

Class Notes: Chapter 3

Diffraction (Basic Idea)

We will develop Bragg's Law by considering Interference (summation of amplitudes, i.e. the electric field vector) of two electro magnetic waves (x-rays) which can be described using a sin function,

$$E = A \sin(2\pi(x/\lambda - t)) \quad \text{the phase angle of a wave, } \phi = 2\pi(x/\lambda - t) \quad (1)$$

$$= 2\pi(x/\lambda) \text{ for fixed time}$$

$$= 2\pi(-t) \text{ for fixed position}$$

E and **A** have direction and magnitude so are vectors. The intensity of a diffracted beam is obtained by considering interference of amplitudes, **E**, then squaring to obtain the intensity. The square of a vector is a scalar which has not direction. **Intensity does not have direction.**

To derive Bragg's law Bragg used a specular (mirror like) analogy for diffraction even though he knew that x-rays don't really reflect like visible light does. The similarity between diffraction and reflection is that the angle of incidence on a set of planes is equal to the angle of diffraction with respect to the set of planes. This is the only similarity.

In derivation of Bragg's law we must consider the phase difference between two waves to tell if the amplitude interference is constructive (added) or destructive (subtracted). The phase difference is defined as ,

$$\phi = 2\pi(x_2 - x_1)/\lambda = 2\pi(x/\lambda) \quad (2)$$

(2) relates a path difference for two waves which begin in-phase $\phi = 0$, to the phase difference. (1) allows the calculation of the relative amplitude for these waves and allows the summation for calculation of the intensity. If ϕ is a multiple of 2π then the waves are in-phase and the amplitudes sum. This is the condition for diffraction. For $\phi = n2\pi$, x must be a multiple of $n\lambda$.

For destructive interference x must be $(1/2 + n)\lambda$.

The Reflection Analogy of Bragg (Specular reflection).

Consider two planes separated by a distance " d_{hkl} " and an x-ray beam incident on the planes at some angle θ to the plane surface. The most tightly bound electrons in the atoms on the planes "vibrate" in response to the imposed oscillating electric field of the incident radiation (the process is really more complicated than just vibration) and these "vibrating" electrons re-emit EM radiation (change in momentum of a charged particle) of the same frequency as the incident beam. At some angles of re-emission the x-rays from the different planes interact constructively and at other angles destructively. It is easy to show that at the Bragg angle of re-emission (θ to the plane or 2θ from the incident beam) the waves constructively interfere.

Figure 3-2 shows that the excess path of the beam in going to the second plane, plane B, is $d_{hkl} \sin \theta$. Since this is done twice, the path difference for incident excess plus diffracted excess is:

$x = 2d \sin \theta$. For constructive interference this path difference must be some multiple of λ so constructive interference is associated with the Bragg angle, θ through,

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

where n is an integer representing the order of diffraction (increasing angles). The number of orders which are observable is limited by the maximum of $\sin \theta$, i.e. for $2\theta = 180^\circ$, or 1.
 $n \leq 2d/\lambda$

Bragg and Bragg's Law (pp. 89)

Bragg worked with NaCl crystals which he knew were FCC and composed of lattice sites of NaCl. He had developed the theory for Bragg's Law but had not idea what the lattice parameters were nor what the wavelength of x-rays were. He was able to determine these through the use of the FCC model and a measurement of the density and atomic weights of Na and Cl.

The bulk density of NaCl crystals is equal to the sum of atomic weights divided by Avogadro's number and the unit cell volume (eqn. 3.6). It was a combination of bulk measurements and diffraction data which lead to the FCC prediction. Bragg's law was then used to determine the wavelength of x-rays so this could be used to determine lattice parameters for other materials.

Diffraction vs Microscopy and other Direct Imaging Approaches (Not in the Book)

It is important to consider the difference between diffraction and microscopy which was emphasized in the first lab. Squaring of the amplitude of the EM wave in measurement of the intensity results in a scalar for intensity which does not contain the details of phase information which were present in the amplitude. **Phase information** is retained in microscopy. Phase information is the information that relates different regions of contrast in a particular arrangement, i.e. it is a picture of the structure. In the absence of phase information we have statistical information such as density, mass, surface area, composition and volume but we can't connect this information to produce an image. Production of an image requires a model from diffraction data and the need for a model is the main distinguishing feature between microscopy and diffraction.

You can think of this as having a statistical description of an elephant which includes its weight, density, average size, composition and surface area but no real picture of what an elephant is. A camera will give you a nice photograph of the elephant which will give you a direct feel for what an elephant is but no real 3-d details. The combination of a photograph and the statistical data on an elephant can give a good idea of the elephant.

In order to interpret the statistical data you need a **model** which is some guess of what an elephant is. You can test this model against what you know statistically about the elephant to see if the two are consistent but you can't rule out other models such as the elephant is a strangely shaped clump of mud.

In XRD we use models to interpret diffraction data. A model in XRD is based on the two components we have discussed, the unit cell structure factor, f^2 , and the lattice structure factor S^2 . We can test the model by comparing the predictions of the model with the diffraction data. Further verification of the model can come from oriented samples for polycrystalline samples. Usually the use of models allows you to think about the structure of crystals in a much deeper way than is yielded by a photograph.

Prior to about 10 years ago there were no tools which could directly image on a molecular scale so it was only models and statistical data from XRD which yielded our current understanding of molecular structure. Now several imaging techniques are available including atomic force microscopy, AFM. XRD remains a valuable tool since the experiment is simple, it can be conducted on real samples with 3-d statistical information resulting which probes a large section of the sample. You can think of the value of diffraction techniques as parallel to the value of tabulated statistical data on a population (i.e. the US population) versus a case study of a single person in the US. The two pieces of data are both valuable in understanding how people feel about some issue.

Diffraction Methods:

For a single crystal, a single wavelength and a single orientation of the crystal to the main beam it is unlikely that the Bragg condition will be met for a given plane. Rotation of the crystal will bring planes into the Bragg condition.

This means that it is desirable to have one of these parameters have variability.

1) **X-ray Spectrometer:** pp. 88 Rotation of a perfect crystal in an x-ray beam is one method to determine the x-ray spectrum using Bragg's Law. By rotation of a single crystal with a fixed detector, or using a position sensitive detector with a fixed crystal we can perform x-ray spectroscopy experiments similar to how a diffraction grating can be used in an IR or UV spectrometer.

2) **Laue Camera:** pp. 92 With a polychromatic incident beam many planes will meet the Bragg condition and tracing the 2-d pattern on a photographic film will reveal the planes of a zone. We will perform this experiment in lab.

3) **Rotating Crystal Method:** For a mono chromatic beam and a single crystal. Rotate the crystal during diffraction experiment to bring Bragg planes into alignment.

4) **Powder Method:** Mono-chromatic beam, polycrystalline sample. Usually done with a flat film in pinhole arrangement.

5) **Diffraction Method:** Similar to the powder method but uses a step-scanner and a line beam. Usually involves a polycrystalline sample.

Scherrer Equation:

Bragg's law states the condition for a sharp diffraction peak from an infinite crystal with perfect 3-d order. Typically the diffraction peak has a finite width which is associated with imperfection in some of the Bragg parameters. These imperfections can be associated with beam divergence, a somewhat polychromatic source, or imperfections in the 3-d order of the crystals. The latter can be a basis for quantitative measurement of the deviation from the Bragg requirement for perfect 3-d order which is infinite in all spatial directions. Deviations from the latter requirement have been explained in terms of 3 features:

- 1) Finite crystallite size. (Scherrer equation)
- 2) Distortions of the first kind, which are random motion of atoms in a crystalline lattice (Debye thermal broadening) or other local randomization of lattice sites which do not disturb the 3-d repetition or crystalline motif.
- 3) Distortions of the second kind, which involve destructive of long range order in the crystal, i.e. at long distances the lattice does not repeat perfectly. These usually lead to preferential broadening of high order peaks.

The Scherrer equation, #1 above, predicts crystallite thickness if crystals are smaller than 1000Å. Since small angular differences in angle are associated with large spatial distances (inverse space), Broadening of a diffraction peak is expected to reflect some large scale feature in the crystal. The simplest way to obtain the Scherrer equation is to take the derivative of Bragg's law holding the wavelength constant and allowing the diffraction angle and the Bragg spacing to vary,

$$2d \sin \theta = \lambda \quad \text{Take Derivative in } d \text{ and } \theta \text{ yields} \quad 2 \lambda \cos \theta = \frac{d \theta}{d} =$$

since θ can be positive or negative the absolute value must be taken and it reflects the half-width of the peak (really half-width at half-height) so $2 \lambda \cos \theta$ is the peak full-width at half-height, B . d reflects the crystallite thickness,

$$\text{Thickness} = t = d = \frac{\lambda}{B \cos \theta}$$

If a Gaussian function (rather than a triangle function) is used to describe the peak a prefactor of 0.9 occurs so the Scherrer equation is given as $t = 0.9 \lambda / (B \cos \theta)$ where B is the full-width at half maximum.

The derivative approach is the approach taken by Alexander in Klug and Alexander's "X-ray Diffraction" to describe the Scherrer equation. It is also easily adaptable to describe the dependence of any two terms in the Bragg equation in terms of variability, for instance peak width on wavelength variation etc.

The Scherrer equation is useful when crystals are smaller than 1000Å in size. For larger grains such as in metals the Debye-Scherrer ring becomes grainy as shown in figure 9-1 on page 283. Such grainy patterns can be analyzed in terms of a statistical analysis to determine grain size although this is rarely done since grain size can be more easily determined from optical or electron microscopy studies in this size range. The ultimate limit of the behavior in figure 9-1 is a single crystal which shows few diffraction peaks.

Disorder of the first kind is described in terms of an exponential function derived by Debye, e^{-2M} , which is discussed in chapter 4 on pages 137-138. We will discuss this in more detail in chapter 4 as it is usually measured in terms of the absolute intensity reduction which is the topic of chapter 4. Debye thermal broadening in terms of angular broadening is described also using an exponential function, the Debye-Waller factor which is basically $\text{Breadth} = K \exp(-q^2 \lambda^2)$ where λ is the mean free path of the lattice sites due to thermal vibration, K is a constant material parameter and q is $4 \pi \sin(\theta) / \lambda$. It is possible to observe crystalline distortions which have the same structural basis as thermal broadening but are not related to temperature, i.e. related to misplacement of atoms in the crystal. These are modeled using the same exponential relationships as Debye thermal broadening.

Thermal motion of atoms in a crystal are related to the heat capacity and Debye's description of thermal broadening is intimately tied with his development of heat capacity theory which you should be familiar with from previous classes.

Disorder of the second kind involves disruption of long-range order in the crystal and leads to loss of high-order peaks in the diffraction pattern as well as broadening of low order peaks. The extreme of disorder occurs in the liquid state where typically a single broad peak is seen. This peak reflects the preferred separation distance (or distances) for the fluid molecules. Figure 3-18 on pp. 105 shows the qualitative diffractometer tracings for a crystal, a liquid and a monoatomic

gas. The peak in the liquid sample is due to exclusion of one molecule or atom from the space occupied by another atom (so called excluded volume).

In a dense, amorphous material there is a high probability that one atom could approach another which leads to a preferred separation distance reflected in a broad peak. For interacting systems this peak becomes more pronounced. As a material is diluted, such as in an ideal gas, the peak dissipates since there is no probability for overlap in the limit of infinite dilution, i.e. no excluded volume. The curve which remains involves no molecular correlations and reflects only the internal structure of the gas atom. The shape and dependence of the decay curve for an ideal gas depends on the Bohr radius of the atom.

The last curve in Figure 3-18, ideal monoatomic gas, is generated by isolated atoms which do not interact. This type condition could be envisioned for all atoms although, in reality, it is not achievable for many atoms. Such an ideal curve can be measured by measurement of the diffraction pattern from perfect crystals and removal of the interatomic correlations using known functions. In this way the last pattern in figure 3-18 has been measured for all atoms and is tabulated as the atomic scattering factor as a function of angle, f . The atomic scattering factor is crucial in calculation of the diffracted intensity in chapter 4.