concentration calculation in any absorption method requires that the thickness and density of the sample be known and requires a homogenous matrix for accurate quantitative results.

8.3.1.1. EXAFS

A recent development in the use of X-ray absorption is a technique called EXAFS, extended X-ray absorption fine structure spectroscopy. A sample is placed in a beam of X-rays and the incident and transmitted intensities are measured as the energy of the X-ray beam is varied. A plot of the absorption vs. energy gives us the position (energy) and exact shape of the absorption edge for the element being measured. The exact energy of the absorption edge and its shape, the "fine structure", does change slightly depending on the oxidation state of the element and the number and type of nearest neighbor atoms. This change in position of the absorption edge is analogous to the chemical shift seen in NMR. EXAFS does provide oxidation state information and molecular structure information, unlike normal X-ray absorption or X-ray fluorescence, which are strictly elemental analysis techniques. Details of the spectral interpretation of EXAFS are beyond the scope of this book. The interested student can consult the text by Teo and Joy listed in the bibliography.

8.3.2. X-Ray Diffraction

X-ray diffraction or X-ray diffractometry (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 8.35 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, 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 Fig. 8.36(a). 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.

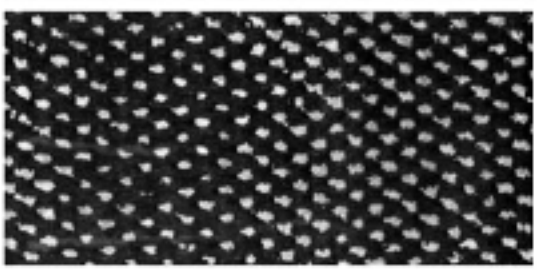

Figure 8.35 An electron micrograph of the (110) plane in crystalline silicon.

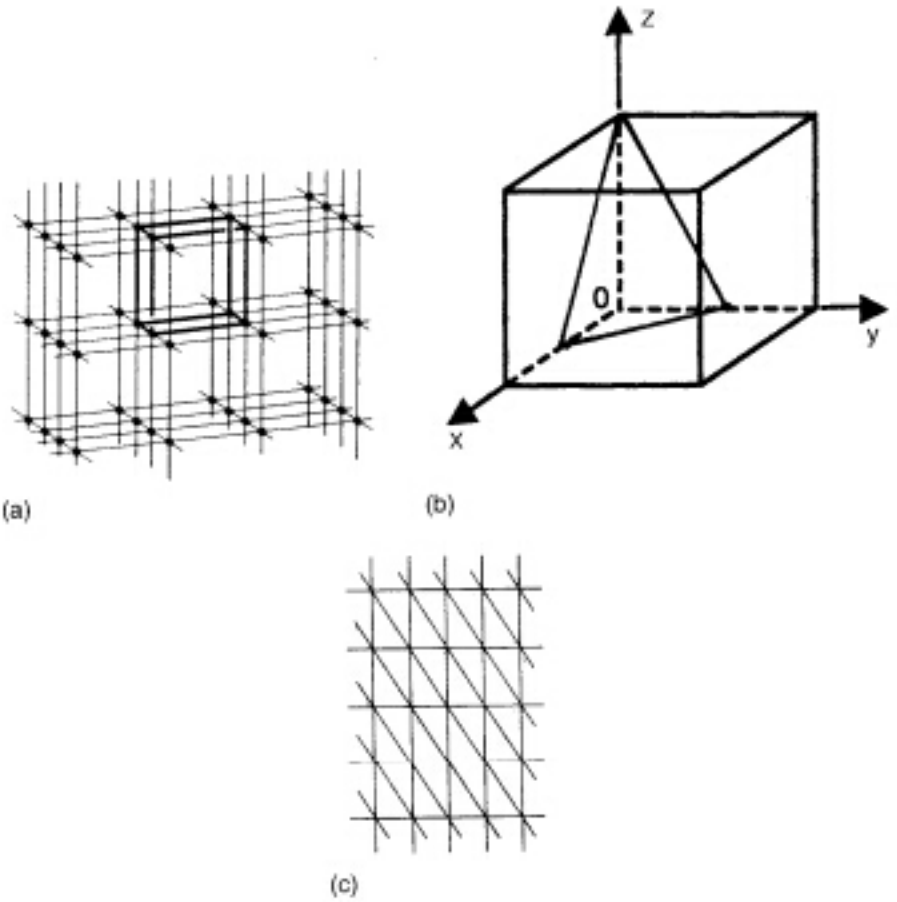

Figure 8.36 (a) A portion of a 3D crystal lattice. The unit cell, or basic repeating unit, of the lattice is shown in heavy outline. The black dots represent the atoms or ions or molecules that make up the crystal. (b) A cubic unit cell, with the corners of the cell located at 1 unit from the origin (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.

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. For example, suppose the unit cell is a cube, with edges equal to 1 unit of length on each axis as shown in Fig. 8.36(b). 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, 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. [What axis is the (110) plane in Si parallel to? Draw the (110) plane in a cubic unit cell such as the one shown in Fig. 8.36(b)]. 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), (440) planes are a family of planes]. These planes in a given family are all parallel, as shown in Fig. 8.36(c), 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).*

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 X-ray diffraction. 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. For example, you could draw a plane extending into the page along one of the dark diagonals in Fig. 8.35, but that plane contains no atoms and therefore will not diffract X-rays.

In Fig. 8.37 radiation from the source falls on the crystal, some on the top atomic plane, 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.

As we derived in Section 8.1.3, $n\lambda = 2d \sin \theta$. 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 θ and a given family of planes, $n\lambda$ is constant. Therefore, if n varies, there must be a corresponding change in λ 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 8.8 will satisfy the Bragg equation. Radiation of wavelength 0.60, 0.30, 0.20, or

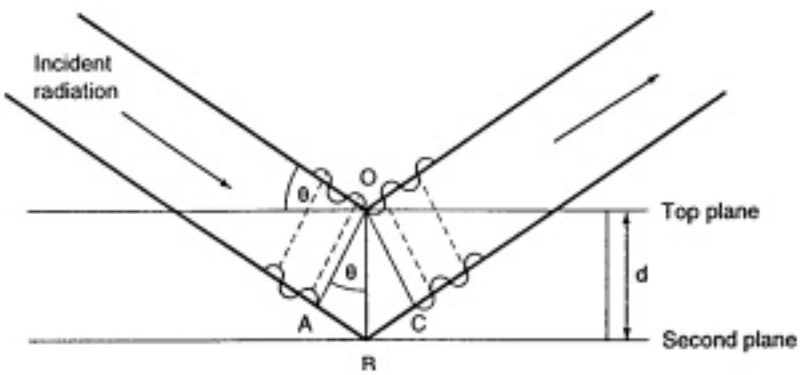

Figure 8.37 Reinforcement of light diffracted from two crystal planes.

Table 8.8 Order of Diffraction for Values of n, λ

n	λ (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

0.15 Å will diffract at the same angle θ in first, second, third, or fourth order, respectively, as seen in Fig. 8.38. 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 Fig. 8.38. Wavelengths 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.

8.3.2.1. X-Ray Diffractometer

The schematic layout of a single crystal diffractometer is given in Fig. 8.39. 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

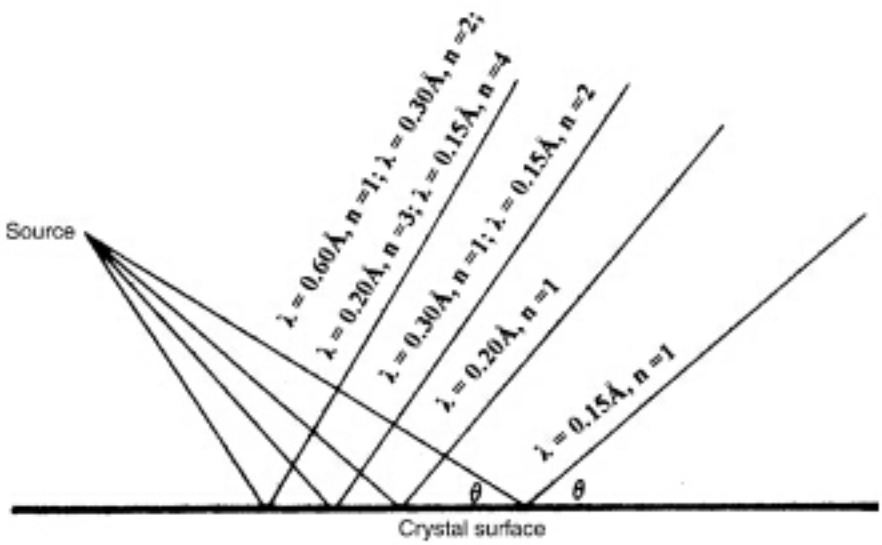

Figure 8.38 Diffraction of radiation of different wavelengths. Overlap can occur when different orders are diffracted at the same angle.

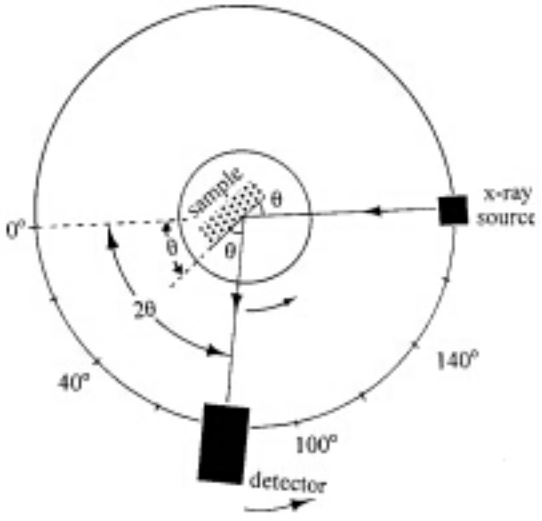

Figure 8.39 Schematic layout of a single-crystal XRD.

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.

In order to determine the structure of a single crystal, such a crystal must be grown from the material to be studied. 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. 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".

For any given experiment, λ is the known wavelength of the monochromatic X-ray beam, θ 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; even with a computer, the data processing can take days. 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.

The diffraction pattern of a single crystal of an inorganic salt is shown in Fig. 8.40. This inorganic salt always gives the same diffraction pattern, and from this pattern we can determine the spacing between planes and the arrangement of planes in the salt crystal. Also, qualitative identification can be obtained by matching this pattern to previously