PH2255 Course:
Introduction to Statistical Methods
Lab 2
X-Ray Diffraction

Thomas Bass

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Abstract

To explore the structure of atoms in crystals, one cannot employ the traditional methods of optical microscopes: the atoms, and the crystal lattice they form, are smaller than the wavelengths of light. Therefore, we must probe the structure of these crystals using radiation of a shorter wavelength. In this case: X-Rays. By employing techniques developed by von Laue and Bragg, the phenomenon of constructive interference with crystal diffraction can be used to determine the crystal diffraction spacing of four alkali halide crystals; LiF, NaCl, KCl, and RbCl, and to estimate the relative sizes of Na^+, K^+, and Rb^+ cations.

1 Equipment

The equipment used in this lab was an online simulation of X-Ray crystal diffraction apparatus. The apparatus, named a diffractometer, consists of a X-Ray tube which accelerates electrons from a hot cathode to a copper anode target at potential difference 30kV. These electrons, of $50\mu A$ current, hit the copper target and produce X-Rays and leave the X-Ray tube through a $250\mu m$ borosilicate window, where they enter the crystal sample. The apparatus is enclosed in a glass-lead dome to prevent the X-Rays entering the body.

To observe the diffraction from the crystal, a Geiger-Muller tube counts the number of radiation events per second. The dependent variable, the angle of incidence of X-Rays, is changed by moving the Geiger-Muller tube along a circular track around the crystal sample. The sample and G-M tube are connected by a drive belt, such that as the crystal rotates θ degrees, the G-M tube is rotated around 2θ.

2 Method

To analyse the internal lattice structure of crystals, we employ a technique developed by von Laue and Bragg. By directing a beam of X-Rays at a crystal, you can observe the beam "reflected" off the lattice planes. However, this reflection is also subject to interference effects, as determined by extra optical path

length travelled by successive rays. If these path lengths are integer multiples of the wavelength, the rays interfere constructively, resulting in a high intensity of X-Rays being reflected. This can be observed as a high count rate in the Geiger-Muller tube in the apparatus.

Bragg developed a law to describe the relationship between the distance between crystal lattice planes, and the required conditions for constructive interference.

$$2d \sin \theta = n\lambda \tag{1}$$

In this condition, a ray of light at wavelength λ enters the lattice structure at angle θ to the crystal planes, and successive rays travel an extra $2d \sin \theta$ optical path difference (or an integer n multiple of it) to emerge from the crystal, constructively interfering to produce an intensity peak.

3 Data and Analysis

An X-Ray diffraction pattern was obtained using the simulated apparatus provided, using the LiF crystal. Measurements were taken at $\Delta\theta = 2 \deg$, unless around an observed peak, where observations were made at $\Delta\theta = 0.1 \deg$ to improve resolution. The G-M tube was set to a 3 second time period. The plot is shown below.
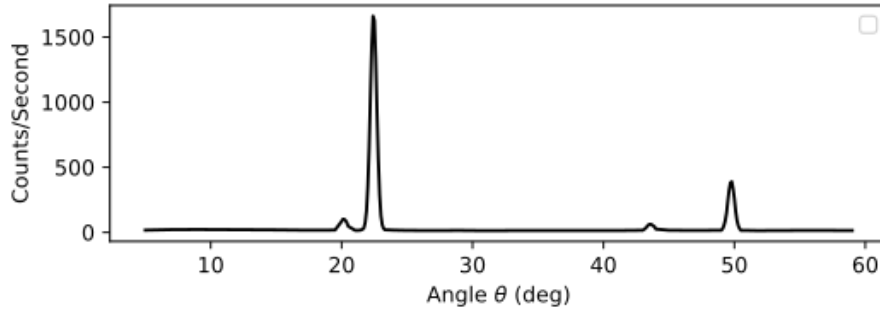

Figure 1: X-Ray diffraction pattern for LiF, between $\theta = 5$ and $\theta = 60$, using a time period of 3 seconds

From these observations, the angles at which the diffraction interference is constructive can be extracted. By writing the Bragg's law in terms of d we obtain:

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

From the plot, the peak wavelengths for $Cu - K_\alpha$ and $Cu - K_\beta$ were estimated, knowing that the K_α peak is the larger of the pair at each order. From these, one can obtain four estimates for d.

To estimate the error, using half of the measurement resolution, and propagating that through the equation, we use the following equation:

$$\sigma_d = d \cdot \sqrt{\left(\frac{\sigma_\theta}{\theta}\right)^2} \tag{3}$$

2

Only the error for θ was included, as the wavelengths are given in the lab script, and the order has no error, as it is an integer.

Angle (deg)	Wavelength (m)	Order	Estimate (m)	Estimate Error (Δm)
20.15	1.392×10^{-10}	1	2.021×10^{-10}	1.076×10^{-11}
22.4	1.542×10^{-10}	1	2.023×10^{-10}	1.094×10^{-11}
43.55	1.392×10^{-10}	2	2.021×10^{-10}	1.394×10^{-11}
49.8	1.542×10^{-10}	2	2.019×10^{-10}	1.564×10^{-11}

Table 1: Estimates for the $Cu - K_\beta$ and $Cu - K_\alpha$ interference peaks for LiF diffraction, with the estimated value d for lattice separation

An estimate of $d = 2.021 \times 10^{-10}$ m is obtained by averaging each of these estimates. To obtain an average error, we can divide the average by the root of the number of measurements, as repeated measurements reduce the overall error. An estimate error of $\sigma_d = 6.41 \times 10^{-12}$ m was be calculated.

The lab simulation also provides a Nickel filter. Measurements were repeated at the same intervals, but this time with the Nickel filter in front of the X-Ray beam generator.
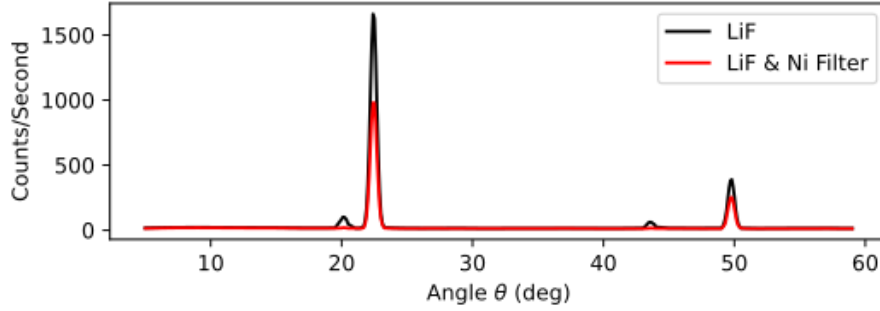

Figure 2: X-Ray diffraction pattern for LiF, with and without the Nickel filter, between $\theta = 5$ and $\theta = 60$, using a time period of 3 seconds

From this graph, one can see that the peaks corresponding to the $Cu - K_\alpha$ lines are reduced to around 60% of their intensity without the filter, but the $Cu - K_\beta$ peaks are not present at all. This is explained by the Nickel atom's absorption edge at $1.448\mathring{A}$, which is between the K_α and K_β lines. Therefore, this method can be used to distinguish K_α lines, present with a Nickel filter, from K_β lines, which would not be present.

The same method can be repeated for NaCl[1], KCl[2], and RbCl[2] crystals.

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[1]Data obtained with permission from Sean Hibbit
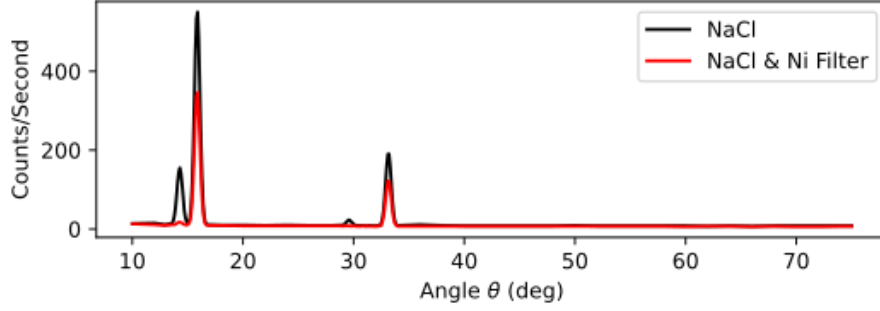[2]Data obtained with permission from Ethan Kosak-Hine

Figure 3: X-Ray diffraction pattern for $NaCl$, with and without the Nickel filter, between $\theta = 5$ and $\theta = 60$, using a time period of 3 seconds

Angle (deg)	Wavelength (m)	Order	Estimate (m)	Estimate Error (Δm)
14.3	1.392×10^{-10}	1	2.818×10^{-10}	1.454×10^{-11}
15.9	1.542×10^{-10}	1	2.814×10^{-10}	1.493×10^{-11}
29.6	1.392×10^{-10}	2	2.818×10^{-10}	1.620×10^{-11}
33.15	1.542×10^{-10}	2	2.820×10^{-10}	1.684×10^{-11}

Table 2: Estimates for the $Cu - K_\beta$ and $Cu - K_\alpha$ interference peaks for $NaCl$ diffraction, with the estimated value d for lattice separation
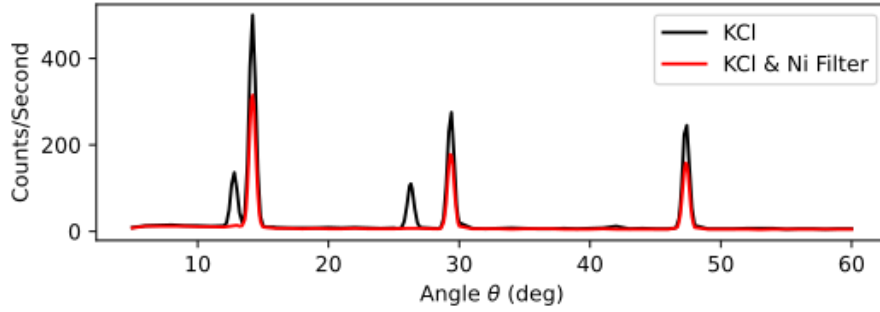

Figure 4: X-Ray diffraction pattern for KCl, with and without the Nickel filter, between $\theta = 5$ and $\theta = 60$, using a time period of 3 seconds

Angle (deg)	Wavelength (m)	Order	Estimate (m)	Estimate Error (Δm)
12.8	1.392×10^{-10}	1	3.142×10^{-10}	1.611×10^{-11}
14.2	1.542×10^{-10}	1	3.143×10^{-10}	1.621×10^{-11}
26.3	1.392×10^{-10}	2	3.142×10^{-10}	1.752×10^{-11}
29.3	1.542×10^{-10}	2	3.151×10^{-10}	1.807×10^{-11}
42	1.392×10^{-10}	3	3.121×10^{-10}	2.100×10^{-11}
47.3	1.542×10^{-10}	3	3.147×10^{-10}	2.320×10^{-11}

Table 3: Estimates for the $Cu - K_\beta$ and $Cu - K_\alpha$ interference peaks for KCl diffraction, with the estimated value d for lattice separation
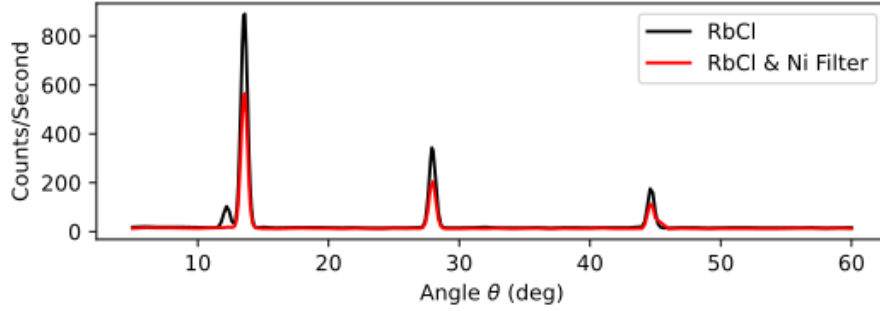
Figure 5: X-Ray diffraction pattern for $RbCl$, with and without the Nickel filter, between $\theta = 5$ and $\theta = 60$, using a time period of 3 seconds

Angle (deg)	Wavelength (m)	Order	Estimate (m)	Estimate Error (Δm)
12.1	1.392×10^{-10}	1	3.320×10^{-10}	1.698×10^{-11}
13.55	1.542×10^{-10}	1	3.291×10^{-10}	1.693×10^{-11}
27.9	1.542×10^{-10}	2	3.295×10^{-10}	1.864×10^{-11}
44.6	1.542×10^{-10}	3	3.294×10^{-10}	2.313×10^{-11}

Table 4: Estimates for the $Cu - K_\beta$ and $Cu - K_\alpha$ interference peaks for $RbCl$ diffraction, with the estimated value d for lattice separation

4 Conclusion

From the same method as used with the LiF crystal, we obtain the following averages:

Crystal	Lattice Spacing Estimate (m)	FCC Lattice Parameter (m)
LiF	$(2.021 \pm 0.0641) \times 10^{-10}$	$(4.042 \pm 0.128) \times 10^{-10}$
$NaCl$	$(2.818 \pm 0.0781) \times 10^{-10}$	$(5.939 \pm 0.156) \times 10^{-10}$
KCl	$(3.141 \pm 0.0763) \times 10^{-10}$	$(6.282 \pm 0.153) \times 10^{-10}$
$RbCl$	$(3.300 \pm 0.0946) \times 10^{-10}$	$(6.600 \pm 0.189) \times 10^{-10}$

Table 5: Estimated values d for lattice separation for crystals LiF, $NaCl$, KCl, and $RbCl$, with error ranges, and Face-Centered-Cubic lattice parameter $a = 2d$.

As the LiF crystal contains F^- ions, whereas the other three crystals contain CL^- ions, we cannot directly relate the size of the LiF lattice parameter to the Li^+ ion size. However, as the other three crystals contain Cl^- ions, we can factor their size out, and compare the Na^+, K^+, and Rb^+ ion sizes with known values taken from Kittel, C. *Introduction to Solid State Physics* (8 ed.).

Cont. overleaf.

Ion	Lattice spacing ($m \times 10^{-10}$)	Relative size	Known size ($\AA$)	Known relative size
Na^+	2.818 ± 0.0781	1	0.98	1
K^+	3.141 ± 0.0763	1.115	1.33	1.357
Rb^+	3.3 ± 0.0946	1.171	1.48	1.510

Table 6: Comparing the calculated relative sizes of Na^+, K^+, and Rb^+ ions to known values.

While these calculated relative sizes (relative to Na^+) do not perfectly line up to the known relative sizes, it is promising to see the expected increase. From looking at a periodic table, we see that Na, K, and Rb are alkali metals of increasing electron configuration, and we would expect Li^+ ions to follow the trend, being smaller than Na^+, but we cannot conclude this due to the F anion, rather than Cl in the rest of the crystals. We can expect a linear progression of ion size, as each increasing electron orbital can be estimated to be the same size.