

## Diffraction of X-Rays by a Powdered Crystalline Sample

All crystals can be classified into one of seven crystal systems – cubic, tetragonal, trigonal, orthorhombic, monoclinic, and triclinic. Each of these crystal systems is divided into a number of crystal classes. Here we will be looking at the cubic crystal system. This system is divided into three classes – primitive, body-centered, and face centered. The cubic class is characterized by unit cells having orthogonal faces and sides of equal length.

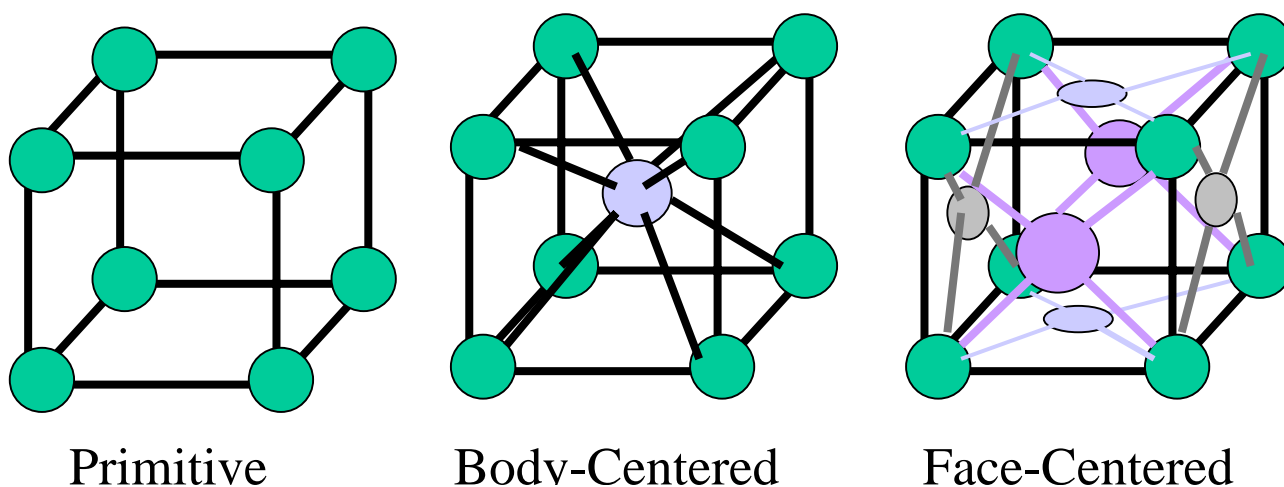


Figure 1. Three classes of the cubic crystal system.

In this experiment the x-ray diffraction pattern from a piece of wire composed of many cubic microcrystals will be analyzed to ascertain the specific cubic class of the microcrystals. The unit cell dimensions and Avogadro's number will also be determined.

Suppose a monochromatic x-ray beam of wavelength  $\lambda$  is directed with an incident angle,  $\theta$ , toward  $N$  parallel atomic planes separated by a distance  $d$ . Here,  $d$  is assumed comparable in magnitude to  $\lambda$ . A fraction of the incident beam will be deflected at each of the surfaces with the angle of incidence equal to the angle of reflection, while the remainder of the beam is transmitted. For a given inter-planar spacing, wavelength, and incident angle, beams reflected from successive layers of atoms will, for the most part, emerge from the crystal out of phase and destructively interfere, producing no appreciable reflected x-ray intensity at the corresponding reflection angle. However, if

the difference in optical path length for rays reflected from successive planes in a whole number,  $n$ , of wavelengths, then the reflected beams will emerge from the crystal in phase and constructively interfere, producing a reflected wave at reflection angle,  $\theta$ , with an intensity  $N$  times stronger than that of a single reflected beam. The diffraction condition is expressed by the Bragg equation.

$$2d \sin \theta_n = n\lambda \quad n = 1, 2, 3, \dots \quad (1)$$

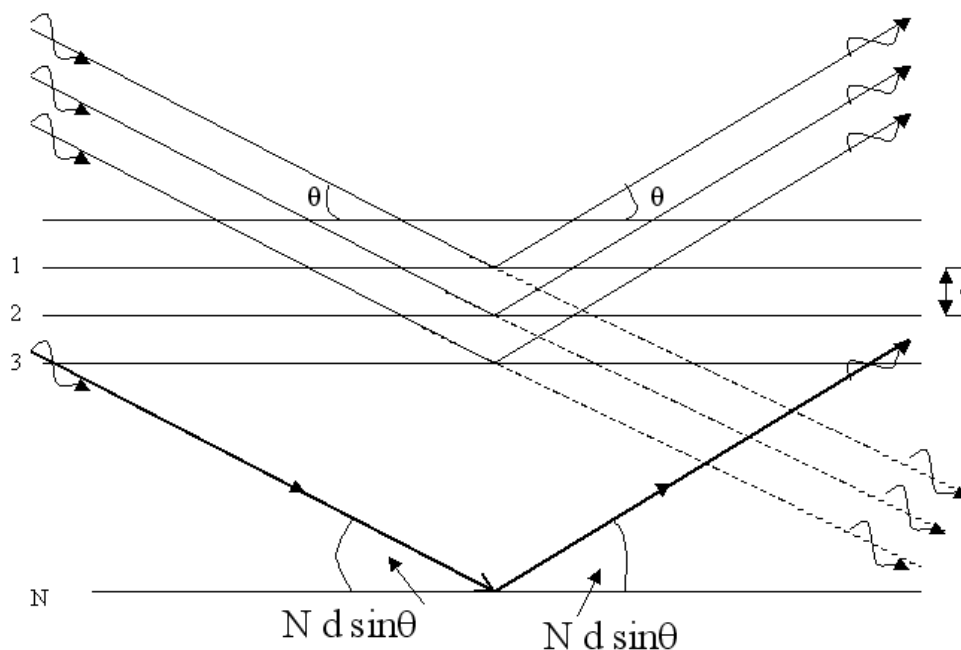


Figure 2. Bragg reflection on a set of  $N$  atomic planes.

The apparatus used to produce the film you will be studying includes an X-ray generator and powder camera. The x-ray generator produces a dichromatic x-ray beam of wavelengths  $\lambda_1 = 1.54050 \text{ \AA}$  and  $\lambda_2 = 1.54434 \text{ \AA}$ . The intensity weighted average is  $\lambda_{\text{avg}} = 1.5418 \text{ \AA}$ . The dichromatic x-ray beam interacts with a piece of wire that rotates within the camera. The wire is composed of very fine microcrystals, which present to the x-ray beam a near infinite variety of crystal orientations. It is therefore highly probable that a set of lattice planes will be oriented to satisfy Bragg's Law.

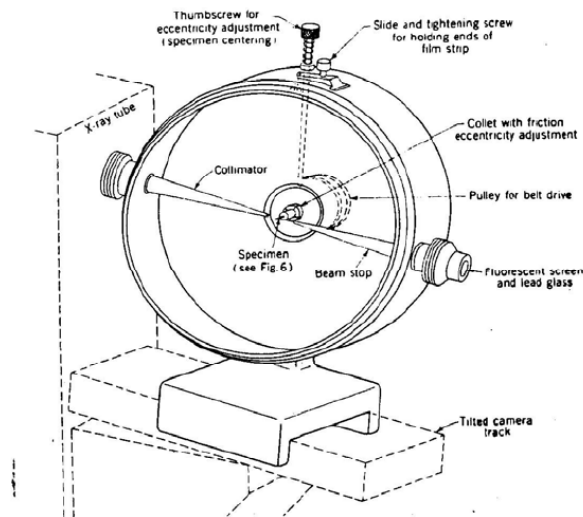


Figure 3. X-ray generator and powder camera

But note that Bragg's Law does not uniquely specify the orientation of a set of lattice planes which are diffracting x-rays. Both of the configurations below satisfy the diffraction condition.

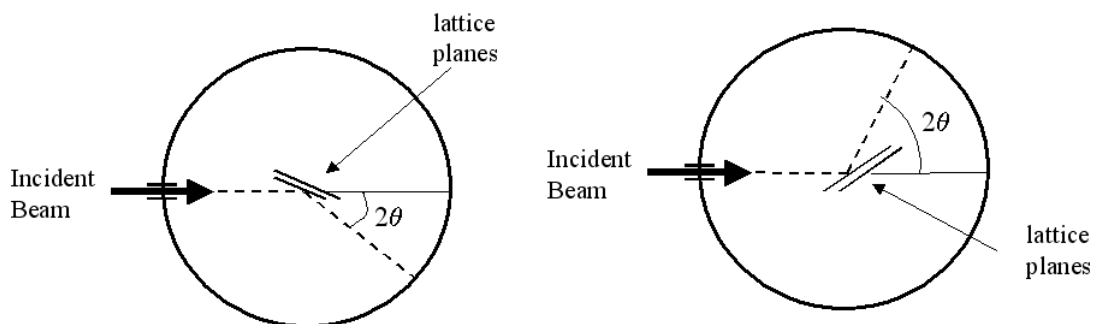


Figure 4. Two possible conditions that satisfy Bragg's Law.

Since microcrystals are oriented randomly in the incident x-ray beams, diffracted beams from the same family of lattice planes will lie on the surface of a cone with has an apex at the sample and spans a angle of  $4\theta$ .

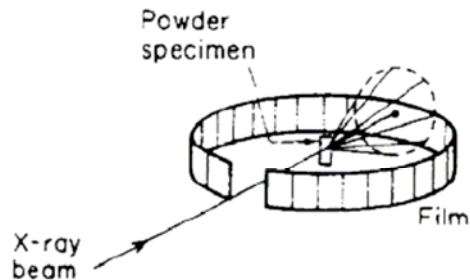


Figure 5. Diffracted beams hitting the film at an angle of  $4\theta$ .

Portions of these cones are recorded as arcs on the photographic film in the camera.

When the film is laid flat after development, it looks something like this:

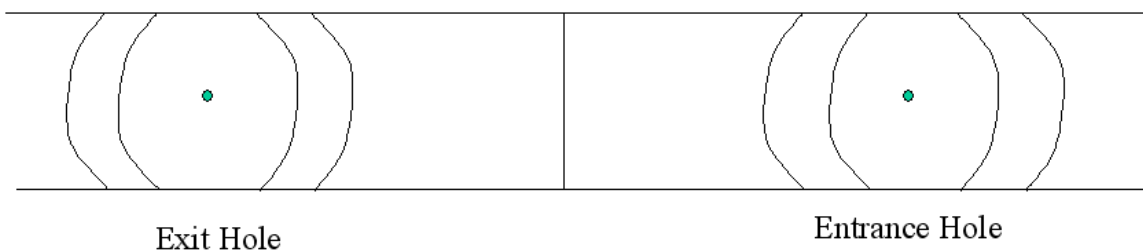


Figure 6. Example of a developed film.

Within a crystal lattice there are many different families of lattice planes. Each set of parallel atomic planes will, in principle, produce a pair of diffraction lines symmetrically disposed about the exit hole for the first, second, third, etc. order reflections.

The diagram below shows a few of the different families of lattice planes arising in each of the cubic crystal classes. Each set of planes is specified by three integers known as Miller indices.

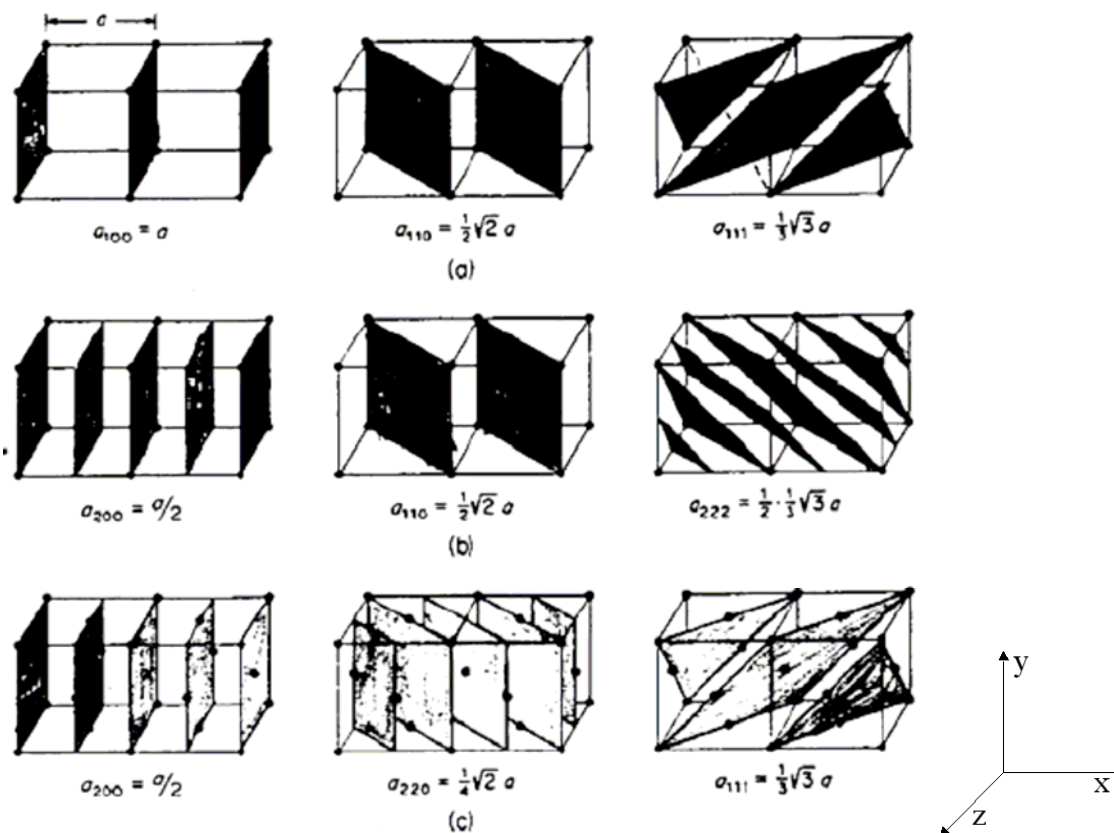


Figure 7. Lattice planes and Miller indices.

If a unit cell is placed on a Cartesian coordinate system, the miller indices,  $h$ ,  $k$ , and  $l$  correspond to the reciprocal  $x$ ,  $y$ , and  $z$  intercepts of that plane closest to, but not including, the origin. By convention, if a plane does not intersect a coordinate axis, its reciprocal intercept is 0. The Miller indices ( $h,k,l$ ) are useful because the inter-planar spacing for a set of atomic planes is conveniently expressed as

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

where  $a$  is the unit cell dimension. Combining this relationship with Bragg's Law one obtains

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} [(nh)^2 + (nk)^2 + (nl)^2] \quad (3)$$

## EXPERIMENTAL

Unfortunately, this lab is no longer performed by the students due to safety concerns and lack of material. However, if you have any questions about how the experiment would be set up, feel free to ask questions. What you will be doing is interpreting the results of a previous experiment. You will be given a piece of developed film. You need to measure positions of all of the lines using the traveling microscope in the darkroom. Make sure to note the relative intensities of the lines, the singlet/doublet structure of the lines and any other remarkable features on the film. Note the absolute error in all measurements.

## CALCULATIONS

- Find the distance between pairs of lines symmetrically disposed around the exit hole. For each pair of lines, determine the corresponding diffraction angle. The diameter of the camera is 11.46 cm.
- Find an appropriate common factor that reduces the value of  $\sin^2\theta$  for each pair of lines to the sum of three squared integers. Use the proportionality factor to determine the unit cell dimension. Calculate  $a$  using a few different proportionality factors. Report the standard deviation.
- Assign Miller indices to each line and determine what class of cubic crystal it is.
- Calculate Avogadro's number using the average value of the unit cell dimension as well as the molecular weight and density of your metal.
- NO ERROR PROPOGATION IS NECESSARY!

## DISCUSSION

- What x-ray diffraction pattern would you expect to see if the example consisted of a single crystal and was not rotated.
- How did relative line intensities vary as a function of Miller index? Even if you did not observe intensity variations, how would you expect the intensity to vary? (HINT: This has to do with the number of atoms per unit area for planes having different Miller indices.)

- When did you use  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_{\text{avg}}$ ? How did you know when to use  $\lambda_1$  rather than  $\lambda_2$ ?
- Draw the lattice planes for any Miller indices not appearing in your diffraction pattern but not in Figure 7.

## REFERENCES

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