

Crystallography for Chemists

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By

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FOREWORD

Crystallographic methods have been very important in the development of modern chemistry. Unlike NMR, crystallographic education in the chemistry curriculum remains at best minimal and frequently non-existent. There are historical and practical reasons for this failure. However, this has led to the situation where most chemists cannot really interpret crystallographic data. This extends from graduate students to journal editors. The goal of this book is to provide assistance and insight into crystallography in a language that chemists can understand. It should be suitable for advanced undergraduate and beginning graduate students.

There have been several motivations for producing this book. The first was my experience in organizing a session on crystallographic education at the American Chemical Society's Biennial Conference on Chemical Education in 2006. Both crystallographers and chemists warned me that there is no interest in this topic and to expect few to attend. It surprised me when I entered the room for the session to see it fairly full. I gave my talk on the importance of crystallographic education and it was received enthusiastically. The first question I was asked is what book I would recommend for such a course. I listed the standard texts but was told that they were too advanced. Faculty from small colleges pointed out that they had no experience with crystallography and found it difficult to understand the topic with enough depth to teach it. They needed a book that would be the main teaching tool and not just a reference.

A second motivation was the graduate course on applied crystallography I taught for many years at Purdue. This provided a platform where I could try different approaches to instruction in crystallography. I quickly learned that most of the students enrolled were synthetic chemists who only wanted to use crystallography as an analytical method. They did not have much interest in the theory of crystallography or topics they could not apply to their research. I always taught this course in a computer lab so the students could run programs instead of studying their input and output. One unintended consequence of providing students with computers was that I received an instant evaluation on my teaching abilities and their interest in the topics covered. If I walked around the lecture room and found most of

the students were checking their email, the news, or sports, I knew this lecture was not of interest. Much of what I learned from this experience is in this book.

Before stating what this book is, let me stress what it is not. This is not, nor was it meant to be a comprehensive text on crystallography. There are already many excellent books at various levels and there is no reason to reinvent the wheel. Nor is this book a reference book used to answer all questions concerning crystallography. Some will complain it is not suitable for training professional crystallographers. However, that is not the intent.

There have been several guiding philosophies in organizing this book. First, was to make it as non-mathematical as possible. Equations are provided when they can provide insight. Statements are presented as facts rather than proved. This is in keeping with what I have observed in teaching. The concepts of typical programs are explained. There is no discussion of the algorithms, formulas, and approaches. Many programs will be considered black boxes where the input and output is more important than what is happening in the program.

The discussion of crystallographic programs presents a problem in writing a book such as this. It is a conscious decision to not spend much time on software. There are several justifications for this decision. First, there are many programs available for running diffractometers, processing data, and solving and refining structures. It is not the place of this book to endorse any of them. Besides, today most software has excellent manuals typically on the internet and in the case of SHELXL there is even a text on its use. The one exception to the above involves SHELXL. This program is the most widely used crystallographic program. Therefore, the appropriate commands are placed in square brackets during discussions of refinement. However, only the name of the command is given and its application and usage will require research elsewhere. With advances in computers and artificial intelligence, software is changing rapidly. No book can keep up with the changes. Undoubtedly, new software will become available which will pass into common usage.

Many topics are introduced and some readers will desire more detail. It is hoped that the references provided will allow for further exploration. Also, as much as possible, terminology and concepts are not used until introduced. This creates some unusual wording in the early chapters.

Chapters 1 to 4 are an introduction that provides information on understanding crystallographic data and results. They should be useful to all chemists even

if they do not perform crystallographic experiments. Chapter 5 introduces the concepts of real and reciprocal space. One theme of this book is the nature of these two spaces which are related by Fourier transforms. This is essential to crystallography. Chapters 6-8 deal with symmetry. Basic symmetry operations are quickly introduced and previous knowledge of the concepts of symmetry will be useful. Chapters 9 to 12 deal with the process and equipment used to go from a crystal to a crystal structure. They will be most useful to those who will actually collect crystallographic data and refine structures. Chapter 13 deals with the determination of absolute structure and absolute configuration and is important to those working with enantiomorphic compounds. Chapter 14 concerns crystals that do not have perfectly repeating motifs. Lastly, Chapter 15 is about diffraction methods beyond X-rays and single crystals.

There are several who have provided graphics that have been used in this book. Larry Falvello and Esteban Urriolabeitia of the University of Zaragoza provided the NMR spectra used. I am grateful to Margret Kastner for the use of drawings found on her Crystallographic Courseware web page. It is a wonderful resource for those learning crystallography. I also thank Kevin Cowtain of York University for allowing me to reproduce figures from his web page <http://www.ysbl.york.ac.uk/~cowtan/fourier/fourier.html>. Lastly I thank the International Union of Crystallography for permission to print pages from the **International Tables of Crystallography, Volume A**.

I never had any formal education in crystallography (and some say it shows). There are a great many people who have taught me much over the years. First, is my friend Larry Falvello who has always answered my ignorant questions with wonderful and frequently humorous explanations. He has helped me to gain insight into the crystallographic experiment. I also thank David Watkin for his help over the years. David has written many articles which clearly explain the workings of crystallography beyond the scope of this book. I also thank Ton Spek for many interesting conversations over the years from which I have gleaned much. I am also most grateful to Mary Hoekstra who proofread this manuscript. Lastly, I thank my wife and soul mate Karen, for her encouragement, patience, and help in assembling this text. I do not think I would have ever taken on this project without her being by my side.

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CHAPTER 1

SINGLE CRYSTAL X-RAY CRYSTALLOGRAPHY AS A METHOD OF CHEMICAL ANALYSIS

During the last fifty years, X-ray crystallography has been an important chemical analytical tool capable of routinely solving problems that would be very difficult by other methods. In this chapter, an example of such an analysis will be discussed as well as the strengths and weaknesses of the technique.

For all but the last chapter, it will be assumed that a high quality crystal was the sample and X-rays were the radiation for the diffraction experiments.

1.1 A Case Study

In 1958 Kotel'nikova and Tronev¹ reported the preparation of a compound of the formula $(C_5H_5NH)^+HReCl_4$. The addition of the hydrogen ion to the chemical formula was required because the oxidation state of the rhenium was determined to be +2. Later a single crystal structure of this compound was published and the result is shown in Figure 1.1.² The major portion of the publication deals with the difficulties in obtaining structural results in 1963. However, there are comments on several chemical aspects that are worthy of discussion. The most noteworthy comments are:

“It should be noted that the Re-Re distance = 2.22 Å is less than the Re-Re distance in the metal.”

“The decrease in the Re-Re distance in this structure, compared with the Re-Re distance in the metal, indicates that the valence electrons of rhenium also take part in the formation of the Re-Re bond. This may explain the diamagnetism of this compound.”

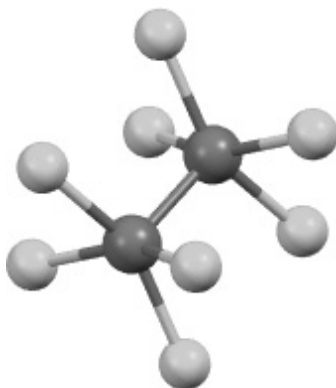


Figure 1.1 $\text{Re}_2\text{Cl}_8^{2-}$

Possible positions for the H^+ ion are provided. However, since there is no solvent or other base that could be protonated, the existence of this ion in a crystal would be unusual. Even with a crystal structure and other supporting chemical analyses, the bonding and even the chemical formula of the $\text{Re}_2\text{Cl}_8^{2-}$ ion failed to be established.

The reported results interested Professor F. Albert Cotton who quickly published three papers dealing with this ion. The first dealt with the chemical formula.³ Electrochemical analysis revealed that the rhenium was in the +3 oxidation state and no hydrogen cation was required to balance the charge. This made the formula from the crystal structure consistent with the chemistry. In the second paper, the structure of the potassium salt of $\text{Re}_2\text{Cl}_8^{2-}$ was determined.⁴ This was both a check on the previously reported structure and provided an improved structure. This structure confirmed the previously reported details. The Re-Re distance was 2.241 Å while the Cl-Cl distance across the Re-Re bond averaged to 3.32 Å which is nearly twice the chlorine van der Waals distance.

The third paper reported on the bonding in the octachlorodirehenate ion.⁵ Unusual features of this ion included the very short rhenium-rhenium distance and the eclipsed configuration of the chlorine atoms when looking down the Re-Re bond. The chlorine atoms are essentially at the minimal non-bonding distance from each other and this results in a Re-Re-Cl angle of 103.7°. Since there are 8 electrons available from the two rhenium atoms that are not involved in the Re-Cl bonding, it was suggested that the bond order between the rhenium atoms was 4. Such a bond would be composed of a σ bond, two π bonds, and a δ bond. For

maximum overlap of the δ bond the chlorine atoms would need to be in an eclipsed configuration as observed. The important point is that the stability provided by the δ bond was greater than the repulsive forces of the chlorine atoms. Hence, the shape of the molecule and the geometrical parameters determined by the structure were used to elucidate the metal-metal bonding.

This is hardly a unique example of the use of crystallography to solve chemical mysteries. There may have been other methods that would have eventually led to the geometry, formula, and bonding in this novel dimetallic ion. However, the information would be more indirect, require much more interpretation, and take more time. The results would have had greater uncertainty and not contained as much information. Crystallography provided a definitive structure and accurate geometrical parameters in a short time. It is for these reasons that crystallography has become an essential tool for chemists and changed the nature of chemical analysis.

1.2 Crystallography and Chemical Analysis

1.2.1 Qualitative and Quantitative Analysis

Qualitative and quantitative analyses are the determinations of what elements are present in a compound and the relative ratios of each element. It appears that crystallography would be perfect for providing this information, but that is not totally correct. From Figure 1.1 it appears that the formula can easily be determined from a crystal structure, since all the atoms are assigned an element. However, these assignments are made by the researcher determining the crystal structure; they are not uniquely provided by the crystallography.

This ambiguity results from the nature of the X-ray crystallographic experiment. The graphical results such as Figure 1.1 falsely imply that crystallography is like a giant microscope able to observe the atoms. Even if that were true, it is not clear how the atomic number could be directly observed. However, the actual result of the X-ray crystallographic experiment is the calculated value of the electron density at any location within the crystal. Throughout most of the crystal the electron density is at or near zero. It is only in some small locations where the electron density is significant. It is assumed this is where the atoms are located.

There is a problem however. There is no simple direct relationship between the electron density and the atomic number of an element in a crystal. There are several reasons for this, most of which have to do with the movement of the atoms in a crystal. All atoms are vibrating even at 0 K. The greater the movement of an atom, the more the electron density will be decreased because of the increasing volume caused by the atomic displacement. There are also problems such as multiple atoms at a site or disorder in the structure which will affect the electron density.

A common example of unusually low electron density is observed for the trifluoromethyl group. This group in some crystals rotates about the C-C bond. If the displacements are small, this will simply lower the electron density and the fluorine atoms will appear to have less electron density than even the carbon atom neighboring them. It is also possible that there will be two sets of positions where the fluorine atoms are located. The electron density observed in the structural analysis will display the density averaged over the entire crystal. In this case, six half fluorine atoms will be observed around the central carbon and the observed electron density will be half of what would be expected. It is also possible that there is nearly free rotation around the C-C bond and the fluorine atoms will be smeared out into a ring of density. It is possible (though not necessarily likely) that the electron density will be so low as to not be observed above the noise. In this case, it will be difficult to assign locations for the fluorine atoms.

How are the element types assigned to the calculated electron density? In most cases there is external information about the sample synthesis, and other analyses are available. This information can be used to guide both a qualitative and quantitative crystallographic analyses. There is always the possibility the crystal contains unexpected fragments such as molecules of solvation. These can usually be assigned, given more information. Therefore, a correct crystal structure contains the chemical formula of the contents of the crystal and not just the fragment that is of interest. It must be emphasized that elemental assignments add a bias to the experiment, not only can that produce an incorrect result but sometimes spectacularly incorrect chemistry as will be discussed later.

For unknown samples the problem is more difficult. The organic part is usually the easiest to assign. First, most elements in an organic fragment have a consistent number of bonds about them and a well-established geometry. The bond order can be determined by the bond length. Besides,

the difference in an incorrect electron density assignment is significant. For example, if a carbon atom is assigned as a nitrogen atom the electron count is too great by 17% while as an oxygen the overage is 33%. This difference makes a significance in the quality of the structure and can readily be observed in a drawing of the molecule that includes atomic displacement parameters (see Chapter 4).

For inorganic compounds or fragments, elemental assignment is much more difficult. First, heavier elements have variable coordination numbers. Their bond distances are not as consistent as main group elements. If the rhenium atom in the structure discussed in Section 1 were replaced by next heaviest element osmium, the electron difference would only be 1.3%. Lastly, substitution of heavier elements does not significantly affect the quality of the structure. Structures containing second or third row transition metals can be “titrated” by trying different elements at the metal location. Invariably, the best fit does not contain the correct element. In the end, if there is any question about the composition of a crystal, further analytical means must be employed to determine what elements are present. For the rest of this text, the assumption is that the elements have been correctly identified and the atoms in the structure have been correctly assigned, except as noted.

1.2.2 Structural Isomerization

The greatest strength of crystallography is to provide unequivocal evidence of the arrangement of the atoms in a molecule. Structural isomers are molecules with the same chemical formula but different connectivities, while stereoisomers have the same connectivity but differ in their three dimensional orientations. Obviously, the drawing of a molecule from a crystal structure analysis provides proof of the isomer.

Crystallography is almost too good at determining isomers. There are standards that must be met if a structure is to be considered a quality structure. This includes standards for quality and quantity of data collected. Also, the calculations required for a finished structure and the quality of the final results are equally specified. The problem is that frequently the isomer can be determined satisfactorily from even the most rudimentary data and calculations. This provides frustration because the structural results may not be publishable, yet the nature of the isomer has been determined. There is a consensus that the quality of the entire structure must be considered and not just some area of interest. Since a

crystal structure is considered indisputable evidence of the arrangement of atoms in the crystal, low quality structures cannot provide this certainty, even if they appear to provide the desired information. It is essential that the proper amount of high quality data be collected and that all calculations be completed before any conclusions can be drawn from a structure. This at times appears to be overkill, but it has proved essential to eliminating incorrect structures.

1.2.3 Geometric Parameters

A quality crystal structure provides accurate geometrical parameters for the contents of the crystal. These include bond distances, bond angles, torsional angles (the dihedral angle between two sets of planes formed by three atoms in which two planes contain two atoms in common), planarity of a group of atoms, and other special parameters which define the shape of unsaturated rings, sugars, *etc.* These parameters may be calculated for molecules or molecule like ions or non-bonded atoms. Likewise, parameters between fragments in a crystal can be determined. This includes intermolecular hydrogen-bonds and π - π interactions.

As shown in the example at the beginning of the chapter, knowledge of intramolecular distances can be used to determine the strength of a bond and its bond order. This is important for the elucidation of functional groups in the molecule. Unusual bonds such as metal-metal bond orders can be assigned. The effect of interactions such as hydrogen bonds on carbon-oxygen and carbon-nitrogen bonds can be studied. While similar results can be obtained from vibrational spectroscopy or NMR, the results provided by a crystal structure are much easier to interpret.

1.2.4 Optical Isomerization

One important use of crystallography is to determine the absolute configuration of optically active molecules. This is important in many cases, such a pharmaceutical compounds. Crystallography is essentially the only technique that can provide this information.

There are certain requirements for this determination to be made. First, the crystal must be enantiomorphically pure. Frequently, crystals grown from non-pure materials will be racemic and therefore no determination can be made. Second, a high quality data set is required for this experiment to succeed. Lastly, the choice of X-ray wavelengths must be considered so

that the calculations will provide a definitive result. All of this will be discussed in Chapter 13.

1.2.5 Other Uses

In no way does the above discussion reflect the total extent of what can be done using crystallography. There are experiments for studying the surface of a crystal. This information can be important to the creation of electronic devices. Changes in the crystal, such as reactions, can be studied using time-resolved crystallography. Experiments have been performed where the geometry of an electronic excited state has been determined. These experiments however are usually performed at national laboratories where high intensity synchrotron X-ray sources are available that allow data collection to be completed in seconds. In the end, crystallography is an extremely versatile technique able to provide analyses for a wide variety of chemical and solid state problems.

The above is based on crystal structures from single crystals. However, one of the most important analytical crystallographic tools is powder crystallography. If crystalline materials are ground up into a fine powder, then the diffraction pattern of this powder can be obtained. The pattern can be matched to previously determined patterns to ensure the material is the correct crystalline phase. Unexpected peaks can be used to establish the presence of impurities. If the powder pattern of the impurity is known, then its concentration can be determined. This type of analysis is very important in pharmaceutical manufacturing where, in general, not only the identity and purity of a compound is required, but also the precise crystalline form. Differences in the crystal structure can change the stability of the pharmaceutical, as well as its efficiency as a drug.

1.3 Limitations of crystallography

There are several important limitations to the crystallographic analysis that must be kept in mind. It appears obvious, but a crystallographic result only provides information about the crystal sample studied. Clearly, if a crystal of a minor product is used, it will not provide any data about the major product of a chemical reaction. Also, some compounds react during crystallization and the crystal may be completely different from the original product.

The second limitation is that the structure only provides information about the packing and geometry of the components in the solid state. The formation of a crystal introduces strong intermolecular forces that can distort a molecule or in some cases even alter the isomer. It can be expected that geometrical information from crystallography may not agree with data from studies done in the gas phase or in solution. In many cases the agreement is excellent.

CHAPTER 2

SCATTERING AND DIFFRACTION— WHAT IS GOING ON WHEN RADIATION INTERACTS WITH A CRYSTAL

In order to understand what is happening in the diffraction experiment, it is important to build a model for the interaction of the radiation and the sample being studied. In this chapter the concept of scattering of radiation will be introduced. The use of constructive interference and diffraction to produce the observed data will be explained. The importance of translation will be emphasized. Finally, the concept of the primitive unit cell will be introduced. The chapter will be presented for X-ray radiation, though much of what is presented can be extended to other forms of radiation.

2.1 Scattering of Radiation

The theory of scattering of radiation by a free electron was first reported by J. J. Thompson in 1906.⁶ This theory was based on classical mechanics and assumed the scattering was elastic *i.e.* the wavelength of the scattered wave was the same as the exciting radiation. Also, relativistic effects were not included. The discussion here will be further simplified in that the polarization of the scattered wave will be ignored. This simplified approach gives a good starting place as to the interaction of the X-ray radiation with the electron and provides a model that can be built upon to understand crystallography.

When the free electron encounters the electromagnetic radiation, it moves opposite to the amplitude of the applied field because of the repulsive nature of the interaction. Since the electron, a charged particle, is now moving, it should emit radiation. The emitted radiation will have the same wavelength as the exciting source but be 180° out of phase. Since this is a new wave it will be emitted from the free electron in all directions. This new radiation is called scattered radiation and it occurs at all exciting wavelengths.

It is also interesting to look at the intensity of the scattered radiation. The intensity will be very much weaker than that of the exciting radiation. A few centimeters from the free electron, the ratio of the intensity of the total scattered radiation to that of the incident radiation is on the order of 10^{-28} .⁷ This value is only slightly less than Avogadro's number. The electrons in a chemical sample will produce considerable scattered intensity. One last point is that if the primary beam is completely unpolarized, then the intensity will fall off by the factor $(1+\cos^2\theta)/2$ where θ is the angle between the incoming beam and the scattered beam.

Obviously, scattering by an atom is more complex. First, the electrons in an atom can hardly be considered free. There are attractive forces with the nucleus and repulsive interactions between them. Classical physics is not a valid description for these electrons. However, the model developed for the free electron can be applied to the atom. The biggest difference is in the calculation of the intensity of the scattering which is much more complicated. However, atoms with more total electrons will scatter more strongly.

2.2 Diffraction in One-dimension

At first, the fact that atoms will weakly scatter X-ray radiation appears to be of little use in determining a crystal structure. If an X-ray beam is directed at any matter regardless of its state, there will be randomly scattered radiation from the sample. The greater the atomic number of the atoms in the sample, the more intense this scattering will be. Waves can interact by constructive or destructive interference as shown in Figure 2.1. Most of the scattering away from the incident beam will be eliminated by destructive interference,

11 Scattering and Diffraction—what is going on when radiation interacts with a crystal

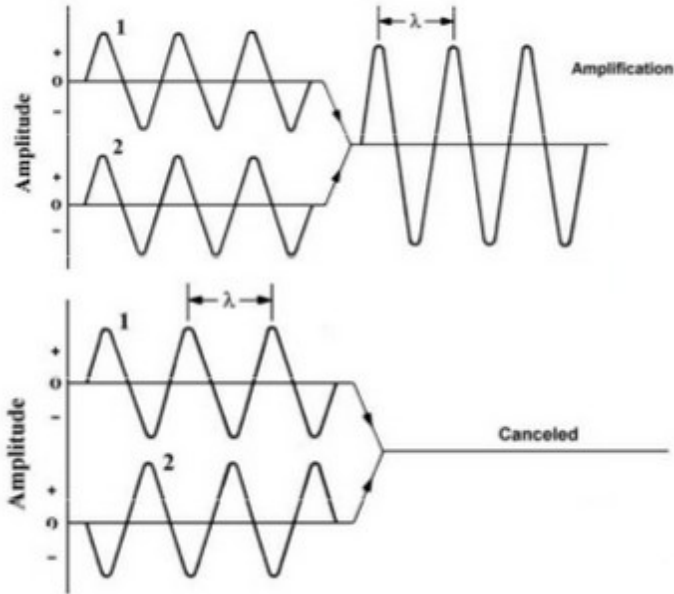


Figure 2.1 Interactions between waves

However, more complicated effects will occur if the atoms or molecules are lined up in a regular repeating pattern. The result of such an interaction is shown in Figure 2.2. The repeat distance between the arrangement (in this case the atoms) will be the vector \mathbf{a} . If the length of \mathbf{a} is on the order of the wavelength emitted, then interference effects will be observed. The repeat distance in a crystal is typically measured in Angstroms (\AA) which is 10^{-10} meters. While the Angstrom is not an SI unit, it is very convenient to use in crystallography. Typical bond distances are on the order of a few Angstroms and repeat distances in crystals typically range from 3 to 100 \AA . Since the wavelength of commonly used X-rays is from 0.5-2 \AA , they will produce interference interactions when multiple waves interact. Two waves can interact either constructively or destructively as shown in Figure 2.1. Constructive interference will occur whenever two waves are in-phase. The result will be a new wave.

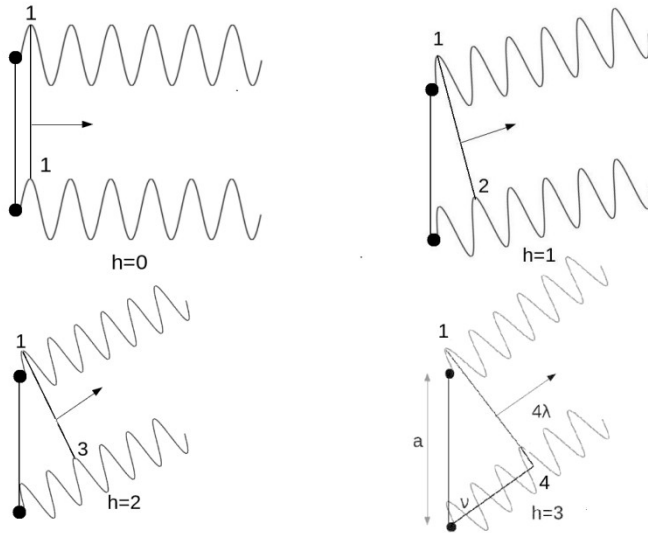


Figure 2.2 Constructive Interference

The case where the incident radiation is perpendicular to the line of the atoms is first studied. The scattered radiation will come out in all directions and will interfere with other waves scattered by other atoms. However, except for the case where the waves are in phase, they will interact destructively and no intensity will be observed. Obviously, scattered waves in the direction of the primary beam will be in phase. The intensity of such scattered X-rays will be very weak compared to the primary beam and cannot be observed. However, as Figure 2.2 illustrates, at certain angles ν the scattered beam from one atom will differ by exactly some integer multiple of wavelengths, and constructive interference will take place. The number of wavelengths difference will be assigned the symbol h which must be integral. If $h=0$ then the scattered beam will be along the primary beam. If $h=1$ then there will be a difference of one wavelength between the scattered radiation. Higher numbers work similarly.

From Figure 2.2 it can be observed that there must be a relationship between the wavelength of the X-ray radiation, the separation distance $|a|$ and the angle ν between a and the diffracted wave. It is obvious that a is the hypotenuse of a right triangle and h times the wavelength (λ) is the side adjacent to ν . Thus, $h \cdot \lambda / |a| = \cos(\nu)$. This provides a simple equation for

diffraction. If an X-ray sensitive film is placed perpendicular to the primary beam, then various lines representing the diffracted beams will be observed. Let θ be the angle between the primary beam and the diffracted beam. The distance between diffracted beams is given by $\sin(\theta)$ times the distance to the film.

However, even in one-dimension this result is too simple. It was assumed that the primary beam was perpendicular to \mathbf{a} , which requires the total phase shift to occur only in the diffracted beam. If the primary beam makes an angle μ with \mathbf{a} , then a phase shift as illustrated in Figure 2.2 can also take place for the primary beam. The phase shift for either the primary beam or the diffracted beam need not be an even number of wavelengths as long as the sum is. This creates the condition

$$|\mathbf{a}|\cos(\mu) + |\mathbf{a}|\cos(\nu) = h\lambda \quad (2.1)$$

This equation is called the Laue Equation and it provides the most liberal description of the conditions for diffraction in one dimension.

In order to place some restrictions on the Laue diffraction, it is useful to make the angles ν and μ equal and call this new angle Λ . In this case, the Laue Equation reduces to $2|\mathbf{a}|\cos(\Lambda) = h\lambda$. (2.2)

A second way to approach this is to add imaginary lines P perpendicular to \mathbf{a} (see Figure 2.3). Initially, the lines will be spaced at $|\mathbf{a}|$ from each other. The angle θ will be the angle between the incoming beam and P and the same for the outgoing beam. The angle Λ was defined previously as the angle between the diffracted radiation and the line defining the distance between the atoms. This means that $90 - \Lambda = \theta$. The cosine of 90 minus an angle is equal to sine of the angle. Therefore, changing to θ and relabeling $|\mathbf{a}|$ as d converts equation 2.2 into

$$2d\sin(\theta) = \lambda \quad (2.3)$$

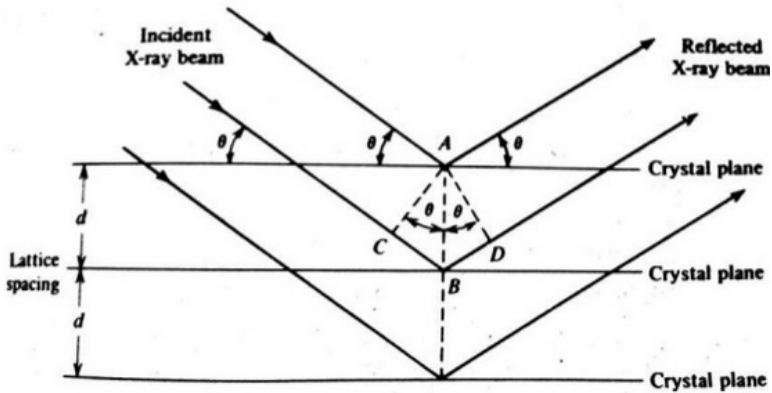


Figure 2.3 Bragg's Law

This is the well-known Bragg's Law if higher and much weaker orders of diffraction are ignored. For the beams to be in phase the length of CB plus BD must be a multiple of the wavelength. It should be pointed out that in Figure 2.3 it appears the primary beam is reflecting off the line P and Bragg's Law is just an example of the familiar equation for reflection that the angle of incidence is equal to the angle of reflection. However, this is not simply reflection but a complicated diffraction process. It also should be pointed out that crystallographers frequently call their data reflections even though that is only what appears to be happening.

The genius of William Lawrence Bragg and his father William Henry Bragg was that they derived an explanation for the different diffracted beams without using phase differences. Since the line P does not exist, it can be modified by changing the distance between the lines by dividing $|a|$ by integers and using this new distance in equation 2.3. The modified Bragg's Law becomes $2(|a|/h)\sin(\theta)=\lambda$ where $|a|/h$ is the distance between the lines P. This is a much easier equation to work with as it relates the angle θ to distances within the crystal. It should be pointed out that in the one-dimensional case P is a line and is perpendicular to the direction of stacking making the distance between lines P easy to figure out. Things become somewhat more difficult in three dimensions as P becomes a plane and the distances between planes are not as simple to determine. It must also be emphasized that the line P is an abstraction and has nothing to do with where the atoms are with respect to the line. The result of both the Laue and Bragg descriptions of diffraction is that the location of the diffracted

radiation is determined only by the repeat distance $|\mathbf{a}|$ and has nothing to do with what pattern is being repeated along the line.

There are some easy conclusions that can be drawn from Bragg's Law. First, as h gets bigger then $\sin(\theta)$ will increase and the angle between the incident beam and the observed diffracted beam will increase. Also, as the wavelength used increases the diffracted beams will become further apart. Lastly, as the magnitude of \mathbf{a} increases, the distance between diffraction intensities will decrease. This is the well-known reciprocal relationship.

2.3 The Primitive Unit Cell

The derivation of the diffraction of X-ray radiation requires that there be a regular repeating pattern. In the example just discussed, this is in one dimension but for a solid obviously this should be in three dimensions. It turns out crystals are composed of just such a repeating pattern. The properties of crystals such as the way they allow light to pass through them are because of this regular structure. In general, non-crystalline solids are not transparent unless they are very thin. Yet even large crystals are 'crystal clear.' Also, non-crystalline solids can be cut smoothly in any direction. Crystals, on the other hand, can only be cleaved along certain planes.

In considering the one-dimensional array of atoms, it is observed that the array is made up of a unique pattern that is translated along the \mathbf{a} vector. In the previously considered array the translation vector was called \mathbf{a} (see Figure 2.4a). The vector \mathbf{a} is the basis vector for a one-dimensional coordinate system. The familiar Cartesian coordinates have basis vectors whose magnitude is 1. However, here the magnitude is $|\mathbf{a}|$. This means that if we pick a particular place on the one-dimensional pattern, then adding or subtracting an integer results in a translation to an equivalent position. This is because the basis vector has length $|\mathbf{a}|$ and any integer translation with respect to this basis vector simply shifts to an equivalent point down the line. If x is a decimal fraction greater than zero and less than one, it refers to a point between the equivalent origins of the coordinate system and x is called a fractional coordinate. Its distance to the origin of the coordinate system is given by $x |\mathbf{a}|$. The repeating pattern can be considered a one-dimensional unit cell.

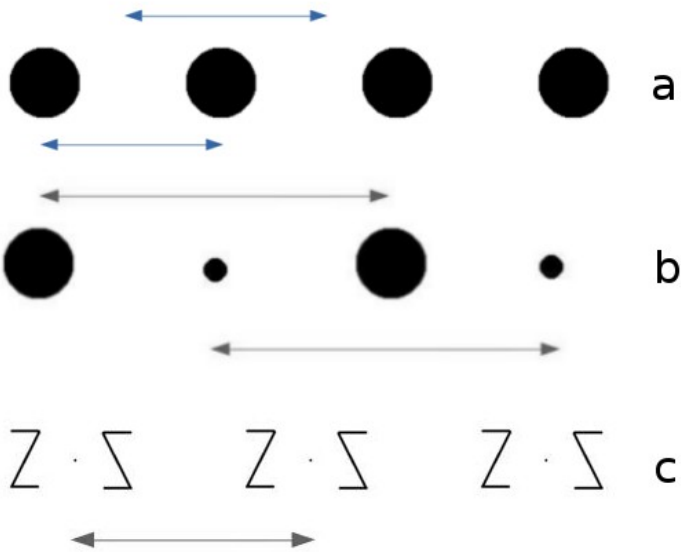


Figure 2.4 One-Dimensional Unit cells

The one-dimensional unit cell will be more complicated and $|a|$ will increase as the number of atoms increases. There is also the question as to where to place the origin. If the array is made up of atoms or ions, it appears easiest to place the origin for the pattern on one of the atoms. However, for linear molecules it is much less clear. Should the origin be placed on an atom, midway between the bonded atoms, or at some other place? Actually, for the cases being discussed, it makes no difference. The only requirement is that the one-dimensional array is formed by translating the basic pattern by $|a|$. Note when two different atoms are placed with the same separation as in Figure 2.4b, the length of the repeat distance doubles as the old a now translates an atom from one type to another.

Figure 2.4c represents a one-dimensional arrangement of Z shaped objects. In creating crystals, nature tries to minimize the cell volume to pack the components efficiently. So, in 2.4c turning one Z upside down with respect to the other may make sense in providing maximum packing efficiency. There is only one type of object in this linear arrangement. The other is related by a symmetry operation between the two objects. This is represented by the dot between them. The two form a pair which is the basic building block of the pattern. Therefore, it makes sense to use the dot as the origin for the axis system.

The discussion of 2.4c illustrates some important points about unit cells. First, an atom does not need to occupy the origin of the unit cell. In the vast majority of structures there is no atom at the origin. Second, a primitive unit cell can contain more than one formula unit in the unit cell. In this example there are two. Lastly, in most cases the origin of the unit cell is determined by the symmetry operations, not the contents.

The one-dimensional idea can be extended to two and even three dimensions. Possible repeating patterns in two dimensions are shown in Figure 2.5. Note that in this figure two different repeating patterns have been selected as unit cells. A second vector called **b** becomes the basis vector in the second direction. It should be noted that in both of the repeating patterns displayed, the vectors **a** and **b** are not orthogonal *i.e.* they do not make a 90° angle with each other. This angle will be called γ . It can be shown that the area of the parallelogram is given by $|\mathbf{a}| \cdot |\mathbf{b}| \cdot \sin(\gamma)$. While the two potential cells have different shapes, the area of the parallelograms is identical. In fact, any cell that has this minimal volume is acceptable as a valid primitive unit cell.

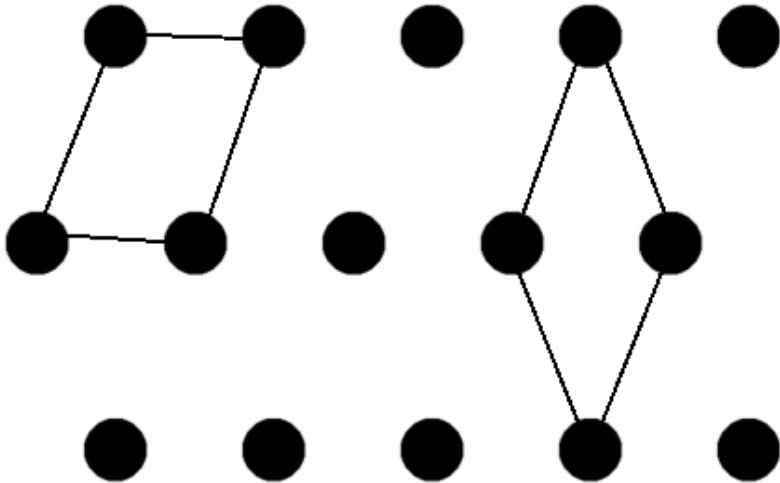


Figure 2.5 Choices for a unit cell

In three dimensions, it takes six parameters to define the unit cell. Three are the basis vectors **a**, **b**, and **c**. Three angles are also required. The angle α is the angle between **b** and **c**, β between **a** and **c** and γ between **a** and **b**.

The easiest way to remember this is that an angle name is the Greek equivalent of the axis **not** involved in the angle.

The unit cells presented here are called primitive because they represent the smallest volume that when repeated forms the crystal lattice. However, for some cells additional translation within the unit cell can be added that will result in a unit cell with higher symmetry. These are called centered cells and will be discussed when unit cell symmetry is considered. This means the primitive unit cell will not always be the cell reported in the final crystal structure.

Since the unit cell axes are typically not identical in three-dimensions, the physical properties of the crystal will depend on the direction of measurement. When properties differ when measured in different directions, they are called anisotropic. If the direction has no effect, it is called isotropic. The existence of anisotropy only occurs naturally in crystalline solids.

2.4 Diffraction in Three-dimensions

Diffraction in three dimensions is much more complicated than in one. If the Laue Equation is to be used, three equations like equation 2.2 are required. In this case, h was an integer that described the offset between waves that constructively interfered along the **a**-axis. Two new integers are required for similar interactions along **b** and **c**. These are assigned k and l , respectively. Likewise, two more equations are required where the angles are measured from **b** and **c**. Therefore, the Laue conditions are fulfilled whenever all three equations are satisfied and at the point in space where the beams intersect. The diffracted waves in three dimensions form spots in space wherever the conditions are satisfied. However, this is not an easy set of equations to work with.

Bragg's Law provides a simpler approach to diffraction in three dimensions. In the one-dimensional approach the trick was to create the line P which is perpendicular to **a**. By using $|\mathbf{a}|/h$ as the distance between lines, the location of the various diffraction intensities can be determined. In three dimensions P must be converted into a plane called the Bragg plane. The various Bragg planes will be defined by the three Miller indices h , k , and l . Each index will indicate the plane intersects the axis **a**, **b**, and **c** at coordinates $1/h$, $1/k$, and $1/l$. The plane (1,2,3) intersects **a** at 1, **b** at $1/2$ and **c** at $1/3$. A value of zero means the plane is parallel to that axis. The

plane (1,0,0) is the plane containing the **b** and **c** axes since it never intersects these axes.

What is important is the distance d_{hkl} between the set of planes. Calculating this distance is more difficult than might be imagined. Take the (1,0,0) plane. It would be expected that the distance between these planes which contain **b** and **c** would be the length of the a-axis. This may or may not be correct. For some unit cells the a-axis is not perpendicular to **b** or **c** and therefore is not perpendicular to the bc-plane. The perpendicular would need to be calculated and this is difficult in non-Cartesian axes. Later the concept of reciprocal space and the reciprocal lattice will be introduced to make the calculation of **d** much easier. Until then, it will be assumed that **d** can be calculated.

If d_{hkl} is known, then Bragg's Law reduces to $2d_{hkl}\sin(\theta)=n\lambda$. Note that addition of n to the equation. The integer n represents the order of the diffraction, which in the case of X-ray crystallography is usually treated as one and can therefore be ignored. However, for very intense radiation it is possible that second order diffraction ($n=2$) or even higher orders will be present with reduced intensity. In nature, $n=2$ results in a double rainbow. If we treat **d** as a vector and know the alignment of the crystal, then diffraction will be observed when **d** bisects the angle between the incoming and diffracted beam. This means it is possible to calculate the diffracting position for any indices hkl .

It is clear that the diffracting position is well-defined by Bragg's Law. However, that does not mean there is only one orientation of the crystal that will satisfy it. The only requirement is that the diffraction vector bisect the angle between the incoming primary beam and the outgoing diffracted beam. However, there is still one degree of freedom. Rotation around the diffraction vector will not change this geometry. Therefore, the same hkl diffraction spot can be observed at many positions during the data collection. This means that it is possible to collect a given reflection at different positions.

Lastly, it must be emphasized that the Bragg planes are an abstraction introduced to make the calculations easier. They are simply a function of the unit cell parameters and have nothing to do with the contents of the unit cell. There is no relationship between the location of the cell contents and the Bragg planes. Also, as mentioned above, the concept that the primary beam is being reflected by a Bragg plane like light by a mirror does not describe what is physically happening.

2.5 Review and Using Diffraction Data

This chapter represents a typical description of X-ray diffraction. It appears that the emphasis has been placed on explaining the existence and location of the diffraction spots. However, the original idea was to use the diffraction to calculate the position of the atoms in the crystal. A piece is still missing.

A review of this chapter will highlight the points made so far. When an X-ray beam interacts with an atom, the atom will produce new intensity which will have the same wavelength as the exciting radiation and be 180° out of phase. If there is no order to the solid, this scattered radiation will be of little use. However, if the material forms a regular array as in a crystal, then interference effects will be observed. The Bragg and Laue approaches were developed to provide a method of calculating where the diffracted beams will be observed. The concept of the unit cell was also introduced. The crystal is formed by translating the unit cell in three dimensions. The directions for translation are the unit cell parameters which form the basis vectors for a coordinate system. These basis vectors are not required to be orthogonal which can greatly complicate any calculations using them. The location of the diffraction spots in space will depend only on the unit cell parameters.

However, none of this has answered the question of where the atoms are in the crystal. If all the unit cells are identical then the problem is reduced to finding all the atoms in a single unit cell. In fact, this problem can be further simplified if the crystal has multiple formula units in the cell related by symmetry. In this case it is only necessary to position the atoms in the unique part of the unit cell called the asymmetric unit to form the entire unit cell.

The key to positioning the atoms is that the diffracted beam is created by constructive interference of waves of differing intensity. The intensity difference is because of the different number of electrons in each scatterer. The observed diffraction is a Fourier transform of the electron density in the unit cell. The indices (h,k,l) are Fourier summation factors and the amplitude of these data are the Fourier coefficients. The information concerning the location of the cell contents is contained in the intensities measured and their phases. It is possible to talk of two Fourier domains like in Fourier spectroscopy. One is real space which is defined by the unit cell parameters and has a dependent value of the electron density (ρ) at any location x,y,z inside the unit cell. The other domain is reciprocal space