Using a Bruker-AXS diffractometer to collect data from a diamond-anvil cell

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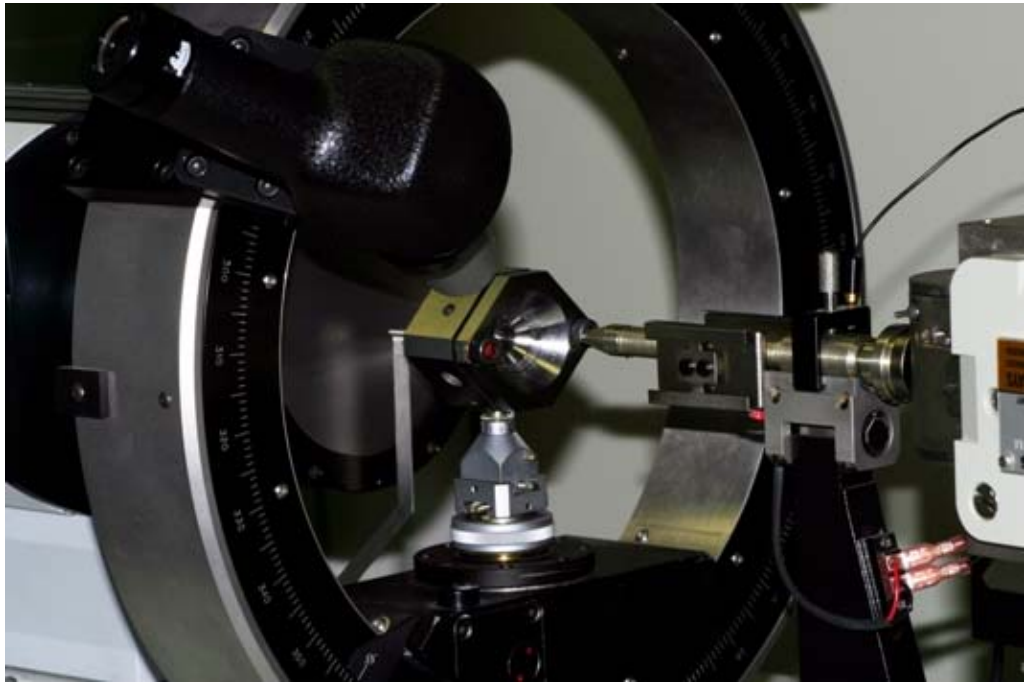
Diffractometer configuration at the XRD-Laboratory of the Natural History Museum, Copenhagen

Bruker-AXS four-circle goniometer with sealed Mo-tube, flat graphite monochromator and Smart 1000CCD detector. Centering-aid: permanently mounted optical microscope on the chi-circle.

Used DACs: ETH-type both Be- and diamond-plate backed (constructed by R. Miletich, Heidelberg) and Diacell Be-backed (shown on the figure).

Specific requirements for measurements with DAC:
- A short collimator and a beam-stop mounted on the goniometer base, as used earlier with the scintillation detector.
- sample-detector distance of 5.5 cm (minimum)

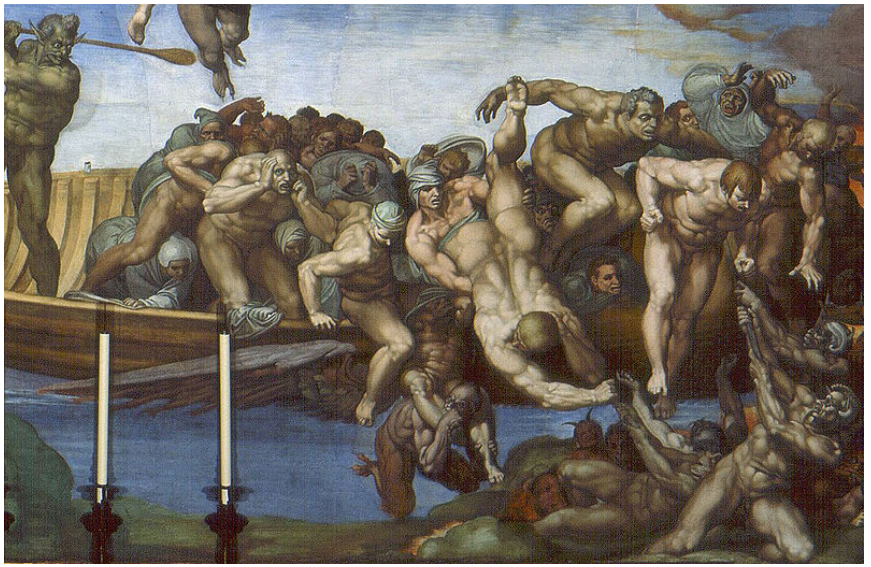


Work phases

Smart phase: data acquisition

Saint phase: data extraction

Correction phase



Refinement phase: on your own…

Smart phase

Controlled through the program SMART (plus GEMINI)

1. **Centering the crystal** (make sure to know exactly the centre of the microscope)

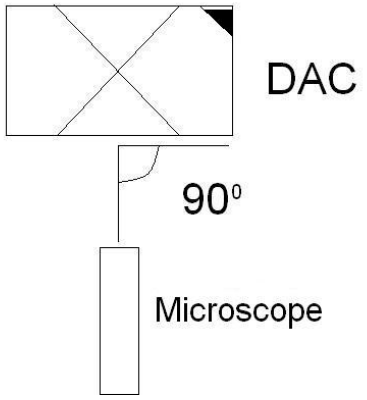
1.1 Mount the DAC perpendicularly to the microscope.

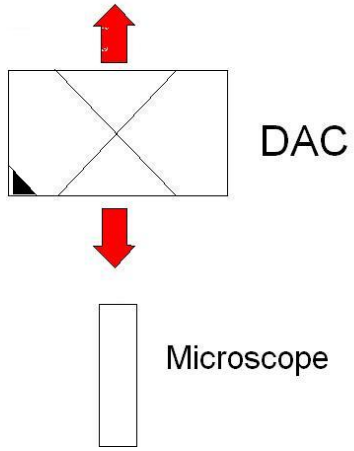
1.2 Focus on the crystal and adjust its lateral and the vertical position in the field of view.

1.3 Turn the DAC 180^0. Focus on the crystal by moving DAC to-from the microscope (and NOT using the microscope focusing) while registering exactly how much you had to turn the adjustment key.

1.4 Turn the key back half of the way.

Voila!



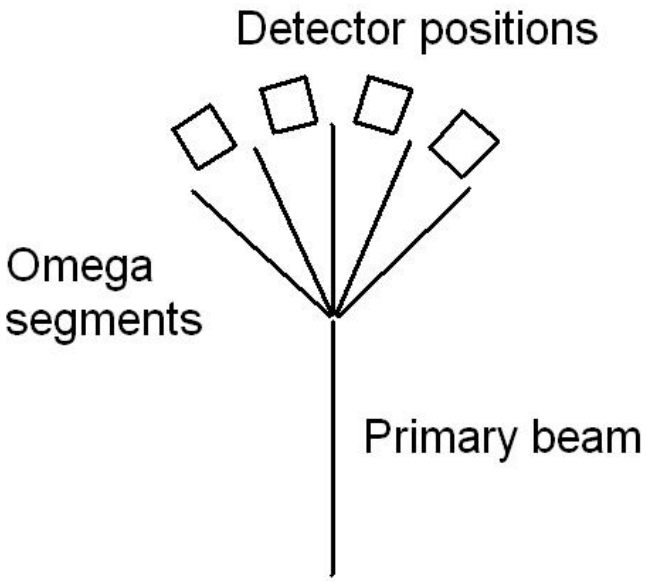


2. Planning the exposures

- I recommend: Make small steps (gives more accurate lattice parameters – important for HP).

- Make exposures from both sides of the cell (also needed for accurate cell parameters).

- Follow as much as possible the cell with the detector (avoids shaded regions and harvests better the measurable reflections).



Multirun example

Our typical 16-run procedure:
4 + 4 omega-scans from both sides of the DAC with chi = 0^0 and with chi = 90^0.

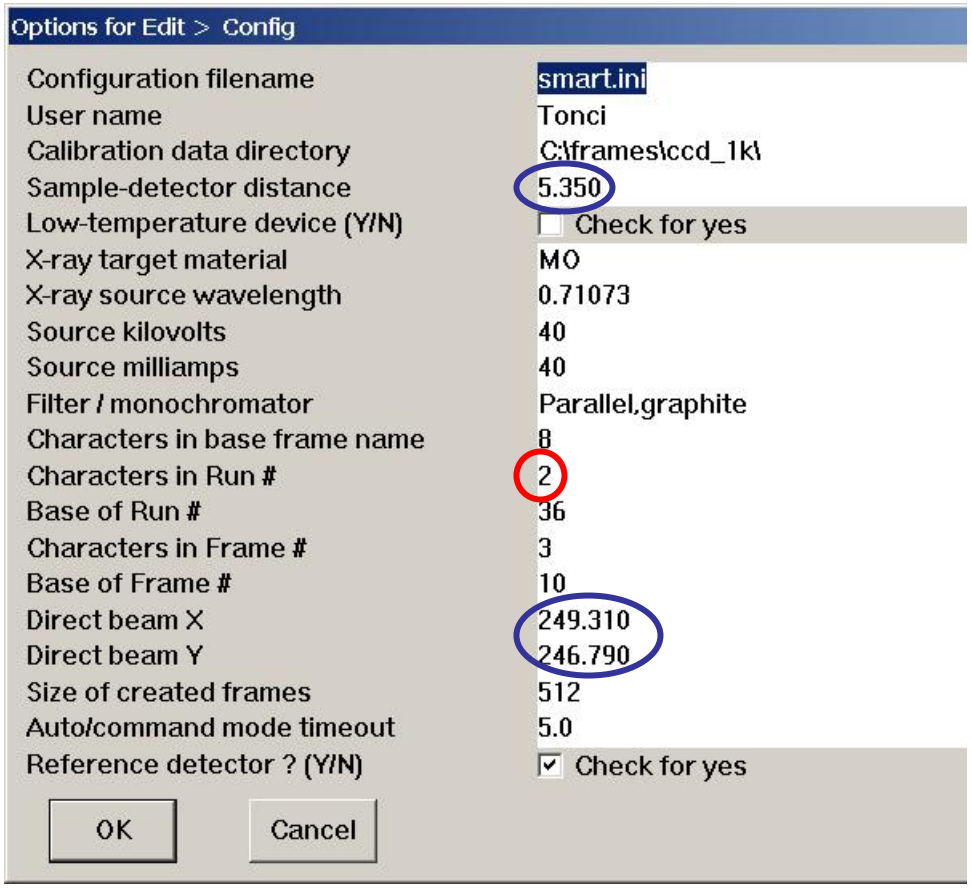
SCAN MultiRun List (50 lines)

Run#	Frame#	2-Theta	Omega	Phi	Chi	Axis	Width	#Frames	Time
1	001	31.00	43.00	0.00	0.00	2	-0.200	120	30.00
2	001	10.50	23.00	0.00	0.00	2	-0.200	125	30.00
3	001	-10.50	2.00	0.00	0.00	2	-0.200	125	30.00
4	001	-31.00	-19.00	0.00	0.00	2	-0.200	120	30.00
5	001	-31.00	-43.00	180.00	0.00	2	0.200	120	30.00
6	001	-10.50	-23.00	180.00	0.00	2	0.200	125	30.00
7	001	10.50	-2.00	180.00	0.00	2	0.200	125	30.00
8	001	31.00	19.00	180.00	0.00	2	0.200	120	30.00
9	001	31.00	43.00	180.00	90.00	2	-0.200	120	30.00
10	001	10.50	23.00	180.00	90.00	2	-0.200	125	30.00
11	001	-10.50	2.00	180.00	90.00	2	-0.200	125	30.00
12	001	-31.00	-19.00	180.00	90.00	2	-0.200	120	30.00
13	001	-31.00	-43.00	0.00	90.00	2	0.200	120	30.00
14	001	-10.50	-23.00	0.00	90.00	2	0.200	125	30.00
15	001	10.50	-2.00	0.00	90.00	2	0.200	125	30.00
16	001	31.00	19.00	0.00	90.00	2	0.200	120	30.00

OK | Cancel | Print... | Write... | Read...

Configuration example

Be sure to calibrate your detector with a standard crystal before running DAC measurement – you need calibrated values for the orientation refinements!



The calibration determines also pitch, roll and yaw values, as well as omega and chi offsets to be used in the LS refinement of the crystal lattice parameters.

Remember enough characters in the names of runs to avoid overwriting!

3. Determining the orientation and lattice parameters

There are two strategies for finding crystal reflections:

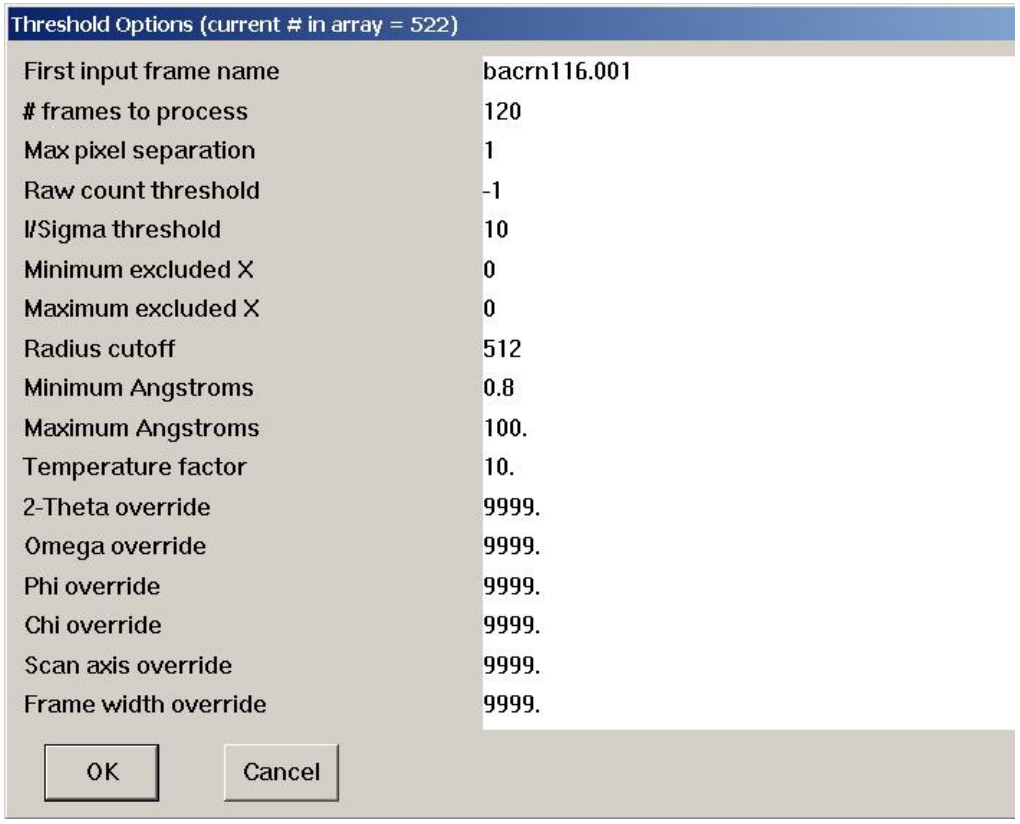
“Automatic”

and

“Manual”

3.1 The automatic procedure (for the patient)

Selecting the parameters in the “threshold” function

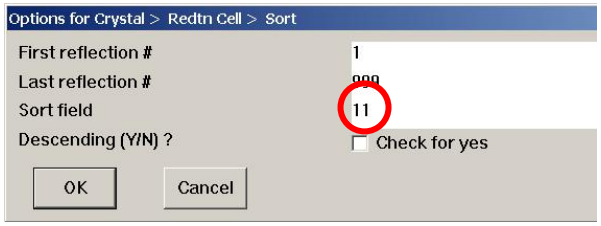


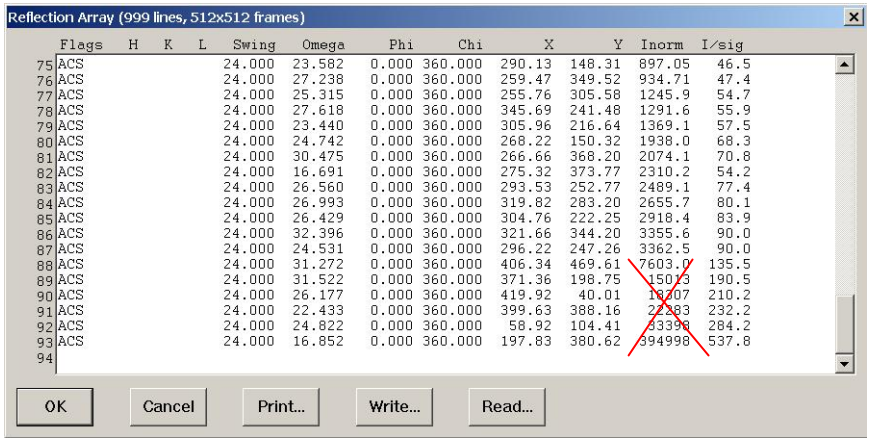
Needs removing diamond reflections, powder rings and “hot spots”.

3.1.1 Removing diamond reflections

Sort the data by intensity

Remove the anomalously strong

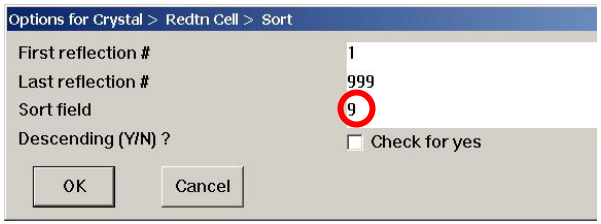


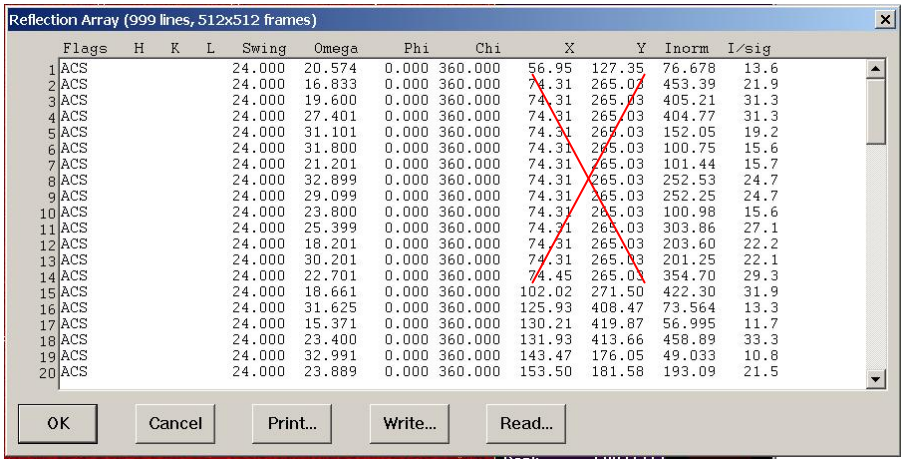


3.1.2 Removing “hot spots”

Sort the data by x-coordinate

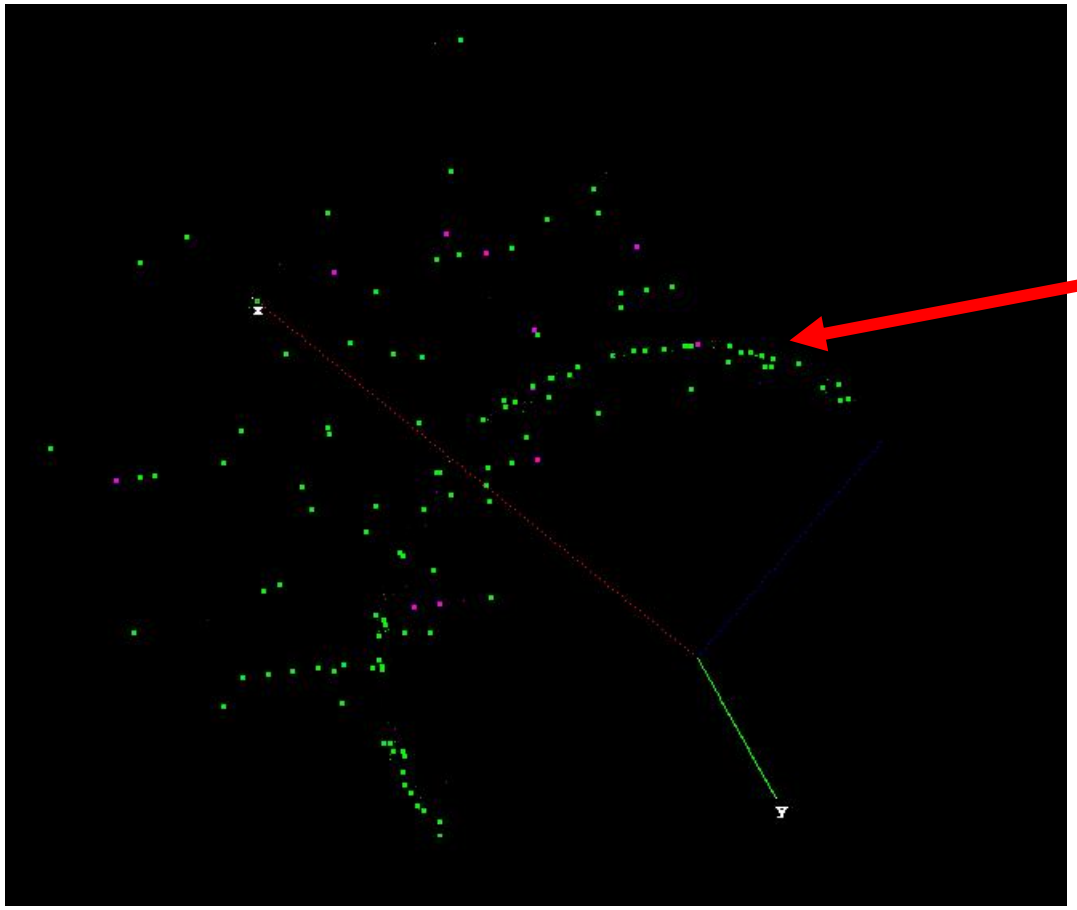
Remove repeating x, y pairs





3.1.3 Removing powder rings

In Rlatt mark the rings and remove marked reflections.



Reflections arranged in a ring-form come from the Be-backing plates.

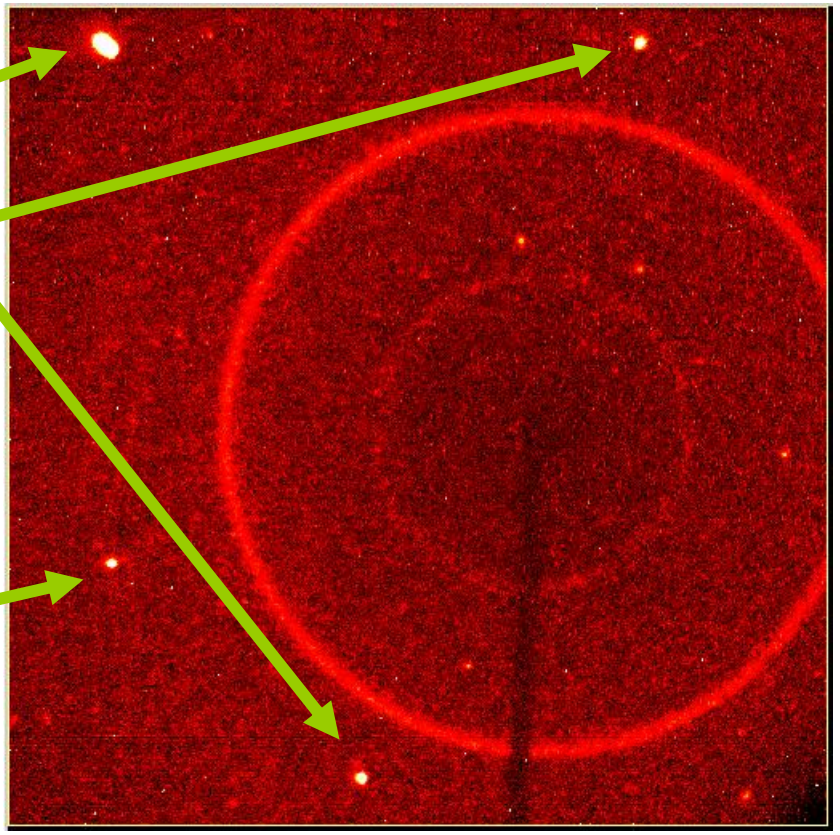
3.2 “Manual” procedure (for the accurate)

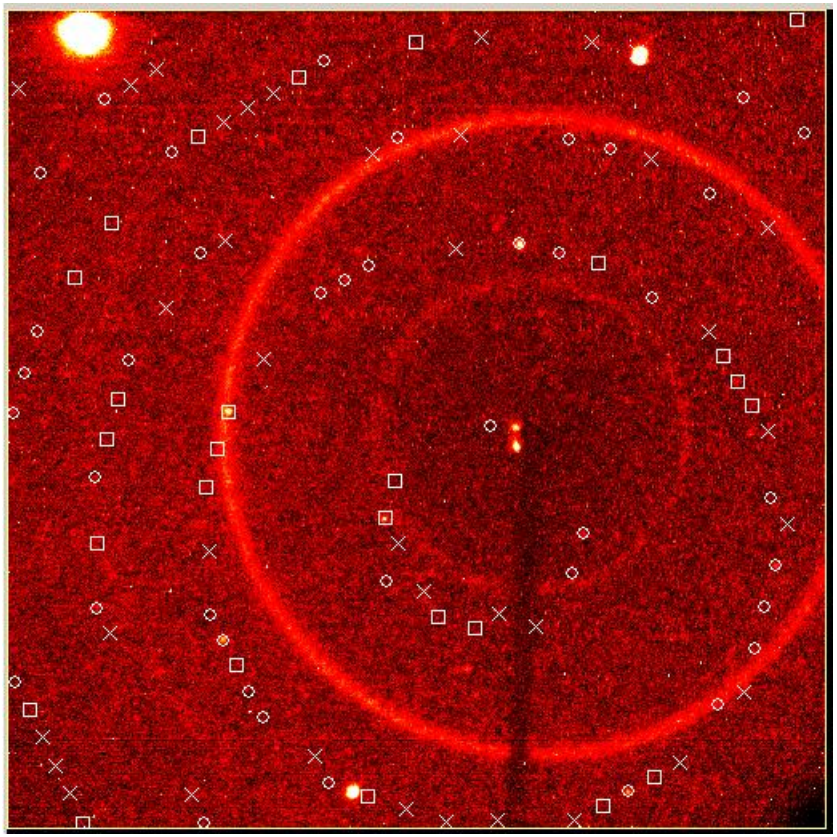
With a bit of experience it is easy to tell the sample and internal standard reflections (small and sharp) from the diamond reflections (huge and moving). Hand-picking reflections might seem slow and tedious but is often less that than the automatic search because the reflection list does not need checking and cleaning.

These are diamond reflections

These could have been sample’s reflections, but on the following frames they are largely shifting the position – diamond!!

This is the sample’s reflection

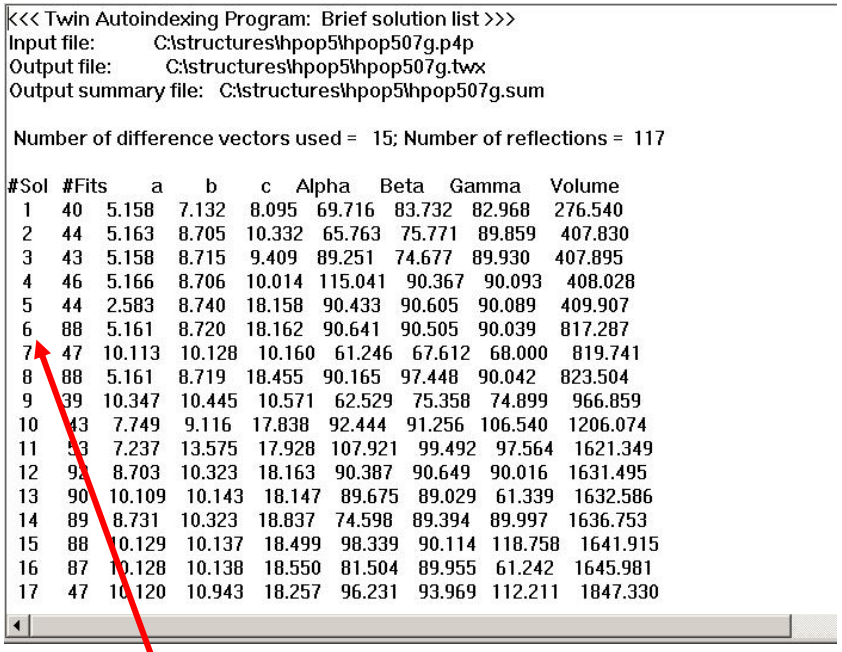




After the crystal lattice orientation is determined for the first run, the marking feature can be used for subsequent runs as a very effective aid for spotting the reflections.

3.3 For the lattice determination from a set of reflections the program GEMINI is recommended. It works much better than the indexing routine in SMART even in cases when there is only one crystal lattice present in the data.

GEMINI is especially advantageous if quartz is used for the pressure calibration, because the program will reveal both lattices (the investigated crystal plus the quartz crystal).

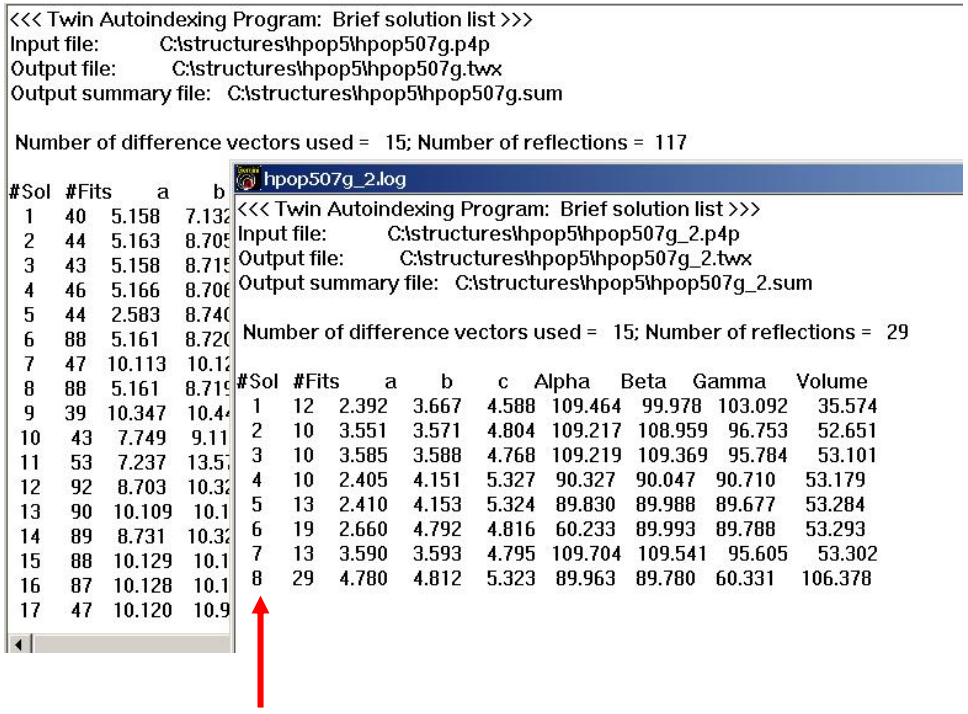


<<< Twin Autoindexing Program: Brief solution list >>>
Input file: C:\structures\hpop5\hpop507g.p4p
Output file: C:\structures\hpop5\hpop507g.twx
Output summary file: C:\structures\hpop5\hpop507g.sum

Number of difference vectors used = 15; Number of reflections = 117

#Sol	#Fits	a	b	c	Alpha	Beta	Gamma	Volume
1	40	5.158	7.132	8.095	69.716	83.732	82.968	276.540
2	44	5.163	8.705	10.332	65.763	75.771	89.859	407.830
3	43	5.158	8.715	9.409	89.251	74.677	89.930	407.895
4	46	5.166	8.706	10.014	115.041	90.367	90.093	408.028
5	44	2.583	8.740	18.158	90.433	90.605	90.089	409.907
6	88	5.161	8.720	18.162	90.641	90.505	90.039	817.287
7	47	10.113	10.128	10.160	61.246	67.612	68.000	819.741
8	88	5.161	8.719	18.455	90.165	97.448	90.042	823.504
9	39	10.347	10.445	10.571	62.529	75.358	74.899	966.859
10	43	7.749	9.116	17.838	92.444	91.256	106.540	1206.074
11	53	7.237	13.575	17.928	107.921	99.492	97.564	1621.349
12	92	8.703	10.323	18.163	90.387	90.649	90.016	1631.495
13	90	10.109	10.143	18.147	89.675	89.029	61.339	1632.586
14	89	8.731	10.323	18.837	74.598	89.394	89.997	1636.753
15	88	10.129	10.137	18.499	98.339	90.114	118.758	1641.915
16	87	10.128	10.138	18.550	81.504	89.955	61.242	1645.981
17	47	10.120	10.943	18.257	96.231	93.969	112.211	1847.330

Solution 6 reveals the investigated crystal (an ortho-pyroxene).



<<< Twin Autoindexing Program: Brief solution list >>>
Input file: C:\structures\hpop5\hpop507g.p4p
Output file: C:\structures\hpop5\hpop507g.twx
Output summary file: C:\structures\hpop5\hpop507g.sum

Number of difference vectors used = 15; Number of reflections = 117

#Sol	#Fits	a	b
1	40	5.158	7.132
2	44	5.163	8.705
3	43	5.158	8.715
4	46	5.166	8.706
5	44	2.583	8.740
6	88	5.161	8.720
7	47	10.113	10.12
8	88	5.161	8.719
9	39	10.347	10.44
10	43	7.749	9.11
11	53	7.237	13.57
12	92	8.703	10.32
13	90	10.109	10.1
14	89	8.731	10.32
15	88	10.129	10.1
16	87	10.128	10.1
17	47	10.120	10.9

hpop507g_2.log

<<< Twin Autoindexing Program: Brief solution list >>>
Input file: C:\structures\hpop5\hpop507g_2.p4p
Output file: C:\structures\hpop5\hpop507g_2.twx
Output summary file: C:\structures\hpop5\hpop507g_2.sum

Number of difference vectors used = 15; Number of reflections = 29

#Sol	#Fits	a	b	c	Alpha	Beta	Gamma	Volume
1	12	2.392	3.667	4.588	109.464	99.978	103.092	35.574
2	10	3.551	3.571	4.804	109.217	108.959	96.753	52.651
3	10	3.585	3.588	4.768	109.219	109.369	95.784	53.101
4	10	2.405	4.151	5.327	90.327	90.047	90.710	53.179
5	13	2.410	4.153	5.324	89.830	89.988	89.677	53.284
6	19	2.660	4.792	4.816	60.233	89.993	89.788	53.293
7	13	3.590	3.593	4.795	109.704	109.541	95.605	53.302
8	29	4.780	4.812	5.323	89.963	89.780	60.331	106.378

The rest of reflections are quartz reflections.

It can always be expected that the crystal is not perfectly centred and this introduces the inaccuraces in the lattice parameters determined from only few runs. They will disappear when data from all the runs are merged. However, the experience shows that it is not easy for the program to find a common cell starting from the full merged dataset. Another tactics showed to be more effective in the most of the cases:

-Determine the lattice orientation from the first run data only (if you are using the “manual” procedure you would anyhow go through this step in order to be able to mark reflections when inspecting subsequent runs).*
-Add reflections from the second run and refine the lattice parameters.
-Save the updated orientation and continue by adding each subsequent run.

*As the HP investigations are usually performed as series of measurements on the same sample under varying pressure, the lattice orientation determined in one run can also be used for spotting the reflections in the subsequent one, thus speeding-up hand-picking.

Saint phase

∫ Obtaining integrated intensities and accurate crystal lattice parameters

Using the SAINT+ program

There might be up to three integrations necessary:

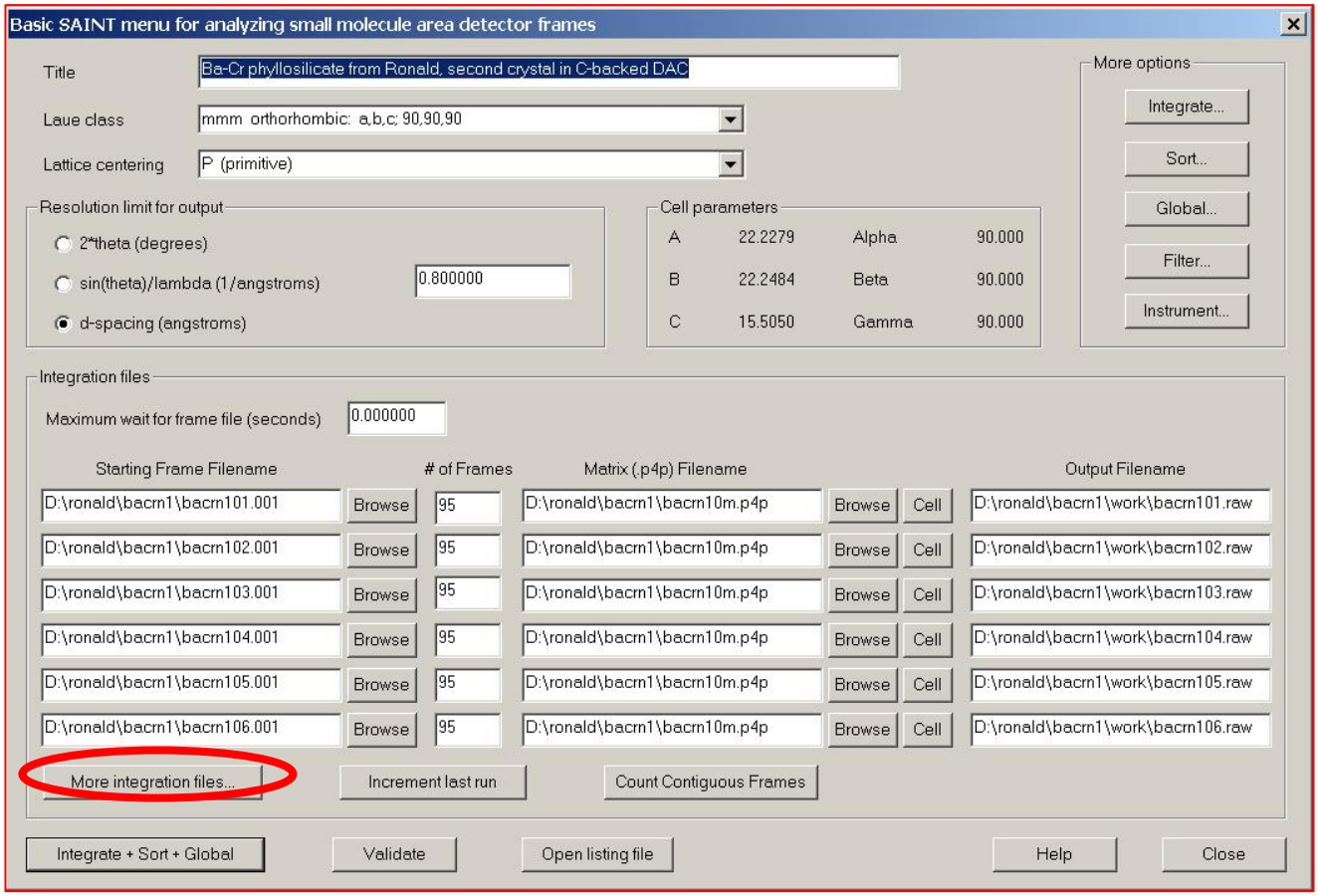
1. Integrating data for the investigated crystal

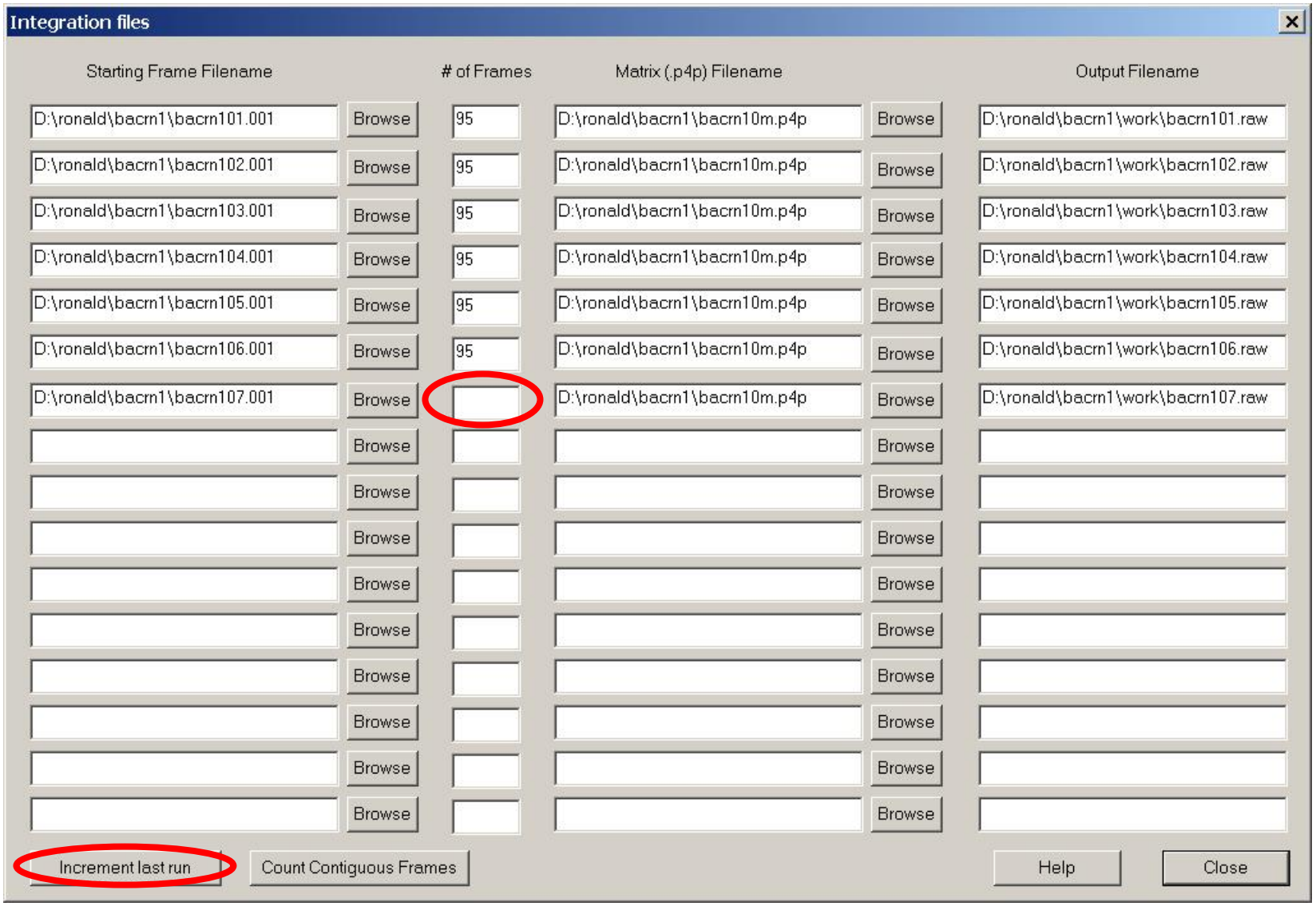
2. Integrating quartz (internal standard) reflections – to obtain accurate crystal lattice parameters

3. Integrating the investigated crystal and the diamond contributions together to register the overlaps

Some important reminders:

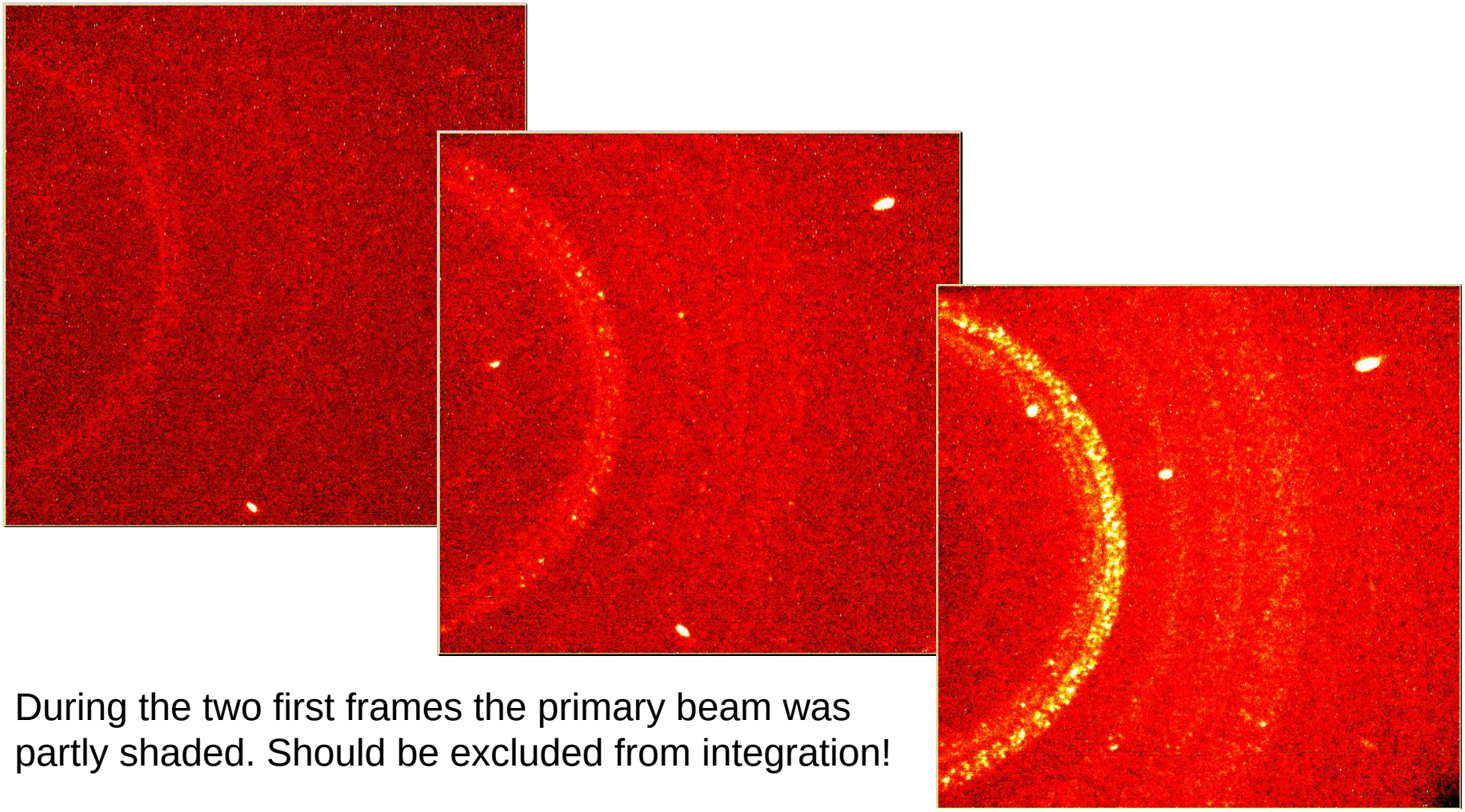
The number of runs in the recommended procedure exceeds the default. One needs to add more runs to the list…





Unfortunately, the program does not recognize automatically that there are more runs than on the starting page, so the remaining must be input one by one. Increment last run helps a lot, but the number of frames must be typed in.

Although the recommended data collection strategy avoids the shaded regions on detector area, there might be a shadowing of the primary beam at the beginning or the end of the sweep sequence, if one tries to use the full opening of the DAC. Check the critical frames and exclude, if necessary, from the integration (but you are routinely visually checking your frames after the data collection, just in case… aren't you?)

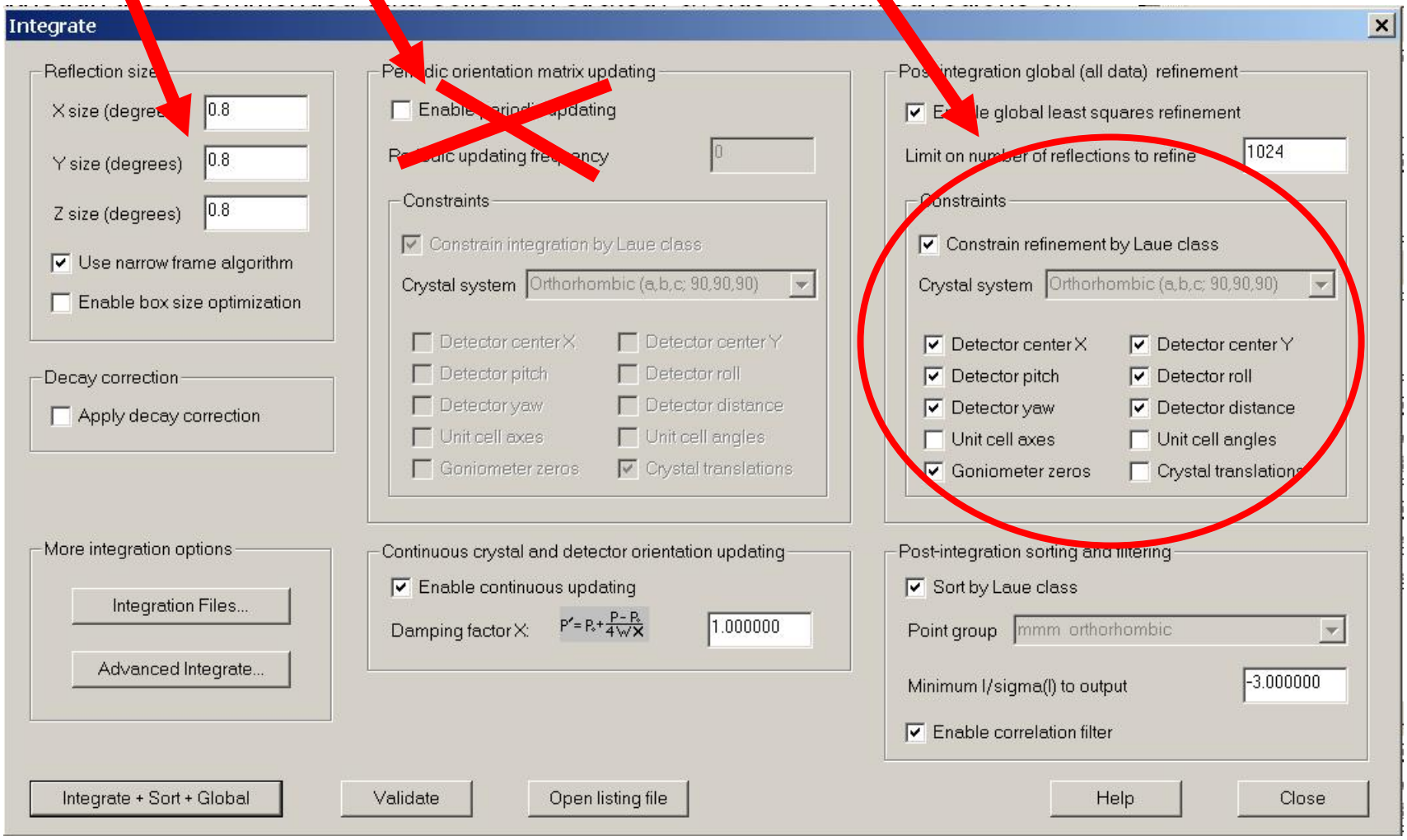


During the two first frames the primary beam was partly shaded. Should be excluded from integration!

Due to the “stormy” background, keep the box size as small as possible.

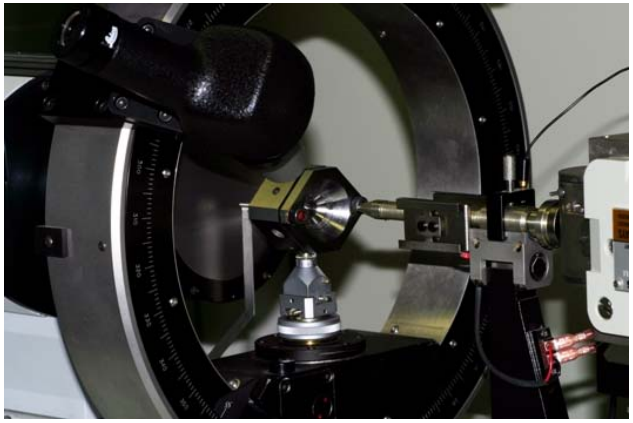
No updating of the orientation!

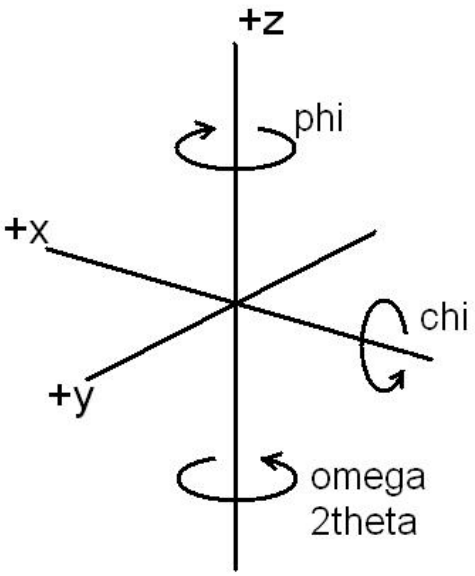
Constrain detector parameters (you are using calibration data from the measurement on standard in your P4P file!)



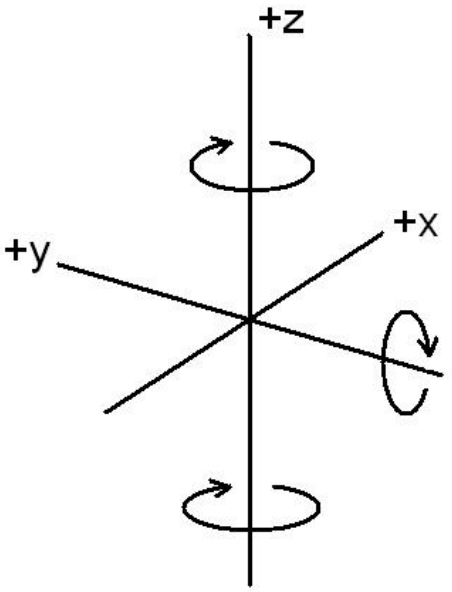
Correction phase

It is highly recommended that you measure your crystal and use ABSORB.
No details here, just the orientation specification for the Smart system. When measuring crystal it is supposed you measured the crystal with the DAC upwards from the goniometer head and looking along the primary beam when all the angles are on zero.





SMART



Busing & Levy (1967)

Lines in *.exp file:

PARITY -1,-1,-1,1
BLAXES 2,-1,3

Few last words about the Bruker-AXS diffractometer:

P4 goniometer or Kappa-geometry preferable!

Old software was and is still very good for HP work.
It allows for a large and versatile intervention from the user and contains some nice functions (e.g. hand picking of the reflections).

There have been developments in hardware which should give a significant improvement (larger and more sensitive detectors, recently stronger sources…) if they work OK.

Software development went unfortunately along the total-automation line taking the initiative from the user. The drawbacks of loosing some important functions and straightforward influence contained in the old software weigh in the opinion of our group more than the advantages of making some programs more “intelligent”. The impression is that the purpose was not to give good crystallographers more versatile tools, but that some good crystallographers tried to solve all the problems in advance for a mediocre user.