X-RAY DIFFRACTION in POWDERS

PURPOSE: **T**o learn x-ray powder-pattern diffraction techniques, to verify Vegard's law for copper-nickel alloys, to determine the nickel content in some American and Canadian "nickels", and to identify an unknown sample.

APPARATUS: Rigaku Miniflex 30 kV x-ray diffraction spectrometer, with water cooling circulator, x-ray power supply and gun, proportional counter detector, safety interlocks; fluorescent paddle; known and unknown samples.

THEORY: An excellent, very readable discussion of all of the aspects of x-ray diffraction that you will need for this experiment can be found in Cullity[1] "Elements of X-ray Diffraction". References to specific sections have been given throughout this write-up. Appendices 5 and 10, which contain useful parameters and information, are attached in the appendix to this write-up.

1. **Crystal Structure and Vegard's Law:** Solids can be classified as being either amorphous or crystalline. In crystalline materials the ions occupy specific locations in a regular lattice. The simplest such lattice is a simple cube with ions on each of the corners of the cube. However, in all materials other crystalline structures are preferred because they have a lower total energy. The most common simple structures are the **face-centered-cubic (fcc)** and the **body-centered cubic (bcc)**. The fcc structure consists of a cube of ions with six additional ions located at the centers of each of the six faces of the cube. Aluminum, copper, and nickel are metals with the fcc structure. The bcc structure consists of a cube of ions with one additional ion located at the center of the cube. Tungsten, molybdenum and iron take on the bcc structure. For both the fcc and bcc structures the distance between the ions on the corners of the cube is called the **lattice constant *a*.** In this experiment you will use x-ray diffraction to determine the lattice constant of a number of different samples.

The size of the lattice constant depends on the size of the ions. In metals the outermost electrons become unbound and wander freely through the lattice (making them good

conductors). This lowers the energy of the crystal and creates an attractive metallic bond that holds the metal together. But when the (positive) ions come so close to each other, the Coulomb repulsion between the ions sets in and prevents the crystal from further compressing. The equilibrium value for the lattice constant is then determined by the balance between the attractive metallic bond and the Coulomb repulsion of the ions. This distance varies from metal to metal.

In this experiment you will study how the lattice constant changes for some alloys of copper in nickel. Copper is totally soluble in nickel. That is, you can form a copper-nickel alloy with any composition: Cu_xCuNi_{1-x} , where x is the **number fraction** of Cu ions, $0 \le x \le 1$. You will study how the lattice constant changes in Cu_xNi_{1-x} alloys as you vary x. For copper a = 3.6148 Å (one Angstrom = 1 Å = $1x10^{-10}$ m), while for nickel, a = 3.5239 Å. If one makes the simplistic assumption that the ions of an alloy behave like hard spheres packed as close together as possible, then **Vegard's law** tells us that the alloy lattice constant should vary linearly with composition:

$$a_{\text{alloy}} = x\, a_{\text{Cu}} + (1-x)\, a_{\text{Ni}} . \qquad (1)$$

Note that **x is defined as the number (not weight) fraction of Cu atoms**. Vegard's law is found to be a fairly good approximation in many alloy systems.

Nickel is a magnetic element with a Curie point of $T_C = 368^{o}$ C. Copper is nonmagnetic. In Cu_xNi_{1-x} alloys the Curie point is found to vary linearly with concentration:

$$T_C = 368 - 1170x \ (^{o}C), \qquad (2)$$

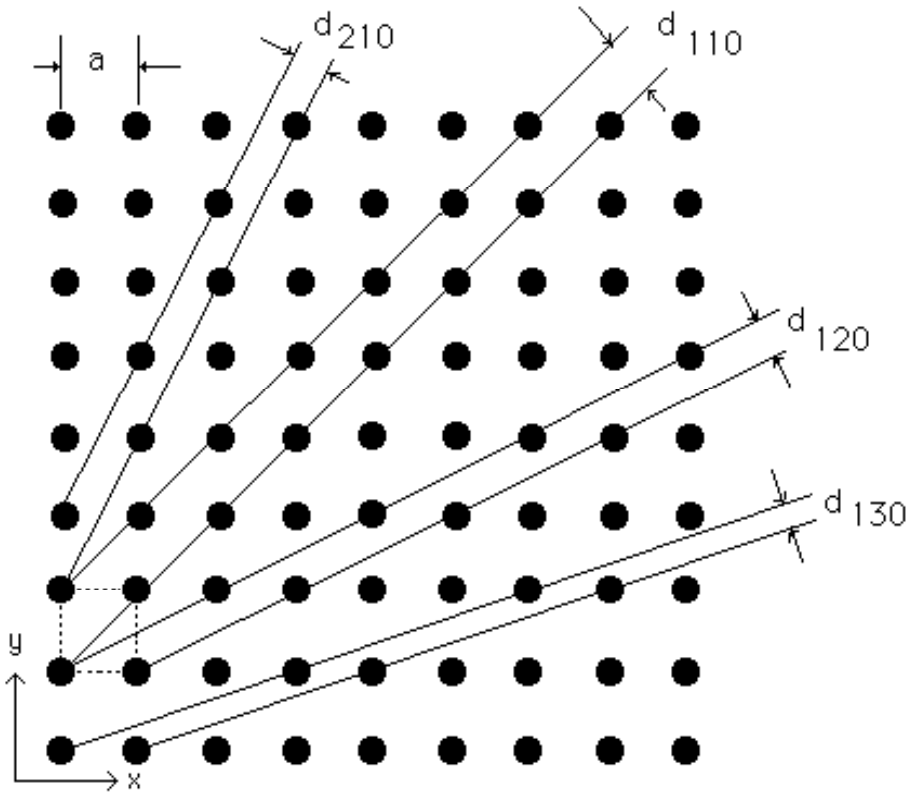
which implies samples with more than about 30% copper are nonmagnetic at room temperature.

2. X-ray Diffraction. In 1912 W.L. Bragg proposed a simple way of understanding x-ray diffraction by crystalline materials. He pointed out that, for any crystal, one can draw a set of equidistant parallel planes that pass through all of the atoms in the crystal, and that there are many different sets of such "Bragg" planes. Figure 1 shows a few of these planes on a simple cubic crystal. The planes are labeled with a set of integers (hkl), called the Miller

indices, which identify the reciprocals of the fractional intercepts which the plane of interest makes with the crystal axes. (See Cullity section 2-6 for a more complete discussion.) Thus in Fig. 1, where the z-axis is out of the page, we see that the plane labeled d_{120} intercepts the cube shown as a dotted box in the figure at x = 1, y = 1/2, and z =∞. So the Miller indices are (1, 2, 0). For a cubic crystal the Miller indices also correspond to the x, y, and z components of a vector perpendicular to the plane.

Notice that the distance d_{hkl} between adjacent Bragg planes becomes smaller as the Miller indices increase. For cubic crystals this distance is:

$$d_{hkl} = a \frac{1}{\sqrt{h^2 + k^2 + l^2}} \quad . \qquad (3)$$



BRAGG PLANES IN A CUBIC SOLID

Figure 1

When a beam of x-rays strikes one of the ions in the crystal, the x-rays are diffracted

in all directions. In general these diffracted waves from different ions will be, on average, out of phase and cancel out. However, Bragg showed that, for an x-ray of wavelength λ and angle of incidence θ with respect to a Bragg plane (not the normal to the plane), scattered waves from the various ions lying in a single Bragg plane will be coherent if the angle of reflection equals the angle of incidence, Fig. 2. Scattering in this direction from successive planes a distance d_{hkl} apart will also be coherent, and will interfere constructively if

$$n\lambda = 2\, d_{hkl} \sin\theta \qquad (4)$$

where n is integer. This is the **Bragg law** of diffraction. Thus the diffracted beam makes an angle θ with the Bragg plane and **the angle between the incident beam and the diffracted beam is 2θ.**

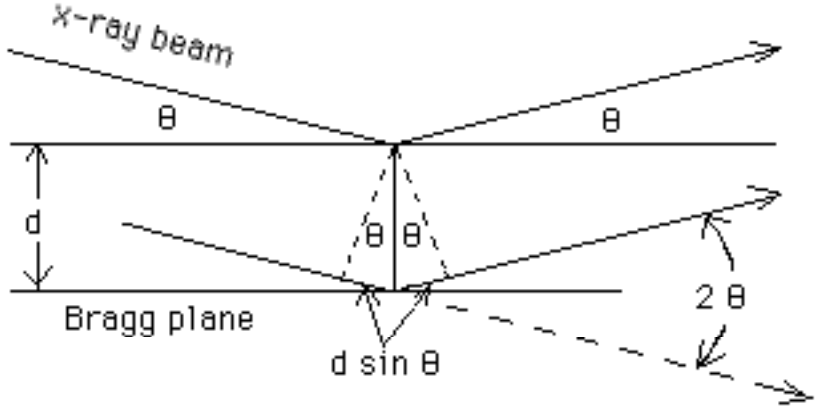


Figure 2

Two different x-ray diffraction techniques are frequently used to study the structure of solids. The **Laue method** (see Cullity, Section 3.6) uses a **single crystal** sample (as distinguished from a powdered sample), so the incident beam makes the same angle with all parts of the sample and the angle of incidence with each set of Bragg planes is fixed. The beam used for the **Laue method contains a continuous distribution of x-ray wavelengths**. The diffraction pattern consists of a set of spots, each corresponding to a different set of (h k l) values, which are formed by those x-rays from the beam which have the appropriate wavelength for the angle of incidence, Eq. (4). The Laue method is a very

powerful crystallographic tool, but the spectra are somewhat hard to interpret.

In this experiment you will use the powder method, which is easier to interpret and is capable of high accuracy, especially for determining the spacing of atoms in a solid. In the **powder method, monochromatic x-rays** are used and the **sample is very finely powdered**. As can be seen from Eq. (4) for a given d_{hkl}, since λ is fixed, there are only a few values of θ (sometimes only one, since $\sin\theta \leq 1$) that will give a diffracted beam. But since the sample is powdered, the beam will encounter small crystallites oriented at random so that there will always be some that are oriented properly for diffraction. The diffracted beams corresponding to each d_{hkl} are recorded by rotating a detector around the sample so that the angle 2θ between the incident beam and the detector sweeps from 0^o to 180^o while the sample itself rotates from 0^o to 90^o.

It is not strictly necessary to have a powdered sample in order to use the powder method. If a metal sample is rapidly cooled, it will form many small crystallites whose x-ray spectra will mimic that of a powdered sample. However, the orientation of these crystallites is frequently not completely random, especially if the sample has been mechanically worked (rolled flat or stretched, etc.), and the relative intensity of the x-ray lines will vary from that of a powder sample. In extreme cases some lines may even be missing. For such samples an accessory that spins the sample is sometimes used to give reproducible intensities for the diffracted lines.

3. Interpretation of Spectra. The interpretation of the powder pattern spectrum for cubic crystals is very straightforward. From the measured value for θ and the known value for λ (1.5418 Å for the x-ray tube you will use), you can use Bragg's law to calculate the spacing of the Bragg planes d_{hkl}. Then, since the lattice constant *a* must be the same for all the lines, a set of Miller indices can be assigned to each line giving the same value of a for each line. (This is called **indexing the spectrum**.). This task is easy, since the order of the reflections is determined by the value of $s = 1/\sqrt{h^2 + k^2 + l^2}$. Then, in order of increasing 2θ, the first few reflections for a simple cubic crystal will be (100), (110), (111), (200), (210), (220). A complication arises for cubic crystals of high symmetry such as fcc

or bcc where total destructive interference occurs for x-rays diffracted from some planes. For example, in an fcc crystal (see Section 2-7 in Cullity) such as copper or nickel, only those reflections are seen for planes for which (h k l) are all odd or all even (counting zero as even). Then the first few reflections for a fcc crystal are (111), (200), (220), ... A complete list of allowed reflections for various crystals is given in Appendix 10 of Cullity. If the crystal structure is unknown, the indexing is carried out by trial-and-error until a consistent set of values is obtained.

For the x-ray apparatus you will be using there can be an error of several tenths of a degree in the measured angle, which can affect how well your data agrees with Vegard's law. To reduce this error, the powdered alloy samples are mixed with powdered silicon. You will **use the silicon x-ray diffraction lines as a reference to correct for systematic errors in** θ. The crystal structure of silicon is the same as that of diamond. Blakemore[3] states:

> "Close packing is not the primary consideration in the diamond lattice. This (e.g., diamond) is the structure adopted by solids for which the existence of four symmetrically placed valence bonds overrides any other consideration, which is the situation in silicon, germanium, and gray tin (20 C), as well as diamond. Diamond has the face-centered cubic (fcc) translational symmetry. We can view diamond as the result of two interpenetrating fcc lattices displaced from each other by one quarter of the cube diagonal distance. Since for diamond the two lattices are of the same type of atom, each atom ends up with four tetrahedrally arranged nearest neighbors just like itself and 12 next-nearest neighbors."

It is interesting to note that some of the diffraction lines seen in the fcc structure are missing in silicon due to destructive interference between the two interpenetrating fcc lattices. Thus the silicon diffraction pattern is even more sparse than the fcc pattern. (See Cullity, Appendix 10). The intensity of the spectrum varies widely from line to line. This variation is due to a number of different factors (see Cullity, Sections 4-12 and 4-13), which make it difficult to use intensity to estimate the relative amount of different crystal phases in a mixed phase sample.

4. Generation of X-rays An x-ray tube generates x-rays by slamming a beam of electrons

that has been accelerated across a large potential difference (30 kV for the Rigaku Miniflex) into a water-cooled copper target. The spectrum has a continuous distribution of **bremsstrahlung** ("braking radiation") wavelengths, with a cutoff at short wavelengths corresponding to the maximum electron kinetic energy (30 keV for the Rigaku Miniflex). The shape of the spectrum is independent of the material used as the target.

Superimposed on this continuous spectrum are narrow, much more intense lines called the **characteristic spectrum**, whose wavelengths are characteristic of the material used in the target, independent of the exciting electron energy. For this experiment we need a monochromatic x-ray beam and will be using one of these characteristic spectral lines for copper. Tungsten or molybdenum targets are used if shorter wavelength x-rays are needed. These lines arise when an incoming electron strikes an atom and ejects one of its orbiting electrons. One of the remaining, less tightly bound atomic electrons then cascades down to the unoccupied orbit and gives up the energy difference as an x-ray characteristic of the element. In a multi-electron atom the shells of electrons are labeled with the letters K, L, M, ... with the K shell being closest to the nucleus (most tightly bound). When a K-shell electron is ejected and an L-shell electron "drops down" into the empty orbit, the emitted x-ray is labeled K_α. When an M-shell electron drops into the K-shell, a K_β x-ray is emitted, etc. In the apparatus you will use, the x-ray tube has a copper target and the K_α line is most intense compared to the other characteristic lines or the continuous spectrum. The K_α line actually consists of two closely spaced lines, $K_{\alpha 1}$ = 0.15406 nanometers (8.047 keV) and $K_{\alpha 2}$ = 0.15444 nm (8.027 keV) , but for most purposes it is sufficient to use an average wavelength weighted ($K_{\alpha 1}$:$K_{\alpha 2}$) by the relative intensities 2:1 (av K_α =0.15418 nm). In some samples you might see a splitting of the x-ray spectrum due to these two source lines (especially for large values of 2θ). A thin nickel foil filter is placed in front of the proportional counter (gas) detector to eliminate most of the higher energy copper K_β line. Nickel is almost transparent to copper K_α radiation but highly absorptive to K_β.

EQUIPMENT: The apparatus you will use is a Rigaku 30 kV Miniflex powder pattern x-ray spectrometer which is extremely easy and safe to use. You will be issued a radiation

badge. **You must wear the radiation badge whenever you are in room 133 and the x-ray machine is in operation.**

1. Safety devices: Improperly controlled X-rays are dangerous and can give serious burns. The machine is well shielded with a series of safety devices and interlocks to insure your safety. **It is important that you do not attempt to defeat these safety measures in any way**. There is a red light mounted on top of the machine that is lit whenever the machine is generating x-rays, to remind you of possible hazards. The door to the machine is made of a special plastic that is highly absorbent to x-rays, even though it is transparent to visible light. When the door is opened the machine will continue to generate x-rays and the light will remain on. However, a shutter automatically covers the source so that it is safe for you to reach into the machine to make adjustments. If for some reason the shutter should fail to cover the source, there is an additional interlock which automatically shuts off the machine. (The shutter moves across the source whenever the handle on the door is turned by even few degrees. Therefore it is important, when recording a spectrum, to be sure that the handle is completely closed. Otherwise your x-ray beam may be partially or totally blocked.)

2. Spectrometer operation: Before you begin using the machine make sure you and your partners have your radiation badges on. Sign in on the USER LOG located on the top of the machine.

a. Mount the sample in the machine by slipping the holder into the two spring clips provided on the machine.

b. Adjust the detector to the desired starting value for 2θ. The mechanism which moves the detector is called a **goniometer**. It turns the sample through an angle θ with respect to the x-ray beam while at the same time moving the detector through 2θ. Note that it always sweeps in the direction of decreasing 2θ. There are two sweep speeds, 2^{o}/minute and 0.5^{o}/minute. The slower sweep speed is for resolving overlapping lines or accurately determining angles. The sweep speed can be adjusted

with the knob located next to a small piece of metal that reads "^{o}/min." Push the knob all the way in for 0.5^{o}/minute, and pull it all the way out for 2^{o}/minute.

To adjust the detector push the chrome metal lever (located inside the machine near the center at the bottom) counter-clockwise, to release the gears that move the detector. Move the detector near the desired angle and release the lever to re-engage the gears. To fine-adjust the detector position, move the sweep speed knob to the center position and turn the degree knob to move the detector. Set the detector at the desired position with the degree knob exactly on zero. Pull the sweep rate knob out to 2^{o}/minute.

c. Close the door to the x-ray machine. **Make sure it closes completely!**

d. Turn on the switch for the cooling water circulator. It is located on the side of the table holding the machine. [Do not run it longer than necessary since the noise can annoy students doing the speed of light experiment.]

e. Turn on the main power switch for the machine and the high voltage power supply switch for the detector. Press the x-ray On switch to begin generating x-rays. The red light on top of the machine should go on. To turn off the x-rays use the red switch beside the On switch.

f. Set the count switch to Count and the count range to a convenient setting, such as 2000 cps.

g. Start the Logger Pro program and make sure that the Universal Lab Interface is turned on. Select "COM1" as the port to scan. Go to "File" →"New." Then go to "Setup" → "Data Collection." In the Sampling tab, you can adjust the experiment length and the number of samples per second. To run the experiment, press the "Collect" button and set the goniometer switch to "Start."

PROCEDURE:

Before you start: Calculate and make a table with the Miller indices, diffraction order , θ and 2θ values for all the Si peaks you expect to see for θ between 10^0 and 40^0 . Include the table in your report.

1. Place the fluorescent paddle in the sample holder (Figure 3) . The

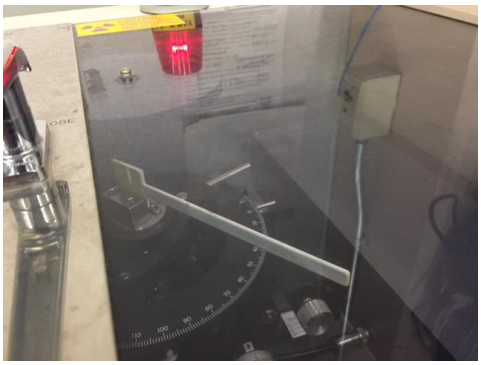


Figure 3. Fluorescent paddle. Left panel – Paddle resting on sample box. Right panel – when exposed to the X-ray beam the paddle emits green light highlighting the location of the bam.

paddle absorbs x-rays and emits visible light, so that you can observe the location of the x-ray beam. Notice how the shape and location of the beam changes for several widely different values of 2θ. You have to be sure that you place your samples in the sample holder so that the beam strikes them as 2θ is swept.

2. Record the x-ray spectrum for silicon, sweeping 2θ from 80^o to 20^o. Silicon has a diamond structure with a lattice constant of 5.4309 Å (see Appendix 5 of Cullity). Calculate the theoretical x-ray spectrum, using this value, and compare with your data. You can expect a discrepancy of several tenths of a degree due to goniometer misalignment. To take this into account, silicon is frequently mixed with other samples to serve as a reference whose spectrum is exactly known. In your report present the data in a table giving for each line the Miller indices, the measured and theoretical angles, and the approximate observed intensity. The only purpose of the intensity measurement is to record whether the lines are weak or strong.

3. For either a copper or a nickel sample, measure as many lines as you can over the entire range of 2θ from 0^o to 160^o and compare with theory using the lattice constant listed in Appendix 5 of Cullity. You doubtless found sweeping over a wide range of angles to be very tedious, even at 2^o/min. Instead of making a wide sweep, predict the location of these lines and then search for them with a small sweep. In your report present the data in a table giving for each line the Miller indices, the measured and theoretical angles, and the

approximate observed intensity.

4. Carefully compare the observed spectra of copper and nickel for the two lowest index lines. You will see that the difference in 2θ between copper and nickel is fairly small (less than 1.5^{o}). To get good results, use Si(220) as a

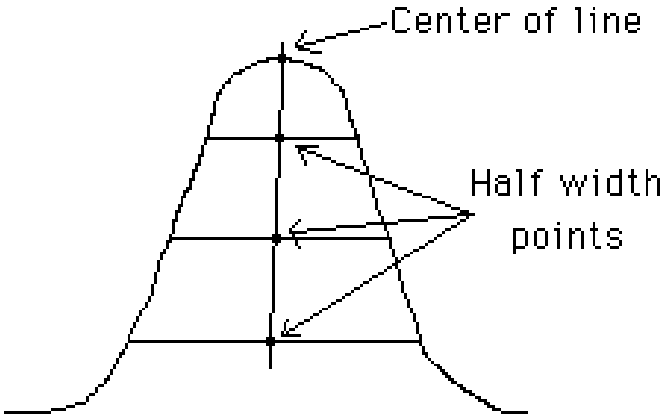


Figure 4. Definition of half width points.

reference assuming you know it's location exactly. Measure the angles as precisely as possible. In order to do this use the 0.5^{o}/min sweep. This will give a spread out spectrum that will be easier to measure accurately. To locate the position of the line by locating the maximum value. It is more accurate to measure the width of the line at several positions to locate the half width points, Fig. 4. From your data for these two lines determine the lattice constant for the two metals and estimate your error. Compare with the accepted value given in Cullity. You may assume the concentrations given for the alloys are accurate to ± 2%.

5. Verify Vegard's law for Cu-Ni alloys. You need **measure only the Ni(Cu) (1 1 1) and the Si (2 2 0) lines**, which can be observed by sweeping from 2θ = 48^{o}to 43^{o}. Use the slow sweep in order to get as accurate a determination of 2θ as possible and follow the procedure outlined in step 4. Present your data as a graph of lattice constant versus copper concentration. **Use you data from step 4 for the lattice constants of pure copper and nickel**; these are good data points too. Make a least square fit to a straight line. On your graph also show the theoretical Vegard's law, Eq. (1), using the accepted lattice constants

for Cu and Ni. Are any of the alloys magnetic? Check with a small, permanent magnet. Do your results agree with Eq. (2)?

6. Determine the nickel concentrations in a U.S. nickel, and in both a 1979 and a 1984 Canadian nickel. Estimate your error. Are any of these nickels magnetic?

7. Record the x-ray spectrum of one of the unknown samples and use Appendix 5 in Cullity to identify it. Be careful; it's easy to miss! Note that there may be very weak or missing lines in these non powdered samples and, even worse, extra lines not associated with the unknown. **If you have trouble indexing the unknown, try dropping one or two of the weakest lines;** they may be spurious. Also note that both a simple cubic lattice and a body-centered cubic lattice can give a 1:2:3:4:5 set of d^2 ratios but there are no simple cubic metals! If you find several metals seem to be possible, try determining the density and whether they are magnetic to help you discriminate between them.

To help with the identification try plotting peak theta value versus peak number for all the candidate materials using the tables in Cullity. On the same graph superpose the theta values of the observed peaks.

REPORT guidelines:

The structure of the report should follow the format of a scientific paper. Include the following: Title, authors, abstract, theory, apparatus, data, analysis, discussion and references. See for example articles published in Physical review letters. We also keep several issues in the lab.

1. Summarize the theory of the X-ray diffraction and discuss how it is tested in your experiment. Discuss the Miller indices, the cause of "missing peaks" and their connection to crystal structure. Discuss the pros and cons of single crystal and powder diffraction techniques. What is the difference between Bremstrahlung and characteristic X-rays. Which ones are used in your experiment and why.
2. In the apparatus section briefly describe the function of each component of the spectrometer- how are X-ray produced and detected in your experiment. Do not copy figures or procedures from the writeup. Discuss how you used the Si reference to

calibrate the θ axis for every sweep.

3. Display the data and analysis in neat compact figures including captions and legends. All the relevant parameters (instrumental settings) should be stated in the caption or legend. Make sure to include error bars on both axis when relevant. In the figures containing the measured spectra list the Miller indices for each peak.
4. Analysis of the data should be presented in close proximity to the relevant figure.
5. Discuss your results, including remarks about whether they support the theory, resolution, accuracy, sources of errors, etc.

In your report include the following:

- Show and discuss the calibration curve of the θ axis using the Si reference.
- Show the full spectra for Si and Cu (or Ni). Include labels of the Miller indices for each peak.
- Include tables listing for each observed peak the Miller indices, expected diffraction angle, observed angle with error bars, deviation from expected vale, and relative intensity. Do this for your Si reference, and the Cu/Si samples. Discuss the possible origin of unidentified peaks.
- For the Cu/Ni samples show the spectra for all the samples in one figure. Plot the measured lattice constant versus Cu concentration together with error bars and a line fit. Indicate the expected concentration separating magnetic and non-magnetic response and compare with your observation.
- For the various coins list the measured lattice constant with error bars, the calculated Cu concentration and compare to expected value. Show the spectra in the appendix.
- For the unknown sample show the spectrum together with the Miller indices obtained after identifying the material.

APPENDIX: Since you will need to frequently refer to them, the Appendices from Cullity are included in the supplementary material

REFERENCES:

1. B.D. Cullity: Elements of X-ray Diffraction, Addison-Wesley, Reading, Mass. 1978

2. D.W. Preston & E.R. Dietz: The Art of Experimental Physics, Wiley, 1991. Section 10, X-ray and Microwave Diffraction by Periodic Structures, Bragg Spectroscopy, pp 180-1952.

3. J. S. Blakemore, Solid State Physics; Saunders, 1969, pp 41,42