

# X-ray Diffraction and Characterisation of Materials

**Summary:** In this assignment, you will use the characteristics X-ray diffraction spectra of differing oriented single crystal materials to identify the materials, measure their lattice spacing and the surface planes of the crystals and verify some of the rules associated with the allowed X-ray diffraction reflections and their intensities. You will then both qualitatively explore and quantitatively measure the X-ray diffraction resulting from a randomly oriented powdered sample of one of the previous single-crystal samples and identify the additional allowed X-ray diffraction reflections and the associated Bragg planes giving rise to these reflections. This will all be done in a standard  $\theta - 2\theta$  measurement geometry. Finally, These same materials, but again in a single crystal form, will be studied by Laue X-ray diffraction.

## I. Introduction

X-rays are electromagnetic radiation with photon energies typically in the range 0.1 keV to 100 keV corresponding to a wavelength range of about 12,000 pm to 12 pm. Apart from medical applications, one of the most important uses of x-rays is the determination of crystal and molecular structure -- a famous example being that of DNA. The structure can be inferred from the diffraction pattern.

X-rays are diffracted by single crystals, according to Bragg's Law  $n\lambda = 2d \sin \theta$ , which describes the condition for which strongest constructive interference occurs.

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

where  $n$  is a positive integer representing the diffraction order,  $\lambda$  is the wavelength of the incoming light,  $d$  is the interplanar distance,  $\theta$  is the scattering angle, as indicated on the diagram in Figure 1.

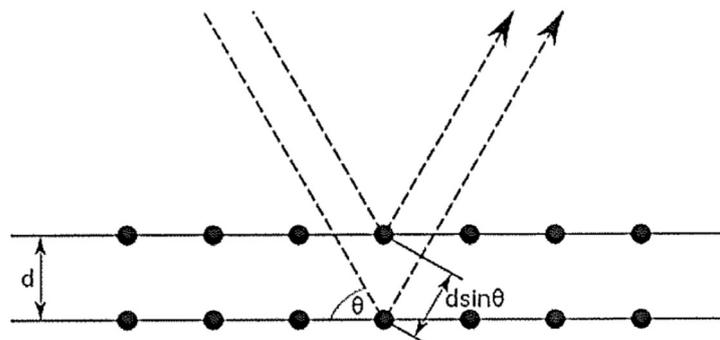


Figure 1- Schematic diagram of Bragg diffraction. Dots represent atoms within a crystalline solid.

The apparatus consists of a crystal diffractometer with a molybdenum x-ray anode target and a number of different crystals. In this set of experiments you will record and interpret the diffraction patterns of single crystals of NaCl, LiF, GaP and Si; there are three crystals of Si – a Si (100) and Si (111) which have faces parallel to (100) and (111) planes respectively, and another offcut of Si(111) whose surface plane is at some unknown angle to the (111) surface and is to be determined. You will then take powder diffraction data from NaCl and LiF. Finally

you will attempt to obtain a Laue diffraction pattern from one or both of a separate set of NaCl and LiF single crystals.

## Notes

- Before commencing any of these experiments read the background material provided in the relevant appendix. In particular, before using the equipment, read Appendix 1 which gives details of its operation. Please try to answer the following questions before your experiment:
  - For a NaCl crystal, can the (100) plane set produce strong coherent interference? Why? How about other crystals?
  - What parameters can you vary when you conduct the  $\theta - 2\theta$  scan? How do they affect the experiment?
- In general, all the crystals are fragile so **handle carefully and only with gloves**, in particular do **NOT** touch the square faces of the NaCl crystal.

## II. Experiment

### II.1 X-ray diffraction of oriented single crystal samples

Aims:

1. To record the x-ray diffraction (XRD) patterns, in the Bragg geometry, of the crystals (100) NaCl, (100) LiF, (111) GaP, (100) Si, (111) Si and (111)- $x^\circ$  Si.
2. To interpret these XRD patterns and in particular, to identify and label all the observed XRD peaks and explain why only these peaks are present.
3. To determine the lattice constant of the conventional cell for LiF, GaP and Si.

Carrying out the experiment

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

- Mount the (100) NaCl crystal on the support such that it is clamped up against the small horizontal bar (**handle carefully and only with gloves, do NOT touch the square faces of the NaCl crystal**). In principle, the intensity should be independent of the orientation of the crystal on the support; in practice, there is a preferred orientation, which is when the white line is facing the experimenter! All the crystals have been marked in this way.
- Operate the x-ray source by selecting  $U = 35 \text{ kV}$ ,  $I = 1 \text{ mA}$
- In coupled scanning mode, set the target to about  $7.2^\circ$  (*Is this value always valid? Why?*) 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 and record the  $2\theta$  value.
- In coupled scanning mode, move the target back by  $7.2^\circ$  (even if this takes you into the negative range! *Why? What would be the error if you did not determine the zero position?*).
- Save these positions as the “zero position of the measuring system” by pressing TARGET, COUPLED and  $\beta$  limits at the same time.

### Recording the diffraction spectrum

- Operate the x-ray source by selecting  $U = 35 \text{ kV}$ ,  $I = 1 \text{ mA}$
- Start the software "X-ray Apparatus". Make sure the apparatus is connected correctly and clear any existing data using the F4 key.
- Set the measuring time per angular step  $\Delta t = 5 \text{ sec}$  and the angular step width  $\Delta\theta = 0.1^\circ$ .
- Press the COUPLED key to select the Bragg geometry ((When operated in a  $\theta$ - $2\theta$  scanning mode this is known as a Debye-Scherrer scan.), and set  $\theta$  limits of  $3^\circ$  and  $35^\circ$  (*Do not choose a lower limit of zero, why?*)
- Start the measurement by pressing the SCAN key. The spectrum of intensity or count rate  $I$  versus  $\theta$  will be recorded and transferred to the PC.
- Attach the zirconium filter onto the collimator and record the full diffraction pattern for the (100) NaCl.
- Repeat the measurements for (100) LiF, (111) GaP, (100) Si, (111) Si and (111)- $x^\circ$  Si. (*Do you need to determine the zero position for each crystal? Why?*)

### Evaluation

- For each crystal, deduce the identity of the diffraction lines, i.e. what are the Miller indices ( $hkl$ ) of the planes concerned and what are the values of the order number  $n$  for each observed diffraction peak?
- Determine the lattice constant (take  $\lambda_{K_\beta} = 63.1 \text{ pm}$ ,  $\lambda_{K_\alpha} = 71.1 \text{ pm}$ ) and compare it with the value in literature (e.g. the conventional unit cell of NaCl has lattice constant  $a = 563 \text{ nm}$ .)
- If you take the wavelength of the Mo  $K_\beta$  and  $K_\alpha$  lines to a more accurate standard than 3 significant figures, how much of an effect would this "error" have on your measurement? (The energies of the Mo  $K_\beta$  and  $K_\alpha$  lines are 17.3743 and 17.47934 keV respectively.)
- What other sources of uncertainty are there?
- Determine the angle of offcut for the (111)- $x^\circ$  Si.

### Notes on presentation

Include printouts or screen captures or Origin plots of all the spectra in your report. On your plot of the XRD scan, all of the XRD peaks must be labelled with both the relevant identifying ( $hkl$ ) label for that Bragg peak and the respective origin of the x-ray line involved, either arising from the  $K_\beta$  or the  $K_\alpha$  lines.

## II.2 X-ray diffraction of powder samples

### Aim

1. To record the x-ray diffraction patterns, in the Bragg geometry, of powdered samples of NaCl and LiF.
2. To interpret these patterns and in particular, to identify all the (additional) peaks and explain why these peaks are now present, and discuss their intensities.
3. To determine the lattice constant of the conventional cell for NaCl and LiF.

### Carrying out the experiment

#### Mount the Goniometer

- Mount the Goniometer in the experiment chamber of the X-ray apparatus. To bring the counter tube out of stray radiation, put the Goniometer to the very left position and use the full length of the sensors arm. See Figure 2

- Mount the Zr filter on the collimator to produce monochromatic Mo  $K\alpha$  X-rays. The filter must be mounted on the left side on the collimator, facing the tube, not on the right hand side, where it would produce a lot of stray radiation into the experiment chamber.

#### *Prepare and Load powder samples onto holders*

- Prepare a powder sample by using the mortar and the pestle. The NaCl (or other) salt is grind in a mortar until no grains can be felt when rubbing the powder between the fingertips. Do not try to prepare too much powder at once, as it will take a lot of time. An amount of 2 times the volume of the powder holder will take approximately 5 minutes to pulverise. (Note: Coarse powder samples yield Debye-Scherrer reflections of inhomogeneous intensity distributions.)
- The powder holder consists of one aluminium frame and a solid aluminium plate. Put the frame onto the plate and fill the powder into the frame, move both aluminium parts together close to the sample holder inside the X-ray apparatus and slide the frame sideways onto the sample holder, so that the powder is always supported either by the aluminium or by the plastic parts.
- Attach strips of scotch-tape to the rear of the powder holder and fill the prepared powder into the frame (Figure 3).
- Squeeze the powder into the frame with the spatula as dense as possible.

#### *Record the spectra*

- Start the software and the x-ray apparatus
- Set the tube high voltage to  $U = 35.0$  kV and the emission current  $I = 1.0$  mA.
- Set the time per angular step  $\Delta t = 10$  sec and the angular step width  $\Delta\theta = 0.1^\circ$ .
- Select "Coupled", set appropriate start and stop angles  $\theta$  for the scan. Usually 10 to 40 deg is sufficient, but up to  $60^\circ$  gives additional lines
- Switch on the high voltage and press the automatic scan button for recording the spectra.
- To check for the existence of the weak, but important  $\langle 111 \rangle$  reflection, scan that region left of the 200 reflex ( $11^\circ$ - $18^\circ$  for NaCl) with  $\Delta t = 30$  sec at least.

#### *Evaluation*

- For each crystal, deduce the identity of the diffraction lines, i.e. what are the Miller indices ( $hkl$ ) of the planes concerned?
- Determine the lattice constant (take  $\lambda_{K\beta} = 63.1$  pm,  $\lambda_{K\alpha} = 71.1$  pm) and compare it with the value in literature (e.g. the conventional unit cell of NaCl has lattice constant  $a = 563.02$  nm. For LiF,  $a = 402.8$  nm)
- The reflections from a NaCl crystal are either all even number or all odd numbers, why?
- Discuss the importance of the 111 reflection for identifying the phase of NaCl (i.e. Can a simple cubic crystal with half the lattice constant match the diffraction peaks?) and verify the structure of NaCl/LiF crystal
- Discuss the benefits of using longer wavelength X-rays for this experiment.

#### *Notes on presentation*

Include printouts or screen captures or Origin plots of all the spectra in your report. On your plot of the XRD scan, all of the XRD peaks must be labelled with both the relevant identifying ( $hkl$ ) label for that Bragg peak and the respective origin of the x-ray line involved, either arising from the  $K\beta$  or the  $K\alpha$  lines.



Figure 2 The experiment Chamber

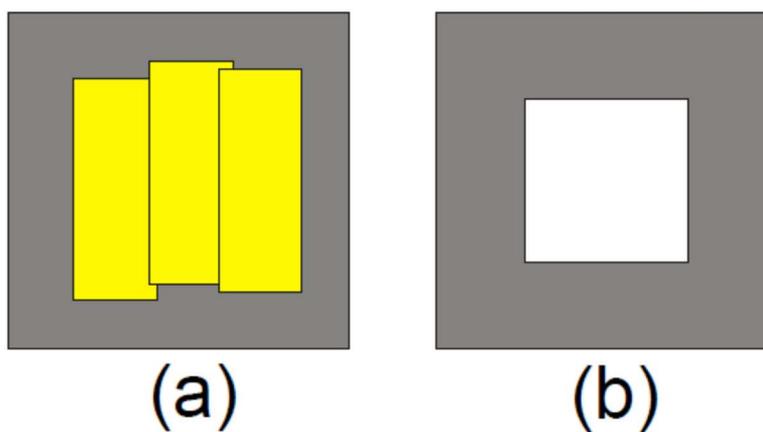


Figure 3 Preparation of the powder holder frame schematically: (a) rear side with strips of scotch tape (b) front side with squeezed powder

## II.2 Laue X-ray diffraction of single crystal samples

### Aim

1. To record the x-ray diffraction patterns, in the Laue geometry, of single crystal samples of NaCl and LiF.
2. To interpret these Laue patterns and assign the set of lattice planes that causes the scattering to the reflection observed, explaining why all of the peaks are seen and why the orientation or pattern recorded in the Laue diagram occurs the way it does.

### Carrying out the experiment

#### Setup the experiment

- The experimental setup is illustrated in Figure 4. The preparation of the film and the positioning of the x-ray film holder may require temporary removal of the goniometer. **This should be supervised by a demonstrator.**

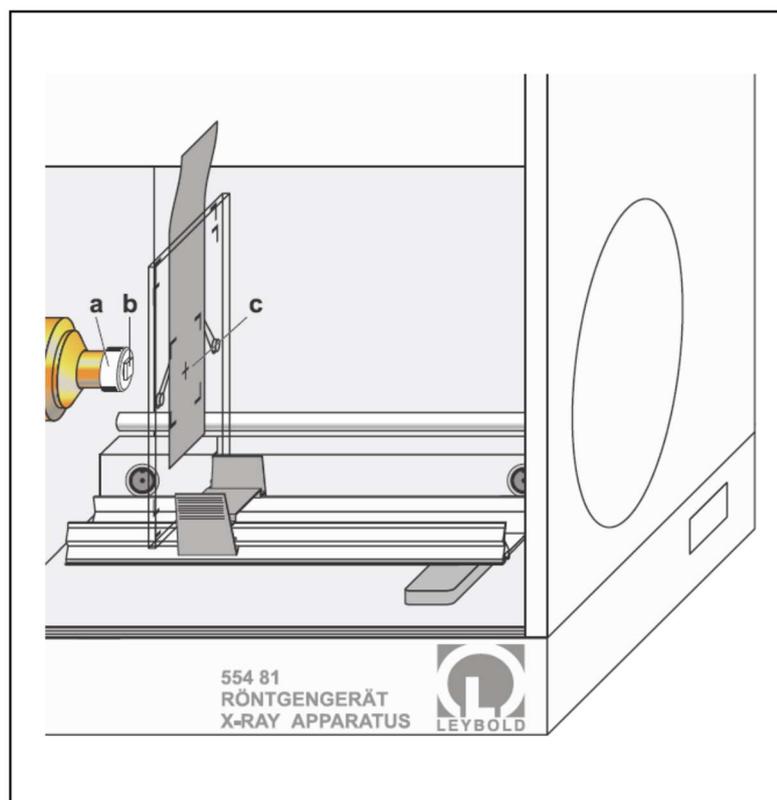


Figure 4 Experimental setup for Laue Diagram measurement (a: pinhole diaphragm; b: crystal; c: x-ray film)

- Please consult a demonstrator for assistance with the mounting of the pinhole aperture and the mounting of the differing set of NaCl (and LiF) crystals on the pinhole aperture. (1) Carefully attach the NaCl/LiF crystal (b in Figure 4) to the pinhole diaphragm (a in Figure 4) (from the scope of supply of the X-ray film holder) with transparent adhesive tape. (2) Attach the collimator, and cautiously turn it so that the outside edges of the crystal are aligned as horizontally (or vertically) as possible.

- Clamp the X-ray film (c in Figure 4) at the film holder so that it is centred, and see to it that the entire surface of the film is planar. Clamp the film holder onto the experiment rail, and mount the experiment rail in the experiment chamber of the X-ray apparatus.
- Make a 15 mm long spacer from paper board and shift the film holder so that the distance between the monocrystal NaCl and the film is 15 mm (by varying the distance between the crystal and the film the area covered in the diagram is changed). Note that the distance is 11 mm for LiF.
- Set the tube high voltage  $U = 35$  kV, the emission current  $I = 1.0$  mA and  $\Delta\theta = 0.0^\circ$ . Select the measuring time  $\Delta t = 1800$  sec ( $\Delta t = 1200$  sec for LiF), and start the exposure timer with the key SCAN. (If the exposure time is longer, the reflections near the centre are blurred by the un-scattered X-rays; however structures which are farer away from the centre become discernible.)
- When the exposure time is over, take the film holder with the experiment rail out of the experiment chamber.
- Remove the X-ray film from the holder, and develop it according to the instruction sheet for the X-ray film.
- Repeat the experiment for LiF.

#### Evaluation

- Read the  $x_Q, y_Q$  coordinates of the reflections and calculate the  $z_Q$  coordinate.
- Identify the indices  $h, k, l$  for each reflection.
- Calculate the spacing of the lattice planes, the Bragg angle and the wavelength.
- Calculate  $x_Q, y_Q$  and compare them with the measured values.
- Use the software "OrientExpress" to simulate the Laue diagram of NaCl (LiF) and compare with the experiment.
- Discuss the symmetry of the Laue diagrams.
- Compare powder x-ray diffraction and Laue measurements.

#### Bibliography

1. Solid State Physics, J. R. Hook and H. E. Hall
2. Introduction to Solid State Physics, C. Kittel
3. X-ray Diffraction, B. E. Warren

## Appendix 1. X-ray equipment

The x-rays are emitted from a molybdenum anode but emission is switched off if the leaded glass door is opened. Depressing the catch to open the door switches off the x-rays.

**Do NOT try to manually rotate the detector or sample support!** This should be done via the control panel.

Set the following parameters by pressing the appropriate button and using the ADJUST dial:

- Tube voltage U (0 – 35 kV).
- Tube current I (0 – 1 mA )
- Measurement time interval (at each angle  $\beta$ )  $\Delta t$
- Step angle  $\Delta\beta$  (during scan)
- The upper and lower limits to  $\beta$ ; these can only be set once COUPLED has been selected. For  $\beta = 0^\circ$  the beam is parallel to the face of the sample and goes straight to the detector so the lower limit of  $\beta$  should always exceed  $0^\circ$ .
- In COUPLED mode the detector is rotated through angle  $2\beta$  as the sample is rotated through angle  $\beta$  so that the Bragg condition may apply (this arrangement is therefore called the *Bragg geometry* and is illustrated in Figure A 1.1 .

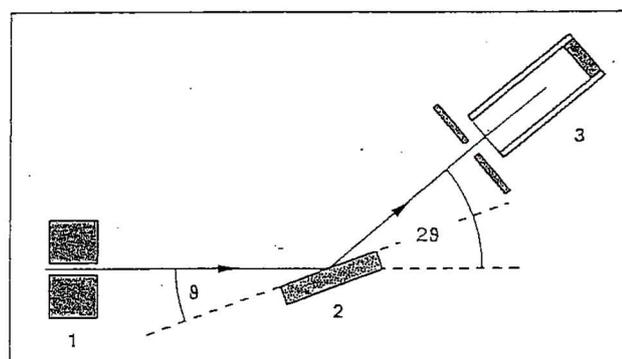
Press SCAN to start a measurement.

RESET causes the target and sensor arms to move to the  $\beta = 0^\circ$  position and resets the parameters to default values; the tube voltage is turned off.

Data is fed to the PC so before beginning a measurement open the software (**the password**, if required, is 'jslab').

Click on the "*clear measurement icon*" to clear existing data before commencing a scan; multiple scans can be displayed simultaneously if none of the data is cleared between scans.

Spectra look better printed in "landscape" than in "portrait".



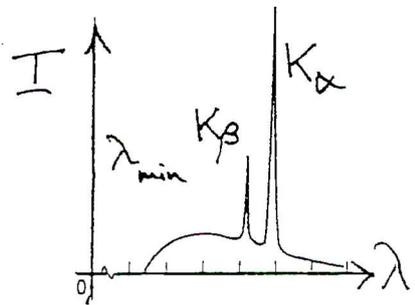
Diffraction of x-rays at a monocrystal and for  $2\theta$  coupling between counter-tube angle and scattering angle (glancing angle)

1 collimator, 2 monocrystal, 3 counter tube

**Fig A 1.1**

## Appendix 2. X-ray spectra

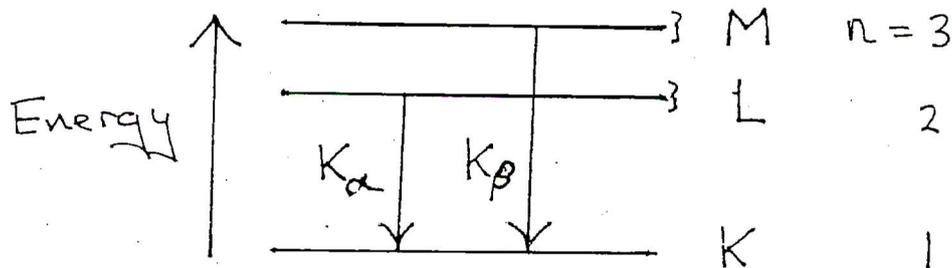
The typical x-ray spectrum is shown in figure A2.1. It consists of sharp lines -- the *characteristic spectrum* -- superimposed on the smooth *continuous spectrum* which extends to a minimum wavelength  $\lambda_{\min}$ .



**Fig A 2.1**

The *continuous spectrum* results from radiation (*bremsstrahlung*) produced by the deceleration of the incident electrons when they strike the target.

The *characteristic spectrum* arises from transitions of electrons between the inner shells of the target atoms. An incident electron may knock an electron out of one of the inner shells of a target atom. Suppose one of the two K shell electrons is removed. As shown in figure A2.2 this vacancy can then be filled by an electron falling in from one of the outer shells such as L, M ... with the emission of a photon whose energy, except for the lightest elements, is in the x-ray region of the spectrum.



**Fig A 2.2**

The terms  $K\alpha$ ,  $K\beta$  refer to transitions from  $L \rightarrow K$  and  $M \rightarrow K$  respectively.

## Appendix 3. Crystal structure and x-ray diffraction

### Crystal Structure

The *structure* of all perfect infinite crystals can be described in terms of a *lattice* and a *basis*. The lattice is a regular periodic array of points in space. The basis is the set of one or more atoms which when associated with each point gives the crystal structure.

The lattice can be defined by three *translation vectors*  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$ , such that the atomic arrangement looks the same in every respect when viewed from a point  $\mathbf{r}$  as from  $\mathbf{r}'$  where

$$\mathbf{r}' = \mathbf{r} + u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3 \quad (1)$$

and  $u_1, u_2, u_3$  are arbitrary integers. These translation vectors are called *primitive* if every lattice point can be generated by (1). The parallelepiped generated by these primitive axes  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$  is called the *primitive unit cell*. This is a minimum volume unit cell and always contains just one lattice point. The basis associated with the primitive cell is called a *primitive basis*; no other basis has fewer atoms than the primitive basis.

By convention a different, non-primitive, set of translation vectors and hence a different, non-primitive, *conventional unit cell* and basis are often used to describe a crystal structure. One of the reasons for this is that the conventional unit cell more obviously shows the full symmetry of the structure than does a primitive cell. For example, consider a crystal with a *face-centred cubic, FCC, structure* as shown in figures A3.1 and A3.2.

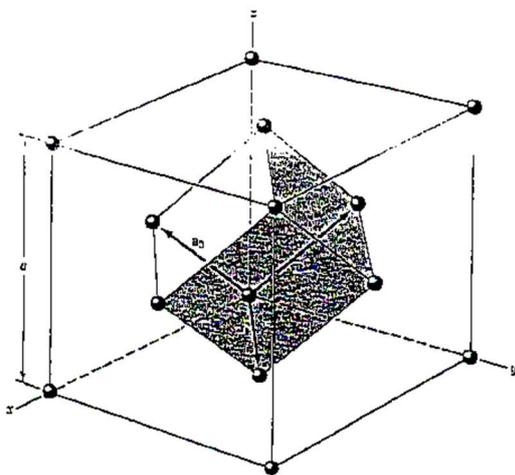


Fig A 3.1

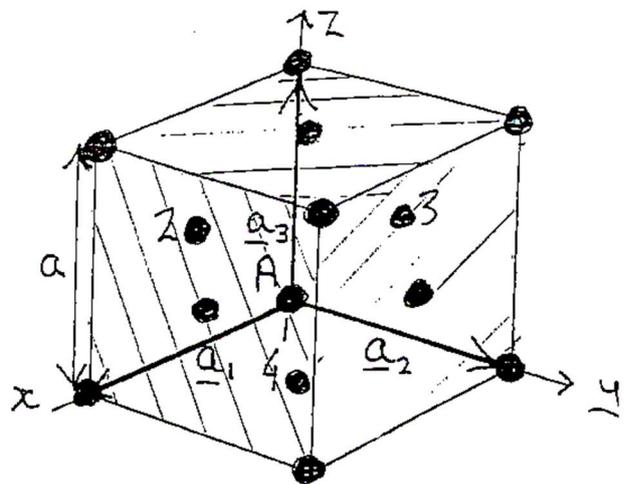


Fig A 3.2

Figure A3.1 shows the (primitive) translation vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$  and corresponding primitive unit cell which, in this case is rhomboidal. There is one lattice point per unit cell and the basis is one atom, which when added to each lattice point generates the structure.

The *conventional unit cell* is shown in figure A3.2 along with the (non-primitive) translation vectors  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ . The structure is equivalent to:

- FCC lattice (4 points per unit cell) + basis of 1 atom at each point.

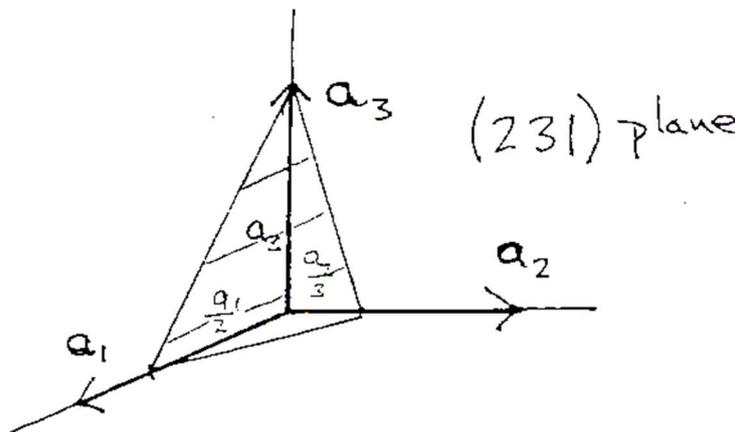
or

- Simple cubic (SC) lattice (1 point per cell) + basis of 4 atoms per point (for example the 4 atoms at positions 1,2,3,4 are associated with lattice point A)

In both cases there are 4 atoms per conventional cell, which is to be expected since it has four times the volume of the primitive cell.

Lattice places are usually identified by their *Miller indices*. These are found using the following rules (see Fig A3.3)

1. Find the intercept on the axes in terms of the lattice constants  $a_1, a_2, a_3$ . The axes chosen are most often those of the conventional unit cell rather than primitive translation vectors.
2. Take the reciprocals of these numbers and reduce to three integers having the same ratio, usually the smallest three integers. The result  $(hkl)$  is called the *index* of the plane.



**Fig A 3.3**

For a cubic lattice, of lattice constant  $a$ , show that the spacing,  $d$ , of the  $(hkl)$  set of lattice planes is given by

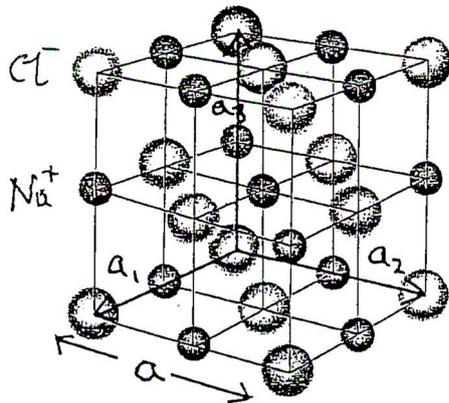
$$d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \quad (\text{here } a_1 = a_2 = a_3 = a)$$

The direction of a vector  $\mathbf{r}$  in the crystal can be written as

$$\mathbf{r} = u \mathbf{a}_1 + v \mathbf{a}_2 + w \mathbf{a}_3$$

and is referred to as the  $[uvw]$  direction. The indices in brackets are not Miller indices but for cubic crystals the symmetry is such that  $[uvw]$  is normal to planes of Miller indices  $(uvw)$ .

NaCl and LiF both have the *sodium chloride* or *rock salt* structure. The conventional unit cell is shown in figure A3.4



**Fig A 3.4** Conventional unit cell of rock salt structure . For NaCl  $a=563\text{pm}$ ,  $a_1, a_2, a_3$  are parallel to cube edges and  $a_1 = a_2 = a_3 = a$

The  $\text{Na}^+$  ions lie on an FCC lattice as do the  $\text{Cl}^-$  ions but the two FCC lattices are displaced relative to one another by one half of a body diagonal.

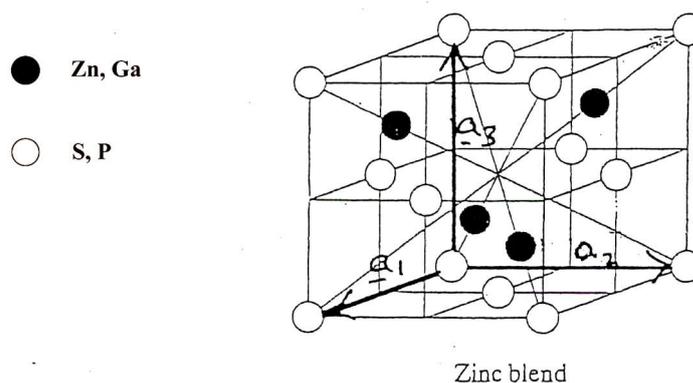
The structure may be regarded as built up from a SC lattice, side  $a$ , with a basis of 8 atoms at

$\text{Cl}^-$  :  $000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$

$\text{Na}^+$  :  $\frac{1}{2}\frac{1}{2}\frac{1}{2}, 00\frac{1}{2}, 0\frac{1}{2}0, \frac{1}{2}00$

The position coordinates  $xyz$  of the atoms are expressed as fractions of the lattice parameters  $a_1, a_2, a_3$  ( here  $a_1 = a_2 = a_3 = a$  ).

GaP has the *zinc blende* (  $\text{ZnS}$  ) structure. The conventional unit cell is shown in figure A3.5.



**Fig A 3.5**

Again  $a_1, a_2, a_3$ , are usually chosen, as shown, parallel to cube edges and  $a_1 = a_2 = a_3 = a$ . The Ga and P atoms both lie again on FCC lattices but here they are separated by one quarter of a body diagonal. There are again 8 atoms per conventional cell with structure equivalent to a SC lattice, side  $a$ , with basis of 8 atoms at

P :  $000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 00\frac{1}{2}$

Ga :  $\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4}$

Silicon has the 'diamond' structure. The conventional unit cell is shown in figure A 3.6

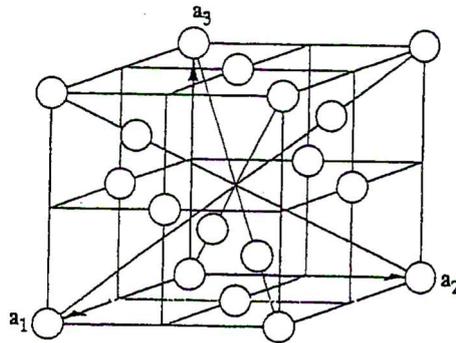


Fig A 3.6

This is the same as for the zinc blende structure apart from the important difference that both Ga and P have been replaced by Si.

X-ray diffraction and crystal structure determination.

The wavelength of x-rays is typically 0.1 nm, comparable to the spacing of atoms in solids. A crystal will therefore act like a 3-dimensional diffraction grating and just as the optical diffraction pattern of a grating provides information about the structure of the grating so too x-ray diffraction patterns can be used to determine the crystal structure. To illustrate this, consider the situation in figure A3.7 where x-rays of wavelength  $\lambda$  are incident on parallel atomic planes of spacing  $d$

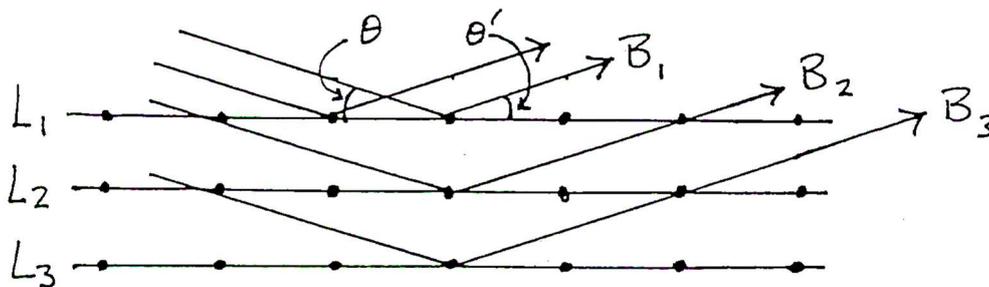


Fig A3.7

Firstly, for there to be constructive interference between x-rays scattered from atoms in the same atomic plane  $\theta'$  must equal  $\theta$ . This is why in your experiments the detector and sample holder are 'COUPLED' such that the detected beam makes the same angle to the face of the sample as does the incident beam. (N.B. on the equipment this angle is labelled as  $\beta$  rather than  $\theta$ ). An important consequence of this is that you will only observe beams diffracted from planes parallel to the sample surface.

Secondly, for a given  $\lambda$ , constructive interference only occurs between beams diffracted from successive layers when

$$2d \sin \theta = n \lambda \quad n = \text{integer (order number)}$$

This is *Bragg's law* and, if  $\lambda$ ,  $n$  are known, measurement of  $\theta$  gives  $d$ .

However although Bragg's law is a necessary condition for a strong diffracted beam it may not be a sufficient condition. For example, suppose that there is a path difference of  $\lambda$  between the beams  $B_1$  and  $B_3$  giving constructive interference between them. However in this case the path difference between  $B_1$  and  $B_2$  is  $\lambda / 2$ . So, if layer  $L_2$  is identical to  $L_1$  complete cancellation occurs and the intensity = 0. However, if  $L_2$  differs from  $L_1$  – maybe the atoms are different so that the amplitude of scattering for an atom in layer 2 is different to that in  $L_1$  then the intensity will be reduced but not to zero.

In summary, *the intensities of the diffracted beams as well as their directions provides information about the structure of the crystal.*

The intensity of the diffracted beam at the detector D depends on the resultant amplitude at D and this is obtained by summing the contributions of the scattered waves from all atoms taking into account their phase differences at D. The latter may be measured with respect to the wave scattered from some reference point O. The incident and scattered waves can be treated as plane waves and so from figure A3.8 it is clear that the phase difference at D between beams 1 and 2 is given by

$$\Delta\phi = \frac{2\pi}{\lambda} (x_1 + x_2) = \Delta \mathbf{k} \cdot \mathbf{r}_n \quad \text{where } \Delta \mathbf{k} = \mathbf{k}' - \mathbf{k}$$

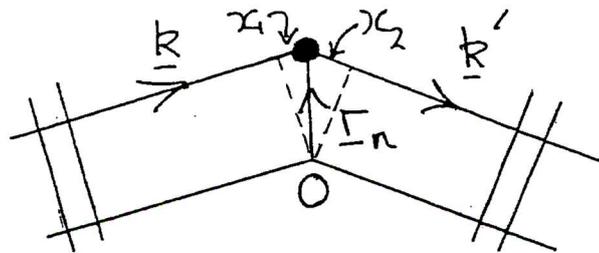


Fig A 3.8

$\mathbf{k}'$ ,  $\mathbf{k}$  are the wavevectors of the scattered and incident beam respectively.

The amplitude at D of the wave scattered from atom  $n$  is therefore proportional to

$$A_n = f_n e^{-\Delta \mathbf{k} \cdot \mathbf{r}_n}$$

$f_n$  is called *the atomic form factor or atomic scattering factor* and is a measure of the dependence of the strength of scattering on the type of atom.

Thus the resultant amplitude at D is proportional  $A$  where

$$A = \sum_n f_n e^{-i\Delta \mathbf{k} \cdot \mathbf{r}_n}$$

One may write

$$\mathbf{r}_n = \mathbf{r}_l + \mathbf{r}_p$$

where

$$\mathbf{r}_l = u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3$$

and  $\mathbf{r}_l$  is the position of the lattice point with which atom  $n$  is associated and  $\mathbf{r}_p$  is the position of the atom relative to this lattice point.

Therefore

$$A = \sum_l e^{-i\Delta \mathbf{k} \cdot \mathbf{r}_l} \times \sum_p f_p e^{-i\Delta \mathbf{k} \cdot \mathbf{r}_p}$$

ie

$$A = (\text{sum over lattice points}) \times (\text{sum over atoms in basis})$$

The first term determines the directions for which diffraction occurs – in effect Bragg's law - and the second term determines the intensities of the diffracted beams. This term is called the *structure factor*,  $F$

$$F = \sum_p f_p e^{-i\Delta \mathbf{k} \cdot \mathbf{r}_p}$$

How does one find  $F$  for the  $(hkl)$  reflection ie the reflection from the  $(hkl)$  plane ?

In this case

$$\Delta \mathbf{k} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

where the *reciprocal lattice vectors*  $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$  are related to  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$

Since

$$\mathbf{r}_p = x_p \mathbf{a}_1 + y_p \mathbf{a}_2 + z_p \mathbf{a}_3$$

where  $x_p, y_p, z_p$  are the coordinates of the atoms in the basis expressed as fractions of  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$  respectively, then

$$F = \sum_p f_p e^{-i2\pi(hx_p + ky_p + lz_p)}$$

For the rock salt, zinc blende and diamond structure the Miller indices are usually given in terms of the axes  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ , of the conventional cells shown in figures A3.4, A3.5, A3.6. In this case summing over  $l$  generates the simple cubic lattice. Therefore the sum over  $p$  must be over the corresponding basis atoms of which there are two sets of 4 atoms.

You will notice that because the atoms in each of these sets lie on a FCC lattice they always have fractional coordinates

$$x_p, y_p, z_p$$

$$x_p + \frac{1}{2}, y_p + \frac{1}{2}, z_p$$

$$x_p + \frac{1}{2}, y_p, z_p + \frac{1}{2}$$

$$x_p, y_p + \frac{1}{2}, z_p + \frac{1}{2}$$

Show that, in this case, for  $hkl$  mixed :  $F_{hkl} = 0$  NB. Miller index 0 is even.

This is how the FCC lattice can be recognized because this condition is characteristic of this lattice.

Show that, in addition to the above condition, for the rock salt structure :

$$hkl \text{ all even : } F_{hkl} = 4(f_c + f_a)$$

$$hkl \text{ all odd: } F_{hkl} = 4(f_c - f_a) \quad \text{where } c, a \text{ stand for the cation, anion respectively.}$$

For the zinc blende structure, in addition:

$$h + k + l = 4n \quad : F^2_{hkl} = 16 (f_{Zn} + f_S)^2$$

$$h + k + l = 2(2n + 1) \quad : F^2_{hkl} = 16 (f_{Zn} - f_S)^2$$

$$h k l \text{ all odd} \quad : F^2_{hkl} = 16 (f_{Zn}^2 + f_S^2)$$

where  $n$  is an integer.  $F^2$  is quoted because  $F$  may here be real or complex:  $F^2 = F F^*$

*Deduce what are the corresponding expressions for silicon.*