X-Ray Powder Diffraction

January 7, 2014

Introduction

In this lab, you will be analyzing four different materials using x-ray powder diffraction. X-ray diffraction is a very powerful tool for characterizing materials, and you will learn not just how to analyze x-ray spectra, but also the theory behind x-ray diffraction and how an x-ray powder diffractometer works. The x-ray diffraction machine is located in Professor Scott Oliver's lab in the Physical and Biological Sciences building. You will spend two lab periods taking data and the remainder of the lab analyzing the data and determining various properties of your materials. The programs JADE and FULLPROF will be useful in fitting your experimental data with a theoretical diffraction spectrum.

Theory of Diffraction

X-ray diffraction is the use of x-rays to determine the crystal structure, grain sizes, and chemical composition of materials. We first explain the simplest case, diffraction from a single crystal with monochromatic x-rays. More complex cases are the Laue method, which uses polychromatic x-rays to scatter from a single crystal, and powder diffraction, which uses monochromatic x-rays on many tiny crystals at once.

When a beam of monochromatic (same wavelength) x-rays strikes a single crystal at an angle satisfying Bragg's law, the x-rays are diffracted in a particular direction depending on the angle θ the incoming rays make with the lattice planes and the orientation of the crystal lattice. Think of a single photon coming in and striking the lattice. Since this photon is also a wave, it does not hit a particular atom in a lattice plane, but rather goes through the lattice plane while being affected by all of the atoms in the plane. This is much like throwing a pebble into a smooth pond and watching the ripples as they move through a line of trees standing in the water. In certain directions, the diffracted waves will interfere constructively and we will get a higher intensity of outgoing radiation. If we sweep a detector through all possible outgoing angles and record the radiation intensity, this constructive interference will show up as a high intensity peak corresponding to a particular angle 2θ. 2θ is the angle the incident x-ray makes with the outgoing x-ray.
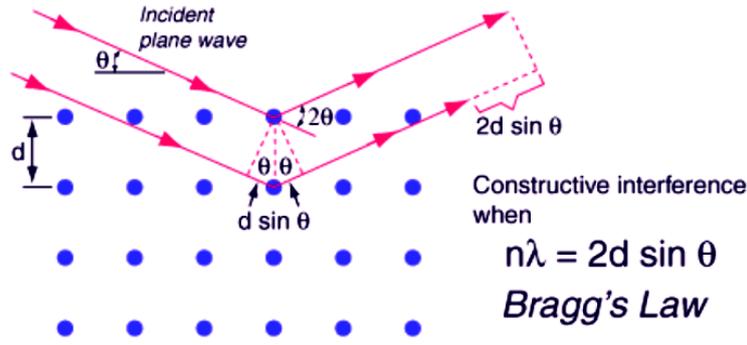
Figure 1: Bragg's law. Image taken from Ref. [1].

Using Bragg's law, we can relate this angle to the spacing, d, of the lattice planes in the crystal:

$$2d sin(\theta) = n\lambda. \tag{1}$$

Here, λ is the wavelength of the x-rays and n is an integer representing the order of reflection. Bragg's law states that there will be constructive interference when the distance $2d \sin(\theta)$ is an integer multiple of the wavelength. The familiar Bragg scattering diagram is shown in Fig. 1.

In addition to Eq. 1, Bragg's law has three more parts which are not often stated explicitly. Constructive interference in a three dimensional lattice only occurs under all four of these specific conditions.

1) $\theta_{out} = \theta_{in}$

The outgoing angle θ_{out} of the x-rays is equal to the incoming angle θ_{in}, where both angles are with respect to the lattice planes rather than the exterior face of the crystal. The angle 2θ used in the diffraction patterns assumes this explicitly.

2) Incident rays and outgoing rays are *coplanar* with the normal to the lattice plane. For example, in Fig. 1, the normal is pointing straight up along the page.

3) $E_{in} = E_{out}$

The incoming energy E_{in} is the same as the outgoing energy E_{out}. If there were a change in the photon's energy, the frequency of the outgoing wave would be different from that of the incoming wave, and constructive interference would not occur. Another way of saying this is that the magnitude of the momentum vector of the incoming ray is the same as that of the outgoing ray. Diffraction is an elastic process, which means that the diffracted photon neither gains energy from or loses energy to the lattice. However, in cases where we want to study atomic excitations or the motion of atoms in a lattice, we can use inelastic scattering and measure the difference between the incoming and outgoing wave vectors as a function of the change in energy of the scattering particle (usually a neutron or a photon).

2

Laue Diffraction

When diffracting from a single crystal with monochromatic radiation, in order to get diffraction peaks the crystal must be aligned very precisely with the beam. Although this is a sensitive and somewhat difficult process, we are rewarded with a strong, sharp, outgoing x-ray beam. One way to get around the crystal alignment, however, is to use many different (polychromatic) wavelengths. Since we are not calibrating the crystal to diffract at a specific wavelength, we do not need to align it with the incoming beam. At one incoming angle, each wavelength may "see" a different set of lattice planes and will diffract if the Bragg's law conditions are met for that particular wavelength. This is called Laue diffraction, after the German physicist Max von Laue.

Powder Diffraction

In contrast to the previous two methods, we will be diffracting *monochromatic* x-rays from a *powder* sample. The x-ray diffractometer you will be using is a powder diffractometer, which uses a sample that is crushed up into many tiny crystals. Ideally, all of these crystals are randomly oriented, so no matter the incident angle, some fraction of the tiny crystals will be aligned in a direction conducive to diffraction. Both the source x-ray beam and the detector move so as to cover the full range of 2θ. In powder diffraction, we compromise the intensity of the outgoing signal for convenience of sample preparation (it is much easier to obtain a material in powder form than it is to grow a single crystal). When diffracting from powders, we actually get a *cone* of outgoing rays instead of a single ray in one direction. This cone is centered along the direction of the incident ray and has an angular size of 2θ. This is because even for many different orientations of the same set of lattice planes, so long as the incident x-rays strike the planes at the same angle, the angle of the outgoing diffracted beam will be the same. However, since the outgoing beam must be coplanar with the incident beam *and* the normal to the lattice plane, the outgoing beam can lie anywhere along a cone. This can be somewhat tricky to visualize, and drawing a picture may help (ask your TA or instructor if you need further clarification). We place our detector so as to look at one particular direction along the cone, but our intensity is significantly reduced from single crystal diffraction as we are only looking at a small subset of the scattered rays.

You can see an example powder x-ray diffraction pattern in Fig. 2. The detector has swept through all outgoing angles and found peaks corresponding to the lattice spacings of this material. A range of $15^o \leq 2\theta \leq 85^o$ is usually sufficient to characterize a material with a relatively simple structure. Higher scattering angles will provide information on higher order reflections, but will tend to be weaker because there are greater effects from thermal fluctuations at these wavelengths.

In this experiment, you will be looking at materials with different space groups (which describe the symmetry of a crystal) and chemical compositions. In the literature, the space group is often given by a series of letters and numbers according to Hermann - Mauguin notation (*i.e.* $P4bm$ or $I\bar{4}c2$). Space groups are divided into 7 different types
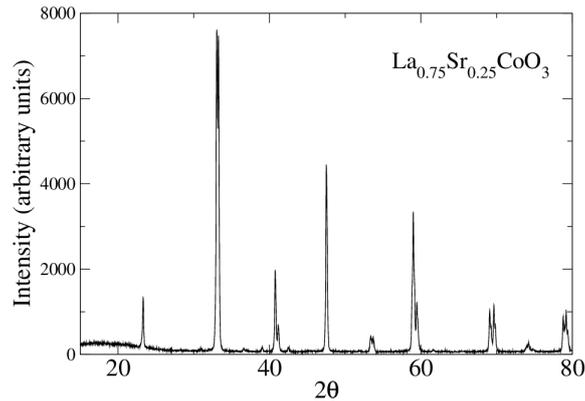
Figure 2: X-ray diffraction pattern of $La_{0.75}Sr_{0.25}CoO_3$, using a Cu $K\alpha_1$ wavelength of 1.54059. This scan was performed with a powder x-ray diffractometer at UC Davis.

of crystal classes: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic. Each crystal class can be subdivided into different types depending on the unit cell of the material. A unit cell is the simplest repeating unit in a crystal - for example, if your crystal were a Rubik's cube, the unit cell would be one of the little cubes making up the large cube [6]. Many materials have the cubic crystal class, which can be either simple/primitive cubic (atoms at all 8 corners of the cube), body-centered cubic (same as simple cubic, but with one more atom in the center of the cube), or face-centered cubic (same as simple cubic, but with one atom at the center of each face of the cube). Fig. 3 shows the different possible unit cells along with the space groups and their relative angles and side lengths.

Each space group gives a unique diffraction pattern, which is a great help when narrowing down the structure of unknown materials. The location of the peaks along the 2θ axis is of primary importance when identifying the space group. However, materials are not always ideal, and the space group can vary within the same material depending on such things as temperature or external pressure. For example, quartz has two phases at atmospheric pressure (101 kPa). At T $< 573^oC$, it is in α-quartz form ($P3_221$), which is trigonal, but once it is heated past 573^oC, it becomes β-quartz ($P6_222$), which is hexagonal. If quartz is placed under increased pressure (on the order of a few GPa), it becomes coesite, which has a monoclinic crystal structure ($C2/c$) [2]. The appearance of extra peaks in your diffraction pattern can indicate material of a different crystal structure, such as a different phase of your material, or unexpected impurities.

As explained in Pecharsky and Zavalij, section 1.14.1 [3], lattices can be seen as made up of sets of crystallographic planes, each parallel to one another and separated by a distance d. Each set contains all of the lattice points, but the absolute orientation of the planes varies between sets. We characterize a set by its d-spacing and the orientation of its planes, the latter of which is represented using the Miller indices h, k, and l. For systems with strictly 90° angles between their axes (i.e cubic, tetragonal, and orthorhombic), these indices are related to d and the magnitudes a, b, and c of the lattice
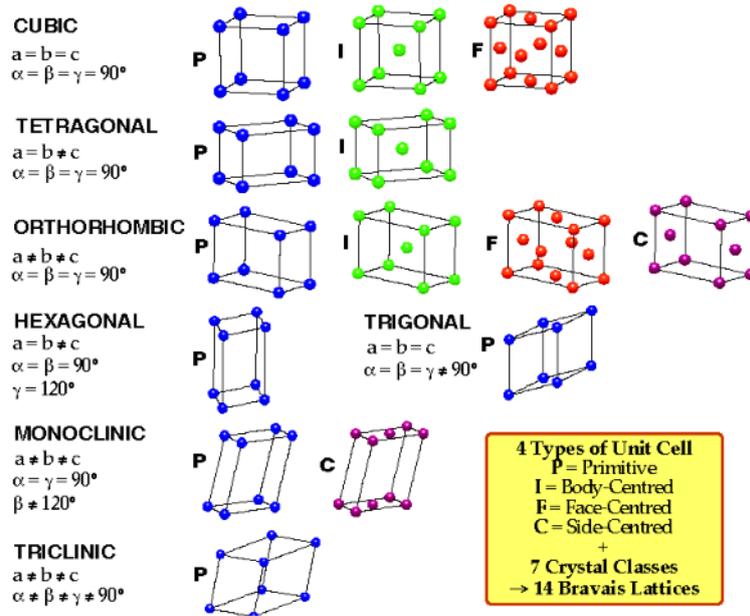
4

Figure 3: Drawings of the seven crystal classes, each with their possible unit cells (i.e. body centered cubic, simple cubic, and face centered cubic). a, b, and c are the lengths of different sides, and α, β, and γ are the different angles in the crystal structure. This graphic was taken from Ref. [4].
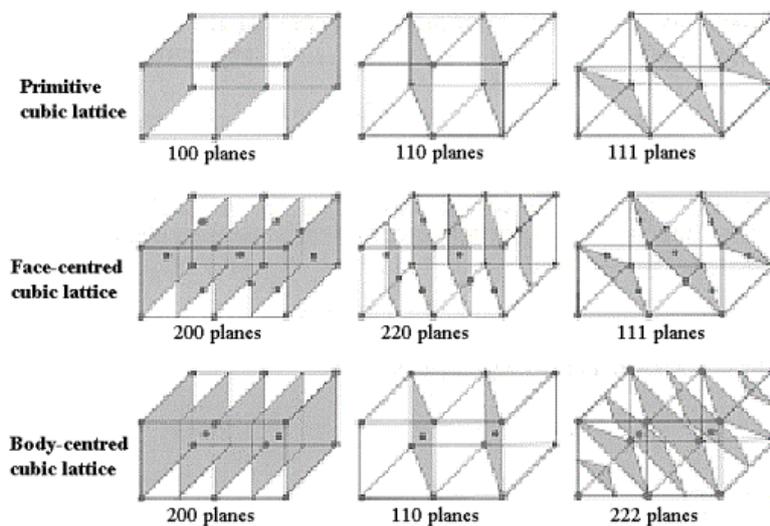

Figure 4: Illustration of the different Miller indices for cubic lattices. The lattice vectors lie along the edges of the rectangular prisms (note that these are not unit vectors in this image), with **a** going along the horizontal to the right, **b** pointing into the page, and **c** pointing towards the top of the page. This graphic was taken from Ref. [7].

vectors **a**, **b**, and **c** with the equation:

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

Here, we are using d_{hkl} to represent the d-spacing for a particular set of planes with a particular set of Miller indices. If we are looking at a system with angles other than 90° between their axes, the equation is modified to take the angles into account. Page 165 in Pecharsky and Zavalij shows the equations for d_{hkl} in each of the seven crystal classes. For a visualization of the lattice planes and an idea of where the lattice vectors point in cubic systems, see Fig. 4. You can think of the indices (hkl), as describing a plane with the points $\mathbf{a}/h$, $\mathbf{b}/k$, and $\mathbf{c}/l$ inscribed in it (an h, k, or l of 0 corresponds to a plane which is along the **a**, **b**, or **c** direction, respectively).

If we are faced with an unknown diffraction pattern, we can use Eq. 2 for d_{hkl} in combination with the Bragg equation (Eq. 1) to make a first stab at identifying the crystal system. We can take $n = 1$ in the Bragg equation, and calculate the d value for a diffraction peak at some θ (note that powder diffractometers put out data in terms of 2θ, so it will be necessary to divide the peak position by 2). We first test if our unknown could have a cubic crystal class ($a = b = c$), since it is the simplest to calculate. The first peak in the diffraction pattern has the smallest θ and hence the largest d of all the peaks, by Bragg's law (verify this for yourself). Our equation for d in terms of Miller indices is:

$$\frac{1}{d} = \frac{1}{a}\sqrt{h^2 + k^2 + l^2} \qquad (3)$$

The quantity $1/d$ will be the smallest for the first peak, so we can choose $(hkl) = (100)$ to minimize the right side of the equation (note that this is equivalent to choosing (010) or (001), as we are in a cubic system). The second peak would then have the second smallest quantity $1/d$, so we can choose $(hkl) = (110)$ for that peak. The lattice parameter a can be determined from Eq. 3, and we can use it to check if our predictions for the Miller indices are correct for all the peaks.

In the case where we do have a cubic crystal, the two main issues with this method are extra peaks and missing peaks. Extra peaks will most likely be due to impurities, and missing peaks will be due to peak *cancellation*. Although we may satisfy all of the Bragg conditions for diffraction, at some predicted diffraction angles we might still see nothing at all - in other words, the peak *intensity* is zero. This peak cancellation happens for certain lattice planes depending on the crystal structure [8]. If you are able to determine which peaks are cancelled in your diffraction pattern, it will help you narrow down the type of structure for an unknown sample (e.g. whether it is face-centered cubic or body-centered cubic).

The intensity, I_{hkl}, of a diffraction peak is directly proportional to the structure factor, $|F_{hkl}|^2$. The structure factor takes into account how the types and positions of the atoms in a material affect the scattering amplitude of the outgoing wave [3]. We can write the structure amplitude, $\mathbf{F}_{hkl}$, as:

$$\mathbf{F}_{hkl} = \sum_j \sum_m f_j \exp(-i\mathbf{K}_{hkl} \cdot \mathbf{r}_{jm}) \tag{4}$$

Here, f_j is called the atomic scattering factor, and depends on the type of atom (j) we are looking at. The sum over m is over each unique atomic position and will be clarified shortly. There are other factors in front of the exponential term in $\mathbf{F}_{hkl}$, but we will not consider them for simplicity's sake (see Pecharsky, page 204 for more information on this). $\mathbf{K}_{hkl}$ is the reciprocal lattice vector, which for a cubic lattice is [15]:

$$\mathbf{K}_{hkl} = \frac{2\pi}{a}(h\hat{x} + k\hat{y} + l\hat{z}) \tag{5}$$

The factor of $2\pi/a$ can be thought of as the "lattice parameter" in reciprocal space. The vectors $\mathbf{r}_{jm}$ represent the positions of the *basis atoms* of the unit cell. For a cubic crystal class, $\hat{x}, \hat{y},$ and $\hat{z}$ correspond to the $\hat{a}, \hat{b},$ and $\hat{c}$ directions. For example, a body-centered cubic lattice will have the basis vectors $\mathbf{r}_{j0} = 0\hat{x} + 0\hat{y} + 0\hat{z}$ (for the atom on the corner of the cube) and $\mathbf{r}_{j1} = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})$ (for the atom in the middle of the cube). These two vectors, translated infinitely, will give a bcc lattice. Note that these vectors are NOT the same basis vectors as the ones in linear algebra which span a space.

We can now plug in the $\mathbf{K}_{hkl}$ and $\mathbf{r}_{jm}$ vectors into Eq. 4, and calculate the dot product. For the bcc lattice made entirely of one element, we end up with:

$$\mathbf{F}_{hkl} = f_j[1 + \exp(-i\pi(h + k + l))] \tag{6}$$

Keeping in mind that $e^{-i\pi} = -1$, we can see that $\mathbf{F}_{hkl}$ will be 0 if the sum $h + k + l$ is odd, and 2 if the sum is even. Therefore, any peaks with (hkl) indices which add up to 0 will not show up in the diffraction pattern (their intensity, I_{hkl}, will be 0). Note that if we have a unit cell made of two or more types of atoms - for example, Element A sitting at $\mathbf{r}_{A0}$ and Element B at $\mathbf{r}_{B1}$, this cancellation will not likely take place due to the f_j being different for each type.

The allowed (hkl) values for non-zero intensity are called the **extinction rules** for a particular lattice. For a more complete set of rules, see Ref. [9]. One of the samples you will be investigating, silicon, is a good example of a material with peak cancellation.

The atomic scattering factor, f_j, depends on the number of electrons in the atom, as x-rays scatter predominantly from electrons rather than nuclei. Elements with a larger number of electrons tend to scatter x-rays more effectively. Note that for neutrons, f_j will be different because neutrons scatter predominantly from the nuclei. As in page 213 of Ref. [3], the x-ray scattering factor f_j is often written as a function of $sin(\theta)/\lambda$, where θ is the Bragg angle and λ is the wavelength of the incoming x-rays:

$$f_j(sin(\theta)/\lambda) = c_0 + \sum_{i=1}^{4} a_i \exp(-b_i sin(\theta)/\lambda) \tag{7}$$

Here, the coefficients c_0, a_i, and b_i vary depending on the element we are looking at. The point to note is that when $sin(\theta)/\lambda = 0$ (forward scattering), f_j is simply the sum

of the coefficients, which is the number of electrons in the atom. As the ratio $sin(\theta)/\lambda$ increases, f_j decreases.

f_j also depends on the radial and angular *distribution* of the electrons about the nucleus. However, this anisotropy is usually a very small effect [3]. The effects of f_j are quite noticeable if we have two different materials with the same space group but different atoms. For example, in NaCl, Na^+ has 10 electrons and Cl^- has 18 electrons, so their f_j's will not cancel according to the extinction rules. The closely related compound KCl, where both K^+ and Cl^- have 18 electrons, will show almost complete cancellation of the (111) peak because the f_j's are so similar. If we had a hypothetical lattice where we replaced all of the K^+ and Cl^- atoms with Ar, we would see complete cancellation because the f_j's would be identical. Another consequence of having K^+ instead of Na^+ is that the lattice parameter is larger, since K^+ has more electrons and hence takes up more room.

As can be seen from the previous discussions, the intensity of the diffraction peaks is of great importance when characterizing a material. It is difficult to analyze, however, as many different things affect the relative and the overall peak intensity. Crystal structure affects relative peak intensity - if there are a high number of lattice planes which have the same periodicity (d), the corresponding Bragg peak will be much larger. An artificial effect which can happen in powder samples is "preferred orientation": if the tiny crystals being examined are not completely randomly oriented, then they will show a higher intensity for certain incoming x-ray angles and a lower one for certain others [3].

The overall peak intensity can be affected by the amount and type of sample you have. That is, if you have a strongly absorbing sample, the x-rays will be absorbed rather than reflected and the x-ray peaks will have a lower intensity. If you have very little of a sample which is not particularly absorbing, the x-rays will be transmitted through the sample, again leading to lower intensity. Overall intensity can also be reduced by strain on the material, which is a problem particularly in samples with small grain sizes. If the lattice is strained, d can vary over a range of values for the same set of planes, leading to shorter, wider diffraction peaks.

The X-Ray Diffractometer

The machine you will be using for most of your x-ray diffraction measurements is a Rigaku Miniflex powder diffractometer. A schematic can be seen in Fig. 5. One can think of an x-ray diffractometer as having three main parts: 1) the x-ray generator and focusing apparatus (collimator and monochromator), 2) the goniometer, a rotating plate upon which the sample sits, and 3) the detector (counter) and filtering apparatus.

The x-ray generator consists of an x-ray tube subjected to a high voltage, in this case 30 kV. The x-ray tube has a tungsten filament at one end which emits electrons when heated, and an anode at the other end which collects electrons accelerated by the high voltage. The anode is usually made of copper, but can also be made of other materials. Copper is preferred because it has a high thermal conductivity and a high melting point (to withstand the temperature from the high voltage), as well as emitting a high intensity wavelength close to 1 Å.
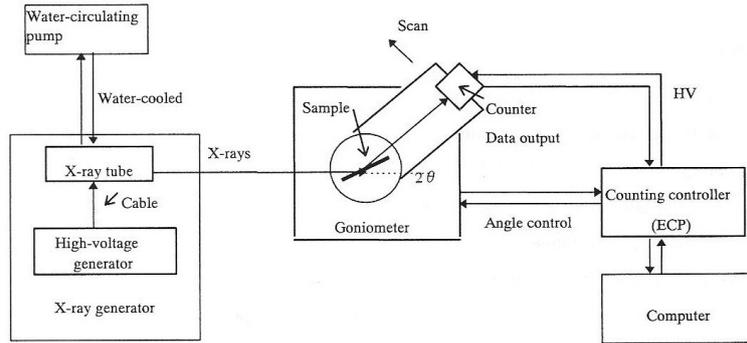
Figure 5: A block diagram of the Rigaku Miniflex desktop diffractometer as seen in the instruction manual [5].

Exercise: Why is 1 Å an ideal wavelength for x-rays scattering off a lattice?

When energetic electrons bombard the Cu anode, they knock out the core (K-shell) electrons from the Cu atoms. Electrons from the outer energy shells then drop down to fill the K-shell vacancies, and in doing so emit x-rays with a characteristic wavelength. For copper, when an electron from the next shell up (L-shell) drops down, it emits x-rays with wavelengths of either 1.54059 Å (called $K\alpha_1$ radiation) or 1.54441 Å ($K\alpha_2$). Whether it is $K\alpha_1$ or $K\alpha_2$ depends on which of the two L electrons drops, as they are at slightly different energies based on their spins relative to their orbital motion. When an electron from the third shell up (M-shell) drops down, the characteristic wavelength emitted is 1.39225 Å ($K\beta$). The characteristic wavelengths are very intense compared to the background radiation, as can be seen in Fig. 6. The background intensity is called "Bremsstrahlung," which is German for "braking radiation." Bremsstrahlung is when an incoming electron is deflected by an atomic nucleus and loses energy in the form of gamma radiation. Since the energy loss can be any amount, the radiation produced has a large range of wavelengths - hence the broad background. Bremsstrahlung is useful for Laue diffraction, which requires polychromatic x-rays.

X-rays are emitted from the anode isotropically, and exit the tube via beryllium windows (usually four) placed at intervals around the anode. We can narrow down, or "collimate" the beam by putting a slit in between the x-ray beam and the sample, which blocks out most of the radiation in any direction other than directly towards the sample.

As you may recall from the previous section, the powder diffractometer requires a single wavelength. In this case, we want the most intense characteristic wavelengths, Cu $K\alpha_1$ and $K\alpha_2$. How do we filter out all of the extra radiation to get the cleanest possible signal? We can use a monochromator, either a β-filter or crystal type, placed in between the x-ray tube and the sample. A β-filter monochromator filters out radiation by absorbing wavelengths below a certain value. The amount of absorption is denoted with the linear absorption coefficient μ, which is a function of the wavelength λ. Conveniently, the continuous parts of μ are more or less proportional to $Z^3\lambda^3$, where Z is the atomic number [3]. A plot of the absorption of nickel can be seen in Fig. 7. The discontinuity
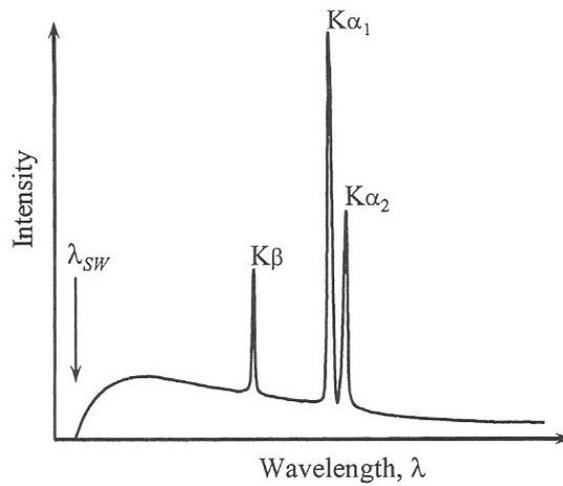
Figure 6: The emission spectrum of an anode material such as Cu. $K\alpha_1$, $K\alpha_2$, and $K\beta$ are the intense characteristic wavelengths, and λ_{SW} is the minimum possible wavelength. The broad background intensity is Bremsstrahlung. Image taken from Ref. [3].
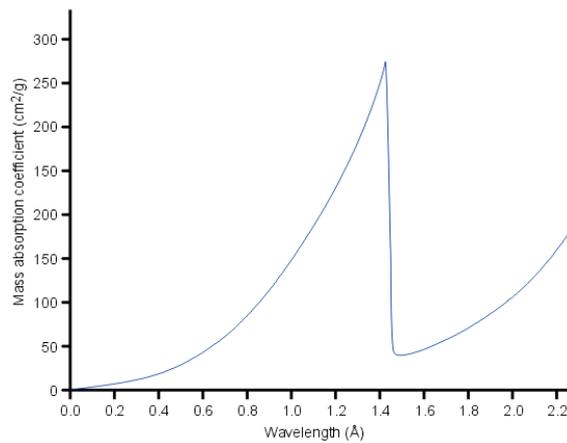

Figure 7: A plot of x-ray absorption for nickel metal, with the K-edge at $\lambda = 1.488$ Å. Note that this shows the mass absorption coefficient, which we will call μ_m (cm^2/gm), instead of the linear absorption coefficient, μ (cm^{-1}). The mass absorption coefficient is simply $\mu_m = \mu/\rho$, where ρ is the density in gm/cm^3 of the material. This image was taken from Ref. [14].

10

at λ = 1.488 Å is referred to as the "K-absorption edge", and will be at different wavelengths depending on Z. If an incoming photon has this particular λ, it will have just enough energy to excite the K shell electrons of nickel, and so will have a high absorption rate. (Remember that the amount of energy an x-ray has is inversely proportional to its wavelength). The higher energy wavelengths to the left of the K-edge are also more likely to be absorbed. As Z increases, the K-shell electrons are more tightly bound, and the location of the K-edge moves to shorter wavelengths. If we choose a filter with a Z that is one less than our anode material, we obtain an edge whose wavelength is above the $K\beta$ line and below the $K\alpha$ lines - effectively filtering out most of the $K\beta$ and higher energy Bremsstrahlung radiation. Since the Rigaku Miniflex diffractometer has a Cu anode, we use a Ni β-filter.

Were the absorption coefficient a perfect step function which eliminated all radiation with energy greater than or equal to the K-edge while keeping the radiation with lower energies at maximum intensity, we would be quite happy with a β-filter. However, this is not the case, and β-filters still leave some of the $K\beta$ line and much of the Bremsstrahlung at lower energies, as well as attenuate the $K\alpha$ lines significantly. Fortunately, if we need high quality data, we can invest in a crystal monochromator, which is a single crystal positioned so as to pick out a single wavelength. A crystal monochromator diffracts only those incoming x-rays which satisfy the Bragg conditions. Placed in the correct orientation, it will "choose" the desired Cu $K\alpha$ wavelength - all other wavelengths will be effectively blocked. We can also place the monochromator between the diffracted x-rays and the detector, with the same effect. *Exercise: Should whether the monochromator is placed before or after the diffracted sample x-rays affect the data? Why or why not?* Monochromators can be crystals of pyrolitic graphite, silicon, or germanium, to name a few [3]. In this way, we eliminate all radiation apart from the $K\alpha_1$ line (though we pay a price in the intensity of the line, as the crystal is not perfectly reflecting). We can also bend the monochromator crystal slightly such that it focuses the outgoing beam more precisely onto the sample. The Rigaku Miniflex is a simple tabletop diffractometer, so it does not have a monochromator - the Ni β-filter suffices for its purposes. The Oliver lab has a much larger and fancier x-ray diffractometer as well, which does have a monochromator.

All of this initial monochromatization is somewhat wasted, however, if we do not take into account another possible source of unwanted radiation - the sample itself! Remember how we used a Ni filter to absorb the $K\beta$ radiation from our Cu anode? Once it absorbs the radiation, the Ni will also fluoresce; that is, its K shell electrons will be knocked out, and when the L and M electrons drop down to fill the vacancies, they will emit photons. Fortunately, the fluorescence from the Ni only adds a small background to our diffraction pattern, as the radiation is emitted isotropically from the filter and only a small fraction of it strikes the sample. The very same fluorescence effect can happen if our sample contains an element which absorbs the Cu $K\alpha$ radiation, such as Co or Fe. The absorption edges of Co and Fe are at 1.608 and 1.74 Å, respectively [3, 12]. These K edges are only slightly higher than the Cu $K\alpha$ lines at around 1.54 Å, and if you refer back to Figure 7 you can see that the absorption coefficient is highest at wavelengths slightly below the K edge. The x-ray fluorescence which results from

these samples absorbing the Cu radiation is a problem, because the x-rays are emitted isotropically from the sample and some make it to the detector. This adds a large, broad background to the diffraction pattern, obscuring smaller diffraction peaks and making it difficult to characterize the sample. One of the samples you will run on the machine is Co_3O_4, so you can see the x-ray fluorescence effect first-hand. If we want to look at samples containing Fe or Co, we can simply swap the anode material with something that has the $K\alpha$ lines at a different location (e.g. molybdenum). Alternately, we can place a monochromator right before the x-rays hit the detector and after they've gone through the sample. This will filter out the extra radiation that does not correspond exactly to the Cu $K\alpha$ wavelengths, and hence significantly reduce the background.

The powder samples for your experiment will be placed in round aluminum sample holders, which can then be loaded into the diffractometer. The Rigaku Miniflex can take multiple samples at once on a rotating goniometer, so there is no need to open up the sample chamber between experiments. The sample is placed in the path of the collimated x-ray beam, and the detector (labeled as a counter in Fig.5) moves along a semi-circular path around the sample to detect outgoing x-rays at various angles 2θ. The goniometer can also tilt along the same axis as the detector, which increases the number of angles that can be observed.

The detector for the Rigaku Miniflex consists of a NaI crystal scintillator with a Be window facing the sample x-rays. As described in Ref. [3], incoming radiation is absorbed by the crystal, which then generates light of a particular wavelength (in this case blue). The blue photons then go into a photomultiplier tube, where they are converted into electrons, resulting in voltage pulses that are recorded as counts. A large number of counts results in a high intensity peak in the diffraction spectrum.

Samples and Analysis

In this experiment, you will be examining 5 different materials using x-ray powder diffraction. Save all of the scans as text files, plot them with your preferred plotting program, and place them in your lab report. Be sure to record all of the specifics of each scan (range, step size, etc.) so that your data are reproducible. You can obtain a crystallographic information file (.cif) from JADE or from the ICSD online database (go to the website in Ref. [16] and click on "Chemistry" under "Advanced Search and Retrieve" on the left hand side to search for a material). A .cif file provides the lattice parameters, atomic positions, and space group (among other things) for a material. You can use it with the free program VESTA to get a neat visualization of the atoms in a material.

If you want to go further with your x-ray analysis, you can download the program FULLPROF and manually refine your data. FULLPROF uses a method called Rietveld refinement to fit the data very closely with a theoretical pattern. It allows you to account for things such as peak widths (as in the case of nanoparticles), temperature factors (atomic positions varying slightly due to temperature), and samples with unusual stoichiometry (e.g. if one atomic position can be occupied by different atoms), to name a few. Most, if not all, scientific articles with x-ray or neutron diffraction data use

Rietveld refinement to characterize their samples, and it is a very important technique for scientists.

When you go to the Oliver lab to perform your scans, please remember that it is a chemistry lab and that you must have proper clothing and protective equipment on at all times. This means: long pants, close-toed shoes, a lab coat, gloves, and safety glasses. We can provide the last three for you (though if you have your own safety glasses, those are preferable).

1. Aluminum sample holder

The sample holders for the Rigaku Miniflex diffractometer are made out of aluminum, and it is important to know the diffraction pattern in order to subtract it out of your later measurements. This is a test run for you to figure out the range of 2θ to scan, the step size in degrees, and the length of time to spend on each step (more time means a higher intensity). Determine values which seem reasonable, then check with your TA or instructor to make sure you are on the right track. Once you have finished with the scan, use the program JADE on the computer near the x-ray machine to determine the unit cell, space group, and the lattice parameters (a, b, and c) of Al. JADE can label each of the peaks with Miller indices - make sure you understand what these mean and how they are calculated. Are there any extra or missing peaks in the Al diffraction pattern? If so, point them out and attempt to identify them (this is not always possible!). Does this Al have any preferred orientation? Why or why not? Keep in mind the background level and intensity of the Al spectrum when you run your other samples; can you think of why Al is used for the sample holders instead of a different material?

2. Silicon

Grind up some of the silicon (Si) powder, place it into an aluminum sample holder, and run a scan on the x-ray diffractometer. Si is an extremely important semiconductor in technology today, and its crystal structure is well known. Note that because Si has a face centered cubic structure and only contains one element, several of its peaks cancel. You may also see Si being referred to as having the "diamond" structure, because it is an fcc structure with extra atoms inside the unit cell. If you use FullProf to refine this sample, note that you must use Fd-3m:1 as the space group (instead of Fd-3m) in order to account for this basis. Keeping this in mind, go through the structure factor ($\mathbf{F}_{hkl}$) calculation for Si and find which peaks cancel. This will be slightly different from the fcc calculation, as you have to take into account the 4 extra basis atoms in the unit cell (see Fig. 8). You can look online to find the position vectors of these atoms. What are the extinction rules for the Si lattice? Label the Miller indices of the x-ray diffraction peaks. Then, calculate the lattice constant a and the d-spacing d using Eq. 3 and Bragg's law. Compare your result for a to a value found by other researchers (i.e. check ICSD).

3. Sodium chloride (salt)

Run a scan with table salt (NaCl) as your sample. Since salt crystals are relatively large, you will need to crush the salt up into a fine powder using a mortar and pestle.
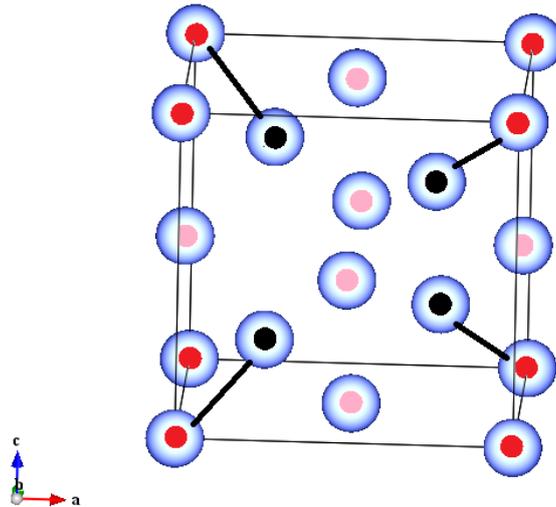
Figure 8: The unit cell of silicon. The fcc lattice is all of the atoms on the corners and faces (red and pink), and the four basis atoms are in black.

NaCl is a face centered cubic (fcc) lattice. However, you can also think of it as two interpenetrating fcc lattices, one with strictly Na^+ ions, and the other with strictly Cl^- ions [8]. Calculate the lattice constant for NaCl and the Miller indices and d-spacing for the peaks. Do any of the NaCl peaks cancel?

4. Cobalt(II, III) oxide

Run a scan with powdered cobalt oxide (Co_3O_4) as your sample and use JADE or FULLPROF/ICSD to characterize the sample. Do you notice anything unusual about the background for this material as compared to your other materials? What is a possible explanation for this? *(Hint: Refer back to the section on X-ray fluorescence).* How might you reduce this background (besides changing the anode)? Run this sample on the larger, fancier X-ray machine in the Oliver lab. How do the scans from each machine differ? Why?

5. Unknown

Run a scan with the unknown sample provided to you by your TA. Characterize it as well you can (lattice constant, Miller indices, d-spacing, type of structure), and see if you can identify or at least narrow down what it could be. *Hint: This material is very similar to one of the other materials you have examined. The first peak is (111) and has a low intensity.*

Appendix

FullProf

To download FullProf, go to *http://www.ill.eu/sites/fullprof/* and go to "Downloads." Download the version of FullProf corresponding to your operating system and follow the instructions on the website. Once FullProf is installed, you will be able to open the FullProf suite, which gives you a narrow window with a bunch of different programs. "ED-PCR" is the program we will use to edit and refine our data files, and "WinPlotr" is the program we will use to view the data files/refinement results, and which provides a text file containing the data, theoretical fit, and difference plot for the refinement (so you can use a different plotting program if you want to tweak the graph). See the addendum: "A Short Guide to FullProf" for an in-depth description on how to run a refinement.

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