

# Xray Diffraction and Absorption

## Experiment XDA

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PHY4803L — Advanced Physics Laboratory

### Objective

The diffraction of xrays from single crystals and powdered crystalline samples will be investigated along with the emission and absorption of xrays by high  $Z$  metals. The diffraction patterns show sharp maxima (peaks) at characteristic angles that depend on the wavelength of the xrays and the structure of the crystal. A Geiger-Müller tube is used to detect the intensity of the diffracted xrays versus scattering angle. Crystal properties are determined from the angular position and intensity of the peaks.

### 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 kV strikes a metal target, two different pro-

cesses simultaneously produce xrays. First, the deceleration of beam electrons from collisions with the target produce a broad continuum of radiation called *bremstrahlung* (braking radiation) having a short wavelength limit that arises because the energy of the photon  $hc/\lambda$  can be no larger than the kinetic energy of the electron. Second, beam electrons can 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  $K_\alpha$  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  $K_\beta$  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 a complete absorption

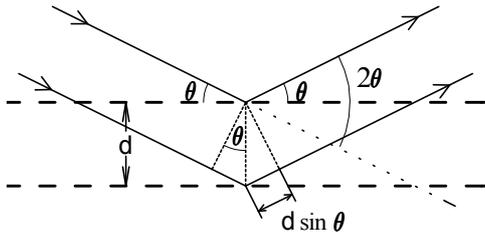


Figure 1: The ray reflected from the second plane must travel an extra distance  $2d \sin \theta$ .

of the initial xray photon and the ejection of an electron—a 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.

## 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  $2\theta$ .

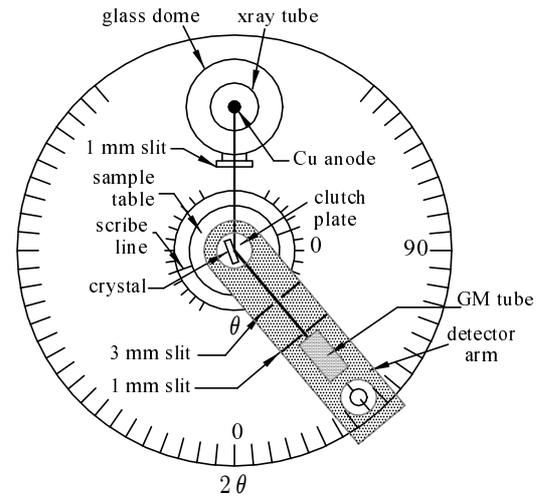


Figure 2: The xray diffraction apparatus.

Constructive interference of the reflected 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  $2\theta$ . In order to obey the Bragg condition, the crystal must rotate to an angle  $\theta$  when the detector is at an angle  $2\theta$ . This  $\theta : 2\theta$  relationship is maintained by gears under the sample table.

Assuming  $d$  is known (from tables of crystal spacings), the wavelength  $\lambda$  of xrays detected

at a scattering angle  $2\theta$  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 xrays—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

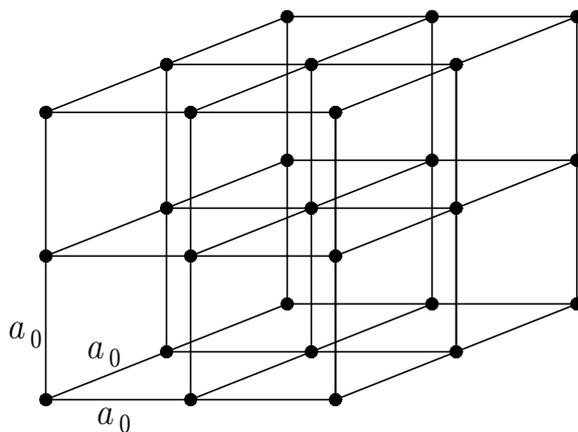


Figure 3: The simple cubic lattice points (dots) and connecting lines showing the cubic structure.

points at the same positions as those of the 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 (rhombohedral) 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  $45^\circ$  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 lattice 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*  $F(hkl)$ :

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

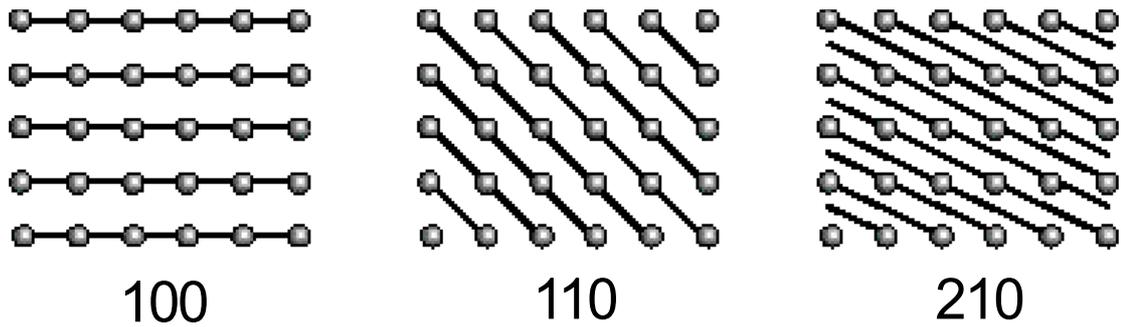


Figure 4: Top view of three possible sets of planes in the simple cubic lattice with their Miller indices.

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  $\theta$ . 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  $\theta$  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  $\lambda$ . 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  $2\lambda$ , and for the Cl planes, it is  $\lambda$ . 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  $F_{\text{fcc}}$  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  $f_{\text{Cl}}$  and  $f_{\text{Na}}$ .

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.

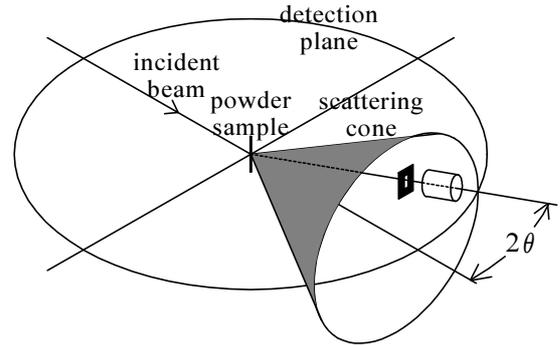


Figure 5: A powder sample illuminated by an x-ray beam scatters radiation for each Bragg angle into a cone.

**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

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  $0^\circ$  and check that the scribe marks on opposite sides of the sample table line up at  $0^\circ$  on the inside  $\theta$  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  $\theta$  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  $0^\circ$  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.
5. 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.
6. Check that the high voltage selector switch on the scattering table (under the motor) is set for 20 kV.
7. 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.
8. Slide the arm around by hand over the full range of angles from about  $13^\circ$  to  $120^\circ$ . 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.
  9. 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  $200 \mu\text{A}$  DC scale). Too high a tube current will load down the high voltage power supply, reducing the voltage below  $20 \text{ kV}$ . The manual warns not to go above  $80 \mu\text{A}$ . Set it to around  $70 \mu\text{A}$  using a small screwdriver on the adjustment at the base of the spectrometer next to XRAY ON button.
  10. 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  $1^\circ$  of  $45^\circ$  and the count rate should be above  $1500/\text{s}$ . If it is below this, recheck that the  $\theta - 2\theta$  table is set properly, then check with an instructor.
  11. Open the shield and tighten the motor mounting against the detector arm gear. The apparatus is now ready to take spectra.
  12. 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  $120^\circ$  and then back down to  $15^\circ$ . 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.

### Xray spectrum

14. Click on the Collect Spectrum to obtain the spectrum of xrays 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 ( $15-120^\circ$ ) 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 xray  $K_\alpha$  and  $K_\beta$  wavelengths as well as the low wavelength cutoff  $\lambda_c$ . Compare the line wavelengths with reference values and  $\lambda_c$  with expectations based on the tube voltage.

### Powder Diffraction

Next, you will take some spectra using powder (microcrystalline) samples. 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  $5^\circ$  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 it for 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  $120^\circ$  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 absorption properties of several metallic elements on xrays emitted by the xray tube. The diffractometer will be used to vary the xray energy incident on a metal foil placed on the detector arm in front of the Geiger-Müller tube. The ratio of the count rate taken with the foil to the count rate taken without the foil (i.e., the transmission fraction or *transmittance* of the foil) will be determined point-by-point at each scattering angle  $2\theta$ . Bragg's law will then be used to determine the xray wavelengths where absorption features are found to occur.

17. Use the LiF crystal on the scattering post.

18. Take one scan without any filter in place for the  $2\theta$  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  $2\theta$  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. For any of the first four use the same settings as for the first reference spectrum and for 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. Plot the transmittance of each foil versus  $2\theta$  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 in the sample spectrum is determined by dividing the two spectra angle by angle. However, keep in mind that if the tube current varies, there will be proportional variations in the xray intensity. For example, if the tube current were to fall at some angle while taking a sample

spectrum, the transmittance ratio would then appear (erroneously) to fall at that angle. As another effect, small random variations in the tube current would cause small random variations in the measured xray intensity and any measured xray count might show random variations above and beyond what would be predicted by the “square-root” statistics appropriate for a source of perfectly uniform intensity. While a jump in the tube current or an unsteady tube current has been observed with our apparatus, neither issue typically affects the analysis to any significant degree. Nonetheless, the principal—that the xray intensity is proportional to the tube current—is worth keeping in mind.

If the tube current were perfectly stable, the spectrum with the absorber should always have a lower count rate than the reference spectrum and the transmittance should be below unity at all angles. An absorption edge due to the foil should appear at some scattering angle above which the transmittance ratio is just a little under unity (indicating a small amount of absorption) and below which the ratio is significantly smaller than unity (indicating a larger absorption of the xrays). However, do not be surprised if the region near the  $K_\alpha$  and  $K_\beta$  peaks shows transmission fractions both much larger and much smaller than one. This will happen if the scattering angles for the reference and sample spectra are slightly shifted in angle from one another. In the regions very close to the peaks where the count rate is changing rapidly, the shift leads to both incorrectly large and incorrectly small transmittance ratios. Taking reference and sample spectra without shutting down the data acquisition program should help minimize any angular shifts. 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 edges.

**C.Q. 2** Read up to learn about the issues involved in xray absorption and answer the following questions. Explain why the absorption edge occurs; why absorption at angles below the edge suddenly increases. How does the absorption depend on the xray energy? What electronic transitions are involved in the absorption? What happens if the xray energy is less than the transition energy? Which foils absorb the copper  $K_\alpha$  line? Which absorb the  $K_\beta$  line? Why doesn't copper self-absorb its own  $K_\alpha$  or  $K_\beta$  emissions? Determine the xray wavelength at the observed absorption edge for each foil and use this to determine the xray energy there, say in keV. Plot the absorption edge energy vs. the atomic number  $Z$  of the foil element. How are these energies expected to depend on atomic number? Do an analysis to demonstrate or verify this prediction.

## Analysis

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  $2\theta$  from which the Bragg angle  $\theta$  is then obtained. For each peak you must then assign (make an educated guess as to) a value for  $\lambda$  (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  $\lambda$  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. 3** 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  $\lambda$ ?

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

**C.Q. 4** 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  $\lambda$  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  $\Delta a$  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  $\kappa$  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.  $2\theta$ . 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. 5** 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?

There are many other experiments that can be performed with this apparatus. The GM tube response can be studied as a function of the operating voltage. The absorption coefficient for aluminum can be determined. Consult the references or discuss with the instruc-

tor if you would like to explore other xray experiments.