Example 3.3: CsLiSO₄

Revised: 17 October 2019

Data	Торіс	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 \rightarrow subgroup transformation.
- Transformation to four times smaller cell.

Initial data

<u>Data</u>

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. <u>Data import</u>

1. Creating new jobname

Start Jana2006

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



New : Selec	t name	of the structure	
Directory		Structure	
	A	00 This is working directory for Example 3	
		CsLiSO4	
		CsLiSO4_red	- 1
		Presentation 1	- 1
		~\$Presentation1	
Y		Y	
ument\Jana Mooc\Examples\Example_03.3_CsLiSC	04\	CsLiSO4	
Drive D: <u>Make new (sub)directory</u>	1		
	I	OH I	

Browse

Cancel

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)



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							
	Complete/correct experimental parameters		Define the reference cell/split by twinning							
Cell parameters:	10.89451 10.88937 8.80485 90.00104 90.02358 119.9455	Cell parameters: 1	0.8945 10.8894 8.8048 90.001 90.024 119	.946						
Number of input indices:	3 AIIII Info about metrics parameters	Target dimension	3	Twinning Twinning matrices						
		1st modulation vec	tor							
		2nd modulation ve	ctor	Data related to domain#						
		3rd modulation ver	tor	Multiply input F(hkl)/I(hkl) by 1						
X-ray tube	Polarization correction:	Max. satellite inde:								
Wave length 0.71073	Circular polarization	Accuracy								
	Perpendicular setting Info	Define to	ransformation ma	TION						
Temperature 293	O Parallel setting Info		All 11132 input reflections	were properly handled						
	O Guinier camera		Ok							
	 Linearly polarized beam 		Inconcentration							
	Monochromator parameters:									
	Perfectness 0.5									
	Glancing angle 6.082144 Set	glancing an								
	Back Next	Car	Back	Next						

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

Step 7	Step 8
Define parameters for absorption and scaling procedure <u>N</u> one or done before importing	
Correction for gaherical sample cadua of the schere [rm] Gaussian integration method pregration grid Egonical correction and/or frame scaling	
Define absorption coefficient => Define formula => Lander of form (a units	
	INFORMATION The import wizard is complete. As a next step you can import another file or modify the previously imported ones.
Back Next Cancel	Back Finish Cancel

3. Data Repository

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





II. <u>Symmetry and data merging</u>

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)



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)



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

We can see the centering vector $(\frac{1}{2},\frac{1}{2},0)$ corresponding to the C centering but also additional vectors $(\frac{1}{2},0,0)$ and $(0,\frac{1}{2},0)$ 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.

								St	e	р6				
			Select cell centering						Select	t spa	ice group			
	Centering	obs/all	ave(I/sig(I))		Space group		obs/all		ave(I/sig(I))		FOM			
0	P	0/0	0.000/0.000	Details	Pmmb	1	20/298	- 1	4.942/0.629	1	0.03130	T		
0	A	823/1405	26.669/16.090	Details	P2mb	1	20/298	I	4.942/0.629	1	0.03130	I.		
0	в	823/1405	26.669/16.090	Details	Pm21b		20/298	1	4.942/0.629		0.08130	I.		
•	с	0/0	0.000/0.000	Details	Pmcb	1	68/588		7.170/1.210	4	0.07685	-		
0	I	4521/5580	51.128/41.615	Details	Pmcn	+	83/883	-	9.016/1.215	+	0.07083	1		
n.a.	R-obverse	2281/3340	51.254/35.336	Details	P21cn	÷.	83/883	i	9.016/1.215	i	0.08098	i.		
n.a.	R-reverse	2246/3310	52,599/36.032	Details	P2221	1	1/13	1	4.308/1.108	T	0.17532	I.		
0	F	823/1405	26 660/16 000	Details	Pmcm	1	48/290	I	8.098/1.807	I	0.32351	1		
~	×(1/2.6.0)	0/0	0.000/0.000	Detaile	P2cm		48/290	I	8.098/1.807	I	0.32351	I.		
16 P	~ (*/*/*/*),	6,0	0.000/0.000		Pmc21		48/290		8.098/1.807		0.32351			
			Further and A second and a second sec		P22121		18/64		5.062/1.743		0.64450			
Warni the or	ng: The cell centerin ogram first transform	ing need not be one	you expect from collection as		P2212		17/51		5.106/1.904		0.97914			
Moree	une after your colori	tion the program of	when another transformation		Pmmm		0/0		0.000/0.000		1.00000			
whene	ever the centring is r	not the standard one	k,		Pm2m	1	0/0	1	0.000/0.000	1	1.00000	1		_
										Det	ails			
			Back Next	Cancel					Back		Next		l P	Ca

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 \rightarrow Structure \rightarrow Save as" and use a new name for example "CsLiSO4-basic" but do not continue with the new structure.

"File \rightarrow Reflection file \rightarrow 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

Select space group												
Space group		obs/all		ave(I/sig(I))		FOM						
Pmmb	1	20/298	I.	4.942/0.629	1	0.03130	1	4				
P2mb	1	20/298	1	4.942/0.629	1	0.03130	1					
Pm21b	1	20/298	1	4.942/0.629	1	0.03130	1					
Pmcb	1	68/588	1	7.170/1.210	1	0.07685	1					
P2cb	1	68/588	1	7.170/1.210	1	0.07685	1					
Pmcn	1	83/883	1	9.016/1.215	1	0.08098	1					
P21cn	1	83/883	1	9.016/1.215	1	0.08098	1					
P2221	1	1/13	1	4.308/1.108	1	0.17532	1					
Pmcm	1	48/290	1	8.098/1.807	1	0.32351	1					
P2cm	1	48/290	1	8.098/1.807	1	0.32351	1					
Pmc21	1	48/290	1	8.098/1.807	1	0.32351	1	1				
P22121	1	18/64	1	5.062/1.743	1	0.64450	1					
P2212	1	17/51	1	5.106/1.904	1	0.97914	1					
Pmmm	1	0/0	1	0.000/0.000	I.	1.00000	1					
Pm2m	1	0/0	1	0.000/0.000	1	1.00000	1					
					Det	oils						
				Back		Next		Cancel				

		510	р С	
	Final	step of the	space group test	
 accept the space group in the 	e standard s	etting:		
Space group: Pmma				
Cell parameters: 9.4301 5.4	505 8.8048 9	0 90 90		
Transformation matrix: a'=	-0.500"a	+0.500*b	+0.000"c	
b'=	-0.500°a	-0.500"b	+0.000*c	
c'=	0.000*a	+0.000"b	-1.000"c	
accept the space group trans	formed into	the original o	cell:	
Space group: 777				
Cell parameters: 10.8919 10	.8919 8.8040	3 90 90 119.9	246	
discard the changes				
Accept twinning matrices inc	juced by the	space group	test	
	1000000000000			

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

Step 9	Step 10
Reflections I< 3 *sig(1) will be sorted as unobserved Note: this number is not interpreted by REFINE use in output file E-format (recommended for data with large dynamical range)	Perform averaging Only sort and apply culling if activated Use non-averaged data
	h k I The slowest varying index ○ ○ ● The fastest varying index ● ○
7493/11132 reflections read from input file 7473/10834 reflections written to output file 20/298 reflections rejected as systematically extinct.	Full print Apply culling Add center of symmetry Apply 1/sig(1) weights in averaging
	Sigma(I(ave)) from: Poisson Equivalents Maximum
Back	Back Next Cancel

Next; OK; Finish

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

Step12

	Stru	acture solution					
C use SIR 2014	Formula	CsUS04		Space group derived fr	om the symme	try operations:	
	Formula ynits Actual space grou	8 ap: Pmma	<u>Calculate density</u>	HM symbol: Pbm Hall symbol: -P Fingerprint: 330	m 2 2b 0320n{041Y03	3}22 (0,0,0)	
allow manual editing of the Bepeat Superflip: Until the of Repeat Superflip: Number of Use local normalization	command file before start an file for forcering unit it convergence detected of runs	<u>B</u> iso: Magaycles:	0	Symmetry operation 1 2 (0,0,1): 2 (1,0,0): -1: 2 [1(0,1,0): m(0,0,1): b (1,0,0): m(0,1,0):	s: -x1 -x1 -x1 -x1 -x1 -x1 -x1 x1	x2 -x2 1/2-x2 -x2 1/2+x2 x2 1/2+x2 1/2-x2	x -x -x -x -x -x x x
Use a specific random seed Define explicitly delta value Beration scheme: © CF LDE ARR Starting model: © Random Pattersor Run solu	For per phases superposition map	ak search use: 0 0 0 0 0	EDMA - flowed composition EDMA - flowed number of atoms EDMA - peak interpretation by Jana2006 Deaks from Jana2006 Peaks from Jana2006 but first run Fourier	Fosition of the origin 0.5570 0.6652 0.78 Agreement factors of i Number smb agreement 6 a 66.69 7 m 0.08 8 m 26.71	n of the spa in the CF m 92 ndividual ge	uce group # ############## Nap: unerators:	

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 \rightarrow Structure \rightarrow Copy in" and select the structure "CsLiSO4-basic"; Rewrite all files; "File \rightarrow Reflection file \rightarrow 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):



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 \rightarrow Twin fractions" (Step2)

			Define/n	nodify bas	ic structural param	neters:					
Cell Symmetry		netry	Composition		Multipole parameters	Ĩ	Magnetic parameter				
Structur	e										
Cell gar	ameters	8.8048	5.4505 9.4301 90	90 90							
E.s.d.'s		0.0006	0.0006 0. <mark>0</mark> 004 0.0	041 0.0041	0.0056						
Twinnin	g	~			∉twin domains	3	-	Matrices			
Dimensi	on = 3										
				Car	ot 1						
				Esc	Ok						

		S	tep 2		
		Ed	it twin fractio	ons	
twvol2	0.333333	two	ol3 0.333333		
		Refine all	<u>Fix all</u>	Reset	
		Sh	ow <u>t</u> winning mat	trix	
			Esc Ok	c [
			Esc Ok		

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) 100/0-1/2-1/2 /03/2-1/2

These twinning matrices are related to the current orthorhombic unit cell





Return to the basic window Start "Edit/view \rightarrow Editing of M90 file" (Step5)

	Step 5					٨	190				
Jana2005 File Edit/View Run Wizards Parameters Tools	Jana2006	• -	3	-1	11	71.2	25.5	1	0	1	0.00
Editing of file Editing of m40 file	File Edit/View Run Wiza	rds	1	0	11	3286.4	35.7	1	0	1	0.00
Editing of m43_file Editing of m42_file	Editing of file		2	0	11	59.4	29.2	1	0	1	0.00
Editing of mSD file Editing of mSD file Editing of mSD file	Editing of m <u>4</u> 0 file	Edit etorns Edit p	3	0	11	867.4	33.1	1	0	1	0.00
Editing of info	Editing of m4 <u>1</u> file	p (c	4	0	11	76.3	37.9	1	0	1	0.00
Editing of atom objects	Editing of m50 file	Eourier Corr	0	1	11	4709.5	78.2	1	0	1	0.00
View of Epurier View of Eput	Editing of m90 file	N I	1	1	11	309.2	33.5	1	0	1	0.00
View of Reflection report	Editing of m95 file	Qist Mətix a	2	1	11	3339.6	47.5	1	0	1	0.00
View of CP report View of Inb report	Editing of saved points		3	1	11	79.1	34.3	1	0	1	0.00
	Editing of atom objects	rofile viewer Gra	1	2	11	2733.2	31.7	1	0	1	0.00
	View of <u>Refine</u>		2	2	11	37.3	24.1	1	0	1	0.00
	View of Dist		2	1	0	879.6	5.7	1	0	2	0.00
``_	View of Dire <u>c</u> t		4	1	0	7.5	6.5	1	0	2	0.00
	View of Reflection report		6	1	0	1358.0	16.8	1	0	2	0.00
> <mark>t</mark> <	View of CP_report		8	1	0	-0.4	8.6	1	0	2	0.00
	View of Inb report		10	1	0	141.4	29.0	1	0	2	0.00
			2	3	0	498.0	9.0	1	0	2	0.00
Structure: D:\document\Jana Mooc\Examples\Example_03.3_CsLISC	24(cal.604		4	3	0	88.8	11.2	1	0	2	0.00

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. <u>Structure solution</u>

"Run \rightarrow 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



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"



IV. <u>Refinements and model improvement</u>

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



2. Twin volume fraction

Start "parameters \rightarrow Twin fractions" (Step1) Activate refinement of the twin fractions Activate refinement of the twin fraction (Step2)



			Step	2
		Edit to	win fraction	s
twvol2 0.333333	\checkmark	twvol3	0.333333	
J	Refine all		Fix all	Reset
	ſ	Show t	winning matri	x
		Esc	Ok	1

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 \rightarrow 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)



OK; YES+START; YES to include new atoms [On the screen: Inserting/replacing of atoms]



OK(Step3) [On the screen: List of peaks] (Step4)

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.



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

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.€	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	sin(th)/lambda		re factors			
			num	nber +		530		530		
			together numerator +			528 1058		528 1058		
					1					
					640.1 -934.4		640.1 -934.4			
			tog	together denominator		1574.5		1574.5		
			der							
			R-factor		2	2.67		2.67		

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

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



[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)



OK; YES+START



contain more information.