

## **Appendix 1:**

### **Rietveld Refinement of Radial x-ray Diffraction Images.**

Processing radial diffraction data is done using the Rietveld method as implemented in the software package Materials Analysis Using Diffraction (MAUD) (Lutterotti et al. 1999). MAUD is written by Lucca Lutterotti and can be downloaded free from <http://www.ing.unitn.it/~maud/>. The program is regularly updated. It is written in java and versions are available for Windows, Mac OS X, Mac OS X 64bit, Linux, Unix, and Linux AMD 64. Below a general procedure is outlined to process and analyze radial diffraction data from compression experiments in the DAC. Of course this procedure can be used to analyze data from compression experiments in other devices such as the D-DIA or the Drickamer apparatus but additional considerations may be required.

#### **Processing Raw Diffraction Data:**

First raw diffraction data must be processed and converted to an .esg file which is the input format for data files in MAUD. Typically raw diffraction data will be in one of two formats. If data was collected using a MAR3450 image plate then the data will be a .mar3450 file. If an x-ray Charge-Coupled Device (CCD) was used then data will be in a .tiff format. Note that CCDs generally have spatial distortion and a correction (.spline) must be applied prior to processing data for MAUD. For diffraction experiments a calibration image measured in the same geometry as the experiment is needed. There are several diffraction standards in use. A few of these are CeO<sub>2</sub>, LaB<sub>6</sub> and Si. The

calibration image is used to determine sample to detector distance, beam center, and detector tilt. You will also need to know the x-ray wavelength and if a CCD was used, the size of the detector pixels.

### **Preparing an .esg file:**

There are two ways to prepare an .esg file for MAUD. One method is to convert data in the program Fit2D (Hammersley 1998) using fit2d2maud.jar, and the other is to process data directly in MAUD. Only the method using fit2d2maud will be described here as a tutorial to processes raw diffraction data in MAUD can be found at <http://eps.berkeley.edu/~wenk/TexturePage/MAUD.htm#Introduction%20MAUD>.

### **Processing data with Fit2D and fit2d2maud:**

To process data using Fit2D the Java utility fit2d2maud.jar is used. Fit2d2maud is written by Sébastien Merkel and can be downloaded free from <http://merkel.zoneo.net/Fit2d2maud/index.php?lang=en>. Essentially what this program does is to write a macro to integrate diffraction images over small arcs (typically 5-10°) and creates a series of .chi files in Fit2D. Fit2d2maud can then be used to convert these files to an .esg file for use with MAUD.

To use this utility the data file of interest must first be opened in Fit2D. At the “Dimensions of Program Arrays” window, make sure that the “First Dimension of Arrays” and the “Second Dimension of Arrays” are large enough for your data. For example if diffraction images were collected using a MAR3450 image plate, set both of these to 3450. Now open the “Powder Diffraction (2-D)” utility. Click input and open the file of

interest. At the start of an analysis you will need to first process your calibration image so that this can be used to calibrate instrument parameters in MAUD. If there are bright spots from the diamonds these can be filtered at this point using the “Mask” function (this will not need to be done for the calibration image). To do this pick the “Threshold Mask” option. When it asks “Less than comparison?” choose “No”. Next enter a value that is less than the intensity of the spots that you wish to remove but greater than the intensity of the peaks of interests. Once any filtering you wish to do is complete select the “Cake” function. You will now be prompted to choose a series of parameters.

- 1) Beam center - If you have already determined the beam center from the calibration image choose “no change”. Otherwise pick the best option.
- 2) Start azimuth – generally this is zero if you have complete diffraction rings.
- 3) End azimuth – generally 360° if full rings are used.
- 4) Inner limit – this corresponds to the lowest  $2\theta$  value that you wish to include in your analysis. Select the inner limit by clicking on the diffraction image.  
Note that if you want to use the entire image click “beam center”
- 5) Outer limit – this corresponds the highest  $2\theta$  value that you wish to include in your analysis. Again select the outer limit by clicking on the diffraction image.

Next select “integrate”. A window will open that says “Experimental Geometry Control Form”. These values should match those obtained from your calibration. If these match the calibration information click “OK”. The next window to open is titled “Type of Azimuth/Radial or 2-Theta Transformation”. Check that the start azimuth and end azimuth are correct and that the scan type is “2-Theta”. Click “OK”. Once Fit2D

has finished calculating you will be shown an “unrolled” image. If this is your calibration image make sure that the diffraction lines are straight. If they are not then the beam center and detector tilt were not calibrated properly. If they are not straight then you can either redo the calibration in Fit2D or refine the beam center and tilt in MAUD when the calibration image is refined. Now that you have made the “Cake” and everything looks fine click “Exchange” to return to the raw diffraction image. If you will be processing many diffraction images the “Cake” process only needs to be done the first time in order to set the calibration parameters and the inner and outer radius for fit2d2maud.

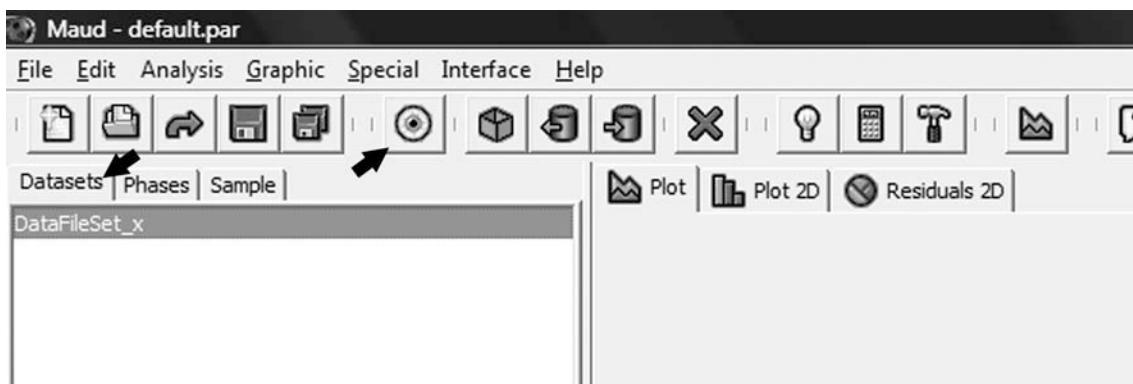
Now that the “Cake” process is finished, open fit2d2maud. Enter in the sample to detector distance in mm and wavelength in Å in the appropriate boxes. You should have these from your Fit2D calibration. Designate the directory that contains the raw diffraction images in the line titled “Directory with diffraction images”. “Directory with chi files” is where fit2d2maud will save the .chi files it creates before converting them to an .esg. This folder must be on on the highest level of your C:\ drive or fit2d2maud will not work. For example C:\Chi will work but C:\Documents and Settings\Chi will not work. Once the .chi files have been converted to an .esg file then the chi files can be deleted if you wish. Choose a directory to save .esg files. It is convenient if this is a different directory than the one containing the raw diffraction images. Once these are all designated, click “Create macro for Fit2D”. Enter in a name for the file that you wish to create. It is best to choose the same name as the raw diffraction image. Designate the start azimuth, end azimuth, and interval. Generally an image will be integrated from 0 - 360° over 5° intervals to yield 72 spectra. If a pattern is quite spotty a larger interval of

10° or even 15° may be used. However if there are bright spots in the diffraction image that need to be removed it is often better to integrate over smaller arcs and remove some spectra from the refinement. If diffraction rings are incomplete choose the start and end azimuth such that only the region of interest is included. Once this information is entered click “OK”.

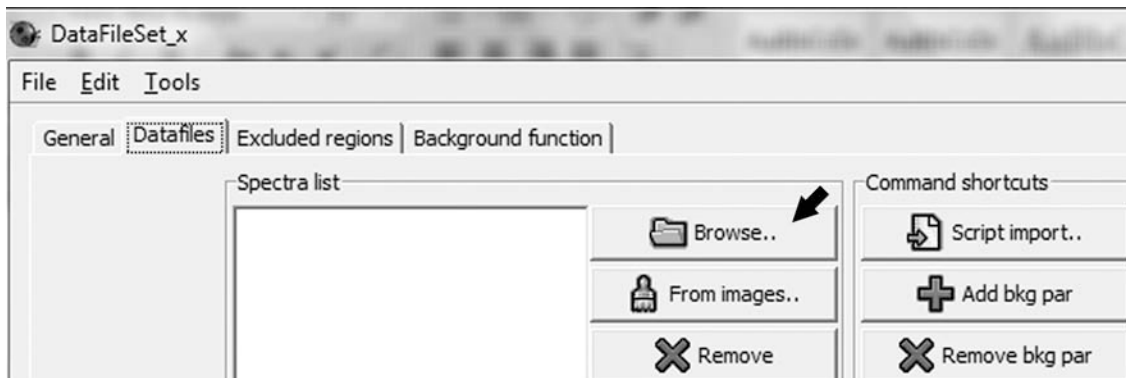
Now you will have to go back to the Fit2D window. Click exit until you return to the welcome window. Under “Fit2D Scientific Interfaces” select “Macro/Log file”, and then choose “Run Macro”. Find the directory with the diffraction data and look for the .mac file you just created in fit2d2maud. Select this file and hit enter to run the macro. This will take a few minutes while Fit2D integrates the image into a series of .chi files. Once the macro has finished running, return to the fit2d2maud window and click “Convert chi to esg”. Enter the same information that you used to create the macro and click “OK”. Fit2d2maud will create an .esg file in the directory that you designated for .esg files.

### Importing Datafiles Into MAUD:

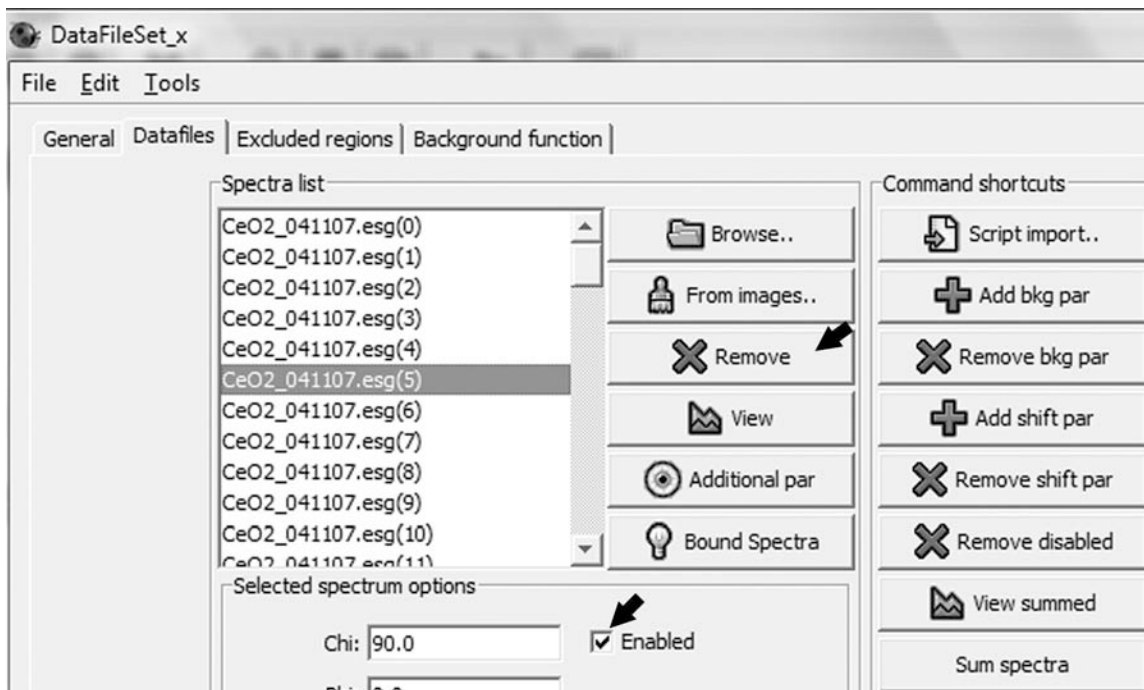
1. Go to the “Datasets” tab and select “DataFileSet\_x” and click the “eye” icon.



2. In the “DataFileSet\_x” window select “Browse” and select the appropriate .esg file. If you are just starting your refinements this will be your calibration file.



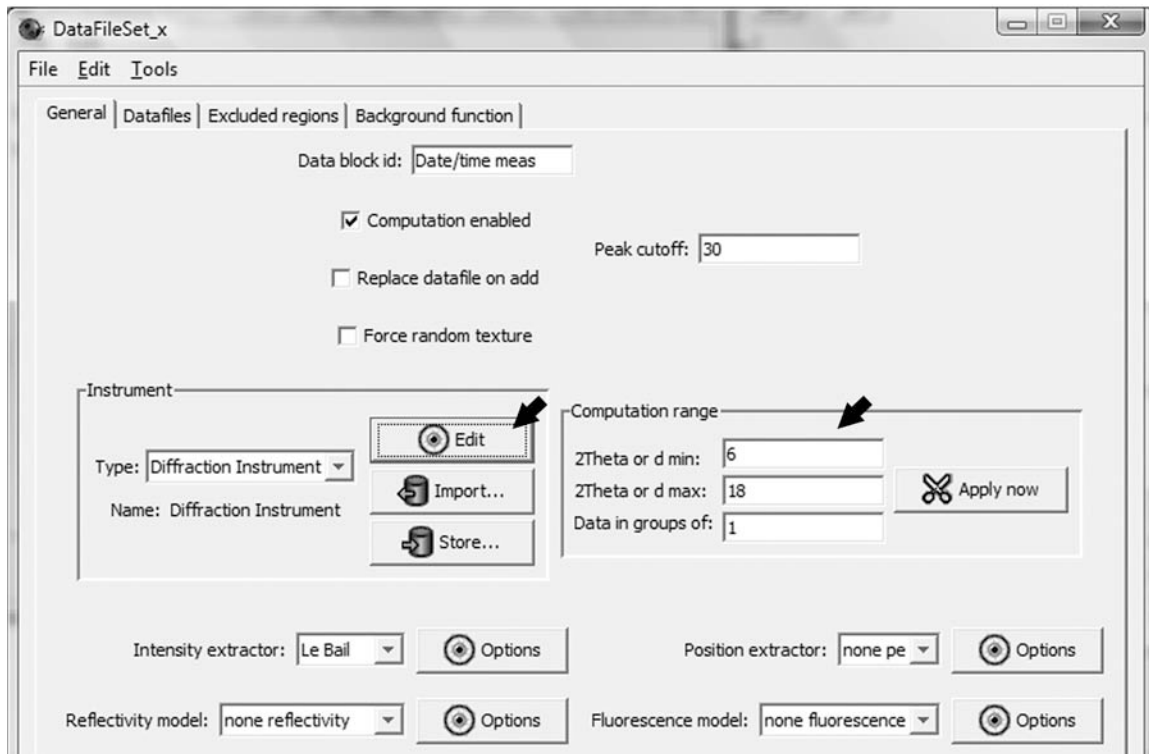
3. Remove or disable any spectra containing the beamstop and/or spots that you wish to remove. To do this highlight the appropriate spectra in the list and click “Remove” or deselect the “Enabled” check box.



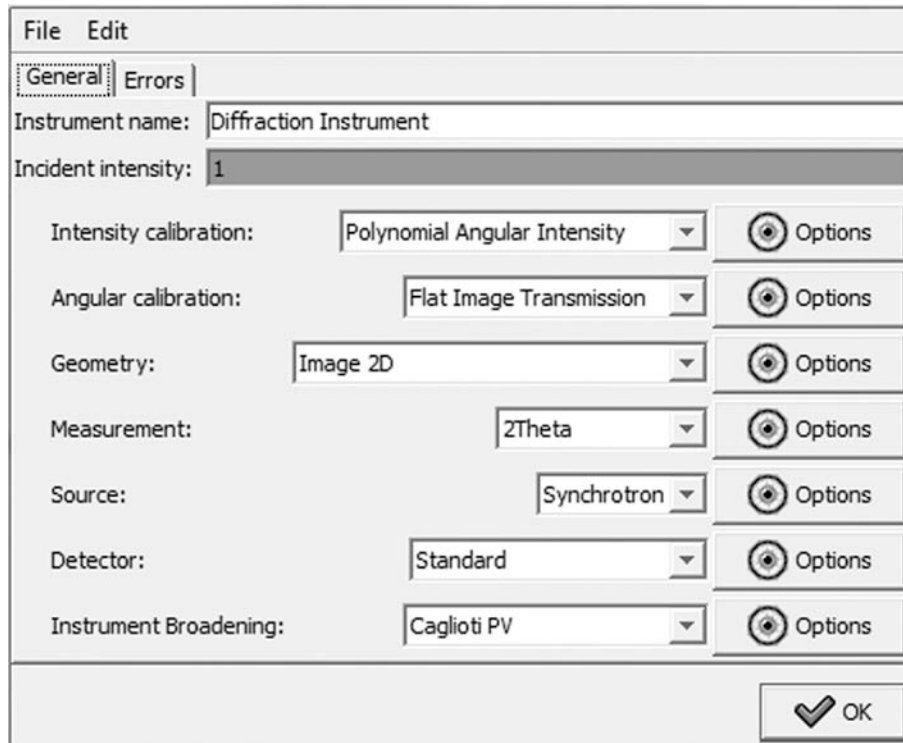
### Instrument Parameters:

1. In the “DataFileSet\_x” window select the “General” tab.

2. In the “Computation Range” box you can designate the  $2\theta$  or d-spacing range that you wish to use for the analysis.
3. In the “Instrument” box it should say “Diffraction Instrument” in the “Type” box. If not select this from the list and click “Edit”.



4. The window that opens will look like the screen shot below. There are several options that you can choose. In general for synchrotron radial diffraction data you will want to select the options as shown.



- a. Intensity calibration: You can often get away with doing no calibration. In this case select “none cal” from the list. There are no options for this setting. However if you notice that the intensities don’t fit well at higher  $2\theta$  when you are refining your calibration image, you will need to do a polynomial angular calibration. In this case select “Polynomial Angular Intensity” from the list and click the corresponding “Options” button. In the “Options” panel add or remove calibration coefficients until you have the number you would like. Generally three coefficients is best.
- b. Angular calibration: Choose “Flat Image Transmission”. Click the “Options” button and enter the sample to detector distance. For now leave everything else at zero except for “Ratio width/height ratio” which should

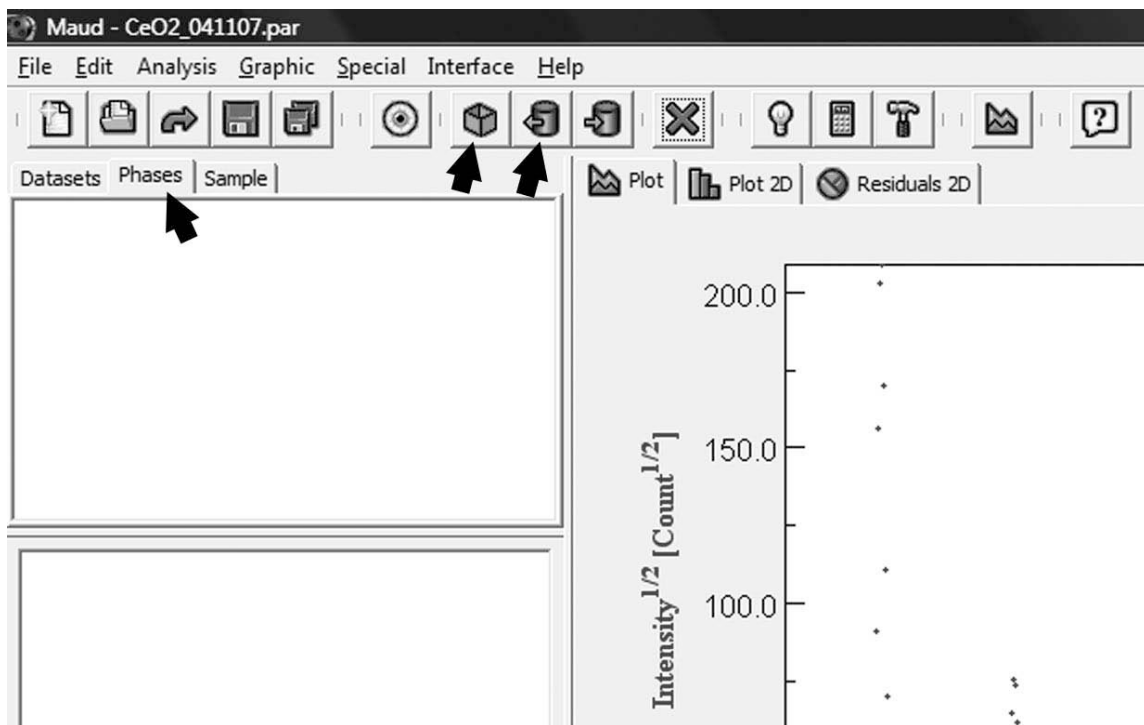


be 1.0 (unless you prepared your .esg file in MAUD and the detector had pixels that were not square).

- c. Geometry: Select image “Image 2D”. You do not need to change anything in the options.
  - d. Measurement: Select “2Theta”. There are no options to change for this setting.
  - e. Source: Select “Synchrotron” and in the “Options” panel input the x-ray wavelength.
  - f. Detector: Choose “Standard”. There are no options for the standard detector.
  - g. Instrument Broadening: Select “Caglioti PV” from the list. Click “Options”. Under the “Asymmetry” tab fix all coefficients to zero if they are not already. To do this highlight the asymmetry coefficients in the list on the right and in the “Value” box below type “0”. Do this for all the asymmetry coefficients. Under the “HWHM” tab add/remove Caglioti coefficients until you have the appropriate number. You shouldn’t need more than three. Under the “Gaussianity” tab you will want to add/remove coefficients. For Gaussian coefficients two should be enough.
5. When you have these set correctly click “Close” and then “OK” to exit the “Diffraction Instrument” panel and then click “OK” to exit the “DataFileSet\_x” window. Be sure to save frequently.

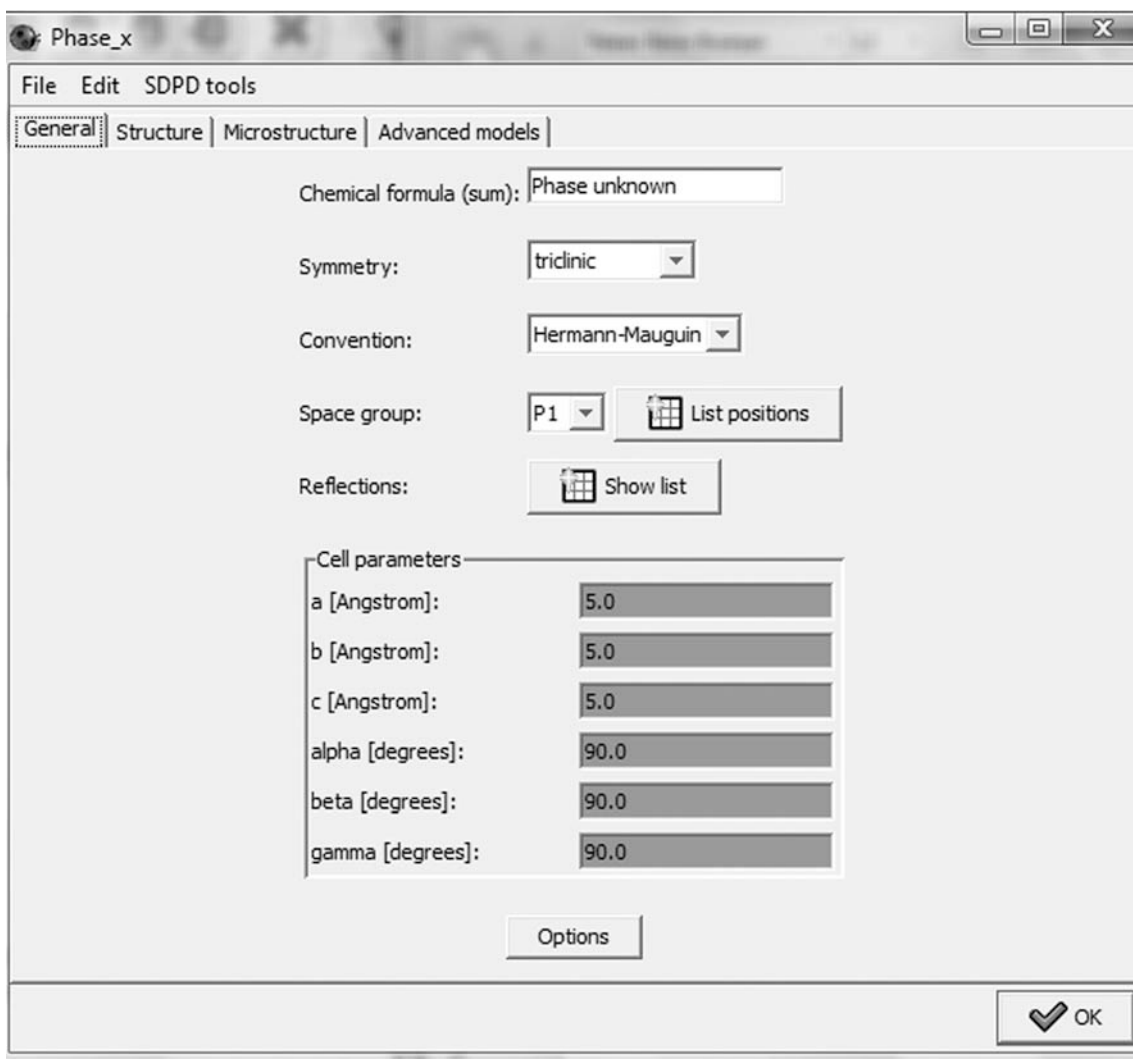
## Phase Information:

You will need to import the appropriate phase file for your calibrant or build one manually in MAUD. To do this click the “Phases” tab.

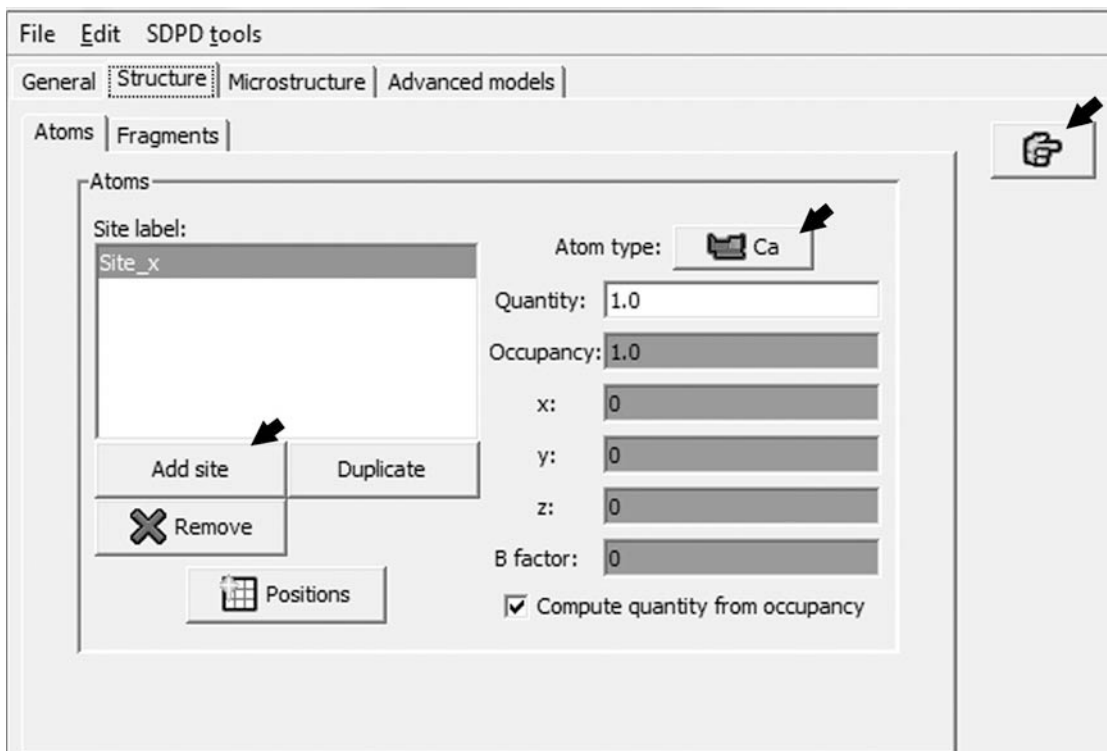


1. If you have a .cif for the calibrant you can import this information into MAUD
  - a. Click the icon with the picture of the cylinder and the arrow or go to the “Edit” menu and select “Load object from CIF...” or hit Ctrl+D.
  - b. Select the appropriate .cif and click “OK”.
2. If you do not have a .cif you will have to build a model manually.
  - a. Click the icon with the picture of the box or in the “Edit” menu select “Add new object” or hit “Ctrl+A”.
  - b. In the “Phases” list “Phase\_x” should appear. You can rename “Phase\_x” by double clicking on it.

- c. Select your phase and click the “eye” icon to open the phase options window.
- d. In the “General” tab enter the appropriate structural information such as symmetry, space group, and crystallographic parameters.



- e. Now select the “Structure” tab and add atomic sites to create you structure. Once you have added a site you can change the name by double clicking the entry in the site list.



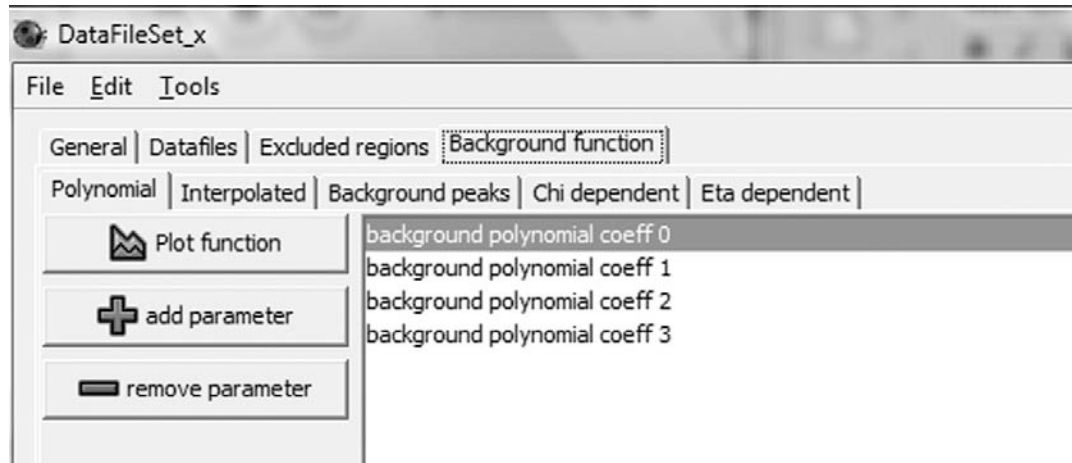
- f. For each site change the atom type by clicking the “Atom type” button and selecting the appropriate atom from the periodic table that will appear. Change the oxidation state in the menu on the bottom right.
- g. You can check how your structure looks by clicking the “pointer finger” icon in the upper right corner of the structure tab window.

### Backgrounds:

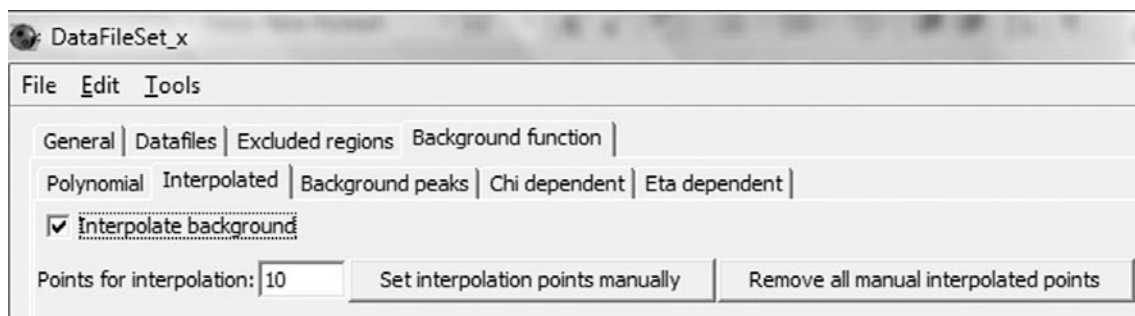
Once you have entered your phase information you need to set up your backgrounds. To do this go back to the “Datasets” tab, highlight “DataFileSet\_x” in the list and click the “eye” button. Now click the “Background function” tab. There are two options that you may wish to use.

1. Polynomial backgrounds: For this option select the “Polynomial” tab and add an appropriate number of background coefficients. For more complex backgrounds

you will need more coefficients. These background coefficients are globally applied to all spectra that are enabled for the refinement. For the calibration image you will probably need 3-4 coefficients.



2. Interpolated backgrounds: For complicated backgrounds a polynomial background may not be sufficient in which case you will need to interpolate backgrounds. This is often the case with radial diffraction data from the DAC particularly when boron-kapton gaskets are used. The scattering from the amorphous gasket material creates complex backgrounds that are very difficult to fit with background polynomials. To interpolate backgrounds first remove any polynomial coefficients that may be under the “Polynomial” tab. Next select the “Interpolated” tab, and check the “Interpolate background” box.

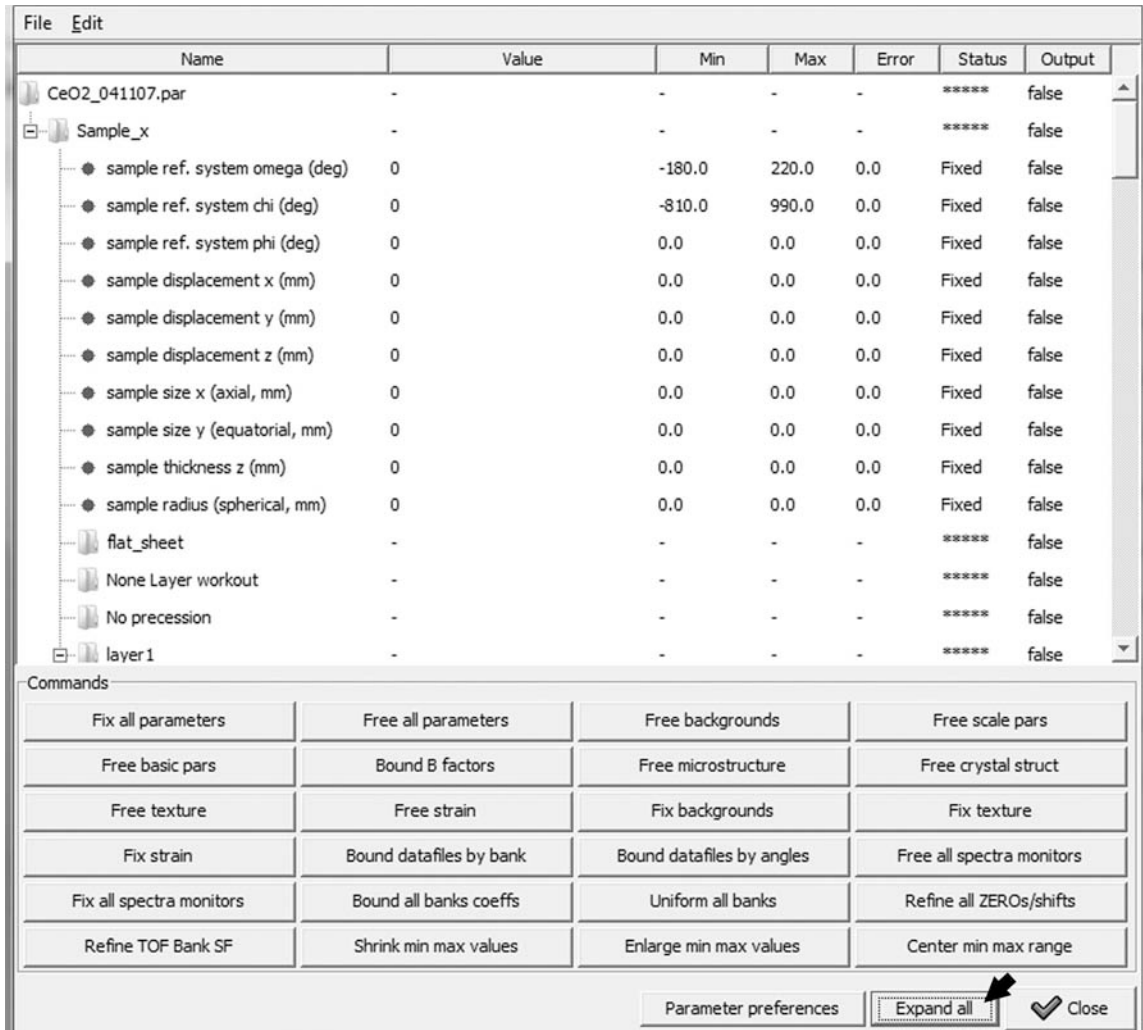


- a) In the “Points for interpolation” box designate the number of points to use. 10 to 15 should be sufficient.
- b) Click the “Set interpolation points manually” button. The new window that opens will show an averaged spectrum of the data. Note that you need to have calculated the spectra using the calculator button in the main window or this window will be blank.
- c) In the “Tools” menu select “Edit interpolated background points” and a set of dots will appear along the spectra.
- d) Right click to remove or add interpolation points. Make sure to only place points between diffraction peaks.

### **Refining the Calibration Image:**

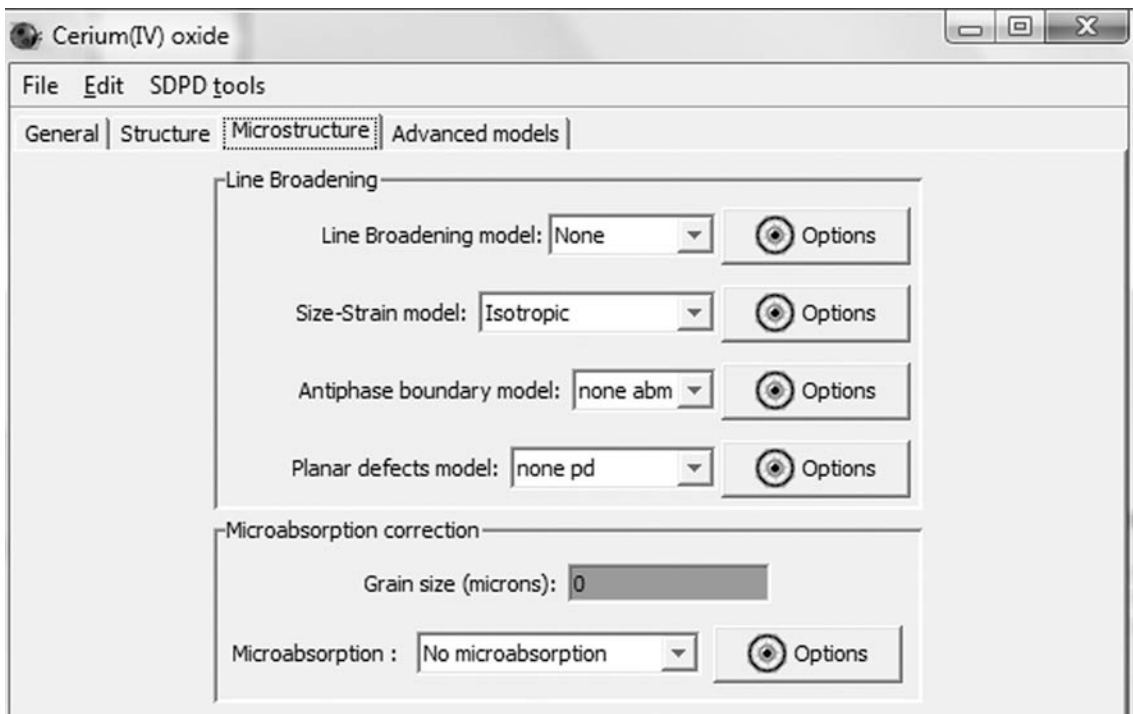
Now that you have loaded your calibration .esg file, phase information, and have set up the initial instrument settings and backgrounds you are ready to begin refining the calibration image. Before you begin refining parameters it is best to manually adjust parameters so that they are close to fitting the data. Otherwise the refinement may not be able to converge. There are several ways to fix or free parameters for refinement. This can be done in the list at the bottom of the main MAUD window. Scroll up or down to find the appropriate parameter and in the “Status” column change the status to either fixed or refined. Alternately go to the “Analysis” pull down menu and select “Parameters List” or hit Ctrl+L. In this window there are several “Command” buttons that allow you to fix or refine multiple parameters such as freeing or fixing all backgrounds. If you click

the “Expand all” button you can view all parameters. Be sure to save frequently between refinements in case the parameters that are being refined diverge wildly.



1. First refine polynomial backgrounds (if you did not interpolate) and intensity by setting them to refine and clicking the “hammer” icon in the main MAUD window. Allow these to keep refining with other parameters as new parameters they are freed in subsequent refinements.
2. If the peak positions are now offset you will need to refine the sample to detector distance.

3. Look at the “Plot 2D” tab and see if the diffraction lines are straight. If not the beam center and/or detector tilt are incorrectly defined. If needed, refine these.
4. When peak positions are fitting correctly you can refine the crystallite size and r.m.s. microstrain. To set up the line broadening model go to the phase window and select the “Microstructure” tab. For the “Line Broadening model” choose “None” (note: only choose the “none” option when you are refining the calibration image). For the “Size-Strain model” choose “Isotropic”. Click the “Size-Strain model” “Options” button. Right click the values for “crystallite size” and “r.m.s. microstrain” and change them from fixed to refined.

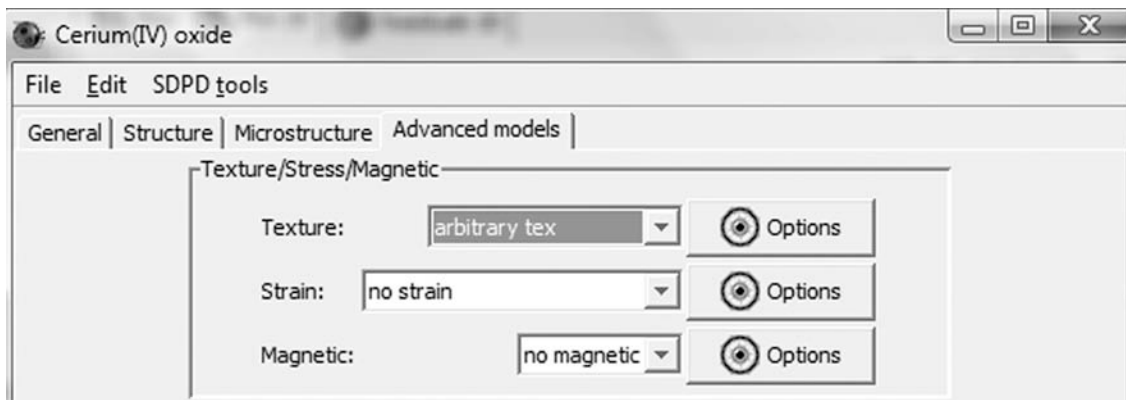


5. After refining crystallite size and r.m.s. microstrain you can refine the Caglioti and Gaussian coefficients. When refining the Caglioti and Gaussian coefficients do not also try to refine crystallite size and r.m.s. microstrain at the same time. First fix the crystallite size and r.m.s. microstrain. Start by freeing coefficient\_0

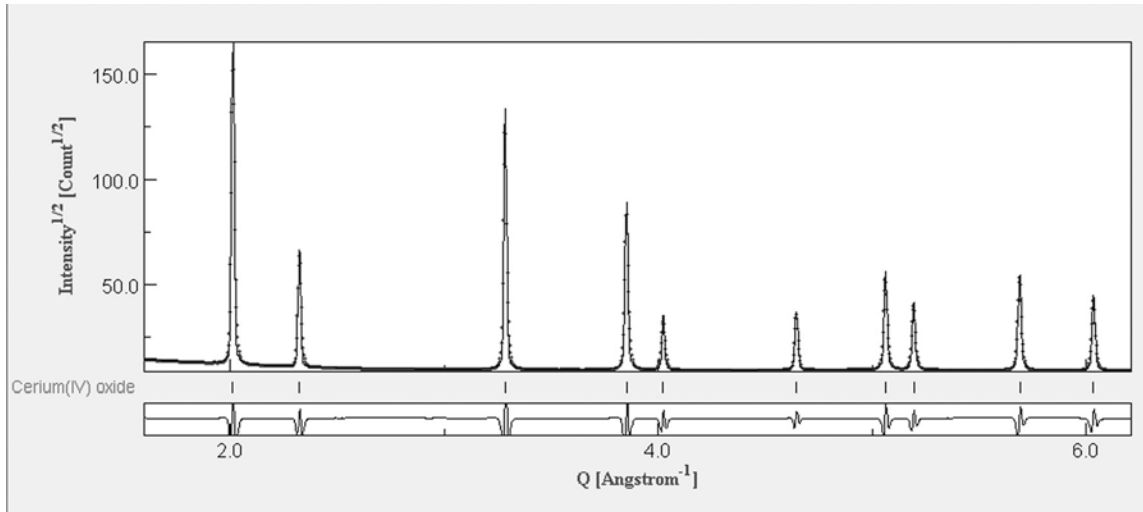


first then free 1 and then 2 etc. At the beginning refine either the Caglioti or the Gaussian coefficients then you can try to refine them all together. Once peak shapes are satisfactory, fix all Caglioti and Gaussian coefficients and free the crystallite size and r.m.s. microstrain.

6. Most likely the calibration image will be very spotty and peak shapes and relative intensities will not fit perfectly. In this case you will need to refine texture in order to fit these. Go to the “Phase” tab select the phase and click the “eye” icon. In the new window that opens select the “Advanced models” tab and in the “Texture” menu choose “arbitrary texture”. In the main window click the refine icon.



7. By now your peak positions and peak shapes should fit nicely. If the relative intensities of the peaks are not well fit yet you will need to refine the polynomial angular intensity calibration coefficients.
8. Once your calibration image has a satisfactory fit, save your refinement (it saves as a .par file) and fix all the parameters.

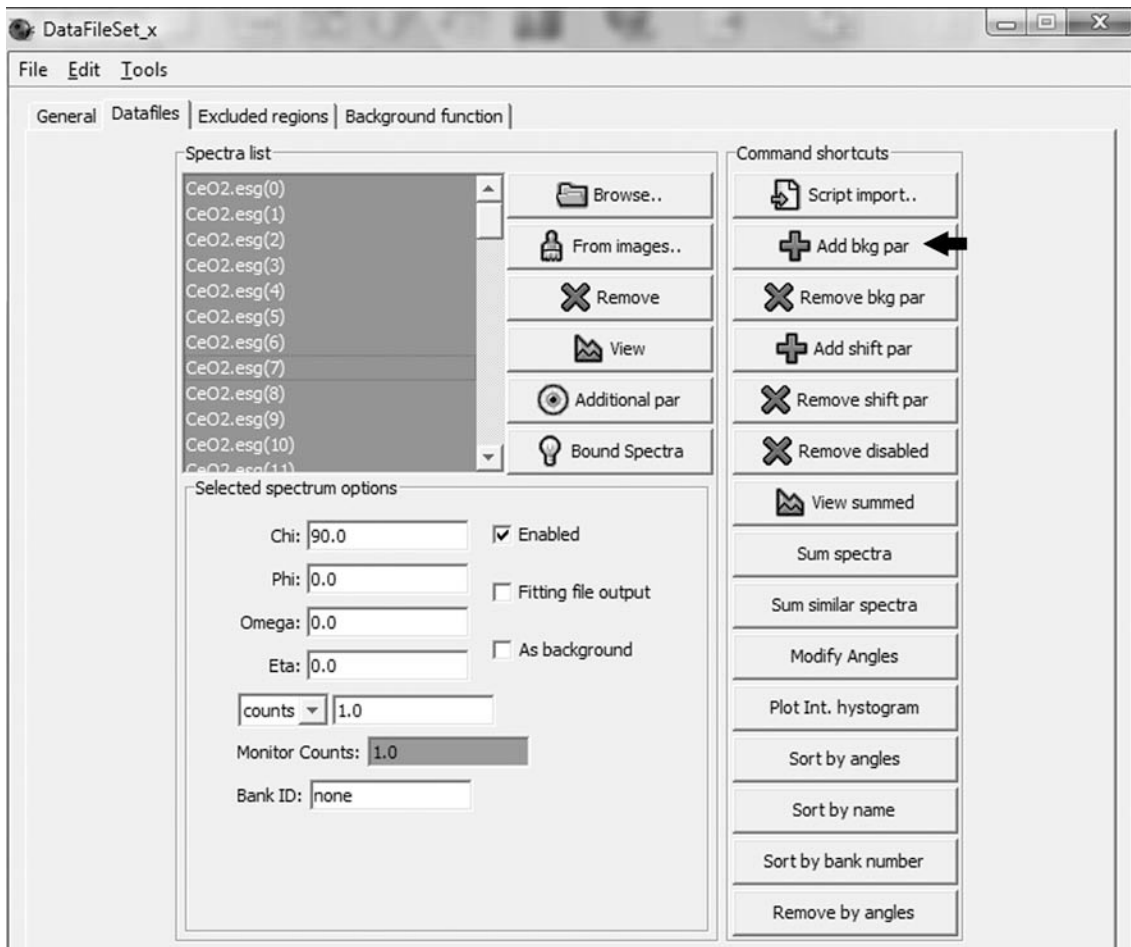


### Setting up the Data Refinement:

Now that the calibration image has been properly refined, data processing can begin.

1. Start with the calibration .par file you just finished. After fixing all the parameters, click “save analysis as...” in the “File” pull down menu. Save this with the name of the first data image you will refine.
2. Open the “DataFileSet\_x” window and select the “Datafiles” tab. Select all the spectra in the “Spectra list” and click remove.
3. Now click the “Browse” button and load the .esg file you wish to analyze. Save.
4. Next load the appropriate phase using a .cif or by building a model manually. If multiple phases are present start with the phase that is the highest volume percentage and adjust parameters for this phase before adding minor phases to the refinement.
5. Setup backgrounds using either polynomial backgrounds or interpolated backgrounds. For many radial diffraction experiments you will just want to use

interpolated backgrounds. This is easier to do and most of the time gives you a better fit than using polynomial backgrounds. If you use polynomial backgrounds you will probably need to add individual backgrounds to each spectra to account for azimuthal and  $2\theta$  variations in absorption. To add individual backgrounds go to the “DataFileSet\_x” window and select the “Datafiles” tab. In the “Spectra list” select all spectra and click the “Add bkg par” button to add an individual background coefficient to each highlighted spectrum. Generally you will want to add 3 or 4 coefficients to each spectrum. To do this click the “Add bkg par” 3 or 4 time respectively.



### **Manually Adjust Basic Parameters:**

Once the .esg file and phase information is loaded and backgrounds are setup, you will need to manually adjust several parameters to get a close fit to the data before you allow MAUD to run refinements. At this point leave these parameters fixed even though you are adjusting them, i.e. do not set them to refine yet.

1. Intensity: Adjust the intensity until it is close to the data. In the parameter list at the bottom of the main window this is in the “Diffraction Instrument” folder.
2. Backgrounds: If you are using polynomial backgrounds adjust the first global background coefficient until the background intensity is close. If you are using interpolated backgrounds you do not need to do anything.
3. Phase proportions: Adjust the phase proportions until the relative intensities of the phases to be refined are close to the data. These parameters are called “phase scale factor / volume fraction #” and are in the “layer 1” folder in the parameter list.
4. Unit cell parameters: Since these experiments are at high pressure it is likely that peak positions will be significantly offset due to the effects of pressure. Adjust the unit cell parameters to bring the peak positions close to those in the data. You should not need to adjust unit cell angles in most cases.
5. Crystallite size: In the phase window select the “Microstructure” tab (as discussed above). For the “Line Broadening model” select “Popa LB”, and for the “Size-Strain Model” select “Isotropic”. Adjust the crystallite size until the peak width is similar to the data. At this point do not worry about the r.m.s. microstrain. If you have anisotropic crystallite shapes you can use the “Popa

rules” for the “Size-Strain Model”. In the “Options” window you can change the number of coefficients by sliding the “Lmax” slider bar to the left or right. 3 – 4 coefficients is generally enough. For “Popa rules” the size coeff (angstrom) 0 and microstrain coeff 0 are the average crystallite size and microstrain respectively. All other coefficients are deviations from this average. Start by adjusting the crystallite size coeff (angstrom) 0 and microstrain coeff 0 and leaving all others set to 0 for now.

### **Stress Models:**

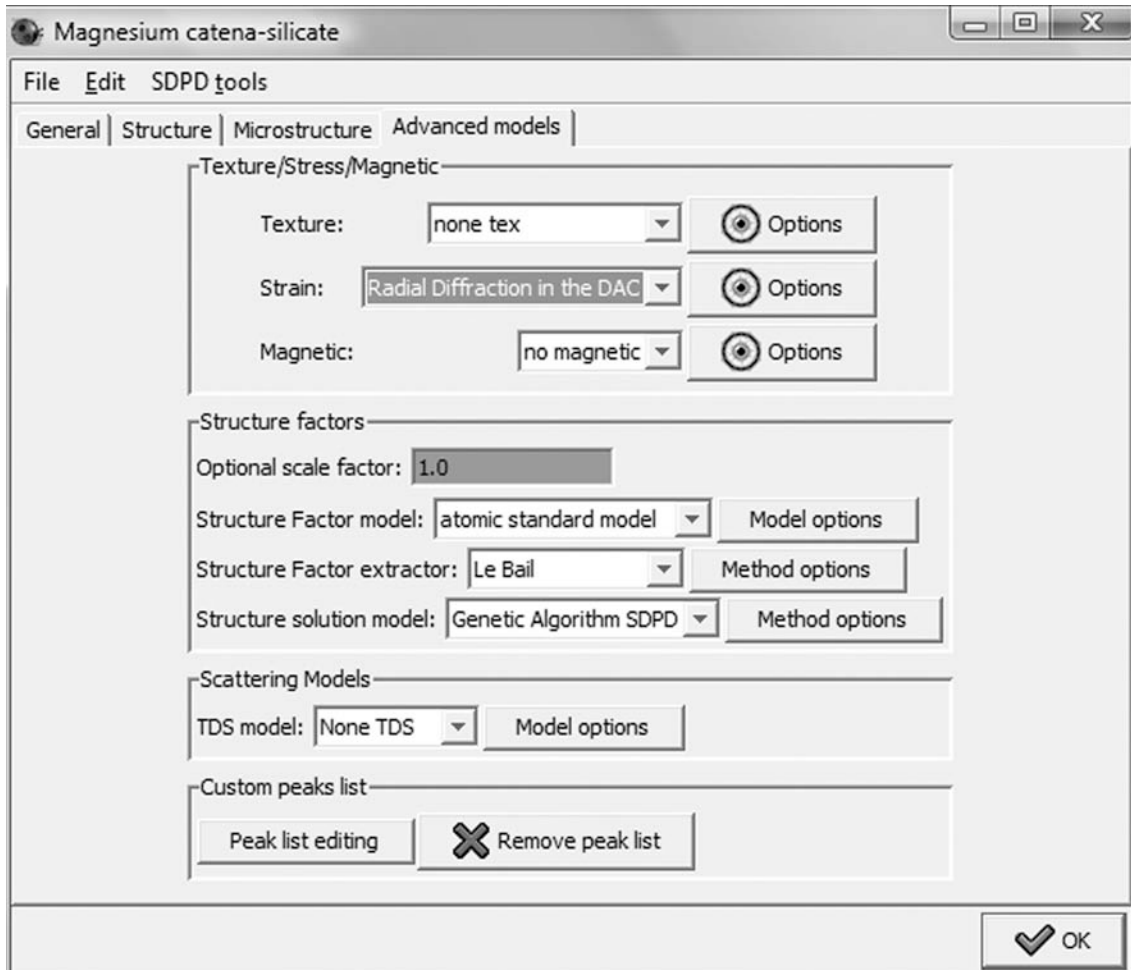
If there are significant elastic lattice strains present in your sample you will notice in the “Plot 2D” tab that the data exhibits sinusoidal oscillations in peak position with azimuth. At this point your fit should have straight lines because you have not setup a stress model. There are three models in MAUD that can be used to fit lattice strains that are generated during axial compression experiments. The first two described are stress models that will convert lattice strains to stress. The third model only fits lattice strains and leaves it up to the user to calculate stresses by hand.

In axial compression experiments in the DAC (and indeed for any compression experiment) the anvils impose both hydrostatic stresses (pressure) and differential stresses. Accordingly the stress tensor  $\sigma_{ij}$  can be separated into hydrostatic  $\sigma_p$  and differential stress  $D_{ij}$  components such that

$$\sigma_{ij} = \begin{bmatrix} \sigma_p & 0 & 0 \\ 0 & \sigma_p & 0 \\ 0 & 0 & \sigma_p \end{bmatrix} + \begin{bmatrix} -t/3 & 0 & 0 \\ 0 & -t/3 & 0 \\ 0 & 0 & 2t/3 \end{bmatrix} = \sigma_p + D_{ij}$$

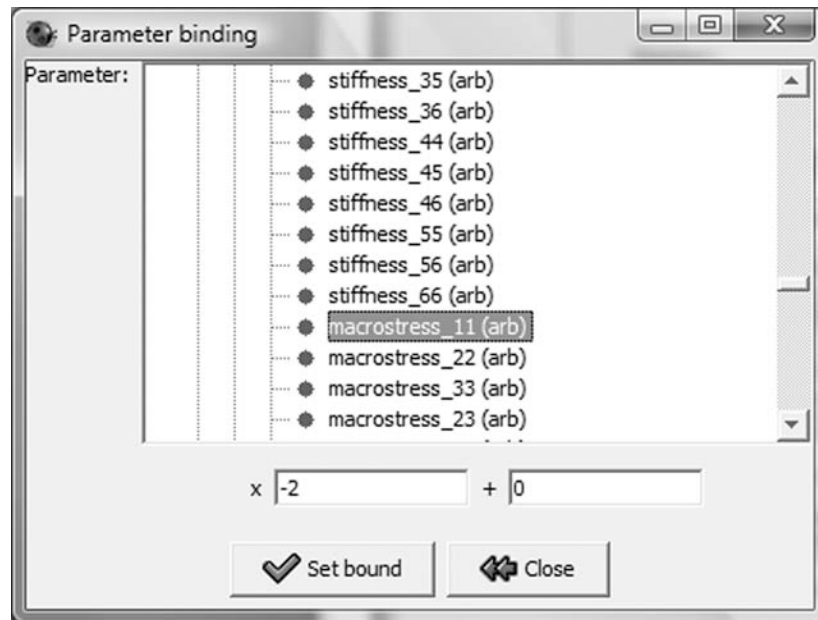
where  $t$  is the axial stress component and provides a lower bounds for the yield strength of the material (Singh 1993, Singh et al. 1998). Consequently for refinement of stresses the differential stresses will be fixed such that  $\sigma_{11} = \sigma_{22}$  and  $\sigma_{33} = -2\sigma_{11}$ , where  $\sigma_{33}$  is the largest principal stress and is negative for compression, according to the conventions in MAUD. For the analysis described here only deviatoric stresses will be fit with the stress model. Hydrostatic stresses are accounted for by refining unit cell parameters which in turn can be converted to pressure by utilizing an appropriate equation of state. The reason for treating these separately is that differential stresses will be calculated assuming a linear stress strain relationship which is only applicable for very small strains. The volume changes in the unit cell due to pressure effects are significantly larger than those due to differential stress, and it is best to use an equation of state which properly accounts for the nonlinearity of larger compressions.

To set up a stress model select the desired phase from under the “Phase” tab in the main window and click the “eye” icon. In the window that opens select the “Advanced models” tab. In the “Texture/Stress/Magnetic” box select one of the following options from the “Strain” menu 1) “Triaxial Isotropic E”, 2) “Moment Pole Stress”, or 3) “Radial Diffraction in the DAC”.



1. Triaxial Stress Isotropic E: Of the three models described this is probably the least useful. This model assumes an isotropic material and as a result generally does a poor job of fitting stresses. However the use of this model is described for completeness.
  - a. Once you have selected “Triaxial Stress Isotropic E” click the “Options” button.
  - b. Enter the Young’s modulus and Poisson ratio for the material being analyzed. To obtain an accurate estimate of stresses you will need to correct the Young’s modulus and Poisson ration for pressure.

- c. Fix the macrostresses with  $\sigma_{ij} = 0$  for  $i \neq j$ ,  $\sigma_{11} = \sigma_{22}$ , and  $\sigma_{33} = -2\sigma_{11}$ . To fix parameters, right click on the “Macrostress22” value and select equal. This will open the “parameter binding” window. Scroll down until you find “Macrostress11” and select it from the list. In the “x” box type 1. In the “+” box type in zero. This means that “Macrostress22” will be set to  $1 * \text{Macrostress11} + 0$ . Set “Macrostress33” equal to -2 times “Macrostress11”. Now that the stresses are fixed only adjust or refine “Macrostress11”.



- d. You will now want to manually adjust “Macrostress11” until the sinusoidal variation in peak position in your fit is close to that observed in the data in the “Plot 2D” window. Leave “Macrostress11” fixed for now.
2. Moment Pole Stress: This model is base on Matthies et al. 2001. To use this model you will need to know the elastic tensor ( $C_{ij}$ ) corrected for pressure for the



material of interest. This is the most sophisticated model of the three. It can account for the effects of texture in the stress analysis and has a variety of methods to average single crystal elastic moduli built into the model.

- a. Once you have selected the “Moment Pole Stress” model click the “Options” button. This will open the “Moment pole figures options panel”
- b. Fix the macrostresses as described above with  $\sigma_{ij} = 0$  for  $i \neq j$ ,  $\sigma_{11} = \sigma_{22}$ , and  $\sigma_{33} = -2\sigma_{11}$ . Again you will only adjust or refine “Macrostress11”.
- c. Enter in the single crystal stiffnesses ( $C_{ij}$ ) for the material of interest. Again it is important to correct these for pressure or the stresses obtained from the model will be incorrect.
- d. In the “Stress/strain model” box in the top right choose the desired stress model. Voigt, Reuss, Hill, PathGEO, and BulkPathGEO are available. If you choose the Hill model you can designate the Voigt-Reuss weighting. If you choose either the PathGEO or BulkPathGEO you can include the effects of texture by checking the “use texture ODF” box. In almost all cases use the BulkPathGEO.

File Edit

Macrostress11 : 3.331638    Macrostress22 : 3.331638    Stress/strain model: BulkPathGEO

Macrostress33 : -6.663276    Macrostress23 : 0    Weight (Voigt-Reuss): 0.5

Macrostress13 : 0    Macrostress12 : 0     Use texture ODF

Stiffness matrix

687.47	270.90	242.81	0	0	0
-	824.34	264.01	0	0	0
-	-	740.73	0	0	0
-	-	-	272.97	0	0
-	-	-	-	218.24	0
-	-	-	-	-	237.33

- e. Adjust “Macrostress11” until the sinusoidal variation in peak position is a close fit to the data. Leave “Macrostress11” fixed for now.
3. Radial Diffraction in the DAC: This model is not a true stress model. It actually only fits the lattice strains and leaves it up to the user to calculate stresses by hand. Where the previous two models can be applied to more complicated deformation geometries than pure axial compression, “Radial Diffraction in the DAC” can only be applied to axial compression. The main advantage of this model is that it allows the user to fit lattice strains for each peak separately whereas the previous two models fit all peaks of a given phase to one stress value. The previous two models may fail if plastic anisotropy of the material is high. In this case some peaks will exhibit much higher lattice strains than other peaks and the “Triaxial Stress Isotropic E” and the “Moment Pole Stress Model” will be unable to provide a satisfactory fit to the data.

The “Radial Diffraction in the DAC” model is built on the model of Singh (1993) and Singh et al. (1998). This model will only be discussed in a cursory manner here and for a full discussion refer to Singh (1993) and Singh et al. (1998). This model fits a  $Q(hkl)$  factor to each diffraction peak. For axial compression the strain produced from deviatoric stresses can be given by

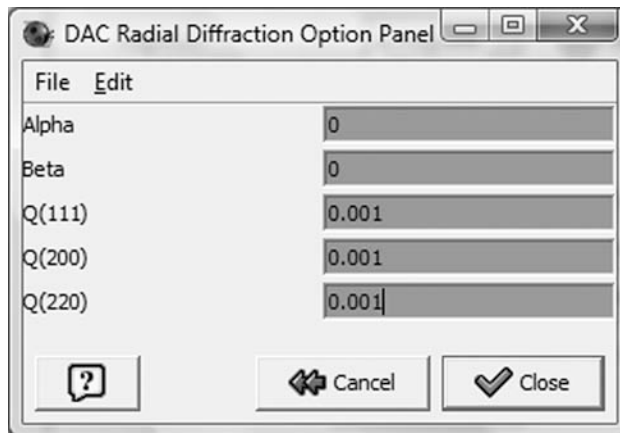
$$d_m(hkl) = d_p(hkl)[1 + (1 - 3\cos^2\psi) Q(hkl)],$$

where  $d_m(hkl)$  is the d-spacing of a given lattice plane (hkl) measured by x-ray diffraction,  $d_p(hkl)$  is the d-spacing of a given lattice plane (hkl) under hydrostatic stress conditions,  $\psi$  is the angle between the direction of maximum compressive stress and the plane normal of the diffracting lattice plane.  $Q(hkl)$  is given by

$$Q(hkl) = (t/3) \{ \alpha [G_R^X(hkl)]^{-1} + (1 - \alpha)(2G_V^{-1}) \}$$

where  $t$  is the axial stress component,  $G$  is the shear modulus, the  $R$  and  $V$  subscripts indicate the Reuss and Voigt assumptions respectively, the superscript  $X$  denotes the average relevant to x-ray diffraction, and  $\alpha$  is a parameter between 0 and 1 that determines the relative Reuss and Voigt weighting.

- a. Once you have selected the “Radial Diffraction in the DAC” model click the “Options” button. This will open the “DAC Radial Diffraction Options Panel”



- b. The first two boxes are titled “Alpha” and “Beta”. “Beta” is the angle between the sample  $Z$  direction and the maximum stress axis. “Alpha” is a rotation around  $Z$ . These two angles allow you to refine the orientation of the maximum stress axis in case it deviates from the sample  $Z$  direction. This does happen fairly frequently at high pressures as the tips of diamond anvils deform elastically and become cupped. For now you will leave these set to zero.

- c. The following boxes will be titled “Q(hkl)” and are the Q(hkl) factor for each lattice plane given in the parentheses. Q(hkl) should be positive and generally falls in the range of 0.001 to 0.007. A good initial estimate is 0.001.
- d. Manually adjust each Q(hkl) until the lattice strains in your model are close to that observed in the data.

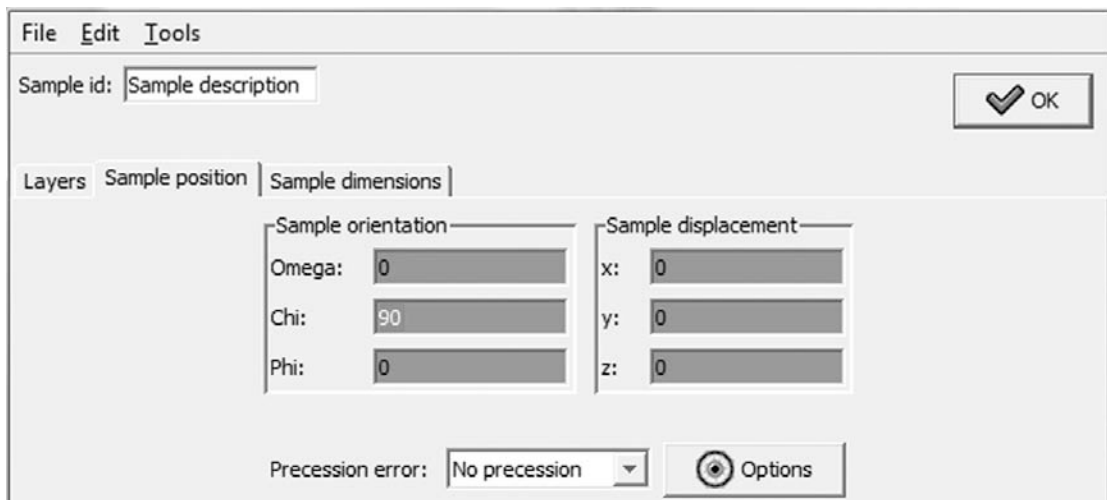
### **Correcting Young’s Modulus and Poisson Ratio or $C_{ij}$ to Pressure:**

It is mentioned above that you will need to correct the elastic moduli to pressure should you choose to use the “Triaxial Stress Isotropic E” on the “Moment Pole Stress” models. Elastic moduli are pressure dependant and often become larger as pressure increases. To correct elastic moduli to pressure you will need an appropriate equation of state for your sample, as well as a set of elastic moduli either calculated or experimentally determined for a range of pressures for your material. If your experiment is also at high temperature you will need to correct for this as well and will also need to know the temperature dependence of the moduli. The easiest way to correct the elastic moduli is to create a spreadsheet which uses an equation of state such as a 3<sup>rd</sup> order Birch-Murnaghan equation of state to calculate pressure from the unit cell parameters. Next you will plot each elastic moduli (e.g.  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ ,  $C_{12}$  etc.) versus pressure. Once this is done fit a best fit line to each of the elastic moduli and determine the equation describing the pressure trend for each moduli. This will allow you extrapolate the elastic moduli to any pressure (within reason). Normally a linear extrapolation will be good enough. Now you

will use the pressure calculated from your unit cell parameters to determine the appropriate value of the elastic moduli using the equations for your best fit lines.

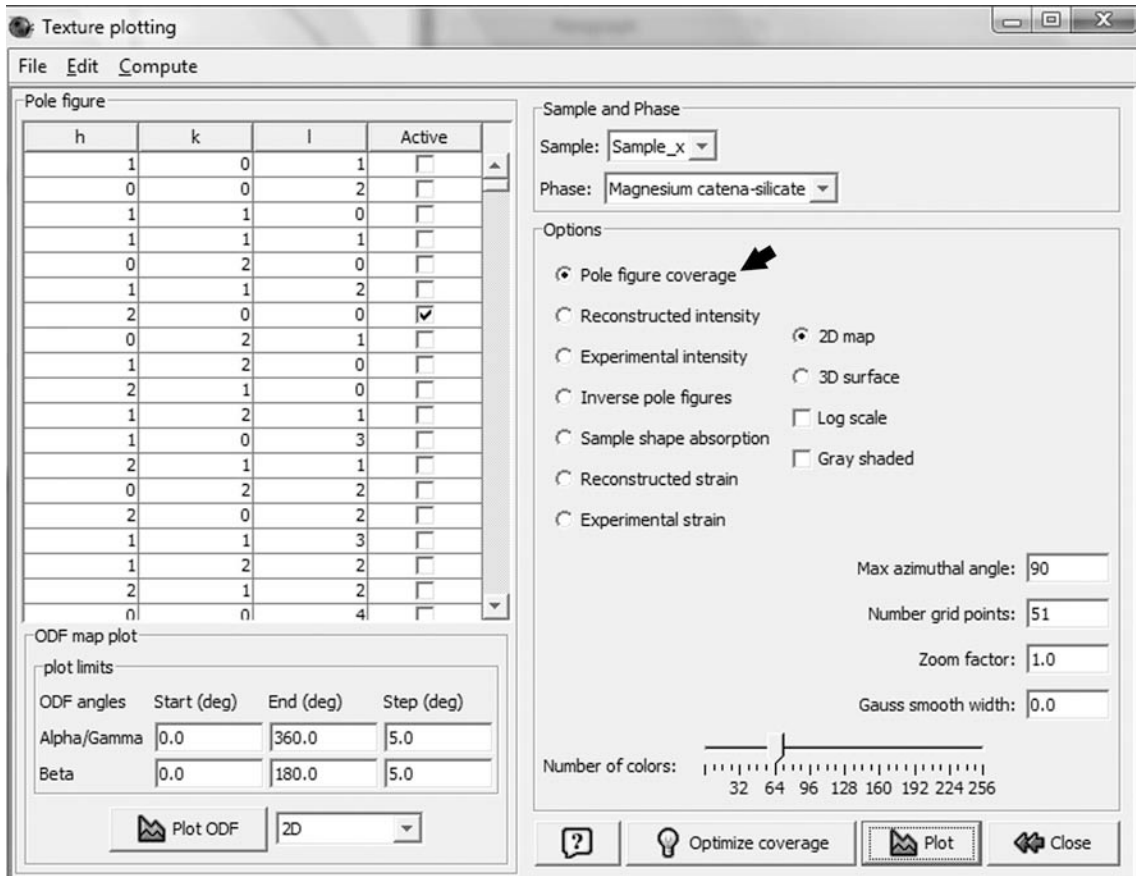
### Sample Orientation:

If the stresses appear to be inverted i.e. “Macrostress 33” is negative or  $Q(hkl)$  is positive but the sinusoidal variations in peak positions are offset from the data by  $90^\circ$  (azimuth) then your sample orientation is wrong. To change the sample orientation select the “Sample” tab in the main MAUD window and highlight “Sample\_x” in the sample list. Click the “eye” icon. In the “Sample\_x” window that opens, select the “Sample position” tab. In the “Sample orientation” box “Omega”, “Chi”, and “Phi” will all be zero. You will need to change one of these to 90. It will probably be “Omega” or “Chi” that will need to be changed depending on the geometry of your experiment, but you may have to find the right orientation by trial and error until the stresses in you model looks like the data.

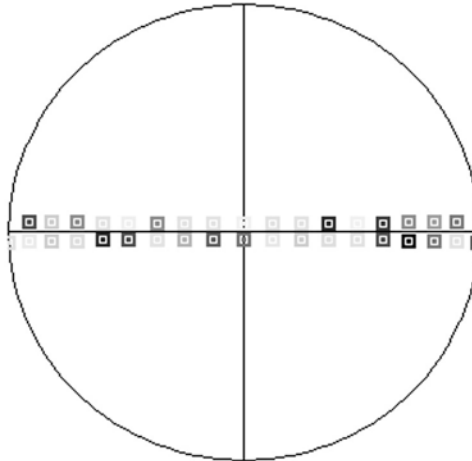


You can also check to see if the sample orientation is correct by going the “Graphic” pull down menu in the main MAUD window and selecting “Texture plot”

from the list or by hitting Ctrl + T. This will open the “Texture plotting” window. In here you will select the option to plot “pole figure coverage” and click the “Plot” button.



The coverage should look like the screen shot below or rotated 90° about the center of the pole figure. If the data points are situated around the periphery of the pole figure the sample orientation is wrong.



### **Refine Parameters:**

Now that the basic parameters listed above are close you will be able to begin to refine some basic parameters. Start by freeing and refining the parameters in the order they are listed below. Refine each parameter or parameters until the fit is not getting better then move on to the next parameter that is listed. After you have refined each parameter leave it free to refine as you free and refine the next parameter in the list.

1. Intensity and backgrounds: If you used interpolated backgrounds you will only need to refine the intensity. If you are using polynomial backgrounds first refine the global background coefficients. Once these have refined satisfactorily fix the global backgrounds and refine the individual parameters you applied to each spectrum. If you did not apply individual background coefficients keep the global backgrounds free to refine.
2. Unit cell Parameters.
3. Crystallite size and r.m.s. microstrain: Do not allow these to go to a negative number. A negative crystallite size is not physically possible. If you are using the “Popa rules” to fit anisotropic grain shapes then the non 0 coefficients can

become negative but can never become more negative than size coeff (angstrom) 0 and microstrain coeff 0 are positive. In other words size coeff (angstrom) 0 + size coeff (angstrom) 1 cannot be less than 0. For refinement of “Popa rules” first refine size coeff (angstrom) 0 and microstrain coeff 0 and once these fit well you can refine the other coefficients.

4. Stress model: Either free “Macrostress11” if you used the “Triaxial Stress Isotropic E” on the “Moment Pole Stress” models or free the Q(hkl) factors if you used the “Radial Diffraction in the DAC” model. For the “Radial Diffraction in the DAC” model some values of Q(hkl) may go wild during refinement if these peaks are of weak intensity or are not well resolved due to peak overlaps. If this happens you will need to fix the appropriate Q(hkl) parameter to a reasonable value.
5. If you are using the “Triaxial Stress Isotropic E” or the “Moment Pole Stress” models, once the stress model has converged (this should only take a few iterations) you will need to use the unit cell parameters to recalibrate pressure. Once you have determined pressure, correct the Young’s modulus and Poisson ratio or the  $C_{ij}$  to the new result for pressure and reenter these in the appropriate model and refine the stresses. You may have to repeat this process a few times before the stresses and unit cell parameters both converge.
6. Beam center and tilt: If your stresses are not fitting you can try to refine the beam center and tilt. After you have refined these fix the beam center and tilt before you continue with the refinement.

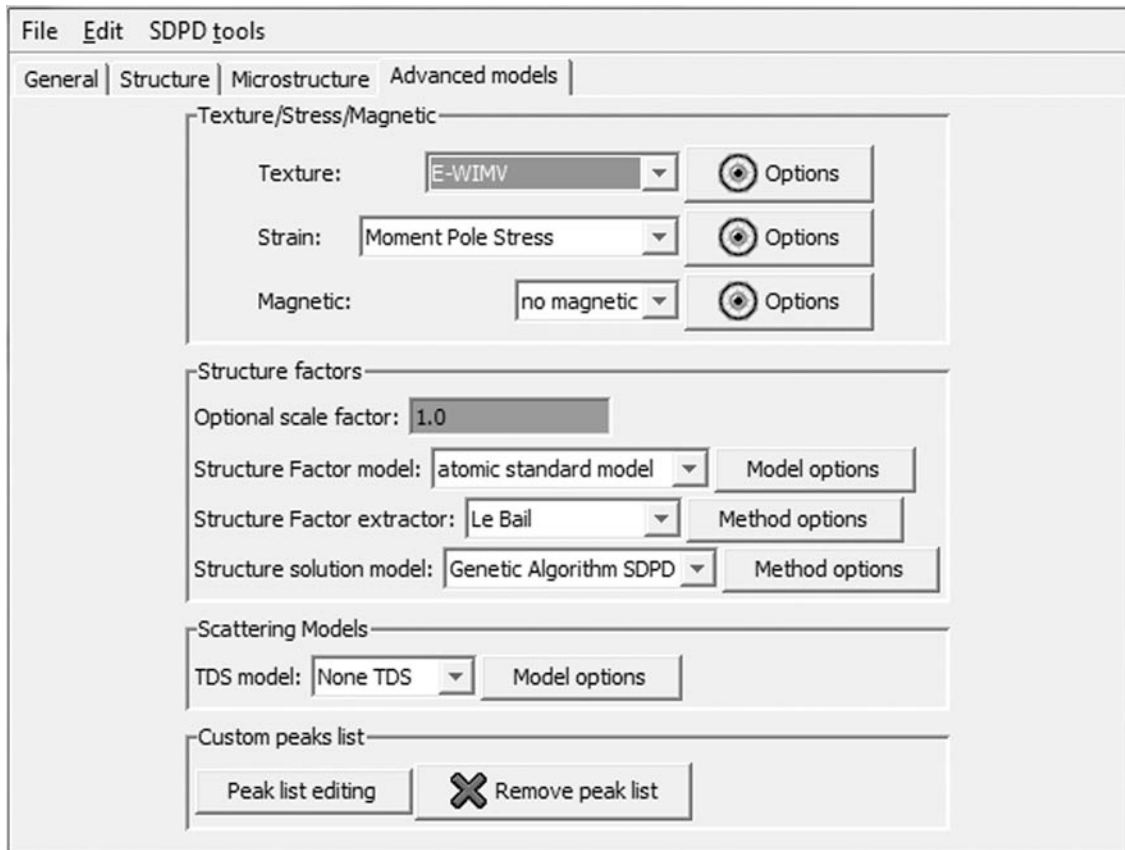


7. If you are using the “Radial Diffraction in the DAC” model you can refine the “Alpha” and “Beta” angles to get a better fit if you wish. Once you have refined these fix them before continuing.

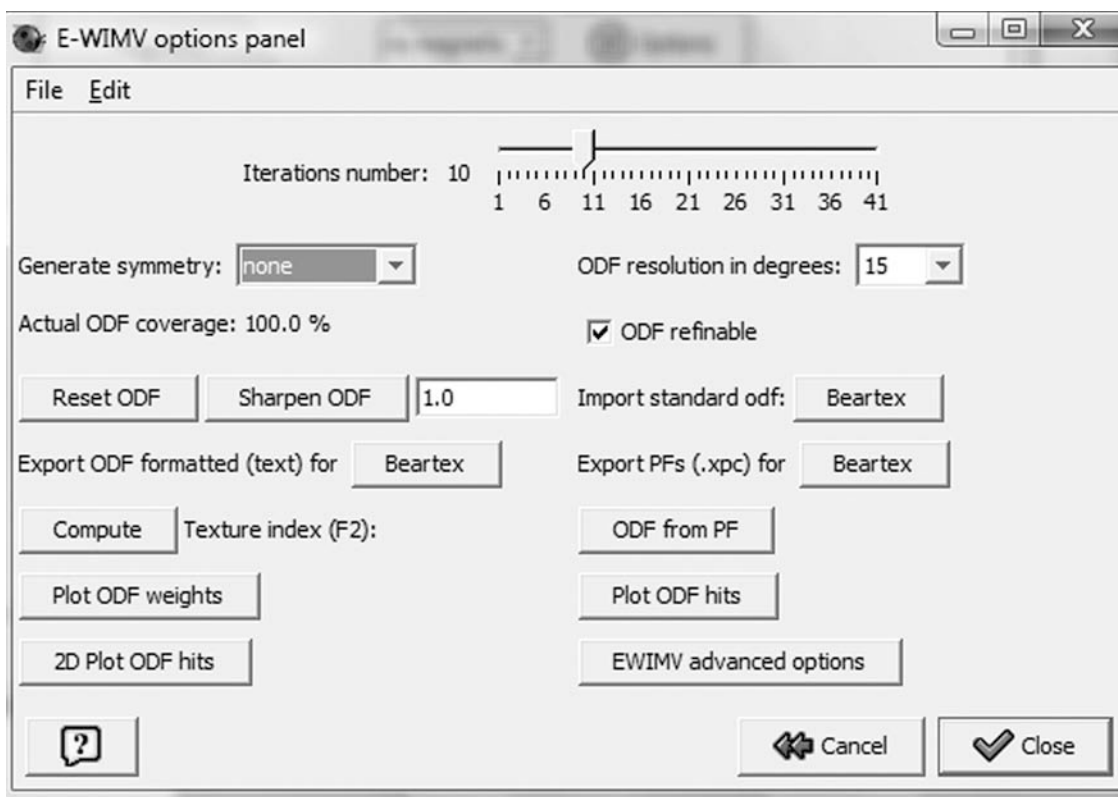
**Texture Refinement:**

By now you should have a pretty good fit to your data. In the “Plot 2D” tab only intensity variations along the diffraction rings will not be fit yet. These systematic intensity variations with azimuth are indicative of texturing. You will now want to refine texture for your sample.

1. Select a phase from the list that is under the “Phases” tab in the main MAUD window. Click the “eye” icon.
2. In the window that opens select the “Advanced models” tab.
3. In the top of the box labeled “Texture/Stress/Magnetic” there is menu labeled “Texture”. Select the E-WIMV model. The E-WIMV model is a tomographic algorithm that is similar to the WIMV model (Matthies and Vinel, 1982) but allows for incomplete and arbitrary pole figure coverage.

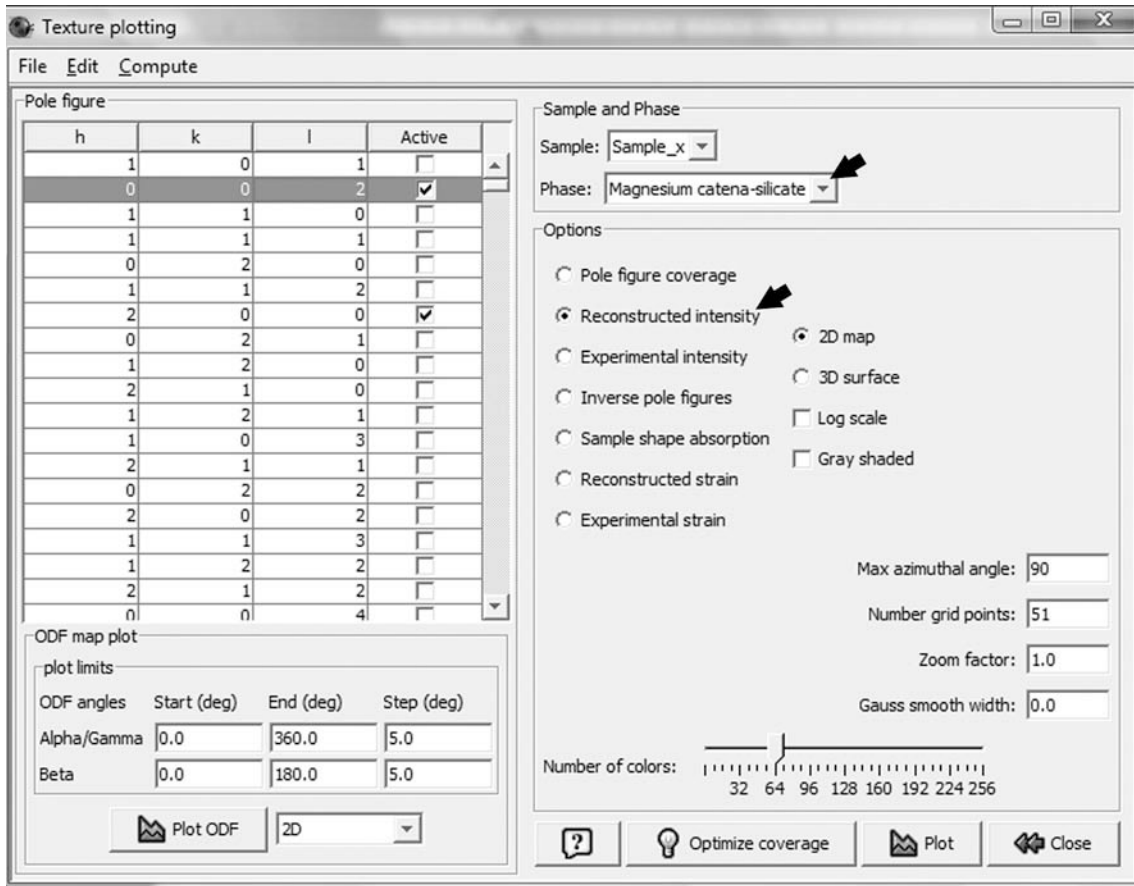


4. Now that you have selected the E-WIMV model click the “Options” button. The “E-WIMV options panel” will open.

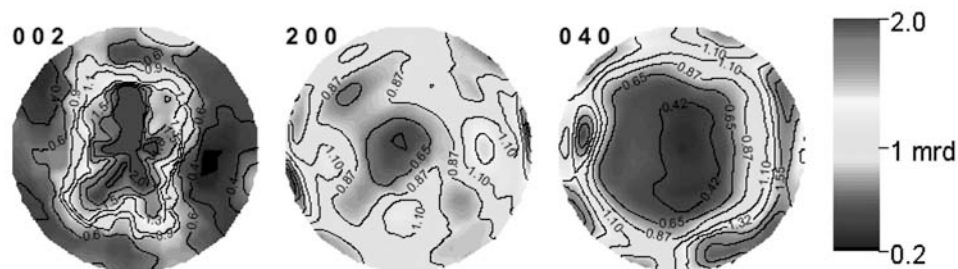


5. Where it says “Generate symmetry” select “none”. Close the “E-WIMV options panel” and click OK in the phase window. Now click the “hammer” icon in the main MAUD window to refine texture.
6. Once texture is finished refining you will want to see if it exhibits cylindrical symmetry about the compression axis. To do this you will need to plot some pole figures.
  - a. Go to the “Graphic” pull down menu and select “Texture plot” form the list or hit Ctrl + T. This will open the “Texture plotting” window.
  - b. In the “Phase” list at the top select the desired phase.
  - c. Select the option that says “reconstructed intensity”

- d. In the list on the left select the pole figures you wish to plot. Generally it is most interesting to plot the primary directions (i.e. 100, 010, 001, or any higher multiple that is parallel to these e.g. 200, 040 etc.).



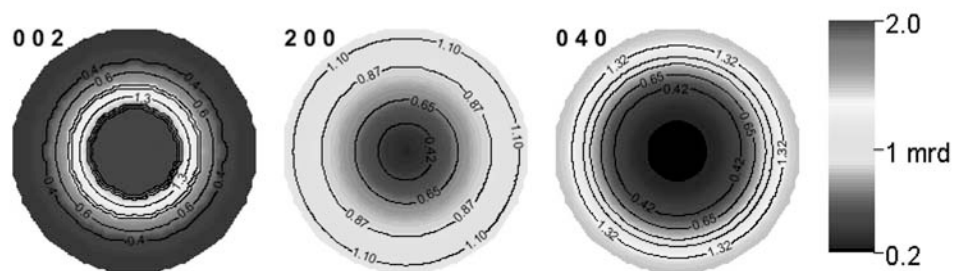
- e. Click "Plot". Check to make sure that the textures are cylindrically symmetric about the compression direction. The compression direction is in the center of you pole figures. Below is a screen shot of pole figures for the 002, 200, and 040 poles for MgPv that exhibit near cylindrical symmetry about the compression axis.



- f. If textures are slightly offset from the center of the pole figure you can adjust the “Omega”, “Chi” and “Phi” angles to center the textures. After changing the angles you will need to go to the “E-WIMV options panel” and click the “Reset ODF” button, refine the textures again, plot pole figures, and check if they are centered. If your textures are pretty close to being centered do not worry for now you can refine the sample orientation in the next step.
7. Now that you have confirmed that you textures have cylindrical symmetry about the compression axis, go back to the “E-WIMV options panel” and where it says “Generate symmetry” select “cylindrical”. Click the “Reset ODF” button. This is critical or MAUD will keep refining the same ODF and it will not actually impose symmetry. Close the “E-WIMV options panel” window and click OK in the phase window.
8. You can now refine the “Omega”, “Chi”, and “Phi” angles if you wish. MAUD will refine the sample orientation based on the stresses and texture. In most cases refining the sample orientations will give a better fit to peak shapes, stresses, and texture. Once you have freed these sample orientation parameters click the “hammer” icon in the main MAUD window to start the refinement. You may

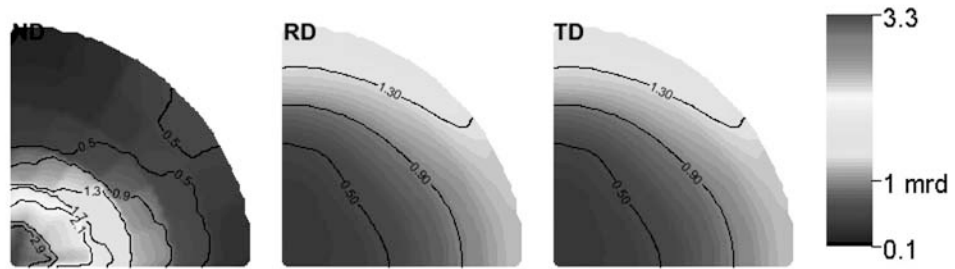
need to run several iterations of refinements before the texture is a good fit to intensity variations.

9. Once the refinement is finished go back to the “Texture plotting” window and plot the reconstructed intensity for the same pole figures you plotted prior to imposing symmetry. They should look similar but perfectly symmetric about compression.



10. Now that you have confirmed that these look similar to before you can plot the inverse pole figure. For axial compression where symmetry about the compression axis can be imposed, the inverse pole figure compactly represents textures. The inverse pole figure shows crystallographic directions with respect to compression.

- a. In the “Texture plotting” window select “Inverse Pole figures” from the “Options” box and click the “Plot” button. For compression you will only need to look at the inverse pole figure on the left. This is the one for the compression direction. The screen shot below shows that the sample has a strong maximum of 001 poles in the compression direction.



- b. Check that this is consistent with what you observed in the pole figures you plotted before. For example, if the 001 pole figure showed a strong maximum in compression, you should see a maximum at 001 in the inverse pole figure. If the inverse pole figures are consistent with your pole figures you are done with this refinement.