

X-Ray Diffraction

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1 Introduction

This laboratory studies the atomic crystalline structure of 5 compounds, including one unknown compound which we are to determine. Using powder X-Ray Diffraction (XRD) and powerful refinement software called FullProf we discovered the inner structure of these compounds. We used two XRD machines courtesy of the chemistry department.

1.1 Historical Background

It is often thought the pioneers of XRD were father and son team of Sir William Henry Bragg and William Lawrence Bragg. However, they merely showed that diffraction can be thought of as reflection between two crystal planes and then used it to determine the crystal structure of numerous compounds. When in fact the first discovery of XRD was done by Max von Laue and his colleagues Paul Knipping and Walter Friedrich in 1912. [4] Laue first hypothesized, after learning that X-rays had wavelengths corresponding on the atomic scale, that X-rays would be diffracted when passing through substances. [3] In Fig. 1 you can see the first ever diffraction pattern done by von Laue. The Bragg's saw von Laue's work and built upon it and refined it the following year in 1913. The Bragg's subsequently won the Nobel Prize in physics for their work on XRD in 1915.



Figure 1: Max von Laue and the first ever XRD pattern (copper sulfate).

Over the following years the equipment improved and the analysis was enhanced, but the major contribution for this laboratory was made by Hugo Rietveld in the 1960's. He used non-linear least squares approach to fit the experimental data. This allows for finer precision in determining the properties of the crystals we are studying. The FullProf software does the Rietveld refinement for us, so we will neglect the theory of it, for sake of clarity.

With out a doubt XRD has been extremely useful in all areas of science, not just physics. For instance, the structure of DNA was discovered by James Watson and Francis Crick in 1954 using the XRD data that Rosalind Franklin had produced, see Fig. 2 for the diffraction pattern of DNA. XRD was the first and is still one of the most efficient and accurate way

to probe the atomic scales. In total there has been 14 Nobel Prizes awarded for study of X-Rays and X-Ray diffraction.[2]

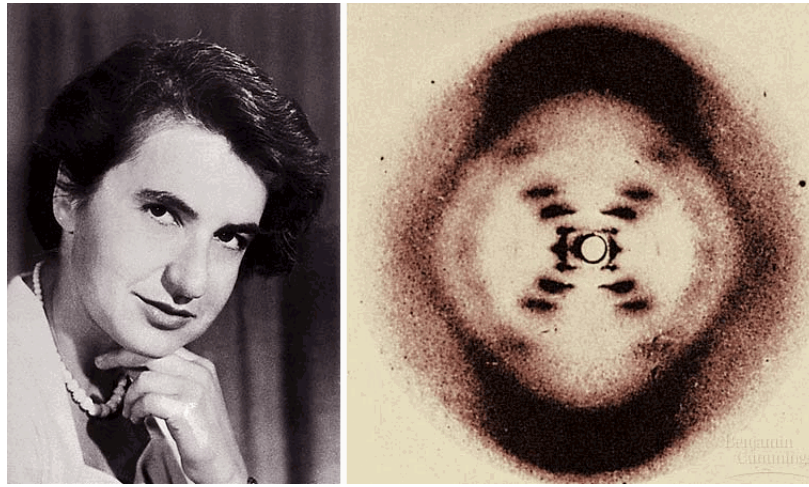


Figure 2: Rosalind Franklin and the XRD pattern of DNA.

1.2 Physics of X-Ray Diffraction

As mentioned previously he Bragg's showed that diffraction is geometrically equivalent to reflection of off parallel lattice planes.

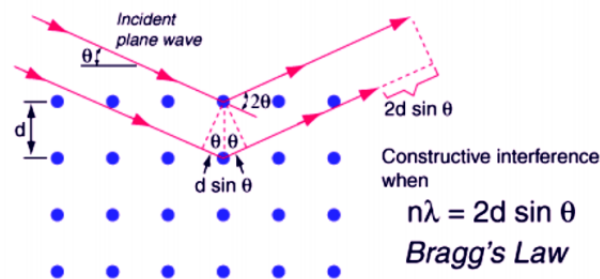


Figure 3: Bragg's Law [?]

As seen in Fig.3 the X-Rays come in parallel and leave parallel. One X-ray reflects off of the lattice plane below the surface lattice plane. Since the lower X-Ray travels a farther distance it will be out of phase with the upper X-Ray. X-Rays being electromagnetic waves however, will have points are constructive (meaning the phase is an even integer times π) or destructive (meaning the phase is an odd integer times π) . In terms of wavelengths the constructive condition is that the extra distance the lower X-Ray must travel are integer wavelengths. The extra distance can be found geometrically using Fig. 3. Going into the sample the lower X-Ray still has the distance $d \sin \theta$ to go until it is reflected. After it is reflected the lower X-Ray has another $d \sin \theta$ to go until it's direction is perpendicular to the upper X-Rays direction at the location of the upper reflection point. This essentially means

that there are certain angles at which you will get constructive interference, since ideally, d is constant. This can be mathematically expressed by Eq. 1

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

Where n is any integer, λ is the wavelength of the X-Rays, d is the atomic lattice plane spacing, and θ is the angle of entry. This equation can be interpreted as (number of wavelengths)=(total extra distance traveled by lower X-Ray).

2 Experimental Setup and Procedure

2.1 Preparing Samples

To use the X-Ray machine for powder diffraction we lathered Vaseline onto the slides then placed the powder onto the slides. The Vaseline is to prevent the powder from falling off of the slides because the sample mount rotated as well as the detector. Due to the large grain size of the table salt and the unknown compound we had to grind the samples until it was a fine powder. The other compounds were already fine enough for accurate readings. We measured the diffraction pattern from a sample holder with Vaseline to compare to our samples to differentiate true signal from background signal.

2.2 Diffractometer

A diffractometer is essentially an X-Ray source and an X-Ray detector on a movable arm. Most commonly the X-Ray source is stationary and the sample mount and X-Ray detector are movable. See Fig. 4 below for a diagram of a Diffractometer.

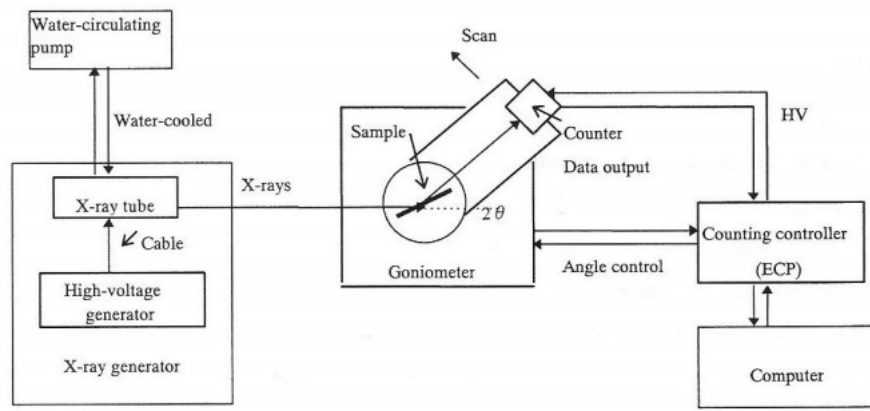


Figure 4: Diagram of diffractometer.

We used two different types of diffractometers (both manufactured by Rigaku) because cobalt oxide fluoresces. The first diffractometer did not have a monochromator in between the sample and the detector. The monochromator blocks all electromagnetic radiation outside

of a given bandwidth. The location of the monochromator is key because if we placed it between the source and the sample then the X-Rays caused by fluorescence of the sample would still be created and picked up by the detector. The difference in intensities can be seen in the cobalt oxide data. For the data without the monochromator we see a large increase in intensity as a function of θ . This for obvious reasons makes it difficult to fit the data to standard purely diffracted peaks. Refer to reference [1] for more details on the diffractometer as well as our lab report on X-Ray fluorescence.

3 Data and Analysis

Our raw data comes in the form of data files which can be either plotted as 2θ vs. intensity (I) or opened using FullProf and analyzed through the program. Through FullProf we also produced visualizations of the crystal lattices. For the following graphs the red line corresponds to the actual data, the black thin line corresponds to the fit function, the blue line is the difference between the fit and the data and the green dashes represent known lattice planes. Note that the relative intensities change between the graphs corresponding to different number of lattice planes, preferred orientations, uniformity of crystal powder.

Our refinement algorithm for all samples is as follows:

1. Vary background polynomial, B factor and intensity scale. Fix all other parameters. Repeat this until fit function peak positions match data.
2. Let a, b, c vary with previous variable parameters fixed.
3. Fix a, b, c values. Then vary (until convergence) u, v, w one at a time.
4. Refine B factor again with new u, v and w values.

This allowed for the most accurate fitting of data. Following this algorithm gives us consistency between fits as well.

3.1 Aluminum and Vaseline Holder

The first peak we analyzed was the sample holder so we distinguish background from actual signal. We use aluminum sample holders because it has very distinct, sharp peaks that are easily subtracted from other data. The grayed out region of the data is due to the Vaseline. We will see a slight bump for the other samples at 2θ angles of less than 25° . Every other peak is characteristic of aluminum as marked by the green dashes. From the ICSD database (reference [5]) we found that the space group for aluminum was F m $\bar{3}$ m. Using the .cif file (crystallographic information file) from the ICSD database we inputted the lattice parameters and ran Rietveld refinement of the fit function.

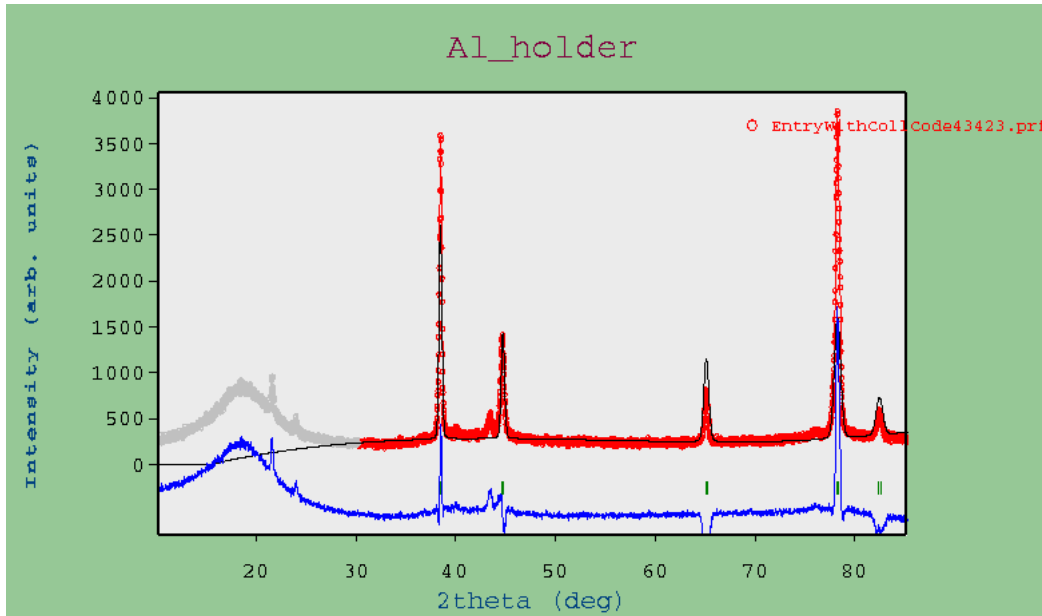


Figure 5: Aluminum sample holder with Vaseline. The gray region corresponds to the Vaseline so we excluded it for fitting the aluminum data.

Note that the fit function peaks are slightly off actual data peaks. This is because of irregularities in the samples crystals. This is most notably seen at the $2\theta = 78.5^\circ$ peak and is indicative of the preferred orientation. Also, note that the double peak at an angle $2\theta = 43.5^\circ$. We believe this is also attributed to the irregularities in the sample such as defects and impurities.

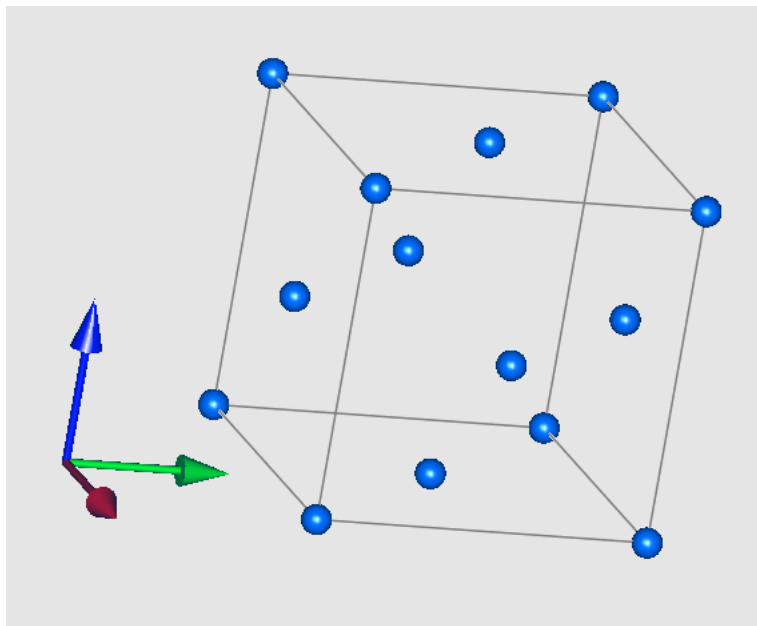


Figure 6: Aluminum crystal structure. It is a face centered cubic with space group $Fm\bar{3}m$.

Since aluminum is face centered cubic (FCC) then we know that $\alpha = \beta = \gamma = 90^\circ$ and that $a = b = c = 4.05 \text{ \AA}$. We summarize our results below.

Table 1: Crystallographic planes and lattice spacing of aluminum.

Peak (2θ)	(hkl)	d_{hkl}
38.5°	(111)	2.34Å
43.5°	(200)	2.03Å
65.0°	(220)	1.43Å
72.0°	(311)	1.22Å
82.5°	(222)	1.17Å

The last column d_{hkl} is the lattice spacing d in Eq. 1. We calculate d_{hkl} by the following formula

$$\frac{1}{d_{hkl}} = \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}} \quad (2)$$

Where h, k, l are the Miller indices and a, b, c are the lattice parameters.

3.2 Silicon Crystals

Silicon is a FCC just like aluminum, however, it has a basis as well that gives it a diamond structure. The space group is F m -3 m: 1. The extra : 1 accounts for the basis vectors. The structure factor comes into play for silicon because we have peak cancellation. The structure factor F tells you how the X-Rays interact with atoms, the f is characteristic of each type of atom. The larger the F the larger the intensity ($I \propto |F|^2$). The structure rules of silicon (and all diamond shaped crystals) are:

- h, k, l have mixed parity then $F^2 = 0$
- h, k, l are all odd then $F^2 = 32f^2$
- h, k, l are all even and exactly divisible by 4 then $F = 8f$
- h, k, l are all even and not divisible by 4 then $F^2 = 0$

This tells us that there are two groups of crystal planes that give us peak cancellation and two groups that don't. We see in Fig. 7 that there is only peak that is canceled in our data corresponding to a $2\theta = 58.5^\circ$. There is also extra peaks corresponding to the same peaks that we saw in the aluminum sample holder. Those peaks are $2\theta = 38.5^\circ, 43.5^\circ, 65.0^\circ$ and 82.5° which all correspond to the peaks of aluminum.

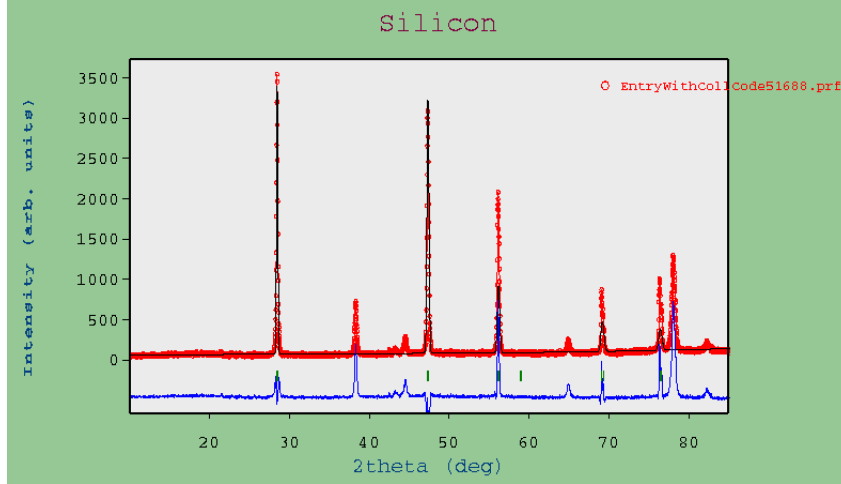


Figure 7: Diffraction pattern of silicon crystals

The lattice vectors are $a = b = c = 5.43\text{\AA}$ and the vector angles are $\alpha = \beta = \gamma = 90.0^\circ$ since silicon is FCC. In Table 2, we can see that the structure factor rules are followed. There are no mixed parity Miller indices and the (222) plane adds up to 6 which is not exactly divisible by four. Notice in Fig. 7 that there are two peaks for the (311) plane which indicates that there is a dislocation defect in line with this plane. The preferred orientation appears to be (111), but with (220) closely behind it. The difference in intensities of these two peaks is approximately 75.

Table 2: Crystallographic planes and lattice spacing of silicon.

Peak (2θ)	(hkl)	d_{hkl}	Canceled
28.5°	(111)	3.13Å	No
47.5°	(220)	1.92Å	No
56.0°	(311)	1.63Å	No
59.0°	(222)	1.57Å	Yes
69.0°	(400)	1.36Å	No
76.5°	(331)	1.25Å	No

Comparing our a value to established a values of 5.431\AA we see that there is very little difference to the number of significant digits. One thing to note here is that even though we have four extra basis vectors, we only get one extra lattice plane. This is due to the symmetry of the diamond structure. We show below the atomic structure of the silicon crystals from two different perspectives. The green, red and blue axis correspond to the a, b and c directions, respectively. However, due to the cubic structure and symmetry of the diamond these are arbitrary and could be switched in any combination without harm.

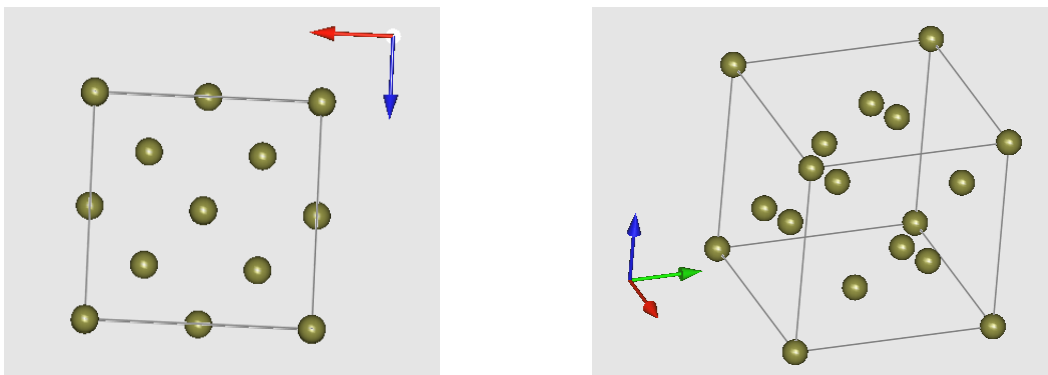


Figure 8: Silicon FCC crystallographic structure. We show two different perspectives of the diamond structure due to its complexity of having four extra basis atoms.

3.3 Table Salt (NaCl)

Sodium chloride is a very common compound with crystalline structure. The average salt crystal is much too large to get accurate data so we first ground the salt to a very fine powder.

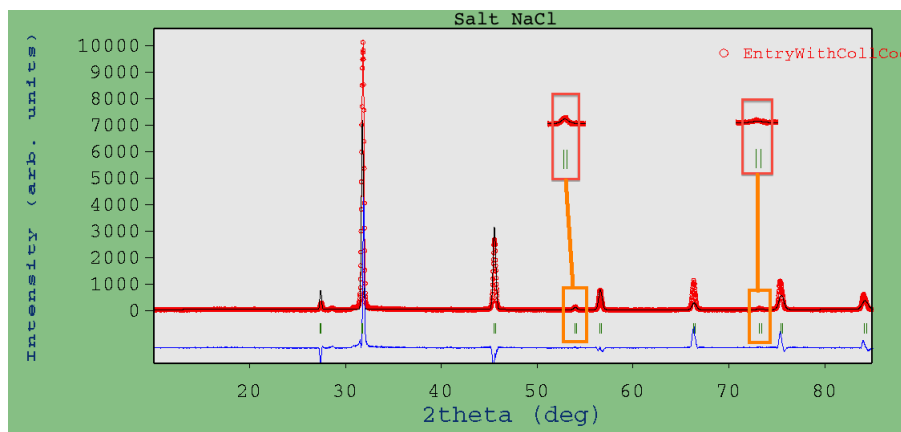


Figure 9: Diffraction pattern of salt crystals.

At first glance of Fig. 9 you may think there are two canceled peaks, however, looking more closely (and looking at difference line) we see that they are actually a near perfect fit. There are no extra peaks so we know all peaks correspond to NaCl. The space group of salt is $Fm\bar{3}m$. Once again we have $\alpha = \beta = \gamma = 90^\circ$ which corresponds to cubic structure, more specifically a body centered cubic (BCC). The lattice vectors are $a = b = c = 5.66\text{\AA}$ and have a basis (corresponding to the Cl^- atoms). In Table 3 we summarize the data of the nine peaks.

Table 3: Crystallographic planes and lattice spacing of table salt.

Peak (2θ)	(hkl)	d_{hkl}
27.0°	(111)	3.27Å
31.5°	(200)	2.83Å
45.5°	(220)	1.99Å
54.0°	(311)	1.71Å
56.0°	(222)	1.63Å
66.0°	(400)	1.41Å
73.0°	(331)	1.30Å
75.0°	(222)	1.27Å

It is clear from the peak shapes that there is a preferred orientation of (200). The small peaks are due to the structure factor rules of NaCl, but we have predicted the intensities quite well using FullProf and Rietveld refinement. As you can see in Fig. 10, it is easier to see NaCl's atomic structure because of the chlorine basis, as compared to the diamond structure of silicon.

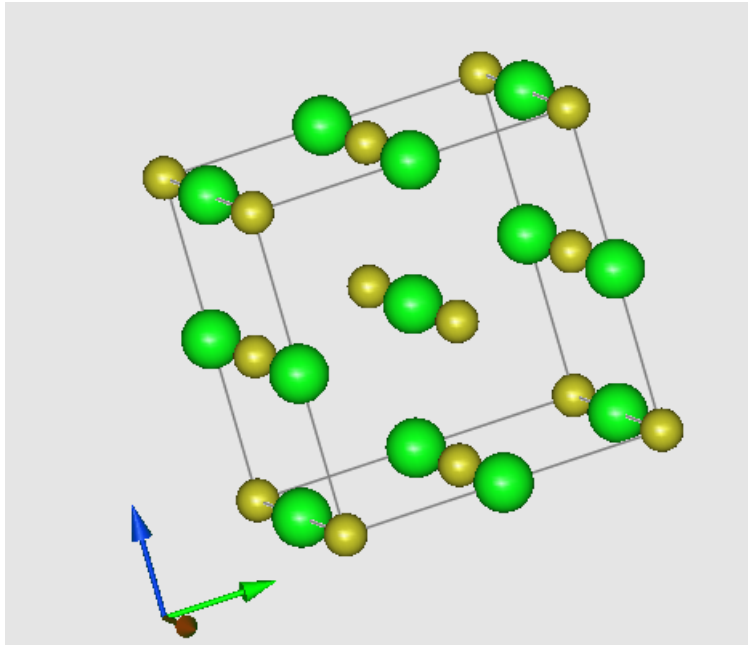


Figure 10: NaCl crystallographic structure. Smaller atoms correspond to the sodium (Na^+) and larger correspond to the chlorine (Cl^-).

3.4 Cobalt (II, III) Oxide Co_3O_4

Cobalt oxide is an antiferromagnet and extremely harmful compound for the environment. Below in Fig. 11 we show a comparison between NaCl (red) and Co_3O_4 (thick dark blue). As you can see its diffraction pattern is very unique. This is because we are actually seeing X-Ray fluorescence of the compound. To learn more about X-Ray fluorescence see our first

lab report. To combat this issue we used a diffractometer that has a monochromator between the sample and the detector so that it filtered all photons outside of a given frequency range.

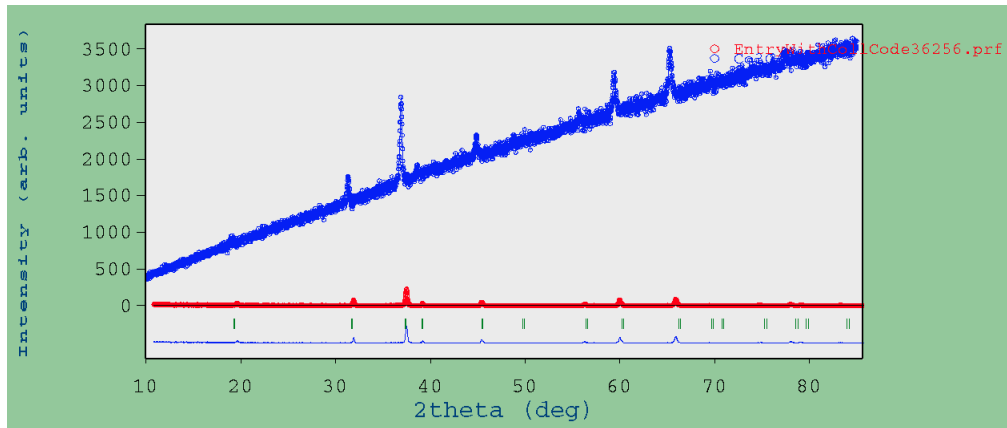


Figure 11: Cobalt (II, III) Oxide Co_3O_4 without monochromator

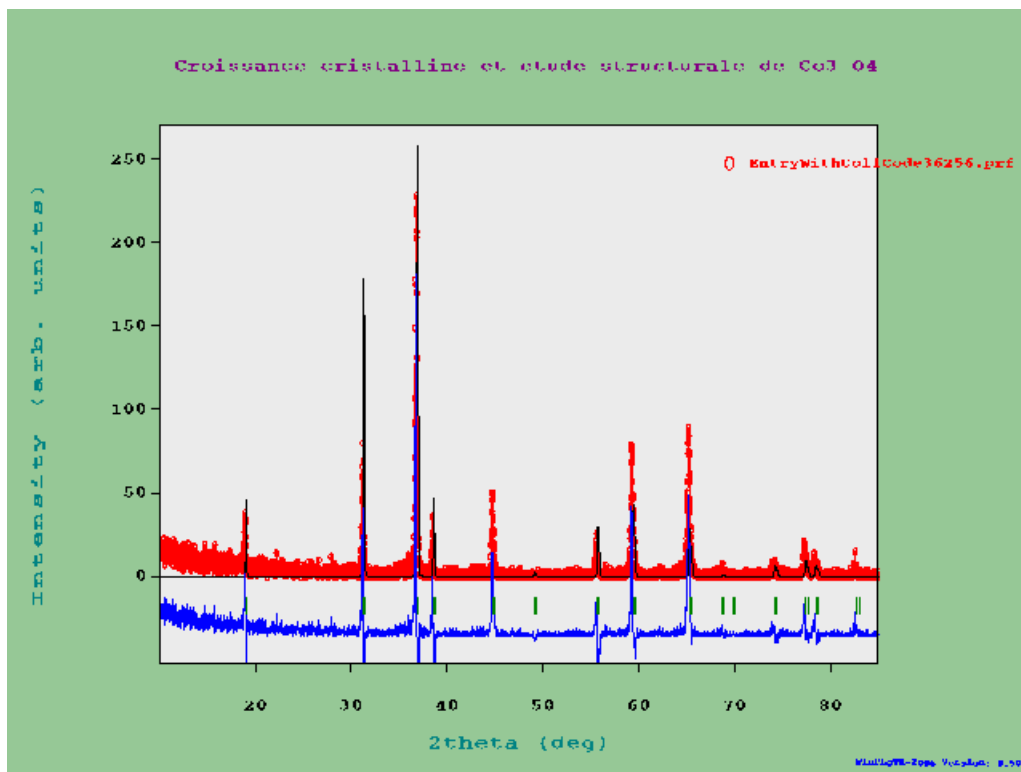


Figure 12: Cobalt (II, III) Oxide Co_3O_4 with monochromator

Below in Table 4 we summarize our results for cobalt oxide.

Table 4: Crystallographic planes and lattice spacing of table salt.

Peak (2θ)	(hkl)	d_{hkl}
19.0°	(111)	4.66Å
31.0°	(220)	2.85Å
37.0°	(311)	2.43Å
38.5°	(222)	2.33Å
45.0°	(400)	2.02Å
49.0°	(331)	1.85Å
56.0°	(422)	1.65Å
59.5°	(333)	1.55Å
59.5°	(511)	1.55Å
65.0°	(440)	1.42Å
68.5°	(531)	1.36Å
70.0°	(442)	1.34Å
74.0°	(620)	1.27Å
77.5°	(533)	1.23Å
78.5°	(622)	1.21Å
83.0°	(444)	1.17Å

In Fig. 13 below we present the atomic structure of the cobalt oxide. The lattice parameters are $\alpha = \beta = \gamma = 90^\circ$ and $a = b = c = 8.07\text{\AA}$.

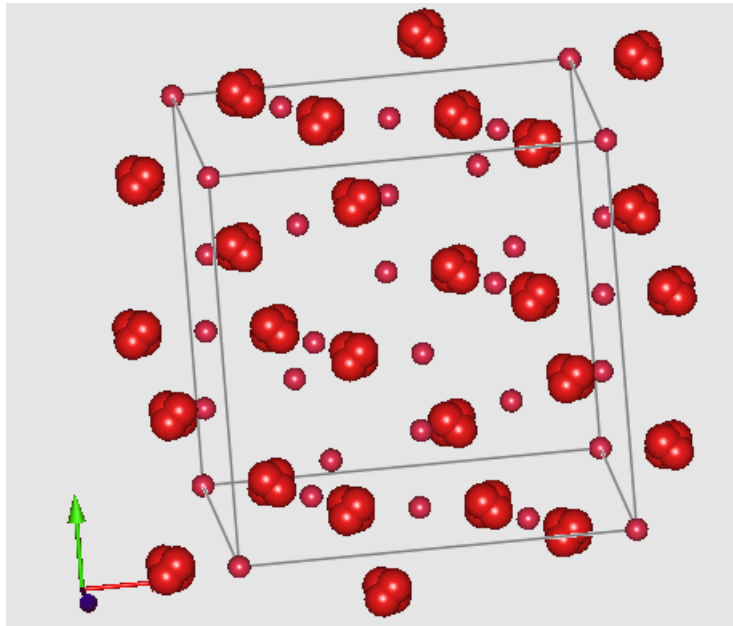
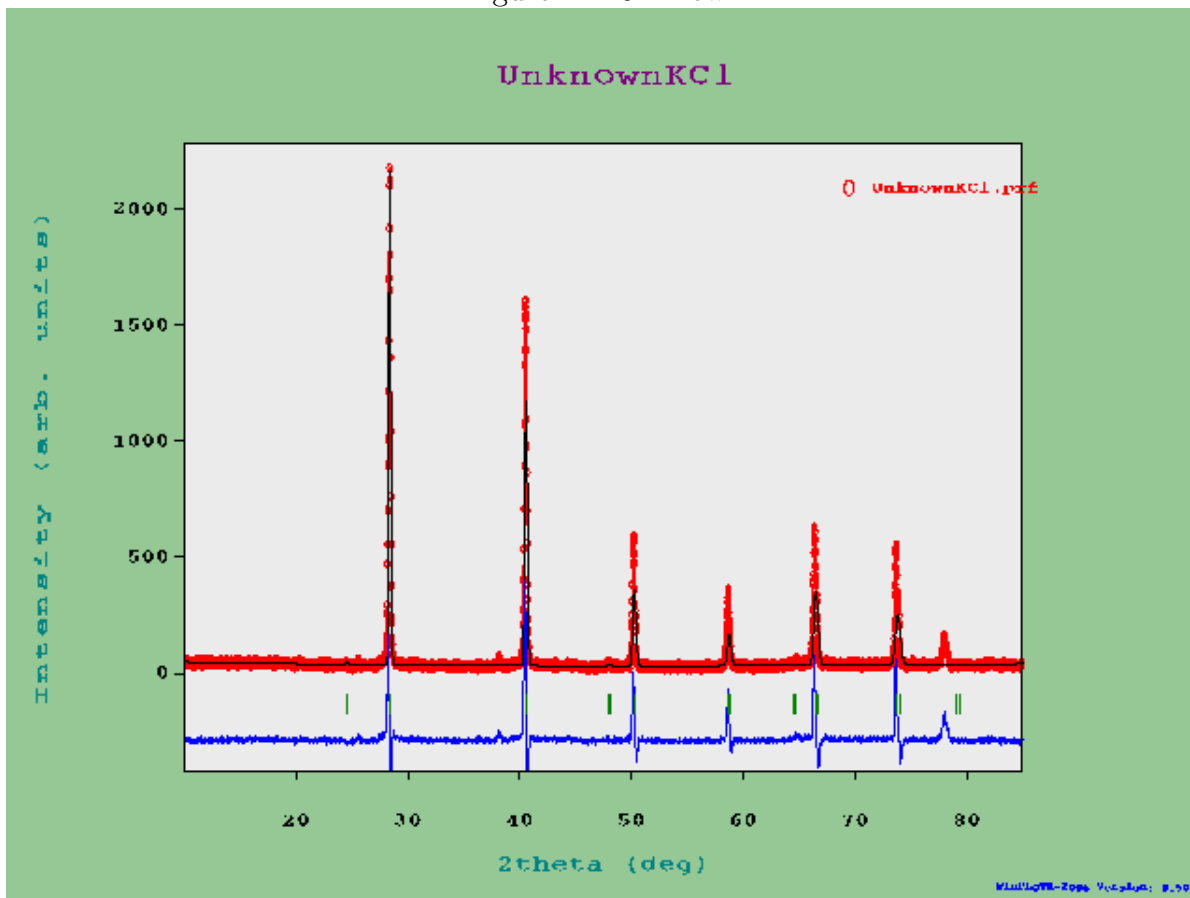


Figure 13: Cobalt (II, III) Oxide Co_3O_4 atomic structure.

3.5 Unknown

For our unknown sample we tried using the .cif files from each compound we had. We found that the NaCl .cif file corresponded the best to the unknown data. Seeing the similarities in crystal structure, space group, and looks to NaCl we decided that it was KCl, another form of table salt.

Figure 14: Unknown



Notice that all peaks are accounted for except the $2\theta = 75^\circ$. This assumed to be due to defects or irregularities for that particular lattice plane. Just as we did for all the other elements we present the results summarized in Table 5 below.

Table 5: Crystallographic planes and lattice spacing of table salt.

Peak (2θ)	(hkl)	d_{hkl}
27.0°	(111)	3.27Å
31.5°	(200)	2.83Å
45.5°	(220)	2.00Å
54.0°	(311)	1.71Å
56.0°	(222)	1.63Å
66.0°	(400)	1.41Å
73.0°	(331)	1.30Å
75.0°	(222)	1.27Å
75.0°	(422)	1.15Å

Comparing Table 5 to Table 3 we see that there is a very close correspondence, supporting our claim that the unknown sample is indeed KCl. The first peak is barely noticeable as mentioned in the lab manual as well. The lattice parameters are $\alpha = \beta = \gamma = 90^\circ$ and $a = b = c = 5.66\text{\AA}$.

4 Conclusion

We have conducted X-Ray diffraction experiments on 4 known samples and one unknown sample. Using powerful software (FullProf) we were able to get the most accurate fits of the diffraction data. This gave us the ability to calculate numerous aspects of atomic structures of crystalline structures. Using FullProf we were also able to extract beautiful crystal structure images from data. We notice that with increasing angle we got a smaller d_{hkl} , which is what we would expect for this data.

We wish we had more time to do a more careful and in depth analysis of each of the diffraction patterns. However, from just aligning peak positions we believe that it was sufficient to get the necessary data.

Some improvements we would suggest is to shorten the lab manual. Just present the actual lab and analysis methods, and let the student to do research onto the nitty gritty details. I believe FullProf should be a requirement as well. It is very powerful and essentially all scientists doing diffraction experiments. The FullProf manual could be accompanied by some screen shots for clarity, but overall it was very well written and explained.

References

- [1] Durand, Alice. Physics 134 Lab Manual XRD. Winter 2014.
- [2] Willmot, Phillip. Introduction to Synchrotron Radiation and its Applications. 2011. Wiley.
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