

Experiences with Twinning

Jim Britten (McMaster)

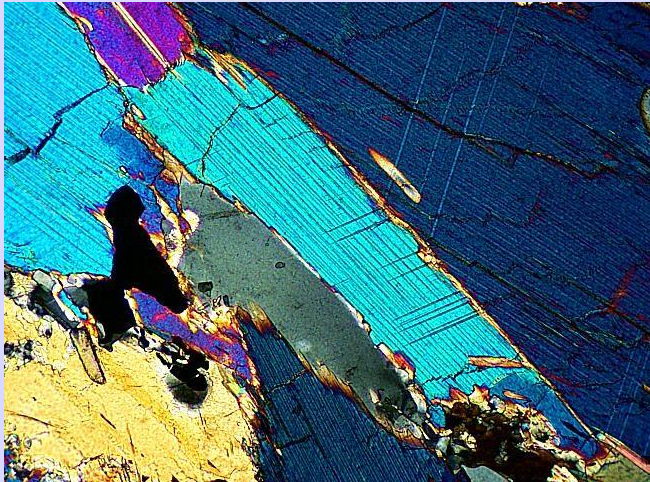
With a lot of input from Regine Herbst-Irmer (Gottingen)
and Ton Spek (Utrecht)

Outline

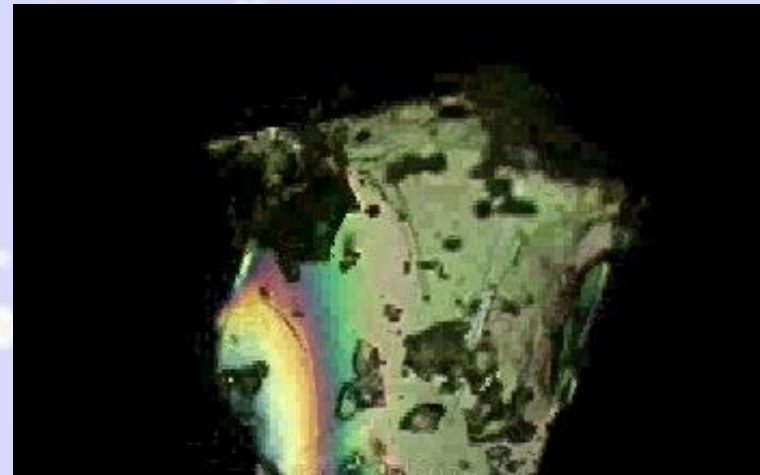
- Twinned crystal growth
- Merohedral twinning
- Non-merohedral twinning
- Pseudo-merohedral twinning
- Twinning that isn't twinning

“Twins are regular aggregates consisting of individual crystals of the same species joined together in some definite mutual orientation.”

from: "Fundamentals of Crystallography", edited by C. Giacovazzo, Union of Crystallography, Oxford University Press 2nd Edn. 2002.



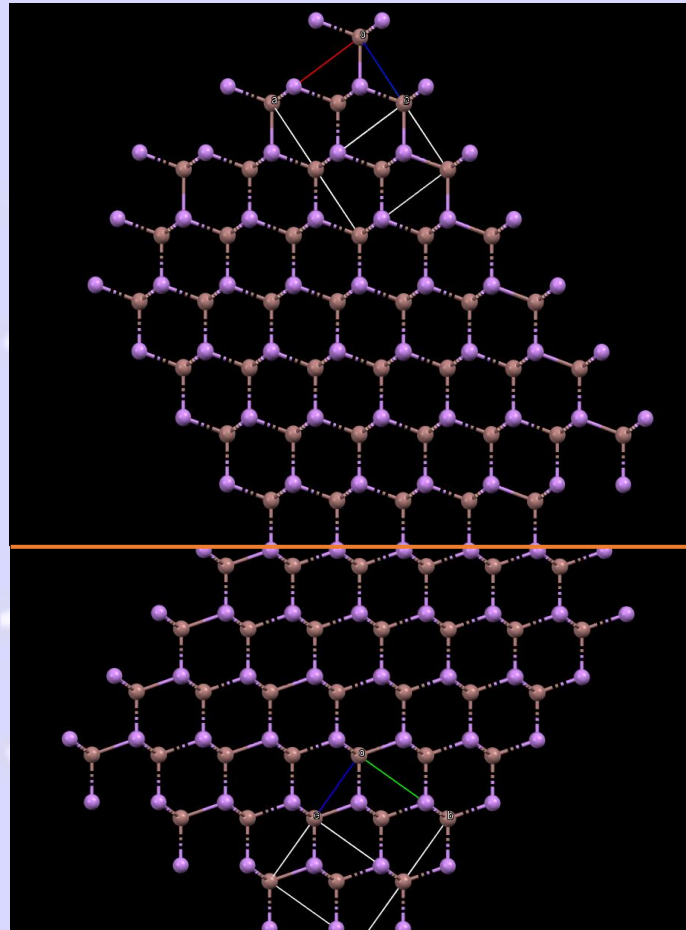
Cross-polarized microscope image of a twinned crystal.
(<https://i.pinimg.com/originals/49/9c/38/499c3896dd4e84bdad20dbe8b4f9e4a2.jpg>)



Cross-polarized microscope image of a single crystal with powder grains on the surface.

Growth of a cubic
 $\text{InAs}_{(1-x)}\text{Sb}_x$ crystal
with a 180° rotation
on the (111) face.

(111) twinning plane →



Merohedral Twinning

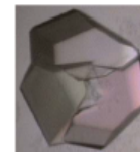
The twin operator is a symmetry operator of the crystal system but not of the point group of the crystal. The result is a 100% overlap of reflections from each component.

This includes racemic twinning for a non centrosymmetric structure (inverted packing). i.e. The space group of the structure does not have a center of symmetry, but the twin component has the inverted structure of the main crystal.

Merohedral twinning can also be due to an operator not part of the Laue group of the crystal. This can only occur for lower symmetry trigonal, tetragonal, hexagonal and cubic space groups. For example, a twinned crystal growing with $P4/m$ symmetry may give a diffraction pattern that appears to have $P4/mmm$ symmetry.



Warning Signs for Merohedral Twinning



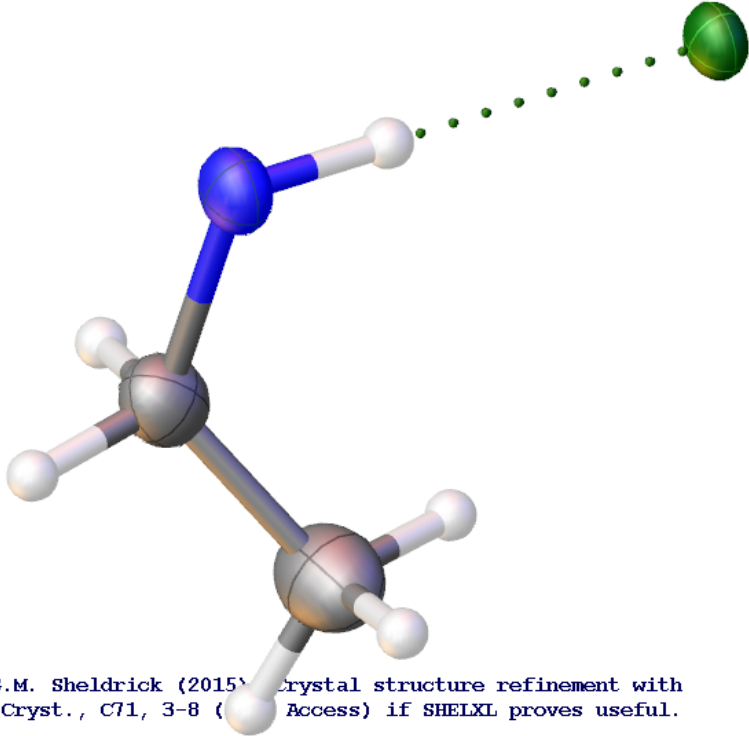
- Metric symmetry higher than Laue symmetry
- R_{int} for the higher symmetry Laue group only slightly higher than for the lower symmetry one
- Different R_{int} values for the higher symmetry Laue group for different crystals of the same compound
- Mean value for $|E^2 - 1| \ll 0.736$
- Apparent trigonal or hexagonal space group
- Systematic absences not consistent with any known space group
- No structure solution
- Patterson function physically impossible (for heavy atom structures)
- High R-Values

Definition Classification Tests Solution Refinement **Warning Signs**

Regine

Olex2

File Edit View Structure Mode Tools Model Select Help



Please cite: G.M. Sheldrick (2015) Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access) if SHELXL proves useful.

```

+++++
+ et3nhcl      finished at 22:43:00   Total elapsed time:    0.19 secs +
+++++
Note: Q-peaks are invisible
Hoof t y: 0.31(6), Flack x: 0.16(9)
>>

```

Et3NHCl

C:\Users\britten\Documents\teach\W...CCW21\Twinning\Et3NHCl\Et3NHCl.res

C₆H₁₆ClN

P3 1 c

a = 8.2862(19) **α** = 90° **Z** = 2
b = 8.2862(19) **β** = 90° **Z'** = 0.333333
c = 7.0249(19) **γ** = 120° **V** = 417.72(18)

R₁ **7.26** %
wR₂ **21.50** %

d min (Mo) **0.75** **I/σ(I)** **18.8** **Rint** **5.44%** **Full 50.5°** **100**
2θ = 56.6°
Shift **0.000** **Max Peak** **0.9** **Min Peak** **-0.6** **Goof** **1.134** **Flack** **.16(9)**

Possible inversion twin or centrosymmetric space group

Home Work View Tools Info

Solve Refine Draw Report

Program XL L.S. Cycles 10 Peaks 1

hkl file Et3NHCl.hkl hkl : Sat Aug 7 22:36:34 2021

Weight ☒ .147 1.146 .000 1.000 EXTI ☐ ACTA

☐ Use Solvent Mask This is the Olex2 implementation of BYPASS (a.k.a. SQUEEZE)

Refinement Settings Extra

Toolbox Work

Labels Labels OFF/ON

C H Cl N ... ☒ Add H

Q to C Q to H ☒ Z' = 0.333333

Select atom(s) and then mFit mSplit Split SAME SHIFT+Move

MAP Show Map Map Settings

Peak & Uiso Sliders

Growing

Finishing

History

Select

Olex2








File Edit View Structure Mode Tools Model Select Help


Et3NHCl P31c

Et3NHCl P31c

C:\Users\britten\Documents\teach\W...CCW21\Twinning\Et3NHCl\Et3NHCl.res

C₆H₁₆ClN

a = 8.2862(19)	$\alpha = 90^\circ$	Z = 2	 25.8 R_1 7.26 % wR_2 21.50 %
b = 8.2862(19)	$\beta = 90^\circ$	Z' = 0.333333	
c = 7.0249(19)	$\gamma = 120^\circ$	V = 417.72(18)	

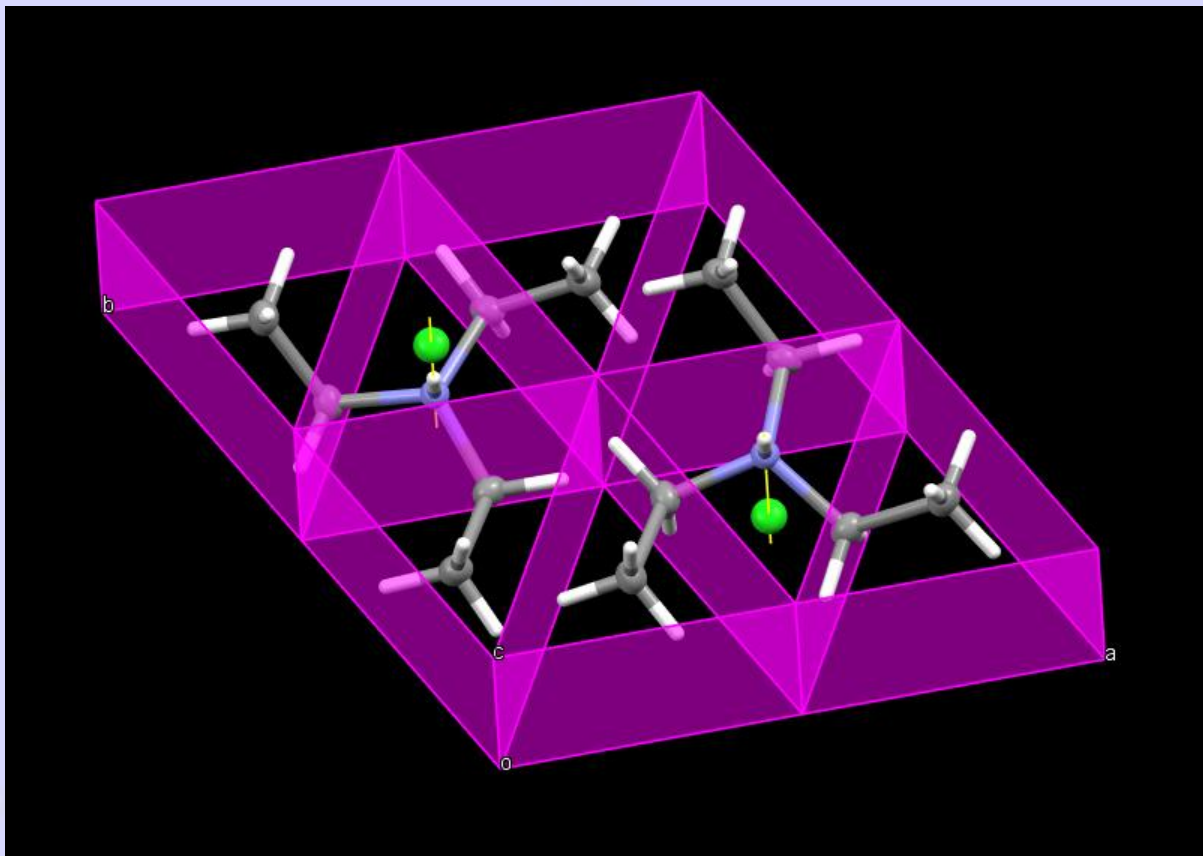
d min (Mo)	0.75	I/ σ (I)	18.8	Rint	5.44%	Full 50.5°	100
Shift	0.000	Max Peak	0.9	Min Peak	-0.6	Goof	1.134
						Flack	.16(9)

Possible inversion twin or centrosymmetric space group

Please cite: G.M. Sheldrick (2015) Crystal structure refinement with SHELXL, Acta Cryst., C71, 3-8 (Open Access) if SHELXL proves useful.

+ et3nhcl finished at 22:43:00 Total elapsed time: 0.19 secs +
 +-----+
 Note: Q-peaks are invisible
 Hoof t y: 0.31(6), Flack x: 0.16(9)
 >>

MAP [Show Map](#) [Map Settings](#)
 Peak & Uiso Sliders
 Growing
 Finishing
 History
 Select



Cell: 0.71073 8.286 8.286 7.025 90.00 90.00 120.00 Spgr: P3lc
Criteria: DeltaI/SigmaI .GT. 4.0, DeltaTheta 0.10 Deg., NselMin = 50
N(refl) = 672, N(selected) = 50, IndMax = 5, CrltI = 0.1, CrltT = 0.10

```

2-axIs ( 1 -2 0 ) ( 0 -1 0 ), Angle ( ) = 0.00 Deg, Freq = 110
*****
(-1.000 -1.000 0.000) (h1) (h2) Nr Overlap = 670
( 0.000 1.000 0.000) * (k1) = (k2) BASF = 0.50
( 0.000 0.000 -1.000) (l1) (l2) DEL-R = -0.025

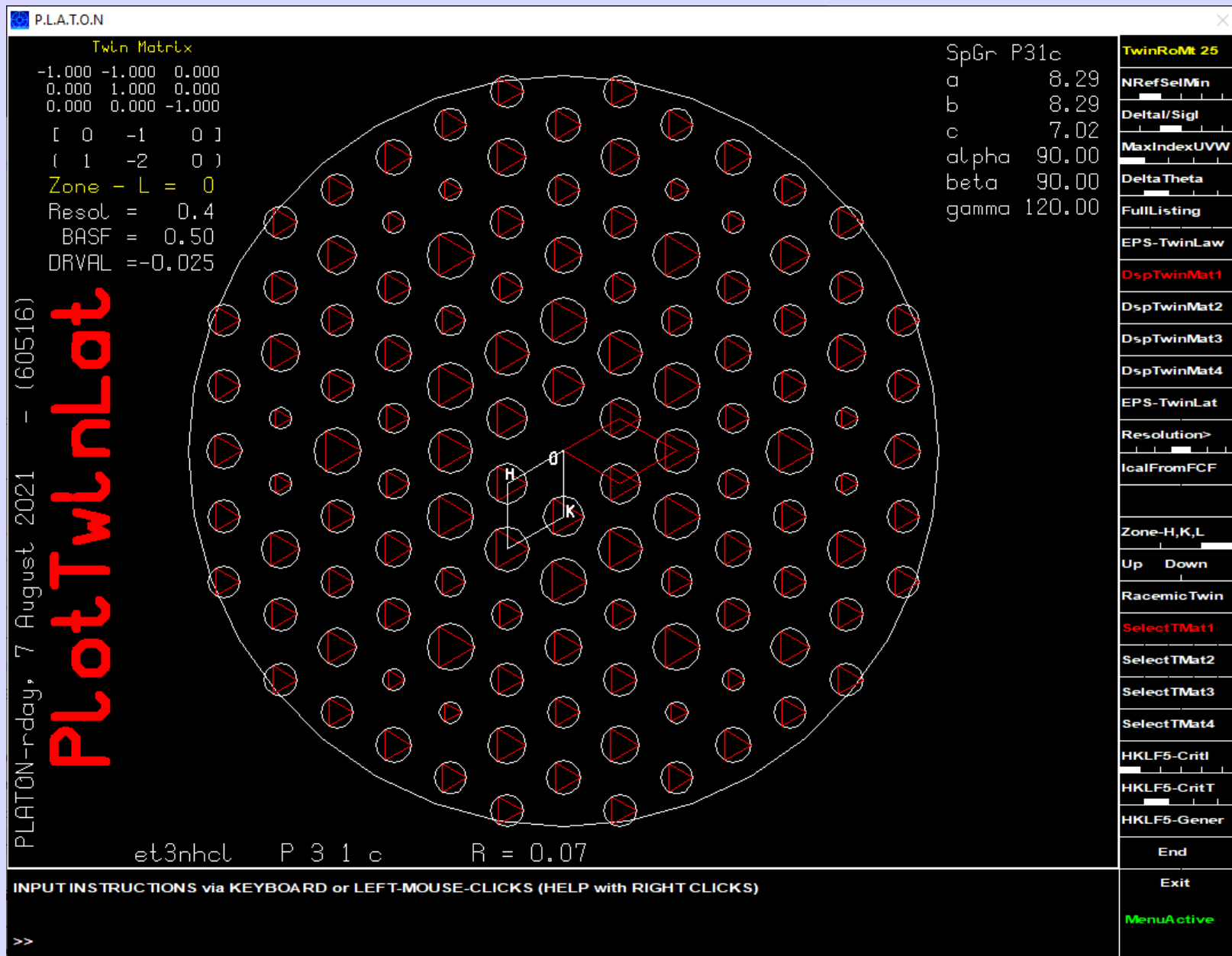
```

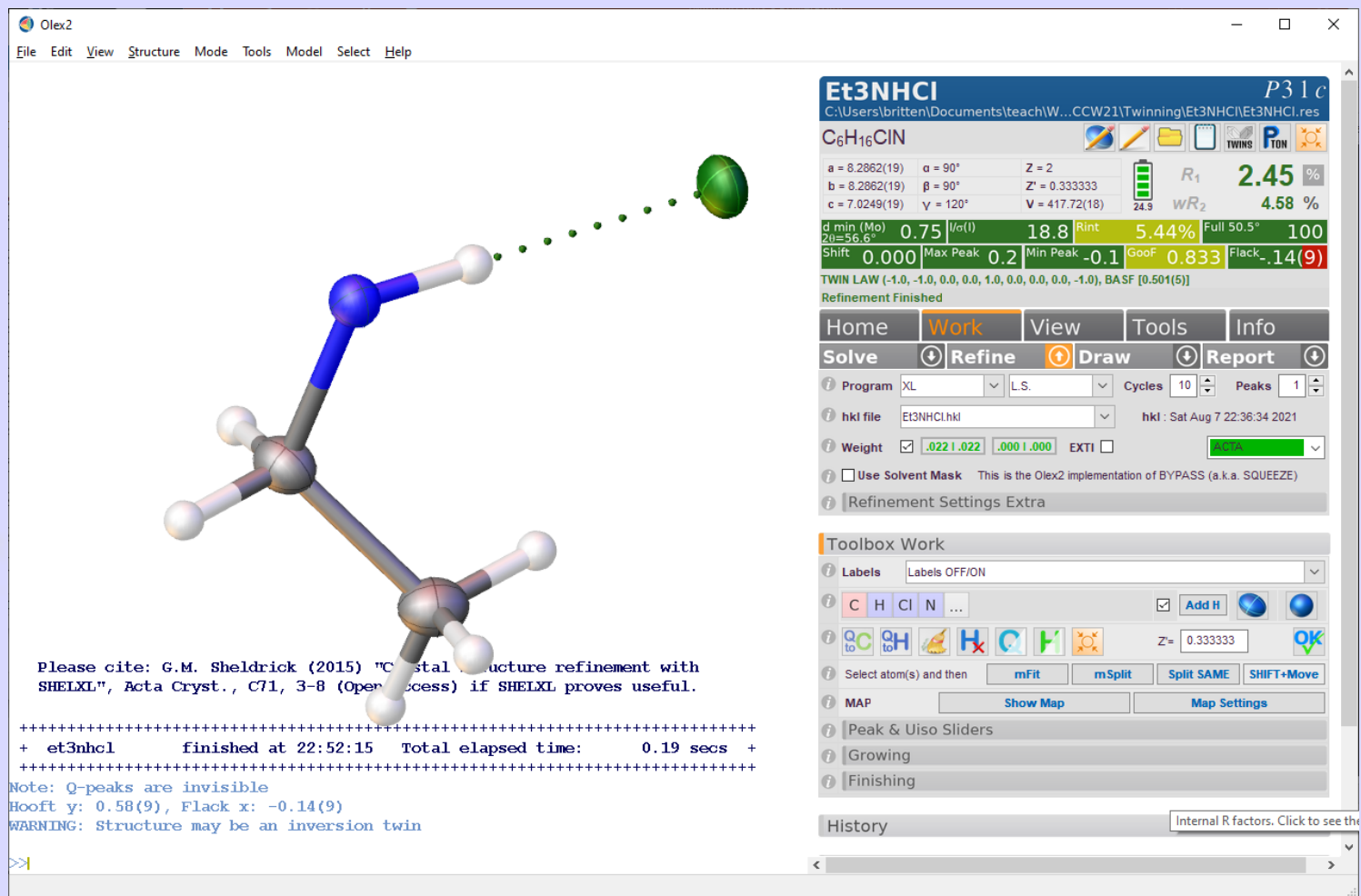
et3nhcl P 3 1 c R = 0.07

1

TwinRoMk 25	
NRefSelMin	
Deltal/Sigl	
MaxIndexUVV	
Delta Theta	
FullListing	
EPS-TwinLaw	
DspTwinMat1	
DspTwinMat2	
DspTwinMat3	
DspTwinMat4	
EPS-TwinLat	
Resolution>	
IcalFromFCF	
Zone-H,K,L	
Up	Down
RacemicTwin	
SelectTMat1	
SelectTMat2	
SelectTMat3	
SelectTMat4	
HKLF5-Critl	
HKLF5-CritT	
HKLF5-Gener	
End	
Exit	
MenuActive	

INPUT INSTRUCTIONS via **KEYBOARD** or **LEFT-MOUSE-CLICKS** (HELP with **RIGHT CLICKS**)






Olex2

File Edit View Structure Mode Tools Model Select Help

Et3NHCl *P3 1 c*
 C:\Users\britten\Documents\teach\W...CCW21\Twinning\Et3NHCl\Et3NHCl.res
 C₆H₁₆ClN

Et3NHCl *P3 1 c*
 C:\Users\britten\Documents\teach\W...CCW21\Twinning\Et3NHCl\Et3NHCl.res

C₆H₁₆ClN

a = 8.2862(19)	α = 90°	Z = 2	 24.9	<i>R</i> ₁	2.45 %
b = 8.2862(19)	β = 90°	Z' = 0.333333		<i>wR</i> ₂	4.58 %
c = 7.0249(19)	γ = 120°	V = 417.72(18)			

d min (Mo)	0.75	I/σ(I)	18.8	Rint	5.44%	Full 50.5°	100
Shift	0.000	Max Peak	0.2	Min Peak	-0.1	GooF	0.833
						Flack	.14(9)

TWIN LAW (-1.0, -1.0, 0.0, 0.0, 1.0, 0.0, 0.0, 0.0, -1.0), BASF [0.501(5)]

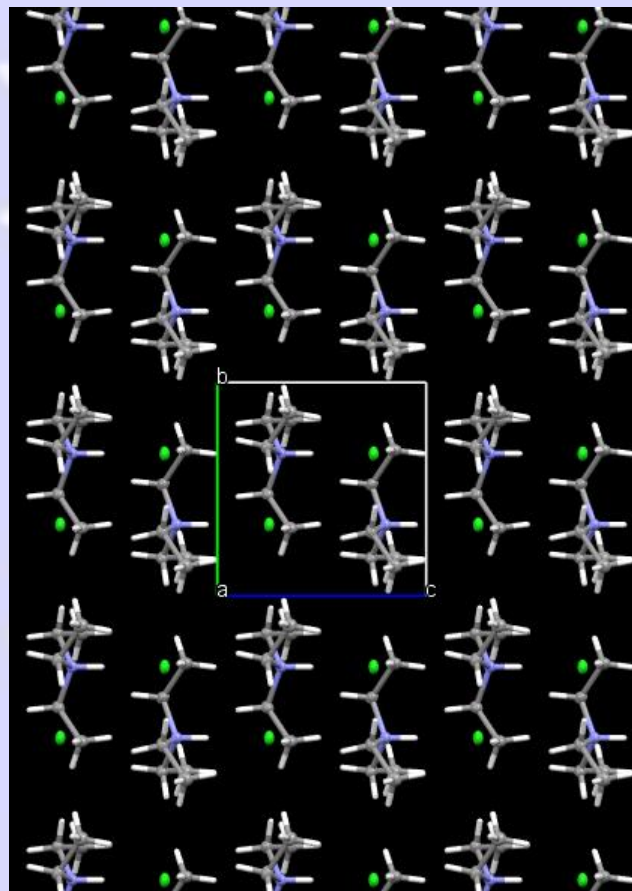
Refinement Finished

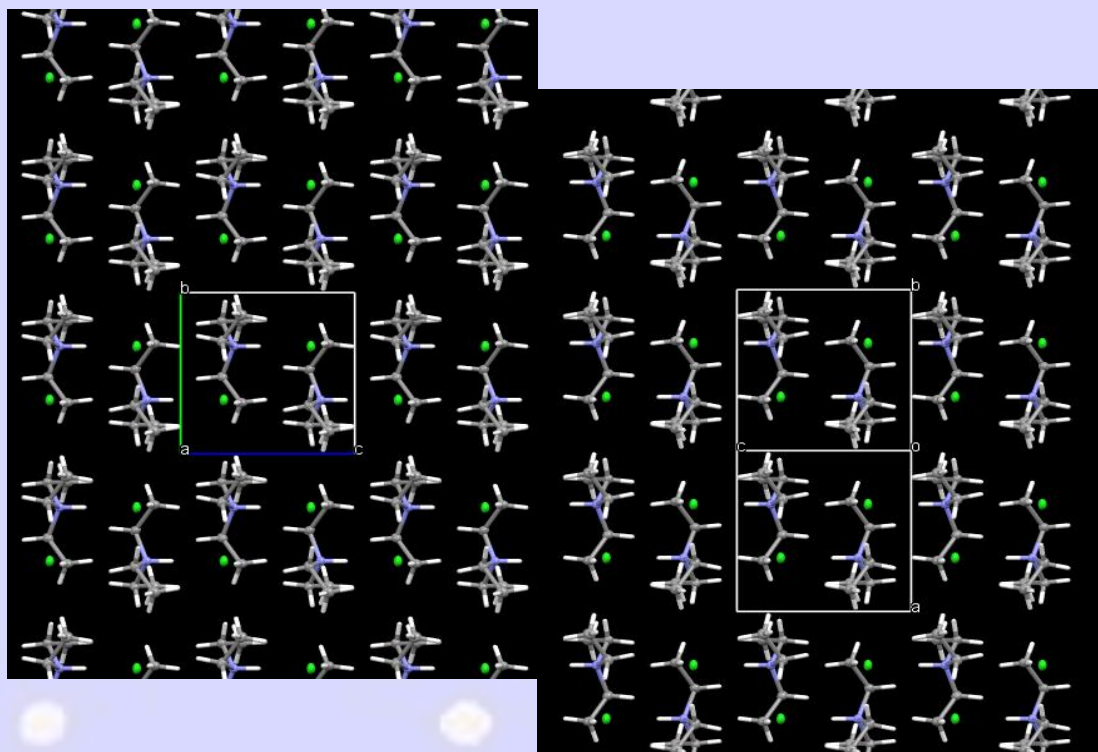
WARNING: Structure may be an inversion twin

History Internal R factors. Click to see the

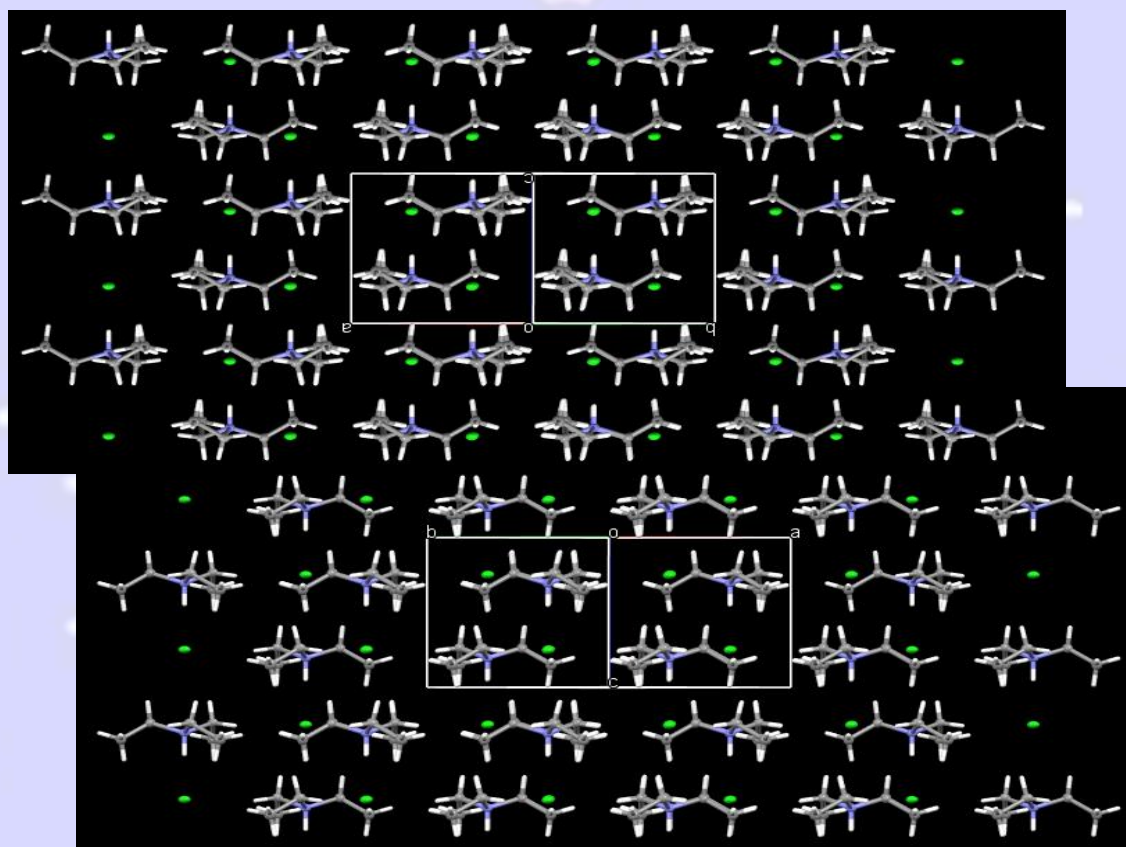
>>|

Crystal structure
of [Et₃N]Cl as
displayed in
CCDC's Mercury

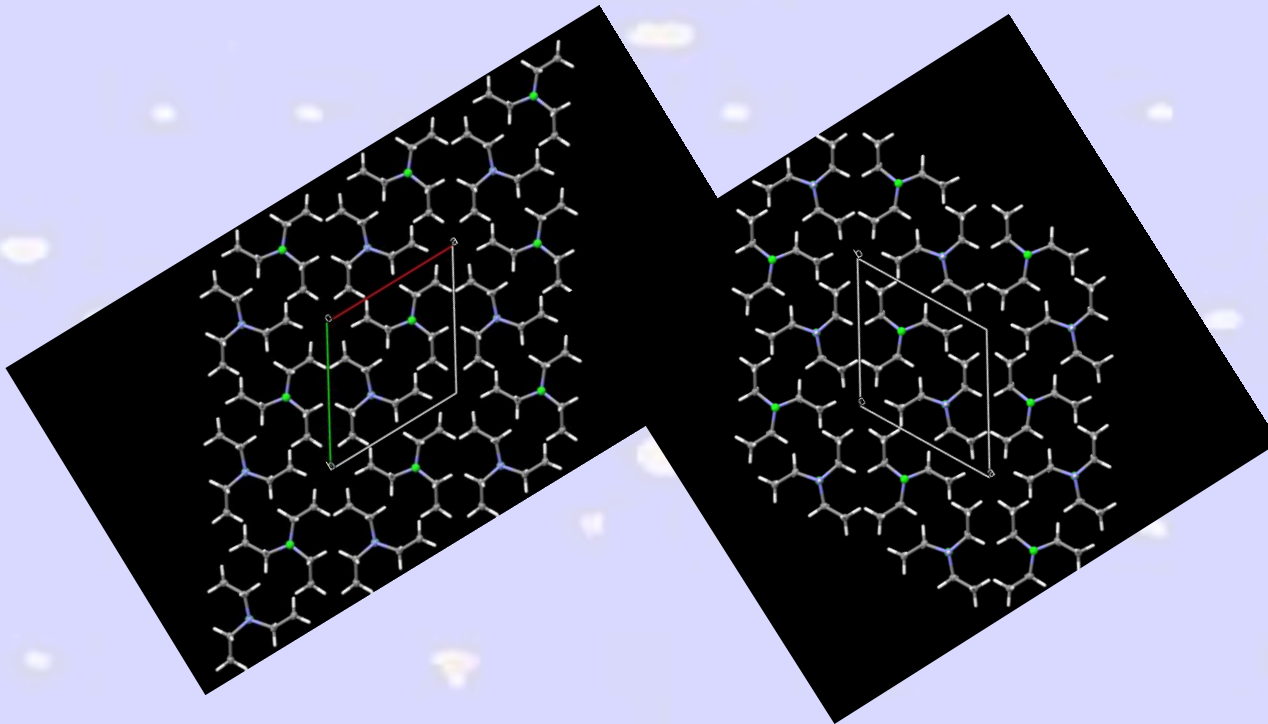




Growth of twin crystal related by
the $\begin{pmatrix} -1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ rotation matrix.



It is not clear which surface of the crystal is acting as the twin interface.



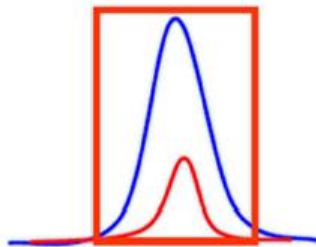
Non-Merohedral Twinning

The twin operator can be represented by an arbitrary operator not related to the Laue Class. It can be a mirror or a 180 degree rotation about a crystal growth surface. There is no exact overlap of diffraction spots and the unit cell may appear too large and not refine well. Spots in the diffraction pattern may be too close or appear split.

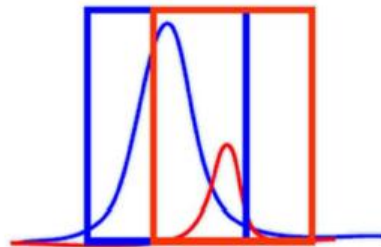
George Sheldrick's program 'cell_now' can be used to find multiple crystal orientations and matrices for integration. An HKLF 5 formatted hkl file contains the multiple sets of indices for overlapping reflections. The twinning can be deconvoluted once a structural model is found.



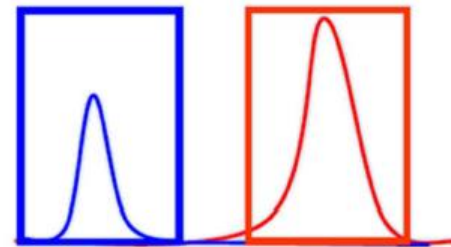
Integration



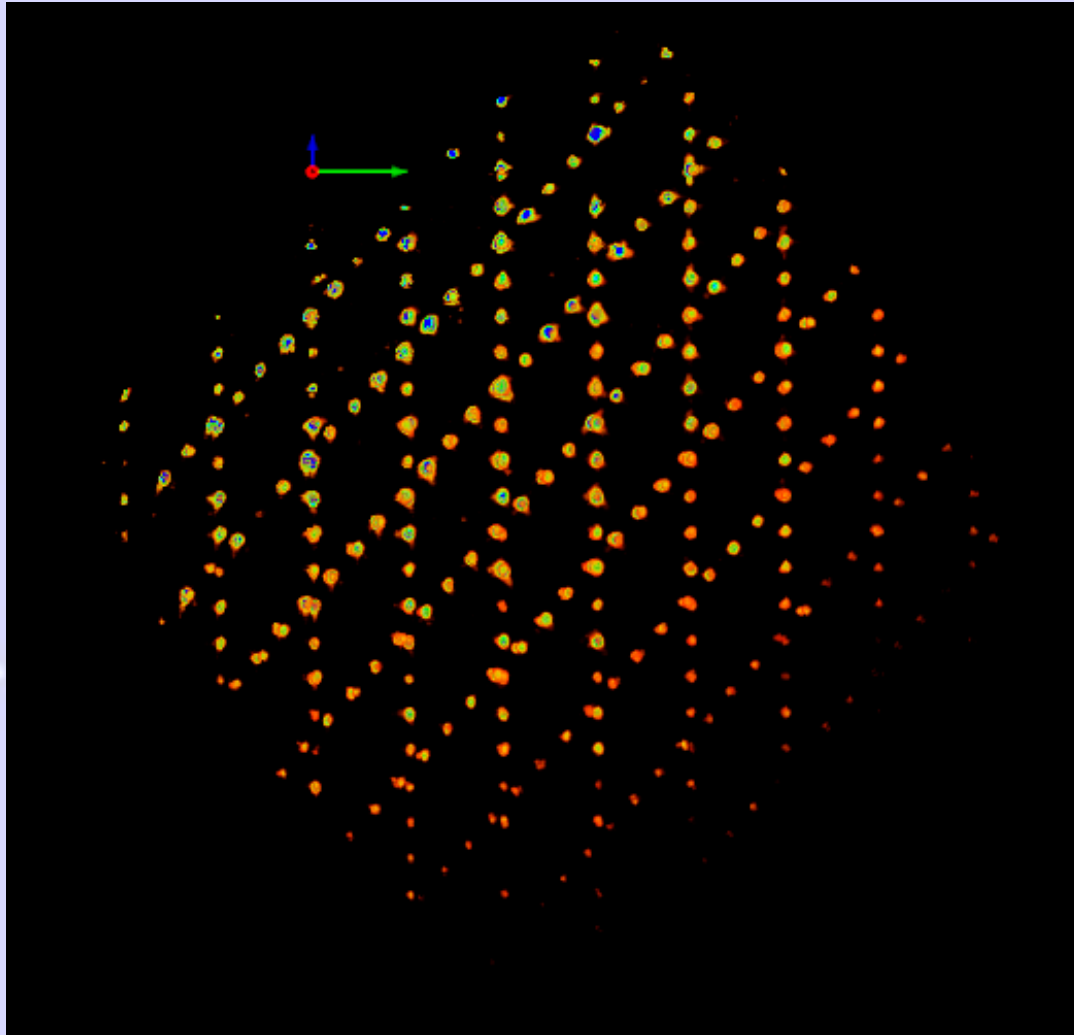
exact
overlaps



partial
overlaps



non-
overlaps



Diffraction pattern from a non-merohedral twin



Cell Determination



CELL_NOW

- Reads .spin, .p4p or .drx-files
- tries to find sets of reciprocal lattice planes that pass close to as many reflections as possible
- The cell may be rotated to locate further twin domains using only the reflections that have not yet been indexed
- Determination of the cell and the twin law in one program
- Writes a .p4p/.spin file for RLATT and SAINT for simultaneous integration of more than one domain
- Determination of very weak domains possible

Twinning Symptoms

- Not all reflections fit in a single lattice
- Statistics $\langle |E^2 - 1| \rangle$ small etc.
- Problems to solve the structure
- Poor refinement
- $wR^2 \gg 2 * R^1$
- Ghost peaks at chemically impossible positions.
- High value of the second Wght parameter
- $F_{obs} \gg F_{calc}$ for a large number of reflections
- Etc.

Ton

Ideas behind the Platon's TwinRotMat Algorithm

- Reflections effected by twinning show-up in the least-squares refinement with $F(\text{obs}) \gg F(\text{calc})$
- Overlapping reflections necessarily have the same Theta value within a certain tolerance.
- Generate a list of implied possible twin axes based on the above observations.
- Test each proposed twin law for its effect on R.

Ton

TwinRotMat

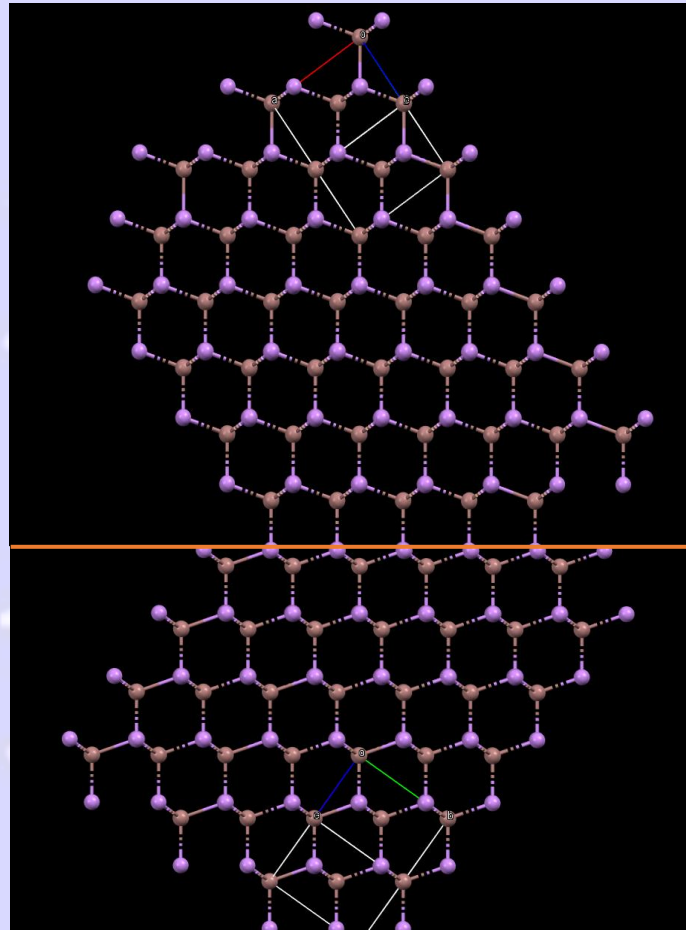
- Points to the effective twin laws to be included in the structure refinement given a partially refined structure model
- Offers a diagnostic tool for possibly missed twinning as part crystal structure validation
- Nowadays possibly less important for the detection of non-merohedral twinning (CCD)

(But cases of missed non-merohedral twinning still arrive for publication)

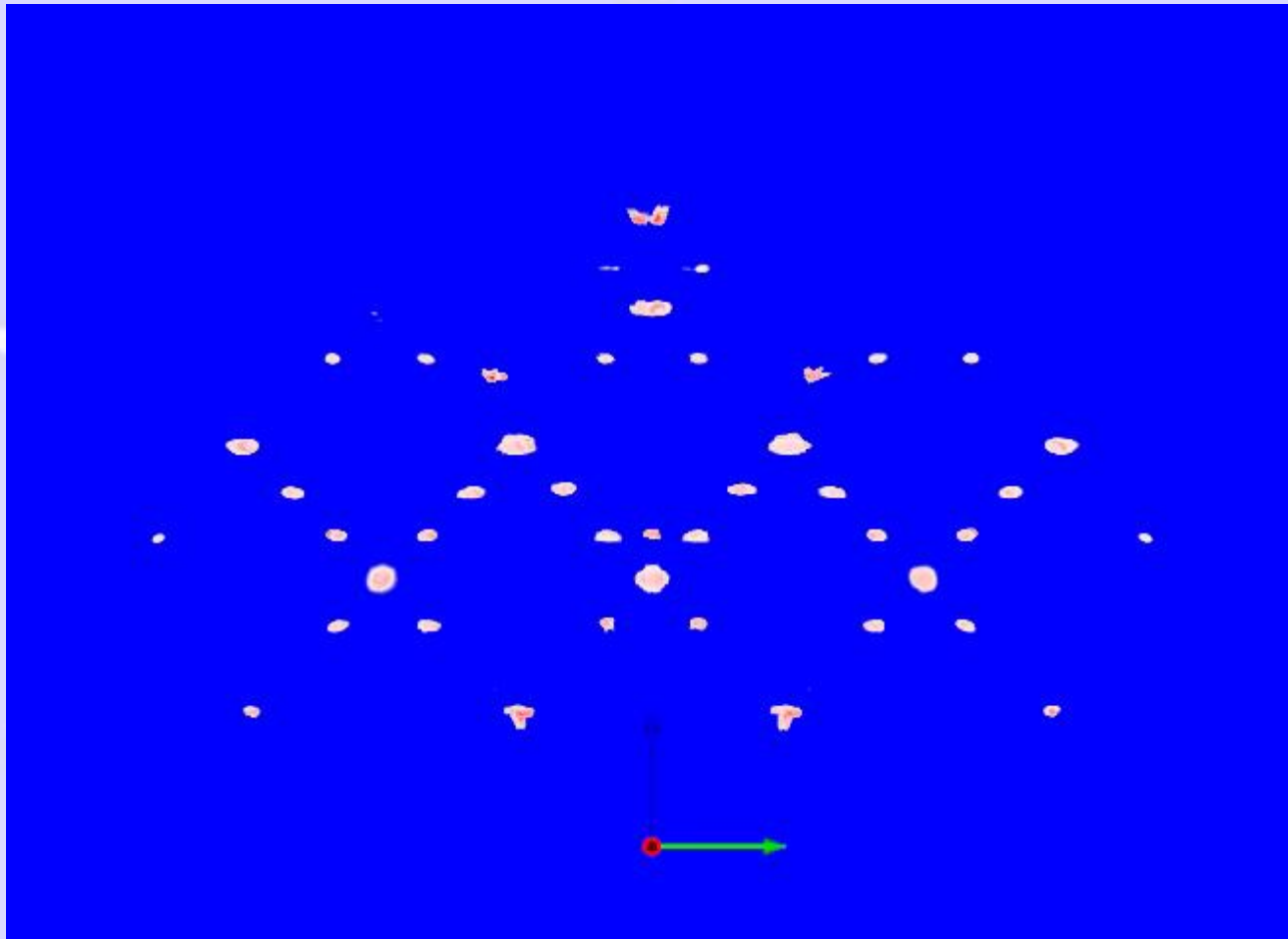
Ton

Growth of a cubic
 $\text{InAs}_{(1-x)}\text{Sb}_x$ crystal
with a 180° rotation
on the (111) face.

(111) twinning plane →

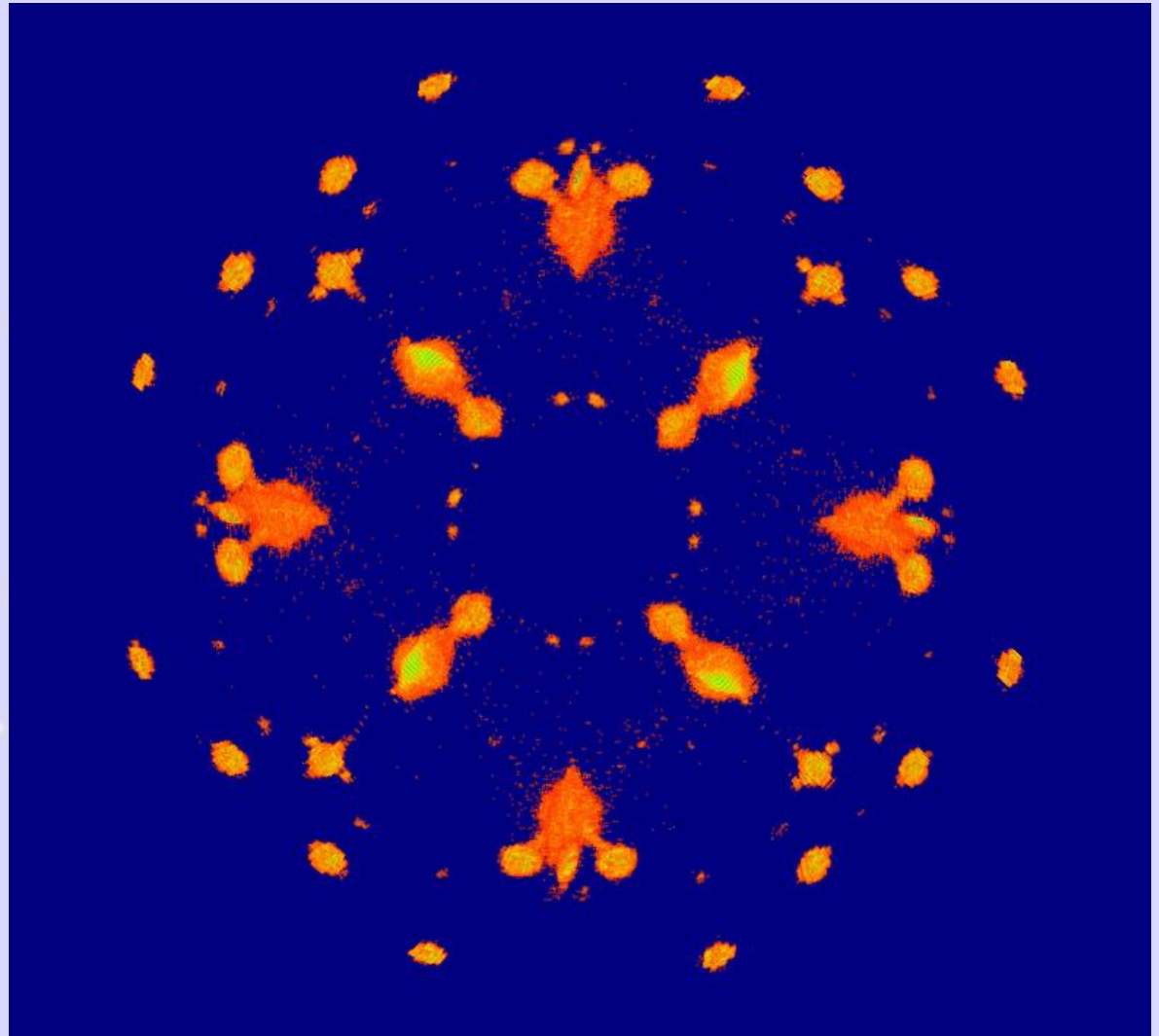


3D diffraction pattern from thin film of $\text{InAs}_{(1-x)}\text{Sb}_x$
nanowires (isolate (111) reflections)



(220) and
(311) shells

Diffuse lines
connect twins



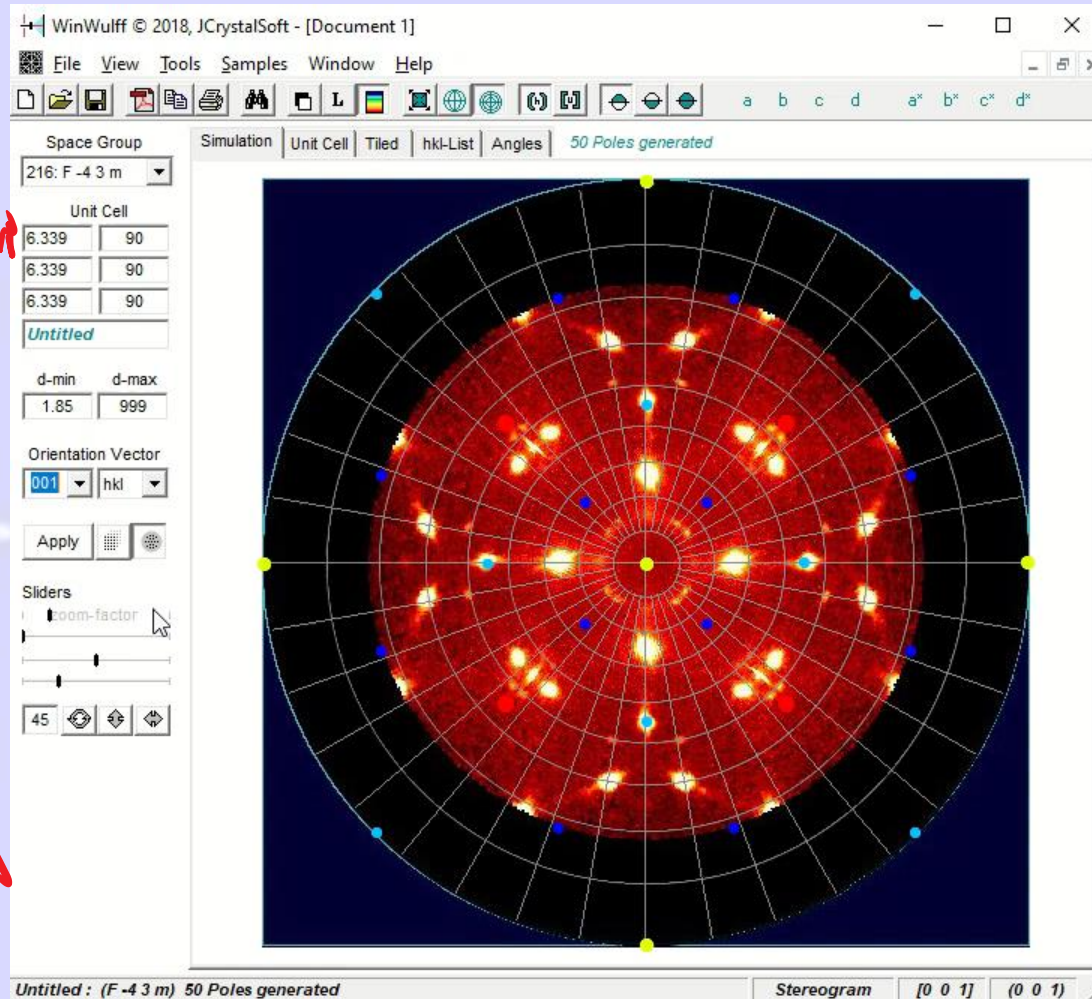
113 POLE FIGURE

IS'T
ORIENTATION

THEN

60° ROT
AROUND 111

THEN
BACK TO
ORIGINAL
ORIENTATION



← SPOT
LABELS

113
MOVES TO
WHERE
220 (110)
WAS

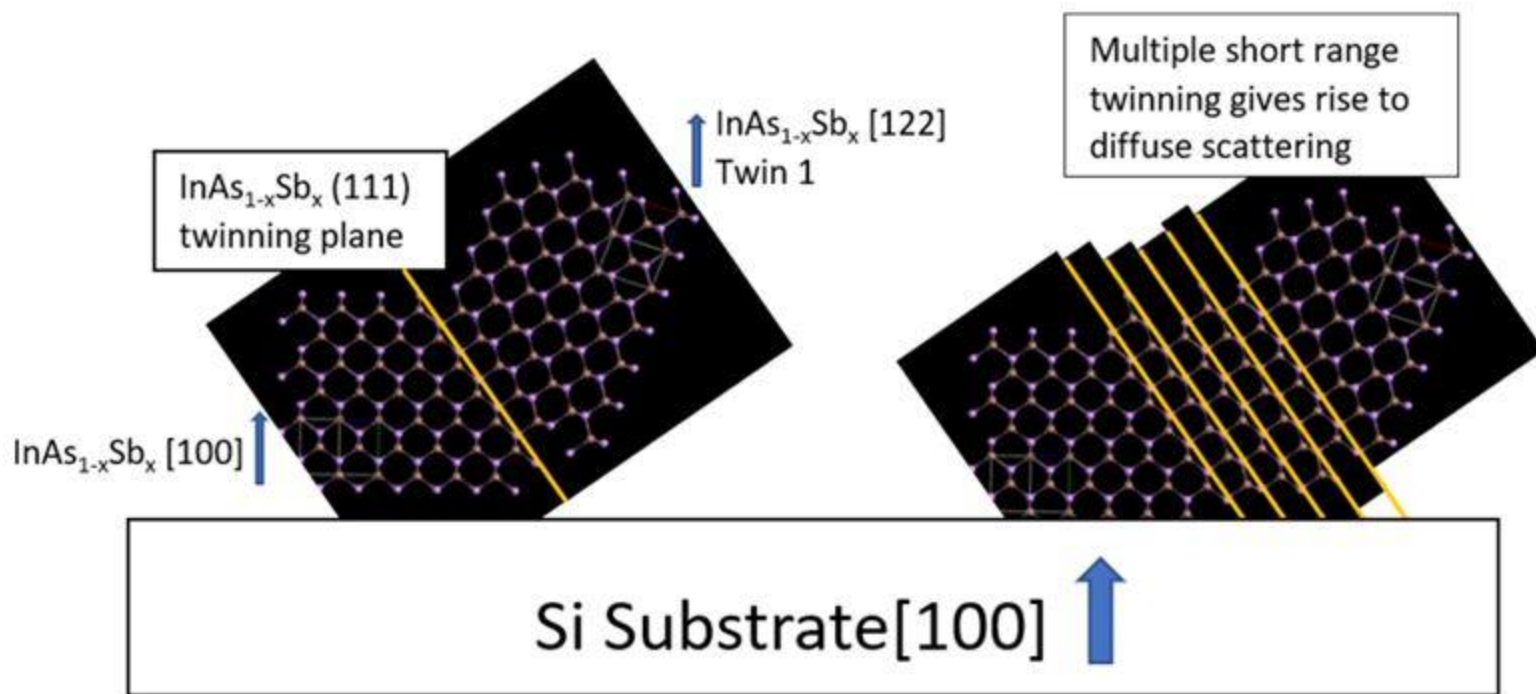


Figure 3. Twinning by 180° (or $\pm 60^\circ$) rotation about the [111] face of $\text{InAs}_{1-x}\text{Sb}_x$. Regions of multiple layer twinning account for the diffuse scattering observed in the 3D diffraction pattern. Twin planes are indicated by yellow lines.

Goosney, Jarvis, Britten, Lapierre, Infrared Physics and Technology

Pseudo-merohedral twinning

The twin operator belongs to a higher crystal system than the true structure.

Metric symmetry appears higher than the Laue symmetry.



Elucidating the structure of the organic spin-liquid candidate $k\text{-(BEDT-TTF)}_2\text{-Cu}_2\text{-(CN)}_3$

Dalini Maharaj
January 29th 2014
Chem 736

- ▶ Some physical and crystallographic properties
- ▶ Data Collection & Processing
- ▶ Refinement in Olex 2
- ▶ Discussion of results



Apex 2: Bravais Cell Selection

Search for higher metric symmetry
Identical indices and Friedel opposites combined before calculating R(sym)

Option A: FOM = 0.183 deg. ORTHORHOMBIC C-lattice R(sym) = 0.198 [4787]
Cell: 13.218 29.197 8.534 90.00 90.00 89.82 Volume: 3293.44
Matrix: 0.0000 0.0000 -1.0000 -2.0000 0.0000 -1.0000 0.0000 1.0000 0.0000

Option B: FOM = 0.000 deg. MONOCLINIC P-lattice R(sym) = 0.016 [3111]
Cell: 13.218 8.534 16.006 90.00 114.21 90.00 Volume: 1646.72
Matrix: 0.0000 0.0000 -1.0000 0.0000 -1.0000 0.0000 -1.0000 0.0000 0.0000

Option C: FOM = 0.182 deg. MONOCLINIC C-lattice R(sym) = 0.208 [3178]
Cell: 29.197 13.218 8.534 90.00 90.00 90.18 Volume: 3293.44
Matrix: 2.0000 0.0000 1.0000 0.0000 0.0000 -1.0000 0.0000 1.0000 0.0000

Option D: FOM = 0.183 deg. MONOCLINIC C-lattice R(sym) = 0.203 [3255]
Cell: 13.218 29.197 8.534 90.00 90.00 89.82 Volume: 3293.44
Matrix: 0.0000 0.0000 1.0000 2.0000 0.0000 1.0000 0.0000 1.0000 0.0000

Current cell not changed

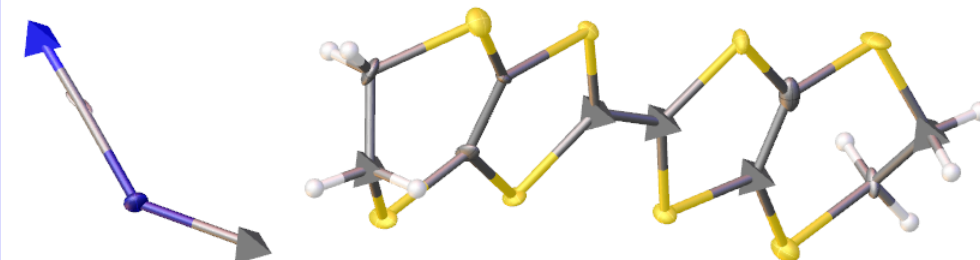
Final choice

Fig 6: Possible space groups obtained from .prp file

Relatively small R values for other possibilities

Olex2

File Edit View Structure Mode Tools Model Select Help



Deepest hole -2.94 at 0.3811 0.5931 0.2976 [1.19 Å from S003]

Please cite: G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3–8 (Open Access) if SHELXL proves useful.

+++++
+ r2d2_0m finished at 23:47:35 Total elapsed time: 0.38 secs +
+++++

Note: Q-peaks are invisible

>>|

R2D2_0m $P2_1/c$
C:\Users\briffen\Documents\teach\W...W21\Twinning\R2D2\test\R2D2_0m.res

$C_{23}H_{16}Cu_2N_3S_{16}$

a = 16.006(3)	$\alpha = 90^\circ$	Z = 2		R_1	21.95 %
b = 8.5336(13)	$\beta = 114.206(3)^\circ$	Z' = 0.5		wR_2	53.13 %
c = 13.218(2)	$\gamma = 90^\circ$	V = 1646.7(5)			

d min (Mo)	0.80	I/e(I)	42.2	Rint	3.48%	Full 50.5°	99.5
Shift	-0.308	Max Peak	4.0	Min Peak	-2.9	Goof	1.191

Warning: 0 atoms may be split and 8 atoms NPD

Home Work View Tools Info

Solve Refine Draw Report

Program XL L.S. Cycles 4 Peaks 2

hkl file R2D2_0m.hkl hkl : Sat Aug 7 16:09:46 2021

Weight ☒ .047 1.039 630 1628 EXTI ☐

☐ Use Solvent Mask This is the Olex2 implementation of BYPASS (a.k.a. SQUEEZE)

Refinement Settings Extra

Toolbox Work

Labels Labels OFF/ON

C H Cu N S ... ☒ Add H

Z' = 0.5 ☒

Select atom(s) and then

MAP

Peak & Uiso Sliders

Growing

Finishing

History

Select

Naming

Cartoon

P.L.A.T.O.N.

TwinRotMat

Analysis of Fo/Fc Data for Unaccounted (Non)Merohedral Twinning for: r2d2_0

Cell: 0.71073 16.006 8.534 13.218 90.00 114.21 90.00 Spgr: P21/c

Criteria: DeltaI/SigmaI .GT. 4.0, DeltaTheta 0.10 Deg., NselMin = 50

N(refl) = 3368, N(selected) = 50, IndMax = 5, CrItI = 0.1, CrItT = 0.10

PLATON-ay, 8 August 2021 - (60516)

Fc from Coordinates

2-axls (1 0 0) [2 0 1], Angle () [] = 0.18 Deg. Freq = 53

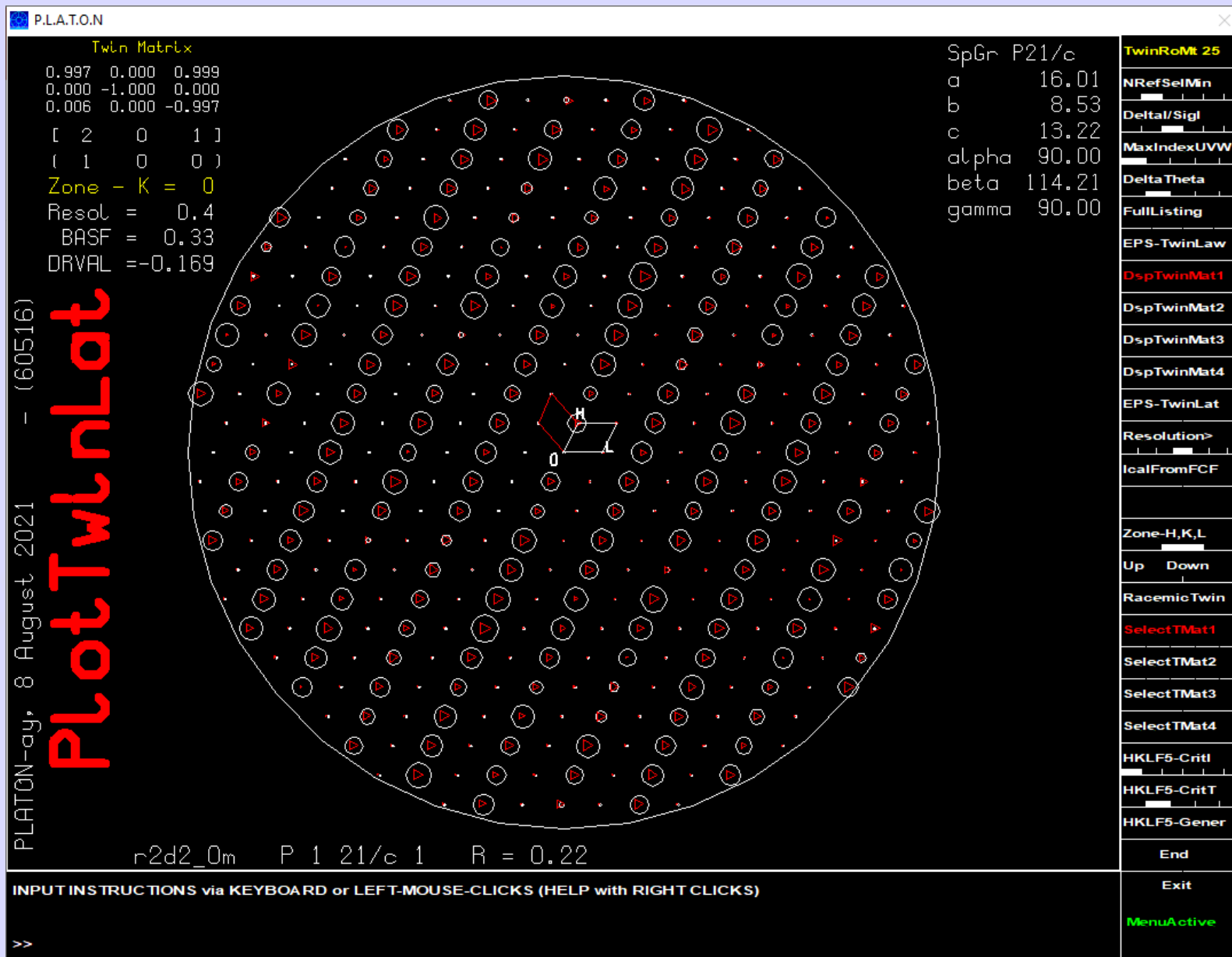
(0.997 0.000 0.999) (h1) (h2) Nr Overlap = 3332
(0.000 -1.000 0.000) * (k1) = (k2) BASF = 0.33
(0.006 0.000 -0.997) (l1) (l2) DEL-R = -0.169

1

r2d2_0m P 1 21/c 1 R = 0.22

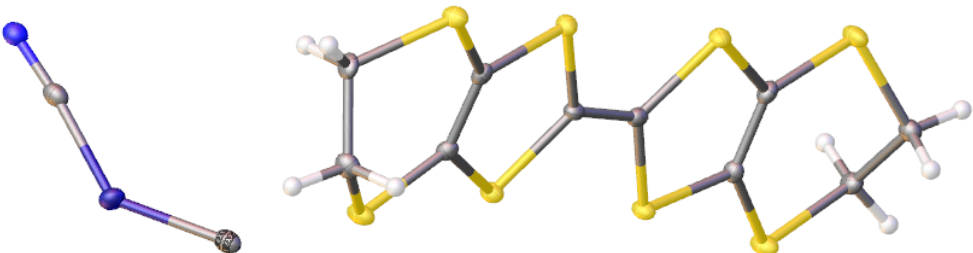
INPUT INSTRUCTIONS via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)

TwinRoMt 25
NRefSelMin
Delta/Sigl
MaxIndexUVW
Delta Theta
FullListing
EPS-TwinLaw
DspTwinMat1
DspTwinMat2
DspTwinMat3
DspTwinMat4
EPS-TwinLat
Resolution>
IcalFromFCF
Zone-H,K,L
Up Down
RacemicTwin
SelectTMat1
SelectTMat2
SelectTMat3
SelectTMat4
HKLF5-CritI
HKLF5-CritT
HKLF5-Gener
End
Exit
MenuActive



Olex2

File Edit View Structure Mode Tools Model Select Help




Highest peak 0.45 at 0.0002 0.8944 0.5820 [0.84 Å from C00A]
 Deepest hole -0.54 at 0.0035 0.1588 0.3785 [0.47 Å from CU01]

Please cite: G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3–8 (Open Access) if SHELXL proves useful.

```

+++++
+ r2d2_0m finished at 23:43:43 Total elapsed time: 0.44 secs +
+++++
  
```

R2D2 0m *P2₁/c*
 C:\Users\brtten\Documents\teach\W...W21\Twinning\R2D2\test\R2D2_0m.res
C₂₂H₁₆Cu₂N₄S₁₆

a = 16.006(3)	α = 90°	Z = 2		R ₁	2.71 %
b = 8.5336(13)	β = 114.206(3)°	Z' = 0.5		wR ₂	6.10 %
c = 13.218(2)	γ = 90°	V = 1646.7(5)			



d min (Mo)	0.80	I/σ(I)	42.2	Rint	3.48%	Full 50.5°	99.5
Shift	-0.001	Max Peak	0.5	Min Peak	-0.5	Goof	1.191








TWIN LAW (1.0, 0.0, 1.0, 0.0, -1.0, 0.0, 0.0, 0.0, -1.0), BASF [0.3341(8)]
 Cell contents from UNIT instruction and atom list do not agree

Home Work View Tools Info
 Solve Refine Draw Report

Toolbox Work

Labels Labels OFF/ON

C H Cu N S ... ☒ Add H  

      Z' = 0.5 

Select atom(s) and then mFit mSplit Split SAME SHIFT+Move

MAP Show Map Map Settings

Peak & Uiso Sliders

Growing

Finishing

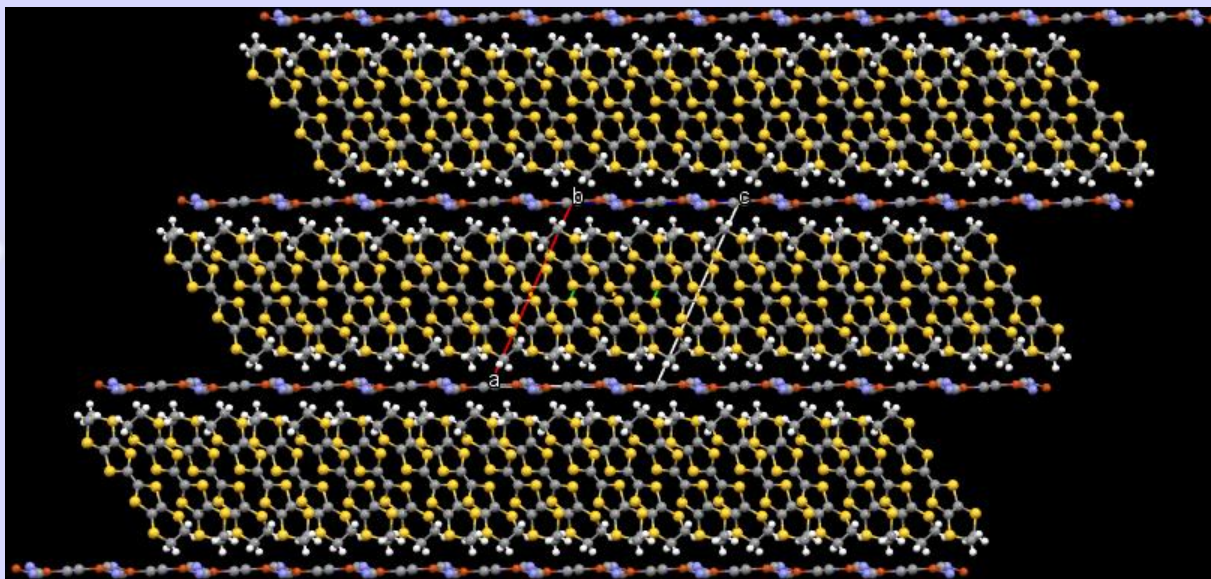
History

Select

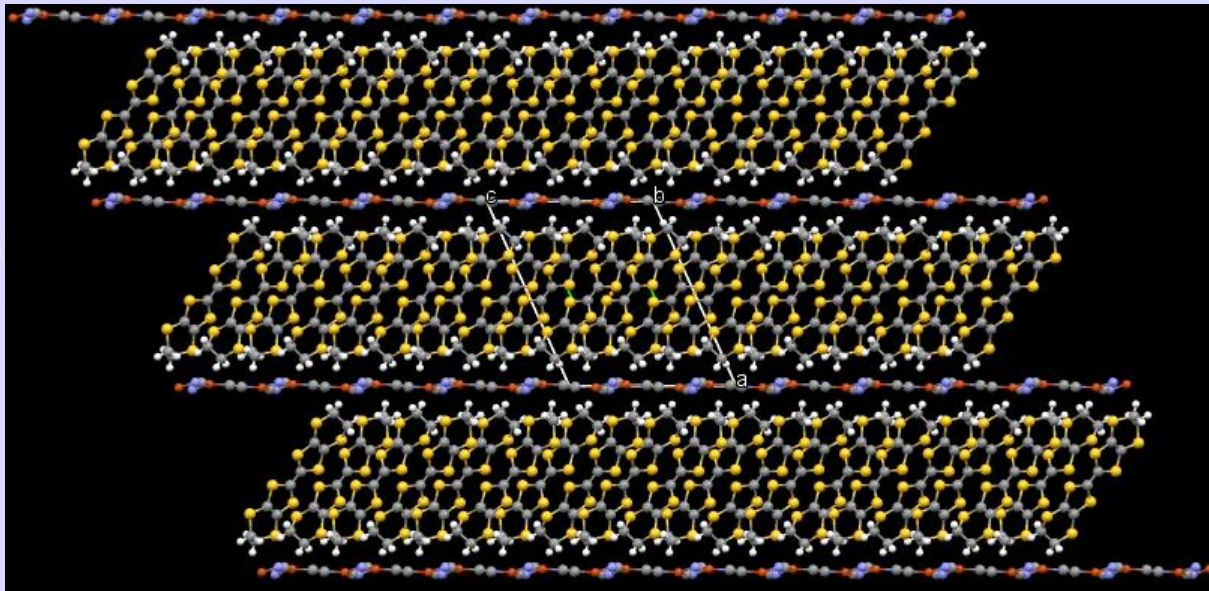
Naming

Sorting

Packing in Dalini's crystal



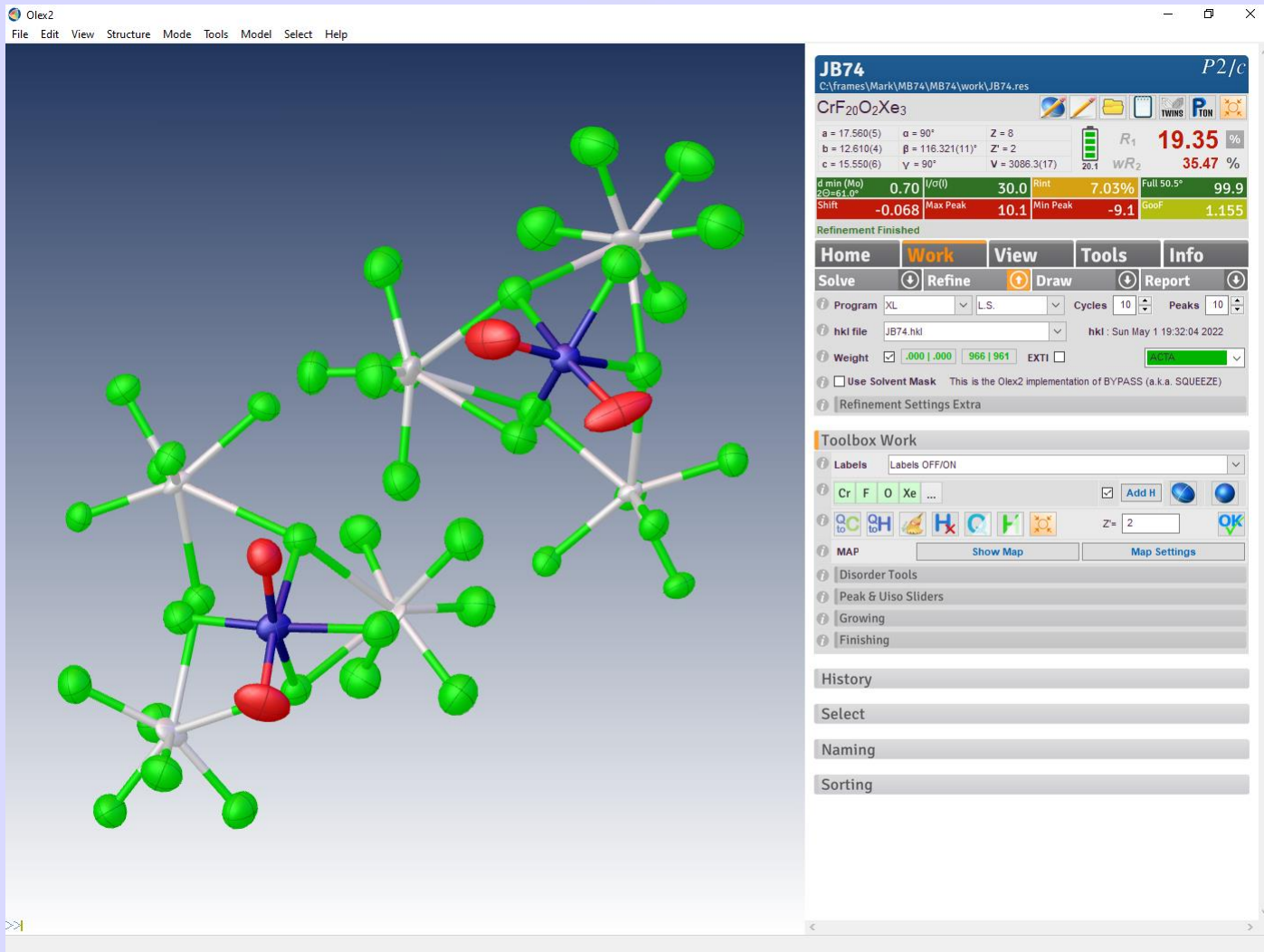
Crystal rotated 180° around a^*



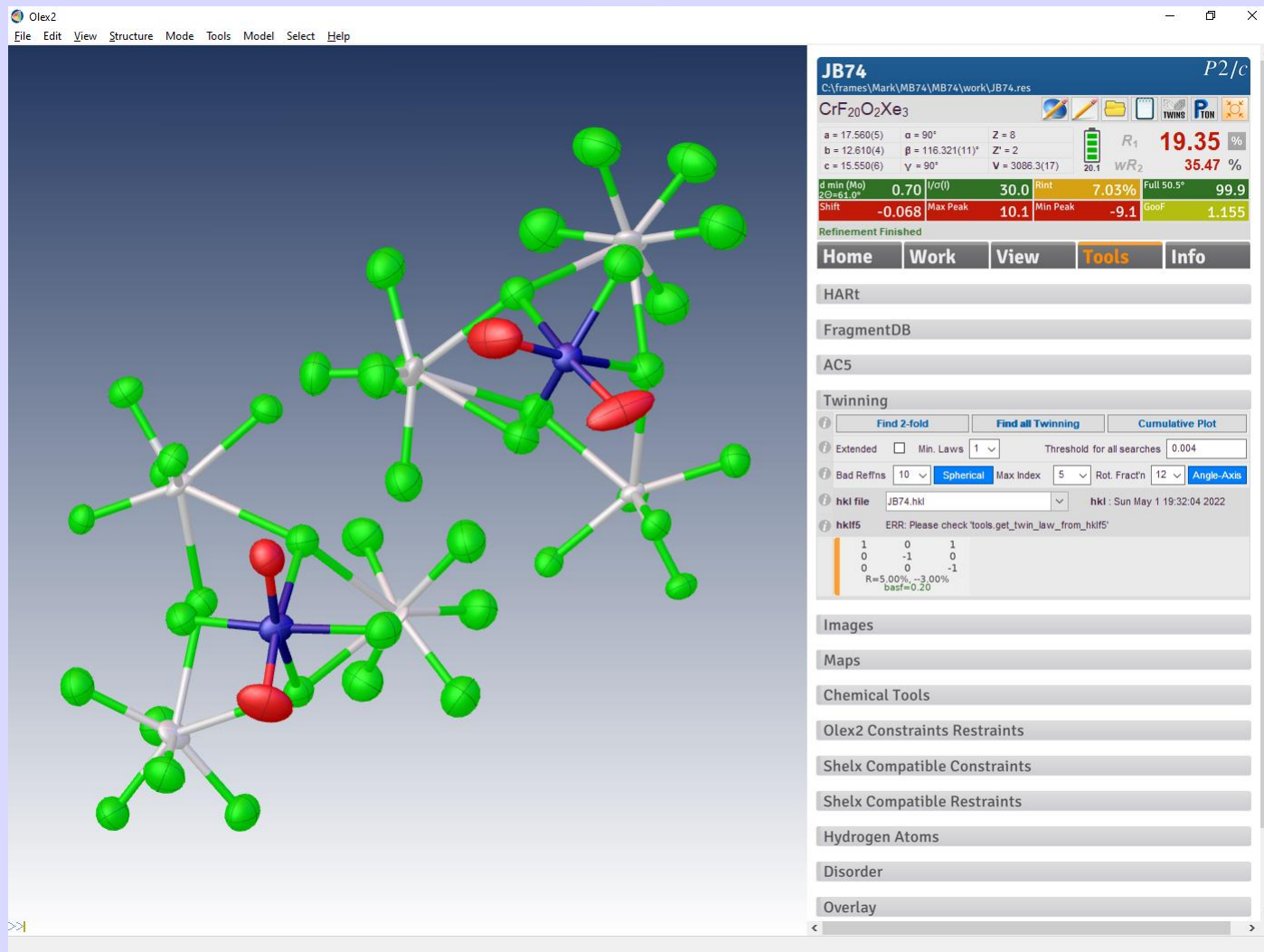
Twinned growth



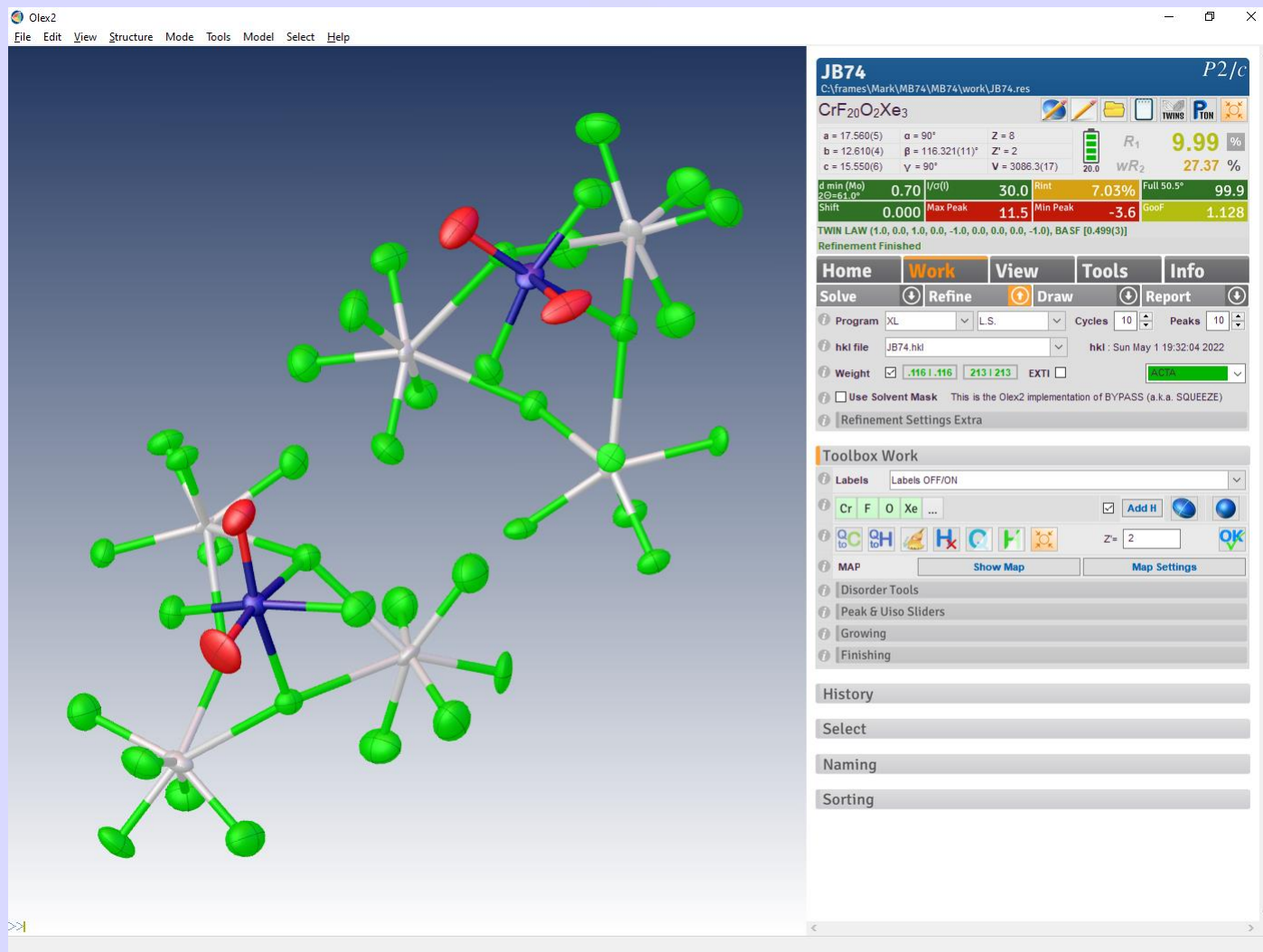
CrF₂₀O₂Xe₃ – Schrobilgen, Bortolus



$\text{CrF}_{20}\text{O}_2\text{Xe}_3$ – Schrobilgen, Bortolus



TWIN 1 0 1 0 -1 0 0 0 -1 2

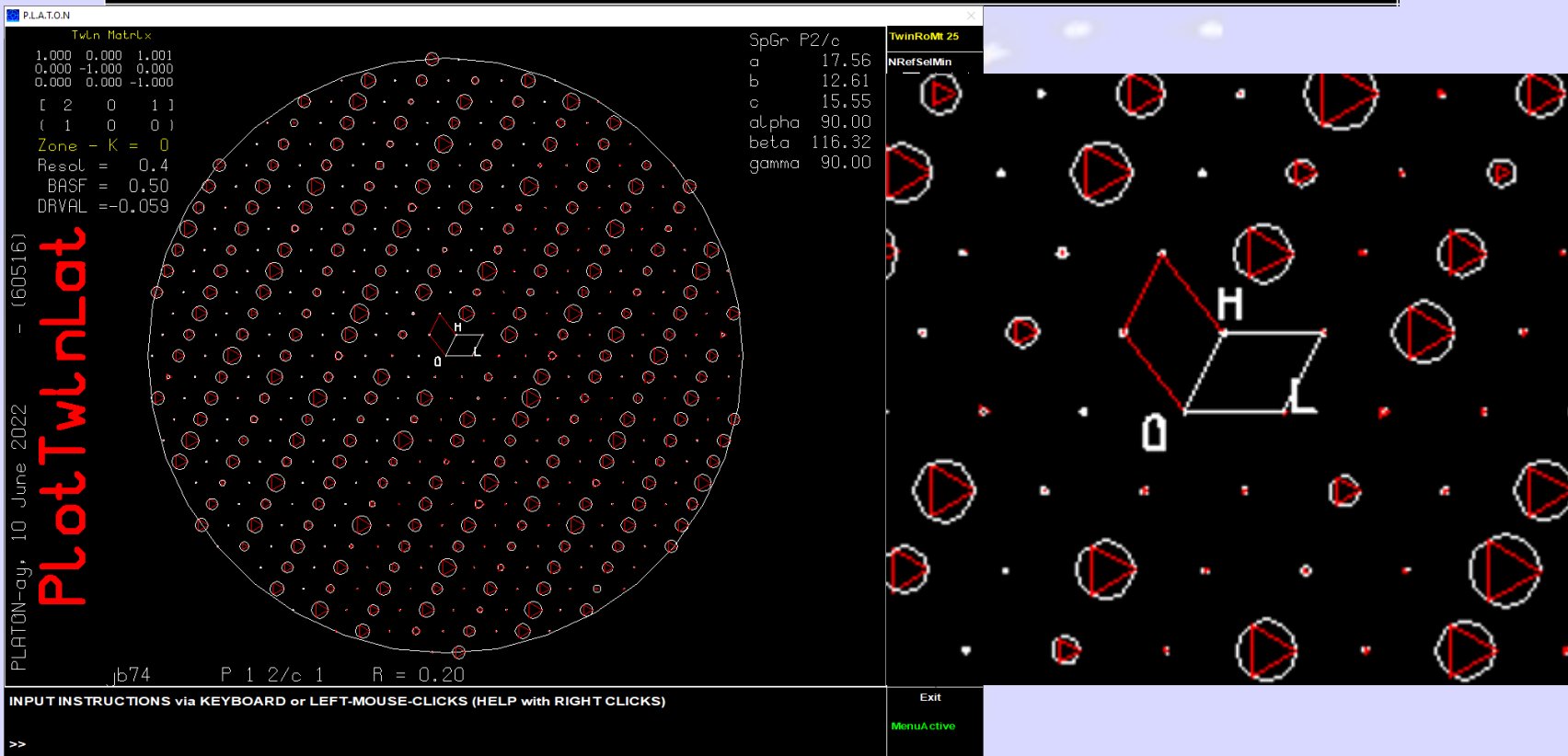


TwinRotMat

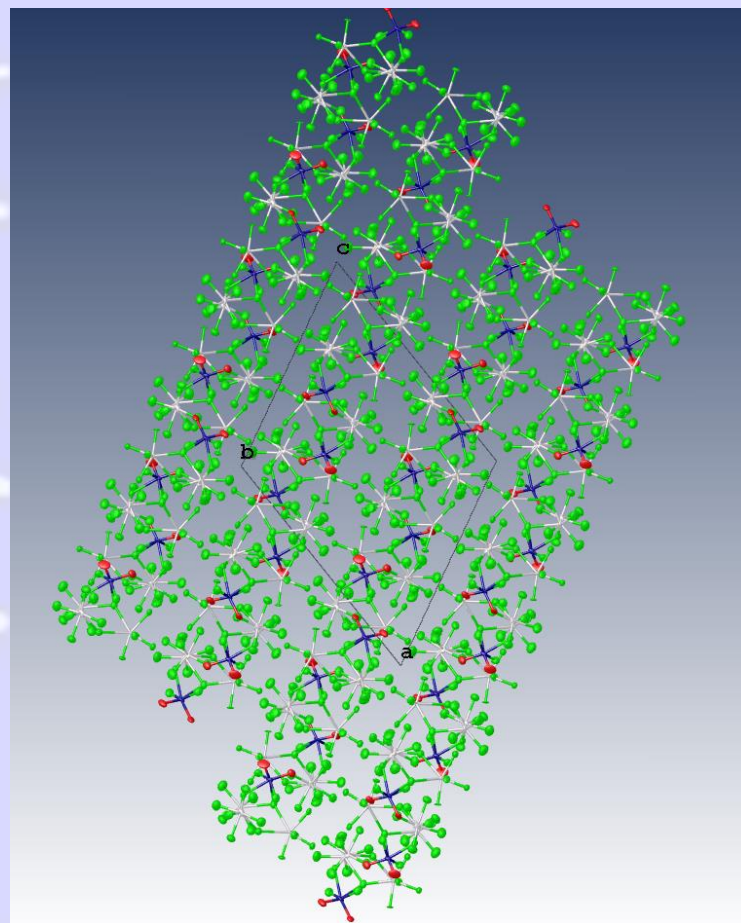
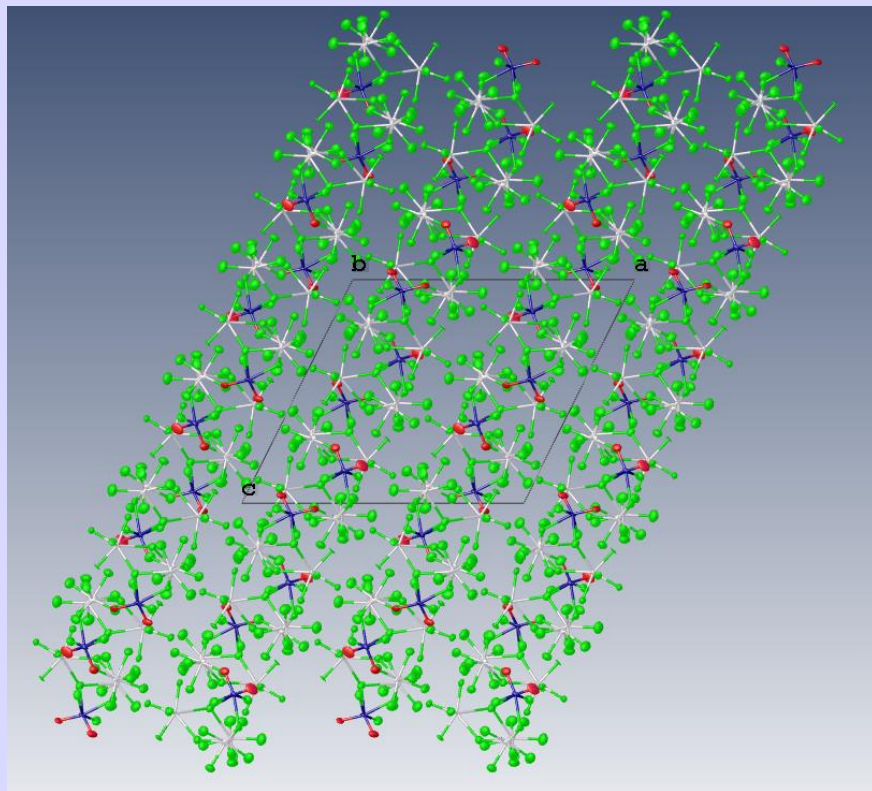
```

2-axls ( 1 0 0 ) [ 2 0 1 ], Angle ( ) [ ] = 0.04 Deg, Freq = 64
*****
( 1.000  0.000  1.001) (h1) (h2)
( 0.000 -1.000  0.000) * (k1) = (k2)
( 0.000  0.000 -1.000) (l1) (l2)

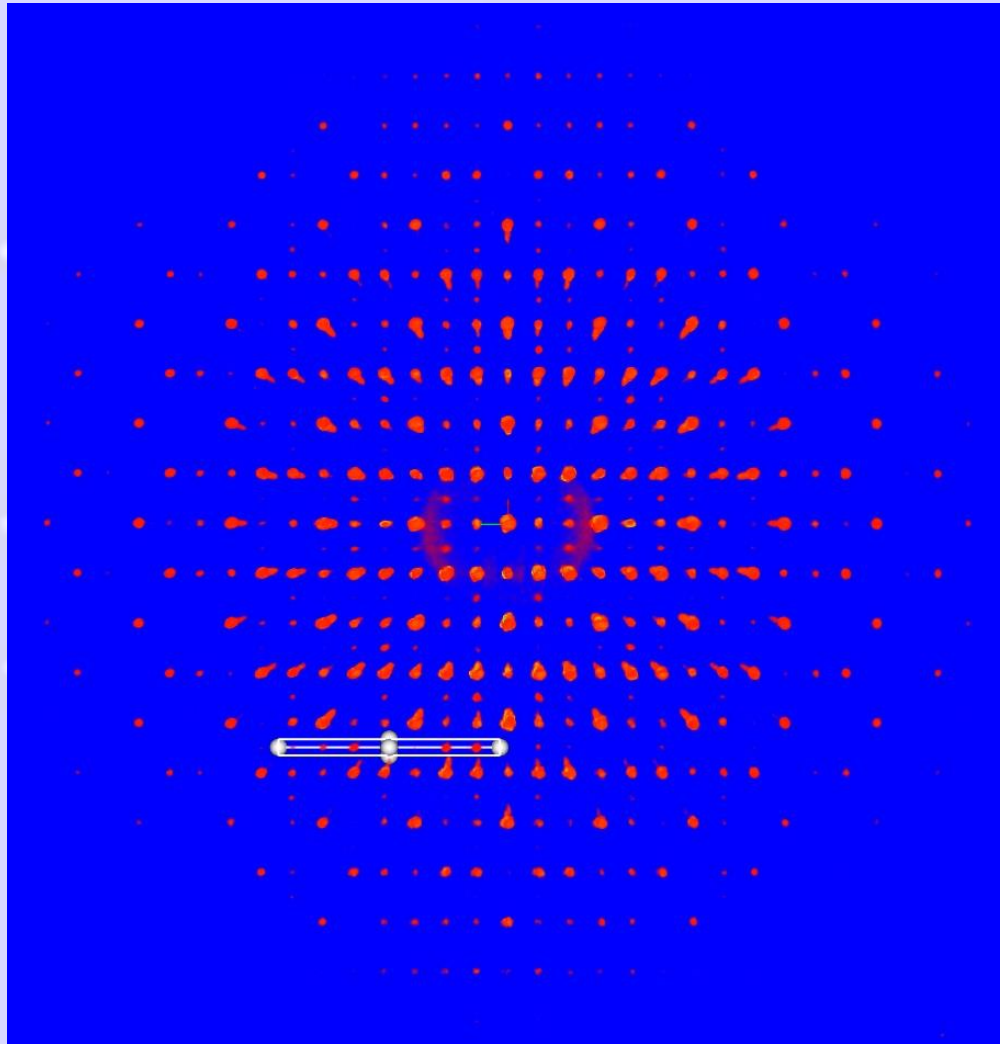
Nr Overlap = 9408
BASF = 0.50
DEL-R = -0.059
    
```



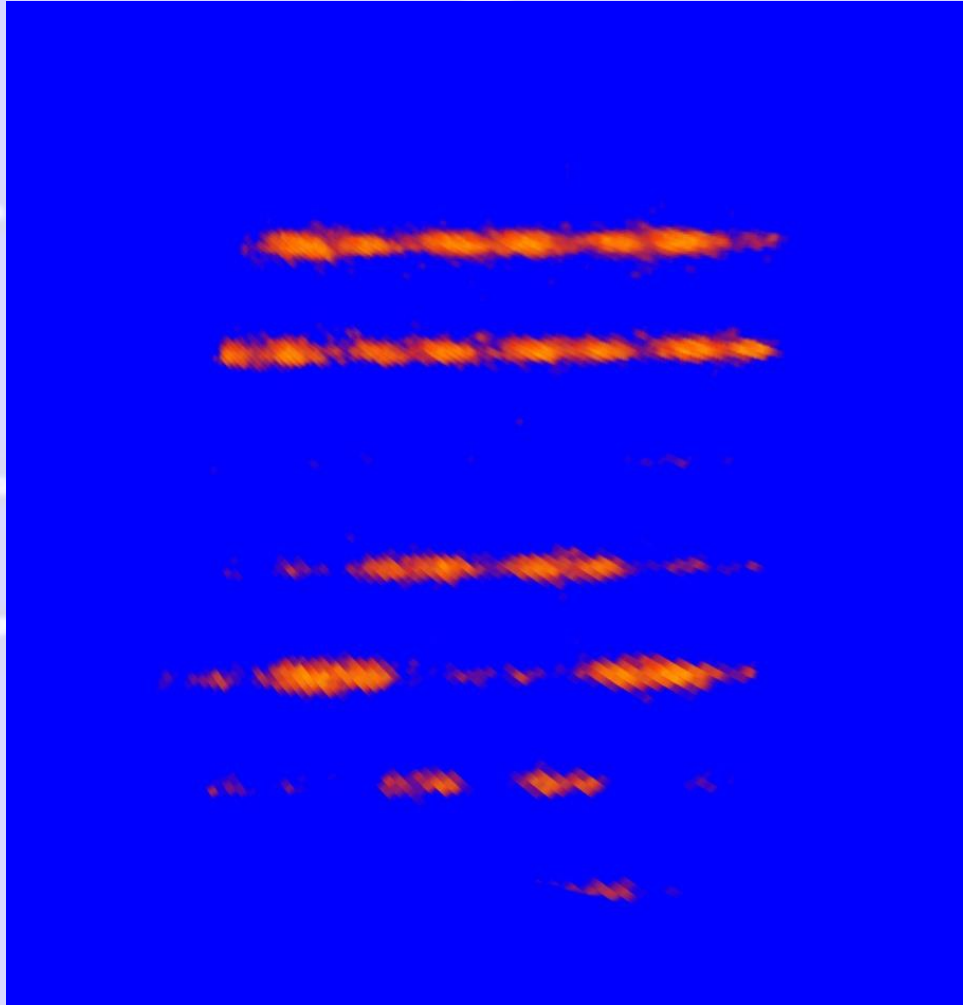
Flip around body diagonal



Strong and weak layer in RS



Diffuse scattering, loss of order in 1D



Twinning that isn't twinning

There is no twin operator, but there are 2 or more crystal orientations. The components are not related by any mathematical rule or twin law.

Cracked crystal. Random angle between orientations.

Growth of thin plate on a thin plate. Random angle between orientations.

Two different crystals stuck to each other. Different cells and space groups. Different compounds.

We can use the same software packages to clean up the mess.

Thanks to Regine Herbst-Irmer and . . .



SHELX-Workshop



Montreal, August 5th, 2014

Twinning

rherbst@shelx.uni-ac.gwdg.de

<http://shelx.uni-ac.gwdg.de/~rherbst/twin.html>

. . . Ton Spek for teaching me about twinning.

The PLATON/TwinRotMat Tool for Twinning Detection

Ton Spek
*National Single Crystal
Service Facility,
Utrecht University,
The Netherlands.*

Delft, 29-Sept-2008



Thank You
Thank you