Example 03.3.1: $CsLiSO_4$

Last update 19.06.2024

Data	Topic	Level
X-ray single crystal data	Structure with pseudo-merohedric 3-fold twinning	Intermediate

Input 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: **$CsLiSO_4$**

References

none

Highlight

none

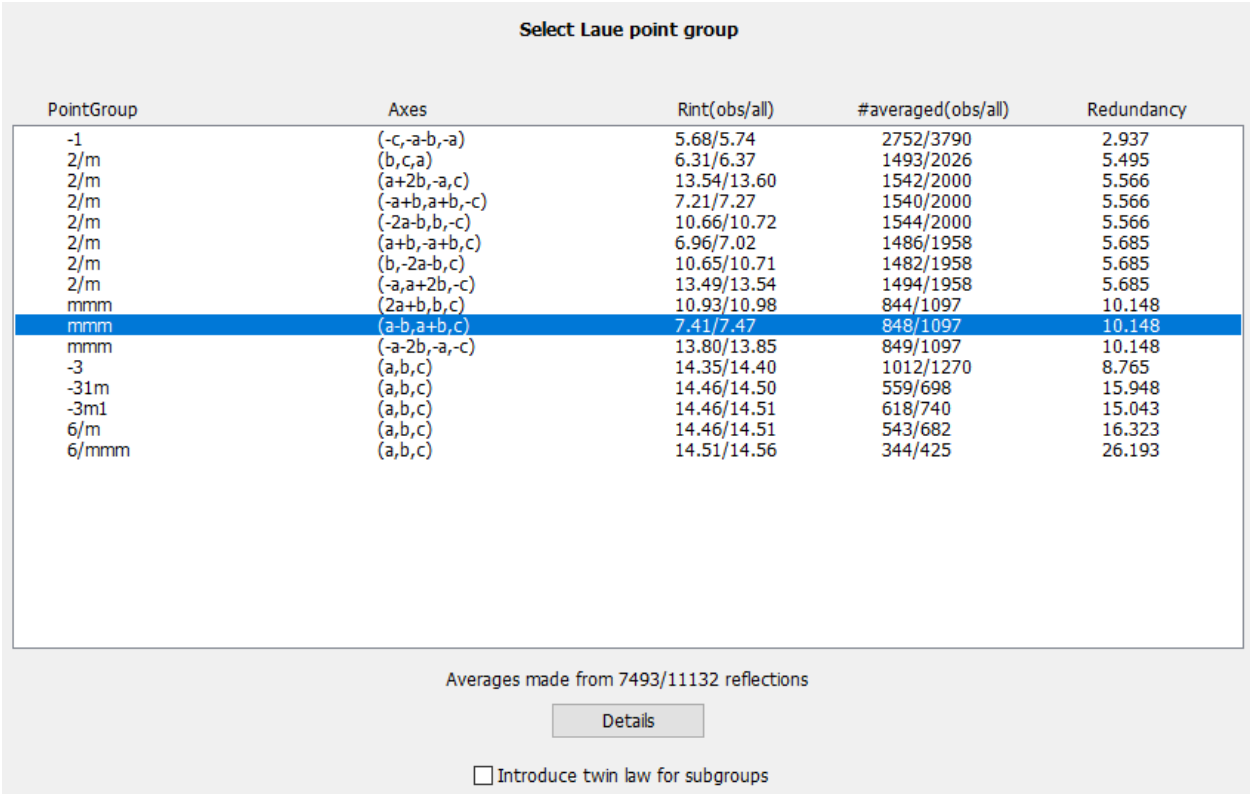
Instructions

1. *Data import*

For details, see Basic tasks:
Start Jana2020
Use “Structure → New” and open a new structure CsLiSO4 in the Example 03.3.1 directory
[On the screen: Specify file to be imported]
Select “Known diffractometer formats”; NEXT
[On the screen: Data reduction file from]
Select “Oxford Diffraction-CCD”; NEXT
Select “Input from “sum” file”; OK**;** OK
[On the screen: Complete/correct experimental parameters]
Leave all settings unchanged; NEXT
[On the screen: Define the reference cell]
Leave all settings unchanged; NEXT; OK
The program reads 11132 reflections from the hkl file
[On the screen: Define parameters for absorption and scaling procedure]
Leave all settings unchanged; NEXT; FINISH
[On the screen: Data repository]
OK; NEXT

2. *Symmetry and data merging*

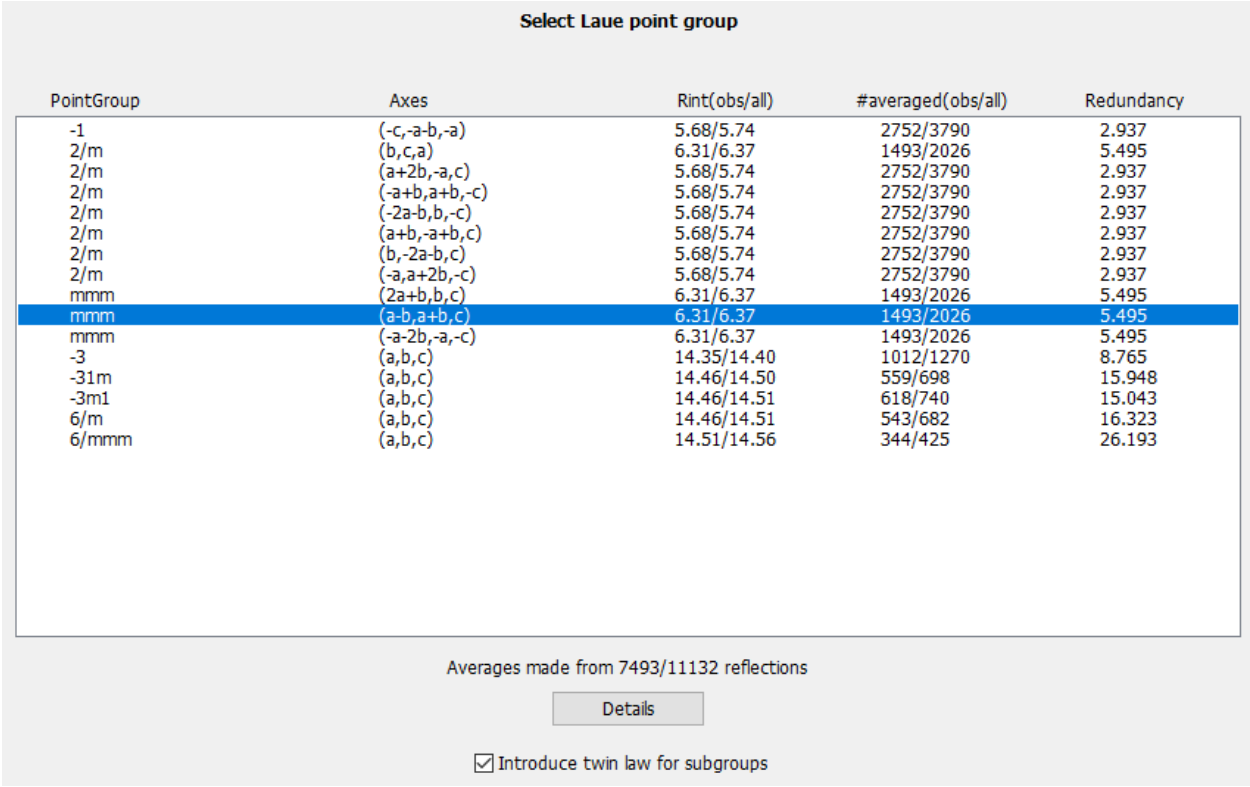
For details, see Basic tasks
[On the screen: “Tolerances for crystal system recognition”]
Leave all other settings default; NEXT
[On the screen: Select Laue point group]



Notes

We can see that hexagonal symmetry is slightly violated because the corresponding R_{int} is about 14%. On the other hand, the orthorhombic symmetry with setting "a-b,a+b" has Rint comparable with the triclinic symmetry, although the redundancy of equivalent reflections is much higher. This indicates the proper symmetry might be mmm with merohedric three-fold twinning.
Another indication of twinning is that the three equivalent orthorhombic settings have quite different Rint. It might be caused by merging reflections belonging to different unequally populated twin domains.

Check „Introduce twin law for subgroups"



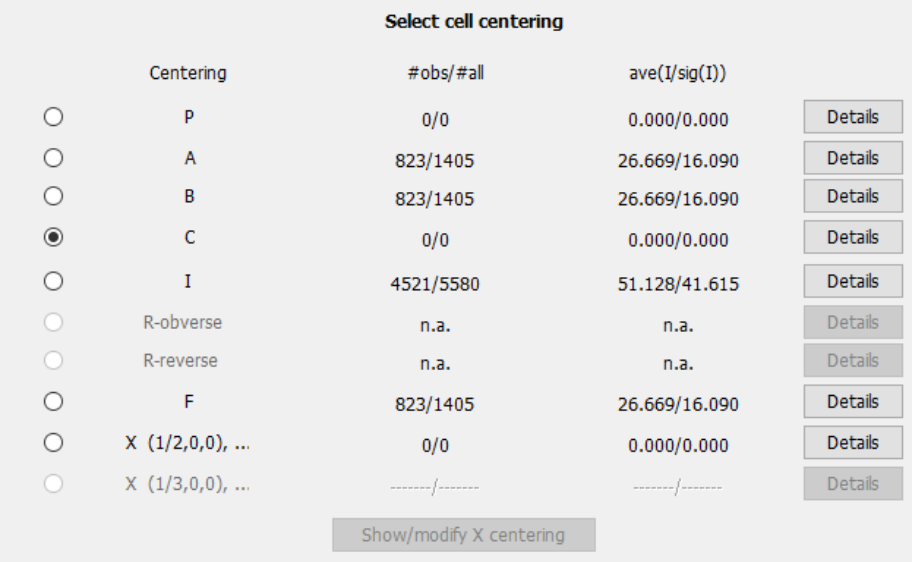
Notes

Now the symmetry test considers twinning. For any subgroup of 6/mmm, the program generates corresponding pseudo-merohedric twinning matrices and merges reflections using only the symmetry elements present in a twinned structure for the general case of not equally populated twin domains.
The three orthorhombic cases now have the same Rint because the influence of unequal twin domains has been eliminated.

Select the highlighted orthorhombic Laue symmetry (setting a-b, a+b); NEXT

Notes

The three orthorhombic cases correspond to three twin domains. The selected one gave us in the previous test the lowest R_{int}. This indicates that such a domain could be more populated than the others.



[On the screen: Select cell centering]
Select C centering; NEXT

Notes
A hexagonal unit cell transformed into an orthorhombic one must be C centered.

[On the screen: Select space group]
Select Ccce space group; NEXT

Notes
There are several possibilities for selecting a space group. At this stage, it is unclear which is the correct one.

[On the screen: Final step of the space group test]
Accept the space group in the **standard setting**
Accept twinning matrices induced by the space group test
FINISH
[On the screen: Processing refinement reflection file for …]
Follow the wizard for the creation of the refinement reflection file
The program reports Rint 6.31% for 1492 observed reflections merged from 7492 observed reflections.
Select "Accept the new DatBlock and calculate coverage"; FINISH; OK;
QUIT the wizard for structure solution without solving the structure

3. *Space group test results*

[On the screen: basic window of Jana]
In the Command tree, expand “Edit structure parameters” and open “Edit basic parameters (cell,symmetry,etc.)”
[On the screen: Define/modify basic structural parameters]
Check new cell parameters and symmetry; ESC

Notes
Cell parameters 18.8654 10.8919 8.8048 90 90 90 *Space group Ccce*

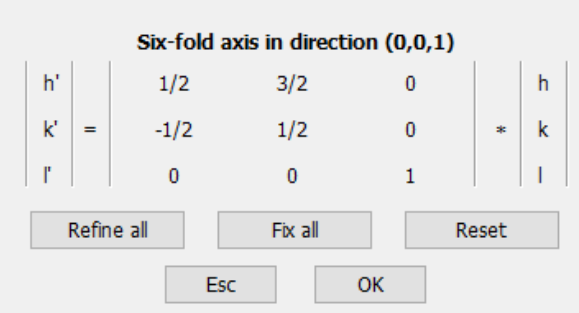
In the Command tree, expand “Edit structure parameters” and open “Edit Twin/phase volume fractions”

[On the screen: Edit twin fractions]

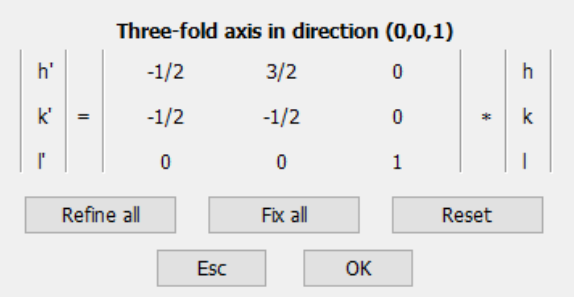
Notes

The initial volume fractions are equal, but we already know they must be different; otherwise, R_{int} for hexagonal Laue symmetry would be lower.

Click the textbox “twvol2” to see the twinning matrix of the second twin domain



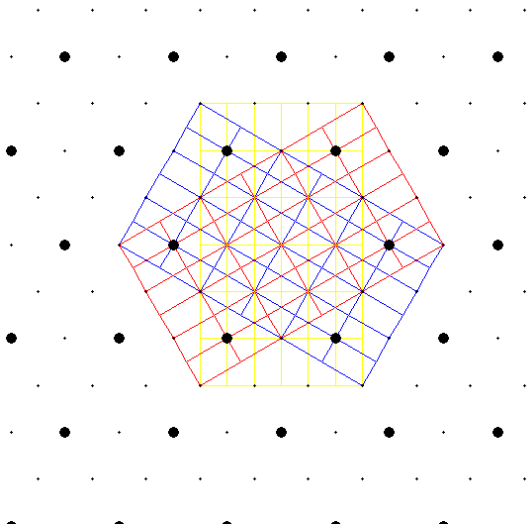
Click the textbox “twvol3” to see the twinning matrix of the third twin domain



Notes

These twinning matrices are related to the orthorhombic unit cell. They correspond to a three-fold twinning around the hexagonal axis. In the next step, we visualize the twins using the reciprocal space viewer.

Return to the basic window
In the command tree, expand “Tools” and run “Run reciprocal space viewer”
In the right pane, select “View along “ c
In the lower toolbar, click the button Options 
Select “Draw individual cells”, “Draw twins”
Define colors according to your preferences
OK
The plot shows three unit cells of the twin individuals:



Quit the Reciprocal space viewer
In the Command tree, expand “Edit File” and double-click “Edit M90 file”

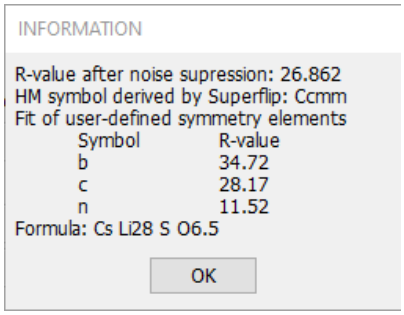
Notes

M90 contains reflection for refinement. The second number from the right is the twin flag. 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 flags “2” and “3” are the ones that cannot be transformed to the first domain because, after such transformation, they would violate systematic absences.

Close the text editor

4. The attempt to solve the twinned orthorhombic structure

[On the screen: basic window of Jana]
In Command tree, expand “Structure Solution” and double-click “Run Superflip”
Quick button for this action: 
[On the screen: Commands for Superflip]
In “Formula” textbox, type Cs Li S O4
“Peaks from Jana2020”; leave other settings default; Press “Run Superflip”
Summary of results of charge flipping:

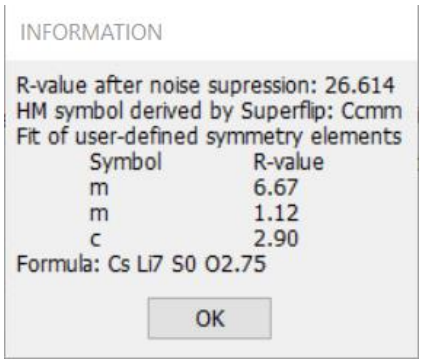


Notes

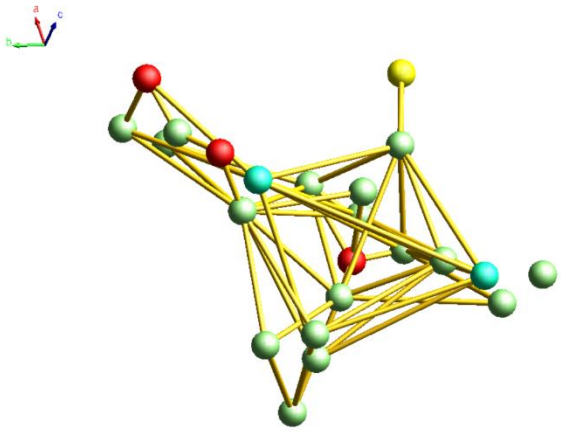
Repeat it several times. Superflip never confirms the originally selected space group, often suggesting Ccmm and other space groups. This is an indication that the structure solution might be difficult.

In the Superflip window, press “Change the space group”
For Space group type Ccmm
OK, YES, to rewrite M50 file

Follow the steps of the wizard for the creation of the refinement reflection file until the program returns to the Structure solution wizard
[On the screen: window of Structure solution]
Press “Run Superflip”
Run Superflip several times. In many cases, it confirms Ccmm symmetry.



Press “Draw structure”;
[On the screen: JanaDraw]
For details, see Basic tasks
Draw the molecule

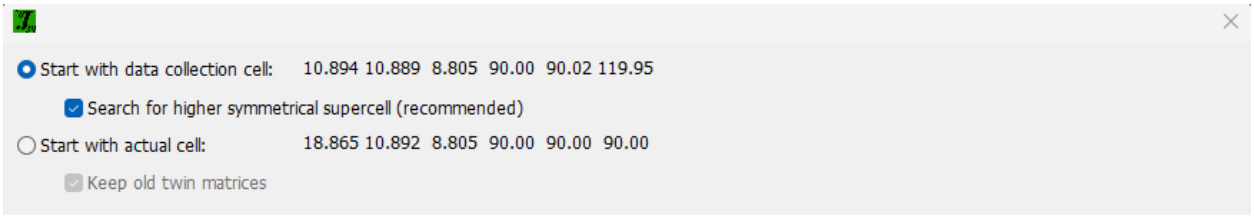


The resulting structure seems to be nonsense
Quit JanaDraw by pressing the red cross on the top of the right pane
Quit the Structure solution wizard (YES to discard the last solution)

5. Application of X centering

Notes
The structure solution in the C-centered orthorhombic unit cell obtained from Symmetry Wizard was problematic. However, the symmetry wizard also indicated X (nonstandard) centering, which has not yet been considered.

In the Command tree, expand “Reflection file” and open “Make space group test”
[On the screen: Tolerances for crystal system recognition]
Select “Start with data collection cell”



NEXT; OK

[On the screen: Select Laue point group]

Check "Introduce twin law for subgroups"

Select the same orthorhombic Laue symmetry as before

NEXT

[On the screen: Select cell centering]

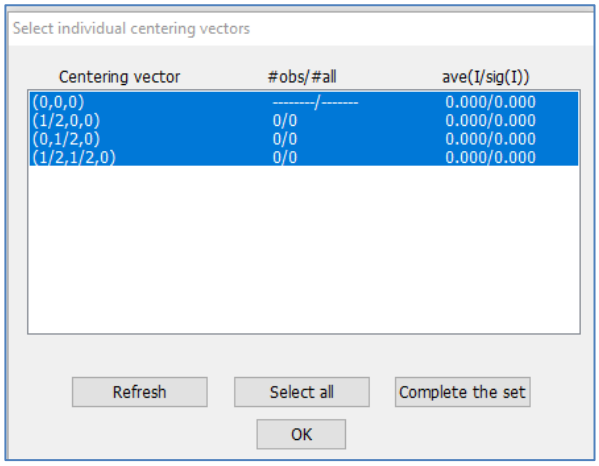
This time, we want to accept X centering instead of C centering

Select X centering

Press "Show/modify X centering" to see the individual centering vectors

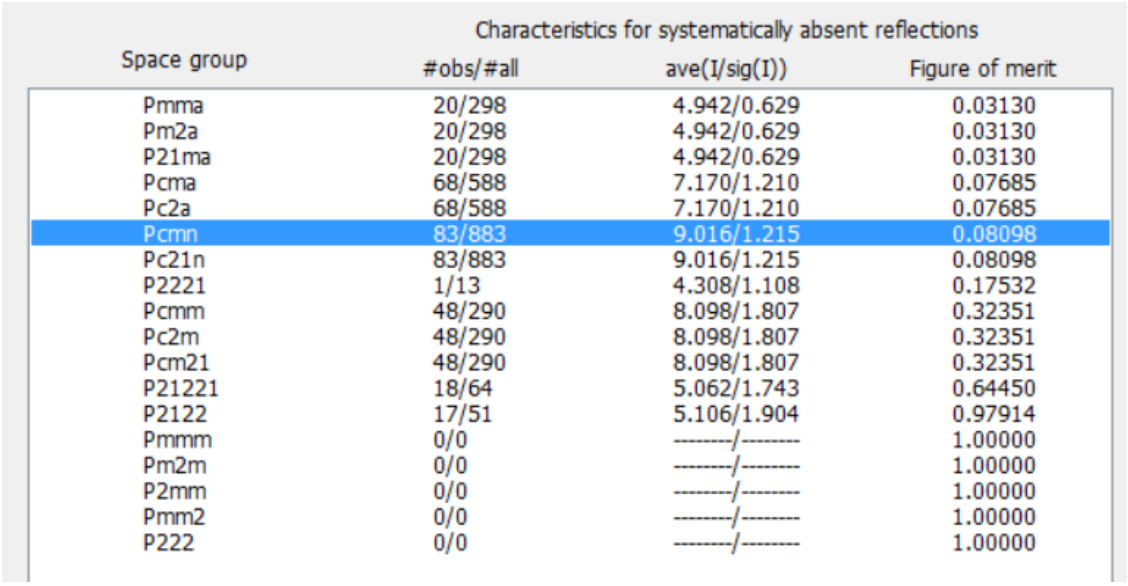
Notes

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.



OK; NEXT

NO to the question about the possibility of repeating the cell centring test



Space group	Characteristics for systematically absent reflections		
	#obs/#all	ave(I/sig(I))	Figure of merit
Pmma	20/298	4.942/0.629	0.03130
Pm2a	20/298	4.942/0.629	0.03130
P21ma	20/298	4.942/0.629	0.03130
Pcma	68/588	7.170/1.210	0.07685
Pc2a	68/588	7.170/1.210	0.07685
Pcmn	83/883	9.016/1.215	0.08098
Pc21n	83/883	9.016/1.215	0.08098
P2221	1/13	4.308/1.108	0.17532
Pcmm	48/290	8.098/1.807	0.32351
Pc2m	48/290	8.098/1.807	0.32351
Pcm21	48/290	8.098/1.807	0.32351
P21221	18/64	5.062/1.743	0.64450
P2122	17/51	5.106/1.904	0.97914
Pmmm	0/0	--------/--------	1.00000
Pm2m	0/0	--------/--------	1.00000
P2mm	0/0	--------/--------	1.00000
Pmm2	0/0	--------/--------	1.00000
P222	0/0	--------/--------	1.00000

Notes

The space group selection is complicated by the presence of spurious peaks in the diffraction pattern. The space group Pcmn has 83 contradicting reflections, but 883 predicted systematic absences. In the other space groups, we would miss an explanation for 883 absent reflections.

[On the screen: Select space group]

Select space group Pcmn; NEXT

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

Accept space group in the standard setting (as Pnma); FINISH

YES to create the refinement reflection file

Follow the steps of the wizard for the creation of the refinement reflection file

Notes

The resulting orthorhombic unit cell has a four times smaller volume than 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 can be seen in the Reciprocal space viewer:

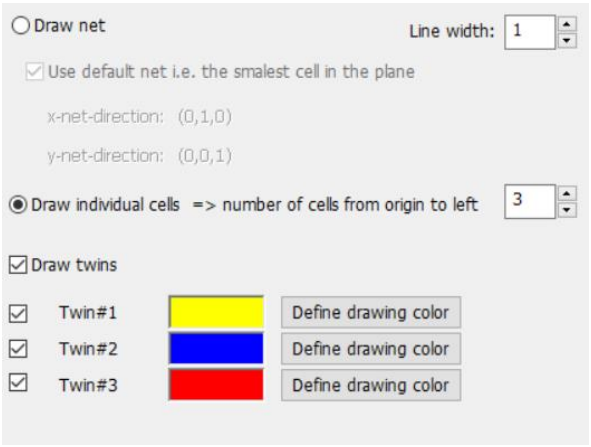
In the “Commands tree”, expand “Tools” and start “Run reciprocal space viewer”

[On the screen: Reciprocal space viewer]

In the bottom toolbar, press “Options”

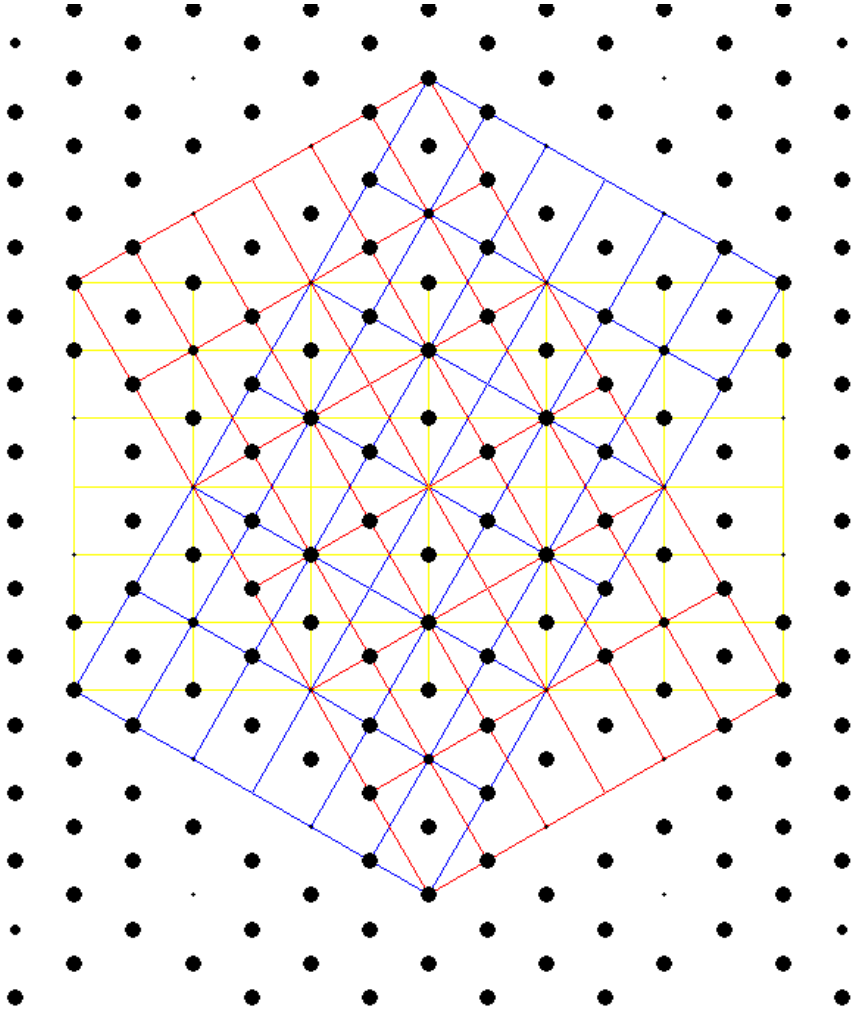
Check “Draw individual cells” and set 3 as the number of cells

Check “Draw twins”, “Twin#1”, “Twin#2” and “Twin#3”

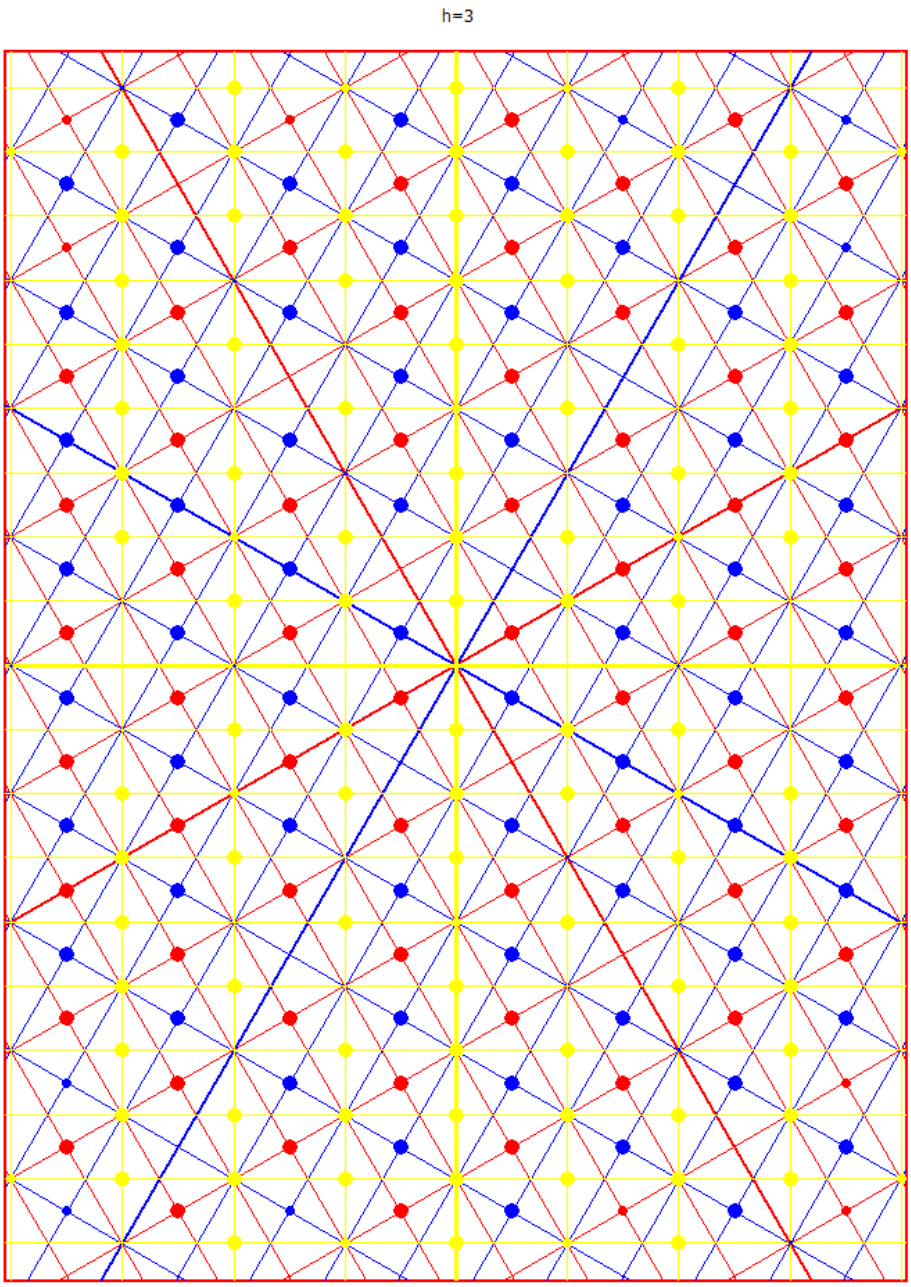


OK

In the right pane, move the “Sensitivity” slider to 10; “zoom” to 65%; change “Layer” to 3; “View along” a;



In the bottom toolbar, press “Options”
Check “Draw net”; OK



Quit the reciprocal space viewer

6. *Structure solution*

In the Command tree, expand “Structure Solution” and double-click “Run Superflip”

The Quick button for Superflip is 

[On the screen: Commands for Superflip]

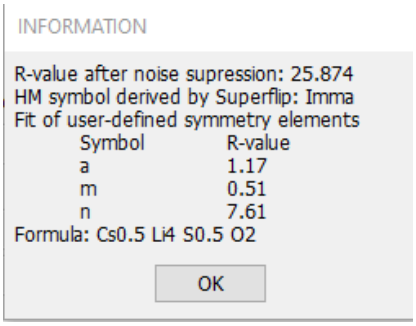
In the “Formula” textbox, type Cs Li S O4

Change Formula units to 4 (based on the density)

A correct number of formula units helps to interpret the peaks, but it is not critical information.

Leave other settings default;

Press “Run Superflip”



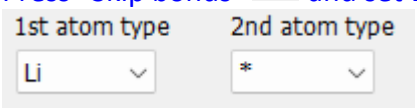
Superflip suggests "I" centering because the test is biased by the presence of the heavy atom

OK; Press "Draw structure"

Li atoms are assigned incorrectly due to noise and twinning.

Delete from the plot all atoms except S1 (click S1; Ctrl-I; Del)

Press "Skip bonds" and set Li as "1st atom type" and * as "2nd atom type"; Rewrite ;



Create the same skipbond command for Cs; OK

Complete coordination of Sulphur using

We should see the SO_4 tetrahedron. Otherwise, repeat the Superflip solution

Quit "JanaDraw"

Press "Accept last solution"

In the Command tree, expand "Edit structure parameters" and open "Edit atoms"

Quick button for this action:

[On the screen: Edit atomic parameters]

Select all Li atoms; Press "Action" and "Delete atoms"; "Yes to all"

OK; YES to save changes

Li atoms are too light to be reliably determined for a twin by charge flipping. They will be found later on from a difference Fourier map.

Change focus to "JanaDraw"

[On the screen: JanaDraw]

Press to draw symmetry-independent atoms

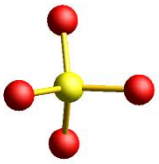
[On the screen: JanaDraw]

Press Crtl+A to select all atoms

Right click out of the atoms to open the "Structure tools" menu -> "Make symmetrically contiguous motif"

Draw symmetry-independent atoms

Press to complete coordination of Sulphur



7. Refinement

[On the screen: JanaDraw]
Open “Refinement commands”
[On the screen: Refine commands]
On the page “Basic”, define 100 cycles, Damping factor 1
OK; YES+START

Notes
R factors : [1235=1058+177/17]
GOF(obs)~8.9 GOF(all)~8.2
Number of reflections excluded due to refinement options: 0+0
R(obs)~8.7 wR2(obs)~22.9 R(all)~9.0 wR2(all)~22.9

8. Twin volume fraction

In the Command tree, expand “Edit structure parameters” and open “Edit Twin/phase volume fraction”
[On the screen: Edit twin fractions]
Activate refinement of both twin fractions; OK; YES
Run refinement

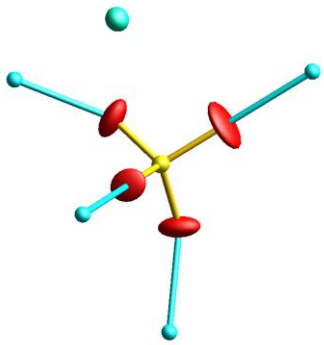
Notes
R factors : [1235=1058+177/19]
GOF(obs)~5.4 GOF(all)~5.0
Number of reflections excluded due to refinement options: 0+0
R(obs)~5.2 wR2(obs)~14.0 R(all)~5.5 wR2(all)~14.1
Twin volume fraction change to 0.26 (twvol2) and 0.31 (twvol3).

[On the screen: JanaDraw]
Press Crtl+A to select all atoms
Open the “Structure tools” menu and select “Define/Edit atoms”
Define/Edit atoms can also be opened by double clicking out of the atoms
Select “harmonic” for ADP parameters; OK
Run refinement”

Notes
R factors : [1235=1058+177/36]
GOF(obs)~4.5 GOF(all)~4.2
R(obs)~4.4 wR2(obs)~11.7 R(all)~4.6 wR2(all)~11.7

9. Find the missing Li atom in a difference Fourier map

[On the screen: JanaDraw]
In the Lower toolbar, press “Show peaks from maps,” 
Highlight Max1; OK



Right-click one of the shown maxima (they are symmetry-equivalent) and add it as Li1
Run refinement

Notes
R factors : [1235=1058+177/39] *GOF(obs)~3.0 GOF(all)~2.7* *R(obs)~2.6 wR2(obs)~7.7 R(all)~2.9 wR2(all)~7.8*

10. Extinction correction

For details, see Example 1.1 – Zn
In Command tree, expand "Refinement" and double-click "View refinement listing"
Press "Go to" and select "Statistics Fo, sin(th)/lambda after refinement"

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	76	72	82	72	51	47	60	
	-	55	56	61	48	62	81	85	71	
	together	134	132	133	130	134	132	132	131	
	av. wd I	45.2984	4.1631	2.3488	4.3462	2.6165	2.3063	2.7095	3.1621	
	numerator +	119.9	96.3	71.4	88.9	79.5	40.5	36.2	67.0	
	-	-472.0	-91.4	-48.7	-70.4	-41.4	-61.3	-84.1	-62.2	
	together	591.8	187.8	120.1	159.4	120.9	101.8	120.3	129.2	
	denominator	11943.5	9489.3	7548.7	7568.8	6031.1	5790.1	5338.9	5343.9	
	R factor	4.96	1.98	1.59	2.11	2.00	1.76	2.25	2.42	

struct. factors

	limits	10.2	14.8	25.7	45.3	59.6	75.6	107.6	347.2	unobs
	number +	71	58	69	72	65	56	81	67	89
	-	61	75	63	60	67	77	51	65	88
	together	132	133	132	132	132	133	132	132	177
	av. wd I	2.6902	31.5610	2.5362	3.5685	4.9055	3.7081	4.0249	14.3432	0.3616
	numerator +	53.8	48.3	36.6	46.8	63.8	63.9	122.9	163.5	105.6
	-	-36.1	-47.2	-46.5	-41.5	-70.9	-83.8	-64.8	-540.9	-74.1
	together	89.9	95.5	83.1	88.3	134.8	147.7	187.7	704.4	179.7
	denominator	1078.9	1643.7	2578.2	4642.9	6959.6	8947.2	11755.0	21448.9	904.7
	R factor	8.33	5.81	3.22	1.90	1.94	1.65	1.60	3.28	19.86

Notes
The Statistics show that the strongest calculated low-angle reflections are systematically weaker, and their partial R factor is increased. This is an indication that extinction correction is needed.

Close the refinement listing by pressing ;
In the Command tree, expand "Edit structure parameters" and open "Edit extinction parameters"
[On the screen: Extinction correction]
Select Isotropic-Becker&Coppens; Type 1; Gaussian;
OK; YES
Run refinement

Notes

R factors : [1235=1058+177/40]
GOF(obs)~2.7 GOF(all)~2.5
Number of reflections excluded due to refinement options: 0+0
R(obs)~2.1 wR2(obs)~7.1 R(all)~2.4 wR2(all)~7.1

In the plot, double-click any of the Li atoms (they are symmetry equivalent)
[On the screen: Define/Edit atom parameters]
Select “harmonic” for ADP parameters; OK
Run refinement

Notes

R factors : [1235=1058+177/43]
GOF(obs)~2.7 GOF(all)~2.5
R(obs)~2.1 wR2(obs)~7.0 R(all)~2.4 wR2(all)~7.0

Conclusions

Three-fold twinning in the primitive orthorhombic unit cell was a clue to successful structure solution and refinement

Anisotropic refinement of Li led to strangely oriented ellipsoids. Due to twinning, the lightness of Li, and the presence of the heavy Cs, data does not bear information for refinement of Li anisotropic displacement

Final plot