X-ray Diffraction and Crystal Structures

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X-Ray Generation

X-rays are electromagnetic radiation with wavelength $\sim 1 \text{ Å} = 10^{-10} \text{ m}$ (visible light $\sim 5.5 \times 10^{-7} \text{ m}$)

X-ray generation: electrons are emitted from the cathode and accelerated toward the anode. Here, Bremsstrahlung radiation occurs as a result of the “braking” process – X-ray photons are emitted.

X-ray wavelengths too short to be resolved by a standard optical grating

$$\theta = \sin^{-1} \frac{m\lambda}{d} = \sin^{-1} \frac{(1)(0.1 \text{ nm})}{3000 \text{ nm}} = 0.0019^\circ$$
The most common metal used is copper, which can be kept cool easily, due to its high thermal conductivity, and which produces strong $K_\alpha$ and $K_\beta$ lines. The $K_\beta$ line is sometimes suppressed with a thin (~10 µm) nickel foil.

**X-Ray Generation**

- **K-alpha ($K_\alpha$)** emission lines result when an electron transitions to the innermost "K" shell (principal quantum number 1) from a 2p orbital of the second or "L" shell (with principal quantum number 2).

- The $K_\alpha$ line is actually a doublet, with slightly different energies depending on spin-orbit interaction energy between the electron spin and the orbital momentum of the 2p orbital.

$$\lambda(K_\alpha) = 0.154 \text{ nm}$$
$$\lambda(K_\beta) = 0.139 \text{ nm}$$


Atomic levels involved in copper $K_\alpha$ and $K_\beta$ emission.
$K_\alpha$ and $K_\beta$ X-ray lines

from Preston and Dietz, p. 191.
X-Ray diffraction

\[ d \sin \theta \]
Diffraction of x-rays by crystal: spacing \( d \) of adjacent crystal planes on the order of 0.1 nm

→ three-dimensional diffraction grating with diffraction maxima along angles where reflections from different planes interfere constructively

\[
2d \sin \theta = m\lambda \quad \text{for } m = 0, 1, 2, \ldots
\]

Note that your measured XRD spectra will most likely reveal only 1\(^{st}\) order diffracted lines (i.e., those for which \( m = 1 \)).
Bragg occupied the Cavendish chair of physics at the University of Leeds from 1909. He continued his work on X-rays with much success. He invented the X-ray spectrometer and with his son, William Lawrence Bragg, then a research student at Cambridge, founded the new science of X-ray analysis of crystal structure.

In 1915 father and son were jointly awarded the Nobel Prize in Physics for their studies, using the X-ray spectrometer, of X-ray spectra, X-ray diffraction, and of crystal structure.

Interplanar spacing $d$ is related to the unit cell dimension $a_0$

$$5d = \sqrt{\frac{5}{4} a_0^2} \quad \text{or} \quad d = \frac{a_0}{20} = 0.2236 a_0$$

Not only can crystals be used to separate different x-ray wavelengths, but x-rays in turn can be used to study crystals, for example determine the type of crystal ordering and $a_0$. 
Planes with different Miller indices in cubic crystals. The inverse of these fractional intercepts yields the Miller indices $h, k, l$. 

from http://en.wikipedia.org/wiki/Miller_index
Crystal structure and Miller indices

Planes with different Miller indices in cubic crystals.

from http://en.wikipedia.org/wiki/Miller_index
Crystal structure and Miller indices

Indexing lattice planes

http://www.msm.cam.ac.uk/doitpoms/tlplib/miller_indices/lattice_index.php
Rock salt (cubic) crystal structure

\[ d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \]

Structure factor for NaCl:

\[ F = \left[ f_{Na} + f_{Cl} e^{i\pi (h+k+l)} \right] \left[ 1 + e^{i\pi (h+k)} + e^{i\pi (h+l)} + e^{i\pi (k+l)} \right] \]

- \( F = 4(f_{Na} + f_{Cl}) \) if \( h, k, l \) are even
- \( F = 4(f_{Na} - f_{Cl}) \) if \( h, k, l \) are odd
- \( F = 0 \) if \( h, k, l \) are mixed

X-Ray diffraction: a practical approach, by C. Suryanarayana, M. Grant Norton
X-Ray diffraction (XRD) pattern (diffractogram) from NaCl

Miller indices: The peak is due to X-ray diffraction from the \{220\} planes.

\[ d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \]

http://web.pdx.edu/~pmoeck/phy381/Topic5a-XRD.pdf
The value of $d$, the distance between adjacent planes in the set $(hkl)$, may be found from the following equations.

**Cubic:**
\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

**Tetragonal:**
\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}
\]

**Hexagonal:**
\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
\]

**Rhombohedral:**
\[
\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}
\]

**Orthorhombic:**
\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]

**Monoclinic:**
\[
\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)
\]

**Triclinic:**
\[
\frac{1}{d^2} = \frac{1}{V^2} \left(S_{11} h^2 + S_{22} k^2 + S_{33} l^2 + 2S_{12} hk + 2S_{23} kl + 2S_{13} hl\right)
\]

In the equation for triclinic crystals,

\[V = \text{volume of unit cell}\]

\[S_{11} = b^2 c^2 \sin^2 \alpha,\]

\[S_{22} = a^2 c^2 \sin^2 \beta,\]

\[S_{33} = a^2 b^2 \sin^2 \gamma,\]

\[S_{12} = abc^2(\cos \alpha \cos \beta - \cos \gamma),\]

\[S_{23} = a^2 bc(\cos \beta \cos \gamma - \cos \alpha),\]

\[S_{13} = ab^2 c(\cos \gamma \cos \alpha - \cos \beta).\]
d spacings for tetragonal, hexagonal, orthorhombic crystals

**Bragg’s Law (1):**

\[
\lambda = \frac{2 \sin \theta_c}{d}
\]  

(1)

\[
d_{hkl} = \frac{\lambda}{\sqrt{h^2 + k^2 + l^2}}
\]  

(2) Plane spacing for cubic crystals

**Combined (1) and (2):**

\[
\left(\frac{n\lambda}{2a}\right)^2 = \frac{\sin^2 \theta}{h^2 + k^2 + l^2} \quad \text{or} \quad \sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)
\]  

(3)

For a particular incident x-ray wavelength and cubic crystal of unit cell size \(a\), this equation predicts all possible Bragg angles at which diffraction can occur from planes (hkl).

**Plane spacings for:**

**Tetragonal:**

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{c^2}
\]  

(4)

**Hexagonal:**

\[
\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2}{a^2} + \frac{hk}{b^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)
\]  

(5)

**Orthorhombic:**

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]  

(6)

If crystal is **tetragonal** with \(a = a \neq c\) then (1) and (4) become:

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

(7)

If crystal is **hexagonal** with \(a = a \neq c\) then (1) and (5) become:

\[
\sin^2 \theta = \frac{\lambda^2}{3a^2} (h^2 + k^2 + hk) + \frac{\lambda^2}{4c^2} (l^2)
\]  

(8)

If crystal is **orthorhombic** with \(a \neq b \neq c\) then (1) and (6):

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

(9)

Diffraction planes are determined solely by the shape and size (lattice parameters) of the unit cell.
CdTe crystal structure (zincblende)

\[ a_0 = 0.648 \text{ nm} \]
CdTe XRD pattern

X-ray diffractograms of thin films at annealing temperatures of a) 350 °C, b) 400 °C and c) 450 °C.

CdTe XRD pattern (intensity vs. $2\theta$)
CdS XRD pattern (intensity vs. 2θ)

\[ a_0 = 0.5832 \text{ nm for zincblende} \]
\[ a = 0.4160; c = 0.6756 \text{ for wurtzite} \]
Scherrer Equation (relationship to Shape Factor)

\[ \tau = \frac{K\lambda}{\beta \cos \theta} \]

K is the shape factor, \( \lambda \) represents the x-ray wavelength used for the measurement, \( \beta \) is the line width (FWHM) in radians, \( \theta \) is the Bragg angle (note, this is not the 2\( \theta \) angle, just \( \theta \)), and \( \tau \) is the mean size of the crystalline domains. The formula yields a lower bound on the possible particle size.

The shape factor enables one to determine the average size of crystal grains within a polycrystalline thin film. Assuming a Gaussian function to fit the peak, the shape factor is 0.9, so that

\[ \tau = \frac{0.9\lambda}{\beta \cos \theta} \]
A CdTe XRD Study

Motivation

Determine why some samples appear shiny, and some appear matte.
Peaks were considered if they were known CdTe peaks. Peaks from other layers (ex. CdS) were not included.
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Calculated Lattice Parameter

Data points calculated using:

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

Orientation factor calculated using: 

\[ p = \frac{I}{\Sigma I} \times \frac{\Sigma I'}{I'} \]

Grain size calculated using: 

\[ \tau = \frac{K\lambda}{\beta \cos \theta} \]

<table>
<thead>
<tr>
<th></th>
<th>Shiny First Location</th>
<th>Shiny Second Location</th>
<th>Matte First Location</th>
<th>Matte Second Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orientation Factor ( p ) for (111) Orientation</td>
<td>1.32</td>
<td>1.60</td>
<td>2.00</td>
<td>1.90</td>
</tr>
<tr>
<td>Average Grain size ( \tau ) (nanometers)</td>
<td>264.86</td>
<td>302.70</td>
<td>302.70</td>
<td>325.99</td>
</tr>
<tr>
<td>Lattice Parameter ( a ) (angstroms)</td>
<td>6.4893 ± 0.0010</td>
<td>6.4906 ± 0.0009</td>
<td>6.4903 ± 0.0011</td>
<td>6.4901 ± 0.0009</td>
</tr>
</tbody>
</table>


G. B. Harris, *Phil. Mag.*, 43, 113-123 (1951)
UT Sample Data (Lab #7, 2013)
Log XRD Intensity (a.u.)

Angle as 2-theat (degrees)

CdTe (square sample)  
cdtefull