

Training for single crystal XRD

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The Team

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Internet: <http://isic.epfl.ch/X-Ray>

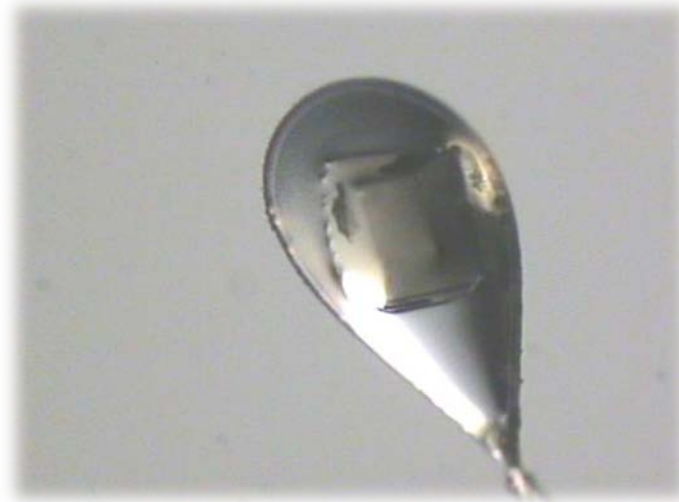
The Instrument



Rigaku Supernova
2 micro-sources, CCD detector,
kappa goniometer,
low temperature device

Single crystal (choose and mount)

- Crystals usually appear as unadulterated, homogenous and with ***well-defined geometric shapes (habits)*** when they are well-formed. However their external morphology is not sufficient to evaluate the crystallinity of a material.
- Crystals are mounted in loops
- Other techniques are also available (capillaries, etc...)



Software

- CrysAlis(Pro)

This software is free of charge and can be downloaded here:

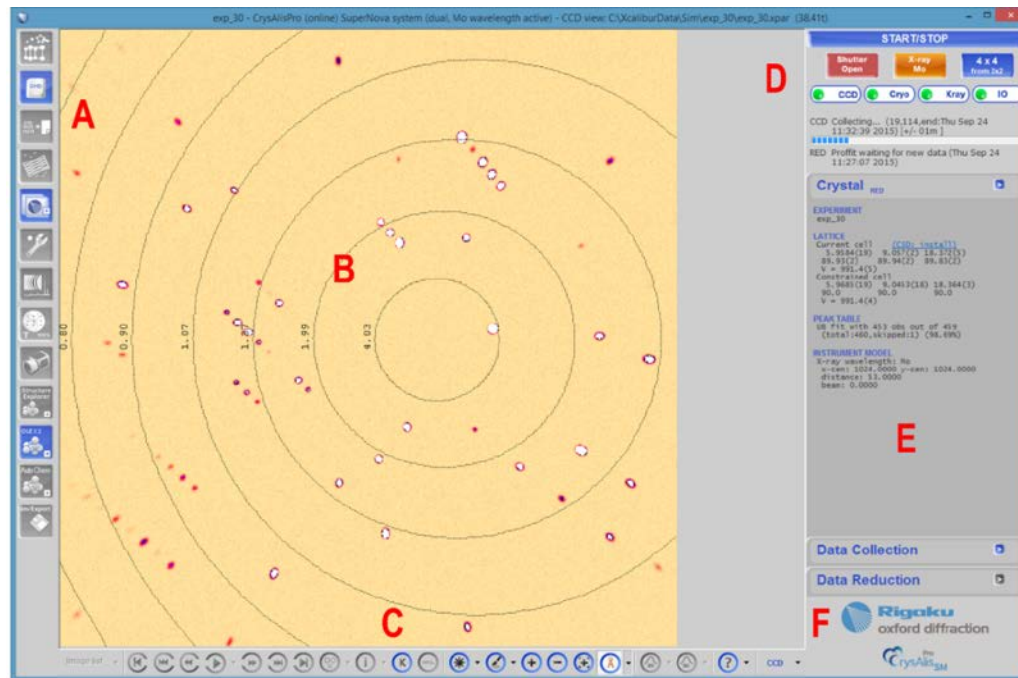
<https://www.rigakuxrayforum.com/> (after registration)

It is divided into two main parts (Online and Offline)

Online takes care about the instrument and the data collection

Offline (RED) allows the user to treat the data

Main Tools of the software



A: **Power tools**: access to the lattice wizard, command shell etc..

B: **Main window**: shows current frame in online mode, and selected frame in offline mode.

C: **Layout and controls**: allows user to scroll through frames, get peak information, change brightness, and use peak profile tools

D: **Device control**: Only shown in the online mode of the software, and shows status of the instrument

E: Provide information about the current unit cell, data collection progress, and a summary of the data reduction.

F: **SM/PX button**: allows the user to switch the software between small molecule and protein modes.

Screening a crystal

SM Screening

Screening

Mount **Screening** >

PEAKS
0 peaks found

UNIT CELL
cell not found

QUALITY
not evaluated

Experiment - Complete data for publication

Name: exp_31

Detector=53.0mm, Res. = 0.837Ang, I/sig =15.0, width=1.0deg, Movie, cryo off, Strategy: Complete data (default mode), Exposure: 2.0s 8.0s

Exposure time: 2.0 s

What is this? **Pre-Exp. (4 m)** **Edit**



SM Screening

Screening

Mount **Screening** >

PEAKS
UB fit with 70 obs out of 76 (92.1%)

UNIT CELL **CSD: 10+0L**

PG: mmm orthorhombic P

5.966(11)	9.04(2)	18.22(5)
90.2(2)	90.26(18)	90.13(18)

V = 983(4)

QUALITY

Resolution(A)	N	I/sig	I/sig0
inf - 1.22	45	128.3	128.3
1.26- 1.22(last)	9	105.9	105.9

Well diffracting sample

Diff. limit: beyond 1.22 (theta res. limit) for I/sig=2.0

Mosaicity: e1=1.3, e2=1.4, e3=2.0 (deg), Iso=1.56 (deg)

Experiment - Complete data for publication

Name: exp_31

Detector=53.0mm, Res. = 0.837Ang, I/sig =15.0, width=1.0deg, Movie, cryo off, Strategy: Complete data (default mode), Exposure: 1.0s 4.0s

Exposure time: 1.0 s

What is this? **Pre-Exp. (2 m)** **Edit**

First **start** a new measurement on the online version, then **mount** and center your crystal.

The screening window will tell you how many peaks have been indexed, it will display the cell parameters and evaluate its quality (based on the intensity of the peaks). If the crystal is good then proceed to the pre-experiment by clicking edit

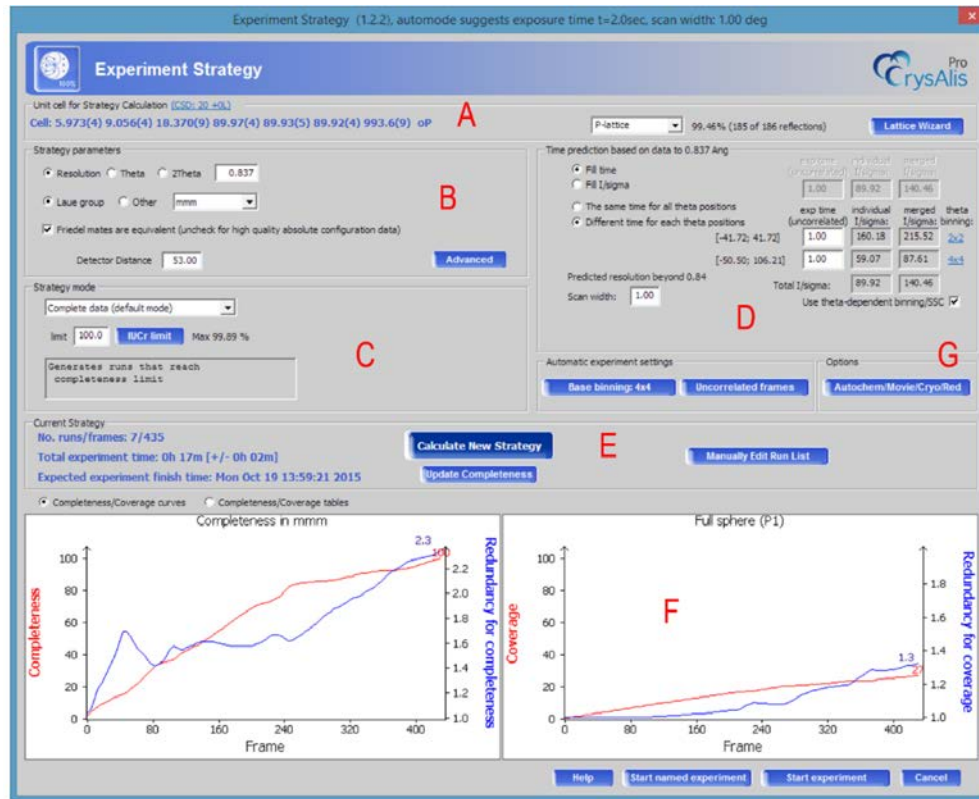
Pre-experiment

The screenshot shows the 'Pre-experiment' window of the Rigaku Oxford Diffraction software. The window title is 'Rigaku Oxford Diffraction fast screening options (1.0.1)'. The interface includes a header with the 'CrysAlis Pro' logo and a 'Pre-experiment' title. Below the header, there are several sections for configuring the experiment:

- Path and user / Sample:** Name: exp_32, Experiment: exp_32 in folder C:\XcaliburData\Sim\exp_32. Buttons: Path is ok!, Browse root folder, Set user.
- Expected chemical formula:** A text input field with a warning: 'AutoChem 2 may not succeed without providing valid chemical formula!'. Button: Get Last used formula.
- Comment:** A text input field. Button: Sample description.
- Experiment options:** Exposure time: A slider control. Detector=53.0mm, width=1.0deg, Movie, cryo off, Strategy: Complete data (default mode), Exposure: 1.0s 4.0s. Total Pre-experiment Time: 0:02, No. Runs/Frames: 6/30, Pre-experiment Finish: Mon Oct 19 13:01:17 2015. Type of experiment: Complete data for publication. Button: Setup.
- Resolution and I/sig:** I/sig: 15.0, Resolution: 0.837.
- Checkboxes:** Interactive strategy after pre, Attempt AutoChem.
- Information:** A section for additional details.
- Buttons:** Help, Exit & start screening, Exit & start preexperiment, Exit.

This window shows the details for the pre-experiment. Insert the name of your sample (and the user), the chemical formula and the sample description. Modify the exposure time and the type of experiment according to your needs. The pre-experiment will collect 30 (Cu) or 15 (Mo) frames in order to get better cell parameters and a good strategy for the real data collection.

Strategy



- A. **Unit cell for Strategy Calculation**: contains the proposed unit cell, calculated from the pre-experiment.
- B. **Strategy parameters**: it is possible to set the maximum resolution of the data collection etc...
- C. **Strategy mode**: includes options such as complete, redundant, and time-limited collections.
- D. **Time prediction**: shows the predicted exposure times, based on the pre-experiment data and desired I/σ value (usually set to 15 for good quality data).
- E. **Current Strategy**: details the number of frames and length of the experiment. If any changes are made to sections A, B, C or D the user must click on the Calculate New Strategy button to update the experiment details.
- F. **Coverage**: graphs or tabulated views of the proposed data collection.
- G. **Settings/Options**
Click on Start Experiment to begin

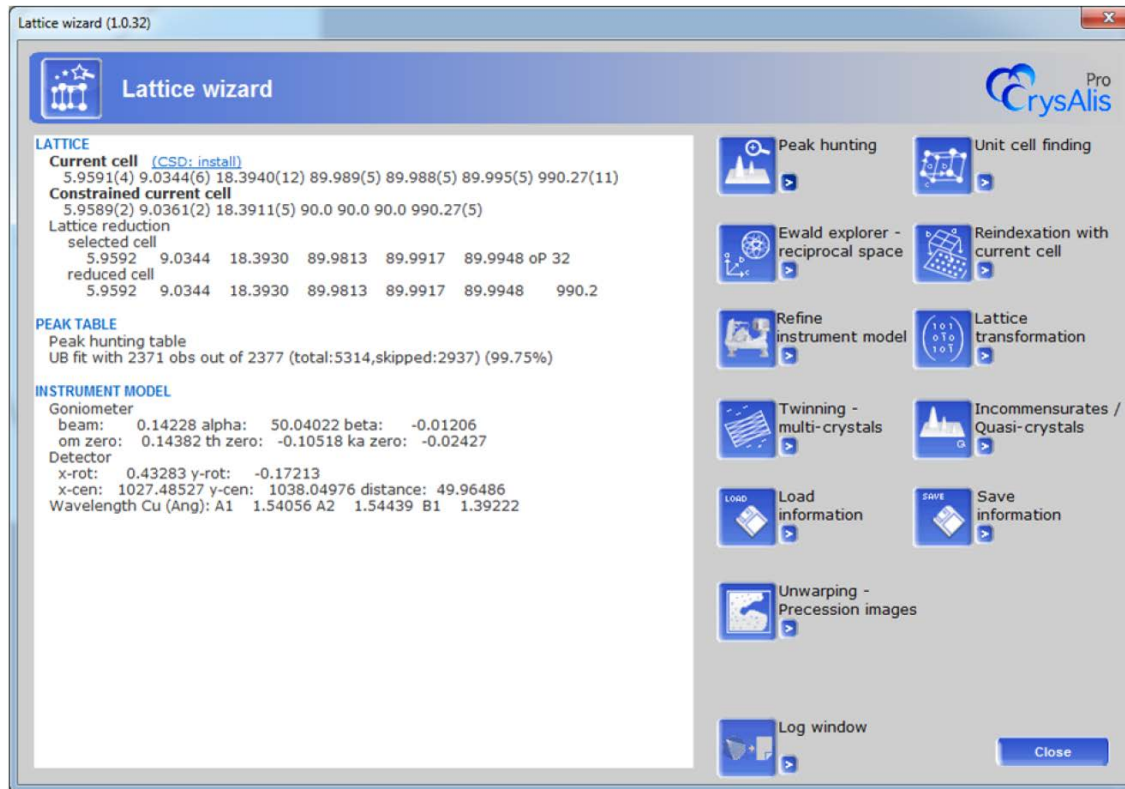
Data Collection and Reduction

- Data reduction starts automatically with the beginning of data collection and uses intelligent routines which tune the parameters to give the best data quality. Processed data are always available and accompanied by real time on-screen feedback of data quality and completeness.
- The measured data can be treated in two ways by the offline version of CrysAlis (Pro): Automatic or Manual (with options)
- Automatic treatment is good for very good samples (if not too absorbing)

Data reductions with options

- First of all, locate your par or run file in the folder containing the measured data
- Open it by clicking on it (it is loaded by Crysalis (Pro) Red (offline version))
- Select the Lattice Wizard from the menu at left

Data reductions with options



This tool will let you find peaks in the collected frames and find the unit cell and evaluate the quality of indexation and determine if twins or incommensurates are present.

Data reductions with options

- To change the settings used by the profile fitting data reduction, click on Start/Stop and select Data reduction with options. There are six windows, and the most commonly used settings are discussed below:
- **Orientation Matrix**: the user can choose which lattice extinctions to filter out. There are also options to choose unit cells from twin components or to use q-vectors determined for incommensurate structures.
- **Experiment run list**: by default the full run list is used during data reduction, but entire runs or individual frames can be removed using this window.

Data reductions with options

- **Basic algorithm parameters:** there are three levels for following crystal movement during a run: moderate sample wobble, significant sample wobble, and discontinuous jumps. This window also gives the user the option to remove any data generated from previous data reduction runs and also to edit several special sample movement parameters.
- **Background evaluation:** the method for determining the background correction can be changed from the standard “Average” method, to a “Smart” correction. For datasets in which the background is non-uniform, using the “Smart” method is often beneficial.

Data reductions with options

- **Outlier rejection**: the choice of outlier rejection is usually based on the chosen Laue group but can be altered.
- **Output**: details about the output, including:
 - re-naming the output files
 - the choice of automatic or manual space group determination via GRAL
 - automatic generation of unwarp (precession) images

Data reductions with options

- Finalization of Data



When data reduction is over, in order to get hkl file we need to apply corrections (based on symmetry, absorption, etc...), to scale the frames and try to determine space group.

The refinalize windows shows:

Sample (contains the cell parameters, the Laue group and the chemical formula)

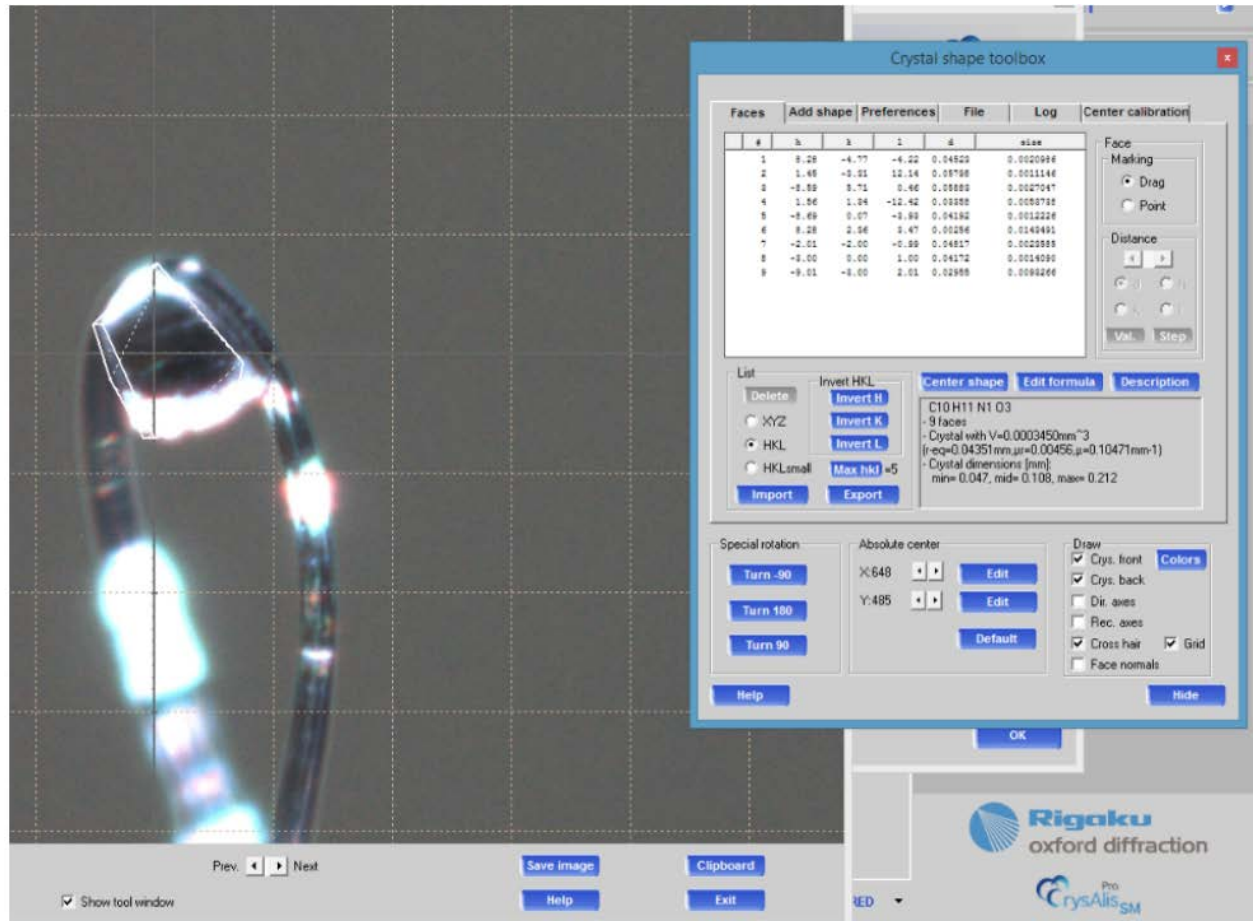
Corrections (empirical absorption correction, frame-scaling and numerical absorption (based on faces))

Space group and Autochem (determination of the space group and try to solve the crystal structure)

Filters and limits: filters and limits (resolution for instance) may be applied

Output: hkl, ins, p4p, cif_od etc are created or overwritten

Crystal shape modelling (face indexing)



It uses the movie registered before starting the data collection and then by simple clicks allows the user to index the faces of the crystal, to determine exactly its size and to apply precise absorption corrections.

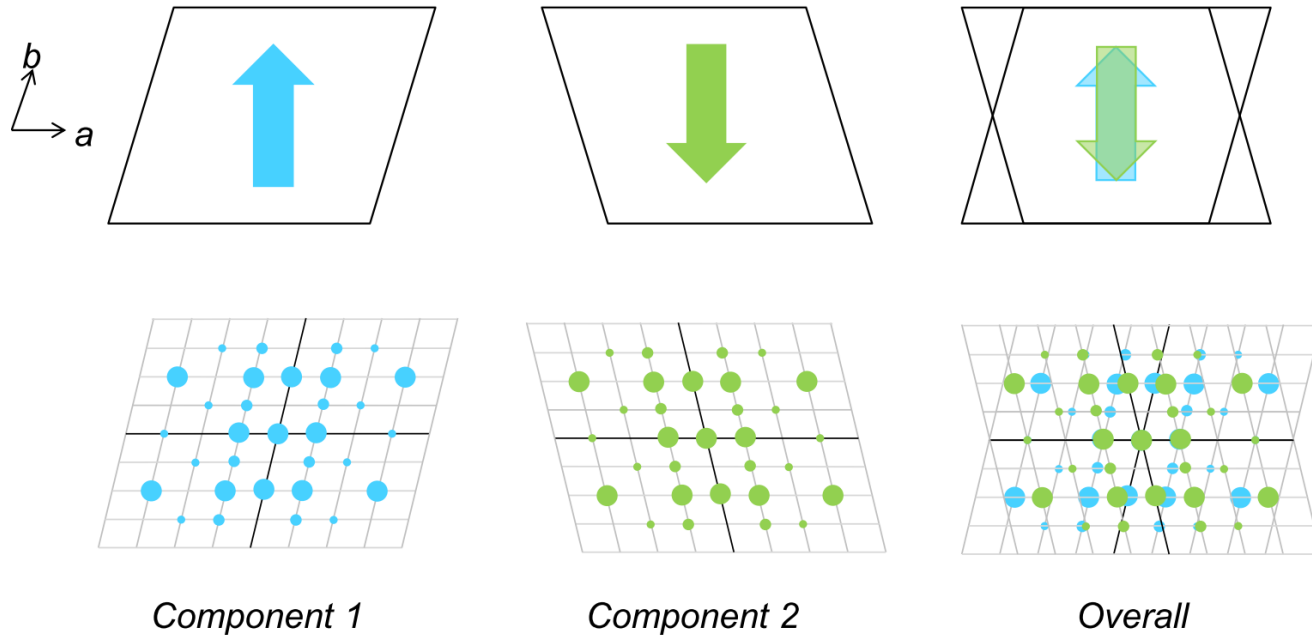
Twins

Introduction to Twinning

Partially overlapped diffraction patterns

This type of twins can be treated during integration

Non-merohedral twins



Twins (diagnosis)

Lattice Wizard

Lattice wizard (1.0.32)

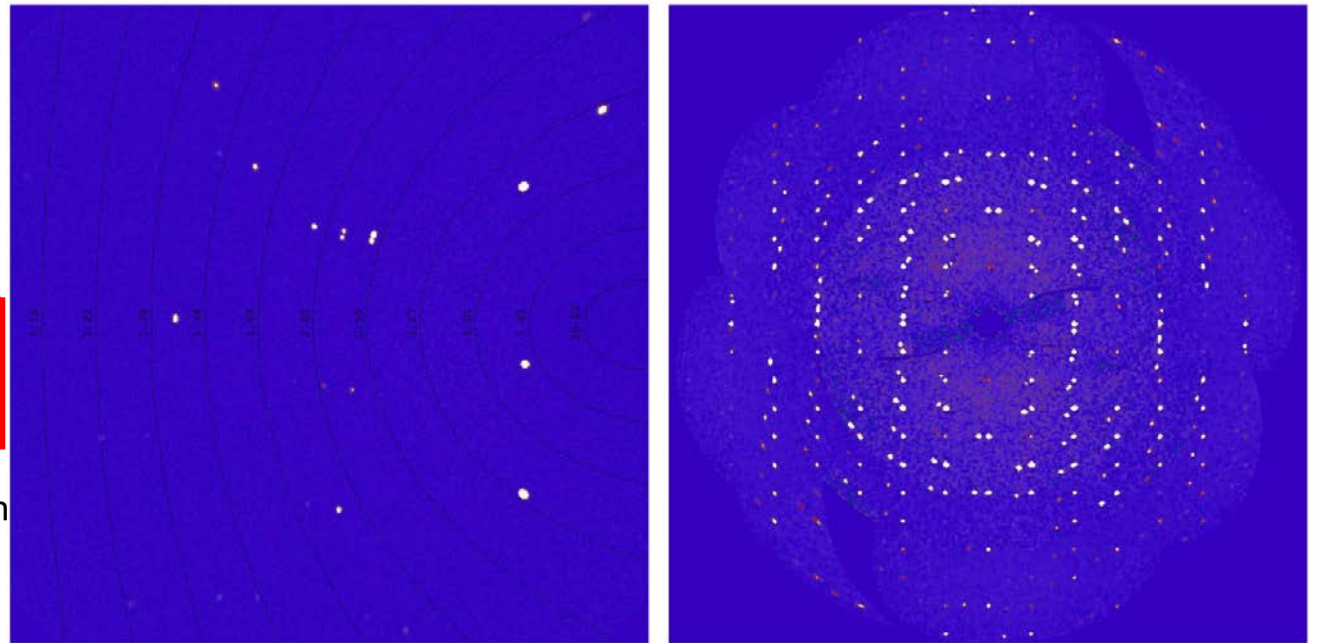
LATTICE
Current cell (CSD: 2 hits)
10.0910(13) 6.9341(8) 29.972(3) 90.068(9) 94.880(10) 90.008(10) 2089.6(4)
Constrained current cell
10.0958(11) 6.9334(17) 29.963(3) 90.0 94.908(9) 90.0 2089.6(6)
Lattice reduction
selected cell
10.0921 6.9338 29.9794 90.1096 94.8911 90.0161 mP 35
reduced cell
6.9338 10.0921 29.9794 94.8911 90.1096 90.0161 2090.2

PEAK TABLE
Peak hunting table
UB fit with 2683 obs out of 4906 (total:4906,skipped:0) (54.69%)

PEAK TABLE
Peak hunting table
UB fit with 2683 obs out of 4906 (total:4906,skipped:0) (54.69%)

Unwarping - Precession images
Log window
Close

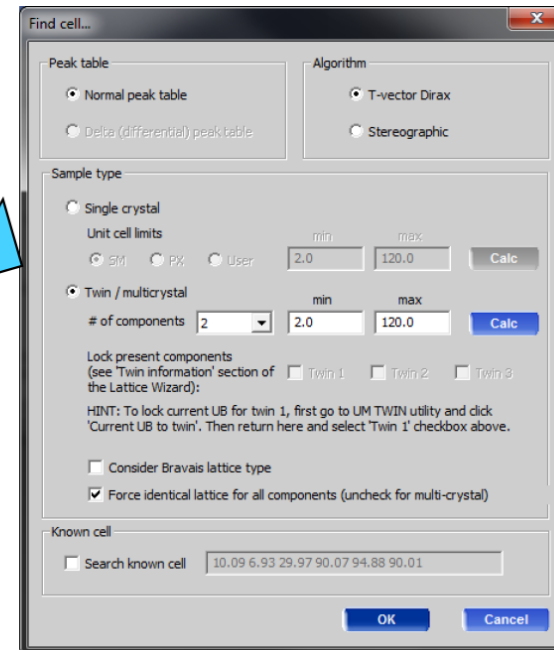
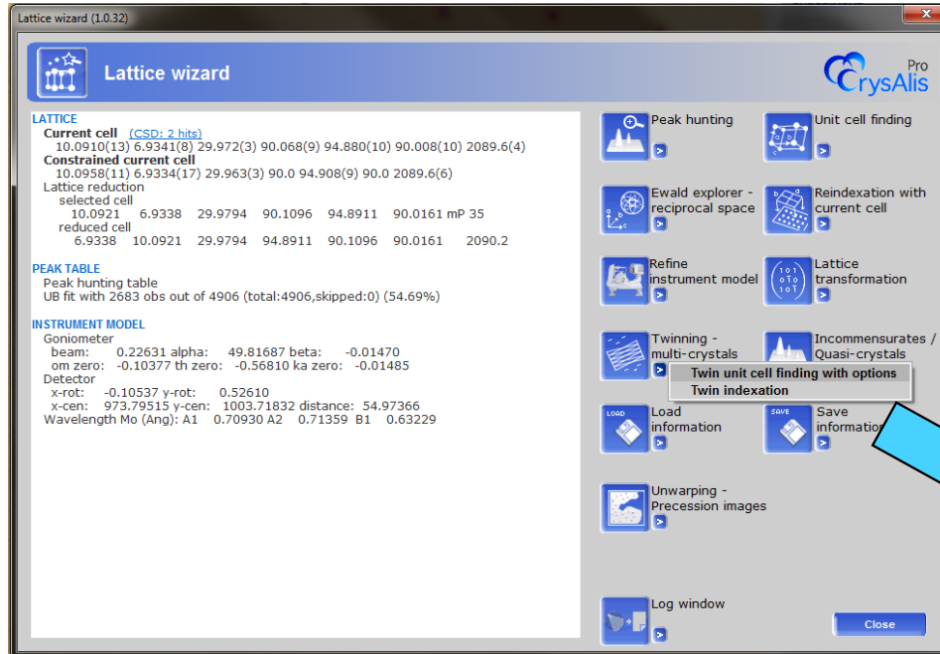
Diffraction and unwarped images



Twins (Automatic indexing)

- Automatic indexing will:
 - 1. try to find an orientation matrix with the highest percentage
 - 2. save it as first component
 - 3. try to obtain another orientation of the cell which indexes the largest % of the remaining unindexed (wrong) peaks
 - 4. save it as next unused component
 - 5. Refine cells simultaneously

Twins (Automatic indexing)



Twins (Automatic indexing)

The image shows two overlapping windows from the CrysAlis Pro software. The background window is the 'Lattice wizard (1.0.32)' and the foreground window is the 'UM TWIN: UB matrix setup for twins (1.0.7)'.

Lattice wizard (1.0.32) - LATTICE

Current cell (CSDP: 2 hits)
10.1001(12) 6.9345(7) 29.952(3) 90.016(8) 94.887(9) 90.010(9) 2090.2(4)

Constrained current cell
10.1040(10) 6.9369(17) 29.930(3) 90.0 94.909(8) 90.0 2090.2(6)

Lattice reduction
selected cell
10.1152 6.9328 29.8793 90.1580 95.0370 90.091
reduced cell
6.9328 10.1152 29.8793 95.0370 90.1580 90.091

Twin information
1: 10.0957 6.9345 29.9666 89.986 94.858 89.989 2090.4
2: 10.1013 6.9352 29.9584 89.958 94.981 89.994 2090.8
1: Total: 3433(51.5%) Separate: 2471(37.1%) Overlapped:
2: Total: 3374(50.6%) Separate: 2412(36.2%) Overlapped:
Unindexed: 819 (12.3%)

PEAK TABLE
Peak hunting table
UB fit with 3436 obs out of 6664 (total:6664,skipped:0) (51.56%)

INSTRUMENT MODEL
Goniometer
beam: 0.22631 alpha: 49.81687 beta: -0.01470
om zero: -0.10377 th zero: -0.56810 ka zero: -0.01485
Detector
x-rot: -0.10537 y-rot: 0.52610
x-cen: 973.79515 y-cen: 1003.71832 distance: 54.97366
Wavelength Mo (Ang): A1 0.70930 A2 0.71359 B1 0.63229

UM TWIN: UB matrix setup for twins (1.0.7) - UB matrix setup for twins

Current UB (orientation matrix)

Current UB:
UM S 0.06255 -0.01560 0.01209 0.01048 -0.08164 -0.01353 0.03074 0.05961 -0.01535
10.10006 6.93454 29.95150 90.0157 94.8866 90.0101 2090.16
Twin component UB:
UM S 0.06259 -0.01567 0.01207 0.01046 -0.08162 -0.01353 0.03074 0.05963 -0.01535
10.09569 6.93449 29.96660 89.9856 94.8576 89.9888 2090.38

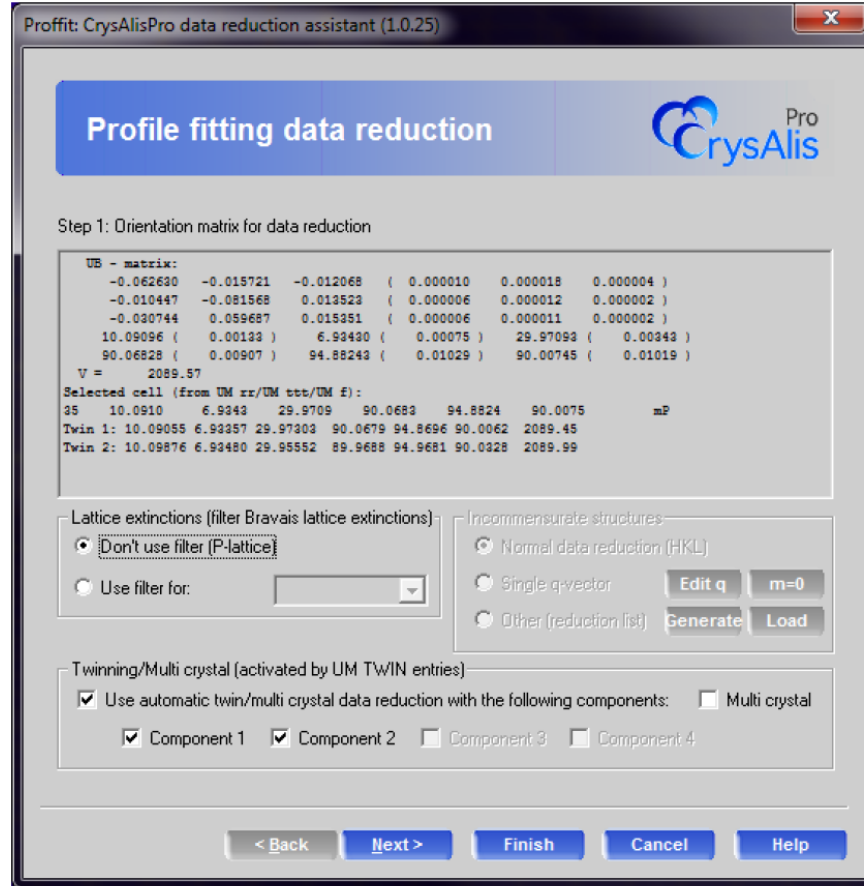
Twin array UB (orientation matrix)

Component 1 Component 3
 Component 2 Component 4

Rot(UB1 UB2)= 179.9411 deg around 0.7077 -0.0000 0.7065 (rec) 0.9906 -0.0006 0.1366 (dir)

TL is the matrix for the TWIN card in SHELXL provided it describes the comp 1 to comp N transf.
TL=UB1-1*UB2: 0.7577 -0.0015 0.2431 0.0001 -0.9999 -0.0001 1.7545 0.0033 -0.7569 det 0.999794
UM SARRAY 0 0.06259 -0.01567 0.01207 0.01046 -0.08162 -0.01353 0.03074 0.05963 -0.01535
10.09569 6.93449 29.96660 89.9856 94.8576 89.9888 2090.38

Twins (Data reduction)



Difficulties

- Overlap prevent accurate determination of 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

Twins (Data reduction)

The screenshot displays the CrysAlisPro software interface. The main window shows a diffraction pattern with two sets of spots, indicating a twin crystal system. The right-hand panel provides detailed data reduction statistics for two twin components.

START/STOP
RED Ready

Crystal RED

Data Collection

Data Reduction

FRAMES / RUNS
In run list: 188/3, used: 188/3

3D PROFILE ANALYSIS (twin component #1)
Frames done: 188
Reflections tested: 9437, used: 4771
Avg mosaicity (in degrees) - 3 run(s)
e1=0.84, e2=0.82, e3=0.95

3D INTEGRATION & FITTING (twin component #1)
Frames done: 188
Fitted: 10666, overflow: 0, hidden: 697
Outliers rejected: 0

FINALIZATION OUTPUT HKL FILE
Filename: MG-2-S1_twin1_hklf4

SCALING / NUMERICAL ABSORPTION (SYM2/m (b-unique)
Empirical abs (e=2, o=0): min=0.99, max=1.03
Frame scales (1/scale): min=0.68, max=1.04

TWIN ANALYSIS

Component	Ratio	Isolated	Overlapped
1	0.52	7281	3338
2	0.48	7256	3338

DECOMPOSED TWIN DATA STATISTICS (<0.80 overlap)

Component	Redundancy	F2/sig(F2)	Rint
1	2.0	11.3	0.088
2	2.0	10.6	0.091

Overlap limit for HKLF4 export: 0.80

TWIN HKLF5 STATISTICS FOR OVERLAPPED OBS

Components	Redundancy	F2/sig(F2)	Rint
1,2	1.8	17.3	0.046

Twins (Data reduction)

The screenshot shows the 'Twin data finalization' dialog box. It contains several sections: 'mpprof files for twin finalization', 'Chemical formula', 'Lattice symmetry', 'Corrections', 'Export options', and 'Merging'. A callout box at the top right highlights the 'Common scales for all twin components' radio button, which is selected. Another callout box at the bottom right highlights the 'HKLF file options' section, which includes checkboxes for 'Use reflections from component 1 only', 'Output multi HKLF4 file containing data from twin 1 and twin:', 'Invert HKLFs of twin:', and checkboxes for twin components #2, #3, and #4. A red arrow points from the text 'Useful for cases where secondary domain(s) are weak' to the 'Common scales' option. Another red arrow points from the text 'Useful for cases where structure solution is difficult due to low completeness of separate reflections' to the 'Output multi HKLF4 file...' option. A third red arrow points from the text 'For non-centrosymmetric twins.' to the 'Invert HKLFs of twin:' option.

Common scales for all twin components
 Separate scales for all twin components

Useful for cases where secondary domain(s) are weak

HKLF file options

Use reflections from component 1 only

Output multi HKLF4 file containing data from twin 1 and twin:
 #2 #3 #4

Invert HKLFs of twin:
 #2 #3 #4

Useful for cases where structure solution is difficult due to low completeness of separate reflections

For non-centrosymmetric twins.