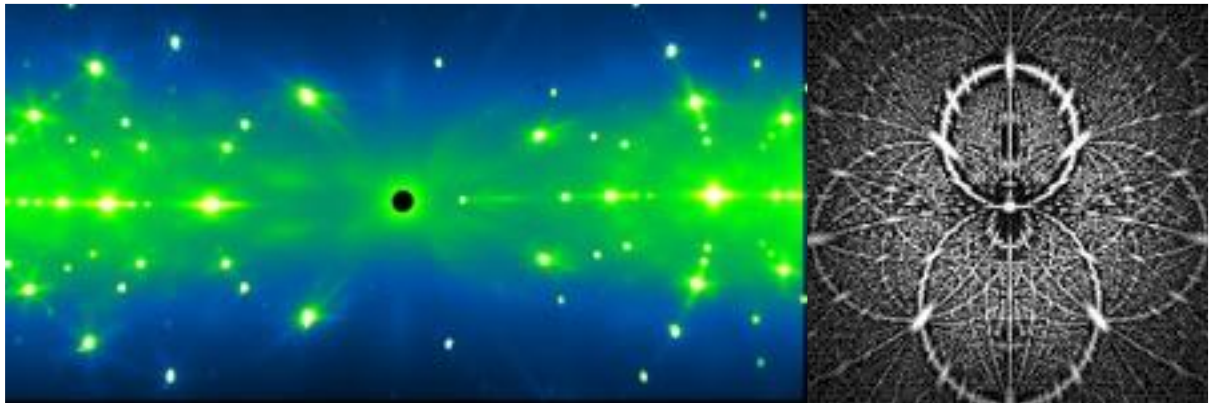




# X-Ray Crystallography



## **1. Aims**

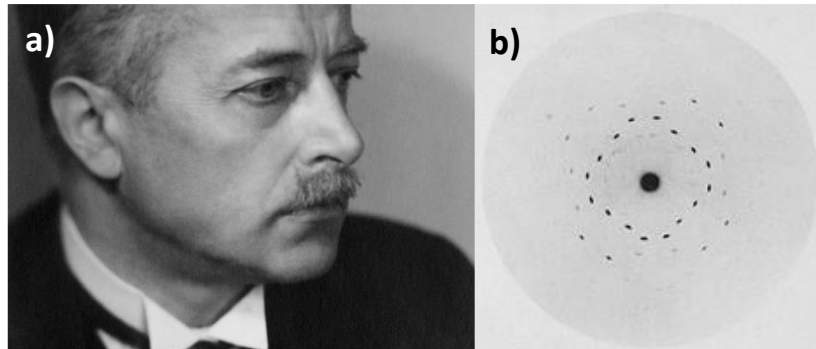
**The main objectives of this laboratory are to:**

- a) Gain a practical understanding of the way in which X-rays scatter from crystals to form distinct diffraction patterns and,
- b) Acquire a practical appreciation of the critical link between diffraction pattern, the reciprocal lattice and the internal structure of crystals.

By performing the experiments in this lab, you will retrace many of the steps taken by Max von Laue and the Braggs (father and son) that resulted in their Nobel Prizes for Physics in 1914 and 1915. While these awards are now over 100 years old, the ramifications of the fundamental principles associated with them translate to today's research: following their work, the interpretation of crystallographic diffraction patterns resulted directly in finding the structures of DNA, haemoglobin, penicillin and nucleic acid (each of which separately resulted in a Nobel Prize between 1962 and 1982), the discovery of quasicrystals (Nobel Prize in 2011) and the birth of the fields of molecular biology and molecular drug design.

## **2. Historical Context**

Around the turn of the 20<sup>th</sup> century, many physicists were trying to understand the nature of both cathode-rays and X-rays (discovered during cathode-ray investigations by Röntgen in 1895, who won the first Nobel Prize ever in 1901 for this work). As had been a theme throughout 20<sup>th</sup> century physics, there was much debate as to whether these different rays resulted from a flow of particles or the propagation of waves. With a background in optics and an awareness of the contemporary view of crystal structures at the time, Max von Laue (Fig. 1a) realised that the expected wavelength of X-rays (if indeed wave-like in nature) should be comparable to, but less than, the expected periodicity of the atomic arrangements in crystals. Hence, crystals might be used as effective diffraction gratings for X-rays and irradiating them might therefore allow distinct interference maxima and minima to be found in the intensity of the diffracted X-ray beams. Initial experiments, by von Laue and his colleagues Friedrich and Knipping, used copper sulphate as the crystal of choice and were deemed insignificant. However, hints of diffraction spots on the photographic plates prompted them to further optimise their experimental geometry and change from copper sulphate to a regular cubic zinc sulphide crystals. With the X-rays passing through one of the square faces of zinc sulphide, a stunningly regular array of diffraction spots was observed which appeared to be entirely consistent with the four-fold symmetry of the macroscopic crystal perpendicular to the beam (Fig. 1b).



**Figure 1. a)** A photograph of Max von Laue and **b)** one of the original X-ray diffraction patterns taken by von Laue and his colleagues on zinc sulphide. Intensity maxima are obvious as is the four-fold symmetry in their spatial distribution.

These experiments allowed two major thrusts in physics to develop: the further use of crystals to allow the investigation of the properties of X-rays (Barkla was awarded the Nobel Prize in 1917 and Siegbahn in 1924 for such studies) and conversely, the use of X-rays to determine the periodicity, symmetry and structure of crystals.

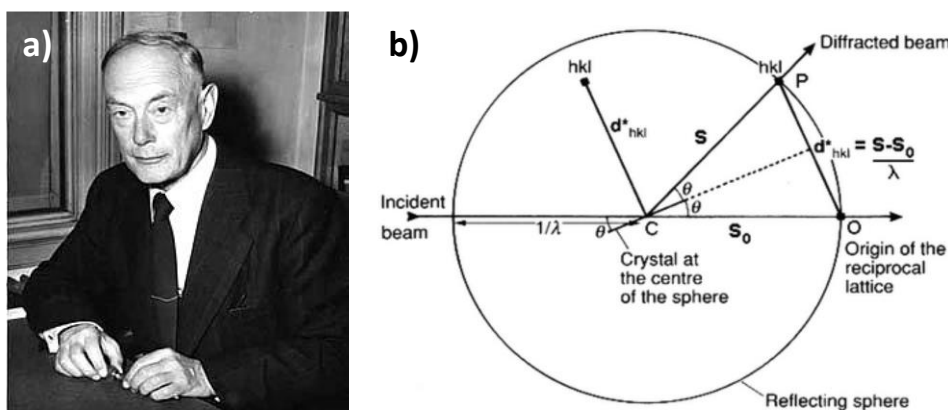
When William Laurence Bragg became aware of von Laue's diffraction patterns, he quickly realised that constructive interference intensity maxima could be interpreted as the result of "reflections" from successive planes of atoms in crystals which obeyed a specific geometrical relationship. This later became known as Bragg's Law:

$$2d \sin \theta = n\lambda \quad \text{(equation 1)}$$

where  $d$  is the perpendicular distance between atomic planes,  $\theta$  is the glancing angle at which the X-rays are reflected,  $n$  is an integer and  $\lambda$  is the wavelength of the X-rays. Using X-rays of a single wavelength, William Laurence and his father William Henry Bragg set up a diffractometer to measure the periodicities of atomic planes in crystals. By taking account of variations in the intensities of the observed maxima, they were able to go further and suggest what the actual crystal structures of a number of simple crystals might be. Establishing "structure determination" in this way is arguably one of the most important landmarks in science.

### 3. Relevance to Queen's University Belfast (QUB)

Two people in QUB were extremely important in the development of the field of X-ray crystallography: Paul Ewald (Fig. 2a) was a lecturer and then Professor of Mathematical Physics during his 10 years at QUB. He came to Belfast in 1939, after leaving Nazi-controlled Germany. His research focused on understanding the dynamical interactions between X-rays and matter and his impact on the field cannot be overstated. Not only did he provide one of the most useful geometric tools for understanding diffraction (The Ewald Sphere – Fig. 2b), which we will use to help understand our experiments, but he was instrumental in the development of the field from its inception.

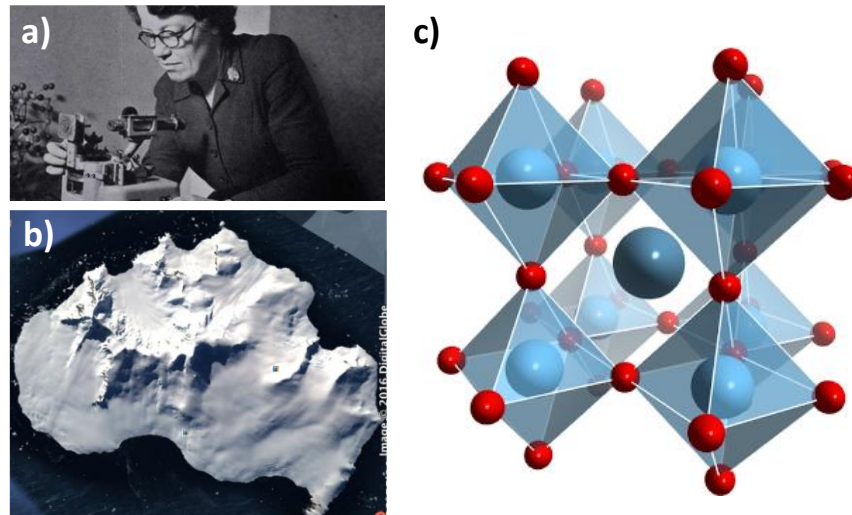


**Figure 2. a)** Photograph of P. P. Ewald and **b)** a 2D diagrammatic representation of the diffraction sphere of “Ewald Sphere”, the surface of which represents all possible solutions to the Bragg equation.

Von Laue said the following in his Nobel lecture:

*“Such was the state of affairs as, one evening in February 1912, P. P. Ewald came to visit me. On Sommerfeld’s instigation he was working on a mathematical investigation into the behaviour of long electromagnetic waves in a space-lattice and subsequently he published a dissertation on the theory of crystal optics which was based upon that work. But he was faced at that time with certain difficulties and came to me with a request for advice. Now it was not, however, possible for me to assist him at that time. But during the conversation I was suddenly struck by the obvious question of the behaviour of waves which are short by comparison with the lattice-constants of the space-lattice. And it was at that point that my intuition for optics suddenly gave me the answer: lattice spectra would have to ensue. The fact that the lattice-constant in crystals is of an order of  $10^{-8}$  cm was sufficiently known from the analogy with other interatomic distances in solid and liquid substances, and, in addition, this could easily be argued from the density, molecular weight and the mass of the hydrogen atom which, just at that time, had been particularly well determined. The order of X-ray wavelengths was estimated by Wien and Sommerfeld at  $10^{-9}$  cm. Thus, the ratio of wavelengths and lattice-constants was extremely favourable if X-rays were to be transmitted through a crystal. I immediately told Ewald that I anticipated the occurrence of interference phenomena with X-rays.”*

Helen Megaw (Fig. 3a) also had links to QUB and played a major role in the history of X-ray crystallography, as a tool for structure determination. Helen studied as an undergraduate in QUB for a year before taking a place in Girton College in Cambridge. She obtained her BA and stayed on for her PhD research from 1930 to 1934. She had an interest in crystallography and spent her initial research career determining the structure of ice. Her seminal contribution in this field is marked by an icy island in the Antarctic (Fig. 3b) which bears her name (Megaw Island). Later in her career, she determined the crystal structure of perovskite oxides (an incredibly important group of materials) and the mineral  $\text{CaSnO}_3$  (Fig. 3c) was named “Megawite”. In 2000, at the age of 93, she was awarded an honorary DSc from QUB.



**Figure 3.** **a)** photograph of Helen Megaw; **b)** Megaw island in the South Atlantic, taken from Google Earth and **c)** the structure of  $\text{CaSnO}_3$  (or Megawite) where the smaller red atoms represent oxygen and the large blue atoms represent the cations.

#### 4. Experiment 1: Laue Photographs

##### Aim:

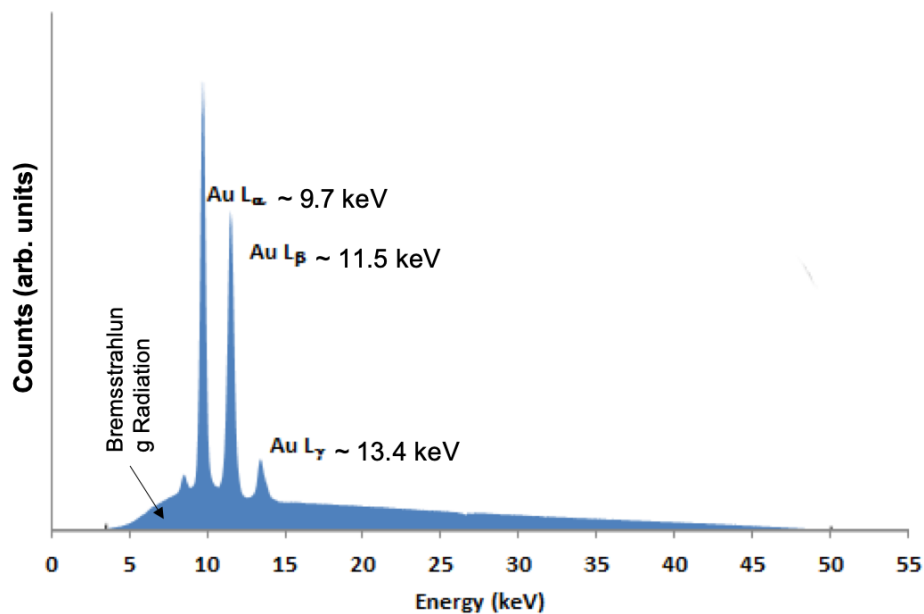
To investigate the x-ray scattering from the crystal lattice plane using a polychromatic wavelength by:

- a) Acquiring a Laue photograph experimentally
- b) Identify symmetry elements in it.

Laue photographs are taken using incident X-rays with a range of wavelengths (or energies). This means that a number of different lattice periodicities can simultaneously satisfy the Bragg equation (eq. 1), for a fixed X-ray beam direction and crystalline sample orientation. To fully analyse the Laue photographs, we should first be familiar with the entire spectrum of X-rays used, in this case this is the X-rays produced from a gold target. Figure 4 shows a typical Au emission spectrum (using a 35 keV electron beam).

Importantly, there are two main contributions to the emission spectrum:

- *Sharp peaks or “characteristic X-rays”.* These are associated with inter-orbital electronic relaxations. The incident electrons impart sufficient energy to some inner orbital electrons (surrounding the Au nuclei) to completely remove them from their potential wells. When this occurs, other electrons in higher energy orbitals can reduce their energy state by relaxing into the unoccupied inner orbitals. By conservation of energy, this relaxation process requires the emission of a photon with a frequency (and energy) characteristic of the inter-orbital energy difference.
- *Bremsstrahlung radiation.* This is a broad continuous background signal which results from the deceleration of incident electrons, usually due to Coulombic interactions with nuclei in the target where, energy loss events can occur from 0 to 35keV. Bremsstrahlung X-rays with energies below about 5keV are absorbed within the gold target and are not emitted.



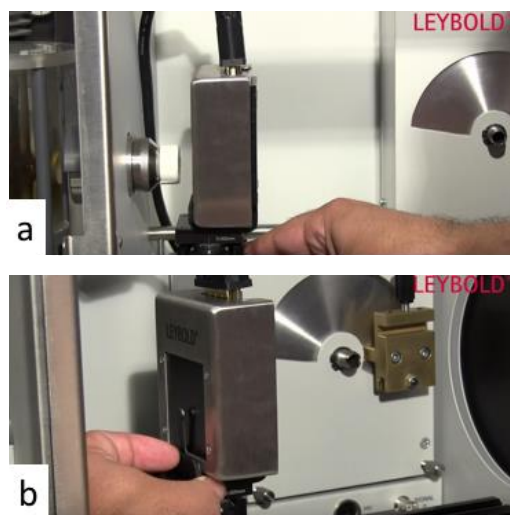
**Figure 4.** Typical Au X-ray energy spectrum upon bombardment by a 35 keV electron beam.

To obtain Laue photographs, the entire spectrum of different X-ray radiation energies must pass through a thin single crystal sample. Some specific wavelengths will be diffracted from periodic atomic planes such that the diffracted rays will interfere constructively, generating spots in a diffraction pattern. These spots, characteristic of in-phase superposition of waves, allowed Laue to state with confidence that X-rays had wave-like characteristics, which led directly to the Nobel Prize.

#### **4.1. Setting up the Apparatus.**

The X-ray system for capturing Laue photographs should be already in place. However, check that this is as shown in Fig. 5 and described below:

- a)** The solid-state X-ray camera should be attached to the optical rail mount that fits into the system (held into place with positioning pins), and this should be connected to the signal processing box and on to the compute.
- b)** The small lead beam stop should be placed approximately where the undiffracted X-ray beam would be expected to hit the detector (but will hopefully be blocked).
- c)** The camera should be placed around 2cm from the diffracting crystal.



**Figure 5.** The Laue photograph experimental configuration. **a)** with the single crystal and plastic cap mounted onto the end of the collimator and the X-ray solid state camera ~2 cm away. **b)** The small beam-stop should be placed onto the front of the camera to block the straight-through beam of undiffracted radiation.

#### 4.2. Acquiring Laue Photographs for NaCl

Once the experimental set up has been checked:

- a)** Identify the NaCl single crystals. These are held in pliable plastic caps.
- b)** Gently mount the crystal on the end of the circular collimator, so that the incident X-ray beam will pass through it.
- c)** Set the accelerating voltage on the X-ray tube to  $U = 35\text{kV}$  and the electron incident beam current to  $I = 1\text{mA}$ .

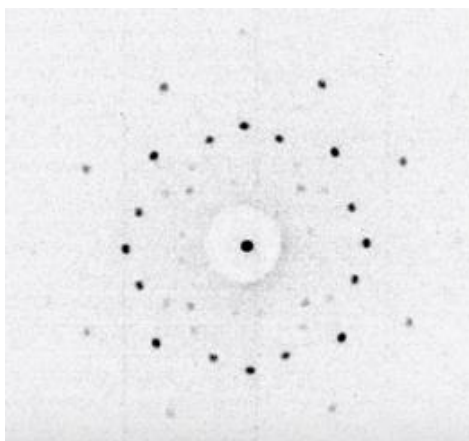
Software: The camera image-capture is driven using the CT software package (the icon with the frog).

- a)** Open the software.
- b)** Within the “Camera” section of the front display (left-hand top): set the integration time should to “3500ms (Laue)”.
- c)** Within the “Radiography” heading: increase the intensity to around 70% of full scale and contrast to around 30% full scale.
- d)** Click the “create offset image using dark frames” within the camera drop-down box. Allow the system to record around 10 images. Stop and then tick the “use offset image” box.
- e)** The X-rays can now be turned on (using the software) and the Laue pattern will be recorded and displayed on the screen.

It is often easier to see the Laue pattern by inverting the image into a “negative”, which can be done from within the radiography drop-down menu.

Images, such as that in Fig. 6 should be obtained and saved. Here is a video [walk-through of the experiment](#).





**Figure 6.** A Laue photograph from white X-ray irradiation of a thin NaCl crystal, taken using the LD X-ray system. 4-fold symmetry is evident and hence the X-ray beam direction is along one of the primary crystallographic axes in NaCl (a  $\langle 100 \rangle$  direction)

Note: If a good quality diffraction pattern cannot be obtained, then it is good idea to check the Au spectrum by following the instructions in the Appendix: Calibration for Laue Photographs.

#### 4.3. Analysing the Data.

The NaCl crystal is oriented with its  $b^*$ -axis parallel to the X-ray beam. Recall that  $a^*$ ,  $b^*$ , and  $c^*$  are the reciprocal lattice vectors, and that in a cubic system they are equivalent to each other ( $a^* = b^* = c^*$ ).

- a) Construct the  $b^*$ - $c^*$  section of the reciprocal lattice to scale for NaCl (cubic with real space lattice parameters  $a=5.64\text{\AA}$ ).
- b) Overlay, to scale, the range of Ewald spheres associated with the energies used (characteristic peaks in the Au X-ray spectrum). Discuss your observations.
- c) Identify the symmetry elements found in the Laue photograph taken.

➤ The Appendix contains a section briefly describing the reciprocal lattice.



## 5. Experiment 2: Bragg-Brentano Diffraction from a Single Crystal

### Aim:

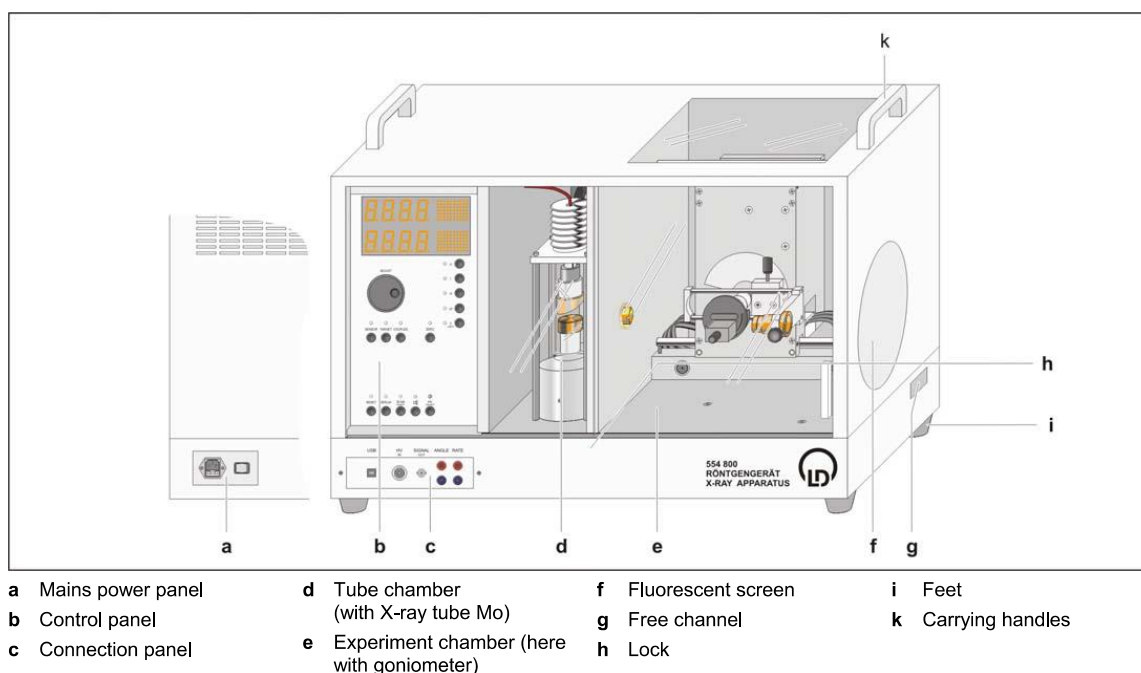
To investigate the x-ray scattering from the crystal lattice plane using Bragg-Brentano set up by:

- a) Acquiring a diffraction pattern
- b) Identify the lattice planes in the diffraction pattern, and calculating their interplanar spacing.

A common quantitative investigative technique is to examine single crystal diffraction under the so-called Bragg-Brentano scanning geometry. This allows for very accurate determination of lattice periodicities and mapping of individual reciprocal lattice points (which can be extremely useful). In this technique, the crystal surface is the entrance and exit reference plane for the X-ray beams. For this reason and because incident and diffracted beams make the same angle with the lattice planes, the Bragg diffraction from a crystal is also known as *Bragg reflection*.

### 5.1 Setting up the Apparatus.

A full overview of the apparatus for the Bragg-Brentano diffraction is shown in Fig. 7. For more information on the keys' functions read the *Appendix*.



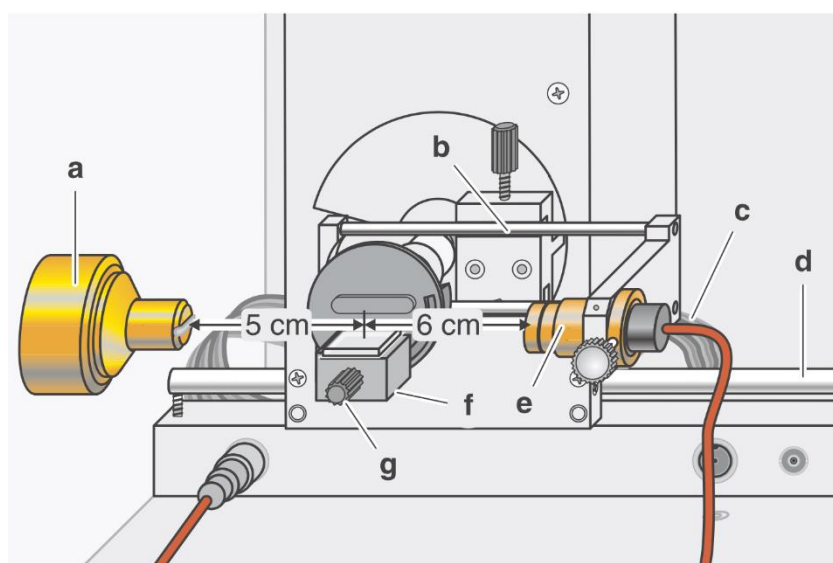
**Figure 7.** Overview of the full apparatus. Taken from the Leybold manual.

A schematic of the apparatus arrangement in more detail is shown in Fig. 8 (without the Zr-filter). Additionally, pay attention to the following:

- a) The X-rays are generated from a Mo target so make sure the X-ray tube is in place (ask Victor to do this, if it hasn't been done already).
- b) The X-rays are detected using a Geiger-Muller (GM) tube.
- c) The X-ray diffraction observed will be in "reflection" mode, for this a larger, thicker free-standing single crystal is used. Both the plastic crystal holder and GM tube should be mounted onto the goniometer drive.

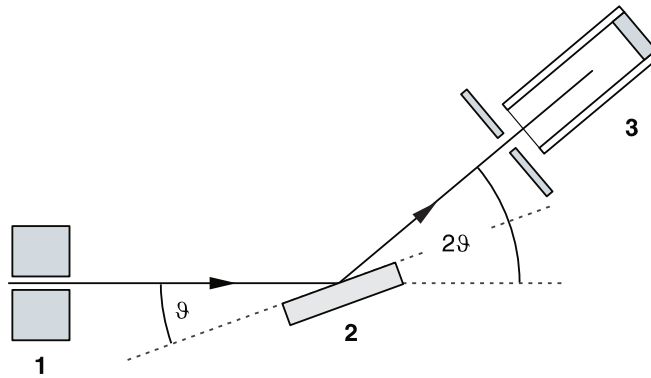
- d) A horizontal slit collimator should be in place.
- e) Monochromatic (single frequency) X-rays are needed; to obtain almost monochromatic X-rays, a Zr metal filter (mounted in another plastic cap) should be placed onto the collimator. By doing this, Mo-K $\alpha$  radiation (with  $\lambda = 0.71\text{\AA}$ ) passes through the Zr filter.
- f) Note the approximate separations between the end of the collimator, the centre of the crystal and the GM detector.

For this experiment you will be using the NaCl single crystal (cubic,  $a = 5.64\text{\AA}$ ), which is the same as that used in Experiment 1. The NaCl crystals are hygroscopic and fragile, so please handle the crystals by the short faces only.



**Figure 8.** Schematic illustration of the experimental arrangement needed for the single crystal Bragg measurements. “a” is the slit collimator; “b” the guiderail holding the GM tube (“e”) and sample stage (“f”) onto the goniometer. “g” is a tightening screw that can be loosened to allow the sample height to be adjusted. Be careful not to over-tighten this screw. Taken from the Leybold manual.

For this experiment, the instrument and the crystal are both pivoted with respect to the incident X-ray beam in a  $2\theta$  coupling, see Fig. 9. Where the zero point ( $\theta = 0^\circ$ ) is characterised by the fact that the lattice planes and the axis of the counter tube (Fig. 8e) are parallel to the incident X-ray beam. In other words, a point detector and sample are moved so that the detector is always at  $2\theta$  to the incident X-ray beam. Since the lattice planes can be considered to be parallel to the surface of the crystal, the zero point of each crystal must be calibrated individually.



**Figure 9.** Schematic diagram of X-rays diffraction at a single crystal showing the  $2\theta$  coupling between the counter-tube and the scattering (glancing) angle. 1 is the collimator, 2 the single crystal and 3 the counter-tube. Taken from the Leybold manual.

**5.2 Setting the Zero Angle for the Detector.** The first stage in any Bragg diffraction measurement on a diffractometer is to make sure that the straight-through X-ray beam is recorded at a detector angle of zero.

- a) Zero the spectrometer (press 'zero')
- b) Manually set the X-ray target voltage (U) 35kV, the emission current associated with the bombarding electron flux (I) to 1mA and lower the specimen holder (without the crystal) so that it will not block the straight-through beam.

Software: The Bragg X-ray experiment is driven using the LD X-ray apparatus software, which you can find through a search for "X-ray" if it is not already on the desktop. Open the software.

- a) By clicking on the control icon (spanners) and clicking on the "detector scan" set up parameters to scan the detector through the zero point (probably scanning  $\beta$  angles from  $-2^\circ$  to  $+2^\circ$  with a time step of  $\Delta t = 1\text{s}$  and an angular step  $\Delta\beta = 0.1^\circ$ ) and run the scan by clicking on the "sensor" box. A peak should be recorded, which should have its centre at  $0^\circ$ , but which is probably shifted a little.
- b) If the peak is not centred at  $0^\circ$ : Manually move the detector (sensor) to the angle at which the centre of the peak is seen and then set this as the new zero position by pressing TARGET, COUPLED and  $\beta$  LIMITS *simultaneously*. The detector zero should now correspond to the centre of the straight-through X-ray beam.
- c) Rescan the detector around the zero position to verify that the zero has been correctly set and record the count rate at the correctly zeroed position.

Notes:

- You can clear any pre-existing measurement using F4.
- $\beta$  is really  $\theta$ .

### 5.3 Positioning the Single Crystal.

Loosen the screw shown in Fig. 8(g) and place the NaCl single crystal onto the sample stage and gently raise the stage up to the point at which the top of the crystal just touches the horizontal plastic setting bar (a protrusion on the sample holder unit).

The next step is to find the maximum counting rate:

- a) Leave the target position unchanged and, in SENSOR scanning mode, manually check that you still have the counting rate from 5.2. This is the maximum counting rate in target mode.
- b) Ideally, the crystal surface will now be sitting in the middle of the X-ray beam. However, this might not be the case. Setting the crystal height is quite important for the accuracy of subsequent measurements, so manually turn on the X-ray HV and see if the count rate has halved over that measured in the zero position before the NaCl crystal had been introduced and sample holder height adjusted. If the count rate is significantly lower than half, then shut off the HV and move the crystal down very slightly; conversely, if the count rate is significantly above half, then raise the holder very slightly. This setting can be fiddley, so be patient and please be careful with the holder and crystal.
- c) If needed check between sensor and target modes and check whether you have actually found the maximum counting rate.

Once the height has been set, you will need to adjust the TARGET angle, so that the crystallographic plane that is parallel, or approximately parallel to the surface of the crystal, and which will be involved in the diffraction to follow is absolutely flat (in this case the {200} plane). To do this, we need to perform what is known as a “*Rocking Curve*”.

**Rocking Curve:** The cubic lattice parameter for NaCl is  $5.64\text{\AA}$  and Mo- $K_{\alpha}$  has a wavelength of  $0.71\text{\AA}$ . This implies the Bragg condition is satisfied for {200} planes when the Bragg angle ( $\theta$ ) is  $\sim 7.2^{\circ}$  (you can verify this for yourself using the Bragg equation).

Steps to perform a rocking curve:

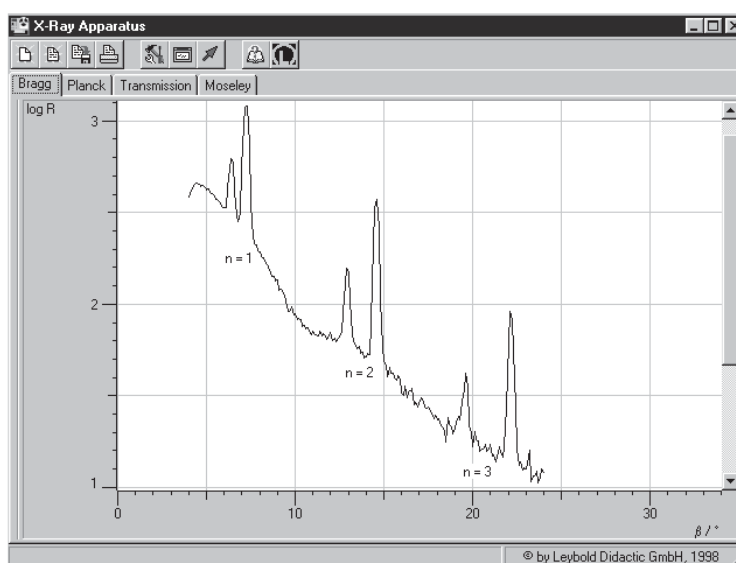
- a) Manually set the GM tube detector position to  $14.4^{\circ}$  (twice the ideal diffraction angle:  $2\theta$ ) and perform a Rocking Curve around  $7.2^{\circ}$ , varying the apparent angle of the crystal surface. This is, a “target scan” from  $\beta_{\min} = 0^{\circ}$  to  $\beta_{\max} = 14.4^{\circ}$ . The ideal scenario is that the diffraction peak in this scan will appear at exactly  $7.2^{\circ}$ , but this is unlikely;

Note: The Bragg peak at  $\sim 7.2^{\circ}$  is much weaker in intensity than the 'half intensity'  $0^{\circ}$  peak (obtained during the 'zeroing' process). The software automatically rescales the y-axis, so it will be very easy to think that there's no peak at  $\sim 7.2^{\circ}$ . To address this, make sure to delete the  $0^{\circ}$  peak on the screen (software) before starting the new scan, so that the small 'blip' (between  $5-8^{\circ}$ ) is more obvious.

- b) In the event that the diffraction peak is not located at exactly  $7.2^\circ$ , manually set the target angle to the point at which the maximum in the measured rocking curve is observed, but **do not save this as the new zero position**;
- c) Switch to “coupled scanning mode” and move the target (and the sensor simultaneously) back by  $7.2^\circ$ , even if this takes it into the negative range. At this point, the {200} planes, the X-ray beam and the GM detector should be perfectly aligned in the same plane;
- d) Save **these** positions as the corrected zero positions for BOTH target and sensor, by again pressing TARGET, COUPLED and  $\beta$  limits **simultaneously**.

**5.4 Taking a Bragg Diffraction Scan.** Now that the sample and diffractometer are aligned, meaningful diffraction scans can be performed:

- a) Within the control panel of the X-ray software, set up a COUPLED scan with a lower limit of  $\beta = 4^\circ$  and upper limit of  $\beta = 35^\circ$  for the target angle.
  - The COUPLED key activates the  $2\theta$  coupling of target and sensor
- b) Run the scan with high resolution (counting times and angular resolution) by pressing the SCAN key.
- c) When you have finished measuring, save the data and graphs. Data (plots) similar to those shown in Fig. 10 should be obtained.



**Figure 10.** X-ray intensities from single crystal diffraction for NaCl. Here, the Zr filter has not been used and so maxima for both  $\text{MoK}_\alpha$  and  $\text{MoK}_\beta$  wavelengths occur.

\* Further advice on data acquisition and analysis can be found in the Appendix.

### 5.5 Analysing the Data.

In the single crystal Bragg experiment, we use knowledge of both the X-ray wavelengths and crystalline lattice parameters to set up the diffractometer accurately. It would hence seem to be a bit of a circular argument to then use the data to determine

either the wavelength of the radiation or the lattice parameters. Thus, the data analysis includes:

- a)** Identify if the experimental diffraction pattern (diffractogram) contains one or more orders of diffraction. Discuss.
- b)** From the diffractogram, using Bragg's Law and equation 2, verify that the Bragg peaks are compatible with the fcc structure. Determine the Miller Indices of lattice planes responsible for the Bragg peaks observed in the diffractogram and calculate their interplanar spacing.
- c)** Draw an  $a^*-c^*$  reciprocal lattice section (for  $b^*=0$ ) and, by superimposing an Ewald Sphere, identify the reciprocal lattice points responsible for the diffraction maxima. Do they match those (hkl) identified in b)?  
Hint for drawing the reciprocal lattice section: consider the rotation of the sample.
- d)** Using a sketch of the NaCl cubic structure, identify the planes associated with each X-ray peak.
- e)** Even then, not all reciprocal lattice points generate X-ray peaks – the 001 / 100 reflection is, for example missing. By performing research on “Structure Factors” and “Systematic Absences”, rationalise why not all spots in the reciprocal lattice are observed in diffraction experiments.

## APPENDIX

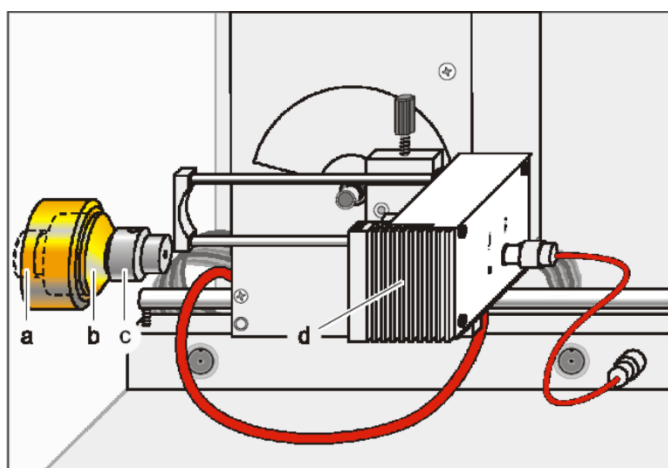
### • Calibration for Laue Photographs

#### **Taking the Energy Spectrum of X-rays from a Gold Anode**

Laue photographs are taken using incident X-rays with a range of wavelengths (or energies). This means that a number of different lattice periodicities can simultaneously satisfy the Bragg equation (eq. 1), for a fixed X-ray beam direction and crystalline sample orientation. To fully analyse the Laue photographs, we should first be familiar with the entire spectrum of X-rays used, in this case this is the X-rays produced from a gold target.

Make sure that the equipment is set up as shown in Fig. A:

1. The X-ray unit is set up with the Au anode (target): X-ray tube inserted.
2. The circular collimator is in place.
3. The attenuating aperture (pin-hole aperture with two red dots) is attached: The aperture reduces the intensity of the X-ray beam to the point where the energy detector will not be damaged. This attenuating aperture needs to be aligned with one red dot vertically above the other.
4. The energy detector should also be attached to the goniometer and placed around 10cm away from the end of the attenuating aperture
5. The goniometer angle is set to zero, so that the straight through collimated and attenuated beam hits the detector window (be aware that there may be slight misalignments, but these can be dealt with later).
6. The X-ray base unit and energy detector are switched on and that the signal output from the energy detector is connected to the SIGNAL IN socket (this can be seen on the right-hand side of Fig. A).
7. The “MCA box” is connected to the computer (USB connection)
8. The SIGNAL OUT output from the X-ray base unit is connected to the MCA box using BNC cable.



**Figure A.** Schematic illustration of the experimental geometry needed to measure the emission spectrum from a gold anode. The collimator is labelled as “b”, the attenuating aperture as “c” and the energy detector unit as “d”.

Taken from LD P6.3.5.3 Instruction Leaflet



**Software:** Open the CASSYLAB software. Within CASSYLAB, click on the drawing of the MCA box. Set measurement parameters (usually on the right-hand side of the CASSYLAB control display) as follows: “multichannel measurement, 512 channels, negative pulses, Factor= -2.5, measuring time= 360s”. Select the tube voltage (the accelerating voltage for the electron beam that will bombard the Au target) to 35kV and the emission current (electron beam flux) to 0.1mA. Switch on the high voltage. Start recording the X-ray energy spectrum using the clock icon and adjust the sensor angle a little if required to optimise the spectrum collection. The spectrum obtained should look like that given in Fig. 4.

- **Experiment 2: Bragg-Brentano Diffraction from a Single Crystal**

**Parameter Selector Keys**

**Key U:** activates display and setting of the tube high voltage  $U$ .

Value range: 0.0-35.0 kV

Step width: 0.1 kV

Default: 5.0 kV

The set value is displayed regardless of whether the tube high voltage is switched on (see keys SCANON/OFF and HV ON/OFF).

**Key I:** activates display and setting of the emission current  $I$ .

Value range: 0.00-1.00 mA

Step width: 0.01 mA

Default: 0.00 mA

The set value is displayed regardless of whether the emission current is flowing.

**Key  $\Delta t$ :** activates display and setting of the measuring time (per angular step)  $\Delta t$ .

Value range: 1-9999 s

Step width: 1 s

Default: 1 s

**Key  $\Delta\beta$ :** when the goniometer is mounted, this activates the display and setting of the angular step width  $\Delta\beta$  for auto-scan mode.

Value range: 0.0°-20.0°

Step width: 0.1°

Default: 0.1°

The setting  $\Delta\beta = 0.0^\circ$  deactivates auto-scan mode and activates “exposure-timer” mode.

**Key  $\beta$  LIMITS:** when the goniometer is mounted, this activates the display and definition of the upper and lower limit angles for auto-scan mode. A measurement cannot be started when the upper limit is less than the lower limit. The display flashes until this situation is corrected.

The first time this key is pressed, the display panel shows a symbol  $\downarrow$ . You can now set the lower limit angle.

The second time this key is pressed, the display panel shows the symbol  $\uparrow$ . You can now set the upper limit angle.

The symbol  $\updownarrow$  in the display panel indicates the setting  $\Delta\beta = 0.0^\circ$ . Auto-scan mode is deactivated.

### Scanning - Mode Keys

**Key SENSOR:** when the goniometer is mounted, this key activates “sensor” scanning in auto-scan or manual scan modes.

You can define the limit angles of the sensor arm for auto-scan. Sensor arm movement can be controlled manually or automatically. The bottom display field shows the angular position of the sensor.

**Key TARGET:** when the goniometer is mounted, this key activates “target” scanning in auto-scan or manual scan modes.

You can define the limit angles of the target arm for auto-scan. Target arm movement can be controlled manually or automatically. The bottom display field shows the angular position of the target.

**Key COUPLED:** when the goniometer is mounted, this key activates “coupled” scanning in auto-scan or manual scan modes. You can define the limit angles of the target arm for auto-scan.

The sensor and target arms can be moved manually or automatically with an angular coupling of 2:1. In A manually controlled movement, the reference point for the 2:1 coupling is the angular position of the target and the sensor before the COUPLED key is pressed, and for automatic movement the reference point is the zero point of the measuring system.

The bottom display field shows the angular position of the target. Pressing the COUPLED key toggles the upper display field between the counting rate and the angular position of the sensor.

**Key ZERO:** when the goniometer is mounted, this key causes the target and sensor arms to move to the zero position of the measuring system (see instruction sheet of the goniometer).

- **Points To Consider For Data Acquisition**

**Step size:** If there is a signal with a peak that you want to resolve, the measurement step size must clearly be less than the peak width. Often, to resolve the peak shape you should have more measurements within or near the peak, in some occasions  $\Delta\theta < 0.1\Delta\theta$  or  $\Delta\theta < 0.25\Delta\theta$  can be used.

**Counting time:** To obtain a good peak, you need to build up signal. However, scattering is a random process and thus, you need to consider that the number of counts (N) in a time given by the counting rate (R) in a time (t):

$$N = Rt$$

So that, the uncertainty in the number of counts is  $\sqrt{N}$ . Therefore, the statistical error in R with a counting time t is  $\sigma_R = \sqrt{R/t}$ . Thus, increasing the counting time decreases the uncertainty in the count rate (but, of course, it also increases the time the experiment takes).

- **Points To Consider For Data Analysis**

**Reciprocal Lattice:** Diffraction patterns generated from crystals are best rationalised by considering the reciprocal lattice construction. Here, each set of parallel lattice planes in the crystal is represented by a vector, oriented perpendicular to the planes with which it is associated and with a magnitude equal to the inverse of the perpendicular spacing between adjacent planes in the set. Because the magnitude of the vector is the inverse of a real space separation, it has units of reciprocal length and so is said to exist in “reciprocal space”. Just as a crystal is defined by a series of lattice of points in real space, the set of vectors generated by the normal vectors from all possible atomic planes in the manner described in reciprocal space also forms a periodic lattice – called the reciprocal lattice. It can be constructed most readily by defining “primary axes” given by the reciprocal lattice vectors associated with the planes that bound the unit cell of the crystal: the (100), (010) and (001) planes (in Miller Index notation). The associated normal vectors in reciprocal space are labelled as  $a^*$ ,  $b^*$  and  $c^*$ . All other reciprocal lattice vectors are linear combinations of the primary  $a^*$ ,  $b^*$  and  $c^*$  reciprocal lattice vectors. For example, the reciprocal lattice vector associated with the plane given by the Miller Index (132) will be:  $[a^*, 3b^*, 2c^*]$  from the origin  $[0,0,0]$ .

The reciprocal lattice is vitally important in studying and understanding crystalline objects for two reasons:

- (a) It allows for many geometric calculations to be done more readily than in real space; and
- (a) As demonstrated by Ewald, all possible solutions to the Bragg equation (all possible conditions under which diffraction maxima / high intensity spots will occur) exist on the surface of a sphere in reciprocal space, with radius equal to the inverse of the wavelength used in the diffraction experiment. When the sphere surface coincides with points from the reciprocal lattice, then a diffraction spot will be seen in the experiment. The specific geometry between the Ewald Sphere and the reciprocal lattice of a general crystal can be seen in Fig. 8, for the  $b^*$ - $c^*$  section of the reciprocal lattice.

