

## 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 recipe 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  $a = 6.1143\text{\AA}$ ,  $b = 3.5870\text{\AA}$ ,  $c = 12.0109\text{\AA}$  and  $\beta = 106.127^\circ$ . The chemical composition is  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ . 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):

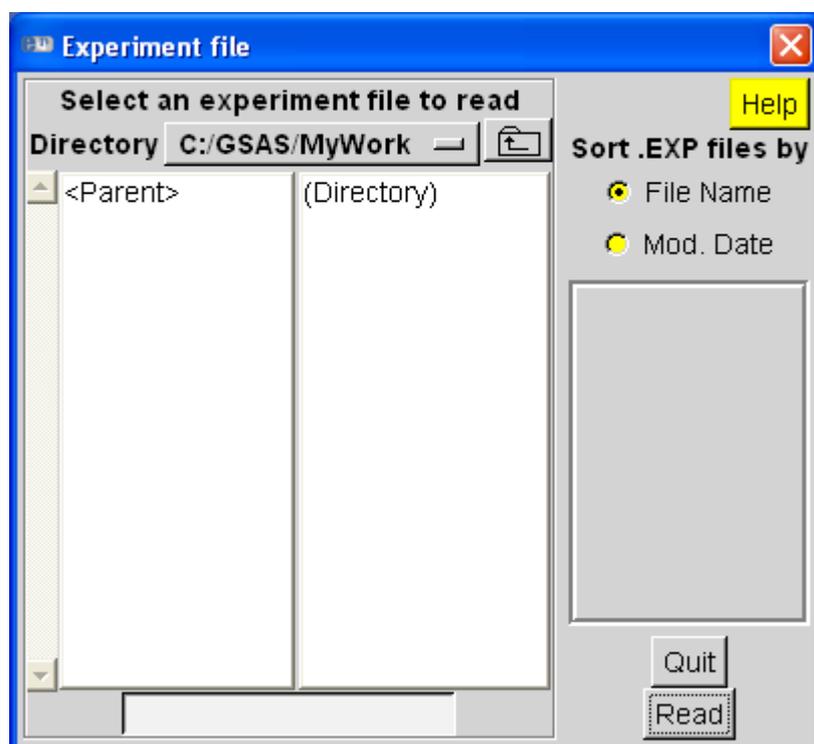


Figure 2: EXPGUI startup screen.

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.

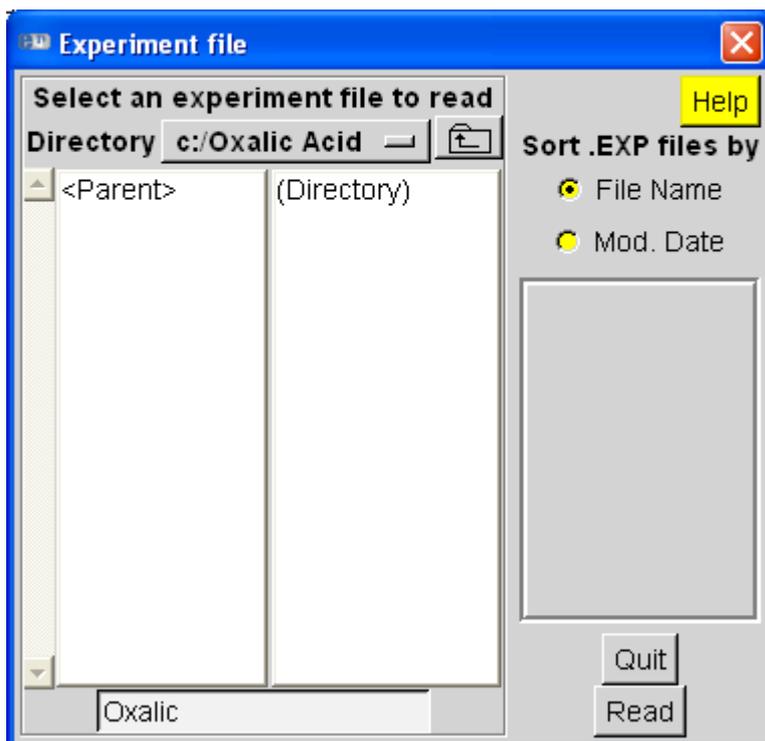


Figure 3: Select the 'C:/Oxalic Acid' folder and specify 'Oxalic' as the job name of this tutorial.

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).

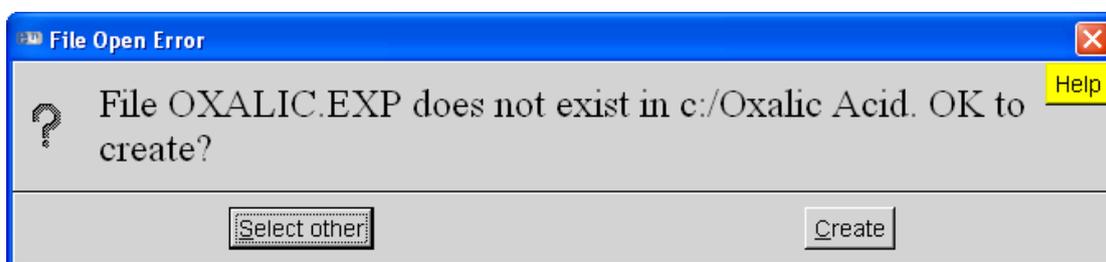


Figure 4: Select 'Create'.

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

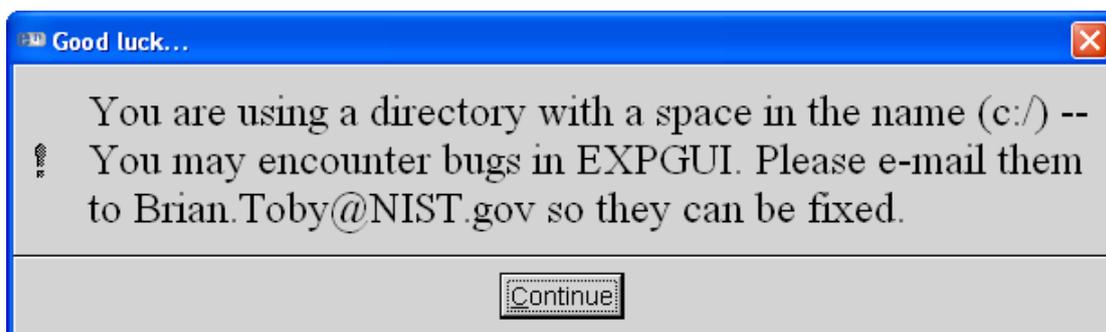


Figure 5: Press 'Continue'.

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).

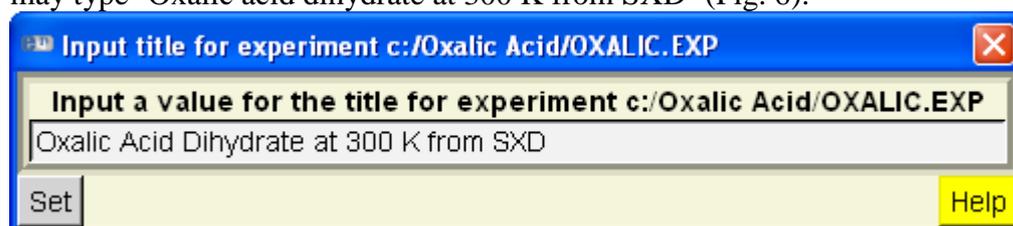


Figure 6: Specify a title and click ‘Set’.

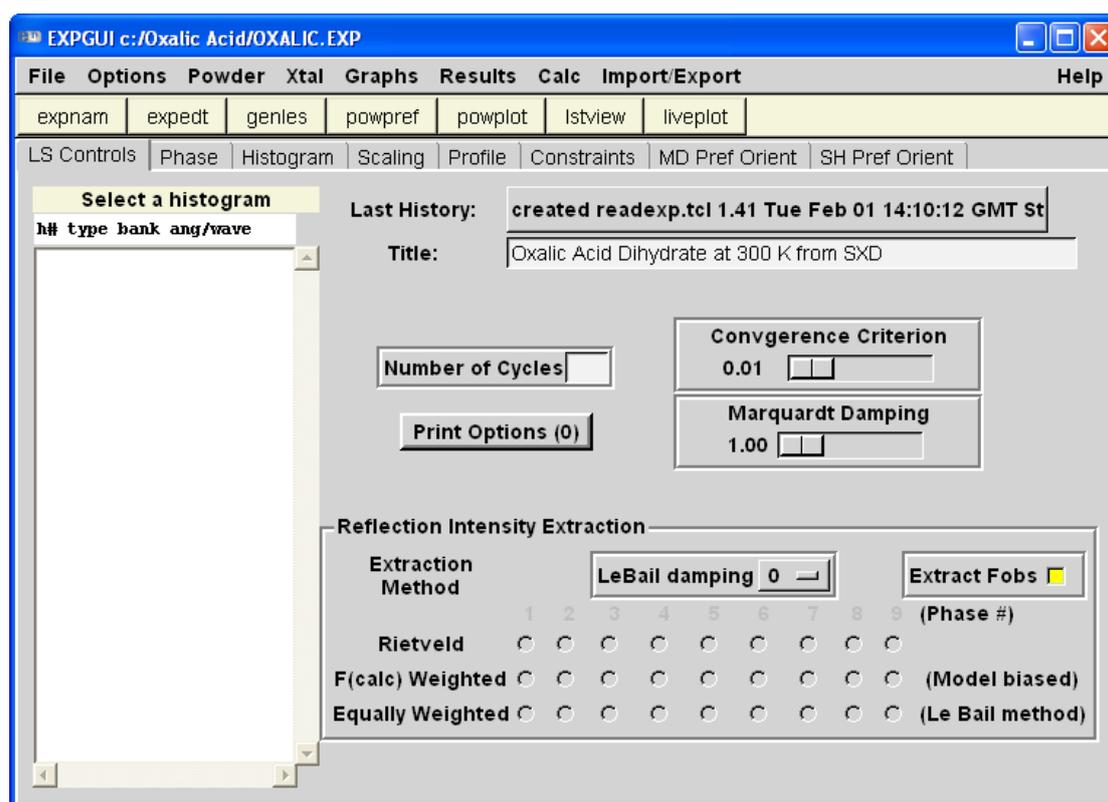


Figure 7: EXPGUI in its full glory.

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).

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/expedt.exe OXALIC
C:\Oxalic Acid>REM a batch file to a DOS command and pause
C:\Oxalic Acid>C:\gsas\exe\expedt.exe OXALIC

-----
Program EXPEDT Version Win32
A menu driven routine to edit .EXP files
Distributed on Fri Apr 16 08:09:02 2004
-----

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

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

The last history record is :
HSTRY 1 created readexp.tcl 1.41 Thu Feb 03 14:40:17 GMT Standard Time 200
5
Is this the file you wish to use? (<?>,K,Q,R,Y) >

```

Figure 8: Start-up screen for EXPEDT.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/expedt.exe OXALIC
-----
Program EXPEDT Version Win32
A menu driven routine to edit .EXP files
Distributed on Fri Apr 16 08:09:02 2004
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Allen C. Larson and Robert B. Von Dreele
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Los Alamos National Laboratory, Los Alamos, NM 87545
-----

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

The last history record is :
HSTRY 1 created readexp.tcl 1.41 Thu Feb 03 14:40:17 GMT Standard Time 200
5
Is this the file you wish to use? (<?>,K,Q,R,Y) >
The options here are:
K - Live dangerously. NO NEW COPY, NO BACKUP!
Q - Quit, exit from the program
R - Review the data in this file
Y - Create a copy of this file and edit it
Is this the file you wish to use? (<?>,K,Q,R,Y) >

```

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

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/expedt.exe OXALIC
The last history record is :
HSTRY 1 created readexp.tcl 1.41 Thu Feb 03 14:40:17 GMT Standard Time 200
5
Is this the file you wish to use? (<?>,K,Q,R,Y) >
The options here are:
K - Live dangerously. NO NEW COPY, NO BACKUP!
Q - Quit, exit from the program
R - Review the data in this file
Y - Create a copy of this file and edit it
Is this the file you wish to use? (<?>,K,Q,R,Y) >Y
Experiment title:
Oxalic Acid Dihydrate at 300 K from SXD
The last history record is :
HSTRY 1 created readexp.tcl 1.41 Thu Feb 03 14:40:17 GMT Standard Time 200
5
EXPEDT data setup option (<?>,D,K,P,R,S,X) >
EXPEDT data setup options:
<?> - Type this help listing
D - Distance/angle calculation set up
K n - Delete all but the last n history records
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>,D,K,P,R,S,X) >S_

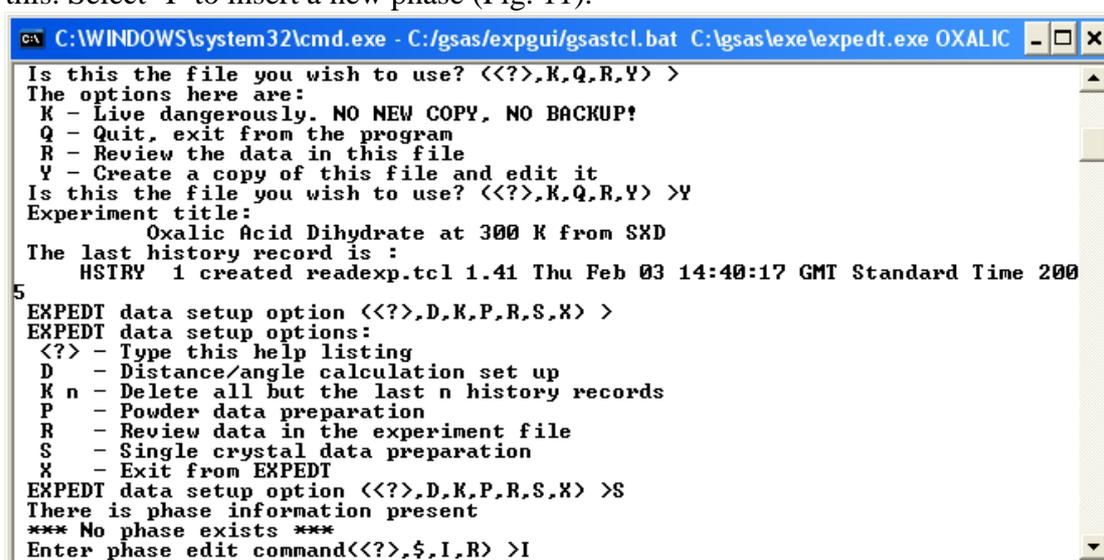
```

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>.

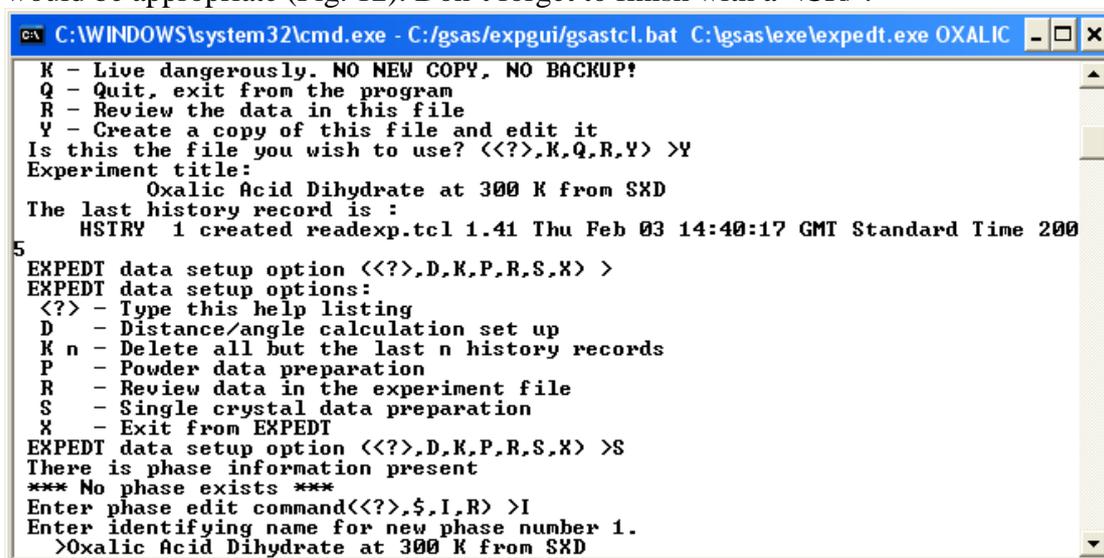
EXPEDT tells us that there is no phase information as of yet. We are about to change this. Select 'I' to insert a new phase (Fig. 11).



```
C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstactl.bat C:/gsas/lexe/lexpedt.exe OXALIC
Is this the file you wish to use? (<?>,K,Q,R,Y) >
The options here are:
K - Live dangerously. NO NEW COPY, NO BACKUP!
Q - Quit, exit from the program
R - Review the data in this file
Y - Create a copy of this file and edit it
Is this the file you wish to use? (<?>,K,Q,R,Y) >Y
Experiment title:
Oxalic Acid Dihydrate at 300 K from SXD
The last history record is :
HSTRY 1 created readexp.tcl 1.41 Thu Feb 03 14:40:17 GMT Standard Time 200
5
EXPEDT data setup option (<?>,D,K,P,R,S,X) >
EXPEDT data setup options:
<?> - Type this help listing
D - Distance/angle calculation set up
K n - Delete all but the last n history records
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>,D,K,P,R,S,X) >S
There is phase information present
*** No phase exists ***
Enter phase edit command(<?>,$,I,R) >I
```

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>.



```
C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstactl.bat C:/gsas/lexe/lexpedt.exe OXALIC
K - Live dangerously. NO NEW COPY, NO BACKUP!
Q - Quit, exit from the program
R - Review the data in this file
Y - Create a copy of this file and edit it
Is this the file you wish to use? (<?>,K,Q,R,Y) >Y
Experiment title:
Oxalic Acid Dihydrate at 300 K from SXD
The last history record is :
HSTRY 1 created readexp.tcl 1.41 Thu Feb 03 14:40:17 GMT Standard Time 200
5
EXPEDT data setup option (<?>,D,K,P,R,S,X) >
EXPEDT data setup options:
<?> - Type this help listing
D - Distance/angle calculation set up
K n - Delete all but the last n history records
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>,D,K,P,R,S,X) >S
There is phase information present
*** No phase exists ***
Enter phase edit command(<?>,$,I,R) >I
Enter identifying name for new phase number 1.
>Oxalic Acid Dihydrate at 300 K from SXD
```

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.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstactl.bat C:/gsas/lexe/lexpedt.exe OXALIC
Y - Create a copy of this file and edit it
Is this the file you wish to use? (<?>,K,Q,R,Y) >Y
Experiment title:
      Oxalic Acid Dihydrate at 300 K from SKD
The last history record is :
      HSTRY 1 created readexp.tcl 1.41 Thu Feb 03 14:40:17 GMT Standard Time 200
5
EXPEDT data setup option (<?>,D,K,P,R,S,X) >
EXPEDT data setup options:
<?> - Type this help listing
D - Distance/angle calculation set up
R n - Delete all but the last n history records
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>,D,K,P,R,S,X) >S
There is phase information present
*** No phase exists ***
Enter phase edit command(<?>,$,I,R) >I
Enter identifying name for new phase number 1.
>Oxalic Acid Dihydrate at 300 K from SKD
No space group information found
Enter space group symbol (ex: P n a 21, P 42/n c m, R -3 c, P 42/m,
R -3 m R for rhombohedral setting) >P 21/n_

```

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  $\beta$  of the unit cell. Just as a reminder, these values are  $a = 6.1143\text{\AA}$ ,  $b = 3.5870\text{\AA}$ ,  $c = 12.0109\text{\AA}$  and  $\beta = 106.127^\circ$  (Fig. 14).

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstactl.bat C:/gsas/lexe/lexpedt.exe OXALIC
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>,D,K,P,R,S,X) >S
There is phase information present
*** No phase exists ***
Enter phase edit command(<?>,$,I,R) >I
Enter identifying name for new phase number 1.
>Oxalic Acid Dihydrate at 300 K from SKD
No space group information found
Enter space group symbol (ex: P n a 21, P 42/n c m, R -3 c, P 42/m,
R -3 m R for rhombohedral setting) >P 21/n_

Space group P 21/n
The lattice is centric primitive monoclinic Laue symmetry 2/m
Multiplicity of a general site is 4
The unique axis is b
The symmetry of the point 0,0,0 contains 1bar

The equivalent positions are:
< 1> X Y Z < 2> 1/2-X 1/2+Y 1/2-Z

Enter real lattice parameters (Angstroms & degrees)
Enter a, b, c and Beta >6.1143, 3.587, 12.0109, 106.127

```

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.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gststcl.bat C:/gsas/lexe/lexpedt.exe OXALIC
Space group P 21/n
The lattice is centric primitive monoclinic Laue symmetry 2/n
Multiplicity of a general site is 4
The unique axis is b
The symmetry of the point 0,0,0 contains 1bar

The equivalent positions are:
< 1>      X      Y      Z < 2> 1/2-X 1/2+Y 1/2-Z

Enter real lattice parameters (Angstroms & degrees)
Enter a, b, c and Beta >6.1143, 3.587, 12.0109, 106.127
Lattice parameters are
a,b,c = 6.114300 3.587000 12.010900
angles = 90.000 106.127 90.000
volume = 253.057
Lattice symmetry is monoclinic
Space group symmetry is monoclinic
Enter phase edit command(<?>,$,D,E,F,M,I,L,R,S,X) >x
Enter Single Crystal data preparation option(<?>,I,P,T,X) >x
EXPEDT data setup option (<?>,$,D,K,P,R,S,X) >x
STOP EXPEDT terminated successfully statement executed

C:\Oxalic Acid>pause
Press any key to continue . . .

```

Figure 15: Just about to exit EXPEDT.

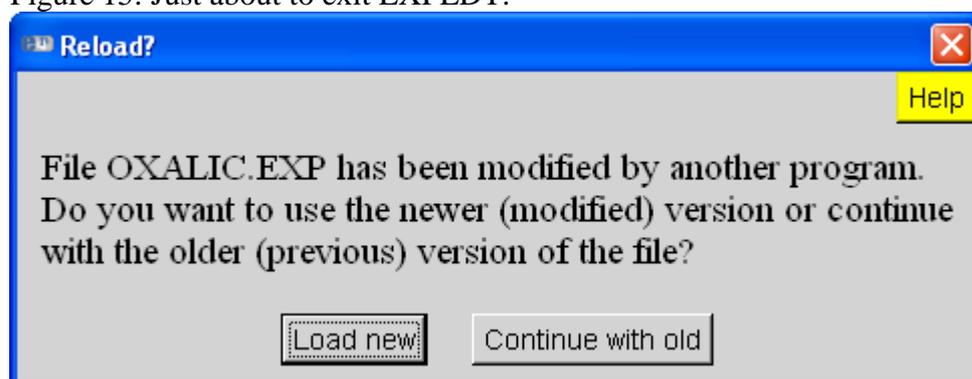


Figure 16: Select 'Load new'.

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  $\text{\AA}^{-3}$ . 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.

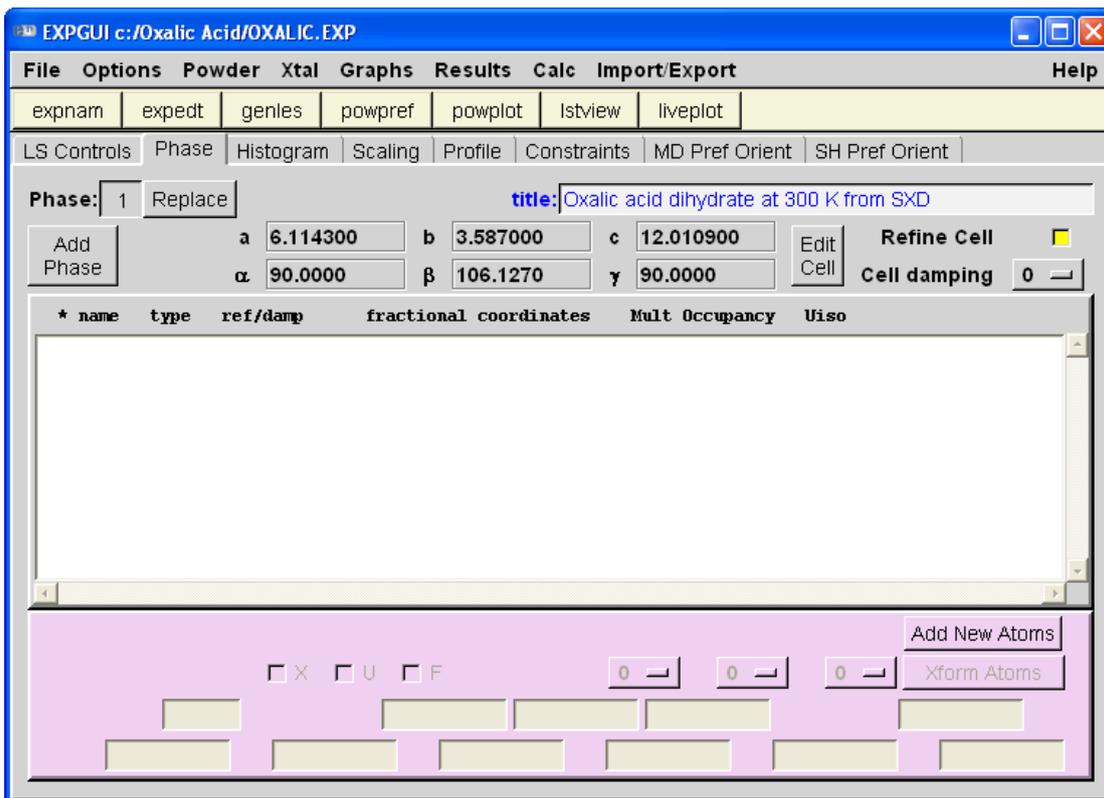


Figure 17: Appearance of the 'Phase' information after completing EXPEDT.

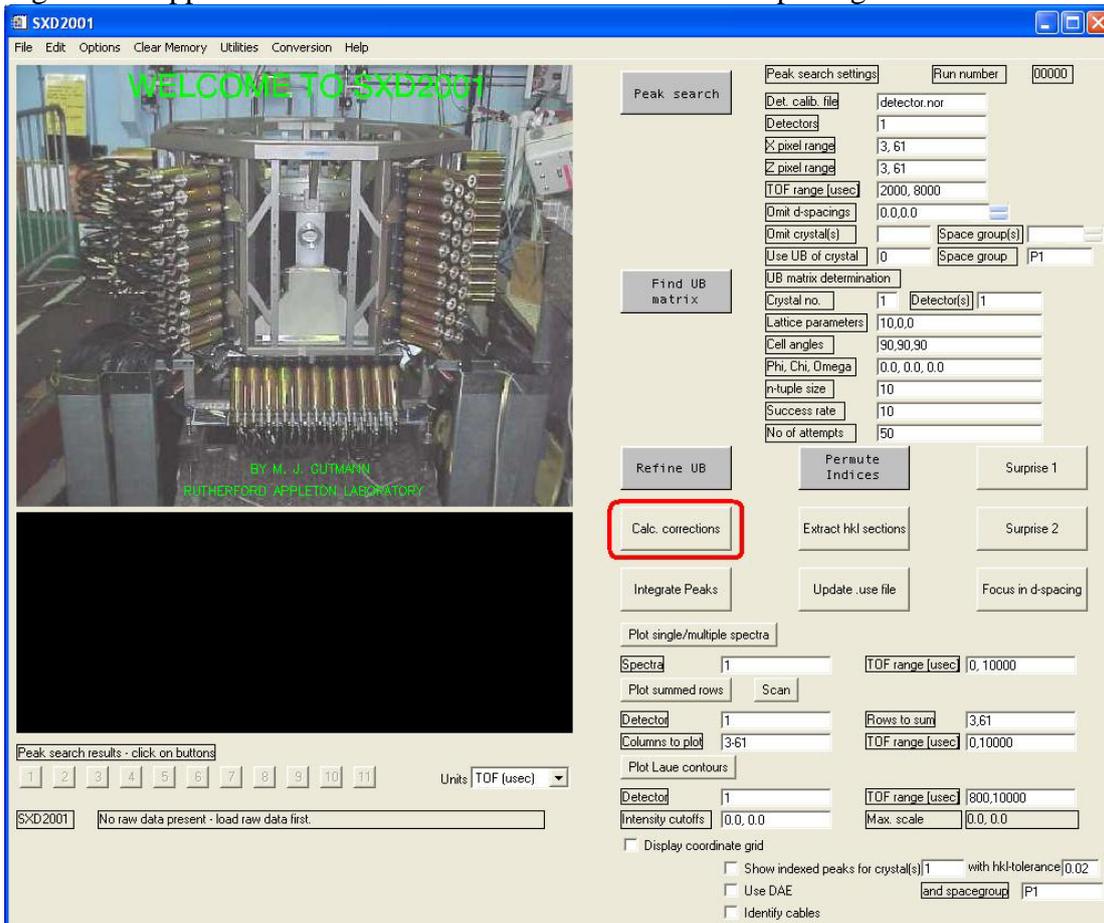


Figure 18: SXD2001 main GUI. The location of the 'Calc. corrections' button is indicated.

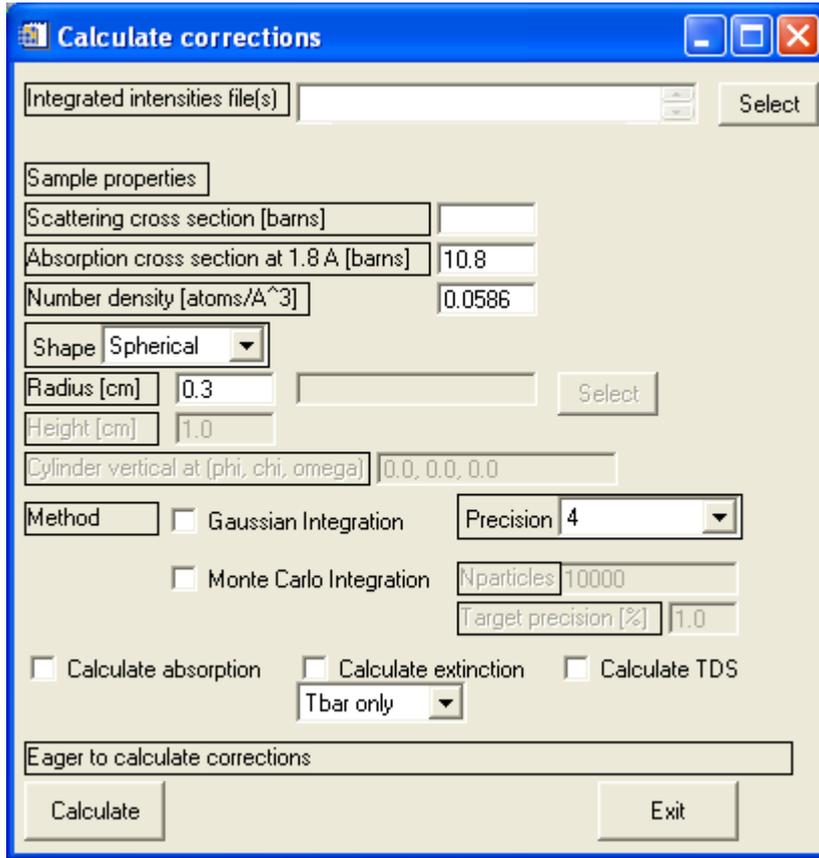


Figure 19: Initial appearance of the calculate corrections GUI.

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  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ . The scattering and absorption cross section per atom are calculated as follows:

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

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

where  $n$  is the number of atoms in the formula and  $\sigma_{abs}^i$ ,  $\sigma_{scat}^i$  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.

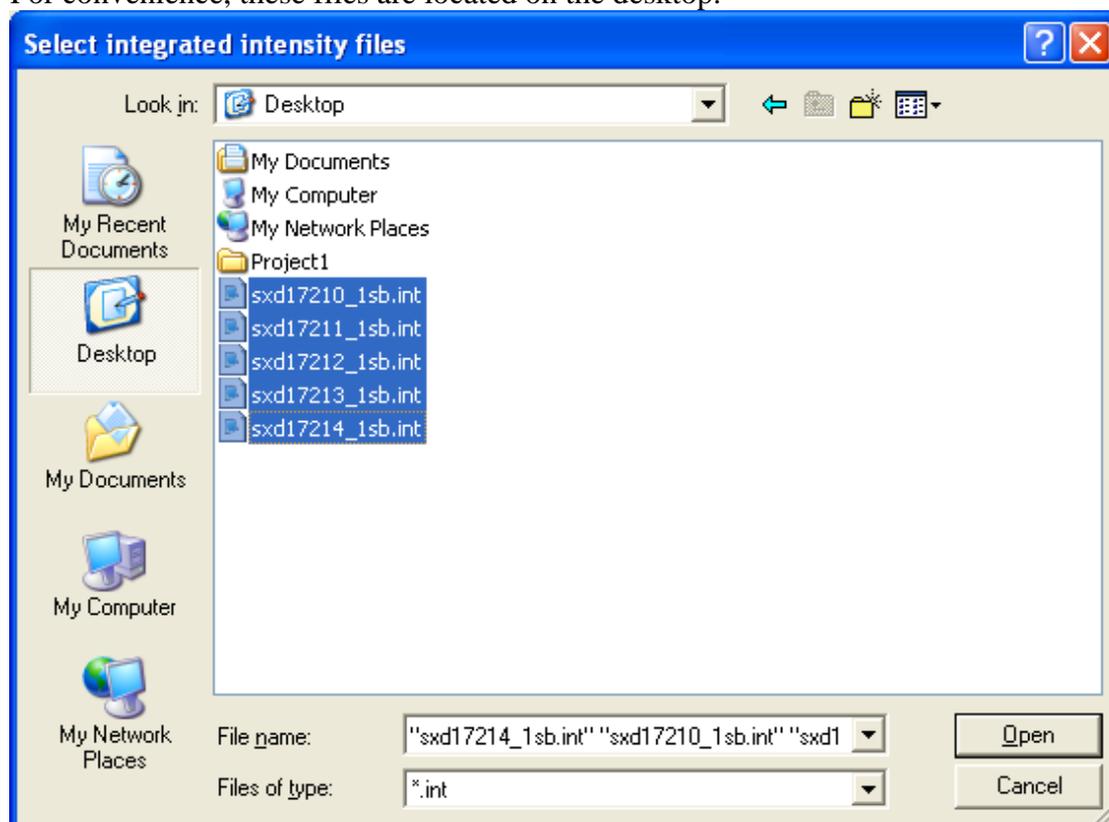


Figure 20: Select the reflection files for use in GSAS.

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!

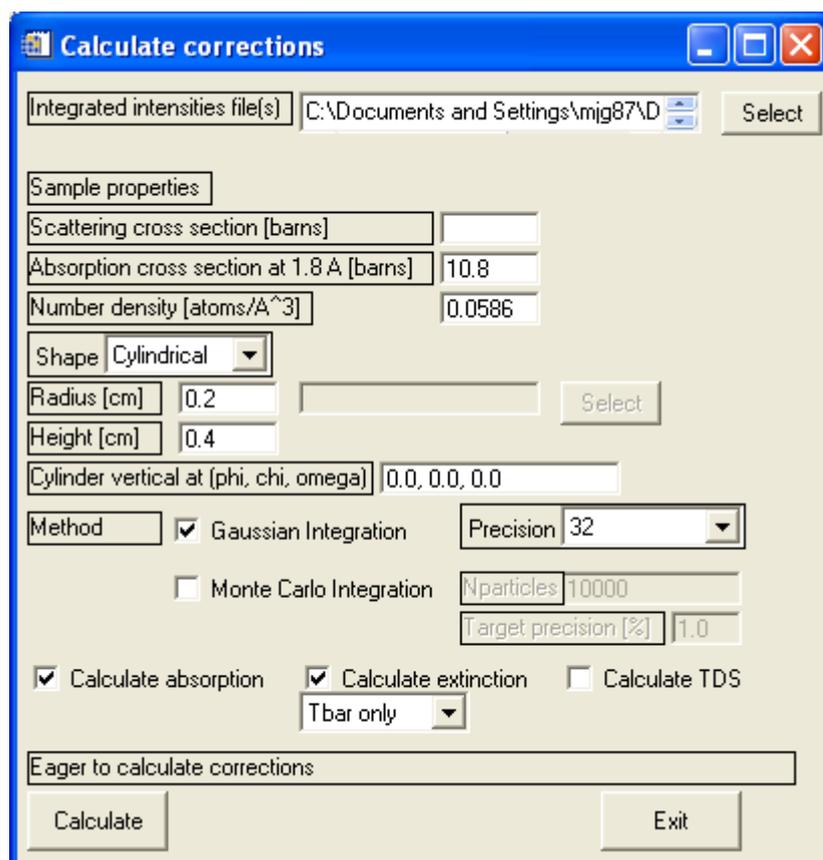


Figure 21: Specify the scattering and absorption cross section as well as the number density.

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’.

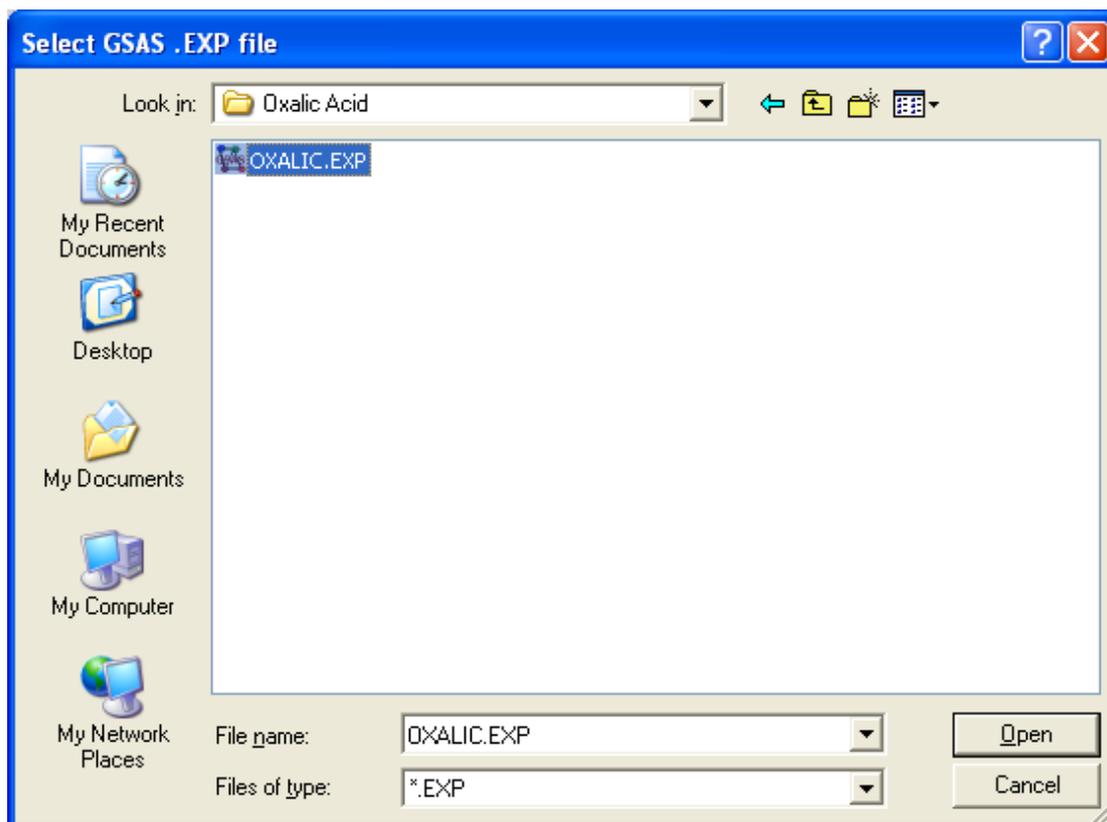


Figure 22: Select 'Oxalic.exp'.

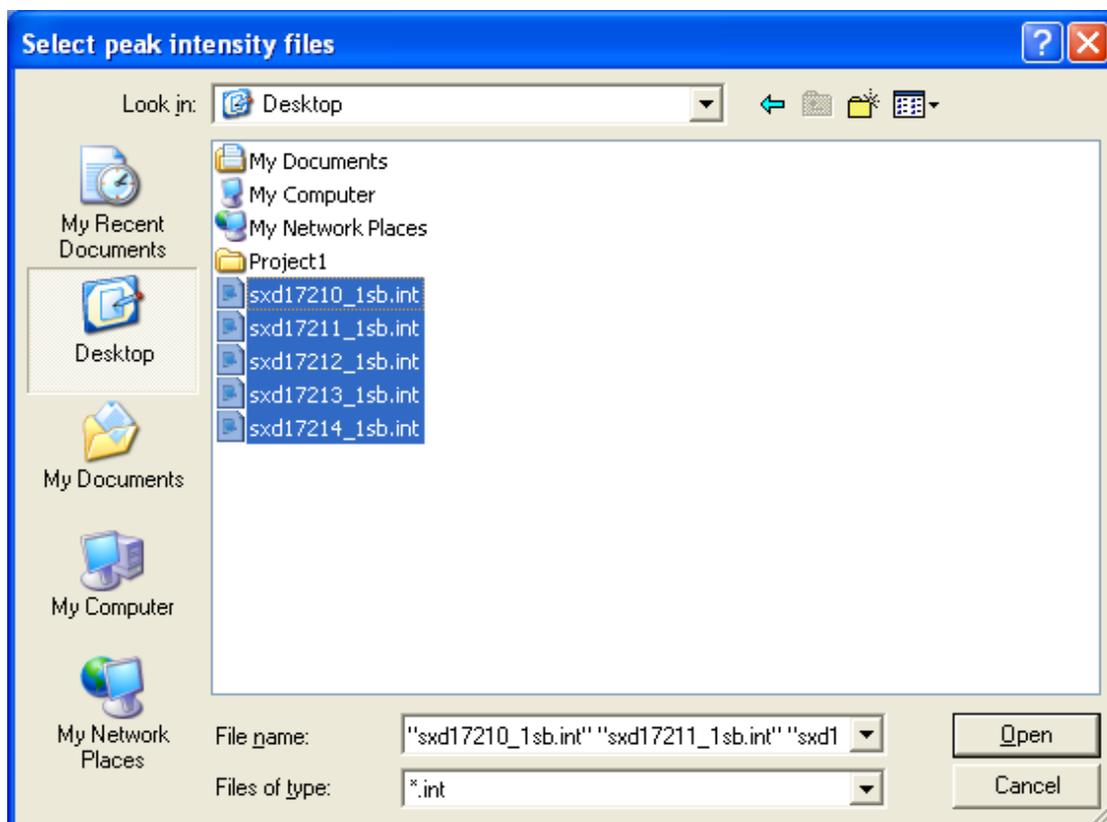


Figure 23: Select the reflection files.

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.

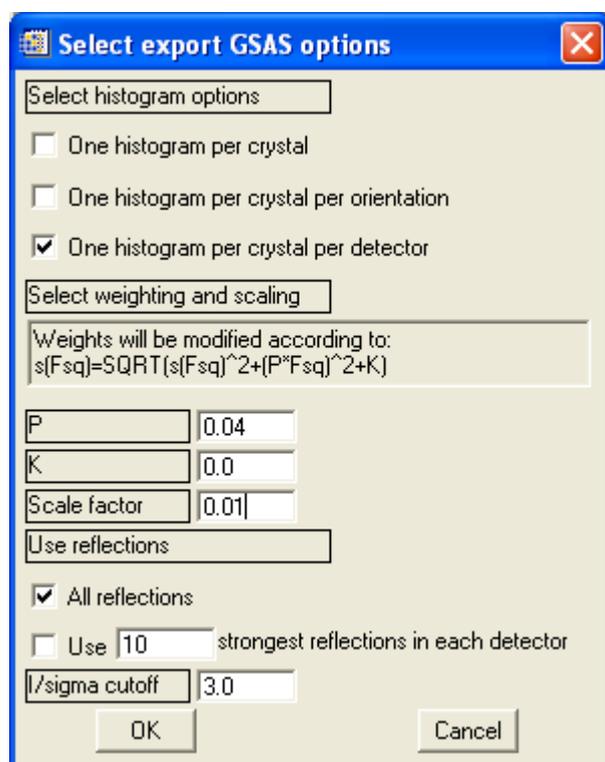


Figure 24: GSAS export options. Select ‘One histogram per crystal per detector’.

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

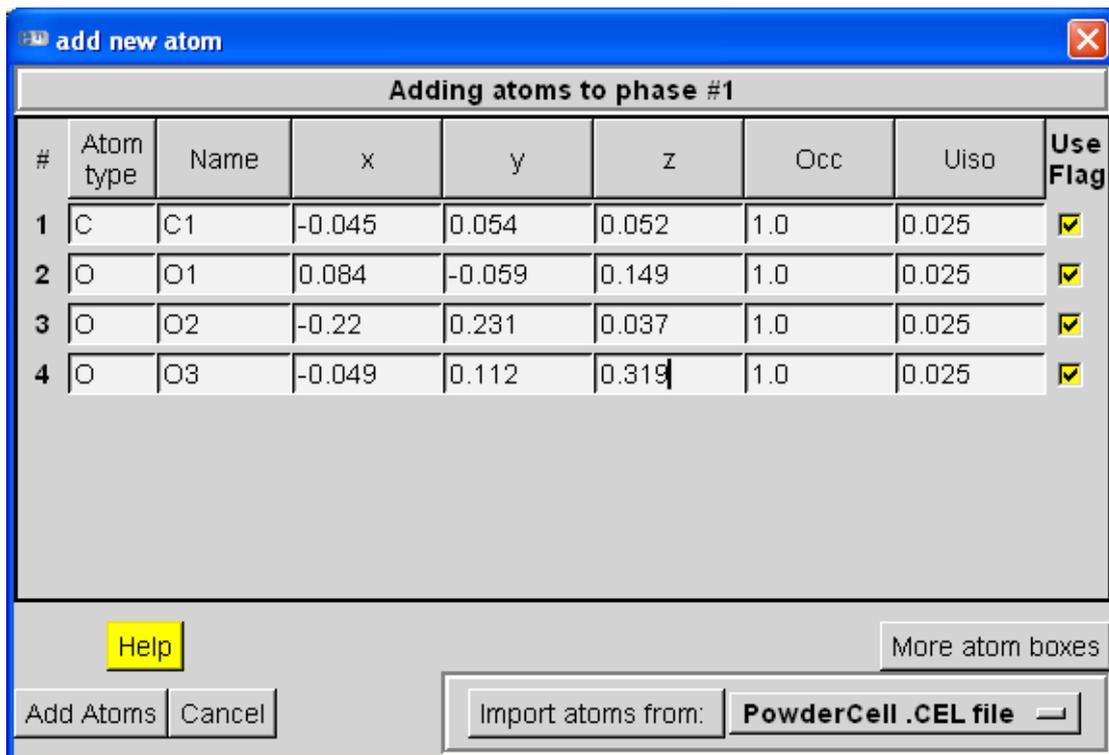


Figure 25: Add new atoms dialog. Click in 'Add Atoms' to finish.

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

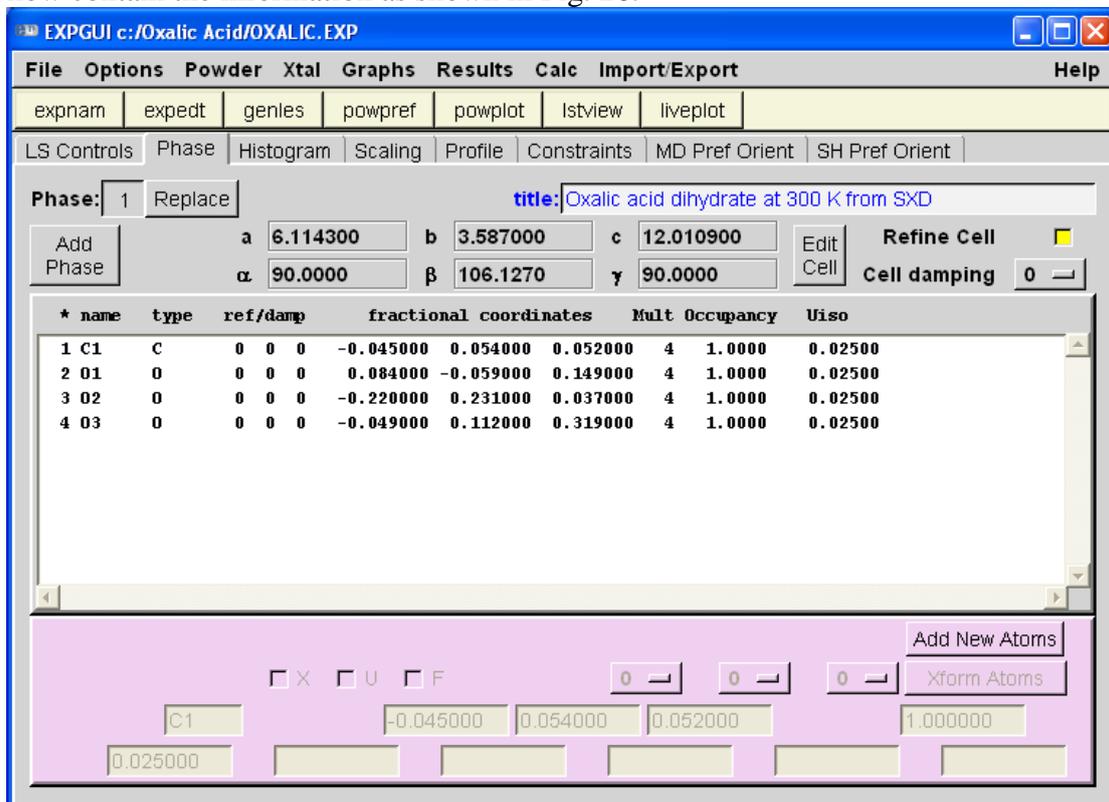


Figure 26: Phase section of EXPGUI after entering the atoms.

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.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gsasctl.bat C:/gsas/lexe/genles.exe OXALIC
Histogram 41 Type SNT Nobs = 15 R(F**2) = 0.6393 CHI**2 = 1.4479E+03
Histogram 42 Type SNT Nobs = 14 R(F**2) = 0.3965 CHI**2 = 8.0556E+02
Histogram 43 Type SNT Nobs = 22 R(F**2) = 0.5024 CHI**2 = 8.2945E+02
Histogram 44 Type SNT Nobs = 11 R(F**2) = 0.4025 CHI**2 = 5.3857E+02
Histogram 45 Type SNT Nobs = 17 R(F**2) = 0.3769 CHI**2 = 5.3823E+02
Histogram 46 Type SNT Nobs = 28 R(F**2) = 0.4524 CHI**2 = 1.3615E+03
Histogram 47 Type SNT Nobs = 30 R(F**2) = 0.7077 CHI**2 = 3.3362E+03
Histogram 48 Type SNT Nobs = 24 R(F**2) = 0.4291 CHI**2 = 1.2985E+03
Histogram 49 Type SNT Nobs = 20 R(F**2) = 0.6213 CHI**2 = 1.8219E+03
Histogram 50 Type SNT Nobs = 31 R(F**2) = 0.3911 CHI**2 = 8.4500E+02
Histogram 51 Type SNT Nobs = 16 R(F**2) = 0.4944 CHI**2 = 6.1065E+02
Histogram 52 Type SNT Nobs = 20 R(F**2) = 0.6656 CHI**2 = 1.9415E+03
Histogram 53 Type SNT Nobs = 14 R(F**2) = 0.3936 CHI**2 = 4.4518E+02
Histogram 54 Type SNT Nobs = 12 R(F**2) = 0.3483 CHI**2 = 2.4584E+02
Histogram 55 Type SNT Nobs = 18 R(F**2) = 0.7475 CHI**2 = 2.2459E+03

Single crystal Rw(Fo**2) = 0.641 for 1088 observations

CPU times for matrix build 0.38 sec; matrix inversion 0.00 sec
Final variable sum((shift/esd)**2) for cycle 7: 0.00 Time: 0.38 sec
Convergence was achieved and
STOP GENLES terminated successfully statement executed

C:\Oxalic Acid>pause
Press any key to continue . . . _

```

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  $R_w(F_o^{**2})$ ' (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  $R_w(F_o^{**2})$  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  $R_w(F_o^{**2})$  slightly decreases to about 0.626. This is still not overwhelming.

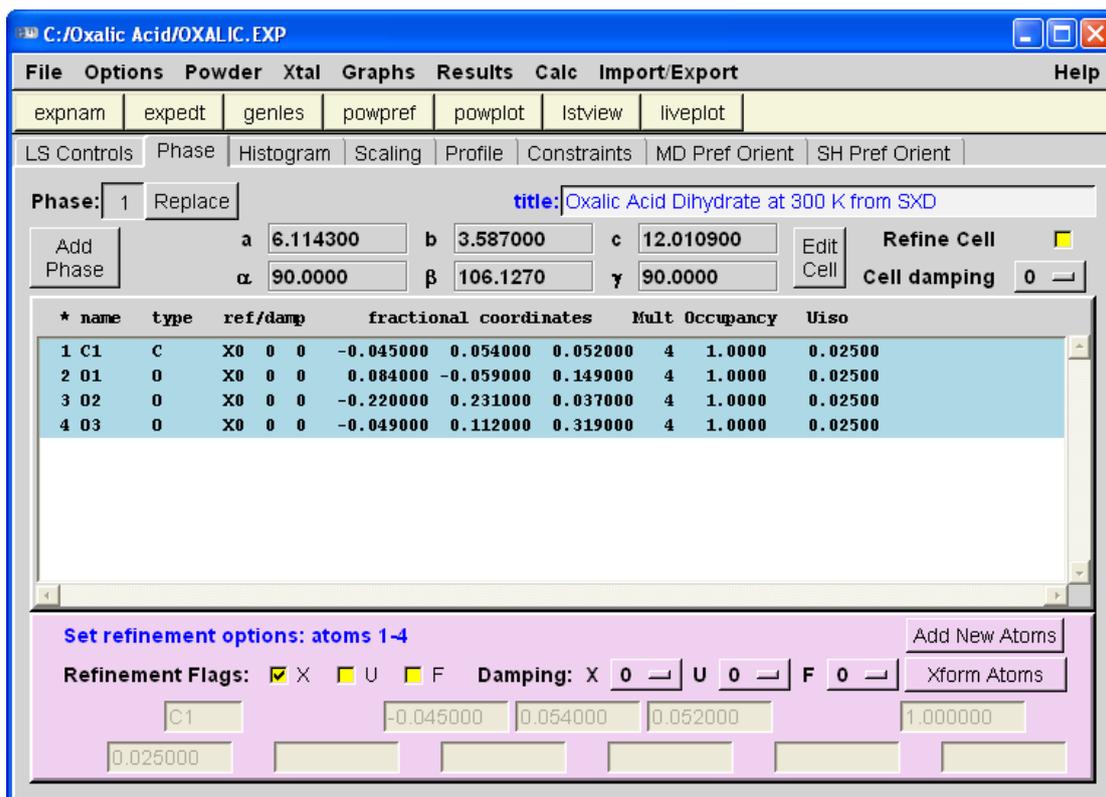


Figure 28: Setting the refinement flag to refine the atomic positions.

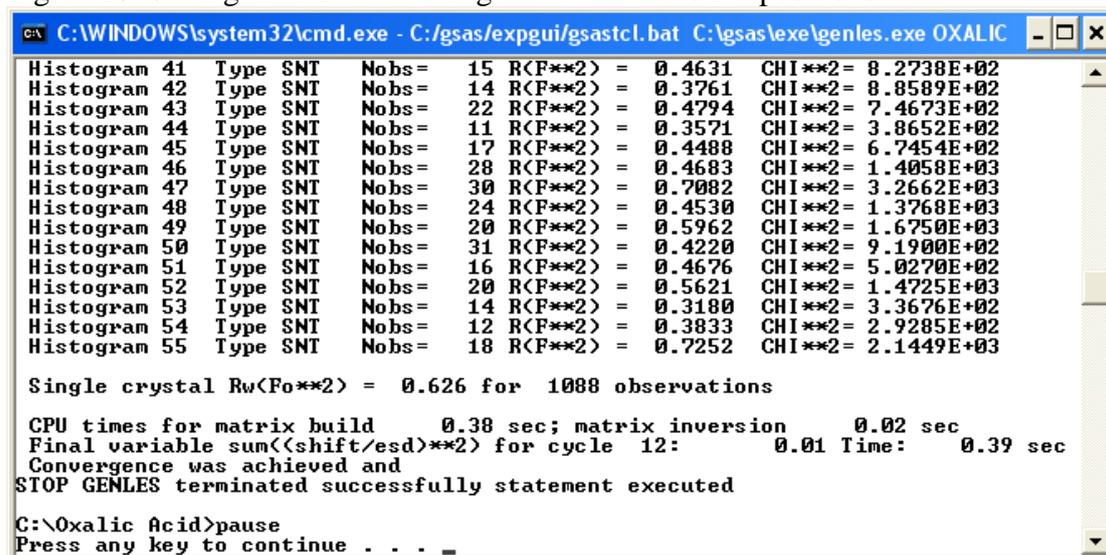


Figure 29: Refinement result after using GENLES.

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).

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/expedt.exe OXALIC
C:\Oxalic Acid>REM a batch file to a DOS command and pause
C:\Oxalic Acid>C:/gsas/lexe/expedt.exe OXALIC

-----
Program EXPEDT Version Win32
A menu driven routine to edit .EXP files
Distributed on Fri Apr 16 08:09:02 2004
-----

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

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

The last history record is :
HSTRY 9 GENLES Win32 Feb 03 14:48:01 2005 Sdsq= 0.699E+05 S/E= 0.913E-02

Is this the file you wish to use? (<?>,D,K,Q,R,Y) >Y_

```

Figure 30: Select 'Y' to use the current file.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/expedt.exe OXALIC

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

The last history record is :
HSTRY 9 GENLES Win32 Feb 03 14:48:01 2005 Sdsq= 0.699E+05 S/E= 0.913E-02

Is this the file you wish to use? (<?>,D,K,Q,R,Y) >Y
Experiment title:
Oxalic Acid Dihydrate at 300 K from SKD
The last history record is :
HSTRY 9 GENLES Win32 Feb 03 14:48:01 2005 Sdsq= 0.699E+05 S/E= 0.913E-02

EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
EXPEDT data setup options:
<?> - Type this help listing
D - Distance/angle calculation set up
F - Fourier calculation set up
K n - Delete all but the last n history records
L - Least squares refinement set up
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >L

```

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

```

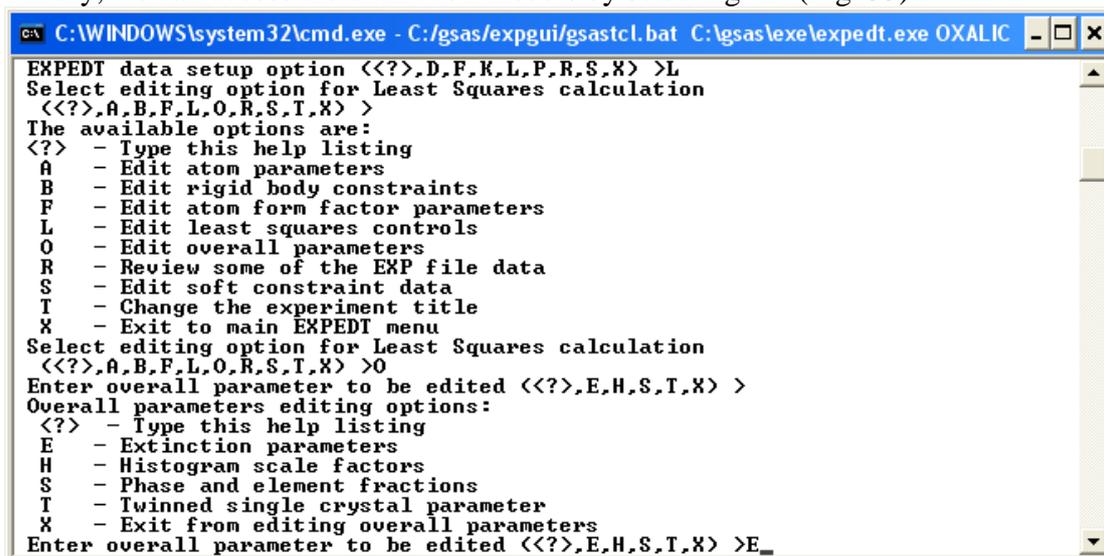
C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/expedt.exe OXALIC

<?> - Type this help listing
D - Distance/angle calculation set up
F - Fourier calculation set up
K n - Delete all but the last n history records
L - Least squares refinement set up
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >L
Select editing option for Least Squares calculation
(<?>,A,B,F,L,O,R,S,T,X) >
The available options are:
<?> - Type this help listing
A - Edit atom parameters
B - Edit rigid body constraints
F - Edit atom form factor parameters
L - Edit least squares controls
O - Edit overall parameters
R - Review some of the EXP file data
S - Edit soft constraint data
T - Change the experiment title
X - Exit to main EXPEDT menu
Select editing option for Least Squares calculation
(<?>,A,B,F,L,O,R,S,T,X) >O

```

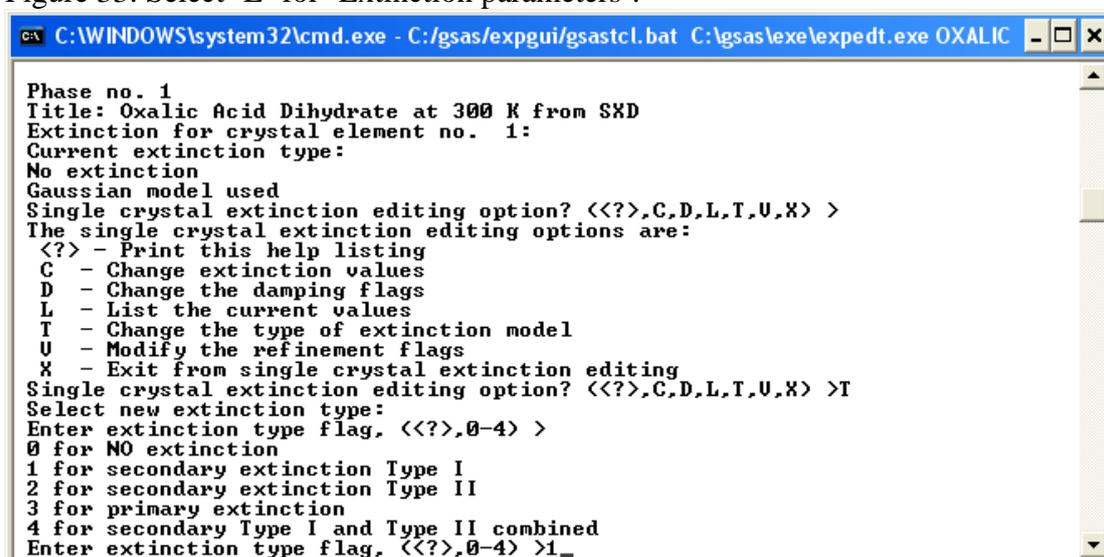
Figure 32: Select 'O' to access the overall parameters.

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



```
C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/lexpedt.exe OXALIC
EXPEDT data setup option <<?>,D,F,K,L,P,R,S,X) >L
Select editing option for Least Squares calculation
<<?>,A,B,F,L,O,R,S,T,X) >
The available options are:
<?> - Type this help listing
A - Edit atom parameters
B - Edit rigid body constraints
F - Edit atom form factor parameters
L - Edit least squares controls
O - Edit overall parameters
R - Review some of the EXP file data
S - Edit soft constraint data
T - Change the experiment title
X - Exit to main EXPEDT menu
Select editing option for Least Squares calculation
<<?>,A,B,F,L,O,R,S,T,X) >O
Enter overall parameter to be edited <<?>,E,H,S,T,X) >
Overall parameters editing options:
<?> - Type this help listing
E - Extinction parameters
H - Histogram scale factors
S - Phase and element fractions
T - Twinned single crystal parameter
X - Exit from editing overall parameters
Enter overall parameter to be edited <<?>,E,H,S,T,X) >E_
```

Figure 33: Select 'E' for 'Extinction parameters'.



```
C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/lexpedt.exe OXALIC
Phase no. 1
Title: Oxalic Acid Dihydrate at 300 K from SXD
Extinction for crystal element no. 1:
Current extinction type:
No extinction
Gaussian model used
Single crystal extinction editing option? <<?>,C,D,L,T,U,X) >
The single crystal extinction editing options are:
<?> - Print this help listing
C - Change extinction values
D - Change the damping flags
L - List the current values
T - Change the type of extinction model
U - Modify the refinement flags
X - Exit from single crystal extinction editing
Single crystal extinction editing option? <<?>,C,D,L,T,U,X) >T
Select new extinction type:
Enter extinction type flag, <<?>,0-4) >
0 for NO extinction
1 for secondary extinction Type I
2 for secondary extinction Type II
3 for primary extinction
4 for secondary Type I and Type II combined
Enter extinction type flag, <<?>,0-4) >1_
```

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).

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gststcl.bat C:/gsas/lexe/lexpedt.exe OXALIC
Phase no. 1
Title: Oxalic Acid Dihydrate at 300 K from SXD
Extinction for crystal element no. 1:
Current extinction type:
No extinction
Gaussian model used
Single crystal extinction editing option? (<?>,C,D,L,T,U,X) >
The single crystal extinction editing options are:
<?> - Print this help listing
C - Change extinction values
D - Change the damping flags
L - List the current values
T - Change the type of extinction model
U - Modify the refinement flags
X - Exit from single crystal extinction editing
Single crystal extinction editing option? (<?>,C,D,L,T,U,X) >T
Select new extinction type:
Enter extinction type flag, (<?>,0-4) >
0 for NO extinction
1 for secondary extinction Type I
2 for secondary extinction Type II
3 for primary extinction
4 for secondary Type I and Type II combined
Enter extinction type flag, (<?>,0-4) >1
Do you want to use the Lorentzian model (Y/N)? >Y

```

Figure 35: 'Y' selects a Lorentzian distribution.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gststcl.bat C:/gsas/lexe/lexpedt.exe OXALIC
U - Modify the refinement flags
X - Exit from single crystal extinction editing
Single crystal extinction editing option? (<?>,C,D,L,T,U,X) >T
Select new extinction type:
Enter extinction type flag, (<?>,0-4) >
0 for NO extinction
1 for secondary extinction Type I
2 for secondary extinction Type II
3 for primary extinction
4 for secondary Type I and Type II combined
Enter extinction type flag, (<?>,0-4) >1
Do you want to use the Lorentzian model (Y/N)? >Y
Current extinction type:
Secondary type-I Value = 1.0000E-10 Refine(N) Damp flag = 0
Lorentzian model used
Single crystal extinction editing option? (<?>,C,D,L,T,U,X) >
The single crystal extinction editing options are:
<?> - Print this help listing
C - Change extinction values
D - Change the damping flags
L - List the current values
T - Change the type of extinction model
U - Modify the refinement flags
X - Exit from single crystal extinction editing
Single crystal extinction editing option? (<?>,C,D,L,T,U,X) >U_

```

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

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gststcl.bat C:/gsas/lexe/genles.exe OXALIC
Histogram 41 Type SNT Nobs = 15 R(F**2) = 0.3838 CHI**2 = 7.5116E+02
Histogram 42 Type SNT Nobs = 14 R(F**2) = 0.3690 CHI**2 = 7.0093E+02
Histogram 43 Type SNT Nobs = 22 R(F**2) = 0.4945 CHI**2 = 8.8378E+02
Histogram 44 Type SNT Nobs = 11 R(F**2) = 0.3475 CHI**2 = 4.0896E+02
Histogram 45 Type SNT Nobs = 17 R(F**2) = 0.2337 CHI**2 = 2.0240E+02
Histogram 46 Type SNT Nobs = 28 R(F**2) = 0.4325 CHI**2 = 1.4263E+03
Histogram 47 Type SNT Nobs = 30 R(F**2) = 0.4378 CHI**2 = 2.2464E+03
Histogram 48 Type SNT Nobs = 24 R(F**2) = 0.5031 CHI**2 = 1.6461E+03
Histogram 49 Type SNT Nobs = 20 R(F**2) = 0.4179 CHI**2 = 1.2508E+03
Histogram 50 Type SNT Nobs = 31 R(F**2) = 0.3764 CHI**2 = 8.2413E+02
Histogram 51 Type SNT Nobs = 16 R(F**2) = 0.4897 CHI**2 = 5.3850E+02
Histogram 52 Type SNT Nobs = 20 R(F**2) = 0.4524 CHI**2 = 1.2190E+03
Histogram 53 Type SNT Nobs = 14 R(F**2) = 0.3723 CHI**2 = 4.9801E+02
Histogram 54 Type SNT Nobs = 12 R(F**2) = 0.4087 CHI**2 = 3.3166E+02
Histogram 55 Type SNT Nobs = 18 R(F**2) = 0.5092 CHI**2 = 1.2542E+03

Single crystal Rw(Fo**2) = 0.543 for 1088 observations

CPU times for matrix build 0.36 sec; matrix inversion 0.02 sec
Final variable sum((shift/esd)**2) for cycle 22: 0.00 Time: 0.38 sec
Convergence was achieved and
STOP GENLES terminated successfully statement executed

C:\Oxalic Acid>pause
Press any key to continue . . .

```

Figure 37: Refinement result after including extinction.

The refinement has improved significantly with  $R_w(F_o^{**2})$  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.

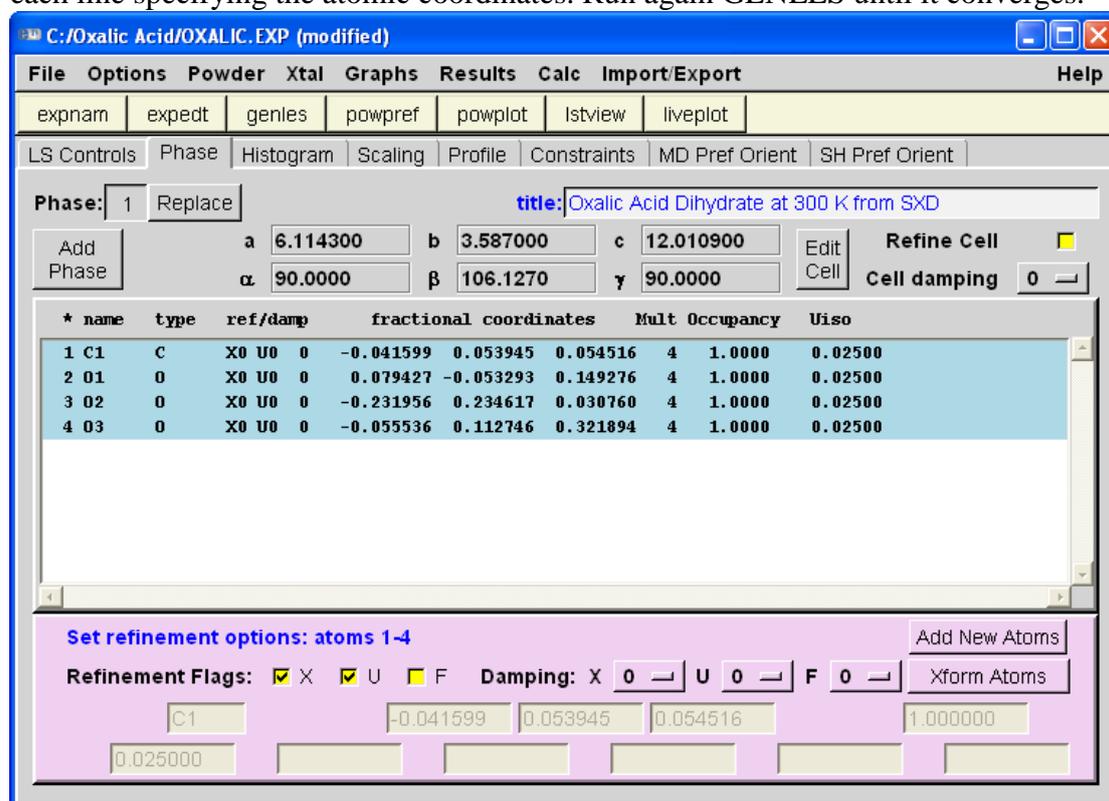


Figure 38: Switching the refinement flag for including isotropic thermal parameters.

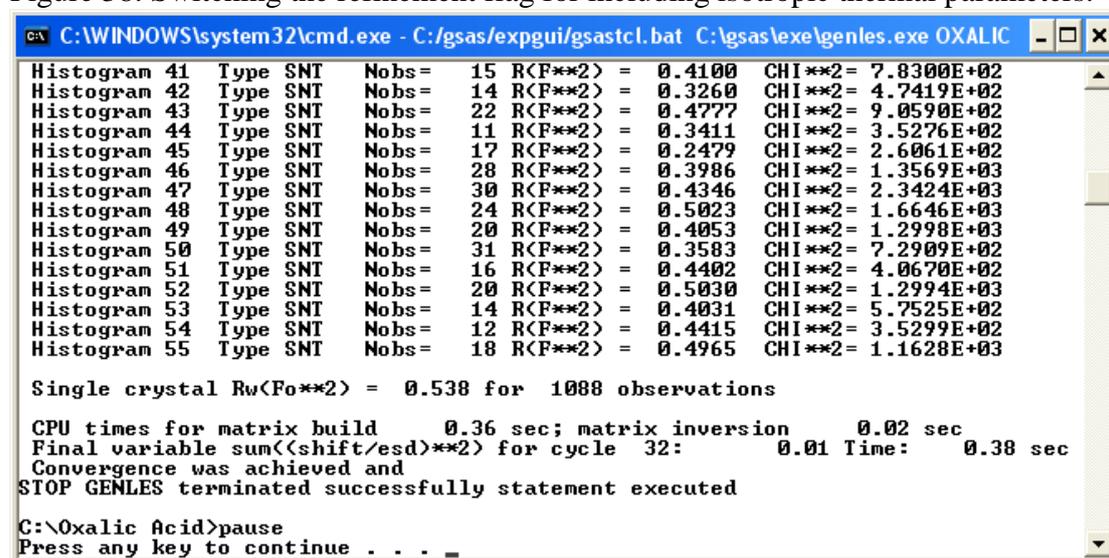


Figure 39: Refinement result after including isotropic thermal parameters.

$R_w(F_o^{**2})$  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.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gststcl.bat C:/gsas/lexe/lexpedt.exe OXALIC
-----
Copyright, 2000, The Regents of the University of California.
-----

The last history record is :
HSTRY 19 GENLES Win32 Feb 03 14:51:46 2005 Sdsq= 0.516E+05 S/E= 0.723E-02

Is this the file you wish to use? (<?>,D,K,Q,R,Y) >Y
Experiment title:
Oxalic Acid Dihydrate at 300 K from SXD
The last history record is :
HSTRY 19 GENLES Win32 Feb 03 14:51:46 2005 Sdsq= 0.516E+05 S/E= 0.723E-02

EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
EXPEDT data setup options:
<?> - Type this help listing
D - Distance/angle calculation set up
F - Fourier calculation set up
K n - Delete all but the last n history records
L - Least squares refinement set up
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >F_

```

Figure 40: Select 'F' for Fourier setup.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gststcl.bat C:/gsas/lexe/lexpedt.exe OXALIC
-----
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >F
Enter desired map (<?>,DELF,FCLC,FOBS,NFDF,PTSN,DPTS,EXIT) >FOBS
Enter section desired (X,Y,Z - choose Z for DSN6 maps) >Z
Do you wish to specify individual map steps for each axis (Y/<N>)? >
Current overall map step size is 0.2000 Å
Enter new overall map step size in Angstroms >/
The a-axis is 6.114300 Å
The new del-x is 0.1911 Å
The cell will be divided into 32 points along x
The b-axis is 3.587000 Å
The new del-y is 0.1793 Å
The cell will be divided into 20 points along y
The c-axis is 12.010900 Å
The new del-z is 0.2002 Å
The cell will be divided into 60 points along z
Old x limits are 0.0000 to 0.0000
Enter minimum and maximum values of x in fractions of the cell edge >-1,1
New x limits are -1.0000 to 1.0000
Old y limits are 0.0000 to 0.0000
Enter minimum and maximum values of y in fractions of the cell edge >-1,1
New y limits are -1.0000 to 1.0000
Old z limits are 0.0000 to 0.0000
Enter minimum and maximum values of z in fractions of the cell edge >-1,1

```

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).

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gststcl.bat C:/gsas/lexe/lexpedt.exe OXALIC
The b-axis is 3.587000 A
The new del-y is 0.1793 A
The cell will be divided into 20 points along y
The c-axis is 12.010900 A
The new del-z is 0.2002 A
The cell will be divided into 60 points along z
Old x limits are 0.0000 to 0.0000
Enter minimum and maximum values of x in fractions of the cell edge >-1,1
New x limits are -1.0000 to 1.0000
Old y limits are 0.0000 to 0.0000
Enter minimum and maximum values of y in fractions of the cell edge >-1,1
New y limits are -1.0000 to 1.0000
Old z limits are 0.0000 to 0.0000
Enter minimum and maximum values of z in fractions of the cell edge >-1,1
New z limits are -1.0000 to 1.0000
At least one asymmetric part of the unit cell is included in the Fourier.
Enter new list of histogram numbers in the order you wish them to be read.
The last occurrence of a reflection will be used.
Include histogram (<0 to terminate list) > 1, 2, 3, 4, 5, 6, 7, 8, 9,10,11
Include histogram (<0 to terminate list) >12,13,14,15,16,17,18,19,20,21,22
Include histogram (<0 to terminate list) >23,24,25,26,27,28,29,30,31,32,33
Include histogram (<0 to terminate list) >34,35,36,37,38,39,40,41,42,43,44
Include histogram (<0 to terminate list) >45,46,47,48,49,50,51,52,53,54,55
Include histogram (<0 to terminate list) >0
Enter FOURIER map option (<?>,A,C,D,E,F,H,I,L,P,R,S,T,W,X) >X_

```

Figure 42: Specification of parameters for Fourier calculation.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gststcl.bat C:/gsas/lexe/fourier.exe OXALIC
C:\Oxalic Acid>REM a batch file to a DOS command and pause
C:\Oxalic Acid>C:/gsas/lexe/fourier.exe OXALIC
Calculation of a FOBS map was requested.
CPU time for reading reflections was 0.31 sec.
CPU time for this FOURIER map was 0.14 sec.
STOP FOURIER completed successfully statement executed
C:\Oxalic Acid>pause
Press any key to continue . . .

```

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.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/forsrh.exe OXALIC
C:\Oxalic Acid>REM a batch file to a DOS command and pause
C:\Oxalic Acid>C:\gsas\exe\forsrh.exe OXALIC

-----
                Program FORSRH Version Win32
                Fourier map peak search program
                Distributed on Fri Apr 16 08:09:06 2004
-----

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

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

A FOBS file has been opened
The range of map values is  -1.010 to  3.806
Enter min. Peak value (negative if negative values are desired) >-0.8
Enter number of peaks to be located (1 to 225) >50
Save the peaks located in the EXP file? (Y,<N>) >

```

Figure 44: Input for forsrh.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/forsrh.exe OXALIC

-----
A FOBS file has been opened
The range of map values is  -1.010 to  3.806
Enter min. Peak value (negative if negative values are desired) >-0.8
Enter number of peaks to be located (1 to 225) >50
Save the peaks located in the EXP file? (Y,<N>) >

Min rho =  -0.80000 No. of peaks = 50 Peaks saved? N

The following peaks were found
      Rho      X      Y      Z
1      3.806  0.9555  0.0564  0.0518
2      2.889  0.0819  0.9409  0.1460
3      2.720  0.7752  0.2302  0.0356
4      2.491  0.5504  0.6153  0.1795
5     -1.010  0.6446  0.4391  0.1582
6     -0.945  0.4176  0.6780  0.1133
7     -0.869  0.0257  0.0213  0.2208

Total CPU time for FORSRH was  0.13 seconds
STOP FORSRH terminated successfully. statement executed

C:\Oxalic Acid>pause
Press any key to continue . . .

```

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).

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/forplot.exe OXALIC
C:\Oxalic Acid>C:/gsas/lexe/forplot.exe OXALIC

-----
                Program FORPLOT Version Win32
                Crystal structure Fourier map drawing program
                Distributed on Fri Apr 16 08:09:06 2004
-----

                Allen C. Larson and Robert B. Von Dreele
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-----

Enter graphic screen option (<?>,A,B,C,D,Z) >
Graphics screen option:
A   black on white graphics always on top
B   white on black graphics always on top
C   black on white graphics not on top
D   white on black graphics not on top
Z   No screen graphics; only hardcopy
Enter graphic screen option (<?>,A,B,C,D,Z) >c
Do you want to save graphics output (Y,<N>)? >

```

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

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/forplot.exe OXALIC
Map X axis divided into 32 steps, from -32 and covering 65 steps
Map Y axis divided into 20 steps, from -20 and covering 41 steps
Map Z axis divided into 60 steps, from -60 and covering 121 steps
Map scaling factor 1.E+00
Rescaled rho limits from -1.01 to 3.81
There were 322465 map elements stored
Selected maptype is FOBS
The map values range from -1.01 to 3.81 with a scaling factor of 1.E+00
5 contours will be drawn between rho = 0.00 and 3.81
with an interval of 0.63
Contours will be drawn at:
0.63 1.27 1.90 2.54 3.17
The map center is at 0.00000 0.00000 0.00000
The map orientation vectors are:
U = 1.00000 0.00000 0.00000
U = 0.00000 1.00000 0.00000
Plot axes to crystal transformation matrix:
0.163551 0.000000 0.047290
0.000000 0.278785 0.000000
0.000000 0.000000 0.086668

Height of section above center is 0.000 A
The map size - center to edge is 5.00 A
The map grid interval is 0.300 A
Enter FORPLOT command (<?>,A,C,D,E,G,F,H,I,L,M,N,O,P,Q,R,S,T,U) >

```

Figure 47: Default settings for drawing Fourier maps.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/forplot.exe OXALIC
Selected maptype is FOBS
The map values range from -1.01 to 3.81 with a scaling factor of 1.E+00
5 contours will be drawn between rho = 0.00 and 3.81
with an interval of 0.63
Contours will be drawn at:
0.63 1.27 1.90 2.54 3.17
The map center is at 0.00000 0.00000 0.00000
The map orientation vectors are:
U = 1.00000 0.00000 0.00000
U = 0.00000 1.00000 0.00000
Plot axes to crystal transformation matrix:
0.163551 0.000000 0.047290
0.000000 0.278785 0.000000
0.000000 0.000000 0.086668

Height of section above center is 0.000 A
The map size - center to edge is 5.00 A
The map grid interval is 0.300 A
Enter FORPLOT command (<?>,A,C,D,E,G,F,H,I,L,M,N,O,P,Q,R,S,T,U) >N 13
Enter values for contours 1 to 13 >-1.0,-0.8,-0.6,-0.4,-0.2,0.0
Enter values for contours 7 to 13 >0.2, 0.4, 0.6, 0.8, 1.0,1.2, 1.4
Contours will be drawn at:
-1.00 -0.80 -0.60 -0.40 -0.20 0.00 0.20 0.40
0.60 0.80 1.00 1.20 1.40
Enter FORPLOT command (<?>,A,C,D,E,G,F,H,I,L,M,N,O,P,Q,R,S,T,U) >_

```

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).

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstactl.bat C:/gsas/lexe/forplot.exe OXALIC
with an interval of 0.63
Contours will be drawn at:
0.63 1.27 1.90 2.54 3.17
The map center is at 0.00000 0.00000 0.00000
The map orientation vectors are:
U = 1.00000 0.00000 0.00000
V = 0.00000 1.00000 0.00000
Plot axes to crystal transformation matrix:
0.163551 0.000000 0.047290
0.000000 0.278785 0.000000
0.000000 0.000000 0.086668

Height of section above center is 0.000 A
The map size - center to edge is 5.00 A
The map grid interval is 0.300 A
Enter FORPLOT command (<?>,A,C,D,E,G,F,H,I,L,M,N,O,P,Q,R,S,T,U) >N 13
Enter values for contours 1 to 13 >-1.0,-0.8,-0.6,-0.4,-0.2,0.0
Enter values for contours 7 to 13 >0.2, 0.4, 0.6, 0.8, 1.0,1.2, 1.4
Contours will be drawn at:
-1.00 -0.80 -0.60 -0.40 -0.20 0.00 0.20 0.40
0.60 0.80 1.00 1.20 1.40
Enter FORPLOT command (<?>,A,C,D,E,G,F,H,I,L,M,N,O,P,Q,R,S,T,U) >G 0.1
Enter FORPLOT command (<?>,A,C,D,E,G,F,H,I,L,M,N,O,P,Q,R,S,T,U) >D
Enter thickness for atom labeling (default=0.25, <=0.0 for no labels) >/
Enter FORPLOT command (<?>,A,C,D,E,G,F,H,I,L,M,N,O,P,Q,R,S,T,U) >_

```

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).

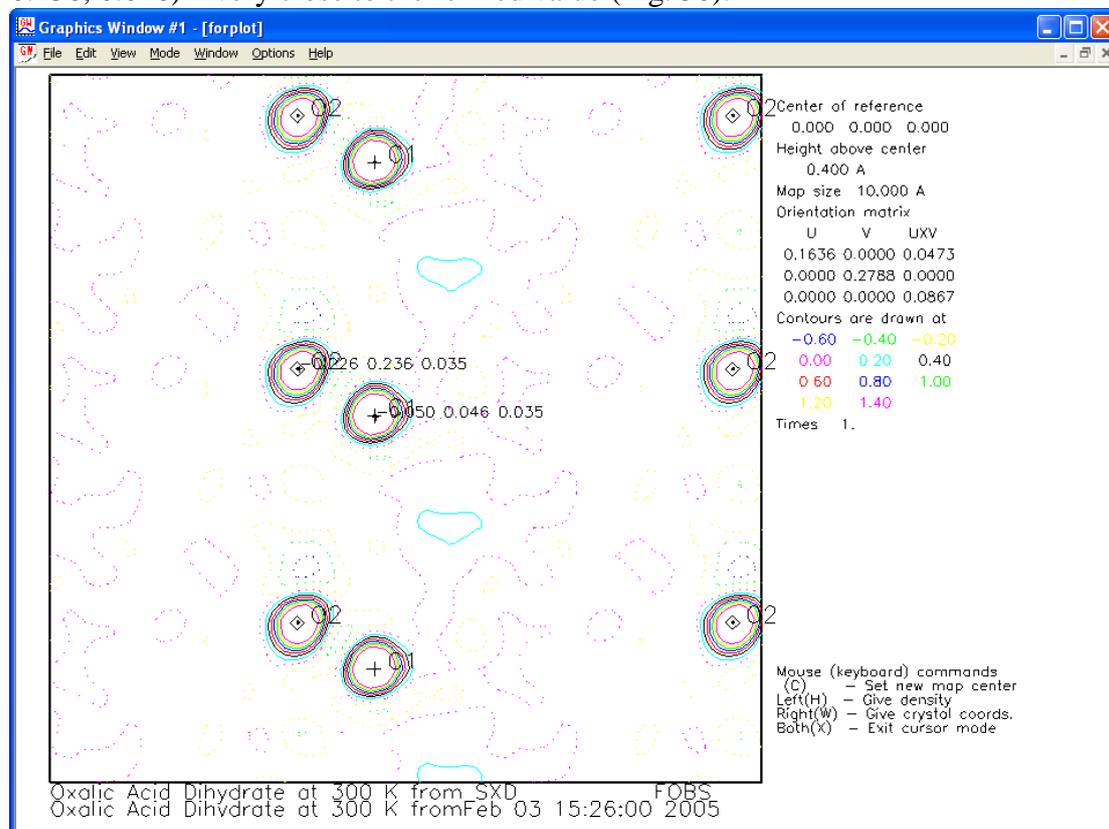


Figure 50: Location of C(1) and O(2) in the Fourier map. Click simultaneously with the left and right mouse button to gain back control over the DOS input window.

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

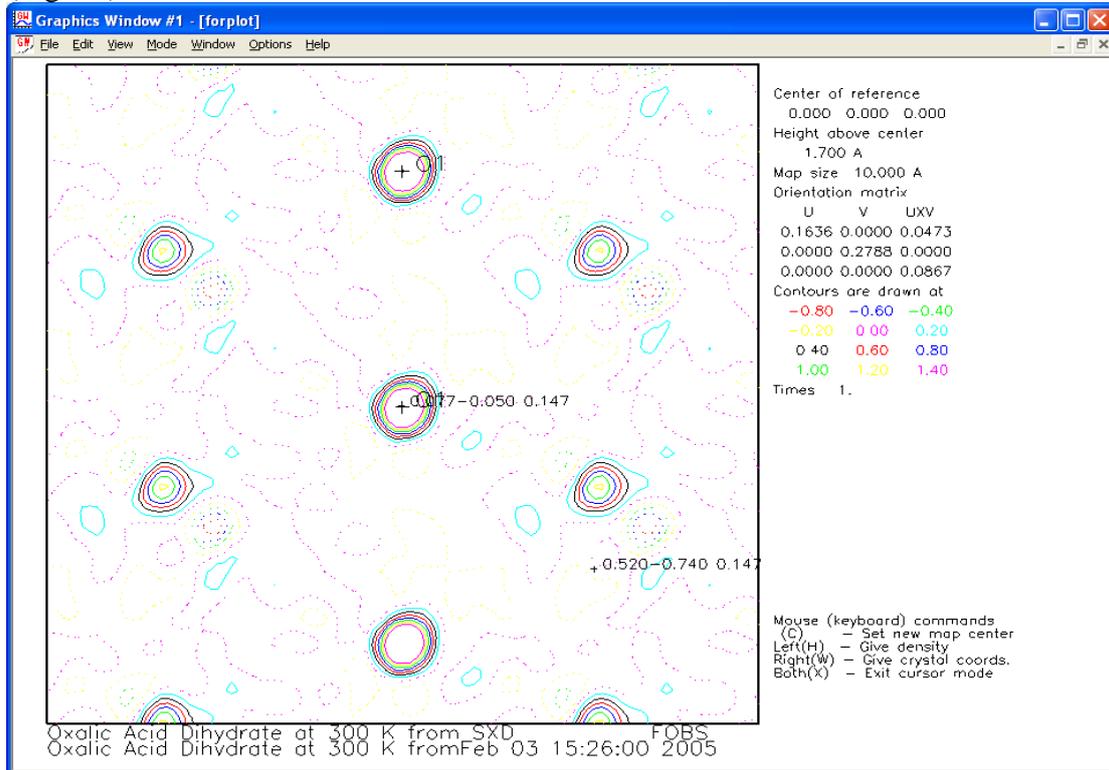


Figure 51: Location of O(1).

'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.

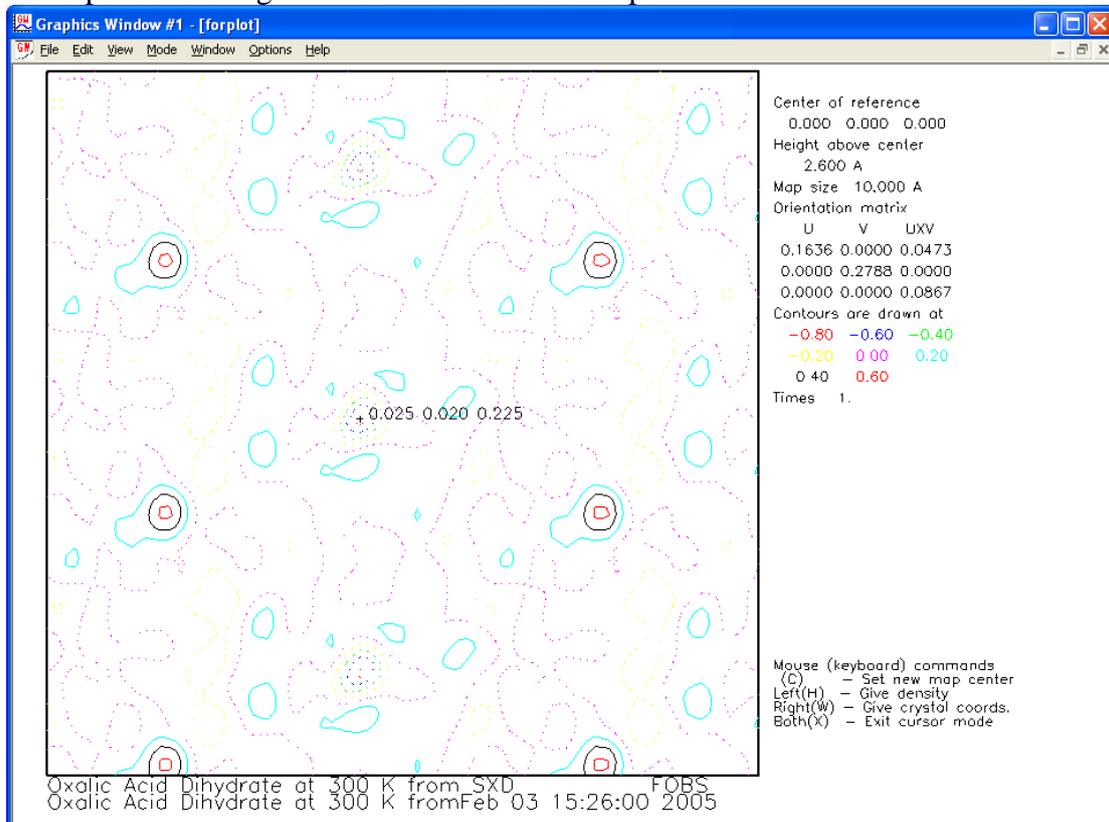


Figure 52: Location of H(2). The residual positive density comes from a nearby O(3).

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

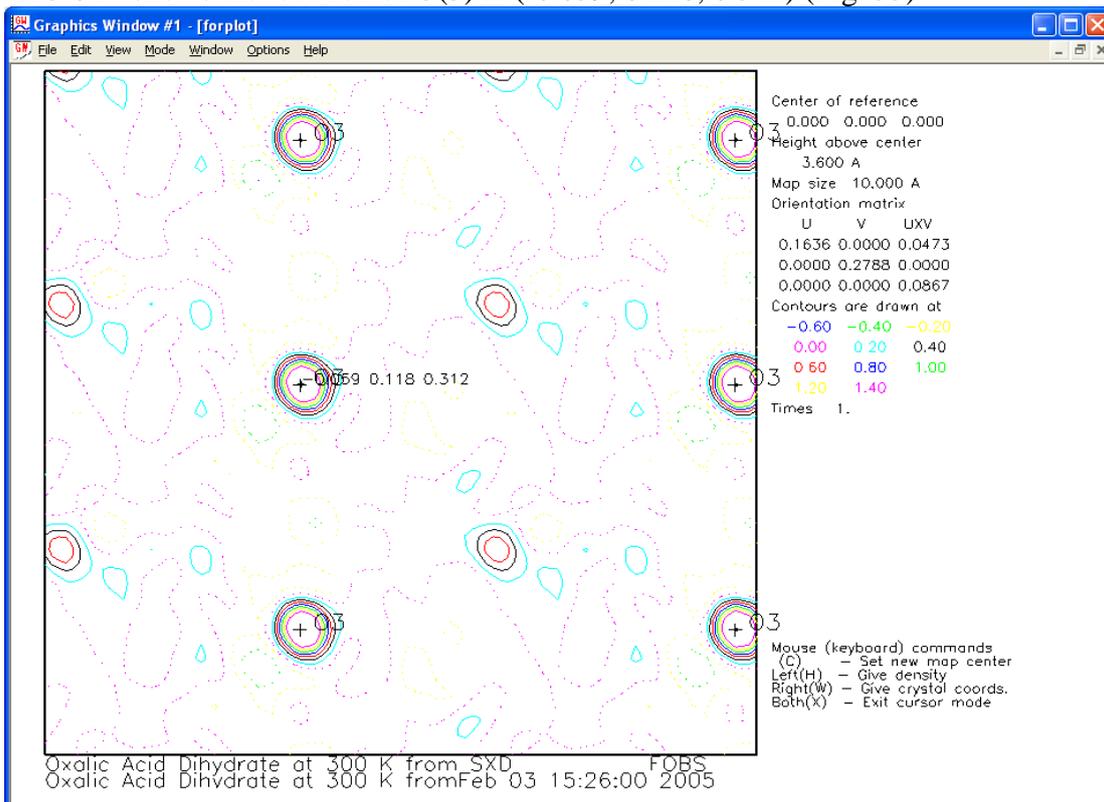


Figure 53: Location of O(3).

'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).

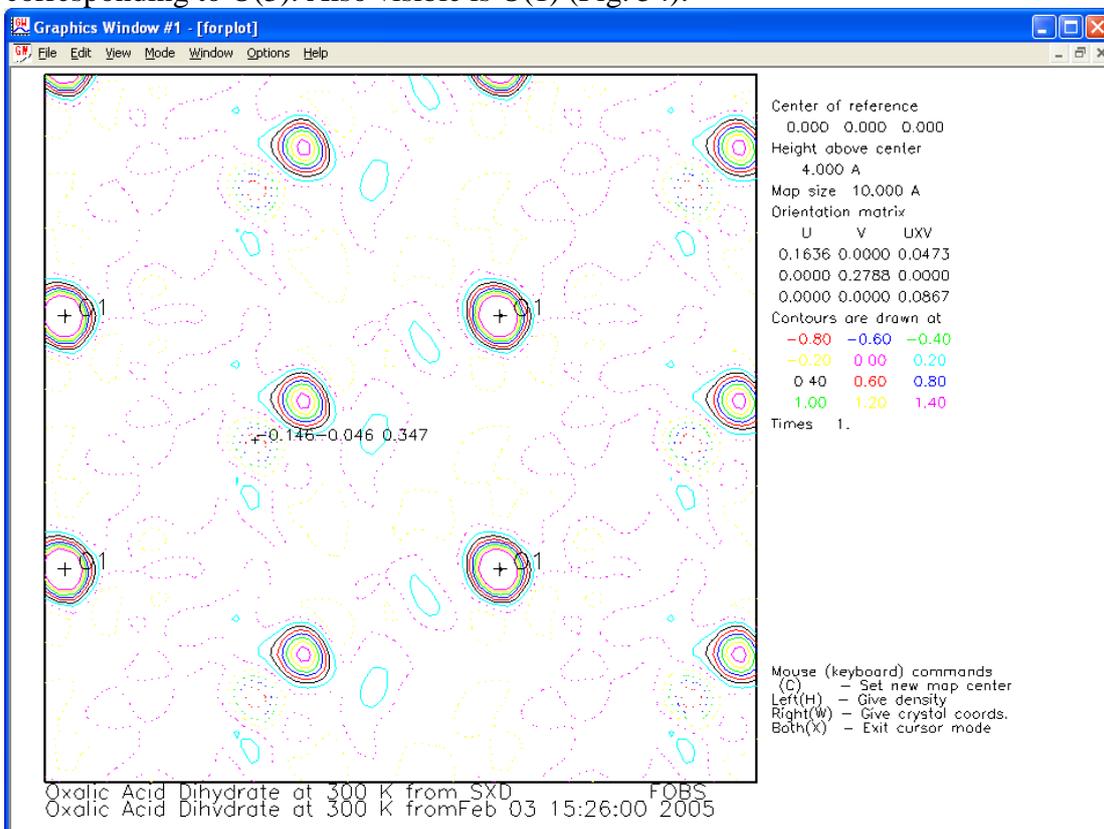


Figure 54: Location of a negative pocket corresponding to H close to O(3).

'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).

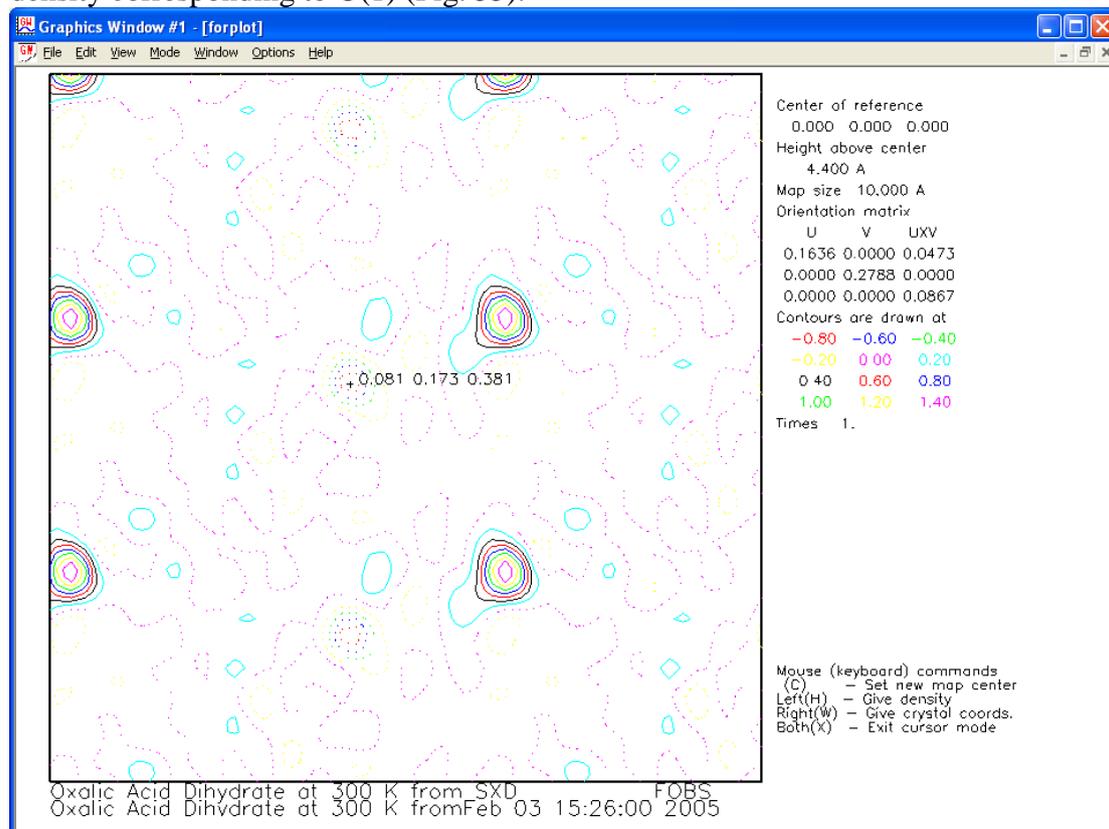


Figure 55: Location of the third hydrogen at a negative pocket.

add new atom

Adding atoms to phase #1

#	Atom type	Name	x	y	z	Occ	Uiso	Use Flag
1	H	H1	0.025	0.02	0.225	1.0	0.025	<input checked="" type="checkbox"/>
2	H	H2	0.081	0.173	0.381	1.0	0.025	<input checked="" type="checkbox"/>
3	H	H3	-0.146	-0.046	0.347	1.0	0.025	<input checked="" type="checkbox"/>

Help More atom boxes

Add Atoms Cancel Import atoms from: PowderCell .CEL file

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  $R_w(F_o^{**2})$  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.

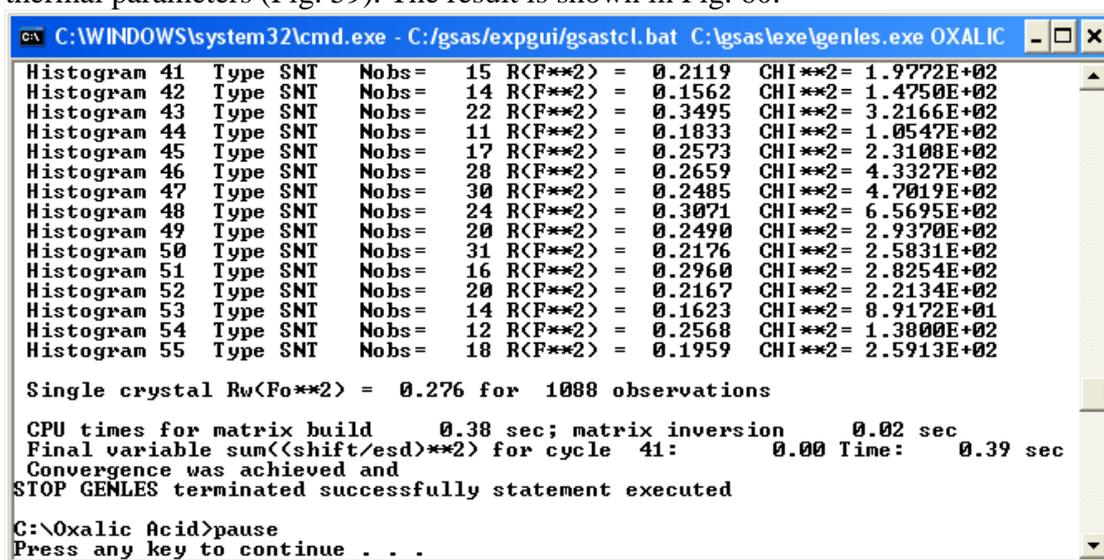


Figure 57: Refinement after including hydrogen.

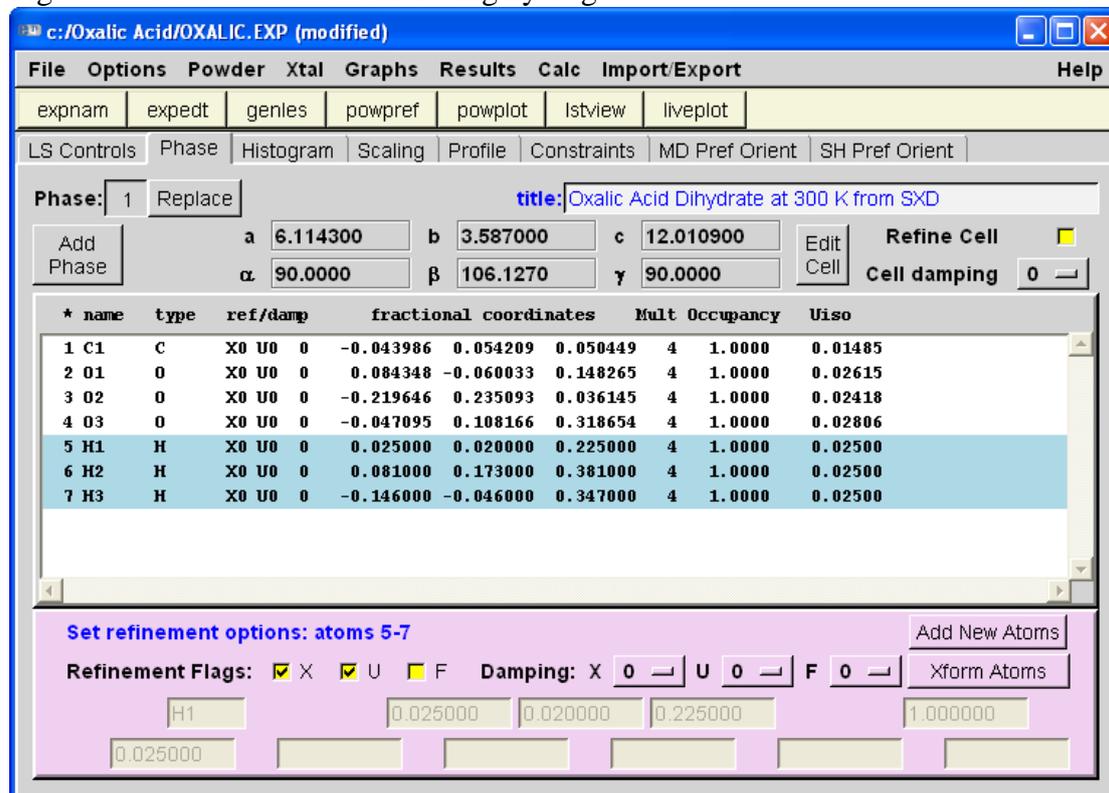


Figure 58: Select the three hydrogens and set the flags 'X' and 'U' by checking the appropriate boxes near 'Refinement Flags'.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/genles.exe OXALIC
Histogram 41 Type SNT Nobs = 15 R(F**2) = 0.1735 CHI**2 = 1.3510E+02
Histogram 42 Type SNT Nobs = 14 R(F**2) = 0.1621 CHI**2 = 9.9961E+01
Histogram 43 Type SNT Nobs = 22 R(F**2) = 0.2981 CHI**2 = 1.9750E+02
Histogram 44 Type SNT Nobs = 11 R(F**2) = 0.1047 CHI**2 = 3.4903E+01
Histogram 45 Type SNT Nobs = 17 R(F**2) = 0.2382 CHI**2 = 1.8012E+02
Histogram 46 Type SNT Nobs = 28 R(F**2) = 0.2234 CHI**2 = 2.3647E+02
Histogram 47 Type SNT Nobs = 30 R(F**2) = 0.1952 CHI**2 = 3.4780E+02
Histogram 48 Type SNT Nobs = 24 R(F**2) = 0.2346 CHI**2 = 4.4900E+02
Histogram 49 Type SNT Nobs = 20 R(F**2) = 0.1937 CHI**2 = 1.9160E+02
Histogram 50 Type SNT Nobs = 31 R(F**2) = 0.2257 CHI**2 = 2.0250E+02
Histogram 51 Type SNT Nobs = 16 R(F**2) = 0.1579 CHI**2 = 7.5941E+01
Histogram 52 Type SNT Nobs = 20 R(F**2) = 0.1815 CHI**2 = 9.9322E+01
Histogram 53 Type SNT Nobs = 14 R(F**2) = 0.1185 CHI**2 = 5.1957E+01
Histogram 54 Type SNT Nobs = 12 R(F**2) = 0.1238 CHI**2 = 3.2483E+01
Histogram 55 Type SNT Nobs = 18 R(F**2) = 0.1310 CHI**2 = 9.7234E+01

Single crystal Rw(Fo**2) = 0.207 for 1088 observations

CPU times for matrix build 0.38 sec; matrix inversion 0.02 sec
Final variable sum((shift/esd)**2) for cycle 47: 0.00 Time: 0.39 sec
Convergence was achieved and
STOP GENLES terminated successfully statement executed

C:\Oxalic Acid>pause
Press any key to continue . . . _

```

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).

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gstcl.bat C:/gsas/lexe/expedt.exe OXALIC
-----
Copyright, 2000, The Regents of the University of California.
-----

The last history record is :
HSTRY 27 GENLES Win32 Feb 03 16:11:45 2005 Sdsq= 0.764E+04 S/E= 0.850E-03

Is this the file you wish to use? (<?>,D,K,Q,R,Y) >Y
Experiment title:
Oxalic Acid Dihydrate at 300 K from SXD

The last history record is :
HSTRY 27 GENLES Win32 Feb 03 16:11:45 2005 Sdsq= 0.764E+04 S/E= 0.850E-03

EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
EXPEDT data setup options:
<?> - Type this help listing
D - Distance/angle calculation set up
F - Fourier calculation set up
K n - Delete all but the last n history records
L - Least squares refinement set up
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDT
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >L

```

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.

```

C:\WINDOWS\system32\cmd.exe - C:\gsas\expgui\gsastcl.bat C:\gsas\lexe\lexpedt.exe OXALIC
<?> - Type this help listing
D - Distance/angle calculation set up
F - Fourier calculation set up
K n - Delete all but the last n history records
L - Least squares refinement set up
P - Powder data preparation
R - Review data in the experiment file
S - Single crystal data preparation
X - Exit from EXPEDIT
EXPEDIT data setup option (<?>,D,F,K,L,P,R,S,X) >L
Select editing option for Least Squares calculation
(<?>,A,B,F,L,O,R,S,T,X) >
The available options are:
<?> - Type this help listing
A - Edit atom parameters
B - Edit rigid body constraints
F - Edit atom form factor parameters
L - Edit least squares controls
O - Edit overall parameters
R - Review some of the EXP file data
S - Edit soft constraint data
T - Change the experiment title
X - Exit to main EXPEDIT menu
Select editing option for Least Squares calculation
(<?>,A,B,F,L,O,R,S,T,X) >A

```

Figure 61: Select 'A' to access the atom parameters.

```

C:\WINDOWS\system32\cmd.exe - C:\gsas\expgui\gsastcl.bat C:\gsas\lexe\lexpedt.exe OXALIC
Atom editing commands:
<?> - Type this help package
x <?> - To give details on command x
$ - Enter DCL command
+,-,*, or / - Modify num. atom parameters
C t/s/s1:s2 codes - Change atom parameters
D t/s/s1:s2 codes - Modify atom damping factors
E t/s/s1:s2 - Erase atoms
F - Fix specific atom parameters
I s - Insert one atom or read atoms from a file
K - Set atom parameter constraints
L t/s/s1:s2 - List atoms, if none specified all atoms will be listed
M - Edit magnetic moment data
S - Modify the space group and unit cell data
T t/s/s1:s2 M U - Transform atom parameters by matrix "M" and vector "U"
U t/s/s1:s2 codes - Convert atom thermal factors
U t/s/s1:s2 codes - Modify refinement flags
X - Exit from editing atoms
Where "t" is an atom type, "s" is an atom sequence number, "s1:s2" refers
to a range of atom sequence numbers, and "codes" are specific to the
command; see the individual help listings for specific instructions
Phase No. 1; Phase has 7 atoms; Title: Oxalic Acid Dihydrate at 300 K from
Give atom editing command
(<?>,$,C,D,E,F,I,K,L,M,S,T,U,U,X,+,-,*,/) >L_

```

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

```

C:\WINDOWS\system32\cmd.exe - C:\gsas\expgui\gsastcl.bat C:\gsas\lexe\lexpedt.exe OXALIC
S - Modify the space group and unit cell data
T t/s/s1:s2 M U - Transform atom parameters by matrix "M" and vector "U"
U t/s/s1:s2 codes - Convert atom thermal factors
U t/s/s1:s2 codes - Modify refinement flags
X - Exit from editing atoms
Where "t" is an atom type, "s" is an atom sequence number, "s1:s2" refers
to a range of atom sequence numbers, and "codes" are specific to the
command; see the individual help listings for specific instructions
Phase No. 1; Phase has 7 atoms; Title: Oxalic Acid Dihydrate at 300 K from
Give atom editing command
(<?>,$,C,D,E,F,I,K,L,M,S,T,U,U,X,+,-,*,/) >L
SER TYPE X Y Z FRAC NAME UIISO CODE STSYM MULT FXU
1 C -0.04550 0.05454 0.05097 1.00000 C1 0.02196 I XU 1 4 000
2 O 0.08344-0.05894 0.14890 1.00000 O1 0.03593 I XU 1 4 000
3 O -0.21961 0.23023 0.03643 1.00000 O2 0.03350 I XU 1 4 000
4 O -0.04839 0.11074 0.32046 1.00000 O3 0.03467 I XU 1 4 000
5 H 0.02746 0.01126 0.21852 1.00000 H1 0.04488 I XU 1 4 000
6 H 0.07036 0.19002 0.38238 1.00000 H2 0.05157 I XU 1 4 000
7 H -0.13891-0.04877 0.34790 1.00000 H3 0.05275 I XU 1 4 000
Phase No. 1; Phase has 7 atoms; Title: Oxalic Acid Dihydrate at 300 K from
Give atom editing command
(<?>,$,C,D,E,F,I,K,L,M,S,T,U,U,X,+,-,*,/) >U 1:7
Enter thermal factor change desired (A,I) >A

```

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  $R_w(F_o^{**2})$  of 0.135. This value is entirely acceptable for time-of-flight single-crystal neutron diffraction data.

```

C:\WINDOWS\system32\cmd.exe - C:/gsas/expgui/gsasctl.bat C:/gsas/lexe/genles.exe OXALIC
Histogram 41 Type SNT Nobs= 15 R(F**2) = 0.1043 CHI**2= 5.5701E+01
Histogram 42 Type SNT Nobs= 14 R(F**2) = 0.1106 CHI**2= 4.5071E+01
Histogram 43 Type SNT Nobs= 22 R(F**2) = 0.1009 CHI**2= 3.4359E+01
Histogram 44 Type SNT Nobs= 11 R(F**2) = 0.0685 CHI**2= 1.0396E+01
Histogram 45 Type SNT Nobs= 17 R(F**2) = 0.1366 CHI**2= 8.0551E+01
Histogram 46 Type SNT Nobs= 28 R(F**2) = 0.0891 CHI**2= 4.7782E+01
Histogram 47 Type SNT Nobs= 30 R(F**2) = 0.1551 CHI**2= 2.6175E+02
Histogram 48 Type SNT Nobs= 24 R(F**2) = 0.1876 CHI**2= 2.7639E+02
Histogram 49 Type SNT Nobs= 20 R(F**2) = 0.1066 CHI**2= 5.4256E+01
Histogram 50 Type SNT Nobs= 31 R(F**2) = 0.1158 CHI**2= 5.5520E+01
Histogram 51 Type SNT Nobs= 16 R(F**2) = 0.0738 CHI**2= 1.5839E+01
Histogram 52 Type SNT Nobs= 20 R(F**2) = 0.0552 CHI**2= 1.9123E+01
Histogram 53 Type SNT Nobs= 14 R(F**2) = 0.0383 CHI**2= 4.1274E+00
Histogram 54 Type SNT Nobs= 12 R(F**2) = 0.0810 CHI**2= 1.2327E+01
Histogram 55 Type SNT Nobs= 18 R(F**2) = 0.0810 CHI**2= 1.2327E+01
Histogram 55 Type SNT Nobs= 18 R(F**2) = 0.0575 CHI**2= 2.4037E+01

Single crystal  $R_w(F_o^{**2}) = 0.135$  for 1088 observations

CPU times for matrix build 0.41 sec; matrix inversion 0.02 sec
Final variable sum((shift/esd)**2) for cycle 51: 0.00 Time: 0.42 sec
Convergence was achieved and
STOP GENLES terminated successfully statement executed

C:\Oxalic Acid>pause
Press any key to continue . . .

```

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).

```

View OXALIC.LST
File Edit Go To Options Font: Courier Help
Histogram 52 Type SNT Nobs= 20 R(F**2) = 0.0552 CHI**2= 1.9123E+01
Histogram 53 Type SNT Nobs= 14 R(F**2) = 0.0383 CHI**2= 4.1274E+00
Histogram 54 Type SNT Nobs= 12 R(F**2) = 0.0810 CHI**2= 1.2327E+01
Histogram 55 Type SNT Nobs= 18 R(F**2) = 0.0575 CHI**2= 2.4037E+01

Single crystal  $R_w(F_o^{**2}) = 0.135$  for 1088 observations

R-factors: weighted and unweighted, based on  $F_o$  and on  $F_o^{**2}$ , for various subsets of the single cr

All data I>0.0 I>3*sigI
NREFL= 1088 1088 1042
 $R_w(F_o^{**2})$  0.135 0.135 0.135
 $R(F_o^{**2})$  0.117 0.117 0.117
 $R_w(F)$  ----- 0.072 0.072
 $R(F)$  ----- 0.065 0.064

The value of the determinant is 0.1451*10.0**( -12)

Atom parameters for phase no. 1
frac x y z 100*Uiso 100*U11 100*U22 100*U33 100*
C ( 1) Values : 1.000 -0.045048 0.055199 0.050919 1.960 2.458 1.578 0.
Sigmas : 0.000301 0.000533 0.000257 0.100 0.088 0.218 0.
shft/esd: 0.00 -0.01 0.00 0.01 0.00 0.00 0.00

Cycle 51 | Chi**2 3.357 | Shift/SU 0.00

```

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).

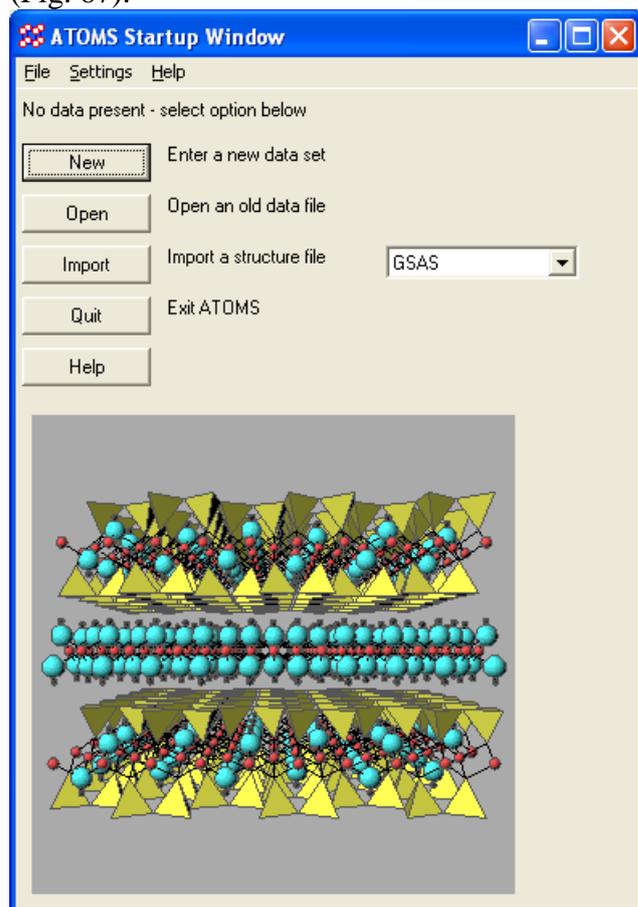


Figure 67: Start-up screen of ATOMS. Select 'Import'.

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

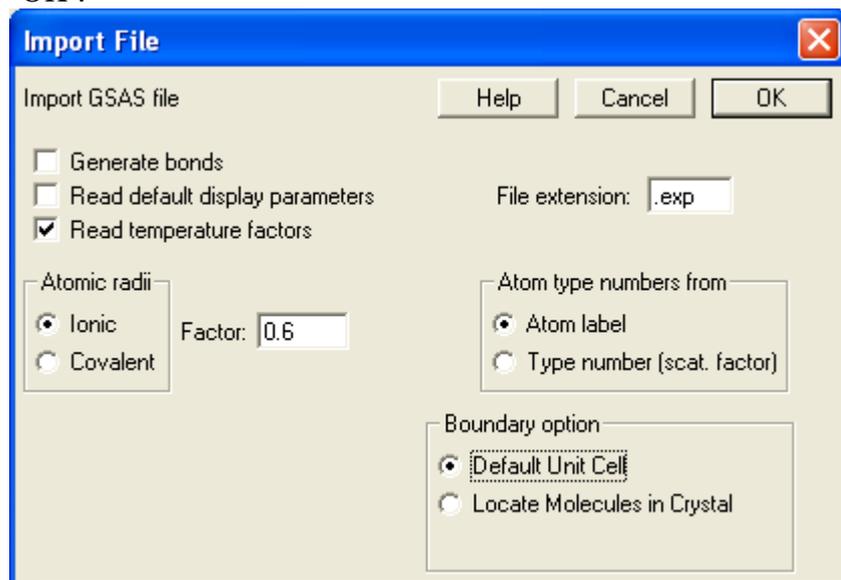


Figure 68: GSAS import dialogue. Click 'OK'.

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

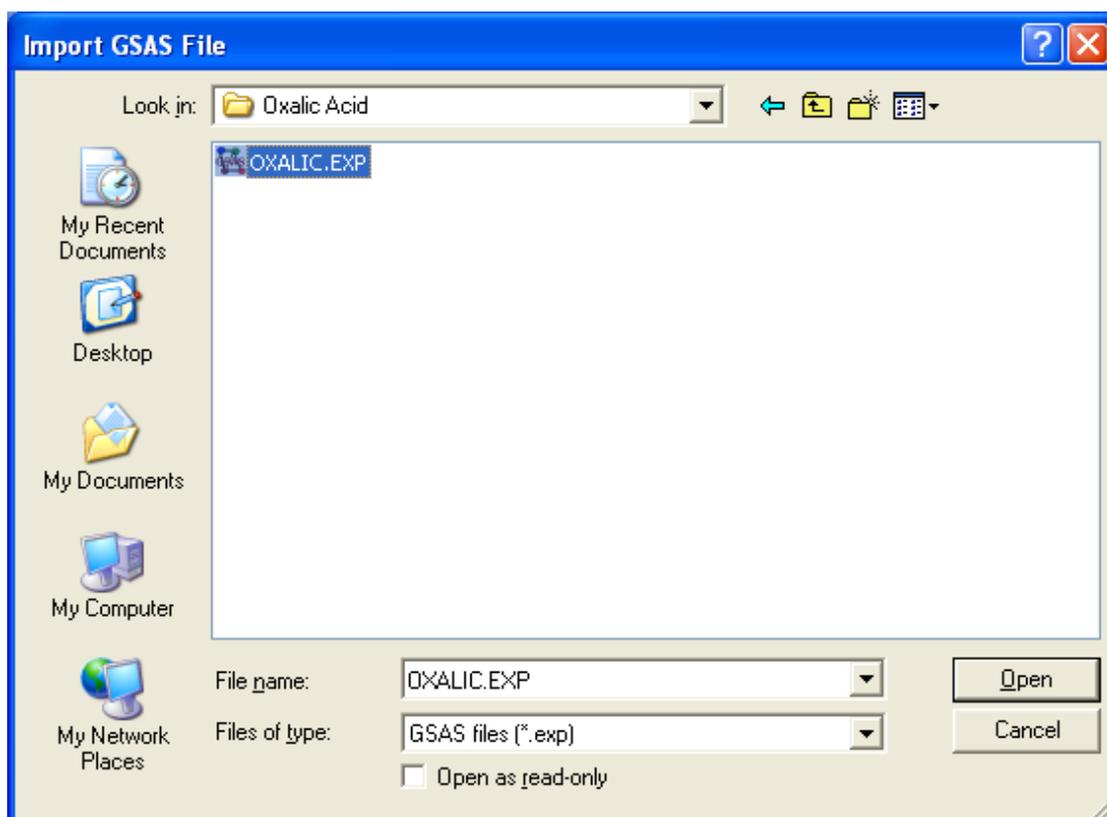


Figure 69: File selection dialog.

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

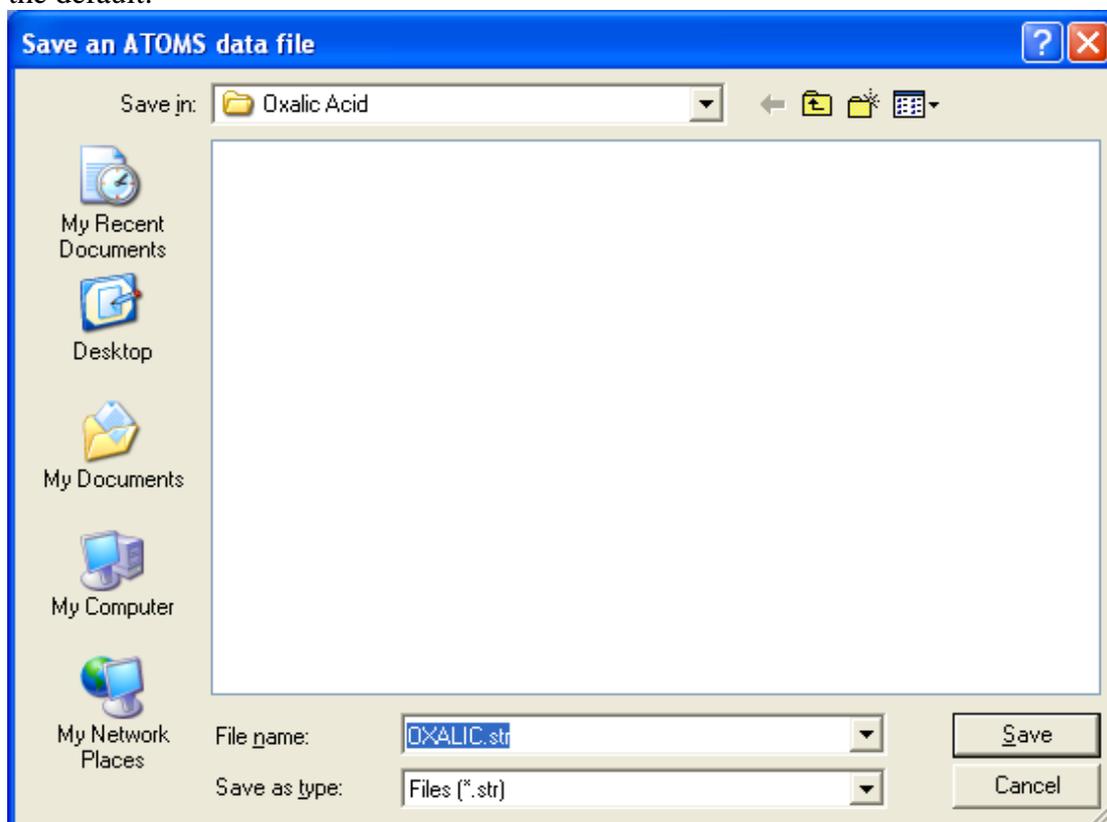


Figure 70: Dialog to specify the structure file name for saving the structure.

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



Figure 71: Click into 'Yes'.

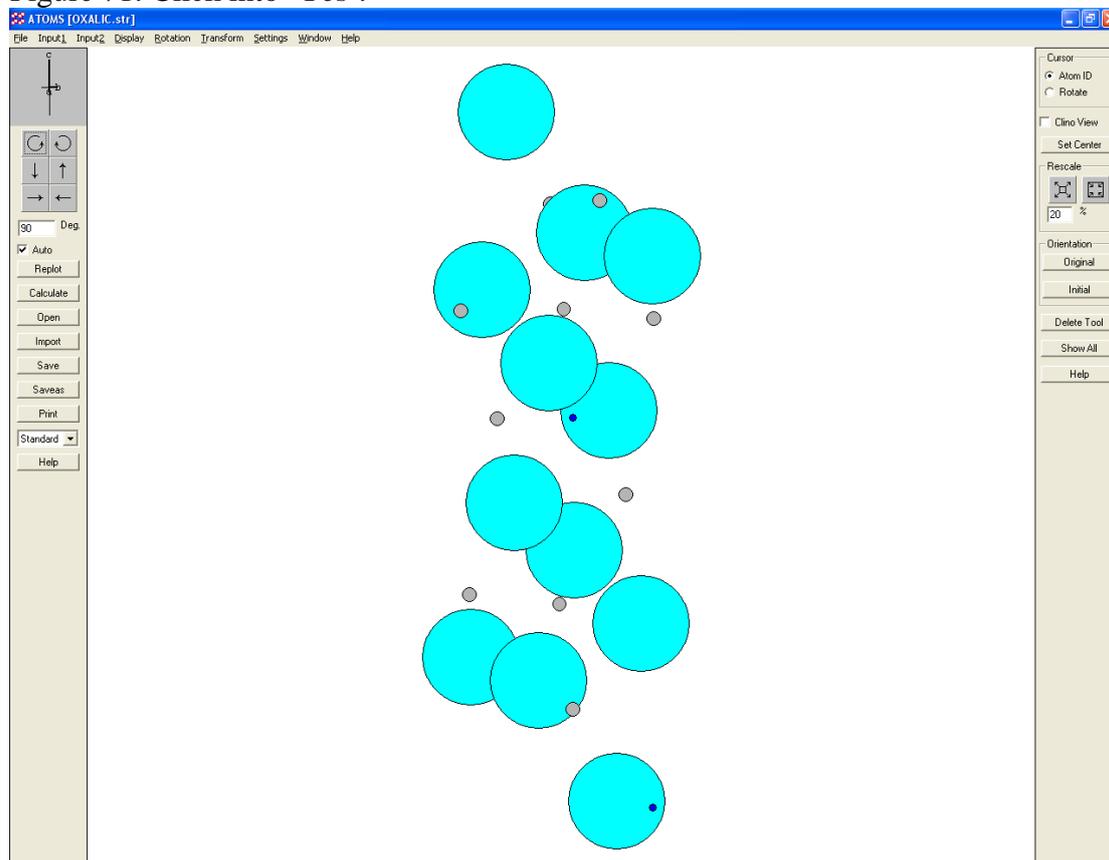


Figure 72: Initial appearance of the structure.

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.

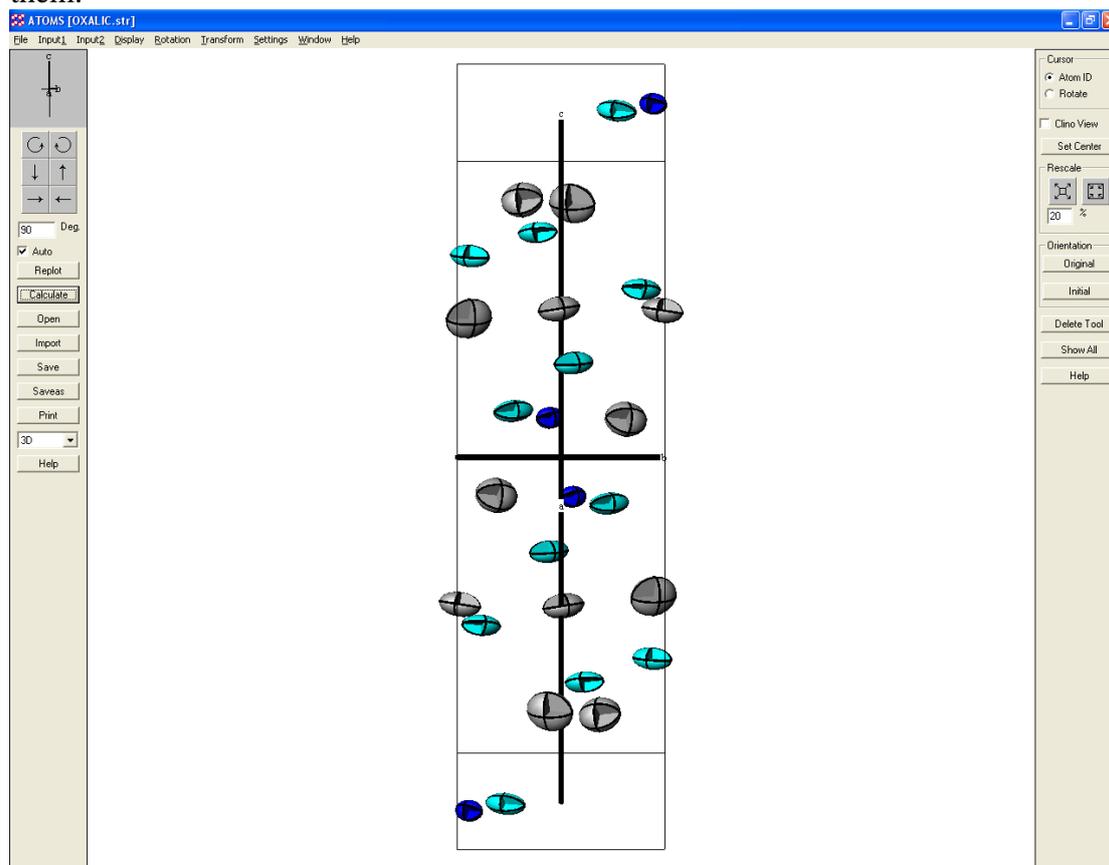


Figure 73: Final appearance of the crystal structure of Oxalic Acid Dihydrate.

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