Practical 2P9

XRD Detective

This practical will run remotely due to COVID restrictions. The teaching assistants, after a brief introduction, will run the experiments and share the raw data they acquired with the students to be used for the lab notebook.

1. Safety Considerations

Hazards	*Control measures*
Ionising radiation (X-rays)	• X-rays are ionising radiation, and therefore are potentially hazardous. • In the diffractometer, X-rays are completely enclosed and the instrument is fully interlocked to prevent the door being opened with the X-ray shutter open. • X-ray workers must be registered with the safety office, so students must be supervised by fully trained Junior Demonstrators.
Powder handling	• None of the materials are toxic but gloves and lab coats should be worn for powder handling.
Waste disposal	• Waste powders must be disposed of using the dedicated waste disposal container.

2. 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 MgB_2 powder sample from the peak broadening.

Practical Skills:

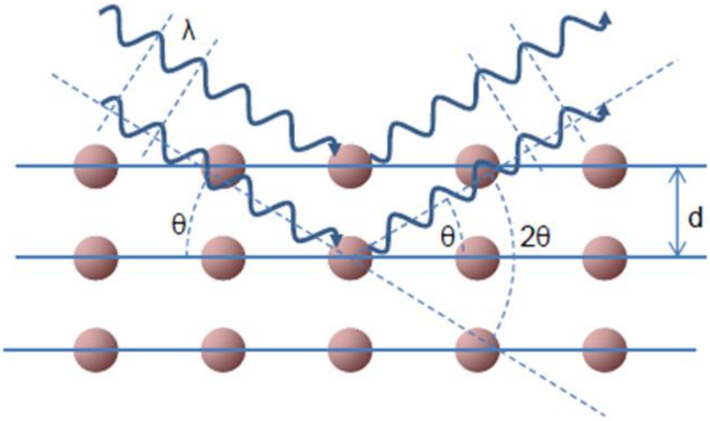
You will learn how an X-ray diffractometer is operated, and how to analyse the data to extract different kinds of information about the sample.

3. 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 1st year Diffraction lecture course and have used more recently in the 2nd year Microstructural Characterisation lectures in relation to electron diffraction.

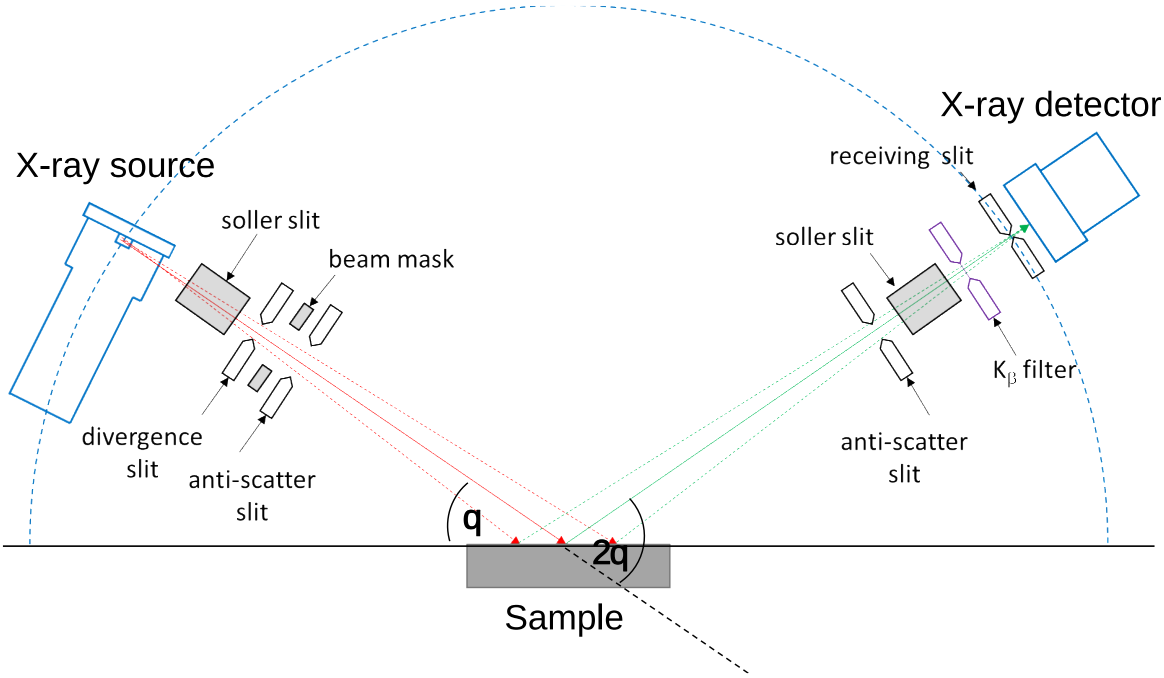
The path difference between X-rays scattered by different atomic planes must be an integer number (n) of wavelengths (λ) for coherent diffraction. This can be written in terms of inter-planar spacing (d) and angle (θ) as Bragg's law: $2d \sin\theta = n\lambda$ where n=1.



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.

θ–2θ XRD scans

In this practical, you will using so-called θ–2θ scans in reflection (Bragg-Brentano) geometry. During the measurement the sample is kept fixed and the X-ray source and the detector are moved in a circular path, keeping the angle of incidence and the angle of diffraction (relative to the sample surface) the same as each other (θ). The scan is called a θ-2θ scan because the angle between the detected beam and the incident beam is 2θ (see diagram below). angles (relative to the source), whilst simultaneously rotating the sample by angle θ 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 (set by the sample)

Angle of incidence/reflection (changed 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 (μ) 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.

4. Experimental Procedure

Instrument	Panalytical Empyrean
X-ray source	Cu K_α X-rays (λ=0.15406 nm) produced using a Cu X-ray tube with a Ni filter to remove the Cu K_β X-rays.
Sample	Rotates about the vertical axis during the measurement for better quality data. X-ray source and detector both stay at angle θ to the sample surface (which should be as flat as possible). The top surface of the sample must be flush with the top of the sample holder to ensure that the surface is at the centre of the diffractometer circle.
Detector	moves through 2θ with respect to the X-ray source (i.e. it measures 2θ). The detector is a Pixcel 1D strip detector (https://www.malvernpanalytical.com/en/products/category

/x-ray-components/detectors/pixcel1d) and for this practical will be used in scanning mode for fast data acquisition.

In general, it is good practice to perform **repeat measurements** in the XRD to reduce error. In θ–2θ 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, it is good practice to perform a third scan 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

Six unknown elemental metal samples will be provided and you only need to analyse two specimens (this is indicated in the excel sheet). θ–2θ scans should be carried out on each of these samples using the following measurement parameters to ensure you see several peaks:

2θ range	Step size	Scan rate
25-100°	0.013°	13.8 s/step

Determining accurate peak positions

The XRD analysis program (Highscore) is used to perform the first stage of the data analysis. The stages below will be demonstrated to you and you will be given the peak lists as well as the raw data for each scan. The first and second columns of the raw data correspond to the angle (2θ in degrees) and the intensity (in counts) respectively.

1) Determine the background. Your background should follow a smooth line.
2) Perform a peak search. This is a rough algorithm for finding peaks. A list of peak positions is generated automatically when you do this, but the peak parameters will not be very accurate.
3) Perform a profile fit (default settings) and check that the fit is good by comparing with the raw data.
4) Export the peak list (list of 2θ positions of each peak) as a text file. This can be imported into Excel or Matlab or your choice of data processing software.

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. 1st year Crystallography and Diffraction / 2nd 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 θ 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. Ideally, to obtain the most accurate lattice parameter value, ideally we want to measure a peak at $2\theta=180^o$, which is impossible. Instead, the lattice parameter is calculated from all peaks in the pattern and extrapolated against a function of θ. The curve of *a* against θ is not linear and so a function of θ which does result in a straight line is chosen. Cullity (chapter 11) discusses the various sources of possible systematic errors and the functions of θ 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

Lab Notebook

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

- XRD scans from each metal samples, presented clearly and 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 the differences observed between the scans taken from the same sample mounted correctly (Metal_1) and incorrectly (Metal_1i)
- Discussion of why the most accurate lattice parameter can be determined from peaks at high 2θ 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	0.542
Ni	fcc	0.352
Cu	fcc	0.361
γ-Fe	fcc	0.363
α-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: CaO and MgO powder mixture

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_2 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_α 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_α is the weight fraction of the α 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 α phase from the intensity ratio (I_α/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_2 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

θ–2θ scans should be carried out on each of these samples using the following measurement parameters:

2θ range	Step size	Scan rate
50-70°	0.013°	24 s/step

Two measurements are needed for each of the calibration samples and the unknown sample X or Y (However, this year you are only provided with one measurement for each specimen). 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

Peak lists generated using the steps detailed above will be provided. The integrated intensities of each peak are given in the peak list and can be exported as a text file for further analysis offline (e.g. using Excel).

You will need to identify which peak in the spectrum comes from each phase. The demonstrators will show you how this is done using the Highscore software, but you can also search the ICSD database (https://icsd.psds.ac.uk/search/basic.xhtml/) which can be accessed on any computer connected to the Oxford University network. **If you are working remotely, you will need to connect to the network via vpn first.**

Quantitative phase fraction analysis

Using the **integrated intensity** values of the {220} MgO (α-phase) peak and the {311} CeO_2 peak, calculate the intensity ratio (I_α/I_s) for each calibration sample. Plot this against w_α (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.

Lab Notebook

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

- An example of an XRD pattern with the all the peaks identified and indexed.
- A table showing the integrated intensities of the {220} MgO and {311} CeO_2 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 briefly on the errors in your analysis. It is not necessary to carry out quantitative error analysis.

Part 3: Crystallite size and strain analysis in heavily ball-milled MgB_2 powder

Data collection

You will be provided with two MgB_2 powder samples. 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 24 hours. θ–2θ scans should be carried out on each of these samples using the following measurement parameters:

2θ range	Step size	Scan rate
5-120°	0.013°	100 s/step

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 2θ 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 λ **is the** X-ray wavelength (0.15406 nm)

θ is the Bragg angle

k is a constant which depends on the shape of the particle and has a value ≈ 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 η 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 θ dependence, using a series of peaks at different 2θ 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.

Lab Notebook

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

- XRD scans of the as-received and 24 hour ball-milled MgB_2 powders.
- Table with FWHM values of the peak widths and θ 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. Briefly comment on the accuracy of your results / errors in the analysis. Quantitative error analysis is not required.

5. What should be in the Lab Notebook?

Your lab book should include all of the data and analysis requested in the three separate parts detailed in section 4 above. The data should be well-presented with suitable annotations. The analysis/calculations should be clear and easy to follow.