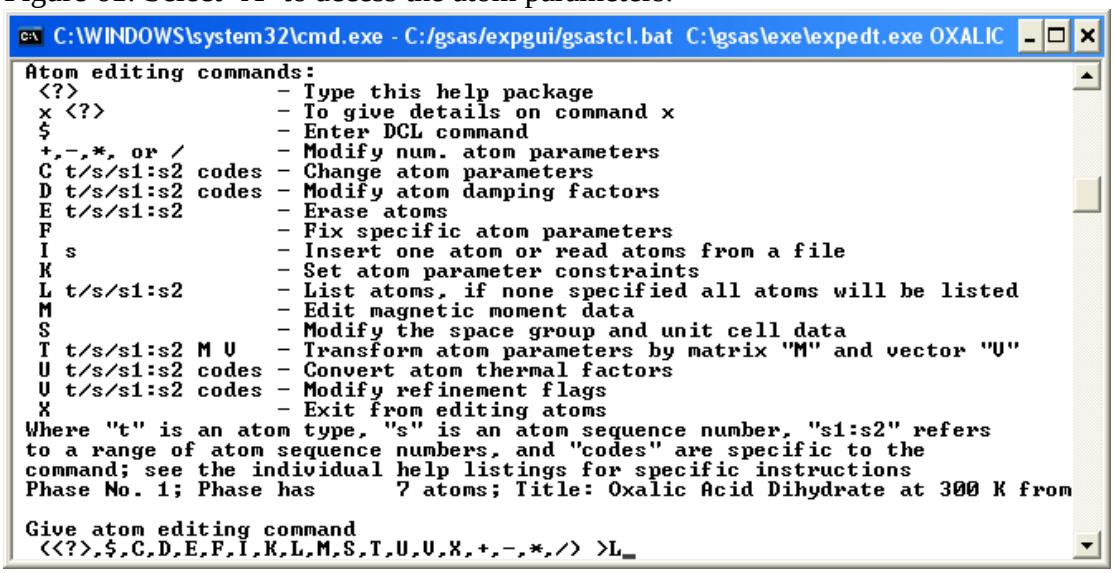

Figure 62: List of options in the ‘Edit atom parameters’ section.

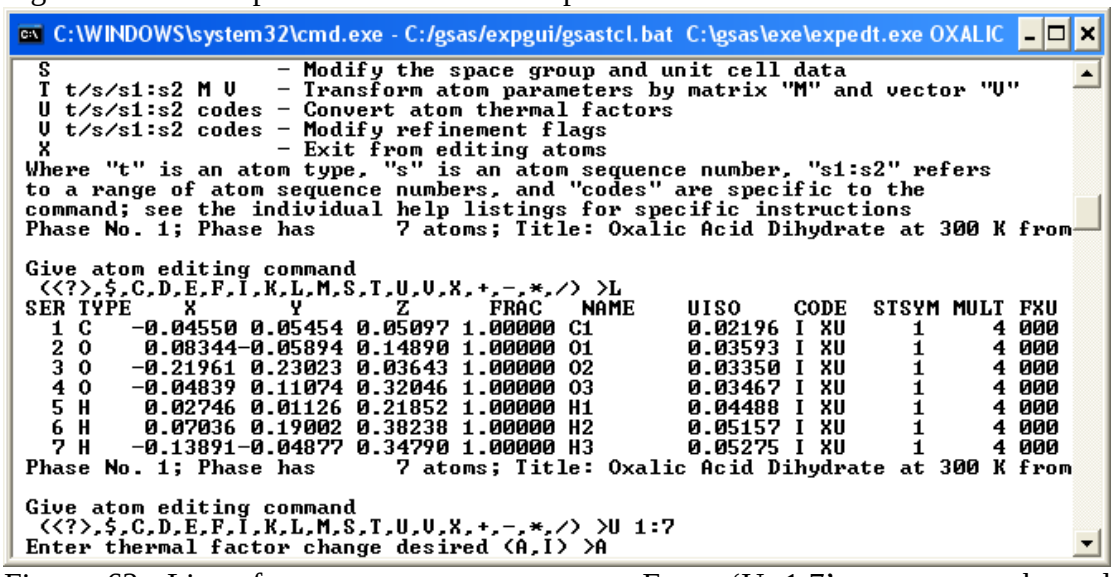

Figure 63: List of current atom parameters. Enter ‘U 1:7’ to convert thermal parameters for atoms 1 – 7. ‘A’ makes them anisotropic.

GSAS knows from the space group and site symmetry which components of the thermal tensor need to be refined. Run now GENLES until it converges. This results now in relatively low Rw(Fo**2) of 0.135. This value is entirely acceptable for time-of-flight single-crystal neutron diffraction data.

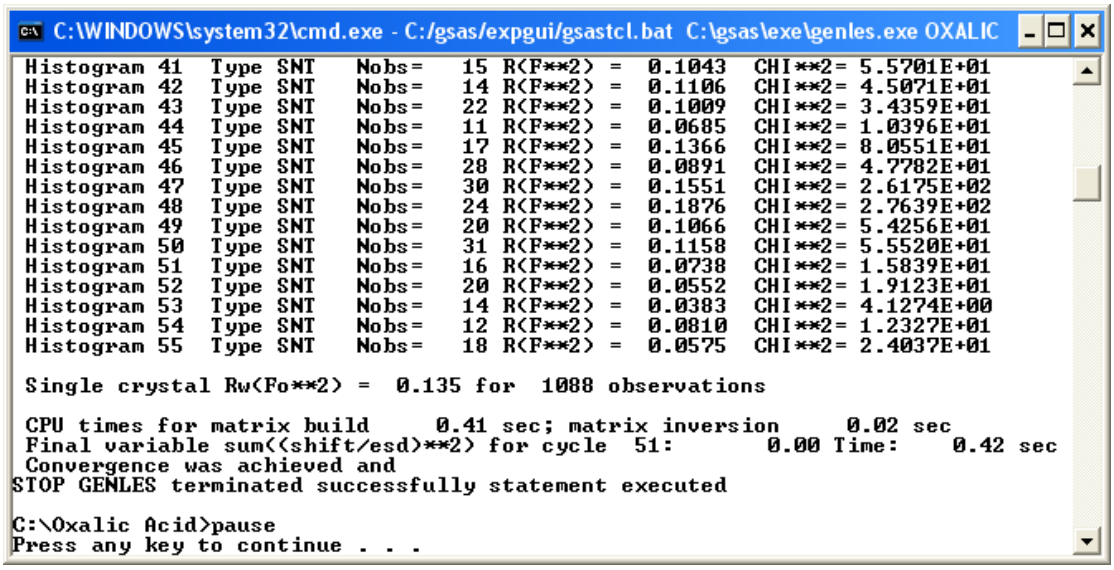

Figure 64: Final converged refinement with all thermal parameters being anisotropic.

To see a summary of the refinement, select 'LSTVIEW' from EXPGUI and scroll down until you see the list of R factors (Fig. 65).

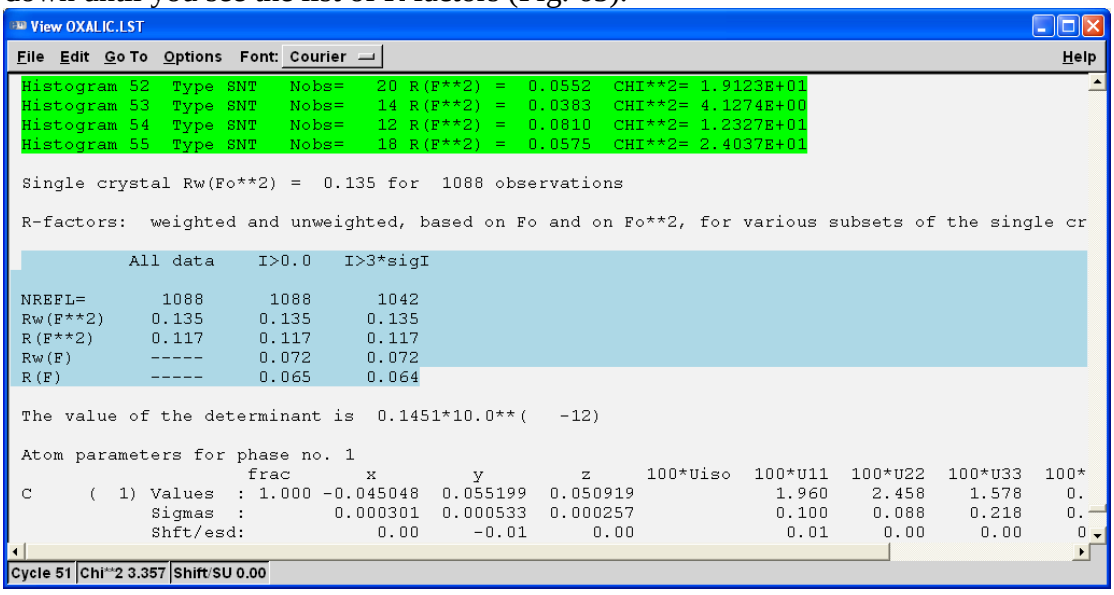

Figure 65: List of R factors. R(F) is 6.4%.

So far, we have only completed a refinement. It is now time to see the resulting crystal structure in its full glory. For this purpose start the program ATOMS61 located on the desktop (Fig. 66).


Figure 66: 'ATOMS' icon.

Conveniently, ATOMS allows to import GSAS files. Click on the ‘Import button’ (Fig. 67).

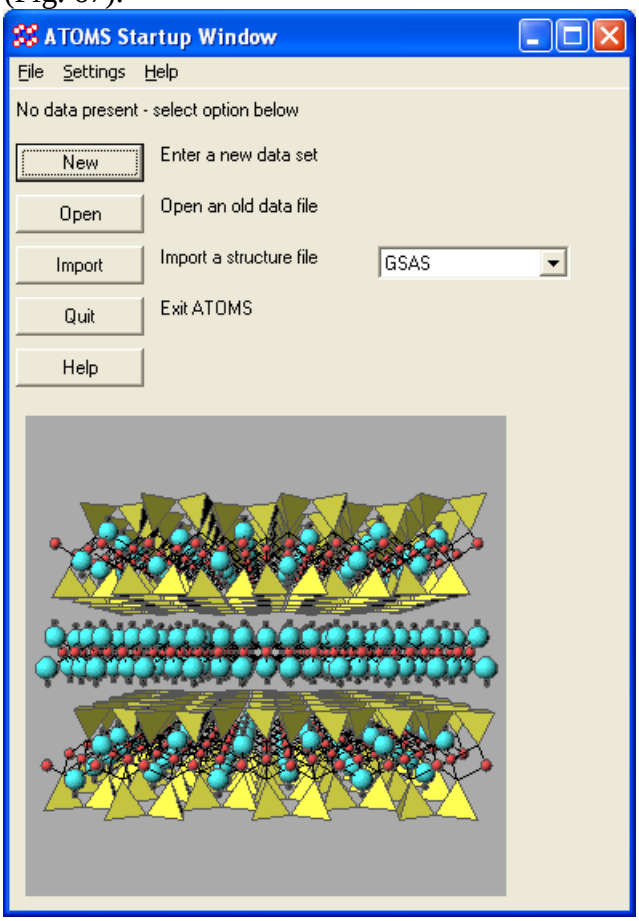

Figure 67: Start-up screen of ATOMS. Select ‘Import’.

This will pop up another window (Fig. 68). Accept all the defaults and click into ‘OK’.

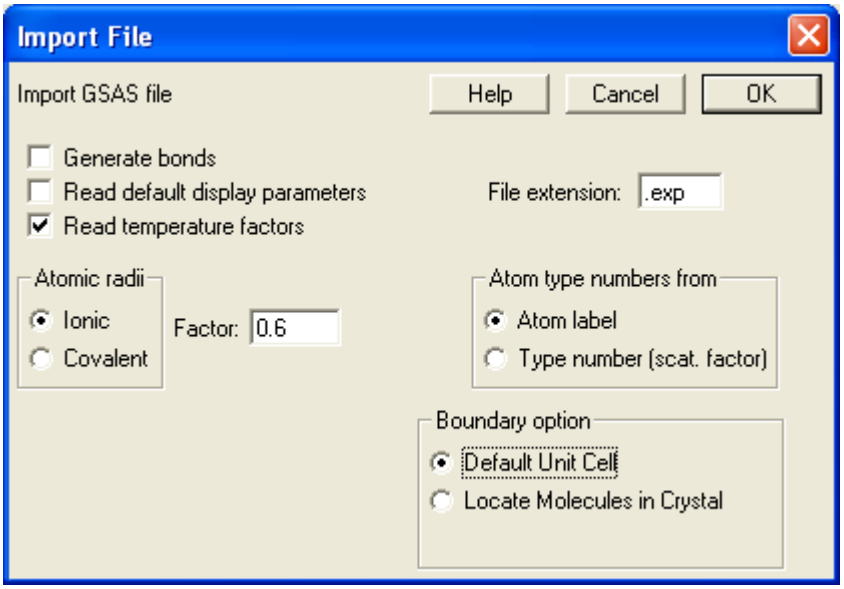

Figure 68: GSAS import dialogue. Click ‘OK’.

A file selection dialogue appears as shown in Figure 69. Navigate to the C:\Oxalic acid folder and select the file ‘Oxalic.EXP’.

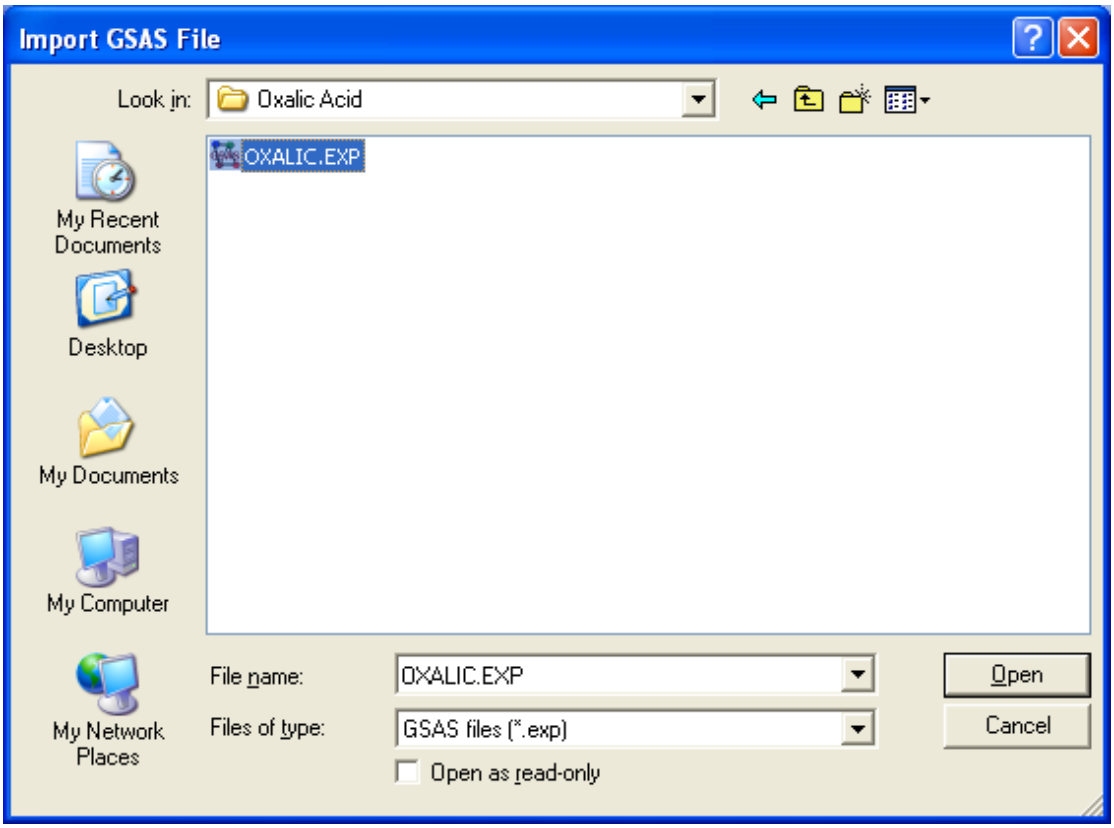

Figure 69: File selection dialog.

The next dialog asks for a file name of the structure to be saved (Figure 70). Accept the default.

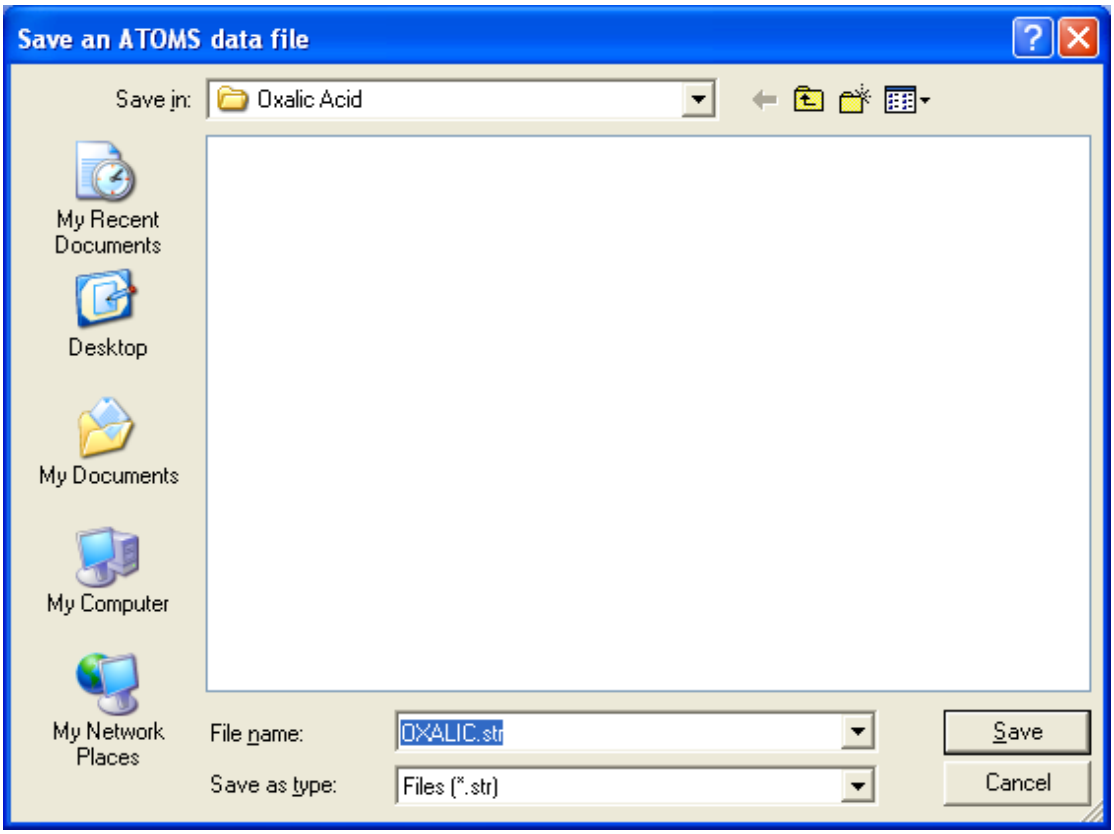

Figure 70: Dialog to specify the structure file name for saving the structure.

Click into ‘Yes’ to finally see an image of the crystal structure (Fig. 71, 72).

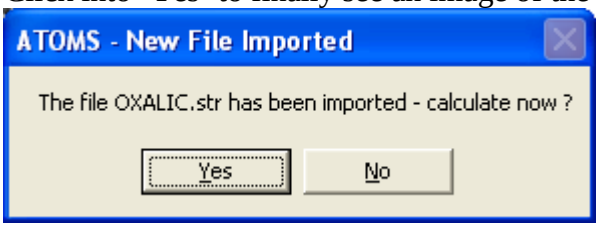

Figure 71: Click into ‘Yes’.

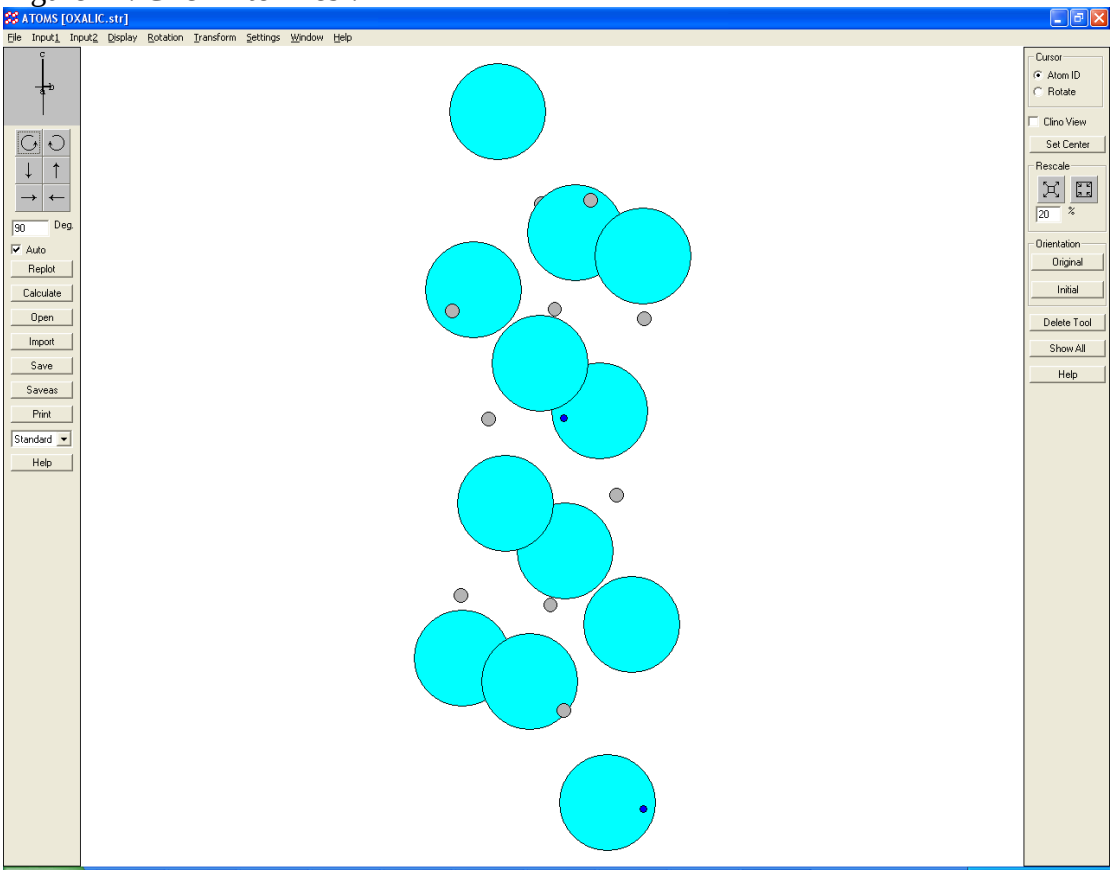

Figure 72: Initial appearance of the structure.

The initial appearance does not look very appealing. We will change this. Do the following:

1. Under the ‘Display’ menu select ‘Display 3D’ – the thermal ellipsoids should now be visible and the structure should appear more 3 dimensional.

2. Under ‘Input 1’ select ‘Boundary’ and choose from 0 to 1 inclusive.

3. Under ‘Input 2’ select ‘Unit cell’ and select ‘Show unit cell’.

4. If desired add the crystal axes under ‘Input 2’ → ‘Movable axes’.

5. Press the ‘Calculate’ button on the left side of the main ATOMS GUI.

After all these modifications the crystal structure should now appear as in Figure 73. If desired, the crystal structure can be rotated. This should be fairly intuitive. Atoms

can be identified by adding labels or simply clicking with the left mouse button on them.

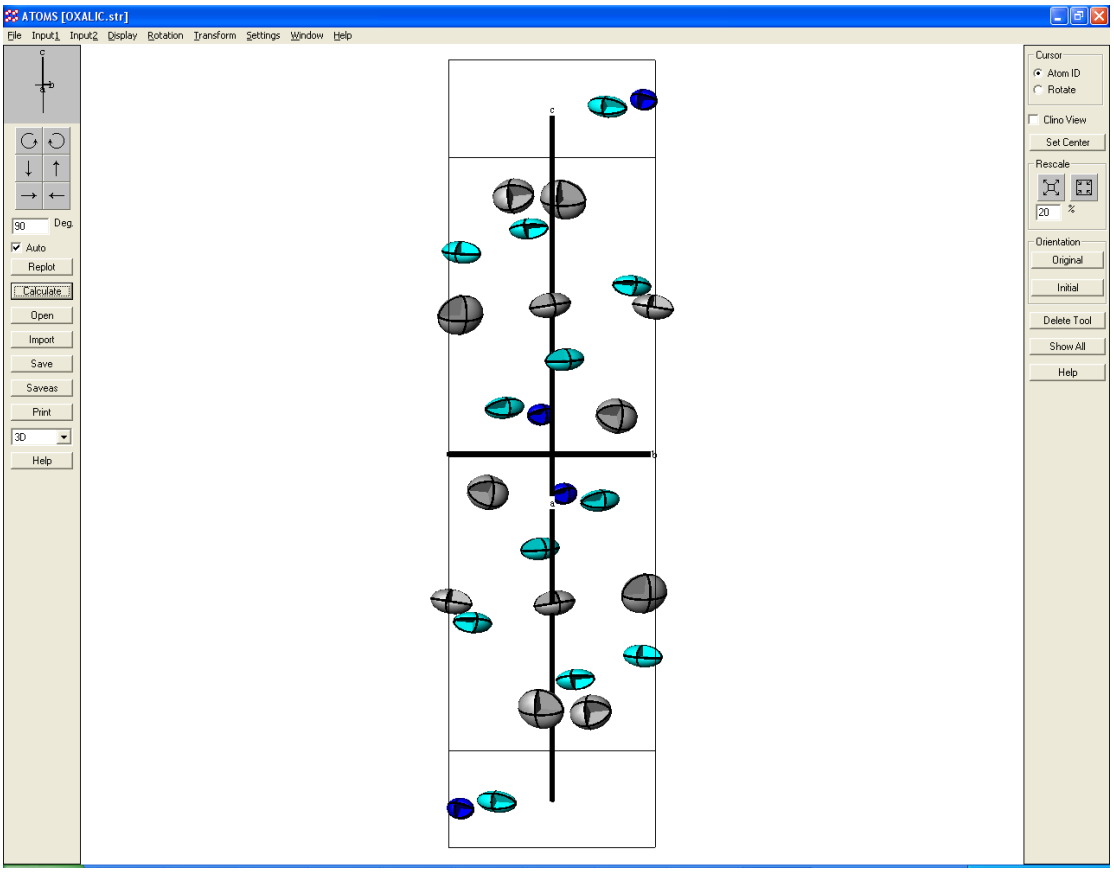

Figure 73: Final appearance of the crystal structure of Oxalic Acid Dihydrate.

This concludes the GSAS and EXPGUI tutorial and it is suggested that the user have some rest now.