Recipros Wokshop

Paris, June 24th, 2019

Twinning in Chemical Crystallography

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http://shelx.uni-ac.gwdg.de/~rherbst/twin.html

Outline

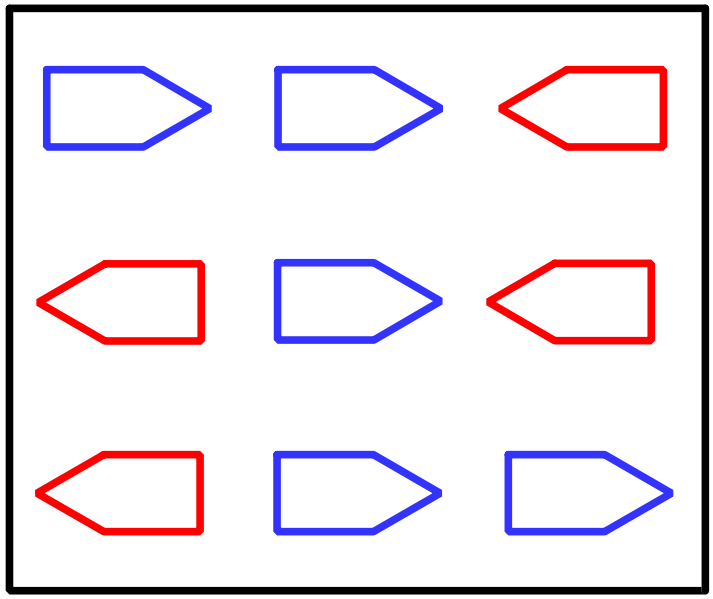
- Theory
  - Definition
  - Classification
  - Test for Merohedral Twinning
  - Solution
  - Refinement
  - Warning Signs
- Examples

Definition

"Twins are regular aggregates consisting of individual crystals of the same species joined together in some definite mutual orientation."

from: "Fundamentals of Crystallography", edited by C. Giacovazzo, Union of Crystallography, Oxford University Press 2nd Edn. 2002.

Simple example for a two-dimensional twin:



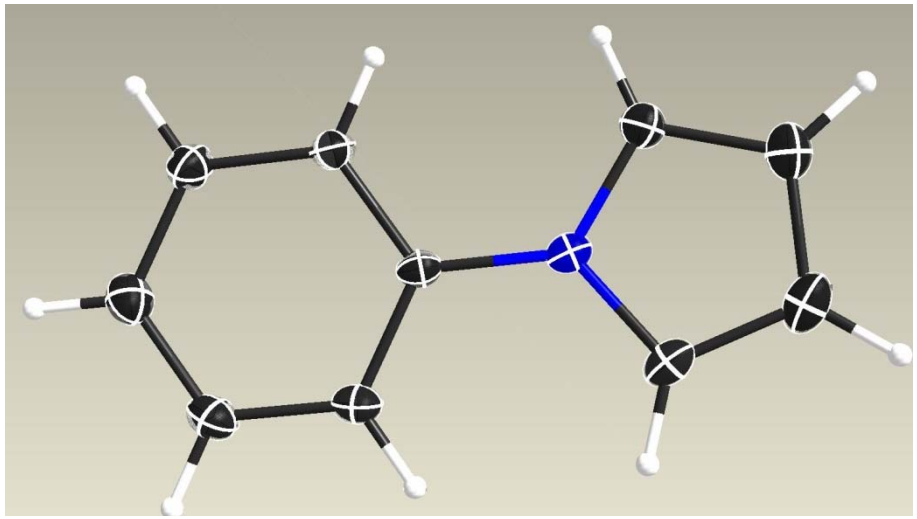
Twin Law: $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

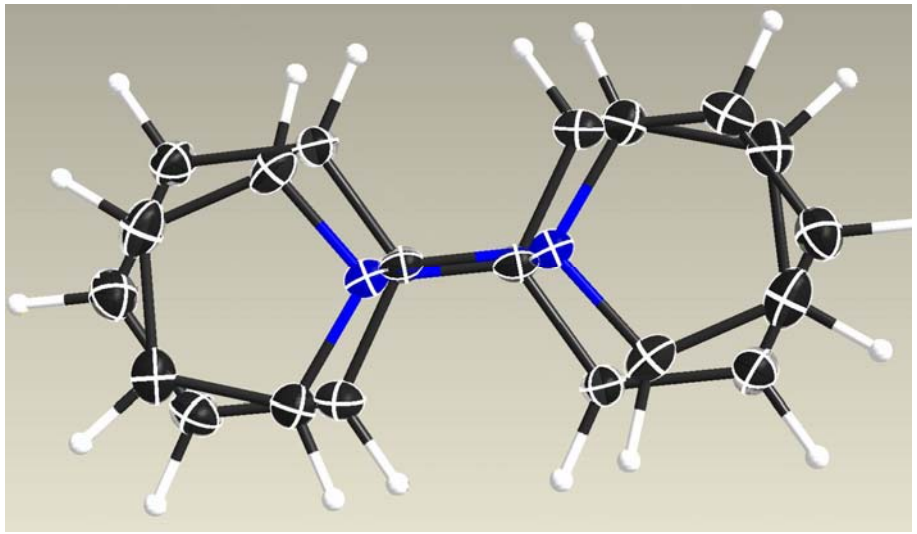
fractional contribution k_1 for twin domain 1: 5/9

fractional contribution k_2 for twin domain 2: 4/9

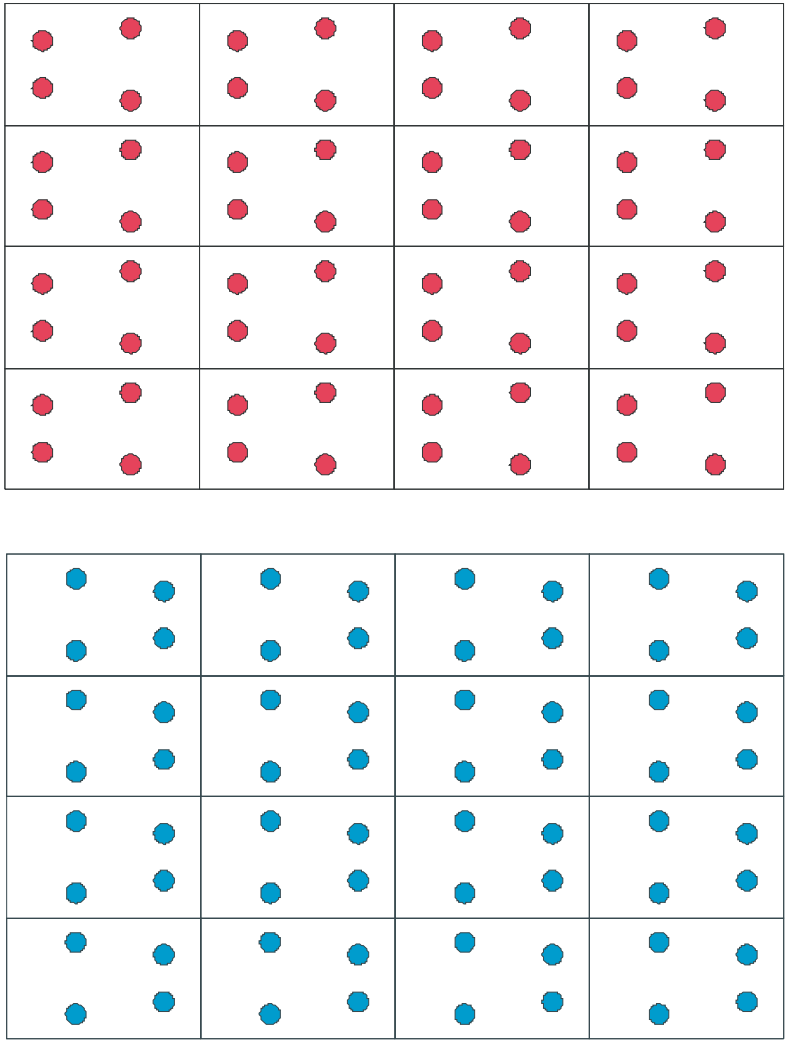
Disorder versus Twinning

A twinned structure can sometimes be mistaken for a disordered one. What is the difference between disorder and twinning?

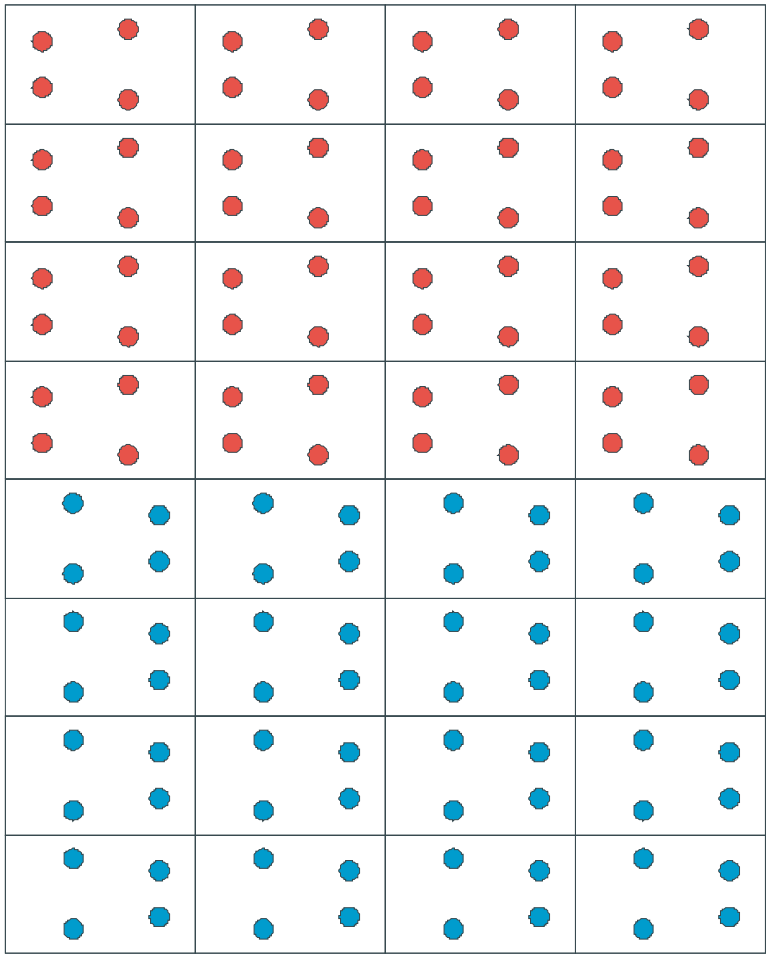




Disorder versus Twinning

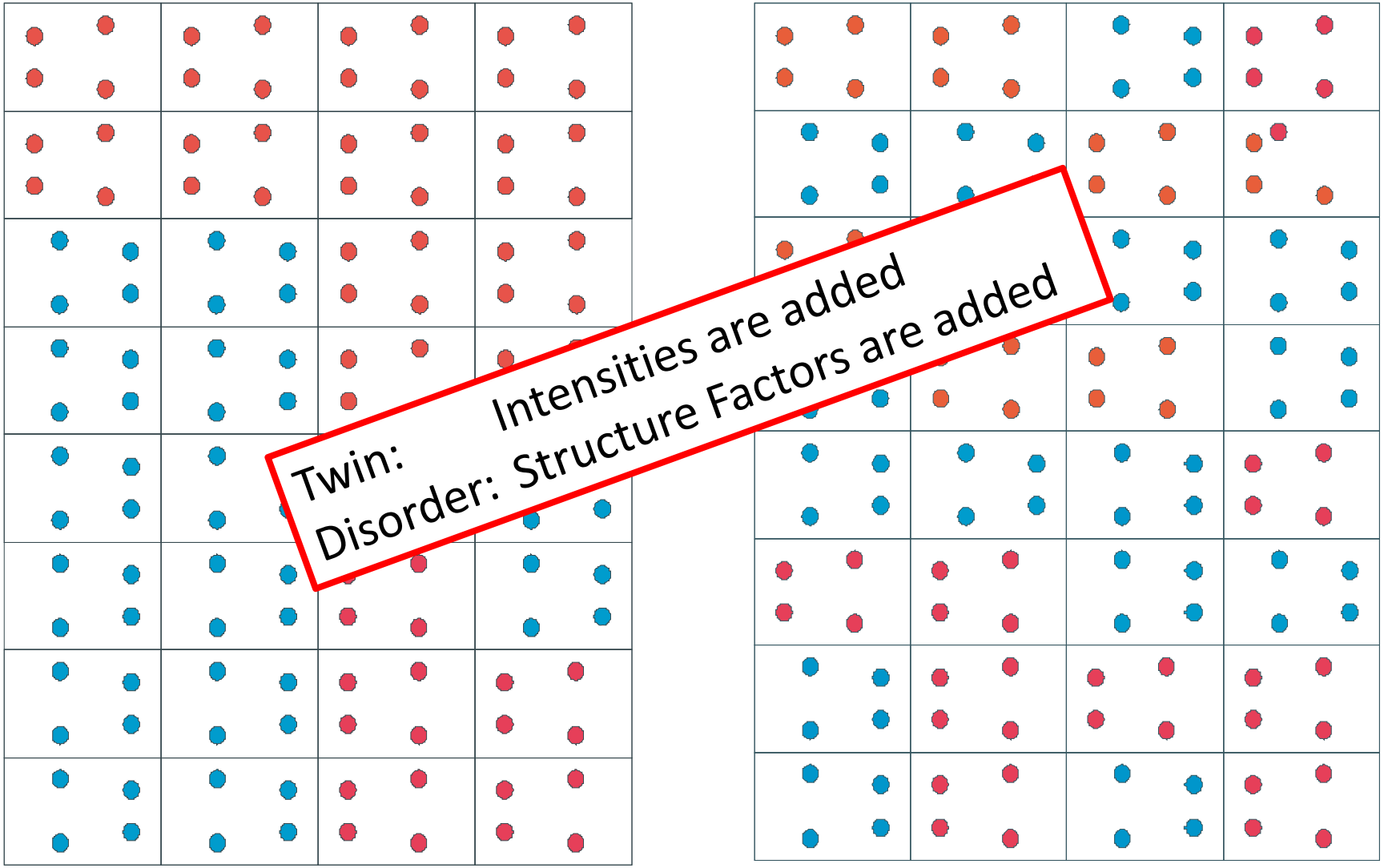


Disorder versus Twinning



Twinning may occur when a unit cell (or a supercell) – ignoring the content – has higher symmetry than implied by the space group of the crystal structure

Disorder versus Twinning



Four Kinds of Twins (I)

1. Twinning by merohedry

   Twin operator: symmetry operator of the crystal system but not of the point group of the crystal

   1.1. racemic twin

   1.2. twin operator: not of the Laue group of the crystal

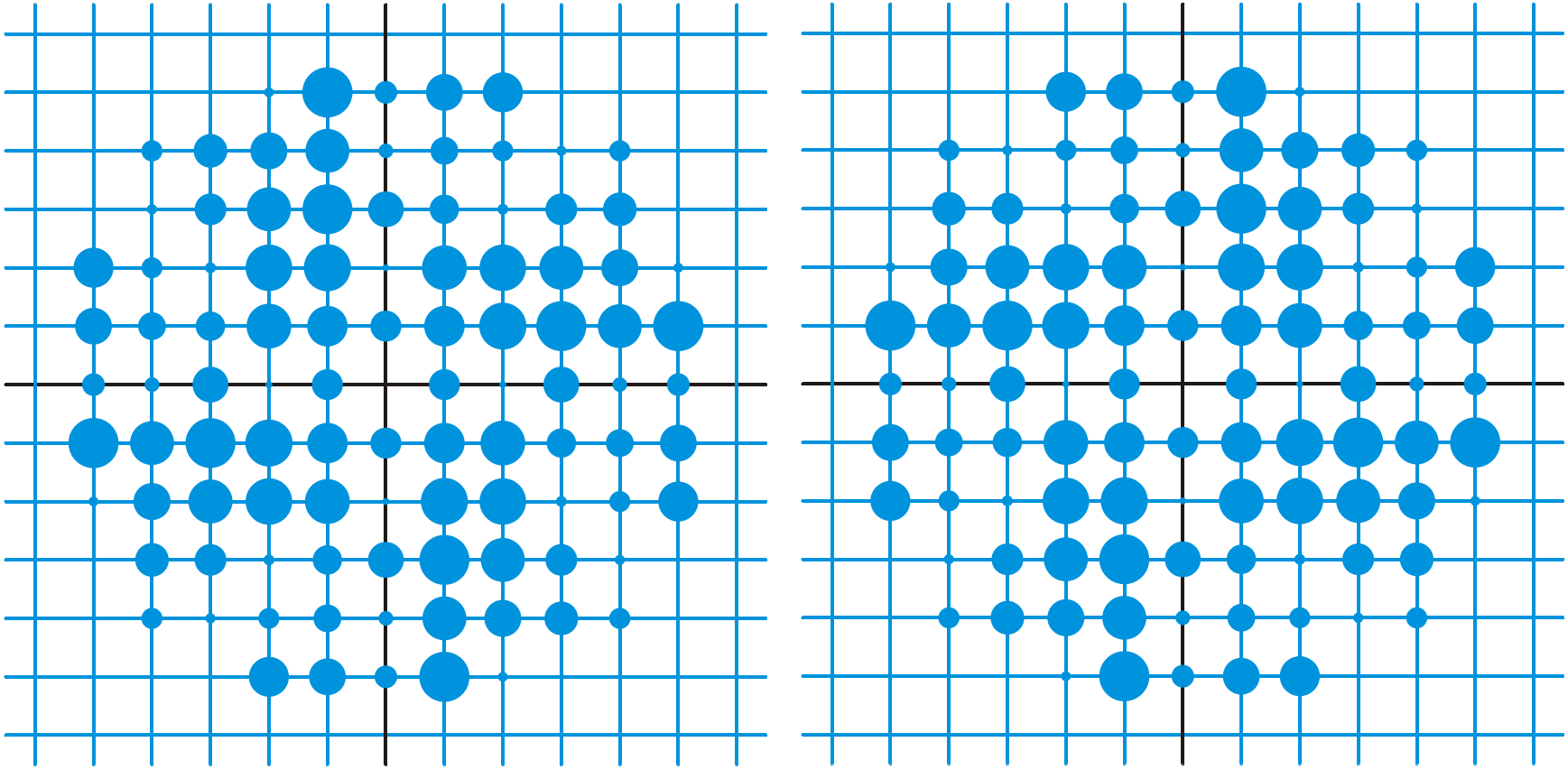
   - only in tetragonal, trigonal, hexagonal and cubic space groups
   - exact overlap of the reciprocal lattices
   - often low value for $<|E^2-1|>$
   - Laue group and space group determination may be difficult
   - structure solution may be difficult

2. Twinning by pseudo-merohedry

   Twin operator: belongs to a higher crystal system than the structure

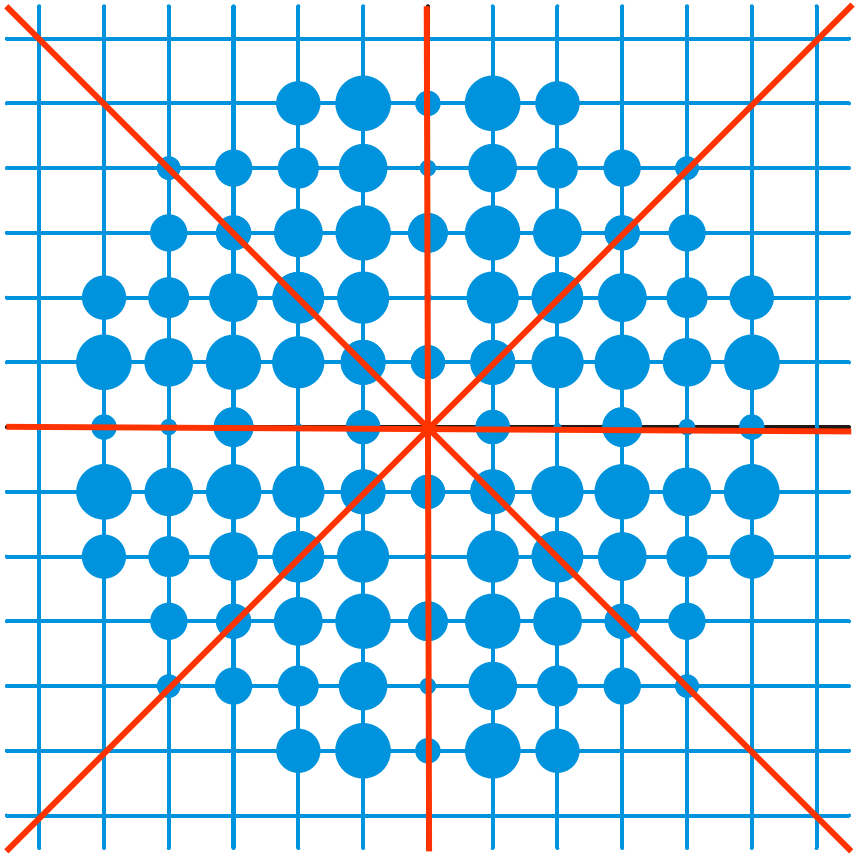
   - Metric symmetry higher than Laue symmetry

Reciprocal Space Plot l = 0



Twin Law

Additional non-crystallographic symmetry



Twin Law

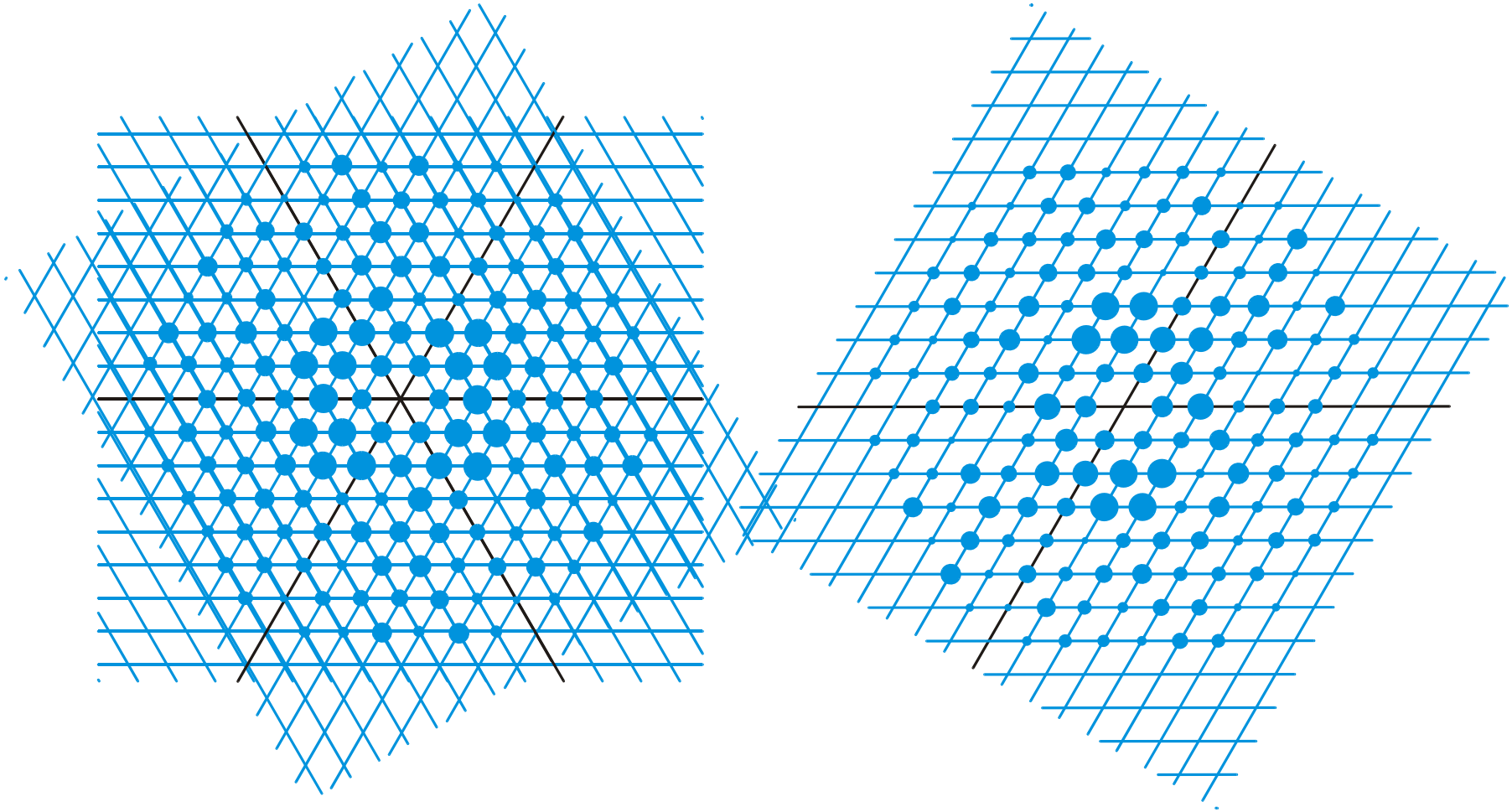
Matrix Notation

0	1	0	1	0	0	0	0	-1
-1	0	0	0	1	0	0	0	-1
0	-1	0	-1	0	0	0	0	-1
1	0	0	0	-1	0	0	0	-1
0	-1	0	-1	0	0	0	0	1
1	0	0	0	-1	0	0	0	1
0	1	0	1	0	0	0	0	1
-1	0	0	0	1	0	0	0	1

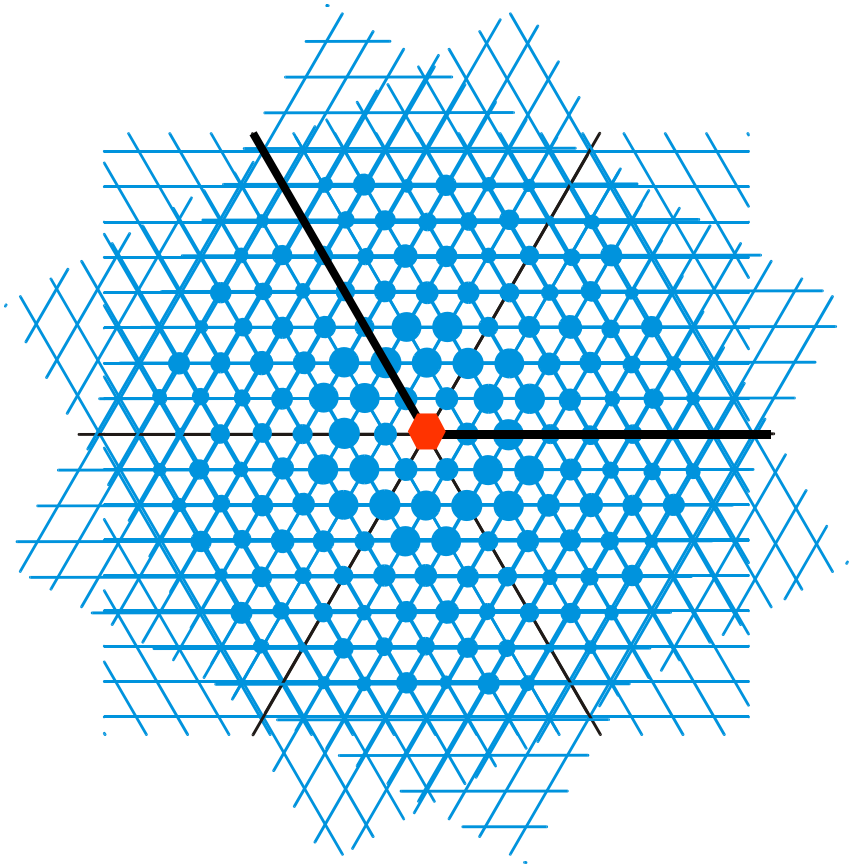
Merohedral Twin Laws

True Laue Group	Apparent	Twin Law								
4/m	4/mmm	0	1	0	1	0	0	0	0	-1
$\bar{3}$	$\bar{3}$1m	0	-1	0	-1	0	0	0	0	-1
$\bar{3}$	$\bar{3}$m1	0	1	0	1	0	0	0	0	-1
$\bar{3}$	6/m	-1	0	0	0	-1	0	0	0	1
$\bar{3}$	6/mmm	0	-1	0	-1	0	0	0	0	-1
		0	1	0	1	0	0	0	0	-1
		-1	0	0	0	-1	0	0	0	1
$\bar{3}$m1	6/mmm	-1	0	0	0	-1	0	0	0	1
$\bar{3}$1m	6/mmm	0	1	0	1	0	0	0	0	-1
6/m	6/mmm	0	1	0	1	0	0	0	0	-1
m$\bar{3}$	m$\bar{3}$m	0	1	0	1	0	0	0	0	-1

Reciprocal Space Plot k = 0



Twin Law



Four Kinds of Twins (II)

3.Twinning by reticular merohedry

e.g. obverse/reverse twinning in case of a rhombohedral crystal

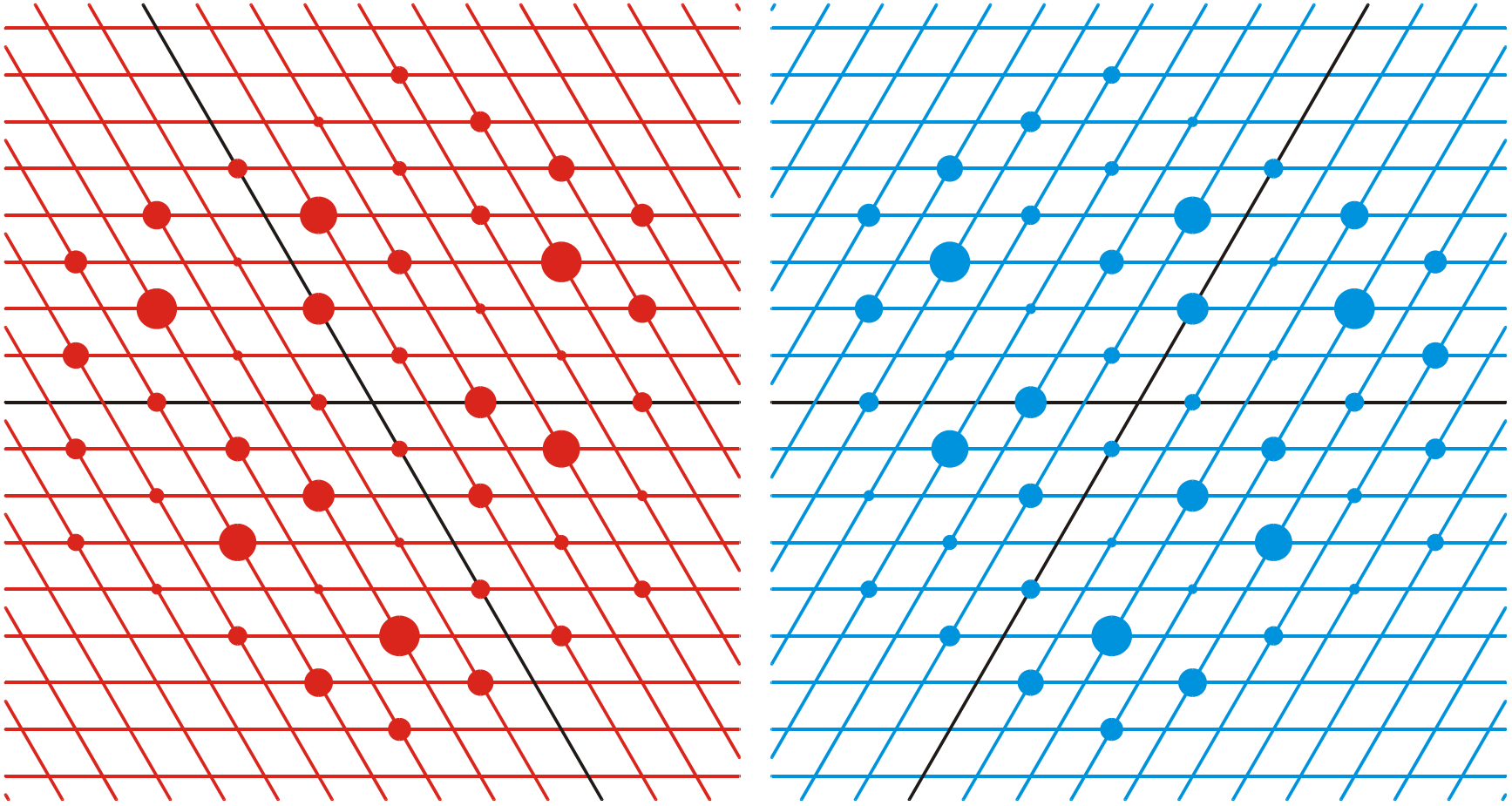
- detection of the lattice centring may be difficult
- structure solution not as difficult as for merohedral twins.

4. Non-merohedral twins

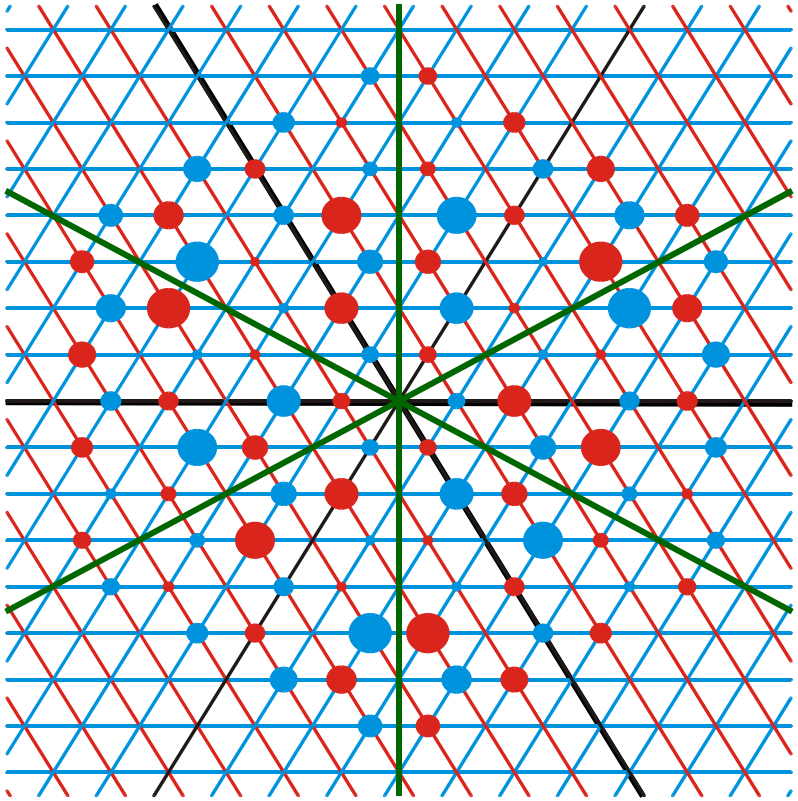
Twin operator: arbitrary operator, often rotation of 180°

- no exact overlap of the reciprocal lattices
- cell determination problems
- cell refinement problems
- some reflections sharp, others split
- data integration complicated (requires more than one orientation matrix)
- structure solution not as difficult as for merohedral twins

Reciprocal Space Plot l = 1



Twin Law



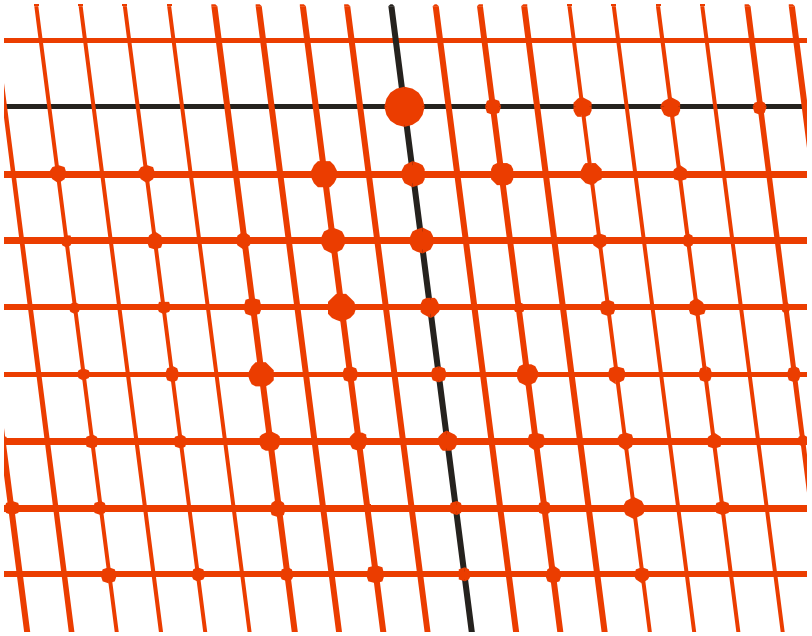
Obverse/ Reverse Twinning

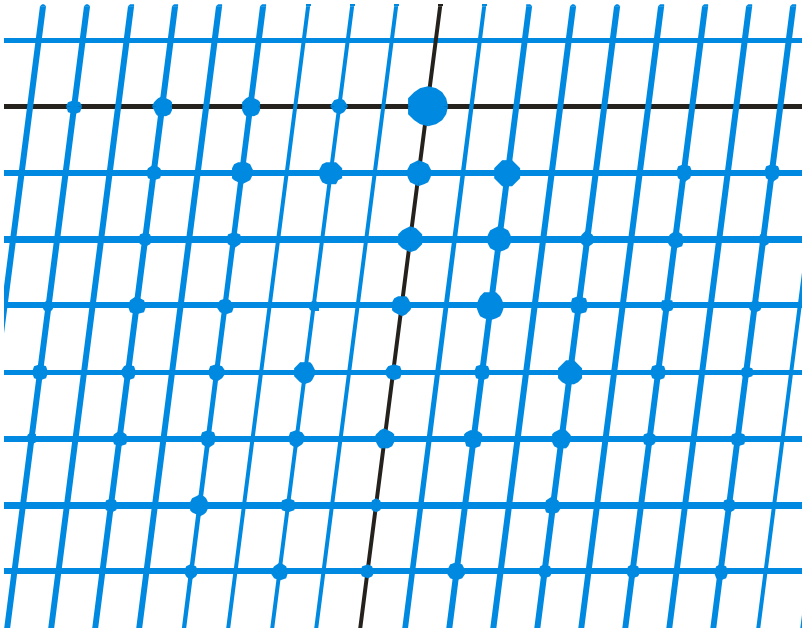
Systematic Absences:

Domain 1:
-h + k + l = 3n
Domain 2:
h - k + l = 3n

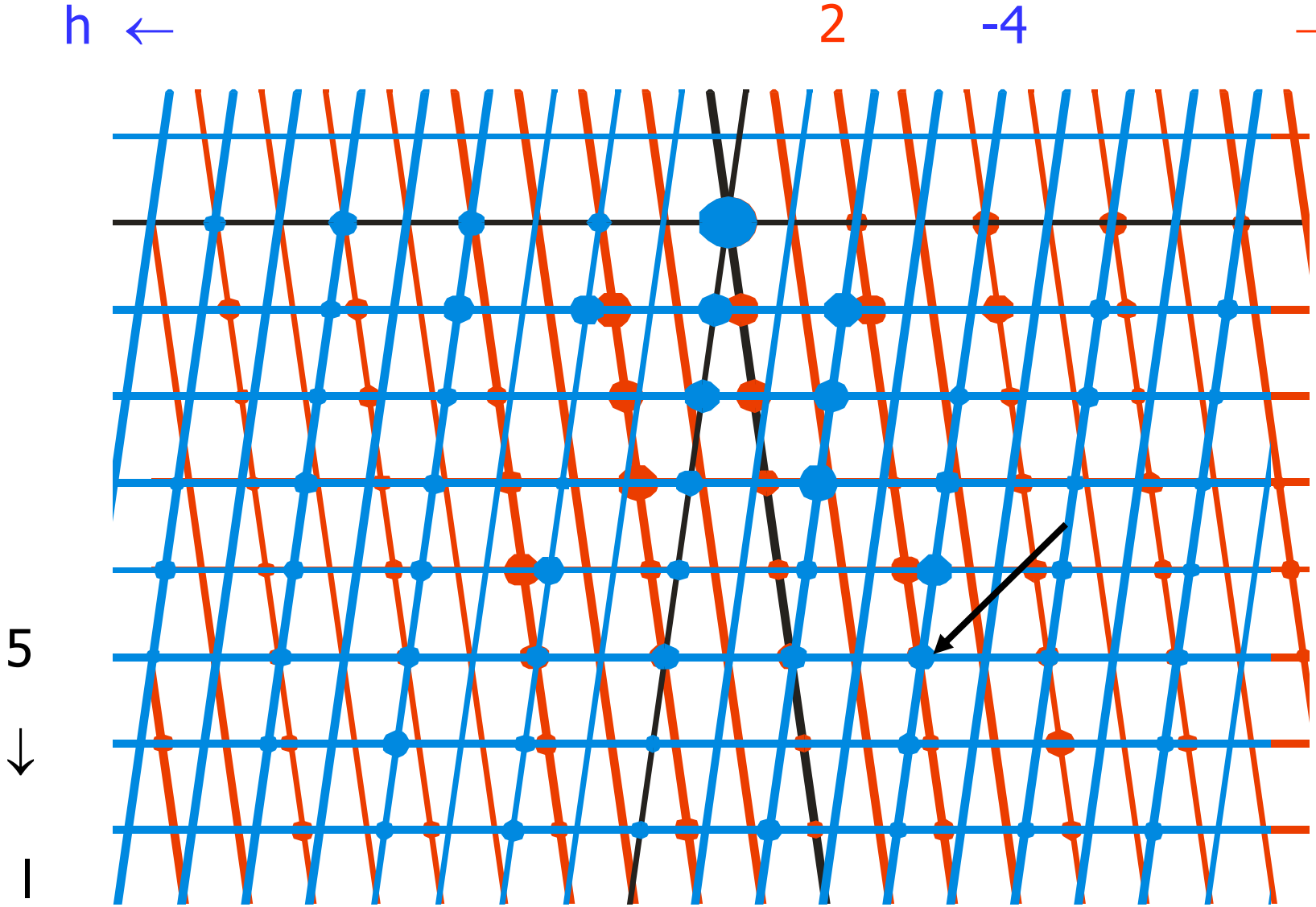
-h + k + l	h – k + l	domain
= 3n	≠ 3n	1
≠ 3n	= 3n	2
≠ 3n	≠ 3n	-
= 3n	= 3n	1 and 2

Reciprocal Space Plot k = 2



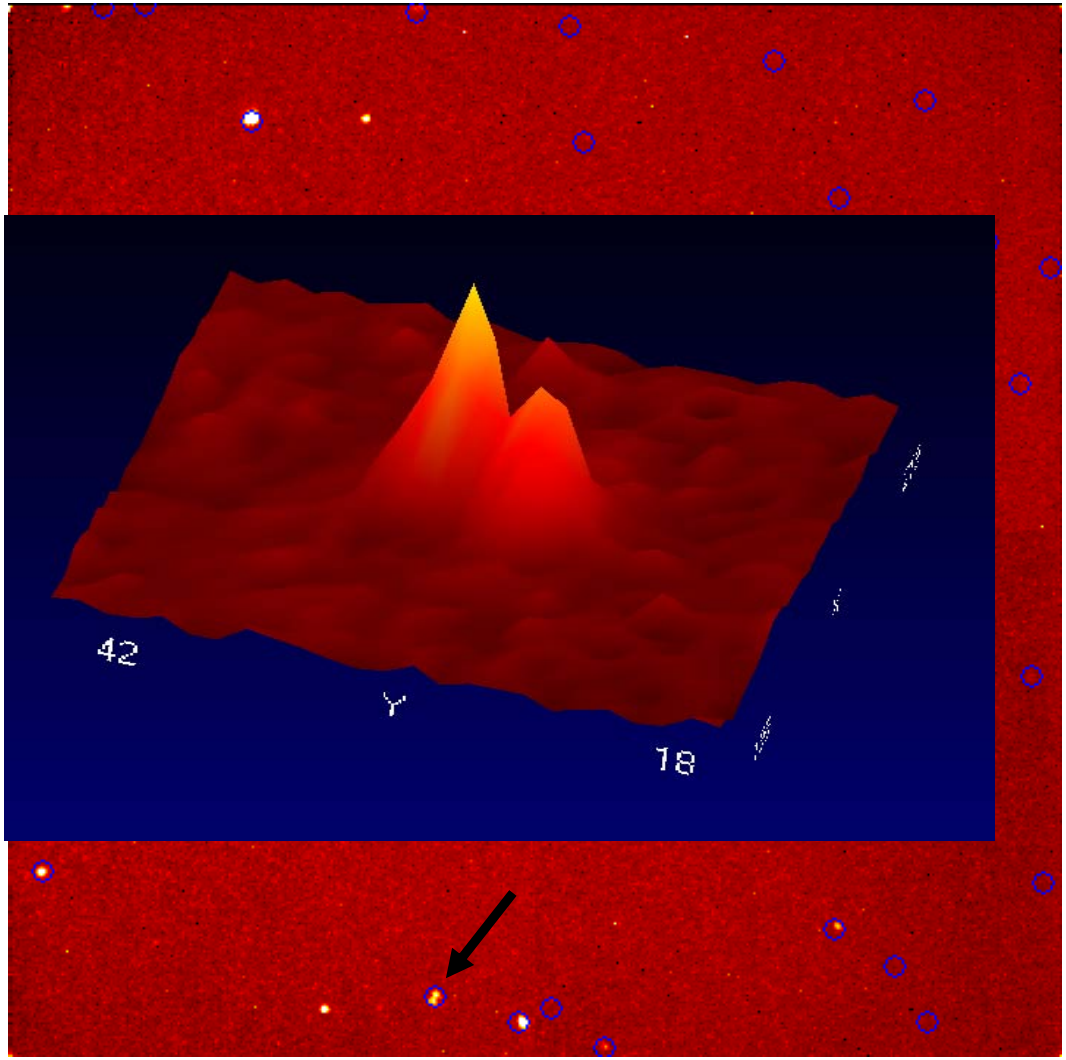


Reciprocal Space Plot k = 2



Reflection Pattern

- Problems with the cell determination
- Some reflections not indexed
- Some reflections very close to each other
- Some split reflections

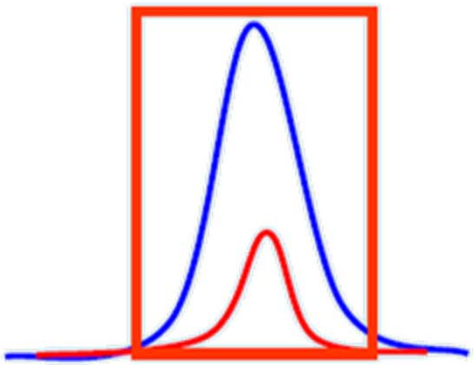


Cell Determination

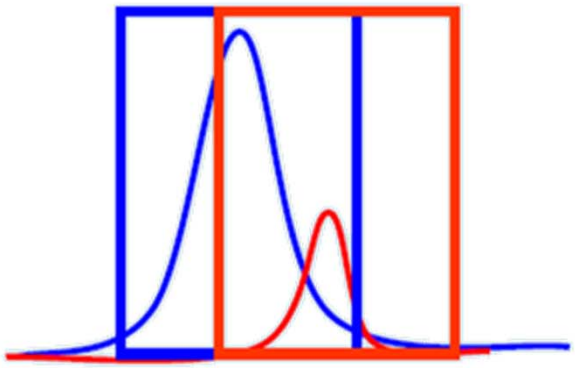
CELL_NOW

- Reads .spin, .p4p or .drx-files
- tries to find sets of reciprocal lattice planes that pass close to as many reflections as possible
- The cell may be rotated to locate further twin domains using only the reflections that have not yet been indexed
- Determination of the cell and the twin law in one program
- Writes a .p4p/.spin file for RLATT and SAINT for simultaneous integration of more than one domain
- Determination of very weak domains possible

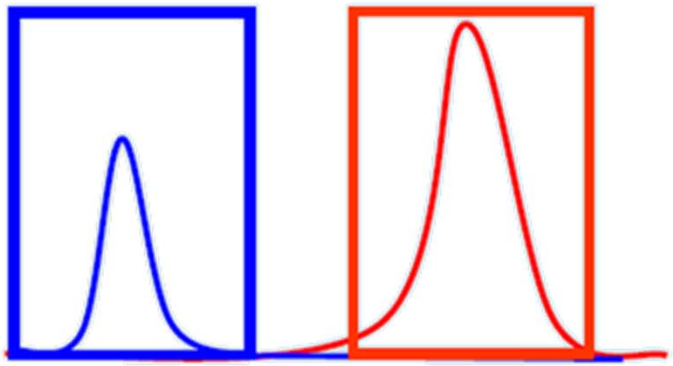
Integration



exact
overlaps



partial
overlaps



non-
overlaps

TWINABS

Twin raw file : *.mul, similar to HKLF5 format

➔ Special version of SADABS: TWINABS

- Scaling and absorption correction
- Merging
- Output
  - detwinned data file (HKLF4) for structure solution
  - HKLF5 file for the refinement:

h'	k'	l'	F^2	$\sigma(F^2)$	-2
h	k	l	F^2	$\sigma(F^2)$	1

with h', k', l' generated by the second orientation matrix

M.Sevvana, M. Ruf, I. Uson, G. M. Sheldrick, R. Herbst-Irmer, *Acta Crystallogr.* **2019**, *D75*, submitted.

Merging

h	*k*	*l*	component	(assuming point group mmm)
1	-2	3	 1	} equivalent singles (non-overlaps)
-1	-2	-3	 1	
-1	-2	-3	 2	— not equivalent to the above singles
-1	-2	-3	..... -2	
2	0	-4	 1	} equivalent groups
1	2	-3	..... -2	
-2	0	-4	 1	
4	1	1	..... -2	} not equivalent to the other groups shown here
1	-2	-3	..... -3	
-1	1	2	 1	

SHELX HKLF 5 format:

- a group of overlapping reflections is defined by negative component numbers for all but the last reflection in the group.
- For scaling purposes the component numbers MUST match.

Tests for Twinning: XPREP

[M] Test for MEROHEDRAL TWINNING

Comparing true/apparent Laue groups. 0.05 < BASF < 0.45 indicates partial merohedral twinning. BASF ca. 0.5 and a low <|E^2-1|> (0.968[C] or 0.736[NC]) are normal) suggests perfect merohedral twinning. For a twin, R(int) should be low for the true Laue group and low/medium for the apparent Laue group.

Test for Merohedral Twinning

[1] -3 / -31m:
R(int) 0.039(801)/0.316(478), <|E^2-1|> 0.624/0.517
TWIN 0 -1 0 -1 0 0 0 0 -1 BASF 0.205 [C] or 0.124 [NC]

[2] -3 / -3m1:
R(int) 0.039(801)/0.406(444), <|E^2-1|> 0.624/0.525
TWIN 0 1 0 1 0 0 0 0 -1 BASF 0.113 [C] or 0.008 [NC]

[3] -3 / 6/m:
R(int) 0.039(801)/0.103(488), <|E^2-1|> 0.624/0.617
TWIN -1 0 0 0 -1 0 0 0 1 BASF 0.319 [C] or 0.269 [NC]

[4] -31m / 6/mmm:
R(int) 0.316(478)/0.097(228), <|E^2-1|> 0.517/0.523
TWIN -1 0 0 0 -1 0 0 0 1 BASF 0.346 [C] or 0.304 [NC]

[5] -3m1 / 6/mmm:
R(int) 0.406(444)/0.114(262), <|E^2-1|> 0.525/0.527
TWIN -1 0 0 0 -1 0 0 0 1 BASF 0.360 [C] or 0.322 [NC]

[6] 6/m / 6/mmm:
R(int) 0.103(488)/0.478(218), <|E^2-1|> 0.617/0.516
TWIN 0 1 0 1 0 0 0 0 -1 BASF 0.178 [C] or 0.090 [NC]

Obverse/ Reverse Twinning

	P	A	B	C	I	F	Obv	Rev	All
N	0	24004	23981	24079	23964	36032	31915	31944	147964
N I>3σ	0	6903	6913	7404	6931	10610	3990	6064	13592
<I>	0.0	80.3	81.4	84.3	80.8	82.0	16.8	66.2	81.0
<I/σ>	0.0	4.1	4.1	4.3	4.1	4.1	1.6	3.4	4.0

Obverse/reverse test for trigonal/hexagonal lattice
Mean I: obv only 145.5, rev only 28.0, neither obv nor rev 4.8
Preparing dataset for refinement with BASF 0.161 and TWIN -1 0 0 0 -1 0 0 0 1
Reflections absent for both components will be removed

Structure Solution

- For small molecules, normal direct methods are often able to solve twinned structures even for perfect twins, provided that the correct space group is used.
- SHELXT often fails!
- SHELXD can use the twin law and the fractional contribution
- Detwinning

$$J_1 = (1\text{-}k_2)\, I_1 + k_2\, I_2 \qquad J_2 = (1\text{-}k_2)\, I_2 + k_2\, I_1$$

$$I_1 = \frac{(1 - k_2)\, J_1 - k_2\, J_2}{1 - 2\, k_2} \qquad I_2 = \frac{(1 - k_2)\, J_2 - k_2\, J_1}{1 - 2\, k_2}$$

G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3-8.
G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122.

Twin Refinement in SHELXL

Method of Pratt, Coyle and Ibers:

$$(F_c^2)_* = osf^2 \sum_{m=1}^{n} k_m F^2{}_{c_m}$$

osf = overall scale factor
k_m = fractional contribution of twin domain m
F_{cm} = F_c of twin domain m

$$1 = \sum_{m=1}^{n} k_m$$

$$k_1 = 1 - \sum_{m=2}^{n} k_m$$

(n-1) of the fractional contributions can be refined.

```
TWIN  r11 r12 r13  r21 r22 r23  r31 r32 r33  n
BASF  k2  k3  ...  kn
```

or

```
MERG  0
BASF  k2  k3  ...  kn
HKLF  5
```


G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3-8.
C. S. Pratt, B. A. Coyle, J. A. Ibers, *J. Chem. Soc.* **1971**, 2146-2151.
G. B. Jameson, *Acta Crystallogr.* **1982**, *A38*, 817-820.

Absolute Structure

Flack absolute structure parameter x:

$(F_c^2)^* = (1\text{-}x)\ F_{c\ hkl}^2 + x\ F_{c\ -h-k-l}^2$

- x = 0 → correct absolute structure
- x = 1 → wrong absolute structure

  Inversion of the structure:

```
MOVE  1  1  1  -1
```

  exceptions for some space groups like Fdd2, $I4_1$ etc.

  sometimes it is necessary to change also the space group, e.g. $P3_1 \rightarrow P3_2$

- 0 < x < 1 →

```
** Possible racemic twinning or wrong absolute structure - try TWIN refinement **
```

```
TWIN  -1  0  0  0  -1  0  0  0  -1  2
BASF  k2
```

=

```
TWIN
BASF  k2
```

H. D. Flack, *Acta Crystallogr.* **1983**, *A39*, 876-881.

Parsons‘ Quotients

$$Q_{(hkl)} = \frac{I(hkl) - I(-h-k-l)}{I(hkl) + I(-h-k-l)}$$

$$Q_{model}(hkl) = (1 - 2\,x)\,Q_{single}(hkl)$$

Cancellation of errors that both effect I(hkl) and I(-h-k-l)

$\Rightarrow$

lower standard uncertainties

Parsons, S., Flack, H., Wagner, T., *Acta Crystallogr.* **2013**, *B69*, 249-259.

Additional Twinning by Inversion

Pseudo-merohedral twinning (HKLF4):

```
TWIN   r11  r12  r13   r21  r22  r23   r31  r32  r33   n
BASF   k2   k3   ...   kn
```

```
TWIN   r11  r12  r13   r21  r22  r23   r31  r32  r33   -2n
BASF   k2   k3   ...   kn  ... 2kn
```

```
Least-squares cycle  10   ...
   N      value        esd     shift/esd  parameter
   1     0.26170     0.00072      0.000    OSF
   2     0.08758     0.00919     -0.001    FVAR  2
   3     0.00418     0.02655     -0.009    BASF  1
   4     0.69759     0.04263     -0.001    BASF  2
   5     0.33588     0.02654      0.009    BASF  3
```

= k_2 merohedral
= k_3 inversion
= k_4 merohedral + inversion

Additional Twinning by Inversion

BASF k2 k3 k4
HKLF 5

Non-merohedral Twins

without twinning by inversion:

0	16	-7	9.56	3.94	-2
0	0	-25	9.56	3.94	1
1	0	-25	2.87	3.16	1
2	0	-25	-0.05	3.12	1
-1	1	-25	1.28	2.53	1
0	1	-25	0.86	2.23	1

HKLF5

with twinning by inversion:

0	-16	7	9.56	3.94	-4	= k_4
0	0	25	9.56	3.94	-3	= k_3
0	16	-7	9.56	3.94	-2	= k_2
0	0	-25	9.56	3.94	1	
-1	0	25	2.87	3.16	-3	
1	0	-25	2.87	3.16	1	
-2	0	25	-0.05	3.12	-3	
2	0	-25	-0.05	3.12	1	
1	-1	25	1.28	2.53	-3	
-1	1	-25	1.28	2.53	1	
0	-1	25	0.86	2.23	-3	
0	1	-25	0.86	2.23	1	

Warning Signs for Merohedral Twinning

- Metric symmetry higher than Laue symmetry
- R_{int} for the higher symmetry Laue group only slightly higher than for the lower symmetry one
- Different R_{int} values for the higher symmetry Laue group for different crystals of the same compound
- Mean value for $|E^2 - 1| << 0.736$
- Apparent trigonal or hexagonal space group
- Systematic absences not consistent with any known space group
- No structure solution
- Patterson function physically impossible (for heavy atom structures)
- High R-Values

Warning Signs for Non-merohedral Twinning

- An unusually long axis
- Problems with cell refinement
- Some reflections sharp, others split
- K = mean(F_o^2)/mean(F_c^2) is systematically high for reflections with low intensity
- For all of the most disagreeable reflections $F_o >> F_c$.
- Strange residual density, which could not be resolved as solvent or disorder.

R. Herbst-Irmer, G. M. Sheldrick, Refinement of Twinned Structures with SHELXL97, *Acta Crystallog.* **1998**, *B54*, 443-449.

P. Müller, R. Herbst-Irmer, A. L. Spek, T. R. Schneider, M. R. Sawaya, Crystal Structure Refinement – A Crystallographer's Guide to SHELXL, Oxford University Press 2006

R. Herbst-Irmer, Twinning in Chemical Crystallography – A Practical Guide, *Z. Kristallogr.*, **2016**, *231*, 573-581.

Non-merohedral Twin: Example 1

Problems with cell determination

Reduced Unit Cells found:

Method: Difference Vectors
Score: 0.61
a=16.84Å, α=80.11°, V=13199Å³
b=17.37Å, β=89.40°
c=45.80Å, γ=89.63°

HKL histogram:
0.1: 58.8% (357/607)
0.2: 85.8% (521/607)
0.3: 99.3% (603/607)

Method: Fast Fourier Transform
Score: 0.57
a=16.85Å, α=88.31°, V=17238Å³
b=17.31Å, β=87.88°
c=59.17Å, γ=89.47°

HKL histogram:
0.1: 59.3% (360/607)
0.2: 87.1% (529/607)
0.3: 99.2% (602/607)

CELL_NOW – Output (I)

The following cells would appear to be plausible, but should be checked using XPREP because they are not necessarily the conventional cells.

FOM, % within 0.2, a..gamma, volume and lattice type for potential unit-cells:

1	1.000	74.5	13.475	16.839	15.568	90.15	107.79	89.63	3363.3	P
2	0.861	75.0	13.475	16.839	17.201	90.17	120.46	89.63	3364.3	P
3	0.300	71.5	17.201	16.839	26.906	89.66	120.41	90.17	6721.2	P
4	0.266	74.3	13.475	15.568	24.039	118.58	110.99	107.79	3362.6	P
5	0.265	74.3	13.475	15.568	24.106	118.24	111.48	107.79	3365.4	P
6	0.245	63.4	13.461	16.839	17.201	90.17	120.29	90.16	3366.7	P
7	0.241	62.3	13.461	16.839	15.601	89.65	107.86	90.16	3365.7	P
8	0.223	73.6	13.475	17.201	22.966	116.71	102.22	120.46	3366.0	P
9	0.208	73.0	13.475	17.201	22.901	117.03	101.72	120.46	3363.8	P
10	0.203	70.5	15.568	16.839	42.815	90.25	116.01	90.15	10086.3	P

CELL_NOW – Output (II)

Cell for domain 1: 13.475 16.839 15.568 90.15 107.79 89.63

Figure of merit: 0.607 %(0.1): 61.4 %(0.2): 74.5 %(0.3): 83.4

Orientation matrix: 0.00257307 0.01269653
0.03501589 0.05319037
-0.04789866 0.03950469

Cell for dom 839 15.5 9.63

Figure of me 1): 97.4 98.1

Orientation 241 0.00257112 -0.06422251
921 0.03481897 -0.01532198
631 -0.0480623 -0.01485831

Rotated from first domain by 179.8 degrees about
reciprocal axis 0.658 0.005 1.000 and real axis 0.999 0.001 1.000

Twin law to convert hkl from first to this domain (SHELXL TWIN matrix):

-0.206 -0.002 0.794
0.010 -1.000 -0.004
1.206 0.004 0.206

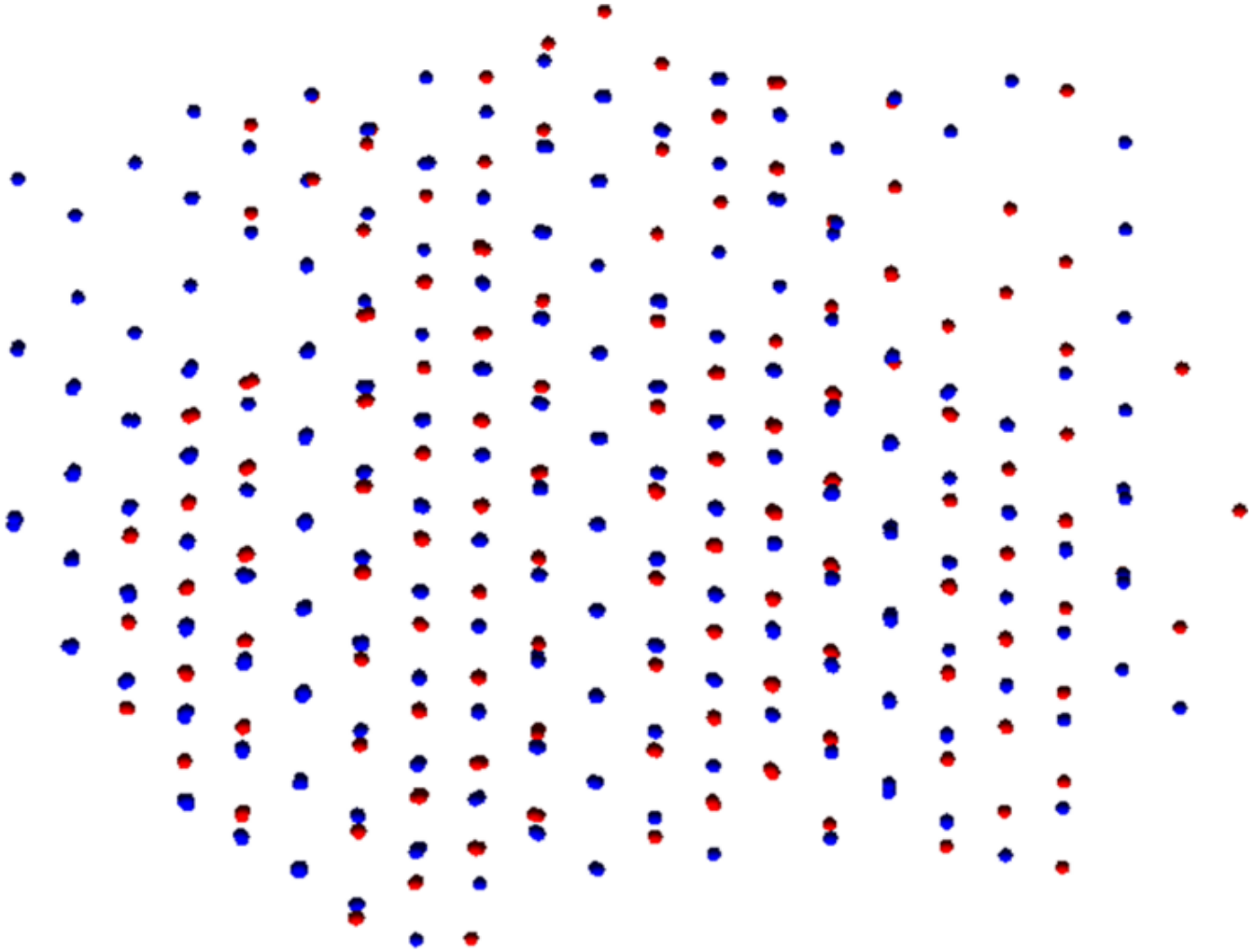
Twin Law

$$\begin{matrix} -\frac{1}{5} & 0 & -\frac{4}{5} \\ 0 & -1 & 0 \\ \frac{6}{5} & 0 & \frac{1}{5} \end{matrix}$$

Reflections with $h + l = 5n$ affected

Graphical Viewer: RLATT

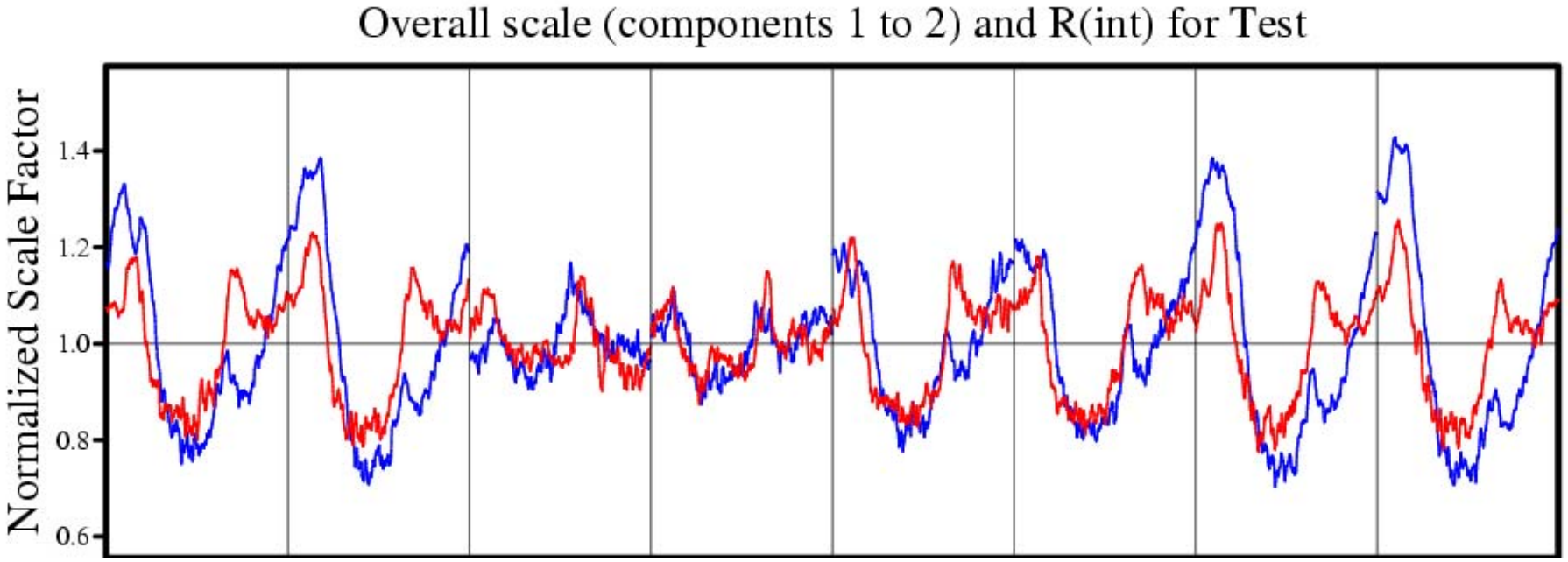
Manual separation of both domains



TWINABS

- SAINT: *.mul instead of *.raw

PART 1 - Refinement of parameters to model systematic errors
38394 data (4516 unique) involve component 1 only, mean I/σ 8.9
37893 data (4445 unique) involve component 2 only, mean I/σ 7.5
17805 data (2699 unique) involve 2 components, mean I/σ 10.1



TWINABS - Detwinning

Unique HKLF 4 data extracted from all observed data

Cycle	N(1)	Rint(1)	N(all)	Rint(all)	Twin fractions	
1	55397	0.0854	92756	0.0865	0.5673	0.4327
2	55470	0.0829	92986	0.0821	0.5665	0.4335
3	55470	0.0800	92986	0.0801	0.5667	0.4333
...						
20	55470	0.0791	92986	0.0794	0.5666	0.4334

N(1) and Rint(1) refer to singles and composites that include domain 1.

Rint = 0.0794 for all 92986 observations and
Rint = 0.0703 for all 52395 observations with I > 3sigma(I)

Rint is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions.

6256 Corrected reflections written to file twin4.hkl
Reflections merged according to point-group 2/m
HKLF 5 dataset constructed from all observations involving domain 1
8825 Corrected reflections written to file twin5.hkl
Reflections merged according to point-group 2/m
Single reflections that also occur in composites omitted

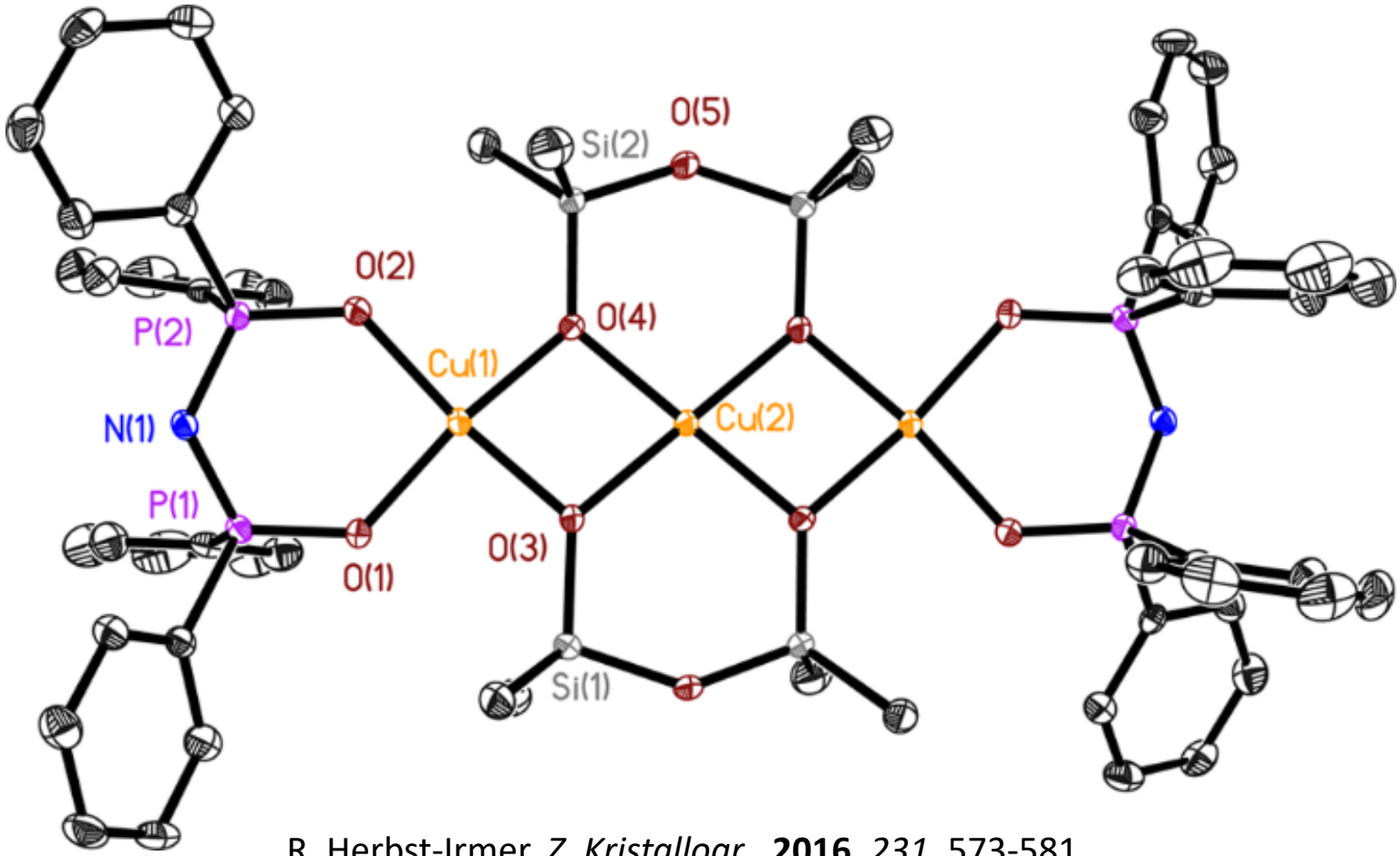
Excerpt of the HKLF 5 File

```
...
   8    0    0       60.5518      2.74215   1
   9    0    0       0.68562      3.61985   1
  -2    0   12       550.733      23.5314  -2
  10    0    0       550.733      23.5314   1
  11    0    0       1.28841      2.55409   1
  12    0    0       159.679      10.4910   1
  13    0    0       -3.1621      4.09349   1
  -3    0   17       247.541      20.5655  -2
  14    0    0       247.541      20.5655   1
   0    1    0       0.00957      0.12846   1
   1    1    0       1536.20      44.4858   1
   2    1    0       438.593      10.3440   1
   3    1    0       413.769      10.2007   1
   4    1    0       127.721      2.64687   1
  -1    1    6       124.490      2.52489  -2
  ...
```

- last column domain number.
- ‘1’ reflection domain 1
- -2’ reflection of domain 2
- it overlaps with the following reflection indicated by the minus sign.

Solution with HKLF4 Data

No problems in space group determination
structure solution and refinement



R. Herbst-Irmer, *Z. Kristallogr.*, **2016**, *231*, 573-581

Integration of the Major Domain

- No problems in space group determination: $P2_1/n$
- SHELXT finds all non-hydrogen atoms:

R1	Rweak	Alpha	Orientation	Space group	Flack_x	File	Formula
0.194	0.045	0.073	as input	P2(1)/n		sad_a	C66 N4 O10 P8 Cu3
0.181	0.017	0.048	as input	Pn	0.49	sad_b	C56 N15 O14 P8 Cu3
0.183	0.029	0.063	as input	P2(1)	0.48	sad_c	C55 N17 O12 P8 Cu3

- Refinement
  - R1 ($F > 4\sigma(F)$) = 11.05 %, wR2 = 34.56 %
  - Residual density: -1.18 – 3.20 e/Å^3
  - $K = < (F_o^2) > / < (F_c^2) > = 10.283$ for the reflections with the lowest intensity.
  - most disagreeable reflections F_o is always larger than F_c.
  - For all these reflections: $h + l = 5n$

h	k	l	F_o^2	F_c^2	Error/esd	$F_c/F_c(max)$	Res.(Å)
-4	9	9	31790.79	918.90	12.81	0.069	1.26
-2	3	7	22611.47	1530.54	11.46	0.090	2.08
-7	9	2	13366.48	198.69	10.85	0.032	1.34
-9	3	4	8506.96	97.35	8.73	0.023	1.45
…							

Platon: TwinRotMat

TwinRotMat

Analysis of Fo/Fc Data for Unaccounted (Non)Merohedral Twinning for: final

Cell: 0.71073 13.576 16.765 15.733 90.00 107.68 90.00 Spgr: P21/n

Criteria: DeltaI/SigmaI .GT. 4.0, DeltaTheta 0.10 Deg., NselMin = 50

N(refl) = 6007, N(sel… …1, CritT = 0.10

2-axis (1 0 -1)

(0.209 0.000 -0.7…

(0.000 -1.000 0.0…

(-1.209 0.000 -0.2…

…eq = 53

…ap = 1132

…SF = 0.37

…R =-0.049

1

0.209 0.000 -0.791

0.000 -1.000 0.000

-1.209 0.000 -0.209

BASF = 0.37

DEL-R = -0.049

PLATON-ay, 16 June 2019 - (230917)

Fc from Coordinates

final P 21/n R = 0.11

INPUT INSTRUCTIONS via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)

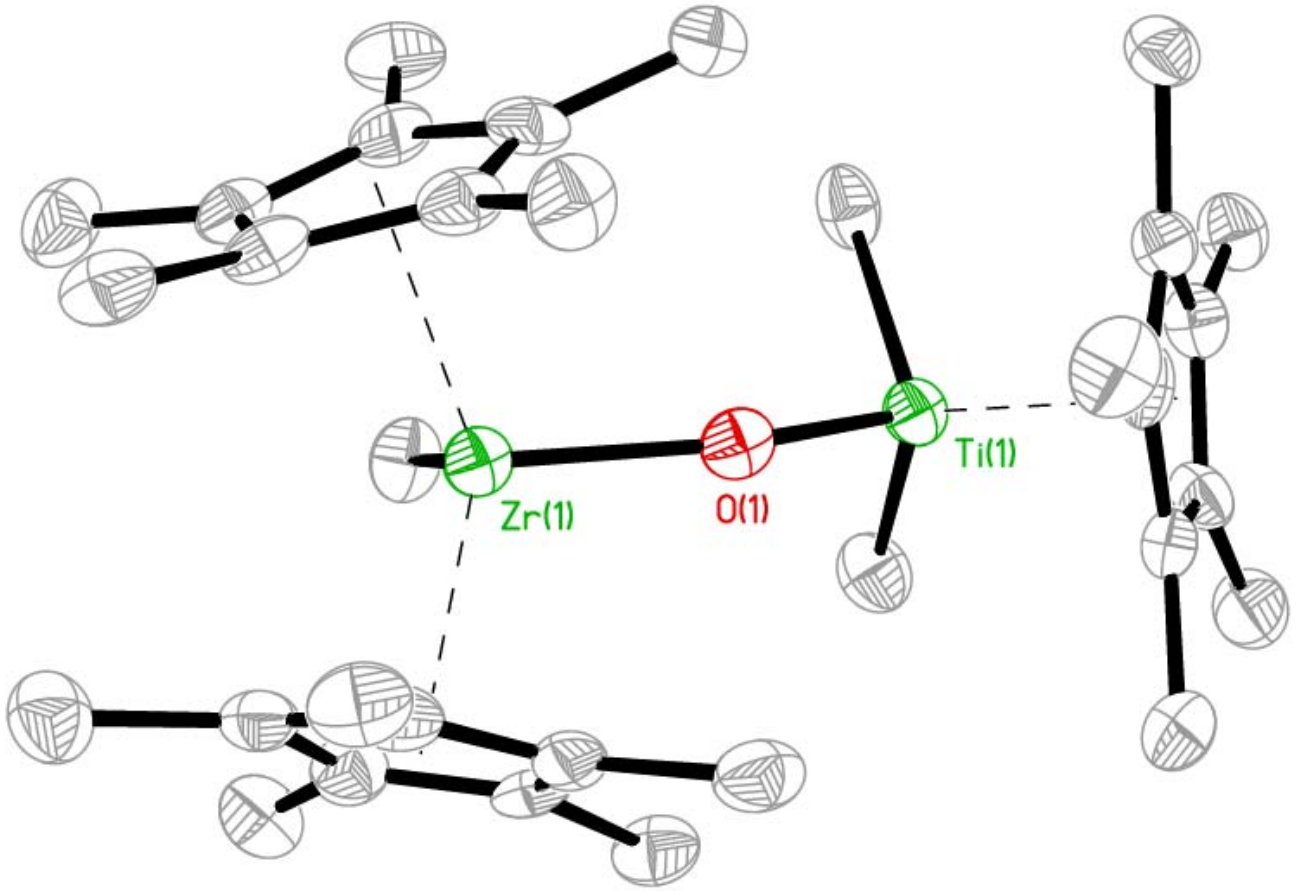
TwinRotM 25
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
FullListing
EPS-TwinLaw
DspTwinMat1
DspTwinMat2
DspTwinMat3
DspTwinMat4
EPS-TwinLat
Resolution>
IcalFromFCF

Zone-H,K,L
Up Down
RacemicTwin
SelectTMat1
SelectTMat2
SelectTMat3
SelectTMat4
HKLF5-CritI
HKLF5-CritT
HKLF5-Gener
End
Exit

Comparison of Different Refinements

	Ignoring twinning	TwinRotMat HKLF 5	detwinned HKLF4	twinned HKLF5
Data	6007	6007	6025	5897
k_2	-	0.327(3)	0.4347	0.431(9)
R1 (I> 2σ(I)	0.110	0.064	0.053	0.036
wR2 (all data)	0.348	0.213	0.130	0.083
R1 (after merging for Fourier)	0.122	0.073	0.070	0.048
K (weakest data)	10.271	3.104	6.712	1.066
s.u. (Cu-O) [Å]	0.0083 - 0.0089	0.0037 - 0.0041	0.0029 - 0.0031	0.0019 - 0.0021
Res. Dens. [eÅ^{-3}]	3.20	1.09	0.44	0.35

Non-merohedral Twin: Example 2



P. M. Gurubasavaraj, H. W. Roesky, P. M. Veeresha Sharma, R. B. Oswald, V. Dolle, R. Herbst-Irmer, and A. Pal, *Organomet.* **26**, 3346, 2007. (Cu data)

M.Sevvana, M. Ruf, I. Uson, G. M. Sheldrick, R. Herbst-Irmer, *Acta Crystallogr.* **2019**, *D75*, submitted. (Mo data, details of the twinning)

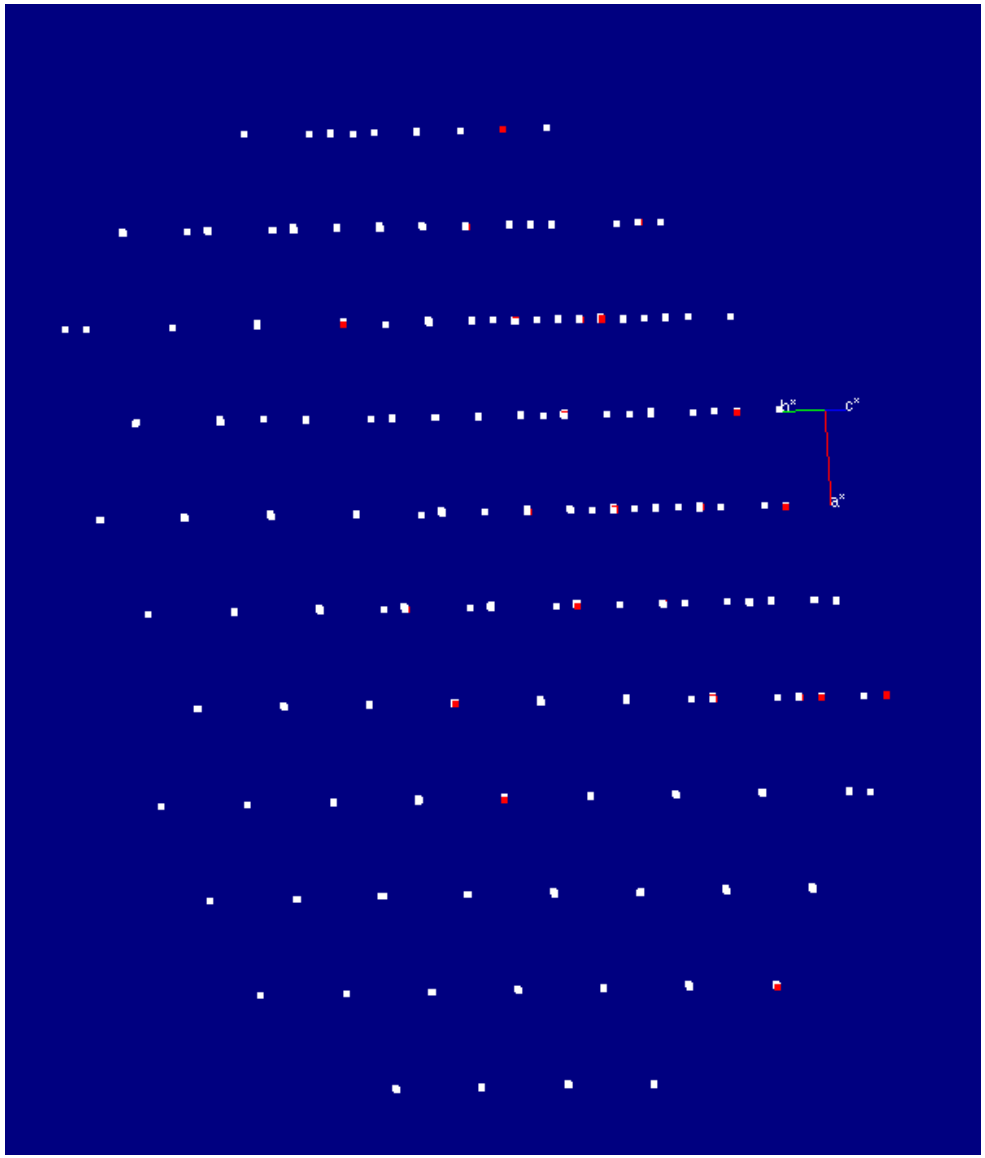
Cell Determination

The following cells would appear to be plausible, but should be checked using XPREP because they are not necessarily the conventional cells.
FOM, % within 0.2, a..gamma, volume and lattice type for potential unit-cells:

1	1.000	70.3	8.681	15.419	11.541	90.04	94.47	90.12	1540.1	I?
2	0.684	70.3	13.889	15.419	8.681	89.88	124.07	90.10	1540.0	C?
3	0.387	87.2	8.681	15.419	23.070	90.07	94.48	90.12	3078.4	P
4	0.347	70.3	8.681	10.367	10.380	96.02	112.08	111.94	769.5	P
5	0.335	70.3	13.889	15.419	21.584	89.93	91.85	90.10	4619.8	C?
6	0.333	70.3	14.973	15.419	20.082	90.12	94.83	89.97	4619.8	C?
7	0.324	70.3	8.681	10.367	10.740	66.22	63.60	68.06	769.6	P
8	0.323	70.3	8.681	10.380	10.752	66.14	63.46	67.92	769.8	P
9	0.301	70.3	8.681	10.740	10.752	91.70	116.54	116.40	769.9	P
10	0.295	70.3	27.646	15.419	11.541	90.04	110.11	89.88	4619.7	C?
11	0.281	70.3	8.681	10.367	11.541	121.53	94.47	111.94	770.4	P

...

RLATT



CELL_NOW (II)

```
-------------------------------------------------------------------------------
Cell for domain  1:    8.681   15.419   23.070    90.07    94.48    90.12
Figure of merit: 0.818   %(0.1):  87.0   %(0.2):  87.2   %(0.3):  89.4
Orientation matrix:  0.00632676  0.03399367  0.03705510
                     0.11366315  0.00778372 -0.00254995
                    -0.01982382  0.05467956 -0.02260331
Percentages of reflections in this domain not consistent with lattice types:
A: 47.6,  B: 49.9,  C: 52.1,  I: 52.1,  F: 74.8,  O: 68.4  and  R: 66.8%
Percentages of reflections in this domain that do not have:
h=2n: 50.4,  k=2n: 51.5,  l=2n: 13.3,  h=3n: 67.0,  k=3n: 69.8,  l=3n: 70.4%
361 reflections within 0.200 of an integer index assigned to domain  1,
  361 of them exclusively;    53 reflections not yet assigned to a domain
-------------------------------------------------------------------------------
```

CELL_NOW (III)

Cell for domain 2: 8.681 15.419 23.070 90.07 94.48 90.12

Figure of merit: 0.941 %(0.1): 100.0 %(0.2): 100.0 %(0.3): 100.0

Orientation matrix: 0.00824846 0.04352904 0.03226658
-0.11331218 -0.00585096 0.00424875
0.02108641 -0.04771791 0.02883242

Rotated from first domain by 180.0 degrees about
reciprocal axis -0.001 0.502 1.000 and real axis 0.185 1.000 0.895

Twin law to convert hkl from first to this domain (SHELXL TWIN matrix):
-1.000 0.000 0.000
0.136 -0.281 0.643
0.269 1.432 0.281

119 reflections within 0.200 of an integer index assigned to domain 2,
53 of them exclusively; 0 reflections not yet assigned to a domain

---

TWINABS: Data files

- HKLF 4 format: unique reflections
  - Make file using all domains
  - Average Friedel opposites
  - Iterative determination of the fractional contributions: 0.6552 : 0.3448
- HKLF 5 format:
  - Average equivalent reflections
  - Make file using only domain 1
  - Average Friedel opposites
  - Leave out single reflections that also occur in composite reflections

Space Group Determination

Crystal system M and Lattice type P selected

Mean |E*E-1| = 0.909 [expected .968 centrosym and .736 non-centrosym]

Systematic absence exceptions:

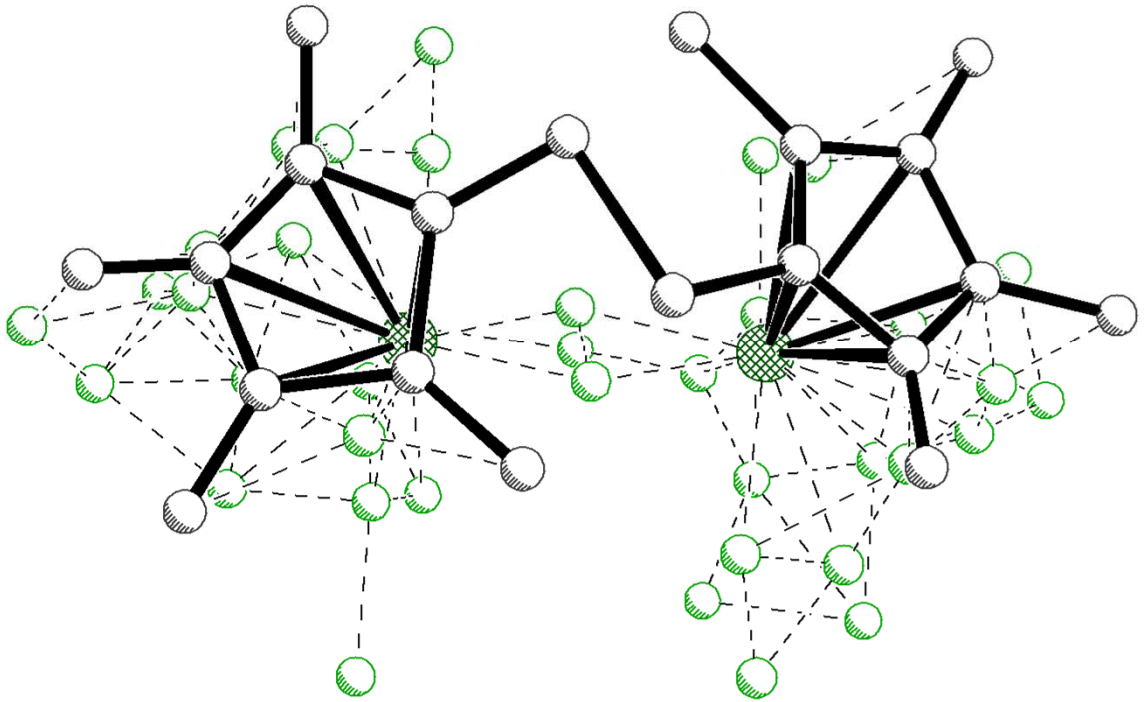
	-21-	-a-	-c-	-n-
N	10	238	239	241
N I>3σ	2	97	4	101
<I>	0.8	18.9	0.3	18.7
<I/σ>	2.0	10.1	0.8	10.0

Opt.	Space Gr.	No.	CSD	R(sym)	N(eq)	Syst. Abs.	CFOM
[A]	P2(1)/c	# 14	19410	0.000	0	2.0 / 10.0	1.48

Solution with Detwinned Data

SHELXT

R1	Rweak	Alpha	Orient.	Space gr.	Flack_x	File	Formula
0.074	0.006	0.007	as input	Pc	no Fp	twin4_a	C68 O2 Ti2 Zr2
0.199	0.021	0.119	as input	P2(1)/c		twin4_b	C60 O6 Ti2 I

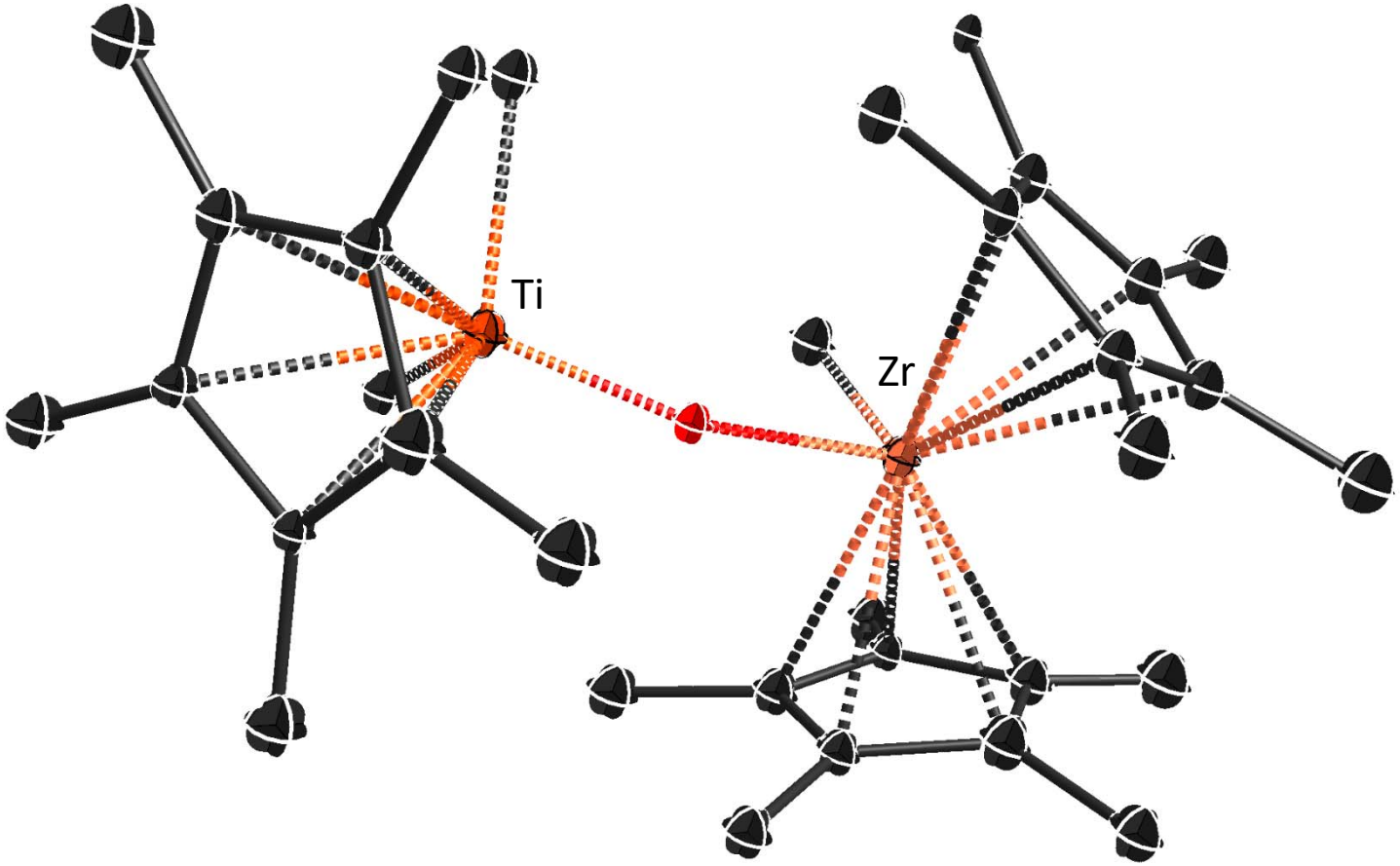


SHELXS

Solution in $P2_1/c$

Solution in Pc

Two molecules



Refinement

	HKLF 4	HKLF 5
R1 $F_o > 4\sigma(F_o)$	0.043	0.050
wR2 (all data)	0.119	0.132
R1 (after merging for Fourier)	0.047	0.051
Data	4401	4735
Unique reflection	4401	4383
k_2	-	0.364(2)
Flack x	0.091(13)	0.078(10)
Unique Friedel pairs found	0	0

No quotients, so Flack parameter determined by classical intensity fit

Refinement

	Friedel MERG		no Friedel MERG	
	HKLF 4	HKLF 5	HKLF 4	HKLF 5
R1 ($F_o > 4\sigma(F_o)$)	0.048	0.058	0.055	0.063
wR2 (all data)	0.119	0.132	0.149	0.177
R1 (after merging)	0.045	0.051	0.047	0.046
Data	4401	4735	8760	18968
Unique reflection	4401	4383	4401	4400
k_2	-	0.364(2)	-	0.342(14)
Flack x	0.091(13)	0.078(10)	0.391(16)	0.666(10)
Parsons	-	-	0.437(8)	0.395(8)

Possible inversion twin or centrosymmetric space group

Additional Twinning by Inversion?

```
BASF  0.37  0.1  0.1
HKLF  5
```

R1 ($F_o > 4\sigma(F_o)$)	0.0576
wR2 (all data)	0.1593
$k_1 = 1 - k_2 - k_3 - k_4$)	0.612
k_2	0.011(18)
k_3	0.025(11)
k_4	0.352(18)

New HKLF file with additional twinning by inversion (extra option in TWINABS)

k_1 (hkl) $\neq 0$ and k_3(-h-k-l) $= 0 \Rightarrow$ correct absolute structure for domain 1

$k_2 = 0$ and $k_4 \neq 0 \Rightarrow$ wrong absolute structure for domain 2

$\Rightarrow$

Inversion of the second domain (possible in TWINABS)

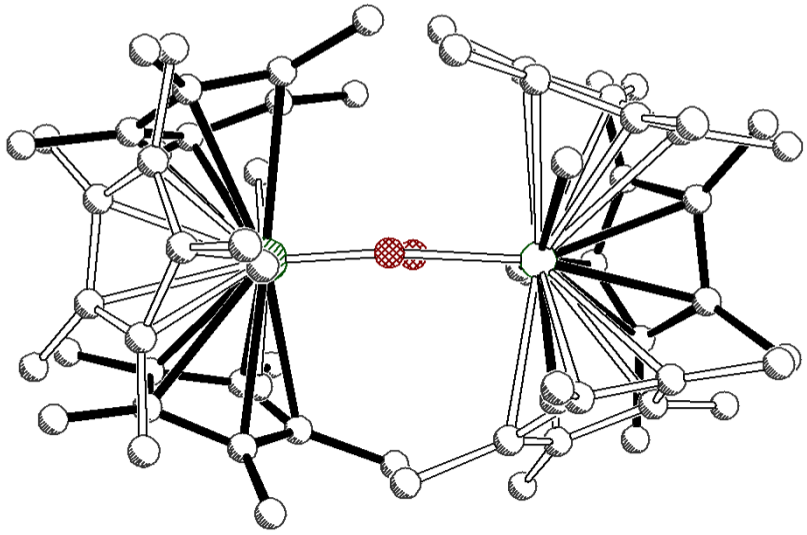
Refinement

	Friedel MERG		no Friedel MERG		Inverted 2nd domain
	HKLF 4	HKLF 5	HKLF 4	HKLF 5	HKLF 5
R1 ($F_o > 4\sigma(F_o)$)	0.048	0.058	0.055	0.063	0.052
wR2 (all data)	0.119	0.132	0.149	0.177	0.138
R1 (after merging)	0.045	0.051	0.047	0.046	0.045
Data	4401	4735	8760	18968	8852
Unique reflection	4401	4383	4401	4400	4383
k_2	-	0.364(2)	-	0.342(14)	0.362(2)
Flack x	0.091(13)	0.078(10)	0.391(16)	0.666(10)	0.035(11)
Parsons	-	-	0.437(8)	0.395(8)	0.040(10)

Pseudosymmetrie: 2_1-Axis

ZR1	4	-0.3521	0.5047	0.0560
TI2	3	0.3518	0.0110	0.4442
TI1	3	-0.1402	0.5153	0.2040
ZR2	4	0.1384	0.0116	0.2961

SYMM -X, Y+0.5, 0.5-Z pseudo $P2_1/c$



Pseudotranslation

ZR1	4	-0.3521	0.5047	0.0560
ZR2	4	0.1384	0.0116	0.2961
TI1	3	-0.1402	0.5153	0.2040
TI2	3	0.3518	0.0110	0.4442

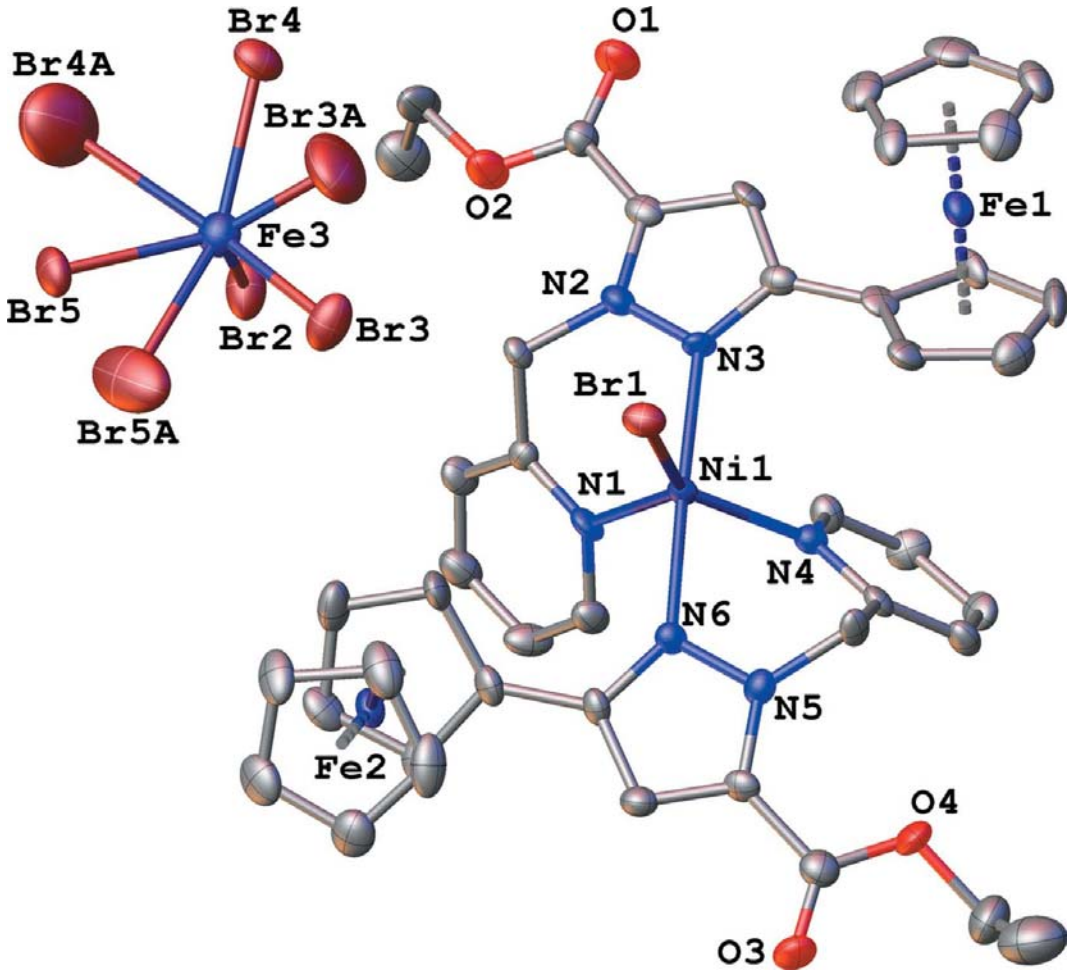
SYMM X+0.5, Y+0.5, Z-0.25

The following cells would appear to be plausible, but should be checked using XPREP because they are not necessarily the conventional cells.
FOM, % within 0.2, a..gamma, volume and lattice type for potential unit-cells:

1	1.000	70.3	**8.681**	**15.419**	**11.541**	**90.04**	**94.47**	**90.12**	**1540.1**	**I?**
2	0.684	70.3	13.889	15.419	8.681	89.88	124.07	90.10	1540.0	C?
3	0.387	87.2	**8.681**	**15.419**	**23.070**	**90.07**	**94.48**	**90.12**	**3078.4**	**P**

.....

Pseudo-merohedral Twin



I. Guzei, R. Herbst-Irmer, A. Munyanezac, J. Darkwad, *Acta Crystallogr.* **2012**, *B68*, 150-157.

Space Group Determination

Option A: FOM = 0.026° ORTHORHOMBIC F-lattice R(sym) = 0.060 [6049]
Cell: 15.218 22.008 28.151 89.98 90.00 89.99 Volume: 9428.45
Matrix: 1.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000 1.000

Crystal system O and Lattice type F selected

Mean |E*E-1| = 0.608 [expected .968 centrosym and .736 non-centrosym]

Systematic absence exceptions:

	d--	-d-	--d
N	741	598	470
N (I>3σ)	502	4	341
<I>	63.2	1.8	171.4
<I/σ>	7.0	0.4	12.8

Identical indices and Friedel opposites combined before calculating R(sym)
Option Space Group No. Type Axes CSD R(sym) N(eq) Syst. Abs. CFOM

No acceptable space group - change tolerances or unset chiral flag
or possibly change input lattice type, then recheck cell using H-option

Crystal System – Option T

Option A: FOM = 0.000 deg. ORTHORHOMBIC F-lattice R(sym) = 0.046 [6066]
Cell: 15.218 22.008 28.151 90.00 90.00 90.00 Volume: 9428.27
Matrix: 1.0000 0.0000 0.0000 0.0000 1.0000 0.0000 0.0000 0.0000 1.0000

Option B: FOM = 0.000 deg. MONOCLINIC C-lattice R(sym) = 0.022 [3916]
Cell: 15.218 22.008 16.001 90.00 118.39 90.00 Volume: 4714.14
Matrix:-1.0000 0.0000 0.0000 0.0000 -1.0000 0.0000 0.5000 0.0000 0.5000

Option C: FOM = 0.000 deg. MONOCLINIC C-lattice R(sym) = 0.045 [3953]
Cell: 15.218 28.151 13.379 90.00 124.66 90.00 Volume: 4714.14
Matrix:-1.0000 0.0000 0.0000 0.0000 0.0000 -1.0000 0.5000 -0.5000 0.0000

Option D: FOM = 0.000 deg. MONOCLINIC I-lattice R(sym) = 0.045 [3953]
Cell: 13.379 28.151 13.379 90.00 110.67 90.00 Volume: 4714.14
Matrix:-0.5000 0.5000 0.0000 0.0000 0.0000 -1.0000 -0.5000 -0.5000 0.0000

Option E: FOM = 0.000 deg. MONOCLINIC C-lattice R(sym) = 0.043 [3994]
Cell: 22.008 15.218 17.866 90.00 128.02 90.00 Volume: 4714.14
Matrix: 0.0000 -1.0000 0.0000 1.0000 0.0000 0.0000 0.0000 0.5000 0.5000

Option F: FOM = 0.000 deg. MONOCLINIC I-lattice R(sym) = 0.043 [3994]
Cell: 17.866 15.218 17.866 90.00 103.96 90.00 Volume: 4714.14
Matrix: 0.0000 -0.5000 -0.5000 1.0000 0.0000 0.0000 0.0000 -0.5000 0.5000

Space Group

Systematic absence exceptions:

Option	B	C	E
	-c-	-c-	-c-
N	598	471	740
N (I>3σ)	4	367	550
<I>	2.3	239.2	85.2
<I/σ>	0.5	8.0	6.8
R(sym)	0.022	0.043	0.045

Option B:

- Lowest R(sym)
- Most probable space group because of systematic absenses

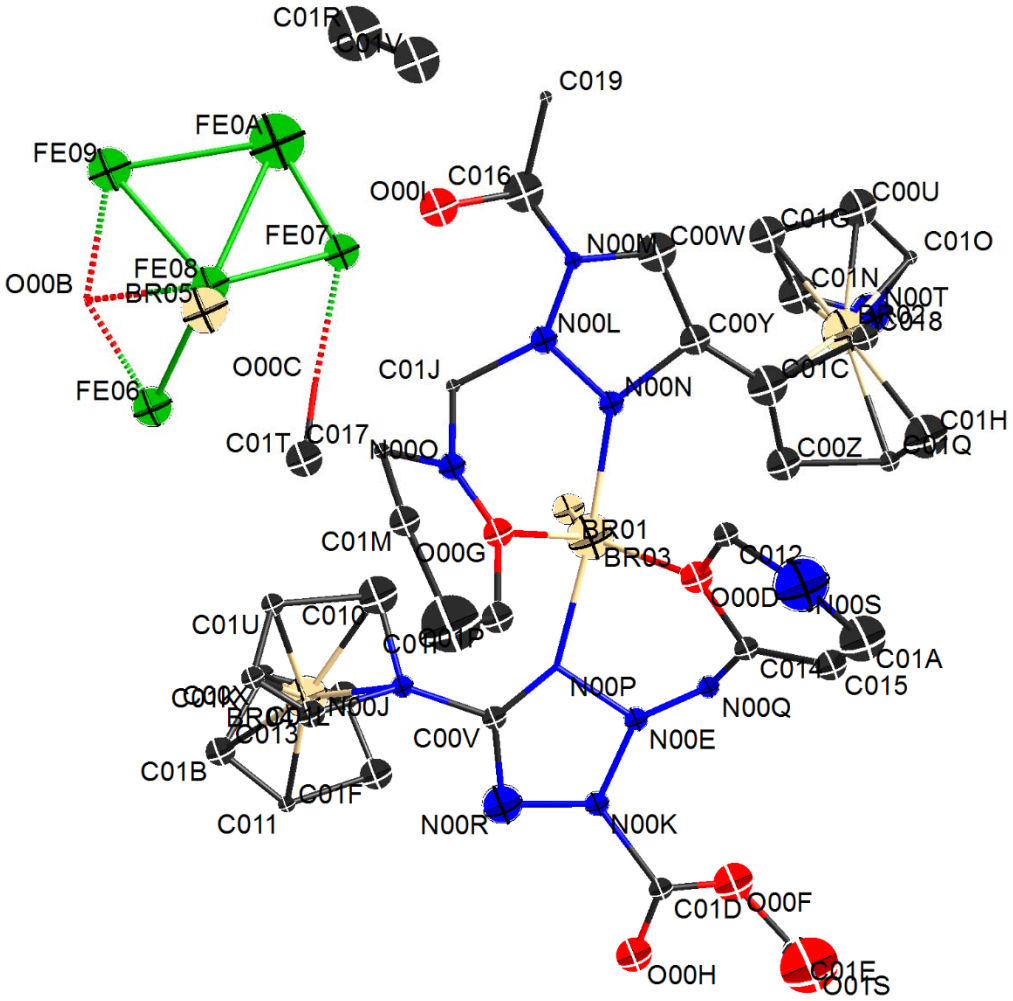
Structure Solution

Option B space group Cc

- SHELXS:
  CFOM 0.0701, RE = 0.288 for C_{46} Ni Fe_4 Br_2
- SHELXD:
  C_{49} Fe_2 Ni Br_5 best final CC 81.3
- SHELXD with TWIN 1 0 0 0 -1 0 -1 0 -1 and BASF 0.45:
  C_{32} O_4 Fe_3 Ni Br_5 best final CC 87.4
- SHELXT :

  space group Cc
  R1 = 0.232, Alpha = 0.028, Flack x= 0.38, C_{37} N_{12} O_8 Fe_5 Br_5

SHELXT Solution – First Refinement



R1 = 0.186
Flack x = 0.32(6)
Parsons = 0.34(2)

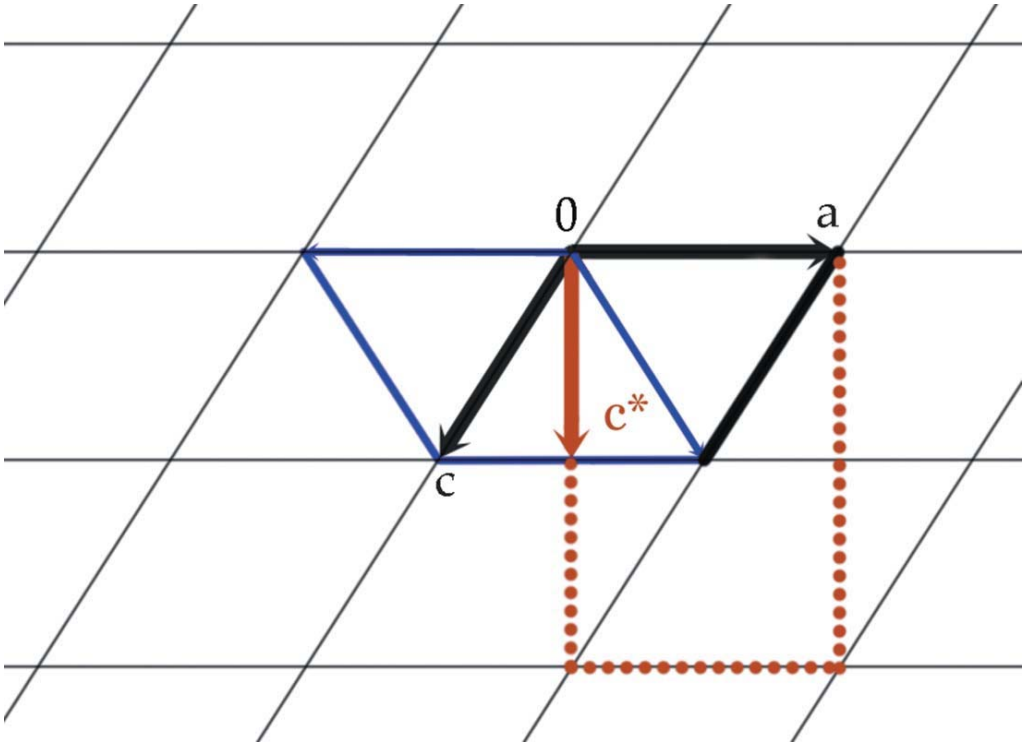
Determination of the Twin Matrix

$$\begin{pmatrix} \text{orthorhombic} \\ \downarrow \\ \text{monoclinic} \end{pmatrix} \quad \begin{pmatrix} \text{twofold} \\ \text{axis} \end{pmatrix} \quad \begin{pmatrix} \text{monoclinic} \\ \downarrow \\ \text{orthorhombic} \end{pmatrix}$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0.5 & 0 & 0.5 \end{pmatrix} \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 0 & 2 \end{pmatrix}$$

$$= \quad \begin{pmatrix} \mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} & \mathbf{0} \\ \mathbf{-1} & \mathbf{0} & \mathbf{-1} \end{pmatrix}$$

Twin Operation



black – monoclinic C-centered unit (option B)

blue – the unit cell related to it by 180° rotation about c*

red dotted line - apparent orthorhombic unit cell (option A)

TwinRotMat

P.L.A.T.O.N

TwinRotMat

Analysis of Fo/Fc Data for Unaccounted (Non)Merohedral Twinning for: solvt_

Cell: 1.54178 15.218 22.007 16.000 90.00 118.39 90.00 Spgr: Cc

Criteria: DeltaI/SigmaI .GT. 4.0, DeltaTheta 0.10 Deg., NselMin = 50

N(refl) = 8007, N(selected) = 50, IndMax = 5, CritI = 0.1, CritT = 0.10

1 0 0 0 -1 0 -1 0 -1

BASF = 0.46

DEL-R = -0.052

2-axis (2 0 ... eg. Freq = 102

(1.000 0.000 ... Overlap = 7954

(0.000 -1.000 ... BASF = 0.46

(-1.000 0.000 ... DEL-R =-0.052

1

2-axis (0 1 ... eg. Freq = 94

(-1.000 0.000 0.000) (h1) (h2) Nr Overlap = 8007

(0.000 1.000 0.000) * (k1) = (k2) BASF = 0.52

(0.000 0.000 -1.000) (l1) (l2) DEL-R =-0.009

2

PLATON-Sep 04 14:26:03 2013 - (170613)

Fc from Coordinates

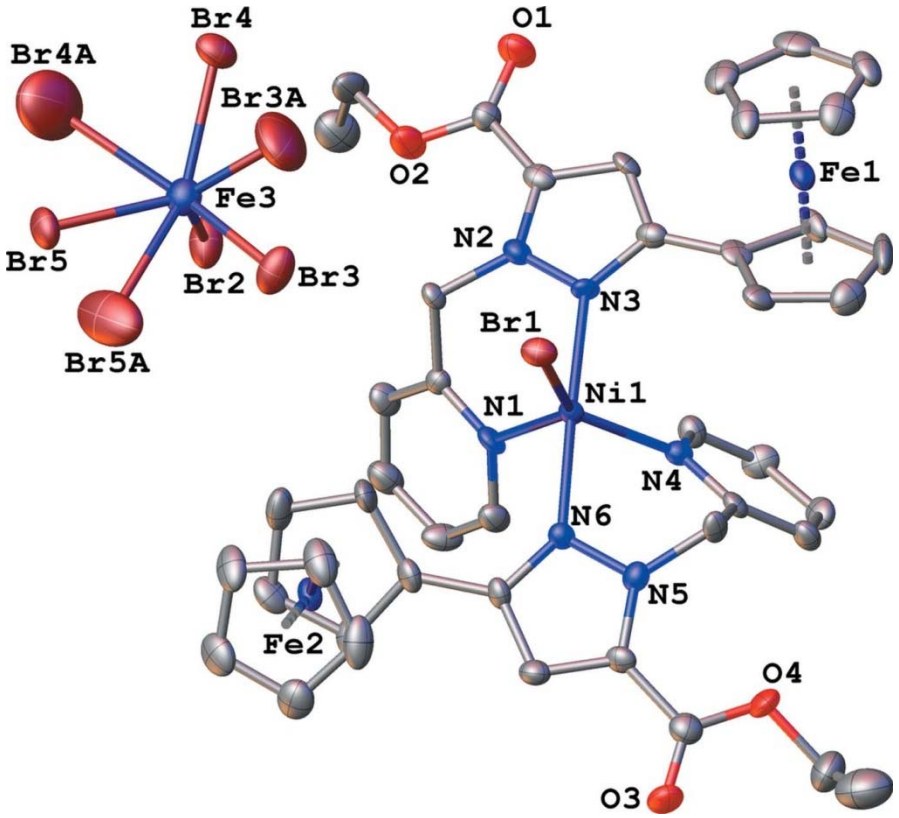
solvt_a1 C c R = 0.19

INPUT INSTRUCTIONS via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)

>>

TwinRoMt 25
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
FullListing
EPS-TwinLaw
DspTwinMat1
DspTwinMat2
DspTwinMat3
DspTwinMat4
EPS-TwinLat
Resolution>
IcalFromFCF
Zone-H,K,L
Up Down
RacemicTwin
SelectTMat1
SelectTMat2
SelectTMat3
SelectTMat4
HKLF5-CritI
HKLF5-CritT
HKLF5-Gener
End
Exit
MenuActive

Final Structure



TWIN -1 0 0 0 -1 0 1 0 1

k_2 = 0.462(4)

R1 = 0.0832

Flack x = 0.932(14) by hole-in-one fit to all intensities

0.715(12) from 3181 selected quotients (Parsons' method)

** Absolute structure probably wrong - invert and repeat refinement **

Additional Twinning by Inversion?

Perhaps four twin domains with following indices:

h, k, l	
h,-k,-h-l	TWIN matrix
-h, -k, -l	inversion
-h, k, h+l	TWIN matrix and inversion

```
TWIN  1 0 0  0 -1 0  -1 0 -1  -4
BASF  .46  .2  .2
```

Parameter	Value	s.u.	Indices
k_1	$1-(k_2+k_3+k_4)$		h, k, l
k_2	0.464	0.004	h,-k,-h-l
k_3	0.546	0.004	-h, -k, -l
k_4	0.004	0.004	-h,k,h+l

k_1 (hkl) = 0 but k_3(-h-k-l) $\neq$ 0 $\Rightarrow$ wrong absolute structure for domain 1

$k_2 \neq 0$ and $k_4 = 0 \Rightarrow$ correct absolute structure for domain 2

No Twinning by Inversion!

```
MOVE  1  1  1  -1
TWIN  -1 0 0  0 -1 0  1 0 1
```

R1 = 0.0271

k_2= 0.461(1)

Flack x = 0.009(4) by hole-in-one fit to all intensities

0.015(2) from 3181 selected quotients (Parsons' method)

Practicals

In ChemicalCrystallography.zip you find

- a demo version of XPREP
- *.p4p (cell dimension and formula)
- and *.hkl of seven example structures

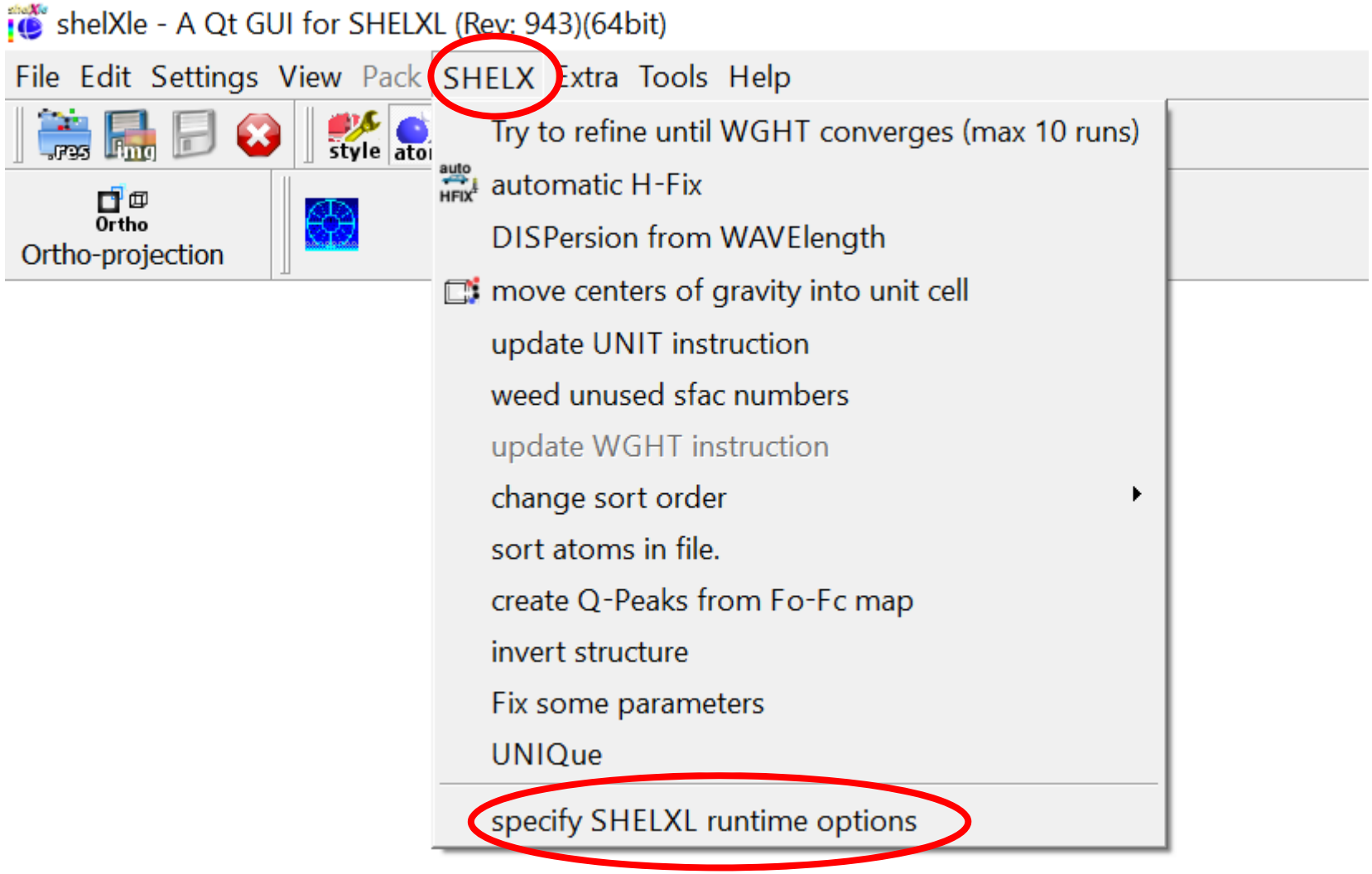
You should have installed

- all SHELX programs (SHELXS, SHELXD, SHELXL, SHELXT)
- PLATON
- Shelxle

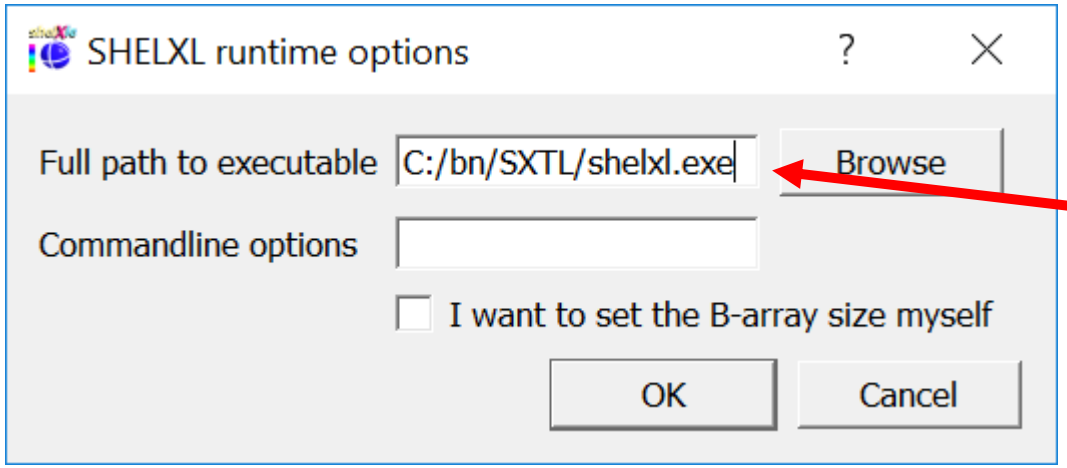
Define in Shelxle the path for

- SHELXL
- Platon

Shelxle: Define SHELXL

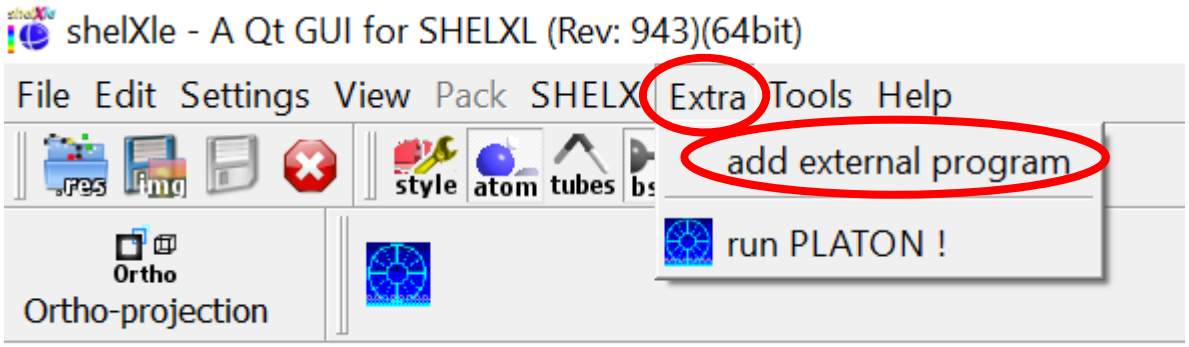


Shelxle: Define SHELXL

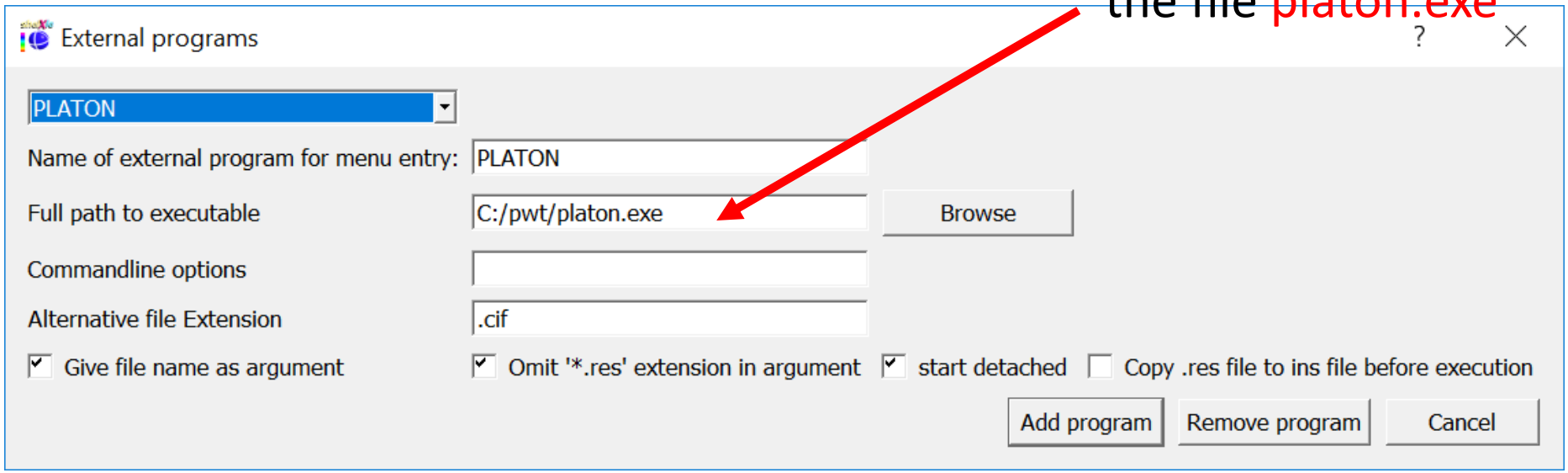


your directory with the file shelxl.exe

Shelxle: Define Platon



your directory with the file platon.exe



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