The PLATON/TwinRotMat Tool for Twinning Detection

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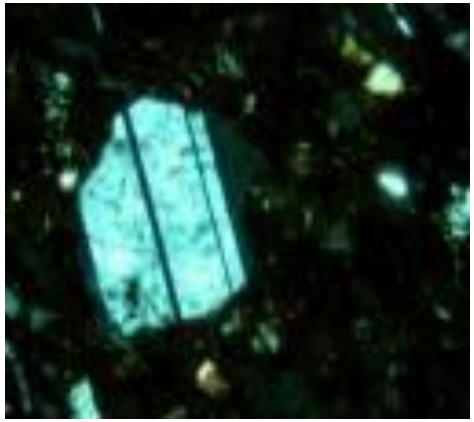
Delft, 29-Sept-2008

Viewpoints on Twinning (I)



- Macroscopic
  - Mineralogy
  - Intergrowth
- Microscopic
  - Extinction pattern under polarized light
- Ways of Formation
  - Deformation, Growth, Pressure, T
- Molecular level
  - Local Pseudo Symmetry

Viewpoints on Twinning (II)

- Data collection
- Processing Procedures
- Refinement Procedures
- Detection of Twinning
- Twinning Matrix

- See: http://www.cryst.chem.uu.nl/lutz/twin/twin_lit.html

Twinning Symptoms

- Not all reflections fit in a single lattice
- Statistics $<|E^2-1|>$ small etc.
- Problems to solve the structure
- Poor refinement
- wR2 >> 2 * R1
- Ghost peaks at chemically impossible positions.
- High value of the second Wght parameter
- Fobs >> Fcalc for a large number of reflections
- Etc.

Twinning Matrix (I)

Non-Merohedral Twins

- Partially overlapped reciprocal lattices
- Problem now largely solved with current area detector images (CCD)
- Twinning Matrix from indexing software (Dirax, CellNow etc.)
- Adequate integration software

  (HKLF 5)

Twinning Matrix (II)

(Pseudo)-Merohedral Twins:

- Overlapping Lattices

  (Lattice symmetry >> Symmetry of the Structure)
- Symmetry elements of the lattice but not of the structure are possible twinning laws.
- Coset Decomposition

  ➔ Possible Twin laws to be tested

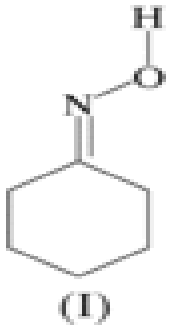
  H.D.Flack (1987). J. Appl. Cryst. A43, 564-568.

Twinning Matrix (III)

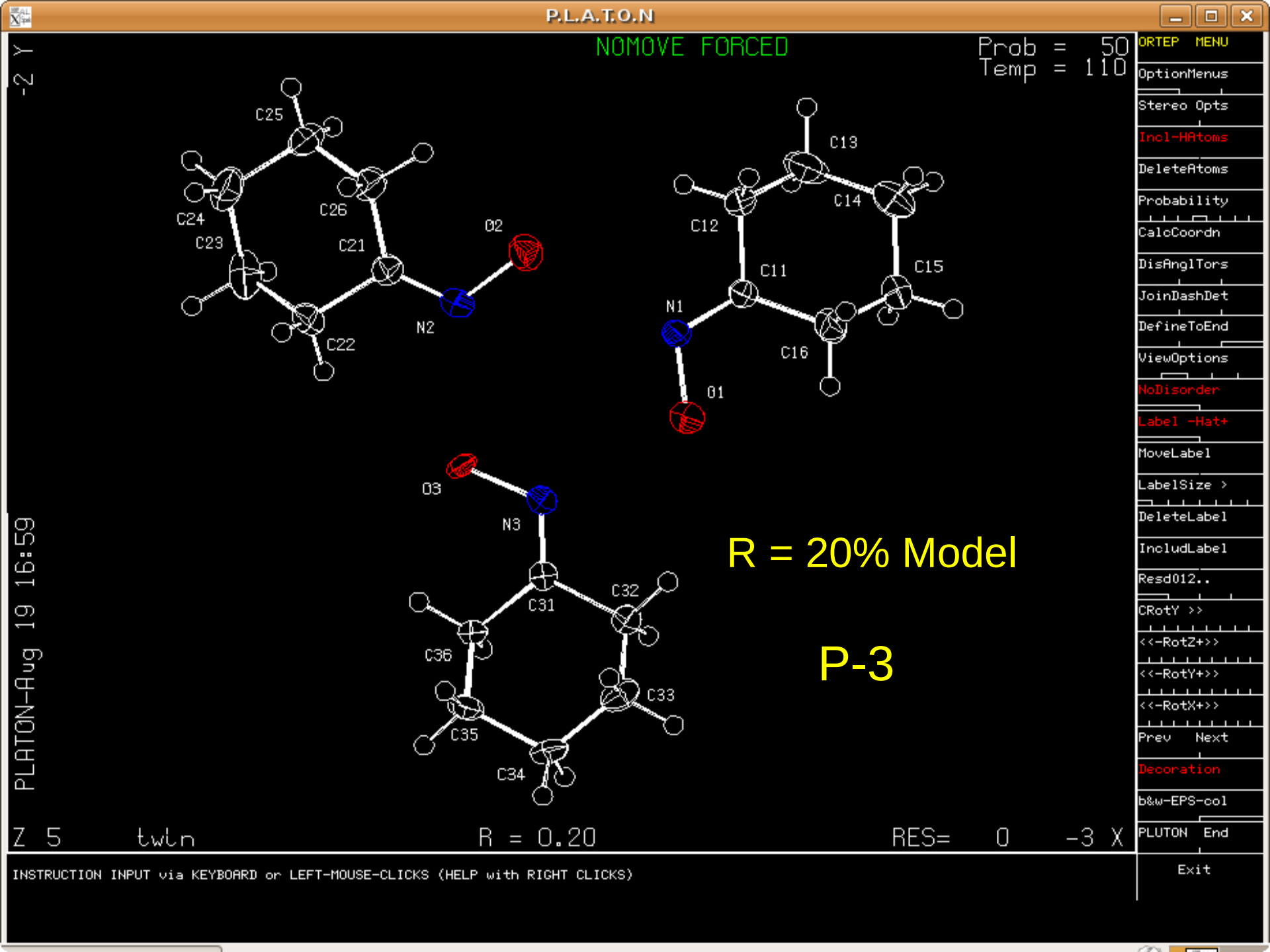
Diagnostic analysis of Fo/Fc CIF

- ROTAX (Simon Parsons & B. Gould)
  Lists possible twin laws from analysis of poorly fitting reflections with Fobs >> Fcalc in .fcf
  Cooper et al., (2002). J.Appl.Cryst., 35, 168-174
- PLATON/TwinRotMat
- Automatically lists the applicable twin law(s) + predicted BASF & R-drop(s)(from .cif & .fcf data)

TwinRotMat Example (I)



- Study of the structure of cyclohexanone oxime. (ZZZVPO)
- Originally published as disordered in P3 with R = 9.25 %.(Acta Cryst. (2001),B57,705)
- But no signs of disorder in the diffraction data.
- Alternative not disordered solution in Space Group P-3.
- Refinement with three independent oxime molecules converged to an unsatisfactorily R= 20%. ORTEP ➔


P.L.A.T.O.N
NOMOVE FORCED
Prob = 50
Temp = 110
-2 Y
C25
C24
C26
C23
C21
O2
N2
C22
C13
C14
C12
C11
C15
N1
C16
O1
O3
N3
C31
C32
C36
C33
C35
C34
R = 20% Model
P-3
PLATON-Aug 19 16:59
Z 5 twin
R = 0.20
RES= 0 -3 X
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
ORTEP MENU
OptionMenus
Stereo Opts
Incl-HAtoms
DeleteAtoms
Probability
CalcCoordn
DisAnglTors
JoinDashDet
DefineToEnd
ViewOptions
NoDisorder
Label -Hat+
MoveLabel
LabelSize >
DeleteLabel
IncludLabel
Resd012..
CRotY >>
<<-RotZ+>>
<<-RotY+>>
<<-RotX+>>
Prev Next
Decoration
b&w-EPS-col
PLUTON End
Exit

TwinRotMat Example (II)

- Noisy difference map etc.
- H’s on O not found
- Twinning ?
- Run PLATON/TwinRotMat on the CIF/FCF of the converged R = 20% model.


P.L.A.T.O.N
P L A T O N
A Multipurpose Crystallographic Tool
(C) 1980-2008 A.L.Spek - 40M-Version: 240908
GRAPHICS | GEOM-CALC | VOIDS FLIP | SYMMETRY | ABSORPTION | REPORT | MISC-TOOLS
PLUTONauto | CALC ALL | CALC SOLV | ADDSYM | DELrefABS | VALIDATION | SYSTEM-S
ORTEP/ADP | CALC INTRA | CALC K.P.I | ADDSYM-EQL | ABSPslScan | ASYM-VIEW | FCF2HKL
NEWMAN | CALC INTER | SQUEEZE | ADDSYM-EXT | ABSTompa | FCF-VALID | EXPAND-P1
RING-PLOTS | CALC COORD | CALC-FCF | ADDSYM-PLT | ABSGauss | SUPPLEMMAT | FCF-GENER
PLANE-PLOT | CALC METAL | CONTOUR-SQ | ADDSYM-SHX | ABSXtal | ANALofVAR | HKL-GENER
POLYHEDRA | CALC GEOM | SOLV F3D | NEWSYM | ABSSphere | ByvoetPair | HKL-TRANSF
CONTOUR-DF | CALC HBOND | SOLV PLOT | NONSYM | MULscanABS | ASYM-EXPCT | EXOR-RES
CONTOUR-Fo | CALC TMA | CAVITY-PLT | LEPAGE | SHXABS | ASYM-VALID | ANIS-RES
AutoMolFit | L.S.-PLANE | | DELRED | | DiffFourier | RENAME-RES
HKL2Powder | DihedAngle | | MOLSYM | | EXPECT-HKL | PDB -pdb
SlmPowderP | AngleLines | FLIP MENU | SPGRfromEX | | CSD-CELL | SPF -eld
RadDistFun | AngLsplLin | FLIP SHOW | ASYM | | CSD-QUEST | SHELXL-res
PATTERSON | CremerPopl | FLIP PATT | ASYMaverF | | StructTidy | CIF -acc
 | BondValenc | FLIPPER 25 | LePageTwl | | StrainAnal | AUTO-RENUM
PLUTONatlv | HFIX - RES | STRUCTURE? | TwinRotMat | Xtal Habit | CIF-LOCAL | CIF2SHELXL
Xtal Data (CIF) ez2088.cif- Set 1(1): I
Refl Data (SHELXL) ez2088.hkl [NO-DIRC] (1): I
Browser - HELP
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
>>
PLATON MENU
OptionMenus
NoMove
Color
Organic
Round
Parentheses
Label-Alias
R/S-Determ
Norm-H-bond
NoSymm
Join-Expand
LstARU RCel
LstCellSymm
ListAtoms
ListBonds
LstFlagRadi
Exclude H
MinQPeakHgt
MinQPeakDis
Q-Peak-Incl
KeyInstruct
Prev Next
SAVE-InstrS
ENTRY-LIST
Reset End
Exit
MenuActive

TwinRotMat Example (III)

- Result: (shown in next slide).
- Twin law with an estimate of the twinning fraction and the estimated drop in R-value when applied
- Note:

  - Green entries indicate significant R-drop

TwinRotMat

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

Cell: 0.71073 20.983 20.983 7.644 90.00 90.00 120.00 Spgr: P-3
Criteria: DeltaI/SigmaI .GT. 16.0, DeltaTheta 0.10 Deg., NselMin = 50
N(refl) = 4445, N(selected) = 50, IndMax = 25, CritI = 0.3, CritT = 0.10

PLATON-Aug 8 17:21:12 2005 - (80805)

2-axis (0 0 1) [0 0 1], Angle () [] = 0.00 Deg, Freq = 47 (-1.000 0.000 0.000) (h1) (h2) Nr Overlap = 4445 (0.000 -1.000 0.000) * (k1) = (k2) BASF = 0.54 (0.000 0.000 1.000) (l1) = (l2) DEL-R =-0.107	1	
2-axis (1 -1 0) [1 -1 0], Angle () [] = 0.00 Deg, Freq = 48 (0.000 -1.000 0.000) (h1) (h2) Nr Overlap = 4445 (-1.000 0.000 0.000) * (k1) = (k2) BASF = 0.01 (0.000 0.000 -1.000) (l1) = (l2) DEL-R =-0.001	2	
2-axis (2 -1 0) [1 0 0], Angle () [] = 0.00 Deg, Freq = 36 (1.000 0.000 0.000) (h1) (h2) Nr Overlap = 4445 (-1.000 -1.000 0.000) * (k1) = (k2) BASF = 0.01 (0.000 0.000 -1.000) (l1) = (l2) DEL-R =-0.001	3	
2-axis (1 3 -1) [10 14 -23], Angle () [] = 0.45 Deg, Freq = 10 (-0.732 0.375 -0.606) (h1) (h2) Nr Overlap = 576 (0.804 0.126 -1.818) * (k1) = (k2) BASF = 0.02 (-0.268 -0.375 -0.394) (l1) = (l2) DEL-R = 0.000	4	
twin R = 0.20		

TwRoMt MENU
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
FullListing
EPS-TwinLaw
DspTwinMat1
DspTwinMat2
DspTwinMat3
DspTwinMat4
EPS-TwinLat
Resolution>
Zone-H,K,L
Up Down
RacemicTwin
SelectTMat1
SelectTMat2
SelectTMat3
SelectTMat4
HKLF5-CritI
HKLF5-CritT
HKLF5-Gener
End

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

>>

Exit
MenuActive

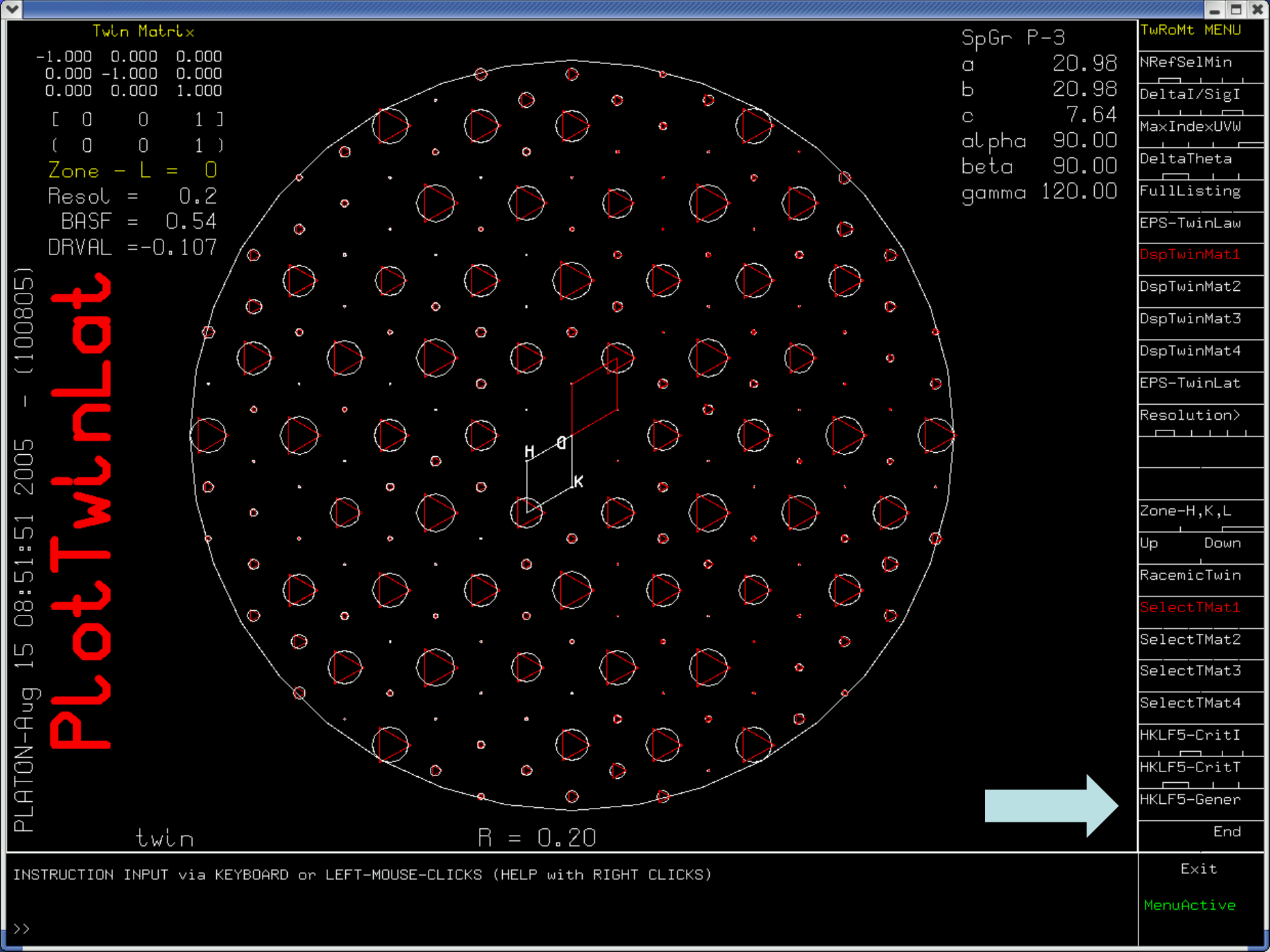
TwinRotMat Example (IV)

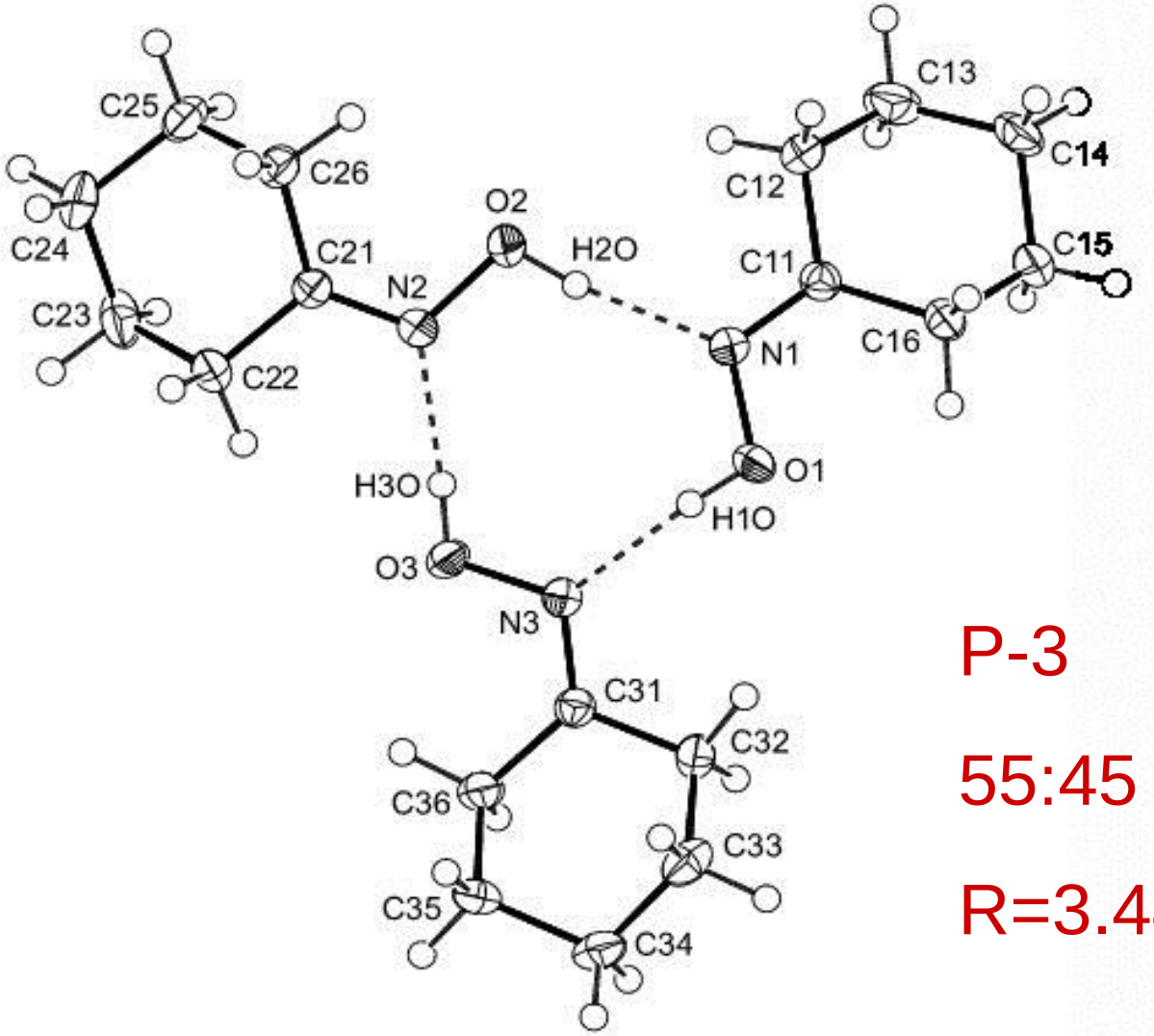
- An HKLF5 file can be generated by clicking on ‘HKLF5-gener’ after selecting the matrices to be used.

or

- TWIN/BASF refinement with the proposed matrix.

- Display the overlap of the two lattices related by the twin law (2-fold axis parallel to c) as viewed down the c-axes.


Twin Matrix
-1.000 0.000 0.000
0.000 -1.000 0.000
0.000 0.000 1.000
[0 0 1]
(0 0 1)
Zone - L = 0
Resol = 0.2
BASF = 0.54
DRVAL =-0.107
SpGr P-3
a 20.98
b 20.98
c 7.64
alpha 90.00
beta 90.00
gamma 120.00
PLATON-Aug 15 08:51:51 2005 - (100805)
PlotTwinLat
H
O
K
twin
R = 0.20
TwRoMt MENU
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
FullListing
EPS-TwinLaw
DspTwinMat1
DspTwinMat2
DspTwinMat3
DspTwinMat4
EPS-TwinLat
Resolution>
Zone-H,K,L
Up Down
RacemicTwin
SelectTMat1
SelectTMat2
SelectTMat3
SelectTMat4
HKLF5-CritI
HKLF5-CritT
HKLF5-Gener
End
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
>>
Exit
MenuActive



P-3

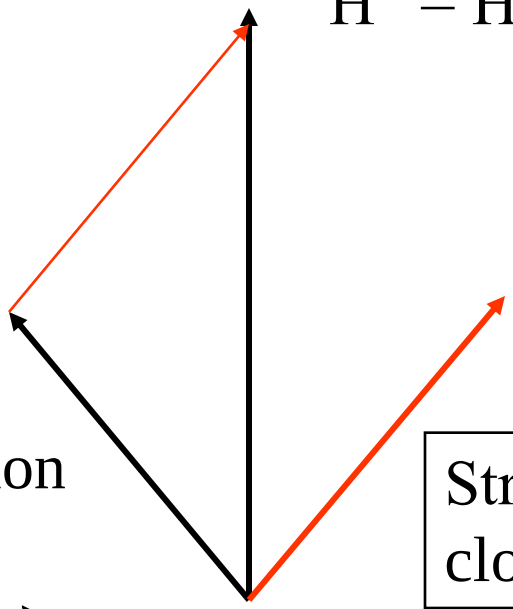
55:45 twin

R=3.44

Ideas behind the Algorithm

- Reflections effected by twinning show-up in the least-squares refinement with F(obs) >> F(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.

Possible Twin Axis



H” = H + H’

Candidate twinning axis
(Normalize !)

H’

H

Reflection
with
F(obs) >>
F(calc)

Strong reflection H’ with theta close to theta of reflection H

TwinRotMat

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

Cell: 0.71073 20.983 20.983 7.644 90.00 90.00 120.00 Spgr: P-3
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PLATON-Aug 8 17:21:12 2005 - (80805)

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2-axis (1 -1 0) [1 -1 0], Angle () [] = 0.00 Deg, Freq = 48 (0.000 -1.000 0.000) (h1) (h2) Nr Overlap = 4445 (-1.000 0.000 0.000) * (k1) = (k2) BASF = 0.01 (0.000 0.000 -1.000) (l1) = (l2) DEL-R =-0.001	2	
2-axis (2 -1 0) [1 0 0], Angle () [] = 0.00 Deg, Freq = 36 (1.000 0.000 0.000) (h1) (h2) Nr Overlap = 4445 (-1.000 -1.000 0.000) * (k1) = (k2) BASF = 0.01 (0.000 0.000 -1.000) (l1) = (l2) DEL-R =-0.001	3	
2-axis (1 3 -1) [10 14 -23], Angle () [] = 0.45 Deg, Freq = 10 (-0.732 0.375 -0.606) (h1) (h2) Nr Overlap = 576 (0.804 0.126 -1.818) * (k1) = (k2) BASF = 0.02 (-0.268 -0.375 -0.394) (l1) = (l2) DEL-R = 0.000	4	
twin R = 0.20		

TwRoMt MENU
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
FullListing
EPS-TwinLaw
DspTwinMat1
DspTwinMat2
DspTwinMat3
DspTwinMat4
EPS-TwinLat
Resolution>
Zone-H,K,L
Up Down
RacemicTwin
SelectTMat1
SelectTMat2
SelectTMat3
SelectTMat4
HKLF5-CritI
HKLF5-CritT
HKLF5-Gener
End

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

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Exit
MenuActive

What about trillings ?

Example: $[PrFe(CN)_6(H_2O)_2].2H_2O$
Langer et al. (2004).Acta Cryst., C60,1104.

Space group Cmcm (R-int = 0.15)
Pseudo hexagonal (R-int = 0.16)
Refinement (via model in P21 etc.) in Cmcm
with TWIN -.5 .5 0 –1.5 -.5 0 0 0 1 3
R = 0.017, wR2 = 0.039
Fractions: 0.6, 0.2, 0.2

TwinRotMat Analysis

- Starting model is the published structure in Cmcm without twinning.
- R = 0.15, wR2 = 0.37
- Large residual density peaks.
- TwinRotMat ➔

TwinRotMat

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

Cell: 0.71073 7.492 12.929 13.790 90.00 90.00 90.00 Spgr: Cmcm

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

N(refl) = 1408, N(selected) = 50, IndMax = 5, CritI = 0.1, CritT = 0.10

PLATON-Sep 28 15:25:17 2008 - (240908)

Fc from Coordinates

2-axis (1 3 0) [1 1 0], Angle () [] = 0.18 Deg, Freq = -50 (-0.497 0.503 0.000) (h1) (h2) Nr Overlap = 1381 (1.497 0.497 -0.000) * (k1) = (k2) BASF = 0.30 (-0.000 -0.000 -1.000) (l1) (l2) DEL-R =-0.110	1
2-axis (1 3 0) [1 1 0], Angle () [] = 0.18 Deg, Freq = 50 (-0.503 0.501 0.000) (h1) (h2) Nr Overlap = 1381 (1.492 0.503 0.000) * (k1) = (k2) BASF = 0.30 (-0.000 0.000 -1.000) (l1) (l2) DEL-R =-0.110	2
2-axis (1 -3 0) [1 -1 0], Angle () [] = 0.18 Deg, Freq = -50 (-0.497 -0.503 -0.000) (h1) (h2) Nr Overlap = 1297 (-1.497 0.497 -0.000) * (k1) = (k2) BASF = 0.40 (0.000 0.000 -1.000) (l1) (l2) DEL-R =-0.093	3
2-axis (1 -3 0) [1 -1 0], Angle () [] = 0.18 Deg, Freq = 50 (-0.503 -0.501 -0.000) (h1) (h2) Nr Overlap = 1281 (-1.492 0.503 -0.000) * (k1) = (k2) BASF = 0.40 (0.000 0.000 -1.000) (l1) (l2) DEL-R =-0.092	4

I C m c m R = 0.02

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

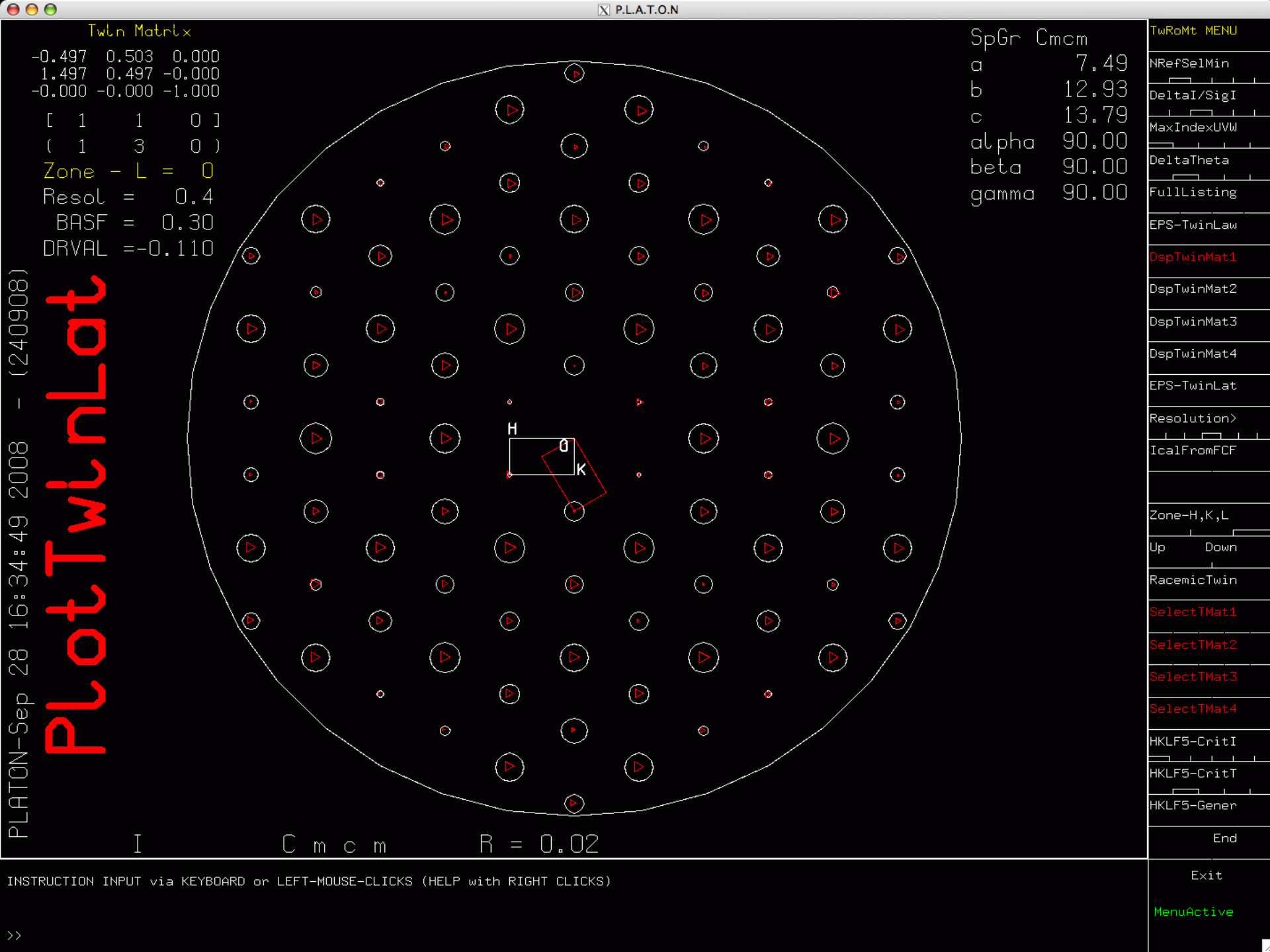
>>

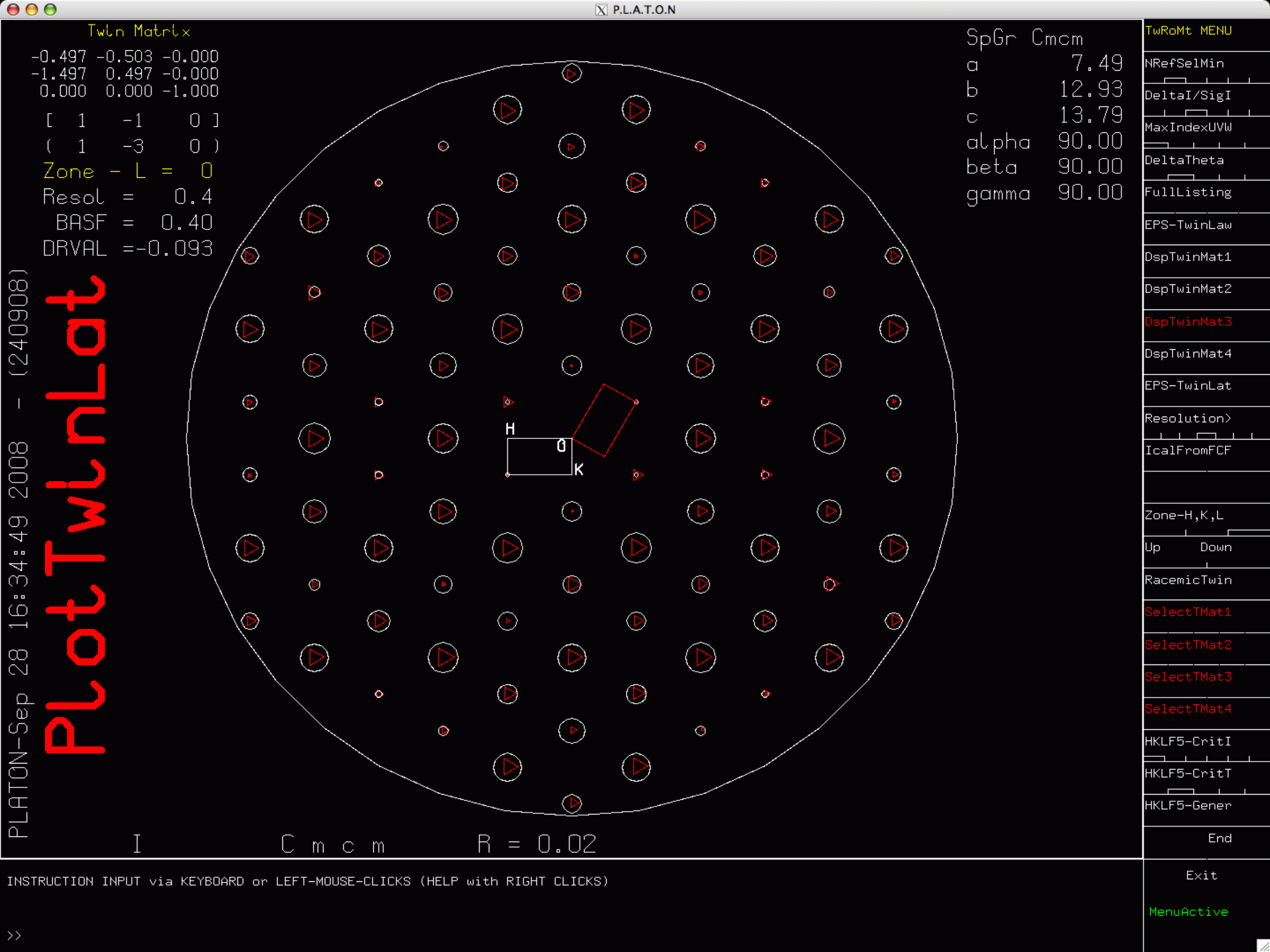
TwRoMt MENU
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
FullListing
EPS-TwinLaw
DspTwinMat1
DspTwinMat2
DspTwinMat3
DspTwinMat4
EPS-TwinLat
Resolution>
IcalFromFCF
Zone-H,K,L
Up Down
RacemicTwin
SelectTMat1
SelectTMat2
SelectTMat3
SelectTMat4
HKLF5-CritI
HKLF5-CritT
HKLF5-Gener
End
Exit
MenuActive

HKLF 5 Generation

- Use the two rotations about the proposed direct lattice directions [1 1 0] & [1 –1 0]

  They have a slightly better overlap than the corresponding reciprocal lattice directions [1 3 0]* & [1 –3 0]*
- See overlap in reciprocal space ➔


P.L.A.T.O.N
Twin Matrix
-0.497 0.503 0.000
1.497 0.497 -0.000
-0.000 -0.000 -1.000
[1 1 0]
(1 3 0)
Zone - L = 0
Resol = 0.4
BASF = 0.30
DRVAL =-0.110
SpGr Cmcm
a 7.49
b 12.93
c 13.79
alpha 90.00
beta 90.00
gamma 90.00
PLATON-Sep 28 16:34:49 2008 - (240908)
PlotTwinLat
H
O
K
I C m c m R = 0.02
TwRoMt MENU
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
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
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
>>
Exit
MenuActive


P.L.A.T.O.N
Twin Matrix
-0.497 -0.503 -0.000
-1.497 0.497 -0.000
0.000 0.000 -1.000
[1 -1 0]
(1 -3 0)
Zone - L = 0
Resol = 0.4
BASF = 0.40
DRVAL =-0.093
PLATON-Sep 28 16:34:49 2008 - (240908)
PlotTwinLat
SpGr Cmcm
a 7.49
b 12.93
c 13.79
alpha 90.00
beta 90.00
gamma 90.00
H
0
K
I C m c m R = 0.02
TwRoMt MENU
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
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
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
>>
Exit
MenuActive

Refinement Results

- Based on HKLF5 file with two matrices
- R = 0.02
- Twin parts 0.6, 0.2, 0.2
- Thus equivalent with the thrilling description.

FCF-VALIDATION

Forthcoming:

Automatic twinning detection as part of the IUCr CheckCif procedure

- Detection of ignored twinning
- Detection of Applied Twinning Correction without being reported

  (Already available via PLATON/Check)

Example of Unreported Twinning (I)

- Sadiq-ur-Rehman et al. (2008). Acta Cryst. E64, e26 & (2007). E63, m2329.
- $Sn_3(CH_3)_9Cl(NO_3)$ reinterpreted as $Sn_3(CH_3)_9Cl(CO_3)$
- But: Still no mention of twinning ! In the paper nor in the CIF (although a correction for twinning was applied)
- No CIF datanames defined yet for twinning
- CIF/FCF Validation ➔ ALERT

Example of Unreported Twinning (II)

```
==========================================================================
Check for Unaccounted Twinning with the TwinRotMat Algorithm - N(selec) =    50
==========================================================================
Note: This Analysis is Based on Fc calculated from Coordinates in the CIF.
==========================================================================

2-axis (   1  -2   0 ) [   0  -1   0 ], Angle () [] =  0.00 Deg, Freq =    50

(-1.000   -1.000   -0.000)    (h1)    (h2)                  Nr Overlap =  1282
( 0.000    1.000    0.000) *  (k1) =  (k2)                        BASF =  0.40
( 0.000    0.000   -1.000)    (l1)    (l2)                     DEL-R =-0.137

2-axis (   0   0   1 ) [   0   0   1 ], Angle () [] =  0.00 Deg, Freq =    53

(-1.000   -0.000   -0.000)    (h1)    (h2)                  Nr Overlap =   435
( 0.000   -1.000    0.000) *  (k1) =  (k2)                        BASF =  0.21
( 0.000    0.000    1.000)    (l1)    (l2)                     DEL-R =-0.017


==========================================================================
Check for Unaccounted Twinning with the TwinRotMat Algorithm - N(selec) =    50
==========================================================================
Note: This Analysis is Based on Fc Taken from Fo/Fc File
==========================================================================

No Applicable Twin Law(s) Detected from Fo/Fc Analysis-or already accounted for
```

Residual Problems

Getting a Preliminary Model from

- a (pseudo-)merohedrally twinned dataset
- Integrated data corresponding to a larger twin lattice rather than the smaller lattice of the structure (e.g. oC <-> mP)

  (Sometimes, but not always showing non space group extinctions)

Concluding Remarks

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)

Additional Info

http://www.cryst.chem.uu.nl

(including a copy of this powerpoint presentation)

Thanks

for your attention !!