HKLF5 Tutorial: $[Br_3F_8][SbF_6]$ twin crystal

This tutorial is divided in two parts. The first part is introductory and describes the initial data processing that was performed in advance. The second part contains the practical instructions for the user to learn the basic functionality of the HKLF5 software. In order to follow this tutorial the user must have a structure refinement software installed on his/her PC. The following instructions will be given for the ShelXL / ShelXle software.

1. Introduction

Octafluoridotribromine(III) hexafluoridoantimonate(V) was synthesized by the following reaction:

$$[BrF_2][SbF_6] + 2\ BrF_3 \rightarrow [Br_3F_8][SbF_6]$$

At room temperature the compound exists as a liquid. The crystallization was done by immersing a vessel with the compound in perfluorinated oil / dry ice bath. The single, solid lump of solidified $[Br_3F_8][SbF_6]$ was crushed under cold perfluorinated oil. The measurement was performed on a Stoe IPDS2T diffractometer equipped with a Mo-Kα sealed X-ray tube and an image plate detector.

The compound crystallizes in the monoclinic crystal system with the cell parameters a = 10.111(2), b = 9.0433(18), c = 9.986(2) Å, β = 94.16(3)°, V = 910.8(3) Å^3 at 100 K. We noticed during indexing that the crystal consisted of two twin components related by a 4-fold rotation axis parallel to the c-axis. An example of one image plate with the reflections of both twin components is shown in Figure 1.

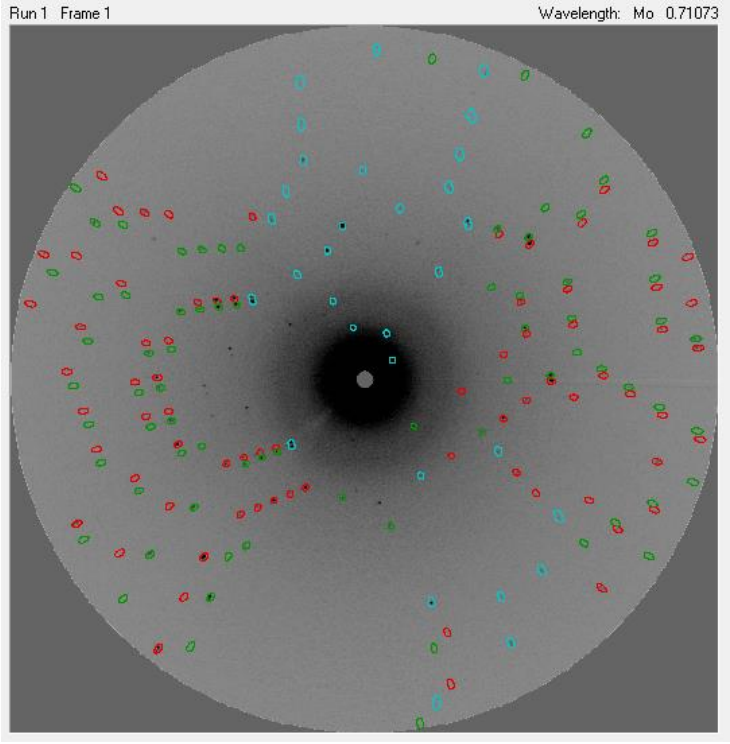


Figure 1. One image plate frame with diffraction spots collected from a crystal of $[Br_3F_8][SbF_6]$. The following colors are used: the 1st twin component in red, the 2nd twin component in green, overlapping reflections of both components in cyan.

After data reduction the following HKL files were created:

1) a file containing non-overlapping reflections of the 1st twin component (HKLF4 format)
2) a file containing non-overlapping reflections of the 2st twin component (HKLF4 format)
3) a file containing all reflections of both twin components (HKLF5 format)

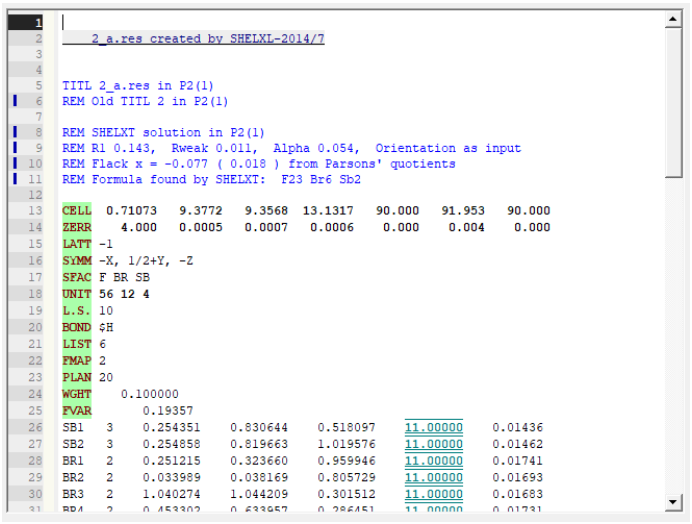
Files 1 and 3 were corrected for absorption using the algorithms implemented in the X-Area software. File 1 was used to solve the structure using the SHELXT software.

2. Practical part

1. Copy the following files from the ZIP archive containing this tutorial to a separate folder:

- tutorial.res (SHELXL .res file)
- tutorial.hkl (reflection file with non-overlapping reflections of the 1st twin component)
- tutorial.hklf5 (reflection file with all reflections of both twin components)
- HKLF5Tools.exe (the software)

2. Open tutorial.res file in the ShelXle software. The following screenshot shows the first lines in this file. For meaning of the keywords please refer to the SHELXL Manual.



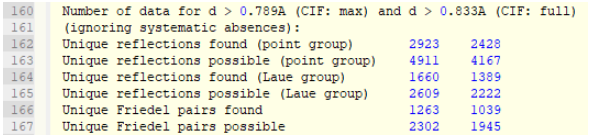
```
    2_a.res created by SHELXL-2014/7


TITL 2_a.res in P2(1)
REM Old TITL 2 in P2(1)

REM SHELXT solution in P2(1)
REM R1 0.143,  Rweak 0.011,  Alpha 0.054,  Orientation as input
REM Flack x = -0.077 ( 0.018 ) from Parsons' quotients
REM Formula found by SHELXT:  F23 Br6 Sb2

CELL  0.71073   9.3772   9.3568  13.1317   90.000   91.953   90.000
ZERR    4.000   0.0005   0.0007   0.0006    0.000    0.004    0.000
LATT -1
SYMM -X, 1/2+Y, -Z
SFAC F BR SB
UNIT 56 12 4
L.S. 10
BOND $H
LIST 6
FMAP 2
PLAN 20
WGHT    0.100000
FVAR       0.19357
SB1   3    0.254351    0.830644    0.518097    11.00000    0.01436
SB2   3    0.254858    0.819663    1.019576    11.00000    0.01462
BR1   2    0.251215    0.323660    0.959946    11.00000    0.01741
BR2   2    0.033989    0.038169    0.805729    11.00000    0.01693
BR3   2    1.040274    1.044209    0.301512    11.00000    0.01683
```

3. Click the button “XL refine”. The refinement should converge to R_1 = 0.0424 and wR_2 = 0.1117, which is good enough for this type of compound. However, the completeness of the dataset suffers from the absence of the overlapping reflections, as they are not included in the HKLF4 dataset. To examine the completeness scroll the .lst file (created after refinement) down to the lines “Unique reflections found” and “Unique reflections possible”.



```
Number of data for d > 0.789A (CIF: max) and d > 0.833A (CIF: full)
(ignoring systematic absences):
Unique reflections found (point group)       2923    2428
Unique reflections possible (point group)    4911    4167
Unique reflections found (Laue group)        1660    1389
Unique reflections possible (Laue group)     2609    2222
Unique Friedel pairs found                   1263    1039
Unique Friedel pairs possible                2302    1945
```

4. To overcome the completeness problem the HKLF5 file must be used. Rename the “tutorial.hklf5” file to “tutorial.hkl”. The old .hkl file will be replaced. If necessary, its copy can be restored from the ZIP archive.

5. In order to run refinement on the HKLF5 data we need to change the “HKLF 4” line in the .res file to “HKLF 5”. Additionally, the BASF keyword must be specified. Add the “BASF 0.4” line, for example, between the “LIST 6” and “FMAP 2” lines. Then click “XL refine”. The refinement should converge to $R_1 = 0.0364$ and $wR_2 = 0.1599$ for all data. The worse wR_2 value may indicate that one of the twin components is of poorer quality than the other. The volume fraction of the 2nd twin component (the BASF parameter) equals 0.341(2).

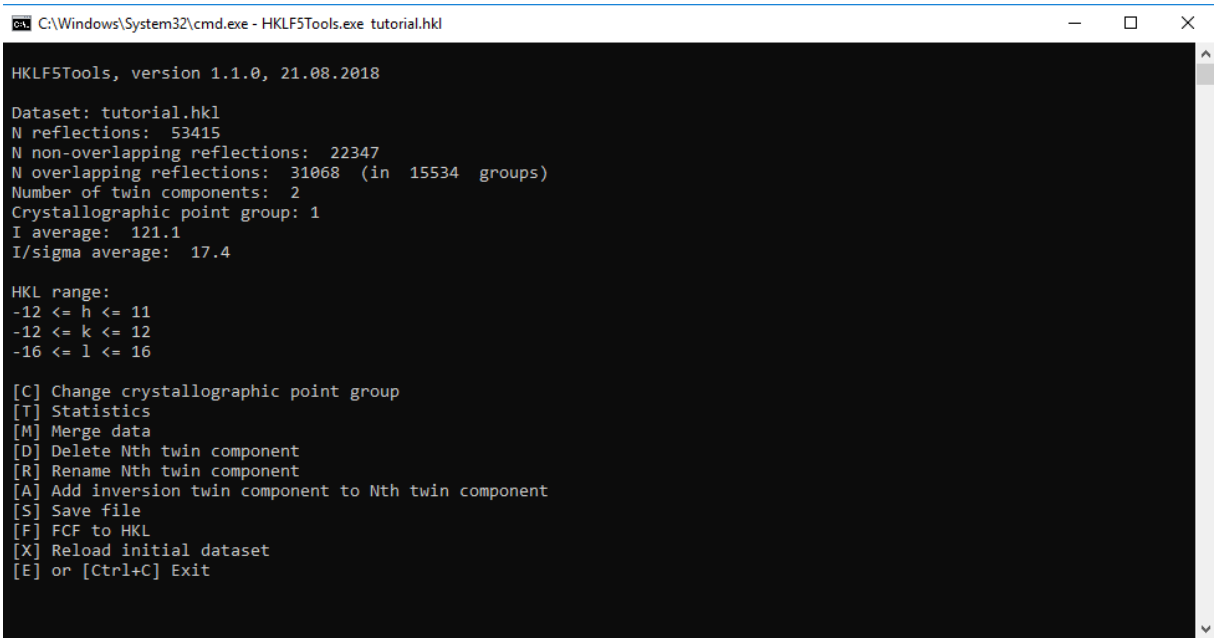
Although the problem of completeness is now solved (check the .lst file), ShelXle reports another two warnings:

- “Possible inversion twin or centrosymmetric space group”. This may indicate presence of inversion twin components.
- “MERG code changed to 0 for compatibility with HKLF and BASF parameters”. This means that ShelXL does not merge the data before refinement. It influences the standard uncertainties of atomic positions, and thus also those of bond lengths and angles.

It is not possible to handle these problems using the ShelXL / ShelXle programs only.

6. Open the command line interface in the tutorial folder. Execute the following command: *hklf5tools.exe tutorial.hkl*

This command starts the software and loads the given reflection file. The screenshot below shows the main menu of the software.



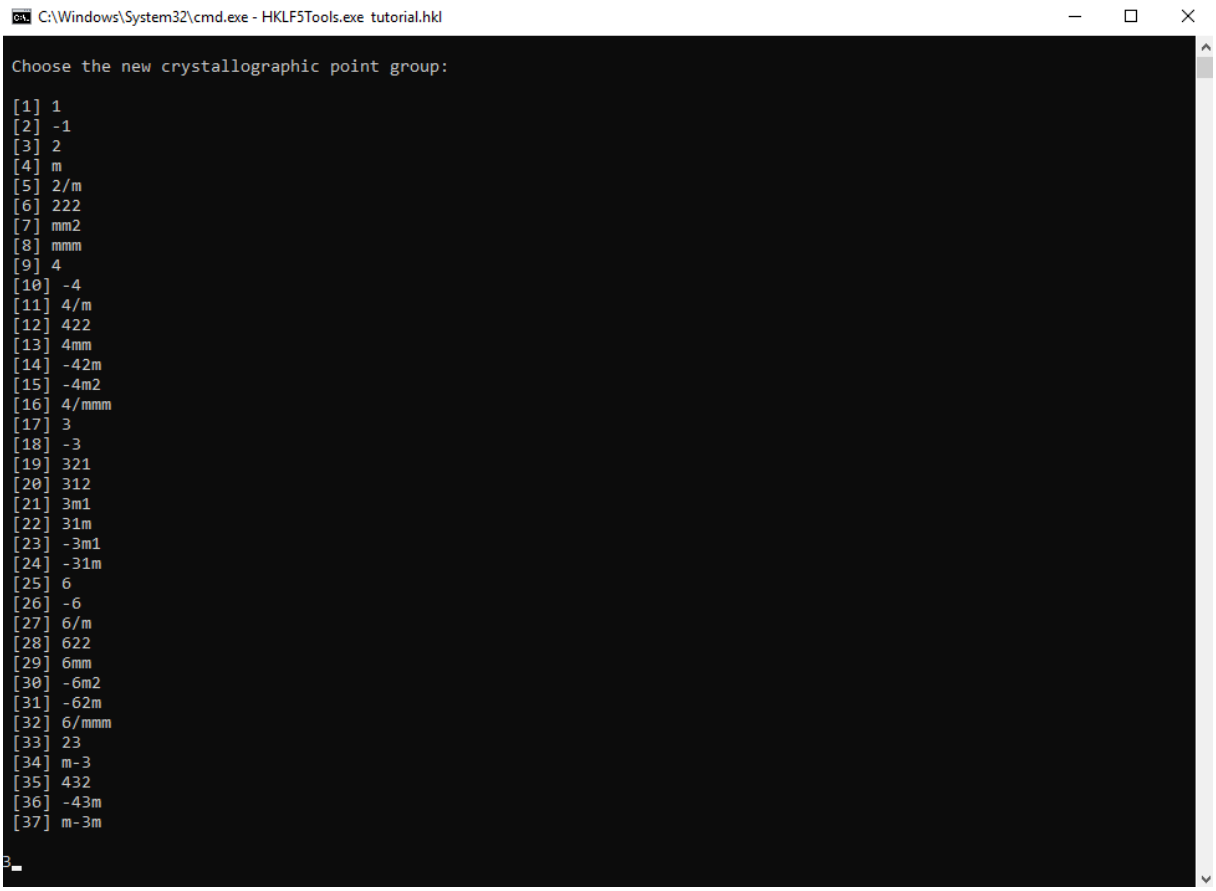
The following information is given in the header of the interface:

- “HKLF5Tools, version 1.1.0, 21.08.2018”: The name, version and release date of the software
- “N reflections: 53415”: Total number of reflections in the given HKL file
- “N non-overlapping reflections: 22347”: The number of non-overlapping reflections
- “N overlapping reflections: 31068 (in 15534 groups)”: The number of overlapping reflections. The reflections that coincide in the same diffraction spot are considered to

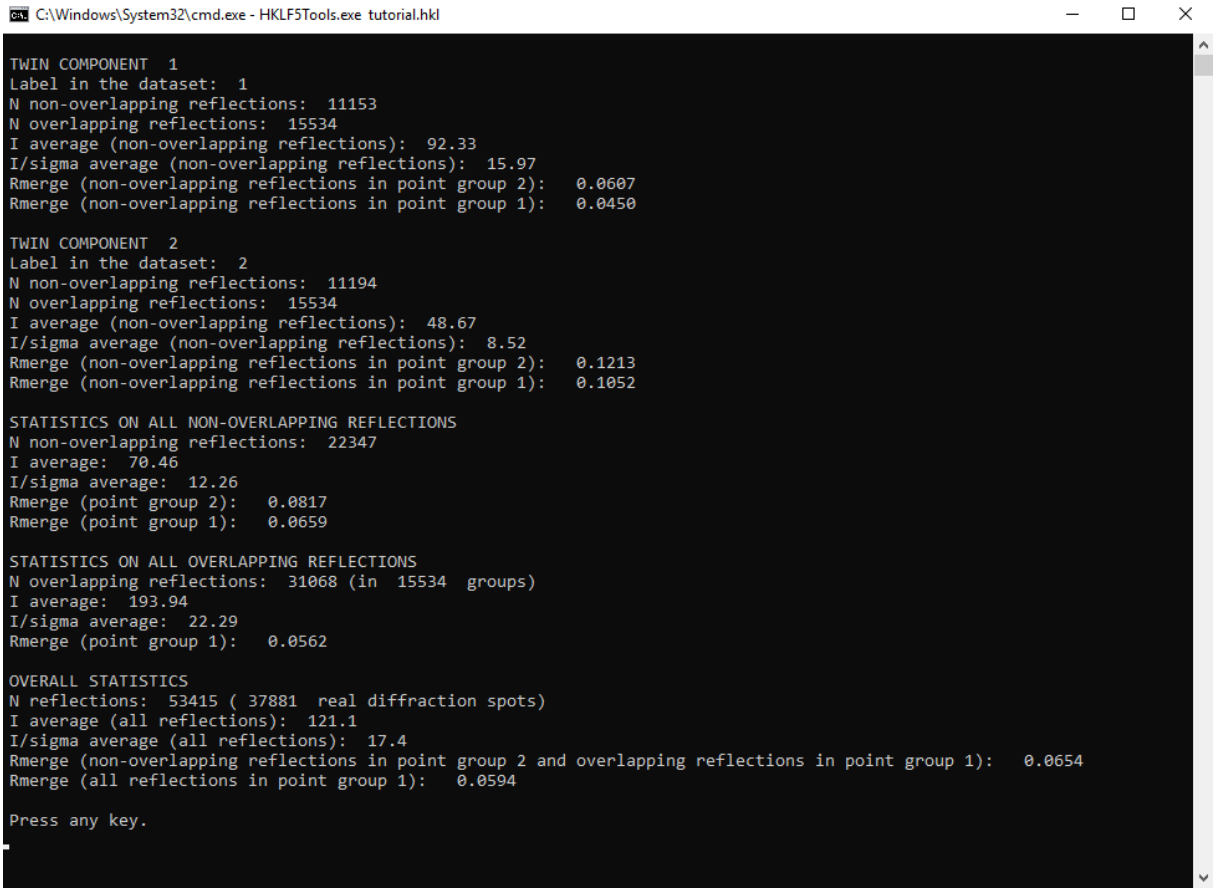
belong to one group (i.e. number of groups is at least twice smaller than number of overlapping reflections).

- "Number of twin components: 2": The number of twin components, which reflections were found in the given HKL file
- "Crystallographic point group: 1": The point group of the crystal that determines which reflections will be considered as symmetry equivalent. By default, it is always 1. The correct point group should be specified by the user.
- "I average": The average intensity of all reflections
- "I/sigma average": the average signal-to-noise ratio for all reflections
- "HKL range": the ranges of the Miller indices of reflections found in the HKL file

7. As the first step, we need to select a proper crystallographic point group. The space group of $[Br_3F_8][SbF_6]$ is $P2_1$, which means that the symmetry equivalent reflections are defined by the point group 2. In the software choose the option "[C] Change crystallographic point group" and then type "3" as in the screenshot below.



8. Choose the option "[T] Statistics" to see important statistical information on the dataset.



The first two blocks give information about non-overlapping reflections of the individual twin components: label in the dataset (as in the HKL file), numbers of overlapping and non-overlapping reflections, average intensities, average signal-to-noise ratios, and R_{merge}-factors for non-overlapping reflections in the chosen point group as well as in point group 1. Then the similar blocks for all non-overlapping, all overlapping, and finally for completely all reflections are shown.

As seen from the R-values, the dataset in general is of good quality. However, the reflections of the 2nd twin component were merged with a significantly worse R-factor than the reflections of the 1st twin component. This is likely due to the fact that the 2nd twin component diffracts weaker in this case. Taking the BASF value from the last refinement into account, this seems reasonable.

9. According to statistical information, the reflections of the 2nd twin component do not improve our structural model. So, it is reasonable to remove the non-overlapping reflections of the 2nd twin component. Return to the main menu by pressing any key and choose the option “[D] Delete Nth twin component”. Then type “2” and choose option “[N] Non-overlapping reflections”.

If now we go to “[T] Statistics”, we can see that no more non-overlapping reflections of the 2nd twin component are present in the dataset.

```
TWIN COMPONENT  2
Label in the dataset:  2
N non-overlapping reflections:  0
N overlapping reflections:  15534
I average (non-overlapping reflections):  0.
I/sigma average (non-overlapping reflections):  0.
Rmerge (non-overlapping reflections in point group 2):   0.0000
Rmerge (non-overlapping reflections in point group 1):   0.0000
```

10. Now go to the main menu and save the updated dataset by choosing “[S] Save file”. Save the file with the file name “tutorial.hkl”. Return to the ShelXle program and click “XL refine”. The refinement now converges to R_1 = 0.0337 and wR_2 = 0.1339. The Flack parameter *x* is still high: classical 0.125(18) or Parsons’ 0.309(22) indicating that we should investigate inversion twinning.

11. Return to the HKLF5Tools and select option “[A] Add inversion twin component to Nth twin component”. Then type “1” that means “1st twin component” and press Enter. The label of the created twin component is “3”. The reflections of the 3rd and 1st twin components are now related to each other by a negative unity matrix (−1 0 0 0 −1 0 0 0 −1 in ShelXL notation).

Repeat the same operation for the 2nd twin component: select option [A], type “2” and press Enter. Now we can see in “[T] Statistics” that we have four twin components in our dataset:

1) 1st twin component
2) 2nd twin component
3) inverted 1st twin component (now called 3rd twin component)
4) inverted 2nd twin component (now called 4th twin component)

12. Save the new reflection file as “tutorial.hkl”. Since we have now two more twin components, we need to add two more numbers to the BASF keyword in ShelXL, for example, as shown below:

```
CELL  0.71073   9.3772   9.3568  13.1317   90.000   91.953   90.000
ZERR    4.000   0.0005   0.0007   0.0006    0.000    0.004    0.000
LATT -1
SYMM -X, 1/2+Y, -Z
SFAC F BR SB
UNIT 56 12 4
L.S. 10
LIST 6
FMAP 2
PLAN 20
WGHT    0.100000
BASF   0.35966 0.1 0.1
FVAR       0.18930
```

Click “XL refine”. The refinement converges with R_1 = 0.0333 and wR_2 = 0.1262. The Flack parameters are now equal to zero within the 3σ criterion. In the .lst file we can find the following information on the refined BASF parameters:

```
    N      value        esd    shift/esd  parameter

    1     0.18952     0.00054     0.000     OSF
    2    -0.03332     0.02140     0.000    BASF  1
    3     0.00469     0.01582     0.000    BASF  2
    4     0.39798     0.02152     0.000    BASF  3

Mean shift/esd =   0.000  Maximum =     0.000 for   z  Sb1

Max. shift = 0.000 A for F13      Max. dU = 0.000 for F5


Largest correlation matrix elements

   -0.992 BASF 3 / BASF 1
```

The BASF 1 (for 2nd twin component) and BASF 2 (for 3rd twin component) equal zero. This means that these twin components do not exist, i.e. their volume fractions are zero.

13. We can remove all reflections of the non-existing twin components. For that choose option "[D] Delete Nth twin component" in the HKLF5Tools, type "2", and then select option "[A] All". Then repeat this operation for the 3rd twin component by typing "3". Check in "[T] Statistics" that only 1st and 4th twin components are present.

14. The ShelXL software works only properly if consecutive labels for the twin components (1, 2, 3, 4, …) are used. In order to rename the 4th twin component into the 2nd twin component, select option "[R] Rename Nth twin component" and type first "4" and then "2".

15. Save the updated reflection file as "tutorial.hkl" and switch to ShelXle. Edit the BASF line to remove the volume fractions of non-existing twin components. Click "XL refine". The refinement converges to essentially the same R-values as before: R_1 = 0.0333, wR_2 = 0.1263.

16. In order to obtain proper standard uncertainties in the refinement, we should merge our dataset. The HKLF5Tools can merge the non-overlapping reflections in the chosen crystallographic point group. The overlapping reflections will be merged in the point group 1. To do that switch to the HKLF5Tools and select option "[M] Merge data". The software will show the reflection statistics before and after merging.

```
Statistics BEFORE merging:
N total:  42221
N non-overlapping reflections:  11153
N overlapping reflections:  31068  (in  15534  groups)

Statistics AFTER merging:
N total:  15995
N non-overlapping reflections:  2923
N overlapping reflections:  13072  (in  6536  groups)

Press any key.
```

Save the dataset under "tutorial.hkl" and click "XL refine" in ShelXle. The refinement converges with R_1 = 0.0357 and wR_2 = 0.0993. Click "XL ANIS refine" to run refinement with anisotropic displacement parameters for all atoms. The refinement converges to R_1 = 0.0317 and wR_2 = 0.0922.

17. As the final step of the refinement, we can extract the detwinned dataset (created by ShelXL and saved in the .fcf file) and refine our model against it. To do that, change the keyword "LIST 6" to "LIST 8" in ShelXle and click "XL refine". Then switch to HKLF5Tools and

select option “[F] FCF to HKL”. Type the file name “tutorial.fcf”. It will create a new reflection file “tutorial.fcf.hkl” with a detwinned dataset in the HKLF 4 format. The intensities in the new dataset will be scaled in order to match the specification of the HKLF 4 format.

18. Rename the “tutorial.fcf.hkl” file to “tutorial.hkl” (it will replace the old reflection file). Switch to ShelXle and comment the BASF line by putting “REM” before it (or delete it). Then change the “HKLF 5” line to “HKLF 4” below the atom list.

```
CELL  0.71073   9.3772   9.3568  13.1317   90.000   91.953   90.000
ZERR    4.000   0.0005   0.0007   0.0006    0.000    0.004    0.000
LATT -1
SYMM -X, 1/2+Y, -Z
SFAC F BR SB
UNIT 56 12 4
L.S. 10
LIST 8
FMAP 2
PLAN 20
WGHT    0.100000
REM BASF   0.37026
FVAR       0.19012
```

Click “XL refine”. The refinement converges with R_1 = 0.0322 and wR_2 = 0.0908. Then go to the “SHELX” menu and click “Try to refine until WGHT converges”. This last refinement should converge to R_1 = 0.0322 and wR_2 = 0.0791.

19. This is the end of the tutorial.