Twinning (maclage)

What do we do with a twinned crystal?

… we recrystallize!

« When twinning occures in crystals grown for structure determination, however, it has usually been a good reason for proceeding no further in view of the difficulties expected.» W. Massa, *Crystal Structure Determination,* **2002**

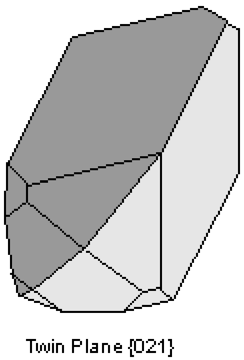
Fin

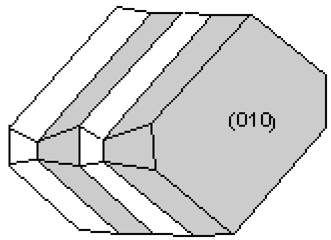
Definition of a twin

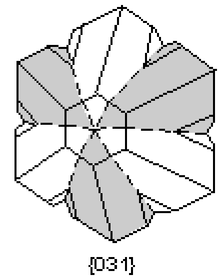
Giacovazzo, 2002:

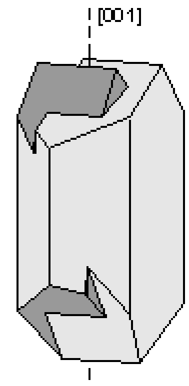
Crystal twins are *regular* aggregates consisting of individual crystals of the same species joined together in some definite mutual orientation.

Classification by appearance









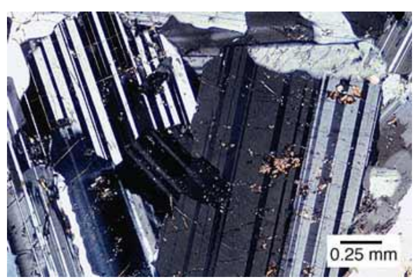
Macle par accolement
Contact twin

Macle polysynthétique
polysynthetic twins

Macle cyclique
cyclical twins

Macle d'interpénétration
Penetration twin

http://www.tulane.edu/~sanelson/eens211/twinning.htm



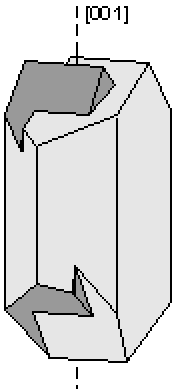
http://www.burmarubies.com; http://mindat.org; http://geology.isu.edu/geostac/Field_Exercise/Cassia_mtns/thinsect.html; http://members.aol.com/vbetz/trading2/tausch.html

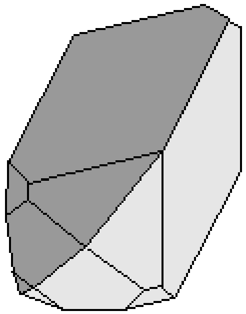
Classification by twin law

A twin is not simply two crystals glued together!

- The two twin domains share a real plane (and thus a reciprocal axis) or a real axis (and thus a reciprocal lattice).
- The twin law desribes the transformation from one domain in the other.

- We can distinguish:
  - **Rotation twins:** The shared axis can be a rotation axis (2-, 3- etc.) and is often an axis of the unit cell.
  - **Reflection twins:** The most abundant twins. The two domains are related by a reflexion on a hkl lattice plane.
  - **Inversion twin/racemic twin:** Those exist only in non-centrosymmetric structures. Inversion twins are the easiest twins to treat.





Classification by origin

Growth twins:

- Two (or more) twin domains started growing from the same nucleation site.
- Typically large domains
- Reflections twins can from time to time be separated by cutting under the microscope.

Deformation twin:

- Twinning was introduced by application of mechanical force.

Transformation twin:

- Twinning accompanied by a phase change, i. e. a transformation (most often loss) of symmetry.
- Formation of microscopic domains (typical origin of polysynthetic twins)
- There are two types of phase transformation:
  - Into a t-subgroup (t = *translationsgleiche* = identical translations): the unit cell does not change, but we loose symmetry elements ($P2_1/c$ into $P2_1$). The lost symmetry elements can be twin operators (twin laws).
  - Into a k-subgroup (k = *klassengleiche* = identical crystal class): Change in centering or the size of the unit cell. Twinning in this case will be racemic twinning.

Classification by the reciprocal lattice

The reciprocal lattice obtained from a twinned crystal depends on the type of the twinning.

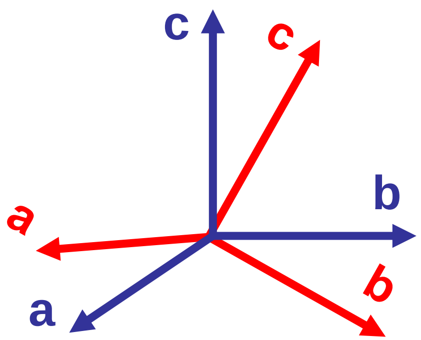
We distinguish 6 types of twinning:

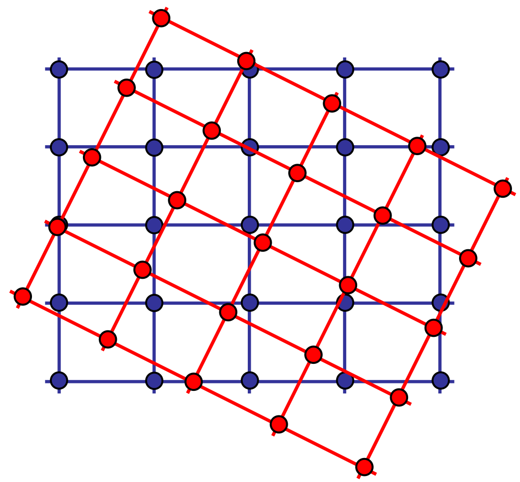
- **Merohedral** twinning / Maclage par **mériédrie**
- **Pseudomerohedral** twinning / Maclage par **pseudomériédrie**
- **Reticular merohedral** twinning / Maclage par **mériédrie réticulaire**
- **Reticular pseudomerohedral** twinning / Maclage par **pseudomériédrie réticulaire**
- **Non merohedral** twinning / Maclage **sans mériédrie**

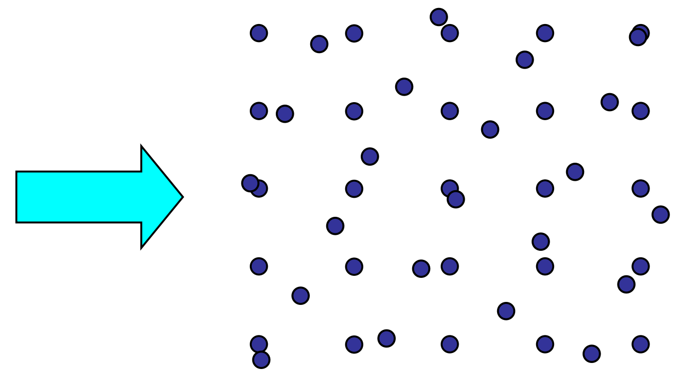
Merohedry:
Superposition of the reciprocal lattices of the two domains of a twin.

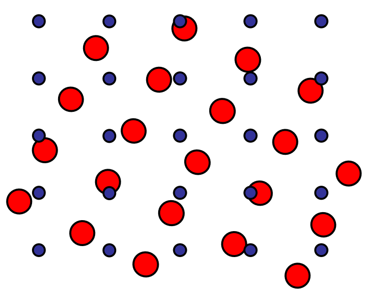
Maclage sans mériédrie («non merohedral twinning»)

- In most of the cases, the twin law (the operation which transforms one domain of a twin into the other) is **neither an element of the Laue group nor of the crystal system**.
- **There is no (systematic) superposition of the two reciprocal lattices**. We have two independant lattices with accidental superposition of isolated reflections.
- Very often we will have severe problems or be unable to index the reflexions, i. e. finding the unit cell.





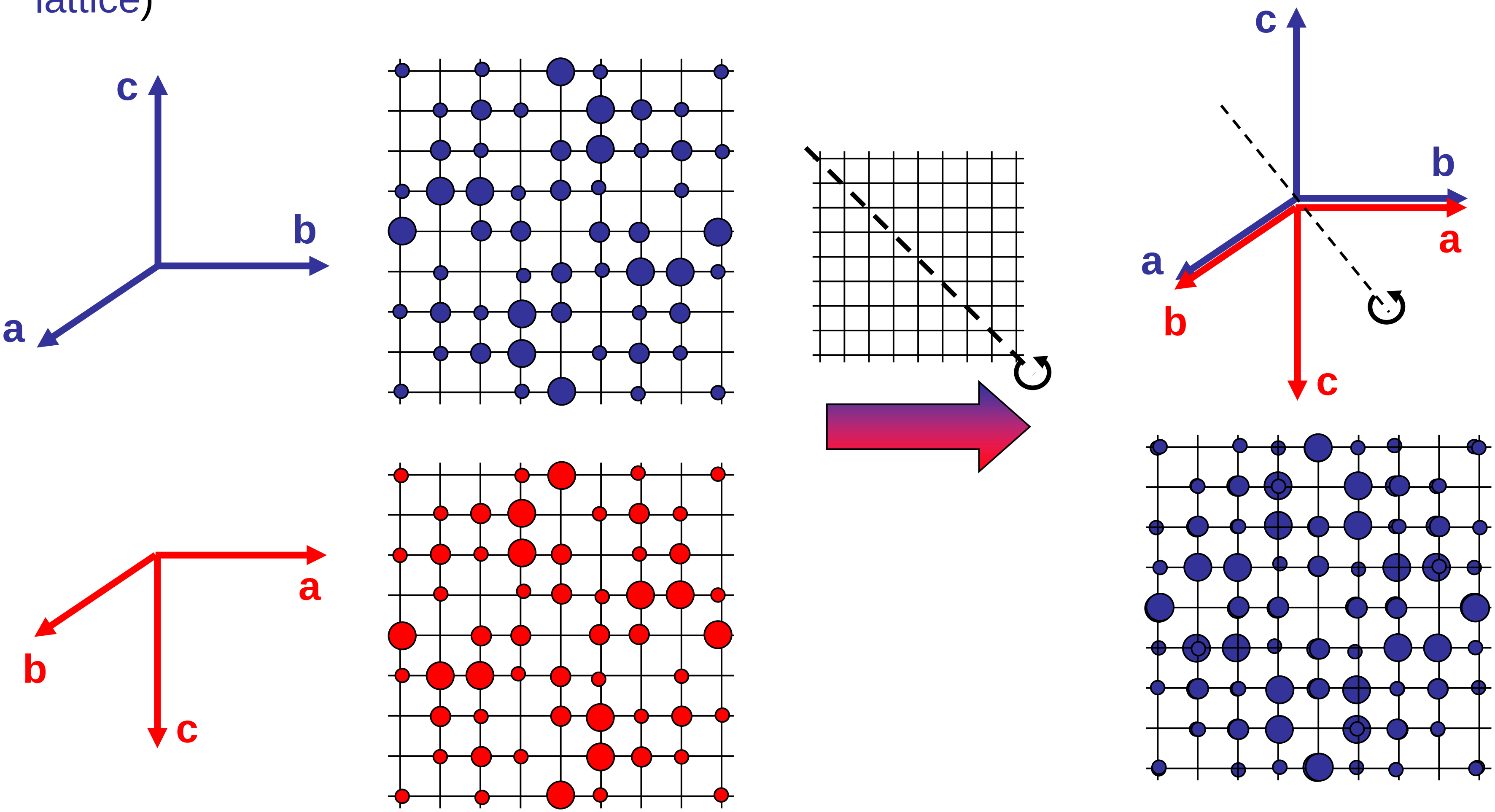




If one domain is significantly bigger than the other one, only this one will yield strong reflexions. The automated indexing normally will proceed without problems. But several reflections will have incorrect intensities, since peaks fo the other domain will overlap.

Maclage par mériédrie («Merohedral twinning»)

Example: Crystal in a tetragonal space group, twinning by rotation around [110] (part of the symmetry of the reciprocal lattice)



Laue group: 4/m **Laue group: 4/mmm**

Maclage par mériédrie («Merohedral twinning»)

1. Merohedral twinning

- **The twinning operation is part of the crystal lattice**, but not part of the Laue group.
- **Superposition of all reflections**
- **Only possible in tetragonal, trigonal, hexagonal and cubic** crystal classes, which have a Laue group with a symmetry which is lower than that of the lattice.
- The number of possible twin laws is limited (11 possibilities for all space groups).

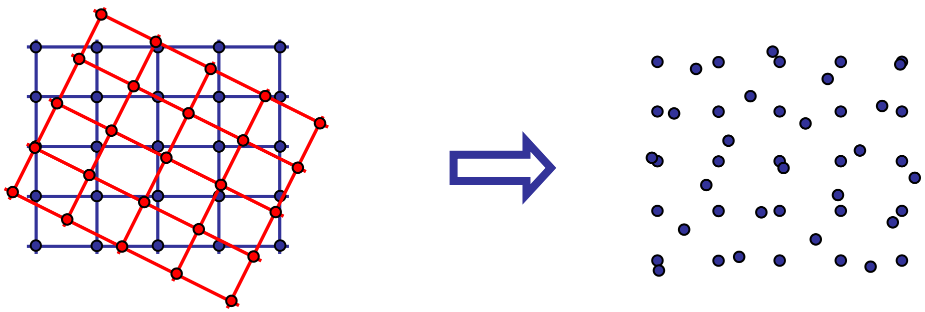
2. Racemic twinning (inversion twin)

- The two reciprocal lattices superimpose exactly.
- In the absence of anomalous dispersion, racemic twinning is not noticeable.
- Only possible in non-centrosymmetric space groups
- **The only twinning by merohedry possible in triclinic, monoclinic and orthorhombic crystal classes.**
- Normally refined using the Flack-x parameter.
- The twin law is:

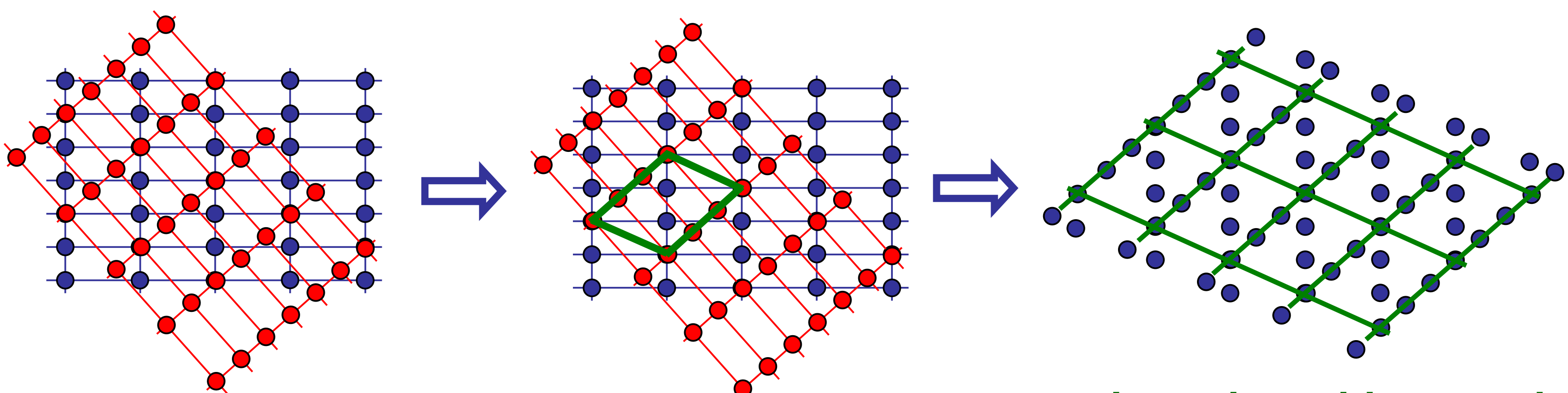
$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Maclage par mériédrie réticulaire
(«reticular merohedral twinning»)

As before (non-merohedral twinning), the twin operator does not have any relation with the space group or the Laue group of the crystal. However, it is part of a “superlattice”, i. e. after a certain number of repetitions the two reciprocal lattices again superimpose at a point.



non-merohedral twinning

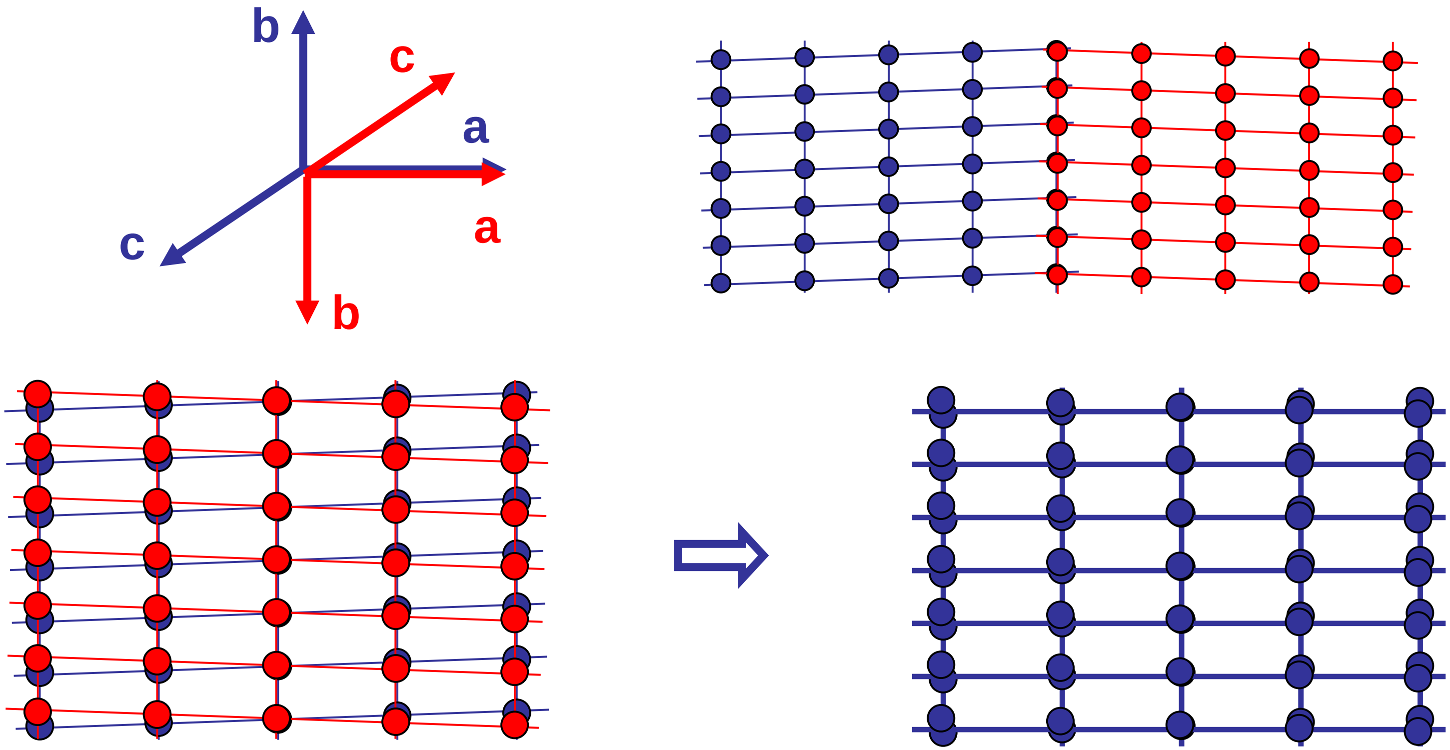


Here: Three times bigger unit cell

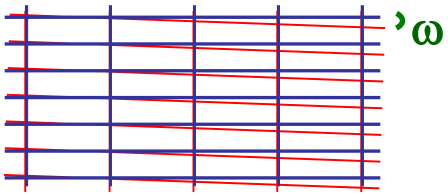
Effect: We obtain a **bigger unit cell**, often with (bizarre) centering, in another crystal system (eventually of higher symmetry).

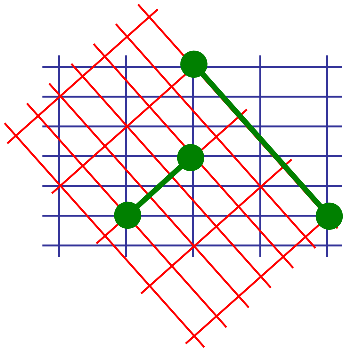
Maclage par pseudomériédrie («Pseudomerohedral twinning»)

- If the geometry of the unit cell is by hazard geometrically close to one of a higher symmetry, the reciprocal lattices of the twin domains superimpose by “geometrical accident” (separation of the reflections smaller than the resolution of the instrument). E. g. monoclinic with $\beta \approx 90°$, combined with twinning by a rotation $C_2 \parallel a$, might mimic orthorhombic.
- Pseudomerohedral twinning normally does not show problems with indexing (finding the unit cell), but eventually in integration since reflections become larger at higher diffraction angles.



Another way to describe twinning





Obliquity ω : The deviation (in °) of the lattice generated by twinning and the original lattice.

Twin index *n* : The periodicity after which a superimposed lattice point of the twin domain superimpose again with the original lattice. The twin index is also the ratio between the twin unit cell and that of the individual (untwinned) crystal.

Merohedral twinning :	$\omega = 0$; $n = 1$
Pseudomerohedral twinning :	$\omega > 0$, but small; $n = 1$
Reticular merohedral twinning :	$\omega = 0$; $1 < n < \approx 6$
Reticular pseudomerohedral twinning :	$\omega > 0$, mais petit; $1 < n < \approx 6$
Non-merohedral twinning :	$\omega >> 0$; $n > 1$

When should we suspect twinning by (pseudo)merohedry ?

1. $|E^2-1|$ is smaller than 0.736 for non-centrosymmetric crystals
2. Metric symmetry is higher than the Laue group symmetry
3. R_{int} for the Laue group of higher symmetry is comparable to that of the lower symmetry
4. Several crystals have different ratios of R_{int} (Laue group of higher symmetry) / R_{int} (Laue group of lower symmetry)
5. Space group is trigonal or hexagonal
6. There are systematic absences which does not exist in the space group (indication of reticular merohedry)

When should we suspect non-merohedral twinning?

1. There are very long unit cell axes
2. Problems with the determination of the unit cell (indexing)
3. Some reflections are sharp, other broad or show two maxima
4. *K* is high (> 4 times) for reflections of low intensity. (Can indicate also the choice of a wrong space group)
5. For all/most of the "most disagreeable reflections" F_o is higher than F_c (addition of reflection intensity from the second, twinned domain to some arbitrary reflections)
6. Strange residual electron density
7. High R values with good data
8. «Weighing scheme» refines to bizarre values (i. e. WGHT 0.00 623.3)
9. « Most disagreeable reflections» have systematic repetitions for h, k or l. (I. e. h = 3, 6, 9)

Merohedral twinning

Reminder:

- Total overlap of all reflections

Solution:

- Unit cell determination and integration proceed normally.
- Twin law has to be found after data reduction
- There is only a limited number of possibilities for merohedral twinning and only in **trigonal, hexagonal, tetragonal or cubic systems.**
- In all cases, the twin law is a rotation C_2. Possible twin laws (depending on the space group) might be found in the « International Tables of Crystallography»
- Specialized programs (ROTAX) can do this for us

Example (manuel SHELX 6.4) :

- **(a)** Twinning by merohedry.

Twinning by reticular (pseudo-)merohedry

Reminder:
- Reflections overlap with a periodicity. Unit cell increased.

Indications:
- Big unit cell, eventually with bizarre centerings (systematic absences)

Solution:
- Unit cell determination (indexing) and integration proceeds normally
- Twin law has to be found after data reduction

Example (manuel SHELX 6.4) :
- **(e)** Rhombohedral obverse/reverse twinning on hexagonal axes.

Pseudomerohedral twinning

Reminder:
- Overlap of all réflexions

Indications:
- Widening of reflections at higher theta angles.

Solution:
- Unit cell determination (indexing) and integration proceeds normally in most cases
- Twin law has to be found after data reduction
- Possible in all space groups
- Use of special programs (GEMINI, TWINROTMAT (Platon)) to find the twin law.

Example (manuel SHELX 6.4) :
- **(b)** Orthorhombic with **a** and **b** approximately equal in length may emulate tetragonal
- **(c)** Monoclinic with beta approximately 90° may emulate orthorhombic
- **(d)** Monoclinic with **a** and **c** approximately equal and beta approximately 120 degrees may emulate hexagonal

Non-merohedral twinning

Reminder:

- No (or only accidental) overlap of the reciprocal lattices. Two independant lattices

Indications:

- Indexation (determination of the unit cell) fails
- Alternatively, a big unit cell might be obtained, which still leaves many reflections unindexed.

Solution:

- Détermination of the orientation matrices for both independant crystals (programs: DIRAX, GEMINI, **CELL_NOW**)
- Twin law is calculated from these orientations
- Twin law has to be determined before data reduction
- Possible in all space groups
- Data reduction yields TWO datasets, one for each crystal domain

- **If the second domain is small**, only one domain might be found in the initial determination of the unit cell and integration proceeds without problems. However, reflections which are superimposed which reflections of the twin domain have artificially high intensities. Corrections (after data reduction) are possible using the programs ROTAX or **TwinRotMat (Platon).**

Additional resources

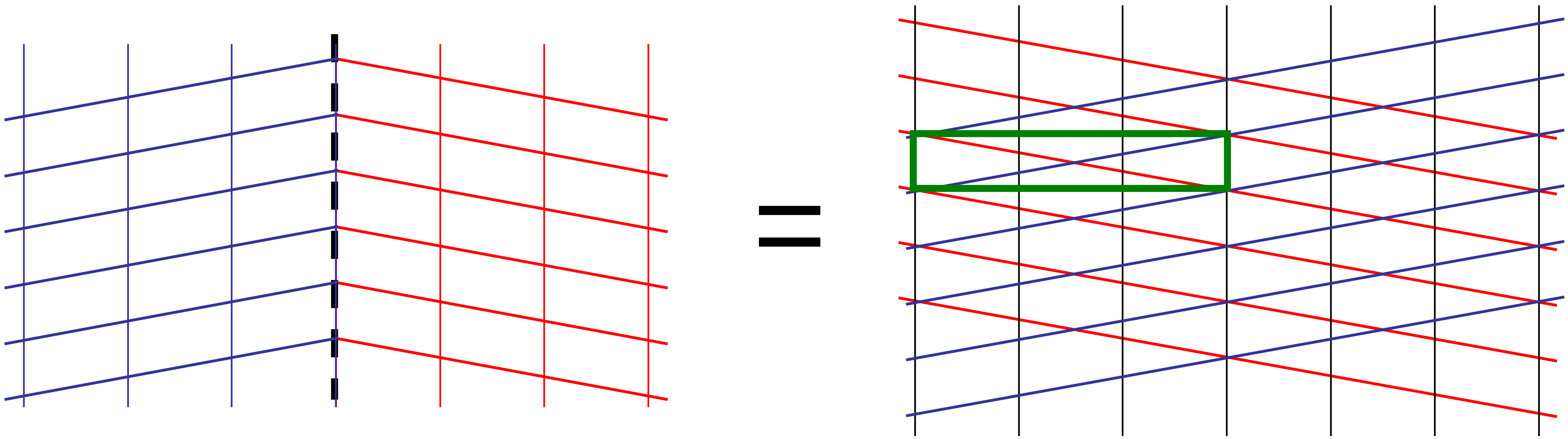
- http://www.lcm3b.uhp-nancy.fr/lcm3b/Pages_Perso/Nespolo/twinning.php
- Twin refinement with SHELXTL (http://shelx.uni-ac.gwdg.de/~rherbst/twin.html)
- http://www.cryst.chem.uu.nl/lutz/twin/gen_twin.html
- http://www.lcm3b.uhp-nancy.fr/mathcryst/twins.htm (IUCR)
- http://www.chem.umn.edu/services/xraylab/twin_workshop.pdf (aussi sur le CD distribué)
- http://acaschool.iit.edu/lectures04/Campana2.pdf (aussi sur le CD distribué)
- http://www.tulane.edu/~sanelson/eens211/twinning.htm (très descriptif)
- http://nihserver.mbi.ucla.edu/Twinning/ (online tool to test for merohedral twinning)
- Twinning. Don't give up - yet. (http://www.xtl.ox.ac.uk/twin.html)

Fin

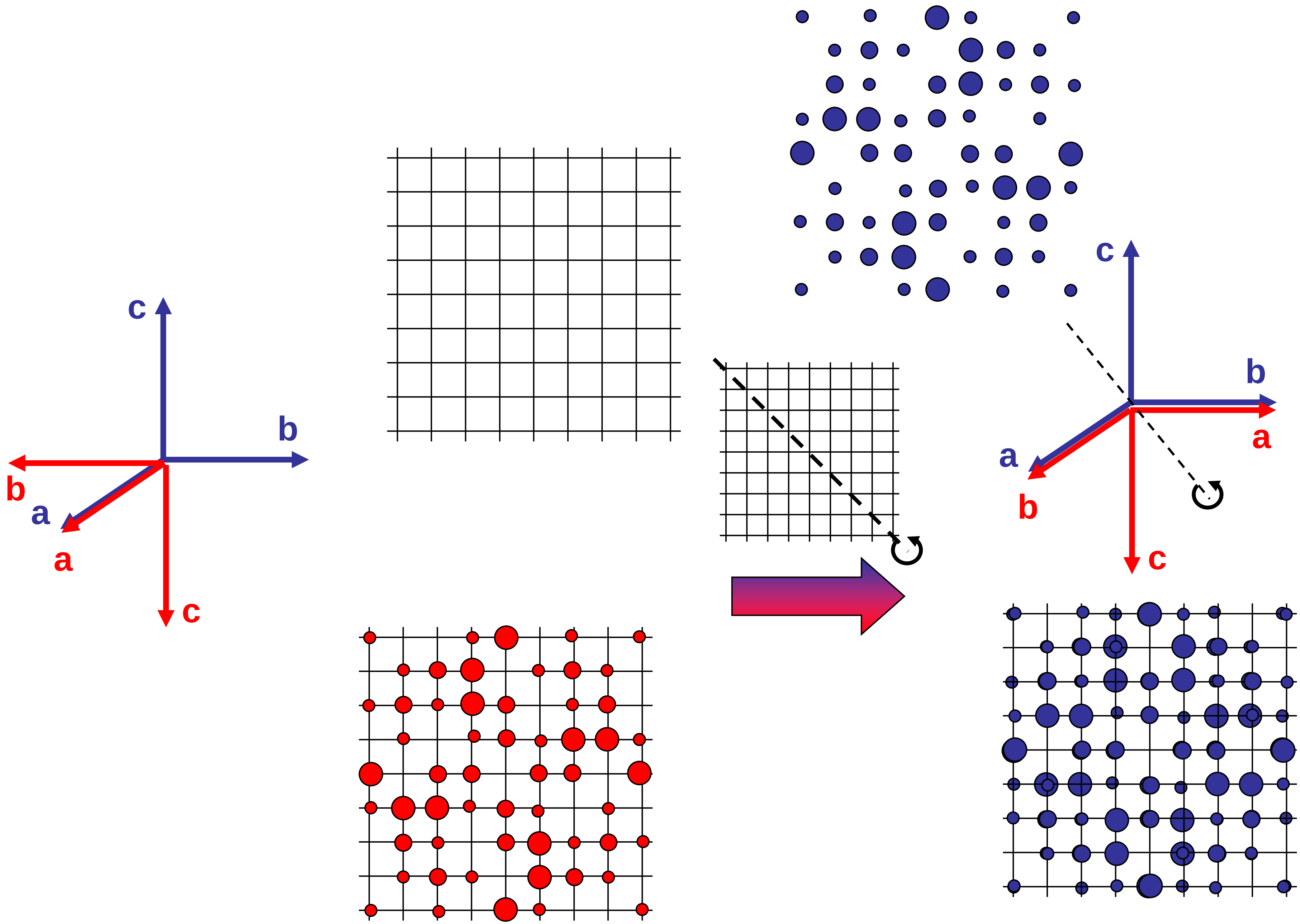
Maclage par mériédrie réticulaire
(«reticular merohedral twinning»)

Comme avant, l'opérateur de maclage n'a pas aucune relation avec la groupe spatial ou Laue de cristal, mais il est part d'une « superlattice ». I. e. que après un certain nombre de répétitions, les deux réseaux superimpose à un point.

Effet: On obtient une **maille plus grande** (souvent avec centrage) dans un **système cristallin de plus haute symétrie.**



Ici: Maille trois fois plus grande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