

## EXPERIMENT 4

### ***POWDER X-RAY DIFFRACTION: STRUCTURAL DETERMINATION OF ALKALI HALIDE SALTS***

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#### **I. Introduction**

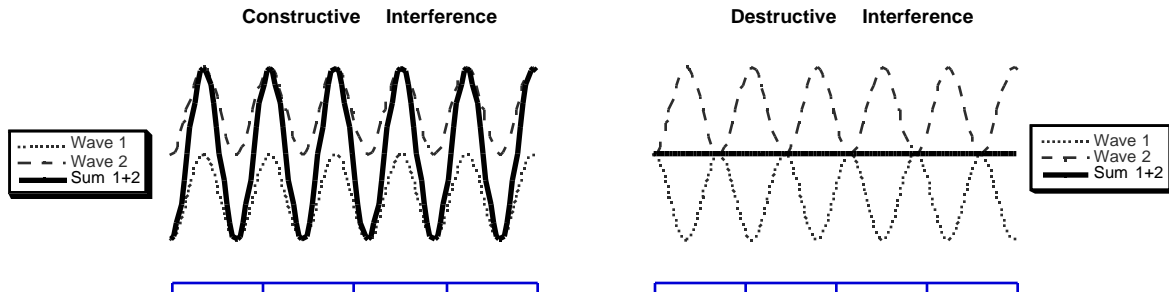
The determination of the chemical structure of molecules is indispensable to chemists in their effort to gain insight into chemical problems. Only a few physical methods are capable of determining chemical structure, and amongst these methods, diffraction methods have been the most successful. Diffraction methods are capable of defining bond lengths, bond angles and the spatial proximity of non-bonded atoms for materials capable of forming crystalline solids. For example, the models of myoglobin which were displayed in the fluoride-myoglobin lab are representations of the myoglobin structure found using x-ray diffraction. The importance of structural determination to science has been recognized with several Nobel Prizes for x-ray diffraction related research.

Year	Prize	Awardee	Topic
1914	Physics	M. Von Laue	Discovery of x-ray diffraction
1915	Physics	W.H. Bragg W.L. Bragg	Analysis of crystal structure using x-ray diffraction
1962	Chemistry	J.C. Kendrew M.F. Perutz	Structural determination of globular proteins (myoglobin and hemoglobin)
1964	Chemistry	D.C. Hodgkin	Structure determinations of important biochemical molecules
1962	Medicine	F.H. Crick J.D. Watson M.H. Wilkins	Structure of DNA
1997	Chemistry	J. Deisenhofer R. Huber H. Michel	Structure of photosynthetic reaction center

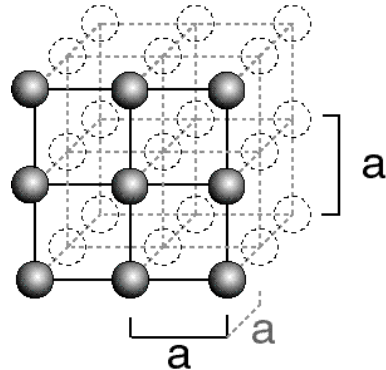
In this final laboratory exercise, you will determine the structure and unit cell dimension of an alkali halide crystal using powder x-ray diffraction, and use the data to construct a chart of ionic radii.

## Experiment 4: X-ray Diffraction

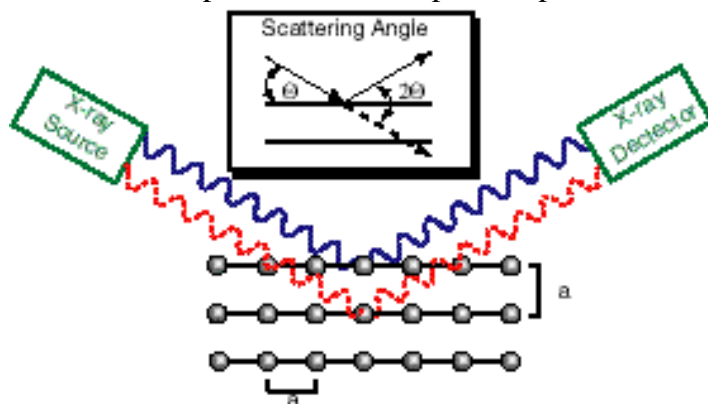
To explain x-ray diffraction it is convenient to think of light as a wave with a wavelength that is related to the energy of the light by the equation,  $E=hc/\lambda$ , where  $h$  is Planck's constant,  $c$  is the speed of light and  $\lambda$  is the wavelength of light. For light within the x-ray region of the spectrum, the wavelength of the light is within the range  $0.1\text{\AA}$  to  $100\text{\AA}$ . One of the fundamental properties of waves is that two waves can interfere with each other if they are in the same spatial region. If the phases of the two waves are coincident they will constructively interfere (increased amplitude) and if their phases are opposed they will destructively interfere (decreased amplitude).



The interference patterns formed in x-ray diffraction originates from the x-rays that are scattered by the electrons of atoms within a crystalline solid. A simple picture of a solid (composed of only one type of atom) is a collection of balls packed together to form a crystal lattice. In a crystalline material the packing of the atoms is well defined, and in fact, the entire crystal can be constructed by repeating a pattern of atoms that define the unit cell (see Chang, chapter 11, Kotz, chapter 13). This is analogous to the fact that a wall can be constructed by stacking bricks; the brick is the unit cell of the wall. The simplest case (the only one that we will consider) is when the unit cell is cubic, that is to say that all of the edges of the cube are equal and the corners form right angles. For cubic unit cells the length of the edge is usually given the symbol 'a'.



Due to the regular spacing of the atoms, imaginary planes can be pictured which contain the nuclei. For example, each face of the cube in the illustration above is one such plane. The electrons of each of these imaginary planes of atoms scatter the x-rays giving a result that can be interpreted as set of parallel partial mirrors; the light (x-rays) is partially



"reflected" by each plane. Although the x-rays originate in-phase from the x-ray source, the scattered x-rays are not necessarily in phase when they emerge from the crystal and reach the detector. The relative phases of scattered x-rays depend critically on the separation distance between these imaginary planes. This is due to the fact that x-rays that penetrate deeper into the

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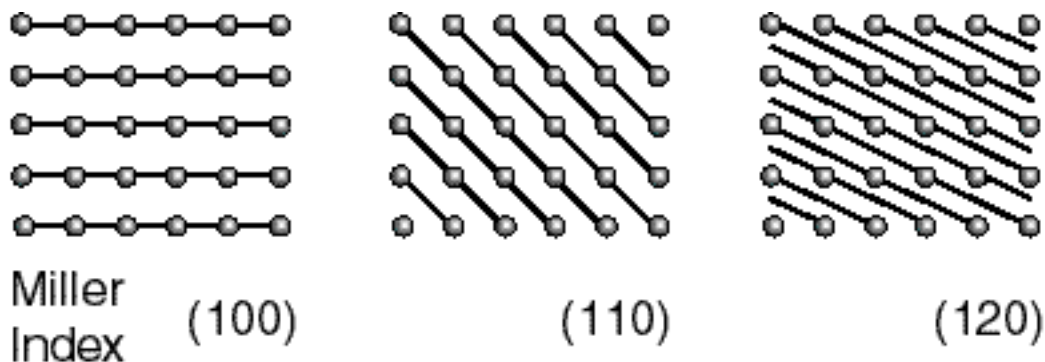
crystal lattice before they are reflected, travel further. Simple geometry demonstrates that for two waves reflected by adjacent planes, the wave that is reflected by the second plane has traveled a distance of  $(2d \sin \theta)$  further than the wave that is reflected by the first plane. In general, the reflected waves from successive planes destructively interfere, however, if the pathlength difference between reflected waves is an integer multiple of the wavelength  $(\lambda)$ , constructive interference is observed (a bright spot). This condition (the Bragg's condition for constructive interference) is summarized by **Bragg's Law**:

$$n\lambda = 2d \sin \theta$$

where  $\lambda$  is the wavelength,  $d$  is the interplanar separation, and  $\theta$  is the **Bragg's angle**. The  $n$  defines the order of the reflection, with  $n=1$  giving first-order,  $n=2$  giving second-order, etc.

From the above equation, it is evident that the structure of the solid (i.e. the distance between the atoms) can be obtained if a monochromatic x-ray source is used (only one  $\lambda$ ) and the intensity of x-rays is measured as a function of  $\theta$ . The constructive interference that results at specific values of theta  $(\theta)$  map out the interplanar spacing of the solid. Further, the total intensity at a spot, not only depends on the fulfillment of the Bragg's condition, but also on the number of electrons, which depends on the chemical identity of the atoms.

There is one further complication however, the planes of atoms can be constructed in several different ways as illustrated below. Each imaginary plane can be indexed using



Miller indices. The Miller index is written as three numbers,  $(h \ k \ l)$ , one for each coordinate in three dimensional space. The protocol for writing these indices are given in the reference<sup>1</sup>, but for now just consider them as labeling scheme for all possible imaginary planes. Each plane can satisfy the Bragg's condition and give a bright spot due to constructive interference. To account for all possible planes, the Bragg's Law is usually rewritten (for a cubic system) as,

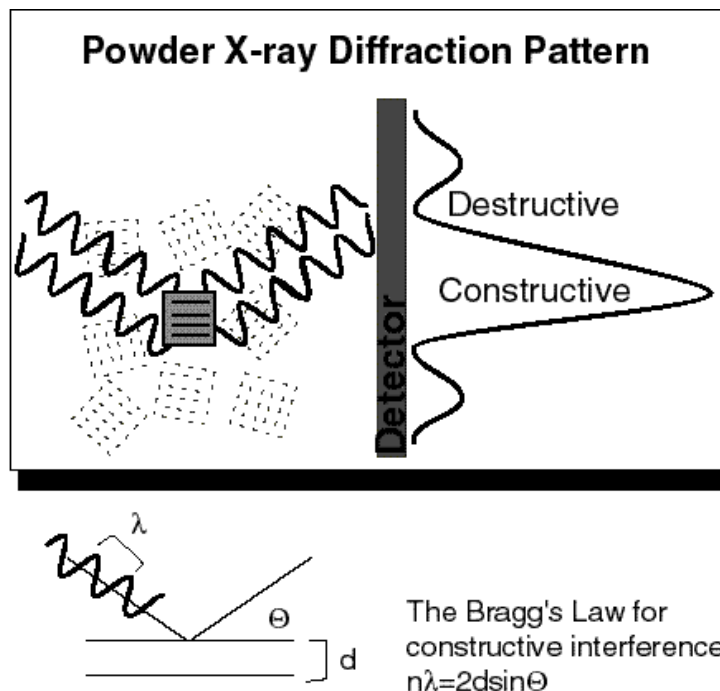
$$\sin^2 \theta = \frac{a^2}{4\lambda^2} (h^2 + k^2 + l^2)$$

<sup>1</sup> Start at the origin of the unit cell, then determine where the point where the plane intersects each of the three axes (a,b,c) of the cell. (abc is used for crystal coordinate rather than xyz) If a plane is parallel to an axis it is assigned an intercept of infinity ( $\infty$ ). The Miller index is form by dividing the cell dimension along each axis (a,b,c), by the intercept to general the Miller indices  $(h,k,l)$  respectively. For example, if the intersection occur half way along a then  $h=a/(a/2)=2$ .

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where  $a$  is the unit cell dimension,  $\lambda$  is the wavelength of the radiation,  $(h, k, l)$  are the Miller indices, and  $\theta$  is the Bragg angle.

In a powder, composed of a very large number of crystallites, all possible orientations of the crystal are simultaneously present. This means that the Bragg's condition for constructive interference will be fulfilled simultaneously for all possible planes consistent with the given crystalline structure. Therefore, a diffraction pattern, intensity as a function of the scattering angle ( $2\theta$ ), is generated and is directly related to the arrangement of atoms within the unit cell as well as to the distances between the atoms.



As you will recall from 4:14 or 4:19 (see Chang, chapter 11, Kotz, chapter 13), ionic solids composed of alkali halides tend to form cubic crystals with either an FCC (face centered cubic) or simple cubic (primitive) unit cell.<sup>2</sup> In this laboratory exercise, you will determine the unit cell structure and unit cell dimension of a series of alkali halide salts. By using the cumulative data of the series you will also determine the cation and anion radii in the lattice. To acquire the data needed to determine these radii, you will use the Chemistry Department's powder x-ray diffractometer (powder XRD) which was purchased in 1996 for ~\$130,000 (needless to say, each student will not have her/his own instrument).

## II. Experimental (groups of four)

The sample preparation and data acquisition for this lab are almost trivial. Each group member will be responsible for one sample from the following set of alkali halides: NaF, NaCl, NaBr, NaI, KCl, KBr, and CsCl. In addition, a powder diffraction pattern of LiCl, will be provided to each group. Each group member should begin her/his numerical analysis on the LiCl data.

Experimental diffraction patterns will be obtained for each of the other samples. The sample preparation consists of grinding the sample in a mortar and pestle and placing a

<sup>2</sup> There is one other variant of the cubic unit cell known as BCC (body centered cubic), but the alkali halides do not crystallize with this structure.

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flattened pile of salt on a glass plate. The plate is then placed into the sample holder and a diffraction pattern is obtained using the wavelength of  $1.5418 \text{ \AA}$  (CuK $\alpha$ , isolated with a Ni foil filter). Your TA or safety monitor will help you with this step. The data will be printed as intensity as a function of scattering angle ( $2\theta$ ). Each set of reflections will be analyzed to determine the structure (primitive or FCC) and the unit cell dimension.

For the simple cubic unit cells, all possible combinations of integer Miller indices are possible. In general for FCC, certain combinations of Miller indices are eliminated by destructive interference caused by the planes formed by the atoms in the faces of the unit cell. The result is that for FCC type lattices reflections occur only if  $h$ ,  $k$ , and  $l$  are all even or all odd. There is one caveat though, in FCC systems in which the scattering power of the two types of atoms is nearly identical (i.e. when the two ions have the same number of electrons) a pseudo-primitive pattern (one that looks primitive) is observed; this is the case for KCl. These results can be used to assign the diffraction patterns and extract the lattice type and cell dimensions from the data.

Simple Cubic ( $h k l$ )	Body Centered Cubic ( $h k l$ )	Face Centered Cubic ( $h k l$ )	$h^2 + k^2 + l^2$
100	—	—	1
110	110	—	2
111	—	111	3
200	200	200	4
210	—	—	5
211	211	—	6
220	220	220	8
221, 300	—	—	9
310	310	—	10
311	—	311	11
222	222	222	12

To correlate the observed Bragg's angle with the predicted values the data must be manipulated to resemble the Bragg's law,  $\sin^2 \theta = \frac{h^2 + k^2 + l^2}{4a^2}$ . This is most easily accomplished using a spreadsheet program such as KaleidaGraph® or Excel®.

- First, enter the position of each reflection and label the column "2-theta".
- Construct a second column that equals  $\sin^2 \theta$ . This is  $c1=(\sin(c0/2))^2$  in KaleidaGraph® (or  $=\text{SIN}(\text{PI}()*A2/360)^2$  in Excel® then fill down).
- Realize that Bragg's law has the form  $\sin^2 \theta = C*i$ , where  $C$  is a constant equal to

$$C = \frac{1}{4a^2} \text{ and } i \text{ is an integer as indicated in the table above. Therefore, divide the}$$

experimental values of  $\sin^2 \theta$  by the  $\sin^2 \theta$  -value of the first reflection ( $c2=c1/\sin^2_{\text{reflection-1}}$ ). If the unit cell is simple cubic, the result of this operation should give an integer series starting with one (see table above). If the unit cell is FCC, the column will need to be multiplied by 3 before the expected integer series is obtained. (There will be some experimental error).

- Once the unit cell type has been established create a column that contains the expected integer values for the appropriate cell type (e.g. 3,4,8,11,12 for FCC).

## Experiment 4: X-ray Diffraction

- Graph  $\sin^2$  vs. the integer column (y vs. x) and fit the result to a straight line to obtain the constant, C.
- Use the wavelength of  $\lambda = 1.5418 \text{ \AA}$  to solve for the constant, 'a' using  $C = \frac{\lambda^2}{4a^2}$ .
- To determine if the constant, 'a', represents the unit cell dimension, half of the unit cell dimension, or twice the unit cell dimension, requires that the density calculated from the cell volume be compared to the actual (macroscopic) density. The simple cubic unit cell contains 1 molecule (AX) and the FCC contains 4 molecules (4 AX). The volume is the cell length cubed, and density is mass divided by volume. The experimental values for density as well as cell parameter data (for comparison to your own) is presented in the table below. You will find that in the case of KCl and CsI the unit cell may need to be contracted or expanded (why are these special cases?).

Salt	$a_0$ (Å)	Density (g/cm <sup>3</sup> )	Molecular Weight (g/mol)	Lattice Type
NaF	Ca. 4.68	2.558	41.99	FCC
LiCl	5.1295	2.068	42.40	FCC
NaCl	5.6405	2.165	58.45	FCC
KCl	6.290	1.984	74.55	FCC (pseudosimple)
CsCl	4.123	3.97	168.37	Simple Cubic
NaBr	5.9732	3.203	102.91	FCC
KBr	6.600	2.75	119.01	FCC
CsI	4.567	4.510	259.83	Simple Cubic (pseudobody-centered)

Data from F.P. Boer, and T.H. Jordan, *J. Chem. Educ.*, **42**, 76 (1965).

- Ionic radii will be calculated following the seminal work of Landé,<sup>3</sup> which was one of the first determinations of the values for ionic radii. Landé assumed that due to the small size of the lithium cation, the unit cell dimension of lithium halides was determined by anion-anion contacts. By inspection of the FCC unit cell, four times the radius of the halide atom is seen to be  $4r_{\text{Cl}} = \sqrt{2}a_0$ . Once this value is set,  $r = 1.81 \text{ \AA}$  in the case of  $\text{Cl}^-$ , other radii can be obtained by assuming that cation-anion contacts determine the edge length. Again inspection of the unit cell leads to the conclusion that:  $a_0 = 2r_{\text{cation}} + 2r_{\text{anion}}$  in the case of FCC and  $\sqrt{3}a_0 = 2r_{\text{cation}} + 2r_{\text{anion}}$  in the case of simple cubic. ( $\text{Br}^-$ , 1.96 Å;  $\text{Na}^+$ , 1.01 Å;  $\text{K}^+$ , 1.34 Å; and  $\text{Cs}^+$ , 1.76 Å)

<sup>3</sup> A. Landé, *Z. Physik*, **1**, 191 (1920).

## Experiment 4: X-ray Diffraction

### Prelab Questions (15 points)

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*Answer these questions in your laboratory notebook.*

1. Go to the Nobel prize web site at the URL, <http://nobel.sdsc.edu/prize/index.html>. For one of the Nobel prizes mentioned in this handout, read any one of the following: presentation/speech, press release or a bibliography of one of the scientist. Write a one-paragraph summary of the historic event or person. (10 points)

2. To obtain the powder diffraction patterns of the alkali halides you will use x-rays of wavelength  $\lambda = 1.54 \text{ \AA}$ . The diffraction pattern will be a plot of x-ray intensity vs. the scattering angle,  $2\theta$ . To better “see” what is going on, go to the Bragg’s Law and Diffraction simulation at: <http://www.journey.sunysb.edu/ProjectJava/Bragg/home.html>

Enter a wavelength of  $\lambda = 1.54 \text{ \AA}$ . Choose on salt: NaF, CsCl, or CsI. Use the table in this handout to the unit cell dimension. (e.g. LiCl is  $a_0 = 5.13 \text{ \AA}$ , do not use this salt, ). Enter the cell dimension into the simulation. Now enter  $5^\circ$  for the beginning angle. Click on the box that says, “details”. Use the greater than sign ( $>$ ) to scan the angle. Record the values of theta that give maximum constructive interference and the value of theta that give maximum destructive interference over the range  $\theta = 5$  to  $35^\circ$ . Mathematically determine the value of theta that gives the first order scattering condition for the salt that you used in the simulation. (5 points)

No purpose or procedure is needed for the pre-lab this week.

### Lab Report (35 points)

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*Your lab report should be completed in your laboratory notebook. Hand in the original to your TA.*

The laboratory report for this lab will consist of all the required calculations, and a brief summary of your results. The report will be turned in at the end of section.

There will also be a short exercise that to determine the line spacing of a diffraction pattern that will also be completed while in the laboratory.