Module 4 : Solid State Chemistry

Lecture 18 : Bragg's Law and X - ray diffraction

Objectives

In this Lecture you will learn the following

- The workings of diffractometers.

- Bragg's law of X - ray diffraction.

- Lattice planes through Miller indices.

- Distances between adjacent planes of the crystal.

18.1 Introduction

X - ray diffraction is one of the earliest methods for studying the structure of solids. In the process of diffraction, electromagnetic waves of a given frequency but different phases interact to produce constructive interference (bright spots on the film exposed to the light) and destructive interference (dark spots). By a careful analysis of the diffraction patterns, very accurate values of the lattice parameters (unit cell dimensions) can be inferred.

18.2 X- ray diffractometers

When high energy electrons are incident on metallic surfaces they knock off the bound electrons from even the inner shells of the atoms. When electrons from the higher shells undergo a transition into the lower (now partially empty) shells, X-rays are emitted. E.g., the K_α line in copper (λ = 154.18 pm) is produced by the n = 2 to the n = 1 transition, while the K_β line (λ = 139.22pm) corresponds to the n = 3 $\rightarrow$ n = 1 transition. Suitable filters are used to obtain monochromatic beams of X-rays. The sample to be studied consists of either a powdered form of the solid or a single crystal. The Debye-Sherrer method is for powders. A photographic film is rolled over the sample and the diffraction pattern traces a cone around the incident beam. The crystallites in the powder are arranged in random directions. If the angle of incident light is θ on any plane, then the diffracted light is at an angle of 2θ from the incident beam.

The powdered sample is also rotated in the plane containing the X-rays to give all possible orientations of the crystallites towards the incident beam. Since the powder of each substance has a characteristic diffraction pattern, powder diffraction is extremely useful in identifying materials.

In the single crystal method developed by Bragg, the single crystal is mounted on a platform. The platform (and the mounted crystal) can be rotated in four different circles along four axes so that the diffraction pattern from every plane of the crystal can be observed in the detector. In modern diffractometers most tasks such as rotating the crystal, analyzing the data (except growing the crystal !) are automated and controlled through computer programs. The schematic diagrams of the powder diffractometer and the single crystal diffractometer are shown in Figures 18.1 (a) and 18.1 (b) respectively.

Figure 18.1 (a) Schematic diagram of a Powder diffractometer.

Figure 18.1 (b) Single crystal diffractometer

18.3 Bragg's Law

This is a simple and elegant law which is central to the analysis of diffraction data. This law relates the angle θ (at which there is a maximum in diffracted intensity) to the wavelength λ of X-rays and the inter-layer distance d between the planes of atoms / ions / molecules in the lattice. Figure 18.2 illustrates the details involved in the derivation of Bragg's Law.

Figure 18.2 Details involved in the derivation of Bragg's Law.

The layers of atoms are indicated by the labels to the right of the lines. The Lattice points are denoted by solid circles. The dashed lines along the row of atoms are only for guiding the eyes. The rays R_1 and R_2 are parallel and they have the same phase till they are at b and e respectively. The ray R_2 traverses an additional distances efg. This additional distance causes a phase difference between rays R_1 and R_2. If rays R_1 and R_2 are at an angle of θ with respect to the atomic planes, then the angles e b f and f b g are also θ and the path length ef and fg are both equal to d sin θ where d is the perpendicular distance between any two adjacent layers. For constructive interference between rays R_1 and R_2, the path difference between R_1 and

R_2 has to be an integral multiple of λ, the wavelength of X-rays used, i.e.,

2d sin θ = n λ (Braggs Law)   (18.1)

The reflection of R_2 is called a first order reflection as it is from the first inner layer. The ray R_3 which is reflected by layer 3 is a second order reflection. The intensities of reflected light from the inner layers (3, 4 (not shown) and so on) is much less and the major diffraction is brought out by the first inner layer. From the intense peaks of the diffraction patterns, the distances between various crystal planes can be determined. We now move on to the labeling of the lattice planes through Miller indices.

18.4 Miller Indices

Consider a square lattice as shown in Fig 18.3(a).

Figure 18.3 (a) A few planes in a lattice.   18.3 (b) The coordinate system.

In this case, an atom occupies each lattice point. The coordinate system used here is also shown in Fig 18.3 (b). Several lines can be drawn in this lattice such that at least one (or more) atoms lie on the lines. A few examples are shown. The unit cell for the Lattice in Fig 18.3 (a) is a square. Lines 1 and 2 are similar in that atoms lie on these at the same separations. Line 3 is less "densely packed", i.e., the distance between adjacent atoms is larger than that in lines 1 and 2. We need a system to label or characterize each of these lines. In three dimensions our interest would be the different planes of atoms.

Figure 18.4

In Fig 18.4 the plane containing the atoms intersects the x axis at a. This plane does not intersect with the y and z axes at all. We may rephrase this by saying that the intersections with y and z axis at $y = \infty$ and $z = \infty$. The x, y and z intersections are at (a, ∞ , ∞). Taking the reciprocals of these, we get (1/a, 0, 0) and since a, b and c are characteristics of the crystal, we can simply refer to it as (100)

These are the Miller indices of this plane. Using the same procedure verify that the Miller indices of the other planes in the figure (18.4) are (110), (111). In a simple cubic lattice, the (100) plane is identical to the (1/2, 0 0)plane, because it has exactly the same density and the relative positions of atoms / ions. Therefore all planes parallel to the (100) planes may be referred to as the (100) planes. In a "body centered" cubic lattice such as the CsCl lattice, the (100) planes containing the Cl^- ions would be different from the (200) planes containing the Cs^+ ions. Now that we can label all these planes accurately, let us see how the distance between the planes can be determined using Bragg's law.

18.5 Interplane spacings in lattices

Now we are in a position to combine Bragg's law which gives the distance between the adjacent planes in the crystal to the Miller's characterization of the planes through the indices (h, k, l). The unit cell edge-lengths are a, b and c.

Consider a square Lattice as shown in Fig 18.5

Figure 18.5 Calculation of the separation between planes.

In Fig 18.5, two adjacent hkl planes are shown. If a is the edgelength of the lattice, then the hkl plane intersects the axes at a / h, b / k, and c / l. For example, if (hkl) was (1,1,1), then this Miller plane would intersect the three axes in a cubic lattice at (a,a,a). If (hkl) is (1,0,0), the intersections would be at (a, ∞, ∞).

Label the two planes in Fig. (18.5) as 1 and 2. Plane 2 intersects the x axis at a / h and the y axis at b / h. The distance perpendicular to the planes 1 and 2 is $d_{h\,k}$. For the planar lattice, $l = 0$.

$\sin\theta = d_{h\,k} / (a / .k)$ and $\cos\theta = d_{h\,k} / (a / h)$ (18.2)

squaring and adding

$$\frac{d^2_{h\,k}}{(a/k)^2 + (a/h)^2} = 1 \quad\text{or}$$ (18.3)

$$\frac{h^2 + k^2}{a^2} = \frac{1}{d^2_{h\,k}}$$ (18.4)

Extending the analogy to three dimensions and for a plane where $l \neq 0$, the distance d_{hkl} will now be given by

$$\frac{1}{d^2_{h\,k\,l}} = \frac{h^2 + k^2 + l^2}{a^2}$$ (18.5)

or

$$d_{h\,k\,l} = a / \sqrt{h^2 + k^2 + l^2}$$ (18.6)

For a general orthorhombic lattice wherein $a \neq b \neq c$, the expression corresponding to (18.5) is

$$\frac{1}{d^2_{h\,kl}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$ (18.7)

18.6 Examples

18.1) What is the distance between the adjacent Miller planes if the first order reflection from X-rays of wavelength 2.29 $\overset{\circ}{\text{A}}$ occurs at 27° 8' ?

Solution :

$n \lambda = 2d \sin \theta$

$n = 1, \lambda = 2.29 \overset{\circ}{A}, \theta = 27^\circ 8'$

$d = 0.5 * 1 * 2.29 * 10^{-8} / \sin (27^\circ 8')$

$= 2.51 \overset{\circ}{A}$

18.2) Gold crystallizes into an FCC structure. The edgelength of the FCC unit cell is $4.07 \overset{\circ}{A}$ Calculate a) the closest distance between two gold atoms and b) the density of gold if its atomic weight is 197

Solution :

Let b = closest distance between gold atoms; $a = 4.07 \overset{\circ}{A}$

$b^2 = a^2 / 4 + a^2 / 4 = 0.25 * 4.07^2$

$b = 2.878 \overset{\circ}{A}$

Density $= \rho =$ mass / volume

volume of the unit cell $= (4.07 \overset{\circ}{A})^3$

mass of the unit cell $= 4 * 197$ g $/ 6.02 * 10^{23}$

as there are four atoms per unit cell in an FCC Lattice

$\therefore \rho = 19.419$ g$/$cm^3

18.3) X rays of $\lambda = 0.1537$ nm from a Cu target are diffracted from the (111) planes of an FCC metal. The Bragg angle is 19.2°. Calculate the Avogadro number if the density of the crystal is 2698 kg $/$ m^3 and the atomic weight 26.98

Solution :

The distance between the 111planes

$d = 0.5 * 1.537 * 10^{-10}$ m $/ \sin (19.2^\circ)$

$= 2.51 * 10^{-10}$ m

We need the edge length a which is related to d by

$a = d (h^2 + k^2 + l^2)^{1/2}$ where hkl = (111) are Miller indices

$a = 2.51 * 10^{-10} \sqrt{3} = 4.0475 * 10^{-10}$ m

$\rho =$ mass / volume $= 2698$ kg $/$ m^3

mass of unit cell $= 4 * 26.98 * 10^{-3}$ kg $/ [N_A * (4.0475 * 10 -10)^3]$

$= 2698$ kg $/$ m^3

This yields $N_A = 6.036 * 10^{23}$ particles / mole

18.7 Problems

18.1 a) Consider the two following planes that cut the crystallographic axes as indicated. Plane 1 cuts the axes at a / 3, b / 2 and c /4 and plane 2 cuts the axes at a / 2, b /3 and ∞ . What are the Miller indices of these planes ?

18.1 b) Draw the planes for which the Miller indices are (112), (200), (120) and (221)

18.2 a) In the Born-Haber cycle for the formation of a crystalline ionic solid, what are the parameters are there which need to be experimentally determined ?

18.2 b) Calculate the electron affinity of the F atom using the data given below. All energies are in kcal / mol.

$\Delta H_{diss} (F_2) = 38$, $\Delta H_f (NaF) = 136$, $\Delta H_{vap} [Na (s)] = 24$

I.E (Na) = 117.7 and $U_L (NaF) = 212.8$

18.3) The Born-Lande equation for the Lattice energy of ionic crystals is

$U_L = - N_A M z$, $z_2 e^2 (1-1/n)/r_0$ (in CGS units)

Where z_1 e and $-z_2$ e are the charges on the cation and the anion, N_A = Avogadro number, M = Madelung constant, r_0 = closest equilibrium distance between the anion and the cation and n = Born exponent. The value of n depends closed shell electronic configuration of the ion. The close shell configuration may resemble any of the rare gas atoms, He, Ne, Ar, Kr and Xe. The values of n for these configurations are 5, 7, 9, 10 and 11 respectively. If the value of n for the anion is n_1 and that for cation is n_2, then an average value of $(n_1 + n_2)/2$ may be taken for the Lattice. Using this formula and M = 1.747, determine the lattice energies for MgO ($r_0 = 2.1 \overset{o}{A}$) and NaCl ($r_0 = 2.81 \overset{o}{A}$). How does this value for NaCl compare with the experimental value of U_L ?

18.4) What are the unit cells for the NaCl and the CsCl structures ? How many atoms are there in these unit cells ?

18.5) The edge length of the Ag FCC structure is 408.6 pm An X-ray beam produces a strong interference (intense reflection) from the 111 planes at 2 θ = 38.2 ^{o} . What is the X- ray wavelength ?

18.6) The X - rays of wavelength 154.2 pm produce reflections from the 200 planes and the 111 plane of Cu which has FCC structure and density of 8.935 g /cm^3 . At what angles will the diffracted intensity be maximum?

18.7) The molecular weight of NaCl is 58.448 and its density 2.165 g / cm^3. What is the edge length of a cube that contains one mole of NaCl ? How many sodium and chloride ions lie along this edge if the distance between the nearest neighbour ions is 2.819 $\overset{o}{A}$? Calculate the Avogadro number using the information given above.

18.8) From the face of a FCC lattice of NaCl, the Bragg diffraction from X-rays of 0.0586 nm wavelength occurs at an angle of 5° 58'. What is the distance separating these planes and what is the smallest distance between Na^+ and Cl^- and Cl^- and Cl^- ? Study the NaCl structure closely for a clear picture of the problem.

18.9) The atoms / ions in a crystal vibrate similar to a mass at the end of a string. For the mass at the end of a string, vibrational frequency increases with decreasing mass. It is found that the heat capacities of solids of lighter atoms such as Be, B and C are lower than the standard equipartion value of 6 cal /mol at room temperature. Can you make a connection between the heat capacity values and the dependence of frequency on mass?

18.10) The lattice parameter of the FCC silver unit cell is 408.6 pm. An X-ray beam produces a strong reflection from the 111 plane at angle 2 θ = 38.2^o . What is the wavelength of the X-ray ?

18.11) X-rays with λ = 154.2 pm produce reflections from the 110 and 200 planes of FCC Cu of density 8.935 g / cm^3. At what angles will these reflections appear?

18.12) X- rays of wavelength = 179 pm produce a reflection at 2 θ = 47.2^o from the 110 planes of BCC

lattice. Calculate the edgelength of the unit cell.

Recap

In this lecture you have learnt the following

Summary

In this lecture you have been introduced to the X- ray diffraction method. The diffraction pattern from adjacent layers of a crystal can be used to get the distance between these layers using Bragg's law. Miller indices are interesting ways of characterizing lattice planes containing atoms /ions or molecules of the crystal and equation 18.7 gives the distance between adjacent layers of an orthorhombic crystal. For less symmetric crystals too, equivalent formulae can be derived. We have also considered in this lecture several numerical examples that use Bragg's law to obtain interplanar distances in a crystal.