Example 3.3: $CsLiSO_4$

Revised: 17 October 2019

Data	Topic	Level
X-ray single crystal data	structure with pseudo-merohedric 3-fold twinning	Advanced

Tasks

Solving a structure with pseudo-merohedric 3-fold twinning using Jana2006 software

- **Finding twinning matrix from group → subgroup transformation.**
- **Transformation to four times smaller cell.**

Initial data

Data

Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files:

CsLiSO4.hkl, CsLiSO4_red.sum

Additional information:

Frame scaling, absorption correction: done by the diffractometer software

Chemical formula: **$CsLiSO_4$**

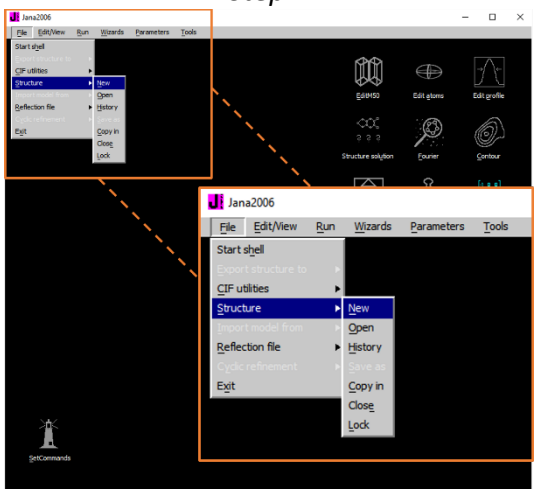
Instructions

I. *Data import*

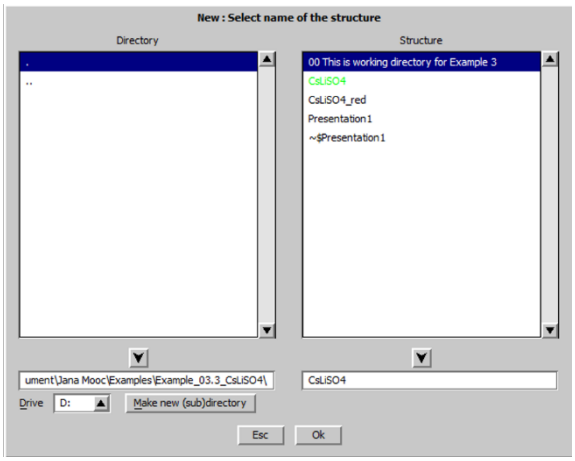
1. Creating new jobname

Start Jana2006
"File → Structure → New" opens a file manager *(Step 1)*
Left pane: locate directory with input files; Right pane: double-click CsLiSO4 *(Step 2)*

Step 1



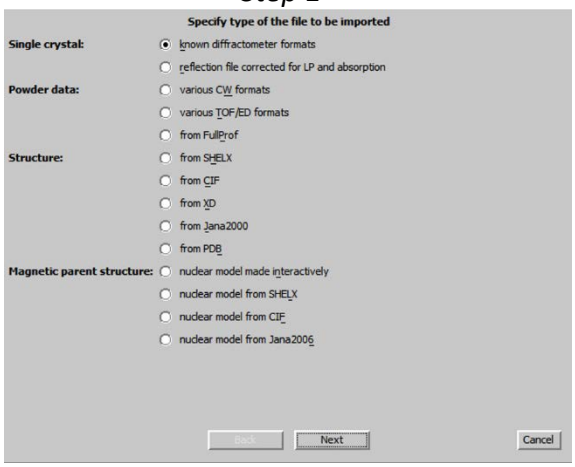
Step 2



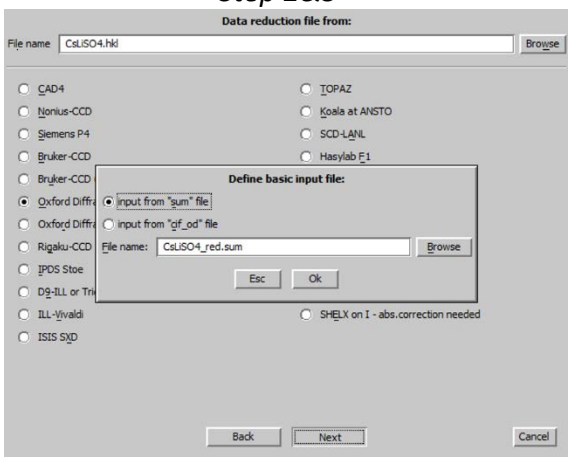
2. Import wizard

Select "Known diffractometer formats"; NEXT *(Step 1)*
Select "Oxford Diffraction → CCD"; NEXT *(Step 2)*
Select "Input from "sum" file"; OK *(Step 3)*

Step 1



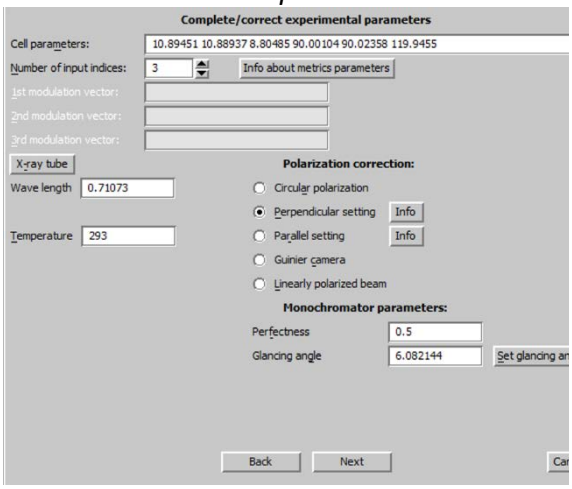
Step 2&3



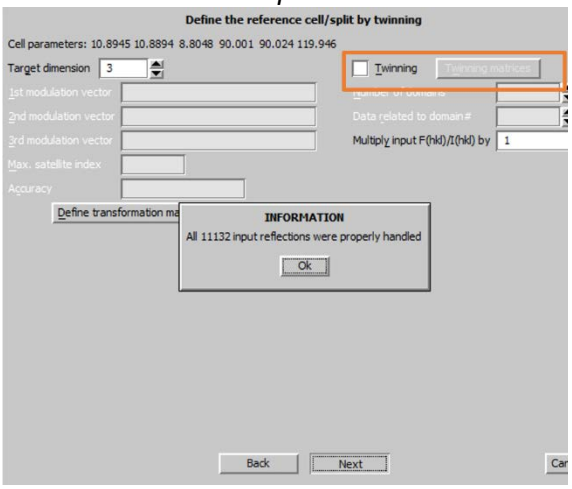
Warning; OK *(Step 4)*

Leave all settings unchanged; NEXT *(Step 5)*
Leave all settings unchanged (leave Twinning checkbox clear); NEXT; OK; *(Step 6)*
The program reads 11132 reflections from hkl file

Step 5

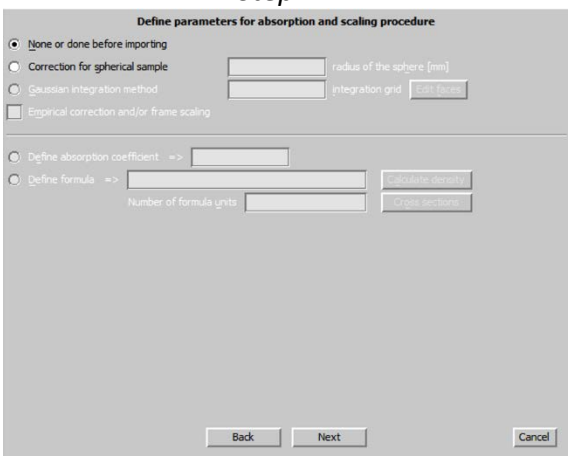


Step 6

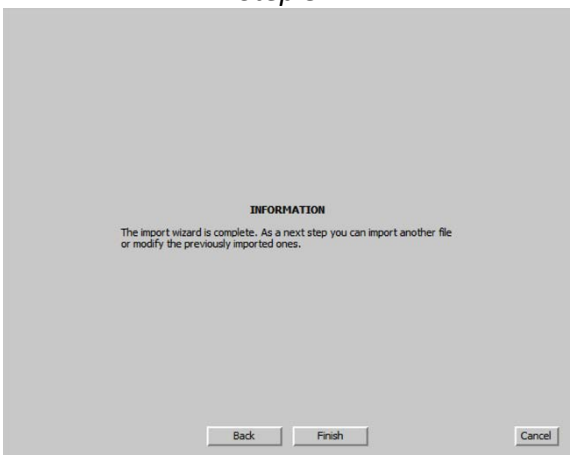


For absorption correction select “None or done before importing”; NEXT *(Step 7)*
FINISH *(Step 8)*

Step 7



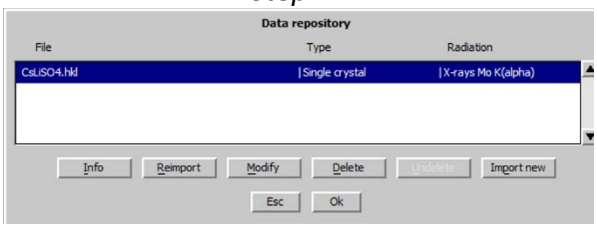
Step 8



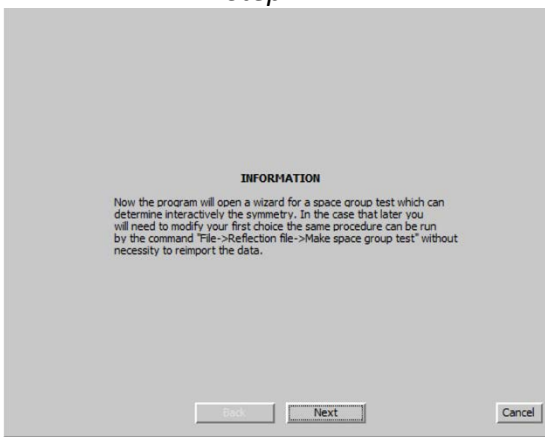
3. Data Repository

OK; YES to accept the data set *(Step 1)*
Nest; *(Step 2)*

Step 1



Step 2

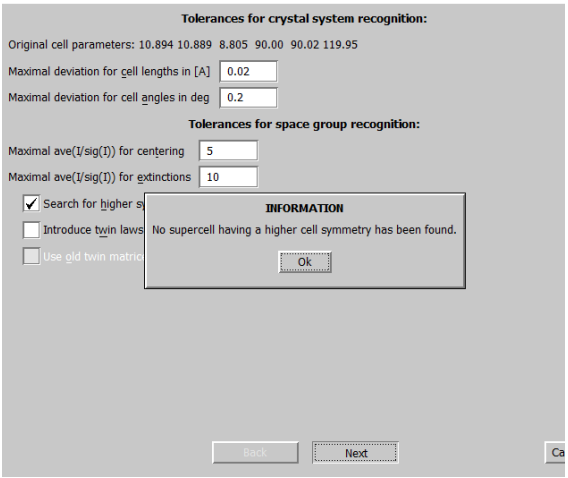


II. ***Symmetry and data merging***

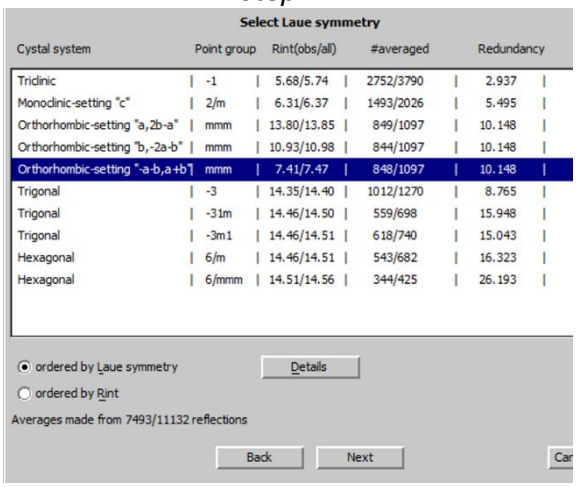
1. Symmetry wizard

[On the screen: "Tolerances for crystal system recognition".]
Leave all other settings default; NEXT *(Step 1)*
[On the screen: Select Laue symmetry] *(Step 2)*

Step 1



Step 2



Notes
We can see that hexagonal symmetry is slightly violated, because corresponding R_{int} is about 14%. On the other hand, an orthorhombic symmetry with setting "-a-b,a+b" has R_{int} comparable with the triclinic symmetry, given much higher redundancy of equivalent reflections.

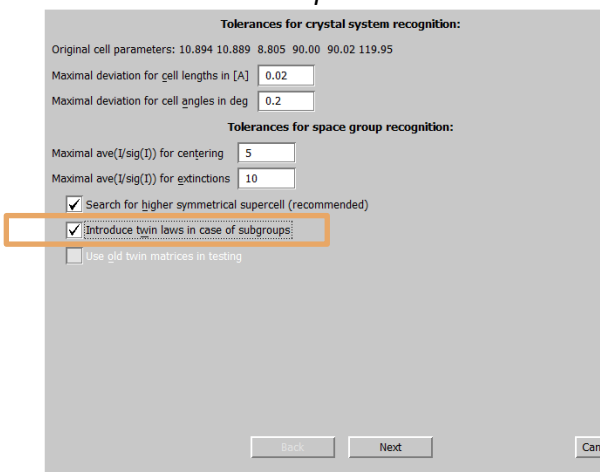
For cell parameters being so close to hexagonal, a metric merohedric twinning is highly probable. However, here the three orthorhombic settings have quite different R_{int}. This indicates that the structure has symmetry lower than hexagonal and that the sample is either not affected by twinning or that twin domains are not equally populated.

In the next step, we will repeat test of Laue symmetry but this time considering twinning. That means for any subgroup of 6/mmm the program will generate corresponding pseudo-merohedric twinning matrices and it will use only symmetry elements, which are present in a twinned structure for general case of not equally populated twin domains.

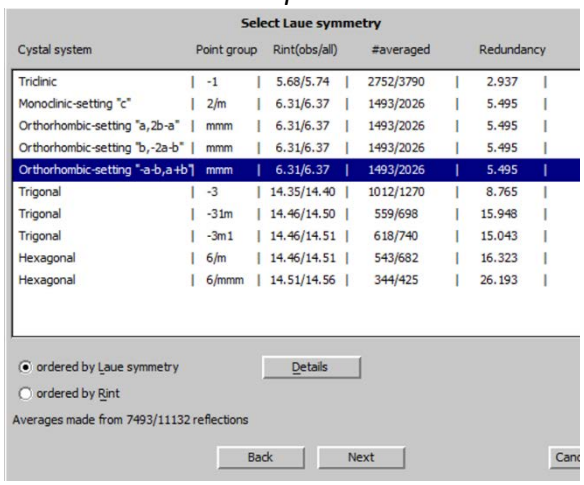
Press BACK

Check „Introduce twin laws in case of subgroups“ *(Step 3)*

Step 3



Step 4



This time, the three orthorhombic cases gives the same internal R factor.

Select the highlighted orthorhombic Laue symmetry; NEXT *(Step 4)*

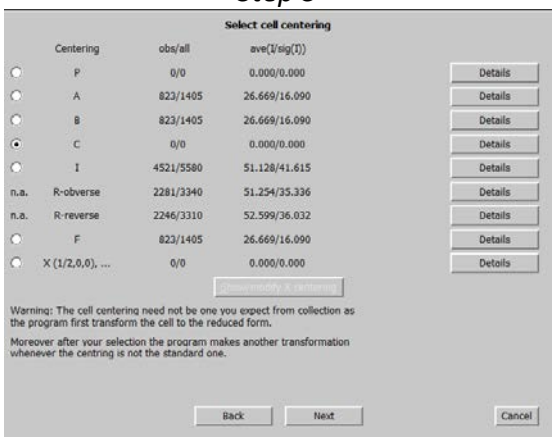
Notes
The three orthorhombic cases are related to the three twin domains. The selected one gave us in the previous test the lowest R_{int}. This means that this domain is more populated than the others.

On the screen: [Select cell centering] *(Step 5)*

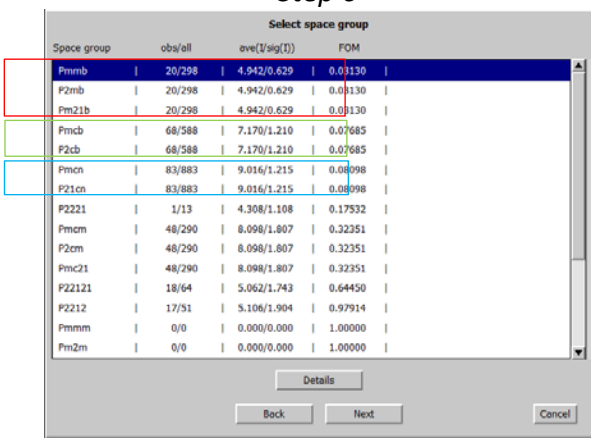
Press “Show/modify X centering” to see the individual centering vectors

Notes
We can see the centering vector (½ ½ 0) corresponding to the C centering but also additional vectors (½ 0 0) and (0 ½ 0) suggesting that a and b unit cell parameters could be halved. Although we cannot conclude unequivocally that the correct cell is really four times smaller than found from diffraction pattern, the natural way is to start with a smaller cell allowing indexing of all diffraction spots.

Step 5



Step 6

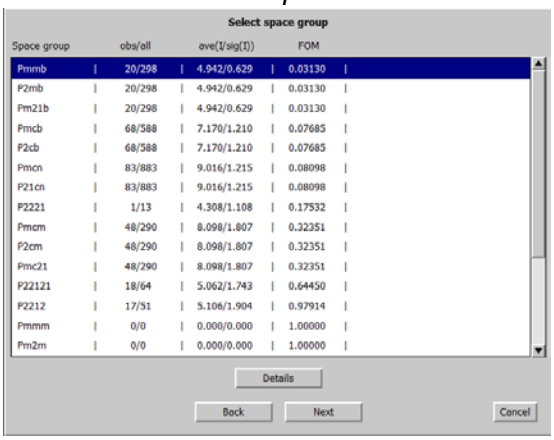


Notes
The space groups highlighted by red, green and blue color (Step 6) have the smallest ratio between the number of reflections violating space group extinctions (I>3σ(I)) and the number of all measured systematically reflections. The first space group in each block is the centrosymmetric space group and the others are its non-centrosymmetric subgroups. In all these cases, the FOM (Figure of Merit) is low and we cannot exclude none of them. In next steps, we will use the Superflip program and test the centrosymmetric space group from each block.

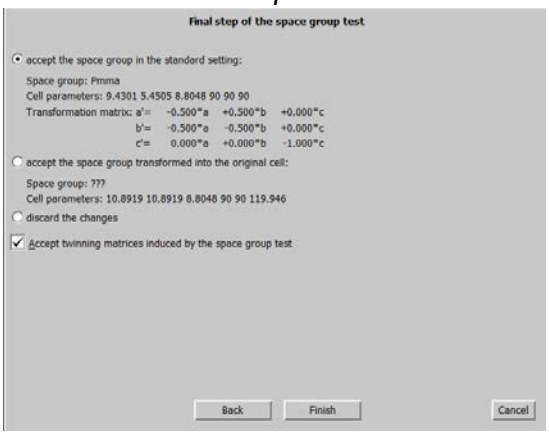
Cancel; No for repeating the test;
"File → Structure → Save as" and use a new name for example "CsLiSO4-basic" but do not continue with the new structure.
"File → Reflection file → Make space group test" and continue to the step for selection of space group; *(Step 7)*
Select the space group Pmmb; NEXT;
Accept space group in the standard setting with twining matrices; FINISH *(Step 8)*

No for repeating the test;

Step 7

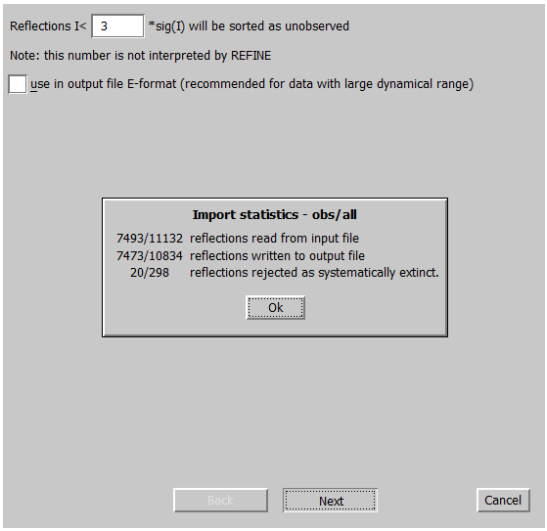


Step 8

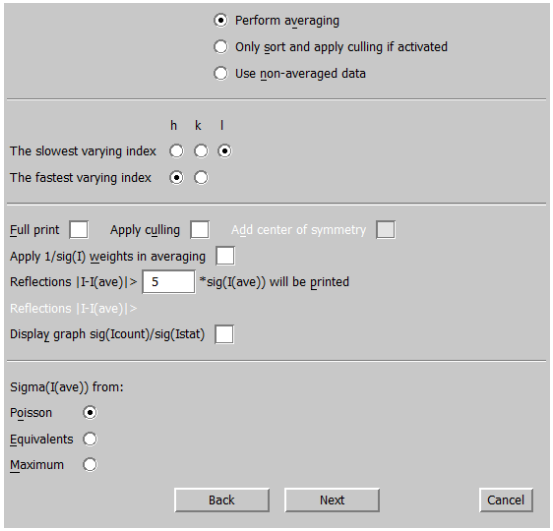


"File → Reflection file → Create refinement reflection file";
Next; *(Step 9)*
OK; OK; *(Step 10)*
Next; OK;
Finish;

Step 9



Step 10



Next; OK; Finish

Start "Structure solution";
Define the formula Cs Li S O4 and run solution; (*Step 11)*

Step 11

Step12

```
-------------------------------------------------
Space group derived from the symmetry operations:
-------------------------------------------------
    HM symbol:      Pbmm
    Hall symbol:    -P 2 2b
    Fingerprint:    3300320n{041Y03}22 (0,0,0)
    Symmetry operations:
                 1:            x1           x2           x3
         2(0,0,1):           -x1          -x2           x3
         2(1,0,0):            x1       1/2-x2          -x3
                -1:           -x1          -x2          -x3
       2_1(0,1,0):           -x1       1/2+x2          -x3
         m(0,0,1):            x1           x2          -x3
         b(1,0,0):           -x1       1/2+x2           x3
         m(0,1,0):            x1       1/2-x2           x3


###############################################
# Search for the origin of the space group #
###############################################


Position of the origin in the CF map:
  0.9570  0.6682  0.7892
Agreement factors of individual generators:
Number smb agreement
   6   a       66.69
   7   m        0.08
   8   m       26.71
```

Notes
The selected space group Pmma was not confirmed by the Superflip as shown in the smb agreement (Step 12). The space group derived by Superflip is Pbmm in the standard setting for Pmma.

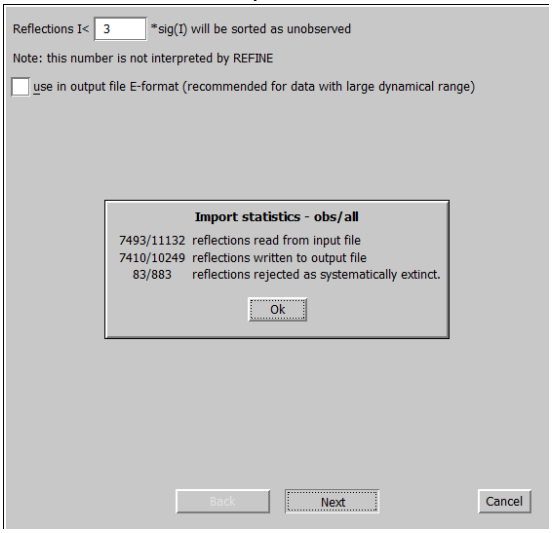
Close the window with Superflip output and press the “Quit” button; Yes to discard the solution;
[On the screen: basic window of Jana]

“File → Structure → Copy in” and select the structure “CsLiSO4-basic”; Rewrite all files;
“File → Reflection file → Make space group test” and continue to the step for selection of space group;
Select the space group Pmcb; NEXT;
Repeat the same procedure as for Pmmb;

Notes
For this choice, Superflip does not converge.

Repeat the whole procedure for Pmcn (in standard setting Pmna):

Step 13



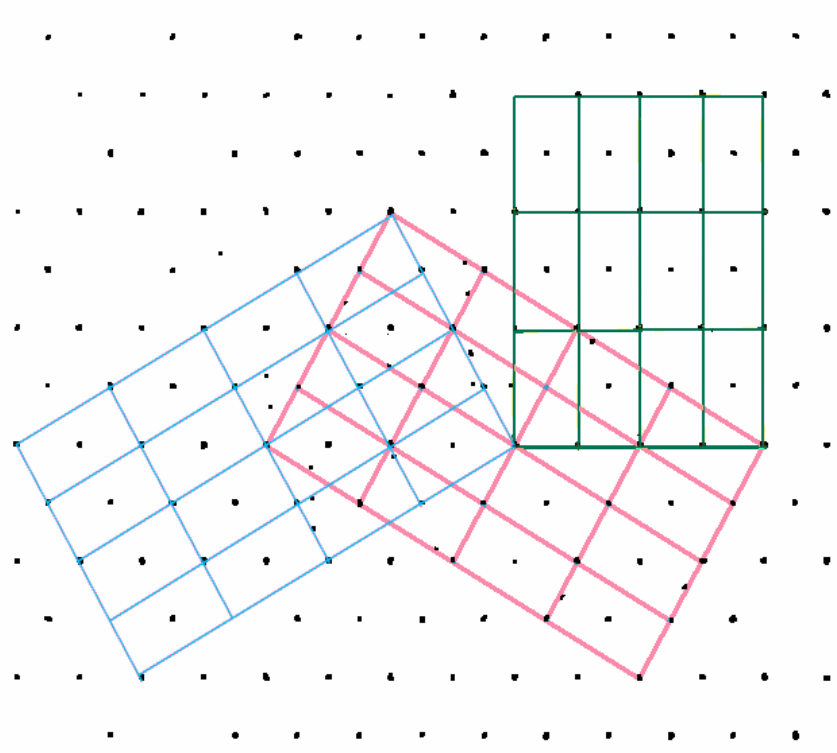
Step14

```
------------------------------------------------
Space group derived from the symmetry operations:
------------------------------------------------
    HM symbol:      Imma
    Hall symbol:    -I 2b 2
    Fingerprint:    33123270n{041Y23}22 (0,0,0)
    Centering vectors:
      0.000  0.000  0.000
      0.500  0.500  0.500
    Symmetry operations:
              1:            x1           x2           x3
       2(0,0,1):           -x1       1/2-x2           x3
       2(1,0,0):            x1          -x2          -x3
              -1:           -x1          -x2          -x3
     2_1(0,1,0):           -x1       1/2+x2          -x3
       b(0,0,1):            x1       1/2+x2          -x3
       m(1,0,0):           -x1           x2           x3
       m(0,1,0):            x1       1/2-x2           x3


###########################################
# Search for the origin of the space group #
###########################################


Position of the origin in the CF map:
  0.5428  0.9452  0.8822
Agreement factors of individual generators:
Number smb agreement
   6   a         6.32
   7   m         0.60
   8   n         1.35
```

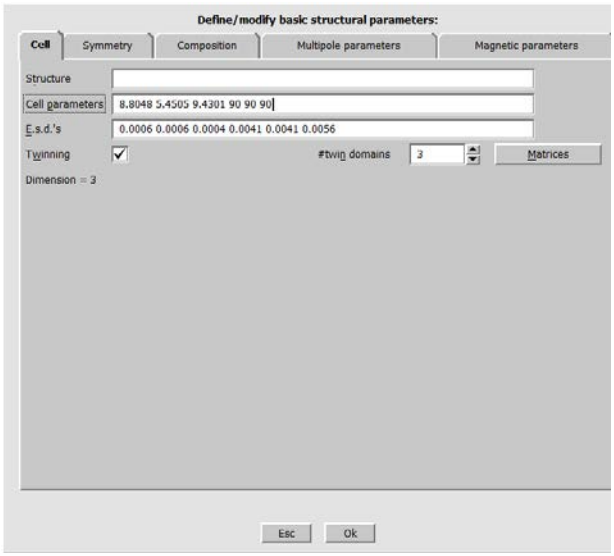
Notes
83 observed reflections will be discarded (see Step13) due to the selected space group. This is probably caused by spurious peaks, which are present in the diffraction pattern. The Superflip confirmed the space group Pnma. The transformation suggested at the final step of the space group test produces an orthorhombic unit cell with four time smaller volume compared with the previously tested orthorhombic unit cell. Such unit cell alone could not index all diffraction spots, but combined with a three-fold twinning it can. The indexing of the hexagonal diffraction pattern with a three-fold twin of this small orthorhombic unit cell is indicated in the next figure.



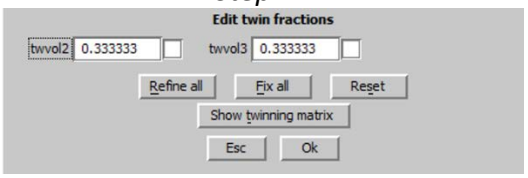
2. Space group test results

[On the screen: basic window of Jana]
Check new cell parameters and symmetry with EditM50 *(Step1)*
Cell parameters 8.8048 5.4505 9.4301 90 90 90
Space group Pnma
ESC
[On the screen: basic window of Jana]
Start "Parameters → Twin fractions" *(Step2)*

Step 1



Step 2



Notes
The initial volume fractions are equal but we already know they will be different; otherwise hexagonal Laue symmetry would be indicated with good R_{int}.

Click inside the textbox “twvol2” and press “Show twinning matrix” *(Step3)*

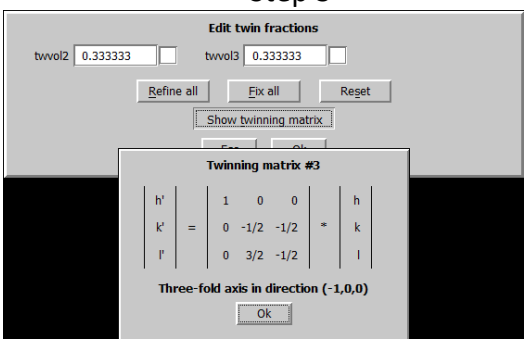
1 0 0 / 0 1/2 -1/2 / 0 3/2 1/2

Click inside the textbox “twvol3” and press “Show twinning matrix” *(Step4)*

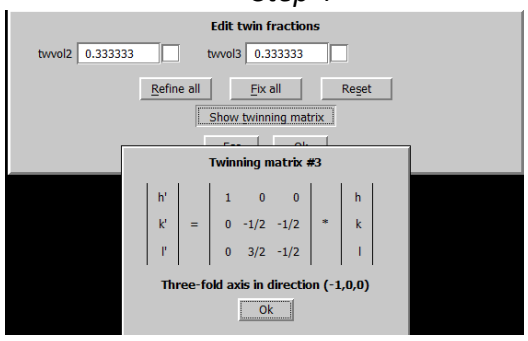
1 0 0 / 0 -1/2 -1/2 / 0 3/2 -1/2

These twinning matrices are related to the current orthorhombic unit cell

Step 3



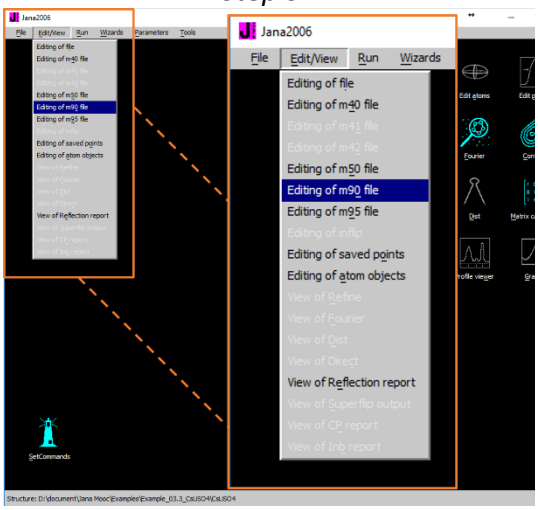
Step 4



Return to the basic window

Start “Edit/view → Editing of M90 file” *(Step5)*

Step 5



M90

3	-1	11	71.2	25.5	1	0	1	0.00
1	0	11	3286.4	35.7	1	0	1	0.00
2	0	11	59.4	29.2	1	0	1	0.00
3	0	11	867.4	33.1	1	0	1	0.00
4	0	11	76.3	37.9	1	0	1	0.00
0	1	11	4709.5	78.2	1	0	1	0.00
1	1	11	309.2	33.5	1	0	1	0.00
2	1	11	3339.6	47.5	1	0	1	0.00
3	1	11	79.1	34.3	1	0	1	0.00
1	2	11	2733.2	31.7	1	0	1	0.00
2	2	11	37.3	24.1	1	0	1	0.00
2	1	0	879.6	5.7	1	0	2	0.00
4	1	0	7.5	6.5	1	0	2	0.00
6	1	0	1358.0	16.8	1	0	2	0.00
8	1	0	-0.4	8.6	1	0	2	0.00
10	1	0	141.4	29.0	1	0	2	0.00
2	3	0	498.0	9.0	1	0	2	0.00
4	3	0	88.8	11.2	1	0	2	0.00

Notes
The numbers inside the orange rectangle are twin flags. All flags except several reflections at the end of the file have the twin flags equal to "1" because most reflections can be indexed in the first domain. The reflections at the end of the file with the twin flag "2" and "3" are the ones, which cannot be transformed to the first domain because after such transformation they would have indices which are not compatible with C centered cell.

III. Structure solution

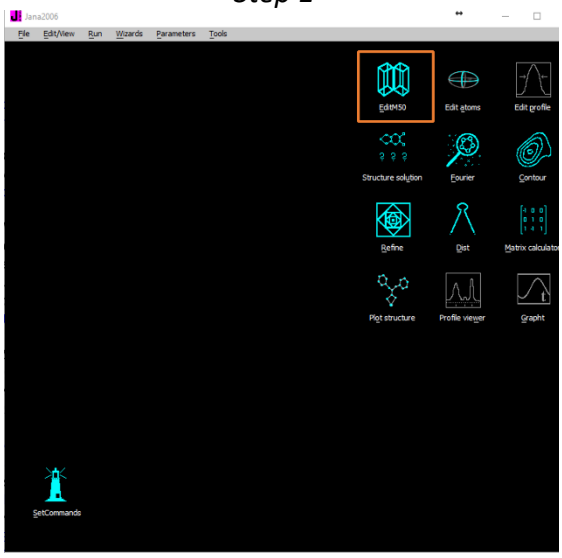
"Run → Structure solution"
[On the screen: window of Structure solution]
In "Formula" textbox check list of chemical elements for CsLiSO4: Cs Li S O
Select "Superflip", "Peaks from Jana2006"; leave other settings default; "Run solution"

Notes
Superflip converges (after noise suppression) with R value 22%. The suggested space group by Superflip is Imma but for twins such prediction is unreliable. On the other hand, Superflip confirms the symmetry elements of the current space group symmetry Pnma.

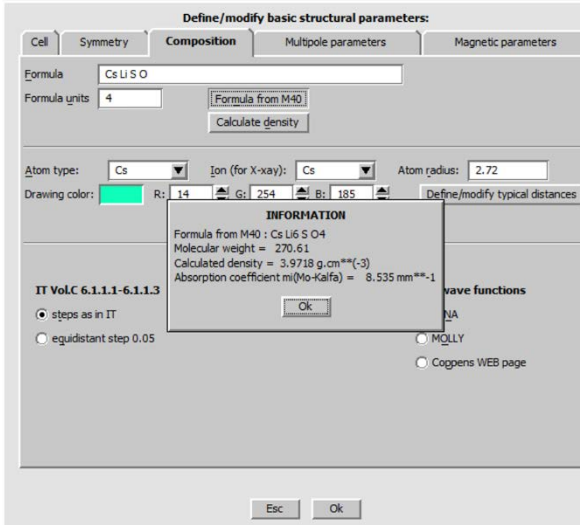
Press CLOSE to leave the listing
Press "Draw structure"
Press "Accept last solution"
Start EditM50; *(Step1)*

Go to page Composition; change Formula units to 4; press Formula from M40; *(Step2)*
OK; Yes; OK

Step 1



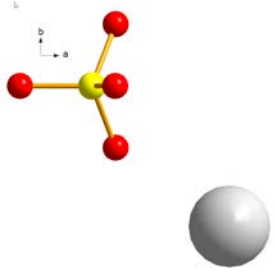
Step 2



Notes
In most cases, the formula will be Cs Li_n S O4, where "n" can be zero, 1 or more. This means all heavy atoms except Li have been properly interpreted. If not, repeat the structure solution.

Start "Edit atoms"; delete all Li atoms
"Plot structure"

Notes
Diamond should show SO4 tetrahedron and Cs. For this plot, all bonds to Cs will need to be disabled through "Build – Connectivity"

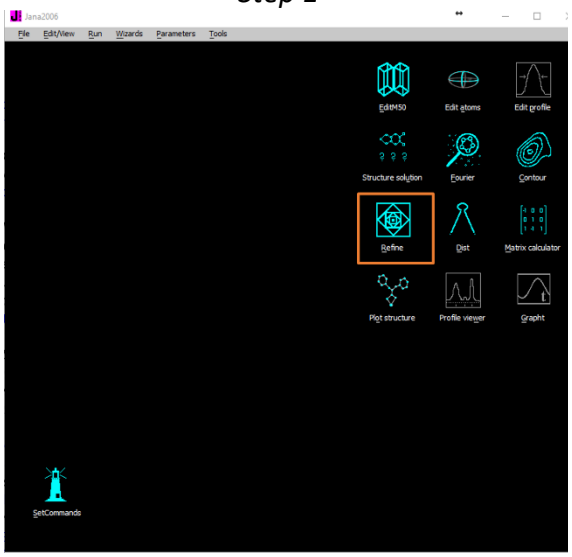


IV. ***Refinements and model improvement***

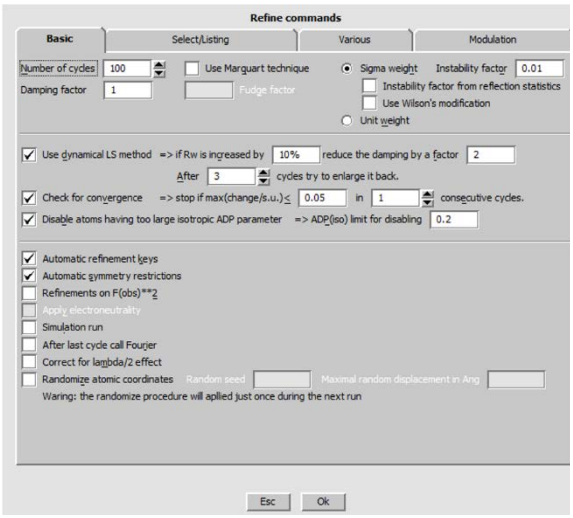
1. Refinement

[On the screen: basic window of Jana]
Right-click the icon of Refine. *(Step1)*
[On the screen: refinement options]
Define 100 of cycles, *(Step2)*
Choose "YES+START"
Refinement converges with R value about 9%, GOF about 9, 17 refined parameters

Step 1



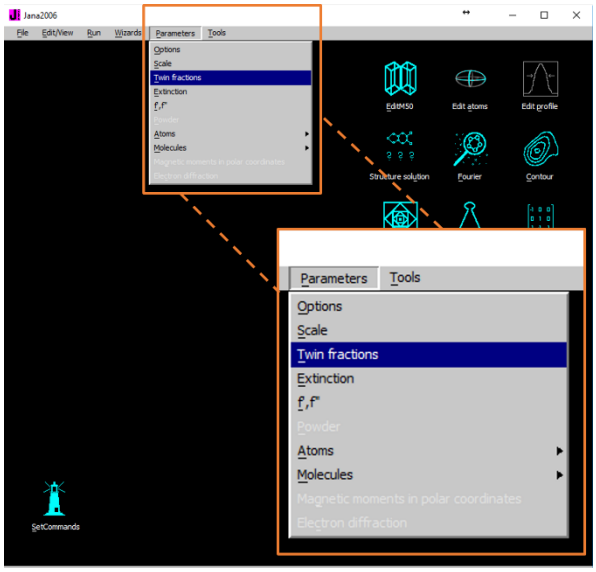
Step 2



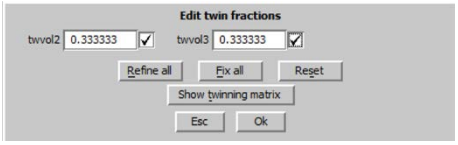
2. Twin volume fraction

Start "parameters → Twin fractions" *(Step1)*
Activate refinement of the twin fractions
Activate refinement of the twin fraction *(Step2)*

Step 1



Step 2



Repeat refinement

Refinement converges with R value about 5%, GOF about 5

Twin volume fraction drops to 0.26 (twvol2) and 0.30 (twvol3).

Start "Edit atoms"

[On the screen: list of atoms]

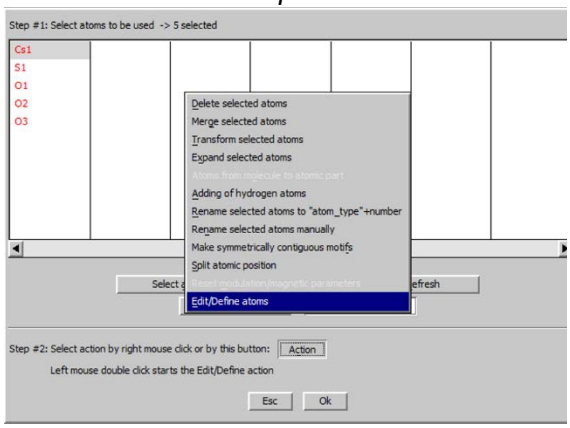
Press "Select all" and "Action → Edit/define" *(Step3)*

Choose "harmonic" for ADP parameters. *(Step4)*

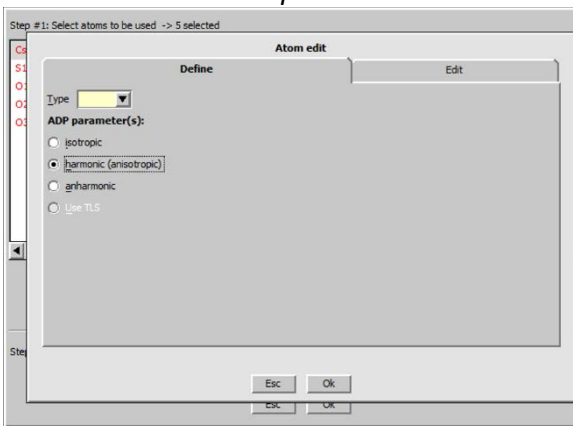
This defines anisotropic temperature parameters for all atoms.

OK, OK, YES to save changes

Step 3



Step 4



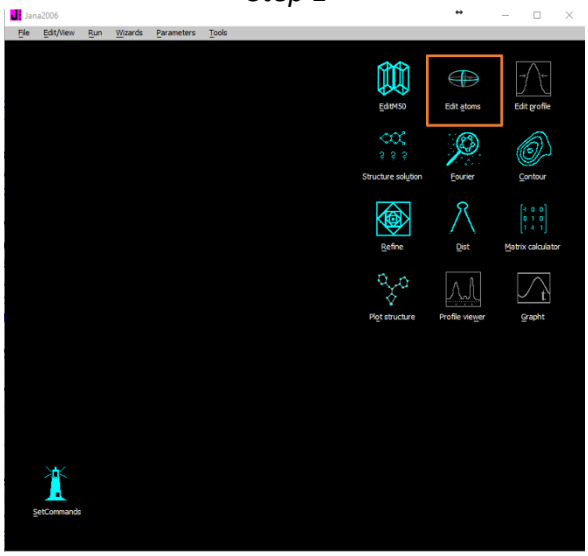
Double-click the icon Refine.

Refinement converges with R value about 4.4%, GOF about 4.4, 36 refined parameters.

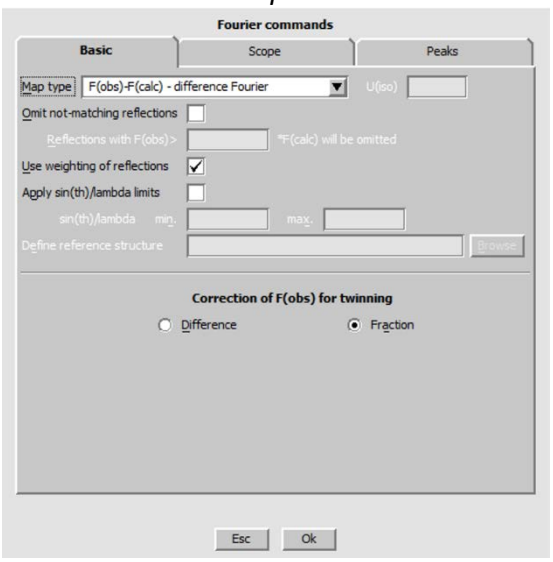
3. Find atoms missing using Fourier

[On the screen: basic window of Jana]
Right-click Fourier *(Step1)*
Select "Map type" = "F(obs)-F(calc) – difference Fourier" *(Step2)*

Step 1

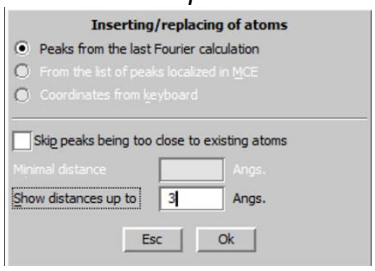


Step 2

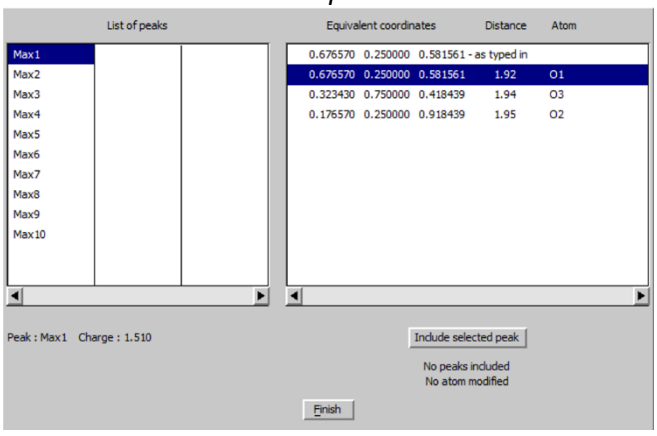


OK; YES+START; YES to include new atoms
[On the screen: Inserting/replacing of atoms]
OK*(Step3)*
[On the screen: List of peaks] (Step4)

Step 3



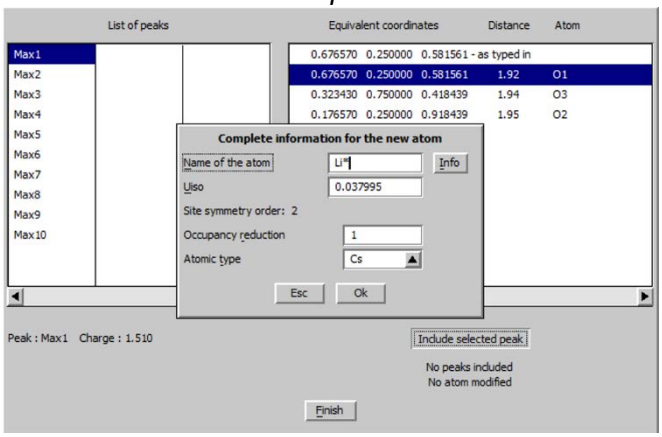
Step 4



Notes
The strongest difference peak (Max1) has reasonable Li-O distances to oxygen atoms. We can add it as Lithium in the first highlighted symmetry position.

Press “Include selected peak”
For “Name of atom” type Li*; *(Step5)*
TAB; OK; FINISH; YES to include the new atom.

Step 5



Run refinement
Refinement converges with GOF ~ 3 and R(obs) ~ 2.7% for 39 parameters

4. Extinction correction

[On the screen: basic window of Jana2006]
Open listing of Refine (by “Edit/View → View of Refine”)
Press “Go to” and select “Statistics Fo, sin(th)/lambda after refinement” *(Step1)*

Step 1

Statistics as a function of sin(th)/lambda and structure factors
sin(th)/lambda

limits	0.300350	0.381961	0.435144	0.480711	0.517336	0.560540	0.589865	0.627326
number +	79	75	73	79	73	45	47	59
-	55	57	60	51	61	87	85	72
together	134	132	133	130	134	132	132	131
av. wd F	43.2864	4.5159	2.5122	4.9112	2.8145	2.5069	3.1005	3.4326
numerator +	122.5	106.8	76.4	95.1	87.9	42.0	38.7	70.7
-	-460.2	-88.2	-49.7	-72.0	-41.3	-65.4	-90.2	-67.4
together	582.7	195.0	126.2	167.2	129.1	107.4	128.9	138.0
denominator	11943.5	9489.3	7548.7	7568.8	6031.1	5790.1	5338.9	5343.9
R factor	4.88	2.05	1.67	2.21	2.14	1.85	2.42	2.58

struct. factors

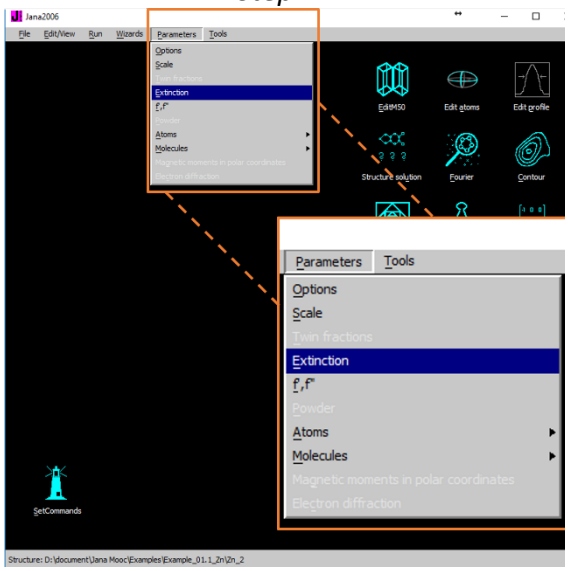
limits	10.2	14.8	25.7	45.3	59.6	75.6	107.6	347.2	unobs
number +	69	57	66	72	62	56	78	70	88
-	63	76	66	60	70	77	54	62	89
together	132	133	132	132	132	133	132	132	177
av. wd F	3.6193	26.2395	2.7545	3.9384	5.4538	4.2044	4.2956	16.9612	0.5491
numerator +	52.3	48.5	37.8	48.9	67.2	67.8	130.8	186.8	106.3
-	-39.2	-49.3	-48.4	-44.0	-75.6	-90.4	-65.2	-522.3	-76.9
together	91.5	97.8	86.3	92.8	142.8	158.1	196.0	709.1	183.2
denominator	1078.9	1643.7	2578.2	4642.9	6959.6	8947.2	11755.0	21448.9	904.7
R factor	8.48	5.95	3.35	2.00	2.05	1.77	1.67	3.31	20.25

final check	sin(th)/lambda	structure factors
number +	530	530
-	528	528
together	1058	1058
numerator +	640.1	640.1
-	-934.4	-934.4
together	1574.5	1574.5
denominator	59054.4	59054.4
R-factor	2.67	2.67

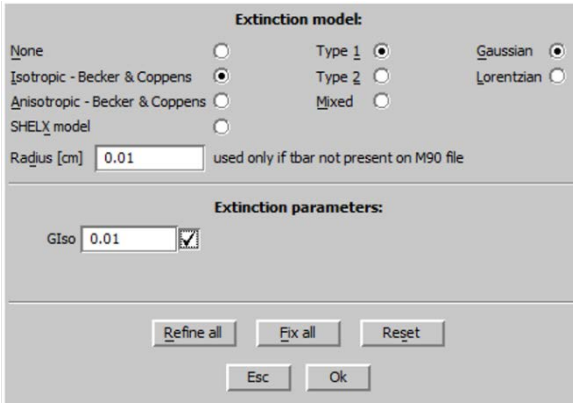
Notes
The Statistics show that the strongest low-angle reflections are systematically weaker. This is an indication that extinction correction is needed.

Close the refinement listing
"Parameters → Extinction" *(Step2)*
Select "Isotropic-Becker&Coppens" "Type 1" "Gaussian"; OK *(Step3)*
Refinement of extinction coefficient is enabled by default

Step 2

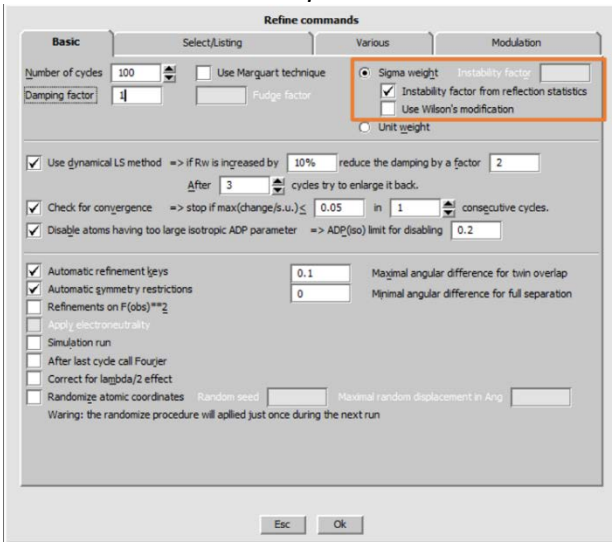


Step 3



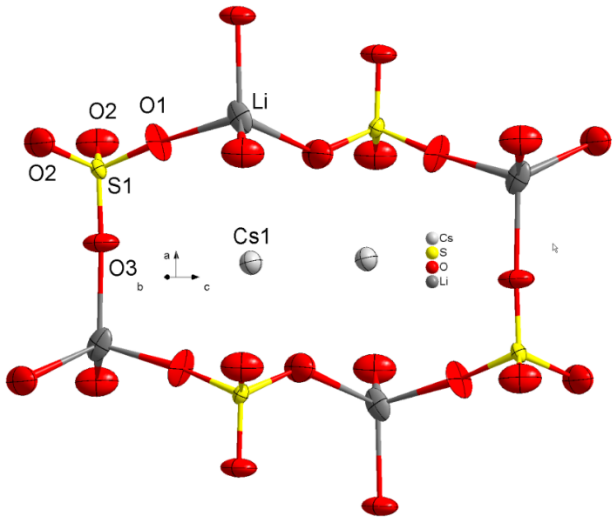
[On the screen: basic window of Jana2006]
Run Refine
Refinement converges with GOF ~ 2.7 and R(obs) ~ 2.2% for 40 parameters
Start "Edit atoms"; change ADP of Lithium to harmonic
Refinement converges with GOF ~ 2.6 and R(obs) ~ 2.2% for 43 parameters
Right-click Refine; go to the page Basic
Check "Instability factor from reflection statistics" *(Step4)*

Step 4



OK; YES+START

Notes



The final structure

Refinement converges with R value around 2.3% and GOF 1.4, for 43 parameters
In this case, the instability factor from reflection statistics seems to be reasonable because the structure of a three-fold twin is fully solved and data are not expected to contain more information.