



Derivation of Results

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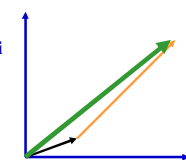
GEOMETRY

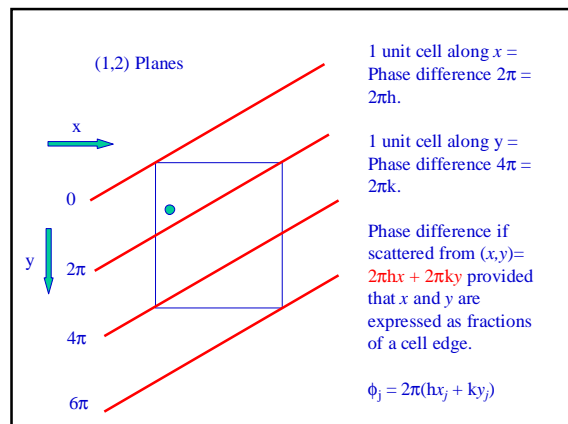
Fractional Coordinates
Bond lengths
Bond and Torsion angles
Planes
Transforming coordinates
Standard Deviations
Hydrogen atoms

Calculating \mathbf{F}

$$\mathbf{F}(hkl) = \sum_j f_j \cos f_j + i \sum_j f_j \sin f_j$$

$$\mathbf{F}(hkl) = \sum_j f_j (\cos f_j + i \sin f_j)$$

$$\mathbf{F}(hkl) = \sum_j f_j \exp(if_j)$$




Fractional Atomic Coordinates

- Fractional atomic coordinates are used because:
 - the structure factor is derived in terms of them (ultimately because of the definition of Miller planes);
 - space group symmetry is readily described in terms of them.
- But, this is not especially convenient for the calculation of geometry.

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Cartesian Coordinates

- Let the X-axis lie along **a**
- Let the Y-axis be perpendicular to **a** in the **ab** plane.
- The Z-axis is given by the vector product

$$\mathbf{Z} = \mathbf{X} \times \mathbf{Y}$$

We'll not go into the derivation in detail, but see Giacovazzo Chapter 2. Note that vector products of direct axis vectors yield reciprocal axis vectors, eg $\mathbf{a}^* = (\mathbf{b} \times \mathbf{c})/V$ etc.

Cartesian Coordinates

- This yields the matrix:

$$\begin{pmatrix} \frac{1}{a} & 0 & 0 \\ -\cos g & \frac{1}{b} & 0 \\ \frac{a \sin g}{a^* \cos b^*} & \frac{b \sin g}{b^* \cos a^*} & c^* \end{pmatrix}$$

- Having expressed coordinates wrt orthogonal axes, ordinary Cartesian methods can be used to work out bond distances etc.

Cartesian Coordinates

- Cartesian coordinates are also useful for fitting purposes, eg expressing two crystal structures on a common frame.
- PDB files contain orthogonal coordinates.
- To convert back to fractional atomic coordinates, simply apply the inverse orthogonalisation matrix.
- There are an infinite number of ways to perform the orthogonalisation.

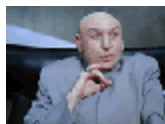
Vectors

- We will examine the determination of distances using vectors. This
 - Illustrates the practical application of vectors;
 - Introduces the *metric tensor*;

Vectors

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 - Illustrates the practical application of vectors;
 - Introduces the *metric tensor*;

- It's a bit mathematical though



Vectors

- The length of a vector **u** is the square root of the dot product **u.u**
- Suppose we have an atom at $(x_1 \mathbf{a} + y_1 \mathbf{b} + z_1 \mathbf{c})$ and another at $(x_2 \mathbf{a} + y_2 \mathbf{b} + z_2 \mathbf{c})$.
- What is the bond length?

- The interatomic vector is:

$$([x_1-x_2]\mathbf{a} + [y_1-y_2]\mathbf{b} + [z_1-z_2]\mathbf{c}) \\ = (\Delta x \mathbf{a} + \Delta y \mathbf{b} + \Delta z \mathbf{c}).$$

- The length (r) is given by

$$r^2 = (\Delta x \mathbf{a} + \Delta y \mathbf{b} + \Delta z \mathbf{c}) \cdot (\Delta x \mathbf{a} + \Delta y \mathbf{b} + \Delta z \mathbf{c}) \\ = ([\Delta x]^2 a^2 + \Delta x \Delta y ab \cos \gamma + \dots \text{etc}).$$

- This simplifies a lot if angles are equal to 90° .

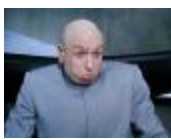
Dot Products

- The dot product $\mathbf{u} \cdot \mathbf{u}$ can be written in matrix notation as: $\mathbf{u}^T \mathbf{u}$.
- Indeed the vector $(\Delta x \mathbf{a} + \Delta y \mathbf{b} + \Delta z \mathbf{c})$ can itself be considered to be a dot product:

$$\begin{pmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix}$$

- The dot product

$(\Delta x \mathbf{a} + \Delta y \mathbf{b} + \Delta z \mathbf{c}) \cdot (\Delta x \mathbf{a} + \Delta y \mathbf{b} + \Delta z \mathbf{c})$
can therefore be written:



$$\begin{pmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix} \begin{pmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix} \\ = (\Delta x \quad \Delta y \quad \Delta z) \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix} \begin{pmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix} \\ = (\Delta x \quad \Delta y \quad \Delta z) \begin{pmatrix} \mathbf{a}\mathbf{a} & \mathbf{a}\mathbf{b} & \mathbf{a}\mathbf{c} \\ \mathbf{b}\mathbf{a} & \mathbf{b}\mathbf{b} & \mathbf{b}\mathbf{c} \\ \mathbf{c}\mathbf{a} & \mathbf{c}\mathbf{b} & \mathbf{c}\mathbf{c} \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix} \\ = (\Delta x \quad \Delta y \quad \Delta z) G \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix}$$

Metric Tensors

- The matrix

$$G = \begin{pmatrix} \mathbf{a}\mathbf{a} & \mathbf{a}\mathbf{b} & \mathbf{a}\mathbf{c} \\ \mathbf{b}\mathbf{a} & \mathbf{b}\mathbf{b} & \mathbf{b}\mathbf{c} \\ \mathbf{c}\mathbf{a} & \mathbf{c}\mathbf{b} & \mathbf{c}\mathbf{c} \end{pmatrix}$$

is very important in crystallography. It is called the metric tensor.

- Likewise,

$$G^* = \begin{pmatrix} \mathbf{a}^*\mathbf{a}^* & \mathbf{a}^*\mathbf{b}^* & \mathbf{a}^*\mathbf{c}^* \\ \mathbf{b}^*\mathbf{a}^* & \mathbf{b}^*\mathbf{b}^* & \mathbf{b}^*\mathbf{c}^* \\ \mathbf{c}^*\mathbf{a}^* & \mathbf{c}^*\mathbf{b}^* & \mathbf{c}^*\mathbf{c}^* \end{pmatrix}$$

can also be defined with the reciprocal axes. This is called the reciprocal metric tensor.

$$G^* = G^{-1}$$

Metric Tensors

- Metric tensors are important because they make geometry calculations computationally simpler.
- The also transform basis vectors between direct and reciprocal space:

$$\mathbf{A} = G \mathbf{A}^*$$

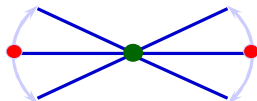
$$\mathbf{A}^* = G^* \mathbf{A}$$

$$\mathbf{x} \cdot \mathbf{h} = hx + ky + lz$$

$$\begin{pmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix} \begin{pmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix} \\ = (\Delta x \quad \Delta y \quad \Delta z) \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix} \begin{pmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix} \\ = (\Delta x \quad \Delta y \quad \Delta z) \begin{pmatrix} \mathbf{a}\mathbf{a} & \mathbf{a}\mathbf{b} & \mathbf{a}\mathbf{c} \\ \mathbf{b}\mathbf{a} & \mathbf{b}\mathbf{b} & \mathbf{b}\mathbf{c} \\ \mathbf{c}\mathbf{a} & \mathbf{c}\mathbf{b} & \mathbf{c}\mathbf{c} \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix} \\ = (\Delta x \quad \Delta y \quad \Delta z) G \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix}$$

Librational Correction

- The values of the displacement parameters can be analysed to test a fit to assumed rigid group motion. This is called TLS analysis (see notes).
- They may also be used to perform a 'librational correction' on bond distances, which can appear to be too short if thermal motion is high.



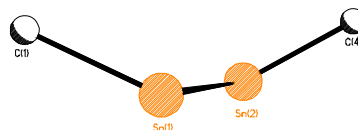
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Bond and Torsion Angles

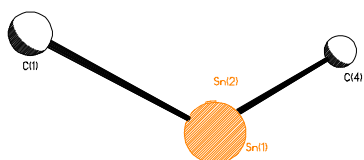
- Bond angles are calculated from distances using the cosine rule or dot products.
- Torsion angles are calculated using vector methods (see Giacovazzo, Ch. 2).
- Torsion angles are also sometimes called dihedral angles, and they must be quoted with a sign.

Torsion Angles



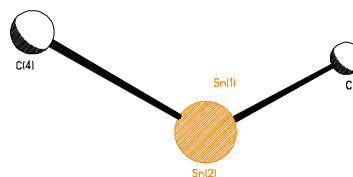
The torsion angle is the angle between the C1Sn1Sn2 and C4Sn2Sn1 planes.

Torsion Angles



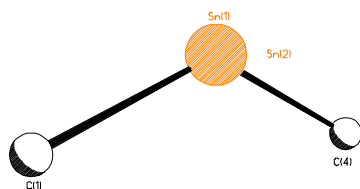
How many degrees should we rotate Sn1-C1 (in front) to bring it into coincidence with Sn2-C4 (behind).
Clockwise is Positive.

Torsion Angles



Notice that the 1-2-3-4 torsion is the same as the 4-3-2-1 torsion angle. But....

Torsion Angles



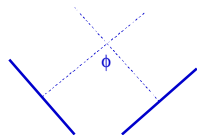
If we invert or reflect a molecule,
the torsion angles *change sign*.

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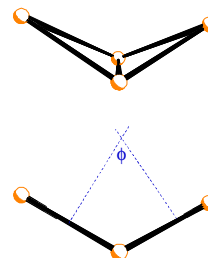
Planes

- Angles between planes are often needed to describe molecular geometry (e.g. angle between Cp ligands)
- The angle between two planes is defined as the angle between the two normals.



Planes

- Sometimes this formal definition can lead to counter-intuitive results.
- In this case it is probably better to quote the hinge angle.
- This is just $180 - \phi$.



Planes Through a Set of Points

- This calculation is often carried out in order to assess how planar a group is.
- Least squares is used to calculate a plane that minimises the deviations (d) of the atoms from the plane.
- Methods for doing this are review in IT volume B (section 3.2).

Type	Serial	XP	YP	ZP
C	43.	1.216	0.662	-0.008
C	42.	1.199	-0.724	-0.032
C	41.	-0.035	-1.385	0.046
C	46.	-1.234	-0.659	-0.021
C	45.	-1.187	0.720	-0.019
C	44.	0.041	1.387	0.033

$$\sum_{atoms} d^2 = \min.$$

Prince Says....

The common practice of fitting a least squares plane through a nearly planar group that has not been constrained to be planar, coupled with the examination of distances of various atoms from this plane to judge whether the group is 'significantly' non-planar, is a procedure designed to answer the wrong question.

Prince Says....

The common practice of fitting a least squares plane through a nearly planar group that has not been constrained to be planar, coupled with the examination of distances of various atoms from this plane to judge whether the group is 'significantly' non-planar, is a procedure designed to answer the wrong question. The question that should be asked, and it can only be addressed through a properly designed constrained refinement, is *Do the data indicate that the group is planar or non-planar?*

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The common practice of fitting a least squares plane through a nearly planar group that has not been constrained to be planar, coupled with the examination of distances of various atoms from this plane to judge whether the group is 'significantly' non-planar, is a procedure designed to answer the wrong question. The question that should be asked, and it can only be addressed through a properly designed constrained refinement, is *Do the data indicate that the group is planar or non-planar?* There are other parameters that must be allowed to find their best values consistent with the constrained model, and it is only this adjusted model that can legitimately be compared with the unconstrained one.

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Transforming Coordinates

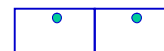
- Sometimes it is necessary to express a set of coordinates wrt a new set of axes.
- This may occur when changing space group, e.g. Pna2₁ to Pnma.
- ...when modelling a structure after a phase transition.

Transforming Coordinates

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- If the basis vectors (the unit cell) is transformed with a matrix R , how do the coordinates transform?

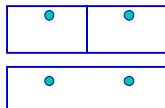
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Transforming Coordinates

- The relationship between the old and new coordinates is **not** the same as between the old and new cell axes.
- In fact the old coordinates should be transformed with the **inverse** transpose of R .

- $(x \mathbf{a} + y \mathbf{b} + z \mathbf{c})$ can be written as

$$\begin{pmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \mathbf{A}^T \mathbf{x}$$

- $(\mathbf{AB})^T = \mathbf{B}^T \mathbf{A}^T$.

Transforming Coordinates

- In fact the old coordinates should be transformed with the **inverse** transpose of R .

$$\begin{aligned} \mathbf{r} &= \mathbf{A}^T \mathbf{x} \\ \mathbf{r} &= \mathbf{B}^T \mathbf{y} \\ \mathbf{A}^T \mathbf{x} &= \mathbf{B}^T \mathbf{y} \\ \mathbf{B} &= \mathbf{R} \mathbf{A} \\ \mathbf{A}^T \mathbf{x} &= (\mathbf{R} \mathbf{A})^T \mathbf{y} \\ \mathbf{A}^T \mathbf{x} &= \mathbf{A}^T \mathbf{R}^T \mathbf{y} \\ \mathbf{x} &= \mathbf{R}^T \mathbf{y} \\ (\mathbf{R}^T)^{-1} \mathbf{x} &= \mathbf{y} \end{aligned}$$

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S.u.'s from Refinement

- The procedure for obtaining s.u.s on refined parameters was discussed in least-squares lectures.

$$\sigma(p_j) = \left((\mathbf{A}^T \mathbf{W} \mathbf{A})^{-1} \sum_{i=1}^N w_i \Delta_i^2 \frac{N}{N-P} \right)^{1/2}$$

$$\begin{aligned} D\mathbf{x} &= \mathbf{y} \\ D^T D \mathbf{x} &= D^T \mathbf{y} \\ \mathbf{x} &= (D^T D)^{-1} D^T \mathbf{y} \\ (D^T D)^{-1} &= \mathbf{A}^{-1} \end{aligned}$$

$$\text{cov}(p_j, p_k) = \left((\mathbf{A}^T \mathbf{W} \mathbf{A})^{-1} \sum_{i=1}^N w_i \Delta_i^2 \frac{N}{N-P} \right)^{1/2}$$

Standard Uncertainties

- Least squares produces s.u.s for refined parameters.
- These s.u.s, and the cell parameter s.u.s, should be propagated into calculated bond distances, angles etc.
- Specific formulae are given in Giacovazzo.

Propagation of Errors

- Suppose we define some function of our refined parameters, $f(x_1, x_2, \dots)$. What is the variance of f ?

$$\sigma^2(f) = \sum_{i,j=1}^N \frac{\partial f}{\partial x_i} \cdot \frac{\partial f}{\partial x_j} \cdot \text{cov}(x_i, x_j)$$

- If co-variances are zero - or not known! - this simplifies.

$$\sigma^2(f) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 \sigma^2(x_i)$$

Example

$$\sigma^2(f) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 \sigma^2(x_i)$$

$$f = x + y$$

$$s^2(f) = \left(\frac{\partial f}{\partial x} \right)^2 s^2(x) + \left(\frac{\partial f}{\partial y} \right)^2 s^2(y)$$

$$s^2(f) = s^2(x) + s^2(y)$$

Correlation

- The s.u.s quoted in output files of refinement programs (e.g. cifs) only contain information on the diagonal terms of the least squares inverse normal matrix.
- BUT in order to propagate errors properly, the off diagonal terms are needed as well!
- Programs external to the refinement package will not have this information, and the calculated s.u.s may be badly wrong.

An Extreme Example

```
AFIX 66
C2A 1 0.691085 0.421897 0.187569 11.00000 0.05831
C3A 1 0.627482 0.230118 0.129289 11.00000 0.05831
C4A 1 0.614620 0.215989 0.013887 11.00000 0.05831
C5A 1 0.665359 0.393640 -0.043235 11.00000 0.05831
C6A 1 0.728962 0.585421 0.015045 11.00000 0.05831
C7A 1 0.741826 0.599552 0.130446 11.00000 0.05831
AFIX 0

C(2A) 0.6911(8) 0.4219(16) 0.1876(15)
C(3A) 0.6275(9) 0.2301(18) 0.1293(17)
C(4A) 0.6146(10) 0.216(2) 0.0139(17)
C(5A) 0.6654(11) 0.394(3) -0.0432(15)
C(6A) 0.7290(11) 0.585(3) 0.0150(15)
```

An Extreme Example

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C(6A) 0.7290(11) 0.585(3) 0.0150(15)
```

_atom_site_refinement_flags

C2A C 0.6911(8) 0.4219(16) 0.1876(15) 0.0583(15) Uiso 1 1 d GD . .

Correlation

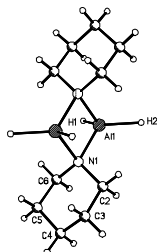
- Important bond lengths and angles should therefore always be calculated using the refinement program.
- In SHELX extra bond lengths etc can be calculated with RTAB instructions.
- In CRYSTALS they may be obtained by extending the LIMITS of a #DISTANCE calculation.

1.GEOMETRY

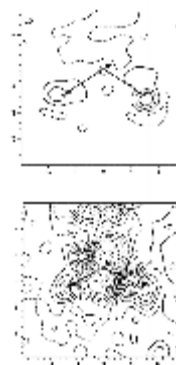
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Hydrogen Atoms

- H-atoms are something of a problem for X-ray crystallography.
- X-rays are scattered by electrons and so H-atoms don't show up very well.
- H-atoms may be of interest for H-bonding, or in hydride compounds.

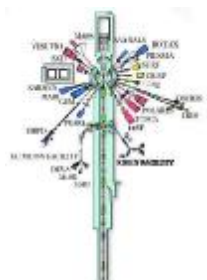


- These are difference maps calculated through the mean plane of an MH_2 moiety where $M = Al$ or Ga .
- The Ga map is much noisier.

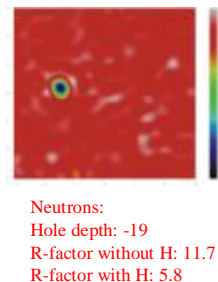


Hydrogen Atoms

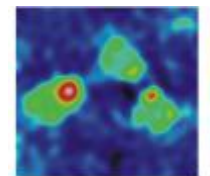
- The best answer is to use neutron diffraction, but this will either require a large crystal or deuteration.
- Ab initio methods are also be useful.



Search for a Missing Water H

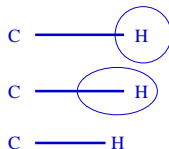


X-Rays
Peak height: +0.6
R-factor without H: 2.9
R-factor with H: 2.7



Hydrogen Atoms

- ...And even if you can find and refine them the X-H bond length will be wrong.
- Typically a C-H bond will be ca 0.1 Å too short.
- The s.u.s may also either be enormous or strongly affected by H-atom treatment in least squares - restraints or constraints.



Hydrogen Atoms

- Some care should be exercised when interpreting H-atom positions, especially if they have been placed in idealised positions.
- It is a good idea to 'normalise' X-H bonds to typical neutron values, but this depends on data available for comparison.
- For D-H...A interactions quote the D...A distance.

Tutorials

Ch 15 Q1-3
Ch 16 Q4, 5

2. Displacement Parameters

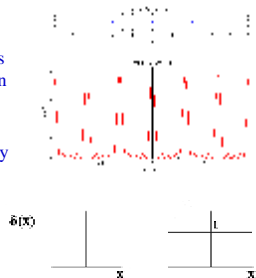
Scattering
Anisotropic Displacement Parameters
Transformation Properties
Uses

Displacement Parameters

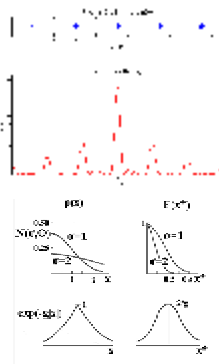
- In most refinements the majority of refined parameters are displacement parameters.
- They are extremely important in modelling diffraction intensities.
- Not usually of much interest, but they are very sensitive to errors (like an error dustbin).

Scattering

- The diffraction pattern of a lattice of point scatterers would show no drop off in intensity with angle.
- This is similar to neutron diffraction (nuclei are very small).
- The reason is that the Fourier transform of a Delta function is a constant.



- X-rays are diffracted by electrons.
- Electron clouds have finite size and are diffusely located around an atomic centre.
- The larger the size the bigger the drop off.
- This accounts for the shape of the scattering factor (form factor) curve in X-ray diffraction.
- A Fourier Transforms goes from long and thin to short and fat.



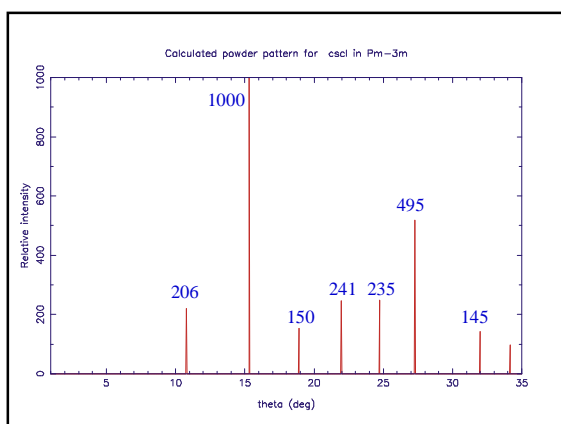
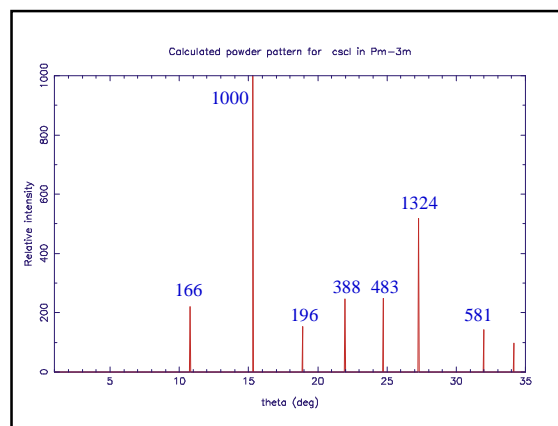
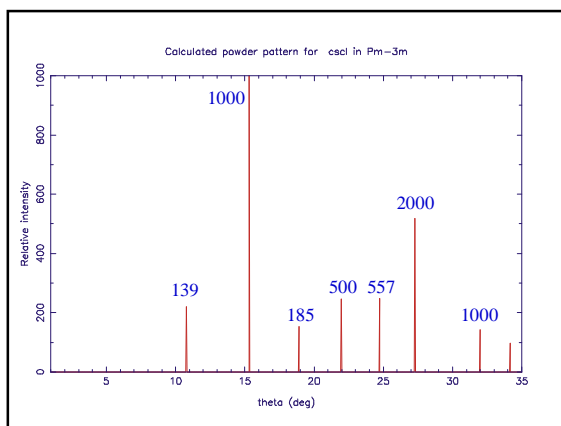
Displacement Parameters

- Thermal motion increases the effective size of an electron cloud (smearing it out).
- Thus thermal motion tends to attenuate the high angle data.
- This is one reason for collecting data at low temperature.

Scattering factor is theta dependent.

$$F(hkl) = \sum_j f_j \cos 2\pi (hx + ky + lz) \exp\left(-B \frac{\sin^2 \theta}{\lambda^2}\right)$$

Accounts for effect of thermal motion on intensities. B = thermal parameter, Debye-Waller Factor. Also expressed as U . ($8\pi^2 U = B$)



Anisotropic Thermal Motion

- Although in the early stages of a refinement atoms are usually refined isotropically, thermal motion is in fact anisotropic.
- In general 6 parameters are needed - 3 for size and 3 for orientation.



Anisotropic Thermal Parameters

$$\begin{aligned}
 & -(b^{11}h^2 + b^{22}k^2 + b^{33}l^2 + 2b^{23}kl + 2b^{13}hl + 2b^{12}hk) \\
 \text{or } & -\frac{1}{4}(B^{11}h^2a^{*2} + B^{22}k^2b^{*2} + B^{33}l^2c^{*2} + 2B^{23}klb^*c^* + 2B^{13}hla^*c^* + 2B^{12}hka^*b^*) \\
 \text{or } & -2p^2(U^{11}h^2a^{*2} + U^{22}k^2b^{*2} + U^{33}l^2c^{*2} + 2U^{23}klb^*c^* + 2U^{13}hla^*c^* + 2U^{12}hka^*b^*)
 \end{aligned}$$

These may also be written in matrix notation, e.g.:

$$-(h \quad k \quad l) \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{12} & b_{22} & b_{23} \\ b_{13} & b_{23} & b_{33} \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

Principal Values

- The eigenvalues of this matrix express the radii of the ellipsoid.
- For an ellipsoid they must all be positive.
- Otherwise, the matrix is described as being **non-positive definite**.
- The average of the principal values is called the equivalent isotropic displacement parameter.

$$\begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{12} & b_{22} & b_{23} \\ b_{13} & b_{23} & b_{33} \end{pmatrix}$$



Transformation Properties

- Space group symmetry operations transform displacement parameters according to: $U' = RUR^T$.
- Since U and U' must be equal if an atom is on a special position this can place constraint on the values of the components.

$$\begin{aligned}
 U' &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{12} & b_{22} & b_{23} \\ b_{13} & b_{23} & b_{33} \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\
 &= \begin{pmatrix} b_{11} & -b_{12} & b_{13} \\ -b_{12} & b_{22} & -b_{23} \\ b_{13} & -b_{23} & b_{33} \end{pmatrix} \\
 U_{12} &= -U_{12} = 0 \\
 U_{23} &= -U_{23} = 0
 \end{aligned}$$
- E.g. If an atom is on a two-fold axis perpendicular to b.