Introduction to Twinning

Twinning

Göttingen, Februar 1st, 2012

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“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

Question 1

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

Question 1

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.

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

Reciprocal Space Plot l = 0
Question 2

What is the twin law?
**Question 2**

**What is the twin law?**

<table>
<thead>
<tr>
<th>Twin Law</th>
<th>True Apparent Twin Law</th>
</tr>
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<tbody>
<tr>
<td>Laue Group</td>
<td></td>
</tr>
<tr>
<td>4/m</td>
<td>4/mmm</td>
</tr>
<tr>
<td>3</td>
<td>31m</td>
</tr>
<tr>
<td>3</td>
<td>3m1</td>
</tr>
<tr>
<td>3</td>
<td>6/m</td>
</tr>
<tr>
<td>3</td>
<td>6/mmm</td>
</tr>
<tr>
<td>m3</td>
<td>m3m</td>
</tr>
</tbody>
</table>

**Merohedral Twin Laws**

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 \(|E - 1|\)
   - 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 k = 0**
Reciprocal Space Plot $k = 0$

Question 3

**What is the twin law?**

1. Twinning by **rectangular merohedry**
   
   e.g. obverse/reverse twinning in case of a rhombohedral crystal

3. Twinning by **reticular merohedry**
   
   e.g. obverse/reverse twinning in case of a rhombohedral crystal
Reciprocal Space Plot $l = 1$

Definition

Classification

Tests

Solution

Refinement

Warning Signs

Reciprocal Space Plot $l = 1$

Obverse/Reverse Twinning

Systematic Absences:

 Domain 1:  
  \(-h + k + l = 3n\)  
  \(-h + k + l \neq 3n\)  
  \(h - k + l \neq 3n\)  
  Domain 1

 Domain 2:  
  \(-h + k + l \neq 3n\)  
  \(h - k + l = 3n\)  
  \(h - k + l \neq 3n\)  
  Domain 2

\(h - k + l = 3n\)  
\(-h + k + l = 3n\)  
\(h - k + l = 3n\)  
1 and 2

\(\rightarrow HKLF 5\)
**Question 4**

**What is the twin law?**

1. **1 1 0 0 -1 0 0 0 1**
2. **-1 0 0 1 1 0 0 0 1**
3. **0 -1 0 -1 0 0 0 0 1**
4. **-1 -1 0 0 1 0 0 0 -1**
5. **1 0 0 -1 -1 0 0 0 -1**
6. **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°
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
**Definition**

**Classification**

**Tests**

**Solution**

**Refinement**

**Warning Signs**

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**Integration**

- exact overlaps
- partial overlaps
- non-overlaps

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**Integration**

- exact overlaps
- partial overlaps
- non-overlaps

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**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
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

Tests for Twinning: XPREP

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

| Test | R(int) | <|E^2-1|> | TWIN | BASF |
|------|--------|---------|------|------|
| 1 | 0.039(801)/0.316(478) | 0.624/0.517 | TWIN 0 -1 0 -1 0 0 0 -1 | BASF 0.205 [C] or 0.124 [NC] |
| 2 | 0.039(801)/0.406(444) | 0.624/0.525 | TWIN 0 1 0 1 0 0 0 -1 | BASF 0.113 [C] or 0.008 [NC] |
| 3 | 0.039(801)/0.103(488) | 0.624/0.617 | TWIN -1 0 0 -1 0 0 0 1 | BASF 0.319 [C] or 0.269 [NC] |
| 4 | 0.316(478)/0.097(228) | 0.517/0.523 | TWIN -1 0 0 -1 0 0 0 1 | BASF 0.346 [C] or 0.304 [NC] |
| 5 | 0.406(444)/0.114(262) | 0.525/0.527 | TWIN -1 0 0 -1 0 0 0 1 | BASF 0.360 [C] or 0.322 [NC] |
| 6 | 0.103(488)/0.478(218) | 0.617/0.516 | TWIN 0 1 0 1 0 0 0 -1 | BASF 0.178 [C] or 0.090 [NC] |
### Test for Merohedral Twinning

<table>
<thead>
<tr>
<th>Test Case</th>
<th>Classification</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1] -3 / -31m:</td>
<td>R(int) 0.039(801)/0.316(478), $&lt;</td>
<td>E^2-1</td>
</tr>
<tr>
<td></td>
<td>TWN 0 1 0 0 0 0 1</td>
<td>BASF 0.205 [C] or 0.124 [NC]</td>
</tr>
<tr>
<td>[2] -3 / 3m1:</td>
<td>R(int) 0.039(801)/0.406(444), $&lt;</td>
<td>E^2-1</td>
</tr>
<tr>
<td></td>
<td>TWN 0 1 0 0 0 0 1</td>
<td>BASF 0.113 [C] or 0.008 [NC]</td>
</tr>
<tr>
<td>[3] -3 / 6/m:</td>
<td>R(int) 0.039(801)/0.103(488), $&lt;</td>
<td>E^2-1</td>
</tr>
<tr>
<td></td>
<td>TWN -1 0 0 1 0 0 0 0 1</td>
<td>BASF 0.319 [C] or 0.269 [NC]</td>
</tr>
<tr>
<td>[4] -31m / 6/mmm:</td>
<td>R(int) 0.316(478)/0.097(228), $&lt;</td>
<td>E^2-1</td>
</tr>
<tr>
<td></td>
<td>TWN -1 0 0 1 0 0 0 1</td>
<td>BASF 0.346 [C] or 0.304 [NC]</td>
</tr>
<tr>
<td>[5] -3m1 / 6/mmm:</td>
<td>R(int) 0.406(444)/0.114(262), $&lt;</td>
<td>E^2-1</td>
</tr>
<tr>
<td></td>
<td>TWN -1 0 0 1 0 0 0 1</td>
<td>BASF 0.360 [C] or 0.322 [NC]</td>
</tr>
<tr>
<td>[6] 6/m / 6/mmm:</td>
<td>R(int) 0.103(488)/0.478(218), $&lt;</td>
<td>E^2-1</td>
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<td></td>
<td>TWN 0 1 0 0 0 0 0 1</td>
<td>BASF 0.178 [C] or 0.090 [NC]</td>
</tr>
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### Tests for Twinning: Todd Yeates

**Twinning Server**

http://www.doe-mbi.ucla.edu/Services/Twinning

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**Perfect Twins ($\alpha = 0.5$)**

- Acentric data:
  - $<I^2>/<I>= 2$ for untwinned data
  - $<I^2>/<I>= 1.5$ for twinned data

- Centric, untwinned
  - $L = \frac{I(h_1) - I(h_2)}{I(h_1) + I(h_2)}$
  - $h_1$ and $h_2$ proximally located in reciprocal space
  - $L = \frac{1}{2}$

- Centric, perfectly twinned
  - $L = \frac{3}{8}$

- Non-centrosymmetric structures:
  - $\alpha = \frac{1}{2}[1 - 2<|H|>/(\pi/2)]$ and $\alpha = \frac{1}{2}[1 - (2<|H|>)/\pi]$}

- Only possible for partial twins ($\alpha \neq 0.5$)

**Japanese twin structure:**


Local Intensity Test

X = |L|
Y = N(|L|) acentrics
DATAMAN Local Intensity Statistics Plot
Cumulative N(|L|) vs. |L| (acentrics)
Dataset P32 File P32.hkl
Comment Read from P32.hkl

<|L|> = 0.388
Perfectly twinned = 0.375

<|E^2-1|> = 0.981
TWIN 0 1 0 0 0 0 -1
BASF 0.043 [C] or -0.082 [NC]

Wrong Merging

[1] 4/m / 4/mmm: R(int) 0.052(20645)/0.794(1070),
<|E^2-1|> 0.981/0.729
TWIN 0 1 0 0 0 0 -1
BASF 0.043 [C] or -0.082 [NC]

Perfect Twinning or Higher Symmetry

[1] 4/m / 4/mmm: R(int) 0.000(0)/0.047(12539),
<|E^2-1|> 0.763/0.765
TWIN 0 1 0 0 0 0 -1
BASF 0.409 [C] or 0.384 [NC]

PLATON -TwinRotMat

www.mit.edu/platon_v40505/platon/docs/platon/pl000315.html
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>24004</td>
<td>23981</td>
<td>24079</td>
<td>36032</td>
<td>31915</td>
<td>31944</td>
<td>147964</td>
<td></td>
</tr>
<tr>
<td>N I&gt;3σ</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>
<td></td>
</tr>
<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/σ&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 -1 0 0 0 1
Reflections absent for both components will be removed

Twin Refinement in SHELXL-97

Method of Pratt, Coyle and Ibers:

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

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

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

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

or

MERG 0
BASF k2 k3 ... kn
HKLF 5


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

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

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


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 \(|E^2 - 1| \ll 0.736\)
- 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
- $K = \text{mean}(F_o^2)/\text{mean}(F_c^2)$ is systematically high for reflections with low intensity
- For all of the most disagreeable reflections $F_o \gg F_c$.
- Strange residual density, which could not be resolved as solvent or disorder.


Acknowledgements

George Sheldrick