POWDER DIFFRACTION

Principles

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CONTENTS

• Diffraction viewed as Bragg’s law.
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• Crystals - Diffraction planes - Miller indices
• Reciprocal space – reciprocal unit cell
• Ewald construction, monochromatic - single-crystal – powder
• Ewald construction, white/pink radiation – single-crystal – powder
• Reciprocal lattice points – the interference function
BRAGG’S LAW

\[ 2d_{hkl} \sin \theta_{hkl} = n \lambda \]

(Geometric interpretation of diffraction)

SINGLE- VS. MULTI-CRYSTAL DIFFRACTION

One crystal

Four crystals

Powder
POWDER DIFFRACTION

CRYSTAL PLANES – MILLER INDICES

Note that the 2, 2 and -2, -2 planes are identical.
CRYSTAL PLANES – d-VALUES

\[
\frac{1}{d_{hkl}^2} = \frac{[h^2 \sin^2 \alpha/ a^2 + k^2 \sin^2 \beta/ b^2 + l^2 \sin^2 \gamma/ c^2 + 2kl(\cos \beta \cos \gamma - \cos \alpha)/(bc) + 2hl(\cos \alpha \cos \gamma - \cos \beta)/(ac)]}{[1 - \cos^2 \alpha \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma]}
\]

\[
\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2 + l^2)}{a^2}
\]

RECIPROCAL SPACE

\[
a^* = \frac{b c}{V_{\text{cell}}} \quad (= \frac{b c \sin \alpha}{V_{\text{cell}}})
\]

\[
b^* = \frac{a c}{V_{\text{cell}}} \quad (= \frac{a c \sin \beta}{V_{\text{cell}}})
\]

\[
c^* = \frac{a b}{V_{\text{cell}}} \quad (= \frac{a b \sin \gamma}{V_{\text{cell}}})
\]

\[
a \cdot a^* = 1 \quad a \cdot b^* = 0
\]

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

Direct space

Reciprocal space

\[ d_{32} = \frac{1}{d_{32}^*} \]

**EWALD CONSTRUCTION**

Single-crystal, monochromatic radiation

\[ R = \frac{1}{\lambda} \]
\[ R \cdot \sin \theta = r_{hk} / 2 \]
\[ r_{hk} = d_{hk}^* = \frac{1}{d_{hk}} \]
\[ 2d_{hk} \sin \theta_{hk} = \lambda \]

Reflections within a radius of 2R can be observed

http://www.doitpoms.ac.uk/tlplib/reciprocal_lattice/ewald.php
SINGLE-CRYSTAL LAUE DIFFRACTION

Single-crystal, white or ”pink” radiation

Max. wavelength
Min. energy

Min. Wavelength
Max. energy

All reflections between the two Ewald spheres can be observed.

POWDER DIFFRACTION

Powder, monochromatic radiation
POWDER DATA COLLECTION

Bragg-Brentano (reflection mode)  
Guinier (transmission mode)

![Bruker D8 Advance](image1)

![Huber G670](image2)

ENERGY DISPERSIVE POWDER DIFFRACTION

Powder, white or "pink" radiation

Max. wavelength
Min. energy

Min. wavelength
Max. energy

Fixed detector angle
Energy dispersive (solid state) detector

Reflections crossing the green line can be observed
\[ f_j = f_0 \exp\{2\pi i(r + \nu) \cdot r^*\} \]
\[ \nu = n_1a + n_2b + n_3c \]
\[ F_{\text{cryo}} = \sum_{\text{cryo}} \exp\{2\pi i \cdot \nu \cdot r^*\} \cdot F_{\text{hal}} = J(r^*) \cdot F_{\text{hal}} \]

\[ \sum_{\text{cryo}} \exp\{2\pi i n_a \cdot r^*\} = (1 - \exp\{2\pi i N_j a \cdot r^*\}) / (1 - \exp\{2\pi i a \cdot r^*\}) = \sin\{\pi N_j a \cdot r^*\} / \sin\{\pi a \cdot r^*\} \]

\[ \sin^2\{\pi N_j x\} / \sin^2\{\pi x\} \]
ANISOTROPIC SIZE EFFECTS

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Fe₂O₃

a = 5.0364(8), c = 13.750(2) Å  D(a) = 399(3) Å, D(c) = 87(2) Å