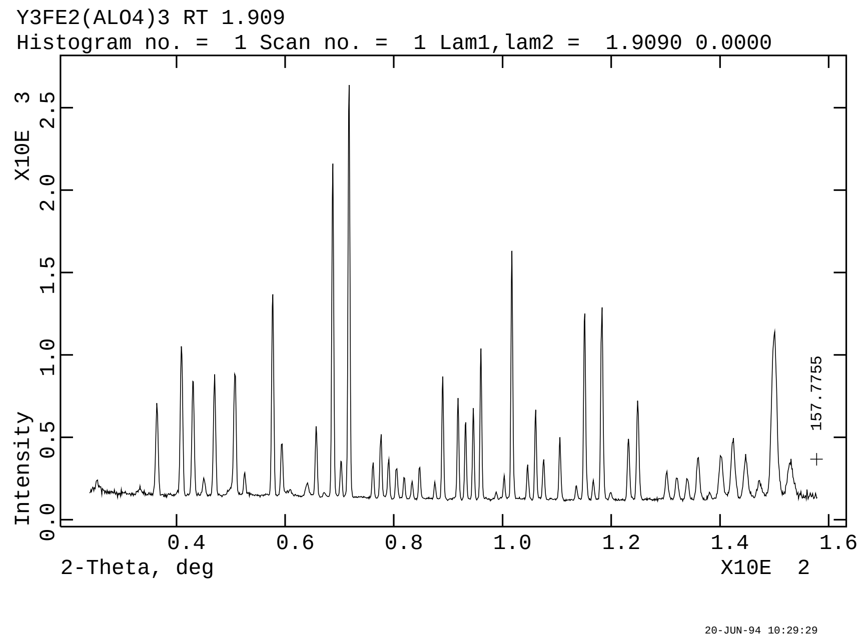
Refinement of Yttrium Iron Garnet

In this training exercise you will refine the structure of a yttrium iron garnet using constant wavelength neutron data . The structure is cubic with four different atomic sites two of which are occupied by both iron and aluminum. The data was taken on the D1a powder diffractometer at the ILL, Grenoble, France using 1.909Å wavelength neutrons. It is presumed that you have already done the nickel powder example and are familiar with many of the facilities in **GSAS**; hence this exercise will only briefly cover those parts. In other parts of this exercise you will be introduced to new features of **GSAS**; and the manual will be more explicit at those points.

Powder Data Setup and Atom Data Entry

The procedure for preparing constant wavelength powder data is essentially identical to that for TOF data as given in the nickel exercise. After entering the **GSAS** command and naming the experiment (**'GARNET'** would be a suitable name) type **'EXPEDT'** to start data preparation. Again the powder data preparation option **'P'** is used to introduce new data to the system. The space group for this garnet is **'I a 3 d'** and the cubic lattice parameter is ca. **'12.19'**. The unit cell contains 24 Y atoms, 16.33 Fe atoms, 23.67 Al atoms and 96 O atoms. This information can be entered into **GSAS** through the phase editing menu. Enter **'F C'** for inserting the chemical formula from the phase editing menu. The raw data can be found in the file **'GSAS_EXERCISES:GARNET.RAW'** (or **'/usr/gsas/gsas_exercises:GARNET.RAW'** for UNIX) and the instrument file is **'GSAS_EXERCISES:INSTPARM.D1A'** (or **'/usr/gsas/gsas_exercises/INSTPARM.D1A'** for UNIX). There is only one histogram corresponding to a scan from 20˚ to nearly 160˚ 2Θ. The scan number for this histogram is **'1'** and the corresponding instrument parameter set is also **'1'**. A plot of the entire histogram is shown below.



The minimum d-spacing sets the upper 2Θ limit for the calculations and is required before you can exit the histogram editing menu. The 2Θ value for end of the scan is noted in the above figure. It is probably easier to set it with the **'T'** option and give a maximum 2Θ of **'159'** which is just beyond the end of the data.

As this was the only histogram to be read you should exit each menu until you reach the **EXPEDT** data setup menu.

```
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

At this point you can continue your editing session by entering **'L'** to start editing of least squares data. As before you will need to enter some atoms, check the least squares controls and perhaps examine the defaults for the other parameters. The atoms you will need to enter are:

SER	TYPE	X	Y	Z	FRAC	NAME	UISO	CODE	STSYM	MULT	FXU
1	Y	0.12500	0.00000	0.25000	1.00000	Y(1)	0.01000	I	222(100)	24	000
2	FE	0.00000	0.00000	0.00000	0.60000	FE(2)	0.01000	I	-3(111)	16	000
3	AL	0.00000	0.00000	0.00000	0.40000	AL(3)	0.01000	I	-3(111)	16	000
4	AL	0.37500	0.00000	0.25000	0.75000	AL(4)	0.01000	I	-4(100)	24	000
5	FE	0.37500	0.00000	0.25000	0.25000	FE(5)	0.01000	I	-4(100)	24	000
6	O	-0.03000	0.05000	0.15000	1.00000	O(6)	0.01000	I	1	96	000

This listing is obtained by entering **'L'** after you have entered all the atoms for this example. The values of U_{iso} are a reasonable guess for this material and the values of FRAC for atoms 2-5 are also reasonable guesses for the distribution of iron and aluminum between the two sites. The full atom editing menu is shown below.

```
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

Because there are atoms that occupy the same site, their atom parameters must be constrained to shift together during least squares refinement. In this case the two sets of atom locations are fixed by symmetry so constraints need only be applied to the thermal parameters and the atom fractions. These constraints are not needed for the initial least squares refinements, but they will be needed for later stages of the refinement and it is convenient to enter them now while you are thinking about them. Enter **'K'** to edit atom constraints.

```
Editing atomic constraints:
Enter atom parameter linear constraint editing command (<?>,D,I,L,X) >
```

You will need to enter four sets of constraints, two for U_{iso} and two for FRAC on each of the two sites. First enter those for U_{iso}; enter **'I'** to insert the first one.

```
Phase no., var_name, atom no. & coeff.?(<CR> to terminate) >
```

Enter **'1 UISO 2 1'** for the first term and **'1 UISO 3 1'** for the second. Then enter **'CR'** to complete the first constraint. This will define U_{iso} for atoms 2 and 3 as one variable in **GENLES**. In a similar fashion enter the constraint on U_{iso} for atoms 4 and 5; this will make U_{iso} for these atoms another single variable in **GENLES**.

The constraints on FRAC for these atoms are set so that both sites remain full regardless how the individual values of FRAC change. For example, if FRAC for atom 2 increases the constraint should make FRAC for atom 3 decrease by an identical amount. The same idea applies to the values of FRAC for atoms 4 and 5. Enter **'I'** for the first one.

```
Phase no., var_name, atom no. & coeff.?(<CR> to terminate) >
```

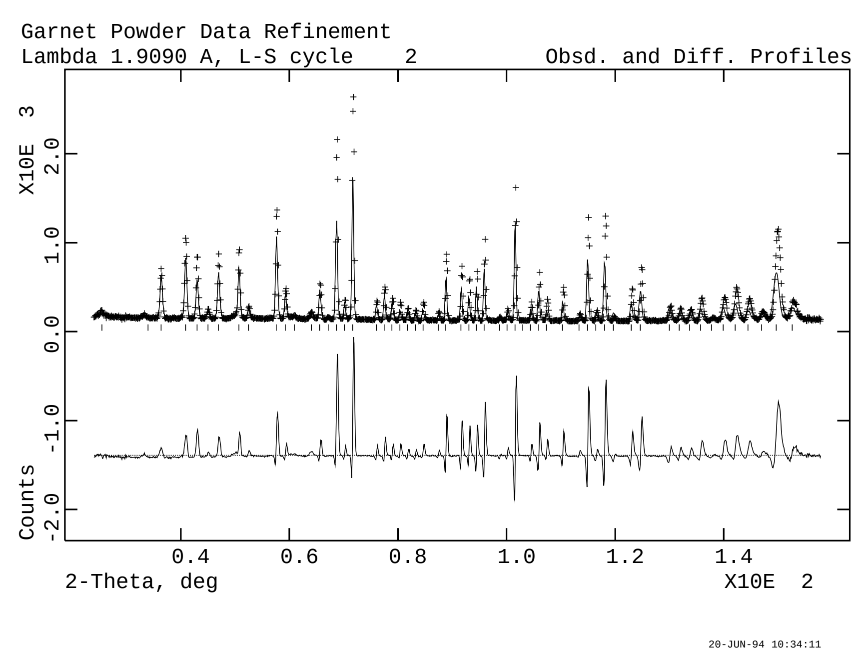
Enter **'1 FRAC 2 1'** followed by **'1 FRAC 3 -1'** and a **'CR'** for the first FRAC constraint. This means that FRAC for atom 3 will decrease if FRAC for atom 2 increases and visa-versa. In a similar fashion enter a constraint on FRAC for atoms 4 and 5; remember to change the sign of the coefficient for the second term. When you are done there should be four constraints for the two pairs of atoms. Enter **'L'** to list them.

```
Linear atomic constraint no.    1
Phase,parm.,atom,coeff. =  1  UISO   2    1.0000
Phase,parm.,atom,coeff. =  1  UISO   3    1.0000
Linear atomic constraint no.    2
Phase,parm.,atom,coeff. =  1  UISO   4    1.0000
Phase,parm.,atom,coeff. =  1  UISO   5    1.0000
Linear atomic constraint no.    3
Phase,parm.,atom,coeff. =  1  FRAC   2    1.0000
Phase,parm.,atom,coeff. =  1  FRAC   3   -1.0000
Linear atomic constraint no.    4
Phase,parm.,atom,coeff. =  1  FRAC   4    1.0000
Phase,parm.,atom,coeff. =  1  FRAC   5   -1.0000
Enter atom parameter linear constraint editing command (<?>,D,I,L,X) >
```

Enter **'X X X'** to return to the main **EXPEDT** menu. You may now exit from **EXPEDT** by entering **'X'**.

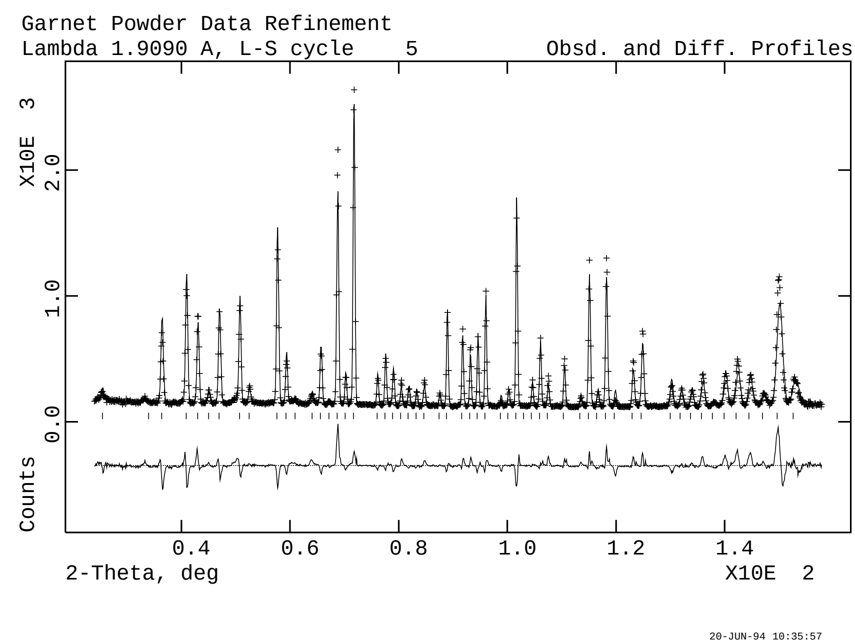
Powder Data Preparation and Refinement

You are now ready to run two batch jobs. The first will run **POWPREF** and the second will run **GENLES**. These may be submitted individually but **POWPREF** must finish before you submit **GENLES**. Alternatively, on a VMS system you may submit them both to be run sequentially by entering **'POWPREF GENLES'** at the **GSAS** command prompt. You will be asked a pair of questions about each of the two batch jobs to be run. By this means a set of up to seven batch jobs may be submitted and the list can have duplicate programs. This option is not available on the UNIX versions of **GSAS**. After both jobs finish use **POWPLOT** to look at the results of the refinement.



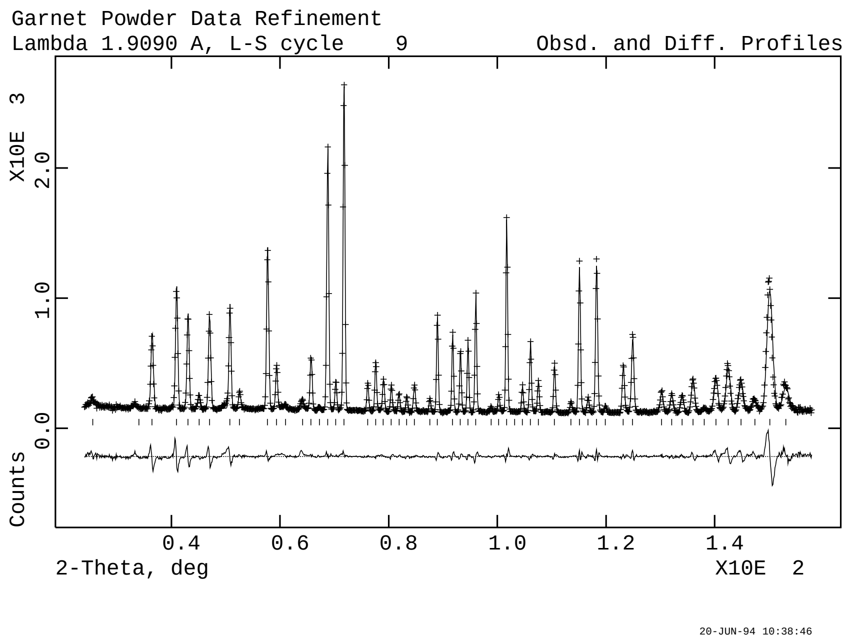
As you can see the fit at this point is quite poor and more parameters need to be varied before the fit will improve. Close examination of the difference curve indicates that a lot of the error arises from lattice parameter and zero point. The list output shows that while the refinement converged rapidly, the residuals are quite high (~32%). You should set the appropriate refinement flags (zero and lattice parameters) for the next least squares run. Because the previous least squares did not modify the peak positions, it is not necessary to rerun **POWPREF** before the next run of **GENLES**.

After refinement of the lattice parameter and zero point to convergence, the residuals are 9-10% and the fit to the pattern is considerably improved.

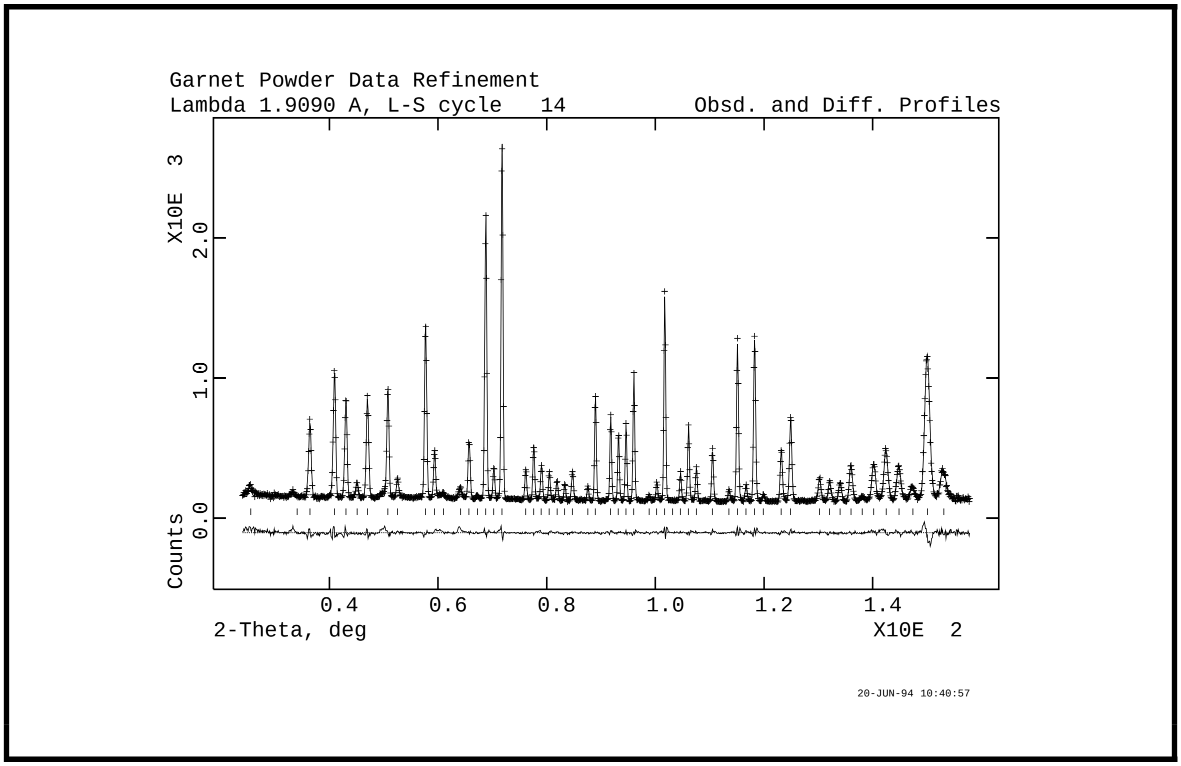


Examination of the fit seems to indicate that the major differences are related to structural details and profile shapes. Notice that several peaks have the wrong calculated intensity; this indicates a structural problem. In this case it is probably a combination of positional errors for the oxygen atom, atom fractions for the iron/aluminum sites and thermal parameters for all atoms. We suggest that you refine all these first; you should also increase the maximum number of L-S cycles to five. The atom constraints which were entered earlier are needed here to control the refinement of the atom fractions and thermal parameters for the Fe/Al atoms. The other major difference is that the peak shapes are in error; especially at the ends of the pattern. Refinement of the profile coefficients will be necessary; this should be done after the atom refinement has converged. In this case you need to run both **POWPREF** and **GENLES** because the previous refinement moved the peak positions relative to the pattern.

After refinement of the atomic parameters the residuals are much lower (5-7%) and the profile fit is much better.



As you can see all the peak intensity errors have disappeared leaving only the peak shape errors at the ends of the pattern. Now refine the first four (U, V, W and asym) peak shape coefficients. You will also want to increase the number of background coefficients to six. Again run both **POWPREF** and **GENLES**. After this refinement has converged the profile should look like the next plot.



Clearly there are no longer any major differences between the observed and calculated profiles; the residuals are 3-5%. An exception is the large peak at ~150˚; the remaining residual is probably due to an incomplete peak shape model. This is suggested by the shape of the difference curve. You may add additional parameters for anisotropic thermal motion and more background and profile coefficients; the improvement will be slight. If you do decide to refine the anisotropic thermal parameters for the Fe/Al sites, the constraints will have to be changed to include those for each u_{ij} on each site. For the final refinement, you should rerun **POWPREF** before the final run of **GENLES**. This assures that the peak positions and widths are correctly calculated.

Fourier Setup and Calculations

Before a Fourier calculation can be performed from powder data, a set of "observed" structure factors must be available. This is done in **GSAS** by the least squares program **GENLES** by dividing up the observed profile intensity above background among the contributing reflections according to their calculated intensity. Thus the "observed" structure factors are biased by the model used in the least squares. Nonetheless, these structure factors can contain sufficient information to find, for example, atoms that are missing from the structure. The appropriate option is set from the least squares controls menu in **EXPEDT**.

```
Maximum number of cycles is   5
Enter L-S control editing option (<?>,C,E,L,P,X) >
```

Enter **'E'** to select the F_o extraction option. As this is selectable for individual histograms, **EXPEDT** requests the histogram number you wish to extract F_o's from.

```
Enter histogram number >
```

Enter **'1'** to select the histogram in the garnet example; the default extraction information for that histogram is presented next.

```
New histogram selected

Histogram no.   1 Bank no.  1 Lambda =  1.90900
Title: Y3FE2(ALO4)3 RT 1.909
Histogram will be used in least-squares
Fo's will not be extracted from this histogram
Experiment phase flags:           1    0    0    0    0    0    0    0    0
Histogram Fo extraction flags :   0    0    0    0    0    0    0    0    0
0 for normal 1 for LeBail method
Fo extraction flag editing options - (<?>,C,E,H,L,N,X) >
```

There are two techniques available in **GSAS** for the extraction of F_O's from powder data. The "normal" method apportions the observed Bragg intensity above background according to the portion of the total calculated intensity contributed by each reflection to give a set of "observed" structure factors with phases. Thus, the extraction is biased by the calculated structure factors and hence the structure model. Nonetheless, there is sufficient information in the extracted F_O's so that meaningful difference Fourier maps can be produced to locate missing atoms, etc. The "le Bail" method begins with a set of calculated structure factors based on a partial or dummy structure to obtain an initial set of F_O's. On subsequent least-squares cycles the set of F_O's extracted from one cycle are used as the F_C's for the next. In this way a set of F_O magnitudes (i.e. no phases) can be obtained even in the absence of a structural model. They can be used to produce Patterson maps or passed on to a direct methods package (SHELX, MULTAN, etc.) for structure solution. The le Bail method can also be used to fit sets of reflections from second phases, sample holders, chambers or other sources that appear as unwanted additions to the pattern. Thus, the extraction method can be selected individually for each phase. The default flags are set so that no extraction will occur and that "normal" is the default method. Enter '**CR'** to see the help listing.

```
Histogram phase flag editing options
 <?> - Type this help listing
 C   - Change Fo extraction method flags
 E   - Toggle main Fo extraction flag
 H m - Select new histogram "m"
 L   - List the current Fo extraction flags
 N   - Select next histogram
 X   - Exit to least squares control editing menu
Fo extraction flag editing options - (<?>,C,E,H,L,N,X) >
```

Select option **'E'** to set calculation of observed structure factors by the "normal" method. This option increases the computation time for a cycle of least squares by 10-20%, thus it should be only used when needed. A message will appear indicating that extraction is to be done.

```
Fo's will be extracted from this histogram
Fo extraction flag editing options - (<?>,C,E,H,L,N,X) >
```

You are now done setting the extraction flag so enter **'X'** to return back to the least squares controls menu. You may also wish to set the number of cycles (**'C'** option) to zero to reduce the computation time; the structure factor and profile calculations will be made but no least squares matrix will be generated. Now return to the main **EXPEDT** menu.

```
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

The next step is to set the Fourier controls; this is a main **EXPEDT** option. Enter **'F'** to select this option.

```
Enter desired map (<?>,DELF,FCLC,FOBS,PTSN,DPTS,EXIT) >
```

The available Fourier calculations include Patterson (**'PTSN'**), difference Patterson (**'DPTS**)', observed Fourier (**'FOBS'**), difference Fourier (**'DELF'**) and calculated Fourier (**'FCLC'**) maps. The first two can be calculated from le Bail extracted intensities; the others require F_O values extracted by the "normal" method. We want you to calculate an observed Fourier map for the garnet so enter **'FOBS'**.

```
Enter section desired (X,Y,Z) >
```

You are now requested to indicate the axis that is to vary from section to section in the Fourier calculation. In the case of garnet, which is cubic, there is no preferred direction so enter **'X'**. If you anticipate that there will be fewer points to be calculated along a particular axis then choose that axis; the calculation will use less computer time than the other choices.

```
Do you wish to specify individual map steps for each axis (Y/<N>)? >
```

Generally, the grid size for a Fourier map should be the same along the three axes; only in special cases might you need different size steps. Respond with **'CR'** to select a single grid size.

```
Current overall map step size is  0.2000 A
Enter new overall map step size in Angstroms >
```

This is a reasonable map step size so enter **'/'**. This choice ensures that the contouring routines **FORPLOT** and **PLOTTER** will draw sensible contours without consuming too much computer time. The next listing shows the chosen step size and number of steps for each cell edge. The step sizes are adjusted so that special sections (1/4, 1/3, 1/2 etc.) are explicitly included according to the cell symmetry.

```
The a-axis is  12.188955 A
The new del-x is  0.2031 A
The cell will be divided into   60 points along x
The b-axis is  12.188955 A
The new del-y is  0.2031 A
The cell will be divided into   60 points along y
The c-axis is  12.188955 A
The new del-z is  0.2031 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 >
```

The next step is to set the axes limits for the Fourier calculation. The old x limits are clearly wrong. Reference to "International Tables for Crystallography, Vol. A" suggests that the limits on the x-axis for this space group are -1/8 to 1/8. Enter **'-1/8   1/8'**.

```
New x limits are -0.1250 to  0.1250
Old y limits are  0.0000 to  0.0000
Enter minimum and maximum values of y in fractions of the cell edge >
```

The new limits for x are shown; they are set to be on a grid point. As was for x the old y limits are wrong; the suggested range is also -1/8 to 1/8. Enter **'-1/8   1/8'.**

```
New y limits are -0.1250 to  0.1250
Old z limits are  0.0000 to  0.0000
Enter minimum and maximum values of z in fractions of the cell edge >
```

The new limits for y are shown; again they are on a grid point. The z limits should be 0 to 1/4. Enter **'0   1/4'.**

```
New z limits are  0.0000 to  0.2500
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) >
```

The new z limits are shown. The message indicates that the volume you have selected contains at least a complete unique part of the unit cell. Next you have to indicate which histograms contribute reflections to the calculation. In case of duplicate reflections between histograms, the last one found will be used in the Fourier calculation. Thus the numerical order of the histograms entered here may be important. For this example there is only one histogram so enter **'1   0'** to include it and terminate the list.

```
Enter FOURIER map calculation option (<?>,A,D,E,F,H,I,L,M,P,R,S,T,W,X) >
```

This is the main Fourier control menu; enter **'CR'** to see the help listing.

```
The FOURIER control data edit options are
<?> - Type this help listing
 A  - Add another map to the set to be calculated
 D  - Change minimum reflection D-spacing for this phase
 E  - Erase a map from the set to be calculated
 F  - Edit phase composition
 H  - Select histograms to include in the map
 I  - Enter new map intervals
 L  - List the current controls
 M  - Select map type to be computed
 P  - Select phase (only one can be processed by FOURIER
 R  - Enter new unit cell limits for the map
 S  - Change the sections control
 T  - Change the experiment title
 W  - Change the map listing options
 X  - Exit to EXPEDT main menu
Enter FOURIER map calculation option (<?>,A,D,E,F,H,I,L,M,P,R,S,T,W,X) >
```

All of the items you have just entered can be now edited separately from this menu. Enter **'L'** to list the current settings.

```
Current Fourier map options for phase 1 are:
Calculate a FOBS map
Do not generate a map listing
Calculate sections at constant X
Divide the cell into   60 points along x
The x interval is 0.2031 A
The range is -0.1250 to  0.1250
Divide the cell into   60 points along y
The y interval is 0.2031 A
The range is -0.1250 to  0.1250
Divide the cell into   60 points along z
The z interval is 0.2031 A
The range is  0.0000 to  0.2500
At least one asymmetric part of the unit cell is included in the Fourier.
There are  1 histograms
The histogram type flags are
 1 PNC
 1 of them are to be used
The ones to be used are:
    1
F000 is  98.071
Enter FOURIER map calculation option (<?>,A,D,E,F,H,I,L,M,P,R,S,T,W,X) >
```

You are all finished with **EXPEDT** so return to the main **GSAS** prompt by entering **'X'** a sufficient number times.

The next section of this manual describes the map display program **FORPLOT** but first you need to extract structure factors and calculate the Fourier. At the **GSAS** prompt on a VMS system enter **'GENLES FOURIER'** and respond to the two pairs of batch job questions. Both runs are relatively short so choose the appropriate queue. Two batch jobs will be submitted to perform the required calculations; after they finish continue with the exercise. The operation is essentially the same for UNIX except that **GENLES** and **FOURIER** are run sequentially.

Fourier Map Display

In this section you will run the Fourier display program **FORPLOT**. It is capable of displaying single slices of the density map calculated by **FOURIER** in any orientation and over any range. A slice is produced by 8 point interpolation for each point in a grid covering the slice area to the computed map and uses symmetry operations to complete the coverage. The plots are always square and are contoured with levels of your choosing. The area covered by the slice is limited by computer memory and is also related to the fineness of the grid. Successive plots may be generated by incremental displacement and rotation from a reference position. This exercise will demonstrate some of these facilities.

To start the program type **'FORPLOT'** at the main **GSAS** prompt; the following will be displayed.

```
               |---------------------------------------------|
               |          Program FORPLOT Version 6.25       |
               | Crystal structure Fourier map drawing program |
               |    Distributed on TEST Vers. 20-JUN-1994     |
               |---------------------------------------------|
       |-------------------------------------------------------------|
       |              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, 1994, The Regents of the University of California. |
       |-------------------------------------------------------------|

Enter terminal type (<?>,A,B,C,D,E,F,G,H,Z) >
```

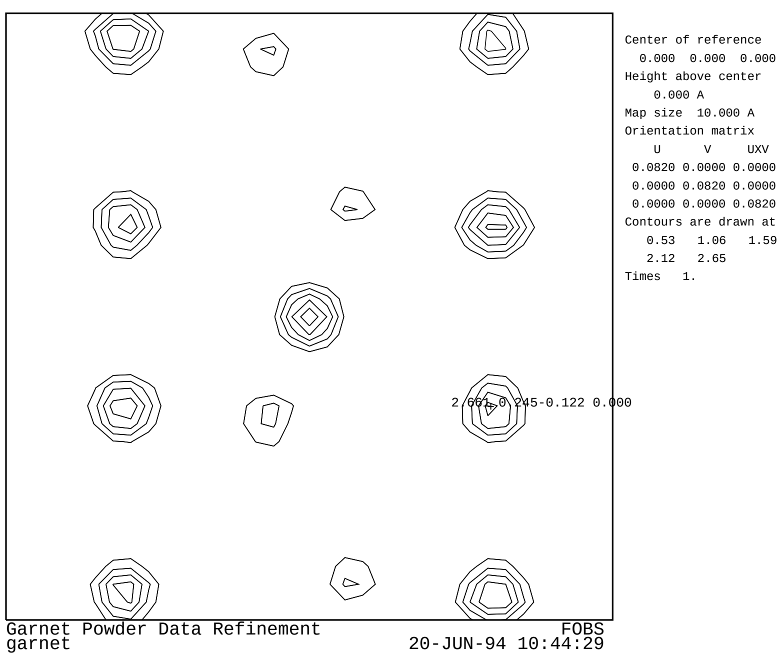
As in the earlier exercises with **EXPEDT** and **POWPLOT**, you need to identify the type of graphics terminal you are now using. Enter the appropriate letter. **FORPLOT** will read the map file output by **FOURIER** and show you a summary of what it found as well as the default plotting parameters.

```
A FOBS file has been opened
Problem title: Garnet Powder Data Refinement
Phase name: garnet
Map parameters:
Map X axis divided into   60 steps, from   -8 and covering   17 steps
Map Y axis divided into   60 steps, from   -8 and covering   17 steps
Map Z axis divided into   60 steps, from    0 and covering   16 steps
Map scaling factor  1.E+00
Rescaled rho limits from  -0.59 to   3.19
There were   4624 map elements stored
The map values range from   -0.59 to   3.19 with a scaling factor of  1.E+00
  5 contours will be drawn between rho =   0.00 and   3.19
with an interval of   0.53
Contours will be drawn at:
  0.53  1.06  1.59  2.12  2.65
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:
   0.082041    0.000000    0.000000
   0.000000    0.082041    0.000000
   0.000000    0.000000    0.082041

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,G,F,H,I,L,M,N,O,P,Q,R,S,T,V) >
```

The first few lines indicate the step sizes and ranges for the Fourier calculations and show the number of elements in the map. The rest of the display shows the default settings. **FORPLOT** has selected 5 contours which are to be drawn at equal intervals between zero and the maximum map density. The default orientation is with the crystallographic *a*-axis horizontal, the *b*-axis up the screen and the *c*-axis out of the picture towards you. In this case they are orthogonal axes. The columns of the transformation matrix indicate the crystallographic real space vectors that are horizontal, vertical and normal to the screen; in this case 100, 010 and 001, respectively. Note that the menu is quite extensive, type **'CR'** to see the help listing.

```
FORPLOT commands:
 <?>   - Type this help listing
 A     - Define map center and orientation by entering 3 or 4 atom seq. numbers
 C c   - Set map center
 D     - Set atom labeling limit
 F     - Read a different Fourier map
 G g   - Set grid interval "g" in A (default = .3)
 H h   - Set height "h" of section above center in A
 I v   - Select contour interval in rho "v"
 L     - List current settings
 M v   - Select minimum rho value "v" (default = 0.0)
 N n   - Select number of contours "n" and assign their values
 P     - Plot map
 Q     - Quit FORPLOT
 R a r - Enter axis (x,y,or z) and angle for rotation of current drawing
 S s   - Set map size - center to edge (default = 5.0 A)
 T x y z  - Display rho at "x,y,z"
 V u v - Set map orientation vectors "u" and "v" (Enter 6 values)
         Map horizontal is u and normal is uxv
Enter FORPLOT command (<?>,A,C,D,G,F,H,I,L,M,N,O,P,Q,R,S,T,V) >
```

There are several types of commands for **FORPLOT**. One set controls the contours (**'G'**, **'I'**, **'N'** and **'M'**), another the map orientation and position (**'A'**, **'C'**, **'H'**, **'R'** and **'V'**) and the rest provide information. To see the default plot type **'P'** and the contoured plot will immediately follow.



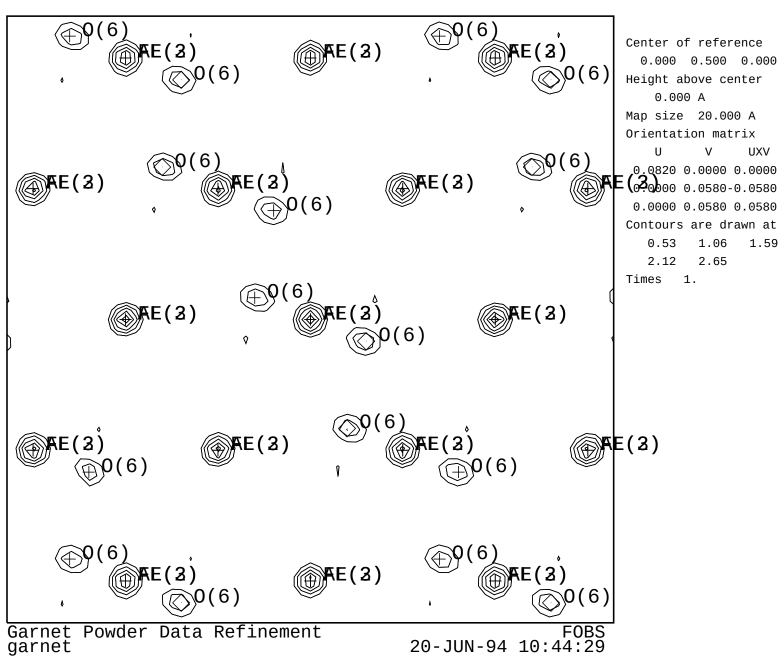
This is a 10 X 10Å *ab*-section centered at 0,0,0 looking down the *c*-axis of the garnet cell. The peak in the center is the first Fe/Al atom, the smaller peaks nearby are close to the O atom positions and the intermediate peaks to the right and left are Y atoms. A graphics cursor and a menu also appears on the plot. To move the cursor push the arrow keys (or mouse) until it is positioned where you want. The picture in this manual has the cursor placed on the peak with the numbers nearby. Move the cursor to that peak and type **'W'** to show its crystallographic coordinates. They are printed to the right. Then type **'H'** to show the density; it is printed to the left. The **'C'** option allows you to set the map center for the next picture. To exit the cursor mode and return to the main **FORPLOT** menu, type **'X'**.

```
Enter FORPLOT command (<?>,A,C,D,G,F,H,I,L,M,N,O,P,Q,R,S,T,V) >
```

The next plot we want you to try is a view with the *a*-axis horizontal and the 110 real axis vertical; this will give a view down the real space 0-11 vector. Enter **'V 1 0 0 0 1 1'**; this will set the U and V vectors. **FORPLOT** will then display the new orientation matrix.

```
New grid to crystal transformation matrix:
   0.08204   0.00000   0.00000
   0.00000   0.05801  -0.05801
   0.00000   0.05801   0.05801
Enter FORPLOT command (<?>,A,C,D,G,F,H,I,L,M,N,O,P,Q,R,S,T,V) >
```

We want the center of the plot to be at 0,1/2,0 and span twice the range as the previous plot. We also want all atoms that fall within 0.5Å of the plot plane to be labeled. All these commands can be entered on one line so type **'C 0 1/2 0 S 10 D 0.5 P'**, the plot will immediately follow.



You may wish to explore this structure using some of the other options of **FORPLOT**. There are some precedence rules for the various options that you should be aware of. The **'R'** commands are cumulative, that is each rotation is applied to the previous orientation to give a new one. A **'V'** or **'A'** command starts a new orientation and wipes out the effect of any previous **'R'** commands. The height option **'H'** is only effective for the next plot to be drawn, after the plot is made the height is reset to zero. A new set of contours is only generated by the **'I'** and **'N'** options. Changing the minimum density with the **'M'** option will not generate extra contour levels until an **'I'** option is given, and **'M'** has no effect on the contour levels set with the **'N'** option..

Distance-Angle Setup and Calculations

There is a set of controls for a distance/angle calculation which are set to some default values. In this part of the exercise you will examine them. The editing of these controls is reached by the **'D'** option in the main **EXPEDT** menu.

```
Select editing option for Distance/angle calculation (<?>,A,D,P,T,X) >
```

This is the distance/angle editing main menu. Here you can completely define a known crystal structure; both phase and atom editing options are available. Enter **'?'** to see the help listing.

```
The available options are:
 <?> - Type this help listing
 A   - Edit atom parameters
 D   - Edit the distance/angle routine controls
 P   - Edit phase data - lattice & sp. group
 T   - Change the experiment title
 X   - Return to main EXPEDT menu
Select editing option for Distance/angle calculation (<?>,A,D,P,T,X) >
```

Since you are interested in distances and angles for the refined structure of yttrium-iron garnet enter **'D'** to examine the controls.

```
Current Distance and Angle options for phase  1 are:
Calculate distances based on atom type limits
Calculate angles based on atom type limits
Atom type   Dist. radii   Angle radii
  Y            2.00       1.80
  FE           1.47       1.27
  AL           1.60       1.43
  O            1.09       0.89
Do not include any Fourier map peaks
Enter DISAGL control data edit option (<?>,C,D,F,L,N,O,X) >
```

The default setup for a distance/angle calculation is shown. The atom radii were obtained from the atom data file and provide a reasonable starting point for upper limits for bond distance and angle calculations. These can be changed with the **'C'** option. You also have the choice of using overall limits for both distance and angle calculations. This choice is also made with the **'C'** option. Enter **'?'** to see the help listing.

```
The DISAGL control data edit options are
 <?>  - Type this help listing
 C   - Change distance limit type and values
 D   - Delete calculation of distances for this phase
 F   - Change the Fourier peak inclusion option
 L   - List the current controls
 N n - Process phase "n"
 O   - Select a new output option
 X   - Exit to DISAGL editing main menu
Enter DISAGL control data edit option (<?>,C,D,F,L,N,O,X) >
```

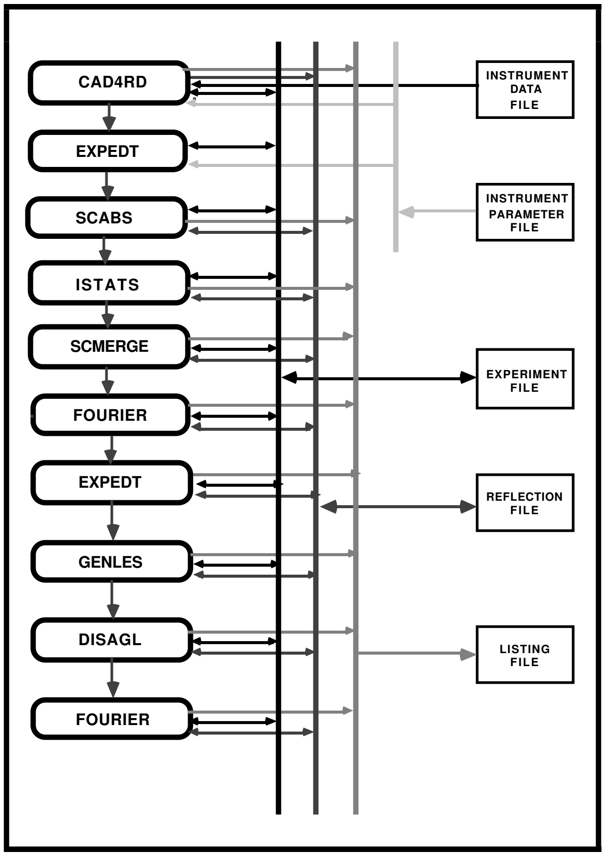
Since the default selections for the controls are reasonable for a distance/angle calculation enter **'X'** a sufficient number of times to exit **EXPEDT**.

To run the distance/angle program enter **'DISAGL'** at the **GSAS** prompt and respond to the two batch run questions. This calculation is quite rapid so select a fast batch queue. The output will be appended to the list file and can be examined after the job completes.

Single Crystal X-ray Data Exercise

As an introduction to the use of **GSAS** to process single crystal data, we present first a flow diagram for the run which we want you to work through. This is given in the box below.

We have prepared an exercise to acquaint you with using **GSAS** for single crystal data analysis. The example which we are using is oxonium hexafluoroantimonate, $(H_3O)^+(SbF_6)^-$. This structure has been published in *Acta Crystallographica* **B**. The compound is cubic and the space group is either Ia3 or $I2_13$. The lattice constant is 10.120(7) and there are eight formula units per unit cell. The raw data for this exercise was collected on a Enraf-Nonius CAD4 single crystal diffractometer.



CAD4 Data Setup

To begin set the default directory to where you wish to run this exercise and enter **'GSAS OXONIUM'** to start the **GSAS** command file and set the experiment name to 'OXONIUM' which is the name we have chosen for this exercise.

```
                       Welcome to GSAS
              The General Structure Analysis System

     Current listing output page length is 60 lines
     Default for running Least-squares and other long jobs is ONLINE
     Enter a ? or a simply a <CR> for information on available commands

%SYSTEM-W-NOSUCHFILE, no such file
 \OXONIUM.EXP\
  The experiment is OXONIUM  creation date =
MIST::GSAS Command? >
```

As with the powder exercises the error message informs you that these is no experiment file for OXONIUM, you will create it in a moment. In the first part of this exercise you create the experiment file at the same time the diffraction data is read. Enter **'CAD4RD'** to begin and you will get the first prompt .

```
Experiment - OXONIUM - was not found.
Do you wish to create it (Y/<N>)? >
```

You want to create the file OXONIUM.EXP, so enter **'Y'** and you will get the next prompt. After it is created you should not see this prompt at the beginning of **CAD4RD** or **EXPEDT** unless you are inadvertently in the wrong directory or have the wrong experiment name.

```
The new experiment - OXONIUM - has been created.
 Enter a title for this experiment
  >
```

Give the experiment a title, '**Single Crystal Exercise'** might be an appropriate one. At this point you will see the program banner and the next prompt.

```
            |-------------------------------------------------------|
            |              Program CAD4RD Version 6.14              |
            |          Convert CAD4 data to a standard form         |
            | Modified by James Fait, University of Calgary Apr 89  |
            |               Modified by ACL Feb, Apr 90             |
            |       Distributed on TEST Vers. 20-JUN-1994           |
            |-------------------------------------------------------|
        |----------------------------------------------------------------|
        |            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, 1994, The Regents of the University of California. |
        |----------------------------------------------------------------|

Enter Single Crystal instrument parameter file name (<?>,$,QUIT)
  >
```

The file **'GSAS_EXERCISES:INSTPARM.CAD4'** (for UNIX use **'/usr/gsas/INSTPARM.CAD4'**) is the instrument parameter file for the CAD4. It contains information that characterizes the Enraf-Nonius CAD4 diffractometer including the relationship between the goniometer and the 'laboratory coordinate system' as well as the sense of rotation and zero positions of the goniometer circles. It also has attenuator data and a nominal wavelength. Notice that the possibility of executing system commands is available here (the '**$'** command).

```
Enter single crystal data file name (<?>,$,QUIT)
  >
```

The next prompt is for the CAD4 data file which contains both the results of the lattice parameter and orientation matrix determination as well as the entire data acquisition results. Enter **'GSAS_EXERCISES:OXONIUM.DAT'** (or **'/usr/gsas/gsas_exercises/OXONIUM.DAT'** for UNIX) so that this information can be introduced to **GSAS**. Again system commands can be used to search for it.

```
First record:  21     1KENT'S H3O+SBF5- LOW TEMP -50C       173 4.0 1.3 5.9
Is this the correct file (<Y>/N/Q)? >
```

The first record on the CAD4 data file is reproduced here and you are given the opportunity to reject it. This is the correct file so enter **'CR'** to accept it.

```
There is no phase information present
Enter identifying name for new phase number 1.
  >
```

We need to enter some phase information as a first step in this process. The first request is for a name of this phase, **'(H3O)+(SbF6)-'** or something else appropriate will do. You will then be asked for further information about this phase.

```
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) >
```

First you need the space group. This data set was collected in a way that places the antimony atom on the intersection of mirrors *bca* at 1/4,1/4,1/4 in Ia3; this is the 8b site. The 8a site at 0,0,0 is taken by the oxygen atom. If you use the alternate name for this space group, Ib3, then these two sites are interchanged so that the antimony atom is at the origin and the oxygen atom at 1/4,1/4,1/4. We have assumed that the alternate choice is used so enter **'I B 3'** as the space group and you will get the following screen..

```
Space group I b 3
The lattice is centric  I-centered cubic         Laue symmetry m 3
 Multiplicity of a general site is  48
 The symmetry of the point 0,0,0 contains 1bar

The equivalent positions are:

 ( 1)     X      Y      Z   ( 2)     Z      X      Y   ( 3)     Y      Z      X
 ( 4)     X  1/2+Y  1/2-Z   ( 5) 1/2-Z      X  1/2+Y   ( 6) 1/2+Y  1/2-Z      X
 ( 7) 1/2-Z  1/2+X     -Y   ( 8)    -Y  1/2-Z  1/2+X   ( 9) 1/2+Y     -Z  1/2-X
 (10) 1/2-X  1/2+Y     -Z   (11)    -Z  1/2-X  1/2+Y   (12) 1/2+X     -Y  1/2-Z

Enter real lattice parameters (Angstroms)
Enter a >
```

As was the case for the powder examples **GSAS** determines that only the *a* lattice parameter is needed for this cubic cell. Enter **'10.12'** and a full list of the lattice constants and calculated cell volume is shown next.

```
Lattice parameters are
    a,b,c  = 10.120001 10.120001 10.120001
    angles =    90.000    90.000    90.000
    volume =  1036.434
Lattice symmetry is cubic
Space group symmetry is cubic
Enter phase edit command(<?>,$,D,E,F,M,I,L,S,X) >
```

Enter **'?'** or **'CR'** to see the options available from this menu.

```
Phase editing commands:
 <?> - Type this help listing
 $   - Enter DCL command
 D n - Delete all data for phase "n"
 E n - Edit phase data for phase "n"
 F n - Enter unit cell contents data for phase "n"
 I   - Insert new phase
 M n - Toggle magnetic flag for phase "n"
 L   - List phase names
 S n - Enter unit cell sigmas
 X   - Exit to EXPEDT main menu
At least one phase must be defined before leaving this menu
Enter phase edit command(<?>,$,D,E,F,M,I,L,S,X) >
```

The CAD4 data file does not contain the error information on the lattice constants so we should enter σ_a into the data file. To do this select option **'S'** from this menu.

```
All sigmas for lattice parameters = 0.00
Enter real lattice parameter Sigmas (Angstroms & degrees)
       ( enter / if current values are OK )
Enter Sigma(a) >
```

As with the lattice parameter input, only the error for the *a* lattice parameter is needed for a cubic cell. Enter **'.007'** and the menu prompt for phase editing is shown.

```
Enter phase edit command(<?>,$,D,E,F,M,I,L,S,X) >
```

The next step is to enter the probable unit cell contents; these are required for the absorption calculation that will be run in a few moments. Enter **'F'**.

```
Unit cell contents not known
Enter unit cell composition edit command (<?>,$,C,E,F,L,X) >
```

You see a message that there is no information on the unit cell contents. To see the entries in this menu enter **'CR'**.

```
Unit cell composition editing commands:
 <?> - Type this help listing
 $   - Enter DCL command
 C   - Change unit cell composition
 E   - Edit unit cell composition data
 F   - Edit form factor information
 L   - List unit cell composition
 X   - Exit to phase editing menu
You are limited to 9 atom types for all phases
Enter unit cell composition edit command (<?>,$,C,E,F,L,X) >
```

You want to change the unit cell contents so enter **'C'**.

```
Enter atom type for type(1) (<CR> to quit) >
```

And now enter **'h 24 o 8 sb 8 f 48'** to define the contents of the unit cell.

```
Enter atom type for type(5) (<CR> to quit) >
```

The entry of chemical formula data is terminated with a blank line; enter **'CR'**. The program will next list the composition, calculated density, absorption coefficients and the F(000) structure factors for both x-rays and neutrons.

```
Unit cell contents for phase 1:
H          24.00 O          8.00 SB          8.00 F          48.00
F(000) neutrons =   27.30              Formula weight = 2038.09
F(000) xrays    =  927.94              The density is     3.265
  X-Ray Abs. Coefs. 1229.96 799.59 441.55  54.09  28.01
Neutron Abs. Coef.     0.48 +   0.48 Lambda
Enter unit cell composition edit command (<?>,$,C,E,F,L,X) >
```

You are finished here so exit formula editing by entering **'X'.**

```
Enter phase edit command(<?>,$,D,E,F,M,I,L,S,X) >
```

You are finished here so exit phase editing by entering **'X'**. You next have the opportunity to edit the information taken from both the CAD4 instrument parameter and data files.

```
Attenuator coefs. are
 1.0000 16.2300  1.0000  1.0000  1.0000  1.0000
Enter new values or a "/"
Enter ATNCOF(1) >
```

These six attenuator coefficients are taken from the instrument parameter file. They are correct for this data set so enter **'/'** to accept them. The program will next process the entire diffraction data file listing all lattice constant and orientation matrix changes which occurred during the data collection. Generally these changes are quite minor and can be ignored. The orientation information in the first one will automatically be accepted, but later ones will be presented for you to choose as to whether or not they are a better representation of the cell orientation than the first one.

```
 Nref =    0 Last iseq =    0   Exposure time =      0.  Lambda = 0.70930
 4.1278001E-02  9.7239995E-03  8.9162000E-02
-8.5389003E-02 -2.5436001E-02  4.2268999E-02
 2.7078001E-02 -9.4682999E-02 -2.5480001E-03
 Lattice constants are 10.1386 10.1502 10.1311   90.20   90.01   90.06
Phi =   64.58 Chi =   -91.29 Omega =   344.01

 Nref = 1460 Last iseq = 1926   Exposure time =   79282.  Lambda = 0.70930
 4.2096000E-02  9.4630001E-03  8.8886999E-02
-8.4546000E-02 -2.7169000E-02  4.3008000E-02
 2.8436000E-02 -9.4355002E-02 -3.5850001E-03
 Lattice constants are 10.1385 10.1375 10.1204   90.06   90.02   90.07
Phi =   64.16 Chi =   -92.02 Omega =   343.16
Save this orientation? (Y,<N>) >
```

The second orientation information is insufficiently different from the first one to warrant using, so don't save it; enter **'N'**.

```
There were  1497 reflections read
There were     2 standard reflections used
Do you wish to list the standard reflection data? (Y,<N>) >
```

You probably don't want to list the individual standard reflection data, so either enter **'CR'** or **'N'**. A summary of the intensity variation for the first standard is shown next.

```
Standard no.  1 is     0    4   -8
It was measured   12 times
Avg(i) = <WI>/<W> is          3520.67
Sigma(I)/Avg(I) =              0.0029
<abs(del(I))>/Avg(I) =         0.0280
rms(del(I))/Avg(I) =           0.0316
Sqrt(<I**2>-<I>**2)/<I> is     0.0316
Fitting of standards to a polynomial
Default number of terms (M) is:  2 The convergence criterion (C) is: 0.0100
Enter the initial number of terms (2-20), M >
```

The program will fit the intensity data to a polynomial series of the type

$$S_i = A + \sum_{n=1}^{M} B_n T_i^n$$

where M is the order of the polynomial and T is the x-ray exposure time for the crystal. The fitting routine will begin with the number of terms, M, entered and will fit the first standard until the convergence criterion is satisfied for that number of terms. Optionally, the routine will increase the number of terms and repeat the fitting until no further improvement can be obtained. The number of terms found for the first standard is then used for all subsequent standards. We shall start the polynomial fitting with two terms by entering**'2'**.

```
Enter the convergence criterion, C >
```

We will use the default convergence criterion of 0.01 by entering **'/'**.

```
Do you want to search for "best" number of terms (<Y>/N)? >
```

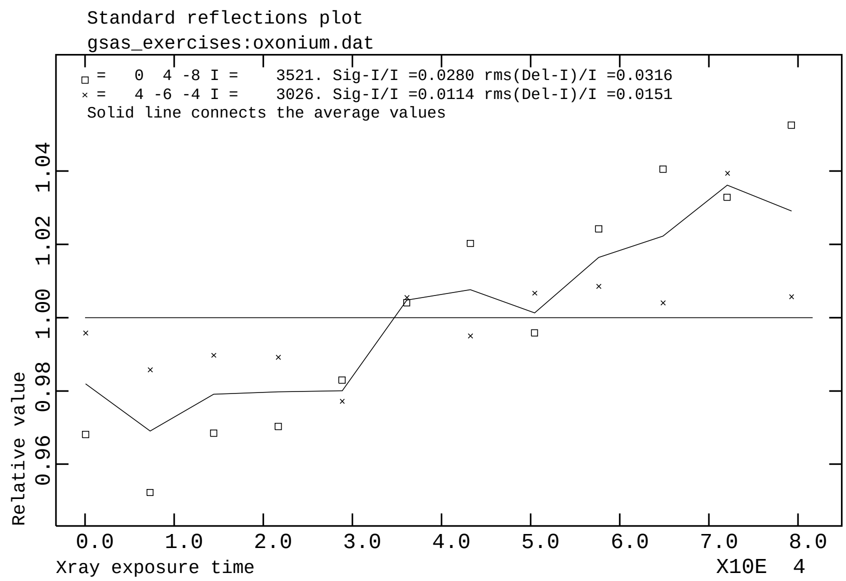
We want the program to search for the best number of terms so enter **'Y'**.

```
Number of terms  =  2 Convergence crit. =    0.01000
Sum of the squares of the residuals =    14690.6     M =  2
Sum of the squares of the residuals =    14280.9     M =  3
Sum of the squares of the residuals =    13175.3     M =  4
Sum of the squares of the residuals =    10963.7     M =  5
Sum of the squares of the residuals =    58296.0     M =  6

Coefficients of normalization polynomial
    1.00000       -0.169575         1.14993        -1.68633        0.800769
Errors for polynomial coefficients
   0.111243E-01    0.174331        0.779324         1.23120        0.628443
Polynomial evaluated at 0. and  81647.   1.00000   1.09480
rms(del(I))/<I> =                0.0476

Standard no.  2 is     4   -6   -4
It was measured   12 times
Avg(i) = <WI>/<W> is            3026.11
Sigma(I)/Avg(I) =                0.0031
<abs(del(I))>/Avg(I) =           0.0114
rms(del(I))/Avg(I) =             0.0151
Sqrt(<I**2>-<I>**2)/<I> is       0.0151
Number of terms  =  5 Convergence crit. =    0.01000
Sum of the squares of the residuals =    9414.70     M =  5

Coefficients of normalization polynomial
    1.00000       -0.385320E-01   -0.690919E-01    0.473014       -0.352103
Errors for polynomial coefficients
   0.116685E-01    0.182595        0.815299         1.28717        0.656700
Polynomial evaluated at 0. and  81647.   1.00000   1.01329
rms(del(I))/<I> =                0.0128
Plot the standards? (<N>/Y/X=EXIT) >
```

As you can see the program tried progressively more terms to fit the first standard. Introduction of the sixth term did not improve the fit so five terms was used for all fitting. The second standard was fit without any further requests from you. You next have the option to plot the standards. Enter **'Y'** for the first plot.

```
Enter terminal type (<?>,A,B,C,D,E,F,G,H,Z) >
```

Enter your terminal type letter followed by **'N'** to have no hardcopy plots. The first plot will immediately follow.



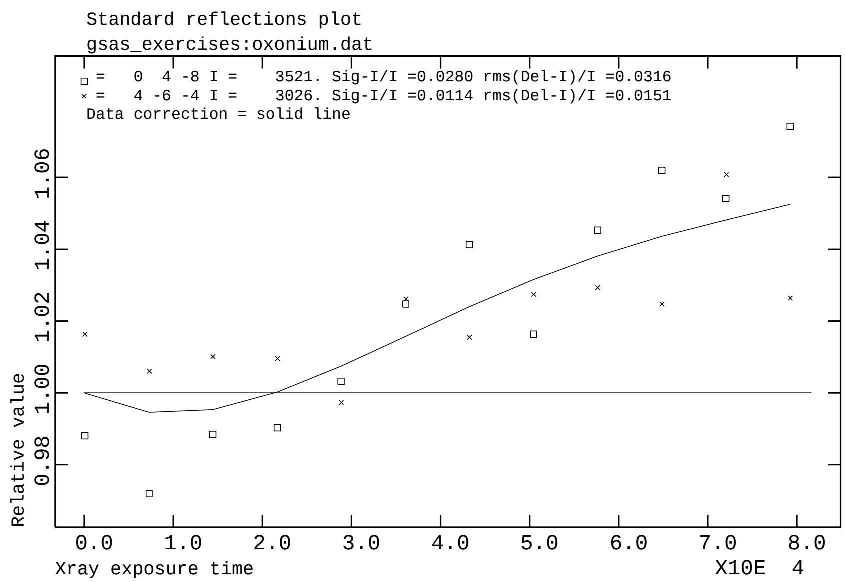
This plot shows the normalized intensities for both standards plotted as symbols along with their average as a solid line. Notice that in this case all three curves are similar so that an average correction is appropriate. On some terminals you need to enter **'CR'** to get the next prompt.

```
Use all of the standards? (<Y>,N) >
```

There is no reason why we should not use all standards measured, so enter **'Y'**.

```
Do you want to use polynomial fit? (<Y>,N) >
```

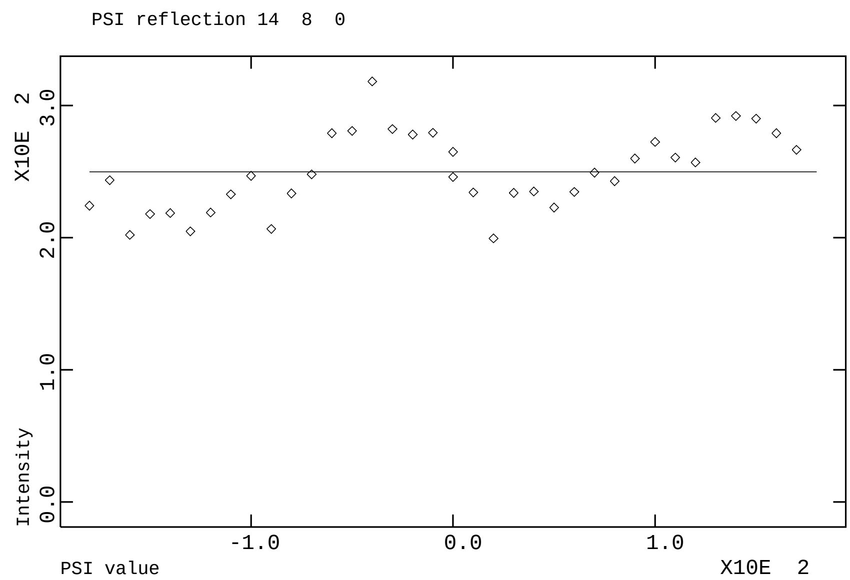
You now need to choose between using the results of the polynomial fit and a simple interpolation of the normalized average standard intensities. Generally the polynomial fit gives a better description of the intensity variations so enter '**Y'.** A plot of the standards and the polynomial fit will follow.



As you can see the five term polynomial fit gives a satisfactory description of the intensity variation. As above you may need to enter **'CR'** to get the next prompt.

```
Data will be corrected with the polynomial fit
Scan no. 1 for hkl  14  8  0 Avg-I      250. has  37 psi values starting at 1461
Do you want to plot this psi scan reflection (<Y>/N)? >
```

You are first advised that the polynomial fit to the standards will be used to correct the intensities. Then **CAD4RD** finds the first ψ-scan data and asks if you want to plot it. Enter **'Y'** and the plot will immediately follow.



This ψ-scan shows the typical sinusoidal variation due to absorption from a non-spherical crystal. If there was more than one ψ-scan reflection set they would be plotted in turn. As for the other plots enter **'CR'** if necessary to get the next prompt.

```
Enter the no. of the PSI reflection you want to use for absorption corrections
 (/ for the last one,<=0 for list) >
```

You will need to select this ψ-scan in order to apply the non-spherical component to the absorption. Enter **'/'** or **'1'** to select it.

```
Reflection  14  8  0 was measured    37 times
 These measurements, given as IREF, PSI, and Intensity, are
1461   0.00    246. 1462  10.00    234. 1463  20.00    199. 1464  30.00    234.
1465  40.00    235. 1466  50.00    223. 1467  60.00    235. 1468  70.00    249.
1469  80.00    243. 1470  90.00    260. 1471 100.00    272. 1472 110.00    261.
1473 120.00    257. 1474 130.00    291. 1475 140.00    292. 1476 150.00    290.
1477 160.00    279. 1478 170.00    266. 1479-180.00    224. 1480-170.00    243.
1481-160.00    202. 1482-150.00    218. 1483-140.00    219. 1484-130.00    205.
1485-120.00    219. 1486-110.00    233. 1487-100.00    247. 1488 -90.00    207.
1489 -80.00    233. 1490 -70.00    248. 1491 -60.00    279. 1492 -50.00    281.
1493 -40.00    318. 1494 -30.00    282. 1495 -20.00    278. 1496 -10.00    279.
1497   0.00    265.
Do you wish to copy them to the .EXP file? (<Y>,N) >
```

This listing shows the measured intensity for all occurrences of the selected ψ-scan reflection in the data set. You should examine it with some care because one that is out of sequence with the others is not part of the ψ-scan and belongs in the reflection data set. You will want to copy the ψ-scan data to the EXP file, so enter **'Y'**.

```
Copy all of this set? (<?>,Y,N) >
```

This question gives you the opportunity to exclude some of the reflections from the ψ-scan set. For example, those observations that were collected during the normal data collection and not part of a ψ-scan could be skipped. In the present case, however, you will want to copy all of them to the EXP file, so enter **'Y'**.

```
Are you finished with the PSI scan data? (<Y>,N) >
```

We are finished with the ψ-scan data, so enter **'Y'**. The display will change the number of reflections until the entire data set is processed after which the **CAD4RD** program will terminate.

```
1475 reflections have been processed
<sigma(I)>/<I> =  0.017
CAD4RD run ended successfully
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >
```

While you were running **CAD4RD**, it was also producing much of the output seen on the screen on the list file. You can examine it by using either of the **GSAS** utilities **ELST** or **TLST**.

Absorption Correction Setup and Calculations

You will need to run **EXPEDT** to set up the absorption calculations. This includes selecting the method for calculating the absorption and entering some coefficients. Enter **'EXPEDT'** at the **GSAS** prompt to get started.

```
                 |-------------------------------------------|
                 |       Program EXPEDT Version 6.50         |
                 | A menu driven routine to edit .EXP files  |
                 | Distributed on TEST Vers. 20-JUN-1994     |
                 |-------------------------------------------|
       |----------------------------------------------------------------|
       |            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, 1994, The Regents of the University of California.  |
       |----------------------------------------------------------------|

The last history record is :
    HSTRY  1 CAD4RD  V-6.14   20-JUN-94 10:51:17
Is this the file you wish to use? (<?>,D,K,N,Q,R,Y) >
```

To make a copy of this experiment file and commence editing enter **'Y'**. If you are brave you can use the **'K'** option which skips the copy operation. Be aware that if you mess up the edit you will have to live with it because the **'Q'**uit option is not available when the **'K'**eep option is selected.

```
Experiment title:
         Single Crystal Exercise
The last history record is :
    HSTRY  1 CAD4RD  V-6.14   20-JUN-94 10:51:17
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

The absorption correction setup is one of the controls for single crystal data preparation, so enter **'S'**.

```
Enter Single Crystal data preparation option(<?>,A,D,I,L,P,T,U,X) >
```

You should look at this menu further, so enter **'CR'** to get the help listing.

```
The available options are:
<?> - Type this help listing
A       - Enter and edit data for SCABS
D n/n:m - Do not use histograms
I       - Enter or change instrument parameter file
L       - List histogram titles
P       - Edit phase information
T       - Change the experiment title
U n/n:m - Use histograms
X       - Exit from single crystal data editing
Enter Single Crystal data preparation option(<?>,A,D,I,L,P,T,U,X) >
```

You need to set up the controls for single crystal absorption calculations by **SCABS** so enter **'A'**.

```
The absorption flag is                    NONE
The radiation type flag is                MoKa
The absorption coefficient is       0.000
The maximum value of d* to be used is  2.000
The instrument error constant is      0.0100
PSI scan data is present
 Scan   1 was measured with the 14  8  0 reflection
 There are  37 values
 PSI  Value    PSI  Value    PSI  Value    PSI  Value    PSI  Value
   0.0 0.9841   10.0 0.9372   20.0 0.7982   30.0 0.9360   40.0 0.9400
  50.0 0.8914   60.0 0.9389   70.0 0.9972   80.0 0.9715   90.0 1.0401
 100.0 1.0904  110.0 1.0429  120.0 1.0281  130.0 1.1630  140.0 1.1687
 150.0 1.1607  160.0 1.1167  170.0 1.0664 -180.0 0.8971 -170.0 0.9743
-160.0 0.8085 -150.0 0.8720 -140.0 0.8748 -130.0 0.8194 -120.0 0.8766
-110.0 0.9314 -100.0 0.9875  -90.0 0.8268  -80.0 0.9343  -70.0 0.9921
 -60.0 1.1167  -50.0 1.1236  -40.0 1.2734  -30.0 1.1293  -20.0 1.1127
 -10.0 1.1179    0.0 1.0601

 Reflection data will not be listed in SCABS
The Absorption type is currently NONE
Enter absorption type desired (<?>,A,G,N,P,S,W,X) >
```

A summary of the available data for the absorption correction including the ψ-scan data is listed. Another new menu, let us look at it by typing **'?'**.

```
The absorption types available are
 <?> - Repeat this help message
 A  - Crystal described by 25 or fewer planes
         Absorption calculated analytically
 G  - Crystal described by 25 or fewer planes
         Absorption by Gauss approximation
 N  - No absorption is to be applied
 P  - PSI-scan data will be used
 S  - Assume a spherical crystal
 W  - Spherical crystal, modified by PSI-scan data
 X  - Exit from absorption type editing
The Absorption type is currently NONE
Enter absorption type desired (<?>,A,G,N,P,S,W,X) >
```

The type of correction that you will use on this data is a combination of a sphere and ψ-scan data. Enter **'W'** to accomplish this.

```
Radius of the sphere in mm.? >
```

The crystal was approximately a 0.2 mm cube, you can assume a .3mm sphere as a good approximation, so enter **'0.15'** to define the radius of the sphere.

```
Do you wish to modify the PSI scan data? (Y,<N>) >
```

No, don't modify the ψ scan data, so enter either **'N'** or **'CR'**.

```
The Absorption type is currently SPHR+PSI
Enter absorption type desired (<?>,A,G,N,P,S,W,X) >
```

You have completed the absorption correction setup so enter **'X'** to exit.

```
SCABS control data editing option (<?>,A,D,F,I,L,M,P,R,X) >
```

Enter **'X'** to exit from **SCABS** control editing.

```
Enter Single Crystal data preparation option(<?>,A,D,I,L,P,T,U,X) >
```

Enter **'X'** to exit from single crystal data editing.

```
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

You are finished with **EXPEDT** for now, so enter **'X'** to exit from **EXPEDT**.

```
EXPEDT terminated successfully
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >
```

Now you are ready to perform the absorption calculations. Enter **'SCABS'** to perform the absorption calculations. This may be run as a batch job on VMS systems or in background on UNIX systems. This job will complete in a few minutes and the output is sent to the list file. Some output will appear on the screen if it is run "online" (or in foreground). When it finishes you are ready for the next step.

Intensity Statistics

After the **SCABS** run completes, you can run **ISTATS** to check on the proper choice of space group. This data set was collected for the primitive space group Pm–3 and it is of interest to check the intensity of the various parity classes to determine the correct space group. Enter **'ISTATS'** at the **GSAS** prompt. The following output will appear on both the screen and the list file. The reflection classes that should be extinct for Ib3 are marked in the manual by asterisks (not in the screen output though), you should look for them on your screen.

```
               |---------------------------------------------|
               |         Program ISTATS Version 6.14         |
               | Program for determining reflection statistics |
               |    Distributed on TEST Vers. 20-JUN-1994     |
               |---------------------------------------------|
       |---------------------------------------------------------------|
       |            Allen C. Larson and Robert B. Von Dreele            |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805      |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545     |
       |                                                                |
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       |---------------------------------------------------------------|

There are  1 histograms
Histogram will be used in least-squares
Histogram 1 has 1460 reflections

Refln1460

Set     Parity      n  <F/sF>   n>3s  n>9s  Max(F/sF)
h00     h = 2n      3  78.024     3     3    83.31
h00     h = 2n+1    2   0.284     0     0     1.48       *
0k0     k = 2n      8  59.157     8     8    83.05
0k0     k = 2n+1    7  -0.456     0     0     0.63       *
00l     l = 2n      8  58.015     8     8    81.39
00l     l = 2n+1    7  -0.778     0     0     0.93       *
hk0     h = 2n     57  33.732    30    30    91.50
hk0     h = 2n+1   49   0.626     3     1    10.10       **
hk0     k = 2n     55  35.290    30    30    91.50
hk0     k = 2n+1   51   0.245     3     1    10.10       **
hk0   h+k = 2n     54  36.190    33    31    91.50
hk0   h+k = 2n+1   52  -0.016     0     0     2.56       *
h0l     h = 2n     64  31.280    33    33    90.11
h0l     h = 2n+1   49   0.370     1     0     8.65       **
h0l     l = 2n     58  34.639    33    33    90.11
h0l     l = 2n+1   55   0.200     1     0     8.65       **
h0l   h+l = 2n     57  35.647    34    33    90.11
h0l   h+l = 2n+1   56  -0.211     0     0     1.88       *
0kl     k = 2n    117  27.626    61    61    91.91
0kl     k = 2n+1  108   1.747    21     6    24.00       **
0kl     l = 2n    117  27.665    61    61    91.91
0kl     l = 2n+1  108   1.705    21     6    24.00       **
0kl   k+l = 2n    113  30.467    82    67    91.91
0kl   k+l = 2n+1  112  -0.194     0     0     1.80       *
hkl   h+k = 2n    733  17.245   272   251    91.91
hkl   h+k = 2n+1  727   3.347   163    79    65.51
hkl   h+l = 2n    734  17.256   276   246    91.91
hkl   h+l = 2n+1  726   3.316   159    84    65.51
hkl   k+l = 2n    733  18.027   323   269    91.91
hkl   k+l = 2n+1  727   2.559   112    61    64.52
hkl h+k+l = 2n    734  20.612   435   330    91.91
hkl h+k+l = 2n+1  726  -0.076     0     0     2.70       *
hhl     l = 2n     58  38.428    49    44    91.50
hhl     l = 2n+1   53   0.005     0     0     2.70       *
hhl   h+l = 2n     56  34.648    33    33    91.50
hhl   h+l = 2n+1   55   5.250    16    11    64.29
hhh     h = 2n      3  77.659     3     3    91.50
hhh     h = 2n+1    3   0.680     0     0     2.64       *
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >expedt
```

As you can see we collected a data set for the primitive lattice. There is no doubt about the I-lattice centering, however the evidence that the space group should really be $I2_13$ is very weak. The extra extinctions needed for Ib3 (marked **) do not show much more intensity than the extinctions common to both space groups (marked *). For the remainder of this exercise we have assumed that Ib3 is the correct choice.

Data Merge and Patterson Calculations

The next step is to merge the equivalent reflections to give the unique set for the space group Ib3. However, you can save a little time by setting up a Patterson calculation and running the data merge program and the Fourier calculations in sequence. Thus, the first step here is to enter **'EXPEDT'** for the Fourier setup of a Patterson map.

```
                 |-----------------------------------------|
                 |       Program EXPEDT Version 6.50       |
                 | A menu driven routine to edit .EXP files |
                 | Distributed on TEST Vers. 20-JUN-1994    |
                 |-----------------------------------------|
       |----------------------------------------------------------------|
       |           Allen C. Larson and Robert B. Von Dreele             |
       |     Manuel Lujan, Jr. Neutron Scattering Center, MS-H805       |
       |     Los Alamos National Laboratory, Los Alamos, NM  87545      |
       |                                                                |
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       |----------------------------------------------------------------|

The last history record is :
    HSTRY  3 SCABS   V-6.16   20-JUN-94 10:57:21 Finished
Is this the file you wish to use? (<?>,D,K,N,Q,R,Y) >
```

To start editing Fourier controls enter **'K F'**. The current experiment file will be opened for editing.

```
Experiment title:
         Single Crystal Exercise
The last history record is :
    HSTRY  3 SCABS   V-6.16   20-JUN-94 10:57:21 Finished
Enter desired map (<?>,DELF,FCLC,FOBS,PTSN,DPTS,EXIT) >
```

You want to calculate a Patterson map, enter **'PTSN'**. **GSAS** will properly compute the Patterson map so that the symmetry is appropriate for the space group Ib3.

```
Enter section desired (X,Y,Z) >
```

Since the unit cell is cubic the choice is immaterial, enter **'X'**.

```
Do you wish to specify individual map steps for each axis (Y/<N>)? >
```

It is not necessary to make the map steps different for the three axes, enter **'CR'**.

```
Current overall map step size is  0.2000 A
Enter new overall map step size in Angstroms >
```

You can get a little better definition of the peak locations with a finer step size than the default, enter **'0.1'**.

```
The a-axis is  10.120001 A
The new del-x is  0.1012 A
The cell will be divided into  100 points along x
The b-axis is  10.120001 A
The new del-y is  0.1012 A
The cell will be divided into  100 points along y
The c-axis is  10.120001 A
The new del-z is  0.1012 A
The cell will be divided into  100 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 >
```

The output shows the number of steps it finds along each cell edge. The next step is to determine the fraction of the cell edge that is the minimum needed to generate a complete map. Reference to the 'International Tables for X-ray Crystallography Vol. A' for this space group suggest that you should enter the limits **'0 1/4 0 1/4 0 1/2'**.

```
New x limits are  0.0000 to  0.2500
Old y limits are  0.0000 to  0.0000
New y limits are  0.0000 to  0.2500
Old z limits are  0.0000 to  0.0000
New z limits are  0.0000 to  0.5000
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) >
```

You entered a sufficient part of the cell to be calculated so that all the unique part of the map is covered. Next you need to select the histograms that are the source of the structure factors needed for the calculation of the Patterson. There is only one histogram available so enter **'1 0'** to include it and terminate the list.

```
Enter FOURIER map calculation option (<?>,A,D,E,F,H,I,L,M,P,R,S,T,W,X) >
```

You are all done entering the Fourier controls so enter **'X'**.

```
At least one asymmetric part of the unit cell is included in the Fourier.
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

You are reassured that the choice of limits is at least one asymmetric unit and you are all finished in **EXPEDT** so enter **'X'** to exit.

```
EXPEDT terminated successfully
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >scmerge fourier
```

Now you are ready for the data merge that we put off from above and the Patterson map calculation. On VMS systems enter **'SCMERGE FOURIER'** and respond to the two sets of batch job questions about log files and queues. On UNIX systems run them sequentially in either foreground or background. The **SCMERGE** program will take longer to run than any of the previous batch jobs in this exercise; however **FOURIER** is quite fast. Both programs will produce results on the list file, consult them at your leisure. After they both finish you will be ready for the map search step.

Map Search and Structure Solution

After the two jobs you submitted above have completed, you will need to determine the location of peaks in the Patterson map. The program **FORSRH** will do this for you, so at the **GSAS** prompt enter **'FORSRH'** and you will get the following screen.

```
                  |-----------------------------------------|
                  |      Program FORSRH Version 6.16        |
                  |     Fourier map peak search program     |
                  | Distributed on TEST Vers. 20-JUN-1994   |
                  |-----------------------------------------|
       |----------------------------------------------------------------|
       |           Allen C. Larson and Robert B. Von Dreele             |
       |     Manuel Lujan, Jr. Neutron Scattering Center, MS-H805       |
       |     Los Alamos National Laboratory, Los Alamos, NM  87545      |
       |                                                                |
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       |----------------------------------------------------------------|

A PTSN file has been opened
The range of map values is -239.091 to 9373.339
Enter min. Peak value (negative if negative values are desired) >
```

The program **FORSRH** opens the PTSN map file and lists the extreme limits on the map density. You are being asked to set the minimum peak value cutoff for the search. For this search you should enter **'50'** to locate all peaks greater than 50. If you were interested in negative peaks as well as positive peaks you could enter a negative number.

```
Enter number of peaks to be located (1 to 225) >
```

The program wants a maximum number of peaks to save, before raising the cutoff value. Enter **'50'** as a reasonable maximum. Thus, the number of peaks listed will be limited to 50 and all will have a density greater than 50.

```
Save the peaks located in the EXP file? (Y,<N>) >
```

There is no need to save these peak locations in the experiment file, so enter **'N'** and wait for the program to scan the Patterson map and then list out its findings.

```
Min rho =   50.00000  No. of peaks =  50  Peaks saved?

The following vectors were found
           Rho       X       Y       Z         Length
   1    9373.339  0.0000  0.0000  0.0000        0.00
   2    8617.319  0.0000  0.0000  0.5000        5.06
   3    1236.617  0.2500  0.2500  0.2500        4.38
   4     329.964  0.1373  0.1019  0.4403        4.78
   5     300.689  0.1023  0.0610  0.3649        3.88
   6     299.863  0.0615  0.1351  0.1034        1.83
   7     293.569  0.0617  0.1353  0.3968        4.29

Total CPU time for FORSRH was   0.49 seconds
FORSRH terminated successfully.
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >
```

After a brief summary of the limits imposed on the peaks list, **FORSRH** finds that the Patterson map has only seven unique peaks. It noted that it was dealing with a Patterson vector map and modified the space group operations properly to determine the unique set of peaks in the map. You might want to examine the Patterson map with either **PLOTTER** or **FORPLOT**, or both at this point.

We know that there are only eight antimony atoms in the unit cell, so we can assume that they are in set 8a at 0,0,0 and the eight oxygen atoms are in set 8b at 1/4,1/4,1/4. Your only task in solving this structure is to choose the Sb-F vector from the remaining four peaks. The choice of space group as Ib3 makes this task easier in that one of the four xyz values is the location of the fluorine atom. Remembering that the lattice parameter is ~10Å, peak number 6 is about the right length (1.83Å) for a Sb-F bond. However, the vector shown points in the direction of the oxygen atom at 1/4,1/4,1/4 so you must choose an alternate location for the fluorine atom. A good choice is to change one sign so the fluorine atom would be at -x,y,z or -0.0615,0.1351,0.1034.

Atom Insertion and Structure Refinement

After you have solved the Patterson, you will need to run **EXPEDT** to enter the atoms into the experiment file and set some least squares controls. Since you have done these operations for both powder exercises we want to demonstrate to the power of the type ahead features in **GSAS** by entering as much as possible long strings of commands. Be very careful when you type them in so that the correct sequence will be executed. To start enter **'EXPEDT'** at the **GSAS** prompt, the following familiar screen will appear.

```
                 |------------------------------------------|
                 |       Program EXPEDT Version 6.50        |
                 | A menu driven routine to edit .EXP files |
                 | Distributed on TEST Vers. 20-JUN-1994    |
                 |------------------------------------------|
       |--------------------------------------------------------------|
       |             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, 1994, The Regents of the University of California. |
       |--------------------------------------------------------------|

The last history record is :
    HSTRY  5 SCMERGE V-6.14   20-JUN-94 10:58:54
Is this the file you wish to use? (<?>,D,K,N,Q,R,Y) >
```

The first steps are to open this experiment file, enter least-squares editing and then atom editing. Enter **'K L A'** to get there.

```
Experiment title:
         Single Crystal Exercise
The last history record is :
    HSTRY  5 SCMERGE V-6.14   20-JUN-94 10:58:54

Phase No. 1 There are   0 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,I,S,X) >
```

Some of the information lines appear before you see the atom editing line. Notice that there are no atoms, you will now enter the three for $(H_3O)^+(SbF_6)^-$. Start by entering **'I 1'**.

```
Enter TYPE, X, Y, Z, FRAC or <?> for help
  >
```

Now enter the antimony atom. It is at the origin and we will take defaults for the name and temperature factor. Enter **'SB 0 0 0 1 / I /'**. Don't worry if the input line wraps on your terminal, all the characters will be accepted. Next you see the data you entered for the antimony atom.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  1 SB   0.00000 0.00000 0.00000 1.00000 SB(1)    0.02500 I     -3(111)   8 000

Phase No. 1 There are   1 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

Next you need to enter the oxygen atom coordinates; for the other data you will use defaults. Enter **'I N O 1/4 1/4 1/4 1 / I /'**, again don't worry about the line wrap.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  2 O    0.25000 0.25000 0.25000 1.00000 O(2)     0.02500 I     -3(111)   8 000

Phase No. 1 There are   2 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

Finally, enter the fluorine atom parameters. Enter '**I N F -0.0615 0.1351 0.1034 1 / I /**'. As you can see quite long strings of commands can be entered into **GSAS**; you will probably never exceed the 132 character buffer available for user input.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  3 F   -0.06150 0.13510 0.10340 1.00000 F(3)     0.02500 I        1     48 000

Phase No. 1 There are   3 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

The next step is to set the flags for refinement of the atom coordinates and temperature factors. Enter **'V 1:3 X U'**. This sets the flags for all three atoms.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  1 SB   0.00000 0.00000 0.00000 1.00000 SB(1)    0.02500 I XU  -3(111)   8 000
  2 O    0.25000 0.25000 0.25000 1.00000 O(2)     0.02500 I XU  -3(111)   8 000
  3 F   -0.06150 0.13510 0.10340 1.00000 F(3)     0.02500 I XU     1     48 000

Phase No. 1 There are   3 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

Notice that the flags to refine coordinates for the Sb and O atoms were both set by this command. **GSAS** will use the symmetry information to hold these values fixed regardless of the refinement flag because both atoms are in special positions. You are finished with atom editing, enter **'X'**

```
Select editing option for Least Squares calculation (<?>,A,B,F,L,O,R,S,T,X) >
```

The next step is to modify the least-squares controls, enter **'L'** to see the menu.

```
Maximum number of cycles is   3
Refine on Fsq
The Single crystal Least Squares weight function is
  W = Wght
 Wght = 1.0/(SigmaFoSq)**2 for FoSq refinements
 Wght = (2*Fo/SigmaFoSq)**2 for Fo refinements
Minimum D-spacing is  0.000
Maximum D-spacing is 99.990
Include all data as observed
Enter L-S control editing option (<?>,C,F,G,I,K,L,M,N,P,S,W,X) >
```

You are told the defaults for single crystal refinements. Enter **'CR'** to see the help listing.

```
 C n - maximum number of cycles
 F   - Change minimization function
 G a - Upper limit on wave-length for SCD data
 I a - Treatment of Negative Obs.
 L   - List current settings
 M n - upper D-spacing limit
 N n - lower D-spacing limit
 P   - Select options for the output listing
 R   - Change the weight modification flag, Robust
 S n - Set a Lower I/SigI cut-off in RFN-F
 U n - Set a Upper I/SigI cut-off in RFN-F
 W n - refinement weight option "n"
 X   - Exit from editing least squares controls
Enter L-S control editing option (<?>,C,F,G,I,K,L,M,N,P,S,W,X) >
```

The modifications that we want you to do are to change the number of least squares cycles to 5, set the I/σI cutoff to 1.5, and set the refinement to be on F rather than F^2. To do all of these enter **'C 5 S 1.5 F N X'**. Some messages will appear as each value is set and you will exit from this menu.

```
Maximum number of cycles is   5
Lower I/SigI cut-off for F refinements is  1.500
Refine on F
Select editing option for Least Squares calculation (<?>,A,B,F,L,O,R,S,T,X) >
```

The last step is to modify the scale factor so that the starting value is closer to what you will obtain when the least squares converges. Normally you would have refined this value first before moving the atoms, but you will change it here this way for the purposes of this exercise. To change this overall parameter enter **'O H C 0.4 X X X'**. Some messages will appear as the scale is changed. You need not set the refinement flag, it is set 'Y' by default.

```
Editing histogram scale factors
Histogram will be used in least-squares

Histo. scale =      1.0000     Refine Y Damping flag =  0
Histogram will be used in least-squares

Histo. scale =     0.40000     Refine Y Damping flag =  0
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

The sequence of exit commands in your last command string brought you to the last menu in **EXPEDT**. This menu can only be exited (and hence out of **EXPEDT**) by entering an **'X'** on a new line. Do that now.

```
EXPEDT terminated successfully
  The experiment is OXONIUM  creation date = 20-JUN-1994 10:51:07.67
MIST::GSAS Command? >
```

The atoms are entered and the least squares controls are now set. Enter **'GENLES'** at the **GSAS** prompt and respond to the log file and queue questions. The run will take a few minutes; when it finishes you can examine the results in the list file.

Anisotropic Refinement and Structure Results

After **GENLES** finishes and you have satisfied yourself that all is going well if might be useful to convert the thermal parameters to anisotropic and then make another pass through **GENLES** followed by a distance and angle calculation and an analysis of the thermal ellipsoids with **DISAGL** and **BIJCALC**. As for the previous section, you will enter several commands in sequence so that the changes are made with minimal output on the terminal. To begin enter **'EXPEDT'** at the **GSAS** prompt.

```
                 |------------------------------------------|
                 |       Program EXPEDT Version 6.50        |
                 | A menu driven routine to edit .EXP files |
                 | Distributed on TEST Vers. 20-JUN-1994    |
                 |------------------------------------------|
       |----------------------------------------------------------------|
       |             Allen C. Larson and Robert B. Von Dreele           |
       |      Manuel Lujan, Jr. Neutron Scattering Center, MS-H805      |
       |      Los Alamos National Laboratory, Los Alamos, NM  87545     |
       |                                                                |
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       |----------------------------------------------------------------|

The last history record is :
    HSTRY  7 GENLES  V-6.48   20-JUN-94 11:02:12 Sdsq= 0.112E+05 S/E= 0.125E-03
Is this the file you wish to use? (<?>,D,K,N,Q,R,Y) >
```

First you need to select this version of the experiment file, least squares editing, atom editing and finally list the atoms. Enter **'K L A L'** to do all of these.

```
Experiment title:
        Single Crystal Exercise
The last history record is :
    HSTRY  7 GENLES  V-6.48   20-JUN-94 11:02:12 Sdsq= 0.112E+05 S/E= 0.125E-03

Phase No. 1 There are   3 atoms for this phase
Title: (H3O)+(SbF6)-
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  1 SB   0.00000 0.00000 0.00000 1.00000 SB(1)    0.01511 I XU  -3(111)   8 000
  2 O    0.25000 0.25000 0.25000 1.00000 O(2)     0.03686 I XU  -3(111)   8 000
  3 F   -0.05996 0.14043 0.10432 1.00000 F(3)     0.02604 I XU     1     48 000

Phase No. 1 There are   3 atoms for this phase
Title: (H3O)+(SbF6)-
Give atom editing command (<?>,$,C,D,E,F,I,K,L,M,S,T,U,V,X,+,-,*,/) >
```

Now you want to make all the atoms anisotropic and then exit as far as possible, enter **'U 1:3 A X X X'**.

```
SER TYPE    X       Y       Z      FRAC   NAME    UISO    CODE  STSYM  MULT FXU
  1 SB   0.00000 0.00000 0.00000 1.00000 SB(1)            A XU  -3(111)   8 000
U11,U22,U33,U12,U13,U23 =   0.01511  0.01511  0.01511  0.00000  0.00000  0.00000
  2 O    0.25000 0.25000 0.25000 1.00000 O(2)             A XU  -3(111)   8 000
U11,U22,U33,U12,U13,U23 =   0.03686  0.03686  0.03686  0.00000  0.00000  0.00000
  3 F   -0.05996 0.14043 0.10432 1.00000 F(3)             A XU     1     48 000
U11,U22,U33,U12,U13,U23 =   0.02604  0.02604  0.02604  0.00000  0.00000  0.00000

Phase No. 1 There are   3 atoms for this phase
Title: (H3O)+(SbF6)-
EXPEDT data setup option (<?>,D,F,K,L,P,R,S,X) >
```

The equivalent anisotropic thermal parameters for each of the atoms is listed and then the last menu in **EXPEDT** is shown. To exit from this one you must enter **'X'** on a new line, do this now.

```
EXPEDT terminated successfully
  The experiment is OXONIUM  creation date = 20-JUN-1994 11:02:07.65
MIST::GSAS Command? >
```

To finish the refinement and calculate some structural results enter **'GENLES DISAGL BIJCALC'** (for VMS systems) and respond to the three pairs of batch questions. The results of these calculations can be found in your list file. You can next work on refining the structure in the correct space group ($I2_13$) as indicated by the relatively few observed *hk0* reflections with *h* and *k* odd seen in the **ISTATS** run.

Structure Drawing

The last part of this exercise consists of an introduction to the structure drawing program **ORTEP**. **ORTEP** was originally written many years ago by C. Johnson of Oak Ridge National Laboratory and it has become one of the most widely used programs for drawing crystal structures. We have modified it for use in **GSAS** to make an interactive version using the **GSAS** menu handling facilities. Most of the original features of **ORTEP** have been retained in this version. We have assumed that you have refined the structure of $(H_3O)^+ (SbF_6)^-$ in the space group Ib3 with anisotropic thermal parameters. To begin enter **'ORTEP'** at the **GSAS** prompt.

```
            |----------------------------------------------------|
            |              Program ORTEP Version 6.17             |
            | Crystal structure plotting program by C.K. Johnson |
            |      Distributed on TEST Vers. 20-JUN-1994          |
            |----------------------------------------------------|
       |--------------------------------------------------------------|
       |           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, 1994, The Regents of the University of California. |
       |--------------------------------------------------------------|

Enter terminal type (<?>,A,B,C,D,E,F,G,H,Z) >
```

As usual for this question enter your terminal type and an **'N'** to avoid creation of a hard copy file. **ORTEP** will next read information from your experiment file and produce a summary of what it found. If you are working in one of the four face-centered cubic space groups that have 192 symmetry operators (Fm3m, etc.), **ORTEP** will reduce the symmetry and add extra atoms as necessary to give 96 operators.

```
Title: Single Crystal Exercise
Phase name: (H3O)+(SbF6)-
Lattice parameters:
a,b,c            =    10.1200   10.1200   10.1200
alpha,beta,gamma =     90.000    90.000    90.000

Space group   I b 3
The lattice is centric  I-centered cubic         Laue symmetry m 3
 Multiplicity of a general site is  48
 The symmetry of the point 0,0,0 contains 1bar

The equivalent positions are:

 ( 1)      X      Y      Z   ( 2)      Z      X      Y   ( 3)      Y      Z      X
 ( 4)      X  1/2+Y  1/2-Z   ( 5) 1/2-Z      X  1/2+Y   ( 6) 1/2+Y  1/2-Z      X
 ( 7) 1/2-Z  1/2+X     -Y   ( 8)     -Y  1/2-Z  1/2+X   ( 9) 1/2+Y     -Z  1/2-X
 (10) 1/2-X  1/2+Y     -Z   (11)     -Z  1/2-X  1/2+Y   (12) 1/2+X     -Y  1/2-Z

Do you want atom list (Y/<N>)? >
```

If you respond **'Y'** here the atoms will be listed, to skip that enter **'N'**. After the atoms are read in the list is examined for duplicate coordinates and the extra atoms are removed from the list. Two additional atoms are added, one is at the unit cell origin and the other is at the unit cell center.

```
New crystal to cartesian transformation matrix:
   0.09881   0.00000   0.00000
   0.00000   0.09881   0.00000
   0.00000   0.00000   0.09881
No atoms in drawing array
Atom names:
  1 SB(1)      2 O(2)      3 F(3)      4 ORIGIN     5 CENTER
Enter model building command (<?>,A,B,D,E,L,S,T,U,X) >
```

The first step is to select a set of atoms to be drawn by **ORTEP**. Most of the facilities in the original version are available as menu selections. You presently have no atoms selected for drawing. Enter **'CR'** to see the help listing.

```
Model building commands:
 <?> - Type this help listing
 A   - Atom designator codes (ADC)
 B   - Box of enclosure
 D   - Subsequent commands will DELETE atoms
 E   - Erase all atoms
 L   - List current contents of atom array
 S   - Sphere of enclosure
 T   - Triclinic cell of enclosure
 U   - Insert unit cell corners
 X   - Exit model building
ADC is the code "acccss" where a is the atom sequence number, ccc is unit cell
designators (1-9) and ss is the symmetry operator number. If a positive ADC is
followed by a negative ADC then all atoms between them are included. Ex. 155501
for 1st atom in center cell & 1st operator; 155501 -2455504 for all atoms in
center cell between atoms 1 and 24 for operators 1 to 4.
Enter <CR> to continue
```

These commands allow you to select single atoms, sets of atoms, all atoms within certain volumes and can even cause chains of atoms to be selected. The atoms are designated by **ORTEP** by a "atom designator code" (ADC) which has three parts. The first part is the atom serial number as listed by **ORTEP**. See the atom name list above for these values. The second part is a three integer code that indicates which unit cell the atom is in. **ORTEP** will permit unit cell designation within a 9x9x9 block of unit cells. The designation "555" refers to the central unit cell within this block. The last part of the ADC is a two integer designator for the symmetry operator. Thus an ADC looks like "acccss" as noted in the help listing. For example, the code "355602" refers to atom number 3, located in unit cell 556 generated from the original position by symmetry operator number 2. Enter **'CR'** to continue.

```
Atom names:
  1 SB(1)      2 O(2)      3 F(3)      4 ORIGIN     5 CENTER
Enter model building command (<?>,A,B,D,E,L,S,T,U,X) >
```

We want you to draw the SbF_6^- ion; to begin you need to select the Sb atom. Enter **'A'** for individual atom selection.

```
Enter  atom designator code (0 to quit,-1 for help) >
```

You want to include the Sb atom in the center cell and first symmetry operator, enter **'155501'**

```
Enter  atom designator code (0 to quit,-1 for help) >
```

That is the only atom you want to select that way, enter **'0'** to terminate individual atom selection.

```
Atom names:
  1 SB(1)      2 O(2)       3 F(3)       4 ORIGIN     5 CENTER
Enter model building command (<?>,A,B,C,D,E,L,R,S,T,U,X) >
```

The easiest way to select the six F atoms is to include those that are inside a sphere about the Sb atom, enter **'S'** to use this option.

```
Enter first origin atom designator code (0 to quit,-1 for help) >
```

The sphere of inclusion can be constructed about a range of atoms. In this case you only want a sphere around just the Sb atom, enter the ADC **'155501'** for it.

```
Enter last  origin atom designator code (0 to quit,-1 for help) >
```

In this case, the list of origin atoms in this case is terminated by the same atom, enter **'155501'**.

```
Enter first target atom number >
```

You want F atoms to be selected when they fall inside the sphere. Since F is the third atom in the list enter **'3'**.

```
Enter last target atom number >
```

Again a range of atoms can be selected if they fall inside the sphere of inclusion. In this case you only want F atoms so enter **'3'** again.

```
Enter max. interatomic bonding distance >
```

You only want those F atoms that are bonded to the Sb atom. The Sb-F bond length is somewhat less than 2Å, so enter **'2.0'**. **ORTEP** will find all atom number 3's that fall within 2Å of the already included Sb atom.

```
Atom names:
  1 SB(1)      2 O(2)       3 F(3)       4 ORIGIN     5 CENTER
Enter model building command (<?>,A,B,C,D,E,L,R,S,T,U,X) >
```

To list the atom ADC's that **ORTEP** found enter **'L'**.

```
Contents of drawing array:
   155501   355501   355502   355503   355513   355514   355515
Drawing array contains  7 atoms
Atom names:
  1 SB(1)      2 O(2)       3 F(3)       4 ORIGIN     5 CENTER
Enter model building command (<?>,A,B,C,D,E,L,R,S,T,U,X) >
```

As you had hoped there is seven atoms in the list, one Sb and six F atoms. Notice that although all seven atoms are in the same unit cell (555), the symmetry operators for the atoms selected might have been difficult to determine manually. You are finished here so enter **'X'**. As you exit from this menu **ORTEP** writes this atom selection list on the experiment file so that when you reenter **ORTEP** later they are read automatically.

```
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

You are now in the main **ORTEP** menu. This menu was skipped earlier when **ORTEP** found that no atoms had been selected for drawing. Enter **'CR'** to see the help listing.

```
ORTEP commands:
 <?>   - Type this help listing
 B     - Edit bond selection controls
 C     - Select origin at centroid & give best view
 E e   - Choose ellipsoid style e
 L     - List structure data
 M     - Build or modify structure model
 N n   - Select a new phase n
 P     - Plot model
 R a r - Enter axis (x,y,or z) and angle for rotation of current drawing
 S a r - Enter axis (x or y) and angle for stereo rotation of current drawing
 T     - Select title & label options
 U u   - Enter viewpoint
 V u v - Enter reference vectors "u" & "v"; resets transformation matrix
 Q     - Quit ORTEP
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

The commands listed here allow you to position the object for drawing by selection of reference vectors or rotation from the previous orientation. There are also commands that determine the ellipsoid style for the atoms and permit labeling of the atoms. You need, however, to complete the model by instructing **ORTEP** how you want the interatomic bonds to be drawn. Enter **'B'** for bond selection.

```
There are no bond selection controls
Atom names:
  1 SB(1)      2 O(2)       3 F(3)       4 ORIGIN     5 CENTER
Enter bond selection command (<?>,I,L,X) >
```

ORTEP informs you that no bond information is present , lists the atom names and gives a short menu. Enter **'CR'** to see the help listing.

```
Bond selection editing commands:
 <?> - Type this help listing
 I   - Insert bond selection control
 L   - List current bond selection controls
 X   - Exit bond selection
Enter bond selection command (<?>,I,L,X) >
```

You want to make a bond selection so enter **'I'** to start.

```
Enter first origin atom number >
```

ORTEP draws bonds from one set of atoms to another set of atoms when the interatomic distance falls within a range of distances. You first have to select the origin set of atoms for the bond drawing. Enter **'1'** so that the bonds are drawn from the Sb atom.

```
Enter last origin atom number >
```

You need to terminate the list of origin atoms, enter **'1'**.

```
Enter first target atom number >
```

Next you have to select the range of target atoms for the bond drawing. Enter **'3'** so that the bonds are drawn to the F atoms.

```
Enter last target atom number >
```

Again the target atom list must be terminated, enter **'3'**.

```
Enter bond type (<1>,2,3,4,5) >
```

ORTEP now wants an indication of how the bond is to be drawn. The bond is drawn with "bond type"*2 number of lines. Enter **'3'** so that six lines are used for each bond.

```
Enter min. (>0.0) and max. bond length & radius >
```

ORTEP now wants the range of distances to use for selecting the bonds to be drawn. It also wants the radius of the stick that is drawn to form the bond. All of these are in Angstroms. Enter **'1 2 0.02'** to draw bonds 0.04Å thick between 1.0 and 2.0 Å long. When you are used to the input of the bond selection controls all eight of these values can be entered on a single line (i.e. **'1 1 3 3 3 1 2 0.02'**).

```
Enter bond selection command (<?>,D,I,L,X) >
```

To see the bond drawing control you have entered, type **'L'**.

```
Bond selection controls:
No.  Ori. ANR  Tar. ANR  Type    D-min   D-max   Radius
   1    1    1    3    3    3  1.0000  2.0000  0.0200
Atom names:
  1 SB(1)      2 O(2)       3 F(3)       4 ORIGIN     5 CENTER
Enter bond selection command (<?>,D,I,L,X) >
```

This is the only bond control needed so enter **'X'** to leave this menu. **ORTEP** writes this information on the experiment file.

```
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

The next step is to set the viewing direction for the SbF_6^- ion. The "best" view is one that looks through the thinnest "diameter" of the molecule. To get the best view enter the **'C'** command.

```
Do you want the best view of the model (<Y>/N)? >
```

Respond with a **'CR'**, a best view through the ion is selected for drawing. After this command is done then any of the other positioning commands (**'R'** or **'V'**) may be used to further refine the viewing direction.

```
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

Next you want to select the ellipsoid style, enter **'E'**.

```
Enter ellipsoid style (<?>,A,B,C,D) and scale >
```

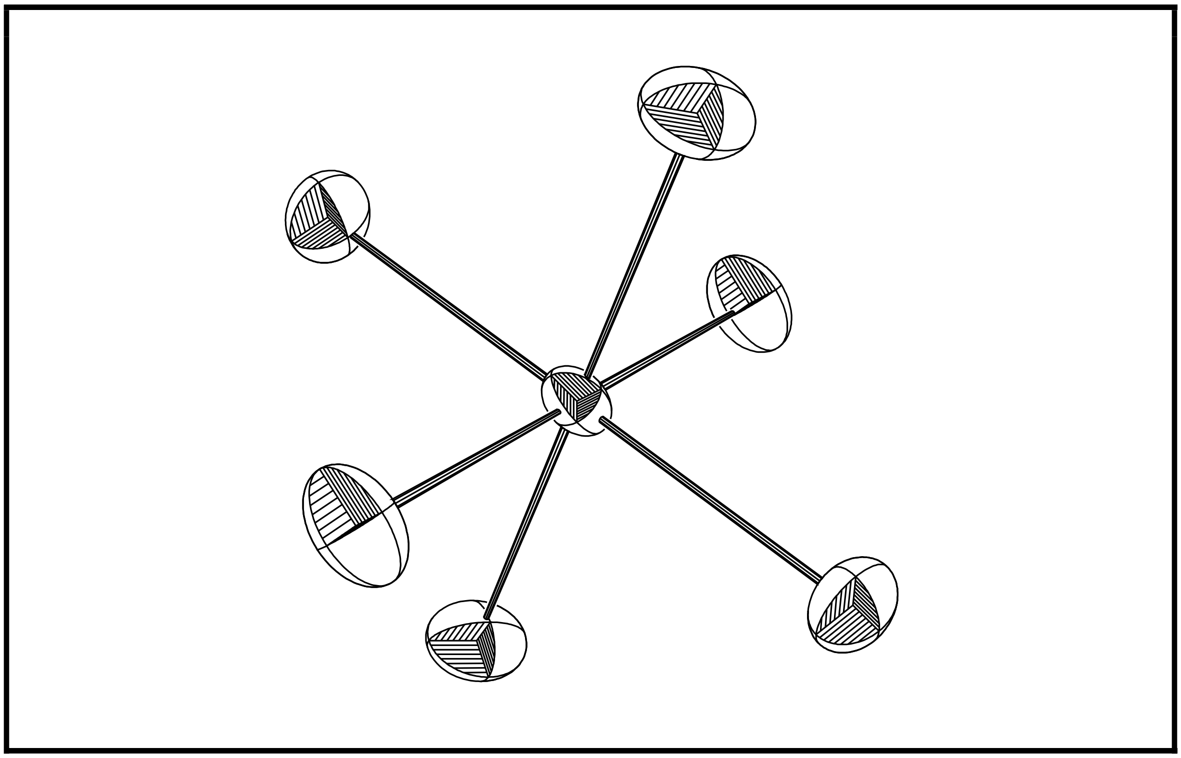
You may enter **'CR'** to see the help listing here, the **'A'** option displays the ellipsoids in the cross-hatched octant style so commonly seen in crystallographic publications.

```
Enter ellipsoid probability (default = 0.50) >
```

ORTEP now asks for the probability value that defines the ellipsoid surface to be plotted for each atom. To take the default enter **'/'.**

```
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

The drawing is now ready to be plotted, enter **'P'** and the plot will immediately follow.



As usual enter **'CR'** to get the next prompt.

```
Enter ORTEP command (<?>,B,C,E,L,M,N,P,R,S,T,U,V,Q) >
```

You may wish to further explore the features of **ORTEP**. We recommend that you try different orientations, viewing positions and distances. Try the labeling options

(**'T'** command) especially the cursor controlled atom labeling feature. To exit from **ORTEP** enter **'Q'**.

```
ORTEP has finished
  The experiment is OXONIUM  creation date =  4-MAY-1994 16:28:08.62
MIST::GSAS Command? >
```

This completes the third exercise. Many of the **GSAS** programs used in this exercise wrote information to a list file. You should examine it with the **GSAS** utilities **ELST**, **TLST** and **SLST**.