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.

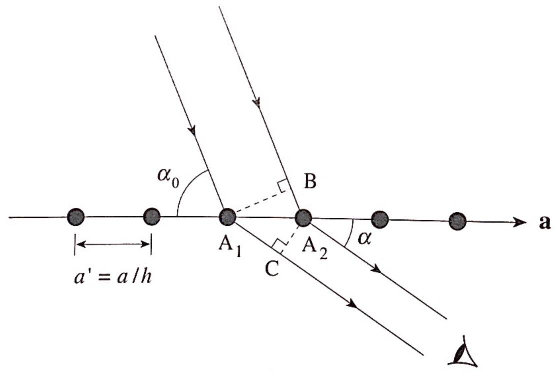

Figure 8.1: Deriving the von Laue equations.

  - 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
$$\Delta = \overline{\mathrm{A_1C}} - \overline{\mathrm{A_2B}}$$
    - Imagine two parallel rays of light incident on points A_1 and A_2 in a crystal lattice.
    - $\overline{\mathrm{A_1C}}$ 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, $\overline{\mathrm{A_2B}}$ 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
$$\overline{\mathrm{A_1C}} = a'\cos\alpha \qquad \overline{\mathrm{A_2B}} = a'\cos\alpha_0$$
as we may readily read from Figure 8.1, we require
$$\begin{aligned} n\lambda &= \Delta \\ &= \overline{\mathrm{A_1C}} - \overline{\mathrm{A_2B}} \\ &= a'(\cos\alpha - \cos\alpha_0) \\ nh\lambda &= a(\cos\alpha - \cos\alpha_0) \end{aligned}$$

- **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.
- $\boldsymbol{n}^{\mathbf{th}}$**-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%.