SHELX-Workshop

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Twinning

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Outline

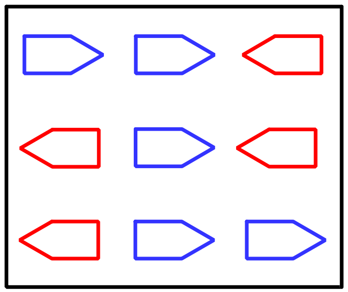
- Theory
  - Definition
  - Classification
  - Test for Merohedral Twinning
  - Solution
  - Refinement
  - Warning Signs
- Examples

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

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. twin by inversion

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

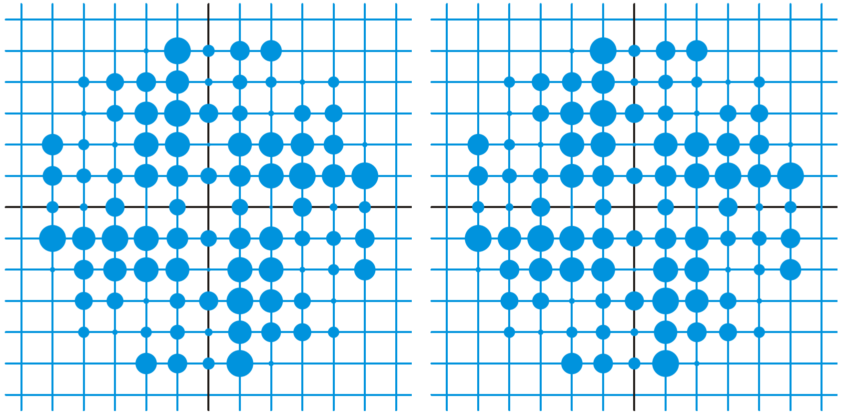
   - only in tetragonal, trigonal, hexagonal and cubic space groups
   - exact overlap of the reciprocal lattices
   - often low value for <|E²-1|>
   - Laue group and space group determination may be difficult
   - structure solution may be difficult

2. Twinning by pseudo-merohedry

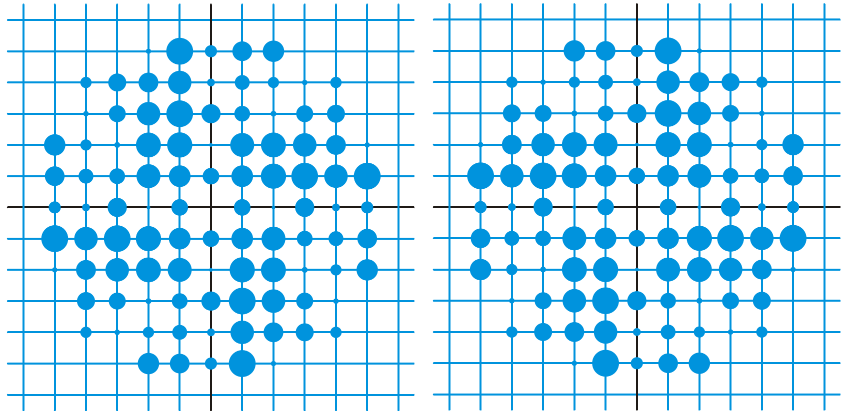
   Twin operator: belongs to a higher crystal system than the structure

   - Metric symmetry higher than Laue symmetry

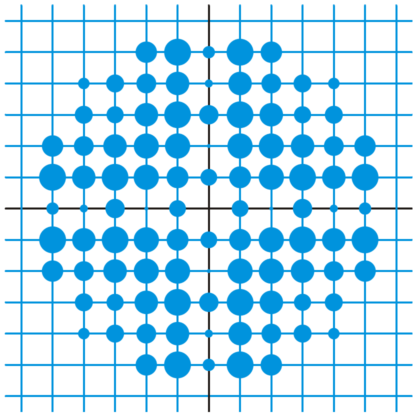
Reciprocal Space Plot l = 0



Reciprocal Space Plot l = 0



Reciprocal Space Plot l = 0



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

Four Kinds of Twins (II)

3.Twinning by reticular merohedry

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

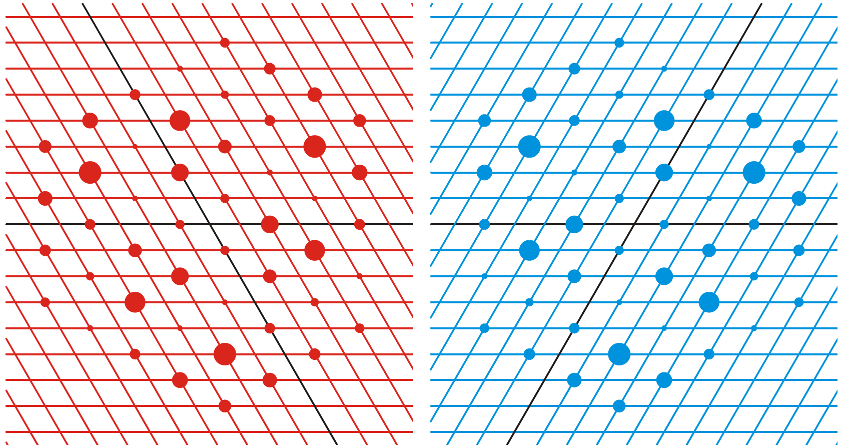
- detection of the lattice centring may be difficult
- structure solution not as difficult as for merohedral twins.

4. Non-merohedral twins

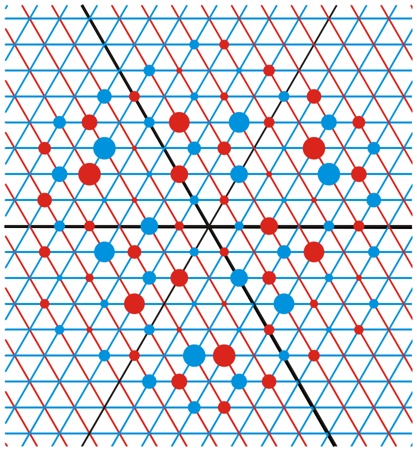
Twin operator: arbitrary operator, often rotation of 180°

- 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



Reciprocal Space Plot l = 1



Four Kinds of Twins (II)

3.Twinning by reticular merohedry

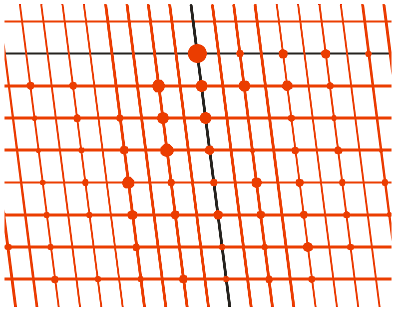
e.g. obverse/reverse twinning in case of a rhombohedral crystal

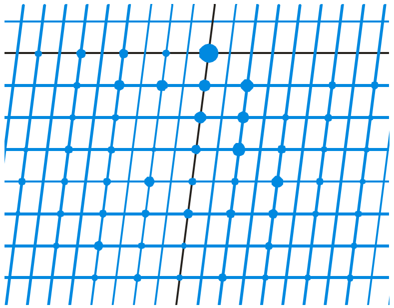
- detection of the lattice centring may be difficult
- structure solution not as difficult as for merohedral twins.

4. Non-merohedral twins

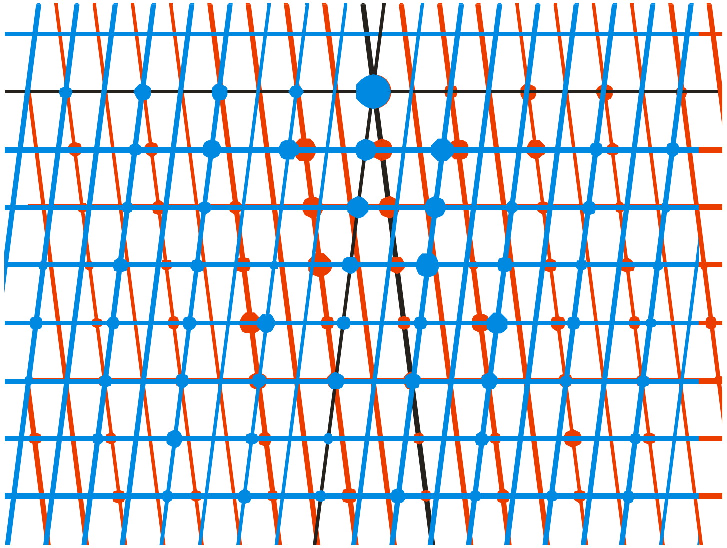
Twin operator: arbitrary operator, often rotation of 180°

Reciprocal Space Plot k = 2



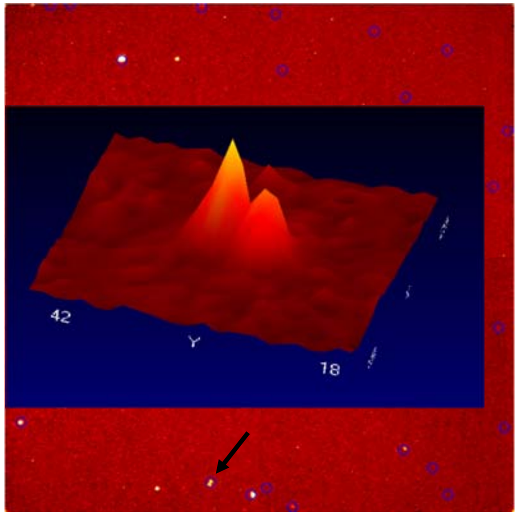


Reciprocal Space Plot k = 2



Reflection Pattern

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



Cell Determination

- One orientation matrix indexes only part of the reflections
- A second run with the yet unindexed reflections with
  - Using the information of the first cell by rotating the first derived orientation matrix

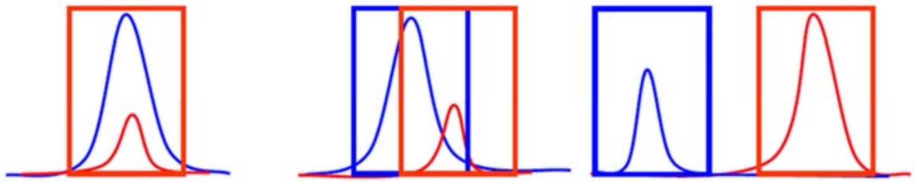
    ⇒ Determination of very weak domains possible and Rotation = Twin law

or

  - Totally new indexing

    ⇒ Determination of different cells possible and Determination of the twin law separately

Integration



exact overlaps

partial overlaps

non-overlaps

Scaling and Data Files

Twin raw file : information about overlap (HKLF5 format)

➔ Special version of scaling programs needed

- 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

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.
- SHELXD can use the twin law and the fractional contribution
- Detwinning

$$J_1 = (1-\alpha)\, I_1 + \alpha\, I_2 \qquad J_2 = (1-\alpha)\, I_2 + \alpha\, I_1$$

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

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
```

C. S. Pratt, B. A. Coyle, J. A. Ibers, *J. Chem. Soc.* 2146, 1971
G. B. Jameson, *Acta Crystallogr. A***38**, 817, 1982

Warning Signs - 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

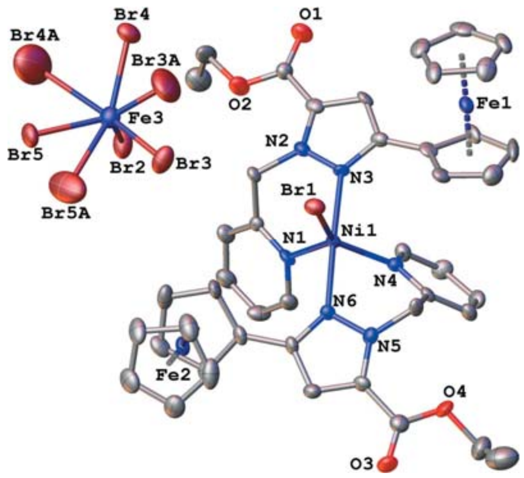
Warning Signs - Non-merohedral Twinning

- 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 Crystallogr. B***54**, 443, 1998

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

Pseudo-merohedral Twin



I. Guzei, R. Herbst-Irmer, A. Munyanezac, J. Darkwad, *Acta Crystallogr. B***68**, 150, 2012.

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 = 0.026° 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

Option B: FOM = 0.022 ° MONOCLINIC C-lattice R(sym) = 0.059 [3941]
Cell: 15.218 28.151 13.377 89.98 124.65 90.00 Volume: 4714.23
Matrix: 1.000 0.000 0.000 0.000 0.000 -1.000 -0.500 0.500 0.000

Option C: FOM = 0.022 ° MONOCLINIC I-lattice R(sym) = 0.059 [3941]
Cell: 13.377 28.151 13.380 89.98 110.67 90.02 Volume: 4714.23
Matrix: 0.500 -0.500 0.000 0.000 0.000 -1.000 0.500 0.500 0.000

Option D: FOM = 0.014 ° MONOCLINIC C-lattice R(sym) = 0.052 [3988]
Cell: 22.008 15.218 17.863 89.99 128.00 90.01 Volume: 4714.23
Matrix: 0.000 1.000 0.000 1.000 0.000 0.000 0.000 -0.500 -0.500

Option E: FOM = 0.014 ° MONOCLINIC I-lattice R(sym) = 0.052 [3988]
Cell: 17.863 15.218 17.870 90.01 103.97 90.01 V olume: 4714.23
Matrix: 0.000 0.500 0.500 1.000 0.000 0.000 0.000 0.500 -0.500

Option F: FOM = 0.026 ° MONOCLINIC C-lattice R(sym) = 0.036 [3905]
Cell: 15.218 22.008 16.000 89.99 118.39 89.99 Volume: 4714.23
Matrix: -1.000 0.000 0.000 0.000 1.000 0.000 0.500 0.000 -0.500

Space Group

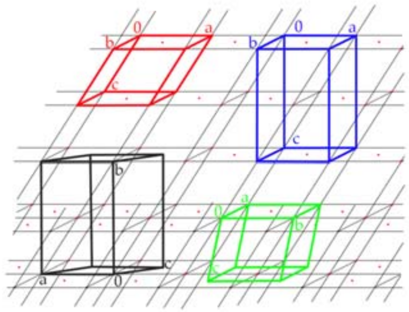
Systematic absence exceptions:

Option	B	E	F
	-c-	-c-	-c-
N	470	741	598
N ($I>3\sigma$)	341	502	4
$<I>$	171.4	63.2	1.8
$<I/\sigma>$	12.8	7.0	0.4
R(sym)	0.059	0.052	0.036

Option F:

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

Crystal System



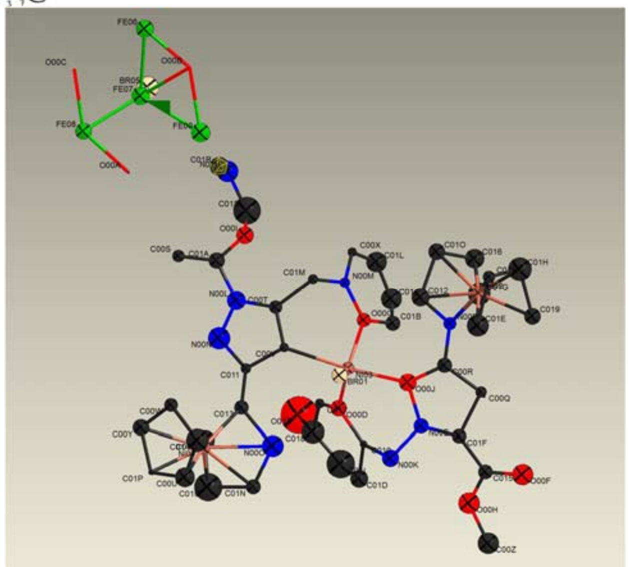
Red - correct C-centered monoclinic cell (option F); blue - orthorhombic F-centered cell (option A); green - monoclinic C-centered cell (option B); black monoclinic C-centered cell (option D). The red dots represent lattice points.

Structure Solution

Option F space group Cc

- SHELXS:
  CFOM 0.0605, RE = 0.267 for C_{62} Fe_5 Br
- SHELXD:
  C_{55} Fe_2 Ni Br_2 best final CC 77.40
- SHELXD with TWIN 1 0 0 0 -1 0 -1 0 -1 and BASF 0.45:
  C_{42} Fe_2 Ni Br_2 best final CC 80.46
- SHELXT:
  space group Cc
  R1 = 0.227, Alpha = 0.067, Flack x= 0.49, C_{39} N_8 O_{10} Fe_4 Ni_3 Br_2

SHELXT Solution



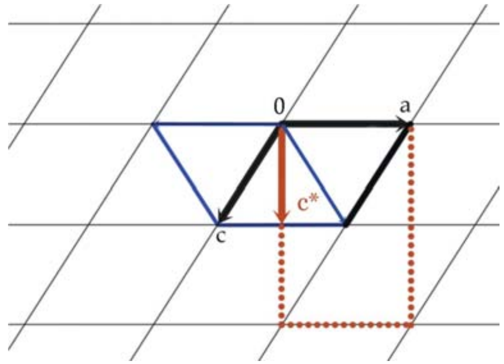
R1 = 0.1903
Flack x = 0.522(8)

Determination of the Twin Matrix

orthorhombic → monoclinic	twofold axis	monoclinic → orthorhombic
$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0.5 & 0 & -0.5 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 1 & 0 & 2 \end{pmatrix}$

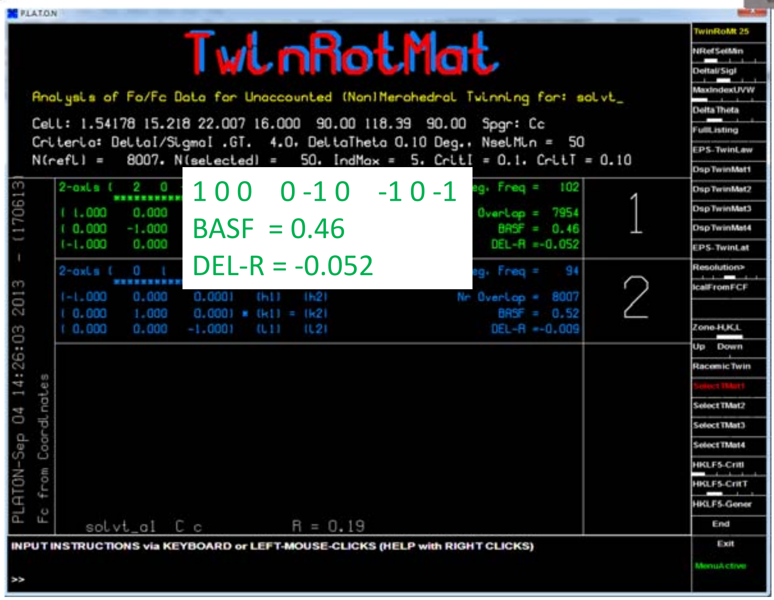
$$= \begin{pmatrix} \mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} & \mathbf{0} \\ \mathbf{-1} & \mathbf{0} & \mathbf{-1} \end{pmatrix}$$

Twin Operation

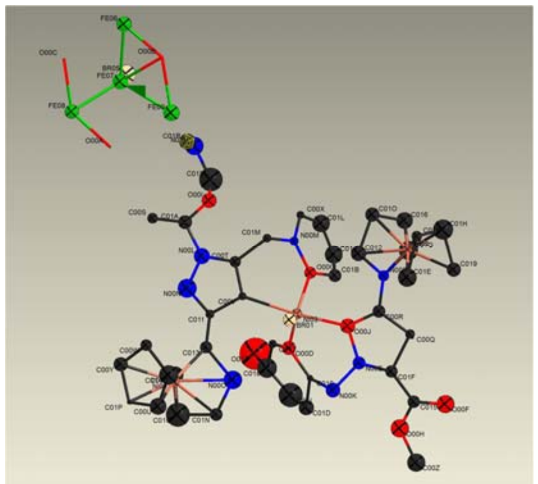


black – monoclinic C-centered unit (option F)
blue – the unit cell related to it by 180° rotation about c*
red dotted line - apparent orthorhombic unit cell (option A)

TwinRotMat



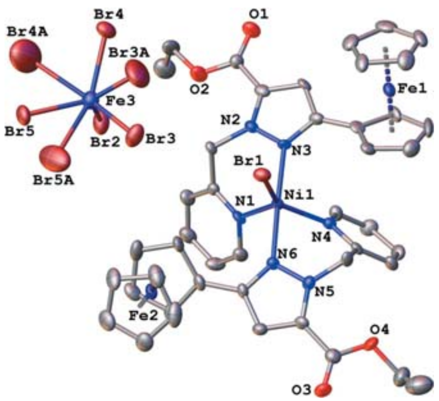
Refinement



Without TWIN/BASF
R1 = 0.1903
Flack x = 0.522(8)

TWIN 1 0 0 0 -1 0 -1 0 -1
BASF = 0.462(4)
R1 = 0.0920
Flack x = 0.209(12)
(Parsons' quotients)

Final Structure



TWIN -1 0 0 0 -1 0 1 0 1
BASF = 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
K1	1-(K2+K3+K4)		h, k, l
K2	0.464	0.004	h,-k,-h-l
K3	0.546	0.004	-h, -k, -l
K4	0.004	0.004	-h,k,h+l

K1 (hkl) = 0 but K3(-h-k-l) $\neq$ 0 $\Rightarrow$ wrong absolute structure for domain 1
K2 $\neq$ 0 and K4 = 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
BASF = 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)

Acknowledgements

I. Guzei, *University of Wisconsin, Madison*

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