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# Example 2.1: PbSO<sub>4</sub>

## Simple structure from powder data

Revised: 4 October 2015

### PbSO<sub>4</sub>

Powder data measured with laboratory diffractometer

Input files: PbSO4.mac (powder profile data)  
PbSO4.txt (additional information)

#### 1. *Creating new jobname*

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click PbSO4

#### 2. *Import Wizard*

Select “Various CW formats”, NEXT

CW stands for constant wavelength

Select “MAC format” and “Another/unknown method”; NEXT

File name is automatically set to “PbSO4.mac”.

Fill cell parameters 8.48 5.4 6.96 90 90 90

For wavelength type first select Kalpha1/Kalpha2 doublet and then select X-ray tube Cu

Select “Parallel setting”, “Glancing angle” 13.28815, “Perfectness 0.5”; NEXT; FINISH

Accept the data in Data repository

Select “Yes, I would like to continue with the wizard”; OK

At this point Jana2006 offers wizard for determining powder profile parameters, space group and structure. We shall use the wizard but all its tools could be also started separately.

#### 3. *Refinement of the powder profile*

*[On the screen: Refinement of the powder profile by the le Bail algorithm]*

“Show powder profile”

Profile viewer shows experimental powder profile

Leave profile viewer

“Edit refinement commands”; set 0 cycles; leave other settings default; OK

“Run Refine”

“Show powder profile”

*Now the profile viewer shows experimental and calculated powder profile.*

*The calculated profile is based on default profile parameters.*

*The calculated profile is stored in PbSO4.prf*

Leave profile viewer

“Edit profile parameters”

*[On the screen: Powder options]*

In “Cell” page select refinement of a, b and c

In “Profile” page select Cutoff to 12\*FWHM; activate refinement of GW;

In “Corrections” page activate refinement of “shift”;

In "Corrections" page select "Legendre polynomials" with 5 terms for background calculation

*Refinement of background terms is enabled by default*

Leave Powder options, save changes

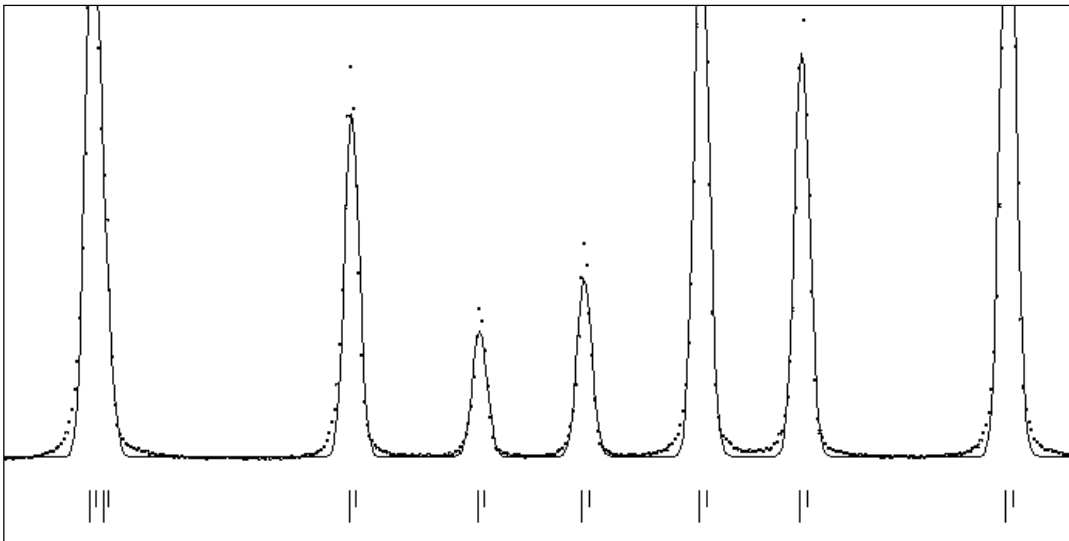
"Edit refinement commands"; set 10 refinement cycles; OK

"Run Refine"

*After 10 refinement cycles  $R_p \sim 11.4\%$ .*

"Show powder profile"

In Powder profile viewer press "Default" and move close to theta 20°



*The observed peaks are systematically broader which may indicate that Lorentzian broadening is to be combined with the Gaussian profiles.*

"Edit profile parameters"

[On the screen: Powder options]

In page "Profile" select Pseudo-Voigt and activate refinement of LY;

"Run Refine"

*After 10 refinement cycles  $R_p \sim 8\%$*

"Show powder profile"

"Edit profile parameters"

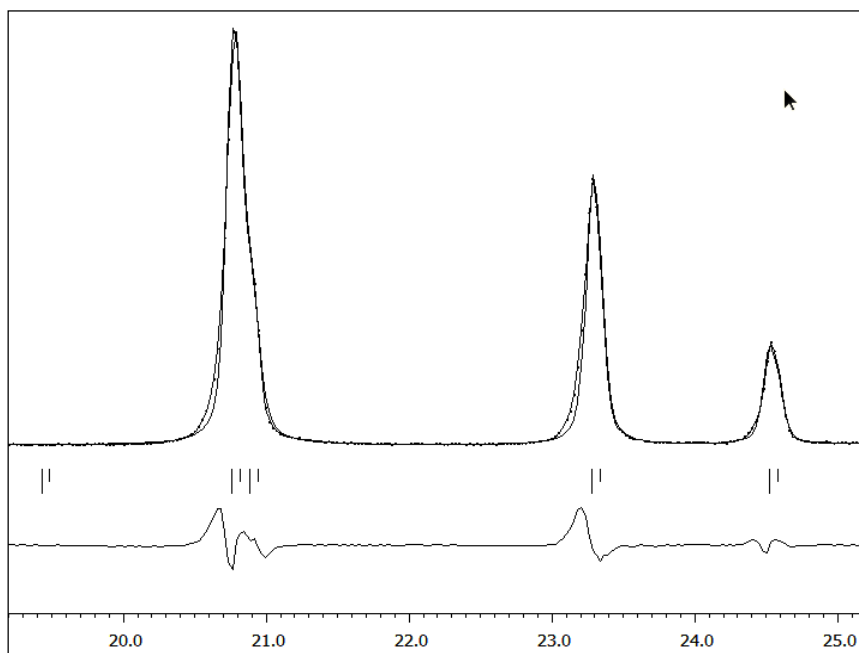
[On the screen: Powder options]

In page "Profile" activate refinement of LX.

"Run Refine"

*After 10 refinement cycles  $R_p \sim 6.2\%$*

"Show powder profile"



The observed peaks at low angles still have some asymmetry. (Use “X+” and “X-“ buttons to see it better)

“Edit profile parameters”

[On the screen: Powder options]

In page “Asymmetry” select the Berar-Baldinazzi correction and activate refinement of asym1, asym2, asym3, asym4;

“Run Refine”

After 10 refinement cycles  $R_p \sim 5.4\%$

FINISH; Yes to close the refinement tool; Next

#### 4. Space group determination

[On the screen: Tolerances for crystal system recognition]

Use default; NEXT

[On the screen: Select Laue symmetry]

Select the highest one – orthorhombic; NEXT

[On the screen: Select cell centering]

The table shows  $R_p$  values calculated for various centering vectors. For instance, when we introduce A centering and discard corresponding extinct Bragg positions,  $R_p$  becomes about 30%. This indicates we don't have A centering. In our case no centering is indicated.

Select P centering as it gives much better profile fit; NEXT

[On the screen: Information about progress of space group tests. It takes some time...]

[On the screen: Select space group];

Among the space groups with good profile fit we are looking – in analogy with a single-crystal experiment – for a space group with maximum number of extinct reflections consistent with the experiment. The space groups  $Pnma$  and  $Pn2_1a$  have good profile fit ( $R_p \sim 5.4\%$ ) and the largest ratio of systematically extinct reflections (about 13%). We shall select the centrosymmetric one.

Select space group  $Pnma$ ; NEXT

[On the screen: Final step of the space group test];

Accept the space group transformed into the original cell; FINISH  
NO to refine profile parameters once more.

## 5. Structure solution

[On the screen: Structure solution]

This part of wizard can be also started separately by “Run → Solution”

Type formula Pb S O4; Formula units 4

Select “Use Superflip”

Check “Repeat Superflip until the convergence is detected”



Set “Maxcycles” to 1000

Press “Run solution” to start Superflip

Jana makes LeBail decomposition and then it starts Superflip.

Superflip confirms space group Pnma

Close listing of Superflip; “Draw structure”; “Draw+continue”.

For plotting with Diamond use button  at the bottom toolbar and plot only Pb and S. In Build → Connectivity adjust limits for S-O distances. The complete coordination of Pb and S with .

The sulphur atom should be coordinated by four oxygen atoms. But as the structure contains one very heavy atom it may happen that some of O atoms are missing or that the solution contains some spurious peaks or that SO<sub>4</sub> tetrahedron is incomplete.

**If the structure model looks strange you may repeat the solution step with “Run → Structure solution”.** Superflip starts from random phases and its results can be different.

Press “Accept last solution”. This action will also close the structure solution wizard.

## 6. Refinement of the structure

[On the screen: basic window of Jana]

Open refinement options (by the right-click on the icon of Refine).

[On the screen: refinement options]

Uncheck "Make only profile matching", OK, Yes+start

Wait for convergence and open the listing. (You can access the listing of Refine also by "Edit/View → View of Refine")

It may happen that Refinement fails. In such case use "Tools → Recover files" and repeat Structure solution. Superflip starts from random phases and may return better result in the next attempt.

Press "Go to" and select "Changes overview":

```
Refinement program                               page= 8
structure :                                       17:29:45 20-09-09

*****
* Changes overview *
*****

More realistic s.u.'s can be achieved by applying the Berar's factor : 2.741
The correction hasn't been applied
The following atoms where disabled as their Uiso was too large:
O4

      scale1  scale2  scale3  scale4  scale5  scale6  ch/su
3      0.273257* 0.000000 0.000000 0.000000 0.000000 0.000000 -1.22
4      0.272774* 0.000000 0.000000 0.000000 0.000000 0.000000 0.13
5      0.272000* 0.000000 0.000000 0.000000 0.000000 0.000000 0.13
```

At the beginning of "Changes overview" there will be probably list of spurious atoms automatically excluded from the refinement as their ADP is larger than the allowed limit. In this example this is O4. The excluded atoms are still present in M40 file with zero occupation. In order to delete them:

Run "Edit atoms", press "Select rejected"

Press the button Action and delete them; OK

Start EditM50, select page "Composition" and press "Formula from M40". It should display "Pb S O4".

## 7. Completing the structure

In the case that some of oxygen atoms are still missing they can be localized from the difference Fourier.

If your structure is complete (EditM50 displays correct formula) but you would like to try this part, please start "Edit Atoms", delete some oxygen and repeat refinement to prepare proper input for Fourier calculation)

Right-click on the Fourier icon opens the command editing procedure for Fourier.

Select "F(obs)-F(calc) – difference Fourier"; OK; Start the program;

Answer "Yes" to start the procedure for including atoms.

[On the screen: Inserting/replacing atoms]

The program transforms each found maximum to various symmetry equivalent positions where it is close to some already existing atoms. In this dialogue we choose that the right panel will show only atoms with distance to some (transformed) Fourier maximum between 1 and 3 Å. By selecting such line we select the maximum and it corresponding symmetry transformation.

**Inserting/replacing of atoms**

Skip peaks being too close to existing atoms

Minimal distance  Angs.

Show distances up to  Angs.

Include all missing atoms, i.e. the maxima with large enough charge and reasonable distance to some of already existing atoms; FINISH

*It may happen there are no such maxima*

Verify the added maxima with plotting tool.

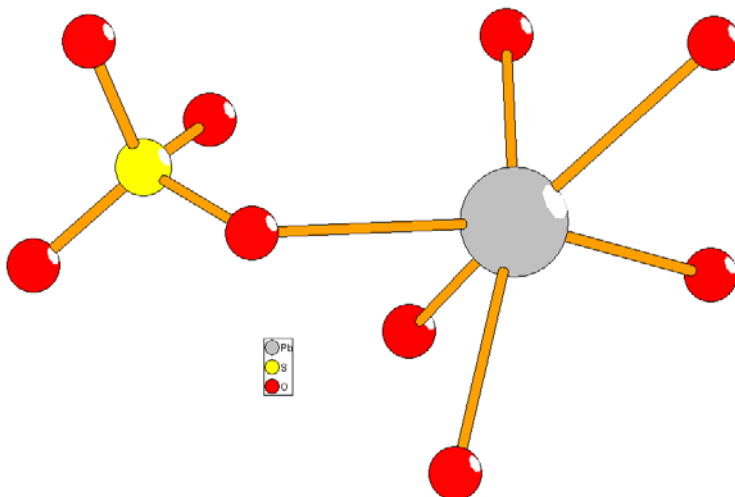
Verify the formula with "Editm50 → Composition → Formula from M40"

Repeat refinement (in case of changes)

*Refinement should converge with Rp around 6.7%, GOF 1.8 and structure R factor around 3.5%.*

"Edit/View → View of Refine"; GoTo; List of serious warnings

*This list should be empty. This means for instance that ADP are positive definite.*



*The resulting structure*

```
R factors : [384=381+3/17]
R(obs)= 3.49 wR(obs)= 4.04 R(all)= 3.54 wR(all)= 4.05
=====
Profile R factors :[5769/16+17], Damping factor: 1.0000
GOF = 1.79 Rp = 6.69 wRp = 8.83
Last wRp: 8.83
Maximum change/s.u. : -0.0070 for b
```

*The resulting R values*



# Example 2.2: Y<sub>2</sub>O<sub>3</sub>

## Le Bail refinement against powder data with strong asymmetry of peaks

Revised: 4 October 2015

Powder data measured with laboratory diffractometer experimental setup with Johansson-type monochromator and transmission mode in asymmetric Guinier type arrangement.

Input files: Y2O3-icsd.cif (crystal structure from data base)  
Y2O3.dat (powder diffraction data)

### 1. Creating new jobname

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click Y2O3

### 2. Import procedure

Select "Structure: from CIF"; NEXT

[On the screen: Select input CIF file]

Select "Y2O3-icsd.cif"; OK

[On the screen: "CIF file does not contain any reflection block"]

Answer "Yes" to the question: "Do you want to import data from file?"

[On the screen: Specify type of the file to be imported]

Select "Powder data: various CW formats" (CW = constant wavelength); NEXT

[On the screen: Powder data from:]

Select "Riet7 formats"; NEXT

[On the screen: Complete/correct experimental parameters]

For wavelength type use "X-ray tube" Cu, Kalpha1/Kalpha2 doublet deselected and wavelength 1.54051

Select "Parallel setting", "Glancing angle" 13.6409 (CuK<sub>α</sub>, Ge[111]) "Perfectness 1"; NEXT; FINISH

Accept the data in Data repository

### 3. Refinement of the powder profile

[On the screen: Basic Jana window]

Start "Edit profile"

[On the screen: Powder options]

In "Cell" page select refinement of the parameter a

In "Profile" page select Cutoff to 12\*FWHM; activate refinement of GW

In "Corrections" page activate refinement of "shift"

In "Corrections" page select "Legendre polynomials" with 5 terms for background calculation

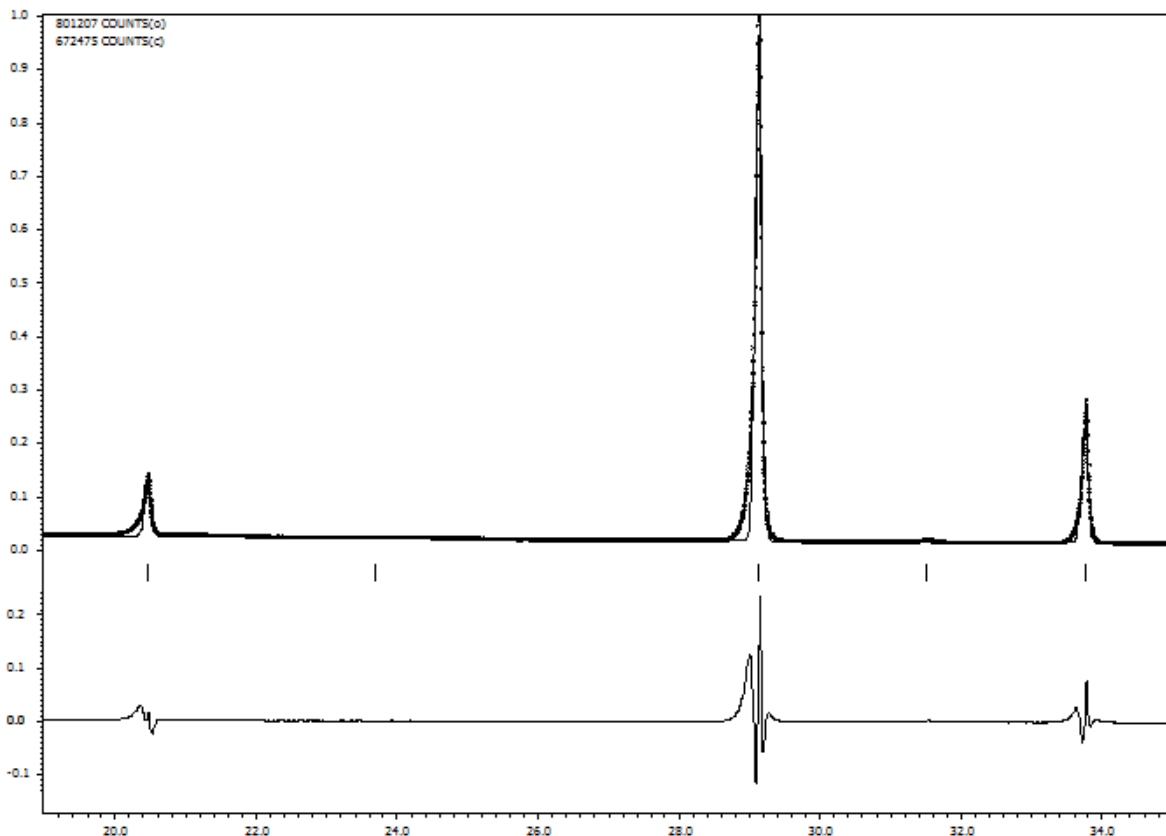
Refinement of background terms is enabled by default

Leave Powder options, save changes

[On the screen: Basic Jana window]

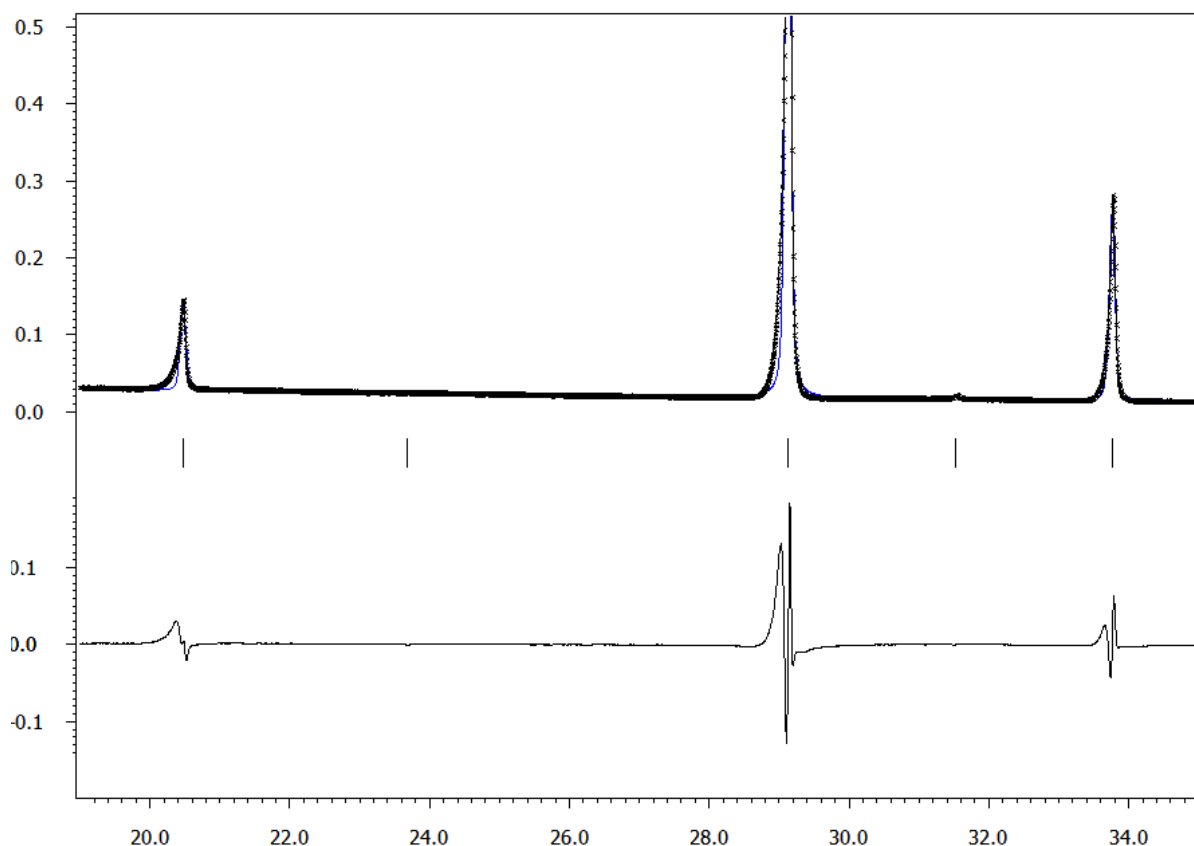
Right click on the Refine icon;

Check "Make only profile matching";  
 Keep default values for another parameters; OK;  
 [On the screen: Do you want to save new command?]  
 Select Yes+start  
 Refinement converges in 10 cycles to  $R_p \sim 7.7\%$   
 Start "Profile viewer"  
 [On the screen: Jana 2006 profile viewer]  
 Press "X exactly" and select the  $2\theta$  interval from 19 to 35.



The observed peaks are systematically broader which can indicate that Lorentzian broadening is to be combined with the Gaussian profiles.

Start "Edit profile"  
 [On the screen: Powder options]  
 In page "Profile" select Pseudo-Voigt and activate refinement of LY; OK  
 Yes to rewrite changes  
 Start refinement (icon Refine)  
 Refinement converges in 10 cycles to  $R_p = 7.1\%$   
 Start "Edit profile"  
 [On the screen: Powder options]  
 In page "Profile" activate refinement of GU; OK  
 Yes to rewrite changes  
 Start refinement (icon Refine)  
 Refinement converges in 10 cycles to  $R_p \sim 7.0\%$   
 Start "Profile viewer"  
 [On the screen: Jana 2006 profile viewer]  
 Press "X exactly" and select the  $2\theta$  interval from 19 to 35.



The experimental peaks have very strong asymmetry which is not explained by the profile model.

#### 4. Asymmetry correction by the Simpson's model

[On the screen: Basic Jana window]

In order to save the basic refinement result for testing of all different asymmetry models a new structure will be opened:

Start "File → Structure → Save As"

[On the screen: File manager for saving structure]

In File manager focus the right-bottom textbox and define a name for testing of the Simpson's model, for instance "Y2O3-Simpson"; OK

Yes to continue with the new structure

[On the screen: Basic Jana window]

Start "Edit profile"

[On the screen: Powder options]

In page "Asymmetry" select "Simpson", use the default value and activate refinement of the "asym1" parameter; OK;

Yes to rewrite changed files

[On the screen: Basic Jana window]

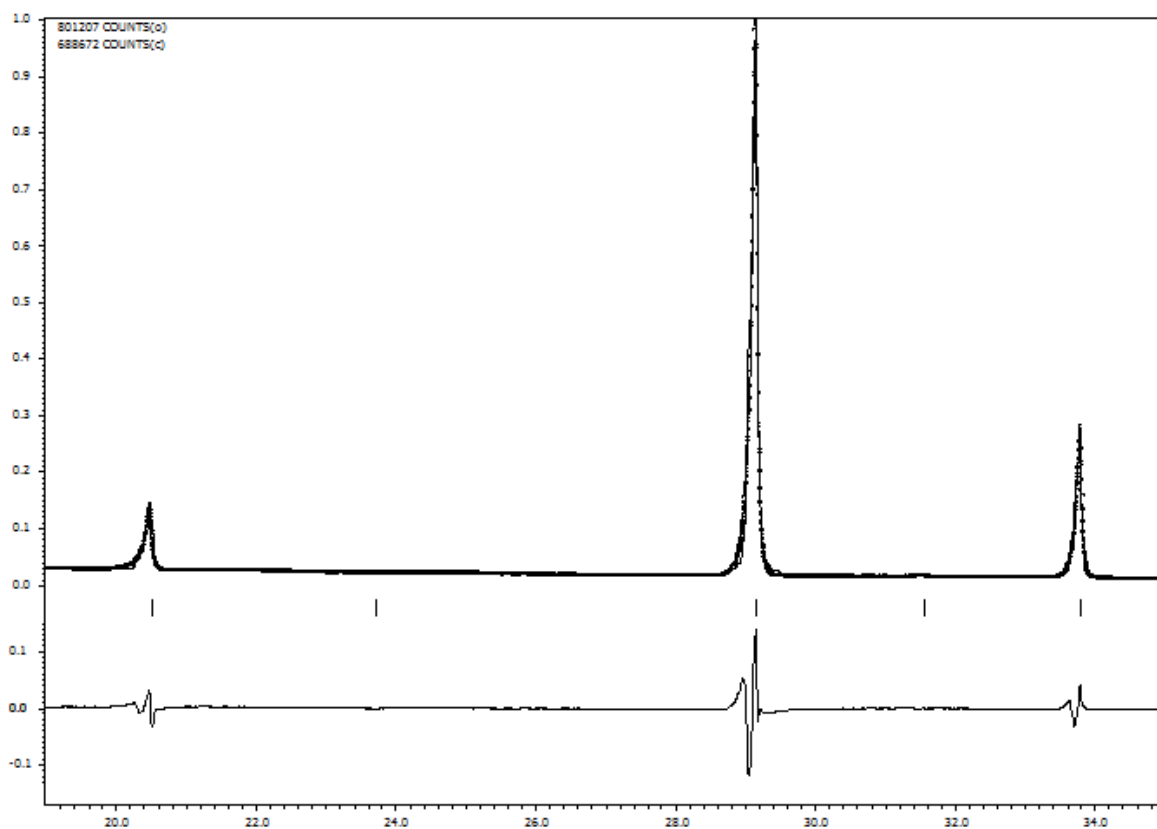
Double-click the icon Refine.

Refinement converges in 10 cycles to  $R_p \sim 6.1\%$

Start "Profile viewer"

[On the screen: Jana 2006 profile viewer]

Press "X exactly" and select the  $2\theta$  interval from 19 to 35.



The Simpson's model improves considerably the profile fit. But some discrepancies due to asymmetry are still visible.

## 5. Asymmetry by Berar-Baldinozzi

[On the screen: Basic Jana window]

Start "File → Structure → History"

[On the screen: History]

Select the original structure Y2O3; OK

[On the screen: Basic Jana window]

Start "File → Structure → Save As"

[On the screen: File manager for saving structure]

In File manager focus the right-bottom textbox and define a name for testing of the Berar-Baldinozzi model i.e. "Y2O3-BB"; OK

Yes to continue with the new structure

[On the screen: Basic Jana window]

Start "Edit profile"

[On the screen: Powder options]

In page "Asymmetry" select "Berar-Baldinozzi", use the default value and activate refinement of the `asym1`, `asym2`, `asym3` and `asym4` parameters; OK;

Yes to rewrite changed files

[On the screen: Basic Jana window]

Start "Refine commands" (right-click on the icon "Refine")

In page "Basic" set 100 refinement cycles and Damping factor 0.3

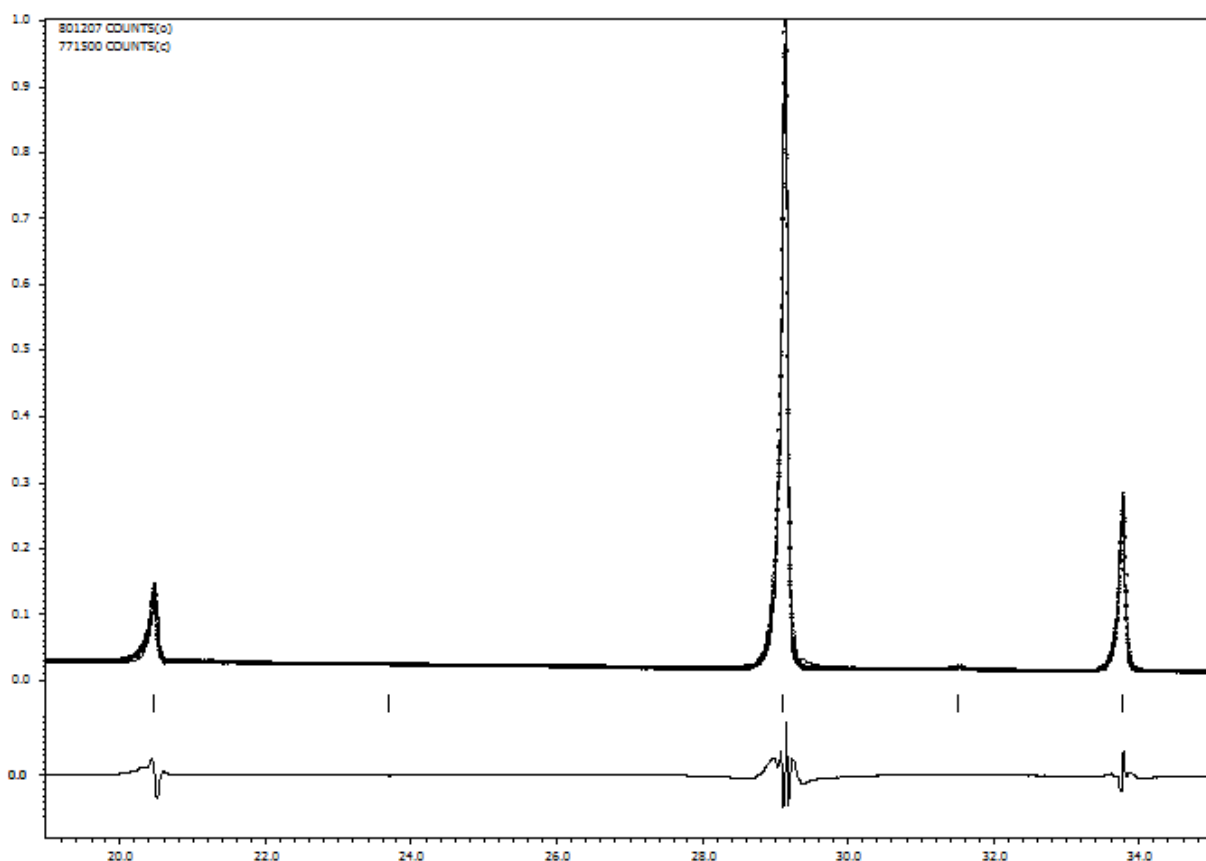
OK; YES+START to save commands and start refinement.

Refinement converges after many cycles to  $R_p \sim 5.8\%$

Start "Profile viewer"

[On the screen: Jana 2006 profile viewer]

Press “X exactly” and select the  $2\theta$  interval from 19 to 35.



The fit is even better than for the previous method but the number of asymmetry parameters is now four.

## 6. Asymmetry by axial divergence

(Finger, Cox, Jephcoat, *J.Appl.Cryst.*(1994). 24, 892-900)

[On the screen: Basic Jana window]

Start “File → Structure → History”

[On the screen: History]

Select the original structure Y2O3; OK

[On the screen: Basic Jana window]

Start “File → Structure → Save As”

[On the screen: File manager for saving structure]

In File manager focus the right-bottom textbox and define a name for testing of the axial divergence correction i.e. “Y2O3-FCJ”; OK

Yes to continue with the new structure

[On the screen: Basic Jana window]

Start “Edit profile”

[On the screen: Powder options]

In page “Asymmetry” select “correction by divergence”, use the default value and activate refinement of the HpS/L and HmS/L parameters; OK;

Yes to rewrite changed files

[On the screen: Basic Jana window]

Right-click the icon Refine

[On the screen: Refine commands]

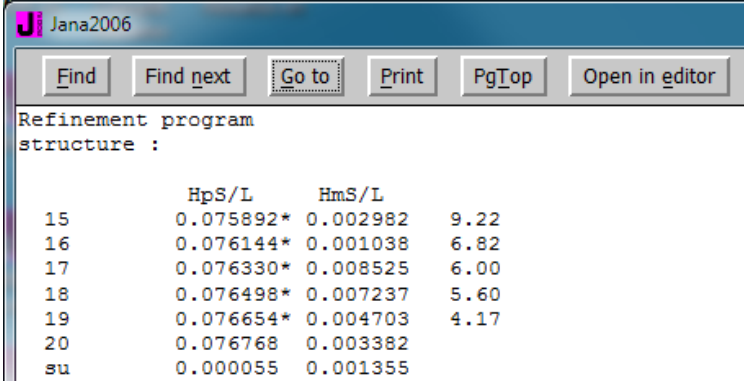
In page "Basic" set 30 refinement cycles and Damping factor 0.5

OK; Yes+start to save the changes and start refinement

Refinement reaches after 20 cycles  $R_p \sim 4.8\%$

Open the refinement listing. (You can access the listing of Refine also by "Edit/View → View of Refine").

Press "Go to" and select "Changes overview":



	HpS/L	HmS/L	
15	0.075892*	0.002982	9.22
16	0.076144*	0.001038	6.82
17	0.076330*	0.008525	6.00
18	0.076498*	0.007237	5.60
19	0.076654*	0.004703	4.17
20	0.076768	0.003382	
su	0.000055	0.001355	

The parameter  $HmS/L$  oscillates, within three times the standard uncertainty, about zero which induces instability in the refinement. For this reason, we can change it to zero and keep it fixed.

Start "Edit profile"

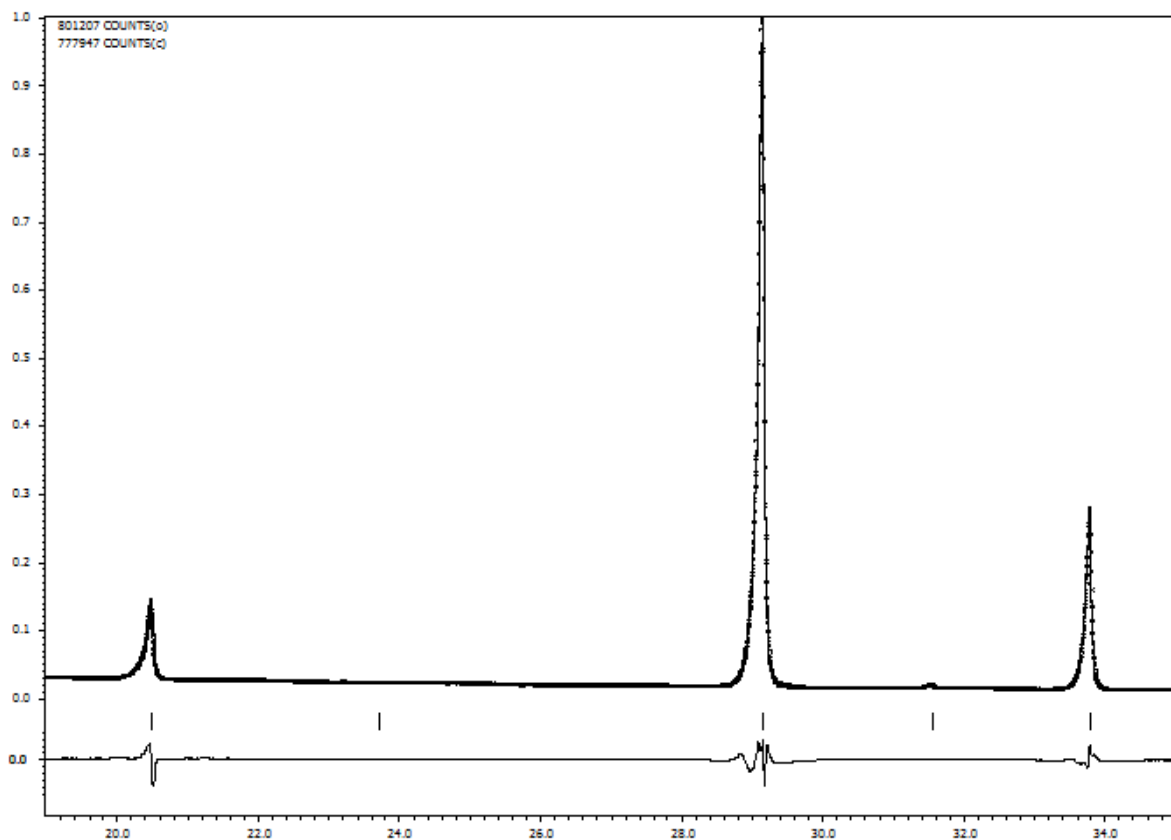
In page "Asymmetry" set  $HmS/L$  to zero and unselect it; OK;

Refinement reaches after 20 cycles  $R_p \sim 4.9\%$

Start "Profile viewer"

[On the screen: Jana 2006 profile viewer]

Press "X exactly" and select the  $2\theta$  interval from 19 to 35.



*With only one additional free parameter the fit is significantly better than for the previous methods.*

*In Jana2006 there is also implemented the fundamental approach following closely the approach described by Cheary and Coelho [J. Appl. Cryst. (1998). 31, 851-861; J. Appl. Cryst. (1998). 31, 862-868]. This method was not applied in our example because it was developed for Bragg-Brentano geometry.*

# Example 2.3.3: MagCag

Solution of simple organometallic structure from powder data, using the rigid body template from M45

Revised: 4 October 2015

Powder data measured with diffractometer Empyrean (PANalytical) using CuK $\alpha$  radiation, focusing mirror and Debye-Scherrer geometry (sample in capillary), at ambient temperature.

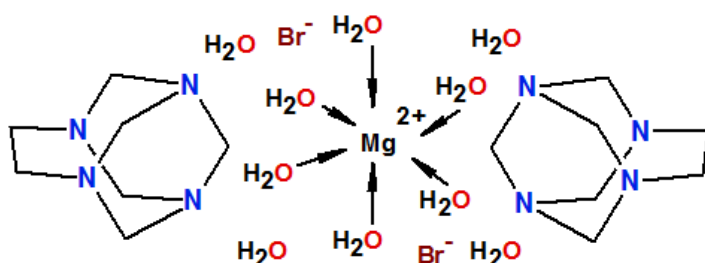
Input files: magcag.xrdml with powder profile

Magcag-symmC1.m45 and Magcag-symmCs.m45: rigid body templates prepared in Example 2.3.2

Additional information:

unit cell 9.19 21.38 8.12 90 113.78 90

Expected scheme:



## 1. Creating new jobname

Start Jana2006

"File → Structure → New" opens a file manager

Left pane: locate directory with input files

Right pane: double-click magcag

## 2. Import procedure

Select "Powder data – various CW formats"; NEXT

[On the screen: Powder data form]

Select "PANalytical XRDML"

For method select "Debye-Scherrer"

[On the screen: Complete/correct experimental parameters]

Fill cell parameters

Check the radiation (should be interpreted from the xrdml file as Copper with doublet):



<input checked="" type="radio"/> X-rays	<input type="text" value="X-ray tube"/>	<b>Polarization correction:</b>
<input type="radio"/> Neutrons		<input type="radio"/> Circular polarization
<input type="radio"/> Electrons		<input type="radio"/> Perpendicular setting <input type="button" value="Info"/>
<input checked="" type="checkbox"/> Kalpha1/Kalpha2 doublet		<input checked="" type="radio"/> Parallel setting <input type="button" value="Info"/>
Wave length #1	<input type="text" value="1.540598"/>	<input type="radio"/> Guinier camera
Wave length #2	<input type="text" value="1.544426"/>	<input type="radio"/> Linearly polarized beam
I(#2)/I(#1)	<input type="text" value="0.5"/>	<b>Monochromator parameters:</b>
Temperature	<input type="text" value="293"/>	Perfectness
		<input type="text" value="0.5"/>
		Glancing angle
		<input type="text" value="13.2776"/> <input type="button" value="Set glancing angle"/>

NEXT; FINISH; OK to close data repository; YES to accept the data set

[On the screen: question how to continue]

Select "Yes, I would like to continue with the wizard"; OK

The typical steps for refinement of powder profile will be offered in the wizard. However, all steps can be also done separately from the basic window of Jana2006.

### 3. Refinement of the powder profile

[On the screen: refinement of the powder profile by the le Bail algorithm]

Press "Show powder profile"

Press "Default" to see more details

Press "Create new" to create a manual background

[On the screen: Options for generating background profile]

For "Number of manual background points" set 60

OK; Quit powder viewer

[On the screen: A manual background has been created]

Select "Accept the new background" and "Reset polynomial coefficients to zero"

The manual background was created because with this data background calculated with Legendre polynomials would not be correct for high angle reflections. (For detail see example 2.4 – PFPhenyl)

Press "Edit profile parameters"

In page "Profile" activate refinement of GW

Unlike for structure parameters, refinement keys of profile parameters are not set automatically

In page Corrections:

Set 30 for "Number of terms" of Legendre polynomials

Polynomial background will be refined in addition to the manual one

Activate refinement of "shift";

OK; Yes to rewrite

Press "Edit refinement commands"

Set 100 refinement cycles

OK

Press "Run Refine"

Refinement of profile slowly converges to the profile R value  $R_p \sim 2.9\%$  and GOF  $\sim 7.3$ .

Waiting for the full convergence is not necessary. Refinement can be interrupted by End or Cancel - in this case End should be used in order to see the latest difference curve in the powder profile viewer.

"Show Powder profile"; "Default"

Move the slider towards low angles; "Fit Y"

*The calculated profile fits quite well with the experimental one but some profiles are too narrow, especially for low angles*

Quit profile viewer

"Edit profile parameters"

In page "Cell" activate refinement of a,b,c,beta

In page "Profile" activate refinement of GV

OK, YES to save changes

Run several cycles of Refine

*Refinement of profile slowly converges to the profile R value  $R_p \sim 2.8\%$  and GOF  $\sim 7$*

*For Gaussian parameters an important rule is that they cannot be refined all together because they are linearly dependent. Usually we refine GW, then GV and finally GU. In our case GU would not improve the fit.*

In page "Profile" change the type of the peak-shape function to "Pseudo-Voigt", activate refinement of LX and LY

OK, YES to save changes

"Run Refine"

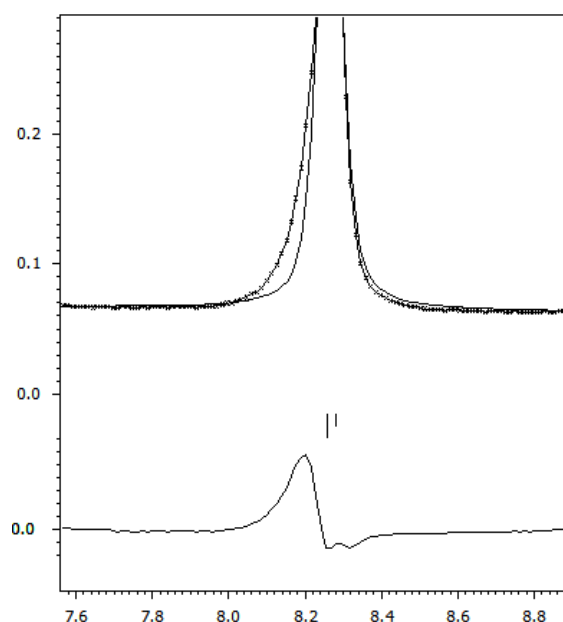
*In case of oscillations press "Parameters" (during the refinement) and change "Damping factor" to 0.5*

*Refinement of profile slowly converges to the profile R value  $R_p \sim 1.7\%$  and GOF  $\sim 4.3$ .*

"Show Powder profile"

Enlarge the profile and investigate details of the fit between the calculated and experimental profile.

*We are especially interesting whether asymmetry of peaks has been correctly described. Not correctly described asymmetry can be found for low angle reflections:*



"Edit profile parameters"

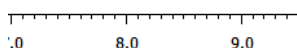
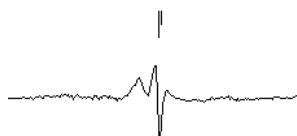
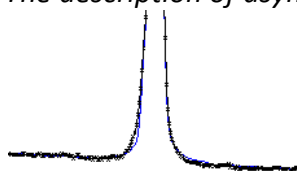
In page "Asymmetry/Diffractometer" select "correction by divergence"

Activate refinement of "HpS/L" (do not refine HmS/L)

"Run Refine"

*Refinement of profile slowly converges to the profile R value  $R_p = 1.4\%$  and GOF  $\sim 3.1$ . "Show Powder profile"*

The description of asymmetry for the low angle peak is considerably improved:



Quit the profile viewer

Press "Save As" and **make a backup copy** of the structure

FINISH to close the Powder wizard

#### 4. **Space group determination**

[On the screen: Tolerances for crystal system recognition]

Use default; NEXT

[On the screen: Select Laue symmetry]

Select the highest one – monoclinic; NEXT

[On the screen: Select cell centering]

Select P centering as it gives the best profile fit; NEXT

[On the screen: Select space group]

Select space group *P21/a*; NEXT

[On the screen: Final step of the space group test];

Accept the space group transformed into the original cell; FINISH

YES to refine profile parameters once more.

*This new profile refinement uses only independent Bragg reflections compatible with *P21/a*.*

*The results are almost the same like for *P-1* but calculation taking into the account the symmetry is faster.*

#### 5. **Structure solution**

[On the screen: information that the solution wizard will start]

OK

Type formula Mg O10 H40 Br2 N8 C14; Formula units 2

Select "Use Superflip"

Check "Repeat Superflip: Number of runs" and choose 10 runs

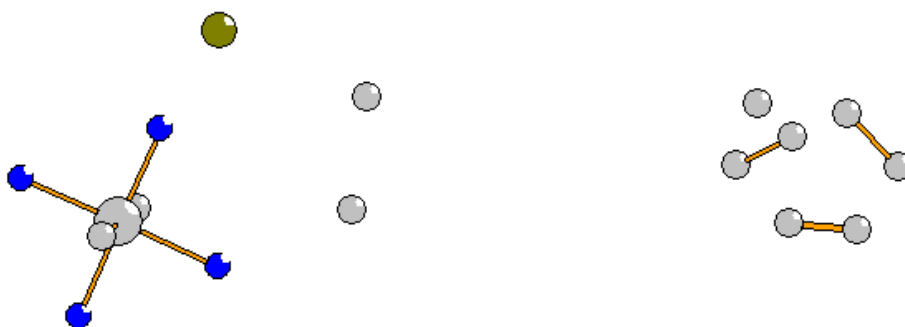
*With this setting Superflip will run ten times and a solution with best R value will be used*

*"Run Solution"*

*In case that Superflip does not converge interrupt the calculation, discard the results and repeat it. It will start from a new set of random phases and the result may be different. The agreement factors of the symmetry printed at the bottom of the Superflip listing will be between 10-20, indicating rather worse fit for the screw axis.*

Press the button "Draw structure"

The initial structure model contains octahedrally coordinated Mg located in one of inversion centers, isolated Br, two oxygens of the water molecules, a fragment of the  $N_4C_7$  cage and probably some false maxima. For instance:



Press button "Accept last solution"

#### 6. Preparation of the starting Rietveld refinement

Start "Edit atoms" and change chemical types of atoms coordinated to Mg to oxygen  
Change to oxygen also the two carbon atoms, which are in fact lattice water molecules  
Rename the changed atoms according to their chemical types

OK; YES to save changes

Start "Refine commads"; go to page "Basic"

Set 100 refinement cycles with Damping factor 0.1

Uncheck "Make only profile matching"

OK; YES to save changes without starting refinement

Start "Edit profile"

Fix all profile parameters: a, b, c, beta, GW, GP, LX, LY, HpS/L, shift

*This means that only Legendre background will be refined*

OK, YES to save changes

Start File → Structure → Save as and **make a backup copy** named "start"

#### 7. Completing the cage

Start "Refine commands"; go to page "Various"

Press "Fixed commands"

Fix all parameters for O\* Mg\* Br\*; OK

Press "Restrictions"

Restrict ADP of C\* to be the same; OK

*Be careful not to restrict coordinates!*

OK; YES+Start

*During refinement you may change damping from 0.1 to 0.5*

*Refinement converges with  $R \sim 11\%$ ,  $R_p \sim 10\%$ ,  $GOF \sim 23$*

Run difference Fourier, YES to start procedure for inserting atoms

Insert new maxima in reasonable distances to the atoms of the cage

Repeat refinement

Repeat difference Fourier and inserting of maxima until 11 carbon atoms is present


“Reasonable distance” should not be taken too strictly for Fourier maxima from powder data

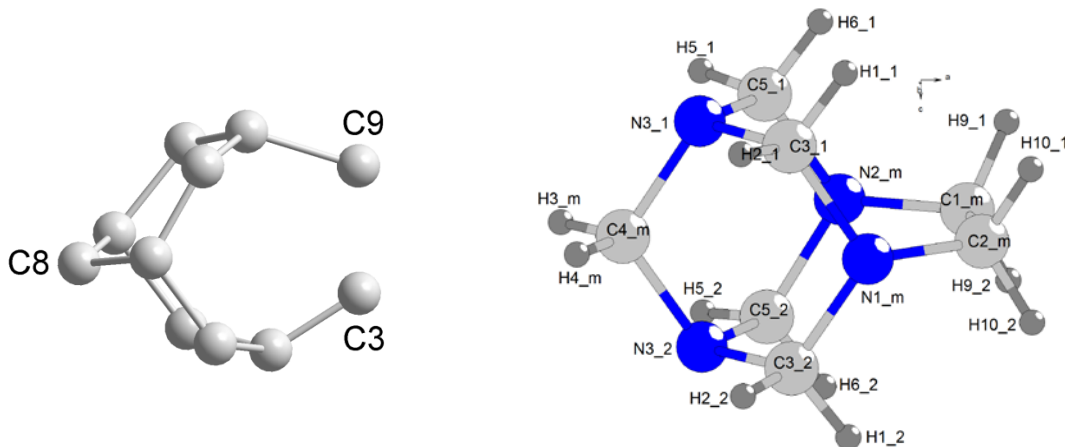
Refinement converges with  $R \sim 5\%$ ,  $R_p \sim 4\%$ ,  $GOF \sim 8$

Start File → Structure → Save as and make a backup copy named “cage\_atomic”

## 8. Placing the cage template with point group symmetry C1

Start “Plot structure”

Using the button  plot the atoms of the cage and ensure they make a symmetry contiguous motif. If not, return to Jana, start Edit atoms and put C\* to symmetry contiguous motif. Otherwise placing of the molecule will not work.



Plot the cage and compare with the template prepared in the previous example. Probably C9 corresponds to C1\_m; C3 corresponds to C2\_m; C8 corresponds to C4\_m (**your labels can be different!**)

Return to Jana2006

Start “Parameters → Molecules → New molecule”

[On the screen: Atoms of the new molecule from:]

Select “Model file”

For name of the molecule type “kage”

We need a name not starting with C, N, O, B, H and M

For “Model name” browse for “Magcag-symmC1.m45” created in the previous example

Keep the scaling distance unchanged

“Show the model molecule” is disabled because we don’t have Magcag-symmC1.jpg

NEXT

[On the screen: Specify atomic types in the model molecule]

Do not change the suggested atomic types; NEXT

[On the screen: Define the molecular reference point]

Select “Explicit”

In “Reference point” textbox type N1\_m

The reference point should be some atom from the mirror plane in order to reflect the symmetry of the molecule. Such atoms in the model molecule have suffix \_m (see Example 2.3.2)

NEXT

[On the screen: Define and complete molecular position #1]

For the pairs “model atoms” – “actual positions” choose c1\_m and C9; C2\_m and C3; C4\_m and C8 (**with actual names** taken previously from Diamond)

For "Maximal coincidence distance" type 0.5

The coincidence ration should be 11/25 but it depends on the previous refinement

Try to adjust the coincidence distance to reach 11 coinciding carbons.

If carbons of the model molecule coincide e.g. with oxygens this means that the cage has been positioned incorrectly, probably because the carbon atoms in the atomic part do not form a symmetry contiguous motif.

Press "Apply+End"

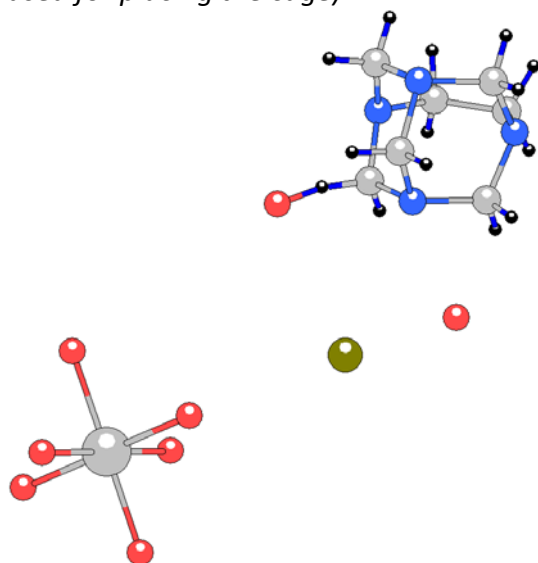
Start "Edit atoms"

Ensure that the atomic part does not contain carbon atoms.

OK, YES to save changes

Start "Plot structure"

The structure with the cage should look like this (depending which carbon positions were used for placing the cage):



In this example one water oxygen is too close to the cage but it may change during the refinement

Return to Jana2006

Start "Refine commands"; go to page "Various"

Press "Fixed commands"

Fix "all parameters" for C\*, H\*, N\* (i.e. for atoms of the cage)

Because the molecule is called "kage", the wild character C\* does not include the molecule and therefore molecular parameters (rotations and translation of the cage), will not be fixed.

OK; OK; YES+START to save changes and start refinement

During refinement you may change damping from 0.1 to 0.5

After many cycles refinement converges with R~4.5%, Rp~4%, GOF~9

Start "Plot structure"

The cage should be now in better position, i.e. without short distances to lattice water

## 9. Refinement of Mg, O and Br

Start "Refine commands"; go to page "Various"

Press "Fixed commands"

Disable or delete the "fixed all" commands for Mg\* O\* Br\*

OK

Go to page "Equations" and define the following equations:

equation : ai[o2]=ai[o1]

equation : ai[o3]=ai[o1]

equation : ai[o4]=ai[o1]

equation : ai[o5]=ai[o1]

*All oxygens belong to water; refinement of their occupancy mimics the missing hydrogens*  
OK

Go to page "Various", press "restrictions"

Define the same ADP for all oxygen atoms (O\*); OK

*Be careful not to make identical coordinates!*

OK; YES to save commands without starting Refine

Start "Edit atoms"

Set harmonic ADP for Br1

*This works because Br is slightly disordered*

Activate refinement of occupancy (ai) of O1

OK, YES to save changes

Start "Refine"

*The refinement converges with R~3%, Rp~2.3%, GOF~5*

## 10. Refinement of atoms of the cage

Start "Edit atoms"

Select all carbon atoms of the cage (blue carbons)

Press "Action → Adding of hydrogen atoms"

*This procedure will not add hydrogens, because they are already present, but it will introduce Keep commands necessary for fixing of their geometry*

OK; YES to save changes

Start "Refine commands"; go to page "Various"

Press "Restrictions"

Define the same ADP for all nitrogen atoms (N\*)

*Be careful not to make identical coordinates!*

OK

Press "Fixed commands"

Disable or delete the "fixed all" command for C\* N\* H\*

OK; go to page Basic

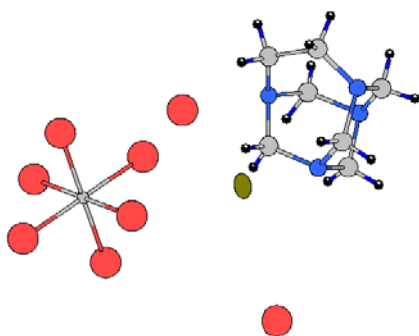
Set "Damping factor" 0.1

OK; YES+START

*The refinement converges with R~2.8%, Rp~2.1%, GOF~4.3*

Start "Plot structure" verify the structure

*Final plot:*



Make backup copy

### 11. Placing the cage template with point group symmetry $C_s$

Now we shall test how the cage with  $C_s$  point symmetry would fit

Start "Edit atoms"

Select the model molecule (blue atoms)

Start "Action → Atoms from molecule to atomic part"

OK; YES to rewrite changes

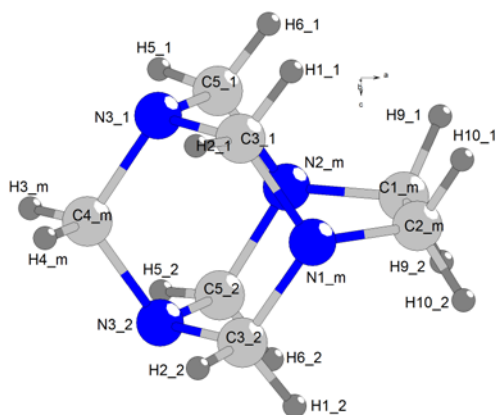
The molecule had only one actual position and therefore this atomic structure model is equivalent with the previous one

Start "Refine"

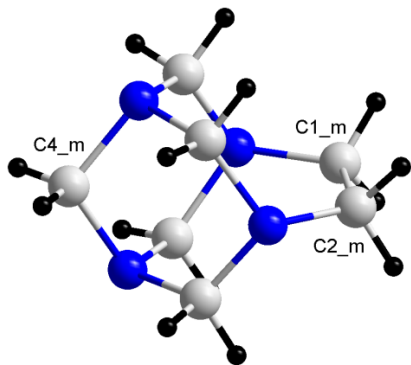
$R$  values must be the same like with the molecule

Now we shall place the template  $C_s$  in such a way that it coincides with the cage present in the atomic part

This is the template how it was created in the example 2.3.2:



Start "Plot structure" and try to orient your cage similarly. Make use of the fact that there is only one C-C bond in the cage.





From the comparison we can see which pairs of atoms should be used for placing the molecule

Return to Jana2006

Start "Parameters → Molecule → New molecule"

[On the screen: Atoms of the new molecule from:]

Select "Model file"

For name of the molecule type "kage"

For "Model name" browse for "Magcag-symmCs.m45" created in the previous example

Keep the scaling distance unchanged

"Show the model molecule" is disabled because we don't have Magcag-symmC1.jpg

NEXT

[On the screen: Specify atomic types in the model molecule]

Do not change the defaults atomic types; NEXT

[On the screen: Define the molecular reference point]

Select "Explicit"

In "Reference point" textbox type N1\_m

This should be some atom from the mirror plane

NEXT

[On the screen: Define and complete molecular position #1]

For the pairs "model atoms" – "actual positions" type the three previously noted pairs

For "Maximal coincidence distance" type 0.6

Press "Show coinciding atoms"

We should see the complete coincidence 25/25 and the coinciding atoms should have the same chemical types.

	Individual atomic positions			distance to	
N1_m	0.773704	0.617148	0.286488	0.068	N2_m
N2_m	0.915984	0.683329	0.081966	0.058	N3_2
N3_1	0.819658	0.573639	0.028719	0.000	N3_1
N3_2	1.046434	0.599749	0.305107	0.020	N1_m
C1_m	0.812606	0.717724	0.144220	0.116	C5_2
C2_m	0.737231	0.682379	0.252867	0.125	C1_m
C3_1	0.715574	0.577568	0.127447	0.047	C5_1
C3_2	0.938936	0.603285	0.399674	0.044	C2_m
H1_1	0.612403	0.593090	0.045690	0.509	H6_1
H1_2	0.978634	0.635256	0.492042	0.139	H10_1
H2_1	0.700096	0.535685	0.163343	0.595	H5_1
H2_2	0.943252	0.563681	0.459695	0.031	H10_2
C4_m	0.977860	0.554390	0.158135	0.137	C3_1
H3_m	1.048065	0.549993	0.096007	0.233	H1_1

Ok

	Individual atomic positions			distance to	
H4_m	0.969985	0.513941	0.207965	0.215	H2_1
C5_1	0.837987	0.634247	-0.048792	0.083	C4_m
C5_2	1.061828	0.660019	0.224019	0.040	C3_2
H5_1	0.898539	0.627373	-0.121264	0.076	H4_m
H5_2	1.141694	0.655369	0.175087	0.047	H2_2
H6_1	0.733458	0.648971	-0.128558	0.118	H3_m
H6_2	1.100287	0.691206	0.318524	0.054	H1_2
H9_2	0.883607	0.752456	0.223110	0.371	H6_2
H9_1	0.723999	0.734079	0.028583	0.155	H5_2
H10_2	0.772972	0.703848	0.372985	0.114	H1c1_m
H10_1	0.618753	0.686092	0.185028	0.391	H2c1_m

Ok

Press "Apply+End"

Start "Edit atoms"

The atomic part should contain only Br1, Mg1 and five oxygens

Start "Plot structure"

The cage should be correctly placed – verify by plotting

In a plot slash "/" means the atoms is transformed by the point group symmetry of the molecule, while "a" indicates the first actual position of the molecule.

## 12. Refinement of the cage with Cs point symmetry

Make backup copy

Start "Refine commands"; go to page "Various"

Press "Keep commands" and delete all of them

OK; OK; YES to save commands without starting Refine  
Start "Edit Atoms"  
Select all carbons  
Start "Action → Adding of hydrogen atoms"  
Select "Try automatic run"  
*The procedure should not add any new hydrogen atoms*  
OK; YES to quit "Edit atoms" and save changes  
Start "Refine Commands"  
Set zero refinement cycles; OK; YES+START  
This applies the previously created keep commands  
Start "Plot structure" and verify hydrogen positions  
Start "Refine commands", set 100 refinement cycles with Damping factor 0.5  
OK; YES+START to save commands and run refinement  
*The refinement has difficulties to reach convergence*  
*The fit is  $R \sim 3.2\%$ ,  $R_p \sim 2.3\%$ ,  $GOF \sim 5$ , 53 structure parameters; i.e. only slightly worse fit comparing with the asymmetric cage*

# Example 6.1: KSm

Modulated structure solved from powder data. Basic steps with powder refinement, mixed sites in 4d.

Revised: 4 October 2015

## K Sm Mo<sub>2</sub> O<sub>8</sub>

Powder data measured with synchrotron radiation

Input files: KSm.dat (powder profile data)  
KSm.txt (additional information)  
KSm.pdf (article about this compound)

### 1. Creating new jobname

Start Jana2006

“File → Structure → New” opens a file manager

Left pane: locate directory with input files

Right pane: double-click KSm

### 2. Import Wizard

Select “Various CW format”, NEXT

*CW stands for constant wavelength*

Type “File name” KSm.dat

Select “Free format of 2th, l, [sig(l)]” and “Another/unknown method”; NEXT

Fill cell parameters 5.5304 5.3019 11.7893 90 90 91.138

*The string can be copied from KSm.txt by CtrlC + CtrlV*

Change “Target dimension” to 4 and fill q vector 0.56883 -0.12885 0

*The string can be copied from KSm.txt by CtrlC + CtrlV*

For wavelength type 0.7114 and select “Linearly polarized beam”; NEXT; FINISH

Accept the data in Data repository

Select “Yes, I would like to continue with the wizard”; OK

### 3. Checking data

*[On the screen: Refinement of the powder profile by the le Bail algorithm]*

“Show powder profile”

*Profile viewer shows experimental powder profile*

*The powder profile is stored in KSm.m95 and in KSm.m90 in analogy to single crystal data*

Leave profile viewer

“Edit refinement commands”; 0 refinement cycles; OK

“Run Refine”

“Show powder profile”

*Now the profile viewer shows experimental and calculated powder profile. The calculated profile is based on default profile parameters. Bragg positions of satellites are green. By default satellites up to the order 1 are used.*

*The calculated profile is stored in KSm.prf*

Leave profile viewer

“Edit profile parameters”

*This opens "Powder options" where profile parameters will be edited  
The profile parameters are stored in file KSm.m41*

#### **4. Refinement of profile parameters**

*[On the screen: Powder options]*

*In the initial state refinement of cell parameters and q-vector is disabled; in page "Profile" only GW has non-zero value and it is also fixed; in "Corrections" page zero background is predefined.*

*In "Profile" page activate refinement of "GW"*

*In "Corrections" page activate refinement of "shift"*

*Refinement of background terms is enabled by default*

*Leave Powder options, save changes*

*"Edit refinement commands"*

*Set 100 refinement cycles; OK; "Run Refine"*

*Refinement converges with  $R_p \sim 3.7\%$*

*The convergence may be slow. You can interrupt the refinement when  $R_p$  reaches 3.7% by button "End" pressed at the moment when LeBail decomposition is not running*

*"Edit profile parameters": activate refinement of cell parameters (a, b, c, gamma) and components (q1,q2) of the modulation vector;*

*set number of Legendre terms for background to 16*

*"Run Refine"*

*Refinement converges with  $R_p \sim 3.1\%$*

*In "Edit profile parameters" switch to the page "Profile" and activate refinement of GU, GV run Refine*

*Refinement converges with  $R_p \sim 2.5\%$ . Waiting for the full convergence is not necessary.*

*Although the profile viewer shows that profile description could be further improved, for structure solution this starting point is sufficient.*

*FINISH; NEXT to open a wizard for the space group test*

#### **5. Space group determination**

*[On the screen: Tolerances for crystal system recognition]*

*Use default; NEXT*

*[On the screen: Select Laue symmetry]*

*Select the highest one – monoclinic; NEXT*

*[On the screen: Select cell centering]*

*Select I centering; NEXT*

*[On the screen: Information about progress of space group tests. It takes some time...]*

*[On the screen: Select space group];*

*Select C2/c; NEXT*

*[On the screen: Final step of the space group test];*

*Accept the space group **transformed into the original cell**; Finish*

*[On the screen: "Do you want to refine profile parameters one more?";*

*Yes*

*Now the used symmetry speeds up the profile refinement.  $R_p$  is slightly higher because we don't use forbidden Bragg positions*

## 6. Structure solution

Select "Use Superflip"

Type formula K Sm Mo<sub>2</sub> O<sub>8</sub>; Formula units 2

Select "Repeat Superflip: Until the convergence detected" and 2000 cycles

Peak from Jana2006

"Run solution"

In case the convergence was detected, press "Accept last solution "

*Because charge flipping for powders is difficult, it may happen that the convergence is not detected but the solution is anyway present in the density map. If the previous procedure has not returned any result, do the following:*

Select "Repeat Superflip: Number of runs", type 10 runs and 3000 cycles

Superflip runs from ten different random phase sets and returns the "best" density in terms of symmetry fit and other criteria

*If the above procedure still does not yield any result, it can be repeated with "Starting model" = "Patterson superposition map"*

*In case no results are obtained please note that there are also different powder-specific procedures like histogram matching. These procedures are described in the Superflip manual.*

"Accept last solution " closes the structure solution wizard

"Quit" closes the structure solution wizard and ignores any solution

### **At this point the powder wizard finishes**

*The components of the powder wizard can be started separately like*

*"Parameters → Powder"*

*"Tools → Powder → Profile viewer"*

*"Run → Solution"*

Start "Edit atoms" or "Edit/View → Editing of M40" and make sure the atomic positions returned by Superflip are as follows (or symmetry transformed):

Sm1 0.500000 0.250000 0.147357

Mo1 0.000000 0.750000 0.120140

*For different result or no convergence of Superflip:*

Start "File → Structure → Copy in"

Import M40 and M50 from the structure "KSm-solution".

## 7. Completing average structure

*Atoms in the initial structure model have already modulation functions, which were found in the electron density map from Superflip. However, for this example it is better to use the classical approach: calculating first the average structure and then refining modulation waves from small starting displacements.*

Start "Parameters → Powder", switch to page "Cell", and check "Use only satellites

corresponding to existing modulation waves” and disable refinement of q vector components.

Start “Edit atoms” and delete all light atoms (if present)

*In our case we will delete all oxygen atoms. Positions of light atoms found from Superflip electron density map may be unreliable.*

In “Edit atoms” dialogue select heavy atoms (Sm1 and Mo1), go to “Action → Edit/define” and delete position modulation wave (if present).

In Refinement options go to page “Basic” and set Damping factor to 0.25

**Uncheck “Make only profile matching”**

Run refinement

*Refinement converges with  $R_p=22\%$ ,  $R=11\%$*

Activate refinement of occupancy (parameter “ai”) for Sm1 and run Refine

*$R_p$  slightly improves, Occupancy of Sm1 changes from 0.5 to 0.4 and ADP of Mo1 becomes positive. The decrease in occupancy of Sm1 indicates that it could be mixed with potassium.*

Open options for Fourier and select difference Fourier map, automatic Scope and default map orientation. In the “Peaks” page – “Interpretation of displacement waves” change “No. of harmonics” to 0.

Run difference Fourier

NO (skip procedure for including new atoms)

*The fact that both heavy atoms are located at the special positions and with interatomic vector about (0,0,0.5) leads to a false symmetry in the map. However, the true maxima should form a tetrahedron around Mo1. In the next steps, we will plot Mo1 and neighboring Fourier maxima in Diamond.*

Run “Plot structure”; Select “Draw average structure”;

Press “Add Fourier peaks”; select all maxima; OK; “Draw+continue” to start Diamond

[On the screen: Diamond]

*Diamond assigns to the Fourier maxima the lightest chemical element in the formula. For our formula, this is the oxygen. Sometimes it may be practical to append another light atom to the end of the formula, for instance hydrogen.*

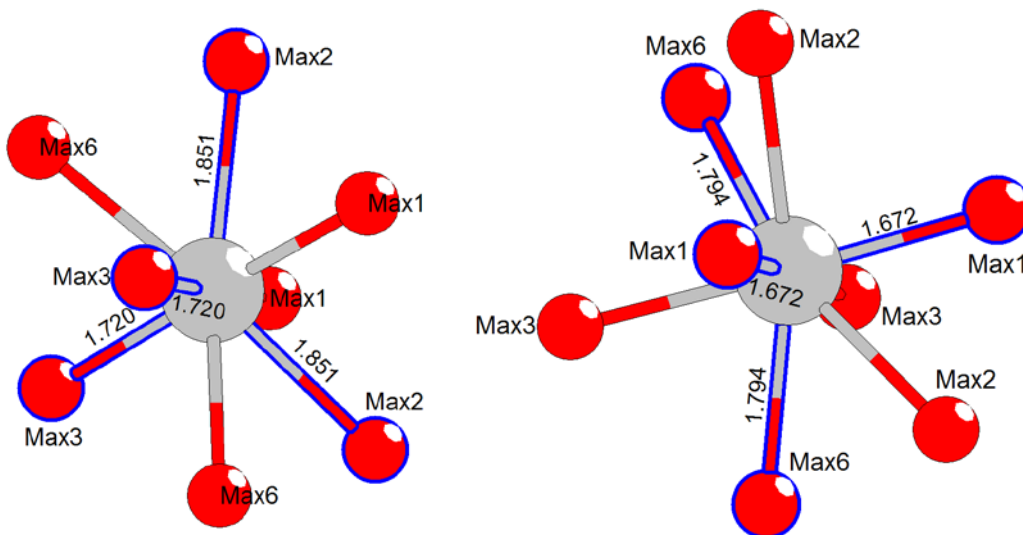
Delete the automatically created structure

With button  from the bottom toolbar select Mo1 as the only atom to be plotted

With “Build → Connectivity” focus Mo-O distance and set the limits above 1.5 Å and below 2 Å; OK

Focus Mo1 and plot its coordination with button 

Rotate the plot until you recognize a tetrahedron formed by four maxima



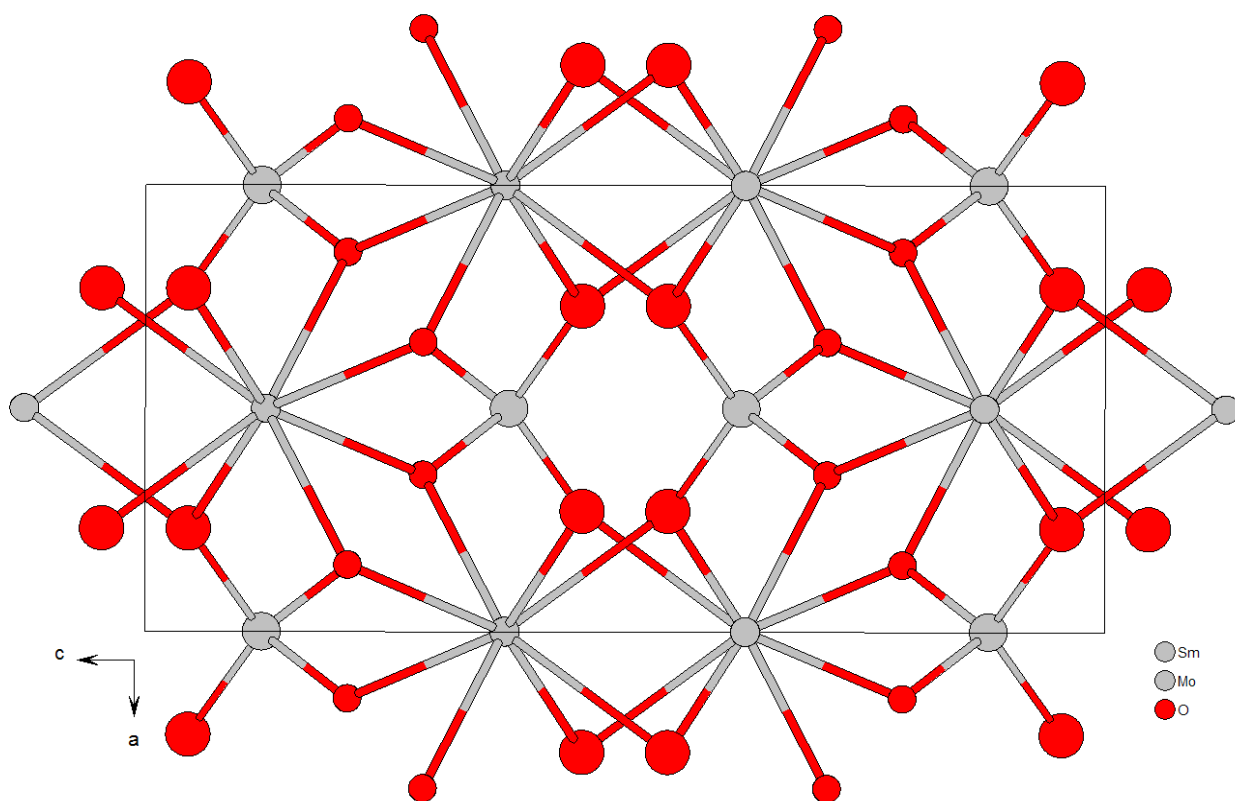
*In our example we can make a tetrahedron from Max2 and Max3 as well as from Max1 and Max6 and they have different bond lengths. The second tetrahedron is a product of the false symmetry induced by additional translation symmetry mentioned above. In our case it is difficult to say which one is better so we will exclude the second one because Max6 may be too weak maximum (maxima are numbered sequentially by their intensity).*

Start "Parameters → Atoms → New" and include the maxima previously selected in Diamond (Max2 and Max3 in our case) as O1 and O2.

Run refinement

Refinement converges with  $R_p=13\%$ ,  $R=6\%$

Start "File → Structure → Save As" and make a backup copy of the average structure, for instance KSm\_ave



## 8. Refinement of modulated structure

Start "Edit atoms" and set one position modulation wave for Sm1

Run refinement

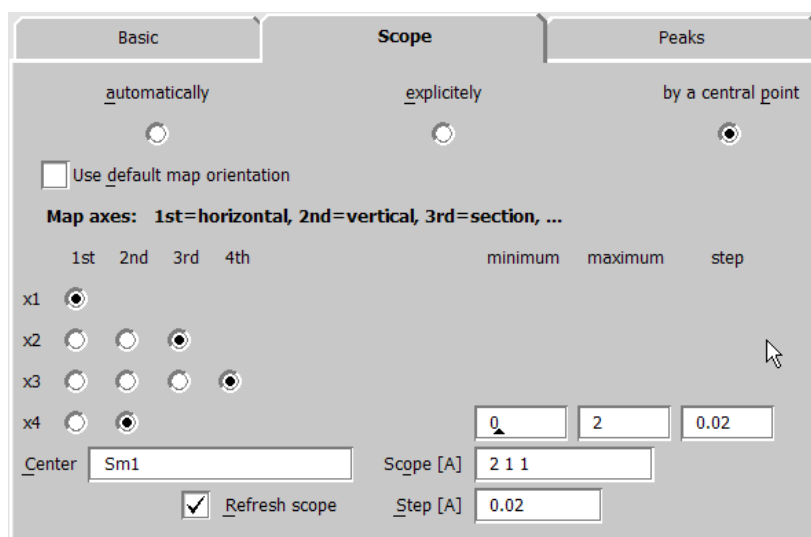
Add one position modulation wave for Mo1

Run refinement

Refinement converges with  $R_p=12\%$ ,  $R(\text{main})=5\%$  and  $R(\text{sat})=15\%$ .

Open options for Fourier, select observed Fourier map

In the page "Scope" choose "by a central point", clear the checkbox "Use default map orientation", select first axis x1 and second axis x4 (i.e. the x1-x4 section), type Sm1 for the Center and "2 1 1" for the section scope.



Run Fourier

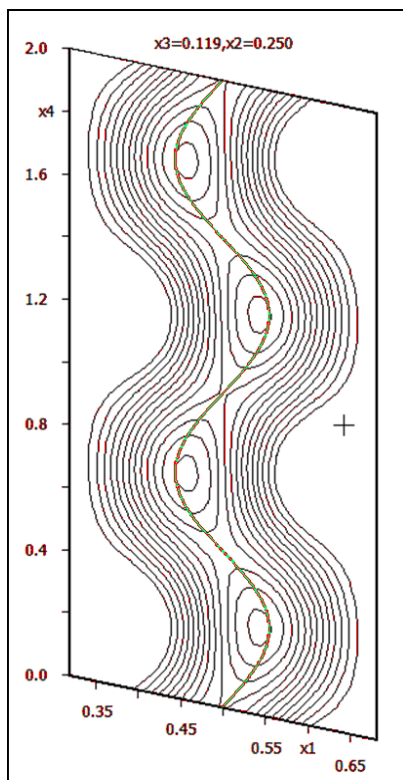
Run Contour, press "New plot", OK

Press "Sum on" and check "x2" and "x3"

Press "Atom edit" and add Sm1 to the list of atoms which will be indicated in the map

The resulting modulation function of Sm1 looks continuously. However, when we follow the line by mouse cursor the Density window in the lower right corner displays fluctuation of density between 68 and 51  $e^{-A^{-3}}$ . Because position of potassium does not appear in the average structure and the occupation of samarium is lower than 0.5 we assume that samarium mixes with potassium. In modulated structure, classical disorder is often replaced by distribution of elements along x4. We can speculate that the area with lower electron density corresponds to the interval (in x4) where potassium exists instead of samarium. However, better background for this consideration will be difference Fourier map.



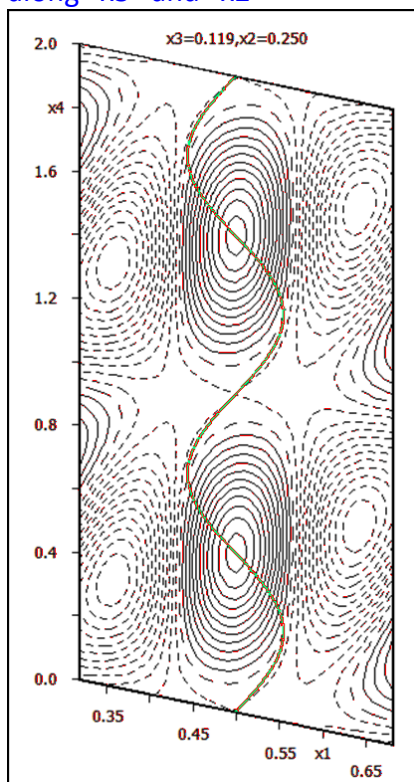


[On the screen: Contour window]

Press "New plot", select "Calculate new ones", OK

In Fourier commands select difference Fourier map, OK

In Contour window that has automatically appeared press "Sum ON" and make summation along "x3" and "x2"



The positive maximum in the difference map indicates region with lack of electron density. This is the area where fully occupied samarium should be present (instead of the partially

occupied one). From this map we can conclude that the definition interval of potassium has centre in  $x_4=0$  and width 0.5. Samarium would occupy a complementary interval with centre at  $x_4=0.5$  and width 0.5.

Leave Contour and start "Edit atoms"

Right-click Sm1 and select "Split atomic position"

In the dialogue that follows:

Type "K1" for "Name of the split atom"

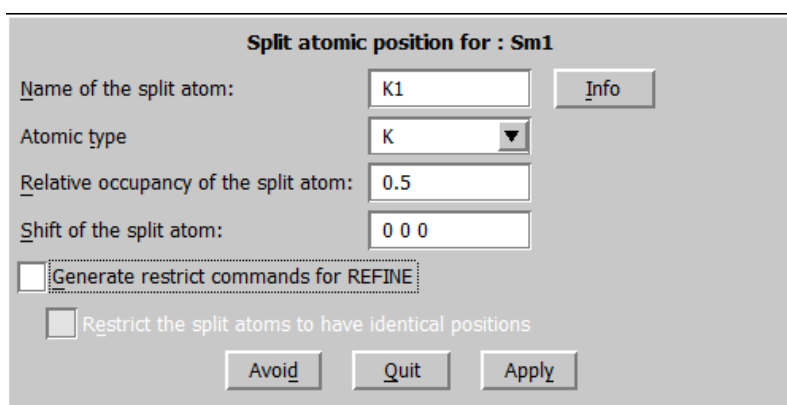
Select "K" for "Atomic type"

Type "0.5" for "Relative occupancy of the split atom"

Type "0 0 0" for "Shift of the split atom"

Clear "Generate restrict command for Refine"

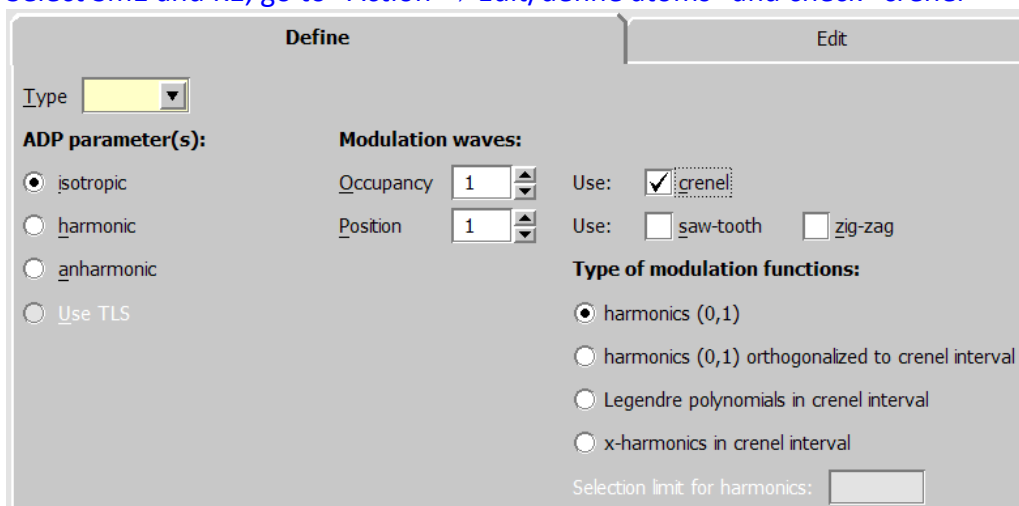
Apply



By this way we have duplicated Sm1, assigned the name K1 and chemical type K to the duplicated atom and reduced occupancy of both atoms by 1/2.

[On the screen: list of atoms in "Edit atoms"]

Select Sm1 and K1, go to "Action → Edit/define atoms" and check "crenel"



Switch to the page "Edit", ensure that "ai" = 0.5 and its refinement is disabled

Press "Occupancy"

Type 0.5 for "delta" and 0.5 for  $x_4$ , OK, OK

By this way we have defined two identical crenel functions for both atoms Sm1 and K1. Note that the occupancy "ai" was recalculated back from 0.25 to 0.5

[On the screen: list of atoms in "Edit atoms"]

Unselect Sm1

Right-click K1, go to "Action → Edit/define atoms"

Switch to page "Edit"; press "Occupancy", change x40 from 0.5 to 0; OK; OK

Close "Edit atoms" and save changes

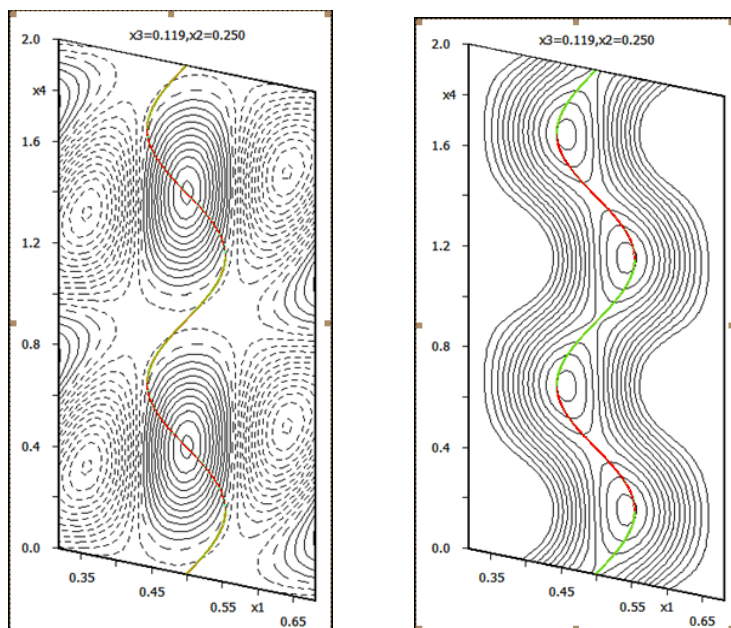
Start Contour and plot the previous difference Fourier map

Make summation

Press "Atoms edit and add K1 to the list"

Make the same for observed Fourier map

*The section shows complementary modulation functions of Sm1 and K1*



Open Refinement options, go to the page "Various", press Restrictions

In the textbox type "Sm1 K1"

Check "Coordinates", "Modulations" and "ADP parameters"

For "Occupancies" select "not restricted"; press "Add"

*This restriction makes the two atoms Sm1 and K1 identical except the definition interval in x4*

Leave Refinement options, save them without starting refinement (YES)

Create backup copy "KSm\_crenel"

Run Refine

*The refinement converges with Rp=6%, R(main)=2% and R(sat)=6.5%*

Add one position modulation wave for O1 and O2

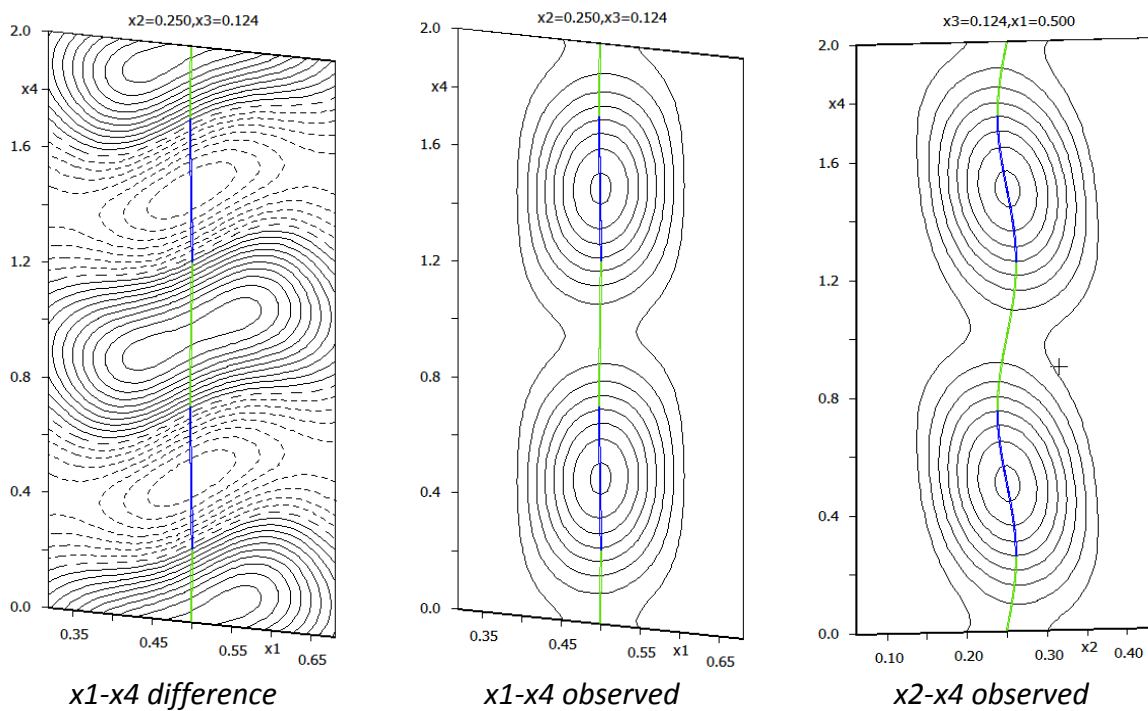
Start "Parameters → Powder", go to the page "Cell" and enable refinement of "q1" and "q2"

*The components of q vector were fixed because they can be refined only when modulation waves are present due to the option "Use only satellites corresponding to existing modulation waves"*

Run Refine

*The refinement converges with Rp=6%, R(main)=2% and R(sat)=5.5%*

Plot observed and difference Fourier map for Sm1

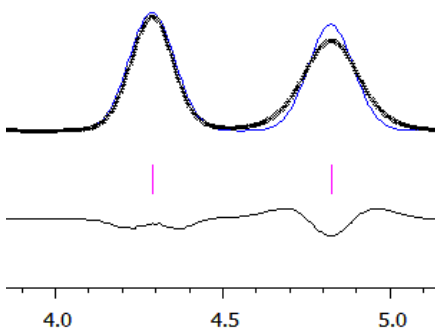


Contour step in the difference map is 0.1. The residua in the difference Fourier map are smaller and in different places than before. The position modulation now occurs in  $x_2$ - $x_4$  section. The previously observed modulation in the  $x_1$ - $x_4$  section was caused by pseudosymmetry.

### 9. Better profile description

Create backup copy KSm\_mod

Start "Tools → Powder → Profile viewer" and examine the first two peaks of the profile



The profile width can be probably better described with anisotropic strain broadening

Start "Parameters → Powder", go to the page "Profile"

Select "Tensor method"

Press "Edit tensor parameters"

Press "Refine all"

Leave "Powder options"

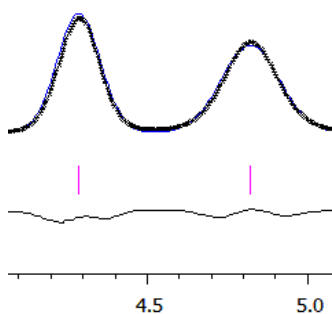
Run Refine

In case that Singularity warning occurs select "Continue refine"

In case the refinement cannot converge note the St parameter responsible for oscillations and fix it to zero in "Edit tensor parameters".

The refinement converges with  $R_p=3.8\%$ ,  $R(\text{main})=1.8\%$  and  $R(\text{sat})=2.9\%$

## Check Powder profile



The width of reflections is now described correctly

Open “Powder options”, go to the page “Profile”

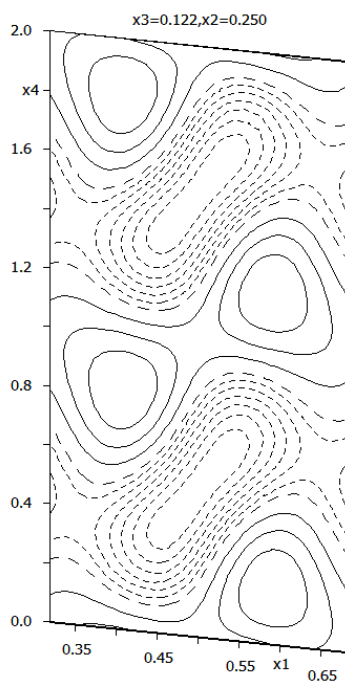
Select “Pseudo-Voight” and activate refinement of “Lx” and “Ly”

Run Refine

*The refinement converges with  $R_p=3.0\%$ ,  $R(\text{main})=1.4\%$  and  $R(\text{sat})=2.1\%$*

*Some St tensor component may cause oscillations. A careful analysis would be needed to select the St components really necessary for profile description. We can for instance fix the components with low parameter-to-sigma ratio (using the button “Show p/sig(p)” to see the ratio)*



Plot difference Fourier for Sm1, section x1-x4

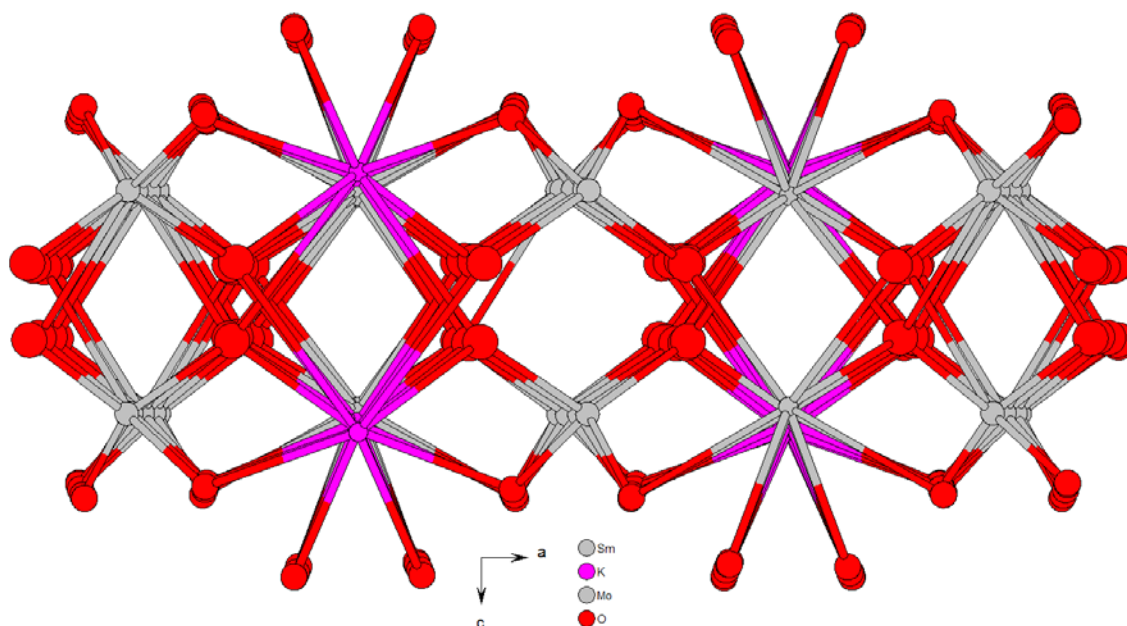


*The section now displays very small residual density. Depending on the fixed St components the resulting section may look differently.*

Start “Plot structure” and try to plot the structure in Diamond

*Sufficiently large area must be selected for the plot because in Diamond we can only plot the supplied atoms. No symmetry transformation (rotation as well as translation) is allowed in Diamond because it does not use modulation functions. The recommended way is to add*

*atoms supplied by Jana2006 using button , connect them using button  and then make only selections and rotations.*



### Alternatives

*The fact that the Sm/K position is half occupied by samarium and potassium makes its scattering power almost identical with Mo atoms. This induces a pseudo-translation symmetry  $(0,0,1/2)$  which strongly affects the solution. The chosen approach is not the only possible one. Another way would be to start – after completing the average structure – with refinement of position modulation of both Mo1 and Sm1 together with harmonic occupation wave of samarium. With this way the “false” modulation in the x1-x4 section would not appear.*