Göttingen, Februar 1st, 2012

Introduction to Twinning

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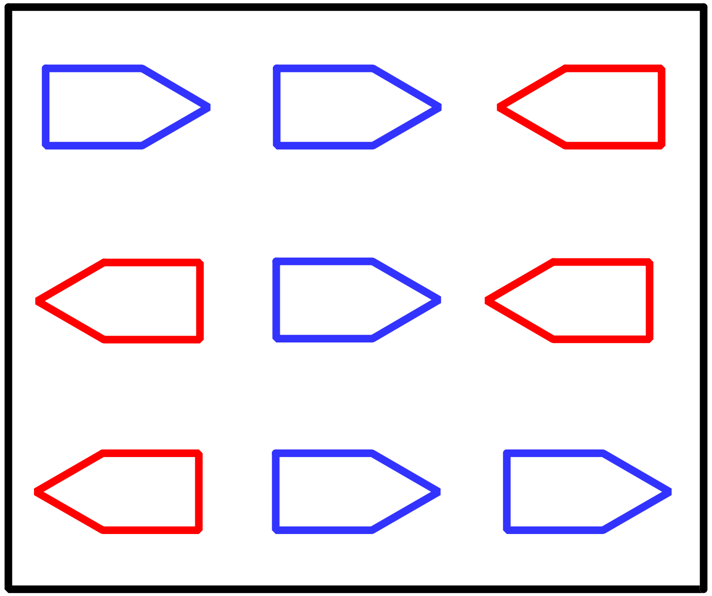
http://shelx.uni-ac.gwdg.de/~rherbst/twin.html

Definition

"Twins are regular aggregates consisting of individual crystals of the same species joined together in some definite mutual orientation."

from: "Fundamentals of Crystallography", edited by C. Giacovazzo, Union of Crystallography, Oxford University Press 2nd Edn. 2002.

Simple example for a two-dimensional twin:



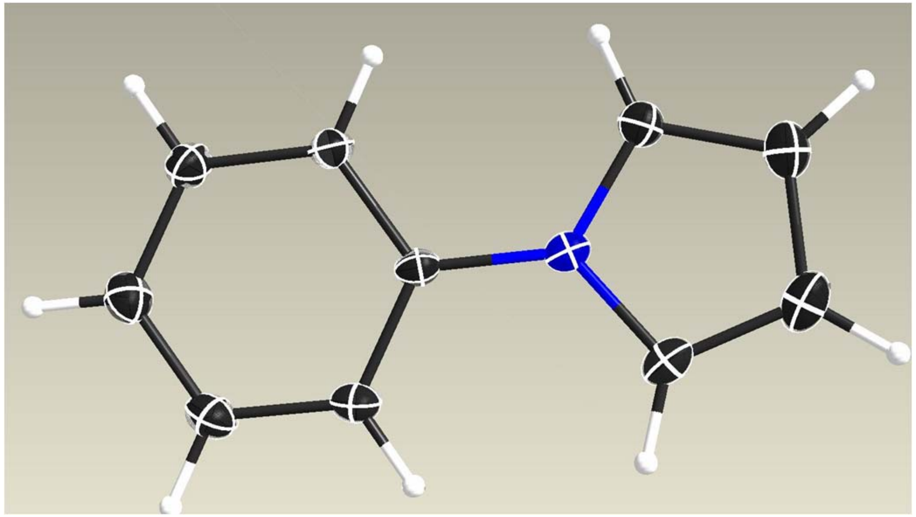
Twin Law: $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

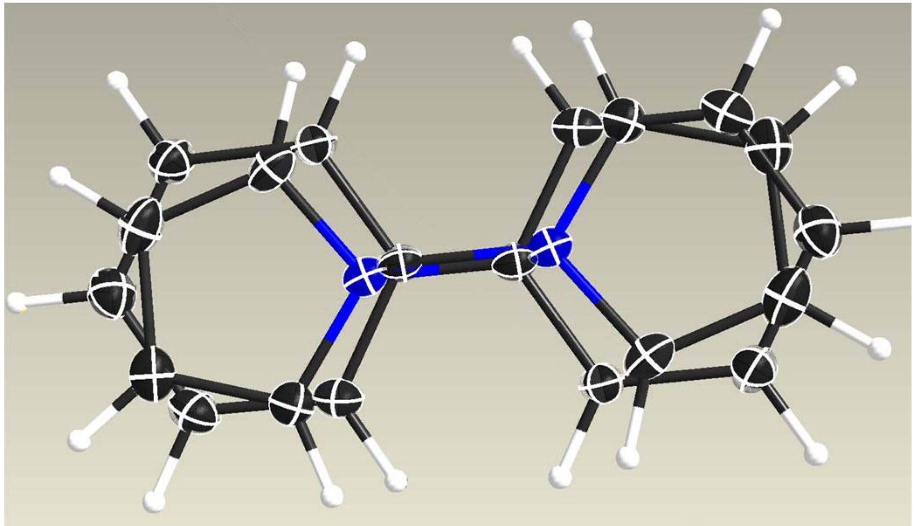
fractional contribution k_1 for twin domain 1: 5/9

fractional contribution k_2 for twin domain 2: 4/9

Question 1

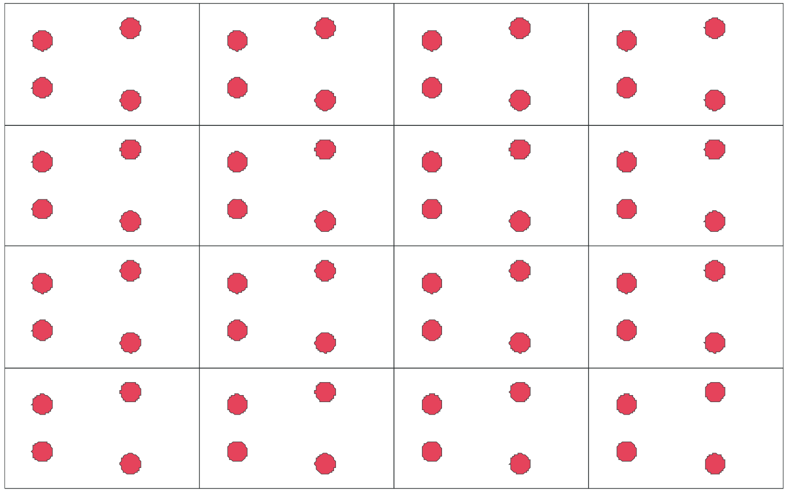
A twinned structure can sometimes be mistaken for a disordered one. What is the difference between disorder and twinning?

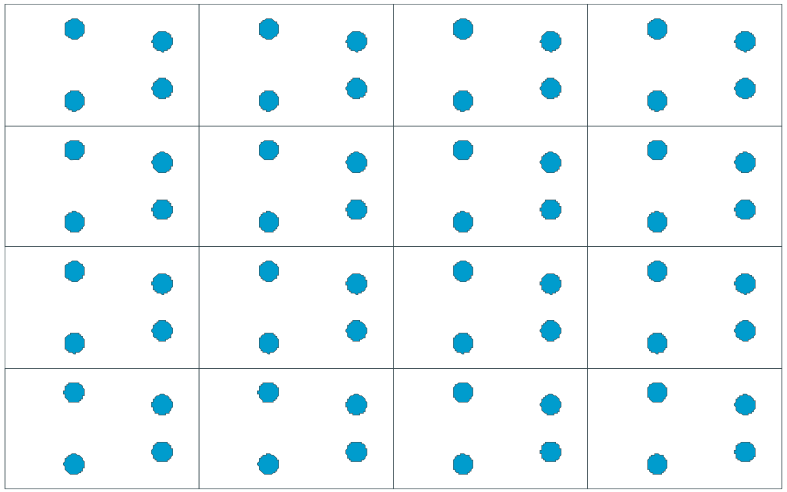




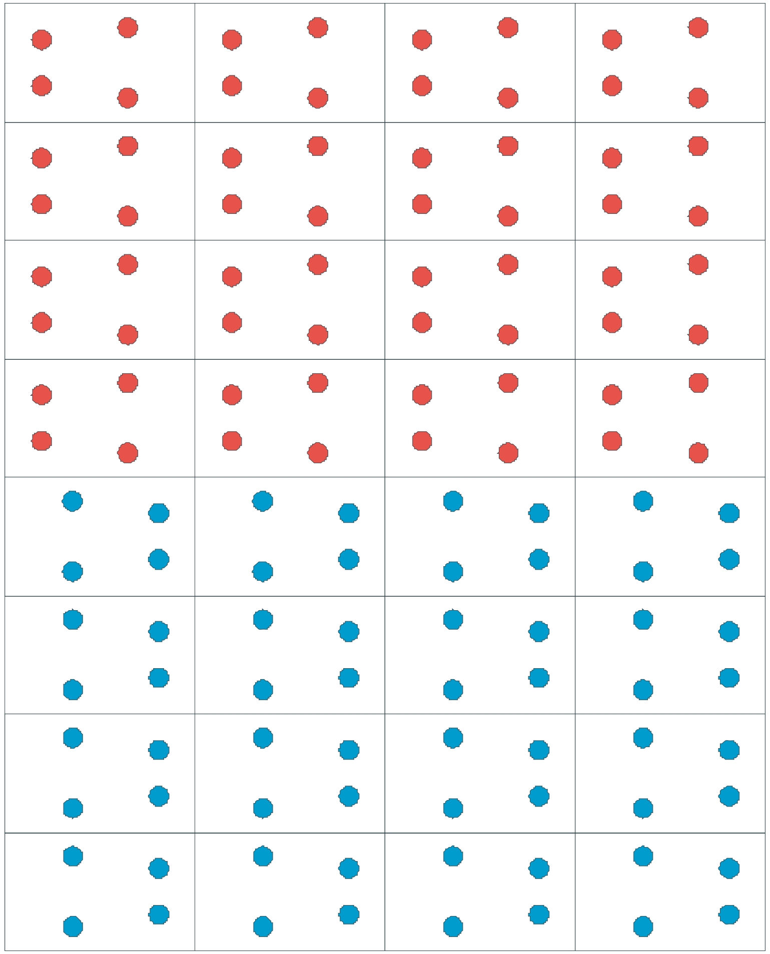
K. Meindl, J. Henn, N. Kocher, D. Leusser, K. A. Zachariasse, G. M. Sheldrick, T. Koritsanszky, D. Stalke, *J. Phys. Chem. A*, **113**, 9684, 2009.

Question 1



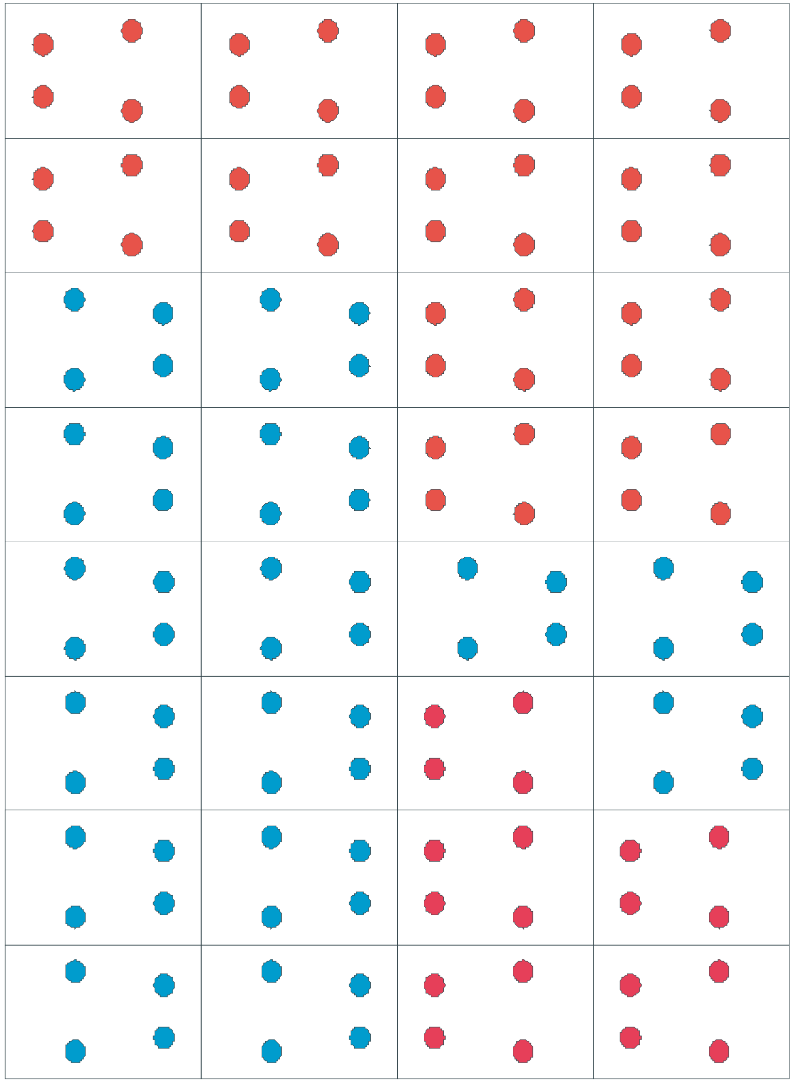


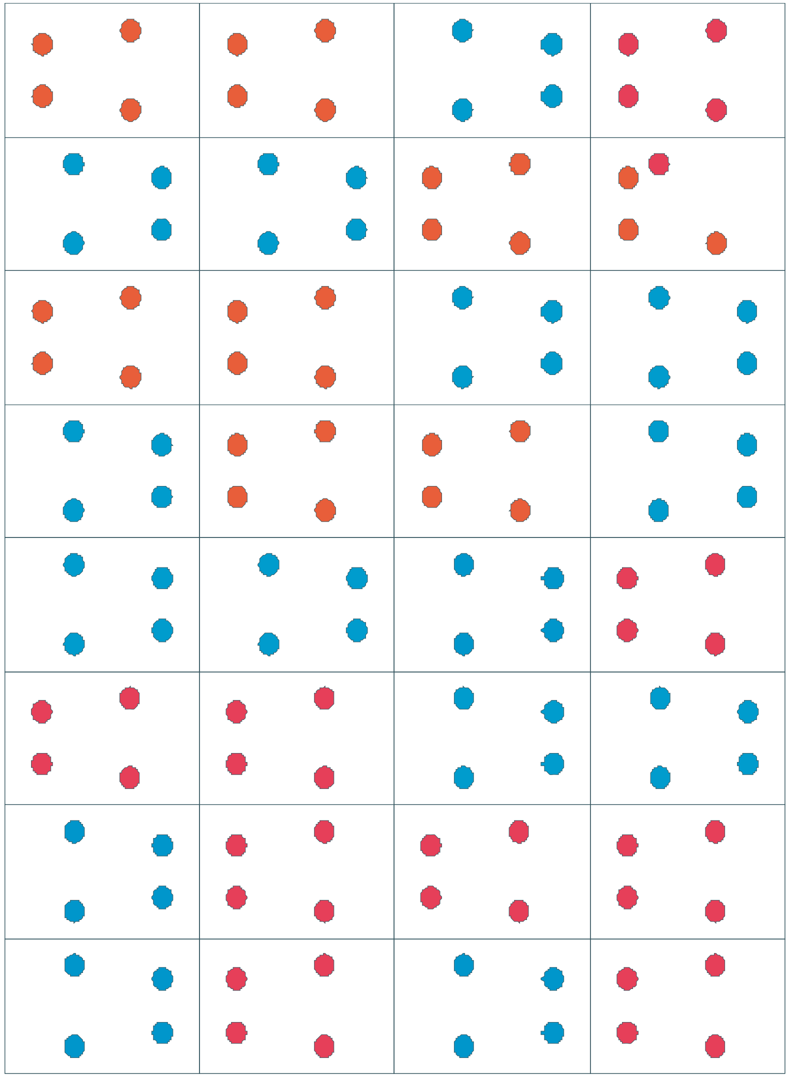
Question 1



Twinning may occur when a unit cell (or a supercell) – ignoring the content – has higher symmetry than implied by the space group of the crystal structure

Question 1

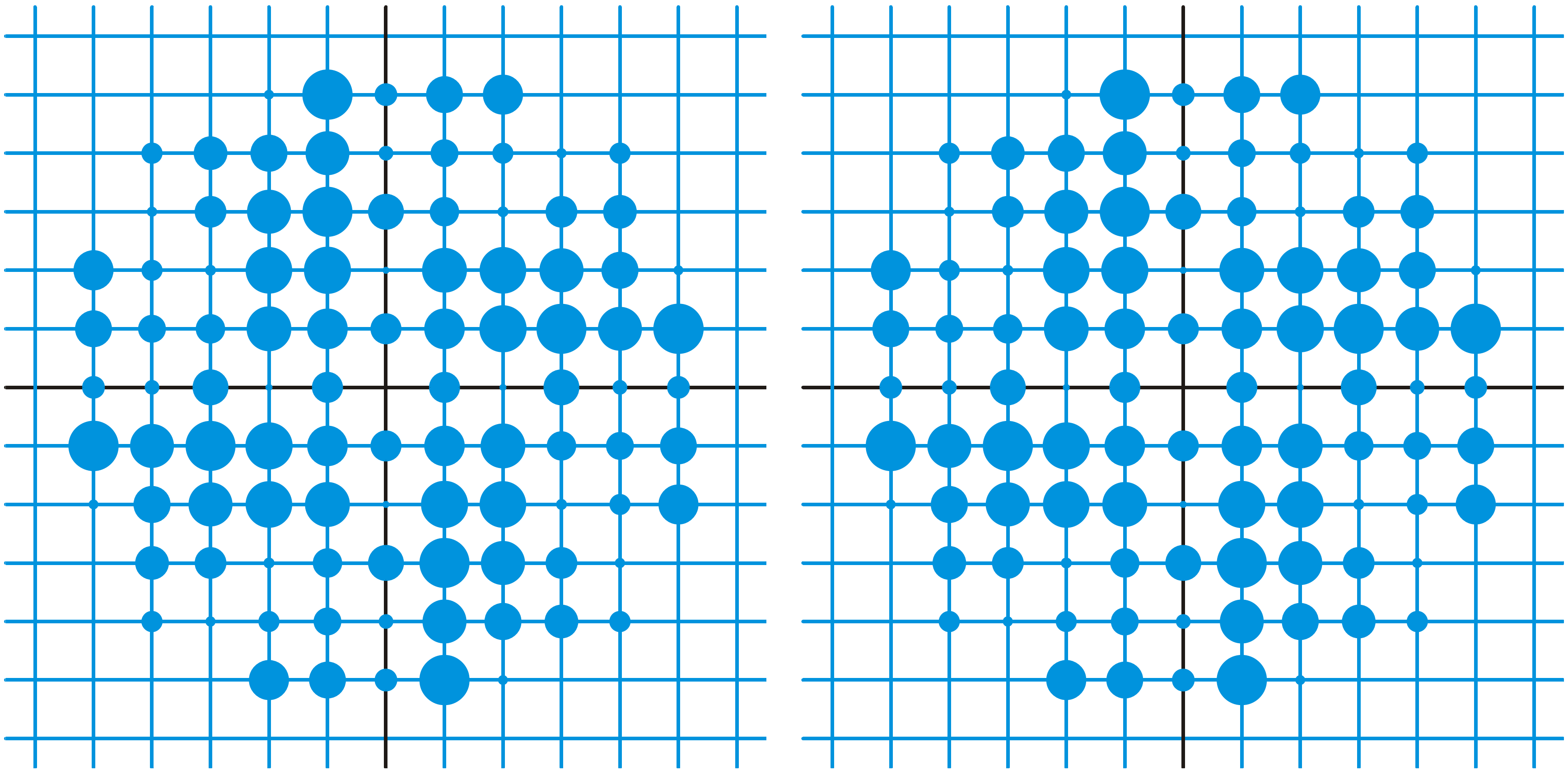




Four Kinds of Twins (I)

1. Twinning by merohedry
   Twin operator: symmetry operator of the crystal system but not of the point group of the crystal
   1.1. racemic twin
   1.2. twin operator: not of the Laue group of the crystal

Reciprocal Space Plot l = 0



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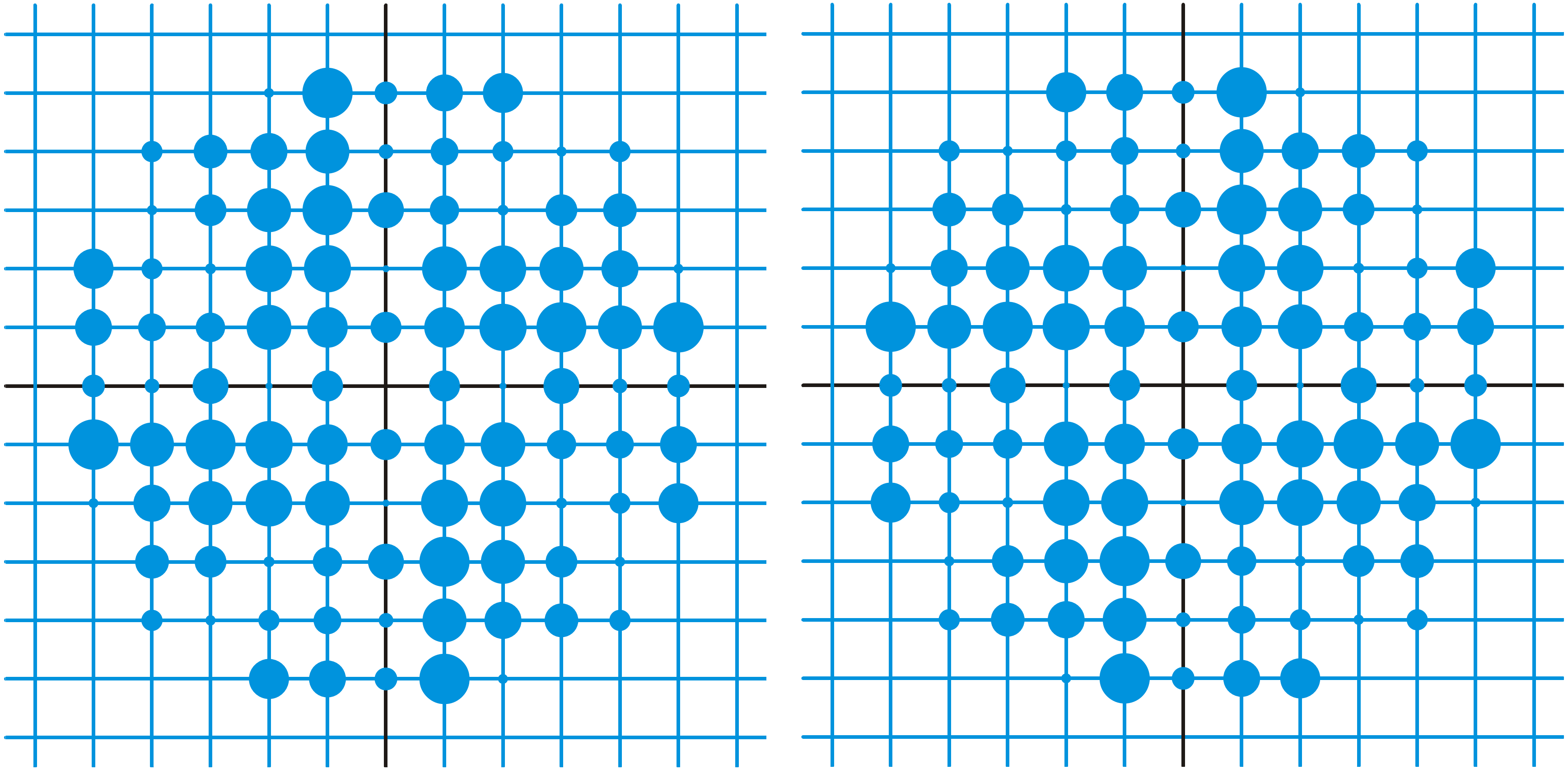

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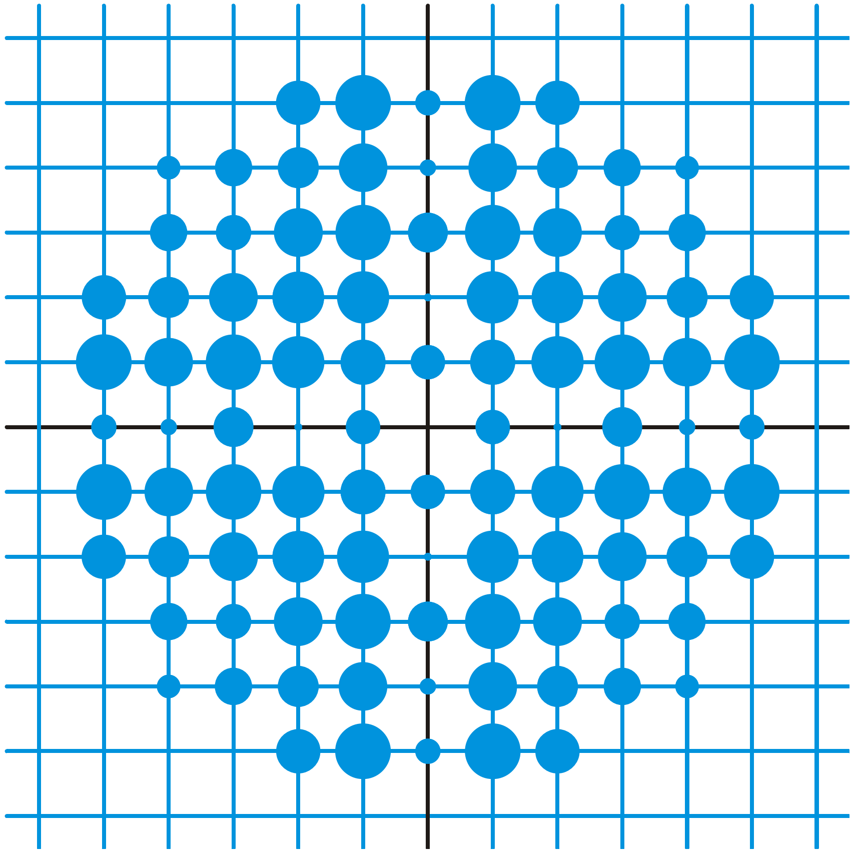
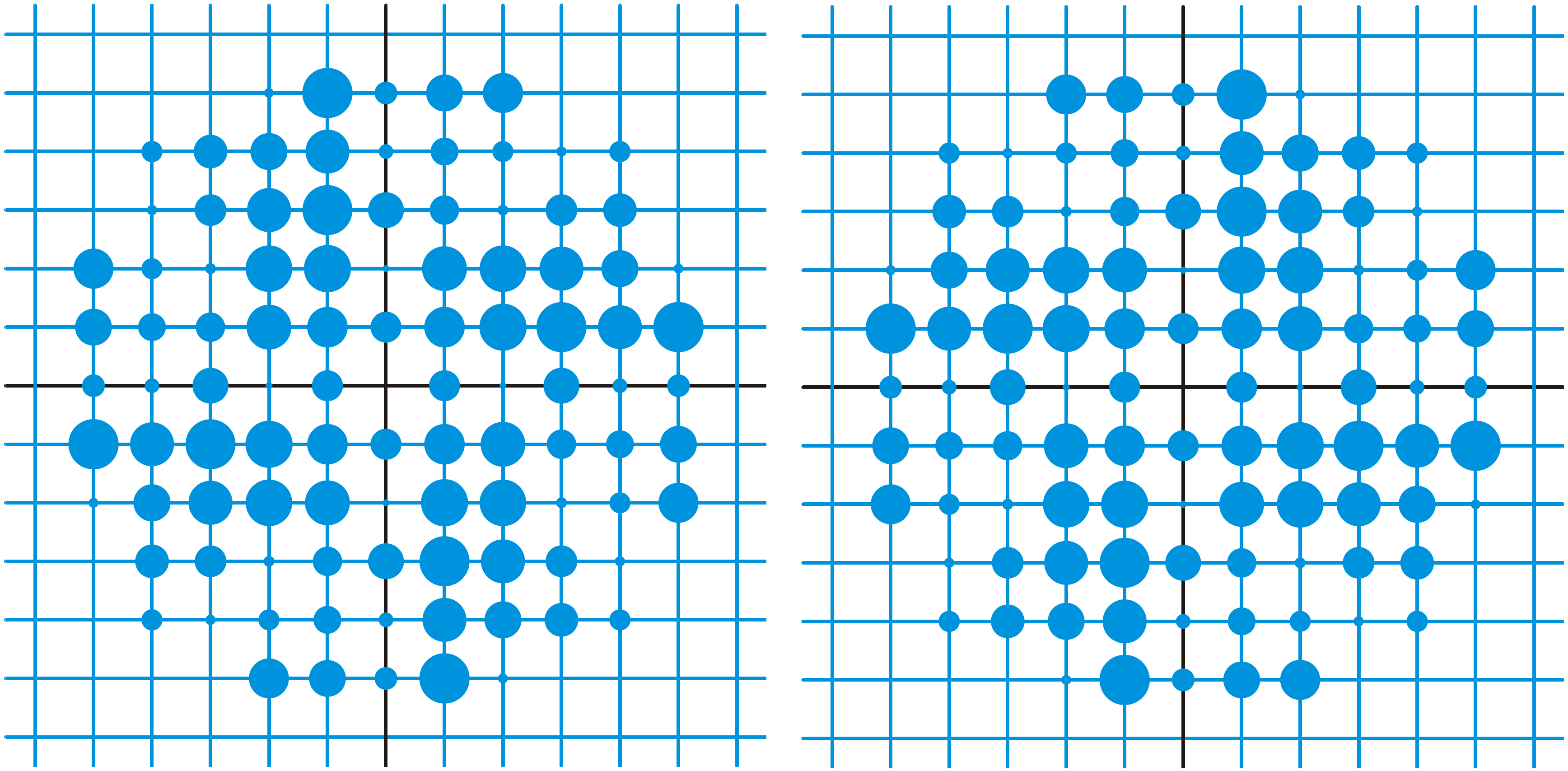


Question 2

What is the twin law?



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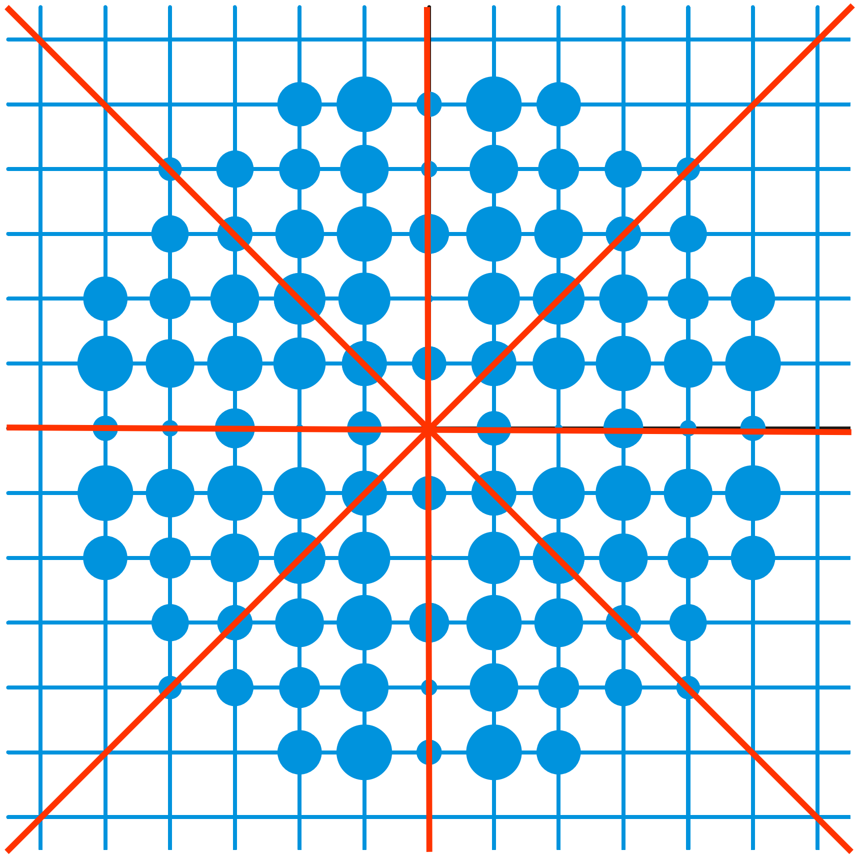

Question 2

What is the twin law?

0	1	0	1	0	0	0	0	-1
-1	0	0	0	1	0	0	0	-1
0	-1	0	-1	0	0	0	0	-1
1	0	0	0	-1	0	0	0	-1
0	-1	0	-1	0	0	0	0	1
1	0	0	0	-1	0	0	0	1
0	1	0	1	0	0	0	0	1
-1	0	0	0	1	0	0	0	1

Merohedral Twin Laws

True Laue Group	Apparent	Twin Law
4/m	4/mmm	0 1 0 1 0 0 0 0 -1
$\bar{3}$	$\bar{3}$1m	0 -1 0 -1 0 0 0 0 -1
$\bar{3}$	$\bar{3}$m1	0 1 0 1 0 0 0 0 -1
$\bar{3}$	6/m	-1 0 0 0 -1 0 0 0 1
$\bar{3}$	6/mmm	0 -1 0 -1 0 0 0 0 -1
		0 1 0 1 0 0 0 0 -1
		-1 0 0 0 -1 0 0 0 1
$\bar{3}$m1	6/mmm	-1 0 0 0 -1 0 0 0 1
$\bar{3}$1m	6/mmm	0 1 0 1 0 0 0 0 -1
6/m	6/mmm	0 1 0 1 0 0 0 0 -1
m$\bar{3}$	m$\bar{3}$m	0 1 0 1 0 0 0 0 -1

Four Kinds of Twins (I)

1. Twinning by merohedry

   Twin operator: symmetry operator of the crystal system but not of the point group of the crystal

   1.1. racemic twin

   1.2. twin operator: not of the Laue group of the crystal
   - only in tetragonal, trigonal, hexagonal and cubic space groups
   - exact overlap of the reciprocal lattices
   - often low value for $<|E^2-1|>$
   - Laue group and space group determination may be difficult
   - structure solution may be difficult

2. Twinning by pseudo-merohedry

   Twin operator: belongs to a higher crystal system than the structure
   - Metric symmetry higher than Laue symmetry

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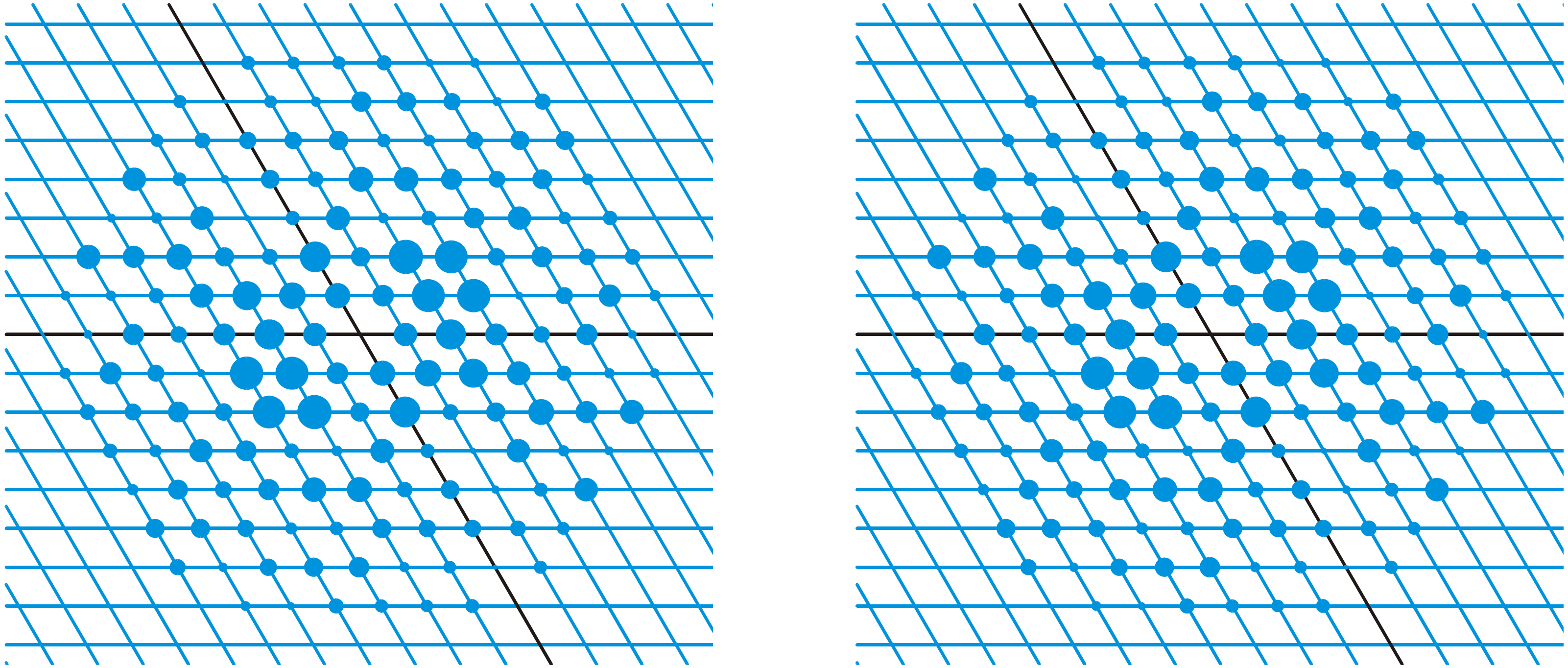

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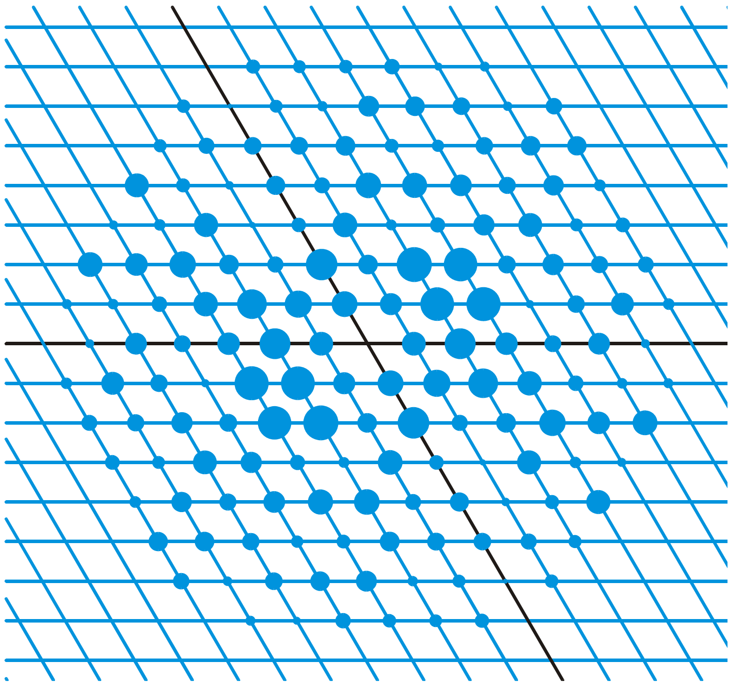

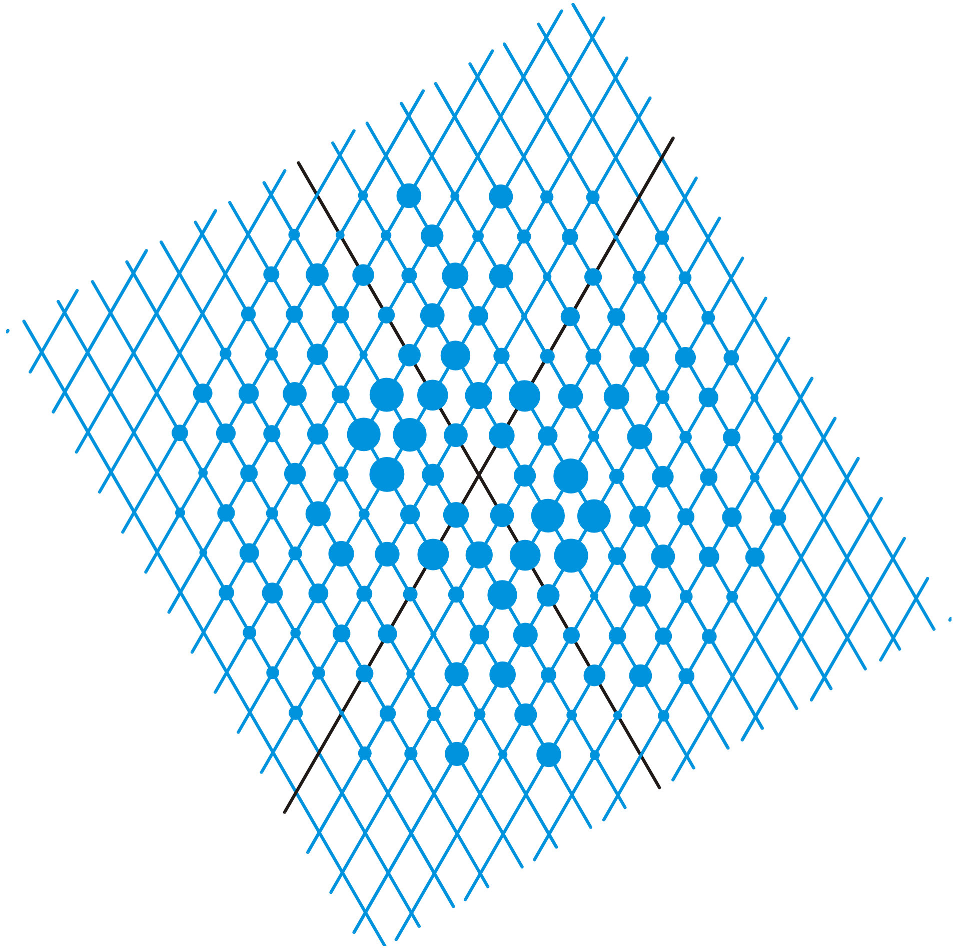

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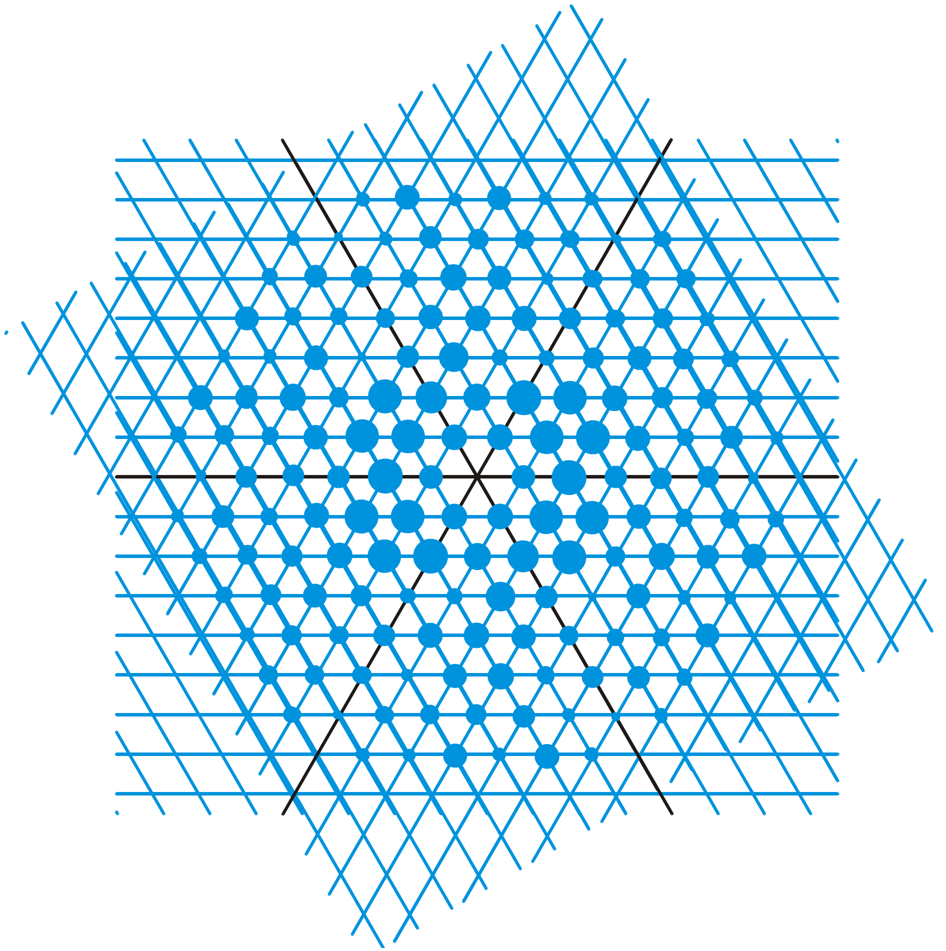

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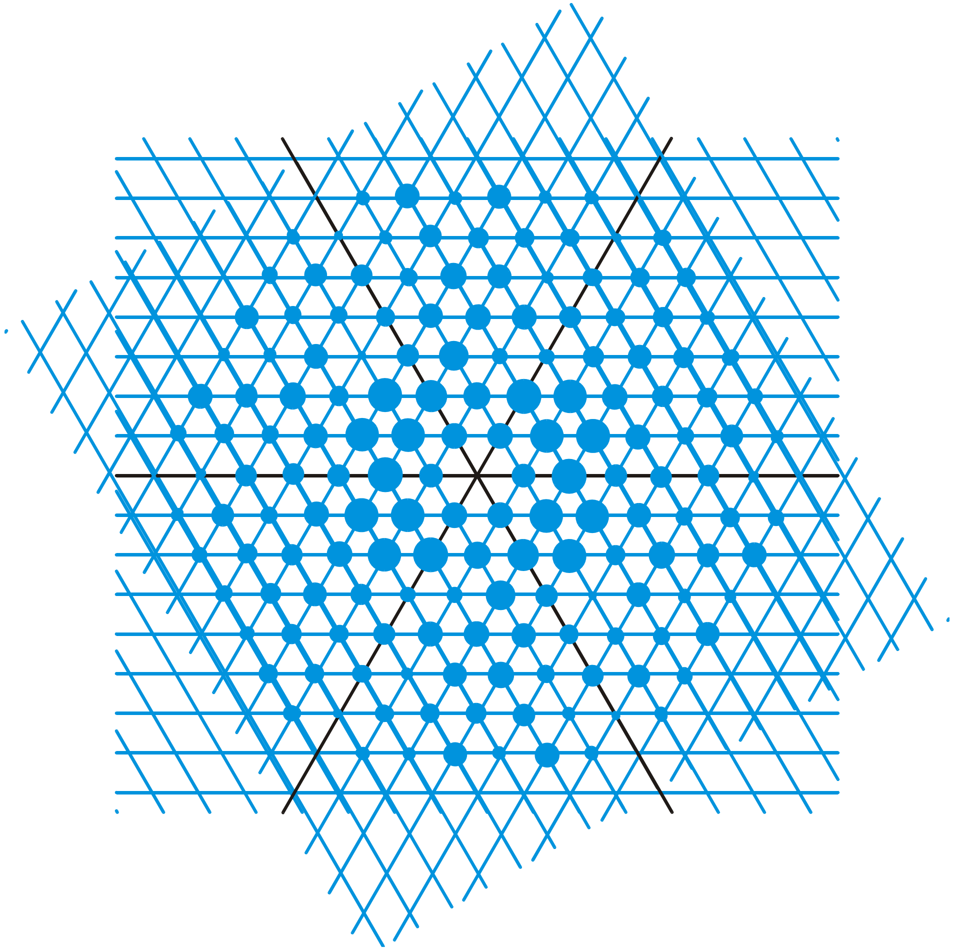

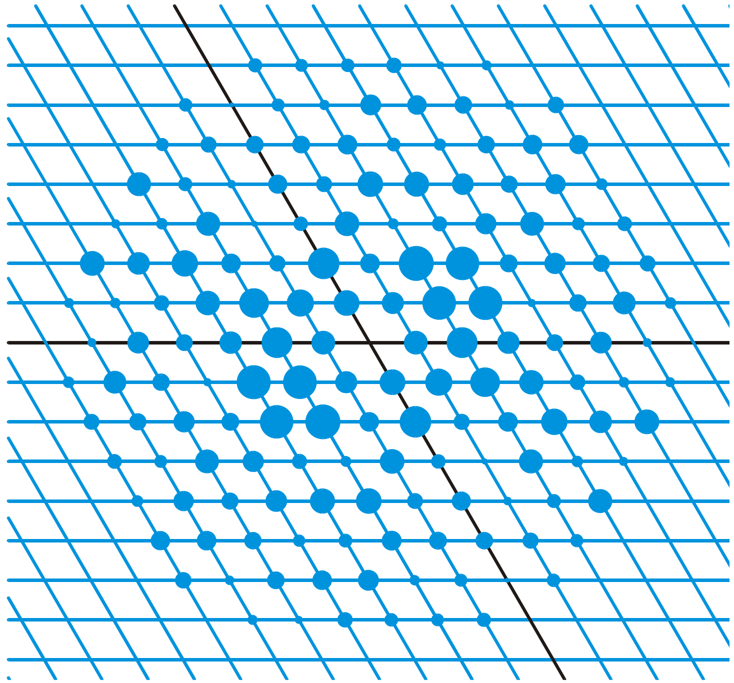

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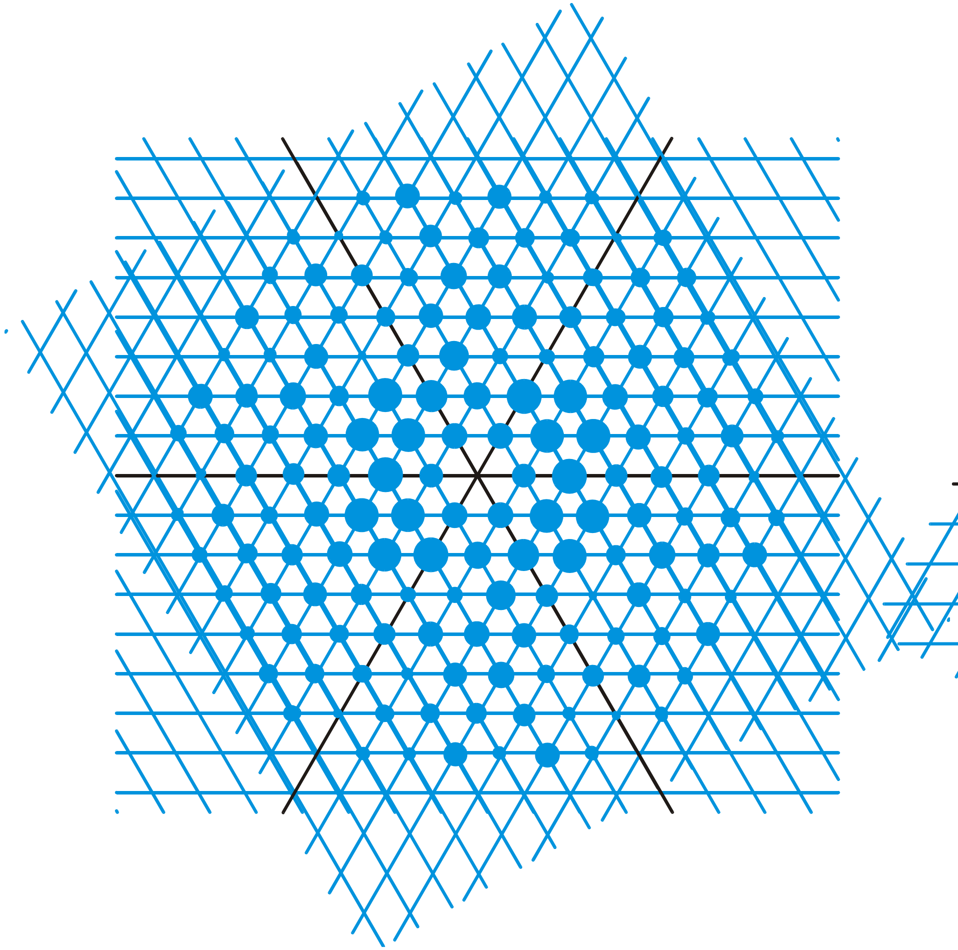
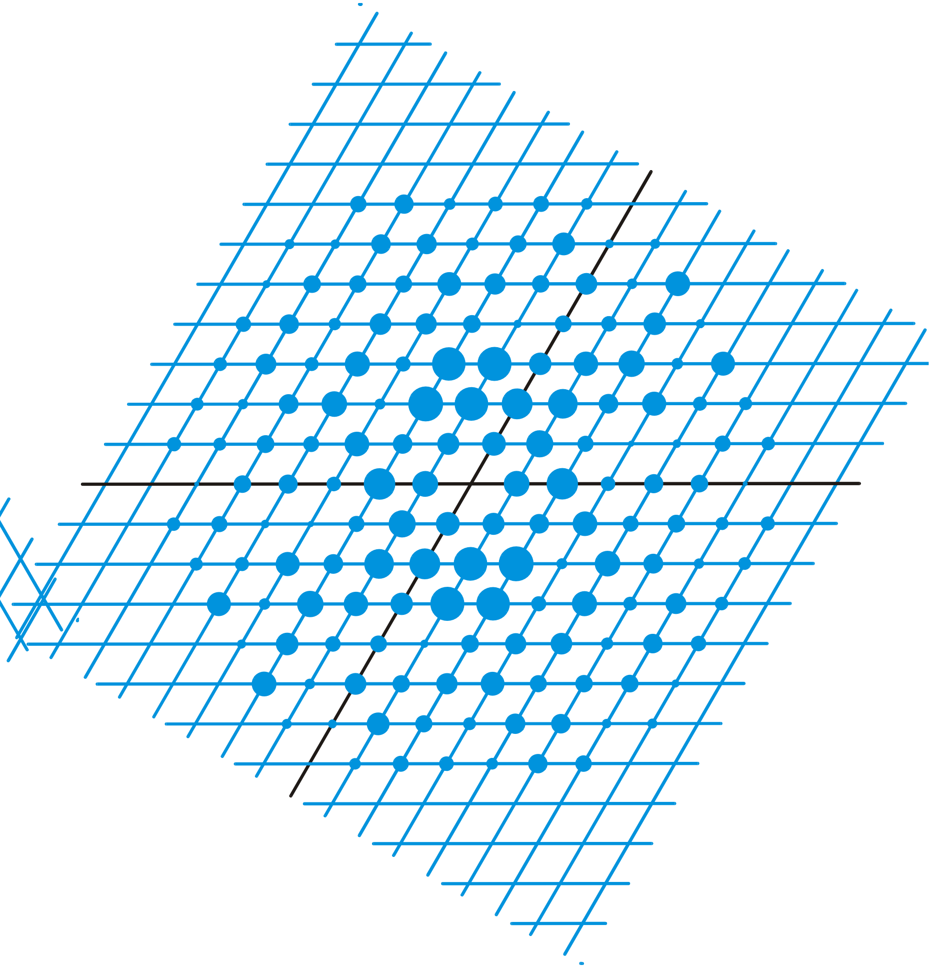
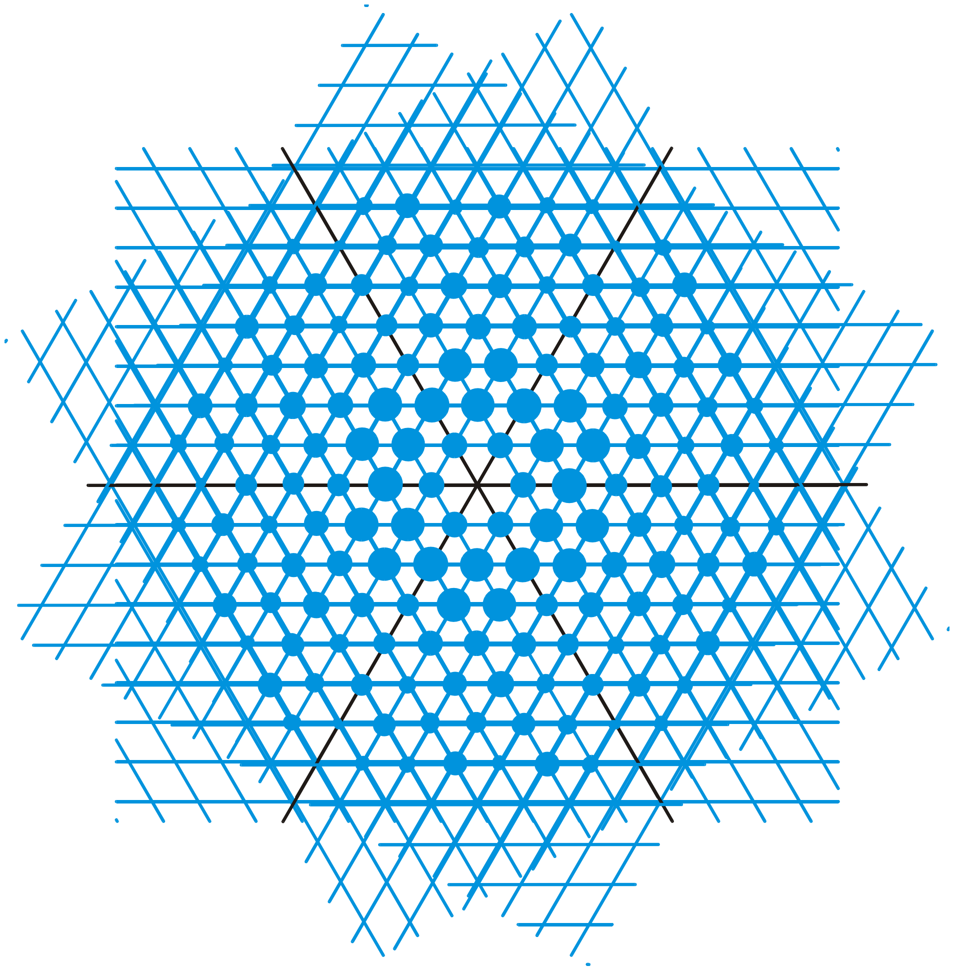




Definition **Classification** Tests Solution Refinement Warning Signs

Reciprocal Space Plot k = 0



Question 3

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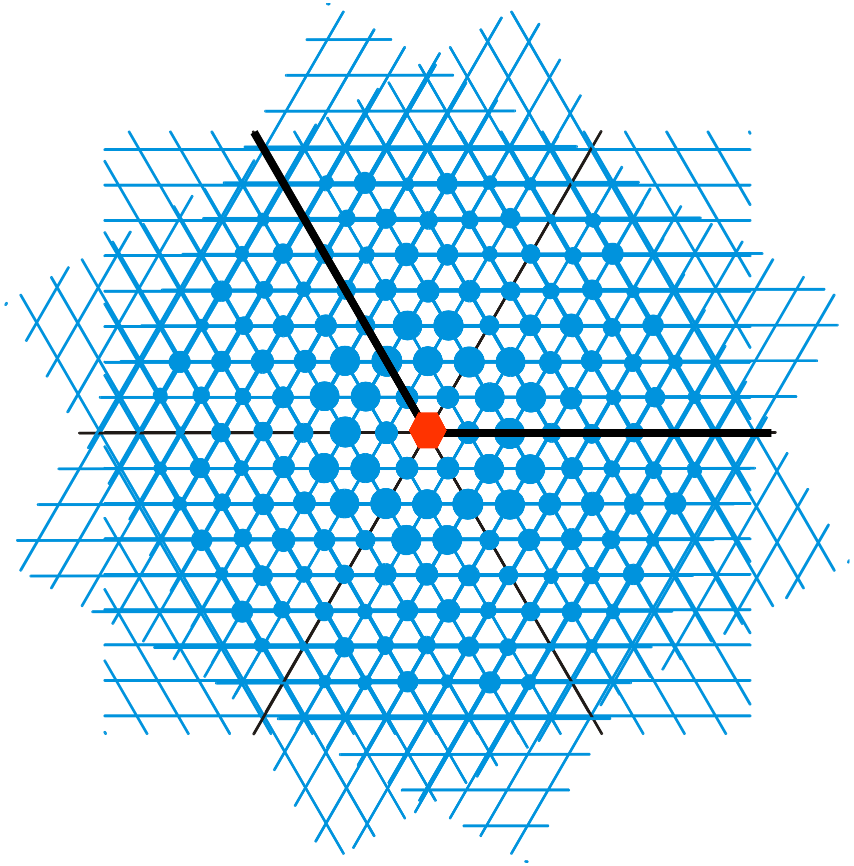


Question 3

What is the twin law?

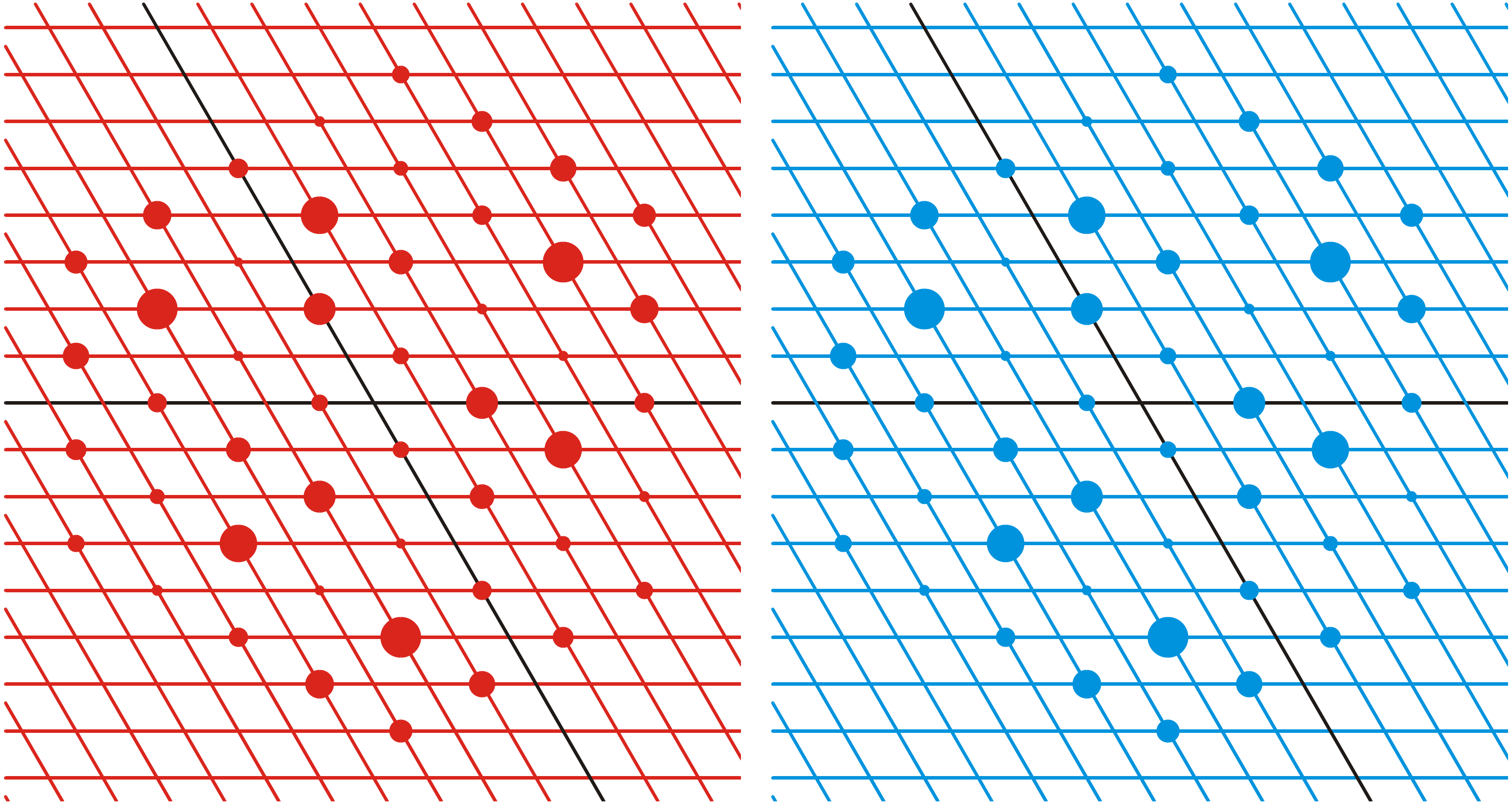
1	0	1	0	1	0	-1	0	0	3
0	0	1	0	1	0	-1	0	-1	
-1	0	-1	0	1	0	1	0	0	3
0	0	-1	0	1	0	1	0	1	
0	0	-1	0	-1	0	1	0	1	3
1	0	1	0	-1	0	-1	0	0	
0	0	1	0	-1	0	-1	0	-1	3
-1	0	-1	0	-1	0	-1	0	-1	

Four Kinds of Twins (II)

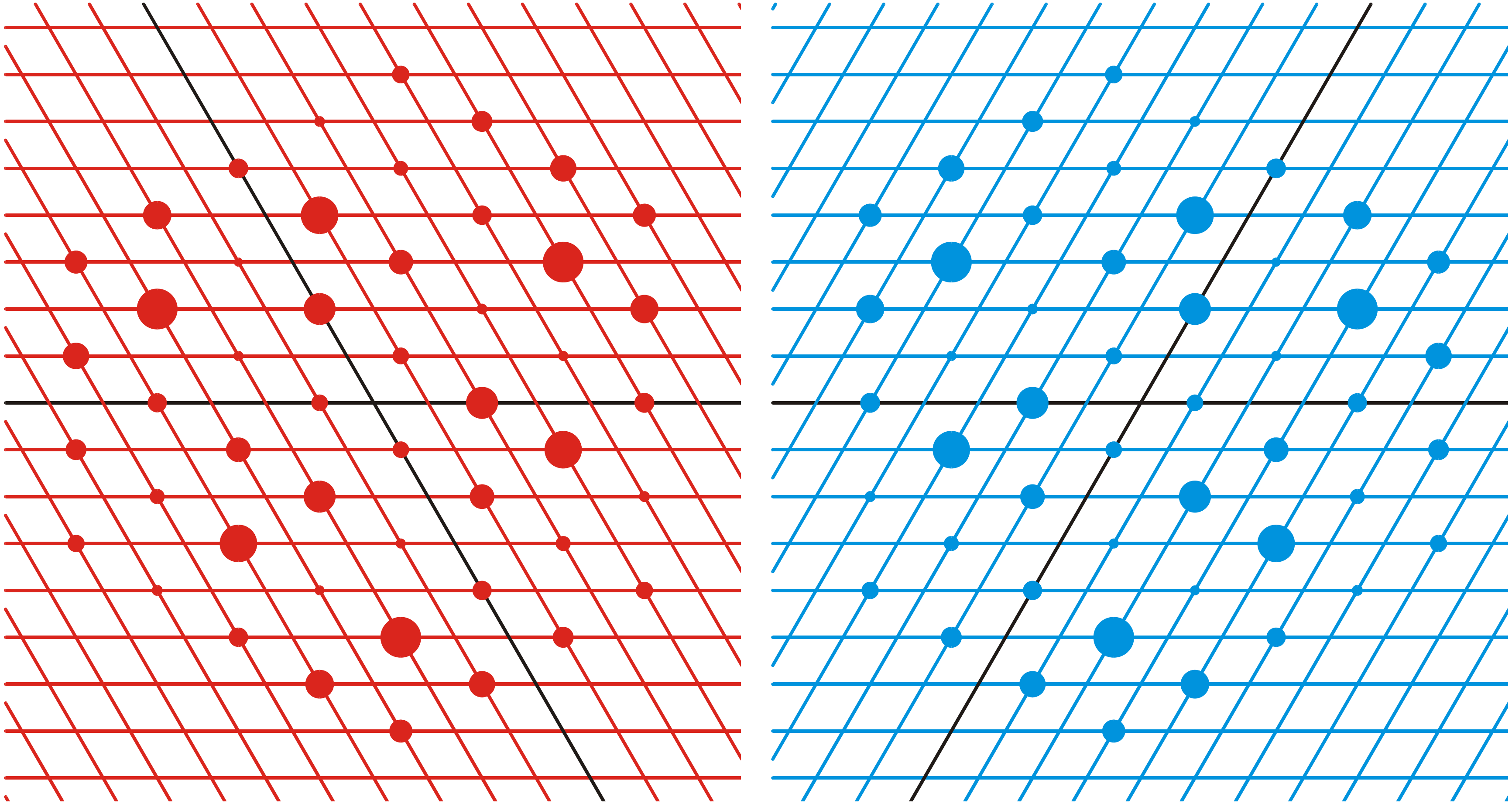
3. Twinning by reticular merohedry

e.g. obverse/reverse twinning in case of a rhombohedral crystal

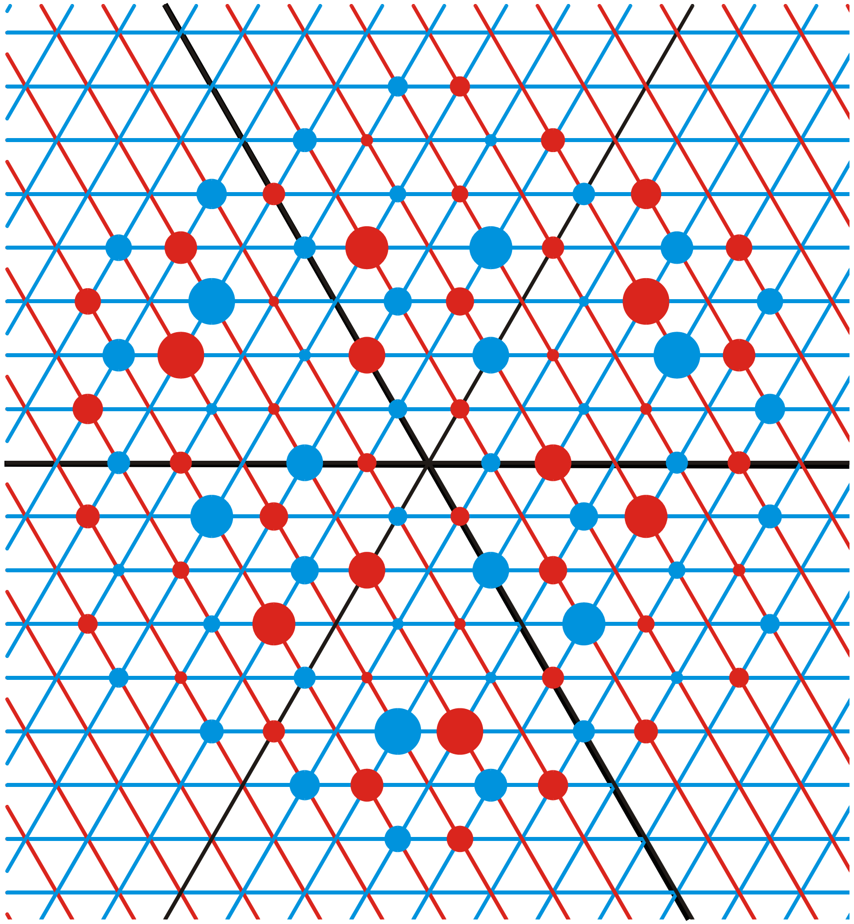
Reciprocal Space Plot l = 1



Reciprocal Space Plot l = 1



Reciprocal Space Plot l = 1



Obverse/ Reverse Twinning

Systematic Absences:

Domain 1:
$-h + k + l = 3n$

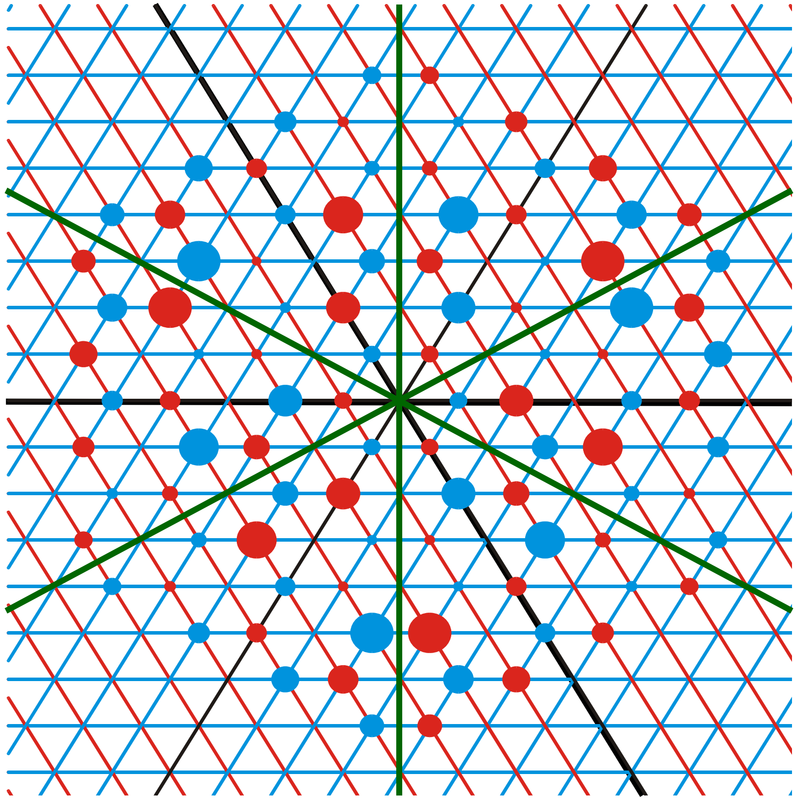
Domain 2:
$h - k + l = 3n$

$-h + k + l$	$h - k + l$	domain
$= 3n$	$\neq 3n$	1
$\neq 3n$	$= 3n$	2
$\neq 3n$	$\neq 3n$	-
$= 3n$	$= 3n$	1 and 2

$\rightarrow$ HKLF 5

Question 4

What is the twin law?



Question 4

What is the twin law?

1	1	0	0	-1	0	0	0	1
-1	0	0	1	1	0	0	0	1
0	-1	0	-1	0	0	0	0	1
-1	-1	0	0	1	0	0	0	-1
1	0	0	-1	-1	0	0	0	-1
0	1	0	1	0	0	0	0	-1

Four Kinds of Twins (II)

3. Twinning by reticular merohedry

e.g. obverse/reverse twinning in case of a rhombohedral crystal

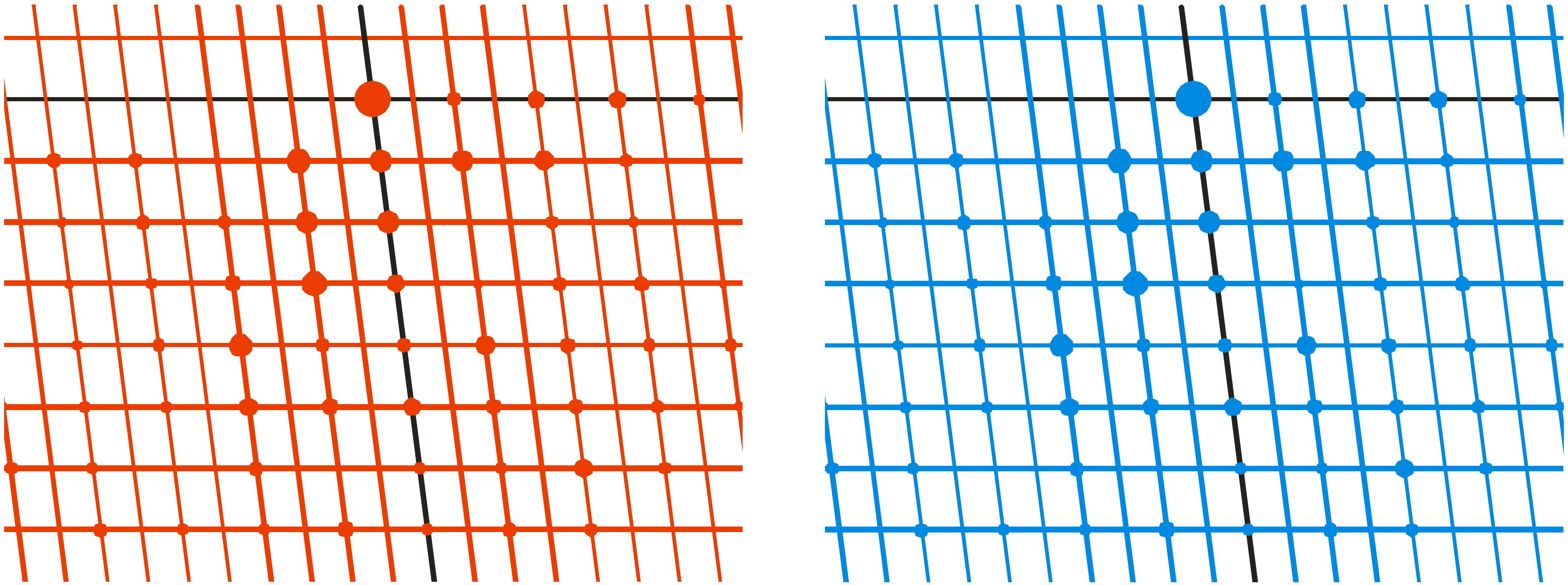
- detection of the lattice centring may be difficult
- structure solution not as difficult as for merohedral twins.

R. Herbst-Irmer, G. M. Sheldrick, Refinement of obverse/reverse twins, *Acta Crystallogr. B* **58**, 477, 2002

4. Non-merohedral twins

Twin operator: arbitrary operator, often rotation of 180°

Reciprocal Space Plot k = 2



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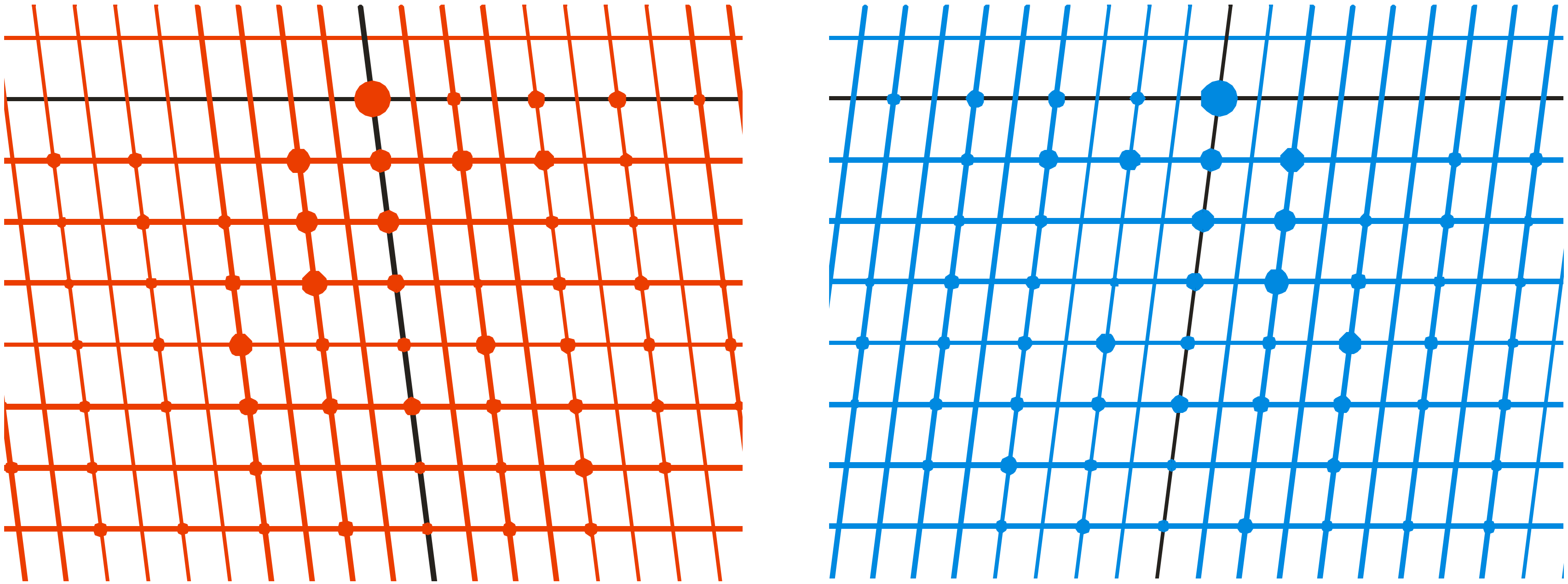

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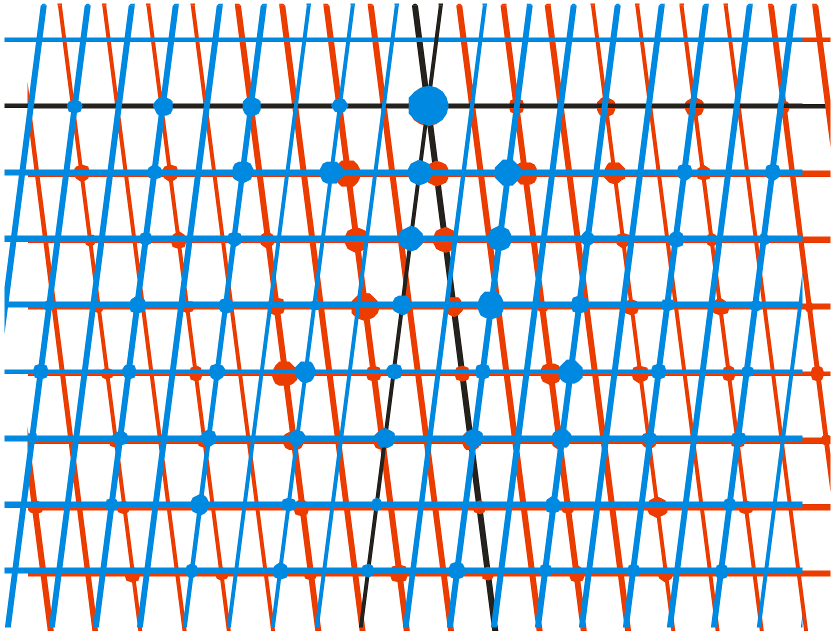
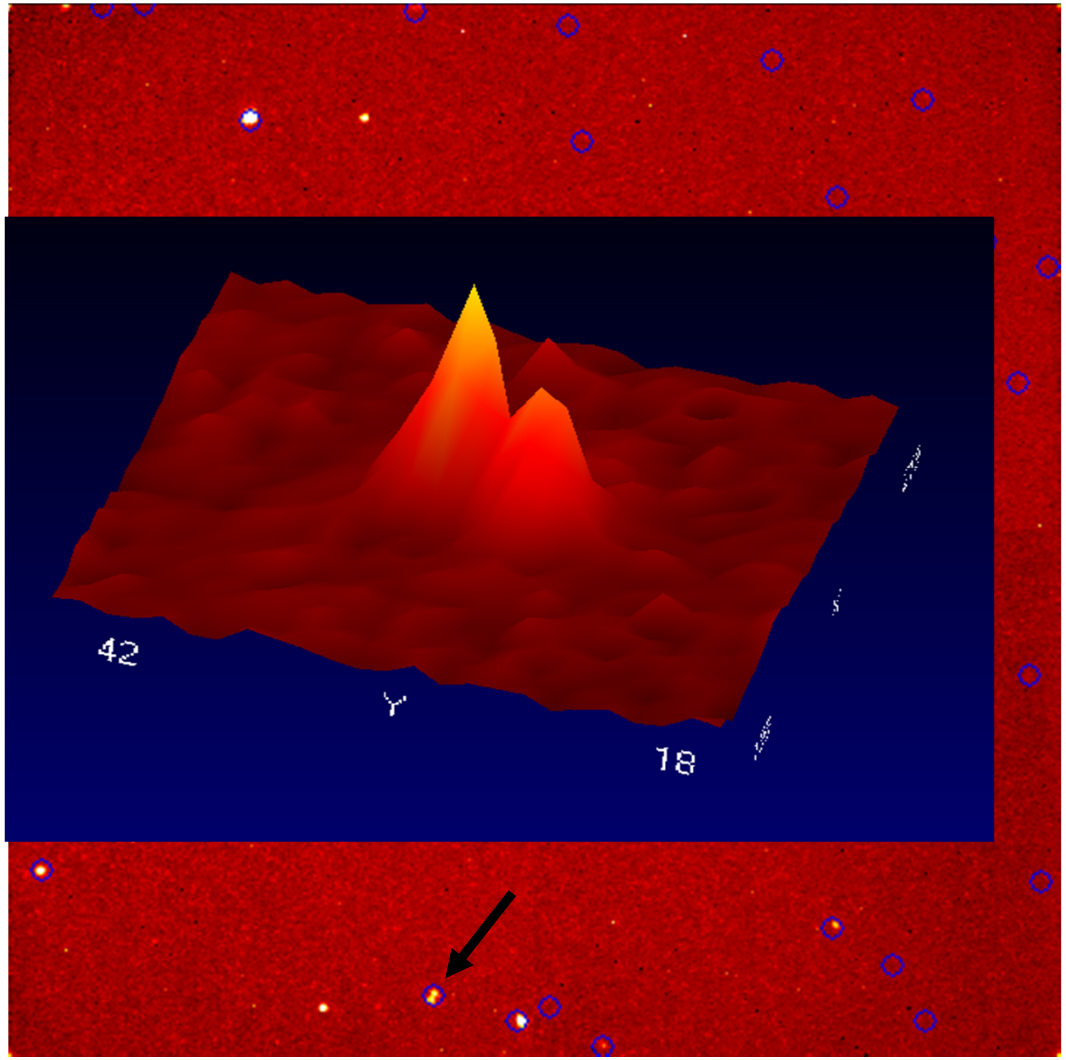


Reflection Pattern

- Problems with the cell determination
- Some reflections not indexed
- Some reflections very close to each other
- Some split reflections

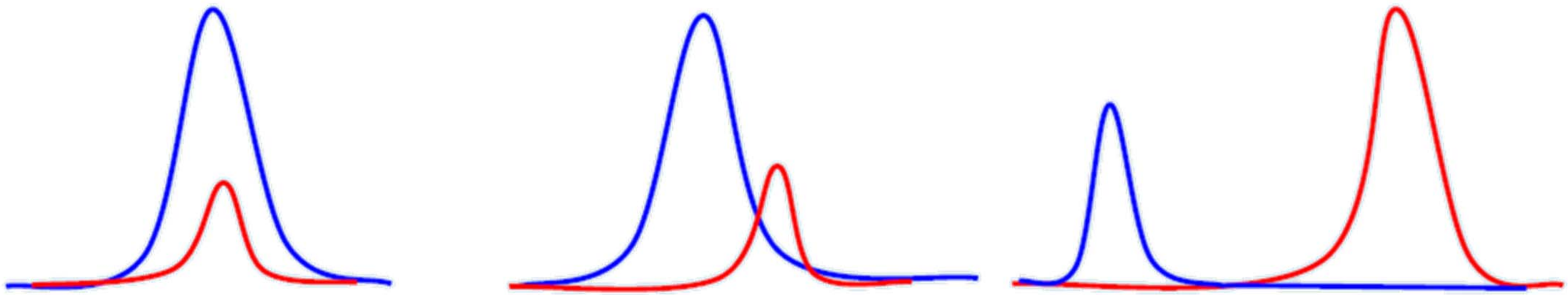


Cell Determination

CELL_NOW

- Reads .spin, .p4p or .drx-files
- tries to find sets of reciprocal lattice planes that pass close to as many reflections as possible
- The cell may be rotated to locate further twin domains using only the reflections that have not yet been indexed
- Determination of the cell and the twin law in one program
- Writes a .p4p/.spin file for RLATT and SAINT for simultaneous integration of more than one domain
- Determination of very weak domains possible

Integration

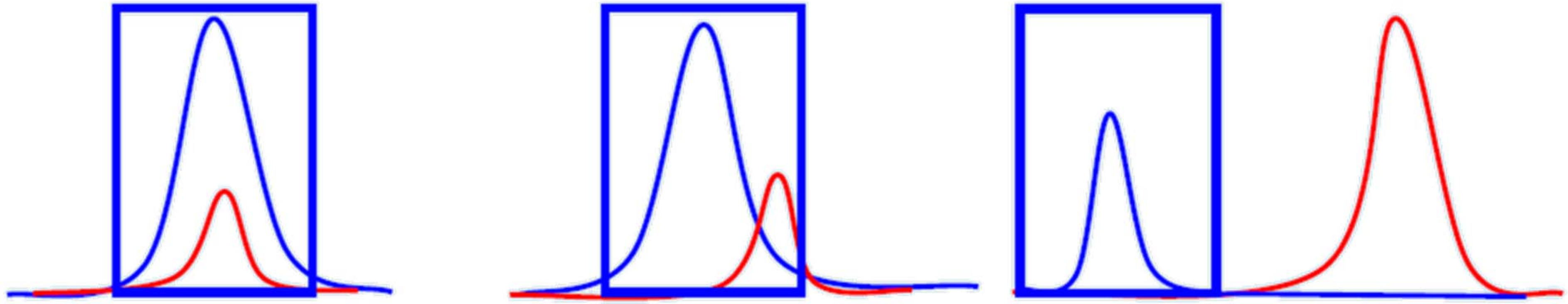


exact
overlaps

partial
overlaps

non-
overlaps

Integration



exact overlaps

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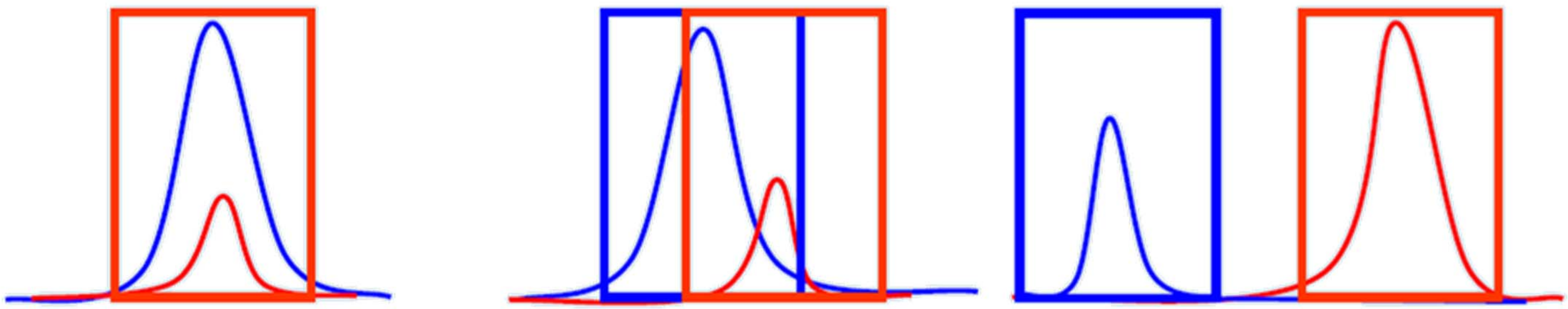
Integration



exact overlaps

partial overlaps

non-overlaps

TWINABS

Twin raw file : *.mul, similar to HKLF5 format

➔ Special version of SADABS: TWINABS

- Scaling and absorption correction
- Merging
- Output
  - detwinned data file (HKLF4) for structure solution
  - HKLF5 file for the refinement:

h'	k'	l'	F^2	$\sigma(F^2)$	-2
h	k	l	F^2	$\sigma(F^2)$	1

with h', k', l' generated by the second orientation matrix

Four Kinds of Twins (II)

3. Twinning by reticular merohedry

e.g. obverse/reverse twinning in case of a rhombohedral crystal
- detection of the lattice centring may be difficult
- structure solution not as difficult as for merohedral twins.

4. Non-merohedral twins

Twin operator: arbitrary operator, often rotation of 180°
- no exact overlap of the reciprocal lattices
- cell determination problems
- cell refinement problems
- some reflections sharp, others split
- data integration complicated (requires more than one orientation matrix)
- structure solution not as difficult as for merohedral twins

Tests for Twinning: XPREP

[M] Test for MEROHEDRAL TWINNING

Comparing true/apparent Laue groups. 0.05 < BASF < 0.45 indicates partial merohedral twinning. BASF ca. 0.5 and a low <|E^2-1|> (0.968[C] or 0.736[NC]) are normal) suggests perfect merohedral twinning. For a twin, R(int) should be low for the true Laue group and low/medium for the apparent Laue group.

Test for Merohedral Twinning

[1] -3 / -31m:
R(int) 0.039(801)/0.316(478), <|E^2-1|> 0.624/0.517
TWIN 0 -1 0 -1 0 0 0 0 -1 BASF 0.205 [C] or 0.124 [NC]

[2] -3 / -3m1:
R(int) 0.039(801)/0.406(444), <|E^2-1|> 0.624/0.525
TWIN 0 1 0 1 0 0 0 0 -1 BASF 0.113 [C] or 0.008 [NC]

[3] -3 / 6/m:
R(int) 0.039(801)/0.103(488), <|E^2-1|> 0.624/0.617
TWIN -1 0 0 0 -1 0 0 0 1 BASF 0.319 [C] or 0.269 [NC]

[4] -31m / 6/mmm:
R(int) 0.316(478)/0.097(228), <|E^2-1|> 0.517/0.523
TWIN -1 0 0 0 -1 0 0 0 1 BASF 0.346 [C] or 0.304 [NC]

[5] -3m1 / 6/mmm:
R(int) 0.406(444)/0.114(262), <|E^2-1|> 0.525/0.527
TWIN -1 0 0 0 -1 0 0 0 1 BASF 0.360 [C] or 0.322 [NC]

[6] 6/m / 6/mmm:
R(int) 0.103(488)/0.478(218), <|E^2-1|> 0.617/0.516
TWIN 0 1 0 1 0 0 0 0 -1 BASF 0.178 [C] or 0.090 [NC]

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Tests for Twinning: Todd Yeates Twinning Server

http://www.doe-mbi.ucla.edu/Services/Twinning

$J_1 = (1-\alpha)\, I_1 + \alpha\, I_2$

$J_2 = (1-\alpha)\, I_2 + \alpha\, I_1$

$H = (J_1 - J_2)/(J_1 + J_2)$

For centrosymmetric structures:

$\alpha = \frac{1}{2}[1 - \langle|H|\rangle(\pi/2)]$ and $\alpha = \frac{1}{2}\, [1 - (2\langle H^2\rangle)^{\frac{1}{2}}]$

non-centrosymmetric structures:

$\alpha \;\; = \frac{1}{2}(1 - 2\langle|H|\rangle)$ and $\alpha = \frac{1}{2}[1 - (3\langle H^2\rangle)^{\frac{1}{2}}]$

Only possible for partial twins ($\alpha \neq 0.5$)

Tests for Twinning: Todd Yeates Perfect Twins (α = 0.5)

- http://www.doe-mbi.ucla.edu/Services/Twinning

  Acentric data:

  $\langle I^2\rangle / \langle I\rangle^2 = 2$ for untwinned data

  $\langle I^2\rangle / \langle I\rangle^2 = 1.5$ for twinned data

  T. O. Yeates, Detecting and Overcoming Crystal Twinning, *Meth. Enzym.* **276**, 344, 1997

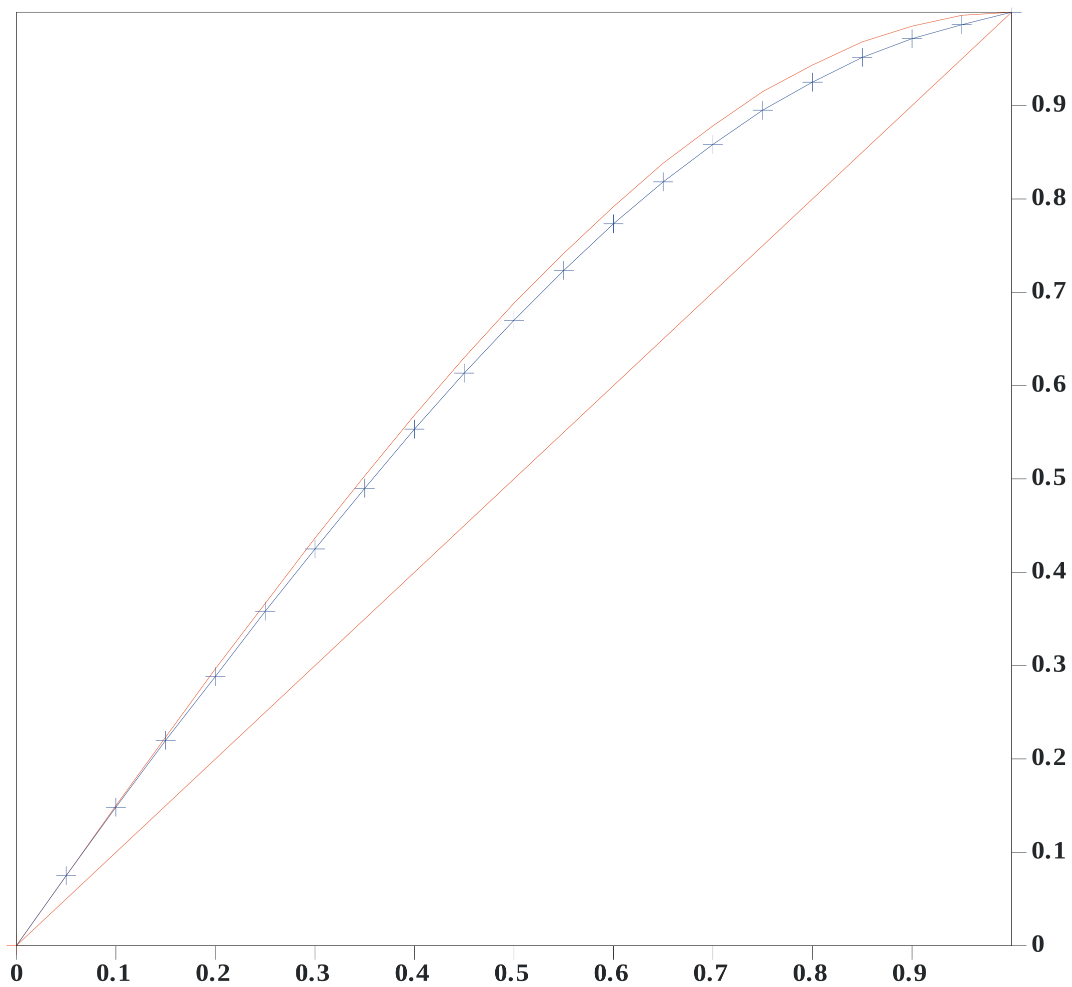
- $$L \equiv \frac{I(h_1) - I(h_2)}{I(h_1) + I(h_2)}$$

  h_1 and h_2 proximally located in reciprocal space

	$\langle \lvert L \rvert \rangle$	$\langle L^2 \rangle$
Acentric, untwinned	1/2	1/3
Centric, untwinned	$2/\pi$	1/2
Acentric, perfectly twinned	3/8	1/5

J. E. Padilla, T. O. Yeates, A statistic for local intensity differences: robustness to anisotropy and pseudo-centering and utility for detecting twinning, *Acta Cryst*, **59**, 1124, 2003

Local Intensity Test



X = |L|

Y = N(|L|) acentrics

DATAMAN Local Intensity Statistics Plot

Cumulative N(|L|) vs. |L| (acentrics)

Dataset P32 File P32.hkl

Comment Read from P32.hkl

<|L|> = 0.388 Untwinned = 0.500
Perfectly twinned = 0.375

<L^2> = 0.215 Untwinned = 0.333
Perfectly twinned = 0.200

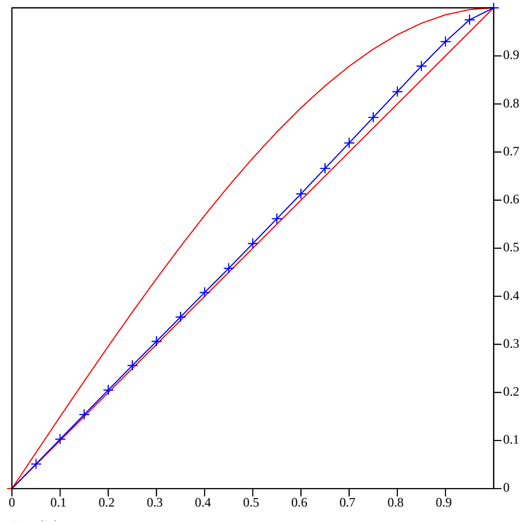
See: JE Padilla & TO Yeates, Acta Cryst D59, 1124 (2003).

Red line = theoretical untwinned

Red curve = theoretical perfectly twinned

Blue curve + points = observed

Wrong Merging

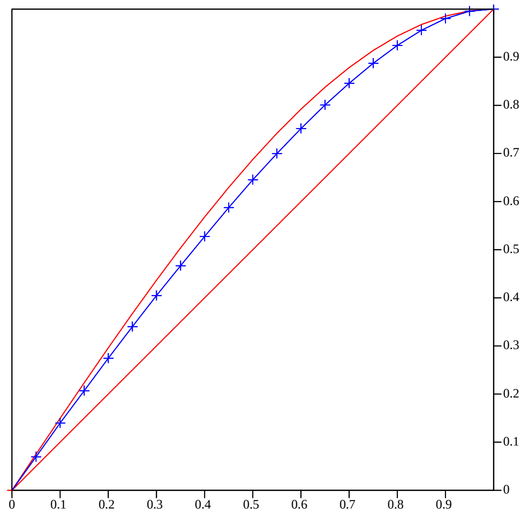


[1] 4/m / 4/mmm: R(int) 0.052(20645)/0.794(1070),

<|E^2-1|> 0.981/0.729

TWIN 0 1 0 1 0 0 0 0 -1

BASF 0.043 [C] or -0.082 [NC]



[1] 4/m / 4/mmm: R(int) 0.000(0)/0.000(0),

<|E^2-1|> 0.752/0.752

TWIN 0 1 0 1 0 0 0 0 -1

BASF 0.500 [C] or 0.500 [NC]

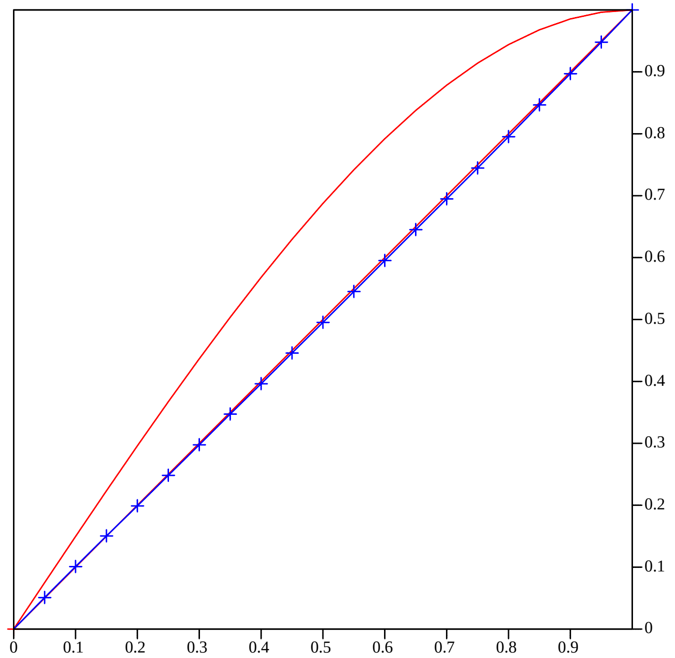
Perfect Twinning or Higher Symmetry

[1] 4/m / 4/mmm: R(int) 0.000(0)/0.047(12539),

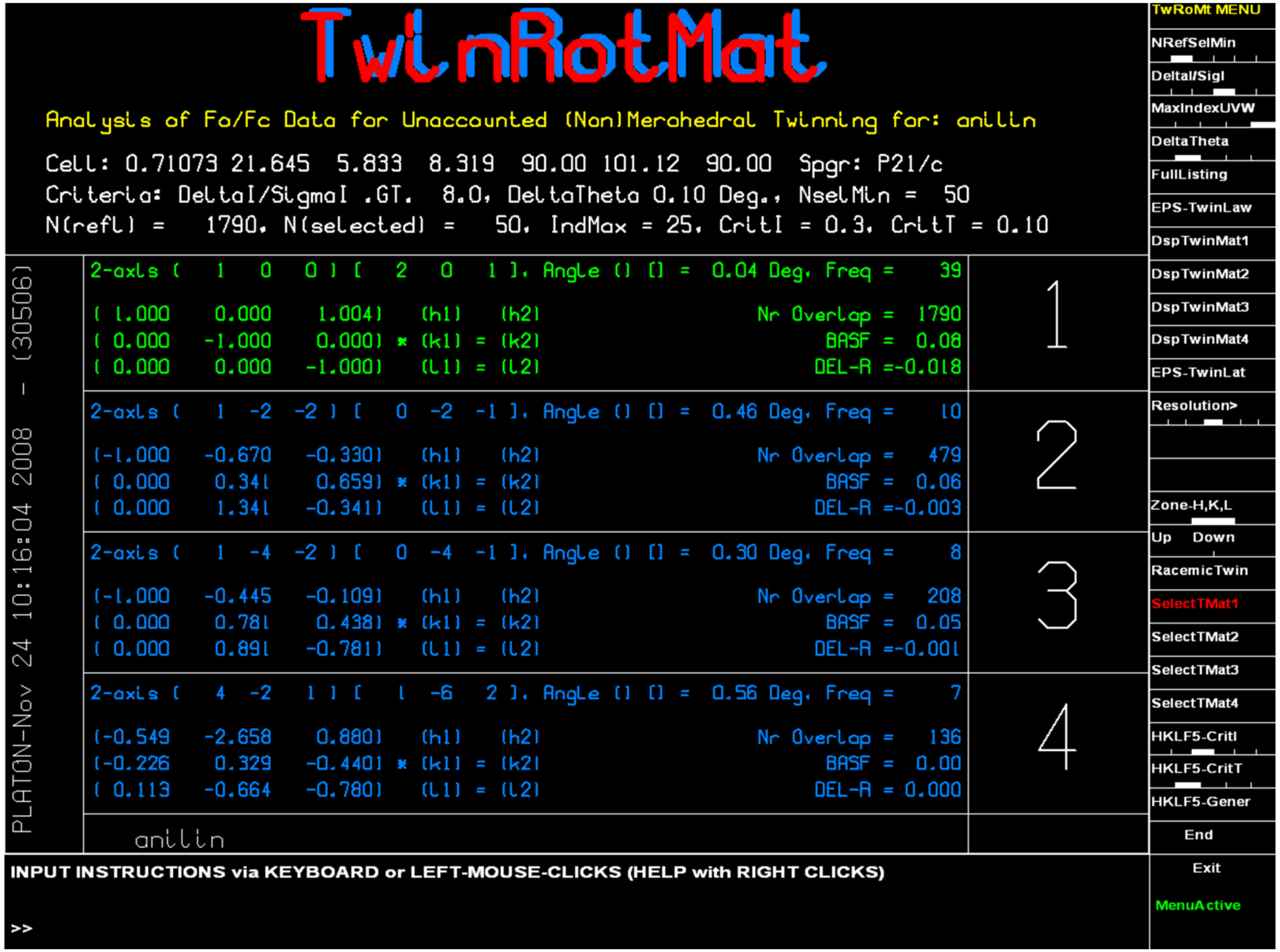
<|E^2-1|> 0.763/0.765

TWIN 0 1 0 1 0 0 0 0 -1

BASF 0.409 [C] or 0.384 [NC]



PLATON -TwinRotMat



www.mit.edu/platon_v40505/platon/docs/platon/pl000315.html

Obverse/ Reverse Twinning

	P	A	B	C	I	F	Obv	Rev	All
N	0	24004	23981	24079	23964	36032	31915	31944	147964
N I>3σ	0	6903	6913	7404	6931	10610	3990	6064	13592
<I>	0.0	80.3	81.4	84.3	80.8	82.0	16.8	66.2	81.0
<I/σ>	0.0	4.1	4.1	4.3	4.1	4.1	1.6	3.4	4.0

Obverse/reverse test for trigonal/hexagonal lattice
Mean I: obv only 145.5, rev only 28.0, neither obv nor rev 4.8
Preparing dataset for refinement with BASF 0.161 and TWIN -1 0 0 0 -1 0 0 0 1
Reflections absent for both components will be removed

Structure Solution

- For small molecules, normal direct methods are often able to solve twinned structures even for perfect twins, provided that the correct space group is used.

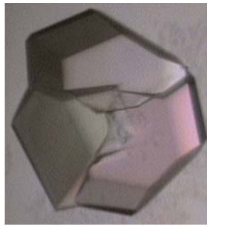
- SHELXD can use the twin law and the fractional contribution

- Detwinning

$$J_1 = (1-\alpha)\, I_1 + \alpha\, I_2 \qquad J_2 = (1-\alpha)\, I_2 + \alpha\, I_1$$

$$I_1 = \frac{(1-\alpha)J_1 - \alpha J_2}{1-2\alpha} \qquad I_2 = \frac{(1-\alpha)J_2 - \alpha J_1}{1-2\alpha}$$

Twin Refinement in SHELXL-97



Method of Pratt, Coyle and Ibers:

$$(F_c^2)^* = osf^2 \sum_{m=1}^{n} k_m F^2{}_{c_m}$$

osf = overall scale factor
k_m = fractional contribution of twin domain m
F_{cm} = F_c of twin domain m

$$1 = \sum_{m=1}^{n} k_m$$

$$k_1 = 1 - \sum_{m=2}^{n} k_m$$

(n-1) of the fractional contributions can be refined.

```
TWIN   r11  r12  r13   r21  r22  r23   r31  r32  r33   n
BASF   k2  k3  …  kn
```

or

```
MERG   0
BASF   k2  k3  …  kn
HKLF   5
```

C. S. Pratt, B. A. Coyle, J. A. Ibers, *J. Chem. Soc.* 2146, 1971
G. B. Jameson, *Acta Crystallogr.* A38, 817, 1982

Warning Signs for Merohedral Twinning

- Metric symmetry higher than Laue symmetry
- R_{int} for the higher symmetry Laue group only slightly higher than for the lower symmetry one
- Different R_{int} values for the higher symmetry Laue group for different crystals of the same compound
- Mean value for $|E^2 - 1| \ll 0.736$
- Apparent trigonal or hexagonal space group
- Systematic absences not consistent with any known space group
- No structure solution
- Patterson function physically impossible (for heavy atom structures)
- High R-Values

Warning Signs for Non-merohedral Twinning

- An unusually long axis
- Problems with cell refinement
- Some reflections sharp, others split
- $K = \text{mean}(F_o^2)/\text{mean}(F_c^2)$ is systematically high for reflections with low intensity
- For all of the most disagreeable reflections $F_o \gg F_c$.
- Strange residual density, which could not be resolved as solvent or disorder.

R. Herbst-Irmer, G. M. Sheldrick, Refinement of Twinned Structures with SHELXL97, *Acta Crystallog. B* **54**, 443, 1998

P. Müller, R. Herbst-Irmer, A. L. Spek, T. R. Schneider, M. R. Sawaya, Crystal Structure Refinement – A Crystallographer's Guide to SHELXL, Oxford University Press 2006

Acknowledgements

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