# Analysis of twinned crystals

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## 1. Introduction

Molecular structure determination has an important role both in fundamental science and applied sciences such as organic chemistry, inorganic chemistry, biochemistry, drug discovery, material chemistry, etc.

A number of analytical methods are routinely used to determine molecular structure: nuclear magnetic resonance (NMR), mass spectrometry (MS), infrared absorption spectroscopy (IR), X-ray diffractometry (XRD), and so on. In particular, single-crystal X-ray structure analysis is the most effective method of obtaining a detailed and overall three-dimensional structure of a molecule.

However, one critical problem is that single-crystal X-ray analysis cannot be performed if the target sample doesn't form a single crystal. Even if the target sample crystallizes, it sometimes turns out to be twinned or a polycrystal.

## 2. Handling of a twinned crystal

A single crystal usually grows from one crystal nucleus without secondary nucleation or impingement on other crystals. On the other hand, a twinned crystal can be thought of as an aggregate of multiple crystals of the same species joined together in certain relative orientations.

In a measurement of diffraction data acquired from a twinned crystal, diffraction spots from different domains are observed simultaneously. If the crystal orientation of each domain can be determined, data collection and processing, and therefore structure analysis, become possible. However, the processing of twin data is usually difficult because indexing and integration are problematic.

Therefore, in the past, when a twinned or polycrystal was acquired, the usual approach was to modify crystallization conditions to avoid twinning.

## 3. Data processing of a twinned crystal

In recent years, the detection and data processing of a twinned crystal have been made easier by advancements in instruments and software.

CrystalClear from Rigaku Corp. is equipped with Reciprocal Lattice Viewer (RLV) and TwinSolve. One can process twinned data by following the steps shown in a flow chart. An operator can easily create the reflection files needed to analyze the structure of a twinned crystal.

### 3.1. Reciprocal Lattice Viewer

The Reciprocal Lattice Viewer (RLV) can be used to view reflections in reciprocal space. This function greatly helps determine whether the crystal is twinned, whether data coverage is sufficient, and whether the indexing is rational.

Figure 1 is a screen shot of the RLV display of a twinned cytidine crystal measured on a desktop X-ray system "XtaLAB mini". The green boxes show the reciprocal lattice corresponding to the current cell parameters. The blue dots represent reflections that are consistent with the lattice, and the pink dots are reflections inconsistent with the lattice. Based on Fig. 1, it seems possible to determine layer lines formed by the pink dots.

This function provides a very effective way to visually grasp the status of twinning. Special knowledge is not required to detect the presence of twinning.

### 3.2. Indexing for a twined crystal

TwinSolve first indexes spots for the major component. The indexed spots are then removed from the reflection list and this step is repeated until no additional domains are found.

A diffraction pattern of a twinned crystal is shown in Fig. 2. Blue and green boxes depict predicted positions of diffraction spots, which were determined from each of two domains. The box positions and the observed diffraction spots mostly overlap. This indicates that the determination of the crystal orientation and indexing of two domains are correct.

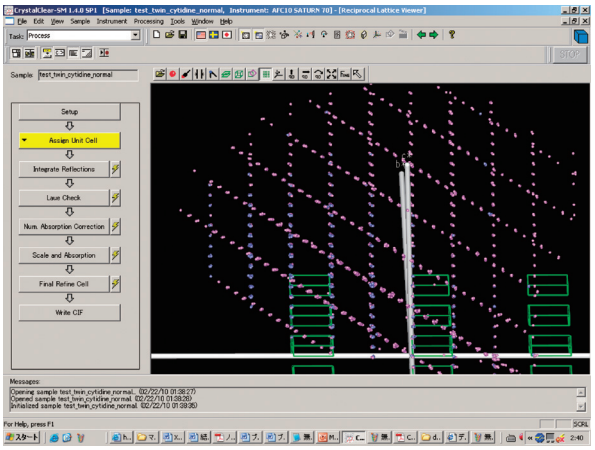


**Fig. 1.** Reciprocal Lattice Viewer.

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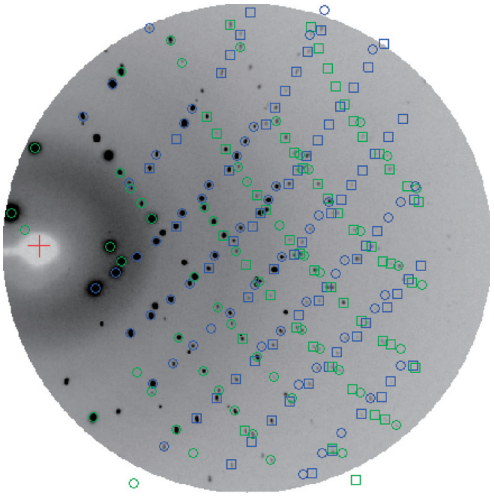

**Fig. 2.** Diffraction pattern of a twinned crystal.

### 3.3. Integration of reflection intensity [1]

In "TwinSolve", integration of reflection intensity is performed using all reflections or reflections from the major domain only. The data processed froma single domain is written in hklf4 format (SHELX[2]), while the data processed assuming two domains is output in hklf5 format.

In Table 1, the numbers in the final column indicate the domain to which that reflection intensity applies, either a "1" or a "2".

**Table 1.** hklf4 format

| | | | | | |
|---|---|---|---|---|---|
| 0 | 0 | 2 | 16863.8 | 31.3125 | 1 |
| 0 | 0 | 3 | 141.970 | 27.3361 | 1 |
| 0 | 0 | 4 | 778.883 | 35.6661 | 1 |
| 0 | 0 | 5 | 130.333 | 39.8200 | 1 |
| 0 | 0 | 6 | 57212.8 | 85.3855 | 1 |
| 0 | 0 | 7 | 92.5154 | 36.7810 | 1 |

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**Table 2.** hklf5 format

| | | | | | |
|---|---|---|---|---|---|
| 0 | 0 | 2 | 16863.8 | 31.3125 | 1 |
| 0 | 0 | 3 | 55.6297 | 28.1459 | 2 |
| 0 | 0 | 3 | 141.970 | 27.3361 | 1 |
| 0 | 0 | 4 | 778.883 | 35.6661 | 1 |
| 0 | 0 | 4 | 956.619 | 36.1883 | 2 |

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### 3.4. Structure solution

In CrystalStrucutre, the initial phases are usually determined using the reflection file in hklf4 format corresponding to one domain (typically the major domain). When most reflections do not overlap, data in hkkl5 format can be used to obtain an initial structure.

Twin refinement is performed after replacing the hklf4 format file with the hklf5 format file.

The analysis of the twinned cytidine crystal resulted in an excellent final structure.

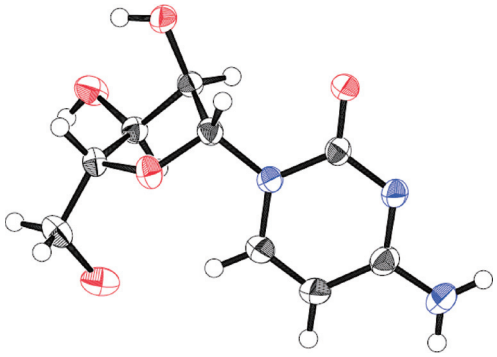

**Fig. 3.** ORTEP of cytidine.

Formula: $C_9H_{13}N_3O_5$
Temperature: 298K
Space group: $P2_12_12_1$
Lattice constants:
a=5.1271 (5) Å
b=14.0186 (16) Å
c=14.8136 (17) Å
2θ max: 55°
Completeness: 100%
GOF: 1.095
R1: 0.0357
wR: 0.0903

## 4. Conclusions

As demonstrated above, even a twinned crystal can yield a good structural result. Twinned crystals do not occur often but a crystallographer using CrystalClear can easily process diffraction data from a twinned crystal by following the steps in the flowchart.

## References


( 1 ) P. Müller, R. Herbst-Irmer, A. L. Spek, T. R. Schneider, M. R. Sawaya: *Crystal Structure Refinement—A Crystallographer's Guide to SHELXL—*, Oxford University Press, (2006).

( 2 ) G. M. Sheldrick: *SHELXL97*. University of Gottingen, Germany, (1997).