PRINT FIRST NAME	PRINT LAST NAME	PRINT STUDENT ID	GRADE

Experiment 1

X-Ray Diffraction

Before starting this experiment, you must be familiar with the concepts of: crystal lattice, unit cell, lattice spacing, Miller indices, X-ray spectrum, crystal diffraction and Bragg diffraction (references 1-4).

Introduction

When X-rays (electromagnetic waves, wavelength order-of-magnitude 1 Å) encounter atoms, they are diffracted (changed in direction of propagation, with a different amplitude and phase, but unchanged in wavelength) by the electron clouds of the atoms. If the atoms are arranged in a crystalline lattice (an array which is periodic in three dimensions), and the incident X-ray wave is a monochromatic parallel beam, then the waves diffracted by the $\cong 10^{23}$ atoms in the crystal will interfere in such a way that only in a few directions constructive interference will take place, and a non-zero intensity diffracted beam will result. The directions of the diffracted beam can be constructed as follows:

- Slice the crystal into planes of atoms, called lattice planes. Each set of lattice planes (two are sketched in figure 1.1) is characterized by its orientation in the crystal (given by the Miller indices h, k and ℓ and its lattice spacing d_ℓ).
- Each lattice plane, when hit by an incoming X-ray beam (direction θ) acts as a mirror, producing a reflected beam as well as a straight-through beam which impinges on the next lattice plane.
- Only when the "reflected" beams from successive lattice planes interfere constructively, that is, when

$$AB + BC - AD = n\lambda \tag{1.1}$$

then the crystal as a whole will produce a diffracted beam with non-zero intensity. The angle between the incident and diffracted beams is then 2θ. This is called Bragg diffraction, and from the geometry of figure 1.1 it can be seen that it will occur when:

$$2d_\ell \sin\theta = n\lambda \tag{1.2}$$

Often the order number n and d_ℓ are combined in a quantity d, given by $d = d_\ell/n$, so that Bragg's Law is written as:

$$2d \sin\theta = \lambda \tag{1.3}$$

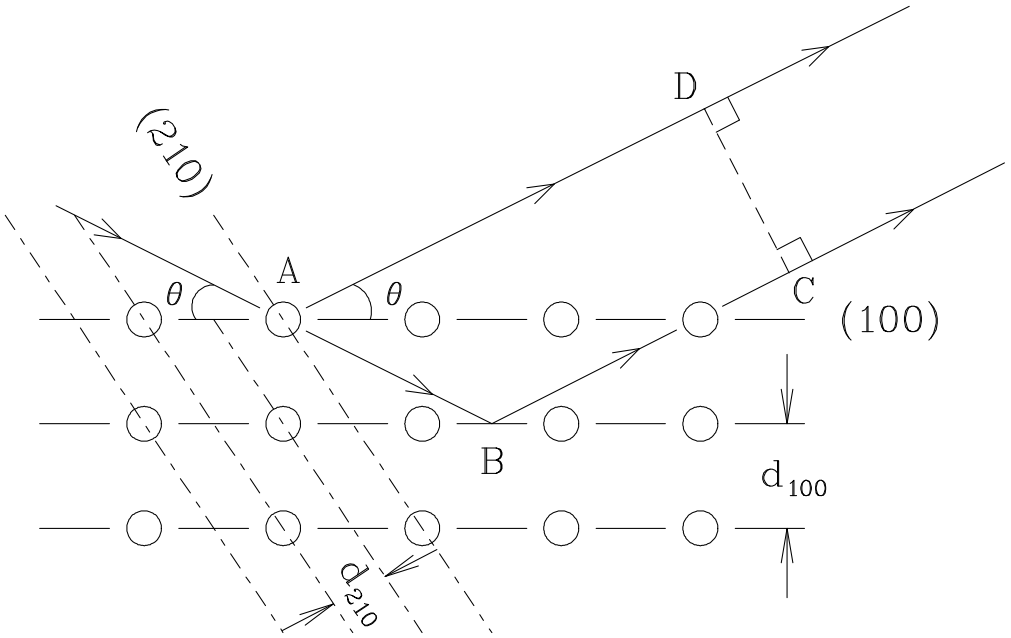

Figure 1.1: X-rays striking a crystal lattice

1.1 The X-Ray Emission Spectrum of Copper

You will determine the wavelength of some of the sharp lines of the Cu X-ray emission spectrum. The diffractometer geometry is shown if figure 1.2. The X-rays emitted by the copper target in the X-ray source are filtered, so that only the spectral lines labelled Cu-$K_{\alpha 1}$, Cu-$K_{\alpha 2}$ and Cu-K_{β_1} (with very low intensity) are present in the X-ray beam. The beam is incident on a single crystal of MgO. Its $(h, k, \ell) = (1, 0, 0)$ lattice planes will be used; they are parallel to the cleaved front face of the crystal. The intensity I of the diffracted beams (at a direction 2θ with respect to the incident beam) is measured by the X-ray counter; the chart output is a graph of I as a function of 2θ.

CAUTION: The instructor will demonstrate the diffractometer. Under no circumstances is the apparatus to be used, or adjusted, without prior permission of the instructor. X-rays are a radiation hazard, so you must observe all safety instructions listed next to the experiment.

Mount the MgO crystal in the sample holder, so that its (100) face is accurately parallel to the sample plane. For the (100) lattice planes the d_ℓ spacing is

$$d_{(100)} = 4.205 \text{ Å}$$

The 2nd order ($n = 2$) Bragg reflection for the CuK_α doublet occurs in the 2θ range $42 \to 44°$; the $n = 4$ reflection occurs in the range $93 \to 95°$. The $n = 2$ reflection of the K_{β_1} line can be seen around $2\theta \cong 38 \to 39°$ with low intensity.

Record the $I(2\theta)$ curves in these ranges, and calculate the wavelength of the observed spectral lines. Compare the experimental results with the literature values.

The wavelength separation of the $K_{\alpha 1}$ - $K_{\alpha 2}$ doublet can be determined quite accurately, in the following way: Let the wavelength of the two lines in the doublet be λ_1 and λ_2 and $\Delta\lambda = \lambda_2 - \lambda_1$, the separation of the recorded lines on the $I(2\theta)$ chart is measured as $\Delta_{2\theta}$ (in radians). By differentiating Bragg's Law show that:

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta_{2\theta}}{2\tan_\theta}.$$

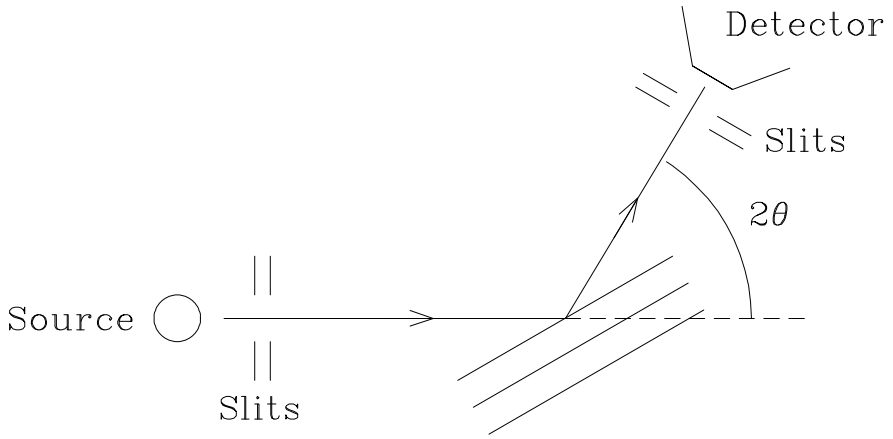

Figure 1.2: Diffractometer geometry

Calculate $\Delta\lambda/\lambda$ for the CuK_α doublet directly from the measured $\Delta_{2\theta}$ at $2\theta \cong 43^\circ$ and $2\theta \cong 94^\circ$; compare your experimental results with the calculated values of

$$\frac{\Delta\lambda}{\lambda} = \frac{2(\lambda_2 - \lambda_1)}{(\lambda_2 + \lambda_1)},$$

where λ_1 and λ_2 are taken from one of the references, or from the *Handbook of Chemistry and Physics.*

1.2 The X-ray diffraction pattern of MgO

Replace the single crystal MgO plate by a sample consisting of a thin layer of MgO powder. In the powder the individual crystals (grains of approximately 10^{-3} cm size) are oriented totally at random. Of the millions of grains only a few will, accidentally, lie such that their (100) planes are parallel to the plane of the sample holder. When the sample holder is therefore at an angle $\theta \cong 21.5^\circ$ with respect to the incident beam, and the detector therefore at an angle $2\theta \cong 43^\circ$, these few grains can produce a Bragg reflection. All the other grains will not give a Bragg reflection, and therefore the $I(2\theta)$ graph will have a (relatively) weak peak at $2\theta \cong 43^\circ$. Similarly, there will be in the powder sample, grains with a different set of lattice planes, say with Miller indices $(h, k, \ell) = (311)$, parallel to the sample plane; these grains will give a Bragg reflection at an angle 2θ satisfying Bragg's Law with $d_{(311)}$. The diffraction pattern $I(2\theta)$ of a MgO powder will therefore consist of a set of peaks, each of which is characterized by its own value of d and of (h, k, ℓ).

Record the $I(2\theta)$ pattern of MgO powder in the range $28^\circ \leq 2\theta \leq 64^\circ$. Calculate the d values of the reflection, use an "average" λ value of $\lambda = 1.5405$ Å. The possible sets of lattice planes have Miller indices: (111), (311), (331), (200) and (222). Calculate the d-value for each of these planes according to:

$$d = \frac{a_0}{\sqrt{h^2 + k^2 + \ell^2}}$$

with the lattice constant $a_0 = 4.205$ Å and compare with the experimental values.

1.3 The XRD pattern of an unknown substance

Each solid crystalline material has its own $I(2\theta)$ diffraction pattern. In general, the position (2θ) of the diffracted beams is determined by the size and shape of the unit cell of the crystalline lattice; the intensity I of a given beam is determined by the kind of atoms and their position inside the unit cell. The XRD pattern is therefore like a fingerprint for each crystalline substance, and can be used for identification.

You will be given a powder of an oxide copper. Two copper oxides are known, with formulae Cu_2O and CuO. Record the XRD pattern of the powder in the range $28° \leq 2\theta \leq 64°$, and calculate d-spacings and relative intensities for each diffraction peak. Compare your results with the patterns for CuO and Cu_2O (patterns 5.0661 and 5.0667 of ref. 5) and determine which copper oxide you have.

References

1. B.D. Cullity, *Elements of X-Ray Diffraction*, Chapters 1, 2, 3. 7.
2. E.W. Nuffield, *X-Ray Diffraction Methods*, Chapters 1, 2, 3, 5.2.
3. D.L. Livesey, *Atomic and Nuclear Physics*, Chapters 4.6 - 4.9.
4. R.T. Weidner and R.L. Sills, *Elementary Modern Physics*, Chapter 5.
5. *Powder Diffraction File*, (Joint Committee on Powder Diffraction Standards, 1968). In library as REF QC 482 P68.