X6 EXPERIMENT

X-RAY POWDER DIFFRACTION

(revised November 2005, L.N. Hand)

Introduction

This experiment is an excellent introduction to crystallography, x-rays and to x-ray diffraction. For starters, read Chapter 1 of Jenkins and Snyder, *Introduction to X-ray Powder Diffractometry*, and Chapter 2 of Kittel's *Introduction to Solid State Physics* (Third Edition).

Get the lecture and the written material on radiation safety from your instructor. Learn how to use the radiation monitor. You both should then sign and date the certificate signifying that you have read and understood the safety material.

Either the instructor or Nick will show you how to operate the x-ray generator and give you darkroom and film handling instruction. The x-ray unit has a copper target, and uses 35 KV and 15 ma. There is a nickel filter, which must be in place when you make the exposures. Learn about copper K_α and K_β radiation.

Photograph the powder patterns of NaCl and KCl first. Do this, and analyze the patterns before proceeding. Show the results to your instructor and look at the sample results for NaCl in these notes. A typical exposure is 3 hours (use the timer). There may be residual K_β lines, so take another picture without the Ni filter for about half the exposure time. When you have identified all the lines on the KCl and NaCl films, you will have understood the difference between simple cubic , body-centered, and face centered cubic lattices.

Next, photograph the lines from one or more of the unknowns. Be sure to record the number of the unknown, so that later you can see if your identification is correct.

Do not forget to make a record in the logbook every time you make an exposure. This, and the signed safety certificate, is a legal requirement by the University.

THE DISCOVERY OF X-RAY POWDER DIFFRACTION

The existence of x-rays was only discovered a little more than a century ago. And yet, x-rays have played an essential role in understanding the structure of materials on an atomic scale. This work is still going on—only a few years ago, a group working at CHESS decoded the complicated structure of the virus responsible for the common cold, using x-rays generated at the Wilson Lab synchrotron.

X-rays were discovered by Roentgen in 1897 serendipitously. You can read the story in the book *Fifty Years of X-ray Diffraction*, edited by P.P. Ewald (Physical Sciences Library, QC482.E94). In 1912, von Laue discovered x-ray diffraction from crystals, after he was told by the famous theoretical physicist Sommerfeld that coherent diffraction from atoms in a crystal was not possible, due to the thermal motion of the atoms.

The subject of this experiment is x-ray powder diffraction. This also came to be found unexpectedly. We quote Scherrer (from the Ewald book, page 643):

For the sample I used the finest grain powder of lithium fluoride; Debye and I were most surprised to find on the very first photographs the sharp lines of a powder diagram, and it took us not long to interpret them correctly as crystalline diffraction on the randomly oriented microcrystals of the powder. The diffraction lines were much too sharp than that they could have been due to the few scattering electrons in each single atom. That in lithium fluoride we picked a cubic crystal powder with exceptionally favourable scattering properties was a piece of good luck.

STEP-BY STEP: A PRACTICAL GUIDE TO POWDER DIFFRACTION

1. For a brief overview, read Jenkins and Snyder, Chapters 1 and 3.1-3.5. (a list of references is at the end of this guide.) Understand Bragg diffraction from a crystal and from a powder. Why does a randomly oriented polycrystalline material diffract x-rays into "cones" of different Bragg angles? What information can you get from these angles. You should read more about x-rays than the minimum suggested above.
2. Examine the powder diffraction camera. Read the "Instructions for operation" (North American Phillips). Learn how to use the alignment on the center wheel.

3. Take a sample of film and practice loading the film with your eyes closed or in total darkness. Show the result to your instructor who will check the film is properly clamped.

4. Mount the camera on the x-ray generator and, with your instructor, check the alignment. You can read the details of how to do this on page12.

5. Fill a 0.4 mm capillary tube with NaCl. See page 10 for hints on how to do this.

6. Get instructions on film handling and development from Nick. It is VERY IMPORTANT that you do not allow the film supply to be exposed to any light.

7. Arrange the exit and entrance collimators so that you can distinguish them in the dark. Then cut the film (2 different cuts) and punch the holes with care about alignment in the jig.

8. Turn on the X-ray generator with your instructor present the first time, sign the log book and expose for 3 hours at 35 KV and 15 ma. Be sure the pulley is connected to the motor, and is turning (very slowly). Set the timer for 3 hours.

9. Develop the film (4 ½ minutes), stop bath, fixer and wash the film. Hang it up to dry.

The analysis of the film is described on pages 7ff. The next three pages are figures taken from the *Instructions for Operation*, North American Phillips Co. Nick has a copy of this manual.

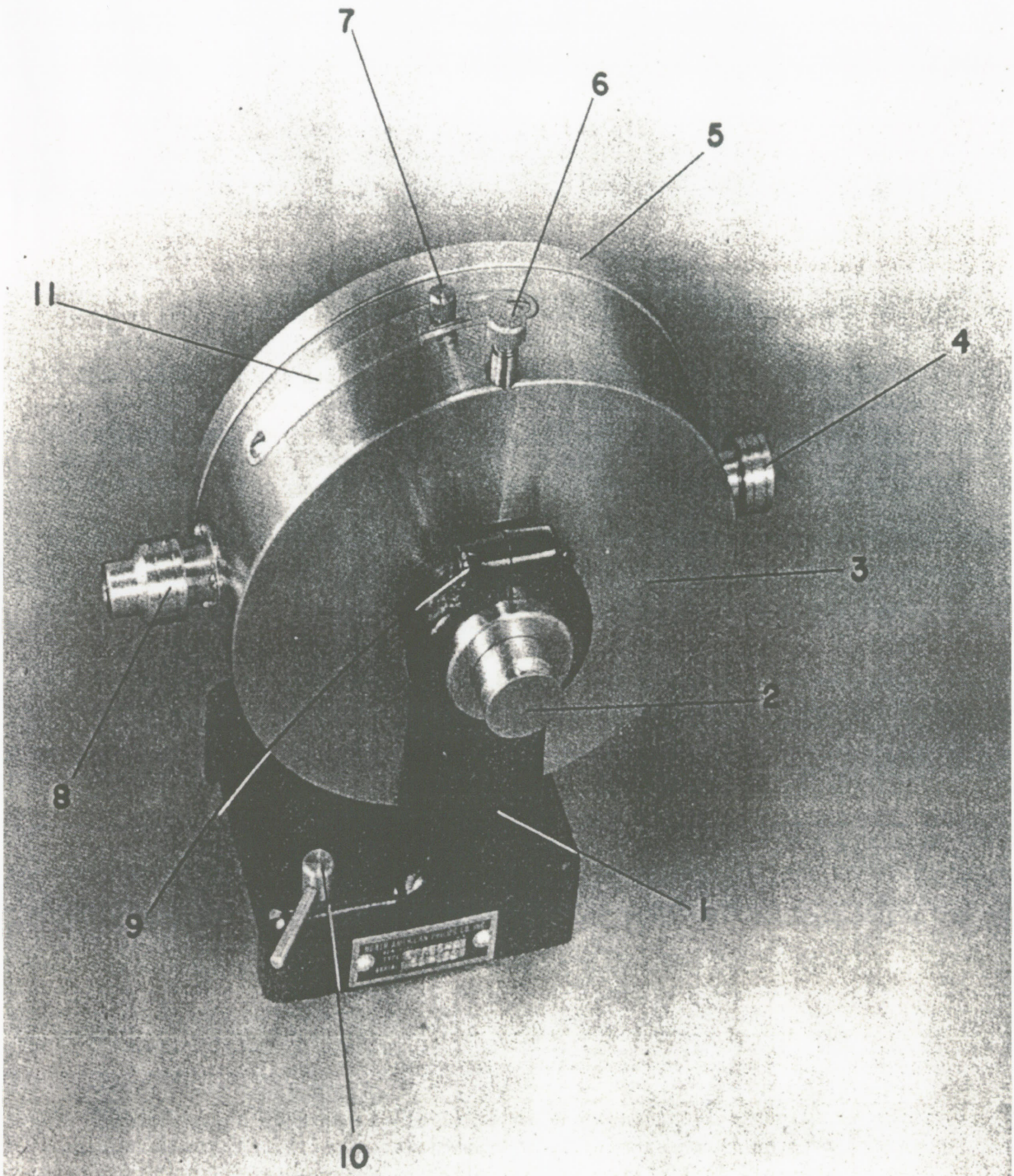
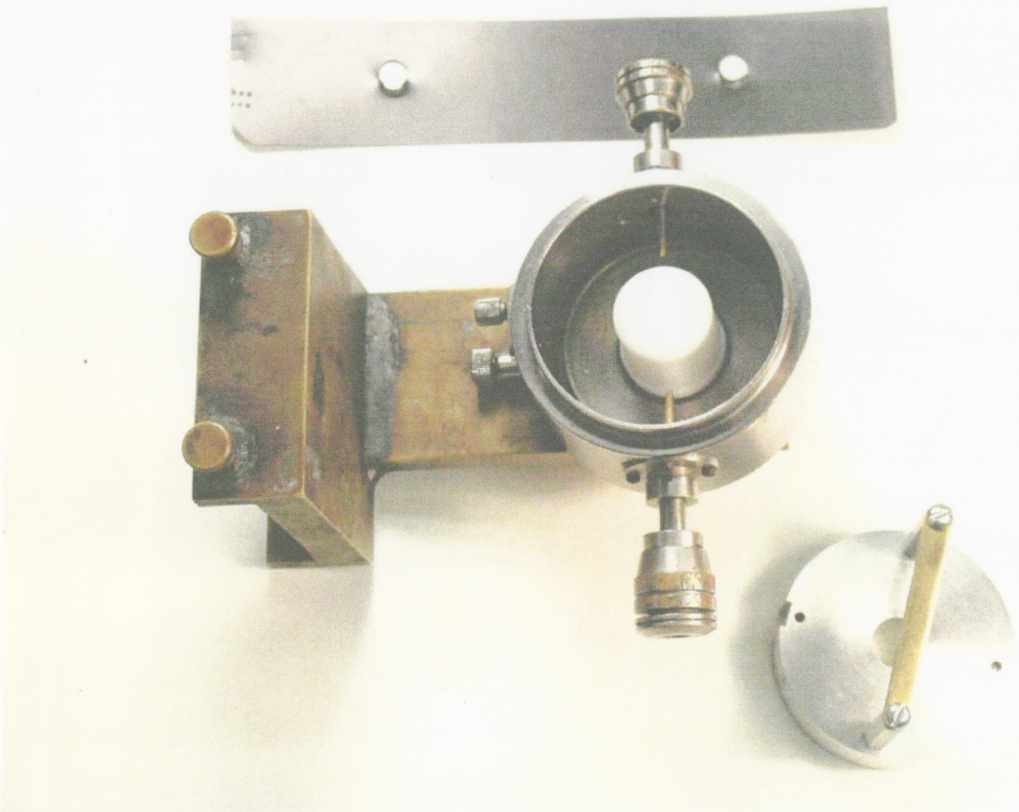


Fig. 1

KEY TO FIGURES

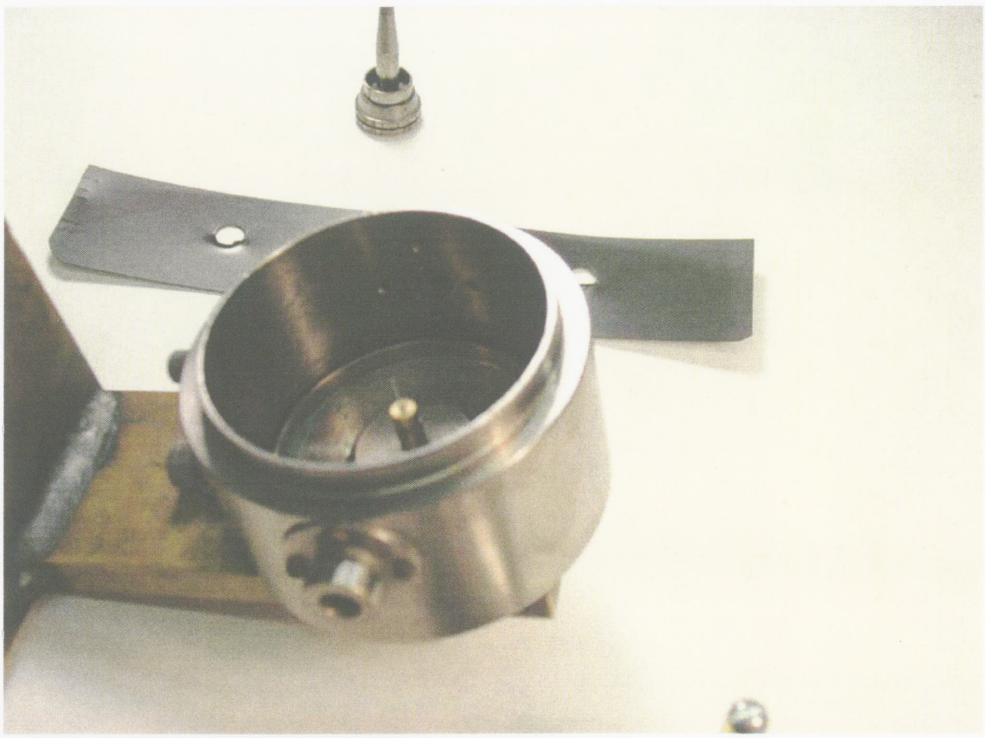
1. Support post
2. Pulley for rubber o-ring for rotation of sample
3. Camera body
4. Entrance Collimator
5. Removable camera back
6. Adjusting screw for sample support base (not used, use jig constructed by Nick instead for alignment.
7. Clamp pin screw. Used for holding down film up against the camera inner wall.
8. Exit Collimator
9. not used here
10. not used on our camera, has screws instead



Components of x-ray powder diffraction camera.

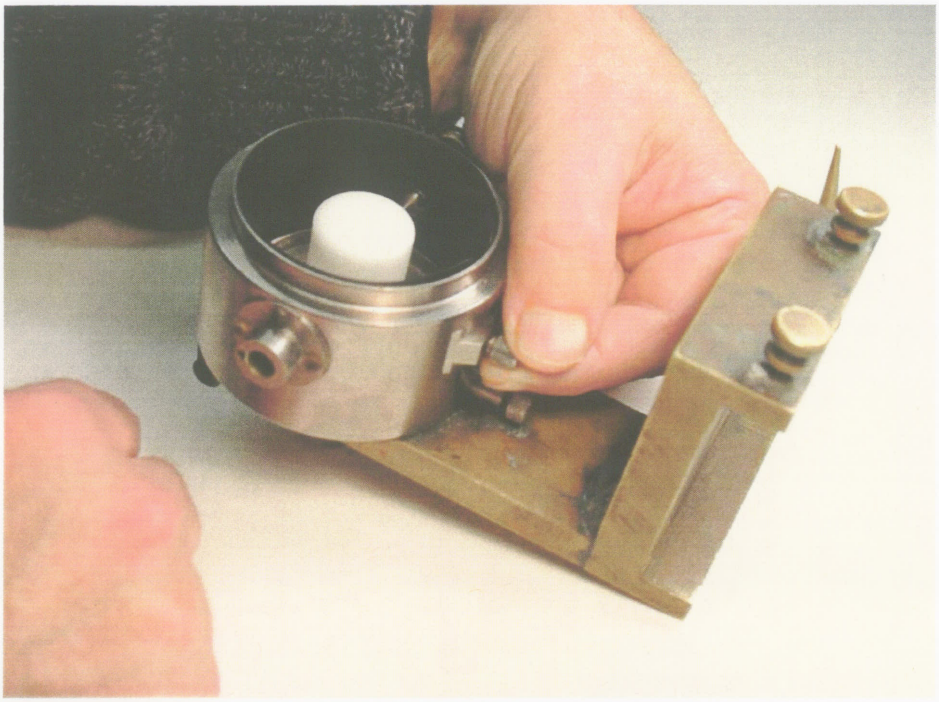
Top: film strip after holes are punched.

Middle: camera with top off, showing plastic capillary guard. Exit collimator and entrance collimator are reversed from correct positions.
Bottom right: alignment tool, to align the rotating wheel holding the brass capillary holder.

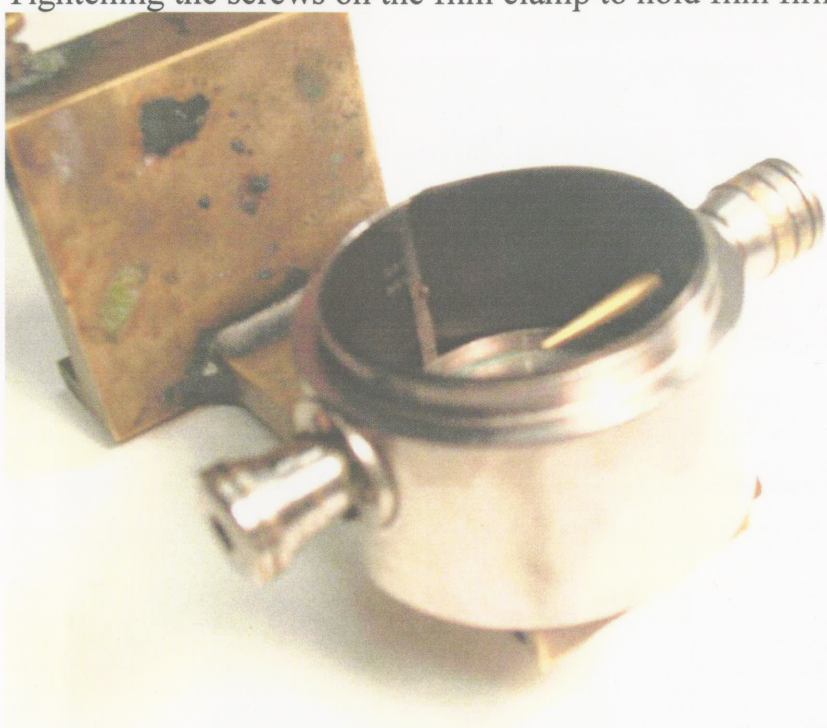


View of brass capillary holder and glass capillary tube filled with powder.

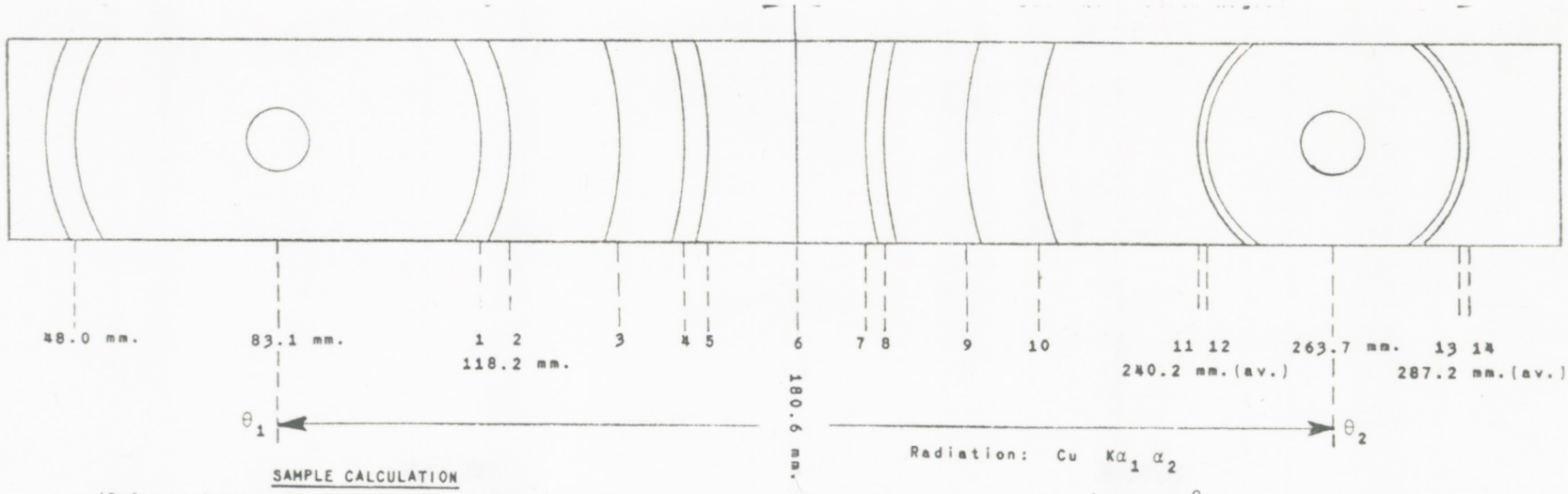
Inserting the film. Use collimator to help hold it in place.



Tightening the screws on the film clamp to hold film firmly against camera body.



Film is now held firmly in position. Plastic guard is removed, and collimators inserted all the way. Ready to put the top on and make an exposure.



SAMPLE CALCULATION

(Refer to Section IV, Measurement and Calculation)

1. Locate positions of lines employing millimeter scale, reading along center line of film. Zero mark on scale meed not coincide with any line. Enter values so obtained as S_1 values in column 2.

2. Determine pattern centers θ_1 and θ_2

   $\theta_1 = (\frac{48.0 + 118.2}{2}) = 83.1$ mm; $\theta_2 = (\frac{240.2 + 287.2}{2}) = 263.7$mm.

   $\theta_2 - \theta_1 = 263.7 - 83.1 = 180.6$ mm., therefore, since correct length on exposure was 180 mm; each measurement must be multiplied by $\frac{180}{180.6} = 0.996$.

3. Subtract 83.1 mm. (θ_1) from each S_1 value. Enter in column 3 as S (uncorrected).

4. Multiply each value in column 3 by 0.996 to get S (corrected). Enter in column 4 as S (corrected).

5. Divide values of S by 2 and enter in column 5. This value gives the Bragg angle in degrees since 2 mm. equals 1^0 Bragg (In the 57.3 mm. camera the figure in column 4 would be employed since 1 mm. on the film equals 1^0 Bragg).

6. In column 6 enter corresponding values of Sin θ.

7. In column 7 enter 2 x Sin θ.

8. In column 8 enter values of "d" from formula $d = \frac{\lambda}{2 \times \text{Sin } \theta}$

9. In column 9 enter relative intensity values of lines

10. Using data in columns 8 and 9, ASTM (Hanawalt) tables may be consulted.

Line #	S_1 mm.	S Uncorr. $(S_1-\theta_1)$	S corr.	$\frac{S}{2}(\theta^0)$	Sin θ	2 Sin θ	d	$\frac{I}{I_1}$
1	118.2	35.1	34.95	17.47	.3000	0.600	2.57	1.0
2	123.7	40.6	40.43	20.21	.3455	0.691	2.22	0.8
3	142.0	58.9	58.71	29.35	.4901	0.980	1.57	0.8
4	153.5	70.4	70.12	35.06	.5743	1.148	1.34	1.0
5	157.0	73.9	73.6	36.8	.5990	1.198	1.29	0.4
6	171.0	87.9	87.55	43.77	.6913	1.383	1.11	0.2
7	181.5	98.4	98.00	49.00	.7547	1.509	1.02	0.6
8	185.0	101.9	101.49	50.74	.7740	1.548	0.997	0.6
9	199.7	116.6	116.13	58.06	.8485	1.697	0.909	0.7
10	211.8	128.7	128.18	64.09	.8993	1.798	0.858	0.8
11	240.2	157.1	156.47	78.23	.9789	1.958	0.785	0.5
1	2	3	4	5	6	7	8	9

DIAGRAM I

ANALYSIS

The basic idea in the analysis is to determine the reciprocal lattice spacing (see definition below), and plot the square of this quantity vs. the sum of squares of 3 integers (Miller indices), in such a way that you get a straight line. Alternatively, you can divide $(d^*)^2$ by the appropriate combination of squares of Miller indices (you have to guess which ones) such that you always get the same number, which is the reciprocal of the lattice constant squared. The detailed procedure for doing this is described below, in a reprint of the manufacturer's instructions.:

The formulas below only apply to the case of cubic crystals. In addition, there are selection rules that exclude certain combinations of indices from consideration, depending on whether your crystal is fcc, bcc, or simple cubic.

IV MEASUREMENT AND CALCULATION

A) STAUMANIS TECHNIQUE

Any film, after development and drying will shrink to a degree that is dependent upon a number of factors. By making use of the Straumanis technique, it is possible to correct for uniform film shrinkage and the film becomes self-calibrating. In this technique, the 114.59 mm diameter Powder Camera is designed so that 2 mm measured on the film, is equivalent to 1° Bragg angle. (see DIAGRAM 1)

The film is laid flat on the film measuring instrument and a 0° reference point in the forward reflection region is estabilshed by bisecting the distance between the corresponding diffraction line on eath side of the beam receiving tube hole in the film. To determine the 180° reference point, the same procedure is followed for the back reflection region, without changing the position of the film. Bisect the distance between the corresponding diffraction line on each side of the beam collimating tube hole in the film. The distance between the 0° reference point and the 180° reference point should be 180 mm. If this does not measure 180 mm, the correction factor will be the ratio of 180 mm to the actual measurement. For example, if the film length is found on measurement to be 178 mm all measured distances must be multiplied by (180)/(178) to get their true value. The distance of the various diffraction lines from the zero reference point is determined by reading from the scale on the film measuring instrument. The correction factor is then applied.

The resulting series of numbers divided by 2 are equal to θ, the Bragg angles. (The resulting series of numbers are equal to θ, the Bragg angles when the 57.3 mm camera is used since 1 mm measured on the film equals 1° Bragg angle).

FROM BRAGGS LAW: $\lambda = 2\, d \sin\theta$

NOW $$d = \frac{\lambda}{2 \sin\theta}$$

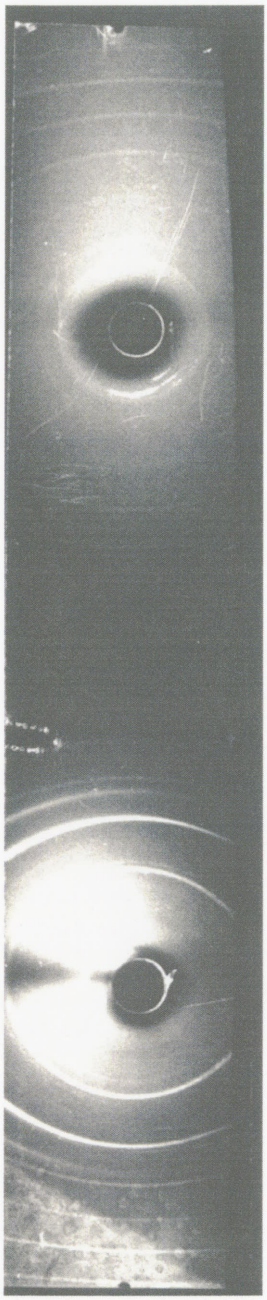
where d = interplanar spacing in A° (Angstrom Units)
λ = wavelength of characteristic radiation in A° (Angstrom Units)
θ = angle between incident x-ray beam and atomic planes in the crystallite of the specimen

Reciprocal Lattice Notation = $d^* = \frac{\lambda}{d}$

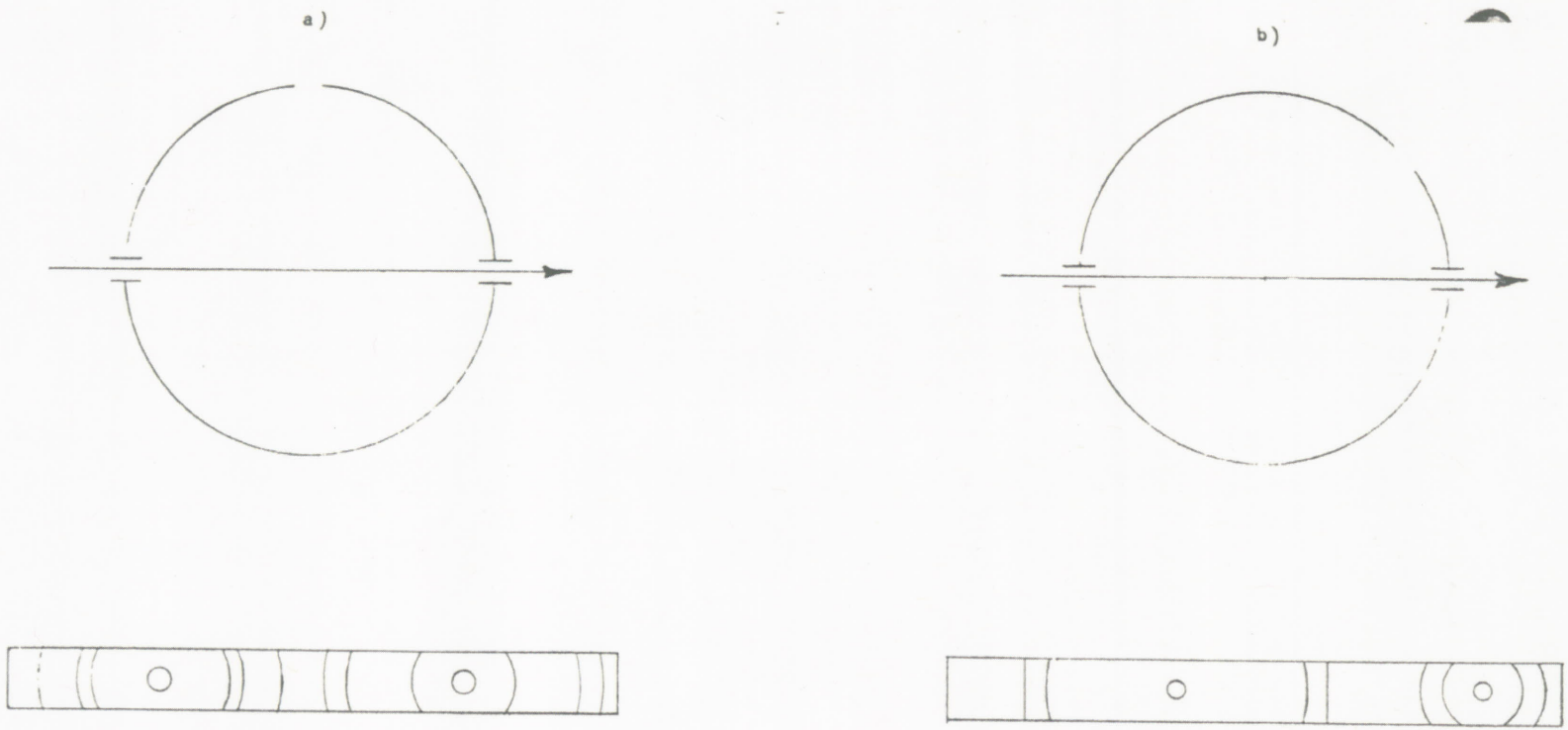
NOW $\lambda = 2d \sin\theta$ (by construction)

so that:- $d^* = 2 \sin\theta$

0.3 mm capillary



0.4 mm capillary



FILM SHRINKAGE CORRECTION METHODS

a) STRAUMANIS TECHNIQUE

b) WILSON TECHNIQUE (MODIFIED STRAUMANIS TECHNIQUE FOR USE WITH SPECIMENS WHICH YIELD NO DIFFRACTION LINES IN THE BACK REFLECTION REGION)

HOW TO FILL A CAPILLARY

The best results are obtained with either 0.3 mm or 0.4 mm capillaries. The 0.3 mm are more difficult to fill than the 0.4 mm tubes, but give slightly better results. Filling these tubes requires a certain degree of care and patience: it pays to follow a standard procedure, and not to rush.

Here is one way that worked for Nick. The NaCl and KCl are available in powder form. A small amount of this powder is placed in a clean vessel and mixed with ethanol (available from Nick). It is then poured into a small test tube and thoroughly shaken. Before it has a chance to settle, pour some of this into the capillary you want to use after you have carefully broken off the small bead at the smaller end of the capillary. Urge the material, which settles fairly quickly, down into the small diameter of the capillary tube with either a tungsten wire(Nick again) or using a glass tube of a larger diameter as a plunger. With some luck and a bit of patience, you should get a small plug of the sample part way down the narrow part of the capillary.

Then repeat this operation until you build up at least one half inch of your sample in the body of the tube.

Finally, break off the tube just below the filled part and insert it into the brass piece which mounts in the camera, placing a very small bit of modeling clay at the bottom of the brass sample holder.

Before even starting to do this, check that the brass holder will actually allow you to insert the capillary all the way to the bottom, then start the filling operation. Also, use the aluminum alignment tool (Nick or your instructor) to set the rotating wheel alignment in the camera so that it is centered. This tool should go all the way to the bottom when you seat it in the camerat. Then, very carefully, seat the holder together with the sample, in the camera.

Important: at least 3/8 inch of the sample should protrude above the top of the sample holder. Check that the beam actually passes through the sample by making a careful inspection after the entrance and exit collimators are inserted .(They have to be removed in order to load film into the camera.).

As a final step, insert the plastic sample cap so that it is secure. Its purpose is to prevent you from accidently breaking the sample when you are loading the film in the dark.

TIPS ON LOADING THE FILM IN THE DARK

Before you turn out the lights, arrange everything on the table so that you can locate: the camera, the two collimators (you do not want to mix them up) and the

brass cap sealing the light from the camera. Now turn off the lights and work in **total darkness.**

We assume you have been briefed by Nick or the instructor on how to get film from the film storage box. Your first priority is to preserve the rest of the film in the storage box, so replace the lead top and velvet curtain after you have made the first (longitudinal) cut to separate the piece you want to use. After the rest of the film is secure, make the second cut to trim a small amount off the length. It is important that the film strip be exactly the right length.

Now carefully insert it into the hole punch (in the light, before you start, check the hole punch is clear and is working freely). Precise alignment of the holes is one key to success! Punch the holes using the press on the right side of the table. If you have trouble removing the film after punching the holes, you may have to loosen the punch, which can get stuck, by using a pair of pliers.

Next, load the camera. Using both hands, form a semicircle. Insert the end of the film so that it is caught by the fixed part of the small clamp on the inner part of the camera body. Then, carefully, place the rest of the film strip around the circumference, and get it under the other(moveable) part of the two part clamp. Tighten the clamp using the set screw on the outside of the camera. Check that it is seated all the way around the circumference, both vertically in the groove at the base of the film and tight against the side everywhere. Now insert the two collimators in the holes, which should be lined up. (It may help to insert these collimators as you insert the film strip, as soon as the hole coincides with where the collimator will be.) Seal off the light with the brass top securely in place.

You can now turn ~~off~~ on the lights and proceed with the exposure. After the exposure, and before taking the film out, it is obvious that you have to remove the collimators (again, only in total darkness).

HOW TO ALIGN THE CAMERA

Proper alignment is critical for success. One simple way to see if the camera is aligned is to remove the exit collimator and measure the radiation level everywhere. (Be careful not to get in the x-ray beam..) It should be < 1 mrad/hr, except in the direct beam exiting the camera. Another test, which your instructor should do, is to remove the brass cap and place the radiation monitor right against the open side. If the collimators are aligned, the radiation level should be about 10 mrad/hr. Do not leave the cap off for longer than it takes to make the measurement. Finally, reinsert the exit collimator and see a rather faint green spot from the fluorescent screen in the collimator. The x-rays first strike a piece of black paper to keep the light out, then about half an inch of plastic, which stops the x-rays completely, and finally a fluorescent screen. No radiation should be observable when the collimator is in place, but the spot should be visible, at least in the dark.

It may be that you discover the camera is not aligned with respect to the x-ray source. The North American Phillips Company Instructions describe how to do the alignment. (Borrow a copy from Nick.)

A simple way to check it is to measure the distance from the top of the far end of the track on which the camera is mounted to the top of the table. It should be 152.8 mm +/- 0.1 mm. The top of the shutter to the track should be 110.1 mm. The track angle should be 4.5^{o} (not 6 deg.), which you can measure with an angle protractor, again from Nick.

The general background level with the camera closed, and mounted properly up against the nickel filter, and the x-ray generator set at 35 Kv and 15 ma, should not exceed 0.2 mr/hr. With an open side, it will be about 9 mr/hr if the radiation monitor is placed right up against the camera on that side. That is with only the entrance collimator in place. With both collimators installed, it drops to 6 mr/hr. If the exit collimator is removed, and the radiation monitor placed in the beam (careful!) it reads 190 mr/hr or higher.

USEFUL REFERENCES

1. *Introduction to X-ray Powder Diffractometry*, by Ron Jenkins and Robert L. Snyder. This book is in the p410-510 library. When you have more time, read Chapter 2 on crystal structure. The crystals you work with are fcc in this experiment, with a sodium chloride structure.
2. *Introduction to Solid State Physics, Third Edition,* by C. Kittel. Chapter 2 is the one you should read first.
3. *X-ray Diffraction*, B.E. Warren. A good succinct overall reference to x-ray physics. Also in our library.
4. *Elements of Modern X-Ray Physics*, by Jens Als-Nielsen and Des McMorrow. This is not in our library, but it should be. It has some of the most modern applications of x-ray physics using synchrotron radiation, and would be very useful if you ever plan to work at CHESS.
5. Mermin and Ashcroft's famous text *Solid State Physics*. This is a good reference to use for both crystal structure and x-ray diffraction in general, and the numerical values of the lattice constants of the alkali halides, which are needed to identify your unknown: Pages 63-110 cover the general topics and pages 80-81 contain tables of the lattice constants you will need to identify your unknown.
6. *Elements of X-Ray Diffraction, Second Edition,* B.D. Cullity. There are useful appendices and tables.

7. In the course library, there are many excellent older books. You should browse through these before finishing the experiment.
8. *Instructions for Operation North American Philips Large and Small Powder Cameras*, North American Philips Company, Inc. Nick has a copy of this on file.