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Module
on

X-Ray Crystallography

By

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Text

Introduction to Properties of X-Rays

X-rays were discovered in 1895 by the German physicist Röntgen and were so named because their nature was unknown at the time. Unlike ordinary light, these rays were invisible, but they travel in straight lines and affect the photographic film in the same way as light. On the other hand, they were much more penetrating than light and could easily pass through the human body, wood, quite thick pieces of metal, and other "opaque" objects.

By placing a source of x-rays on one side of the object and photographic film on the other, a shadow picture, or *radiograph*, could be made, the less dense portions of the object allowing a greater proportion of the x-radiation to pass through than the more dense. In this way the point of fracture in a broken bone or the position of a crack in a metal casting could be located.

Today it is clear that x-rays are electromagnetic radiation of exactly the same nature as light but of very much shorter wavelength. The unit of measurement in the x-ray region is the angstrom (Å) and x-rays used in diffraction have wavelengths lying approximately in the range 0.5-2.5 Å, whereas the wavelength of visible light is of the order of 6000 Å. X-rays therefore occupy the region between gamma and ultraviolet rays in the complete electromagnetic spectrum.

X-rays are produced when any electrically charged particle of sufficient kinetic energy rapidly decelerates. Electrons are usually used for this purpose, the radiation being produced in an *x-ray tube* which contains a source of electrons and two metal electrodes. The high voltage maintained across these electrodes, some tens of thousands of volts, rapidly draws the electrons to the anode, or *target*, which they strike with very high velocity. X-rays are produced at the point of impact and radiate in all directions. If e is the charge on the electron (1.60×10^{-19} coulomb) and V the voltage across the electrodes, then the kinetic energy (in joules) of the electrons on impact is given by the equation

$$KE = eV = \frac{1}{2}mv^2$$

where m is the mass of the electron (9.11×10^{-31} kg) and v its velocity in m/sec just before impact. At a tube voltage of 30,000 volts, this velocity is about one-third that of light. Most of the kinetic energy of the electrons striking the target is converted into heat, less than 1 percent being transformed into x-rays.

When the rays coming from the target are analyzed, they are found to consist of a mixture of different wavelengths, and the variation of intensity with wavelength is found to depend on the tube voltage. Figure 1 below shows the kind of curves obtained. The intensity is zero up to a certain wavelength, called the *short-wavelength limit* (λ_{SWL}), increases rapidly to a maximum and then decreases, with no sharp limit on the long wavelength side. When the tube voltage is raised, the intensity of all wavelengths increases, and both the short-wavelength limit and the position of the maximum shift to shorter wavelengths. Consider the smooth curves in this Figure, which correspond to applied voltages of 20 kV or less in the case of a molybdenum target. The radiation represented by such curves is called *polychromatic, continuous*, or *white* radiation, since it is made up, like white light, of rays of many wavelengths.

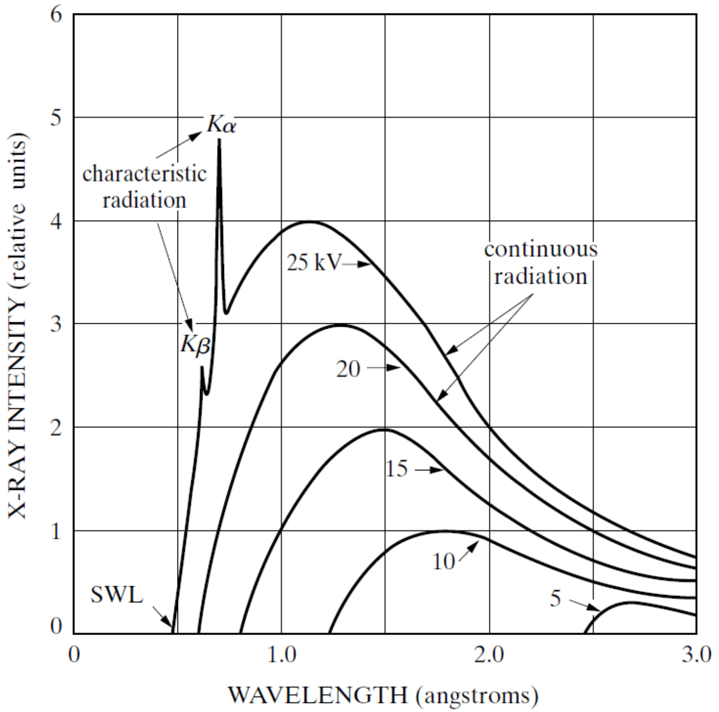


Figure 1. X-ray spectrum of molybdenum as a function of applied voltage (schematic). Line widths not to scale.

When the voltage on an x-ray tube is raised above a certain critical value, characteristic of the target metal, sharp intensity maxima appear at certain wavelengths, superimposed on the continuous spectrum. Since they are so narrow and since their wavelengths are characteristic of the target metal used, they are called *characteristiclines*. These lines fall into several sets, referred to as *K, L,M*, etc., in the order of increasing wavelength, all the lines together forming the *characteristic spectrum* of the metal used as the target. For a molybdenum target the *K* lines have wavelengths of about 0.7 Å, the *L* lines about 5 Å, and the *M* lines still longer wavelengths.

Ordinarily only the *K* lines are useful in x-ray diffraction, the longer-wavelength lines being too easily absorbed. There are several lines in the *K* set, but only the three strongest are observed in normal diffraction work. These are the $K_{\alpha 1}$, $K_{\alpha 2}$, and $K_{\beta 2}$, and for molybdenum their wavelengths are approximately:

$K_{\alpha 1}$: 0.709 Å

$K_{\alpha 2}$: 0.71 Å

$K_{\beta 2}$: 0.632 Å

The α1 and α2 components have wavelengths so close together that they are not always resolved as separate lines; if resolved, they are called the K_{α}*doublet* and, if not resolved, simply the *Kα line*. Similarly, $K_{\beta 1}$ is usually referred to as the K_{β}*line*, with the subscript dropped. $K_{\alpha 1}$ is always about twice as strong as $K_{\alpha 2}$, while the intensity ratio of $K_{\alpha 1}$ to $K_{\beta 1}$ depends on atomic number but averages about 5/1.

These characteristic lines may be seen in the uppermost curve of Fig. 4. Since the critical *K excitation voltage*, i.e., the voltage necessary to excite *K* characteristic radiation, is 20.01 kV for molybdenum, the *K* lines do not appear in the lower curves of Fig. 4. An increase in voltage above the critical voltage increases the intensities of the characteristic lines relative to the continuous spectrum but *does not change their wavelengths*. Figure 5 shows the spectrum of molybdenum at 35 kV on a compressed vertical scale relative to that of Fig. 4; the increased voltage has shifted the continuous spectrum to still shorter wavelengths and increased the intensities of the *K* lines relative to the continuous spectrum but has not changed their wavelengths.

The intensity of any characteristic line, measured above the continuous spectrum, depends both on the tube current *i* and the amount by which the applied voltage *V* exceeds the critical excitation voltage for that line. For a *K* line, the intensity is given approximately by

$$I_{K\mathrm{line}} = Bi(V - V_K)^n$$

where *B* is a proportionality constant, V_K the *K* excitation voltage, and *n* a constant with a value of about 1.5.

The characteristic x-ray lines were discovered by W. H. Bragg and systematized by H. G. Moseley. The latter found that the wavelength of any particular line decreased as the atomic number of the emitter increased. In particular, he found a linear relation (Moseley's law) between the square root of the line frequency *v* and the atomic number *Z*:

$$\sqrt{v} = C(Z - \sigma)$$

where *C* and σ are constants

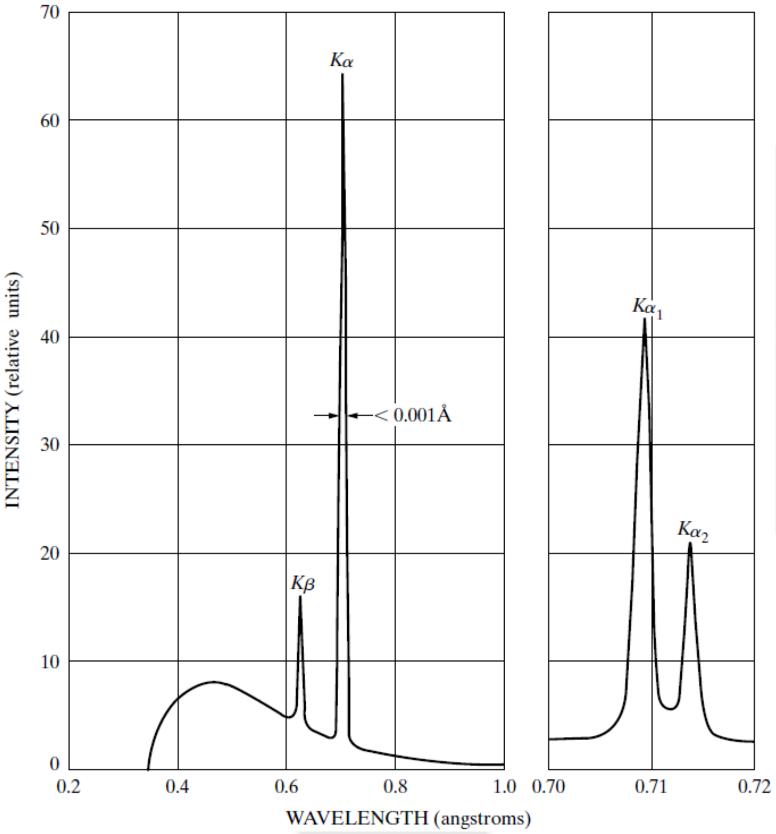


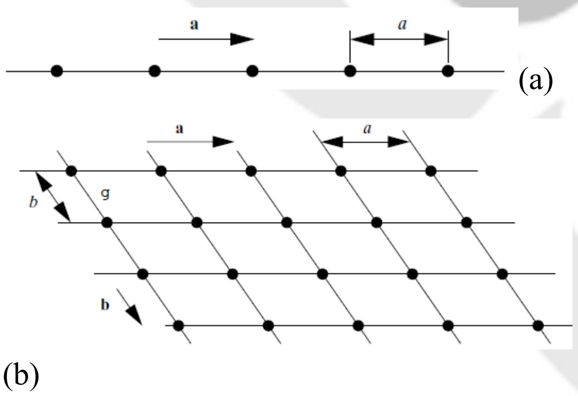
Figure 2: Spectrum of Mo at 35 kV (schematic). Line widths not to scale. Resolved *K*α doublet is shown on an expanded wavelength scale at right.

Geometry of crystals

Turning from the properties of x-rays, consider next the geometry and structure of crystals in order to discover what there is about crystals in general that enables them to diffract x-rays.

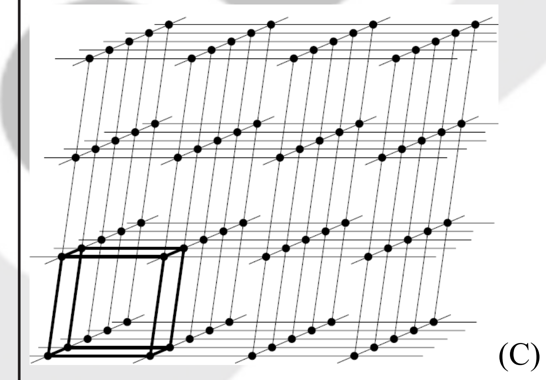
A crystal may be defined as *a solid composed of atoms, ions or molecules arranged in a pattern periodic in three dimensions*. As such, crystals differ in a fundamental way from gases and liquids because the atomic, ionic or molecular arrangements in the latter do not possess the essential requirement of periodicity. Many solids are crystalline; if they are not single-crystals they consist of many contiguous crystals, i.e., they are polycrystalline. Not all solids are crystalline, however; some are *amorphous*, like glass, and do not have any regular interior arrangement of atoms, ions or molecules.

The crystal is then represented as a *lattice*, that is, a three-dimensional array of points (*lattice points*), each of which has identical surroundings. As mathematical constructs, lattices are infinite in extent whereas crystals are not. Diagrammatic representation of lattice is given in Figure 3

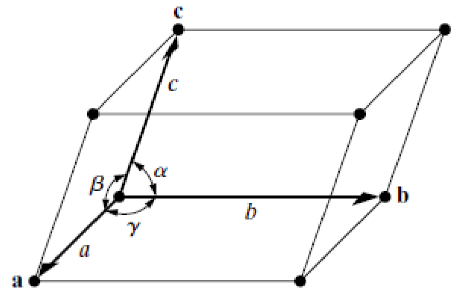


(a) One-dimensional lattice with parameter *a*.

(b) Two-dimensional lattice with lattice translation vectors **a** and **b** and interaxial angle γ .

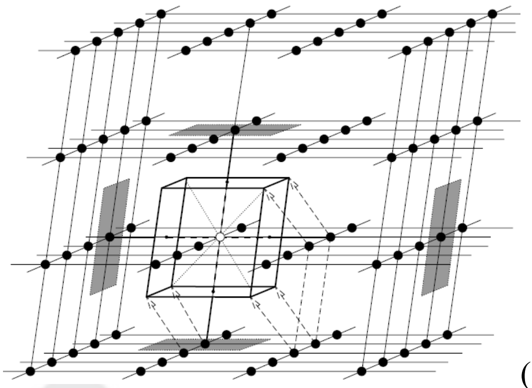


(c) Three-dimensional lattice with a primitive unit cell highlighted in bold. Lattice points are represented by the solid circles/spheres.



(d)

(d) Illustration of lattice vector and interaxial angle designations



(e)

(e) Unit cells with the lattice points located at the cell corners and an alternative unit cell centered on one lattice point.

The fourteen Bravais lattices are described in Figure 4 below. A lattice point in the interior of a cell "belongs" to that cell, while one in a cell face is shared by two cells and one at a corner is shared by eight. The number of lattice points per cell is therefore given by

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$

where N_i= number of interior points, N_f= number of points on faces, and N_C= number of points on corners. Any cell containing lattice points on the corners only is therefore primitive, while one containing additional points in the interior or on faces is nonprimitive.

Structure of some common materials

Metals	**Ceramics**
Copper: FCC (Face centered cubic)	SiC: Diamond Cubic
Iron: BCC (Body centered cubic)	Al_2O_3: Hexagonal
Zinc: HCP (Hexagonal close packed)	MgO: NaCl type
Silver: FCC (Face centered cubic)	
Aluminium: FCC (Face centered cubic)	

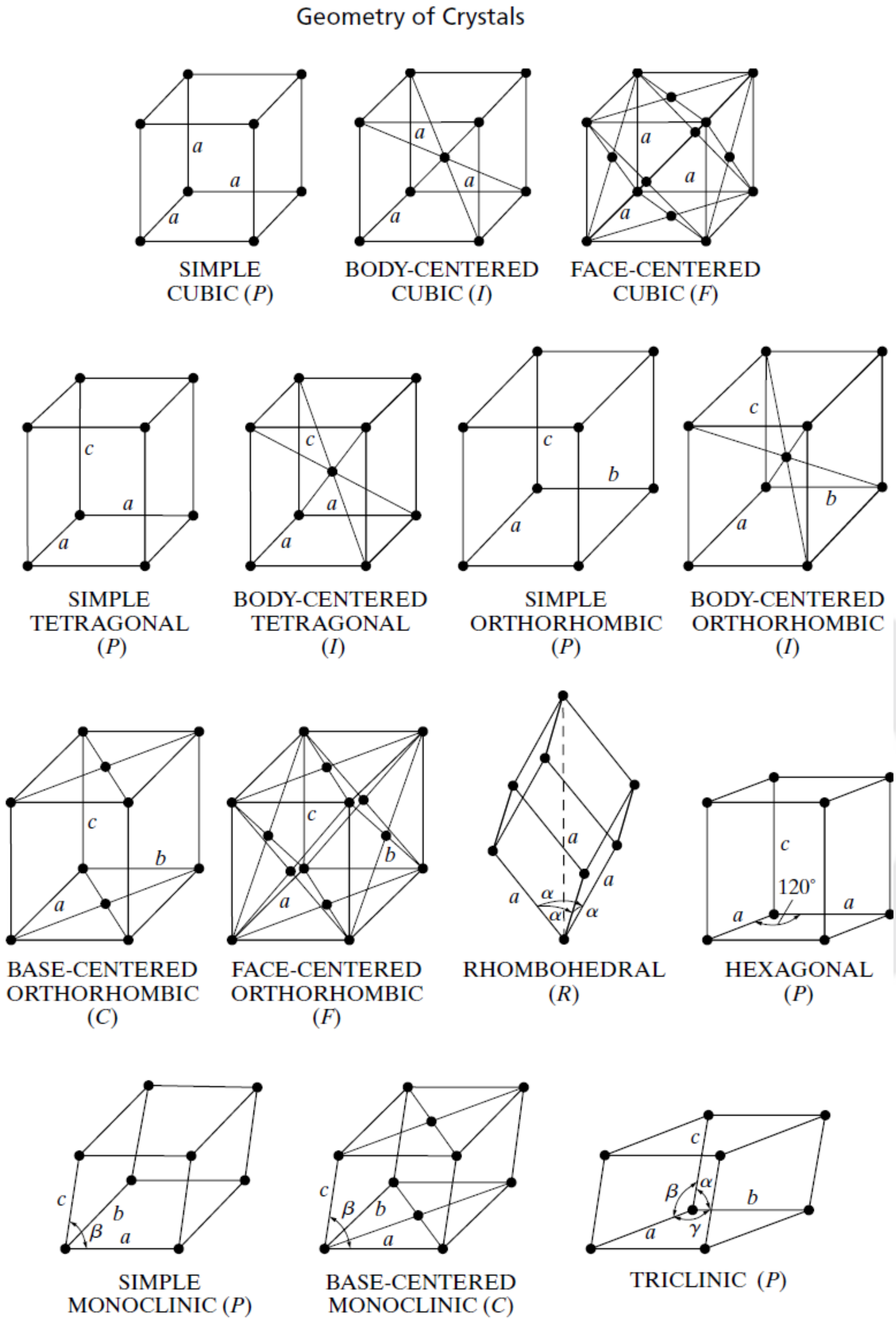


Figure 4: The fourteen Bravais lattices

X-Ray crystallography

There are two features of waves that are important to x-ray crystallography: *Interference and diffraction*. When waves interact, the superposition principle predicts that the areas of overlap will have amplitude equal to the sum of the interfering waves. It is that simple: Where waves overlap, add the amplitudes. For example, if two waves are in *phase*, the amplitudes will add up to form a bigger wave. If they are out of phase, the resulting waves will have amplitude equal to zero.

Diffraction is the bending of light around small objects. This is a phenomenon of all waves and is as simple as it sounds. If an object is in the way of an advancing wave front, the waves will bend around the object. This makes sense in the context of all waves: Water waves will bend around a rock, sound waves will pass through a doorway and fill another room, etc. Similarly, X-rays bend around electron clouds.

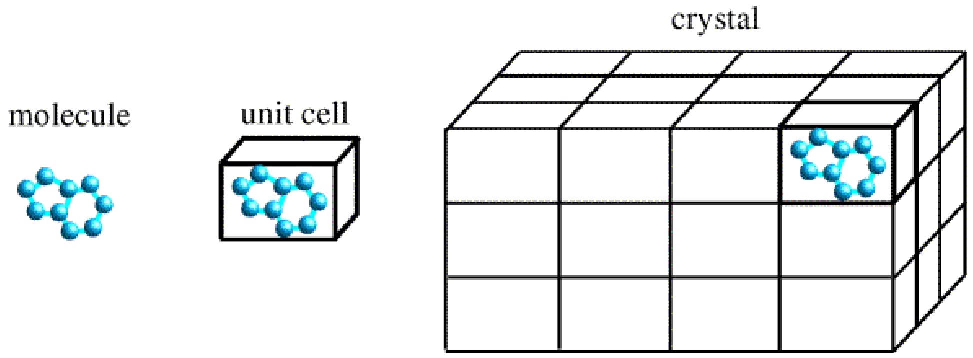


Figure 5: Molecule to crystal hierarchy

Aside from electromagnetic radiation, the only other concept necessary to understanding x-ray crystallography is basic crystal structure. In solid molecules, the atoms are arranged in a specific pattern. This pattern varies with the size and the charge of the atoms (or ions involved), but each compound has only one arrangement of atoms. This arrangement is called a crystal lattice. On a final note, a unit cell is the smallest group of atoms that when repeated, make up the crystal (Fig. 5).

The actual process of performing x-ray crystallography consists of three basic steps (as seen in Fig. 6). The first step, obtaining a crystal, is often the most difficult. The crystal must be large enough (0.1-0.5 mm) and growing crystals can be a time consuming process. The crystal must also be pure, meaning that there are no internal imperfections or twinning (when two identical crystals grow together).

Once the crystal is obtained, it is mounted in front of an x-ray source (a generator, for example). The crystal is slowly rotated and x-rays are passed through it. When the x-rays pass through the crystal they are diffracted by the electrons in the atoms of the crystal and detected by an x-ray detector.

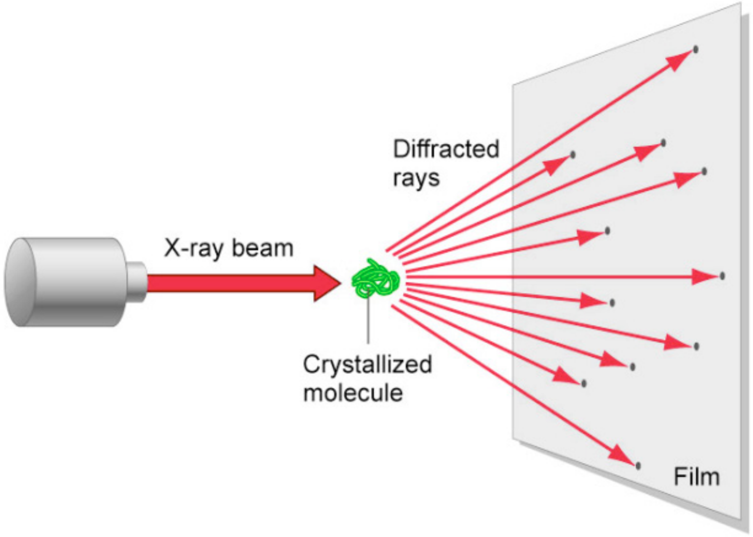


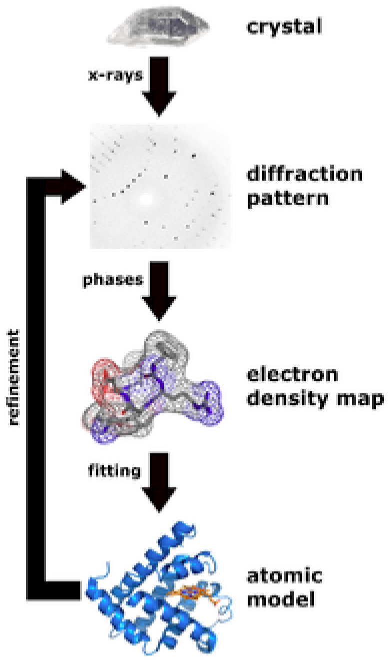
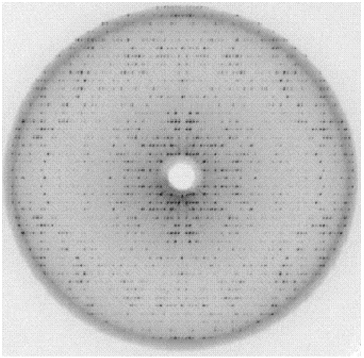
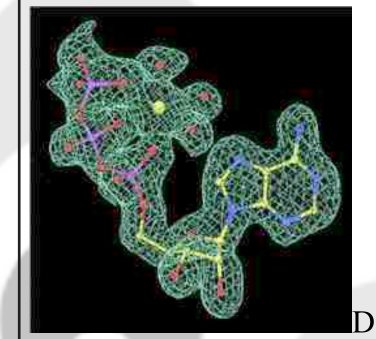
Figure 6: Schematic representation of X-ray crystallography steps

Creation of a molecule’s image from a crystal is similar to creating an image from a lens. Analogously, the wavelength of light used must correspond to the size of the structures that are being visualized. Typical bond distances are on the order of angstroms (0 to 5 Å, or 0 to 0.5 nm). Correspondingly, the wavelength of x-rays (0.01-10 nm) is of the appropriate size for this distance. The wavelengths must be of a similar magnitude to the bond length of atoms in order to produce an interpretable diffraction pattern.

X-ray crystallography will produce unique data for tens of thousands of diffraction spots because of the unique angles and spacing of the atoms in the structure. The diffraction pattern obtained does not resemble any particular kind of molecular structure, so each of the diffraction spots must go through several refinement steps to obtain the structure of the crystal.

X-rays are diffracted around the fluctuating electric fields created by the electrons surrounding the atoms. The resulting diffraction pattern is then used to produce an electron density map. The map can be used to determine the location of atoms relative to each other, bond lengths, and bond angles. It is important to note that crystals with more electrons scatter electrons more effectively. This is because simple molecules/atoms do not have the electron density or complexity to produce scattering detectable over background noise. The electron density map is then used to determine the structure of the crystal.

The electron density pattern is only a measure of the number of received x-ray photons at a given location, not an actual measure of electron densities. In order to obtain the electron density map, the diffraction pattern is analyzed by a computer using an inverse Fourier transform. The specific details involved in Fourier transformations are beyond the scope of the course. (If for some reason you feel a burning desire to learn about Fourier transforms, you can read more about them here.)

 	  Diffraction spots Electron Density

For simplicity's sake, it is easiest to think of the desired electron density as a mathematical function and the diffraction pattern as the Fourier transform of that function. In order to interpret the diffraction pattern, two things are needed: the amplitude and the phase of the diffracted waves.

Because the diffraction pattern is the received number of x-ray photons in each spot, it is a measure of the intensity. From basic wave principles, we know that the intensity is the amplitude of the wave squared, and thus, amplitude can be determined.

There are significant problems, however, when trying to determine the phase of the diffracted waves. Because what is measured in the experiment is essentially a count of the number of X-ray photons in each spot, there is no practical way of measuring the relative phase angles for the different diffracted spots experimentally. To deduce the phase indirectly, there are three approaches.

The first is isomorphous replacement, where a crystal that is nearly identical to the one being studied (except that a few atoms have been replaced or added) is scanned. If these atoms are "heavy" (i.e. they have a large atomic number), they will perturb the diffraction pattern. It is possible to deduce the positions of the few heavy atoms and from that to deduce possible values for the phase angles.

The second techniques is multiple-wavelength anomalous dispersion, which uses just one crystal that contains atoms called anomalous scatterers. By changing the wavelength of the X-rays, the degree to which the anomalous scatterers perturb the diffraction pattern changes, which gives the same kind of information as isomorphous replacement.

A third technique is called molecular replacement. This is used if the researchers already have some idea of the structure of the molecule being analyzed (i.e. it is derived from another compound). In this technique, you replace a unit of the crystal with the model compound and then compute guesses for the phases.

Applications of X-Ray Crystallography

Currently, X-ray crystallography is the most accurate and precise method available for chemical structure determination (although some NMR technologies are coming close). However, due to the nature of diffraction and need for uniform samples, only crystalline compounds can be used. “Growing” or designing these samples is relatively easy for simple and/or small compounds, but as the complexity increases (proteins, viruses, DNA), creating crystal lattices to analyze becomes more difficult. The crystal structure ensures uniform distribution and orientation of one molecule relative to the molecules surrounding it, which is crucial to ensure the diffraction pattern is only determined by the bond orientation *within*the molecules. Non-crystallized samples on the other hand have molecules in random relative orientations, which would produce jumbled, and essentially useless diffraction patterns.

X-ray crystallography has applications in almost every area of science that requires comprehensive knowledge of chemical structure. Because structure and function are affiliated qualities in biological and physical situations, determining the physical structure of a compound is crucial to conducting further research. For example, many pharmaceutical compounds are generated synthetically in labs due to their limited or non-existent) natural abundance. However, the exact structure and connectivity of the compound must be known before pharmacists can attempt to replicate it. One important note is that X-ray crystallography does *not*determine which atoms are present, but rather determines their relative connectivity (bond lengths and bond angles). Nevertheless, since other techniques exist for determining chemical composition, X-Ray Crystallography remains an invaluable tool in chemical research.

Conclusion

Powder x-ray diffraction (XRD) uses x-rays to investigate and quantify the crystalline nature of materials by measuring the diffraction of x-rays from the planes of atoms within the material. It is sensitive to both the type of and relative position of atoms in the material as well as the length scale over which the crystalline order persists. It can, therefore, be used to measure the crystalline content of materials; identify the crystalline phases present (including the quantification of mixtures in favourable cases); determine the spacing between lattice planes and the length scales over which they persist; and to study preferential ordering and epitaxial growth of crystallites. In essence it probes length scales from approximately sub angstroms to a few nm and is sensitive to ordering over tens of nanometres. Atoms or molecules that compose a substance are generally arranged at a distance of 0.1 nm to 0.5 nm from one another. When such a substance is irradiated with X-rays having a wavelength roughly equivalent to the interatomic or intermolecular distance, the X-ray diffraction phenomenon will take place. X-ray crystallography is widely used in the several fields because it is nondestructive and yields crystal structure information relatively easily in an atmospheric environment.