

Diffraction Basics

(prepared by James R. Connolly, for EPS400-001, Introduction to X-Ray Powder Diffraction, Spring 2007)

Introduction

The utilization of X-ray diffraction for crystallographic analysis relies on a few basic principals:

1. When an incident beam of x-rays interacts with a target material (i.e., the specimen), one of the primary effects is scattering (spherical radiation of the incident x-rays without change in wavelength) of those x-rays from atomic scattering centers within the target material.
2. In materials with some type of regular (i.e., crystalline) structure, x-rays scattered in certain directions will be in-phase (i.e., amplified), while most will be out of phase (i.e., attenuated). The process of in-phase scattering is called diffraction.
3. Measurement of the angular relationships between the incident and diffracted x-rays can be used to discern the crystal structure and unit cell dimensions of the target material.
4. The intensities of the amplified x-rays can be used to work out the arrangement of atoms in the unit cell.

For the x-rays to yield useful information about the structure of the analyzed material, the wavelength of the incident x-rays should be of that same order of magnitude as the interatomic spacing in the crystal structure.

In this section we will discuss this process of diffraction and how we make use of it to elucidate the structure of the material(s) in the target. The goal of this section is to give the student sufficient background in the mathematics and crystallography underlying the practice of x-ray diffraction so that understanding of the results of a diffraction experiment will rise above the level of a “black box” technique.

The first part of the material (including the illustrations) in this section is abstracted from Chapter 3 of Nuffield (1966). The remainder of the material (from Bragg’s Law through the reciprocal lattice) is from Jenkins and Snyder (1996) and Bloss (1994). I thank Dr. Cornelis Klein for his suggestions and assistance with this material.

The Geometry of Diffraction

As discussed previously, there are many types of secondary effects that occur when x-rays interact with matter. Fortunately the dominant effect at the energies involved in powder diffraction experiments is *scattering*. In this process, an electron in the path of the x-ray beam vibrates with the frequency of the incoming radiation thus becomes a secondary point source of x-rays of the same energy as the incident x-rays (Fig 3-1). The atom (or its nucleus) is not actually the point source of x-rays, but the electrons surrounding the atom will

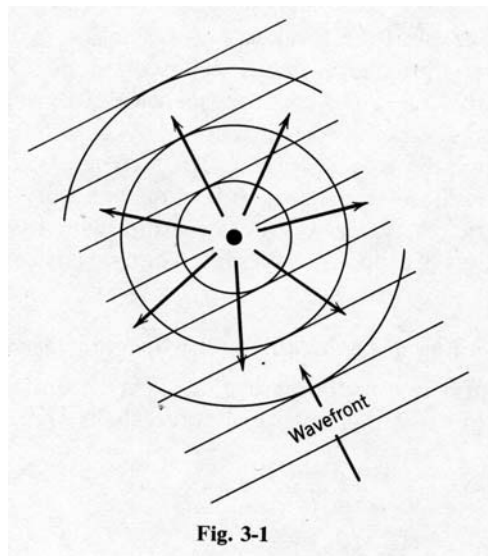


Fig. 3-1

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scatter x-rays that appear to emanate from the center of the atom.

A crystal is a complex but orderly arrangement of atoms and all atoms in the path of an x-ray beam scatter x-rays simultaneously. In general, the scattered x-rays interfere, essentially canceling each other out. In certain specific directions, where the scattered x-rays are “in-phase”, the x-rays scatter cooperatively to form a new wave. This process of constructive interference is *diffraction*.

The directions of possible diffractions depend only on the size and shape of the unit cell. Certain classes of diffraction are systematically extinguished by lattice centering and by certain space-group symmetry elements. The *intensities* of the diffracted waves depend on the kind and arrangement of atoms in the crystal structure. The study of the geometry of the diffraction pattern from a crystal is used to discern the unit cell dimensions, and the missing diffractions yield information about the symmetry of the crystal. The intensities of the diffraction peaks are used to work out the arrangement of atoms.

The Laue treatment of the geometry of diffraction, developed by Max von Laue in 1912, is presented in the following sections because of its geometric clarity and the rigor with which the concepts are treated. As will be discussed, Laue diffraction occurs with polychromatic (i.e., “white”) rather than the monochromatic radiation that we use in powder diffractometry.

Later we will present the Bragg treatment of diffraction that allows diffraction of monochromatic x-rays to be treated as reflection. The Bragg treatment greatly simplifies the mathematics involved in diffraction calculations, and, when combined with the somewhat difficult (but very useful) concept of the reciprocal lattice, simplifies the experimental measurement of a diffraction pattern, thus making diffraction a useful routine tool for crystallographic studies.

Diffraction by a Row of Identical, Equally Spaced Atoms

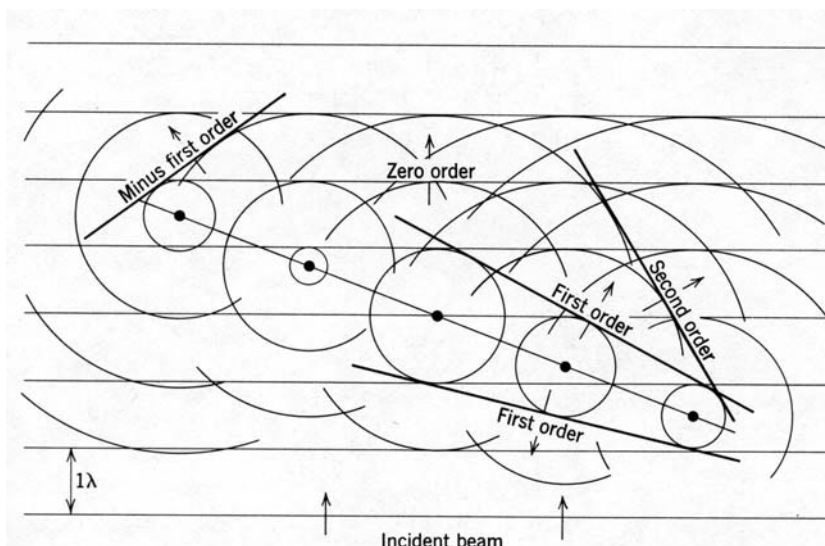


Fig. 3-2. Cooperative scattering by a row of equally spaced, identical atoms.

Consider the hypothetical case of a one-dimensional row of equally spaced atoms. Each atom in the path of an x-ray beam can be considered to be the center of radiating, spherical wave shells of x-rays (Fig 3-2).

In general the scattered waves interfere, cancel out and no diffraction occurs. However, when the scattered waves happen to be in phase, they form wave fronts as

shown in Figure 3-2. Since wavelengths of λ , 2λ and 3λ will all add to produce a different wavefront, we call these first-, second- and third-order wavefronts. By convention,

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wavefronts to the right of the diffracted beam are positive, those to the left are negative (i.e., minus first-order, etc.).

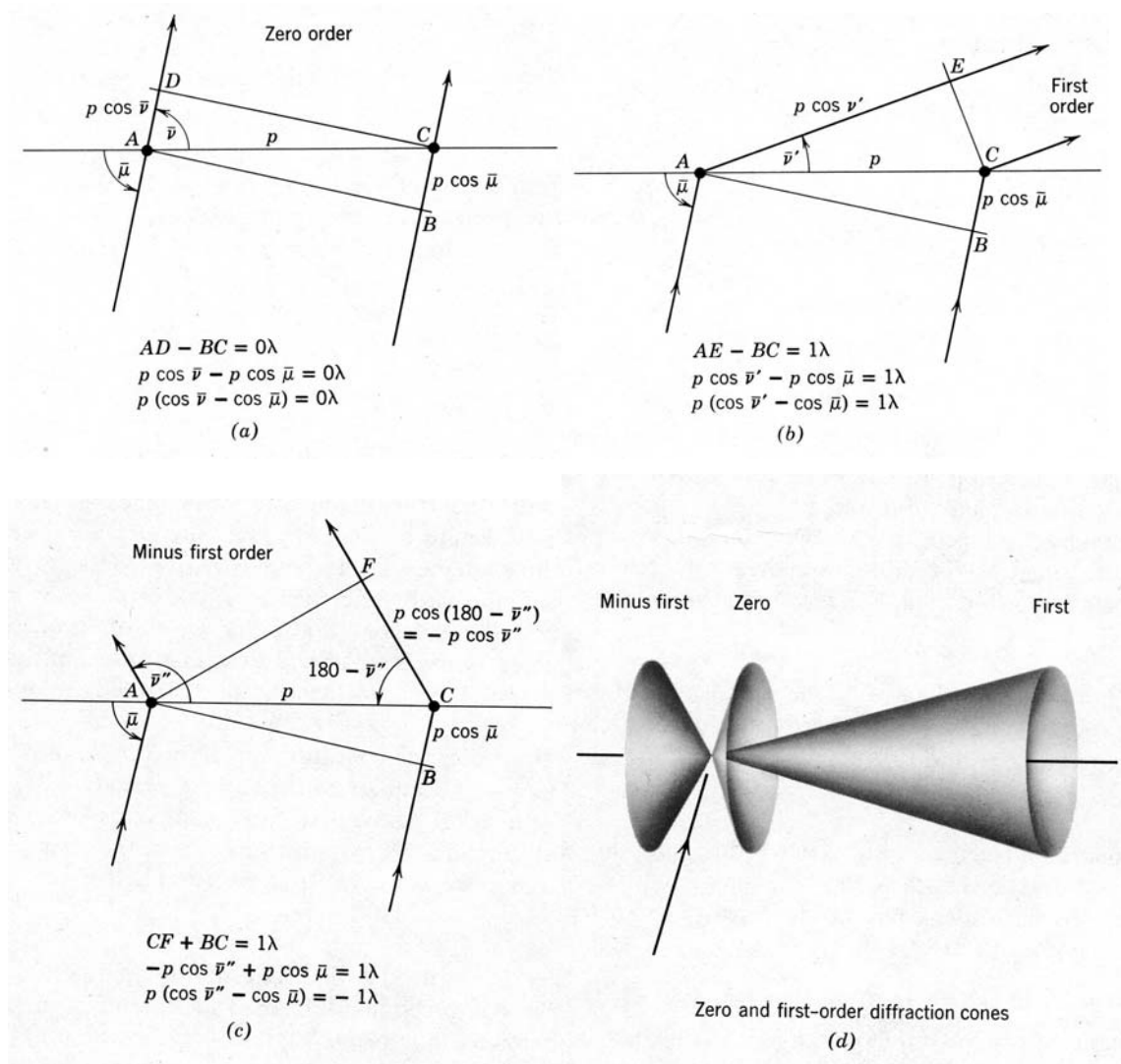


Figure 3-3. Condition for diffraction from a row

Figure 3-3 illustrates the conditions for diffraction from a row of atoms. Two x-rays strike the row of periodicity p , at an angle of incidence $\bar{\mu}$, to form zero-, first- and second-order diffractions. The angle of diffraction, $\bar{\nu}$, is measured from the left (positive) end of the row. The diffracted rays are only in phase if:

$$p(\cos \bar{\nu} - \cos \bar{\mu}) = \pm h\lambda$$

where h is the order of the diffraction, in this case 0 or 1. The condition for diffraction is met not only in the directions AD, AE and AF shown in the diagrams, but in all directions that make angles of $\bar{\nu}$, $\bar{\nu}'$ and $\bar{\nu}''$. These outline three concentric cones as shown in figure 3-3d. The cones define the locus of in-phase scattering (diffraction).

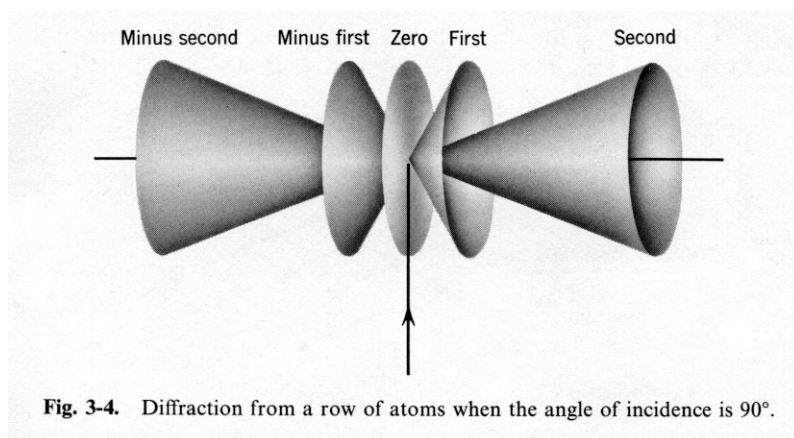
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The expression above is the Laue equation for diffraction by a row. Note that for zero-order diffractions, $h = 0$, and that $\bar{\nu}$ is equal to $\bar{\mu}$. The significance of this is that the incident beam is always a line in the zero-order cone.

When the angle of incidence, $\bar{\mu}$, is 90° , the Laue equation reduces to:

$$p \cos \bar{\nu} = \pm h\lambda$$



Under this condition the angle $\bar{\nu}$ for zero order diffractions is also 90° and the zero-order cone has the shape of a disk. Higher-order cones occur in pairs, symmetrically placed about the zero-order disk (Fig. 3-4)

Diffraction by a Plane Lattice-Array of Atoms

A plane lattice-array of atoms (Fig. 3-5) may be defined by two translation periods, a and b , in the rows OA and OB and the angle γ . Basically this extends the concept of diffraction by a row to include simultaneous diffraction by two non-parallel rows of atoms.

The diffraction directions for the row OA comprise a set of concentric cones coaxial with OA (Fig 3-5b), and have half-apical angles defined by the Laue equation for a row. The directions for the row OB comprise another set of cones (Fig 3-5c) with a different orientation.

When both diffractions are combined, only at the intersection of the diffraction cones will diffraction occur (since the other diffractions will interfere and thus cancel). Those lines of intersection are shown as OX and OY (Fig 3-5d). The Laue equations for diffraction by the plane may be expressed in terms of the Laue equations for the rows OA and OB :

$$a(\cos \bar{\nu}_1 - \cos \bar{\mu}_1) = \pm h\lambda$$

$$b(\cos \bar{\nu}_2 - \cos \bar{\mu}_2) = \pm k\lambda$$

where a and b are periods of the rows
 $\bar{\mu}_1$ and $\bar{\mu}_2$ are the angles at which the beam meets the rows
 $\bar{\nu}_1$ and $\bar{\nu}_2$ are the diffraction angles referred to the respective rows.

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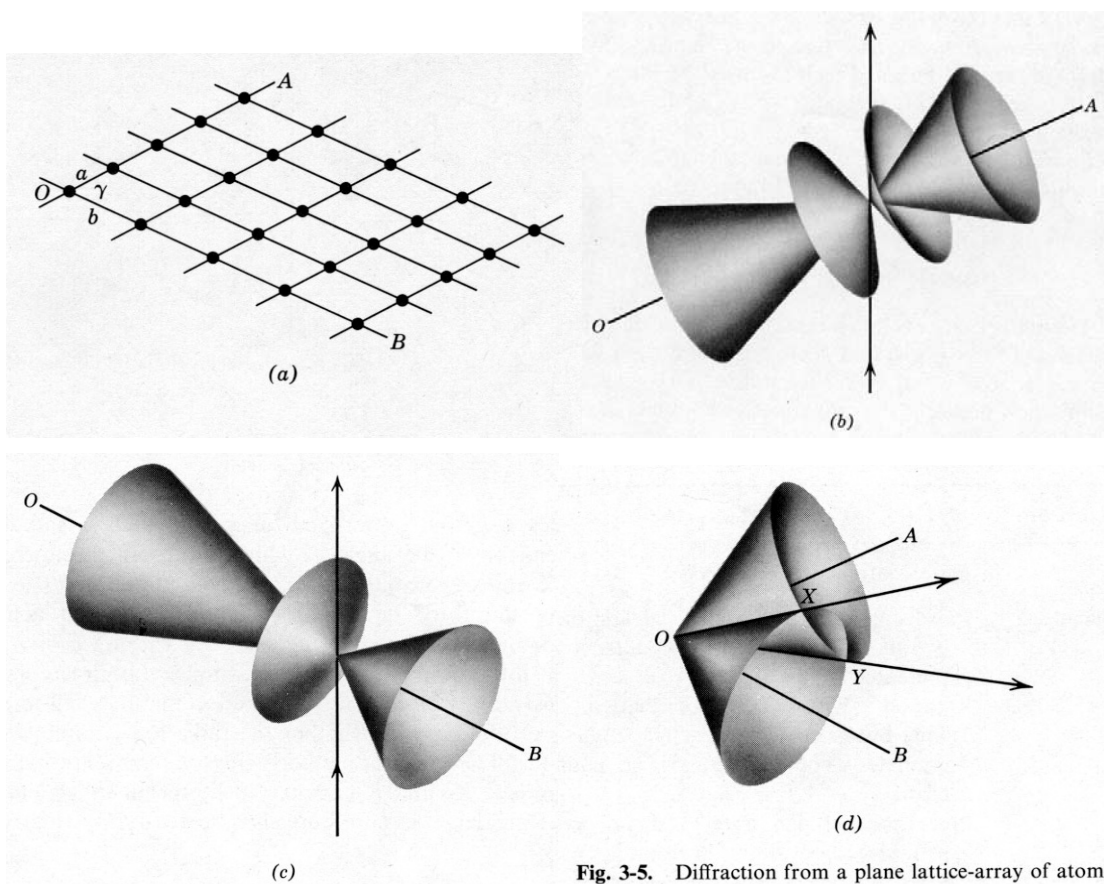


Fig. 3-5. Diffraction from a plane lattice-array of atoms.

Diffraction occurs when the two equations are simultaneously satisfied, i.e., when the angles \bar{v}_1 and \bar{v}_2 define the same direction. As illustrated in Fig 3-5d, when the beam meets the plane at such an angle that the h th-order cone about OA intersects the k th-order cone about OB along OX and OY . The angle between OA and OX (and OY) is \bar{v}_1 and that between OB and OX is \bar{v}_2 .

Diffraction by a Three-Dimensional Lattice-Array of Atoms

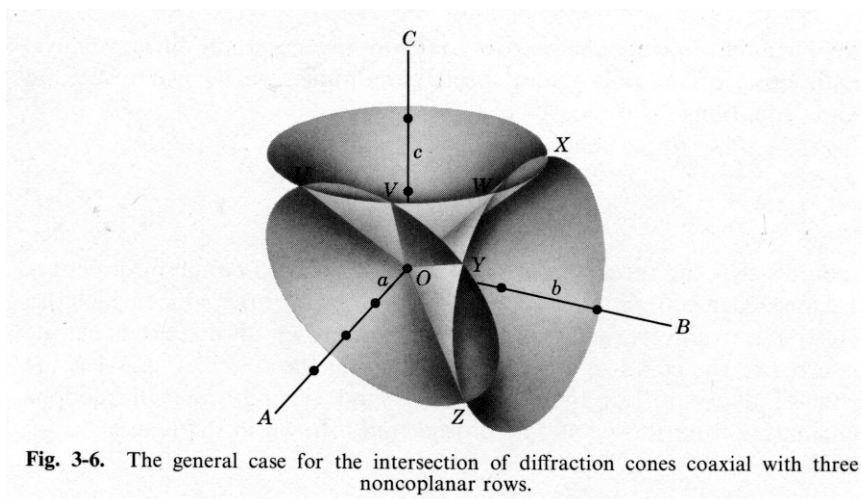


Fig. 3-6. The general case for the intersection of diffraction cones coaxial with three noncoplanar rows.

The diffraction directions for a three-dimensional array may be described by three sets of diffraction cones coaxial with three non-coplanar reference rows (Fig 3-6). In general, each cone will form two diffraction lines by intersection with each of the other two

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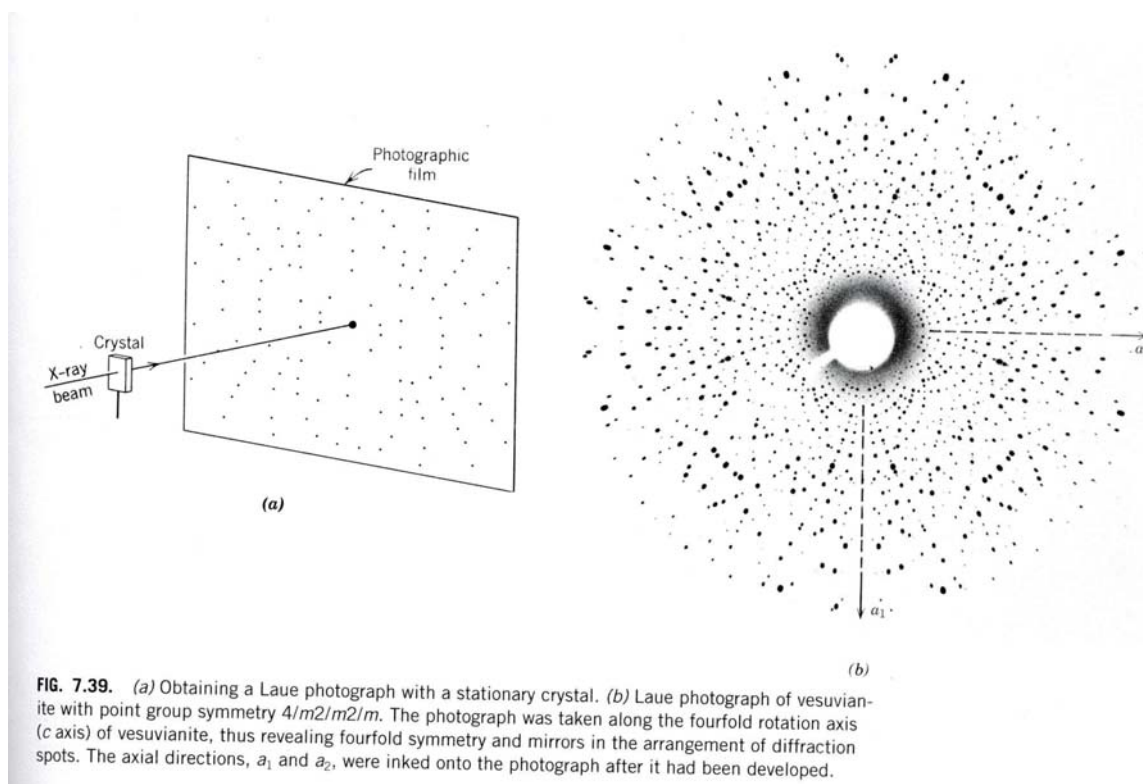
resulting in 6 diffraction lines shown as OU and OV (a-c), OY and OZ (a-b), OW and OX (b-c). For the material to diffract (i.e., interfere constructively) the three diffractions OV , OW , and OY would need to be coincident, a condition satisfied by the following Laue equations only when the diffraction angles, $\bar{\nu}_1$, $\bar{\nu}_2$ and $\bar{\nu}_3$ define a common direction:

$$a(\cos \bar{\nu}_1 - \cos \bar{\mu}_1) = \pm h\lambda$$

$$b(\cos \bar{\nu}_2 - \cos \bar{\mu}_2) = \pm k\lambda$$

$$c(\cos \bar{\nu}_3 - \cos \bar{\mu}_3) = \pm l\lambda$$

The a , b and c directions are fixed (and define the unit cell), thus the $\bar{\nu}$ values depend on $\bar{\mu}$ (the angle at which the beam meets the reference rows) and λ , (the wavelength of the incident radiation). The possibility of satisfying the three equations simultaneously can be increased by varying either $\bar{\mu}$ or λ during analysis. In Laue diffraction, λ is varied by using continuous (or “white”) radiation while keeping the orientation of the crystal ($\bar{\mu}$) fixed. Monochromatic radiation is used in most modern diffraction equipment, so for single crystal analysis the crystal must be progressively moved in the X-ray beam to vary $\bar{\mu}$ sufficiently so that diffractions may be obtained and recorded. Below is a sample Laue diffraction pattern (Fig 7.39 from Klein, 2002).



The table below summarizes the different diffraction methods and the radiation used. Most of this course is concerned with powder methods.

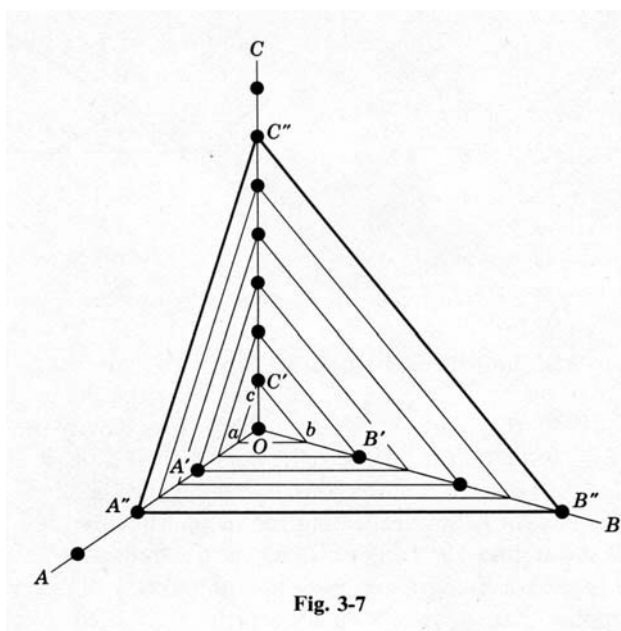
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Radiation	Method
White	Laue: stationary single crystal
Monochromatic	<p>Powder: specimen is polycrystalline, and therefore all orientations are simultaneously presented to the beam</p> <p>Rotation, Weissenberg: oscillation,</p> <p>De Jong-Bouman: single crystal rotates or oscillates about chosen axis in path of beam</p> <p>Precession: chosen axis of single crystal precesses about beam direction</p>

Diffraction as Reflection: The Bragg Law

In 1912, shortly after von Laue's experiments were published, Sir W.L. Bragg discovered that diffraction could be pictured as a reflection of the incident beam from lattice planes. He developed an equation for diffraction, equivalent to the simultaneous solution of the three Laue equations by monochromatic radiation, which allows diffraction to be treated mathematically as reflection from the diffracting planes.



Nuffield's (1966) explanation of the Bragg condition is particularly clear. In Figure 3-7 at left, an x-ray beam encounters a three dimensional lattice-array of atoms shown as rows OA, OB and OC. In this case we assume that the third-order cone about OA, the second-order cone about OB and the first-order cone about OC intersect in a common line to satisfy the Laue condition for diffraction.¹

The x-rays scattered by adjacent atoms on OA have a path difference of three wavelengths, those around OB have a path difference of two wavelengths and those around OC, one wavelength difference. These three points of coherent

scatter define a plane with intercepts $2a$, $3b$, $6c$. The Miller index of this plane (the reciprocal of the intercepts) is (321) . Because A'' , B'' and C'' are six wavelengths out of

¹ Keep in mind that diffraction is not really reflection, but coherent scattering from lattice points, such that each point may be thought of as an independent source of x-rays. Diffraction occurs when the scattered x-rays are in phase.

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phase with those scattered at the origin, they scatter waves that differ by zero wavelengths from one another.

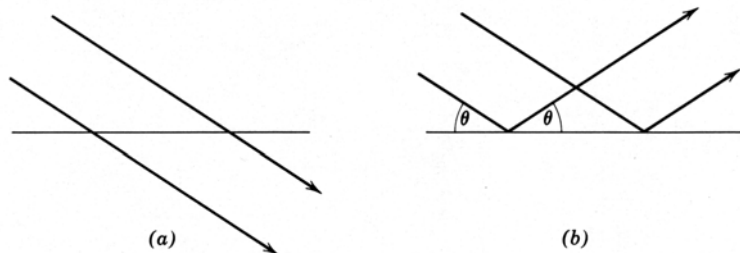


Fig. 3-8. Parallel rays with no difference in path length.

To maintain the same path length (and remain in phase) the rays must pass through the plane (Fig 3-8a) or be deviated at an angle equal to the angle of incidence, θ (Fig 3-8b). Though it is not really reflecting the X-rays, the effective geometry is that of

reflection. Since the lattice is three-dimensional and any lattice point will act as the origin, (321) defines an infinite number of parallel planes that diffract simultaneously. The relationship may be stated as follows: ***A diffraction direction defined by the intersection of the h^{th} order cone about the a axis, the k^{th} order cone about the b axis and the l^{th} order cone about the c axis is geometrically equivalent to a reflection of the incident beam from the (hkl) plane referred to these axes.*** This geometric relation provides the basis for Bragg diffraction. Referring to Figure 3-7, diffraction from each parallel plane shown will be exactly one wavelength out of phase at the proper value of θ .

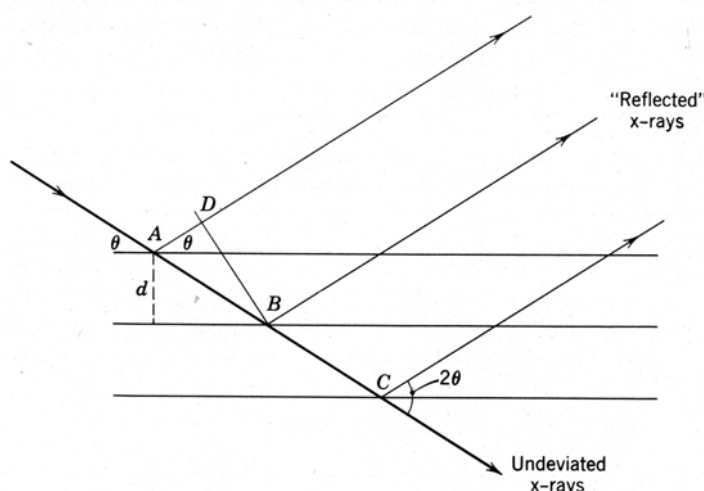


Fig. 3-9. The condition for reflection—the Bragg law.

Figure 3-9 shows a beam of parallel x-rays penetrating a stack of planes of spacing d , at a glancing angle of incidence, θ . Each plane is pictured as reflecting a portion of the incident beam. The “reflected” rays combine to form a diffracted beam if they differ in phase by a whole number of wavelength, that is, if the path difference $AB - AD = n\lambda$ where n is an integer. Therefore

$$AB = \frac{d}{\sin \theta} \quad \text{and}$$

$$AD = AB \cos 2\theta = \frac{d}{\sin \theta} (\cos 2\theta)$$

Therefore:

$$\begin{aligned} n\lambda &= \frac{d}{\sin \theta} - \frac{d}{\sin \theta} (\cos 2\theta) \\ &= \frac{d}{\sin \theta} (1 - \cos 2\theta) = \frac{d}{\sin \theta} (2 \sin^2 \theta) \\ n\lambda &= 2d \sin \theta \end{aligned}$$

The last equation is the Bragg condition for diffraction.

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The value of n gives the “order” of the diffraction. Note that the value of the diffraction angle, θ , will increase as the order of diffraction increases up to the limit where $n\lambda = 2d$. The diagram below (from Bloss, 1994) illustrates this graphically. **A** indicates light reflection from a polished (111) face of an NaCl crystal. **B** indicates diffraction by Cu K α x-rays at successive orders of diffraction, with the first-order diffraction at $\theta = 13.7^\circ$ ($2\theta = 25.4^\circ$). **C** shows the wavelength difference producing the different orders of diffraction. These reflections are commonly referred to as multiples of the Miller index for the planes without the parentheses, i.e., 111, 222, 333, 444, but are represent the same value of d .

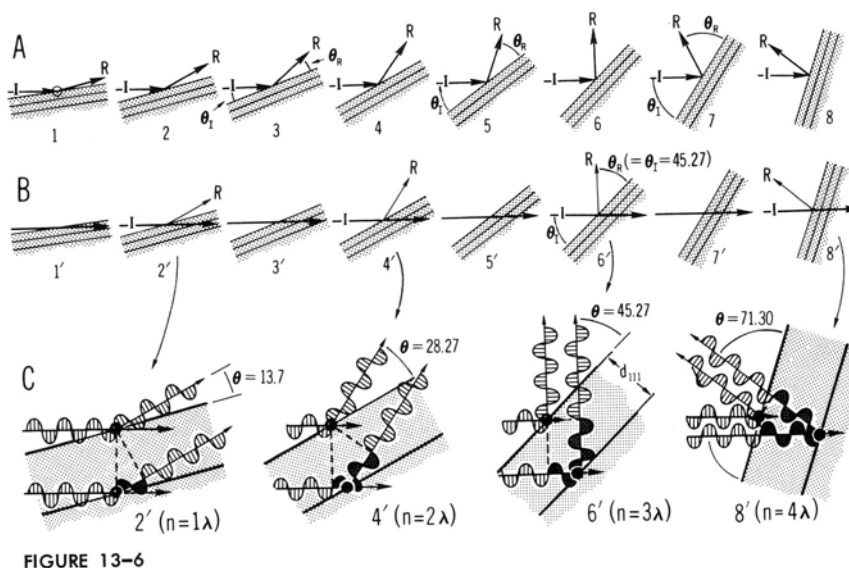


FIGURE 13-6

It can be easily shown that Bragg diffraction occurs in any set of planes in a crystal structure. ***Because of geometrical considerations related to multiple out-of phase diffractions (a.k.a. extinction) in some types of point groups and space groups, not all lattice planes will produce measurable diffractions.*** As will be discussed later, these missing diffractions provide valuable information about the crystal structure.

The Reciprocal Lattice

The most useful method for describing diffraction phenomena has the intimidating name “reciprocal lattice.” It was developed by P.P. Ewald, and is also called “reciprocal space.” It makes use of the reciprocal of d_{hkl} to fabricate a geometrical construction which then serves as a very effective way to understand diffraction effects. Most of the discussion in this section is abstracted from Jenkins and Snyder (1996).

When setting up an arrangement of x-ray source, specimen and detector, it is useful to be able to predict the various motions that will have to be applied to see particular diffraction effects. Consider the diffraction from the (200) planes of a (cubic) LiF crystal that has an identifiable (100) cleavage face. To use the Bragg equation to determine the orientation required for diffraction, one must determine the value of d_{200} . Using a reference source (like the ICDD database or other tables of x-ray data) for LiF, $a = 4.0270 \text{ \AA}$, thus d_{200} will be $\frac{1}{2}$ of a or 2.0135 \AA . From Bragg’s law, the diffraction angle for Cu K α 1 ($\lambda = 1.54060$) will be 44.986° 2θ . Thus the (100) face should be placed to make an angle of 11.03° with the incident x-ray beam and detector. If we had no more complicated orientation problems, then

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we would have no need for the reciprocal space concept. Try doing this for the (246) planes

and the complications become immediately evident.

The orientation problem is related to the fact that the diffracting Bragg planes are inherently three dimensional. We can remove a dimension from the problem by representing each plane as a vector –

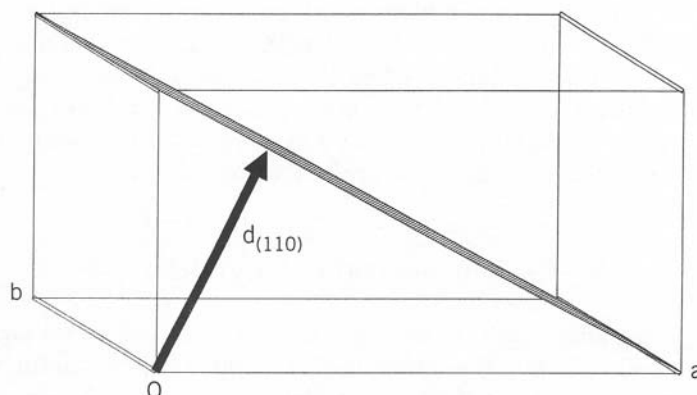


Figure 3.2. Here d_{110} is represented as a vector with magnitude equal to the value of d in angstroms and in the direction from the origin of the unit cell meeting the plane at a right angle.

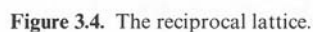
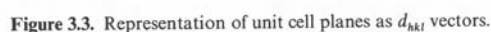
d_{hkl} is defined as the perpendicular distance from the origin of a unit cell to the first plane in the family hkl as illustrated in Figure 3.2. While this removes a dimensional element, it is evident that the sheaf of vectors representing all the lattice planes (see Fig. 3.3 on the following page) will be extremely dense near the center and not ultimately very useful.

Ewald proposed that instead of plotting the d_{hkl} vectors, that the reciprocal of these vectors should be plotted. The reciprocal vector is defined as:

$$\mathbf{d}_{hkl}^* \equiv \frac{1}{d_{hkl}}$$

Figure 3.3 can now be reconstructed plotting the reciprocal vectors instead of the d_{hkl} vectors. Figure 3.4 shows this construction. The units are in reciprocal angstroms and the space is therefore a **reciprocal space**. Note that the points in this space repeat at perfectly periodic intervals defining a space lattice called a **reciprocal lattice**. The repeating translation vectors in this lattice are called \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* . The interaxial (or reciprocal) angles are α^* , β^* and γ^* where the reciprocal of an angle is defined as its complement, or 180° minus the real-space angle. For orthogonal systems the angular relations are quite simple. For non-orthogonal systems (monoclinic and triclinic), they are more complex.

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shape that is directly related to the shape of the of the real-space unit cell. Thus the

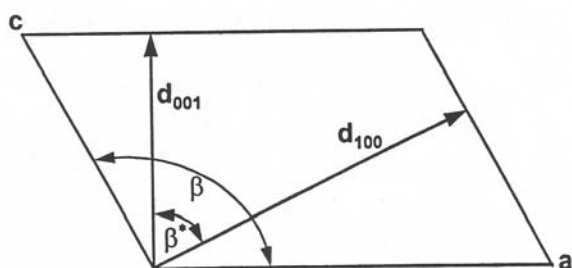
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symmetry of the real space lattice propagates into the reciprocal lattice. Any vector in the lattice represents a set of Bragg planes and can be resolved into its components:

$$d_{hkl}^* = ha^* + kb^* + lc^*$$

In orthogonal crystal systems, the relationship between d and d^* is a simple reciprocal. In non-orthogonal systems (triclinic, monoclinic, hexagonal), the vector character of the reciprocals complicates the angular calculations. The figure at left shows the relations for the



ac plane of a monoclinic unit cell. d_{001} meets the (100) plane at 90° . Because the angle β between the a and c directions is not 90° , the a unit cell direction and the d_{100} are not equal in magnitude or direction, but are related by the sin of the angle between them. This means that the reciprocal lattice parameters d_{100}^* and a^*

will also involve the sin of the interaxial angle.

Table 3.1 (at right) lists the direct and reciprocal space relationships in the different crystal systems. The parameter V shown for the Triclinic system is a complicated trigonometric calculation required for this system because of the absence of 90°

Table 3.1. Direct and Reciprocal Space Relationships

System	a^*	b^*	c^*
Orthogonal	$a^* = \frac{1}{a}$	$b^* = \frac{1}{b}$	$c^* = \frac{1}{c}$
Hexagonal	$a^* = \frac{1}{a \sin \gamma}$	$b^* = \frac{1}{b \sin \gamma}$	$c^* = \frac{1}{c}$
Monoclinic	$a^* = \frac{1}{a \sin \beta}$	$b^* = \frac{1}{b}$	$c^* = \frac{1}{c \sin \beta}$
Triclinic	$a^* = \frac{bc \sin \alpha}{V}$	$b^* = \frac{ac \sin \beta}{V}$	$c^* = \frac{ab \sin \gamma}{V}$

angles. It is derived by Jenkins and Snyder (1994, p. 53) and listed below:

$$V^* = \frac{1}{V} = a^* b^* c^* (1 - \cos^2 \alpha^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \cos \beta^* \cos \gamma^*)^{1/2}$$

The Ewald Sphere of Reflection

Figure 3.6 (following page) shows a cross section through an imaginary sphere with a radius of $1/\lambda$ with a crystal at its center. The reciprocal lattice associated with the crystal's lattice is viewed as tangent to the sphere at the point where an x-ray beam entering from the left and passing through the crystal would exit the sphere on the right. The Ewald sphere contains all that is needed to visualize diffraction geometrically.

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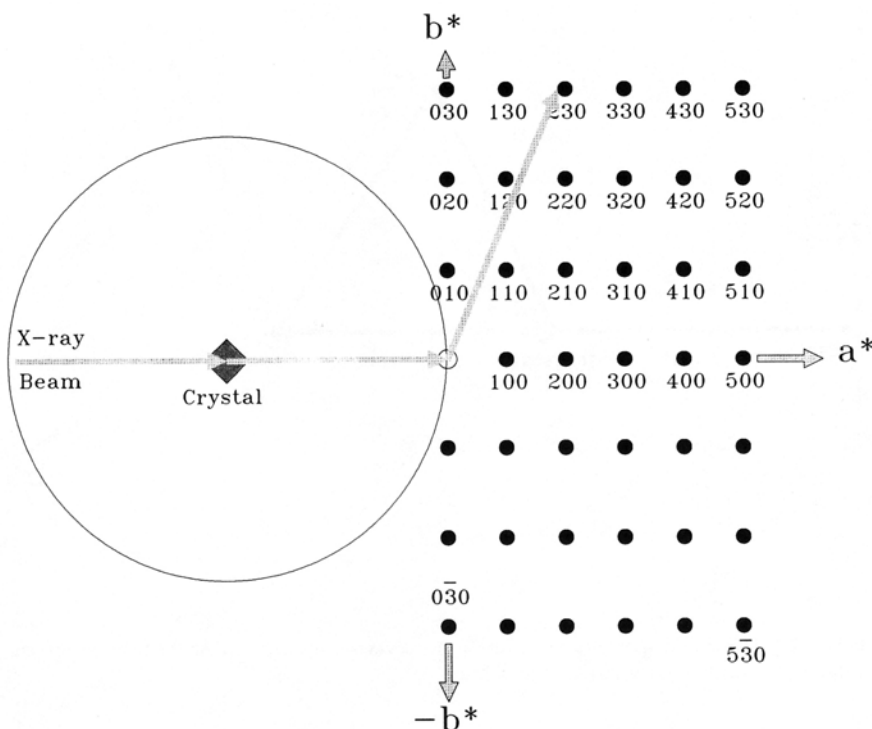


Figure 3.6. The Ewald sphere of reflection with a crystal in the center and its associated reciprocal lattice tangent to the sphere, at the point where the X-ray beam exits.

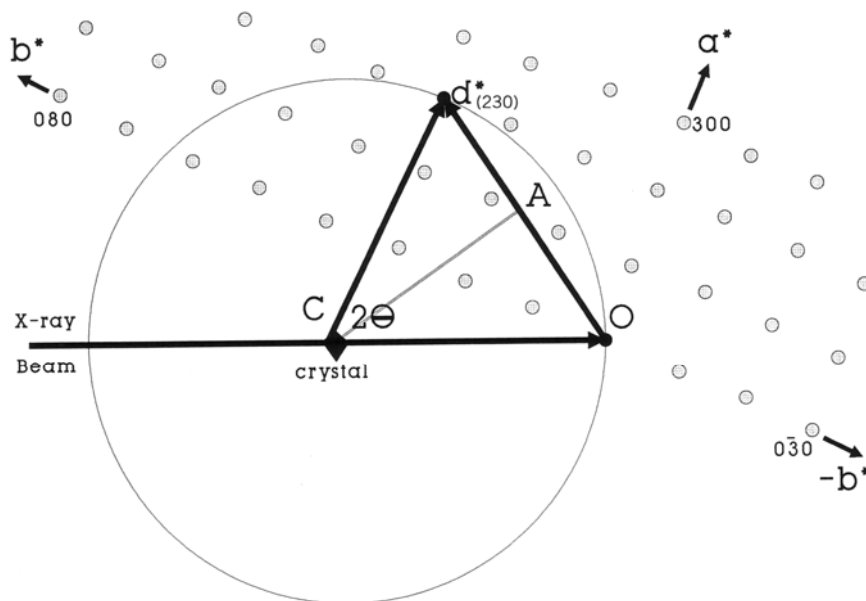


Figure 3.7. The Ewald sphere of reflection with the crystal rotated so that the (230) reciprocal lattice point touches it, permitting it to diffract.

point, representing a \mathbf{d}^* -value, touches the sphere of reflection, the diffraction condition is met and diffraction occurs. In terms of Bragg notation, the real-space lattice plane, represented by \mathbf{d}^* , “reflects” the incident beam. Note that the angle between the incident x-

Rotation of the crystal (and its associated real-space lattice) will also rotate the reciprocal lattice because the reciprocal lattice is defined in terms of the real-space lattice. Figure 3.7 shows this arrangement at a specific time when the (230) point is brought into contact with the sphere. Here, by definition:

$$CO = \frac{1}{\lambda} \text{ and}$$

$$OA = \frac{\mathbf{d}_{(230)}^*}{2} \text{ hence}$$

$$\sin \theta = \frac{OA}{CO} = \frac{\mathbf{d}_{(230)}^* / 2}{1/\lambda}$$

or

$$\lambda = \frac{2 \sin \theta}{\mathbf{d}_{(230)}^*}$$

from the definition of the reciprocal vector:

$$d_{(230)} \equiv \frac{1}{\mathbf{d}_{(230)}^*}$$

therefore:

$$\lambda = 2d_{(230)} \sin \theta$$

which is the Bragg equation.

As each lattice

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ray beam and the diffraction point on the Ewald sphere is 2θ ; this is directly related to the use of 2θ as a measurement convention in x-ray diffraction data.

In the notation of the Ewald sphere, the diffracted intensity is directed from the crystal in the direction of the lattice point touching the sphere. The Ewald sphere construction is very useful in explaining diffraction in a manner that avoids the need to do complicated calculations. It allows us to visualize and effect using a pictorial, mental model, and permits simple analysis of otherwise complex relationships among the crystallographic axes and planes.

The Powder Diffraction Pattern

Methods of single crystal diffraction are not germane to this course. Most of the previous discussions have been in relation to diffraction by single crystals, and most modern methods of single crystal diffractometry utilize automated three-axis diffractometers to move the specimen in a systematic manner and obtain a diffraction pattern.

Most materials are not single crystals, but are composed of billions of tiny crystallites – here called a polycrystalline aggregate or powder. Many manufactured and natural materials (including many rocks) are polycrystalline aggregates. In these materials there will be a great number of crystallites in all possible orientations. When a powder with randomly oriented crystallites is placed in an x-ray beam, the beam will see all possible interatomic planes. If we systematically change the experimental angle we produce and detect all possible diffraction peaks from the powder. Here's how it works in the context of the Ewald sphere:

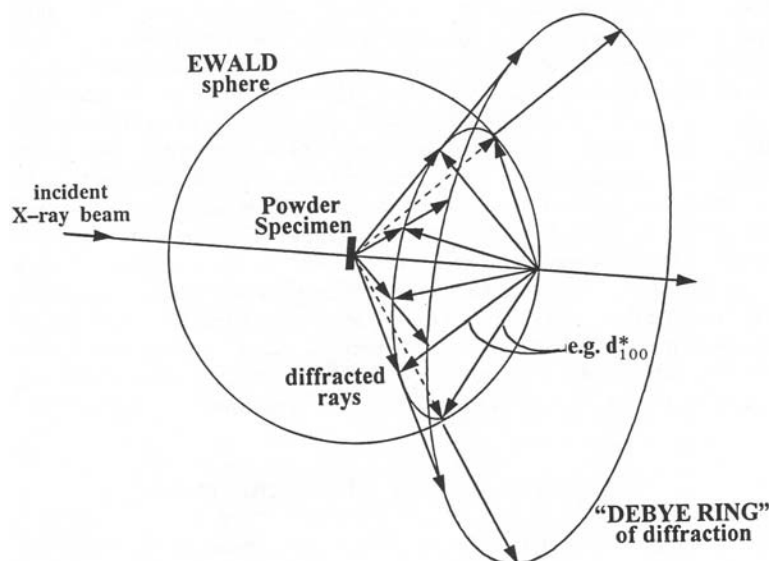


Figure 3.9. The intersection of d_{100}^* vectors from a powder with the Ewald sphere.

- There is a d_{hkl}^* vector associated with each point in the reciprocal lattice with its origin on the Ewald sphere at the point where the direct X-ray beam exists.
- Each crystallite located in the center of the Ewald sphere has its own reciprocal lattice with its orientation determined by the orientation of the crystallite with respect to the X-ray beam.

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The Powder Camera

Figure 3.9 shows this geometry from the d^*_{100} reflection, which forms a sphere of vectors

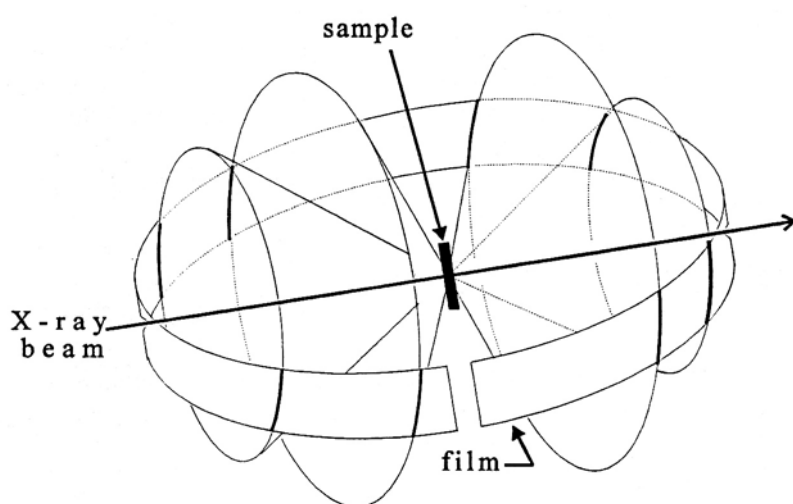
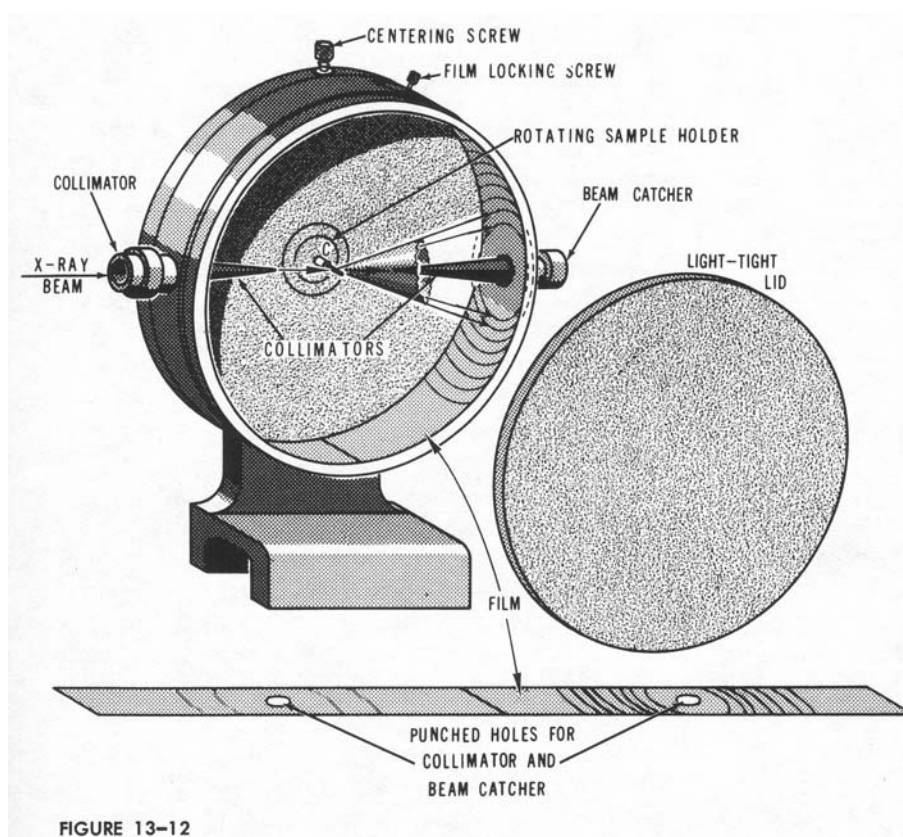


Figure 3.10. The origin of Debye diffraction rings.

emanating from the point of interaction with the beam. The number of vectors will be equal to the number of crystallites interacting with the x-ray beam. The angle between the beam and the cone of diffraction (refer to Fig 3.7) is 2θ . In the diagram at left (Fig 3.10), the diffraction cones from the (100) reflection are shown. In the powder camera, these rings intersect a 360° ring of film, and parts of the

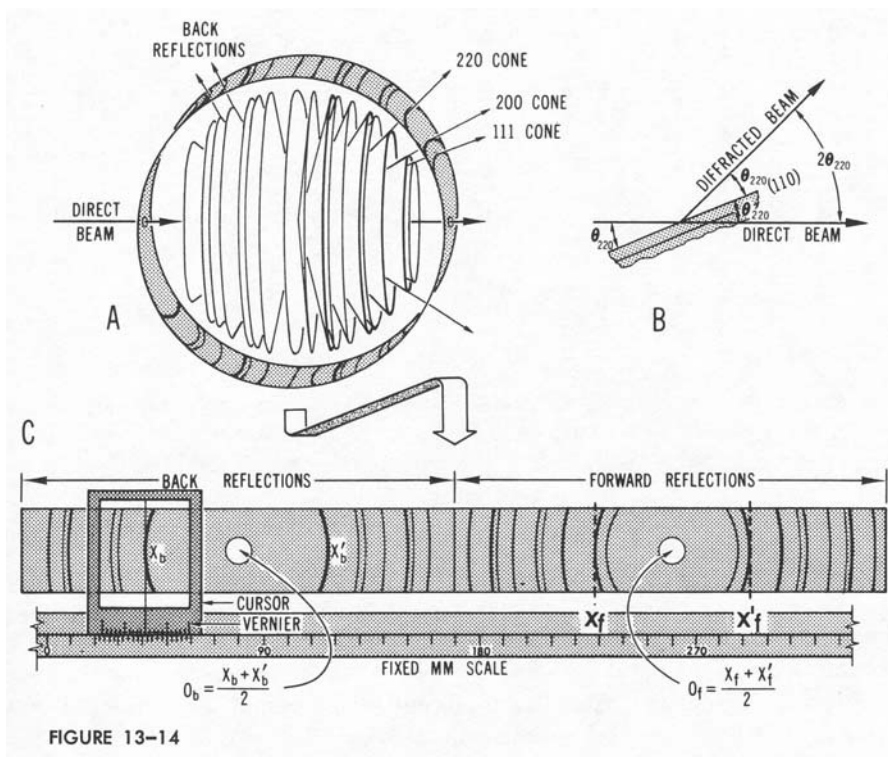
cones are captured on film as Debye rings, producing a Debye-Scherrer diffraction photograph.

Debye-Scherrer powder cameras (illustrated at left) have been largely supplanted in analytical laboratories by automated diffractometers. The powder patterns recorded on film in these devices accurately record the true shape of the diffraction cones produced.



Diffraction Basics

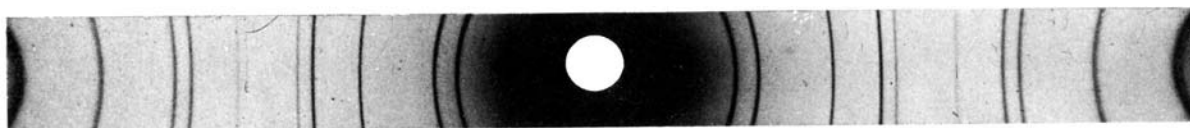
(prepared by James R. Connolly, for EPS400-001, Introduction to X-Ray Powder Diffraction, Spring 2007)



The schematic at left shows the Debye cones that intersect the film in the camera, and how diffractions are measured on the film to determine the d-spacings for the reflections measured.

Two Debye-Scherrer powder camera photographs are shown below. The upper film is gold (Au), a Face centered cubic structure (Fm3m) that exhibits a fairly simple diffraction

pattern.



The film below is of Zircon (ZrSiO_4). Zircon is a fairly complex tetragonal structure ($4/m2/m2/m$) and this complexity is reflected in the diffraction pattern.



The Powder Diffractometer

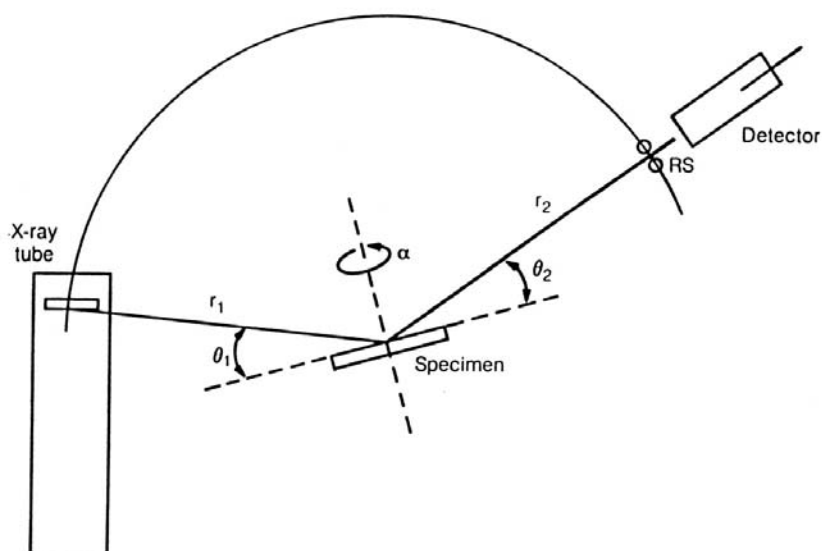
Most modern X-ray diffraction laboratories rely on automated powder diffractometers. While diffractometers differ in the geometry, their purpose is the measurement of the d_{hkl} values and diffraction intensities for powder specimens. In essence, the powder diffractometer is designed to measure diffractions occurring along the Ewald sphere from a powder specimen. It can be thought of as a system for moving through the reciprocal lattice, measuring d-spacings as they occur. By convention (but not by accident – see Fig. 3.7) diffraction angles are recorded as 2θ . We will discuss our Scintag diffractometer in more detail later in this course.

Figure 7.4 (following page from Jenkins and Snyder, 1996) shows the geometry and common mechanical movements in the different types of diffractometers. The table shows the

Diffraction Basics

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diffractometer type, and how the various components move (or don't move). In the table r_1 is the distance between the tube (usually taken as the anode) and the specimen, and r_2 the distance between the specimen and the receiving slit.



Type	Tube	Specimen	Receiving Slit	r_1	r_2
Bragg-Brentano $\theta:2\theta$	Fixed	Varies as θ^*	Varies as 2θ	Fixed	$= r_1$
Bragg-Brentano $\theta:\theta$	Varies as θ	Fixed *	Varies as θ	Fixed	$= r_1$
Seeman-Bohlin	Fixed	Fixed *	Varies as 2θ	Fixed	Variable
Texture Sensitive (Ladell)	Fixed	Varies as θ precesses about α	Varies as 2θ	Fixed	Variable

*Generally fixed, but can rotate about α or rock about goniometer axis.

Figure 7.4. Common mechanical movements in powder diffractometers.

The Seeman-Bolin diffractometer fixes the incident beam and specimen and moves the receiving slit (detector) assembly, varying r_2 with 2θ to maintain the correct geometry.

The Bragg-Brentano diffractometer is the dominant geometry found in most laboratories. In this system, if the tube is fixed, this is called θ - 2θ geometry. If the tube moves (and the specimen is fixed), this is called θ : θ geometry. The essential characteristics are:

- The relationship between θ (the angle between the specimen surface and the incident x-ray beam) and 2θ (the angle between the incident beam and the receiving slit-detector) is maintained throughout the analysis.
- r_1 and r_2 are fixed and equal and define a diffractometer circle in which the specimen is always at the center.

A detailed schematic of this geometry is on the following page (Fig. 7.6 from Jenkins and Snyder).

Diffraction Basics

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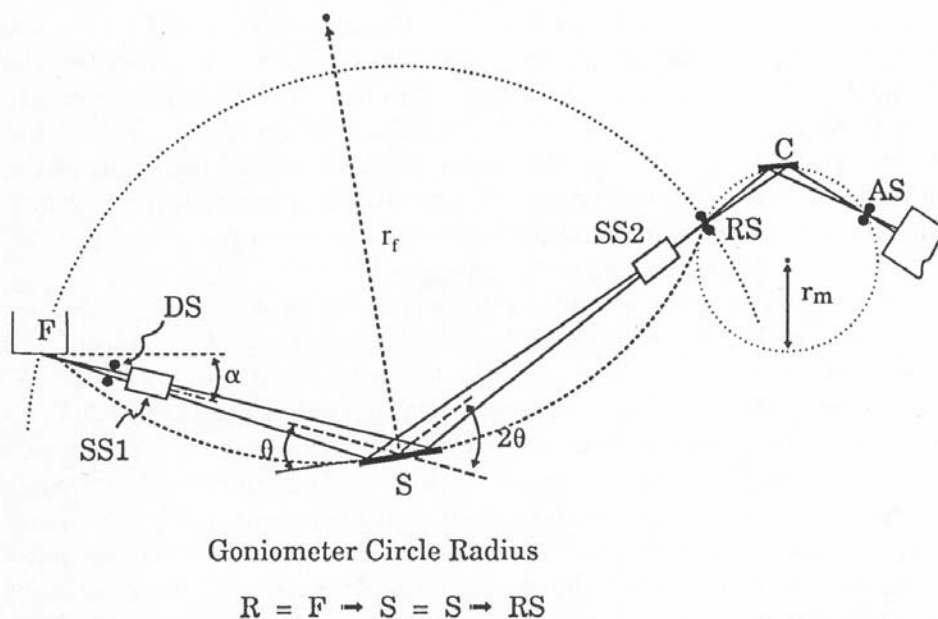


Figure 7.7. Geometric arrangement of the Bragg-Brentano diffractometer.

The arrangement above includes the following elements:

- F – the X-ray source
- DS – the divergence scatter slit
- SS – Soller slit assembly (SS1 on “tube” side, SS2 on detector side), a series of closely spaced parallel plates, parallel to the diffractometer circle (i.e., the plane of the paper), designed to limit the axial divergence of the beam.
- α -- the “take off” angle – the angle between the anode surface and the primary beam
- θ and 2θ are as defined above.
- RS – the receiving slit, located on the diffractometer circle (which remains fixed throughout diffractometer movement)
- C – the monochromator crystal. r_m is the radius of the monochromator circle on which RS, C and AS (the detector slit) lie.
- r_f is the radius of the focusing circle. F, S and RS all fall on this circle. r_f is very large at low θ values and decreases as θ increases.

We will discuss the Bragg-Brentano diffractometer in more detail in subsequent weeks.

Conclusions

This introduction to diffraction has been primarily concerned with development of an understanding of the source of diffraction and understanding how crystalline spacings can be determined experimentally by x-ray diffraction methods.

What is missing in the treatment so far is related to the intensity of diffraction. Basically not all diffractions are created equal – some are much more intense than others and some that one assumes should be present are missing altogether. The source of the variations in intensity of diffraction and the relationship to crystal structure and chemistry will be the topic of Part 2.