Göttingen, Februar 15th, 2012

Examples of (Pseudo-) Merohedral Twins

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

Space Group Determination

Crystal system H and Lattice type P selected

Mean |E*E-1| = 0.529 [expected .968 centrosym and .736 non-centrosym]

Systematic absence exceptions:

	$6_1/6_5$	$6_2=3_1$	6_3	-c-	--c
N	15	12	9	553	301
N I>3σ	1	1	1	535	279
<I>	1.3	1.3	1.4	265.5	253.1
<I/σ>	1.1	1.1	1.3	42.6	40.3

Opt.	Space Gr.	CSD	R(int)	N(eq)	Syst. Abs.	CFOM
[A]	$P6_1$	62	0.061	5574	1.3 / 34.8	6.18
[B]	$P6_5$	62	0.061	5574	1.3 / 34.8	6.18
[C]	$P6_122$	20	0.149	5954	1.3 / 34.8	85.55
[D]	$P6_522$	20	0.149	5954	1.3 / 34.8	85.55

Symmetry Operators in P6/mmm

Atomic Coordinates		Indices	
P-3			
x, y, z	-x, -y, -z	h, k, l	-h, -k, -l
-y, x-y, z	y,-x+y, -z	k, -h-k, l	-k, h+k, -l
-x+y,-x, z	x-y, x, -z	-h-k, h, l	h+k, -h, -l
P-31m			
-y, -x, -z	y, x, z	-k, -h, -l	k, h, l
-x+y, y, -z	x-y, -y, z	-h, h+k, -l	h, -h-k, l
x, x-y, -z	-x, -x+y, z	h+k, -k, -l	-h-k, k, l
P-3m1			
y, x, -z	-y, -x, z	k, h, -l	-k, -h, l
x-y, -y, -z	-x+y, y, z	h, -h-k, -l	-h, h+k, l
-x, -x+y, -z	x, x-y, z	-h-k, k, -l	h+k, -k, l
P6/m			
-x, -y, z	x, y, -z	-h, -k, l	h, k, -l
y, -x+y, z	-y, x-y, -z	-k, h+k, l	k, -h-k, -l
x-y, x, z	-x+y, -x, -z	h+k, -h, l	-h-k, h, -l

Merohedral Twins in the Trig./Hex. Crystal System

Laue group	Apparent Laue Group	Indices related by Twinning	Twin Law
-3	-31m	-k,-h, -l	0 -1 0 -1 0 0 0 0 -1
-3	-3m1	k, h, -l	0 1 0 1 0 0 0 0 -1
-3	6/m	-h,-k, l	-1 0 0 0 -1 0 0 0 1
-3	6/mmm	-k,-h, -l	0 -1 0 -1 0 0 0 0 -1
		k, h, -l	0 1 0 1 0 0 0 0 -1
		-h,-k, l	-1 0 0 0 -1 0 0 0 1
-3m1	6/mmm	-h,-k, l	-1 0 0 0 -1 0 0 0 1
-31m	6/mmm	-h,-k, l	-1 0 0 0 -1 0 0 0 1
6/m	**6/mmm**	**k, h, -l**	**0 1 0 1 0 0 0 0 -1**

XPREP 6.12

[1] -3 / -31m:
R(int) 0.060(4612)/0.142(898), <|E^2-1|> 0.505/0.487
TWIN 0 -1 0 -1 0 0 0 0 -1 BASF 0.382 [C] or 0.350 [NC]
[2] -3 / -3m1:
R(int) 0.060(4612)/0.156(824), <|E^2-1|> 0.505/0.486
TWIN 0 1 0 1 0 0 0 0 -1 BASF 0.365 [C] or 0.328 [NC]
[3] -3 / 6/m:
R(int) 0.060(4612)/0.012(962), <|E^2-1|> 0.505/0.514
TWIN -1 0 0 0 -1 0 0 0 1 BASF 0.481 [C] or 0.475 [NC]
[4] -31m / 6/mmm:
R(int) 0.142(898)/0.021(444), <|E^2-1|> 0.487/0.505
TWIN -1 0 0 0 -1 0 0 0 1 BASF 0.479 [C] or 0.474 [NC]
[5] -3m1 / 6/mmm:
R(int) 0.156(824)/0.022(518), <|E^2-1|> 0.486/0.506
TWIN -1 0 0 0 -1 0 0 0 1 BASF 0.481 [C] or 0.476 [NC]
[6] 6/m / 6/mmm:
R(int) 0.012(962)/0.183(380), <|E^2-1|> 0.514/0.505
TWIN 0 1 0 1 0 0 0 0 -1 BASF 0.365 [C] or 0.328 [NC]

Solution and Refinement

Patterson in $P6_1$: 1 Cs

```
TWIN  0 1 0  1 0 0  0 0 -1
BASF  .4
```

Difference Fourier with these coordinates:

	without	with TWIN
R1(F > 4σ(F))	0.245	0.133
wR2 (all data)	0.617	0.384
K2		0.355(9)
E-density	only few peaks	nearly the whole structure interpretable

R1 = 0.022
wR2 = 0.057
K2 = 0.341(1)

BUT:

** Possible racemic twinning or wrong absolute structure
- try TWIN refinement **

Flack x: 0.87(5)

Absolute Structure

Flack absolute structure parameter x:

$$(F_c^2)^* = (1-x)\, F_{c\,hkl}^2 + x\, F_{c\,-h-k-l}^2$$

- x = 0 → correct absolute structure
- x = 1 → wrong absolute structure

  Inversion of the structure: `MOVE 1 1 1 -1`

  exceptions for some space groups like Fdd2, $I4_1$ etc.

  sometimes it is necessary to change also the space group, e.g. $P3_1 \rightarrow P3_2$
- 0 < x < 1 →

** Possible racemic twinning or wrong absolute structure - try TWIN refinement **

```
TWIN  -1 0 0  0 -1 0  0 0 -1  2
BASF  k2
```

H. D. Flack, *Acta Crystallogr.* A39, 876 (1983)

Additional Racemic Twinning ?

Perhaps four twin domains with following indices:

h, k, l	
k, h, -l	TWIN matrix
-h, -k, -l	Racemic twinning
-k, -h, l	TWIN matrix and racemic twinning

```
TWIN  0 1 0  1 0 0  0 0 -1  -4
BASF  .2  .2  .2
```

Parameter	Value	s.u.	Indices
K1	1-(K2+K3+K4)		h, k, l
K2	0.00395	0.02478	k, h, -l
K3	0.69754	0.03486	-h, -k, -l
K4	0.33611	0.02478	-k, -h, l

correct space group $P6_5$:

```
MOVE  1  1  1  -1
TWIN  0 1 0  1 0 0  0 0 -1
```

Different Refinements

A: Space group $P6_1$
TWIN 0 1 0 1 0 0 0 0 -1

B: Space group $P6_1$
TWIN 0 -1 0 -1 0 0 0 0 1

C: Space group $P6_5$
TWIN 0 -1 0 -1 0 0 0 0 1

D: Space group $P6_5$
TWIN 0 1 0 1 0 0 0 0 -1

	R1	wR2	K2	Flack x	s.u. (C - C)
A	0.022	0.057	0.341(1)	0.87(5)	0.011 - 0.013
B	0.021	0.054	0.341(1)	0.35(3)	0.010 - 0.012
C	0.020	0.049	0.340(1)	0.09(3)	0.009 - 0.011
D	0.018	0.046	0.340(1)	-0.03(4)	0.008 - 0.010

Example of a Pseudo-Merohedrally-Twinned Structure

Very instable compound, difficult to mount,

But good crystal quality

unknown Al-compound, possible composition
$C_{27}H_{26}AlN_2$, perhaps some I from the starting material

cell: 16.934 16.934 12.603 90.00 90.00 120.00

hexagonal metric

Crystal System

Search for higher metric symmetry

Option A: FOM = 0.00 deg. HEXAG. P-lattice R(sym) = 0.653 [10906]
Cell: 16.934 16.934 12.603 90.00 90.00 120.00 Volume: 3129.81
Matrix: 1.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000 1.000

Option B: FOM = 0.00 deg. ORTHO. C-lattice R(sym) = 0.493 [11989]
Cell: 16.934 29.330 12.603 90.00 90.00 90.00 Volume: 6259.63
Matrix: 0.000 1.000 0.000 2.000 1.000 0.000 0.000 0.000 -1.000

Option C: FOM = 0.00 deg. ORTHO. C-lattice R(sym) = 0.493 [12004]
Cell: 16.934 29.330 12.603 90.00 90.00 90.00 Volume: 6259.63
Matrix: 1.000 1.000 0.000 -1.000 1.000 0.000 0.000 0.000 1.000

Option D: FOM = 0.00 deg. ORTHO. C-lattice R(sym) = 0.033 [12024]
Cell: 16.934 29.330 12.603 90.00 90.00 90.00 Volume: 6259.63
Matrix: 1.000 0.000 0.000 1.000 2.000 0.000 0.000 0.000 1.000

Orthorhombic?

Crystal system O and Lattice type C selected

Mean |E*E-1| = 0.702 [expected .968 centrosym and .736 non-centrosym]

Systematic absence exceptions:

	c--	n--	-c-	-n-	--a	--b	--21
N	1259	1259	785	785	1602	1602	41
N I>3s	891	891	548	548	0	0	0
<I>	29.2	29.2	65.3	65.3	0.2	0.2	0.1
<I/s>	28.0	28.0	35.0	35.0	0.3	0.3	0.3

Opt. Space Gr. No. CSD R(sym) N(eq) Syst. Abs. CFOM

No acceptable space group - change tolerances or unset chiral flag
or possibly change input lattice type, then recheck cell using H-option

Monoclinic Space Group?

Cell: 16.934 12.603 16.934 90.00 120.00 90.00

Monoclinic P R_{int} = 0.026

Crystal system M and Lattice type P selected

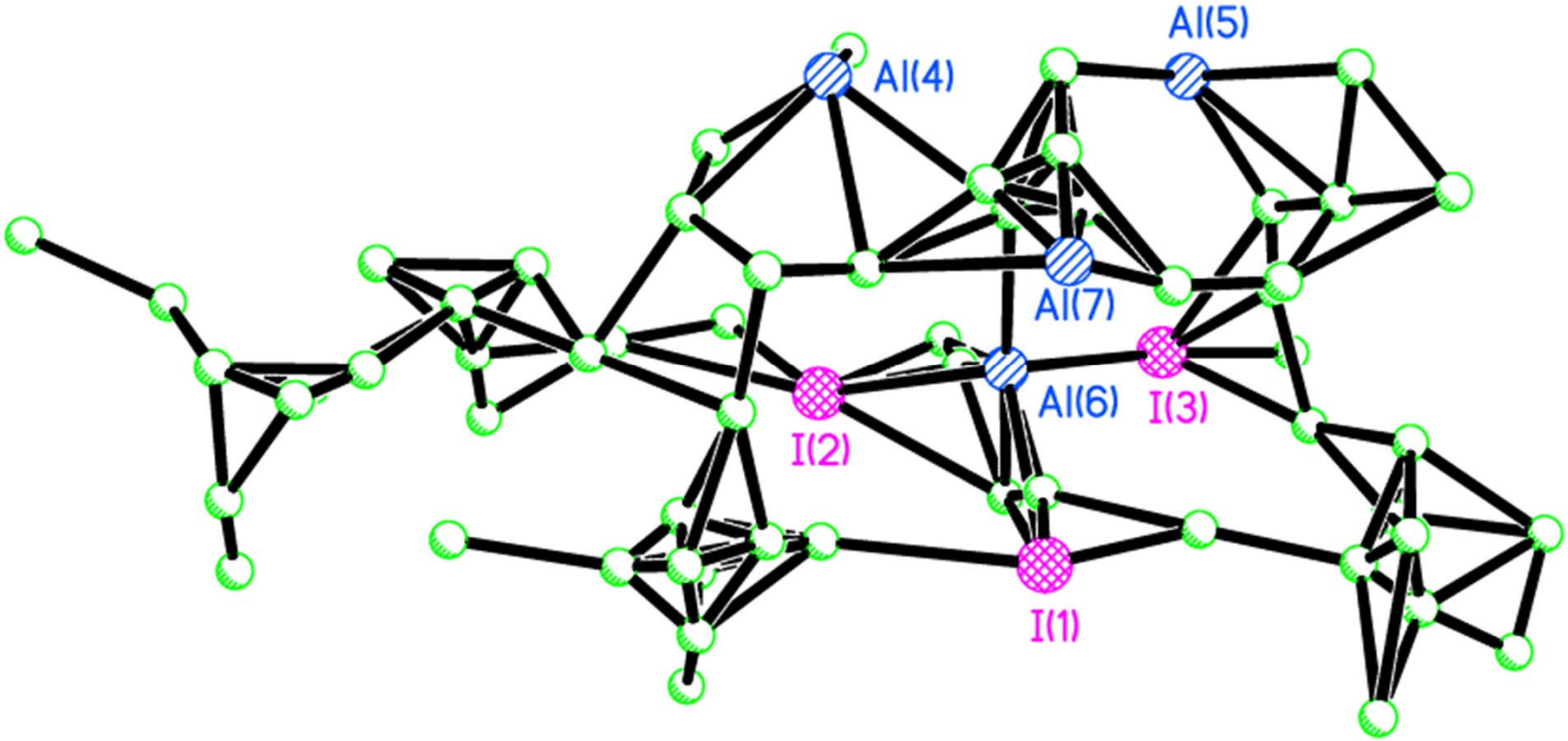
Mean |E*E-1| = 0.708 [expected .968 centrosym and .736 non-centrosym]

Systematic absence exceptions:

	-21-	-a-	-c-	-n-
N	41	1732	1602	1726
N (I>3σ)	0	839	0	839
<I>	0.1	35.3	0.2	35.4
<I/σ>	0.3	17.9	0.3	18.0

Opt.	Space Gr.	No.	CSD	R(sym)	N(eq)	Syst. Abs.	CFOM
[A]	P2(1)/c	# 14	19410	0.026	7746	0.3 / 17.9	7.35

Solution in $P2_1/c$



RE = 0.365 for 48 atoms and 2982 E-values

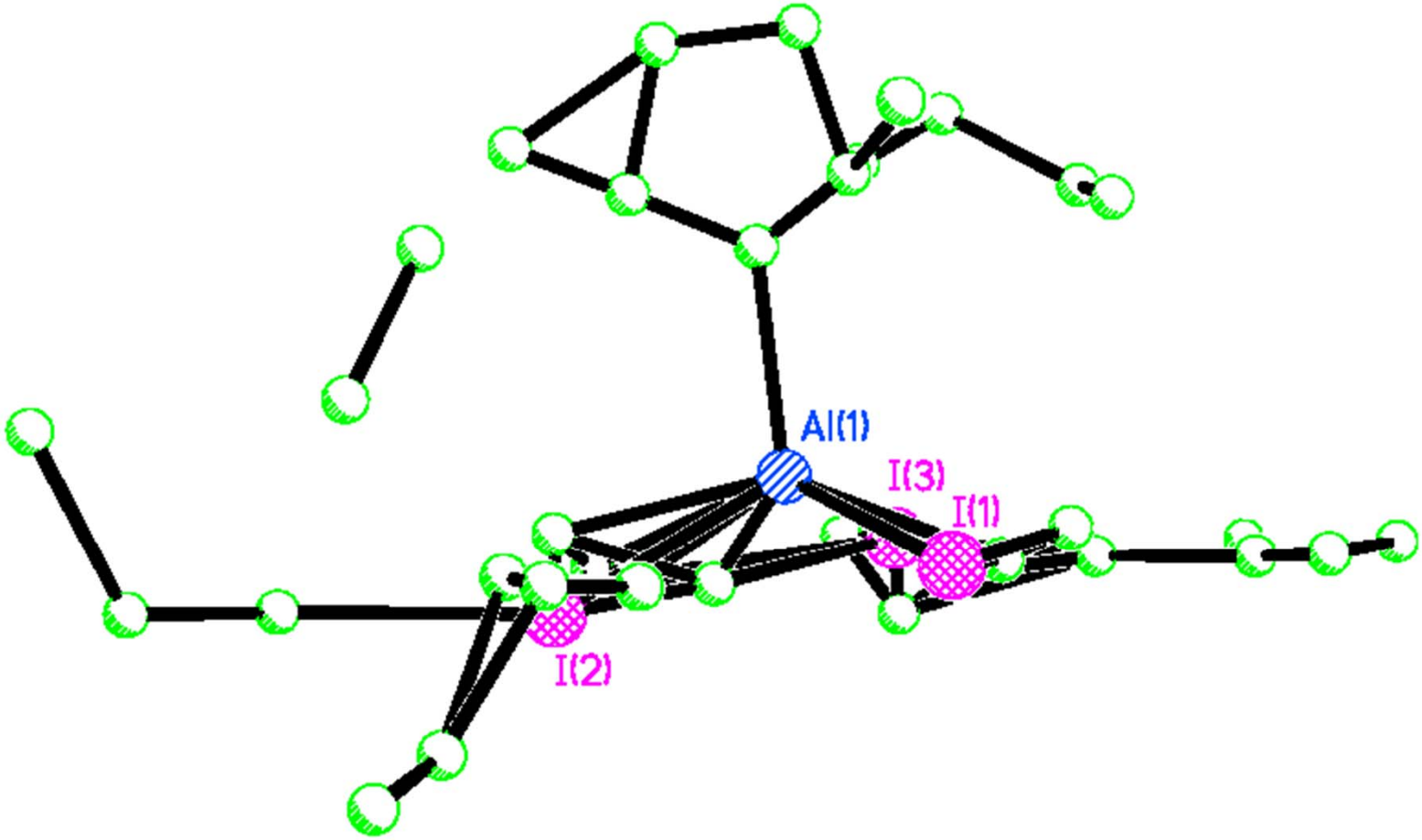
AlI_3 unit can be identified

Refinement in $P2_1/c$

Refinement of the AlI_3 unit

R1 = 0.3427

wR2 = 0.7607



Determination of the Twin Matrix

$$\begin{pmatrix}\text{orthorhombic}\\ \downarrow \\ \text{monoclinic}\end{pmatrix} \qquad \begin{pmatrix}\text{twofold}\\ \text{axis}\end{pmatrix} \qquad \begin{pmatrix}\text{monoclinic}\\ \downarrow \\ \text{orthorhombic}\end{pmatrix}$$

$$\begin{pmatrix} 0.5 & -0.5 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix} \qquad \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \begin{pmatrix} 0 & 0 & -1 \\ -2 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} \mathbf{1} & \mathbf{0} & \mathbf{1} \\ \mathbf{0} & \mathbf{-1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{-1} \end{pmatrix}$$

Check of the Matrix

- The matrix must transform the cell into an equivalent cell.
- The matrix must not be a symmetry operator of the Laue group of the structure.
- The refinement of the BASF factors is reasonable (i.e. the value is in between 0 and 1 and the s.u. is relatively small).
- The TWIN command must improve your refinement.

ROTAX / TwinRotMat -Theory

- Generation of matrices for possible two-fold axis about reciprocal or real axes with small indices
- Use of the data with the largest (F^2_{obs}-F^2_{calc})/sigma values)
- Transformation of the indices by the possible rotation matrix.
- Deviation from integral values as figure of merit
- A small figure of merit means that most (or all) of the indices were transformed to integers and this makes it a likely candidate for a twin law.

TwinRotMat - Output

P.L.A.T.O.N

TwinRotMat

Analysis of Fo/Fc Data for Unaccounted (Non)Merohedral Twinning for: p21c

Cell: 0.71073 16.934 12.603 16.934 90.00 120.00 90.00 Spgr: P21/c
Criteria: DeltaI/SigmaI .GT. 4.0, DeltaTheta 0.10 Deg., NselMin = 50
N(refl) = 8918, N(selected) = 50, IndMax = 5, CritI = 0.1, CritT = 0.10

PLATON-Aug 30 10:05:00 2011 - (300311)
Fc from Fo/Fc File

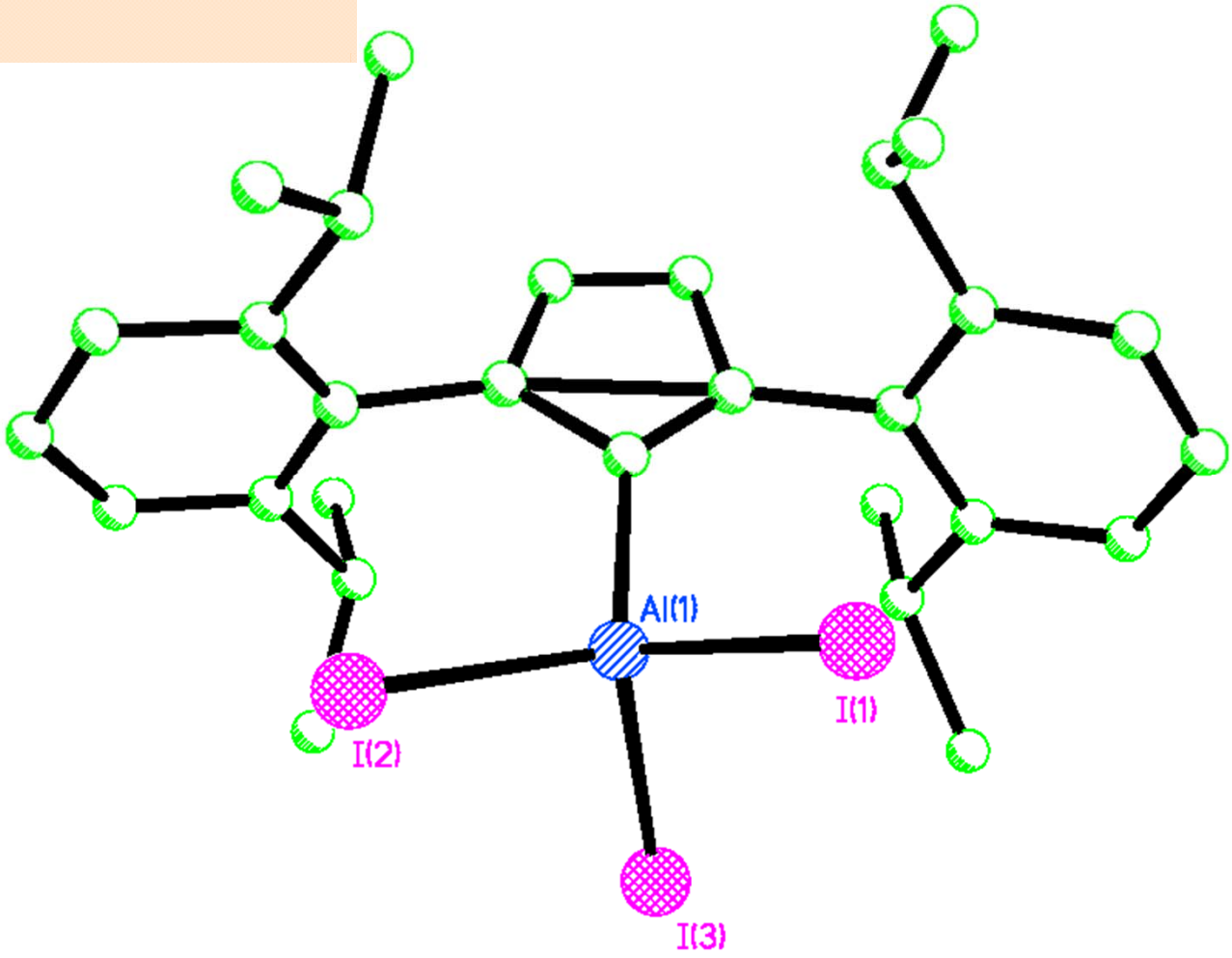
2-axis (1 0 0) [2 0 1], Angle () [] = 0.00 Deg, Freq = 50		1
(1.000 0.000 1.000) (h1) (h2)	Nr Overlap = 8918	
(0.000 -1.000 0.000) * (k1) = (k2)	BASF = 0.50	
(0.000 0.000 -1.000) (l1) (l2)	DEL-R =-0.200	
2-axis (0 0 1) [1 0 2], Angle () [] = 0.00 Deg, Freq = 55		2
(-1.000 0.000 0.000) (h1) (h2)	Nr Overlap = 8740	
(0.000 -1.000 0.000) * (k1) = (k2)	BASF = 0.17	
(1.000 0.000 1.000) (l1) (l2)	DEL-R =-0.034	
2-axis (1 0 -1) [1 0 -1], Angle () [] = 0.00 Deg, Freq = 50		3
(0.000 0.000 -1.000) (h1) (h2)	Nr Overlap = 8735	
(0.000 -1.000 0.000) * (k1) = (k2)	BASF = 0.18	
(-1.000 0.000 0.000) (l1) (l2)	DEL-R =-0.034	
2-axis (0 1 -1) [-2 5 -4], Angle () [] = 2.27 Deg, Freq = 14		4
(-1.000 0.000 0.000) (h1) (h2)	Nr Overlap = 1542	
(-0.425 0.150 -0.850) * (k1) = (k2)	BASF = 0.14	
(0.425 -1.150 -0.150) (l1) (l2)	DEL-R =-0.007	
p21c		

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

TwinRoMt 25
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
FullListing
EPS-TwinLaw
DspTwinMat1
DspTwinMat2
DspTwinMat3
DspTwinMat4
EPS-TwinLat
Resolution>
IcalFromCIF
Zone-H,K,L
Up Down
RacemicTwin
SelectTMat1
SelectTMat2
SelectTMat3
SelectTMat4
HKLF5-CritI
HKLF5-CritT
HKLF5-Gener
End
Exit

Refinement as Twin

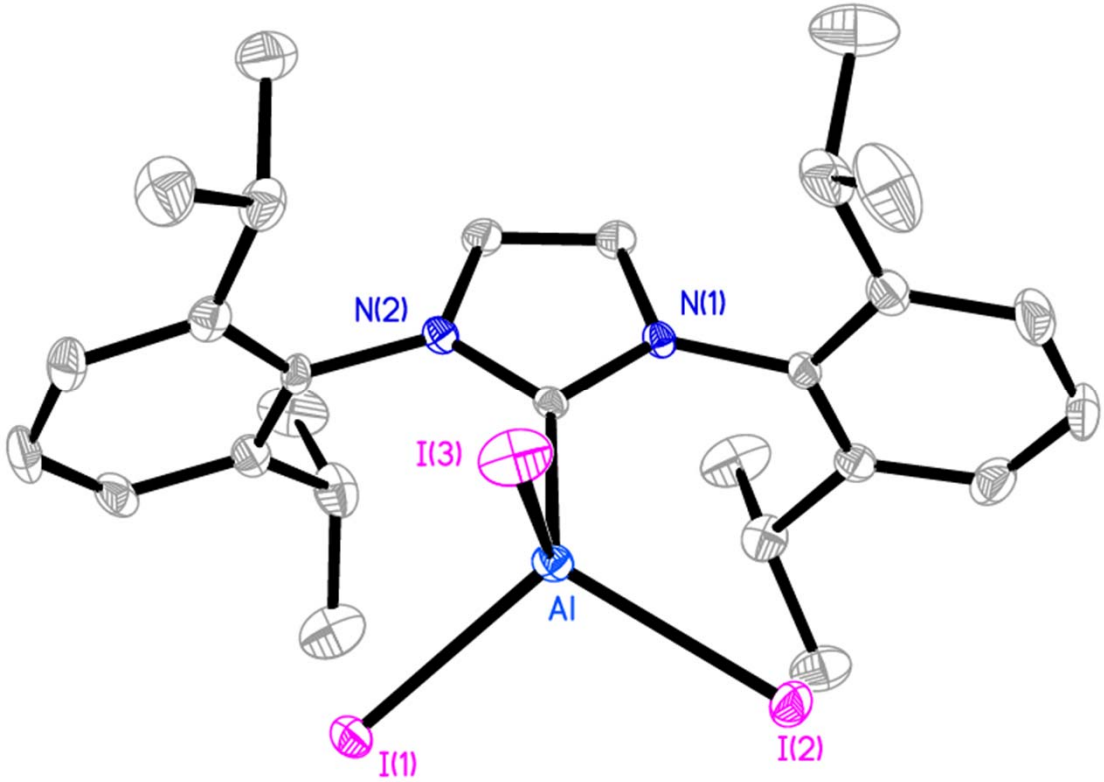
```
TWIN  1 0 1   0 -1 0   0 0 -1
BASF  0.5
```



R1 = 0.1487

wR2 = 0.4103

Final Results

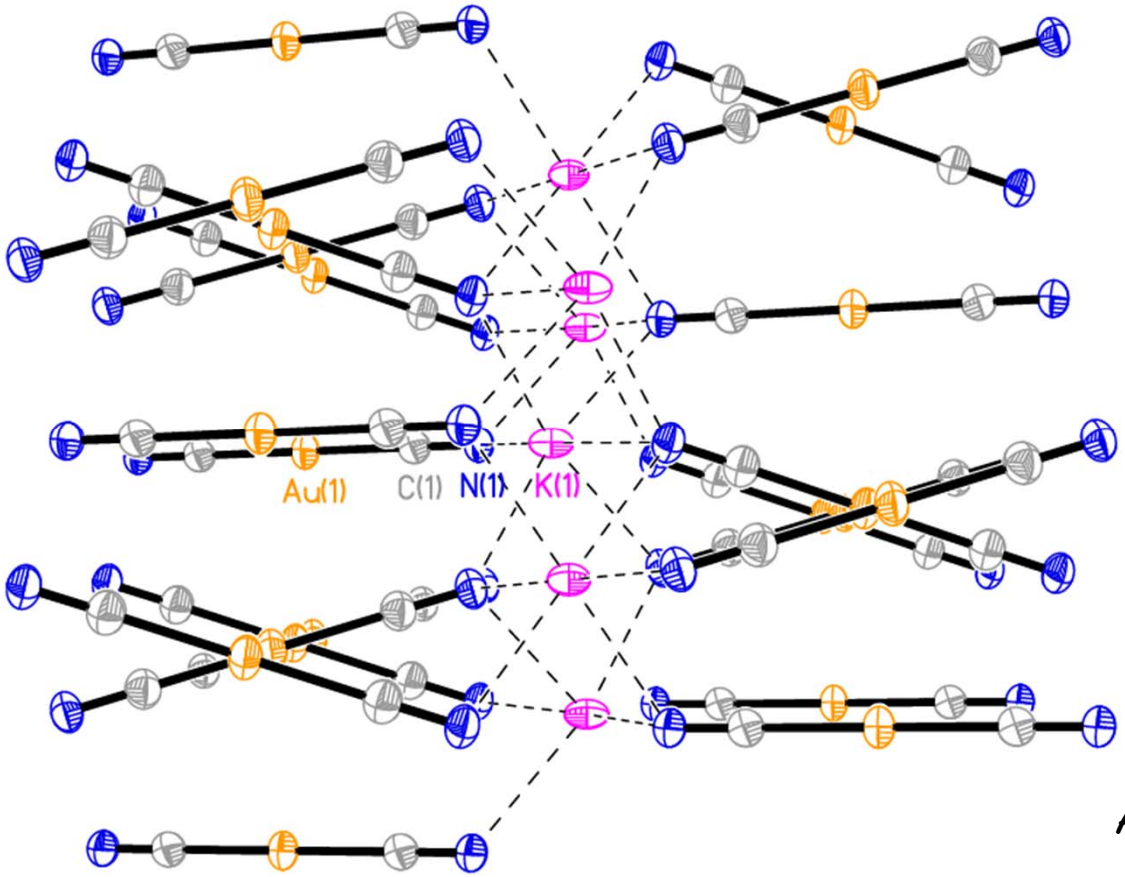


R1 (F > 4σ(F))	0.022	wR2 (all data)	0.046
K2	0.4982(4)	Parameter	307
Data	8918	Residual Density [eÅ^{-3}]	1.07

R. S. Ghadwal, H. W. Roesky, R. Herbst-Irmer, P. G. Jones, N-Heterocyclic Carbene Adducts of Aluminum Triiodide, *Z. Anorg. Allgem. Chem*, **635**, 431, 2009.

Twinning by Reticular Merohedry

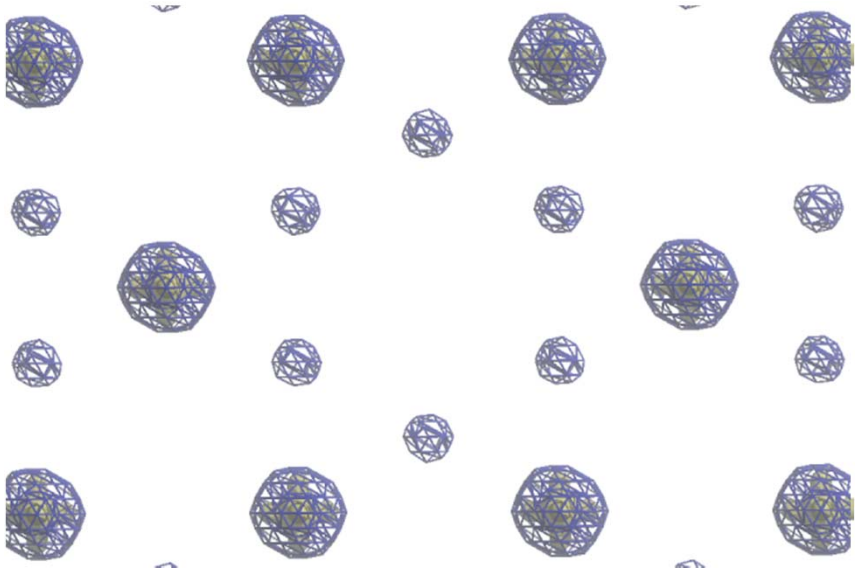
Structure of $K[Au(CN)_2]$
cell: 7.240 7.240 26.445 90 90 120, space group R $\bar{3}$

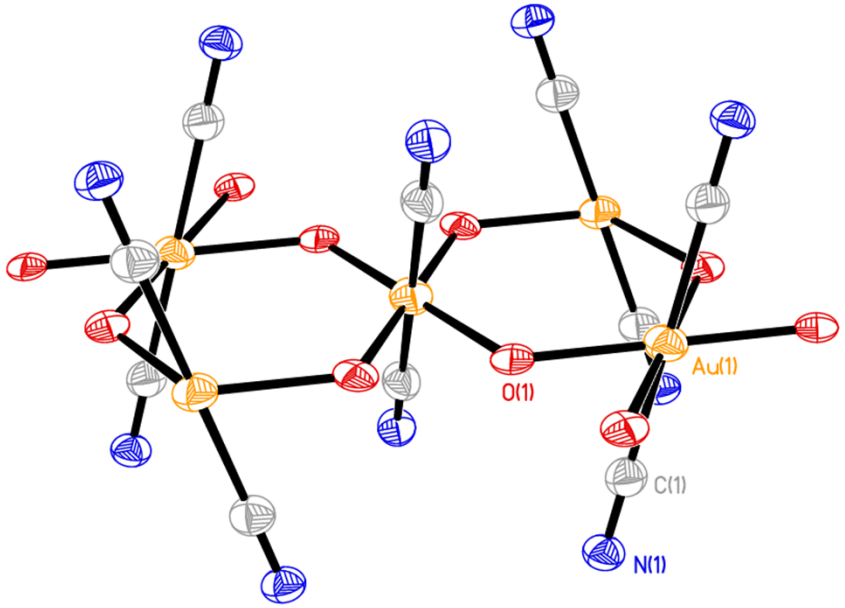


A. Rosenzweig, D. T. Cromer,
Acta Cryst. (1959). 12, 709.

$K[Au(CN)_2]$

R1 = 0.074 for 640 $F_o > 4\sigma(F_o)$, wR2 = 0.170 for all 648 data





R1 = 0.027 for 640 Fo > 4σ(Fo), wR2 = 0.076 for all 648 data
Residual density: 1.18/-1.48 e/A^3

Warning Signs

Systematic Absences Violations:

2	0	0	8.08	2.00	observed but should be systematically absent
-1	0	1	507.42	32.65	observed but should be systematically absent
-1	0	1	610.89	37.97	observed but should be systematically absent
1	0	-1	517.12	34.48	observed but should be systematically absent
0	-1	-1	540.26	33.43	observed but should be systematically absent
1	-1	1	512.14	35.24	observed but should be systematically absent
10	-1	-1	557.75	34.37	observed but should be systematically absent

...

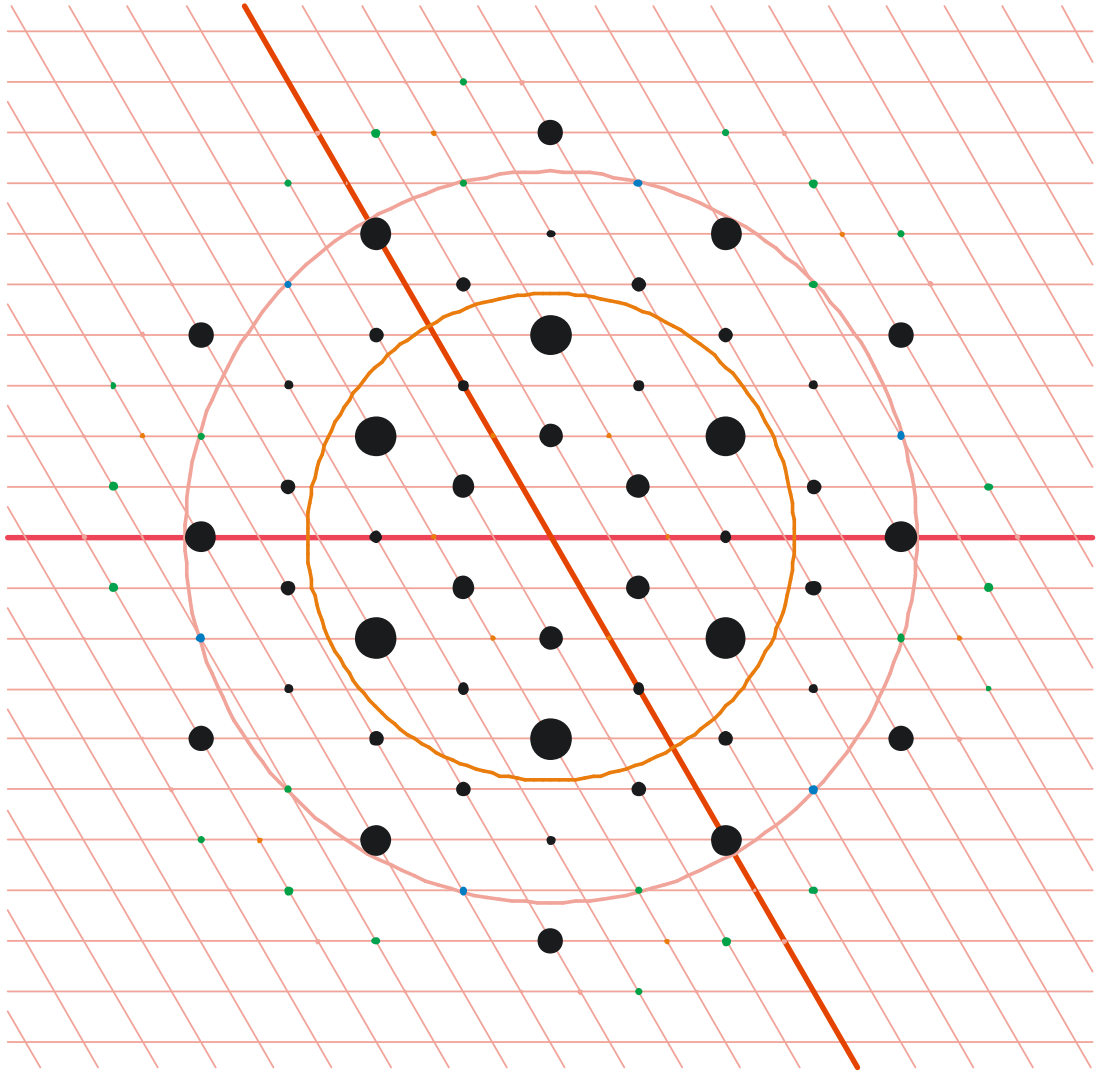
Most Disagreeable Reflections

h	k	l	F_o^2	F_c^2	$\Delta(F^2)/\sigma$	F_c/F_{cmax}	Res.(Å)
0	3	0	1907.04	407.73	11.79	0.026	2.09
-1	2	6	7075.12	11145.69	6.78	0.137	2.80
1	1	6	1275.08	818.27	3.69	0.037	2.80
-1	2	0	27026.22	32870.20	3.53	0.235	3.60
-1	2	3	47884.52	56252.36	2.98	0.307	3.35
-1	2	12	7698.09	9417.93	2.98	0.126	1.88
-5	4	6	642.68	966.24	2.77	0.040	1.31

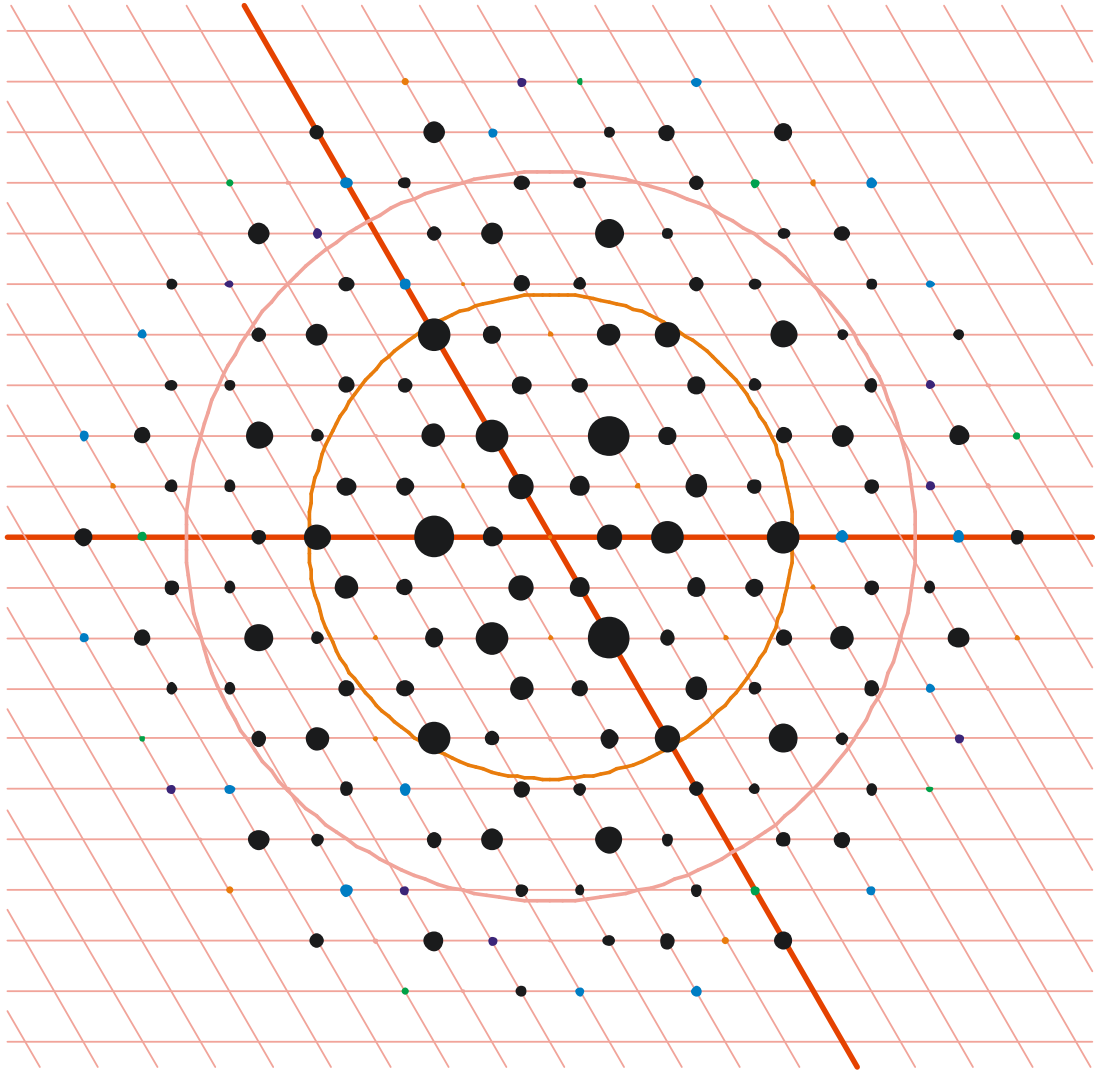
...

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

Reciprocal Space Plot l = 0



Reciprocal Space Plot l = 2



Obverse/Reverse Twinning

	P	A	B	C	I	F	Obv	Rev	All
N	0	4252	4264	4282	4258	6399	5663	5715	8516
N I>3σ	0	2177	2189	2180	2198	3273	1698	1887	4447
<I>	0.0	303.7	302.2	132.1	303.5	245.8	93.4	246.6	341.6
<I/σ>	0.0	6.0	6.0	5.4	6.0	5.8	3.3	4.2	6.1

Obverse/reverse test for trigonal/hexagonal lattice

Mean I: obv only 619.5, rev only 252.1, neither obv nor rev 0.5,

Preparing dataset for refinement with BASF 0.289 and TWIN -1 0 0 0 -1 0 0 0 1

Reflections absent for both components will be removed

Obverse/Reverse Twinning

P.L.A.T.O.N

TwinRotMat

Analysis of Fo/Fc Data for Unaccounted (Non)Merohedral Twinning for: hp33

Cell: 0.71073 7.240 7.240 26.445 90.00 90.00 120.00 Spgr: R-3

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

N(refl) = 648. N(selected) = 50. IndMax = 5. CritI = 0.1, CritT = 0.10

PLATON-Sep 02 09:57:00 2011 - (300311)

Fc from Fo/Fc File

2-axis (0 1 0) [1 2 0], Angle () [] = 0.00 Deg, Freq = 50 ********** (-1.000 0.000 0.000) (h1) (h2) Nr Overlap = 223 (1.000 1.000 0.000) * (k1) = (k2) BASF = 0.27 (0.000 0.000 -1.000) (l1) (l2) DEL-R =-0.044	1	
2-axis (0 0 1) [0 0 1], Angle () [] = 0.00 Deg, Freq = 46 ********** (-1.000 0.000 0.000) (h1) (h2) Nr Overlap = 223 (0.000 -1.000 0.000) * (k1) = (k2) BASF = 0.23 (0.000 0.000 1.000) (l1) (l2) DEL-R =-0.039	2	
2-axis (1 -2 0) [0 -1 0], Angle () [] = 0.00 Deg, Freq = 50 ********** (-1.000 -1.000 0.000) (h1) (h2) Nr Overlap = 648 (0.000 1.000 0.000) * (k1) = (k2) BASF = 0.03 (0.000 0.000 -1.000) (l1) (l2) DEL-R = 0.000	3	
hp33		

TwinRoMt 25
NRefSelMin
DeltaI/SigI
MaxIndexUVW
DeltaTheta
FullListing
EPS-TwinLaw
DspTwinMat1
DspTwinMat2
DspTwinMat3
DspTwinMat4
EPS-TwinLat
Resolution>
IcalFromCIF
Zone-H,K,L
Up Down
RacemicTwin
SelectTMat1
SelectTMat2
SelectTMat3
SelectTMat4
HKLF5-CritI
HKLF5-CritT
HKLF5-Gener
End

Refinement as Twin – SHELXL-97

```
MERG  0
BASF  0.3
HKLF  5
```

original hkl-file
after merging in XPREP

h	k	l	F^2	$\sigma(F^2)$
-3	2	1	547.68	13.89
-2	2	1	3919.92	91.76
-1	2	1	0.4728	0.786
-1	2	0	792.98	19.51
-5	4	3	1287.24	31.66

new hkl-file

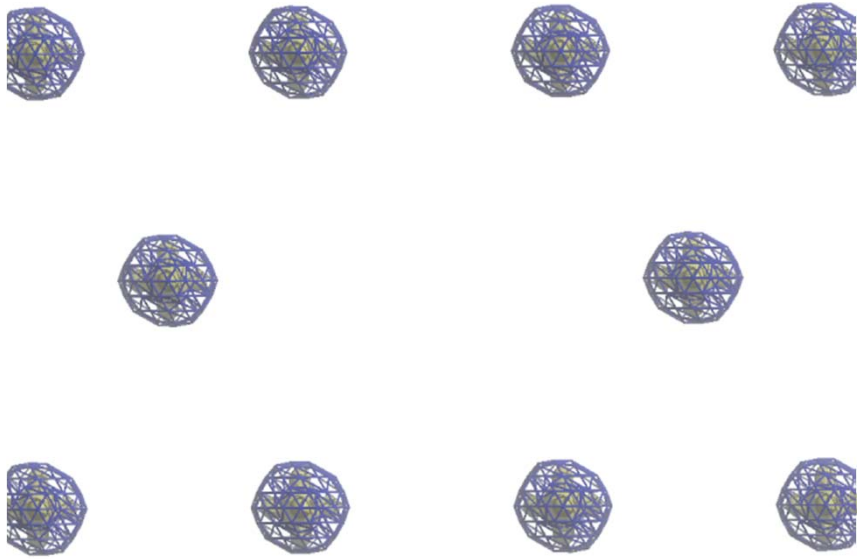
h	k	l	F^2	$\sigma(F^2)$	N
-2	2	1	3919.92	91.76	1
2	-1	0	792.98	19.51	-2
-1	2	0	792.98	19.51	1
4	-5	3	1287.24	31.66	-2
-5	4	3	1287.24	31.66	1

Refinement as Twin – SHELXL-2012

```
TWIN  0 -1 0  -1 0 0  0 0 -1
BASF  0.3
HKLF  4
```

Refinement as Twin - Results

R1 = 0.0178 for 640 $F_o > 4\ \sigma(F_o)$
wR2 = 0.0430 for 648 data
K2 = 0.290(4)



Residual density maximum = 1.03 e/Å^3

S. R. Hettiarachchi, B. K. Schaefer, R. L. Yson, R. J. Staples, R. Herbst-Irmer, H. H. Patterson, *Inorg. Chem.*, **46**, 6997, 2007.

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