X-RAY DIFFRACTION (DEBYE-SCHERRER METHOD)

In this experiment, the diffraction patterns of x-rays of known wavelengths will be analysed to determine the lattice constant for the diffracting crystal (NaCl).

Theory:

In 1912, Max von Laue, a German physicist, discovered that x-rays could be diffracted, or scattered, in an orderly way by the orderly array of atoms in a crystal. That is, crystals can be used as three-dimensional 'diffraction gratings' for x-rays. The phenomenon of x-ray diffraction from crystals is used both to analyze x-rays of unknown wavelength using a crystal whose atomic structure is known, and to determine, using x-rays of known wavelength, the atomic structure of crystals. As mentioned, it is the second application of x-ray diffraction that will be studied in this experiment.

The atomic structure of crystals is deduced from the directions and intensities of the diffracted x-ray beams. A crystal is built of 'unit cells' repeated regularly in three dimensions. The directions of diffracted x-rays depend on the repeat distances of the unit cells. The strengths of the diffracted beams depend on the arrangement of atoms in each unit cell. Figure 1 shows the arrangement of Na^+ and Cl^- ions in a unit cell of NaCl.
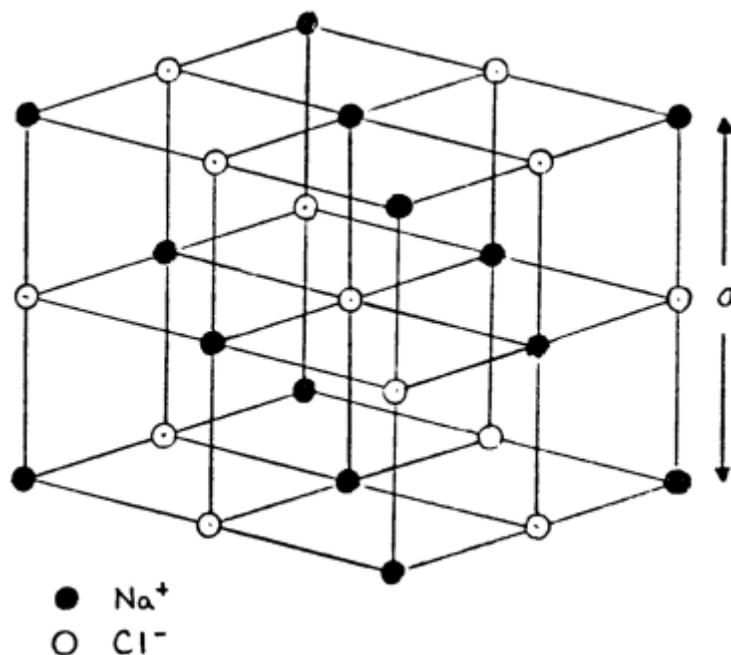
Figure 1

One method of interpreting x-ray diffraction is the Bragg formulation. The x-ray waves are considered as being reflected by sheets of atoms in the crystal. When a beam of monochromatic (uniform wavelength) x-rays strikes a crystal, the wavelets scattered by the atoms in each sheet combine to form a reflected wave. If the path difference for waves reflected by successive sheets

is a whole number of wavelengths, the wave trains will combine to produce a strong reflected beam.
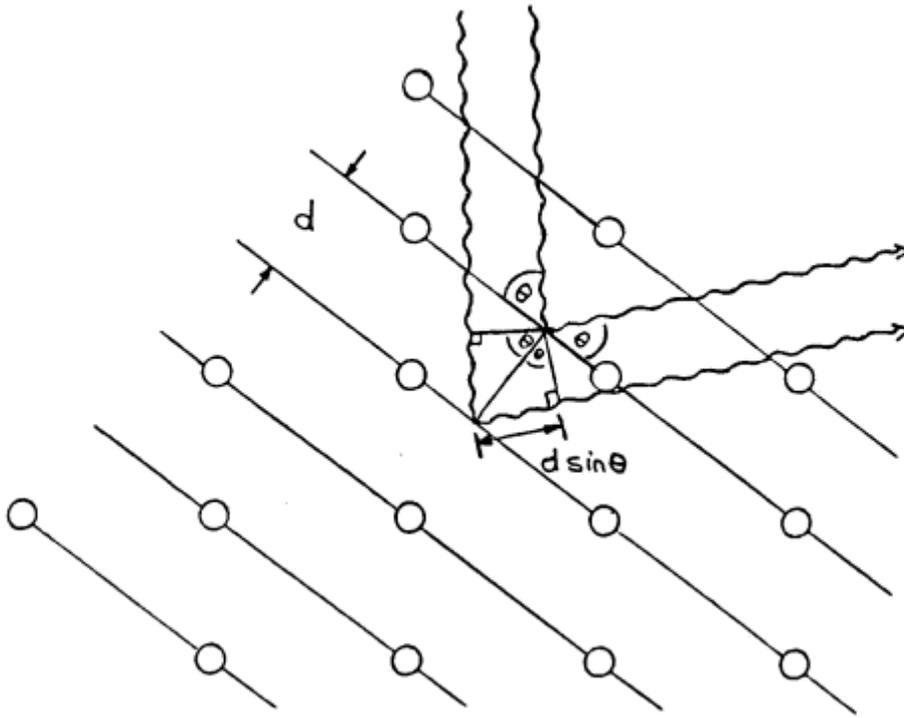
Figure 2

From Figure 2 it is seen that if the spacing between reflecting planes is d and the glancing angle of the incident x-ray beam is θ, the path difference for waves reflected by successive planes is $2d \sin \theta$. Hence the condition for diffraction (the Bragg condition) is

$$n\lambda = 2d \sin \theta$$

where n is an integer and λ is the x-ray wavelength.

The atoms of a given crystal can be arranged in sheets in a number of ways; three of the many possible arrangements of sheets in a crystal of sodium chloride are shown in Figure 3.

a) (200)

b) (220)

c) (111)
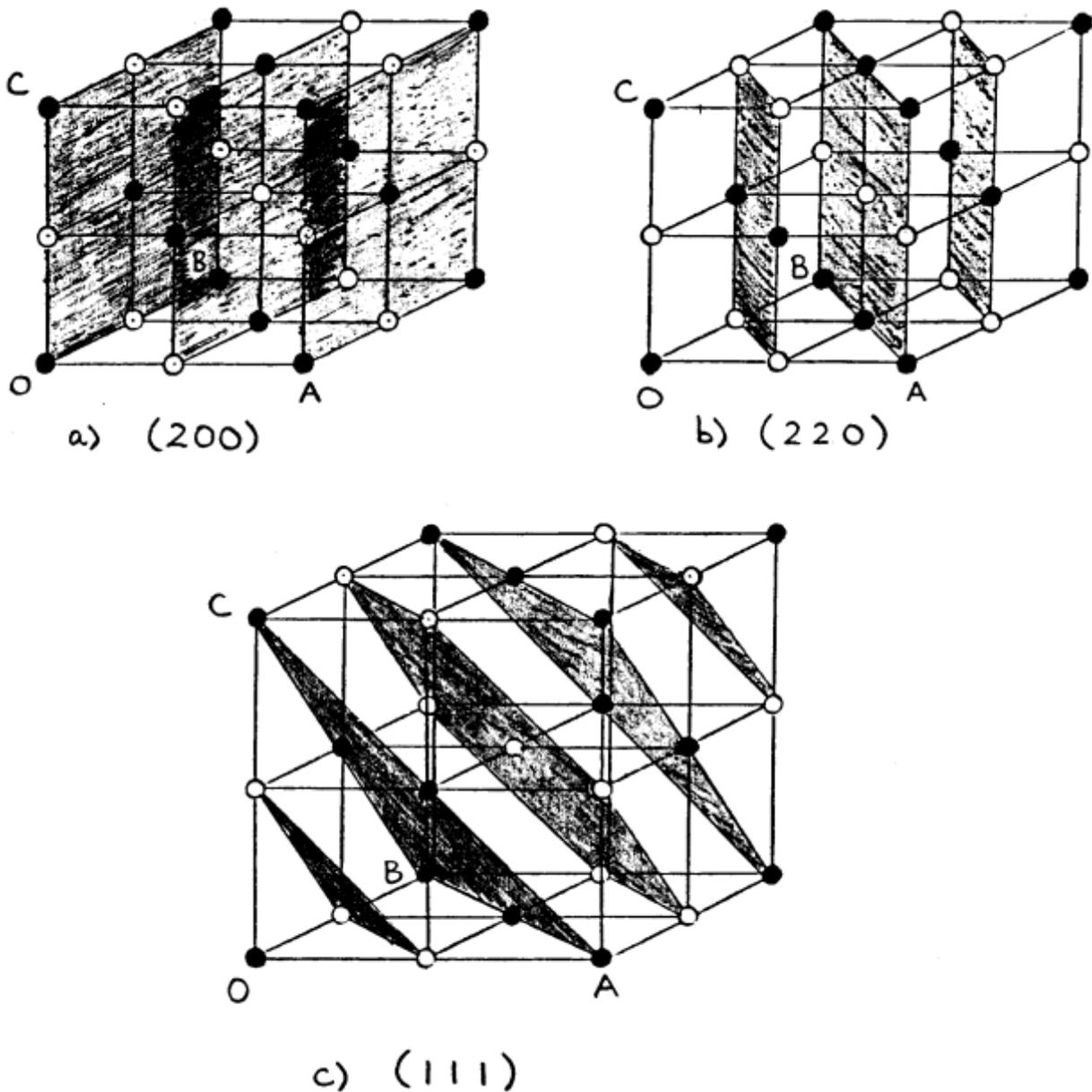
Figure 3

In these structural diagrams, the crystal axes are denoted by the letters 0A, 0B, 0C, these being the intervals at which the crystal pattern repeats. Since NaCl is a cubic crystal, $0A = 0B = 0C = a$ = the length of the edge of the unit cell, also called the lattice constant.

The equation for reflection (Bragg condition) can be satisfied for any set of planes whose spacing is greater than half the wavelength of the x-rays used (if $d < \lambda/2$, then $\sin\theta > 1$, which is impossible). This condition sets a limit on how many orders of diffracted waves can be obtained

from a given crystal using a x-ray beam of a given wavelength. Since the crystal pattern repeats in three dimensions, forming a three-dimensional diffraction grating, three integers, denoted h, k, ℓ are required to describe the order of the diffracted waves. These three integers, the Miller indices used in crystallography, denote the orientation of the reflecting sheets with respect to the unit cell and the path difference in units of wavelength between <u>identical</u> reflecting sheets.

   The wavelength path difference, m, between <u>identical</u> sheets is the greatest common divisor of h, k, ℓ. The sheet orientation is the plane containing the three points found by moving along the 0A axis h/m units, along the 0B axis k/m units, and along the 0C axis ℓ/m units, where one unit, a, is the length of the edge of the unit cell (lattice constant). If any of h, k, $\ell = 0$, the sheet is parallel to the corresponding axis. Note that for NaCl the edge of the unit cell (distance, along crystal axes, between identical atoms) is twice the Na–Cl separation.

   The sheets in Figure 3 a) are denoted $(200) = 2(100)$, indicating a path difference of 2λ between the sheet containing 0 and the sheet containing A. This is the first reflection to appear from the planes perpendicular to 0A because of the presence of the intermediate sheet located halfway between 0 and A. If the path difference between the sheet containing 0 and the sheet containing A is $(2j + 1)\lambda$, j an integer, destructive interference occurs due to the immediate sheet and no reflection is obtained. In fact for any set of sheets, each sheet of which contains both sodium and chlorine atoms, the Miller indices must be all even for reflection to occur. The other possible type of sheet orientation is to have sheets alternately occupied by sodium and chlorine atoms (see Figure 3 c)). In this case it is possible to obtain a reflection even for path differences of odd numbers of wavelengths between identical sheets (for example those containing only chlorine atoms). The reason for this is that although the reflections from a chlorine sheet and the neighbouring sodium sheet are exactly out of phase for an identical sheet path difference of odd numbers of wavelengths, the strength of the reflection from a chlorine plane is stronger than for a sodium plane, so only partial cancellation occurs. The net result is that for NaCl, reflections occur for h, k, ℓ all even, or all odd, with the odd order reflections being weaker compared to the even orders.

   From geometric considerations, the separation of <u>consecutive</u> reflecting sheets, d, is given by

$$d = \frac{a/2}{\sqrt{\left(\dfrac{h}{m}\right)^2 + \left(\dfrac{k}{m}\right)^2 + \left(\dfrac{\ell}{m}\right)^2}}$$

where, as mentioned before, a = length of edge of unit cell (= twice Na–Cl separation) and m = wavelength path difference between identical sheets = greatest common divisor of h, k, ℓ.

$$d = \frac{ma}{2\sqrt{h^2 + k^2 + \ell^2}}$$

From the Bragg condition,

$$n\lambda = 2d \sin \theta$$

where n is the wavelength path difference between <u>consecutive</u> reflecting sheets.

The structure of NaCl is such that because of the symmetric spacing of the Na and Cl atoms, the separation between <u>identical</u> sheets is simply <u>twice</u> the separation between <u>consecutive</u> sheets. Therefore $m = 2n$.

$$d = \frac{na}{\sqrt{h^2 + k^2 + \ell^2}}$$

and the Bragg condition is

$$\lambda = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + \ell^2}}$$

Note that because of the unequal scattering strengths for Na and Cl, the Bragg condition is less restrictive for NaCl than it is in general, allowing consecutive sheet path length differences of an integral number of <u>half</u> wavelengths for odd Miller indices (h, k, ℓ).

The following table contains the first few allowed sets of h, k, ℓ values:

h	k	ℓ	$h^2 + k^2 + \ell^2$	$\sqrt{h^2 + k^2 + \ell^2}$
1	1	1	3	1.732
2	0	0	4	2.000
2	2	0	8	2.828
3	1	1	11	3.317
2	2	2	12	3.464
4	0	0	16	4.000
3	3	1	19	4.359
4	2	0	20	4.472
4	2	2	24	4.899
3	3	3	27	5.196
etc.				

Apparatus:

The experiment consists of analysing two x-ray films exposed in a powder diffraction camera. In the powder (Debye-Scherrer) method, the x-rays fall on a mass of tiny crystals in all orientations, and the diffracted beams of each order h, k, ℓ form a cone. Arcs of the cones are intercepted by a film surrounding the specimen. Figure 4 shows a schematic diagram of the

apparatus. The x-ray beam passes through a collimator and strikes the sample (powdered NaCl crystals). A film strip placed along the cylindrical camera wall will be exposed by the scattered radiation and display, after sufficient time and development, the diffraction pattern. The unscattered radiation leaves the camera via the exit port.

collimator

powder sample

X-Ray Tube

exit port

film

exit hole

Diffraction Pattern on Film
After Exposure
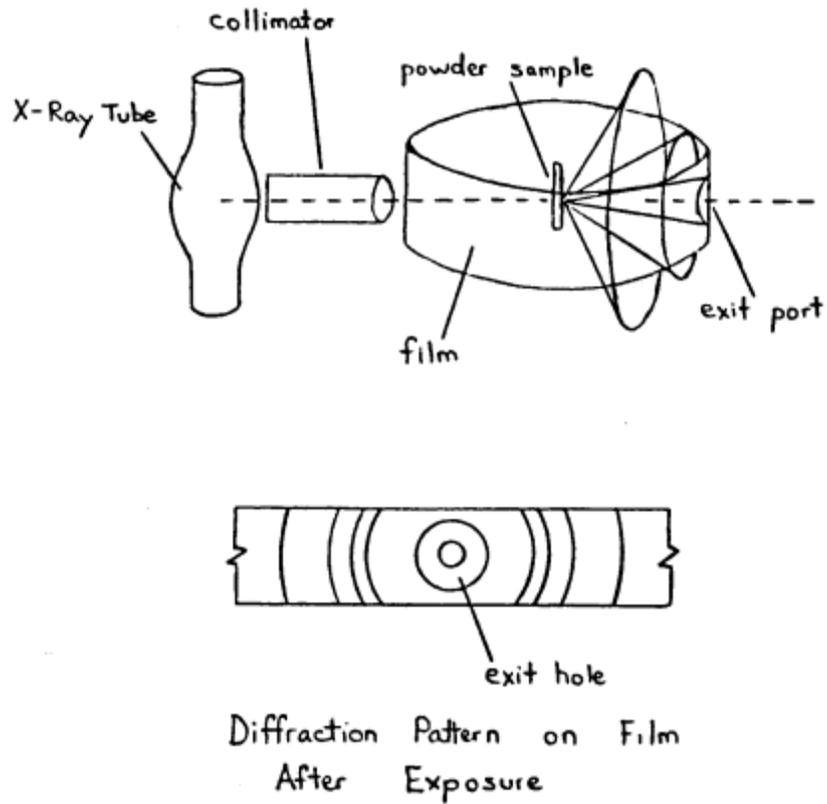
Figure 4

The Debye-Scherrer method is explained as follows:

Figure 5

n^{th} order

2θ

d_i

θ

a)

n^{th} order

2θ

b)

n^{th} order

(1) (2)

m^{th} order

c)

(3)

d)
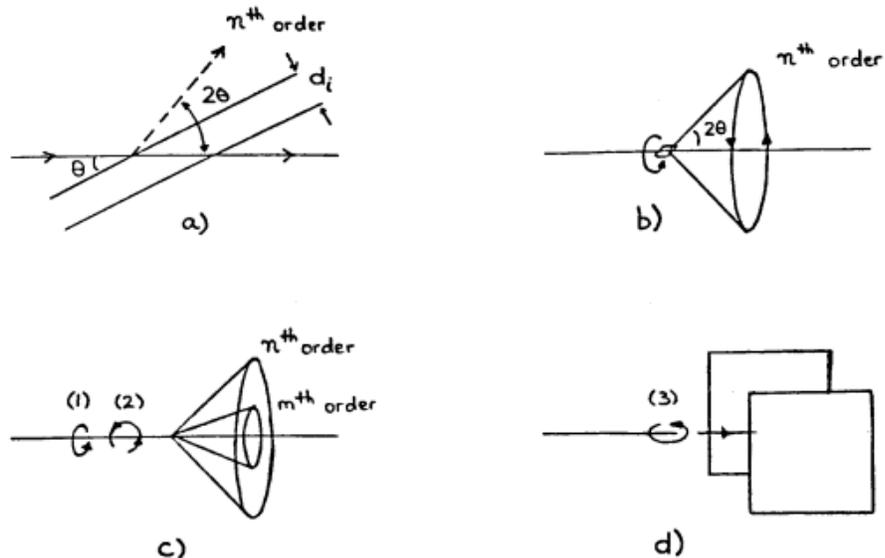
Consider first a single crystal. Consider one set of reflecting sheets of separation d_i. Only one angle, θ, exists for which reflection of the nth order occurs. (Figure 5 a)). Now the crystal is rotated about an axis along the incoming beam direction. The diffracted beam sweeps out a circle as shown in Figure 5 b). This assumes however, that the angle was chosen correctly to get a reflection. To ensure this is so, at least during part of the experiment, the crystal is rotated about an axis perpendicular to the incoming beam, (Figure 5 c)). Thus there will be a ring for each set of sheets in the crystal and each order of reflection from each set of sheets. Finally, there may have been sheets oriented parallel to the paper (Figure 5 d)) and in order to get reflections from them, the crystal is rotated about a third axis perpendicular to the x-ray beam and parallel to the paper. The three rotations result in circular patterns for every sheet separation d_i and every order of reflection. Since the three rotations result in the crystal being oriented in every possible position in space, it is equivalent to use powdered crystals which, because of their random orientation, are already oriented in every possible direction. To further ensure randomisation, the powder sample mounting is rotated about axis 2 by an external motor. Thus, for monochromatic x-rays, the diffraction pattern from a powdered sample consists of one circle for each order of each sheet separation d_i .

The x-rays are produced by bombarding a copper target with electrons. The x-ray spectrum consists of a continuous distribution on which are superimposed the characteristic line spectrum of copper (mainly K_α, $\lambda = 0.154$ nm, and K_β, $\lambda = 0.139$ nm). Using a Ni filter, all but the K_α radiation is absorbed, providing a reasonably monochromatic x-ray beam. Since the continuous spectrum is of much lower intensity than the characteristic lines, it can be considered low-level background.

Procedure and Experiment:

Two previously developed x-ray powder diffraction films are provided. These were produced by allowing x-rays from a copper target to strike a NaCl powder sample. One diffraction pattern was obtained using a Ni filter (hence $\lambda = 0.154$ nm), the other diffraction pattern was obtained using no filter (hence $\lambda = 0.154$ nm and 0.139 nm). The glancing angles corresponding to the rings on the films can be calculated by measuring the ring diameters (s) and knowing the camera radius ($R = 2.877$ cm) (see Figure 6).

Figure 6
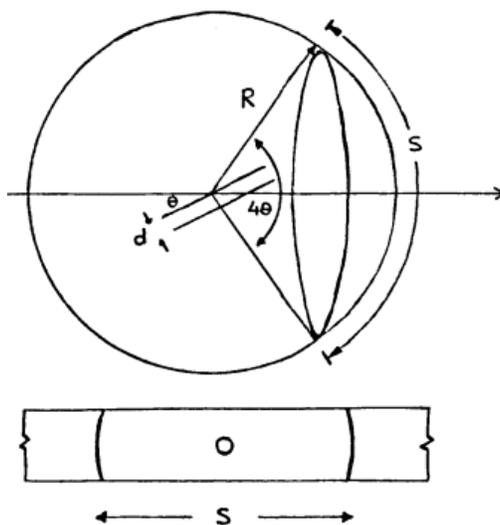
Using the calculated θ value and the appropriate λ, and substituting values for a few sets of Miller indices into the equation

$$\lambda = \frac{2a \sin\theta}{\sqrt{h^2 + k^2 + \ell^2}}$$

a number of values of a, the lattice constant, are obtained for each diffraction ring. Since a is a constant for a given sample type, the correct indices for a ring are those that yield an a value which agrees with a values obtained for other rings (i.e. one value for a should recur for all the rings when the correct indices for each ring are used in the calculation.)

Note that the correct values of $\sqrt{h^2 + k^2 + \ell^2}$ will increase with ring diameter for a given λ, and the first ring should have h, k, ℓ = 1,1,1, second ring 2,0,0, third ring 2,2,0, and so on.

However, since some of the rings may be of too low an intensity to measure, it is best to use the method described (substitute a few sets of h, k, ℓ and choose the one yielding a constant a), rather than simply assigning indices in order.

1. Measure the diameters of as many diffraction rings as possible for each of the two films. For each ring, also record the relative intensity (faint, light, medium, dark, etc.)

2. Determine the average lattice constant, a, for rings produced by the λ = 0.154 nm x-rays.

3. Determine the average lattice constant a, for rings produced by the λ = 0.139 nm x-rays.

4. Calculate the theoretical value for a, given that a unit cell of NaCl contains 4 NaCl molecules, the molecular weight of NaCl is 58.44 g, and the density of NaCl is 2.165 g/cm^3. (Avogadro's number = 6.022 x 10^{23}).

5. Compare the overall average experimental value and the theoretical value for the lattice constant ,a.

6. Comment on the relative intensities of rings corresponding to odd and even indices for a given x-ray wavelength.

References:

Fretter, <u>Introduction to Experimental Physics</u>, QC 41
Halliday and Resnick, <u>Physics, Part II</u>
Harnwell, <u>Experimental Atomic Physics</u>, QC 173
Nuffield, <u>X-Ray Diffraction Methods</u>, QD 945
Woolfson, <u>X-Ray Crystallography</u>, QD 945

<u>PHOTOGRAPHIC DARKROOM TECHNIQUES</u>

This experiment is intended to introduce basic film processing and develop good habits in the use of a photographic darkroom. The experiment consists of developing sheet film which has been exposed to a laser diffraction pattern. Since the experiment is concerned only with the experimental technique, and no measurements are made, no report is required. Attach your developed film to a page of your notebook, and submit it with your X-ray Diffraction report.

Apparatus:

WARNING: LASER LIGHT IS POTENTIALLY DANGEROUS TO YOUR EYES. TO AVOID EYE DAMAGE DO <u>NOT</u> LOOK INTO THE BEAM, AND AVOID VIEWING THE BEAM'S DIRECT REFLECTION.

The experimental apparatus consists of a He-Ne laser light source, a diffraction slide, and a film holder stand. A cardboard cover with an aperture for the laser beam is provided. Also a black cloth should be placed over the back of the laser source to reduce stray light from its on/off indicator light. A sheet of black cardboard is available to be used as a shutter for the laser light. The laser light source is turned on by a key switch at the back.

If the supervisor has not already done so, the laser should be turned on, and the relative positions of the laser, diffraction slide, and film holder stand adjusted to obtain the sharpest possible pattern. A piece of white cardboard placed in the film holder stand can be used as a temporary screen for better viewing of the diffraction pattern. The film holder stand should be roughly 50 cm from the diffraction slide. When the apparatus is correctly positioned, the laser should be switched off.

** All negative film, exposed or not, is to be handled in complete darkness – no safelight is permitted with panchromatic film at any time. Before beginning any work in the dark, <u>lock the door!</u> Also, room lights should be switched off using the darkroom controls, rather than the wall switch, since they turn on a warning light in the hallway when the darkroom lights are off.

The plastic film holder ('camera') has two sliding shutters, one on each side, so that two sheets of film may be loaded at once.

The film holder must be loaded in TOTAL DARKNESS. The film is placed in the holder with the emulsion toward the object to be photographed. The emulsion side of the film is up when the film is held in the right hand, with the corner notches under the index finger.

In the darkroom, keep one side 'Dry' – no chemicals or wet hands to be allowed in this area. Use this side for cutting, or loading and unloading film. The other side, or 'Wet' side, will be the sink side where all developing and printing is done.

Set out four trays in order, starting furthest from the sink. These will be:

1. Developer tray
2. Stop Bath tray
3. Fixer tray
4. Hypo-Clearing Solution tray

To avoid contamination, always use the same tray for the same solution each time. Use about 1 to 2 cm solution in each tray. Use D-76 developer, indicator stop bath, and fixer solutions direct from stock. The hypo-clear solution is mixed one part stock to 4 parts water.

Procedure: - each member of the group is to develop one sheet of film.

1. Set the timer for eight (8) minutes. Place a large tray in the sink under the temperature-controlled tap. Turn on tap so that a steady stream flows into the tray.

2. In TOTAL DARKNESS, load the film holder if this has not already been done. Once the holder is loaded, and the film box is closed, the lights may be turned on.

3. Place the holder in the stand.

4. Place the black cardboard shutter over the laser aperture, and turn on the laser.

5. In TOTAL DARKNESS, open the sliding shutter on the film holder.

6. Remove the black cardboard shutter from the laser for an exposure time of 6 seconds, then replace.

7. Turn off the laser.

8. The film is now ready to be developed. Remove the exposed film from the holder and immerse, emulsion side up, in the developer solution. Start timer. Agitate slowly but continuously by gently rocking the tray.

9. When time has expired, remove the film from the developer tray, immerse briefly in water, then place in stop bath solution. Count off 30 seconds, agitating tray twice during this period, then remove film, briefly rinse, and place in the fixer tray.

10. The film is left in the fixer for 2 minutes with agitation every 30 seconds. After the film has been in the fixer for 30 seconds, the lights may be turned on.

11. Remove film and wash in running water at 20°C for one minute, then immerse film in hypo-clearing solution.

12. Let film remain in hypo-clearing solution for 2 minutes, agitating every 30 seconds, then remove and wash in running water for 5 minutes.

13. Hang developed film to dry.

At the end of the lab, discard all used chemicals in the container that is provided (ask the lab instructor which container to use). Always leave the darkroom the way you would like to find it – CLEAN. Ensure all spills are wiped up, counters washed and dried, all used utensils washed and dried, and all stock chemicals properly stored.

The developed film is to be submitted, suitably mounted, in your lab notebook.