Single Crystal X-Ray Emission and Diffraction

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April 9th, 2017

Abstract

This experiment was broken down into two parts; both were based on x-ray diffraction. The first part was to determine Plank's constant. This was done by analyzing the diffraction pattern over a range of angles coming from bremsstrahlung x-rays diffracting from a single crystal of LiF or NaCl. The angle of diffracted x-rays is related to their energy by Bragg's Law. By analyzing the angles which correspond to the highest energy of the bremsstrahlung radiation you can extrapolate data and deduce Plank's constant. The second experiment was to determine the crystal spacing for four different single crystals (LiF, NaCl, RbCl, and KCl). This was done by analyzing the diffraction pattern over a range of angles coming from atomic transition type x-rays diffracting off of each crystal. The atomic transitions of the x-ray source and thereby the wavelengths were known. These x-rays were also the highest intensity from our source, this results in peaks in the diffracted intensity versus angle data, and thereby a method of determining the location in angle of the atomic transition wavelengths. With the wavelength and angle information from the diffraction experiment you can deduce the crystal spacing via Bragg's Law. In general, x-ray diffraction give us information about the internal structures of materials. This is a remarkable thing, being able to peer inside of a material and to learn about its structure and chemical bonds; this I would say is the motivation behind this experiment. The results of our experiment were acceptable given the questionable quality of our crystals, and simple experimental set-up. The overall results were as follows. For part one Plank's constant was found to be 4.32*10^-34±5.64 J*s. For part two, the crystal spacing's were found to be: LiF: 2.0 ± 0.2 Å, NaCl: 2.8 ± 0.2 Å, 3.1 ± 0.2 Å, and RbCl: 3.3 ± 0.2 Å.

Introduction

X-ray diffraction in general is a name given to a variety of techniques used to probe the inner workings of structures too small to resolve with visible light. This includes atomic and molecular structures. In this experiment, we utilized a specific technique of x-ray diffraction known as Bragg diffraction to determine atomic spacing distances and to filter out certain x-rays from a continuous source. X-ray diffraction as you may have guessed involves the use of x-rays. X-rays are a form of electromagnetic radiation with a wavelength on the order of atomic scales. The science of x-ray diffraction began with the discovery of x-rays by Wilhelm Rontgen in 1895. In 1913, a chap by the name of William Lawrence Bragg along with his father William Henry Bragg observed interesting patterns of reflected x-rays off of crystalline solids. They proposed a rather geometric theory to explain these patterns, and in 1915 they were jointly awarded the Nobel Prize in physics, hence we have Bragg Diffraction. The idea behind Bragg Diffraction is what follows. Say you have x-rays of a

single wavelength incident from a single direction on a structure composed of objects arranged in a periodic fashion (single crystal). The x-rays will interact with the objects. If these interactions result in reflections then the angle of reflection will be equal to the angle of incidence and the reflections will interfere with each other. The reflections will produce constructive interference only for specific angles of incidence for the particular wavelength because of the constant periodic structure of objects. So, by detecting the angle of reflection for constructive interference of a particular wavelength you can determine the spacing of the constant periodic structure. The relation which relates the angle, wavelength, and spacing is known as Bragg's Law. The effect of Bragg Diffraction can be used for at least two experiments. These two experiments are the two we conducted, and the topic of this report. They are: (1) the determination of the crystal spacing for four single crystals (LiF, NaCl, KCl, and RbCl), and (2) the determination of Plank's constant. The determination of Plank's constant is done by utilizing the nifty filtering effect Bragg diffraction has on the x-rays. Imagine a continuum (all wavelengths) of x-rays all coming from the same direction (same angle of incidence) and interacting with a single crystal. A lot of the wavelengths will be reflected from the crystal, however, only one specific wavelength will undergo constructive interference and be distinctly noticeable in the detector. This is the key concept and it will be explained in the theory section how we use this effect to determine Plank's constant.

Theory

This experiment utilized the theories of Bragg Diffraction and single crystals to determine crystal spacing's and the value of Plank's constant. To understand the physics behind the experiment we must understand the basics of these two theories.

To begin, let us define diffraction. Diffraction refers to various phenomena that occur when a wave encounters an obstacle or a slit. It is defined as the bending of light around the corners on an obstacle or aperture into the region of geometrical shadow of the obstacle. (Wikipedia, 2017) The bending of x-rays around atoms (the obstacle) is not what you should be trying to reconcile. The important effect from diffraction and the primary reason why this experiment is called x-ray diffraction is the interference pattern produced after the x-ray interacts with the atoms, not the specifics that happen in the interaction. As mentioned above, Bragg Diffraction is a result of reflection and interference, not diffraction and interference; the pattern produced is a diffraction pattern in the sense that it is that same pattern that occurs when plane waves actually diffract through a diffraction grating of slit spacing equal to that of the atomic lattice spacing. Also, I should mention that the effects of diffraction are most prominent when the wavelength is comparable to the size of the aperture or object, hence more spreading. In this experiment, the objects are the atoms in the lattice of the crystal. The x-rays observed for the lattice spacing experiment have wavelengths less than the lattice spacing and therefore were able to interact with the individual objects in the lattice; this is important because if the wavelength of the x-rays was bigger than or equal to the lattice spacing then interaction and reflections among collections of atoms would occur and resolution of individual objects would not be possible.

Next is the single crystal. The term single crystal refers to a crystal where all of the atoms are part of the same lattice that faces the same plane throughout the entire crystal, it can also be called a

monocrystalline solid. The opposite type of crystal is called a ploy-crystal. In a poly-crystal, individual domains in the crystal exist where each domain consists of atoms in the same lattice facing the same plane, however different domains are arranged in different planes. A single crystal is the simplest type of crystal, and has the structure of a single lattice, it is also the most difficult type of crystal to manufacture. The unit cell of a single crystal is a cube with the length of one side equaling the parameter called the crystal spacing which we refer to as "d". For all four of the single crystals we analyzed in our experiment, we analyzed the same plane, called the (100) plane in miller index notation. This is the plane where the faces of all the cubes of each unit cell of the lattice are in the plane of the crystal's physical face.

Below are some illustrations showing the single crystal structure of NaCl, and Bragg Diffraction showing the process of reflections of x-rays from a single crystal producing interference. (Credit: Wikipedia, 2017)

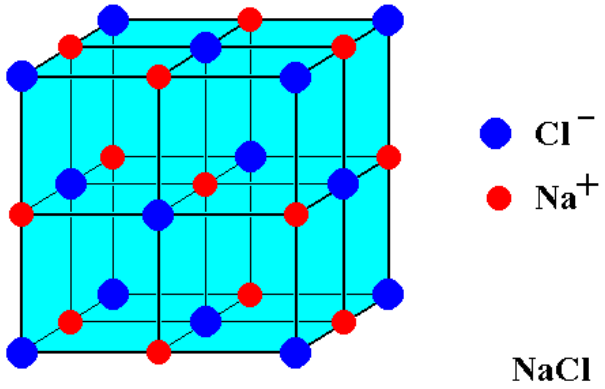


Figure 1: Single Crystal of NaCl

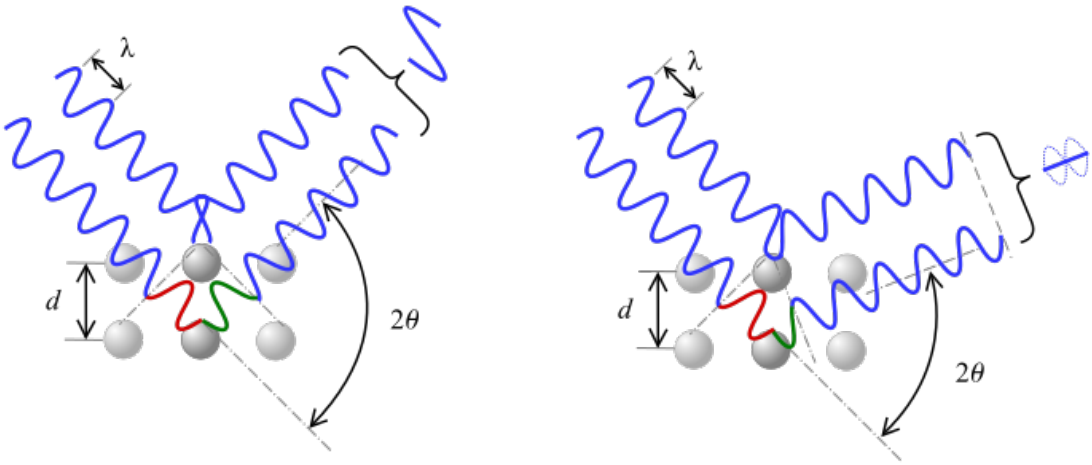


Figure 2: Bragg Diffraction, showing the reflection and interference from a single crystal.

Derivation of Bragg's Law:

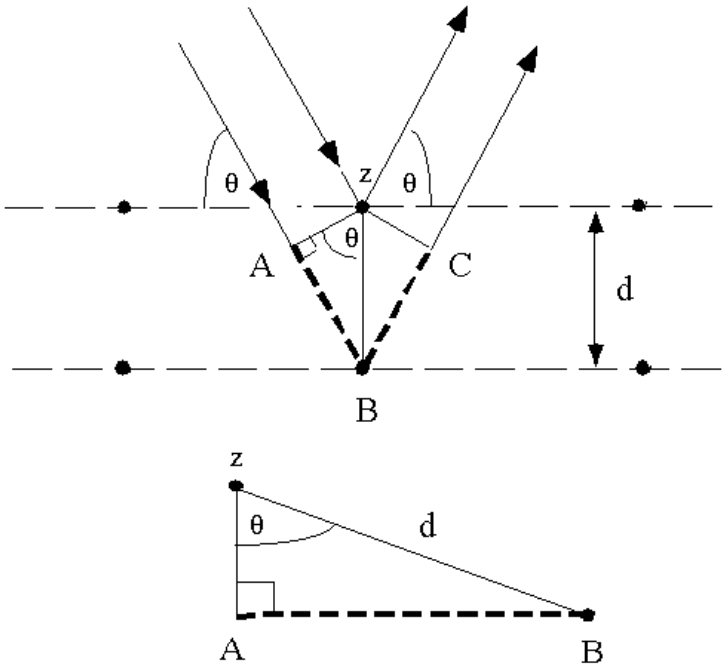


Figure 3: Geometry of Single Crystal X-Ray Reflection

Figure 3 accurately depicts two layers of a single crystal in the (100) plane with the incident x-rays as in that same plane as in our experiment. The two rays are initially in phase and parallel until they interact with and scatter elastically off of their respective atoms in a process known as Rayleigh Scattering. If the two rays both underwent the same elastic scattering process then they will be perfectly reflected and will continue traveling adjacent and parallel to each other. The x-ray that interacted with the second layer must then "travel" the extra distance (AB + BC) to remain in-phase with the upper ray. The extra distance must be an integral multiple of the ray's wavelength:

$$n\lambda = (AB + BC) = 2AB, \text{ where } n = 1, 2, \ldots$$

However, we also know that:

$$AB = d \sin(\theta)$$

Relating these two equations:

$$n\lambda = 2AB$$

$$n\lambda = 2\, d \sin(\theta)$$

Where the last equation is the revered Bragg's Law.

The second to last topic to cover in the theory section is that regarding the Bremsstrahlung experiment. This is the experiment which determined Plank's constant. Bremsstrahlung is a German

term referring to braking radiation or the continuous band of x-ray radiation originating from the x-ray source. The x-ray source used in the experiment is called a Geiger–Müller tube. This device works by heating up a cathode, or a negatively charged electrode of a suitable metal such that thermionic emission of electrons results. The electrons are then accelerated across a potential difference of 30kV or 20kV where they strike the anode or positively charged electrode, which is made of copper. The process of striking the copper electrode gives rise to two distinct classes of x-ray radiation: Bremsstrahlung and Quantum Transition radiation. The Bremsstrahlung radiation is a continuous band of x-rays that result from the continuous deceleration of the electrons when they interact with the copper. The highest energy Bremsstrahlung x-rays will have an energy equal to the energy of the highest possible energy an electron could obtain while accelerating from the cathode to the anode. This maximum energy is either 20,000 eV or 30,000 eV depending on which cavity voltage the tube is set to. The Bremsstrahlung radiation is used for the Plank constant experiment. The known values in this experiment are: (1) the energy of most energetic Bremsstrahlung x-rays, (2) the crystal spacing values [which by the way are determined in the other experiment with knowledge of Plank's constant (Quantum Theory is used to determine the Quantum Transition radiation wavelengths 1.542 and 1.392, and Quantum Theory relies on Plank's constant) … so therefore this second experiment is not a valid verification or determination of Plank's constant, unless a method exists to determine the crystal spacing's in a way that is independent of Plank's constant], (3) The wavelength of the most energetic Bremsstrahlung x-rays (this is found by the knowledge of the crystal spacing and the angle of diffraction of these most energetic x-rays). The infamous Plank constant is related to wavelength and energy via E=hf. Since we know E and f we can determine the constant. This is how Plank's constant is determined. One last critical piece of knowledge is how we determine the angle at which these maximum energy Bremsstrahlung x-rays are striking our detector. One characteristic feature of the Bremsstrahlung x-rays is that the continuum of them forms a Plank distribution. That is the plot of their intensity vs. wavelength resembles a Plank Distribution as shown in Figure 4. This characteristic intensity pattering is what we search for by analyzing the most energetic portion of the diffraction pattern (lowest angles). When we located the intensity pattern in the collected diffraction pattern we are able to fit that portion to a blackbody curve and extrapolate to determine which angel corresponds to the maximum energy.

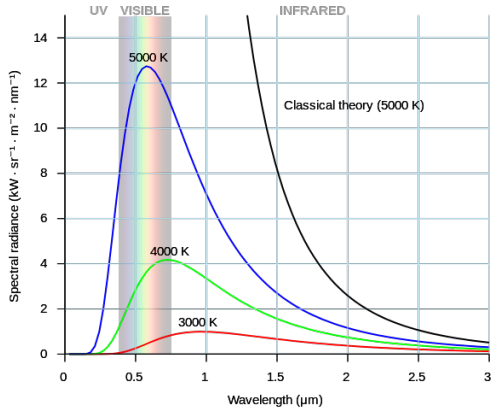


Figure 4: Plank Distribution

The final topic to cover is the determination of the crystal spacing using Bragg diffraction. This experiment utilizes the Quantum Transition x-ray radiation from the Geiger–Müller tube. This

radiation has a much higher intensity than the Bremsstrahlung x-ray radiation. Like the Plank constant experiment, this experiment depends on Bragg's law, but it is also critically dependent on the intensity pattern of the x-ray source. The intensity pattern of the Quantum Transition x-rays from the copper resemble sharp peaks centered about specific wavelengths. Illustrated below in figure 5 is the intensity pattern of both the Bremsstrahlung and Quantum Transition x-rays from our specific copper source. The peaks of the atomic transitions are centered about the wavelengths 0.1392 and 0.1542 nano-meters.

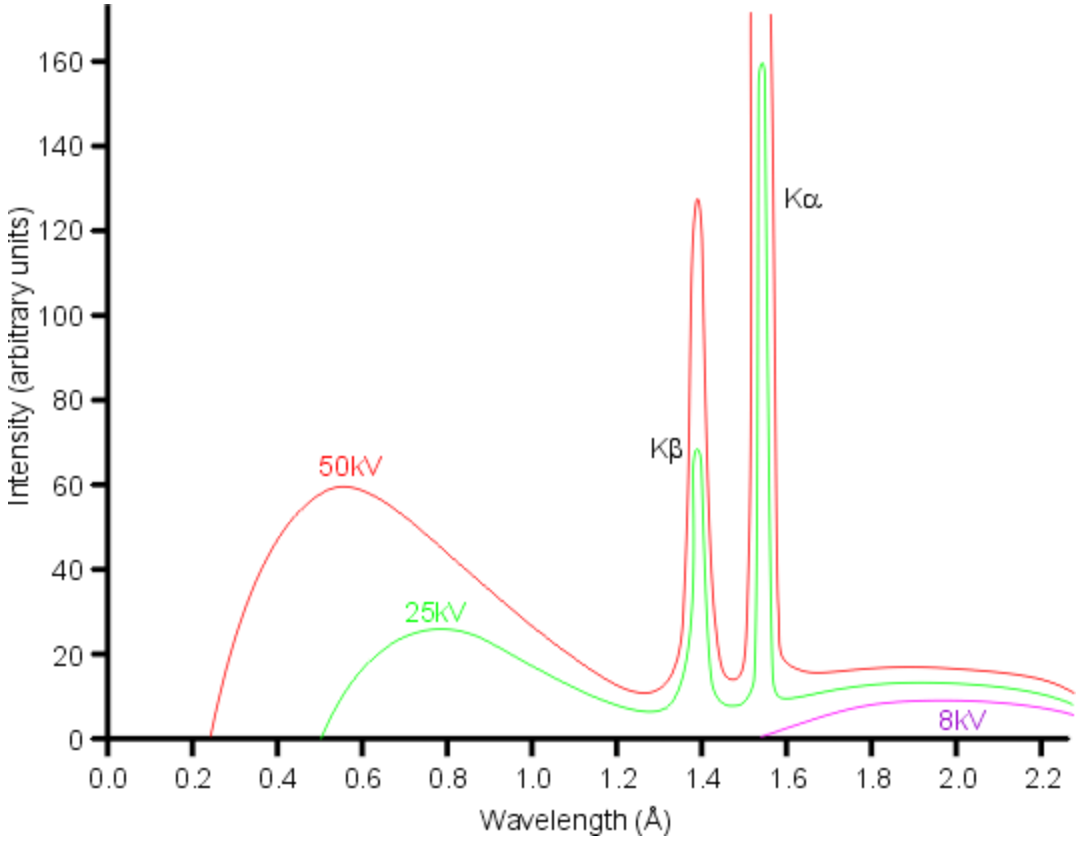


Figure 5: Intensity Pattern of X-Ray Source

The crystal spacing's were deduced by Bragg's Law by knowledge of these specific wavelengths and by knowledge of the diffraction angles which we observed these intensity peaks at. (As a final side note: all of the diffracted x-rays are a result of constructive interference, it is only by way of these variable intensity patterns that we are able to determine what wavelength we are observing and then the angle and Bragg's Law become useful).

Experimental Methods

Below I show a diagram of the experimental apparatus and the experimental device used for data collection.

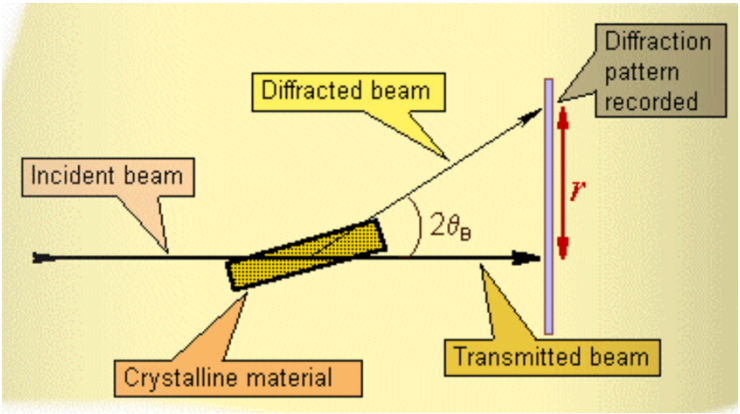


Figure 6: Top Down View of Diffraction

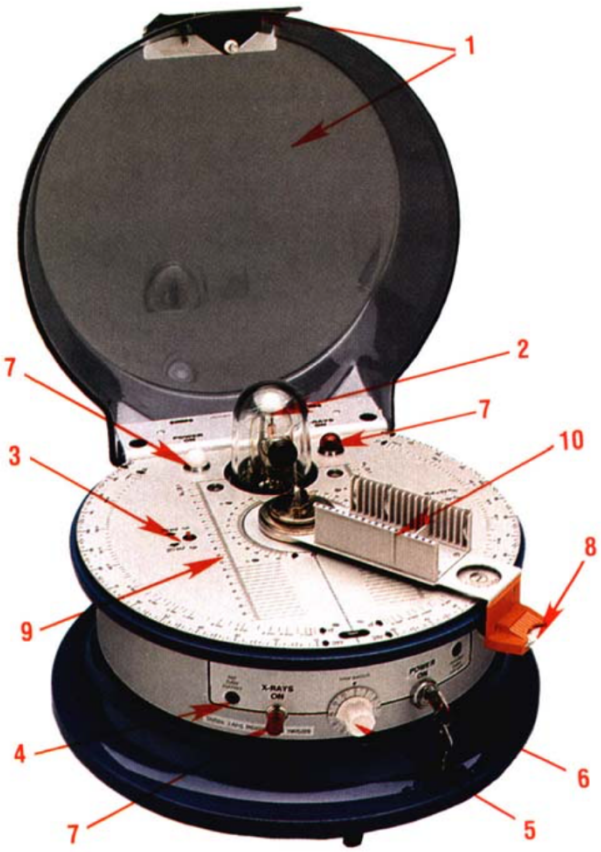


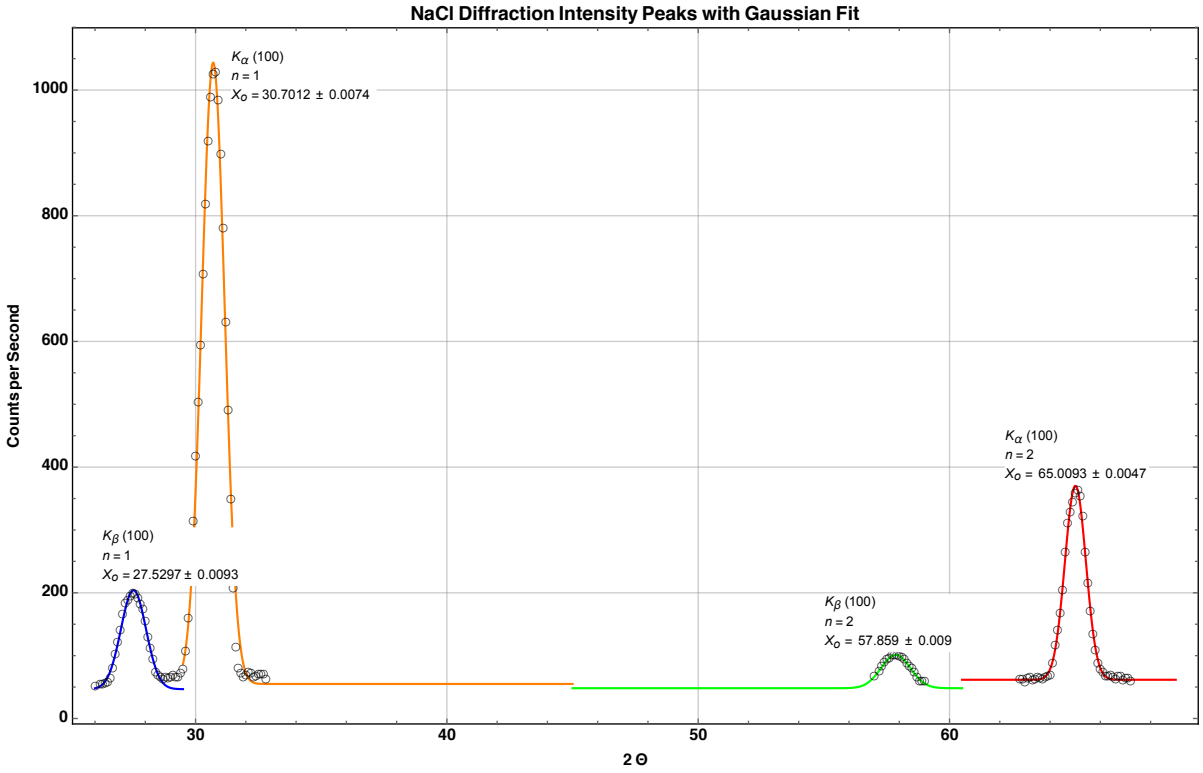
Figure 7: Tel-X-Ometer, Experimental Device

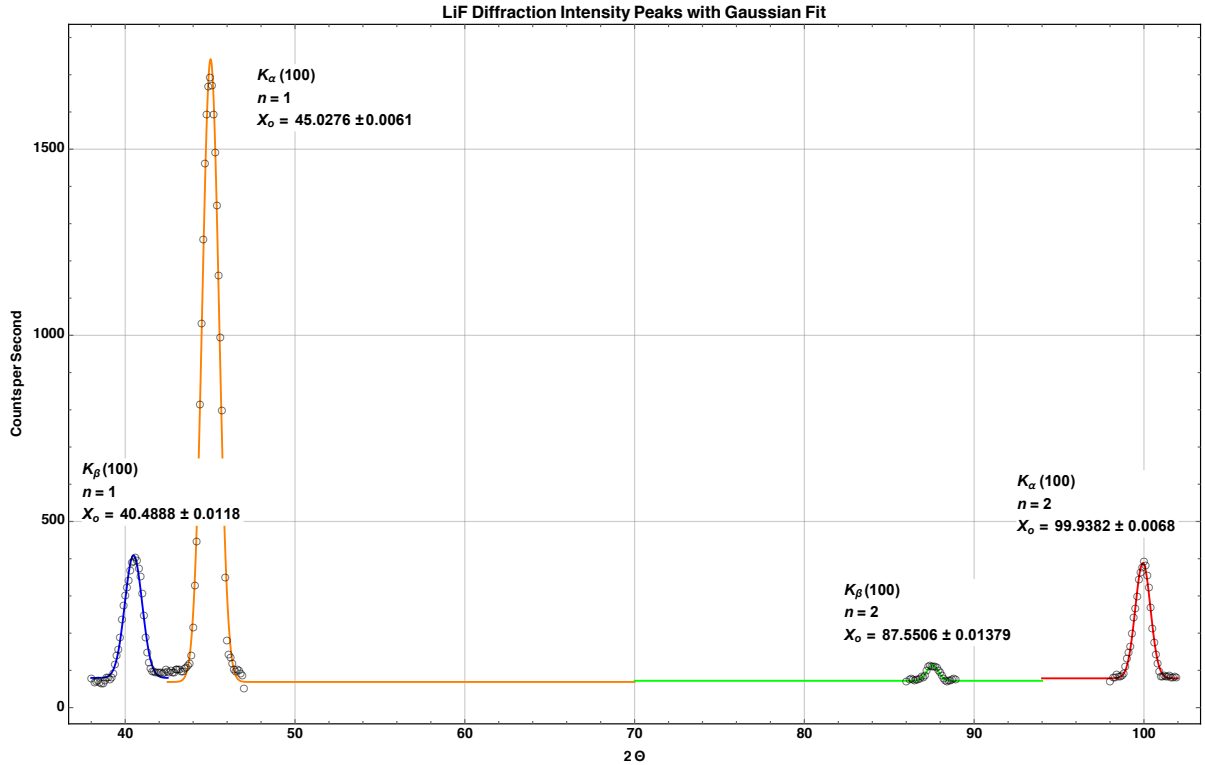
In figure 7, the Tel-X-Ometer is shown. This is the device used for both experiments. Arrow 2 corresponds to the x-ray source which is where the "Incident beam originates from in Figure 6. Arrow 10 corresponds to the position where the detector is placed and the "Diffracted Beam" in Figure 6 is intercepted. The crystal is placed in the very center of the device, where Arrow 9 is pointing in Figure 6.

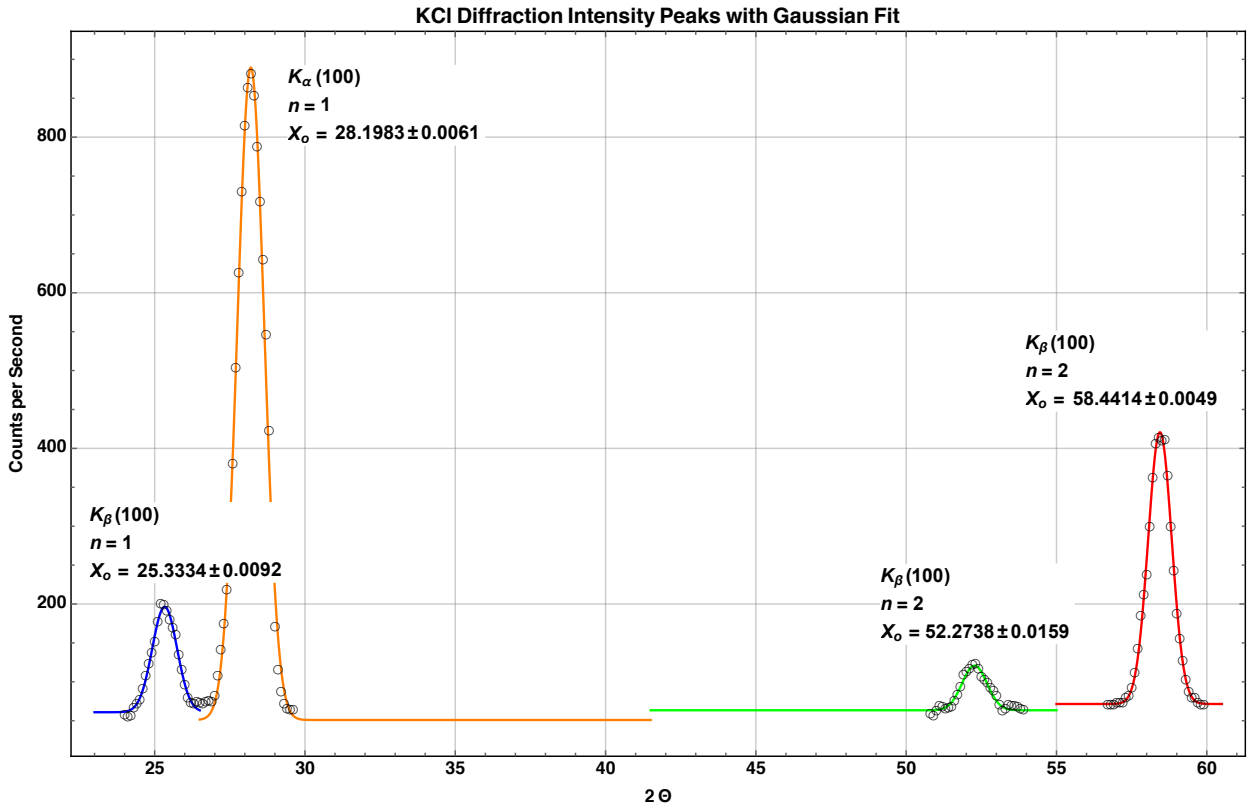
As a general overview of the main steps for data collection. First the crystal is placed inside the mount located in the center of the Tel-X-Ometer. Next detector arm (Arrow 10, Fig. 6) is set to its initial angle by hand. Next, the radiation lid (Arrow 1, Fig. 6) is closed, and the x-ray source is turned on and using a computer the initial and final angles are set and the program is run. The detector collects data in terms of counts per second and saves that information along with the angle information to a text file on the computer.

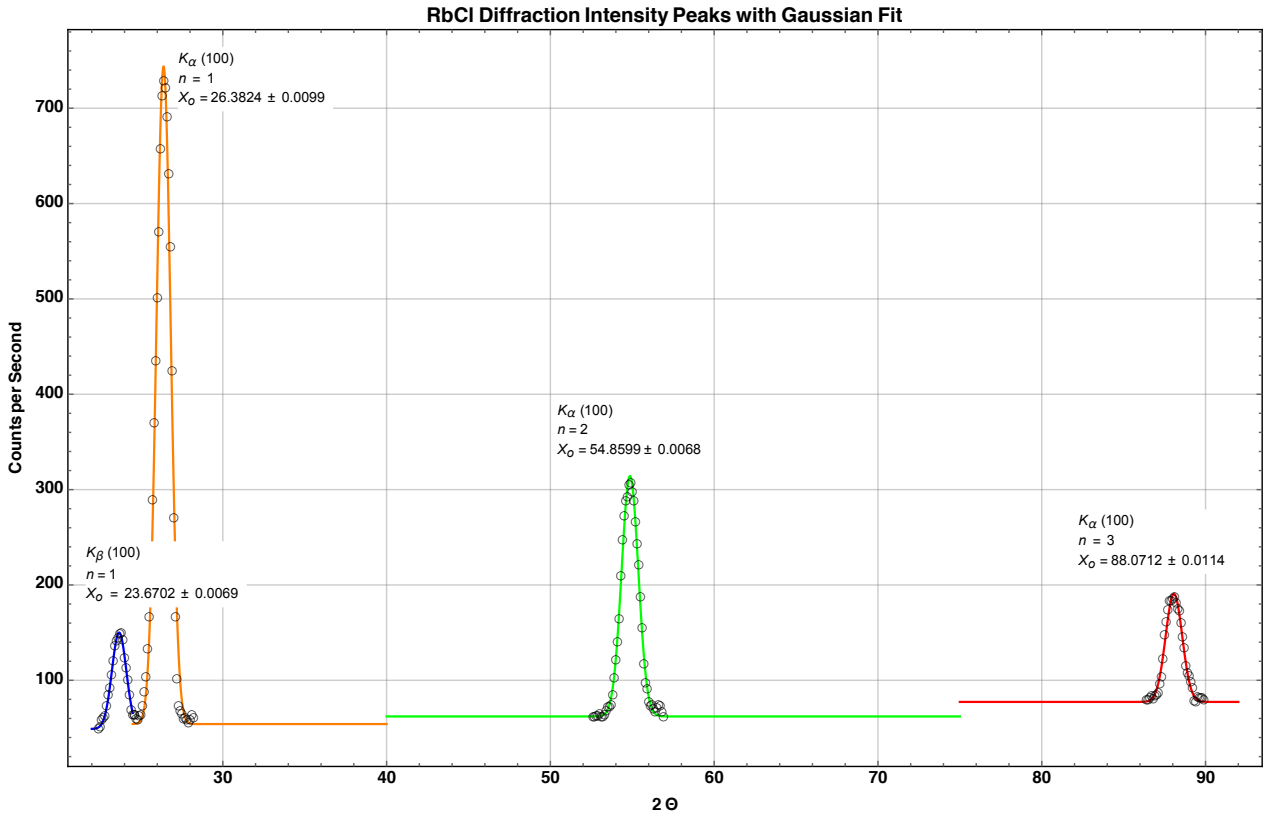
Results, Analysis, and Data

Bragg Experiment:






KCl Diffraction Intensity Peaks with Gaussian Fit
K_α (100)
$n = 1$
$X_o = 28.1983 \pm 0.0061$
K_β (100)
$n = 1$
$X_o = 25.3334 \pm 0.0092$
K_β (100)
$n = 2$
$X_o = 52.2738 \pm 0.0159$
K_β (100)
$n = 2$
$X_o = 58.4414 \pm 0.0049$
Counts per Second
2 Θ


RbCl Diffraction Intensity Peaks with Gaussian Fit
K_α (100)
$n = 1$
$X_o = 26.3824 \pm 0.0099$
K_β (100)
$n = 1$
$X_o = 23.6702 \pm 0.0069$
K_α (100)
$n = 2$
$X_o = 54.8599 \pm 0.0068$
K_α (100)
$n = 3$
$X_o = 88.0712 \pm 0.0114$
Counts per Second
2 Θ

As a quick overview of the above figures. The data is plotted Intensity vs. Degrees. The actual collected data is shown overlaid on top of fitted Gaussian functions. The fits and plots were done in Mathematica. The K-alpha/beta labels represent the wavelength that the peaks correspond to. The values for n represent the excited mode in the crystal. The value of the angle for the center of the peaks is X-not. These values were determined from the Gaussian fit functions in Mathematica. Below I present the calculated values of the crystal spacing using the above values of X-not as the angle in the Bragg Law.

Table 1: Crystal Spacing's

Crystal	True Value (Å)	Measured Mean Value (Å)
LiF	2.005	2.0 ± 0.2
NaCl	2.82	2.8 ± 0.2
KCl	3.14	3.1 ± 0.2
RbCl	3.27	3.3 ± 0.2

Bragg Error Analysis:

The uncertainties: $\delta\lambda = \pm 0.001$Å, this is due to the uncertain lifetime of quantum states resulting in uncertainty in energy and thereby wavelength. $\delta\theta = \pm 1°$, this is due to parallax error; when you are initially setting up the device the initial angle you set it to is uncertain due to parallax. The Bragg equation for crystal spacing is:

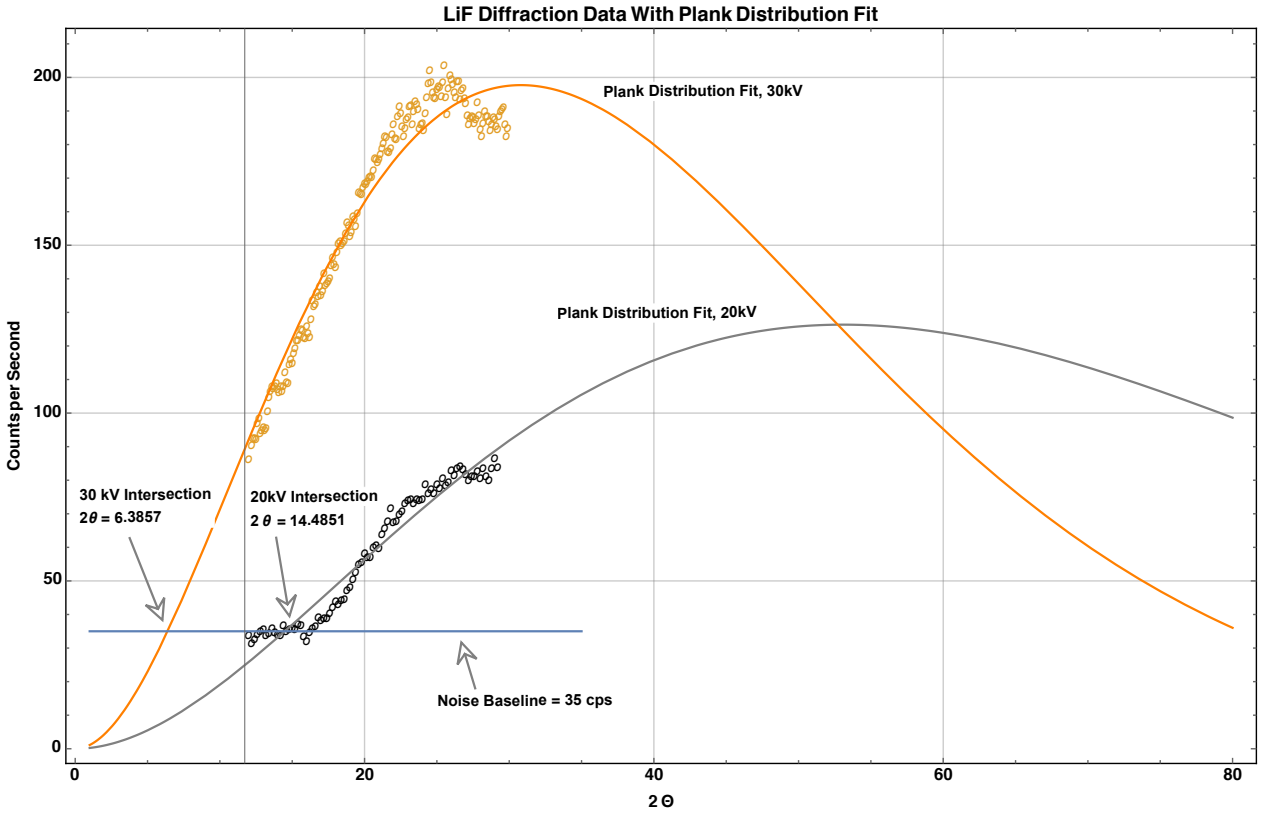
$$d = \frac{n\,\lambda}{2\sin\,\theta}$$

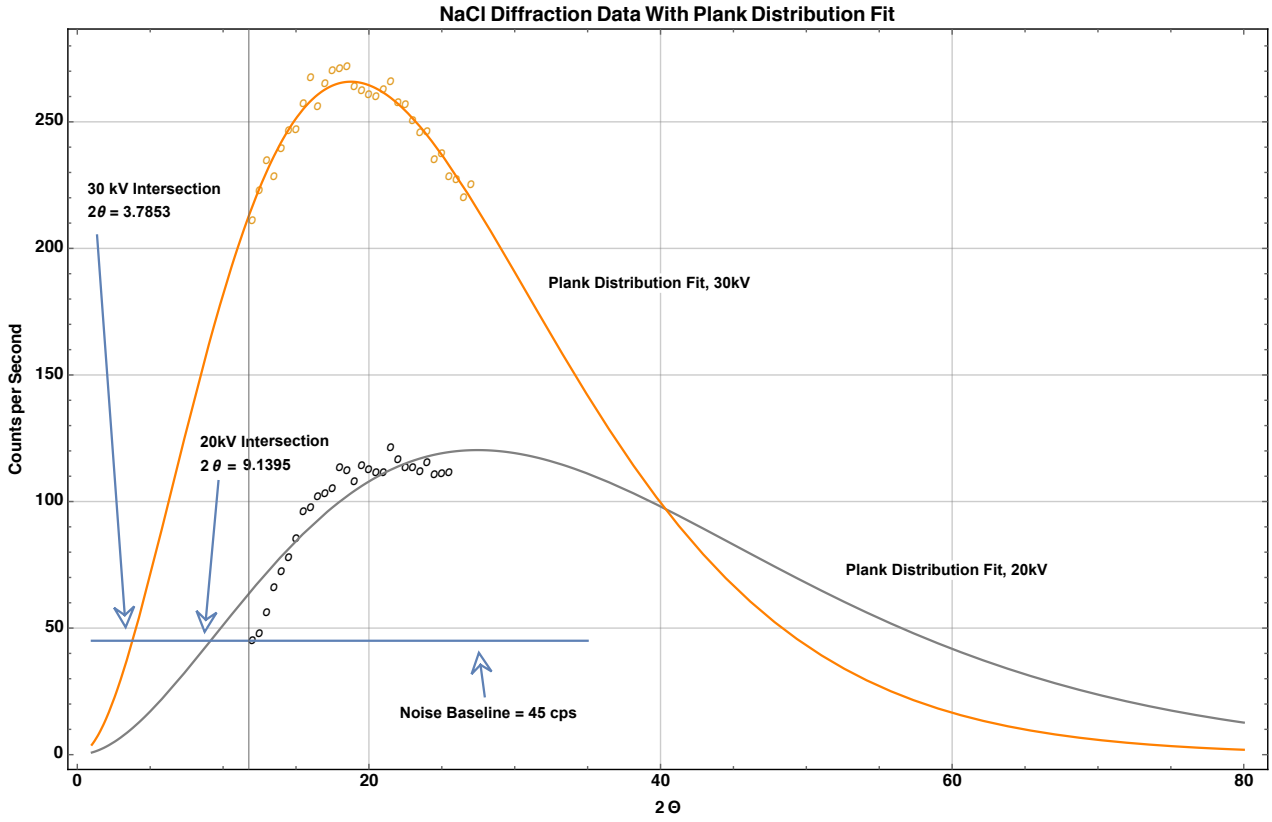
and the error propagation calculation results in:

$$\delta d(n,\lambda,\theta) = \sqrt{\left(\delta\theta\,\frac{1}{2}\,n\lambda\cot(\theta)\csc(\theta)\right)^2 + \left(\delta\lambda\,\frac{1}{2}\,n\csc(\theta)\right)^2}$$

When you consider the range of angles and two possible values of wavelength considered for the experiment, the maximum value you can really obtain for $\delta d(n,\lambda,\theta)$is ~1.9. I have rounded this value to 0.2. I also note that the assumption of $\delta\theta = \pm 1°$ may be an over estimate. I urge the reader to look at the Mathematica notebook titled "Bragg Analysis Overall" for a much more complete look at the data.

Bremsstrahlung experiment:





As a quick overview of the figures. The collected data for each trial is overlaid on top of a fitted Plank Distribution, the fits along with the plots were done in Mathematica. The noise baseline for each plot was taken at the point where the data for the 20kV trial ends. The intersection of the fitted curve with the noise baseline gives the angle of the maximum energy Bremsstrahlung x-rays. This angle along with the corresponding energy is then used to tabulate the value of Plank's constant by the following equation:

$$E_{photon} = h\,f = \frac{h\,c}{\lambda}$$

$$E_{max} = V\,e$$

$$E_{photon} = E_{max}$$

$$h = \frac{V\,e\,\lambda}{c}$$

$$\lambda = \frac{2\,d\,\sin(\theta)}{n}$$

Therefore, Plank's constant is determined by $h = \frac{V\,e\,\lambda\,2\,d\,Sin(\theta)}{c\,n}$

Where V=the voltage, e=electron's charge, d=crystal spacing, c=speed of light, and n=the mode of constructive interference in the diffraction pattern. The overall uncertainty only exists in λ since we are taking d to be a known value and the rest to be constants of the experiment. The calculation of the uncertainty in λ is as follows:

$$\delta\lambda = \frac{2\,d\,Cos(\theta)}{n}\,\delta\theta$$

$$\delta\lambda = \pm\,2d$$

This value of 2d comes from setting everything but 2d equal to 1. This is valid I believe since $\delta\theta$ = 1 and the maximum value of cos(x) = 1 and a typical value for n at low angles is 1. Taking into account this value of uncertainty, below I report the measure values for Plank's constant.

Trial	True Value	Measured Value
LiF 20 kV	6.626	5.392±4.001
LiF 30 kV	6.626	3.573±4.001
NaCl 20 kV	6.626	4.79±5.64
NaCl 30kV	6.626	2.98±5.64
Overall Average	6.626	4.32±5.64

Conclusion

Overall this experiment was enlightening. I learned a tremendous amount on x-ray diffraction, and on data analysis. Particularly using Mathematica to fit experimental data. The results for both experiments I think are good. Particularly for the Bragg experiment where we determined the crystal spacing's I believe our results are quite satisfactory, the primary contribution to the error is the initial experimental setup parallax. Even with this large one degree error however the true values all are included within the uncertainty which is a reassurance that we were able to verify the theory behind Bragg's Law. The second experiment, which as I discussed earlier, really is not an experiment since the analysis relies on the information we are trying to measure, was not as accurate as we hoped it to be. The uncertainty in the value for Plank's constant turned out to be much larger than the value we measured. This however, seems necessary since the true value of Plank's constant is included, in some cases just barely by our uncertainty fluctuation. All in all, I believe this experiment was a tremendous learning process, and I would recommend it to anyone who is curious about understanding the theory and process of x-ray diffraction.