Algorithms and methods for the handling of twin crystals

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http://www.cryst.chem.uu.nl/lutz/twin/twin_lit.html
Outline

• Introduction
• Coset decomposition to find twin laws
• Le Page algorithm
• Non-systematic extinctions
• ROTAX
• TwinRotMat
• Difference Fourier synthesis
Definition

Twinning is the oriented association of two or more individuals of the same crystalline phase, in which pairs of individuals are related by a geometrical operation termed *twin operation*.

http://www.lcm3b.uhp-nancy.fr/mathcryst/twins.htm
Non-merohedral Twins

- Twin operation does not belong to the Laue group or point group of the crystal.
- Reflections of the two lattices do not overlap exactly.
- Indexing software can be used to find the twin operation:
  - Dirax (A.J.M. Duisenberg)
  - Cellnow (G.M. Sheldrick)
- Non-merohedral twins should be handled by the integration software.
(Pseudo-)merohedral Twins

• The reciprocal lattices of all twin components superimpose.
• Consequently, the diffraction pattern is similar to a single crystal.
• Intensities of the Bragg reflections are modified due to the twinning.
• The (point group) symmetry of the crystal is lower than the symmetry of the lattice.
Coset decomposition

Acta Cryst. A43, 564-568
Point groups

• Good news: here, only point groups matter!
Oviedo (19-8-2011)
Holohedries

• We call the maximum point symmetry of a crystal system “holohedry”. It is thus the point symmetry of the lattice.

• Consequently, there are seven holohedries:
  – cubic: m-3m
  – hexagonal : 6/mmm
  – tetragonal : 4/mmm
  – trigonal : -3m
  – orthorhombic : mmm
  – monoclinic : 2/m
  – triclinic : -1
Definitions

• **Merohedral twins**: The twin element belongs to the holohedry of the lattice, but not to the point group of the crystal. Reflections overlap exactly.

• **Pseudo-merohedral twins**: The symmetry of the crystal belongs to a different holohedry as the symmetry of the lattice. Overlap of reflections is only approximate and depends on temperature, pressure, impurities, etc.
Theory

- $H$ is the (point group) symmetry of the crystal.
- $G$ is the (point group) symmetry of the lattice.
- $H$ is a subgroup of $G$.
- The coset decomposition of $G$ with respect to $H$ gives the possible twin operations.
Procedure

• the subgroup $H$ is the first coset
• if $g_2 \in G$ and $g_2 \notin H$, then $g_2H$ is the second coset
• if $g_3 \in G$ and $g_3 \notin H$ and $g_3 \notin g_2H$ then $g_3H$ is the third coset
• continue until no element of $G$ is left
Example

M. Lutz (2010). *Acta Cryst.* **C66**, m330-m335
Room temperature: P-31c

\[
\begin{array}{c}
\text{[N}_2\text{M(N}_2\text{)}_2\text{SO}_4^{2-}]^2+
\
M = \text{Zn, C}
\end{array}
\]
Zinc complex

Room temperature: P-31c
Low temperature: P-3 (twinned)

High temperature: sulfate disordered (D$_3$ site)
Low temperature: sulfate ordered (C$_3$ site)

Metric symmetry: 6/mmm
Crystal symmetry: -3
Zinc complex

• Supergroup 6/mmm
  \{1, 3^+, 3^-, 2, 6^-, 6^+; 2, 2, 2, 2, 2, -1, -3^+, -3^-, m, -6^-, -6^+, m, m, m, m, m, m}\n
• 4 Cosets
  \{1, 3^+, 3^-, -1, -3^+, -3^-\} \cup
  \{2, 6^-, 6^+, m, -6^-, -6^+\} \cup
  \{2, 2, 2, m, m, m\} \cup
  \{2, 2, 2, m, m, m\}

• **Note:** Bilbao Crystallographic Server helps! (In the moment, there is only coset decomposition of space groups).
Important: The 4 cosets are provided for \((x,y,z)\).
To use it on \((h,k,l)\) you must use the transpose matrix.
Zinc complex
Copper complex

Room temperature: P-31c
Low temperature: P-1 (twinned, non-merohedral)

High temperature: complex and sulfate disordered (D₃ sites)
Low temperature: complex and sulfate ordered (C₁ sites)

Metric symmetry at room temperature: 6/mmm
Crystal symmetry at low temp.: -1 (b=2*a, γ = 119.8°)
Left coset decomposition of the group 191 (P\text{6}/mm\text{m}) with respect to the subgroup 2 (P-1)

\[ G = H + g_1 H + g_2 H + \ldots + g_n H \]

The transformation matrix that relates the basis of the supergroup G=191 (P\text{6}/mm\text{m}) with that of the subgroup H=2 (P-1) is:

\[
\begin{bmatrix}
1 & 0 & 0 & 1 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0
\end{bmatrix}
\]

The cosets in the decomposition of G with respect to H (in the basis of H) are given below:

**Coset 1:**
\[
\begin{array}{l}
(x, y, z) \\
(x, -y, z)
\end{array}
\]

**Coset 2:**
\[
\begin{array}{l}
(-y, x-y, z) \\
(y, -x+y, z)
\end{array}
\]

**Coset 3:**
\[
\begin{array}{l}
(-x+y, -x, z) \\
(x-y, x, -z)
\end{array}
\]

**Coset 4:**
\[
\begin{array}{l}
(-x, -y, z) \\
(x, y, -z)
\end{array}
\]

12 cosets! (5 twin domains occupied.)
Copper complex
Algorithm, Step 1

- As a first step, the metric symmetry must be determined:
Algorithm, Step 2

**Coset decomposition:** Cross-out the operations in \( G \)

Set all operations in \( G \) TRUE

Loop over \( G[i] \)

IF \( G[i] \) is flagged TRUE, then loop over \( H[j] \)

Loop over \( G[k] \). If \( G[k] == G[i]H[j] \) then flag \( G[k] \) as FALSE

END LOOP \( G[k] \)

END LOOP \( H[j] \)

ENDIF

END LOOP \( G[i] \)
Le Page algorithm

*J. Appl. Cryst.* **35**, 175-181
Law of Mallard

• A twin plane is always a lattice plane.
• A twin axis is always a lattice row.

http://www.lcm3b.uhp-nancy.fr/mathcryst/twins.htm
Sublattice

**Problem:** The crystal lattice is sometimes a sublattice of the twin lattice. Because all reflections overlap, it is difficult for the indexing software to determine the correct sublattice.
Twin index

$m_I$, $m_T$: multiplicity of the unit cell (Individual, Twin)

$V_I$, $V_T$: volume of the unit cell (Individual, Twin)

$$\sum = \frac{V_T m_I}{V_I m_T}$$

$m = 1$ (P, R lattice)
$m = 2$ (A, B, C, I lattice)
$m = 4$ (F lattice)

Principles

• The Le Page algorithm for **unit cell reduction** is searching for all twofold axes in a crystal lattice. A vector in the direct lattice is a twofold axis, if there is a collinear vector in the reciprocal lattice (angle between direct and reciprocal vector $\delta = 0^\circ$).

• The Le Page algorithm for **twins** is an extension of this. It searches for twofold axes in sub- and superlattices and $\delta$ is allowed to deviate slightly from $0^\circ$ (obliquity).
Definitions

<table>
<thead>
<tr>
<th>$\Sigma$</th>
<th>$\delta = 0^\circ$</th>
<th>$\delta &gt; 0^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma = 1$</td>
<td>merohedry</td>
<td>pseudomerohedry</td>
</tr>
<tr>
<td>$\Sigma &gt; 1$</td>
<td>reticular merohedry</td>
<td>reticular pseudomerohedry</td>
</tr>
</tbody>
</table>

Mallard’s criterion:

\[ \Sigma \leq 5 \]
\[ \delta \leq 6^\circ \]
Le Page algorithm (1)

- Determine the reduced (primitive) unit cell
  - 7 matrices with $det = 2$
  - 13 matrices with $det = 3$
  - 35 matrices with $det = 4$
Le Page algorithm (2)

\[ h \text{ reciprocal-lattice vector} \]
\[ u \text{ direct-lattice vector} \]
\[ h \times u = 0 \]
\[ h \cdot u = n \]

In unit cell reduction \( n \) can take values of 1 and 2.

In the twin algorithm \( n \) can be larger than 2. The modulus of an index of \( h \) can not exceed \( 3\Sigma \) (\( \Sigma = \text{twin index} \)).
Example 1: djurleite $\text{Cu}_{1.97}\text{S}$

Twin cell: 31.34, 31.34, 26.92, $\alpha=\beta=90^\circ, \gamma=120^\circ$

\[
\begin{pmatrix}
1/4 & -1/4 & 0 \\
-1/2 & -1/2 & 0 \\
0 & 0 & -1
\end{pmatrix}
\]  \hspace{1cm} \text{det} = 1/4

Crystal cell: 13.57, 15.67, 26.92, $\alpha=\beta=\gamma=90^\circ$
Example 2: L-Aspartic acid

Twin cell: 5.1, 6.9, 15.1, $\beta=100^\circ$

$$
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1/2
\end{pmatrix}
$$

$\text{det} = 1/2$

Crystal cell: 5.1, 6.9, 7.55, $\beta=100^\circ$

| Rows  | Products |  |  \\
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>direct</td>
<td>reciprocal</td>
<td>dot</td>
<td>$\delta$</td>
</tr>
<tr>
<td>1 0 0</td>
<td>4 0 -1</td>
<td>4</td>
<td>0.28</td>
</tr>
<tr>
<td>0 1 0</td>
<td>0 1 0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1 0 4</td>
<td>0 0 1</td>
<td>4</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Non-systematic extinctions
Non-systematic extinctions

• Twinned crystal structures are often characterized by non-systematic extinctions.

• Example obverse/reverse twinning
  – oR-lattice: hkl: -h+k+l=3n (2/3 absent)
  – rR-lattice: hkl: h-k+l=3n (2/3 absent)
  – twin lattice: -h+k+l=3n OR h-k+l=3n (1/3 absent)
ROTAX


*J. Appl. Cryst.* **35**, 168-174
Observation: If twinning has been overlooked, all reflections in the list of most disagreeable reflections are characterized by $F_{\text{obs}} \gg F_{\text{calc}}$.

Rotax

• Search for 30 reflections with largest values of $(F_{\text{obs}}-F_{\text{calc}})/\sigma$
• Generate all direct- and reciprocal-lattice vectors with $-12 < h < 12$, $-12 < k < 12$, $0 < l < 12$
• Derive matrices corresponding to twofold rotations about these vectors
• Apply the matrices to $(h,k,l)$ of the 30 reflections
• Calculate a figure of merit based on the distance of $(h',k',l')$ to the nearest lattice point
• Remove non-fitting reflections from the calculation of the figure of merit
Rotax

• If the twin matrix has been determined, it can be used for a twin refinement (not recommended for non-merohedral twins).
• For SHELXL you have to prepare a special reflection file (non-merohedral).
• The programs CRYSTALS and JANA2006 can determine the reflection overlap within the program (non-merohedral).
PLATON - TwinRotMat

http://www.platonsoft.nl/PLATON-MANUAL.pdf
Observation 1: If twinning has been overlooked, all reflections in the list of *most disagreeable reflections* are characterized by $F_{\text{obs}} \gg F_{\text{calc}}$.

Observation 2: Overlapping reflections have (approximately) the same $\theta$ value.
TwinRotMat

- Search for reflections with large values of \( \frac{(F_{\text{obs}}-F_{\text{calc}})}{\sigma} \)
- For every such reflection \((h,k,l)\) search for reflections \((h',k',l')\) with approximately the same theta value.
- Calculate the (reciprocal) rotation axis, which transforms \((h,k,l)\) into \((h',k',l')\)
- Select the rotation axis, which explains most of the observed intensity differences
TwinRotMat

• Only rotation axes, which are independent by symmetry, need to be considered
• A twin operation cannot be part of the point group symmetry of the crystal
• If a reciprocal twin axis is close to a direct axis, the direct axis is tested as well
• For every potential rotation axis, a twin fraction (BASF) and the improvement of the R-value can be calculated
• A HKLF-5 file for the refinement program SHELXL can be written (non-merohedral)
### TwinRotMat

**Analysis of Fo/Fc Data for Unaccounted (Non)Merohedral Twinning for: m029b**

- **Cell:** 20.983 20.983 7.644 90.00 90.00 120.00
- **Spgr:** P-3

**Criteria:**
- DeltaI/SlgmaI GT. 4.0
- DeltaTheta 0.10 Deg.
- NselMln = 50
- N(refl) = 4446, N(selected) = 50, IndMax = 5, CrrlI = 0.1, CrrlT = 0.10

<table>
<thead>
<tr>
<th>2-axls ( 0 0 1 ) [ 0 0 1 ]; Angle ( ) = 0.00 Deg.; Freq. = 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-1.000 -0.000 -0.000) (hl) (h2)</td>
</tr>
<tr>
<td>( 0.000 -1.000 0.000) * (kl) = (k2)</td>
</tr>
<tr>
<td>( 0.000 0.000 1.000) (l1) (l2)</td>
</tr>
<tr>
<td><strong>Nr Overlap:</strong> 4446</td>
</tr>
<tr>
<td><strong>BASF:</strong> 0.53</td>
</tr>
<tr>
<td><strong>DEL-R:</strong> -0.202</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2-axls ( 1 0 0 ) [ 2 1 0 ]; Angle ( ) = 0.00 Deg.; Freq. = 66</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.000 1.000 0.000) (hl) (h2)</td>
</tr>
<tr>
<td>( 0.000 -1.000 -0.000) * (kl) = (k2)</td>
</tr>
<tr>
<td>( 0.000 0.000 -1.000) (l1) (l2)</td>
</tr>
<tr>
<td><strong>Nr Overlap:</strong> 4446</td>
</tr>
<tr>
<td><strong>BASF:</strong> 0.05</td>
</tr>
<tr>
<td><strong>DEL-R:</strong> -0.008</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2-axls ( 1 -2 0 ) [ 0 -1 0 ]; Angle ( ) = 0.00 Deg.; Freq. = 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-1.000 -1.000 -0.000) (hl) (h2)</td>
</tr>
<tr>
<td>( 0.000 1.000 0.000) * (kl) = (k2)</td>
</tr>
<tr>
<td>( 0.000 0.000 -1.000) (l1) (l2)</td>
</tr>
<tr>
<td><strong>Nr Overlap:</strong> 4446</td>
</tr>
<tr>
<td><strong>BASF:</strong> 0.03</td>
</tr>
<tr>
<td><strong>DEL-R:</strong> -0.005</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2-axls ( 3 -1 0 ) [ 5 1 0 ]; Angle ( ) = 0.00 Deg.; Freq. = 21</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.143 0.429 0.000) (hl) (h2)</td>
</tr>
<tr>
<td>(-0.714 -1.143 -0.000) * (kl) = (k2)</td>
</tr>
<tr>
<td>( 0.000 0.000 -1.000) (l1) (l2)</td>
</tr>
<tr>
<td><strong>Nr Overlap:</strong> 642</td>
</tr>
<tr>
<td><strong>BASF:</strong> 0.14</td>
</tr>
<tr>
<td><strong>DEL-R:</strong> -0.003</td>
</tr>
</tbody>
</table>

**m029b**  P -3  R = 0.04

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

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**MenuActive**
Difference Fourier
Difference Fourier Synthesis

• In the case of a twin, the observed structure factors must be corrected.

• The Jana2006 software offers two methods:

\[ F_{obs} = \sqrt{I_{obs} - \sum_{i=2,n} v_i F_{c,i}^2} \]

\[ F_{obs}^{corr} = F_{obs} \frac{F_{calc1}}{F_{calc}} \]