X-RAY Diffraction Lab Manual

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Basic Physics

Diffraction

The discovery of x-rays by Wilhelm Röntgen in 1895 was followed rapidly by the development of x-ray diffraction by Max von Laue, Paul Peter Ewald, William Lawrence Bragg and William Henry Bragg. The ability to determine how the atoms were arranged in essentially any crystalline solid led directly to the establishment of solid state physics as a quantitative discipline. Atomic structure and bonding control all of the physical properties of a solid. One measure of the importance of x-ray diffraction can be seen in the 25 people who have received Nobel Prizes for x-ray diffraction work (this does not include those recognized for electron and neutron diffraction) since x-rays were discovered.

The value of x-ray diffraction starts with the observation that the wavelengths of conveniently generated x-rays are comparable to the interatomic distances found in solids. This means that it is possible to use a crystal as a diffraction grating for x-rays in the same way that lines ruled on a glass or metal plate can be used to diffract light. The same equation is used:

$$n\lambda = 2d \, \text{Sin}(\theta)$$

where λ is the wavelength of the x-ray, d is the spacing between the diffracting planes and θ is half of the scattering angle, as shown in Figure 1. However, in crystal diffraction, n is always set to 1.

Figure 1. Illustration of Bragg's Law for diffraction of x-rays from the planes of a crystal. The blue dots represent the atoms in the solid forming a series of equally spaced (by d) planes.
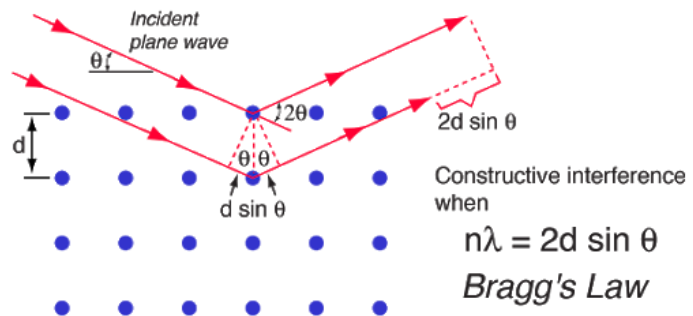
A deeper mathematical approach, due originally to Max von Laue, reproduces Bragg's law but goes further. Not only does it yield that condition that must be met for diffraction to occur, but it provides a way to calculate the *intensity* of the diffracted beam. Furthermore, the mathematical language used shows that the observed pattern of diffraction peaks is actually the Fourier transform of the crystal structure, meaning that, in principle, if you collect enough of the diffraction pattern, then you can back-transform to obtain a complete description of the crystal structure.

One historical irony is that, although the Laue formalism is far superior and is the one universally used to analyse diffraction patterns, the language of lattice planes and indexing established the Braggs dominates the presentation of the results.

Crystal Structure

A crystalline solid consists of a regular 3-dimensional packing of building blocks, called "cells". (Think of a tiled floor covered by a regular pattern of 2-dimensional tiles, but extended as blocks in 3-dimensions). To fully describe the structure we need two pieces of information:

(1) The shape (really symmetry) of the blocks – cubes, etc.
(2) The nature and arrangement of the atoms within the cell

The first are extremely limited in number as they must pack to fill 3-dimensional space (there are only 14 lattice types "Bravais Lattices" grouped into 7 crystal systems – see Figure 2), the second are essentially unlimited. The arrangement will fall into one of 230 allowed by various symmetries, but the units that are arranged according to those rules can range from atoms, through molecules of arbitrary complexity up to entire virus particles. A crystal cell could have just one atom in it, or millions, yet the complete structure can often be determined with great accuracy.
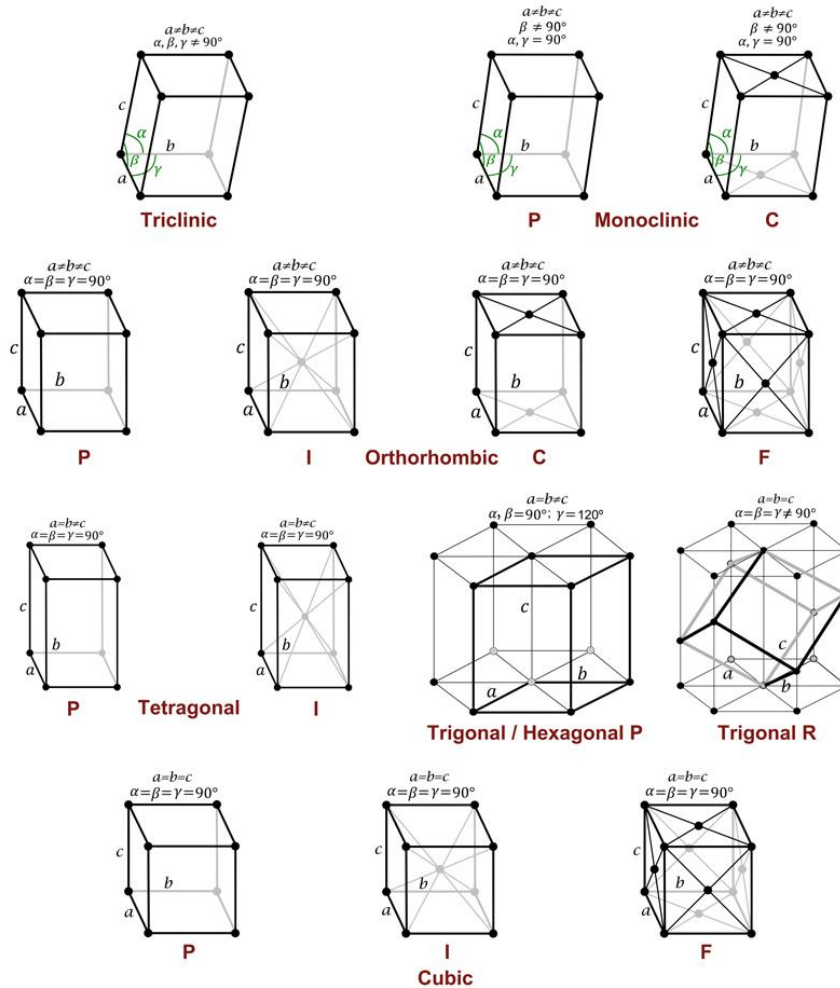

Figure 2. The fourteen Bravais Lattices grouped into the seven possible crystal systems that form the building blocks of all crystal structures.

Indexing diffraction planes

You may have noticed as you walked or drove past a regular plantation of trees, that at some positions you can see right through the array of trees and the trees appear to be arranged in parallel lines extending into the distance, then as you move on, this is lost only to appear again with different trees forming the new parallel lines, as shown in Figure 3. In each case, the set of parallel lines of trees includes *all* of the trees in the plantation.

Figure 3. Some examples of how a 2-dimensional array of points can be viewed as forming a series of parallel lines.
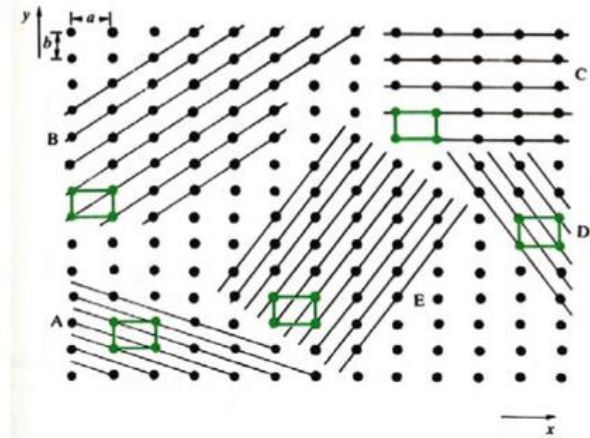
The same is true of 3-dimensional crystals where the atoms form parallel sheets or planes. The easiest to visualise is probably the face of a cube (100 in Figure 4), but there are many other simple ones like a corner diagonal (110 in Figure 4) or the body diagonal (111 in Figure 4). The labelling of these planes uses "Miller Indices" and pre-dates formal crystallography. The indexing is generated by extending the plane to cut the axes that define the crystal system (three equal length orthogonal axes in the case of a cube) and then taking the reciprocal of the three cut points and reducing them the three smallest integers. So, for a cube face, the plane cuts one axis one unit out, but only hits the other two at infinity (as the plane is necessarily parallel to those axes. The reciprocals are then just 1, 0 and 0, hence the (100) plane. The body diagonal in Figure 4 cuts all three axes at one unit out, so it is the (111). Higher-order planes like the (200) cut one or more axes closer to the origin and thus yield larger indices. NOTE: This is why the "n" in
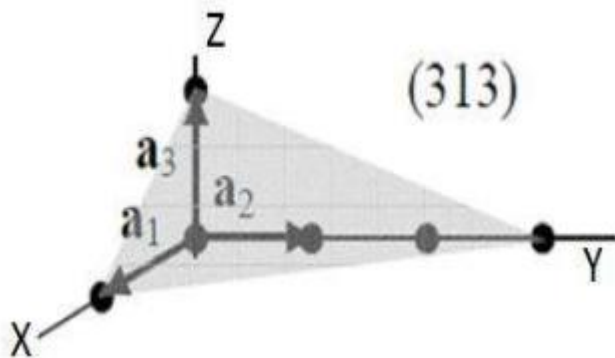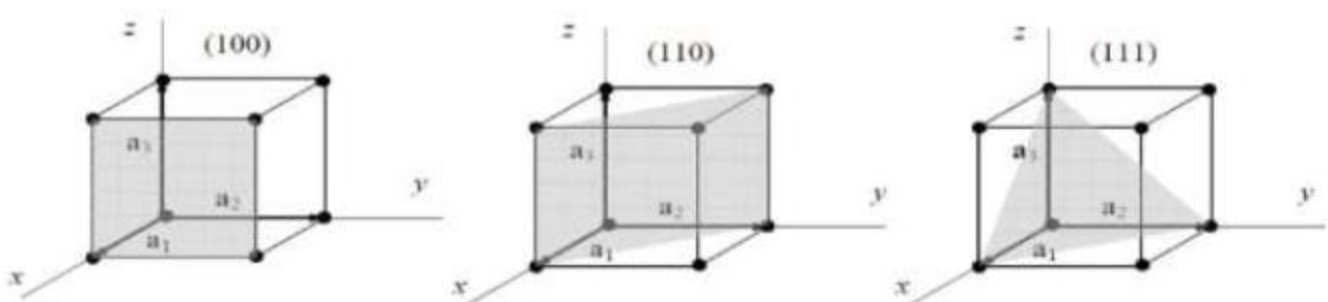

Figure 4.

(left) Example showing the construction of the 313 plane.

(below) Several simple planes indexed in a cubic system.

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Bragg's law is set to 1: For diffraction from a cube face, "n=2" corresponds to diffraction from the (200) plane and it is *not* equivalent to diffraction from the (100) plane.

Each plane, defined by its Miller indices (*hkl*), has a well-defined inter-planar distance *d* (see appendix 3 in Cullity). For a cubic crystal the distance is given by:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

where *a* is the length of the cube edge. It is clear that as the (*hkl*) increase, the inter-planar separation decreases. For each *d*, Bragg's law yields a corresponding θ (up to the limit where θ exceeds 90° and the diffraction condition is no longer physical). By determining the locations of the diffraction peaks we obtain a list of inter-planar distances in the crystal, and if know the corresponding indices, we can determine the lattice parameter (or parameters, if the crystal is not cubic). Furthermore, depending on how the cell is packed (see Chapter 2 of Kittel's book) some (*hkl*) planes yield zero diffracted intensity and so those peaks are systematically absent from the observed pattern – these missing peaks can be used to identify the corresponding Bravais lattice.

Equipment

Automated diffractometer

The diffraction patterns were collected using an automated diffractometer using Copper K_α radiation. As shown in Figure 5, the powder sample is mounted on a flat plate and the instrument runs in θ–2θ mode: Starting (in principle) with the x-ray beam parallel to the sample surface and pointing directly into the detector, the instrument rotates the sample in steps of Δθ and the detector in steps of 2Δθ, so that the simple reflection condition is maintained, and collects counts to measure the scattered intensity.
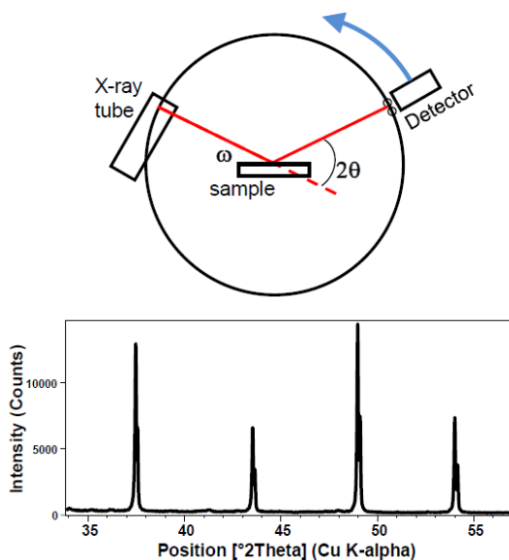

Figure 5. (Top) Schematic layout of an x-ray diffractometer showing the x-ray tube, sample and detector. The pattern is collected as a function of 2θ and the sample rotates at half the rate of the detector (ω = θ = 2θ/2) so as to preserve simple reflection geometry. Note: As the motion of the sample stage is, in principle, independent of that of the detector arm, the angle of the sample stage is often denoted as ω.

(Bottom) Typical diffraction pattern showing a series of peaks as a function of the scattering angle (2θ).

The EXPERIMENT

Basic analysis.

A simple data set is provided to start with: A series of Cu—Ni alloys.

We suggest that you start with the pure copper data.

Can you locate and index the observed peaks?

Can you fit them?

What function works best to fit the peaks?

Can you identify the correct Bravais lattice?

How well can you determine the lattice parameter? (Many tables only list two or three digits, you should be able to do much better)

Deeper analysis.

What happens to the diffraction pattern as nickel is alloyed with copper?

What can you say about the crystal structure?

What can you say about the lattice parameter?

How might Vegard's law apply here? Does it?

The Lead—Tin system.

This system is more complex, not least because tin adopts a tetragonal structure.

What can you say about the Lead—Tin alloy system?

How does it differ from the Copper—Nickel system?

The Mystery Samples.

This zip contains diffraction patterns for several different elements.

Can you identify the structures?

How well can you determine the lattice parameters?

Can you identify the elements?

Cu_3Au.

This is a more interesting challenge.

The two diffraction patterns were taken from pieces of the same ingot so they have precisely the same composition, however they were subjected to different heat treatments.

What can you say about the differences between the two samples based on their diffraction patterns?

RESOURCES

APPENDICES (In the "Literature" Section)

The first two chapters of "Introduction to Solid State Physics" by Kittel
(a discussion of crystal structure from a solid state perspective)

The first four chapters of "Elements of X-Ray Diffraction" by Cullity
(a discussion of crystal structure from a diffraction perspective)

Chapter seven of "Elements of X-Ray Diffraction" by Cullity
(a discussion of diffractometers)

Selected appendices from "Elements of X-Ray Diffraction" by Cullity
(some useful equations and data)

Software

McPhysics & Spinmob

We maintain a user-friendly python library [McPhysics](#), which provides pedagogical tools and interfaces with specific equipment and data files in the McGill Physics Department student labs. You can read more about it on the [GitHub page](#) (including how to install!), but the most relevant features for this lab are:

mcphysics.data

mcphysics.instruments

mcphysics.functions for some potentially useful distribution functions.

Underneath McPhysics is a more general-purpose python library [Spinmob](#) aimed at simplifying the tasks of loading, processing, visualizing, and fitting data. It also includes a quick graphical user interface builder tailored to scientific laboratories.