

## Lecture 4

Let's review what we have been doing so far.

- Bravais Lattice
- Examples for common crystal structures and identified their Bravais Lattice types
- Miller indices for planes and directions.
- Packing fraction & closely packed structures

Let's refresh the closely-packed structures

### HCP and CCP Structures

Both hexagonal close packed (hcp) and cubic close packed (ccp) structures have the highest packing fraction equals to 0.74.

Look at the slides for a review.

ABABAB → Hexagonal Close Packed

ABCABCABC → Cubic Close Packed

### Line and Planar Density:

Previously we have calculated the packing fractions, that is the ratio between the space occupied by the atoms and the total volume of the cell.

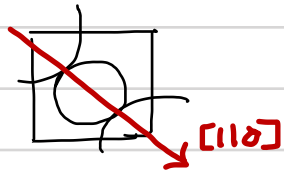
In the similar way, we can calculate the Linear Density & the Planar Density

Atomic Packing Fraction =  $\frac{\text{Volume of Atoms in the cell}}{\text{total unit cell volume}}$

LD =  $\frac{\text{Number of Atoms centered on Direction Vector}}{\text{Length of the Direction Vector}}$

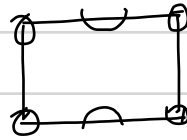
$$PD = \frac{\text{Number of Atoms Centered on a Plane}}{\text{Area of the Plane}}$$

For example, if you think about  $[110]$  direction in FCC (Look at the slide)



$$\begin{aligned} \text{Linear Density in } [110] \text{ of FCC} &= \frac{2 \text{ atoms}}{4R} \\ &= \frac{1 \text{ atom}}{2R} \end{aligned}$$

$(110)$  Plane of FCC:



$$\text{Planar Density} = \frac{2 \text{ atoms}}{a(\sqrt{2}a)}$$

$$= \frac{2 \text{ atoms}}{\sqrt{2} a^2} \quad \begin{aligned} \sqrt{2}a &= 4R \\ a &= 2\sqrt{2}R \end{aligned}$$

$$= \frac{2 \text{ atoms}}{\sqrt{2} (2\sqrt{2}R)^2}$$

That said, we can find that for some crystal structures, several non-parallel directions with different indices are crystallographically equivalent. This means that the atomic density, i.e. atomic arrangement are the same along these directions.

For examples, in cubic crystals  $[100]$ ,  $[\bar{1}00]$ ,  $[010]$ ,  $[0\bar{1}0]$ ,  $[001]$ ,  $[00\bar{1}]$  directions are equivalent each other.

In that case we call it  $\langle 100 \rangle$  Family.

In hexagonal crystals however, the directions with equivalent crystallographic properties do not have the same Miller indices. This problem is solved by introducing 4-axis indices for hexagonal systems. The 4-integer indices are called Bravais-Miller Indices.

This 4-axis system notation is kind of redundant. But convenient.

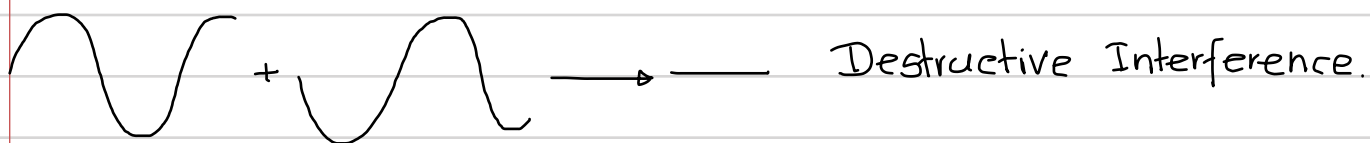
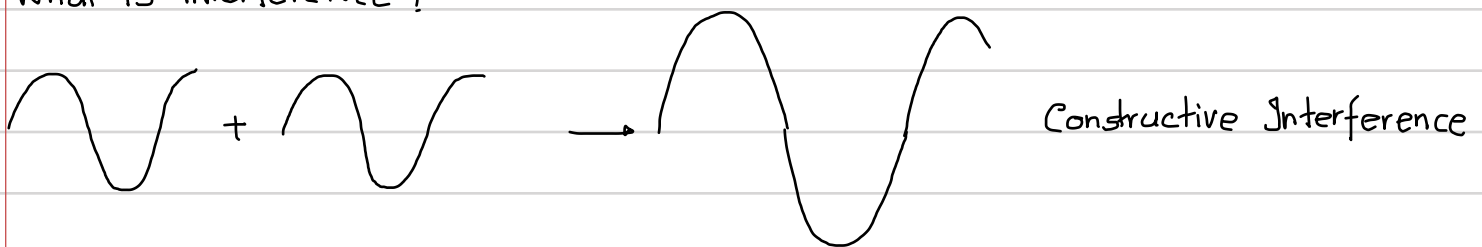
(Look at the slides)

## X-Ray Diffraction

(Determination of Crystal Structures)

Diffraction occurs when a wave sees a series of obstacles. Strictly speaking, a regularly spaced obstacles. The waves scatter from the obstacles and interfere constructively or destructively.

What is interference?



Whether the interference is constructive or destructive is determined by the arrangement of obstacles.

⇒ Diffracted beam composed of a large number of scattered waves.

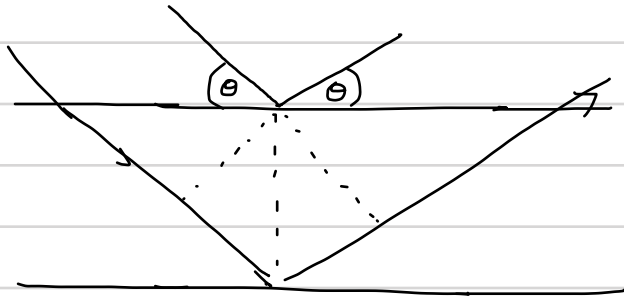
The diffracted intensity is a signature of the arrangement of the obstacles. In order to have a successful diffraction pattern, the separation of the obstacles and wave length of the incident beam has to be of the same order.

X-Rays:

X-Rays are a form of electromagnetic radiation with short wave length of the atomic spacing in solid.

⇒ Now we will examine the conditions for X-Ray diffraction by a periodic arrangement of atoms and how to analyze them.

If we consider the X-Ray diffraction from the plane (hkl)



The condition for a constructive interference

$$2d \sin \theta = n \lambda \leftarrow \text{Bragg Condition}$$

Bragg Law is necessary, but not a sufficient condition for a successful diffraction peak. (We will discuss about this later)

How do we identify the atomic structure related to a given Diffraction pattern.

Let us try to relate the Bragg condition to the atomic structure.

The X-Ray diffraction is related to the electron density of the system.

Electron density is a periodic function. We are going to study about the electron density as follows.

The crystal is invariant under the translation vector  $T$ .

$$T = u_1 \bar{a}_1 + u_2 \bar{a}_2 + u_3 \bar{a}_3$$

Electron density is a periodic function of the position. With the translation vector we can write this as,

$$n(r+T) = n(r)$$

Any periodic function can be explained using Fourier analysis.

## Fourier Analysis of Electron Density:

Let us consider a function  $n(x)$  in one-dimension with a periodicity  $a$  in the direction  $x$ . We expand  $n(x)$  in a Fourier series as,

$$n(x) = n_0 + \sum_{p>0} \left[ C_p \cos \frac{2\pi p x}{a} + S_p \sin \frac{2\pi p x}{a} \right] \quad \text{where } p \rightarrow \text{positive integers.}$$

$C_p, S_p \rightarrow$  Real Constants (Fourier Coefficients)

The factor  $\frac{2\pi}{a}$  appears to ensure the periodicity of 'a'.

We can simply prove that  $n(x) = n(x+a)$  where in one-dimension,  $a$  is the translation vector  $T$ .

$$\begin{aligned} n(x+a) &= n_0 + \sum_p C_p \cos \frac{2\pi p (x+a)}{a} + \sum_p S_p \sin \frac{2\pi p (x+a)}{a} \\ &= n_0 + \sum_p C_p \cos \left( \frac{2\pi p x}{a} + 2\pi p \right) + \sum_p S_p \sin \left( \frac{2\pi p x}{a} + 2\pi p \right) \\ &= n(x) \end{aligned}$$

For different values of  $p$ , we define a series of points  $\frac{2\pi p}{a}$ . This is also a long-range order. That is called a Reciprocal Lattice.

The reciprocal lattice in fact gives the allowed terms in Fourier series

It is also convenient to write this as:

$$n(x) = \sum_p n_p e^{i \frac{2\pi p}{a} x}$$

### Reciprocal Lattice in 3D.

$$n(\mathbf{r}) = \sum_{\mathbf{g}} n_{\mathbf{g}} e^{i \mathbf{g} \cdot \mathbf{r}}$$

$$n(\mathbf{r}+\mathbf{T}) = \sum_{\mathbf{g}} n_{\mathbf{g}} e^{i \mathbf{g} \cdot (\mathbf{r}+\mathbf{T})} = \sum_{\mathbf{g}} n_{\mathbf{g}} e^{i \mathbf{g} \cdot \mathbf{r}} e^{i \mathbf{g} \cdot \mathbf{T}}$$

Now in order to satisfy

$$n(r) = n(r+T)$$

$$e^{iG.T} \rightarrow 1$$

$$G.T = 2\pi i$$

Now if we define  $G = v_1 \bar{b}_1 + v_2 \bar{b}_2 + v_3 \bar{b}_3$

$$\text{with } \bar{b}_1 = 2\pi \frac{\bar{a}_2 \times \bar{a}_3}{\bar{a}_1 \cdot \bar{a}_2 \times \bar{a}_3} \quad b_2 = 2\pi \frac{\bar{a}_3 \times \bar{a}_1}{\bar{a}_1 \cdot \bar{a}_2 \times \bar{a}_3} \quad b_3 = 2\pi \frac{\bar{a}_1 \times \bar{a}_2}{\bar{a}_1 \cdot \bar{a}_2 \times \bar{a}_3}$$

This gives  $G.T = 2\pi i$