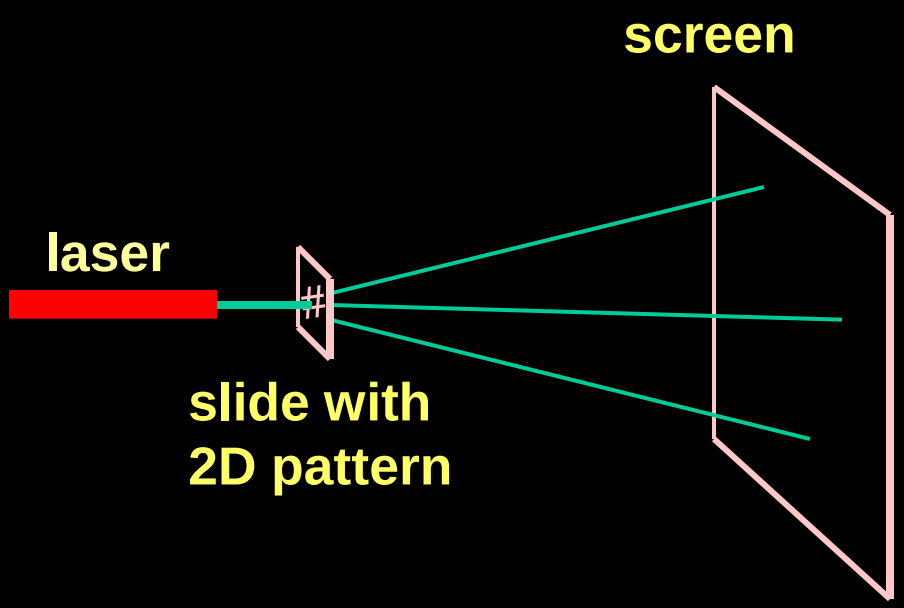
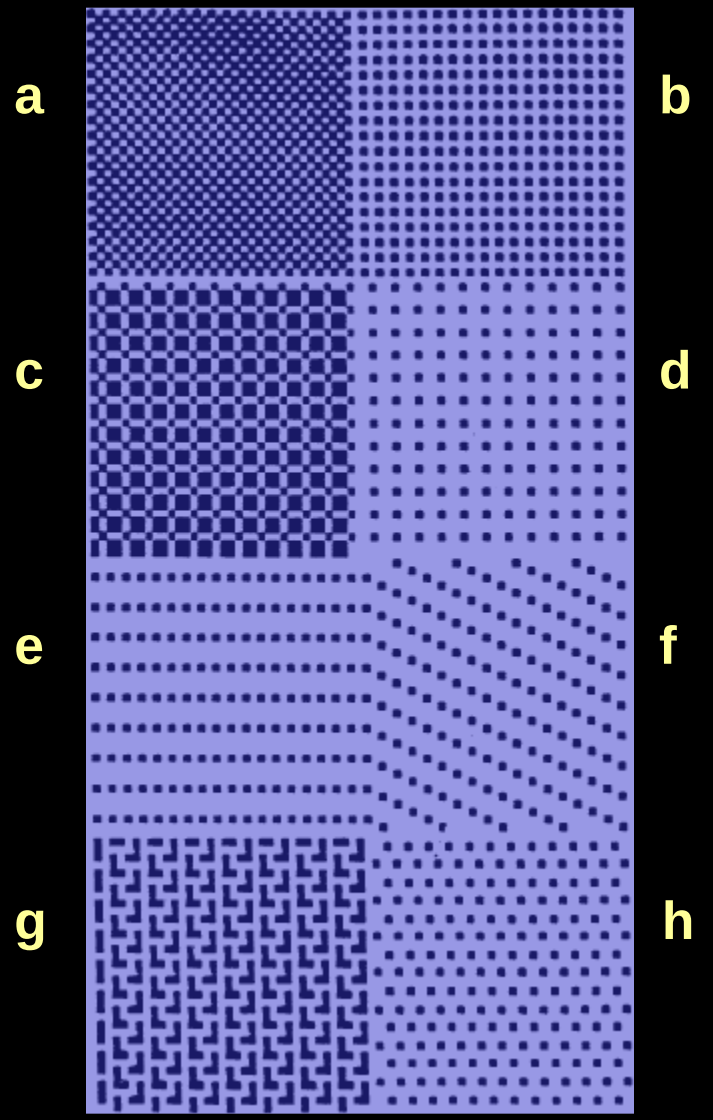
A diffraction experiment





The sides of the unit-cell on the slide are about 10^5 times longer than those in the crystal; the wavelength of the laser is about 10^4 times larger than that of the X-ray beam, so the diffraction angles in this demonstration are about 10 times smaller.

Methods in Chemistry III – Part 1
Modul M.Che.1101 WS 2010/11 – 5

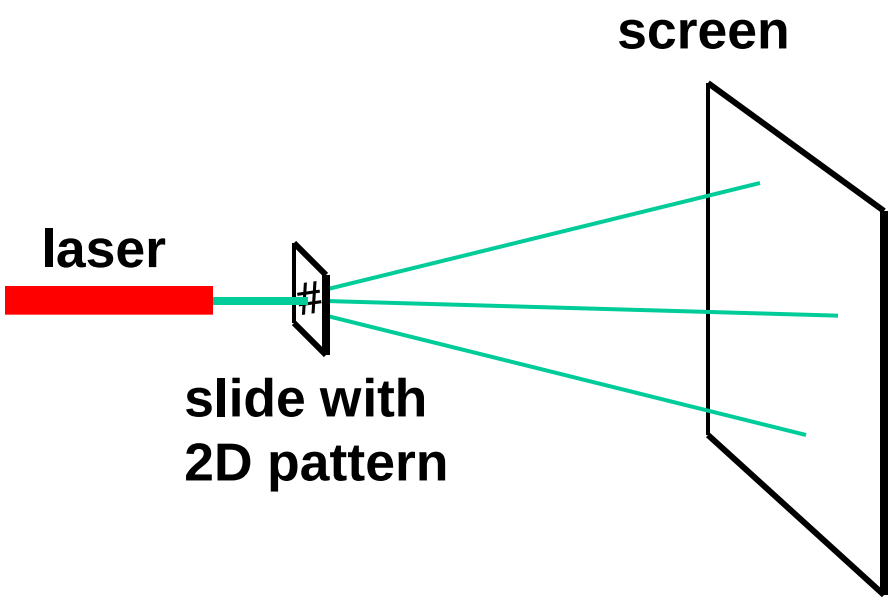
Modern Methods of Inorganic Chemistry

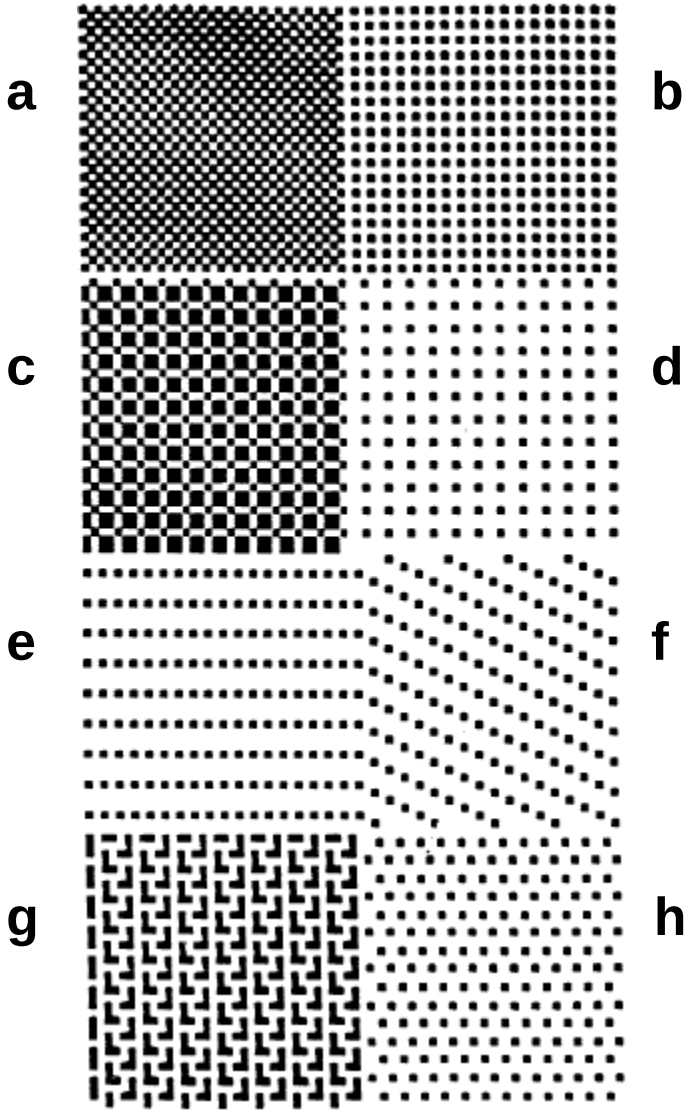
Mi 10:15-12:00, Hörsaal II

George Sheldrick

gsheldr@shelx.uni-ac.gwdg.de

A diffraction experiment





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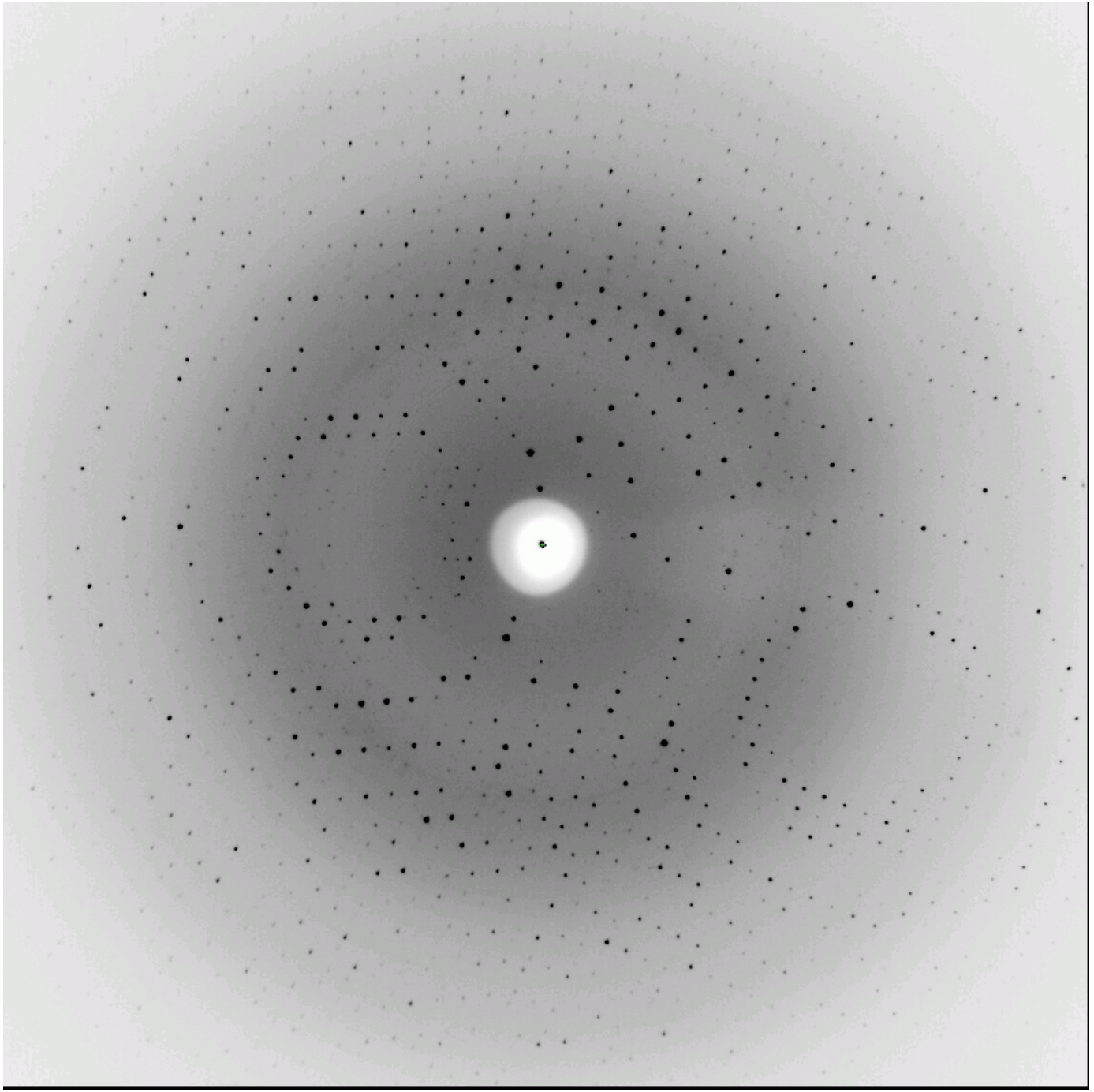
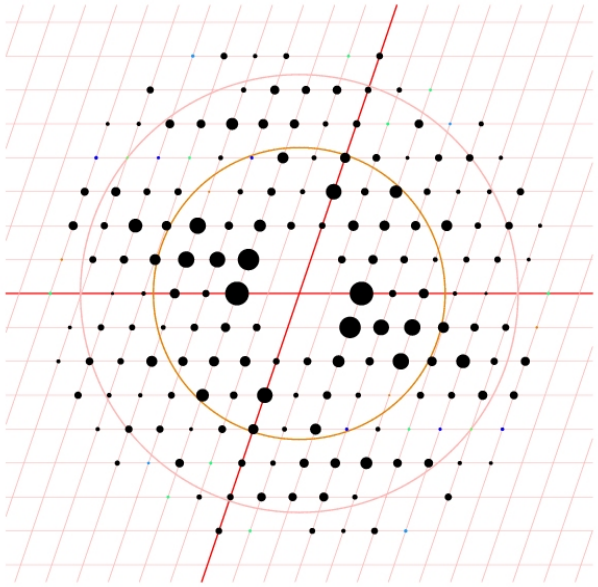
X-ray data collection

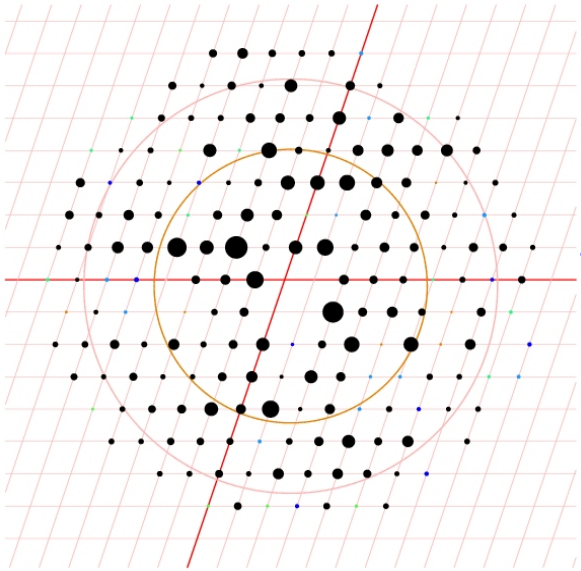
Diffraction data are usually collected in ‘frames’ using an integrating CCD detector. The detector records the X-ray photons that hit it within a finite crystal rotation range (here one degree) on the same frame.
(Viscotoxin A1; animation by Bernhard Rupp).



X-ray diffraction patterns (simulated)

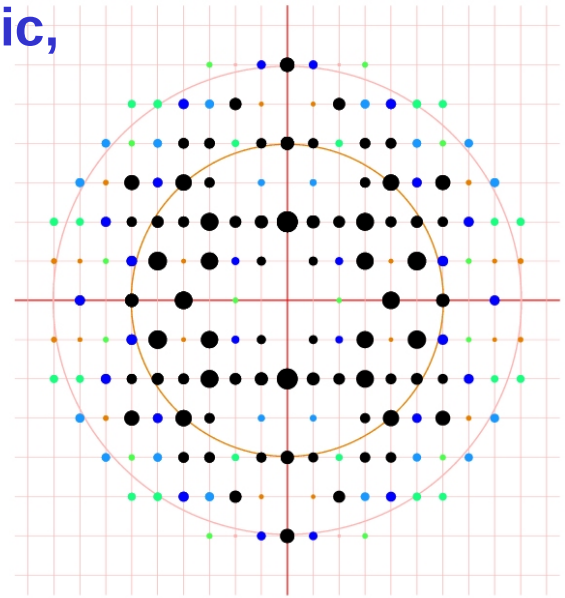
triclinic,
*hk*0 layer

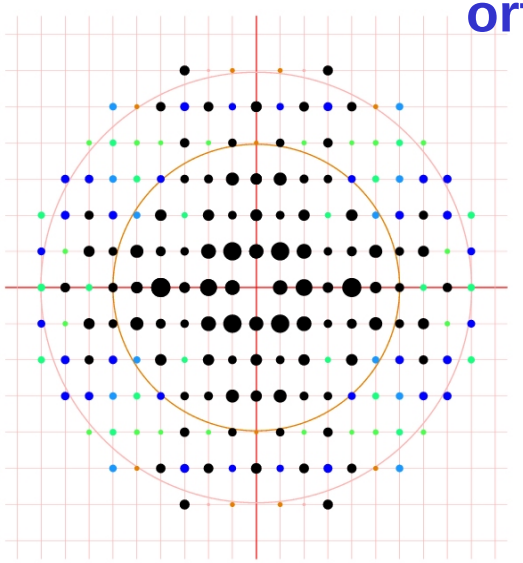




triklinic,
*hk*1 layer

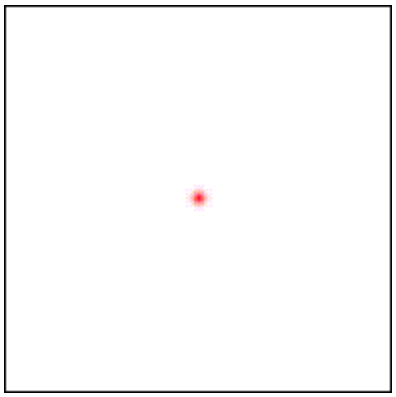
orthorhombic,
*hk*0 layer





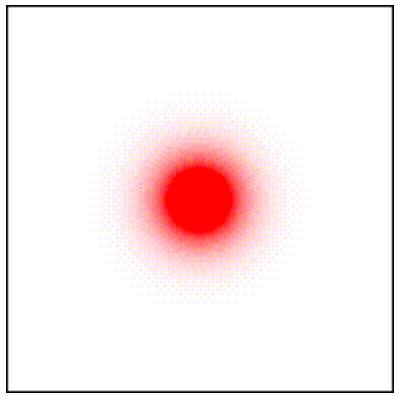
orthorhombic,
*hk*1 layer

Diffraction of atoms and molecules



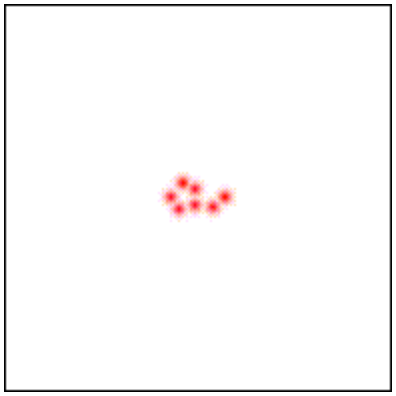
FT

FT



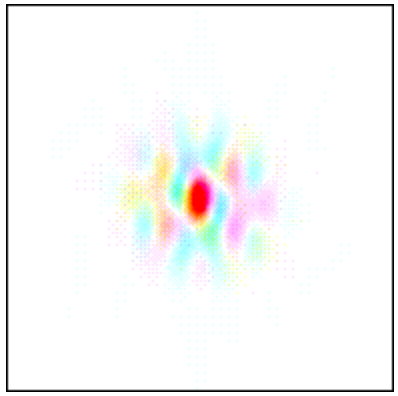
FT of one atom

1 atom



FT

FT



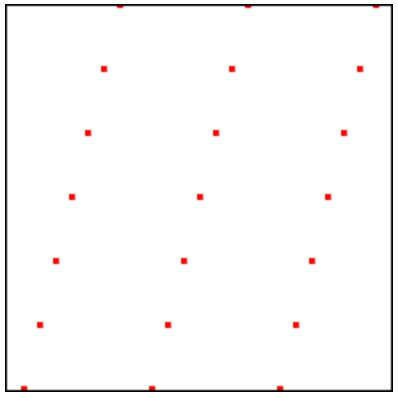
FT of one molecule

1 molecule

Kevin Cowtan http://www.ysbl.ac.uk/~cowtan/

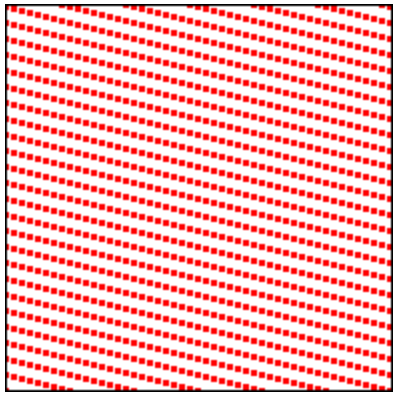
Diffraction of lattices and crystals

lattice



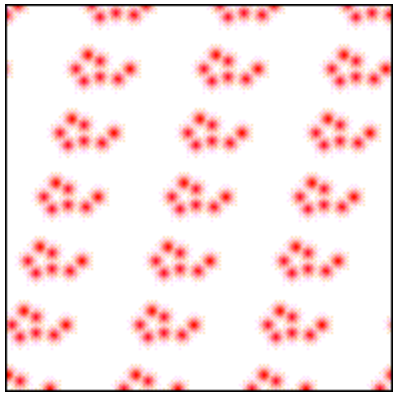
FT

FT



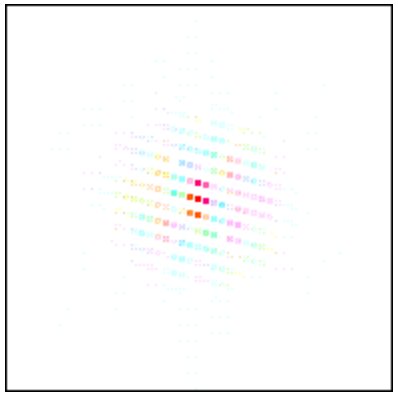
FT of a lattice

crystal



FT

FT

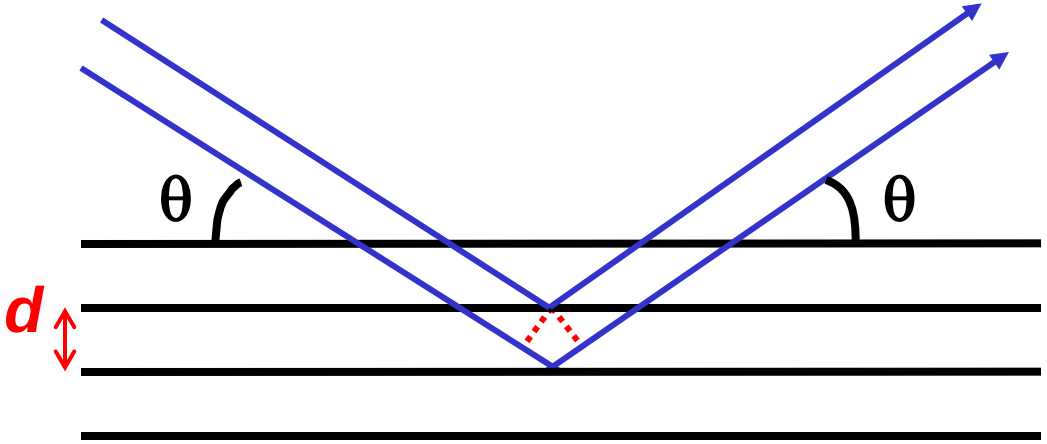


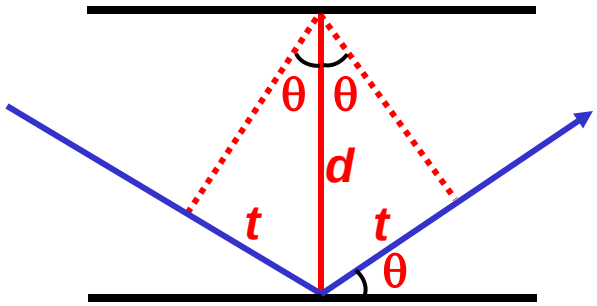
FT of a crystal

Kevin Cowtan http://www.ysbl.ac.uk/~cowtan/

The Bragg equation

$$n\lambda = 2d \cdot \sin(\theta)$$





An X-ray reflection is created by diffraction (reflection) from parallel lattice planes. Only those diffraction angles θ are possible for which the difference in path length $2t = 2d \cdot \sin\theta$ is equal to an integer multiple of the wavelength λ:

$$n\lambda = 2d \cdot \sin\theta \quad (n = 1, 2, 3 \ldots)$$

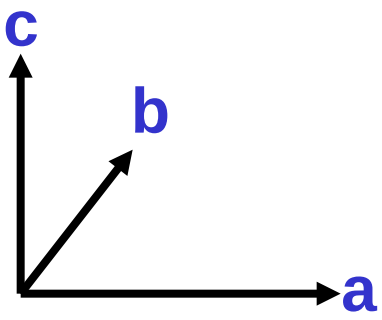
Usually this equation is applied with $n = 1$.

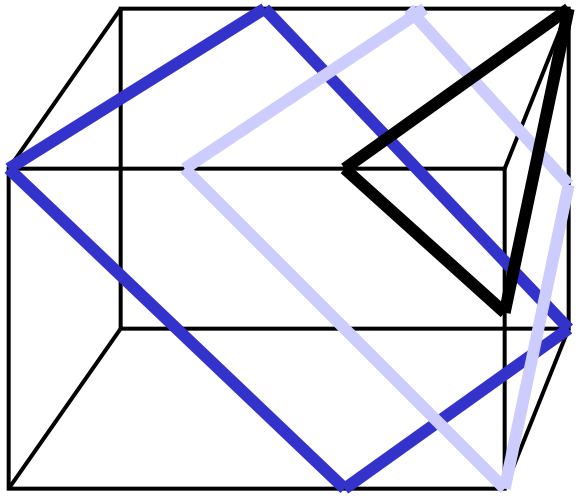
The Bragg indices *h*, *k* and *l*

The X-ray reflection ***h*,*k*,*l*** is caused by reflection from the planes ***h*,*k*,*l*** that cut the three sides of the unit-cell in the rational fractions 1/***h***, 1/***k*** and 1/***l***.

Sets of planes in ***real space*** (distance ***d*** from one another) correspond to points (reflections) in ***reciprocal space*** (distance ***d**** from the origin). The direction of the vector ***d**** is determined by the diffraction geometry of the reflection; ***d**** is at right angles to the planes ***h*,*k*,*l*** and its length can be calculated from $|d^*| = 2\sin\theta/\lambda$.

The reflections constitute a lattice in reciprocal space with integer reflection indices ***h***, ***k*** and ***l*** based on the reciprocal cell **a*, b*, c*.**





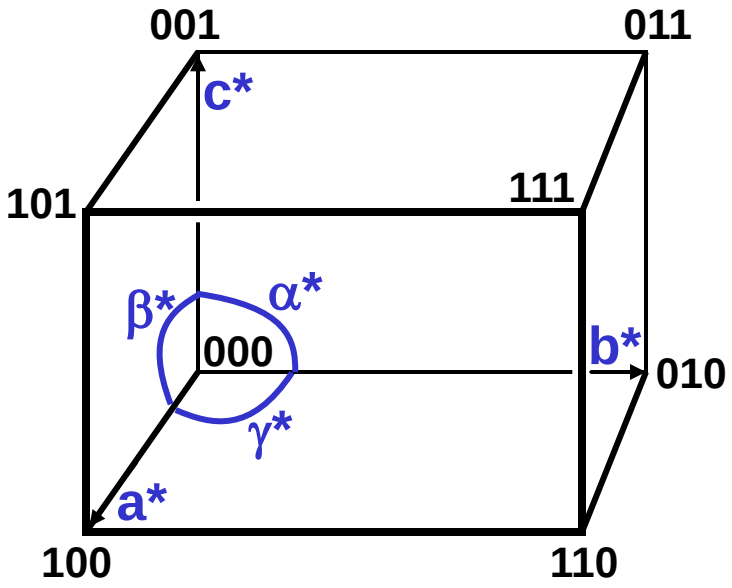
planes 3 –1 2
(or –3 1 –2)

Reciprocal space

An X-ray diffraction experiment measures the intensities of the reflections *h*,*k*,*l*. These reflections can be displayed as a three-dimensional lattice with reflection indices *h*,*k*,*l*. This lattice is based on a reciprocal unit-cell with axis lengths *a, *b** and *c** and angles α^*, β^* and γ^*. The dimensions of the reciprocal cell are inversely proportional to those of the real cell.**

This concept is called *reciprocal space*.

The reciprocal cell



The X-ray reflections constitute a lattice in reciprocal space based on the reciprocal cell.

In the case of orthorhombic cells:

$a = 1/a^*$, $b = 1/b^*$ und $c = 1/c^*$

For triclinic cells the transformation is a little more complicated:

$$1/V = V^* = a^*b^*c^* \left[1 - \cos^2\alpha^* - \cos^2\beta^* - \cos^2\gamma^* + 2\cos\alpha^*\cos\beta^*\cos\gamma^* \right]^{1/2}$$

$$a = b^*c^*\sin\alpha^* / V^* \quad \text{and} \quad \cos\alpha = (\cos\beta^*\cos\gamma^* - \cos\alpha^*) / (\sin\beta^*\sin\gamma^*)$$

The calculation of b, c, $\cos\beta$, $\cos\gamma$ is analogous, as is the calculation of a^*, $\cos\alpha^*$ etc. from the real cell parameters.

The Laue group

The shape of a crystal does not always reveal its symmetry because the faces can grow at different rates. The angles between the crystal faces – but not the lengths of the edges – must have the same metric symmetry as the crystal lattice.

The *Laue symmetry* of the diffraction pattern, which takes the intensities of the reflections into account, reveals more. For example a fourfold symmetry axis in the diffraction pattern must correspond to a 4, $\bar{4}$, 4_1, 4_2 or 4_3 axis in the space group. The diffraction pattern always possesses an inversion center (Friedel's law):

$$I_{-h-k-l} = I_{hkl}$$

Crystals may belong to 230 possible *space groups*, 32 possible *point groups* but only 11 possible *Laue groups*. For example the three orthorhombic point groups *222* (9 space groups), *mm2* (22 space groups) and *mmm* (28 space groups) correspond to the same Laue group *mmm*.

Symmetry in reciprocal space

The Laue symmetry in reciprocal space may also be described using the reflection indices. In the *triclinic* system the only symmetry is given by Friedel's law:

$$I_{hkl} = I_{-h-k-l}$$

For *monoclinic* crystals the twofold axis along b creates the additional relation:

$$I_{hkl} = I_{-hk-l}$$

so combining the two:

$$I_{hkl} = I_{-hk-l} = I_{-h-k-l} = I_{h-kl}$$

In the *orthorhombic* system there are three mutually orthogonal twofold axes plus an inversion center:

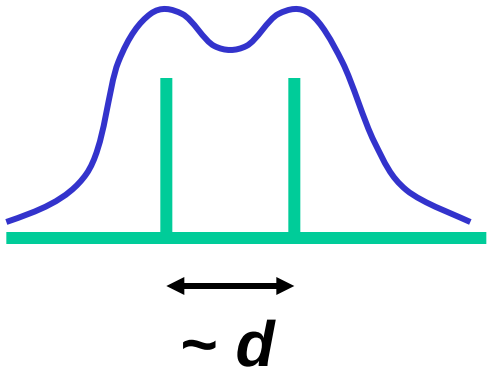
$$I_{hkl} = I_{h-k-l} = I_{-hk-l} = I_{-h-kl} = I_{-h-k-l} = I_{-hkl} = I_{h-kl} = I_{hk-l}$$

The resolution of diffraction data

The maximum resolution *d* can be calculated with the help of the Bragg equation:

$$d = \lambda / 2 \sin(\theta_{max})$$

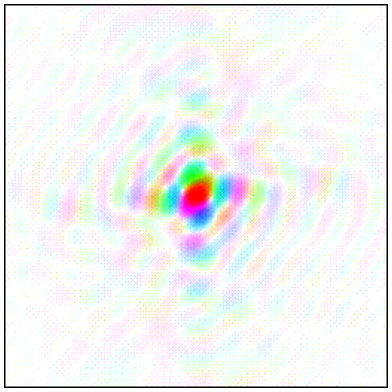
d **corresponds roughly to the distance apart of two equal atoms that can just be resolved from one another in an electron density synthesis calculated from diffraction data with a maximum resolution *d*.**



The number of unique reflections per non-hydrogen atom in a dataset with maximum resolution *d* is about $80/d^3$ for a centrosymmetric structure; this number should be halved for a non-centrosymmetric structure.

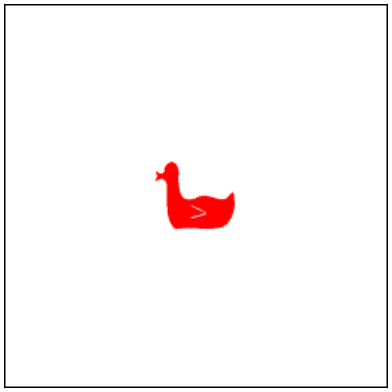
A low resolution duck

FT of a duck



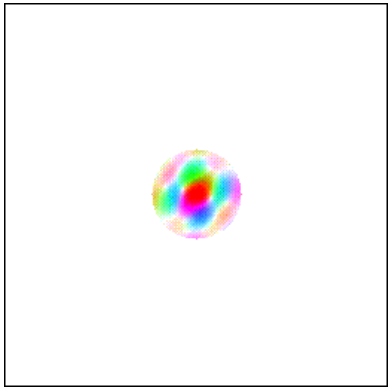
FT

FT



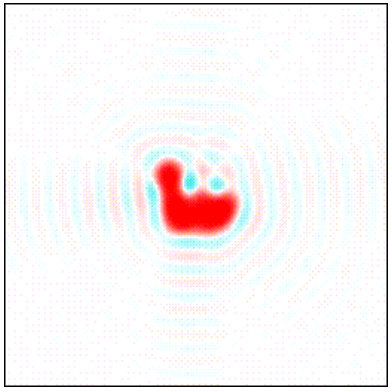
duck

FT of a duck after removal of the high resolution data



FT

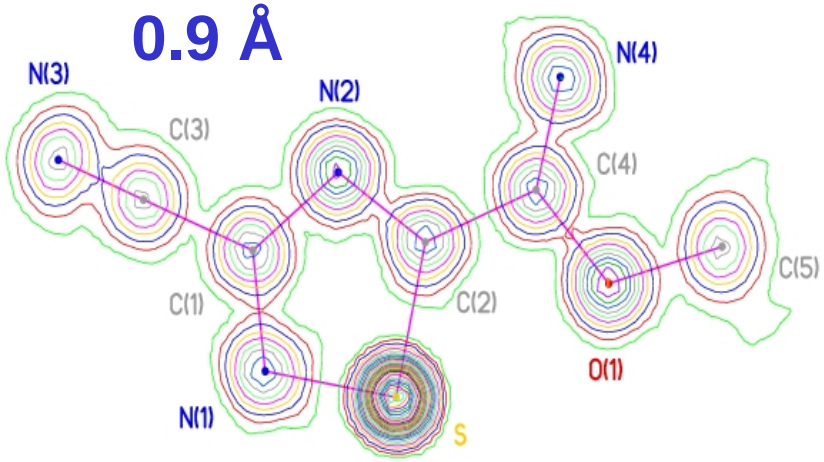
FT

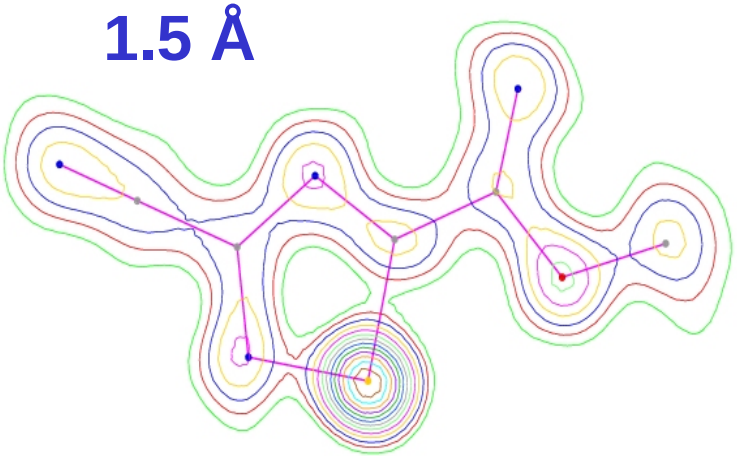


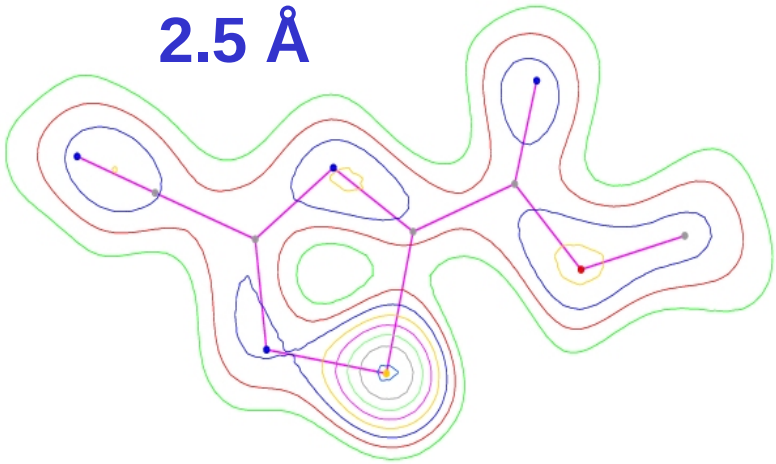
a low resolution duck

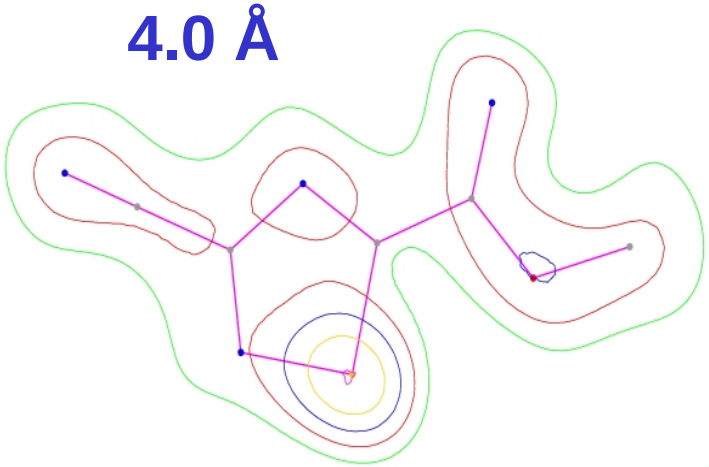
Kevin Cowtan http://www.ysbl.ac.uk/~cowtan/

The influence of the resolution









The contour lines are drawn at multiples of 0.1 eÅ^{-3}

Exercises

1. **Image plate X-ray detectors usually stand perpendicular to the primary beam that passes through the middle of the circular (340 mm diameter) active area of the detector. Calculate the maximum resolution that can be reached with a distance of 45 mm between crystal and detector (a) with CuKα radiation, λ = 1.5418 Å and (b) with MoKα, λ = 0.7107 Å.**

2. **Draw a projection of an orthorhombic unit-cell with *a* = 7.0, *b* = 8.0 and *c* = 12.0 Å viewed down a. Draw in the planes (012) and calculate their distance apart using Pythagoras and the formula for the area of a triangle (½*gh* where *g* is the length of the base and *h* the height perpendicular to it).**

   In a separate drawing show part of the 0*kl* layer of the reciprocal lattice and calculate *b, *c** and thus *d**(012). How are *d* and *d** related to one another?**