CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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Lecture 44: The Structure Factor

So, continuing from the previous lecture, I am going to introduce a term called the *structure factor*. Let me first summarize briefly from the previous lecture. From the previous two lectures, we considered an incident beam falling on point scatterers located at the corners of a unit cell, and the scattered beam propagating in a certain direction. We were trying to determine the intensity at a point Q far away from a finite-sized crystal. Point A was taken as the origin and B as another arbitrary lattice point. The incident beam direction was given by the unit vector $\hat{s}_0$, and the scattered beam direction by the unit vector $\hat{s}$. The distance to the observation point Q was denoted by $\bar{r}$.

The vector $\bar{r}$ was shown to be the lattice translation vector and could be written as

$$\bar{r} = u\bar{a} + v\bar{b} + w\bar{c},$$

where u, v, and w are integers. We also saw that the amplitude at the point Q could be written as

$$Y = \frac{\phi_0}{r} e^{i\omega t} \sum e^{i\frac{2\pi}{\lambda}\bar{r}\cdot\bar{S}},$$

where the summation is over all lattice translation vectors of the finite crystal, and the scattering vector $\bar{S}$ is defined as the difference between the two unit vectors, $\hat{s} - \hat{s}_0$.

We further observed that this summation term attains a maximum when the Laue conditions are satisfied, namely,

$$\bar{S}\cdot\bar{a} = h\lambda, \quad \bar{S}\cdot\bar{b} = k\lambda, \quad \bar{S}\cdot\bar{c} = l\lambda,$$

where h, k, and l are integers. These indices (hkl) can be considered as representing a plane in crystal space that is perpendicular to the scattering vector $\overline{S}$. One additional comment is that ϕ_0 is called the *scattering power* of an atom. In this equation, it represents the amplitude of the wave scattered at a unit distance from the scattering center. The value of ϕ_0 is larger for heavier atoms with higher atomic numbers and smaller for lighter atoms. Therefore, the intensity of scattered X-rays is governed by the kind of atoms present in the crystal.

In our previous analysis, we considered scattering centers located only at the corners of the unit cell. However, real crystals contain atoms not only at the corners but also at other locations within the unit cell, depending on the crystal structure. In this lecture, we extend this analysis.

Let us consider a crystal that has atoms at the corners and also an atom at the body-centered position. Effectively, there are two atoms in the unit cell, and the body-centered atom may be the same as or different from the corner atom. Accordingly, their scattering powers may be different. Let the scattering power at the corner be ϕ_1 and that at the body center be ϕ_2. A crystal such as cesium chloride is an example of this type.

More complex structures are also possible. For example, in sodium chloride, chlorine ions occupy the corners and face centers, while sodium ions occupy the body-centered and edge-centered positions. In this case, there are four chlorine ions and four sodium ions per unit cell, giving a total of eight atoms. In general, there may be m atoms per unit cell, each with a scattering power $\phi_1, \phi_2, \ldots, \phi_m$, and position vectors $\overline{\rho}_1, \overline{\rho}_2, \ldots, \overline{\rho}_m$.

For example, in cesium chloride,

$$\overline{\rho}_1 = (0, 0, 0), \quad \overline{\rho}_2 = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right).$$

These vectors are defined in crystal space with respect to a chosen origin and are expressed using fractional coordinates.

If the crystal has N_1 unit cells along the a-axis, N_2 along the b-axis, and N_3 along the c-axis, and each unit cell contains m atoms, then the total number of atoms in the finite crystal is $N_1N_2N_3m$. The summation over scattered waves must therefore include contributions from positions $\bar{r} + \bar{\rho}_j$, where

$$\bar{r} = u\bar{a} + v\bar{b} + w\bar{c}$$

with

$$u = 0 \dots N_1 - 1, \quad v = 0 \dots N_2 - 1, \quad w = 0 \dots N_3 - 1$$

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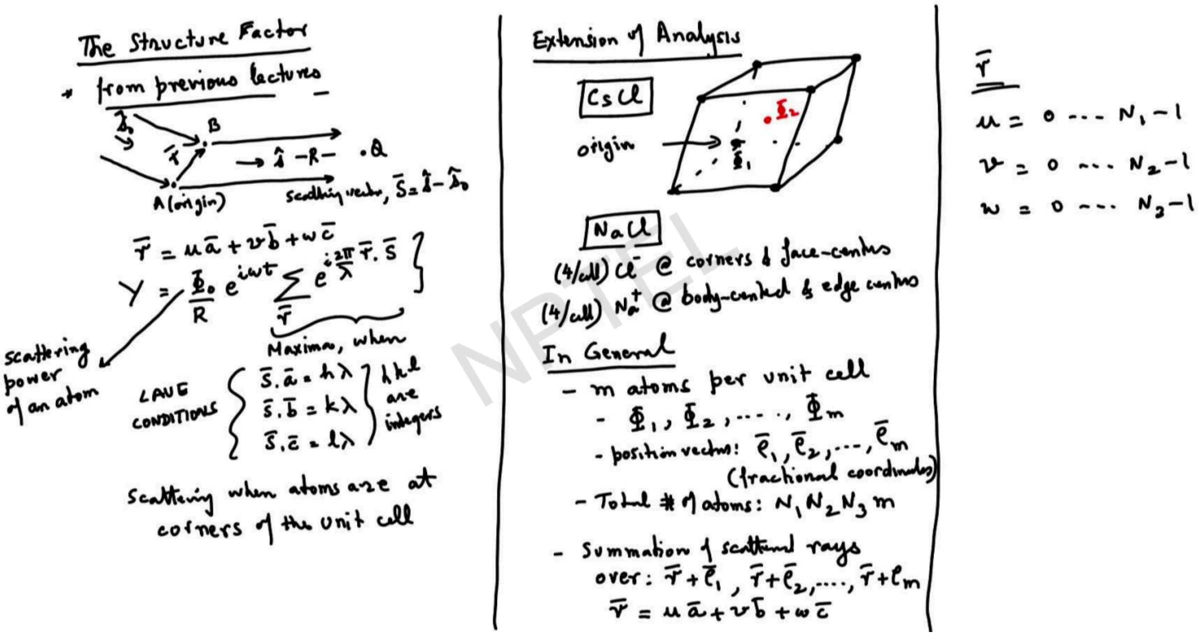

The Structure Factor

- from previous lectures

$\hat{s}_0$ $\hat{s}$ $-R-$ $\bar{r}$

scattering vector, $\bar{S} = \hat{s} - \hat{s}_0$

$$\left.\begin{aligned}\bar{r} &= u\bar{a} + v\bar{b} + w\bar{c}\\ Y &= \frac{\Phi_0}{R} e^{i\omega t} \underbrace{\sum_{\bar{r}} e^{i\frac{2\pi}{\lambda}\bar{r}\cdot\bar{S}}}_{\text{Maxima, when}}\end{aligned}\right\}$$

scattering power of an atom

LAUE CONDITIONS $\left\{\begin{aligned}\bar{S}\cdot\bar{a} &= h\lambda\\ \bar{S}\cdot\bar{b} &= k\lambda\\ \bar{S}\cdot\bar{c} &= l\lambda\end{aligned}\right\}$ $h\,k\,l$ are integers

Scattering when atoms are at corners of the unit cell

Extension of Analysis

$\boxed{\text{CsCl}}$

$\boxed{\text{NaCl}}$

(4/cell) Cl^- @ corners & face-centres

(4/cell) Na^+ @ body-centred & edge centres

In General

- m atoms per unit cell
  - $\Phi_1, \Phi_2, \dots, \Phi_m$
  - position vectors: $\bar{\rho}_1, \bar{\rho}_2, \dots, \bar{\rho}_m$ (fractional coordinates)
- Total # of atoms: $N_1N_2N_3m$
- Summation of scattered rays over: $\bar{r}+\bar{\rho}_1, \bar{r}+\bar{\rho}_2, \dots, \bar{r}+\rho_m$

$\bar{r} = u\bar{a} + v\bar{b} + w\bar{c}$

$\bar{r}$

$u = 0 \dots N_1 - 1$

$v = 0 \dots N_2 - 1$

$w = 0 \dots N_3 - 1$

The wave disturbance at point Q can then be written as

$$Y = \frac{e^{i\omega t}}{r} \sum_{r} \left[\phi_1 e^{i\frac{2\pi}{\lambda}(\bar{r}+\bar{\rho}_1)\cdot\bar{S}} + \phi_2 e^{i\frac{2\pi}{\lambda}(\bar{r}+\bar{\rho}_2)\cdot\bar{S}} + \dots + \phi_m e^{i\frac{2\pi}{\lambda}(\bar{r}+\bar{\rho}_m)\cdot\bar{S}} \right]$$

The common factor $e^{i\frac{2\pi}{\lambda}\bar{r}\cdot\bar{S}}$ can be factored out, yielding

$$\frac{e^{i\omega t}}{r}\left[\phi_1 e^{i\frac{2\pi}{\lambda}\bar{\rho}_1\cdot\bar{S}} + \phi_2 e^{i\frac{2\pi}{\lambda}\bar{\rho}_2\cdot\bar{S}} + \cdots + \phi_m e^{i\frac{2\pi}{\lambda}\bar{\rho}_m\cdot\bar{S}}\right]\sum_r e^{i\frac{2\pi}{\lambda}\bar{r}\cdot\bar{S}}.$$

The summation over r reaches a maximum only when the Laue conditions are satisfied. Under these conditions, the intensity is governed by the remaining bracketed term, which is called the *structure amplitude*, denoted by A. It contains information about the atoms and their positions within the unit cell.

Thus, $A = \sum_{j=1}^{m} \phi_j e^{i\frac{2\pi}{\lambda}\bar{\rho}_j\cdot\bar{S}}$.

Writing ρ_j in crystal space; $\bar{\rho}_j = u_j\bar{a} + v_j\bar{b} + w_j\bar{c}$,

and applying the Laue conditions, we obtain $A = \sum_{j=1}^{m} \phi_j e^{i2\pi(hu_j + kv_j + lw_j)}$

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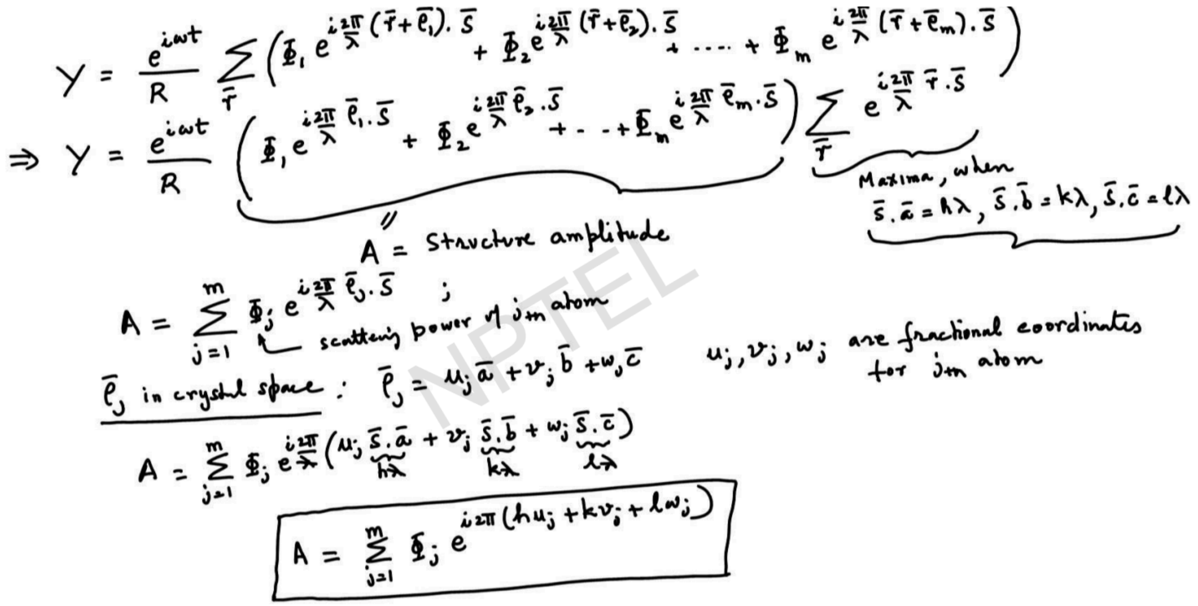

$$Y = \frac{e^{i\omega t}}{R}\sum_{\bar{r}}\left(\Phi_1 e^{i\frac{2\pi}{\lambda}(\bar{r}+\bar{\rho}_1).\bar{S}} + \Phi_2 e^{i\frac{2\pi}{\lambda}(\bar{r}+\bar{\rho}_2).\bar{S}} + \cdots + \Phi_m e^{i\frac{2\pi}{\lambda}(\bar{r}+\bar{\rho}_m).\bar{S}}\right)$$

$$\Rightarrow Y = \frac{e^{i\omega t}}{R}\underbrace{\left(\Phi_1 e^{i\frac{2\pi}{\lambda}\bar{\rho}_1.\bar{S}} + \Phi_2 e^{i\frac{2\pi}{\lambda}\bar{\rho}_2.\bar{S}} + \cdots + \Phi_m e^{i\frac{2\pi}{\lambda}\bar{\rho}_m.\bar{S}}\right)}_{\substack{\parallel \\ A = \text{Structure amplitude}}}\underbrace{\sum_{\bar{r}} e^{i\frac{2\pi}{\lambda}\bar{r}.\bar{S}}}_{\substack{\text{Maxima, when} \\ \bar{S}.\bar{a} = h\lambda,\ \bar{S}.\bar{b} = k\lambda,\ \bar{S}.\bar{c} = l\lambda}}$$

$$A = \sum_{j=1}^{m} \underset{\uparrow\ \text{scattering power of } j\text{th atom}}{\Phi_j} e^{i\frac{2\pi}{\lambda}\bar{\rho}_j.\bar{S}} \quad ;$$

$\bar{\rho}_j$ in crystal space : $\bar{\rho}_j = u_j\bar{a} + v_j\bar{b} + w_j\bar{c}$ $\quad u_j, v_j, w_j$ are fractional coordinates for jth atom

$$A = \sum_{j=1}^{m} \Phi_j e^{i\frac{2\pi}{\lambda}(u_j \underbrace{\bar{S}.\bar{a}}_{h\lambda} + v_j \underbrace{\bar{S}.\bar{b}}_{k\lambda} + w_j \underbrace{\bar{S}.\bar{c}}_{l\lambda})}$$

$$\boxed{A = \sum_{j=1}^{m} \Phi_j e^{i2\pi(hu_j + kv_j + lw_j)}}$$

Now we define the *atomic scattering factor* f as the ratio of the amplitude scattered by an atom to that scattered by a single classical electron.

$$f = \frac{amplitude\ of\ wave\ scattered\ by\ an\ atom}{amplitude\ of\ wave\ scattered\ by\ a\ single\ classical\ electron}$$

Similarly, the *structure factor* F is defined as the amplitude scattered by all atoms in the unit cell divided by that scattered by a single classical electron.

$$F = \frac{amplitude\ of\ wave\ scattered\ by\ all\ atoms\ in\ unit\ cell}{amplitude\ of\ wave\ scattered\ by\ a\ single\ classical\ electron}$$

Dividing the structure amplitude by the electron scattering amplitude gives

$$F = \sum_{j=1}^{m} f_j e^{i2\pi(hu_j+kv_j+lw_j)}.$$

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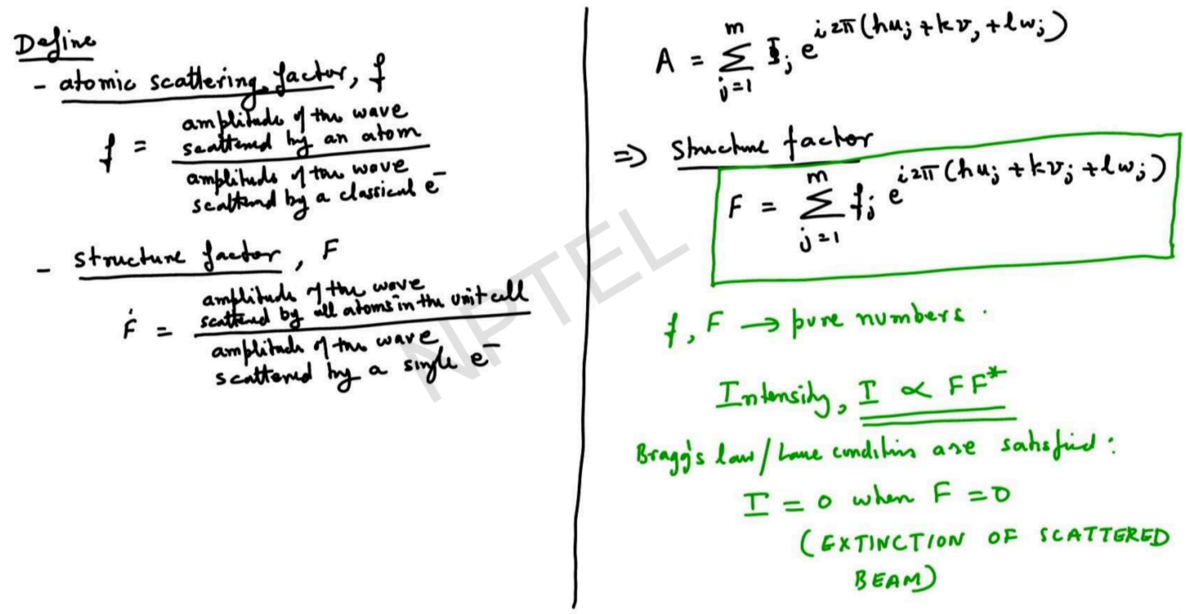

Define

- atomic scattering factor, f

$$f = \frac{\text{amplitude of the wave scattered by an atom}}{\text{amplitude of the wave scattered by a classical } e^-}$$

- structure factor, F

$$F = \frac{\text{amplitude of the wave scattered by all atoms in the unit cell}}{\text{amplitude of the wave scattered by a single } e^-}$$

$$A = \sum_{j=1}^{m} f_j e^{i2\pi(hu_j+kv_j+lw_j)}$$

$\Rightarrow$ Structure factor

$$\boxed{F = \sum_{j=1}^{m} f_j e^{i2\pi(hu_j+kv_j+lw_j)}}$$

$f, F \rightarrow$ pure numbers.

Intensity, $I \propto FF^*$

Bragg's law / Laue condition are satisfied:

$I = 0$ when $F = 0$

(EXTINCTION OF SCATTERED BEAM)

Both the atomic scattering factor f and the structure factor F are dimensionless quantities. The intensity of the diffracted beam is proportional to

$$I \propto FF^*$$

the product of the structure factor and its complex conjugate. Even when the Bragg or Laue conditions are satisfied, the diffracted intensity becomes zero if $F = 0$, a phenomenon known as *extinction* of scattered beam.

With this, I conclude this lecture. In the next lecture, we will perform calculations based on the structure factor. Thank you.