

Example 5.1: YPO

Simple modulated structure with crenel

Revised 16 October 2019

$\text{Y}(\text{PO}_3)_3$

Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files: YPO.hkl, YPO_red.sum

Frame scaling, absorption correction: done

1. Creating new jobname

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click YPO

2. Import Wizard

Select "Known diffractometer formats"; NEXT

Select "Oxford Diffraction → CCD"; NEXT

[On the screen: "Define basic input file:"]

Select "Input from sum file"; file name "ypo_red.sum"; OK

[On the screen: "Warning about appended data reduction runs"]

OK

[On the screen: "Complete/Correct experimental parameters"]

Leave all settings unchanged; NEXT

[On the screen: "Define the reference cell/split by twinning"]

Leave all settings unchanged; NEXT

For absorption correction select "None or done before importing"; NEXT

FINISH

3. Data Repository

The line in data repository window corresponds to one data set.

OK; YES to accept the data set

[On the screen: "Information about starting symmetry wizard"]

NEXT

4. Symmetry Wizard

[On the screen: "Tolerances for crystal system recognition".]

Symmetry wizard can be started separately by "File → Reflection file → Make space group test".

Leave all settings default; NEXT

[On the screen: Select supercell]

Select "Continue with the basic cell"; NEXT

[On the screen: Select Laue symmetry]

Select Monoclinic Laue symmetry; NEXT

[On the screen: Select cell centering]

Select I centered unit cell; NEXT

[On the screen: Select space group]

Select C2/c; NEXT

[On the screen: Select superspace group]

C2/c(0b0)s0

[On the screen: Final step of the superspace test]

Accept the superspace group in the standard setting: C2/c(0b0)s0; FINISH

5. Creating refinement reflection file

We have finished creation of the file M95 (reflections converted from diffractometer format to Jana format) and M50 (cell parameters, symmetry). At this step we shall create the file M90 containing data set merged by symmetry, with extinct reflections omitted.

NEXT to confirm threshold 3sigma

[On the screen: settings for merging of reflections]

Leave all settings default; NEXT

Accept the data block and calculate coverage; FINISH

[On the screen: Information that structure solution will start]

6. Structure Solution Wizard

[On the screen: window of Structure solution]

In "Formula" textbox type list of chemical elements for $\text{Y}(\text{PO}_3)_3$: Y P O

Select "use Superflip"; "Peaks from Jana2006"

Select "Use a specific random seed" and type value 5555

"Run solution"

Superflip converges (after noise suppression) with R value 21%. It confirms the symmetry C2/c(0b0)s0.

Generally, each starting random seed can give a different result, which in most cases allows correct solving the structure. However, the number of localized atoms and/or origin selection can be different. Fixing the random seed to 5555 guarantees that the Superflip returns the same result like described in this cookbook.

For your own practice, we strongly recommend using the method, which repeats the Superflip run with several times. Then Superflip is choosing the best fitting result.

Close the listing and press "Accept last solution" to leave the structure solution wizard

7. Verification of the structure solution

Start "Edit/View → editing of M40 file".

It shows the structure parameter file. Experts knowing exactly the file format can edit individual parameters here. Much safer is to use corresponding utilities like "Edit atoms" allowing a user-friendly editing of structural parameters and modifications of the structural model.

Start "Edit atoms". It shows the same in a graphical interface; parameters of atoms can be accessed by double clicking on atom or by "Action → Edit/Define atoms";

OK

Start EditM50, go to page Composition, change "Formula units" to 4

Press "Formula from M40"

[On the screen: Information about formula]

The reason why the value of formula units was modified from 8 to 4 is that this number

leads to integer multiplicities for all atoms. This reduction also means that Y, P and some of O atoms are localized at special positions if the symmetry as proposed by the space group test. For the solution with previously used "randomseed 5555" the formula should be Y P3 O8 (for Z=4).

OK; YES for updating the formula

Modify the formula to Y P3 O9; OK, YES to rewrite M50 file.

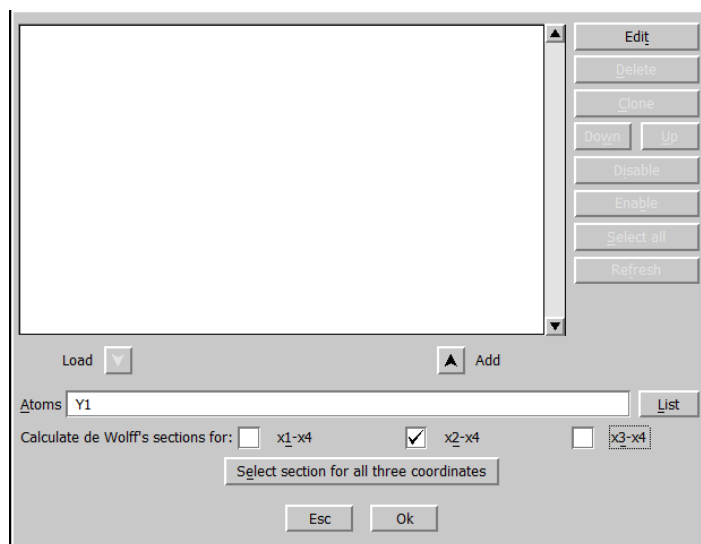
This change was made to keep the ratio P to O 1:3 as expected. The correct structure formula and formula units can help in the process of completing the structure from difference Fourier maps. However, for structure factor calculation only type of atoms and their order in the formula are relevant.

Run Contour; start "New plot"; select "Show de Wolff's sections";

New map to draw "F(obs) – Fourier";

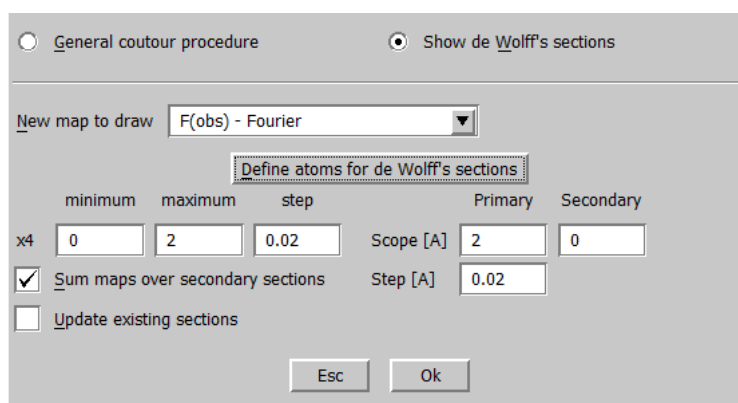
Press "Define atoms for de Wolff's sections";

Select atom Y1 and section x2-x4:



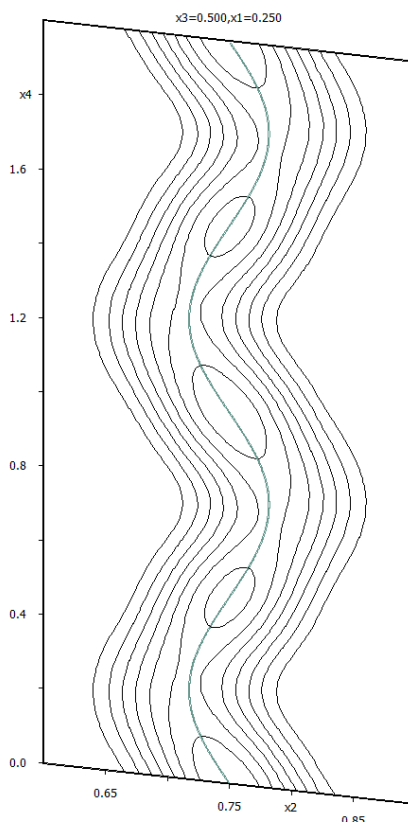
Press "Add"; OK

Leave rest setting default;



OK;

Then the modulation density will appear.



The plot illustrates that the electron density from Superflip contains reliable information about position modulation. The modulation curve results by interpretation of the electron density map by Jana.

[Quit Contour](#)

8. Origin shift to the position of Y1

The atom Y1 should be localized at the inversion center in one of the following Wyckoff positions:

4d $(1/4, 1/4, 1/2); (3/4, 1/4, 0) + (1/2, 1/2, 0)$

4c $(1/4, 1/4, 0); (3/4, 1/4, 1/2) + (1/2, 1/2, 0)$

4b $(0, 1/2, 0); (0, 1/2, 1/2) + (1/2, 1/2, 0)$

4a $(0, 0, 0); (0, 0, 1/2) + (1/2, 1/2, 0)$

In the next step we shall shift the origin to the position of the Y1 atom. This step is not necessary for the structure solution and refinement but it assures that the coordinates and plots will look as described in this cookbook

[Start "Tools → Transformations → Origin shift"](#)

[On the screen: Move the origin to:]

[Select Atom Y1 and press OK.](#)

[Run "Edit atoms"; Select P and O atoms;](#)

[Press "Action" and choose "Make symmetrically contiguous motifs;](#)

This will not only make an contiguous motif from PO, but also it will move motifs to the basic

cell.

9. Verification of modulated functions found by Superflip

Right-click the icon of Refine and select thumbnail "Various". Use the button "Fixed commands", select "Modulation parameters" and type * to the Atoms/parameters textbox.

This fixes modulation parameters for all atoms.

Press the button "Add"; OK; OK

Start Refinement.

The refinement should finish with R(obs) factors about 13%, 11%, 15% and 22% for all, main, 1st order satellite and 2nd order satellite reflections. This means that we have reasonably good starting point to continue the solution.

The screen output of Refine is closed after a delay. It is saved in refinement listing ("Edit/View → View of Refine → Go to → R-factors overview")

10. Refinement of the modulated structure

Right-click the icon of Refine and select thumbnail "Various". Use the button "Fixed commands" and disable or delete the previously used "Fixed command"

Run refinement.

You should get R values about 13%, 10%, 14% and 20% for 24 parameters.

Start "Edit atoms"

Press "Select all" and "Action → Edit/define"

Choose "harmonic" for ADP parameters.

OK; OK; Yes to rewrite changes

Start Refinement.

Refinement converges with R value about 11%, 8%, 12% and 20% for 94 parameters.

11. Localization of the missing oxygen atom

Right-click the icon of Fourier and select thumbnail "Basic" – select "Map type" "F(obs)-F(calc) – difference Fourier"

In the thumbnail "Scope" select: "Automatically" and "Use default map orientation"

OK

Run Fourier

The modulation curve of this additional atom is rather complicated and therefore we have to look at the density maps to see more details. First, we should check if the peak, representing possible position of the new oxygen atom, has been really localized in the difference Fourier map.

[On the screen: Do you want to start the procedure for including of new atoms?]

Answer yes.

[On the screen: Inserting/replacing of atoms – setting of distance limits]

Use default 3 Å; OK

(The dialogue for adding maxima is also available through "Parameters → Atoms → New")

The dominating maximum (with the largest charge) should be close to the special position at (3/4, 3/4, 1/2) or to some of its equivalents, with reasonable distances to the atom P1 (about 1.5 Å).

Note the coordinates of the dominating maximum in equivalent position close to P1

For the current structure model (random seed 5555) it should be 0.749, 0.725, 0.495

Round the coordinates to the closest special position and note them

For the current structure model (random seed 5555) it should be: 0.75, 0.75, 0.5

Leave the form **without** adding the new atom.

Adding new atoms would add oxygen to a general position because its localized position is about 0.16 Å out of special position.

Use Contour to see difference Fourier sections through the point (3/4, 3/4, 1/2).

Start Contour, press “New plot”; Select “General contour procedure”

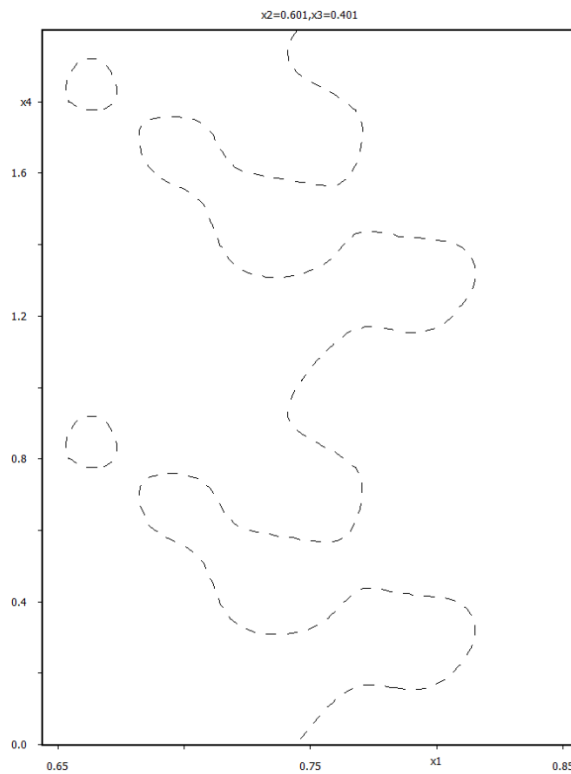
Select “Calculate new ones” and “Draw maps as calculated”; OK

In Basic thumbnail select “F(obs)-F(calc) – difference Fourier” and in the thumbnail “Scope” define the vicinity of the point (3/4, 3/4, 1/2):

The screenshot shows the 'Fourier commands' dialog box with the 'Scope' tab selected. The 'Scope' tab has three sub-tabs: 'automatically', 'explicitly', and 'by a central point'. The 'explicitly' sub-tab is active. The 'Map axes' section shows '1st=horizontal, 2nd=vertical, 3rd=section, ...'. The '1st' axis is set to 'x1', '2nd' to 'x2', and '3rd' to 'x3'. The '4th' axis is set to 'x4'. The 'minimum' value is 0, 'maximum' is 2, and 'step' is 0.02. The 'Center' field is set to '3/4 3/4 1/2'. The 'Scope [Å]' field is set to '3 2 2'. The 'Step [Å]' field is set to '0.05'. The 'Refresh scope' checkbox is checked. The 'Reset to default' button is visible. The 'Esc' and 'Ok' buttons are at the bottom.

OK starts Fourier calculation

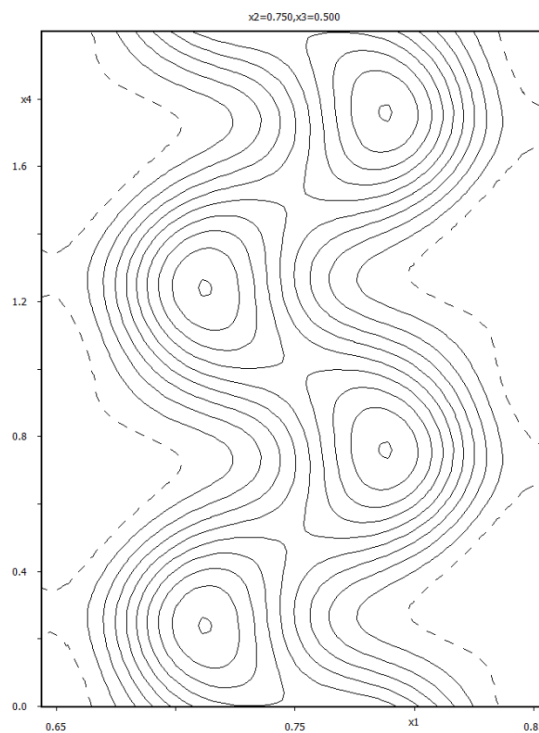
The first section is immediately plotted:



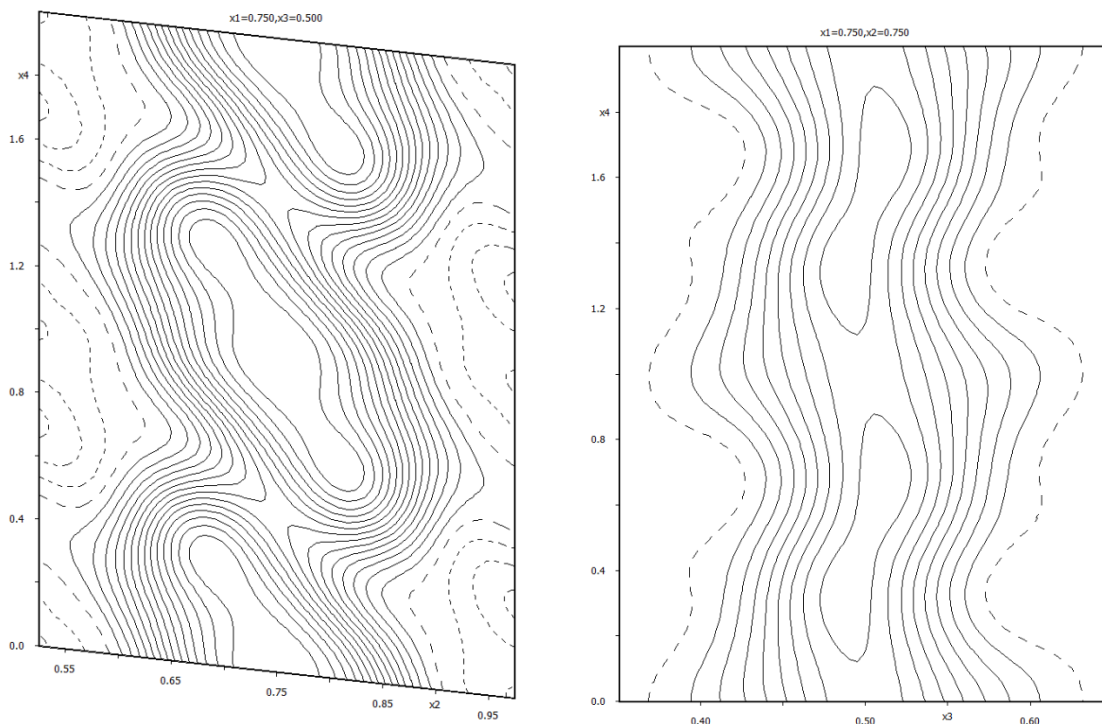
The resulting map must be summed over x_2, x_3 direction to see the correct modulation curve

Press “Sum ON”; select “ x_2 ” and “ x_3 ” leaving the intervals defaults; OK

The resulting map shows the shape of modulation:



Analogously (starting with button “New plot” followed by “Calculate new ones”), calculate and plot the section x_2 - x_4 and the section x_3 - x_4 :



The modulation has a discontinuity at the point with $x_4=0$. This is clearly visible from the map showing evolution of the x_2 atomic coordinate (the x_2 - x_4 section).

Very weak effects like modulation of light atoms in a structure containing heavy atoms are usually not directly detectable from the regular Fourier map. However, they can be detected from the difference Fourier maps calculated for a structure where the relevant atom is omitted. For this reason, we will save this map for future use.

Close "Contour"

"File → Structure → Save as" and use a new name for example "YPO-for-maps" but do not continue with the new structure.

12. Inserting the missing oxygen atom

From the previous we know that the modulation function of the new atom at $(3/4, 3/4, 1/2)$ has a discontinuity and therefore a crenel function will be used. In the x_2 - x_4 difference section we found that the length (delta) of crenel is one and its center (x_{40}) is located at 0.

"Parameters → Atoms → New", select "Coordinates from keyboard"; OK

Type the coordinates $3/4, 3/4, 1/2$, press "Use new coordinates"

Select the symmetrical position making the shortest distance to P1 and press "Include selected peaks".

[On the screen: Complete information for the new atom]

For "Name of atom" type "O*" followed by TAB

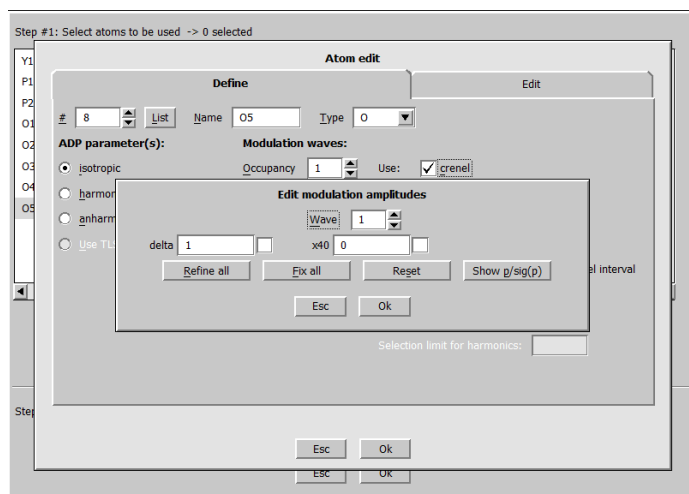
This selects the chemical type oxygen and the label with the first available sequence number.

OK; Finish; YES to include new atom

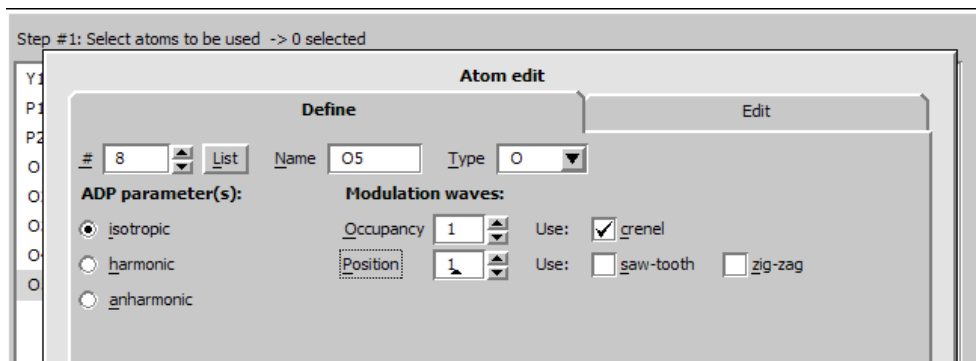
Now we have to define the crenel function

Run "Edit atoms" and select the new atom (probably O5).

"Action → Edit/define" check "crenel" and define "1" for "delta" and "0" for "x40"; OK
This is width and centre of the crenel function



add one position modulation wave in the textbox "Position"



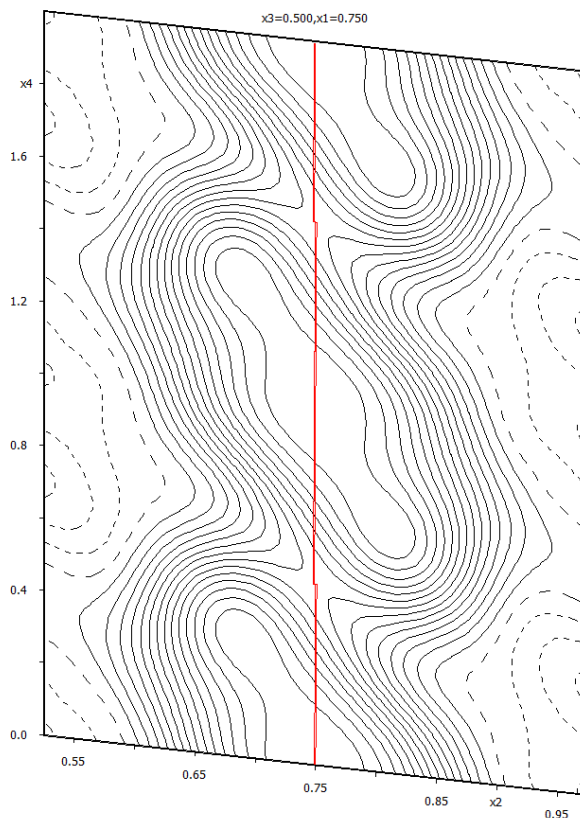
Select "Legendre polynomials in crenel interval"

OK; OK; Yes to rewrite

Draw Contour section x2-x4 for (3/4 3/4 1/2) - like previously

Press "Atoms edit" and add O5; OK

The Contour plot shows the initial modulation function for O5



13. Refinement of the complete structure

Right click on the Refine icon, switch to "Basic"

Define there number of cycles 100 and damping factor 0.2.

Damping factor multiplies the parameters changes

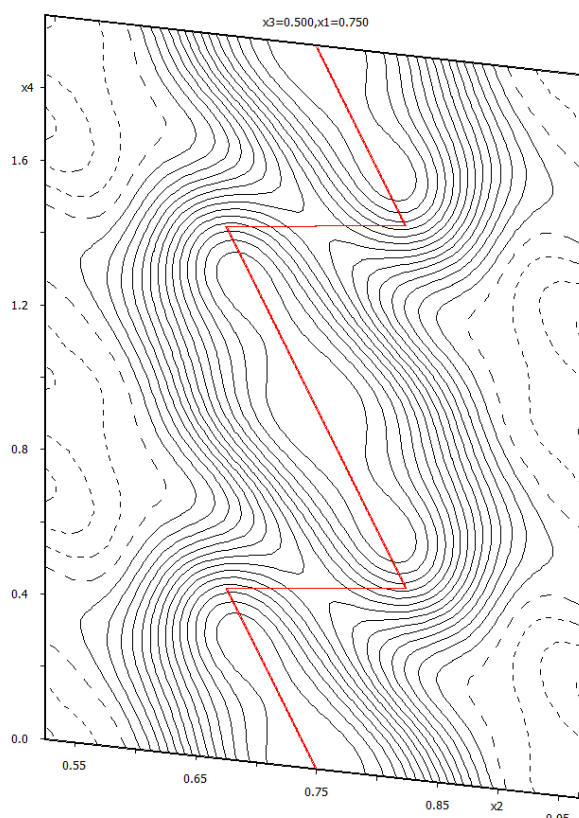
Start refinement

→ R about 9%, 6%, 10%, 20% for 98 refined parameters

Draw Contour section (without Fourier calculation!) x4-x2 for (3/4 3/4 1/2) - like previously

Press "Atoms edit" and add O5; OK

The Contour plot shows the crenel modulation function for O5 combined with one modulation wave



Run “Edit atoms”, select all atoms, press “Action” and select “Edit/Define atoms”

Modify all ADP parameters to harmonic ones by double-clicking the corresponding radio button

Yellow indicates locked objects. Locking occurs when the corresponding parameters are not the same (or of the same type) for the selected atoms. In our case ADP is harmonic for most of atoms but isotropic for the newly added O5, this is the reason for locking of radio buttons. The text box for site occupancy is also locked because some atoms are in special positions. A locked object can be unlocked by double-click.

Add another one positional modulation wave for all atoms using the textbox “Position”.

Save changes and start refinement

→ *R* about 5.6%, 3.4%, 6%, 18% for 141 refined parameters

Run “Edit atoms”, select all atoms and (using the button “ADP^{2nd}”) define two ADP modulation waves for all atoms.

Start refinement

→ *R* about 3.4%, 2.5%, 3.5%, 9.0% for 297 refined parameters

“File → Structure → Save as” make a backup copy with name e.g. ypo-final

14. Check modulation curves with maps for O5

In this part we will check whether the refined modulation function for oxygen O5 corresponds to the electron density map found previously from the difference Fourier maps. We are making this check because refinement of sawtooth function for oxygen in the structure containing the heavy yttrium could be unreliable

Return to the result saved previously (YPO-for-maps):

“File → Structure → Open”: select the name of the previously saved structure (“YPO-for-maps”)

Run Refine to re-generate phases

(R factors 11%, 8%, 12% and 20%.)

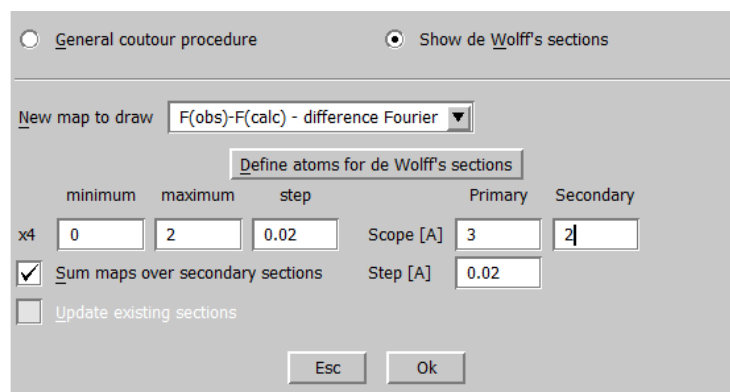
“File → Structure → Copy in” copy only (!!!) m40 from the final structure

(From this point Refine must not be started)

Run “Contour”; Choose “Show de Wolff’s sections” and difference Fourier;

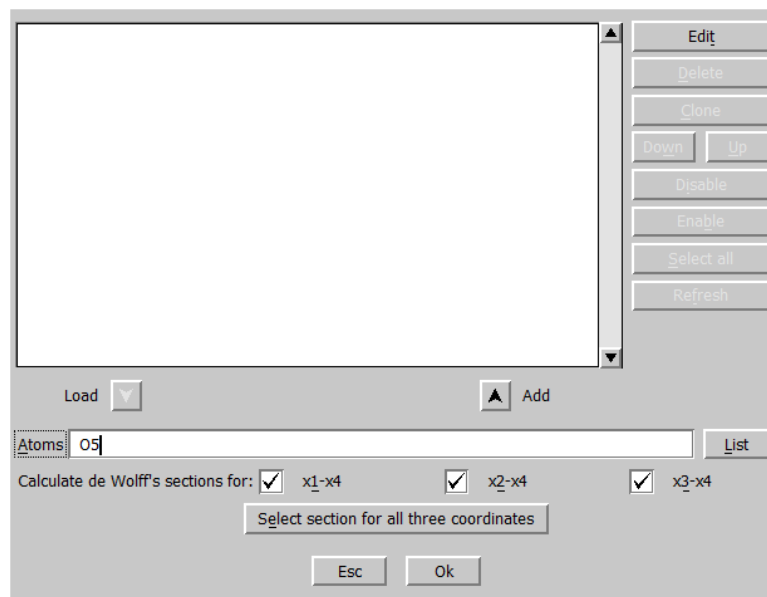
Define primary and secondary scope, 3 and 2 respectively;

Activate summation of the maps over secondary directions:

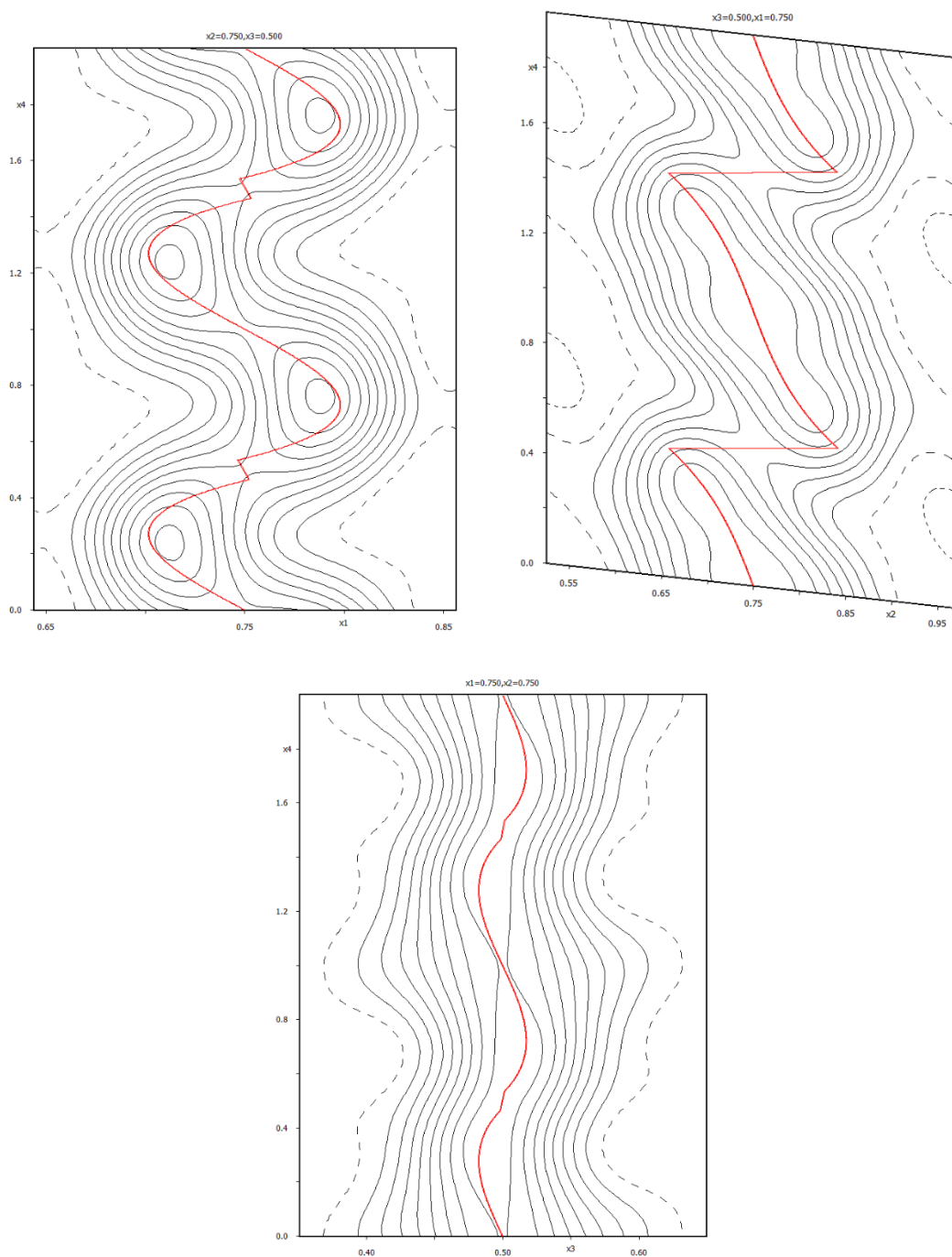


Press the button “Define atoms for de Wolff’s section:

Select atom O5 and activate calculations for all three sections x1-x4, x2-x4 and x3-x4:



The following maps will be obtained:



By this procedure we plot the final refined modulation curve of O5 together with the previously calculated Fourier map. The technical trick consists in the fact that Fourier calculation does not use M40; it uses M80 created by Refine. Only the modulation curve displayed by Contour is based on parameters from M40.

15. Drawing of refined modulated structure

[Return back to the refinement result using “File → Structure → History”](#)

Drawing programs such as Diamond cannot draw a modulated structure directly. Jana2006

creates an approximant based on the refined modulated functions. During this process, the superspace symmetry is used to generate all atomic positions and the symmetry is reduced to $P1$. The size of approximant and the starting t value are to be chosen to visualize different portions of the non-periodic matter. In our case the most convenient supercell is $1 \times 8 \times 1$ as follows from the modulation vector being close to $(0, 3/8, 0)$.

“Plot structure”

In Diamond symmetry operations must not be used for the approximant (no automatic structure, no supercell, no coordinations). This is because Diamond does not know modulation displacements of newly created positions.

16. Checking of refinement listing

Start “Edit/View → View of Refine”

Press “GoTo → List of serious warnings”

The listing contains information that modulation of ADP leads to non-positive values for some values of t coordinate:

```
*****
* List of serious warnings *
*****

Modulated harmonic ADP tensor of the atom "O1" is not positive in some regions
  For more details run "Grapt" and draw U(min) value
Modulated harmonic ADP tensor of the atom "O4" is not positive in some regions
  For more details run "Grapt" and draw U(min) value
Modulated harmonic ADP tensor of the atom "O5" is not positive in some regions
  For more details run "Grapt" and draw U(min) value

There were no correlations larger than 0.900 in the last refinement cycle
```

Start “Grapt”

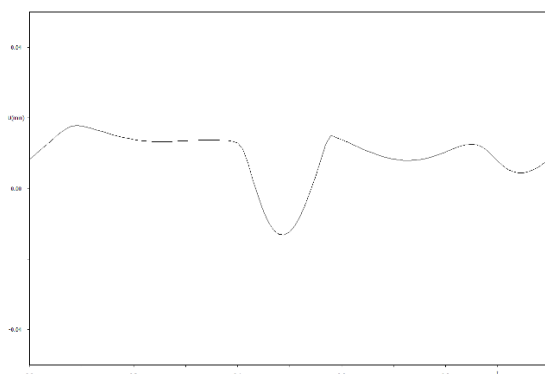
Press New/Edit

For “Parameter to draw” select “ADP parameter”

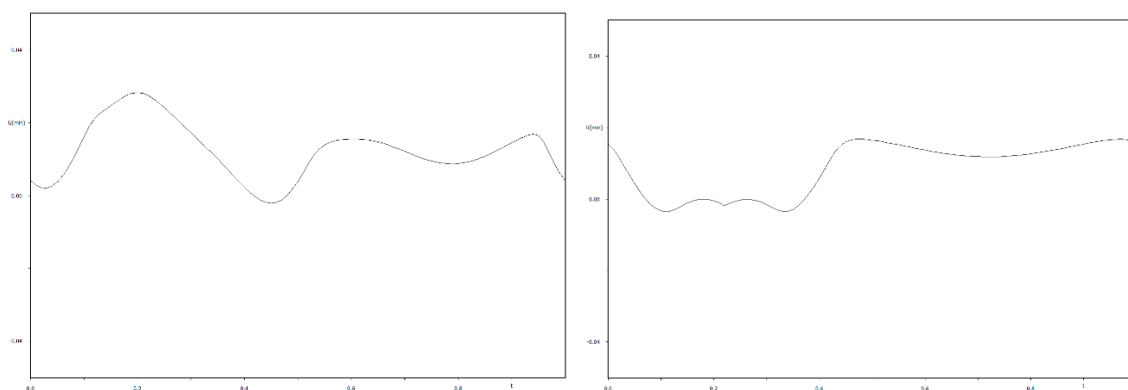
For “Central atom” use “O1” (the label may differ)

For “Principal” select “U(min)”; OK

The following plot shows that $U(\min)$ is negative for a small region of t



Create the same graphs for O4 and O5



Decreasing of number of ADP modulation waves often solves such situation:

*In Atoms/Edit select all oxygen atoms and decrease number of ADP modulation waves to 1
Check refinement listing and Graphs graphs*

In our case it only helps for O4. The reason for bad ADP modulation of some oxygen atoms is probably caused by the fact the sample is more complicated than presented here. High exposition reveals another set of weak satellites, which need another q -vector for their indexing. The five-dimensional structure remains unsolved.