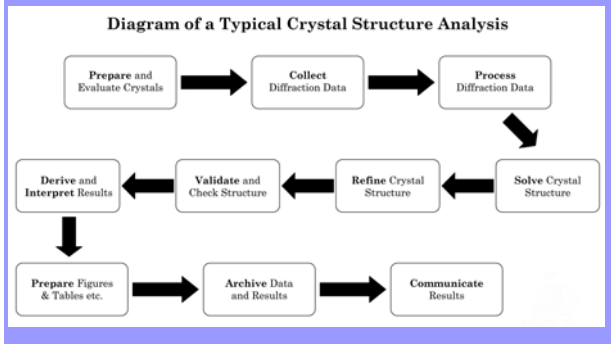
Durham 2005

Crystal Structure Analysis



Uses of X-ray Crystallography

Question 1.

You are given 10mg of a white crystalline substance obtained by processing 100 tonnes of bark from the Pacific yew tree (Taxus brevifolia).

What is it?

Uses of X-ray Crystallography

Question 2

You are given a 1Kg bag of a white, sweet tasting, crystalline material.

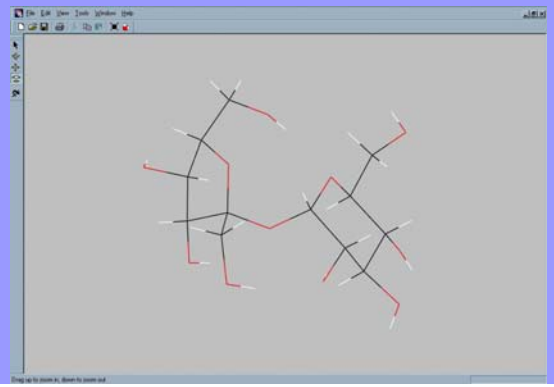
The bag is labelled Tate and Lyle.

What is the material?

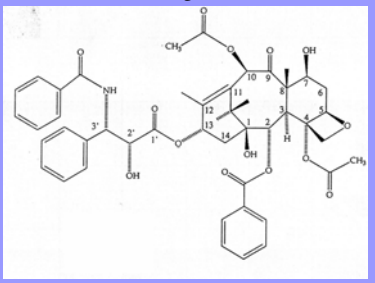
Answer to Question 2

Pupils and teacher from St Edwards School, Oxford, March 2005

Answer to Question 2



Answer to Question 1



In the 1970's it took Wall and Wani four years to elucidate the structure.

Today, it might take 3 hours – if you have a nice crystal

What are we trying to find?

1. Connectivity – what does the material look like.
2. Chemical composition – what atoms are present.
3. Geometry – what are the bond lengths and angles.
4. Absolute configuration.
5. Electron density distribution.

What is the Physics?

X-rays interact with the electrons orbiting the nucleus. *X-rays 'see' electrons*.

If the atoms are repeated in a periodic way, interference between wave fronts occurs, leading to emergent diffracted beams.

The ***position*** of these beams is related to the periodicity of the electron density.

The ***intensity*** is related to the electron density.

What are we trying to find?

X-rays tell us about the *continuous electron distribution* throughout the crystal.

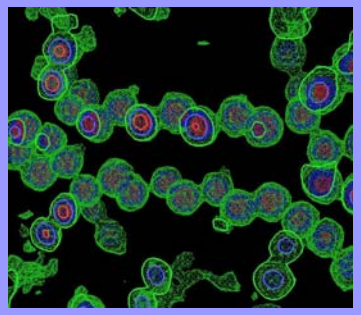
The experiment takes a long (compared with atomic motions) time, so we get a *time average*.

The experiment requires a large number of regularly ordered unit cells, so we also get a *space average.*

What do we find?

If all goes well, we can create an image of the periodic electron density.

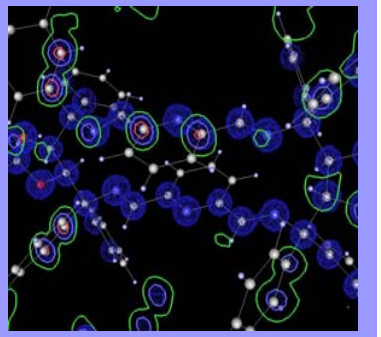
Electron density displayed using Michael Husak's MCE viewer and CRYSTALS



What Next?

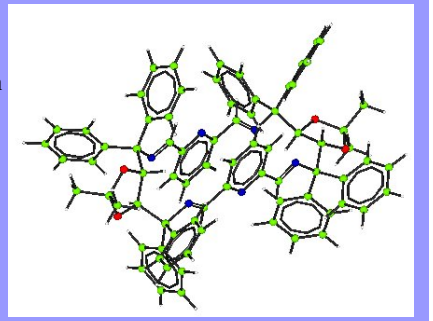
At a resolution of 3 points per Angstrom, a 10x10x10 A cell would require 27,000 sampling points.

Insert atoms into the electron density.



Why bother with the electron density?

In fact, for much structural work the electron density is discarded, and replaced by an atomic model.

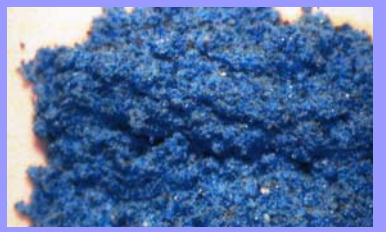


What do we Need? Good Crystals

Powders

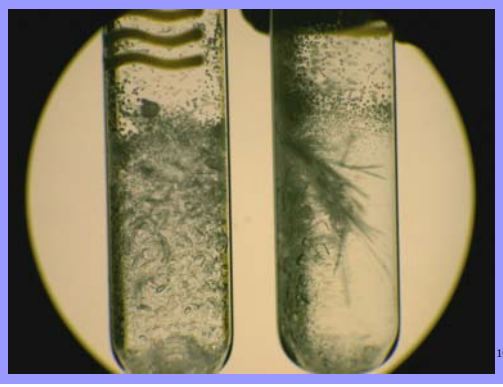
The white powder is freeze dried and non-crystalline.

The blue powder is microcrystalline

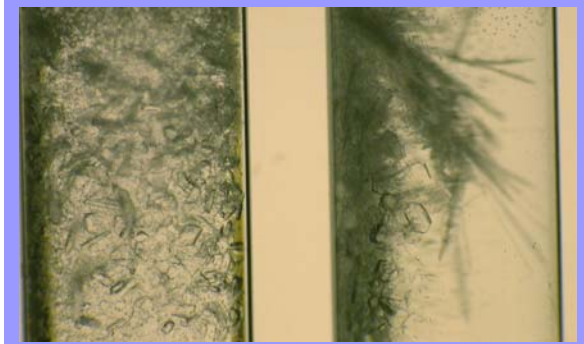


Good Crystals

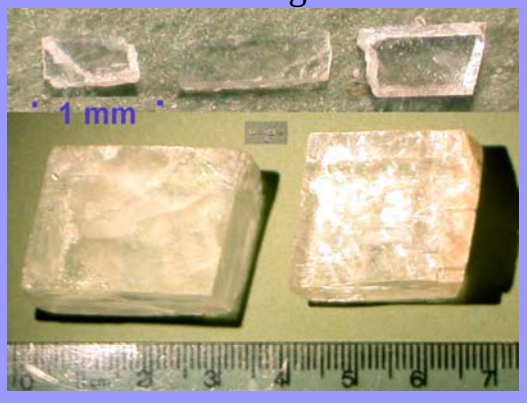
Uninspiring Crystals



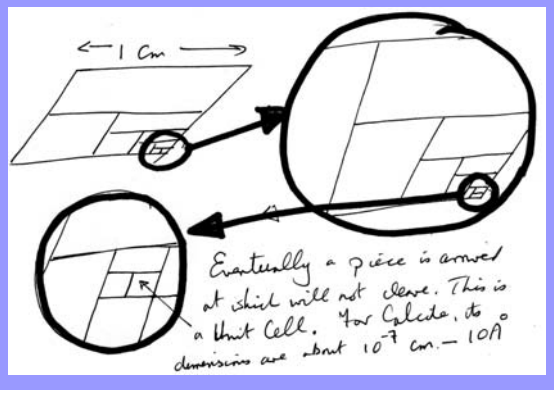
Some Tiny Crystals which might do



Calcite Fragments



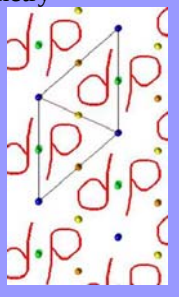
Cleaving Crystals



Symmetry Operators

Symmetry operations inside the unit cell mean that the contents of the cell can be represented by an asymmetric unit plus a list of symmetry operations.

Though this may seem complicated to a human, it greatly simplifies the computations.



Symmetry in the Unit Cell

The motifs within the cell may be related to each other by operations which are not simple translations.

These operations include

Centre of Symmetry

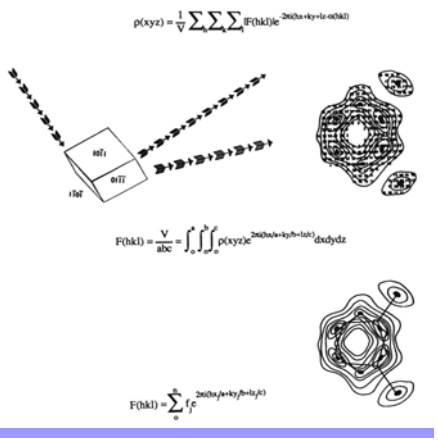
Rotation

Rotation-translation – called Screw operations

Reflection

Reflection-translation – called Glide operations

The 3 key equations



The experiment

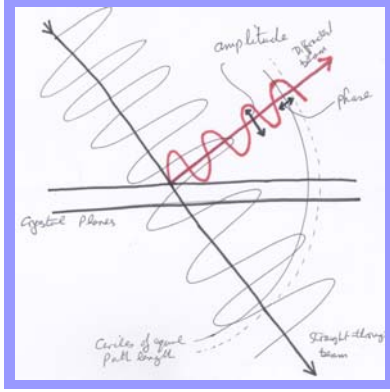
$$F(hkl) = \frac{V}{abc} = \int_o^a\int_o^b\int_o^c \rho(xyz)e^{2\pi i(hx/a+ky/b+lz/c)}dxdydz$$

The structure factors are a transform of the continuous electron density, ρ.

Note the 'i' in the exponent. This means that the structure factor has both magnitude and phase.

We can easily observe the magnitude, but only measure phases with great difficulty.

The Problem



The phase of a diffracted beam is actually the phase lag with respect to the incident beam.

It is not easy to measure.

The reconstruction

$$\rho(xyz) = \frac{1}{V}\sum_h\sum_k\sum_l |F(hkl)|e^{-2\pi i(hx+ky+lz-\alpha(hkl)}$$

Given the magnitude of the structure factors, $|F|$, and the phases, α, we can reconstruct the electron density.

The task of structure solution programs is to determine good estimates of the unobservable phases.

The approximation

$$F(hkl) = \frac{V}{abc} = \int_o^a\int_o^b\int_o^c \rho(xyz)e^{2\pi i(hx/a+ky/b+lz/c)}dxdydz$$

The continuous electron density is replaced by an **atomic model**. *x,y,*and *z* are the location of atoms with properties *f*. An atom will fit into a 3x3x3A box. At 3 points per Angstrom, the atom can be represented by 700 electron density values.

$$F(hkl) = \sum_o^n f_j e^{2\pi i(hx_j/a+ky_j/b+lz_j/c)}$$

An atomic model normally consists of 4 or 9 values. There is an evident opportunity for mis-representation.

Fourier Duck

Demo Kevin Cowtan's Fourier Duck

The nature of the model

$$F(hkl) = \sum_{o}^{n} f_j e^{2\pi i(hx_j/a+ky_j/b+lz_j/c)}$$

The centre of each atom is located at *x*,*y*,*z*. The atomic properties, *f*, consist of two parts.

1. The form factor. This quantifies the interaction of the electrons with X-rays as a function of Bragg angle, and is structure independent.
2. The *atomic displacement parameters*. These must be determined.

Form Factors

These are atom-specific, and consist of 3 components:

$$f_{effective} = f + f' + f''$$

f , the normal part, is wavelength independent.

f' is the real part of the anomalous dispersion, and changes rapidly near an absorption edge.

f'' is the imaginary part of the anomalous dispersion, and for non-centrosymmetric structures leads to information about the absolute structure.

Atomic Displacement Parameters

adps are now measured in Angstrom^2.

Small molecule studies are usually reported in terms of Uiso, Uaniso, Uij or Uequiv

Macromolecular studies are reported in terms of Biso, Baniso, Bij or Bequiv

$$B = 8\pi^2 U$$

Older papers use b or β, which are dimensionless and make comparisons between different axial directions difficult.

Anisotropic Atomic Displacement Parameters

The tensor is symmetric, so only the 6 unique terms need to be determined.

The size and orientation are determined by all 6 terms together.

For an atom on a special position, the terms may not be independent.

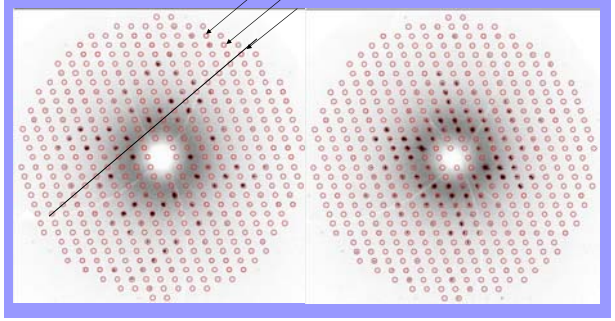
$$adp = \begin{matrix} U_{11} & U_{12} & U_{13} \\ U_{21} & U_{22} & U_{23} \\ U_{31} & U_{32} & U_{33} \end{matrix}$$

The Machine

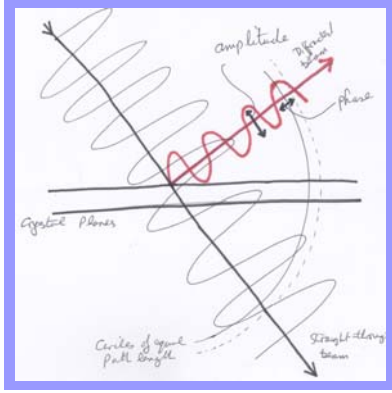
Oxford Diffraction ***Gemini*** Diffractometer

The Diffracted Image

The diffraction pattern is a regular lattice



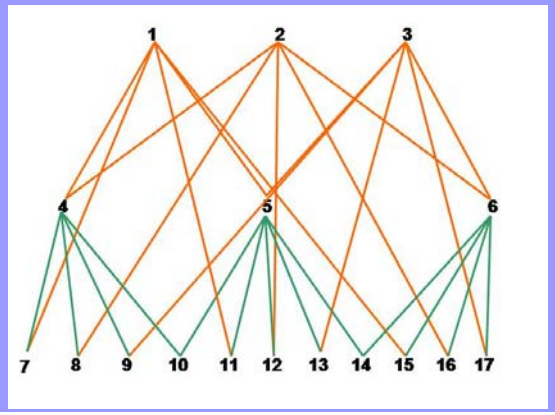
The Problem



The phase of a diffracted beam is actually the phase lag with respect to the incident beam.

It is not easy to measure.

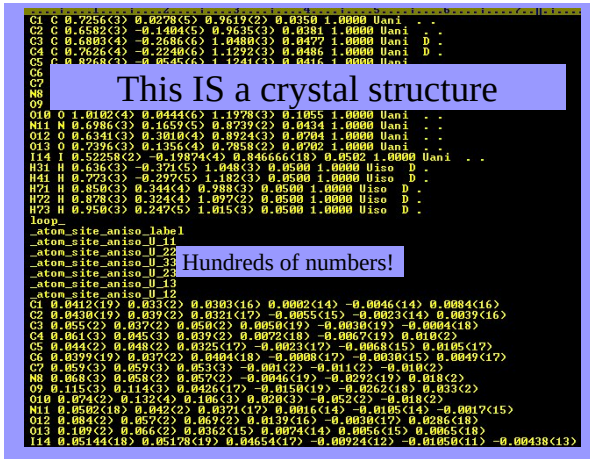
Phase Extension



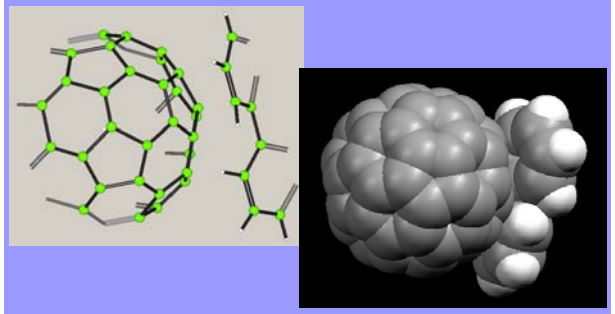
What do we get?

Many thousands of X-ray observations, the Structure Factors, go into the computer, the hkl file.

Many hundreds of numbers come out of the computer, the 'cif' file.



Crystal Structures. Some times it all works out nicely …



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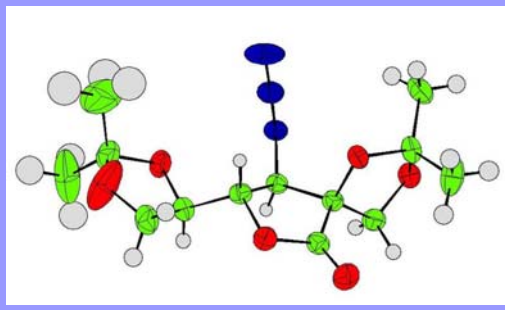
Disordered Azide

(Soengas , Harding, Shallard-Brown)

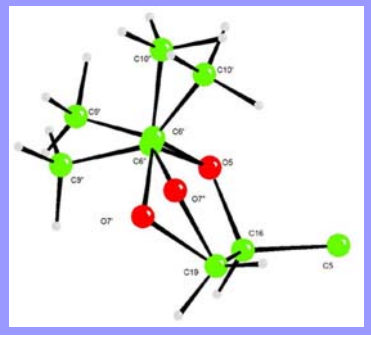
- Note that the left hand end has high adps



Disordered Azide

(Soengas , Harding, Shallard-Brown)

The disordered part modelled as ‘split’ atoms



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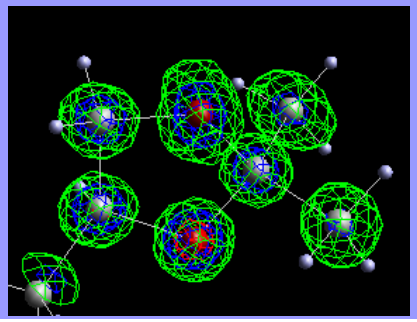
Disordered Azide

(Soengas , Harding, Shallard-Brown)

Actual electron density. Note elongations.



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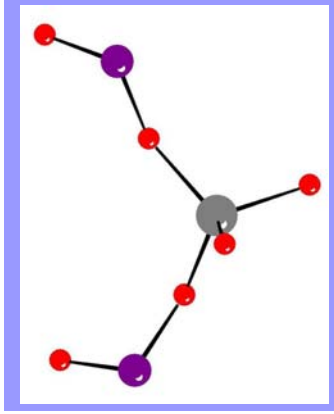
Extended Lattice



The asymmetric unit consists of $Al O_6 P_2$

The oxygen with only one bond are in fact bridging to other atoms in the unit cell.

Applying the SG symmetry operators fills out the stucture.

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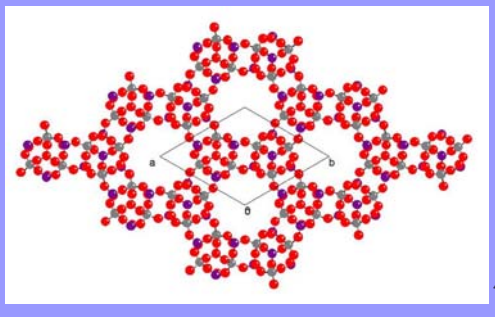
Extended Lattice

The space group is $P\bar{3}$. The ‘holes’ in the structure are in fact channels running all through the crystal, which can contain other molecules



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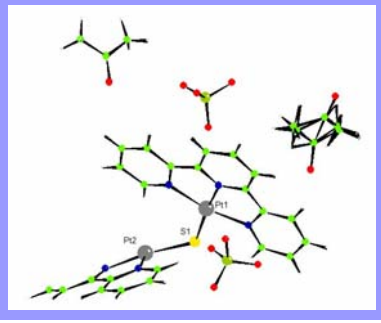
Example: Solvent of crystallisation

As well as the ClO_4 counter ions, there is acetone of solvation.



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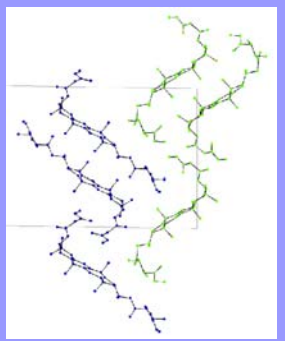
Types of Z′ > 1

- Different conformations.
  - The ‘green’ molecules have the same connectivity as the ‘blue’, but have an extra kink



Only one molecular species present

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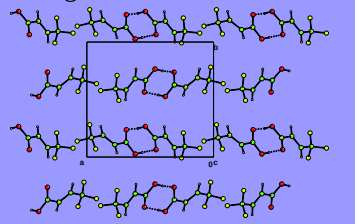
Types of Z′ > 1: tf-butenoic acid

Pseudo-symmetry: The molecules are related by a non-crystallographic symmetry element. Usually the symmetry does not extend beyond the immediately neighbouring molecules.

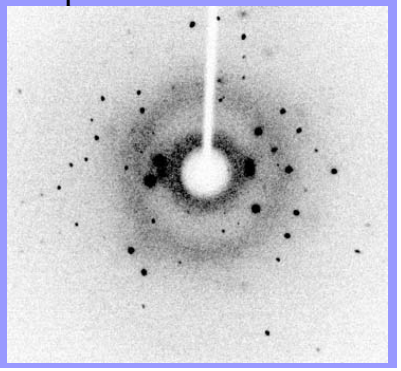
The H-bonded dimer has a local centre of symmetry. The sg is $P2_1/c$



4,4,4-trifluoro-trans-2-butenoic acid

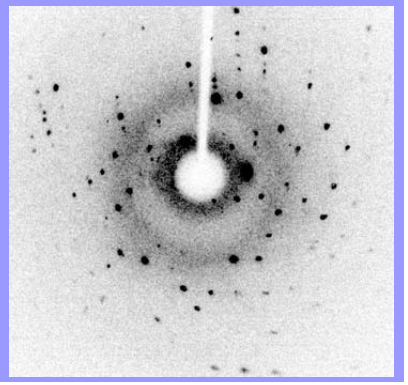
tf- butanoic acid High Temperature Form

- Frame 74
- Time 4:43:57
- 230K



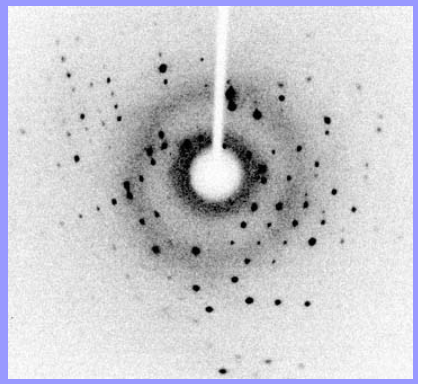
Transition

- Frame 76
- Time 4:44:47
- Interval : 50 sec
- 230K



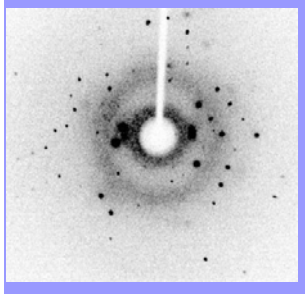
Low Temperature Form

- Frame 79
- Time 4:46:02
- Interval : 75 sec
- 230K

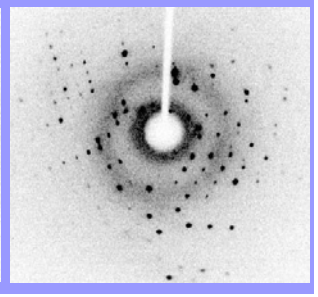


tf-butanoic acid

High temp form



Low temp form



Conclusions

1. X-rays see electrons – where there are electrons there are usually atoms.
2. All the electrons contribute to each structure factor – we need all the structure factors to see any electron.
3. The experiment needs a lot of unit cells, and a lot of time. We see a time & space average.
4. Atoms are very mobile, even in the solid state.
5. Local geometry of atoms is now well established, but molecular packing in not understood (at all?).

Refinement Exercises

Structure development and refinement are often the most time consuming stage of difficult analyses. The talks cannot cover all eventualities.

The book contains about 50 refinement problems. Look at them asap and tell your Group Tutor which ones you find most interesting or difficult.

If there is anything which bothers a lot of people, |I will try to cover it in my talks.

Refinement Lectures

In response to the student's comments in 2003, we have introduced two new refinement topics:

1. One lecture on refinement from powder data.
2. Two lectures on refinement of inorganic/ extended lattice structures.

The time available for the general discussion of refinement has been halved. PPTs showing the topics covered in 2003 will be on display.

All the PPTs will be available as PDFs on request.