Introduction to Twinning

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Outline

- Theory
  - Definition
  - Classification
  - Test for Merohedral Twinning
  - Solution
  - Refinement
  - Warning Signs
- Examples
“Twins are regular aggregates consisting of individual crystals of the same species joined together in some definite mutual orientation.”


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
Reciprocal Space Plot $l = 0$
Reciprocal Space Plot $l = 0$
<table>
<thead>
<tr>
<th>True Laue Group</th>
<th>Apparent Laue Group</th>
<th>Twin Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/m</td>
<td>4/mmm</td>
<td>0 1 0 1 0 0 0 0 -1</td>
</tr>
<tr>
<td>(\bar{3})</td>
<td>(\bar{3}12)</td>
<td>0 -1 0 -1 0 0 0 0 -1</td>
</tr>
<tr>
<td>(\bar{3})</td>
<td>(\bar{3}21)</td>
<td>0 1 0 1 0 0 0 0 -1</td>
</tr>
<tr>
<td>(\bar{3})</td>
<td>6/m</td>
<td>-1 0 0 0 -1 0 0 0 1</td>
</tr>
<tr>
<td>(\bar{3})</td>
<td>6/mmm</td>
<td>0 -1 0 -1 0 0 0 0 -1</td>
</tr>
<tr>
<td>(\bar{3}21)</td>
<td>6/mmm</td>
<td>-1 0 0 0 -1 0 0 0 1</td>
</tr>
<tr>
<td>(\bar{3}12)</td>
<td>6/mmm</td>
<td>0 1 0 1 0 0 0 0 -1</td>
</tr>
<tr>
<td>6/m</td>
<td>6/mmm</td>
<td>0 1 0 1 0 0 0 0 -1</td>
</tr>
<tr>
<td>m(\bar{3})</td>
<td>m(\bar{3}m)</td>
<td>0 1 0 1 0 0 0 0 -1</td>
</tr>
</tbody>
</table>
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 $|\langle E^2 - 1 \rangle|$
       - 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
3. Twinning by reticular merohedry

 e.g. obverse/reverse twinning in case of a rhombohedral crystal
Reciprocal Space Plot \( l = 1 \)
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 $k = 2$
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
    \[ \Rightarrow \text{Determination of very weak domains possible and } \]
    \[ \text{Rotation } = \text{Twin law} \]
  - or
  - Totally new indexing
    \[ \Rightarrow \text{Determination of different cells possible and } \]
    \[ \text{Determination of the twin law separately} \]
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:
      
      \[
      \begin{array}{cccccc}
        h' & k' & l' & F^2 & \sigma(F^2) & -2 \\
        h & k & l & F^2 & \sigma(F^2) & 1 \\
      \end{array}
      \]

      with \(h', k', l'\) generated by the second orientation matrix
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
Comparing true/apparent Laue groups. 0.05 < BASF < 0.45 indicates partial merohedral twinning. BASF ca. 0.5 and a low $\langle |E^2-1| \rangle$ (0.968[C] or 0.736[NC]) are normal) suggests perfect merohedral twinning. For a twin, $R(\text{int})$ 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

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>I</th>
<th>F</th>
<th>Obv</th>
<th>Rev</th>
<th>All</th>
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<tbody>
<tr>
<td>N</td>
<td>0</td>
<td>24004</td>
<td>23981</td>
<td>24079</td>
<td>23964</td>
<td>36032</td>
<td>31915</td>
<td>31944</td>
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<tr>
<td>N (\sigma)</td>
<td>0</td>
<td>6903</td>
<td>6913</td>
<td>7404</td>
<td>6931</td>
<td>10610</td>
<td>3990</td>
<td>6064</td>
<td>13592</td>
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<tr>
<td>(&lt;I&gt;)</td>
<td>0.0</td>
<td>80.3</td>
<td>81.4</td>
<td>84.3</td>
<td>80.8</td>
<td>82.0</td>
<td>16.8</td>
<td>66.2</td>
<td>81.0</td>
</tr>
<tr>
<td>(&lt;I/\sigma&gt;)</td>
<td>0.0</td>
<td>4.1</td>
<td>4.1</td>
<td>4.3</td>
<td>4.1</td>
<td>4.1</td>
<td>1.6</td>
<td>3.4</td>
<td>4.0</td>
</tr>
</tbody>
</table>

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
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

\[ J_1 = (1-\alpha)I_1 + \alpha I_2 \]
\[ J_2 = (1-\alpha)I_2 + \alpha I_1 \]

\[ I_1 = \frac{(1-\alpha)J_1 - \alpha J_2}{1-2\alpha} \]
\[ I_2 = \frac{(1-\alpha)J_2 - \alpha J_1}{1-2\alpha} \]
Twin Refinement in SHELXL

Method of Pratt, Coyle and Ibers:

\[
(F_c^2)^* = \text{osf}^2 \sum_{m=1}^{n} k_m F_{cm}^2
\]

\[
osf = \text{overall scale factor}
\]

\[
k_m = \text{fractional contribution of twin domain m}
\]

\[
F_{cm} = F_c \text{ of twin domain m}
\]

\[
1 = \sum_{m=1}^{n} k_m
\]

\[
(n-1) \text{ of the fractional contributions can be refined.}
\]

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

<table>
<thead>
<tr>
<th>TWIN</th>
<th>r11</th>
<th>r12</th>
<th>r13</th>
<th>r21</th>
<th>r22</th>
<th>r23</th>
<th>r31</th>
<th>r32</th>
<th>r33</th>
<th>n</th>
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<tbody>
<tr>
<td>BASF</td>
<td>k2</td>
<td>k3</td>
<td>...</td>
<td>kn</td>
<td></td>
<td></td>
<td></td>
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</table>

or

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>BASF</td>
<td>k2</td>
</tr>
<tr>
<td>HKLF</td>
<td>5</td>
</tr>
</tbody>
</table>


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
- $K = \text{mean}(F_o^2)/\text{mean}(F_c^2)$ 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.


Pseudo-merohedral Twin

Space Group Determination

Option A:  FOM  = 0.026°  ORTHORHOMBOIC  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:

<table>
<thead>
<tr>
<th>d--</th>
<th>-d-</th>
<th>--d</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>741</td>
<td>598</td>
</tr>
<tr>
<td>N (I&gt;3σ)</td>
<td>502</td>
<td>4</td>
</tr>
<tr>
<td>&lt;I&gt;</td>
<td>63.2</td>
<td>1.8</td>
</tr>
<tr>
<td>&lt;I/σ&gt;</td>
<td>7.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

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

Examples
### Crystal System – Option T

<table>
<thead>
<tr>
<th>Option</th>
<th>FOM</th>
<th>Classification</th>
<th>Lattice</th>
<th>R(sym)</th>
<th>Cell: 15.218 22.008 28.151 89.98 90.00 89.99</th>
<th>Volume: 9428.45</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.026°</td>
<td>ORTHORHOMBIC</td>
<td>F-lattice</td>
<td>0.060</td>
<td>[6049]</td>
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<tr>
<td>Matrix:</td>
<td></td>
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<td></td>
<td></td>
<td>1.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000</td>
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<tr>
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<td>MONOCLINIC</td>
<td>C-lattice</td>
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<td>[3941]</td>
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<tr>
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<td></td>
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<td></td>
<td>15.218 28.151 13.377 89.98 124.65 90.00</td>
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<td>C</td>
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<tr>
<td>D</td>
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<td>[3988]</td>
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<tr>
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<td>[3988]</td>
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<tr>
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<td>[3905]</td>
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</table>
Space Group

Systematic absence exceptions:

<table>
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<tr>
<th>Option</th>
<th>B</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
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<tr>
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<td>470</td>
<td>741</td>
<td>598</td>
</tr>
<tr>
<td>N (</td>
<td>I</td>
<td>&gt;3σ)</td>
<td>341</td>
</tr>
<tr>
<td>&lt;</td>
<td>I</td>
<td>&gt;</td>
<td>171.4</td>
</tr>
<tr>
<td>&lt;</td>
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<tr>
<td>R(sym)</td>
<td>0.059</td>
<td>0.052</td>
<td>0.036</td>
</tr>
</tbody>
</table>

**Option F:**
- Lowest R(sym)
- Most probable space group because of systematic absenses
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

- „Intrinsic Phasing“: 
  space group Cc 
  R1 = 0.227, Alpha = 0.067, Flack x = 0.49, C$_{39}$ N$_8$ O$_{10}$ Fe$_4$ Ni$_3$ Br$_2$
“Intrinsic Phasing” Solution

R1 = 0.1903
Flack x = 0.522(8)
Determination of the Twin Matrix

\[
\begin{pmatrix}
\text{orthorhombic} \\
\downarrow \\
\text{monoclinic}
\end{pmatrix}
\begin{pmatrix}
\text{twofold} \\
\text{axis}
\end{pmatrix}
\begin{pmatrix}
\text{monoclinic} \\
\downarrow \\
\text{orthorhombic}
\end{pmatrix}
\]

\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0.5 & 0 & -0.5
\end{pmatrix}
\begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
1 & 0 & 2
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
-1 & 0 & -1
\end{pmatrix}
\]
Twin Operation

black – monoclinic C-centered unit (option F)
blue – the unit cell related to it by $180^\circ$ rotation about $c^*$
red dotted line - apparent orthorhombic unit cell (option A)
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/StdvI GT. 4.0, DeltaTheta 0.10 Deg., NselMln = 50
N(refl) = 8007, N(selected) = 50, IndMax = 5, CritI = 0.1, CritT = 0.10

2-axls ( 2 0 0 )
  ( 1.000 0.000 )
  ( 0.000 -1.000 )
  ( -1.000 0.000 )
  2-axls ( 0 1 0 )
  ( -1.000 0.000 0.000 ) ^ (h1) ^ (h2)
  ( 0.000 1.000 0.000 ) * (k1) = (k2)
  ( 0.000 0.000 -1.000 ) ^ (l1) ^ (l2)

Also:

BASF = 0.46
DEL-R = -0.052

100 0 -10 -10 -1

1

2

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>s.u.</th>
<th>Indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>$1-(K2+K3+K4)$</td>
<td>0.004</td>
<td>$h, k, l$</td>
</tr>
<tr>
<td>K2</td>
<td>0.464</td>
<td>0.004</td>
<td>$h, -k, -h-l$</td>
</tr>
<tr>
<td>K3</td>
<td>0.546</td>
<td>0.004</td>
<td>$-h, -k, -l$</td>
</tr>
<tr>
<td>K4</td>
<td>0.004</td>
<td>0.004</td>
<td>$-h, k, h+l$</td>
</tr>
</tbody>
</table>

$K1 (hkl) = 0$ 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)
Twinning by Reticular Merohedry

Structure of $\text{K[Au(CN)₂]}$

cell: $7.240 \ 7.240 \ 26.445 \ 90 \ 90 \ 120$, space group $R\overline{3}$

K[Au(CN)₂]

R₁ = 0.074 for 640 F₀ > 4σ(F₀), wR₂ = 0.170 for all 648 data

R₁ = 0.027 for 640 Fo > 4σ(Fo), wR₂ = 0.076 for all 648 data
Residual density: 1.18/-1.48 e/A³
### Warning Signs

#### Systematic Absences Violations:

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>$F_o^2$</th>
<th>$F_c^2$</th>
<th>$\Delta(F^2)/\sigma$</th>
<th>$F_c/F_{c_{\text{max}}}$</th>
<th>Res.(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>8.08</td>
<td>2.00</td>
<td>observed but should be systematically absent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>507.42</td>
<td>32.65</td>
<td>observed but should be systematically absent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>610.89</td>
<td>37.97</td>
<td>observed but should be systematically absent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>517.12</td>
<td>34.48</td>
<td>observed but should be systematically absent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>540.26</td>
<td>33.43</td>
<td>observed but should be systematically absent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>512.14</td>
<td>35.24</td>
<td>observed but should be systematically absent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>-1</td>
<td>-1</td>
<td>557.75</td>
<td>34.37</td>
<td>observed but should be systematically absent</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Most Disagreeable Reflections

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>$F_o^2$</th>
<th>$F_c^2$</th>
<th>$\Delta(F^2)/\sigma$</th>
<th>$F_c/F_{c_{\text{max}}}$</th>
<th>Res.(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3</td>
<td>0</td>
<td>1907.04</td>
<td>407.73</td>
<td>11.79</td>
<td>0.026</td>
<td>2.09</td>
</tr>
<tr>
<td>-1</td>
<td>2</td>
<td>6</td>
<td>7075.12</td>
<td>11145.69</td>
<td>6.78</td>
<td>0.137</td>
<td>2.80</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>6</td>
<td>1275.08</td>
<td>818.27</td>
<td>3.69</td>
<td>0.037</td>
<td>2.80</td>
</tr>
<tr>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>27026.22</td>
<td>32870.20</td>
<td>3.53</td>
<td>0.235</td>
<td>3.60</td>
</tr>
<tr>
<td>-1</td>
<td>2</td>
<td>3</td>
<td>47884.52</td>
<td>56252.36</td>
<td>2.98</td>
<td>0.307</td>
<td>3.35</td>
</tr>
<tr>
<td>-1</td>
<td>2</td>
<td>12</td>
<td>7698.09</td>
<td>9417.93</td>
<td>2.98</td>
<td>0.126</td>
<td>1.88</td>
</tr>
<tr>
<td>-5</td>
<td>4</td>
<td>6</td>
<td>642.68</td>
<td>966.24</td>
<td>2.77</td>
<td>0.040</td>
<td>1.31</td>
</tr>
</tbody>
</table>

Reciprocal Space Plot $l = 2$
**Obverse/Reverse Twinning**

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>I</th>
<th>F</th>
<th>Obv</th>
<th>Rev</th>
<th>All</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0</td>
<td>4252</td>
<td>4264</td>
<td>4282</td>
<td>4258</td>
<td>6399</td>
<td>5663</td>
<td>5715</td>
<td>8516</td>
</tr>
<tr>
<td>N I&gt;3σ</td>
<td>0</td>
<td>2177</td>
<td>2189</td>
<td>2180</td>
<td>2198</td>
<td>3273</td>
<td>1698</td>
<td>1887</td>
<td>4447</td>
</tr>
<tr>
<td>&lt;I&gt;</td>
<td>0.0</td>
<td>303.7</td>
<td>302.2</td>
<td>132.1</td>
<td>303.5</td>
<td>245.8</td>
<td>93.4</td>
<td>246.6</td>
<td>341.6</td>
</tr>
<tr>
<td>&lt;I/σ&gt;</td>
<td>0.0</td>
<td>6.0</td>
<td>6.0</td>
<td>5.4</td>
<td>6.0</td>
<td>5.8</td>
<td>3.3</td>
<td>4.2</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Obverse/reverse test for trigonal/hexagonal lattice

Mean I: obv only 619.5, rev only 252.1, neither obv nor rev 0.5,

Preparing dataset for refinement with BASF 0.289 and TWIN -1 0 0 0 -1 0 0 1

Reflections absent for both components will be removed
# Possible Twin Laws

<table>
<thead>
<tr>
<th>True Laue Group</th>
<th>Apparent Laue Group</th>
<th>Twin Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \overline{3} )</td>
<td>6/mmm</td>
<td></td>
</tr>
<tr>
<td>( 0 -1 0 )</td>
<td>( -1 0 0 )</td>
<td>( 0 0 -1 )</td>
</tr>
<tr>
<td>( 0 1 0 )</td>
<td>( 1 0 0 )</td>
<td>( 0 0 -1 )</td>
</tr>
<tr>
<td>( -1 0 0 )</td>
<td>( 0 -1 0 )</td>
<td>( 0 0 1 )</td>
</tr>
</tbody>
</table>

\( R\overline{3} \Rightarrow \text{Systematic Absences: } -h + k + l = 3n \)

- \( 0 1 0 \quad 1 0 0 \quad 0 0 -1 \) \( \Rightarrow \text{merohedral twin} \)
- \( 0 -1 0 \quad -1 0 0 \quad 0 0 -1 \) \( \Rightarrow \text{obverse/reverse twin} \)
- \( -1 0 0 \quad 0 -1 0 \quad 0 0 1 \) \( \Rightarrow \text{obverse/reverse twin} \)
Obverse/Reverse Twinning

Analysis of Fα/Fc Data for Unaccounted (Non)Merohedral Twinning for: hp33

Cell: 0.71073 7.240 7.240 26.445 90.00 90.00 120.00 Spgr: R3
Criteria: DeltaI/SlgmaI, GT, 4.0, DeltaTheta 0.10 Deg., NselMin = 50
N(refl) = 648, N(selected) = 50, IndMax = 5, CrtTI = 0.1, CrtIT = 0.10

2-axls ( 0 1 0 ) [ 1 2 0 ], Angle () = 0.00 Deg., Freq = 50

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

DEL-A = -0.044

2-axls ( 0 0 1 ) [ 0 0 1 ], Angle () = 0.00 Deg., Freq = 46

-1 0 0 0 -1 0 0 0 1

DEL-A = -0.099

2-axls ( 1 -2 0 ) [ 0 -1 0 ], Angle () = 0.00 Deg., Freq = 50

0 1 0 1 0 0 0 0 -1

DEL-A = 0.000

Examples
Refinement as Twin

SHELXL-97:

<table>
<thead>
<tr>
<th>TWIN</th>
<th>0-1 0 -1 0 0 0 -1</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASF</td>
<td>0.3</td>
</tr>
<tr>
<td>HKLF</td>
<td>5</td>
</tr>
</tbody>
</table>

SHELXL-13

<table>
<thead>
<tr>
<th>TWIN</th>
<th>0-1 0 -1 0 0 0 -1</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASF</td>
<td>0.3</td>
</tr>
<tr>
<td>HKLF</td>
<td>4</td>
</tr>
</tbody>
</table>
## Refinement as Twin

<table>
<thead>
<tr>
<th>TWIN</th>
<th>0-1 0 -1 0 0 0-1</th>
<th>TWIN</th>
<th>-1 0 0 0-1 0 0 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASF</td>
<td>0.3</td>
<td>BASF</td>
<td>0.3</td>
</tr>
</tbody>
</table>

- **R1** = 0.0215
- **wR2** = 0.0533
- **BASF** = 0.284(1)
- **Res. Dens.** = 0.75 e/Å³
- **BASF** = 0.0510
- **wR2** = 0.1433
- **BASF** = 0.278(3)
- **Res. Dens.** = 2.88 e/Å³

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