Week 8

Crystal Structure and Surface Chemistry

8.1 X-Ray Diffraction Fundamentals

• 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.
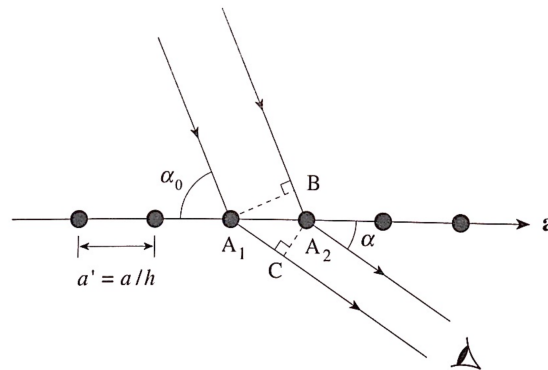

Figure 8.1: Deriving the von Laue equations.

  - 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
    $$\overline{A_1C} = a' \cos \alpha \qquad\qquad \overline{A_2B} = a' \cos \alpha_0$$
    as we may readily read from Figure 8.1, we require
    $$n\lambda = \Delta$$
    $$= \overline{A_1C} - \overline{A_2B}$$
    $$= a'(\cos \alpha - \cos \alpha_0)$$
    $$nh\lambda = a(\cos \alpha - \cos \alpha_0)$$

- **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*

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

  – The integral $4\pi \int_0^\infty \rho(r) r^2 \, \mathrm{d}r$ 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

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

  - 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

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

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

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

    - ■ 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

$$F(hkl) = 1 \times f_- e^{\pi i(h+k+l)} + \frac{1}{8}\times f_+\left[e^0 + e^{2\pi ih} + e^{2\pi ik} + e^{2\pi il} + e^{2\pi i(h+k)} + e^{2\pi i(k+l)} + e^{2\pi i(h+l)} + e^{2\pi i(h+k+l)}\right]$$

$$= f_-(-1)^{h+k+l} + \frac{1}{8}f_+[8]$$

$$= \begin{cases} f_+ + f_- & h+k+l \text{ is even} \\ f_+ - f_- & h+k+l \text{ is odd} \end{cases}$$

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

8.3 Continuous Structure Factors and Adsorption

5/20:
- More on the CsCl example today.

  - We simplify $e^{i\pi(h+k+l)}$ to $(-1)^{h+k+l}$ by expanding to $\text{cis}[\pi(h+k+l)]$, ignoring the imaginary part to get $\cos[\pi(h+k+l)]$, the sign of which does depend on whether the natural number $h+k+l$ is even or odd exactly like $(-1)^{h+k+l}$.

- CsI example.

  - Cs^+ and I^- are **isoelectronic**.
  - We have that
  $$f_+(Cs^+) = f_-(I^-)$$

- The structure factor and the electron density are related by a Fourier transform.

  - In both atomic and molecular crystals, the electron density is not localized at individual points within the unit cell.
  - We should consider the unit cell of the crystal to have a continuous electron density distribution $\rho(x, y, z)$.
  - The structure factor is no longer simply a sum over discrete atoms but now becomes an integral over the continuous electron density distribution in the unit cell, as follows.

  $$F(hkl) = \int_0^a \int_0^b \int_0^c \rho(x, y, z) e^{2\pi i(hx/a + ky/b + lz/c)} \, dx \, dy \, dz$$

  - For the entire crystal, we have the following.

  $$F(hkl) \propto \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(x, y, z) e^{2\pi i(hx/a + ky/b + lz/c)} \, dx \, dy \, dz$$

  - $F(hkl)$ is related to $\rho(x, y, z)$ by a **Fourier transform**.

  $$\rho(x, y, z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F(hkl) e^{-2\pi i(hx/a + ky/b + lz/c)}$$

  - If we let $F(hkl) = A(hkl) + iB(hkl)$, then it follows that the intensity is
  $$I(hkl) \propto |F(hkl)|^2 = [A(hkl)]^2 + [B(hkl)]^2$$

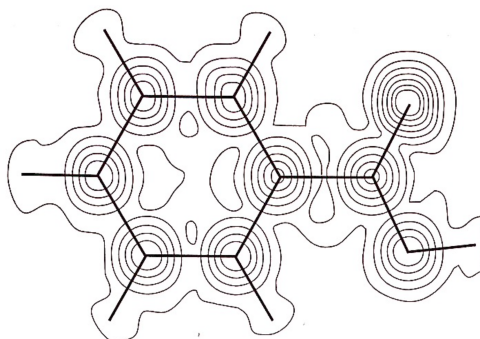- An electron-density map of a benzoic acid molecule.

Figure 8.2: The electron density of benzoic acid.

- An electron-density map of a benzoic acid molecule determined from the X-ray diffraction pattern of a benzoic acid crystal.

- Each contour line corresponds to a constant value of the electron density.

- The location of the nuclei are readily deduced from this electron-density map and are represented by the vertices of the solid lines.

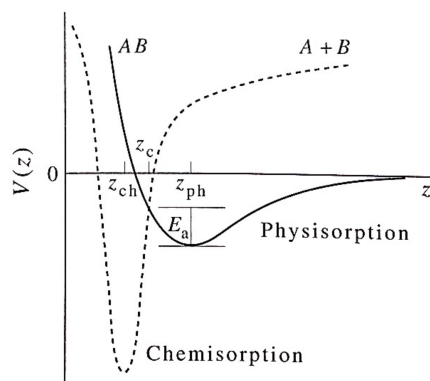- A gas molecule can physisorb or chemisorb to a solid surface.

Figure 8.3: Comparing physisorption and chemisorption.

- Figure 8.3 shows one-dimensional potential-energy curves for the physisorption of molecule AB (solid line) and the dissociative chemisorption of AB (dashed line).

- The quantity z is the distance from the surface.

- In the physisorbed state, the molecule AB is bound to the surface by van der Waals forces.

- In the chemisorbed state, the $A-B$ bond is broken, and the individual atoms are bound covalently or ionically on the surface.

  - As such, chemisorbed molecules are bound more strongly, are held closer to the surface.
  - As $z \to \infty$, V approaches a value greater than zero because AB is dissociated here. The asymptote is the bond dissociation energy (BDE).
  - Additionally, while $A + B$ may be at zero, what we have here is $A^+ + B^-$. As such, we have the Coulomb potential, and the charged ions are unstable to be apart.

- The points z_{ch} and z_{ph} are the surface-molecule bond lengths for a chemisorbed and physisorbed molecule, respectively. The length of the substrate-adsorbate bond is shorter for a chemisorbed molecule than for a physisorbed molecule.

- The two potential curves cross at z_c. The activation energy for the conversion from physisorption to chemisorption is measured from the bottom of the physisorbed potential and is E_a.

- **Adsorption isotherm**: A plot of surface coverage as a function of gas pressure at constant temperature.

- Langmuir's assumptions.

  - The adsorbed molecules do not interact with one another.
  - The enthalpy of adsorption was independent of surface coverage.
  - There are a finite number of surface sites where a molecule can adsorb.

– The process of adsorption and desorption is depicted by the reversible elementary process

$$\text{A}\,(\text{g}) + \text{S}\,(\text{s}) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \text{A}{-}\text{S}\,(\text{s})$$
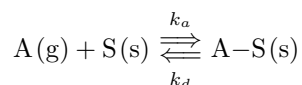
with equilibrium constant

$$K_c = \frac{k_a}{k_d} = \frac{[\text{A}{-}\text{S}]}{[\text{A}]\,[\text{S}]}$$

where k_a and k_d are the rate constants for a̲dsorption and d̲esorption, respectively.

- The fact that k_a and k_d are constants independent of the extent of surface coverage implies that adsorbed molecules do not interact with one another.

- An analysis of surface coverage.

  – Let σ_0 be the concentration of surface sites in units of m^{-2}.

  – If the fraction of surface sites occupied by an adsorbate is θ, then σ (the adsorbate concentration on the surface) is $\theta \sigma_0$ and the concentration of empty surface sites is give by $\sigma_0 - \theta \sigma_0 = (1-\theta)\sigma_0$.

  – We have that

$$v_d = k_d \theta \sigma_0 \qquad\qquad v_a = k_a (1-\theta)\sigma_0 [\text{A}]$$

  where v_d is the rate of desorption, v_a is the rate of absorption, and $[\text{A}]$ is the number density or the concentration of $\text{A}\,(\text{g})$.

  – It follows that at equilibrium,

$$k_d \theta = k_a (1-\theta)[\text{A}]$$
$$\frac{1}{\theta} = 1 + \frac{1}{K_c[\text{A}]}$$

  – Additionally, since

$$[\text{A}] = \frac{P_\text{A}}{k_\text{B}T}$$

  the Langmuir adsorption isotherm is

$$\frac{1}{\theta} = 1 + \frac{1}{bP_\text{A}}$$

  where we have defined $b = K_c/k_\text{B}T$.

- For different materials, the same mass may correspond to orders of magnitude different surface areas (consider MOFs for instance).

- Langmuir adsorption isotherm for the case in which a diatomic molecule dissociates upon adsorption to the surface.

  – This reaction can be written as

$$\text{A}_2(\text{g}) + 2\,\text{S}\,(\text{s}) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} 2\,\text{A}{-}\text{S}\,(\text{s}) \qquad\qquad K_c = \frac{k_a}{k_d} = \frac{[\text{A}{-}\text{S}]^2}{[\text{A}_2]\,[\text{S}]^2}$$

  – Two surface sites are involved in the adsorption and desorption process.

$$v_a = k_a[\text{A}_2](1-\theta)^2 \sigma_0^2 \qquad\qquad v_d = k_d \theta^2 \sigma_0^2$$

– At equilibrium, these rates are equal, i.e.,

$$k_a[A_2](1-\theta)^2 = k_d\theta^2$$

$$\theta = \frac{K_c^{1/2}[A_2]^{1/2}}{1 + K_c^{1/2}[A_2]^{1/2}}$$

– Having defined $[A] = P_A/k_BT$ and $b = K_c/k_BT$, we have

$$\theta = \frac{b_{A_2}^{1/2}P_{A_2}^{1/2}}{1 + b_{A_2}^{1/2}P_{A_2}^{1/2}}$$

$$\frac{1}{\theta} = 1 + \frac{1}{b_{A_2}^{1/2}P_{A_2}^{1/2}}$$

8.4   Office Hours (Tian)

- The whole $F \propto \sigma\rho$ thing from Lecture 4.

- The presence of lack thereof of the $1/2$ coefficient in Z_{AA} and Z_{AB}.

- Lecture 13 example problems.

  – Equilibrium constants appear in reversible reactions.
  – Only applicable for reversible elementary steps.
  – If there's a problem that involves equilibrium constants, he will identify it; tell us that a reaction is reversible and equilibrium constants need to be considered.

- Will there be extra office hours before the final?

- Midterm info.

  – The midterm had a bimodal (2 peaks) distribution.

- Miller indices.

  – We define 100 planes by convention.
  – The middle plane in Figure 31.9a intersects the a-axis at $(1,0,0)$, and never intersects the b or c axes. However, we can conceptually define an intersection at ∞, leading to $k = b/\infty = 0$ and similarly for l.

- Final info.

  – Homeworks 5-6 for the computation problem.
  – Rest are true/false and conceptual (like defining the Miller indices, for example).
  – Open note, calculator, but not open internet.
  – We can bring our computer for online notes, but we cannot search anything.
  – Only conceptual problems on X-ray diffraction.
  – No class on Friday Week 9.

- X-ray diffraction info.

  – Some people who have taken Advanced Inorgo will have already seen this, but it's the first time for most people.

## 8.5   Chapter 31: Solids and Surface Chemistry

From McQuarrie and Simon (1997).

5/24:
- The experimental setup for X-ray diffraction.

    - Generating X-rays.
        - A metal target (often copper) is bombarded with high-energy electrons inside a vacuum tube.
        - This bombardment generates electronically excited copper cations which relax back to their ground state by emitting a photon.
        - A copper sample generates two types of photons: One with $\lambda = 154.433\,\text{pm}$ and another with $\lambda = 154.051\,\text{pm}$.
    - One of these two wavelengths is directed at a single sample crystal.
    - The crystal is located on a rotatable mount, enabling the scientist to orient the incident X-rays with respect to the three crystallographic axes.
    - Most radiation passes through a given crystal, but a little bit is diffracted, giving rise to the **diffraction pattern**.

- **Diffraction pattern**: The image recorded on the detector, where dark spots correspond to concentrated diffracted X-rays.

- The positions and intensities of the diffraction spots are determined by the spacing between the different sets of parallel *hkl* planes of the crystal lattice.

- Comments on Figure 8.1.

    - Lattice points A_1, A_2 lie in neighboring *hkl* planes along the **a** axis of the crystal and are separated by a'.
    - α_0 is the angle of incidence of the X-ray beam.
    - α is the angle of diffraction of the X-ray beam.
    - Δ is the difference in path length of the X-rays diffracted at lattice points A_1, A_2 by the time they reach the observer (or collection sheet).
    - "If we extend [our discussion of constructive and destructive interference] to include diffraction from all the atoms in the row shown in [Figure 8.1], then to observe a diffraction signal, the light diffracted from each atom in the row must interfere constructively. This means that the crystal plane must be oriented with respect to the incident X-rays so that Δ is equal to an integral multiple of the wavelength of the X-ray radiation" (McQuarrie & Simon, 1997, p. 1283).
    - The substitution $a' = a/h$ allows us to write the diffraction equation in terms of the Miller index and the unit cell length.

- Describing the diffraction pattern generated by the first-order reflections of the *h*00 planes in a primitive cubic crystal that is oriented such that the incident X-rays are perpendicular to the **a** axis of the crystal.

    - The perpendicular orientation tells us that $\alpha_0 = 90°$.
    - Thus, the von Laue equations become

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

    - The first equation says that each value of h (i.e., each incremental plane spacing) corresponds to a specific scattering angle α.
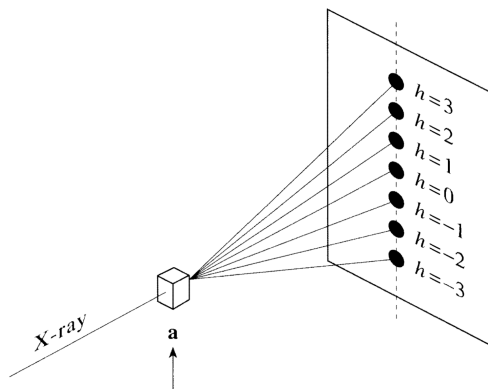
Figure 8.4: The diffraction pattern of the $h00$ planes in a primitive cubic crystal.

■ For $h = 0$, we have $\cos \alpha = 0$ and thus $\alpha = 90°$.
■ For $h = 1$, we have $\cos \alpha = \lambda/a$.
■ For $h = 2$, we have $\cos \alpha = 2\lambda/a$.
■ And on and on.

– Since $k, l = 0$ in all of these planes, the second and third equations say, respectively, that $\beta = \beta_0$ and $\gamma = \gamma_0$.

– Thus, we obtain the diffraction pattern in Figure 8.4.

• Example: Calculating the spacing between lattice points along the **a** axis in a primitive cubic crystal from the first-order reflections of the 000 and 100 planes.
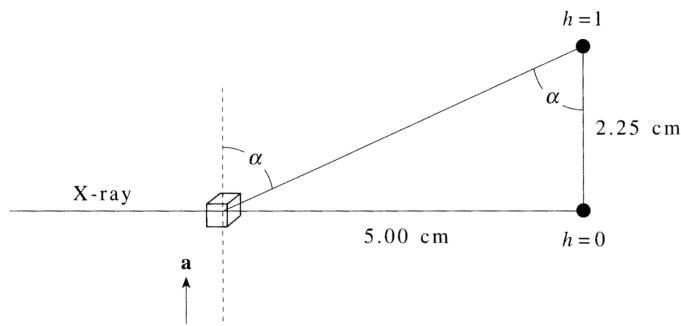

Figure 8.5: Primitive cubic lattice spacing.

– In our experimental setup, we use the $\lambda = 154.433\,\text{pm}$ line of copper as an X-ray source.

– We want to find a. We know that $a \cos \alpha = \lambda$. We also know that $\tan \alpha = 5.00/2.25$. Therefore,

$$a = \frac{\lambda}{\cos\left(\tan^{-1}(5.00/2.5)\right)} = 376.37\,\text{pm}$$

• Arbitrary hkl planes.

– The direction of diffraction with respect to the **a** axis is the same as that for $h00$ planes, but there is also componentwise diffraction with respect to the **b** and **c** axes.

– Thus, the diffraction spots lie along the surface of a cone (see Figure 8.6a) that makes an angle α with respect to the incident X-ray beam in the plane defined by the X-ray beam and the **a** axis (i.e., the plane of the page in Figure 8.5).
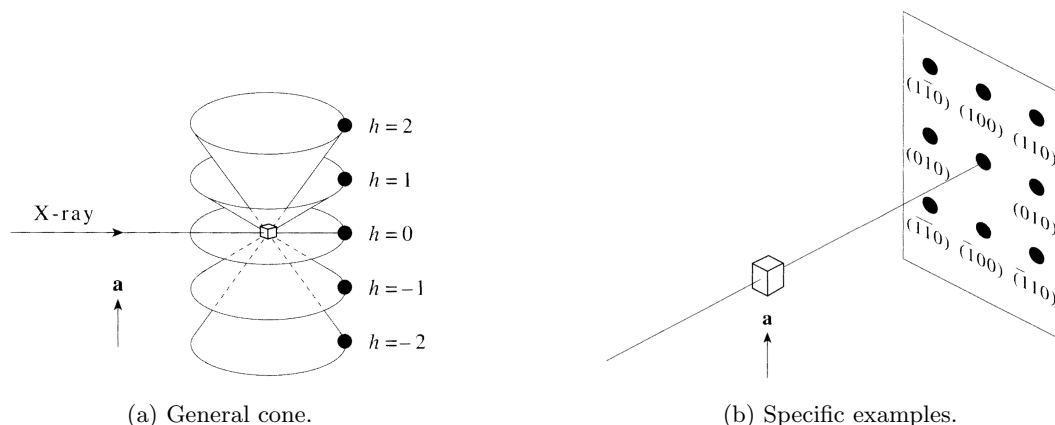
(a) General cone.

(b) Specific examples.

Figure 8.6: The diffraction pattern of the hkl planes in a primitive cubic crystal.

- Where exactly these spots lie depends on the other two von Laue equations.
- Some examples of spots corresponding to hkl planes are given in Figure 8.6b.

- Bragg's approach to diffraction.

    - William Bragg (an English chemist) "modeled the diffraction of X-rays from crystals as originating from the reflection of X-rays from the various sets of parallel hkl lattice planes" (McQuarrie & Simon, 1997, pp. 1286–87).
    - The Bragg equation is

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

    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-rays, $n = 1, 2, \ldots$ is the order of the reflection, and d is the lattice plane spacing.

        ■ For Bragg's derivation, see Problem 31-29.
    - By squaring the above and substituting for d^2 the lattice plane spacing for a cubic unit cell, we obtain

$$\sin^2 \theta = \frac{n^2 \lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

    - Bragg's equation can be derived from the von Laue equations and vice versa (see Problems 31-44 and 31-45), so the two formulations are equivalent.

- In practice, diffraction spots are not observed from all hkl planes and the intensity can vary significantly as well.

    - "For example, an atomic crystal whose unit cell is body-centered cubic shows no diffraction from the hkl planes in which $h + k + l$ is an odd number" (McQuarrie & Simon, 1997, p. 1287).
    - The key to understanding what determines the intensity of a diffraction spot lies in the details of how atoms diffract X-rays.

- X-rays are scattered by the electrons in an atom, but since different atoms have different sized orbitals filled by different numbers of electrons, the scattering efficiency varies atom to atom. Hence we define the **scattering factor**.

- **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 $k = (4\pi/\lambda) \sin(\theta)$. In turn, θ is the scattering angle and λ is the wavelength of the X-radiation. *Denoted by f. Given by*

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

– Wavelengths of X-rays are comparable in size to an atom, so the scatterings from different regions interfere with each other. The integrand accounts for this interference with the $\sin(kr)/kr$ term.

– The scattering factor increases as the number of electrons ($\rho(r)$) increases, and decreases as the angle of diffraction θ increases.

– The scattering factor for the case where $\theta = 0°$ reduces to the total number of electrons in the atom or ion.

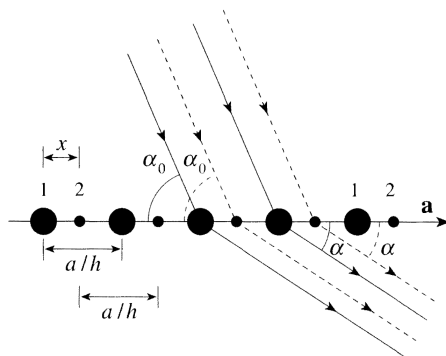• Deriving an expression for the scattering intensity.

Figure 8.7: The scattering from a lattice consisting of two types of atoms.

– Consider a one-dimensional lattice consisting of two different types of atoms, 1 and 2. Let these atoms have scattering factors f_1, f_2, respectively.

– The differences Δ_{11} and Δ_{22} in path length traveled by X-rays diffracted by successive 1 atoms and 2 atoms, respectively, and corresponding to first-order reflections are equal and given by the following, as can easily be determined from Figure 8.7 and the von Laue equations.

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

– Similarly, the difference Δ_{12} in path length traveled by X-rays diffracted by consecutive 1 and 2 atoms and corresponding to a first-order reflection is given by the following and is not equal to an integral number of wavelengths.

$$\Delta_{12} = x(\cos\alpha - \cos\alpha_0)$$

– An alternate form for Δ_{12} can be obtained by solving the expression for $\Delta_{11} = \Delta_{22}$ for $\cos\alpha - \cos\alpha_0$ and substituting into the above equation to yield

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

– This difference in path length corresponds to a phase offset

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

■ Note that to derive this expression, we first take the difference in path length and divide by λ to determine the phase offset in "number of waves." We then multiply by 2π to convert to radians.

■ For instance, if $\Delta_{12} = 1.5\lambda$, then $\Delta_{12}/\lambda = 1.5\,\text{waves} = 3\pi$ radians, as should make intuitive sense.

– It follows that the total amplitude of the light scattered from successive 1 and 2 atoms is

$$A = f_1 \cos \omega t + f_2 \cos(\omega t + \phi)$$

  ■ Technically, what's given is a wave function in terms of time t.
  ■ Also note that the left term in the above expression gives the contribution of the light scattered by successive 1 atoms and the right term gives the contribution of the light scattered by successive 2 atoms. By the superposition principle, the total wave function is the sum of the two partial wave functions, as we have above.

– For convenience, we may switch the above expression to exponential notation.

$$A = f_1 e^{i\omega t} + f_2 e^{i(\omega t + \phi)} = \left(f_1 + f_2 e^{i\phi} \right) e^{i\omega t}$$

– Since the intensity of electromagnetic waves is proportional to the square of the magnitude of the amplitude[1], we have that

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

  ■ The first two terms above 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 accounts for the interference between these two sets.

– The intensity does not depend on the frequency ω of the radiation or the time t but only on the phase offset ϕ (this is because the $e^{i\omega t}$ terms canceled upon complex multiplication). As such, we may define the **structure factor** as the like amplitude but without the $e^{i\omega t}$ term. Naturally, $I \propto |F(h)|^2$.

• **Structure factor** (1D): The following expression, the magnitude squared of which is proportional to the intensity of diffracted radiation between planes spaced h apart. *Denoted by $\boldsymbol{F(h)}$. Given by*

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

• We may generalize the 1D structure factor to three dimensions.

• **Structure factor**: The following expression, the magnitude squared of which is proportional to the intensity of diffracted radiation between hkl planes. *Denoted by $\boldsymbol{F(hkl)}$. Given by*

$$F(hkl) = \sum_j f_j e^{2\pi i (h x_j / a + k y_j / b + l z_j / c)}$$

where the unit cell contains atoms of type j located at points x_j, y_j, z_j, a, b, c are the side lengths of the unit cell, f_j is the scattering factor of atom j, and hkl are the Miller indices of the diffracting planes.

• If we express x_j, y_j, z_j in terms of a, b, c, then

$$F(hkl) = \sum_j f_j e^{2\pi i (h x_j' + k y_j' + l z_j')}$$

• Since $I \propto |F(hkl)|^2$, if $F(hkl) = 0$ for any set of Miller indices h, k, l, then those planes will not give rise to an observable diffraction spot.

• McQuarrie and Simon (1997) computes the structure factor for NaCl and CsCl lattices, the former as in PSet 6 and the latter as in class.

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[1]See the definitions of power and intensity on pages 6 and 13, respectively, of Labalme (2021)

- Improving the scattering factor's realism.

  - In our previous definition of the 3D scattering factor, we model the electron density within a crystal as localized at the atoms.
  - However, in reality, there is a continuous electron distribution throughout the unit cell and the crystal overall.
  - We may account for this distribution in the unit cell with the following analogous integral over the 3D electron density function ρ.

  $$F(hkl) = \int_0^a \int_0^b \int_0^c \rho(x,y,z) \mathrm{e}^{2\pi i(hx/a+ky/b+lz/c)} \, \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z$$

  - For a crystal of dimensions A, B, C along the **a**, **b**, and **c** axes, we get

  $$F(hkl) = \int_0^A \int_0^B \int_0^C \rho(x,y,z) \mathrm{e}^{2\pi i(hx/a+ky/b+lz/c)} \, \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z$$

  or, accounting for the fact that $\rho(x,y,z) = 0$ outside of the crystal, we may take the bounds to be the equivalent

  $$F(hkl) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(x,y,z) \mathrm{e}^{2\pi i(hx/a+ky/b+lz/c)} \, \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z$$

- The above equation shows that F and ρ are related by a Fourier transform (see Chapter 10 in Labalme (2020)). Thus,

  $$\rho(x,y,z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F(hkl) \mathrm{e}^{-2\pi i(hx/a+ky/b+lz/c)}$$

  - Experimental diffraction patterns give $|F(hkl)|^2$, not $F(hkl)$, presenting a problem in determining ρ from the above equation.
  - One first step is to let $F(hkl) = A(hkl) + iB(hkl)$ so that $I(hkl) \propto [A(hkl)]^2 + [B(hkl)]^2$ as we showed in class.
  - However, this still does not determine A and B entirely, and the problem of determining said quantities is known as the **phase problem**.
  - There are, however, several methods of circumventing the phase problem, which allows us to construct electron density maps as in Figure 8.2.

- Michael Faraday proposed in 1834 that the first step of a surface-catalyzed reaction was sticking the reactant to the surface. This proved to be correct, but surfaces are now known to play a much more important role than simply increasing the apparent concentration of the reactants.

- **Adsorption**: The process of trapping molecules or atoms that are incident on a surface.

  - "A molecule approaching a surface experiences an attractive potential" (McQuarrie & Simon, 1997, p. 1295).
  - Always exothermic ($\Delta_{\mathrm{ads}}H < 0$).

- **Adsorbate**: The adsorbed molecule or atom.

- **Substrate**: The surface to which the adsorbate adsorbs.

- **Physisorption**: Physical adsorption, wherein the attractive forces arise from van der Waals interactions.

  - Weak interaction; the strength of the bond is typically less than $20 \, \mathrm{kJ \, mol^{-1}}$; long bond length.

- **Chemisorption**: Chemical adsorption, wherein the attractive forces are covalent or ionic in nature.

  - Strong interaction; the strength of the bond is typically between 250-500 $kJ\,mol^{-1}$; short bond length.
  - First proposed by American chemist Irving Langmuir in 1916.
  - Herein, a molecular bond is broken and new chemical bonds are formed between the substrate and the molecular fragments of the adsorbate.
  - Because bond formation to the atoms at the surface of the substrate is important here, only a monolayer of molecules can chemisorb to the surface.

- **Monolayer**: A single layer of molecules.

- We can model the physisorbed and chemisorbed states in terms of a one-dimensional Lennard-Jones potential as in Figure 8.3, assuming that. . .

  - The substrate has only one type of binding site;
  - The angle at which the adsorbate approaches the substrate is not important;
  - The orientation of the adsorbate with respect to the substrate is not important.

- We take the zero of energy in Figure 8.3 to be the infinite separation of the substrate and the diatomic molecule AB.

- **Dissociative chemisorption**: The chemisorption of a diatomic molecule, which involves breaking the molecular bond between the two atoms and then forming bonds between the atomic fragments and the substrate.

- **Precursor**: A physisorbed molecule that will later become chemisorbed.

  - The energy at z_c (Figure 8.3) is typically less than the strength of the AB$-$S bond. However, there are cases (e.g., H_2 on the 110 surface of copper) for which the energy of the curve crossing is greater than the AB$-$S bond.

- **Adsorption isotherm**: A plot of surface coverage as a function of gas pressure at constant temperature.

- "Adsorption isotherms can be used to determine the equilibrium constant for the adsorption-desorption reaction, the concentration of surface sites available for adsorption, and the enthalpy of adsorption" (McQuarrie & Simon, 1997, p. 1297).

- Langmuir derived in 1918 the simplest expression for an adsorption isotherm.

- Comments on Langmuir's derivation, as covered in class.

  - We assume that the pressure of A is sufficiently low that the ideal gas law can be used. This is how we get

$$P_A V = nk_B T$$
$$\frac{P_A}{k_B T} = \frac{n}{V}$$
$$[A] = \frac{P_A}{k_B T}$$

- **Langmuir adsorption isotherm**: The following equation. *Given by*

$$\frac{1}{\theta} = 1 + \frac{1}{bP_A}$$

- "Experimental adsorption data are often tabulated as the equivalent volume of gas V that will adsorb onto the surface at a particular temperature and pressure," often STP (1 atm and $273.15\,\mathrm{K} = 0\,^{\circ}\mathrm{C}$) (McQuarrie & Simon, 1997, p. 1299).

- Example: From pressure vs. adsorbed volume data for nitrogen on a mica surface, calculate the values of b, V_m (the volume of gas that corresponds to a monolayer coverage), and the total number of surface sites.

  - A monolayer coverage corresponds to $\theta = 1$.
  - The value of θ is related to V_m by
  $$\theta = \frac{V}{V_m}$$

  - Substituting this into the Langmuir adsorption isotherm and rearranging gives
  $$\frac{1}{V} = \frac{1}{PbV_m} + \frac{1}{V_m}$$

  - It follows that a plot of $1/V$ vs. $1/P$ will have slope $1/bV_m$ and y-intercept $1/V_m$.
  - From a line of best fit, we can thus determine that $V_m = 3.96 \times 10^{-8}\,\mathrm{m^3}$ and $b = 2.14 \times 10^{12}\,\mathrm{torr^{-1}}$.
  - Since 1 mol of gas occupies $22.4\,\mathrm{L} = 2.24 \times 10^{-2}\,\mathrm{m^3}$ at STP, the number of moles of gas in V_m is

  $$\frac{3.96 \times 10^{-8}\,\mathrm{m^3}}{2.24 \times 10^{-2}\,\mathrm{m^3\,mol^{-1}}} = 1.77 \times 10^{-6}\,\mathrm{mol}$$

  which corresponds to
  $$(1.77 \times 10^{-6}\,\mathrm{mol})N_{\mathrm{A}} = 1.06 \times 10^{18}\,\mathrm{molecule}$$

  - Since each molecule of gas occupies a single surface site, it follows that there are 1.06×10^{18} total surface sites.

- McQuarrie and Simon (1997) derives the Langmuir adsorption isotherm for the case in which a diatomic molecule dissociates upon adsorption to the surface, as in class.

- McQuarrie and Simon (1997) discusses a physical interpretation of k_d.

Problems

31-29. ...

31-44. ...

31-45. ...