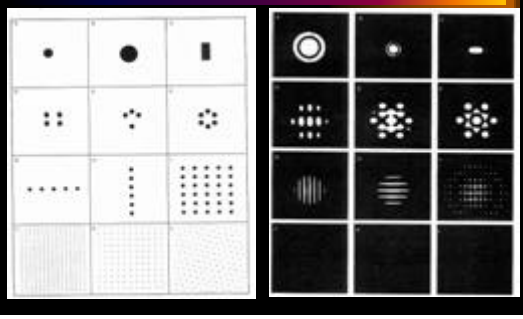
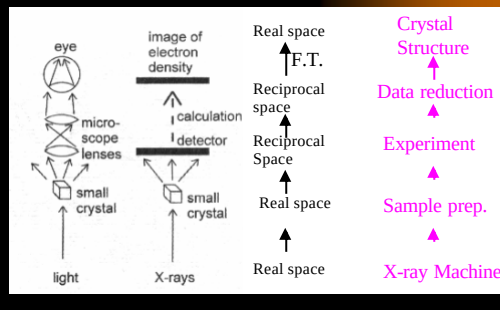
Optical diffraction images



The X-ray microscope: Reciprocal Space



Single-crystal diffraction machines

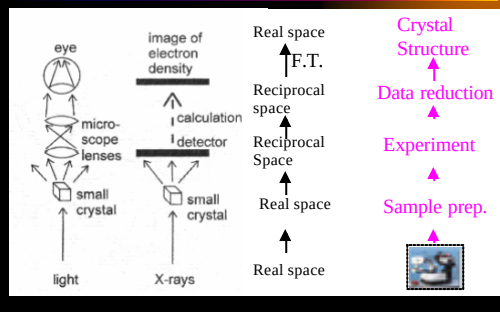
X = X-ray source

M = microscope

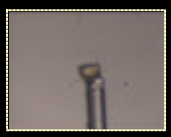
C = crystal

D = detector

The X-ray microscope: Reciprocal Space

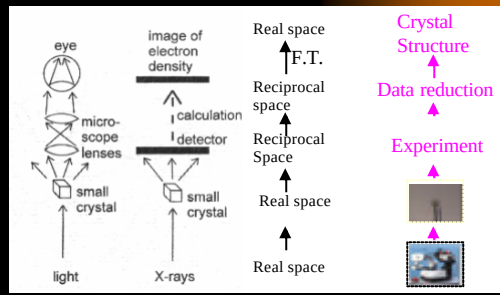


Crystal sample

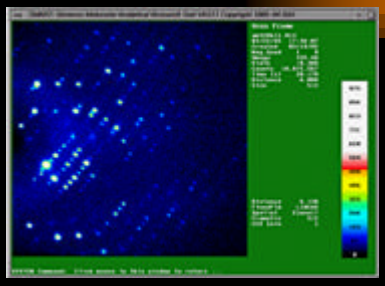


crystal on glass fibre

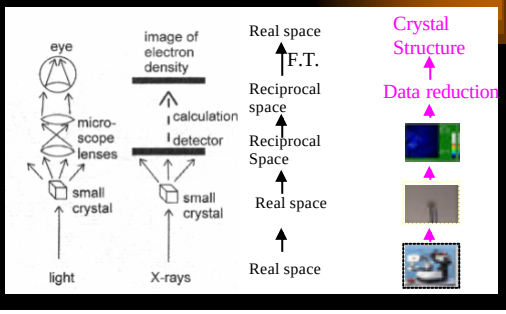
The X-ray microscope: Reciprocal Space



Single-crystal diffraction patterns



The X-ray microscope: Reciprocal Space



Extracting Structure Factors, F, of each hkl reflection

$$I \propto |F|^2$$

and

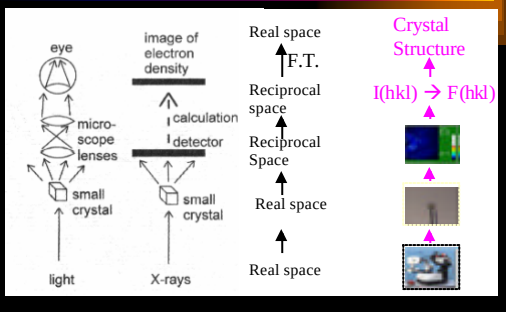
$$I = cL(\theta)p(\theta)A(\theta)E(\lambda)d(t)m|F_{hkl}|^2$$

Data correction terms

Intensity of the diffraction spot measured for each hkl reflection

F is the amplitude of the diffracted X-ray beam: the 'structure factor' (what we need for the Fourier transform)

The X-ray microscope: Reciprocal Space



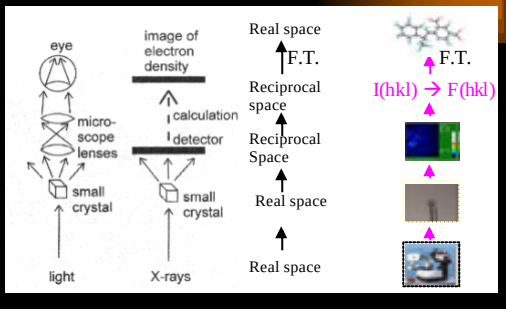
$F_{hkl} \rightarrow \rho(r)$

$$F = \sum_{j=1}^{N} f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

↓ F.T.

$$r(r) = \frac{1}{V} \sum_{h,k,l=-\infty}^{+\infty} F_{hkl} \exp[-2\pi i(hx_j + ky_j + lz_j)]$$

The X-ray microscope: Reciprocal Space

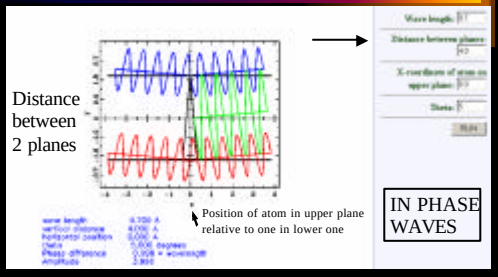


Diffraction: the theory behind the experiments

- Geometry of X-ray diffraction
- Indexing
- UB matrix
- Data collection strategy/procedure
- Integration
- Data reduction

Bragg's Law: $\lambda = 2d\sin\theta$

Bragg's Law (interactive)



http://www.uni-wuerzburg.de/mineralogie/crystal/teaching/iinter_bragg.htm

Bragg's Law: $\lambda = 2d\sin\theta$

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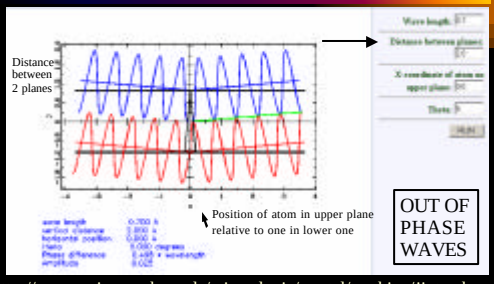

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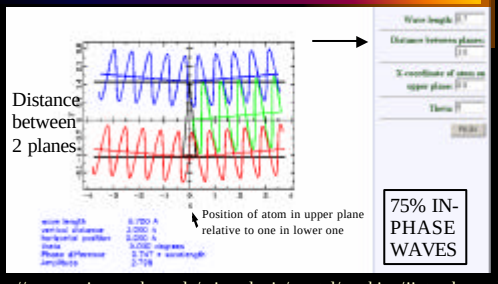

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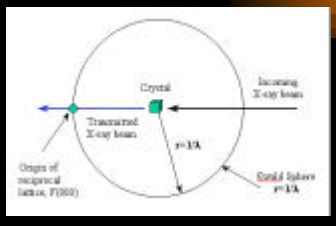
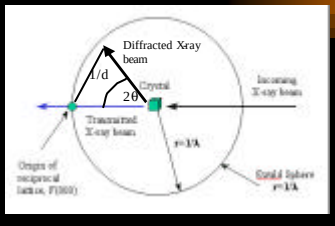
The Ewald sphere



Ewald sphere simulations:
(http://www.uni-wuerzburg.de/mineralogie/crystal/teaching/ibasic_d.html)

The Ewald sphere



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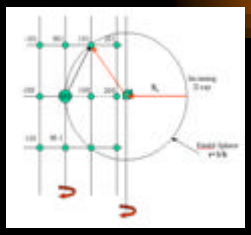


The diffraction condition is met when a reflection touches the surface of the Ewald sphere

Ewald sphere simulations:
(http://www.uni-wuerzburg.de/mineralogie/crystal/teaching/ibasic_d.html)

Indexing

Each observed diffracted beam can be labelled by three integers, or indices, hkl, that uniquely specify it BUT ONLY IF the unit cell geometry is known.

To determine the unit cell, we can use one of two methods:
(a) a real-space method called 'auto-indexing'
(b) The reciprocal space method.

Then we need to identify the orientation of the unit cell with respect to the orientation of the crystal on the diffractometer. The relationship of the diffractometer axes with the unit cell parameters is defined via the orientation matrix.

Determining the unit cell

Collect data from several small parts of reciprocal space

Generate a list of vectors between the reflections collected

Find the three shortest non-coplanar vectors in this list

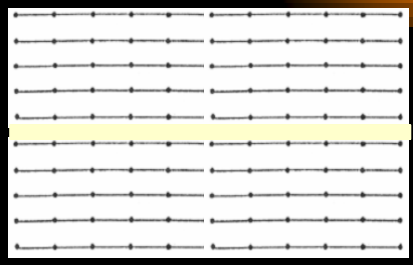
The three non-co-planar vectors are a (primitive) sub-set of the unit cell, if they are not indeed the correct unit cell.

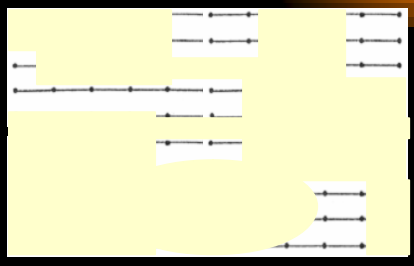
Generate the list of hkls (or vectors) from this cell for the list reflections.

Check that all hkl reflections are integral

Multiply each lattice vector by the three shortest non-co-planar vectors. The unit cell is the product that is integral for every reflection

Determine the metric symmetry.





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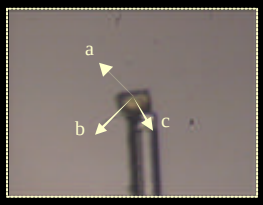
Determining the orientation matrix



Orientation matrix is a 3 x 3 matrix containing information about the unit cell and the crystal orientation.

Data collection strategy

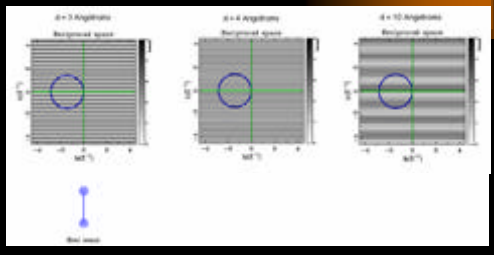
Collect data as a function of increasing value of d (data resolution)

Rotate sample to access different lattice planes (use orientation matrix to obtain best data collection strategy)

Collect data using oscillatory scans.

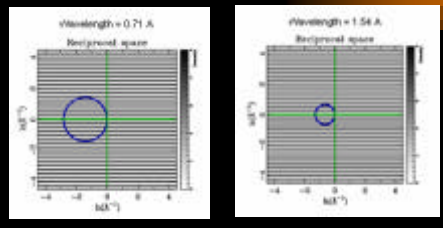
Use any knowledge of symmetry to avoid having to collect the whole sphere of reciprocal space [number of reflections collected typically range from 200 (cubic) to 7000 (triclinic) for 20-30 atoms in the asymmetric unit].

Varying d (data resolution)



(http://www.uni-wuerzburg.de/mineralogie/crystal/teaching/ibasic_d.html)

Choice of X-ray source (an alternative way of changing resolution)



(http://www.uni-wuerzburg.de/mineralogie/crystal/teaching/ibasic_d.html)

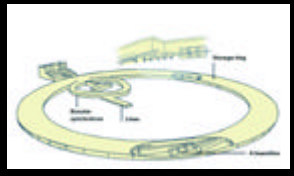
Wider choice of wavelength

Possible X-ray wavelengths depend on available X-ray sources:

Lab X-ray sources:

Targets: Mo (0.71A);
Cu (1.54A); Ag (0.45)

Synchrotron X-rays (any λ):



For interactive tour, see: http://www. esrf.fr/AboutUs/GuidedTour/Anim

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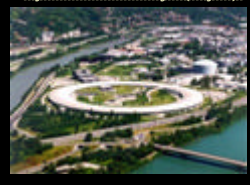

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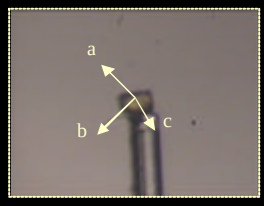

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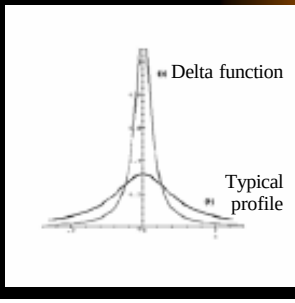
The importance of oscillatory scans



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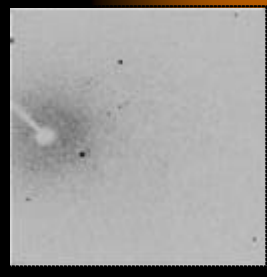
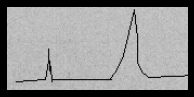
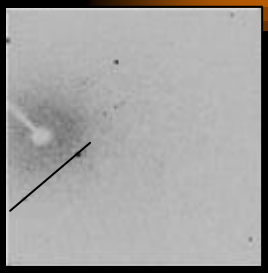
1-D, 2-D and 3-D data



1-D, 2-D and 3-D data



1-D peak image extraction



1-D, 2-D and 3-D data

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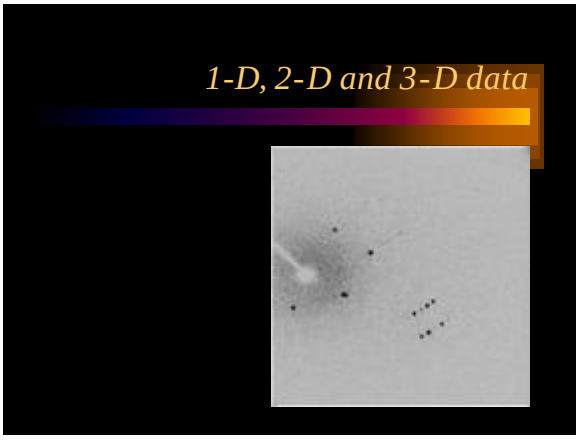
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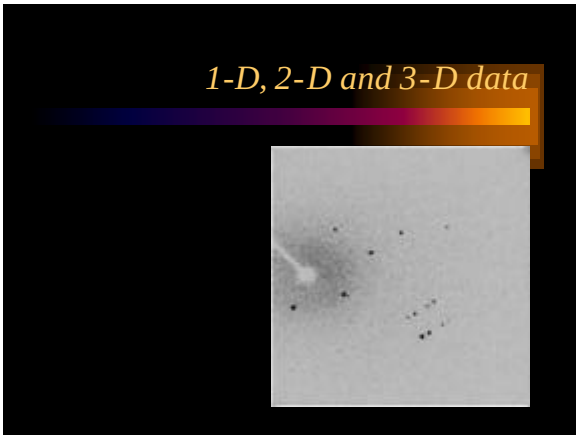
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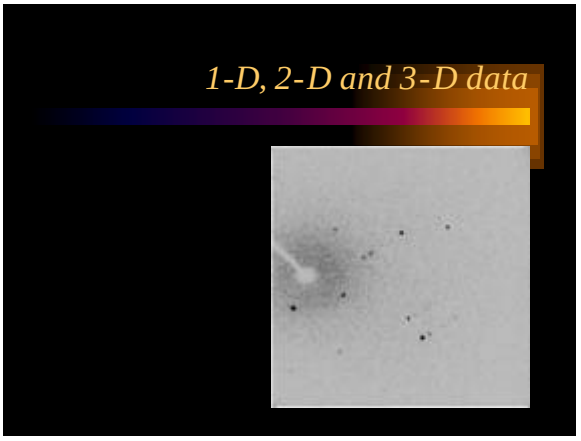
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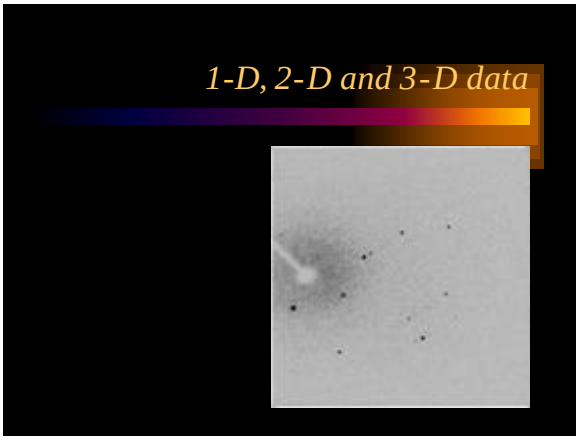
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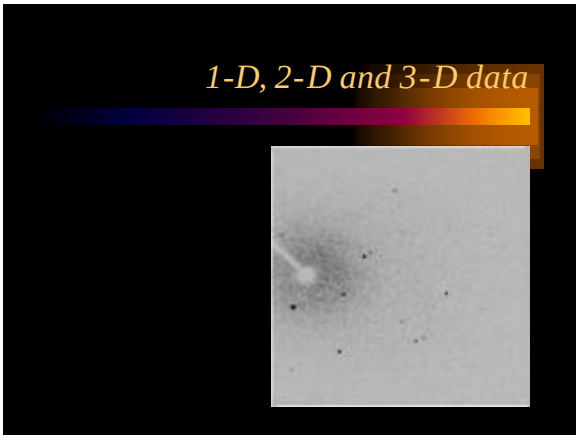
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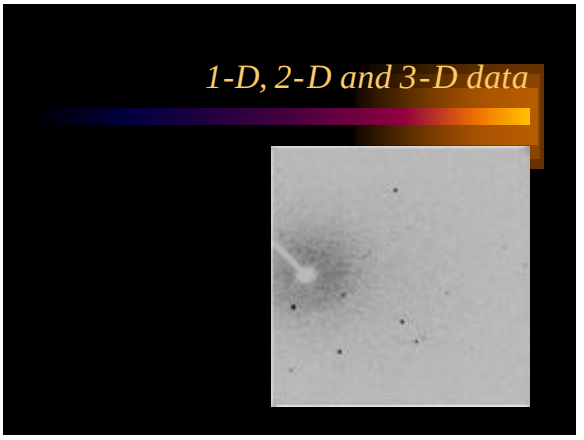
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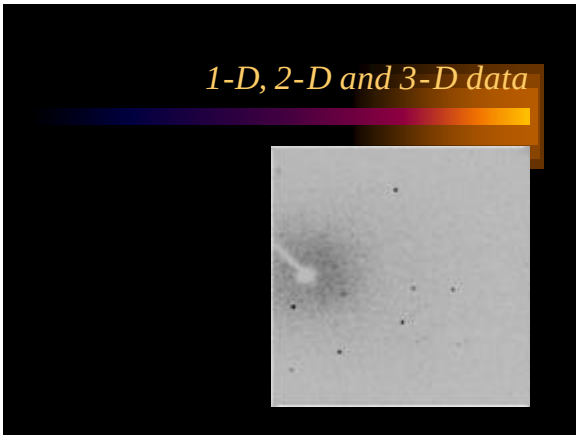
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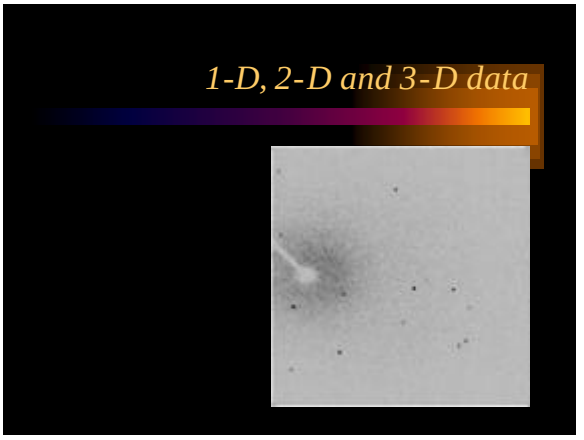
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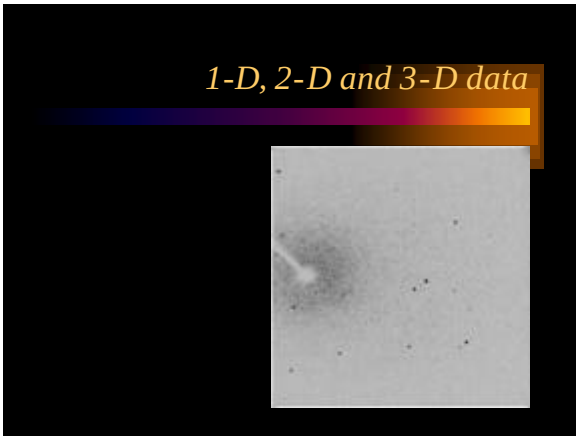
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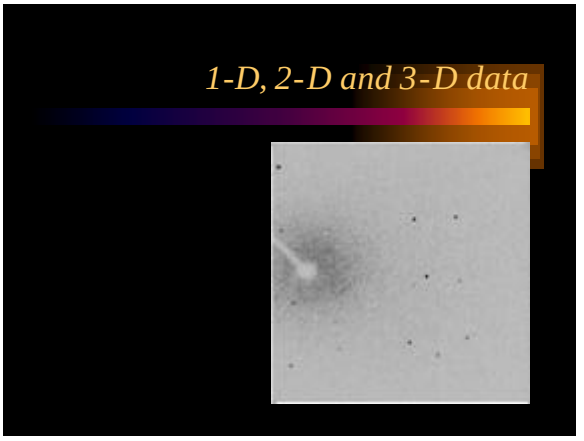
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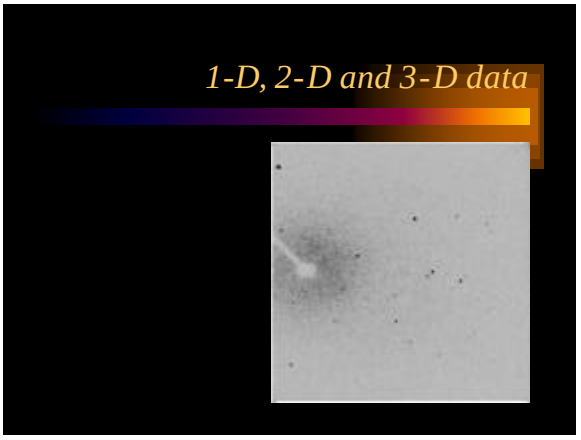
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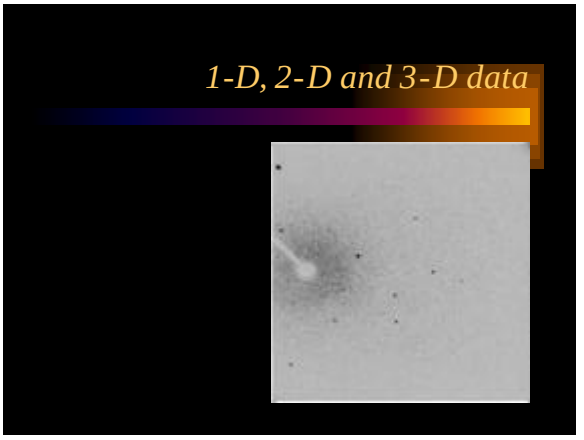
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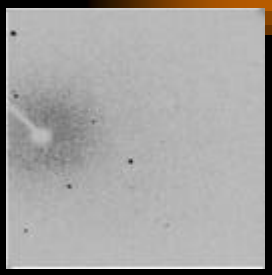

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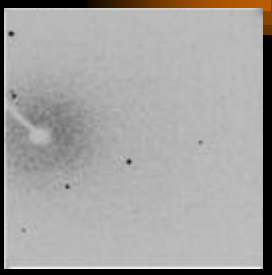

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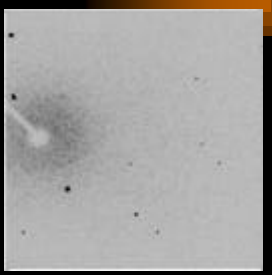
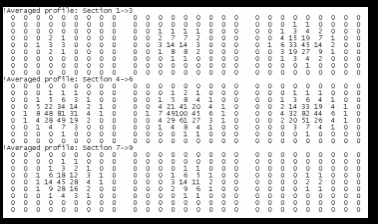


Wide verses narrow scans

Bruker (default: narrow)	Enraf Nonius CCD (default: wide)
0.3deg default scan step	1-2deg calculated scan step
Narrower scans mean more info. obtained	Wider scans generally mean quicker data collections
Generally obtain more accurate data: more profile information	Optimised where fast data collections are required.

Integration of data

Put a 'box' round all reflections and sum (integrate) the values of all the pixels inside (use a good orientation matrix to locate reflections wholly inside each box). This yields a 3-D Intensity of each reflection.



Profile analysis: modelling of weak reflections

Hard to obtain accurate integrated volumes of weak spots, as their signal may be only just greater than the instrument background.

=> Use the profiles of the strong reflections

First-pass of integration (processes strong reflections)

↓

Library of strong reflection profiles created (in bins of similar resolutions)

↓

Second-pass of integration (use of libraries to model weak reflections)

Extracting Structure Factors, F, of each hkl reflection

$I \propto |F|^2$ $\qquad$ $I = cL(\theta)p(\theta)A(\theta)E(\lambda)d(t)m|F_{hkl}|^2$

where I is the intensity of the diffraction spot measured for each hkl and F is the amplitude of the diffracted X-ray beam: the 'structure factor' (what we need to carry out the Fourier transform)

$I = cL(\theta)p(\theta)A(\theta)E(\lambda)d(t)m|F_{hkl}|^2$

Data reduction

- Scale Factor: c
- Lorentz correction: L(θ)
- Polarisation correction: p(θ)
- Absorption correction: A(θ)
- Extinction correction: E(λ)
- Decay correction: d(t)
- Multiplicity: m (for powder diffraction only)

- Additional possible corrections required, e.g.:
- Multiple scattering
- Thermal diffuse scattering

$I = cL(\theta)p(\theta)A(\theta)E(\lambda)d(t)m|F_{hkl}|^2$

Data reduction

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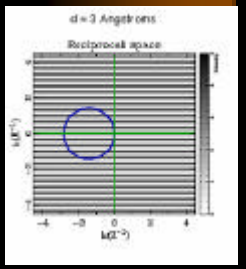
Lorentz correction

A geometric correction to account for the fact that some hkl reflections pass through the surface of the Ewald sphere for longer than others.

i.e. some are measured for longer than other reflections.



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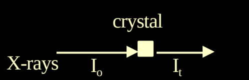
Absorption of X-rays



Io = It → transmittance
Io≠It → absorbance (and/or reflection)

It = Io exp(-μt)

Where t is the path length Through the crystal

And μ is the absorption coefficient which is dependent on the sample (heavy elements absorb more) and the incident X-ray wavelength (longer λ, more absorption).

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Moving from reciprocal to direct (real) space

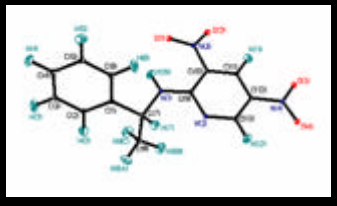
In turn, F is related to the electron density of a compound via a Fourier transform:

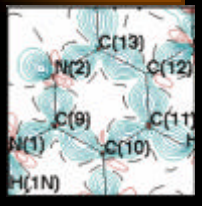
$$F = \sum_{j=1}^{N} f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

F.T. $\downarrow$ $r(r) = \int F(r^*)\exp[-2\pi i r^* \cdot r]dr^*$

$$r(r) = \frac{1}{V}\sum_{h,k,l=-\infty}^{+\infty} F_{hkl} \exp[-2\pi i(hx_j + ky_j + lz_j)]$$

A crystal structure and electron density map using X-ray diffraction





End of lecture