

Algorithms and methods for the handling of twin crystals

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

Outline

- Introduction
- Coset decomposition to find twin laws
- Le Page algorithm
- Non-systematic extinctions
- ROTAX
- TwinRotMat
- Difference Fourier synthesis

Definition

Twinning is the oriented association of two or more individuals of the same crystalline phase, in which pairs of individuals are related by a geometrical operation termed *twin operation*.

http://www.lcm3b.uhp-nancy.fr/mathcryst/twins.htm

Non-merohedral Twins

- Twin operation does not belong to the Laue group or point group of the crystal.
- Reflections of the two lattices do not overlap exactly.
- Indexing software can be used to find the twin operation:
 - Dirax (A.J.M. Duisenberg)
 - Cellnow (G.M. Sheldrick)
- Non-merohedral twins should be handled by the integration software.

(Pseudo-)merohedral Twins

- The reciprocal lattices of all twin components superimpose.
- Consequently, the diffraction pattern is similar to a single crystal.
- Intensities of the Bragg reflections are modified due to the twinning.
- The (point group) symmetry of the crystal is lower than the symmetry of the lattice.

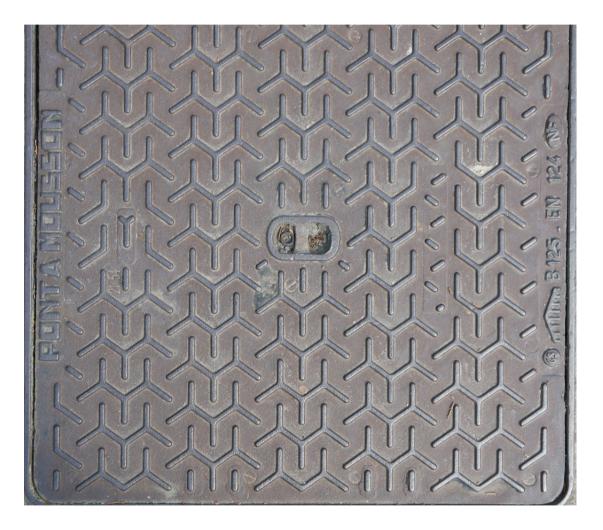
Coset decomposition

H. D. Flack (1987). *Acta Cryst.* **A43**, 564-568

Point groups

 Good news: here, only point groups matter!

Oviedo (19-8-2011)



Holohedries

- We call the maximum point symmetry of a crystal system "holohedry". It is thus the point symmetry of the lattice.
- Consequently, there are seven holohedries:
 - cubic: m-3m
 - hexagonal : 6/mmm
 - tetragonal : 4/mmm
 - trigonal : -3m
 - orthorhombic : mmm
 - monoclinic : 2/m
 - triclinic : -1

Definitions

- **Merohedral twins:** The twin element belongs to the holohedry of the lattice, but not to the point group of the crystal. Reflections overlap exactly.
- **Pseudo-merohedral twins**: The symmetry of the crystal belongs to a different holohedry as the symmetry of the lattice. Overlap of reflections is only approximate and depends on temperature, pressure, impurities, etc.

Theory

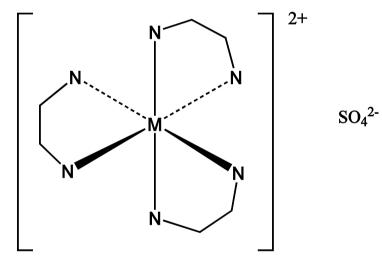
- *H* is the (point group) symmetry of the crystal.
- *G* is the (point group) symmetry of the lattice.
- H is a subgroup of G.
- The coset decomposition of *G* with respect to *H* gives the possible twin operations.

Procedure

- the subgroup *H* is the first coset
- if g2 ∈ G and g2 ∉ H, then g2H is the second coset
- if $g3 \in G$ and $g3 \notin H$ and $g3 \notin g2H$ then g3H is the third coset
- continue until no element of *G* is left

Example

M. Lutz (2010). *Acta Cryst.* **C66**, m330-m335 Room temperature: P-31c





Zinc complex

Room temperature: P-31c Low temperature: P-3 (twinned)

High temperature: sulfate disordered (D_3 site) Low temperature: sulfate ordered (C_3 site)

Metric symmetry: 6/mmm Crystal symmetry: -3

Zinc complex

- Supergroup 6/mmm {1, 3⁺, 3⁻, 2, 6⁻, 6⁺, 2, 2, 2, 2, 2, 2, 2, -1, -3⁺, -3⁻, m, -6⁻, -6⁺, m, m, m, m, m, m]
- 4 Cosets

 $\{1, 3^+, 3^-, -1, -3^+, -3^-\} \cup \\ \{2, 6^-, 6^+, m, -6^-, -6^+\} \cup \\ \{2, 2, 2, m, m, m\} \cup \\ \{2, 2, 2, m, m, m\} \}$

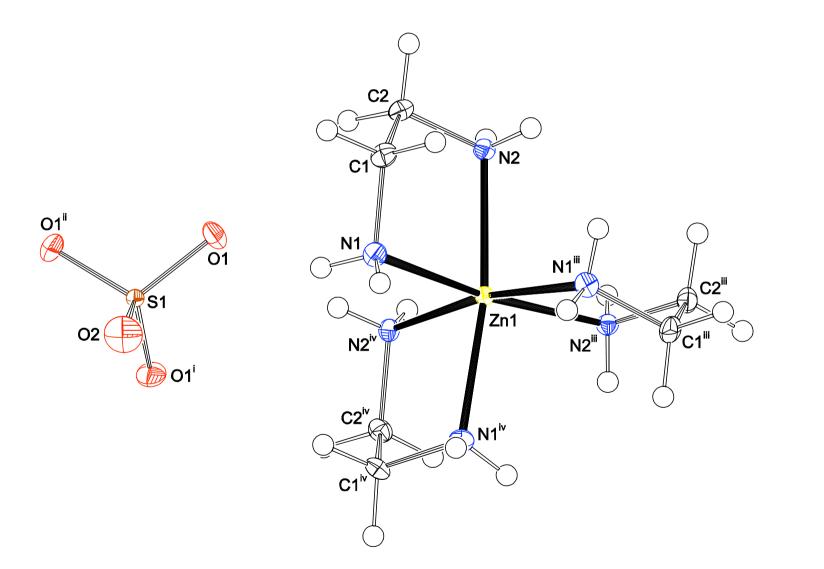
• Note: Bilbao Crystallographic Server helps! (In the moment, there is only coset decomposition of space groups).

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	Lefference (de la compactifica de fille compactifica)	
	Left coset decomposition of the group 191 (P	
	with respect to the subgroup 147 (<i>P</i> -3))
	G = H + g ₁ H + g ₂ H + + g _n H	
The transformation matrix tha	t relates the basis of the supergroup G=191 (<i>P6/mmm</i>) with that of the subgroup H=147 (<i>P</i> -3)) is:
[1 0 0][0]	
	0] 0]	
	tion of G with respect to H (in the basis of H) are given below:	
	tion of 6 with espect to 11 (in the basis of 1) are given below.	
Coset 1:		
(x,y,z) (-y,x-y,z)		
(-x+y,-x,z)		
(-x,-y,-z) (y,-x+y,-z)		
(x-y,x,-z)		
Coset 2:		
(-x,-y,z)		
(y,-x+y,z)		
(x-y,x,z) (x,y,-z)		
(-y, x-y, -z)		
(-x+y,-x,-z)		
Coset 3:		
Done		

Important: The 4 cosets are provided for (x,y,z).

To use it on (h,k,l) you must use the transpose matrix.

Zinc complex



Copper complex

Room temperature: P-31c

Low temperature: P-1 (twinned, non-merohedral)

High temperature: complex and sulfate disordered $(D_3 \text{ sites})$

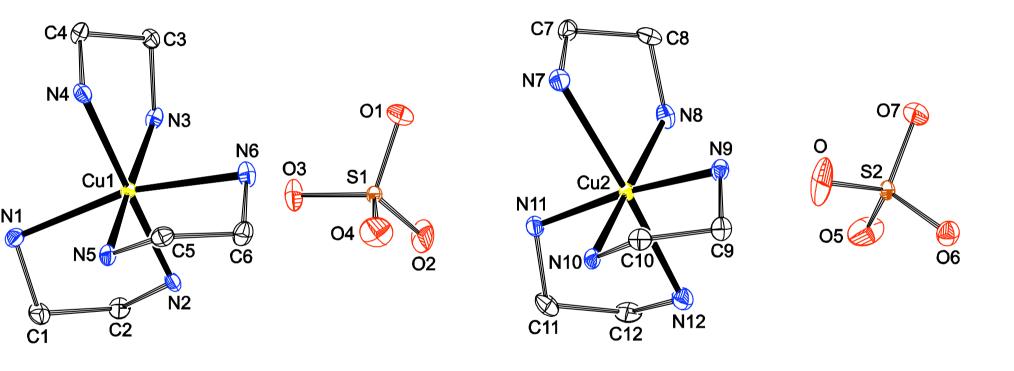
Low temperature: complex and sulfate ordered $(C_1 \text{ sites})$

Metric symmetry at room temperature: 6/mmm Crystal symmetry at low temp.: -1 (b=2*a, γ = 119.8°)

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Coset Decomposition ÷	*					
Bilbao Crystallographic Server → Full cosets	Help					
Left coset decomposition of the group 191 (<i>P6/mmm</i>) with respect to the subgroup 2 (<i>P</i> -1)						
G = H + g ₁ H + g ₂ H + + g _n H	E					
The transformation matrix that relates the basis of the supergroup G=191 (P6/mmm) with that of the subgroup H=2 (P-1) is:						
[0 1 0][0] [0 0 1][0]						
The cosets in the decomposition of G with respect to H (in the basis of H) are given below:						
Coset 1:						
(x,y,z) (-x,-y,-z)						
Coset 2:						
(-y, x-y, z) (y, -x+y, -z)						
Coset 3:						
(-x+y,-x,z) (x-y,x,-z)						
Coset 4:						
(-x, -y, z) (x, y, -z)	-					
Done						

12 cosets! (5 twin domains occupied.)

Copper complex



Algorithm, Step 1

- As a first step, the metric symmetry must be determined:
 - -Y. Le Page (1982) J. Appl. Cryst. 15, 255-259
 - H. Zimmermann, H. Burzlaff (1985) *Z. Kristallogr.* **170**, 241-146
 - R. W. Grosse-Kunstleve, N. K. Sauter,
 P. D. Adams (2004) *Acta Cryst.* A60, 1-6

Algorithm, Step 2

Coset decomposition: Cross-out the operations in *G*

Set all operations in G TRUE

Loop over G[i]

IF G[i] is flagged TRUE, then loop over H[j]

Loop over G[k]. If G[k]==G[i]H[j] then flag G[k] as FALSE

END LOOP G[k]

END LOOP H[j]

ENDIF

END LOOP G[i]

Le Page algorithm

Y. Le Page (2002). J. Appl. Cryst. **35**, 175-181

Law of Mallard

- A twin plane is always a lattice plane.
- A twin axis is always a lattice row.

http://www.lcm3b.uhp-nancy.fr/mathcryst/twins.htm

Sublattice

Problem: The crystal lattice is sometimes a sublattice of the twin lattice. Because all reflections overlap, it is difficult for the indexing software to determine the correct sublattice.

Twin index

 m_1 , m_T : multiplicity of the unit cell (Individual, Twin)

 V_1 , V_T : volume of the unit cell (Individual, Twin)

$$\Sigma = \frac{V_T m_I}{V_I m_T}$$

m = 1 (P, R lattice)= 2 (A, B, C, I lattice) = 4 (F lattice)

M. Nespolo, G. Ferraris (2004). Acta Cryst. A60, 89-95

Principles

- The Le Page algorithm for unit cell reduction is searching for all twofold axes in a crystal lattice. A vector in the direct lattice is a twofold axis, if there is a collinear vector in the reciprocal lattice (angle between direct and reciprocal vector δ = 0°).
- The Le Page algorithm for twins is an extension of this. It searches for twofold axes in sub- and superlattices and δ is allowed to deviate slightly from 0° (obliquity).

Definitions

	$\delta = 0^{\circ}$	$\delta > 0^{o}$
$\Sigma = 1$	merohedry	pseudomerohedry
$\Sigma > 1$	reticular merohedry	reticular pseudomerohedry

Mallard's criterion:

$$\Sigma \leq 5$$

 $\delta \leq 6^{\circ}$

Le Page algorithm (1)

- Determine the reduced (primitive) unit cell
- Generate sub- and supercells by looping over the (unique) matrices, given in A. Santoro, A.D. Mighell (1972). Acta Cryst. A28, 284-287
 - -7 matrices with *det* = 2
 - -13 matrices with *det* = 3
 - -35 matrices with *det* = 4

Le Page algorithm (2)

- h reciprocal-lattice vector
- u direct-lattice vector
- $h \times u = 0$

 $h \cdot u = n$

In unit cell reduction *n* can take values of 1 and 2.

In the twin algorithm *n* can be larger than 2. The modulus of an index of **h** can not exceed 3Σ (Σ = twin index).

Example 1: djurleite Cu_{1.97}S

Twin cell: 31.34, 31.34, 26.92, $\alpha = \beta = 90$, $\gamma = 120^{\circ}$

$$\begin{vmatrix} 1/4 & -1/4 & 0 \\ -1/2 & -1/2 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$
 det = 1/4

Crystal cell: 13.57, 15.67, 26.92, $\alpha = \beta = \gamma = 90^{\circ}$

Example 2: L-Aspartic acid

Twin cell: 5.1, 6.9, 15.1, β =100°

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1/2 \end{vmatrix} det = 1/2$$

Crystal cell: 5.1, 6.9, 7.55, β=100°

Rows		Products	
direct	reciprocal	dot	δ
100	4 0 -1	4	0.28
010	010	1	0
104	0 0 1	4	0.28

Non-systematic extinctions

Non-systematic extinctions

- Twinned crystal structures are often characterized by non-systematic extinctions.
- Example obverse/reverse twinning
 - oR-lattice: hkl: -h+k+l=3n (2/3 absent)
 - rR-lattice: hkl: h-k+l=3n (2/3 absent)
 - twin lattice: -h+k+l=3n OR h-k+l=3n (1/3 absent)

ROTAX

R. I. Cooper, R. O. Gould, S. Parsons, D. J. Watkin (2002). *J. Appl. Cryst.* **35**, 168-174

ROTAX

Observation: If twinning has been overlooked, all reflections in the list of *most disagreeable reflections* are characterized by F_obs >> F_calc.

 R. Herbst-Irmer *in* Crystal Structure Refinement – A Crystallographer's
 Guide to SHELXL (P. Müller, editor). Oxford University Press, 2006, pp. 106-149.

Rotax

- Search for 30 reflections with largest values of (F_obs-F_calc)/σ
- Generate all direct- and reciprocal-lattice vectors with -12<h<12, -12<k<12, 0<l<12
- Derive matrices corresponding to twofold rotations about these vectors
- Apply the matrices to (*h*,*k*,*l*) of the 30 reflections
- Calculate a figure of merit based on the distance of (h',k',l') to the nearest lattice point
- Remove non-fitting reflections from the calculation of the figure of merit

Rotax

- If the twin matrix has been determined, it can be used for a twin refinement (not recommended for non-merohedral twins).
- For SHELXL you have to prepare a special reflection file (non-merohedral).
- The programs CRYSTALS and JANA2006 can determine the reflection overlap within the program (non-merohedral).

PLATON - TwinRotMat

http://www.platonsoft.nl/PLATON-MANUAL.pdf

TwinRotMat

Observation 1: If twinning has been overlooked, all reflections in the list of *most disagreeable reflections* are characterized by F_obs >> F_calc.

Observation 2: Overlapping reflections have (approximately) the same *theta* value.

TwinRotMat

- Search for reflections with large values of (F_obs-F_calc)/σ
- For every such reflection (h,k,l) search for reflections (h',k',l') with approximately the same theta value.
- Calculate the (reciprocal) rotation axis, which transforms (h,k,l) into (h',k',l')
- Select the rotation axis, which explains most of the observed intensity differences

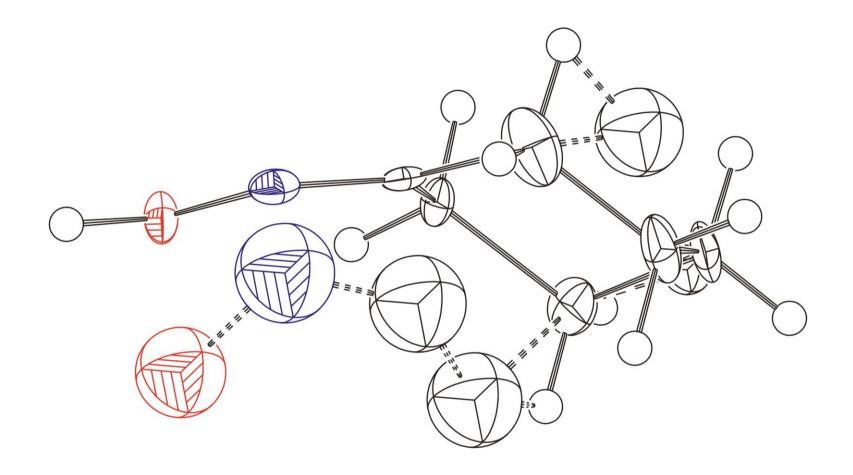
TwinRotMat

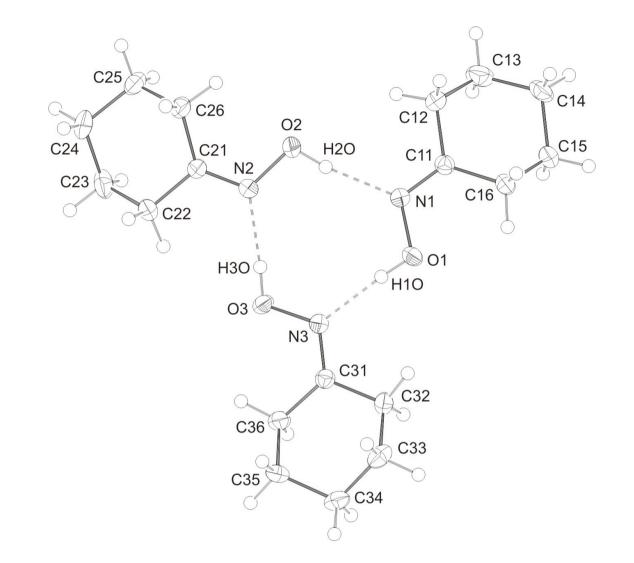
- Only rotation axes, which are independent by symmetry, need to be considered
- A twin operation cannot be part of the point group symmetry of the crystal
- If a reciprocal twin axis is close to a direct axis, the direct axis is tested as well
- For every potential rotation axis, a twin fraction (BASF) and the improvement of the R-value can be calculated
- A HKLF-5 file for the refinement program SHELXL can be written (non-merohedral)

TruinRotting Analysis of Fo/Fc Data for Unaccounted (Non)Merchedral Twinning for: m029b Cell: 0.71073 20.983 20.983 7.644 90.00 90.00 120.00 Spgr: P-3 Criteria: DeltaI/SigmaI .GT. 4.0, DeltaTheta 0.10 Deg., NselMin = 50 N(refl) = 4446, N(selected) = 50, IndMax = 5, CritI = 0.1, CritT = 0.10	TwinRoMt 25 NRefSelMin DeltaI/SigI MaxIndexUVW DeltaTheta FullListing EPS-TwinLaw DspTwinMat1
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INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)

MenuActive





M. Lutz, A.L. Spek, R. Dabirian, C.A. van Walree, L.W. Jenneskens (2004). *Acta Cryst.* **C60**, o127-o129

Difference Fourier

Difference Fourier Synthesis

- In the case of a twin, the observed structure factors must be corrected.
- The Jana2006 software offers two methods:

$$F_{obs} = \sqrt{I_{obs} - \sum_{i=2,n} v_i F_{c,i}^2}$$
$$F_{obs}^{corr} = F_{obs} \frac{F_{calc1}}{F_{calc}}$$

http://jana.fz.cz/doc/manual98.pdf