

# X-ray Diffraction - Background

Rochester Institute of Technology\*

January 29, 2017

## X-Rays - Introduction

X-rays were discovered in 1895 by Roentgen. He named them x-rays because their nature was unknown. These rays travel in straight lines, and darken photographic film, just as light does, yet they pass through objects that are opaque to visible light. They were almost immediately put to use for medical imaging. In 1912, the diffraction of x-rays by crystals was found. This proved the wave nature of x-rays and immediately provided an invaluable tool for investigating the structure of matter at the atomic scale.

Now, of course, we know that x-rays are part of the electromagnetic spectrum. Their wavelengths range from several nanometers (soft x-rays) to about a picometer (hard x-rays). The x-rays used for crystallographic work typically have wavelengths of about an Angstrom (0.1 nanometers), since this is comparable to the spacing of crystalline planes within most solids. X-rays, therefore, have shorter wavelengths (higher energy) than visible light or ultraviolet light, but have longer wavelengths (lower energy) than gamma rays.

X-rays can act, through both diffraction and spectroscopy techniques, to provide information about the structure and elements within a material. In diffraction techniques, the angles, wavelengths, and scattered intensity are all used to determine the atomic arrangements with an impressive degree of accuracy. It is not uncommon to have 5 significant figures, with the uncertainties being on the order of 10s of femtometers. Likewise, just a elements and molecules have distinct, unique optical spectra, so to do they have both unique diffraction profiles. Such diffraction data can rapidly be reduced to determine the materials present in a substance.

An example of this is shown in Figure 1. This is a two dimensional diffraction pattern. There is a series of concentric rings due to the presence of many different lattice planes satisfying the diffraction conditions within the sample. This particular sample contains a mixture of minerals such as feldspar, pyroxenes, olivine, and amorphous volcanic rock. This also happens to be data taken by the CheMin x-ray diffraction instrument on the Curiosity rover on Mars. (<http://mars.jpl.nasa.gov/msl/mission/instruments/spectrometers/chemin/>)

---

\*Prepared by L. Barton and M. Pierce

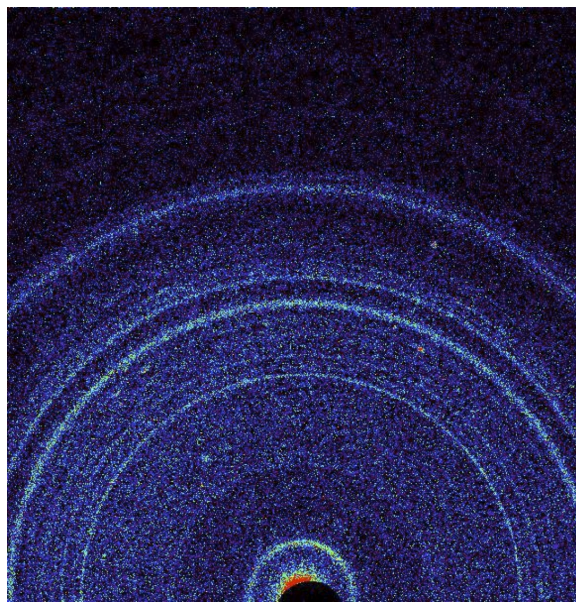


Figure 1: X-ray powder diffraction data from the Curiosity Mars rover.

## Generation of X-rays

When fast moving electrons slam into a target, they decelerate. As they decelerate they radiate (any accelerating charge radiates). This broad spectrum radiation (low intensity at many wavelengths) is known as bremsstrahlung. Within our x-ray tube, electrons are accelerated with a high voltage (up to 35 kV for our instrument) and they hit a Copper metal target. The bremsstrahlung produced would not be a very useful source of x-rays for crystallographic work, since it is of many wavelengths. If you want to do diffraction, you need a monochromatic source!

If the electrons have sufficient energy, they can ionize the copper atom that they hit. A higher energy electron within the copper then falls into the just vacated energy state. Thus, if a K shell electron is ionized out of the copper, then a L shell electron falls into that state, a strong emission line corresponding to the energy difference between the L and the K shells is produced. This is the **characteristic spectra**, which are very sharp emission lines that depend on the target material (copper, in our tube).

Thus there are two types of emission from the copper anode X-ray tube: the broad spectrum low intensity bremsstrahlung, and the strong monochromatic emission lines from the atomic spectra of the copper, which is added to the bremsstrahlung.

## Bremsstrahlung

Bremsstrahlung is produced by all processes that slow the electrons down. The highest energy bremsstrahlung is produced if the electron loses all its energy in a single collision with the copper. If that happens,

$$E_{Potential} = h\nu_{max} = E_{\gamma Max} \quad (1)$$

This defines the shortest wavelength bremsstrahlung that can be produced, since

$$\lambda_{Min} = \frac{hc}{E_{\gamma Max}} \quad (2)$$

where  $hc = 12400 \text{ eV}\text{\AA}$ .

## Copper Characteristic Spectra

The energy levels of copper are given in Figure 2. In your Prelab, you use this to calculate the energy levels of the transitions shown.

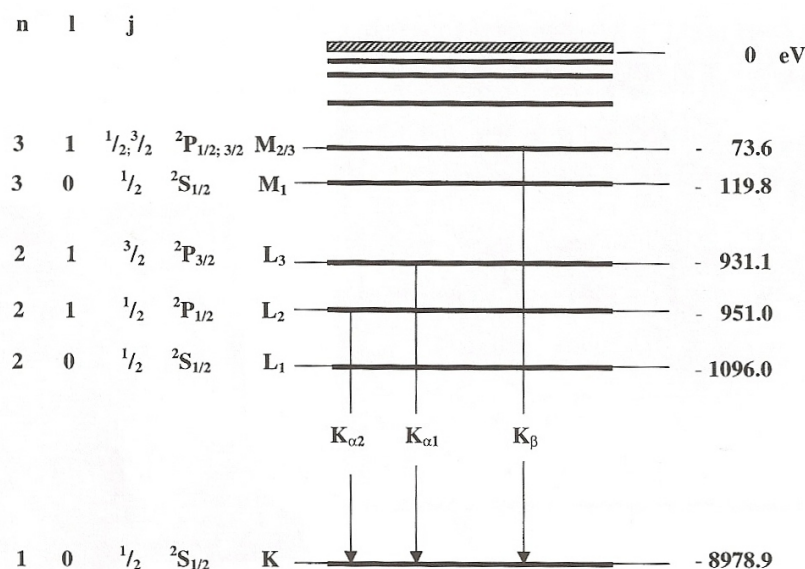


Figure 2: Energy Levels of Copper (taken from Phywe manual)

In order to study the radiation emitted by this copper anode x-ray tube, we use a LiF single crystal as an analyzer. This material has a known interplanar spacing of  $d=2.014 \text{ \AA}$ . In essence, we can use it the same way we would use a diffraction grating to analyze visible light; the crystal provides us with a regularly spaced array of planes at a spacing that is appropriate for x-rays.

Bragg reflection occurs from lattice planes, and constructive interference occurs when the extra path length traveled ( $2\Delta$ ) is equal to the wavelength  $\lambda$ , as usual. Figure 3 shows the typical Bragg condition, where

$$n\lambda = 2d\sin\theta \quad (3)$$

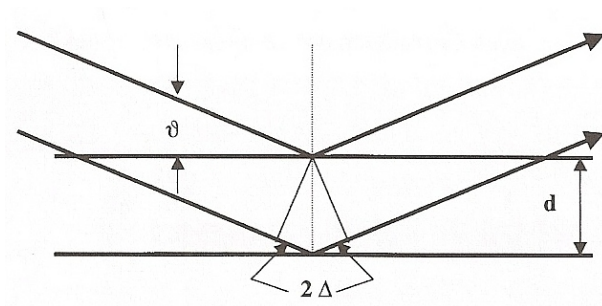


Figure 3: Bragg Diffraction

Note that for x-ray diffraction the angle  $\theta$  is defined from the plane, not from the perpendicular as it is in optics.

## X-ray Diffraction as a Probe of Crystal Structure

Solids are comprised of atoms arranged in regular repeating patterns known as crystals. Their underlying geometry is described by what is known as a lattice the lattice is composed of points in space (the atoms are added to this description later, once we understand just the points).

There are only fourteen lattices that describe all three dimensional solids. These are known as the Bravais lattices, and are shown in Figure 4. The point lattices have basic lattice vectors  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$  as their edges, these are the coordinate system for the solid. The large-scale material is made up by translation along integer numbers of these lattice vectors and then repeating the basic cell. The entire lattice is absolutely periodic in three dimensions, points are periodic along any line you choose to draw through the lattice

The symmetry arguments and group theory behind crystal structure is well beyond the scope of this lab. However, by simple inspection you can see that for the three cubic systems (simple, face centered cubic or fcc, body centered cubic or bcc), the three lattice vectors are of equal magnitude and are all at 90 degrees with respect to each other. This is a highly symmetric system under rotations or mirrors, etc. Tetragonal systems have one lattice vector unequal to the others but all angles are still 90 degrees. As you move down in this figure, the lattices become less symmetric; a triclinic material has three different lattice vectors and has three different non-90 degree angles its not very symmetric at all!

Obviously there are more than 14 materials in the world, and it is difficult to understand how they all can be described by only 14 Bravais lattices. The explanation is that the Bravais lattice points can be decorated with more than one atom. For example, diamond structure describes elemental Si, Ge, and other materials. It is based upon a fcc point lattice. Each point in the fcc point lattice then has two identical atoms, one at the point and a second that is displaced  $(1/4, 1/4, 1/4)$  away from it. The NaCl structure is also based upon an fcc lattice, except that each lattice point has a Na at the point and a Cl displaced by  $(1/2, 1/2, 1/2)$ . This works out to regularly spaced alternating Na and Cl atoms along each of the three cubic atoms. The key to understanding any of these more complex structures is

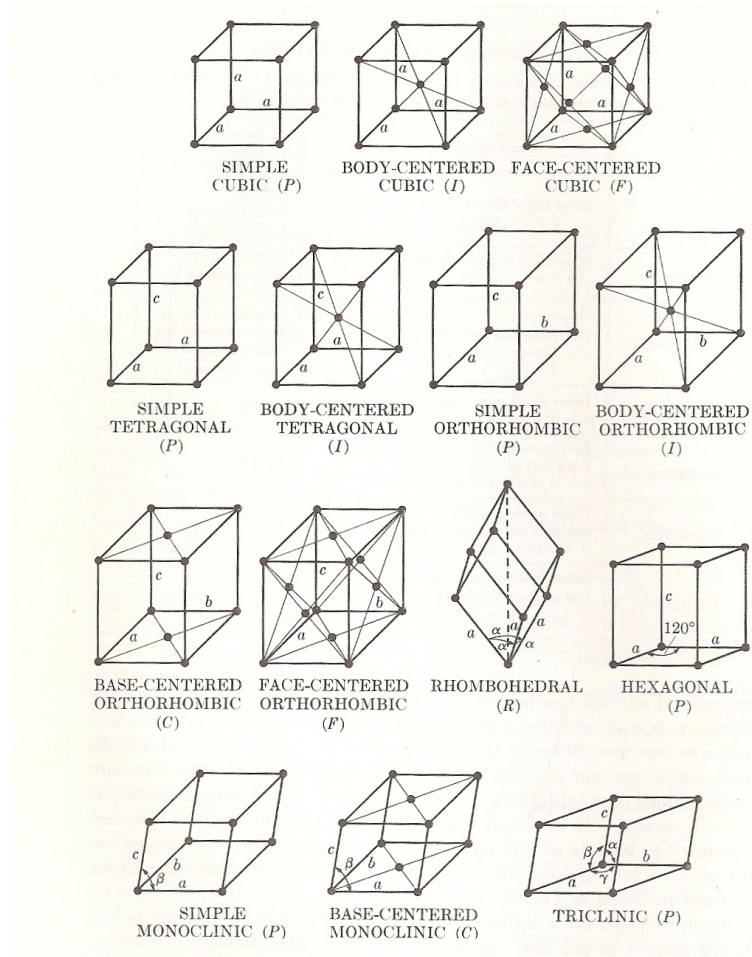


Figure 4: The 14 Bravais lattices. (taken from Cullity, Elements of XRay Diffraction)

that translations based upon the underlying point lattice always take you back to the same type of atom; that is what defines the underlying structure. Complex materials may have a many-atom basis, which is placed at each site of the underlying point lattice.

## Lattice Planes and Miller Indices

There are many planes within a crystal. Since the crystal is perfectly periodic, they form families of parallel planes. (hence one can do diffraction off of them!). There is a standard notation used to describe these families of parallel planes.

Start at a lattice point, and call that the origin. Now figure out where the plane intersects with the three crystallographic axes. Since some planes are parallel to the crystal axes, the plane will only intersect at infinity which would make an inconvenient notation. Therefore we describe these intersections by the inverse of the number of steps out the crystallographic axis. Thus three integers ( $hkl$ ) describe the plane: the (210) plane intersects the **a** axis half way, the **b** axis one unit out, and never hits the **c** axis. These integers ( $hkl$ ) are known as



Miller indices. The parentheses indicate the entire family of parallel identical planes. A bar over one of the integers means the negative. Some lattice planes are shown below in Figure 5.

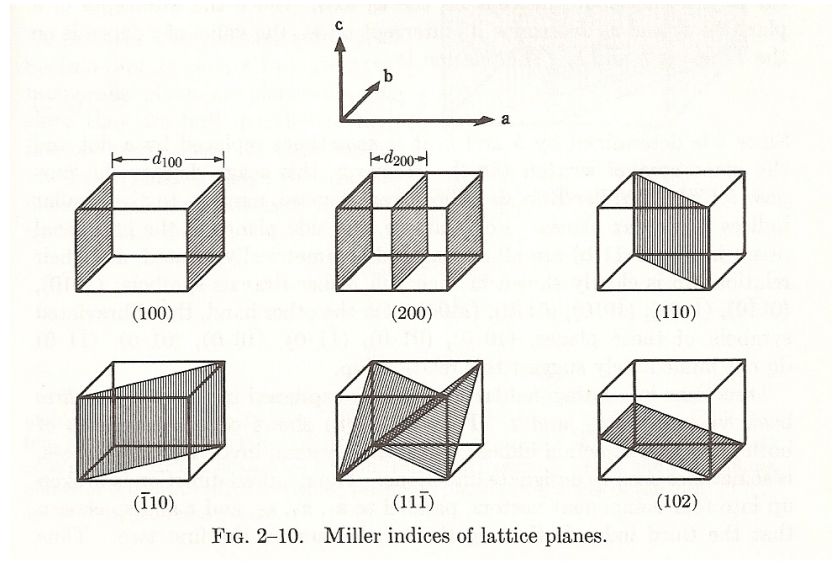


FIG. 2-10. Miller indices of lattice planes.

Figure 5: Some lattice plane examples (taken from Cullity, Elements of XRay Diffraction)

Lattice planes with higher Miller indices are closer together. For cubic systems, the spacing between lattice planes ( $hkl$ ) can be shown to be

$$d_{h,k,l} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (4)$$

where  $a$  is the lattice constant. Therefore, Bragg's law becomes:

$$n\lambda = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \quad (5)$$

Note that we can treat all reflections as first order  $n=1$ , since a reflection from the (100) plane in second order occurs at the exact same angle as a reflection from the (200) plane in first order! With this, the more useful form of the Bragg law for diffraction becomes:

$$\lambda = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \quad (6)$$

For fcc or bcc lattices, some reflections are not allowed. The “extra” atom at the face center or body center produces cancellation of the interference for some planes. The derivation of which reflections are allowed for which lattice types is simple but quite tedious. This is included as an appendix, for fcc lattices.

Table A1, in the appendix, summarizes the allowed reflections for the three types of cubic lattices.

Using this table, it is clear that one could determine both the lattice constant, and the type of cubic lattice (simple cubic, face centered cubic fcc, body centered cubic bcc) from the observed reflections angles. The difficulty becomes one of assigning the correct ( $hkl$ ) to each angle where a reflection is observed!

Using this kind of experimental technique and approach, it is possible to clearly measure both the chemical composition and atomic arrangement within a substance. You are likely familiar that elementally graphite and diamond are the same. However the arrangement and bonding of the atoms produces wildly different substances. Likewise zinc sulfide has two common polymorphs. Both contain equal parts of zinc and sulfur. There is Wurtzite, a hexagonal structure, and Sphalerite, a cubic structure. These structures produce very different diffraction profiles and allow easy determination of the substance, as shown in figure 6.

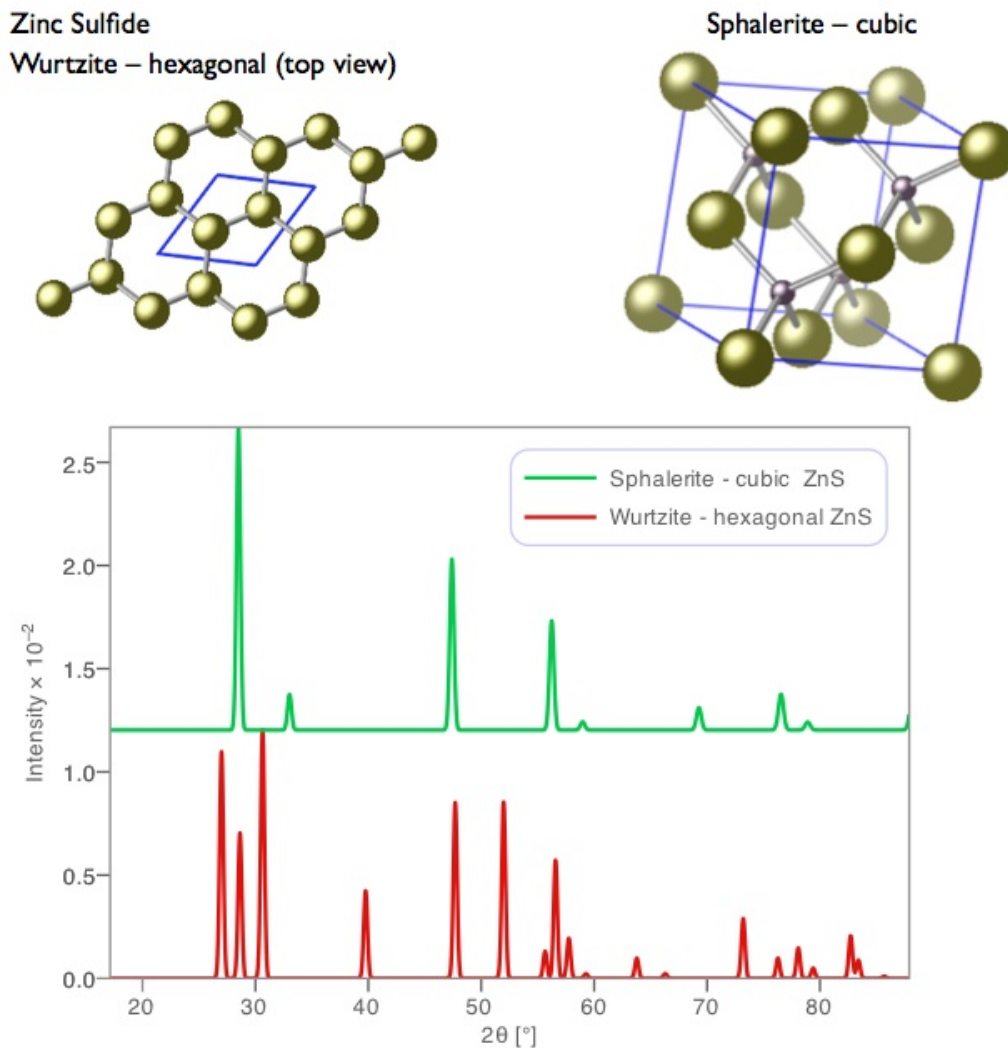


Figure 6: Zinc sulfide unit cell structures at top, and diffraction patterns at bottom.