**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:
\[ \{ \hat{E} = \hat{T}_1, \hat{T}_2, \ldots \hat{T}_n \} \]

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

\[ \{ a_1^*, a_2^*, a_3^* \} \xrightarrow{\hat{E}} \{ a_1^*, a_2^*, a_3^* \} \]

\[ \{ a_1^*, a_2^*, a_3^* \} \xrightarrow{\hat{T}_2} \{ \hat{T}_2 a_1^*, \hat{T}_2 a_2^*, \hat{T}_2 a_3^* \} \]

\[ \ldots \]

\[ \{ a_1^*, a_2^*, a_3^* \} \xrightarrow{\hat{T}_n} \{ \hat{T}_n a_1^*, \hat{T}_n a_2^*, \hat{T}_n a_3^* \} \]

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 → subgroup relations:

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

Twinning operations:

\( \{ \hat{E} \equiv \hat{T}_1, \hat{T}_2, \cdots \hat{T}_n \} \)

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 $H$:

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

$4^+ 0,0,z$, $4^- 0,0,z$, $2 x,x,0$, $2 x,\bar{x},0$

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

$\bar{4}^+ 0,0,z$, $\bar{4}^- 0,0,z$, $m x,\bar{x},0$, $m x,x,0$
Diffraction pattern combines **intensities** of twin individuals.

Structure factor of a merohedric twin:

\[ \mathcal{F}^2(H) = v_1 F^2(H \cdot T_1) + v_2 F^2(H \cdot T_2) + \ldots + v_n F^2(H \cdot T_n) \]

where \( v_i \) are domain fractions  

\( T_i \) are twin operations  

The sum of domain fractions \( \sum v_i = 1 \)

Symmetry element of the crystal structure:

\( S_i \in G \Rightarrow |F(H \cdot S_i)| = |F(H)| \)

Transformation of the structure factor of a twin:

\[ \mathcal{F}^2(H \cdot S_i) = v_1 F^2(H \cdot S_i \cdot T_1) + v_2 F^2(H \cdot S_i \cdot T_2) + \ldots + v_n F^2(H \cdot S_i \cdot T_n) \]

The condition \( \mathcal{F}^2(H \cdot S_i) = \mathcal{F}^2(H) \) is fullfilled only when  

\[ H \cdot S_i \cdot T_k = H \cdot T_k \cdot S_j \Rightarrow S_j = T_k^{-1} \cdot S_i \cdot T_k \]

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:

\[ v_1 = v_2 = v_3 \ldots = v_n = 1/n \]
Fourier coefficients for twin

\[ F_{obs}(H) = \frac{\mathcal{F}_{obs}(H) F_{calc}(H)}{\mathcal{F}_{calc}(H)} \]

\[ F_{obs}(H) = \sqrt{\mathcal{F}_{obs}^2(H) - v_2 F_{calc}^2(H \cdot T_2) \ldots - v_n F_{calc}^2(H \cdot T_n)} \]

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

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

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: $m_x$
2$^{nd}$ domain fraction: 50%
Twins with partial overlaps (m > 3)
$Y(HP_2O_7)(H_2O)_3$
Cell parameters: 6.422 6.890 9.817 81.65 80.27 88.35; symmetry: P-1

Twinning matrix:
\[
\begin{pmatrix}
-1.0000 & 0.0517 & 0.0000 \\
0.0000 & 1.0000 & 0.0000 \\
0.0000 & 0.4161 & -1.0000
\end{pmatrix}
\]
(h' = $T\cdot h$, h is a column)
Rot= 180° around $b$
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:

\[
W = \begin{pmatrix}
-1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & -1 & 0 \\
0 & 1 & 0 & 0 \\
\end{pmatrix}, \quad H^1 = H^2 W
\]
Sometimes the splitting is tiny.
In this case it would be hidden for normal CCD measurement.

\[
\text{NiCd(CN)}_4\text{O}_3
\]

Cell parameters: 8.522 16.012 7.651 90 90.32 90
Symmetry: C2/c(α0γ)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
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.

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: \((-1 \ 0\ 0.733| \ 0\ -1\ 0| \ 0\ 0\ 1)\)
Frame scaling, absorption correction: done with software of diffractometer

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%

\[ \begin{pmatrix} h' \\ k' \\ l' \end{pmatrix} = \begin{pmatrix} -1 & 0 & -0.733 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix} \]
3. Discarding partially overlapped reflections: \( R \approx 4\% \)
Where to stop?
We want to discard as little reflections as possible

<table>
<thead>
<tr>
<th>$L1$</th>
<th>$L2$</th>
<th>$R_{obs}$</th>
<th>$GOF$</th>
<th>discarded</th>
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<td>8.2</td>
<td>0</td>
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<td>0</td>
<td>12.7</td>
<td>4.7</td>
<td>0</td>
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</tr>
<tr>
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<td>0</td>
<td>7.1</td>
<td>3.5</td>
<td>0</td>
</tr>
<tr>
<td>0.4</td>
<td>0</td>
<td>9.8</td>
<td>5.5</td>
<td>0</td>
</tr>
<tr>
<td>0.35</td>
<td>0</td>
<td>9.6</td>
<td>5.4</td>
<td>0</td>
</tr>
<tr>
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<td>0</td>
<td>9.3</td>
<td>5.3</td>
<td>0</td>
</tr>
<tr>
<td>0.3</td>
<td>0.4</td>
<td>6.9</td>
<td>3.6</td>
<td>778</td>
</tr>
<tr>
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<td>0.5</td>
<td>7.4</td>
<td>3.8</td>
<td>1264</td>
</tr>
<tr>
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<td>0.6</td>
<td>7.9</td>
<td>4.1</td>
<td>1916</td>
</tr>
<tr>
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<td>0.3</td>
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<td>0.4</td>
<td>5.7</td>
<td>3.0</td>
<td>1193</td>
</tr>
<tr>
<td>0.15</td>
<td>0.3</td>
<td>5.3</td>
<td>2.4</td>
<td>709</td>
</tr>
<tr>
<td>0.1</td>
<td>0.3</td>
<td>4.8</td>
<td>1.9</td>
<td>1120</td>
</tr>
</tbody>
</table>
| 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
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

\[
\begin{align*}
\mathbf{a} &= 10.89451(0.00058) \\
\mathbf{b} &= 10.88937(0.00058) \\
\mathbf{c} &= 8.80485(0.00041) \\
\alpha &= 90.00104(0.00407) \\
\beta &= 90.02358(0.00406) \\
\gamma &= 119.94547(0.00557) \\
V &= 905.11 
\end{align*}
\]
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
Triclinic -1  5.68/5.74  2752/3790  2.937
Monoclinic-setting "c" 2/m
Trigonal -3
Trigonal -31m
Trigonal -3m1
Hexagonal 6/m

Averages made from 7492/1

Select space group

<table>
<thead>
<tr>
<th>Space group</th>
<th>obs/all</th>
<th>ave(I/sig(I))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P6/mmm</td>
<td>0/0</td>
<td>0.000/0.000</td>
</tr>
<tr>
<td>P-62m</td>
<td>0/0</td>
<td>0.000/0.000</td>
</tr>
<tr>
<td>P-6m2</td>
<td>0/0</td>
<td>0.000/0.000</td>
</tr>
<tr>
<td>P6mm</td>
<td>0/0</td>
<td>0.000/0.000</td>
</tr>
<tr>
<td>P622</td>
<td>0/0</td>
<td>0.000/0.000</td>
</tr>
<tr>
<td>P6322</td>
<td>1/13</td>
<td>4.311</td>
</tr>
<tr>
<td>P63/mmc</td>
<td>51/532</td>
<td>7.874</td>
</tr>
</tbody>
</table>

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
The discarded symmetry operations will be used as twinning operations. They are two -> we have created three-fold twin.
Finally a transformation is offered to standard symmetry Cmcm. We can check new cell parameters in EditM50.
Header of M95 now contains transformation from hexagonal to new orthorhombic elementary cell. It is applied when making M90 before merging of reflections.
Flags in M90 show that all reflections are indexed in the first domain. This is correct because the twin is merohedric.
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?
### Summary of systematic extinctions

- **n(all):** 883, **n(obs):** 81
- **Average(I/Sig(I)):** 1.12

**List of the strongest absent reflections:**

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>I</th>
<th>Sig(I)</th>
<th>I/Sig(I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>20.3</td>
<td>0.7</td>
<td>29.0</td>
</tr>
<tr>
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<td>0</td>
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<td>0.8</td>
<td>22.8</td>
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<tr>
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</tr>
<tr>
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<td>0.8</td>
<td>20.8</td>
</tr>
<tr>
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</tr>
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<td>0</td>
<td>16.8</td>
<td>0.9</td>
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</tr>
<tr>
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<td>1</td>
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<td>9.7</td>
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</tr>
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<td>0.9</td>
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<td>1</td>
<td>0</td>
<td>15.6</td>
<td>0.9</td>
<td>16.4</td>
</tr>
</tbody>
</table>

### 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
M95 with all transformations cumulated

M90 should contain three domains: 1,2,3
Solution with Superflip

Correction of false Li

Final refinement: $R \sim 2.5\%$