Experiment 2b
X-Ray Diffraction*


Introduction

Inorganic chemists, physicists, geologists, and materials scientists use X-ray diffraction to determine molecular structures in the solid state. Depending on the type of sample and the information desired, a number of diffraction techniques are available: however, they all depend on the same principles of diffraction. In this laboratory experience, you will learn how diffraction works using optical diffraction, and identify an unknown mineral from its powder x-ray diffraction pattern. You will work with a partner for the optical diffraction experiments, but everyone must turn in their own report. The lab report will consist of a separate sheet of paper with your typed answers to the questions from the various sections, a data table, and sample calculations.

Optical Diffraction Experiments

Purpose

To discover how a diffraction pattern is related to a repeating dot array; to use the diffraction pattern to measure the dimensions of the repeating dot array.

Introduction

Diffraction of a wave by a periodic array is due to phase differences that result in constructive and destructive interference (illustrated in Figure 1). Diffraction can occur when waves pass through a periodic array if the repeat distance of the array is similar to the wavelength of the waves. Observation of diffraction patterns when beams of electrons, neutrons, or X-rays pass through crystalline solids thus serves as evidence both for the wave nature of those beams and for the periodic nature of the crystalline solids. However, X-rays are hazardous and they require special detectors.
Figure 1. When waves line up (the oscillations are in phase), they add to give a bigger wave. When the peak of one wave is aligned with the trough of another, the waves annihilate each other.

Atoms, with spacings of about $10^{-10}$ m, require X-rays to create diffraction patterns. In this experiment, you make a change of scale. By using dots with spacings of about $10^{-4}$ m, visible light can be used instead of X-rays to create diffraction patterns. You will shine red laser light (633 nm wavelength) through a slide containing repeating arrays of dots, and observe Fraunhofer diffraction (see Figure 2).

![Figure 2](image)

**Figure 2.** The Fraunhofer diffraction experiment.

Mathematically, the equations for Fraunhofer and Bragg diffraction (the basis of X-ray diffraction) are similar and embody the same functional dependence on the dot spacing ($d$), wavelength ($\lambda$), and scattering angle ($\phi$ or $\theta$), (see Figure 3).

In this experiment, you will first check how the size and orientation of the diffraction pattern is related to the periodic array that produced it, and then you will measure distances in diffraction pattern spacings in order to calculate the repeat distance for the array in the slide. By measuring the distances between the diffraction peaks ($X$) and the distance between the slide and the wall ($L$), shown in Figure 2, you can solve for $\phi$ by using the trigonometry definition that $\tan \phi = X/L$. Use of the Fraunhofer equation (below) then gives the lattice spacing ($d$) when the radiation wavelength ($\lambda$) is known.

$$d \sin \phi = n\lambda$$

**Procedure**

Obtain slides containing greatly reduced versions of arrays like those in the bottom half of Figure 4. Each photographic slide contains eight patches with a different periodic array.

**Question 1.** Look through a slide at a point source of white light. What do you see? Is the slide a diffraction grating? Why?

Shine a He-Ne laser (633-nm wavelength), or a diode laser pointer (approximately 650 nm) at a white piece of paper several meters away. Fasten the laser in place. **CAUTION: The laser is**
potentially dangerous. Do not look directly into a laser beam or shine a laser toward other people, as damage to the eye can occur.

**Question 2.** Look through a slide at the laser dot on the paper. What do you see? Why?

**Question 3.** Put the slide in the laser beam and watch the paper. What happens? Light travels from the laser to the paper and then to your eye. Are the same results obtained if the beam goes through the slide before it hits the paper as after it hits the paper?

![Fraunhofer diffraction and Bragg diffraction](image)

**Figure 3.** A comparison of Fraunhofer diffraction with Bragg diffraction. When waves are scattered by a periodic array, the path difference between any two waves must be a whole number of wavelengths, \( n \), if the waves are to remain in phase and give constructive interference.

**Question 4.** Pretend that you want to sketch the shape of the diffraction pattern from an array. Why should you use the laser light source? Should you shine the beam through the slide or look at the spot through the slide? Pretend that you want to measure the spacing between the spots. What method is easiest?

Use a hand lens to examine the arrays on the slide. For ease of interpretation, you may prefer to keep a consistent orientation for the slide.

Devise and conduct experiments to answer the following questions. You may need to sketch an array and the resulting diffraction pattern to answer some of the questions, and should include any measurements of distances.
Figure 4. Arrays of dots that can be used to generate diffraction patterns with a laser. The actual patterns on the slide are those shown on the lower-half of the figure, and are much smaller.
**Question 5.** This question regards how the orientations of the diffraction patterns relate to the orientation of the array of dots. Be sure to indicate which array leads to a particular diffraction pattern. For example, array e is a rectangular dot-array that leads to a rectangular diffraction pattern. The ‘long axis’ of the array exhibits shorter diffraction spacings due to the inverse relationship between lattice spacing and diffraction angle.

What is the diffraction pattern of:

A square array of dots?

A rectangular array of dots?

A parallelogram array of dots where the angle is not 90°?

A hexagonal array of dots?

**Question 6.** Find two similar arrays that differ only in size. How does the repeat distance of the array relate to the repeat distance of the diffraction pattern?

**Question 7.** Choose two arrays, and calculate the size of the unit cell for those arrays by carefully measuring some distances in the diffraction pattern.

**Question 8.** What happens if you put an additional dot in the array in the center of the unit cell? Does it matter if the dot placed in the center is the same size as those in the original array? (array a vs. b, or array d vs. c)

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**X-Ray Diffraction Experiment**

**Introduction**

X-rays are electromagnetic radiation of wavelength about 1 Å (10^-10 m), which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are etc. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. We can determine the size and the shape of the unit cell for any compound most easily using the diffraction of x-rays.

**Instrumentation Description**

The X-ray diffraction experiment requires an X-ray source, the sample under investigation and a detector to pick up the diffracted X-rays. Fig 5 is a schematic diagram of a powder X-ray diffractometer.
Figure 5. Schematic of an X-ray powder diffractometer.

The X-ray radiation most commonly used is that emitted by copper, whose characteristic wavelength for the K radiation is $\lambda = 1.5418\text{Å}$. When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of $2\theta$. The diffracted beam may be detected by using a moveable detector such as a Geiger counter, which is connected to a chart recorder. In normal use, the counter is set to scan over a range of $2\theta$ values at a constant angular velocity. Routinely, a $2\theta$ range of 5 to 70 degrees is sufficient to cover the most useful part of the powder pattern. The scanning speed of the counter is usually $2\theta \sim 2^\circ$ per minute; therefore, about 30 minutes are needed to obtain a typical trace.

Figure 6 Reflection of x-rays from two planes of atoms in a solid.

The path difference between two waves:

$$2\lambda = 2d \sin \theta$$
For constructive interference between these waves, the path difference must be an integral number of wavelengths (figure 6):

\[ n\lambda = 2x \]

This leads to the **Bragg equation**:

\[ n\lambda = 2d \sin \theta \]

Figure 7 shows the x-ray diffraction pattern from a single crystal of a layered clay. Strong intensities can be seen for a number of values of \( n \); from each of these lines we can calculate the value of \( d \), the interplanar spacing between the atoms in the crystal.

**Figure 7.** X-ray diffraction pattern from a layered structure of vermiculite clay.

**EXAMPLE: Unit Cell Size from Diffraction Data**

The diffraction pattern of copper metal was measured with x-ray radiation of wavelength of 1.315Å. The first order Bragg diffraction peak was found at an angle \( 2\theta = 50.5 \) degrees. Calculate the spacing between the diffracting planes in the copper metal.

The **Bragg equation** is

\[ n\lambda = 2d \sin \theta \]

We can rearrange this equation to solve for the unknown spacing \( d \). \( \theta \) is 25.25 degrees, \( n = 1 \), and \( \lambda = 1.315\text{Å} \).

\[ d = \frac{1 \times 1.315}{(2 \times 0.4266)} = 1.541 \text{ Å} \]

In this lab you will be provided the x-ray powder diffraction pattern from a single compound, which is your unknown. The unknowns are layered minerals, and the diffraction peaks result from the spacing between layers.

You should measure all the values of \( 2\theta \) from your powder diffraction, and after converting them into \( d \) values calculate the layer spacings in your unknown. You will probably need to interpolate
some peak positions by use of a ruler. In your lab report, reproduce the data table below, and list all the 2θ values with their corresponding values of n and d. Then calculate the mean and median values of the unit cell. From this, you will be able to identify your unknown sample.

Results

| Data Table of X-ray Diffraction Peaks |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2θ              | θ               | sin(θ)          | n               | d = n × λ / sin θ | lattice spacing = n x d |
| 1               |                 |                 |                 |                 |
| 2               |                 |                 |                 |                 |
| 3               |                 |                 |                 |                 |
| 4               |                 |                 |                 |                 |
| 5               |                 |                 |                 |                 |
| 6               |                 |                 |                 |                 |
| 7               |                 |                 |                 |                 |
| 8               |                 |                 |                 |                 |

λ = 1.5418 Å for Cu Kα

X-ray simulation software

Use the program “X-Rays and Diffraction”, by R. P. Grosso, J. T. Fermann, and W. J. Vining to answer the following questions.

Look through the “Generation and Diffraction” module. There is some very interesting information in this module, and you are responsible for learning the material in the following three sections:

How are X-Rays Generated? (Pictures)

How X-Rays Interact with Atoms. (Movie and Pictures)

Bragg’s Law

Then look through the “Diffraction and Structure” module. There is some very interesting information in this module, and you are responsible for learning the material in the following two sections:

Unit Cell Type and Lattice Extinctions (Interactive)

Unit Cell Lengths and X-Ray Line Splitting (Interactive)

Answer the following questions.
Question 9. Place the following metals in order of increasing wavelength for the $K_{\alpha 1}$ radiation: Mg, Al, Fe, Ni, Cu

Question 10. From the Bragg’s Law Interactive, you observed how to derive Bragg’s Law: $n\lambda = 2d \sin \theta$. Explain (in words) why $n$ cannot be a half-integer value.

Question 11. Unit Cell Type. Fix the length of $a$ axis at 5.0 Å. From what you know about Bragg’s law, why do the body-centered (I) and face-centered (F) unit cells exhibit powder diffraction peaks at shorter values of $2\theta$ than the primitive (P) unit cell? Think outside the box…