X-Ray Diffraction

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Abstract

The aim of this experiment was to examine the crystal structure of various atoms and molecules using x-ray diffraction. The lattice constants and miller indices were found for each crystal.

Crystal	Miller Index (hkl)	Lattice Constant (A)
NaCL	(100)	$5.61{\pm}.05 \AA$
LiF	(100)	$4.06{\pm}.05 { m \AA}$
GaP	(111)	$5.45{\pm}.07 m \AA$
Si	(100)	$5.42{\pm}.07 m \AA$
Si	(111)	$5.52{\pm}.08{ m \AA}$

Introduction and Basic Theory

A crystalline solid is a material which is composed of basis of atoms or molecules that are packed in an orderly and repeating lattice. The structure of these crystals can be quite varied, and there are many different types of lattice. As the wavelength of x-rays is comparable to the spacing of atoms in a solid (~ 0.1 nm) a crystal acts as a diffraction grating. Using the resulting diffraction pattern it is possible to analyse even complex crystal structures.

For this experiment, the Bragg method was used. If the structure as shown in Fig 1 is considered, where x-rays of wavelength λ are incident on parallel atomic planes of spacing d. It is clear that the rays will have a path difference of $dsin\theta$. As such, constructive interference will occur between beams diffracted from successive layers when :

$$2dSin\theta = n\lambda \qquad (n = 1, 2, 3...) \tag{1}$$



Figure 1: Bragg Diffraction

This is known as Bragg's law. If a crystal is scanned using x-ray diffraction, the intensity peaks will give values of θ . Using that, d can be found if λ is known.

In addition, the relative intensities of the peaks can give more information. If a wave is scattered by an atom from some reference point O, the incident and scattered waves can be treated as plane waves. As such, the phase difference between the beams at a detector point D is given by:

$$\Delta \phi = \frac{2\pi}{\lambda} (x_1 + x_2) = \Delta k \cdot r_n \qquad (\Delta k = k' - k) \tag{2}$$

k' and k are the wavevectors of the scattered and incident waves.

The amplitude at D of the wave scattered from atom n is therefore proportional to:

$$A_n = f_n e^{-\Delta k \cdot r_n} \tag{3}$$

 f_n is known as the atomic form factor. If r_l is the position of the lattice point with which atom n is associated and r_p is the position of the atom relative to the lattice point, it follows that:

$$A = \sum_{l} e^{-i\Delta k \cdot r_l} \sum_{p} f_p e^{-i\Delta k \cdot r_p}$$
(4)

The first term determines the directions for which diffractions occurs, this is essentially Bragg's Law. The second term determines the intensities of the diffracted beams. This is called the structure factor, F. This term can also be expressed in terms of miller indices (hkl) and atomic basis coordinates (x_p, y_p, z_p) :

$$F = \sum_{p} f_p e^{-i2\pi(hx_p + ky_p + lz_p)}$$
(5)

From this, it is possible to derive useful constraints for different lattice shapes:

Condition	F_{hkl}
hkl all odd	0
hkl all mixed	0
hkl unmixed	$4[f_a + f_2 e^{\pi i(h+k+l)}]$
hkl all even	$4(f_1 + f_2)$
hkl all odd	$4(f_1 - f_2)$
hkl mixed	0
h+k+l=4n	$\sqrt{16(f_1+f_2)^2}$
h + k + l = 2(2n + 1)	$\sqrt{16(f_1-f_2)^2}$
hkl all odd	$\sqrt{16(f_1^2+f_2^2)}$
	Condition hkl all odd hkl all mixed hkl unmixed hkl all even hkl all odd hkl mixed h + k + l = 4n h + k + l = 2(2n + 1) hkl all odd

The points at which $F_{hkl} = 0$ are called systematic absenses as there will be no intensity peak at those points.

It is also possible to derive a useful formula that can be used to compare the ratios of $sin^2\theta$ values:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
$$\lambda = 2a\sqrt{\frac{1}{h^2 + k^2 + l^2}}sin\theta$$
$$sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

As h,k,l must be integers, the values of $sin^2\theta$ must all have a common multiplier. By comparing the ratios of the $sin^2\theta$ values for different peaks, and by knowing which combinations

are disallowed for each structure it is now possible to find the miller indices and the atomic lattice spacing of the sample crystals.

Experimental Setup

Initially, a crystal of NaCl was placed in the X-Ray diffractor as shown in Fig 2. A tube voltage of 35kV amd a current of 1mA was used, and the count rate over 5s was found over steps of $\theta = 0.1^{\circ}$ Using the coupled mode, the detector was rotated through 2θ and the sample was rotated through θ for the Bragg condition to apply. The count rate and angle were recorded by the computer and graphed. The process was repeated for four other crystals; LiF, GaP and two different Si crystals.



Figure 2: Bragg Diffraction

Results

In the following graphs, the k_{α} peaks are given positive integer values and the k_{β} peaks are given negative integer values for clarity.



NaCl

Figure 3: NaCl: Intensity vs angle

k_{α} peaks (°)	sin heta	$sin^2\theta$
6.5	0.113	0.0129
13.0	0.225	0.0506
19.8	0.339	0.1147
k_{β} peaks (°)	sin heta	$sin^2\theta$
7.3	0.127	0.0161
14.7	0.254	0.0644
22.3	0.379	0.1440

The ratio of the $sin^2\theta$ values corresponds to 1:4:9 meaning the crystal has (100) miller index. (This is also equivalent to a (010) or a (001) index.) A graph of n vs $\frac{2sin(\theta)}{\lambda}$ was then plotted to find the spacing between the atomic planes:



Figure 4: NaCl: n vs $\frac{2sin(\theta)}{\lambda}$

The spacing d is the slope of the graph. In this case it was the average of the two slopes, represented by the k_{α} and k_{β} peaks. As the crystal has the rock salt structure, we have a = 2d and as such, the atomic lattice constant is 5.61Å The error is ± 0.05 Å. This was found using analytical methods.

The method is the same for the other crystals.

 \mathbf{LiF}

k_{α} peaks (°)	sin heta	$sin^2\theta$
8.9	0.155	0.024
18.1	0.311	0.097
27.9	0.468	0.219
k_{β} peaks (°)	$sin\theta$	$sin^2\theta$
10.0	0.174	0.030
20.5	0.350	0.123
31.7	0.525	0.276





 $\begin{array}{l} {\rm Ratio: 1:4:9} \\ {\rm Miller \ Indices: \ (100)} \\ a=4.03\pm0.05 {\rm \AA} \end{array}$

GaP

k_{α} peaks (°)	sin heta	$sin^2\theta$
5.7	0.099	0.010
11.5	0.201	0.039
17.5	0.315	0.090
23.7	0.414	0.162
k_{β} peaks (°)	sin heta	$sin^2\theta$
6.5	0.113	0.013
13.1	0.227	0.051
19.8	0.339	0.115
26.8	0.451	0.203





Ratio : 3:12:27 Miller Indices: (111) As GaP has the Zinc Blend structure and the miller indices are (111) we have $a = \sqrt{3}d$ instead. $a = 5.45 \pm 0.07 \text{\AA}$

Si(100)

k_{α} peaks (°)	sin heta	$sin^2\theta$
13.5	0.233	0.054
27.8	0.466	0.218
44.4	0.799	0.489
k_{β} peaks (°)	sin heta	$sin^2\theta$
15.2	0.262	0.069
31.6	0.524	0.275
51.7	0.785	0.616



Figure 7: Si(100): n vs $\frac{2sin(\theta)}{\lambda}$

Ratio : 1:4:9 Miller Indices: (10) As Si has the diamond structure and the miller indices are (100) we have a = 4d. $a = 5.42 \pm 0.07 \text{\AA}$

Si(111)

k_{α} peaks (°)	sin heta	$sin^2\theta$
5.5	0.096	0.009
17.3	0.297	0.088
23.5	0.399	0.159
30.0	0.500	0.25
k_{β} peaks (°)	$sin\theta$	$sin^2\theta$
6.2	0.108	0.012
19.6	0.335	0.113
26.6	0.448	0.200
22.2		



Figure 8: Si(111): n vs $\frac{2sin(\theta)}{\lambda}$

Ratio : 3:27:54:81 Miller Indices: (111) Si has the diamond structure and the miller indices are (111) so we have $a = \sqrt{3}d$. $a = 5.52 \pm 0.08 \mathring{A}$

Conclusion

While in theory, Bragg Diffraction may be a very simple model that doesn't account for many complexities, it still provides very accurate results. All values found for the lattice constant using this method were correct to within a relatively small margin of error. ($\sim 5\%$)

The biggest problem that was encountered during the experiment was the fact that the number of diffraction peaks found was quite small. As the intensity diminished quite rapidly as θ increased, noise in the measurement ensured any peaks after the 3rd or 4th were unreadable. It is possible that the accuracy could be improved if the noise level could be reduced somewhat, possibly by taking more time to measure at higher θ

The errors in this experiment were quite small, the main source of error being the fact that 0.1° was the smallest possible step. As the peaks were well defined, there was no need to take errors in the intensities into account.

Sources

http://epswww.unm.edu/xrd/xrdclass/04-Crystalography-for-XRD.pdf Neil W. Ashcroft and N. David Mermin, Solid State Physics (Harcourt: New York, 1976) http://en.wikipedia.org