

Orthopyroxene

Last update 23.03.2021

Data	Topic	Level
Electron diffraction	Complete procedure from data reduction to structure refinement using the dynamical approach	Intermediate

Warning: this is a time-consuming example. The computations in the last stages may take up to several hours.

Input data

Data

Electron diffraction data were measured on a transmission electron microscope Tecnai with a precession device DigiStar. Accelerating voltage 200 kV (wavelength = 0.0251 Å).

Input files

directory “dp” with the set of experimental data (diffraction patterns)

opx.pts: input file for PETS2.0 – the data reduction program

opx_reference.cif_pets and opx_dyn_reference.cif_pets are the output files of the data reduction. They are provided to warrant reproducibility of the results and can be used without the processing part.

opx_reference.cif_pets: this file is dedicated to the structure solution and the kinematical refinement.

opx_dyn_reference.cif_pets: This file is provided for the refinement using dynamical approach.

References

For further information about the data processing in PETS2.0 see:

- L. Palatinus et al. Specifics of the data processing of precession electron diffraction tomography data and their implementation in the program PETS2.0. Acta Cryst. B 75: 512-522 (2019).
- PETS2.0 manual pets.fzu.cz/download/

For further information about the dynamical refinement and associated parameters:

- L. Palatinus et al. Structure refinement using precession electron diffraction tomography and dynamical diffraction: theory and implementation. Acta Cryst. A71: 235–244 (2015).
- L. Palatinus et al. Structure refinement using precession electron diffraction tomography and dynamical diffraction: tests on experimental data. Acta Crystallogr B71: 740–751 (2015)

Instructions

PART 1 - Data treatment in PETS2.0

1. Prepare (check) input file for PETS2.0

File opx.pts is the input for PETS2.0. The file was prepared by the software used for the data collection. However, you can prepare easily such input file for your own data.

You can open the file opx.pts in any plain-text editor (Notepad, Wordpad, Notepad++, Vim, ...) to view its contents.

Below are the important parameters you can find in the PETS input file:

```
lambda 0.0251
Aperpixel 0.00138
dstarmax 1.4
phi 1.20
omega 58.000
reflectionsize 34
I/sigma 10
noiseparameters 6.5 100.
bin 4
skipsaturated yes

imagelist
dp/TS_p120_0001.tif 45.00 0.0
dp/TS_p120_0002.tif 44.00 0.0
dp/TS_p120_0003.tif 43.00 0.0
...
...
...
Endimagelist
```

lambda: relativistic wavelength of the incident electrons in Angstroms (100 kV = 0.0370 Å, 120 kV = 0.0335 Å, 200 kV = 0.0251 Å, 300 kV = 0.0197 Å)

Aperpixel: Scale of the images given as the size of one pixel in reciprocal angstroms

phi: Precession angle in degrees used during the data collection. Can be zero, of course.

omega: orientation of the tilt axis of the sample holder with respect to the positive horizontal axis of the image. Must be estimated either by calibration, or by visual inspection of the series of images. Should be close to the correct value within +/-20 deg. Can be refined later in PETS2.0.

bin: Binning of the images prior to any treatment. Saves time, makes nicer pictures, and seems to make the whole analysis somewhat more robust. bin 2 is a good choice from our experience for most data sets. Important: All parameters in the input file that are given in pixels refer to the original, unbinned images. This concerns Aperpixel, center, reflectionsize, mask.

reflectionsize: Diameter of the spots on the images in pixels. Used for peak search and integration, should be large enough to encompass also the strong spots, but small enough to avoid overlaps of neighboring spots.

noiseparameters: two parameters for the determination of $\sigma(I)$. The first value is Gy, the second is ψ . The uncertainty on each pixel γ is then calculated as:

$$\sigma^2(p) = G\gamma p + \psi$$

For more information see Waterman, D. & Evans, G. (2010). J. Appl. Cryst. 43, 1356-1371.

imagelist – endimagelist: Multiline keyword. Each line contains one image. The format is: name, alpha, beta. Name is the file name of the image (including possible relative or absolute path), alpha is the tilt angle, and beta is the possible second tilt value of the double tilt holder.

Reconstruction – endreconstruction: Multiline keyword to generate reciprocal space sections. Each line contains a specification of one layer in the reciprocal space that should be reconstructed by PETS2.0. The format is: filename, base vector 1, base vector 2, origin vector, where each vector is given by three reciprocal-space coordinates. The first two vectors define the orientation of the plane, and the third vector defines the origin of the plane. The standard set is $hk0, hk1, hk2, hk3, h0l, h1l, h2l, h3l, 0kl, 1kl, 2kl, 3kl$. You can determine a specific set of sections later in the graphical interface or directly in the input file using the keywords “reconstruction” and “endreconstruction”.

Close opx.pts

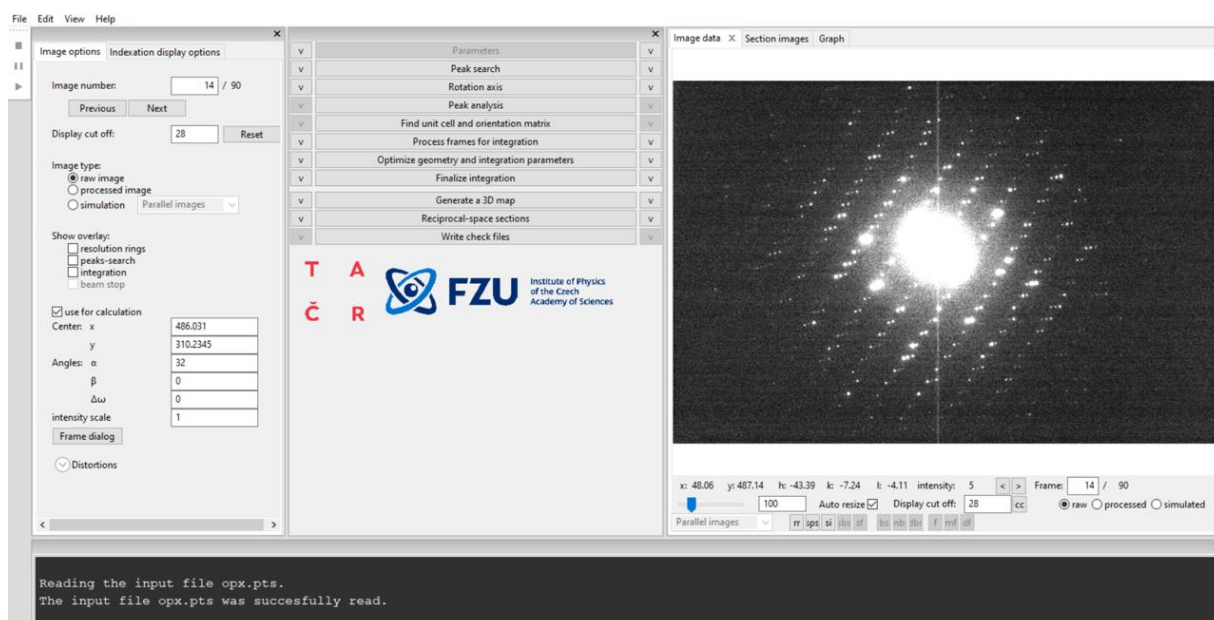
2. Run PETS2.0 and prepare files for indexation

Start PETS2.0 by double clicking the executable

Go to File->Open in the upper menu

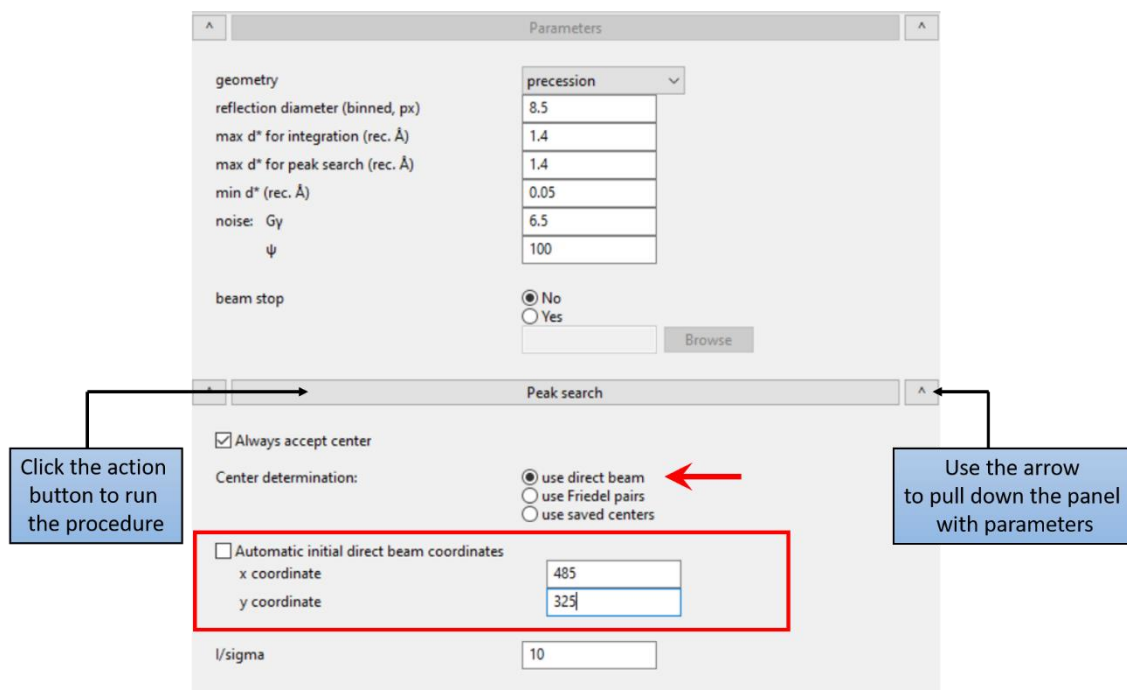
Open the file opx.pts

In the Main panel (Image data tab) you can view individual diffraction frames of orthopyroxene dataset stored in the directory “dp” using the arrows at the bottom of the panel. The contrast of the images can be adjusted by changing the value in the Cutoff-box. The parameters of the input files are visible in the console and in the menus of the tabs “Parameters” and “Peak search”. The arrows to the left of “Picture” (at the bottom controls of the Image data panel in blue) and the value next to it control the image that is shown. The radio buttons “raw” and “processed” show you the raw diffraction pattern as recorded and the processed frame (some background correction etc.), respectively.



Data reduction steps are run by clicking the respective action button. The action options can be modified in the panel which opens after clicking the small arrow next to the action button. The “Parameters” action button (first in the list of action buttons) is gray because there is no associated action. Note that you can adapt the size of the different window components (e.g.

make the plot window more narrow or wider) and decouple the action bar or the console from the main window.



3. Peak search

Click on the arrows (v) next to “Parameters” and “Peak search” to display the panels with parameters.

Keep all the parameters by default

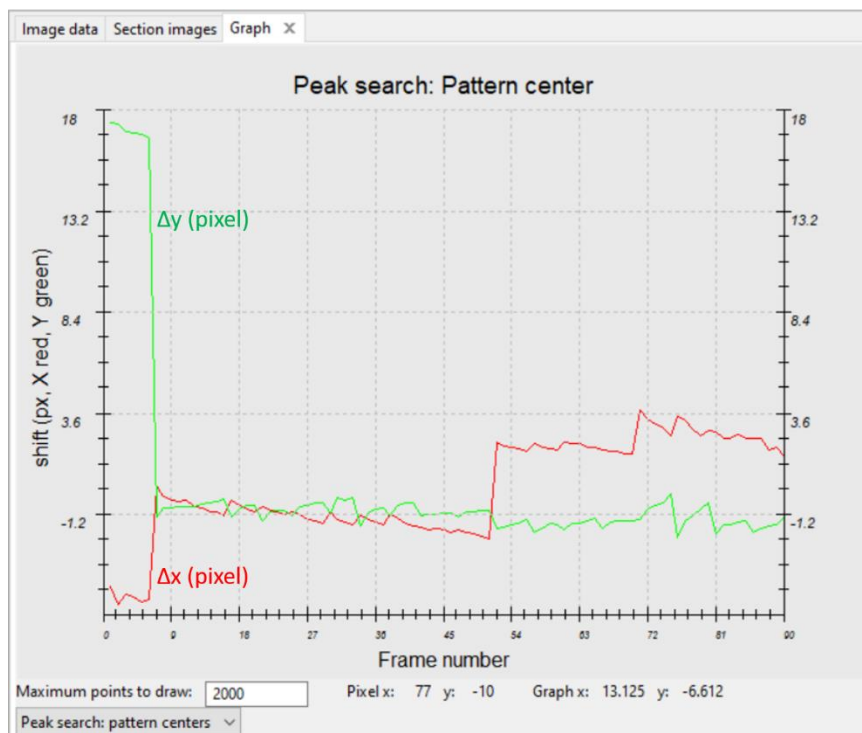
in Peak search parameters - Always accept center checked, use direct beam,

Unselect “Automatic initial direct beam coordinates” and enter x = 485 and y = 325

Check I/sigma 10.

Click the action button “Peak search” to start the procedure. The progress of the Peak search can be followed in the Image data panel.

In the main panel (image data), diffraction images are sequentially displayed with circles at points found by PETS2.0 as significant peaks (above I/sigma specified in the Peak search parameters). Crosses appear in the if the peak’s Friedel pair was detected (if you select Friedel pairs option). At the end, the deviation of the x- (red) and y-coordinates (green) of the estimated direct-beam position is displayed in the Main panel in pixels (tab Graph):



In the console, for each frame the estimated position of the primary beam and the number of significant peaks is given. The process ends with the following message in the console:

```
Number of peaks in the image:      70. Total peaks:  8492
Minimum, average and maximum position of the primary beam:  481.98  486.99
490.39 |      308.70  310.87  490.39.
Finished reading  8471 peaks from the file opx.rpl.
```

4. **Rotation axis**

The next step after peak hunting is the refinement of the angle between the horizontal axis (x axis of the diffraction image) and the projection of the rotation axis. This angle depends on the experimental setup, and needs to be refined for each data set.

Click the action button “Rotation axis” to start the procedure.

Switch to the tab “Cylindric projection” in the main panel to see the progress of the refinement

In the main panel “Cylindric projection”, a cylindrical projection of the difference space of the extracted peak positions is displayed. A correct azimuthal angle refinement results in the image containing sharp peaks aligned on sinusoidal curves.

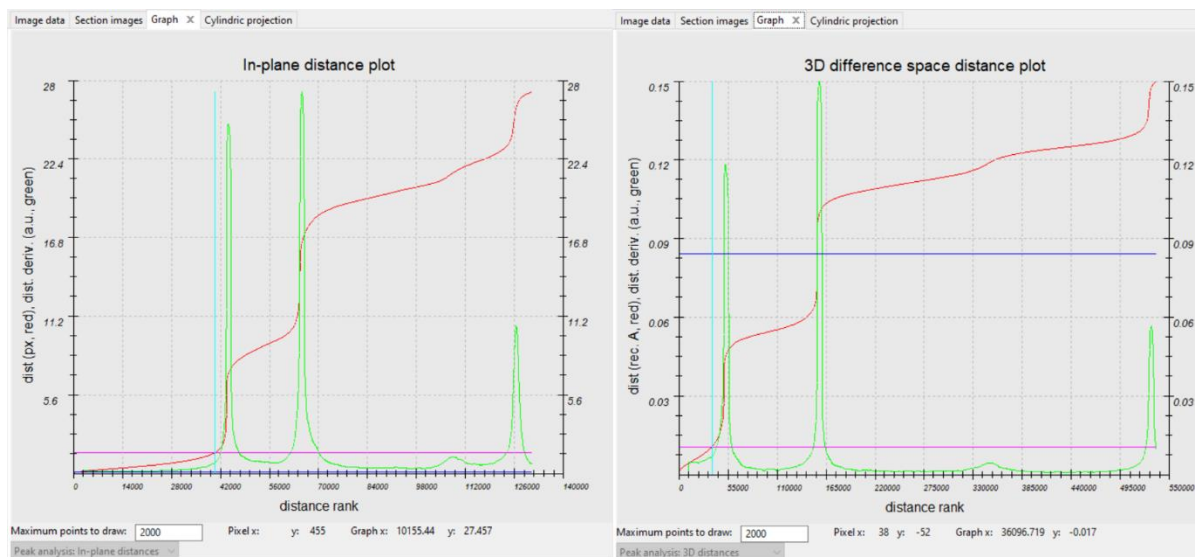
This step provides a first estimation of data quality. At the end of the refinement the omega angle is 57.969 degree for a score of 1.05136.



5. Peak analysis

Click the action button “Peak analysis”.

PETSc 2.0 starts the analysis of the peak positions obtained in the peak hunting procedure. In the first step, distance distribution between peaks in the image plane is analyzed. A sorted plot of inter-peak distances is displayed in the Processing tab (red curve) with its derivative (green):



For good quality data set, the red curve contains distinct steps, and, consequently, the green curve has distinct peaks. The steps are well visible for orthopyroxene showing the good quality of the data.

Click “Peak analysis (continue)”

In the next step, an auto convolution of the diffraction pattern (difference space) is analyzed, and the groups of peaks in the auto convolution (clusters) are replaced by the cluster centers. Again, a distance distribution is displayed (right screenshot), and clear-cut steps on the curve indicate a well-defined lattice.

Click “Peak analysis (continue)”

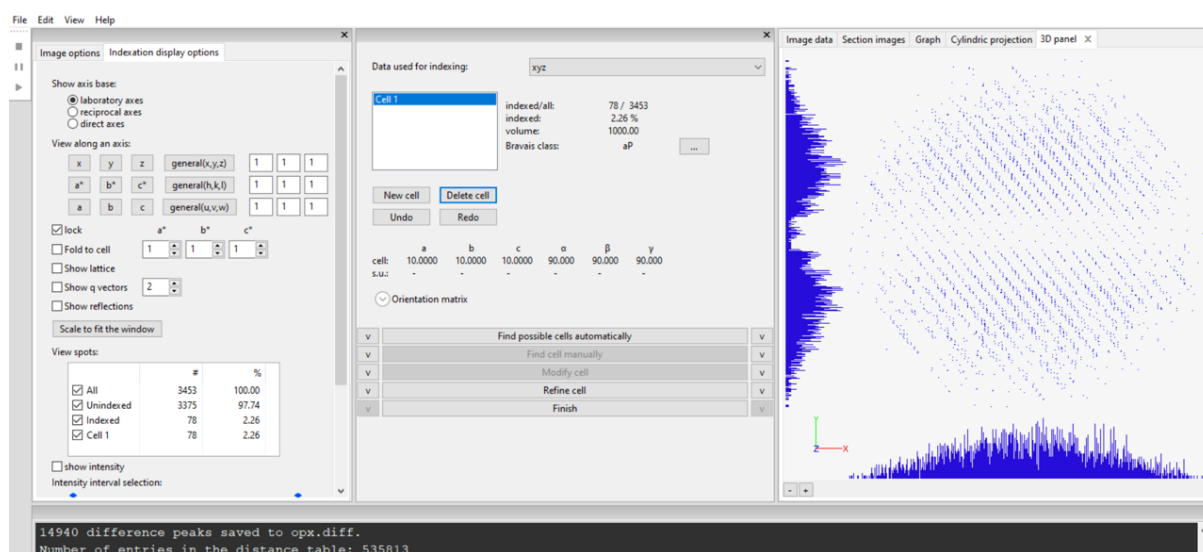
Now the first step is finished and PETS2.0 prepared the files needed for unit cell indexing.
At the end of this step, you should get the following message in the console:

Thresholds for considering two peaks the same: 0.0102 reciprocal angstroms.
 14432 peaks merged into 5628 clusters, 2546 with more than one peak. Find unit cell and orientation matrix

Click “Find unit cell and orientation matrix” to access the indexing options.

New set of buttons with parameters opens as well as a new tab “3D panel” that displays the data used for indexing. The data can be enlarged by scrolling the wheel of your mouse, and rotated by holding the left mouse button.

In the Drop-down list “Data used for indexing” select xyz (should be set by default)



Open the menu below “Find possible cells automatically” by clicking on the arrow next to the action button.

You can see the parameters used in the procedure as well as the possible unit cells found later by PETS2.0.

Check that the selected option is “from difference space” and keep the other parameters default.

Run “Find possible cells automatically”

Data used for indexing: xyz

Cell 1

indexed/all: 2186 / 2732
 indexed: 80.01 %
 volume: 859.63
 Bravais class: mP

New cell Delete cell
 Undo Redo

	a	b	c	α	β	γ
cell:	18.4754	5.2381	8.8838	89.970	90.935	90.031
S.U.:	-	-	-	-	-	-

Orientation matrix

Find possible cells automatically

☒ from difference space ☐ from triplets

Maximal d^* difference for indexing (rec.Å): 0.018
 Angular tolerance for rec. direction (deg): 2
 Maximal volume (Å³): 5000
 Symmetry search: tolerance for lengths (%): 3
 tolerance for angles (deg): 0.6

	a	b	c	α	β	γ	V	Bravais	ind/all
1	18.475	5.238	8.884	89.970	90.935	90.031	859.630	mP	2546/2546
2	20.372	5.234	9.939	90.421	90.934	90.025	1059.650	mP	865/2546
3	20.369	5.235	9.602	90.224	93.381	90.003	1022.058	mP	865/2546
4	20.373	5.236	10.890	89.885	99.528	90.045	1145.653	mP	865/2546
5	20.367	5.238	8.130	89.762	91.636	90.009	867.021	mP	712/2546
6	5.235	12.101	20.427	80.572	85.014	81.784	1275.708	aP	840/2546

Several unit cells are found (see below) and the initial unit cell 10 10 10 90 90 90 is replaced by the first one in the list that indexes most of the reflections with $a = 18.474 \text{ Å}$, $b = 5.2381 \text{ Å}$, $c = 8.8838 \text{ Å}$, $\alpha = 89.970^\circ$, $\beta = 90.935^\circ$, $\gamma = 90.031^\circ$.

PETS2.0 suggests a Bravais class "monoclinic primitive" for the unit cell because the beta angle is almost 1 degree far from the orthorhombic settings. We know that it should be orthorhombic. The difference can be due to a misorientation of the frames in the data sets and/or the distortions of the data.

Before refining the unit cell, we need to exchange the b and c parameters to get the standard settings of the literature.

Go in the "Modify cell" parameters,
 Enter the transformation matrix as displayed below to invert b and c parameters.
 Press "Transform by matrix"

	a	b	c	α	β	γ
cell:	18.4754	8.8838	5.2381	90.030	90.031	89.065
s.u.:	-	-	-	-	-	-

Orientation matrix

Find possible cells automatically

Find cell manually

Modify cell

Reduce cell Check centering Go to supercell

Transformation matrix:

☐ direct space ☒ reciprocal space

$a^* = 1 \cdot a^* + 0 \cdot b^* + 0 \cdot c^*$

$b^* = 0 \cdot a^* + 0 \cdot b^* + -1 \cdot c^*$

$c^* = 0 \cdot a^* + 1 \cdot b^* + 0 \cdot c^*$

☐ transform centering for changed cell volume

Transform by matrix Reset to unit matrix

In the Drop-down list “Data used for indexing” select “cor”,
Click on the arrow next to “Refine cell” to access the options,
Select the option “refine cell and distortions”,
In symmetry, select “orthorhombic”
Check the boxes “refine cell” and “refine distortions”
Pull down the Distortions’ parameters and select the zero order and the second order distortions as shown on the screen shot.
Uncheck the center x and y of the distortions.

Note: The center of the zero order distortions (in this case barrel and spiral) does not generally coincide with the primary beam. If these distortions are small (like in this case), the refinement of the center of distortion become unstable especially in the presence of a large elliptical distortion.

Refine cell

☐ refine UB + cell
☐ refine cell from d
☒ refine cell and distortions

Maximal d* difference for indexing[Inv(A)]: 0.018

☒ symmetry orthorhombic

☐ fixed cell parameters
10 10 10 90 90 90
☐ fixed up to a scale factor

☒ refine cell ☒ refine distortions

Distortions

Center: x 0
y 0

rad lin quad cub phase

0 ☐ 0 ☐ 0 ☒ 0 ☐ 0

1 ☐ 0 ☐ 0 ☐ 0 ☐ 0

2 ☒ 0.01 ☐ 0 ☐ 0 ☒ 0

sg terms ☐ 0 ☐ 0 ☐ 0

tan lin quad cub phase

0 ☐ 0 ☐ 0 ☒ 0 ☐ 0

1 ☐ 0 ☐ 0 ☐ 0 ☐ 0

2 ☐ 0.01 ☐ 0 ☐ 0 ☐ -45

sg terms ☐ 0 ☐ 0 ☐ 0

☒ tie elliptical distortion

Run “Refine Cell”

The refined unit cell parameter is $a = 18.474(8) \text{ \AA}$, $b = 8.880(4) \text{ \AA}$, $c = 5.268(2) \text{ \AA}$ and $\alpha = \beta = \gamma$ set to 90° . The refined distortion parameters are displayed below.

Distortions

Center: x
y

	rad	lin	quad	cub	phase
0	<input type="checkbox"/>	<input type="text" value="0"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="text" value="-0.5667"/>
1	<input type="checkbox"/>	<input type="text" value="0"/>	<input type="checkbox"/>	<input type="text" value="0"/>	<input type="text" value="0"/>
2	<input checked="" type="checkbox"/>	<input type="text" value="6.0285"/>	<input type="checkbox"/>	<input type="text" value="0"/>	<input checked="" type="checkbox"/>

sg terms ☐ ☐ ☐

	tan	lin	quad	cub	phase
0	<input type="checkbox"/>	<input type="text" value="0"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="text" value="4.0133"/>
1	<input type="checkbox"/>	<input type="text" value="0"/>	<input type="checkbox"/>	<input type="text" value="0"/>	<input type="text" value="0"/>
2	<input type="checkbox"/>	<input type="text" value="6.0285"/>	<input type="checkbox"/>	<input type="text" value="0"/>	<input type="text" value="97.7564"/>

sg terms ☐ ☐ ☐

☒ tie elliptical distortion

Leave the indexing panel by clicking “Finish”

The file *opx.cellist* is now created. This file contains the orientation matrix and the unit cell parameters.

6. Create reciprocal-space sections

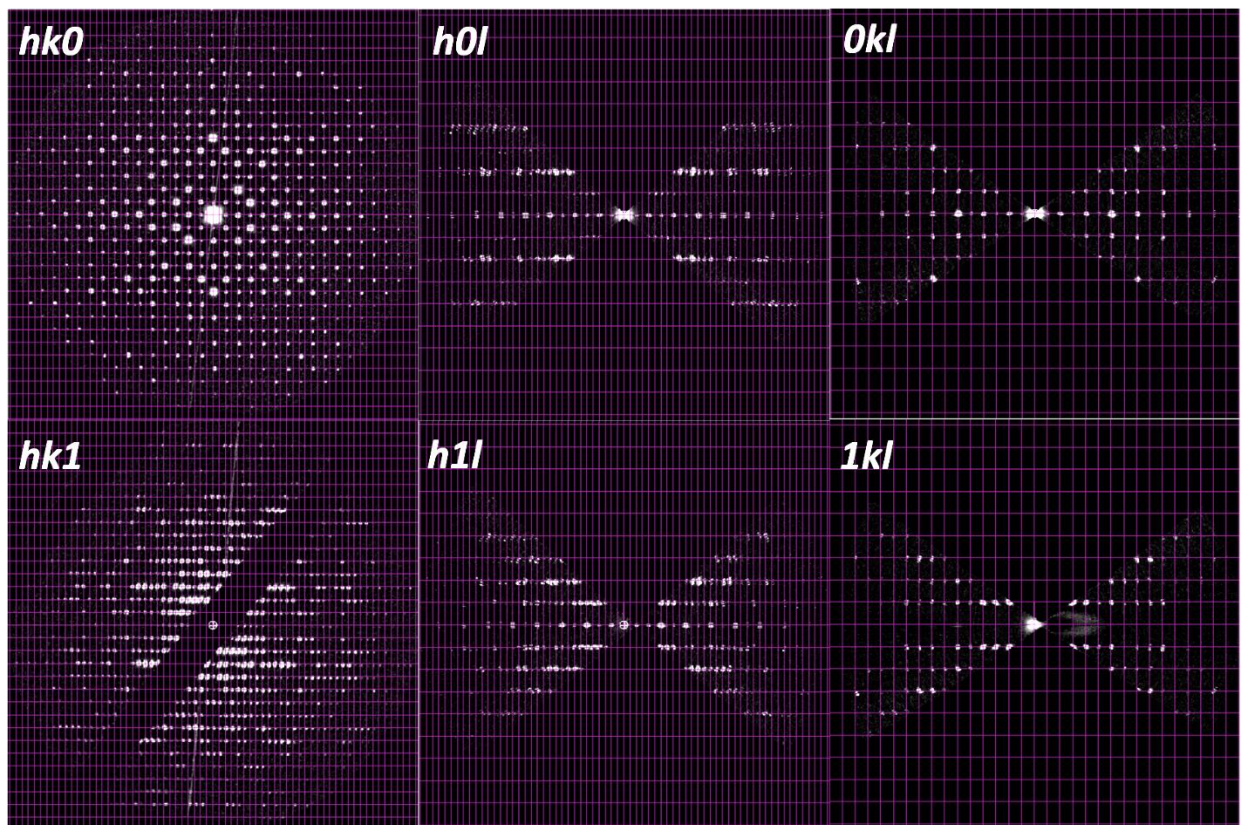
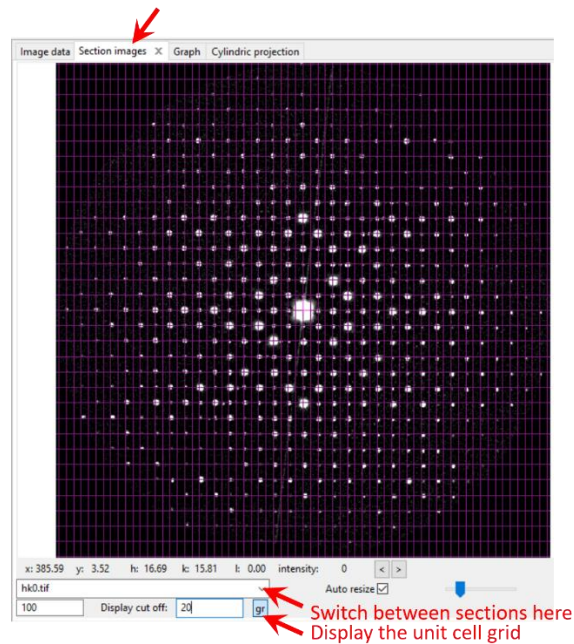
PETS2.0 scans all images and reconstructs sections through reciprocal space at planes $hk0$, $hk1$, $hk2$, $h0l$, $h1l$, $h2l$, $0kl$, $1kl$, $2kl$ (default set). These sections are used as an aid to determine the space group. Sections are saved in the folder “section” as TIF-files.

In the main panel, select “Reciprocal-space sections”,
Use the standard set; OK.

This step can take some time.

You can visualize the sections in the tab “Section images” of the main panel and choose the section as shown on the picture below.

To display the unit cell grid, press the icon “gr” on the bottom of the “section images” panel.



From electron diffraction data, it is often difficult to select the correct space group. In particular, the presence or absence of glide planes and screw axes is hard to assess, knowing that kinematically absent reflections may have significant intensities due to dynamical diffraction effects. To detect the extinct reflections despite the dynamical effects, we compare the intensities in the layers 0 and 1.

Looking at $hk0$ and $hk1$, the condition $h = 2n$ on $hk0$ seems possible and reflects the presence of a a -glide plane perpendicular to c -axis. On $h0l$, you will see that the rows $l = 2n+1$ present much weaker intensity than the even rows. In the higher layer $h1l$ these differences are no more visible indicating a c -glide plane. On $0kl$, we can suspect a b glide plane perpendicular to the a -

axis. Further extinction conditions are visible on the rows $h00$, $0k0$ and $00l$: $h = 2n$, $k = 2n$ and $l = 2n$ respectively. The space group with the highest possible symmetry is $Pbca$. If the space group is not obvious at this stage, it will be confirmed later during the structure solution steps.

7. Integrate intensities

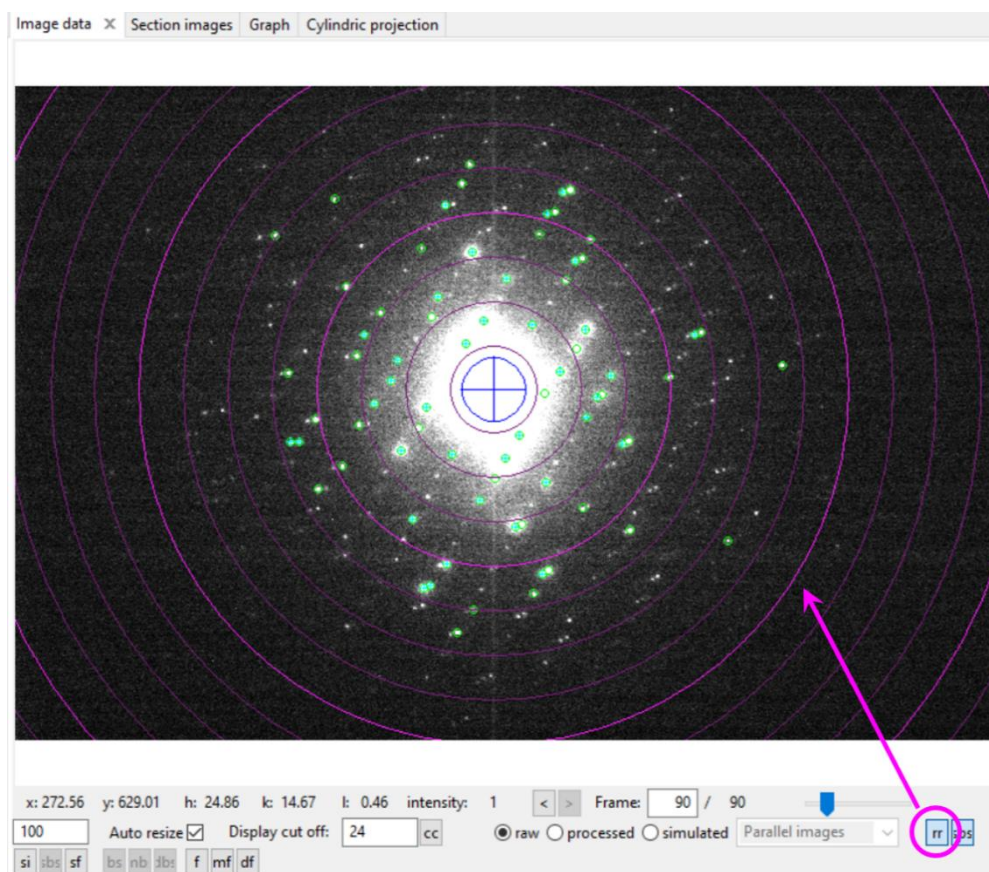
(a) Process frames for integration

Open the parameter sections of “process frames for integration” and change the RC width to 0.0025 reciprocal Å.

Select “shift integration box to maximum intensity”

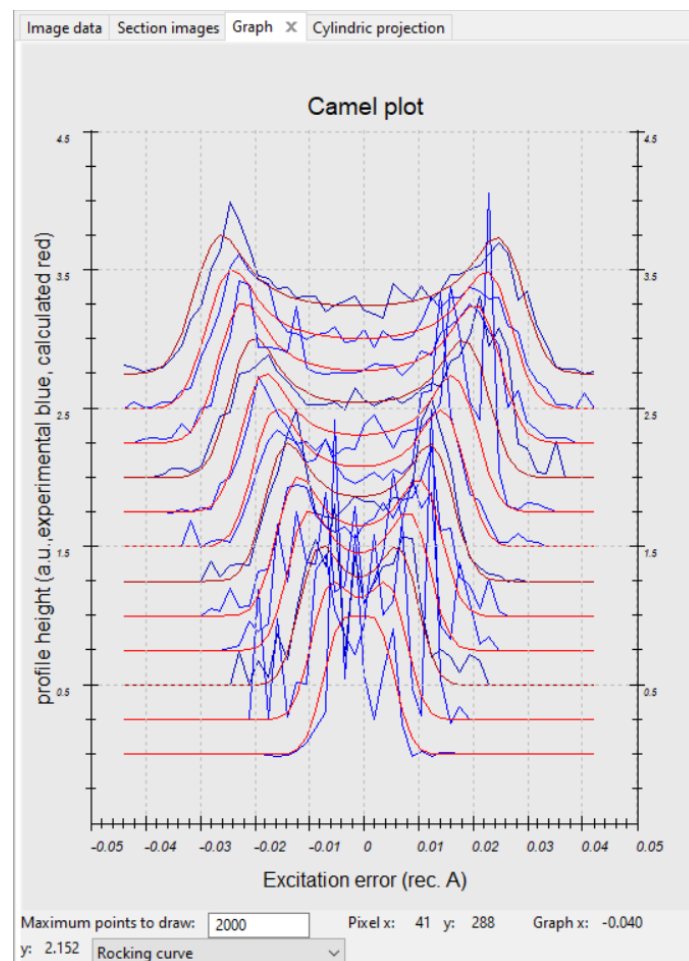
Start the procedure by clicking the action button “Process frames for integration”.

In the Image data tab, diffraction frames with circles drawn at positions predicted from the orientation matrix are displayed. A green circle means that a peak with $I > 3\sigma(I)$ was found. A brown diamond means that a reflection is expected on upcoming frame(s) or was present on previous frame(s). To assess the resolution of your data, you can also display the resolution rings by selecting the option “rr” in the Image data panel (see below).



At the end of the integration process, in the Graph tab, the camel plots (rocking curves profiles) are displayed (data - blue, fit - red). On the horizontal axis of the plot there is the excitation error of reflections. Each curve shows an average rocking curve of reflections in one resolution shell, starting from 0.2-0.3 Å⁻¹ in steps of 0.1 Å⁻¹. Notice the splitting of the humps with

increasing diffraction angle due to the precession. By changing the parameters, you can observe their effect on the curve. The reflections considered for the visualization of the camel plots are affected by the $I/\sigma(I)$ threshold.



Before doing any further optimization, it is good to “Finalize the integration” after the data processing. The statistics will allow the user to track the improvements of the data reduction before and after optimizations (number of the reflections, R_{int} , etc.).

(b) Finalize integration

Open the parameters for “Finalize integration”

Check that both “kinematical” and “dynamical” integration are checked

Select the radio button “fit profile” next to “intensity estimation”.

Default value for intensity estimation is “integrate profile”, which is the more robust technique and works well even for poorer data. However, for average to good data the “fit profile” option gives better results.

Select “frame scaling” and choose the mmm Laue class for scaling,

Interframe correlation range = 3 and

Interframe correlation weight = 1 (see below).

The two latest parameters are used to make the scaling smoother and avoid irrelevant points.

Run the procedure by clicking the action button.

Finalize integration

☒ kinematical

intensity estimation: ☒ fit profile
☐ integrate profile
☐ maximum intensity
☐ Bragg position

integration parameters: min. number of reflection measurements
 reflection width multiplier

☒ frame scaling

Laue class for scaling:

Interframe correlation range:

Interframe correlation weight:

☒ dynamical

virtual frames: number of frames:
step between frames:

After the integration, PETS2.0 shows the table of Rint values in the console for the different Laue classes. For the Laue class mmm the Rint of observed reflections is 22.78 % for 918/1089 observed /all unique reflections (see below). It is possible to view the scale factors for individual frames on the tab Graph

```
Intensity statistics:
Observed/Total number of reflections: 4078/ 5509
Laue class  Rint(obs)  Rint(all)  Nobs/Nall  redundancy
-1          13.61    13.89    2238/ 2815    1.957
2/m         20.37    20.66    1572/ 1877    2.935
112/m       17.17    17.44    1329/ 1664    3.311
2/m11       21.03    21.32    1548/ 1842    2.991
mmm         22.78    23.05     918/ 1089    5.059
4/m         50.93    51.17    1129/ 1361    4.048
4/mmm       59.05    59.28     731/  849    6.489
-3          64.39    64.54    1666/ 2011    2.739
-31m        82.94    83.05    1127/ 1299    4.241
-3m1        82.66    82.78    1162/ 1348    4.087
6/m         65.70    65.90     978/ 1164    4.733
6/mmm       83.18    83.32     697/  789    6.982
m-3         44.20    44.50     820/  973    5.662
m-3m        72.84    73.04     597/  674    8.174
Integration finished successfully.
```

. When the integration finishes, files `opx.cif_pets` and `pyrite_dyn.cif_pets` are created. `pyrite.cif_pets` is used to solve the structure and for kinematical refinement, while `pyrite_dyn.cif_pets` is used for dynamical refinement.

(c) Geometry optimizations

Now we can try to improve the integration by optimizing the frame orientation, the center of the diffraction patterns, the frame by frame apparent mosaicity and the frame by frame distortions.

In "Optimize geometry and integration parameters",
Unselect "refinement using rocking curve profile"

Select “refinement using frame simulation” with the options orientation angles, center of the diffraction patterns, mosaicity, distortion and use the simulation mode “integrated intensity” (see picture).

The option “integrated intensity” can be used only if a kinematical integration has been performed before and gave acceptable results. This is our case now. When the camel plot or the integration is not satisfying, use the simulation mode “uniform intensity” that do not require to finalize the integration.

Press the action button “Optimize geometry and integration parameters” to start

Optimize geometry and integration parameters

☐ refinement using rocking curve profile (camel plot)

☒ RC width (rec. Å) 0.0025

☒ apparent mosaicity (deg.) 0.05

☐ precession angle (deg.) 1.2

☐ calibration constant (rec. Å, binned) 0.00552

minimum I/sigma 10

☒ refinement using frame simulation

☒ orientation angles

☒ center of the diffraction patterns

☐ RC width

☒ mosaicity

☒ distortion

☐ Transfer to global

for simulation use:

☐ uniform intensities

☒ integrated intensity

Advanced settings

The frame orientation refinement optimizes the rotation angles α , β and ω together with the position of the diffraction pattern centers, the apparent mosaicity of each frame and the frame by frame distortions.

The routine generates diffraction patterns based on the previous finalized integration. The least-squares minimization routine tries then to reduce the pixel-wise differences of the generated pattern to the background-subtracted experimental diffraction pattern. You can find more details about the method in Palatinus, L. et al. (2019). Acta Cryst B 75, 512-522.

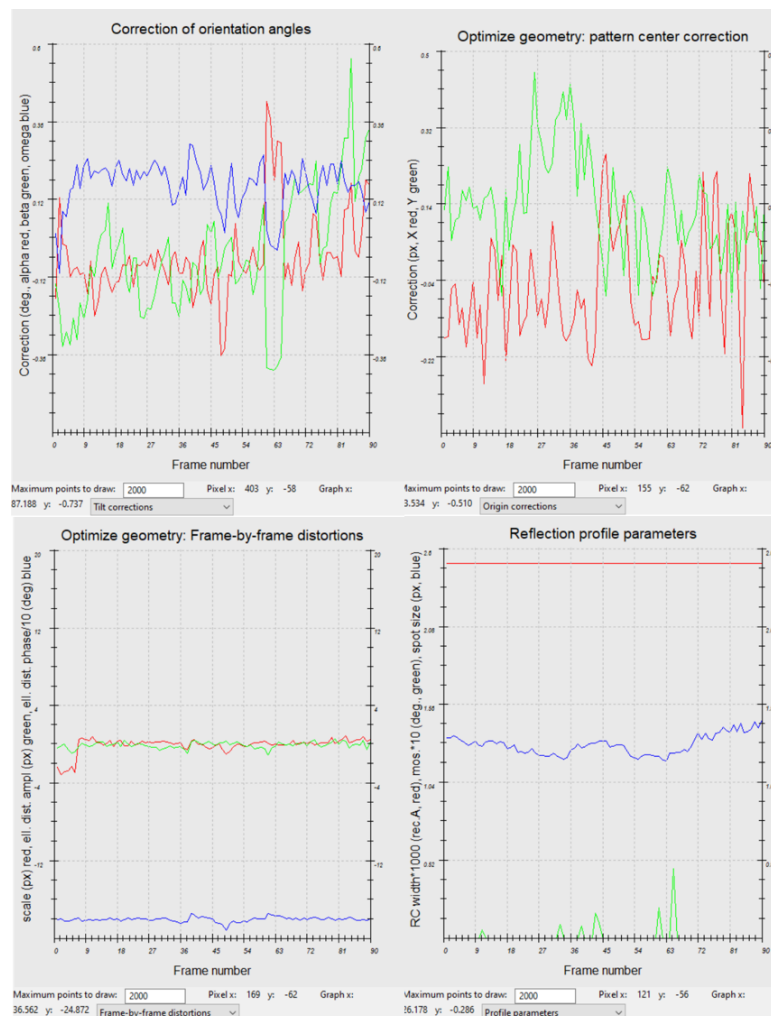
The results are visible on several Graphs accessible in the drop-down menu at the bottom of the Graph tab

-By selecting “Tilt corrections” you access a curve $\Delta\alpha$, $\Delta\beta$, $\Delta\omega$ (pixel) as a function of the frame number. In this example, there is a small trend for each curve. We can consider that the optimization is successful.

-Select “origin corrections” to see how the x and y origin are shifted from their initial position.

-The frame by frame distortions are displayed in “Frame-by-frame distortions” with the scale of each frame (ref), the amplitude of the elliptical distortions (second order) (green) and its phase (blue).

-The evolution of the RC width and the apparent mosaicity frame by frame are in the option “Profil parameters”.



Because the frame orientations and the integration parameters have changed, we need to redo some of the data processing steps, namely “refine the cell” and “Process frames for integration” and refinement of the rocking curve profile

Go to “Find unit cell” and select the xyz file.

In the refinement parameters, select “refine UB + cell” and select the triclinic symmetry.

Run “Refine cell”.

Finish

The new parameters are now very compatible with an orthorhombic unit cell. The optimizations significantly improved the unit cell parameters, especially the gamma angle that was far from 90 degree before.

	a	b	c	α	β	γ
cell:	18.4699	8.8771	5.2769	90.058	89.970	89.996
s.u.:	0.0025	0.0011	0.0022	0.019	0.019	0.011

Click the action button “Process frames for integration” with the same parameters as previously.

Switch to the tab Graph to view the new camel plot.

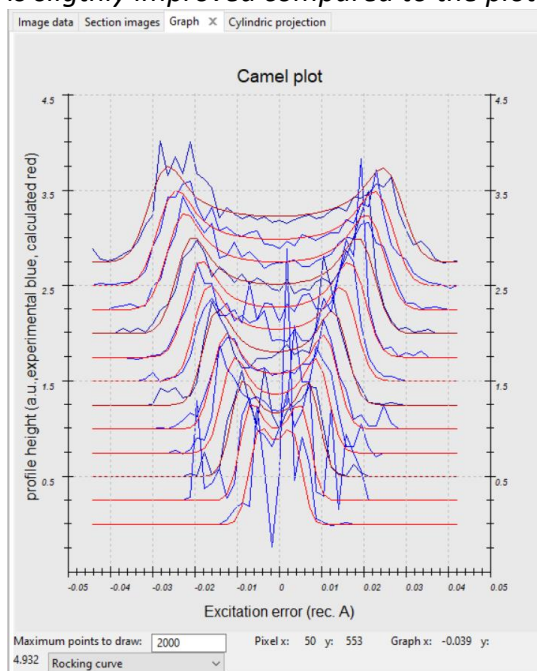
(d) Optimize geometry and integration parameters

Go to the options of “Optimize geometry and integration parameters”

Unselect “refinement using frame simulation”,

Select “refinement using rocking curve profile” and check that the refinement using rocking curve profile is checked as well as the RC width and mosaicity parameters. Start the fitting procedure by clicking on the action button.

The optimized values for the camel plot are now RC width = 0.00152 \AA^{-1} and apparent mosaicity = 0.084 deg . The camel plot is slightly improved compared to the plot before frame orientation.

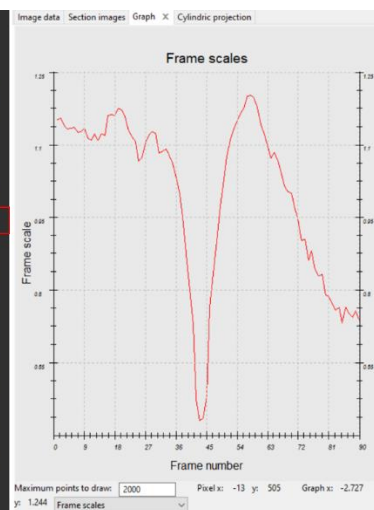


In the Finalize integration options, check that fit profile is still selected as well as the frame Select the Laue class for scaling “mmm”, interface correlation range = 3 and interface correlation weight = 1.

When the frame scaling is used, it optimizes frame scales by matching the intensities to the theoretical refraction profiles. In our case, we use Laue class mmm, which is consistent with the space group derived earlier from the reciprocal-space sections. The Rint values are slightly improved.

Run Finalize integration

```
Intensity statistics:
Observed/Total number of reflections: 4018/ 5491
Laue class  Rint(obs)  Rint(all)  Nobs/Nall  redundancy
-1          11.95    12.27    2228/ 2809  1.955
2/m         18.69    19.03    1565/ 1874  2.930
112/m       13.65    13.95    1314/ 1659  3.310
2/m11       18.63    18.98    1547/ 1840  2.984
mmm         19.58    19.91    905/ 1086   5.056
4/m         49.58    49.87    1118/ 1356  4.049
4/mmm       58.76    59.05    723/  847   6.483
-3          64.53    64.65    1653/ 2008  2.735
-31m        83.54    83.62    1128/ 1295  4.240
-3m1        83.58    83.66    1153/ 1343  4.089
6/m         64.83    65.02    975/ 1165   4.713
6/mmm       83.64    83.76    698/  786   6.986
m-3         42.17    42.53    813/  971   5.655
m-3m        73.47    73.66    589/  674   8.147
Integration finished successfully.
```



Close PETS

Answer “Yes” to the question about saving the project

The current state of the project is saved in the file opx.pts2. Opening this file with PETS next time allows you to continue from the current state of processing. If you open opx.pts, you must start from scratch again, because opx.pts is not overwritten by PETS and still stores the initial settings.

PART 2 - Structure solution and kinematical refinement in Jana2020

1. Create new structure

***Important!** The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can reproduce the following part of the tutorial, do not use the file opx.cif_pets that you have just created, but use the file opx_reference.cif_pets provided with the example files. Using your own cif_pets file is also possible, but your results may slightly differ from the results described in this tutorial.*

Start Jana2020

In the Main menu bar, use “Structure → New” and open new structure “opx” in directory of the Example 13.6

2. Import Wizard

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

Select “Single crystal: known diffractometer formats”; NEXT

[On the screen: Data reduction file from]

Select “Pets electron diffractometer”

For “Input file”, browse the file opx_reference.cif_pets (or your file)

This file produced by PETS2.0 contains all important information, including the list of intensities.

NEXT

[On the screen: Complete/correct experimental parameters]

Leave all settings unchanged; NEXT

Leave all settings unchanged; NEXT

The program reads 5489 reflections from the file

OK

For absorption correction select “None or done before importing” (default); NEXT

FINISH; OK to accept the data set

You just read in the cell parameters and the intensity list. If you do not have the data in the cif_pets format, you can read them in from a general hkl file using the option “reflection file corrected for LP and absorption” at the beginning of the import wizard. You then have to input the radiation type, wavelength and cell parameters by hand.

3. Symmetry Wizard

NEXT to close the information window and start the symmetry wizard.

Symmetry Wizard can be started separately by expanding “Reflection file” in the Command tree and selecting “Make space group test”. The default settings are prepared for x-ray diffraction. For electron diffraction we have to increase the tolerances.

Change the tolerances according to this screenshot:

Tolerances for crystal system recognition:

Original cell parameters: 18.470 8.877 5.277 90.06 89.97 90.00

Maximal deviation for cell lengths in Ang:

Maximal deviation for cell angles in degs:

Maximal deviation for modulation vector:

Tolerances for space group recognition:

Maximal ave(I/sig(I)) for systematic extinctions induced by cell centering:

Maximal ave(I/sig(I)) for systematic extinctions induced by other symmetry:

☒ Search for higher symmetrical supercell (recommended)

☐ Introduce twin laws in case of subgroups

☒ Use old twin matrices in testing

NEXT, OK

[On the screen: Select Laue point group]

Select Laue point group

Crystal system	Point group	Rint(obs/all)	#averaged(obs/all)	Redundancy
Triclinic	-1	10.39/10.74	2139/2782	1.957
Monoclinic-setting "a"	2/m	16.49/16.92	1488/1818	2.994
Monoclinic-setting "b"	2/m	16.40/16.83	1506/1852	2.939
Monoclinic-setting "c"	2/m	11.81/12.15	1265/1646	3.307
Orthorhombic	mmm	17.26/17.68	872/1074	5.068

Select orthorhombic mmm; NEXT

The internal R-values would be rather high for x-rays, but are acceptable for electron diffraction data.

[On the screen: Select cell centering]

Select cell centering

Centering	#obs/#all	ave(I/sig(I))	
<input checked="" type="radio"/> P	0/0	0.000/0.000	Details
<input type="radio"/> A	2010/2768	40.675/29.843	Details
<input type="radio"/> B	1823/2738	39.920/26.881	Details
<input type="radio"/> C	1997/2742	46.850/34.420	Details
<input type="radio"/> I	2038/2759	44.358/33.062	Details
<input type="radio"/> R-obverse	n.a.	n.a.	Details
<input type="radio"/> R-reverse	n.a.	n.a.	Details
<input type="radio"/> F	2915/4124	42.554/30.381	Details
<input type="radio"/> X (1/2,0,0), ...	-----/-----	-----/-----	Details
<input type="radio"/> X (1/3,0,0), ...	-----/-----	-----/-----	Details

[Show/modify X centering](#)

The statistics clearly excludes a centered cell. The choice of a primitive cell is also in agreement with our visual inspection of the reciprocal space sections.

Select primitive unit cell; NEXT

[On the screen: Select space group]

The window shows possible space groups.

The list of the strongest reflections contradicting the selected space group can be displayed by "Details" button.

Select space group			
Characteristics for systematically absent reflections			
Space group	#obs/#all	ave(I/sig(I))	Figure of merit
P21221	2/26	9.071/0.836	0.05946
P2122	2/26	9.071/0.836	0.05946
Pmca	130/646	12.155/2.798	0.58811
P21ca	130/646	12.155/2.798	0.58811
Pbca	170/706	12.191/3.299	0.65799
Pmmm	0/0	-----	1.00000
Pm2m	0/0	-----	1.00000
P2mm	0/0	-----	1.00000
Pmm2	0/0	-----	1.00000
P2221	0/0	-----	1.00000
P222	0/0	-----	1.00000
Pbma	93/570	16.190/2.941	1.25369
Pb21a	93/570	16.190/2.941	1.25369
Pmma	53/510	19.119/2.265	1.44653
Pm2a	53/510	19.119/2.265	1.44653
P21ma	53/510	19.119/2.265	1.44653

In Section 7 of the data reduction (Create reciprocal-space sections), we saw that the space group was probably *Pbca*, despite some violations. JANA2020 offers the expected space group although with large Figure of merit.

Note that a wrong choice of the space group is not detrimental for the structure solution, because we will use the program *Superflip* for structure solution. This program makes additional check for the most probable space group.

Select *Pbca*; NEXT

Accept the space group transformed into the original cell or Accept the space group in the standard settings.

In this case, the two options are the same because we already have the standard settings.

FINISH

Symmetry is saved in file *opx.m50*.

4. Creating refinement reflection file

In this step, the program creates file *pyrite.m90* containing the data set merged by symmetry and with discarded forbidden reflections. This file will be used for refinement.

Proceed with the wizard, leaving all settings default. NEXT

The Import statistics-obs/all gives 4011/5489 reflections read from input file, 3841/4783 reflections written to output file and 170/706 reflections rejected as symmetrically extinct.

OK,

OK again; NEXT

Summary after averaging

Rint(obs/all) = 19.17/19.24 for 844/898 reflections
averaged from 3841/4783 reflections

Redundancy = 5.326

h(min) = 0, h(max) = 25
k(min) = 0, k(max) = 12
l(min) = 0, l(max) = 5

R(obs/all) from e.s.d. of I : 0.96/ 1.04

Information from culling : no reflection was culled

OK

The Rint(obs/all) = 19.17%/19.24% for 844/898 independent reflections.

OK; FINISH

5. Structure Solution Wizard

OK to close the information window and start the solution wizard

[On the screen: window of Structure solution]

Structure solution wizard can be executed separately from the Command tree. JANA020 does not contain solution procedures, it calls external programs. By default, Jana uses Superflip (using charge flipping as the solution method). Superflip is distributed with Jana2020.

In "Formula" textbox type the expected formula: Fe Mg Si2 O6

Superflip does not need information about the chemical composition but it will be required for the peak assignment based on the electrostatic potential map calculated by Superflip. If Jana2020 is used for peak assignment, a list of expected chemical elements is sufficient. If you know the expected formula (like here), you may enter it and use EDMA for peak search (at the bottom of the window). If the formula is correct, EDMA often gives cleaner and more complete interpretations of the solution.

Click the radio button "EDMA – fixed composition"

EDMA is an external program for interpretation of electron densities. It can take the chemical formula and interpret the density using this formula.

Leave other settings default; Run Superflip

[On the screen: window of Superflip appears]

Commands for Superflip

Basic commands | Advanced commands

Formula: Fe Mg Si2 O6 Phase: ▼

Formula units: 8 ▲▼ Calculate density Sum formula from structure model

Actual space group: Pbca Change the space group

☐ use in le Bail decomposition structure information for already identified phases

☐ allow manual editing of the command file before start

☐ use previously prepared input file for Superflip

☐ use old solution and reinterpreted

☐ Repeat Superflip: Until the convergence detected Bis: 0

☒ Repeat Superflip: Number of runs => 10 Maxcycles: 2000

☐ Use local normalization

☒ Use a specific random seed => 111

☒ Define explicitly delta value => 0.9

Iteration scheme: ☒ CF ☐ LDE ☐ AAR

For peak search use: ☒ EDMA - fixed composition ☐ EDMA - fixed number of atoms => 0 ☐ EDMA - peak interpretation by Jana2020 ☐ Peaks from Jana2020 ☐ Peaks from Jana2020 but first run Fourier

Starting model: ☒ Random phases ☐ Patterson superposition map

Run Superflip Open the listing Draw structure Draw 3d map

Replace the result with tutorial files Accept last solution Quit

Window of Superflip appears with iteration running. After ten runs, listing of Superflip log file is displayed.

Press OK at the end of the procedure to close the "Information" window

Click on "Replace the result with tutorial files" for reproducibility of the results;OK.

You can switch between your solution and tutorial one by clicking on the same button.

Open the listing

Superflip performed ten solution attempts. Check the space groups derived by Superflip from each of the attempts. In all cases the proposed space groups are $Pbca$ or $P2_1ca$. But the b -glide plane in the suggested $P2_1ca$ space group is close to the limit of 25 below which it is considered as agreeing with the proposed symmetry. It is thus likely (though not guaranteed!) that $Pbca$ is indeed the correct space group.

Properties of the saved density:

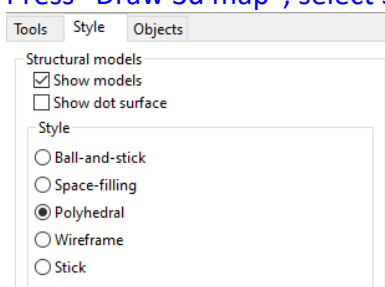
Run Rvalue Peaks Symm. Der.SG

10 40.92 2.28 12.95 $Pbca$

Electron density written to file opx_Superflip.m81.

[Close the listing](#)

Let's have a look at the raw solution that is 3d electrostatic potential map
[Press "Draw 3d map", select Style "Polyhedral".](#)



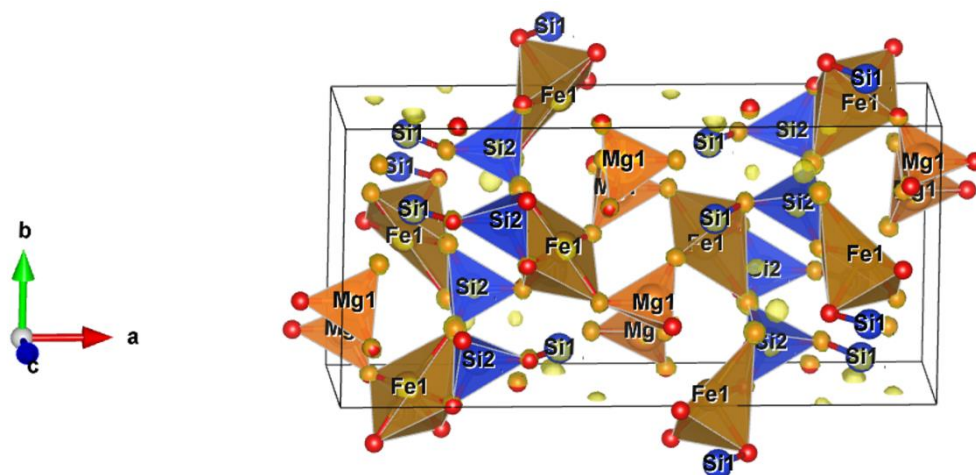
VESTA opens with a 3d electrostatic potential shown as isosurfaces, and an atomic model overlaid (in the default settings the shown isosurface level corresponds to the 2σ level based on the statistics of the 3D electrostatic potential map). Rotate the view to inspect the structure. Try to recognize the structural motifs.

The main expected motifs are SiO_4 tetrahedra and $(\text{FeMg})\text{O}_6$ octahedra.

Viewing the structure solution in VESTA has the advantage that you can directly check, if the raw density was correctly interpreted. In this case, the solution is perfect and all atoms are properly located. The only problem is that some cations have been assigned a wrong atomic type. By inspecting the structure, you should conclude that the following two atoms need to be changed:

Mg1 -> Si

Si1 -> Mg or Fe – we will choose Mg for the moment

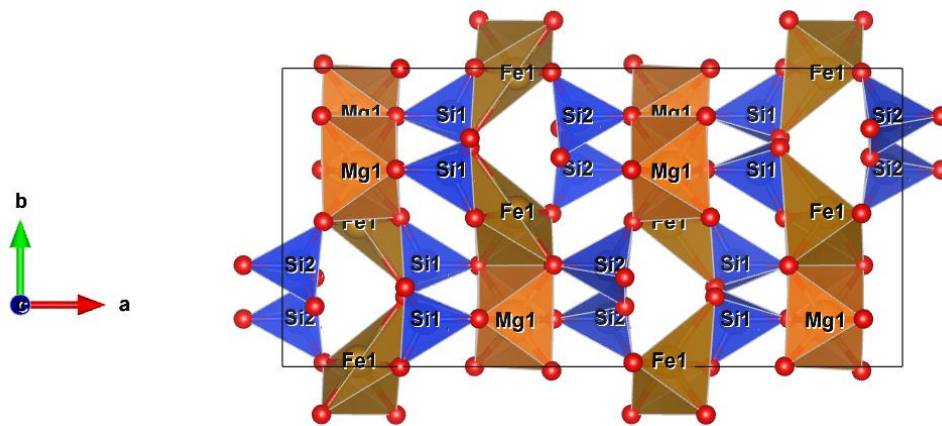


In vesta, if you want to change the atom type to visualize the result as it should be,

Close Vesta, Accept last solution.

Go to Edit, Edit data, Structure parameters,

Change the atom types that need to be changed (Fe1 into Mg, Si1 into Fe and Mg1 into Si).



The program creates file pyrite.m40 with atoms of the structure model

To access the list of atoms with their positions and atomic displacement parameters, you can open the pyrite.m40 using “Edit file” menu in Command tree, or using “Edit structure parameters → Edit atomic parameters”, or using the quick button “Edit atoms”.

Now we need to adjust the atom types that need to be changed as we saw in vesta.

Click on the icon “Edit atoms”  on the left side of the main panel,

Double click on Si1 (or click once to select Si1 and then Press “Action” → Define/Edit atom parameters).

In the “Define” panel, select “Mg” for the atomic type.

In the same define tab, press “Select atom(s) from list” and select the second atom that need to be adjusted: change the atom type of Mg1 into Si

Press OK.

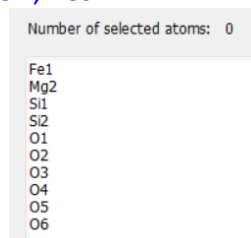
In “Edit atomic parameters”, select all the atoms,

Press Action and “Rename atoms “atom_type” +number”.

All atoms are renamed according to their atom type and their order in the list. This is a useful tool but to help in the interpretation later in the tutorial, it will be easier to rename Mg1 in Mg2.

Rename manually Mg1 to Mg2.

OK; Yes.



You should end up with a similar list of atoms.

6. Kinematical refinement

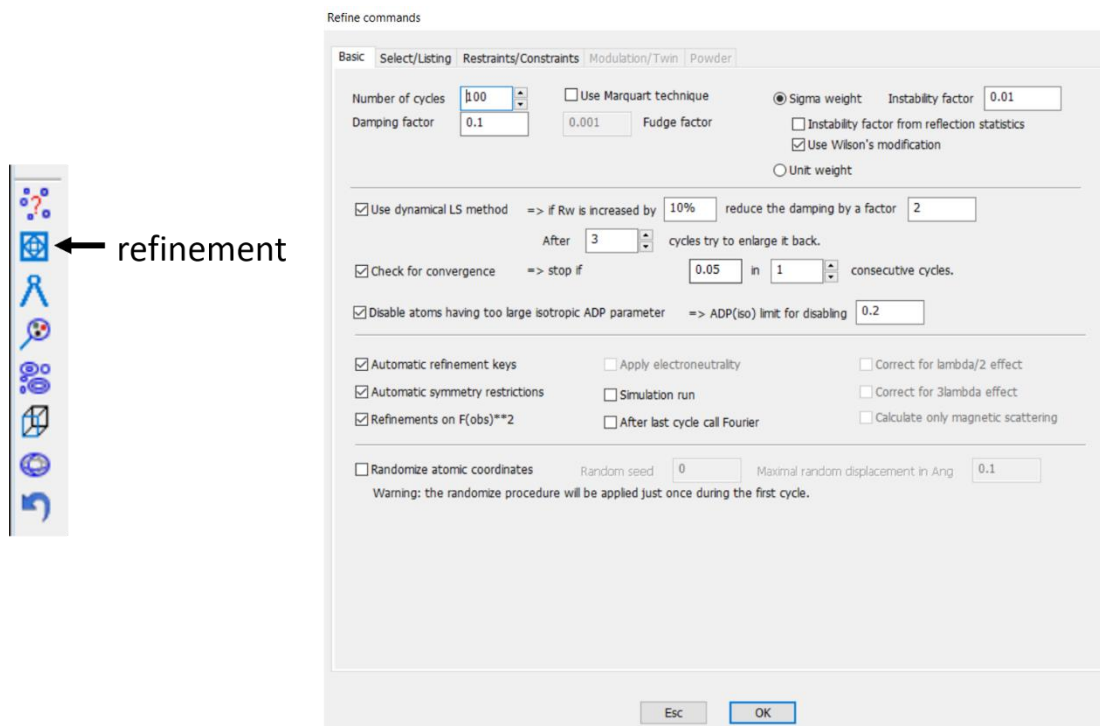
We suggest to save the structure under a new name to keep track of previous results

Structure/Save as/ opx_kin (or any name you will find suitable)

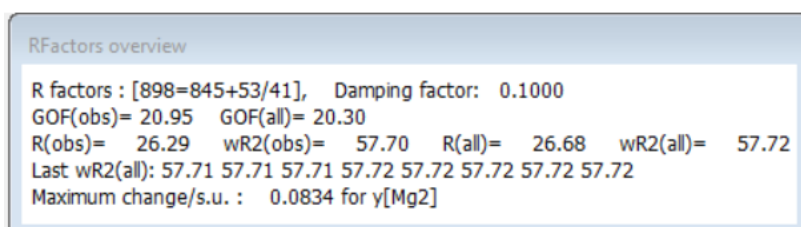
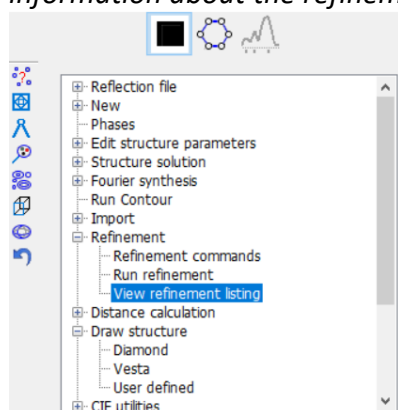
Yes, to continue with the new structure.

Right-click the quick button “Run Refinement” .

Change the number of cycles to 100 the damping factor at 0.1;
OK, Yes+Start.



Refinement converges with R values of $R(\text{obs}) = 26.29\%$, $wR2(\text{obs}) = 57.70\%$ for 845/898 observed over all reflections and 41 refined parameters. At this moment you may check the refinement listing (Command tree → Refinement → View refinement listing”) with a lot of information about the refinement procedure and the results.



7. The resulting structure

The kinematical refinement is usually not accurate to determine the ADPs parameters. It happens that some values are slightly below zero even when the atom type is correctly

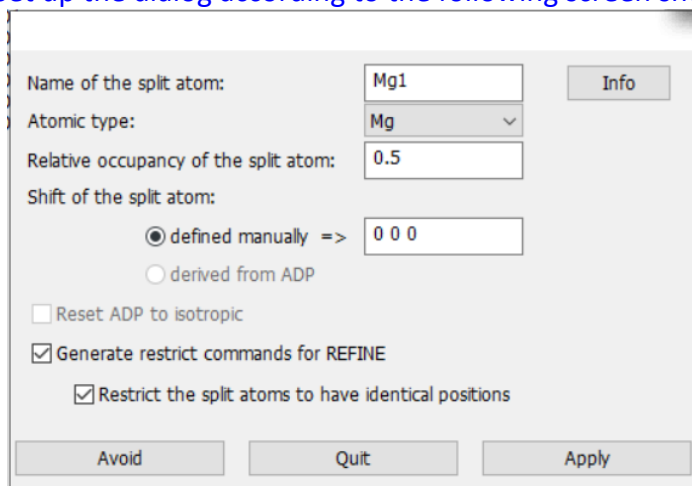
assigned. Too high values or too small mean usually that this is the wrong atomic type, or the occupancy is not correct.

However, for orthopyroxene, we can already use the Uiso to understand some characteristic of the structure. You will notice that Uiso values for Fe1 is very high compare to the other atoms and Mg2 has a negative Uiso. Without more information, this can be an artifact of the kinematical refinement, which does not correct properly for multiple scattering effects, or, the octahedral positions are not exclusively occupied by iron or magnesium, but by both elements. In that case, we have to refine the mixed occupancy in these sites.

Click icon Edit atoms on the quick menu

Select Fe1 and Right-click atom Fe1 → Split atomic position

Set up the dialog according to the following screen shot:



Apply;

Repeat the procedure with Mg2 to generate atom Fe2 at the same position.

Ok, Yes.

Right-click Refine icon → Restrictions/Constraints

Press Restrictions to access the list.

Click on the restriction on atoms Mg2 and Fe2 (restric Mg2 1 Fe2).

The coordinates and the ADP parameters are restricted to be the same, and the sum of occupancies is restricted, too.

Exchange the order of atoms in the restriction, so that Fe is always the “master” atom.

Click Rewrite

When finished, the dialog should look like this:

Define restrictions

<pre> restric Fe1 1 Mg1 restric Fe2 1 Mg2 </pre>	Edit Delete Disable Enable Down Up Select all Refresh Clone
--	--

Rewrite

Make identical:
☒ Coordinates
☒ Modulations
☒ ADPs
☐ Magnetic parameters
☐ Population of valence electrons
☐ Kappa
☐ Kappa*

Occupancies:
☐ Modulated identically
☐ Modulated complementarily
☒ Keep overall sum
☐ not restricted

Atoms/molecules:

Esc OK

OK; OK; Yes (do not start refinement yet!)

Now we have restricted the atomic pairs, but the occupancies are still fixed and would not be refined. We have to allow their refinement explicitly:

Click the icon "Edit atoms"

Double click atom Fe1

On the card "Edit" check the box next to the parameter "occ"; OK

Repeat for atom Fe2

OK to close the Edit atoms dialog; Yes

Click the Refine icon to start refinement

Refinement converges to $R(\text{obs}) = 25.18\%$. The refined atomic occupancies are:

Fe1: 0.45(6)

Fe2: 0.46(6)

PART 3 - Dynamical refinement in Jana2020

1. Preparation of reflection file for the dynamical refinement

At this moment there is very little we can do with the kinematical refinement. We have a satisfactory refinement, the structure makes sense, the occupancies have been refined, but their accuracy cannot be estimated from the kinematical refinement. We will now proceed to the structure refinement using dynamical diffraction theory.

During the integration procedure in PETS2.0, an input file for dynamical refinement was created. The integration for the dynamical refinement considers each diffraction image separately. The result is a list with the hkl indices, the measured intensity with the respective $\sigma(I)$ and the number of the frame in which the intensity is present. PETS2.0 creates the file `opx_dyn.cif_pets` with all this information, which will be used in Jana2020. Note that the same

hkl reflection might be present in several frames, with different intensity due to the multiple scattering relative to different crystal orientation and thickness at this condition.

In the main menu bar, use “Structure → Save as” and save a new structure *opx_dyn* for the dynamical refinement

YES to Continue with the new structure.

*This step saves the structure you refined kinematically as a new job, which will be used for dynamical refinement. Now we need to replace the current data file for kinematical refinement by the *opx_dyn.cif_pet* one dedicated to the dynamical approach.*

In Command Tree, expand „Reflection file“ and start „Import-modify reflection file“
Click „Reimport“

*Again, if you want to be sure that you can exactly reproduce the following part of the tutorial, use the file *pyrite_reference_dyn.cif_pets* provided with the example files.*

Select the *opx_reference_dyn.cif_pets* as the new reflection file

Make sure the box “Make the reflection file for dynamical refinement” is checked.

NEXT,

NEXT, NEXT,

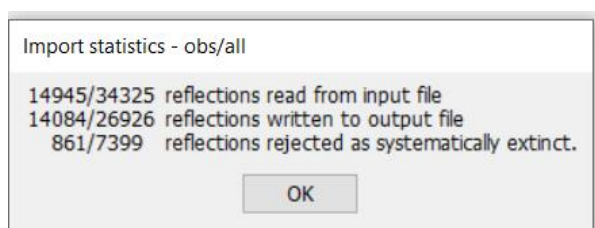
You get the message “All 34325 input reflections were properly handled”

OK

NEXT, FINISH, OK

Then on the panel Processing refinement reflection file for : Block 1,

NEXT, OK, OK, FINISH



You can find this information in the file *.rre (Edit/View → Reflection report).

2. Dynamical refinement parameters

In Command Tree, expand “Edit structure parameters” and start “Edit parameters for electron diffraction”

The default values for the selection of the intensities are: $g(\max)=1.6 \text{ \AA}^{-1}$, maximal excitation error $Sg(\text{matrix})=0.01$, maximal excitation error (refine) = 0.1, $Rsg(\min) = 0.4$, $DSg(\min) = 0$ and the number of integration steps 108. These values are “safe” to produce good quality refinement, but they are not optimized for speed. In this case, parameters more optimized for speed still produce good result.

Change the parameters according to the following image ($g(\max)$ and Number of integration steps):

Orientation matrix: U11 0.03367 U12 0.08821 U13 -0.00011
 U21 -0.04236 U22 0.06999 U23 -0.00827
 U31 -0.00186 U32 0.00322 U33 0.18933

Maximal diffraction vector g(max): 1.7 Number of integration steps: 96 Geometry: ☒ precession ☐ rotation
 Maximal excitation error (Matrix): 0.01 Use dynamic approach: ☒
 Maximal excitation error (Refine): 0.1 Use twin version: ☐
 RSg(max): 0.4 Apply correction for crystal tilt: ☒
 DSg(min): 0 For Fourier rescale to Fcalc: ☐
 Number of threads: 6
 Dyngo commands:

Select zones for refinement Define zones of equal thicknesses

Run optimizations except of scale, optimize also: ☐ Thickness ☐ Orientation Show thickness plots

Zone#: 1 uvw: (-0.242,0.403,1.000) R(all)= Select zones for editing

Precession angle 1.2 Alpha 44.815 Beta -0.14
 EDScale 1 EDThick 400 EDPhi 0 EDTheta 0

Esc OK

You can set the number of threads to the number of cores on your processor to speed up the calculation.

3. Sample thickness

The sample thickness is an important parameter of the dynamical refinement. The default value is 400 Å. The refinement is rather time consuming, so we will only select one every three frames. Go to “Select zones for refinement” and select each 3 frames.

Select zones for refinement

Zone#1	Zone#21	Zone#41	Zone#61	Zone#81
Zone#2	Zone#22	Zone#42	Zone#62	Zone#82
Zone#3	Zone#23	Zone#43	Zone#63	Zone#83
Zone#4	Zone#24	Zone#44	Zone#64	Zone#84
Zone#5	Zone#25	Zone#45	Zone#65	Zone#85
Zone#6	Zone#26	Zone#46	Zone#66	Zone#86
Zone#7	Zone#27	Zone#47	Zone#67	Zone#87
Zone#8	Zone#28	Zone#48	Zone#68	Zone#88
Zone#9	Zone#29	Zone#49	Zone#69	Zone#89
Zone#10	Zone#30	Zone#50	Zone#70	Zone#90
Zone#11	Zone#31	Zone#51	Zone#71	
Zone#12	Zone#32	Zone#52	Zone#72	
Zone#13	Zone#33	Zone#53	Zone#73	
Zone#14	Zone#34	Zone#54	Zone#74	
Zone#15	Zone#35	Zone#55	Zone#75	
Zone#16	Zone#36	Zone#56	Zone#76	
Zone#17	Zone#37	Zone#57	Zone#77	
Zone#18	Zone#38	Zone#58	Zone#78	
Zone#19	Zone#39	Zone#59	Zone#79	
Zone#20	Zone#40	Zone#60	Zone#80	

From the zone# 1 select each 3 rd zone

Select all Refresh

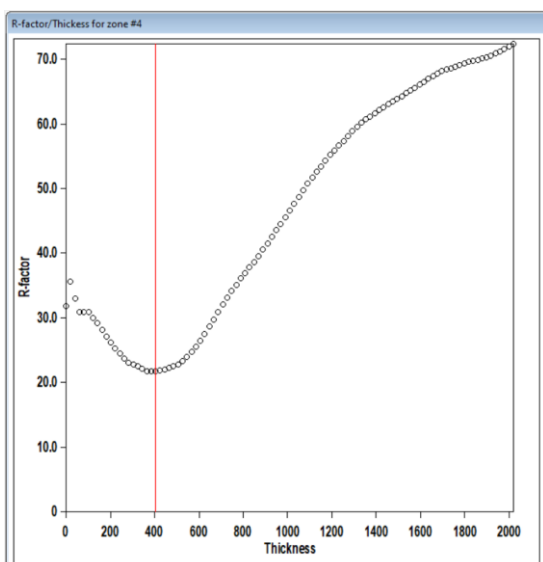
Esc OK

Enable “Except of scale, optimize also: Thickness”

Click “Run optimizations”

Dyngo calculates wR-factor for the thickness varying from 0 to 2000 Å.

“Show thickness plots”. Check the variation of the thickness of the crystal for the frames. Quit.



Most frames have well defined wR -factor minima for one thickness. However, few frames either have poorly defined minimum or the minimum is at a very different thickness. You can check the $wR(\text{all})$ going through the zones in the main window of “parameters for electron diffraction data” or while viewing the graphs. Looking at the typical position of the minimum across the frames you can see that 400 Å is usually a reasonable starting point for the refinement.

“Select zones for editing → Select all → OK”

Click in the field EDThick, click the button Unlock and type 400 for “EDThick”.

Disable “Except of scale, optimize also: Thickness”

Click “Run optimizations”

Neither the Thickness nor the Orientation check box should be checked: only the scale factors of individual frames are optimized with the new common thickness and sets a good starting point for the least-squares refinement.

Click OK and YES to return to the main screen of Jana2020.

4. Initial refinement

This refinement can be too time-consuming for the workshop. If the procedure takes too long on your computer, you can use the reference refinement to get directly to the result.

The JANA2020 jobs `opx_dyn` and `opx_dyn_orientation` are in the folder `Jana2020_reference/2_dyn`.

Right-click on quick button “Refine”, confirm the number of cycles is set to 100 and the damping factor to 1.

OK; “Yes+Start”.

The refinement converges after 8 cycles in 20 minutes. Depending on your computer’s performances, you might need to use the reference result (`opx_dyn` in `Jana/2_dyn`).

You can see the details of the refinement in the file `opx_dyn.ref` on the screen or in refinement listing (Command Tree → Refinement → View refinement listing). The refinement converges with $R(\text{obs})/wR2(\text{obs}) = 9.52\% / 21.48\%$ for 1436 observed reflections and 73 parameters. It is important to check the ratio observed reflections to refined parameters, which is around 20 in the present case (1436/73). It is recommended to keep this ratio above 10. It can be increased by increasing $RSg(\text{max})$ (selecting more reflections for the refinement).

Another important aspect to check is the number of observed reflections per zone (frame). Also, in the *opx_dyn.ref* file (refinement listing), you can see “R-factors for individual zones”, where the list of zones with the respective R-factors and number of reflections is shown.

```
-----
|R factors : [2206=1436+770/73],      Damping factor:  1.0000
|GOF(obs)=  4.71      GOF(all)=  3.85
|R(obs)=   9.52      wR2(obs)= 21.48      R(all)=   12.22      wR2(all)= 21.85
|Last wR2(all): 21.99 21.86 21.85 21.85 21.85
|Maximum change/s.u. :    0.0234 for EDThick[Zone#1]
|
*****
* R-factors for individual zones *
*****
```

	Robs	wRobs	Rall	wRall	nobs	nall
Zone#1	10.93	23.49	14.13	23.90	49	78
Zone#4	9.51	17.93	14.60	18.76	45	80
Zone#7	15.91	36.20	16.86	36.29	58	70
Zone#10	11.73	24.67	13.08	24.83	63	81
Zone#13	8.16	17.84	9.89	18.26	60	81
Zone#16	13.08	22.77	16.09	23.13	48	76
Zone#19	7.98	17.64	12.75	18.17	40	74
Zone#22	8.55	18.07	15.46	19.23	34	79
Zone#25	6.12	11.88	9.12	12.49	45	67
Zone#28	8.22	16.97	11.52	17.53	42	70

Note that the displacement parameters of both Fe1/Mg1 and Fe2/Mg2 are positive.

The occupancies are Fe1 = 0.49(2) and Fe2 = 0.08(2).

These results can be improved.

5. Optimization of orientation

[On the screen: Main window of Jana2020].

Save a new structure “Structure→Save as→opx_dyn_orient”; OK; YES

In Commads Tree, expand “Edit structure parameters” and start “Edit parameters for electron diffraction”

[On the screen: Parameters for electron diffraction data]

Enable “Except of scale, optimize also: Orientation”

Click “Run optimizations”

[On the screen: Intensity calculation for optimizing of orientation]. This step takes some time.

Using “Zone #” box, check the resulting EDTheta for the individual frames.

EDTheta is the amplitude of the correction of the frame orientation. It should be a small number, a few tenths of a degree at most because the misorientation were corrected in PETS during the data reduction. A deviation of 0.5° is already high and signifies a failure of the optimization procedure for this individual frame. In such case, the frame should be removed from the refinement. In the current case no value of ED Theta exceeds 0.5°.

OK; YES to save file M42

Start the refinement.

The refinement converges after 9 cycles with $R(\text{obs})/wR2(\text{obs}) = 7.35\%/15.51\%$ for 1405/2168 observed/all reflections and 73 refined parameters (42 structural parameters + crystal thickness + 30 frame scales).

The refined thickness is 502(5) Å.

```

-----
|R factors : [2168=1405+763/73],      Damping factor:   1.0000
|GOF(obs)=   3.46      GOF(all)=   2.88
|R(obs)=    7.35      wR2(obs)=  15.50      R(all)=   10.32      wR2(all)=  16.08
|Last wR2(all): 16.43 16.23 16.13 16.10 16.09 16.08 16.08 16.08
|Maximum change/s.u. :   0.0167 for EDThick[Zone#1]
-----

```

```

*****
* R-factors for individual zones *
*****

```

	Robs	wRobs	Rall	wRall	nobs	nall
Zone#1	8.40	14.64	12.96	15.83	48	79
Zone#4	9.65	18.47	14.87	19.27	42	77
Zone#7	10.20	18.87	11.47	19.07	61	75
Zone#10	9.27	16.03	10.48	16.23	59	78
Zone#13	5.91	13.69	7.76	14.22	56	77
Zone#16	10.17	18.65	13.03	19.06	51	77
Zone#19	7.37	16.04	11.01	16.55	48	81
Zone#22	8.19	17.31	15.09	18.61	35	78
Zone#25	6.35	11.74	9.52	12.38	44	69

6. Difference Fourier map

Difference Fourier map is used to check if there is any missing electrostatic potential that has not been described by the structure model yet. This is not the case here, the structure is very simple, but in general you have to check it.

[On the screen: main window of Jana]

Right-click the quick button “Run Fourier synthesis”

Select the following parameters to calculate the Fourier map.

Basic Scope Peaks

Map type: **F(obs)-F(calc) - difference Fourier**

☒ Use weighting of reflections

☐ Omit not-matching reflections

Reflections with *|F(calc)| will be

☒ Apply sin(th)/lambda limits

sin(th)/lambda max.

Define reference structure:

Correction of |F(obs)| for ☐ based on difference F(obs)²-sum(w

OK; “Yes+start”

Choose “No” to avoid the procedure for including new atoms.

Choose “No” to avoid opening the listing.

In Command Tree, double-click “Run Contour”

In Command Tree of Contour, expand “Use old Fourier map” and start “Draw maps as calculated”

[On the screen: Contour program]

In the right panel, use “Go to map” to display next/previous two-dimensional section

In bottom toolbar, press the button “Run Vesta”

To adjust the display of the potential map, go to Properties in VESTA, tab Isosurfaces. Click on isosurface No 1 and change it to Positive and its level. To display the isosurface corresponding to 3σ , multiply the value of the isosurface level by 1.5.

No significant isosurface can correspond to a missing atom.

Close Contour

7. The resulting structure

You can view the resulting structure in JanaDraw or by using your favorite program associated with Jana2020 - see "Draw structure" in the Command Tree.

The most interesting result is the refinement of the occupancies for Fe1/Mg1 and Fe2/Mg2.

We can compare the occupancies obtained from the differentes procedures: kinematical and dynamical approach with the new data processing, the old dynamical refinement with the old data processing, the x-ray refinement.

The new features in the data processing bring significant improvements in the accuracy of the results. If we take the x-ray refinement as a reference, the dynamical refinement with the new data processing is more precise than the refinement from 2015.

occupancies	Kinematical New data processing (2021)	Dynamical New data processing (2021)	Dynamical Old data processing (2015)	x-ray data
Fe1	0.45(6)	0.47(1)	0.59(3)	0.432(3)
Fe2	0.46(6)	0.14(1)	0.22(2)	0.157(3)