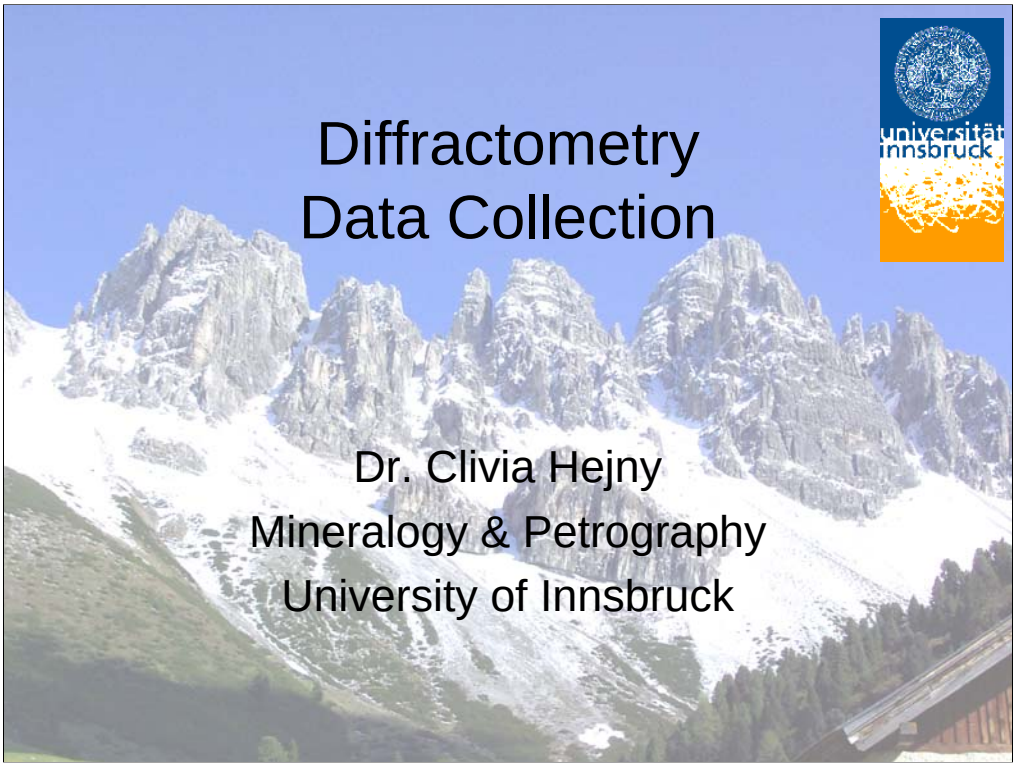


Hi everyone who finds these notes. These are my personal notes for the presentation given on 3rd of September at the satellite “Methods of high- pressure single-crystal x-ray diffraction” attached to the 26h European Crystallography Meeting in Darmstadt. I am happy if my notes help you to understand things that are not clear from the transparencies, but please understand that these notes are just notes and not an elaborate publication.

Practical considerations before the experiment:

Make room for DAC on diffractometer: short collimator

longer beam-stop distance

longer sample – detector distance

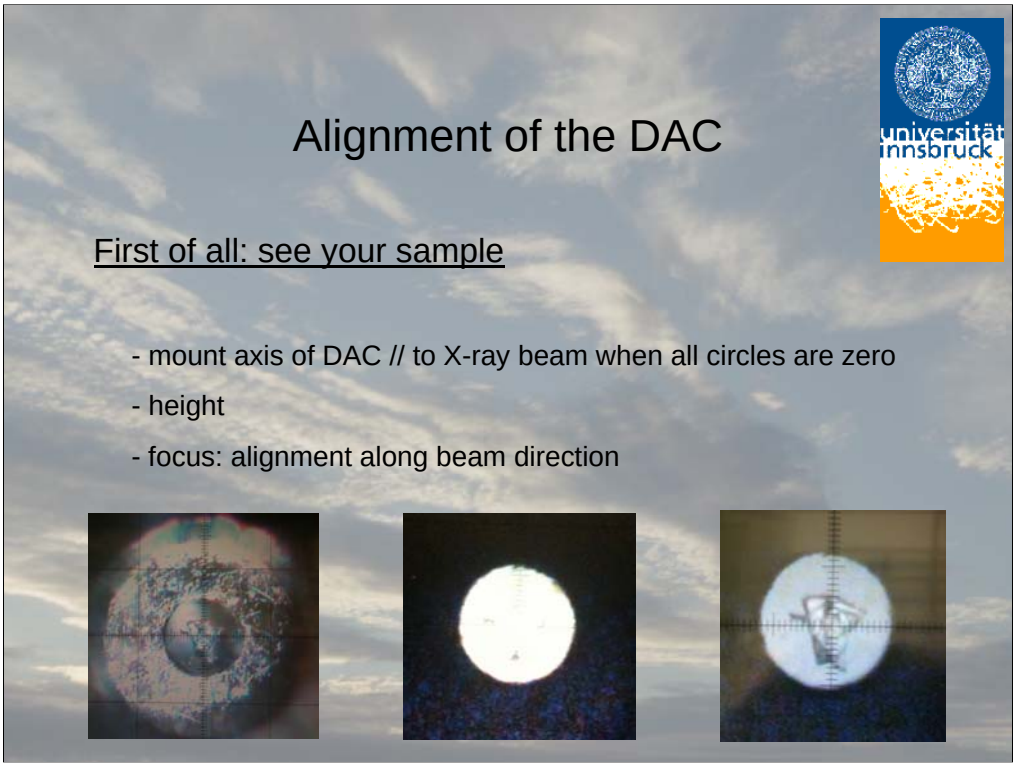
remove telescope (Eulerian

get cooling / heating devise

Fix DAC WELL to goniometer head

-Ways to fix DAC WELL to goniometer head:

- Glue DAC with superglue on little table with pin to go into goniometer head
- cell holder with pin that goes into goniometer head, as done by the Heidelberg group
- Weak point with cells on the heavy side: screw that holds pin – too easy to rotate



Mount - axis of DAC // to X-ray beam when all circles are zero, e.g. // diffractometer x-axis

When you put on DAC for first time: You will see nothing

Telescope on diffractometer is aligned to crystal in air at center of goniometer

What you are likely to see is an unfocused imaged of backing plate but not your crystal through the diamond

So first: get height approximately right:

-compare with xtal on goniometerhead that was centered

- direct comparison

- measure hight and note in your lab book / experiment routine

- one goniometer head dedicated to HP experiment with fixed DAC holder in correct height position

- Next step: Focus:

- in my experiment procedure fixed note: to change telescope from standard to HP as rough estimate

-Before this in more detail a note on illumination:

-First image: sample with light source standard equipment of diffractometer

-Better: light from back

- -- but not direct!

-Indirect!

Alignment of the DAC

First of all: see your sample

- mount axis of DAC // to X-ray beam when all circles are zero
- height
- focus: alignment along beam direction

-Focus: alignment along beam direction, e.g. DAC axis

-Cannot be viewed from side, gasket is in the way

-(1)

-Focus with telescope – turn DAC 180° so you can see sample through other diamond – focus again but remember how many turn you need - then go have way back and move DAC to be in focus

-Or (2): TONCI:

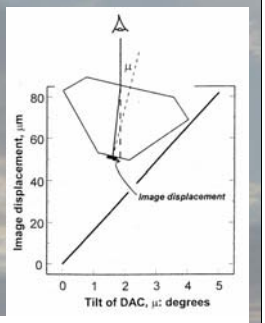
-Leave telescope and use mark on gonimeter key to focus – same principle see one side – see other side – go half way in between

Alignment of the DAC

First of all: see your sample

- IMPORTANT: look exactly perpendicular to diamond!

first estimate: optically



Angel, Downs and Finger, Reviews in Mineralogy Vol. 41

-IMPORTANT: make sure you look perpendicular to diamond surface!

-WHY perpendicular to diamond surface? Refractive index of diamond 2.47 – if you look at an angle you see the sample not where it is but displaced from its actual position, e.g. Misalignment of 2° - displacement of 30 microns

-Optically: first estimate cell aligned to goniometer head

Use all information available!

→ e.g. Check you see all side walls of diamond indent cylindrically

→ if telescope is well aligned – sample should stay in same position when defocusing and not wonder le/ri

-Possibility of using some tool to get DAC parallel to e.g. Chi circle of Eulerian cradle (0.5° - if diamond back is exaclty parallel to DAC!) or some other fixed part of the diffractometer, e.g. Old polaroid film casette

Alignment with laser: setting up the laser is a nuisance

Back-reflection of laser from back of diamond perpendicular beam

Positive: very accurate, especially when path length of laser is long, even small differences of angle are seen

Negative: nuisance setting up the laser

2 person job –one on the computer turning the cell around and one on the telescope centering

How to do in practice:

(1) Telescope must be perfectly aligned and focus onto the centre of the diffractometer

(2) Position of laser: opposite telescope and as far away from diffractometer as possible!

(3) Align laser so that the laser light is back-reflected from the telescope onto the laser source

Hint 1: optionally use mirror in front of telescope – make sure mirror is parallel telescope lens

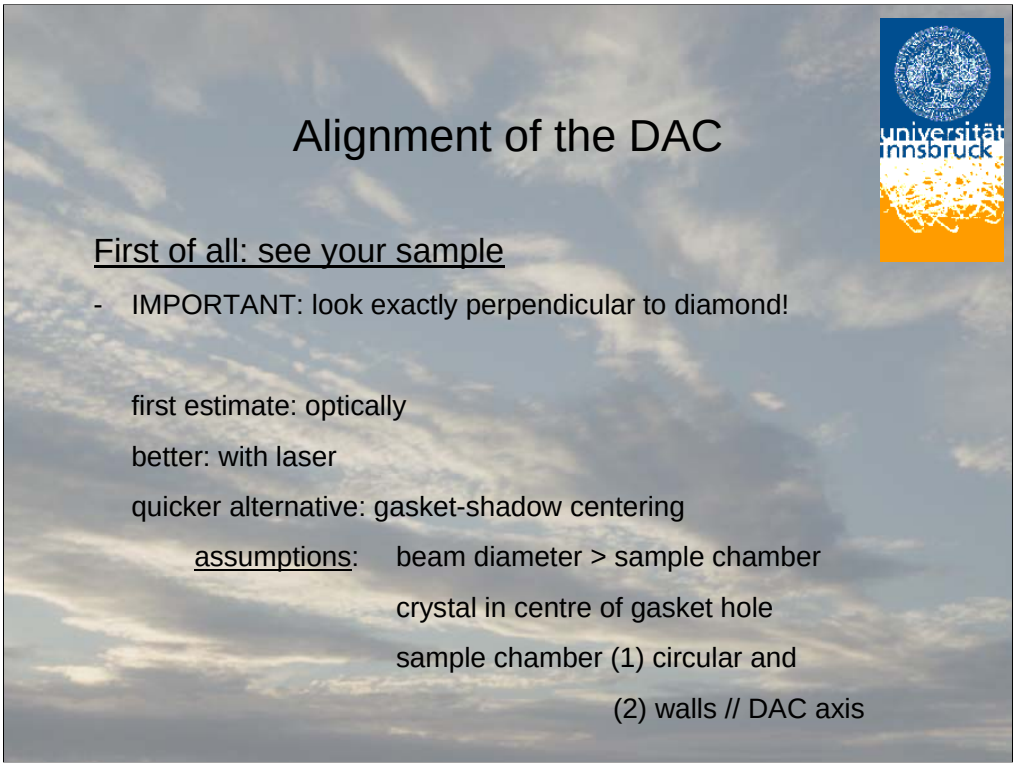
Hint 2: Paper around laser source helps to see back-reflected laser beam, that is otherwise somewhere on the wall

(4) Put on DAC and rotate omega and phi until back-reflection of laser from diamond is going exactly back into laser light source

(5) Use these omega and phi positions to centre the sample in the DAC

Gasket shadowing: quick, easy, relatively precise

Circular sample chamber in x-ray transparent gasket



Gasket shadowing: quick, easy, relatively precise

Circular sample chamber in x-ray transparent gasket

Alignment of the DAC

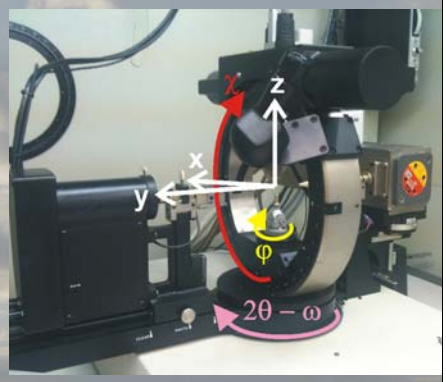
Gasket-shadow centering: alignment along the beam

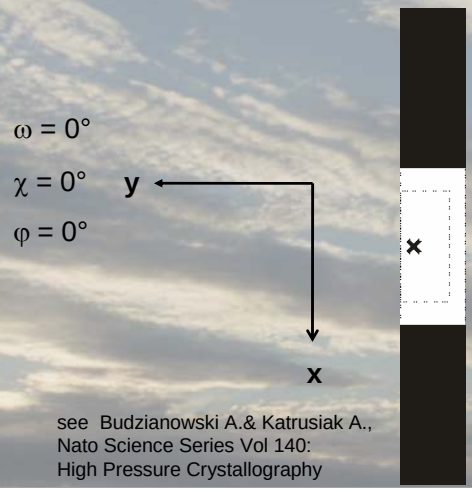
diffractometer y axis

ω = 0°

χ = 0°

φ = 0°





see Budzianowski A.& Katrusiak A., Nato Science Series Vol 140: High Pressure Crystallography

-Looking down on DAC mounted on diffractometer, down z of diffractometer

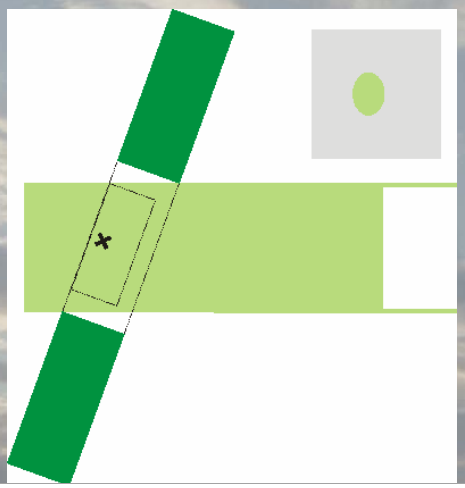
Alignment of the DAC

Gasket-shadow centering: alignment along the beam

$\omega = 0°$

$\chi = 0°$

$\varphi = + 25°$



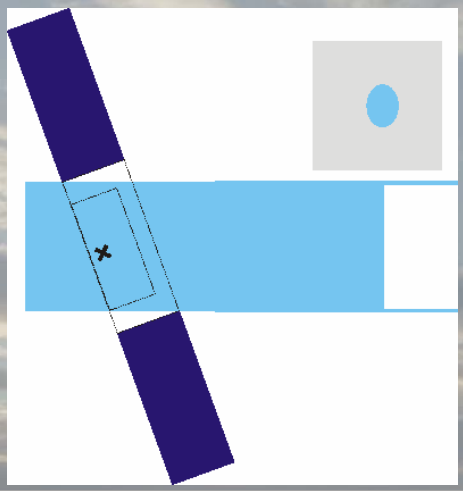
Alignment of the DAC

Gasket-shadow centering: alignment along the beam

ω = 0°

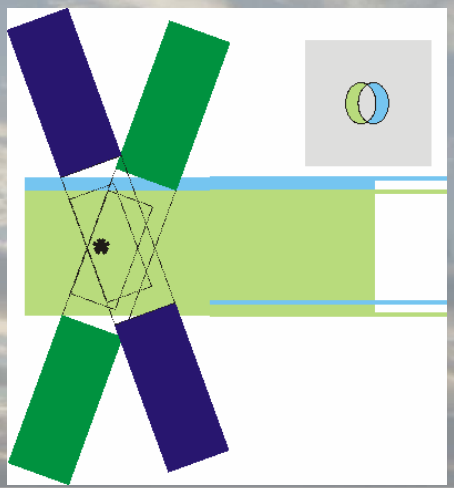
χ = 0°

φ = - 25°



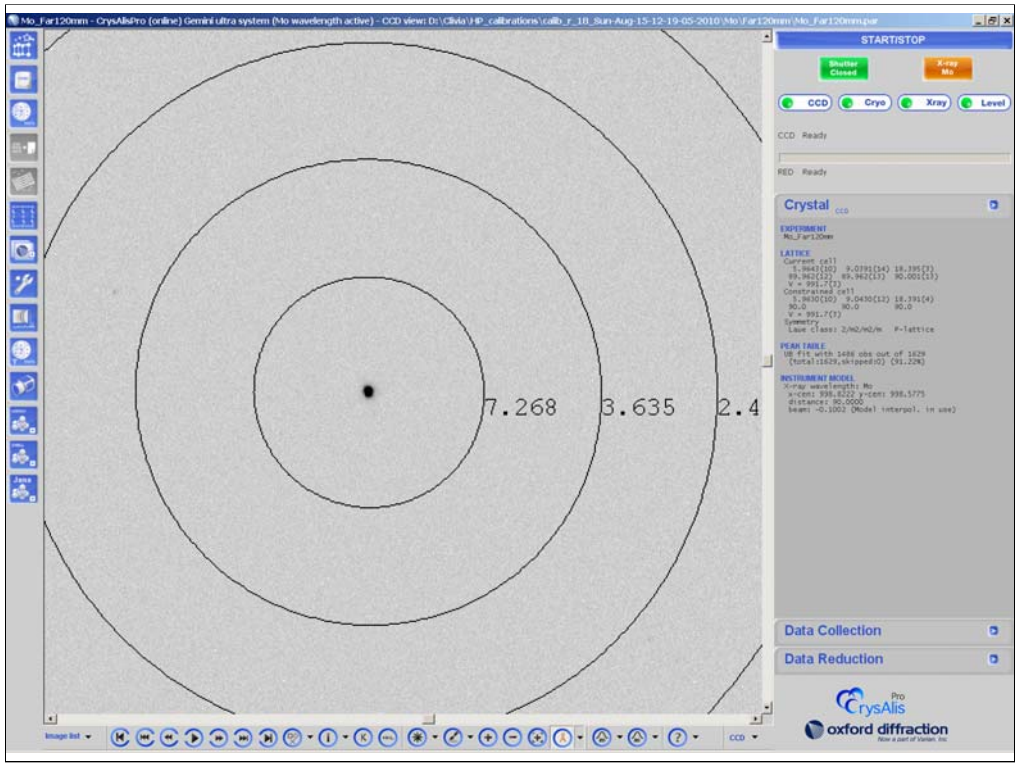
Alignment of the DAC

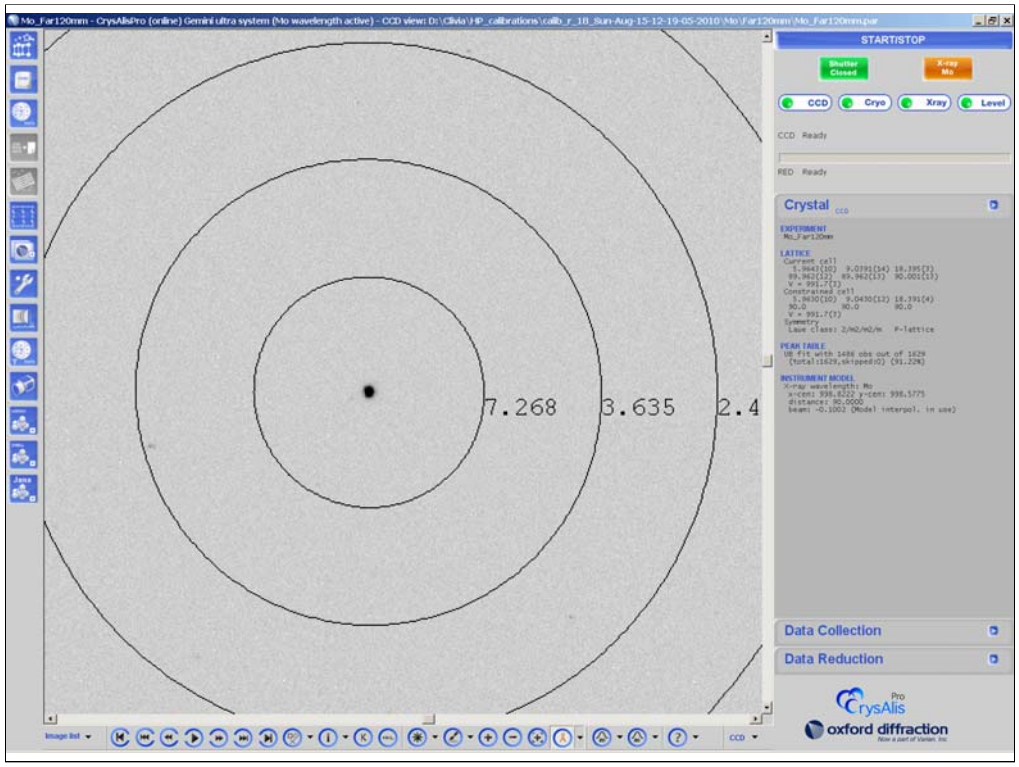
Gasket-shadow centering: alignment along the beam



This is actually centring the sample chamber and not the crystal in the sample chamber!!!

So for a crystal of 50 microns thickness in a sample chamber of 100 microns thickness the error along the beam is 25 microns! This should be corrected before the start of the datacollection.


Mo_Far120mm - CrysAlisPro (online) Gemini ultra system (Mo wavelength active) - CCD view: D:\Olivia\HP_calibrations\calib_r_18_Sun-Aug-15-12-19-05-2010\Mo\Far120mm\Mo_Far120mm.par
7.268
3.635
2.4
START/STOP
Shutter Closed
X-ray Mo
CCD
Cryo
Xray
Level
CCD Ready
RED Ready
Crystal
Data Collection
Data Reduction
CrysAlis Pro
oxford diffraction


7.268
3.635
START/STOP
Shutter Closed
X-ray Mo
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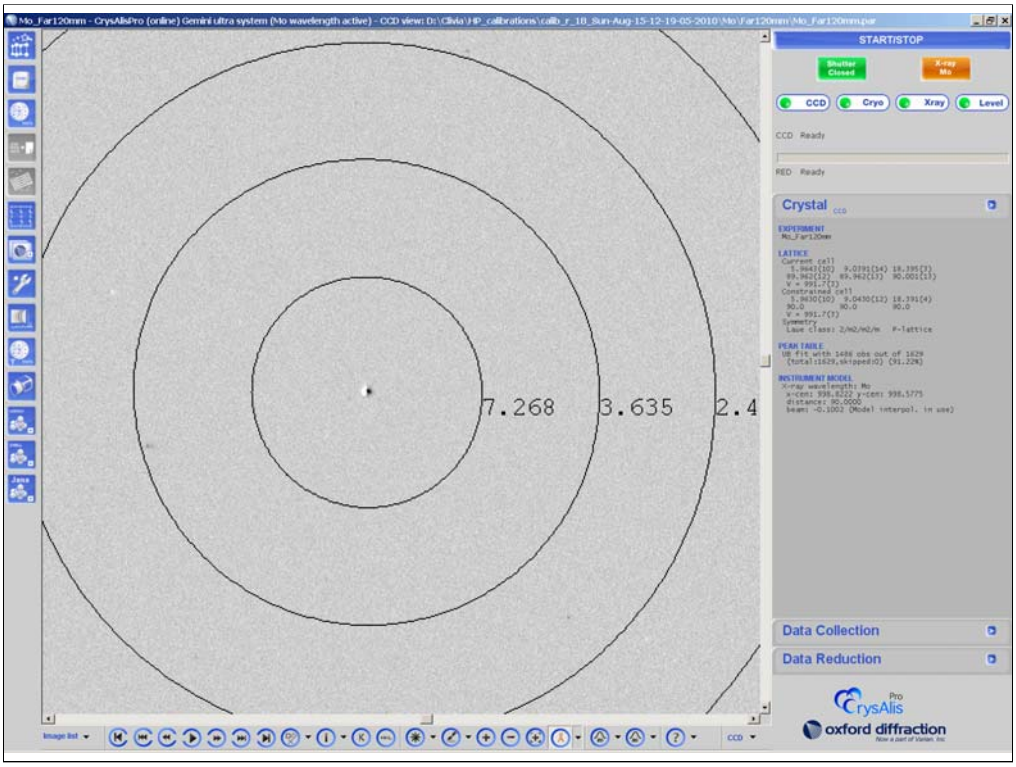
Cryo
Xray
Level
Crystal
Data Collection
Data Reduction
CrysAlis Pro
oxford diffraction



-Procedure:

-Rotate – expose – save – rotate – expose – save –subtract images – rotate cell back to zero

-Best to write a macro: write an e-mail to me, I can supply the macro and info how to run the macro or contact Olly at Oxford Diffraction. The macro can also be downloaded from the OD forum

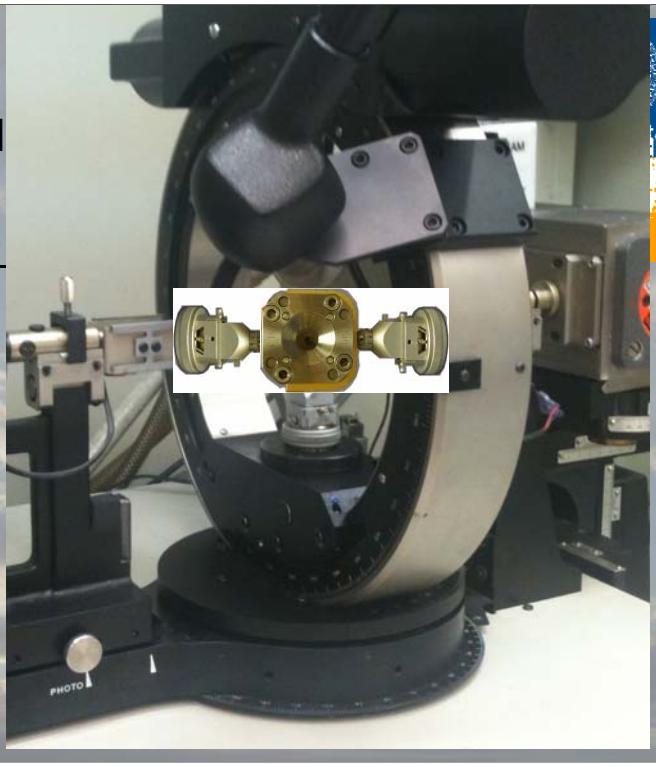
Al

Gasket-shadow

ω = 0°

χ = 90° / -90°

φ = 0°



Alignment of the DAC

Gasket-shadow centering:

~ equally off-centred along x and z | off-centred along x | off-centred along z | ideally centred

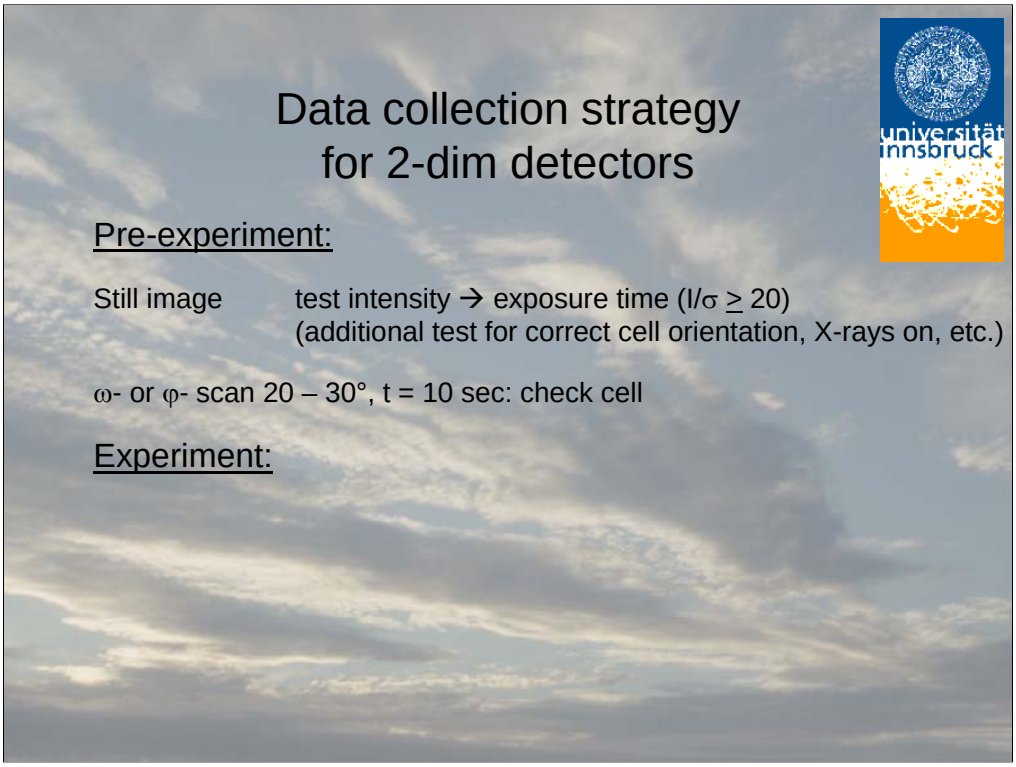
So far the easiest missalignments. For combinations, such as off along beam AND off in x – see Budzianowski A.& Katrusiak A.,

Nato Science Series Vol 140: High Pressure Crystallography

-Note: Center along beam back into crystal and away from center of gasket hole.

-Important especially for crystal e.g. 50 micron in 100 micron gasket hole: center of crystal at 25micron from dia, center of hole 50 micron

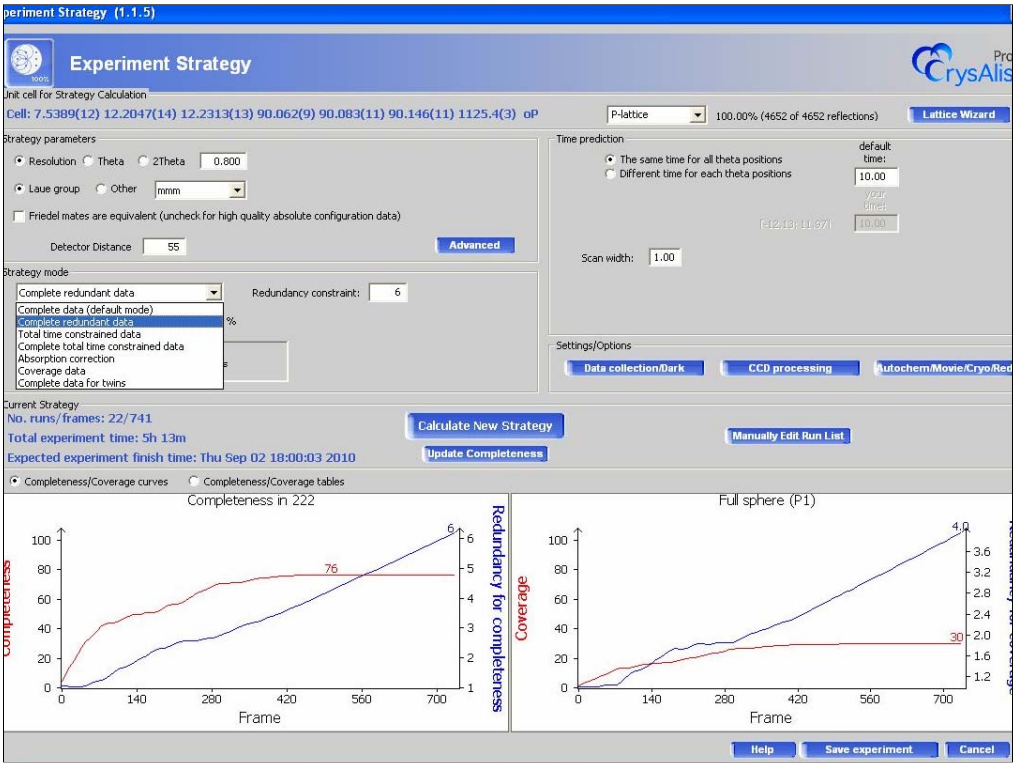
-How to do practically? – which way to turn screw on goniometer head and how much turn is a micron on the goniometerhead? When does screw on goniometer head bite?



pre-experiment: omega or phi-scan – is the same for chi = 0 and here I am not interested in intensity, only in lattice parameter and quality of the diffracted reflections: was there a phase transtion, are reflections still reasonable good, or are they split because crystal is broken due being squeezed by shrinking gasket hole

For data collection always omega-scan

Optimum way of collection data is phi= 0 mode, this ensures maximum completeness of the accessible reflections and minimum absorption if the DAC positioned for each reflection



I must admid, that most of the time I now use the oxford diffraction experiment strategywindow-

You can click several options, play around, check the time needed for this and that

Several test runs of one HP sample in DAC with different strategy modes

e.g. Complete data – complete redundant

Never time constrainded – for HP datacollection I now do take my time

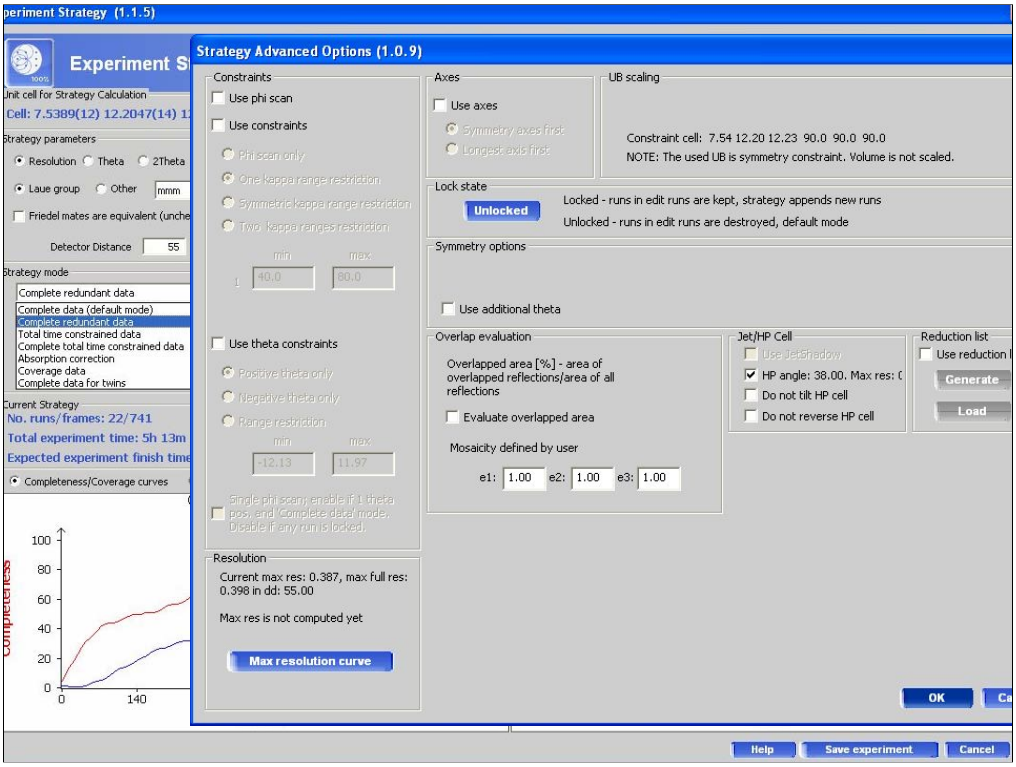
Different redundancy constrains when measured a hemisphere, e.g. 1,3,5

But there is only so much you can get out of a cell – for good data collection no matter which mode it takes about 5-6 hours with exposure time 10sec if I want all info out of the cell

Redundancy 5 gave more runs – longer experiments, but additional runs were frames with lots of shaded region and did not gain quality

So now: I mostly use hemisphere or sphere complete redundant data

BUT what I do use: fill I/sigma to be > 20!!!!



OD software: strategy tool: select HP cell and enter opening angle

HINT: not bigger than actual opening angle – this gives a lot of shaded region and this is much more work after data collection for good and usefull data integration

Data collection strategy for 2-dim detectors

Pre-experiment:

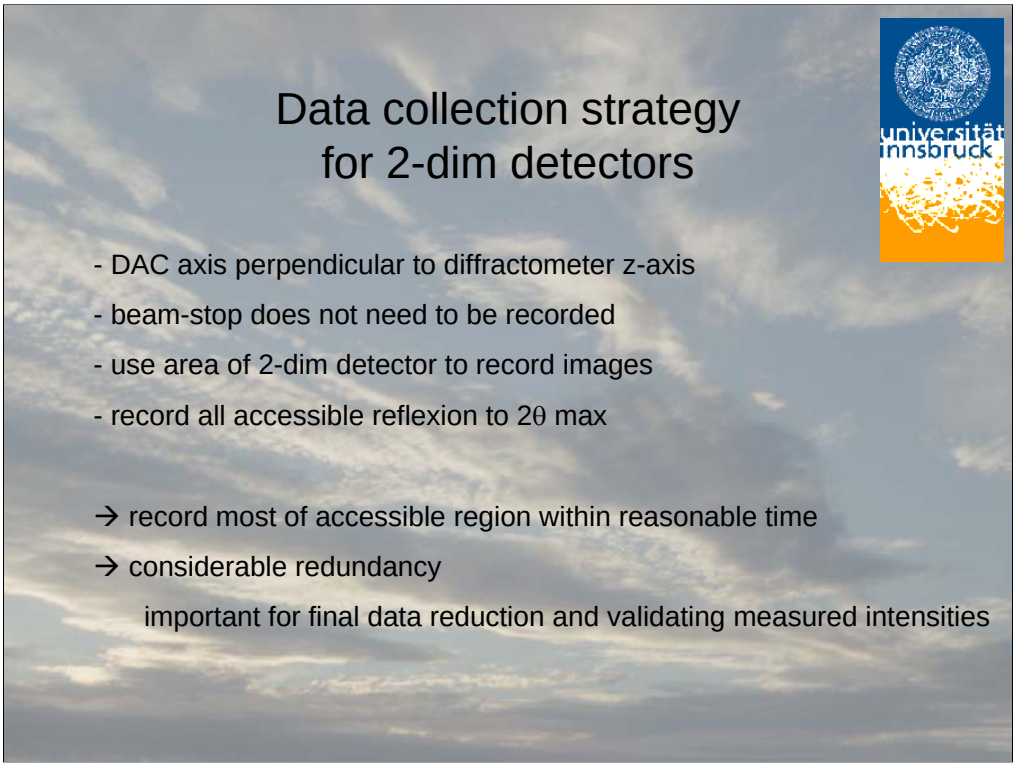
Still image test intensity → exposure time ($I/\sigma \geq 20$)
(additional test for correct cell orientation, X-rays on, etc.)

ω- or φ- scan 20 – 30°, t = 10 sec: check cell

Experiment:

Scan all accessible region of reciprocal space

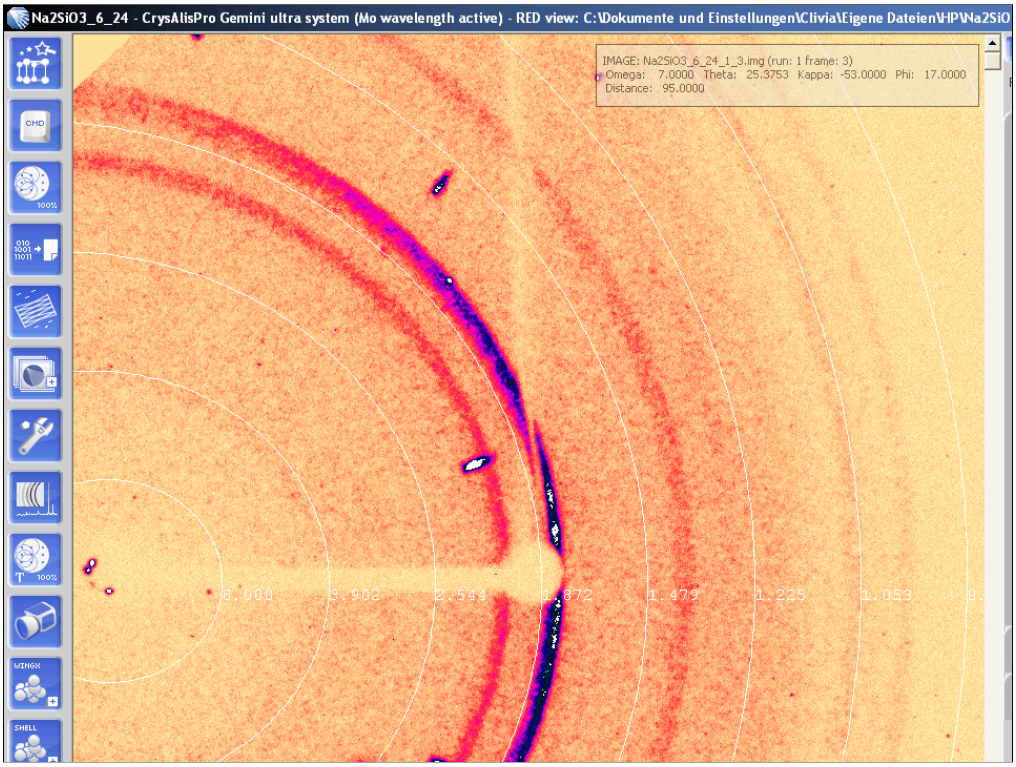
ω - scan



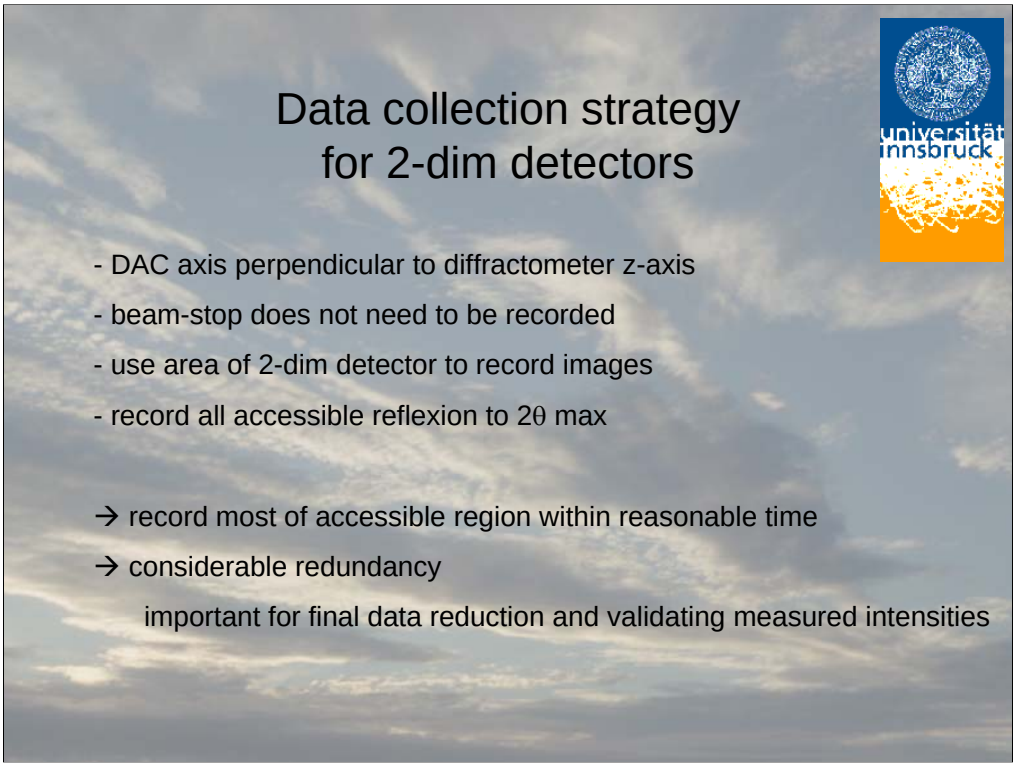
Use are for recording information that you can use – not beamstop and not shadow

Rather have overlapping

No frames with less than 25% info from sample, no more than 75% shaded



Notice reflections around the beamstop – double reflected in diamond to go parallel direct beam



How to get the most information out of the cell:
Rotate cell to get full information

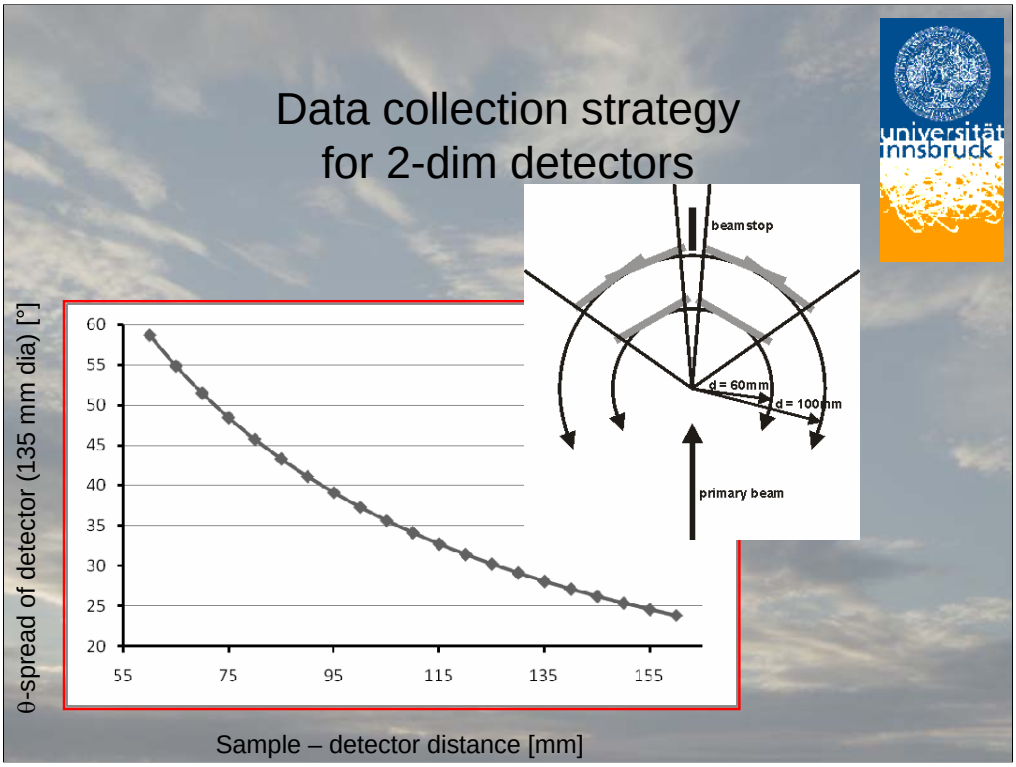
- but 2 different detector positions
- plus turning cell 180° and again 2 different detector positions
→ 4 runs for this
for bigger distance: 2 x 4 or 3 x 4 detector positions

Then chi 30° and again 4 runs
Chi 60° and 90°

Convert from eulerial geometry (chi = 0, 30, 60, 90) to kappa geometry
Test for collision (program)

Time dependent on exposure time
16 runs with 1 min exposure – 29hr
Accordingly 30sec – 16 hr
20sec < 10hr

Time is important!
e.g. Shortly after phase transition new weak reflections →



-Theta range that can be collected out of DAC gives position of detector

-But it also gives overlapping area

-E.g. Even further out 3 detector positions necesarra but with less overlap and hence less redundancy

Data collection strategy for 2-dim detectors

important parameter to set up run list :

- opening angle of your cell → max available 2θ
- sample - detector distance

➔16 runs (2 or 3 times 16 runs if necessary)

4 runs each for χ = 0, 30, 60, 90°

if κ – geometry: convert angles accordingly

EXPOSURE TIME!

Time dependent on exposure time

16 runs with 1 min exposure – 29hr

Accordingly 30sec – 16 hr

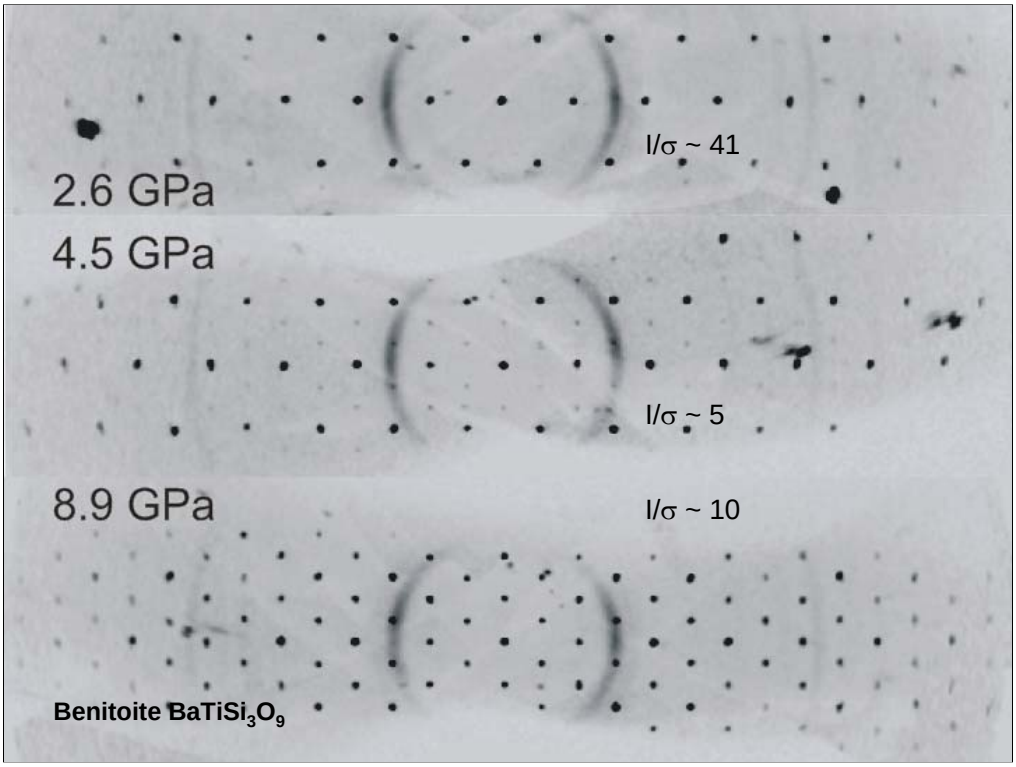
20sec < 10hr

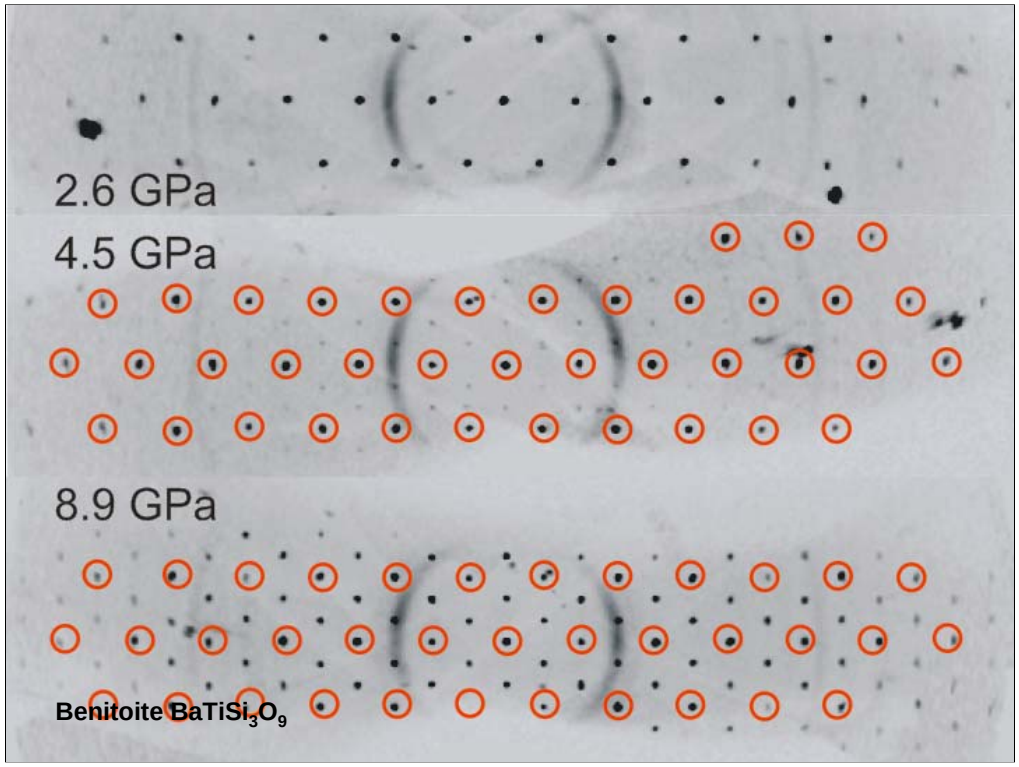
Time is important!

e.g. Shortly after phase transition new weak reflections → need longer exposure time for reasonable I/sigma than further away from phase transition with reflections srong

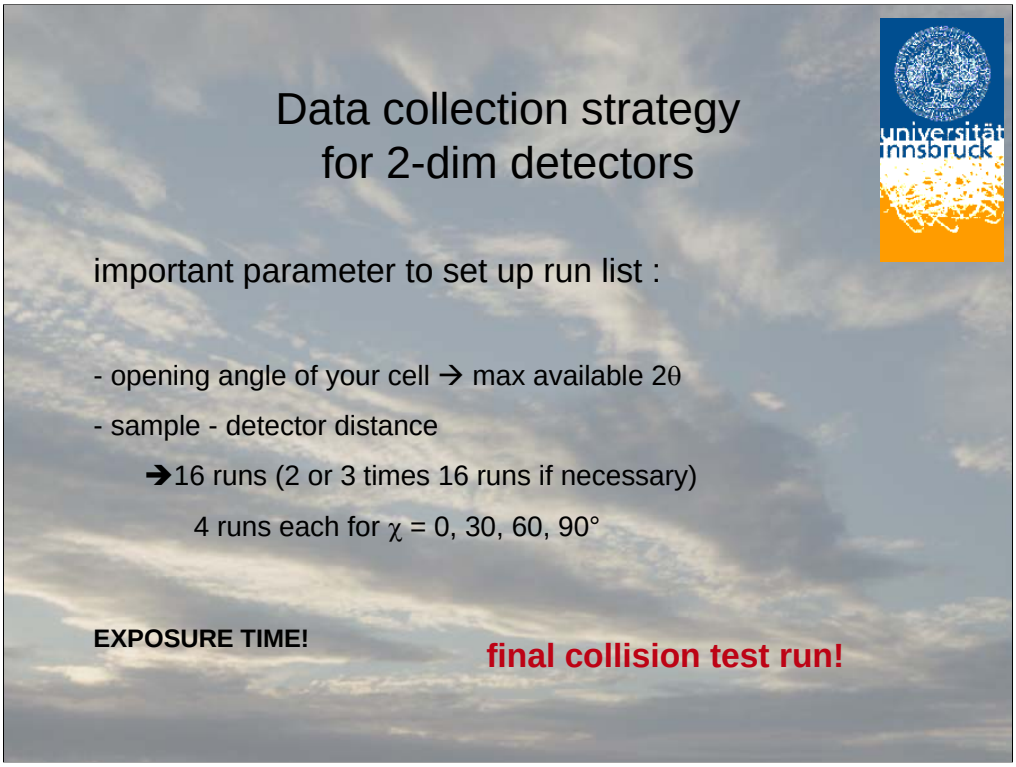
Weak scatterer: lab source for reasonable data even with low I/sigma exposure time of 10 minutes necessary → do you really want to risk burning holes from diamond reflections onto your detector?

And for good I/sigma 1,5 months necessary → go to the synchrotron!


2.6 GPa
I/σ ~ 41
4.5 GPa
I/σ ~ 5
8.9 GPa
I/σ ~ 10
Benitoite $BaTiSi_3O_9$

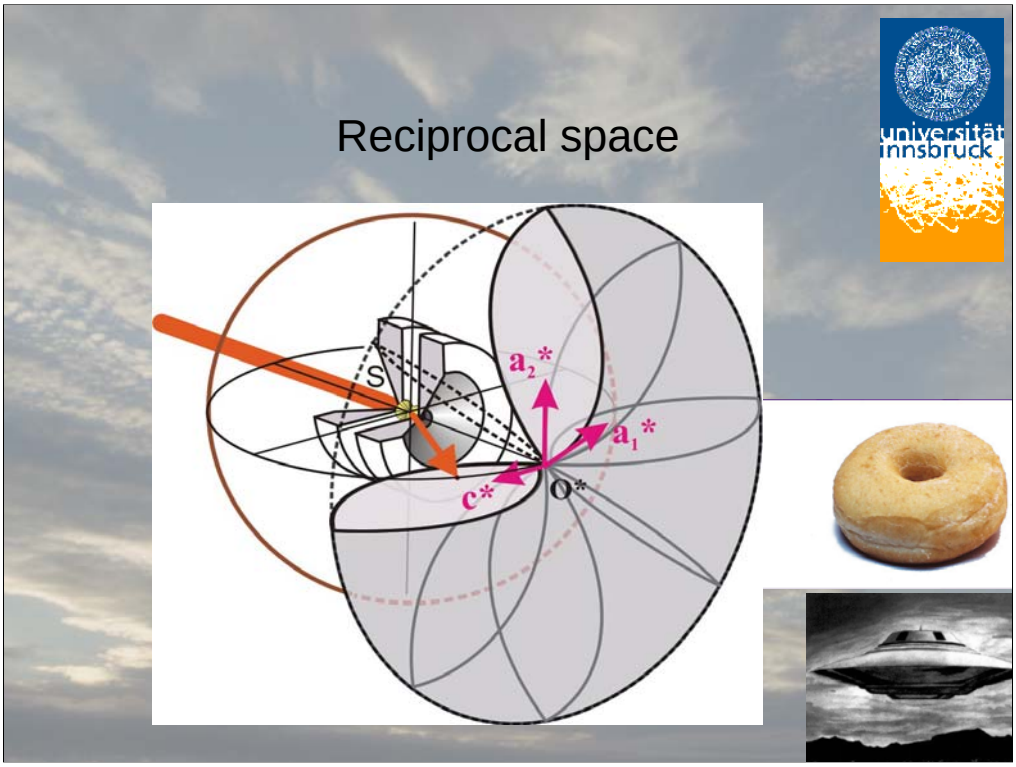


Benitoite $BaTiSi_3O_9$



Actually ready to go

But helpful – especially when something fundamentally on diffractometer has changed: Dry run though all different positions for last collision test



Toroidal shape of accessible reciprocal space

For those who do not know what toroidal mean: mixture between donat and UFO → Unidentified flying donat

Now imagine you have a tetragonal crystal with two a equal axis and and one different c axis

-- how do you want your axis to be oriented in this donat to get good information on a and c

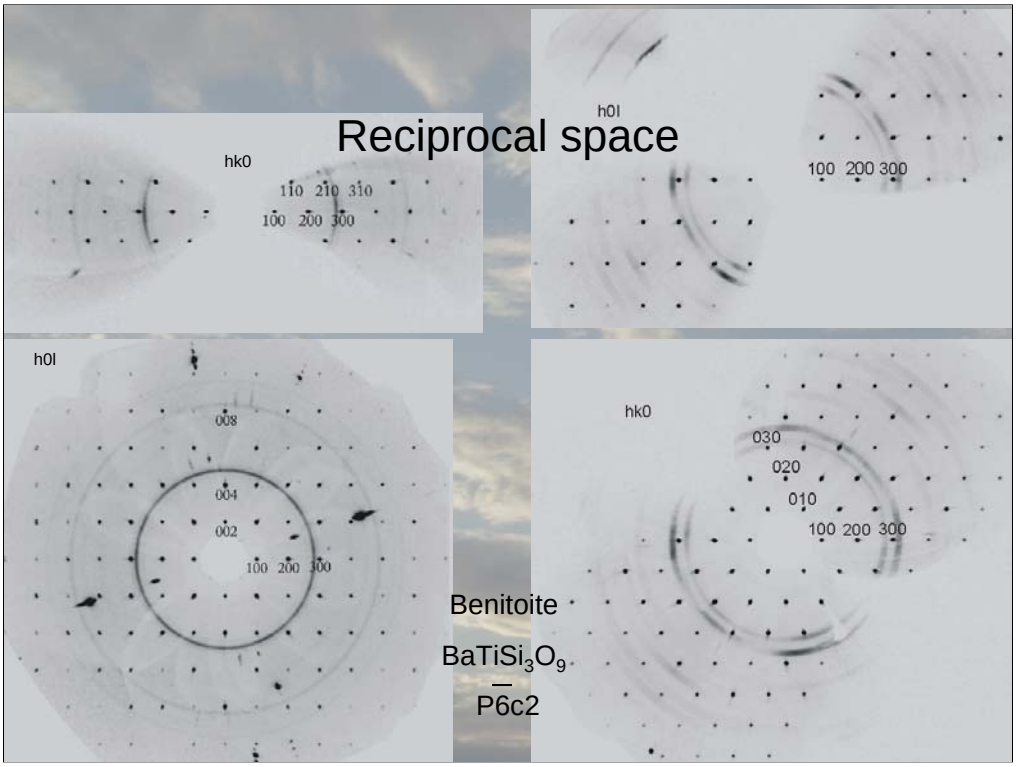
So a good orientation for the crystal in the DAC is with a* and c* axis parallel to anvil faces and the other a* axis (info already in donat) // DAC axis

Cubic: no restictions on orientation

Uniaxial: a* and c* parallel culet

Lower symmetries: reduced resolution of reciprocal space direction that is perpendicular to culet

→Load two crystal with different orientations in cell, or two cell loadings, or reduced resolution in all direction with use of 111 slice

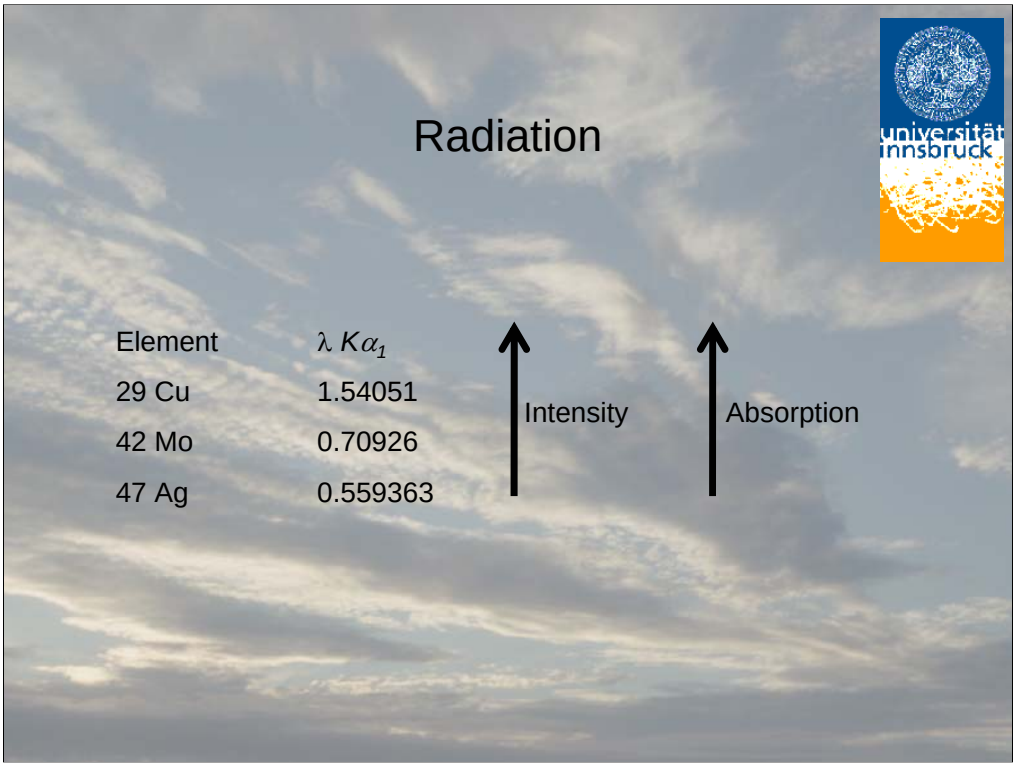


→Another orientaion-problem: find correct space group

→00l reflections missing: valuable information is missing!Left side: right orientation of crystal in DAC

Right side: wrong orientation of crystal in DAC: no 00l-refelctions, no 001, 002, 003,.....!


What else is important?

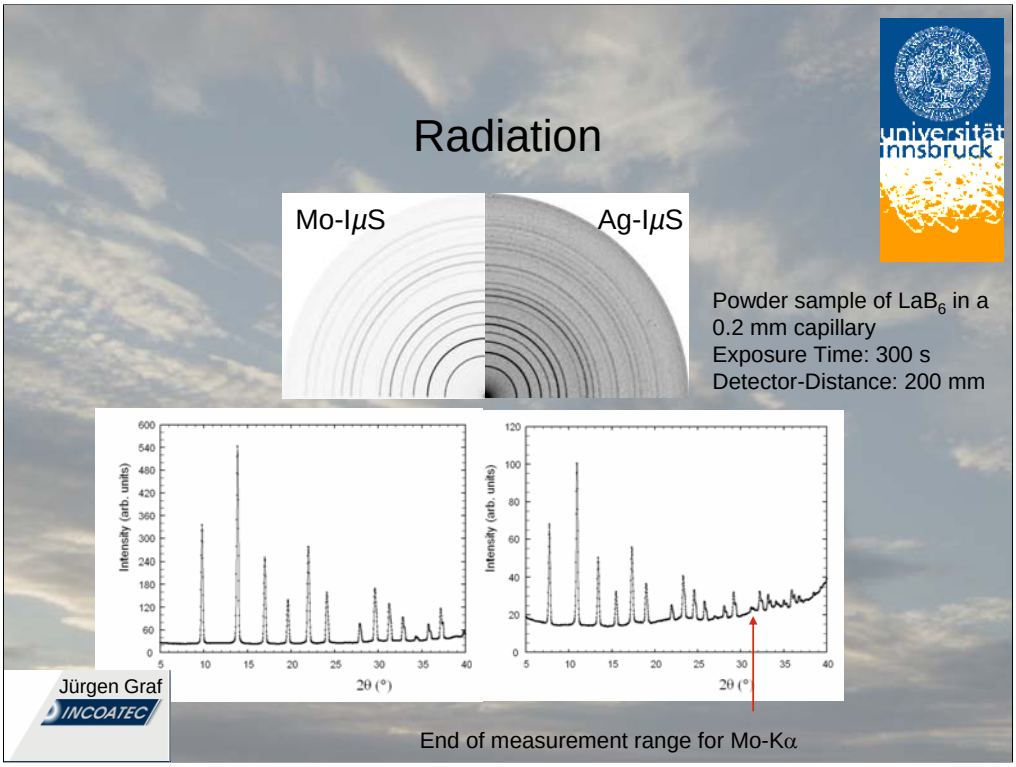


Cu-radiation: NO NO NO for DAC: althought Cu has more intensity, it is more strongly absorbed by the diamond!

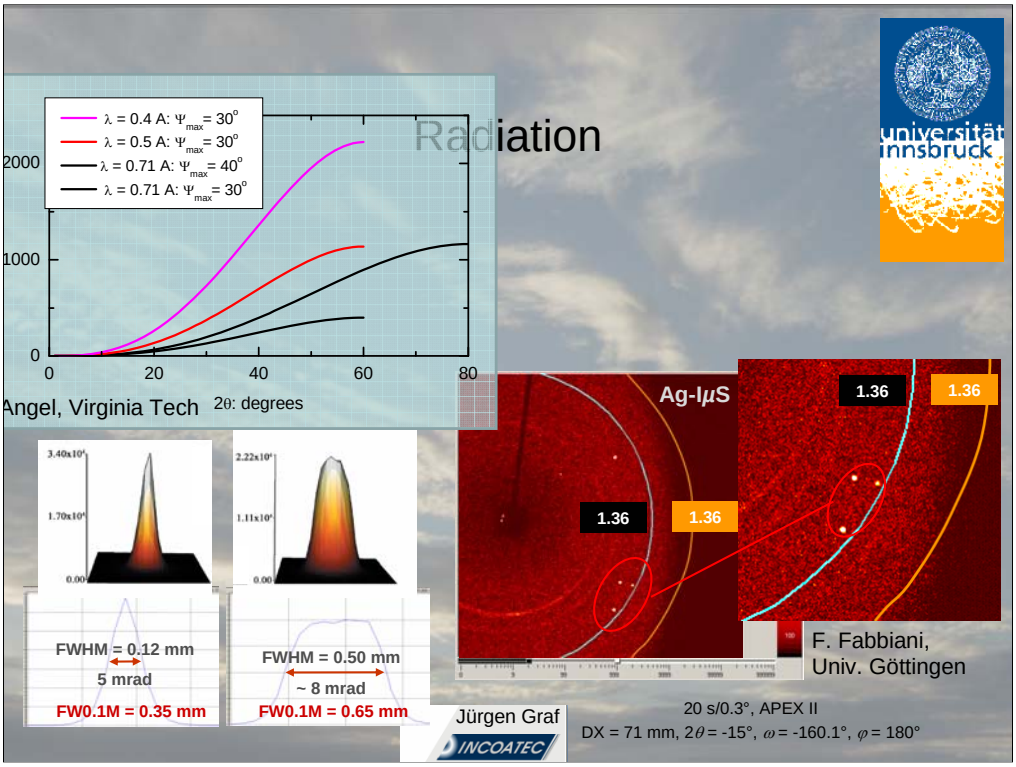
Furthermore too little reflections with Cu!

Mo: okay

Ag: more reflections out of DAC, but less intensity → overcome by new micro focus tubes



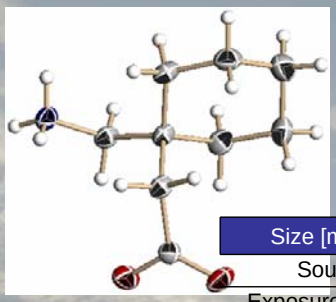
Ag – shorter wavelength: more information to come out of DAC



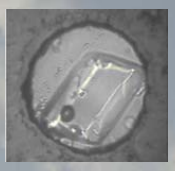
Ag – shorter wavelength: more information to come out of DAC

Synchrotron: even shorter wavelength than Ag → even more reflections to get out of the DAC

Furthermore: beam profile of micro focus tube → less scattering from the gasket



Gabapentin crystal in **300 µm gasket** of Be-free DAC



$C_9H_{17}NO_2 \cdot 2\ H_2O$

Gabapentin Heptahydrate, *P*-1, *Z* = 2,

μ = 0.12 mm^{-1}

Size [mm^3]	0.25 × 0.20 × 0.20	
Source	**Ag-IμS**	**2 kW Mo-ST**
Exposure [s/0.3°]	**20**	**20**
Resolution [Å]	**0.90 (1.00 – 0.90)**	**0.90 (1.00 – 0.90)**
< I/σ >	19.6 (3.2)	18.3 (4.7)
Unique data	**866 (170)**	**721 (135)**
<Redundancy>	1.5 (0.9)	1.1 (0.7)
<Completeness>	**40.6 (28.9)**	**33.7 (22.6)**
R_{int}	0.0306 (0.1636)	0.0342 (0.1489)
Data used (I > 2σ(I))	**860 (630)**	**705 (523)**
$R1$; $wR2$	**0.0487; 0.1025**	**0.0532; 0.1232**

Jürgen Graf

INCOATEC

F. P. A. Fabbiani, Universität Göttingen

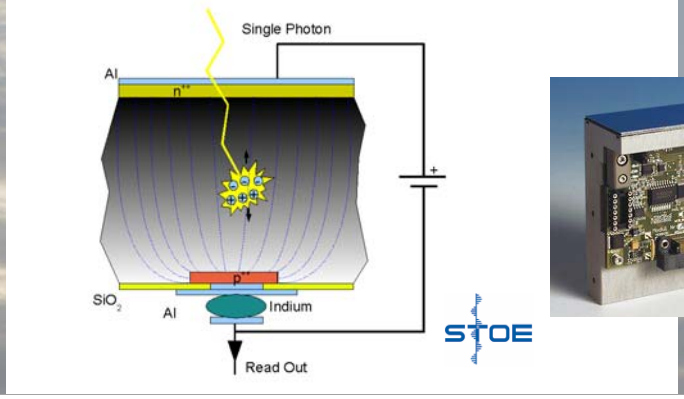
Detectors

2-dim detectores:

Image plate

CCD

pixel detector



-Image plate: very good, high sensitivity, high dynamic range, but slow

-CCD: quicker than image plate, but more expensive

-Pixel detector: as good as image plate regarding quality and quicker!

Point detector

High-precision determination of peak position

very precise lattice parameters (constant temperature!)

accurate measurement of 3-dimensional setting angles

Careful analysis of profile of Bragg reflection

e.g. $K\alpha_1 - K\alpha_2$: for low θ splitting below resolution

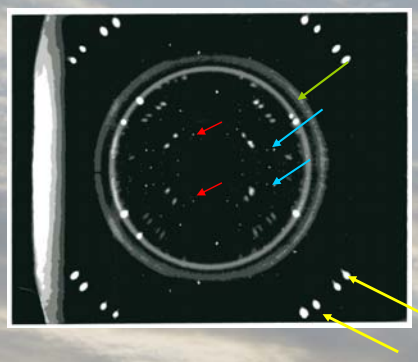
inhomogeneous scattering from different parts of sample with high deviation from goniometer centre & centre of diffraction

➔ 8-position centering: measure reflection at 8 different positions

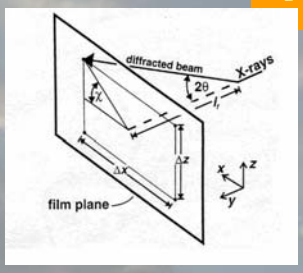
drawbacks: (1) difficulty of determining UB (2) time!

- 2-dim detector: polaroid film
- or CCD/image plate/ new silicon strip detector on other diffractometer
-Transform UB and search for one reflection
-Create a list

Point detector



Polaroid film of DAC loaded with realgar AsS & quartz SiO2



Geometry of rotation on polaroid

$$2\theta = \arctan\left(\frac{\sqrt{\Delta x^2 + \Delta y^2}}{2l}\right)$$

$$\chi = \arctan\left(\frac{\Delta z}{\Delta x}\right)$$

-Yellow: gasket (powder ring) and diamond (strong reflection)

-Blue: realgar reflection

-Red: quartz reflection

-UB from polaroid film:

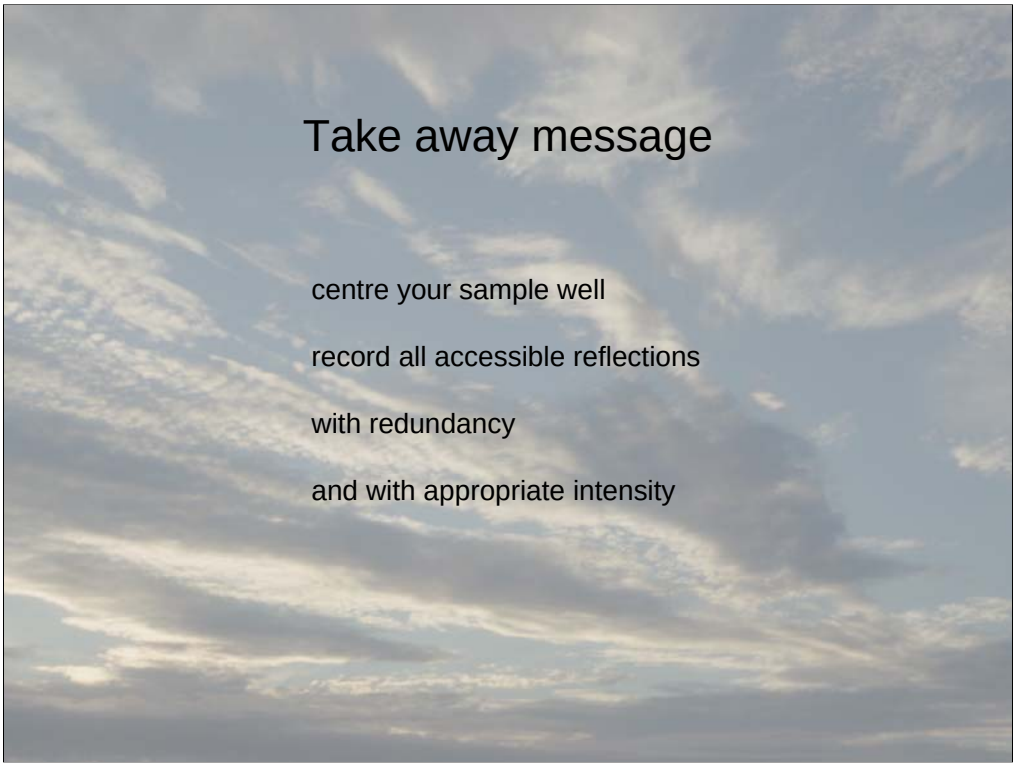
-Measure distance between equivalent reflections and calculate setting angles theta a chi, search for phi with scanning

-Get d value and index hkl (attention for high pressure hkl lower d than for AP crystal

-2 reflections with known setting angles and indeces are sufficient to calculate UB

-Make list of other reflections that are available and scan then to refine UB

-E.g. 15 – 20 reflections for sample and 15-20 reflections for quarz crystal


Take away message
centre your sample well
record all accessible reflections
with redundancy
and with appropriate intensity