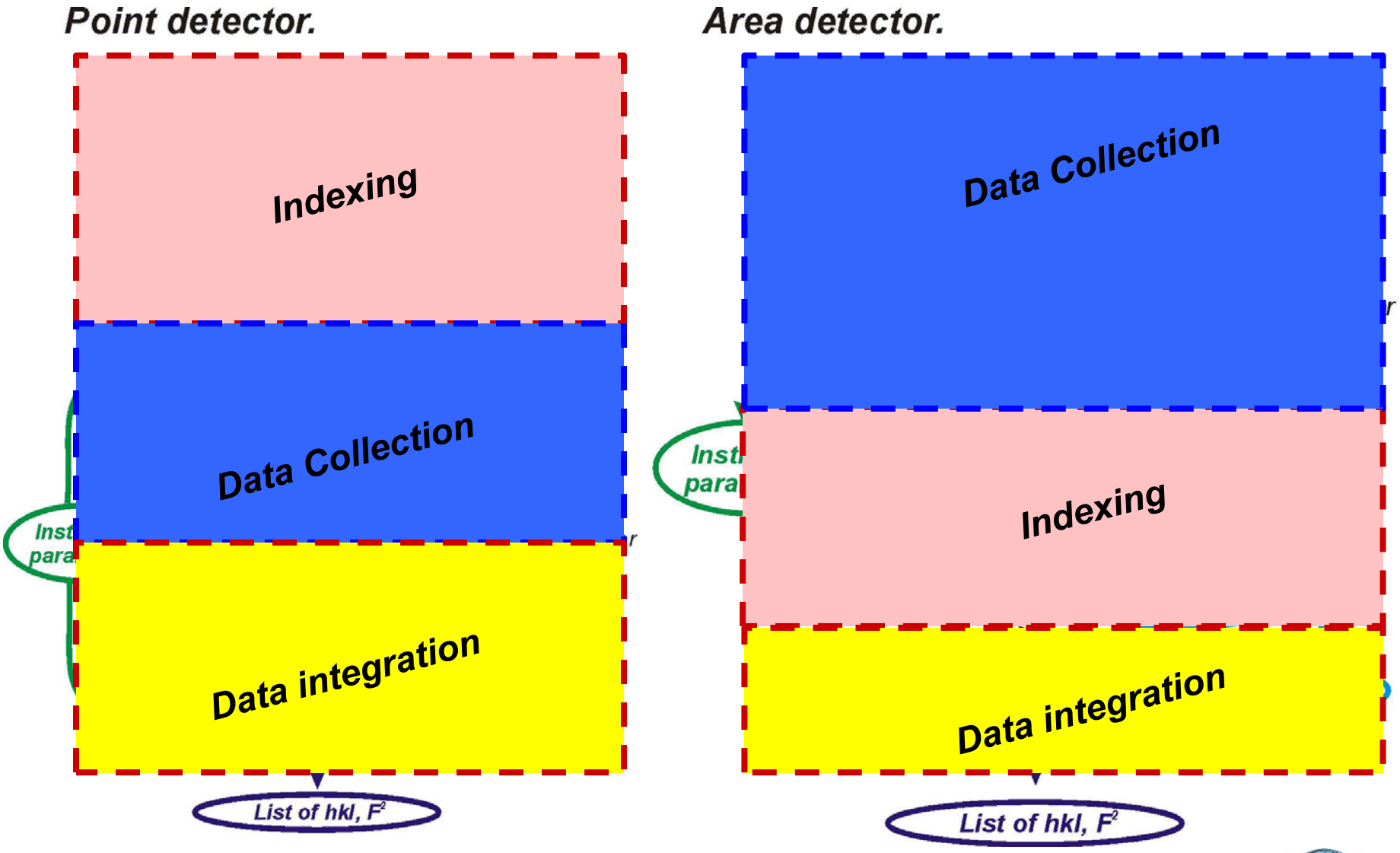
Absorption and Intensity Corrections

Ross Angel
Dipartimento di Geoscienze, Universita di Padova

- ***Overview***
- ***Absorption –***
  - ***the principles***
  - ***the information needed***
- ***And what we cannot correct!***

Data collection….done and integrated!



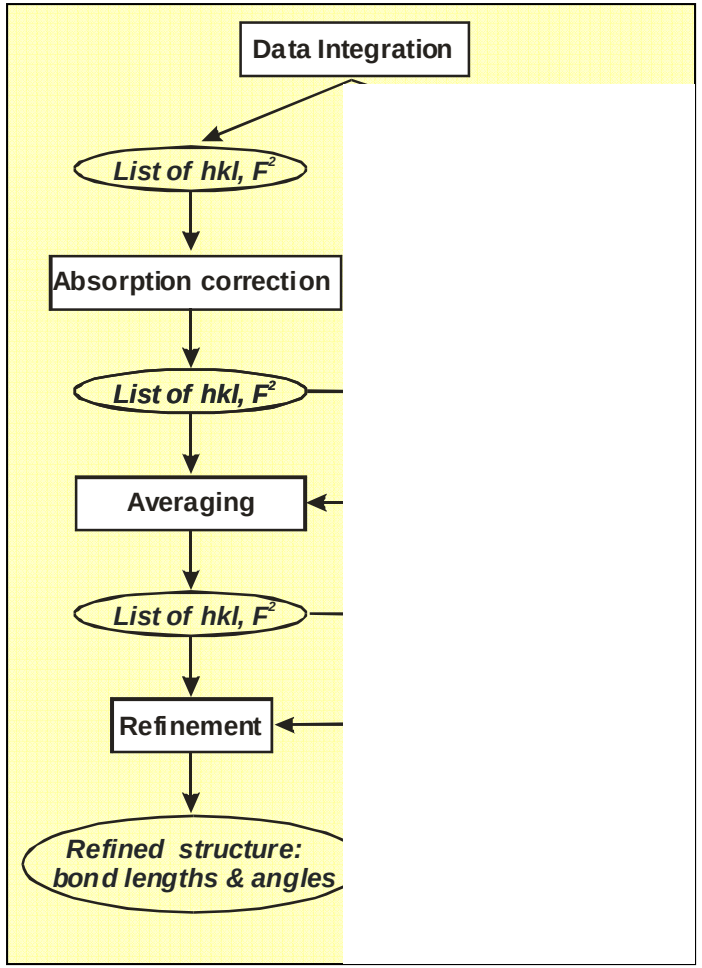
Intensity data quality:

- **Intensity data is degraded by:**

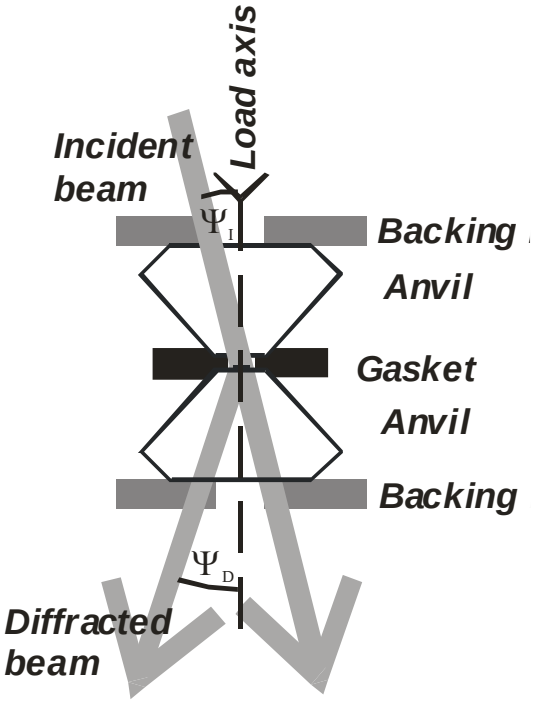
Limited access Low signal	Experiment design Integration
Scattering by cell components Shadowing by cell components	Experiment design Integration
Beam decay (synchrotron data) Absorption by cell components Diamond dips	Data Reduction

Post-integration steps

- **Data reduction**
  - Critical for HP data
  - Absorption corrections
  - Averaging
- **Refinement**
  - Robust-resistant weighting
  - Restraints
  - Careful evaluation of outliers
- **Structure validation**

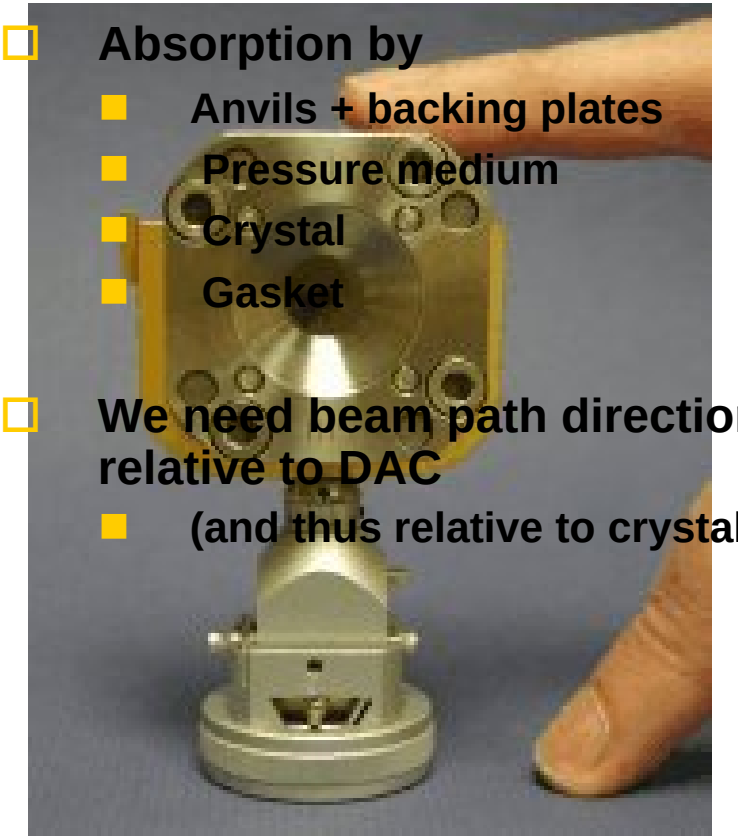


Absorption in the DAC: geometry

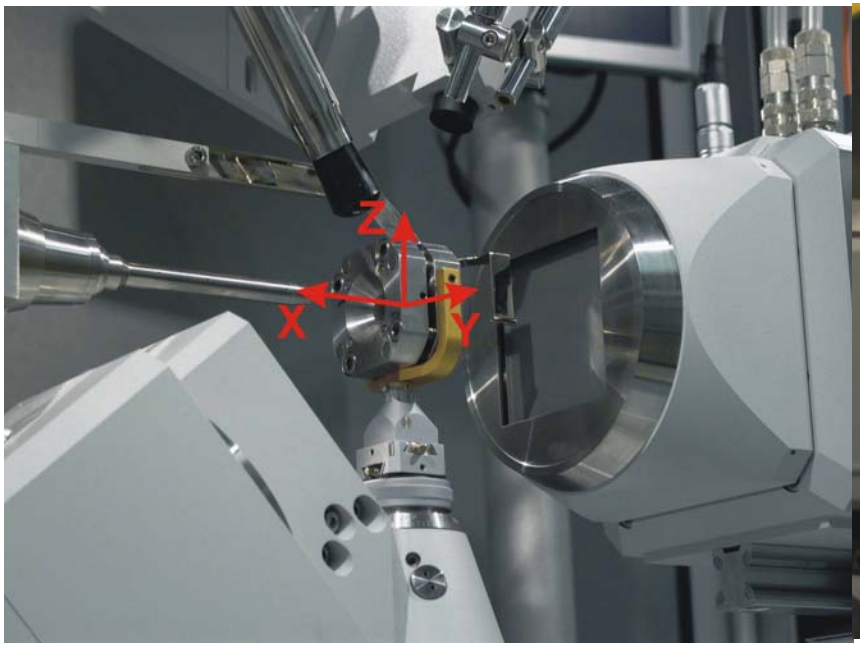


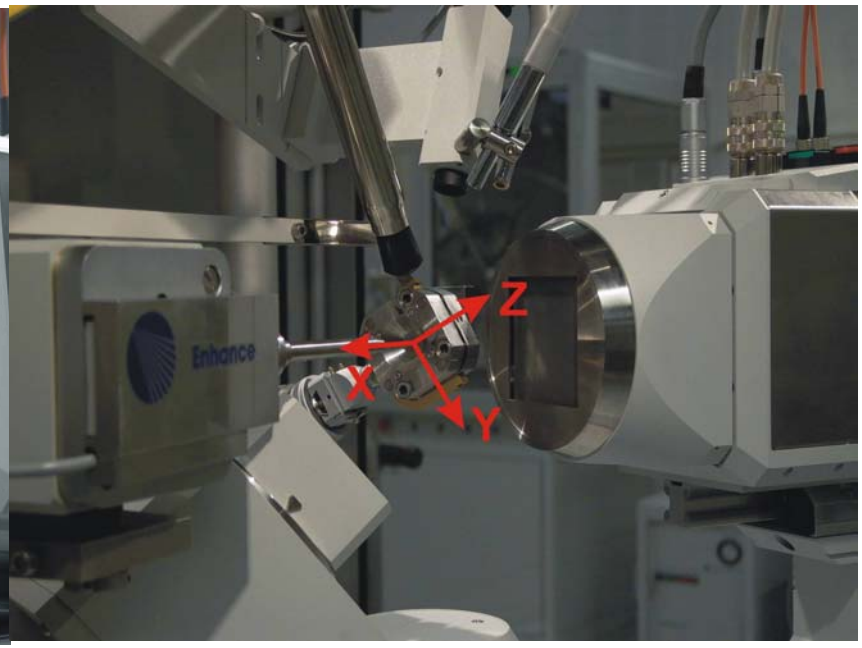
Transmission mode

- Absorption by
  - Anvils + backing plates
  - Pressure medium
  - Crystal
  - Gasket
- We need beam path directions relative to DAC
  - (and thus relative to crystal as well)



Absorption in the DAC: defining beam paths



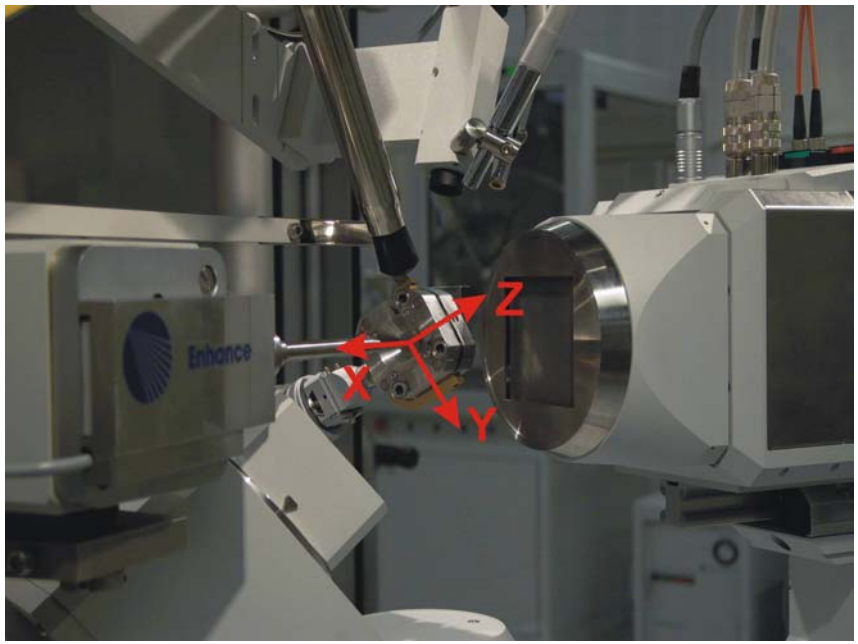


- The DAC is fixed to the goniometer head
- A natural Cartesian reference basis is therefore a basis fixed to the goniometer head (phi-axis system)
- Define beam paths on this axial system

Busing, Levy (1967) Acta Cryst 22:457

Defining beam paths

- Incident beam path
  - Only goniometer angles
- Diffracted beam path
  - Goniometer angles
  - Detector position
  - Spot position on the detector (area detectors only)



- Information can be provided in two ways:

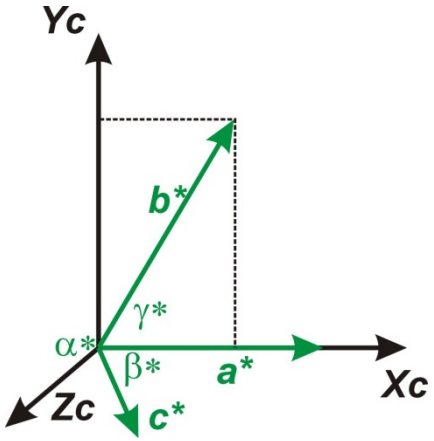
- PD: goniometer angles
- PD & AD: Direction cosines of I-beam and D-beam
  - In SHELX hkl files, direction cosines relative to crystal axes!

The orientation matrix, UB

- Defines the orientation of the reciprocal lattice vectors of the crystal with respect to the goniometer:

$$\underline{h\phi} = UB.\underline{h}$$

- B is a matrix that transforms reciprocal space vectors (hkl) from reciprocal lattice basis to an orthonormal basis:

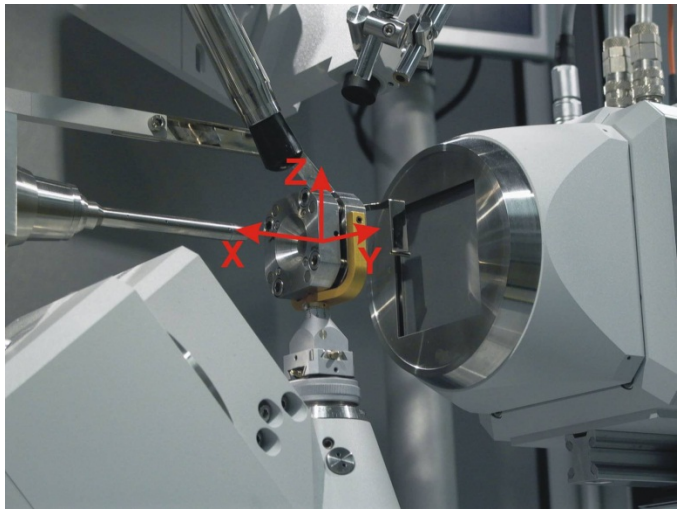


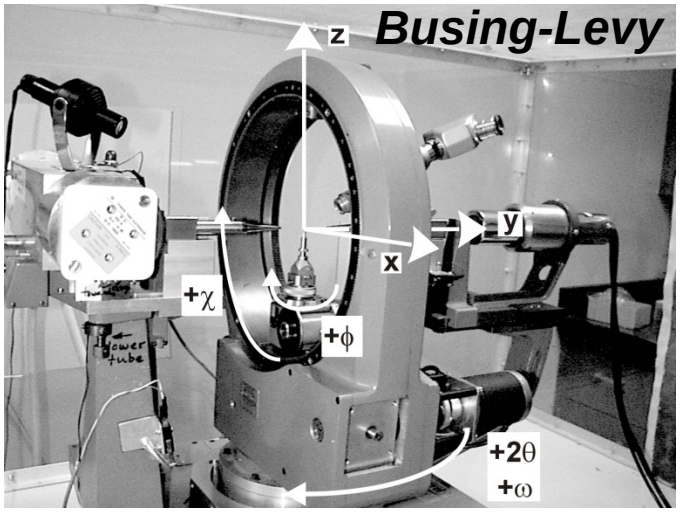
$$\mathbf{B} = \begin{pmatrix} a^* & b^*\cos\gamma^* & c^*\cos\beta^* \\ 0 & b^*\sin\gamma^* & -c^*\sin\beta^*\cos\alpha \\ 0 & 0 & 1/c \end{pmatrix}$$

- The B matrix (or UB) is needed to convert the SHELX direction cosines from crystal system to phi-axis system (Allen et al, 2000)

Defining beam paths with the UB matrix

- The definition of the phi-axis system, and thus U and UB, is different in different software!
  - Axis directions when diffractometer circles at zero



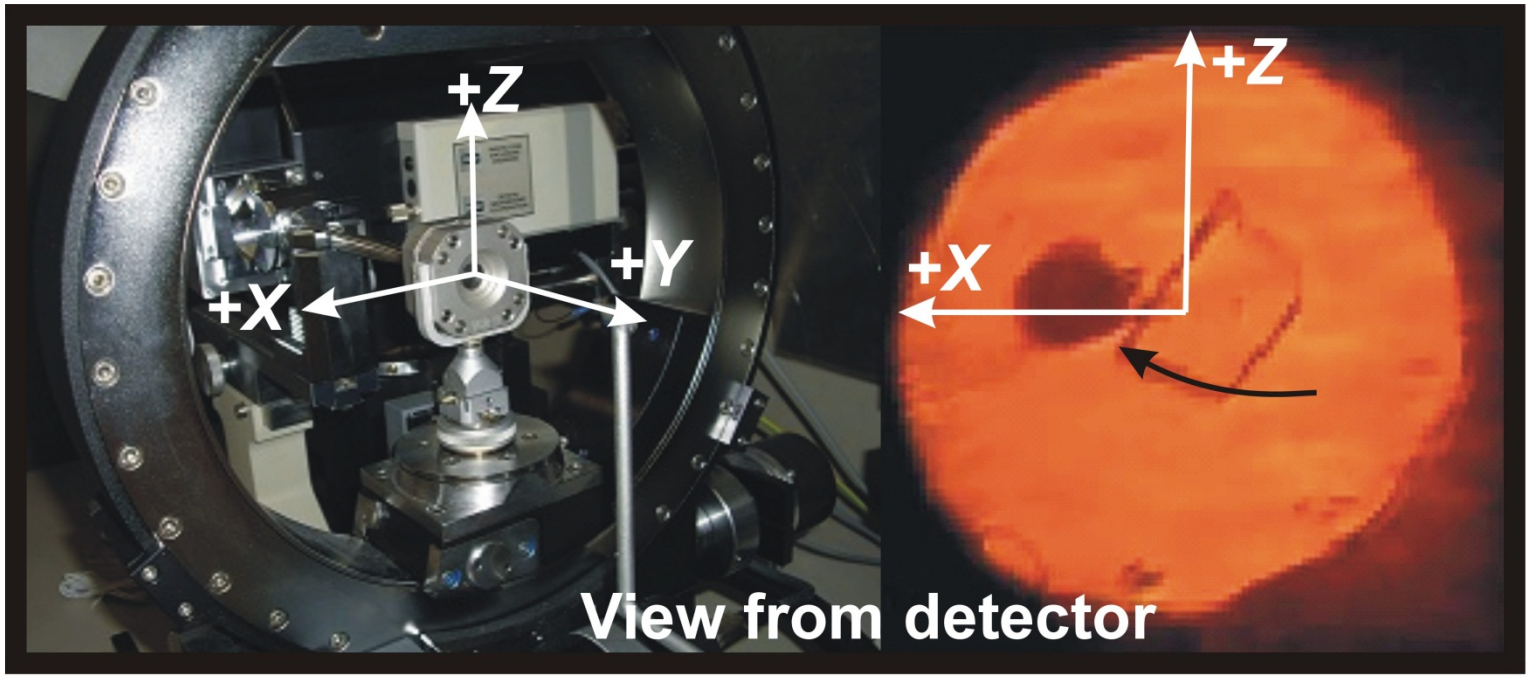


- And you need to know:
  - Conventions used by your absorption program
- For PD data and setting angles in datafile:
  - Type of goniometer (kappa or Eulerian)
  - Circle parities

Describing the crystal

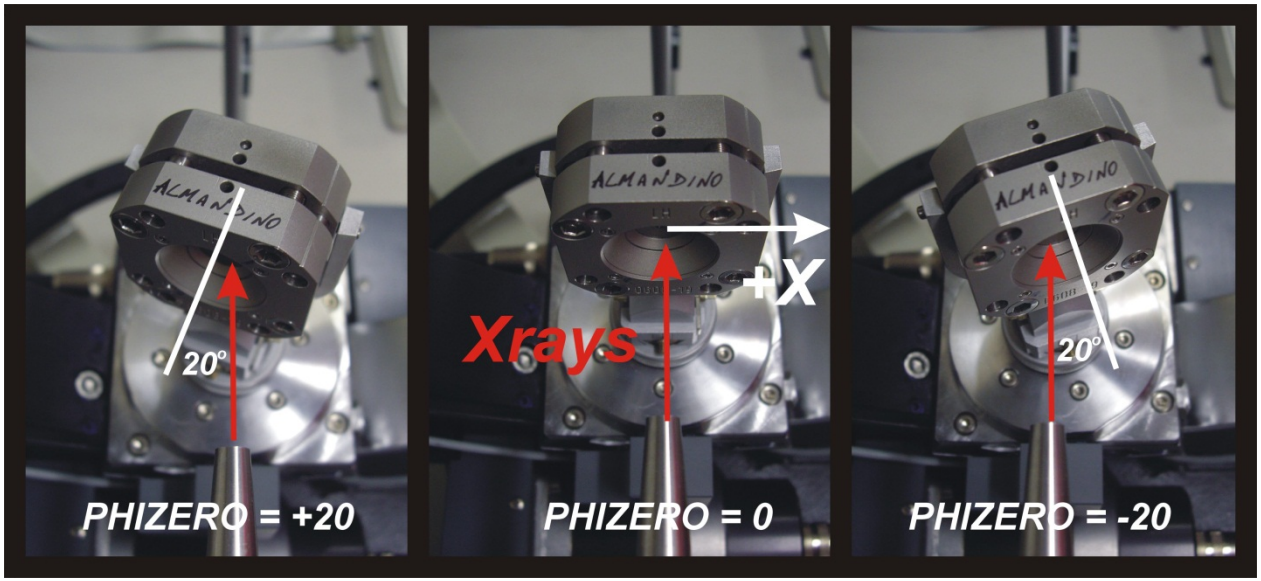
- The crystal position in the DAC can be described by:
  - The Miller indices and distances of faces
  - Coordinates of the corners

- In addition, the position of the crystal relative to the gasket centre must be defined for gasket shadowing:



The DAC on the goniometer

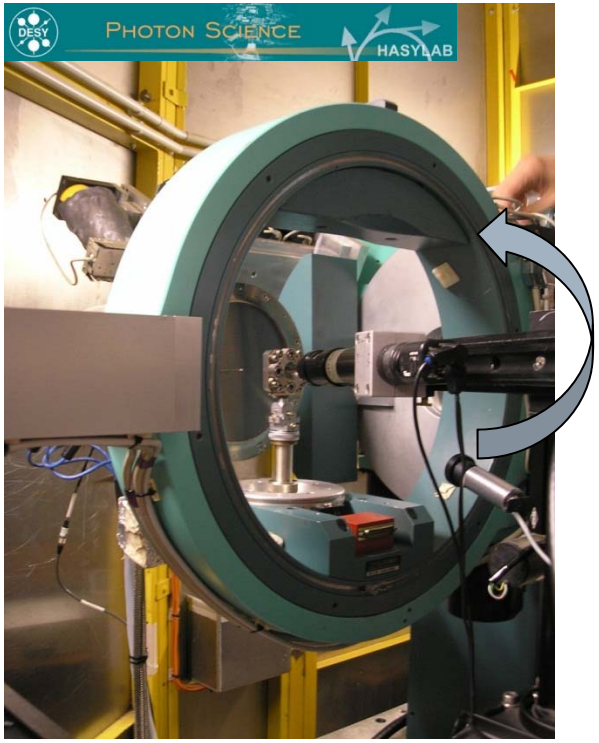
- It is **strongly recommended** that you always collect data with the DAC face-on to the beam when the diffractometer angles are at zero.

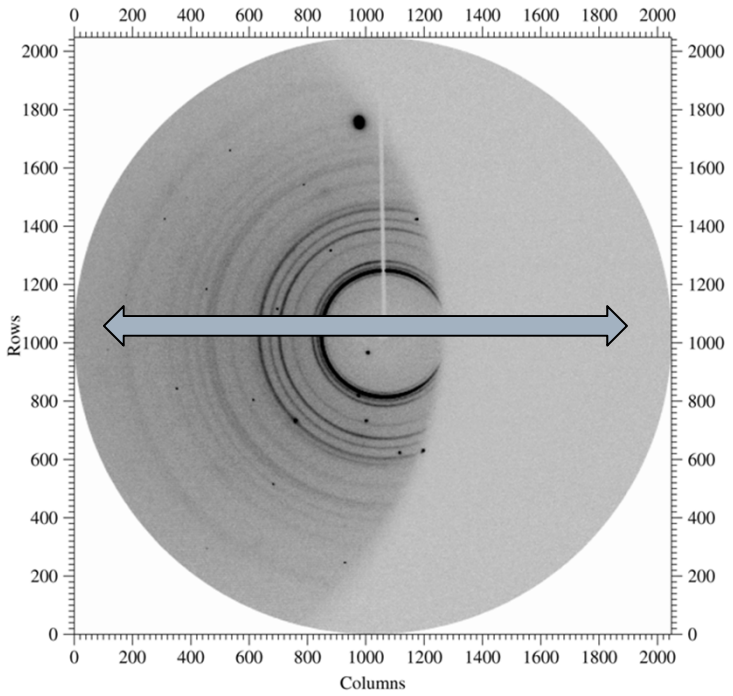


- If not, be very very very careful in defining:
  - The opening angle and DAC to the integration program
  - The size and shape and position of the crystal in the DAC

At synchrotrons….

- **Also worry about the detector orientation!**
  - **Look at the frames…cell shadow and beamstop**



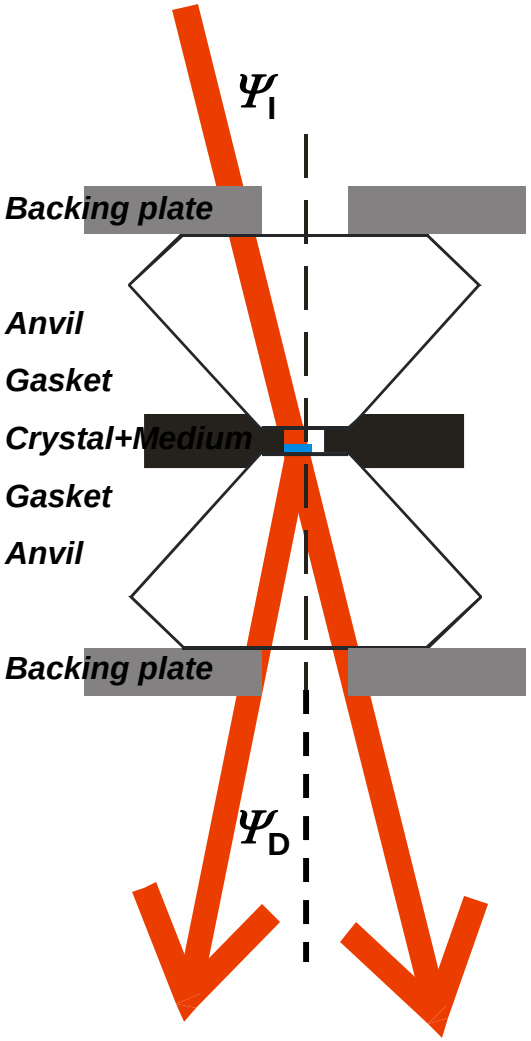


D3 (HASYLAB)

4(3)-circle HUBER & MAR165 (CCD)

Pictures: Andrzej Grzechnik

Absorption corrections

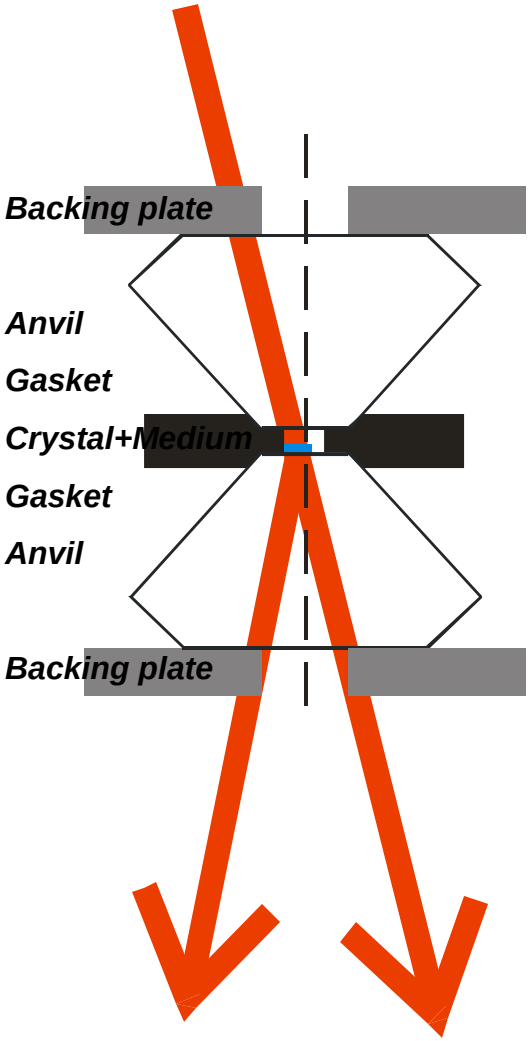


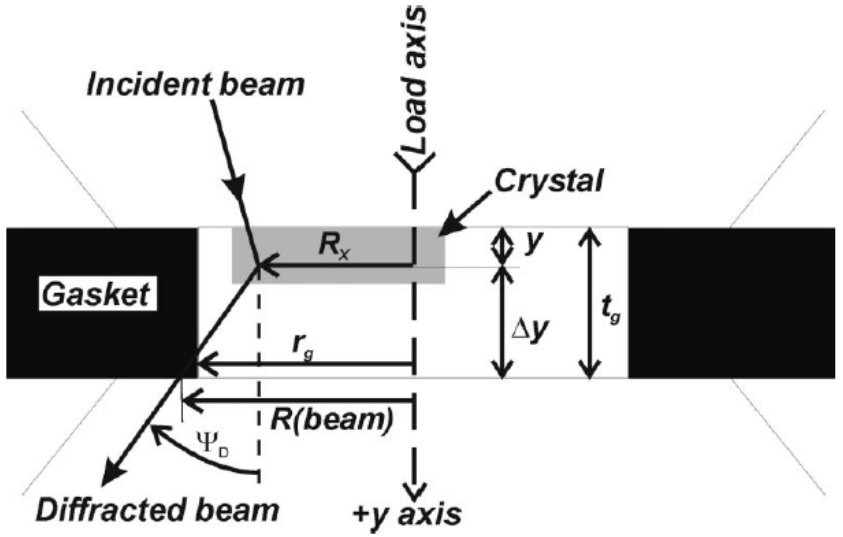
- **Absorption by**
  - Anvils + backing plates
  - Pressure medium
  - Crystal
  - Gasket
- **Psi scans or SADABS**
  - Not recommended
- **Integration over the crystal**
  - Non-analytic
  - Replace by summation over Gaussian grid of points on the crystal:

$$T = V^{-1} \int_V \exp\left[-\sum_i \mu_i (t_{Ii} + t_{Di}) \right] dV.$$

$$T = V^{-1} T(\Psi_I) T(\Psi_D) \int_V \exp\left[-\sum_i \mu_i (t_{Ii} + t_{Di}) \right] dV,$$

Gasket shadowing

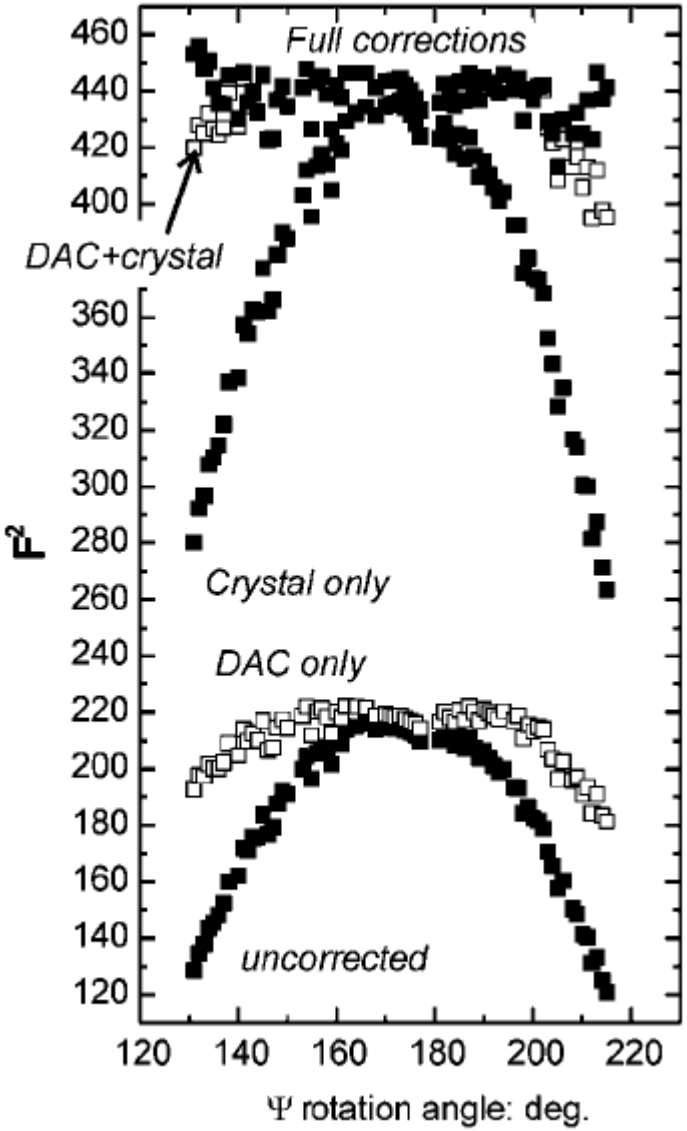




$$T = V^{-1} T(\Psi_I) T(\Psi_D) \int_V \exp[-\mu_x(t_{I,x} + t_{D,x})] \times \exp[-\mu_g(t_{I,g} + t_{D,g})] \exp[-\mu_m(t_{I,m} + t_{D,m})] \, dV.$$

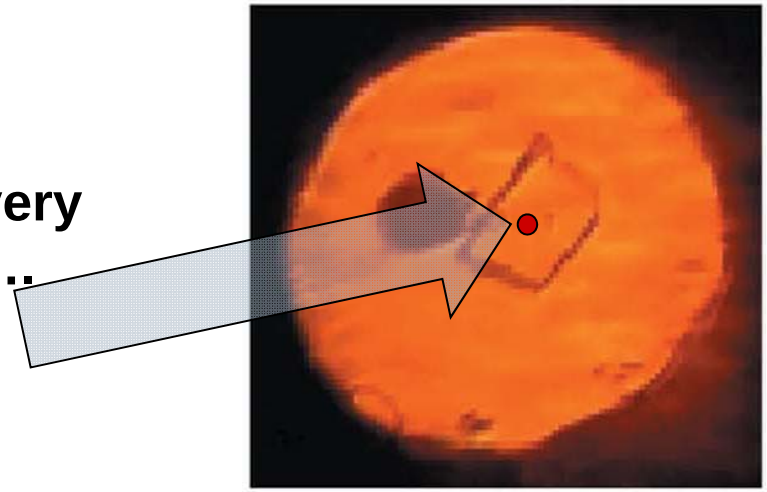
- **Need description of:**
  - *Anvils + backing plates*
  - *Pressure medium*
  - *Crystal*
  - *Gasket*

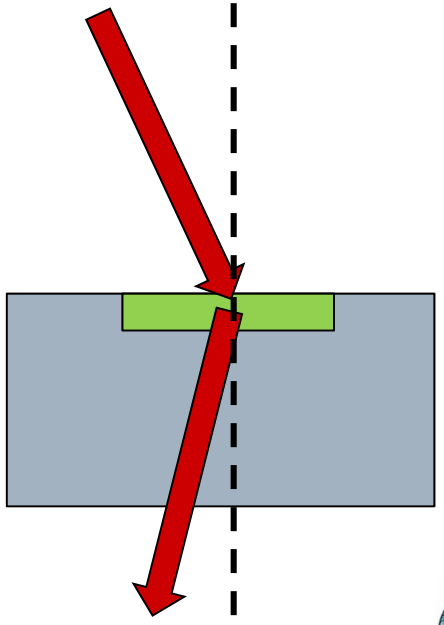
Test models with psi scans



Small beam case

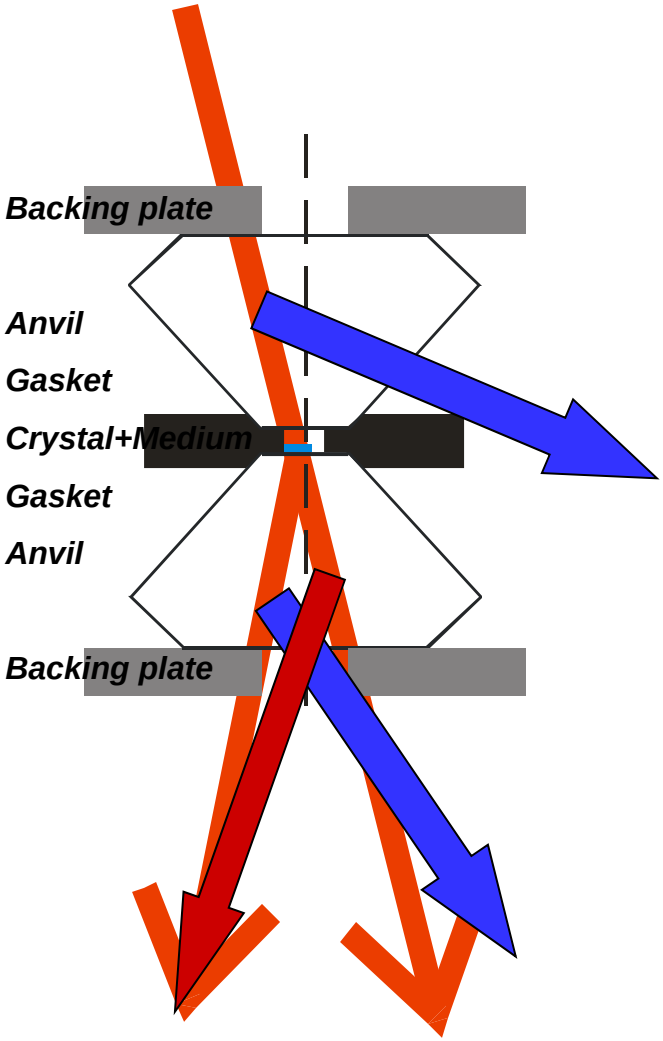
- **If the spot size of the beam is very small compared to the crystal….**
  - **No edge effects**
  - **No gasket shadowing**
  - **Absorption by crystal is just same as infinite flat plate**



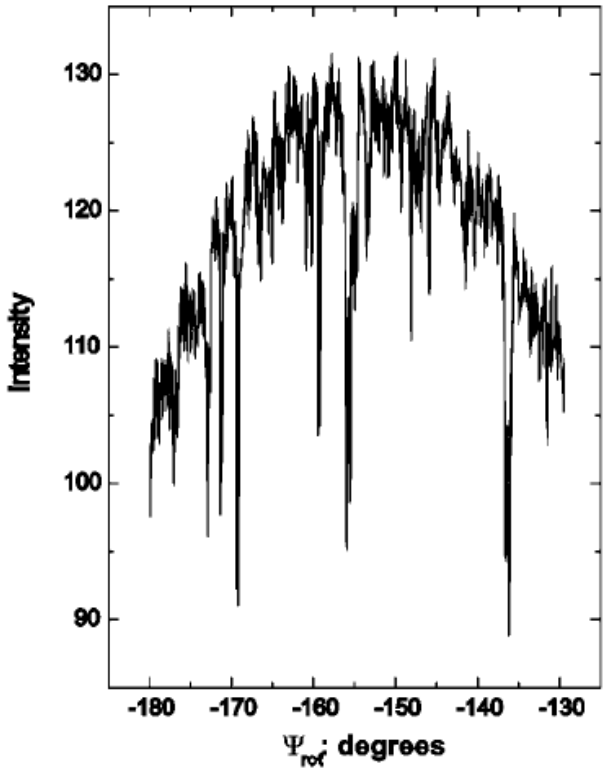


$$T \propto \exp\left[-\frac{\mu t}{2}\left(\frac{1}{\cos\Psi_I}+\frac{1}{\cos\Psi_D}\right)\right]$$

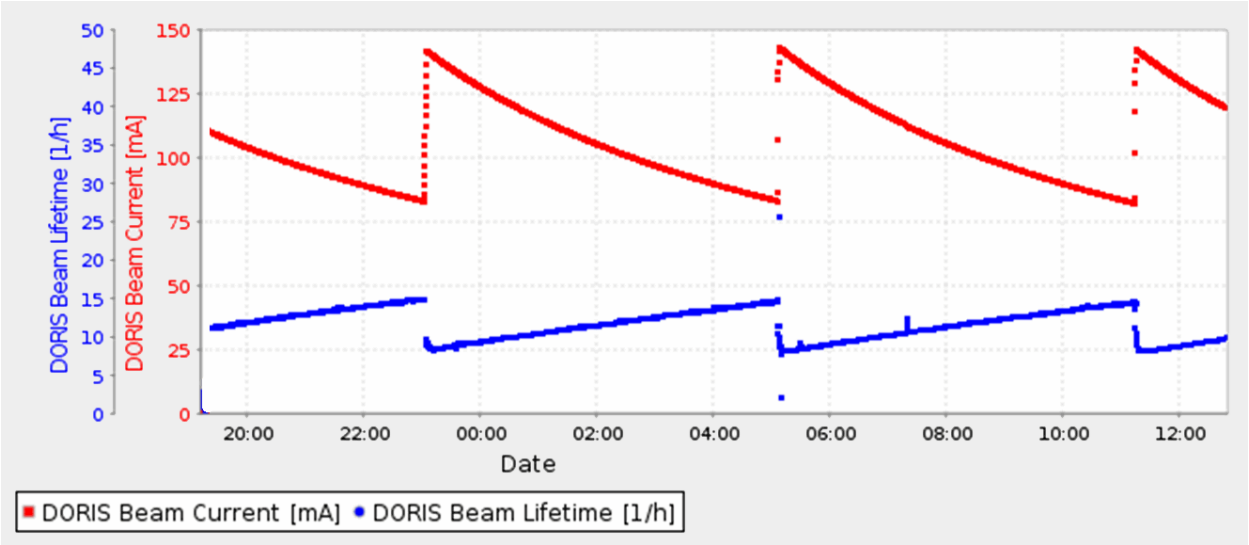
What we cannot correct: Diamond reflections



- *Diamond reflections in to detector*
- *Diamond dips*



Inter-frame scales



- **Synchrotron incident intensity variation:**
  - **Monitor incident beam and correct at integration**

- **Inter-frame scaling on area detectors:**
  - **Arises from several sources**
  - **Often determined from symmetry-equivalent intensities**
  - **Apply after absorption corrections**

Absorption in DAC – key points

- **For corrections on a physical basis, the DAC, crystal and data must be described on a common reference system**
  - **Orientation matrix**
  - **Axial systems**
- **Keep things simple:**
  - **DAC face-on to beam at circles zero**
  - **Use hkl files with d-cosines**
- **Do inter-frame detector scaling afterwards**
- **Diamond dips and other outliers:**
  - **Identify in averaging or in refinemnnt (Fo vs Fc)**