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

X-rays scattered by electrons - electrons are in atoms



Scattering power f of atom at $\theta = 0^{\circ}$ is no. electrons (atomic no.) × scattering power of one e⁻

Because of path length difference, scattering power decreases as θ increases

Decrease is gradual since path length difference δ is small compared to λ

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



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, y, z, But distanted wangle atoms much larger than between e⁻s

Wave from each atom has:

amplitude - fphase factor - exp $(2\pi i\Phi_i) = exp (2\pi i(hx_i + ky_i + lz_i))$

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

$$\mathbf{F}_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

$$\mathbf{F}_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

Since F_{hkl} is an amplitude

$$|\mathbf{I}_{hkl} \sim |\mathbf{F}_{hkl}|^2$$

In general, F is imaginary so

F = A + iB and $F^*F = (A - iB)(A + iB)$

$$\mathbf{F}_{hk1} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

Simple example calculation:

Cu: Fm3m a = 3.614 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:

 $F_{hkl} = f_{Cu} \left(e^0 + e^{\pi i (h+l)} + e^{\pi i (h+k)} + e^{\pi i (k+l)} \right)$

Since $e^{i\phi} = \cos \phi + i \sin \phi$ (Euler's rule)

 $F_{hkl} = 0 \text{ or } 4f_{Cu}$

$$\mathbf{F}_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

Derivation of extinction rule for I centering:

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

$$F_{hkl} = \sum_{j=1}^{N/2} f_j \{(\exp (2\pi i(hx_j + ky_j + lz_j) + \exp (2\pi i(h(x_j + 1/2) + k(y_j + 1/2) + l(z_j + 1/2)))\}$$

exp (2\pi i(h(x_j + 1/2) + k(y_j + 1/2) + l(z_j + 1/2)))\}
Since $e^{A + B} = e^A e^B$
 $F_{hkl} = \sum_{j=1}^{N/2} f_j (\exp (2\pi i(hx_j + ky_j + lz_j)))(1 + e^{\pi i(h + k + 1)})$

$$\mathbf{F}_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

Derivation of extinction rule for I centering



$$\mathbf{F}_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

A slightly more complex structure:

HoZn₂ is I 2/m 2/m 2/a, with a = 4.456 ± 1, b = 7.039 ± 3, c = 7.641 ± 5Å Ho in 4e (0,1/4,z) (0,3/4, \bar{z}) + I, z = 0.5281 ± 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 ± 9, z = 0.1663 ± 8

F(hkl) = f_{Ho} (exp (2 π i(k/4 + l(0.5281))) + exp (2 π i(3/4k + l(0.4719)))

+ exp $(2\pi i(1/2h + 3/4k + I(0.0281))) + 1$ more term)

+ f_{Zn} (exp (2 π i(k(0.0410) + l(0.1663))) + 7 more terms)

Example - cubic $\{100\} = (100), (010), (001), (\overline{100}), (0\overline{10}), (00\overline{1}) \quad p = 6$ $\{110\} = (110), (101), (011), (\overline{110}), (\overline{101}), (0\overline{11}), (1\overline{10}), (10\overline{1}),$ $(01\overline{1}), (\overline{110}), (\overline{101}), (0\overline{11}) \quad p = 12$

accounts for differing probabilities that symmetry

equivalent planes (hkl) will reflect

p = multiplicity

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

$$\mathbf{F}_{hk1} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

Intensities

Now

$$\mathbf{F}_{hkl} = \sum_{j=1}^{N} \mathbf{f}_{j} \mathbf{e}^{2\pi i (hx_{j} + ky_{j} + lz_{j})}$$

Now

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 2θ increased

$$\mathbf{F}_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

Now

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

Lorentz factor corrects for geometrical broadening of reflections as 2θ increased

Which reflection is more intense?



$$\mathbf{F}_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

Now

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

LP = Lorentz-polarization factor

 $LP = (1 + \cos^2 2\theta) / \sin^2 \theta \cos \theta$



$$\mathbf{F}_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

Now

A = absorption factor

In standard X-ray powder diffractometers, when specimen is dense and thick, A is considered constant over all 20 $\,$

$$\mathbf{F}_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

Now

 $e^{-2M(T)}$ = temperature factor (also called Debye-Waller factor) 2M(T) = $16\pi^2 \mu(T)^2 (\sin \theta)^2 / \lambda^2$

 μ^2 = mean square amplitude of thermal vibration of atoms direction normal to planes (hkl)

$$\frac{I(\text{high T})}{I(\text{low T})} = \frac{e^{-2M(\text{high T})}}{e^{-2M(\text{low T})}} = \frac{1}{e^{2M(\text{high T}) - 2M(\text{low T})}}$$

Intensities —> 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 × formula wt/cell volume × Avogadro's no.

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

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

Intensities —> crystal structure $\rho(xyz) = \left(\frac{1}{V}\right) \sum_{h} \sum_{k} \sum_{l} \mathbf{F}(hkl)e^{-2\pi i(hx+ky+lz)}$

Electron density distribution tells where the atoms are

ρ(XYZ) is plotted and contoured to show regions of high electron density



Intensities -> crystal structure But WAIT!!! I_{hkl} = K |F_{hkl}|² = K F_{hkl}* × 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 $\rho(XYZ)$!!

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

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

Here, have set of planes reflecting in-phase at θ (Bragg condition) X-rays at non- θ 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



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



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

Scherrer eqn.:

 $B_{size} = (180/\pi) (K\lambda / L \cos \theta) \quad (K - 0.9, usually)$ $B_{tot}^2 = B_{instr}^2 + B_{size}^2$

Must subtract broadening due to instrument. Measure peak width from suitable standard (ex: LaB₆ -NIST SRM 660)



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

Scherrer eqn.:

 $B_{size} = (180/\pi) (K\lambda / L \cos \theta) \quad (K - 0.9, usually)$ $B_{tot}^2 = B_{instr}^2 + B_{size}^2$

- 10^{4} Å $B_{size} = (180/\pi) (1.54 / 10^{4} \cos 45^{\circ}) = 0.0125^{\circ} 2\theta$
- 10^{3} Å $B_{size} = 0.125^{\circ} 2\theta$
- 10^2\AA B_{size} = 1.25° 20
- 10\AA B_{size} = 12.5° 20

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

Williamson-Hall method:

strain broadening - $B_{strain} = \langle \epsilon \rangle$ (4 tan θ) size broadening - $B_{size} = (K\lambda / L \cos \theta)$ $(B_{obs} - B_{inst}) = B_{size} + B_{strain}$

 $(B_{obs} - B_{inst}) = (K\lambda / L \cos \theta) + 4 \langle \epsilon \rangle (\tan \theta)$ $(B_{obs} - B_{inst}) \cos \theta = (K\lambda / L) + 4 \langle \epsilon \rangle (\sin \theta)$

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

Williamson-Hall method:

$$(B_{obs} - B_{inst}) \cos \theta = (K\lambda / L) + 4 < \varepsilon > (\sin \theta)$$



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
- 3. peak shape
- 4. background structure

Obvious structural information in background - due to noncrystalline character of material (disorder)

