Twinning tools in PLATON

Detection and Absorption Correction

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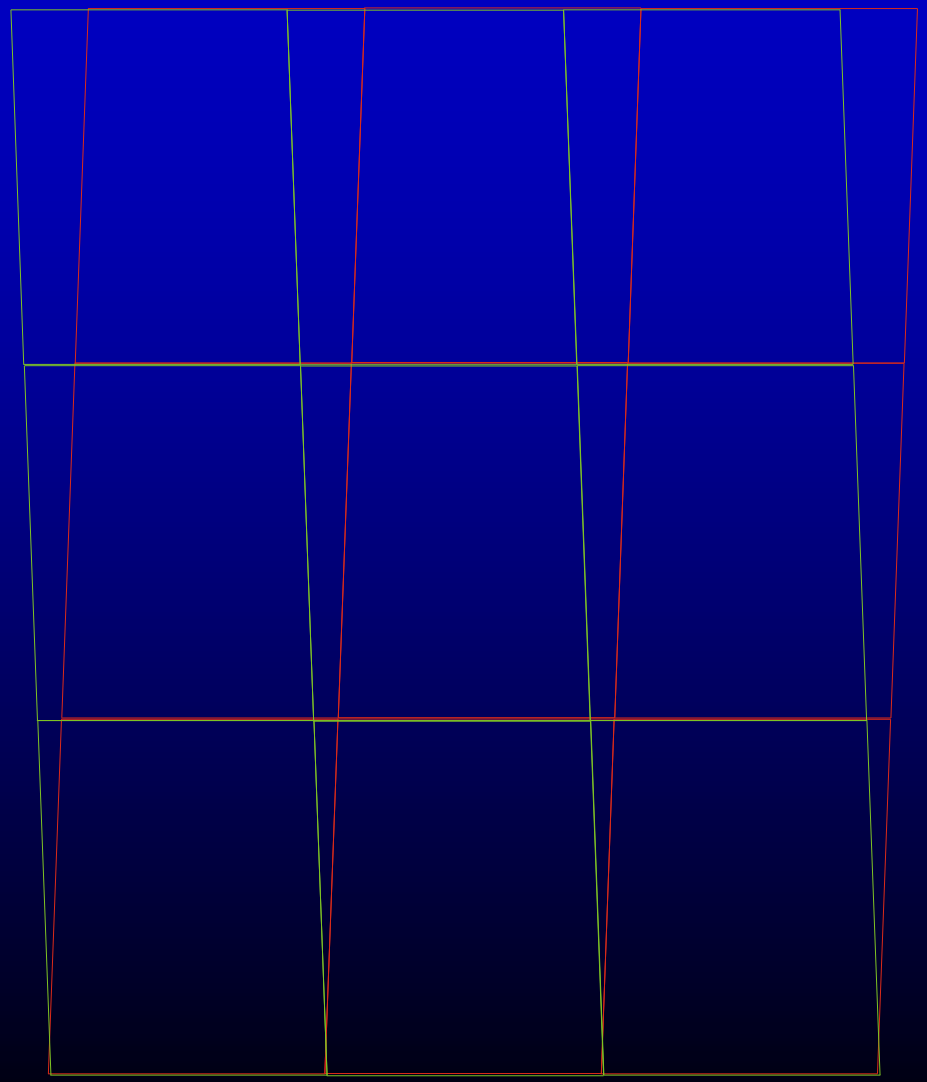
Merohedral Twins

- The twin element belongs to the holohedry of the lattice, but not to the point group of the crystal.
- The reciprocal lattices of all twin domains superimpose exactly.
- In the triclinic, monoclinic and orthorhombic crystal systems, the merohedral twins can always be described as inversion twins.

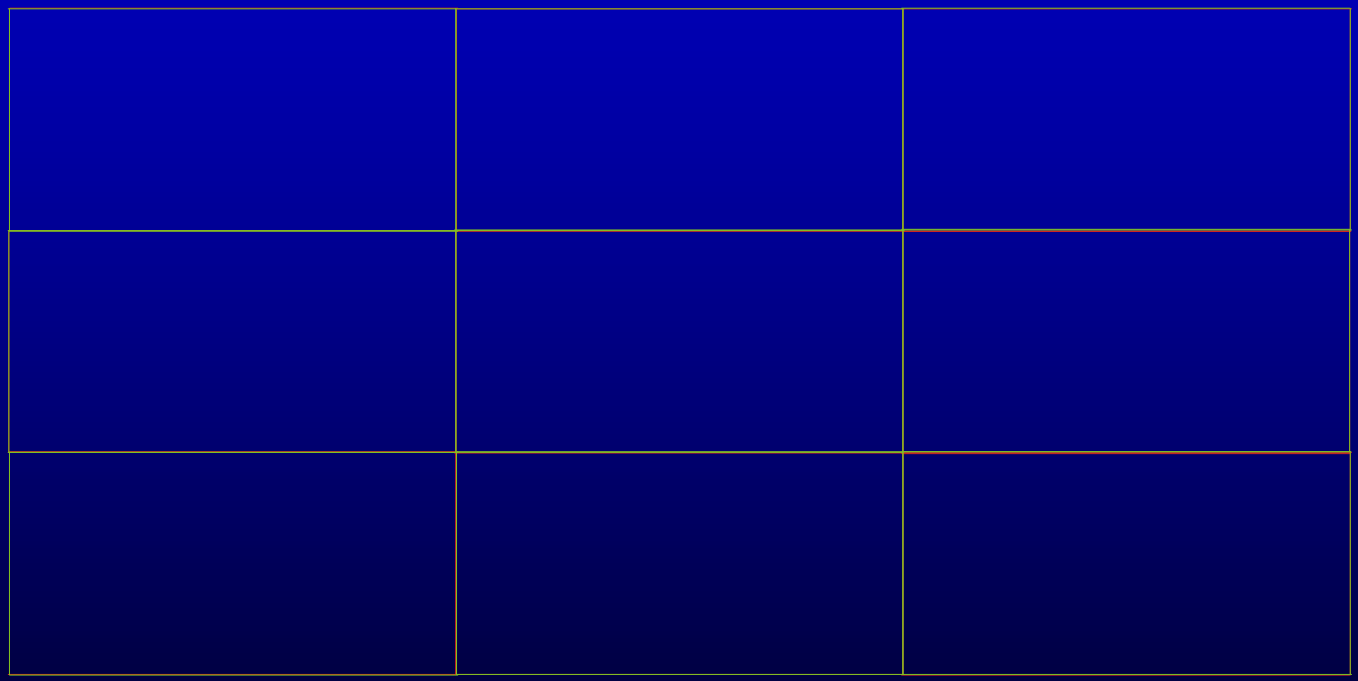
Non-merohedral Twins

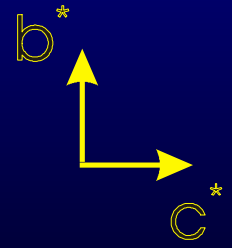
- Twin operation does not belong to the Laue group or point group of the crystal.
- In practice there are three types of reflections:
  - Reflections belonging to only one lattice.
  - Completely overlapping reflections belonging to both lattices.
  - Partially overlapping refections belonging to both lattices.

Non-merohedral Twins



Non-merohedral Twins





Warning signs

- The R_{int} value for the higher-symmetry Laue group is only slightly higher than for the lower-symmetry Laue group
- The mean value for $|E^2-1|$ is much lower than the expected value of 0.736
- The space group appears to be trigonal or hexagonal
- The apparent systematic absences are not consistent with any known space group
- For all of the most disagreeable reflections F_o is much greater than F_c

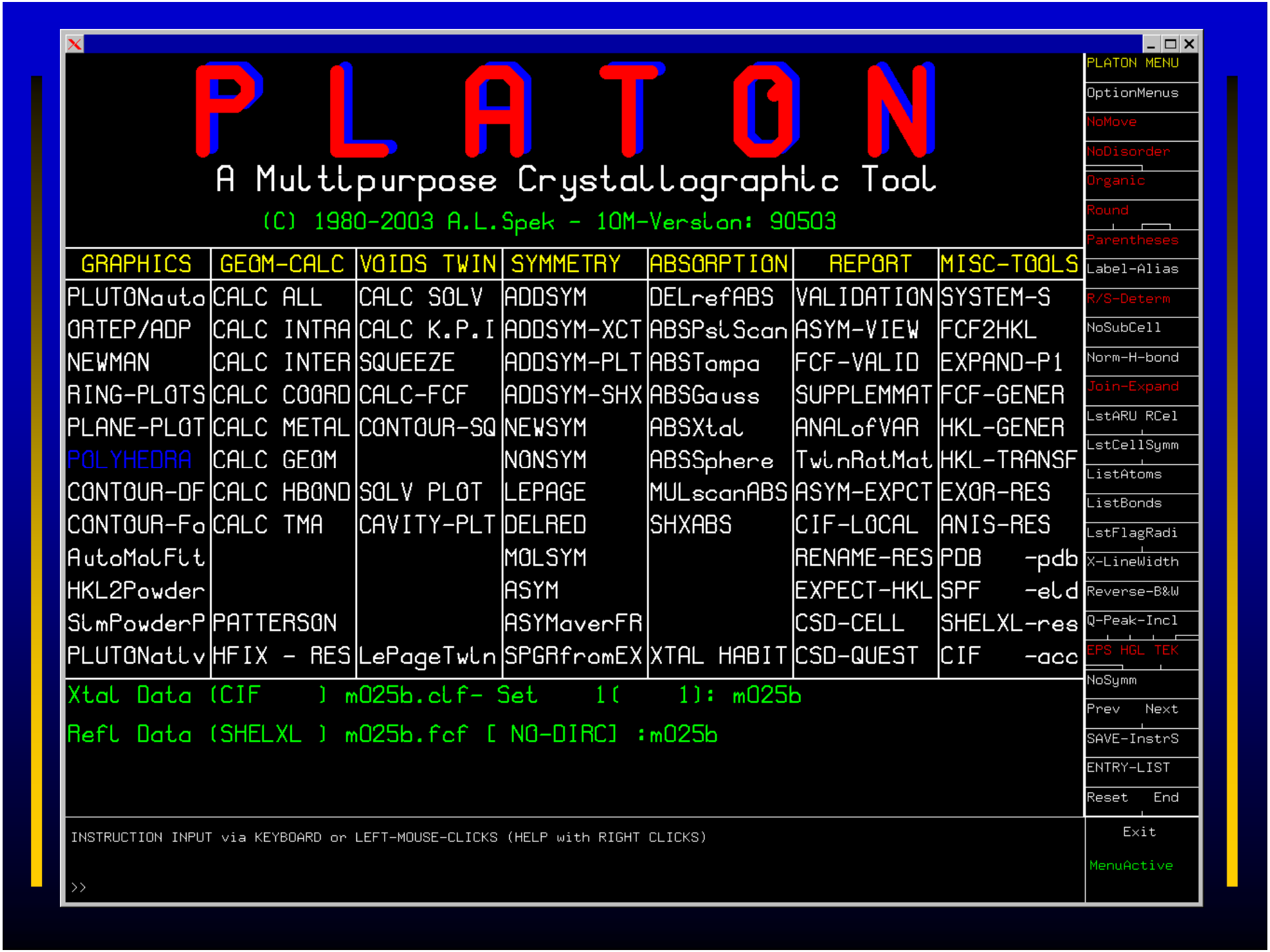
(Herbst-Irmer & Sheldrick, 1998)

Non-merohedral Twins

- Non-merohedral twins should be detected on the diffractometer.
- Indexing problems can be solved with
  - Phi- and Phi/Chi-Scans
  - Dirax as indexing program
- Intensities can be obtained with EvalCCD
  - Output: SHELX HKLF5 file

Non-merohedral Twins

- If the structure can be solved and refined, non-merohedral twins can be detected with PLATON
  - Input file: *compound.fcf*
  - GUI: TwinRotMat
  - Command line: *platon –T compound.fcf*


PLATON
A Multipurpose Crystallographic Tool
(C) 1980-2003 A.L.Spek - 10M-Version: 90503
GRAPHICS
PLUTONauto
ORTEP/ADP
NEWMAN
RING-PLOTS
PLANE-PLOT
POLYHEDRA
CONTOUR-DF
CONTOUR-Fo
AutoMolFit
HKL2Powder
SlmPowderP
PLUTONatlv
GEOM-CALC
CALC ALL
CALC INTRA
CALC INTER
CALC COORD
CALC METAL
CALC GEOM
CALC HBOND
CALC TMA
PATTERSON
HFIX - RES
VOIDS TWIN
CALC SOLV
CALC K.P.I
SQUEEZE
CALC-FCF
CONTOUR-SQ
SOLV PLOT
CAVITY-PLT
LePageTwln
SYMMETRY
ADDSYM
ADDSYM-XCT
ADDSYM-PLT
ADDSYM-SHX
NEWSYM
NONSYM
LEPAGE
DELRED
MOLSYM
ASYM
ASYMaverFR
SPGRfromEX
ABSORPTION
DELrefABS
ABSPslScan
ABSTompa
ABSGauss
ABSXtal
ABSSphere
MULscanABS
SHXABS
XTAL HABIT
REPORT
VALIDATION
ASYM-VIEW
FCF-VALID
SUPPLEMMAT
ANALofVAR
TwlnRotMat
ASYM-EXPCT
CIF-LOCAL
RENAME-RES
EXPECT-HKL
CSD-CELL
CSD-QUEST
MISC-TOOLS
SYSTEM-S
FCF2HKL
EXPAND-P1
FCF-GENER
HKL-GENER
HKL-TRANSF
EXOR-RES
ANIS-RES
PDB -pdb
SPF -eld
SHELXL-res
CIF -acc
Xtal Data (CIF) m025b.clf- Set 1(1): m025b
Refl Data (SHELXL) m025b.fcf [NO-DIRC] :m025b
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
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PLATON MENU
OptionMenus
NoMove
NoDisorder
Organic
Round
Parentheses
Label-Alias
R/S-Determ
NoSubCell
Norm-H-bond
Join-Expand
LstARU RCel
LstCellSymm
ListAtoms
ListBonds
LstFlagRadi
X-LineWidth
Reverse-B&W
Q-Peak-Incl
EPS HGL TEK
NoSymm
Prev Next
SAVE-InstrS
ENTRY-LIST
Reset End
Exit
MenuActive

TwInRotMat

Cell 7.4014 8.0163 8.2906 89.41 77.54 74.65 P-1

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

Criteria: DeltaI/SigmaI .GT. 2.5, DeltaTheta 0.10 Deg.

N(refl) = 2104, N(selected) = 149

2-Rotation about [1 4 0] [0 1 0] Flt: 42(68)

(-0.995	0.499	-0.006)	(h1)	(h2)	Alpha () [] = 0.78 Deg.
(0.020	0.995	-0.024)	* (k1) =	(k2)	TPA = 0.23
(0.000	0.000	-1.000)	(L1) =	(L2)	

2-Rotation about [1 -1 0] [6 -5 -1] Flt: 12(18)

(0.081	-0.919	-0.199)	(h1)	(h2)	Alpha () [] = 1.23 Deg.
(-1.081	-0.081	0.199)	* (k1) =	(k2)	TPA = 0.28
(0.000	0.000	-1.000)	(L1) =	(L2)	

2-Rotation about [0 1 1] [-6 12 11] Flt: 12(22)

(-1.000	0.000	0.000)	(h1)	(h2)	Alpha () [] = 0.33 Deg.
(-0.530	0.044	0.956)	* (k1) =	(k2)	TPA = 0.09
(-0.530	1.044	-0.044)	(L1) =	(L2)	

2-Rotation about [0 1 0] [-4 12 1] Flt: 12(36)

(-1.000	0.000	0.000)	(h1)	(h2)	Alpha () [] = 2.60 Deg.
(-0.596	1.000	0.095)	* (k1) =	(k2)	TPA = 0.22
(0.000	0.000	-1.000)	(L1) =	(L2)	

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

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TwRoMt MENU

TwinMatrix1

TwinMatrix2

TwinMatrix3

TwinMatrix4

HKLF5

End

Exit

MenuActive

TwinRotMat

Cell 7.4046 8.0125 8.2856 89.37 77.49 74.67 P-1

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

Criteria: DeltaI/SigmaI .GT. 5.0, DeltaTheta 0.10 Deg.

N(refl) = 2103, N(selected) = 166

2-Rotation about (1 4 0) [0 1 0] Flt: 53(82)

(-0.995 0.499 -0.006) (h1) (h2) Alpha () [] = 0.82 Deg.
(0.021 0.995 -0.025) * (k1) = (k2) TPA = 0.98
(0.000 0.000 -1.000) (L1) = (L2)

2-Rotation about (0 1 0) [-4 12 1] Flt: 20(52)

(-1.000 0.000 0.000) (h1) (h2) Alpha () [] = 2.64 Deg.
(-0.595 1.000 0.094) * (k1) = (k2) TPA = 0.68
(0.000 0.000 -1.000) (L1) = (L2)

2-Rotation about (1 1 0) [9 7 -2] Flt: 15(35)

(0.140 0.860 -0.230) (h1) (h2) Alpha () [] = 1.11 Deg.
(1.140 -0.140 -0.230) * (k1) = (k2) TPA = 0.61
(0.000 0.000 -1.000) (L1) = (L2)

2-Rotation about (1 0 1) [12 -3 8] Flt: 12(24)

(0.189 -0.300 0.811) (h1) (h2) Alpha () [] = 0.52 Deg.
(0.000 -1.000 0.000) * (k1) = (k2) TPA = 0.65
(1.189 -0.300 -0.189) (L1) = (L2)

TwRoMt MENU

TwinMatrix1
TwinMatrix2
TwinMatrix3
TwinMatrix4
HKLF5
End

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

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Exit

MenuActive

TwinRotMat

Cell 7.4104 8.0097 8.2895 89.38 77.51 74.62 P-1

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

Criteria: DeltaI/SigmaI .GT. 2.5, DeltaTheta 0.10 Deg.

N(refl) = 2109, N(selected) = 206

2-Rotation about [1 4 0] [0 1 0] Flt: 74(99)

(-0.996	0.499	-0.006)	(h1)	(h2)	Alpha () [] = 0.76 Deg.
(0.018	0.996	-0.024) *	(k1)	= (k2)	TPA = 0.47
(0.000	0.000	-1.000)	(l1)	= (l2)	

2-Rotation about [0 1 0] [-4 12 1] Flt: 22(51)

(-1.000	0.000	0.000)	(h1)	(h2)	Alpha () [] = 2.62 Deg.
(-0.596	1.000	0.094) *	(k1)	= (k2)	TPA = 0.35
(0.000	0.000	-1.000)	(l1)	= (l2)	

2-Rotation about [1 0 1] [12 -3 8] Flt: 16(27)

(0.189	-0.301	0.811)	(h1)	(h2)	Alpha () [] = 0.54 Deg.
(0.000	-1.000	0.000) *	(k1)	= (k2)	TPA = 0.28
(1.189	-0.301	-0.189)	(l1)	= (l2)	

2-Rotation about [1 1 0] [9 7 -2] Flt: 16(38)

(0.138	0.862	-0.229)	(h1)	(h2)	Alpha () [] = 1.09 Deg.
(1.138	-0.138	-0.229) *	(k1)	= (k2)	TPA = 0.36
(0.000	0.000	-1.000)	(l1)	= (l2)	

TwRoMt MENU

TwinMatrix1

TwinMatrix2

TwinMatrix3

TwinMatrix4

HKLF5

End

Exit

MenuActive

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

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Non-merohedral Twins

- TwinRotMat has an option to generate a HKLF5 file based on the twin matrix.
- Warning: The amount of overlapping reflections depends not only on the twin matrix:
  - (Anisotropic) mosaicity
  - Crystal size
  - Detector distance and rotation angle
  - Etc.
- Better: EvalCCD

Example

- Three different crystals of the same compound
- Crystal 1 [BASF 0.0878(19)]:
  - R1 (obs.) 0.0233, wR2 (all) 0.0591, -0.47/1.38 e/Å^3
  - R1 (obs.) 0.0211, wR2 (all) 0.0534, -0.38/0.50 e/Å^3
- Crystal 2 [BASF 0.5482(7)]:
  - R1 (obs.) 0.1323, wR2 (all) 0.3361, -2.29/12.99 e/Å^3
  - R1 (obs.) 0.0282, wR2 (all) 0.0693, -0.59/0.64 e/Å^3
- Crystal 3 [BASF 0.228(2)]::
  - R1 (obs.) 0.0481, wR2 (all) 0.1340, -0.62/3.83 e/Å^3
  - R1 (obs.) 0.0261, wR2 (all) 0.0658, -0.48/0.51 e/Å^3

Pseudo-merohedral Twins

- These are non-merohedral twins, where all reflections seem to overlap because of the limited resolution of the equipment.
- Because cell parameters are temperature dependent, a temperature change can lead to splitting of reflections.
- Pseudo-merohedral twins are optimally suited for TwinRotMat.

Absorption Correction

- With reflections in HKLF4 format, all methods of absorption correction in PLATON are applicable:
- ABSPsiScan
- ABSTompa/ABSGauss
- MULscanABS
- DELrefABS
  - TWIN/BASF card in *compound.res* is treated properly.

Absorption Correction

- With reflections in HKLF5 format, only analytical absorption corrections are possible (ABST/ABSG).
- Direction cosines of all twin domains must be based on the same orientation matrix (e.g. of the first domain).
- In PLATON the option *check direction cosines* must be switched off.

Absorption Correction

- The shape of the crystal can be optimized using the program EUHEDRAL based on a HKLF4 file.
- The refined crystal shape can then be applied to a HKLF5 file using PLATON.

EUHEDRAL

- A computer program for the refinement of the crystal shape for an analytical absorption correction

EUHEDRAL

- The difficulty with the analytical absorption correction is the determination of the crystal shape
  - Errors in crystal size measurement
  - Presence of other absorbing material (glass, oil, grease)
  - Unclear face indices

EUHEDRAL

- In many laboratories the crystal shape is refined before the absorption correction is performed
- We want to offer a computer program for this purpose, which
  - makes use of the redundancy of area detector data
  - is as flexible as possible
  - is independent of the diffractometer type
  - is running on many UNIX/LINUX platforms

EUHEDRAL

- EUHEDRAL was developed in close relation to the PLATON package.
- A running version of PLATON is therefore needed. (http://www.cryst.chem.uu.nl/platon)
- The reflection data must contain direction cosines as described for SHELX76 (crystal coordinate system).

EUHEDRAL

- All minimizations in EUHEDRAL are based on a merging R-value R2

$$R2 = w_1 * R_{int} + w_2 * R_{psi}$$

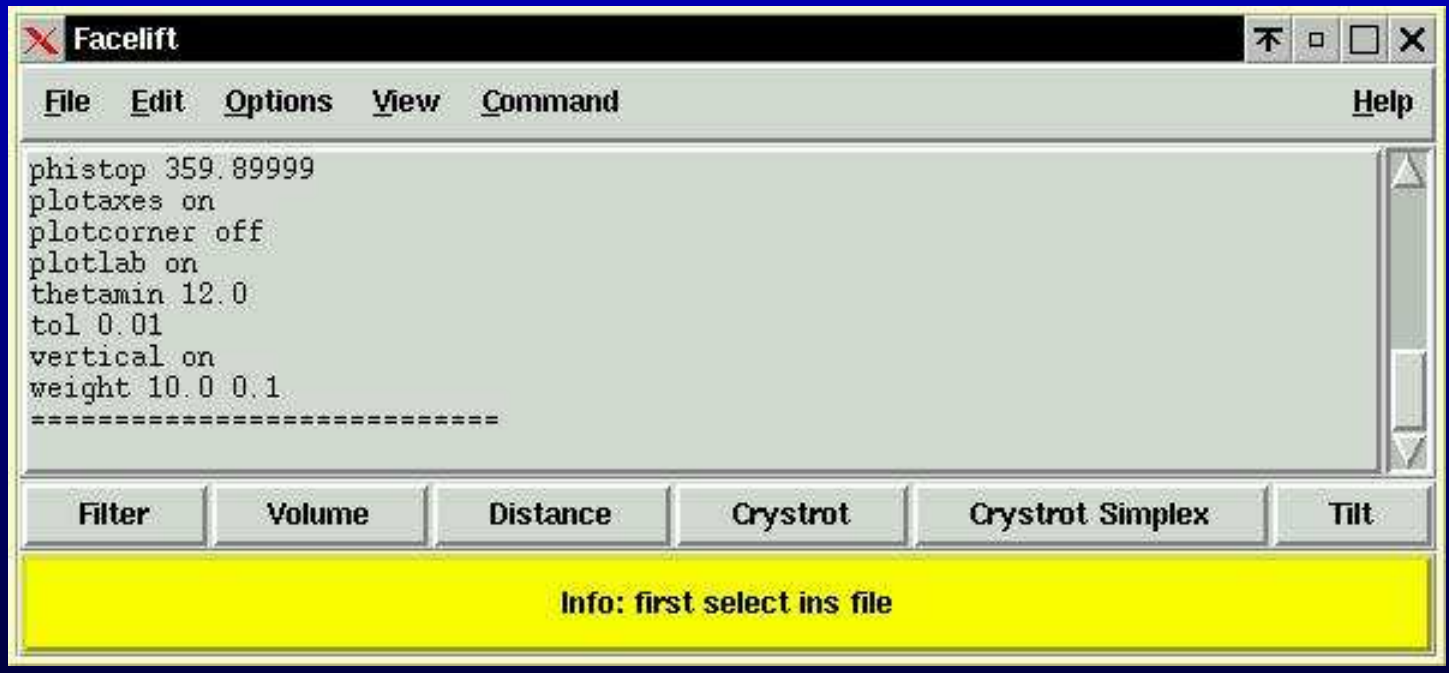
$$R_{int} = \sum [abs(int - intmean)] / \sum (int)$$

$$R_{psi} = \frac{1}{n} \sum [(intmax / intmin) - 1]$$

EUHEDRAL

- The program EUHEDRAL can be run on the command line
- or with a graphical user interface (GUI) based on Tcl/Tk

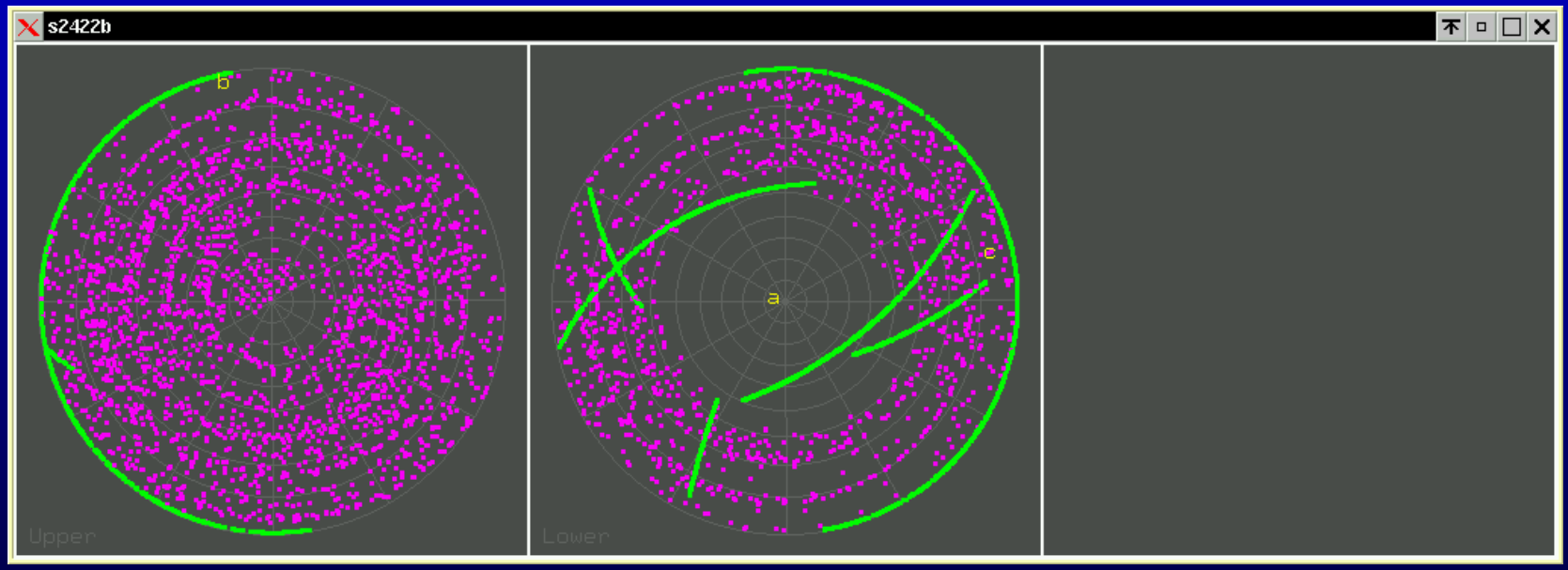
EUHEDRAL


Facelift
File Edit Options View Command Help
phistop 359.89999
plotaxes on
plotcorner off
plotlab on
thetamin 12.0
tol 0.01
vertical on
weight 10.0 0.1
==========
Filter
Volume
Distance
Crystrot
Crystrot Simplex
Tilt
Info: first select ins file

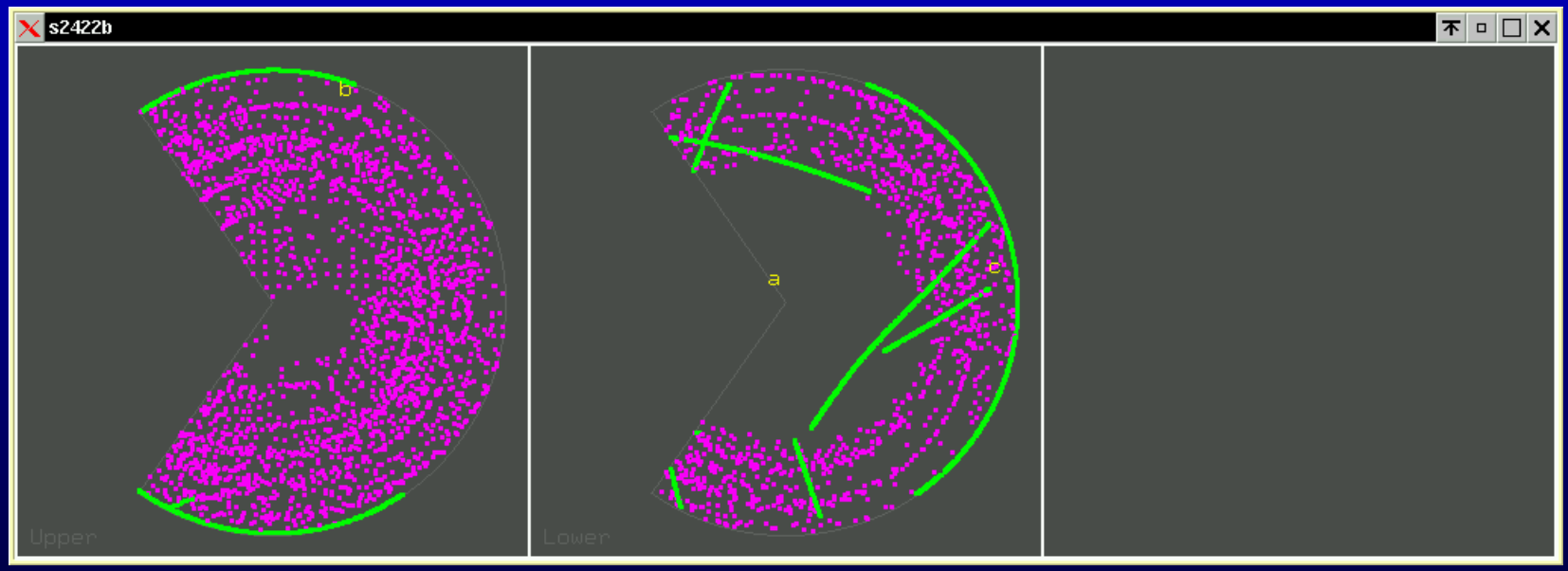
EUHEDRAL

- In a first step the number of reflections is reduced with the routine *filter*.
- The suitability of this subset can be judged from different projections.
- Several filter criteria are available: Minimal intensity, minimal theta, minimal redundancy, and angular distribution.

EUHEDRAL



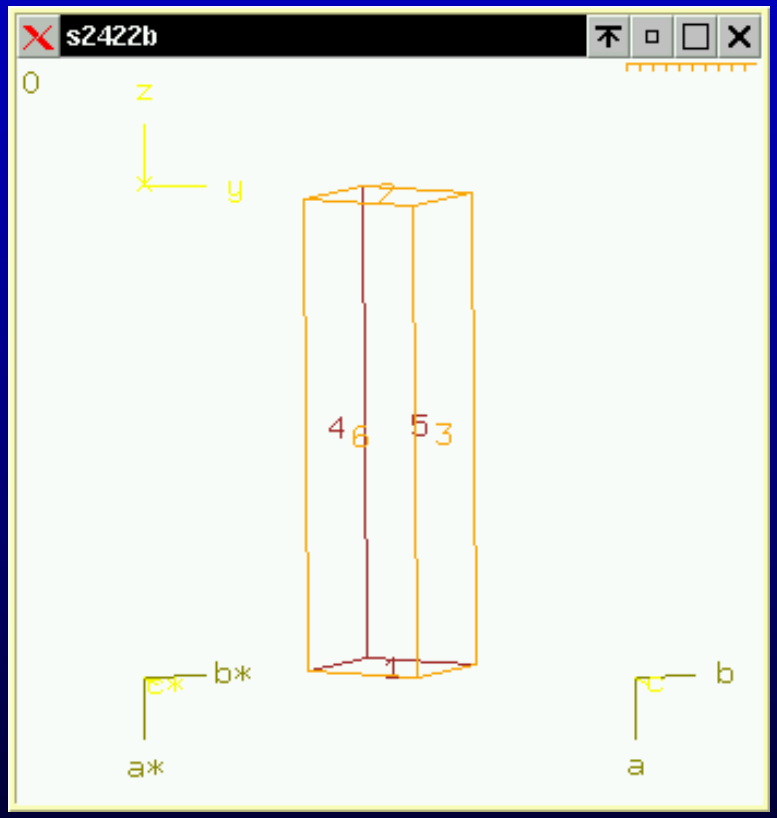
EUHEDRAL



EUHEDRAL

- Situation 1
  - Start with a measured crystal shape (faces are indexed and crystal size determined)
  - Refine volume and distances
  - Fine-tune the description by tilting the faces

EUHEDRAL



EUHEDRAL

- Ex. s2422b (Pt-complex, μ = 13.60 mm^{-1})
- Without correction: R2=1.069
- Measured crystal shape+size: R2=0.592
- Refined crystal shape+size: R2=0.497

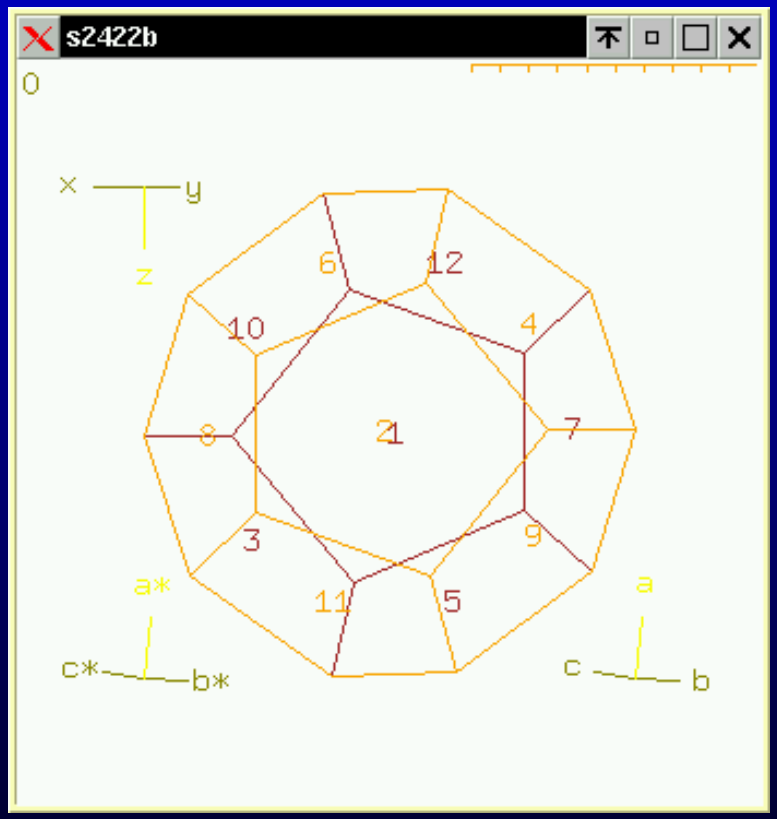
EUHEDRAL

- Situation 2
  - Crystal shape known, faces not indexed
  - Refinement of crystal orientation with respect to the reciprocal axes
  - Then refinement of volume, distance and tilt

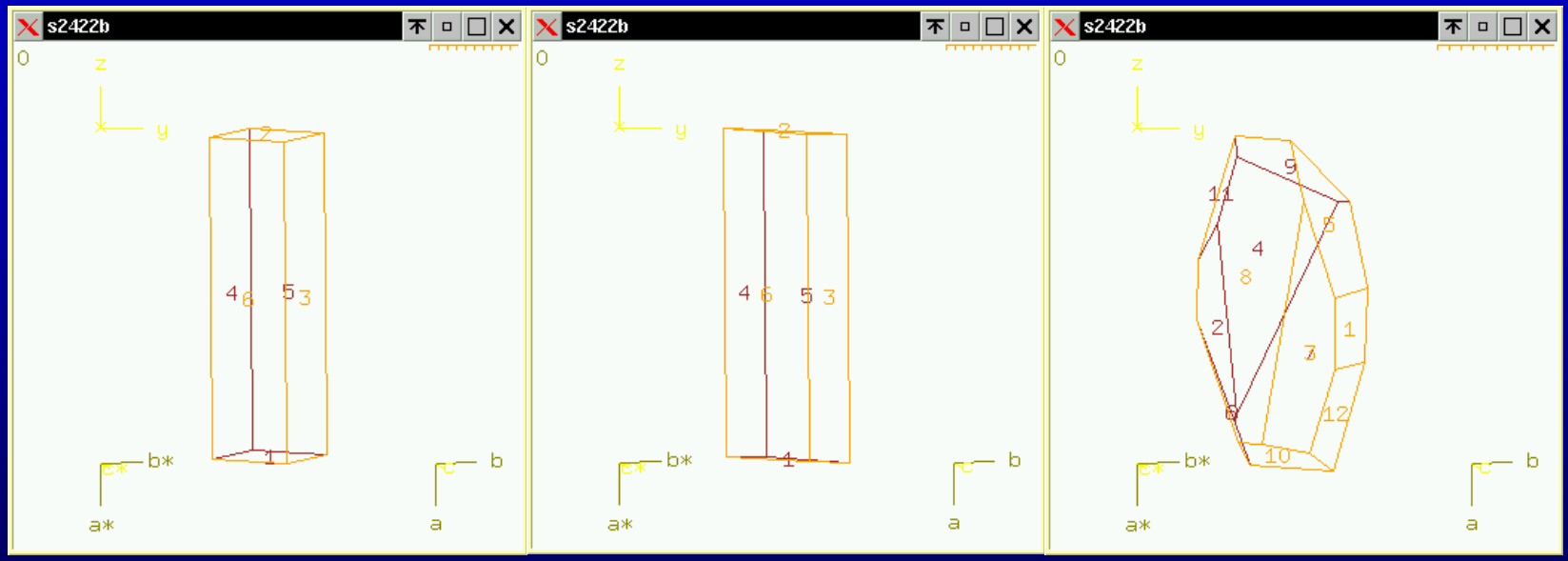
EUHEDRAL

- Situation 3
  - Nothing known about crystal size and shape
  - Start with a dodecahedron model (EUHEDRAL offers 7 different dodecahedrons)
  - Refinement of volume and distance
  - Refinement of orientation and tilt

EUHEDRAL



EUHEDRAL



R2=0.592 R2=0.497 R2=0.480

EUHEDRAL

- No correction
  - R_{int}=0.1082
  - R1(obs. refl.)=0.0353
  - Res. dens. –3.05/2.05
  - Ellipticity Pt: 1.99
- EUHEDRAL
  - R_{int}=0.0553
  - R1(obs. refl.)=0.0310
  - Res. dens. –2.20/1.13
  - Ellipticity Pt: 1.71

EUHEDRAL

- EUHEDRAL
  - 0.101-0.342 transmission
  - R_{int}=0.0553
  - R1(obs. refl.)=0.0353
  - Res. dens. –2.20/1.13
  - Ellipticity Pt: 1.71
- DELABS (PLATON)
  - 0.280-0.728 transmission
  - R_{int}=0.0504
  - R1(obs. refl.)=0.0291
  - Res. dens. –1.64/1.08
  - Ellipticity Pt: 1.58

EUHEDRAL

- Home page:
  www.crystal.chem.uu.nl/distr/euhedral/

Thanks

- Many thanks
  - A.L. Spek and A.M.M. Schreurs for useful discussions.
  - Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) for financial support.