**X-ray Diffraction**

*Mineral identification*

*Mode analysis*

*Structure Studies*

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**X-ray Generation**

- X-ray tube (sealed)
- Pure metal target (Cu)
- Electrons remove inner-shell electrons from target.
- Other electrons “fall” into hole to emit an X-ray photon.

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**X-ray Spectrum from Tube**

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**Diffraction**

- Diffraction is the coherent scattering of waves from a periodic array of scatterers.
- The wavelength of light is about half a micron
- Light is diffracted by the tracks in a CD.
- The wavelengths of X-rays is about the same as the interatomic distances in crystals.
**X-ray Scattering**

- A single atom in space interacts with an X-ray photon.

**X-Ray Diffraction**

- Atoms in a periodic array separated by distance \( d \) will scatter in phase when the path length difference is an integral number of wavelengths.
- Path length difference \( B-C-D = n\lambda \)
- \( n\lambda = 2d \sin \theta \)

**Single-crystal Diffraction**

- The unit cell \( a, b, c, \alpha, \beta, \gamma \)
- Crystal System
- Lattice type (\( P, A, B, C, I, F, R \))
- Point Group (Laue symmetry)
- Space Group
- Crystal Structure Determination
  - Atom position (fractional coordinates)
  - Element ordering (# electrons per site)

**Diffraction**

- Intensities can be calculated knowing the position and scattering characteristics of each atom.
- \( F_{hkl} \) = square root of integrated intensity.
- \( f_j \) = scattering of atom \( j \) at angle \( 2\theta \)
- Atom \( j \) located at fractional coordinates \( x_j, y_j, z_j \).
### Structure Factors

- The structure factor, $F$, is the square root of the measured integrated intensity.

### Structure Factors (complex number)

$$ F_{hkl} = \sum_{j=1}^{n} f_j (\cos \phi + i \sin \phi) $$

$$ \phi = 2\pi (hx_j + ky_j + lz_j) $$

### Structure Factors (Centro-symmetric crystals)

- If, for every atom, $j$, at $(x_j, y_j, z_j)$, there is an identical atom at $(-x_j, -y_j, -z_j)$.
- The imaginary term in the equation is zero.

$$ F_{hkl} = \sum_{j=1}^{n} 2f_j (\cos \phi) $$

### Systematic Extinction

- If, for every atom, $j$, at $(x_j, y_j, z_j)$, there is an identical atom at $(1/2+x_j, 1/2+y_j, 1/2+z_j)$, (body centering)
- The structure factor is zero for $h + k + l = 2n+1$ (h+k+l odd) for all hkl.
- So, systematic extinction of structure factors tells us which symmetry operators are present.

### Systematic Extinction

- Lattice centering Operations
  - For all hkl
  - F: hkl all even or all odd
  - I: $h+k+l = 2n$
  - A: $k+l = 2n$
  - B: $h+l = 2n$
  - C: $h+k = 2n$
- The Structure Factor, $F$, is zero for all hkl not meeting above relations.

- This means that lattice centering operations are determined from systematic absences.
**Systematic Extinction**

- Glide planes
  - a glide normal to c: for hk0, \( h = 2n \)
  - b-glide normal to c: for hk0, \( k = 2n \)
  - n-glide normal to c: for hk0, \( h+k = 2n \)
  - a-glide normal to b: for h0l, \( h = 2n \)
  - c-glide normal to b: for h0l, \( l = 2n \)
  - n-glide normal to b: for h0l, \( h+l = 2n \)
  - b-glide normal to a: for 0kl, \( k = 2n \)
  - c-glide normal to a: for 0kl, \( l = 2n \)
  - n-glide normal to a: for 0kl, \( k+l = 2n \)

**Reciprocal Lattice**

- The reciprocal lattice is a mathematical construct of points each corresponding to a given Miller index, \( hkl \).
- It is a three dimensional lattice where the nodes are diffracted intensities and the spacing between points is inversely proportional to the unit cell parameters in real space.

**Reciprocal Lattice**

- Reciprocal axes are denoted
  - \( a^* \), \( b^* \), \( c^* \), \( \alpha^* \), \( \beta^* \), \( \gamma^* \)
- For Orthorhombic
  - \( a^* = 1/a \) ; \( b^* = 1/b \) ; \( c^* = 1/c \)
- Scale is arbitrary

**Wadsleyite Imma**

<table>
<thead>
<tr>
<th>H K L</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5.7Å</td>
<td></td>
</tr>
<tr>
<td>11.5Å</td>
<td></td>
</tr>
<tr>
<td>8.3Å</td>
<td></td>
</tr>
</tbody>
</table>

Each spot is a 'reflection'
Tail is from white radiation

**Four-Circle Diffractometer**

![Four-Circle Diffractometer Diagram]
Four-Circle Diffractometer

CCD Image
Single crystal
0.5° rotation
10s exposure
72 images for orientation.

Gives unit cell:
\( a, b, c, \alpha, \beta, \gamma \)

Crystal system
Point group
**Four-Circle Diffractometer**

**Diffraction Experiment**

- Mount Crystal (~100μm)
- Measure 50 – 100 ‘random’ frames
- Locate Bragg reflections
- Index and obtain UB matrix
- Refine unit cell parameters (1/10^4)
- Measure Intensities (1000 - 10000)
- Determine or refine atom position and displacement parameters

Crystal on goniometer head:
- Crystal is ~100μm.
- Glued on a glass fiber.
- Mount is in 3mm Al tube.
- Goniometer has x, y, z translations for centering.

CCD Image
- Single crystal
- 0.5° rotation
- 10s exposure
- 72 images for orientation.

Reciprocal Lattice from orientation images
Indexed Unit Cell from 60 reflections

Reduced Unit Cell found:

<table>
<thead>
<tr>
<th>Method: Difference Vectors</th>
<th>HKL histogram:</th>
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<tbody>
<tr>
<td>Score: 0.06</td>
<td>1.0: 0.35 (560)</td>
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<tr>
<td>a = 3.07Å, c = 75.10°, V = 93Å³</td>
<td>0.25: 25.05 (1560)</td>
</tr>
<tr>
<td>b = 3.39Å, β = 75.10°</td>
<td>0.3: 56.75 (1462)</td>
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<tr>
<td>c = 4.72Å, γ = 90.01°</td>
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<table>
<thead>
<tr>
<th>Method: Fast Fourier Transform</th>
<th>HKL histogram:</th>
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<tr>
<td>Score: 380</td>
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<td>a = 4.77Å, c = 90.40°, V = 293Å³</td>
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<td>b = 6.28Å, β = 92.29°</td>
<td>0.3: 56.75 (1462)</td>
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<td>c = 3.99Å, γ = 90.01°</td>
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</table>

Bravais Symmetry chooses Orthorhombic P

<table>
<thead>
<tr>
<th>Bravais Lattice</th>
<th>FUM</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>α°</th>
<th>β°</th>
<th>γ°</th>
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<tr>
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<td>12.75</td>
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<td>10.22</td>
<td>90.26</td>
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<td>111.39</td>
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<td>21.70</td>
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<tr>
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<tr>
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<td>10.22</td>
<td>90.26</td>
<td>90.06</td>
<td>90.29</td>
</tr>
</tbody>
</table>

Flip b and c- axes
a = 4.75Å
b = 10.19Å
c = 5.98Å
α = β = γ = 90°
To match known cell.

Set up data collection:
6232 images of 10s each (~24h).

Integrate images: Find reflections and calculate intensities.
Integrate images: Refine cell and matrix

Scale: find reflections in more than one scan and determine scale factor for scans.

Scale: find reflections in more than one image and determine scale factor for scans.

Scale: Determine \( R_{\text{int}} \) for the various scans and get \( hkl \) file:

\[
\begin{array}{ccc}
 h & k & l \\
 F^2 & \sigma & r_d \\
\end{array}
\]

A list of relative intensities of ‘reflections’

INS file for SHELX:

TITL
CELL
LATT
SYMM
SFAC
UNIT
L.S.
LIST
Atom list
Typical refinement procedure:

1. Overall scale with atoms from known structure.
2. Atom positions (fractional coordinates within unit cell) and isotropic displacements
3. Occupancies
4. Anisotropic displacements

R-factors

1. \( R_1 = \frac{\text{sum} (F_{\text{obs}} - F_{\text{calc}})}{\text{sum} (F_{\text{obs}})} \)
2. Program (SHELXL) minimizes \( \text{sum} (F_{\text{obs}} - F_{\text{calc}}) \) or \( (F^2_{\text{obs}} - F^2_{\text{calc}}) \) by least squares adjustments of atom \( x, y, z \) coordinates, occupancy, and displacements.

Each atom modeled with a scattering factor, position, occupancy, and displacement (sphere (1) or ellipsoid(6))

Objectives:

Determine new structure.

Refine atom positions \( x, y, z \) to get interatomic distances.

Determine site occupancies to get cation ordering or determine vacancies (thermal or pressure history).

INS file for SHELXL:

SHELXL reads INS and hkl files and refines coordinates and displacement parameters to minimize \( F_{\text{obs}} - F_{\text{calc}} \). Output is .res file in same format as .ins. Also a list file of changes.

INS file for SHELXL:

Look at list file to see results.

Edit the .res file and rename it as .ins and run it again.