

Introduction to X-ray Powder Diffraction

(prepared by James R. Connolly, for EPS400-002, Introduction to X-Ray Powder Diffraction, Spring 2005)

X-Ray Analytical Methods

X-rays were discovered by W.C. Röntgen in 1895, and led to three major uses:

- X-ray radiography is used for creating images of light-opaque materials. It relies on the relationship between density of materials and absorption of x-rays. Applications include a variety of medical and industrial applications.
- X-ray crystallography relies on the dual wave/particle nature of x-rays to discover information about the structure of crystalline materials.
- X-ray fluorescence spectrometry relies on characteristic secondary radiation emitted by materials when excited by a high-energy x-ray source and is used primarily to determine amounts of particular elements in materials.

This course is primarily concerned with the x-ray crystallography of powders. In course materials you will commonly find X-ray Diffraction, X-ray powder diffraction, and the abbreviation XRD used interchangeably. This is intellectually somewhat sloppy, but is also common practice.

Uses of X-Ray Powder Diffraction

The most widespread use of x-ray powder diffraction, and the one we focus on here, is for the identification of crystalline compounds by their diffraction pattern. Listed below are some specific uses that we will cover in this course:

- Identification of single-phase materials – minerals, chemical compounds, ceramics or other engineered materials.
- Identification of multiple phases in microcrystalline mixtures (i.e., rocks)
- Determination of the crystal structure of identified materials
- Identification and structural analysis of clay minerals
- Recognition of amorphous materials in partially crystalline mixtures

Below are some more advanced techniques. Some of these will be addressed in an introductory fashion in this course. Many are left for more advanced individual study.

- Crystallographic structural analysis and unit-cell calculations for crystalline materials.
- Quantitative determination of amounts of different phases in multi-phase mixtures by peak-ratio calculations.
- Quantitative determination of phases by whole-pattern refinement.
- Determination of crystallite size from analysis of peak broadening.
- Determine of crystallite shape from study of peak symmetry.
- Study of thermal expansion in crystal structures using in-situ heating stage equipment.

Introduction to X-ray Powder Diffraction

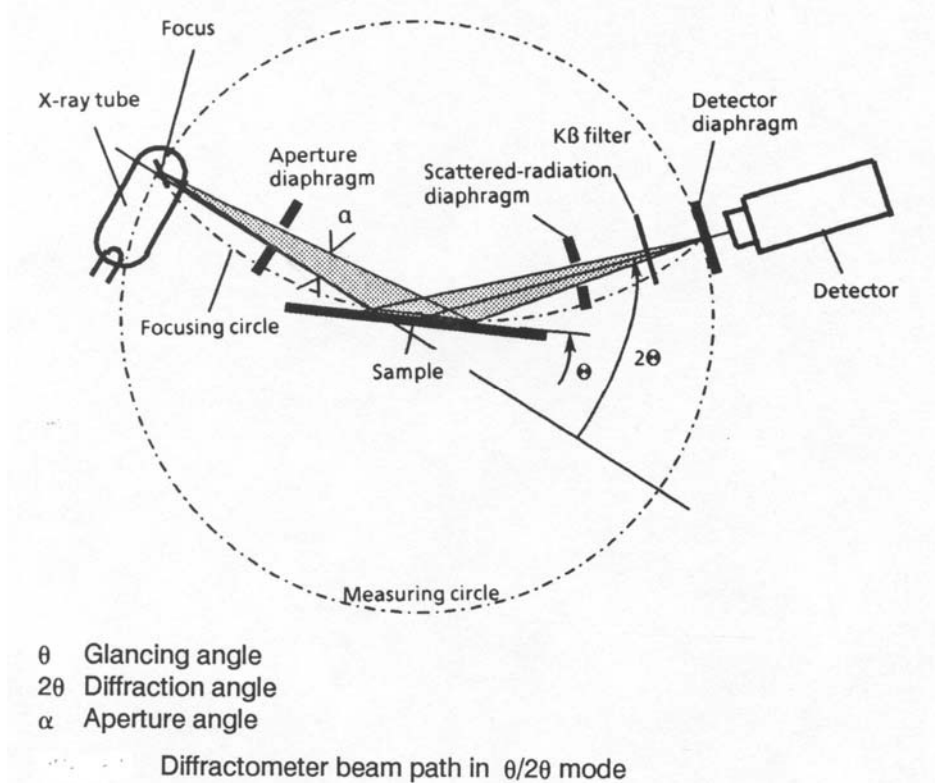
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XRD for Dummies: From Specimen to analyzed sample with minimal math

The physics and mathematics describing the generation of monochromatic X-rays, and the diffraction of those X-rays by crystalline powders are very complex (and way beyond my limited abilities to expound upon them). Fortunately a complete understanding of the mathematics involved is not required to obtain, interpret and use XRD data. What *is* required is a basic understanding of what is happening, how the X-rays interact with your specimen, the sources and nature of possible errors, and what the data tell you about your sample¹.

What follows is a generalized explanation of the process of going from X-rays to diffraction data for math-challenged geologists like me. Some of these processes will be treated a bit more rigorously later in the course. For those who want to delve into the physics of X-ray diffraction, any of the books in the bibliography at the end of this chapter will provide all that you desire (and probably more). The intent here is to provide a conceptual framework for what is happening.

Below is a schematic diagram of a diffractometers system and on the next page is a photograph of our Scintag PAD V goniometer with many of the parts discussed below labeled.



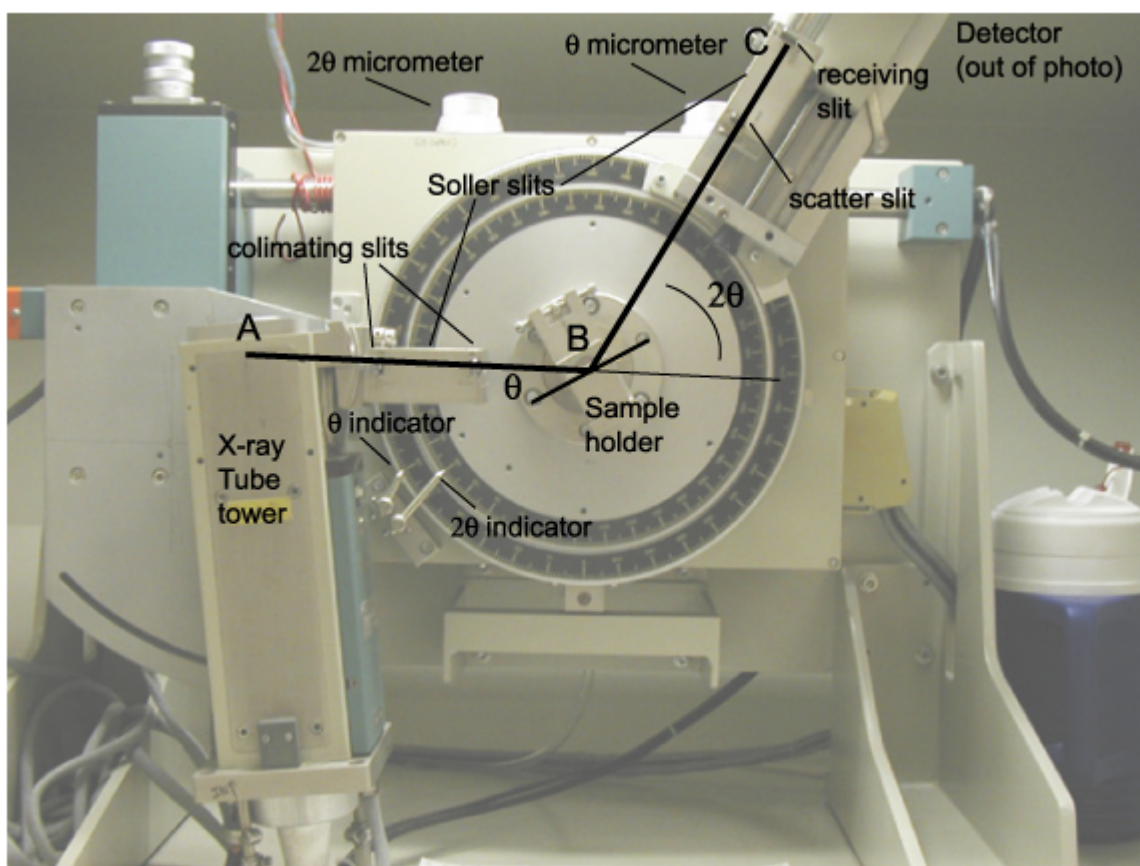
The diagram above is from the Siemens (now Bruker AXS) manual for the D5000 diffractometer. While placement and geometry is somewhat different between different systems, all the basic elements of a Bragg-Brentano diffractometer are present:

¹ It is important to understand the difference between the terms sample and specimen. “Sample” refers to the material, *in Toto*, that you want to analyze. “Specimen” refers to the prepared fraction of your sample which you will be analyzing in a particular diffraction experiment. Though we frequently mix these terms in conversation, this is a very important distinction. An ideal specimen will exactly represent your sample in your experiment; if it does not, it is important to at least understand how it deviates from that ideal.

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- The X-ray tube
- The flat specimen (labeled sample in the diagram)
- The goniometer circle (labeled measuring circle in the diagram) which remains constant through the analysis and is defined by the position of the (Cu) target in the X-ray tube, the center of the sample, and the position of the receiving slit (labeled detector diaphragm) on the detector side.
- The X-ray tube, specimen and receiving slit also lie on the arc of the focusing circle. Unlike the goniometer circle which remains fixed, the radius of the focusing circle is a function of θ - 2θ , with the radius decreasing as θ increases.
- The incident angle θ defined as the angle between the incident beam and the sample, and 2θ defined as the angle between the incident and diffracted beams. The detector is moved (rotated) at twice the angular rate of the sample to maintain the θ - 2θ geometry.
- A filter (on the diffracted beam side) is used (in this example) to remove all but the desired $K\alpha$ radiation from the diffracted beam before it enters the detector.
- A slit (labeled aperture diaphragm) on the incident beam side is used to narrow the beam so that it is confined within the area of the specimen.



The photo above labels the important parts of our Scintag PAD V diffractometer. The following items are noted with differences between the Scintag and Bruker systems.

- The path $AB=BC$ is the radius of the diffractometer circle.
- The tube position is fixed and the θ - 2θ geometry is maintained by rotating the sample holder at $\frac{1}{2}$ the angular rate of the detector.
- There are Soller slits on both the tube and detector side, and two collimating and receiving slits.
- Note the easy-to-read angular indicators and micrometer dials for visually reading θ and 2θ .
- The detector on this system also includes a graphite monochromator adjacent to the scintillation detector (off the photo, top right) eliminating the need for any filters in the system.

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Sample preparation

The Ideal Specimen is a statistically infinite amount of randomly oriented powder with crystallite size less than 10 μm , mounted in a manner in which there is no preferred crystallite orientation.

In this day of automated data collection and analysis, the preparation of your specimen is usually the most critical factor influencing the quality of your analytical data. Sample preparation will be a significant topic in this course.

Generate Analytical X-rays

A coherent beam of monochromatic X-rays of known wavelength is required for XRD analysis

Striking a pure anode of a particular metal with high-energy electrons in a sealed vacuum tube generates X-rays that may be used for X-ray diffraction. By the right choice of metal anode and energy of accelerated electrons, a known wavelength (i.e., energy) or group of wavelengths will dominate the X-rays generated. Copper (Cu) X-ray tubes, for which the wavelength of the strongest radiation ($K\alpha$) is approximately 1.54 angstroms (\AA), are most commonly used for X-ray diffraction of inorganic materials. Other anodes commonly used in X-ray generating tubes include Cr ($K\alpha$ 2.29 \AA), Fe ($K\alpha$ 1.94 \AA), Co ($K\alpha$ 1.79 \AA), and Mo ($K\alpha$ 0.71 \AA).

The full spectrum of radiation produced, and how it is “processed” to get to a (more or less) monochromatic character will be discussed in more detail later. For most X-ray diffraction applications, the closer we can get to monochromatic radiation in our X-ray beam, the better our experimental results will be. The radiation produced in the tube includes $K\alpha_1$, $K\alpha_2$, and $K\beta$ as the highest energy X-rays and a whole host of lower energy radiation. We generally use the $K\alpha$ for our analytical work. The $K\beta$ radiation is generally removed by use of a filter or a monochromator, and the $K\alpha_2$ radiation is removed from the X-ray data electronically during data processing.

Direct the X-rays at a Powdered Specimen

An approximately parallel beam of X-rays is directed at the powdered specimen.

In most powder diffractometers systems a series of parallel plates (soller slits) arranged parallel to the plane of the diffractometer circle and several scatter and receiving slits (arranged perpendicular to the diffractometer circle) are used to create an incident beam of X-rays that are (approximately) parallel. Soller slits are commonly used on both the incident and diffracted beam, but this will vary depending on the particular system. The scatter slits (on the incident beam side) may be varied to control the width of the incident beam that impinges upon the specimen and the receiving slits may be varied to control the width of the beam entering the detector.

Filters for removing $K\beta$ may be located in the beam path on the generator or detector side of the path; a monochromator, if present, is usually located on the detector side between the receiving slit and the detector.

Measure X-Rays “Diffracted” by the specimen and obtain a diffraction pattern

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Interaction of X-rays with sample creates secondary “diffracted” beams (actually generated in the form of cones) of X-rays related to interplanar spacings in the crystalline powder according to a mathematical relation called “Bragg’s Law”:

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

where n is an integer
 λ is the wavelength of the X-rays
 d is the interplanar spacing generating the diffraction and
 θ is the diffraction angle

λ and d are measured in the same units, usually angstroms. We will derive the Bragg law a bit more rigorously later but for a powder specimen in a diffractometer having a statistically infinite amount of randomly oriented crystallites, diffraction maxima (or peaks) are measured along the 2θ diffractometer circle.

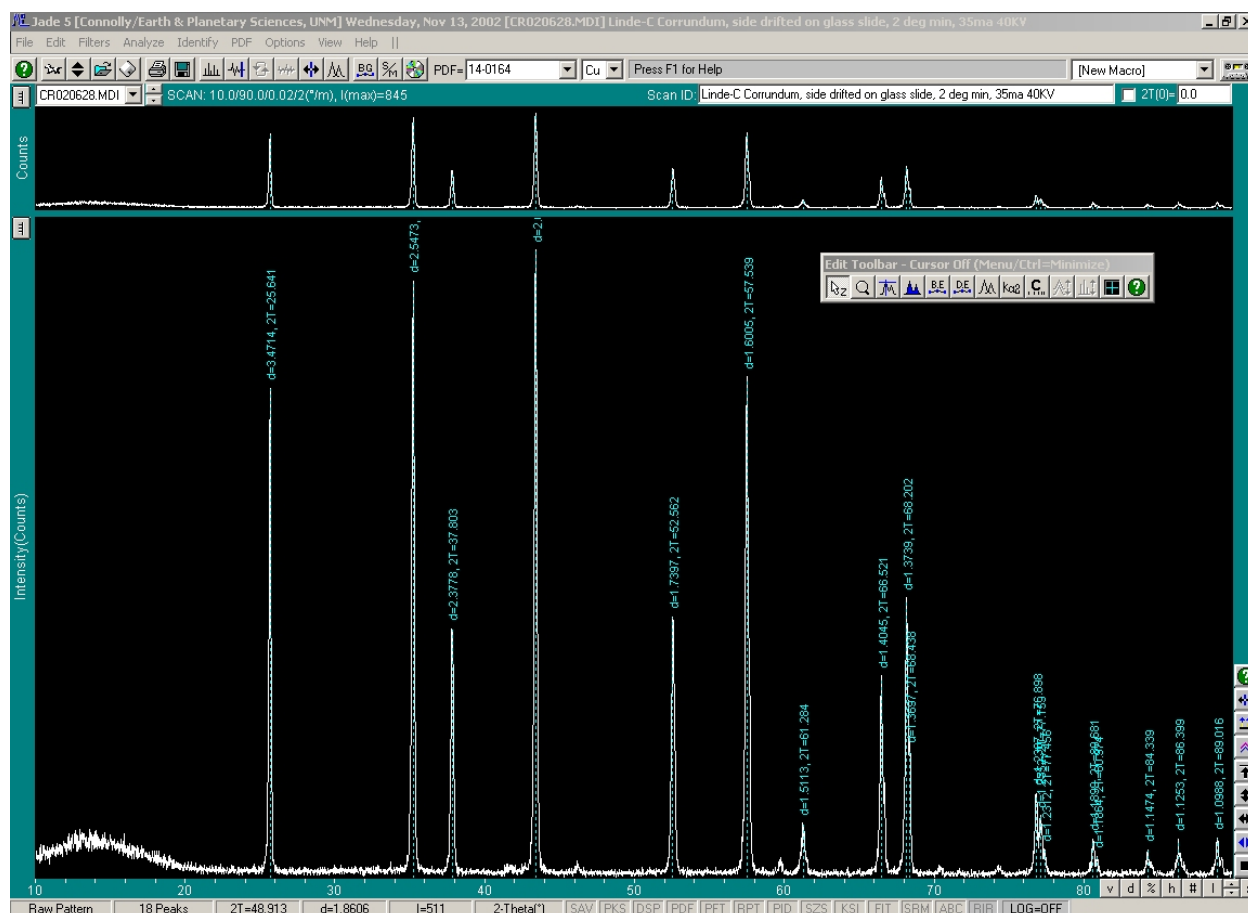
Diffractometers come in two basic varieties: θ - θ in which the X-ray tube and detector move simultaneously or a θ - 2θ in which the X-ray tube is fixed, and the specimen moves at $\frac{1}{2}$ the rate of the detector to maintain the θ - 2θ geometry. Our Scintag PAD V system is a θ - 2θ system; the Siemens D5000 systems located in the Chemistry Department are θ - θ systems. In both systems the essential geometry as shown in the previous diagrams is maintained during data collection.

The “angle” of the diffraction (recorded as 2θ by convention) is related to the interplanar spacing, d , by the Bragg law, and the intensity of the diffraction maximum is related to the strength of those diffractions in the specimen. X-ray data are recorded in terms of 2θ (x-axis) vs. intensity (y-axis).

The angles and intensities of diffractions are recorded electronically using a detector, electronics and specialized software resulting in a plot of 2θ (horizontal axis) vs. intensity (vertical axis) for the specimen. See the sample plot (from MDI Jade 5.0) below:

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Detectors: There are a variety of detectors used in XRD systems. The Scintag system in our laboratory uses a scintillation counter. In the Chemistry XRD lab, the Siemens systems have either scintillation counters or a large-window position sensitive detector or PSD (covering 8° 2 θ simultaneously). Scintillation counters are some of the oldest technology available, but are still widely used because of their relatively low cost, ease of use and durability. Newer detector technologies can deliver improved quality data or deliver it faster, but not without tradeoffs in cost and/or maintenance. We will briefly discuss detector technologies later in the course.

“Legacy” Methods: Before the advent of computerized data collection, X-ray diffraction data were derived by film methods or by diffractometers using paper strip-chart recorders. In both cases, the resultant data were derived by physically measuring peak positions and intensities, and the diffraction data recorded as a list of peaks (in degrees 2 θ) and relative intensities (scaled from 0 to 100). Modern automated diffractometers and the associated automation software collect data electronically, process and calculate it digitally removing much of the tedium from the acquisition of powder XRD data. Some of the “legacy” methods are useful for understanding the process of diffraction, and we will address some of these in this course.

Determine the Crystalline Phases Present in the specimen

For most samples, the aim of the analysis is to identify the crystalline phases present. Even for work where other information is sought (i.e., unit cell calculations, quantitative determinations, etc.), identification of the phase(s) present is usually the first step.

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Phase identification is accomplished by comparing the data (peaks and relative intensities) from your specimen with peaks and relative intensities from a very large set of “standard” data provided by the International Center for Diffraction Data (ICDD). The current release (2004) contains well over 150,000 XRD patterns, both experimental (about 94,000) and calculated (about 59,000), from almost every known inorganic and many organic crystalline substances. In our lab we use Jade (from Materials Data, Inc., a.k.a. MDI) facilitate the access to this massive (and continually growing) database.

Jade includes an automated search-match function that compares the sample pattern with the ICDD database. With good data from a single-phase sample, Jade’s automated search-match program will usually identify the phase successfully with little or no effort on your part. For most two-phase samples identification of the dominant phase will usually be successful, but the second may require more hunting. With three or more phases (and virtually all bulk rocks), some knowledge of the likely constituents will be required to successfully “sleuth” the constituents. Fortunately the ability to visually compare your sample pattern to a large number of possible phases is a manageable task. We will spend considerable laboratory time learning to use this powerful software.

Prior to the advent of automated XRD software like Jade, manual methods required the listing of all the 2θ -intensity values for your sample and the use of paper indexes to identify phases. These methods are rarely used today outside of the classroom environment, but the methodology is useful to understand and will be discussed briefly in this course.

XRD Bibliography

There is a vast literature concerned with X-Ray diffraction many good texts available. Unfortunately, most of the textbooks available are (in your instructor’s opinion) exorbitantly priced, particularly for new users unsure of how they will be using XRD for their research. Rather than specify a particular textbook for this course, we will be using instructor-prepared materials.

The Internet is an excellent resource for information about many aspects of XRD and most of this information is available for free.

For anyone using XRD on a regular basis, investment in a comprehensive text is strongly advised. Below (listed alphabetically by author) are some texts good tutorial/reference materials with annotations:

Bish, D.L., and Post, J.E., eds., 1989, Modern Powder Diffraction, Min. Soc. America Reviews in Mineralogy Vol. 20, 369 p.

This is a surprisingly comprehensive yet very readable volume summarizing powder diffraction. The first four articles alone (on Principles or XRD, Instrumentation, Experimental Procedures, and Sample Prep) are worth the cost of the volume, and there is a lot more. Highly recommended and affordable. (Price \$28 only from Mineralogical Society of America)

Buhrke, Victor E., Jenkins, Ron, and Smith, Deane K., eds., A Practical Guide for the Preparation of Specimens for X-Ray Fluorescence and X-Ray Diffraction Analysis, John Wiley, 333 p.

Expensive but very comprehensive volume on sample preparation methods with

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discussions of sources of errors in analyses of prepared specimens for XRD and XRF. Probably more extensive than required by most XRD users. (Current Retail Price: \$115)

Cullity, B.D. and Stock, S.R., 2001, *Elements of X-Ray Diffraction*, Third Edition, Addison-Wesley, 664 p.

The 2nd edition (1978) was a widely used introductory text in X-ray diffraction. This recent update incorporates more recent developments. (Current Retail Price: \$110)

Guinier, Andre, 1994, *X-Ray Diffraction: In Crystals, Imperfect Crystals, and Amorphous Bodies*, Dover Publications, 378 p.

Opens with a rigorous introduction to diffraction theory using Fourier transforms, and moves into advanced topics in analysis of amorphous bodies, crystals and imperfect crystals. Good advanced text for crystallographers and materials scientists studying complex materials by one of the pioneers. A “bargain” reissue of the original Wiley edition, translated from the 1956 French edition. (Current Retail Price: \$18.95)

Jenkins, Ron and Snyder, Robert L., 1996, *Introduction to X-ray Powder Diffraction*, John Wiley, 403 p.

A good introduction to XRD for new users includes good sections on instrumentation, equipment alignment, specimen preparation, and modern computer-based analytical methods. Much of the training at the ICDD XRD courses is based on material in this volume, and of all the texts this is probably the best general introduction to XRD. (Current Retail Price: \$105)

Klein, Cornelis, 2002, *Mineral Science* (22nd Edition), John Wiley, 641 p.

The classic mineralogy text includes a very succinct discussion of X-ray diffraction. This volume provides the basic framework for the mineral chemistry and crystallography needed to make optimal use of your X-ray diffraction data. The excellent interactive CD-ROM is a crystallography tutorial on its own. This volume should be in every geologist's library. (Current Retail Price: \$102.95; CD-ROM only: \$69.95)

Klug, Harold P., and Alexander, Leroy E., 1977, *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, Second Edition, John Wiley, 966 p.

This book which has not been revised for 25 years, is still the most comprehensive single-volume work on X-ray diffraction, and highly recommended for anyone who will be doing a lot of XRD work or running a laboratory. Unfortunately, the astronomical cost of this volume (which was \$126 ten years ago) puts it out of the range of most students. (Current Retail Price: \$325)

Moore, Duane E., and Reynolds, Robert C., Jr., 1997, *X-Ray Diffraction and the Identification and Analysis of Clay Minerals*

Indispensable and (still) affordable volume which should be owned by anyone planning to do analyses of clay minerals by XRD. Chapters 2 and 3 contain a very lucid introduction to the X-rays and diffraction processes; the rest of the volume is very specific to the preparation, analysis and structure of clay minerals. (Current Retail Price: \$49.95)

Nuffield, E.W., 1966, *X-ray Diffraction Methods*, John Wiley & Sons, 408 p.

This out-of-print volume is a comprehensive, classic text on X-ray diffraction. Contains thorough, mathematically rigorous yet understandable discussions of diffraction

Introduction to X-ray Powder Diffraction

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phenomena and is still an excellent reference text. (Check Barnes & Noble – <http://www.bn.com> – used booksellers for availability. I got a copy at Powell's books in Portland, Oregon for \$18 plus shipping.)

Pecharsky, V.K. and Zavalij, P.Y., 2003, Fundamentals of Powder Diffraction and Structural Characterization of Materials, Kluwer Academic Publishers, 713 p. and CD ROM. This new volume focuses on XRD data acquired from conventional sources (i.e., the equipment we have in our lab), and how to make the most of that data using modern computerized methods of data analysis. The first three chapters cover the basics (crystallography, diffraction, and experimental methods) in a comprehensive and rigorous manner. The balance of the text covers data analysis, unit cell determination and refinements, and crystal structure determination and refinements. The CD includes all the figures from the book in a variety of formats, solutions to problems in the chapters and links to related websites. Overall a great book, if somewhat advanced for an introductory class. (Current Retail price: \$163)