XRD Intensity Calculations

-Example FCC Cu (centric) \( e^{ix} = \cos x \)

\[
I_{hkl} \propto |F_{hkl}|^2 \quad \text{Consider Copper which is } F = \frac{4}{3} \frac{2}{m} \text{ with } a=3.615\text{Å}; \text{ atoms in positions } [0,0,0] \\
[\frac{1}{2},\frac{1}{2},0][\frac{1}{2},0,\frac{1}{2}][0,\frac{1}{2},\frac{1}{2}] \text{ and } \lambda=1.54\text{Å}
\]

\[
F_{hkl} = f_{Cu}(e^{2\pi(0)} + e^{2\pi(h/2+k/2)} + e^{2\pi(h/2+l/2)} + e^{2\pi(k/2+l/2)})
\]

\[
F_{hkl} = f_{Cu}(1 + e^{2\pi(h+k)} + e^{2\pi(h+l)} + e^{2\pi(k+l)})
\]

\[
I = |F|^2 p \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \quad [3]
\]

Know this

where \( I = \text{relative integrated intensity (relative area under the curve of intensity vs. } 2\theta) \), \( F = \text{structure factor} \), \( p = \text{multiplicity factor} \), see handout appendix 13 (table); and \( \theta = \text{Bragg angle} \). The trig. terms in parentheses are the Lorentz-polarization (LP) factor (in degrees).

-This is an approximate solution, since other factors contribute slightly such as temperature and absorption factors.

<table>
<thead>
<tr>
<th>( S )</th>
<th>( (hkl) )</th>
<th>( F_{hkl} )</th>
<th>( I_{hkl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>110</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>111</td>
<td>4f_{Cu}</td>
<td>16f^2_{Cu}</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>4f_{Cu}</td>
<td>16f^2_{Cu}</td>
</tr>
<tr>
<td>5</td>
<td>210</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>211</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>220</td>
<td>4f_{Cu}</td>
<td>16f^2_{Cu}</td>
</tr>
</tbody>
</table>

All \((hkl)\) reflections will have different intensities! Let’s determine why….

• Agreement between calculated and observed intensities is satisfactory.
• Note how the \( p + \text{LP} \) values have a strong influence on line \((hkl)\) intensity.

\[
\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)
\]

Column 4:

\[
F^2 = 16f^2_{Cu}
\]

Column 12: Eqn. [3]

Column 13: values from column 12 are recalculated to normalize the intensity to 10

Column 14: observed intensities

(with visual scale: \( vs = \text{very strong} \), \( s = \text{strong} \), \( m = \text{medium} \), \( w = \text{weak} \))

\[
I_{hkl} \propto \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}
\]

Relative integrated intensity

<table>
<thead>
<tr>
<th>( \frac{I_{hkl}}{F^2} )</th>
<th>( p )</th>
<th>( 1 + \cos^2 2\theta )</th>
<th>( \text{Calc.} )</th>
<th>( \text{Calc.} )</th>
<th>( \text{Obs.} )</th>
</tr>
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<tbody>
<tr>
<td>6464</td>
<td>8</td>
<td>12.03</td>
<td>6.22 \times 10^6</td>
<td>10.0</td>
<td>vs</td>
</tr>
<tr>
<td>5776</td>
<td>6</td>
<td>8.50</td>
<td>2.94</td>
<td>4.7</td>
<td>s</td>
</tr>
<tr>
<td>3844</td>
<td>12</td>
<td>3.70</td>
<td>1.71</td>
<td>2.7</td>
<td>m</td>
</tr>
<tr>
<td>3181</td>
<td>24</td>
<td>2.83</td>
<td>2.16</td>
<td>3.4</td>
<td>s</td>
</tr>
<tr>
<td>3003</td>
<td>8</td>
<td>2.74</td>
<td>0.66</td>
<td>1.1</td>
<td>m</td>
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<tr>
<td>2500</td>
<td>6</td>
<td>3.18</td>
<td>0.48</td>
<td>0.8</td>
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</tr>
<tr>
<td>2190</td>
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<td>2.52</td>
<td>4.1</td>
<td>w</td>
</tr>
<tr>
<td>2079</td>
<td>24</td>
<td>6.15</td>
<td>3.06</td>
<td>4.9</td>
<td>w</td>
</tr>
</tbody>
</table>
PDF#01-071-6715 (RDB): QM=Blank(B); d=Calculated; I=Calculated

Zirconia, (Zirconium Oxide) ZrO₂

Radiation=CuKα  Lambda=1.5405999  Filter=
Calibration=  2Theta=31.495-140.153

Cubic - Profile Analysis, Fm-3m (space group 225)

CELL: 4.916 x 4.916 x 4.916 <90.0 x 90.0 x 90.0>  P.S.=cF12.00
Density(c)=6.889  Mwt=123.22  Ref: Ibid.

<table>
<thead>
<tr>
<th>2-Theta</th>
<th>d(Å)</th>
<th>I(f)</th>
<th>( h k l)</th>
<th>Theta(θ)</th>
<th>1/(2d)</th>
<th>2pi/d</th>
<th>n^2</th>
</tr>
</thead>
<tbody>
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<td>31.495</td>
<td>2.8383</td>
<td>100</td>
<td>(1 1 1)</td>
<td>15.747</td>
<td>0.1762</td>
<td>2.2138</td>
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<tr>
<td>36.526</td>
<td>2.4580</td>
<td>19.4</td>
<td>(2 0 0)</td>
<td>18.263</td>
<td>0.2034</td>
<td>2.5562</td>
<td>4</td>
</tr>
<tr>
<td>52.615</td>
<td>1.7381</td>
<td>47.5</td>
<td>(2 2 0)</td>
<td>26.308</td>
<td>0.2877</td>
<td>3.6150</td>
<td>8</td>
</tr>
<tr>
<td>62.622</td>
<td>1.4822</td>
<td>28.8</td>
<td>(3 1 1)</td>
<td>31.311</td>
<td>0.3373</td>
<td>4.2390</td>
<td>11</td>
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<tr>
<td>65.748</td>
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<td>(2 2 2)</td>
<td>32.874</td>
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<td>77.624</td>
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<td>(3 3 1)</td>
<td>43.079</td>
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<td>0.4549</td>
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<tr>
<td>100.283</td>
<td>1.0035</td>
<td>8.8</td>
<td>(4 2 2)</td>
<td>50.142</td>
<td>0.4983</td>
<td>6.2615</td>
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</tr>
<tr>
<td>109.015</td>
<td>0.9461</td>
<td>6.4</td>
<td>(5 1 1)</td>
<td>54.508</td>
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<td>124.844</td>
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<td>(4 4 0)</td>
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<td>0.5754</td>
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<td>135.943</td>
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<td>(5 3 1)</td>
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<td>140.153</td>
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<td>(4 4 2)</td>
<td>70.077</td>
<td>0.6103</td>
<td>7.6687</td>
<td>36</td>
</tr>
</tbody>
</table>

Where 1/(2d) = sinθ/λ and n^2 = S (=h^2+k^2+l^2)

(111) allowed

(110) extinct

class26/2
The effect of changes in symmetry on the multiplicity and peak intensity of diffraction peaks

XRD Intensity Calculations
-Example Rutile (TiO$_2$) (centric)

\[ e^{ix} = \cos x \]
Calculate $I_{110}$ for TiO$_2$, CuKα, powder diffractometer. Ignore scale, absorption, and temperature factors.

TiO$_2$ is $P4_2/mnm$ with $a = 4.5929$, $c = 2.9591$ Å, and Ti atoms in 2a and O atoms in 4f $(x = 0.3056)$.

\[
e^{ix} = \cos x
\]
XRD Intensity Calculations

-Example Rutile (TiO$_2$) (centric)

\[
I_{001} = ?
\]

Expect to see $I_{001}$ since primitive unit cell

\[
\frac{1}{d^2} = \frac{\frac{1}{h^2} + \frac{1}{k^2} + \frac{1}{l^2}}{2a^2} = \frac{1}{(2.954)^2} = 0.1142 \Rightarrow d = 2.954 \Rightarrow \frac{1}{2d} = \frac{1}{5 \sin \theta} \Rightarrow \frac{I}{0.1690} = 0.1690 \Rightarrow \frac{I}{5} = 0.1690
\]

\[
\theta = 15.081^\circ
\]

\[
F_{001} = \sum f e^{-2\pi i (2h)}
\]

\[
F_{001} = \int f(x, y, z) e^{-2\pi i (2x)} dx dy dz
\]

\[
= 15.206 \left[ 1 - 1 \right] + 6.275 \left[ 1 + 1 - 1 - 1 \right] = 0 + 0 = 0
\]

This example shows that primitive cell has additional extention because have more than one element. Atomic model for this crystal...
Atomic Scattering Factors for TiO$_2$ (Rutile)

- Ti$^{4+}$ (f values from appendix 12)
- O$^{-2}$ (f values from appendix 12)
- Ti$^{4+}$ (f values interpolated for I$_{110}$ & I$_{001}$)
- O$^{-2}$ (f values interpolated for I$_{110}$ & I$_{001}$)

Graph showing the relationship between atomic scattering factor (f) and sin(θ)/λ for Ti$^{4+}$ and O$^{-2}$ ions in TiO$_2$ (Rutile).
1. For ZnTe (Zincblende structure), $SG \# 216: F\bar{4}3m$
   
   Zn in $4a (0,0,0) + F = (0,\frac{1}{2},\frac{1}{2}) (\frac{1}{2},0,\frac{1}{2})$  
   Te in $4c (\frac{1}{4},\frac{1}{4},\frac{1}{4}) + F = (\frac{1}{4},\frac{3}{4},\frac{3}{4}) (\frac{3}{4},\frac{1}{4},\frac{3}{4}) (\frac{3}{4},\frac{3}{4},\frac{1}{4})$

a. Draw the unit cell, $a=6.1026\text{Å}$
b. Calculate the structure factor, $F$
c. Determine the selection rules for $hkl$ reflections. You should be able to determine the selection rules going from $S=1$ to $S=16$. Show all your work.
d. Based on your answers in (b) and (c), which set of reflections will have the highest diffraction intensity and the lowest diffraction intensity? Do not calculate the Intensities, just look at your answers. You may want to draw the $(hkl)$ planes to help you.
e. Now calculate $I_{111}$ and $I_{200}$ and $I_{220}$ with CuKα (x-ray wavelength is 1.54Å). How do these values compare with your answer in (d).
XRD Intensity Calculations
-Example Zincblende (ZnTe) (non-centric)

Te atoms in ZnTe at \((1/4,1/4,1/4)\) \((1/4,3/4,3/4)\) \((3/4,1/4,3/4)\) \((3/4,3/4,1/4)\) → 
\((3/4,3/4,3/4)\) \((3/4,1/4,1/4)\) \((1/4,3/4,1/4)\) \((1/4,1/4,3/4)\) “Non-Equivalent points thus non-centric”

\[ e^{ix} = \cos x + i \sin x \]
XRD Intensity Calculations

- Example Zincblende (ZnTe) (non-centric)

\[ F_{222} = 4 \left( f_{zn} - f_{te} \right) \]

\[ F_{400} = 4 \left( f_{zn} + f_{te} \right) \]

Based on all \( s = 1 \) to \( s = 16 \) selection rules are:

(a) \( h, k, l \) mixed odd and even, \( F = 0 \)

(b) \( h + k + l \) is odd, as in \( s = 3 \) and \( s = 11 \).

Have to multiply by its complex conjugate.

\[ F_{311} = 4 \left( f_{zn} + i f_{te} \right) \]

\[ |F_{311}|^2 = F_{311}^* F_{311} = 16 \left( f_{zn} + f_{te} \right)^2 \]

(c) \( s = 4 \) \( F_{200} = 4 \left( f_{zn} - f_{te} \right) \) and \( F_{200}^* = 16 \left( f_{zn} - f_{te} \right)^2 \) for each.

\[ |F_{200}|^2 = 16 \left( f_{zn} - f_{te} \right)^2 \]

(d) \( s = 8 \) \( F_{222} = 4 \left( f_{zn} + f_{te} \right) \) and \( F_{222}^* = 16 \left( f_{zn} + f_{te} \right)^2 \) for each.

\[ |F_{222}|^2 = 16 \left( f_{zn} + f_{te} \right)^2 \]
XRD Intensity Calculations

- Example Zincblende (ZnTe) (non-centric)

(d) As we went over in class and from your handout $f_{\text{ZnTe}} > f_{\text{Zn}}$ since $\frac{2}{2} > \frac{5}{2} > \frac{3}{2}$

For (111): \[ \text{High Int.} \]

For (200): \[ \text{Low Int.} \]

For (220): \[ \text{High Int.} \]

For (311): \[ \text{Low Int.} \]

For (222): \[ \text{High Int.} \]

For (400): \[ \text{Low Int.} \]

\[ I_{\nu} = \left| \mathbf{F}_{\nu} \right|^2 \mathbf{P} \]

\[ I_{(111)} = \left| \mathbf{F}_{(111)} \right|^2 \mathbf{P} \]

\[ \sin^2 \theta = \frac{\mathbf{P}}{4a^2 (h+k+l)} \Rightarrow \sin^2 \theta = (1.4)^2 \]

\[ \frac{46,1026}{i(111)} \Rightarrow \sin^2 \theta = 0.04776 \]

\[ \theta = 12.62^\circ \]

\[ \sin \theta = 0.21854 \]

\[ i = 0.14 \]

\[ f_{\text{ZnTe}} = 26.8 - [26.8 - 22.4] \cdot 0.4 = 25.04 \]

\[ f_{\text{Zn}} = 42.7 - [42.7 - 41.3] \cdot 0.4 = 45.14 \]

\[ \left| \mathbf{F}_{(111)} \right|^2 = 16 \left( f_{\text{ZnTe}}^2 + f_{\text{Zn}}^2 \right) = 16 \left( (25.04)^2 + (45.14)^2 \right) = 42634 \]

\[ p = 8 \]

\[ \mathbf{P} = \left( \frac{1 + \cos^2 \theta}{\sin^2 \theta} \right) = 24.03 \]

\[ I_{200} = \left| \mathbf{F}_{200} \right|^2 \mathbf{P} \]

\[ \sin^2 \theta = \frac{\mathbf{P}}{4a^2 (h+k+l)} \Rightarrow \sin^2 \theta = (1.4)^2 \]

\[ \frac{46,1026}{i(200)} \Rightarrow \sin^2 \theta = 0.06368 \Rightarrow \theta = 14.62^\circ \]

\[ \sin \theta = 0.21854 \]

\[ f_{\text{ZnTe}} = 26.8 - [26.8 - 22.4] \cdot 0.6 = 24.16 \]

\[ f_{\text{Zn}} = 42.7 - [42.7 - 41.3] \cdot 0.6 = 43.86 \]

\[ \left| \mathbf{F}_{(200)} \right|^2 = 16 \left( f_{\text{ZnTe}}^2 - f_{\text{Zn}}^2 \right) = 16 \left( 24.16 - 43.86 \right) = 6.204 \]

\[ p = 6 \]

\[ \mathbf{P} = \left( \frac{1 + \cos^2 \theta}{\sin^2 \theta} \right) = 28.57 \]

\[ I_{220} = \left| \mathbf{F}_{220} \right|^2 \mathbf{P} \]

\[ \sin^2 \theta = \frac{\mathbf{P}}{4a^2 (h+k+l)} \Rightarrow \sin^2 \theta = (1.4)^2 \]

\[ \frac{46,1026}{i(220)} \Rightarrow \sin^2 \theta = 0.12736 \Rightarrow \theta = 20.91^\circ \]

\[ \sin \theta = 0.21854 \]

\[ f_{\text{ZnTe}} = 22.4 - [22.4 - 18.6] \cdot 0.7 = 21.26 \]

\[ f_{\text{Zn}} = 41.7 - [41.7 - 31.4] \cdot 0.7 = 29.07 \]

\[ \left| \mathbf{F}_{(220)} \right|^2 = 16 \left( f_{\text{ZnTe}}^2 + f_{\text{Zn}}^2 \right) = 16 \left( 21.26 + 29.07 \right) = 59.127 \]

\[ p = 12 \]

\[ \mathbf{P} = 13.07 \]

\[ I_{220} = \left| \mathbf{F}_{220} \right|^2 \mathbf{P} \]

\[ \sin^2 \theta = \frac{\mathbf{P}}{4a^2 (h+k+l)} \Rightarrow \sin^2 \theta = (1.4)^2 \]

\[ \frac{46,1026}{i(220)} \Rightarrow \sin^2 \theta = 0.06368 \Rightarrow \theta = 14.62^\circ \]

\[ \sin \theta = 0.21854 \]
Intensity values calculated in (e) agree well with planar packing in (d) as well as the intensities from the PDF (on right) for ZnTe.
Simple Problems for XRD from Callister with Solutions given out

• Problem 1: For Aluminum compute the interplanar spacing for the (110) set of planes.

• Problem 2: Determine the expected diffraction angle for the 1st order reflection from the (310) set of planes for BCC Chromium when monochromatic radiation of wavelength \( \lambda = 0.0711 \) nm is used.

• Problem 3: The metal Rhodium is FCC crystal structure. If the angle of diffraction for the (311) plane occurs at 36.12° (first order reflection) when monochromatic radiation of wavelength 0.0711 nm is used, compute (a) the interplanar spacing for this set of planes and (b) the atomic radius for a rhodium atom.

• Problem 4: For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of 44.53° for FCC Nickel when monochromatic radiation having a wavelength of 0.1542 nm is used?

• Problem 5: Below shows first 5 peaks of the XRD pattern for Tungsten (BCC crystal structure). Monochromatic radiation of wavelength 0.1542 nm was used. (a) Index \((h,k,l)\) for each of these peaks. (b) Determine the interplanar spacing for each of these peaks. (c) For each peak, determine the atomic radius for W and compare these with tabulated value of 0.1371.