Twins? and TwinSolve

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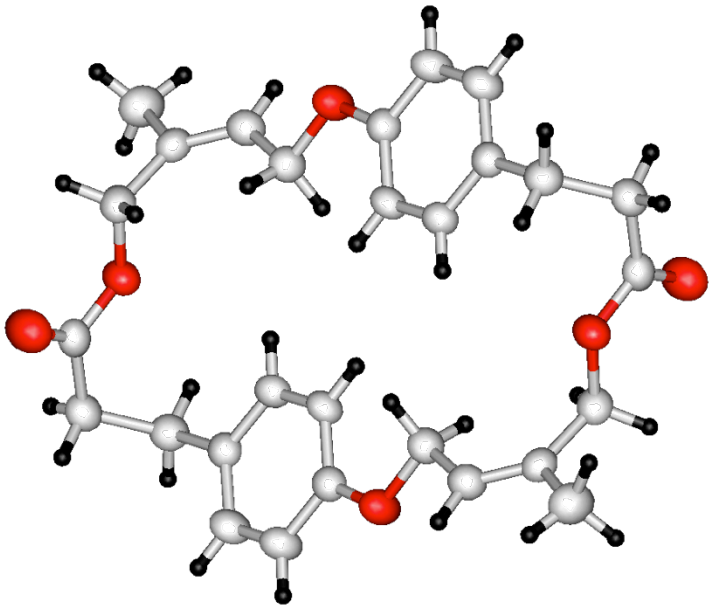
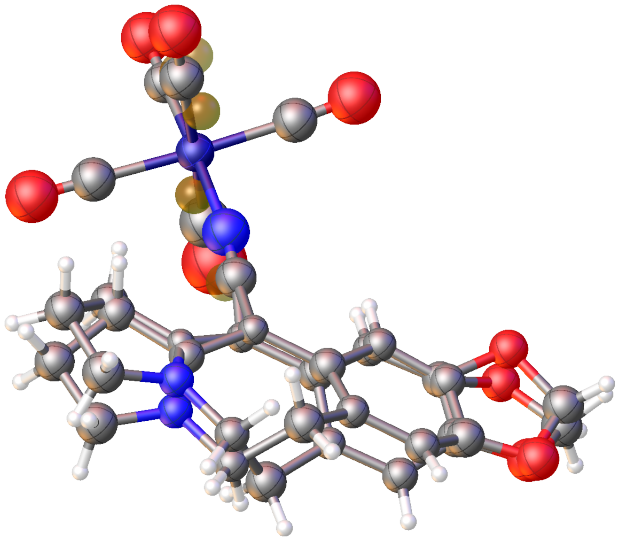
What We Will Cover

- Basics of twinning
- Process, solve and refine an example from start to finish
- Explore pitfalls in a second example





What is twinning?

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

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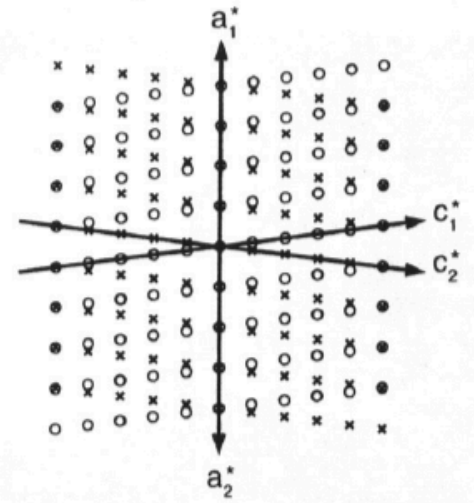
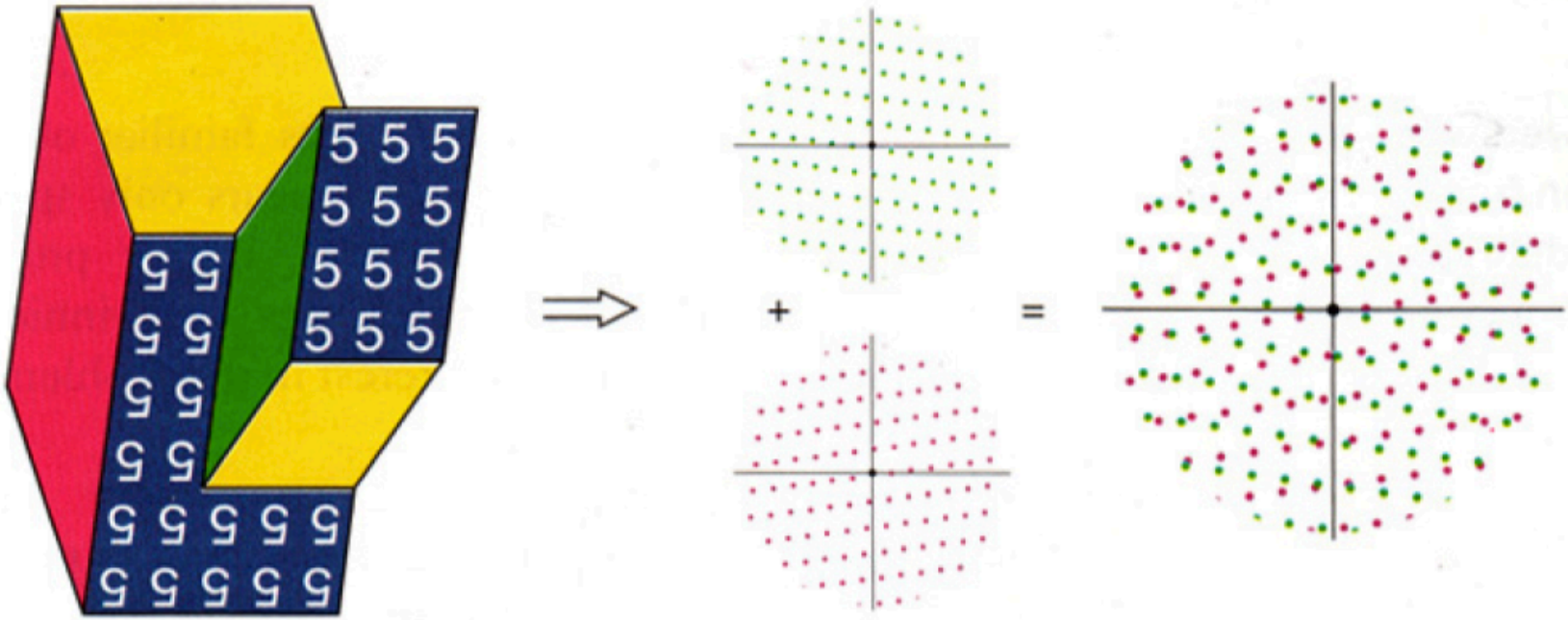
Non-merohedral twins (epitaxial)

In non-merohedral twinned crystals, the separate domain lattices align in fewer than three dimensions (e.g. at a sueface where they meet); the diffraction pattern contains interpenetrating lattices.



Along twin axis



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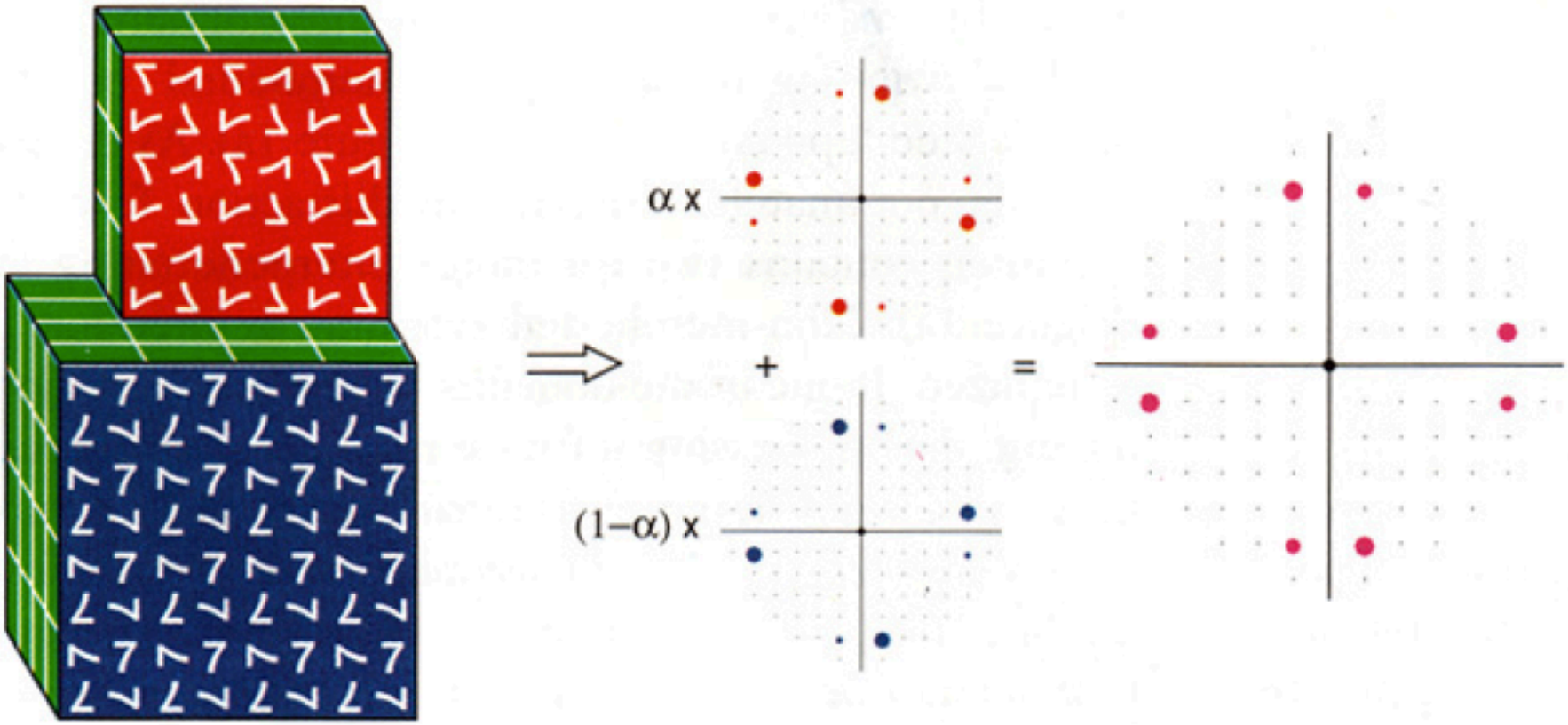
Merohedral twinned crystals

Lattice of two or more distinct domains coincide exactly in all three dimensions. Since the real space lattices coincide, the reciprocal lattices of different domain overlap exactly.



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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 acentric 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

- 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 itself.
    - For some compounds this second type of twin is present in all the suitable crystals.

Non-merohedral Twins

- These must be treated as multiple crystals.
- They must be indexed so that the orientation matrices of each component is be determined.
- Once this is done, the integration program 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

The Twin Law

- There is a relationship between the two components – if they are the same unit cell.
- 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 rejection
  - The final R factor will be somewhat larger than if the twinning is treated.

Rigorous Refinement

- Must integrate the data set for each separate component using Twinsolve.
- Scale the data using TwinSolve.
- 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 known 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.

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.

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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 quite good.
- Can sometimes get some ideas from PLATON or other software.

What We Will Cover

- Path 1
  - Setup
  - Cell Determination
  - Integration
  - Scale
  - Solve
  - Refine
- Path 2
  - Setup
  - Cell Determination
    - Repeat
  - Integration
  - Scale
    - Repeat
  - Solve
  - Refine
    - Repeat

Let's Talk about the Steps

- Cell Determination
  - Find
  - Index
  - Refine
  - Bravais lattice
  - Refine
  - Predict

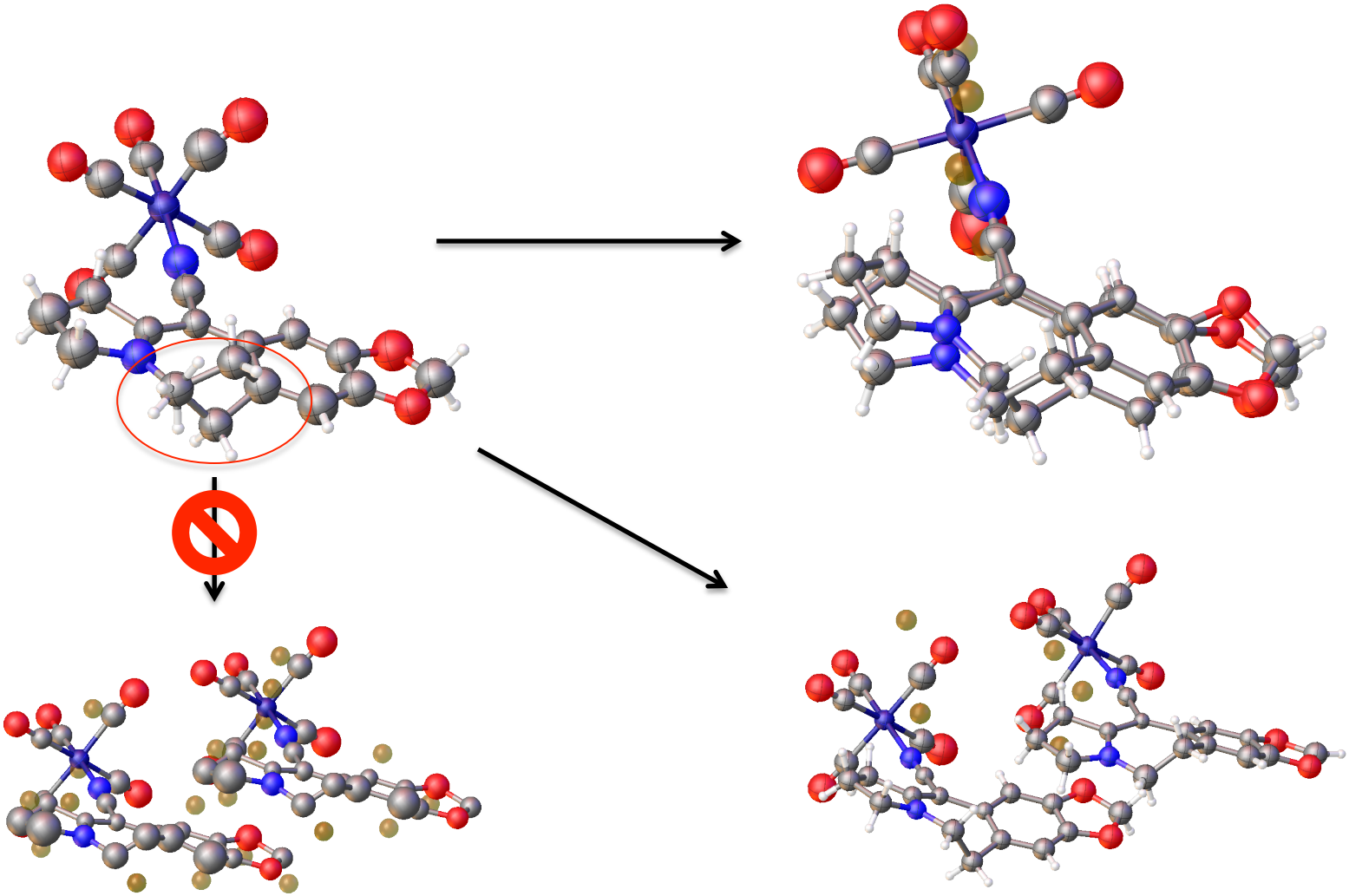
Let's Talk about the Steps

- Scale
  - Determine Laue group
  - Empirical absorption
  - Merge and reject
  - Output files: hklf4 and hkl5

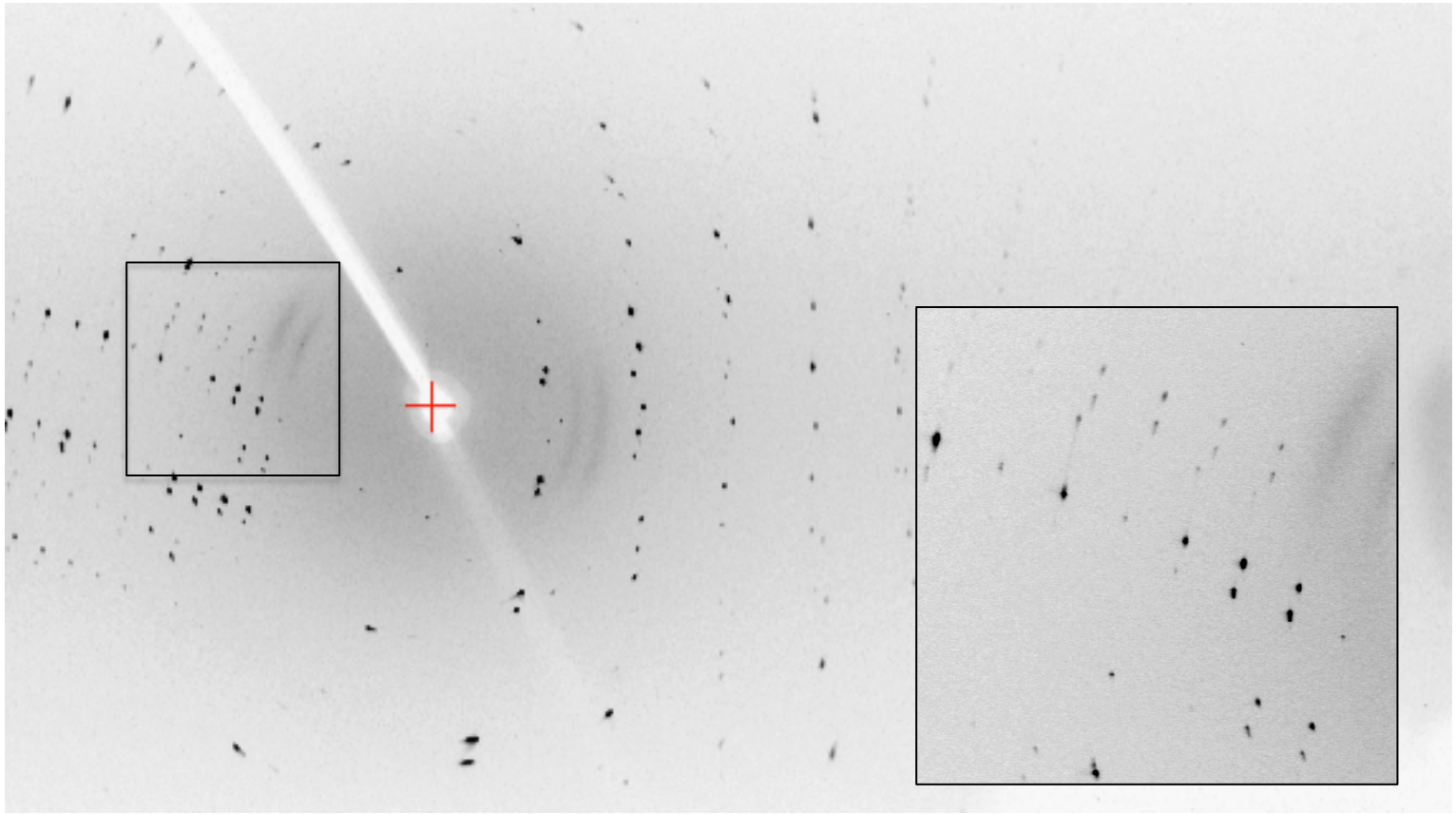
Let's Talk about the Steps

- Solve
  - Use hklf4 from a single component
- Refine
  - Assign atoms, go aniso, add hydrogens
  - Adjust error model
  - Replace HKLF4 with HKLF5 and add BASF

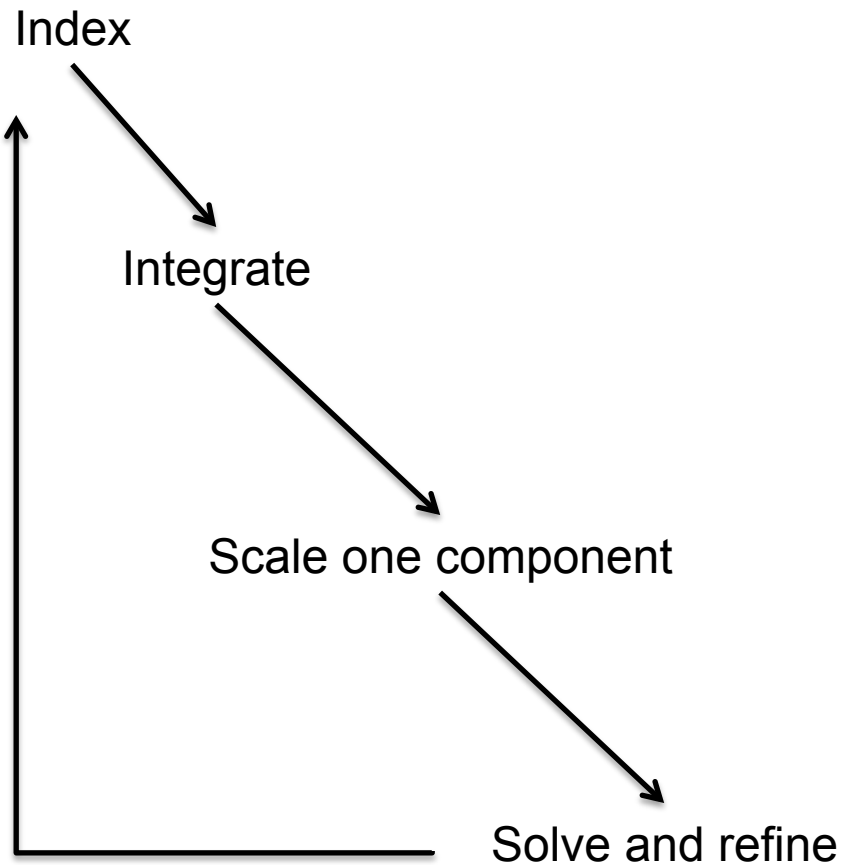
Disorder can be fun

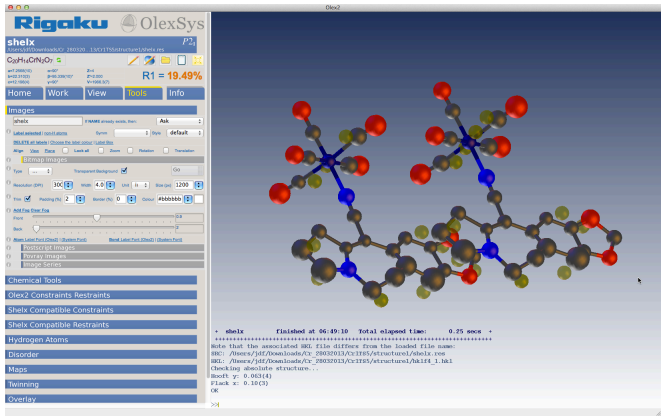


Our problem was images with lots of reflections…

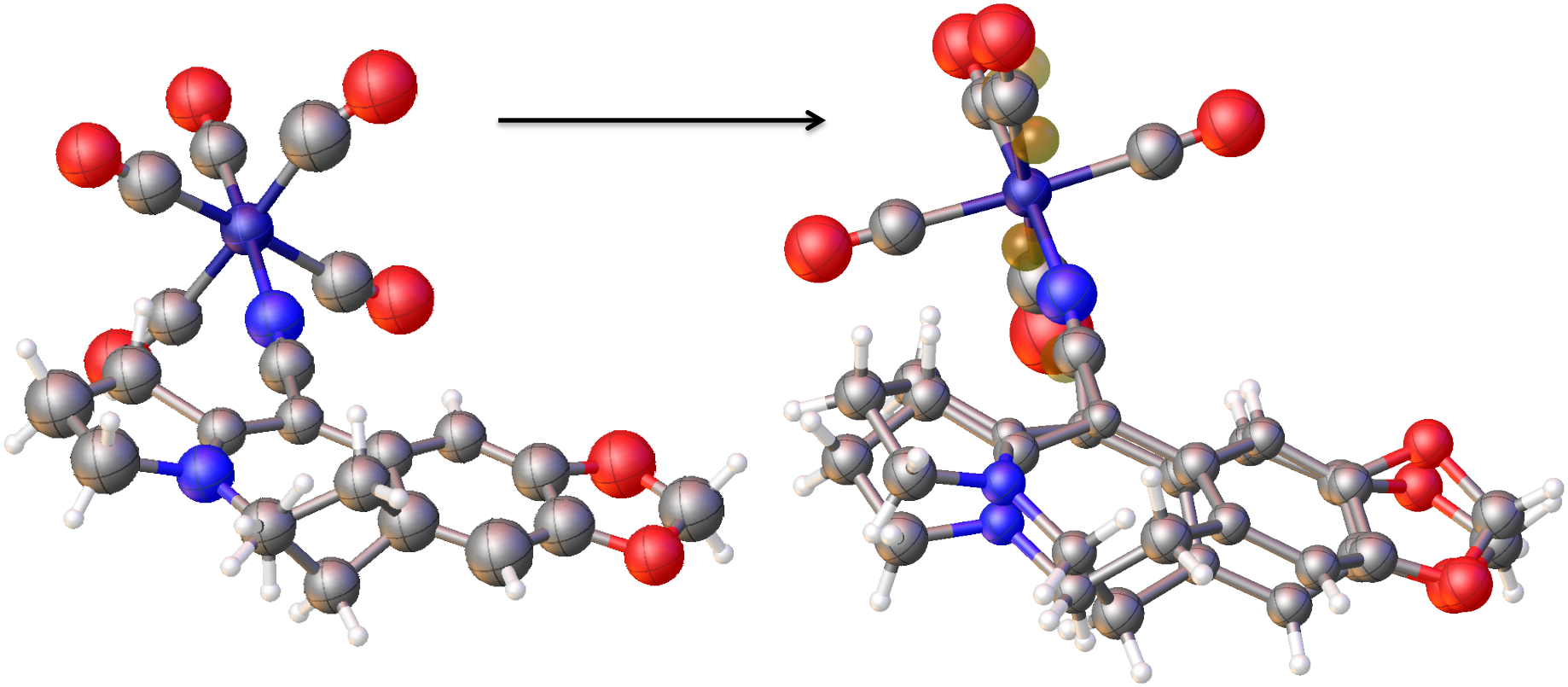


From spots to structure





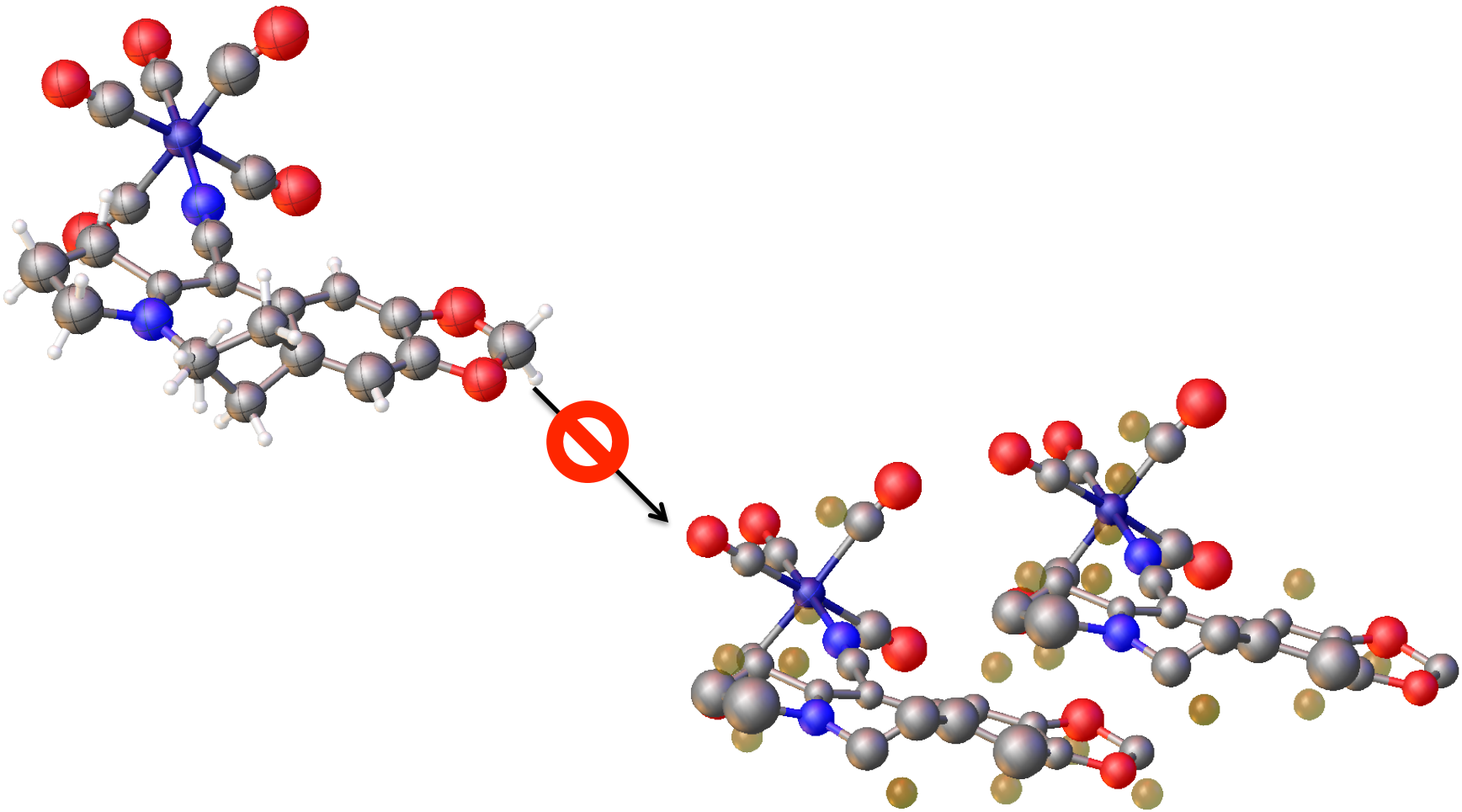
Single molecule with disorder



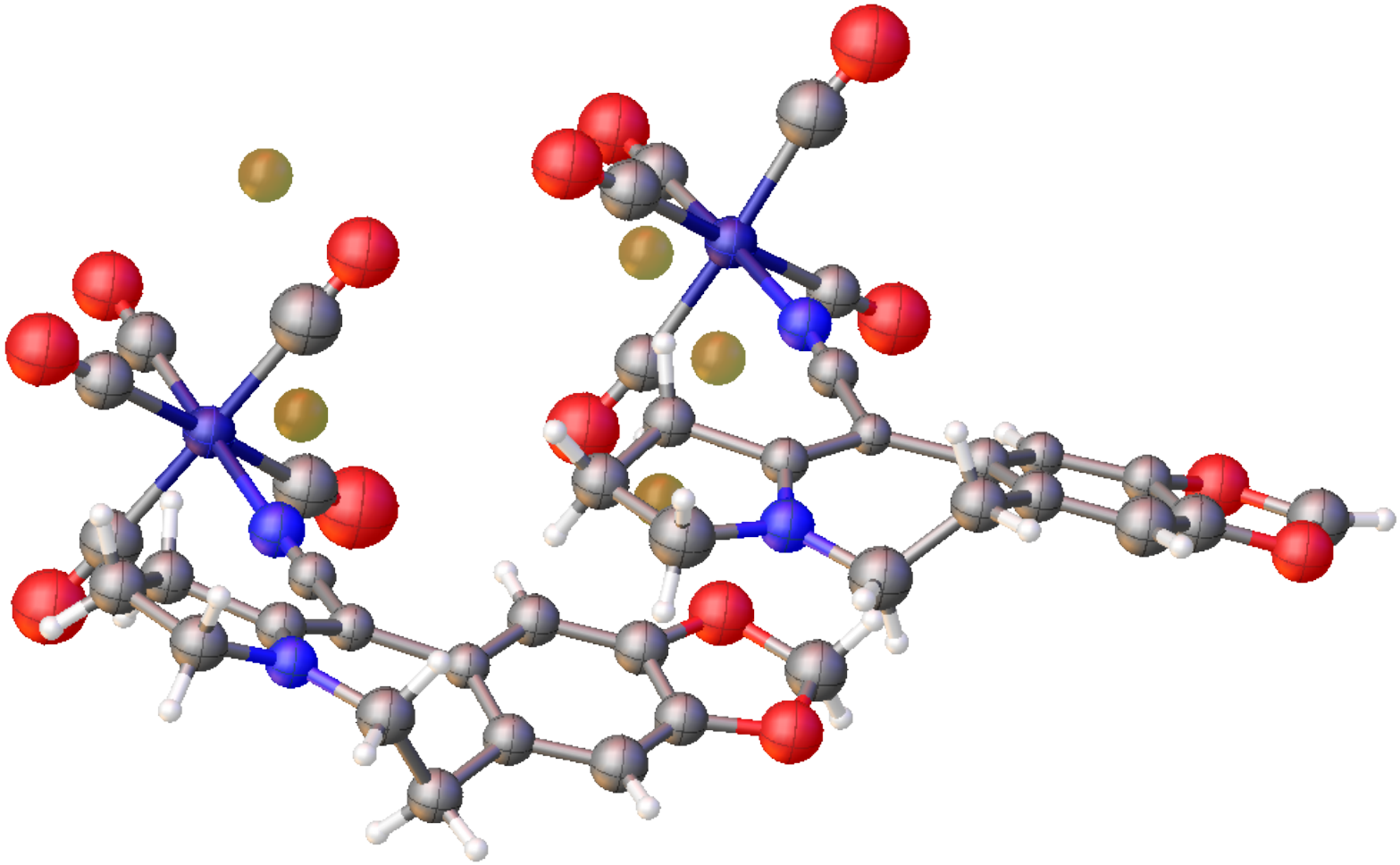
How to refine the disorder

- Use the split command to separate both tetracycles
- Refine
- Walk around the tetracycle and reassign atoms to Part 1 or Part 2 based on the most reasonable bond lengths and angle given the chemistry
- Add a few restraints (ADPs only)
- Refine and repeat

Two molecules with disorder



Two molecules with no disorder



The relationship of the cells seen in the indexing step

	a	b	c	β	V
Single, disorder	6.82 6.12	22.29 22.29	7.25 7.24	116.9 95.1	984 984
Double, disorder	7.26	22.29	12.19	95.4	1964
Double, no disorder	7.38	22.31	11.98	94.3	1966