Lecture 2:

short repetition (primitive cells lattice planes and Miller indices)

distance between lattice planes

x-ray diffraction

reciprocal space
Crystal structure I

- In bulk, many solids are crystalline.
- Have discrete translational and rotational symmetries.
- Real-space structure is periodic - repetitions of a single unit cell.
- Smallest unit cell that gives full structure: primitive unit cell
- Can describe structure by a lattice and a basis.

![Diagram of crystal structure with lattice and basis points](image)
Lattice Planes and Miller Indices

Atoms or ions in lattices can be thought of as being connected by lattice planes. Each plane is a representative member of a parallel set of equally spaced planes.

A family of crystallographic planes is always uniquely defined by three indices, \( h, k, l \), (Miller indices) usually written \((h, k, l)\)

The Miller indices are defined by

\[
\begin{align*}
    h &= \frac{1}{X}, \quad k = \frac{1}{Y}, \quad l = \frac{1}{Z} \\
\end{align*}
\]

\(X, Y, Z\) are the intersections of one plane with on a, b, c respectively

Note - plane // to axis, intercept = \(\infty\) and \(1/\infty = 0\)

\((0kl)\)  \(x\)
\((h0l)\)  family of lattice planes parallel to \(y\)
\((hk0)\)  \(z\)
How to Determine Miller Indices

1.

- Intercepts are \( \infty, 1, \infty \)
- Miller indices of the plane are:

\[
\left( \frac{1}{\infty}, \frac{1}{1}, \frac{1}{\infty} \right) = (010)
\]

2.

- Intercepts are \( \infty, 1/2, \infty \)
- Miller indices of the plane are:

\[
\left( \frac{1}{\infty}, \frac{1}{1/2}, \frac{1}{\infty} \right) = (020)
\]
Inter-Planar Spacing, \(d_{hkl}\), and Miller Indices

The inter-planar spacing (\(d_{hkl}\)) between crystallographic planes belonging to the same family \((h,k,l)\) is denoted \((d_{hkl})\).

Distances between planes defined by the same set of Miller indices are unique for each material.

Inter-planar spacings can be measured by x-ray diffraction (Bragg’s Law)
The lattice parameters $a$, $b$, $c$ of a unit cell can then be calculated.

The relationship between $d$ and the lattice parameters can be determined geometrically and depends on the crystal system.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>$d_{hkli}$, lattice parameters and Miller indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$</td>
</tr>
</tbody>
</table>

The expressions for the remaining crystal systems are more complex.
The angles at which x-rays are diffracted depends on the distance between adjacent layers of atoms or ions. X-rays that hit adjacent layers can add their energies constructively when they are “in phase”. This produces dark dots on a detector plate.
Derivation of Bragg’s Law

Bragg’s Law can be derived using simple geometry by considering the distances traveled by two parallel X-rays reflecting from adjacent planes. The X-ray hitting the lower plane must travel the extra distance AB and BC. To remain in phase with the first X-ray, this distance must be a multiple of the wavelength thus:

\[ n\lambda = AB + BC = 2AB \]

(since the two triangles are identical)

The distance AB can be expressed in terms of the interplanar spacing (d) and incident angle (θ) because d is the hypotenuse of right triangle \( zAB \) shown at right.

\[ \sin(\theta) = AB/d \text{ thus } AB = d \sin(\theta) \]

Therefore:

\[ n\lambda = 2 \ d \sin(\theta) \]
Reflection (signal) only occurs when conditions for constructive interference between the beams are met.

These conditions are met when the difference in path length equals an integral number of wavelengths, \( n \). The final equation is the BRAGG’S LAW

\[
n\lambda = 2d \sin \theta
\]

Data are collected by using x-rays of a known wavelength. The position of the sample is varied so that the angle of diffraction changes.

When the angle is correct for diffraction a signal is recorded.

With modern x-ray diffractometers the signals are converted into peaks.
Reciprocal Lattice

Because of the reciprocal nature of d spacings and θ from Bragg’s Law, the pattern of the diffraction we observe can be related to the crystal lattice by a mathematical construct called the *reciprocal lattice*. In other words, the pattern of X-ray reflections makes a lattice that we can use to gain information about the crystal lattice.
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Constructing the reciprocal lattice

Choose a point to be the origin in the crystal lattice.

Let the vector normal to a set of lattice planes in the real lattice radiate from that origin point such that the distance of the vector is thereciprocal of the d spacing for each family of planes. i.e. the vector for the plane (hkl) has a distance of 1/d(hkl) (or, more generallyK/d(hkl)).

Repeat for all real lattice planes.
Reciprocal Lattice

This procedure constructs a reciprocal lattice in which each lattice point corresponds to the reflection that is generated by a particular family of planes. This lattice can easily be indexed by assigning the proper (hkl) value to each lattice point.