Diffraction Experiments of Arbitrary Geometry

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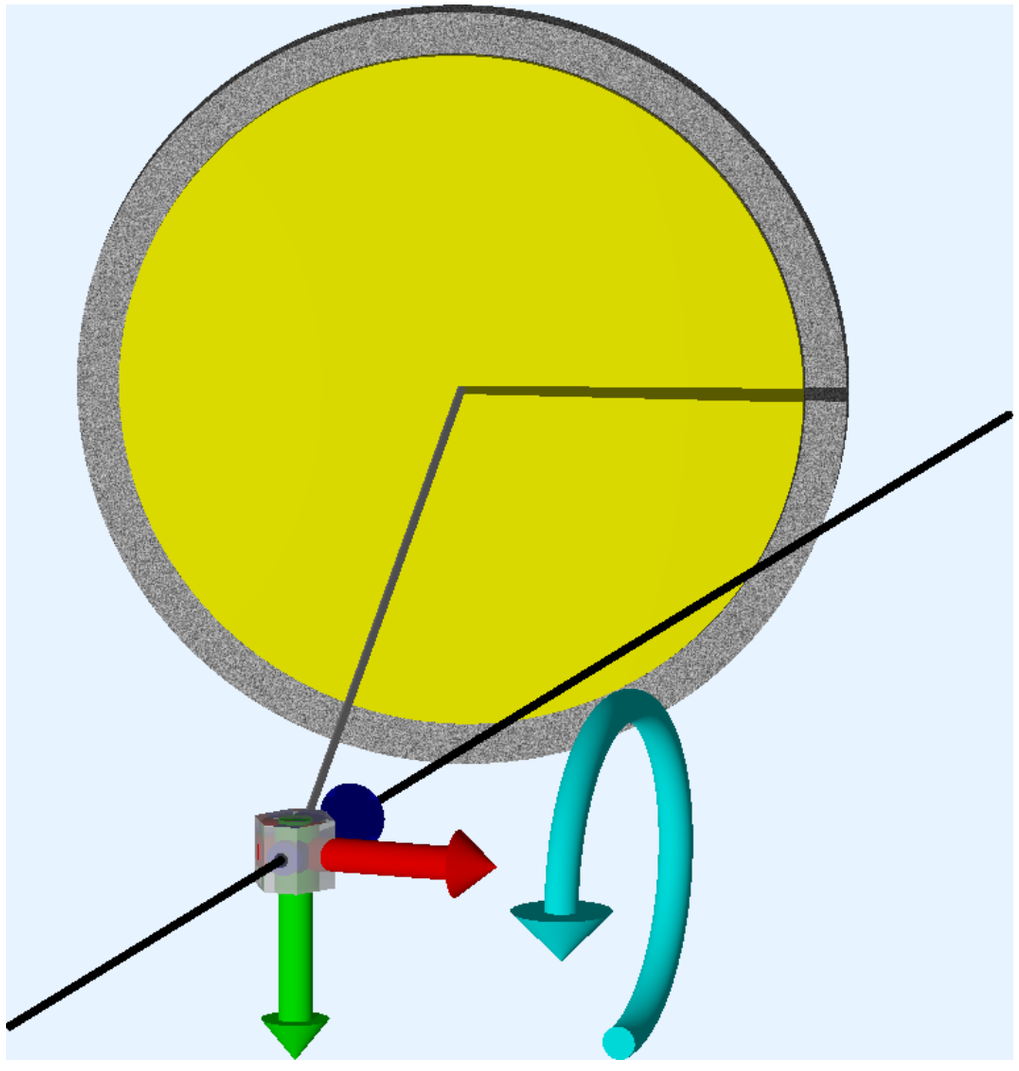
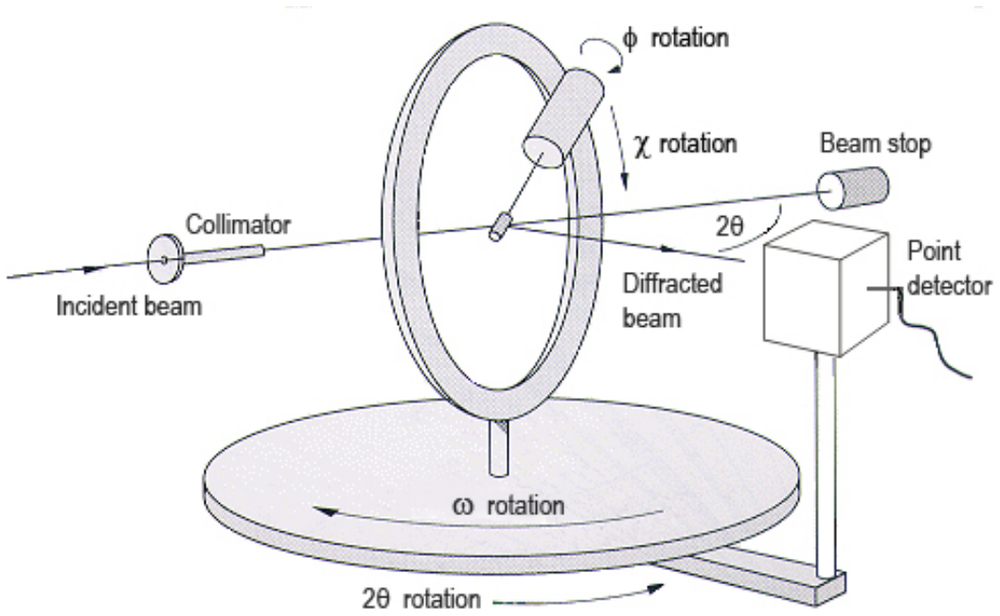
Laboratory Coordinate System



- Green: Y–axis (gravity)
- Blue: Z–axis (idealised source → crystal)
- Red: X–axis (right handed coordinate system)

Angles and Rotation Axes



(CSIC http://www.xtal.iqfr.csic.es/Cristalografia/index-en.html)

Name	Axis Definition	Remark
2θ	Detector normal against (000)	
ϕ	Crystal rotation axis “about crystal pin”	Common for MX
ω	Crystal rotation abous vertical axis	better completeness
χ	Rotation of ϕ axis about $S_0(000)$ at $\omega = 0°$	
κ	Rotation about ϕ, but pin axis off	

Reasons for “non–standard” Data Collection

- Real Multiplicity: reduction of random (and systematic) errors
  - S–SAD phasing
  - Chirality from light atoms (C, N, O)*
- Data Completeness
  - Long wavelength *vs.* high resolution data
  - Well diffracting crystal hit Bragg limit $d_{\text{min}} \geq \lambda/2$
  - Low Symmetry Space Group (P1)

*Parsons, Flack, Wagner (2013), Acta Cryst. B69, 249–259

Description of Diffraction Geometry (in XDS)

Detector

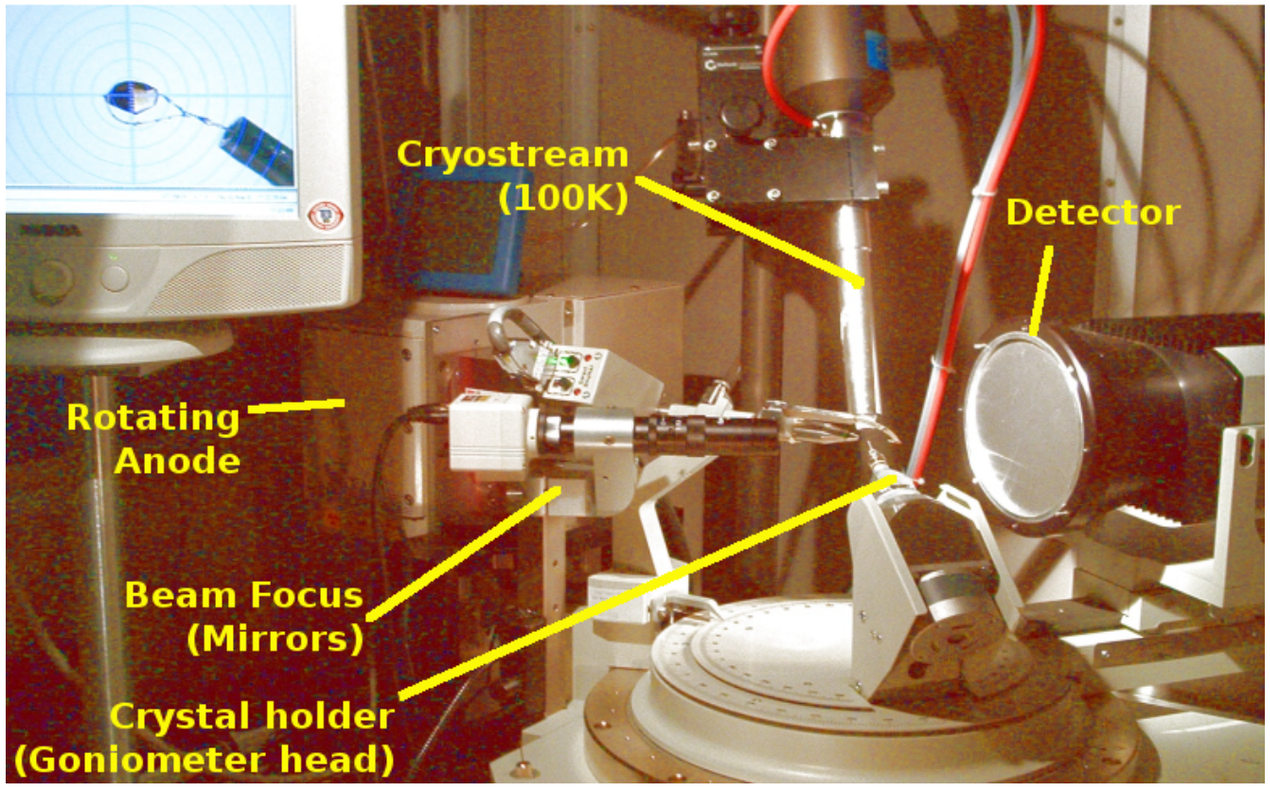
- `DIRECTION_OF_DETECTOR_X-AXIS`, `DIRECTION_OF_DETECTORY-AXIS`
- `ORGX`, `ORGY`
- `DETECTOR_DISTANCE`

Beam

- `INCIDENT_BEAM_DIRECTION`
  seldomly changed from $(0, 0, 1)$

Experiment

- `ROTATION_AXIS`
- `OSCILLATION_RANGE` always $> 0°$!



Detector Orientation

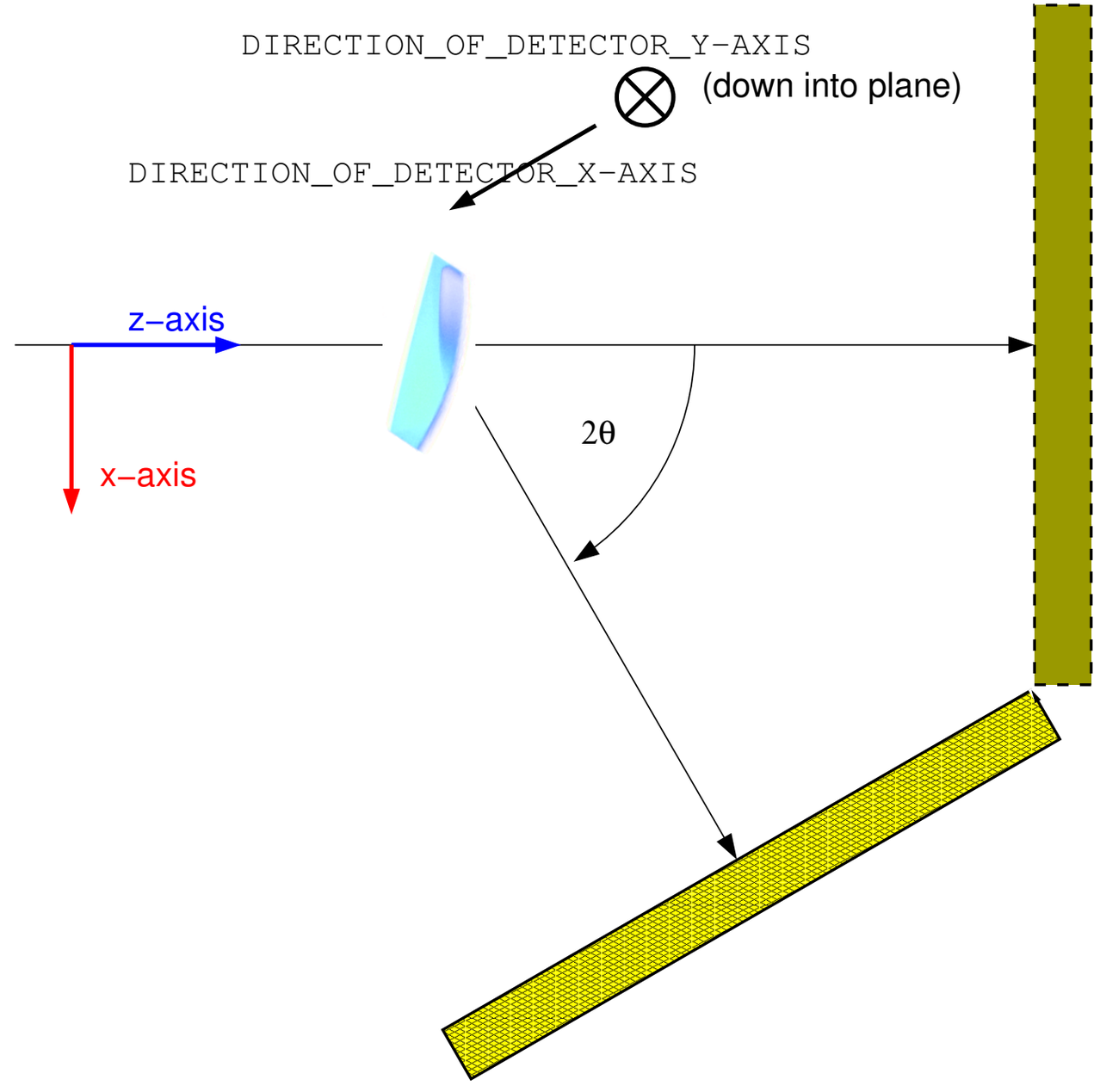
Detector described by `DIRECTION_OF_DETECTOR_X-AXIS` and `DIRECTION_OF_DETECTOR_Y-AXIS`

- Detector must be planar (for XDS)
- Several segments allowed (e.g. Pilatus 12M at I23, Diamond)

`ORGX, ORGY`: Detector point closest to crystal in detector plane, `ORGX` $\approx$ `NX/2`, `ORGY` $\approx$ `NY/2`

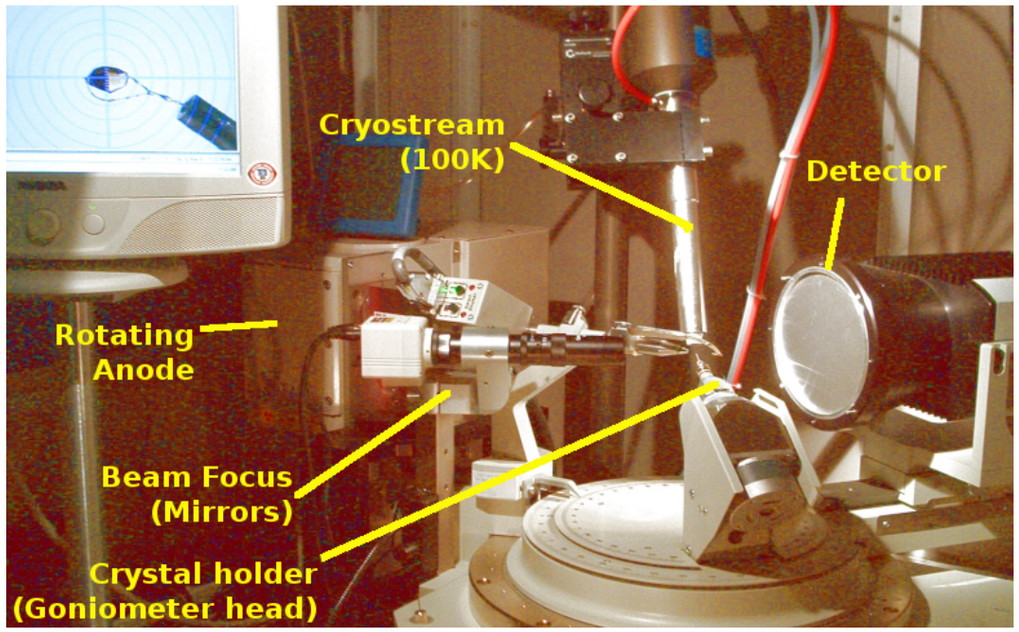
Detector Orientation

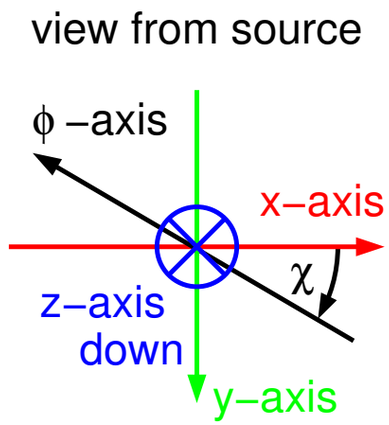
- $2\theta = 0°$: $X = (1,0,0)$, $Y = (0,1,0)$
- Rotation of Detector about vertical axis:
  - $X = (\cos 2\theta, 0, -\sin 2\theta)$, $Y = (0,1,0)$,
  - NB: how is 2θ measured?
  - ORGX, ORGY unchanged

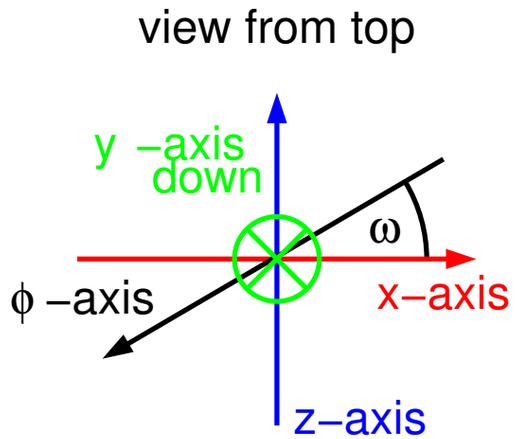


Manual Computation of Axes

Break down orientation into simple rotations:







$$\vec{r}' = \begin{pmatrix} \cos\chi & -\sin\chi & 0 \\ \sin\chi & \cos\chi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix}$$

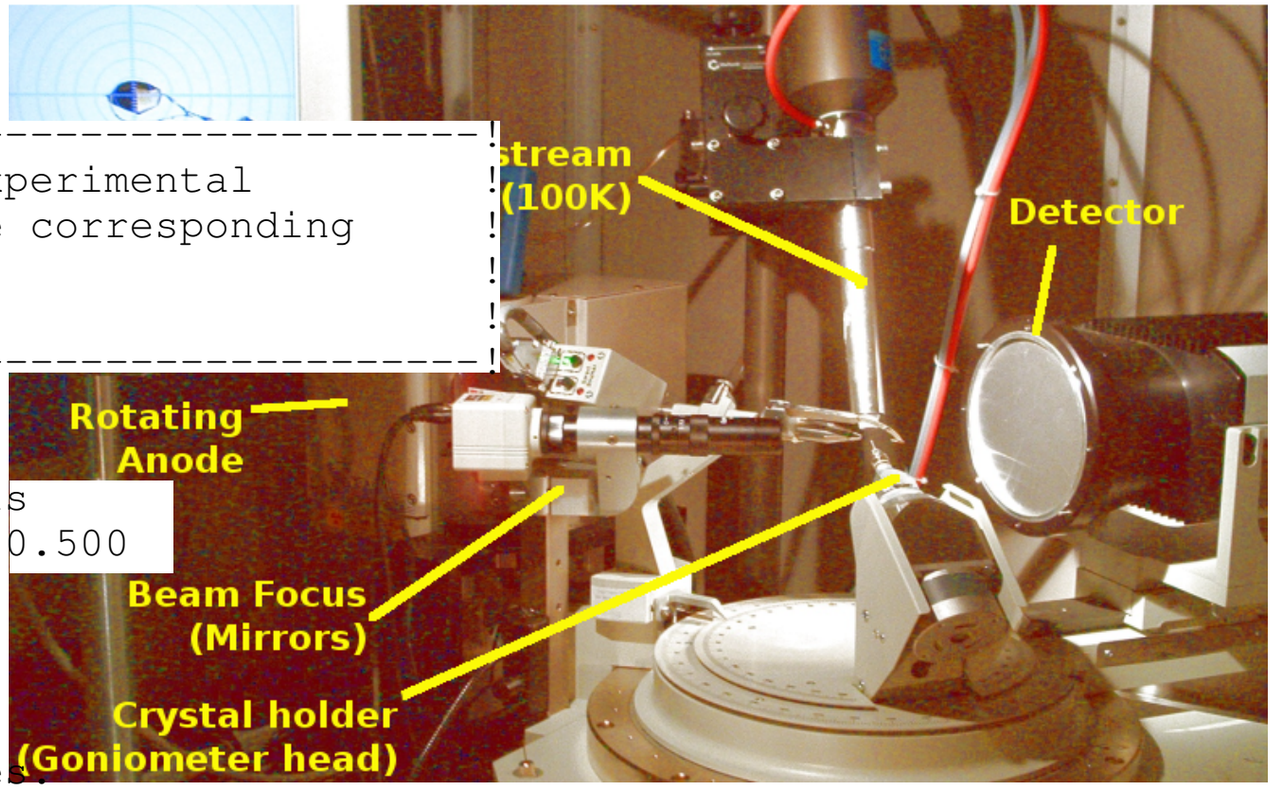
$$\vec{r}'' = \begin{pmatrix} \cos -\omega & 0 & -\sin -\omega \\ 0 & 1 & 0 \\ \sin -\omega & 0 & \cos -\omega \end{pmatrix} \vec{r}'$$

sfrmtools

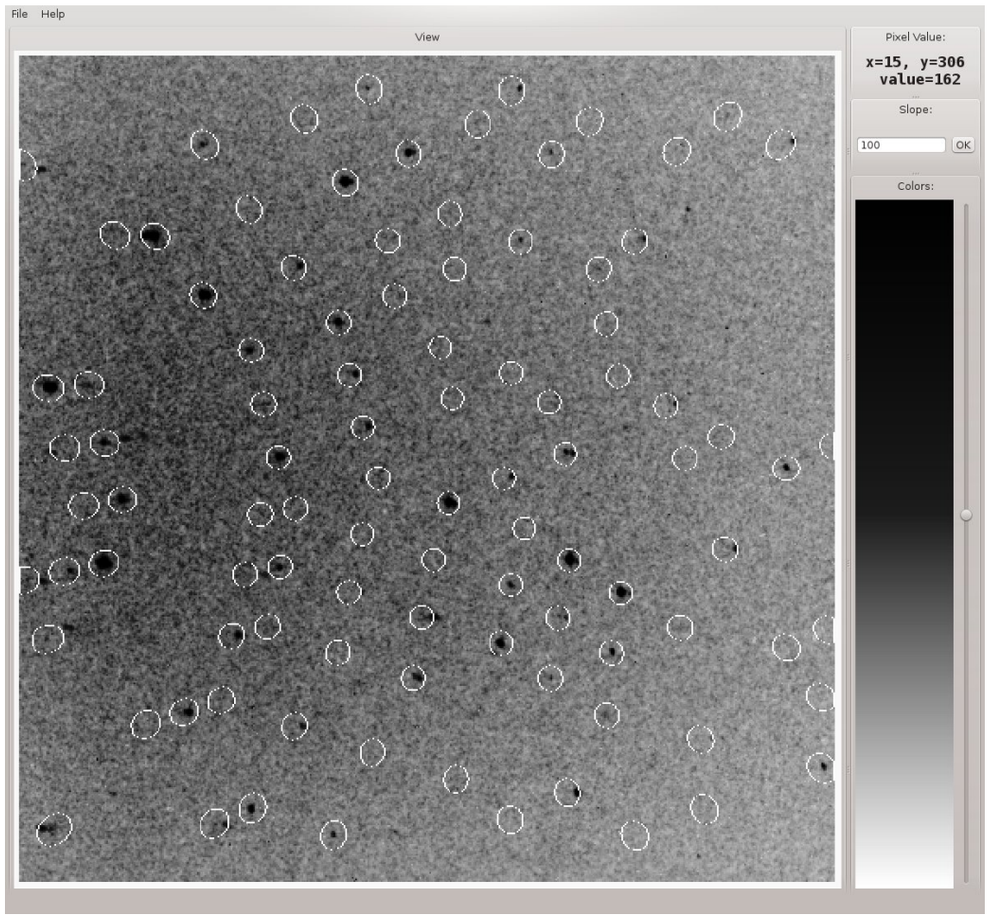
Setup for `XDS.INP` from Bruker `sfrm` frames:

- Combination of rotations at non–right angles
- E.g. Bruker machines: $\chi = 54.7°$

```
#>  sfrmtools lid1_c2_am_03_0001.sfrm
!-------------------------------------------------------------!
! sfrmtools:    Read an sfrm-file, extract experimental       !
!               parameters and convert to the corresponding    !
!               XDS parameters.                                !
! Copyright:    Tim Gruene, 2014                               !
!-------------------------------------------------------------!
! Data extracted from file
! lid1_c2_am_03_0001.sfrm
! 2theta = 30deg, assuming vertical swing axis
DIRECTION_OF_DETECTOR_X-AXIS=  0.866025 0.0   0.500
DIRECTION_OF_DETECTOR_Y-AXIS= 0.0 1.0 0.0
X-RAY_WAVELENGTH= 1.541884   !Angstroem
OSCILLATION_RANGE= 0.179993
ORGX= 505.730011 ORGY= 513.440002
!! WARNING: Header contains 2 distance entries!
!! Probably the second one is correct, please verify!
DETECTOR_DISTANCE= 50.000000 !(mm)
DETECTOR_DISTANCE= 53.000000 !(mm)
DATA_RANGE= 39 58
! Rotation about phi axis
ROTATION_AXIS= -0.817105 -0.576489 -0.000000
```



Example Data Set I [1]



- Wavelength $\lambda = 0.7107$
- 5 high resolution runs $0.44\text{Å} \leq d_{\text{min}} \leq 0.93\text{Å}$
- 5 low resolution runs $0.66\text{Å} \leq d_{\text{min}} \leq 11.1\text{Å}$
- Spacegroup $P\bar{1}$
- Unit cell parameters
  $10.23 \times 12.33 \times 17.40\text{Å}^3$,
  $101.597°$, $91.192°$, $112.090°$
- Detector axis
  $X = (0.20791, 0, -0.97814) = (\cos 78°, 0, \sin 78°)$
  (highest resolution at $2\theta_{\text{max}} = 106.6°$)

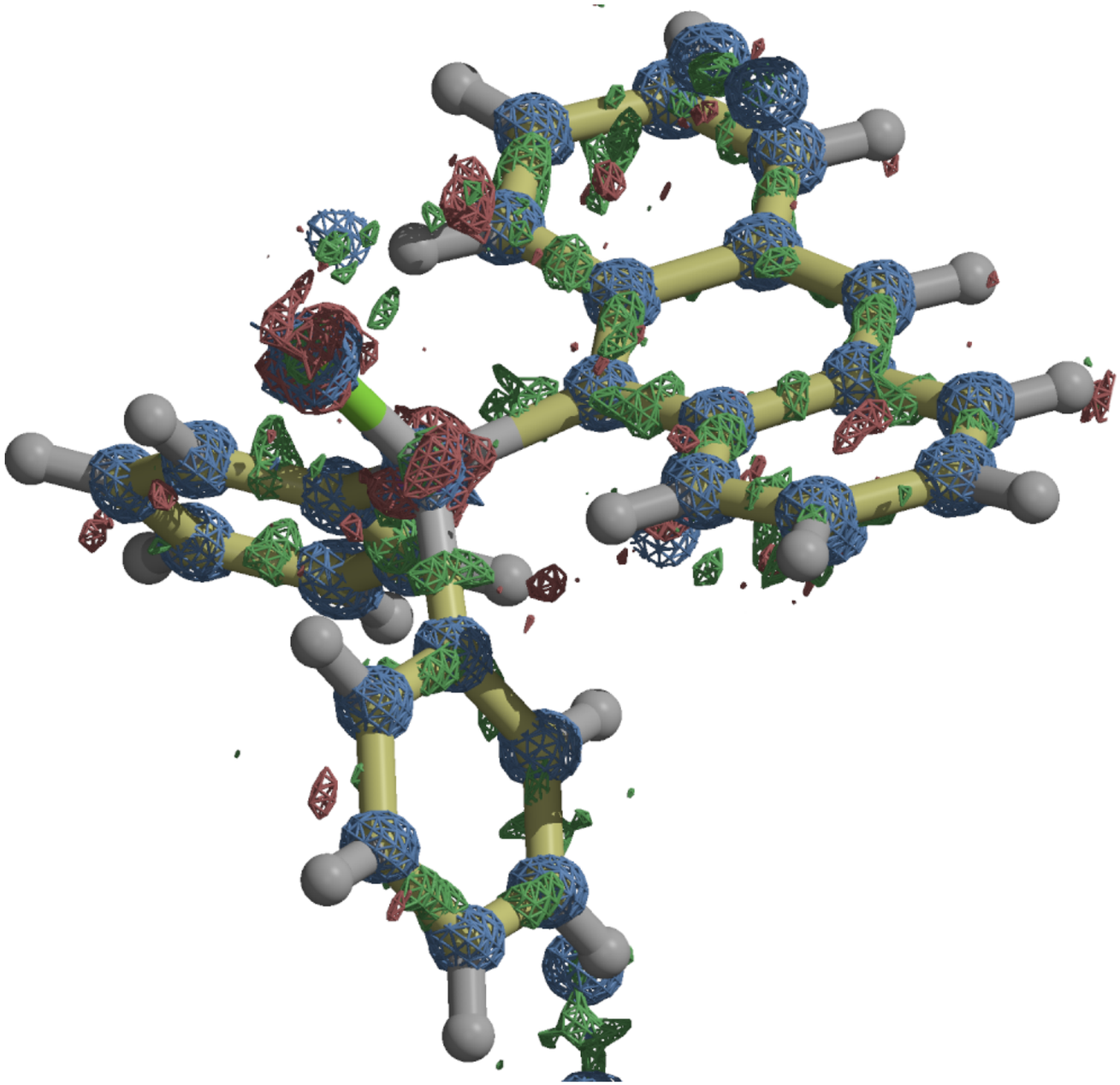
Data Statistics in $P\bar{1}$ [1]

RESOLUTION LIMIT	NUMBER OF REFLECTIONS OBSERVED	UNIQUE	POSSIBLE	COMPLETENESS OF DATA	R-FACTOR observed	COMPARED	I/SIGMA	R-meas	Rmrgd-F
0.79	1324	1323	8356	15.8%	4.6%	2	29.68	6.5%	4.6%
0.70	1753	1753	3669	47.8%	-99.9%	0	-99.00	-99.9%	-99.9%
0.64	1832	1831	4036	45.4%	4.5%	2	22.21	6.3%	4.5%
0.59	1871	1871	4461	41.9%	-99.9%	0	-99.00	-99.9%	-99.9%
0.55	1922	1920	4802	40.0%	7.1%	4	16.76	10.0%	7.2%
0.51	1892	1891	5093	37.1%	15.8%	2	12.31	22.3%	15.9%
0.49	1903	1901	5422	35.1%	6.1%	4	9.96	8.7%	6.2%
0.46	1835	1835	5714	32.1%	-99.9%	0	-99.00	-99.9%	-99.9%
0.44	1589	1589	5967	26.6%	-99.9%	0	-99.00	-99.9%	-99.9%
total	15921	15914	47520	33.5%	6.0%	14	16.73	8.5%	6.4%

Merging High & Low Resolution Runs [1]

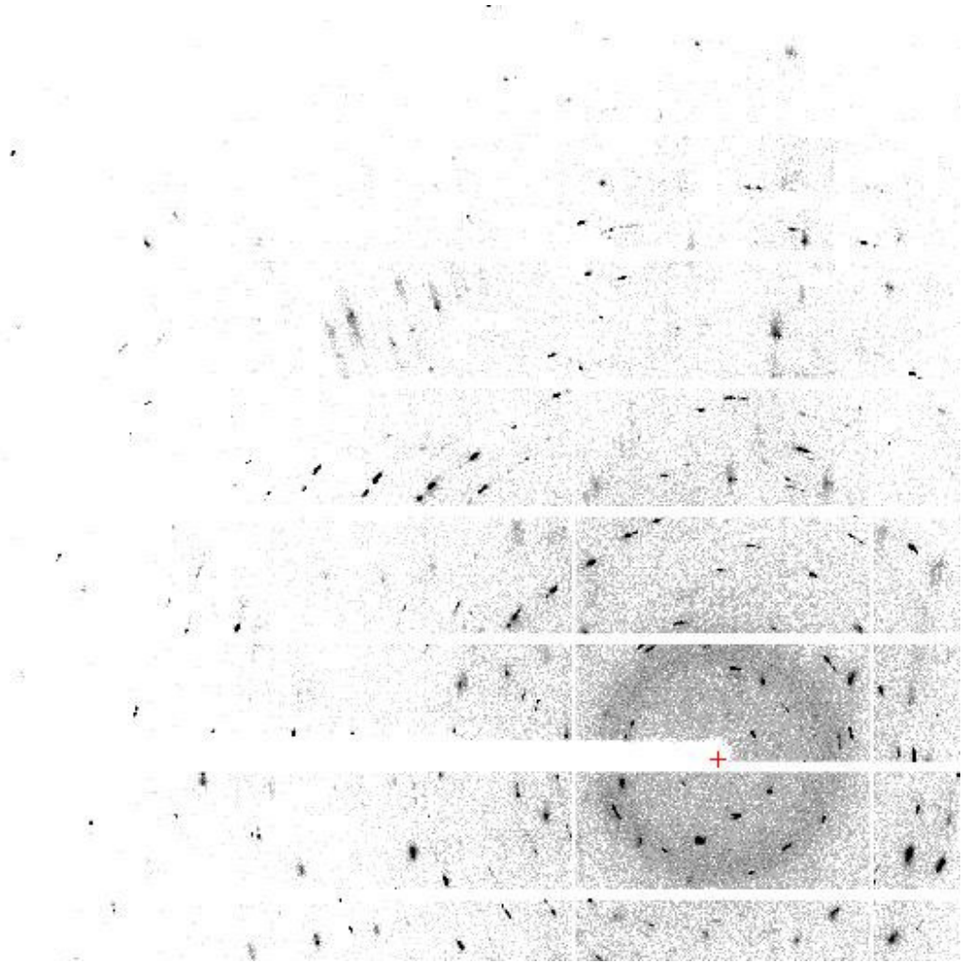
RESOLUTION LIMIT	NUMBER OF REFLECTIONS OBSERVED	UNIQUE	POSSIBLE	COMPLETENESS OF DATA	R-FACTOR observed	COMPARED	I/SIGMA	R-meas	CC(1/2)
1.99	1911	504	531	94.9%	1.1%	1898	48.84	1.3%	100.0*
1.40	3728	970	971	99.9%	1.5%	3727	41.99	1.8%	100.0*
1.15	4245	1249	1251	99.8%	1.9%	4245	33.41	2.3%	100.0*
0.99	4453	1501	1499	100.1%	2.6%	4453	26.50	3.2%	99.9*
0.89	5244	1685	1689	99.8%	13.7%	5244	23.99	15.9%	99.8*
0.81	8237	1866	1869	99.8%	33.5%	8236	28.26	37.3%	99.9*
0.75	8608	1992	1998	99.7%	30.3%	8587	25.81	33.8%	91.4*
0.70	8862	2153	2204	97.7%	26.7%	8844	22.68	29.9%	92.7*
0.66	6485	2222	2311	96.1%	25.9%	6323	17.83	30.6%	61.8*
0.63	4771	2328	2446	95.2%	27.7%	4381	15.88	34.7%	57.9*
0.60	4793	2408	2563	94.0%	27.2%	4302	14.26	34.0%	68.7*
0.57	4860	2516	2709	92.9%	26.4%	4284	13.01	33.3%	70.6*
0.55	4963	2598	2827	91.9%	22.6%	4319	11.37	28.7%	77.5*
0.53	4840	2641	2899	91.1%	22.7%	4082	9.47	29.3%	72.6*
0.51	4797	2698	2989	90.3%	20.2%	3939	7.97	26.4%	82.8*
0.50	4900	2829	3184	88.9%	19.0%	3901	6.85	25.0%	83.9*
0.48	4766	2856	3218	88.8%	17.3%	3636	6.17	22.9%	87.1*
0.47	4624	2863	3298	86.8%	20.9%	3369	5.99	28.0%	75.9*
0.46	4609	2944	3431	85.8%	19.5%	3213	5.87	26.3%	74.0*
0.44	3892	2676	3504	76.4%	17.3%	2393	5.41	24.0%	77.9*
total	103588	43499	47391	91.8%	15.4%	93376	14.85	17.8%	98.0*

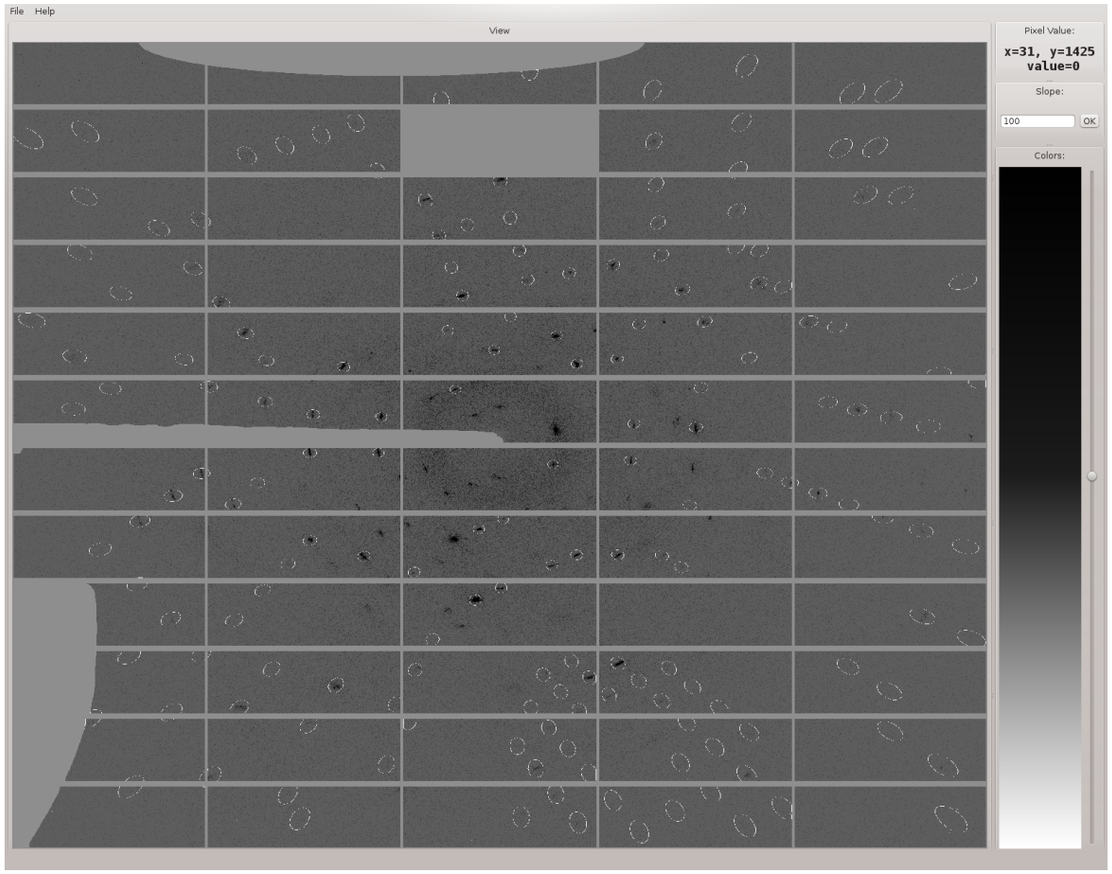
The Structure [1]



R1=5.66%, $R_{\text{complete}} = 5.759\%$

Example Data Set II [2]





Cell: 10.934Å, 12.778Å, 17.592Å, $72.652°$ $80.303°$ $85.568°$;
Spacegroup: $P\bar{1}$

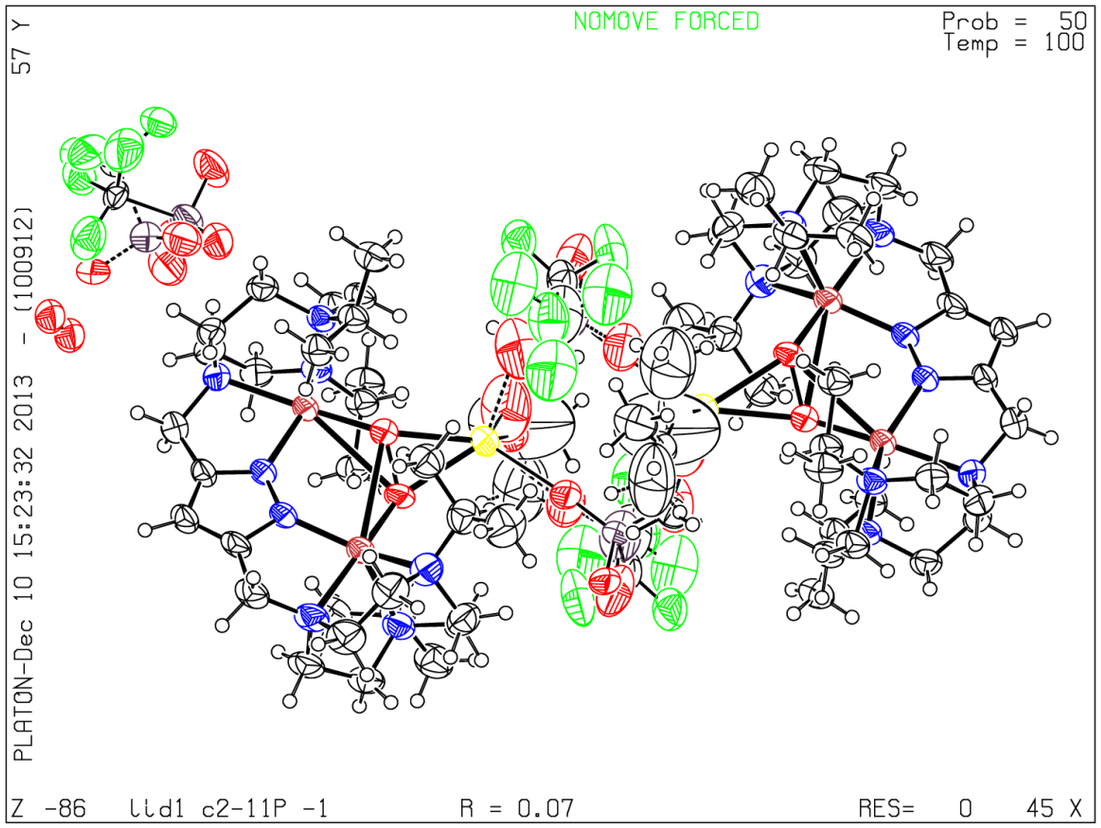
K. Dalle *et al.*, J. Am. Chem. Soc. 2014

Improving Data Quality with κ–Goniometer [2]

Data collected at BESSY with four κ–settings $0 - 30°$

INTENSITY STATISTICS FOR DATASET # 1 Lid1_C2.HKL

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.60	101	101	100.0	13.47	450.5	33.96	0.0789	0.0277
3.60 - 2.43	238	238	100.0	12.74	200.3	31.71	0.0708	0.0304
2.43 - 1.92	344	347	99.1	12.66	135.4	30.17	0.0701	0.0300
1.92 - 1.68	328	334	98.2	12.88	78.7	29.56	0.0749	0.0295
1.68 - 1.52	353	360	98.1	13.52	58.9	29.45	0.0686	0.0307
1.52 - 1.41	337	347	97.1	12.35	46.7	26.50	0.0655	0.0318
1.41 - 1.33	309	320	96.6	12.71	38.4	26.74	0.0725	0.0330
1.33 - 1.26	345	361	95.6	12.63	39.6	26.46	0.0709	0.0336
1.26 - 1.20	360	378	95.2	13.00	28.9	25.10	0.0741	0.0318
1.20 - 1.15	364	386	94.3	11.40	22.6	21.28	0.0787	0.0371
1.15 - 1.11	340	358	95.0	12.12	19.0	22.37	0.0828	0.0375
1.11 - 1.08	277	292	94.9	12.50	15.4	20.91	0.0862	0.0362
1.08 - 1.05	335	358	93.6	12.51	12.5	20.11	0.0882	0.0383
1.05 - 1.02	337	363	92.8	11.66	11.6	19.07	0.0937	0.0406
1.02 - 0.99	399	429	93.0	11.42	12.5	19.36	0.0966	0.0397
0.99 - 0.97	267	287	93.0	11.72	10.8	17.89	0.0988	0.0428
0.97 - 0.95	350	380	92.1	11.55	8.7	17.34	0.1078	0.0431
0.95 - 0.92	433	547	79.2	8.68	8.1	14.96	0.1126	0.0485
0.92 - 0.90	249	426	58.5	5.43	9.3	14.96	0.1201	0.0536
0.90 - 0.87	316	719	43.9	3.71	7.1	12.39	0.1256	0.0631
0.87 - 0.82	328	1479	22.2	1.19	4.5	7.98	0.1334	0.1033
0.92 - 0.82	893	2624	34.0	2.57	6.8	11.49	0.1246	0.0693
Inf - 0.82	6710	8810	76.2	9.20	42.6	21.82	0.0756	0.0324

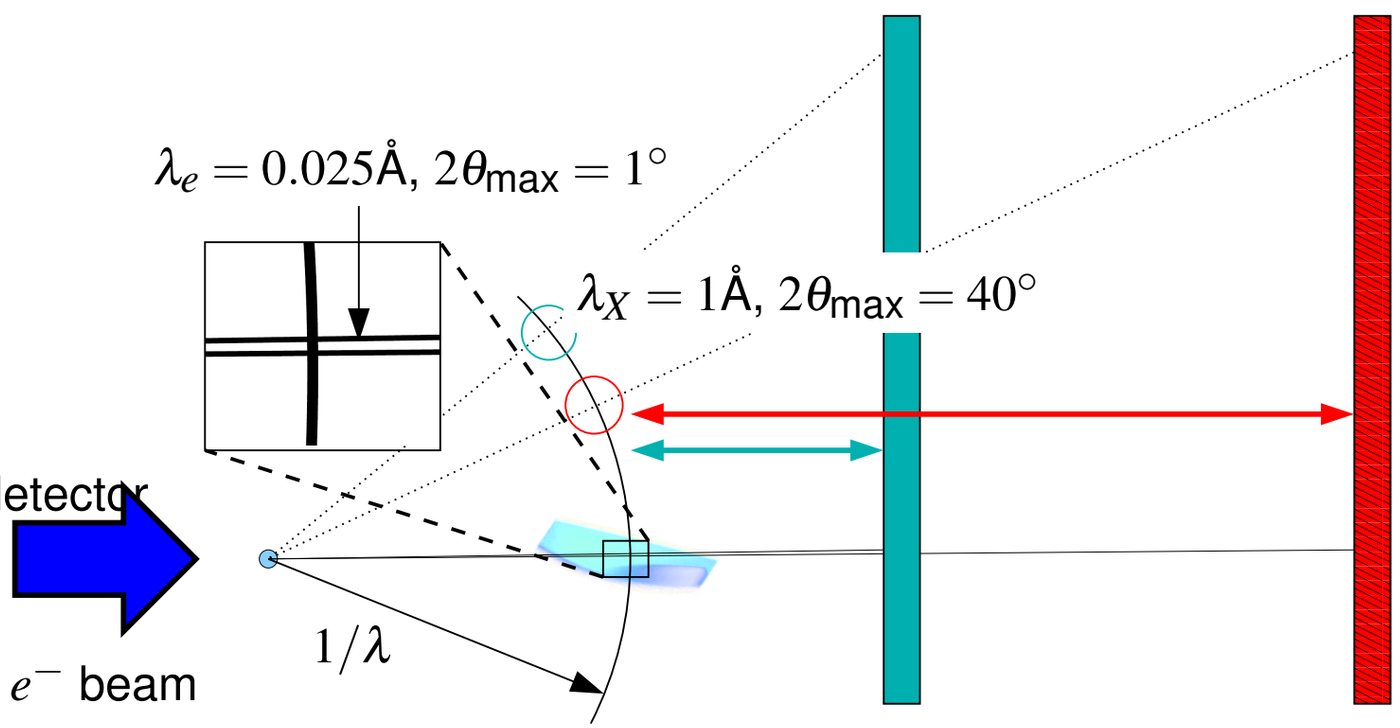


$R1 = 6.95\%, R_{\text{complete}} = 7.61\%$ [4]

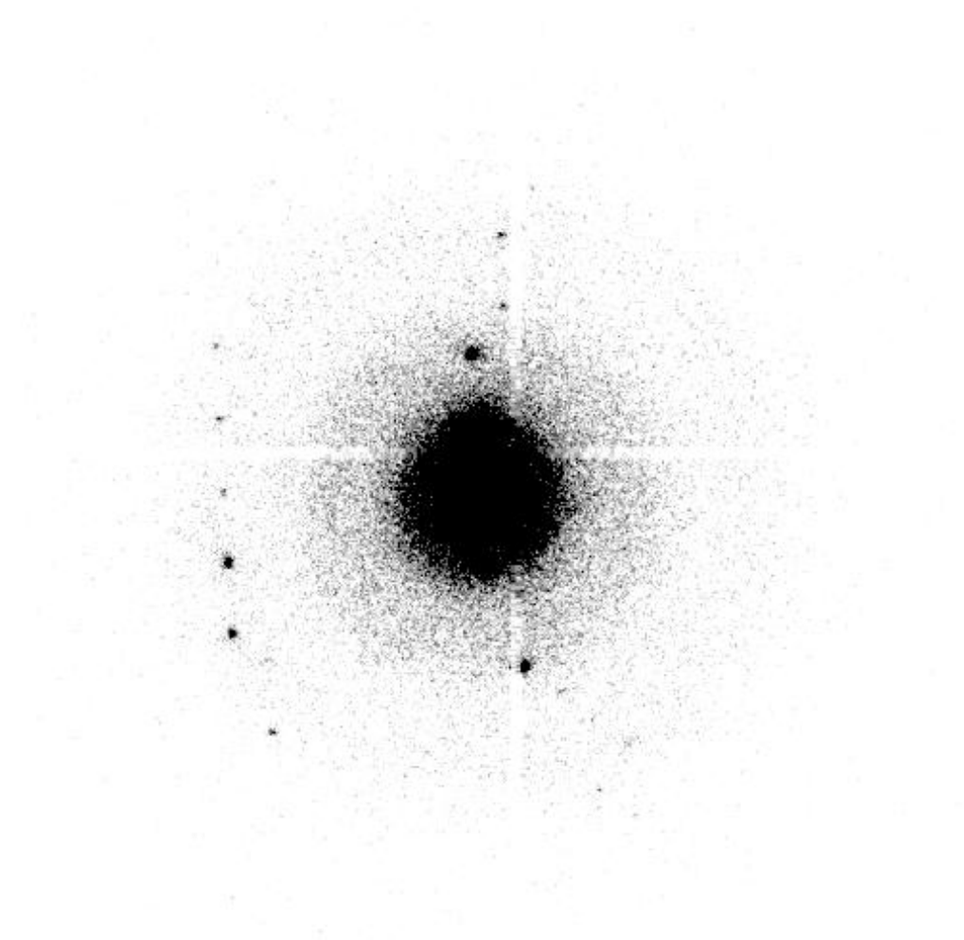
Example Data Set III: Electron Diffraction [3]

Features of electron diffraction

- measurement of nanocrystals
- several orders of less radiation damage
- wavelength $\lambda = 0.025$Å
- no dedicated diffractometer
  $\Rightarrow$ incomplete data
- multiple scattering
  $\Rightarrow$ inappropriate scaling models
- $2\theta_{\text{max}} \leq 1^\circ$ at 1Å
  $\Rightarrow$ heavy correlation between cell and detector



Special Options in XDS [3]



ROTATION_AXIS= 0.632385 0.774647 -0.003443
X-RAY_WAVELENGTH=0.02508
AIR=0.000
OSCILLATION_RANGE=0.0183 ! 50° in $P2_1/n$
MAXIMUM_ERROR_OF_SPOT_POSITION=16.0 ! default: 3
MAXIMUM_ERROR_OF_SPINDLE_POSITION=64.0 ! default: 2
REFINE(INTEGRATE)=!
REFINE(CORRECT)=BEAM ORIENTATION CELL AXIS
DELPHI= 10
BACKGROUND_PIXEL=3.

Resulting Data Quality [3]

SUBSET OF INTENSITY DATA WITH SIGNAL/NOISE >= -3.0 AS FUNCTION OF RESOLUTION

RESOLUTION LIMIT	NUMBER OF REFLECTIONS OBSERVED	UNIQUE	POSSIBLE	COMPLETENESS OF DATA	COMPARED	I/SIGMA	R-meas	CC(1/2)
2.50	67	45	104	43.3%	44	9.90	8.0%	97.7*
1.79	145	78	166	47.0%	130	10.57	8.6%	97.7*
1.47	177	90	206	43.7%	167	9.33	8.3%	98.4*
1.27	197	105	239	43.9%	176	7.13	14.2%	96.9*
1.14	243	129	272	47.4%	219	6.99	13.8%	96.0*
1.04	281	147	304	48.4%	257	5.10	18.2%	96.9*
0.96	284	151	316	47.8%	258	3.85	23.2%	92.3*
0.90	349	179	363	49.3%	322	3.36	27.2%	91.6*
0.85	326	171	368	46.5%	293	2.27	37.4%	65.8*
total	2069	1095	2338	46.8%	1866	5.55	11.8%	98.7*

- Incomplete Data
- Poor R–value, possibly due to dynamic scattering
- Resonable Multiplicity due to Space group ($P2_1/n$)

Direct Methods: Atom Type Assignment [3]

- Structure solved with direct methods
- all atom positions found
- no false positives
- even atom types assigned with very few errors

Final $R1 = 28.0\%, R_{\text{complete}} = 32.2\%$ [4]

Conclusions

- Data processing with XDS from virtually all experimental setups

- Preliminaries

  1. Detector built up from planar segments
  2. Single wavelength
  3. Sinlge crystal

- Integration of X–ray, electron, and neutron diffraction

- Small and Macromolecular compounds

- Scaling model applies to X–ray and neutron data

References

1. R. Herbst–Irmer, “Experimental charge density studies: Discard valid data and overfit?”, Acta Cryst. (2014), **A**70, C282

2. K. Dalle, T. Gruene, S. Dechert, S. Demeshko, and F. Meyer, “A weakly coupled biologically relevant $Cu_2^{II}(\mu-\eta^1:\eta^1-O_2)$ *cis*-peroxo adduct that binds side-on to additional metal ions” J. Am. Chem. Soc. (2014), 136, 7428–7434

3. E. van Genderen, MTB. Clabbers, PP. Das, A. Stewart, I. Nederlog, KC. Barentsen, Q. Portillo, NS. Pannu, S. Nicolopoulos, T. Gruene, JP. Abrahams, “*Ab initio* structure determination of nanocrystals of organic pharmaceutical compounds by electron diffraction at room temperature using a Timepix quantum area direct electron detector”, Acta Cryst (2015) **A**, under revision.

4. J. Luebben & T. Gruene, “New Method to compute R_{complete} enables Maximum Likelihood Refinement for Small Data Sets”, PNAS (2015), 112, 8999–9003