

Week 8

Crystal Structure and Surface Chemistry

8.1 X-Ray Diffraction Fundamentals

5/16:

- Final exam next Wednesday in class.
 - 50 minutes.
 - Questions like the midterm.
 - We can bring our notes and textbook, but cannot search online.
 - Can we bring notes on a computer, like mine, or do we have to print?
 - 1 computation problem.
 - We will write answers on paper.
- Review of last lecture.
- Tian goes through some examples of naming crystallographic planes from pictures of them intersecting a unit cell.
 - The first example is a 111 plane.
 - If asked to identify a 111 plane, it is enough to identify it as a 111 plane; we do not have to identify it as a possible 222 plane, too.
 - Consider a plane intersecting the **a**, **b**, and **c** axes at $a' = 2a/5$, $b' = b/2$, and $c' = c/5$, respectively.
 - Then $h = \frac{5}{2}$, $k = 2$, and $l = 5$.
 - An easier way to show this, however, is with $h = 5$, $k = 4$, and $l = 10$. Aren't these planes spaced twice as close together, though?
 - Consider a plane intersecting the **a**, **b**, and **c** axes at $a' = a/2$, $b' = b/2$, and $c' = -c/4$, respectively.
 - A convenient point to use as the origin in this case is the upper-left corner.
 - Thus, the plane is $(2, 2, -4)$.
 - The question of could we denote the plane by $(1, 1, -2)$: These two sets of planes are parallel, but the spacing of $(1, 1, -2)$ would skip every plane like $(2, 2, -4)$. Thus, we need $(2, 2, -4)$ for the spacing.
- Rules.
 1. If you see a fraction, convert to integers.
 2. But do not reduce a ratio.

- The fundamentals of X-ray diffraction.

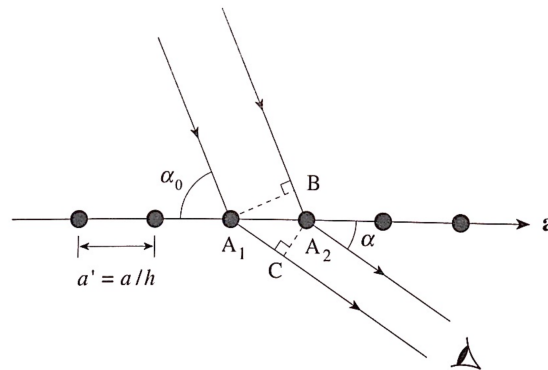


Figure 8.1: Deriving the von Laue equations.

- An X-ray diffraction pattern is a collection of spots of varying intensity.
 - The arrangement of the spots provides a great deal of information on the crystal structure, as we will soon see.
- We define

$$\Delta = \overline{A_1C} - \overline{A_2B}$$

- Imagine two parallel rays of light incident on points A_1 and A_2 in a crystal lattice.
- $\overline{A_1C}$ is the distance that the bottom beam travels after being scattered at A_1 and before the top beam is scattered at A_2 .
- Symmetrically, $\overline{A_2B}$ is the distance that the top beam travels after the bottom beam is scattered at A_2 and before being scattered at A_2 .
- Either way, Δ represents a kind of phase offset that occurs upon scattering. Say, for instance, that the two waves are in phase before scattering. Then from the perspective of the top wave, the bottom wave gets offset by Δ relative to it during the scattering process, and vice versa from the perspective of the bottom wave.
- If the distance Δ is equal to an integral multiple of the wavelength of the X-ray radiation, the two diffracted beams will interfere constructively. Mathematically, since

$$\overline{A_1C} = a' \cos \alpha \qquad \overline{A_2B} = a' \cos \alpha_0$$

as we may readily read from Figure 8.1, we require

$$\begin{aligned} n\lambda &= \Delta \\ &= \overline{A_1C} - \overline{A_2B} \\ &= a'(\cos \alpha - \cos \alpha_0) \\ nh\lambda &= a(\cos \alpha - \cos \alpha_0) \end{aligned}$$

- **First-order reflection:** A diffraction spot that corresponds to $n = 1$ in the above equation.
- **Second-order reflection:** A diffraction spot that corresponds to $n = 2$ in the above equation.
- **n^{th} -order reflection:** A diffraction spot that corresponds to n in the above equation.
- **von Laue equations:** The following three equations, which relate the quantities involved in a first-order reflection. *Given by*

$$a(\cos \alpha - \cos \alpha_0) = h\lambda \qquad b(\cos \beta - \cos \beta_0) = k\lambda \qquad c(\cos \gamma - \cos \gamma_0) = l\lambda$$

where $\alpha_0, \beta_0, \gamma_0$ are the angles of incidence of the X-ray radiation with respect to the **a**, **b**, and **c** axes of the crystal, respectively, and α, β , and γ are the corresponding diffraction angles.

- An example of how to use the von Laue equations.
 - Consider the diffraction pattern obtained when an X-ray beam is directed at a crystal whose unit cell is primitive cubic.
 - Orient the crystal such that the incident X-rays are perpendicular to the **a** axis of the crystal.
 - Then the relevant von Laue equation reduces to $a \cos \alpha = h\lambda$.
 - It follows that discrete angles will yield discrete spots?
- A more general situation.
 - For an arbitrary hkl plane, the direction of diffraction with respect to the **a** axis is the same as that for the $h00$ planes. But there is also diffraction with respect to the **b** and **c** axes.
 - The diffraction spots from an hkl plane (with fixed h) will lie along the surface of a cone that makes an angle α with respect to the **a** axis of the crystal.
- The Bragg diffraction.
 - We have

$$\lambda = 2 \left(\frac{d}{n} \right) \sin \theta$$

where θ is the angle of incidence (and reflection) of the X-rays with respect to the lattice plane, λ is the wavelength of the X-ray radiation, and $n = 1, 2, \dots$ is the order of the reflection.
 - d in terms of the Miller indices for a cubic unit cell gives

$$\sin^2 \theta = \frac{n^2 \lambda^2}{4a^2} (h^2 + k^2 + l^2)$$
 - Tian will not go through the details, but there will be a homework problem in which we will explore this.
- Rotating the sample vs. rotating the incident beam in an X-ray diffraction experiment.
 - In most cases, we fix the incident beam orientation and rotate the sample on the sample stage.
- Midterms back today or tmw.
- The grade distribution in the course.
 - A or A- is typically 65-70%.

8.2 The Scattering Factor and Intensity

5/18:

- Reviews the Bragg diffraction.
 - There is no such thing as a 222 or a 333 lattice plane; rather, there are 111 lattice planes with higher order diffractions.
 - Tian says something about higher order reflections?
- **Scattering factor** (of an atom): The following quantity, where $\rho(r)$ is the spherically symmetric electron density (number of electrons per unit volume) of the atom and $k = 4\pi \sin(\theta)/\lambda$. In turn, θ is the scattering angle and λ is the wavelength of the X-radiation. *Denoted by **f**. Given by*

$$f = 4\pi \int_0^\infty \rho(r) \frac{\sin kr}{kr} r^2 dr$$

- The integral $4\pi \int_0^\infty \rho(r) r^2 dr$ gives the total number of electrons in the atom.

- The total scattering intensity is related to the periodic structure of the electron density in the crystal.
 - If the crystal is oriented such that the von Laue equation governing scattering from atoms along the a axis is satisfied, then

$$\Delta_{11} = \Delta_{22} = \frac{a}{h}(\cos \alpha - \cos \alpha_0) = \lambda \qquad \Delta_{12} = x(\cos \alpha - \cos \alpha_0)$$

- Combining these two equations, we learn that

$$\Delta_{12} = \frac{\lambda h x}{a}$$

- The difference in path length corresponds to a phase difference between the diffracted beams from successive 1 and 2 atoms of

$$\phi = 2\pi \frac{\Delta_{12}}{\lambda} = 2\pi \frac{\lambda h x / a}{\lambda} = \frac{2\pi h x}{a}$$

- The amplitude of the light scattered from successive 1 and 2 atoms is then

$$\begin{aligned} A &= f_1 \cos \omega t + f_2 \cos(\omega t + \phi) \\ &= f_1 e^{i\omega t} + f_2 e^{i(\omega t + \phi)} \end{aligned}$$

- The detected intensity is proportional to the square of the magnitude of the amplitude.

$$\begin{aligned} I \propto |A|^2 &= [f_1 e^{i\omega t} + f_2 e^{i(\omega t + \phi)}][f_1 e^{-i\omega t} + f_2 e^{-i(\omega t + \phi)}] \\ &= f_1^2 + f_1 f_2 e^{i\phi} + f_1 f_2 e^{-i\phi} + f_2^2 \\ &= f_1^2 + f_2^2 + 2f_1 f_2 \cos \phi \end{aligned}$$

- The first two terms reflect the constructive interference of the X-rays scattered from the set of parallel planes through the 1 atoms and 2 atoms, respectively.
 - The third term takes into account the interference of the scattering from these two sets of parallel planes.
- We can therefore ignore the $e^{i\omega t}$ term and define

$$F(h) = f_1 + f_2 e^{i\phi} = f_1 + f_2 e^{2\pi i h x / a}$$

- The intensity is then proportional to $|F(h)|^2$.
- Generalizing to three dimensions for a unit cell that contains atoms of type j located at points x_j, y_j, z_j gives

$$F(hkl) = \sum_j f_j e^{2\pi i (hx_j/a + ky_j/b + lz_j/c)} = \sum_j f_j e^{2\pi i (hx'_j + ky'_j + lz'_j)}$$

where $x'_j = x_j/a$, $y'_j = y_j/b$, and $z'_j = z_j/c$.

- An analysis of the CsCl body-centered cubic lattice, where we take the unit cell to have eighth chloride atoms at every corner and one cesium ion in the center.
 - Taking f_+ to be the scattering factor of the Cs^+ cations and f_- to be the scattering factor of the Cl^- anions, we get

$$\begin{aligned} F(hkl) &= 1 \times f_- e^{\pi i (h+k+l)} + \frac{1}{8} \times f_+ \left[e^0 + e^{2\pi i h} + e^{2\pi i k} + e^{2\pi i l} + e^{2\pi i (h+k)} + e^{2\pi i (k+l)} + e^{2\pi i (h+l)} + e^{2\pi i (h+k+l)} \right] \\ &= f_- (-1)^{h+k+l} + \frac{1}{8} f_+ [8] \\ &= \begin{cases} f_+ + f_- & h+k+l \text{ is even} \\ f_+ - f_- & h+k+l \text{ is odd} \end{cases} \end{aligned}$$

where we substitute $e^{\pi i} = -1$ and $e^{2\pi i} = 1$ to get from the first line to the second.