

Twinning

Twinning occurs when two or more individuals of the **same phase** exist in the sample. The individuals are related by twin operations.

Set of twinning operators :

$$\{\hat{E} \equiv \hat{T}_1, \hat{T}_2, \dots, \hat{T}_n\}$$

Their application to the base reciprocal vectors of the first individual :

$$\{\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*\} \xrightarrow{\hat{E}} \{\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*\}$$

$$\{\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*\} \xrightarrow{\hat{T}_2} \{\hat{T}_2 \mathbf{a}_1^*, \hat{T}_2 \mathbf{a}_2^*, \hat{T}_2 \mathbf{a}_3^*\}$$

.....

$$\{\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*\} \xrightarrow{\hat{T}_n} \{\hat{T}_n \mathbf{a}_1^*, \hat{T}_n \mathbf{a}_2^*, \hat{T}_n \mathbf{a}_3^*\}$$

The operations give rise to m independent vectors.

$m=3$	complete overlap
$3 < m \leq 3n$	partial overlap
$m=3n$	no overlap

Possible twinning operations can be determined from group \rightarrow subgroup relations:

G ... point group of the structure
H ... point group of the crystal lattice

$$G \subset H$$

Twinning operations:

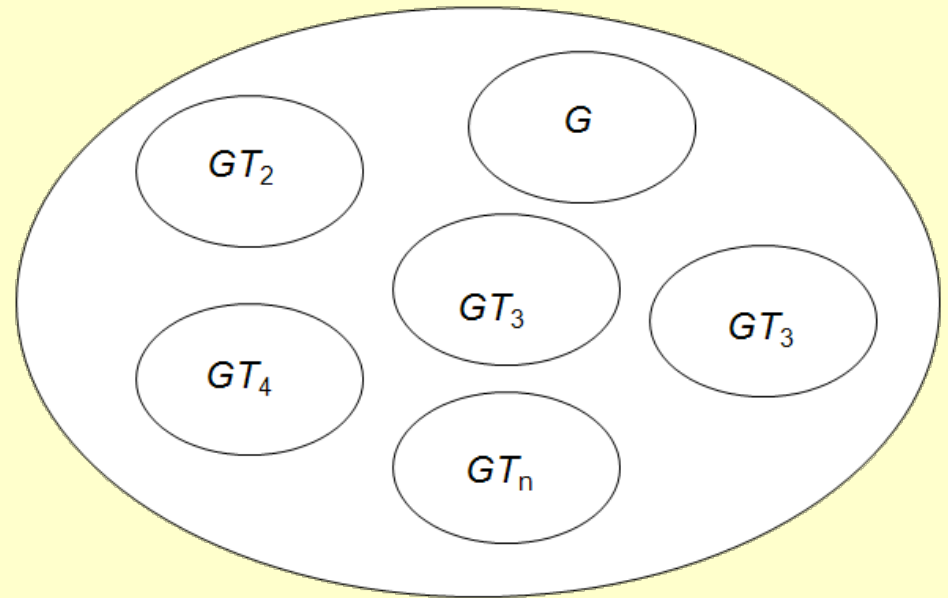
$$\{\hat{E} \equiv \hat{T}_1, \hat{T}_2, \dots, \hat{T}_n\}$$

With twinning operations we can get indices of a selected reflection in all twin domains

$$\mathbf{h}_i = \mathbf{h} \cdot \mathbf{T}_i$$

Decomposition of H to right classes according to G:

- take element T_1 of H which is not part of G
- create set of elements GT_1 (this is not necessarily subgroup)
- find element T_2 of H which is member neither of G nor of GT_1
- create set of elements GT_2
- Finally H is decomposed to so called right classes. Each element of H belongs to one and only one right class. Each member of the right class can be taken as twinning operation.



Example: $H = 4/mmm$, $G = mmm$

Order H is 16, order G is 8 \Rightarrow index of the twin is 2 and twin operation can be any from the following symmetry operations of H :

$$\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$4^+ 0,0,z$

$$\begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$4^- 0,0,z$

$$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$2 x,x,0$

$$\begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$2 x,\bar{x},0$

$$\begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$\bar{4}^+ 0,0,z$

$$\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$\bar{4}^- 0,0,z$

$$\begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$m x,\bar{x},0$

$$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$m x,x,0$

Diffraction pattern combines **intensities** of twin individuals.

Structure factor of a merohedric twin:

$$\mathcal{F}^2(\mathbf{H}) = v_1 F^2(\mathbf{H} \cdot \mathbf{T}_1) + v_2 F^2(\mathbf{H} \cdot \mathbf{T}_2) + \dots + v_n F^2(\mathbf{H} \cdot \mathbf{T}_n)$$

where v_i are domain fractions

\mathbf{T}_i are twin operations

The sum of domain fractions $\sum v_i = 1$

Symmetry element of the crystal structure:

$$\mathbf{S}_i \in G \Rightarrow |F(\mathbf{H} \cdot \mathbf{S}_i)| = |F(\mathbf{H})|$$

Transformation of the structure factor of a twin:

$$\mathcal{F}^2(\mathbf{H} \cdot \mathbf{S}_i) = v_1 F^2(\mathbf{H} \cdot \mathbf{S}_i \cdot \mathbf{T}_1) + v_2 F^2(\mathbf{H} \cdot \mathbf{S}_i \cdot \mathbf{T}_2) + \dots + v_n F^2(\mathbf{H} \cdot \mathbf{S}_i \cdot \mathbf{T}_n)$$

The condition $\mathcal{F}^2(\mathbf{H} \cdot \mathbf{S}_i) = \mathcal{F}^2(\mathbf{H})$ is fulfilled only when

$$\mathbf{H} \cdot \mathbf{S}_i \cdot \mathbf{T}_k = \mathbf{H} \cdot \mathbf{T}_k \cdot \mathbf{S}_j \Rightarrow \mathbf{S}_j = \mathbf{T}_k^{-1} \cdot \mathbf{S}_i \cdot \mathbf{T}_k$$

The conditions

$$\mathbf{H} \cdot \mathbf{S}_i \cdot \mathbf{T}_k = \mathbf{H} \cdot \mathbf{T}_k \cdot \mathbf{S}_j$$

means that the argument of structure factor is always from the same right class of the decomposition.

Otherwise the argument would “skip” between domains.

Diffraction symmetry of a twin is given by a set of symmetry operations invariant with respect to the twinning operations. It can be maximally equal to the point group of the lattice, when the domain fractions are equal:

$$v_1 = v_2 = v_3 \dots = v_n = 1/n$$

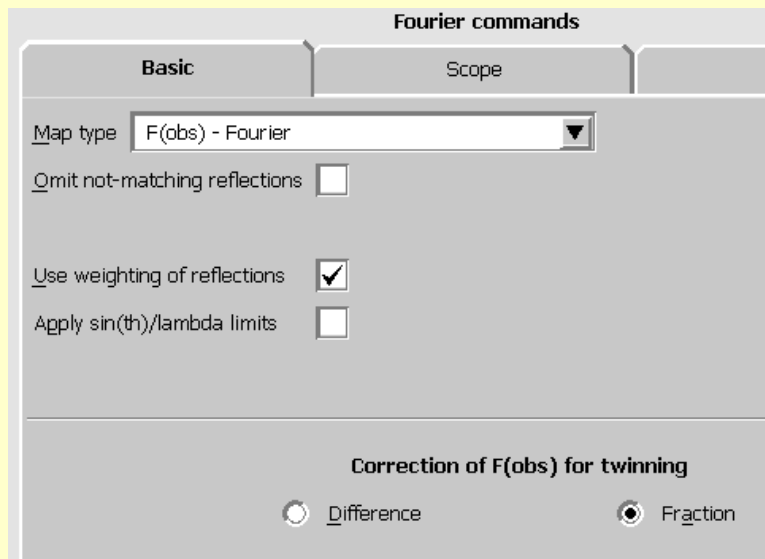
Fourier coefficients for twin

$$F_{obs}(\mathbf{H}) = \mathcal{F}_{obs}(\mathbf{H}) \frac{F_{calc}(\mathbf{H})}{\mathcal{F}_{calc}(\mathbf{H})}$$

$$F_{obs}(\mathbf{H}) = \sqrt{\mathcal{F}_{obs}^2(\mathbf{H}) - v_2 F_{calc}^2(\mathbf{H} \cdot \mathbf{T}_2) \dots - v_n F_{calc}^2(\mathbf{H} \cdot \mathbf{T}_n)}$$

$\mathcal{F}_{obs}(\mathbf{H})$ Structure factors from all domains

$F_{obs}(\mathbf{H}), F_{calc}(\mathbf{H})$ Structure factors from one domain (needed for calculation of Fourier map)



Fourier commands

Basic Scope

Map type: F(obs) - Fourier

Omit not-matching reflections

Use weighting of reflections

Apply sin(theta)/lambda limits

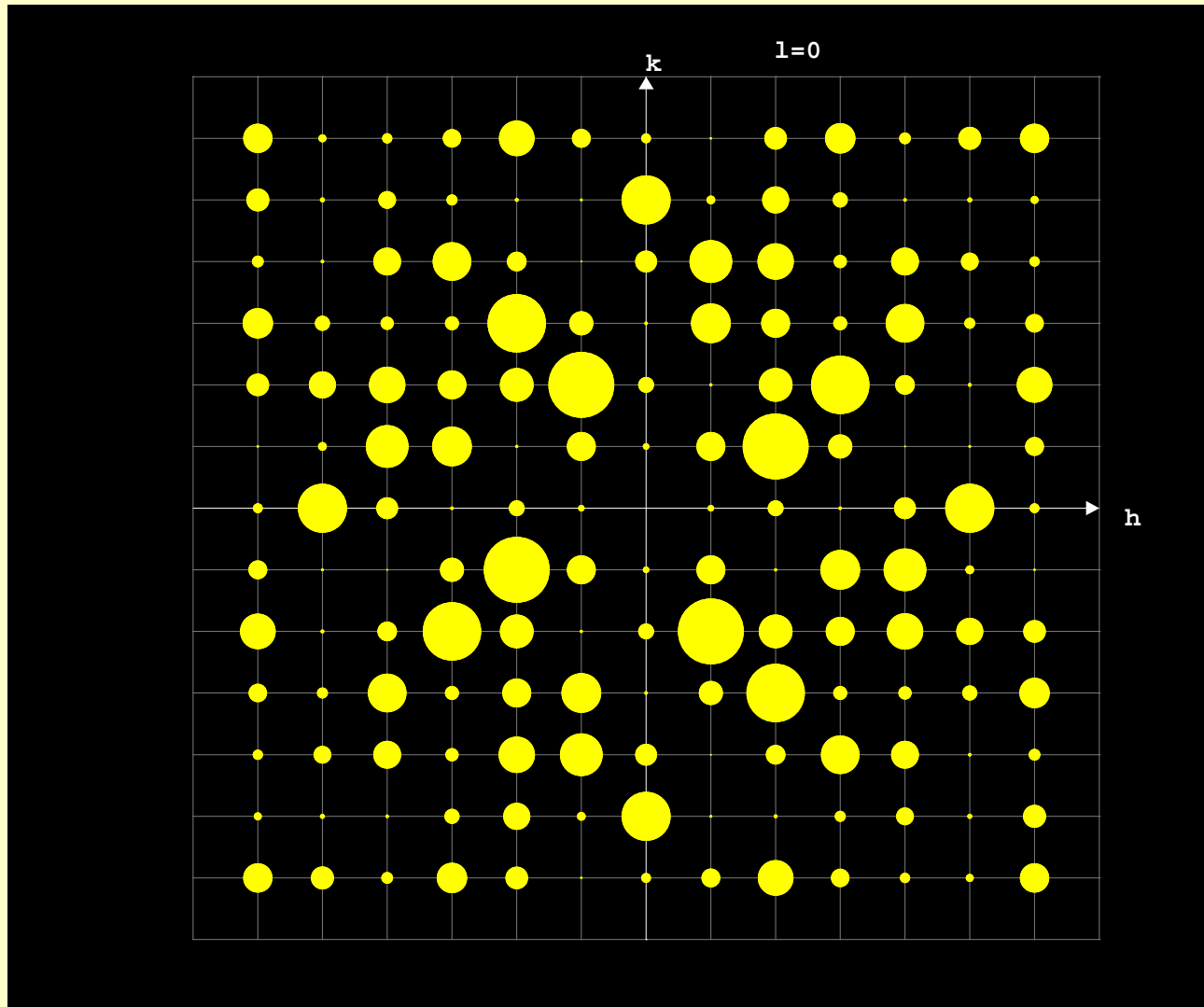
Correction of F(obs) for twinning

Difference Fraction

The precision of “fraction” method grows with completing of the structure model

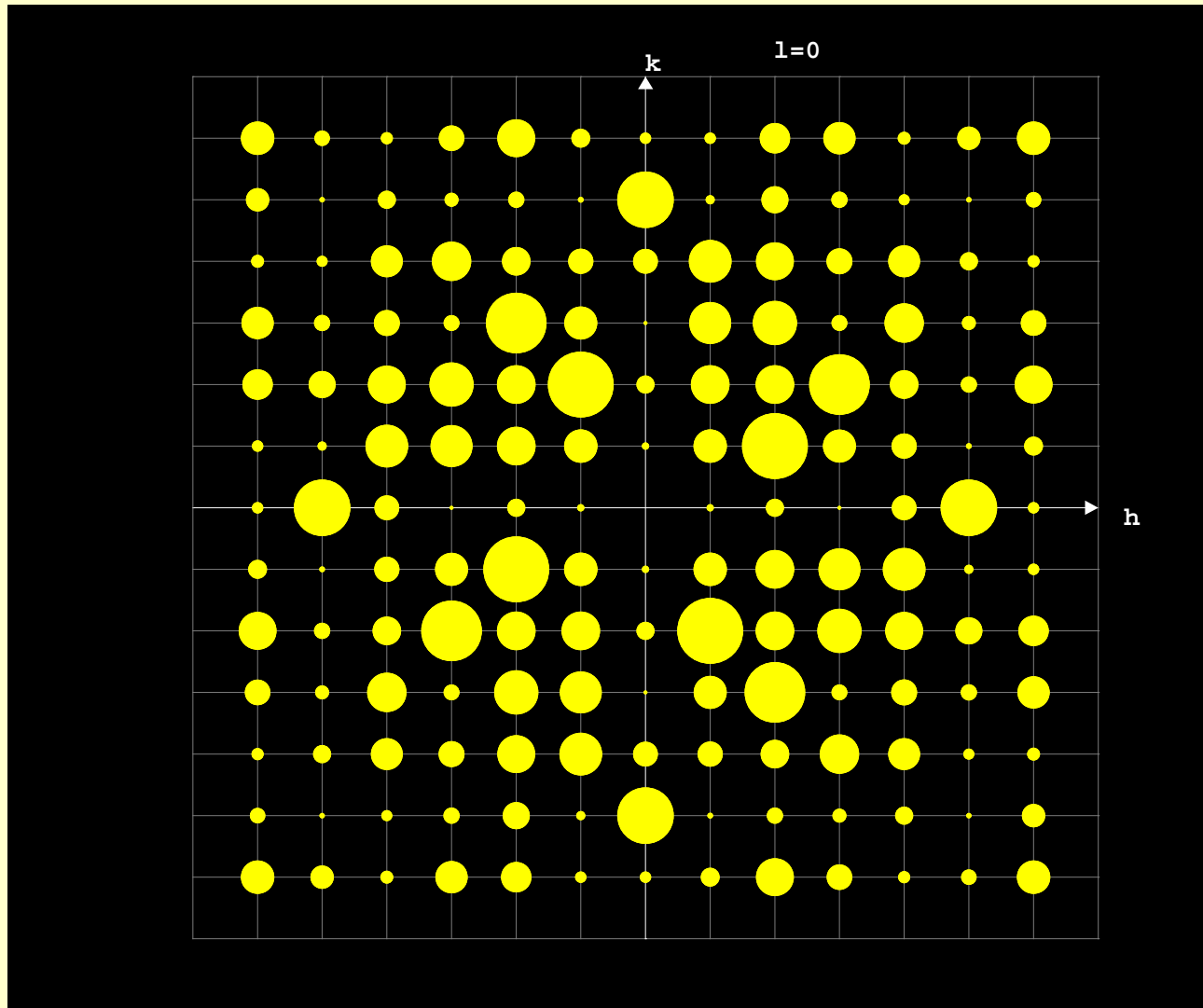
If the Fourier map is not satisfactory switching the method may help

Diffraction symmetry of a merohedric twin: The chance to recognize proper symmetry from the diffraction pattern of merohedric twin depends on the twin domains ratio.



Lattice:
4/mmm
Structure:
4/m
Twin operation:
none

For non-equal domains ratio the proper symmetry is still evident.



Lattice:

4/mmm

Structure:

4/m

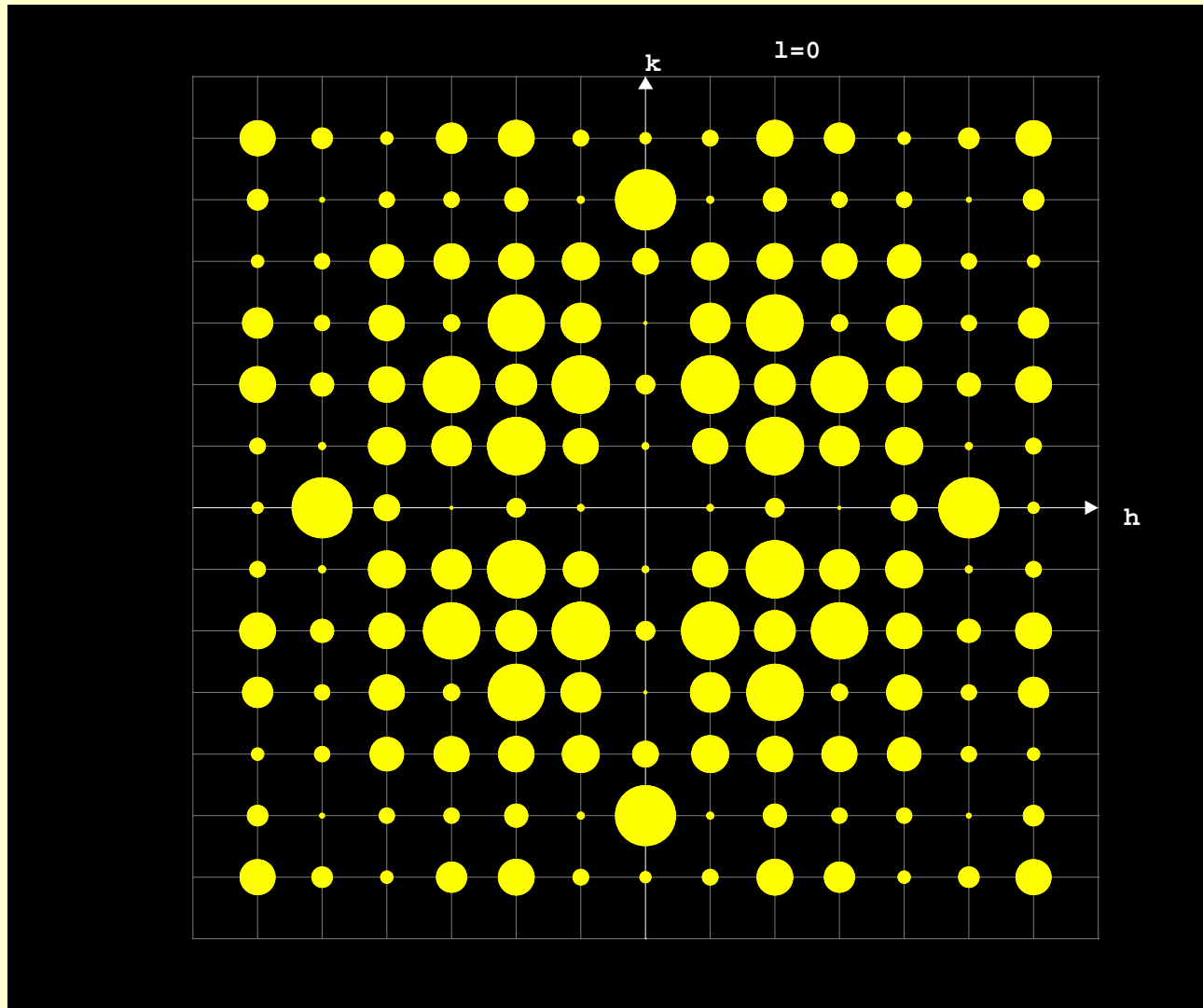
Twin operation:

m_x

2nd domain fraction:

25%

For equal domains ratio false higher symmetry is detected.



Lattice:

4/mmm

Structure:

4/m

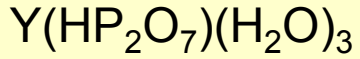
Twin operation:

m_x

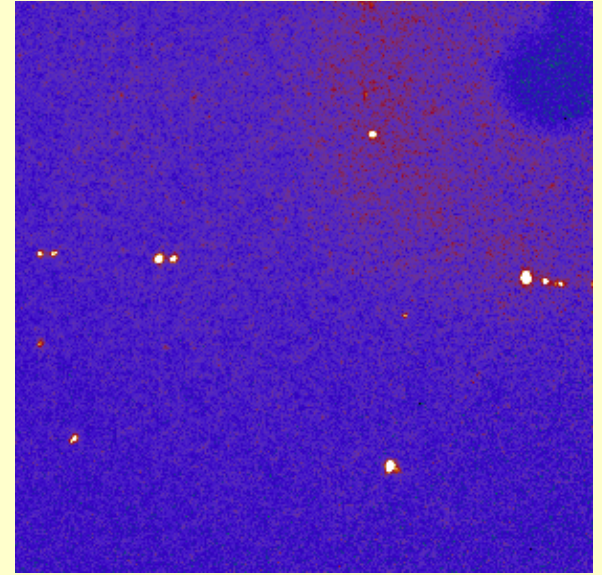
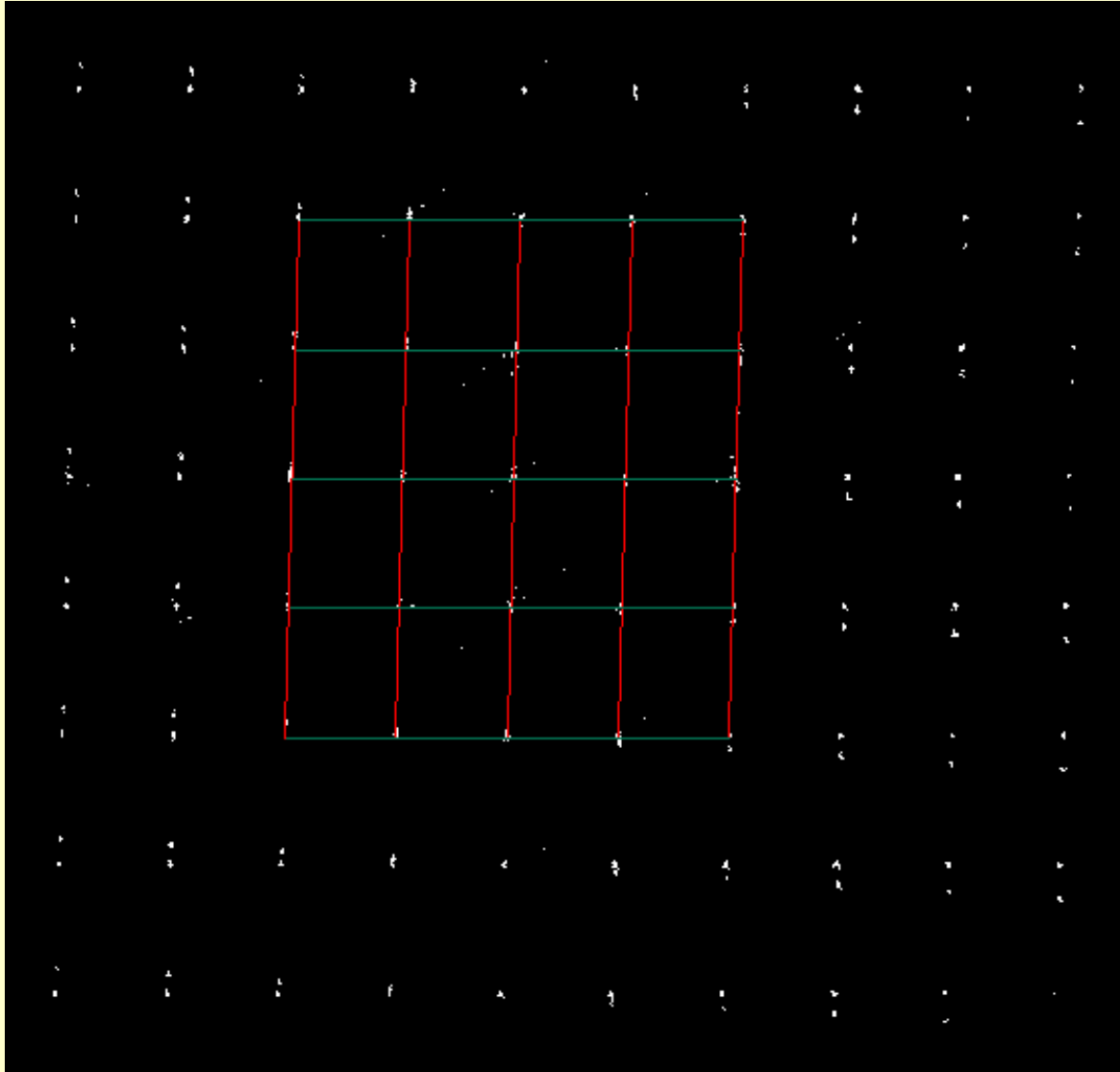
2nd domain fraction:

50%

Twins with partial overlaps ($m > 3$)



Cell parameters: 6.422 6.890 9.817 81.65 80.27 88.35; symmetry: P-1



Twinning matrix:

-1.0000	0.0517	0.0000
0.0000	1.0000	0.0000
0.0000	0.4161	-1.0000

$(\mathbf{h}' = \mathbf{T} \cdot \mathbf{h}, \mathbf{h}$ is a column)

Rot= 180° around \mathbf{b}

T applies to indices as a column, therefore **T** inverted transposed will apply to reciprocal base vectors as a column. For two fold twin $\mathbf{T}^{-1} = \mathbf{T}$.

$$\begin{pmatrix} -1 & 0 & 0 \\ 0.0517 & 1 & 0.4161 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}^* \\ \mathbf{c}^* \end{pmatrix} = \begin{pmatrix} -\mathbf{a}^* \\ 0.0517\mathbf{a}^* + \mathbf{b}^* + 0.4161\mathbf{c}^* \\ -\mathbf{c}^* \end{pmatrix}$$

The twinning operation yields one new reciprocal vector:

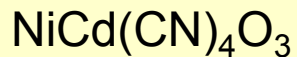
$$\mathbf{q} = (0.0517\mathbf{a}^* + \mathbf{b}^* + 0.4161\mathbf{c}^*)$$

We can index the complete diffraction pattern using four indices h,k,l,m. The first twin individual will have indices h,k,l,0; the second twin individual will have indices -h,m,-l,0. The relationship between the individuals can be expressed by 4x4 matrix:

$$\mathbf{W} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad \mathbf{H}^1 = \mathbf{H}^2\mathbf{W}$$

Sometimes the splitting is tiny.

In this case it would be hidden for normal CCD measurement.



Cell parameters: 8.522 16.012 7.651 90 90.32 90

Symmetry: C2/c($\alpha 0 \gamma$)0s

q vector (0.4346, 0, 0.13)

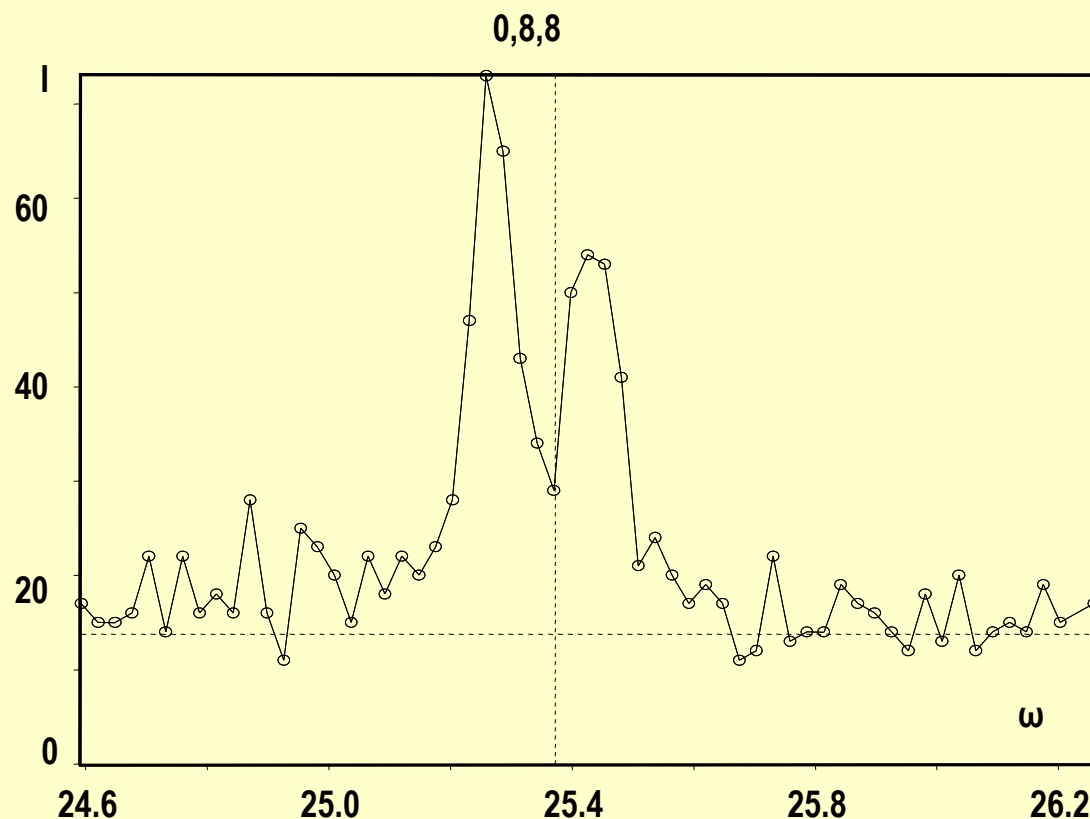
Twinning matrix:

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ -0.0124 & 0 & 1 \end{pmatrix}$$

Transformed indices:

$$(-h - 0.0124l, -k, l)$$

Almost complete overlap
of main reflections, clear
separation of satellites.



Example 3: AD3

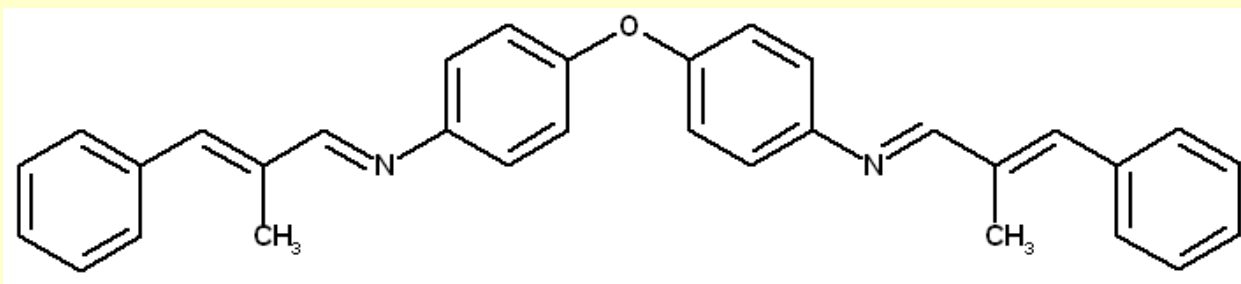
Simple structure with pseudo-merohedric twinning. Finding twinning matrix from group-subgroup transformation. Creating publication CIF.

Bis[N-(2-benzylidenepropylidene)phenyl]ether

Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files: AD3.hkl, AD3.sum

Frame scaling, absorption correction: done with software of diffractometer



Test of space group: the option “Introduce twin law” is selected based on the “suspicious” unit cell parameters

Tolerances for crystal system recognition:

Original cell parameters: 6.018 7.467 55.844 90.05 90.02 89.96

Maximal deviation for cell lengths in [A]

Maximal deviation for cell angles in deg

Tolerances for space group recognition:

Maximal ave(I/sig(I)) for centering

Maximal ave(I/sig(I)) for extinctions

Search for higher symmetrical supercell (recommended)

Introduce twin laws in case of subgroups

Use old twin matrices in testing

Check non-standard centering:

look for centering vectors composed from 0 and $1/2$

look for centering vectors composed from 0, $1/3$ and $2/3$

Back

Next

Cancel

Meaning of "Introduce twin law" : if the selected Laue symmetry is lower than the highest possible for the given unit cell, the program will introduce twinning by the lost symmetry elements

Select Laue symmetry

Crystal system	Point group	R _{int} (obs/all)	#averaged	Redundancy
Triclinic	-1	1.50/1.51	7330/7492	2.084
Monoclinic-setting "a"	2/m	17.38/17.38	4135/4225	3.695
Monoclinic-setting "b"	2/m	17.36/17.36	4059/4161	3.752
Monoclinic-setting "c"	2/m	1.61/1.61	3841/3910	3.993
Orthorhombic	mmm	17.90/17.90	2292/2345	6.657

ordered by Lae symmetry

ordered by Rint

Averages made from 15193/15611 reflections

Cell parameters:
7.4728 55.89 6.0235
90 90.0418 90

R_{int} for mmm: 17.9%
R_{int} for 2/m: 1.6%
(setting b)

Lost symmetry mmm
-> 2/m: x -y -z can be
used like twinning
operation

Here the twinning is finally accepted

Final step of the space group test

accept the space group in the standard setting:

Space group: P21/n

Cell parameters: 7.4667 55.8439 6.0185 90 90.042 90

Transformation matrix: a'= 1.000*a +0.000*b +0.000*c

b'= 0.000*a +1.000*b +0.000*c

c'= 0.000*a +0.000*b +1.000*c

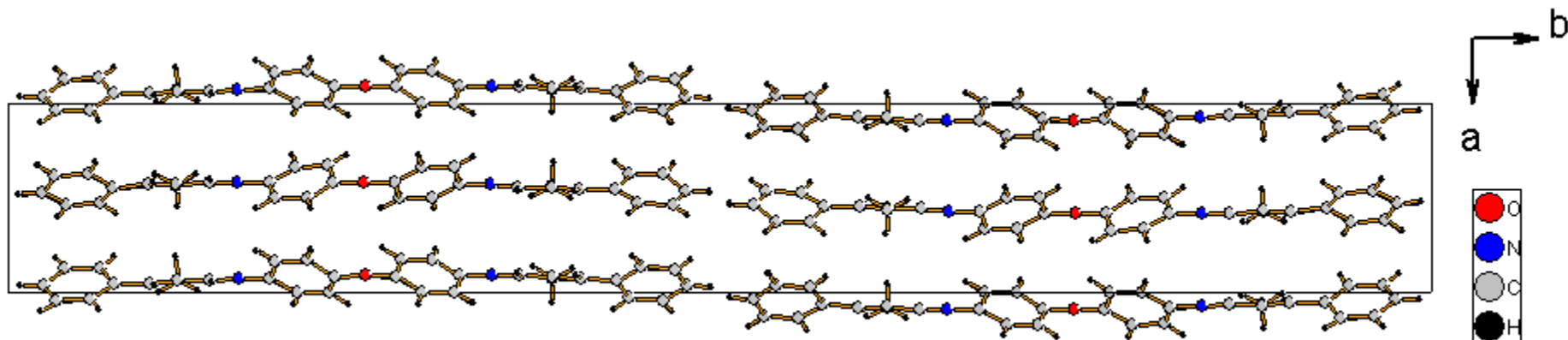
accept the space group transformed into the original cell:

Space group: P21/n

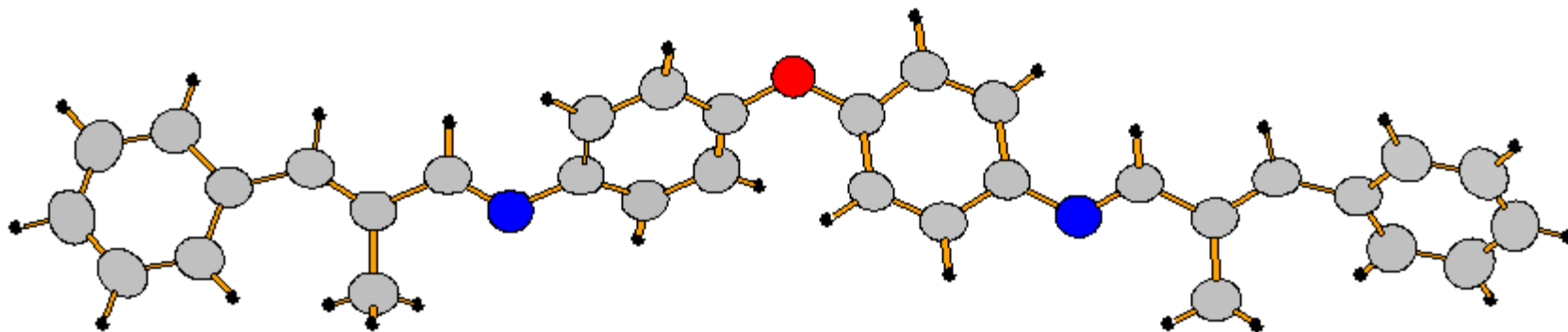
Cell parameters: 7.4667 55.8439 6.0185 90 90.042 90

discard the changes

Accept twinning matrices induced by the space group test



Charge flipping
 Correcting chemical types
 Anisotropic ADP
 Hydrogens



R=20% without twinning, 3.44% with twinning - Refined twin fractions: 0.72, 0.28

Example 3.2: PyNinit

Simple structure with non-merohedric twinning. Handling twin overlaps in Jana2006

Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files:

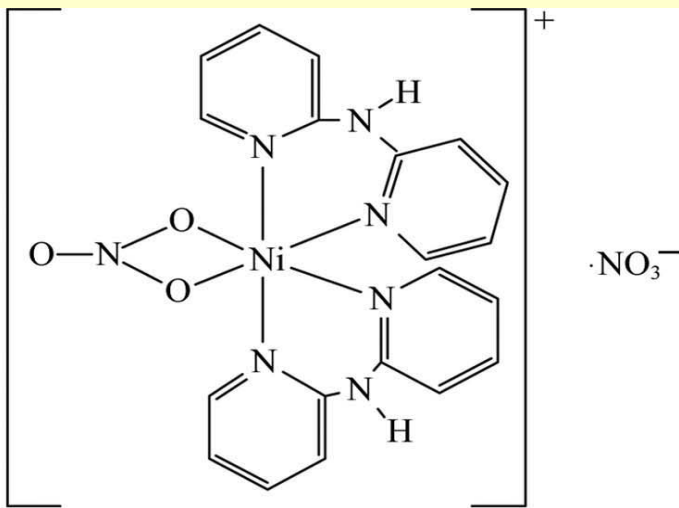
1st twin domain: pyNinit_twin1.hkl, pyNinit_twin1.sum

2nd twin domain pyNinit_twin2.hkl, pyNinit_twin2.sum

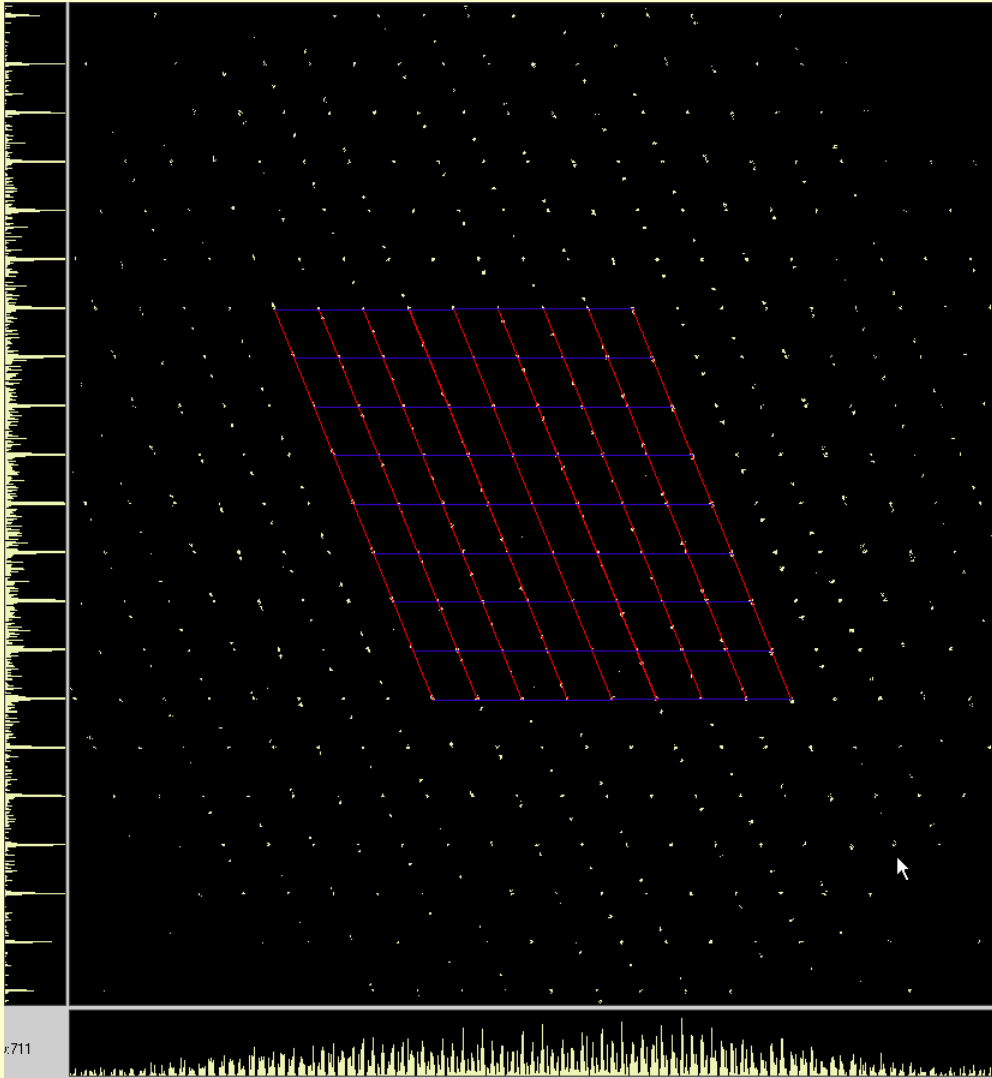
hklf5: pyNinit_twin1_hklf5.hkl

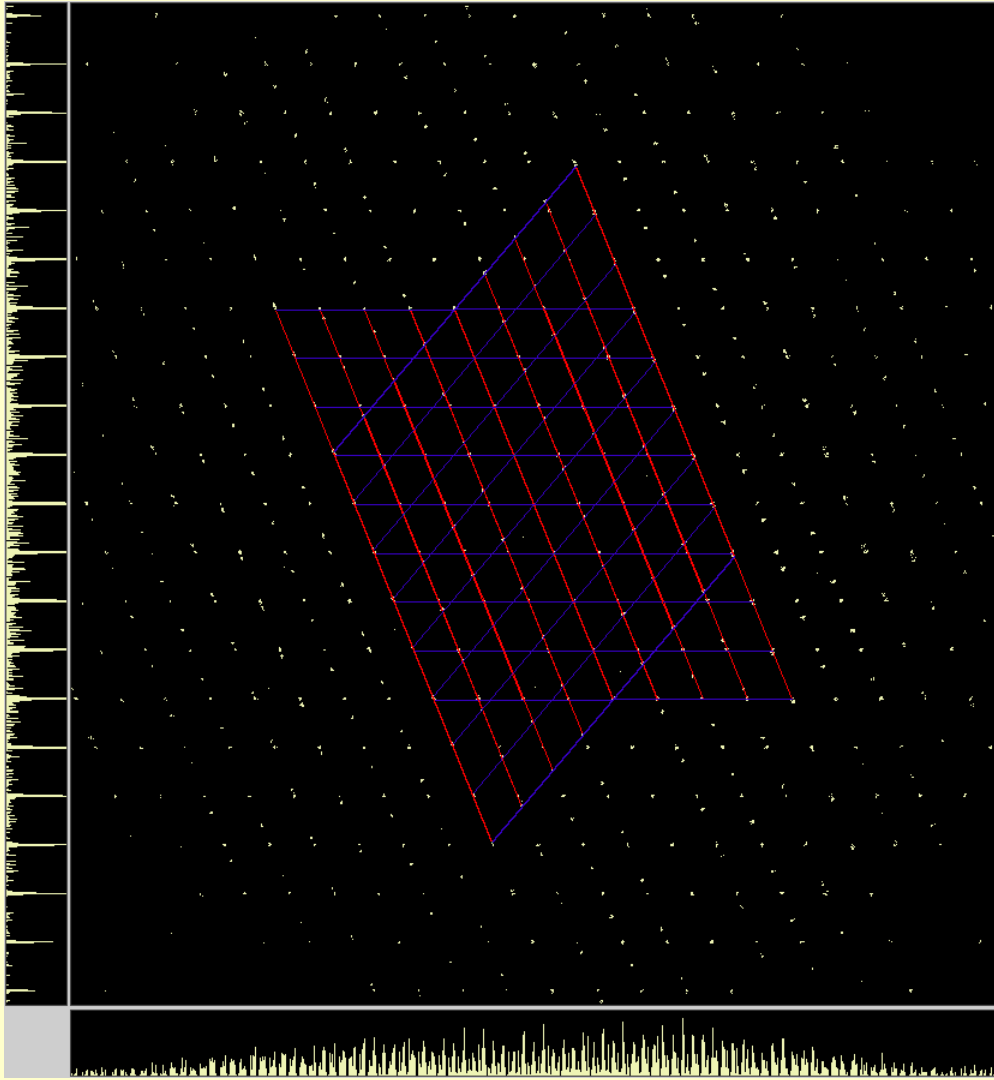
Twinning matrix: $\begin{pmatrix} -1 & 0 & -0.733 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Frame scaling, absorption correction: done with software of diffractometer



J. Černák, M. Dušek, K. Fejfarová, Acta Cryst. (2009). C65, m260-m262.





LATTICE

Current cell

14.5940(15) 9.8526(5) 16.0519(11) 90.005(5) 113.739(8) 90.016(6) 2112.8(3)

Constrained current cell

14.6005(13) 9.8578(7) 16.0454(17) 90.0 113.814(12) 90.0 2112.8(3)

Lattice reduction

selected cell

14.5993 9.8527 16.0514 90.0061 113.7692 90.0239 mP 35

reduced cell

9.8527 14.5993 16.0514 113.7692 90.0061 90.0239 2113.0

Twin information

1: 14.5934 9.8530 16.0502 90.007 113.720 90.008 2112.9

2: 14.6015 9.8542 16.0544 90.002 113.764 90.030 2114.1

1: Total: 4970(61.1%) Separate: 3201(39.3%) Overlapped: 1769(21.7%)

2: Total: 4930(60.6%) Separate: 3161(38.8%) Overlapped: 1769(21.7%)

Unindexed: 9 (0.1%)

1. Structure solution using 1st twin domain only: R ~ 17%
2. Introduction of twinning: R ~ 13%

2nd twinning matrix

h' = * h + * k + * l

k' = * h + * k + * l

l' = * h + * k + * l

Rotation axis

in direct base
 Proper rotation

in reciprocal base
 Improper rotation

Rotation angle:

0 deg
 120 deg
 270 deg

60 deg
 180 deg
 300 deg

90 deg
 240 deg
 explicitly

$$\begin{pmatrix} h' \\ k' \\ l' \end{pmatrix} = \begin{pmatrix} -1 & 0 & -0.733 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

Original cell parameters:

14.623	9.873	16.083	90.00	113.72	90.00
--------	-------	--------	-------	--------	-------

Twin cell parameters:

14.632	9.873	16.083	90.00	113.81	90.00
--------	-------	--------	-------	--------	-------

Do you want to accept the twinning matrix?

3. Discarding partially overlapped reflections: $R \sim 4\%$

Refine commands

Basic Select/Listing Various Modulation

Number of cycles: Use damping method Sigma weight Instability factor

Damping factor Use Marguart technique Unit weight

Use dynamical LS method => if R_w tolerance larger than reduce the damping by a factor
After cycles try to enlarge it back.

Check for convergence => stop if $\max(\text{change/s.u.}) \leq$ in consecutive cycles.

Disable atoms having too large isotropic ADP parameter => ADP(iso) limit for disabling

Automatic refinement keys Maximal angular difference for twin overlap

Automatic symmetry restrictions Minimal angular difference for full separation

```
R factors : [2993=1921+1072/317], Damping factor: 0.5000
GOF(obs)= 1.36 GOF(all)= 1.30
Number of reflections excluded due to refinement options: 0+1898
R(obs)= 3.83 Rw(obs)= 3.11 R(all)= 8.63 Rw(all)= 3.84
Last Rw(all): 3.84
Maximum change/s.u. : -0.0190 for U23[N7]
```

Where to stop?

We want to discard as little reflections as possible

<i>L1</i>	<i>L2</i>	<i>R_{obs}</i>	<i>GOF</i>	<i>discarded</i>
0	0	15.2	8.2	0
0.1	0	12.7	4.7	0
0.2	0	7.4	3.6	0
0.3	0	7.1	3.5	0
0.4	0	9.8	5.5	0
0.35	0	9.6	5.4	0
0.31	0	9.3	5.3	0
0.3	0.4	6.9	3.6	778
0.3	0.5	7.4	3.8	1264
0.3	0.6	7.9	4.1	1916
0.2	0.3	6.2	3.0	415
0.2	0.4	5.7	3.0	1193
0.15	0.3	5.3	2.4	709
0.1	0.3	4.8	1.9	1120
0.1	0.4	3.9	1.4	1848

4. Using data of the second domain

5. Testing scale of domains

6. Using HKLF5 file: R ~ 5.5% without discarding reflections

The diffractometer software should know more about overlaps than Jana2006

```
-4 -7 -12 132.825 55.5172 -2
13 7 -12 132.825 55.5172 1
-5 -7 -12 19.9661 56.6859 -2
14 7 -12 19.9661 56.6859 1
-6 -7 -12 24.2907 52.1818 -2
15 7 -12 24.2907 52.1818 1
0 -4 -11 421.765 31.9614 -2
8 4 -11 421.765 31.9614 1
-1 -4 -11 42.9233 24.2092 -2
9 4 -11 42.9233 24.2092 1
-2 -4 -11 322.224 34.3002 -2
10 4 -11 322.224 34.3002 1
-3 -4 -11 48.0177 31.7279 -2
11 4 -11 48.0177 31.7279 1
-4 -4 -11 471.881 52.0069 -2
12 4 -11 471.881 52.0069 1
-5 -4 -11 383.447 52.9024 -2
13 4 -11 383.447 52.9024 1
-6 -4 -11 348.428 62.3163 -2
14 4 -11 348.428 62.3163 1
-7 -4 -11 162.334 70.3329 -2
15 4 -11 162.334 70.3329 1
-8 -4 -11 289.451 54.9913 -2
16 4 -11 289.451 54.9913 1
-9 -4 -11 81.6937 39.9522 -2
17 4 -11 81.6937 39.9522 1
```

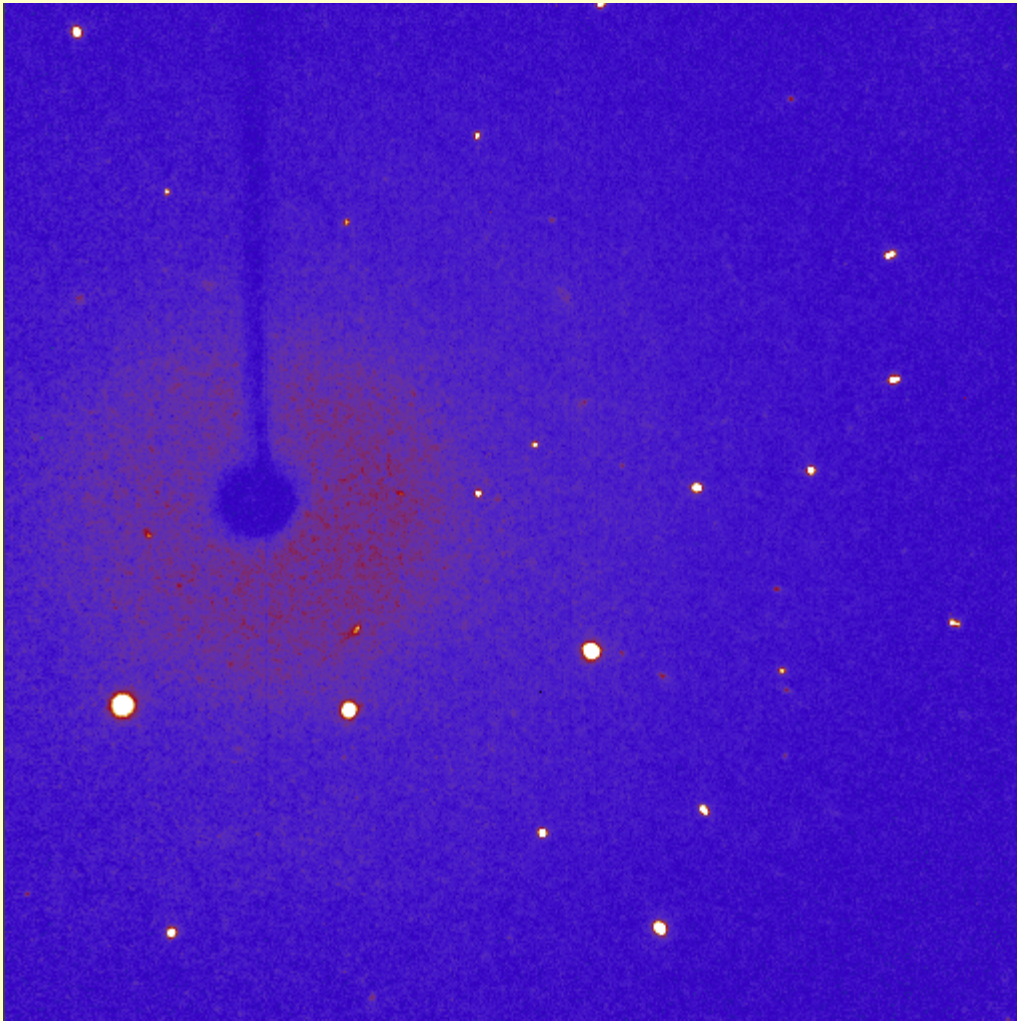

Example 3.3: CsLiSO₄

Simple structure with pseudo-merohedric 3-fold twinning. Finding twinning matrix from group->subgroup transformation. Transformation to four times larger reciprocal cell.

Single crystal data measured with Oxford Diffraction four-circle diffractometer

Input files: CsLiSO4.hkl, CsLiSO4.sum

Frame scaling, absorption correction: done with software of diffractometer

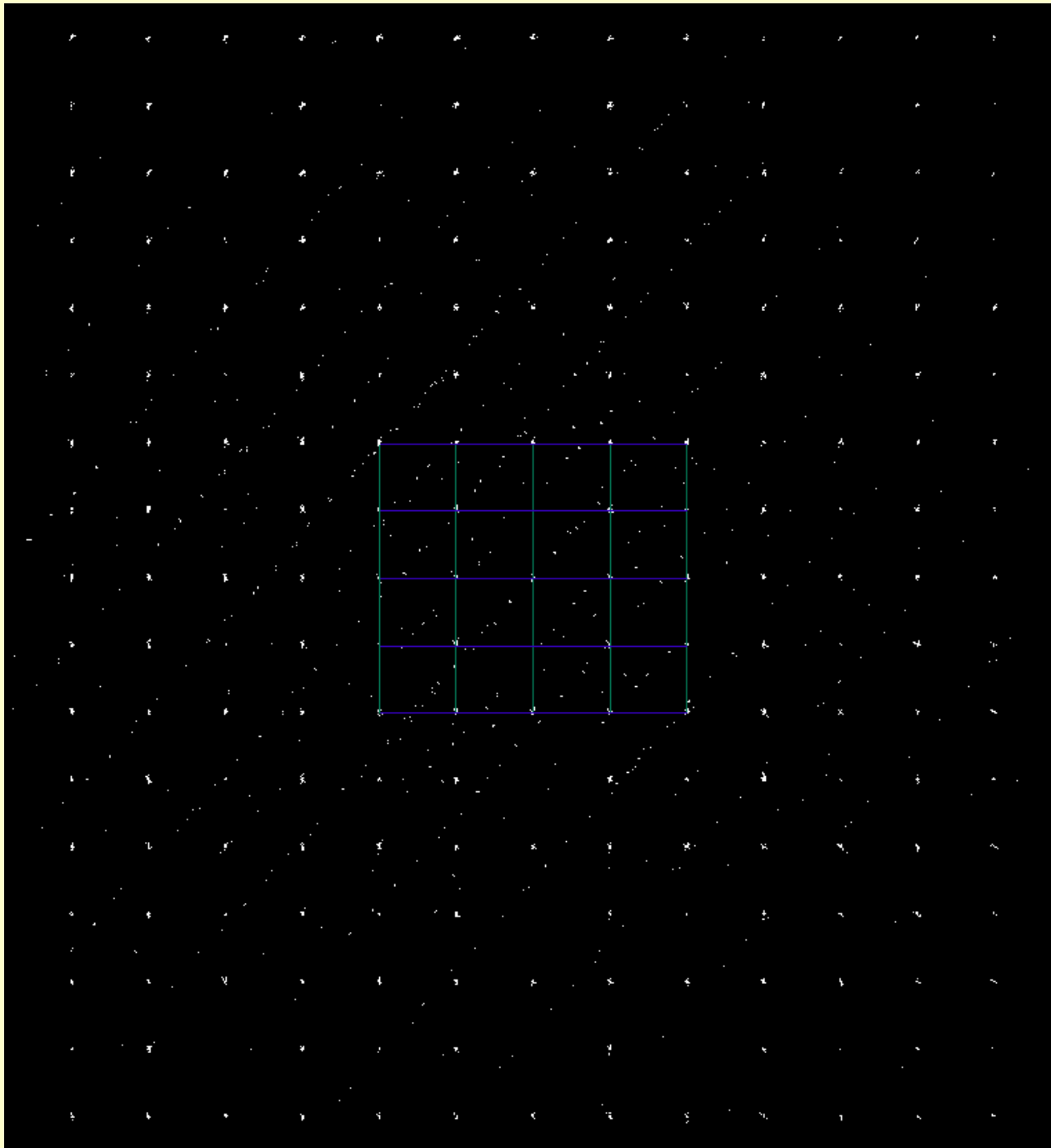


Good data

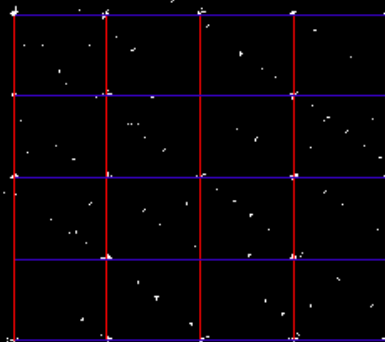
No split reflections

No overlaps

Peaks projected along a^*

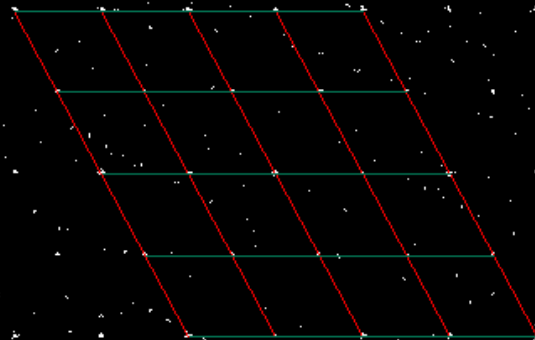


Peaks projected along b^*



Peaks projected along c^*

hexagonal unit cell



$$a = 10.89451(0.00058)$$

$$b = 10.88937(0.00058)$$

$$c = 8.80485(0.00041)$$

$$\alpha = 90.00104(0.00407)$$

$$\beta = 90.02358(0.00406)$$

$$\gamma = 119.94547(0.00557)$$

$$V = 905.11$$

Symmetry wizard

Select Laue symmetry

		Rint(obs/all)	#averaged	Redundancy
<input type="radio"/> Triclinic	-1	5.68/5.74	2752/3790	2.937
<input type="radio"/> Monoclinic-setting "c"	2/m	6.31/6.37	1493/2026	5.494
<input type="radio"/> Trigonal	-3	14.35/14.40	1012/1270	8.765
<input type="radio"/> Trigonal	-31m	14.46/14.50	559/698	15.947
<input type="radio"/> Trigonal	-3m	14.46/14.51	618/740	15.042
<input type="radio"/> Hexagonal	6/m	14.46/14.50	543/682	16.321
<input checked="" type="radio"/> Hexagonal	6/mmm	14.51/14.56	344/425	26.191

Averages made from 7492/11131 reflections

Select cell centering

Centering	obs/all	ave(I/sig(I))
<input checked="" type="radio"/> P	0/0	0.000/0.000
<input type="radio"/> A	3185/5616	32.662/18.990
<input type="radio"/> B	3269/5636	30.220/17.981
<input type="radio"/> C	3466/5624	40.898/25.600
<input type="radio"/> I	3017/5599	37.134/20.509
<input type="radio"/> F	4960/8438	34.735/20.856

From symmetry wizard this is evident that hexagonal symmetry is violated. Because cell parameters are exactly hexagonal merohedric twinning is highly probable. In order to get twinning matrices easily we shall use the highest hexagonal symmetry and use group-subgroup transformation tool.

The symmetry wizard does not list orthorhombic possibilities because they are in contradiction with cell parameters. Orthorhombic cells will be available in group-subgroup transformation.

Select Laue symmetry

	Rint(obs/all)	#averaged	Redundancy
<input type="radio"/> Triclinic -1	5.68/5.74	2752/3790	2.937
<input type="radio"/> Monoclinic-setting "c" 2/m			
<input type="radio"/> Trigonal -3			
<input type="radio"/> Trigonal -31m			
<input type="radio"/> Trigonal -3m1			
<input type="radio"/> Hexagonal 6/m			
<input checked="" type="radio"/> Hexagonal 6/mmm			

Averages made from 7492/1

Back

Select space group

Space group	obs/all	ave(I/sig(I))
P6/mmm	0/0	0.000/0.000
P-62m	0/0	0.000/0.000
P-6m2	0/0	0.000/0.000
P6mm	0/0	0.000/0.000
P622	0/0	0.000/0.000
P6322	1/13	4.311/0.000
P63/mmc	51/532	7.874/0.000
P-62c	51/532	7.874/0.000
P63mc	51/532	7.874/0.000

Back

Final step of the space group test

accept the space group in the standard setting:

Space group: P63/mmc

Cell parameters: 10.9139 10.9139 8.8226 90 90 120

Transformation matrix: a' = 0.000*a -1.000*b +0.000*c
b' = -1.000*a +0.000*b +0.000*c
c' = 0.000*a +0.000*b -1.000*c

accept the space group transformed into the original cell:

Space group: P63/mmc

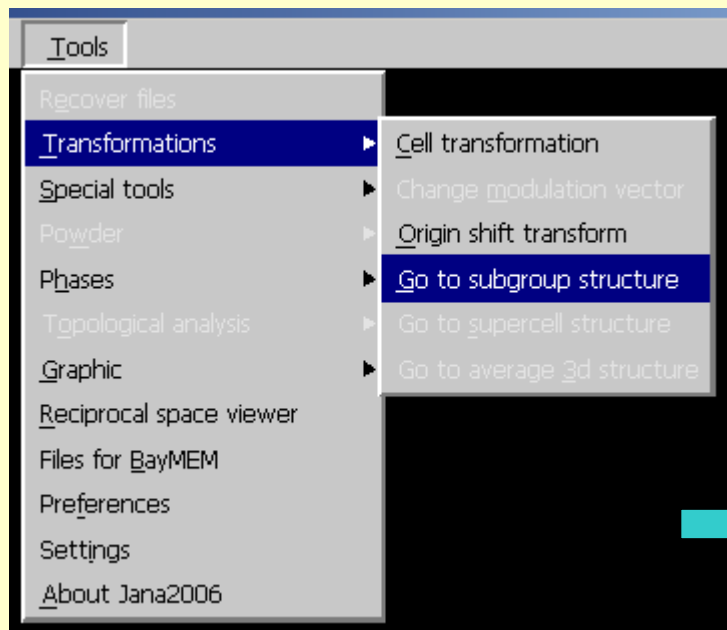
Cell parameters: 10.9139 10.9139 8.8226 90 90 120

discard the changes

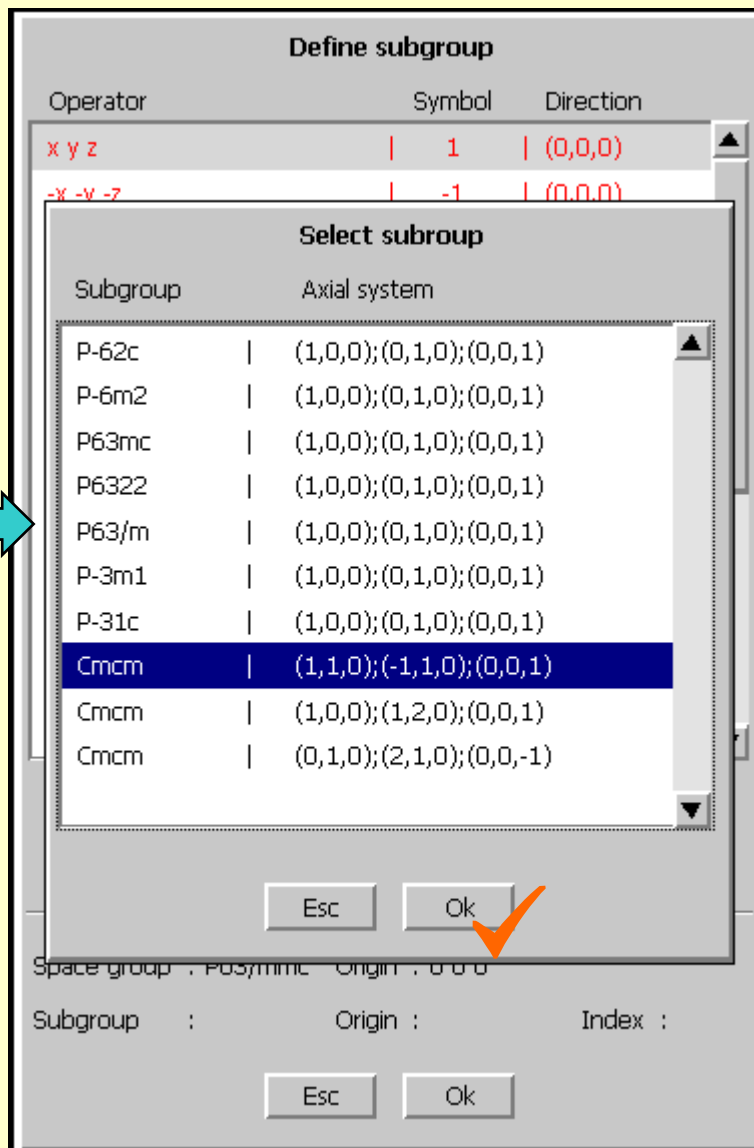
Back

Finish

Cancel



Transformation to orthorhombic cell



Select one representative of the 2nd coset

	Symbol	Direction
-x -x+y -z	2	(0,1,0)
x x-y z	m	(0,1,0)
-y x-y z	3	(0,0,1)
y -x+y z+1/2	63	(0,0,1)
y -x+y -z	-3	(0,0,1)
-y x-y -z+1/2	-6	(0,0,1)
x x-y -z+1/2	2	(2,1,0)
-x -x+y z+1/2	c	(2,1,0)

Esc Ok

Select one representative of the 3rd coset

	Symbol	Direction
x-y -y -z	2	(1,0,0)
-x+y y z	m	(1,0,0)
-x+y -x z	3	(0,0,1)
x-y x z+1/2	63	(0,0,1)
x-y x -z	-3	(0,0,1)
-x+y -x -z+1/2	-6	(0,0,1)
-x+y y -z+1/2	2	(1,2,0)
x-y -y z+1/2	c	(1,2,0)

Esc Ok

Specify the output structure

Name of structure: CsLiSO4_twin

Make as twinning structure

Save the selected coset representative as local operators

Esc Ok

Summary after averaging

Rint(obs/all) = 6.31/6.37 for 1492/2021 reflections
 averaged from 7491/11118 reflections

Redundancy = 5.501

h(min) = -13, h(max) = 11
 k(min) = 0, k(max) = 13
 l(min) = 0, l(max) = 11

R(obs/all) from e.s.d. of I: 0.67/ 0.89

Ok

The discarded symmetry operations will be used as twinning operations. They are two -> we have created three-fold twin.

The selected subgroup wouldn't be at the standard setting unless the following transformation is applied:

$$\begin{aligned} a' &= 1.000*a + 1.000*b + 0.000*c \\ b' &= -1.000*a + 1.000*b + 0.000*c \\ c' &= 0.000*a + 0.000*b + 1.000*c \end{aligned}$$

Do you want to make the proposed transformation?

Yes

No

Summary after averaging

Rint(obs/all) = 6.31/6.37 for 1492/2021 reflections
averaged from 7491/11118 reflections

Redundancy = 5.501

h(min) = -13, h(max) = 13

k(min) = 0, k(max) = 23

l(min) = 0, l(max) = 11

R(obs/all) from e.s.d. of I : 0.67/ 0.89

Ok

Edit M50 file

Cell Symmetry Composition Multipole parameters Magnetic parameters

Structure

Cell parameters 10.9229 18.8984 8.8226 89.9867 90.025 90.0309

E.s.d.'s 0 0 0 0 0

Twinning #twin domains 3 Matrices

Dimension = 3

Finally a transformation is offered to standard symmetry Cmcm. We can check new cell parameters in EditM50.

```

Commcell 10.9165 10.9114 8.8226 90.001 90.024 119.946
trcell
      1.0000   -1.0000    0.0000
      1.0000    1.0000    0.0000
      0.0000    0.0000    1.0000
refblock Block1
sourcefile CsLiS04.hkl
filedate 23/01/2008 filetime 10:46:40
difcode 5 correspond 1 corrlp -1 corrrabs 0
lambda 0.71073 radtype 1 polarization 1 datcolltemp 293
monangle 6.0821 perfmono 0.5
nref 11131 ndim95 3 nlines 22262 twidth 1 scmax 1 scale 1
cell 10.9165 10.9114 8.8226 90.001 90.024 119.946
ormat
      0.071904   -0.022060    0.042037
     -0.045981   -0.092164   -0.055632
      0.062385    0.046966   -0.089360
end
Data Block1
      1 -13   3   0   0.00   0.00  26.30  26.30   0.111946E+03   0.838333E+03   1.000   1   1
      0.100000E+01   0.100000E+01   0.0000   0.5782   0.7640   0.6042  -0.2860   0.5019   0.6038   0.0000

```

Header of M95 now contains transformation from hexagonal to new orthorhombic elementary cell. It is applied when making M90 before merging of reflections.

```

datblock Block1
nref 2021 obslim 3 norefitems 1 diffscaler 1 dataave 1 scalelim 10
indslowest 3 indfastest 1 addcentrsymm 0 sigimethod 1 multave 1
flimprint 5 flimcull -1
lambda 0.71073 radtype 1 dattype 1 lpfactor 1 monangle 6.082 perfmono 0.5
datcolltemp 293
end
Data Block1
  2  0  0  166.8  3.4  1  0  1  0.0000
  4  0  0 115151.2  357.3  1  0  1  0.0000
  6  0  0   13.8  9.2  1  0  1  0.0000
  8  0  0  56835.4  139.6  1  0  1  0.0000
 10  0  0   -8.5  16.5  1  0  1  0.0000
 12  0  0  10219.7  72.2  1  0  1  0.0000
-13  1  0  -20.7  30.6  1  0  1  0.0000
-11  1  0   9.2  17.3  1  0  1  0.0000
 -9  1  0  -3.9  34.2  1  0  1  0.0000
 -7  1  0   9.1  10.9  1  0  1  0.0000
 -5  1  0   8.5   7.2  1  0  1  0.0000

```

Flags in M90 show that all reflections are indexed in the first domain. This is correct because the twin is merohedric.

2nd twinning matrix

$$\begin{aligned} h' &= -1/2 * h + 1/2 * k + 0 * l \\ k' &= 3/2 * h + 1/2 * k + 0 * l \\ l' &= 0 * h + 0 * k + -1 * l \end{aligned}$$



Rotation axis

- in direct base Proper rotation
 in reciprocal base Improper rotation

Rotation angle:

- 0 deg
 60 deg
 90 deg

Original cell parameters:
10.923 18.898 8.823 89.99 90.03 90.03
Twin cell parameters:
10.917 18.909 8.823 89.98 90.02 90.07

Do you want to accept the twinning matrix?

Yes

No

3rd twinning matrix

$$\begin{aligned} h' &= -1/2 * h + -1/2 * k + 0 * l \\ k' &= -3/2 * h + 1/2 * k + 0 * l \\ l' &= 0 * h + 0 * k + -1 * l \end{aligned}$$



Rotation axis

- in direct base Proper rotation
 in reciprocal base Improper rotation

Rotation angle:

- 0 deg
 60 deg
 90 deg

Original cell parameters:
10.923 18.898 8.823 89.99 90.03 90.03
Twin cell parameters:
10.911 18.918 8.823 90.03 90.00 89.96

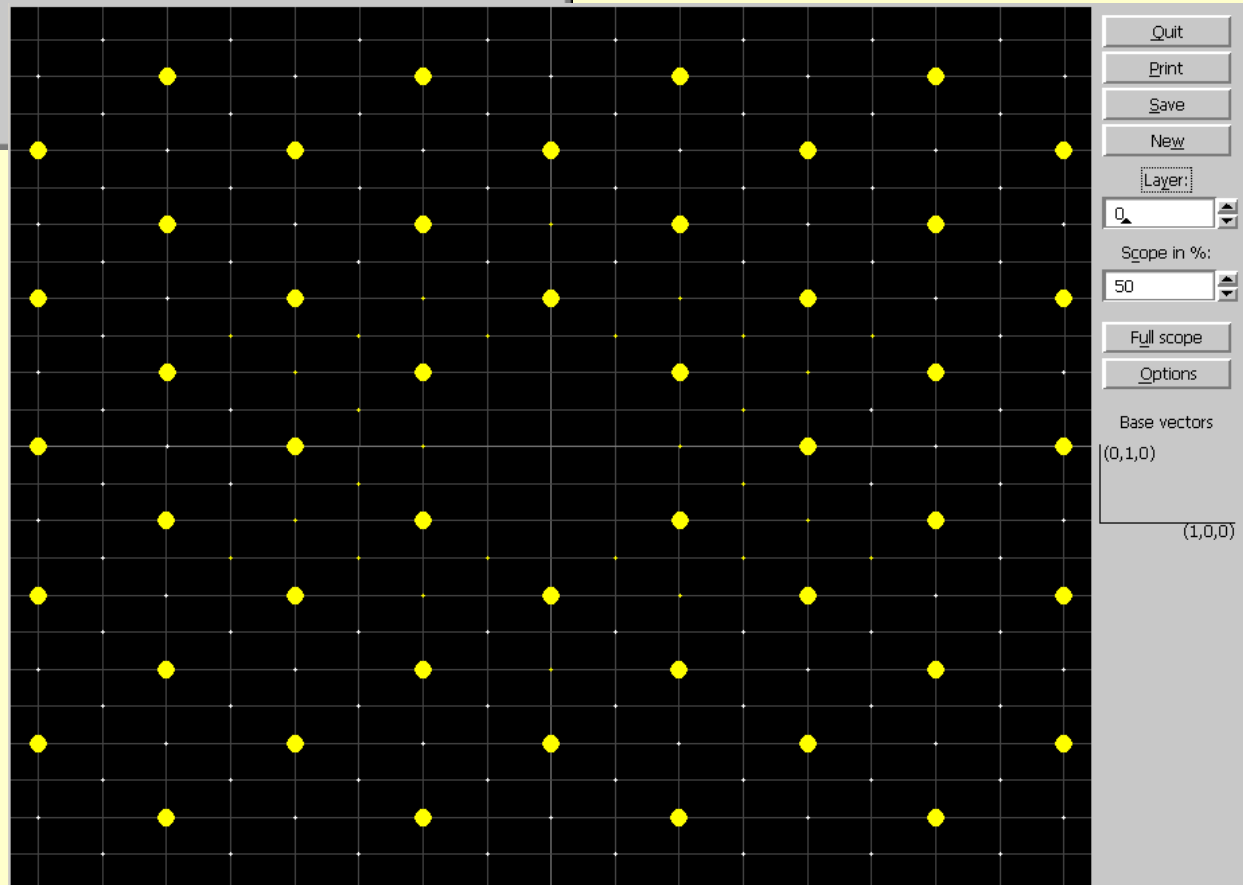
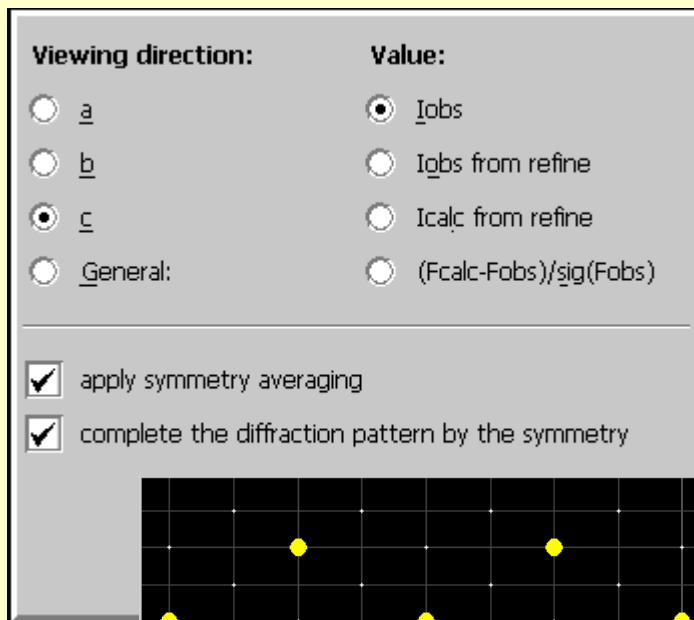
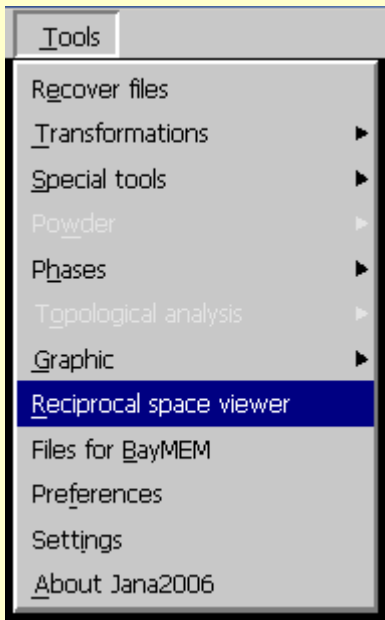
Do you want to accept the twinning matrix?

Yes

No

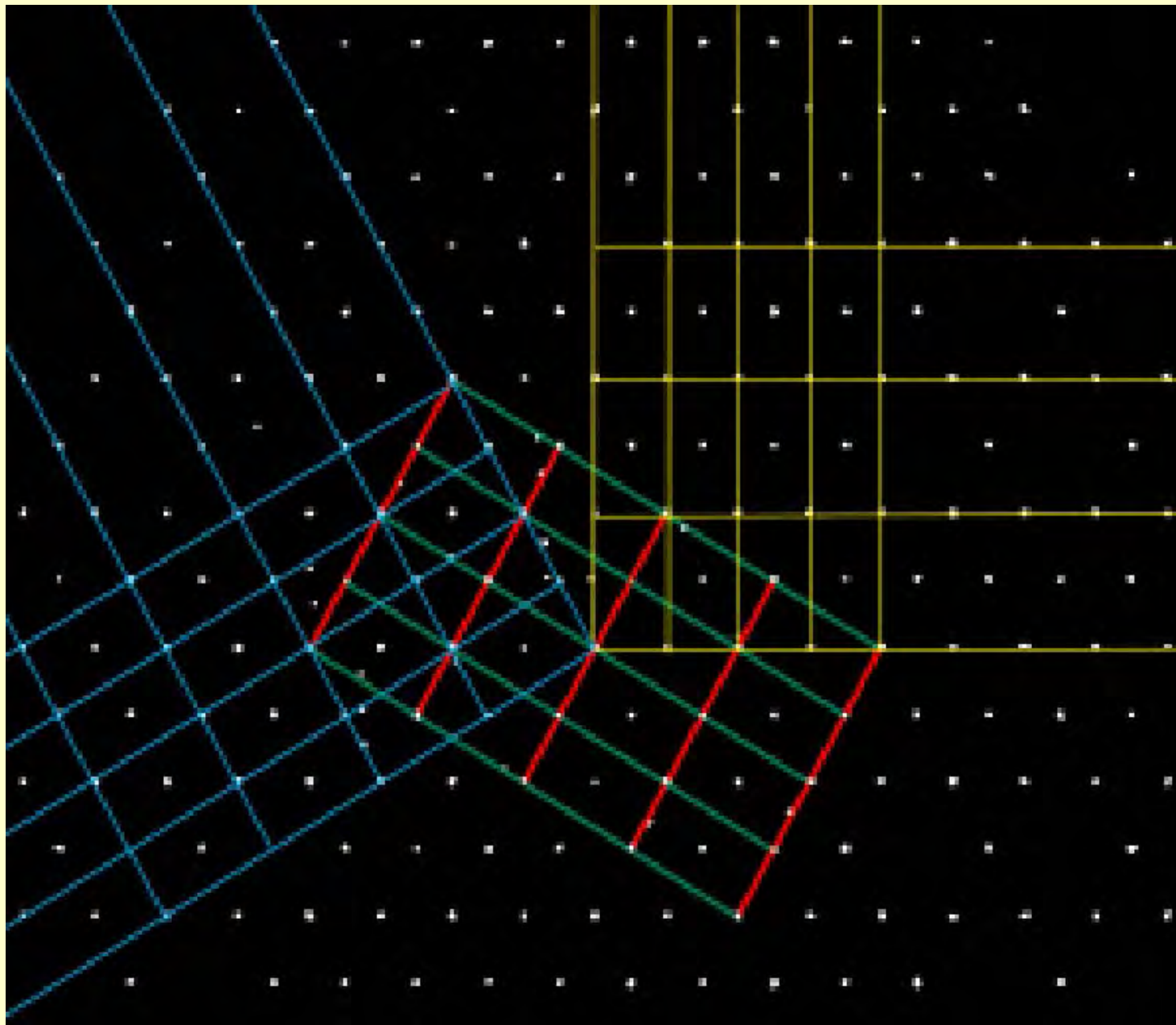
Twinning matrices

Attempts to solve structure fail!!



This will start Jana2006 to show Reciprocal space viewer.

Can we use four times larger reciprocal cell + three-fold twinning?



Transformation

Tools

- Recover files
- Transformations**
 - Cell transformation
 - Change modulation vector
 - Origin shift transform
 - Go to subgroup structure
 - Go to supercell structure
 - Go to average 3d structure
- Special tools
- Powder
- Phases
- Topological analysis
- Graphic
- Reciprocal space viewer
- Files for BayMEM
- Preferences
- Settings
- About Jana2006

Transformed cell parameters - Volume

10.9139 18.9034 8.8226 90.000 90.000 90.000 1820.2

Back

Cumulative matrix

a' = 1.000*a + 0.000*b + 0.000*c
b' = 0.000*a + 1.000*b + 0.000*c
c' = 0.000*a + 0.000*b + 1.000*c

Forward

Transform:

to the reduced cell to those from data collection

Transformation matrix

a' =	1/2	*a+	0	*b+	0	*c
b' =	0	*a+	1/2	*b+	0	*c
c' =	0	*a+	0	*b+	1	*c

Set unit matrix Set to zeros

Esc Ok

discard changes

rewrite the old structure

create a new one

Ok

Reflections I < *sig(I) will be sorted as unobserved

Note: this number is not interpreted by REFINE

Import statistics - obs/all

7487/11131 reflections read from input file

7406/10248 reflections written to output file

81/883 reflections rejected as systematically extinct

Ok

Back

Next

Cancel

Summary of systematic extinctions

n(all) : 883, n(obs) : 81

Average(I/Sig(I)) : 1.12

List of the strongest absent reflections:

h	k	l	I	sig(I)	I/sig(I)
-1	1	0	20.3	0.7	29.0
0	1	0	17.9	0.8	23.5
0	-1	0	18.9	0.8	22.8
0	1	0	17.2	0.8	21.0
0	-1	0	16.8	0.8	20.8
0	1	0	15.5	0.8	19.9
0	1	0	16.8	0.9	19.3
-1	1	0	9.7	0.5	19.0
0	-1	0	16.7	0.9	18.0
-3	-1	0	14.4	0.8	18.0
0	-1	0	17.1	1.0	17.1
0	-1	0	15.9	0.9	16.8
0	1	0	15.6	0.9	16.8
0	1	0	15.6	0.9	16.4

Ok

Summary after averaging

Rint(obs/all) = 6.39/6.43 for 1057/1235 reflections
averaged from 7406/10248 reflections

Redundancy = 8.298

h(min) = 0, h(max) = 11

k(min) = -6, k(max) = 6

l(min) = 0, l(max) = 11

R(obs/all) from e.s.d. of I : 0.55/ 0.64

Ok

File Edit/View Run Parameters Tools

Start shell

Export structure to ▶

Structure ▶

Reflection file ▶ Import/modify the reflection file

Exit Make space group test

Create refinement reflection file

Select supercell

Cell	n*Volume
8.823 18.903 18.904 120.00 90.00 90.00	6*455.05
continue with the basic cell	

Select Laue symmetry

	Rint(obs/all)	#averaged	Redunda
<input type="radio"/> Triclinic -1	5.44/5.47	1478/1886	2.92
<input type="radio"/> Monoclinic-setting "a" 2/m	6.27/6.31	858/1048	5.255
<input type="radio"/> Monoclinic-setting "b" 2/m	6.12/6.16	805/1010	5.452
<input type="radio"/> Monoclinic-setting "c" 2/m	5.94/5.97	803/1006	5.474
<input checked="" type="radio"/> Orthorhombic mmm	6.45/6.48	479/589	9.35

Averages made from 4026/5507 reflections

Select space group

Space group	obs/all	ave(I/sig(I))
Pmcb	24/204	6.238/1.179
P2cb	24/204	6.238/1.179
Pmmb	17/105	7.296/1.753
P2mb	17/105	7.296/1.753
Pm21b	17/105	7.296/1.753
Pmnb	31/300	8.848/1.321
P21nb	31/300	8.848/1.321
Pmab	24/201	10.359/1.691
P21ab	24/201	10.359/1.691

Final step of the space group test

accept the space group in the standard setting:

Space group: Pnma

Cell parameters: 8.8226 5.457 9.4517 90 90 90

Transformation matrix: a' = 0.000*a + 0.000*b - 1.000*c
 b' = -1.000*a + 0.000*b + 0.000*c
 c' = 0.000*a + 1.000*b + 0.000*c

Summary after averaging

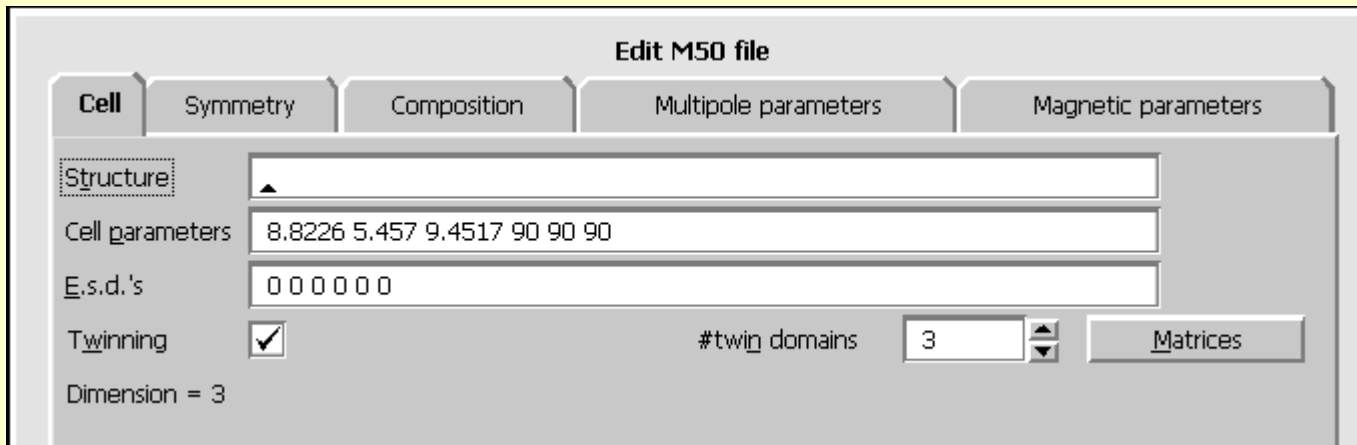
Rint(obs/all) = 6.18/6.20 for 650/743 reflections
 averaged from 3995/5207 reflections

Redundancy = 7.008

h(min) = 0, h(max) = 11
 k(min) = -6, k(max) = 6
 l(min) = 0, l(max) = 11

R(obs/all) from e.s.d. of I : 0.50/ 0.57

Ok



```

commcell 10.9165 10.9114 8.8226 90.001 90.024 119.946
trcell

```

```

  0.0000    0.5000   -0.5000
  0.0000    0.5000    0.5000
  1.0000    0.0000    0.0000

```

```
refblock Block1
```

```
sourcefile CsLiS04.hkl
```

```
filedate 23/01/2008 filetime 10:46:40
```

```
difcode 5 correspond 1 corrlp -1 corrab
```

```
lambda 0.71073 radtype 1 polarization 1
```

```
monangle 6.0821 perfmono 0.5
```

```
nref 11131 ndim95 3 nlines 22262 twidth
```

```
cell 10.9165 10.9114 8.8226 90.001 90.0
```

```
ormat
```

```
  0.071904  -0.022060   0.042037
 -0.045981  -0.092164  -0.055632
  0.062385   0.046966  -0.089360

```

```
end
```

```
Data Block1
```

```
datblock Block1
```

```
nref 743 obslim 3 norefitems 1 diffscals 1 dataave 1 scalelim 10
```

```
indslowest 3 indfastest 1 addcentrsymm 0 sigimethod 1 multave 1
```

```
flimprint 5 flimcull -1
```

```
lambda 0.71073 radtype 1 dattype 1 lpfactor 1 monangle 6.082 perfmono 0.5
```

```
datcolltemp 293
```

```
end
```

```
Data Block1
```

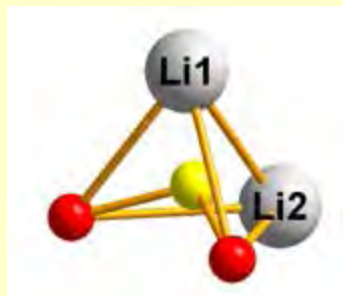
2	0	0	21338.2	51.8	1	0	1	0.0000
4	0	0	120500.5	371.6	1	0	1	0.0000
6	0	0	29054.0	94.2	1	0	1	0.0000
8	0	0	19811.9	131.8	1	0	1	0.0000
10	0	0	14985.7	133.1	1	0	1	0.0000
2	1	0	1491.4	9.5	1	0	1	0.0000
4	1	0	8.6	5.6	1	0	1	0.0000
6	1	0	2380.5	20.9	1	0	1	0.0000
8	1	0	-1.1	27.3	1	0	1	0.0000
10	1	0	272.2	29.4	1	0	1	0.0000
0	2	0	115151.2	357.3	1	0	1	0.0000

M95 with all
transformations
cumulated

M90 should contain three domains: 1,2,3

Solution with Superflip

Correction of false Li



Final refinement: $R \sim 2.5\%$

