Twinning and Incommensurate Data Processing in CrysAlis Pro

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X-ray Product Configurations
Modular Products - Tuned to Application

4-circle Goniometer

X-ray Sources

CCD Detectors
Crystallographic Software: CrysAlis\textsuperscript{Pro}

CrysAlis\textsuperscript{Pro} has been designed to be as simple to use as possible:

- User friendly GUI
- Simple workflow
- Fully integrated platform
- Supporting SM and PX
- Highly automated......
- ...but full of manual features for those who want them
A Perfect Tool from Crystal to Structure!

- Mounting
- Screen/Pre
- Strategy
- Experiment
- Structure
Overview

Twinned data
- Introduction
- Data collection tips
- Diagnosis and indexing tools
- Data reduction

Incommensurate data
- Introduction
- Data collection tips
- Diagnosis and indexing tools
- Data reduction
Introduction to Twinning
Fully overlapped diffraction patterns

*Merohedral twins*

Component 1

Component 2

Overall
Introduction to Twinning
Partially overlapped diffraction patterns

Non-merohedral twins

Component 1

Component 2

Overall
Introduction to Twinning
Partially overlapped diffraction patterns

Multi-crystals – different unit cells

Component 1
Component 2
Overall
Introduction to Twinning

Fully overlapped diffraction patterns can’t be separated at integration

Partially overlapped reflections can be treated during integration
Collecting twinned data

General Tips

• Use copper radiation (where possible and appropriate)
  ➢ Longer wavelength increases peak separation

• Use longer sample to detector distances
  ➢ Again, gives better peak separation

• Use fine slicing
  ➢ This enables better profiling for those peaks which can’t be separated

• Use the twin mode in strategy planner
  ➢ More information enhances success of data processing algorithms

• Use lower detector binning modes
  ➢ Improves spatial resolution improving separation and profile fitting
Twinning Diagnosis

Diffraction and unwarped images
Twinning Diagnosis

Diffraction and unwarped images
Twinning Diagnosis

Lattice Wizard

Indexed percentages

< 85%  Possible twin - check
> 85%  Probably single
Twinning Diagnosis
Automatic indexing will…

1. Attempt to find an orientation matrix which indexes the largest percentage of all peaks
2. Store as first component
3. Attempt to find another orientation of the cell which indexes the largest % of the remaining unindexed (wrong) peaks
4. Store as next unused component
5. Repeat step 3 and 4 until requested number of components (up to 4) have been found
6. Refine cells simultaneously
Twinning
Automatic Indexing

Lattice wizard

Current cell (CSD: 2 hits)
10.0910(10) 8.9344(2) 29.972(2) 90.068(9) 94.886(10) 90.008(10) 90.008(10) 2089.6(4)
Constrained current cell
10.0938(11) 8.9334(17) 29.966(2) 90.0 94.908(9) 90.0 2089.8(6)
Lattice reduction
selected cell
10.0921 6.9388 29.9794 90.1096 94.8911 90.0161 mP 35 reduced cell
6.9328 10.0921 29.9794 94.8911 90.1096 90.0161 2090.2

Peak hunting
Unit cell finding

Twinned explorer - reciprocal space
Reindexation with current cell

Refine instrument model
Lattice transformation

Twinning - multi-crystals
Incommensurates / Quasi-crystals

Load information
Save information

Twinned unit cell finding with options
Twinned indexing

Find cell

Peak table
Normal peak table
T-vector Dirax

Detector
Peak (HKL or I) peak table
Stereo graphic

Sample type
Single crystal
Unit cell limits

Twin / multi-crystal

Agilent Technologies

09/10/2013
Twinning

Indexing results

[Image of software interface showing lattice wizard and UB matrix setup for twins]
Twinning
Indexing problems

Sometimes, with slight rotation of twin components the majority of reflections overlap. This can sometimes confuse indexing routines.
Twinning
Manual indexing with Ewald\textsuperscript{Pro}
Twinning
Manual indexing with Ewald Pro
Twinning
Manual indexing with Ewald\textsuperscript{Pro}

![Ewald Pro interface showing manual indexing process]

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Twinning EwaldPro Video

http://www.agilentxrdforum.com
Twinning Integration

- **Difficulties**
  - Overlap obscures individual peak intensities
  - Data completeness can be too low for structure solution

- **Goals**
  - Extract accurate intensities for all reflections for good refinement results
  - Where possible, accurately deconvolute (de-twin) overlapped peaks to improve completeness
Twinning Integration
Twinning Integration
Twinning Integration

Component 1 contribution
Component 2 contribution
Overall profile
Twinning
Improved Algorithm!!

For Cr ysAlisPro v171.37 .x onwards, the twin processing algorithm has been overhauled

• Faster processing
• Easier to use
• Better results

<table>
<thead>
<tr>
<th>Dataset no.</th>
<th>R1 (old method)</th>
<th>R1 (new method)</th>
<th>Improvement</th>
<th>Overlapped reflections</th>
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<tbody>
<tr>
<td>1</td>
<td>5.9%</td>
<td>3.8%</td>
<td>2.1%</td>
<td>51%</td>
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<td>2</td>
<td>7.0%</td>
<td>5.4%</td>
<td>1.6%</td>
<td>26%</td>
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<td>3</td>
<td>5.4%</td>
<td>4.1%</td>
<td>1.3%</td>
<td>50%</td>
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<td>4</td>
<td>4.0%</td>
<td>2.8%</td>
<td>1.2%</td>
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<td>6</td>
<td>3.2%</td>
<td>2.3%</td>
<td>0.9%</td>
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<tr>
<td>7</td>
<td>6.4%</td>
<td>5.5%</td>
<td>0.9%</td>
<td>92%</td>
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</table>
Twinning integration results
Twinning
Integration output

Exp_1_twinN_HKLF4.hkl
Use for structure solution
Contains:
• Domain N only reflections
• Domain N portion of reflections below full overlap threshold (i.e. de-twinned data)
• Usually N=1 for most purposes but others are available if needed.

Exp_1_twin1_HKLF5.hkl
Use for structure refinement
Contains:
• All reflections
• Any overlapped reflections are not de-twinned
The Twin Problem
Integration treatments – profile size

With typical masks, in this example, few reflections are fully separated…

Component 1 profile mask
Component 2 profile mask
Twinning
Integration treatments – profile size

Using smaller masks can reduce overlap meaning more separate reflections
Twinning
Integration treatments – profile size

Alternatively, if separation is small enough, and depending on the nature of the twin, twinning can sometimes be ignored entirely by *increasing* profile mask sizes and treating as a single crystal.
Twinning
Integration treatments – profile size

Altering profile mask sizes in CrysAlisPro
Twinning
Integration treatments – smart background

• For datasets with uneven backgrounds, smart background can help.

• From v37 upwards, smart background is now twin enabled

• See previous webinar on data reduction at…
  http://www.agilent.com/chem/x-ray_eSeminars
  …for more details
Twinning
Post Integration treatments – overlap threshold

Increasingly difficult deconvolution

De-twinning attempted for structure solution

De-twinning not attempted
Twinning
Post Integration treatments – overlap threshold

Version 36 or lower

Version 37 or higher
Twinning
Additional options

Useful for cases where secondary domain(s) are weak:
- Common scales for all twin components
- Separate scales for all twin components

Useful for cases where structure solution is difficult due to low completeness of separate reflections:
- Use reflections from component 1 only
- Output multi HKLF4 file containing data from twin 1 and twin:
  - #2
  - #3
  - #4

For non-centrosymmetric twins:
Incommensurate Structures

Introduction

• A unit cell describes the smallest repeating pattern of a crystal

• In some cases, whilst some parts agree with the defined unit cell, other parts may not giving rise to a superstructure, i.e. longer-range ordering.
Incommensurate Structures

Introduction

• Superstructures can be broadly categorised as:
  
  • commensurate, long-range ordering is related to a whole number of unit cells
    
    • e.g. satellites at $\frac{1}{2}$ along a particular axis indicate long-range ordering of 2 unit cells.
    
    • processing possible using larger unit cell.
  
  • incommensurate, long range ordering is unrelated to the main unit cell
    
    • e.g. satellites can appear at any fraction position, e.g. 0.312 along an axis
    
    • process using $q$-vectors to describe higher dimensionality of diffraction pattern
Incommensurate Structures

Introduction

- Diffraction effects...
Incommensurate Structures
Data collection

- Use copper radiation (where possible and appropriate)
  - Longer wavelength increases peak separation
  - High intensity enhances weak satellites
- Use longer sample to detector distances
  - Again giving better peak separation
- Use fine slicing
  - This enables better profiling for those peaks which can’t be separated
- Use lower detector binning modes
  - Improves spatial resolution improving separation and profile fitting
Incommensurate Structures

q-vectors

• To index satellite peaks a 1, 2 or 3 dimensional q-vector is used to describe their position relative to the main lattice.

• Here a vector (0.30, 0.00, 0.15) describes the position of the satellites.
Incommensurate Structures

EwaldPro

- Refining and visualising q-vectors
Incommensurate Structures

Ewald\textsuperscript{Pro}

To aid visualisation of satellites, Ewald\textsuperscript{Pro} can set the size of peaks according to their intensity

NaCO reciprocal space
Incommensurate Structures
Indexing with q-vectors
Incommensurate Structures

Processing data

- Advanced processing options
- Data reduction lists allow use of advanced extinction rules with incommensurates and quasicrystals
Incommensurate Structures

Processing data

- Integration setup
- Integration output

Main reflections

Statistics vs resolution - point group symmetry: P2/m (b-unique)

<table>
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<tr>
<th>resolution(A)</th>
<th>measured</th>
<th>kept</th>
<th>unique</th>
<th>average redundancy</th>
<th>mean F2</th>
<th>mean F2/sig(F2)</th>
<th>Rint</th>
<th>Rsigma</th>
<th>RsigmaA</th>
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<td>772</td>
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<td>1404</td>
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| inf-0.81      | 9479     | 9398 | 1060   | 8.9                | 62591.22  | 16.19           | 0.027| 0.028  | 0.027   |
| inf-0.82      | 9406     | 9326 | 1020   | 9.1                | 63057.36  | 16.29           | 0.027| 0.028  | 0.027   |

Satellite reflections

Statistics vs resolution - point group symmetry: P2/m (b-unique)

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<td>429</td>
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<td>18996.45</td>
<td>9.11</td>
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<td>0.056</td>
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<td>8.64</td>
<td>0.051</td>
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<td>0.087</td>
<td>0.080</td>
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<td>6.62</td>
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<tr>
<td>0.95-0.91</td>
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<td>3333.17</td>
<td>4.45</td>
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<td>0.129</td>
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<td>0.110</td>
<td>0.117</td>
<td>0.145</td>
</tr>
</tbody>
</table>

| inf-0.81      | 38265    | 38081 | 4241 | 9.0                | 13850.78 | 7.37         | 0.051| 0.067  | 0.068   |
| inf-0.82      | 38246    | 38062 | 4227 | 9.0                | 13853.90 | 7.37         | 0.051| 0.068  | 0.068   |
Incommensurate Structures
Jana Integration

http://www.agilent.com/chem/library
Search ‘xrd’ for all application notes
Software Updates

- **CrysAlisPro** is frequently updated with fixes for known problems
- New features are introduced in annual major updates
- All updates are **Free** and available from our user forum, www.agilentxrdforum.com
- **Free** multi-user, multi-site license
Please type your question into the chat box. Send a direct chat to the “Host” which is private, or a chat to “All Participants” which is public.
Q&A

Please type your question into the chat box. Send a direct chat to the “Host” which is private, or a chat to “All Participants” which is public.
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All feedback and comments are welcome

» xrdapplications@agilent.com

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