Introduction: X-Ray Diffraction

- XRD is a powerful experimental technique used to determine the
  - crystal structure and its lattice parameters (a,b,c,α,β,γ) and
  - spacing between lattice planes (hkl Miller indices) → this interplanar spacing ($d_{hkl}$) is the distance between parallel planes of atoms or ions.
- Diffraction is result of radiation’s being scattered by a regular array of scattering centers whose spacing is about same as the λ of the radiation.
- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- We know that atoms and ions are on the order of 0.1 nm in size, so we think of crystal structures as being diffraction gratings on a sub-nanometer scale.
- For X-rays, atoms/ions are scattering centers (photon interaction with an orbital electron in the atom). Spacing ($d_{hkl}$) is the distance between parallel planes of atoms….
Recall incoming X-rays **diffract** from crystal planes:

Reflections must be in phase for a detectable signal. I.e., for diffraction to occur, x-rays scattered off adjacent crystal planes must be in phase.

Measurement of critical angle, $\theta_c$, allows computation of interplanar spacing ($d_{hkl}$).

$\theta$ is scattering (Bragg) angle.

**Bragg's Law** (1)

$$d = \frac{\lambda}{2 \sin \theta_c}$$

**Cubic** ($d_{hkl}$)

$$d_{hkl} = \frac{\sqrt{h^2 + k^2 + l^2}}{a}$$

Combine (1)+(2):

Adapted from Fig. 3.37, *Callister & Rethwisch 3e*.
The interplanar \((d_{hkl})\) spacings for the 7 crystal systems

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

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

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

**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,
\[
V = abc\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}
\]
\[
S_{11} = h^2c^2 \sin^2 \alpha,
S_{22} = a^2c^2 \sin^2 \beta,
S_{33} = a^2b^2 \sin^2 \gamma,
S_{12} = abc^2(\cos \alpha \cos \beta - \cos \gamma),
S_{23} = a^2bc(\cos \beta \cos \gamma - \cos \alpha),
S_{13} = ab^2c(\cos \gamma \cos \alpha - \cos \beta).
\]

- **As crystal symmetry decreases, the number of XRD peaks observed increases:**
  - **Cubic crystals,** highest symmetry, fewest number of XRD peaks, e.g. \((110) = (101) = (011)\), since a=b=c → all 3 have same interplanar \((d_{hkl})\) spacing.
  - **Orthorhombic crystals,** lower symmetry, larger number of XRD peaks, e.g. \((110) \neq (101) \neq (011)\), since a\(\neq\)b\(\neq\)c → all 3 have different interplanar \((d_{hkl})\) spacings.
Geometry of XRD (F.Y.I.)

- A single (monochromatic) wavelength of x-ray radiation is often used to keep the number of diffraction peaks to a small workable number, since samples often consist of many small crystal grains orientated randomly.

- The diffracted beam intensity is monitored electronically by a mechanically driven scanning radiation detector.

Bragg angle = \( \theta \)
Diffraction angle, what's measured experimentally = \( 2\theta \)

- Counter/detector is rotated about O-axis; \( 2\theta \) is its angular position.
- Counter and specimen are mechanically coupled such that a rotation of the specimen through \( \theta \) is accompanied by a \( 2\theta \) rotation of the counter.
- This assures that the incident and reflection angles are maintained equal to one another.
More on Bragg’s Law

• Bragg’s Law is a necessary **but** insufficient condition for diffraction.
• It only defines the diffraction condition for **primitive unit cells**, e.g. P cubic, P tetragonal, etc., where atoms are only at unit cell corners.
• Crystal structures with non-primitive unit cells have atoms at additional lattice (basis) sites.
• These extra scattering centers can cause out-of-phase scattering to occur at certain Bragg angles.
• The net result is that some of the diffraction predicted by Bragg’s Law (eqn. 1) does not occur, i.e. certain sets of planes do not exist (**forbidden reflections**).

**Selection (or Reflection) rules:**

<table>
<thead>
<tr>
<th>Bravais Lattice</th>
<th>Example Compounds/Structures</th>
<th>Allowed Reflections</th>
<th>Forbidden Reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primitive (P) Cubic</td>
<td>Simple Cubic (α-Po)</td>
<td>Any h,k,l</td>
<td>None</td>
</tr>
<tr>
<td>Body-centered (I) Cubic</td>
<td>Body-Centered Cubic metal</td>
<td>h+k+l even</td>
<td>h+k+l odd</td>
</tr>
<tr>
<td>Face-centered (F) Cubic</td>
<td>Face-Centered Cubic metal</td>
<td>h,k,l all odd or all even</td>
<td>h,k,l mixed odd or even</td>
</tr>
<tr>
<td>Face-centered (F) Cubic</td>
<td>NaCl-rocksalt, ZnS-zincblende</td>
<td>h,k,l all odd or all even</td>
<td>h,k,l mixed odd or even</td>
</tr>
<tr>
<td>Face-centered (F) Cubic</td>
<td>C, Si, Ge - Diamond cubic</td>
<td>As FCC, but if all even and h+k+l≠4n, then absent (n is integer)</td>
<td>h,k,l mixed odd or even and if all even and h+k+l≠4n</td>
</tr>
<tr>
<td>Primitive (P) Hexagonal</td>
<td>Hexagonal closed packed metal</td>
<td>All other cases</td>
<td>h+2k=3n, l odd</td>
</tr>
</tbody>
</table>

*These rules are calculated based on atomic scattering factors (f) and structure factors (F), which we will discuss next class (you will also see them on final exam).*
Selection Rules for Cubic

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

where “S” is line #,
e.g. for (100) S=1 and
for (200) S=4

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>I</th>
<th>F</th>
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<tbody>
<tr>
<td>S (hkl)</td>
<td>S (hkl)</td>
<td>S (hkl)</td>
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As we will determine later when we calculate the structure factors, these selection rules also hold for other non-primitive Bravais lattices, e.g. I-tetragonal, F-orthorhombic, etc.
The unit cell size and geometry may be resolved from the angular positions of the diffraction peaks. When the distance between the peak spacings are all pretty much the same (2θ) it is likely cubic. The arrangement of atoms within the unit cell is associated with the relative intensities of these peaks.

Diffraction pattern for polycrystalline α-iron (BCC)

$d$-spacing decreases according to Bragg’s Law

\[ h+k+l \text{ even are only allowed according to previously shown selection rules for BCC metal.} \]
Review of Systematic Absences in the Diffraction Patterns of 4 Cubic Structures

When indexing XRD data for your material always try cubic first (least amount of diffracting planes since most symmetric lattice parameters).

<table>
<thead>
<tr>
<th>h^2 + k^2 + l^2</th>
<th>100</th>
<th>110</th>
<th>111</th>
<th>200</th>
<th>210</th>
<th>211</th>
<th>220</th>
<th>300, 221</th>
<th>310</th>
<th>311</th>
<th>222</th>
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