Chemical Crystallography and Structural Chemistry

(VO 270287)

Lecture 9

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Previous Lecture

1. Example of constraints and data:parameter ratio
2. Validation - why and how

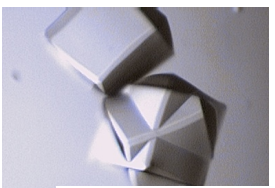
Today's Lecture

1. Twinning
2. types of twinning
3. how to deal with twinning
4. warning signs of twinning

Twinning

According to G. Friedel[3], 1904

> "A twin is a complex crystalline edifice built up of two or more homogeneous portions of the same crystal species in contact (juxtaposition) and oriented with respect to each other according to well-defined laws."

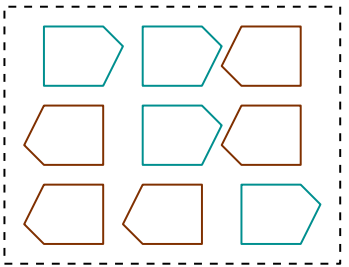


Courtesy M. Sevvana

Single insulin crystal and two insulin crystal grown into each other as an example of *non-merohedral twins*.

Twin Law

A two-dimensional twin:



idea by R. Herbst-Irmer

Twin law: $\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$ (rotation by $180°$)

Contribution of **orientation 1** to diffraction: 4/9

Contribution of **orientation 2** to diffraction: 5/9

Usually each orientation forms **domains** of a large number of unit cells

$\Rightarrow$ not one larger unit cell

$\Rightarrow$ both orientations contribute independently to diffraction pattern

How to Deal with Twinned Crystals

Life is easier with a single, non-twinned crystal. When faced with a twin it is worth putting **some** effort into improving the crystallisation conditions and growing a single crystal.

But sometimes one does not have a choice.

Do not throw away your twinned crystal — the data can often be integrated and refined.

Types of Twinning

One can distinguish four different types of twinning in crystallography:

1. **non-merohedral** twinning
2. Twinning by **merohedry**
3. Twinning by **pseudo-merohedry**
4. Twinning by **reticular merohedry**

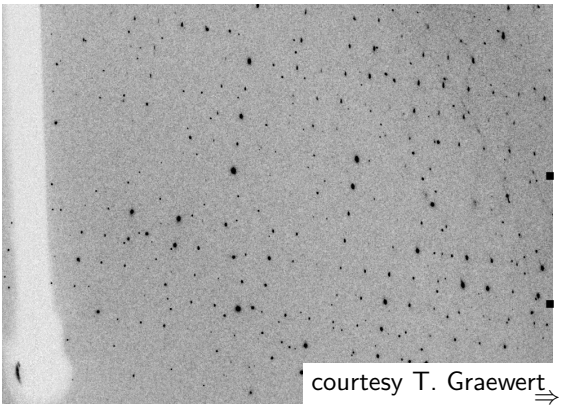
Mineralogists distinguish many more phenotypes and subgroups of twins

Non-Merohedral Twinning

- Two or more crystals attached together
- **Arbitrary** orientation (not related to crystal's symmetry)
- Often: "satellites", small crystals attached to one main crystal

→ try to separate crystals before mounting, *e.g.* with a cats whisker. Sometimes crystals break apart during transfer into cryo-solution.

Example of Non-Merohedral Twinning



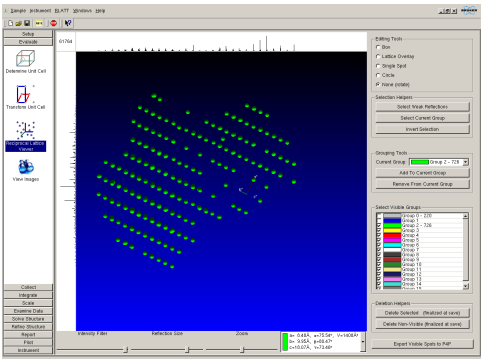
courtesy T. Graewert

- Main lattice, strong spots
- Small spots interspersed inbetween main lattice

$\Rightarrow$ Small'ish satellite crystal

$\Rightarrow$ Most spots **do not** overlap

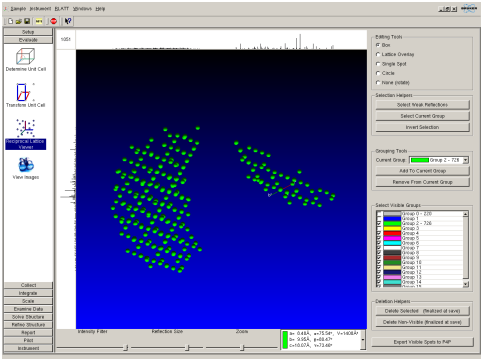
Example of Non-Merohedral Twinning



courtesy C. Grosse

- View of reciprocal lattice of a dataset
- this orientation: apparently single lattice

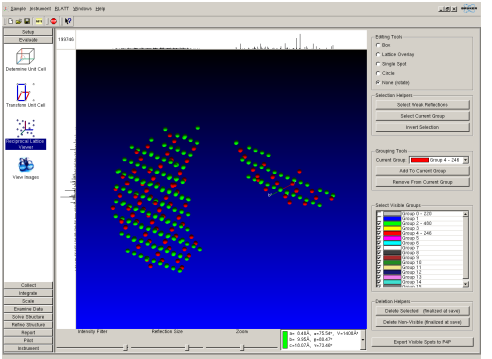
Example of Non-Merohedral Twinning



courtesy C. Grosse

- View of reciprocal lattice of a dataset
- different orientation: systematic absences?

Example of Non-Merohedral Twinning

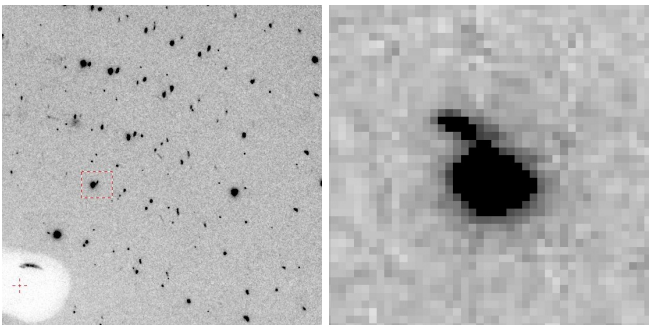


courtesy C. Grosse

- View of reciprocal lattice of a dataset
- Correct indexing with two domains in two orientations

Non-Merohedral Twinning

Easiest solution: ignore smaller domain, only integrate reflections belonging to main/ one crystal.
Works ok if only very few spots overlap. One could even integrate the two different lattices separately.



Overlapping spots are difficult to integrate for software: difficult assignment of pixel to correct spot.

Merohedral Twinning

The reciprocal lattice of **merohedral twins** overlap perfectly, because the

twin law is a symmetry operator of the *crystal system*, but **not** the *point group*.

The crystal system describes the symmetry of the pure lattice (triclinic, monoclinic, orthorhombic, tetragonal, tri-/hexagonal, and cubic).

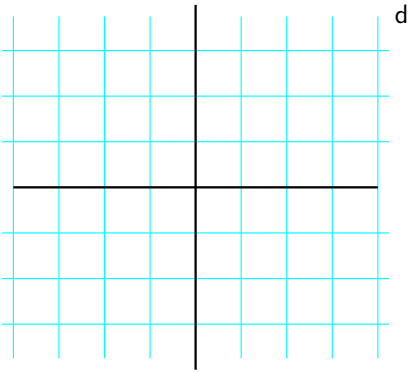
Merohedral Twinning

Merohedral Twinning can only occur when the real space group belongs to the lower Laue group, *i.e.*

Crystal System	Real Laue	"Twinned" Laue
tetragonal	$4/m$	$4/mmm$
trigonal	$\bar{3}$	$\bar{3}m1$
hexagonal	$6/m$	$6/mmm$
cubic	$m\bar{3}$	$m\bar{3}m$

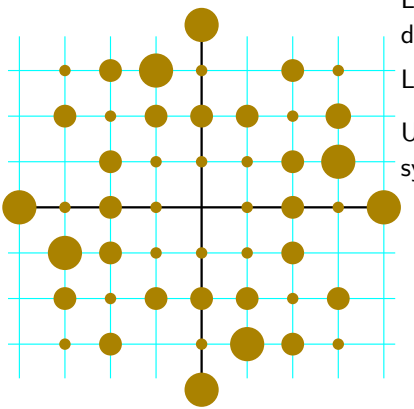
Merohedral twinning cannot occur in monoclinic, triclinic, or orthorhombic space groups — they only contain 1 Laue group.

Merohedral Twinning: Example



Lattice with 4-fold symmetry perpendicular to plane also has mirror planes.

Merohedral Twinning: Example

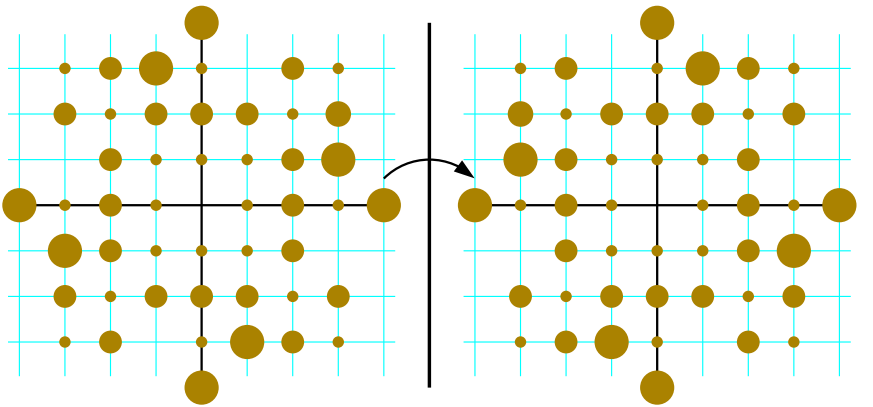


Lattice with 4-fold symmetry perpendicular to plane also has mirror planes.

Lattice: mirror planes (strong lines)

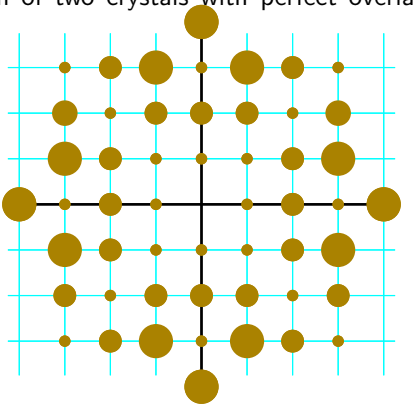
Unit cell (and intensities) with 4-fold symmetry, but not a mirror plane.

Merohedral Twinning: Example



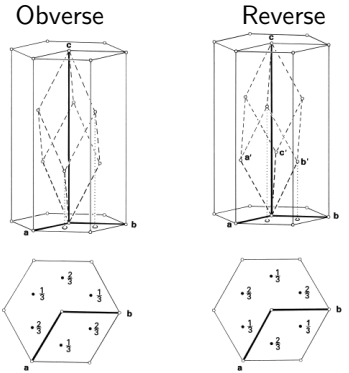
Merohedral Twinning: Example

Observed data: sum of two crystals with perfect overlap of the reciprocal lattices.



Each spot on detector = sum of two reflections from two "crystals".

Twinning by Reticular Merohedry



- *E.g.* twin consisting of obverse and reverse settings of rhombohedral crystals
- About $1/3$ of reflections overlap perfectly, the remaining do not overlap
- Once detected, structure solution less difficult than for merohedral twins

from Massa [4]

Pseudo-Merohedral Twins

The twinned crystal pretends a **higher** symmetry than it really has.
Overlaps are incomplete, *i.e.* not perfect as they are in the case of merohedral twinning (hence the name).

Data Processing with Twinning

Twinned data are best coped with as early as possible, *i.e.* at the data processing step.

Keep in mind: processing software **predicts** the position of the reflections on the detector from the experimental parameters (unit cell, wavelength, crystal orientation, ...).

Three different situations occur.

1) Non-overlapping reflections

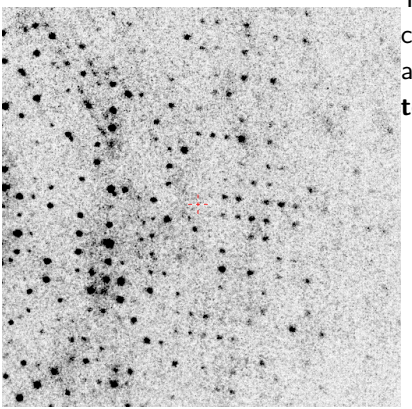
Especially in the case of non-merohedral twinning, a large number of reflections do not overlap and can be treated as normal reflections:

1. Predict position from appropriate cell and orientation
2. Subtract background
3. Measure intensity

The integration software, however, has be to set-up for twinning and be capable of dealing with more than one **orientation matrix** for the crystal.

2) Partially Overlapping Reflections

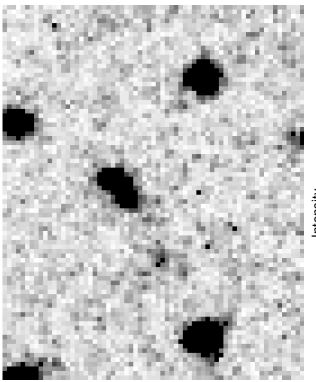
Some of the reflections of a non-merohedral twin overlap partially and the main problem is to assign the detector values at the border between the overlapping pixels.

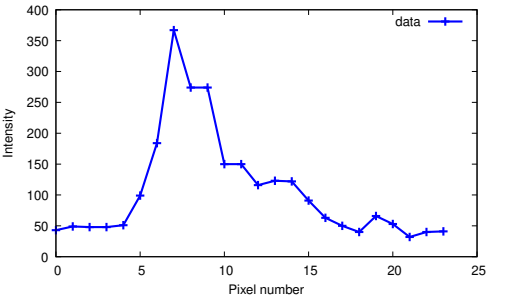


The same phenomenon can occur with crystals of **large unit cell** parameters, and can be improved by increasing **detector distance** to the crystal.

2) Partially Overlapping Reflections

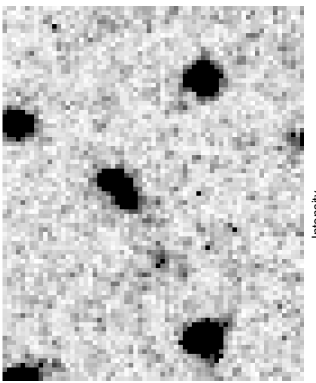
The pixels in the **overlapping region** contain photons from both spots. The contributions have to be split up correctly.

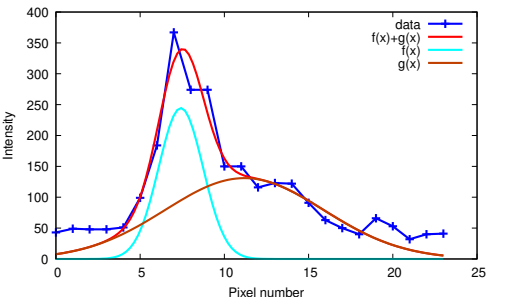




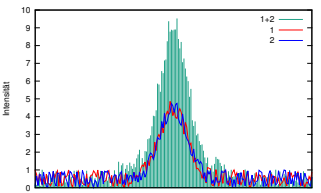
2) Partially Overlapping Reflections

The pixels in the **overlapping region** contain photons from both spots. The contributions have to be split up correctly.
This may be achieved by **profile fitting**.





3) Perfectly Overlapping reflections



Perfect overlaps happen *e.g.* in the case of merohedral twins.

Deconvolution during *data processing* is not possible.

Data can be handled during refinement, refinement includes the **twin fraction** α:

$$I_{1+2}(hkl) = (1-\alpha)I_1(hkl) + \alpha I_2(h'k'l')$$

α: Volume of domain one / crystal volume

$1-\alpha$: Volume of domain two / crystal volume

Dealing with Twinned Data (1/2)

(Obviously) Twinned data are best dealt with starting at the data processing stage.
SAINT (from Bruker AXS) in combination with TWINABS for scaling and SHELXL for refinement are probably the most sophisticated work flow.

Dealing with Twinned Data (2/2)

Unfortunately, many data processing software do not support twinned data. In case of one major domain, one can

1. Ignore twinning
   - poor results
2. Omit **all** overlapping reflections
   - May lead to (very) incomplete data
3. Omit partial overlaps, split exact overlaps (refinement of twin fraction)
   - May still lead to incomplete data
   - Special file format required (SHELXL HKLF5 format)

Warning Signs: (Pseudo-) Merohedral Twinning

- Laue group appears higher than true Laue group
- The matching of symmetry equivalent reflections (R_{merge}) in the higher (pretended) Laue group is only slightly worse than in the lower (correct) Laue group
- Twinning disturbs the **expected** intensity distribution of the reflections: The mean of $|E^2 - 1|$ is lower than expected ($\ll 0.736$)
- Trigonal and hexagonal space groups are suspicious
- systematic extinctions are not consistent with any space group
- Refinement: Structure cannot be solved or R-values very high

list compiled by G. Sheldrick

Warning Signs: Non-Merohedral Twinning

- Some split reflections, others are sharp
- Difficult indexing/ determination of cell dimensions
- unusually long cell edge ("supercell" for near-180° domain rotation)
- No suitable space group
- Refinement: Many outliers $|F_{\text{obs}}| \gg |F_{\text{calc}}|$, especially for reflections with low $|F_{\text{calc}}|$ (integration of two spots as one)
- Strange left-over electron density, which cannot be assigned to disorder or solvent molecules (especially for small-molecule structures)

list compiled by G. Sheldrick

References

1. C. Giacovazzo (ed.), *Fundamentals of Crystallography*, Union of Crystallography, Oxford University Press (2002)

2. T. Hahn (ed.), *International Tables for Crystallography, Vol. A*, Union of Crystallography

3. E. Prince (ed.), *International Tables for Crystallography, Vol. C*, Union of Crystallography

4. W. Massa, *Crystal Structure Determination*, Springer (2004)

End of lecture