X-RAY DIFFRACTION TECHNIQUES (XRD)

Ever since the discovery of X-rays by Wilhelm Conrad Roentgen in 1895, and the first application of an X-ray experiment to the study of crystalline material in 1912 by Max von Laue (see p. 7), X-ray diffraction techniques have been fundamental to crystal structure analysis. All that is now known about the location of atoms, their sizes, and their bonding in crystal structures—as well as our knowledge of a structure’s space group symmetry and chemical composition of its unit cell—has been derived largely from X-ray diffraction studies. X-ray crystallography is a science that is pursued by researchers with a broad knowledge base in mathematics, physics, chemistry and computational skills.

This section of the text briefly introduces X-rays and their diffraction effects, and then there is a short overview of crystal structure analysis, using single-crystal techniques and an introduction to the X-ray powder diffraction method, which is routinely used in mineral identification. Powder diffraction equipment is generally available in most Geology departments and this identification method is especially powerful in the study of minerals (and other materials) that are too fine-grained to be evaluated by optical microscope techniques. Examples of such materials are members of the clay mineral and zeolite groups.

**X-Ray Spectra**

Electromagnetic waves form a continuous series varying in wavelength from long radio waves with wavelengths of the order of thousands of meters to cosmic radiation whose wavelengths are of the order of $10^{-12}$ meters (a millionth of a millionth of a meter). All forms of electromagnetic radiation have certain properties in common, such as propagation along straight lines at a speed of 300,000 km per second in a vacuum, reflection, refraction according to Snell’s law, diffraction at edges and by slits or gratings and a relation between energy and wavelength given by the Einstein equation:

$$E = hv = hc/\lambda$$

where $E$ is energy, $v$ frequency, $c$ velocity of propagation, $\lambda$ wavelength, and $h$ Planck’s constant. Thus, the shorter the wavelength the greater its energy and the greater its powers of penetration. X-rays occupy only a small portion of the spectrum, with wavelengths varying between slightly more than 100 Å and 0.02 Å (see Fig. 7.31). X-rays used in the investigation of crystals have wavelengths of the order of

<table>
<thead>
<tr>
<th>Wavelength in centimeters</th>
<th>300,000</th>
<th>30</th>
<th>$3 \times 10^{-2}$</th>
<th>$3 \times 10^{-5}$</th>
<th>$3 \times 10^{-8}$</th>
<th>$3 \times 10^{-11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Radio waves</td>
<td>Infrared</td>
<td>Ultraviolet</td>
<td>X-rays</td>
<td>Gamma rays</td>
<td>Cosmic rays</td>
</tr>
</tbody>
</table>

**FIG. 7.30.** Photomicrograph of a polished section of opaque minerals from Balam, New York, as obtained with a reflecting light microscope. The minerals are: white, pyrite; light gray with triangular pits, galena; dark gray, sphalerite. (Courtesy of Charles Grocetti, Harvard University.)
In a modern X-ray tube there is nearly a complete vacuum. The tube is fitted with a tungsten filament as a cathode that provides the source of electrons. The anode consists of one of a number of metals such as Mo, Cu, or Fe, and acts as the target for the electrons. When the filament is heated by passage of a current, electrons are emitted which are accelerated toward the target anode by a high voltage applied across the tube. X-rays are generated when the electrons impact on the target (anode). The nature of the X-rays depends on the metal of the target and the applied voltage. No X-rays are produced until the voltage reaches a minimum value dependent on the target material. At that point a continuous spectrum is generated. With increasing potential, the intensity of all wavelengths increases, and the value of the minimum wavelength becomes progressively less (Fig. 7.33a). The continuous spectrum, also referred to as white radiation, is caused by the stepwise loss of energy of bombarding electrons in series of encounters with atoms of the target material. When an electron is instantaneously stopped, it loses all of its energy at once and the X-ray radiation emitted is that of the shortest wavelength (see Fig. 7.33a). The stepwise energy losses from a stream of electrons produce a continuous range of wavelengths that can be plotted as a smooth function of intensity against wavelength (Fig. 7.33a). The curve begins at the short wavelength limit, rises to a maximum, and extends toward infinity at very low intensity levels.

If the voltage across the X-ray tube is increased to a critical level, which is dependent on the element
of the target, there becomes superimposed on the continuous spectrum a line spectrum of characteristic radiation peculiar to the target material. This characteristic radiation, many times more intense than the continuous spectrum, consists of several isolated wavelengths, as shown in Fig. 7.33b by β and α peaks.

The characteristic X-ray spectrum is produced when the bombarding electrons have sufficient energy to dislodge electrons from the inner electron shells in the atoms of the target material. When these inner electrons are expelled, they leave vacancies that are filled by electrons from surrounding electron shells. The electron transitions, from outer to inner shells, are accompanied by the emission of X-radiation with specific wavelengths. Electron transitions from the L- to the K-shell produce Kα radiation, and those from the M- to the K-shell cause KB radiation (see Fig. 7.54). The KB peak can be eliminated by an appropriate filter yielding essentially a single wavelength, which by analogy to monochromatic light is called monochromatic X-ray. The Kα radiation consists of two peaks, Kα1 and Kα2, which are very close together in wavelength.

The wavelengths of the characteristic X-radiation emitted by various metals have been accurately determined. The Kα wavelengths (weighted averages of Kα1 and Kα2) of the most commonly used metals are:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Wavelength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdenum</td>
<td>0.7107</td>
</tr>
<tr>
<td>Copper</td>
<td>1.5418</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1.7902</td>
</tr>
<tr>
<td>Iron</td>
<td>1.9373</td>
</tr>
<tr>
<td>Chromium</td>
<td>2.2909</td>
</tr>
</tbody>
</table>

**Diffraction Effects and the Bragg Equation**

Crystals consist of an ordered three-dimensional structure with characteristic periodicities, or identity periods, along the crystallographic axes. When an X-ray beam strikes such a three-dimensional arrangement, it causes electrons in its path to vibrate with a frequency of the incident X-radiation. These vibrating electrons absorb some of the X-ray energy and, acting as a source of new wave fronts, emit (scatter) this energy as X-radiation of the same frequency and wavelength. In general, the scattered waves interfere destructively, but in some specific directions they reinforce one another, producing a cooperative scattering effect known as diffraction.

In a row of regularly spaced atoms that is bombarded by X-rays every atom can be considered the center of radiating, spherical wave shells (Fig. 7.34). When the scattered waves interfere constructively, they produce wave fronts that are in phase, and diffraction will occur. Figure 7.35 illustrates that rays 1 and 2 will be in phase only when distance AB represents an integral number of wavelengths—in other words, when \( AB = n\lambda = c \cos \phi \) (where \( n \) represents whole numbers such as 0, 1, 2, 3, . . . , \( n \)). For a specific value of \( n\lambda \), \( \phi \) is constant, and the locus of all possible diffracted rays will be represented by a cone with the row of scattering points as the central axis. Because the scattered rays will be in phase for the same angle \( \phi \) on the other side of the incident beam, there will be another similar but inverted cone on that side (see Fig. 7.36). The two cones with \( n = 1 \) would have \( \phi \) (as in Fig. 7.36) as the angle between the cone axis and the outer surface of the cone. When \( n = 0 \), the cone becomes a plane that includes the incident beam. The greater the value of \( n \)
cones in Fig. 7.6 can be expressed by three independent equations (the Laue equations) in which the three cone angles \( \phi_1, \phi_2, \) and \( \phi_3 \) define a common direction along the path of the arrow (the common intersection of the three cones). In order to produce a diffraction effect (a spot on a photographic plate or film) these three geometric equations must be simultaneously satisfied. The three equations are named after Max von Laue, who originally formulated them.

Shortly after the publication of these equations, W. L. Bragg, working on X-ray diffraction in England, pointed out that although X-rays are indeed diffracted by crystals, the diffracted X-rays act as though they were reflected from planes within the crystal. Unlike the reflection of light, however, X-rays are not "reflected" continuously from a given crystal plane. Using a given wavelength, \( \lambda \), Bragg showed that a "reflection" takes place from a family of parallel planes only under certain conditions. These conditions must satisfy the equation: \( n \lambda = 2d \sin \theta \), where \( n \) is an integer \( (1, 2, 3, \ldots, n) \), \( \lambda \) the wavelength, \( d \) the distance between successive parallel planes, and \( \theta \) the angle of incidence and "reflection" of the X-ray beam from the given atomic plane. This equation, known as the Bragg law, expresses in a simpler manner the simultaneous fulfillment of the three Laue equations.

We have seen that the faces most likely to appear on crystals are those parallel to atomic planes having the greatest density of lattice nodes. Parallel to each face is a family of equispaced identical planes. When an X-ray beam strikes a crystal, it penetrates it, and the resulting diffraction effect is not from a single plane but from an almost infinite number of parallel planes, each contributing a small bit to the total diffraction maximum. In order that the diffraction effect ("reflection") be of sufficient intensity to be recorded, the individual "reflections" must be in phase with one another. The following conditions necessary for reinforcement were demonstrated by W. L. Bragg.

In Fig. 7.38 the lines \( p \), \( p' \), and \( p'' \), represent the traces of a family of atomic planes with spacing \( d \). X-rays striking the outer plane \( pp \) would be reflected at the incident angle \( \theta \), whatever the value of \( \theta \). However, to reinforce one another in order to give a "reflection" that can be recorded, all "reflected" rays must be in phase. The path of the waves along \( DEF \) "reflected" at \( E \) is longer than the path of the waves along \( ABC \) "reflected" at \( B \). If the two sets of waves are to be in phase, the path difference of \( ABC \) and \( DEF \) must be a whole number of wavelengths \( (n \lambda) \). In Fig. 7.38 \( BG \) and \( BH \) are drawn perpendicular to \( AB \) and \( BC \), respectively, so that \( AB = DG \) and \( BC = HF \). To satisfy the condition that the two waves be in phase, \( GE + EH \) must be equal to an integral number of wavelengths. \( BE \) is perpendicular to the lines \( p \) and

---

FIG. 7.36. Diffraction cones from a row of atoms.

FIG. 7.37. Diffraction cones from three noncoplanar rows of scattering atoms, intersecting in a common line.
the incident beam makes an angle $\theta$ that satisfies the Bragg equation, with $n = 1$. On continued rotation there are further "reflections" only when the equation is satisfied at certain $\theta$ angles with $n = 2, 3$, and so on. These are known are the first-, second-, third-order, etc., "reflections." These "reflections" are in actuality the diffraction effects that occur when the three diffraction cones about three noncoplanar rows of atoms intersect in a common direction (see Fig. 7.37).

**Single-Crystal X-ray Diffraction and Structure Analysis**

Single-crystal X-ray diffraction, as the name implies, concerns itself with the interaction of an X-ray beam with a very small single-crystal (about 1 mm in size or smaller) of a mineral (or other crystalline substance). The X-ray beam and the crystalline structure produce X-ray diffraction effects that can be recorded on film or measured by an electronic device, an X-ray counter (or detector). Until about 1970 almost all X-ray diffraction studies involved film methods which consist of a crystal positioned in an X-ray beam at a fixed distance from a film wrapped in a light-tight envelope. Figure 7.39a shows this arrangement for the Laue method in which the crystal is stationary and...
the X-ray beam is unfiltered (meaning that it contains X-rays represented by Kβ radiation as well as the continuum in addition to the Kα radiation). Although the Laue method is now mainly of historic interest, it is mentioned here because the resulting diffraction effects, as recorded on a flat film, display the symmetry of the crystal as long as one of the crystallographic axes of the crystal is aligned parallel with the X-ray beam. Figure 7.39b illustrates the fourfold symmetry arrangement of X-ray diffraction spots (about the center of the film) for the mineral vesuvianite. Here the X-ray beam was parallel to the c axis, the fourfold axis in vesuvianite, which is tetragonal in symmetry.

In other single-crystal film methods the film is generally not stationary and furthermore, the film may not be contained in a flat but instead in a cylindrical housing. The most commonly used single-crystal method in which a flat film and a single crystal move on a complex gyroratory motion, is known as the precession method. An example of an X-ray single-crystal precession photograph of vesuvianite is shown in Fig. 7.40.

Although an enormous number of crystal structures have been solved on the basis of data obtained on film using single-crystal camera techniques, the modern approach to data acquisition is not by film technique, but by single-crystal diffractometer. In such instrumentation (see also "X-ray Powder Diffraction and Mineral Identification," later in this chapter) the intensity of X-ray reflections is not evaluated from the intensity of a spot on an X-ray film, but instead is measured by an electronic device, an X-ray counter (or detector). Such detectors greatly improve the accuracy of X-ray intensity measurements over those obtained by film techniques. Furthermore, in automated instrumentation, such detectors can measure large numbers of X-ray reflections with high accuracy. The most commonly used automated technique in X-ray structure analysis is the four-circle diffractometer. The name four-circle arises from its possession of four arcs that are used to orient the single crystal so as to bring desired (atomic) planes into reflecting positions. An automated four-circle diffractometer is shown in Fig. 7.41.

The Determination of Crystal Structures
The orderly arrangement of atoms in a crystal is known as the crystal structure. It provides information on the location of all the atoms, bond positions and bond types, space group symmetry, and the chemical content of the unit cell.

The first steps in determining the atomic structure of a crystal are the measurement of its unit cell size and the evaluation of its space group. The systematic measurement of the geometric distribution of diffracted X-ray beams on single crystal X-ray photographs in one or more crystallographic orientations (precession photographs are most convenient) yields
FIG. 7.41. (a) Schematic illustration of the P4 single-crystal X-ray diffractometer manufactured by Siemens Industrial Automation, Inc. (b) Close-up of the four-circle goniometer for controlling the orientation of the single crystal (in center of photograph). To the right is the X-ray tube, and to the left is the X-ray detector, a scintillation counter. (Courtesy of Siemens Industrial Automation, Inc., Madison, Wis.)
information about the geometry of that crystal's unit cell, specifically the lengths of the unit cell edges and the angles between them. Information about the space group and the crystal structure (i.e., the symmetry of the atomic arrangement and the coordinates of atoms within the unit cell) is contained in the intensities of the diffracted beams, which are measured either from X-ray single crystal photographs, or more commonly with quantum counting detectors on single-crystal diffractometers. The diffracted beams are identified by Bragg indices $hkl$ associated with the lattice planes of the same indices.

The relationship between the intensity $I$ of the diffracted beam associated with lattice planes having Bragg diffraction indices $hkl$ and coordinates $x_{j}, y_{j}, z_{j}$ of atom $j$ in the unit cell is

$$I = k \left[ \sum_{j} f_{j} e^{2\pi i (hx_{j} + ky_{j} + lz_{j})} \right]^{2} = kF_{hkl}^{2},$$

where $k$ is a term containing several physical constants and experimental factors, including a scale factor; $f_{j}$ is the scattering factor of atom $j$ (which depends on atomic number and scattering angle and includes corrections for atomic thermal motion); and the summation is over all atoms in the unit cell. The summation is termed the structure factor, $F_{hkl}$, and its value clearly depends on the kinds of atoms in the cell and their positions.

Because the intensities of diffracted beams are related to $F_{hkl}$ rather than $F_{hkl}$, the atomic coordinates cannot be extracted straightforwardly from measured intensities. Over the past 70 years a great deal of effort has been devoted to methods by which these intensities can be made to yield atomic positions, with remarkable success. Modern methods are based either on analysis using Fourier techniques, which are very powerful, particularly when the positions of a small number of heavy atoms are known, or on so-called direct methods, which are essentially statistical in nature and have become extremely successful as computing power has increased. An illustration of a now-classical electron density map (and the structure derived therefrom) by W. L. Bragg in 1929 is given in Fig. 7.42. Once the atom positions are known crudely, they can be refined to high precision, using least-squares analysis on many measured $F_{hkl}$, a procedure that can yield amplitudes of atomic

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**FIG. 7.42.** (a) The summation of Fourier series for diopside, CaMgSi$_2$O$_6$, projected on (010). The distribution of scattering matter is indicated by contour lines drawn through points of equal density in the projection. (b) The atomic positions of diopside (with space group $C2/c$) projected on (010), as derived from the distribution in (a). (Re-drawn after W. L. Bragg, 1929, *Zeitschrift für Kristallographie* 70:488.)
thermal vibration as well as site occupancies of substituting atomic species in minerals that are members of solid solution series. Accurate interatomic distances (bond lengths) can then be calculated from refined atomic coordinates. In recent years highly accurate electron density maps, calculated as a Fourier series in which the structure factors are the Fourier coefficients, have yielded information about bonding and the spatial distribution of valence electrons. Examples of such detailed electron density maps are given in “Molecules as models for bonding in silicates,” by G. V. Gibbs (1982); complete reference is given at the end of this chapter.

Supplementing structure analyses based on diffraction phenomena (these are X-ray, neutron, and electron diffraction techniques), a variety of spectroscopic methods, including infrared, optical, Mössbauer, and resonance techniques such as nuclear magnetic resonance (NMR) yield information about the local environments or ionization states of certain atomic species. Thus a complete structural picture of a mineral at the atomic level usually requires information obtained by both diffraction and spectroscopy.

X-Ray Powder Diffraction and Mineral Identification

The relative rarity of well-formed crystals and the difficulty of achieving the precise orientation required by single-crystal methods led to the discovery of the powder method of X-ray investigation. In X-ray diffraction studies of powders, the original specimen is ground as finely as possible and bonded with an amorphous material into a small spindle (for powder film methods) or mounted on a glass slide, or in a special rectangular sample holder (for powder diffractometer techniques). The powder mount consists ideally of crystalline particles in completely random orientation. To ensure randomness of orientation of these tiny particles with respect to the impinging X-ray beam, the spindle mount (used in film cameras) is generally rotated in the path of the beam during exposure.

When a beam of monochromatic X-ray strikes the mount, all possible diffractions take place simultaneously. If the orientation of the crystalline particles in the mount is truly random, for each family of atomic planes with its characteristic interplanar spacing (d), there are many particles whose orientation is such that they make the proper θ angle with the incident beam to satisfy the Bragg law: nλ = 2d sin θ. The diffraction maxima from a given set of planes form cones with the incident beam as axis and the internal angle 4θ. Any set of atomic planes yields a series of nested cones corresponding to “reflections” of the first, second, third, and higher orders (n = 1, 2, 3, . . .). Different families of planes with different interplanar spacings will satisfy the Bragg law at appropriate values of θ for different integral values of n, thus giving rise to separate sets of nested cones of “reflected” rays.

If the rays forming these cones are permitted to fall on a flat photographic plate at right angles to the incident beam, a series of concentric circles will result (Fig. 7.43). However, only “reflections” with small values of the angle 2θ can be recorded in this manner.

In order to record all the possible diffraction cones that may occur in three dimensions (see Figs. 7.36 and 7.37) a film method is used in which the film is wrapped around the inside of a cylindrical camera. This camera is known as a powder camera in which the film fits snugly to the inner curve of the camera (see Fig. 7.44a). This type of mounting is known as the Straumanis method. Figure 7.44b shows the circular film strip with two holes cut into it, one to allow the X-ray beam to enter the camera and the other for a lead-lined beam catcher. Although this powder camera method has been used extensively for mineral identification, the X-ray powder diffractometer is the instrumental method currently used most often. This powerful analytical tool uses essentially monochromatic X-radiation and a finely powdered sample, as does the powder film method, but records the information about the “reflections” present as a graphical recording, or as electronic counts (X-ray counts) that can be stored and printed out by computer.

The sample for powder diffractometer analysis is prepared by grinding it to a fine powder, which is then spread uniformly over the surface of a glass slide, using a small amount of adhesive binder. (If enough powder is available it can be compressed

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**FIG. 7.43.** X-ray diffraction from a powder mount recorded on a flat plate.
into a rectangular sample holder. The instrument is so constructed that the sample, when clamped in place, rotates in the path of a collimated X-ray beam while an X-ray detector, mounted on an arm, rotates about it to pick up the diffracted X-ray signals (see Fig. 7.45). When the instrument is set at zero position, the X-ray beam is parallel to the base of the sample holder and passes directly into the X-ray detector. The slide mount and the counter are driven by a motor through separate gear trains so that, while the sample rotates through the angle $\theta$, the detector rotates through $2\theta$.

FIG. 7.45. Schematic illustration of the essential components of a powder X-ray diffractometer. In such an instrument the sample holder rotates ($\theta^\circ$) while the detector arm rotates $2(\theta^\circ)$. 
If the specimen has been properly prepared, there will be thousands of tiny crystalline particles in random orientation. As in powder photography, all possible "reflections" from atomic planes take place simultaneously. Instead of recording all of them on a film at one time, however, the X-ray detector maintains the appropriate geometrical relationship to receive each diffraction maximum separately.

In operation, the sample, the X-ray detector, and the recording device are activated simultaneously. If an atomic plane has an interplanar spacing \( d \) such that a reflection occurs at \( \theta = 20^\circ \), there is no evidence of this reflection until the counting tube has been rotated through 20 or 40°. At this point the diffracted beam enters the X-ray detector, causing it to respond. The pulse thus generated is amplified and causes an electronic response on a vertical scale that represents peak height. The angle 2\( \theta \) at which the diffraction occurs is read on a horizontal scale. The heights of the peaks are directly proportional to the intensities of the diffraction effects. An example of a diffractometer tracing for low quartz is given in Figure 7.46. The 2\( \theta \) positions of the diffraction peaks in such a tracing can be read off directly or they can be tabulated as 2\( \theta \) positions by an online computer. The interplanar spacings giving rise to them are calculated using the equation \( n \lambda = 2d \sin \theta \).

Once a diffractometer tracing has been obtained and the various diffraction peaks have been tabulated in a sequence of decreasing interplanar spacings \( d \), together with their relative intensities \( I \), with the strongest peak represented by 100 and all the other peaks scaled with respect to 100, the investigator is ready to begin the mineral identification process. Through a computer search technique (doing searches for comparable or identical diffraction patterns on the basis of the strongest lines or the largest interplanar spacings), the diffraction pattern of an unknown can be compared with records stored in the Powder Diffraction File (PDF) published by the International Center for Diffraction Data (ICDD). This file is primarily available on CD-ROM and is compatible with PC, VAX/VMS, and Macintosh platforms.

The Powder Diffraction File is the world's largest and most complete collection of X-ray powder diffraction patterns. The PDF contains more than 70,000 experimental patterns compiled by the ICDD since 1941, as well as more than 42,000 calculated patterns. Each pattern includes a table of interplanar \( d \) spacings, relative intensities \( I \), and Miller indices, as well as additional information such as chemical formula, compound name, mineral name, structural formula, crystal system, physical data, experimental parameters, and references. An example printout for low quartz from this file is shown in Fig. 7.47. Entries are indexed to allow for subfile searches of inorganics, organics, minerals, metals and alloys, common phases, pharmaceuticals, zeolites, and many others.

By this outlined comparative search procedure, a completely unknown substance may generally be identified in a short time using a very small volume of sample.

**FIG. 7.46.** X-ray powder diffractometer tracing for a finely powdered sample of low quartz.
The powder method is of wider usefulness, however, and there are several other applications in which it is of great value. Variations in chemical composition of a known substance involve the substitution of ions, generally of a somewhat different size, in specific sites in a crystal structure. As a result of this substitution the unit cell dimensions and hence the interplanar spacings are slightly changed, and the positions of the lines in the powder diffractogram corresponding to these interplanar spacings are shifted accordingly. By measuring these small shifts in position of the lines in powder patterns of substances of known structure, changes in chemical composition may often be accurately detected. Figure 7.48 illustrates a variation diagram that correlates unit cell dimensions (b and unit cell volume, V) and changes in the position of a specific diffraction maximum (1, 11, 0) with composition in the cummingtonite-grunerite series.
Further, the relative proportions of two or more known minerals in a mixture are often conveniently determined by the comparison of the intensities of the same peaks in diffractometer patterns of prepared control samples of known composition.

Several student exercises using X-ray powder diffraction film and diffractometer techniques are given in Klein (1994; see reference list for complete reference).

Until recent years, most of the structural studies of crystalline materials were based on single-crystal X-ray and neutron diffraction experiments, but a newly developed X-ray powder diffraction technique, the Rietveld refinement method, allows the extraction of structural information from powdered instead of single-crystal specimens. This is an especially important development for the determination of the crystal structures of minerals that are typically finely crystalline and are not found in well-developed single crystals. Examples of such finely crystalline or poorly ordered minerals are clay minerals, manganese and iron oxides and hydroxides, and some zeolites. There are three basic requirements of the Rietveld refinement:

1. Accurate powder diffraction intensity data measured at specific intervals of $2\theta$
2. A basic understanding ("starting model") of the actual crystal structure of the material that is being studied
3. A quantitative understanding of shapes, width, and any systematic errors in the positions of X-ray peaks in the powder pattern.

For further discussion of the Rietveld method, see Post and Bish (1989; see reference list for complete reference).

**TRANSMISSION ELECTRON MICROSCOPY (TEM)**

A transmission electron microscope consists of a finely focused electron beam that impinges on a very thin foil of an object (the unknown material under investigation) and that, upon transmission through the object, can be used to display electron diffraction patterns and high resolution transmission electron microscope (HRTEM) images. A schematic drawing of the electron column in a TEM with its electromagnetic lenses was shown in Fig. 1.13 and a photograph of a modern instrument was shown in Fig. 1.12. The thin foil of the material to be investigated is produced by ion bombardment or sputter-etching methods for nonconducting materials or by ultramicrotomy. For metals and conducting materials, foil preparation is done by electrochemical methods. The thin foil, which is on the order of a few nanometers thick, is held in place with a sample holder centered in the electron beam (see Fig. 1.12).