Electron Diffraction Patterns

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Lecture 3

\[ \vec{g}_{hkl} \perp \text{plane (hkl)} : \text{The } g \text{ is the plane normal} \]

\[ \text{Angles between } g = \text{Angles between the corresponding planes} \]

\[ |\vec{g}_{hkl}| = \frac{2\pi}{d_{hkl}} \]

\[ Rd_{hkl} = \lambda L \]

Diffraction Patterns (DPs):

Lattices in the Intersecting plane of the Ewald Sphere and the reciprocal lattice - ZOLZ

- The diffraction planes are almost // the beam (angle~30’)
- Beam direction is approximately the zone axis  \( hu + kv + lw = 0 \)

DPs  \[ \rightarrow \]  \( g \), angles between \( g \)  \[ \rightarrow \]  \( R \), angles between \( R_s \)  \[ \rightarrow \]  \( \text{Planes, angles between planes} \)  \[ \rightarrow \]  \( \text{Beam direction} \)
Electron diffraction Patterns

- Polycrystalline: Ring Pattern
  - Identification of phase
    - extraction replicas
    - Fine grain size polycrystalline, CVD foils

- Single-crystal:
  - Spot
    - The foil orientation
    - Accessibility of certain orientations/diffracting vectors
    - Well-defined tilt axis
    - Identify: precipitates, twins, martensite plates etc.
    - Orientation relationship between phases
    - Details of the fine structures
  - Kikuchi line (Pairs of parallel bright/dark lines)
    - Reasonably thick: ~1/2 maximum usable penetration
    - Low defect density
Selected-Area Diffraction Patterns

- Accuracy of operation of the TM is important
  - SADP: the image and selector aperture coplanar (objective lens in focus)
  - Spherical aberration
  - Sample height
  - Instability of lens current and/or high tension

- Indexing?
  - Indices of diffraction spots $hkl$
    - spacing between lattice planes, lattice constants
  - The orientation of the crystal and beam direction
Indexing: Ring Patterns

- **Known materials**
  - Measure $\phi_n$, (diameters of the rings)
  - Determine the ratios of $\phi_n / \phi_1$ ($\phi_1$ innermost ring)
  - Check the ratios against the table of ratios of the inter-planar spacing

- **Unknown substance**
  - Measure $\phi_n$, (diameters of the rings)
  - Convert the $\phi_n$ into inter-planar spacing (camera constant)
  - Use ICDD index to identify the phase... starting from the most likely...
  - Or... Determine the ratios of $\phi_n / \phi_1$ .. (depending on the crystal structures)
  - If failed... try XRD and X-ray microanalysis!

- **Use of Ring Pattern**
  - Calibrate the Camera Length
  - Identify phases

ICDD: The international Centre for Diffraction Data
Indexing: simple spot patterns

- Spots are in one zone axis
  - By inspection: Cubic... yes; Hexagonal...no (for particular c/a patterns are similar for different zone axis)

- Indexing
  - Determine the \{hkl\} indices of the spot
    - Camera constant: measure \( R \) – work out \( d \)
    - Ratios: measure \( d_n/d_1 \) – check low index planes
  - Assign specific \((hkl)\) to the individual spot
    - Closest spot (to the direct beam): arbitrarily indexed
    - The other two spots, check
      - Vector addition
      - Angles between them
    - All the others: vector addition with opposite spots \((-h-k-l),(hkl)\)
  - Determine beam direction \( B \)
    - \([uvw]\): \( z = B = g_1 \times g_2 \)
    - Anticlockwise indexing rule: \( B \) upward normal from the pattern to the incident beam
Example: Pure Nickel

American Mineralogist Crystal Structure database

FCC, $a = 3.524 \text{ Å}$

http://rruff.geo.arizona.edu/AMS/amcsd.php
For cubic system:
\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{N}{a^2}
\]
\[
R_{d_{hkl}} = \lambda L
\]

\[
d_1^2 = \frac{R_1^2}{R_2} = \frac{N_1}{N_2}
\]
\[
d_2^2 = \frac{R_2}{R_1} = \sqrt{\frac{N_2}{N_1}}
\]

\[N \equiv h^2 + k^2 + l^2\]
The Distances in Diffraction Pattern

Finite sizes of spots

http://imagej.nih.gov/ij/

\[ R_1 = \frac{503.337}{6} = 83.89 \]
The distances in diffraction pattern
The distances in diffraction pattern

- Work out the ratios

\[
\frac{d_1}{d_3} = \frac{R_3}{R_1} = 2.518
\]

\[
\frac{d_1}{d_2} = \frac{R_2}{R_1} = 2.497
\]

**Systematic absence:**

f.c.c: hkl mixed odd and even

\(d_1\) (largest spacing): \{110\}
\(d_2\): \{222\}
\(d_3\): \{320\}

\(d_1\) (largest spacing): \{111\}
\(d_2\): \{331\}
\(d_3\): \{420\}
Deciding indices

- Arbitrarily deciding $d_1$: (111)

Angle between $(h_1k_1l_1)$ and $(h_2k_2l_2)$

\[ \cos \phi = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}} = \frac{h_2 + k_2 + l_2}{\sqrt{3(h_2^2 + k_2^2 + l_2^2)}} \]

$(h_1k_1l_1)$: (111)

In the cubic system planes having the same indices regardless of order or sign are equivalent.
Measuring the Angles

Angles between the normal of \{331\} and \{111\}

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>\cos \phi</th>
<th>\phi</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3</td>
<td>1</td>
<td>0.927173</td>
<td>22.01287</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>-1</td>
<td>0.662266</td>
<td>48.55168</td>
</tr>
<tr>
<td>-3</td>
<td>3</td>
<td>1</td>
<td>0.132453</td>
<td>82.43041</td>
</tr>
<tr>
<td>-3</td>
<td>3</td>
<td>-1</td>
<td>-0.13245</td>
<td>97.66089</td>
</tr>
<tr>
<td>-3</td>
<td>-3</td>
<td>1</td>
<td>-0.66227</td>
<td>131.5396</td>
</tr>
<tr>
<td>-3</td>
<td>-3</td>
<td>-1</td>
<td>-0.92717</td>
<td>158.0784</td>
</tr>
</tbody>
</table>

\[
\cos \phi = \frac{h^2 + k^2 + l^2}{\sqrt{3(h^2 + k^2 + l^2)}}
\]

Note -331, 3-31, -313,.etc give the same result
Measuring the Angle

Angle between \((h_1k_1l_1)\) and \((h_3k_3l_3)\)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th>(\cos \phi)</th>
<th>(\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2</td>
<td>0</td>
<td>0.774597</td>
<td>39.25142</td>
</tr>
<tr>
<td>-4</td>
<td>2</td>
<td>0</td>
<td>-0.2582</td>
<td>105.0165</td>
</tr>
<tr>
<td>-4</td>
<td>-2</td>
<td>0</td>
<td>-0.7746</td>
<td>140.8399</td>
</tr>
</tbody>
</table>
Deciding indices: Vector Addition

\[ \vec{d}_2 - \vec{d}_3 = \vec{d}_1 \]

Possible pairs

\begin{align*}
(-420)&(-331) & (-402)&(-313) \\
(2-40)&(3-31) & (20-4)&(31-3) \\
(0-42)&(1-33) & (02-4)&(13-3)
\end{align*}

<table>
<thead>
<tr>
<th></th>
<th>-331</th>
<th>-313</th>
<th>3-31</th>
<th>31-3</th>
<th>1-33</th>
<th>13-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>-420</td>
<td>111</td>
<td>1-13</td>
<td>7-51</td>
<td>1-1-3</td>
<td>5-53</td>
<td>51-3</td>
</tr>
<tr>
<td>-402</td>
<td>13-1</td>
<td>111</td>
<td>1-3-1</td>
<td>71-5</td>
<td>5-31</td>
<td>53-5</td>
</tr>
<tr>
<td>2-40</td>
<td>-571</td>
<td>-553</td>
<td>111</td>
<td>15-3</td>
<td>-113</td>
<td>-17-3</td>
</tr>
<tr>
<td>20-4</td>
<td>-535</td>
<td>-517</td>
<td>1-35</td>
<td>111</td>
<td>-1-37</td>
<td>-131</td>
</tr>
<tr>
<td>0-42</td>
<td>-37-1</td>
<td>-351</td>
<td>31-1</td>
<td>35-5</td>
<td>111</td>
<td>17-5</td>
</tr>
<tr>
<td>02-4</td>
<td>-315</td>
<td>-3-17</td>
<td>3-55</td>
<td>3-11</td>
<td>1-57</td>
<td>111</td>
</tr>
</tbody>
</table>
Deciding indices: the other spots

\[
\begin{align*}
(-420)\cdot(-331) &= (\cos \phi_{\{331\} \wedge (\overline{420})} = \frac{(-3) \times (-4) + 3 \times 2}{\sqrt{(9 + 9 + 1)(16 + 4)}} = 0.9234 \\
\phi_{\{331\} \wedge (\overline{420})} &= 23^\circ
\end{align*}
\]

Check Vector addition

\[(-4, 2, 0) = (-3,3,1) + (-1, -1, -1)\]

• Use vector addition to index the other spots
Deciding Zone Axis

The \( g \) vectors belong to the ZOLZ

The zone axis \([uvw]\) \perp all the \( g \) vectors

\[
\vec{B} = \vec{g}_1 \times \vec{g}_2
\]

\[
\vec{B} = \vec{g}_1 \times \vec{g}_2
\]

\[
\begin{vmatrix}
\vec{a} & \vec{b} & \vec{c} \\
1 & 1 & 1 \\
-3 & 3 & 1 \\
\end{vmatrix}
\]

\[
= (1-3)\vec{a} + (-3-1)\vec{b} + (3-(-3))\vec{c}
\]

\[
= -2\vec{a} + (-4)\vec{b} + 6\vec{c}
\]

\([uvw] = [-1 -2 3]\)
Uniqueness in indexing DP: other possibilities

• 180°: \( g \) and \(-g\) - diffraction from both sides of the reflecting plane (From one zone)

\[
\vec{B} = \vec{g}_1 \times \vec{g}_2
\]

\[
\begin{bmatrix}
\vec{a} & \vec{b} & \vec{c} \\
-1 & -1 & -1 \\
3 & -3 & -1 \\
\end{bmatrix}
\]

\[
= (1 - 3)\vec{a} + (-3 - 1)\vec{b} + (3 + 3)\vec{c}
\]

\[
= -2\vec{a} - 4\vec{b} + 6\vec{c}
\]

\[
[uvw] = [-1 \ 2 \ 3]
\]

The same beam direction

• Coincidence ambiguity: \{hkl\} the same inter-planar spacing
• Solved by tilt sample
Beam direction: Source of Errors

- Uniform intensity: $B < 0.5^\circ$
- Rings of bright spots: $B > 1^\circ$
- Nonuniform intensity: $B \sim 15^\circ$
- Kikuchi lines: $B \sim 0.1^\circ$
- For high accuracy
  - $Cs$
  - Errors in lattice parameters/beam energy
  - Errors in measurement of SADP
- $B$: average for the selected region
  - Bent, defective
  - K lines not for deformed/phase transformations
Sketch Zero Laue Zone

FCC (421)

In the reciprocal space, (421) Intercepts are:

\[ 4 \left( \frac{1}{4}, \frac{1}{2}, 1 \right) = 1, 2, 4 \]

100, 020, 004

Consider the plane passing through the origin: lets move (1,0,0) to the origin

1,0,0; 0,2,0; 0,0,4 \rightarrow 0,0,0; -1,2,0; -1,0,4

For FCC: must be all even/odd numbers

0,0,0; -2,4,0; -2,0,8

The angle between (-2,4,0) and (-2,0,8) is \( 83^\circ 49' \)

Length ratio is

\[ \frac{R_{240}}{R_{208}} = \frac{\sqrt{20}}{\sqrt{68}} = \frac{1}{1.844} \]

Simple pattern
low zone axis
Weiss zone law

\[ h_1 u + k_1 v + l_1 w = 0 \]
ZOLZ of the example

Zone axis [-1-23] ⊥ The plane in the reciprocal space (-1-23)
Intercepts of the plane: (-1,0,0) (0,-1/2,0) (0,0,1/3) \rightarrow (-6,0,0) (0,-3,0) (0,0,2)
Move this plane to the origin: (0,0,0) (6,-3,0) (6,0,2)
fcc requires: (0,0,0) (12,-6,0) (6,0,2)
Angle : 32°
The length ratio: 2.1
Kikuchi Lines

- 1928 Kikuchi
- More accurate than spot for
  - Specimen orientation
  - Accessibility of certain orientation/diffracting vectors
  - A well-defined tilt axis
  - Orientation relationship
- Kikuchi map: distribution of K lines
  - A unit triangle of the stereogram
  - Identify K pattern rapidly, determine B
  - Tilt sample in a self-consistent manner
- Determine the magnitude and sign of the deviation \( s \)
- Define the sense of tilt (moves in the same sense as the crystal)
- Small angle tilt can be estimated
- Large angular tilts can be measured
- Determine crystal symmetry – real crystal symmetry
Kikuchi Lines

- The diffraction of electrons which have been previously inelastically scattered
  - Inelastically scattered
    - Small Energy loss < 50 eV and change direction
    - A diffuse halo (small angle)/overall faint background
  - The Bragg law (hkl)
    - Not satisfied for the incident beam
    - Satisfied for the inelastically scattered beam
      - Removed from the T beam: local reduction in background intensity
      - Fewer will be diffracted back to the background (angle distribution)
  - Cones of radiation
    - Centre: the sample
    - Cone I: high intensity; Cone II: low intensity
    - Cones attached to the crystal
      » Move about a radius: $1/\lambda$
      » Spots move about: $g \approx 1/25\,1/\lambda$
    - Cones intersect Ewald sphere ($\lambda' \approx \lambda$): hyperbolae
Summary

• Indexing simple patterns
  – Diffraction spots
  – Beam direction
  – ZOLZ

• Kikuchi Lines
Lecture 5

• Dynamical Diffraction Theory
• Diffraction Contrast
SUPPLEMENTARY
Indexing

For cubic system: \[ \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{N}{a^2} \]

N: Sum of squares of three integers \( N \neq 4^n(8m+7) \)

bcc: \( N = 2m; \) fcc: \( N=4n; \) \( 8n+3 \)

Assume two spots: \( R_1 \) and \( R_2 \) \[ R_{d_{hkl}} = \lambda L \]

Camera Length: \[ \frac{d_2^2}{d_1^2} = \frac{R_1^2}{R_2^2} = \frac{N_1}{N_2} \]

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

For \( l=0 \): \( A, 2A \) must in the series

For Hexagonal system: \[ \frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} = \frac{4}{3} \frac{H}{a^2} + \frac{l^2}{c^2} \]

For \( l=0 \): \( H, 3H \) must in the series
Diffraction Symmetry

Note: All diffraction patterns are centro-symmetric even if the crystal is not (Friedel’s law)

Some ZOLZ patterns thus exhibit higher rotational symmetry than the structure has.
Indexing: Kikuchi Patterns

• B = low zone axis
  – a high degree of symmetry
  – Direct comparison: standard patterns

• Two features
  – Kikuchi line spacing $D_d = \lambda L$: no error because of $s$
  – Angles between K lines – angles between planes

• Simple patterns: in the same zone
  – Identical for spot patterns
  – B is close to zone axis: T beam away from the centre of the K pattern
  – $180^\circ$ ambiguity
Kikuchi Lines: Complex pattern

- Three non-parallel line pairs
Kikuchi Maps

- Help to eliminate the trial and error stage of indexing K patterns
- Rapidly obtain: B with $2^\circ$
Use of diffraction patterns: Basic

• Specimen tilting
• Orientation relationship determination
• Twining
• Second phases
• Crystallographic information
USE: The fine structures

• Extra spots
• Spot splitting and satellite spots
• Streaks
• Diffuse scattering Effects
Indexing: Complicated patterns

• Large lattice para
  – Thin sample: high-order laue zero – at the edge of the pattern
  – Thin sample: far away from low zone axis
    • Fragmentary arrays of spots – avoid this!
    • Laue zones: hu+kv+lw = n
Indexing: Imperfect patterns

• Spots: from different zero-order Laue zones
  – Remove ambiguity in indexing
• Indexing: Three vectors $g_1, g_2, g_3$, form a circle
  – $T$ is inside the circle:
    • $O$ lying below the plane
    • Labelled anticlockwise
  – $T$ is outside
    • $O$ lying above the plane
    • Labelled clockwise
  – Evaluate $\{hkl\}$: use camera length
  – Arbitrarily index on $(hkl)$, label $g_2, g_3$ according to the above rule
  – Zone axis = $g_1 \times g_2$
  – All zone axes: close
  – Check $g_1.(g_2 \times g_3) > 0$
  – Work out $B$:

$$B = |g_1|^2 (g_2 \times g_3) + |g_2|^2 (g_3 \times g_1) + |g_3|^2 (g_1 \times g_2)$$