Important notes about the twinning.

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These notes were based on some lecture notes and important crystallography books. For more details, see the references below. All material presented here is compiled from these references.

1) Fundamentals of Crystallography", by C. Giacovazzo, Union of Crystallography, Oxford University Press 2nd Edn. 2002.
2) Müller, Peter and others, *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL*, International Union of Crystallography Texts on Crystallography (Oxford, 2006; online edn, Oxford Academic, 1 Sept. 2010).

Twin crystals: A short Introduction:

For typical crystal structures that have thousands of unique reflections, indices (hkl) can be assigned to each reflection, showing its position within the diffraction pattern, describing the unit cell parameters. This pattern has a reciprocal relationship with the crystal lattice and the unit cell in real space. This step is fundamental for the solution of the crystal structure. However, when the framework has problems, these steps may not be trivial. Often, the ***reflection profiles usually split in the diffraction pattern***, is described by twinning.

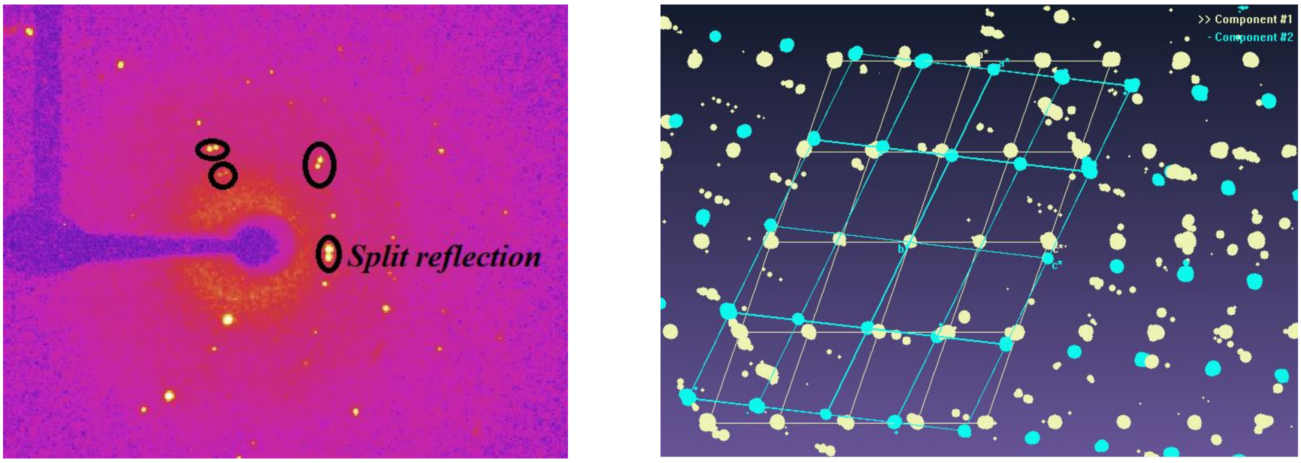


Figure 01 – Diffraction Pattern and Reciprocal lattice with two domains (component 1 and 2).

And according to the definition of twinning:

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

“From a geometrical point of view a twin is characterized by the symmetry operations which relate one individual to the other individuals in the composite crystal. The operation is very frequently a rotation through n about a zone axis.”

• Consider two hypothetical two-dimensional crystals growing together (A + B) as well as their contents and unit cells:

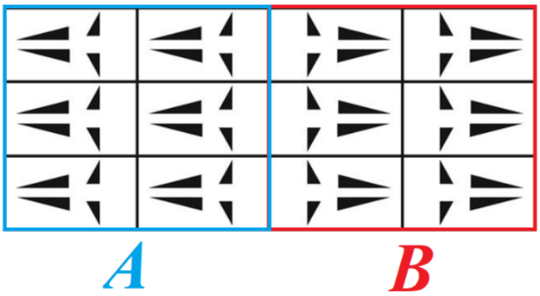


Figure 02 – 2D perfect twin with two domains.

The content of the unit cell in **A** has mirror symmetry in one direction as well in **B** (Figure 02), while the symmetry of the cell (metric symmetry) has an additional mirror perpendicular to the first mirror. Crystal **A** can be transformed into crystal **B** by applying an external symmetry operation to the unit cell. In this case, a mirror (metric symmetry), and in this case, If the two crystals grow together, it has a twin situation.

- The twin operation of this twin (twin law) is the mirror plane which transforms one domain into the other.
- Both domains are the same size, the fractional contributions of both domains are **50%**, and this case is known as a perfect twin.

In figure 03, it is possible to see a twin crystal with fractional contributions of 0.67:0.33, and corresponding to a partial twin, however, with same twin-law.

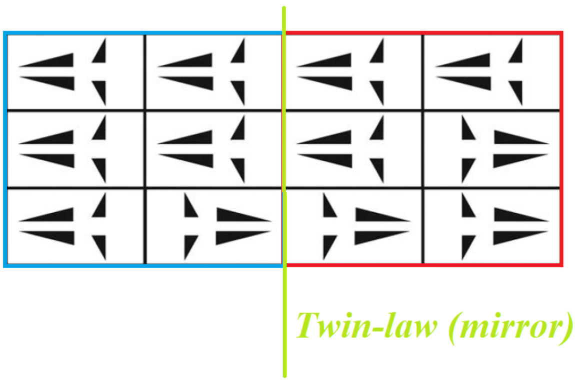


Figure 03 – Partial twin (ratio 0.67:0.33).

The twin-law can be expressed as a matrix which transform the *(hkl)* indices of one species into the other. For simple example, the twin law for 2D crystal can be expressed by the matrix (1 0 0 -1).

These two features- twin law and fractional contribution- are necessary for description of a twin. Multiple twins consist of three or more components. However, in this case, it can be difficult to find the twin-law for the components. Keep in mind that separating and identifying the reflections and intensities of each component is not always a trivial task.

What happens to the diffraction pattern when twinning occurs?

If the crystal (A+B) is transformed, the reciprocal lattice can also be transformed by applying the symmetry operation that correlates both crystals. Thus, the intensities of both reciprocal lattices are added, and the collection data contains the set referring to the two crystals, Figure 04.

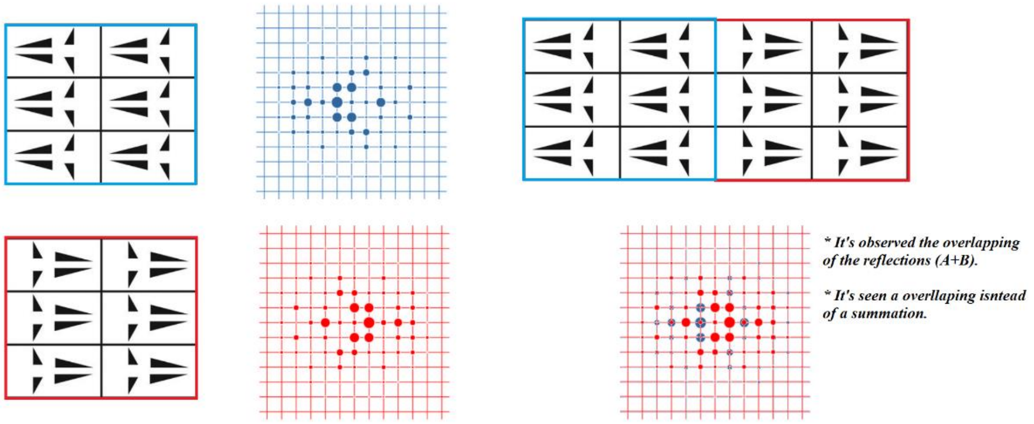
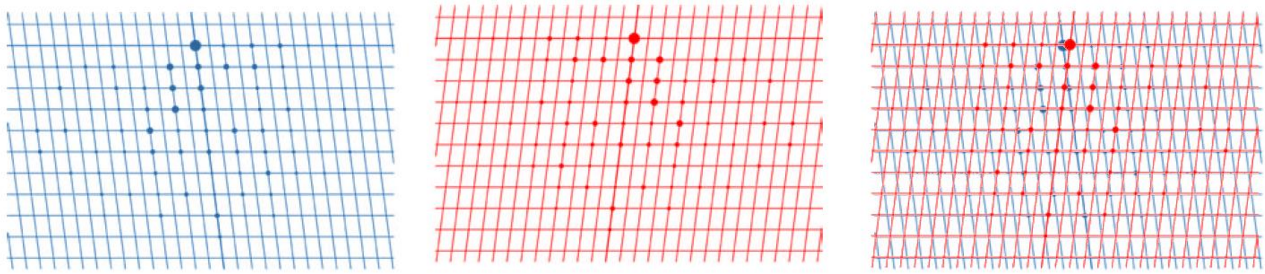


Figure 04 – Reciprocal space plot for crystal (A+B) in perfect twin situation.

There are several systems of twin classification. For Figure 04, the twins are classified as <u>merohedral twins</u>, as there is a reciprocal lattice overlap between the reciprocal points and an additional mirror symmetry appears for this situation, a strong feature for it.

- **<u>For non-merohedral twins.</u>**

For non-merohedral twins, the twin law doesn't belong to the crystal class of the structure or to the metric symmetry of the unit cell. In this case, the different reciprocal lattices do not overlap exactly and, <u>there are some reflections</u> which overlap or can't be distinguished from each other, but most part of the reflections are not affected by the twining, Figure 05. All most of the points don`t overlap and are separate.



A *B* *C*

Figure 05 – Reciprocal lattice plot of the k = 0 layer of a monoclinic C-centred crystal in ***A***. Same layer as in ***A*** with rotate by 180° about ***c***-axis in ***B***. Overlapping of ***A*** and ***B*** in ***C***. Some reflections overlap and some do not overlap.

An example to this form of twinning is an orthorhombic crystal structure where 2***a*** ~ ***b*** (Fig. 6). For more details about this example, consult (*Parsons, Acta Cryst. (2003). D59, 1995-2003*).

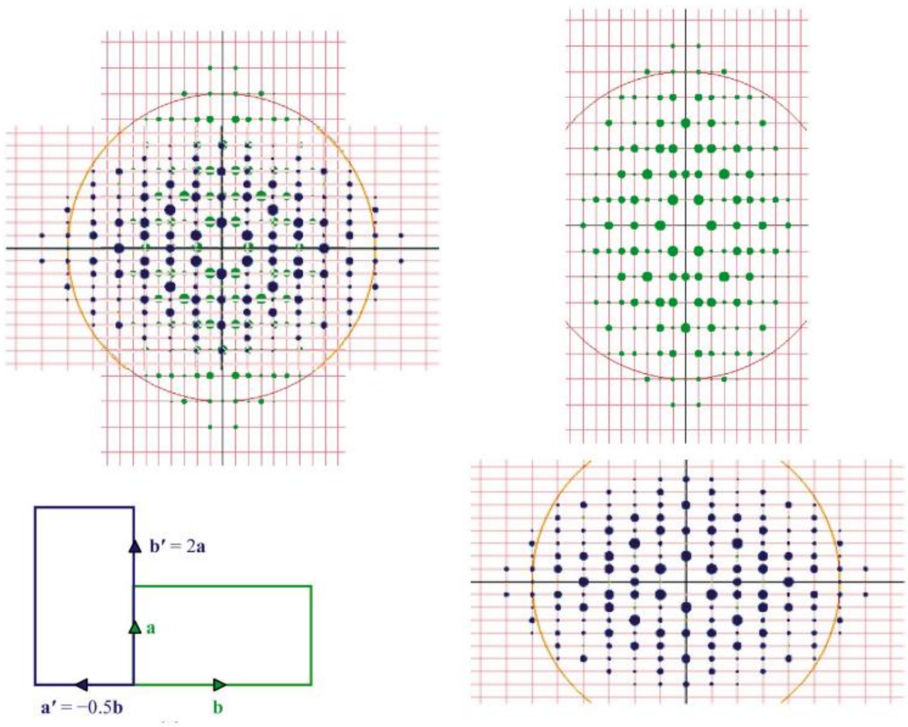


Figure 06 – Reciprocal lattice of crystals and their symmetry element relationship.

The diffraction pattern from one domain of the crystal is related to that from the other by a 90° rotation about ***c****. Overlapping of the two diffraction patterns (Blue and Green) shows that data from the first domain are only affected by overlap with data from the second domain when ***k*** is even. Then, this twin law needs to be expressed with respect to the axes of the true orthorhombic cell. From Fig. 4, **a**′ = -0.5**b**, **b**′ = 2**a**, **c**′ = **c**, and that the twin law is (0 -1/2 0 2 0 0 0 0 1) and the effect of this matrix on the data is (0 -1/2 0 2 0 0 0 0 1) (***h k l***) = (-***k***/2 2***h l***). Confirming that only data with ***k = 2n*** are affected by the twinning. Thus, the reflections from the first domain (green) is overlapped with the reflection from the second (blue) domain where most of the reflections in the green domain doesn't overlap and are unaffected by twinning.

Normally this kind of twinning is detected at the diffractometer, because the automatic cell determination fails or have a lot of problems. Split reflections profiles or un-indexed reflections are typical warming. In case of a two domain non-merohedral twin such as previous examples, two orientation matrices must be determined. And so, the usual programs take into account that only a particular fraction of the reflections will fit an individual solution. As a result, a list of possible solutions is presented. If second domain is much weaker, the determination of the orientation matrix of this domain could be problematic because there are only a few strong reflections that fit only this weak domain. However, If the solution is accepted, all the reflections that do not fit this first solution are placed in a new reflection list to re-run the cell determination process.

- **H**ow to work with non-merohedral twins.

There are three different types of reflections:

1) Reflections that do not overlap with any reflection of the second domain,
2) Reflections that overlap exactly with a reflection of the second domain,
3) Reflections that overlap partially with a reflection of the second domain.

The last type is the most problematic, because usually the degree of overlap is not known and differs from reflection to reflection.

In general, only reflections with a contribution from the main domain should be used, because in most cases this domain is much better determined. Even if data of both domains are similar in quality, the addition of reflections having only a contribution from the second domain does not usually improve the structure determination.

For small molecules, normal direct methods are often able to solve twinned structures even for perfect twins, provided that the correct space group is used.

For partially twinned structures, mathematical detwinning is possible if the fractional contribution is not too close to 0.5.

- Initially check the indexing percentage of the unit cell parameters, indexing below 80% is a Red Flag to start the investigation by twin.
- Try to find split reflection sets, it is indicative of twinning.
- Try to determine the cell and the twin law in a program, generally, a 180° rotation is more common to define the law.

- Consider that your crystal may be cracking rather than twinned. Check the rotation matrix and search for integers.
- Reduces and writes a .p4p file to new .hkl files (hklf4 and hklf5) for more than one domain integration.

This detwinned data can be used for structure solution, while refinement should be performed against the original data.

- Use the hklf4 file for the structure solution normally, and after finding the crystalline phase as well as all the atoms of the structure, use the hklf5 file.

For overlapping lattices, a normal intensity data file (standard HKLF4 format) can be used together with the following two instruction lines:

TWIN *rij n*

BASF n

The matrix *rij* is the twin law and *n* the number of twin domains.

The batch scale factor BASF is followed by *n*−1 starting values for the fractional contributions.

The default value for *n* is 2, which corresponds to a twin with two domains.

If only part of the reflections have a contribution from the second domain (twinning by reticular merohedry and non-merohedral twins), a special reflection file is necessary, which is read in by the command

HKLF 5

The HKLF 5 is given at the end of the .ins file, replacing the line that reads HKLF 4.

BASF is used as in the case before.

As merging is no longer allowed the default value for MERG assumed by SHELXL is now 0.

Check the example, DHPM28 and their files. Even when constraints are employed, the distribution of displacement and residual parameters characteristics in a difference electron density map may be less satisfactory than for a normal structure determination.

Justification will likely be required during the Checkcif Process.