

### 8.3 X-RAY ABSORPTION

If the wavelength of an X-ray beam is short enough (high energy), it will excite an atom that is in its path. In other words, the atom absorbs X-rays that have enough energy to cause it to become excited. As a rule of thumb, the X-rays emitted from a particular element will be absorbed by elements with a lower atomic number. The ability of each element to absorb increases with atomic number.

Beer's law states that

$$\log \left( \frac{P_0}{P_x} \right) = \mu_x t \quad (8.20)$$

where

$\mu_x$  is the linear absorption coefficient

$t$  is the path length through the absorbing material

$P_0$  is the X-ray power before entering sample

$P_x$  is the X-ray power leaving sample

However,

$$\left( \frac{\mu_x}{\rho} \right) = \mu_m \quad (8.21)$$

where

$\mu_m$  is the mass absorption coefficient

$\rho$  is the density

But

$$\mu_m = \left( \frac{CN_0Z^4\lambda^3}{A} \right) \tag{8.22}$$

where

- C is a constant
- $N_0$  is Avogadro's number
- Z is the atomic number
- A is the atomic weight
- $\lambda$  is the wavelength of the radiation

It can be seen that at a given wavelength,  $\mu_m$  is proportional to  $Z^4$  divided by the atomic weight. This relationship is shown in Figure 8.56. The setup for X-ray absorption is slightly different than that for XRF, as seen in Figure 8.57. The sample is placed directly in line with the X-ray tube, in

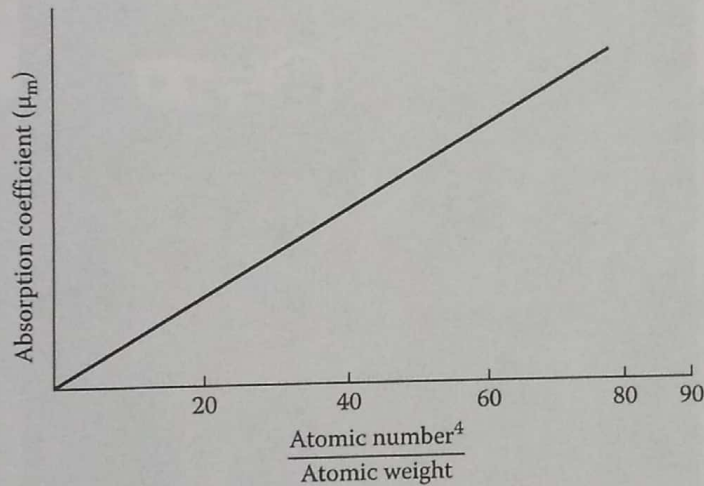


Figure 8.56 Relationship between atomic number and X-ray absorption coefficient.

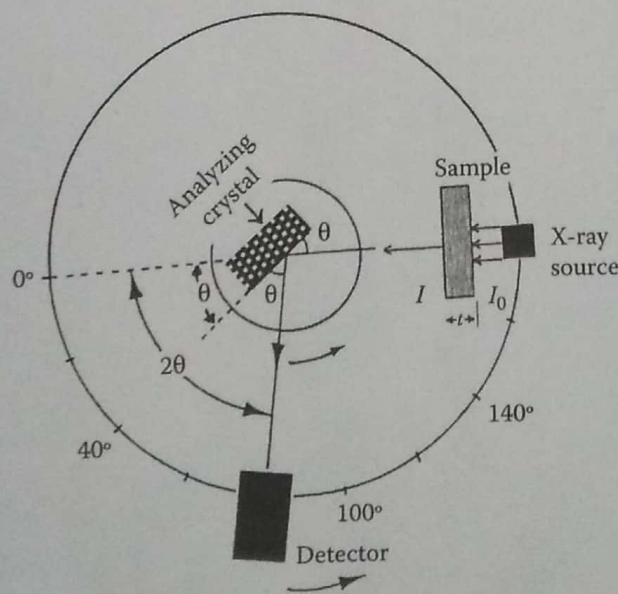


Figure 8.57 X-ray absorption. The sample is placed between the X-ray tube and the detector. The intensity of the source is  $I_0$ . The intensity of light reaching the detector after passing through a sample of thickness  $t$  is  $I$ .  $I$  will be less than  $I_0$  if absorption occurs.

*Configuration:*

*It passing sample*

a configuration very similar to UV/VIS absorption spectrometry. The parameter measured is the decrease in intensity of the incident beam after passing through the sample. The same detectors described for XRF may be used for X-ray absorption spectrometry. Older systems and some current medical systems use photographic film for detection (radiography).

*Radiography:*

The most familiar example (and the oldest use) of X-ray absorption does not provide chemical information, but rather physical information. That is the use of X-ray absorption in medical radiography, but it is based on the relationship between absorption coefficient and atomic number. For example, the human arm consists of flesh, blood, and bone. The flesh or muscle is made up primarily of carbon, nitrogen, oxygen, and hydrogen. These are all low atomic number elements, and their absorptive power is very low. Similarly, blood, which is primarily water, consists of hydrogen and oxygen, plus small quantities of sodium chloride and trace materials. Again, the absorptive power of blood is quite low. In contrast, bone contains large quantities of calcium and phosphorus, primarily as calcium phosphate. The atomic numbers of these elements are considerably higher than those in tissue and blood, and so the absorptive power is considerably higher. When an X-ray picture is taken of a hand (Figure

*Absorption Coefficient  $\propto Z$*

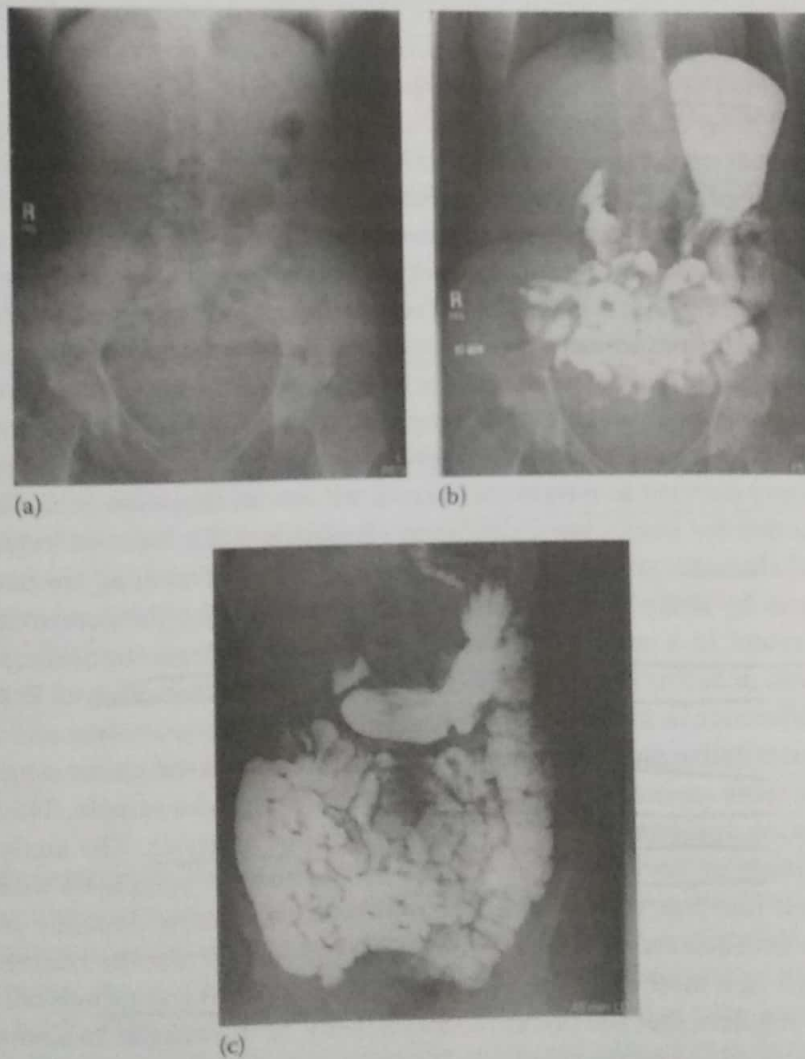


Figure 8.58 X-ray photograph of a human hand.

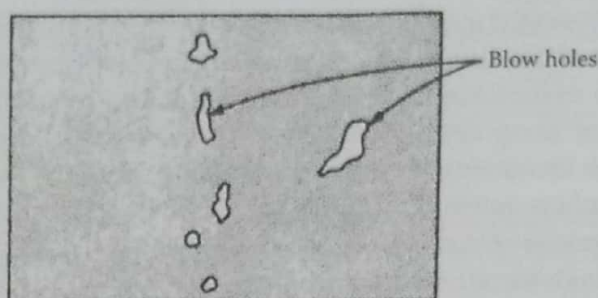


*medical diagnose of bones disease:*  
 8.58), the x-radiation penetrates the muscle tissue and blood quite readily, but is absorbed significantly by the bone. A photograph of this absorption indicates the location of the bones in the hand. The procedure is routinely used in medicine to detect broken bones, fractures, and arthritic changes in joints.

Another application of X-ray absorption in medicine is to define the shapes of arteries and capillaries. Normally, the blood absorbs only poorly; however, it is possible to inject a solution of strongly absorbing cesium iodide into the veins. The material is then swept along with the blood and follows the contours of the arteries. An X-ray video is recorded as the highly absorbing cesium iodide flows through the arteries, showing the contours of the arteries. This can be used to identify breaks in the veins or arteries that could cause internal bleeding. Such internal bleeding can be the cause of a stroke. The technique may also be used to indicate a buildup of coating (plaque) on the inside of the veins. This is particularly dangerous in the heart, where deposits of cholesterol restrict the flow of blood through the heart. If this is left unchecked, a heart attack will result. X-ray absorption can be used to diagnose this problem and to locate exactly the position of deposits. Surgery is made much easier by this technique. In a similar fashion, a barium-containing liquid ingested by a patient permits the detailed observation of the colon since barium, a high Z element, absorbs very strongly (Figure 8.59a through c).



**Figure 8.59** X-ray photographs of a human colon before and after ingestion of a barium-containing liquid. (a) Before ingestion of the barium solution, the colon cannot be seen at all. (b) 10 min after ingestion, the highly absorbing barium has entered the colon. (c) After 45 min, the entire colon can be clearly seen.



**Figure 8.60** Schematic X-ray absorption photograph of a mechanical weld.

### *metallurgy:*

In the field of metallurgy, applications of X-ray absorption include the detection of voids or the segregation of impurities, such as oxides, in welds and other joints. Figure 8.60 shows an idealized X-ray absorption photograph of a mechanical weld that contains voids or internal holes. Such holes indicate that the weld is mechanically weak and might break in use. If the weld is weak, it must be strengthened to form a sufficiently strong joint. This type of nondestructive testing is used to check the manufacturing quality of ships, aircraft, bridges, and buildings. It is also used to check these structures during routine maintenance. X-ray absorption is routinely used for measuring the thickness of thin metal films. *liquid levels:*

The technique of X-ray absorption can also be used to determine the levels of liquids in enclosed vessels or pipes without opening or breaking them. The same process can be used to detect metal supports or metal fillings inside constructed objects as diverse as buildings and small works of art. A major advantage is that X-ray techniques are usually nondestructive. Sometimes artists paint over old paintings, using the canvas for their own work and covering unrecognized masterpieces in the process. Using X-ray absorption, it is possible to reveal the covered painting without removing the top painting. When used to examine a metal horse sold for several million dollars as an ancient Greek art piece, X-ray absorption showed that the horse contained internal metal supports and was therefore a fake. This was done without destroying the art piece, in case it had been authentic.

For quantitative elemental analysis, X-ray absorption is not particularly useful except in the case of a single heavy element in a light matrix. As we saw in Equation 8.10, the mass absorption coefficient needed for Beer's law calculation (Equation 8.20) must be calculated from the weight fractions of elements present in the sample. The weight fractions are usually unknown. Quantitative analysis by X-ray absorption is usually only used for the determination of a high atomic number element in a matrix of lower atomic number elements. Examples include the determination of lead or sulfur in hydrocarbon fuels and the determination of Pt catalyst in polymers, where the difference in mass absorption coefficients between analyte and matrix is large. One approach to quantitative analysis using X-ray absorption is based on the measurement of the intensities of two or more monochromatic X-rays passed through the sample. This is called X-ray preferential absorption analysis or dual-energy transmission analysis. The analysis depends on the selective absorption of the transmitted X-rays by the analyte compared with absorption by the rest of the sample (the matrix). The sensitivity of the analysis also depends on the difference in mass absorption coefficients of the analyte and sample matrix for the transmitted X-rays; a big difference results in a more sensitive analysis. The analyte concentration calculation in any absorption method requires that the thickness and density of the sample be known and requires a homogeneous matrix for accurate quantitative results.

One of the most common applications of X-ray absorption (transmission) is the determination of sulfur in



## 8.4 X-RAY DIFFRACTION

*Significance:*

XRD is a technique that is useful for the analysis of solid crystalline or semicrystalline materials. Most organic and inorganic compounds, minerals, metals, and alloys, and many types of polymers form crystals and can be analyzed by XRD. XRD can provide the exact crystal structure of a pure single-crystal material. In addition, XRD can provide the qualitative and quantitative identification of the molecules present in pure crystalline powders or mixtures of crystalline powders.

The ions or molecules that make up a crystal are arranged in well-defined positions, called a crystal lattice. Figure 8.62 is an electron micrograph of the (110) plane of crystalline silicon. Three coordinates, called Miller indices, identify the plane in space; the Miller indices for this plane are 1,

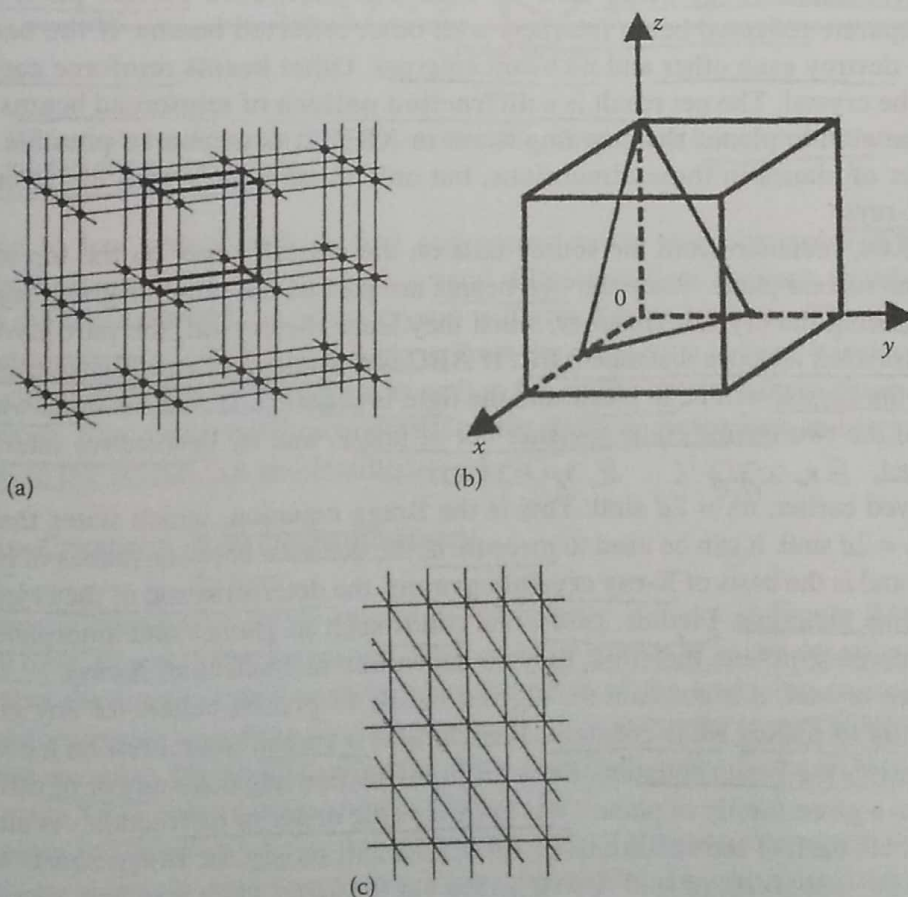


**Figure 8.62** An electron micrograph of the (110) plane in crystalline silicon.

### structure of crystal lattice:

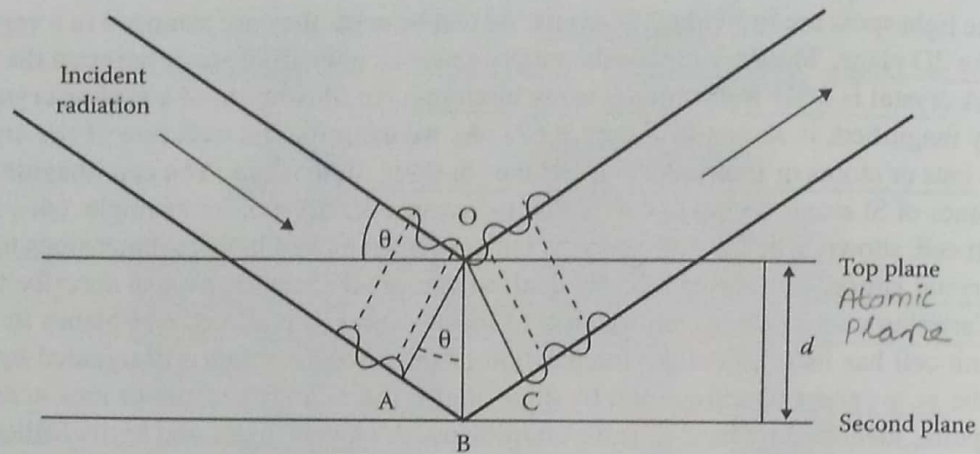
1, and 0. The light spots are individual Si atoms. As can be seen, they are arranged in a very regular pattern in the 2D plane. The dark area is the empty space or interstitial space between the atoms in the lattice. A crystal is a 3D well-ordered array of atoms. An illustration of a typical crystal structure, greatly magnified, is shown in Figure 8.63a. As we examine the structure of the crystal, we see that the ions or atoms or molecules form planes in three dimensions. You can imagine stacking identical planes of Si atoms on top of each other to create a 3D crystal, for example. *Unit cell:*

The **unit cell**, shown in heavy outline in the lattice, can be moved in three dimensions to recreate the entire crystal lattice. The unit cell is the smallest volume that can be used to describe the entire lattice. A Cartesian coordinate system is used to locate points, directions, and planes in a crystal lattice. A unit cell has its origin at the intersection of the three axes and is designated by its edge lengths in the x-, y-, and z-directions and by three angles. An atom (molecule or ion) in the crystal lattice is a point, identified by its x, y, and z coordinates. A plane is identified by its Miller indices, the reciprocals of the intersection points of the plane with the x, y, and z axes. A triangular plane is shown within the unit cell. The plane intersects the x-axis at 1/2, the y-axis at 1/2, and the z-axis at 1; it has intercepts of 1/2, 1/2, and 1. The reciprocals are 2, 2, and 1, so the Miller indices for this plane are (221). A plane that is parallel to a given axis has an intercept of infinity; the reciprocal of infinity is 0. A crystal lattice will have many parallel planes, each uniformly spaced from each other. Such groups of planes are called families of planes and will have related Miller indices [e.g., the (110), (220), (330), and (440) planes are a family of planes]. These planes in a given family are all parallel,



**Figure 8.63** (a) A portion of a 3D crystal lattice. The unit cell, or basic repeating unit, of the lattice is shown in heavy outline. The black dots represent the atoms or ions or molecules that make up the crystal. (b) A cubic unit cell, with the corners of the cell located at 1 unit from the origin (O). The triangular plane drawn within the unit cell intersects the x-axis at 1/2, the y-axis at 1/2, and the z-axis at 1. This plane has Miller indices of (221). (c) A family of planes shown in a 2D lattice.





**Figure 8.64** Reinforcement of light diffracted from two crystal planes.

as shown in Figure 8.63c, just at different distances from the origin specified for the coordinate system. The (110) plane is the farthest from the origin, and the (440) plane is the closest to the origin of the set of planes (110), (220), (330), and (440). Miller indices for commonly used analyzing crystals were given in Table 8.7. *Phenomenon of diffraction:*

If a monochromatic X-ray beam falls on such a crystal, each atomic plane reflects the beam. Each separate reflected beam interacts with other reflected beams. If the beams are not in phase, they destroy each other and no beam emerges. Other beams reinforce each other and emerge from the crystal. The net result is a **diffraction pattern** of reinforced beams from many planes. It is the atomic planes that are important in XRD. It is of course possible to draw an infinite number of planes in three dimensions, but only those planes with electron density on them reflect X-rays.

In Figure 8.64, radiation from the source falls on the crystal, some on the top atomic plane and some on the second plane. Since the two beams are part of the same original beam, they are in phase on reaching the crystal. However, when they leave the crystal, the part leaving the second plane has traveled an extra distance ABC. If ABC is a whole number of wavelengths, the two beams leaving the crystal will be in phase and the light is coherent. If ABC is not a whole number of wavelengths, the two beams come together out of phase, and by destructive interference, the light is destroyed. *Bragg's Equation:*

As we derived earlier,  $n\lambda = 2d \sin\theta$ . This is the Bragg equation, which states that coherence occurs when  $n\lambda = 2d \sin\theta$ . It can be used to measure  $d$ , the distance between planes of electron density in crystals, and is the basis of **X-ray crystallography**, the determination of the crystal structure of solid crystalline materials. Liquids, gases, and solids such as glasses and amorphous polymers have no well-ordered structure; therefore, they do not exhibit diffraction of X-rays.

For any given crystal,  $d$  is constant for a given family of planes; hence, for any given angle  $\theta$  and a given family of planes,  $n\lambda$  is constant. Therefore, if  $n$  varies, there must be a corresponding change in  $\lambda$  to satisfy the Bragg equation. For a given diffraction angle, a number of diffracted lines are possible from a given family of planes;  $n$  is known as the order of diffraction. As an example, if  $2d \sin\theta$  equals 0.60, each of the conditions of Table 8.12 will satisfy the Bragg equation. Radiation of wavelength 0.60, 0.30, 0.20, or 0.15 Å will diffract at the same angle  $\theta$  in first, second, third, or fourth order, respectively, as seen in Figure 8.65. This is called order overlap and can create difficulty in interpretation of crystal diffraction data.

It should be noted that radiation of 0.30 Å would also be diffracted at a different angle in first order from the same family of planes (same  $d$  value), as shown in Figure 8.65. Wavelengths



Table 8.12 Order of Diffraction for Values of  $n, \lambda$ .

$n$	$\lambda$ (Å)	$n\lambda$	Order
1	0.60	0.60	First
2	0.30	0.60	Second
3	0.20	0.60	Third
4	0.15	0.60	Fourth

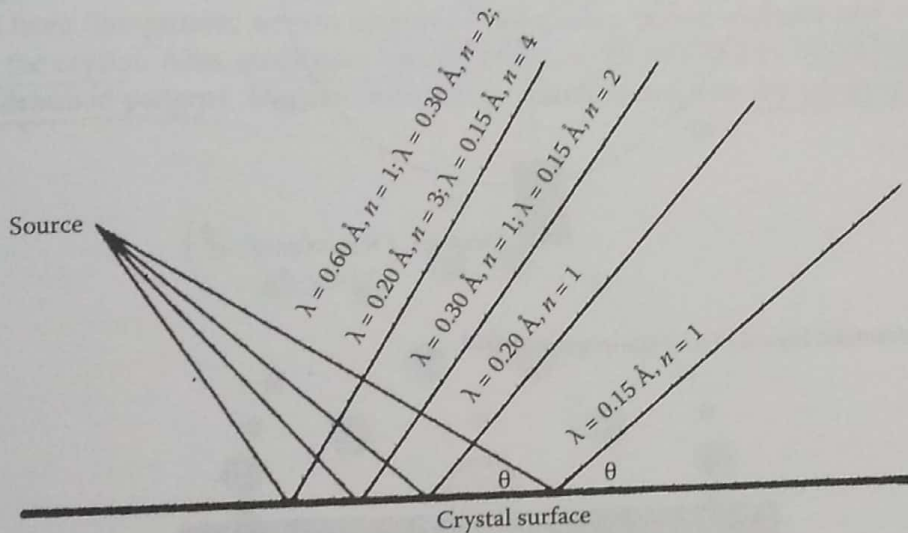


Figure 8.65 Diffraction of radiation of different wavelengths. Overlap can occur when different orders are diffracted at the same angle.

corresponding to low orders such as first and second order give observable diffraction lines. Consequently, a single plane will generate several diffraction lines for each wavelength. Each of the planes in the three dimensions of the crystal will give diffraction lines. The sum total of these diffraction lines generates a diffraction pattern. From the diffraction pattern, it is possible to deduce the different distances between the planes as well as the angles between these planes in each of the three dimensions. Based on the diffraction pattern, the physical dimensions and arrangement of the atomic planes in the crystal can be identified.

#### 8.4.1 Single-Crystal X-Ray Diffractometry

##### *Instrumentation:*

The schematic layout of a single-crystal diffractometer is given in Figure 8.66. This system uses an X-ray tube, a sample specimen, and a detector that rotates in an arc described by a Rowland circle. Note that the single-crystal sample takes the place of the analyzing crystal in a WDXRF analyzer. The goniometer mounting for a single-crystal diffractometer is very complex, because the crystal must be moved in three dimensions to collect data from many planes. A commercial bench-top single-crystal XRD instrument is shown in Figure 8.67.

For any given experiment,  $\lambda$  is the known wavelength of the monochromatic X-ray beam;  $\theta$  is controlled and varied by the goniometer. From this information,  $d$  can be calculated. By rotating the goniometer and examining various sides of the crystal, hundreds (or thousands) of diffracted X-rays are collected. This data is processed to identify the positions of the planes and atoms in the crystal in three dimensions. Modern single-crystal diffractometers use computers to control the goniometer and to process the data. The diffraction data is usually converted to a 2D electron density map by

Fourier transformation. The electron density map shows the location of atoms. A 2D electron density map is produced for each angle. The computer program uses the 2D maps plus the rotation angle data to generate the 3D coordinates for atoms (molecules, ions) in the crystal. The mathematical treatment of the experimental data to produce a crystal structure from an unknown single-crystal diffraction pattern is complicated and beyond the scope of this text, but an example of the results will be shown in the following. *Example:*

The diffraction pattern of a single crystal of an inorganic salt is shown in Figure 8.68; an actual diffraction pattern is shown in Figure 8.69. A given molecule always gives the same diffraction pattern, and from this pattern, we can determine the spacing between planes and the arrangement of planes in the crystal. Also, qualitative identification can be obtained by matching this pattern to previously identified patterns. Modern instruments are equipped with 2D imaging detectors such as CCDs.

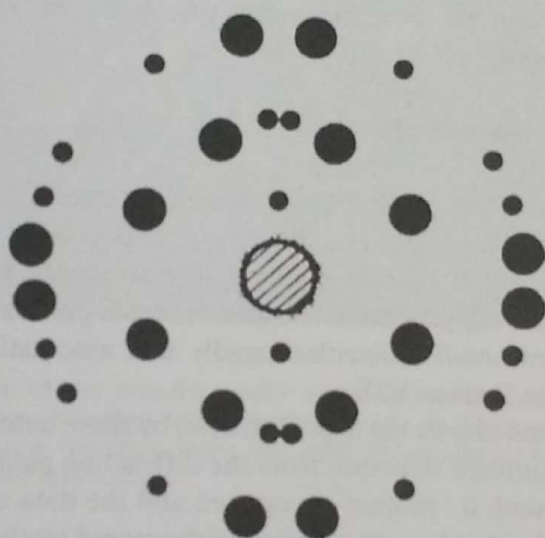


Figure 8.68 Diffraction pattern in two dimensions of a single crystal of an inorganic salt.

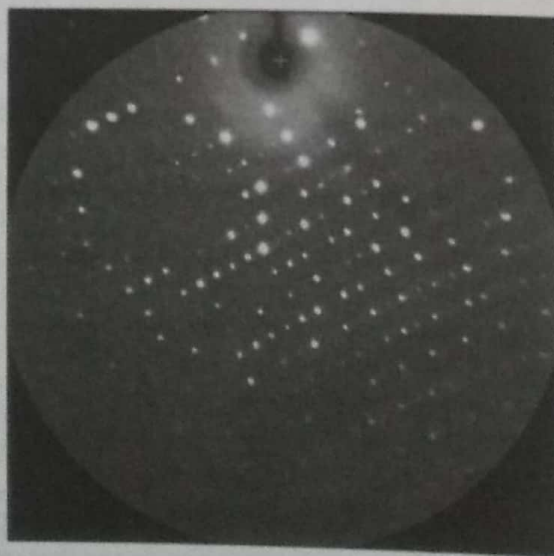


Figure 8.69 Actual single-crystal diffraction pattern of a small molecule collected with a Rigaku XtaLAB mini™. (Used by permission of Rigaku Corporation. [www.rigaku.com](http://www.rigaku.com).)



### 8.4.2 Crystal Growing

In order to determine the structure of a single crystal, such a crystal must be grown from the material to be studied. The crystal quality determines the quality of diffraction results obtained. One limitation of XRD is that data is obtained on only one single crystal of the bulk material, unlike other techniques where multiple replicates are usually analyzed. The growth of single crystals of materials often is not easy. Simple inorganic salts and small organic molecules can be crystallized as single crystals by very slow evaporation of a supersaturated solution of the salt or compound. Once one tiny single crystal forms, it will grow in preference to the formation of more small crystals. Sublimation under vacuum can be used. Proteins and other biomolecules are more difficult to grow as single crystals because they are complex. One method that often works is to suspend a drop of protein solution over a reservoir of buffer solution. Water diffusion from the drop often results in single-crystal growth. Different techniques are required to form metal crystals. The interested student can find many references and resources on the Internet, by searching the term "X-ray crystallography." The single crystal then has to be mounted; various mount types are available depending on the instrument and goniometer being used.

### 8.4.3 Crystal Structure Determination

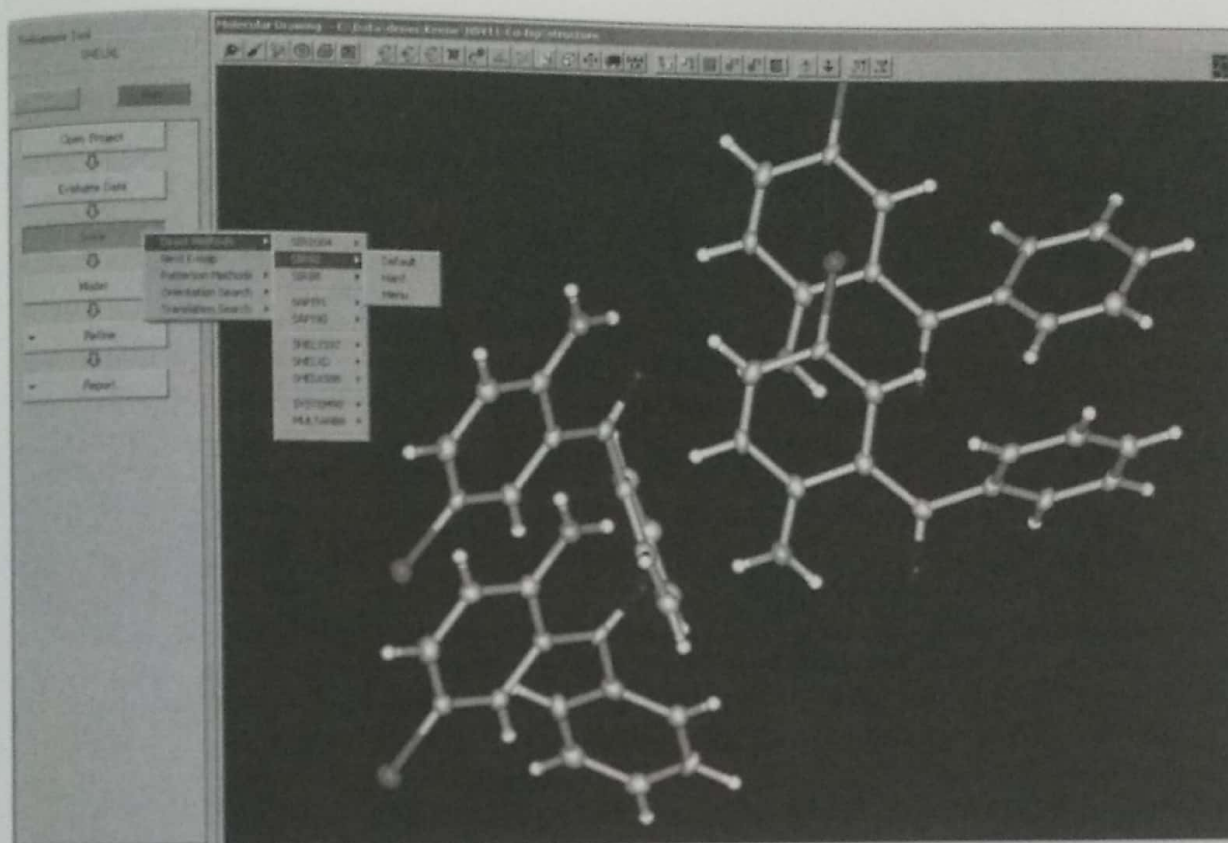
From the diffraction pattern, the crystal structure can be determined mathematically and the compound identified. While the discussion of the details is beyond the scope of this text, small, benchtop automated single-crystal XRD systems have come into use. These instruments possess a variety of powerful data processing programs and libraries that permit the determination of high-resolution crystal structures of small molecules rapidly and automatically. Systems include the Rigaku XtaLAB mini™ and the Bruker X2S.

The XtaLAB mini™ software shows the approach used by these automated systems. Figure 8.70 lists the steps involved in obtaining a structure from the diffraction pattern. Once the single crystal of the analyte has been mounted, a "project" is opened and the data collected. Then, the data is evaluated and the structure solved using one or more of the stored mathematical approaches. Some of the various methods and programs can be seen on the computer screen. A model is created and refined, and a report with the crystal structure, lattice parameters, and molecular identification is produced. Figure 8.71 shows the refinement results for a particular crystal obtained using the program SHELX. The results after five cycles of refinement (which requires over 2000 observations and 231 variables) give a "goodness of fit" of 1.066, an indication that the result is highly probable. Perfect fit would be 1.000. The number of cycles, observations, and variables makes it clear that without modern computer processing, determination of a structure from an XRD pattern would take days or weeks of work, as it used to.

Measurement times for crystals of small molecules using such a system vary and depend on the complexity of the molecule. Potassium tetrachloroplatinate II,  $K_2PtCl_4$ , required less than 2 h of measurement time using the XtaLAB mini™, while a structure like raffinose,  $C_{18}H_{32}O_{16} \cdot 5H_2O$ , required 5 h and 30 min. The overall results from an analysis of the diffraction pattern would include the chemical structure, the name of the compound, the formula weight, the space group to which the crystal belongs, and the crystal lattice constants.

### 8.4.4 Powder X-Ray Diffractometry

Powdered crystalline samples can also be studied by XRD. The sample is loaded onto the specimen holder, which is placed in the X-ray beam in a setup similar to that used for single-crystal XRD. The sample must be powdered by hand or by mechanical grinding and is pressed into a sample

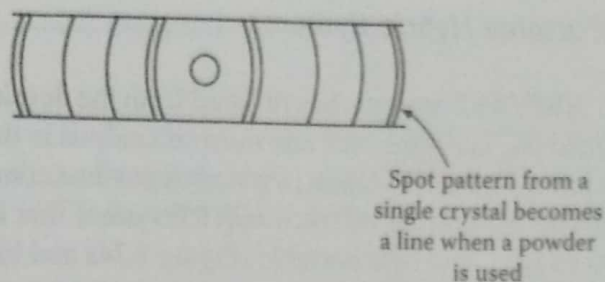


**Figure 8.70** Computer screen of the XtaLAB mini™ showing the automated program steps for solving a crystal structure, including a list of some of the mathematical methods available and the molecular structure resulting from the data processing. (Used by permission of Rigaku Corporation. [www.rigaku.com](http://www.rigaku.com).)

holder to form a flat surface or packed into a thin glass or polymer capillary tube. After mounting, the specimen is rotated relative to the X-ray source at a rate of (degrees  $\theta$ )/min. Diffracted radiation comes from the sample according to the Bragg equation. The detector is simultaneously rotated at (degrees  $2\theta$ )/min, using traditional  $\theta$ - $2\theta$  geometry. Alternatively, instruments such as the Thermo Fisher Scientific ARL X'TRA powder diffraction system are available using a  $\theta$ - $\theta$  geometry (Bragg-Bretano geometry).

A powdered crystalline material contains many thousands of tiny crystals. These crystals are oriented in all possible directions relative to the beam of X-rays. Hence, instead of the sample generating only single diffraction spots, it generates cones of diffracted X-rays, with the point of all the cones at the sample (Figure 8.72). Each family of planes will have a different circular diameter, so the result is a series of concentric cones radiating from the sample. Imagine that inside the Rowland circle opposite the sample, we have a strip of X-ray film as shown in Figure 8.72 on the right. The circular cones of X-rays will hit the film, resulting in a series of curved lines on the film (Figure 8.72 left). A typical diffraction pattern from a powdered sample collected on film is shown in Figure 8.73. These are called Laue photographs, after Max von Laue, the German scientist who developed the technique. Film has been replaced by automated scanning with a standard X-ray detector as discussed for XRF or by the use of imaging detectors such as CCDs or image plates to give a 2D image. A cylindrical image plate detector used by Rigaku Corporation has an active area of 454 mm  $\times$  256 mm, a pixel size of 100  $\mu$ m  $\times$  100  $\mu$ m, extremely rapid readout, and a sensitivity of 1 X-ray photon per pixel for Cu  $K_{\alpha}$  radiation. One X-ray photon per pixel is a quantum efficiency of 100%. The major advantage of these imaging detectors is that the images can be stored and





**Figure 8.73** A typical diffraction photograph, called a Laue photograph, from a powdered crystalline sample.

manipulated electronically without the need for a photographic film-developing lab. The Thermo Fisher Scientific ARL X'TRA uses a Peltier-cooled Si(Li) solid-state detector, which can be cooled to about  $-100^{\circ}\text{C}$ , resulting in extremely low internal noise. This solid-state detector allows the user to electronically select photons based on their energy signature, which eliminates the need for beta filters or diffracted beam monochromators to remove Bremsstrahlung and sample fluorescence.

In order to obtain accurate XRD spectra, the sample must be ground finely and pressed, so that there is sufficient random orientation of the crystals in the sample. Nonrandom orientation (preferred orientation) will result in a distorted spectral pattern, like a broken line or series of spots instead of a complete curved line. Some materials exhibit preferred orientation, either naturally or by design, and can be identified through these distortions. Powder diffractometers come in a variety of sizes, including small benchtop units and field-portable units (Section 8.4.5.1).

#### 8.4.5 Hybrid XRD/XRF Systems

Hybrid systems are designed to combine the speed and flexibility of XRD and XRF systems in one spectrometer. Such systems permit more complete characterization of a given crystalline sample. These systems are varied: some are XRF systems with a few powder XRD-based channels to identify compounds, such as a system designed with a CaO channel for the cement industry. The combination can go as far as including a complete powder diffractometer and XRF spectrometer for flexible compound identification and quantification. These types of systems are generally used in industries, including metal and alloy production, cement production, mining, and refractory materials production, for both R&D and process control.

Thermo Fisher Scientific's ARL 9900 series hybrid systems offer a variety of configurations of the XRF and powder XRD components for R&D, fast process analysis, qualitative and quantitative elemental analysis, and phase analysis. The system can be configured in many ways: with up to 32 monochromators for fast elemental analysis, up to three goniometers for analysis of specific elements (quantitative and standardless analysis), scanning the XRF spectrum (qualitative and semiquantitative analysis), a compact XRD system for process control, or a full powder XRD system. With the XRF unit, up to 83 elements (B to U) can be determined from ppm levels to 100%. The full XRD goniometer, called the NeXRD, provides qualitative and quantitative phase analysis. Full-pattern quantitative phase analysis results can be obtained in 5 min using automatic interpretation of the XRD pattern. The 9900 series has options for a variety of automated sample changers (12 or 98 position) and can be integrated with the ARL robotic sample preparation systems, allowing unattended continuous operation of the instrument. This system is a floor-mounted laboratory unit. The advantages of a hybrid unit for the laboratory are that it provides a single user interface for both XRF and XRD techniques, minimizes occupied floor space, merges elemental and phase analysis into a single report, and permits rapid, precise analysis of solid samples. One limitation of such systems is that they can only handle solid samples. Pictures and details are available at [www.thermo.com./xray](http://www.thermo.com./xray).

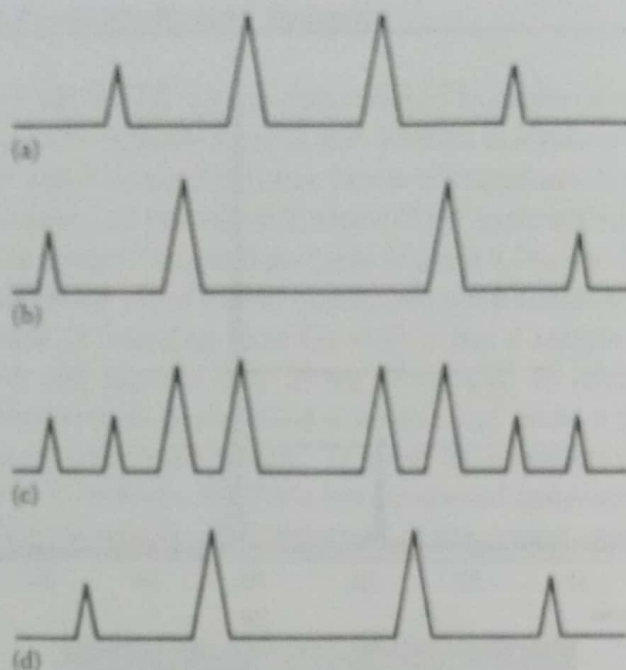
#### 8.4.6 Applications of XRD

##### *structure determination.*

The analytical applications of XRD are numerous. The method is nondestructive and gives detailed information on the structure of crystalline samples. Comparing powder diffraction patterns from crystals of unknown composition with patterns from crystals of known compounds permits the identification of unknown crystalline compounds. The number of peaks or lines, intensities of peaks or lines, and the angular positions of peaks or lines (in terms of  $2\theta$ ) are used to identify the material (Figure 8.75).

Diffraction patterns are unique for each compound and serve as a fingerprint for a crystalline material. For example, as shown in Figure 8.76a and b, pure crystals of compound A and pure crystals of compound B give different diffraction patterns. A mixture containing both A and B will show diffraction peaks from both pure compounds (Figure 8.76c). If we had a mixture of 15% KCl and 85% NaCl, the diffraction pattern would show strong NaCl peaks with a weak pattern of KCl intermixed. A mixture containing 15% NaCl and 85% KCl would show the diffraction pattern of KCl





**Figure 8.76** Schematic X-ray powder diffraction patterns for simple inorganic salts. (a) Pure salt A. (b) Pure salt B. (c) A physical mixture of salt A and salt B. Note that the peaks for both pure salts can be seen in the mixture; every peak matches a peak in either (a) or (b). (d) A diffraction pattern for a mixed crystal containing the same elements present in both A and B, but chemically combined in the same crystal lattice. The diffraction pattern for the mixed crystal (a unique structure) is unique; it does not match either pure A or pure B.

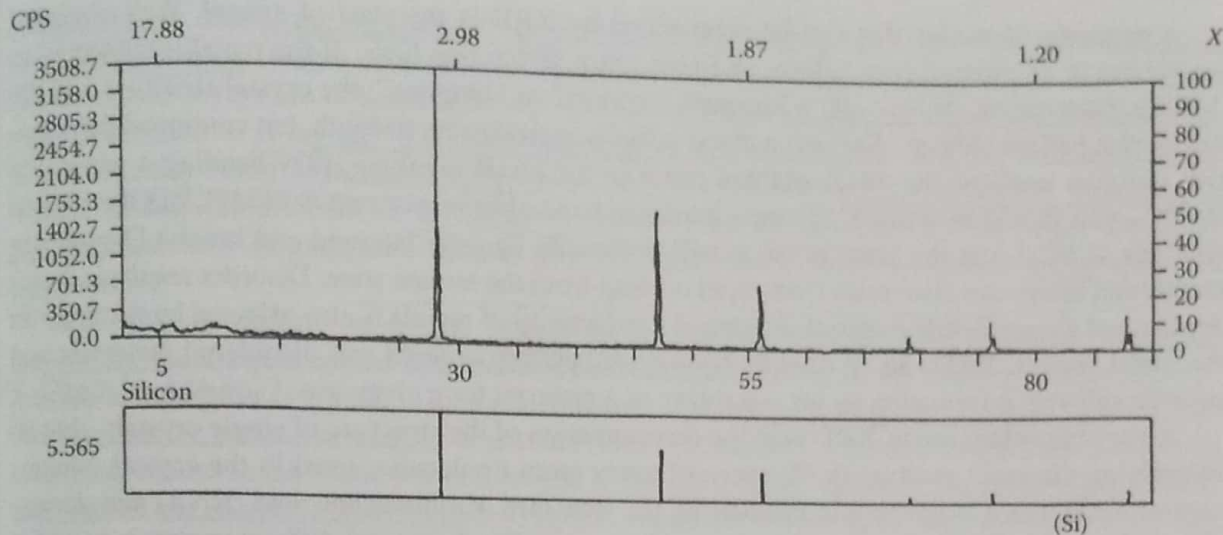
### Multiphase material.

with a weak pattern of NaCl. Such a mixture is a multiphase material, and interpretation of multiphase patterns is more difficult than for single-phase (pure) materials. If, on the other hand, the crystal were a mixed crystal of sodium potassium chloride, in which the sodium and potassium ions are in the same crystal lattice, there would be changes in the crystal's lattice size from that of pure NaCl or pure KCl. However, the mixed crystal is a single-phase material, resulting in a unique diffraction pattern as shown in Figure 8.76d. X-ray powder diffraction therefore can be used to distinguish between a mixture of crystals, which would show both diffraction patterns, and a mixed crystal, which would give a separate unique diffraction pattern. The exact crystallographic lattice constants can be measured using XRD. Powder diffraction pattern matching to identify unknowns is now done with a computer, software, and a powder diffraction pattern spectral library or database that can be searched by the computer. An example is shown in Figure 8.77. The International Centre for Diffraction Data (ICDD), located in Newtown Square, PA, United States, maintains a database of more than 50,000 single-phase powder XRD patterns ([www.icdd.com](http://www.icdd.com)). polymers:

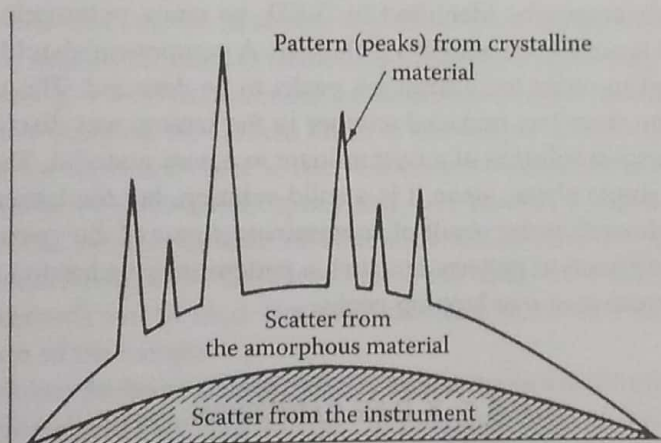
In polymer characterization, it is possible to determine the degree of crystallinity of semicrystalline polymers. The noncrystalline (amorphous) portion simply scatters the X-ray beam to give a continuous background, whereas the crystalline portion gives diffraction lines. A typical schematic diffraction spectrum of a semicrystalline polymer is shown in Figure 8.78. The ratio of the area of diffraction peaks to scattered radiation is proportional to the ratio of crystalline to noncrystalline material in the polymer. The ultimate quantitative analysis must be confirmed using standard polymers with known percent crystallinity and basing the calculation on the known ratio of crystalline diffraction to amorphous scattering.

Using an XRD pattern and looking at the intensity of peaks, it is possible to determine if the crystals of a polymer or a metal are oriented in any particular direction. "Preferred orientation" can occur after the material has been rolled out into a sheet, for example. This is sometimes a very undesirable property, since the material may be very weak in one direction and strong in another, with

$\frac{\text{Area of diffraction peak}}{\text{Total area}} \propto \frac{\text{crystalline}}{\text{non-crystalline}}$



**Figure 8.77** The X-ray powder diffraction pattern of an unknown material is shown in the upper spectrum. A search of a computerized database identified the unknown as silicon, based on the match to the stored spectrum for silicon (lower spectrum).



**Figure 8.78** Schematic diffraction pattern from a semicrystalline polymer, showing how both crystalline and amorphous phases may be detected. The amorphous portion results in broad scattering while the crystalline portion shows a typical diffraction peak pattern. A totally amorphous polymer would show no diffraction peaks. (There are no 100% crystalline polymers.) The units on the x-axis are degrees  $\theta$ .

### *Industrial uses:*

the result that it tears easily in one direction. Sometimes, however, this is a desirable property, as, for example, in packaging material that we may wish to tear easily in one direction to open the package.

Powder XRD is used for phase analysis and compound identification in a variety of industries, especially mineral, mining, and metal production and for materials such as rocks, minerals, oxide materials, and products. Typical examples include the levels of Fe phases such as FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and FeC; determination of free lime in clinker and slags in the cement industry; phases related to the electrolysis of Al; and CaO, CaCO<sub>3</sub>, and Ca(OH)<sub>2</sub> content. *Phase transition:*

XRD at different temperatures can be used to study phase transitions between different crystallographic forms of a material (e.g., tetragonal vs. monoclinic forms of yttria-stabilized zirconia). This approach can be used to measure thermal expansion coefficients and to study crystalline-to-amorphous transitions in materials.



A property of metals that can be determined by XRD is the state of anneal. Well-annealed metals are in an ordered crystal form and give sharp diffraction lines. If the metal is subjected to drilling, hammering, or bending, it becomes “worked” or “fatigued”; the crystal structure and the diffraction pattern change. Working a metal initially increases its strength, but continued deformation (fatigue) weakens the metal and can result in the metal breaking. (Try bending a paper clip slowly—you should note that it becomes harder to bend after one or two workings, but then if you continue to bend it at the same point, it will eventually become fatigued and break.) Disorder in metals and alloys can also result from rapid cooling from the molten state. Disorder results in lower density and a more brittle material. Electrical conductivity of metals is also affected by the order in the metal crystal. XRD can be used to distinguish between ordered and disordered materials and provide valuable information on the suitability of a material for a given use. *single crystal:*

A very important use of XRD is in the determination of the structure of single crystals, that is, identifying the exact position in 3D space of every atom (molecules, ions) in the crystal. Single-crystal XRD was a major tool in elucidating the structure of ribonucleic acid (RNA) and deoxyribonucleic acid (DNA), insulin, vitamins, and proteins. Single-crystal diffractometry is used for structural determination of biomolecules, natural products, pharmaceuticals, inorganic coordination complexes, and organometallic compounds.