

X-Ray Spectroscopy

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The aim of this experiment was to use X-ray spectroscopy to determine: the properties of the crystal structure of NaCl and Si, Planck's constant, and the Rydberg constant. From the X-ray diffraction patterns produced, the peaks were observed and a graph was plotted using the equation $n\lambda = 2d \sin \theta$ to determine the interplanar spacing for each crystal. For NaCl: $d = 2.82 \pm 0.018 \text{ \AA}$, $a = 5.65 \pm 0.061 \text{ \AA}$ and $\rho = 2.15 \pm 0.070 \text{ g/cm}^3$. These values were within 0.5% of accepted values. For Si $d = 3.16 \pm 0.030 \text{ \AA}$, $a = 5.48 \pm 0.052 \text{ \AA}$ and $\rho = 2.26 \pm 0.065 \text{ g/cm}^3$. These values were within 3.0% of the accepted values. To determine the Rydberg constant, filters of different elements were used on the X-ray tube and the absorption spectra were compared to the NaCl spectrum. A graph was plotted using the equation $\frac{1}{\sqrt{\lambda}} = \sqrt{R}(Z - \sigma)$. The Rydberg constant was found to be $11820000 \pm 860000 \text{ m}^{-1}$, this value was within 7.76% of the accepted value. To determine Planck's constant, the voltage of the X-ray apparatus was varied, and the minimum of each Bremsstrahlung continuum of NaCl was recorded. The relationship $\lambda_{\min} = \frac{hc}{eV}$ was used to plot a graph, from which Planck's constant was found to be $(6.12 \pm 0.105) \times 10^{-34} \text{ J Hz}^{-1}$, which is within 6.9% of the accepted value.

INTRODUCTION

This experiment is an exercise in utilising X-ray spectroscopy in many different ways to determine fundamental constants and investigate the properties of crystal structures. X-rays have a very short wave length at 0.1 to 100 \AA . This means that they can interact with matter at the atomic scale. This experiment is so important as its a way of taking advantage of this property to examine the microscopic properties of matter we otherwise couldn't. In 1901 Wilhelm Roentgen was awarded a Nobel Prize discovering X-rays [1]. In 1913 during the early stages of X-ray spectroscopy W.L. Bragg conducted experiments to understand how X-rays interacted with crystalline structures. His aim was to work out information about the atomic structure of materials by studying how the crystals scattered X-rays [2]. He observed how X-rays were diffracted by planes of atoms within the crystal, which was used to determine the spacing between atomic planes and reveal the crystal structure. During these experiments Bragg's law was derived $n\lambda = 2d \sin \theta$, where d refers to the interplanar spacing in a crystal lattice. From 1913-1914, an English physicist named Henry Moseley was able to establish a relationship between the frequencies of emitted by elements and their atomic number. Before Moseley's work, elements on the periodic table were ordered based on their atomic weights. Moseley's research provided a more accurate way of ordering the periodic table, that being based on atomic number, and it was observed that the reordering the elements more accurately reflected their chemical properties. Moseley's work supported Bohr's model of atomic structure as it established that atomic number corresponds to number of protons in the nucleus [3]. Moseley's law can be expressed as $\sqrt{\nu} = K(Z - \sigma)$ where ν is the frequency of the x-ray and Z is the atomic number of the element

THEORY

X-ray Production

Electrons are produced at the cathode filament through thermionic emission. The electrons are then accelerated by applying a voltage between the anode and the cathode. The voltage is known as the kilo-voltage peak (kVp). It produces a strong negative charge in the filament that forces electrons across the x-ray tube to the anode. The electrons slam into the anode of the x-ray tube, when they are decelerated and the lost energy is released as x-rays. The number of x-rays released is determined by the tube current and increasing the kVp increases the energy of the x-rays. Increasing kVp may also increase the number of electrons as high energy electrons get converted to x-rays.

Theory of X-ray diffraction

When x-rays are directed at a crystalline substance, they are scattered by the atoms in the crystal. The scattered waves interfere with each other, and under certain conditions, constructive interference occurs. This produces a diffraction pattern, where the position of the peaks depend on the wavelength of the x-rays and the spacing of the lattice planes. This means that the intensity and shape of the pattern provides information about the structure of the crystal.

Bragg's law can be used alongside the diffraction pattern of a crystal to determine the interplanar spacing. The law states that when the x-ray is incident onto a crystal surface, its angle of incidence θ , will reflect back with the same angle of scattering, θ . Furthermore, when the path difference is equal to a whole number of wavelengths, constructive interference will occur. This relationship can be shown by the equation

$$n\lambda = 2d \sin \theta \quad (1)$$

where n is the order of diffraction, λ is the wavelength of

the x-ray, d is the interplanar spacing and θ is the angle of incidence.

Theory of X-ray Absorption

An x-ray will strike a material and the atom can absorb the x-ray. When the electron of an atom absorbs an X-ray, if the X-ray has enough energy the electron will be excited and leave the atom. This creates vacancies and electrons from higher energy levels will fall into the vacancies and release X-rays in the process. [4] The energy of the emitted X-ray depends on the difference in energy between the electron shells involved. This means that we can gain information about the atomic structure by studying the X-ray spectrum.

Moseley's law describes the relationship between the frequency of the X-ray and the atomic number of the element.

$$\sqrt{\nu} = K(Z - \sigma) \quad (2)$$

where ν is the frequency of the X-ray, K is a constant that relates to the Rydberg constant R , Z is the atomic number of the element and σ is the shielding constant. The Rydberg constant represents the limit of the highest frequency of light that can be emitted or absorbed by an electron in a hydrogen atom as it transitions between energy levels. The shielding constant represents the extent to which the nuclear charge experienced by an electron in the outer shell is reduced due to the presence of lower energy shells.

Crystal Structure

It is important to understand what properties of a crystal we are trying to work out using X-ray spectroscopy. The first part of the experiment focuses on the lattice constant of a crystal. The lattice constant represents the length of one edge of the cubic unit cell. The unit cell is the smallest repeating structural unit of a crystal lattice. The crystal structure represents the specific arrangement of atoms within a unit cell. NaCl is an example of a face centred cubic and Si is a diamond cubic. These structures can be seen in Fig 1 and 2.

The crystal structure of a substance can provide insights into many aspects such as density, packing efficiency, diffraction patterns and super conductivity. In this experiment we will aim to use the lattice constant to calculate the density of the material. Another factor when considering crystal structure are miller indices and lattice planes. Miller indices are used to describe the orientation of planes in a crystal lattice. They are related to the lattice constant by the following relationship:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3)$$

A quantity called the structure factor can be used to determine the intensity of diffraction from a set of lattice planes. For a

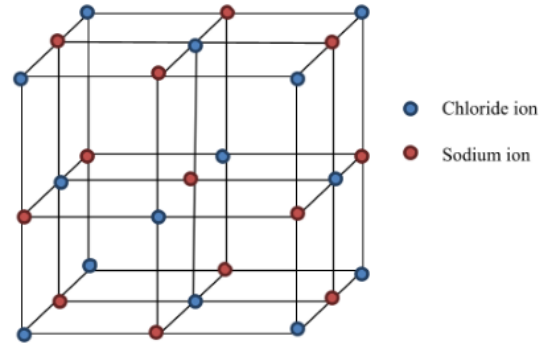


FIG. 1. NaCl, face centred cubic

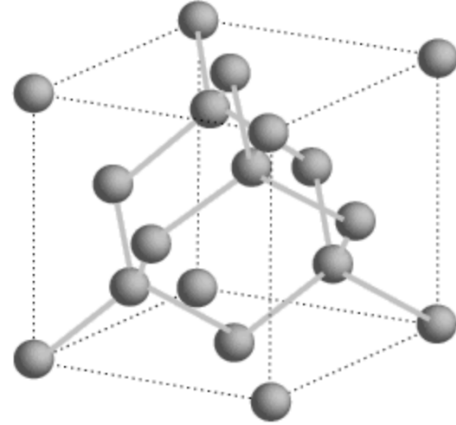


FIG. 2. Si, diamond cubic [5]

diamond cubic structure the formula is

$$F_{hkl} = f \left[1 + e^{i\frac{\pi}{2}(h+k+l)} \right] \quad (4)$$

When calculating the structure factor for Silicon with miller indices (1, 1, 1) it can be seen that that F_{111} is equal to 0 for the $n = 2$ peak. This happens because of destructive interference due to the structure of Silicon.

EXPERIMENTAL METHODS

Determination of the lattice constants of NaCl and Si

The x-ray apparatus was set to 35kv, 1mA and $\Delta T = 5$ and the NaCl was placed on the stage. A diagram of the apparatus can be seen in Fig 3. The machine was started and x-rays were fired at the NaCl at different angles, each for ΔT seconds. The data was logged to the computer and the x-ray diffraction pattern was produced as seen in Fig 4. The same process was repeated for Si and the diffraction pattern seen in fig 5 was produced. An observation is that the characteristic peaks come in pairs. This is because each one corresponds to a K_α and K_β transition. These represent specific electron transitions from

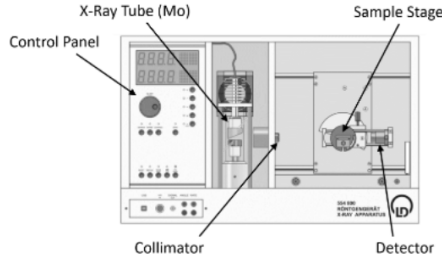
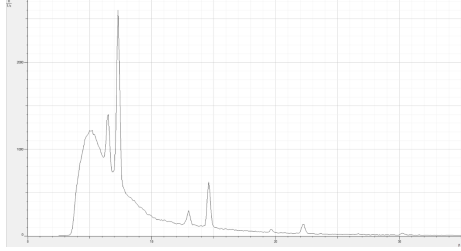


FIG. 3. The Leybold X-Ray Apparatus

FIG. 4. NaCl Spectrum of θ against counts

an L to a K shell or an M to a K shell. As we can see, the $n = 2$ peak is missing for Silicon as predicted from theory.

Attenuation Spectra

The goal of this part of the experiment was to calculate the Rydberg constant by using equation 2. This could be achieved by locating a characteristic drop before a peak as seen in Fig 6. Filter caps were placed on the collimator and the machine was turned on. As before, the machine fired x-rays at different angles and the data was logged to the computer. The elements of the filter caps used were: Indium, Niobium, Zirconium, Silver and Molybdenum. From these scans, x-ray absorption spectra were produced.

Planck's Constant

The bremsstrahlung continuum in the emission spectrum of an x-ray tube is 0 at characteristic wavelength λ_{min} . At this value, we are able to use the relationship $\lambda_{min} = \frac{hc}{eV}$ to calculate Planck's constant. To do this, the x-ray apparatus was turned on with NaCl on the stage. It was ran until an increase in counts was observed, as this is past the point at which λ_{min} occurs. The interplanar spacing calculated from part 1 of the experiment was used to convert from θ to λ_{min} . This was repeated at different voltages so a graph of λ_{min} against $\frac{hc}{eV}$ could be plotted. The gradient of this graph would give Planck's constant.

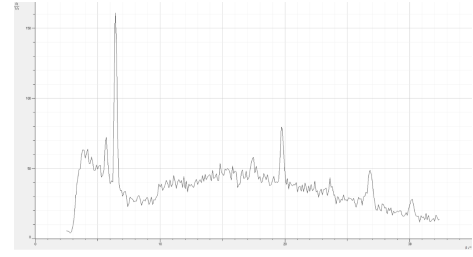
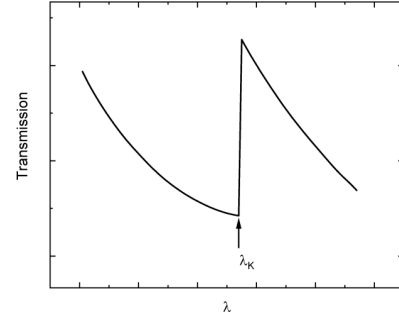
FIG. 5. Si Spectrum of θ against counts

FIG. 6. Graph of NaCl counts/filter counts

ANALYSIS OF RESULTS

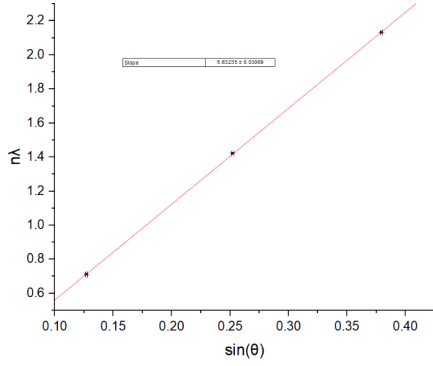
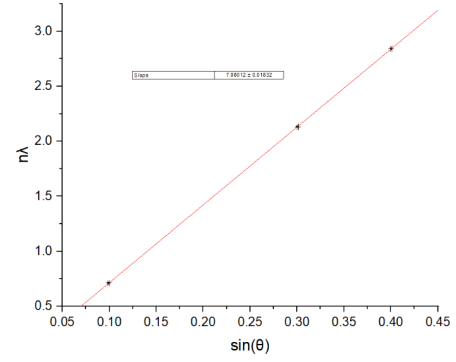
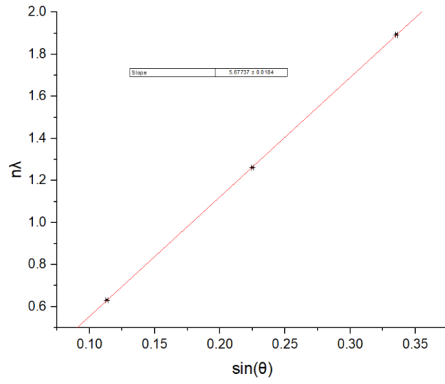
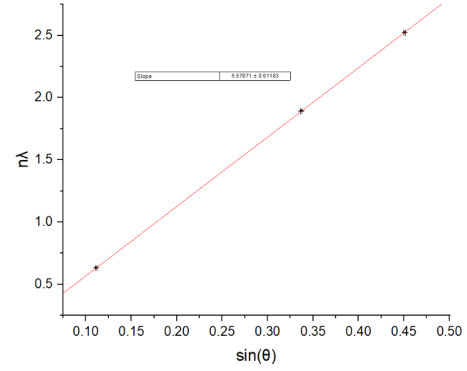
Determination of the lattice constants of NaCl and Si

In order to determine the lattice constant of NaCl the interplanar spacing needed to be calculated, as seen in equation 3. A graph was plotted of $n\lambda$ against $\sin \theta$, to use the relationship seen in equation 1, to calculate the interplanar spacing d . The data was plotted into two separate graphs where one graph corresponds to the k_α peaks and another corresponds to the k_β peaks. The values of $\sin \theta$ corresponding to the peaks in Fig 4 were used. The values of $n\lambda$ were calculated using the reference values from the table provided in the exam script as seen in table 1. The value of $n\lambda$ was calculated by multi-

| Line | Wavelength (\AA) |
|------------|-----------------------------|
| k_α | 0.7108 |
| k_β | 0.6309 |

TABLE I. Wavelength values for different spectral lines

plying the number of the peak by the relevant wavelength. $n\lambda$ was plotted against $\sin \theta$ as seen in fig 7 and 8. The gradient of both these graphs is equal to twice the interplanar spacing of NaCl. The gradients were averaged and the mean interplanar spacing was found to be $d = 2.83 \pm 0.061 \text{ \AA}$. Using equation 3, the lattice constant was calculated to be $a = 5.65 \pm 0.061 \text{ \AA}$. The accepted value lies in this range and has a %D of 0.24%. The same method was applied to Silicon which produced the graphs seen in fig 9 and 10. By

FIG. 7. $n\lambda$ plotted against $\sin \theta$ for the k_α transition (NaCl)FIG. 9. $n\lambda$ plotted against $\sin \theta$ for the k_α transition (Si)FIG. 8. $n\lambda$ plotted against $\sin \theta$ for the k_β transition (NaCl)FIG. 10. $n\lambda$ plotted against $\sin \theta$ for the k_β transition (Si)

analysing the line from the graphs the mean interplanar spacing was found to be $d = 3.16 \pm 0.030 \text{ \AA}$. The lattice constant for Si_{111} was then calculated as $a = 5.48 \pm 0.052 \text{ \AA}$. The accepted value falls within this range and the %D is 0.9%.

Attenuation Spectra

Five absorption spectra was produced for each filter and each graph was divided by the spectrum of unfiltered NaCl. Of the resulting lines, they were normalised by dividing the graphs by their max value to make the characteristic drop, as seen in Fig 6, more visible. The resulting graph can be seen in Fig 11. Afterwards, the drop was identified for each filter and $\sin \theta$ was converted to λ using equation 1. A modified version of equation 2 was used to plot a graph,

$$\frac{1}{\sqrt{\lambda}} = Z\sqrt{R} - \sigma\sqrt{R} \quad (5)$$

$\frac{1}{\sqrt{\lambda}}$ was plotted against the atomic number of each element of each filter and the graph seen in fig 11 was produced. By extracting the gradient from this graph, the Rydberg constant was found to be $R = 11825000 \pm 86000/\text{m}$.

Planck's Constant

The voltage of the x-ray apparatus was varied and the theta of each minimum on the bremsstrahlung continuum was recorded. Examples of the graphs these points were taken from are seen in fig 13 and 14. The relationship,

$$\lambda_{\min} = \frac{hc}{eV} \quad (6)$$

can be used to plot a graph of λ_{\min} against $\frac{c}{eV}$. Minimums were recorded from spectrums ranging from 15kV to 35kV and the following graph was produced seen in fig 15. The value of Planck's constant extracted from the gradient of the graph was $(6.17 \pm 0.104)E - 34 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}$. This has a %D of 6.9%

Calculating Densities of NaCl and Si

The volume V of the unit cell can be calculated by taking the cube of the lattice constant. The density can be calculated by taking the mass of the unit cell and dividing by the volume of the unit cell. In the case of NaCl we have to account for 4 Na^+ ions and 4 Cl^- ions residing in the unit cell. When

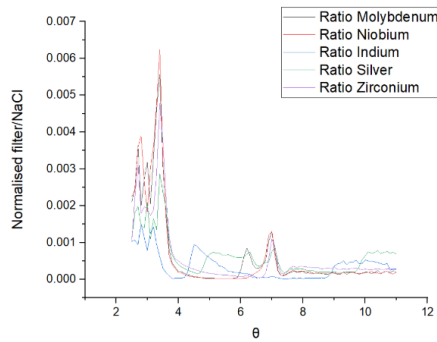


FIG. 11. Normalised graph of filtered counts over NaCl counts.

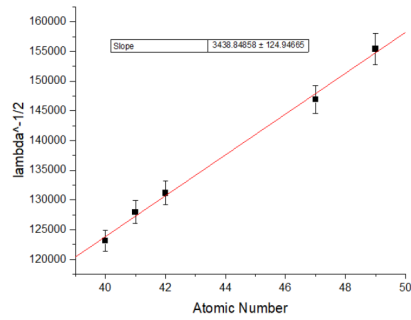


FIG. 12. plot of $\frac{1}{\sqrt{\lambda}}$ against atomic number

we take their molar masses and divide it by the volume, the resultant density is $\rho = 2.15 \pm 0.07 \text{ g/cm}^3$. The percentage difference from the true value is 0.46%. Silicon has a diamond cubic crystal structure, therefore it as 8 atoms in a unit cell. Taking the molar mass of Silicon, the resultant density is $\rho = 2.26 \pm 0.065 \text{ g/cm}^3$. This has a percentage difference of 3% from the true value.

DISCUSSION AND CONCLUSION

In this experiment we obtained accurate values for many quantities. Firstly, for the lattice constants of NaCl and Si we had percentage differences of 0.24% and 0.9% respectively. These are very accurate results, so we can say we successfully used x-ray diffraction and Bragg's law to determine the lattice constants of materials.

In part 2 we tried to determine the Rydberg constant. The constant is used to describe the wavelengths of light emitted or absorbed by an atom when an electron transitions between energy levels. We used different filters and observed the absorption spectra. Using Moseley's law, we were able to determine the Rydberg constant by plotting the atomic number of the element of the filter against the characteristic wavelength. In this part we learned how to systematically identify a characteristic transmission of λ as seen in fig 6. The value we got for R had a %D of 7.76%. A source of error could've been

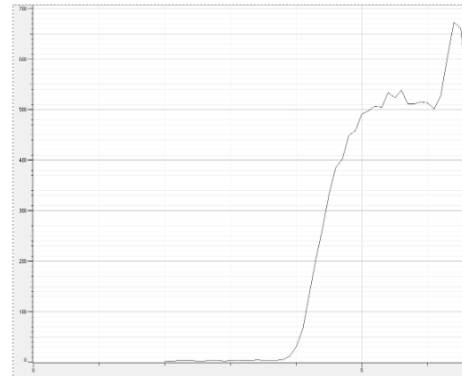


FIG. 13. Spectrum of NaCl with kvp at 30kV

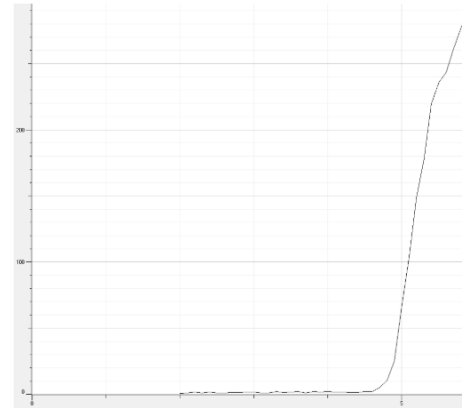


FIG. 14. Spectrum of NaCl with kvp at 25kV

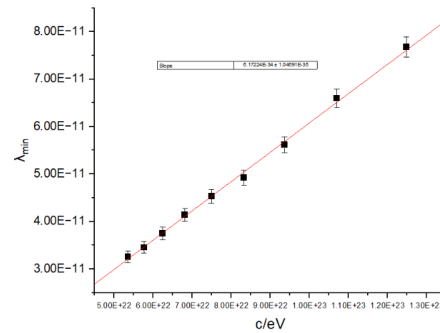


FIG. 15. plot of λ_{min} against c/eV

because we used our calculated value of d rather than the true value.

In part 3 the value of Planck's constant by using the relationship seen in equation 6. The voltage was varied and each time λ_{min} was identified. λ_{min} was plotted against V and the calculated value of Planck's constant had a %D of 6.9% from the true value.

Overall I would consider this experiment a success as we determined accurate values using x-ray apparatus.

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