Data processing and reduction

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International School on Fundamental Crystallography 2012

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Class Plan

• Determination of $I_{hkl}$
  – single crystal intensities
    • unique data, use of equivalent reflections
  – powder intensities
    • intensity overlap and peak deconvolution

• Intensity corrections
  – Lorentz and polarization
  – Absorption
  – Extinction (Primary and Secondary)

• Intensity scaling and statistics
  – Scale factor and thermal parameters (Wilson plot)
  – Intensity statistic (centric-acentric distributions)
Reciprocal lattice

Reciprocal lattice vectors:

\[ a^* = \frac{b \times c}{V} \]
\[ b^* = \frac{c \times a}{V} \]
\[ c^* = \frac{a \times b}{V} \]

HKL to d:

\[ d_{h'k'l'} = \frac{1}{d_{h'k'l'}} \]

HKL to d*:

\[ d_{hkl} = \frac{1}{d_{hkl}} \]
Reciprocal lattice and Ewald sphere
Reciprocal lattice and Ewald sphere

Rayos X difractados

Rayos X incidentes

\[ d_{hkl}^* = \frac{1}{d_{hkl}} \]

\[ \frac{1}{\lambda} \sin(\theta) = \frac{d_{hkl}^*}{2} = \frac{1}{2d_{hkl}} \]

\[ 2d_{hkl} \sin(\theta) = \lambda \]

\[ |s| = \frac{2}{\lambda} \sin(\theta) = d_{hkl}^* = \frac{1}{d_{hkl}} \]
Reciprocal lattice and Ewald sphere

\[ |s_{hkl}| = \frac{2}{\lambda} \sin(\theta) = d_{hkl}^* = \frac{1}{d_{hkl}} = h\hat{a}^* + k\hat{b}^* + l\hat{c}^* \]
Single crystal data collection

- Modern CCD/CMOS area detectors allow for simultaneous collection of hundreds/thousands of diffraction intensities (reflections).
- Data is collected in frames produced by rotation of the crystal by a fraction of degree.
- Programs automatically integrate the images into individual indexed intensities.
Single crystal intensities

- For each indexed reflection (dots inside the circles) an intensity value will be determined by a numerical integration procedure to provide the output in a $h,k,l, I_{hkl}$ list that is used for structure determination.
Single crystal intensities

• Imagine you have just entered the diffractometer room (where the pride and treasure of the department is located). The last single crystal of your thesis work has been used for a successful automatic x-ray diffraction data collection procedure overnight.

• Your data was collected, indexed and integrated in each of the plates/frames of the CCD and put together in a file containing a large number of $h,k,l,I_{hk\ell}$, $\sigma I_{hk\ell}$ lines (shelx format) but the diffractometer software is malfunctioning and you cannot make it finish the work and solve the structure for you.

• You have been left with a file containing a long list of reflections plus the unit cell parameters of the conventional cell and a thesis to finish.
Single crystal intensities

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- what should I do now?
Single crystal intensities

• Since the reciprocal space is the Fourier Transform of the crystal and the crystal is (assumed) periodic, all the information in the reciprocal space is condensed in the reciprocal lattice points.

• Therefore the intensities of the RL points contain all the structural information and should allow to determine the structure, or at least the symmetry first.

• Intensities in the reciprocal lattice are related to the structure factors ($F_{hkl}$) through a series of factors that should be accounted for correctly, so one can determine the structure from the intensities after proper data Processing and Reduction.
Reflections, all, unique, observed

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- Part of the reflection list for the compound $\text{Gd}_2\text{Ca}_3\text{C}_{24}\text{O}_{40}\text{H}_{44}$
- During data collection, some reflections are measured more than once (red).
- Some are equivalent by symmetry (blue).
- Some are not observed ($I<2\sigma I$) (grey).
- Etc...
Reflections, all, unique, observed

- For the compound Gd$_2$Ca$_3$C$_{24}$O$_{40}$H$_{44}$ (cubic Fd3c) a=26.5954 Å:
  - 98706 intensities were integrated.
  - 36302 were different
  - 10764 were observed (|l>2s|)
  - 824 were unique (unrelated by symmetry)
  - 521 of the unique were observed.
Reflections, all, unique, observed

• Identification of useful intensities is required before structure determination since we need to know the degree of over-determination of the problem to know if the structure determination procedure will succeed.

• `For the compound Gd$_2$Ca$_3$C$_{24}$O$_{40}$H$_{44}$ (cubic Fd3c) a=26.5954 Å:
  – 521 of the unique were observed.
  – With these number of observed intensities only a small number of atomic parameters can be determined. Since the symmetry is high the problem is reduced to a few atoms in the asymmetric unit.
Reflections, all, unique, observed

• Even though we don’t need 98185 of the 98706 collected intensities for the structure determination and refinement, the redundancy allows for symmetry and data consistency checks, for the determination of other effects such as absorption or radiation damage of the crystal and to reduce the total uncertainty of the refined parameters due to a reduction in the uncertainty of the observed intensities.

• $R_{\text{int}}$ and $R_{\text{sigma}}$ are good measures of the consistency between equivalent reflections (symmetry-related reflections that should have equal intensities) and the overall uncertainty of the recorded intensities respectively.
Powder Intensities

• If one set of reciprocal lattice points can be associated to each crystal in the powder the reciprocal space for a powder sample (composed of an infinite number of small (~1μm) randomly oriented crystals) becomes populated with infinite copies of the same RL but randomly oriented. Therefore the RL nodes at a distance $s_{hkl}$ from the origin form spheres of that radii and intersection of the spheres with the Ewald sphere produce circles through where diffracted rays come out of the sample forming diffraction cones.
Powder diffraction data collection

- A policrystalline sample (powder) is composed of an “infinite” (>10^{10}) number of micrometric (1-10 μm) crystal with a perfectly random order and its Fourier Transform
Powder diffraction data collection

- The powder pattern is obtained from the intersection of the reciprocal lattice of the powder and the Ewald sphere.
Powder diffraction data collection

- Depending on the detector system geometry (and the sample shape and orientation respect to the beam different kinds of diffraction patterns are obtained.)
Powder diffraction data collection

- Depending on the detector system geometry (and the sample shape and orientation respect to the beam different kinds of diffraction patterns are obtained.)
Powder diffraction data collection

Rayos X ($\lambda$)
En función de la geometría del detector de rayos X se obtienen los distintos tipos de diagramas de polvo. Debye-Scherrer
Powder diffraction data collection

- En función de la geometría del detector de rayos X se obtienen los distintos tipos de diagramas de polvo. Con una pantalla plana (Image Plate)
Powder diffraction data collection

- En función de la geometría del detector de rayos X se obtienen los distintos tipos de diagramas de polvo. Con una pantalla plana (Image Plate)
Powder diffraction pattern

Powder diffraction pattern of $\text{Gd}_2\text{Ca}_3\text{C}_{24}\text{O}_{40}\text{H}_{44}$
Powder Intensities

• Either for systematic properties or for experimental conditions in a powder pattern a large number of reflections overlap and it is impossible to determine their individual intensities:
  – Metric overlap due to equal d-spacing of different reflections with different hkl
  – Symmetry overlap of equivalent reflections (all showing identical dhkl)
  – Accidental overlap for independent reflections with $\Delta 2\theta <$instrumental resolution
Powder Intensity Extraction

• In modern times two methods are systematically used for intensity extraction from Powder Data:
  – Pawley fit
  – Le Bail fit

• In both cases the procedure provides a set intensities corresponding to hkl indices of the corresponding contributions to each peak.

• In the case of severe overlap (no true multiplet is visible) the intensity extraction gives equal intensity to all the components of the fitted peak.
Powder Intensity Extraction

- Both Pawley and LeBail method are based on Rietveld equation:

\[ y_{obsi} = y_{bi} + S \sum_j s_j \sum_{hkl} LPAI_{hkl} \phi(2\theta_i - 2\theta_{hkl}) \]

**Pawley:**

- \( I_{hkl} \) is refined as a variable intensity \( I_{hkl} \) to fit the corresponding peak/s.

**Le Bail:**

- \( I_{hkl} \) is inserted arbitrarily in the first cycle and then through the LS procedure to achieve a list of integrated \( I_{hkl} \).
Powder Intensity Extraction

• After a Powder Intensity Extraction an h,k,l,Ihkl list is obtained but all available hkl values are those non-overlapping so they are all “unique” reflections.

• Accidental peak overlap reduces the number of observations further by a percentage up to 25% for large-cell/low-symmetry materials.
Powder vs Single Crystal intensities

- Conventional X-ray powder diffraction data for Gd$_2$Ca$_3$C$_{24}$O$_{40}$H$_{44}$ (cubic Fd3c) down to a resolution of 0.8 Å (2θ=140° for CuK$_\alpha$) provides ~353 unique reflections of which ~261 do not overlap significantly of which ~255 are observed (I>2σ$_i$ criterion).

- Conventional X-ray single crystal diffraction data for Gd$_2$Ca$_3$C$_{24}$O$_{40}$H$_{44}$ (cubic Fd3c) down to a resolution of 0.8 Å (2θ=55° for MoK$_\alpha$) provides ~851 unique reflections (none overlapping) of which ~512 are observed (I>2σ$_i$ criterion).

Peak overlap produces a reduction of at least 40% of the candidate observed intensities, and these calculations are made for a cubic unit cell (large) so things get worse for low-symmetry/large-cell problem.
Powder vs Single Crystal intensities

- In either case for $\text{Gd}_2\text{Ca}_3\text{C}_{24}\text{O}_{40}\text{H}_{44}$ (cubic Fd3c) we ended up with files containing $h, k, l, I_{hkl}$ and $\sigma I_{hkl}$ lists that have to be correctly processed before submitting the problem for structural determination.

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Intensity-Structure Factor relation

- The intensities can be related to the structure factors of the crystal by the equation:

\[ I_{hkl} = kALp|F_{hkl}|^2 \]

- \( k \): scale factor
- \( A \): absorption correction
- \( L \): Lorentz correction
- \( p \): Polarization correction
Intensity-Structure Factor relation

\[ I_{hkl} = kA\lambda p |F_{hkl}|^2 \]

\( k = \text{scale factor} \)
Intensity-Structure Factor relation

\[ I_{hkl} = kALp |F_{hkl}|^2 \]

A = absorption correction
Intensity-Structure Factor relation

\[ I_{hkl} = kAL_p |F_{hkl}|^2 \]

L = Lorentz correction

\[ L = \frac{1}{2} \sin(\theta) \]
Intensity-Structure Factor relation

\[ I_{hkl} = kALp |F_{hkl}|^2 \]

\[ p = \text{Polarization correction} \]

Sealed tube with filter: \( p = 1/2 + \cos^2(2\theta)/2 \)

Synchrotron radiation: \( p = 1 \)

Sealed tube with IBM: \( p = 1/2 + \cos^2(2\theta_m)\cos^2(2\theta)/2 \)
Further Corrections: Extinction

• One factor that significantly affect single crystal intensities is called extinction and comes in two types:
  – Primary Extinction
  – Secondary Extinction
Further Corrections: Extinction

- **Primary Extinction:**

  The primary extinction is responsible for the loss of intensity due to dynamic effect inside every block of a mosaic crystal. At the Bragg angle, each incident wave can undergo multiple reflections from different atomic planes; each scattering introduced causes a phase difference of $\lambda/4 = \pi/2$ so that along each direction waves differing by an even number of scattering, *i.e.* by $n\pi$ in phase, interfere, whose intensity decreasing rapidly with the number of scatterings. Because of the decrease in intensity of waves multiply scattered, the effect of waves differing by more than two scatterings can normally be neglected: in each direction one observes then the destructive interference between waves having a significant difference in intensity and an overall reduction of the intensity with respect to the intensity given by the kinematical theory.

http://reference.iucr.org/dictionary/Primary_extinction
Further Corrections: Extinction

- **Secondary Extinction:**

  The secondary extinction is responsible for the loss of intensity occurring when the incident beam crosses a crystal. Each plane of a family \((hkl)\) satisfying Laue equations (or Bragg's law) diffracts the incident beam, and thus subtracts part of the intensity to the incident beam. Successive planes of the same family will then experience a weakening of the incident beam and as a consequence the diffracted beams will result from the positive interference of waves not having the same intensities, as it is instead considered by the kinematical theory.

  Secondary extinction is equivalent to an increase of the linear absorption coefficient and is negligible for sufficiently small crystals.
Further Corrections: Extinction

- Both primary and secondary extinction cause intensity reduction that changes with $2\theta$ and the crystal morphology (hkl), therefore are experiment-dependent.

- None of these two extinctions affect powder diffraction data since crystallites in the powder are assumed to be similar in size to the mosaic blocks.

- It is very difficult to predict the presence of extinction in single crystal data until the structure is solved and observed and reasonable calculated intensities can be compared.

- Single crystal data affected by extinction in general can be used for structure determination (except for very special cases) but should be corrected during the refinement procedure. Almost never is corrected before structural determination and refinement.

http://reference.iucr.org/dictionary/Secondary_extinction
Further Corrections: Microabsorption

• In powder diffraction when two phases show a very strong absorption contrast (mixture of light element phase with heavy element phase) the intensity of the diffracted beam by the highly absorbing phase is decreased respect to the intensities of the diffracted beam coming from low-absorbing phase.

• This problem often produces erroneous results when quantitative phase analysis is performed using powder diffraction data and the Rietveld method.
Intensity-Structure Factor relation

• For a spherical (or low absorbing $\mu<1$) crystal:

$$|F_{\text{rel}}(hkl)| = \frac{I(hkl)}{Lp}^{1/2} = (Lp(hkl))^{1/2}$$

$$k |F_{\text{rel}}(hkl)|^2 = kLp(hkl) = |F(hkl)|^2$$

$|F_{\text{rel}}(hkl)|$ is the relative structure factor modulus (determined assuming k includes all unknown corections to the intensity that are independent of hkl or $\theta$.
Wilson Plot

• With a little help of mathematics we can estimate \( k \) to get the structure factors to its correct magnitude, and as a bonus we can estimate the average \( B \) for the crystal:

\[
\tilde{F}(hkl) = \sum_{j} f_{aj} e^{2\pi i (hx_j + ky_j + lz_j)} e^{-B_j \left(\frac{\sin(\theta)}{\lambda}\right)^2}
\]

\[
g_{aj} = f_{aj} e^{-B_j \left(\frac{\sin(\theta)}{\lambda}\right)^2}
\]

\[
\tilde{F}(hkl) = \sum_{j} g_{aj} e^{2\pi i (hx_j + ky_j + lz_j)}
\]

Atomic scattering factor

Atomic displacement (thermal, Debye-Waller) parameter
Wilson Plot

- With a little help of mathematics we can estimate $k$ to get the structure factors to its correct magnitude, and as a bonus we can estimate the average $B$ for the crystal:

$$f_a = \begin{cases} 
B = 2 \\
B = 5 
\end{cases}$$

$$g_a = f_a e^{-B_a \left( \frac{\sin(\theta)}{\lambda} \right)^2}$$
Wilson Plot

• With a little help of mathematics we can estimate $k$ to get the structure factors to its correct magnitude, and as a bonus we can estimate the average $B$ for the crystal:

$$\ln\left( \frac{\left\langle I^L_p(hkl) \right\rangle_{\theta}}{\sum_j f_{aj}(\theta)^2} \right) = -2B_{ave}\left( \frac{\sin(\theta)}{\lambda} \right)^2 + \ln(k)$$
Intensity scaling and statistics

- Normalized Structure Factor $E(hkl)$:
  \[ F(hkl) = \sum_j g_{aj} e^{2\pi i (hx_j + ky_j + lz_j)} \]
  \[ \left| \tilde{E}(hkl) \right|^2 = \frac{\left| \tilde{F}(hkl) \right|^2}{\sum_j f_{aj}(\Theta)^2} \]
  \[ < |E(hkl)|^2> = < |F_o(hkl)|^2>/ \Sigma_j f_{aj}^2 = \Sigma_j f_{aj}^2 / \Sigma_j f_{aj}^2 = 1 \]
Intensity scaling and statistics

- The Normalized Structure Factors $E(hkl)$ are a way of expressing the structure factors considering only the effect of amplitude decay by interference among radiation scattered by atoms and thermal motion.
- With the calculation of $E(hkl)$ we eliminate the effect of scattering amplitude decay with the scattering angle.
Intensity scaling and statistics

- $E(hkl)$ are fundamental for structural determination both from single crystal or powder diffraction data by Direct Methods or the Patterson Method.
- The distribution of $E(hkl)$ values with $2q$ is also useful since it follows the symmetry of the structure.
- A number of statistic indicators based on $E(hkl)$ are in general used to distinguish among centric and acentric space groups (task that cannot be performed only by inspecting the systematic absences in many cases) or to analyze the symmetry of special projections of the structure that may be useful to solve disorder problems or other rarities of crystal structures.
Intensity scaling and statistics

• We have shown that $<|E(hkl)|^2> = 1$

• It is possible to demonstrate that if a structure is:
  – Centrosymmetric: $<|E(hkl)^2-1|> = 0.968$
  – Non-centrosymmetric: $<|E(hkl)^2-1|> = 0.736$

• This is not only valid for every hkl but for special groups of them such as 0kl, h0l and hk0 that are the projections of crystal structure in the A (yz), B (zx) and C (xy) faces of the unit cell.
S.G. determination (example 1)

• Using systematic absences and intensity statistics the space group could be univocally determined if the data quality is high enough.

• Example: Orthorhombic cell

Reflection list shows the following systematic absences:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>P lattice</th>
<th>Intensity Statistics $&lt;E^2-1&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl:</td>
<td>no absences</td>
<td></td>
<td>hkl: 0.867 ambiguous</td>
</tr>
<tr>
<td>hk0:</td>
<td>h odd</td>
<td>a glide $\perp c$</td>
<td>hk0: 0.774 acentric</td>
</tr>
<tr>
<td>h0l:</td>
<td>no absences</td>
<td>m $\perp b$ or $2_1//b$</td>
<td>h0l: 0.981 centric</td>
</tr>
<tr>
<td>0kl:</td>
<td>k+l odd</td>
<td>n glide $\perp a$</td>
<td>0kl: 0.743 acentric</td>
</tr>
<tr>
<td>h00:</td>
<td>h odd</td>
<td>a glide</td>
<td></td>
</tr>
<tr>
<td>0k0:</td>
<td>k odd</td>
<td>n glide</td>
<td></td>
</tr>
<tr>
<td>00l:</td>
<td>l odd</td>
<td>n glide</td>
<td></td>
</tr>
</tbody>
</table>

Possible Space groups $Pn2_1a$ and $Pnma$