X-ray Powder Diffraction

Aims and Objectives

- Measure and analyse the X-ray diffraction from simple materials such as Si, NaCl, KCl and CsCl.

- Investigate a known or unknown material of your choice by X-ray diffraction

- Learn to operate an X-ray generator and a two-circle powder diffractometer.

Introduction

Most solids have crystal structures, where the position of individual atoms is well known. To find out the structure of a given material, X-ray diffraction is the most commonly used experimental tool. X-rays are fired at a sample and interact with density fluctuations (i.e. the atomic positions), leading to reflections off atomic planes. By measuring these reflections, the structure can be determined. In this experiment, you will look at a variety of salts and determine their structures.

Background

A crystalline solid is an ordered state. If we know where one atom is, then we know where all of the other atoms in the material are. In practice, of course, atoms are constantly moving due to thermal and quantum fluctuations. This information is contained in two portions: the **lattice**, and the **basis**. The **lattice** consists of a series of lattice points that are symmetrically identical, i.e. if the lattice extended infinitely, it would be impossible to distinguish between the lattice points. These lattice points are commonly placed on atomic sites, although this is merely as a convenience. By means of a tiling system, the entire lattice can be constructed by designating a **unit cell**, which is defined by **lattice translation vectors**, and then tiling it across 3D space as necessary to represent the crystal in question. There may be more than one atom associated with each lattice point, or there may be more than one lattice point in the unit cell, in which case the position of the atoms in the unit cell may be described using **basis vectors**, which are fractional coordinates of the unit cell construction vectors.

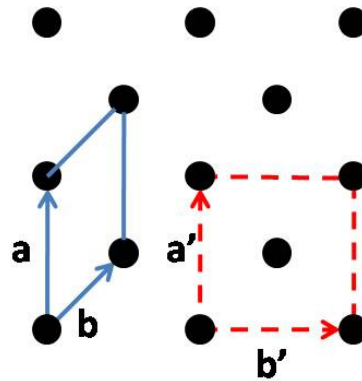*How might atomic motion affect the discussion below?*

Figure 1: A sample two-dimensional lattice, illustrating possible unit cells and associated lattice translation vectors. For the dashed unit cell, the basis vectors for the lattice points are (0,0) and (1/2, 1/2).

Planes

Crystals that we observe on the macroscopic level often have facets, e.g. salt crystals form cubes. These faces correspond to particular crystal planes. If a crystal can be cleaved along a particular plane, an interface that is flat on an atomic scale can be formed. Knowing where planes are and the distances between them is very important for categorizing and identifying crystal structures.

Planes are labelled using **Miller indices**. Consider a plane as shown in Fig. 2 in red. Choose the unit cell and lattice translation vectors that you wish to use. Choose a particular lattice point and then find where the planes intercept along the lattice translation vectors. In this case, the planes intercept along the **b** axis at the next lattice point, and half-way to the lattice point in the **a** direction. The intercepts are therefore at $(\frac{\mathbf{a}}{2}, \frac{\mathbf{b}}{1})$. The Miller indices for these planes are (21). If the planes of interest lie parallel to a particular lattice translation vector, than the corresponding index in that case is 0.

In 3D, if the planes intercept the unit cell axes at

$$\left(\frac{\mathbf{a}}{h}, \frac{\mathbf{b}}{k}, \frac{\mathbf{c}}{l}\right) \tag{1}$$

then the Miller indices describing the plane are (*hkl*).

In high symmetry conditions, such as cubic lattices, several planes or directions may be symmetrically identical, e.g. the (100) plane looks the same as the (010) and (001) planes. To refer to all of these symmetrically equivalent planes, we use curly brackets: {100}.
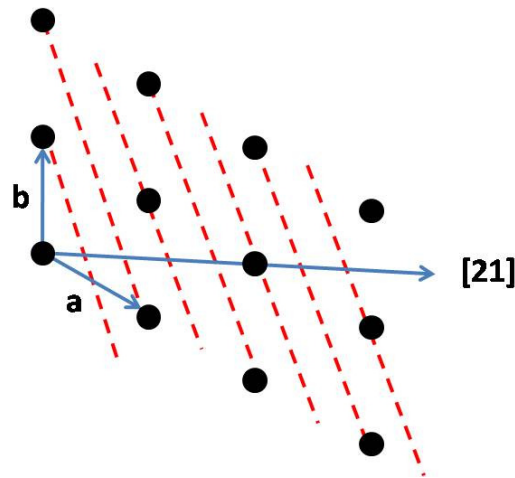
Figure 2: (21) planes.

Bragg's Law

Suppose we have a crystal of unknown origin that we wish to identify. We want to identify the unit cell, and so we need to know the size and direction of the lattice vectors, and the position of atoms in the basis, as well as the type of atoms. One way to get some of this information is via diffraction.

Consider the planes that we discussed earlier. They consist of uniform density variations in the material separated by a distance d. Suppose a plane wave of some radiation, such as light, is incident on these planes at some angle θ. Let us assume that the radiation will be specularly reflected by these planes of atoms.
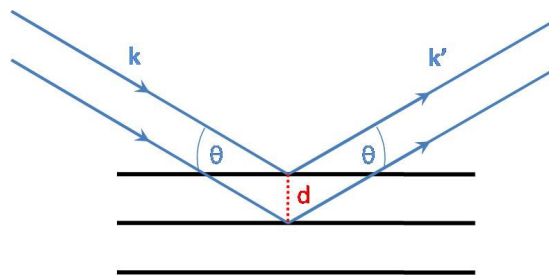
Figure 3: Reflection from planes of spacing d.

To get constructive interference at the detector from the two planes, the waves must be in phase. The extra path length from the plane below is $2d \sin \theta$, and so if

$$2d \sin \theta = n\lambda \tag{2}$$

where n is an integer and λ is the wavelength of the incident radiation, the outgoing beams will be in phase and give a strong reflected beam. If this condition is not met, there will be no constructive interference signal. This equation is **Bragg's law**.

This means that λ must be in the right range for probing atomic distances. A typical inter-atomic distance is ~ 3 Å. This means that X-rays are the right type of photon. If the wavelength is a fixed, known value, we can look for strong reflected signals at certain angles. By measuring the angle at which they appear, usually referred to as 2θ, we can calculate d and hence characterize the plane spacings. If we know several plane spacings, then with some detective work, we can extract the crystal structure.

For a cubic material, the plane spacings are given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}. \tag{3}$$

What is the general formula?

The Laue condition

Max von Laue developed a more rigorous derivation for the appearance of strong reflections from crystals that also introduces the useful concept of reciprocal space. You can find out about this method in the recommmended reading. This method makes no assumptions about planes, but merely relies on individual atoms scattering elastically. The final result is that the scattered X-ray amplitude varies as

$$\psi_{sc} \propto \sum_l e^{-i\boldsymbol{K}\cdot\mathbf{r}_l} \sum_m b_m e^{-i\boldsymbol{K}\cdot\mathbf{r}_m}. \tag{4}$$

where $\kappa = \mathbf{k}' - \mathbf{k}$ is the **scattering vector**, $\mathbf{r}_l$ is the position vector of a given unit cell and $\mathbf{r_m}$ is the position vector of atoms inside a unit cell. $\mathbf{r}_l$ is written in terms of the lattice translation vectors and κ is written in terms of reciprocal lattice vectors, which are defined as:

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b}\times\mathbf{c}}{[\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}]} \; ; \; \mathbf{b}^* = 2\pi \frac{\mathbf{c}\times\mathbf{a}}{[\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}]} \; ; \; \mathbf{c}^* = 2\pi \frac{\mathbf{a}\times\mathbf{b}}{[\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}]}. \tag{5}$$

These vectors are the reciprocals of the unit cell axes, and are inverse lengths. The space defined by them may be referred to as **reciprocal space**.

When the scattering vector has the following value

$$\mathbf{G}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \tag{6}$$

it matches a reciprocal lattice vector, and will give rise to a strong reflected signal. Diffraction occurs when the scattering vector κ is a reciprocal lattice vector $\mathbf{G}_{hkl}$, where (hkl) are the Miller indices of the plane being reflected off.

Can you confirm that this is true?

Structure factor

Having dealt with the lattice, we now turn to the effects of the contents of the unit cell.

$$F = \sum_m b_m e^{-i\boldsymbol{K}\cdot\mathbf{r}_m} \tag{7}$$

This is commonly referred to as the **structure factor**. In a unit cell containing only one atom, this term reduces to $F = b_m$, since $\mathbf{r}_m = 0\mathbf{a} + 0\mathbf{b} + 0\mathbf{c}$. However, many materials have more than one atom per unit cell. Silicon has a face-centered cubic structure, with atoms at (0,0,0), (1/2,1/2,0), (1/2,0,1/2) and (0,1/2,1/2) inside the unit cell. What effect does this have on the structure factor for planes of the type 100, 200, 110, 111 etc.? Can you determine a general rule?

Experimental Method

The X-rays generated in this experiment have an energy of ~ 8 keV. Such X-rays are readily absorbed by bodily tissue and can cause severe burns if proper precautions are not taken. The Siemens system contains several safety measures and hardware interlocks that must be in place before you can turn on the X-ray set and open the X-ray shutter.

Observe the indicator lights on the X-ray tube. Do not open the window to load a sample if the red 'SHUTTER OPEN' light is on – the X-rays would be cut off by an interlock if you did this by mistake.

The X-ray tube has a copper anode. The characteristic wavelengths produced by this tube are:

Cu K_{α_1}	1.54056 Å
Cu K_{α_2}	1.54439 Å
Cu K_β	1.39222 Å

The K_β X-rays can be filtered out using a nickel filter - one has been placed in front of the detector.

Starting the X-Ray generator and software

To turn the Siemens X-ray set on, you will need a key for the front panel switch of the X-ray generator. You can obtain this from one of the demonstrators. Check that the glass door is closed before attempting to turn the generator on – if the interlocks are not satisfied, it will not work. Even when the X-ray tube is running, a shutter prevents X-rays from leaving the tube shield if the door is open.

- Turn on the green switch marked 'Mains' on the left hand side of the front panel. If this does not come on, check the mains switch on the wall.

- Turn the water on, using the tap on the wall behind the diffractometers. If there is no water flowing, the X-ray generator will not turn on.

- Use the key to turn the keyswitch to position I.

- Switch on the temperature controller.

- Turn the X-ray generator on by pressing the middle button for 1-2 seconds, until the green light appears. This puts the X-ray machine in standby.

- Pull out the keyboard on the right hand side of the front panel, and press 'SHIFT' then 'X-RAY' then '1' and then 'ENTER'.

- Press the ON button next to the middle standby button. The X-ray warning light should come on. The software will automatically set the correct X-ray tube voltage and current.

- You are now ready to start the software, which can be found in the Windows Start menu, under "DIFFRACplus Measurement Part".

- Open DIFFRAC, select configuration (password: DIFFRAC). Use the second ⇓ button, or the File menu to download TC/FDC to the temperature controller. This initialises the temperature controller, which you have to do even if you are not using it.

- Open XRD Commander

Shutting down

The X-ray tube current (in mA) should never exceed the voltage (in kV). Maintain this relationship when you turn the machine off at the end of the day, as follows:

- Reduce the current to its minimum value, using the software

- Reduce the voltage to its minimum value, using the software

- Press the red off button

- Leave the water running for several minutes to cool the tube, then turn off the mains switch and the water.

Running a scan

From the XRD commander File menu, choose 'Select Diffractometer', and select the D5000 named after the PC you are on. On first operation after the machine has been switched off, the 'theta' and '2Theta' motors need initialising. Click the 'Requested' tick box on the main screen, and then in the Diffractometer menu, select 'Init Drives'. You should hear and be able to see the motors moving. The '2Theta' motor rotates the detector about the sample position, and the 'theta' motor rotates the sample about its centre.

You are now ready to start a scan. Having loaded a sample (see below), start with a 'Locked Coupled' scan type (this is the default option on starting). In this scan type, the two motors are locked, so that 'theta' rotates by exactly half the amount that '2Theta' rotates. A scan is set up by specifying the start and end angles in the boxes below the graph window. You should alter the step size and scan speed according to whether you wish to priorise speed or accuracy. Select degrees/minute for the scan speed setting. Limit your scans from $10°$ to $140°$. Avoid going close to $0°$ as you risk overloading the detector and damaging it. Click 'Start' to start the scan. The kV and mA indicators should go up to the programmed 40 kV and 30 mA, and the scan should strt, with data appearing on the screen.

Once you have collected some data, save it as a text file, so that you can access it using standard analytical software such as fityk to examine your data in more detail.

Sample preparation

If using the room-temperature sample stage, powder samples must be loaded into the plastic plates. The powder should be packed down and then a strip of Magic™tape placed across it to stop the powder from spilling out. You may find it useful to use one piece of tape to pick up spilled bits of powder from the plate, and then remove this and replace with a fresh piece of tape. Please check that no powder will escape before installing a new sample. Clean out the chamber of this happens. Remember to label

your samples. Ask a demonstrator to show you how to load a sample, or see the video on Canvas.

If using the temperature-controlled sample chamber, the sample must go in the specially shaped metal sample holder with a thermometer inserted. Ask a demonstrator to show you how this works.

Suggested investigations

Prepare a sample using some of the table salt provided. This consists of small crystalline grains. Start with 20-100°, at 0.2°/s, with 1s counts. You should be able to see peaks within five minutes, but the data will be of poor quality. A reliable, detailed scan may take an hour to collect over the full range. Calculate the lattice parameter of silicon, and compare this with the standard literature value. You could also do a high resolution scan over just one peak, and try to explain its shape.

Can you explain the origin of all of the peaks observed?

To understand the operation of the diffractometer, try changing the slits and monitor the effect on the intensity and resolution of the peaks that you observe, in particular the slit just in front of the detector - ask a demonstrator to show you how to change the slits. You may find the cartoons of the diffractometer positioning that are available in XRD Commander helpful here.

After measuring this, using a pestle and mortar, grind some of these crystals into a powder, and compare the diffractograms obtained from the two samples. Explain the diffractograms and any differences that you observe.

Other samples are available, including are potassium chloride and low-sodium table salt. What can you say about these materials?

What structure do they have?

The general procedure for finding the lattice constant a from a powder diffraction pattern is to use Eq. 2 to get the plane spacings, then use equation 3 (in the cubic case) to determine the Miller indices h, k and l, using the fact that these must be small integers. Equation 3 should then give a consistent value of a for all peaks. It is helpful to work with the squares of the equations. See, e.g., Warren (1990) section 5.3.

Suggested temperature-dependent investigation

$BaTiO_3$ is a solid that is used in electronic applications as a capacitor dielectric and transducer. It has a structural phase transition just above 100 °C. Study the X-ray

reflections to track the change of symmetry as you change its temperature, and plot out the course of the phase transition. Consult a demonstrator about the temperature-controlled sample stage.

Recommended Reading

S. A. Holgate, *Understanding Solid State Physics*, pp 125-139, CRC Press (2010).

J.-A. Nielsen and D. McMorrow, *Elements of Modern X-Ray Physics*, Wiley (2001).

W. L. Bragg, *The Structure of Some Crystals as Indicated by their Diffraction of X-Rays*, Proc. Roy. Soc. **89**, 248 (1914).

B.E. Warren, *X-Ray Diffraction*, Dover 1990.