Treatment of a Non-Merohedral Twin Using CrysAlis^{Pro}

Application Note

X-ray Crystallography

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An Illustration of the Agilent Software Approach to Twin Data Set Decomposition

For the vast majority of routine crystal samples, a Pre-experiment will reveal an unequivocal unit cell with a high percentage fit of indexed reflections. In general, problems are encountered when this fit percentage drops significantly. In fact, some institutions have a policy not to collect data on any crystal with a fit lower than around 70%. However, a low % fit can often be explained by the presence of a secondary lattice, caused by non-merohedral twinning in the crystal lattice, or simply by the presence of a second crystal fragment. Advances in CrysAlis^{Pro}'s software tools for dealing with such data sets mean that obtaining a good quality structure can be a remarkably routine procedure.

Figure 1. Xcalibur S system at the Indian Institute of Technology, Mumbai, India.

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The example data described in this application note was collected using an Xcalibur S system (Figure 1) by Prof. Mathur's group at IIT, Mumbai. As is often the case with non-merohedral twins, in this data set the diffraction images look good, but many reflections are suspiciously close together and many do not fit a single unit cell (Figure 2).

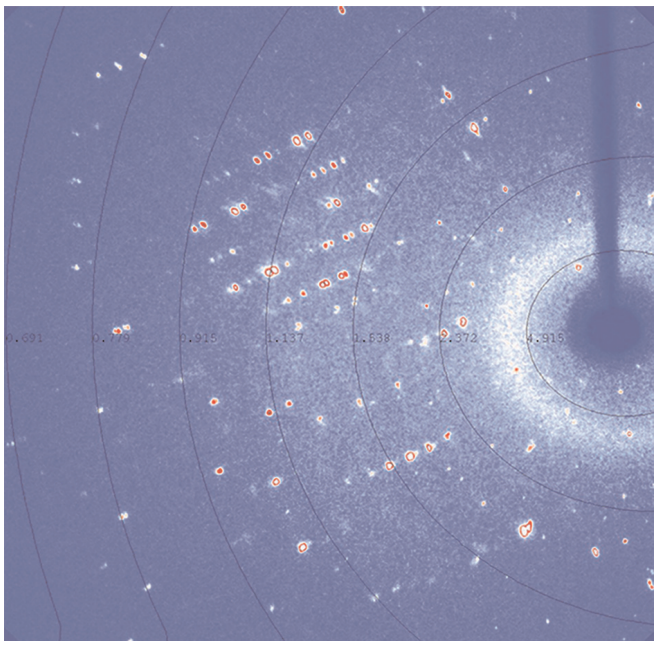

Figure 2. Diffraction image with apparent "twin" reflections.

A single unit cell can be found but this fits only 42% of the lattice reflections. However, two cells can be easily found using the multiple unit cell finding tool in CrysAlis^{Pro}. The user simply specifies how many components to look for and may suggest minimum and maximum unit cell dimensions. This helps to prevent the finding of suspiciously large cells which are sometimes found due to the presence of reflections from the second lattice. Multiple unit cells can then be easily visualised using the Ewald Explorer module (Figure 3). In this case 82% of the total reflections fit two identical unit cells, which are related by a 180° rotation in c.

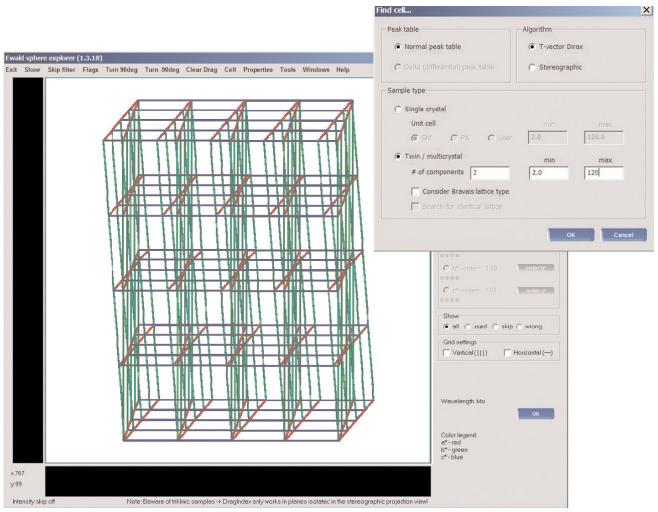

Figure 3. Multiple lattice finding tool and Ewald Explorer module with twin lattices superimposed.

The extent of twinning is most clearly observed in a 2D precession image of the h0l layer, reconstructed using CrysAlis^{Pro} (Figure 4). In fact, more than 90% of the 30,000 reflections are considered to be overlapped with a reflection from the second lattice.

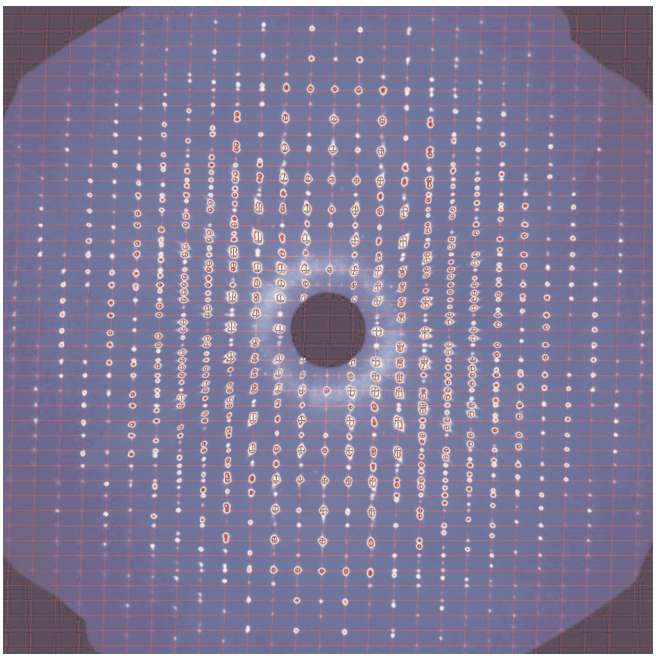

Figure 4. Reconstructed h0l precession image.

CrysAlis^{Pro}'s twin data reduction module outputs R_{int} statistics for both isolated and overlapped reflections (Figure 5). R_{int} figures of 4–5% are on a par with many more routine data sets and so this is a sign of very good quality twin data. A single hklf4 file is output for each defined lattice component in the data set. However, only reflections where the overlap factor with a second reflection is less than 80% are written to the hkl file. This value can be changed by the user, but it is designed to help in cases where the corrupting influence of the secondary lattice makes it impossible to solve the structure. In the example, default overlap factors were used and the hkl file from the major component was successfully employed for structure solution.

HKLF 5 merged

RINT ANALYSIS FOR OVERLAPPED REFLECTIONS

Components	measured	kept	unique	redundancy	F2/sig(F2)	Rint	Rsigma
1,2	26686	24252	13460	1.80	18.93	0.051	0.064

RINT ANALYSIS FOR ISOLATED REFLECTIONS

Component	measured	kept	unique	redundancy	F2/sig(F2)	Rint	Rsigma
1	1390	1294	823	1.57	34.41	0.039	0.029
2	1362	1257	814	1.54	31.03	0.040	0.031

Figure 5. Twin data reduction output statistics.

The twin data reduction module also outputs a single hklf5 file containing reflections from both lattices, where an overlap decomposition algorithm is employed to resolve the overlapping reflections. This file is used in conjunction with a BASF parameter (also output by CrysAlis^{Pro}) for final structure refinement.

A face-indexed analytical absorption correction was applied to this data to help account for the high absorption coefficient (7 mm^{-1}) and anisotropic crystal shape (Figure 6).

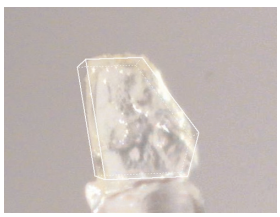

Figure 6. Face-indexed model for application of an analytical absorption correction.

In this example, solution and refinement using a single lattice and no twin treatment affords a R_1 of 18.6%, with residual Q peaks as large as 22 e/Å^3. The refinement is also not particularly stable, with many atoms becoming non-positive definite when refined anisotropically. Full treatment as a twin results in a R_1 of 8.5%, and this drops to 5.9% (with Q peaks of 4.66 e/Å^3) on application of an analytical absorption correction. (Table 1 and Figure 7).

Table 1. Refinement Statistics

	Single lattice (no specialist abs, correction)	Twin	Twin + analytical abs, correction
R_1 [> 2sig(I)]	18.63%	8.53%	5.94%
R_1 (all data)	20.27%	9.97%	7.01%
Largest diff. peak/hole	+ 22.11 e/Å^3	–12.97 e/Å^3	–4.66 e/Å^3
GOOF	1.213	1.030	0.944

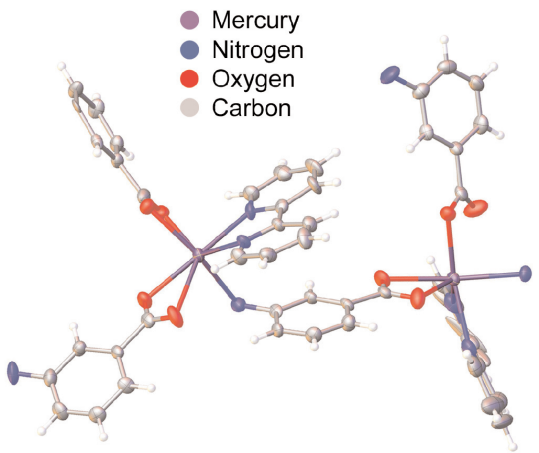

Figure 7. Refined molecular structure (ellipsoids at 50% probability level).

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