http://www.cryst.chem.uu.nl/lutz/twin/gen_twin.html

Twinning tools in Eval15

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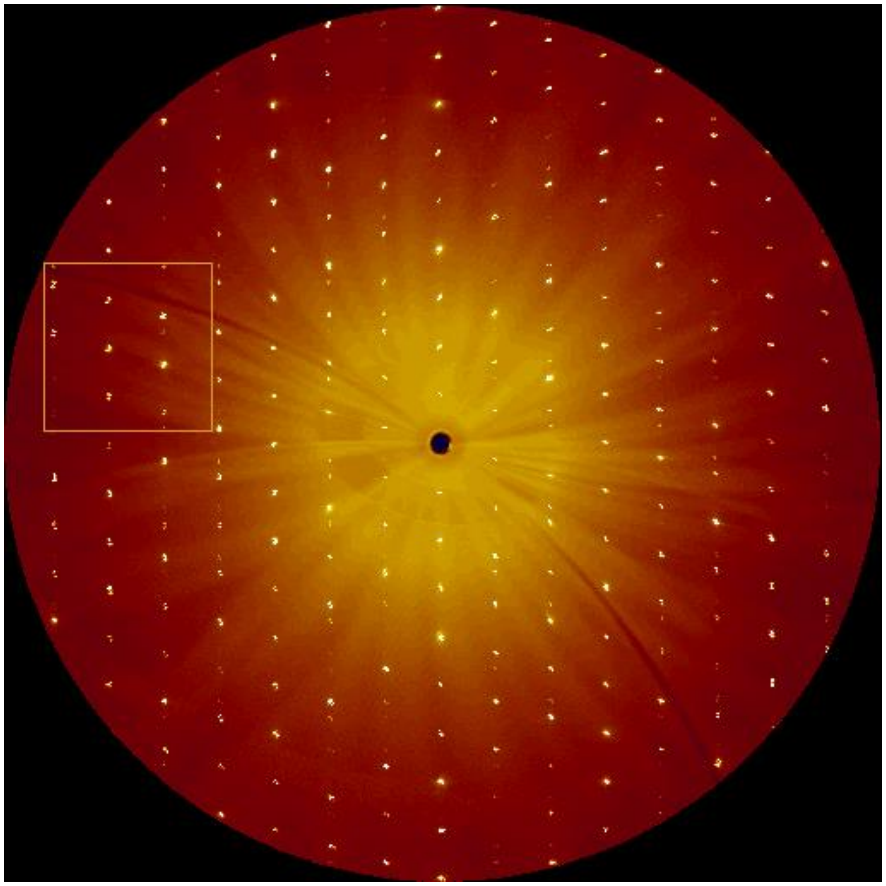
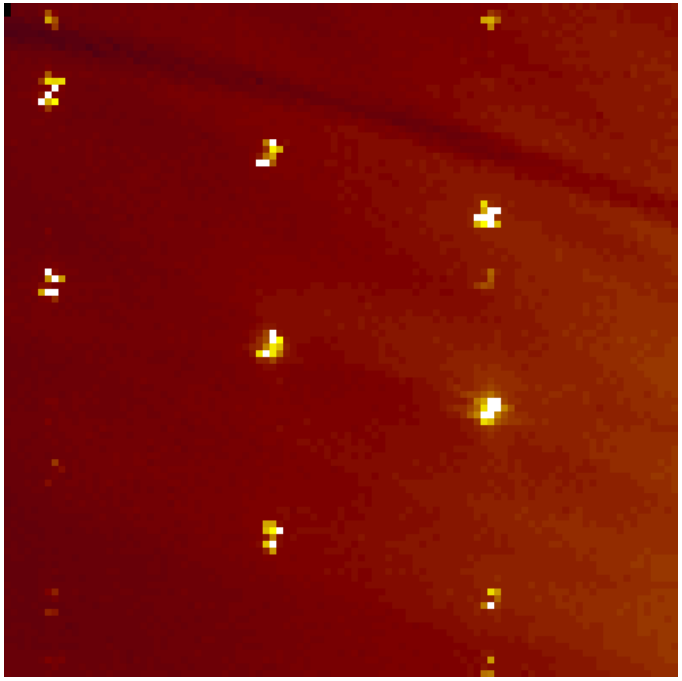
Not a Twin… (1)

Simulated precession image

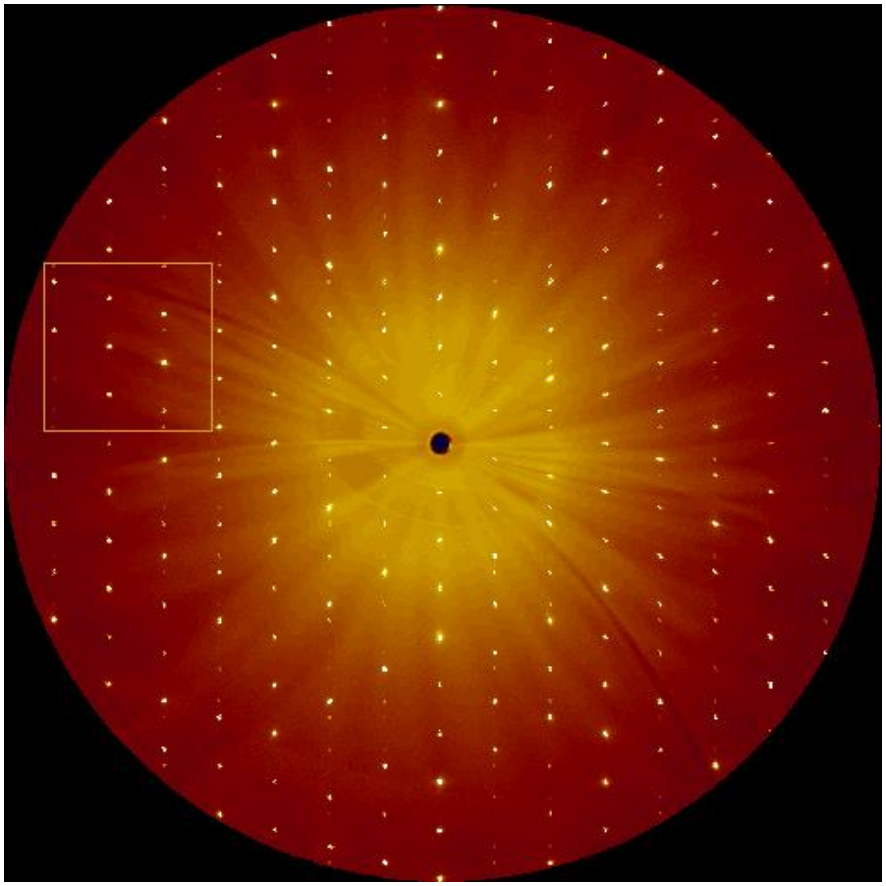


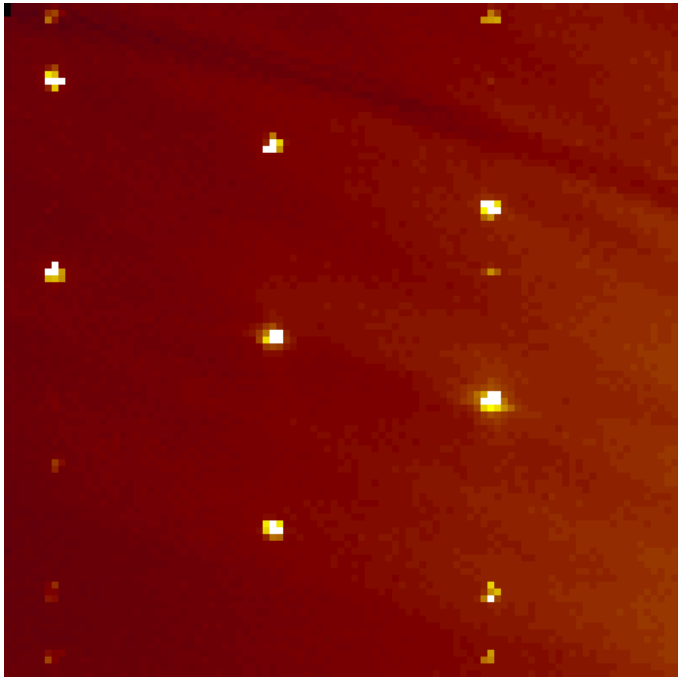


Problem and solution

- Orientation matrix in first frame differs by 1.011° from last frame. The rotation vector in the laboratory system is
  x, y, z= -0.02, -0.02, 1.00
- Solution: overrule phi increment by a factor of 1.0028.

Simulated precession image (2)





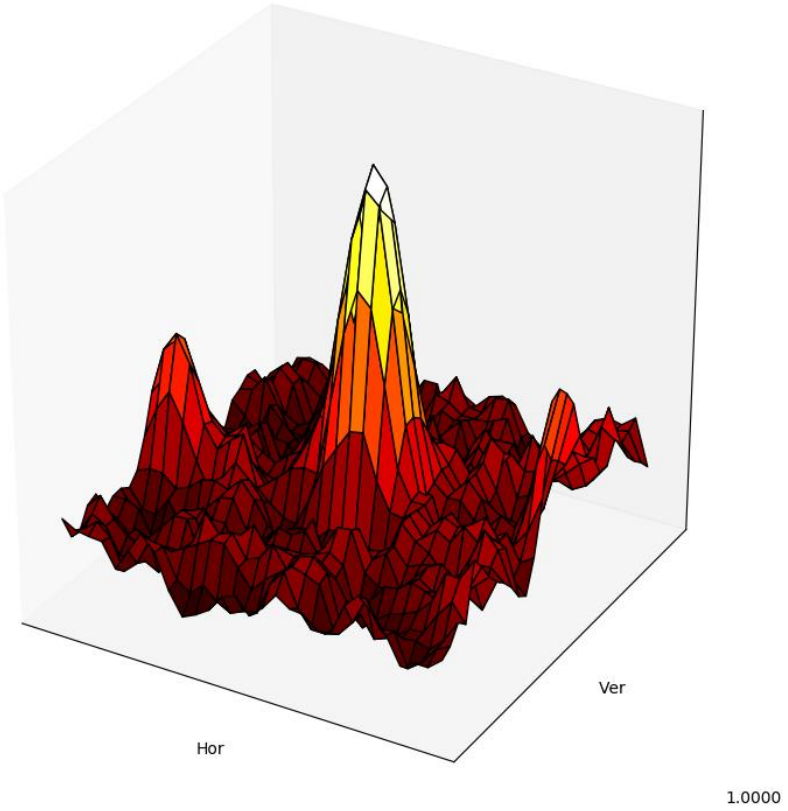
Not a Twin… (2)

“Cracked” crystal

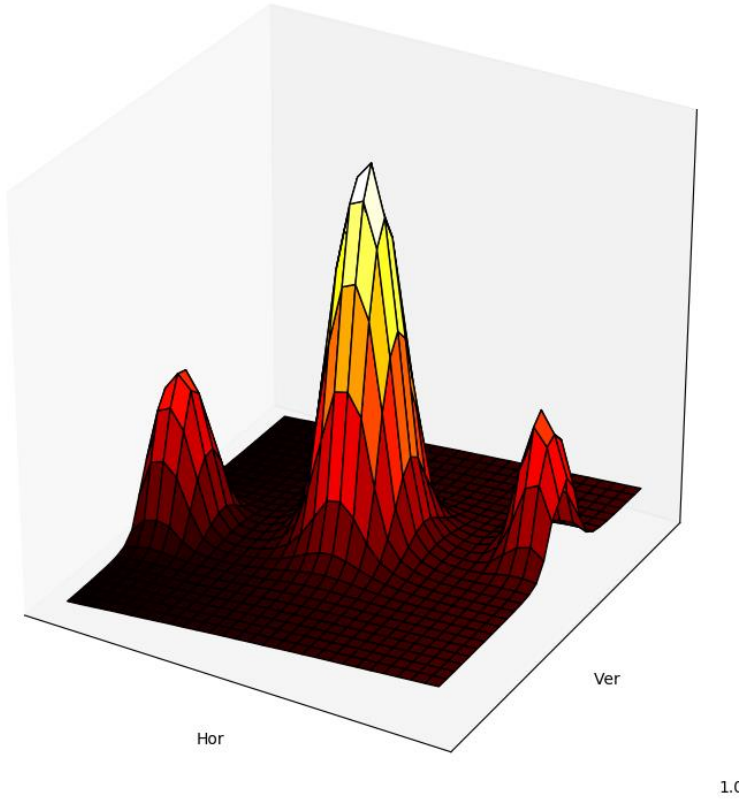
- Two crystal fragments related by a small rotation angle
- Rather common in needle/plate-shaped crystals
- Peak maxima close together

Krachko, Ehlers, Nieger, Lutz, Slootweg (2018). *Angew. Chem. Int. Ed.* **57**, 1683-1687.

refl3d

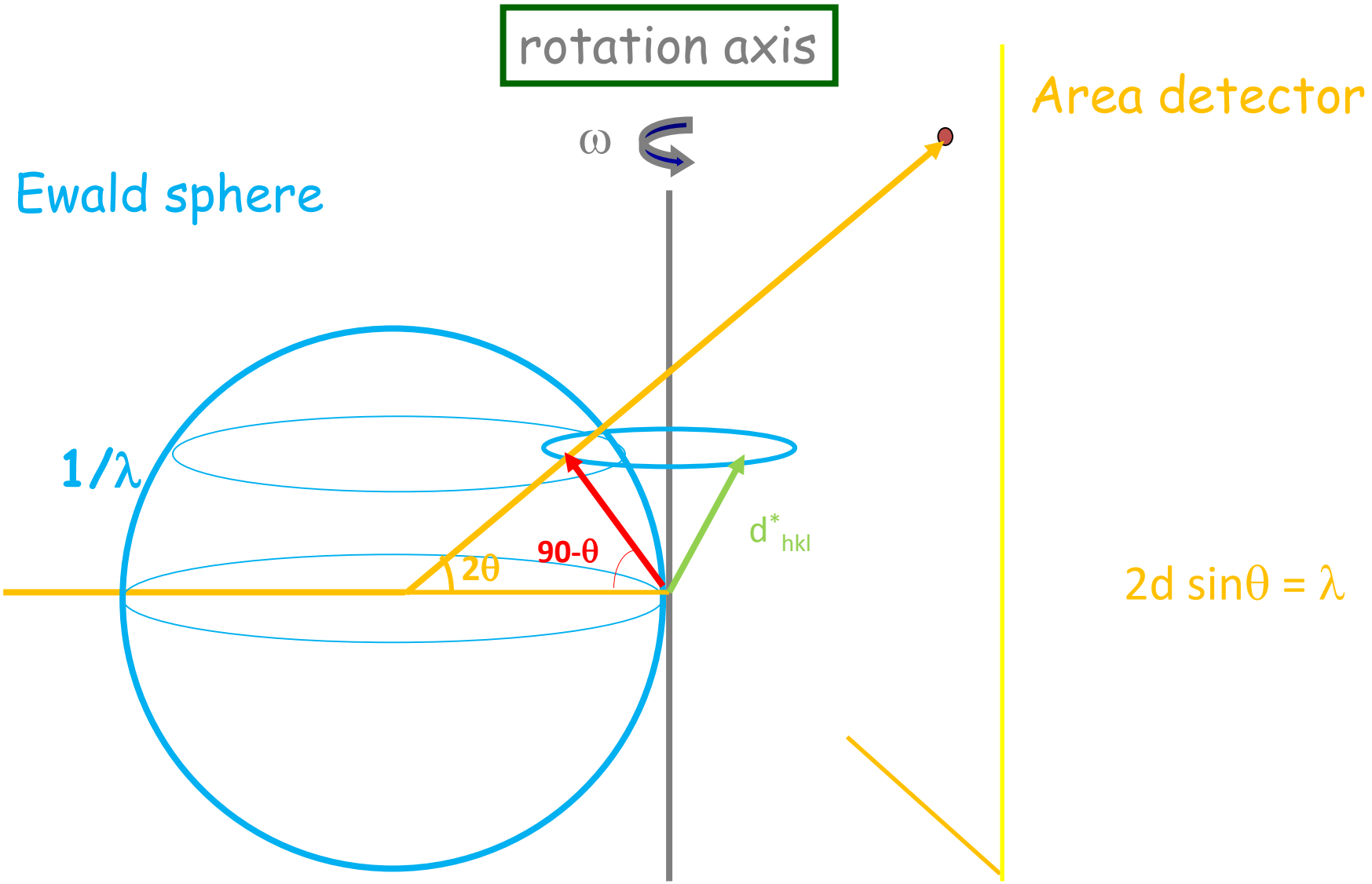


observed



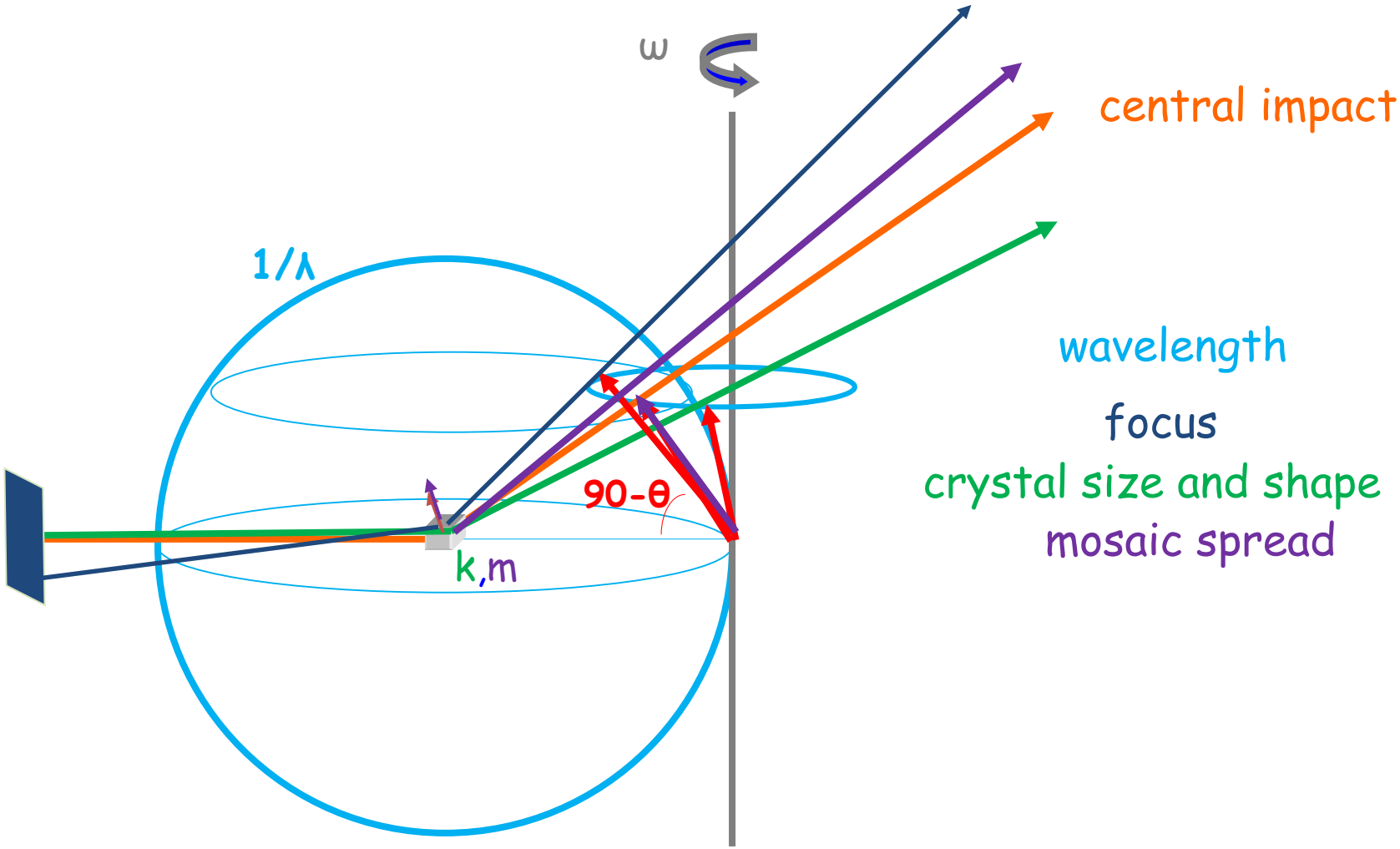
model

Diffraction geometry



General impact

ω rotation to Bragg condition at ζ: $\cos \zeta = (\sin \theta - \sin \chi_{fk})/(\cos \chi_{fk} \cos \chi)$



Least squares (SVD)

$$\chi^2 = \sum_{i=1}^{N} w_i \left[\rho_i - JP_i - \sum_{m}^{M} J_m P_{im} - ax_i - by_i - c \right]^2$$

$$I = J \sum_{i=1}^{N} P_i \qquad \sigma_i = \sqrt{\rho_i + bgnoise^2} \qquad w_i = \frac{1}{\sigma_i^2}$$

Standard deviation of integrated reflection

$$\sigma_I^2 = \sigma_J^2 \left(\sum_{i=1}^{N} P_i \right)^2$$

$$fom_{box} = \left[\frac{\sum_{i=1}^{N} w_i (\rho_i - \rho_i^{calc})^2}{N - N_p} \right]^{1/2}$$

Variances and co-variances available

Overlap fraction

- For the integration with EVAL15, the parameter *nbcommonfraction* was set to 0.2
- If the number of pixels shared by main and interfering reflection is smaller than $0.2*Npix_{main}$, the reflections are split

Covariance

- For the integration with EVAL15, the parameter *nbcovariance* was set to 0.05
- If |Covariance| is smaller than $0.05*\text{Variance}_{\text{Main}}$, the reflections are split

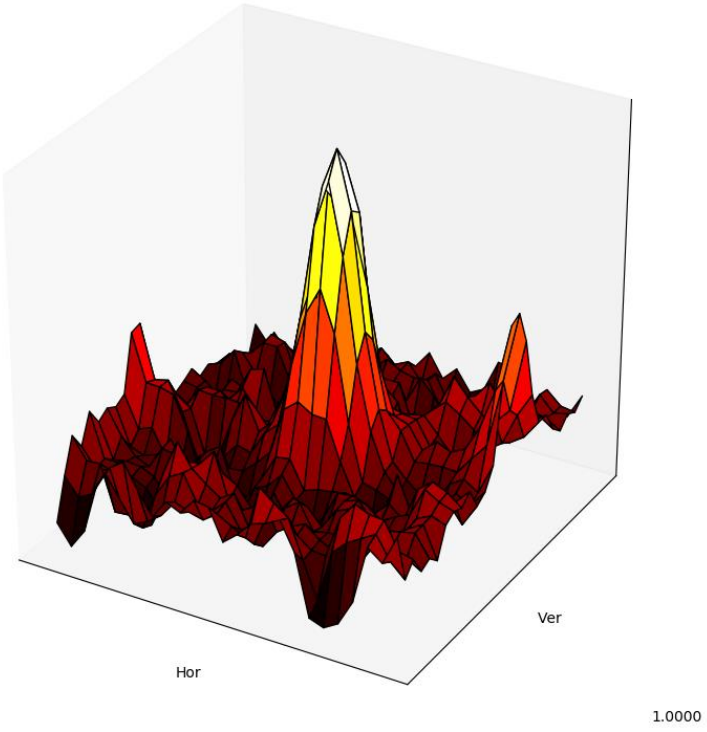
Result

- Eval15 integration with two orientation matrices
- Rotation of 1.53° with respect to each other
- Absorption correction and scaling with TWINABS (G. Sheldrick, Göttingen University)
- HKLF5 refinement
- R1= 0.0533, wR2=0.1506

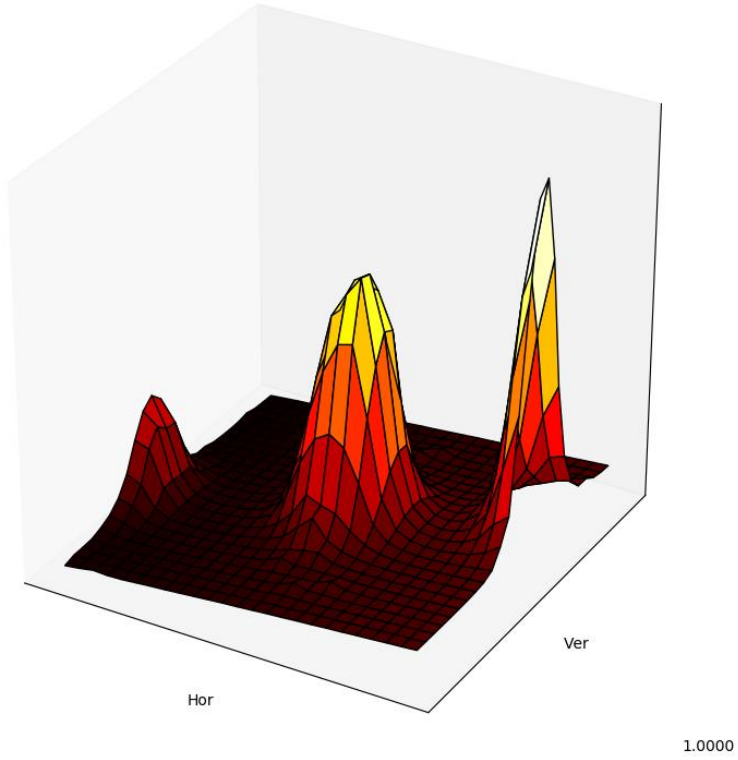
“Split mosaic” model

- In Eval15 the mosaicity is a distribution (lorentzian, gaussian or block distribution)
- The distribution can be isotropic or anisotropic
- It can also be a convolution of more than one distributions (“split mosaic”)
- Advantage: result is HKLF4 file
- Disadvantage: parametrization in Eval15 can be challenging

refl3d



observed



model

Comparison

- “Twin” integration:
  R1= 0.0533, wR2=0.1506
- “Split mosaic” model:
  R1= 0.0470, wR2=0.1246

Not a Twin… (3)

Two polymorphs in one crystal

- Component 1: triclinic (space group P-1)
  a=14.9515(9), b=12.2358(9), c=19.9234(11) Å
  α=104.710(2), β=110.223(3), γ=96.656(1) °
  V=3223.7(4) Å^3
- Component 2: monoclinic (space group P2$_1$/c)
  a=14.9737(7), b=22.9567(10), c=19.9168(8) Å
  α=90, β=110.001(2), γ=90 °; V=6433.4(5) Å^3

Filonenko, Conley, Copéret, Lutz, Hensen, Pidko (2013). *ACS Catal.* **3**, 2522-2526.

Dirax

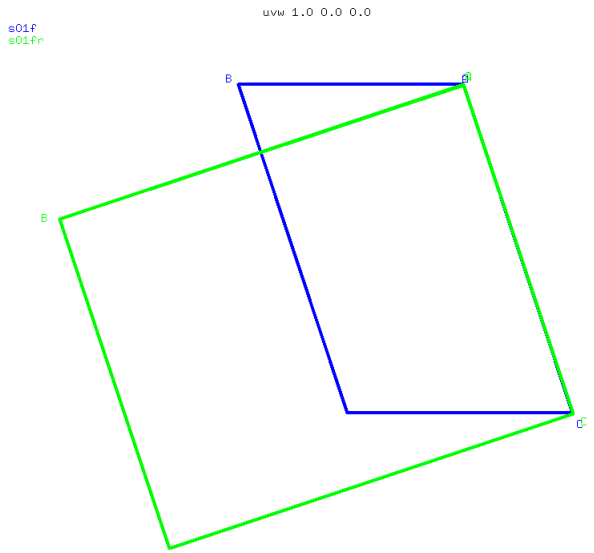
- The program *dirax* finds the triclinic cell directly.

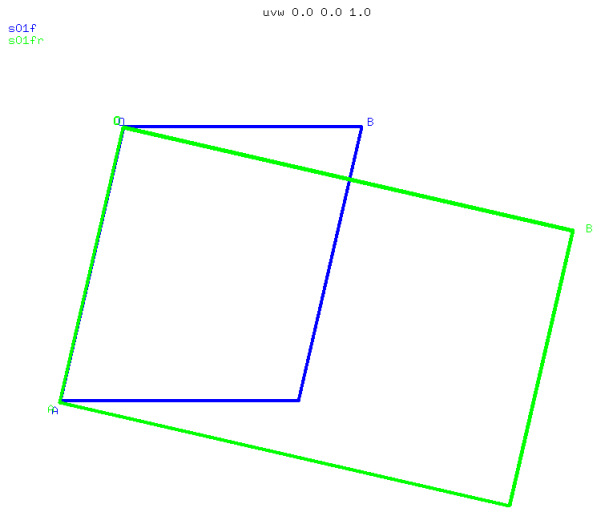
Duisenberg (1992). *J. Appl. Cryst.* **25**, 92-96.

Search “rest” peaks

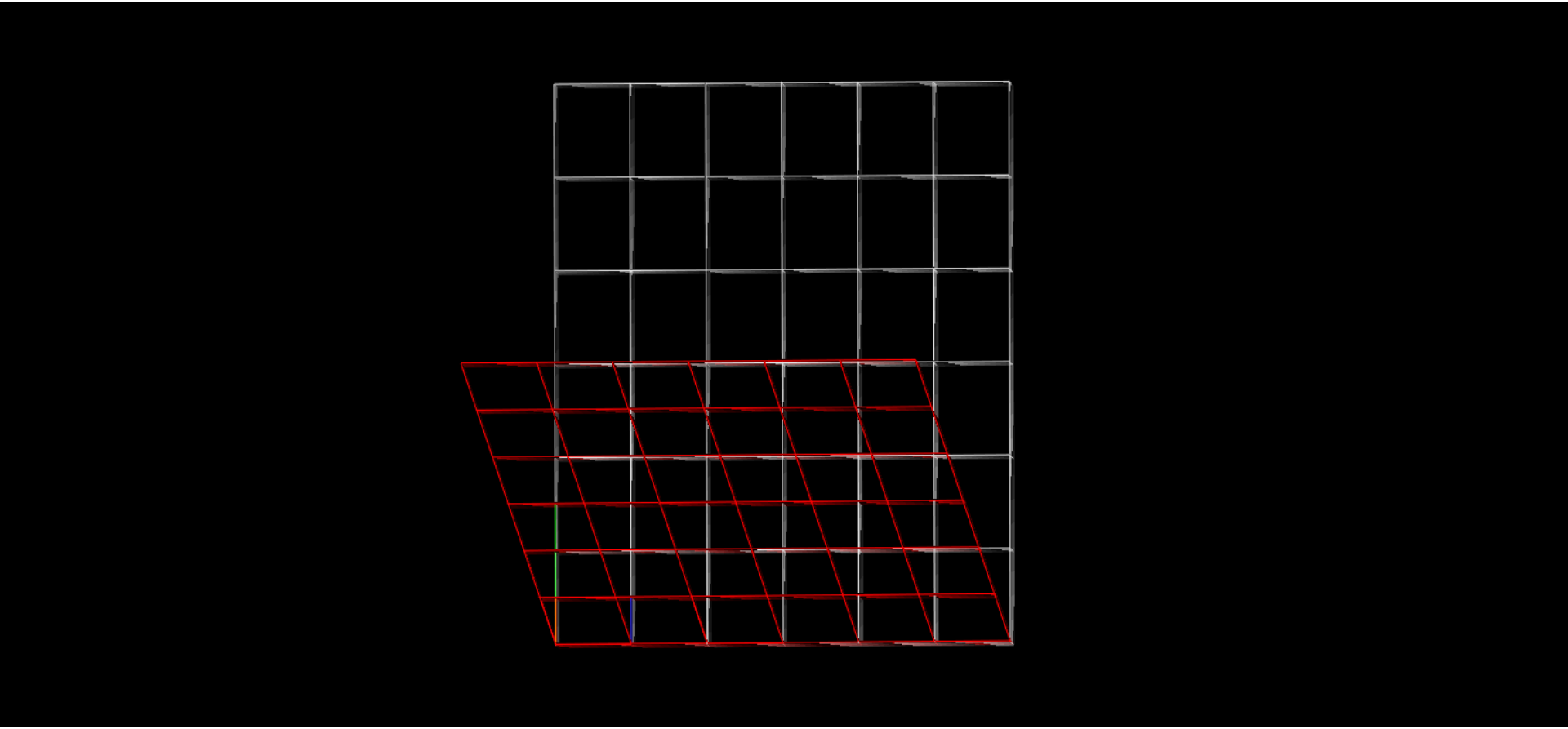
- Search peaks that are not predicted by the first unit cell.
- The program *dirax* finds the second unit cell directly.

cellplot





rmat2pdb



Display using the program *pymol*

Structure analysis

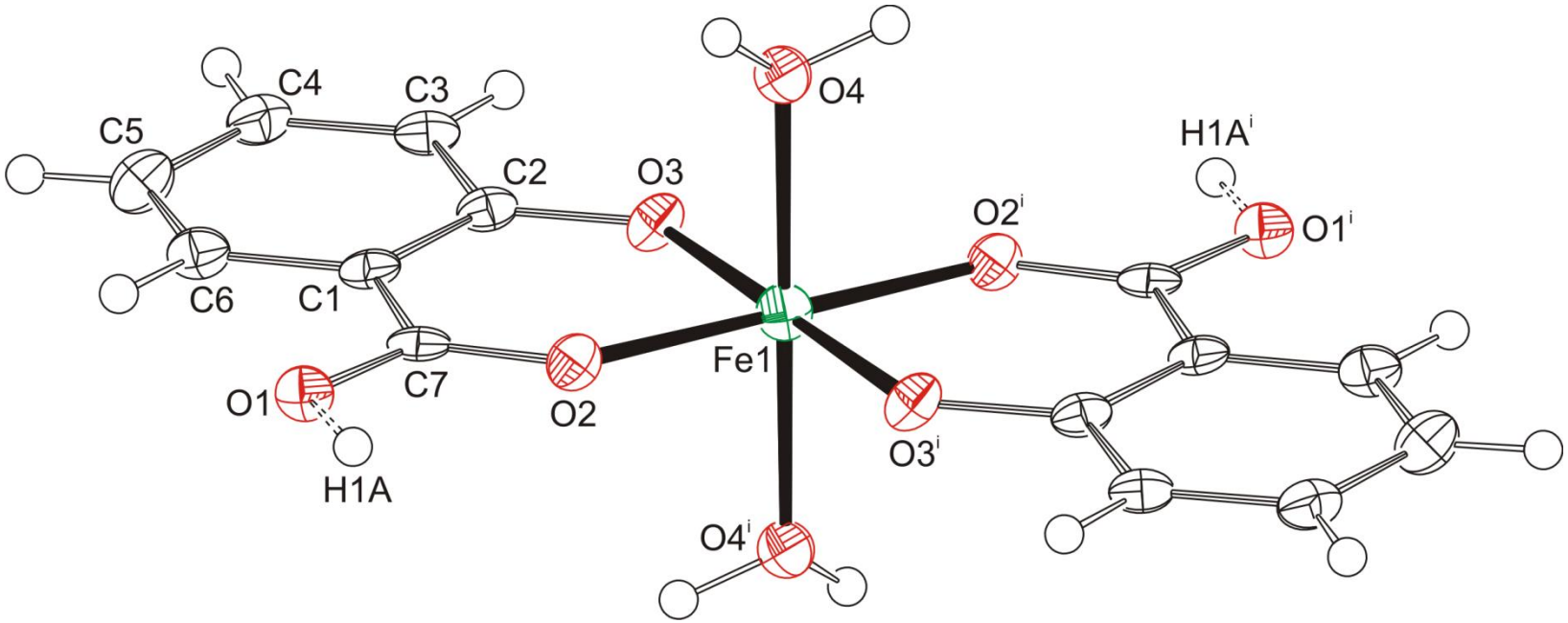
- Perform “twin” integration with Eval15.
- Structure solution and refinement based on non-overlapping reflections.
- Calculate structure factors with PLATON.
- “De-twin” observed data based on calculated structure factors. (Small self-written program).
- Final refinements on “de-twinned” data.

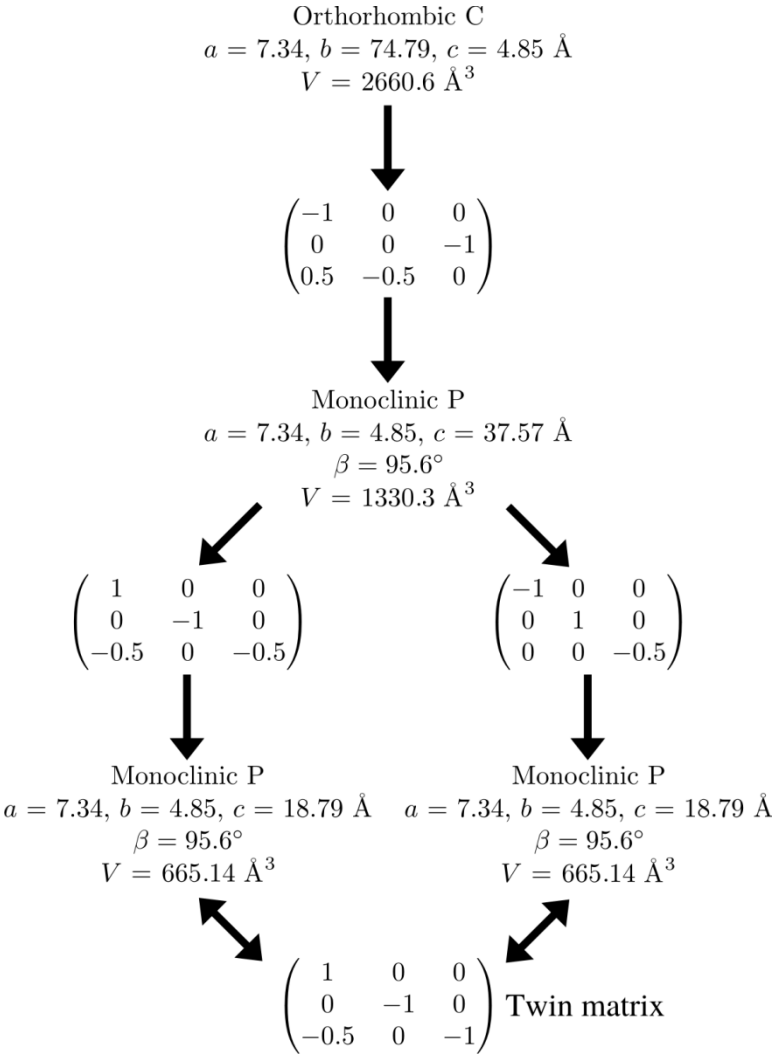
Results

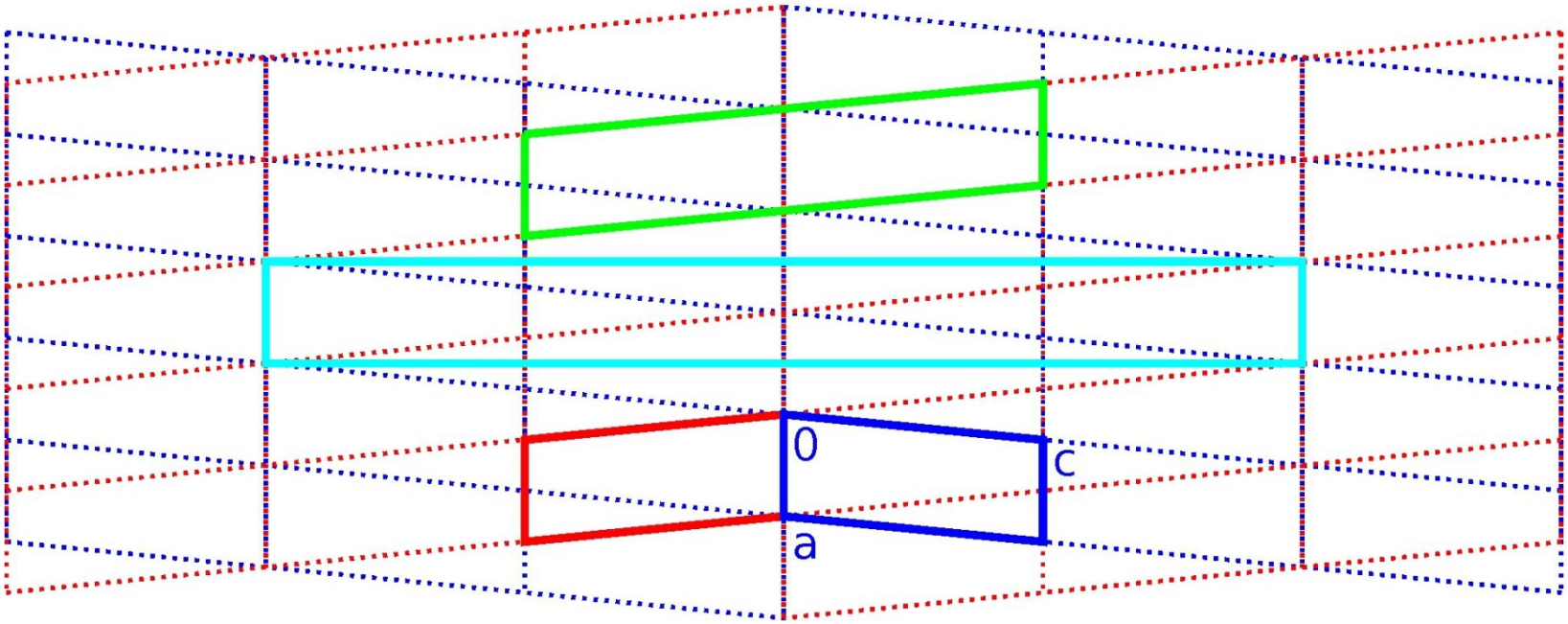
- Component 1: R1=0.0345, wR2=0.0914
- Component 2: R1=0.0429, wR2=0.1277

Reticular twinning in Iron(III) Salicylate

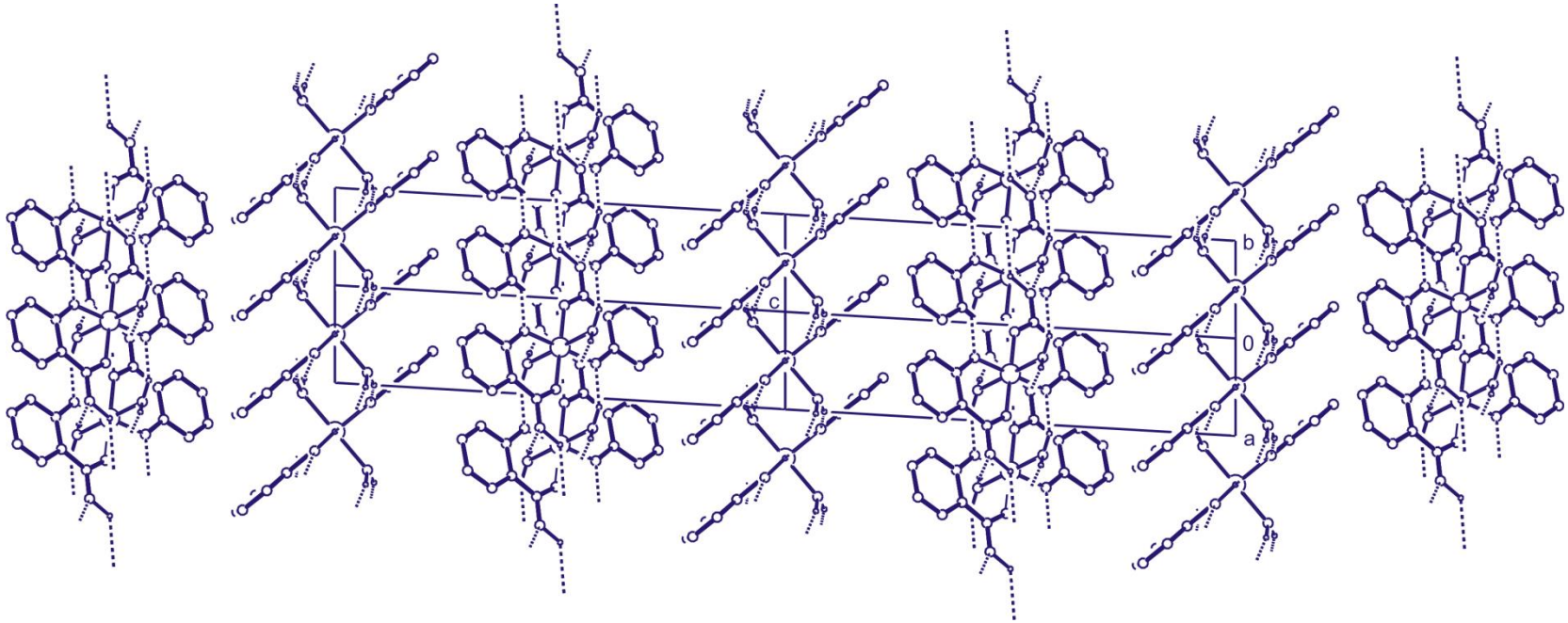
van der Horn, Souvignier, Lutz (2018). *Crystals* **7**, 377.


C4
C3
C5
C2
O3
O4
H1A^{i}
O2^{i}
O1^{i}
C6
C1
C7
Fe1
O1
O2
O3^{i}
H1A
O4^{i}

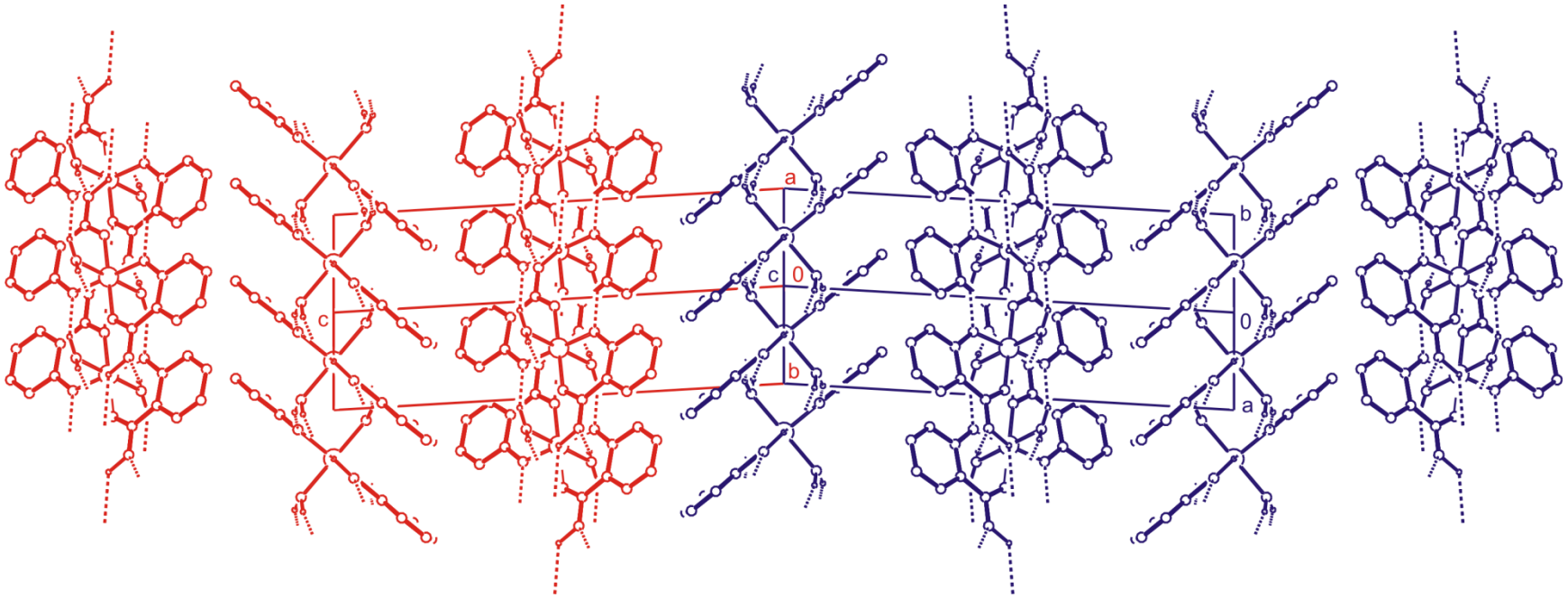

Orthorhombic C
$a = 7.34$, $b = 74.79$, $c = 4.85$ Å
$V = 2660.6$ Å^3
$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0.5 & -0.5 & 0 \end{pmatrix}$
Monoclinic P
$a = 7.34$, $b = 4.85$, $c = 37.57$ Å
$\beta = 95.6°$
$V = 1330.3$ Å^3
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -0.5 & 0 & -0.5 \end{pmatrix}$
$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -0.5 \end{pmatrix}$
Monoclinic P
$a = 7.34$, $b = 4.85$, $c = 18.79$ Å
$\beta = 95.6°$
$V = 665.14$ Å^3
Monoclinic P
$a = 7.34$, $b = 4.85$, $c = 18.79$ Å
$\beta = 95.6°$
$V = 665.14$ Å^3
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -0.5 & 0 & -1 \end{pmatrix}$ Twin matrix


0
c
a

Packing in layers

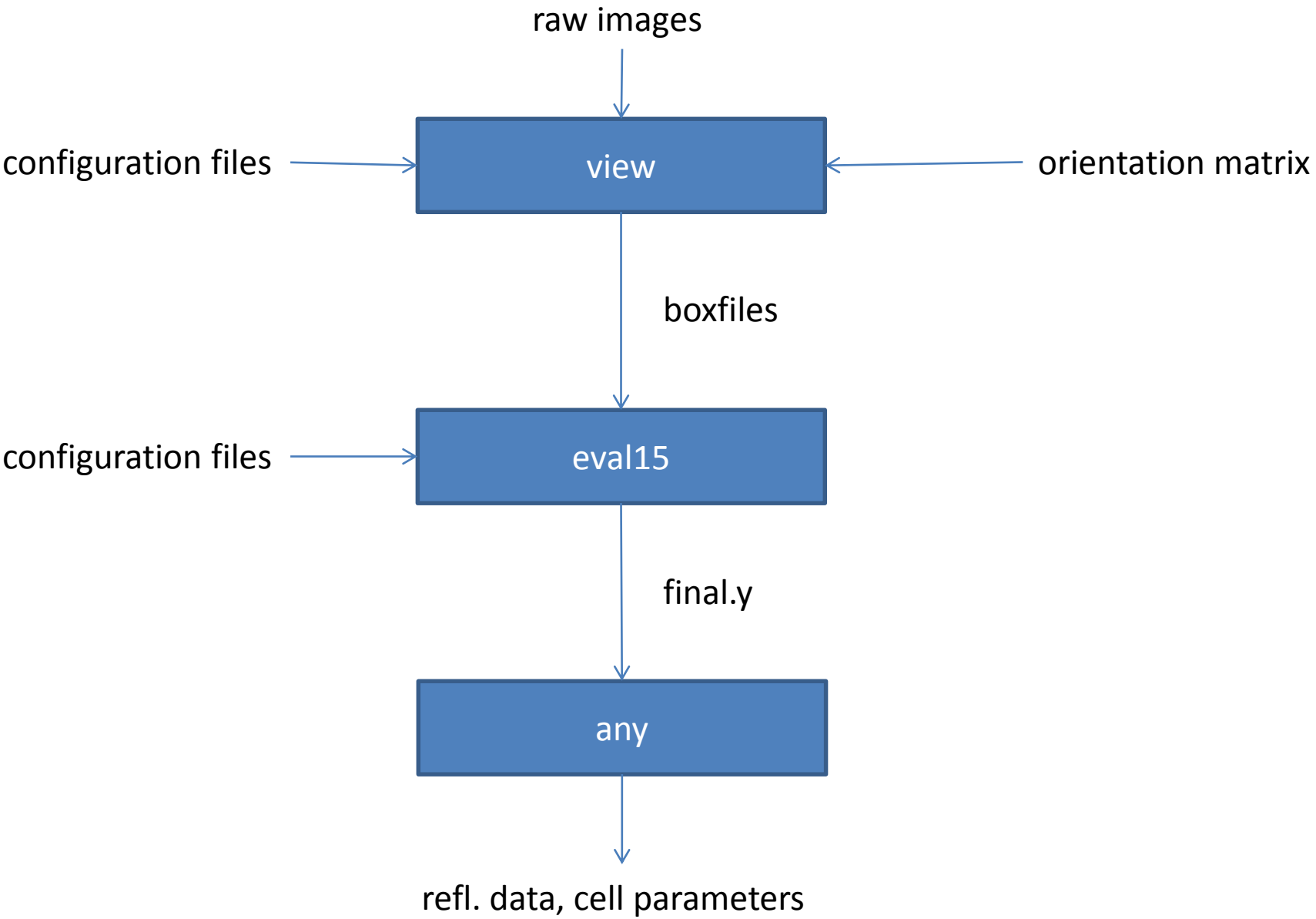


Twinning by stacking faults

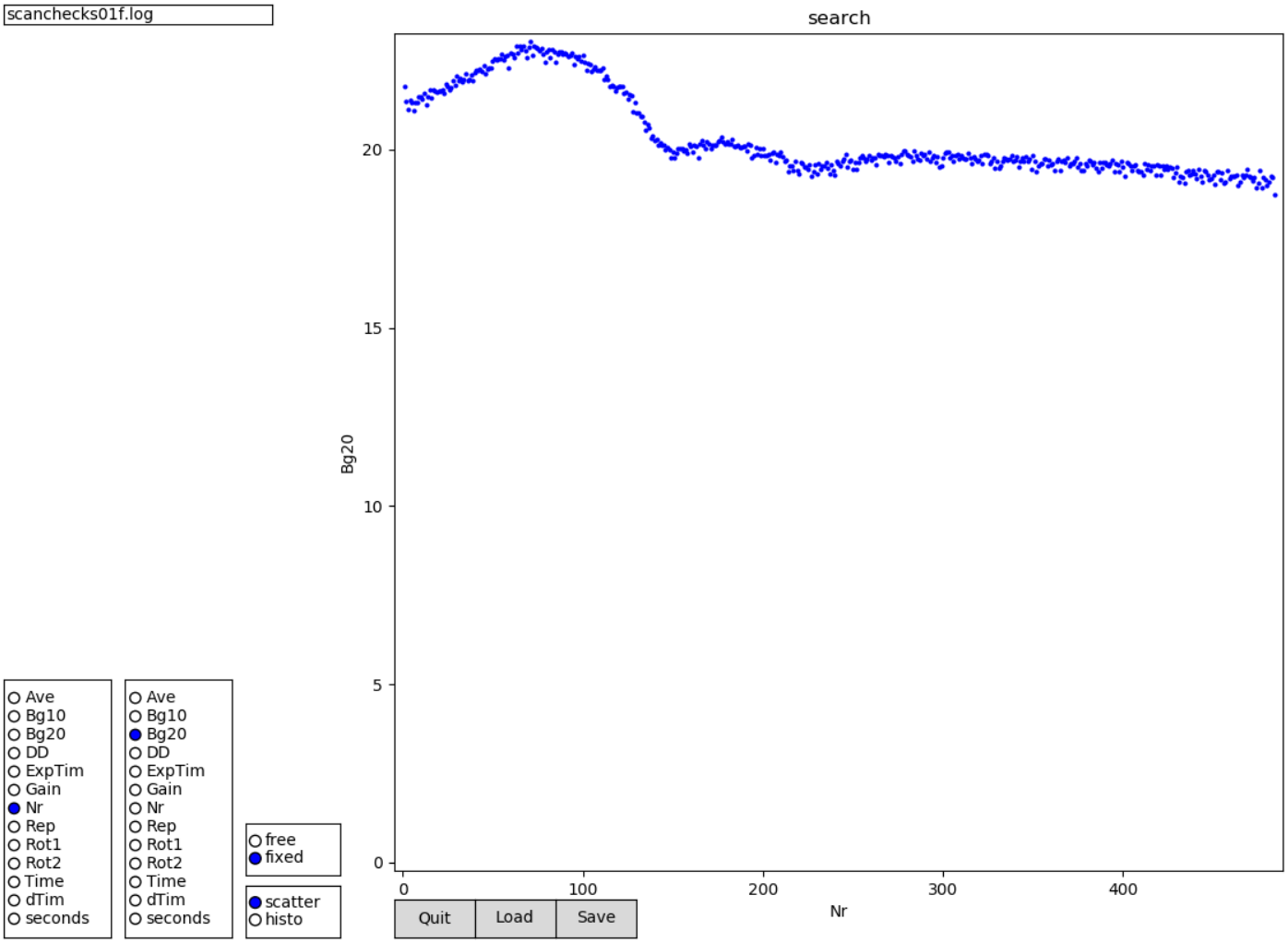


Tools in Eval15

A.M.M. Schreurs, X. Xian, L.M.J. Kroon-Batenburg,
J. Appl. Cryst. (2010). **43**, 70-82.


raw images
configuration files
view
orientation matrix
boxfiles
configuration files
eval15
final.y
any
refl. data, cell parameters

scancheck/scancheckplot



low3

- Create artificial dark image
- The lowest pixel intensities over all frames is considered as being background
- The influence of diffuse scattering is reduced

- **Important:** low-images are not meant to be used during intensity integration

Peak search

- Poor crystal quality
- Additional crystal fragments
- Ice reflections

- Advise: only search for the strongest peaks

dirax

Acl	nH	a	b	c	alpha	beta	gamma	Volume	S
90	140	12.168	17.604	38.883	102.41	98.10	93.90	8012	
89	132	7.356	4.844	37.644	90.03	95.53	90.00	1335	
85	134	7.356	4.843	37.659	89.96	95.56	90.02	1335	
80	100	4.844	7.351	18.801	95.96	90.10	90.00	666	
73	99	7.352	4.843	18.826	89.97	95.85	90.01	667	
19	27	4.830	7.346	9.889	105.53	100.32	90.39	332	
10	7	2.538	4.188	6.812	76.24	88.03	88.60	70	?
9	12	4.389	4.627	7.012	96.76	103.02	115.05	122	?
8	14	4.844	7.338	10.352	77.00	85.97	89.89	358	
7	9	3.762	4.004	4.535	106.51	109.32	94.60	61	?

dirax

Acl	nH	a	b	c	alpha	beta	gamma	Volume	S
90	140	12.168	17.604	38.883	102.41	98.10	93.90	8012	
89	132	7.356	4.844	37.644	90.03	95.53	90.00	1335	
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80	100	4.844	7.351	18.801	95.96	90.10	90.00	666	
73	99	7.352	4.843	18.826	89.97	95.85	90.01	667	
19	27	4.830	7.346	9.889	105.53	100.32	90.39	332	
10	7	2.538	4.188	6.812	76.24	88.03	88.60	70	?
9	12	4.389	4.627	7.012	96.76	103.02	115.05	122	?
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7	9	3.762	4.004	4.535	106.51	109.32	94.60	61	?

dirax

Acl	nH	a	b	c	alpha	beta	gamma	Volume	S
90	140	12.168	17.604	38.883	102.41	98.10	93.90	8012	
89	132	7.356	4.844	37.644	90.03	95.53	90.00	1335	
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80	100	4.844	7.351	18.801	95.96	90.10	90.00	666	
73	99	7.352	4.843	18.826	89.97	95.85	90.01	667	
19	27	4.830	7.346	9.889	105.53	100.32	90.39	332	
10	7	2.538	4.188	6.812	76.24	88.03	88.60	70	?
9	12	4.389	4.627	7.012	96.76	103.02	115.05	122	?
8	14	4.844	7.338	10.352	77.00	85.97	89.89	358	
7	9	3.762	4.004	4.535	106.51	109.32	94.60	61	?

acl 80
store a
lchi (→ invert indexing state)

dirax (second run)

```
Acl  nH      a      b      c  alpha   beta  gamma Volume S
(lines omitted)
 48  95  7.353  4.842 18.823  89.96  95.79  90.06    667
```

acl 48
store b
compare a b

```
Nr Rotangle       Rotvec(xyz)           RotVec(hkl)     ( angle)     RotVec(uvw)     ( angle) Obliq     Fom
 2  179.955 -0.2754  0.9304  0.2418   0.00  0.00 -1.00 (  0.17)  -0.03 -1.03 -4.00 (  0.20)  0.36   0.530  <
b0b0*a00*0a00aabaa00*0*ab0*0ba0b00*0aa*0*aba*aba00*b00000000*a0***00b0000b0a000*
a00*b0b*a00a000a00b0b*0b0aa0*0000b00a0**a*000a0a00*b**00*bb0a0000b0*0a00*0b000*0
0b*0aa*b00a0b*b**00aa0000000000a*000*00*0b000*0*000aa*a0*b000a00b0b0*0a00b*0a000
000*0*a0*bb000b0*00ba*a00b00**0aa000a0**0b00b*00bb0*b00
a=46 b=41 0=154 *=54
```

Dirax: extra output

- Extra output can be switched-on
- The entry V/H gives an indication of the information content
- For volume 1335, V/H=10
- For volume 667, V/H=7
- This is a warning sign for reticular twinning

Alternative approach

- Select the 667 $Å^3$ cell in dirax
- Perform a peak search for reflection that do not fit: program buildrest
- Re-run dirax on these new reflections

Note

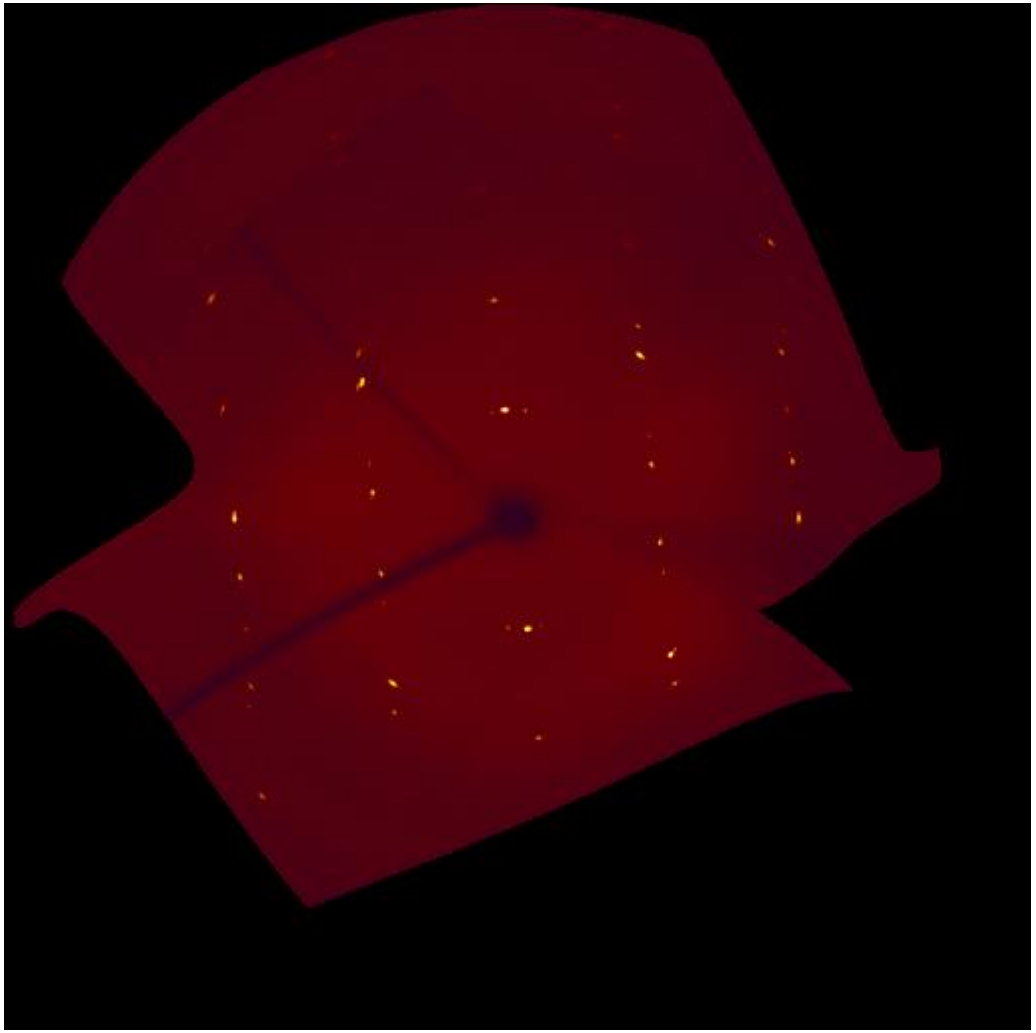
- Dirax always (!) results in a triclinic P-cell
- Use the program *rmatrix* to detect higher Bravais symmetry

2view

```
 a       b       c      alpha    beta   gamma    volume
iar :   7.356   4.845  18.829   89.94   96.01   89.99      667.4
ibr :   7.347   4.847  18.795   89.92   95.41   89.99      666.3
Volume ratio = 1.002 Trying 8 solutions
Nr Rotangle       Rotvec(xyz)           RotVec(hkl)    ( angle)     RotVec(uvw)    ( angle) Obliq     Fom
 1  179.918 -0.1098 -0.2796  0.9538  -4.00 -0.00  1.04 (  0.21)  -1.00 -0.00 -0.00 (  0.20)  0.40   1.260
 2  179.980 -0.2744  0.9309  0.2413   0.00  0.00 -1.00 (  0.19)  -1.04  0.02 -4.00 (  0.22)  0.41   1.060 U
```

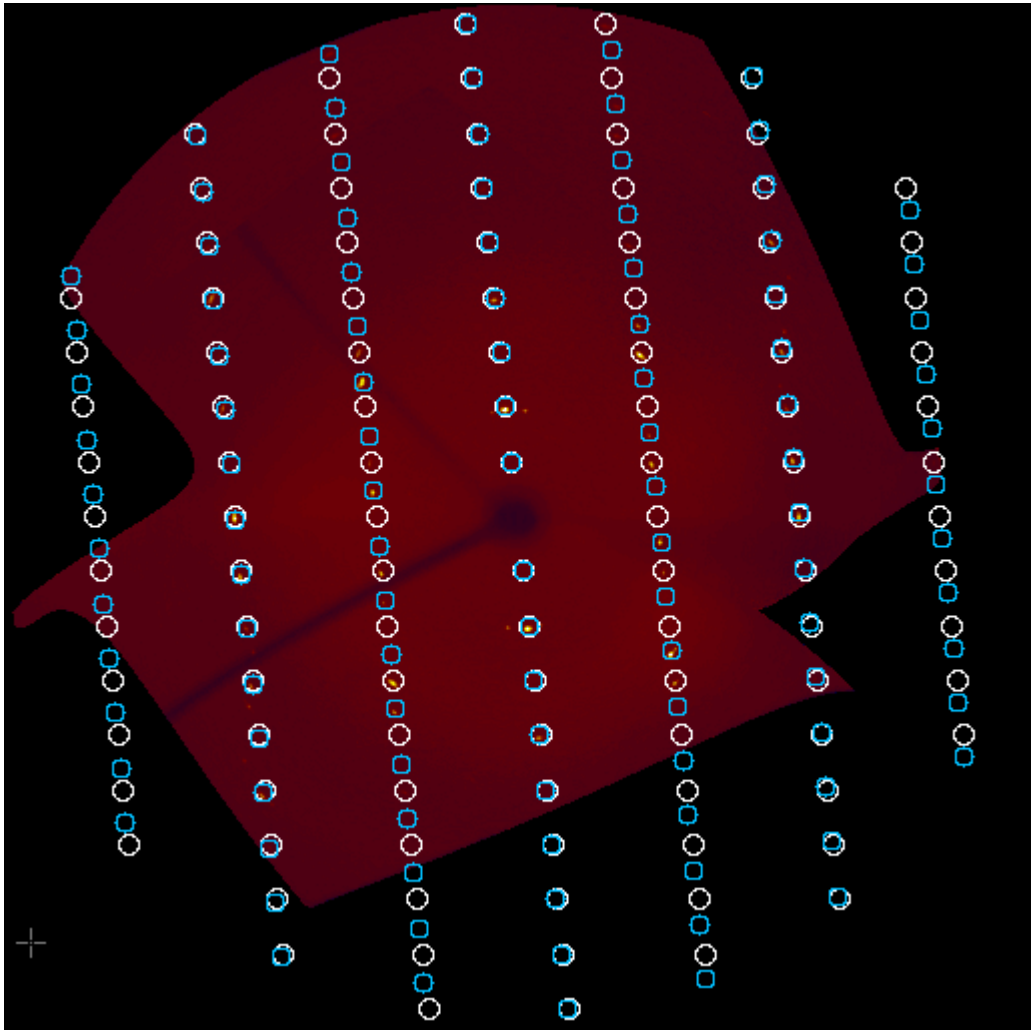
The program 2view also has the option to write the rotated orientation matrix into a file.

Simulated precession image



low-image subtracted

Simulated precession image



white: unit cell 1
blue: unit cell 2

Integration

- From two orientation matrices first.rmat and second.rmat, two subdirectories are created:
  - first-second
  - second-first
- The program *any* reads from first-second the single and overlapping reflections, from second-first only the single reflections
- In the program *any*, direction cosines can be based on one orientation matrix: numerical absorption correction is possible (in PLATON switch-off “check direction cosines”)

Statistics

One scan, directory first-second.

```
Flags for all reflections
Good 100 Not Good 155 (Weak 37 Not Weak 118) Total: 255
Total Percent NonWeak Percent
  100  39.216     100  45.872 GOOD
   37  14.510                 WEAK
    2   0.784       2   0.917 EDGEVER
  130  50.980     115  52.752 OVERLAPSUM
    1   0.392       1   0.459 BIGROT
    1   0.392                 BADUNIF
```

Further processing

- Twinabs (G. Sheldrick, Göttingen University)
- mergehklf5
- euhedral (analytical absorption correction) optimize crystal shape on non-overlapping reflection, apply to all reflections
- anafcf (variance analysis). In the case of twins, the use of the LIST 8 command in SHELXL is recommended.

Structure solution

- In many cases it is sufficient to write the non-overlapping reflections into a HKLF4 file for structure solution.
- Structure refinement on HKLF5 file.

Suggestion

- For data deposition with cif-files I advise to include the orientation matrix
- In the case of twins, these are usually more than one orientation matrix

Acknowledgements

- Loes Kroon-Batenburg, Toine Schreurs
- Jitse van der Horn

Change Keyboard setting on LiveUSB

- Blue icon in top-left
- Settings
- Keyboard
  - Layout
  - Unmark button “Use System Defaults”
  - Add
    - French
  - Delete
    - English(US)