Using APEX2 to Analyze Twinned Crystals

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Innovation with Integrity
Welcome

• What are twins?
  • Types of twinning
  • Warning signs of twinning
• Indexing
  • RLATT
  • Cell_Now
• Integration
• Scaling
• Structure solution
• Structure refinement

Speakers

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What are twins?

- Twins are regular aggregates consisting of individual crystals of the same species joined together in some definite mutual orientation.
Types of twins –
Non-merohedral twin

- Twin operator is arbitrary but often a rotation of 180°
- no exact overlap of reciprocal lattice points
- Close, split and overlapping reflections
- Special tools for cell determination
- Data integration requires more than one orientation matrix
- Structure solution not difficult after “de-twinning”
Types of twins –
Partial merohedral twin

- Twin operator is always(?) a rotation of 180°
- No overlap and exact overlap of reflection in reciprocal space
- Every n-th lattice row overlaps completely
- Special tools for cell determination
- Difficult to index with Cell_now
- Data integration requires more than one orientation matrix
- Structure solution not difficult after “de-twinning”
Types of twins –
Pseudo Merohedral Twin

- Twin operator emulates a higher crystal system than the true crystal system
- Metric symmetry higher than Laue symmetry
- Often low value for E-Value statistics
- Laue group and space group determination may be difficult
- Structure solution may be difficult
Types of twins – Merohedral Twin

- Twin law: symmetry operator of the crystal system but not of the point group of the crystal
- Possible in tetragonal, trigonal, hexagonal and cubic crystal systems
- Exact overlap of reciprocal lattices
- Often low value for E-Value statistics
- Laue group and space group determination may be difficult
- Structure solution may be difficult
Non-Merohedral Twin – Twin operator and Lattice

- Twin operator is a 15° rotation within the paper plane
Partial-Merohedral Twin – Twin operator and Lattice

- Twin operator is a 180° rotation out of the paper plane
Merohedral Twin –
Twin operator and Lattice

• Twin operator is a 180° rotation in the paper plane
“Anthra” –
A Partial Merohedral twin

• Structure existed for room temperature data
• Low temperature data gave a different cell, but structure could not be solved
• Crystals from Arnie Rheingold
“Anthra” –
A Partial Merohedral twin

- Visual inspection of the frames does not suggest twinning
- Unless, maybe, if you already know what you are looking for
“Anthra” – Indexing

- Indexing is straightforward
- Orthorhombic C centered cell
- Overlay looks reasonable
- But if you go down this path the trouble starts!
“Anthra” – Visual Indexing

- Event in RLATT the lattice looks reasonable
- Until one looks along c*
- Why are there alternating rows of wide spacing and narrow spacing?
“Anthra” – Visual Indexing

- This is a partial merohedral twin with the index 2
- Every second row overlaps completely
“Anthra” – Visual Indexing

- Use the lattice overlay tool or the box cursor to mark every second row including the 0 layer
- Assign these reflections to the red group
- Use the lattice overlay tool to select a lattice that includes all red reflections and every second grey reflection
“Anthra” – Visual Indexing

- Use the lattice overlay tool or the box cursor to mark every second row including the 0 layer
- Assign these reflections to the red group
- Use the lattice overlay tool to select a lattice that includes all red reflections and every second grey reflection
"Anthra" – Visual Indexing

- Switch to Unit cell determination and index the “red reflection”
- This gives a smaller Monoclinic unit cell
- This is the unit cell of the first domain
“Anthra” – Visual Indexing

• Switch back to RLATT and change the even layers (complete overlap) from red to grey
“Anthra” – Visual Indexing

- Switch to Unit cell determination and index the “grey reflection”
- This gives a smaller Monoclinic unit cell
- This is the unit cell of the second domain
“Anthra” –
Unit cell overlay

- Incorrect Orthorhombic cell
- Correct Monoclinic cell
  - Domain 1
- Correct Monoclinic cell
  - Domain 2
“Anthra” – Comparing Unit Cells

- The “compare unit cell” plugin calculates the twin law
- The twin operator is a 180° rotation about c*
- The “index 2” of the twin is reflected in the superposition matrix
- \[-1 \ 0 \ 0 \ 0 -1 \ 0 \ 0.5 \ 0 \ 1\]
This is a brute-force algorithm which can index multicomponent nonmerohedral and partial merohedral twins, given enough CPU time.

Multiple random real-space starting vectors $d$ with lengths between user-input limits are refined by iterative linear least-squares refinement.

A weighting scheme strongly downweights reflections that do not fit well and so concentrates the refinement on the better-fitting reflections, which in general will belong to the same twin domain.
• The reflections that do not fit the first twin domain can be used to search for a second domain. The cell for the first domain is rotated to give a good fit to as many of these reflections as possible.

• The rotation required (often 180° about a real or reciprocal axis) provides a description of the type of twinning.

• After assigning reflections to the second domain, the reflections that do not fit either domain may be used to search for a third domain etc. in the same way.

• Cell_now can write the multidomain .p4p file needed for integration of such twins with SAINT.
Input for Cell Now

- Prepare reflection array in APEX2
  - 800-1200 reflections
  - Well-distributed in space
- Write .p4p file
- Open command prompt
  - Sample → Run Command...
Cell_Now
Non-Merohedral Twin

G:\frames\twinning\twin\work>cell_now -t

CELL_NOW - Version 2008/2
-------------------------

- Launch Cell_Now (cell_now -t)
- Input .p4p file name
- Accept defaults or change
- Cell_now calculates best-fit cell
The following cells would appear to be plausible, but should be checked using XPREP because they are not necessarily the conventional cells.

FOM, % within 0.2, a..gamma, volume and lattice type for potential unit-cells:

<table>
<thead>
<tr>
<th></th>
<th>0.100</th>
<th>69.0</th>
<th>5.525</th>
<th>7.079</th>
<th>7.610</th>
<th>80.20</th>
<th>84.30</th>
<th>87.92</th>
<th>291.8</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.821</td>
<td>67.3</td>
<td>5.525</td>
<td>7.079</td>
<td>7.612</td>
<td>80.17</td>
<td>84.25</td>
<td>87.92</td>
<td>291.8</td>
<td>P</td>
</tr>
<tr>
<td>3</td>
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<td>68.3</td>
<td>5.525</td>
<td>7.079</td>
<td>8.930</td>
<td>97.03</td>
<td>122.29</td>
<td>92.08</td>
<td>290.9</td>
<td>P</td>
</tr>
<tr>
<td>4</td>
<td>0.653</td>
<td>69.1</td>
<td>5.525</td>
<td>7.610</td>
<td>8.819</td>
<td>94.27</td>
<td>126.68</td>
<td>95.70</td>
<td>291.7</td>
<td>P</td>
</tr>
<tr>
<td>5</td>
<td>0.586</td>
<td>67.2</td>
<td>5.525</td>
<td>7.079</td>
<td>8.928</td>
<td>97.08</td>
<td>122.27</td>
<td>92.08</td>
<td>290.8</td>
<td>P</td>
</tr>
</tbody>
</table>

**Cell for domain 1:** 5.525  7.079  7.610  80.20  84.30  87.92

**Figure of merit:** 0.623  %(0.1):  58.6  %(0.2):  69.0  %(0.3):  78.7
Cell_Now

- Presentation of candidate cells
- Fit reflections
- Look for centering
- Reorient cell
- Write .p4p file for first domain
- Search for second domain

.p4p or .spin file to write domain to:

?  
bcntw.p4p  
548 reflections within tolerance assigned to domain 1,  
548 of them exclusively; 287 reflections not yet assigned to a domain

Re-refine initial cell (R), search for next domain (S), quit (Q) or choose new cell from list (enter number) [S]:

05.05.2011
Cell_Now: Search for Second Domain

Cell for domain 2: 5.525  7.079  7.610  80.20  84.30  87.92

Figure of merit: 0.964  %(0.1): 96.9  %(0.2): 96.9  %(0.3): 97.6
Rotated from first domain by 179.9 degrees about
reciprocal axis 0.000  0.000  1.000 and real axis -0.128 -0.179 1.000

Twin law to convert hkl from first to this domain (SHELXL TWIN matrix):
-1.000  -0.002  0.001
0.002  -1.000  0.000
-0.255  -0.359  1.000

.p4p or .spin file to write domain to:
? bcntw2.p4p

539 reflections within tolerance assigned to domain 2,
278 of them exclusively;  9 reflections not yet assigned to a domain
Cell_Now: Import to APEX2

- Return to APEX2
- Sample → Import → .p4p
  - Import file created in Cell_Now
  - Import reflections
- Add Bravais Class
  - Determine Unit Cell plug-in
  - Edit → Bravais lattice type
Input for APEX2

- Prepare reflection array in APEX2
- 800-1200 reflections
- Well-distributed in space
- Write .p4p file
- Open command prompt
- Sample
- Run Command
Data integration – SAINT

- SAINT allows integration of up to 8 domains simultaneously
- It will switch into “twinning” mode automatically if more than one orientation matrix is provided
- SAINT will create a HKLF 5 style file (*.mul) that needs further processing with TWINABS
SAINT uses a profile-based twin-pairing method to determine when spots start to overlap.

Multi-component spot overlap is computed based on overlap of the model profiles.

In the case of twin overlaps SAINT estimates the intensities of individual spot components and writes them to the output reflection file.
Data integration – SAINT

- The intensity ESDs are equal for each spot component and correspond to the ESD of the aggregate intensity sum.
- The additional intensity information has been added to increase the information available for scaling and absorption correction with TWINABS and subsequent structure solution and refinement using SHELXTL
Data integration – SAINT integration options

Twin overlap determination
- Minimum common volume
- Separation factor
- Maximum range
Data integration –
SAINT integration options

Minimum Common Value

- The relative overlap of model profile volumes necessary for two spots to be classified as overlapping. The default is 0.04 (4%).
- Lower values produce more overlaps in the output file; higher values, fewer overlaps.
Separation Factor

- The difference vector between the two spot centroids is divided by this factor prior to computation of the overlapping volume.
- Normally, this can be left at its default of 1.0.
- If you find that you need to specify very small relative overlap volumes in order to obtain overlapping spots in the output, you can effectively bring the spots closer together by increasing the separation factor.
- If you do so, specify a larger relative overlap to make the volume calculation more stable.
Twin Box Size Ratio

- This is the maximum range over which spots are considered candidates for overlap, in units of the integration box size.
- The default is 1.3. Normally, this will not need to be changed.
Data integration – SAINT refinement options

- SAINT allows one of two types of inter-component constraints to be applied in twin refinements, to support cases where one or more components exhibit much weaker diffraction than the first component.
Data integration –
SAINT refinement options

Unit cell as component 1
• The first constrains the unit cell parameters a, b, c, alpha, beta, and gamma in the target component to those refined for the first component

All as component 1
• The second constraint is for use in extreme cases where there are too few strong reflections from a component to perform orientation refinement
• On read-in of the .p4p file, the inter-component rotation between the target component and component 1 is determined.
• In subsequent refinements, all parameters of the target component are constrained to those of component 1, then rotated by the fixed inter-component rotation to give the new orientation of the target component.
TWINABS for absorption correction and scaling

- Multiscan method
  - Many sets of equivalent reflections analyzed and scaled.
  - Used for each domain.
- Applied similar to SADABS.
  - Input reduced data from SAINT.
  - Calculate absorption model
  - Apply model to complete data set
  - Write corrected data set to .hkl files
- Output for structure solution and refinement
  - HKLF 4 file for XPREP and structure solution
  - HKLF 5 file for structure refinement
TWINABS: data input

- Choose proper Laue group
- Choose centrosymmetric or noncentrosymmetric model
  - Treat Friedel opposites as equal
    - Centrosymmetric crystal
    - Small anomalous differences
  - Treat Friedel opposites independently
    - Must have strong anomalous differences
- Input file name
- Transformation matrix and space group
  - Transform system to standard setting
  - Eliminate systematic absences from composite reflections
PART 1 - Refinement of parameters to model systematic errors

680 data ( 571 unique ) involve domain 1 only, mean I/\sigma 12.6
669 data ( 566 unique ) involve domain 2 only, mean I/\sigma 11.2
459 data ( 408 unique ) involve 2 domains, mean I/\sigma 14.6

• Data summary
  • Reflections in each domain
  • Singles and Composites
  • Average I/\sigma

• Choose data for error model
  • Enter number of strong domain
  • 0 to use singles from all domains
  • -N to use singles and composites from domain 1 to N
Enter mean(I/sigma) threshold (must be positive) [1.5]:
Highest resolution for parameter refinement [0.1]:
Factor g for initial weighting scheme \( w = 1/(\sigma(I)^2 + (g <I>)^2) \), where \( \sigma(I) \) is estimated by SAINT and \( <I> \) is mean intensity [0.04]:
The following restraint esd should be increased for strong absorbers.
Restraint esd for equal consecutive scale factors [0.005]:
Suitable spherical harmonic orders are 4,1 for weak absorption and 8,5 for strong. Highest even order for spherical harmonics (0,2,4,6 or 8) [6]:
Highest odd order for spherical harmonics (0,1,3,5 or 7) [3]:
Number of refinement cycles [40]:

- Defaults have been carefully chosen
  - Mean I/\( \sigma \)
  - Scale factor g
  - Restraint esd
  - Even/odd order for spherical harmonics
  - Refinement cycles
TWINABS: reject outliers

1808 total and 1545 unique reflections assuming Friedel's law.

High resolution limit [0.1]:
|I-<I>|/su ratio for rejection [4.0]:

\[ g\text{-value for use in: } su^2 = \sigma^2 + (g<I>)^2 \text{ (} \sigma(I) \text{ from SAINT).} \]

This is only used for rejections, not for final \( \sigma(I) \) values [0.04000]:

1808 total and 1545 unique reflections left after |I-<I>|/su test

- Examine rejections
Iterative extraction of best unique reflection data

<table>
<thead>
<tr>
<th>Cycle</th>
<th>N(1)</th>
<th>Rint(1)</th>
<th>N(all)</th>
<th>Rint(all)</th>
<th>Twin fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1081</td>
<td>0.0404</td>
<td>1663</td>
<td>0.0465</td>
<td>0.5458 0.4542</td>
</tr>
<tr>
<td>:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1139</td>
<td>0.0243</td>
<td>1808</td>
<td>0.0261</td>
<td>0.5452 0.4548</td>
</tr>
</tbody>
</table>

N(1) and Rint(1) refer to singles and composites that include domain 1.

Rint = 0.0261 for all 1808 observations and
Rint = 0.0244 for all 1185 observations with I > 3\sigma(I)

- Calculate R(int), twin ratio, intensity data files
TWINABS: prepare .hkl files

Generate HKLF 4 format file (4) with crude averaged intensities for structure, solution or more accurate HKLF 5 format file (5) for refinement, reindex (I), repeat (R) or quit (Q) [5]:

Average equivalent reflections (Y or N) [Y]:
Enter name of output file [twin5.hkl]:
Mu*r of equivalent sphere for additional spherical abs. corrn. [0.2000]:
Make file using domain N only, -N to use domains 1..N or 0 to use all [1]:
Average Friedel opposites in output file (Y or N) [Y]:
Leave out single reflections that also occur in composites (Y or N) [Y]:

1380 Corrected reflections written to file twin5.hkl

Reflections merged according to point-group -1
Minimum and maximum apparent transmission: 0.636559 0.745451

- HKLF 4 format for XPREP and structure solution
- HKLF 5 format for final refinement
XL: structure refinement

TITL twin4 in P-1
CELL 0.71073  5.5072  7.0648  7.5920  80.174  84.069  87.928
ZERR 1.00  0.0015  0.0019  0.0022  0.005  0.006  0.008
LATT 1
basf 0.5
.
(Atom coordinates and other instructions)
.
hklf 5

- Insert BASF scale factor
  - N-1, where N is number of domains
  - Can include racemic twinning (TWINABS)
- Replace HKLF 4 with HKLF 5
  - Include transformation matrix if needed
  - Or repeat TWINABS with matrix and space group
Final Results

Refinement against HKLF 4:
R1= 0.0436 wR2= 0.1035

Refinement against HKLF 5:
R1= 0.0325 wR2= 0.0724
BASF= 0.462(2)
Any Questions?

Please type any questions you may have for our speakers in the Ask a Question panel and click Submit.

Thank you for your attention!

Please give us your feedback. Click View Polls, then Take Poll next to each question, select your answer and send.