

Twinning tools in PLATON

Detection and Absorption Correction

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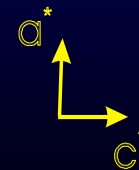
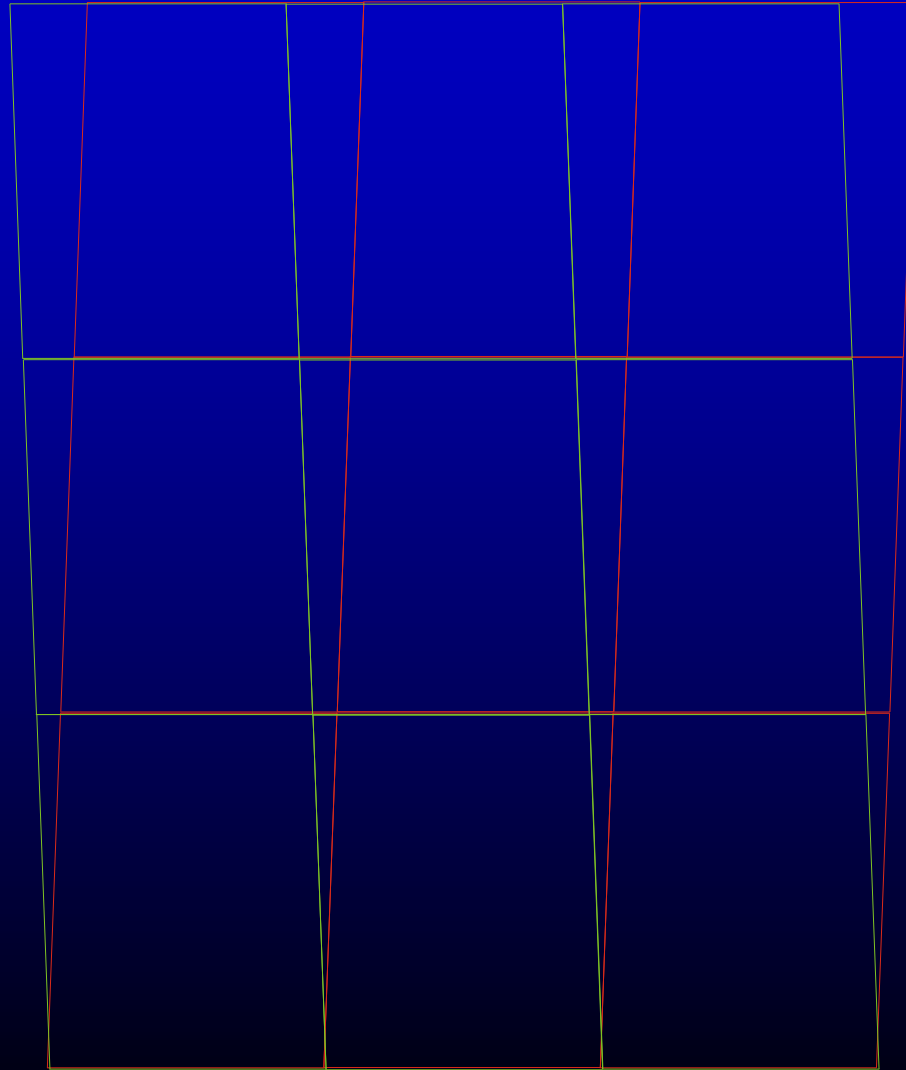
Merohedral Twins

- 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

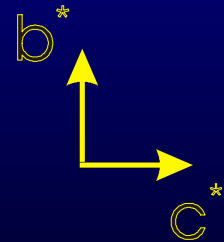
- Twin operation does not belong to the Laue group or point group of the crystal.
- In practice there are three types of reflections:
 - Reflections belonging to only one lattice.
 - Completely overlapping reflections belonging to both lattices.
 - Partially overlapping reflections belonging to both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

Non-merohedral Twins



Non-merohedral Twins

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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 | GEOM-CALC | VOIDS TWIN | SYMMETRY | ABSORPTION | REPORT | MISC-TOOLS |
|------------------------|------------|------------|-------------------------|-------------------------|------------------------|------------|
| PLUTON _{auto} | CALC ALL | CALC SOLV | ADDSYM | DEL _{ref} ABS | VALIDATION | SYSTEM-S |
| ORTEP/ADP | CALC INTRA | CALC K.P.I | ADDSYM-XCT | ABSP _{sL} Scan | ASYM-VIEW | FCF2HKL |
| NEWMAN | CALC INTER | SQUEEZE | ADDSYM-PLT | ABST _{empa} | FCF-VALID | EXPAND-P1 |
| RING-PLOTS | CALC COORD | CALC-FCF | ADDSYM-SHX | ABSG _{auss} | SUPPLEMENT | FCF-GENER |
| PLANE-PLOT | CALC METAL | CONTOUR-SQ | NEWSYM | ABSX _{tal} | ANAL _{of} VAR | HKL-GENER |
| POLYHEDRA | CALC GEOM | | NONSYM | ABSS _{sphere} | TwlnRotMat | HKL-TRANSF |
| CONTOUR-DF | CALC HBOND | SOLV PLOT | LEPAGE | MUL _{scan} ABS | ASYM-EXPT | EXOR-RES |
| CONTOUR-F _o | CALC TMA | CAVITY-PLT | DELRED | SHXABS | CIF-LOCAL | ANIS-RES |
| AutoMolFit | | | MOLSYM | | RENAME-RES | PDB -pdb |
| HKL2Powder | | | ASYM | | EXPECT-HKL | SPF -eld |
| SLmPowderP | PATTERSON | | ASYM _{aver} FR | | CSD-CELL | SHELXL-res |
| PLUTON _{atLv} | HFIX - RES | LePageTwln | SPGR _{from} EX | XTAL HABIT | CSD-QUEST | CIF -acc |

Xtal Data (CIF) m025b.cif- 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

LetARU RCel

LetCellSymm

ListAtoms

ListBonds

LetFlagRadi

X-LineWidth

Reverse-B&W

Q-Peak-Incl

EPS HGL TEK

NoSymm

Prev Next

SAVE-InstrS

ENTRY-LIST

Reset End

Exit

MenuActive

TwlnRotMat

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

TwLnRotMat

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)

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

>>

TwRoMt MENU

TwinMatrix1

TwinMatrix2

TwinMatrix3

TwinMatrix4

HKLF5

End

Exit

MenuActive

TwLnRotMat

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)

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

>>

TwRoMt MENU

TwinMatrix1

TwinMatrix2

TwinMatrix3

TwinMatrix4

HKLF5

End

Exit

MenuActive

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/Å³
 - R1 (obs.) 0.0211, wR2 (all) 0.0534, -0.38/0.50 e/Å³
- Crystal 2 [BASF 0.5482(7)]:
 - R1 (obs.) 0.1323, wR2 (all) 0.3361, -2.29/12.99 e/Å³
 - R1 (obs.) 0.0282, wR2 (all) 0.0693, -0.59/0.64 e/Å³
- Crystal 3 [BASF 0.228(2)]:
 - R1 (obs.) 0.0481, wR2 (all) 0.1340, -0.62/3.83 e/Å³
 - R1 (obs.) 0.0261, wR2 (all) 0.0658, -0.48/0.51 e/Å³

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

$$R_2 = w_1 * R_{int} + w_2 * R_{psi}$$

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

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

EUHEDRAL

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

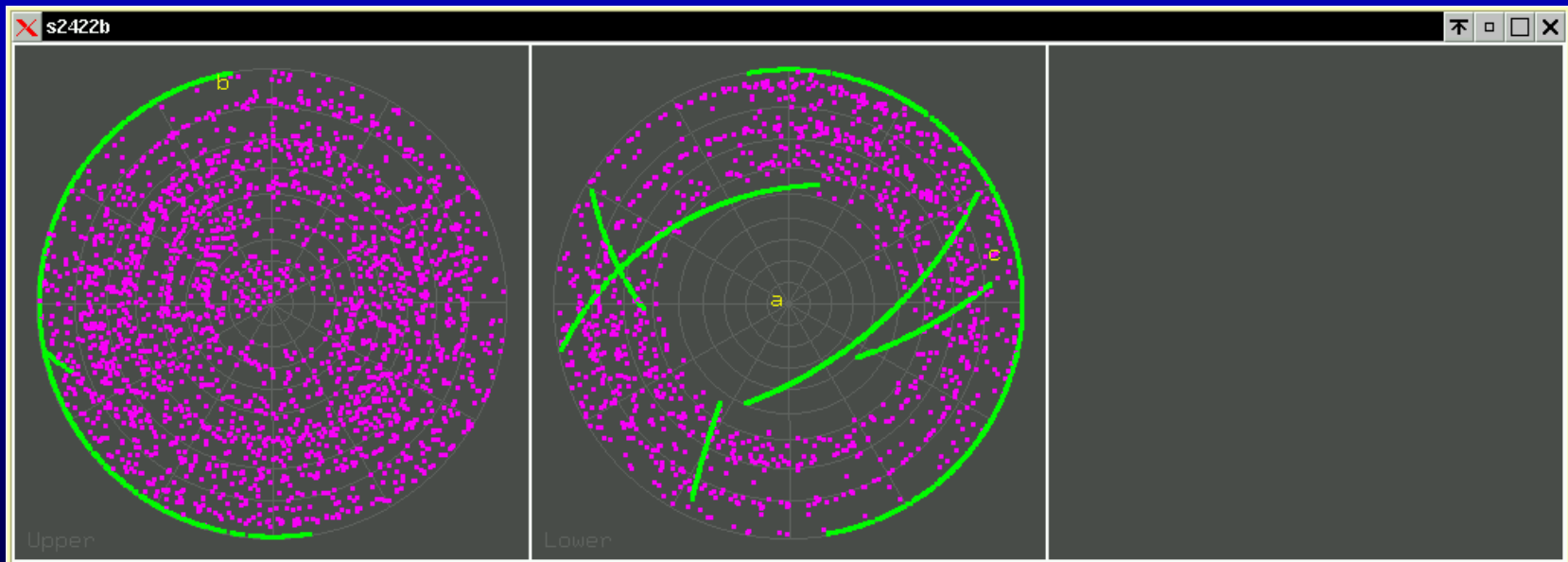
EUHEDRAL



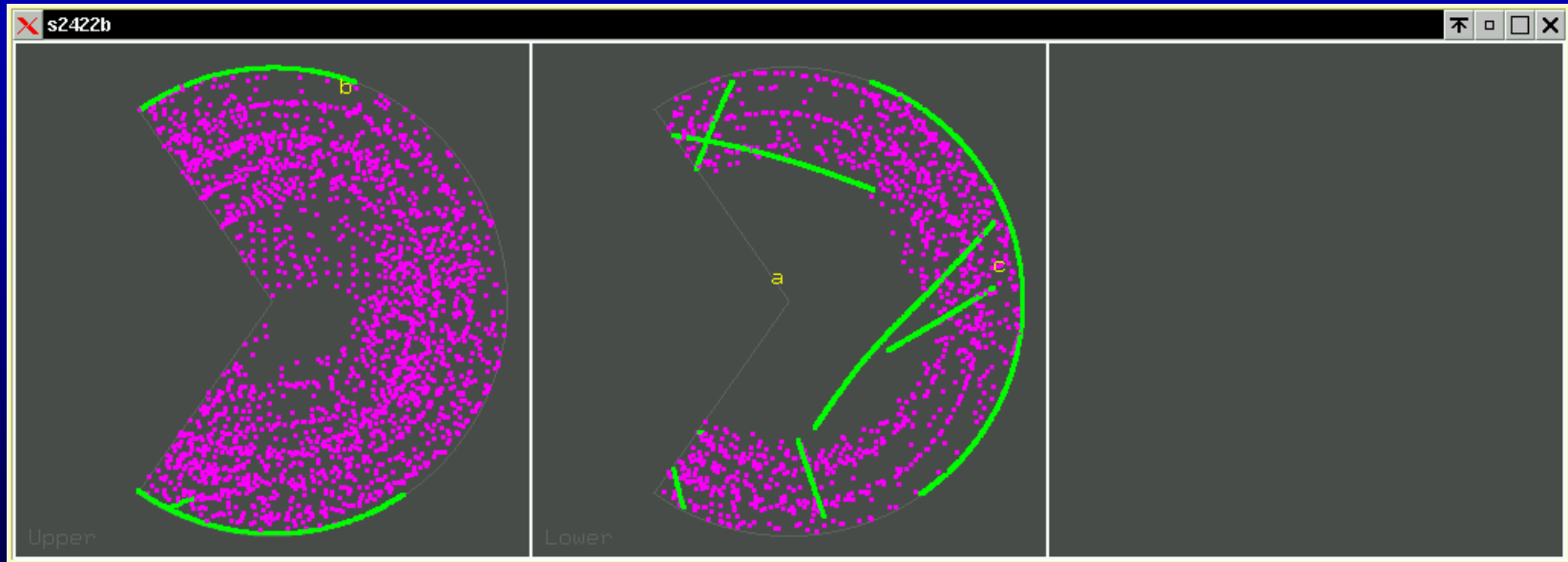
EUHEDRAL

- 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



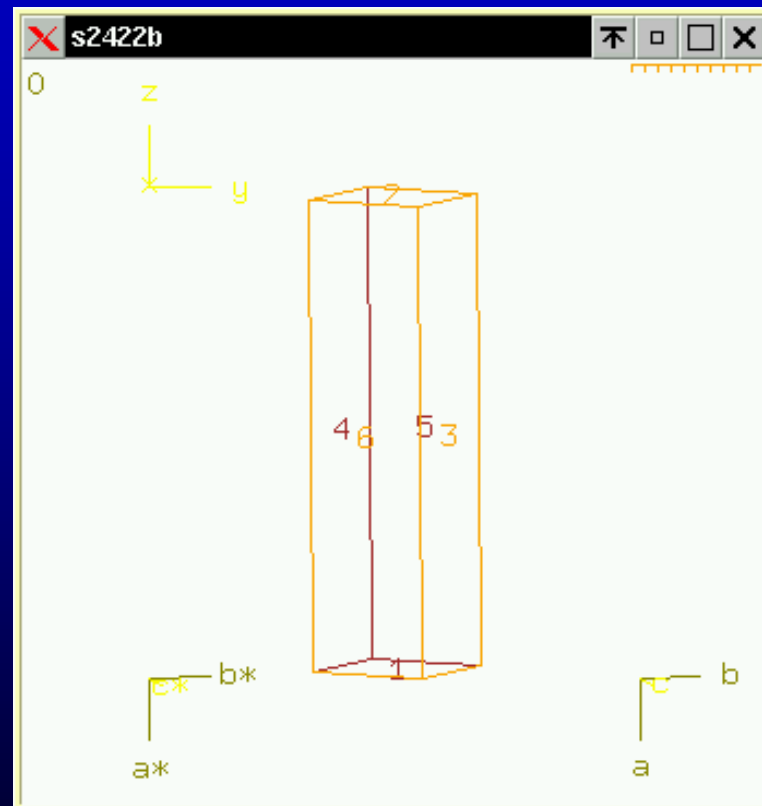
EUHEDRAL



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, $\mu = 13.60 \text{ mm}^{-1}$)
- Without correction: $R2=1.069$
- Measured crystal shape+size: $R2=0.592$
- Refined crystal shape+size: $R2=0.497$

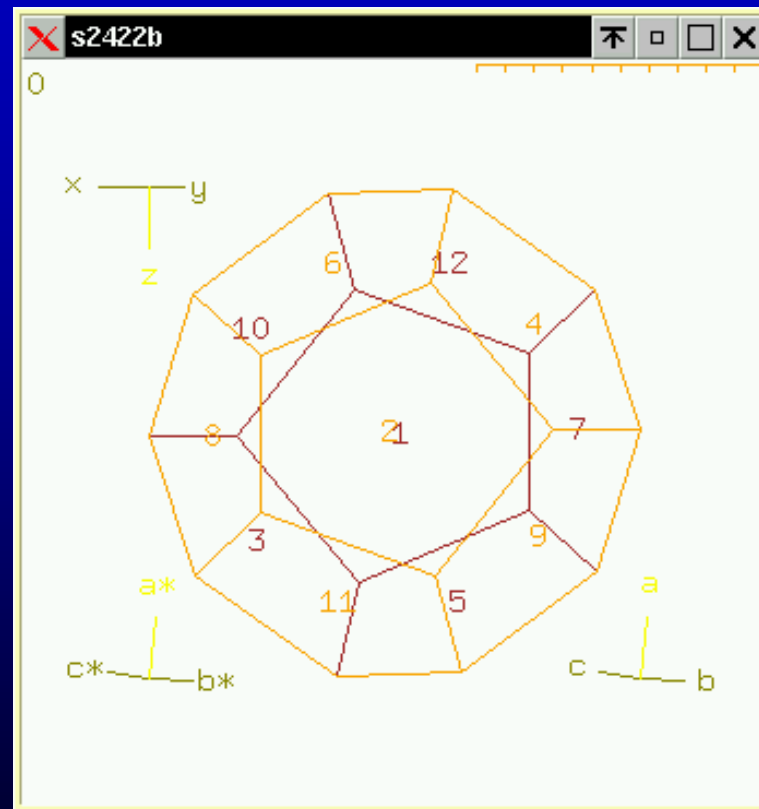
EUHEDRAL

- 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

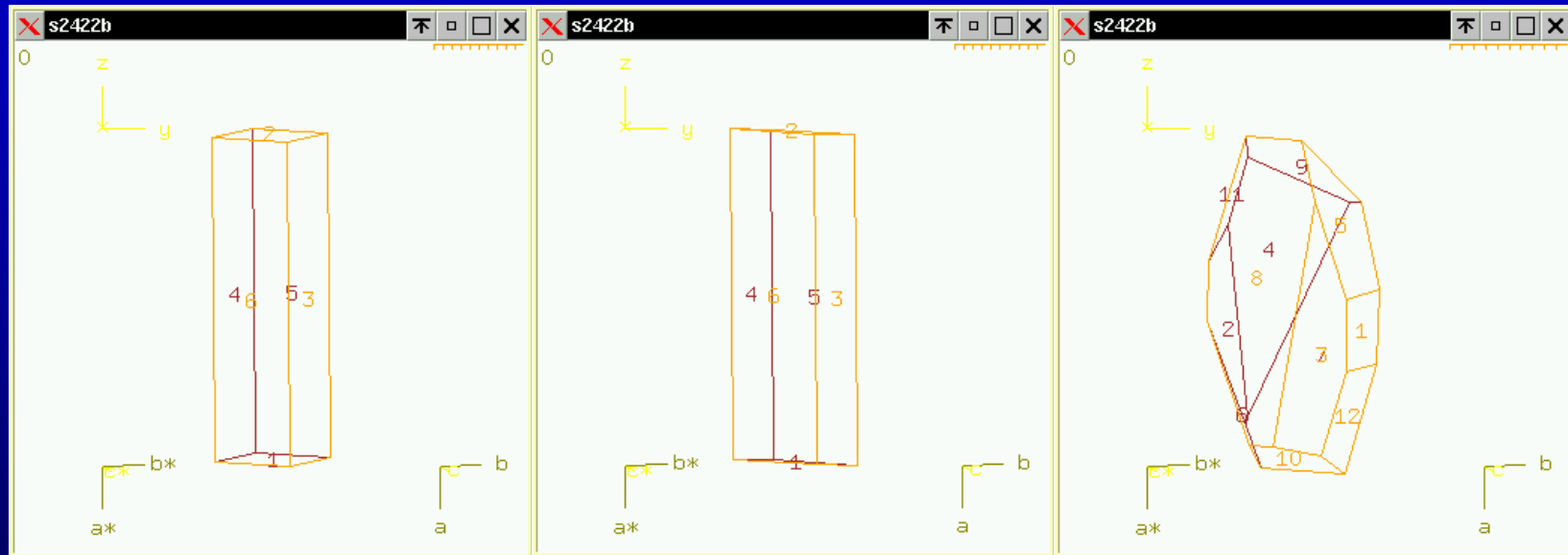
EUHEDRAL

- 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
 - $R_{\text{int}}=0.1082$
 - $R1(\text{obs. refl.})=0.0353$
 - Res. dens. $-3.05/2.05$
 - Ellipticity Pt: 1.99
- EUHEDRAL
 - $R_{\text{int}}=0.0553$
 - $R1(\text{obs. refl.})=0.0310$
 - Res. dens. $-2.20/1.13$
 - Ellipticity Pt: 1.71

EUHEDRAL

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