

# X-ray Diffraction

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## Overview

In this lab you will learn the basics of scattering and determine the structure of several different materials using x-ray diffraction.

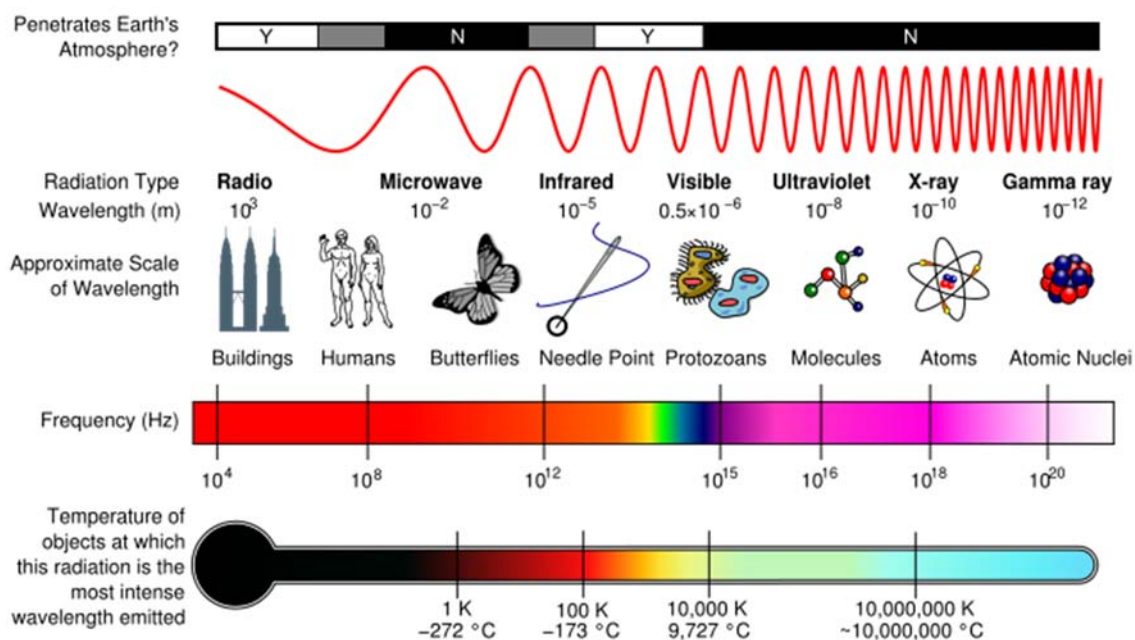
X-rays are a form of high energy electromagnetic radiation. Their wavelength  $\lambda$  varies with frequency  $f$  with the usual equation

$$f\lambda = c \quad (1)$$

where  $c$  is the speed of light. X-rays have energies from  $\sim 100$  eV to 100 KeV. In comparison, the energy of visible light is around 1 eV. The energy  $E$  is related to the frequency by the equation

$$E = hf \quad (2)$$

where  $h$  is Planck's constant. Fig. 1 shows x-rays in comparison to other types of electromagnetic radiation.



**Fig. 1.** Electromagnetic spectrum. Notice that x-rays have a wavelength comparable to the size of an atom, making them suitable for probing distances close to atomic size, ideal for studying the properties of solids where atoms are close together.

From: [urbanshakedown.files.wordpress.com/2011/03/675px-em\\_spectrum\\_properties\\_edit\\_svg.png](http://urbanshakedown.files.wordpress.com/2011/03/675px-em_spectrum_properties_edit_svg.png)

X-rays were discovered by W. C. Röntgen, a German scientist, near the end of the 1800's, and in 1901 he became the first winner of the Nobel Prize in physics for this work. Since that time, 14 additional Nobel prizes have been given for work using x-rays. In the early days, x-rays were thought to be healthy, and prescribed to treat headaches and other ailments.

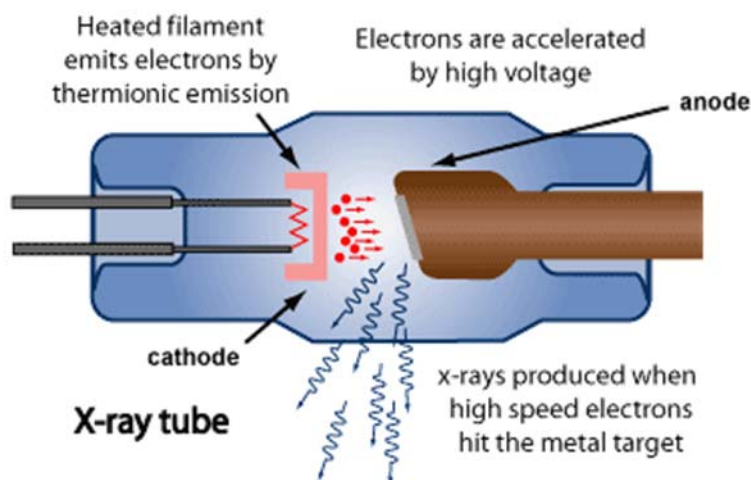
In addition to their wide use in medicine, x-rays are used to identify materials, determine crystal structures, create micro-machines, inspect for flaws in mechanical parts, and a myriad of other things. In this lab, we will use x-rays to study different forms of matter, and to determine how atoms are arranged in materials, a field called crystallography.

### Production of X-rays

In classical electromagnetism, radiation is produced whenever a charge is accelerated. The power  $P$  which is radiation depends on the charge  $q$  and the acceleration  $a$ . In SI units the equation is given by

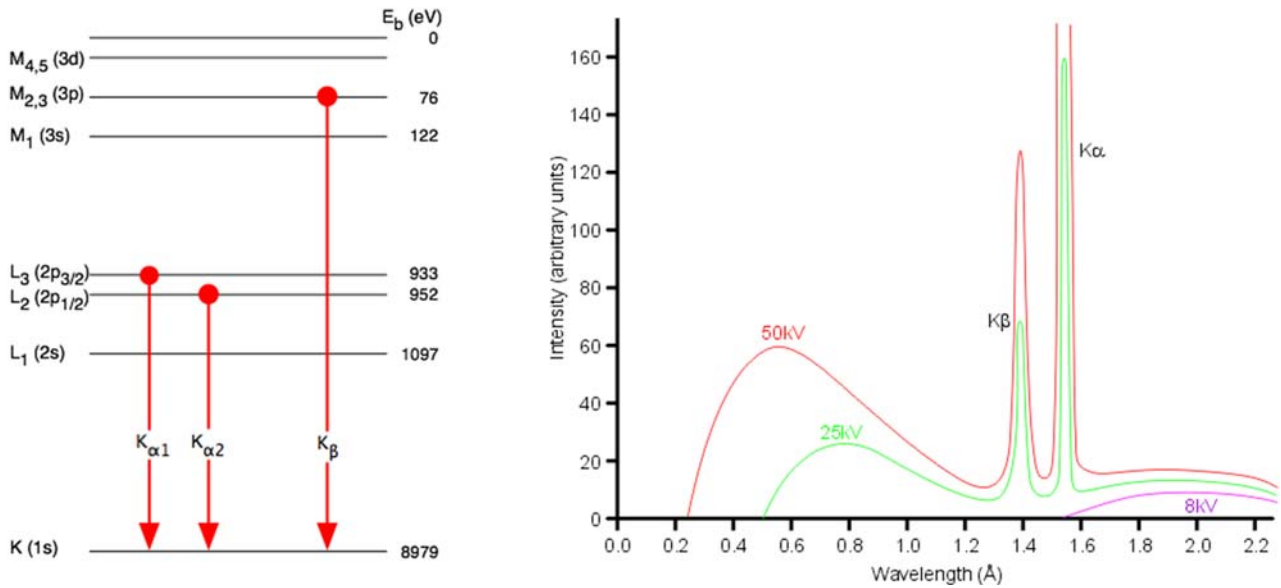
$$P = \frac{q^2 a^2}{6\pi\epsilon_0 c^3} \quad (3)$$

Here  $q$  is the charge of the particle,  $a$  is the acceleration,  $\epsilon_0$  is the permittivity of free space, and  $c$  is the speed of light. Thus to get substantial power radiated you need a high acceleration. For laboratory sources, this is generally achieved by accelerating electrons to high speeds by means of a large potential difference and then slamming them into a target which stops them abruptly (i.e., gives a large negative acceleration). A diagram of the process is shown in Fig. 2 below.



**Fig. 2** X-ray tube operation. A heated filament releases x-rays which are accelerated by a high voltage (in our case 45 kV). Electrons collide with a copper anode, causing the emission of radiation. From [www.arpana.gov.au/images/basics/xraytube.png](http://www.arpana.gov.au/images/basics/xraytube.png).

In addition to the continuous radiation from the electrons being decelerated (called Bremsstrahlung radiation, from the German word for braking), there is additional radiation from the material the electrons are shot into; in our case this will be copper. When the electrons collide with the copper, they often knock out the copper electrons. If they knock out for instance a ground state electron ( $1s$  orbital, often called the  $K$  shell for historical reasons) there will also be x-rays produced as higher energy electrons fall into this ground state. The orbitals are shown in Fig. 2a. These lines are called characteristic x-ray lines, and are often very strong. They have a very narrow energy range and are useful for x-ray studies.



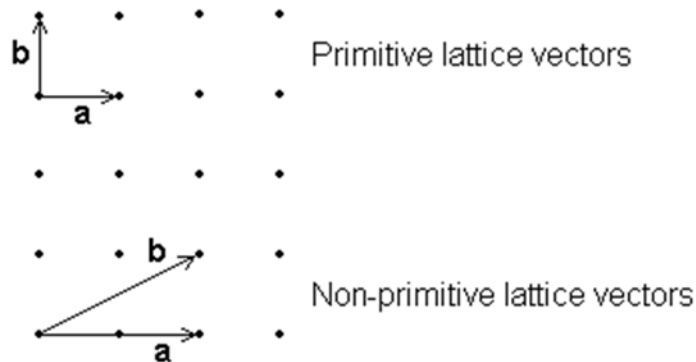
**Fig. 3 a)** X-ray energy levels for copper. The collision of the accelerated electron with the copper knocks an electron out from the ground state  $K$  shell ( $1s$  orbital). Electrons from higher orbitals fall into the ground state, emitting x-rays with characteristic energies with high intensity, labeled as  $K_{\alpha 1}$ , etc. Figure from [www.arpansa.gov.au/images/basics/xraytube.png](http://www.arpansa.gov.au/images/basics/xraytube.png). **b)** Output of an x-ray tube, showing a broad background of energies from the electron decelerating, as well as the characteristic lines from the copper. The three different color lines correspond to different voltages across the tube. Note that at  $8\text{keV}$ , the energy is too low to knock out a ground state electron (which requires  $8.979\text{ keV}$  as shown in a). Figure by Pieter Kuiper from [commons.wikimedia.org/w/index.php?curid=2239415](https://commons.wikimedia.org/w/index.php?curid=2239415).

### Crystals

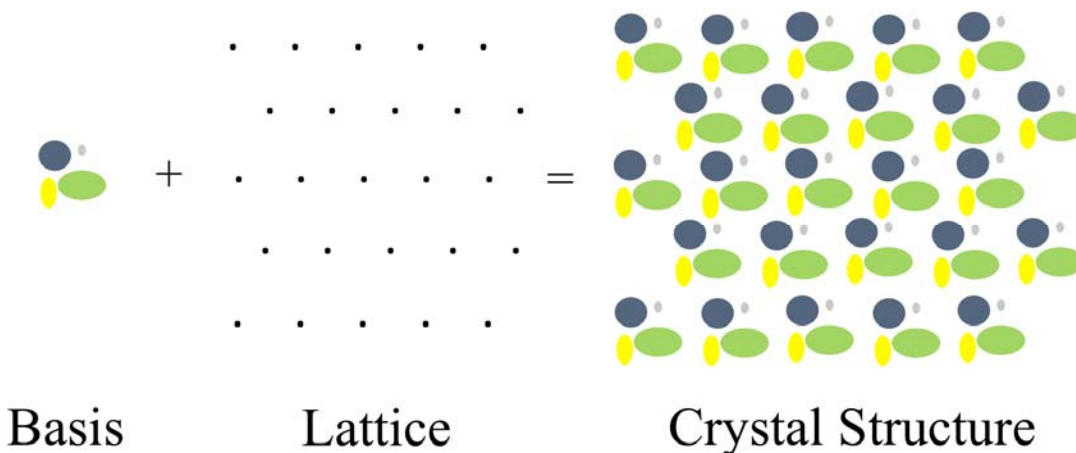
The atoms in crystals sit at regular positions in a lattice. – see Fig. 4. In a perfect crystal, there is a basic structural unit which repeats itself. A set of lattice vectors move you from one point to the next – see Fig., 4 Top.

While there could be one atom at each lattice position, it is possible to have more than one associated with a lattice point – for instance you could have a molecule (such as  $\text{H}_2\text{O}$ ) at each lattice point. Then you would have an ice crystal. If there is more than one atom per lattice point, you have what is called a **basis** – that is, you have the lattice points, and a basis consisting of several atoms which are associated with that lattice point (see Fig. 4, Bottom).

You might think that there would be an infinite number of possible crystal lattices, but if you want the structure to fill all space you are actually limited to 14 different types of structure (called Bravais Lattices). For instance, the simple cubic lattice is one possible structure. Of course, the distance between the atoms can vary, but the basic structure remains the same. You might also think there are an infinite number of possible combinations when you add a basis, but again, if you want to have a crystal which is built out of repeating blocks, there are only a finite number of possibilities, in this case 230 **space groups**. Any crystal belongs to one of these space groups.



**Fig. 4. Top** Lattice vectors for a 2d lattice. Generally, the simplest primitive lattice vectors are used. From <http://www.chm.bris.ac.uk/webprojects2003/cook/periodicstructures.htm>  
**Bottom** Crystal is made up of a basis, typically different atoms, put on a lattice, to give the crystal structure. From <https://andreaslm.wordpress.com/2015/06/21/crystallography-i-basis-and-lattice>.



### X-ray Diffraction

Sir William Lawrence Bragg discovered the law that bears his name (Bragg's Law). For his work on x-ray scattering (carried out with his father, William Henry Bragg), he received the Noble Prize (at age 25, the youngest winner so far in Physics).

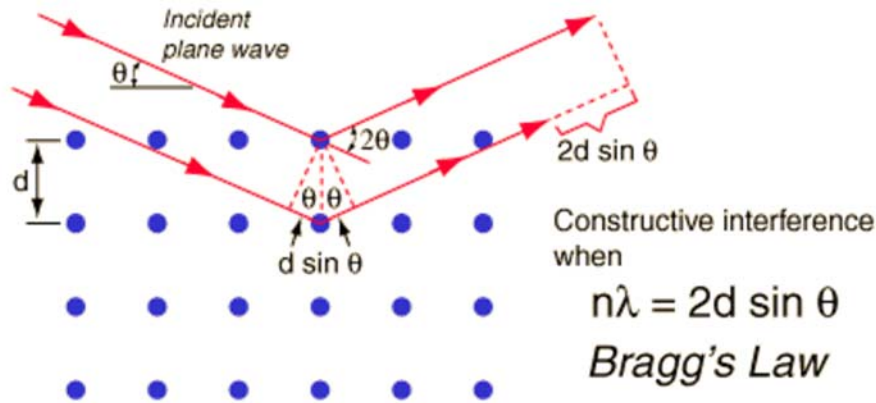
The basic idea, shown in Fig. 5, is that x-rays are incident on a sample. An x-ray that bounces off the top of the sample has a shorter path than one that bounces off the layer below. The difference in the path lengths is  $2d \sin(\theta)$  as shown in Fig. 5. Recalling optics, if the path difference is an integral number of wavelengths, the two waves will exhibit constructive interference. That is the signal becomes a maximum when

$$2d \sin(\theta) = n\lambda \quad (4)$$

This equation is Bragg's Law. It tells us that if we know the wavelength of the x-ray, there will be a maximum at an angle corresponding to the distance between the planes in the crystal. Note that if you solve Eq. 5 for the angle, it will be inversely proportional to the distance; that is **large** distances correspond to scattering at **small angles** and vice versa.

The atoms in crystals define a series of planes which act to reflect the x-rays – see Fig. 5. Planes are indicated by three numbers (called the Miller indices) – you can look this up online for more details. Use the Wolfram Demonstration entitled *Crystallographic Planes for Cubic Lattices*, which is on the lab computer to see how the indices correspond to different planes. You will find that there are a large number of different possible planes for a given crystal, and each plane will reflect x-rays at a certain angle. Powder

diffraction is based on the idea that if you put a large number of tiny crystals in an x-ray beam they will have random orientations, so every possible plane in a crystal will reflect x-rays at the angle corresponding to that plane. By looking at a wide range of angles, you will see a large number of peaks corresponding to different sets of planes. (Not just powders are this way; many solid materials are actually made up of a huge number of small single crystals randomly oriented and joined together.) For such a system, you will see **every** allowed reflection at the appropriate angle, since by chance you expect a large number of the small single crystals to happen to have the correct orientation. Note, however, that some reflections may be forbidden based on the crystal structure. By working backwards from the reflections you can determine a crystal structure.



**Fig. 5.** Bragg's Law, which shows the relationship between the x-ray wavelength and the lattice spacing which leads to constructive interference. When the x-rays interfere constructively, the signal is largest. By knowing the wavelength  $\lambda$  and measuring the angle  $\theta$  for constructive interference, it is possible to determine the spacing  $d$  in the crystal lattice. From <http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html>.

A more modern treatment involves using the scattering of an incoming plane wave from a regular lattice of atoms. What this analysis shows is that the scattering observed from a crystal does not directly give the positions of the atoms, but rather provides the **Fourier Transform** of the structure. In order to get the actual atomic locations, it would be necessary to take the data and do an inverse Fourier transform on it, which would yield the positions. However, to do such a transform, it is necessary to know both the amplitude and the phase of the scattered wave. But our instruments are only capable of determining the amplitude. Therefore, analysis of the data has to involve comparing the scattering result with the expected signal from possible structures, and trying to find a match. In the old days this was done by hand, but now of course it is handled by sophisticated computer programs.

When you do the Fourier transform, you go from the real crystal lattice into what is known as reciprocal space. The reciprocal space lattice can be found from the following equations

$$b_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$b_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$b_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

Here the  $\mathbf{a}$ 's refer to the basis vectors for the crystal (shown in Fig. 4).

While the angle of the peak gives information about the distance between the lattice planes being reflected from, there is additional information in the intensity of the peaks. The intensity depends on which atoms are in the crystal (there may be more than one type) as well as the crystal structure. The intensity depends on the **structure factor** for the crystal, which tells how strong a given reflection is. The structure factor depends on the atoms in the basis, and how they are arranged. There can also be a so-called multiplicity factor if there are more than one set of planes which can give the same value.

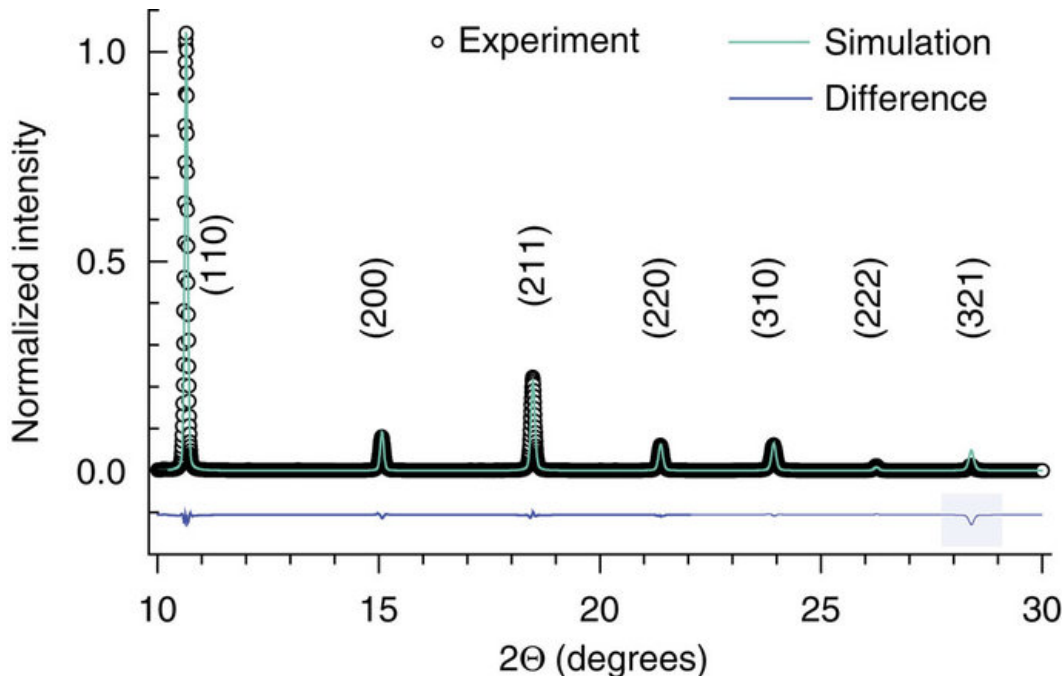
### Amorphous materials

In addition to crystal structures, some materials are amorphous. In these materials, there is no regular structure which repeats itself. Rather, the atoms are fixed in positions without a regular pattern. However, there is still often a well-defined **average** distance between the atoms. Scattering is increased at the angle corresponding to this average distance, but the peak tends to be broad (since there is significant spread around the average distance). Most liquids are amorphous, and some other materials such as glasses.

### Preparatory Calculations

- 1) We will be using an x-ray machine with a copper tube. Using the data in the Fig. 3a, find the energy which corresponds to the copper  $K_{\alpha 1}$  line. What is the wavelength of this radiation? Also find the wavelength for the  $K_{\alpha 2}$ . These are the strongest wavelengths, so we will approximate the x-ray signal as coming just from these wavelengths.
- 2) Consider a crystal with a simple cubic (sc) structure. Assume that the distance between the atoms (called the **lattice** constant) is 0.3 nm. For the wavelength you found above, determine the angle  $\theta$  from Bragg's law corresponding to the (1 0 0), (1 1 0) and (1 1 1) reflections. Using the Wolfram Demonstration *Crystallographic Planes for Cubic Lattices* will allow you to see what these reflections look like.

Note that few materials crystallize in a sc lattice, so you should also look at the body centered cubic (bcc) and face centered cubic (fcc) lattices, which are much more common.



**Fig. 6.** X-ray powder diffraction pattern from superdense Al created by laser-induced micro-explosion. The different crystal planes for the bcc structure are labeled using Miller indices. From <http://www.nature.com/articles/ncomms1449>.

### Experimental details

The instrument which we will use to take measurements is a Panalytic Empyrean x-ray powder diffractometer. Powder samples will be ground up and placed in special sample holders. Other holders are suitable for solid objects. Your instructor will show you how to use the instrument.

### Safety

The Panalytic x-ray machine produces a strong x-ray beam, so it is important to avoid contact with the x-rays. The entire instrument is enclosed in a shielded chamber. The glass looking into the system is leaded glass, since lead is good at reducing x-ray intensities. The instrument has an extensive safety interlock system, and won't allow x-rays to be emitted if any of the doors are open. However, in order to operate the system alone, a radiation safety course is required, so for this lab you will need to have the instructor present in order to do the measurements.

### Procedure

We are going to use the Reflection/Transmission Spinner in order to study several samples; a couple of samples of powder, a piece of metal, and a piece of glass. We will measure a *diffraction pattern*, which is simply a measurement of the x-ray intensity at different angles. An example of such a pattern is shown in Fig. 6. The spinner is so named since it continuously rotates the sample (**think about why you would want to do this**).

**Data taking.** We will take data on a number of different samples. Our samples may include

- 1) Salt or NaCl (the first structure ever determined with x-rays).
- 2) Copper metal

- 3) Aluminum metal
- 4) A glass slide
- 5) Wood
- 6) Clay
- 7) An unknown mixture of materials. Based on the x-ray data you will use HighScore software to determine what the materials are and their relative concentration.
- 8) Other stuff?

### Data analysis

For any x-ray experiment, it is important to know how deep you are probing a sample – depending on the material, x-rays will only penetrate a certain depth into the system. Since x-rays are scattering from the electrons, heavier atoms with more electrons have more scattering and the x-rays penetrate a smaller distance. The intensity ( $I$ ) of x-rays falls off exponentially as a function of depth  $d$  in the material following the equation below:

$$I = I_0 e^{-d/l} \quad (5)$$

where  $I_0$  is the intensity incident on the sample, and  $l$  is a property of the material called the attenuation length.

- 1) For the materials studied, you should determine the approximate depth of material probed, which can be found using the online calculator in Highscore or at the Center for X-ray Optics (CXRO) website: [http://henke.lbl.gov/optical\\_constants/atten2.html](http://henke.lbl.gov/optical_constants/atten2.html).
- 2) For the crystalline materials, you will need to determine the crystal structure and the lattice constant for the materials. You should also show the simulated data from Highscore with the actual data and discuss any discrepancies.
- 3) For the amorphous samples, find the position of the largest peak in the scattering. This should correspond to the average distance between the atoms or molecules in the material. Use this number to predict a value for the density in the material, and compare this result with the known value. They are likely to be roughly comparable, but not exactly the same.
- 4) For the unknown material mixture, attempt to determine what the materials are and their proportion.

### Background material

You will want to look up some basic material on scattering and crystal structures (online or in a solid state physics book). For the software, tutorials are available in the program or online. If you are having trouble finding a good reference let me know and I can help.