

# X-ray Diffraction and Absorption

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by

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## Objective

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

## References

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## X-ray Emission and Absorption

When an electron beam of energy around 20 keV strikes a metal target, two different processes simultaneously produce x-rays. First, the deceleration of beam electrons from collisions with the target produce a broad continuum of radiation called *bremsstrahlung* (braking radiation) having a short wavelength limit that arises because the energy of the photon  $\frac{hc}{\lambda}$ , 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 x-rays lines characteristic of the target material are emitted.

The x-ray tube used in this experiment has a copper target, and only two emission lines of appreciable intensity are emitted. Copper  $K_{\alpha}$  x-rays ( $\lambda = 0.1542 \text{ nm}$ ) are produced when an  $n = 2$  electron makes a transition to a vacancy in the  $n = 1$  shell. A weaker  $K_{\beta}$  x-ray with a shorter wavelength ( $\lambda = 0.1392 \text{ nm}$ ) occurs when the vacancy is filled by an  $n = 3$  electron.

The reverse process of x-ray absorption by an atom also occurs if the x-ray 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 x-ray energies and metals considered in this experiment, the ionization of a K-shell electron is the dominant mechanism when the x-ray energy is high enough, which leads to a complete absorption of the initial x-ray photon and the ejection of an electron — a process known as the photoelectric effect. If an x-ray does not have enough energy to cause a transition or to ionize an atom, the only available energy loss mechanism is Compton scattering.

## The X-ray Diffractometer

Thus, the spectrum of x-rays from an x-ray 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 x-rays 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 x-ray spectroscopy.

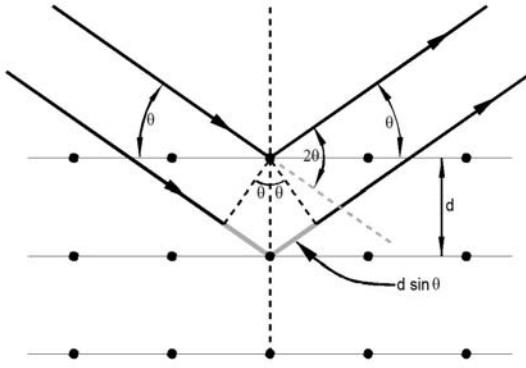


Figure 1. The ray reflected from the second plane must travel an extra distance  $2d \sin \theta$ .

The incident x-ray 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 Figure 1 where the plane spacing is denoted  $d$ , the pathlength 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  $2\theta$ .

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 x-ray diffraction is sometimes used to orient single crystals and determine crystal axes.

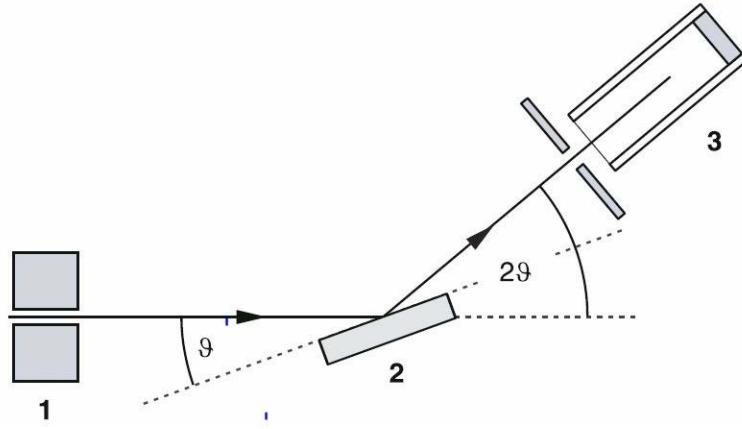


Figure 2: Schematic diagram of x-ray diffraction apparatus.

The schematic of the apparatus is shown in Figure 2. The x-rays from the tube are collimated to fine beam and reflect from the crystal placed on the sample stage. The detector, a Geiger-Müller (GM) tube, is placed behind a collimating slit on the detector arm which can be rotated 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 electronically by stepping motors working independently but with electronic control.

Assuming  $d$  is known (from tables of crystal spacings), the wavelength  $\lambda$ , of x-rays detected at a scattering angle  $2\theta$  can be obtained from Equation 1.

Crystal	category	$a_0$
LiF	Face Centered Cubic (FCC)	0.405
NaCl	Face Centered Cubic (FCC)	0.564
CsCl	Body Centered Cubic (BCC)	0.411
KF	Face Centered Cubic (FCC)	
KCl	Face Centered Cubic (FCC)	0.629
NaF	Face Centered Cubic (FCC)	0.462
KI	Face Centered Cubic (FCC)	
KBr	Face Centered Cubic (FCC)	0.659

Table 1. Alkali halide crystals, their structure and lattice constants.

## 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 as

$$lattice + basis = crystal . \quad (2)$$

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

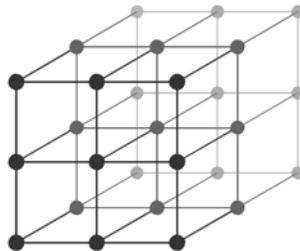


Figure 3. The simple cubic lattice points (dots) and connecting lines showing the cubic structure.

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  $(u, v, w) = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  within each “pulled-back” unit cell.

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  $d = \frac{a_0}{\sqrt{2}}$ , 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 Equation 1 with this  $d$ . It turns out that the spacing 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 Equation 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 Figure 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 Equation 1.) The 110 reflections are from the 110 planes through opposite edges of the cube, and so on.

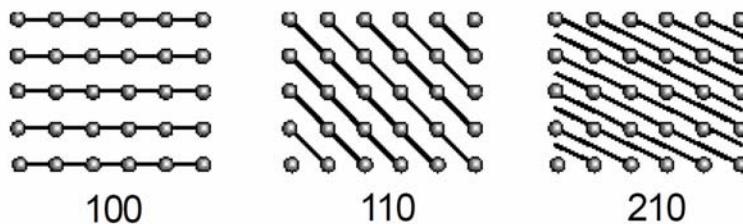


Figure 4. Top view of three possible sets of planes in the simple cubic lattice with their Miller indices.

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 Equation 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*  $F(hkl)$  where

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

and the sum extends over all atoms in a single unit cell. For certain integers of  $hkl$ , 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  $f_j$  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 Equation (5) so that

$$F(100) = f_{Cs} - f_{Cl}. \quad (6)$$

While for a  $200$  reflection

$$F(200) = f_{Cs} + f_{Cl}. \quad (7)$$

In this case, the path length 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

$$F(hkl) = f_{Cs} + f_{Cl} e^{i\pi(h+k+l)} \quad (8)$$

and gives  $f_{Cs} + f_{Cl}$  when  $h+k+l$  is even and  $f_{Cs} - f_{Cl}$  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:

$$F_{bcc}(hkl) = f(1 + e^{i\pi(h+k+l)}) \quad (9)$$

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:

$$F_{fcc}(hkl) = f(1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}) \quad (10)$$

Then use this result to show that  $F_{fcc}$  is zero unless  $h, k$ , and  $l$  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

$$\begin{aligned} \text{Na: } & 0,0,0; \frac{1}{2},\frac{1}{2},0; \frac{1}{2},0,\frac{1}{2}; 0,\frac{1}{2},\frac{1}{2} \\ \text{Cl: } & \frac{1}{2},0,0; 0,\frac{1}{2},0; 0,0,\frac{1}{2}; \frac{1}{2},\frac{1}{2},\frac{1}{2} . \end{aligned}$$

**Exercise 3.** Evaluate the crystal structure factor for the NaCl crystal. Show that  $F$  is still zero unless  $h, k$ , and  $l$  are all even or all odd and give the structure factor in terms of the atomic form factors  $f_{Cs}$  and  $f_{Cl}$ .

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 x-rays nearly equally well, i.e., have nearly the same atomic form factors.

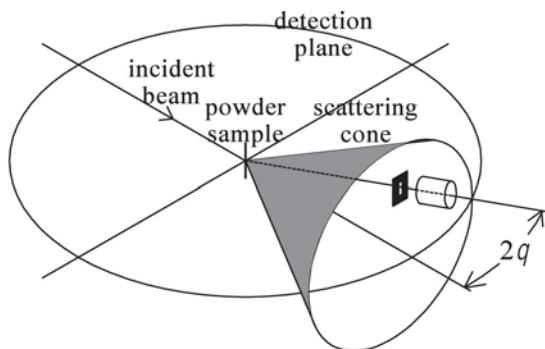


Figure 5: A powder sample illuminated by an x-ray beam scatters radiation for each Bragg angle into a cone.

**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:  $f_{Na} = f_{Cl}$ . Use the results derived in the previous exercise along with Equation (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 Equation (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 Figure 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.



Figure 6. Leybold Didactic (LD) Model 554 800 X-ray apparatus.

## Apparatus

The apparatus for this experiment is shown in Figure 6 and consists of the following: (1) Leybold Didactic (LD) Model 554 800 X-ray apparatus, (2) LD Model 554 862 copper anode x-ray tube, (3) LD Model 554 831 goniometer, (4) and samples consisting of LD model 554 77 LiF crystal, LD model 554 78 NaCl crystal, LD model 554 842 crystal powder holder with LiF powder.



Figure 7. Leybold Didactic (LD) x-ray diffraction system control panel.

The x-ray diffraction instrument is composed of 3 sections. The left hand section contains the control panel that has: (1) an adjustment knob to change the operating parameters, (2) buttons to choose the adjustment parameters, and (3) a readout display to read the set values. See Figure 7. The high voltage, the tube current, the time to measure the number of scattered x-rays at each position in the scanning process, the incremental angle change, the beginning angular position, and the final angular position can be chosen to be changed with the adjustment knob. In addition, there are a number of other buttons for various options. The middle row of buttons allows the sample and detector positions be adjusted separately or coupled together. The sample and detector angular positions can be set to their zero positions with the reset button. The bottom row of buttons are used to turn the high voltage on and off and to initiate scanning. The audio sound for the rate meter can be controlled with the button with the speaker symbol. Scans can be reset and replayed with 2 of the other buttons in that row.

The middle section contains the x-ray tube. For this experiment an x-ray tube with a copper anode is used. The copper x-ray tube produces 2 characteristic x-rays, the  $K_{\alpha}$  and  $K_{\beta}$  x-rays, having wavelengths  $0.154 \times 10^{-9}$  m and  $0.138 \times 10^{-9}$  m respectively. The tube can be seen through a leaded glass door that is interlocked to the high voltage power supply. The high voltage cannot be turned on unless the door is closed and locked in place by the interlock system. If the door is moved, the interlock system will trip the high voltage off. Electrical shock from the power supply could be fatal if it were possible to make contact with the anode when the high voltage is on, and this is as much a hazard as exposure to the x-rays.

The right hand section is the “business” section where the x-rays are diffracted and detected. This section contains the goniometer module that rotates the detector around the sample to measure the diffracted x-rays as a function of their scattering angle. Most importantly about this module is that the goniometer rotates the crystalline samples at  $\frac{1}{2}$  the angular change of the detector. This is

important to fulfill the Bragg condition where the angle of incidence has to equal the angle of diffraction for the position of the detector. This can be observed by setting the detector and sample to zero, and with the coupled option chosen, rotate the detector to some angle and observe the angular position of the sample. The display can be set to read either the sample or detector position by depressing the appropriate button on the panel.

The Leybold Didactic x-ray diffraction instrument can be computer controlled via a LabView data acquisition system. All the controls on the control panel can be accessed, adjusted, and set with the computer attached via a USB cable. Diffracted and detected x-rays are counted, recorded, and plotted at each angular position as the sample and detector are scanned from some initial angular value to some final value.

## Safety



Exposure to x-ray radiation can be dangerous to a person's health if sources of x-rays are used improperly or exposures are excessive. The Leybold Didactic (LD) x-ray instrument is approved for school use and is stated to have a dose rate at a distance of 10 cm of less than 1  $\mu\text{Sv}/\text{h}$ . This is equivalent to less than 0.1 mrem/hr, i.e. since 1 Sv = 100 rem,

$$(1 \mu\text{Sv}/\text{h} = 1 \times 10^{-6} \times 100 \text{ rem}/\text{hr} = 1 \times 10^{-4} \text{ rem}/\text{hr} = 0.1 \text{ mrem}/\text{hr})$$

One of the State of Tennessee's most stringent regulations for radiation protection is that a pregnant female should receive a dose of no more than 500 mrem. A dose of 500 mrem with dose rate of 0.1 mrem/hr would take an exposure time of 5000 hours, or more than 200 24-hour days of exposure at the 10 cm distance. Typically an operator of this instrument would be located a greater distance away from the instrument and would spend much less time with the machine.

The instrument has two independent safety circuits for doors, high voltage and emission current. It has automatic door locking; the doors can be opened only, when no high voltage is present i.e. no x-ray radiation can be generated. It has a built-in rate meter and has a loudspeaker that can act as an acoustic rate meter and as an audible warning that radiation is being produced.

## Procedure

### Sample Mounting

1. Samples are mounted on a rotating stage that consists of a gray polymer plastic block. The stage is attached to a rod that is inserted in the goniometer. The rod is aligned with the use of a pin in the rod and by seating this pin in a v-groove in the threaded portion of the goniometer that rotates. The rod is secured in place with a knurled aluminum fastener that screws onto the threaded goniometer part. Proper alignment is necessary for the sample and detector positions to coincide at the zero position and to have the 2:1 relative motion. See Figure 8.



Figure 8. Alignment of sample holder rod with goniometer receiver using rod pin and receiver v-groove.

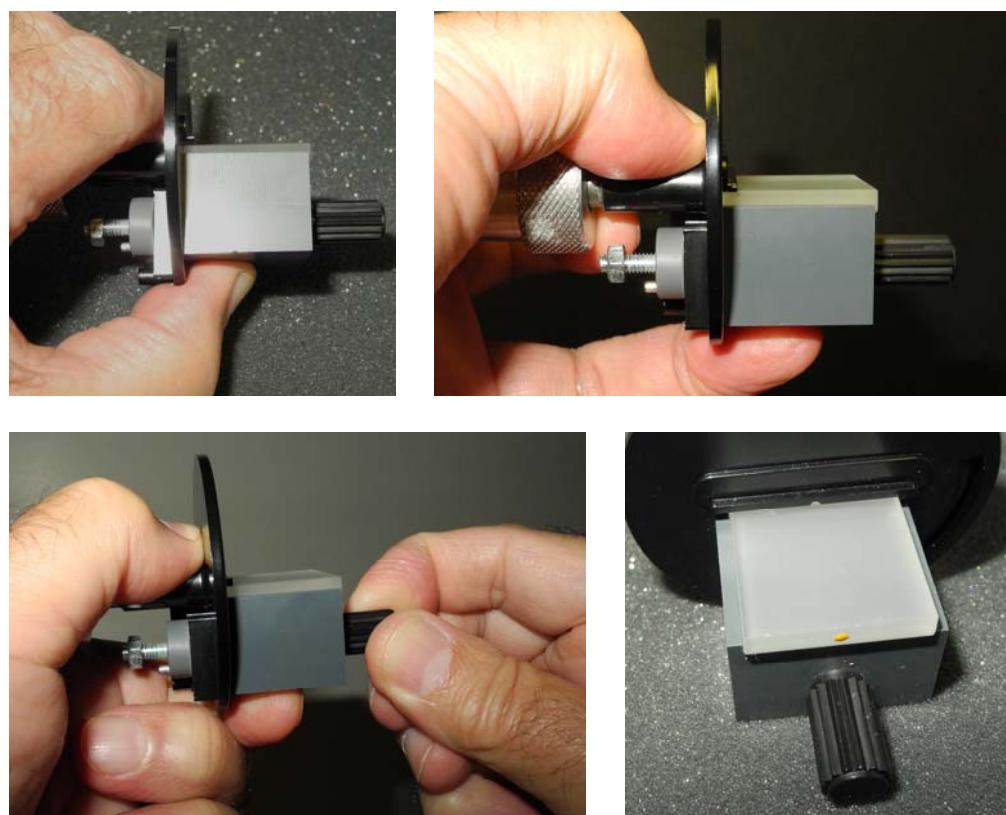


Figure 9. Illustrations of proper mounting of a sample.

2. A black plastic disk is attached to the goniometer rod and the gray block is attached to it. The gray block can be loosened and tightened with a screw so that the block can be moved to and from the axis of rotation to allow different sample thicknesses to be mounted. The black disk has several other functions for other experiments, but in this experiment a sample can be positioned on the gray block so that the top surface of the sample is against a protruding ledge that has one edge perfectly in line with the axis of rotation. This allows

the top surface of the sample to rotate about the axis of the rod's rotation. Figure 9 illustrates the mounting of the sample and how to apply a little pressure on the block while tightening the screw that affixes the block to the black disk. A thumb and forefinger can be placed such that one is underneath the block and the other is on the rod, or vice versa, while tightening the block in place. There is also a ledge on the gray block to prevent the sample from sliding off as the stage rotates if the sample is not held securely enough.

3. For the first measurement mount the single crystal sample of LiF. Be careful not to let the sample fall to the floor.

#### Adjust Operating Parameters

1. Turn on the Leybold Didactic (LD) Model 554 800 X-ray apparatus. The power switch is located on the left side, facing the unit, and as shown in Figure 10.
2. Depress the high voltage button, marked "U", on the control panel, and set the high voltage to its maximum value of 35kV by turning the adjustment knob.



Figure 10. Instrument power switch and close-up view of control panel.

3. With the adjustment dial, set the x-ray tube current to its maximum value of 1 mA by first depressing the current button labeled "I". See Figure 11.



Figure 11. Readout display indicating current value of 1mA and 1 second of counting time.

- The total time to make a measurement of a diffraction spectrum depends on: (1) the range of angles over which the measurement is made, (2) the incremental change in angle as the sample and detector change angular positions, and (3) the time that the sample and detector remain stationary at their specific positions while the number of x-rays is being counted and recorded. The total time is simply the range of angles divided by the angular increment (i.e. the number of angular positions that data is collected) times the increment of time that diffracted x-rays are counted.
- Determine a reasonable incremental angle in degrees and a reasonable incremental time in seconds to measure the number of diffracted x-rays counted with the sample and detector located at their respective angular positions. Set these incremental angles and times by depressing the  $\Delta\beta$  and  $\Delta t$  buttons and using the adjustment control.
- The initial angle and the final angle can be set for the range over which the diffracted x-rays will be determined. The range is set with the  $\beta$  LIMITS button and this button is a toggle button that allows both the initial and final angles to be set. To set the initial angle, the lower limit of the scan, toggle the button until a down arrow is shown in the readout display as shown in Figure 12a. Then change the value with the adjustment control to the desired value. Set the final angle to end the scan by toggling the  $\beta$  LIMITS button so that an up arrow appears in the readout display (see Figure 12b). Then the value can be set with the adjustment control.

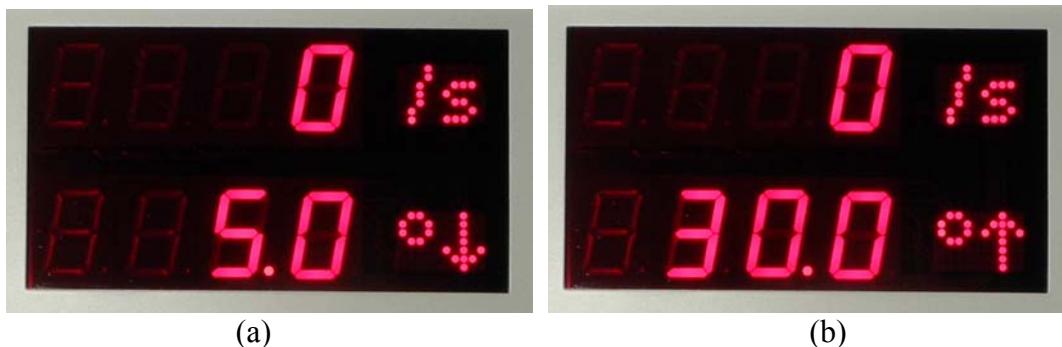


Figure 12. Readout display for setting the initial and final angular values for the spectral range of x-ray diffraction measurements.

- Press the Coupled button and turn the adjustment knob to rotate the sample and detector about the axis of rotation. Change the angle sufficiently in order to observe that the detector's change in angle is twice the sample's change of angle.

**Caution:** Move the detector from its minimum value to determine the maximum value that it can move and not become obstructed by any part of the apparatus that would impede its motion. This is important to keep the detector from being damaged. Also note that the angle being displayed is the sample angle and not the detector angle.

- The detector for the diffracted x-rays is a Geiger-Mueller detector and is shown in Figure 13. The x-rays enter the detector through a thin metallic window at the end of the detector. Care should be taken to touch and possibly damage this end window



Figure 13. End-window Geiger-Mueller tube for detecting and counting diffracted x-rays.

- All of these adjustments can be set and read from the Leybold Didactic (LD) program that is used for data acquisition. The software for this program can be run by clicking on the x-ray diffraction apparatus program icon and then clicking on the tools icon to bring up the Settings panel as shown in Figure 14. The settings that were made using the buttons on the control panel can be viewed or they can be entered or changed by inputting the parameters in the settings panel.

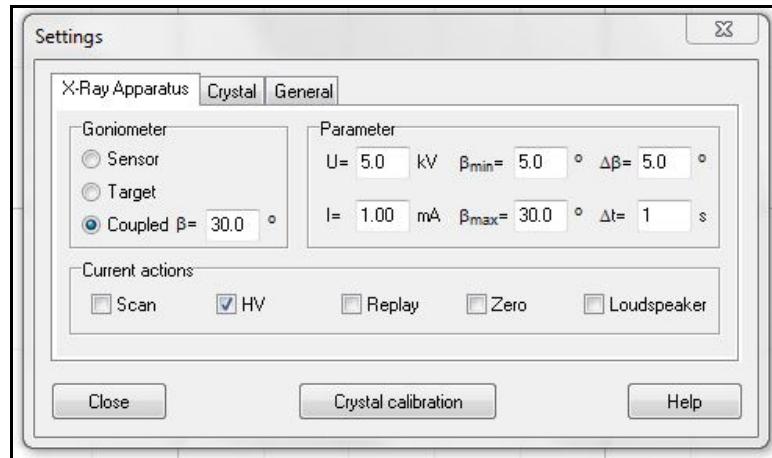


Figure 14. Settings panel contained in the Leybold Didactic (LD) data acquisition system program.

## Diffraction Measurements—Single Crystals

1. Mount the LiF crystal on the rotation stage as shown in Figure 15. Turn on the main power switch for the apparatus and start the x-ray diffraction system program by clicking the icon,  . Using either the front control panel or the settings panel in the computer program, adjust the control parameters as follows:
  - a. High Voltage (U): 35 kV
  - b. Current (I): 1 mA
  - c. Increment of Time for Each Angle ( $\Delta t$ ): 0.2 seconds
  - d. Incremental Scan Angle ( $\Delta\beta$ ): 0.1°
  - e. Initial Starting Angle ( $\beta\downarrow$ ): 5°
  - f. Final Ending Angle ( $\beta\uparrow$ ): 60°

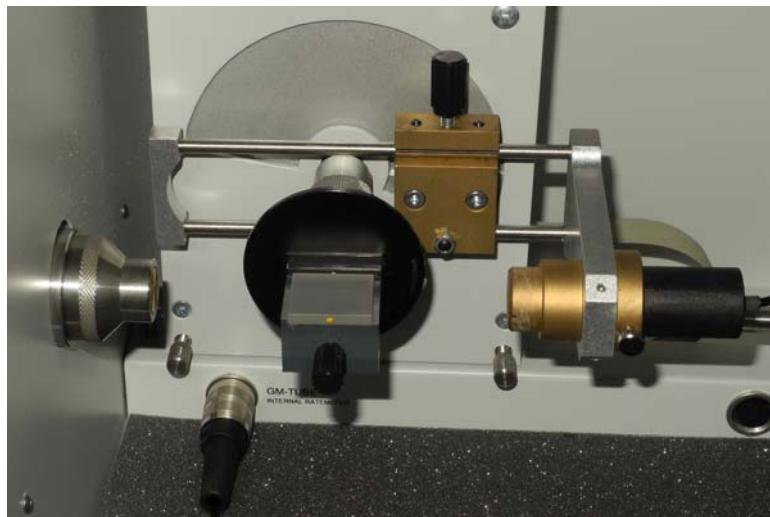


Figure 15. Diffraction apparatus with mounted sample and detector in the zero positions ready for a scan.

2. Initialize the system by setting the detector and sample stage to the zero position by depressing the Zero button or by clicking on the Zero check box in the Settings panel of the program.
3. Using these parameters, calculate the length of time for completing a scan and note whether this time is reasonable for making a measurement. If not make adjustments as appropriate.
4. With the designated button on the control panel or settings panel, select the Coupled mode of operation.
5. Similarly as an option you may also turn on the Loudspeaker to listen as the diffracted x-rays reach their peak values.

6. Make sure the glass doors are closed and start the scan by clicking on the start-stop icon, , of the computer program or depressing the Scan on/off button on the control panel.
7. The data acquisition system will measure and record the diffraction spectrum and the display should look similar to the one shown in Figure 16. The display shows the numerical data and a plot of the data.
8. This spectrum should be saved by clicking on the Save Measurement As icon, , and providing a filename. The file will have the extension “xry” attached to the file name. Saved files of this type can be loaded back into the program for further use.
9. Right clicking on any part of the window will bring up a menu as shown by the example in Figure 17. Choosing Copy Table by left clicking on it allows you to copy all of the headings and numbers in the data table and then copy it into an Excel spreadsheet to plot and analyze as desired. Plotting your data in Excel may lead to a graph similar to the one shown as an example in Figure 18.

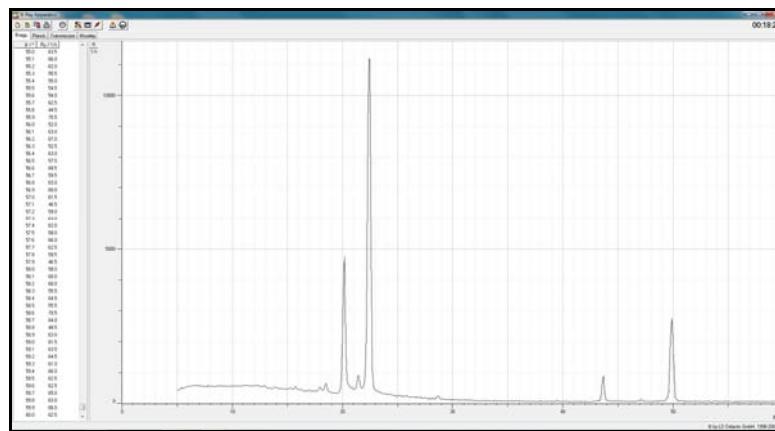


Figure 16. Typical x-ray diffraction spectrum of Cu x-rays diffracted by LiF crystal.

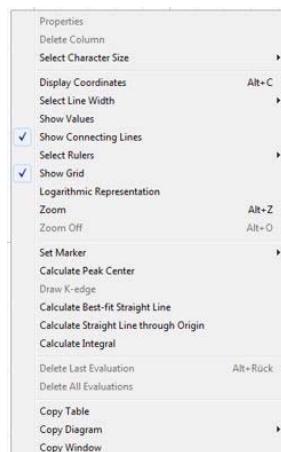


Figure 17. Menu for copying the table data into an Excel spreadsheet.

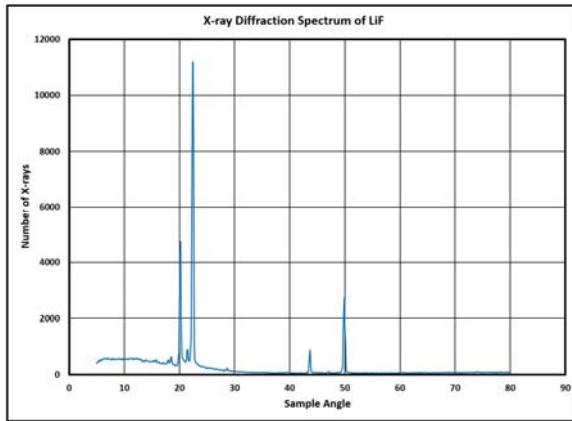


Figure 18. Typical graph of spectrum processed with Excel.

### Analysis of Results with Single Crystal

1. Label the prominent peaks of the x-ray diffraction spectrum and determine the diffraction angle for each one.
2. Prepare an Excel spreadsheet similar to the one shown in Figure 19.

Peak #	$\theta$	n	X-ray, $\lambda$	d	$a_0$
1					
2					
3					
4					

Figure 19. Example of Excel spreadsheet for analyzing LiF crystal spectrum and calculating the lattice constant.

3. Assign the diffraction order, n, and the x-ray wavelength,  $\lambda$ , to each peak and enter the data in the table.
4. Use the Bragg diffraction equation to calculate the separation of planes, d, and the lattice constant,  $a_0$ .
5. Compare your results with known accepted values.

### Diffraction Measurements—Powdered Sample

1. Obtain the prepared sample of powdered LiF that is secured in place in an aluminum frame. Then mount it on the sample stage of the goniometer.

**Note:** The powdered sample of LiF was made by mixing LiF powder with clear fingernail polish, making a thick paste, and quickly filling the paste into the aluminum frame with a clear scotch tape backing to keep it in place.

2. The LiF powder sample is made up of tiny crystals, all randomly oriented with respect to the x-ray beam. Diffraction from any of all the crystals will only be detected for the ones that are oriented correctly to satisfy the Bragg condition, i.e. the angle of incidence of x-rays is equal to the angle of diffracted x-rays. Different orientations that meet the Bragg condition are specified by the Miller indices.
3. Diffraction of x-rays from the powder will be small and dependent on the orientations of the microscopic crystals. As a result, measurement times will need to be much larger. Leaving the operating parameters to be the same as the single crystal, change the time increment to a value that results in the total time being approximately 2 hours. Longer times would result in a better, smoother spectrum, but would be more detrimental to the x-ray tube and would lessen its useful lifetime.
4. Scan the diffraction of x-rays from  $10^\circ$  to  $60^\circ$ . Save your data and copy it to an Excel spreadsheet. The spectrum should look something like the one in Figure 20.

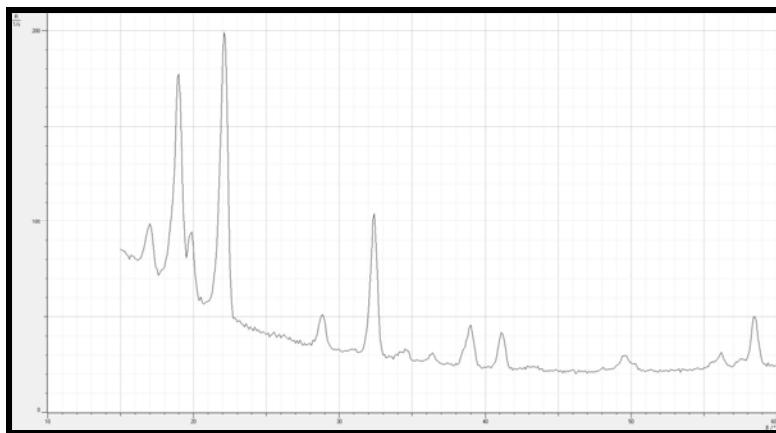


Figure 20. Example of diffraction spectrum of sample of LiF powder.

### Analysis of Results of LiF Powder

1. Label the prominent and other discernable peaks of the x-ray diffraction spectrum and determine the diffraction angle for each one.
2. Prepare an Excel spreadsheet similar to the one shown in Figure 21 and enter the observed peak angle values.

Computed Values of $a_0$ for Measured Values of Theta at Observed Peak Positions								
	Peak Label #	Observed Peak Angle Values	h	k	l	lambda type	Computed $a_0$	
LiF Powder	1					alpha		
	2					beta		
						alpha		
						beta		
						alpha		
	28.61128107	2	2	0	0	beta	4.0755E-10	
						alpha		
						alpha		
						beta		
						alpha		Mean
	11					alpha		Stddev
	12					alpha		Stddev/Mean

Figure 21. Example of Excel spreadsheet for entering peak values and analyzing a LiF powder spectrum.

- The goal of the analysis is to determine the Miller indices, i.e. the crystal orientations, that are responsible for each of the observed peaks. Regardless of the orientation, the crystals all have the same lattice constant and this value can be calculated if the Miller indices are known. The Miller indices can be found by trial and error, but trial guesses can be limited to ones that the theory predicts. In the case of LiF, LiF is a face centered cubic FCC (100) crystal and theory predicts that peaks occur only when h, k, and l are all even or all odd.
- It is suggested that to aid in guessing the correct Miller indices, an Excel spreadsheet like the one in Figure 22 be prepared. This table has combinations of all even values for the Miller indices, h, k, and l, and of all odds values. Note that 0 is an even value for the theory. The theory also predicts that the intensity of diffraction peaks decreases with higher values for the indices and there is no point in trying values higher than 5.

Trial Values of $a_0$ for alpha and beta Cu X-rays for a Single Value of a Peak Diffraction Angle and Selections of All Even and All Odd Values of h, k, and l.								
Experimental Value of theta		h	k	l	$h^2+k^2+l^2$	$a_0$ alpha	$a_0$ beta	
28.61128107	even	0	0	2	4	3.21594E-10	2.88182E-10	
		0	2	2	8	4.54803E-10	4.0755E-10	$a_0$ 4.03E-10
		2	2	2	12	5.57017E-10	4.99145E-10	K_alpha 1.54E-10
		0	0	4	16	6.43188E-10	5.76363E-10	K_beta 1.38E-10
		0	2	4	20	7.19106E-10	6.44394E-10	F_alpha 0.0365429
		2	2	4	24	4.48657E-10	7.05898E-10	F_beta 0.029344
		2	4	4	36	9.64782E-10	8.64545E-10	
		4	4	4	48	1.11403E-09	9.9829E-10	
		0	0	6	36	9.64782E-10	8.64545E-10	
	odd	1	1	1	3	2.78509E-10	2.49573E-10	
		1	1	3	11	5.33303E-10	4.77895E-10	
		1	3	3	19	7.00898E-10	6.28077E-10	
		3	3	3	27	8.35526E-10	7.48718E-10	
		3	3	5	43	1.05442E-09	9.44867E-10	
$a_0 = \lambda * \sqrt{(h^2+k^2+l^2)} / 2 * \sin\theta$ $\lambda = \frac{2a_0}{\sqrt{h^2+k^2+l^2}} \sin\theta$								

Figure 22. Example of an Excel spreadsheet to assist in determining the correct values for the Miller indices for the various peaks in a LiF powder diffraction spectrum.

- The table contains 2 columns for calculating the lattice constant, one for the Cu alpha x-rays and one for the Cu beta x-rays. The table calculates values for the lattice constant  $a_0$  for the

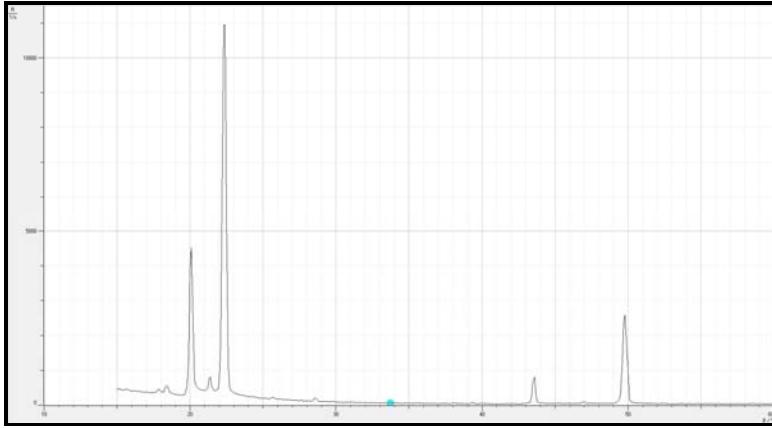
different combinations of the feasible Miller indices, the x-ray wavelength, and the angle position of the diffraction peak. Once an angle value is entered, the spreadsheet calculates a value for each combination and the differing results can be scanned for a lattice constant value that agrees with the previous value determined with the LiF single crystal.

6. The table shows the calculated values for a peak measured at the angle  $28.611^\circ$ . Crystals oriented with Miller indices (220) and diffracted with Cu beta x-rays yield the correct result and are highlighted in green.
7. Determine the Miller indices for all the peaks in your diffraction spectrum and enter your results in your spreadsheet.
8. Using all your results for the lattice constant, determine the average value, standard deviation, and the percent value for the standard deviation divided by the average value.

#### Further Investigations

1. Your instructor can assign additional samples to be measured and analyzed. Samples listed in Table 1 may be assigned. NaCl is another FCC single crystal, but CsCl is a BCC crystal. A powder sample of CsCl would be interesting since the guidelines for determining the Miller indices for BCC crystals at different orientations are different from those of FCC crystals.

THE END



$\beta / ^\circ$        $R_0 / 1/s$

### Notes:

1. LiF is a FCC (100) crystal: *Peaks occur only when  $h, k$ , and  $l$  are all even or all odd.*
2. NaCl is a FCC (100) crystal: Peaks are zero unless  $h, k$ , and  $l$  *are all even or all odd.*
3. CsCl is BC i.e. for  $h+k+l$  being even, the peaks are larger than those for which  $h+k+l$  is odd.
4. KCl is a FCC crystal.
5. For a FCC crystal

### Procedure:

1. Construct Excel Spreadsheet

Computed Values of $a_0$ for Measured Values of Theta at Observed Peak Positions								
	Peak Label #	Observed Peak Angle Values	$h$	$k$	$l$	lambda type	Computed $a_0$	
LiF Powder	1					alpha		
	2					beta		
						alpha		
						beta		
						alpha		
		28.61128107	2	2	0	beta	4.0755E-10	
						alpha		
						alpha		
						beta		
						alpha		Mean
	11					alpha		Stddev
	12					alpha		Stddev/Mean

Trial Values of $a_0$ for alpha and beta Cu X-rays for a Single Value of a Peak Diffraction Angle and Selections of All Even and All Odd Values of h, k, and l.									
Experimental Value of theta		h	k	l	$h^2+k^2+l^2$	$a_0$ alpha	$a_0$ beta		
28.61128107	even	0	0	2	4	3.21594E-10	2.88182E-10		$a_0$ 4.03E-10
		0	2	2	8	4.54803E-10	4.0755E-10		K_alpha 1.54E-10
		2	2	2	12	5.57017E-10	4.99145E-10		K_beta 1.38E-10
		0	0	4	16	6.43188E-10	5.76363E-10		F_alpha 0.0365429
		0	2	4	20	7.19106E-10	6.44394E-10		F_beta 0.029344
		2	2	4	24	4.48657E-10	7.05898E-10		
		2	4	4	36	9.64782E-10	8.64545E-10		
		4	4	4	48	1.11403E-09	9.9829E-10		
		0	0	6	36	9.64782E-10	8.64545E-10		
	odd	1	1	1	3	2.78509E-10	2.49573E-10		
		1	1	3	11	5.33303E-10	4.77895E-10		
		1	3	3	19	7.00898E-10	6.28077E-10		
		3	3	3	27	8.35526E-10	7.48718E-10		
		3	3	5	43	1.05442E-09	9.44867E-10		

$a_0 = \lambda * \sqrt{(h^2 + k^2 + l^2)} / 2 * \sin\theta$        $\lambda = \frac{2a}{\sqrt{h^2 + k^2 + l^2}} \sin\theta$