

# Twins? and TwinSolve

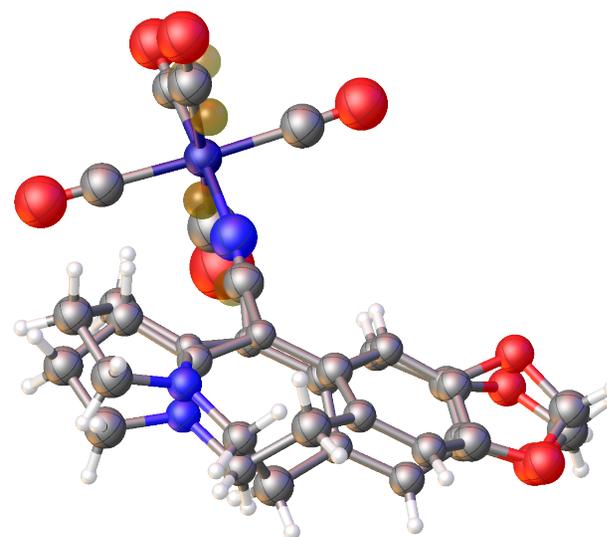
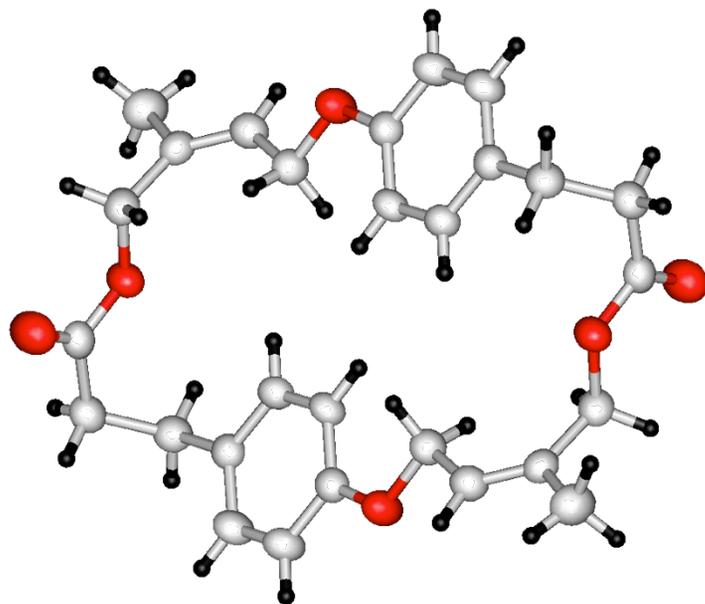
Joseph D. Ferrara, Ph. D.  
*CSO, RAC, USA*  
*VP XRL, RC, Japan*

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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



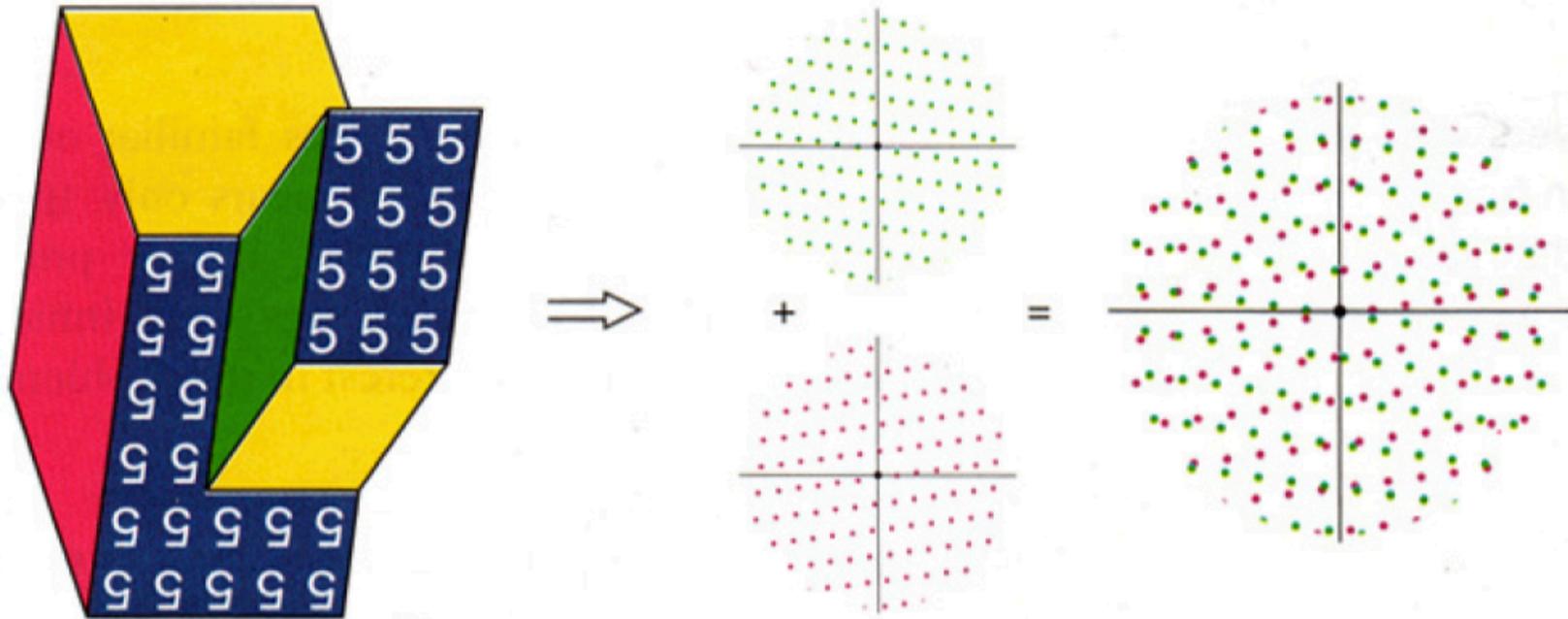
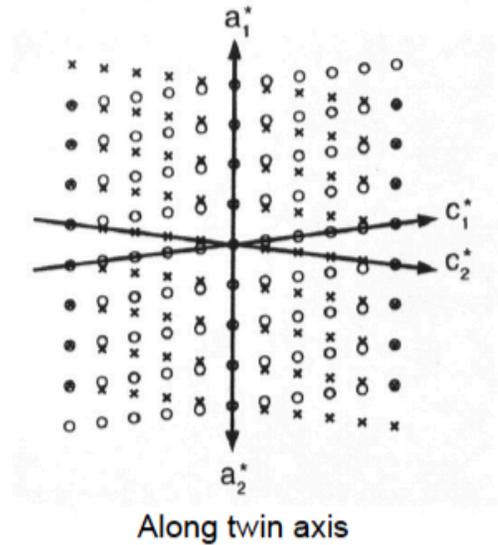
# What is twinning?

- At one time this meant something, today it 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



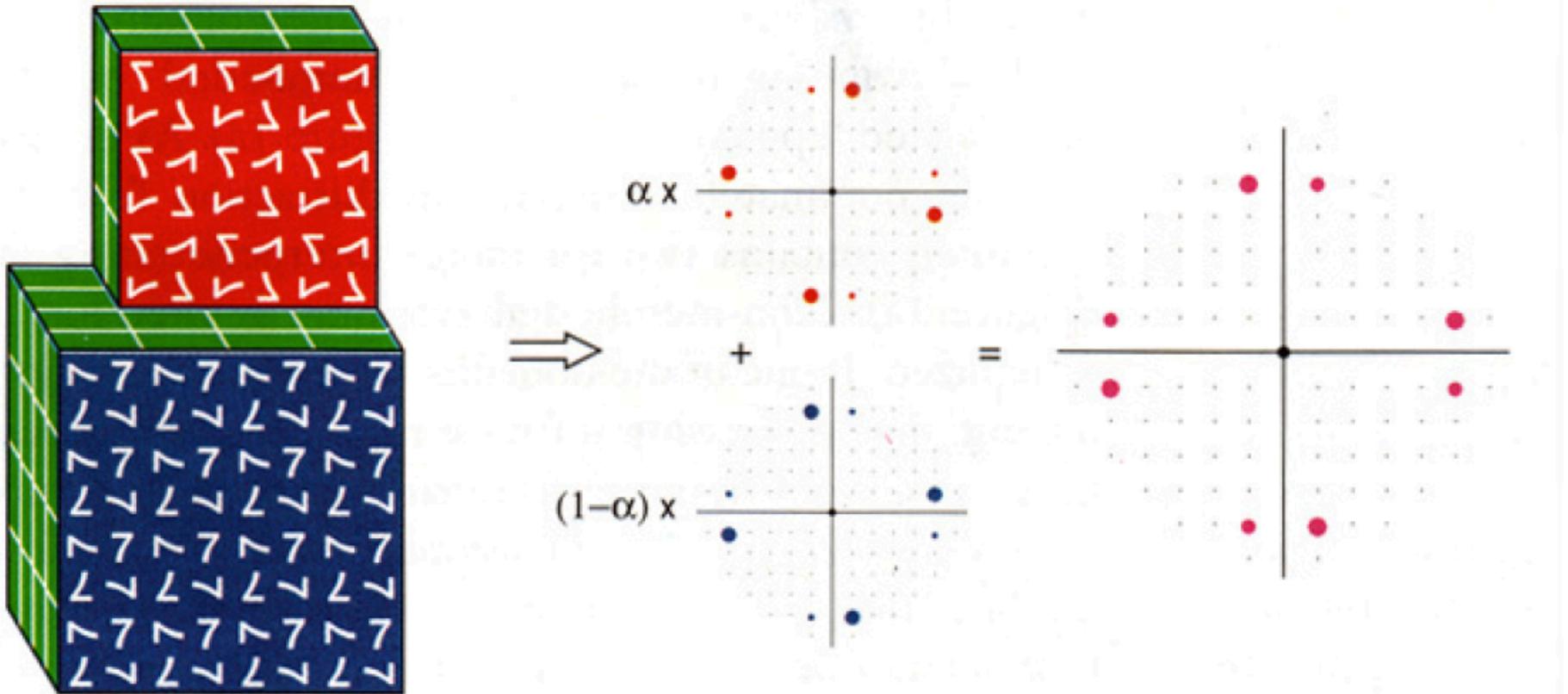
## Non-merohedral twins (epitaxial)

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



## 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.



# 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  $180^\circ$  rotation around a reciprocal axis
    - This is only possible for triclinic or monoclinic crystals as a  $180^\circ$  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  $R_{int}$ .
  - 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.

# 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  $R_{int}$  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



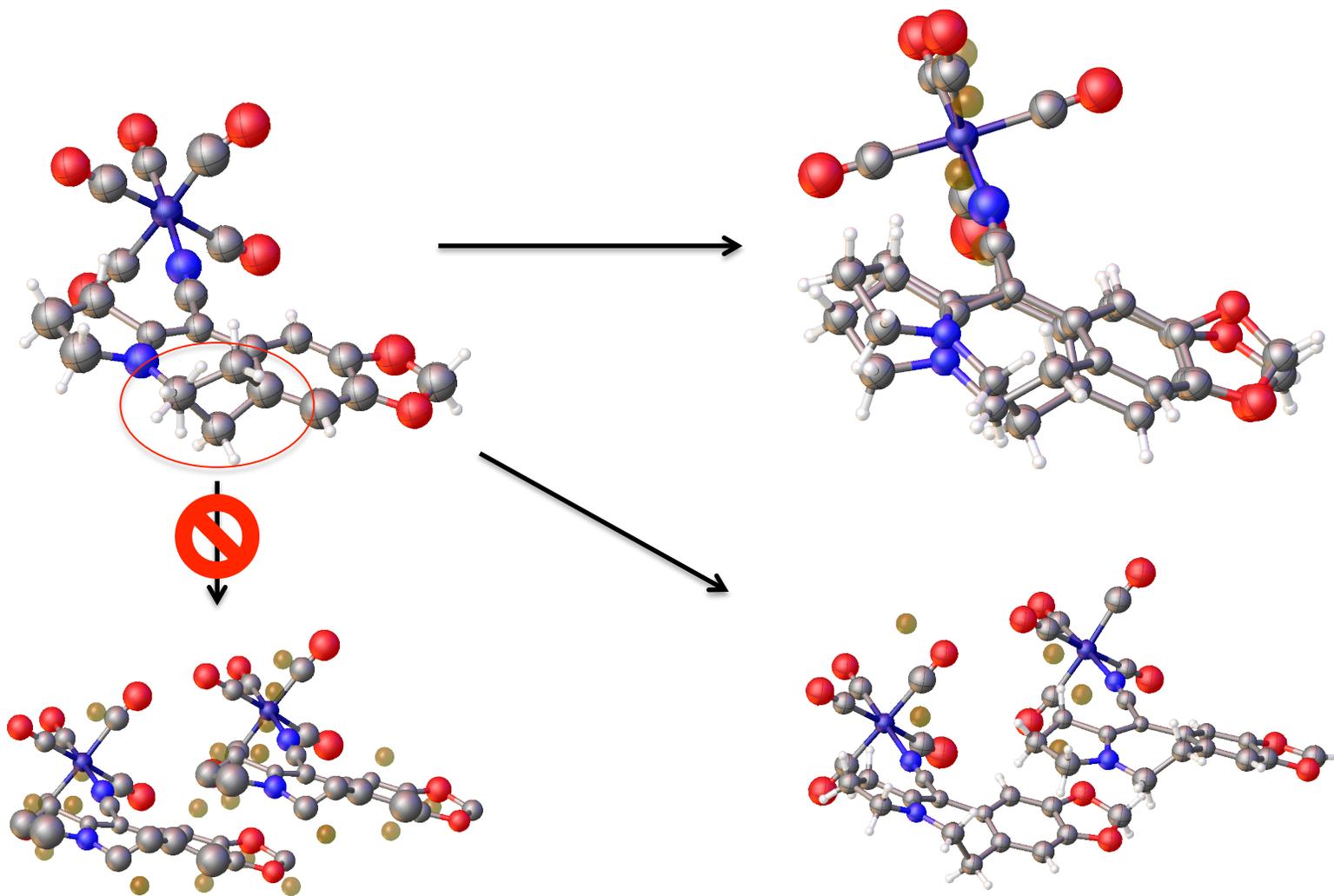
# Let' s Talk about the Steps

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

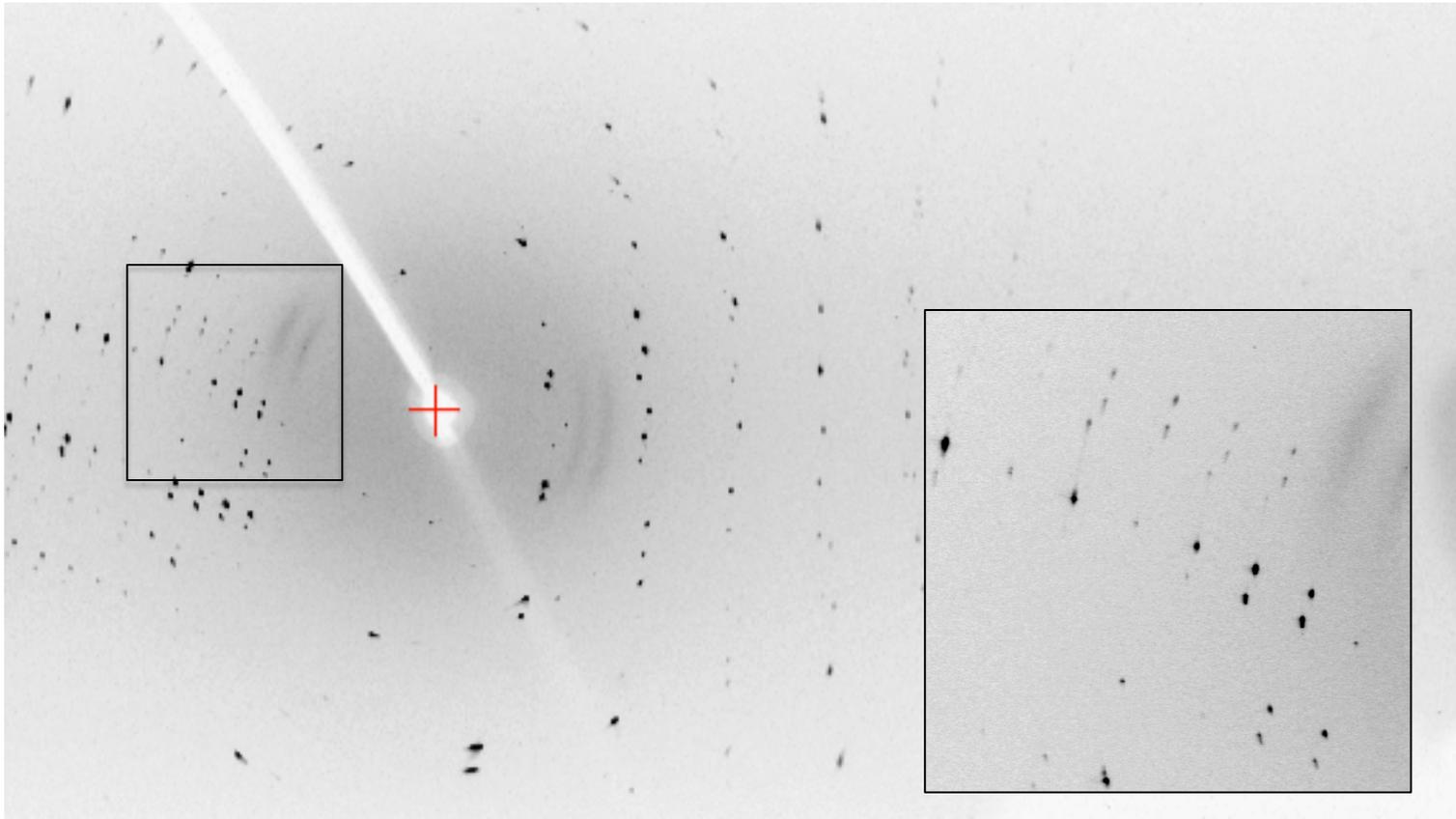
# Let's Talk about the Steps

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

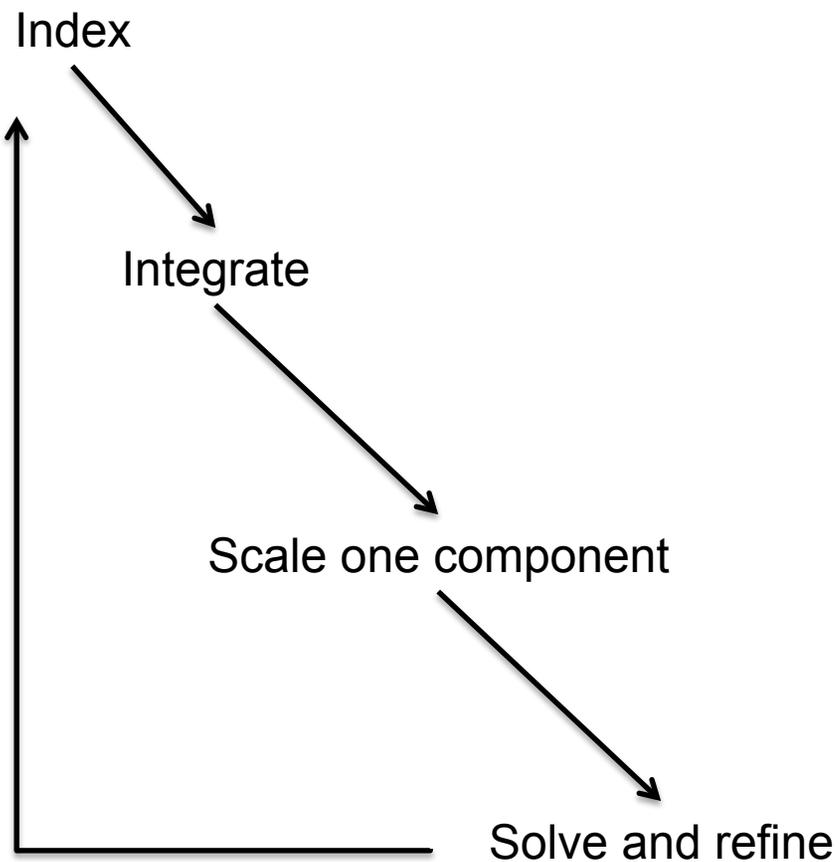
# Disorder can be fun



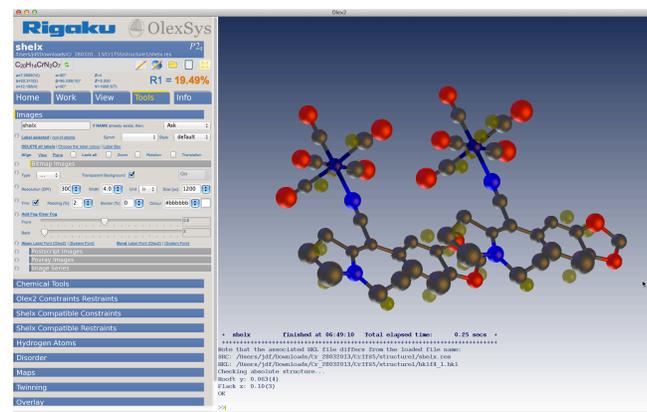
# Our problem was images with lots of reflections...



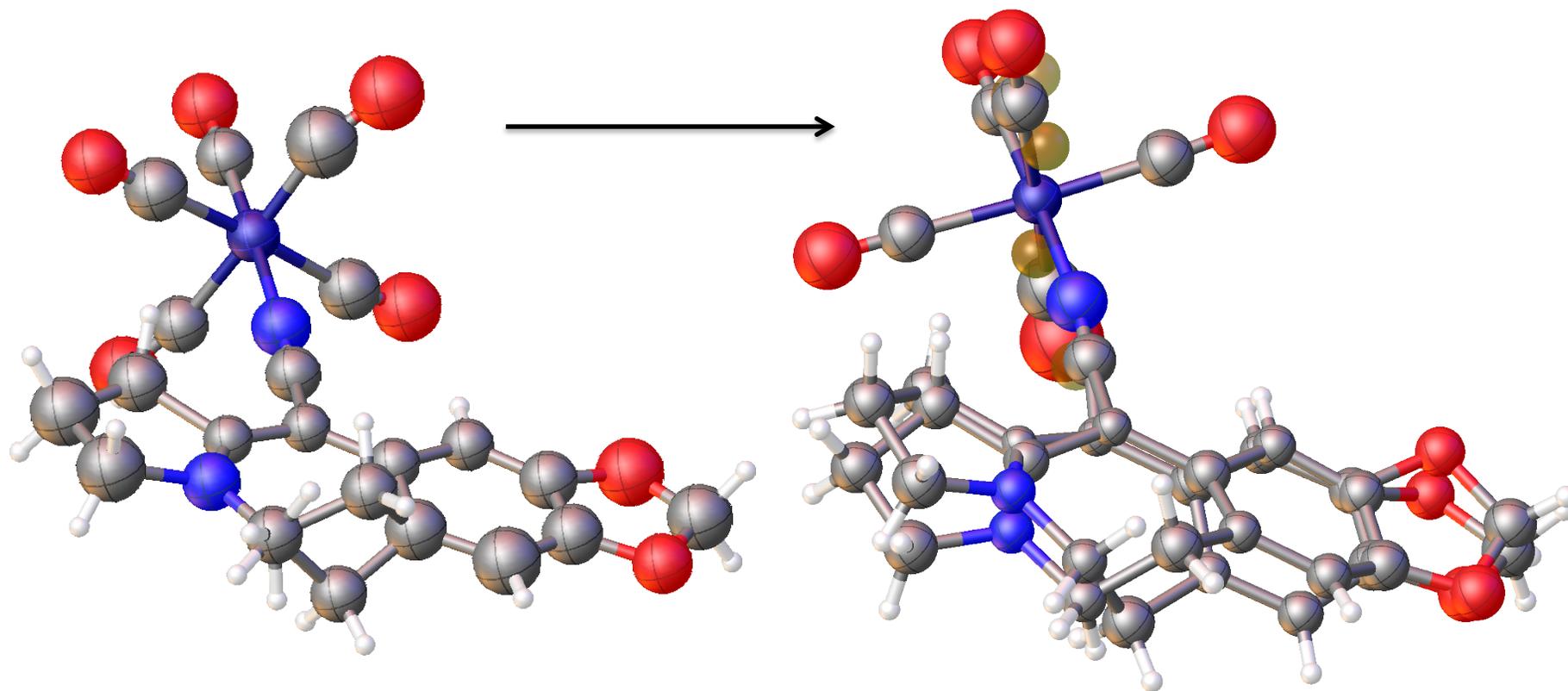
# From spots to structure



```
6 1 -0.5712
6 5 -0.6241
14 5 -0.6355
14 6 0.6835
14 12 -0.6157
19 13 -0.6016
=====
Cycle 3
Refinement flags: 110110000011111010
No. of reflections used: 2179, from a total of 5371
No. of reflections, C: 0( 0), and Q: 2179( 5371) 0.00
Twotheta range: 7.85 to 112.08 d range: 11.248 to 0.929
Rms devs. of position and rotation: 2.0710 1.3868 0.0156
Rms deviations of h,k,l: 0.055 0.056 0.035
Goodness of fit and max. shift/esd: 0.8788 -2.580 (par. 14)
New parameters and esd's; final shifts in parentheses:
beam x,y -0.062 0.023 < 0.062 0.017>
distance 0.066 0.056 < 0.000>
rotations 0.054 0.143 -0.117 < 0.005 0.060 -0.129>
xtal origin 0.055 0.042 0.105 < 0.000 0.000 0.000>
o,c offsets 0.008 0.043 0.144 < 0.000 0.000 0.000>
xtal orient. -0.294 -0.003 0.000 < 0.000 0.000>
xtal orient. -38.894 -42.593 126.887 < -0.114 0.012 0.260>
0.000 0.000 0.000
0.055 0.041 0.101
U11 - 13 -0.0135079 0.1247282 0.0588930
U21 - 23 -0.0374734 0.0071015 -0.0236352
U31 - 33 -0.0898926 -0.0531348 0.1265588
Cell parameters 7.2446 22.2867 6.1194 90.000 95.148 90.000
0.0059 0.0173 0.0054 0.000 0.071 0.000
< -0.0059 -0.0056 0.0010 0.000 0.096 0.000>
Cell volume 984.04
-1.42
< -1.03>
Indexed, but not used: 94 Not indexed: 3098
Distribution of 'indexed, not used' over nine areas of the detector surface
5 0 2
0 78 2
0 7 0
Ave. rms and max offsets for 2179 Q reflections: 0.14 1.17 2.49
hkl deviations from integers, and rotation errors, for 2179 indexed spots:
.05 .10 .15 .20 .25 .30 .35 .40 .45 .50
h 1757 148 206 68 0 0 0 0 0 0
k 1559 400 150 52 0 0 0 0 0 0
l 1842 288 38 11 0 0 0 0 0 0
r 1954 0 2 0 2 0 4 0 0 217
>Accept these parameters? <N/Y> IN1: y
Rigaku UB matrix U-matrix part of the R&P&D UB
-0.013508 -0.037473 -0.089893 -0.097464 -0.035156 -0.0541308
0.124728 0.007102 -0.053135 0.899961 0.158269 -0.486227
0.058893 -0.023635 0.126559 0.424935 -0.526749 0.736183
```



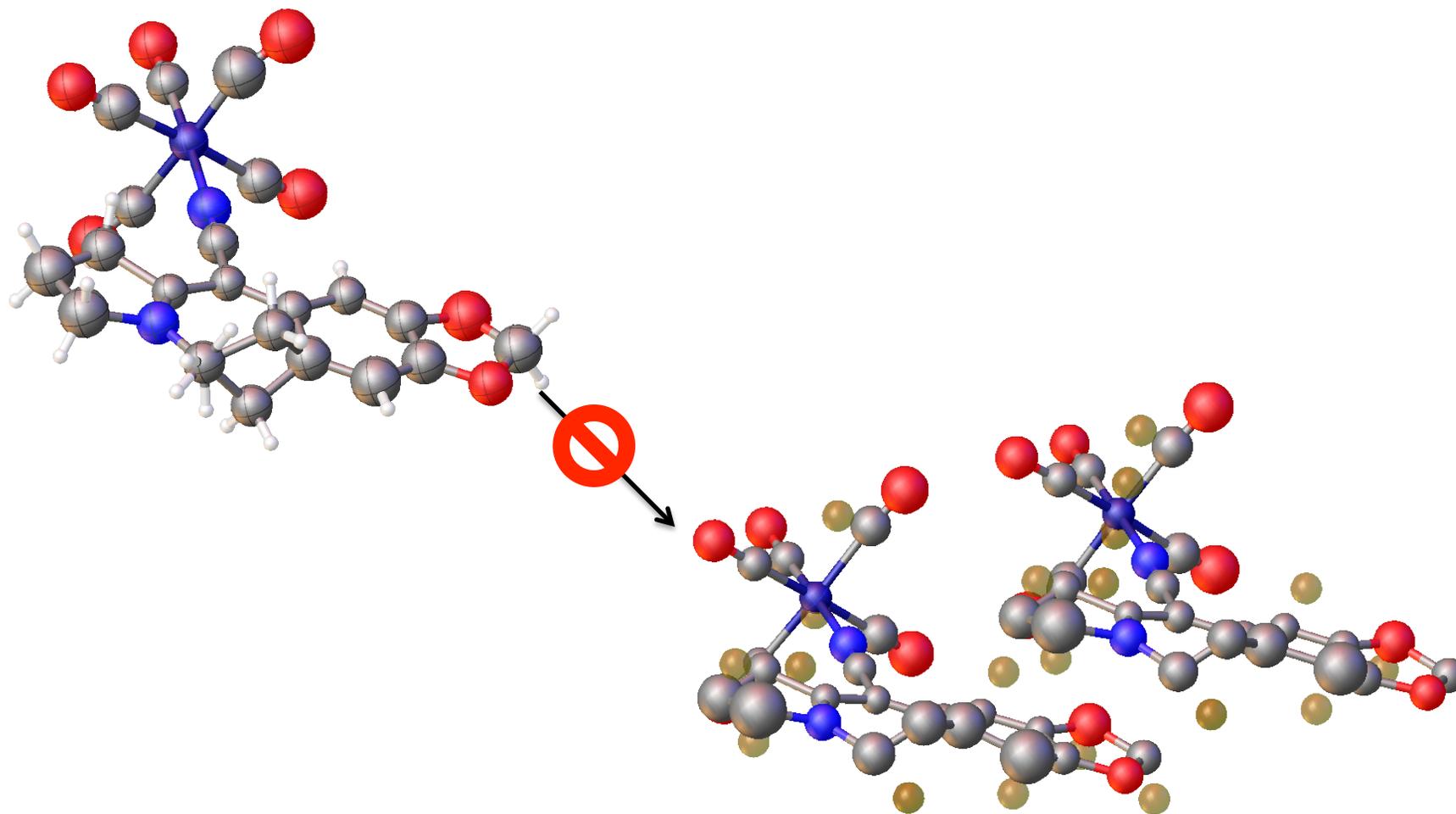
# Single molecule with disorder



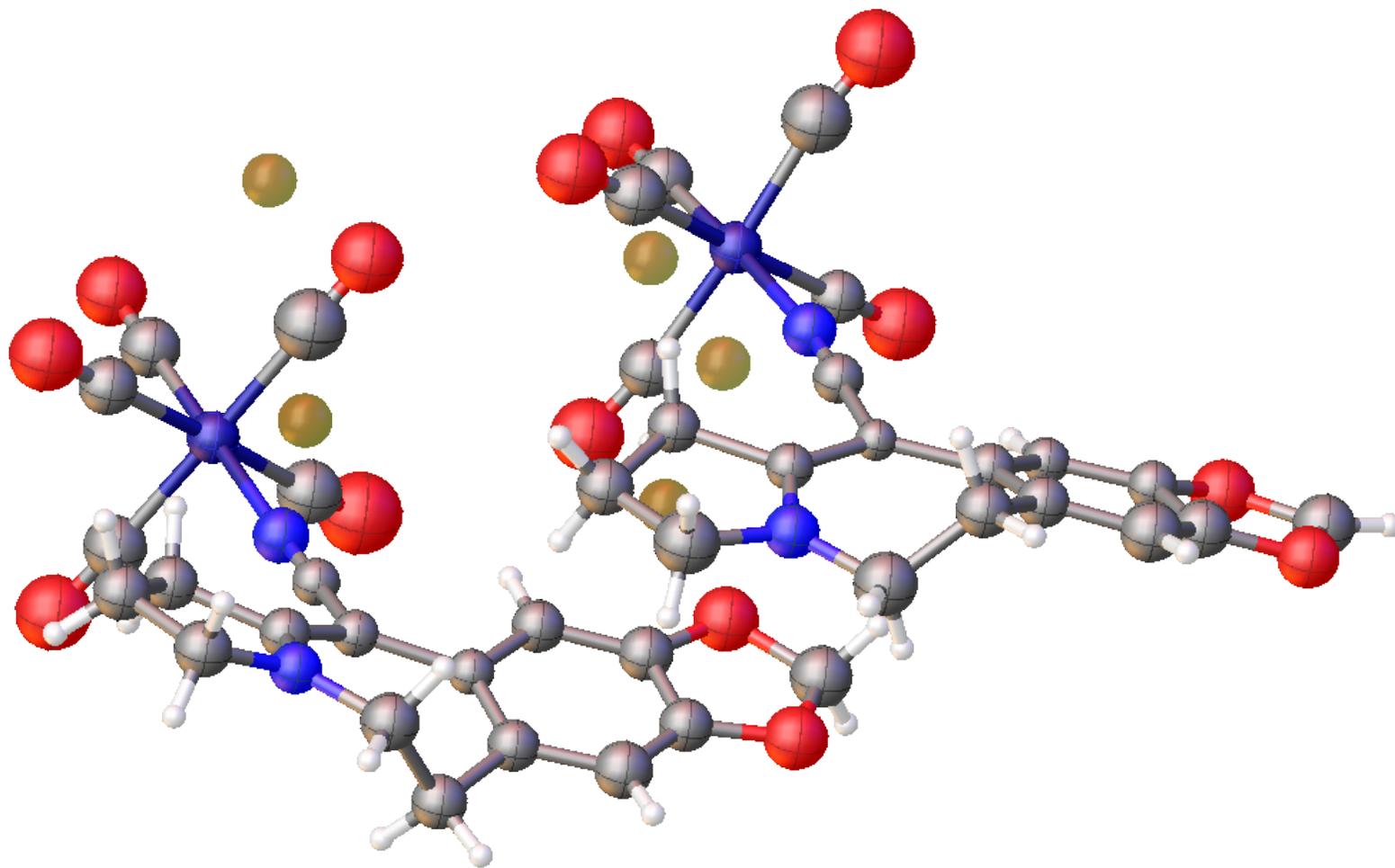
# How to refine the disorder

- 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	$\beta$	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