

Xray Diffraction and Absorption

Experiment XDA

University of Florida — Department of Physics
PHY4803L — Advanced Physics Laboratory

Objective

You will investigate the diffraction of xrays from crystalline samples and the absorption of xrays passing through metal foils. Diffraction patterns show sharp maxima (peaks) at characteristic angles that depend on the wavelength of the xrays and the structure and orientation of the crystal. Absorption edges appear at xray energies that depend on the atomic number of the foil material. A Geiger-Müller tube is used to detect the xrays as the scattering angle is varied.

References

Generally look in the QC481 and QD945 sections.

A. H. Compton and S. K. Allison, *Xrays in Theory and Experiment*

C. Kittel, *Introduction to Solid State Physics*

B. D. Cullity, *Elements of Xray Diffraction*

Teltron manual, *The Production, Properties, and Uses of Xrays*

Xray Emission and Absorption

When an electron beam of energy around 20 keV strikes a metal target, two different processes produce xrays. In one process, the

deceleration of beam electrons from collisions with the target produces a broad continuum of radiation called *bremstrahlung* (braking radiation) having a short wavelength limit that arises because the energy of the photon hc/λ can be no larger than the kinetic energy of the electron. In the other process, beam electrons knock atomic electrons in the target out of inner shells. When electrons from higher shells fall into the vacant inner shells, a series of discrete xrays lines characteristic of the target material are emitted.

In our machine, which has a copper target, only two emission lines are of appreciable intensity. Copper K_α xrays ($\lambda = 0.1542$ nm) are produced when an $n = 2$ electron makes a transition to a vacancy in the $n = 1$ shell. A weaker K_β xray with a shorter wavelength ($\lambda = 0.1392$ nm) occurs when the vacancy is filled by an $n = 3$ electron.

The reverse process of xray absorption by an atom also occurs if the xray has either an energy exactly equal to the energy difference between an energy level occupied by an atomic electron and a vacant upper energy level, or an energy sufficient to eject the atomic electron (ionization). For the xray energies and metals considered in this experiment, the ionization of a K -shell electron is the dominant mechanism when the xray energy is high enough, which leads to the absorption of the initial xray photon and the ejection of an electron—a

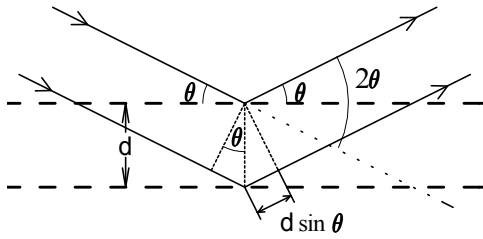


Figure 1: The ray reflected from the second plane must travel an extra distance $2d \sin \theta$.

process known as the *photoelectric effect*). If an xray does not have enough energy to cause a transition or to ionize an atom, the only available energy loss mechanism is Compton scattering from free electrons.

The Xray Diffractometer

Thus, the spectrum of xrays from an xray tube consists of the discrete lines superimposed on the bremsstrahlung continuum. This spectrum can be analyzed in much the same way that a visible spectrum is analyzed using a grating. Because xrays have much smaller wavelengths than visible light, the grating spacing must be much smaller. A single crystal with its regularly spaced, parallel planes of atoms is often used as a grating for xray spectroscopy.

The incident xray wave is reflected specularly (mirror-like) as it leaves the crystal planes, but most of the wave energy continues through to subsequent planes where additional reflected waves are produced. Then, as shown in the ray diagram of Fig. 1 where the plane spacing is denoted d , the path length difference for waves reflected from successive planes is $2d \sin \theta$. Note that the scattering angle (the angle between the original and outgoing rays) is 2θ .

Constructive interference of the reflected

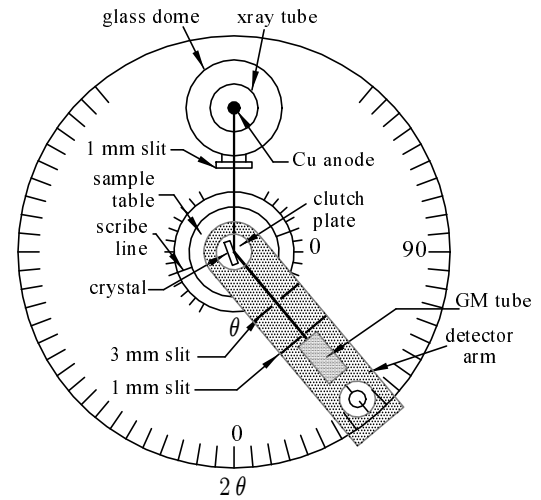


Figure 2: The xray diffractometer apparatus.

waves occurs when this distance is an integral of the wavelength. The *Bragg condition* for the angles of the diffraction peaks is thus:

$$n\lambda = 2d \sin \theta \quad (1)$$

where n is an integer called the order of diffraction. Note also that the lattice planes, i.e., the crystal, must be properly oriented for the reflection to occur. This aspect of xray diffraction is sometimes used to orient single crystals and determine crystal axes.

Our apparatus is shown schematically in Fig. 2. The xrays from the tube are collimated to a fine beam (thick line) and reflect from the crystal placed on the sample table. The detector, a Geiger-Müller (GM) tube, is placed behind collimating slits on the detector arm which can be placed at various scattering angles 2θ . In order to obey the Bragg condition, the crystal must rotate to an angle θ when the detector is at an angle 2θ . This $\theta : 2\theta$ relationship is maintained by gears under the sample table.

Assuming d is known (from tables of crystal spacings), the wavelength λ of xrays detected at a scattering angle 2θ can be obtained from

Eq. 1.

Powder Diffraction

An ideal crystal is an infinite, 3-dimensional, periodic array of identical structural units. The periodic array is called the *lattice*. Each point in this array is called a *lattice point*. The structural unit—a grouping of atoms or molecules—attached to each lattice point is called the *basis* and is identical in composition, arrangement, and orientation. A crystal thus consists of a basis of atoms at each lattice point. This can be expressed:

$$\text{lattice} + \text{basis} = \text{crystal} \quad (2)$$

The general theoretical treatment for the determination of the diffracted x-rays—their angles and intensities—was first derived by Laue. Starting with Huygens' principal, it involves constructions such as the Fourier transform of the crystal's electron distribution and develops the concept of the reciprocal lattice. The interested student is encouraged to explore the Laue treatment. (See *Introduction to Solid State Physics*, by Charles Kittel.) However, we will only explore crystals that can be described with a cubic lattice for which a simpler treatment is sufficient.

There are three types of cubic lattices: the simple cubic (sc), the body-centered cubic (bcc) and the face-centered cubic (fcc). The simple cubic has lattice points equally spaced on a three dimensional Cartesian grid as shown by the dots in Fig. 3. As a viewing aid the lattice points are connected by lines showing the cubic nature of the lattice.

The body-centered cubic lattice has lattice points at the same positions as those of the sc lattice and additional lattice points at the center of each unit cube defined by the grid. The face-centered cubic lattice also has lattice points at the same positions as those of the

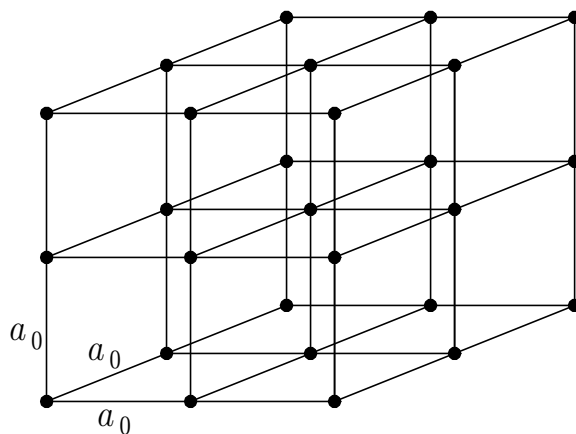


Figure 3: The simple cubic lattice points (dots) and connecting lines showing the cubic structure.

sc lattice but it has additional lattice points at the center of each unit square (cube face) defined by the grid.

A *primitive unit cell* is a volume containing a single lattice point that when suitably arrayed at each lattice point completely fills all space. The number of atoms in a primitive unit cell is thus equal to the number of atoms in the basis. (There are many ways of choosing a primitive unit cell.) The primitive unit cell for the sc lattice is most conveniently taken as a cube of side a_0 . a_0 is called the lattice spacing or lattice constant.

The bcc and fcc primitive unit cells (rhombohedra) will not be used. Instead, bcc and fcc crystals will be treated using the sc lattice and sc unit cell (which would then not be primitive).

A crystal is completely described by specifying the lattice (sc, bcc, or fcc) and the position of each atom in the basis relative to a single lattice point. For the sc lattice, the basis atom positions are specified by their relative Cartesian coordinates (u, v, w) within the sc unit cell. u , v , and w are given in units of the lattice spacing a_0 , so that, for example, the

body-centered position would be described by the relative coordinates $(u, v, w) = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

When a sc lattice is used to describe a bcc or fcc crystal, one still specifies the position of atoms using relative coordinates (u, v, w) . But all atoms within the sc unit cell must be given—including the extra basis atoms that would occur at the body-centered or face-centered positions, respectively.

If the unit cell is taken so that its corners are at lattice points, each corner lattice point is shared among the eight cells that meet at that corner. In order to avoid having lattice points shared among different unit cells, the corner of the cell is usually given an infinitesimal backward displacement in all three directions so that of all the eight corner lattice points $(0, 0, 0)$, $(0, 0, 1)$, ..., $(1, 1, 1)$, only the $(0, 0, 0)$ site remains in the cell. Then, for example, the bcc lattice—with lattice points at the corners and the body center of the sc unit cell—would be described as having lattice points only at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ within each “pulled-back” unit cell.

Exercise 1 Use a drawing to show that the fcc lattice—with lattice points at the corners and face centers of the sc cell—would be described as having lattice points at $(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, 0)$; $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$ in the “pulled-back” unit cell.

A simple cubic crystal with a one-atom basis has an infinite number of atomic plane sets, though different sets have different spacings. There is an obvious set of planes separated by a_0 , passing through opposite faces of the unit cell. There is also a set of equally spaced planes separated by $d = a_0/\sqrt{2}$, turned 45° from the planes along the cube faces and passing through opposite edges of the cube. There should also be constructive interference for reflection angles given by Eq. 1 with this d . It turns out that the spacings for all possible lat-

tice planes in the sc lattice can be represented by

$$d(hkl) = n \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad (3)$$

where hkl are integers—called the Miller indices and n is an integer. Together with Eq. 1 this leads to the Bragg scattering relation giving the angular position of the Bragg peaks

$$\lambda = \frac{2a_0}{\sqrt{h^2 + k^2 + l^2}} \sin \theta. \quad (4)$$

The Miller indices are used to classify the possible reflections as shown in Fig. 4. For $hkl = 100$, we speak of the 100 (*one-zero-zero*) reflection, which is from the 100 planes, i.e., the planes along the cube faces. The 200 reflection, ($hkl = 200$) is from the 200 planes which are the 100 planes and an additional set midway between. (It can be considered the 100 planes with $n=2$ in Eq. 1.) The 110 reflections are from the 110 planes through opposite edges of the cube, and so on.

Not all reflections are of equal intensity. As hkl get large, the density of atoms in each plane decreases and the corresponding peak gets weaker. For plane spacings smaller than $\lambda/2$, the formula gives $\sin \theta > 1$, and these reflections cannot occur. Most importantly, as in the case of the bcc or fcc lattices, or when there is more than one atom in the basis, the additional atoms can cause reflections which can contribute either constructively or destructively to the reflection.

The position of each atom j in the unit cell can be described by its relative coordinates u_j, v_j, w_j . Then, the angular position of the Bragg peaks is still described by Eq. 4. However, because of the scattering sites within each cell, the intensity of the peak will be proportional to the square of the magnitude of the *crystal structure factor* $F(hkl)$:

$$F(hkl) = \sum_j f_j e^{2\pi i(hu_j + kv_j + lw_j)} \quad (5)$$

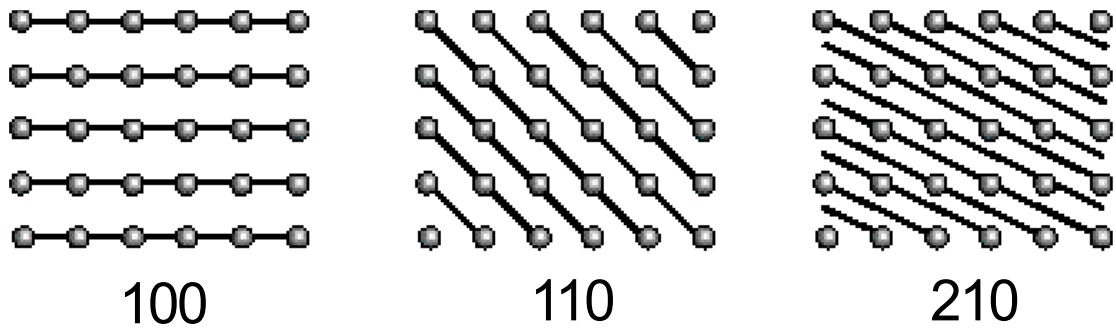


Figure 4: Top view of three possible sets of planes in the simple cubic lattice with their Miller indices.

where the sum extends over all atoms in a single unit cell. For certain hkl , this factor may be zero and the corresponding Bragg peak will be missing.

The *atomic form factor* f_j above depends on the type of atom at the site u_j, v_j, w_j . It also varies with θ . For $\theta = 0$, it is approximately proportional to the number of electrons in the atom. For larger reflection angles, it decreases due to interference effects of scattering from different parts of the atom. Determining f as a function of θ from measurements of intensities in the Bragg peaks is possible, but difficult because the apparatus collection efficiency usually also depends on the scattering angle.

Nonetheless, qualitative information is obtainable from the intensity of the Bragg peaks. Consider the CsCl structure. It has a simple cubic lattice structure and a basis of two atoms. One atom, say Cs, can be considered at the corners of the sc unit cell $(0, 0, 0)$ and the other, say Cl, will then be at the body centered positions $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The 100 reflection corresponds to waves reflected from adjacent 100 planes of Cs atoms having a path length difference of λ . This reflection should now be reduced in intensity due to reflections from the mid-planes of Cl atoms which would be in phase with one another but out of phase

with the reflections from the Cs planes. This may be verified from Eq. 5.

$$F(100) = f_{\text{Cs}} - f_{\text{Cl}}$$

While for a 200 reflection

$$F(200) = f_{\text{Cs}} + f_{\text{Cl}}$$

In this case, the pathlength difference for the Cs planes is 2λ , and for the Cl planes, it is λ . Thus, the reflections from each kind of plane are in phase.

In fact, the CsCl structure factor for the general (hkl) is

$$F(hkl) = f_{\text{Cs}} + f_{\text{Cl}}e^{i\pi(h+k+l)} \quad (6)$$

and gives $f_{\text{Cs}} + f_{\text{Cl}}$ when $h + k + l$ is even and $f_{\text{Cs}} - f_{\text{Cl}}$ when $h + k + l$ is odd. Thus, one might expect that superimposed on a gradual reduction in peak intensities as the scattering angle increases, the spectrum would show that peaks for which $h + k + l$ is even are larger than those for which $h + k + l$ is odd.

Consider next a body-centered cubic crystal with a single atom basis. Using the sc unit cell we would have to include one atom at the sc lattice site $(0, 0, 0)$ and an identical atom at the body-centered site $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The crystal structure factor becomes:

$$F_{\text{bcc}}(hkl) = f(1 + e^{i\pi(h+k+l)}) \quad (7)$$

which shows that the crystal structure factor for the bcc lattice is non-zero (and equals $2f$) only if $h + k + l$ is even. Thus peaks with $h + k + l$ odd would be entirely missing.

Exercise 2 Show that the crystal structure factor for a crystal with the fcc lattice type and a one atom basis is given by:

$$F_{\text{fcc}}(hkl) = f(1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}) \quad (8)$$

Then use this result to show that F_{fcc} is zero unless hkl are all even or all odd.

Next consider the class of crystals having the NaCl structure. NaCl has an fcc lattice structure with a two-atom basis. Putting the Na atoms at the normal fcc sites of the sc cell—the corners and the face centers—the Cl atoms will be at the body-centered position and at the midpoint of each edge of the cell. The relative coordinates in the sc unit cell are

$$\text{Na: } 0,0,0; \frac{1}{2},\frac{1}{2},0; \frac{1}{2},0,\frac{1}{2}; 0,\frac{1}{2},\frac{1}{2}$$

$$\text{Cl: } \frac{1}{2},0,0; 0,\frac{1}{2},0; 0,0,\frac{1}{2}; \frac{1}{2},\frac{1}{2},\frac{1}{2}$$

Exercise 3 Evaluate the crystal structure factor for the NaCl crystal. Show that F is still zero unless hkl are all even or all odd and give the structure factor in terms of the atomic form factors f_{Cl} and f_{Na} .

While there are no simple cubic crystals with a one-atom basis in nature, the potassium chloride (KCl) crystal behaves nearly so. Potassium chloride has the NaCl structure with the potassium having atomic number 19 and the chlorine having atomic number 17. However, because of the ionic bonding, each atomic site has roughly the same number of electrons (18) and scatter xrays nearly equally well, i.e., have nearly the same atomic form factors.

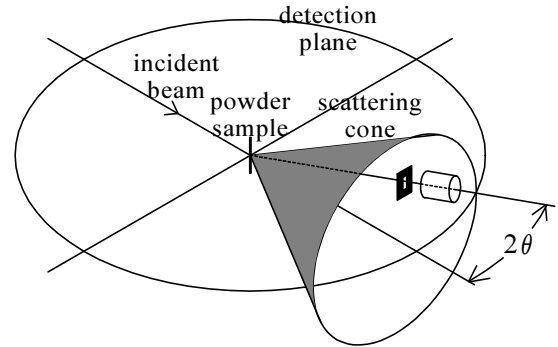


Figure 5: A powder sample illuminated by an x-ray beam scatters radiation for each Bragg angle into a cone.

Exercise 4 Visualize an NaCl-type crystal with a lattice spacing a_0 and explain how, if both atom types are identical, the crystal is equivalent to a simple cubic crystal with a one atom basis and a lattice spacing $a_0/2$. Now, show how this works out in the math. Assume the atomic form factors in an NaCl-type crystal are exactly equal: $f_{\text{Na}} = f_{\text{Cl}}$. Use the results derived in the previous exercise along with Eq. 4 to show that the x-ray scattering would then be the same as that of a simple cubic crystal with a one atom basis and half the original lattice spacing. Keep in mind that for a simple cubic crystal with a one atom basis, the crystal structure factor is just the atomic form factor for that one atom and all hkl in Eq. 4 lead to non-zero scattering. (Don't be concerned about a factor of 8 difference in the structure factors. It is just the ratio of the number of atoms in the unit cells for the two cases.)

For single crystal diffraction, the crystal must be properly oriented to see reflections from particular lattice planes at particular angles. With a powder sample, all crystal orientations are present simultaneously and the outgoing scattered radiation for each Bragg diffraction angle forms a cone centered about

the direction of the incident radiation as shown in Fig. 5. As the detector slit passes through a particular cone, the GM tube behind the slit detects an increase in the radiation and a peak in the spectrum will be recorded.

Procedure

Setup

The shielding dome over the top of the apparatus has several interlocks that de-energize the xray high voltage supply (and thus shut off the production of xrays) if the shield is bumped. The interlocks will also prevent the high voltage supply from coming on unless the shield is closed properly. Have an instructor show you how the interlocks operate.

Opening the shield must be performed carefully and gently. **Do not force the shield open** as this will easily break the interlock mechanisms. Pay particular attention to rear hinge-bar, which must slide to one side before it will rotate and allow the shield to open. To open the shield, grab it with both hands—one near the front interlock pin and one near the back hinge bar—and slide it to the right. The interlock pin on the front must move about 1 cm to the right to allow the pin to release from the front interlock, and the hinge-bar on the back must slide about 1 cm to the right to a click-stop before the hinge will rotate. The shield should lift with little effort when the interlocks are properly disengaged.

1. Open the shield and completely unscrew the plastic posts holding the motor gear against the detector arm gear. Move the motor completely out of the way of the inner angular scale around the sample table. The motor/detector arm gears simply drive the detector arm. Gears under

the sample table are responsible for maintaining the $\theta : 2\theta$ relationship but they must be set properly at one angle first. First, rotate the arm around by hand and note how the sample post rotates half as much. Then, set the arm at precisely 0° and check that the scribe marks on opposite sides of the sample table line up at 0° on the inside θ scale. The raised, chamfered, semicircular post must be on the side away from the motor. The sample table can be rotated independently of the detector arm if the knurled clutch plate is first loosened sufficiently. If both scribe marks cannot be made to line up exactly at the zeros of the θ scale, they should be made to give equal angles on the same side of a line connecting the zeros. Carefully retighten the clutch plate. Finger-tighten only! Do not use pliers or wrenches.

2. Place the primary collimator (button with 1 mm slit) on the exit port of the glass dome surrounding the xray tube. Orient the slit vertically by sighting past a vertical edge of the sample post. Use the 3 mm slit in slot 13 on the detector arm bench, and the 1 mm slit in slot 18.
3. Place the LiF single crystal with the flat matte side centered against the sample post (see section D27.30 of the Teltron manual).
4. Turn on the keyed switch and move the automatic shutoff timer off 0. The filament should light but the high voltage will remain off and xrays will not be present. Set the arm back to 0° and sight through the detector slits, past the crystal sample and through the primary collimator. All edges should be vertical and you should see a reflection of the filament

- light from the slanted surface of the copper anode just skimming past the crystal face.
- Put the GM tube (with the connector wire pointing up) in slot 26. Make sure the GM tube BNC cable is connected to the top BNC output on the TEL 2807 Ratemeter. **This output will have dangerously high voltage.** Make sure **nothing** but the GM tube is connected to this output. Push the CHANNEL SELECT button to monitor channel 3—G/M TUBE voltage. Set it to about 420 V.
 - Check that the high voltage selector switch on the scattering table (under the motor) is set for 20 kV.
 - Move the detector arm out of the way of the locking mechanism and close the shield. The shield enters the interlock off-center, and must be clicked into a central position before the xrays will come on. Xray emissions begin when you depress the red XRAY ON button to turn on the high voltage supply. If the xrays do not come on, the shield may need some jiggling to get the interlocks engaged. If the machine crackles, leave on the filament, but turn off the high voltage by bumping the shield. Wait about 5 minutes for the things to dry out before trying again.
 - Slide the arm around by hand over the full range of angles from about 13° to 120° . There has been some trouble with the arm rubbing into the shield and getting stuck during a computerized run. Play around with the positioning of the shield so that it interlocks properly allowing the xrays to come on, but such that it does not interfere with the free motion of the rotating arm.
 - To measure the xray tube current, install the xray tube current cable, plugging one end into the jack on the base of the spectrometer and the other end into the Keithley model 175 multimeter (set to 200 μA DC scale). Too high a tube current will load down the high voltage power supply, reducing the voltage below 20 kV. The manual warns not to go above 80 μA . Set it to around 70 μA using a small screwdriver on the adjustment at the base of the spectrometer next to XRAY ON button.
 - Activate the XRAY data acquisition program. If it is not running, click on the LabVIEW run button in the tool bar. Click on the Monitor Counts button. This displays counts collected in a fixed time interval as chosen by the control just under the button. Slide the arm around to $45-46^\circ$ where there is a strong diffraction peak. Find the angle where the count rate maximizes. It should be within about 1° of 45° and the count rate should be above 1500/s. If it is below this, recheck that the $\theta-2\theta$ table is set properly, then check with an instructor.
 - Open the shield and tighten the motor mounting against the detector arm gear. The apparatus is now ready to take spectra.
 - Click on the Initialize Angle button. This brings up a new window to initialize the program so it knows the angle of the spectrometer arm. Click as necessary on the Step button while checking the angle on the spectrometer to bring the arm to some degree marking on the scale imprinted on the spectrometer. Enter the angle for this marking in the Present Angle control and then click on the Done button.

13. Set the **Angle** control to bring the arm to 120° and then back down to 15° . Then try this again. If there is any problem with the free and accurate movement of the spectrometer arm using the stepper motor, fix it or notify the instructor before continuing.

X-ray spectrum

In this investigation, you will determine the spectrum of x-rays emitted by the source. Using the LiF single crystal and assuming the crystal plane spacing d is known, Bragg's law will be used to determine the wavelengths of the K_α and K_β emission lines and the wavelength of the bremsstrahlung cutoff.

14. Click on the **Collect Spectrum** to obtain the spectrum of x-rays emitted from the tube. You will then be asked to enter a file name in which to store the data. Remember to store all data in the My Documents area of the disk. The data is only saved at the end of the run (or after aborting). **If you hit the stop button in the tool bar while taking data, that data will be lost forever.** Use the **Abort** button under the **Collect Spectrum** button to stop a run prematurely. Use the LiF single crystal on the sample post and scan over the full range of scattering angles (15 - 120°) with a step size of $1/8^\circ$. Because the single crystal scattering is strong, you can set the **Time per channel** short, around 5-10 seconds and the signal to noise will be quite reasonable. Be sure to start at $2\theta = 15^\circ$ to get data at the bremsstrahlung cutoff wavelength.

C.Q. 1 Explain the spectrum you see. Use Eq. 1 to convert the angles of the various spectral features to wavelengths. The crystal face is along the 100 sc lattice plane and, for LiF, $a_0 = 0.403$ nm. Because LiF is an fcc crystal, there are two planes of atoms per (simple cubic) lattice spacing a_0 and thus the appropriate plane spacing d for use in Eq. 1 is given by $d = a_0/2$. Obtain best estimates of the x-ray K_α and K_β wavelengths as well as the low wavelength cutoff λ_c . Compare the line wavelengths with reference values and λ_c with expectations based on the tube voltage.

Powder Diffraction

Next, you will take spectra using powder (microcrystalline) samples. Here, the microcrystals are oriented randomly in all possible directions and the Bragg condition will be met for several different possible plane spacings in the crystal—each at a particular scattering angle. From an analysis of the angles where diffraction maximum are observed, the crystal lattice constant as well as the crystal structure can be determined.

The scattering for powder samples is much weaker than for single crystals because only a fraction of the crystals are in the proper orientation for any particular scattering angle. Thus, for powders, you will need to run overnight scans. You might want to take a one- or two-hour spectrum in class, setting the starting and stopping angles to scan over a small range of about 5° around the strongest expected peak to check the signal (peak height) to noise (background height) ratio for this peak. If the signal to noise is reasonable, then set up an overnight scan. You should be able to get a reasonable signal to noise ratio at 100 seconds per channel. A full scan from $2\theta = 15$ to 120° in $1/8^\circ$ steps will

then take about 24 hours. Thus, start a spectrum before leaving and come back the following day to turn off the xray machine and analyze the data. Increase or decrease the time per channel to fully utilize the time the xray machine is on. For example, if you start the run at 10:00 am and will not be back until 3:00 pm the next day, then adjust the time per channel for a total running time of 28-29 hours. There is no point in having the xray tube running with the machine not taking data. No run should be made longer than 30 hours or so without first discussing it with the instructor. The clamp on the shut-off timer knob is needed to keep the xrays from shutting off after 55 minutes.

15. Replace the LiF crystal with a powder sample of LiF. Take an overnight run.

16. Repeat with the KCl powder sample.

CHECKPOINT: C.Q. 1 should be answered. Spectra for all crystal and powder samples should be acquired and the angles for all peaks in each spectrum should be measured and tabulated.

Xray absorption

In this last investigation, you will study the xray absorption properties of several metallic elements. The experimental procedure is similar to that used to determine the spectrum of xrays emitted by the tube: the LiF crystal is placed on the scattering post and counts are measured for fixed time intervals over a range of scattering angles. To measure xray absorption, a sample spectrum is taken with a metal foil placed on the detector arm in front of the Geiger-Müller tube and the ratio of the counts obtained with the foil to a reference spectrum taken under identical conditions but without

the foil is determined point-by-point at each scattering angle. This ratio is called the foil *transmittance*, i.e., the fraction of xrays transmitted through the foil. The transmittance depends on the xray energy and this dependence will be determined from your data.

17. Properly install the LiF crystal on the scattering post.

18. Take one scan without any filter in place for the 2θ region from $30^\circ < 2\theta < 55^\circ$ with a $1/4^\circ$ step size and an acquisition time of 10-20 s per point. This will be one of the reference spectra. Take a second reference spectrum, again without any absorber, for the 2θ region from $45^\circ < 2\theta < 75^\circ$ again with a $1/4^\circ$ step size and about 30-60 s per point. (At the larger angles the source xray intensity is weaker and longer acquisition times are needed.)

19. Next take sample spectra with at least four, but preferably all eight foil samples available: Zn, Cu, Ni, Co, Fe, Mn, Cr, and V, inserted (one at a time) into the detector arm in front of the GM tube (slot 16). For any of the first four use the same settings as for the first reference spectrum and for any of the last four use the settings for the second reference spectrum. It is best to take all reference and sample spectra without turning off the data acquisition program or re-calibrating the angle. This way, all spectra should have the least amount of angular shift between them.

20. Import the spectra into Excel or some other analysis program and plot the transmittance of each foil versus 2θ by dividing the appropriate spectra point-by-point. The transmittance at any angle

is the ratio of the spectrum with the absorber to the reference spectrum without the absorber.

The xray source intensity varies with energy and that is why a reference spectrum is taken and the amount of absorption due to the foil is determined by dividing the two spectra angle by angle. You will be looking for an *absorption edge*, which appears at a particular scattering angle—a different angle for each foil—above which the transmittance suddenly increases. (C.Q. 5 asks you to learn about and describe why this behavior is expected.)

Because placing the foil in front of the detector can only attenuate the xrays reaching it, the spectrum with the foil should always have a lower count rate than the reference spectrum and the transmittance should be below unity at all angles. However, you should be aware of two possible experimental problems that can cause systematic errors in the transmittance. One is associated with small shifts in the scattering angle between the reference and sample spectra and the second is associated with changes in the xray tube current. Neither problem prevents you from getting great data, but as described next, you should be aware of the issues.

In the region near the K_α and K_β peaks, the xray intensity changes rapidly with scattering angle. Consequently, if the reference and sample spectra are slightly shifted in angle from one another, transmission fractions both much larger and much smaller than one can result. It is useful to try to understand this problem for the trivial case where the sample spectra is taken with no added foil in place; where both the reference and sample spectra should be identical and the transmittance should be unity at all angles. If the two spectra were slightly offset from one another in angle, why would the apparent transmittance

in the regions near the peaks come out incorrectly above unity on one side of a peak and incorrectly below unity on the other? And why would the transmittance still be near unity at other angles where the xray intensity does not vary as rapidly with angle?

Taking reference and sample spectra without shutting down the data acquisition program or recalibrating the angle should help minimize any angular shifts between spectra. If the affect of the offset is observed, try to ignore the errors in the transmittance near the peaks and concentrate on finding the absorption edge.

Another experimental problem can arise if the tube current is not steady. While our tube current is steady enough to get excellent data you should keep in mind the basic principal that the xray intensity is proportional to the tube current. Thus, for example, if the tube current were to jump up or down at some particular angle during the acquisition of a sample spectra with the foil in place, the transmittance would also incorrectly appear to jump up or down at that angle.

Even if the tube current doesn't jump, but only varies randomly about some average value, there can still be observable effects. With a perfectly steady xray source there would still be random variations in any measured count that should follow Poisson or "square root" statistics. However, if the tube current is varying randomly, any measured count will show additional random variations above and beyond those predicted by Poisson statistics.

Optional measurements

Feel free to explore other measurements that can be made with this apparatus. One interesting possibility is to do a powder diffraction sample (perhaps the SiC) having a Ni filter

in place so that only the K_α line contributes, thus simplifying the spectrum and analysis.

Analysis

Powder diffraction

Determining the best crystal lattice constant a_0 from the xray spectrum is not trivial. First, use the LabVIEW xray program and cursor to determine the center of each scattering peak. This is the scattering angle 2θ from which the Bragg angle θ is then obtained. For each peak you must then assign (make an educated guess as to) a value for λ (either 0.154 or 0.138 nm) and a set of values for (hkl) . Using these in Eq. 4 produces a value for a_0 . Of course, if either the λ or hkl are not the actual values for the scattering peak, the a_0 will not be correct. In fact, you must try to hit upon *logical* combinations that produce, within experimental error, the same lattice constant for each peak.

What does logical mean? For example, if the scattering for a given hkl is strong enough, two peaks should be observed—a stronger peak from 0.154 nm xrays and a weaker one from 0.138 nm xrays; with the same hkl both should give the same a_0 . If the scattering is too weak, the peak due to the weaker 0.138 nm xrays will become difficult or impossible to detect and only the peak due to the 0.154 nm xrays will be observed. You must also keep in mind how the atomic form factor and crystal structure factor are expected to behave. For example, if the crystal is fcc, then only scattering with all even or all odd values of hkl will occur. If it is bcc then only scattering with an even hkl sum can occur. Furthermore, the atomic form factors decrease with increasing scattering angle. Then, since the scattering angle increases as hkl increases, the strongest peaks always have the smallest hkl consistent with the crystal structure factor.

C.Q. 2 Explain why it should be impossible to observe a given hkl peak for the 0.138 nm xrays without also detecting the same hkl peak for the 0.154 nm xrays. With a crystal having the NaCl structure, if the last observed peak corresponds to $\lambda = 0.154$ nm and $hkl = 331$, which other hkl peaks (at lower angles) should also be observable for this λ ?

21. Prepare a table for each powder sample, with a row for each Bragg peak and columns for:
 - (a) the scattering angle 2θ .
 - (b) the true angle θ .
 - (c) the appropriate xray wavelength (0.154 or 0.138 nm).
 - (d) the values for h , k and l .
 - (e) the calculated lattice constant a_0 .

C.Q. 3 For each sample, print out the xray spectrum, labeling the Miller indices hkl and the value of a_0 for each peak.

With the correct assignments of λ and hkl , the values for a_0 determined from each peak should be close, but not identical. There are random errors associated with the determination of the scattering angle and systematic errors inherent in xray diffraction work. Systematic errors arise from xray absorption and from various kinds of misalignments in the apparatus. They are typically smaller at larger scattering angles and thus better values for the lattice constant are obtained at higher angles. Careful modeling of possible sources of systematic error (Cullity, *Elements of Xray Diffraction*, Ch. 11) leads to several predictions for systematic effects.

One prediction is that if the xray beam hits the sample either to the left or right of the

centerline there will be an error Δa in the calculated lattice constant given by

$$\frac{\Delta a}{a_0} = -\frac{D \cos^2 \theta}{R \sin \theta} \quad (9)$$

where R is roughly the distance from the source to the sample and D is the xray beam displacement—positive if the beam is displaced toward the detector side.

Another prediction is that scattering from atoms deeper into the sample will produce a lattice error

$$\frac{\Delta a}{a_0} = \kappa \cos^2 \theta \quad (10)$$

where κ depends on the thickness of the sample and its xray absorption coefficient.

Thus, the measured values of a_0 (let's now call them a_m) are predicted to be

$$a_m = a_0 + c_1 g_1 + c_2 g_2 \quad (11)$$

where

$$g_1(\theta) = \frac{\cos^2 \theta}{\sin \theta} \quad (12)$$

$$g_2(\theta) = \cos^2 \theta \quad (13)$$

and a_0 is the true lattice constant.

Make spreadsheet columns for a_m , g_1 , and g_2 with values for g_1 and g_2 in adjacent columns. Perform a multiple linear regression to Eq. 11 selecting the a_m values for the **Input Y Range** (y -variable) and selecting both the g_1 and g_2 columns for the **Input X Range** (x -variables). The fitted **Constant** is the best estimate of a_0 and the fitted **X Variable** (1 and 2) are the best estimates of c_1 and c_2 . Add a column for a_m according to the fitting formula using the regression values for a_0 , c_1 and c_2 . Make a graph with plots of the measured a_m (markers, no line) and fitted a_m (smooth line, no markers) vs. 2θ . Both g_1 and g_2 go to zero for backscattering ($2\theta = 180^\circ$) and thus a_0 may

be considered the extrapolated fitted value at this angle.

The general trend of the fitted curve away from horizontality ($c_1 = c_2 = 0$) indicates the size of the systematic errors while the scatter of the data about the fit (the rms deviation) represents the size of the random errors. This suggests two ways to judge the significance of the systematic errors. (1) Determine whether or not c_1 and c_2 are consistent with zero (in comparison with their 68 or 95% confidence intervals) and discuss if the g_1 or g_2 systematic errors are present in the apparatus or too small to be observable. (2) Look at the difference between the rms deviation of the fit and a direct evaluation of the standard deviation of the measured a_m (equivalent to the rms deviation of a fit with $c_1 = c_2 = 0$). Report on these two deviations and discuss how they demonstrate the significance of systematic errors.

If you found systematic errors are significant, you might then look to see if your data can distinguish between g_1 - and g_2 -type errors. The g_1 and g_2 functions are relatively similar in that both monotonically decrease with angle. They differ in that g_1 has a larger range of values. Try fitting with only one and then only the other as the x -variable and report on the differing values for the lattice constant and the rms deviation of the fit. What conclusions can you draw regarding the systematic errors based on the three ways you used to include them?

There may also be a systematic error in the measured scattering angles. The gears on the motor and rotating table would dictate that the detector arm should move exactly $1/16^\circ$ per pulse sent to the motor. After a long scan there may be a difference between the angle as determined by the scale on the xray machine and the computer value. While there might be a problem with the stepper motor

and gears, e.g., slippage, the cause of the discrepancy may be as simple as inaccuracies in the silk screened angular scale imprinted on the spectrometer. You should investigate this issue and how it might affect your results.

C.Q. 4 For each sample, explain the values of hkl observed, give a single best estimate of the lattice constant and uncertainty and compare with reference values. Discuss the observed intensity pattern of the peaks with respect to the calculations of the crystal structure factor. Include error estimates where appropriate and tell in the report how you determined them. Also report on the consistency (or lack of consistency) in the systematic error parameters c_1 and c_2 for different samples. Use a representative c_1 value to get a rough estimate of the beam displacement D . Is this D reasonable?

Xray absorption

C.Q. 5 Read up to learn about the issues involved in xray absorption and answer the following questions. How is the transmittance you measure versus angle related to the absorption versus the xray photon's wavelength and energy? Why is there an absorption edge; why does the absorption at angles below the edge suddenly increase? What electronic transitions are involved in the absorption? How is the xray energy at the edge expected to depend on atomic number of the foil material? Which foils absorb the copper K_α line? Which absorb the K_β line? Why doesn't copper self-absorb its own K_α or K_β emissions?

Determine the xray wavelength at the observed absorption edge for each foil and use this to determine the xray energy E there, say in eV. Plot E vs. the atomic number Z of the foil element and fit this data to the theoretical prediction made in the comprehension question above and comment on the results.