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Principles of Diffraction

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1. INTRODUCTION TO X-RAY DIFFRACTION

1.1 Why do an X-ray Structure Determination?

a) Advantages

The X-ray diffraction experiment provides a 3-dimensional map of electron density. If the data collection and analysis are done carefully, the results provide the "definitive" answer to the analysis of the substance; an answer with which it is usually very difficult to argue. Not only can the accurate 3-dimensional geometrical arrangement of the atoms in the molecules be determined, but also, with care, the correct chemical composition, should this be uncertain. Neutron diffraction gives similar information, but in this case a 3-dimensional map of the locations of the nuclei is obtained. The process also requires a source of neutrons! The combination of data from X-ray and neutron experiments can be a very powerful source of information.

Other analytical techniques do not give as complete a picture as the X-ray experiment. Microanalysis, IR and MS only give partial information about composition and connectivity within molecules. They rarely give full 3-dimensional information, or a complete connectivity description. NMR is a powerful tool, is constantly becoming more powerful and some experiments do deliver three-dimensional information, which can be complementary to the X-ray method.

One drawback of spectroscopic techniques, such as IR and NMR, is that the spectra need to be interpreted based on past experience. A "direct" picture of the molecule is not obtained. Therefore these methods leave ambiguities about the structure. How often is a structure incorrectly assigned because a weak NMR peak was overlooked or a strong peak was misinterpreted? MS can be misleading if the experiment is stopped at a mass just above the *expected* mass of the molecule and the information from a dimer is not measured at all, or if the molecule is so unstable that the molecular mass peak is not observed.

X-ray analysis also gives information about intermolecular interactions in the solid state, such as hydrogen bonding. This may be both useful and a hindrance when one is trying to compare conformations in the solid state with those in solution, where reactions usually take place.

b) Disadvantages

The X-ray diffraction method requires that the substance of interest be not only in the solid state, but in a crystalline form. Moreover, the crystals must be of very high quality, of sufficient size and a single crystal, not intergrown multiple crystals. Much of the time between synthesising a substance and knowing its actual structure can be spent just waiting for crystals to grow. This is a process that cannot, and should not, be hurried! In other frustrating cases, suitable crystals refuse to appear and the answer to the problem remains unresolvable. Techniques for analysing microcrystalline powders to give reasonable structural information do exist (very time consuming and not always successful), but if a substance precipitates in an amorphous (non-crystalline) form there is no hope. Proteins present special problems and a great deal of effort is required to obtain, and maintain, suitable crystals.

The contents of any one crystal is not always representative of the composition of the bulk material. Ensuring high purity of the sample being crystallised helps to avoid this problem. For example, solutions with a high, but not perfect, enantiomeric excess can sometimes yield racemic crystals as the best quality crystals. Solid solutions are rare. The least soluble energetically most stable component or composition always crystallises first, so a mixture might give just one component in the crystals, or a co-crystal with a stoichiometric ratio not representative of the ratio in the bulk and all this can lead to ambiguous conclusions. Ambiguity can be avoided by ensuring proper purity

before attempting crystal growth.

The results of an X-ray study show molecular conformations in the solid state. Intermolecular interactions can influence the conformation of individual molecules in a way that is not the case in solution. Some molecules may adopt conformations in solution that enable them to react readily because of low energy barriers to free rotation of certain bonds, whereas, in the solid state, intermolecular interactions caused by the crystal packing might force the molecules to adopt conformations which would lead one to deduce that the compound was non-reactive. You should always be wary of this possibility when comparing an X-ray structure with solution processes.

In the past, the X-ray diffraction experiment itself was quite slow when compared with the time needed to run an MS, IR or a standard NMR. During the 1960's to early 1990's, data collection typically required from 24 hours to 7 days, and was dependent on the size of the molecule, its packing in the crystal and the diffracting power of the crystal. Each diffracted intensity was measured individually and sequentially by a detector, so larger molecules meant that more intensities had to be collected. In the 1950's, a single structure determination even occupied the entire time of a PhD candidature! New X-ray detector technology and brighter X-ray sources have now reduced the time required to just a few hours for a routine sample and puts a structure determination on a competitive footing with other analytical methods, once good crystals have been grown. However, the presence of disorder in the structure, or unusual difficulties with the refinement can still require several days of work before the best solution is found.

c) Advances in the technique

In the late 1980's, new data collection techniques were developed which use image plates or area detectors to sample regions of space rather than measuring one diffracted intensity at a time. The data collection time then becomes independent of the size of the molecule. This method was originally used to collect data from protein crystals, but the introduction of Charge Coupled Device (CCD) detectors in 1994 revolutionised the speed of data collection for small molecules and a complete data set can now be collected from any suitable crystal in 2-24 hours. The sensitivity of CCD detectors also allows reasonable data to be collected from crystals that would previously have been too small. Since about 2012, noise-free hybrid pixel area detectors (HPAD) have become available for standard diffractometers, further increasing the ability to record good data from very small or weakly diffracting crystals, or allowing even faster data collections.

d) Philosophical considerations

An X-ray analysis can be speeded up even further by collecting less data (lower resolution) and at a faster speed. By doing this, the structure could be obtained more rapidly, but the data quality suffers significantly. The structure may be unambiguously determined, but the geometric parameters might be too imprecise to make any useful deductions from the structure. The same applies to using low quality crystals. Pollution of the crystallographic databases with sub-standard data is to be avoided and the results may even be unpublishable. Such procedures might be adequate if all that is required is a confirmation that the molecule is as predicted and there is no intention to publish any of the structural information, or even to mention the structure in a publication.

My philosophy is that if the job is worth doing at all, it is worth doing as well as possible. In this way, it is never necessary to waste time remeasuring a "quick and dirty" structure when it is suddenly decided, 2 years later, that the work should now indeed be published. If the original crystal no longer exists and the substance is not readily available, the temptation to publish sub-

standard work is too great. If the best possible data is measured the first time, adequate information is always available for more detailed and accurate analyses at a later date, even if the intention at the outset was to have no more than a basic structural confirmation.

Crystal quality is a very important factor affecting the quality of the results. Poor crystals are to be avoided if at all possible. The extra effort is worth it!

Remember: **GARBAGE IN ⇒ GARBAGE OUT!**

1.2 X-rays and Crystals

a) A comment on units

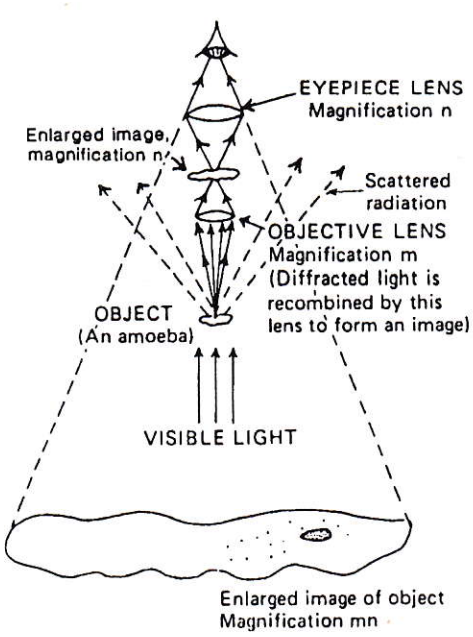
Following IUPAC recommendations, an appropriate unit of length for use in crystallography is the pm (10^{-12} m) and many crystal structure publications do use these units. Historically, the Ångstrom (10^{-10} m) was first adopted by the early crystallographers, and because interatomic distances conveniently fall within the order of 1-3 Å, compared with the more bulky 100-300 pm, the use of Å units has remained a popular and accepted alternative. We will continue to work with Å in this course.

b) Why use X-rays?

Look at ripples in a pond. If they encounter a large object, such as a brick, there is a "shadow" behind the brick in which there are no ripples. If they encounter a small object, such as a thin stick, the ripples appear to go around the stick with virtually no distortion or "shadow", as if the stick was not there. The feature to note here is that if the width of the object is significantly smaller than the wavelength of the ripples, there is no distortion, or scattering, of the waves and therefore the wave pattern after it encounters the object contains no information about the nature of the object.

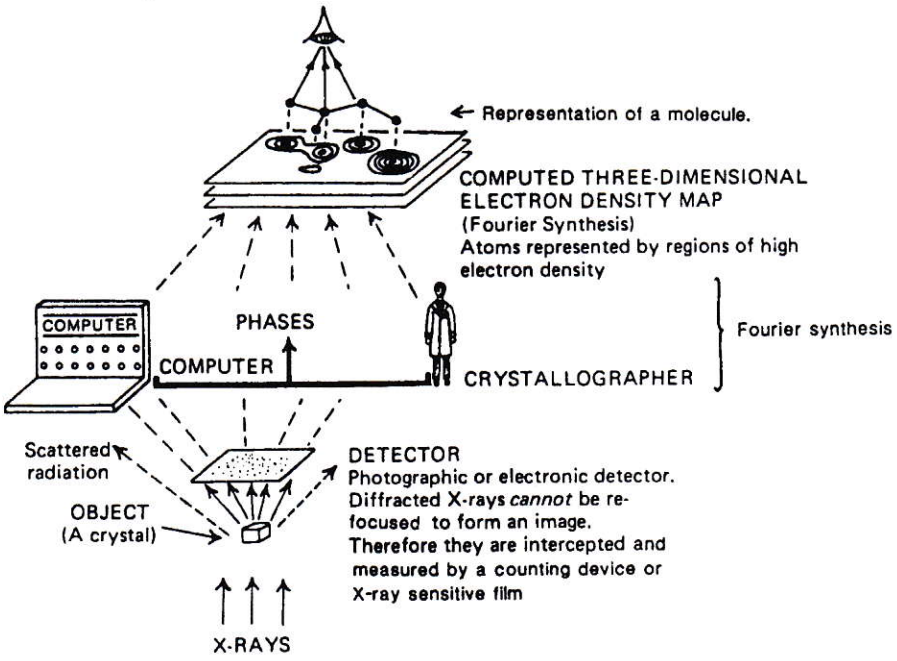
A similar principle applies when using a microscope, since electromagnetic radiation (light) can be thought of, on a simplified level, as having wave-like properties. If the size of an object is of a smaller order of magnitude than the wavelength of the light being used to view it, the object will not scatter and we cannot see the object, no matter how powerful the microscope. Visible light has a wavelength on the order of 10^{-7} m. Thus, if we are interested in looking at the internal structure of molecules, where the size of the atoms including electron clouds is of the order of 10^{-10} m (1 Å), we must use radiation of a similar wavelength. X-rays belong to this region of the electromagnetic spectrum, and the commonly used X-rays have wavelengths in the range 0.5-1.6 Å.

It follows, in principle, that we should be able to view atoms and molecules under a microscope if we irradiate them with X-rays (and use a camera rather than our naked eye to view the image!). So why all the bother with doing a diffraction experiment? Radiation scattered by an object contains information about the appearance of that object. With a microscope we are able use a lens to recombine the scattered radiation to form an image of the object. The main problem is that there is no lens known powerful enough to refract X-rays sufficiently to recombine them to form an image. Therefore we use X-ray diffraction and collect the diffracted radiation, which contains similar information to the light scattered by an object. The "lens" must be provided by the crystallographer using computer programs and his wit.



(a) MICROSCOPE

FIGURE 1.1 Analogies Between Light Microscopy and X-ray Diffraction.



(b) X-RAY DIFFRACTION

Molecular structure may also be studied by neutron or electron diffraction, since neutrons and electrons are scattered by atoms in a similar way to X-rays, although the actual part of the atom with which each radiation interacts is different. However, there is no "lens" available for neutrons either and the electrons have such high energy that, as yet, they generally cannot be focused sufficiently well to resolve individual atoms.

c) X-rays interact with electrons

One of the key concepts to remember is that X-rays interact only with the electrons surrounding atoms, not with the nuclei. Therefore, the results of the X-ray diffraction experiment is a map of

electron density. It can usually be assumed that the atomic nuclei lie at the centres of these regions. For most elements this is a reasonable assumption, since the core electrons will exhibit the highest electron density, and any distortion of the valence electrons due to bonding effects will have an almost negligible effect on the measurable electron density distribution around an atom. The major exception to this is the hydrogen atom, since the only electron it possesses is involved with the covalent bond to another atom. The electron density around the hydrogen nucleus is distorted towards the atom to which it is bonded, and from X-ray data the bond appears to be shorter than the true internuclear separation. For example, the C-H distance is usually found to be 0.95 Å from X-ray data, but the internuclear separation is known from neutron diffraction data to be 1.083 Å.

The fact that we are looking at regions of electron density, and not the actual positions of the nuclei, should always be born in mind when interpreting the results of an X-ray study. The effects of disorder or strong thermal motion on the electron density distribution, and the subsequent interpretation of the positions of the nuclei will be discussed at a later stage.

d) Why crystals diffract

Crystals have long been recognised as having a very high degree of internal order; that is, the objects of which a crystal is composed are arranged in a regular way that is repeated over and over again identically in all directions.

In the 17th century it was recognised that although the faces of crystals of a given substance, e.g. quartz, differ in shape and size, the angles between pairs of similar faces on different crystals were always the same. This constancy reflects the regularity of the internal structure of the crystal. Before the advent of crystallography, these interfacial relationships were used to categorise crystals visually and enabled the classification and separation of many compounds. Crystals tend to develop fastest those faces that are the most densely packed in the underlying structure.

The precise internal order of crystalline materials enable the crystal to be used as a 3-dimensional diffraction grating for radiation that has a wavelength comparable to the interatomic distances within the crystal. This concept actually led, in 1912, to an experiment to prove that X-rays were wave-like with wavelengths of approximately 1 Å, by using crystals as diffraction gratings. In other words, crystals were used to study X-rays *first*. Within one year, it was realised that the X-rays could be used to determine the spacing and positions of the atoms in the crystal, and so crystallography was born.

If, then, crystals are ordered arrangements of "objects" that repeat regularly and identically in 3 dimensions, and thus act as diffraction gratings, how can we utilise this property to deduce the form and orientation of these objects?

In order to fully complete a crystal structure analysis, two things must be determined:

1. **The size of the unit that is regularly repeated to form the 3-dimensional array.**
2. **The contents and the arrangement of the contents of this unit.**

These are the two fundamental problems that the crystallographer faces. The answer to the first question is relatively easily determined, the second is far more complex, but with modern computers and programs this can also be dealt with routinely. In the days of hand calculations, this was an arduous task. One or two crystal structure determinations could occupy the entire time of a Ph.D. study! It is not necessary to fully understand how the computer programs process the data and perform the calculations, but certain basic concepts must be grasped in order to interpret the results produced along the way, and to make critical decisions which the computer is sometimes (or

always) unable to make. It is these basic principles that will be the focus of most of this course.

1.3 Principles of X-ray Diffraction

A brief description only is given here. For those interested, a detailed discussion of Diffraction is given in Glusker & Trueblood, Chapter 3.

a) The one-dimensional case

Consider, firstly, the diffraction of monochromatic light from narrow slits. If there is only one slit there is a strong direct beam which becomes weaker at the sides followed by one or more weak "side bands". This is because each point within the slit acts as a point source, scattering in all directions. As the angle from the direct beam increases, the path lengths from each point source to any given point start to vary, therefore the waves from each point become more and more out of phase and so start to cancel each other, thus the intensity decreases. At sufficiently high angles some waves may again be in phase, and so weak side bands are observed. Note that the wider the slit (Fig. 3.1b), the narrower the overall spread of the pattern.

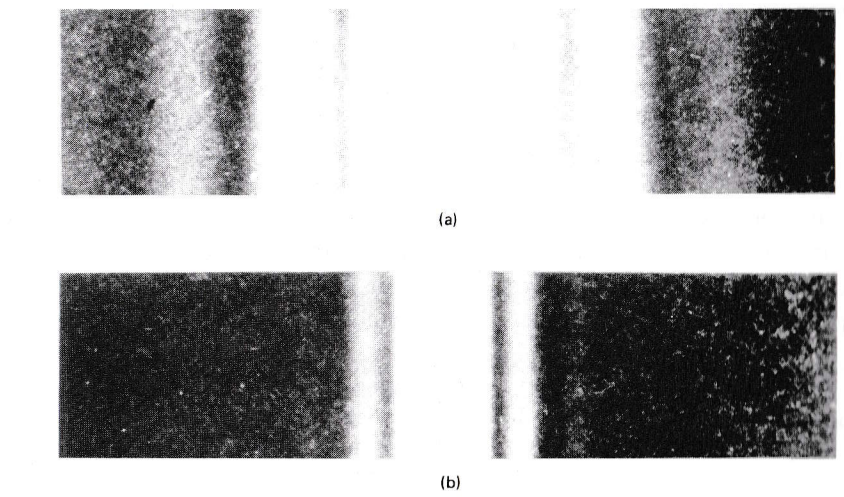


FIGURE 3.1 Diffraction Patterns of Single Narrow Slits.

Diffraction from a single slit generates an "envelope" of intensity, as shown below.

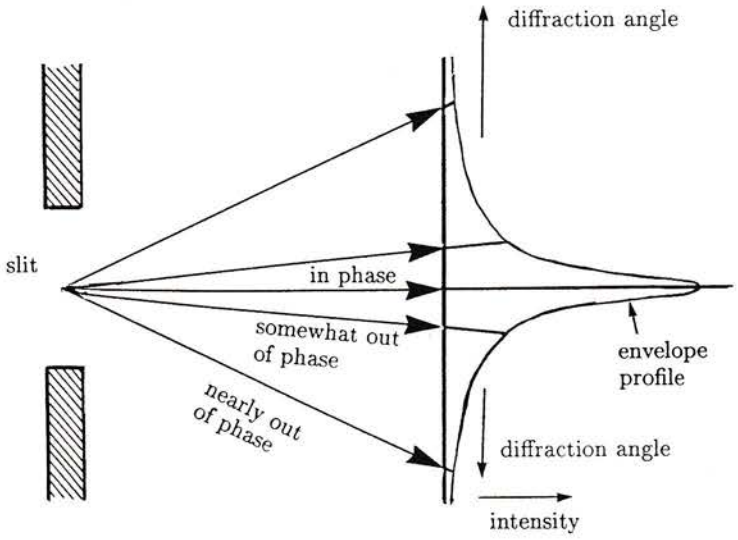


FIGURE 3.5. An illustration of the reason that the diffraction pattern of a single slit has width to its profile (the envelope profile, compare with Figure 3.4). This is because of varying degrees of interference between waves traveling in the directions indicated in this figure. Waves traveling in the direction of the direct beam (if the incident light is perpendicular to the slit) are in phase and give a maximum intensity. At angles other than that of the direct incident beam, the scattered waves are more out of phase. Therefore their intensities decrease because of increased interference. The result is a diffraction pattern with the envelope profile shown here.

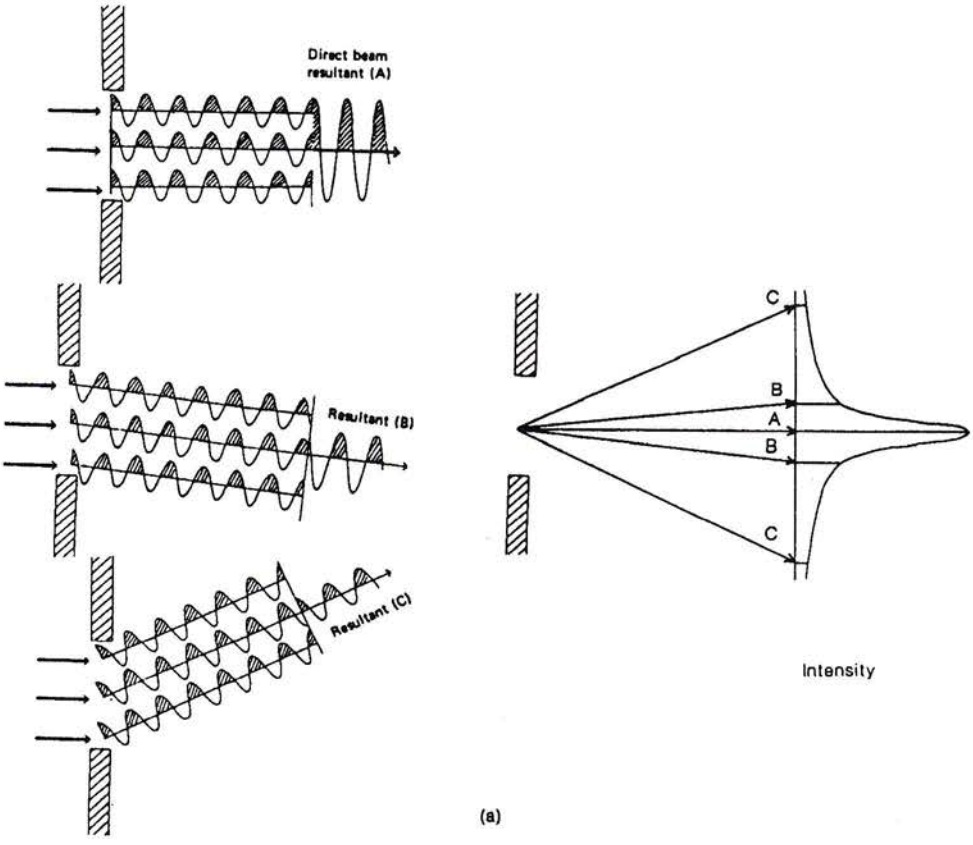
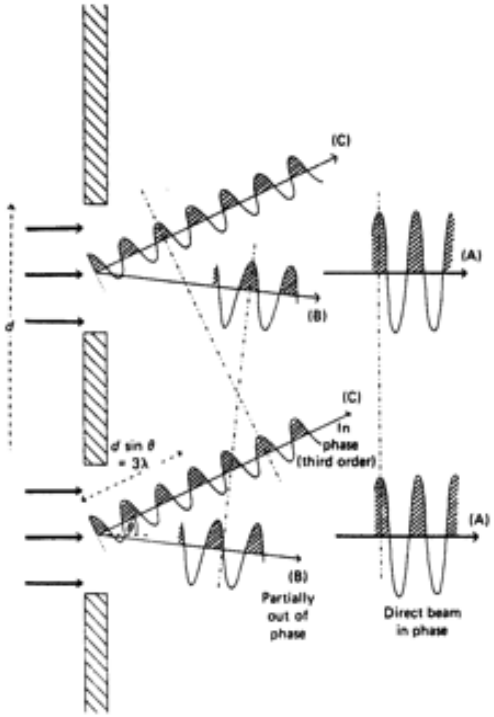


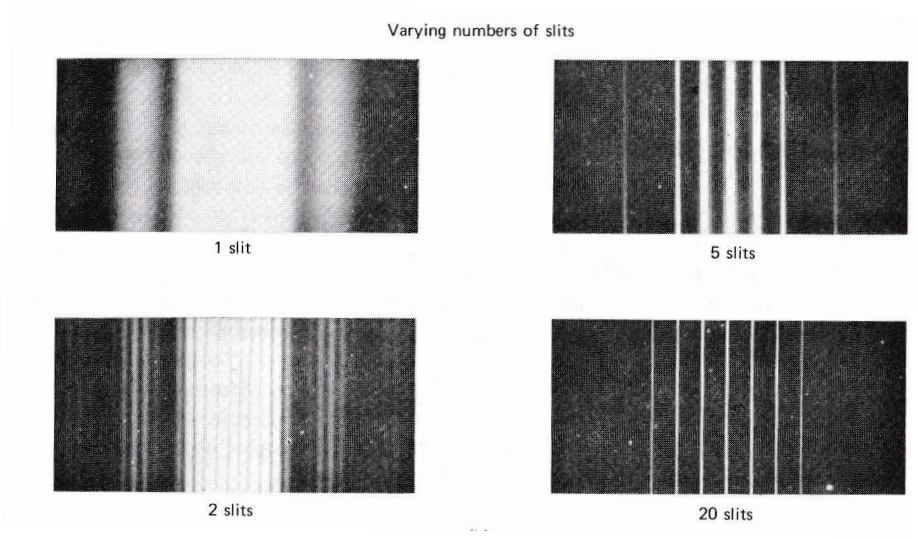
FIGURE 3.3 Diffraction as the Interference of Waves.

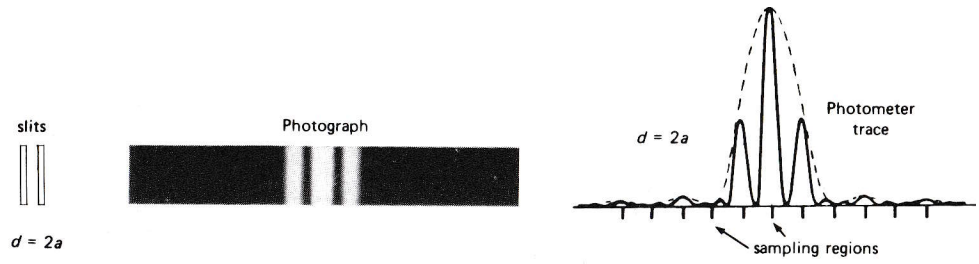
When diffraction occurs from two slits there are two effects to consider. Firstly, the variation in intensity with angle as a result of interference of the waves generated within each slit separately, as shown above, to create an "envelope" of intensity. Secondly, the interference of scattered waves at a given angle with those at the same angle from the adjacent slit. At angles of constructive interference, when the resultant two waves from the two slits are in phase, sampling of the "envelope" takes place. As shown on the next page, waves are in phase when the path length difference for the waves is exactly an integral number of wavelengths. At certain other angles, no diffraction is observed because the waves from adjacent slits are out of phase and destructive interference occurs.

At intermediate angles, the waves from two slits would be partially out of phase and weak intensity would be observed. However, in the case of multiple slits, the phase differences at these intermediate angles will range over all possibilities, so that the sum of all the waves is almost zero and the intensity in directions other than for which the waves are exactly in phase will be so small, relative to the in-phase maxima, as to be undetectable. Thus sharp diffraction lines are observed. The diagram at the top of the next page shows how an increasing number of slits increases the sharpness of the diffraction pattern, and how the minor maxima from waves that are only partially in phase disappear.

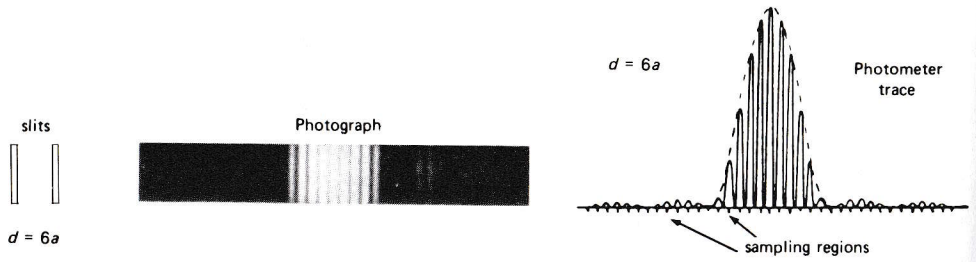


From the diagram above it can also be seen that the angle at which the waves from the two slits are exactly in phase is dependent upon the spacing, d, between the slits. If the path length difference is n wavelengths, then the relationship can be written as $n\lambda = d\sin\theta$. It should be clear from this that the smaller the spacing between the slits, the larger the angle at which a given order of diffraction occurs. This can be seen clearly in the lower diagram on the following page.





Narrow spacing between slits. Wide spacing between sampling regions



Wide spacing between slits. Narrow spacing between sampling regions.

(a)

In the above diagram, as the spacing between the slits increases, the spacing of the diffraction lines decreases proportionally, so that the relationship $n\lambda = d\sin\theta$ is obeyed. The graphs on the right show how the observed intensity (solid line) comes from a combination of the intensity envelope from single slit diffraction (dashed line) with the discreet sampling regions generated by the two slits. In other words, the intensity of a diffraction band is just the intensity of the single slit diffraction envelopes at those, and only those, angles at which the waves from the two slits are exactly in phase.

This concept has important significance for the determination of a crystal structure. The spacing of the diffraction pattern will tell us about the spacing of the repeating units from which the crystal is made up, and therefore the size of each individual unit, while the intensity of each point in the

diffraction pattern should contain information about the contents of the individual unit itself, which in chemical terms means the arrangement of the individual atoms, and this is what we really want to know in the first place.

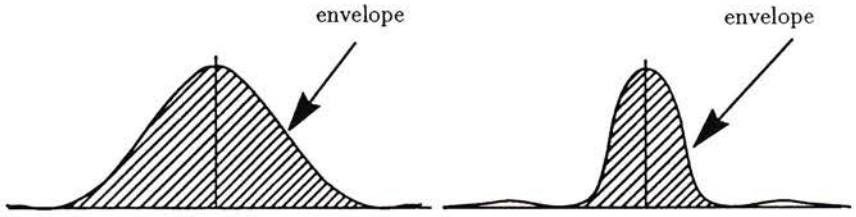


FIGURE 3.4. Scattering by a single slit. (a) Diffraction by a narrow slit and (b) the diffraction pattern of a slit that is wider than that in (a). In both cases the intensity variation shown is referred to as the "envelope." The zero point of the horizontal axis represents the direction of the direct beam (cf. Figure 3.5).

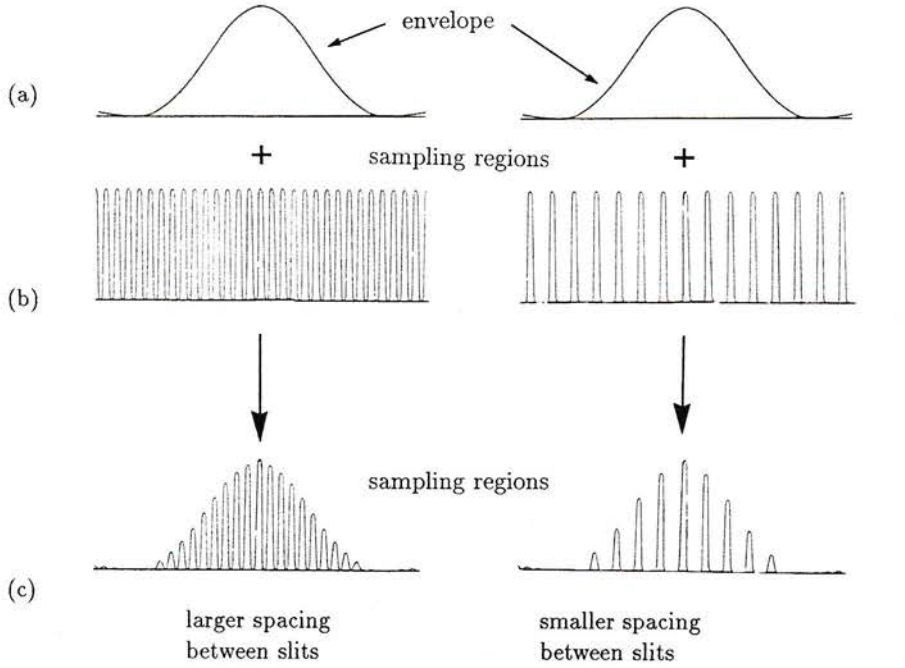
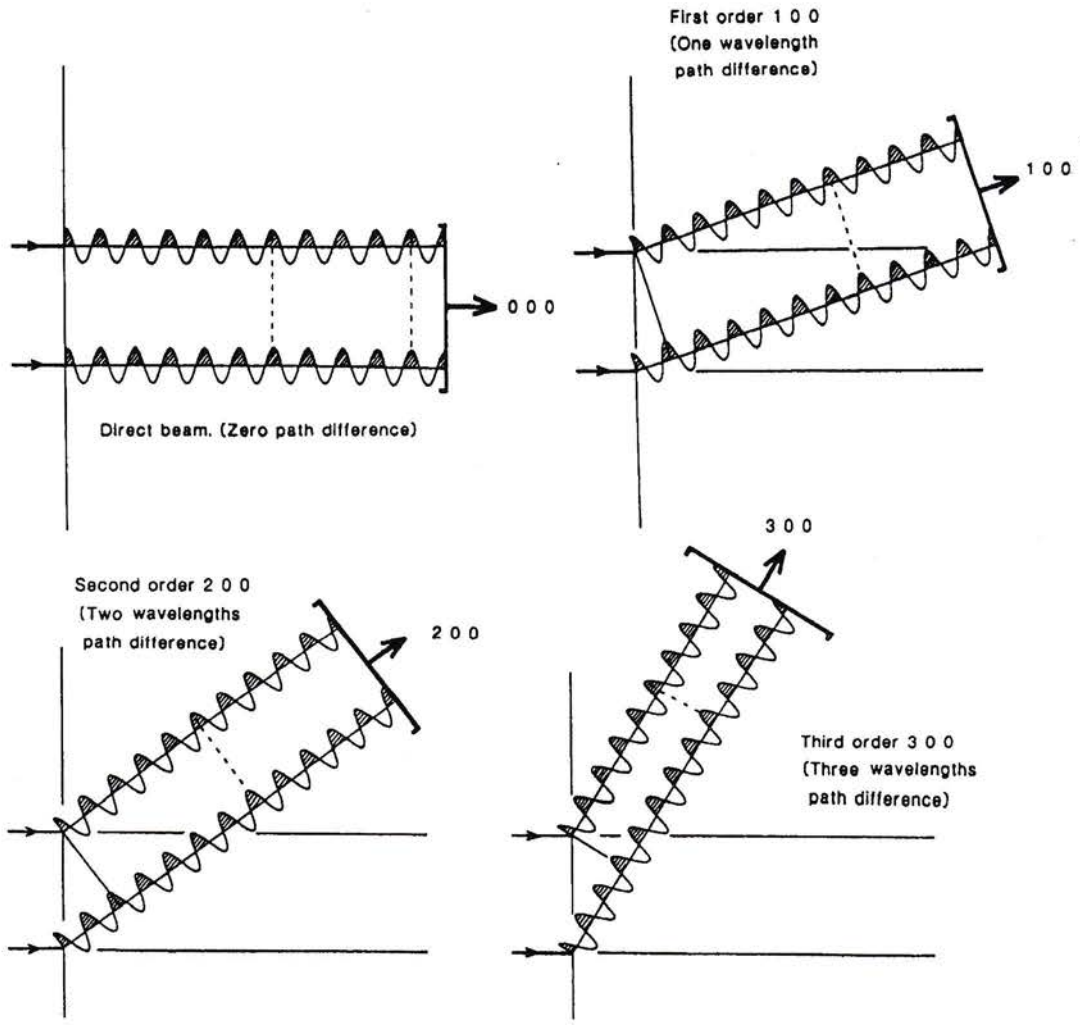


FIGURE 3.6. The diffraction patterns of series of slits. Shown in (a) is the diffraction pattern of a single slit. The sampling regions (from the grating periodicity) are shown in (b). The diffraction pattern is the combination of the envelope profile and the sampling regions, that is, the sampling of the envelope profile at sampling regions only. The results for a series of parallel, regularly spaced slits are shown in (c). The spacing between the slits is greater in the diagrams on the left than in those on the right.

First, second, third and higher orders of diffraction are obtained as scattered waves which differ by one two, three, and more exact wavelengths, as shown below. In one dimension, the index, h, can be used to indicate the order of diffraction, or the number of wavelengths by which the path lengths differ.



In summary:

1. The size and shape of the "envelope" are determined by the diffraction pattern of a single slit.
2. The positions of the regions in which the envelope is sampled are determined by the spacings between the slits.
3. The diffraction pattern is increasingly sharp, the greater the number of slits.

b) Extension to two and three dimensions

The one-dimensional diffraction pattern of parallel lines produced by a row of equally spaced slits will also be produced if the slits are replaced by holes. If a one-dimensional array of holes is punched in a card, the diffraction pattern of monochromatic light passing through the holes will consist of lines which run perpendicular to the direction of the line of holes (Fig. 3.5a&b, below). This is because interference effects between light scattered from adjacent holes reduce the scattered light intensity effectively to zero in all directions except that perpendicular to the repeat direction of the original grating. Hence lines of diffracted light are formed.

If two one-dimensional arrays of holes are combined and intersect at some angle, γ, then each of the arrays acts independently and the only regions in which there is not destructive interference of the diffracted light are at the intersections of the two sets of lines produced by the one-dimensional gratings. Thus, for a completely two dimensional array (or lattice) of holes, a two dimensional lattice of diffracted points of light is obtained, which is related to, yet different from, the original

pattern (Fig. 3.5c). This diffracted array is known as a reciprocal lattice. As in the one-dimensional case the distances between successive rows of points in the reciprocal lattice are inversely proportional to the corresponding distances in the original lattice. The actual relationships between the real and reciprocal lattice spacings can be seen in Fig. 3.5d.

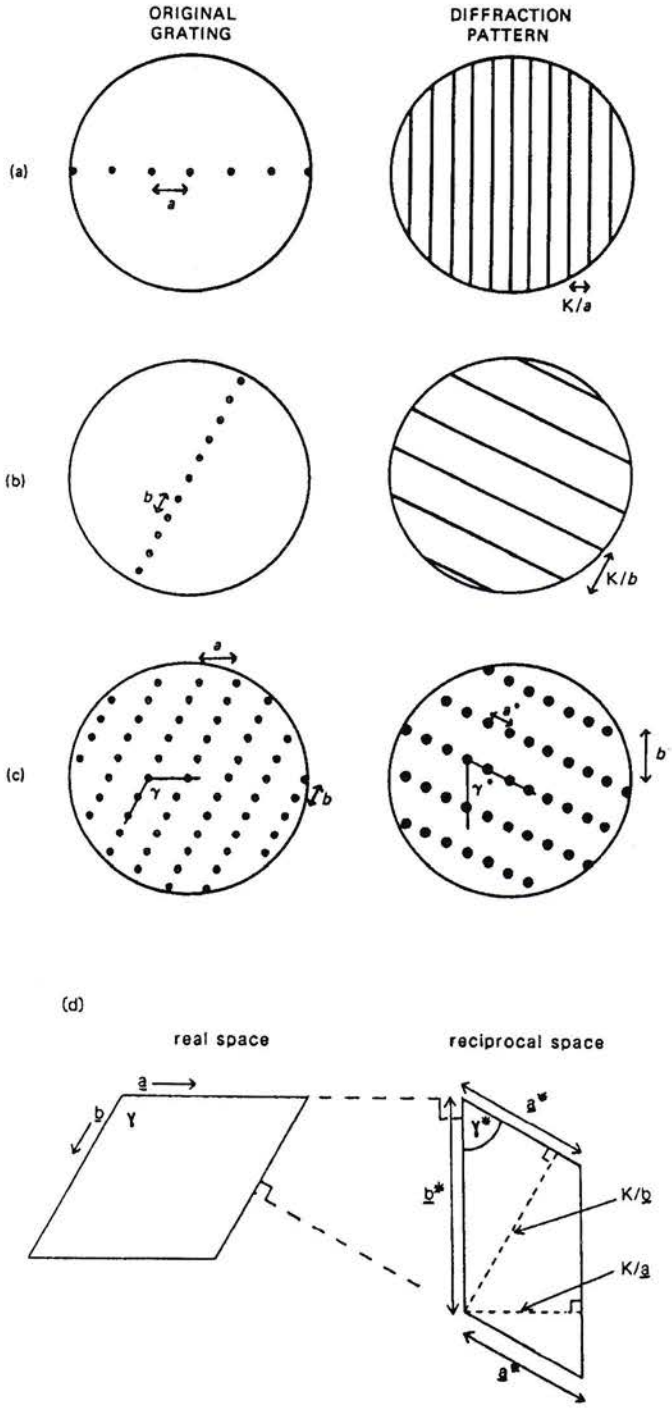


Figure 3.5. Production of a two-dimensional diffraction pattern.

A further example of the relationship between direct and reciprocal lattices is below and in the appendix to this chapter.

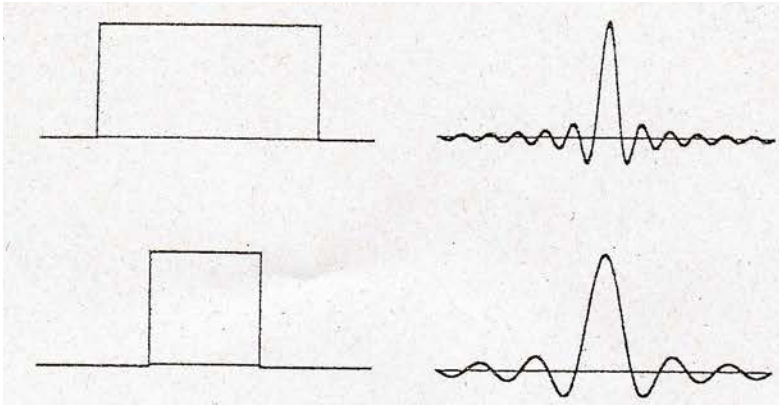


Fig. 4.13 Wide and narrow top-hat functions and their Fourier transforms.

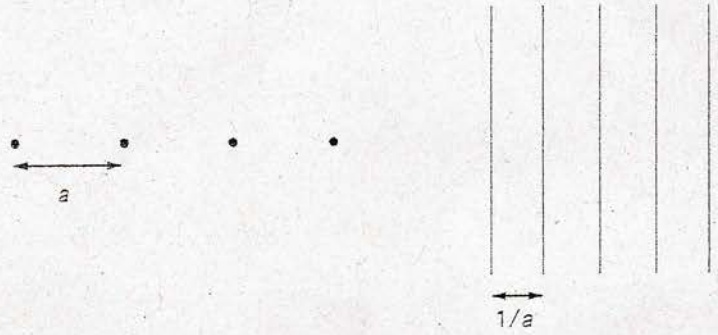


Fig. 4.17 A line of dots and its diffraction pattern (based on Holmes and Blow 1966).

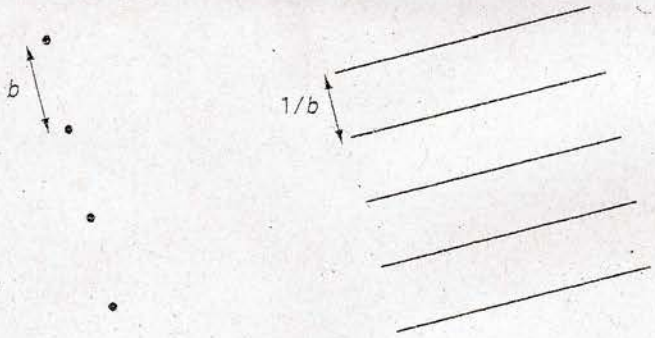


Fig. 4.18 A different line of dots and its diffraction pattern (based on Holmes and Blow 1966).

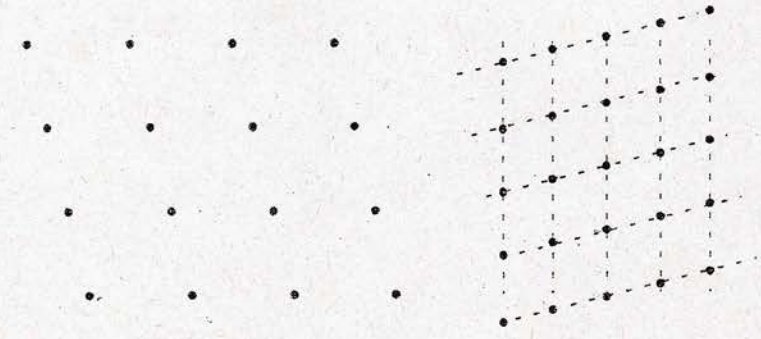


Fig. 4.19 A two-dimensional lattice and its diffraction pattern (based on Holmes and Blow 1966).

The extension of the two-dimensional argument to three dimensions follows the same principles, so that the 3-dimensional diffraction pattern will be points of intensity which also occupy 3-dimensional space. In this case the reciprocal lattice so produced is known as reciprocal space.

The principle of reciprocal space is a fundamental cornerstone to the understanding of the mathematics of X-ray diffraction and for the necessary calculations. However, it is not necessary to have a full understanding of the mathematics of this concept at this stage. For the most part the computer programs take care of that for us. It is more important to recognise that the repeating unit in a crystal can be related to the "holes" which produced the diffraction grating in the above discussion. This means that the spacing of the points in the diffraction pattern of a crystal is inversely related to the size of the basic repeating structural unit (the unit cell) that makes up the crystal lattice. The more closely spaced that the pattern is, the larger will be the repeating unit. In addition, the shape of the pattern or the angles between rows of points tells us, also in an inverse sense, the shape of the unit cell.

Fig. 3.5c shows that if a diffraction pattern is recorded on a surface, the spacing of rows in the pattern can easily be measured and the spacing of identical points in the original lattice can be directly calculated. In X-ray diffraction, the surface used to record the diffraction pattern can be a film. For a 3-dimensional crystal lattice the problem is not quite so simple, but if the direction of one of the crystal axes is kept perpendicular to the X-ray beams at all times, the projection of the other two axes will appear as a grid similar to that in Fig. 3.5c and the lengths of these axes may be readily calculated. [A crystal axis can be thought of as one of the directions in which the repeating structural units, or unit cells, are stacked (just as boxes would be stacked), and the axis length is just the distance to the same point on the next box in the stack; i.e.. the spacing between the slits in the one-dimensional case.] An alternative way of calculating the spacing of rows in a diffraction pattern, and hence the size of the repeating unit or the unit cell dimensions, is to measure the angles through which the beam is diffracted to give each individual point of the pattern. This is the method by which modern X-ray diffractometers calculate the unit cell dimensions.

We have now satisfied the first requirement for determining a crystal structure. That is, to be able to determine the size of the unit that is regularly repeated to form the 3-dimensional lattice of the crystal. To do this it is only necessary to know the positions of the points on the diffraction pattern, not the intensities of these points. In the early days of crystallography this was the easy part of the experiment. It actually provides a lot of information about simple substances. If the unit cell volume is known together with the density of the crystal, a great deal can be inferred about the contents of the repeating unit.

In three dimensions the order of diffraction can be represented by three indices, h, k, and l. Each index gives the order of diffraction in one of the principle directions of the unit cell as if each was a one-dimensional case. Only when all three of the one-dimen-sional diffraction patterns are in phase will a diffracted beam be observed, thus it is valid to express the order of a beam diffracted in three dimensions in terms of the individual one-dimensional orders. The three indices are written *hkl* and are termed Miller indices. Miller Indices will be discussed further in the section on space groups.

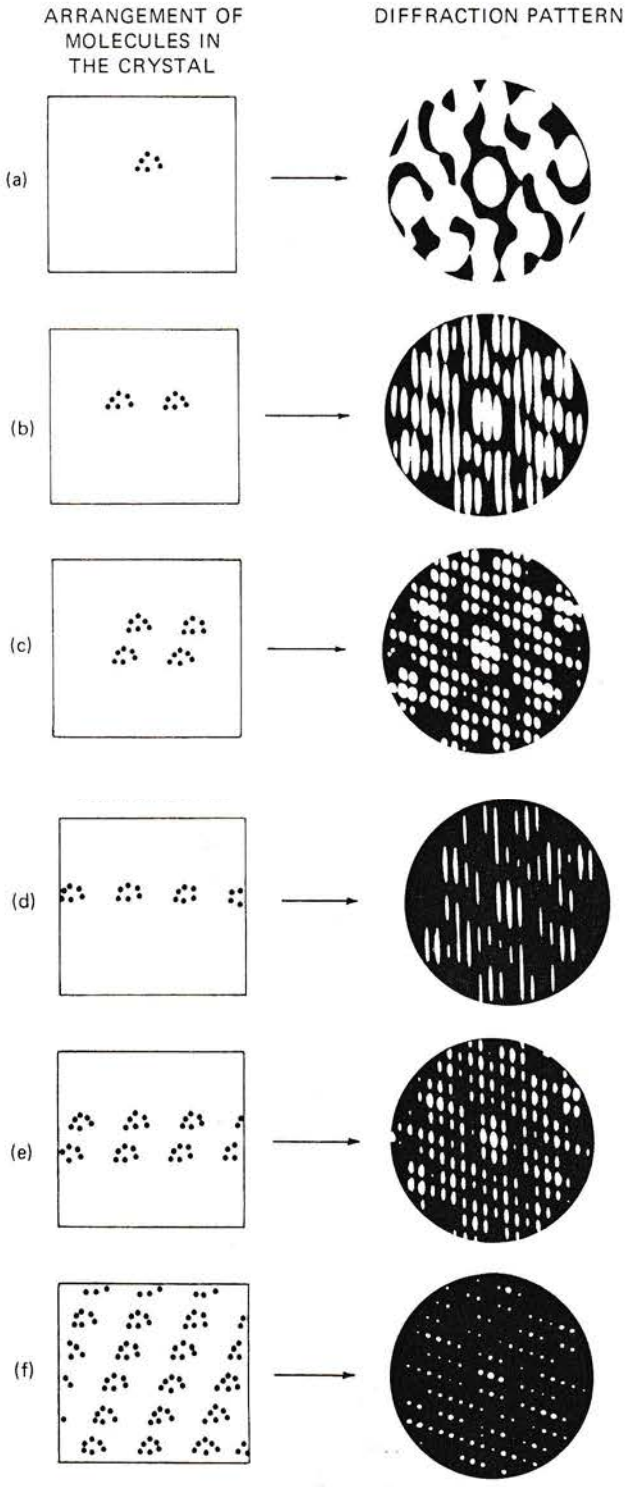
c) The information in the diffraction intensities

Until now we have considered the repeating unit in a lattice to be made up of a single "hole" or object. What happens if the "hole" takes on some internal structure or becomes an arrangement of small holes, not related by translational symmetry, which are then repeated in a regular fashion? Such an arrangement can be thought of as simulating a molecule, or a group of molecules, unrelated by translational symmetry, in a crystal lattice.

The figures below demonstrate how the diffraction pattern of a molecule can be simulated by repeating a small arrangement of holes in a card in two dimensions, and reinforces some of the concepts discussed so far.

Picture (a) resembles the single slit scenario in which the "envelope" is produced. This pattern actually contains the structural information of the single arrangement of holes (or molecule).

Pictures (b) and (d) resemble the effect of having two and then a whole row of slits; (d) contains the same number of lines as (b), the pattern merely becomes sharper. The gaps in some of the lines are caused by the internal structure of the "molecules".



Pictures (c), (e) and (f) represent the development of the two-dimensional diffraction pattern shown in Fig. 3.5. Again, the intersection of diffraction lines from the overlap of two one-dimensional arrays leads to the formation of points of intensity. Pictures (c), (e) and (f) become increasingly sharp as the number of repeating units is increased.

Finally, in (f), a diffraction pattern quite similar to that in Fig. 3.5c is obtained. Rows of points can clearly be seen, the spacing of which relates inversely to the spacing between the "molecules" on the card. The one clear difference is that not all of the points in (f) have the same intensity. The intensity variation is caused by the "molecule" from which the repeating unit is built. Thus diffraction intensity contains the information about the internal structure of each unit cell.

A further example is shown on the next page. From these diagrams, it can be seen that the sharpness of a diffraction pattern is dependent upon the number of repeating units producing the pattern. A well ordered crystal will have large numbers of well aligned unit cells, and a sharp diffraction pattern will result. If order breaks down in a crystal, so that there are only small numbers of unit cells aligned in a particular orientation, the diffraction pattern will tend to become "fuzzy". This property can be used to examine the quality of a crystal to see if it is sufficiently ordered to be used for a structural determination.

A real diffraction photograph is shown on the right. Note the similarities to Picture (f) above.

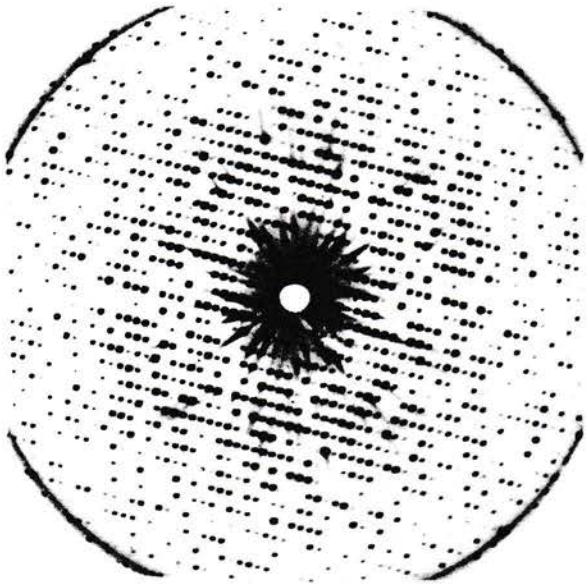


FIGURE 3.6 X-Ray Diffraction Photograph Taken by the Precession Method.

Now we know how to satisfy the second requirement for the determination of a crystal structure. That is, to determine the contents and arrangement of atoms within the unit cell. This information is obtained by measuring the intensities of the diffracted beams. In early days this was done by estimating, by hand, the densities of each diffracted spot recorded on a piece of photographic film. This was a huge task, since there were many hundreds of such spots to be measured in order to determine the structure of even quite small molecules. By comparison, the determination of the unit cell dimensions by merely measuring the spacings of rows of spots on the film was a trivial task. Today the hard labour is undertaken by the diffractometer, which automatically measures the intensities of each point in the diffraction pattern with an electronic detector.

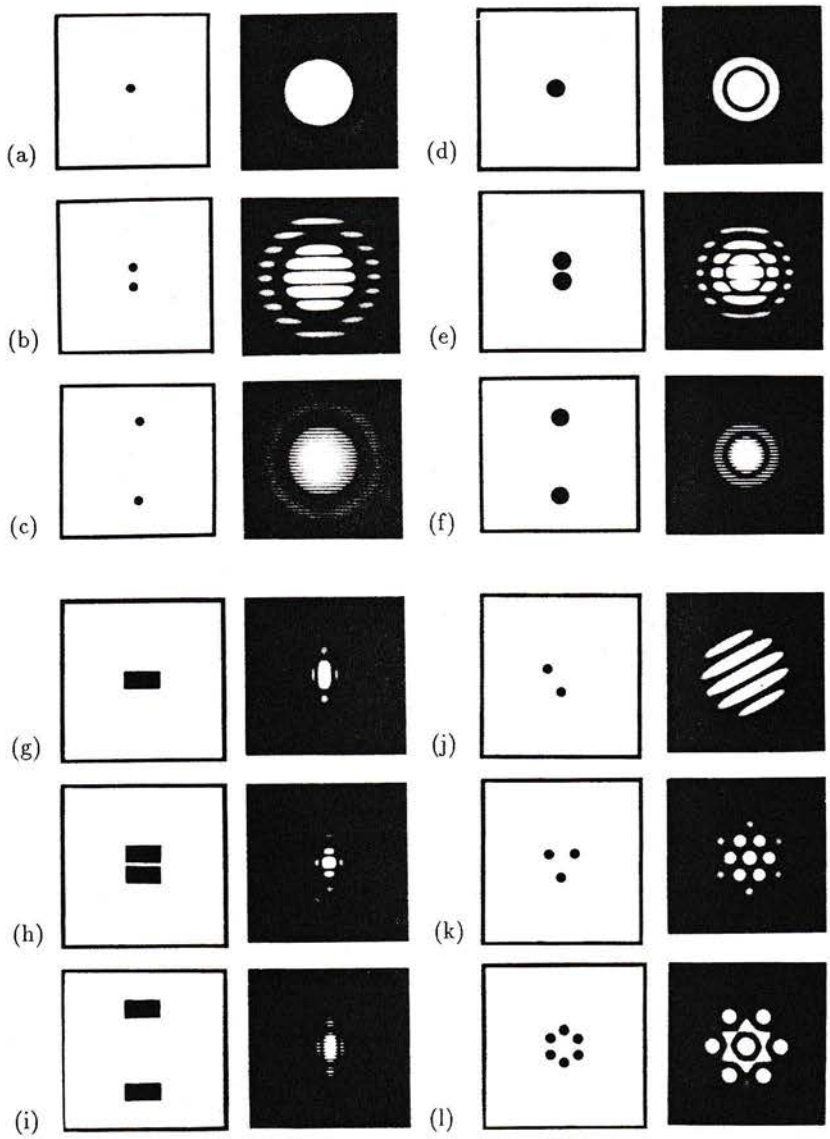


FIGURE 3.7. Examples of diffraction patterns from a variety of masks. The mask with the holes in it is to the left and its diffraction pattern is to the right. The diffraction pattern of (a) a single round hole in a mask, (b) two round holes, and (c) two round holes further apart. Note that in (b) and (c) the diffraction pattern is sampled (in lines) with a spacing that is inversely proportional to the distance between holes in the mask. The diffraction effects when the sizes of the holes in the masks are increased are shown in (d), (e), and (f). The holes are larger than in (a), (b), or (c), but the spacings between their centers are the same. Recall that the experimental diffraction pattern is now more compact, illustrating the reciprocal relationship between the size of an object and its diffraction pattern. Since the spacings of holes in the masks are the same in (a), (b), and (c), and in (d), (e), and (f), the distances between sampling regions are also the same. The effect of changing the shape of the holes in the mask is shown in (g), (h), and (i), where the holes are rectangular in shape. Again, the reciprocal relationship between dimensions in real space and in the diffraction pattern is shown. The wider part of the hole gives a narrower diffraction pattern. The spacings between holes are the same as in (a) to (f). Finally, the effect of different arrangements of holes on the diffraction pattern. In (j) there are two holes in the mask, and the resulting diffraction pattern is similar to that in (b), although one mask is rotated with respect to the other. In (k) the effect of three holes, equivalent to three superpositions of the diffraction pattern in (j), each at 120° to each other is seen. In (l) the diffraction pattern of six holes is shown. (Reprinted from G. Harburn, C. A. Taylor and T. R. Welberry: *Atlas of Optical Transforms.*)

d) Diffraction by atoms

In the above discussion, the principles of diffraction of light by slits or holes in a card have been described and an analogy to the diffraction of X-rays by crystals has been made assuming crystals behave like diffraction gratings. This is an experimentally proven fact, but some explanation is required.

When X-rays interact with the electrons of an atom, the electrons are excited by the electric field of the X-rays. These oscillating electrons then act as a secondary source of radiation of the same wavelength as that of the incident beam. This radiation is scattered in all directions, just as every point within a single slit acts as a secondary source and scatters light in all directions. The scattered radiation from each atom within a unit cell then interferes with that from the other atoms in exactly the same way as the radiation from points within a single slit. In addition, the radiation scattered by the identical atom in the same position in each unit cell interferes as if it came from a row of slits, and so the analogy to a diffraction grating can be seen. [It is also a fortunate fact of physics that the phase change between the incident and scattered radiation from *any* atom is *always* the same (180°) and therefore can be ignored. Strictly this is not quite true when anomalous dispersion from heavy atoms is considered. However, the effect of anomalous dispersion is very weak and can be ignored here. The significance and use of the effects of anomalous dispersion will be discussed later.

We have seen that the observed X-ray diffraction patterns can be explained in terms of a theory analogous to that used for diffraction by gratings. This was the theory used by von Laue who discovered the diffraction of X-rays by crystals in 1912. An alternative theory was developed by Bragg in 1913, and it is discussed briefly here because it explains why the terminology "reflection" has traditionally been used to describe diffracted beams; a term which will be used throughout this course.

Bragg deduced that the angular distribution of scattered radiation could be understood by considering that the diffracted beams behave as if they were reflected from planes passing through points of the crystal lattice. This "reflection" is analogous to that from a mirror for which the angles of incidence and reflection must be the same. Waves scattered from adjacent lattice planes will be exactly in phase when the difference in paths travelled by these waves is an integral number of wavelengths. This led to the famous Bragg equation: $n\lambda = 2d\sin\theta$. Here λ is the X-ray wavelength, $n\lambda$ is the path length difference between waves scattered from adjacent parallel lattice planes, d is the perpendicular spacing between these planes, and θ is the complement of the angle of incidence (and scattering) of the X-ray beam. Since the diffracted beam appears as if reflection had occurred from these lattice planes, with the beam deviated through an angle 2θ, diffracted beams are commonly referred to as "reflections".

It is important to note that the lattice planes referred to above are planes through the crystal lattice, not planes of atoms. Lattice planes, as will be explained later, are defined as having specific fractional intercepts along each of the unit cell edges. They are planes that sub-divide the unit cell. For a given unit cell there are specific orientations of the crystal that will bring each lattice plane into the reflecting position. The intensity of the diffracted beam at this point is then determined by how many atoms, if any, lie on or near a particular lattice plane. If, co-incidentally, a planar fragment of a molecule lies in a specific lattice plane, a very intense reflection will be observed when this plane is brought into the reflecting position. If no atom lies on a particular lattice plane, no intensity will be observed.

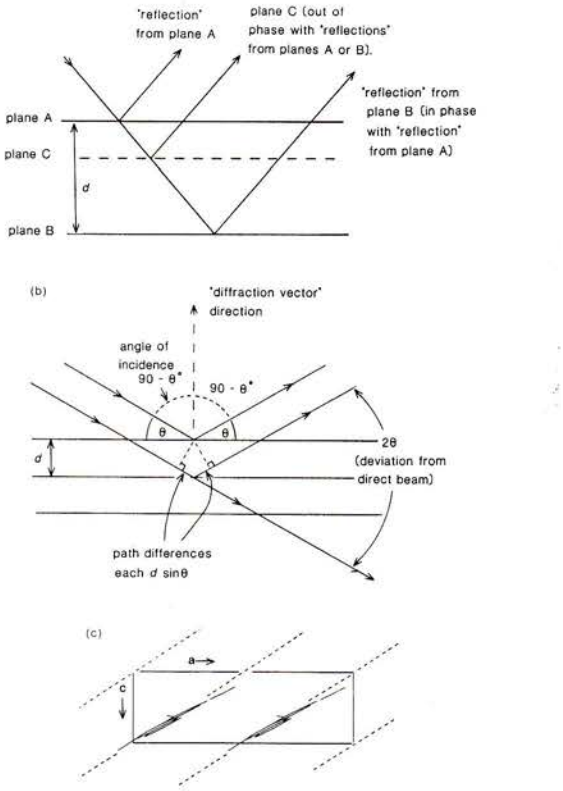


FIGURE 3.9 Diagram of "Reflection" of X Rays by Imaginary Planes Through Points in the Crystal Lattice.

(a) Constructive and destructive interference as waves are "reflected" from imaginary planes, spacing d, in a crystal.

(b) This leads to the Bragg equation $n\lambda = 2d \sin \theta$. Since the path difference (causing phase differences) of waves scattered by two adjacent planes is $2d \sin \theta$, this must equal $n\lambda$ for reinforcement to occur to give a diffracted beam (as illustrated in Figure 3.2).

(c) Planes 2 0 1 in a crystal (see Figure 9.3b). The planes lie perpendicular to the plane of the paper. Note that the planes intersect the unit cell edges once in the **c** direction and twice in the **a** direction. A portion of the crystal structure, which diffracts to give an intense 2 0 1 reflection, is shown.

1.4 Summary

Now we know what we need to measure in order to determine a crystal structure and how the information is generated. Next we must discuss how to go about obtaining the data that we need, and how to interpret the information buried in the data in order to finally "see" the molecular structure that we seek.

It is worth reiterating that the arrangement of the internal contents of the repeating unit does not affect the spacings of the points in the diffraction pattern at all. The size of the unit cell affects the positions of the diffracted beams. The contents of the unit cell only affect the intensities of the diffracted beams.

Appendix – Comparison of Bragg and Laue equations
– The Reciprocal Lattice

Some comments on the Laue diffraction equation and the Bragg equation and their relationship. Taken from **G.H. Stout & L.H. Jensen: X-ray Structure Determination - A Practical Guide** 2nd Edition - Wiley Interscience, 1989, ISBN: 0471607118, chapter 2 and Appendix A.

2.2. X-RAY DIFFRACTION

The diffraction of X-rays by crystals was discovered by Max von Laue in 1912, and the sequence of events that led to the discovery is one of the most fascinating chapters in the history of science.[9] Although X-rays had been discovered in 1895 by Roentgen, their nature was not known. During the years following their discovery, a number of determined efforts were made to prove them particles or waves. It was not, in fact, until diffraction by crystals was observed that their wave character was proved.

Following the experimental observation of X-ray diffraction early in 1912, von Laue showed that the phenomenon could be described in terms of diffraction from a three-dimensional grating.[10] In the same year, however, while engaged in experimental studies, W. L. Bragg[11] noticed the similarity of diffraction to ordinary reflection and deduced a simple equation treating diffraction as "reflection" from planes in the lattice. In order to

[6]It is standard crystallographic practice to place minus signs *over* indices. The plane $(\bar{1}00)$ is one that cuts the $-x$ axis at $-a$ and lies parallel to the y and z axes.
[7]*International Tables*, Vol. I, pp. 15–21.
[8]Buerger, *X-Ray Crystallography*, pp. 10–28.
[9]See P. P. Ewald in *Fifty Years of X-Ray Diffraction*, P. P. Ewald, Ed., International Union of Crystallography, Utrecht, 1962, pp. 6–75.
[10]M. von Laue, *Sitz. math. phys. Klasse Bayer. Akad. Wiss.*, 303 (1912).
[11]W. L. Bragg, *Proc. Camb. Phil. Soc.*, **17**, 43 (1913).

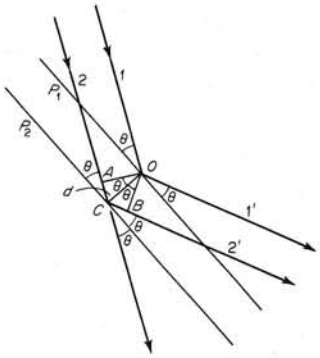


Figure 2.8. Construction showing conditions for diffraction.

derive the equation, we consider an X-ray beam incident on a pair of parallel planes P_1 and P_2 with interplanar spacing d (Fig. 2.8). The parallel incident rays 1 and 2 make an angle θ with these planes. Electrons assumed at O and C will be forced to vibrate by the oscillating field of the incident beam and, as vibrating charges, will radiate in all directions. For that particular direction[12] where the parallel secondary rays 1′ and 2′ emerge at angle θ as if reflected from the planes, a diffracted beam of maximum intensity will result if the waves represented by these rays are in phase. Dropping perpendiculars from O to A and B, respectively, it becomes evident that $\angle AOC = \angle BOC = \theta$. Hence $AC = BC$, and waves in ray 2′ will be in phase, that is, crest to crest, with those in 1′ if $AC + CB\ (= 2AC)$ is an integral number of wavelengths λ. This is expressed by the equality

$$2AC = n\lambda \tag{2.1}$$

where n is an integer. By definition, $AC/d \equiv \sin\theta$, and by substitution in Eq. (2.1),

$$2d \sin\theta = n\lambda \tag{2.2}$$

This is *Bragg's law*.

The process of reflection is described above in terms of incident and reflected rays each making an angle θ with a fixed crystal plane. It can also be viewed as involving a fixed incident beam, in which case reflection occurs from planes set at the angle θ with respect to the beam and generates a reflected ray deviating through 2θ. This description resembles

[12]It can be shown (see Appendix A) that if one considers the simultaneous reflection of a large number of such rays, interference prevents the appearance of radiation in any other direction.

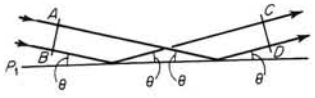


Figure 2.9. Reflection from two points in a plane.

more closely the actual experimental arrangements and is the more commonly used.

Though Fig. 2.8, on which the derivation is based, represents a special case, the result is, in fact, general. What holds for points O and C can be shown to hold for any pair of points in planes 1 and 2. This can be seen by recalling the elementary treatment of reflection. Figure 2.9 shows two parallel incident and reflected rays, where the angles θ between the rays and the plane are all equal. The path length by way of these rays (or any parallel rays) from the incident wave front AB to the emergent wave front CD is always the same provided the incident rays, the normals to the plane P at the points of incidence, and the reflected rays all lie in a plane. Thus the emergent rays shown, or any others similarly constructed, are in phase. It can now be seen by reference to Fig. 2.8 that any ray parallel to 1′ but from another point in plane P_1 will differ in phase by just $n\lambda$ not only from ray 2′ emergent from point C but also from any other parallel ray from any other point in plane P_2.

In the derivation of Bragg's law, electron density was assumed to be in the planes of Fig. 2.8. In actual structures, however, the electron density is distributed throughout the unit cell and does not lie in special planes. Nevertheless, the derivation is valid, since it can be shown that waves scattered from electron density not lying in the plane P (Fig. 2.10) can be added to give a resultant as if reflected from the plane. It is the variation in these resultants that accounts for the differing intensities of reflection observed for various planes (see Chapter 8).

In the derivation, reflections from only two planes were considered. In such a case the diffraction maxima would be broad and the various diffracted rays would virtually merge. In crystals, however, many hundreds or thousands of planes make up each of the mosaic blocks (see Chapter 4) that constitute the macroscopic crystal. Under these conditions, the diffraction maxima will be sharp and will occur only at clearly defined values of θ. Indeed, for real crystals the breadth of a reflection as measured in terms of the range of θ over which it can be observed is usually a small fraction of a degree and due mostly to the slight misalignment of the mosaic blocks.

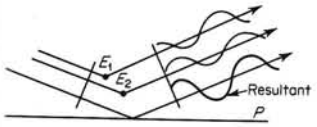


Figure 2.10. Diffraction from E_1 and E_2 as if reflected from plane P.

BRAGG'S LAW

Although Bragg's law can be justified by showing that its results are the same as those predicted by more rigorous analysis of diffraction from a three-dimensional grating,[1] in the absence of such an analysis students often wonder whether the analogy drawn with reflection is truly legitimate. In particular, doubts arise as to whether diffraction can occur only in the special directions corresponding to reflection from lattice planes.

The correctness of this assumption can easily be demonstrated,[2] however, for the following two-dimensional case of an orthogonal lattice (Fig. A.1), and the arguments can be generalized to three dimensions and a nonorthogonal system. Consider the three noncollinear points A, B, C, each of which scatters one of the parallel incident beams (1, 2, 3) in a direction (1′, 2′, 3′) such that constructive reinforcement occurs. By dropping perpendiculars and considering the requirement that for such reinforcement the difference in path for waves scattered from any two lattice points must be a whole number of wavelengths, it is clear that

$$a - b = h\lambda \tag{A.1}$$

$$c + d = k\lambda \tag{A.2}$$

If ψ and ψ' are the angles of incidence and reflection (not necessarily

[1]For an excellent and simple analysis, see W. L. Bragg, *The Crystalline State*, Vol. I, Macmillan, New York, 1934, pp. 13–20. H. Lipson and W. Cochran, *The Determination of Crystal Structures*, Cornell University Press, Ithaca, NY, 1966, pp. 4–7, give similar results using vectors.

[2]This argument follows closely that of L. R. B. Elton and D. F. Jackson, *Am. J. Phys.*, **34**, 1036 (1966).

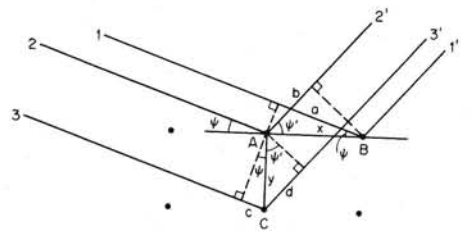


Figure A.1. Parallel scattering from three points in a lattice.

equal) formed with the lattice row AB, Eqs. (A.1) and (A.2) can be rewritten as

$$x \cos \psi - x \cos \psi' = h\lambda \tag{A.3}$$

$$y \sin \psi + y \sin \psi' = k\lambda \tag{A.4}$$

Now consider (Fig. A.2) a plane RS drawn to make equal angles θ with the incident and scattered beams and an angle α with the row AB. Then

$$\theta = \psi + \alpha = \psi' - \alpha \tag{A.5}$$

Rearranging for ψ and ψ' and substituting in (A.3) and (A.4) gives

$$x[\cos(\theta - \alpha) - \cos(\theta + \alpha)] = h\lambda \tag{A.6}$$

$$y[\sin(\theta - \alpha) + \sin(\theta + \alpha)] = k\lambda \tag{A.7}$$

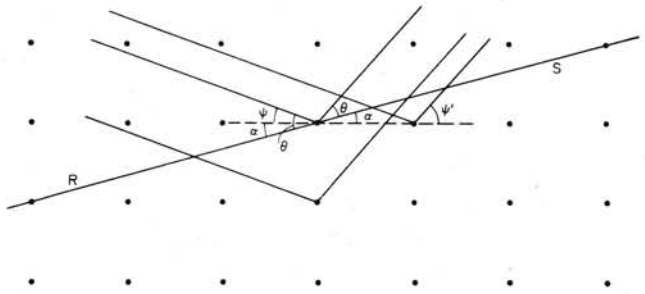


Figure A.2. Equivalent reflection from a lattice plane RS.

Expanding these leads to

$$x(\cos\theta\cos\alpha + \sin\theta\sin\alpha - \cos\theta\cos\alpha + \sin\theta\sin\alpha) = h\lambda \tag{A.8}$$

$$y(\sin\theta\cos\alpha - \cos\theta\sin\alpha + \sin\theta\cos\alpha + \cos\theta\sin\alpha) = k\lambda \tag{A.9}$$

or

$$2x \sin\theta \sin\alpha = h\lambda \tag{A.10}$$

$$2y \sin\theta \cos\alpha = k\lambda \tag{A.11}$$

Thus by division

$$\frac{\sin\alpha}{\cos\alpha} = \tan\alpha = \frac{hy}{kx} \tag{A.12}$$

The interpretation of Eq. (A.12) is that the plane RS, after leaving A, passes repeatedly through other lattice points successively shifted by h units along y and k units along x. This is equivalent to the definition of a lattice plane (h, k), so the conditions that permit constructive scattering in arbitrary directions are seen to correspond to simple reflection from a suitably oriented lattice plane. Thus the assumption inherent in the usual derivation of the Bragg law is justified.

THE RECIPROCAL LATTICE

The relation between the crystal lattice (real space) and the reciprocal lattice (reciprocal space) may be expressed most simply in terms of vectors. If we denote the fundamental translation vectors of the crystal lattice by **a**, **b**, and **c**, and the volume of the unit cell by V_c, and then use the same symbols, starred, for the corresponding quantities of the reciprocal lattice, the relation between the two lattices is:

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V_c}, \qquad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{V_c}, \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V_c} \tag{A2.1}$$

with $V_c = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c} = 1/V_c^*$.

The vectors of the crystal lattice and the reciprocal lattice are thus oriented as follows: any fundamental translation of one lattice is perpendicular to the other two fundamental translations of the second lattice. Thus $\mathbf{a}^*$ is perpendicular to both **b** and **c**, **b** is perpendicular to both $\mathbf{a}^*$ and $\mathbf{c}^*$, and so on.

From a consideration of Bragg's law in the form

$$\sin\theta = \frac{n\lambda}{2}\left(\frac{1}{d}\right) \tag{2.3}$$

it is seen that $\sin\theta$ is inversely proportional to d, the interplanar spacing in the crystal lattice. Since $\sin\theta$ is a measure of the deviation of the diffracted beam from the direct beam, it is evident that structures with large d will exhibit compressed diffraction patterns, and conversely for small d. Interpretation of X-ray diffraction patterns would be facilitated if the inverse relation between $\sin\theta$ and d could be replaced by a direct one. What amounts to this can be achieved by constructing a reciprocal lattice based on $1/d$, a quantity that varies directly as $\sin\theta$

TABLE 2.1 Orthorhombic Direct/Reciprocal Relationships

$a^* = 1/a$	$a = 1/a^*$	$\alpha = \beta = \gamma = \alpha^* = \beta^* = \gamma^* = 90°$
$b^* = 1/b$	$b = 1/b^*$	$V^* = 1/V = a^*b^*c^*$
$c^* = 1/c$	$c = 1/c^*$	$V = 1/V^* = abc$

The relationships between the direct and reciprocal lattices in three dimensions depend on the angles between the axes in the direct lattice. Consider the cases shown in Figs 2.14, 2.16, and 2.19. In Fig. 2.14 the three direct axes are mutually perpendicular but the axial lengths are not the same (an orthorhombic cell, see Chapter 3). The planes (100), (010), and (001) are perpendicular to the a, b, and c axes, respectively, so their normals are along these axes. Thus the r.l. point 100 can be considered to be on the a axis at a distance $1/a$ from the origin. The line connecting this point to the origin is one edge of the unit cell in reciprocal space and is thus a^*. In the same way the reciprocal axes b^* and c^* can be seen to coincide with the corresponding direct axes b and c, and all three reciprocal axes are mutually perpendicular. The result is a reciprocal unit cell with the relationships summarized in Table 2.1 and pictured in Fig. 2.15.

Matters become somewhat more complex when the direct axes are not orthogonal. Figure 2.16 shows the case of a monoclinic cell in which two axes (by convention a and c) meet in an obtuse angle while the third (b) is perpendicular to both. The normal to (100) still lies in the ac plane and is still perpendicular to b but no longer coincides with a. Similarly, the normal to (001) also lies in ac but does not coincide with c. A plane view of these relationships as seen down the b axis is shown in Fig. 2.17. The r.l. point 100 will lie as usual on the normal to (100) at a distance $1/d_{100}$ from the origin. Note, however, that d_{100} is the interplanar separation measured

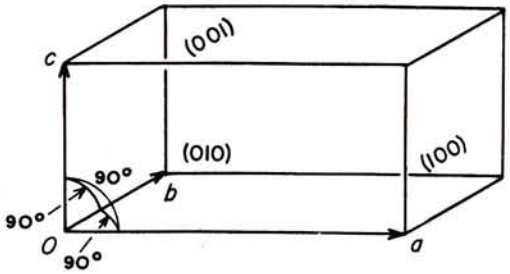


Figure 2.14. Orthorhombic direct cell.

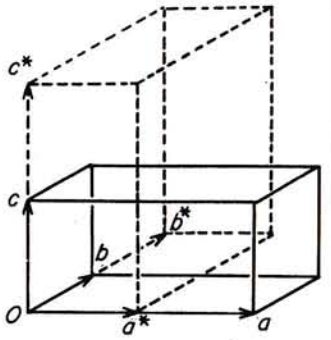


Figure 2.15. Orthorhombic direct and reciprocal cells.

along the (100) normal and is not, in this case, equal to a. If the ac angle is β,

$$d_{100} = a \sin(180° - \beta) \tag{2.11}$$

or

$$d_{100} = a \sin \beta \tag{2.12}$$

Thus the distance to the r.l. point 100, that is, a^*, is given by

$$a^* = 1/(a \sin \beta) \tag{2.13}$$

Similarly,

$$c^* = 1/(c \sin \beta) \tag{2.14}$$

On the other hand, since b is perpendicular to the ac plane (010), b^* still lies along it and

$$b^* = 1/b \tag{2.15}$$

The angular relationships between the two cells can be deduced from Figs. 2.16 and 2.17 and are given in Table 2.2, while Fig. 2.18 shows the shapes of a monoclinic cell and its reciprocal.

In the general, triclinic, case none of the axes are perpendicular, and as a result none of the plane normals that define the reciprocal axes coincide with their direct counterparts. Figure 2.19 shows this arrangement. The relationships between the direct and reciprocal axes are quite complex and will not be derived here. One form in which they can be expressed is given in Table 2.3, although others are possible and may be advantageous in particular cases.[14] A comparison of Tables 2.1–2.3 shows that the equalities in the first two can be easily obtained from those in the third by setting the proper angles to 90°. Special relationships for the other crystal classes (Chapter 3) can be similarly derived from the general expressions as needed.

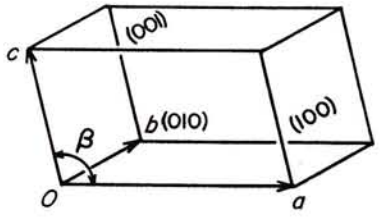


Figure 2.16. Monoclinic direct cell.

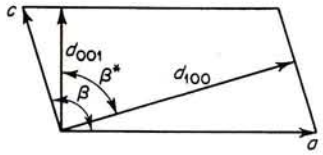


Figure 2.17. The ac face of the cell in Fig. 2.16.

It is important to note that the relationship between the direct and reciprocal axes is strictly reciprocal. That is, whatever is true in going from one to the other is equally true if the process is reversed. Put another way, any true statement about the two lattices remains true if all the unstarred symbols are replaced by starred ones and the starred by unstarred. An examination of Table 2.3 will reveal examples.

One vital conclusion that may be reached either from this principle or from an analysis similar to that at the beginning of this section relates the planes of r.l. points to the direct lattice axes. By construction, an r.l. axis (e.g., a^*) must be perpendicular to one face of the unit cell [e.g., (100), the bc plane]. By changing stars, it can be seen that similarly the b^*c^* plane of the reciprocal lattice must be perpendicular to the a direct axis. This plane contains the r.l. points $0kl$ and is parallel to those containing $1kl$, $2kl$, and so on. This result is general, and thus any direct axis has a family of r.l. planes perpendicular to it, each plane containing points of constant value for the index associated with that axis (Fig. 2.20).

TABLE 2.2 Monoclinic Direct/Reciprocal Relationships

$a^* = 1/(a \sin \beta)$	$a = 1/(a^* \sin \beta^*)$	$\alpha = \gamma = \alpha^* = \gamma^* = 90°$
$b^* = 1/b$	$b = 1/b^*$	$\beta^* = 180° - \beta$
$c^* = 1/(c \sin \beta)$	$c = 1/(c^* \sin b^*)$	$V^* = 1/V = a^*b^*c^* \sin \beta^*$
	$V = 1/V^* = abc \sin \beta$	

TABLE 2.3 Triclinic Direct and Reciprocal Relationships

$$a^* = \frac{bc \sin \alpha}{V} \qquad a = \frac{b^* c^* \sin \alpha^*}{V^*}$$

$$b^* = \frac{ac \sin \beta}{V} \qquad b = \frac{a^* c^* \sin \beta^*}{V^*}$$

$$c^* = \frac{ab \sin \gamma}{V} \qquad c = \frac{a^* b^* \sin \gamma^*}{V^*}$$

$$V = \frac{1}{V^*} = abc\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

$$V^* = \frac{1}{V} = a^* b^* c^* \sqrt{1 - \cos^2 \alpha^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \cos \beta^* \cos \gamma^*}$$

$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma} \qquad \cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*}$$

$$\cos \beta^* = \frac{\cos \alpha \cos \gamma - \cos \beta}{\sin \alpha \sin \gamma} \qquad \cos \beta = \frac{\cos \alpha^* \cos \gamma^* - \cos \beta^*}{\sin \alpha^* \sin \gamma^*}$$

$$\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta} \qquad \cos \gamma = \frac{\cos \alpha^* \cos \beta^* - \cos \gamma^*}{\sin \alpha^* \sin \beta^*}$$

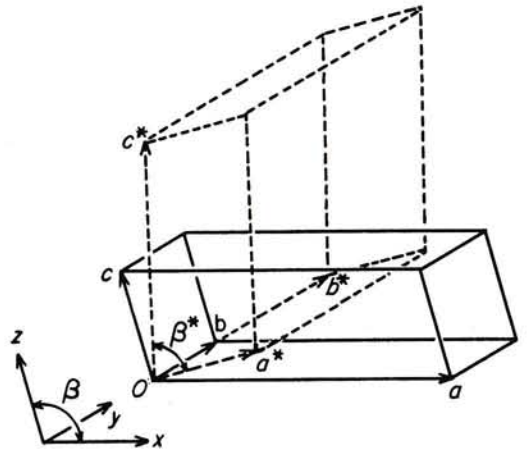


Figure 2.18. Monoclinic direct and reciprocal cells.

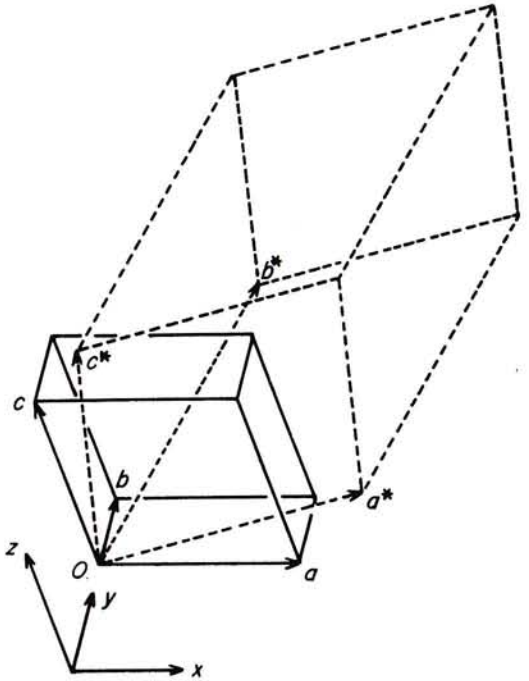


Figure 2.19. Triclinic direct and reciprocal cells.