Twinning

- Non-merohedral twinning
- Merohedral twinning

Twinning

- At one time this meant something, today if simply means not a single crystal.
- Basically there are two types
  - A sample contains more than one crystal—non-merohedral twin
  - A crystal that is sort of a huge disorder that adds non-existent symmetry –merohedral twin

Racemic Twinning

- In this case each unit cell is enantiomorphically pure but the crystal is made up of both d and l cells
- This is rare for polar space groups but common in non-polar accentric cells.
- The twinning will effect the r-factor and the adp's
- Add two cards to SHELX .ins
  - TWIN
  - BASF 0.5 --this is the ratio of the two types of cells.

Non-merohedral Twins

- These must be treated as multiple crystals.
- They must be indexed so that the orientation matrices of each component must be determined. This cannot be done with DENZO.
- Once this is done must recognize there are two types of diffraction spots.
  - Spots that are well defined and belong to a single component
  - Spots that overlap and belong to more than one component

Non-merohedral Twins

- There are two types
  - Two or more random multiple crystals—unless sample is in short supply there is no reason to use such crystals.
  - Cases where the twinning is a 180° rotation around a reciprocal axis
    - This is only possible for triclinic or monoclinic crystals as a 180° rotation in higher symmetry takes an axis into -axis.
  - For some compounds this second type of twin is present in all the suitable crystals.

The twin law

- Obviously there is a relationship between the two components.
- This is called the twin law and is a 3x3 matrix that translates one cell into the other.
- The programs that index twins provide the twin law.

Refining Twins

- There are several approaches to refining twins.
- The first is to simply ignore the twinning.
  - During data averaging some reflections will have contributions from multiple components this will result in large values of Rint.
  - There will also be some data where the intensity is too large because of overlap. The worst of these can be removed using OUTLIER
  - The final R factor will be somewhat larger than if the twinning is treated.
  - The greater separation on the Cu image plate makes this more practical

Output

FILE USED IS xl.ins
0.2000 0.0000

	H	K	L	FO	FC	IND	d
REJECTED REFLECTION	10	1	0	1629.2	286.4	8.48	1.51
REJECTED REFLECTION	11	1	0	4132.7	629.3	9.26	1.37
REJECTED REFLECTION	15	1	0	999.9	2.6	8.50	1.01
REJECTED REFLECTION	14	2	0	720.6	123.6	6.46	1.06
REJECTED REFLECTION	8	3	0	3824.6	939.8	7.31	1.59
REJECTED REFLECTION	10	3	0	3862.8	423.8	10.42	1.35
REJECTED REFLECTION	14	3	0	1442.4	266.8	7.66	1.02
REJECTED REFLECTION	10	4	0	1373.6	353.8	6.81	1.24
REJECTED REFLECTION	14	4	0	455.4	49.0	6.18	0.97
REJECTED REFLECTION	-1	1	1	19.5	41565.9	7.49	7.17
REJECTED REFLECTION	0	1	1	17.7	21648.7	7.49	8.06
REJECTED REFLECTION	1	1	1	26.5	34089.8	7.49	7.10
REJECTED REFLECTION	-1	2	1	50472.2	15562.8	6.35	4.05
REJECTED REFLECTION	8	2	1	2083.7	130.4	11.14	1.74
REJECTED REFLECTION	10	2	1	2669.9	661.2	7.26	1.44
REJECTED REFLECTION	10	3	1	703.1	143.4	7.36	1.34
REJECTED REFLECTION	-11	6	1	479.4	51.5	8.51	0.99
REJECTED REFLECTION	-8	6	1	1531.3	327.3	7.14	1.14
REJECTED REFLECTION	-10	7	1	596.9	93.5	6.27	0.95
REJECTED REFLECTION	0	1	2	8.1	28471.4	7.50	7.08
REJECTED REFLECTION	-13	2	2	300.5	1.0	8.35	1.13

And Many More

Rigorous Refinement

- Must integrate the data set for each separate component
- This will produce two data sets
  - An HKLF 4 data set which is one component
  - An HKLF 5 data set which is for twins.
  - The next to last card in SHELX indicates the type of data
- Solve with HKLF 4 and finish with HKLF 5
- Add a BASF card with HKLF 5

Another Approach in SHELX

- If the twin law is know use it instead of HKLF 5
- Add a card TWIN followed by the nine numbers of the twin law.
- Add a BASF card.
- This will correct for overlap without an additional data set.

PLATON

- Twinrotmat option calculates if the sample is a non-merohedral twin.
- Must be run with a cif file as input—i.e.
  - platon xl.cif

Will give basf values for several possible twins

- If basf greater than zero by some amount than can generate an hklf5 file to use in shelxl.

Merohedral Twins

- A merohedral twin results when disorder adds symmetry to the crystal that is not there.
- This makes the symmetry of the crystal look like it belongs to a higher class than it really is.
- A simple example: an orthorhombic crystal where a and b are about equal. In this case it is possible that a and b may disorder making the crystal appear to be tetragonal.

Lets look at an extreme example

As is

- The coins in the wrappers are very disordered with respects to heads and tails and also to the orientation of the coin.
- This is an example of a one dimensional crystal.
- It is ordered along the wrapper but random in the other two dimensions.

Add Some Ordering

- Lets put a nick in all the coins so we can ensure they face in the same directions.
- If the crystals are all in the wrapper face up or face down then there is exact translational symmetry along the wrapper. This is the only symmetry.
- Now imagine the coins are aligned in the wrapper but are placed in randomly with respect to face up or face down.

- In this case each edge will be ½ heads and ½ tails.
- The two faces will be identical.
- In this case there will be a two-fold between the coins and in the middle of the coin.
- This symmetry was created by the disorder and is not real.
- This is a merohedral twin.

Recognizing Merohedral Twins

- These will only contain one component and therefore will not appear to be twinned.
- The data will look quite normal
- There is no space group that fits the data.
- The value of Rint for data averaging is bad.
- Frequently it is impossible to solve.

Refinement

- The HKLF 5 method will not work
- Need to place the twin law on a TWIN card and add a BASF card.
- Frequently this data goes nowhere even when it looks quit good.
- Can sometimes get some ideas from PLATON or other software.
- Send to Vic Young at U. of Minnesota.