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REVIEW ARTICLE

Basic View of X- Ray Crystallography

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ABSTRACT

X-ray crystallography is an experimental technique that exploits the fact that X-rays are diffracted by crystals. It is not an imaging technique. X-rays have the proper wavelength (in the angstrom range, ~10^{-8}cm) to be scattered by the electron cloud of an atom of comparable size. Based on the diffraction pattern obtained from X-ray scattering off the periodic assembly of molecules or atoms in the crystal, the electron density can be reconstructed. Additional phase information must be extracted either from the diffraction data or from supplementing diffraction experiments to complete the reconstruction. A model is then progressively built into the experimental electron density, refined against the data and the result is a quite accurate molecular structure.

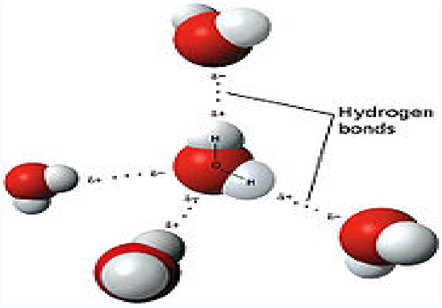
Key words: X-ray crystallography, molecular structure, angstrom range.

INTRODUCTION

Prior to the discovery of X-rays by Conrad Roentgen in 1895, crystallographers had deduced that crystals are made of an orderly arrangement of atoms and could infer something about this orderly arrangement from measurements of the angles between crystal faces. The discovery of X-rays gave crystallographers a powerful tool that could see of crystals and allow for detailed determination of crystal structures and unit cell size. Here we discuss the application of X-rays, not so much in terms of how they are used to determine crystal structure, but how they can be used to identify minerals.

X-ray crystallography can locate every atom in a zeolite, an aluminosilicate with many important applications, such as water purification.

X-ray crystallography is a method of determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and diffracts into many specific directions. From the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.



X-ray crystallography shows the arrangement of water molecules in ice, revealing the hydrogen bonds that hold the solid together. Few other methods can determine the structure of matter with such sub-atomic precision

Since many materials can form crystals — such as salts, metals, minerals, semiconductors, as well as various inorganic, organic and biological molecules — X-ray crystallography has been fundamental in the development of many scientific fields. In its first decades of use, this method determined the size of atoms, the lengths and types of chemical bonds, and the atomic-scale differences among various materials, especially minerals and alloys. The method also revealed the structure and functioning of many biological molecules, including vitamins, drugs, proteins and nucleic acids such as DNA. X-ray crystallography is still the chief method for characterizing the atomic structure of new materials and in discerning materials that appear similar by other

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experiments. X-ray crystal structures can account for unusual electronic or elastic prope of a material, shed light on chemical interact and processes, or serve as the basis for desig pharmaceuticals against diseases.

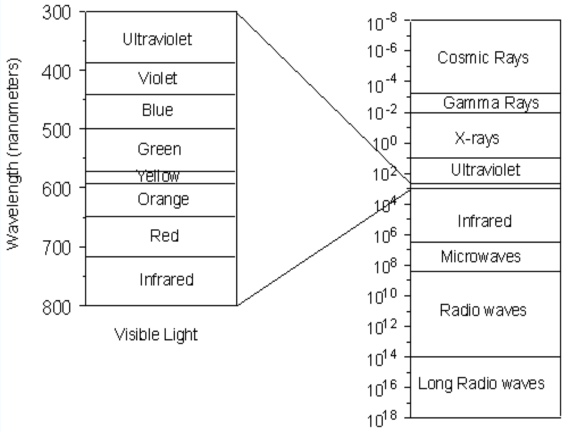
Fundamental Concepts

- X-rays are diffracted by electrons
- Diffraction: constructive or destruc interference of scattered waves
- Pattern of diffracted x-rays useful to ob orientation of atoms in space

A variety of x-ray technique & methods are in .But we shall classify all methods in to three r categories such as x-ray absorption, x fluorescence, and x-ray diffractions methods.

X-rays and the Production of X-rays

X-rays are electromagnetic radiation wavelengths between about 0.02 Å and 100 Å = 10^{-10} meters). They are part of electromagnetic spectrum that incl wavelengths of electromagnetic radiation ca visible light which our eyes are sensitive (different wavelengths of visible light appear t as different colors). Because X-rays have wavelengths similar to the size of atoms, they are useful to explore within crystals.



The energy of X-rays, like all electromagnetic radiation, is inversely proportional to their wavelength as given by the Einstein equation:

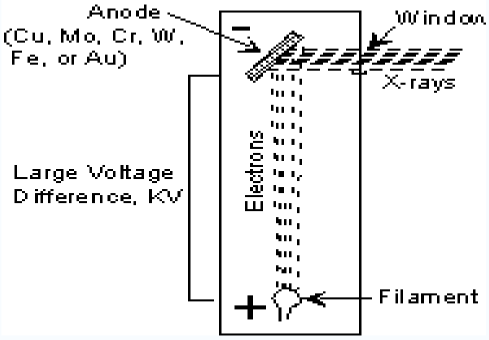
$E = hn = hc/l$
E = energy
h = Planck's constant, 6.62517 x 10^{-27} erg·sec
n = frequency
c = velocity of light = 2.99793 x 10^{10} cm/sec
l = wavelength

Since X-rays have a ssmaller wavelength than visible light, they have higher energy. With their higher energy, X-rays can penetrate matter more easily than can visible light. Their ability to penetrate matter depends on the density of the matter, and thus X-rays provide a powerful tool in medicine for mapping internal structures of the human body.

X-r ays are produced in a device called an X-ray tube. Such a tube is illustrated here. It consists of an evacuated chamber with a tungsten filament at one end of the tube, called the cathode, and a metal target at the other end, called an anode. Electrical current is run through the tungsten filament, causing it to glow and emit electrons. A large voltage difference (measured in kilovolts) is placed between the cathode and the anode, causing the electrons to move at high velocity from the filament to the anode target. Upon striking the atoms in the target, the electrons dislodge inner shell electrons resulting in outer shell electrons having to jump to a lower energy shell to replace the dislodged electrons. These electronic transitions results in the generation of X-rays. The X-rays then move through a window in the X-ray tube and can be used to provide information on the internal arrangement of atoms in crystals or the structure of internal body parts [5].

Continuous and Characteristic X-ray Spectra

When the target material of the X-ray tube is bombarded with electrons accelerated from the cathode filament, two types of X-ray spectra are produced. The first is called the continuous Spectra



$nl = 2a$

but, from trigonometry, we can figure out what the distance 2a is in terms of the spacing, d, between the atomic planes.

$a = d \sin q$

or $2a = 2 d \sin q$

thus, $\mathbf{nl = 2d \sin q}$

This is known as **Bragg's Law** for X-ray diffraction.

What it says is that if we know the wavelength ,l , of the X-rays going in to the crystal, and we can measure the angle q of the diffracted X-rays coming out of the crystal, then we know the spacing (referred to as ***d-spacing***) between the atomic planes.

$\mathbf{d = nl /2 \sin q}$

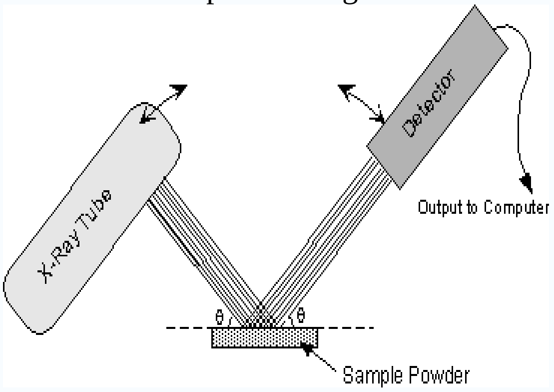
Again it is important to point out that this diffraction will only occur if the rays are in phase when they emerge, and this will only occur at the appropriate value of n (1, 2, 3, etc.) and q.

In theory, then we could re-orient the crystal so that another atomic plane is exposed and measure the d-spacing between all atomic planes in the crystal, eventually leading us to determine the crystal structure and the size of the unit cell [15].

The X-ray Powder Method

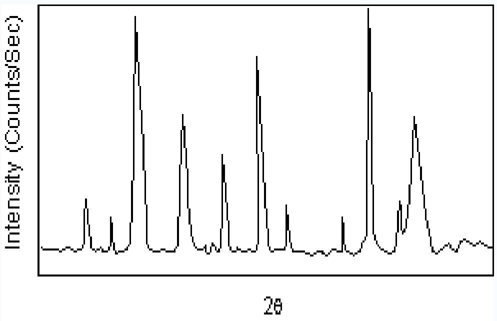
In practice, this would be a time consuming operation to reorient the crystal, measure the angle q, and determine the d-spacing for all atomic planes. A faster way is to use a method called the powder method. In this method, a mineral is ground up to a fine powder. In the powder, are thousands of grains that have random orientations. With random orientations we might expect most of the different atomic planes to lie parallel to the surface in some of the grains. Thus, by scanning through an angle q of incident X-ray beams form 0 to 90^{o}, we would expect to find all angles where diffraction has occurred, and each of these angles would be associated with a different atomic spacing[3].

The instrument used to do this is an x-ray powder diffractometer. It consists of an X-ray tube capable of producing a beam of monochromatic X-rays that can be rotated to produce angles from 0 to 90^{o}. A powdered mineral sample is placed on a sample stage so that it can be irradiated by the X-ray tube. To detect the diffracted X-rays, an electronic detector is placed on the other side of the sample from the X-ray tube, and it too is allowed to rotate to product angles from 0 to 90^{o}.



The instrument used to rotate both the X-ray tube and the detector is called a goniometer. The goniometer keeps track of the angle q, and sends this information to a computer, while the detector records the rate of X-rays coming out the other side of the sample (in units of counts/sec) and sends this information to the computer.

After a scan of the sample the X-ray intensity can be plotted against the angle q (usually reported as 2q because of the way older diffractometers were made) to produce a chart, like the one shown here. The angle 2q for each diffraction peak can then be converted to d-spacing, using the Bragg euation



One can then work out the crystal structure and associate each of the diffraction peaks with a different atomic plane in terms of the Miller Index for that plane (hkl).

A group known as the Joint Committee on Powder Diffraction Standards (JCPDS) has collected data such as this on thousands of crystalline substances.

X-ray Diffraction Methods

X-ray diffraction methods are generally used for investigating the internal structures. However, the following methods are used:

(1) Laue photographic method- Laue has studied the phenomenon of diffraction of crystal by two methods
(2) Bragg X-ray spectrometer method
(3) Rotating crystal method
(4) Power method [9]

Details of the above methods:

Transmission Method: This experimental equipment required for this is relatively simple and is shown in fig.

A is a source of X-rays. This emits beams of continuous wave length, known as white radiation which is obtained from a tungsten target at about 60000 volts.

B is pinhole collimator. When X-rays obtained from A are allowed to pass through this pinhole collimator, a fine pencil of X-rays is obtained. The diameter of the pinhole is of importance from the stand point of detail in diffraction pattern. The smaller is the diameter, the sharper is the interference.

C is a crystal whose internal structure is to be investigated. The crystal is set on a holder to adjust its orientation.

D is a film arranged on a rigid base. This film is proved with beam stop to prevent direct beam from causing excessive fogging of the film.

The position of crystal is held stationary in a bean of X-rays. The x-rays after passing through the crystal are diffracted and are recorded on a photographic plate. This sort of diffraction pattern obtained is shown in fig. On examining the Laue photograph; it is observed that the spots actually occur at the position to be expected from the reflection law. When the X-ray beam is passed along the axis of symmetry of the crystal, the Laue pattern would contain a series of “spots” whose loci are ellipses which pass through the “central image” made by the X-ray beam. The spots of any one ellipse are produced by planes belonging to the same zone, i.e., planes which are parallel to one common direction.

Back reflection method: This method provides similar information as the transmission method. However, the back reflection method is the only method for the investigation of large and thick specimens.

The main disadvantages of Laue’s method are that a big crystal is required and furthermore there is uncertainty in the significance due to unhomogeneous nature of X-rays.

The Bragg’s X-ray spectrometer Method. According to Laue, if a beam of X-rays is passed through a crystal, the emitted X-rays by the crystal are obtained on a photographic plate in the form of pattern known as Laue’s photograph. Using the photographs, Bragg analysed the structures of crystals of NaCl, KCl and ZnS. Bragg devised a spectrometer to measure the intensity of X-ray beam. The spectra obtained in this way canbe employed for crystallographic analyses. This method is based on Bragg’s law which has been deduced in Art. The Bragg’s equation is as follow where n is an integer, λ is the wavelength of the X-ray beam, d is the distance between the crystal planes, and θ is the angle of incidence of the X-ray beam. Equ. Gives the condition which most be satisfied for the reflection of X-rays from a set of atomic planes [12].

Rotating Crystal Method:

The rotating crystal method is shown in fig.

The X-rays are generated in the X-ray tube and then the beam is made monochromatic by a filter.

From the filter, the beam is then allowed to pass through collimating system which permits a fine pencil of parallel X-rays.

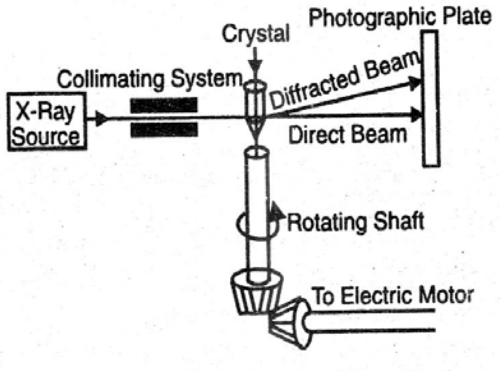
From the collimator, the X-ray beam is made to fall on a crystal mounted on a shaft which can be rotated at a uniform angular rate by a small motor.

Now the shaft is moved to put the crystal into slow rotation about a fixed axis. This cause the set of planes coming successively into their reflecting positions i.e. the value of θ satisfies the Bragg’s relation. Each plane will produce a spot on the photographic plate. One can take a photograph of a diffraction pattern upon a photographic plate perpendicular to X-ray beam or upon a film in a cylindrical camera, the axis of which coincides with the axis of rotation of the crystal. One can take photographs in two ways

Complete rotation method. In this method there occurs a series of complete revolutions. It is observed that each set of planes in the crystal diffracts four times during the rotation. These four diffracted beams are disturbed into a rectangular pattern about the central point of the photograph.

Oscillation method. In this method, the crystal is oscillated through an angle of 150 or 200. The photographic plate is also moved back and forth with a same period as that of the rotation of the crystal. The position of a spot on the plate indicates the orientation of the crystal at which the spot was formed.

By the rotating crystal method, one can measure the size of unit cell[8].

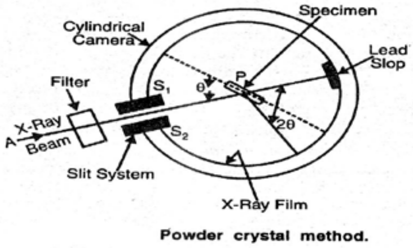


Rotating crystal method.

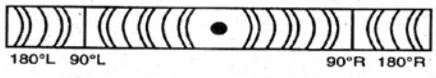
Powder Crystal Method:

In all the above described methods, a single crystal is required whose size is much larger than microscopic dimensions. However, in the power method, the crystal sample need not be taken in large quantity but as little as 1 mg of the material is sufficient for the study.

The powder method was devised independently by Debye and Scherrer in Germany and by Hull in America at about the same time.



Powder crystal method.



Arrangement of line in a powder photograph.

The experimental arrangement of powder crystal method is shown in fig. their main features are outlined as below:

A is a source of X-rays which can be made monochromatic by a filter

Allow the X-ray beam to fall on the powdered specimen P through the slits S1 and S2. The function of these slits is to get a narrow pencil of X-rays.

Fine powder, P, struck on a hair by means of gum is suspended vertically in the axis of a cylindrical camera. This enables sharp lines to be obtained on the photographic film which is surrounding the powder crystal in the form of a circular arc.

The X-rays after falling on the powder passes out of the camera through a cut in the film so as to minimize the fogging produced by the scattering of the direct beam.

On a flat photographic plate the observed pattern consists of traces as shown in fig.

Theory, when a monochromatic beam of X-rays is allowed to fall on the powder of a crystal, then the following possibilities may happen:

There will be some particles out of the random orientation of small crystals in the fine powder, which lie within a given set of lattice planes (marketing the correct angle with the incident beam) for reflection to occur.

While another fraction of the grains will have another set of planes in the correct position for the reflections to occur and so on.

Also, reflections are also possible in the different order for each set.

All the like orientation of the grains due to reflection for each set of planes and for each order will constitute a diffraction cone whose interaction with a photographic plate gives rise to a trace as shown in fig. The crystal structure can be obtained from the arrangement of the traces and their relative intensities.

Applications:

The method is most useful for cubic crystals

The method is used for determining the complex structures of metals and alloys. However there structures could not be revealed by the earlier studies.

This method is useful to make distinction between the allotropic modifications of the same substance [5].

Advantages of a crystal:

In a liquid, powder or amorphous sample, molecules within that sample are in random orientations. Such samples have a continuous Fourier spectrum that uniformly spreads its amplitude thereby reducing the measured signal intensity, as is observed in Saxs. More importantly, the orientational information is lost. Although theoretically possible, it is experimentally difficult to obtain atomic-resolution structures of complicated, asymmetric molecules from such rotationally averaged data. An intermediate case is fiber diffraction in which the subunits are arranged periodically in at least one dimension [1].

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