X

X-RAY TECHNOLOGY

1. Introduction

Analytical X-ray instruments are used to characterize materials in several different ways. As with medical X-ray instruments, there are analytical instruments that can produce images of internal structures of objects that are opaque to visible light. There are instruments that can determine the chemical elemental composition of an object, that can identify the crystalline phases of a mixture of solids, and others that determine the complete atomic and molecular structure of a single crystal. These are the most common applications for X-ray instruments.

The determination of particle size and structural information for fibers and polymers, and the study of stress, texture, and thin films are applications that are growing in importance and can be examined with X-ray instruments.

Because of recent advances in hardware, particularly detector hardware, and computer software, X-ray instruments have become very powerful. Problems that could not be solved several years ago can be solved with the newer instrumentation. Also, the instruments have become much more automatic so that the more routine problems can be solved much faster than a few years ago.

2. Characterization and Generation of X-Rays

2.1. X-Ray Electromagnetic Spectrum. X-rays are a form of electromagnetic radiation and have a wavelength, λ, much shorter than visible light. The center of the visible light spectrum has a wavelength of $\sim 0.56 \times 10^{-6}$m. The range of wavelengths for X-rays used in the applications discussed here are from $\sim 0.01 \times 10^{-9}$m to $\sim 7.0 \times 10^{-9}$m. The energy of an X-ray photon expressed in kiloelectronvolts (1.0 keV = 1000 eV) is related to wavelength expressed in nanometers (1.0 nm = 1.0 × 10^{-9}m) as follows:

$$E\,(\text{keV}) \sim 1.24/\lambda\,(\text{nm})$$

There are several ways to produce X-rays that have the range of energies appropriate for the various applications discussed here. The most commonly used methods are discussed below.

2.2. Synchrotron Radiation. X-rays are produced when very energetic electrons traveling close to the speed of light are decelerated. A continuous X-ray spectrum of intensity versus wavelength is produced. Very intense X-ray sources are available at synchrotron installations around the world. The Stanford Linear Accelerator in California is typical of these installations. Electrons are accelerated with electromagnets while traveling along a linear path of 2 miles. Then, they are inserted into a nearly circular path that is maintained by bending magnets. In this circular path, the electrons lose energy by producing X-ray photons whose paths are tangential to the circle. X-ray instruments designed for many different applications are placed around the synchrotron ring.

Synchrotrons were originally designed for high energy particle physics studies. The synchrotron X-ray radiation was not desirable for those studies. Later, synchrotrons were designed not for high energy particle physics studies, but instead were designed to optimize the desirable features of the X-ray and ultraviolet (uv) radiation produced. The so-called third-generation synchrotrons are the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, the Advanced Photon Source (APS) at Argonne in the United States and the Super Photon Ring (Spring-8) in Harima, Japan. These facilities produce high energy X-ray beams at least 10,000 times brighter than the early synchrotrons. They have straight sections in their otherwise circular paths to allow the insertion of wiggler and undulator magnets. These magnets cause the electrons to oscillate in the plane of the ring causing a large increase in the intensity of the synchrotron radiation.

An undulator produces X-ray radiation as sharp peaks at several harmonics of some fundamental radiation energy. At higher magnetic field strength, the higher harmonics tend to smooth out producing a continuous and very intense spectrum of X-ray wavelengths. The insertion device operating under these conditions is called a wiggler.

2.3. X-Ray Tubes. X-ray tubes are the most widely used source for the generation of X-rays. In these tubes, electrons are accelerated by a high electric potential (20−120 kV). These electrons strike the target (anode) of the tube. The electrons decelerate as they pass through the electron clouds of the atoms. This phenomenon produces a continuous spectrum similar, but much less intense, to that of the synchrotron. In addition, some high energy electrons knock electrons out of the atomic orbitals of the atoms of the target material. When these orbitals are refilled by electrons, X-ray photons are generated. The resulting X-ray spectrum of intensity versus wavelength has a series of peaks known as characteristic lines. The wavelengths and intensities of these lines are dependent on the elemental composition of the target material (synchrotron radiation has no characteristic lines). The most intense peaks are the two lines known as $K_{\alpha 1}$ and $K_{\alpha 2}$ (or together known as K_{α}). The next most intense lines are the K_{β} lines.

Unlike synchrotron radiation, the maximum intensity of X-rays from an X-ray tube is limited by how fast heat can be removed from the target to prevent its melting. In a conventional sealed tube, the target is stationary, relatively small, and must be continually cooled with water. In a rotating anode tube, the target is larger and is continually rotated so that the heat can be distributed over a larger surface. With such a tube the amount of heat, and hence, the intensity of X-rays can be greater than in a stationary target tube. The materials that are used as targets in X-ray tubes depend on the application.

3. Properties of X-Rays

X-rays impinging on an object interact primarily with the electrons in the object, ie, there is very little interaction with the atomic nuclei that comprise most of the mass of the object. An X-ray photon can interact with an object in the following ways: The X-ray photon does not interact and is transmitted through the object in the same direction that it impinged on the object. The energy of the photon does not change. The X-ray photon is completely absorbed. No X-ray photon leaves the object. All of the energy of the X-ray photon is transferred to the electrons within the object.

The X-ray photon is absorbed and another X-ray photon of longer wavelength (lower energy) is produced. In this process, an electron (or electrons) gains the lost energy. The new X-ray photon may travel in any direction from the site of the event. This phenomenon is known as incoherent, inelastic, or Compton scattering. Because there is a transfer of energy at a localized position within the object the incident X-ray photon can be considered to behave as a particle.

The X-ray photon produces an oscillating electric field in the object. This electric field in turn causes a photon of the same wavelength as the original photon to be generated. The resulting photon may leave the object at many different angles with respect to the incident photon. No energy is transferred to the object. This phenomenon is known as coherent, elastic, or Rayleigh scattering. The incident X-ray photon can be considered to behave as a wave and the phenomenon of diffraction takes place (see below).

All of these properties of X-rays are used to measure various properties of materials. X-ray applications can be placed into three categories based on which of the above phenomena are exploited. These categories are X-ray radiography, X-ray fluorescence spectrometry, and X-ray diffraction.

X-rays were discovered by Wilhelm Roentgen in 1895. Soon after their discovery Roentgen used X-rays to image the bones in a human hand. The X-rays transmitted through the hand (phenomenon 1) were recorded on photographic film. The bones or other dense objects absorb X-rays more than soft tissues or less dense materials (phenomenon 2). This method of imaging the internal structure of an object is known as X-ray radiography.

X-ray fluorescence spectrometry consists of the measurement of the incoherent scattering of X-rays (phenomenon 3 above). It is used primarily to determine the elemental composition of a sample.

X-ray diffraction consists of the measurement of the coherent scattering of X-rays (phenomenon 4 above). X-ray diffraction is used to determine the identity of crystalline phases in a multiphase powder sample and the atomic and molecular structures of single crystals. It can also be used to determine structural details of polymers, fibers, thin films, and amorphous solids and to study stress, texture, and particle size. Each of these categories of applications and the associated X-ray instruments are discussed in this article.

4. X-Ray Diffraction Principles

4.1. Interference of Waves. The coherent scattering property of X-rays is used in X-ray diffraction applications. Two waves traveling in the same direction with identical wavelengths, λ, and equal amplitudes (the intensity of a wave is equal to the square of its amplitude) can interfere with each other so that the resultant wave can have anywhere from zero amplitude to two times the amplitude of one of the initial waves. This principle is illustrated in Figure 1. The

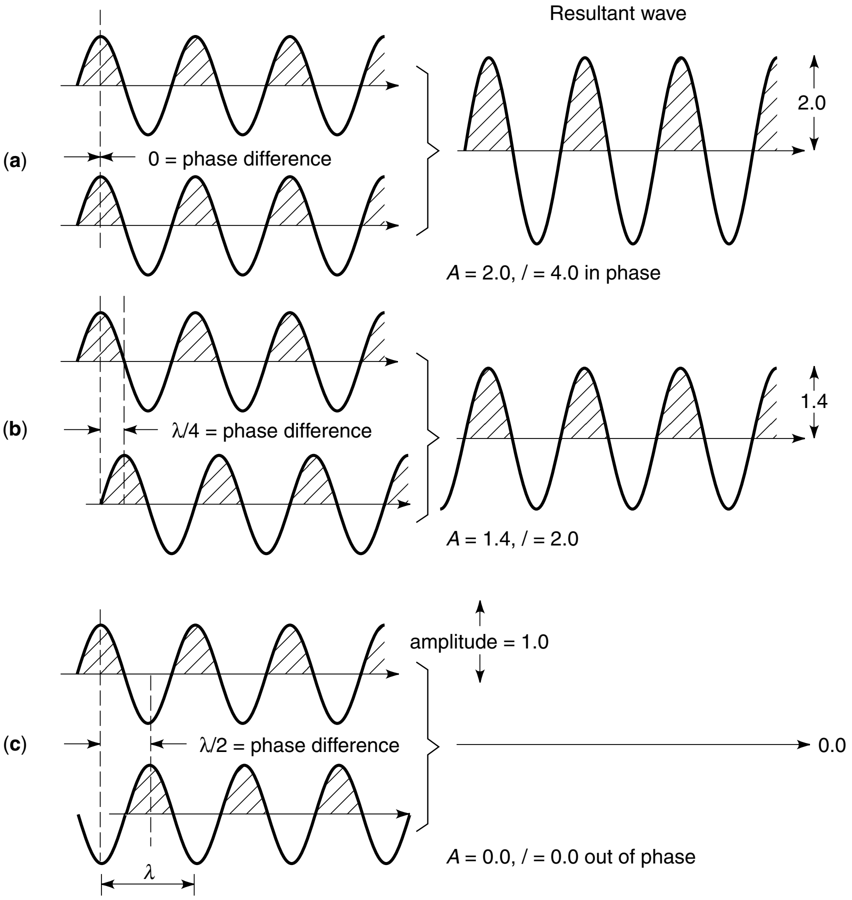

Fig. 1. Interference of two waves. (See text for explanation of (**a**), (**b**), (**c**).)

resultant amplitude is a function of the phase difference between the two initial waves.

In Figure 1**a**, the two waves have a zero phase difference and the resultant amplitude is twice that of each of the initial waves. In this case, the waves are in phase with one another and the interference is "constructive". In Figure 1**b**, the two waves have a phase difference of one-fourth of the wavelength, λ/4, and the resultant amplitude is the square root of two times that of each of the initial waves. In Figure 1**c**, the two waves have a phase difference of one-half of the wavelength, λ/2, and the resultant amplitude is zero. In this case, the waves are out of phase with one another and the interference is "destructive". In each of the three cases, the resultant wave has the same wavelength, λ, as the initial waves.

4.2. Diffraction Patterns. A classical experiment in physics is the diffraction of light through slits or holes. If the size of the slits or holes are about the same size as the wavelength of the incident light, a diffraction pattern results. The diffraction pattern through a single slit is shown in Figure 2. The

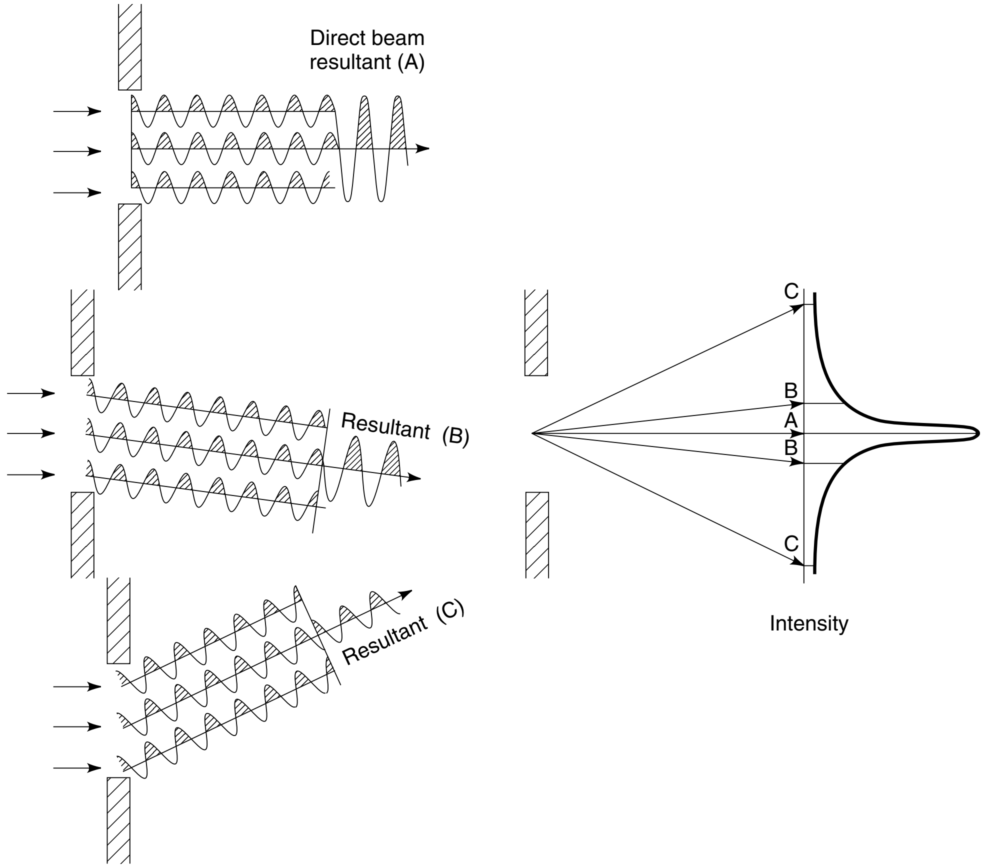

Fig. 2. Diffraction through a slit. Superposition of events A, B, C, from the same slit, plus all other possible angles of diffraction gives the resultant intensity profile.

resulting pattern is a bell-shaped curve that is wider than the slit. The analogue of the slit or hole in an X-ray diffraction experiment is an electron that is the entity that produces the scatter of an X-ray photon. An electron in an atom has a size on the same order of magnitude as the wavelength of the X-rays used in a diffraction experiment.

Diffraction of X-rays from many atoms with many electrons results in a two-dimensional (2D) continuous pattern of peaks and valleys. Diffraction from a liquid or an amorphous (noncrystalline) solid results in a continuous pattern with few features, mainly broad peaks and valleys.

4.3. Unit Cells and Crystal Lattice.

A single crystal, unlike a liquid or amorphous solid, is made up of identical units, each of which has the same three-dimensional (3D) arrangement of atoms (and hence, electrons). This basic unit is called a unit cell. It is a parallelopiped (a six-sided box whose opposite faces are parallel). The unit cell parameters are the lengths of the edges, a, b, and c, and the angles, α, β, and γ (Fig. 3). The edge lengths are usually expressed in angstroms $(1.0 = 10^{-10}\mathrm{m})$ and the angles are expressed in degrees. A crystal can be thought of as consisting of many of these unit cells that are stacked like bricks. Figure 4 shows a 2D projection of a 3D crystal structure. The positions of the atoms are shown as dots. The parallelograms are 2D projections of the unit cells. The corners of the unit cells are the crystal lattice points. The crystal lattice consists of all of the lattice points in the crystal. Note that each unit cell has exactly the same configuration of atoms as every other unit cell.

4.4. Diffraction from a Crystal Lattice.

An X-ray diffraction pattern from a single crystal has sharp peaks and regions of zero intensity between these peaks. An analogy is a diffraction pattern obtained by passing visible light through a series of equally spaced holes of uniform size (Fig. 5). In this case, each hole is analogous to a unit cell in the crystal.

For a 2D array of equally spaced holes, the diffraction pattern is a 2D array of spots. The intensity between the spots is very small. The crystal is a 3D lattice of unit cells. The third dimension of the X-ray diffraction pattern is obtained by rotating the crystal about some direction different from the incident beam. For each small angle of rotation, a 2D diffraction pattern is obtained. In principle,

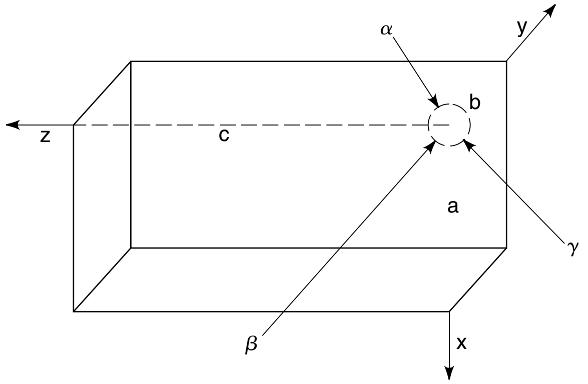

Fig. 3. Conventions for naming axes and angles for a unit cell.

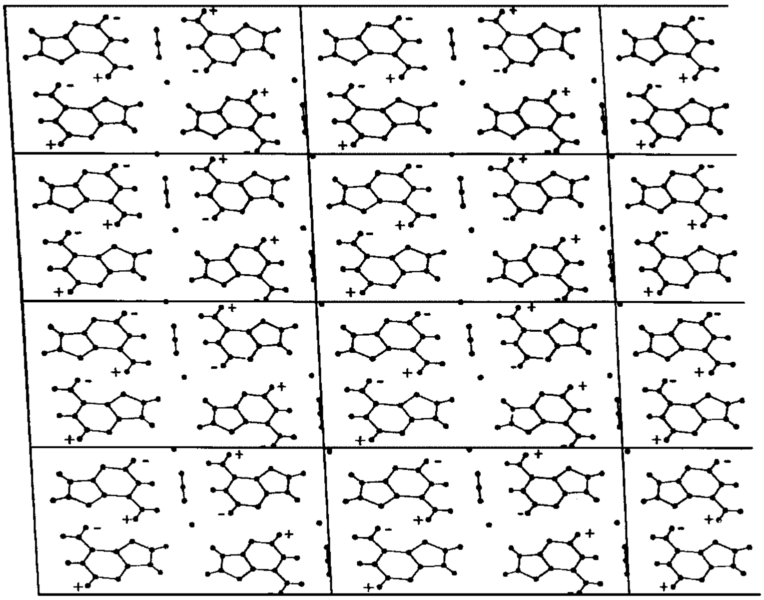

Fig. 4. Translational symmetry. For each atom in a unit cell there are corresponding atoms in neighboring unit cells.

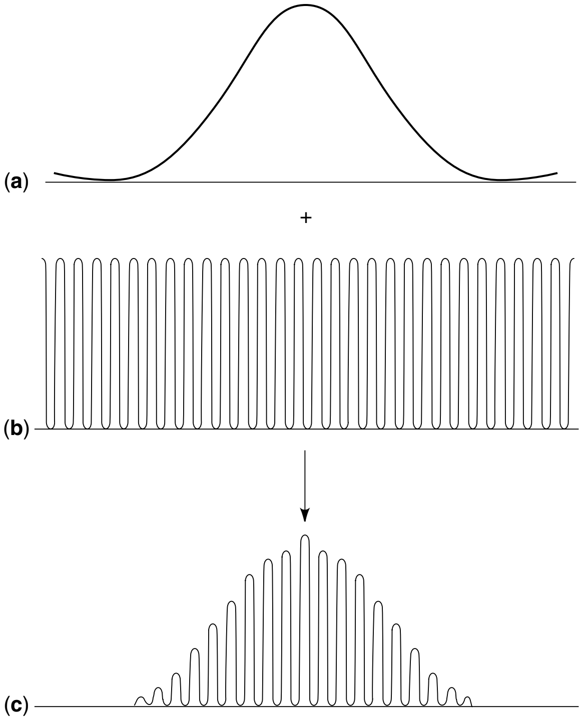

Fig. 5. Diffraction profile from (**a**) a single slit and (**c**) many slits. (**b**) The sampling region from many slits.

it is possible to calculate the detailed 3D electron density distribution in a unit cell from the 3D X-ray diffraction pattern.

4.5. Bragg's Law. In 1913, Bragg showed that the positions of the discrete X-ray spots in the diffraction pattern can be explained by assuming that the diffracted X-ray photons behave as if they were "reflected" from certain families of equally spaced parallel planes passing through the crystal lattice. Figure 6 illustrates the principle known as Bragg's law. The two paths, A and B, for the incident and diffracted beams differ in length by $2d\sin\theta$; where d is the perpendicular distance between two adjacent parallel planes. The parameter θ is equal to the angle between the incident beam and each plane and is equal to the angle between the diffracted beam and each plane. For constructive interference to take place, this difference must be equal to a whole number of wavelengths. Bragg showed that diffraction takes place only if all the lattice points of the crystal are on the parallel planes.

Bragg's law is

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

where n is an integer. An example of parallel planes that pass through all of the lattice points is shown in Figure 7.

Because of Bragg's explanation of diffraction of X-rays from a crystal as being like reflections from families of planes, the diffraction spots are usually called "reflections". Each reflection is identified with three integer indexes, h,

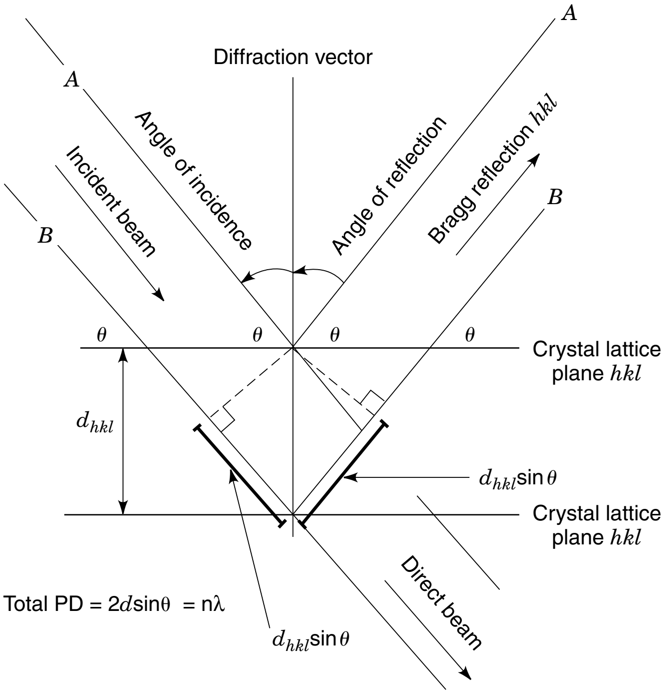

Fig. 6. Geometry of diffraction and its relationship to Bragg's law.

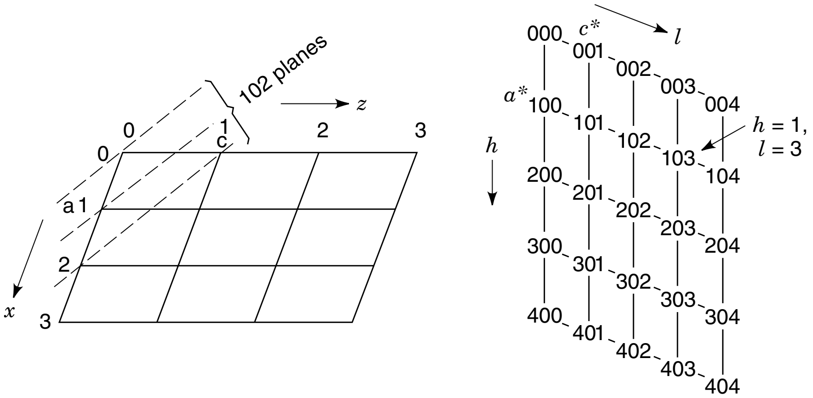

Fig. 7. Indexes of reflections and the reciprocal lattice.

k, and *l*. For the set of planes shown in Figure 7, the indexes of the corresponding reflection are $h = 1$, $k = 0$, and $l = 2$.

5. Instruments for X-Ray Single-Crystal Diffraction

An X-ray single-crystal diffraction experiment consists of mounting a single crystal on a diffractometer, finding a few reflections, assigning indexes to these reflections, determining the unit cell parameters and the orientation of the crystal on the diffractometer. Then, it systematically measures the intensities of all of the reflections. An X-ray single-crystal diffractometer consists of the following:

An X-Ray Source. Either synchrotron radiation or X-radiation from an X-ray tube is used (see above). The target materials for X-ray tubes for single-crystal diffraction experiments are usually copper or molybdenum. The resulting wavelengths are 15.418 and 7.1073 nm for CuK_α and MoK_α, respectively.

An X-Ray Monochromator. A monochromator is a large single crystal (usually graphite) that is oriented so that a very intense reflection is directed toward the sample. All wavelengths are absorbed by the monochromator except a small range of wavelengths used for the diffraction experiment. Usually, only the K_α characteristic radiation is used if an X-ray tube is the X-ray source.

The X-ray photons generated by the X-ray tube diverge from the target of the tube in all directions. Normally, only those photons that are directed toward the monochromator and are diffracted from the monochromator toward the sample can be diffracted from the crystal and measured by the detector. Recently, graded multilayer devices have been used instead of single-crystal monochromators. The graded multilayers consist of 20–100 layers of alternating light elements (eg, silicon) and heavy elements (eg, tungsten). The layer thickness is graded from one side of the device to the other. Useful thicknesses are 1.5–10 nm. The devices are also curved so that they form a piece of a parabola (Fig. 8). A divergent beam of

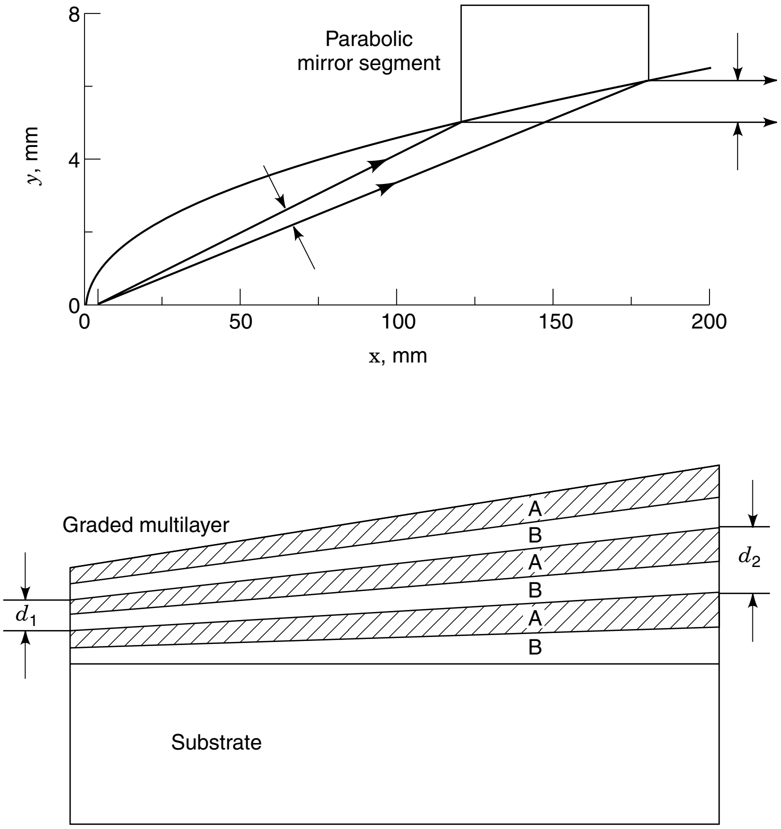

Fig. 8. A parabolically curved graded multilayer device. $\Delta y = 1$ nm. $\Delta\alpha = 0.4°$.

X-rays entering this device will exit as a parallel beam of monochromatic X-rays. The advantage compared to conventional monochromators is that the resulting intensity is several times larger and the parallel nature of the beam makes it possible to measure the intensities of reflections from crystals with large unit cell dimensions. A divergent beam causes reflections to overlap for samples with large unit cells (proteins).

A Goniometer. The crystal is mounted in the center of a goniometer, which with computer control, can orient the single crystal in many different directions in 3D space (Fig. 9).

An X-Ray Detector. Two different types of detectors are commonly used.

A single-reflection detector measures the intensity of one reflection at a time. It is necessary to orient the crystal and the detector (with the goniometer) with respect to the monochromatic incident X-ray beam for each reflection so that the Bragg condition is satisfied. A common single-reflection detector consists of a NaI crystal doped with Tl. The crystal is coupled to a photomultiplier tube that is followed by a voltage discriminator. This type of detector is called a scintillation detector. An X-ray photon hitting the NaI crystal is converted to many

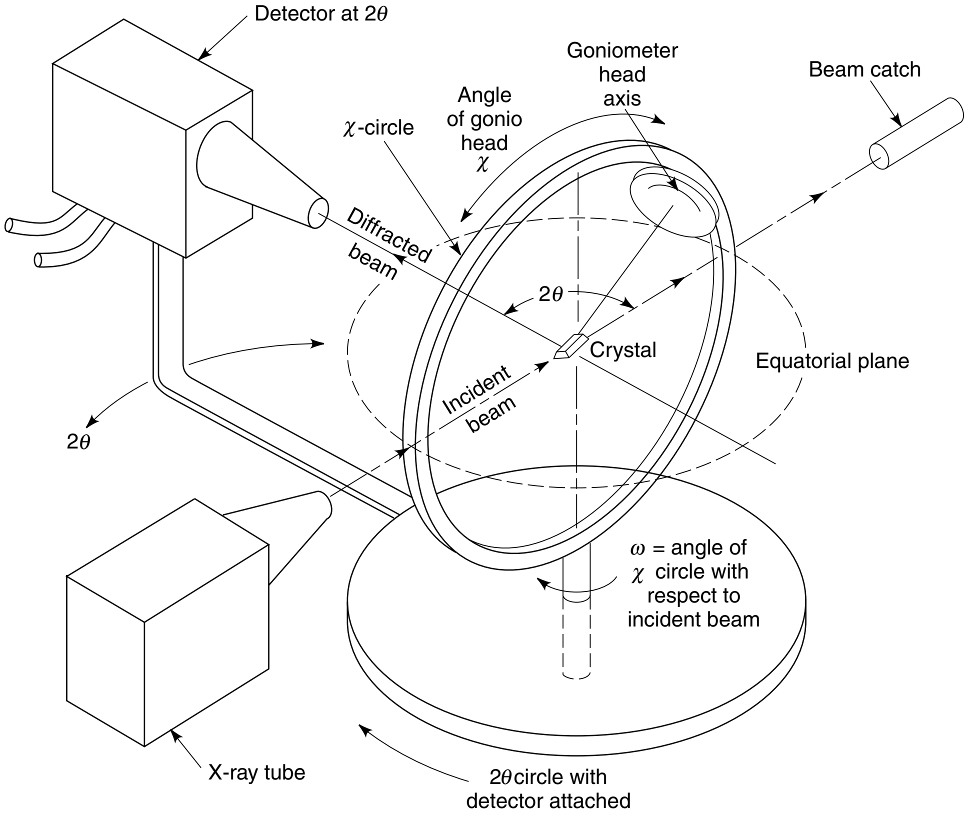

Fig. 9. A four-circle single-crystal diffractometer system.

visible light photons, that are then multiplied by the photomultiplier tube, producing a voltage signal. For each signal that is in the correct range, a count of one is added to the accumulated counts in the computer.

An X-ray area detector can be used to collect the intensities of many reflections at a time. The crystal must be oriented in many different settings with respect to the incident beam, but the detector needs to be positioned at only a few positions to collect all of the data. A charge coupled device (CCD) is used as the area detector on the Siemens SMART single-crystal diffractometer system. The SMART detector consists of a flat 6-cm circular phosphorescent screen that converts X-ray photons to visible light photons. The screen is coupled to a tapered fiber optics bundle that is then coupled to a 1 × 1 in. square CCD chip. The CCD chip has 1024 × 1024 pixels each, which stores an electrical charge proportional to the number of X-ray photons detected at that point. When an X-ray image has been collected, it can then be converted from analogue to digital and read into computer memory (Fig. 10).

Typically, it takes 2–3 days to collect a complete data set using a single-reflection detector. The new SMART diffractometer with its CCD detector can collect two or three data sets per day. Figures 11 and 12 are diagrams of commonly used diffractometers.

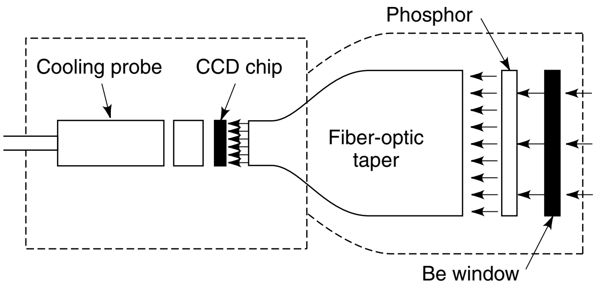

Fig. 10. Siemens SMART CCD detector.

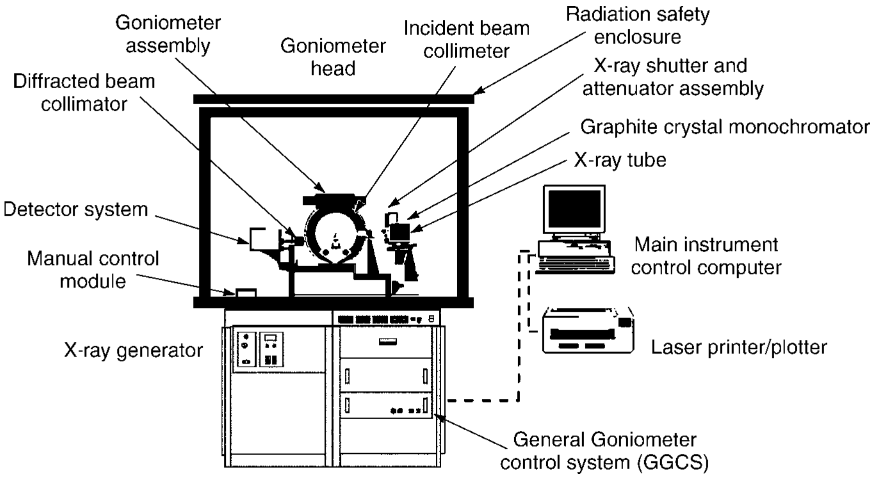

Fig. 11. Siemens P4 single-crystal X-ray diffractometer system.

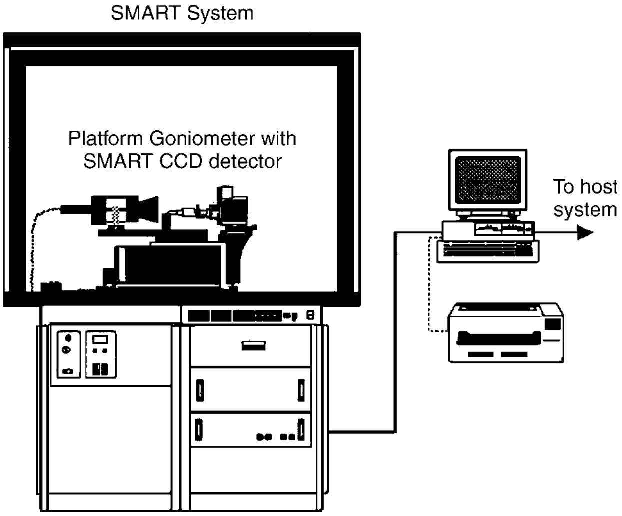

Fig. 12. Siemens SMART single-crystal X-ray diffractometer system.

6. Small-Molecule Single-Crystal Structure Determination

For the following discussion, small molecules are considered to have fewer than 200 nonhydrogen atoms. Macromolecules, primarily proteins, polynucleic acids, and viruses, can have many thousands of atoms. A typical small-molecule structure determination using a SMART system proceeds in the following way:

Step 1. A single crystal with the largest dimension equal to ~0.01–0.3 mm is mounted on a glass fiber that in turn is mounted on a copper pin. The copper pin is placed on a goniometer head that in turn is placed on the goniometer (Fig. 13). The crystal is positioned manually in the center of the goniometer. In this position, the crystal is always in the center of the monochromatic incident X-ray beam (whose diameter is ~1.0 mm).

Step 2. The computer opens a shutter, bathing the crystal in a monochromatic X-ray beam. The computer rotates the crystal for about 1 min and the rotation diffraction image is stored on the detector. Then it is read into the computer memory. When the operator examines the image and is confident that the sample is indeed a single crystal, the experiment can proceed.

Step 3. The computer collects ~45 frames of data. The crystal is rotated about the vertical axis for 0.3° for each frame. Usually, the crystal is exposed to X-rays for ~5 s for each frame. The computer finds the centers of many reflections (typically 25 to several hundred) and determines

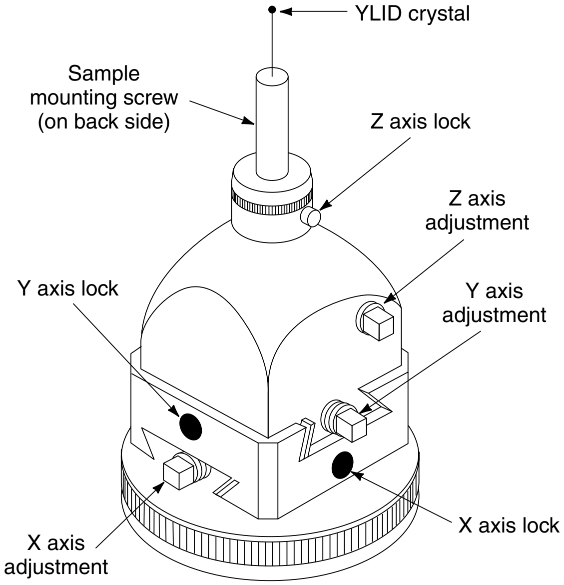

Fig. 13. Goniometer head with a mounted crystal.

indexes for these reflections. It then determines the unit cell parameters and the orientation of the unit cells with respect to the diffractometer.

Step 4. The user may then search for a match of the measured unit cell parameters against all unit cell parameters that have been published. Currently, there are ~197,500 entries in the National Institute of Standards and Technology (NIST) Crystal Data File. An exhaustive search takes ~1 min. Unit cell parameters are very definitive. Usually, only one or a few hits are found and the appropriate literature reference(s) are listed. If no hits are found, the structure has not been previously reported.

The time for these four steps is typically ~15–20 min. It takes 1–2 h with the older single-reflection detector instruments. Because all reflections with weak, as well as moderate-to-strong, intensities are measured with the SMART system, the probability of obtaining an incorrect unit cell parameters is less than for conventional instruments.

For small crystals, the 5 s/frame must be increased, but because so many reflections can be measured in a short period of time, it is possible to determine the unit cell parameters and identify crystals considerably smaller than was possible with conventional instruments. In 1996, the smallest sample for which this method has been used had dimensions of ~0.01 × 0.01 × 0.01 mm (~2 n). Consequently, the SMART system is one of the most powerful tools for determining the identity of very small samples.

Step 5. If the crystal structure has not been previously reported, a complete data set is then collected automatically. The time for this operation is from 3 h for strongly diffracting crystals to 24 h for the weakly diffracting or small crystals. At this point, the crystal may be removed from the diffractometer making the instrument available to analyze another sample.

Step 6. The intensities are measured by the computer for each reflection in the dataset.

The techniques for determining and refining the atomic parameters obtained from a crystal structure are not described in detail in this article. For more details see the book by Glusker and Trueblood. The steps that the crystallographer takes to determine and refine the structure follow.

Step 7. The computer determines the symmetry among the intensities of the reflections collected. The computer also looks for the absence or presence of intensity for certain classes of reflections. The computer determines which of 230 space groups the crystal belongs to from this information.

Step 8. To be able to calculate the 3D electron density distribution of the crystal structure, it is necessary to know the phase-angle change from the incident to the diffracted beam for each reflection, as well as the intensity of each reflection. Unfortunately, the phase-angle information cannot be measured. This missing information leads to the so-called phase problem of X-ray crystallography. However, it is known that the electron density must be everywhere positive and that the electron density is distributed primarily at the positions of the atoms. From this information and the intensity of the reflections, very powerful computer programs have been written to solve the "phase problem". As a result, almost every structure with <200 nonhydrogen atoms in the unit cell is solved with these programs.

Step 9. After obtaining phase angles for many of the reflections (phase determination programs do not determine the phase angles of all of the reflections), a 3D electron density map is generated. Because there are many reflections whose phase angles are not determined, this map has some false detail. The computer generates a list of the strongest peaks on this map.

Step 10. The crystallographer, using their knowledge of chemical information, eg, bond distances and bond angles, analyzes the peak information and assigns labels and atomic types (eg, C, N, O, Si, Fe) to those peaks that make good chemical sense.

Step 11. At this point, a computer program refines the atomic parameters of the atoms that were assigned labels. The atomic parameters consist of the three position parameters (x, y, and z) for each atom. Also, one or six atomic displacement parameters that describe how the atom is "smeared" (due to thermal motion or disorder) are refined for each atom. The atomic parameters are varied so that the calculated reflection intensities are made to be as nearly equal as possible to the observed intensities. During this process, estimated phase angles are obtained for all of the reflections whose intensities were measured. A new 3D electron density map is calculated using these calculated phase angles and the observed intensities. There is less false detail in this map than in the first map.

The crystallographer assigns more labels and atomic types to more peaks and repeats the refinement. After a few cycles of refinement and assignment of atoms, all of the atoms, with the possible exception of some hydrogen atoms, are included in the model.

Step 12. Finally, the crystallographer analyzes the results, tabulates some critical information (eg, bond distances, bond angles, torsion angles, planarity of groups of atoms), and prepares a report on the structure determination. The time for structure solution and refinement as outlined here is normally 2–8 h, depending on the complexity of the structure.

7. Macromolecule Single-Crystal Structure Determination

The procedures for solving and refining macromolecular structures are similar to those for small molecules. The class of macromolecular structures solved consists mostly of proteins, some polynucleic acids, and some viral structures. These structures usually contain thousands of atoms.

These structures do not diffract as well as small molecules, and as a result, there are many weak reflections. The data collection takes much longer than for small molecules. Also, the solution of the phase problem is more difficult and usually requires the collection of data sets with monochromatic radiation at several different wavelengths. Because of the much longer data collection times, area detectors are almost always used. Also, because of the long data collection times, crystallographers like to use the very intense synchrotron sources where it is possible to collect all of the data in a few days instead of the weeks that may be required with X-ray tubes.

These structures tend to have a lot of disorder. It is rare that any hydrogens can be observed in the final electron density maps. In fact, many groups of atoms (water molecules and some side chains) may be so disordered that it is usually difficult to determine positions for these groups.

7.1. The Wealth of Information from Single-Crystal Determinations.

The amount of information that is determined from a crystal structure experiment is much greater and more precise than for any other analytical tool for structural chemistry or structural molecular biology. Indeed, almost all of the structural information that has been determined for these two fields has been derived from X-ray single-crystal diffraction experiments.

There are several databases that contain the structural information that has been published. The Cambridge Structural Database (CSD) contains information from studies of organic and organometallic compounds and metal–organic complexes. This database has almost 100,000 structures and is growing at the rate of 7000 entries per year. The Inorganic Crystal Structure Database (ICSD) has >3000 entries and is increasing at ~1200 entries per year. The Protein Databank (PDB) has structural information for ~1800 macromolecular structures (1993). The National Research Council of Canada maintains a Metals Crystallographic Data File (CRYSTMET) that contained ~6000 entries in 1987.

There are very sophisticated programs to search these databases. The databases are used by chemists to design new chemical compounds and by drug companies to design new drugs for a great variety of diseases. Of special interest is the design of drugs that fit into the active sites of proteins.

8. Instruments for Powder Diffraction

8.1. Bragg-Brentano Powder Diffractometer.

A powder diffraction experiment differs in several ways from a single-crystal diffraction experiment. The sample, instead of being a single crystal, usually consists of many small single crystals that have many different orientations. It may consist of one or more crystalline phases (components). The size of the crystallites is usually ~1–50 μm in diameter. The sample is usually prepared to have a flat surface. If possible, the experimenter tries to produce a sample that has a random distribution of crystallite orientations.

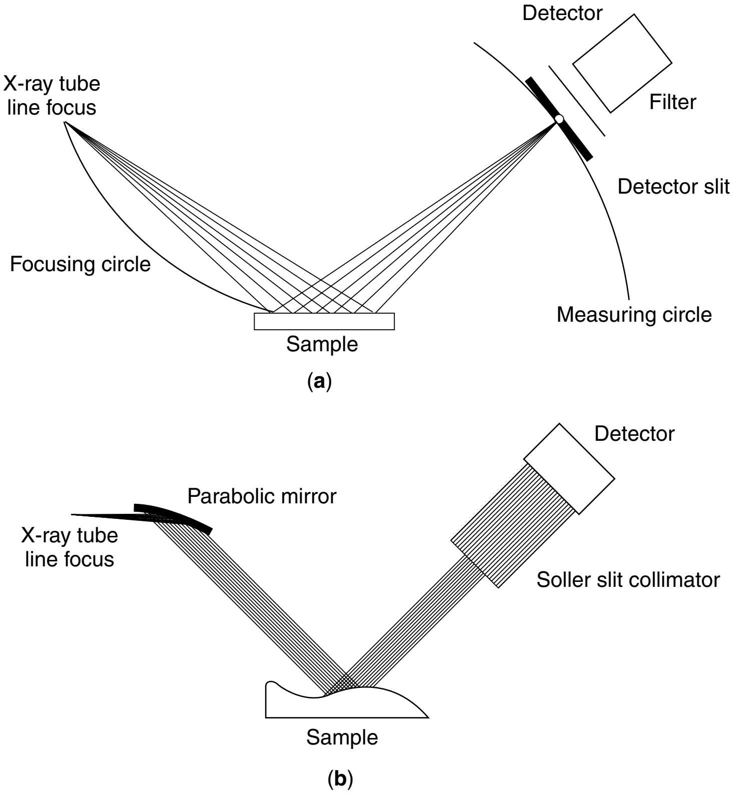

Fig. 14. Focusing schemes in powder diffraction: (**a**) conventional parafocusing Bragg-Brentano diffractometer; (**b**) parallel-beam diffractometer using a parabolic graded multilayer device.

See Figure 14**a** for the design of the most commonly used powder diffractometers. The instruments are designed so that a divergent beam of X-rays impinges on the sample. A convergent beam of X-rays is diffracted from the sample and passes through a narrow slit. The normal to the flat surface of the sample bisects the angle between the incident and diffracted beams. Usually, a single-crystal monochromator is placed after the diffraction slit to remove X-ray photons of unwanted wavelengths. A conventional scintillation detector (see above) is usually used to measure the intensity of the diffracted beam. This kind of powder diffractometer is called a Bragg-Brentano diffractometer. This type of diffractometer gives best results if the sample is very flat.

8.2. Graded Multilayer Device. Recently, a new diffractometer design takes advantage of the graded multilayer device. Figure 8 shows the principle of this device. With this device, parallel incident and diffracted beams are produced. No diffracted beam monochromator is necessary. The advantage over the Bragg-Brentano design is that the sample does not have to be flat (Fig. 14**b**).

8.3. Applications. The most common application for the Bragg-Brentano and graded multilayer powder diffractometers is to measure the 2θ-values

(2θ is the angle between the incident and diffracted X-ray beams; see Bragg's law above) and intensities for the peaks in a powder diffraction pattern. A typical experiment consists of mounting the specimen in the center of the instrument, and then slowly rotating the specimen and detector (the detector moves at twice the speed of the specimen) so that the diffraction angle (2θ) increases. While the detector and specimen rotate, the X-ray photons that reach the detector are counted by the computer. Figure 15 is an example of a typical powder pattern. This pattern is analyzed by the computer in various ways.

Search–Match. The computer identifies which crystalline phases (components) match the unknown pattern by using a file of known powder patterns maintained by the International Center for Diffraction Data (ICDD). The Powder Diffraction File contains interplanar d spacings [$d = \lambda/(2\sin\theta)$] and intensities of the diffraction maxima for each crystalline powder pattern submitted to the ICDD. Currently, there are ~65,000 patterns in the file. Current search–match programs can successfully identify up to seven components in an unknown pattern. A typical diffraction pattern of an unknown sample and the components identified by the computer search–match program is shown in Figure 15.

Quantitative Phase Analysis. Once the identity of the components in a sample are known, it is possible to determine the quantitative composition of the sample. There are several different methods for doing a quantitative analysis, but the most reliable method is to use mixtures of known composition as standards. The computer can determine quantitatively the relative amounts of each component in the unknown sample. For accurate calculations of relative amounts in the unknown sample, it is necessary that the sample and standards have uniform distributions of crystallites. Often the sample and standards are rotated during data collection to provide a more even distribution of crystallites that diffract.

Indexing and Lattice Parameter Determination. From a powder pattern of a single component, it is possible to determine the indexes of many reflections. From this information and the 2θ values for the reflections, it is possible to determine the unit cell parameters. As with single crystals, this information can then be used to identify the material by searching the NIST Crystal Data File (see the section 'Small Molecule Single Structure Determination').

Structure Determination from a Powder Pattern. In many cases, it is possible to determine atomic positions and atomic displacement parameters from a powder pattern. The method is called the Rietveld method. Single-crystal structure determination gives better results, but in many situations where it is impossible to obtain a suitable single crystal, the Rietveld method can produce adequate atomic and molecular structures from a powder pattern.

Crystallite Size. From the width of the peaks the computer can determine the size of the crystallites in the sample. The smaller the crystallite size, the broader are the diffraction peaks. This kind of analysis is important for determining particulate size of certain materials (eg, silica) where a range of crystallite size may be a health hazard if inhaled into the lungs.

Measurement of Residual Stress and Strain. The displacement of the 2θ value of a particular line in a diffraction pattern from its nominal, nonstressed position gives a measure of the amount of stress retained in the crystallites

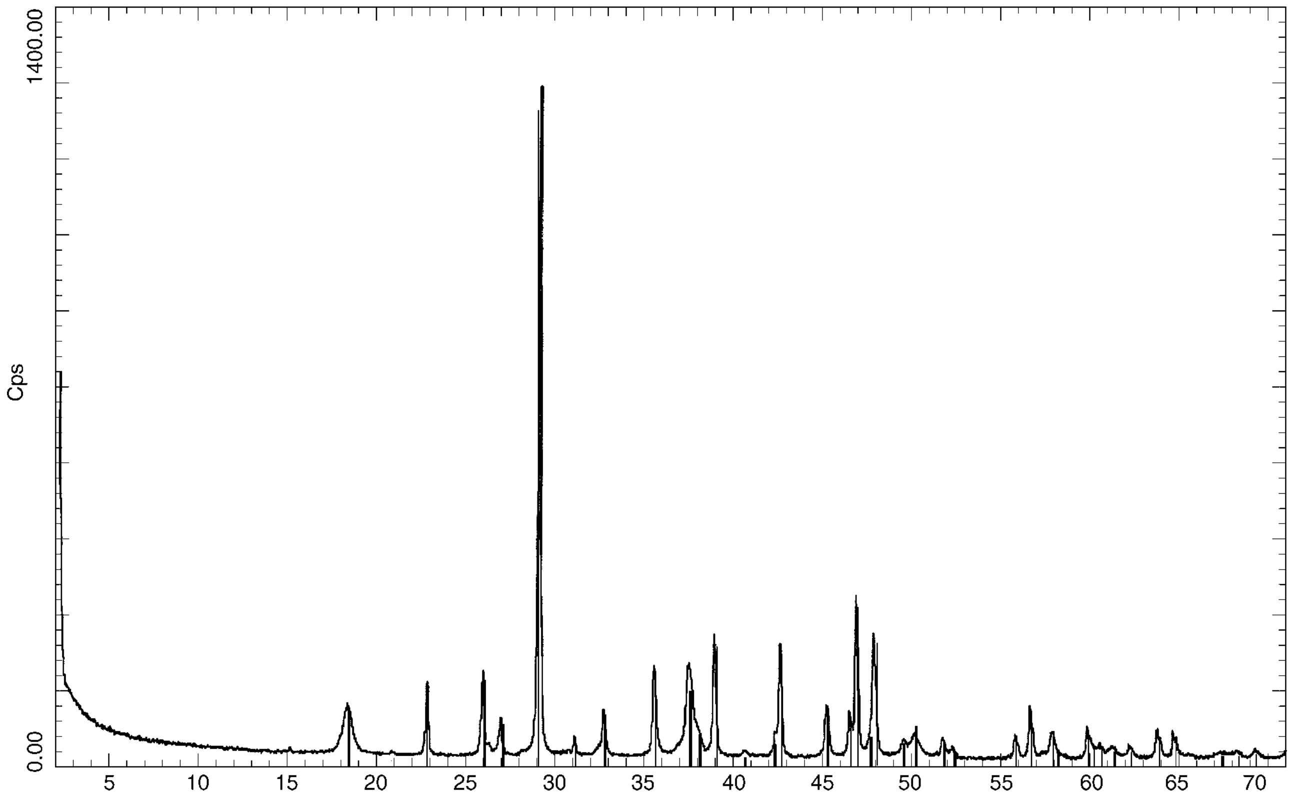

Fig. 15. A typical powder pattern with three phases: Calcite (—), Aragonite (—), and Brucite (〰). The lines below the peaks are the powder lines from the ICDD powder diffraction file.

during the crystallization process. Thus metals prepared in certain ways (eg, cold rolling) have stress in their polycrystalline form. Strain is a function of peak width, but the peak shape is different than that due to crystallite size. Usually, the two properties, crystallite size, and strain, are determined together by a computer program.

Percent Crystallinity. For samples that consist of a mixture of crystalline and amorphous material, it is possible to determine the percent of crystallinity by measuring the integrated intensity of sharp Bragg reflections and the integrated intensity of the very broad regions due to the amorphous scattering.

Texture Analysis. For many rigid polycrystalline materials (eg, metals) an analysis of the orientation of the crystallites is important to understanding the mechanical properties of the sample. In a texture analysis, the sample must be oriented in many different directions with respect to the incident beam. Special texture attachments that provide the necessary tilting of the sample are required. In a pole figure analysis, the intensity of one specific diffraction line (eg, the 2 0 0 reflection) is measured many times at a given 2θ value (the detector is held fixed). The measurements are made at different settings of the sample by rotating about two different axes (called φ and χ). From pole figures for several different reflections, the computer can generate an orientation distribution function (ODF) that contains all of the information concerning the 3D distribution of the orientation of the crystallites.

9. Instruments for Special Applications

Because so many new and exotic materials are being manufactured, special X-ray instruments have been designed to measure properties of these materials.

9.1. X-Ray Reflectometer. Thin films can be deposited on single-crystal substrates. Such materials have special properties (eg, YBCO deposited on silicon is used as a superconductor that can detect very small magnetic fields). To be able to measure the thickness of thin layers, an X-ray reflectometer has been designed. Although this instrument measures the reflected X-ray photons rather than diffracted photons, the design is very similar to that of a conventional powder diffractometer. As with visible photons, total reflection can take place from a surface if the angle between the incident and reflected beams is small enough. Because the wavelengths of X-rays are very small, total reflection occurs at angles on the order of several tenths of a degree. A diagram of an X-ray reflectometer is shown in Figure 16. With this instrument it is possible to measure the thickness of several layers deposited on top of one another. It is also possible to measure the roughness of each layer. Typical measured thicknesses are tens of nanometers and typical measured roughnesses are several tenths of nanometers.

9.2. Position Sensitive Detectors. By replacing the scintillation detector in a conventional powder diffractometer with a Position Sensitive Detector (PSD), it is possible to speed data collection. For each X-ray photon received a PSD records the angle at which it was detected. Typically, a conventional scintillation detector records X-ray photons in a range of a few hundredths of a degree at a time. A PSD can measure many degrees (in 2θ) of a powder pattern

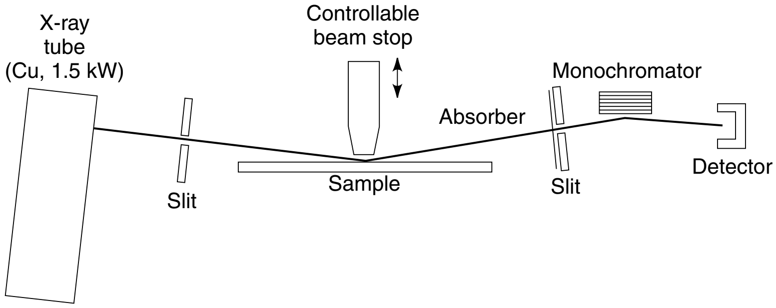

Fig. 16. Diagram of the Siemens X-ray reflectometer.

simultaneously. Thus, for small samples, data collection, which could require hours with a conventional detector, could take minutes or even seconds with a PSD.

9.3. Area Detectors. A 2D or area detector attached to a powder diffractometer can greatly decrease data collection time. Many diffraction applications require so much time with a conventional detector that they are only feasible if an area detector is attached to the instrument. The Siemens General Area Detector Diffraction System (GADDS) uses a multiwire area detector (Fig. 17). This detector measures an x and a y position for each X-ray photon detected. The applications follow.

Texture Analysis with GADDS. With a conventional detector, a data collection for a pole figure analysis with a powder diffractometer with a texture attachment could take 12 h or more. With an area detector, it is possible to collect enough data for several pole figures (required for an ODF analysis) in a few minutes.

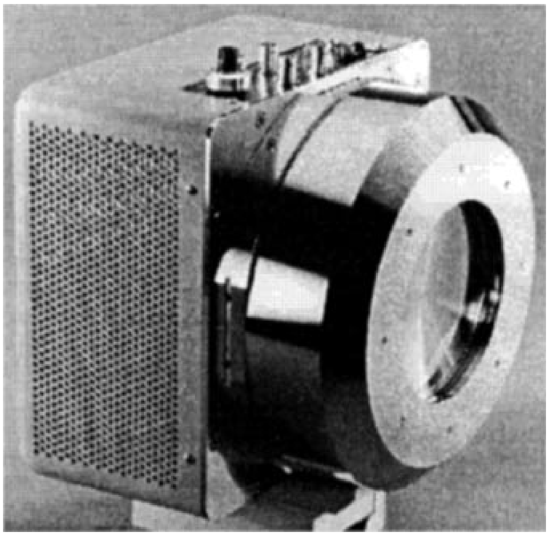

Fig. 17. Siemens HI-STAR multiwire proportional detector.

Small Angle X-Ray Scattering (SAXS). Diffraction at small angles gives information about large-scale structure (d spacings up to 100 nm). Usually the intensity at such small angles is weak and the ability of the area detector to collect complete diffraction rings makes this application feasible. SAXS is used to characterize polymeric or fiber materials.

Polymer or Fiber Diffraction. Polymers and fibers are often ordered in one or two dimensions, but not ordered in the second or third dimension. The resulting diffraction patterns have broad diffuse diffraction maxima. The ability to collect 2D images makes it possible to collect and analyze polymer and fiber diffraction patterns.

Microdiffraction. By concentrating the incident X-ray beam on a small portion of a sample, it is possible to get a complete diffraction pattern of very small regions of a sample. Of course, the intensity from such small regions is weak and an area detector that can collect a large portion of the diffraction pattern at one time makes this application practical. A typical region size is ~50 μm in diameter.

10. X-Ray Fluorescence Spectrometry

X-ray fluorescence (XRF) spectrometry is a technique for measuring the elemental composition of samples. The basis of the technique is the relationship between the wavelength or energy of the emitted incoherently scattered X-ray photons and the atomic number of the element. This relationship established in 1913 is

$$E/1.24 = 1/\lambda = K\,(Z - s)^2$$

where E is the energy in kiloelectronvolts (keV), λ is the wavelength in nanometers, Z is the atomic number of an element, and K and s are constants that depend on the spectral series of the emission line in question. When an atom is bombarded with X-ray photons of sufficient energy, an inner-orbital electron may be displaced leaving the atom in an excited state. As an example, if a molybdenum atom were bombarded in this way, a vacancy in the innermost shell (K shell) might be created by removal of one or the *1s* orbital electrons (see Fig. 18). The energy to remove the K shell electron from the atom is, in the case of molybdenum, ~20 keV. The atom can return to the ground state by transference of a higher orbital electron into the K shell vacancy (the resulting higher level vacancy is filled by an electron from a still higher level, and so on). In so doing, the difference in energy between the electron in the K shell and the energy of the electron in the shell from which it came is emitted as an X-ray photon. For molybdenum, an L shell electron transfering to the K shell causes an X-ray photon with an energy of 17.6 keV to be emitted. For the L to K shell transition, the emitted X-ray photon is called a K_α photon. The L series X-ray photons are produced when L shell vacancies are filled with higher level electrons. The fluorescent yield is ~1 for the high atomic number elements and may be as small as 0.01 for the low atomic elements (eg, Be, Na, Mg, and Al). Most commercially available X-ray spectrometers can measure X-ray photons with wavelengths in the range of ~0.02–8.0 nm (60–0.18 keV), which means that the K series can

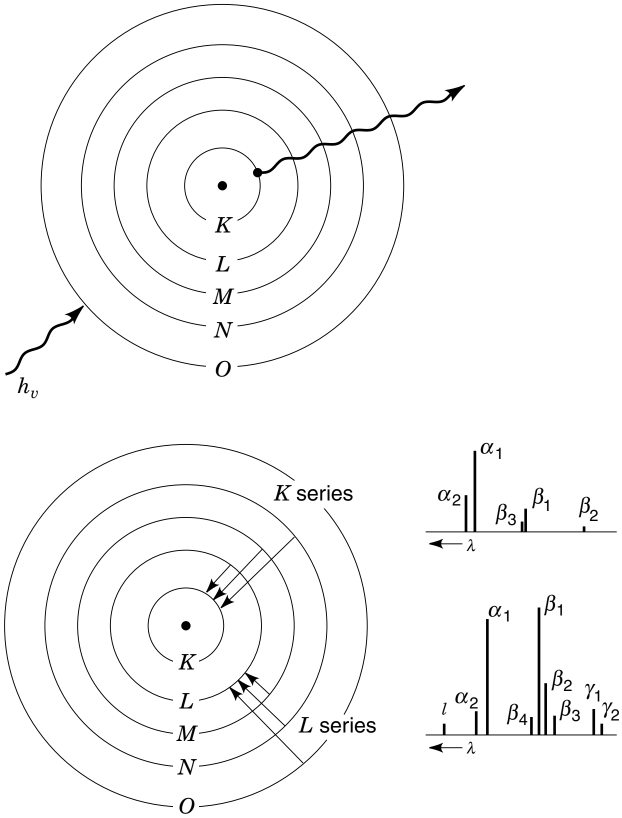

Fig. 18. Production of X-ray fluorescence K and L series from the molybdenum atom.

be measured for atomic numbers 4(Be) to 71(Lu) and the L series from 25(Mn) to 92(U). Each element produces a fluorescence spectrum of intensity versus wavelength that is characteristic of that element.

10.1. X-Ray Spectrometers.

An X-ray spectrometer is an instrument that measures the fluorescence spectra of samples. The associated computer software then determines the qualitative and quantitative elemental composition of the samples from the resulting spectra.

The primary X-ray source is usually a sealed tube with a Rh anode. The tube usually has an end window so that the sample is as close to the anode as possible. This arrangement ensures that the surface of the sample is irradiated with a beam with nearly uniform intensity.

10.2. Wavelength Dispersive Spectrometer.

A wavelength dispersive spectrometer uses an analyzing crystal to measure the spectrum. The analyzing crystal is a single crystal positioned so that a specific Bragg reflection can be used to measure the intensity of the various wavelengths of the fluorescence spectrum. The analyzing crystal is continuously rotated. At each position of the crystal, X-ray photons with only a narrow band of wavelengths are diffracted into a detector. The detector is usually a scintillation detector like that used in a conventional powder diffractometer. The detector is rotated at twice the speed of the analyzing crystal so that the Bragg condition (Fig. 6) is maintained for each wavelength.

Because such a wide range of wavelengths must be measured (see above), no single analyzing crystal is best for all elements. The 1 0 0 reflection of LiF (*d* spacing; $2d = 0.403$ nm) is useful for measuring the K_α lines for elements K to Xe. A pentaerythrite (PET) *d* spacing; $2d = 0.874$ nm analyzing crystal is useful for measuring the K_α lines for elements Al to Ti. Special multilayer materials (eg, alternating layers of W and C; *d* spacing; $2d = 16.0$ nm) are useful for the K_α lines for the lowest atomic number elements. By changing the thickness of each layer, large *d* spacing ($2d = 30$ nm) is available for light element analysis. Other analyzing crystals are used for measuring other ranges of wavelengths.

10.3. Energy Dispersive Spectrometer. An energy dispersive spectrometer (EDS) uses a detector that can measure the energy of each detected X-ray photon. The detector is usually a lithium-drifted silicon [Si(Li)] detector that is a proportional detector of high intrinsic resolution. The resolution of this type of detector is typically 130−160 eV, compared to 20−200 eV for the wavelength dispersive systems. A multichannel analyzer (MCA) is used to sort the arriving pulses into memory locations corresponding to the energy of the X-ray photons. Figure 19 shows the analytical process in the pulse height analysis. The signal output from the energy dispesive X-ray (EDX) detector is a pulse, whose height corresponds to X-ray energy. After the pulses are amplified, the signals are analyzed by the MCA. Each channel independently records the number of the pulses as a function of their height; therefore, simultaneous energy analysis for multielements is achieved. No analyzing crystal is needed for the energy dispersive systems. The complete spectrum is collected with no mechanical movement of the spectrometer. However, the crystal of energy dispersive X-ray detector must be cooled normally by liquid N_2 to minimize the electronic noise in the detector. Therefore, the total size of the EDS becomes large due to a big vessel of liquid N_2.

Energy dispersive spectrometers can, in general, collect the spectrum faster and are less expensive than the more sophisticated wavelength dispersive spectrometers. However, they do not have the resolution and cannot separate closely spaced lines as easily as the wavelength dispersive spectrometers in some cases. The advantage of EDX detector is that simultaneous energy analysis for multielements is possible. In addition, a new type of EDX detector like Silicon drift detector (SDD) has been developed. It has a Peltier cooling device ($\sim -20^\circ$) instead of liquid N_2. The size of the SDD is quite small, leading to downsizing total analytical system. The SDD that has a good energy resolution of <140 eV [full width at half-maximum (FWHM) at Mn Kα] is commercially available. However, the sensitive volume (thickness of the crystal) of the SDD is limited to be $\sim$500 μm. Therefore, it is difficult to detect high energy X-rays. This is one of the drawbaks of the SDD. A Si-PIN detector is also a promising EDX detector, operated without liquid nitrogen. This is a low cost and compact detector having an acceptable energy resolution of 150−180 eV depending on the size of crystal and shaping time.

The great flexibility and range of the two types of X-ray spectrometers make them ideal for quantitative analysis. The precision of a well-designed X-ray spectrometer is typically $\sim$0.1%. Systematic errors in quantitative X-ray spectrometry

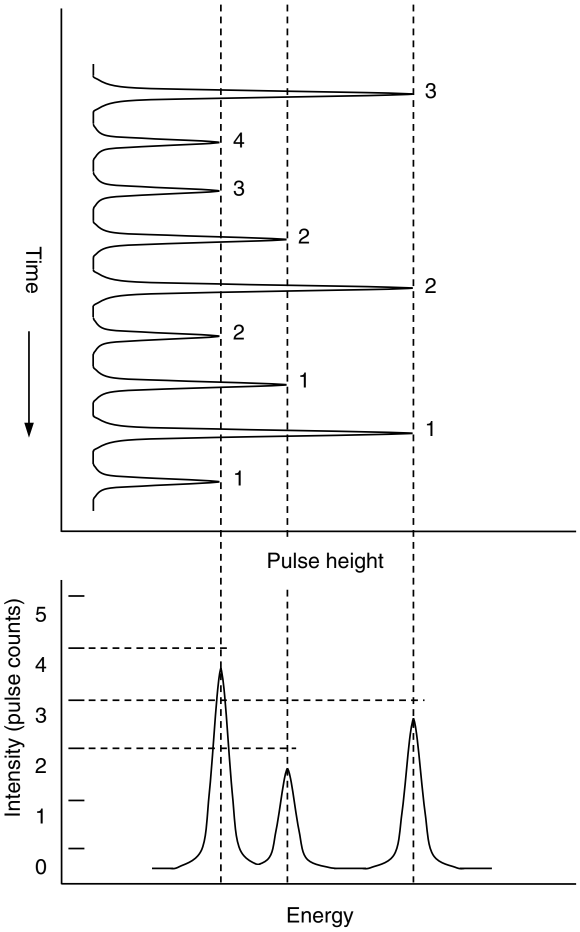

Fig. 19. Principle of pulse height analysis.

arise mainly from absorption and specimen related phenomena, including particle size and heterogeneity. Although these effects are complex, computer programs have been developed for handling them. Relative amounts of the elements in a sample can usually be determined with an accuracy of a few tenths of a percent.

11. Total Reflection X-Ray Fluorescence

When an X-ray beam irradiates a flat surface of solid material at grazing angles of less than the critical angle, the X-ray beam is totally reflected. This critical angle (θ_c) depends on the energy (wavelength: λ) of the X-rays and the density (ρ) of the solid material. Accoding to Snell's law, θ_c is given as follows:

$$\theta_c = \sqrt{2\delta} \propto \lambda\sqrt{\rho}$$

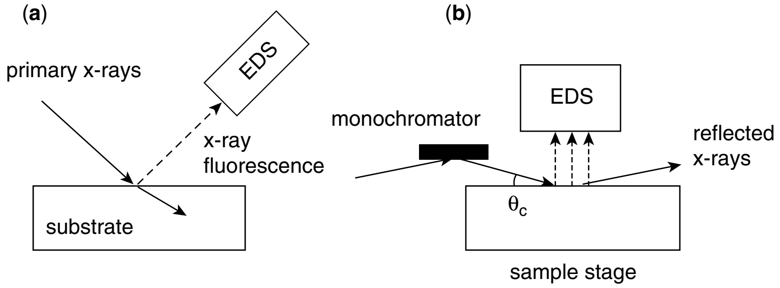

Fig. 20. Experimental arrangements. (**a**) Normal X-ray fluorescence spectrometry, (**b**) total reflection X-ray fluorescence spectrometry.

where δ appears in the real part of the refractive index ($n = 1 - \delta - i\beta$). The parameters δ and β are real and imaginary parts in the refractive index, respectively. These values depends on the X-ray energy and material of the substrate. For example, θ_c of Mo Kα (17.44 keV) on a glass (SiO_2) is ~0.10°.

This total reflection phenomenum is useful for X-ray analysis. In the normal XRF analysis, the primary X-rays are irradiated at large incident angles, as shown in Figure 20**a**. In this case, scattered primary X-rays from the sample cause large continuous X-ray background in the X-ray spectrum. In the total reflection arrangement (Fig. 20**b**), the primary X-rays are totally reflected on the flat substrate; therefore, the primary X-rays do not affect the X-ray spectrum. The X-ray fluorescence emitted from the surface on the substrate is detected usually by the EDX detector. The X-ray detector having a large sensitive area (~80 mm^2) is placed near the sample; therefore, X-ray fluorescence is detected with high efficiency. This analytical technique is called TXRF (total reflection X-ray fluorescence) spectrometry. Since the background intensity is considerably reduced in the TXRF, the S/B ratio and detection limit are improved, leading to trace elemental analysis.

Figure 21 shows penetration depth of primary X-rays of Mo Kα (17.44 keV) on a Si wafer as a function of incident angle. In the angle range below θ_c, the

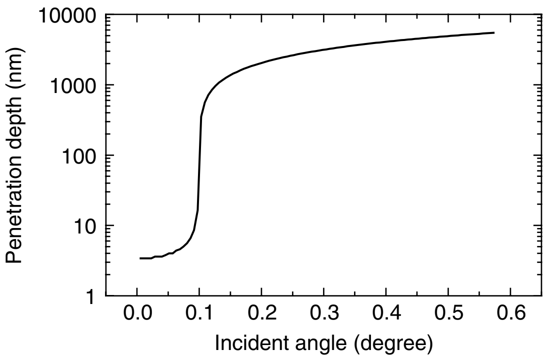

Fig. 21. Penetration depth of Mo Kα (17.44 keV) on Si as a function of incident angle. In this case, the critical angle is ~0.1°.

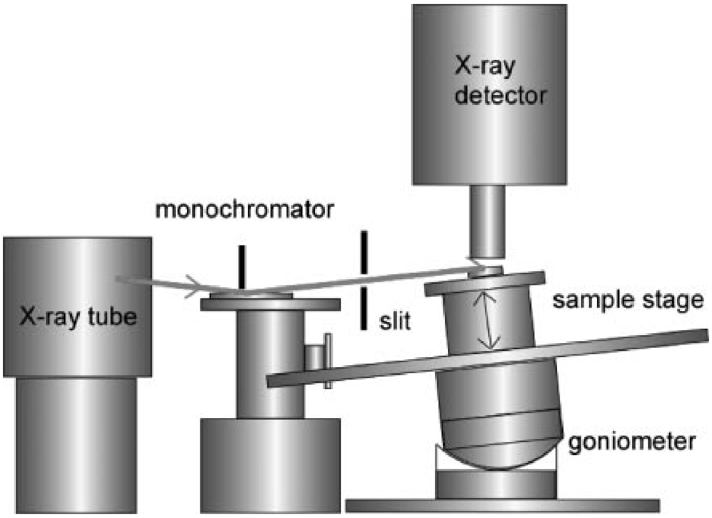

Fig. 22. Schematic drawing of TXRF spectrometer.

penetration depth is quite small, ~3 nm. Therefore, TXRF spectrometry is considered to be a surface-sensitive method. Actually, the TXRF has been applied for the analysis of contaminations on Si wafers in semiconductor industry. The detection limits $<10^9$ atoms/cm^2 for contaminations on Si wafer have been reported.

Since total reflection phenomenon is related to energy of the X-rays, monochromatic X-rays are usually applied for TXRF analysis. A commercially available TXRF instrument consists of a powerful X-ray source, a monochromator like a W/C multilayer, a precise sample stage (X, Y, Z, θ, ϕ) and an X-ray detector. Figure 22 shows an experimental setup of TXRF spectrometer in the laboratory. Powerful monochromatic synchrotron radiation (SR) is a suitable X-ray source for TXRF. Actually, the smallest detection limit is obtained in the SR–TXRF analysis. In addition, to improve the detection limit, preconcentration of contaminations on Si wafer is performed in some cases. Vapor-phase decomposition (VPD) is one of the techniques for chemical preconcentration. After the Si wafer sample is exposed to HF vapor, the solution that includes surface contaminations is collected into a small droplet, and then dried. Besides the trace analysis for Si wafers, TXRF spectrometry has been applied for trace analysis of environmental samples (water, air, soil, etc), medical samples (blood, urine, hair, liver, etc), arts (pigments) and forensic samples (gunshot residue, finger prints, etc).

12. Micro X-Ray Fluorescence

Micro X-ray fluorescence (MXRF) analysis is XRF analysis with a spatially restricted X-ray beam. This is an area that is gaining interest by its ability to solve materials characterization problems rapidly. Micro X-ray fluorescence is done with the aid of a spatially restricted X-ray beam that can range from

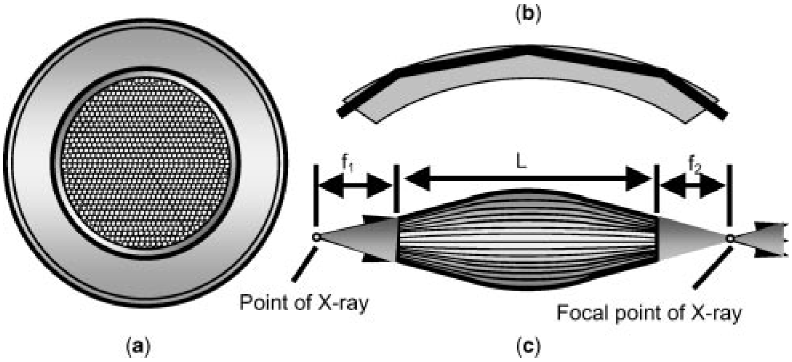

Fig. 23. Drawings of cross section of polycapillary X-ray lens (**a**), total reflections in each capillary (**b**), and side view of polycapillary full lens (**c**).

submicrometers at synchrotron facility to >300 μm in commercially available bench top instruments. At a synchrotron radiation facility, various focusing optics like a K-B mirror, Zone plate, and refractive lens can be applied to obtain micro X-ray beam. However, in the laboratory, the primary X-ray does not have enough intensity; therefore, these focusing optics are not always effective in the laboratory. One alternative focusing optic is capillary optics. A single capillary made of glass is useful to make a micro X-ray beam (10 μm in diameter) with small divergence of the beam; however, a flux density gain, which is defined as the ratio of X-ray intensity obtained by single capillary lens to the X-ray intensity obtained by a simple pinhole, is not so high. Therefore, XRF analysis of low concentrations is difficult in some cases. On the other hand, a polycapillary X-ray lens consists of >100 thousand small capillaries. Each capillary has a diameter of a few micrometers. As shown in Figure 23, X-rays emitted from a small X-ray source are propagated into the polycapillary lens with a large solid angle. Multiple total reflections occur on the inner wall of each capillary, as a result, X-rays are focused into a small point. The gain obtained for this polycapillary lens is >10 times higher that that of a single capillary. A gain of a few thousand is reported for polycapillary lens.

A spot size at focal point critically depends on the X-ray source size. The smaller the X-ray source size, the smaller the spot size. Therefore, the polycapillary lens is usually applied with a microfocus X-ray tube, whose source size is $<50 \times 50$ μm. The spot size at focal point depends on the energy of the X-rays. The small spot size is available for high energy X-rays. A small spot size of ~15 μm for Mo Kα has been reported.

Transmission efficiency is also an important factor for analytical performance of the polycapillary lens. Since the θ_c for low energy X-rays is larger than that for high energy X-rays, the transmission efficiency decreases in the high energy range. The shape of the curve of transmission efficiency as a function of energy critically depends on the design of the polycapillary lens. Therefore, it is important for users to use a proper polycapillary lens considering the analytical sample, required information and XRF instrument.

Micro XRF instrument consists of a microfocus X-ray tube, an X-ray focusing optic, an X–Y–Z sample stage, and an X-ray detector. Figure 24 shows a

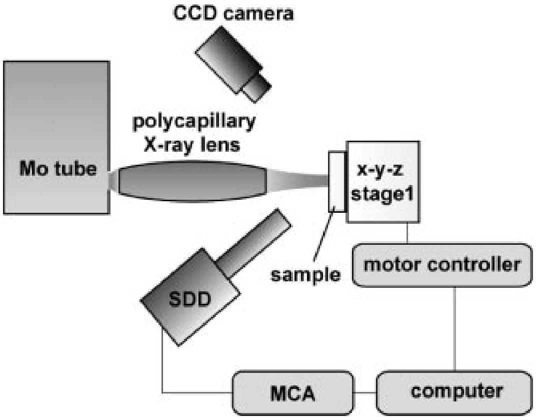

Fig. 24. A typical experimental setup of micro XRF analysis.

typical experimental setup for micro XRF analysis. Micro XRF has been applied for elemental analysis of a small region near the surface of the sample. The analyzing region depends on the spot size of the X-ray beam on the sample. In this case, X-ray fluorescence emitted in certain depth is detected. This analyzing depth depends on the X-ray energy and matrix component of the sample. The analysis depth can be several millimeters in the case of a low Z matrix sample and a high Z analyte. Usually, the sample is placed on a precise $X-Y-Z$ stage, which is automatically controlled by using stepping motors and a computer. By scanning the sample in the $X-Y$ plane, 2D elemental X-ray images can be obtained. A number of elemental images are simultaneously obtained by using an EDX detector. There are commercially available micro XRF instruments. Micro XRF spectrometry has been applied for analyses of semiconductor devices, food materials, medical samples, and paintings.

13. 3D X-Ray Fluorescence

X-rays penetrate to a considerable depth into the sample, depending on X-ray energy and sample matrix composition. X-ray fluorescence having chemical information is produced in the X-ray penetrating path. This suggests elemental depth profiling and 3D elemental analyses. One of the techniques for 3D-XRF is confocal micro XRF spectrometry, as shown in Figure 25. In this method, two focusing X-ray optics like polycapillary X-ray lens are applied. One X-ray lens is used to obtain a micro X-ray beam for excitation of X-ray fluorescence. Another X-ray lens is used to detect X-ray fluorescence. Usually, a polycapillary half-lens is attached to the top of the EDX detector. If the EDX detector that has a large sensitive area (eg, 5–10 mm^2) is used, it is preferable to use the entire sensitive area of the EDX detector. Therefore, XRF is collected and collimated by the half-lens, and then detected by the EDX detector. In the confocal configuration, X-ray fluorescence emitted only from a spatially small region, where two focal points are overlapped, is detected. Therefore, 3D elemental X-ray images are obtained by scanning the sample position in X, Y, and Z axes using stepping motors. The

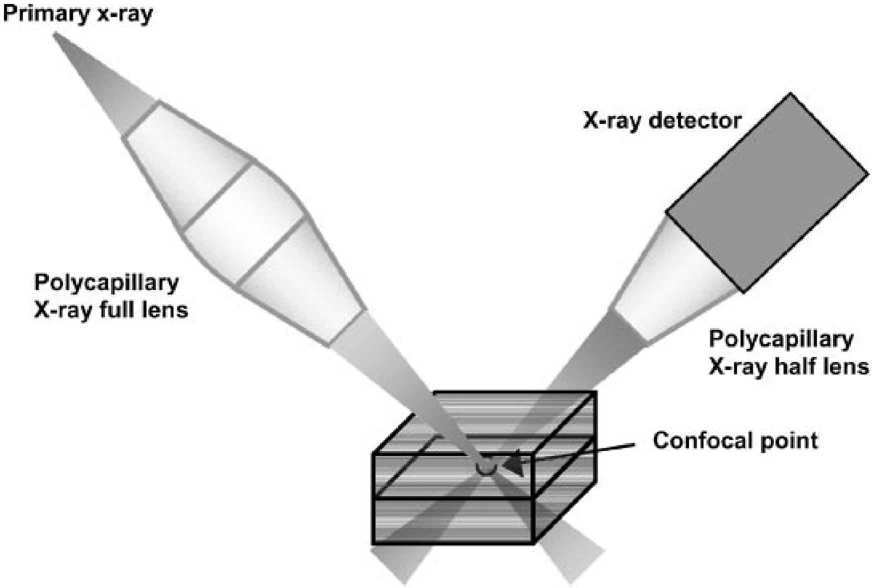

Fig. 25. Schematic drawing of confocal setup of 3D-XRF analysis.

analyzing volume is related to the X-ray beam focal spot sizes. An analyzing volume of several tens of micrometers has been reported.

Using the confocal micro XRF instrument, elemental depth profiling has been performed for paintings and trace elements in wheat grain, etc. Three-dimensional images have also been taken for an iron oxide particle in BN and trace elements in embryo of rice grain.

14. X-Ray Radiography

X-ray imaging tests are widely used to examine interior regions of metal castings, fusion welds, composite structures, and brazed components. Radiographic tests are made on pipeline welds, pressure vessels, nuclear fuel rods, and other critical materials and components that may contain 3D voids, inclusions, gaps, or cracks that are aligned so that the critical areas are parallel to the X-ray beam. Since penetrating radiation tests depend on the absorption properties of materials on X-ray photons, the tests can reveal changes in thickness and density and the presence of inclusions in the material.

X-ray fluoroscopy is used for direct on line examination. A fluorescent screen is used to convert X-ray photons into visible light photons. A television camera receives the visible image and displays it on a television screen (see Fig. 26). This type of system is used for security screening of carry-on luggage at airports.

As in medical X-ray imaging, computerized tomography (CT) can reveal the details of the internal structure of complex objects. Many detectors are used to measure the transmittance of X-rays along many lines through the object. A

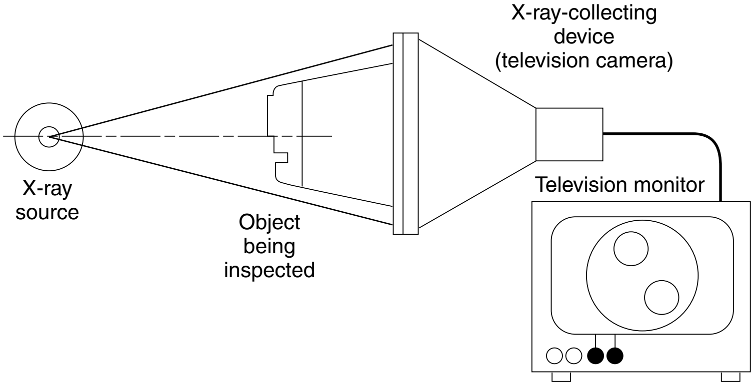

Fig. 26. Basic hardware for X-ray fluoroscopic inspection.

computer uses this information to produce an image of the internal structure of a slice of the object. One of the methods under investigation by the Federal Aviation Administration is a computerized tomographic scanning system for automatically detecting bomb materials in bags loaded onto airplanes. Digital detectors are becoming increasing importance in X-ray radiography, for medial applications (dental, mammograms, bone density, etc) as well as industrial applications. Fujifilm Co. has produced a computed radiography from 1983. The FCR series are digital X-ray imaging instruments with a 50-μm resolution and 20 pixel/mm sampling pitch, applied for mammography. The XCUBE produced by Hamamatsu Co. is a compact X-ray CCD camera with CsI X-ray scintillators and an effective are of 25-mm diameter.

15. Applications Using Synchrotron Radiation

Because of the unique features of the X-ray radiation available at synchrotrons, many novel experiments are being conducted at these sources. Some of these unique features are the very high intensity and the brightness (number of photons per unit area per second), the nearly parallel incident beam, the ability to choose a narrow band of wavelengths from a broad spectrum, the pulsed nature of the radiation (the electrons or positrons travel in bunches), and the coherence of the beam (the X-ray photons in a pulse are in phase with one another). The applications are much more diverse than the applications described in this article. The reader may wish to read the articles in the Proceedings of the Materials Research Society listed in the bibliography.

Just two of the many experiments being conducted that are of special interest to chemists are described here. Recent results using synchrotron radiations can be known from following websites: SSRL (Stanford Synchrotron Radiation Laboratory), APS (Advanced Photon Source) as well as websites of other synchrotron facilities.

15.1. Extended Absorption Fine Structure.

As indicated above, it is possible to obtain very detailed structural information from the X-ray diffraction of single crystals. For samples that are not single crystals, it is possible to obtain structural information around the site of certain heavy atoms. The procedure is called Extended Absorption Fine Structure (EXAFS). As indicated in the section, "X-Ray Fluorescence Spectrometry", when an X-ray photon of a specific wavelength impinges on an atom of a given type (eg, Fe), the incident photon may be absorbed by the atom and an X-ray photon with longer wavelength is emitted. The intensity of the transmitted X-rays at this specific wavelength decreases correspondingly. The resulting absorption spectrum of intensity versus wavelength will have a sharp peak at this specific wavelength. There is, however, a fine structure to this absorption spectrum that is dependent on the chemical structure of the atoms bonded to the atom of interest. By measuring the absorption fine structure spectrum of intensity versus wavelength, one can determine this bonding structure. Because of the large intensities and fine wavelength tunability of the incident X-ray photons available at synchrotrons, these measurements can be routinely performed, but they are difficult or impossible to perform using conventional X-ray sources. Much information about the structures of catalysts has been obtained using EXAFS.

15.2. Laue Method for Macromolecule X-Ray Diffraction. As indicated above, it is possible to determine the structures of macromolecules from X-ray diffraction; however, it normally takes a relatively long period of data collection time (even at synchrotrons) to collect all of the data. A new technique, the Laue method, can be used to collect all of the data in a fraction of a second. Instead of using monochromated X-rays, a wide spectrum of incident X-rays is used. In this case, all of the reflections that are diffracted on to an area detector are recorded at just one setting of the detector and the crystal. By collecting many complete data sets over a short period of time, the Laue method can be used to follow the reaction of an enzyme with its substrate. This technique cannot be used with conventional X-ray sources.

16. Portable EDXRF Instruments

As mentioned previously, the compact Si-PIN EDX detector is useful for miniaturizing total X-ray analysis system. This detector has a sufficient energy resolution of 150–200 eV at 5.9 keV. NITON has produced several types of portable EDXRF instruments depending on the samples such as plastics, metals, and soils. This handheld EDXRF instrument has a radioactive X-ray source, eg, ^{109}Cd and ^{241}Am, a small EDX detector, eg, Si-PIN or CdZnTe detectors, and a display to show the analyzed quantitative data. The similar handheld EDXRF instruments have been developed by other companies; AMPTEK, EDAX, Thermo Measure Tech, etc. These portable EDXRF instruments are useful for *in situ* environmental analysis, analysis of cultural heritages (paintings, monuments, etc), and analysis of soils of MARS.

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