X-Ray Crystallography of NaCl and other Alkali Halides

This lab introduces you to the technique of x-ray diffraction in mineralogic studies. We will use as our subject material the alkali halides to see what information can be derived about their crystal chemistry from x-ray diffraction.

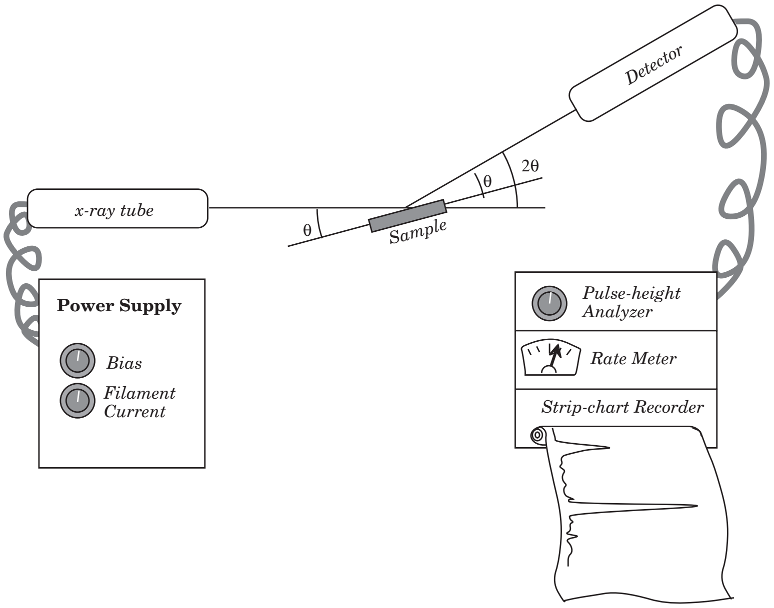
X-rays are very similar to visible light. They are both forms of electromagnetic radiation. They are generated by oscillating electrons in atoms and by electronic transitions in atoms and molecules. They are absorbed by electrons, causing other electronic transitions. The generation and absorption of x-rays and light are governed by the rules of quantum mechanics. However, the propogation of the electromagnetic radiation is very well described by classical mechanics. This means that, for our purposes, we can treat the radiation as waves. They possess all the properties of waves: wavelength, period, frequency, amplitude, energy, and so on. Visible light has wavelengths in the range of 400 to 700 nm. X-rays have wavelengths on the order of about 0.1 nm (= 1 Å).

When waves hit an interface, as light waves traveling from air to mineral, they are reflected or refracted. If the waves impinge on several objects that are spaced by distances comparable to the wavelength, the waves are diffracted, or scattered. This is the case for x-rays and crystal structures, which have spacings of about 1 nm between atoms. The scattered waves then interfere with each other, sometimes causing constructive interference, other times causing destructive interference. The directions in which constructive interference occurs are the diffraction directions. To determine these directions, we need to figure under which conditions constructive interference takes place. This occurs when the waves are completely in phase or when the waves are an integral number of wavelengths out of phase.

W. L. Bragg figured out that this occurs when the spacing between interatomic planes, d, and the angle at which the x-rays strike the planes, θ, are related by a relation called Bragg's law, proved in the adjacent figure. The law is simple and allows us to determine the interatomic spacings by measuring the angles at which diffraction takes place. Each set of planes, (001), (111), (110), and so on, is spaced a different distance in a lattice. Each angle of diffraction measures these distances. Because each mineral has a unique structure and composition, the pattern of angles of diffraction is unique to each mineral and acts as a fingerprint of the mineral. We will see what the fingerprints of the alkali halides looks like in this lab.

The machine we use is the x-ray powder diffractometer. In this machine, a powdered sample of the mineral is placed on a holder. The holder can rotate through an angle θ; a detector rotates through an angle of 2θ to measure the positions of diffracted beams. Refer to the diagram below.

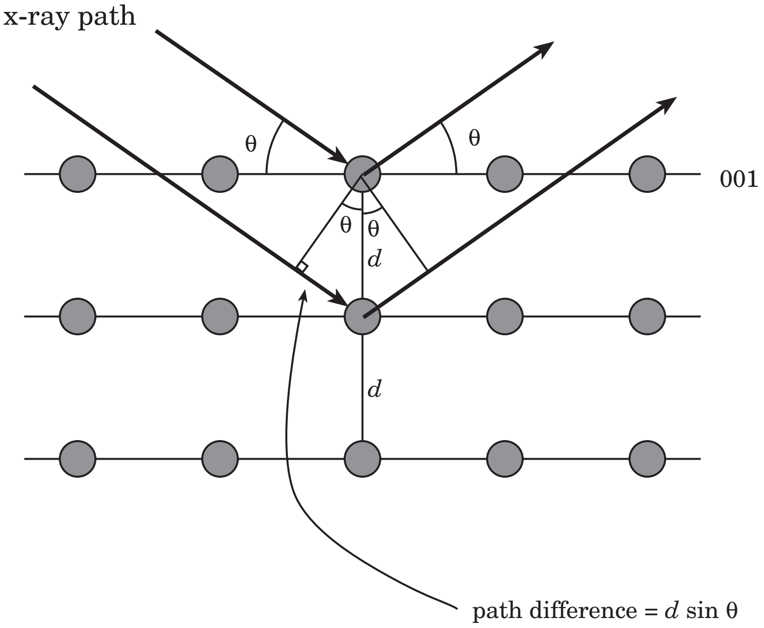
X-ray Powder Diffractometer



The intensities of diffracted beams, in counts per second are recorded in a data file in which each angle 2θ is paired with an intensity I. The computer program makes a plot of I versus 2θ, which looks similar to the strip chart shown on the right. Each peak on the plot represents a plane of atoms having a d spacing appropriate for diffraction at the angle θ. The value of d can be determined from Bragg's law.

Bragg Condition for x-ray diffraction

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



The intensity of a diffracted beam is related to the density of electrons on the plane and on the symmetry of the crystal. It is customary to pick the most intense peak and assign it the intensity 100. All other peaks are then assigned intensities as fractions of the most intense peak: 90, 75, 30, etc.

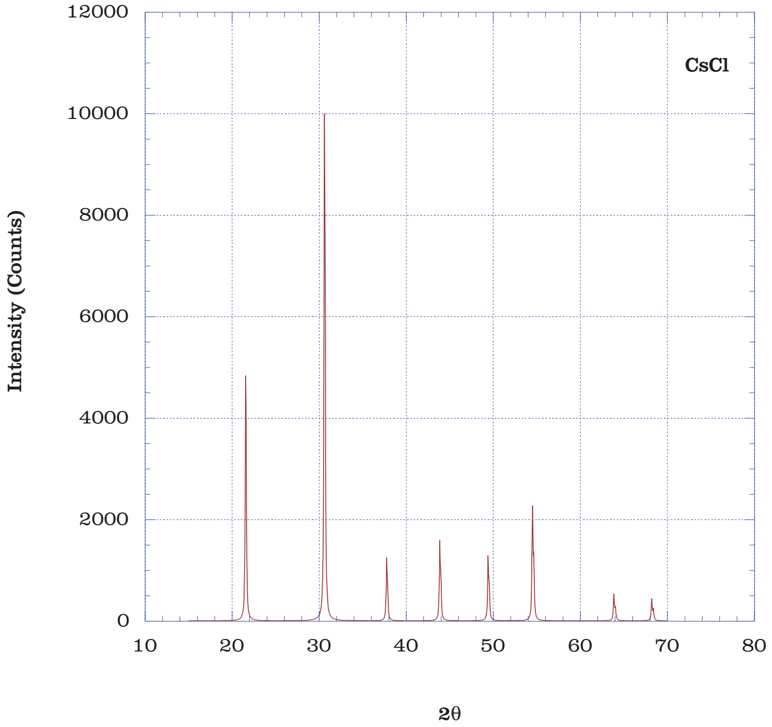
The number of peaks is related to the symmetry of the crystal. Cubic minerals, for example, can have only one peak for the planes (100), (010), and (001) because the d spacings are all the same. Orthorhombic crystals have three peaks, one for each plane, because the d spacings for (100), (010), and (001) (equivalent to the axis lengths a, b, c) are distinct.

Each mineral possesses its own diffraction pattern. This means that the combination of d spacings, number of peaks, and intensities of peaks is unique for each mineral. Even two minerals like halite and sylvite, which have the same symmetry, crystallize in the same space group, and have the same arrangement of alkali and halide ions, possess different diffraction patterns. This happens because Na^+ and K^+ are different in size and have different numbers of electrons. The alkali-halide distances are different, and, therefore, d_{100} (= a, the unit-cell edge) is different.

1. You will measure the diffraction patterns of halite and sylvite (both have the point symmetry $4/m\bar{3}2/m$, space group $Fm3m$). Determine the values of d from the patterns using Bragg's law. Compare the patterns to see whether they possess the same number of peaks, same intensity of peaks, and the same values of d.

2. Compare the patterns with those of fluorite (point symmetry $4/m\bar{3}2/m$, space group $Fm3m$) and CsCl (point symmetry $4/m\bar{3}2/m$, space group $Pm3m$). Is the number of peaks the same? How about values of d? Discuss the effects of symmetry on the x-ray diffraction patterns.

3. Use the graphing program Kaleidegraph to plot the x-ray data and determine the locations of the peaks and their intensities. In your notebook, you should present the plots and tables of peak locations, d values for the peaks, and intensities of the peaks. The data files are in the mineralogy folder on the file server. Some examples are given below.



No.	2θ	d	Relative Intensity	Maximum Intensity	Integrated Intensity	Width	Type
1	21.557	4.1223	48.300	4811.0	985.85	0.20500	KA
2	30.615	2.9202	100.00	9963.0	2246.2	0.22500	KA
3	37.766	2.3821	12.400	1237.0	280.75	0.22700	KA
4	43.862	2.0641	15.800	1579.0	374.38	0.23700	KA
5	49.407	1.8446	12.800	1276.0	310.20	0.24300	KA
6	54.502	1.6836	22.600	2255.0	572.92	0.25400	KA
7	63.846	1.4579	5.3000	527.00	132.93	0.25200	KA
8	68.194	1.3740	4.4000	439.00	73.310	0.16700	KA1
9	68.309	1.3754	2.4000	244.00	41.340	0.16900	KA2