Twinning

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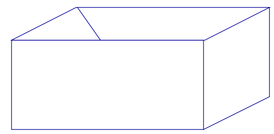
Simple Model for Twinning



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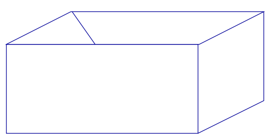

It's a Brick!

http://www.michiganbrick.com/

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What Is A Brick?

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Brick Advantages

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* Brick will not dent.

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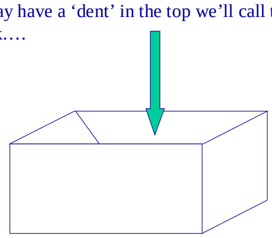
What Is A Brick?

Brick Advantages

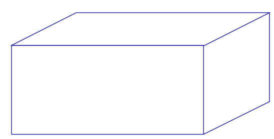
* Brick will not dent.

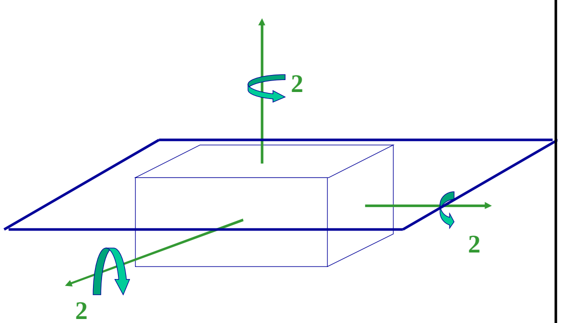
* Brick will not limit your personal expression.

A Brick may have a 'dent' in the top we'll call this the 'contents' of the brick....



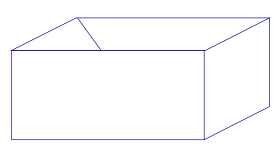
...But consider just the outline, or shape, of the brick.

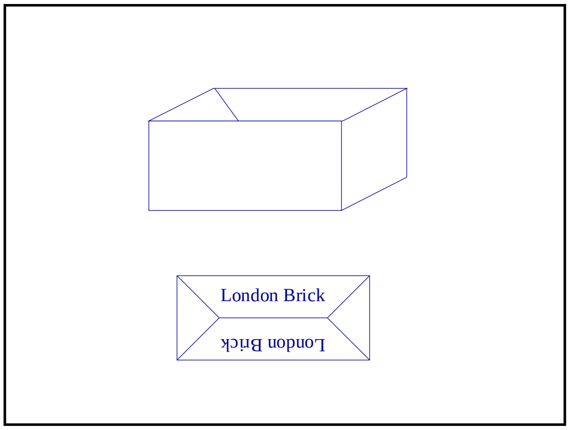


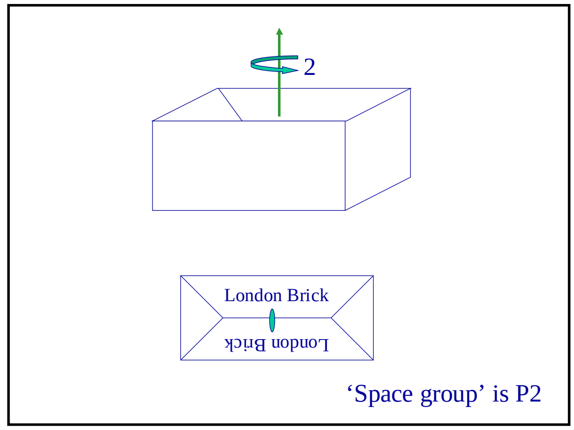


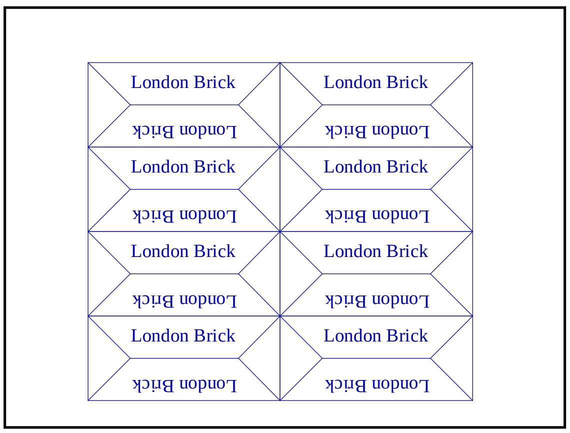
Point Group of overall shape is 2/m 2/m 2/m = mmm

Now consider the symmetry of the brick with 'contents'...




London Brick
London Brick


2
London Brick
London Brick
‘Space group’ is P2


London Brick
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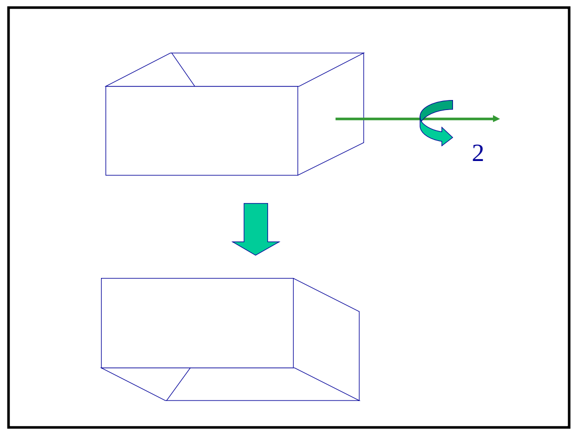
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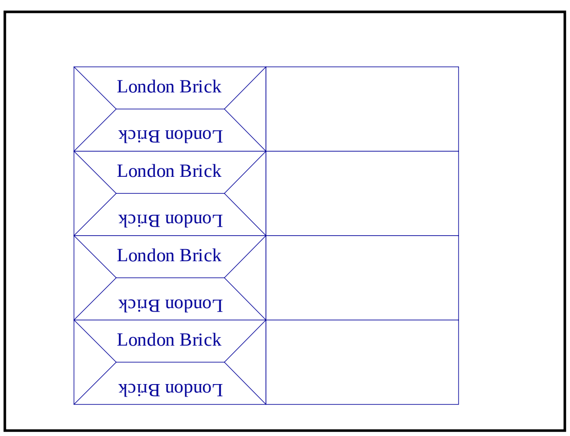
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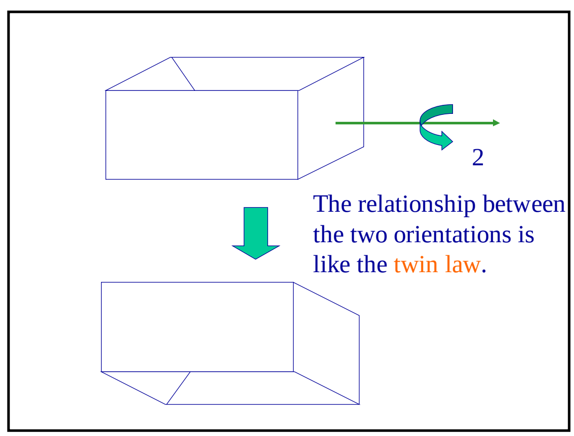
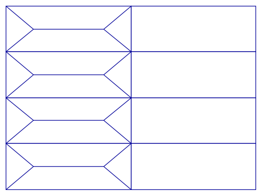
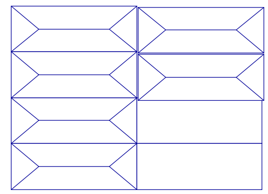

2
The relationship between the two orientations is like the twin law.

The relative number of the bricks in the two domains corresponds to the twin scale factor.
Here it is 0.5, or 50%.

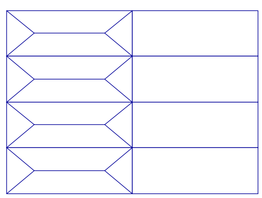


The relative number of the bricks in the two domains corresponds to the twin scale factor.
Here it is 0.25, or 25%.

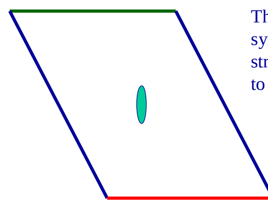


Twinning

- How does all this apply to crystals?
- Two (or more) crystals stuck together with a symmetry relationship between the two *domains* which are related by a symmetry element of the unit cell, which is not present in the space group of the structure.



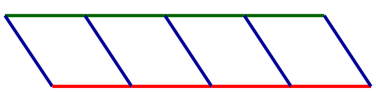
Monoclinic Unit Cells



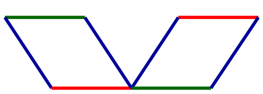
The only crystallographic symmetry that a monoclinic structure can exhibit is wrt to b-axis

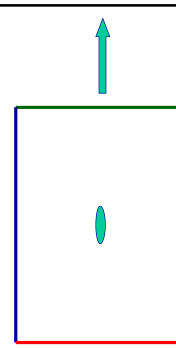
Twinning

Monoclinic crystal viewed on ac plane

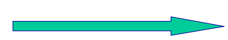


No chance of making a mistake by putting one cell the wrong way up.

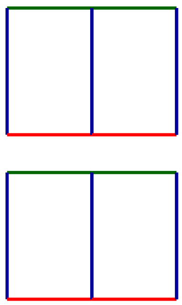




But if the angle beta is accidentally 90° the unit cell has higher symmtery than the structure. (Cf the brick!)



But if beta is near 90° a mistake may occur….



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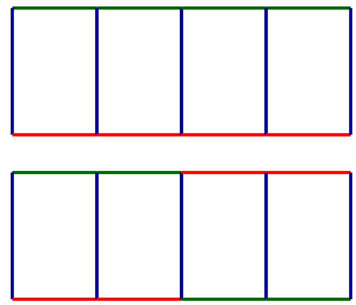
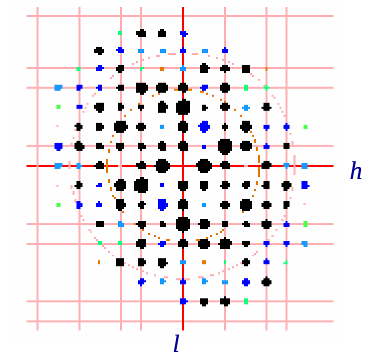


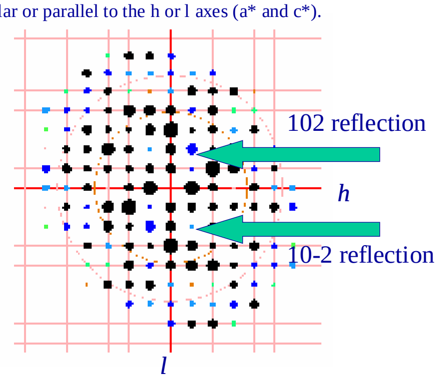
What effect does this have on the diffraction pattern?

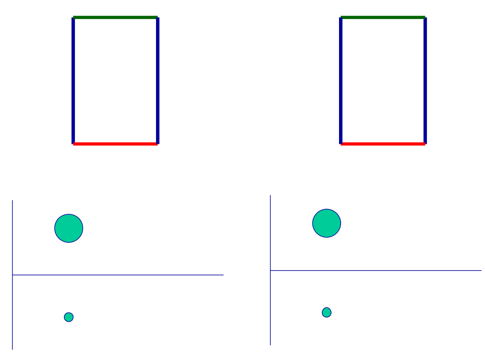
- Each domain of the twinned crystal will give rise to a diffraction pattern
- But the two patterns will be rotated (or reflected) with respect to one another.
- The matrix describing this operation is the same as that defining the relationship between the two domains of the crystal.

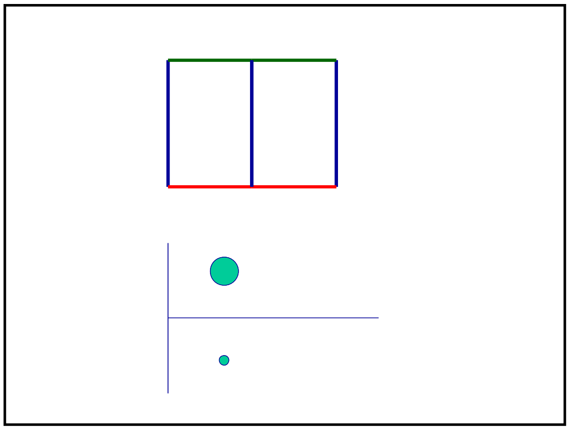
Here is a diffraction pattern (k=0 layer) from a monoclinic crystal, where β happens to be 90° (shape is orthorhombic!)

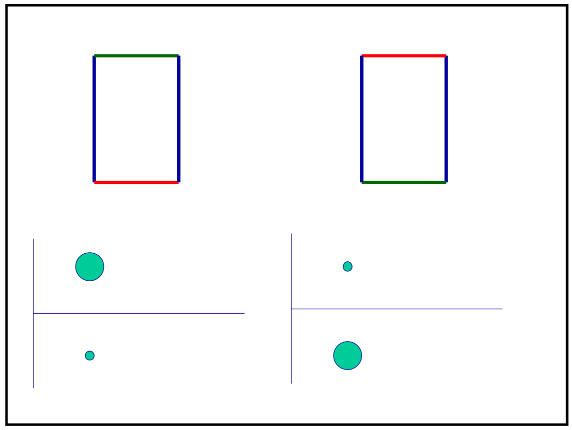


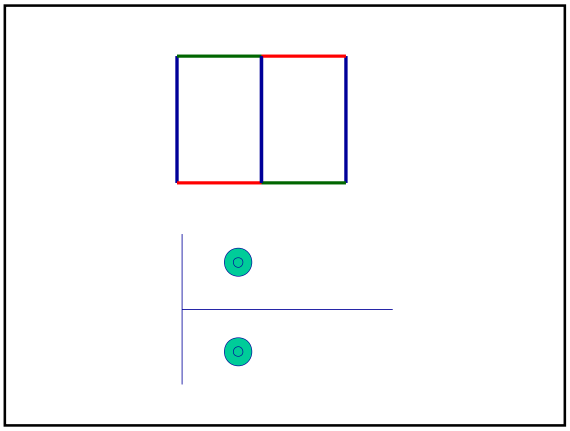
We can see that it is monoclinic because there is no symmetry perpendicular or parallel to the h or l axes (a* and c*).



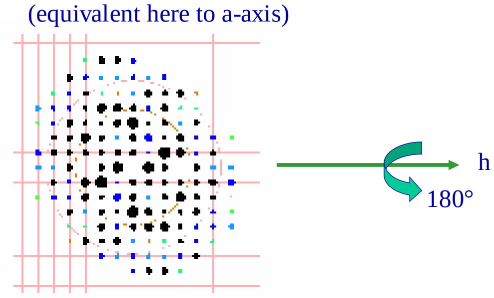


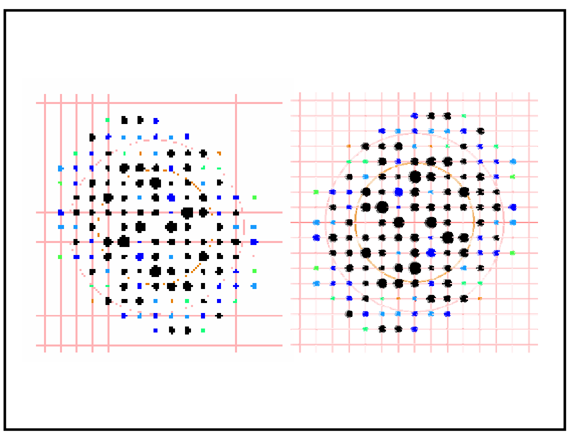


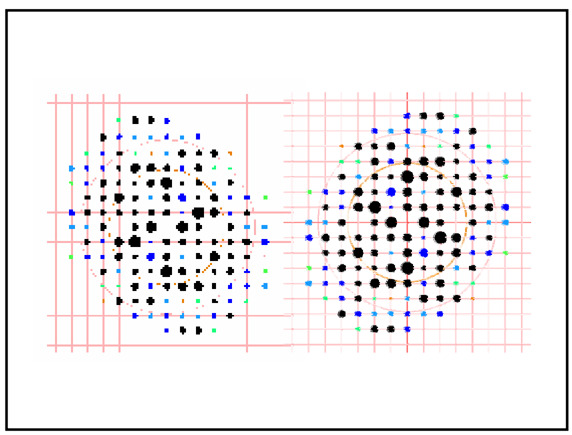


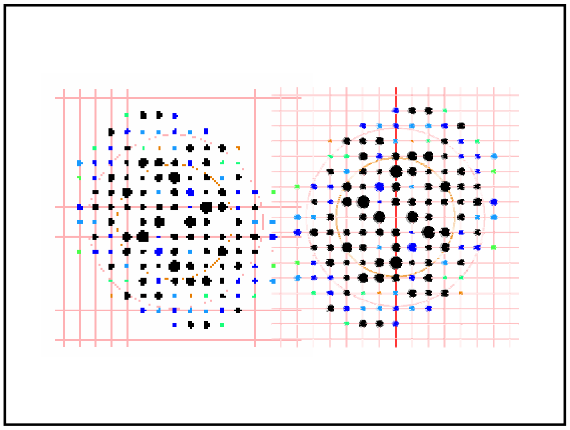


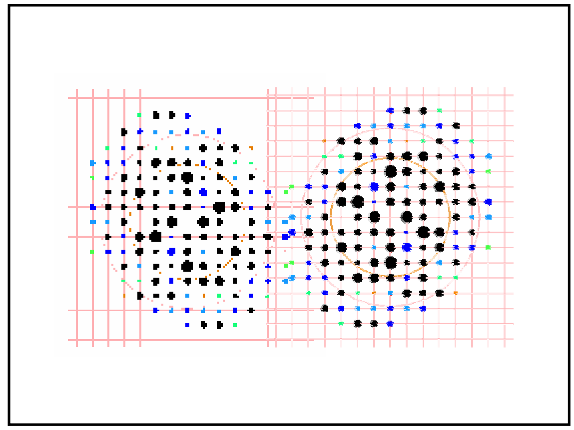
Consider a 2-fold rotation about the h-axis
(equivalent here to a-axis)

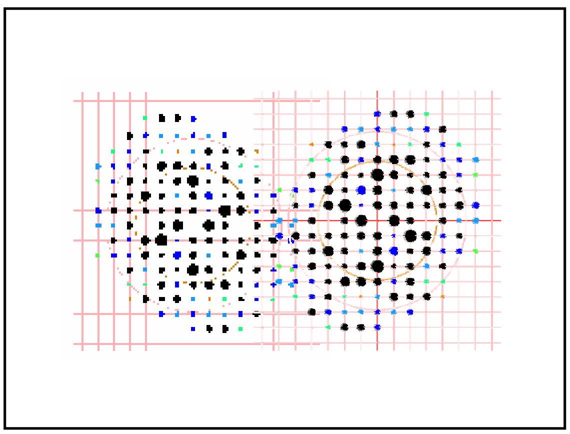


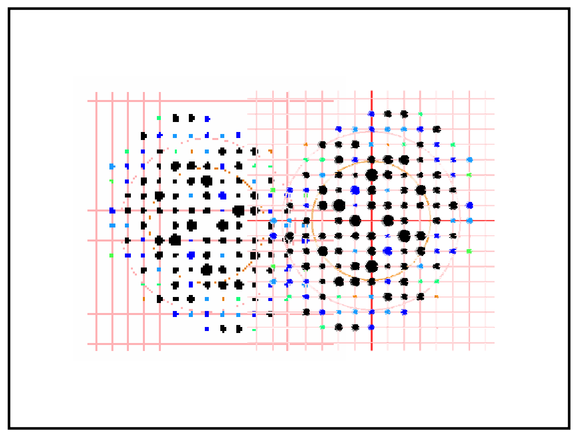


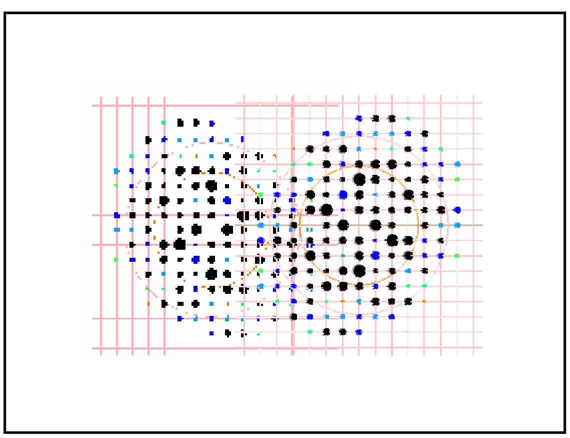


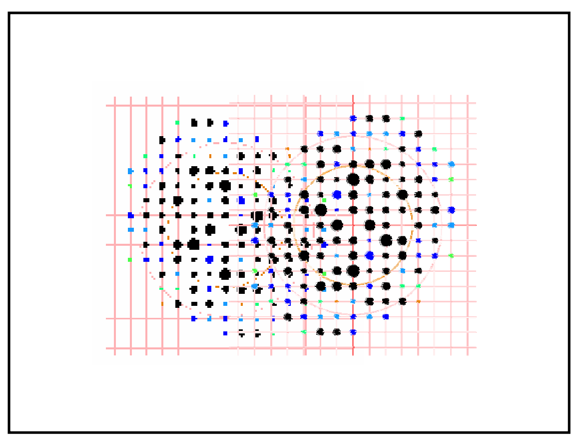


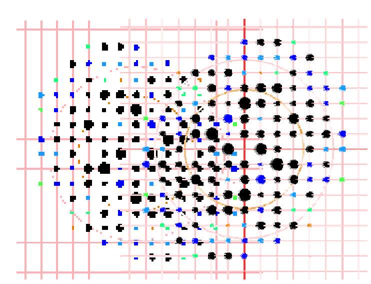


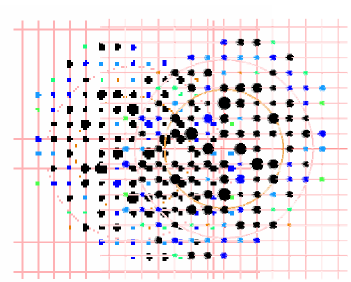


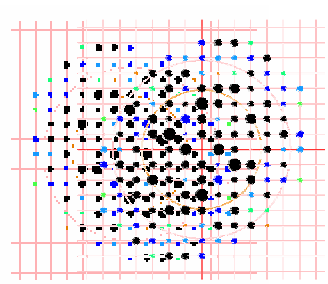


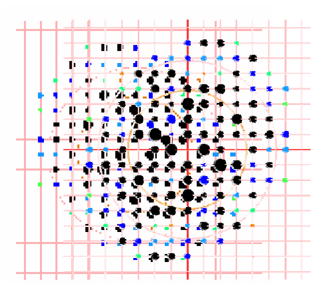


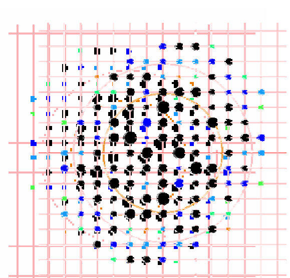


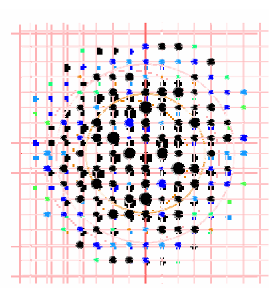


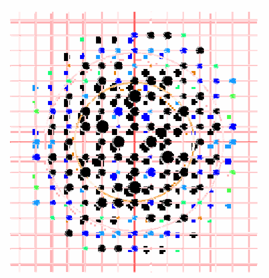






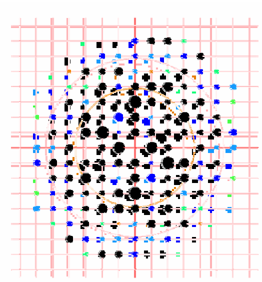






The reflections can only overlap in this way because the unit cell has high enough symmetry for this to happen (mmm) - even though the contents of the cell have monoclinic symmetry (2/m).
[Remember this is a *monoclinic* crystal with $\beta = 90°$ - a reasonably common situation actually.]

In order to treat the twinning during refinement we need to say which reflections overlap…



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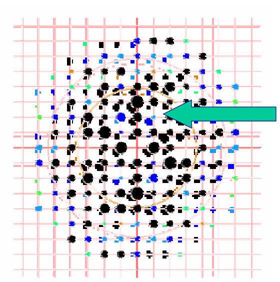


This was measured as the 1,0,2 reflection.
But actually it is a composite of the 1,0,2 reflection from one domain and the 1,0,-2 reflection from the second domain.

Which reflections contribute to a measured reflection?

- This can be derived by the **twin law**

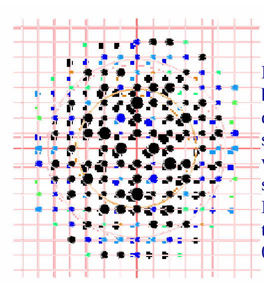
$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} h \\ k \\ l \end{pmatrix} = \begin{pmatrix} h \\ -k \\ -l \end{pmatrix}$$

This is a 2-fold about **a** written as a matrix.

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 2 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ -2 \end{pmatrix}$$

Which Reflections Overlap?

- Notice that operation of this matrix gives integral transformed hkl's for any values of h, k and l.
- Hence all reflections measured will have contributions from *both* twin domains. (The significance of this will be more evident later).
- This is why twinned structures like this are so hard to solve.



Notice that there now appears to be extra symmetry in the diffraction pattern. If the twin scale factor is 0.5 then the data would have a low R_{int} in mmm symmetry (orthorhombic). Merging would get worse as the scale factor departed from 0.5.

This accounts for one of the most common signs of twinning: you see rather similar merging R-factors for different Laue groups.

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Another common sign is that the space group is hard to determine: this is because reflections from one domain can overlap with systematic absences from the other domain.

Suppose we have a $P2_1/c$ structure with the following twin law:

$$\begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} h \\ 0 \\ l \end{pmatrix} = \begin{pmatrix} l \\ 0 \\ h \end{pmatrix}$$

The 201 reflection, which is absent in domain 1 overlaps with the 102 reflection from domain 2. If the 102 reflection is strong, what you think is the 201 reflection has significant intensity! Here the space group would appear to be $P2_1$.

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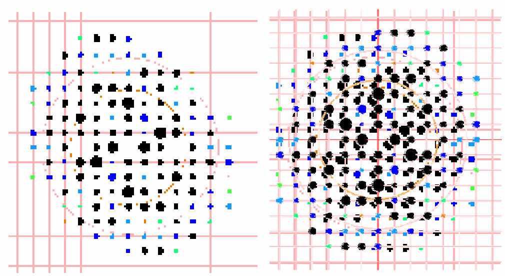
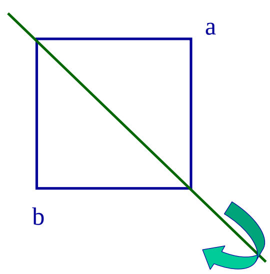
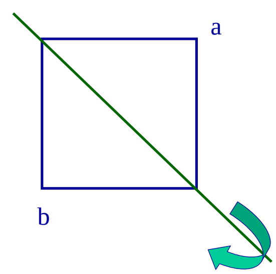


A common sign of twinning is a low value for <|E^2-1|>.

Susceptible Structures

- All trigonal crystals.
- All low-symmetry tetragonal, rhombohedral, hexagonal and cubic crystals.
- For example, tetragonal structures may belong to Laue groups 4/m or 4/mmm, but tetragonal unit cells always have 4/mmm symmetry.
- Hence a 2-fold about [110] can act as a twin law for lower symmetry tetragonal structures. This works for low-symmetry trigonal, hexagonal and cubic cells too.





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

More Susceptible Structures

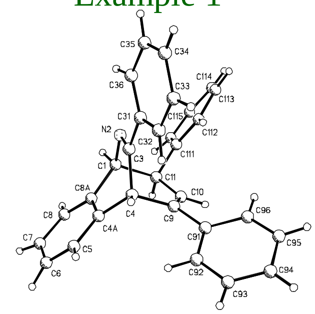
- Orthorhombic with two edges equal.
- Monoclinic with $\beta = 90°$
- Triclinic with two angles near 90°.
- These may not be immediately evident in primitive settings - see problem 3(ii).
- A cell-reduction program should pick this up!

Refinement

- Assuming that a structure can be solved this kind of twinning presents little problem during refinement
- Most refinement programs simply require a twin law to be specified and a scale factor refined.
- Potential twin laws should be obvious from the symmetry of the unit cell.

- THE problems arise
  - Assigning the space group
  - Solving the structure.
- There are no rules here which work for every case.
- The best weapon is probably persistence.
- http://shelx.uni-ac.gwdg.de/SHELX/index.html

Example 1



Statistics

- Unit cell
  - a = 8.28, b = 12.92, c = 41.67, all angles 90°.
- Formula: $C_{30}H_{23}N$ => Z = 8
- $<|E^2-1|>$ = 0.725 - nothing very odd.

	R_{int}
Orthorhombic	14%
Monoclinic (a)	13%
Monoclinic (b)*	6%
Monoclinic (c)	9%

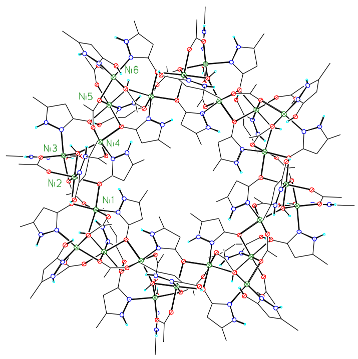
* 2_1 absence up this axis. Apparent space group assuming orthorhombic symmetry is $P22_12$, but this is very unusual- 44 in entire CSD.

Solution

- It looks like a twin!
- Direct methods failed to give a recognisable solution.
- Solution was achieved in $P2_1$ in the end using a Patterson search on the rigid part of the molecule: one molecule (/4) located.
- Lengthy process of Fouriers and LS.
- Final R was 10%…. not very good but neither was the crystal!

Solving twinned structures

- Look carefully at merging statistics.
- Does the space group look plausible (is it very unusual?)
- If direct methods don't give a recognisable solution try
  - Patterson methods for heavy atom compounds
  - Patterson search using a rigid fragment either from the CSD or from molecular modelling.



Example 2: Ni_{24} Structure

- Tetragonal cell - but what is the Laue group?
- Absences consistent with P4/n or P4/nmm, which are both centrosymmetric.
- <|E^2-1|> = 0.797.

	R_{int}	No in CSD
P4/n	9%	233
P4/nmm	18%	80

Solution

- Dropped out of an automatic Patterson program. The structure completed routinely by difference syntheses and least-squares refinement.
- But R=25%
- Try the ‘standard’ 2[110] matrix as a twin law:

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

	No Twin	Twinned
R	25%	7%
ΔF	±2	±0.7
Scale	-	0.38

Equivalent Twin Laws

Original	2-fold about *a*	2-fold about *c*
h k l	h –k -l	-h -k l
h –k l	h k –l	-h k l
-h k –l	-h –k l	h –k –l
-h –k –l	-h k l	h k -l

The same indices would have been obtained with mirrors perp. to *a* and *c*.

Equivalent Twin Laws

	2 about *a*	2 about *b*	2 about *c*
h k l	h –k –l	-h k –l	-h –k l
-h –k –l	-h k l	h –k l	h k –l

Here because the crystal structure is triclinic, faking orthorhombic the three rotations are NOT equivalent.

How Many Twin Laws are Possible?

- Point group of structure = G
- Point group of lattice = H
- No of twin laws =

$$\frac{h_H}{h_G}-1$$

Monoclinic 2/m. h = 4
Orthorhombic mmm. h = 8
1 twin law possible.

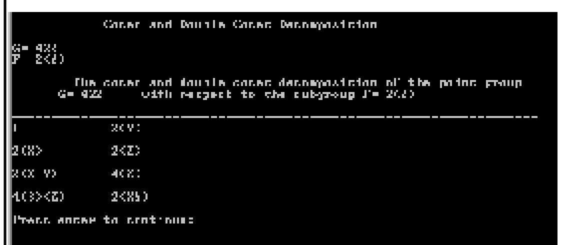
Triclinic. -1 h = 2
Orthorhombic mmm. h = 8
3 twin laws possible.

Orthorhombic mm2. h = 4
Cubic. m-3 h = 24
5 twin laws possible.

Coset Decomposition

http://www.bk.psu.edu/faculty/litvin/Download.html

Coset Decomposition



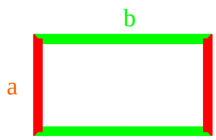
Tutorials

1, 2, 3, 4i-iii, 6

Non-Merohedral Twinning

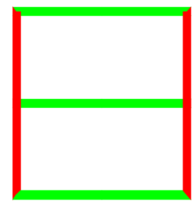
- Merohedral and pseudo-merohedral twinning arises because of extra symmetry in the unit cell dimensions.
- Overlap affects all diffraction spots
- Non-merohedral twinning can arise when extra symmetry occurs in a supercell.
- Only some zones affected by overlap.

Consider an orthorhombic unit cell.
It happens that b ~ 2a



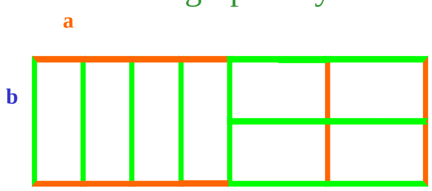
Clearly this cell has mmm symmetry.

But now consider what we have if we put two such cells together:

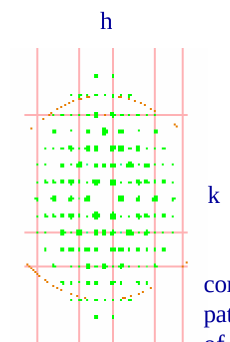


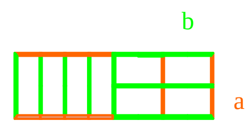
This is a metrically tetragonal supercell with 4/mmm symmetry.

Building-up a Crystal

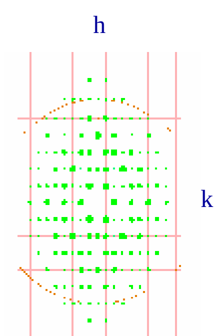


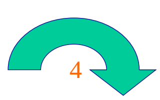
We can still build up a twin, but now we must use a symmetry element of the supercell.

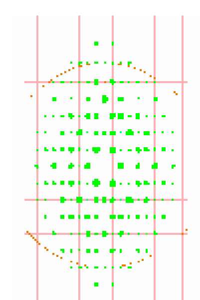


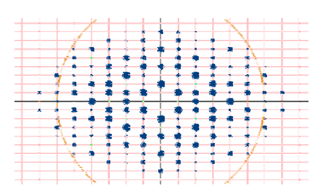


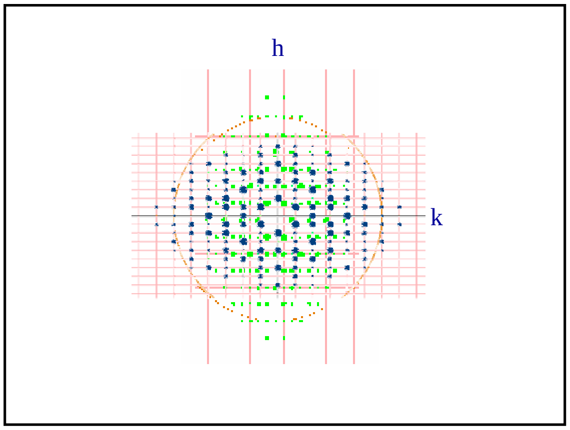
consider diffraction pattern from this half of the crystal.

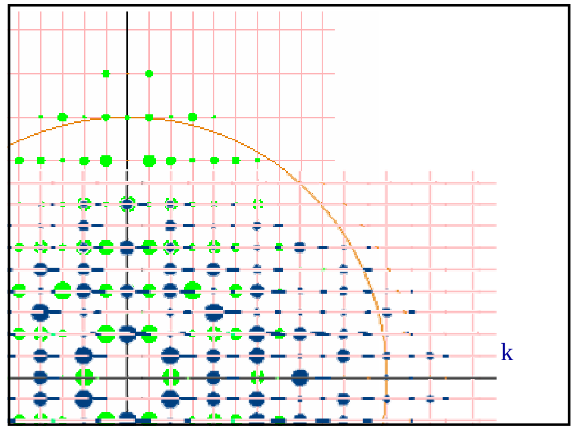


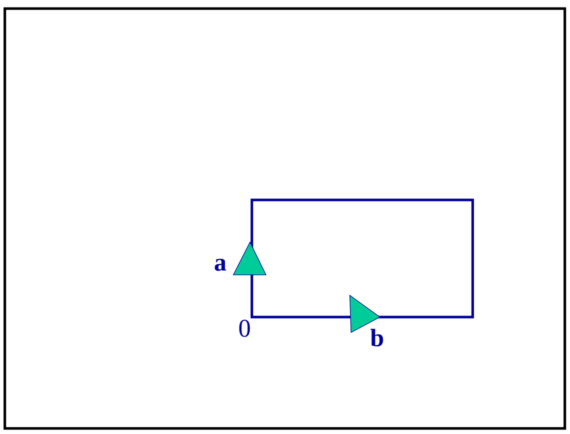


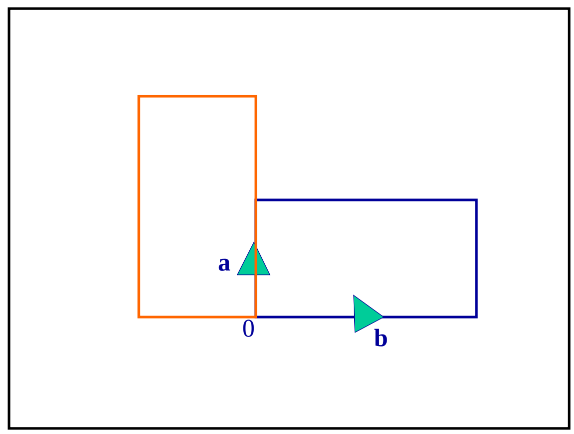


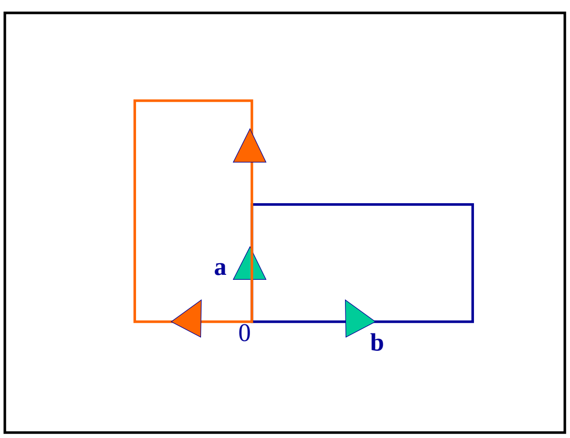


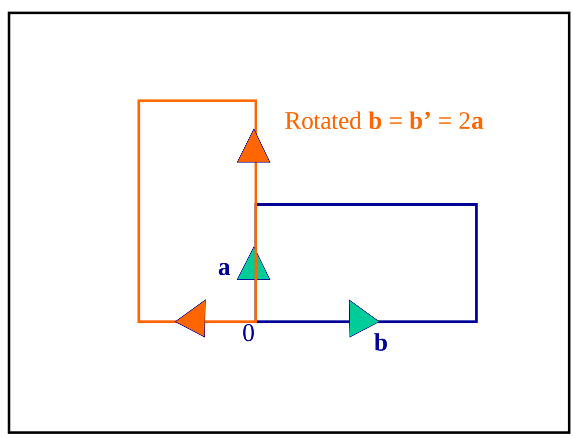

h
k

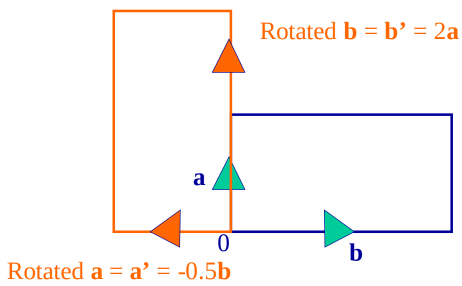

k


a
0
b


a
0
b


a
0
b


Rotated **b** = **b’** = 2**a**
a
0
b



a' = 0**a** - 0.5**b** + 0**c**

b' = 2**a** + 0**b** + 0**c**

c' = 0**a** + 0**b** + 1**c**

The twin law is therefore: $\begin{pmatrix} 0 & -0.5 & 0 \\ 2 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Twin Laws

$$\begin{pmatrix} \tfrac{1}{2} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & -\tfrac{1}{2} & 0 \\ 2 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} 0 & -\tfrac{1}{2} & 0 \\ 2 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix} = \begin{pmatrix} -k/2 \\ 2h \\ l \end{pmatrix}$$

Examples of this Approach

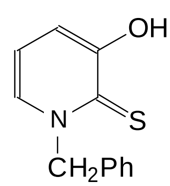
- Petricek et al:
  - Acta B56, 972-979, 2000
  - Acta B57, 221-230, 2001
- *Note that these papers refer to structures refined with JANA-2000, in which the twin laws are transposed wrt those that would be used in Shelx or Crystals.*
- References to more papers on twinning are available from Ton Spek's and Martin Lutz's website: www.chem.uu.nl.

Non-Merohedral Twinning

- Structures will normally solve more-or-less routinely
- Refinement usually unacceptable
  - High R factor
  - Noisy difference map
- It is necessary to try a twinned refinement- but what's the twin law?
- The diffraction pattern may have been hard to index.
- *DIRAX; GEMINI; TWINSOLVE; RECEIPE*
- *ROTAX*

Example 1

- Monoclinic, $P2_1/n$
- The structure solved easily, but R stuck at 15%.
- More details are given in *J. Appl. Cryst. (2002)*, **35**, 168-174.
- Quick diagnosis with ROTAX

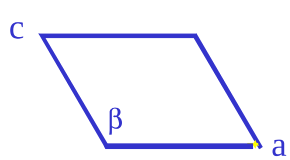


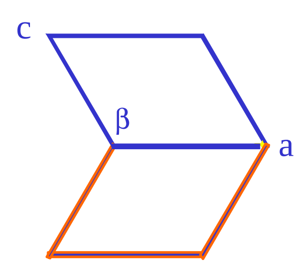
Method 1: Using DIRAX

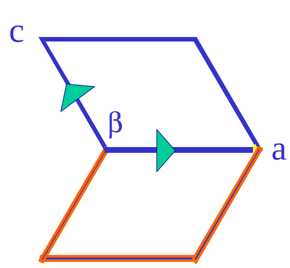
- 50 reflections located in a random search
- Orientation matrix 1: 18/50 unindexed
- Orientation matrix 2: 26/50 unindexed
- Matrix 1: Matrix 2:
- -0.041089 0.072637 -0.043333 0.027103 0.072571 0.043433
- 0.018636 0.071131 0.047086 -0.003457 0.071183 -0.047107
- 0.129867 0.012936 -0.015103 -0.134820 0.013005 0.015141
- 2View output:
  - H'= +0.999*H -0.001*K +0.000*L
  - K'= +0.000*H -1.000*K -0.001*L
  - L'= -0.322*H +0.001*K -0.999*L

$$Ah = X$$
$$A'h' = X$$
$$Ah = A'h'$$
$$h' = Rh$$
$$Ah = A'Rh$$
$$A = A'R$$
$$(A')^{-1}A = R$$

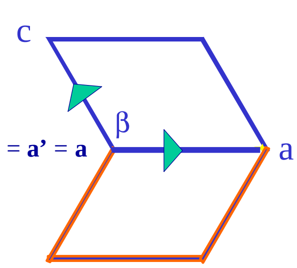
Method 2: Cell Transformation

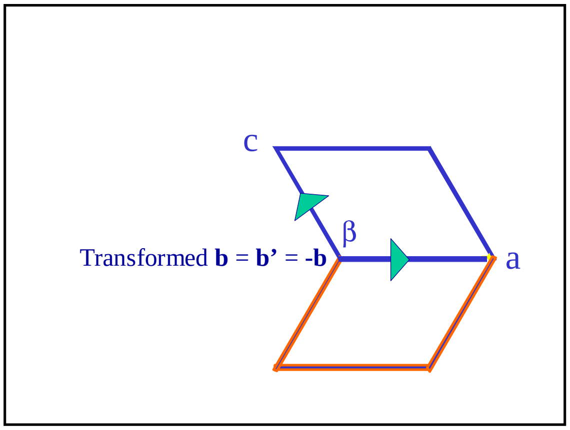


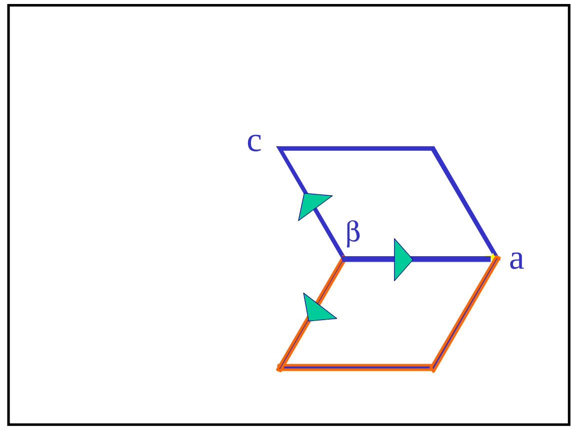


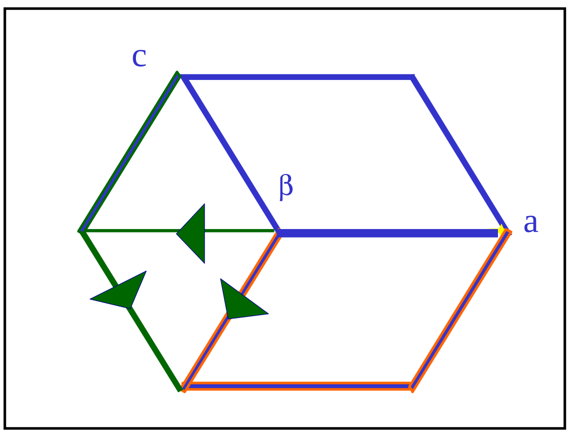


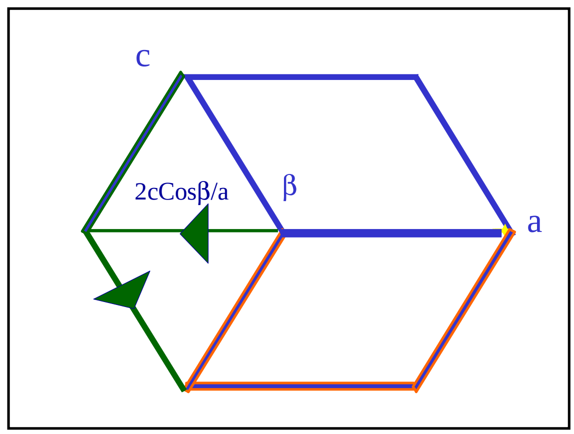
Transformed **a** = **a’** = **a**











2-fold about **a** for a monoclinic cell

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ \frac{2cCosb}{a} & 0 & -1 \end{pmatrix}$$

Method 2: Rational Transformation

- a = 7.28, b=9.74, c=15.23 Å, β= 94.39°
- First consider 2-fold rotations about a and c
- 2cCosβ/a = -0.32 (2-fold about a)
- 2aCosβ/c = -0.07 (2-fold about c)

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -0.32 & 0 & -1 \end{pmatrix}$$

Reflections with greatest unexpected extra intensity:

h	k	l	(Fo2-Fc2)/s	Fo^2	Fc^2	Sigma
-3	3	3	47.805	84.2	2.6	1.7
0	1	3	43.461	279.3	195.0	1.9
-3	1	1	32.794	65.3	22.7	1.3
0	1	2	32.701	385.5	316.7	2.1
0	2	2	29.611	111.0	74.6	1.2
-3	4	5	28.808	61.5	12.0	1.7
0	2	3	26.745	150.1	108.8	1.5
-3	2	7	25.694	35.6	1.1	1.3
0	0	8	23.609	189.5	129.0	2.6
0	2	7	22.423	160.3	109.8	2.3
3	1	3	21.837	28.9	5.4	1.1

Method 3: Poorly Agreeing Data

Reflections with greatest unexpected extra intensity:

h	k	l	(Fo2-Fc2)/s	Fo^2	Fc^2	Sigma
-3	3	3	47.805	84.2	2.6	1.7
0	1	3	43.461	279.3	195.0	1.9
-3	1	1	32.794	65.3	22.7	1.3
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-3	2	7	25.694	35.6	1.1	1.3
0	0	8	23.609	189.5	129.0	2.6
0	2	7	22.423	160.3	109.8	2.3
3	1	3	21.837	28.9	5.4	1.1

Method 3: Poorly Agreeing Data

- If twinning is not taken into account overlapping zones will be poorly-modelled.
- Analysis of poorly-fitting data shows that they belong to distinct zones for which $|F_o|^2 > |F_c|^2$.
- Trends in the indices may give a clue to the twin law.

Method 3: Poorly Agreeing Data

- If, for a certain operation **R**, the transformed indices **Rh** are near-integral, then **R** is a possible twin law.
- Two-fold axis are the most common symmetry element by far.

Rotax Output

```
180.0 degree rotation about   1.   0.   0. direct lattice direction:
[   1.000    0.000    0.000]
[   0.000   -1.000    0.000]
[  -0.320    0.000   -1.000]
Figure of merit =   1.82 ***********
 2 reflections omitted
Figure of merit with no omissions =   3.28
```

This matrix times a vector with $h = 3n$ gives a near integral transformed vector.
The two reflections overlap.

Rotax Output

```
180.0 degree rotation about   1.   0.   0. direct direction:
[   1.000    0.000    0.000]   =[-100]
[   0.000   -1.000    0.000]
[  -0.320    0.000   -1.000]
Figure of merit =   1.82 ***********

180.0 degree rotation about  -6.   0.   1. reciprocal direction:
[   0.999    0.000   -0.003]
[   0.000   -1.000    0.000]
[  -0.333    0.000   -0.999]
Figure of merit =   1.37 ***********
```

We have parallel direct and reciprocal lattice vectors whose dot-product is more than 2. (Le Page & Flack's Rule)

This information will help us to work out what the higher symmetry supercell is.

Method 4: Higher Symmetry Supercell

- A close look at the Rotax output shows that there are related 2-fold axes along the [1 0 0] and [1 0 6] direct lattice directions.
- This gives a metrically orthorhombic supercell.

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 1 & 0 & 6 \end{pmatrix}$$

a = 7.29 Å
b = 9.74 Å
c = 91.12 Å

Higher Symmetry Supercell

- This information is (usually) much easier to derive using CREDUC.
- Use the dot product of the parallel direct and reciprocal vectors as input.
- *CREDUC is part of the XTAL and NRCVAX systems of programs available from CCP14.*
- The algorithm is also available in *PLATON/LEPAGE*

Method 4: Identify a Supercell

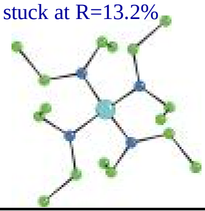
$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -1/6 & 0 & 1/6 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 1 & 0 & 6 \end{pmatrix}=\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -1/3 & 0 & -1 \end{pmatrix}$$

Higher Symmetry Supercell

- It is important to know what the symmetry of the supercell is, as coset decomposition can then be used to predict the presence of other domains.
- mmm (order = 8) is 2/m (order = 4) with an extra 2-fold about *x* or *z*.
- Use Daniel Litvin's program TWINLAWS for this (www.ccp14.ac.uk).

Example 2: $V(NEt_2)_4$

- Very dark liquid.
- Non-merohedral twin, indexed with Gemini to give a triclinic unit cell. *Z* =4
- A second orientation matrix was also derived.
- The twin law was a 2-fold about [100].
- Integrated with the first matrix.
- Isotropic refinement stuck at R=13.2%



Example 2: Rotax Output

Reflections with greatest unexpected extra intensity:

h	k	l	(Fo2-Fc2)/s	Fo^2	Fc^2	Sigma
-10	-6	6	8.528	391.0	37.2	41.5
-2	-2	1	7.462	86.3	4.7	10.9
0	0	8	6.570	181.8	42.8	21.2
-2	2	0	6.529	50.0	1.9	7.4
0	2	6	6.375	33.3	2.5	4.8
5	-2	3	6.147	37.9	3.1	5.7
-2	-2	4	6.139	141.4	46.0	15.5
2	-5	3	6.113	35.4	5.5	4.9
0	10	0	5.923	99.0	23.8	12.7
0	-10	5	5.865	102.6	25.8	13.1

Example 2: Rotax Output

```
180.0 degree rotation about   1.  0.  0. direct lattice direction:
[   1.000    0.000    0.000]
[  -0.019   -1.000    0.000]
[  -0.551    0.000   -1.000]
Figure of merit =   1.82 ***********
```

This is the same matrix that GEMINI suggested, and clearly it is the most sensible twin law to try first.

Incorporating this matrix gives R=11.4%, and twin scales of 0.75 and 0.25.

Example 2: Supercell Symmetry

Rotax output showed [100] was parallel to [-401]*; [010]//[0-41]*;[114]//[001]*.

Run CREDUC with ‘DOT’=4

```
 Pseudo orthorhombic  F    Max delta       .863
 A =   1.0   .0   .0    8.2490  Alpha=    90.155
 B =    .0 -1.0   .0   15.8270  Beta =    89.188
 C =  -1.0 -1.0 -4.0   65.5495  Gamma=    89.710
```

Coset decomposition of mmm into -1 gives 2 fold axes about the orthorhombic *x*, *y* and *z* -axes. (Other schemes are possible)

In principle there are **four** domains in this twin!

Multi-domain Twin Model

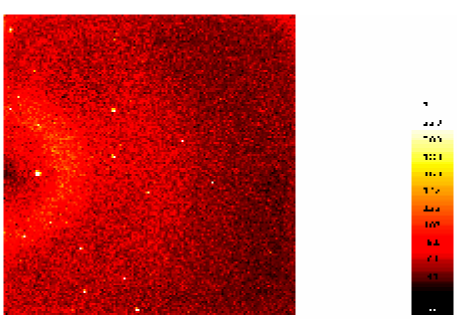
```
180.0 degree rotation about   [1.  0.  0.]
[   1.000    0.000    0.000]
[  -0.019   -1.000    0.000]
[  -0.551    0.000   -1.000]

180.0 degree rotation about   [0.  1.  0.]
[  -1.000   -0.005    0.000]
[   0.000    1.000    0.000]
[   0.000   -0.504   -1.000]

180.0 degree rotation about   [1.  1.  4.]
[  -1.004   -0.004   -0.014]
[  -0.001   -1.001   -0.005]
[   0.501    0.501    1.005]
```

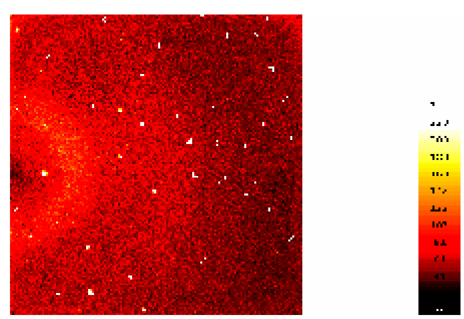
Results

- R-Factor drops further to 11.1%
- One twin scale factor is small, and can be removed.
- Anisotropic refinement with H-atoms etc gives a final R of 5%.

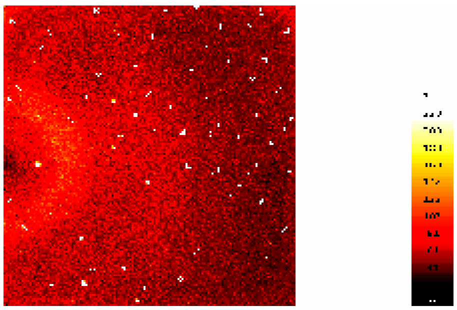
	0.67
[100]	0.17
[010]	0.14
[114]	0.03

But is it right?

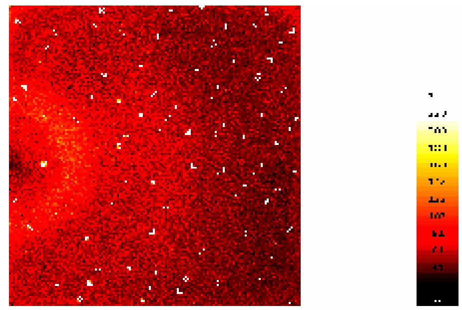




Indexing with matrix 1



Indexing with matrices 1 & 2



Indexing with matrices 1, 2 and 3