Twinning

Carmelo Giacovazzo:

"Twins are regular aggregates consisting of individual crystals of the same species joined together in some definite mutual orientation".

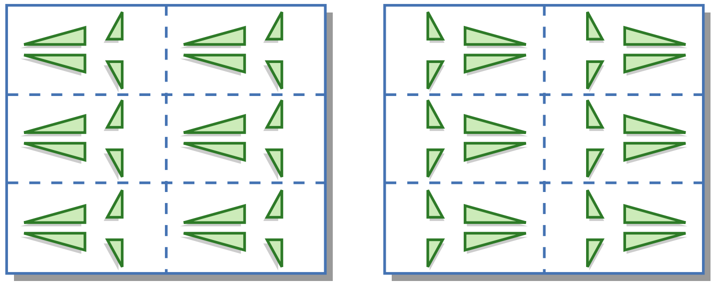

Figure by MIT OpenCourseWare.

The two two-dimensional crystals are related by a vertical mirror. This mirror is part of the metric symmetry of the unit cell but not of the contents of the unit cell!

Fusing the two crystals results in a twin. The vertical mirror operation is the twin law:

$$\begin{matrix} 1 & 0 \\ 0 & -1 \end{matrix}$$

(if x is going down and y to the right).

Twinning

Twinning can occur when a unit cell – ignoring the contents of the cell – has higher symmetry than implied by the space group of the crystal structure.

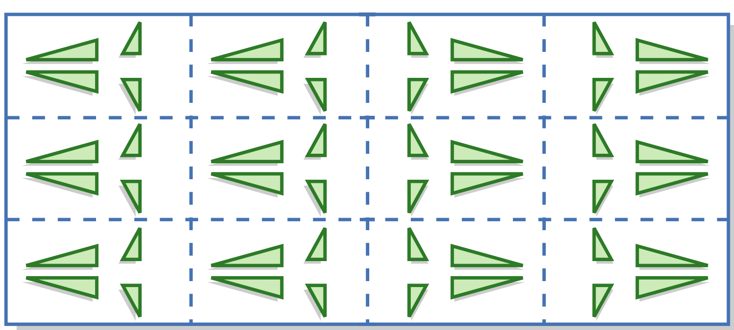

Figure by MIT OpenCourseWare.

The ratio of unit cells of one orientation to unit cells of the other orientation is called the "twin ratio". In the example above it is 0.5 (a "perfect twin").

Twinning

When you put two identical crystals in two different orientation in the X-ray beam at the same time, you'll observe an overlay of the two identical but differently oriented diffraction patterns:

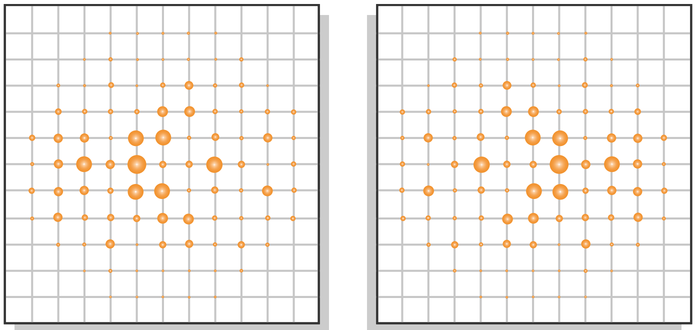

Figure by MIT OpenCourseWare.

As with the twinned crystals, the two diffraction patterns are related by a vertical mirror.

Twinning

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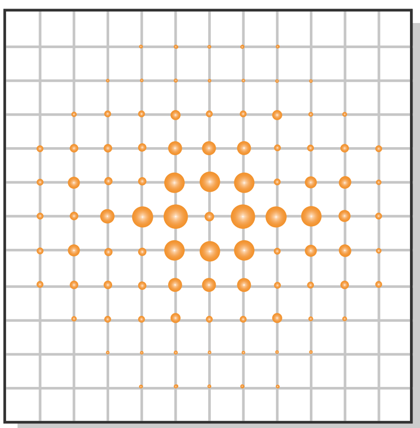
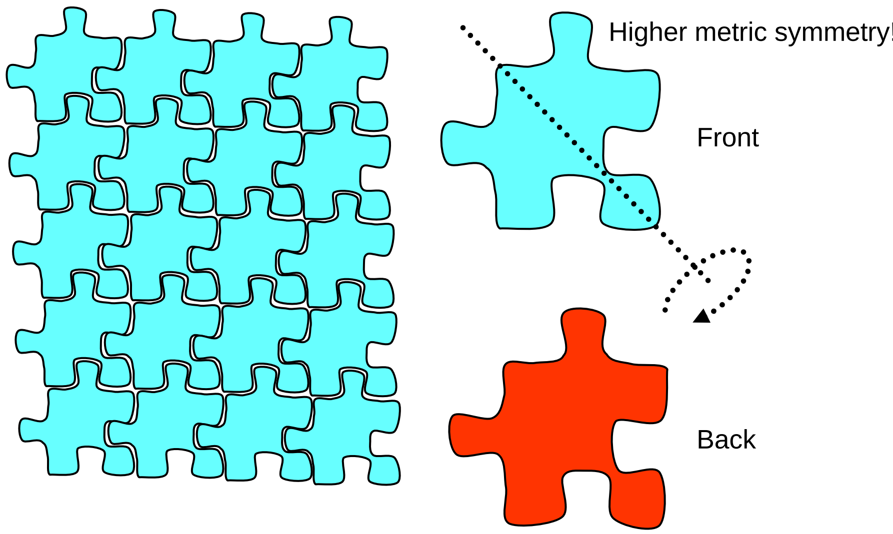


Figure by MIT OpenCourseWare.

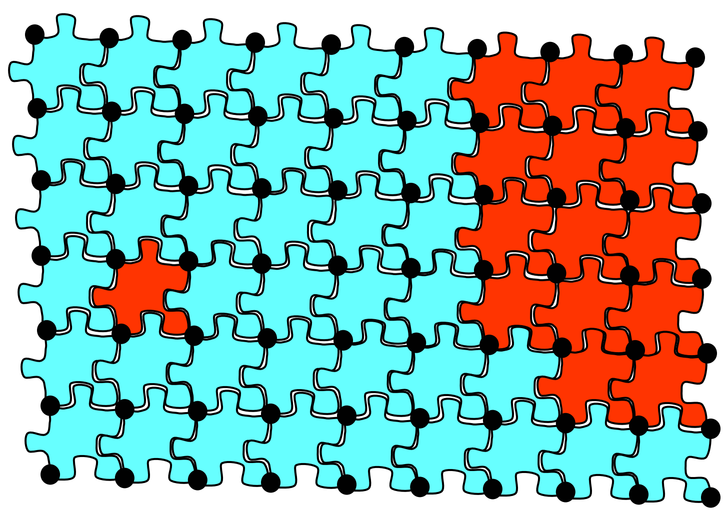
We observe the superposition of the two diffraction patterns.
The resulting pattern has higher symmetry than the true Laue symmetry and the intensity distribution of the twinned diffraction pattern is more even, resulting in a lower value for the $|E^2-1|$ statistic.

Twinning and jigsaw puzzles



Jigsaw Puzzle Cartoon by Dr. Thomas Schneider

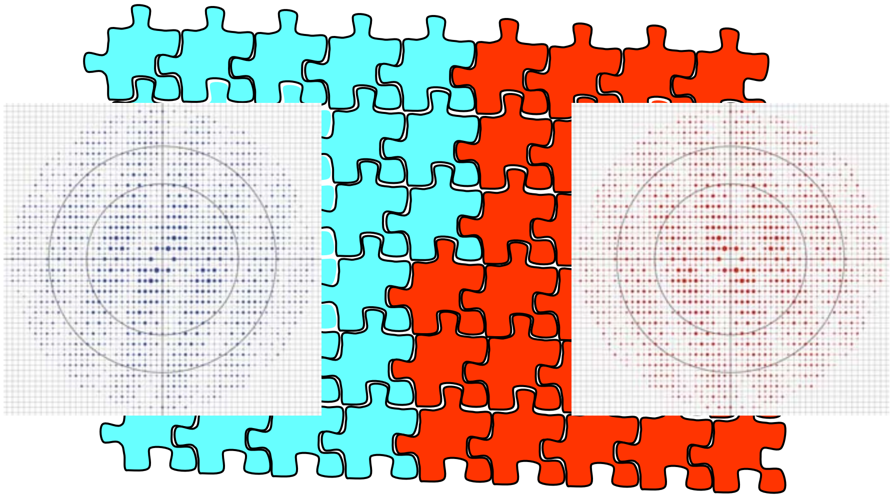
Jigsaw puzzles in the dark – can we tell the difference?



Same lattice, same unit cell, but in a different orientation!
If the crystal lattices overlap, the reciprocal lattices will too!

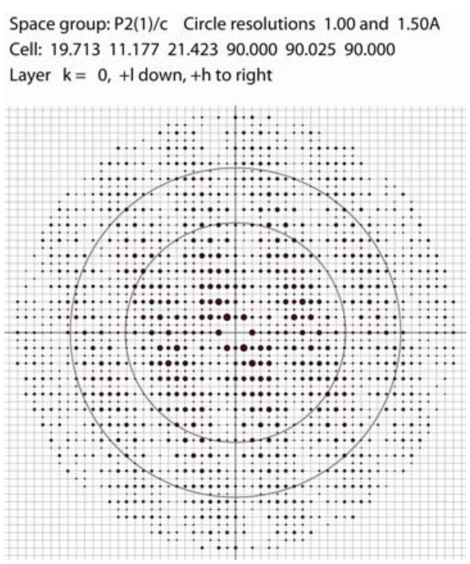
Jigsaw Puzzle Cartoon by Dr. Thomas Schneider

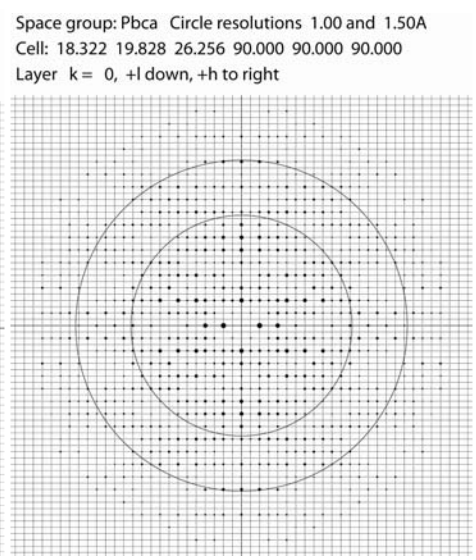
Jigsaw puzzles in the dark – can we tell the difference?



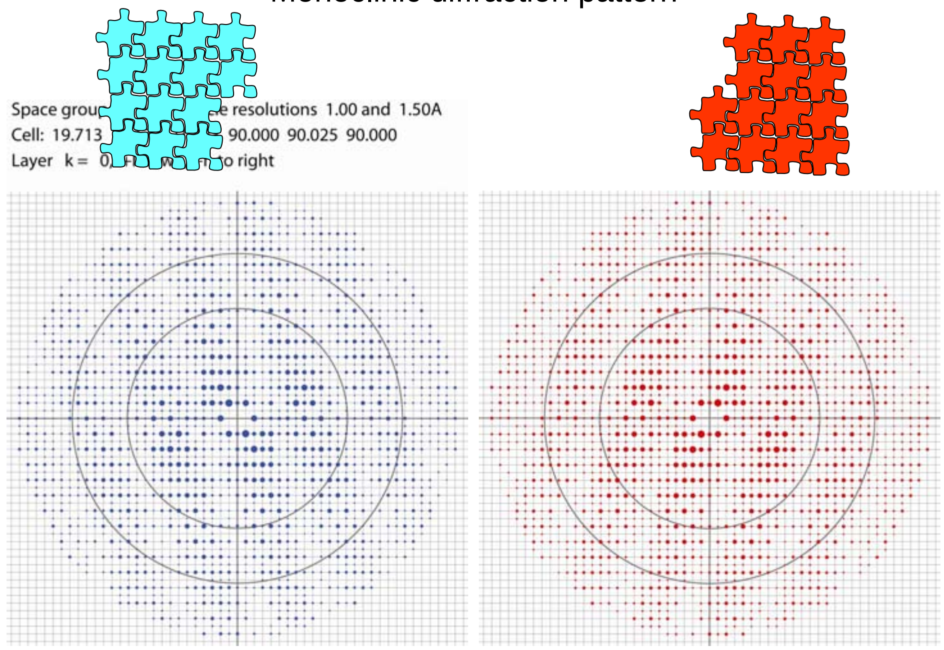
Jigsaw Puzzle Cartoon by Dr. Thomas Schneider

Laue groups 2/*m* versus *mmm*

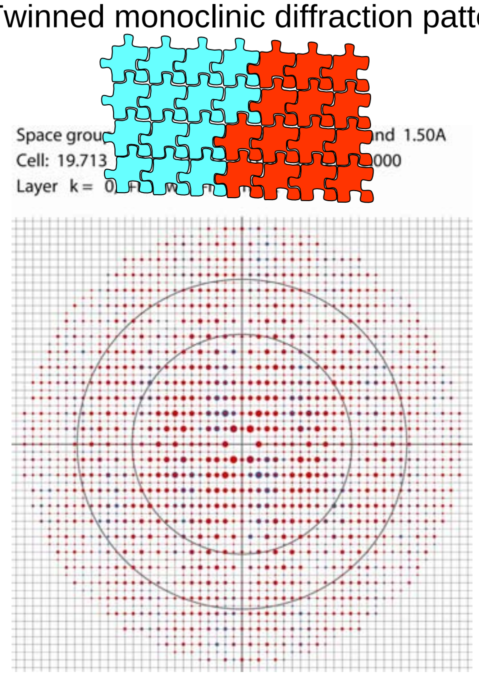




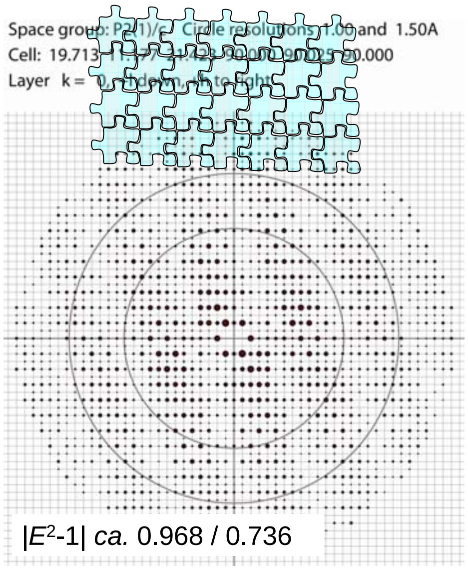
Monoclinic diffraction pattern



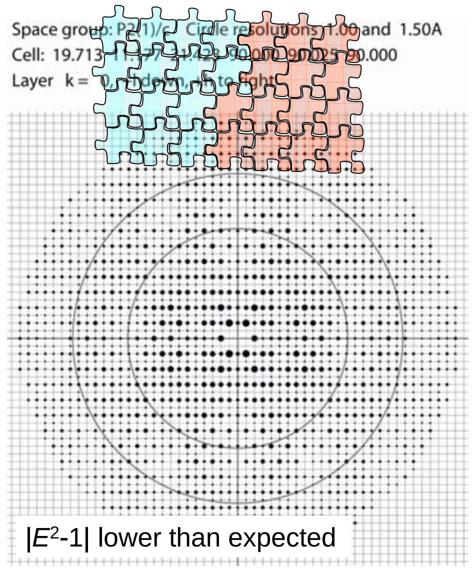
Twinned monoclinic diffraction pattern



Twinned monoclinic diffraction pattern looks orthorhombic and intensity distribution is more even



$|E^2-1|$ *ca.* 0.968 / 0.736



$|E^2-1|$ lower than expected

Classification of Twins

“Twins are regular aggregates consisting of individual crystals of the same species joined together in some **definite** mutual orientation” (definite as in ‘*twin law*’).

Twinning can occur when a unit cell – ignoring the contents of the cell – has higher symmetry than implied by the space group of the crystal structure.

Two possibilities: either the crystal lattice after application of the twin law overlaps with the original or not.
If yes: merohedral, pseudo-merohedral or reticular-merohedral twin.
If no: non-merohedral twin.
These four classes were introduced by Friedel in 1928.

NB: The preceding examples (jigsaw puzzle *etc.*) dealt with the first case. Non-merohedral twinning is different.

Merohedral Twinning

The twin law is a symmetry operator of the crystal system, but not of the point group / Laue group of the crystal. This leads to perfect overlap of the reflections of both domains.

For example: Say the true space group is $P4_1$ (Laue group $4/m$) and the twin law is a mirror perpendicular to *a* and *b* (part of the crystal system but not of the Laue group). This will generate an apparent mirror in the diffraction pattern, making the Laue group **look like** $4/mmm$ (somewhat depending on the twin ratio).

Merohedral twinning is possible only in the trigonal, tetragonal, hexagonal and cubic crystal systems.

Racemic twinning is a special case of merohedral twinning. The twin operator is an inversion center.

Twin Refinement

Each observed reflection has contributions of two diffracting domains, each giving raise to their individual reflections, related by the reciprocal twin law.

If *osf* is the overall scale factor (first Free Variable), k_m is the fractional contribution of the twin domain *m*, and F_{c_m} is the calculated structure factor if the twin domain *m*, we calculated for the combined structure factor F_c:

$$\left(F_c^2\right) = osf^2 \sum_{m=1}^{n} k_m F_{c_m}^2$$

SHELXL uses this equation to refine against the twinned data.
Never refine against mathematically un-twinned data See book for details)!

In most cases there are only two twin domains and k_1 = 1-k_2, but the general case looks like that:

$$k_1 = 1 - \sum_{m=2}^{n} k_m$$

Racemic Twinning and Absolute Configuration

For racemic twinning, the twin operator (that is the twin law) is inversion.

In order to determine the absolute configuration of a molecule, Howard Flack suggested to refine the structure as a racemic twin and determine the twin ratio (Flack-x parameter).

If the configuration is correct, the twin ratio will be zero (meaning 100% of the structure has the configuration as given in the .ins file). If the configuration is wrong, the twin-ratio will be one (meaning 0% of the structure is as given).

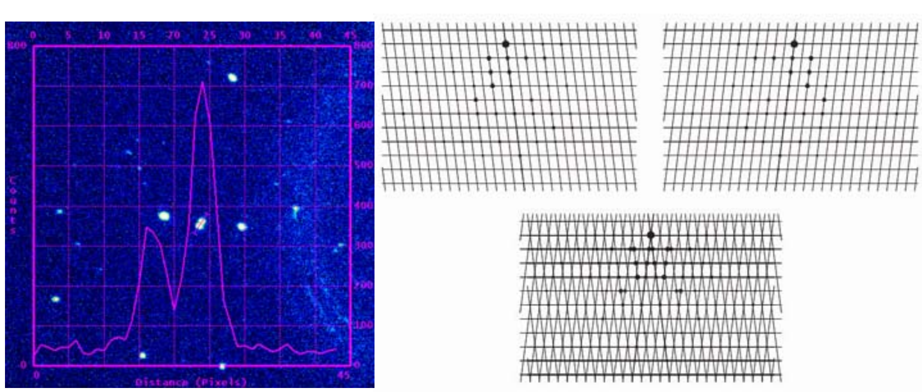
Values for the Flack-x between 0 and 1 mean that the structure is in fact racemically twinned.

$$\left(F_c^2\right)^* = (1-x)F_c^2(hkl) + xF_c^2(-h-k-l)$$

In this special case of the equation for F_c, x is the Flack parameter.

Non-Merohedral Twinning

The twin law does not belong to crystal system or metric symmetry or anything. It is just two identical crystals (not necessarily of identical size) morphed into one. Most usually the second domain is rotated by 180° against the first one. Some reflections in the resulting diffraction patterns are not affected, some are perfect overlaps of two reflections and some are partial overlaps (split reflections).



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Two or more independent orientation matrices need to be determined (cell_now) and taken into account during the integration (SAINT). Each reflection that corresponds to an overlap (or partial overlap) appears twice (or more often for higher numbers of twin components) in the .hkl file with two different sets of hkl integers. This requires a different format for the .hkl file: HKLF 5. See, for example, page 147 in the book.

In the case of non-merohedral twining, data must not be merged. The R_{int} value is not defined for non-merohedral twins.

In the .ins file: Give HKLF 5 instead of HKLF 4 and *n*-1 BASF parameters for *n* twin domains.

Warning Signs for Twinning

Long list of warning signs in the book. The most important ones are:

- Metric symmetry higher than Laue symmetry.
- R_{int} for higher symmetry Laue group is only slightly higher than for lower symmetry Laue group.
- $|E^2-1|$ statistic lower than expected.
- Trigonal or hexagonal space group.
- Systematic absences inconsistent with any space group.
- No solution can be found or refinement gets stuck at high R-values.

Specifically for non-merohedral twins:

- Some reflections split some not.
- Difficulty finding and refining the unit cell.
- $F_o >> F_c$
- Spurious residual electron density maxima.

5.067 Crystal Structure Refinement
Fall 2009