JUNIOR SOPHISTER EXPERIMENTAL PHYSICS LABORATORY REPORT

X-Ray Diffraction

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1 Abstract

In this experiment, the X-ray diffraction pattern of various crystal samples (NaCl (100), LiF(100), GaP (111), Si (100), Si (111)) were recorded. Using the Bragg condition and diffraction order selection rules, these patterns were interpreted to determine the lattice constant for each of the crystals. The calculated values for the lattice constant (556 ± 5 pm, 405 ± 2 pm, 537 ± 5 pm, 534 ± 11 pm) were found to agree with experimentally-verified values, within experimental error.

2 INTRODUCTION

2.1 Crystal Structure

Crystalline materials consist of a highly ordered make-up of its constituents and are uniquely determined by a lattice, an array of periodically repeating points in space, and a basis, a set of atoms attributed to each lattice point. A lattice can be described by the vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 by the expression

$$\mathbf{r}' = \mathbf{r} + u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3,\tag{1}$$

where the lattice at **r** is identical to that at **r**', and u_1 , u_2 and u_3 are arbitrary integers. While this experiment deals with crystals of different structure, each of these can be described by a cubic lattice, i.e. $a_1 = a_2 = a_3 \equiv a$, where a is the lattice constant of the crystal.

2.2 MILLER INDICES

When dealing with samples of crystals, specifically samples with a smoothly cut face, it is often useful to denote which plane of the lattice the crystal has been cut. This is done using Miller indices; for a given lattice plane that intersects the \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 axes at $(ua_1, 0, 0)$, $(0, va_2, 0)$ and $(0, 0, wa_3)$, respectively, the Miller indices (hkl) are given by the expression

$$h:k:l = \frac{1}{u}:\frac{1}{v}:\frac{1}{w}.$$
(2)

A relationship between the lattice plane spacing d and the lattice constant a of a cubic crystal can be derived. Consider the reciprocal vector $\mathbf{r} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$. The magnitude of this vector is simply $\frac{1}{d^2}$, and since $\mathbf{b}_1^2 = \mathbf{b}_2^2 = \mathbf{b}_3^2 = \frac{1}{a^2}$, this reduces to

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \implies d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}.$$
(3)

2.3 X-RAY RADIATION

In X-ray production, electrons are accelerated through a high voltage towards a target, where their collisions in the target produce two notable X-ray spectra: the characteristic spectrum and the continuous spectrum.

When the accelerated electrons are in the vicinity of the target, a portion of their kinetic energy may be absorbed by electrons in certain energy levels of the atoms in the target. These electrons enter an excited energy level and, after returning back to their original energy level, emit electromagnetic radiation. Specific energy transitions correspond to specific radiation wavelength, giving rise to the characteristic X-ray spectrum. In this experiment, $K\alpha$ and $K\beta$ radiation are produced, corresponding to the energy transitions $L\rightarrow K$ and $M\rightarrow K$ and wavelengths 71.1 pm and 63.1 pm, respectively (as shown in Figure 1).



Figure 1: Energy transitions corresponding to $K\alpha$ and $K\beta$ radiation.

The continuous spectrum, on the other hand, is produced by the general deceleration of electrons as it collides with the target. Since this is not associated with specific energy transitions, this deceleration can produce X-rays across a continuous range of wavelengths, also known as bremsstrahlung.

In this experiment, X-ray radiation is diffracted from a crystal into a detector. By varying the angle of diffraction, a spectrum of intensities is produced due to Bragg's Law, consisting of both characteristic and continuous spectra components.

2.4 BRAGG'S LAW

When electromagnetic radiation is focused towards a crystal, it is scattered in a predictable fashion; for a given radiation wavelength (similar to the atomic spacings, i.e. X-rays), certain angles of incidence lead to constructive interference of the reflected waves. This is known as Bragg's Law, and is a foundation in X-ray crystallography. The so-called Bragg condition for constructive interference is given by

$$n\lambda = 2d\sin\beta,\tag{4}$$

where n is the order of diffraction, λ is the wavelength of the incident radiation, d is the spacing between the lattice planes of the crystal, and β is the angle of incidence of the radiation. This expression can be derived from Figure 2, where in order for constructive interference to occur between the reflected waves, the segments highlighted in blue, equalling a length of $2d \sin \beta$, must be an integer number of wavelengths, $n\lambda$.



Figure 2: Diffraction of waves from planes of a crystal lattice.

For cubic crystals, Equation 3 and Equation 4 can be combined to result in

$$a = \frac{n\lambda\sqrt{h^2 + k^2 + l^2}}{2d\sin\beta}.$$
(5)

2.5 Selection Rules

While the characteristic spectrum obtained from X-ray diffraction must obey the Bragg condition, not every diffraction order satisfying Equation 4 will result in a peak on the spectrum. This is due to the specific make-up of the lattice and basis of the crystal.

For a given crystal A, the amplitude of a scattered wave is proportional to the structure factor F_A , given by [1]

$$F_{A} = \sum_{p} f_{p} e^{-2\pi i (hx_{p} + ky_{p} + lz_{p})},$$
(6)

where \sum_{p} denotes a sum over all basis atoms in the conventional unit cell, f_p is the atomic form factor of atom p, (x_p, y_p, z_p) is the location of atom p in the unit cell, and (hkl) are the miller indices of the crystal.

A face-centred cubic crystal made up of atoms of atomic form factor f can be considered as a simple cubic lattice with a basis of atoms located at (0,0,0), $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$ and $(0,\frac{1}{2},\frac{1}{2})$. Equation 6 thus reads

$$F_{\text{FCC},f} = f \left[e^{-2\pi i (0+0+0)} + e^{-2\pi i \left(\frac{h}{2} + \frac{k}{2}\right)} + e^{-2\pi i \left(\frac{h}{2} + \frac{l}{2}\right)} + e^{-2\pi i \left(\frac{k}{2} + \frac{l}{2}\right)} \right]$$

$$= f \left[1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l} \right]$$

$$F_{\text{FCC},f} = \begin{cases} 4f \quad h, k, l \text{ are all even or all odd} \\ 0 \quad h, k, l \text{ are of mixed parity} \end{cases}.$$
 (7)

A rock salt structure, such as that observed in NaCl and LiF, can be considered as a face-centred cubic lattice with a basis of atom σ at (0, 0, 0) and atom ρ at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Using Equation 7 results in

$$F_{\text{rock salt},f_{\rho},f_{\sigma}} = F_{\text{FCC},f}|_{f \to F_{f_{\rho},f_{\sigma}}}$$

$$= \begin{cases} 4 \left[f_{\sigma} e^{-2\pi i (0+0+0)} + f_{\rho} e^{-2\pi i \left(\frac{h}{2} + \frac{k}{2} + \frac{l}{2}\right)} \right] & h,k,l \text{ are all even or all odd} \\ 0 & h,k,l \text{ are of mixed parity} \end{cases}$$

$$F_{\text{rock salt},f_{\rho},f_{\sigma}} = \begin{cases} 4(f_{\sigma} + f_{\rho}) & h,k,l \text{ are all even} \\ 4(f_{\sigma} - f_{\rho}) & h,k,l \text{ are all odd} \\ 0 & h,k,l \text{ are of mixed parity} \end{cases}$$
(8)

For a zincblende structure, such as GaP, a similar method as above can be used. Considering instead the basis points of (0, 0, 0) and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ leads to

$$F_{\text{zincblende}, f_{\sigma}, f_{\rho}} = \begin{cases} 4(f_{\sigma} + f_{\rho}) & h + k + l = 4N \\ 4(f_{\sigma} \pm if_{\rho}) & h + k + l = 2N + 1 \\ 4(f_{\sigma} - f_{\rho}) & h + k + l = 4N + 2 \end{cases}$$
(9)

where N is an arbitrary integer.

A diamond crystal structure is simply a zincblende structure with σ and ρ being identical atoms, i.e. $f_{\sigma} = f_{\rho} \equiv f$, and so

$$F_{\text{diamond},f} = \begin{cases} 8f & h+k+l = 4N\\ 4f(1\pm i) & h+k+l = 2N+1\\ 0 & h+k+l = 4N+2 \end{cases}$$
(10)

While the Miller indices in the above expressions for the structure factor are given as (hkl), for diffraction orders greater than 1 these are replaced with ((nh)(nk)(nl)). This gives rise to a set of selection rules imposed on the diffraction order n for different crystal structures.

3 Method

- 1. Initialise the X-ray diffraction apparatus using the following parameters:
 - Tube voltage U = 35 kV
 - Tube current I = 1 mA
 - Measurement time interval $\Delta t = 1$ s
- 2. Mount the NaCl (100) crystal on the support and secure it in place.
- 3. Pressing the SCAN button on the apparatus and using the X-ray software on the supplied PC, record the intensity spectrum for each of the four orientations of the crystal.
- 4. Identify the strongest intensity spectrum and record the diffraction pattern for the corresponding orientation, setting $\Delta t = 5$ s.
- 5. Using the selection rules discussed in subsection 2.5, determine the diffraction order n for each of the K α and K β peaks.
- 6. Using Equation 5, calculate the lattice constant a of the crystal.
- 7. Repeat steps 1-6 for the LiF (100), GaP (111), Si (100) and Si (111) crystals.

4 Results & Discussion

4.1 NACL

NaCl has a rock salt structure, and so from the selection rules in Equation 8, only even diffraction orders, i.e. n = 2N, can be diffracted. After choosing the optimal orientation from Figure 8, the following intensity spectrum, peak locations and lattice constant for NaCl (100) were found:



Figure 3: Intensity spectrum of NaCl (100) with $\Delta t = 5$ s, the corresponding locations of the K α and K β lines, and the calculated lattice constant *a* for each peak.

The average value of a for NaCl was calculated to be 556 ± 5 pm, within experimental error of the true value of 563 pm. [1]

- Step angle $\Delta\beta = 0.1^{\circ}$
- Angle limits β_{\min} , $\beta_{\max} = 3^{\circ}$, 35°
- Detector mode: COUPLED

4.2 LIF

LiF also has a rock salt structure, and so again only even diffraction orders are considered. After choosing the optimal orientation from Figure 9, the following intensity spectrum, peak locations and lattice constant for LiF (100) were found:



	n	β , °	a, pm		
	2	10.1	405 ± 4		
$K\alpha$	4	20.6	404 ± 2		
	6	31.8	405 ± 2		
	2	8.9	408 ± 5		
$K\beta$	4	18.2	404 ± 3		
	6	28.0	403 ± 2		

Figure 4: Intensity spectrum of LiF (100) with $\Delta t = 5$ s, the corresponding locations of the K α and K β lines, and the calculated lattice constant *a* for each peak.

The average value of a for LiF was calculated to be 405 ± 2 pm, agreeing with the true value of 403 pm. [2]

4.3 GAP

From Equation 9, the Bragg condition is the only restriction on X-ray diffraction, and so any order peak can be observed. The spectra obtained in Figure 10 contained a significant amount of noise, and so the spectra were recorded again with a longer time interval around the first K α peak using the provided K α filter. After choosing the optimal orientation from Figure 11, the following intensity spectrum, peak locations and lattice constant for GaP (111) were found:



Figure 5: Intensity spectrum of GaP (111) with $\Delta t = 8$ s, the corresponding locations of the K α and K β lines, and the calculated lattice constant *a* for each peak.

The average value of a for GaP was calculated to be 537 ± 5 pm, within experimental error of the true value of 545 pm. [2,3]

4.4 SI

From Equation 10, the only allowed diffraction orders for Si (100) are n = 1, 3, 4, 5, 7, 8, ...The spectra obtained in Figure 12 were too noisy to choose an orientation, and so similarly as was done with GaP, a more accurate spectra was obtained around the first K α peak. After choosing the optimal orientation from Figure 13 (and noting that the n = 1 diffraction was amongst the peak of the bremsstrahlung and thus neglected), the following intensity spectrum, peak locations and lattice constant for Si (100) were found:



Figure 6: Intensity spectrum of Si (100) with $\Delta t = 7$ s, the corresponding locations of the K α and K β lines, and the calculated lattice constant *a* for each peak.

From Equation 10, the only allowed diffraction orders for Si (111) are n = 1, 3, 4, 5, ... As with Si (100), a second set of spectra were obtained after an initial noisy spectra in Figure 14. After choosing the optimal orientation from Figure 15, the following intensity spectrum, peak locations and lattice constant for Si (111) were found:



Figure 7: Intensity spectrum of Si (111) with $\Delta t = 8$ s, the corresponding locations of the K α and K β lines, and the calculated lattice constant *a* for each peak.

The average value of a for Si across both crystal samples was calculated to be 534 ± 11 pm, agreeing with the true value of 543 pm. [3]

5 ERROR CALCULATIONS

The uncertainty $\Delta \lambda$ in the wavelengths of the Mo K α and Mo K β lines were taken to be 0.1 pm. The uncertainty $\Delta \beta$ in the angle β was taken to be the step angle, 0.1°.

The uncertainty Δa in the lattice constants a was calculated using Gauss's law of error propagation

$$f = f(x, y) \implies \Delta f = \sqrt{\left(\frac{\partial f}{\partial x}\Delta x\right)^2 + \left(\frac{\partial f}{\partial y}\Delta y\right)^2}.$$
 (11)

Using Equation 5 and Equation 11, the uncertainty was calculated as follows:

$$\begin{aligned} a(\lambda,\beta) &= \frac{n\lambda\sqrt{h^2 + k^2 + l^2}}{2\sin\beta} \\ \Delta a &= \sqrt{\left(\frac{\partial a}{\partial\lambda}\Delta\lambda\right)^2 + \left(\frac{\partial a}{\partial\beta}\Delta\beta\right)^2} \\ &= \sqrt{\left(\frac{n\sqrt{h^2 + k^2 + l^2}}{2\sin\beta}\Delta\lambda\right)^2 + \left(-\frac{n\lambda\sqrt{h^2 + k^2 + l^2}}{2\sin^2\beta}\cos\beta\Delta\beta\right)^2} \\ &= \frac{n\sqrt{h^2 + k^2 + l^2}}{2\sin\beta}\sqrt{(\Delta\lambda)^2 + (\Delta\beta\cdot\lambda\cot\beta)^2} \end{aligned}$$

When finding the uncertainty in the average value \bar{a} of a over multiple peaks, the standard deviation σ was taken as the uncertainty, namely

$$\sigma^2 = \sum_{i=1}^{N} \frac{(\bar{a}-a)^2}{N}.$$

6 CONCLUSION

The calculated values of the lattice constants were found to agree with their experimentallyverified values within experimental error. This confirmation further upholds both the Bragg condition and the diffraction order selection rules for X-ray diffraction.

Possibly the largest source of unaccounted error was due to the precision of the cuts of the provided crystal samples. While a slight difference in the cut would result in different Miller indices, and thus differing values of the peaks in the diffraction spectra, it was not possible to verify the precision of these cuts with the limited equipment and timeframe for this laboratory. This possible source of error, however, did not prove to be an obstacle, as the largest percentage error between the calculated and true value of a lattice constant was 1.7% (Si).

7 References

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8 APPENDIX



Figure 8: Intensity spectra for the different orientations of NaCl (100), with $\Delta t = 1$ s.



Figure 9: Intensity spectra for the different orientations of LiF (100), with $\Delta t = 1$ s.



Figure 10: Intensity spectra for the different orientations of GaP (111), with $\Delta t = 1$ s.



Figure 11: Intensity spectra for the different orientations of GaP (111) using the K α filter, with $\Delta t = 5$ s.



Figure 12: Intensity spectra for the different orientations of Si (100), with $\Delta t = 1$ s.



Figure 13: Intensity spectra for the different orientations of Si (100) using the K α filter, with $\Delta t = 5$ s.



Figure 14: Intensity spectra for the different orientations of Si (111), with $\Delta t = 1$ s.



Figure 15: Intensity spectra for the different orientations of Si (111) using the K α filter, with $\Delta t = 5$ s.