1 Safety First

During this experiment we are using a strong x-ray source. It is well shielded. Before switching it on, check if all unused x-ray outlets have filter set to lead (green colour).
2 Objectives

A Debye-Scherrer method will be used to obtain and to analyse the x-ray diffraction pattern produced by a polycrystalline substance. The dimensions of the unit cell and the density of the polycrystalline material will be found by measurement of this pattern.

3 Theory

X-rays have a wavelength of the same order as the inter-atomic spacing in most crystalline substances. X-ray diffraction is thus an ideal way of probing the cell structure of a crystalline substance. In this experiment, we mainly consider crystals whose basic or unit cell is a cube (of side $a$). We restrict ourselves to this simple type to make the interpretation easier - the method, however, is most powerful and can be applied generally to all types of crystal structure. There are three basic types of cubic cell: the simple cubic, the face centred cubic and the body centred cubic.

The differences in these three types are shown in Fig. 13-1.

An interesting variant occurs when a cubic crystal is composed of equal numbers of two types of atoms. The common salt (sodium chloride) is a good example and is shown in Fig. 13-2.

Another interesting variant is diamond (silicon has the same structure). Although complicated to draw, it is most easily visualised in terms of 5 slices through the unit cube. These are shown in Fig. 13-3.

The technique in this experiment is to use metal samples in the form of wires composed of small crystals orientated in every direction.

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2Max von Laue (1879 - 1960) won the Nobel Prise in Physics 1914 for his discovery of the diffraction of x-rays by crystals.
3You can take challenge to do this as an optional part of this experiment.
Fig. 13-2 Cell structure for crystals of the sodium chloride type.

Fig. 13-3 Cell structure for crystals of the diamond type: (a) top and bottom slice, (b) a/4 from top slice, (c) a/2 from top slice and (d) 3a/4 from top slice. (All atoms are identical, different colours for slices are used exclusively to simplify the drawing.)
The starting point in our reasoning is the Bragg’s scattering law which states that x-rays will constructively interfere (and form a high intensity spot on the film) when x-rays scattered from neighbouring planes have path differences differing by an integer number of wavelengths. Fig. 13-4 illustrates this.

![Fig. 13-4 Bragg’s reflection of x-rays from a family of planes.](image)

The extra path length is \(2d \sin \theta = n\lambda\); \(n\) is the order of the reflection. Note that \(\theta\) is different from the normal angle of incidence usually defined in optics. For first order reinforcement, therefore, we have

\[
\sin \theta = \frac{\lambda}{2d}
\]

There are, however, many families of planes of various inclinations which can be drawn through the scattering centres. Each family of planes consists of an almost infinite set of members, all parallel and all equally spaced.

Each family of planes is characterised by its Miller indices \((h, k, l)\) which are the inverses of the intercepts on the axes of the plane closest to the origin (in cell co-ordinates). Thus the Miller indices \((0, 0, 1)\) would describe a family of planes all parallel with the xy plane and all separated by the same distance \(a\). For a general family of planes \((h, k, l)\) it is easy to show that

\[
d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}
\]

so that the Bragg’s condition can be written as:

\[
\sin^2 \theta = \left(\frac{\lambda}{2a}\right)^2 (h^2 + k^2 + l^2) = \left(\frac{\lambda}{2a}\right)^2 N
\]

Clearly \(N\) must be an integer. Please note that equation (3) already covers higher orders of reflection for \(N = n^2\). In crystallography Miller indices are usually given in the lowest terms, i.e., their greatest common divisor should be 1. In x-ray diffraction we often allow Miller indices

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4 After Sir William Henry Bragg (1862 - 1942) and his son Sir William Lawrence Bragg (1890 - 1971) (born in Adelaide, Australia) British physicists who won the Nobel Prize in Physics 1915.

5 Miller indices were introduced in 1839 by the British mineralogist William Hallowes Miller.

6 Although equation (1) is valid for any crystal, equations (2) and (3) are true only for isometric systems.
to brake this rule to accommodate automatically higher orders of reflection. For example a first order reflection from (2, 0, 0) plane can be considered as a second order reflection from (1, 0, 0) plane.

Whenever an x-ray photon hits a crystal with the correct angle of incidence constructive interference will occur from the corresponding family of planes \((h, k, l)\) forming a reinforced scattered beam (the angle of deflection of the beam is obviously \(2\theta\)).

Note also that since we are dealing with a polycrystalline metal specimen containing many crystals of all possible orientations, the scattered beams will form a cone (rather than a bright spot) with an opening angle \(2\theta\) with respect to the incident beam direction (see Fig. 13-5 and Fig. 13-8).

The camera used in this experiment utilises a strip of film wrapped around the inner surface (covered with a rare earth intensifying screen) and enclosing the specimen. Thus instead of circular rings being seen if the screen is flat perpendicular to the incident beam direction, we see ellipsis or two elliptical arcs for each value of \(N\). The aim is to ascribe a value of \(N\) to each ring seen, thus allowing one to estimate the basic cell size, \(a\), (provided the wavelength of the x-ray is known and the value of \(\sin^2\theta\) is calculated).

![Fig. 13-5](Formation of elliptical arcs on the film for a polycrystalline sample.)

For simple cubical crystals all values of \(h, k\) and \(l\) are allowed. All \(N\), however, are NOT allowed as numbers such as 7, 15, 23, 28, 31 and 39 etc. cannot be made up from the sum of three squares.

For face centred crystals we add extra planes due to the additional scatterers in the middle of each face. This results in some destructive interference; so that some further \(N\) values are missing. Let us consider two slices through a face centred crystal perpendicular to the \(z\) axis as shown in Fig. 13-6.

The two horizontal slices (slice 1 and 2) have equal numbers of atoms (2) per unit slice area.
In FCC type of crystal, the two horizontal slices of the unit cell are just different selections from the same pattern of atoms. But are separated by half the unit cell size (i.e. by a/2) so there will be destructive interference causing suppression of the reflection $hkl = 001$ ($N = 1$). By extension this will mean suppression of $hkl = 010$ and $hkl = 100$. If this argument is applied to other planes, the result is that only cases when $hkl$ are all odd and where $hkl$ are all even are allowed (i.e. $h$, $k$ and $l$ must have the same parity).

An interesting effect occurs in crystals like sodium chloride. A plane 111 is entirely occupied by sodium ions and the next 111 plane is entirely occupied by chloride ions. This pattern is repeated through the crystal and it causes destructive interference to occur. The interference is only partially destructive in NaCl as x-ray scattering is stronger from the chlorine atoms which have a higher atomic number than sodium. The result is that the line $N = 3$ (due entirely to $hkl = 111$) is weak in NaCl. The $N = 3$ line is extremely weak (effectively missing) in crystals like NaF and KCl because the component atoms are near neighbours in the periodic table. As a general rule, if the planes have atoms of near equal $Z$ then we will see lines with $h$, $k$ and $l$ all even.

Diamond and silicon lattices have a face centred arrangement of atoms with four extra atoms in the cell, arranged as already shown in Fig. [13-3]. The two extra planes cause destructive interference with $hkl = 200$ ($N = 4$). A similar interference occurs with $hkl = 222$ ($N = 12$), with $hkl = 420$ ($N = 20$) and $N = 30$, 36 and 44. As a consequence, the allowed interval between successive values of $N$ goes 5, 3, 5, 3 etc.

We finally come to the body centred cubic crystals; destructive interference is caused by the atom in the unit cell’s centre and produces a simple result: $N$ has to be even.

**Question 1:** Why would radio waves be useless to investigate structure of crystals? Hint: Can radio wave fulfils the Bragg’s equation? Can gamma radiation be used for diffraction on crystals? Please comment.

**Question 2:** What influences relative intensity of the lines produced by diffracted x-ray? Hint: Read [1], ch.2.
4 Experimental procedure

4.1 Loading the sample

1. It is first necessary to position the wire sample in the central mount of the camera, holding it in place by means of the plasticine. It needs to stay central within the field of view of the x-rays for a complete rotation.
2. Remove the lead glass from the beam exit tube and attach the lens.
3. Rotate the sample and centre it by means of the screw at the top of the camera. Be sure this screw is turned back several turns between each centring adjustment and left fully unscrewed so that it does not touch the shaft as it rotates.

4.2 Loading the film

1. The film must be loaded in the darkroom-box illuminated with the infra-red light and observed using the CCD camera. The film has been pre-cut to size.
2. Remove the collimator, the exit tube and the cover plate, placing them carefully aside.
3. Insert the film carefully, not touching the specimen, with the emulsion side (less reflecting) facing the rare earth intensifying screen (white material on the wall of the camera). One end of the film should rest against the fixed pin. Push the other end with the finger till it is tight against the case, and slide the moving pin to hold it in position.
4. Replace the collimator, the exit tube and the cover plate.
5. Bring the powder camera out of the darkroom-box.

4.3 The x-ray generator

1. Put the camera on the end of its appropriate bracket.
2. Lift the flap and push up the camera till the collimator touches the filter plate.
3. Slide the motor on to the camera shaft, lock it and turn it on.
4. Rotate the filter selector to the Ni position.\(^7\)

4.4 The switch-on procedure

1. Check that the cooling water supply is turned on.
2. Turn both current and high voltage controls to minimum (fully anticlockwise).
3. Switch on x-ray machine.
4. Increase high voltage one step up and adjust current to 10 mA.
5. Wait for 1 min and increase high voltage 1 notch up.
6. Repeat the above step until high voltage reaches 40 kV.
7. Turn up current to 20 mA.

\(^7\)The x-ray tube has a copper target; the nickel filter removes \(K\beta\) radiation.
4.5 Exposure

1. The exposure time is around 25 minutes.
2. Check the current and the water flow from time to time.
3. To turn off, turn back the current control to its stop, then turn back the high voltage control.
4. Push in the red button. This is a ‘panic’ button and you should use it to turn machine off immediately in case of emergency.

4.6 Development of the film

1. The exposed film must be first removed from the camera and placed in the developing tank. This should be done using the darkroom-box.
2. Prepare 50 ml of developer by mixing 25 ml of “part A” with 25 ml of “part B”.
3. Pour the x-ray film developer into the developing tank containing the exposed film and wait for 3 minutes.
4. Dispose the developer to the sink (it cannot be reuse for other films) and rinse the film with running water for 1 minute.
5. Dispose the water and fill the tank with the 50 ml of the x-ray film fixer. After 2 minutes the tank can be open and the film inspected under normal light.
6. When all whiteness has disappeared from the film, remove the fixer from the tank to its container (it can be reuse later) and wash the film thoroughly for at least 3 minutes under the running water.
7. Dry the film.

5 Measurement of the film

1. Upon development, the film should appear as in Fig. 13-7. Obviously the number and the placement of the arcs depends on the sample used for diffraction. The illustrated case is obtained with the sample labelled “w10”. We will refer to this particular case in the following text. If your sample is different you should adjust this description to your results.
2. Using the flat bed optical scanner connected to the computer, scan the film with a resolution of 600 dpi as a grey-scale image and save it to the file (as usual make your own folder in the “My Documents” to keep all your documents there).

3. Open the image file in a painting application “Gimp” and try to improve the contrast to make rings well visible. You may use different setting for the light and the dark parts of the image.

4. Read the x coordinate of the cursor placed over the ring and write it down. Those values of the x coordinate are in the pixel units. You don’t need to convert them to the length units. Why?

5. In recording the measurements the arcs should be numbered as shown in the Fig. 13−7. Those between the $X_0$ and $X_{\pi/2}$ positions are numbered sequentially $x_1, x_2, \ldots$. Those outside the $X_0$ and $X_{\pi/2}$ positions, which form matching pairs with arcs between $X_0$ and $X_{\pi/2}$, are numbered $x'_1, x'_2, \ldots$ in accordance with which arcs they are matched.

6. For all matched forward rings (i.e. those for which $\theta < \pi/4$) $x_i + x'_i$ should be a constant viz $2X_0$ whilst $x_i + x'_i$ for the matched backward rings (i.e. those for which $\theta > \pi/4$) should all equal another constant viz $2X_{\pi/2}$.

7. Investigate any greater deviations in these sums.

6 Analysis of data

6.1 Theory

In cross-section we have the situation for a particular ring shown in Fig. 13−8. Obviously $x_i - X_0 = 2R\theta_i$ where $R$ is the camera’s radius. Therefore

$$\theta_i = \frac{x_i - X_0}{2R}$$

Now $R$ is given by the relation $S = \pi R$ and thus we obtain

$$\theta_i = \frac{\pi(x_i - X_0)}{2S} \quad (4)$$

As explained above the $X_0$ and $X_{\pi/2}$ can be calculated from the formulas:

$$X_0 = \left( \sum_{i=1}^{i=4} \frac{x_i + x'_i}{2} \right)/4$$

$$X_{\pi/2} = \left( \sum_{i=5}^{i=9} \frac{x_i + x'_i}{2} \right)/5$$

The Bragg’s equation (3) implies

$$\Delta \sin^2 \theta = \left( \frac{\lambda}{2a} \right)^2 \Delta N$$

Consequently, apart from a constant multiplying factor, $\left( \frac{\lambda}{2a} \right)^2$ which is the same for all the arcs, we expect $\sin^2 \theta$ to increase in the same step sizes as does $N$. Your sample will be one of the
four types of cubic crystal studied in this experiment. The allowed values of N are given in Table [13-1].

The list of values of \( \theta \) as \( \theta \) increases from 0 to \( \pi/2 \) enables values of \( \Delta N \) and thus \( N \) to be assigned. This in turn allows identification of the crystal type.

Apart from the destructive interference effects described earlier, there will be intensity variations from ring to ring due to the fact that some of the \( N \) values can be produced by more than one combination of hkl e.g. \( N = 17 \) can be produced from 410 and 322.

Once we have determined \( N \) and \( \sin^2 \theta \) for each ring, it simply remains to insert the correct value of \( \lambda \) to obtain the estimate of \( a \), the side dimension of the basic cubic cell.

\[
a = \frac{\lambda \sqrt{N}}{2 \sin \theta}
\]

The x-rays are produced by electrons being brought to rest suddenly in a copper target. Apart from a general bremsstrahlung background, lines of particular wavelengths are emitted as a result of inner electrons being knocked out of the atom and higher-level electrons dropping down to fill the vacancy. We are interested in particular in the K shell vacancy. The first level above the K shell \( (n = 1) \) is the L shell \( (n = 2) \). For \( n = 2 \) we are allowed both orbital quantum numbers \( l = 0 \) and \( l = 1 \) so we have for copper the energy level diagram shown in Fig. [13-9].

There are only two lines from the \( n = 2 \) level because of the selection rules:

\( \Delta l = +1 \) or -1, and \( \Delta J = 0 \) or +1 or -1.

The \( K_\beta \) lines (coming from the \( n = 3 \) level) are removed by the insertion of a nickel filter. If this was not the case, each ring would appear double because of the two quite different wavelength groups \( K_\alpha \) and \( K_\beta \). The difference between the \( K_{\alpha 1} \) and \( K_{\alpha 2} \) lines is sufficiently small not to be a bother except at large angles where rings are usually resolved into a doublet (same \( N \), slightly different \( \lambda \)). In such a case use the weighted average position of both arcs: 2/3 of the more intense plus 1/3 of the weaker.
Because the $K_{\alpha_1}$ line has twice the weight of the $K_{\alpha_2}$ line ($J = 3/2$ has 4 projections, $J = 1/2$ only has 2), we use a weighted average for this experiment.

$$\lambda = \frac{2}{3}(154.05) + \frac{1}{3}(154.434) \text{ pm} = 154.178 \text{ pm}$$

There may be a systematic variation in your estimates of $\alpha$. This comes about mainly from absorption of the x-rays in the sample giving off-centre rings (see [1], page 210). This absorption effect goes roughly as $\cos^2 \frac{\theta}{\sin \theta}$ and vanishes when the $\theta$ reaches $\pi/2$.

### 6.2 Calculations

1. To simplify the calculations and data analysis we provide a template called “w10.ods”. Open it in the “LibreOffice Calc” application and save it under a different name (depending on your sample) in your folder.
2. Type in your results for $x_i$ and $x'_i$ in the appropriate columns. If $x_i$ does not have matching $x'_i$, input $x_i$ and leave the $x'_i$ cell empty.
3. Adjust the number of cells in the $x$ column and a definition of $X_0$ and $X_{\pi/2}$ accordingly to your data.
4. From plot of values of $\alpha$ as a function of $\cos^2 \frac{\theta}{\sin \theta}$ obtain the best estimate of $\alpha$ for your sample.
5. The “LibreOffice Calc” spreadsheet (as well as Microsoft’s “Excel”) does not have ability to fit linear function using weighted data and calculate an error of this fit taking into account the data errors. The “Qtiplot” application is much better for this task. Export the data which is used to produce the $\alpha$ vs $\cos^2 \frac{\theta}{\sin \theta}$ plot to the “Qtiplot” and fit a linear function.
6. Compare the results achieved from the “OpenOffice Calc” and the “Qtiplot”.
7. By using reference books (see [4, 3]) identify the sample that you have by using your value of $\alpha$.
8. Note the extreme accuracy that this method allows.
9. Find out from the demonstrator the identity of your sample and see if you are correct.

**Question 3:** From the equation (5) derive formula for $\Delta \alpha$ used in the above spreadsheet.
6.3 Cell size and density

By knowing the crystal structure of your sample it is possible to count the number of atoms (of each type if applicable) in the unit cell. Consider separately the different categories of atoms:

- those in corners of the cell (there are 8 cells which share these atoms)
- those along the cell edges (there are 4 cells which share these atoms)
- those on cell cube faces (there are 2 cells which share these atoms)
- those inside the cell (there is only one cell that holds these atoms)

Using this number, the mass of each atom species involved and the cell size $a$, calculate the crystals density. The result can be compared with values given in reference books (see [4, 3]).

7 Investigation of non-isometric crystal structure (optional)

Not all crystals have a structure the basic cell of which has a cubical form. In this part of the experiment you may investigate the structure of such a crystal. The procedure is very similar to the one used previously, but the reading of additional materials (such as [1], ch.8) is necessary. Two very common elements which you can investigate are: Zinc and Tin (respectively hexagonal and tetragonal crystal structure). Also you may propose any other material, to investigate the structure of, using the x-ray diffraction method. We do not provide detailed notes for this part of the experiment to give you a chance to show your creativity.

To proceed, discuss your proposal with the demonstrator.

References


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Table 13-1 N numbers which occurs for different cell structure.