

# Practical 2P9

## XRD Detective

### Safety

<i>Hazards</i>	<i>Control measures</i>
Ionising radiation (X-rays)	<ul style="list-style-type: none"><li>• X-rays are completely enclosed and the X-ray diffraction (XRD) instrument is fully interlocked to prevent door being opened with shutter open.</li><li>• Follow instructions, training and supervision.</li></ul>
Powder handling	<ul style="list-style-type: none"><li>• None of the materials are toxic but gloves and lab coats should be worn for powder handling.</li><li>• Follow instructions, training and supervision.</li></ul>

#### Safety Rules:

- Operate XRD machine as instructed by Demonstrators.
- Take care when handling powders and ensure spillages are cleared up.
- Put waste powders in dedicated waste disposal container.
- Listen and follow instructions carefully. If you do not understand instructions, then ask before you perform the tasks.

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## 1. What you should learn from the practical

### Science:

This practical has three parts. In the first part you will use X-ray diffraction to identify two metal elements and accurately determine their lattice parameters.

In the second part you will work out the composition of an unknown two-phase mixture, using the **internal standard** method to determine the phase fractions in your mixture.

In the third part you will estimate the strain and crystallite size in a heavily ball-milled  $\text{MgB}_2$  powder sample from the **peak broadening**.

### Practical Skills:

You will learn how to operate an X-ray diffractometer, and how to analyse the data to extract different kinds of information about the sample.

## 2. Overview

### Day 1:

- Learning the basic operation of the XRD.
- Collect data from the two unknown metal samples for **part 1**.
- Prepare standard samples for **part 2** and start to measure standards and unknown sample in the XRD.

### Day 2:

- Complete data collection for **part 2**.
- Measure two  $\text{MgB}_2$  powder samples for **part 3**.
- Ensure you have done preliminary analysis using PDXL2 software and export results for further independent analysis.

### Day 3:

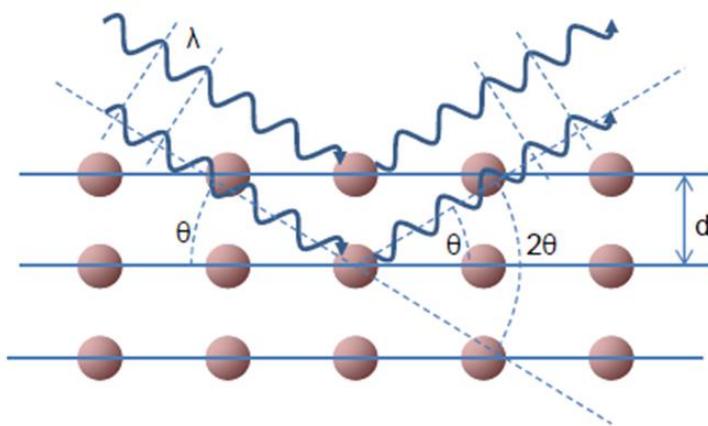
- You should be able to complete all the data collection and initial analysis (that requires the analysis software) in the first 2 days. There is a considerable amount of further analysis that you need to do independently and can be completed on your own computers using tools such as Excel.

## 2. Background Information

### X-ray diffraction technique

X-ray diffraction is a powerful technique for probing the structure of crystalline materials because X-ray wavelengths are slightly smaller than typical lattice spacings in crystals. The fundamental principle that is the basis of this technique is **Bragg Diffraction**, which you will be familiar with from 1<sup>st</sup> year Diffraction lecture course and have used more recently in the 2<sup>nd</sup> year Microstructural Characterisation lectures in relation to electron diffraction.

The path difference between X-rays scattered by different atomic planes must



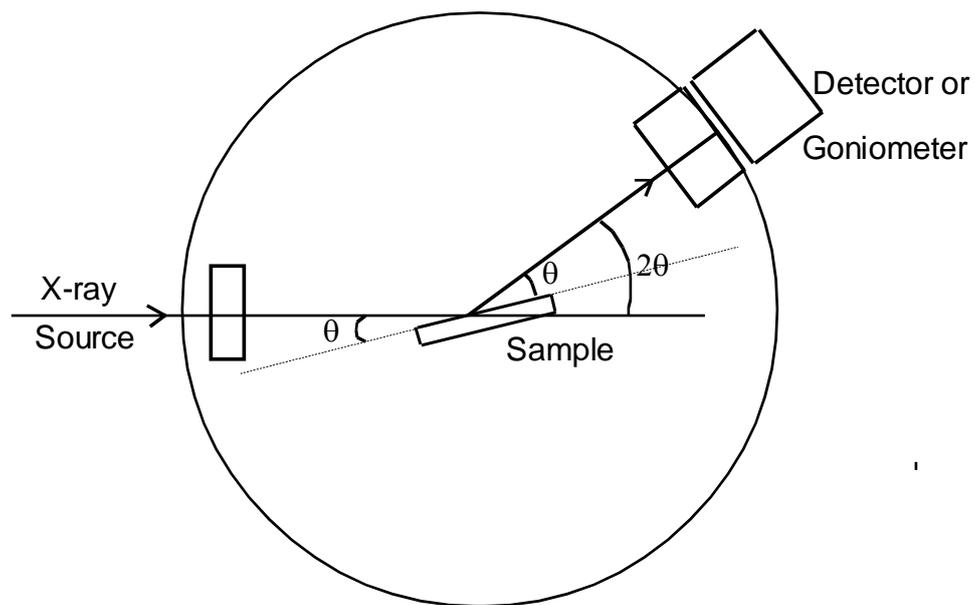
be an integer number ( $n$ ) of wavelengths ( $\lambda$ ) for coherent diffraction. This can be written in terms of inter-planar spacing ( $d$ ) and angle ( $\theta$ ) as Bragg's law:  $2d \sin\theta = n\lambda$  where  $n=1$ .

This relationship is the

basis of X-ray diffraction and describes the effects of X-ray scattering from a crystal lattice. The X-rays are visualised as diffracting from imaginary planes defined by the Miller indices. In fact, the electron shells around each atom are the scattering particles, and the intensity of X-rays scattered by a crystal can only be determined by an analysis of the scattering from each atom in a periodic structure. Information that can be extracted from XRD spectra include phase identification, crystal structure determination, lattice parameter determination, texture analysis (preferred orientation), strain and crystallite size measurements and quantitative phase fraction analysis.

## $\theta$ - $2\theta$ diffractometer set-up

In this practical, you will be carrying out so-called  $\theta$ - $2\theta$  scans in reflection (Bragg-Brentano) geometry. The X-ray source is fixed during the measurement and the scan involves rotating the detector over a selected range of  $2\theta$  angles (relative to the transmitted beam), whilst simultaneously rotating the sample by angle  $\theta$  to maintain the symmetric geometry (as shown in the figure below). At certain angles, constructive interference occurs when the Bragg condition is satisfied and a high X-ray intensity is detected. Each peak in intensity is related to a particular interplanar spacing for a set of  $\{hkl\}$  planes ( $d_{hkl}$ ) and therefore to the crystal structure of the sample.



Bragg Equation

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

X-ray wavelength  
(fixed by source)

Interplanar spacing  
of  $(hkl)$  planes  
(sample dependent)

Angle of  
incidence/reflection  
(scanned in the  
measurement)

All X-ray goniometers will have a **background** number of counts even when no crystallographic planes are aligned at the Bragg angle. Any two diffractometers will show have different characteristic backgrounds, but they are usually only important for small grained-powder samples or those which have a low peak/background ratio for other reasons.

**Peak position:** gives information about lattice parameter and crystal structure.

**Peak intensity:** gives information about phase fractions in a polyphase mixture.

However, the relationship is not generally linear because the diffracted intensity is dependent on the X-ray yield, the fluorescence and the absorption coefficient ( $\mu$ ) which in turn varies with concentration. In addition, peak intensity is also influenced by texture (preferred orientation) in the sample, but this is not usually a problem for powder samples.

**Peak broadening:** occurs in samples with fine grains (referred to as crystallites) and/or inhomogeneous strain. Analysis involves comparing peak widths of a series of (*hkl*) diffraction peaks from the sample of interest with a standard large grained, unstrained sample.

### 3. Experimental Procedure

<b>Instrument</b>	Rigaku MiniFlex
<b>X-ray source</b>	Cu $K_{\alpha}$ X-rays ( $\lambda=0.15406$ nm) produced using a Cu X-ray tube with a Ni filter to remove the Cu $K_{\beta}$ X-rays.
<b>Sample</b>	moves through angle $\theta$ with respect to X-ray source
<b>Detector</b>	moves through $2\theta$ with respect to the X-ray source (i.e. it measures $2\theta$ )

Appendix A gives the method for loading samples and taking XRD measurements in the Rigaku MiniFlex instrument. In general, it is good practice

to perform **repeat measurements** in the XRD to reduce error. In  $\theta-2\theta$  diffractometers, the main source of error is likely to arise from inaccurate positioning of the sample surface (i.e. sample height) and so it is important to remove the sample from the holder and re-mount it before repeating the measurement. Here, it is expected that **two spectra** are presented in each case (unless otherwise stated). If they are appreciably different, a third scan is expected to confirm which scan is best to use for the subsequent data processing.

## Part 1: Identification of cubic metal samples and accurate determination of their lattice parameters

### Data collection

Two unknown elemental metal samples will be provided.  $\theta-2\theta$  scans should be carried out on each of these samples using the following measurement parameters to ensure you see several peaks:

$2\theta$ range	Step size	Scan rate
25-100°	0.02°	10°/min

### Determining accurate peak positions

The XRD analysis program (PDXL2) should be used to subtract the background and generate a peak list (list of  $2\theta$  positions of each peak) following the method given in appendix B. Export this peak list as a .csv file using the “export” button for further analysis offline (e.g. using Excel).

### Crystal structure determination

From knowledge of the atomic positions in a particular crystal structure it is possible to calculate the **structure factor** which tells you which lattice planes will diffract strongly and which are expected to be **systematic absences** (c.f. 1<sup>st</sup> year

Crystallography and Diffraction / 2<sup>nd</sup> year Microstructural Characterisation lecture courses).

Using Bragg's law and the expression for interplanar spacing for a cubic

structure,  $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$  where  $a$  is the lattice parameter, it is possible

to relate  $h, k, l$  values with  $\theta$  by the equation:  $\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$

Therefore, by calculating values of  $\sin^2 \theta$  from the experimental data a characteristic pattern of  $(h^2 + k^2 + l^2)$  values can be found and the crystal structure for each metal sample can be determined.

#### Accurate lattice parameter determination

After indexing the XRD spectra from the two metal samples (i.e. assigning the correct Miller indices to the peaks), the equations above can be used to estimate the lattice parameter ( $a$ ) from each peak position. However, it is likely that there will be some variation in the values calculated from each peak owing to systematic measurement errors. To obtain the most accurate lattice parameter value, ideally we want to measure a peak at  $2\theta=180^\circ$ , which is impossible. Instead, the lattice parameter is calculated from all peaks in the pattern and extrapolated against a function of  $\theta$ . The curve of  $a$  against  $\theta$  is not linear and so a function of  $\theta$  which does result in a straight line is chosen. Cullity (chapter 11) discusses the various sources of possible systematic errors and the functions of  $\theta$  which should be used in each case.

e.g.	$\cos^2 \theta$	flat specimen and absorption
	$\cos^2 \theta / \sin \theta$	displacement from diffractometer axis

## Write up

The following should be included in your lab book for part 1 of the experiment:

- XRD scans from each metal samples (including repeat measurement), annotated with the Miller indices associated with each peak.
- Accurate lattice parameter determination for each sample. Clearly indicate the extrapolation function you have used in your calculation, giving your reasons.
- Discussion of why the most accurate lattice parameter can be determined from peaks at high  $2\theta$  angles.
- Identification of the two metals with an explanation of your reasoning.

The following table may be of assistance:

Element	Structure	Lattice parameter (nm)
Si	Diamond cubic	0.357
Ni	fcc	0.352
Cu	fcc	0.361
$\gamma$ -Fe	fcc	0.363
$\alpha$ -Fe	bcc	0.286
Al	fcc	0.404
Ag	fcc	0.408
Cr	bcc	0.288
V	bcc	0.303
Mo	bcc	0.314
W	bcc	0.316

## Part 2: Quantitative phase fraction analysis in a two-phase mixture of CaO and MgO powders

### Internal standard method

To obtain quantitative phase fractions from a mixture of phases, it is generally necessary to determine a calibration curve using a series of standards of known composition. There are several different methods that can be used, but you will use the **internal standard** method in which a series of samples of known composition are prepared with a fixed amount of a known standard material (CeO<sub>2</sub> powder in this case) added to each. The ratio of the integrated intensity of a chosen peak in one of the sample phases with a chosen peak in the added standard material is calculated for each sample of known composition to generate a calibration curve.

$$\frac{I_{\alpha}}{I_s} = K w_{\alpha}$$

where  $I_{\alpha}$  is the intensity of the phase of interest in the sample  
 $I_s$  is the intensity of the internal standard  
 $K$  is the slope of the calibration curve  
 $w_{\alpha}$  is the weight fraction of the  $\alpha$  phase in the sample

The same fixed amount of the internal standard material is also added to the sample of interest with unknown composition. The calibration curve can then be used to extract the weight fraction of the  $\alpha$  phase from the intensity ratio ( $I_{\alpha}/I_s$ ) measured in the unknown sample.

### Sample preparation

The following series of CaO+MgO powder mixtures should be prepared in a fume cupboard wearing gloves and a lab coat: 20, 40, 60, 80 and 100 wt% MgO. A total of 1g of each mixture should be prepared. For each sample, **including sample X of unknown composition**, add 0.1g of CeO<sub>2</sub> powder to 1g of

the CaO+MgO mixture. Mix well by shaking in a plastic bottle. Take care to weigh the powders carefully and mix them really well. The Junior Demonstrators will show you how to pack your powder sample into the dedicated sample holder for XRD measurements. **Take care to ensure the powder is not too loose as the sample tilts during the measurement.**

#### Data collection

$\theta$ - $2\theta$  scans should be carried out on each of these samples using the following measurement parameters:

$2\theta$ range	Step size	Scan rate
50-70°	0.02°	5°/min

**Two** measurements are needed for each of the calibration samples and the unknown sample X. The powder should be removed from the holder after the first measurement, re-mixed with the rest of the batch of powder, and then the sample mounting process should be repeated for the second measurement.

#### Determining integrated intensities

Carry out basic analysis using the PDXL2 software to subtract the background, generate a peak list and fit the profile (as in part 1) and identify which peak in the spectrum comes from each phase (procedure given in appendix B). The integrated intensities of each peak are given in the peak list and can be exported as a .csv file using the “export” button for further analysis offline (e.g. using Excel).

#### Quantitative phase fraction analysis

Using the **integrated intensity** values of the {220} MgO ( $\alpha$ -phase) peak and the {311} CeO<sub>2</sub> peak, calculate the intensity ratio ( $I_{\alpha}/I_s$ ) for each calibration sample. Plot this against  $w_{\alpha}$  (the known weight fraction of MgO) to generate the calibration curve for the experiment. This curve can then be used to extract the composition of X from the intensity ratio of the same peaks.

## Write up

For part 2, the following should be included in your write up:

- An example of an XRD spectrum with the peaks identified.
- A table showing the integrated intensities of the {220} MgO and {311} CeO<sub>2</sub> peaks for measurement on the calibration sample and the unknown sample (giving the values for the repeat measurements as well).
- Your calibration curve and an explanation of how you have fitted the curve through the discrete data points. Show clearly how you have used the calibration curve to extract the weight percent of MgO in your unknown sample.
- Discuss why a standard is needed for quantitative XRD analysis and comment on the errors in your analysis.

## **Part 3: Crystallite size and strain analysis in heavily ball-milled MgB<sub>2</sub> powder**

### Data collection

You will be provided with two MgB<sub>2</sub> powder samples, already mounted in XRD holders. One is the as-received powder, which can be assumed to be strain-free and have large grains. The other is the same powder after high energy ball-milling for 40 hours.

**Please take care with these samples as there is a limited amount of ball-milled powder available, so these samples will be used by every practical group.**

$\theta$ - $2\theta$  scans should be carried out on each of these samples using the following measurement parameters:

$2\theta$ range	Step size	Scan rate
25-100°	0.02°	10°/min

**Do not take repeat the measurements for this part of the practical.**

### Correcting for instrumental broadening

In addition to peak broadening arising from the microstructure of the sample, there is always a contribution to the broadening from instrumental effects. This contribution needs to be removed from the total peak widths to determine the peak broadening arising from the sample itself. To remove instrumental broadening, the peak width is compared to a standard material where we know that crystallite broadening and strain broadening are not contributing to the peak width – i.e. one with a large grain size and no inhomogeneous strain. The peak broadening in the sample of interest ( $B$ ) is usually calculated by the Warren formula which assumes a Gaussian peak profile:

$$B^2 = B_M^2 - B_S^2$$

where  $B_M$  is the measured peak width from the sample of interest **in radians** at half peak height – i.e. its full-width at half-height (FWHM) value.

$B_S$  is the corresponding FWHM from a standard material of a peak at a similar  $2\theta$  angle. In this case the as-received  $MgB_2$  powder can be used as the standard material.

### Peak broadening due to small crystallite size

$B_{crystallite}$  is the contribution to peak broadening resulting from small crystallite thickness ( $t$ ) is given by the Scherrer formula:

$$t = \frac{k\lambda}{B_{crystallite} \cos \theta}$$

where  $\lambda$  is the X-ray wavelength (0.15406 nm)

$\theta$  is the Bragg angle

$k$  is a constant which depends on the shape of the particle and has a value  $\approx 1$

### Peak broadening due to lattice strain

Inhomogeneous strain leads to peak broadening because different regions of the crystal will effectively have different lattice parameters and therefore will satisfy the Bragg condition at slightly different angles. Peak broadening due to inhomogeneous lattice strain ( $B_{strain}$ ) is given by:

$$B_{strain} = \eta \tan \theta$$

where  $\eta$  is the strain in the material.

### Crystallite size and strain analysis

In samples with both small crystallite size and inhomogeneous strain, the peak broadening from each contribution must be added together.

$$B = B_{crystallite} + B_{strain}$$

Since each of these terms has a different  $\theta$  dependence, using a series of peaks at different  $2\theta$  values enables a linear function to be plotted where the gradient is related to strain and the y-intercept is related to the crystallite size.

### Write up

For part 3 of the practical, the following should be included in your write up:

- XRD scans of the as-received and 40 hour ball-milled  $MgB_2$  powders.
- Table with FWHM values of the peak widths and  $\theta$  values for the  $MgB_2$  peaks for the as-received and ball-milled samples and B values for the ball-milled sample after removal of the instrumental broadening.
- Calculation of crystallite size and strain in ball-milled sample along with the linear graph used to calculate them.
- Have you chosen to remove any outliers from the data analysis? If so, explain your reasons. Comment on the accuracy of your results / errors in the analysis.

#### 4. What should be in the lab book?

The lab book should include all of the data and analysis requested in section 3 above. The data should be well-presented with suitable annotations. The analysis/calculations should be clear and easy to follow.

**In addition, include:**

- A brief description of what you did. Please do not reproduce large portions of the practical script.
- A comparison between X-ray and electron diffraction techniques.
- What techniques (other than XRD) could be used (i) to measure crystallite size and (ii) for phase identification? Comment on their benefits/drawbacks compared to XRD.

## Appendix A: Data collection in the Rigaku MiniFlex XRD

### Loading the sample

1. The JD will show you how to mount powder and bulk samples in the special XRD. It is very important that the surface of the sample is level with the top of the sample holder.
2. Press the “door lock” button on front panel of MiniFlex to unlock the door. It will start to beep to indicate that the door is unlocked. Open the door and insert the sample according to instructions from the JD.
3. The beep will continue until you have closed the door and pressed the “door lock” button to re-lock the door.
4. The JD will double check (by referring to table below) that the correct optics are loaded into the XRD instrument and will change them if necessary.

### Data Collection

1. Click on “General measurement” yellow box in the Package/Macro measurement window. Check the box for measurement number 1, leaving all of the other measurements unchecked. For measurement 1, browse to the desired folder to save the data files and set the file name for the scan. You can also add a sample name and measurement conditions and save the program for further use if needed.
2. Click on “measurement conditions” box to open the Measurement condition window. The table below gives the correct slit and optics settings to select:

Slit condition		Variable+Fixed slit system
Soller(inc)	Incident beam path	5.0 deg
IHS	Incident beam path	10.0 mm
DS	Incident beam path	1.250 deg
SS	Diffracted beam path	1.250 deg
SS(rec)	Diffracted beam path	5.0 deg
RS	Diffracted beam path	0.3 mm
Monochromator	Diffracted beam path	kb filter (x1)

3. Run the measurement by pressing the “run” button.

## Appendix B: Data analysis using PDXL2 software

### Data analysis

1. Open the PDXL2 software and log in (username: demonstrator, pwd is left blank).
2. Select “manual” processing in right hand window.
3. Press “load” button in flow chart in the left hand window and browse to find the .RAS file for your measurement.
4. Click on “data processing” button.
5. In right hand window, press button to select the same conditions as the automatic analysis. Work through the analysis stages stepwise (checking that you are happy with the results at each stage). You are aiming for the calculated curve (which can be viewed by making sure the icon “display raw data only” is unchecked) to be as similar as possible to the raw data. If peaks are not picked up in the peak search stage, reduce the “sigma” value and try again. The automatic analysis (on loading) should be avoided unless you have already confirmed manually that the settings give a good fit to the data.

6. The peak list will automatically be displayed in the lower central window when the “peak search” procedure has been completed. The subsequent profile fitting stage is essential for accurate peak positions, FWHM and integrated intensities to be calculated.
7. The peak list can be exported as a .csv file by selected all of the lines in the peak list table, ensuring they are selected and then clicking the “export” button.

### Comparing XRD spectra with database patterns

For parts 2 and 3 of the practical, you may wish to use the PDXL2 software to search the COD (Crystallography Open Database) and help identify the peaks in the measured spectra.

1. Click on “load card info” on the Left hand flow diagram.
2. In the window that opens, you can choose how to search the database. The best method is probably to use an “elements” search to choose which elements you expect to have in your sample using the periodic table that pops up.
3. When you have clicked “OK” on the periodic table pop up window, press “search” to find database entry that fit your restrictions.
4. Select patterns of interest and click “add” button. Then close this window.
5. In the right hand window, the chosen patterns appear in the pattern list. Select them and press the down arrow button to move them to the “candidates” window. When you click on a specific pattern, the crystallographic information for that panel appears in the bottom right window. The pattern peaks can also be compared with the measurement scan by selecting the “pattern” tab on the main window.