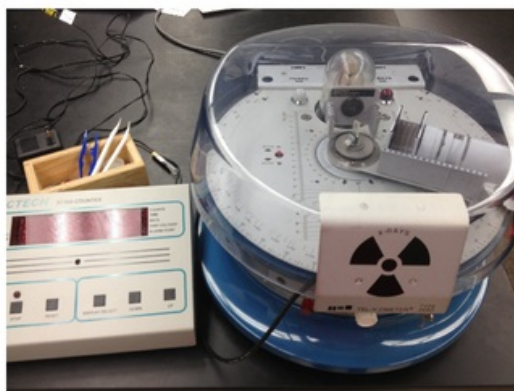


1. PURPOSE

The aim of the experiment is to determine the length of the atomic spacing between the planes of the sodium chloride crystal through the analysis of the spectrum intensity of the X-rays scattered by the surface of the sodium chloride crystal as a function of the scattering angle.

2. EXPERIMENTAL SETUP

The instruments used for this experiment include: Teltron LTC X-ray Spectrometer (Tel-X-Ometer), a Spectech ST360 Counter, a Geiger-Muller Tube, several collimating slits, a sodium chloride crystal, a couple of connecting coaxial cables, and a pair of tweezers.



Spechtch ST360 Counter(left) and Tel-X-Ometer(right)

In the Tel-X-Ometer a beam of high-speed electrons is released from the heated cathode through thermionic emission and an electric potential accelerates them into the copper anode. As the electrons travel towards the metal target two phenomena take place.

First, the electrons encounter electric forces created by the atoms of copper that decelerates them. As it is expected from classical electrodynamics, the process releases a form of radiation called Bremsstrahlung, which is observed as a continuous spectrum. Second, some electrons knock off the electrons of the inner shell (the K-shell in the Bohr model) of the metal target (the copper metal). These holes are rapidly filled by other electrons decaying from higher atomic levels (the L- and M-shells), which cause the emission of x-rays with sharply defined frequencies associated with the difference between the atomic energy levels of these target copper atoms; however, not all the transitions are allowed. This is known as K-shell emission. The outgoing high energy x-rays are emitted from the x-ray tube, which are then narrowed with a collimator and the resulting x-ray beam is allowed to elastically strike the NaCl crystal. The collision is considered elastic since there are no free electrons available to produce Compton scattering, and the energies are too high to undergo Photoelectric effect. The x-ray photons are then diffracted at an angle into a Geiger-Mueller tube, which is essentially a charged cylindrical capacitor. An incoming x-ray photon ionizes the gas in the capacitor and leads to a discharge, which produces a small current pulse that is detected electronically by a counter whose output is linearly proportional to the intensity of the x-rays detected.

The experimental set up is as follows. A 1 mm vertical slit (TEL 582.001) is attached to the X-ray tube window. Similarly a 3 mm vertical slit (TEL562.016) is placed in slot number 13 on the slide carriage and a 1 mm slit (TEL562.015) in slot number 18. These slits serve as collimators, which make the beam of incoming X-ray photons as parallel as possible; this is a required condition for the next set of calculations. Then, the Geiger-Muller tube holder is placed with the locating plates in slots 22 and 26. Next, the slide carriage is slowly

rotated until the cursor gives an accurate zero reading on the 2θ scale and the θ scale, which also reads zero. This step is important since it properly calibrates the scattering angles of the X-rays that will be analyzed. Next, the small NaCl crystal is carefully positioned in its mount with the aid a pair of tweezers.

Afterwards, the output of the Geiger-Muller tube is connected with a coaxial cable to the Spechttech ST360 counter and is set up at 400-420V. The Tel-X-Ometer voltage selector is set at 30kV and the plastic cover is properly closed. Then, its timer is turned to 55 minutes and the main power is turned on with the key. Finally, the red button that turns on the X-rays is pressed and the instruments are ready to begin taking measurements.

The counter timer is set to 10 seconds and the intensity at each angle will be measured from 20° to 90° . The intensity of X-rays is proportional to the number of counts detected. However, there is a considerable amount of noise and fluctuations that will be taken into account later. After locating the peaks a careful and more precise analysis must be done to locate them to a precision of $10'$.

3. DATA

A. Parameters

Wavelength of $K\alpha$: 1.542 Å

Wavelength of $K\beta$: 1.532 Å

B. Experimental Data

The following data will be used to locate the possible neighborhood of spectrum of scattered X-rays intensity peaks.

Degrees	Counts	Degrees	Counts	Degrees	Counts
20°	281	44°	49	68°	91
21°	282	45°	70	69°	73
22°	263	46°	58	70°	78
23°	240	47°	74	71°	86
24°	224	48°	70	72°	72
25°	208	49°	55	73°	76
26°	206	50°	65	74°	67
27°	188	51°	72	75°	79
28°	183	52°	70	76°	79
29°	860	53°	74	77°	72
30°	357	54°	79	78°	76
31°	174	55°	65	79°	86
32°	3084	56°	83	80°	81
33°	869	57°	58	81°	72
34°	125	58°	59	82°	78
35°	107	59°	85	83°	77
36°	93	60°	166	84°	76
37°	102	61°	77	85°	78
38°	83	62°	77	86°	83
39°	82	63°	69	87°	89
40°	80	64°	80	88°	86
41°	83	65°	79	89°	78
42°	72	66°	86	90°	106
43°	77	67°	336		

C. Precise Measurements of Peak Positions

Once four pronounced peaks have been located, a more precise analysis is registered measuring the intensity at a precision of $10'$.

Peak 1 ($K\beta$ Order 1):

$$\left\{ \begin{array}{l} 29^\circ = 808 \\ 29^\circ + 10' = 666 \\ 29^\circ - 10' = 854 \\ 29^\circ - 20' = 753 \end{array} \right.$$

Peak 2 ($K\alpha$ Order 1):

$$\left\{ \begin{array}{l} 32^\circ = 3142 \\ 32^\circ + 10' = 2118 \\ 32^\circ - 10' = 2190 \end{array} \right.$$

Peak 3 ($K\beta$ Order 2):

$$\left\{ \begin{array}{l} 60^\circ = 152 \\ 60^\circ + 10' = 116 \\ 60^\circ - 10' = 175 \\ 60^\circ - 20' = 168 \\ 60^\circ - 30' = 183 \\ 60^\circ - 40' = 190 \\ 60^\circ - 50' = 133 \end{array} \right.$$

Peak 4 ($K\alpha$ Order 2):

$$\left\{ \begin{array}{l} 67^\circ = 367 \\ 67^\circ + 10' = 301 \\ 67^\circ - 10' = 417 \\ 67^\circ - 20' = 496 \\ 67^\circ - 30' = 516 \\ 67^\circ - 40' = 383 \end{array} \right.$$

It is important to point out that several measurements have been taken in the neighborhood of the second diffraction order due to the lower intensities of the diffracted x-rays that need a better treatment in order to avoid misleading results due to the fluctuations of the values. On the other hand, few measurements are taken for the first diffraction order since the peaks are sharp and easier to locate.

4. CALCULATIONS

A. Assumptions

The following assumptions have been made in order to minimize calculations:

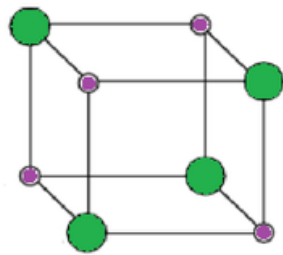
1. The x-rays beams are coherent and in phase with each other.
2. The x-rays scatter elastically from the sodium chloride crystal.
3. The intensity of spectrum registered is mainly obtained from the $K\alpha$ and $K\beta$ rays.
4. The output of the counter is linearly proportional to the intensity of the x-rays.
5. The uncertainty of the registered counts is the square root of the number of counts.
6. The given wavelengths for the $K\alpha$ and $K\beta$ are precise and to a high degree of accuracy.

B. Theoretical Crystalline Structure Approach

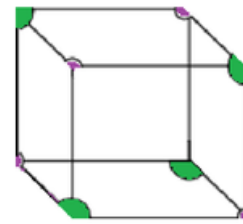
Before attempting to find the length of atomic spacing of Sodium Chloride crystal experimentally, an approximate mathematical calculation based on its structure will be considered. This will provide a rough idea of the order of magnitudes of the desired length that will be compared with the experimental results later.

From knowledge of the crystalline structure of NaCl, it can be reasonably assumed that the atomic spacing between the atomic planes is equal to the distance between the atoms of the crystals itself; namely the distance between Na^+ and Cl^- ions. This comes from the fact that the arrangement of the ions of NaCl is cubical.

Now, let the larger green spheres represent Cl^- ions and the smaller purple spheres represent Na^+ ions. From the NaCl crystal, consider the smallest possible enclosed Sodium Chloride structure represented as a simple cube unit with either a Sodium or Chlorine ion at each vertex. Such a structure will have eight atoms in total, but more importantly it would be composed of four NaCl molecules, and the length of its edges is the length of the atomic spacing.



NaCl Structure



NaCl Simple Cube

However, the fraction of the NaCl ions that are actually inside the enclosed cube is half of the NaCl ions since each corner contains an octant of an atom. Therefore, the equation for the actual mass of one unit cell of a Sodium Chloride crystal is the following:

$$\text{mass / unitcell} = \frac{1}{2}[(\text{Na}^+) + (\text{Cl}^-)] \quad \text{mass / unitcell} = \frac{1}{2} \left[58.44 \frac{\text{g}}{\text{mol}} \right]$$

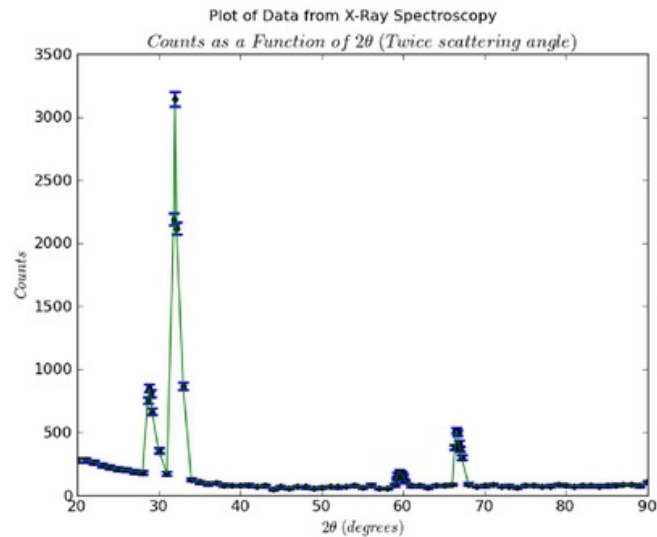
$$\text{mass / unitcell} = 29.22 \frac{\text{g}}{\text{mol}}$$

Then the atomic spacing length can be calculated as shown:

$$d = \sqrt[3]{\frac{m}{\rho}} \quad d = \sqrt[3]{\frac{29.22}{(2.16)(6.022 \times 10^{23})}} \left[\sqrt[3]{\frac{\text{g}}{\text{mol}} \cdot \frac{\text{cm}^3}{\text{g}} \cdot \text{mol}} \right] = 2.821 \text{ \AA}$$

C. Plotting of the Experimental Data

The next plot depicts the position of the peaks as a function of twice the scattering angle. The uncertainty has been taken to be the square root of the number of counts due to fluctuations and noise.

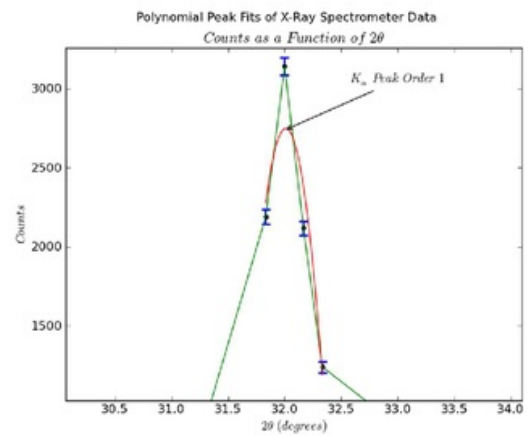
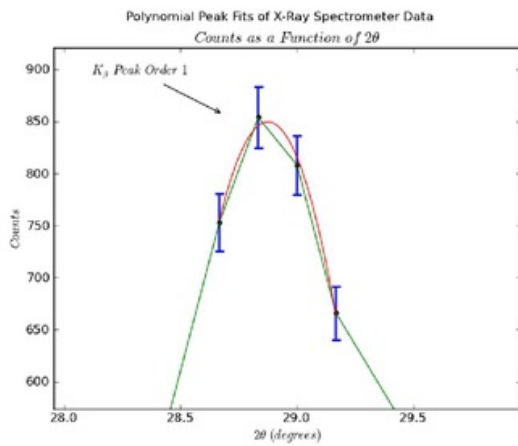


It can be inferred from the graph that only two different x-ray wavelengths are present and not four as might be thought. The reasoning behind this is that the first two observable peaks' intensities in the graph are nearly proportional to the last two, indicating that these correspond to the next diffraction order of the same wavelengths.

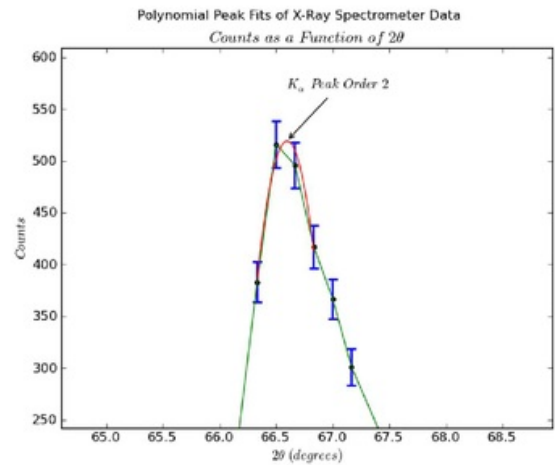
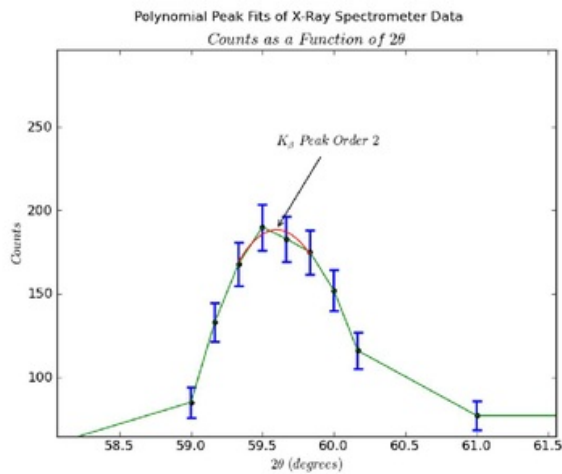
D. Polynomial Fitting of $K\alpha$ and $K\beta$ Peaks

In order to obtain a more accurate measurement of the position of peaks, parabolas have been fitted in the peak's neighborhood as shown.

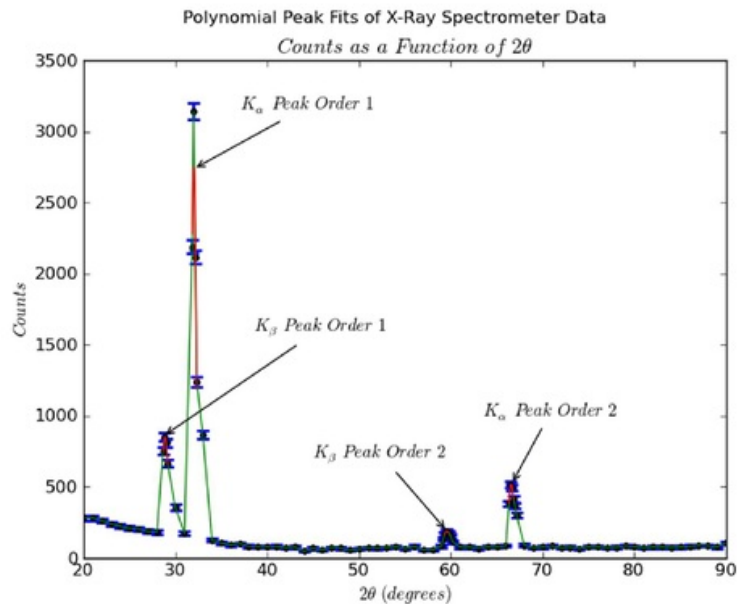
1st Order Polynomial Fit



2nd Order Polynomial Fit



The next plot summarizes the information about the peaks and its corresponding diffraction order. The angles shown correspond to the values at which the peaks occur.



The value at which the maxima occur is such that the derivative of the quadratic equation at that point is equal to zero. Therefore;

$$\frac{d}{d(2\theta)}(a(2\theta)^2 + b(2\theta) + c) = 0 \quad 2a(2\theta) + b = 0 \quad 2\theta = \frac{-b}{2a}$$

Using the equations mentioned above, the following values for the position (2θ) of maxima are obtained to 4 significant figures:

$$K_{(n=1)}\alpha = 32.01^\circ$$

$$K_{(n=2)}\alpha = 66.60^\circ$$

$$K_{(n=1)}\beta = 28.87$$

$$K_{(n=2)}\beta = 59.60^\circ$$

It might have been assumed that the first two peaks correspond to diffraction order one. However, this assumption might be incorrect since the range of angle measurement is from 20° to 90° and the first diffractions could have occurred at less than 20° . Let the following explanation be presented:

The diffraction order is proportional to the sine of the scattering angle.

$$\frac{n}{n+1} = \frac{\sin \theta_n}{\sin \theta_{n+1}}$$

Solving for n and substituting the values previously acquired. Remark: the angles obtained above are twice the angle that must be used. Thus:

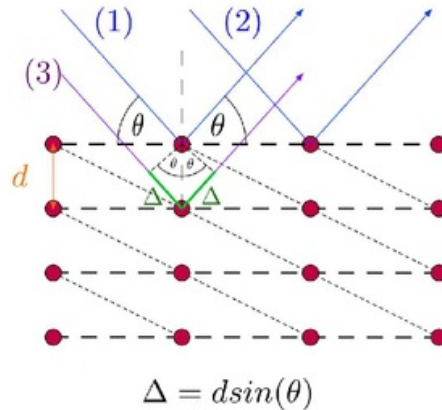
$$n = \frac{\sin \theta_n}{\sin \theta_{n+1} - \sin \theta_n}$$

$$n = \frac{\sin 16^\circ}{\sin 33.3^\circ - \sin 16^\circ} = 1.008 \qquad n = \frac{\sin 14.4^\circ}{\sin 29.8^\circ - \sin 14.4^\circ} = 1.002$$

This clearly shows that the first diffraction order observed is indeed of order one.

E. Calculations of Spacing from X-ray Peaks

The locations of the intensity peaks in the plots represent the positions where constructive interference takes place. The next graph sketches the concept that will be conveyed to calculate the length of atomic spacing (d):



As it is observed the path difference between two consecutive X-ray beams is:

$$2\Delta = 2d \sin \theta$$

Constructive interference occurs when the path difference is equal to an integer multiple of the wavelength of the incoming beam resulting in the following equation, known as Bragg's condition:

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

Then, the order of diffraction will be plotted as a function of the scattering angle and a line fit will be properly adjusted for $K\alpha$ and $K\beta$ individually. The slope of the line will be the ratio of length spacing to wavelength of the beam (known). Then, d should be found as follows:

$$\underbrace{n}_{y} = \frac{2d}{\underbrace{\lambda}_{m}} \underbrace{\sin \theta}_{x} \qquad \frac{2d}{\lambda} = m(\text{slope}) \qquad d = \frac{m\lambda}{2}$$

F. Calculation of Uncertainty in the Scattering Angle for Constructive Interference

There are two sources of uncertainty for the scattering angle of constructive interference; one of them is associated with the resolution of the instrument and the ability to resolve the value, which in this case will be considered to be about $\pm 10^\circ$. The other source of error is related to the uncertainty of the position of the maxima given by the quadratic fitting. This uncertainty must be calculated from the variances and covariances of the coefficients of the parabolas.

From the equation for θ , the value of the uncertainty follows:

$$\theta = -\frac{b}{4a} \quad \sigma_\theta = \left(\left(\frac{\partial\theta}{\partial a} \sigma_a \right)^2 + \left(\frac{\partial\theta}{\partial b} \sigma_b \right)^2 + 2 \frac{\partial\theta}{\partial a} \frac{\partial\theta}{\partial b} \sigma_{ab} \right)^{1/2}$$

Where σ_a , σ_b , and σ_{ab} are the variance of a , the variance of b and the covariance of a and b respectively.

Then taking the partials with respect to a and b , and simplifying:

$$\frac{\partial\theta}{\partial a} = \frac{b}{4a^2} \quad \frac{\partial\theta}{\partial b} = -\frac{1}{4a}$$

$$\sigma_\theta = \left(\left(\frac{b}{4a^2} \sigma_a \right)^2 + \left(\frac{1}{4a} \sigma_b \right)^2 - 2 \frac{b}{4a^2} \frac{1}{4a} \sigma_{ab} \right) \quad \sigma_\theta = \frac{b}{4a} \left(\left(\frac{\sigma_a}{a} \right)^2 + \left(\frac{\sigma_b}{b} \right)^2 - 2 \frac{\sigma_{ab}}{ab} \right)^{1/2}$$

It should be emphasized that in this case the contribution of the covariances plays an important role in the uncertainty calculations; this can be seen in the covariance matrix for the quadratic fitting.

$$\text{cov}(K - \beta - 1) = \begin{pmatrix} 1.75e+11 & -1.21e+10 & 2.09e+8 \\ -1.21e+10 & \mathbf{8.37e+8} & \mathbf{-1.45e+7} \\ 2.09e+8 & \mathbf{-1.45e+7} & \mathbf{2.50e+5} \end{pmatrix}$$

$$\text{cov}(K - \alpha - 1) = \begin{pmatrix} 7.21e+11 & -4.49e+10 & 7.00e+8 \\ -4.49e+10 & \mathbf{2.80e+9} & \mathbf{-4.36e+7} \\ 7.00e+8 & \mathbf{-4.36e+7} & \mathbf{6.80e+5} \end{pmatrix}$$

$$\text{cov}(K - \beta - 2) = \begin{pmatrix} 7.29e+11 & -2.45e+10 & 2.05e+8 \\ -2.45e+10 & \mathbf{8.20e+8} & \mathbf{-6.89e+6} \\ 2.05e+8 & \mathbf{-6.89e+6} & \mathbf{5.78e+4} \end{pmatrix}$$

$$\text{cov}(K - \alpha - 2) = \begin{pmatrix} 2.88e+12 & -8.66e+10 & 6.51e+8 \\ -8.66e+10 & \mathbf{2.60e+9} & \mathbf{-1.95e+7} \\ 6.51e+8 & \mathbf{-1.95e+7} & \mathbf{1.47e+5} \end{pmatrix}$$

The previous equations give the uncertainties for the position of each peak from the parabola fittings:

$$\sigma_{K_{(n=1)}\alpha} = \pm 1.7'$$

$$\sigma_{K_{(n=2)}\alpha} = \pm 0.4'$$

$$\sigma_{K_{(n=1)}\beta} = \pm 0.2'$$

$$\sigma_{K_{(n=2)}\beta} = \pm 0.9'$$

As can be observed these uncertainties are small compared to those obtained from the experimental measurements ($\pm 10'$), except perhaps for $\sigma_{K_{(n=1)}\alpha}$. The final errors are therefore;

$$\sigma_{K_{(n=1)}\alpha} = \pm 11.7'$$

$$\sigma_{K_{(n=2)}\alpha} = \pm 10.4'$$

$$\sigma_{K_{(n=1)}\beta} = \pm 10.2'$$

$$\sigma_{K_{(n=2)}\beta} = \pm 10.9'$$

G. Calculation of Uncertainty in the Slope of the Linear Fit

The value of the slope is calculated by the change in order of diffraction over the change of sine of the scattering angle:

$$m = \frac{1}{\sin \theta_2 - \sin \theta_1}$$

Then, the propagation error is calculated as shown:

$$\frac{\partial m}{\partial \theta_2} = \frac{\cos \theta_2}{(\sin \theta_2 - \sin \theta_1)^2} \qquad \frac{\partial m}{\partial \theta_1} = \frac{-\cos \theta_1}{(\sin \theta_2 - \sin \theta_1)^2}$$

$$\sigma_m = \frac{\sqrt{(\cos \theta_2 \sigma_{\theta_2})^2 + (\cos \theta_1 \sigma_{\theta_1})^2}}{(\sin \theta_2 - \sin \theta_1)^2}$$

After plugging the values for each set of data:

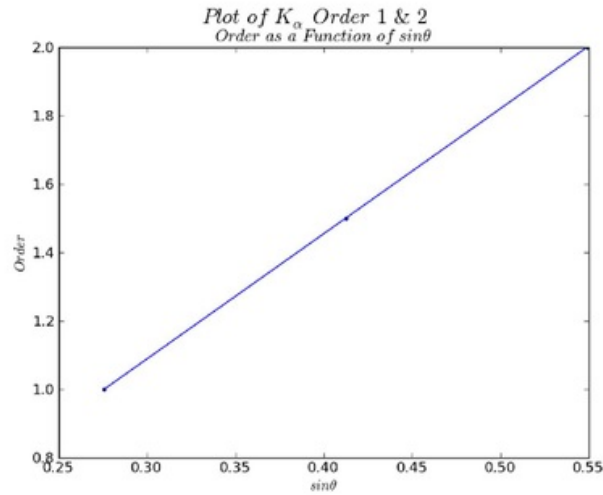
The absolute uncertainty in the slope evaluated for K-alpha is 0.055

The absolute uncertainty in the slope evaluated for K-beta is 0.067

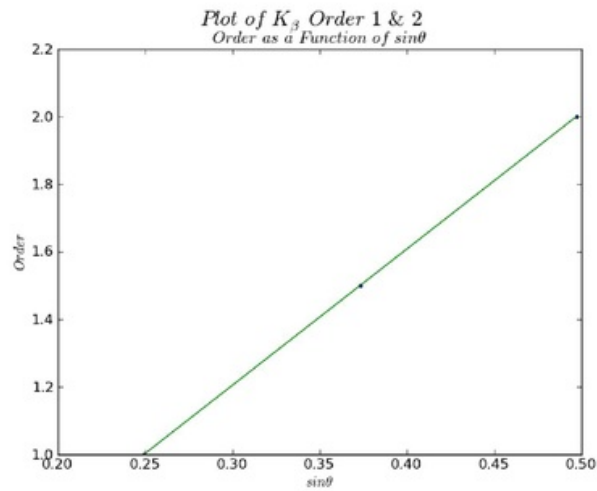
The largest contribution of uncertainty is due to the constraint and limitations in the precision of the instrumental measurement rather than the fitting itself.

5. RESULTS

The next plots show the linear fit for each x-ray wavelength and their corresponding slope and uncertainty:



Slope of linear fit: 3.659 ± 0.055



Slope of linear fit: 4.038 ± 0.069

The corresponding relative uncertainty in the slope obtained for each wavelength is 1.50% and 1.71% for K_{α} and K_{β} respectively.

Finally, applying the calculations previously explained the resulting atomic spacing length from the $K\alpha$ and $K\beta$ plots are given by:

$$\begin{aligned}d_{K\alpha} &= \frac{m\lambda}{2} & d_{K\beta} &= \frac{m\lambda}{2} \\d_{K\alpha} &= \frac{(3.659)(1.542\text{\AA})}{2} & d_{K\beta} &= \frac{(4.039)(1.392\text{\AA})}{2} \\d_{K\alpha} &= 2.821 \pm 0.042\text{\AA} & d_{K\beta} &= 2.810 \pm 0.048\text{\AA}\end{aligned}$$

The average is the final result for the atomic spacing length:

$$\begin{aligned}d_{avg} &= \frac{2.821\text{\AA} + 2.810\text{\AA}}{2} \\d_{avg} &= 2.816 \pm 0.045\text{\AA}\end{aligned}$$

6. CONCLUSIONS

The results of the experiment show that both the calculation of the crystalline structure and the experimental results, with the aid of Bragg's condition, lead to the very close values for the length of the atomic spacing for sodium chloride $2.816 \pm 0.045 \text{ \AA}$ and 2.821 \AA respectively, compared to the current accepted value of 2.8201 \AA . This indicates that the assumptions of crystalline structure are correct and that the ionic arrangement of NaCl is indeed geometrically cubical. The results also imply that there has been a change in the size of the NaCl ions from their corresponding atoms, since the Van der Waals radius of Sodium is 227 pm and 175 pm for Chlorine, which will make an atomic spacing of 4.02 \AA . This is expected from Bohr's atomic model and theory of bonding.

Another important consequence of the results is that x-ray spectroscopy should be considered as a reliable method to measure the spacing between atoms (or ions) in a crystal, and it may be used to analyze more complex structures as well. Furthermore, this method can be utilized to identify elements from the corresponding constructive scattering angle if the wavelength of characteristic x-rays is known. On the other hand, if the atomic spacing is known, the wavelength of characteristic x-rays from the different materials can be obtained. This will give insight regarding the x-ray K-shell emission; hence, in the interactions between high Z elements and high-energy photons.

Regarding the uncertainties, it is important to mention that more measurements should have been taken in the neighborhood of the peaks in order to attain a more accurate quadratic fit. It would have been interesting to also measure a longer range of scattering angles to observe the third order diffraction, which could help for the line fitting of diffraction order as a function of the angle. However, a more precise instrument would also be required in order to conduct careful measurements of the intensities of higher diffraction orders. Finally, it has been observed that the largest uncertainty comes from the resolution of the instrument and the ability of the operator.