What do X-ray powder diffraction patterns look like?
Powder patterns - what information available in pattern?

1. peak positions
2. peak intensities - get crystal structure
3. peak shape
4. background structure

Intensities give atom positions
Intensities

X-rays scattered by electrons - electrons are in atoms

Scattering power $f$ of atom at $\theta = 0^\circ$ is no. electrons (atomic no.) $\times$ scattering power of one $e^-$
**Intensities**

Because of path length difference, scattering power decreases as $\theta$ increases.

Decrease is gradual since path length difference $\delta$ is small compared to $\lambda$.

Atomic scattering factor $f$ plotted as a function of $(\sin \theta)/\lambda$. $f$ values given in various tables, and as analytical functions.
Intensities

Now think of atoms in unit cells of a lattice

Waves reflected (diffracted) from the same atoms at the same x, y, z positions in all unit cells will be in phase

Thus, need to consider scattering in only one unit cell

Out-of-phaseness depends on:
As before, the scattered waves out of phase

a. relative positions of atoms $x_i, y_j, z_j$

b. diffraction angle $\theta$

But distances between the atoms much larger than between e–s
Intensities

Wave from each atom has:

\[ \text{amplitude} - f \]
\[ \text{phase factor} - \exp(2\pi i \Phi_j) = \exp(2\pi i(hx_j + ky_j + lz_j)) \]

\( x_j, y_j, z_j \) are positions  \( h, k, l \) related to diffraction angle

The scattering power for all atoms in unit cell obtained by adding up all scattered waves. This is the structure factor or structure amplitude

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

\[ F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (h x_j + k y_j + l z_j)} \]

Since \( F_{hkl} \) is an amplitude

\[ I_{hkl} \sim |F_{hkl}|^2 \]

In general, \( F \) is imaginary ....... so

\[ F = A + iB \quad \text{and} \quad F^*F = (A - iB)(A + iB) \]
Intensities

Simple example calculation:

Cu: Fm3m \[ a = 3.614 \text{ Å} \]

Cu atoms in 4a - (000) (1/2 0 1/2) (1/2 1/2 0) (0 1/2 1/2)

Equipoint 4a → 4 atoms/cell → 4 terms:

\[ F_{hkl} = f_{Cu} (e^0 + e^{\pi i(h + l)} + e^{\pi i(h + k)} + e^{\pi i(k + l)}) \]

Since \[ e^{i\phi} = \cos \phi + i \sin \phi \] (Euler’s rule)

\[ F_{hkl} = 0 \text{ or } 4f_{Cu} \]
Intensities

Derivation of extinction rule for I centering:

For every atom at \((x_j, y_j, z_j)\), there must be an atom at \((x_j + 1/2, y_j + 1/2, z_j + 1/2)\)

Then

\[
F_{hk\ell} = \sum_{j=1}^{N/2} f_j e^{2\pi i (hx_j + ky_j + lz_j)}
\]

Since \(e^{A+B} = e^A e^B\)

\[
F_{hk\ell} = \sum_{j=1}^{N/2} f_j (\exp (2\pi i (hx_j + ky_j + lz_j)))(1 + e^{\pi i (h + k + l)})
\]
Intensities

\[ F_{hkl} = \sum_{j=1}^{N} f_j \ e^{2\pi i (hx_j + ky_j + lz_j)} \]

Derivation of extinction rule for I centering

Since \( e^{A+B} = e^A e^B \)

\[ F_{hkl} = \sum_{j=1}^{N/2} f_j \ (\exp (2\pi i (hx_j + ky_j + lz_j)))(1 + e^{\pi i (h + k + l)}) \]

Every term in sum contains \( 1 + e^{\pi i (h + k + l)} \)

\[ = 1 + \cos (\pi (h + k + l)) + i \sin (\pi (h + k + l)) \]

\( \rightarrow 0 \) when \( h + k + l = \) odd number

Extinction rule for I centering: \( (hkl), h + k + l = 2n \)
Intensities

\[ F_{hk\ell} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]

A slightly more complex structure:

HoZn\textsubscript{2} is I 2/m 2/m 2/a, with \( a = 4.456 \pm 1 \), \( b = 7.039 \pm 3 \), \( c = 7.641 \pm 5 \text{Å} \)

Ho in 4e (0,1/4,z) (0,3/4,\bar{z}) + I, \( z = 0.5281 \pm 4 \)

Zn in 8h (0,y,z) (0,\bar{y},\bar{z}) (0,1/2 + y,\bar{z}) (0,1/2 - y,z) + I,
\( y = 0.0410 \pm 9 \), \( z = 0.1663 \pm 8 \)

\( F(hkl) = f_{Ho} (\exp (2\pi i(k/4 + l(0.5281)))) + \exp (2\pi i(3/4k + l(0.4719)))) \)
+ \( \exp (2\pi i(1/2h + 3/4k + l(0.0281)))) + 1 \text{ more term} \)
+ \( f_{Zn} (\exp (2\pi i(k(0.0410) + l(0.1663)))) + 7 \text{ more terms} \)
Intensities

\[ F_{hkl} = \sum_{j=1}^{N} f_j \ e^{2\pi i (hx_j + ky_j + lz_j)} \]

Now

\[ I_{hkl} = \text{scale factor} \cdot p \cdot LP \cdot A \cdot |F_{hkl}|^2 \cdot e^{-2M} \]

\( p = \text{multiplicity} \)

accounts for differing probabilities that symmetry equivalent planes \((hkl)\) will reflect

Example - cubic

\{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1}) \hspace{1cm} p = 6

\{110\} = (110), (101), (011), (\bar{1}10), (\bar{1}01), (0\bar{1}1), (1\bar{1}0), (10\bar{1}),

(01\bar{1}), (\bar{1}10), (\bar{1}0\bar{1}), (0\bar{1}\bar{1}) \hspace{1cm} p = 12
Intensities

\[ F_{hk\ell} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]

Now

\[ I_{hk\ell} = \text{scale factor} \cdot p \cdot LP \cdot A \cdot |F_{hk\ell}|^2 \cdot e^{-2M} \]

LP = Lorentz-polarization factor

P accounts for polarization state of incident beam (in most powder x-ray diffractometers, unpolarized)

Lorentz factor corrects for geometrical broadening of reflections as 2\(\theta\) increased
Intensities

\[ F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]

Now

\[ I_{hkl} = \text{scale factor} \cdot p \cdot LP \cdot A \cdot |F_{hkl}|^2 \cdot e^{-2M} \]

Lorentz factor corrects for geometrical broadening of reflections as \(2\theta\) increased

Which reflection is more intense?
Intensities

\[ F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]

Now

\[ I_{hkl} = \text{scale factor} \cdot p \cdot LP \cdot A \cdot |F_{hkl}|^2 \cdot e^{-2M} \]

LP = Lorentz-polarization factor

\[ LP = \frac{(1 + \cos^2 2\theta)}{\sin^2 \theta \cos \theta} \]

No monochromator

20\,M \approx 26.5^\circ
Intensities

\[
F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}
\]

Now

\[
I_{hkl} = \text{scale factor} \cdot p \cdot \text{LP} \cdot A \cdot |F_{hkl}|^2 \cdot e^{-2M}
\]

\(A = \text{absorption factor}\)

In standard X-ray powder diffractometers, when specimen is dense and thick, \(A\) is considered constant over all \(2\theta\)
**Intensities**

\[
F_{hk\ell} = \sum_{j=1}^{N} f_j \ e^{2\pi i (hx_j + ky_j + lz_j)}
\]

Now

\[
I_{hk\ell} = \text{scale factor} \cdot \ p \cdot L\ P \cdot A \cdot |F_{hk\ell}|^2 \cdot e^{-2M(T)}
\]

\[e^{-2M(T)} = \text{temperature factor (also called Debye-Waller factor)}\]

\[2M(T) = 16\pi^2 \mu(T)^2 (\sin \theta)^2 / \lambda^2\]

\[\mu^2 = \text{mean square amplitude of thermal vibration of atoms direction normal to planes (hk\ell)}\]

\[
\frac{I(\text{high } T)}{I(\text{low } T)} = \frac{e^{-2M(\text{high } T)}}{e^{-2M(\text{low } T)}} = \frac{1}{e^{2M(\text{high } T) - 2M(\text{low } T)}}
\]
Intensities $\rightarrow$ crystal structure

So, OK, how do we do it?

Outline of procedure:

Measure reflection positions in x-ray diffraction pattern - index, get unit cell type and size, possible space groups

Measure density, if possible, to get number formula units/unit cell (N) density = N x formula wt/cell volume x Avogadro's no.

Measure reflection intensities, get F-values, calculate electron density distribution from

$$
\rho(xyz) = \left(\frac{1}{V}\right) \sum_h \sum_k \sum_l F(hkl) e^{-2\pi i(hx+ky+lz)}
$$
Intensities $\rightarrow$ crystal structure

$$\rho(\text{xyz}) = \left( \frac{1}{V} \right) \sum_{n} \sum_{k} \sum_{l} F(hkl)e^{-2\pi i(hx+ky+lz)}$$

Electron density distribution tells where the atoms are

$\rho(\text{XYZ})$ is plotted and contoured to show regions of high electron density
Intensities $\rightarrow$ crystal structure

But WAIT!!!

\[ I_{hkl} = K |F_{hkl}|^2 = K F_{hkl}^* \times F_{hkl} \]

\[ = K (A_{hkl} - iB_{hkl}) (A_{hkl} + iB_{hkl}) = K (A_{hkl}^2 + B_{hkl}^2) \]

\[ \sqrt{I_{hkl}/K} = \sqrt{(A_{hkl}^2 + B_{hkl}^2)} \]

So, can't use \( I_{hkl} \)'s directly to calculate \( F_{hkl} \)'s and \( \rho(XYZ) \)!!

\[ \rho(xyz) = \left( \frac{1}{V} \right) \sum_h \sum_k \sum_l F(hkl) e^{-2\pi i (hx+ky+lz)} \]

Many techniques for using \( I_{hkl} \)'s to determine atom positions have been developed, most of which, at some stage, involve formulating a model for the crystal structure, and then adjusting it to fit the intensity data.
Powder patterns - what information available in pattern?

1. peak positions
2. peak intensities
3. peak shape - peak broadening
4. background structure

Two effects
Peak broadening

Here, have set of planes reflecting in-phase at \( \theta \) (Bragg condition)

X-rays at non-\( \theta \) angles won't reflect; every reflected ray has a mate deeper in the crystal which is 180° out of phase with it - reflection is narrow

Small crystallite size broadens reflections - becomes significant below 1 micron
Peak broadening

Microstrain & chemical inhomogeneity distort the structure so that interplanar distances not constant - vary a little from an average value - broadens peaks
Peak broadening

If broadening due to small crystallite size only, simple technique to determine that size, $L$, from the breadth, $B$

**Scherrer eqn.**:

\[ B_{\text{size}} = \left( \frac{180}{\pi} \right) \left( \frac{K\lambda}{L \cos \theta} \right) \quad (K = 0.9, \text{ usually}) \]

\[ B_{\text{tot}}^2 = B_{\text{instr}}^2 + B_{\text{size}}^2 \]

Must subtract broadening due to instrument. Measure peak width from suitable standard (ex: LaB$_6$ - NIST SRM 660)
Peak broadening

If broadening due to small crystallite size only, simple technique to determine that size, L, from the breadth, B

Scherrer eqn.:

\[ B_{\text{size}} = \left( \frac{180}{\pi} \right) \left( \frac{K\lambda}{L \cos \theta} \right) \quad (K - 0.9, \text{ usually}) \]

\[ B_{\text{tot}}^2 = B_{\text{instr}}^2 + B_{\text{size}}^2 \]

\[ 10^4\text{Å} \quad B_{\text{size}} = \left( \frac{180}{\pi} \right) \left( \frac{1.54}{10^4} \cos 45^\circ \right) = 0.0125^\circ 2\theta \]

\[ 10^3\text{Å} \quad B_{\text{size}} = 0.125^\circ 2\theta \]

\[ 10^2\text{Å} \quad B_{\text{size}} = 1.25^\circ 2\theta \]

\[ 10\text{Å} \quad B_{\text{size}} = 12.5^\circ 2\theta \]
Peak broadening

If broadening due to small crystallite size & microstrain, simple technique to determine size, L, & strain, $<\varepsilon>$, from the breadth, B

Williamson-Hall method:

\[
\text{strain broadening} - B_{\text{strain}} = <\varepsilon> \left(4 \tan \theta \right)
\]

\[
\text{size broadening} - B_{\text{size}} = \left( \frac{K\lambda}{L \cos \theta} \right)
\]

\[
(B_{\text{obs}} - B_{\text{inst}}) = B_{\text{size}} + B_{\text{strain}}
\]

\[
(B_{\text{obs}} - B_{\text{inst}}) = \left( \frac{K\lambda}{L \cos \theta} \right) + 4 <\varepsilon>(\tan \theta)
\]

\[
(B_{\text{obs}} - B_{\text{inst}}) \cos \theta = \left( \frac{K\lambda}{L} \right) + 4 <\varepsilon>(\sin \theta)
\]
Peak broadening

If broadening due to small crystallite size & microstrain, simple technique to determine size, \( L \), & strain, \(<\varepsilon>\), from the breadth, \( B \)

Williamson-Hall method:

\[
(B_{\text{obs}} - B_{\text{inst}}) \cos \theta = (K\lambda / L) + 4 <\varepsilon>(\sin \theta)
\]
Peak broadening

If broadening due to small crystallite size & microstrain, can use other more complex methods for analysis:

- Warren-Averbach
- double Voigt
- x-ray tracing
Powder patterns - what information available in pattern?

1. peak positions
2. peak intensities - get crystal structure
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Obvious structural information in background - due to non-crystalline character of material (disorder)