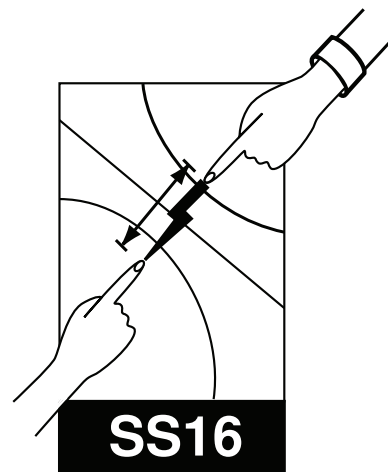


# X-ray diffraction



RAT October 2010



X-rays are dangerous. Safety interlocks have been built into the equipment but you must ensure that everything is correctly set up to minimize the radiation hazard. If in doubt, consult a demonstrator. Before switching on inspect the apparatus for damage. The high voltage should turn off when the sliding doors are opened.

Note required by the Ionizing Radiation Regulation 1985:

The enclosure for the X-ray diffraction apparatus is fully interlocked, and the dose rate outside the equipment is  $<1 \mu\text{Sv h}^{-1}$ . There is, therefore, no requirement for a supervised area either inside or outside the equipment. The apparatus is monitored and the interlocks checked by staff at intervals of not more than 3 months.



If you are planning to carry out the mini-project on this experiment, you will need to write your own risk assessment, stating the hazards involved, and the control measures in place to avoid these risks, in your logbook **BEFORE STARTING THE EXPERIMENT**. Demonstrators will help you write the risk assessment once you have read the script through and looked at (but not touched) the apparatus.

► If you are not doing the mini-project, ask the demonstrator to see the risk assessment for this experiment and discuss it with them before you start the experiment.

► If you are doing the mini-project, discuss the risk assessment you have written with a demonstrator before starting the experiment.

## 1 Introduction

In this set of experiments, you will become familiar with a number of basic X-ray diffraction techniques that are particularly relevant to your eventual examination papers. These are:

- Powder diffraction.
- Diffraction using single crystals.

These days much X-ray diffraction is carried out by modern diffractometers using electronic counters automatically guided by computers. In this experiment a combination of electronic detection and photography will be used. The use of photographs provides a more intuitive and simpler means to enable

you to understand the X-ray diffraction process. In the basic two-day experiment you will obtain the diffraction pattern from single crystals of NaCl and LiF as well as from an unknown semiconductor. You will also use a powdered specimen of NaCl. Instructions on how to use the apparatus and on how to develop the film are to be found in the supplementary script SS16a — *X-ray diffraction apparatus*.

## 2 Basic theory of X-ray diffraction

### 2.1 Bragg's Law

The first X-ray diffraction photographs were demonstrated in a landmark experiment by Max von Laue and co-workers in 1912, designed initially to prove that X-rays were wave phenomena rather than particles. However, Laue could not explain the observed pattern of spots in full, because he assumed that the X-rays being diffracted were all of the same fixed wavelength. It was W. L. Bragg in the same year who realised that if a polychromatic source of X-rays was assumed, Laue's diffraction patterns immediately became understandable. In order to work out the arrangement of spots in a particular case, Bragg, according to a suggestion put to him by C. T. R. Wilson (of cloud-chamber fame), decided to treat the diffracted beams as if they had been specularly reflected from planes of atoms within the crystal. Experiments conducted with his father, W. H. Bragg, soon confirmed that this idea worked in practice. This led eventually to the establishment of a most important equation, known as Bragg's Law and to the possibility of solving the structures of crystals.

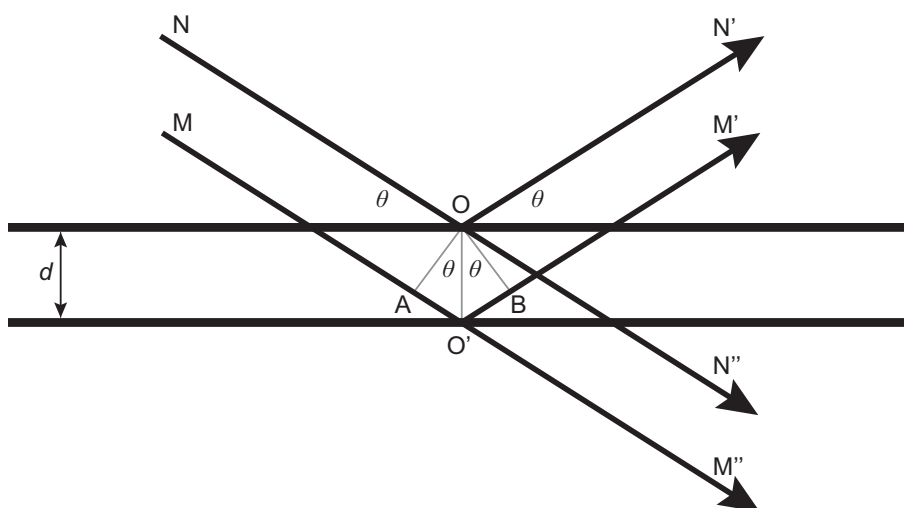


Figure 1: Path of X-rays for derivation of Bragg's Law. Note that the angle labelled  $\theta$  in this diagram is referred to as  $\beta$  on the instrument and accompanying software

In order to find the Bragg expression for specular reflection, consider X-ray beams being reflected by two adjacent planes of atoms with inter-planar spacing  $d$ . The angle between the X-ray beam and the plane is the Bragg angle. From figure 1 above, the path difference between the two sets of rays is given by

$$AO' + O'B = 2d \sin \theta$$

and so if there is to be constructive interference between the two beams this must equal a whole number of wavelengths. This gives the famous Bragg's Law equation

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

Note that the angle  $N'ON''$  between the reflected beam and the incident beam is  $2\theta$ .

This expression shows that for a particular choice of wavelength, there is a particular angle at which a reflection can occur for a particular set of parallel planes. Therefore we can see from this that a stationary

crystal in a monochromatic beam is unlikely to produce many diffraction spots, and so it was fortuitous that in Laue's original experiment the X-rays were actually polychromatic, thus satisfying Bragg's Law for many different wavelengths at the same time. One may wonder whether the discovery of X-ray diffraction might have been substantially delayed had the source been monochromatic!

It is because Bragg treated the diffraction problem as if it were a matter of specular reflection that today we refer to a diffraction spot observed in a diffraction pattern from a crystal by the term reflection. However, it is important to emphasise that the process of diffraction is not the same as for reflection. For instance, the treatment described above implies that if the crystal is made larger i.e. we include more crystal planes, more X-rays will be reflected to form a larger spot in the detector. This is in fact not the case. Provided that the crystal size lies within the coherence length of the X-rays, the opposite is true - the larger the crystal the smaller the width of the diffraction peak. This fact is, for example, used in the study of suspensions of micro-crystallites in solution, where a measurement of the diffracted peak width can be used to estimate the average particle size. So if Bragg's treatment is incorrect, wherein does its value lie? What Bragg's Law does for us correctly is to enable us to calculate the angle at which a reflection can occur, and this is a major part of interpreting the diffraction patterns obtained. Thus, Bragg's Law is applicable as a geometric law, even though it was obtained through oversimplified reasoning. It turns out that it comes out in the same form in any case if one applies the full diffraction theory due to Laue.

### 3 Brief introduction to crystals

We now give a brief explanation of the important terms that you need to understand in this experiment. Fuller details about crystals can be found in [1].

- **Crystal:** this consists of a repeating pattern of 'objects' (e.g., atoms or molecules) in an effectively infinite three-dimensional array. A convenient way of describing this is in terms of a *lattice* combined in some way with a physical object or *basis*.
- **Lattice:** A regular array of points (note that it is a mathematical construction that has no physical reality, but serves to denote how molecules are laid down to form the crystal).
- **Basis:** Any object (atom or collection of atoms, such as a molecule).

For instance in figure 2a we show a lattice (for simplicity we assume orthogonal axes) and in figure 2b, a possible basis.

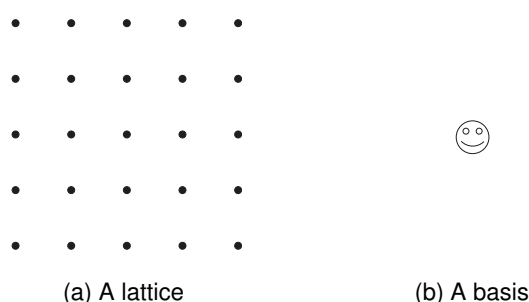


Figure 2: Schematic representations of a lattice and a basis.

We combine this object with the lattice in an operation known as *convolution*, which essentially means that the basis is repeated throughout out space according to the repeating(translational) symmetry of the lattice to give a 'crystal' of smiling faces! Note that in the simplest cases, the basis may consist of single atoms so that the resulting crystal structure looks more like the picture of the lattice (but note that they are not actually the same; the lattice consists of *points*, not *atoms*). See figure 3.

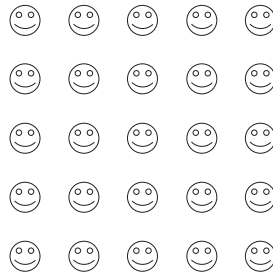


Figure 3: A 'crystal' formed by convolving figure 2a with figure 2b.

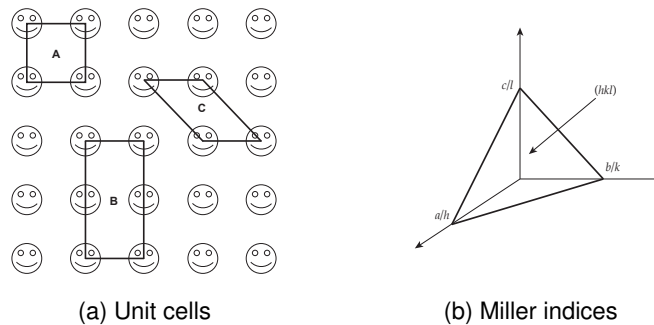


Figure 4:

- **Unit cell:** this is a region of space that when repeated fills all space. In any crystal structure there is an infinite set of choices of unit cell, three of which, A, B and C, are illustrated below in figure 4a. Unit cells A and C are the smallest volume cells possible in this structure and are known as *primitive unit cells*. Unit cell B has twice the volume of A or C, and is known as a centred unit cell. There are two types of centred cell that will concern you. In the *body-centred cell*, there are two lattice points, one at a corner  $(0,0,0)$  and one at the centre of the unit cell  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . This means that in such a crystal every atom in the basis will have an exact copy at a distance  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , thus doubling the number of atoms in the unit cell. The other type of centred cell of interest is the all *face-centred cell*. Here, there are four lattice points per unit cell, at the positions  $(0,0,0)$   $(\frac{1}{2}, \frac{1}{2}, 0)$   $(\frac{1}{2}, 0, \frac{1}{2})$   $(0, \frac{1}{2}, \frac{1}{2})$ .

► Sketch diagrams of these for yourself.

- **Cubic Crystal:** this contains four three-fold axes of symmetry. This is the formal definition of the term cubic, but its effect is that the unit cell is shaped like a cube, i.e., it has three orthogonal axes of equal length  $a$ , the so-called lattice parameter.
- **Miller indices:** these are integers  $(hkl)$  that refer to the intercepts made by a plane on the unit cell axes. Thus we can define sets of planes drawn through atomic groups in the crystal structure that can be described by Miller indices — see figure 4b. These planes are separated by the distance  $d_{hkl}$ .

For crystallographers, a more convenient form of Bragg's Law can be written thus:

$$\lambda = 2d_{hkl} \sin \theta$$

You will note that the quantity  $n$ , the order of diffraction, has been dropped. The reason for this is that instead of talking about the order of diffraction, which is perfectly sensible in a one-dimensional diffraction pattern, it makes no sense in three dimensions. In such a case, there would be a different series of orders for each different set of planes, and rather than try to talk about, say, the 2<sup>nd</sup> order diffraction

from the (111) planes and the 3<sup>rd</sup> order diffraction from the (213) planes, it is easier to treat the problem in terms of diffraction from (222) and (639) planes. Thus we can use the relationships:

$$\begin{aligned}d_{222} &= \frac{1}{2}d_{111} \\d_{639} &= \frac{1}{3}d_{213}\end{aligned}$$

One way of interpreting this is to imagine that the diffraction is occurring from hypothetical planes whose  $d$  spacings are fractions of the fundamental sets of planes. In this case we then talk about 222 and 213 reflections, rather than use the idea of diffraction order specifically. Note a convention that when talking about the indices denoting a reflection, no parentheses or brackets are used. It is worth pointing out here that by treating diffraction as specular reflection in this way, the Braggs, father and son, were able to explain the spots found on Laue's photographs, and by applying this to simple materials such as NaCl, they eventually were able to propose realistic models for their crystal structures. Thus the science of crystal structure determination was born, for which the Braggs shared the Nobel Prize. Today, the solution of far more complex crystals, such as proteins and viruses, where tens of thousands of atoms occupy a single unit cell, has become almost routine.

A useful relationship that you should know between the interplanar spacings and the Miller indices of the planes is

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

provided that the unit cell axes are orthogonal, and the three lattice parameters are  $a$ ,  $b$  and  $c$ . Such a crystal is known as *orthorhombic*.

In a so-called tetragonal crystal, the parameters  $a = b$ , and then

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

and in a cubic crystal:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{N^2}{a^2}$$

where  $N$  is an integer.

### 3.1 Allowed reflections

It can be shown that the reflections observed are influenced by the arrangement of atoms in the crystal and the lattice type. In the case of the lattice type, certain reflections have zero intensity and this is a useful guide in determining the lattice type of a particular crystal. The conditions for reflections to be present are:

Crystal Type	Allowed Reflections
Primitive lattice	all reflections possible
Body-centred lattice	$h + k + l = 2n$
Face-centred lattice	$(h, k, l \text{ all odd})$ or $(h, k, l \text{ all even})$
Diamond structure	$(h, k, l \text{ all odd})$ or $((h, k, l \text{ all even}) \text{ and } (h + k + l = 4n))$

Thus in a cubic crystal, the following reflections can be observed (ordered in increasing angle):

$N^2$	Primitive	Body-centred	Face-centred	Diamond
1	100	—	—	—
2	110	110	—	—
3	111	—	111	111
4	200	200	200	—
5	210	—	—	—
6	211	211	—	—
7	—	—	—	—
8	220	220	220	220
9	300	—	—	—
10	310	310	—	—
11	311	—	311	311
12	222	222	222	—
13	320	—	—	—
14	321	321	—	—
15	—	—	—	—
16	400	400	400	400
17	410, 322	—	—	—
18	411, 330	411, 330	—	—
19	331	—	331	331

Note that it is not possible to have a sum of squares of integers equal to 7, so that in all cases the seventh line is missing. For diamond-like structures, reflections from 333, 444 and 555 are all allowed, but note that 222 is NOT. By permuting the indices, different reflections lie on top of one another. This defines a multiplicity value for each  $hkl$ . For example, in the cubic case, the multiplicity of the 100 line is 6:

100	010	001	$-100$	$0-10$	$00-1$
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and for 111 it is 8:

111	$-111$	$1-11$	$11-1$	$-1-11$	$-11-1$	$1-1-1$	$-1-1-1$
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► Determine for yourself the multiplicities for 110 and 213.

In a tetragonal crystal the multiplicities for the  $h00$  type of reflections are:

$h00, -h00, 0h0, 0-h0$	4
$001, 00-1$	2

If the density  $\rho$  and unit cell volume  $V_{\text{cell}}$  of a material are known, it is possible to calculate number of formula units  $Z$  in the unit cell, according to:

$$Z = \frac{\rho V_{\text{cell}}}{(M_f / N_A)}$$

where  $M_f$  is the mass of one mole of the formula unit and  $N_A$  is Avogadro's number.

## 4 Bragg reflection: determining the lattice constants of single crystals

In this experiment we will use the X-ray apparatus to determine the lattice constants of single crystals of NaCl, LiF and an unknown elemental semiconductor. From Bragg's law we see that it is necessary to measure the diffraction angle  $\theta$  for a known wavelength  $\lambda$ . N.B. This method becomes more precise for larger diffraction angles.

► Use your knowledge of calculus and the Bragg formula to derive the accuracy of determining the plane spacing  $d$  as a function of the diffraction angle  $\theta$ .

The X-ray tube in the apparatus has a molybdenum anode emitting a broad range of X-rays known as Bremsstrahlung and 2 sharp lines from K-shell emission at:

Line	$\lambda / \text{pm}$
$K_\alpha$	71.08
$K_\beta$	63.09

If it is not already in place, mount the goniometer in the apparatus with the Geiger-Müller counter tube as detector (see the description of the goniometer in section 2.2 of the apparatus script, the mounting procedure for the components can be found overleaf).

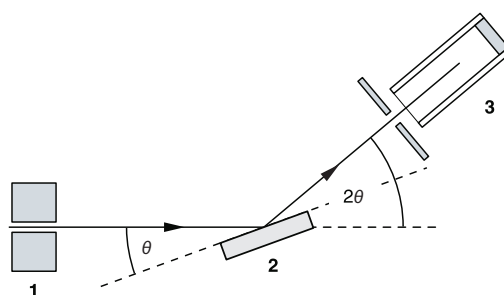


Figure 5: Schematic diagram of diffraction of X-rays at a single crystal and  $2\theta$  coupling between the counter-tube angle and the scattering angle (glancing angle). **1** collimator, **2** single crystal, **3** counter tube.

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This instrument and the crystal are both pivoted with respect to the incident X-ray beam in  $2\theta$  coupling — the counter tube is turned by twice the angle of the crystal (see figure 5). **Note that the angle  $\theta$  is labelled  $\beta$  on the apparatus** The zero point  $\theta = 0^\circ$  is characterized by the fact that the lattice planes and the axis of the counter tube are parallel to the incident X-ray beam. As the lattice planes are seldom precisely parallel to the surface of the crystal, the zero point of each crystal must be calibrated individually.

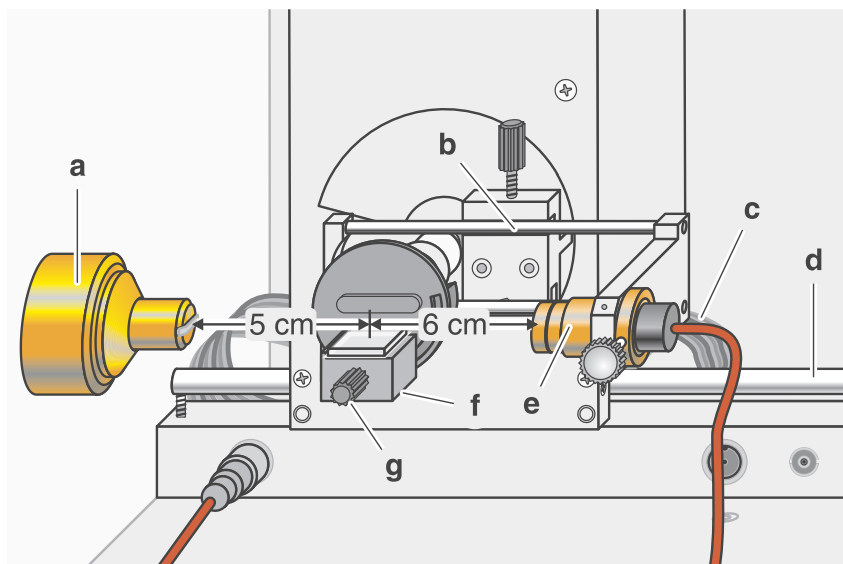


Figure 6: Schematic diagram of the arrangement for zeroing the system before taking data.  
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Figure 6 below shows some important details of the experimental setup. To set up the experiment proceed as follows:

Mount the collimator in the collimator mount (a) (note the guide groove). If the collimator is already mounted remove it to check that the Zr filter is not still attached to the rear of the collimator

Attach the goniometer to guide rods (d) so that the distance between the slit diaphragm of the collimator and the target arm is approx. 5 cm. Connect ribbon cable (c) for controlling the goniometer.

Remove the protective cap of the end-window counter, place the end-window counter in sensor seat (e) and connect the counter tube cable to the socket marked GM TUBE.

By moving the sensor holder (b), set the distance between the target arm and the slit diaphragm of the sensor seat to approx. 6 cm.

Mount the target holder (f) with target stage.

Align the target manually and sensor arm horizontally using the **ADJUST** knob and save these positions as a first attempt at a “zero position of the measuring system” by pressing **TARGET**, **COUPLED** and  $\beta$  limits at the same time. This will be done more precisely with the crystal in place in section 6.2.



The NaCl and LiF crystals are hygroscopic and extremely fragile. Store the crystals in the dry jar beside the experiment, avoid mechanical stresses and handle the crystals by the short faces only. It is part of the experimental procedure to return all samples to their proper packets to the desiccator on the end of the bench. These samples are delicate, hygroscopic and expensive, and there are no spares available. Failure to observe these instructions indicate poor experimental practice, which will be reflected in your final assessment.

If the counting rate is too low, you can reduce the distance between the target and the sensor. However, the distance should not be too small, as otherwise the angular resolution of the goniometer is no longer sufficient to separate the characteristic  $K_\alpha$  and  $K_\beta$  lines.



## 4.1 Bragg reflection from a LiF single crystal

Loosen knurled screw (**g**), place the LiF crystal flat on the target stage, carefully raise the target stage with crystal all the way to the stop and gently tighten the knurled screw (prevent skewing of the crystal by applying a slight pressure).

Set the tube voltage  $U = 35.0$  kV and the emission current  $I = 1.00$  mA.

### 4.1.1 Determining the zero position of the measuring system

In coupled scanning mode, set the target to about  $10.2^\circ$  using the **ADJUST** knob.

Switch on the tube high voltage with **HV ON/OFF**.

Leave the target position unchanged and, in sensor scanning mode, manually find the counting rate maximum for the first reflection maximum of the  $K_\alpha$  line.


Leave the sensor unchanged in the maximum counting rate position and manually find the maximum of the counting rate in target mode.

Switch between sensor and target modes and check whether you have found the counting rate maximum.

In coupled scanning mode, move the target back by  $10.2^\circ$  (even if this takes you into the negative range!).

Save the positions of the target and the sensor as the “zero position of the measuring system” by pressing **TARGET**, **COUPLED** and  $\beta$  **LIMITS** simultaneously.


### 4.1.2 Recording the diffraction pattern

Start the software “X-ray Apparatus”, check to make sure that the apparatus is connected correctly, and clear any existing measurement data using the  button or the F4 key.

Set the measuring time per angular step  $\Delta t = 10$  s and the angular step width  $\Delta\beta = 0.1^\circ$ .

Press the **COUPLED** key to activate  $2\theta$  coupling of target and sensor and set the lower limit of the target angle to  $4^\circ$  and the upper limit to  $34^\circ$ .

Start measurement and data transfer to the PC by pressing the **SCAN** key.

When you have finished measuring, save the measurement series under an appropriate name by pressing the  button or the **F2** key.

### 4.1.3 Bragg reflection from a NaCl single crystal

Press the **ZERO** key to return the target and sensor to the current zero position.

Remove the LiF crystal and carefully mount the NaCl crystal in its place.

Determine the zero position of the measuring system in the same way as that above, except that the first reflection should now be at  $7.2^\circ$ .

Record the diffraction pattern in the same way as above.

You should have a saved pattern displayed on screen similar to the one shown in figure 7.

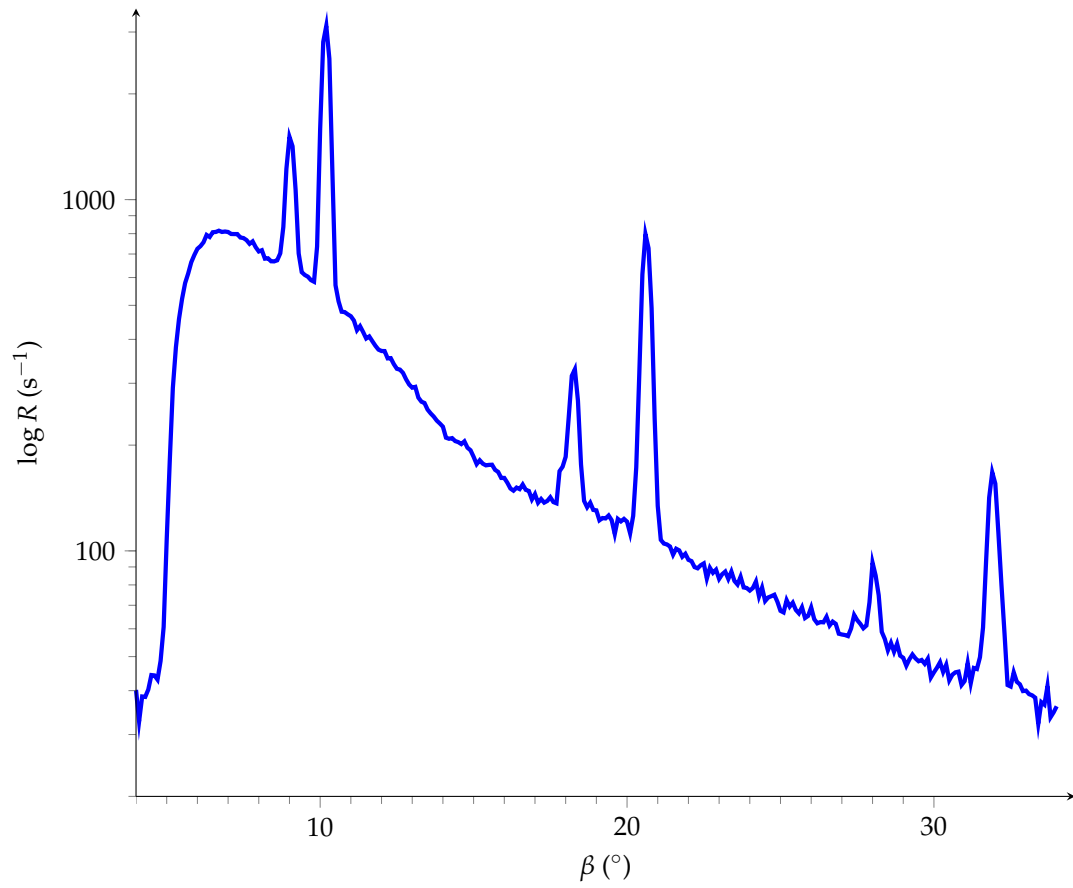


Figure 7: Diffraction pattern of X-rays in Bragg reflection to the third diffraction order for a LiF single crystal (note logarithmic display of the counting rate  $R$ ).

## 4.2 Analysis

**Note:** the NaCl and LiF crystals are both cut so that the X-rays diffract from planes parallel to the (100) direction. They have a face-centred cubic structure (see the table in section 3.1) so the first reflection will be 200.

In each window, click the right mouse button to access the evaluation functions of the software “X-ray Apparatus” and select the command “Calculate Peak Center” to evaluate the diffraction spectra.

Using the left mouse button, mark the “full width” of each peak and write down the centre values in a table as diffraction angle.

► For each diffraction angle  $\theta$  ( $= \beta$ ), calculate the values  $\sin \theta$  and plot  $n\lambda$  versus  $\sin \theta$ .

In each case, the results should lie along a straight line through the origin; in accordance with the Bragg formula — if the graph does not pass through the origin, your zeroing of the apparatus was at fault. As this is a constant error, how can you compensate for it without re-aligning your system?

► Calculate the lattice constant  $a_0$  and the indices of reflection for the peaks seen for both NaCl and LiF. Comment on the accuracy of your determination of  $a_0$ . What can you conclude about the ionic radii of the ions involved?

## 4.3 Identification of an unknown semiconductor

Repeat the experiment above with the semiconductor single crystal labelled X that has been supplied.

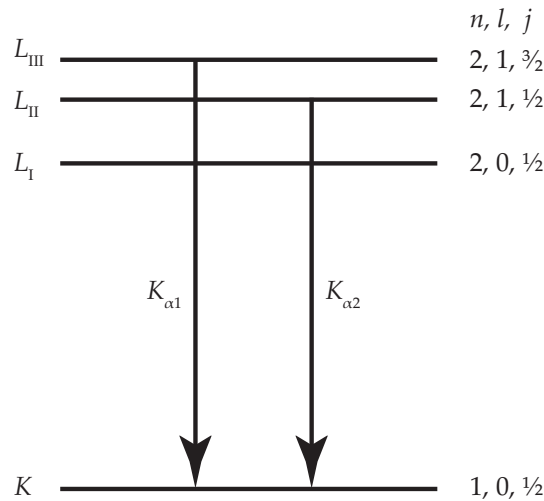
This crystal has a zincblende structure (face centred cubic lattice with a basis of two different atoms) and is oriented such that reflections parallel to the (111) direction are seen. Use the internet to determine its identity from your measured lattice constant.

Now repeat the experiment with the semiconductor crystal labelled Y. This semiconductor also crystallises in a zincblende structure — but for the purpose of this experiment, calculate the lattice constant as if the unknown semiconductor has a diamond structure.

► Discuss the spectra obtained from the semiconductor samples with a demonstrator. Carefully consider which of the (111) family of reflections will be seen in a diamond structure using the tables in section 3.1.

## 5 Fine structure of the characteristic X-radiation of a molybdenum anode

On closer examination, the characteristic  $K_\alpha$  and  $K_\beta$  lines of the X-radiation prove to be line doublets. The two doublets can be resolved by means of Bragg reflection from a single crystal of NaCl when measured in a high diffraction order. However, they differ in their physical nature. The  $K_\beta$  doublet consists of the pure  $K_\beta$  line, *i.e.* transitions of excited atoms from the *M*-shell to the *K*-shell, and the  $K_\gamma$  line, *i.e.* transitions from the *N*-shell to the *K*-shell. The wavelength interval  $\Delta\lambda$  between the two lines is just 1.2 pm (see table below), so that they can only be split using high resolution.

Figure 8: Diagram of the fine structure of the characteristic line  $K_\alpha$ .

Line	$E/\text{kV}$	$\lambda/\text{pm}$	Relative proportion
$K_\alpha$	17.44	71.08	1.000
$K_\beta$	19.60	63.26	0.170
$K_\gamma$	19.97	62.09	0.027
Doublet $K_\beta + K_\gamma$	19.65	63.09	

The fine structure of the  $K_\alpha$  line arises from the fine structure of the  $L$ -shell, and thus ultimately from the spin-orbit characteristic of the electrons. The  $L$ -shell actually consists of three sub-shells, designated  $L_I$ ,  $L_{II}$  and  $L_{III}$  in X-ray spectroscopy. The transitions from these sub-shells to the  $K$ -shell with emission of an X-ray is subject to the selection rules:

$$\Delta l = \pm 1, \quad \Delta j = 0, \pm 1$$

for the change of the orbital angular momentum  $l$  and the total angular momentum  $j$  on transition. Thus, two transitions from the  $L$ -shell to the  $K$ -shell are permitted; designated  $K_{\alpha 1}$  and  $K_{\alpha 2}$  (see figure 8). The table below shows the values generally found in the literature for molybdenum. According to these, the wavelength interval within the  $K_\alpha$  doublet is  $\Delta\lambda = 0.43 \text{ pm}$ .

Line	$\lambda/\text{pm}$	Relative proportion
$K_{\alpha 1}$	70.93	1.000
$K_{\alpha 2}$	71.36	0.55

## 5.1 Experiment

Using the same technique as in section 6.2 above, check that the first reflection around  $7^\circ$  is still present and strong. In order to see the fine structure a long exposure is necessary.

You will need to run this part of the experiment overnight — note that it will take **about 9 hours**.

Set the lower limit of the target angle to  $32.5^\circ$  and the upper limit to  $40.5^\circ$ , and set the measuring time per angular step to  $\Delta t = 400$  s.

Start the measurement and data transfer to the PC by pressing the **SCAN** key.

When the measurement is finished, open the “Settings” dialog with the **F5** key and enter the lattice plane spacing for NaCl to show the wavelength-dependency of the counting rate.

Save the measurement series under a suitable name using the **F2** key.

The fine structure pattern should now be evident in your data. Check the splittings seen against the tables above.

► **Show your results to a demonstrator before proceeding.**

## 6 Powder diffraction experiment

Another technique for recording X-ray diffraction patterns is known as Debye-Scherrer photography. We have seen from Bragg’s Law that the X-ray diffraction pattern from a single crystal consists of a series of spots, whose angular positions are given by scattering through  $2\theta$ . If instead we use a powdered (polycrystalline) material, Bragg’s Law then predicts that the diffraction pattern will consist of a series of rings subtending cones of semiangle  $2\theta$ , provided that we filter the X-rays to make them monochromatic (see figure 9).

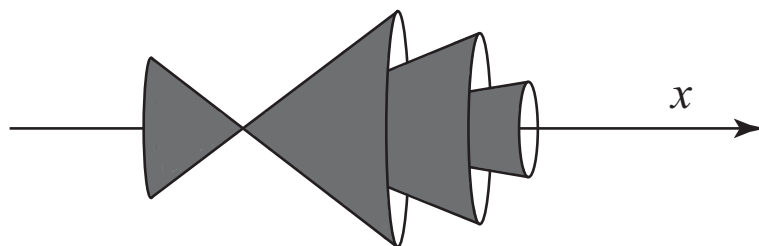


Figure 9: Schematic diagram of the rings of X-rays produced in Debye-Scherrer diffraction.

Suppose we now place a photographic film or X-ray luminescence plate<sup>1</sup> in front of the specimen: then the cones will give rise to rings on the film or plate. The radius of these rings is given by:

$$R = L \tan 2\theta$$

where  $L$  is the distance between the sample and the plate. The geometry is illustrated for a particular lattice plane in figure 5.

Thus the Bragg angles for the diffraction pattern can be obtained from the radii of the circles on the X-ray plate, provided the distance  $L$  is known accurately.

### 6.1 Experiment

In this experiment, Debye-Scherrer photographs of a powdered sample of NaCl are to be taken. The sample is already mounted in a circular holder which fits on the front of the collimator. The experimental

<sup>1</sup>We have both photographic film and X-ray luminescence plates available in the lab, however the required exposure time for the photographic film is approximately 10 times longer for the film than the luminescence plate. We will therefore use the luminescence plate for all the exposures in this practical, as doing so reduces the exposure time from 1 hour to 5 minutes.

setup is shown in figure 10.

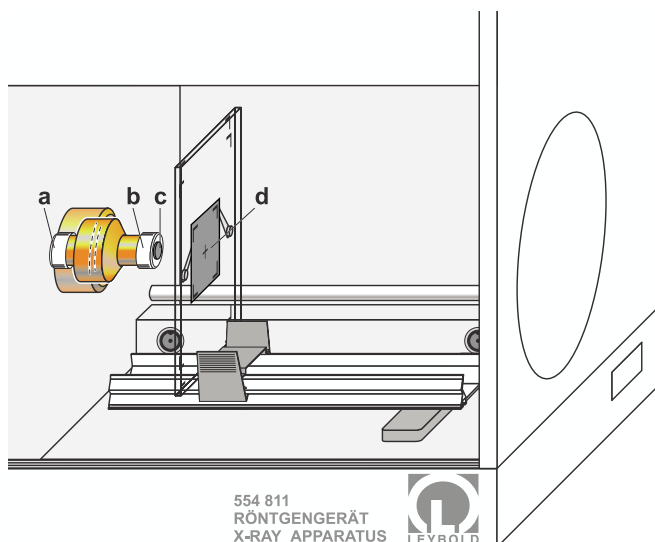


Figure 10: Schematic diagram of the arrangement for powder diffraction of X-rays, showing (a) the Zr filter, (b) the pinhole filter, (c) the sample position, and (d) the position of the luminescence plate and holder.

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Remove the goniometer (see X-ray apparatus script), then use figure 10 to mount the Zr filter on the ray entrance side of the collimator and re-insert the collimator. This will produce monochromatic X-rays from the  $K_{\alpha}$  line of the molybdenum cathode at 71.1 pm. Mount the pinhole filter on the collimator, then place the powdered NaCl sample immediately in front of the pinhole, as shown in figure 10.

Mount the X-ray plate holder assembly in the experimental chamber apparatus as shown, after clamping a luminescence plate in one of the black hygienic bags, in position (d). Ensure that it is centred on the masked area and see to it that the entire surface of the plate is planar.

Use the 20 mm long plastic spacer provided to shift the holder so that the distance between the sample and the plate is 20 mm (by varying the distance between the sample and the plate, the area covered in the photograph is changed).

Set the tube high voltage  $U = 35 \text{ kV}$ , the emission current  $I = 1.0 \text{ mA}$  and  $\Delta\beta = 0.0^{\circ}$ . Select the measuring time  $\Delta t = 300 \text{ s}$ , and start the exposure timer with the key "Scan". If the exposure time is longer, the reflections near the centre are blurred by the unscattered X-rays; however structures which are farther away from the centre become discernible.

**N.B. Close the software acquisition program before you take the exposure, otherwise the software may terminate the exposure before the time set.**

When the exposure time is over, take the plate holder with the experiment rail out of the experiment chamber. Remove the X-ray plate from the holder, and scan it using the "Planmeca" plate scanner according to the separate instructions provided with that system.

## 6.2 Analysis

Scan the film to create a bitmap image using the transparency scanner near the demonstrators' desk. You can then use a package such as GIMP to determine the exact diameters of the rings. The picture below shows the kind of image that you might expect to achieve:

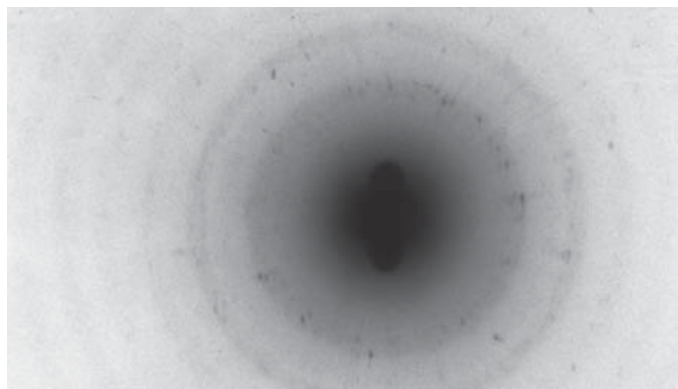


Figure 11: Powder diffraction image from NaCl.

It is therefore possible to calculate the Bragg angle  $\theta$  to obtain  $\sin^2 \theta$ . From the theory in section 4 we have:

$$\sin^2 \theta = \frac{\lambda^2}{4d^2} = \frac{\lambda^2(h^2 + k^2 + l^2)}{4a^2} = \frac{\lambda^2}{4a^2} I$$

where  $I$  is an integer. By using the table of allowed reflections you should be able to determine the integers  $I$  from your values for  $\sin^2 \theta$  and thus calculate the lattice constant for NaCl. Compare this with the value that you obtained in section 6. Estimate the errors in your determination of the ring diameters, and remembering the angular dependence of the accuracy, make an estimate of the accuracy of your value of  $a_0$  using the Debye-Scherrer method. Given that the density of NaCl is  $2.164 \times 10^3 \text{ kg m}^{-3}$ , calculate the number of formula units  $Z$  for this material.

**Optional** If time permits, repeat experiment 6.1 using a powdered sample of KCl, which has a similar structure to NaCl. Comment on any differences in the X-ray spectra. (No extra credit available)

## 7 Project

In this mini-project section we have given you a choice of investigations. We anticipate that you should do two of the three sections described below, taking about two days in the lab, but you may end up doing all three or just one.

► **Discuss your plans with a demonstrator before starting.**

### 7.1 Laue photography

Take Laue photographs of the existing crystals to orient them relative to their crystal axis. Instructions are provided in [2], but you should go beyond this document in the analysis and discussion.

### 7.2 X-ray spectroscopy

X-ray spectroscopy involves measuring the spectra by scanning the tube voltage ([3], [4]). The technique and possible results are described for a few samples in the Leybold script, but we expect you to investigate a variety of other metal films, available from the technician on request.

Firstly, you should verify Moseley's law. Next, experiment with using this as a method of chemical analysis on metallic alloys. This could interestingly be done on a selection of metal coinage (say foreign coins also) to determine what the alloy contents are and how these have changed with time (the UK changed the metal content of its coins quite recently).

### 7.3 X-ray analysis of a non-cubic crystal

The aim of this part is to perform an X-ray analysis of a non-cubic crystal. This is a more open-ended option which will involve experimenting with different crystals to determine what is possible with this kit.

### Bibliography

- [1] A. M. Glazer, *The structure of crystals*, IoP Publishing (1987)
- [2] Laue diagrams: investigating the lattice structure of monocrystals, *Leybold Physics Leaflets* P7.1.2.2 [https://www.ld-didactic.de/literatur/hb/e/p7/p7122\\_e.pdf](https://www.ld-didactic.de/literatur/hb/e/p7/p7122_e.pdf)
- [3] Determination of the chemical composition of a brass sample by X-ray fluorescence analysis, *Leybold Physics Leaflets* P7.5.1.2 <https://www.ld-didactic.de/documents/en-US/EXP/P/P7/P7512cle.pdf>
- [4] Application of X-ray fluorescence for the non-destructive analysis of the chemical composition, *Leybold Physics Leaflets* P7.5.1.1 <https://www.ld-didactic.de/documents/en-US/EXP/P/P7/P7511cle.pdf>