

SOLID STATE PHYSICS

This book presents a comprehensive study of important topics of **Solid State Physics** for the undergraduate students of pure and applied sciences and engineering disciplines in a brief, coherent and lucid manner. The text is divided into ten chapters incorporating crystal structure, X-ray diffraction, bonding, lattice vibrations and free electron theory of metals. It is followed by the physics of semiconductors based on band theory of solids and magnetic, dielectric and superconducting properties. The text acquaints the reader with the fundamental properties of solids starting from their properties. This book has the following salient features :

- The coverage of basic topics is developed in terms of simple physical phenomena supplemented with theoretical derivations and relevant models which provides strong grasp of the fundamental principles of physics in solids in a concise and explanatory manner.
- It incorporates interaction of electrons, phonons and atoms in solids based on classical laws as well as elements of quantum mechanics.
- A set of solved examples based on S.I. system of units are given at the end of each chapter.
- A summary is given at the end of each chapter for a quick review of the various topics.
- A set of questions and unsolved problems are given for a better comprehension of every topic.

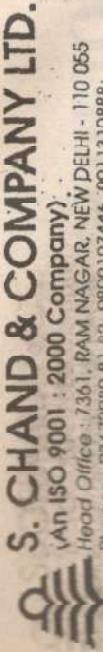
SOLID STATE PHYSICS

R.K. PURI
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PREFACE TO THE THIRD EDITION

The present edition is brought up to incorporate the useful suggestions from a number of readers and teachers for the benefit of students. Keeping in view the present style of University Question Papers, a number of Very Short, Short and Long questions are given at the end of each chapter. The manuscript has been thoroughly revised and corrected to remove the errors which crept into earlier editions. We hope the present improved edition would serve the students in a better way. However, the comments and suggestions from readers for further improvement of the book will be gratefully acknowledged.

R.K. PURI
V.K. BABBAR

PREFACE TO THE FIRST EDITION

A number of Indian universities have revised their curricula at the undergraduate level and have included various topics which earlier formed a part of the postgraduate curricula. Ever since the new syllabi were introduced, there had been a dearth of good books which strictly follow the revised syllabi. A number of standard texts are available on Solid State Physics but these are of advanced level. The present book is written specifically to meet the requirements of the undergraduate students and is in accordance with the common prescribed syllabi of most of the Indian universities.

The general approach and aim of this book is to provide a comprehensive introduction to the subject of Solid State Physics to the undergraduate students in a coherent, simple and lucid manner. The coverage of basic topics is concise, brief and self-explanatory. The topics such as Lasers, Magnetic Resonances, and the Mossbauer Effect are excluded as their advanced treatment is generally covered at the postgraduate level. The text is divided into ten chapters and each chapter is followed by a set of solved examples which acquaint the students with the application of the various principles and formulae used in the text and give them a feeling of the magnitude of the physical quantities involved therein. The SI units are followed throughout the book and their conversions to other practical units are appropriately introduced. Some of the conversion factors are also listed in appendix I. A summary of each chapter is given for a quick review of the topics. Each chapter is concluded with a set of questions and unsolved problems to help the students to comprehend these topics. A list of useful references is given for the indepth study of the subject.

We hope that the undergraduate students will find this book useful as well as concise for the subject of Solid State Physics. The comments and feedback from the students as well as teachers about this book will be gratefully appreciated.

We thank our friends and families, particularly our spouses, for their inspiration and encouragement. We also thank the publishers for quality printing and timely publication of this book.

R.K. PURI

V.K. BABBAR

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Add additional sheet(s) if the space provided is not sufficient, and if so required.*

(i) What topic(s) of your syllabus that are important from your examination point of view are not covered in the book ?

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CHAPTER - I

CRYSTAL STRUCTURE

1.1 INTRODUCTION

Matter, consisting of one or more elements or their chemical compounds, exists in nature in the solid, liquid and gaseous states. As the atoms or molecules in solids are attached to one another with strong forces of attraction, the solids maintain a definite volume and shape. The solid state physics is the branch of physics dealing with physical properties of solids, particularly crystals, including the behaviour of electrons in these solids. The solids may be broadly classified as *crystalline* and *non-crystalline* depending upon the arrangement of atoms or molecules.

The crystalline state of solids is characterized by regular or periodic arrangement of atoms or molecules. Most of the solids are crystalline in nature. This is due to the reason that the energy released during the formation of an ordered structure is more than that released during the formation of a disordered structure. Thus crystalline state is a low energy state and is, therefore, preferred by most of the solids. The crystalline solids may be subdivided into *single crystals* and *polycrystalline* solids. In single crystals, the periodicity of atoms extends throughout the material as the case of diamond, quartz, mica, etc. A polycrystalline material is an aggregate of a number of small crystallites with random orientations separated by well-defined boundaries. The small crystallites are known as *grains* and the boundaries as *grain boundaries*. It may be noted that although the periodicity of individual crystallites is interrupted at grain boundaries, yet the polycrystalline form of a material may be more stable compared with its single crystal form. Most of the metals and ceramics exhibit polycrystalline structure.

The non-crystalline or *amorphous* solids are characterized by the completely random arrangement of atoms or molecules. The periodicity, if at all present, extends up to a distance of a few atomic diameters only. In other words, these solids exhibit *short range order*. Such type of materials are formed when the atoms do not get sufficient time to undergo a periodic arrangement. Glass is an example of amorphous materials. Most of the plastics and rubbers are also amorphous.

The science which deals with the study of geometrical forms and

physical properties of crystalline solids is called *crystallography*. The study of crystallography is necessary to understand the strong correlation between the structure of a material and its physical properties. The present chapter deals with some of the basic concepts of crystallography which are fundamental to the study of solid state physics.

1.2 CRYSTAL LATTICE AND TRANSLATION VECTORS

Before describing the arrangement of atoms in a crystal, it is always convenient to describe the arrangement of imaginary points in space which has a definite relationship with the atoms of the crystal. This set of imaginary points forms a framework on which the actual crystal structure is based. Such an arrangement of infinite number of imaginary points in three-dimensional space with each point having identical surroundings is known as *point lattice* or *space lattice*.

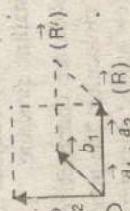
The term 'identical surroundings' means that the lattice has the same appearance when viewed from a point r in the lattice as it has when viewed from any other point r' with respect to some arbitrary origin. This is possible only if the lattice contains a small group of points, called *pattern unit*, which repeats itself in all directions by means of a translation operation T given by

$$T = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \quad (1.1)$$

where n_1, n_2 and n_3 are arbitrary integers and the vectors \mathbf{a}, \mathbf{b} and \mathbf{c} are called the *fundamental translation vectors*. Thus, we have

$$\mathbf{r}' = \mathbf{r} + T = \mathbf{r} + n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \quad (1.2)$$

In a perfect lattice, Eq. (1.2) holds good, i.e., point r' can be obtained from r by the application of the operation (1.1). However, in an imperfect lattice, it is not possible to find \mathbf{a}, \mathbf{b} and \mathbf{c} such that an arbitrary choice of n_1, n_2 and n_3 makes \mathbf{r}' identical to \mathbf{r} . The translation vectors \mathbf{a}, \mathbf{b} and \mathbf{c} are also called the *crystal axes* or *basis vectors* and shall be described later.



where two sets $\mathbf{a}_1, \mathbf{b}_1$ and $\mathbf{a}_2, \mathbf{b}_2$ of translation vectors are drawn. Considering first the translation vectors \mathbf{a}_1 and \mathbf{b}_1 , the point \mathbf{R}' can be obtained from \mathbf{R} using the translation operation given by

$$T = 0\mathbf{a}_1 + 1\mathbf{b}_1$$

which contains integral coefficients. Thus \mathbf{R}' is related to \mathbf{R} by the equation

$$\mathbf{R}' = \mathbf{R} + T = \mathbf{R} + 0\mathbf{a}_1 + 1\mathbf{b}_1$$

Such translation vectors which produce a translation operation containing integral coefficients are called *primitive translation vectors*. Referring to the second set of translation vectors \mathbf{a}_2 and \mathbf{b}_2 , the point \mathbf{R}' can be obtained from \mathbf{R} by using the equation

$$\mathbf{R}' = \mathbf{R} + \frac{1}{2}\mathbf{a}_2 + \frac{1}{2}\mathbf{b}_2$$

which contains non-integral coefficients of \mathbf{a}_2 and \mathbf{b}_2 . Such translation vectors for which the translation operation contains non-integral coefficients are called *non-primitive translation vectors*. Either type of translation vectors may be used to describe the structure of a crystal inspite of the fact that the non-primitive translation vectors involving non-integral coefficients are not in accordance with the periodicity of the crystal. Usually, a set of orthogonal and the shortest possible translation vectors is preferred for describing a lattice.

1.3 UNIT CELL

The parallelograms formed by the translation vectors (Fig. 1.1) may be regarded as building blocks for constructing the complete lattice and are known as *unit cells* of the lattice. For a three-dimensional lattice, the unit cells are of the form of a parallelepiped. An application of the translation operation (1.1) for some values of n_1, n_2 and n_3 takes the unit cell to another region which is exactly similar to the initial region. On repeatedly applying the same operation with all possible values of n_1, n_2 and n_3 , one can reproduce the complete lattice. Thus a unit cell may be defined as the smallest unit of the lattice which, on continuous repetition, generates the complete lattice. Both primitive and non-primitive translation vectors may be used to construct a unit cell. Accordingly, a unit cell is named as a *primitive unit cell* or a *non-primitive unit cell*. In Fig. 1.2, the parallelogram ABCD represents a two-dimensional primitive cell, whereas the parallelograms EFGH and KLMN represent non-primitive cells. Primitive unit cell is the smallest volume cell. All the lattice points belonging to a primitive cell lie at its corners. Therefore, the effective number of lattice points in a primitive unit cell is one. A non-primitive cell may have the lattice points at the corners as well as at other locations both

Consider, for simplicity, a part of a two-dimensional lattice as shown in Fig. 1.1. The translation vectors \mathbf{a} and \mathbf{b} can be chosen in a number of ways. Two such possibilities are shown in this figure

Fig. 1.1. Primitive ($\mathbf{a}_1, \mathbf{b}_1$) and non-primitive ($\mathbf{a}_2, \mathbf{b}_2$) translation vectors in a two-dimensional lattice.

1.5 SYMMETRY OPERATIONS

A *symmetry operation* is that which transforms the crystals to itself, i.e., a crystal remains invariant under a symmetry operation. These operations are *translation*, *rotation*, *reflection* and *inversion*. The translation operation applies to lattices only while all the remaining operations and their combinations apply to all objects and are collectively known as *point symmetry operations*. The inversion operation is applicable only to three-dimensional crystals. These operations are briefly described below:

(i) Translations

The translation symmetry follows from the orderly arrangement of a lattice. It means that a lattice point \mathbf{r} , under lattice translation vector operation \mathbf{T} , gives another point \mathbf{r}' which is exactly identical to \mathbf{r} , i.e.,

$$\mathbf{r}' = \mathbf{r} + \mathbf{T}$$

where \mathbf{T} is defined by Eq. (1.1).

(ii) Rotations

A lattice is said to possess the rotation symmetry if its rotation by an angle θ about an axis (or a point in a two-dimensional lattice) transforms the lattice to itself. Also, since the lattice always remains invariant by a rotation of 2π , the angle 2π must be an integral multiple of 0 , i.e.,

$$n\theta = 2\pi \quad (1.3)$$

The factor n takes integral values and is known as *multiplicity of rotation axis*. The possible values of n which are compatible with the requirement of translation symmetry are 1, 2, 3, 4 and 6 only. Thus, for example, for n equal to 6, θ is 60° which means that the lattice repeats itself with a minimum rotation of 60° . Such a rotation is illustrated in Fig. 1.5. Regular hexagon is an example such a lattice. A rotation corresponding to the value of n is called *n-fold rotation*. A two-dimensional square lattice has 4-fold rotation symmetry. It may be noted that a rotation axis may or may not pass through a lattice point. The fact that 5-fold rotation is not compatible with translation symmetry operation and that only 1, 2, 3, 4 and 6-fold rotations are permissible is proved as follows:

Consider a row of lattice points A, B, C and D as shown in Fig. 1.6. Fig. 1.5. Six-fold rotation about the point O in two dimensions.

Fig. 1.6. Geometry used to prove that only 1, 2, 3, 4 and 6-fold rotation axes clockwise and anticlockwise directions respectively yield points B' and C' which must be identical to B and C . Thus the points B' and C' must also be lattice points and should follow lattice translation symmetry. Hence $B' C'$ must be some integral multiple of BC , i.e.,

$$B' C' = m(BC)$$

$$2T \cos \theta + T = mT$$

$$\cos \theta = (m - 1)/2$$

where m is an integer. Since $| \cos \theta | \leq 1$, the allowed values of m are 3, 2, 1, 0 and -1 . These correspond to the allowed values of θ as 0° or 360° , 60° , 120° and 180° respectively. Hence from Eq. (1.3), the permissible values of n are 1, 6, 4, 3 and 2. Thus we conclude that 5-fold rotation is not permissible because it is not compatible with lattice translation symmetry. Similarly, other rotations, such as 7-fold rotation, are also not permissible.

Figure 1.7 gives a convincing demonstration of non-existence of 5-fold rotation axis. As shown in the figure, the pentagons placed side by side do not cover the complete space. This is because no sets of vectors exist which satisfy translation symmetry operation throughout and hence this arrangement of pentagons cannot be regarded as a lattice. The array itself, however, has a 5-fold symmetry about the point A.

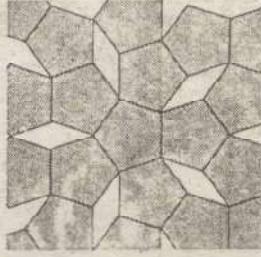


Fig. 1.7. Demonstration of non-existence of a five-fold rotation axis in a lattice.

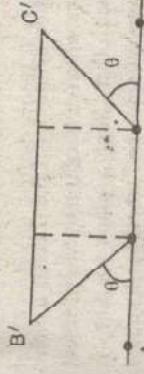


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$$B' C' = m(BC)$$

$$2T \cos \theta + T = mT$$

where m is an integer. Since $| \cos \theta | \leq 1$, the allowed values of m are 3, 2, 1, 0 and -1 . These correspond to the allowed values of θ as 0° or 360° , 60° , 120° and 180° respectively. Hence from Eq. (1.3), the permissible values of n are 1, 6, 4, 3 and 2. Thus we conclude that 5-fold rotation is not permissible because it is not compatible with lattice translation symmetry. Similarly, other rotations, such as 7-fold rotation, are also not permissible.

Figure 1.7 gives a convincing demonstration of non-existence of 5-fold rotation axis. As shown in the figure, the pentagons placed side by side do not cover the complete space. This is because no sets of vectors exist which satisfy translation symmetry operation throughout and hence this arrangement of pentagons cannot be regarded as a lattice. The array itself, however, has a 5-fold symmetry about the point A.

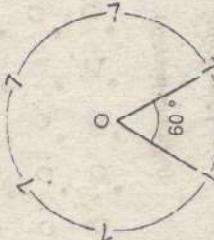
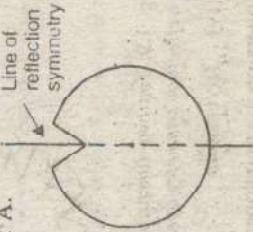


Fig. 1.5. Six-fold rotation about the point O in two dimensions.

Fig. 1.8. Reflection symmetry of a notched wheel about a line.



(iii) Reflections

A lattice is said to possess reflection symmetry if there exists a plane (or a line in two dimensions) in the lattice which divides it into two identical halves which are mirror images of each other. Such a plane (or line) is represented by m . The reflection symmetry of a notched wheel is illustrated in Fig. 1.8. Considering the combinations of reflections with allowed rotations, we note that each allowed rotation axis can be associated with two possibilities : one is rotation with reflection and the other rotation without reflection. Since there are five allowed rotation axes, the possible number of such combinations is 10. These are designated as

$$1, 1m, 2, 2mm, 3, 3m, 4, 4mm, 6, 6mm$$

where the numerals represent the type of rotation axis, the first m represents a plane (or line) parallel to the rotation axis and the second m refers to another plane (or line) perpendicular to the rotation axis. These ten groups of symmetry operations are shown in Fig. 1.9.

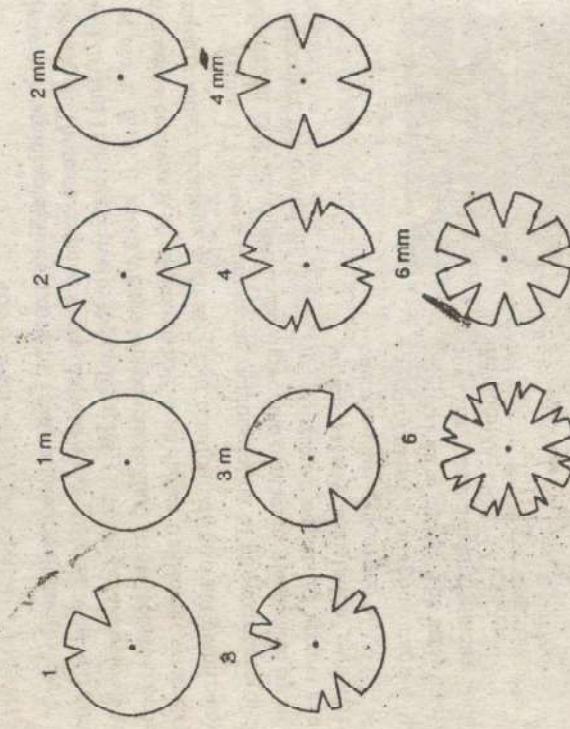


Fig. 1.9. Ten two-dimensional point groups consisting of rotation and reflection symmetry operations illustrated using notched wheels.

(iv) Inversions

Inversion is a point operation which is applicable to three-dimensional lattices only. This symmetry element implies that each point located at \mathbf{r}

relative to a lattice point has an identical point located at $-\mathbf{r}$ relative to the same lattice point. In other words, it means that the lattice possesses a centre of inversion denoted by $\bar{1}$.

It may be noted that, apart from these symmetry operations, a three-dimensional lattice in particular may have additional symmetry operations formed by the combinations of the above-mentioned operations. One such example is *rotation-inversion operation*. These operations further increase the number of symmetry elements. These symmetry elements are further employed to determine the type of lattices possible in two and three-dimensional spaces.

1.6 POINT GROUPS AND SPACE GROUPS

We have seen that there are mainly four types of symmetry operations, i.e., translation, rotation, reflection and inversion. The last three operations are point operations and their combinations give certain symmetry elements which collectively determine the symmetry of space around a point. The group of such symmetry operations at a point is called a *point group*.

In two-dimensional space, rotation and reflection are the only point operations. As described earlier, their combinations yield 10 different point groups designated as 1, $1m$, 2, $2mm$, 3, $3m$, 4, $4mm$, 6, and $6mm$ which are shown in Fig. 1.9. In three-dimensional space, however, the situation is complicated due to the presence of additional point operations such as inversion. There are a total of 32 point groups in a three-dimensional lattice.

The crystals are classified on the basis of their symmetry which is compared with the symmetry of different point groups. Also, the lattices consistent with the point group operations are limited. Such lattices are known as *Bravais lattices*. These lattices may further be grouped into distinct crystal systems.

The point symmetry of crystal structure as a whole is determined by the point symmetry of the lattice as well as of the basis. Thus in order to determine the point symmetry of a crystal structure, it should be noted that

- (i) a unit cell might show point symmetry at more than one locations inside it, and
- (ii) the symmetry elements comprising combined point and translation operations might be existing at these locations.

The group of all the symmetry elements of a crystal structure is called *space group*. It determines the symmetry of a crystal structure as a whole. There are 17 and 230 distinct space groups possible in two and three dimensions respectively.

1.7 TYPES OF LATTICES

As described earlier, the number of point groups in two and three dimensions are 10 and 32 respectively. These point groups form the basis for construction of different types of lattices. Only those lattices are permissible which are consistent with the point group operations. Such lattices are called *Bravais lattices*. It is beyond the scope of this book to describe the details of formation of various Bravais lattices from the possible point group operations. It can be stated that 10 and 32 point groups in two and three dimensions produce only 5 and 14 distinct Bravais lattices respectively. These Bravais lattices further become parts of 4 and 7 distinct *crystal systems* respectively and are separately described below.

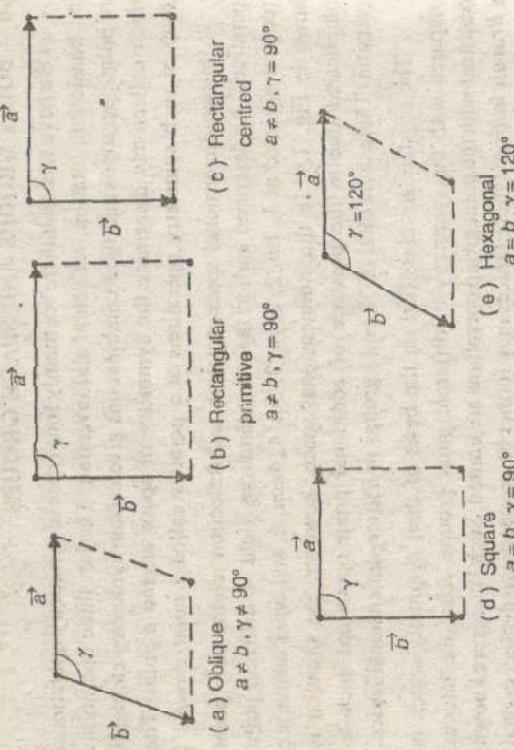


Fig. 1.10. Bravais lattices in two dimensions.

(i) Two-Dimensional Lattices

The four crystal systems of two-dimensional space are oblique, rectangular, square and hexagonal. The rectangular crystal system has two Bravais lattices, namely, rectangular primitive and rectangular centred. In all, there are five Bravais lattices which are listed in Table 1.1 along with the corresponding point groups. These lattices are shown in Fig. 1.10.

TABLE 1.1. Crystal systems and Bravais lattices in two dimensions

S. No.	Crystal system	Characteristic Point group	Bravais lattice	Conventional unit cell symmetry	Unit cell characteristics
1	Oblique	1, 2	Oblique	1. Rectangular primitive	$a \neq b, \gamma \neq 90^\circ$
2	Rectangular	1m, 2mm	1. Rectangular primitive	2. Rectangular centred	$a \neq b, \gamma = 90^\circ$
3	Square	4, 4mm	Parallelogram	Square	$a = b, \gamma = 90^\circ$
4	Hexagonal	3, 3m, 6, 6mm	Hexagonal	Hexagons	$a = b, \gamma = 120^\circ$

(ii) Three-Dimensional Lattices

All the seven crystal systems of three-dimensional space and the corresponding Bravais lattices are listed in Table 1.2 in the decreasing order of symmetry. The crystallographic axes a , b and c drawn from one of the lattice points determine the size and shape of a unit cell. The angles α , β and γ represent the angles between the vectors b and c , c and a , and a and b respectively. The lengths a , b and c and angles α , β and γ are collectively known as *lattice parameters* or *lattice constants* of a unit cell. These Bravais lattices are also shown in Fig. 1.1.1 in the form of their conventional unit cells. The symbols P, F and I represent simple or primitive, face-centred, and body-centred cells respectively. A base or end-centred cell is that which has lattice points at corners and at one of the pairs of opposite faces. It is designated by the letter A, B or C. The designation A refers to the cell in which the faces defined by b and c axes contain the lattice points, and so on. The symbol R is specifically used for rhombohedral lattice.

13 Crystal Structure

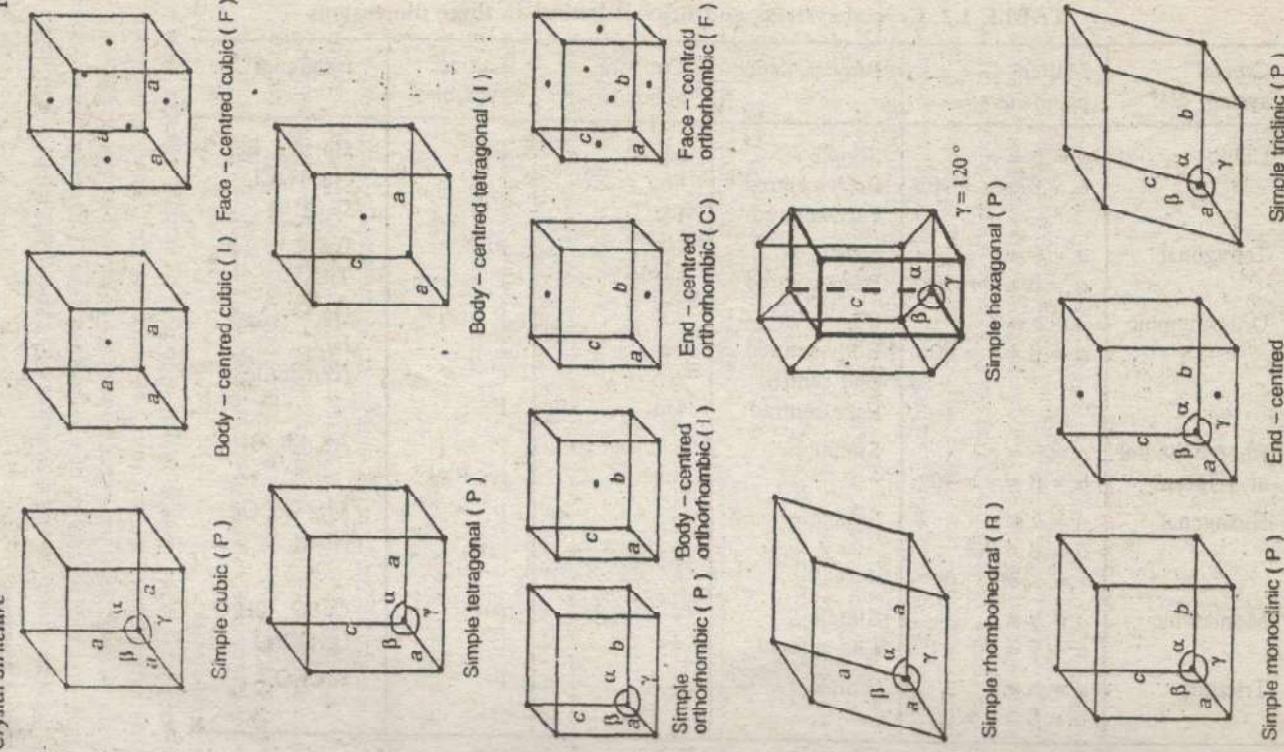


Fig. 1.11. The Bravais lattices in three dimensions

1.8 LATTICE DIRECTIONS AND PLANES

The direction of a line in a lattice is defined by assigning certain indices to this line. If the line passes through the origin, its indices are determined by taking a point on this line and finding out the projections of the vector drawn from the origin to that point on the crystallographic axes. Let these projections be u , v and w . Apparently, u , v and w also represent the coordinates of that point. These coordinates are then simplified to get a set of the smallest possible integers which when enclosed in square brackets represent the indices of the line. As an example, to determine the indices of the direction OQ in a cubic crystal (Fig. 1.13), we may take either a point P ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) or Q (1, 1, 1) on this line; either of these points yields the indices of the direction OQ as [111]. The same are the indices of any other direction parallel to OQ because by shifting the origin to an appropriate position, the new direction can be made to pass through the points O, P and Q. The origin is shifted in such a way that the orientation of the axes remains unchanged. If a direction is perpendicular to a certain axis, its index corresponding to that axis is zero as it does not form any projection on the axis. A direction having projections on the negative sides of the axes possess negative indices which are written by putting bars over the indices.

Consider the direction AB as shown in Fig. 1.14. The indices of this

family of face diagonals is represented by <110> and that of body diagonals by <111>. The number of members in the families of cube edges, face diagonals and body diagonals is 6, 12 and 8 respectively.

The angle θ between the two crystallographic directions $[hk\ell]$ and $[h'k'l']$ is given by

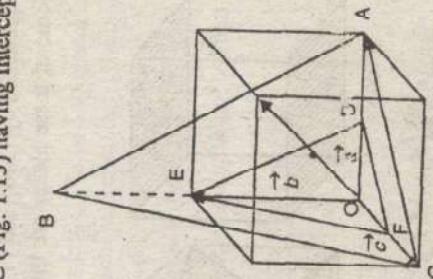
$$\cos\theta = \frac{hh' + kk' + ll'}{\sqrt{(h^2 + k^2 + l^2)^{1/2} (h'^2 + k'^2 + l'^2)^{1/2}}} \quad (1.6)$$

The scheme to represent the orientation of planes in a lattice was first introduced by Miller, a British crystallographer. The indices of planes are, therefore, known as the *Miller indices*. The steps involved to determine the Miller indices of a plane are as follows :

- Find the intercepts of the plane on the crystallographic axes.
- Take reciprocals of these intercepts.
- Simplify to remove fractions, if any, and enclose the numbers obtained into parentheses.

In step (i), the intercepts are taken in terms of the lengths of fundamental vectors choosing one of the lattice points as the origin. If a plane is parallel to a certain axis, its intercept with that axis is taken as infinity. In step (ii) the reciprocals are taken in order to avoid the occurrence of infinity in the Miller indices.

As an example, consider a plane ABC (Fig. 1.15) having intercepts 1,



2 and 1 with the crystallographic axes a , b and c respectively of a cubic lattice. The Miller indices of this plane are determined as follows :

- Intercepts : 1, 2, 1
- Reciprocals : 1, $\frac{1}{2}$, 1
- Simplification : 2, 1, 2

Hence the Miller indices of the plane ABC are (212); the numbers within the parentheses are written without commas. The Miller indices of a plane, in general, are written as (hkl) .

It may be noted that another plane DEF which is parallel to the plane ABC and lies completely inside the lattice, has intercepts 1/2, 1 and 1/2 with the axes a , b and c . The Miller indices of this plane are (112).

Fig. 1.14 shows some directions in a cubic lattice. The indices of a few more directions are indicated as <100>, <110>, etc. These constitute a family of cube edges designated as <100> which includes all the directions of this type. Similarly, a

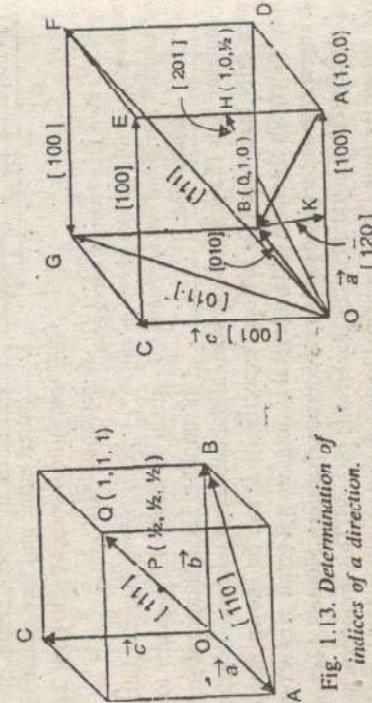


Fig. 1.13. Determination of indices of a direction.

direction can be obtained by shifting the origin to the point A. The projections of AB on the axes then become -1, 1, and 0 and hence the indices of the line AB are [110]. The indices of a few more directions are illustrated in Fig. 1.14. The cube edges are represented by the indices of the type [100], [010], [100], etc. These constitute a family of cube edges designated as <100> which includes all the directions of this type. Similarly, a

Fig. 1.15. Miller indices of parallel planes and the planes passing through the origin.

axes and hence carries the same Miller indices as the plane ABC. Thus we conclude that the parallel planes have the same Miller indices. The plane DEF is rather more convenient to deal with as it lies completely inside the lattice. If a plane intercepts an axis on the negative side, a bar is put above the corresponding number of the Miller indices. The intercepts of a plane passing through the origin cannot be determined as such. In such a case, we take another plane parallel to this plane and determine its Miller indices. The same are the indices of the given plane. Alternatively, we shift the origin from the plane to some other suitable lattice point without changing the orientation of the axes and then find the Miller indices. For example, the indices of the plane OCGA in Fig. 1.15 become $(0\bar{1}0)$ if the origin is shifted to the point E. The importance of orientation of the axes can be realized with reference to Fig. 1.12. The indices of the shaded plane are of the type (100) when referred to the axes of the face-centred tetragonal cell, whereas these become of the type (110) when referred to the axes of the simple tetragonal cell indicated by dotted lines.

A family of planes of a particular type is represented by enclosing the Miller indices of any one of the planes of that family into braces. Thus $\{100\}$ represents a family of planes which has the planes (100) , (010) , (001) , $(\bar{1}00)$, $(0\bar{1}0)$ and $(00\bar{1})$ as its members. These six planes represent the faces of the cube. Similarly, the families of diagonal planes and close-packed planes are represented by $\{110\}$ and $\{111\}$, and contain 6 and 8 members respectively. Some of these planes are illustrated in Fig. 1.16.

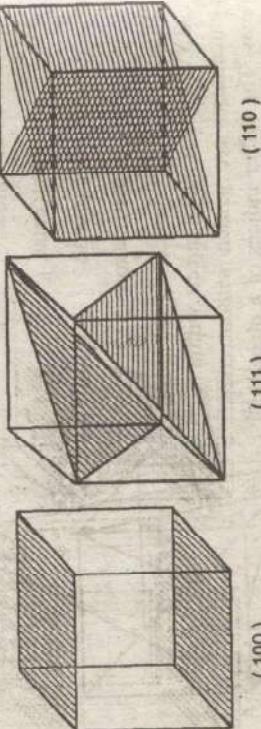


Fig. 1.16. Two parallel planes belonging to each one of the families $\{100\}$, $\{111\}$ and $\{110\}$ in a cubic lattice.

1.9 INTERPLANAR SPACING

Consider a set of parallel planes with indices $(hk\ell)$. Take origin on a

$$\begin{aligned} x = na, \quad y = nb, \quad z = nc \\ k = \frac{na}{a}, \quad h = \frac{nb}{b}, \quad \ell = \frac{nc}{c} \\ \Rightarrow x = n/a, \quad y = b/k, \quad z = n/c \end{aligned}$$

Solve for n

lattice point of one such plane and draw crystallographic axes a , b and c . Now consider another similar plane adjacent to this plane. Since the second plane also has the Miller indices $(hk\ell)$, the lengths of the intercepts on a , b and c are ah , bk and cl respectively. If we draw a normal from the origin to the second plane, the length of the normal represents the interplanar distance d . From Fig. 1.17, it follows that

$$d = OP = \frac{a}{h} \cos \alpha = \frac{b}{k} \cos \beta = \frac{c}{l} \cos \gamma \quad (1.7)$$

where α , β and γ represent the angles between the normal and the axes a , b and c respectively and $\cos \alpha$, $\cos \beta$ and $\cos \gamma$ represent the direction cosines of the normal to the plane $(hk\ell)$. The Eq. (1.7) indicates that the direction cosines of the normal are proportional to $1/ha$, $1/bk$ and $1/cl$.

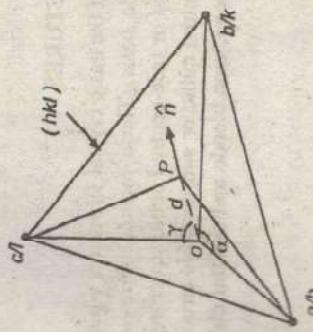


Fig. 1.17. An $(hk\ell)$ plane at a distance d from another similar parallel plane and \hat{n} , \hat{a} , \hat{b} , \hat{c} respectively and Eqs. (1.7) passing through the origin.

$$d = \hat{n} \cdot \hat{a}/h = \hat{n} \cdot \hat{b}/k = \hat{n} \cdot \hat{c}/l \quad (1.8)$$

Thus the value of d can be determined if \hat{n} is known. In an orthogonal lattice, where a , b and c point along x , y and z directions respectively, the equation of the plane $(hk\ell)$ with intercepts ah , bk and cl on the axes is

$$f(x, y, z) = hx/a + ky/b + lz/c = 1$$

For a surface $f(x, y, z) = \text{constant}$, ∇f represents the vector normal to it.

$$\therefore \hat{n} = \frac{\nabla f}{|\nabla f|} = \frac{(h/a)\hat{i} + (k/b)\hat{j} + (l/c)\hat{k}}{(h^2/a^2 + k^2/b^2 + l^2/c^2)^{1/2}} \quad (1.8)$$

Hence from Eqs. (1.8), we obtain

$$\hat{d} = \frac{\hat{n} \cdot \hat{a}}{h} = \frac{[(h/a)\hat{i} + (k/b)\hat{j} + (l/c)\hat{k}] \cdot (a/h)\hat{i}}{(h^2/a^2 + k^2/b^2 + l^2/c^2)^{1/2}} \quad (1.9)$$

$$\text{or } d = \frac{1}{(h^2/a^2 + k^2/b^2 + l^2/c^2)^{1/2}} \quad (1.9)$$

This equation is valid for orthogonal lattices only. For non-orthogonal lattices, such an expression may not be obtained easily; one may need to find \hat{n} by some other method and then use Eq. (1.8) to determine d . For a cubic lattice, a , b and c are equal and we get

$$(1.10) \quad d = \frac{a}{\left(h^2 + k^2 + l^2 \right)^{1/2}}$$

It may also be noted that for a cubic lattice, the direction $[hkl]$ is perpendicular to the plane (hkl) .

1.10 SIMPLE CRYSTAL STRUCTURES

We shall now describe some of the basic crystal structures which are either monoatomic or contain simple basis. These include *close-packed structures* like hexagonal close-packed or face-centred cubic structures. *Loose-packed structures* like body-centred cubic or simple cubic structures. Besides these, the structures of diamond, zinc blende and sodium chloride are also described.

1.10.1. Close-Packed Structures

Close-packed structures are mostly found in monoatomic crystals having non-directional bonding, such as metallic bonding. In these structures, the coordination number of each atom is 12, i.e., each atom is surrounded by twelve similar and equal sized neighbours. Out of these twelve neighbours, six lie in one plane, three in an adjacent parallel plane above this plane and three in a similar plane below it. There are two types of close-packed structures:

- (i) Hexagonal close-packed (*hcp*) structure
- (ii) Face-centred cubic (*fcc*) structure

These structures are described as follows :

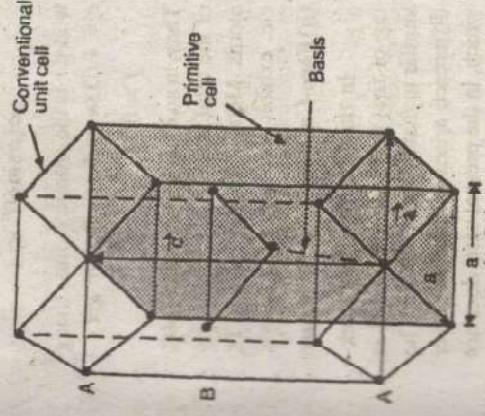


Fig. 1.10. Conventional and primitive cells of hexagonal close-packed structure.

This type of stacking is called *hcp* stacking and the structure is known as *hexagonal close-packed structure*.

The name corresponds to the shape of the conventional unit cell which is hexagonal and is shown in Fig. 1.19. There are twelve atoms located at the corners, two at the centres of the basal planes, and three completely inside the hexagon forming a part of the B-layer. The effective number of atoms in a unit cell is

$$12(1/6) + 2(1/2) + 3 = 6$$

The interatomic distance for the atoms within a layer is a . The distance between the two adjacent layers is $c/2$, c being the height of the unit cell. For an ideal *hcp* structure, $c = 1.633a$.

It may be noted that although the structure is *hcp*, the space lattice is simple hexagonal with basis consisting of two atoms placed in such a way that if one atom lies at the origin, the other atom lies at the point $(2/3, 1/3, 1/2)$. The shaded portion in Fig. 1.19 represents the primitive cell of this structure. It contains 2 atoms instead of one which is due to the presence of the basis. Also, the volume of the primitive cell is exactly one-third of the volume of the hexagonal cell.

The *packing fraction*, f , is defined as the ratio of the volume occupied by the atoms present in a unit cell to the total volume of the unit cell. It is also referred to as the *packing factor* or *packing efficiency* of the unit cell. From the primitive cell, we find

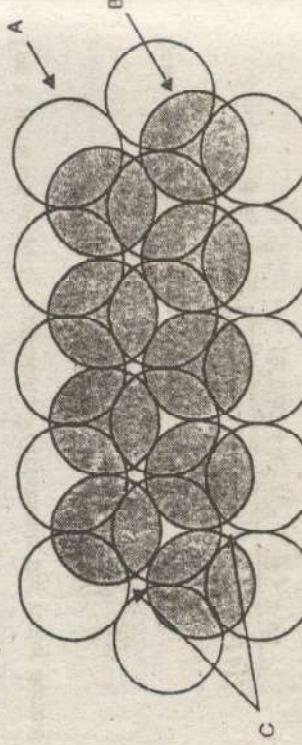


Fig. 1.18. Layered arrangement of close-packed structures.

$$f = \frac{2(4/3)\pi r^3}{a(a \sin 60^\circ)c}$$

where r is the atomic radius. Using $c = 1.633a$ and $a = 2r$, we get

$$f = 0.74$$

Thus, in an ideal hcp structure, 74% of the total volume is occupied by atoms. Metals like Mg, Zn, Cd, Ti, etc. exhibit this type of structure.

(ii) Face-Centred Cubic Structure

In this structure, the stacking of first two layers A and B is similar to that of hcp structure. The difference arises in the third layer which, in the present case, does not overlap the first layer. The atoms of the third layer occupy the positions of those valleys of the A-layer which are not occupied by the B-layer atoms. The third layer is designated by the letter C. The fourth layer exactly overlaps the first layer and the sequence is repeated. Thus fcc. structure is represented by the following stacking sequence :

..... ABCABCABC

The conventional unit cell is face-centred cubic and is shown in Fig. 1.20. It is a non-primitive cell having effective number of atoms equal to $8(1/8) + 6(1/2) = 4$. The atoms touch one another along the face diagonals. The length of the cube edge, a , and the atomic radius, r , are related to each other as

$$4r = \sqrt{2}a$$

The packing fraction, f , is given by

$$f = \frac{4(4/3)\pi r^3}{a^3} = 0.74$$

Thus the packing fraction of fcc structure is exactly the same as that of hcp structure which is expected because of the close-packed nature of both the structures. Also, the coordination number of each atom is 12. Examples of materials having this type of structure are Cu, Ag, Au, Al, etc.

1.10.2. Loose-Packed Structures

A loose-packed structure is that in which the coordination number of an atom is less than 12 or the packing fraction is less than 0.74. Among the various possible loose-packed structures, the most common and the simplest are the *body-centred cubic* (bcc) and the *simple cubic* (sc) structures. These structures are described as follows :

(i) Body-Centred Cubic Structure (bcc)

The conventional unit cell of bcc structure is non-primitive and is shown in Fig. 1.21. It has cubical shape with atoms located at the corners and the body centre. Thus the effective number of atoms per unit cell is $8(1/8) + 1 = 2$. The coordination number of each atom is 8. The atoms touch one another along the body diagonal. Thus a is related to r as

$$4r = \sqrt{3}a$$

The packing fraction is given by

$$f = \frac{2(4/3)\pi r^3}{a^3} = 0.68$$

The examples of materials exhibiting bcc structure are Na, K, Mo, W, etc.

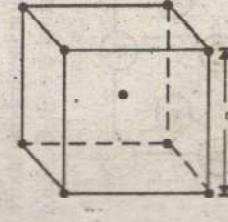


Fig. 1.21. Conventional unit cell of bcc structure.

(ii) Simple Cubic Structure (sc)

The conventional unit cell of sc structure is the same as its primitive cell and is shown in Fig. 1.22. The atoms are located at the corners only and touch one another along the cube edges. Thus in sc structures, we have $a = 2r$.

The coordination number of each atom is 6. The packing fraction is given by

$$f = \frac{(4/3)\pi r^3}{a^3} = 0.52$$

Only plonium exhibits this type of structure at room temperature.

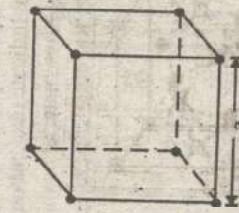


Fig. 1.22. Unit cell of sc structure.

1.11 STRUCTURE OF DIAMOND

Diamond exhibits both cubic and hexagonal type structures. The diamond cubic (*dc*) structure is more common and is described here. The space lattice of the diamond cubic structure is *fcc* with basis consisting of two carbon atoms, one located at the lattice point and the other at a distance of one quarter of the body diagonal from the lattice point along the body diagonal. The unit cell of the *dc* structure is shown in Fig. 1.23. The carbon atoms placed along the body diagonals, in fact, occupy the alternate tetrahedral void positions in the *fcc* arrangement of carbon atoms. This opens up the otherwise close-packed *fcc* arrangement which decreases the packing efficiency considerably. The packing efficiency of the *dc* structure is only 34% as compared to 74% for the *fcc* structure. The coordination number of each carbon atom is 4 and the nearest neighbour distance is equal to $\sqrt{3}a/4$ where a is the lattice parameter.

The *dc* structure may also be viewed as an interpenetration of two *fcc* sublattices with their origins at $(0, 0, 0)$ and $(1/4, 1/4, 1/4)$. A plan view of the positions of all the carbon atoms in the unit cell is shown in Fig. 1.24. The fractional heights of the carbon atoms relative to the base of the unit cell are given in the circles drawn at the atomic positions. Two numbers in the same circle indicate two carbon atoms at the same position located one above the other. Other materials exhibiting this type of structure are Si, Ge, SiC, GaAs, gray tin, etc.

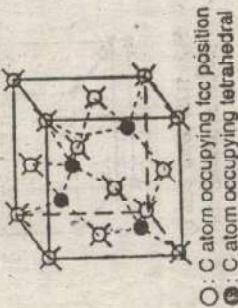


Fig. 1.23. The unit cell of *dc* structure. The lattice is *fcc* with carbon atoms located at *fcc* positions and at alternate tetrahedral sites.

1.12 ZINC BLENDE (ZnS) STRUCTURE

The zinc blende structure is similar to the *dc* structure except that the two *fcc* lattices in it are occupied by different elements. The structure is similar to the one shown in Fig. 1.23 where the dark circles now represent one type of atoms, say Zn, and the light circles represent the other type of atoms, i.e., S.

1.13 SODIUM CHLORIDE (NaCl) STRUCTURE

The unit cell of NaCl structure is shown in Fig. 1.25. In NaCl structure, the radii of Na^+ and Cl^- ions are such that each Na^+ ion is octahedrally coordinated to six Cl^- ions. The unit cell is *fcc* with four Cl^- ions occupying all the four *fcc* positions and the four Na^+ ions occupying all the four octahedral voids. The *fcc* positions and the octahedral void positions are, however, interchangeable. The NaCl structure can, therefore, be viewed as two interpenetrating *fcc* sublattices, one belonging to Na^+ ions with its origin at the point $(0, 0, 0)$ and the other belonging to Cl^- ions with its origin at the point $(a/2, 0, 0)$. In the terminology of lattice and basis, the structure can be interpreted as an *fcc* lattice with basis consisting of two ions, one of Na^+ and the other of Cl^- . One of these ions occupies one of the *fcc* positions and the other ion occupies the corresponding octahedral void position. A unit cell of NaCl comprises four molecules. The position of various ions in the unit cell are as follows :

$$\begin{aligned}\text{Na}^+ : & 0, 0, 0; 1/2, 1/2, 0; 1/2, 0, 1/2; 0, 1/2, 1/2 \\ \text{Cl}^- : & 1/2, 1/2, 1/2; 0, 0, 1/2; 0, 1/2, 0; 1/2, 0, 0\end{aligned}$$

SOLVED EXAMPLES

Example I.1. Determine the relationships between the lattice parameter a and the atomic radius r for monoatomic *sc*, *bcc* and *fcc* structures.

Solution. In *sc* structure (Fig. 1.26), the atoms touch one another along the cube edges.

$$a = 2r$$

In *bcc* structure, the atoms touch along the body diagonals.

$$\sqrt{3}a = 4r$$

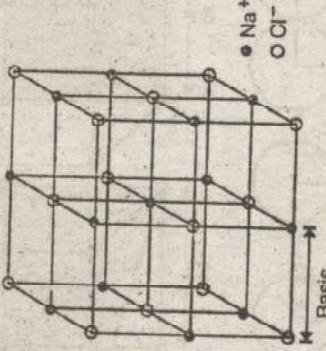
$$a = 4r/\sqrt{3}$$

In *fcc* structure, the atoms touch along the face diagonals

$$\sqrt{2}a = 4r$$

$$a = 2\sqrt{2}r$$

Fig. 1.25. Unit cell of sodium chloride structure.



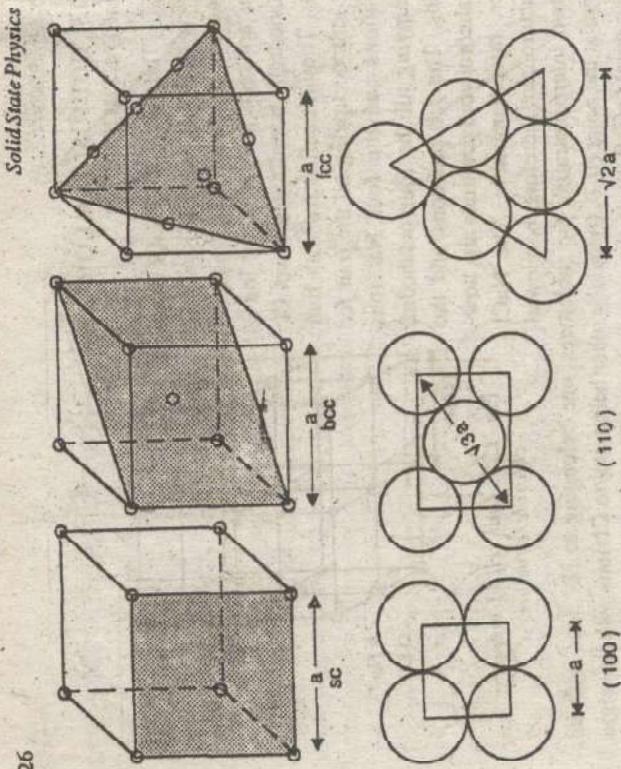


Fig. 1.26. Monatomic sc, bcc and fcc structures along with their (100), (110) and (111) type planes respectively.

Example 1.2. Draw (101) and (111) planes in a cubic unit cell. Determine the Miller indices of the directions which are common to both the planes.

Solution. Intercepts of the plane (101) with the axes

$$\begin{aligned} &= 1/1, 1/0 \text{ and } 1/1 \\ &\approx 1, \infty \text{ and } 1 \\ &\approx 1, 1 \text{ and } 1 \end{aligned}$$

Intercepts of the plane (111) with the axes

Taking the point O as origin and the lines OA, OB and OC as the axes a , b and c respectively, the plane with intercepts 1, ∞ and 1 is the plane ADGC and that with intercepts 1, 1 and 1 is plane ABC as shown in Fig. 1.27. Therefore, the line common to both the planes is the line AC. It corresponds to two directions, i.e., AC and CA.

Projections of the direction AC on the (111) axes = -1, 0 and 1
Projections of the direction CA on the axes = 1, 0 and -1

Fig. 1.27. Planes (101) and (111) in a cubic lattice.

$$h_1 = \frac{3}{1}; h_2 = \frac{2}{2}; h_3 = \frac{1}{1}, l_1 = \frac{1}{0}, l_2 = \frac{1}{1}, l_3 = \frac{1}{0}$$

Therefore, the required indices are $(\bar{1}01)$ and $(10\bar{1})$.

Example 1.3. A plane makes intercepts of 1, 2 and 0.5\AA on the crystallographic axes of an orthorhombic crystal with $a:b:c = 3:2:1$. Determine the Miller indices of this plane.

Solution. Taking the lengths of the axes OA, OB and OC as 3, 2 and 1\AA respectively, the plane with intercepts of 1, 2 and 0.5\AA on the axes is the plane DBE as shown in Fig. 1.28. The intercepts of this plane relative to full lengths of the axes are

$$\begin{aligned} &h = \frac{1}{1/3} \Rightarrow h = 3 \\ &l = \frac{2}{2/3} \Rightarrow l = 3 \\ &k = \frac{0.5}{1/6} \Rightarrow k = 3 \\ \text{or } &h = \frac{1}{1/3}, l = \frac{1}{1/2} \\ \text{Reciprocals : } &3, 1 \text{ and } 2 \\ &z = \frac{1}{1/2} \Rightarrow z = 2 \end{aligned}$$

Therefore, the Miller indices of the plane DBE are (312) .

Example 1.4. In a cubic unit cell, find the angle between normals to the planes (111) and (121).

Fig. 1.28. Plane (312) in an orthorhombic lattice.

Solution. Since the crystal is cubic, the normal to the planes (111) and (121) are the directions [111] and [121] respectively. Let θ be the angle between the normals,

$$\begin{aligned} \cos\theta &= \frac{h_1k_2 + h_2k_1 + l_1l_2}{(h_1^2 + k_1^2 + l_1^2)^{1/2} (h_2^2 + k_2^2 + l_2^2)^{1/2}} \\ &= \frac{1 \times 1 + 1 \times 2 + 1 \times 1}{(1^2 + 1^2 + 1^2)^{1/2} (1^2 + 2^2 + 1^2)^{1/2}} \\ &= 0.9428 \end{aligned}$$

or $\theta = 19.47^\circ$ or $19028'$

Example 1.5. Calculate the packing efficiency and density of sodium chloride from the following data :

$$\begin{aligned} \text{Radius of sodium ion} &= 0.98 \text{\AA} \\ \text{Radius of chloride-ion} &= 1.81 \text{\AA} \\ \text{Atomic mass of sodium} &= 22.99 \text{ amu} \\ \text{Atomic mass of chlorine} &= 35.45 \text{ amu} \end{aligned}$$

Solution. The unit cell of NaCl structure is shown in Fig. 1.25. The Na^+ and Cl^- ions touch along the cube edges.

$$\begin{aligned} \text{Lattice parameter, } a &= 2(\text{Radius of } \text{Na}^+ + \text{Radius of } \text{Cl}^-) \\ &= 2(0.98 + 1.81) = 5.58 \text{\AA} \end{aligned}$$

$$\text{Packing fraction} = \frac{\text{Volume of ions present in the unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{4(4/3)\pi r_{N_a^+}^3 + 4(4/3)\pi r_{Cr}^3}{a^3}$$

$$= \frac{16\pi}{3} \left[\frac{(0.98)^3 + (1.81)^3}{(5.58)^3} \right]$$

$$= 0.663 \text{ or } 66.3\%$$

$$\text{Density} = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{4(22.99 + 35.45) \times 1.66 \times 10^{-27}}{(5.58 \times 10^{-10})^3} \text{ kg m}^{-3}$$

$$= 2234 \text{ kg m}^{-3} \text{ or } 2.23 \text{ g cm}^{-3}$$

SUMMARY

1. The solids may be broadly classified as crystalline and non-crystalline (or amorphous). The crystalline solids may be further sub-divided into single crystals and polycrystalline materials.

2. Crystallography is the study of formation, structure and properties of crystals.

3. A crystal structure results from the combination of a space lattice and a basis. A space lattice is a regular arrangement of infinite number of imaginary points in three-dimensional space. A basis is a structural unit comprising a single atom or a group of atoms which is placed on each lattice point in a regular fashion to generate the crystal structure.

4. A unit cell is a small group of points which acts as a building block for the entire lattice. It may be primitive or non-primitive. A primitive cell is the smallest volume unit cell and contains only one lattice point per cell. A non-primitive cell contains more than one lattice points per cell. The conventional unit cell has the highest possible symmetry and the lowest possible volume. It may be primitive or non-primitive.

5. The effective number of lattice points belonging to a unit cell is:

$$N = N_i + N_f/2 + N_c/8$$

where N_i , N_f and N_c denote the number of lattice points present inside, at the face centres, and at the corners of the cell respectively.

6. A crystal remains invariant under the application of various symmetry operations like translation, rotation, reflection, inversion etc. Some rotational operations, such as 5-fold and 7-fold rotations, are not permissible as these are not compatible with lattice translation symmetry.

7. A point group is the combination of certain symmetry operations like rotation, reflection and inversion. It determines the symmetry of space around a point. The number of point groups in three-dimensional space is 32. These point groups produce only 14 Bravais lattices.

8. The set of all the symmetry elements of a crystal structure is called the space group. The number of distinct space groups possible in three dimensions is 230.

9. The Miller indices of a crystallographic plane and a direction are denoted by (hkl) and $[hkl]$ respectively where h , k and l are integers. The parallel planes and the parallel directions have the same indices.

10. The angle between two directions $[hkl]$ and $[h'k'l']$ is given by

$$\cos\theta = \frac{hh' + kk' + ll'}{(h^2 + k^2 + l^2)^{1/2} (h'^2 + k'^2 + l'^2)^{1/2}}$$

11. The interplanar distance for the parallel (hkl) planes for an orthorhombic lattice is

$$d = (h^2/a^2 + k^2/b^2 + l^2/c^2)^{-1/2}$$

where a , b and c are the lengths of the axes.

12. A close-packed structure is that in which each atom has twelve identical nearest neighbours. A close-packed structure may be either fcc or hcp with the following sequence of layers :

hcp :ABABABAB.....

fcc :ABCABCABC.....

VERY SHORT QUESTIONS

1. Define a single crystal.
2. How does a crystal differ from a grain?
3. What is short-range order?
4. What are amorphous materials? Give an example of such a material.
5. What is crystallography?
6. What is a unit cell?
7. How does a crystal differ from a lattice?
8. What is the maximum number of possible Bravais lattices?
9. What are Miller indices? What is their importance?
10. Write the indices of all the twelve edges of a cube.
11. Write the indices of all the face diagonals of a cube.
12. What is packing efficiency? What are its values for sc, bcc, fcc and hcp structures?
13. Give at least one example each of materials exhibiting sc, bcc, fcc and hcp structures.
14. Calculate the number of carbon atoms per unit cell of diamond.

SHORT QUESTIONS

1. Define primitive and non-primitive translation vectors. Which type of translation vectors are preferred for describing a lattice?
 2. Prove that the crystals cannot have five-fold symmetry.
 3. Differentiate primitive cell, non-primitive cell and conventional cell from one another. How is a Weigner-Seitz cell constructed?
 4. Describe the scheme to determine the Miller indices of a plane. Show that the parallel planes have the same Miller indices.
 5. What is the relationship between the Miller indices and reciprocal lattice vectors corresponding to any plane?
 6. Find the Miller indices of cube faces and diagonal planes of a unit cube.
 7. Explain the concepts of lattice, basis and crystal structure. How are they related?
 8. Draw primitive cells corresponding to bcc and fcc unit cells.
 9. How does hcp structure differ from bcc structure?
 10. What is Bravais lattice? What is the maximum number of Bravais lattices possible? How will you account for the existence of thousands of structures from these lattices?
 11. The end-centred orthorhombic is one of the Bravais lattices but the end-centred tetragonal is not. Give reasons.
 12. The primitive cell of fcc lattice is rhombohedral. Why then is the rhombohedral lattice included separately in the Bravais list?
 13. State the points of similarity and difference of the monoatomic, sc, monoatomic bcc, and CsCl structures?
 14. Calculate the volume of the primitive cell and the number of nearest neighbours for an fcc lattice.
 15. Obtain an expression for the packing fraction for hcp structure.
 16. Show that the c/a ratio for an ideal hcp lattice is $\sqrt{8/3}$.
 17. Determine the values of packing fraction for fcc, bcc and sc structures.
 18. Assuming one of the basis atoms lying at the origin, find the coordinates of the other atoms for an hcp structure.
 19. Explain, without calculation, why fcc and hcp structures have the same packing factor.
 20. Show that for a cubic lattice, the lattice constant, a , is given by

$$a = \sqrt[3]{\frac{nM}{N\rho}} \quad M(\text{Weight}) = m(\text{Mass}) \quad N_A$$
- where the symbols have their usual meanings.
21. What type of lattice and basis do the following structures have?
 - (i) Sodium chloride
 - (ii) Diamond cubic ?
 22. Diamond is the hardest substance known in spite of the fact that the packing fraction and the coordination number of carbon atom in the dc structure are quite low. Explain.
 23. There are four vacant tetrahedral sites in a unit cell of the dc structure. Can four additional carbon atoms occupy these sites? Give reasons.
 24. How many crystal directions constitute the family of body diagonals of a unit cube? Draw all such directions.

LONG QUESTIONS

1. What are symmetry operations? Describe the principal symmetry operations applicable to a three-dimensional lattice. Show that the five-fold rotational axis is not permissible in case of lattices.
2. What are point group and space group? Give their number for two- and three-dimensional lattices. List all the point groups of a two-dimensional lattice.
3. Determine the interplanar spacing between the two parallel planes with Miller indices (h, k, l) in a cubic crystal of side a .
4. Which is the most densely packed structure amongst the various cubic structures? Determine the packing fraction and porosity of this structure. Can the porosity be reduced by some means? What type of solids generally exhibit this type of structure and why?
5. Draw a plan view of sodium chloride structure. In how many ways can this structure be interpreted?
6. Draw a plan view of *hcp* unit cell and give coordinates of all the atoms. Are all the atoms located at equivalent sites? Discuss implications of your answer.
7. Draw the following:
 - (i) $[1\bar{1}1], [1\bar{2}\bar{1}]$ and $[0\bar{1}2]$ directions in cubic and tetragonal lattices.
 - (ii) $(\bar{1}11), (1\bar{1}2)$ and $(2\bar{1}0)$ planes in cubic and orthorhombic lattices.

4. A plane makes intercepts of 1, 2 and 3 Å on the crystallographic axes of an orthorhombic crystal with $a : b : c = 3 : 2 : 1$. Determine the Miller indices of this plane.
5. Determine the number of the nearest neighbours and the closest distance of approach in terms of lattice parameter for monatomic sc, *bcc* and *fcc* structures.
6. Calculate the linear density (number of atoms per unit length) along cube edge, face diagonal and body diagonal of an *fcc* unit cell of side length a .
7. Nickel (*fcc*) has the lattice parameter of 3.52 Å. Calculate the atomic planar density (number of atoms per unit area) on (100) , (110) and (111) planes. Is it possible to pack the atoms more closely than in (111) plane? $(1.61 \times 10^{19}, 1.14 \times 10^{19}, 1.86 \times 10^{19}$ atoms m^{-2} ; No)
8. Calculate the angles which $[111]$ direction of a cubic lattice makes with $[100]$ and $[110]$ directions.
9. Show (111) and (222) planes in a cubic unit cell of side a . Compute the distances of these planes from a parallel plane passing through the origin.
10. Calculate the distances between the adjacent parallel planes of the type (100) , (110) and (111) in an *fcc* lattice of lattice constant a . Check the validity of the statement "The most close-packed planes are the most widely spaced."
11. Copper (*fcc*) has density of 8960 kg m^{-3} . Calculate the unit cell dimension and the radius of Cu atom, given the atomic mass of Cu as 63.54 amu.
12. Prove that c/a ratio for an ideal *hcp* structure is 1.633.
13. Zinc (*hcp*) has lattice parameters a and c as 2.66 Å and 4.95 Å respectively. Calculate the packing fraction and density of zinc, given the atomic radius and the atomic mass of Zn as 1.31 Å and 65.37 amu (62%, 7155 kg m^{-3})
14. Calculate the distance between two atoms of a basis of the diamond structure, if the lattice constant of the structure is 5 Å. (2.17 \AA)

PROBLEMS

- $\chi = \frac{\sqrt{a^2 + b^2 + c^2}}{K} = \frac{\sqrt{a^2 + b^2 + c^2}}{K}$
1. Find the Miller indices for planes with each of the following sets of intercepts:

(i) $2a, 3b, 2c;$	(ii) $a, 2b, \infty;$	(iii) $5a, -6b, c;$
(iv) $a, b/2, c;$	(v) $a, b, -c;$	(vi) $a/2, b, \infty$

where a, b and c are lattice parameters.

2. Draw a $(1\bar{1}0)$ plane in a cubic unit cell. Show all the $\langle 111 \rangle$ directions that lie on this plane and give the Miller indices of each direction. $([111], [1\bar{1}1] \text{ and } [\bar{1}\bar{1}1])$

CHAPTER - II

X-RAY DIFFRACTION AND RECIPROCAL LATTICE

2.1 INTRODUCTION

X-rays, being electromagnetic radiations, also undergo the phenomenon of diffraction as observed for visible light. However, unlike visible light, x-rays cannot be diffracted by ordinary optical grating because of their very short wavelengths. In 1912, a German physicist Max Von Laue suggested the use of a single crystal to produce diffraction of x-rays. Since all the atoms in a single crystal are regularly arranged with interatomic spacing of the order of a few angstroms, a crystal can act as a three-dimensional natural grating for x-rays. Friedlich and Knipping later successfully demonstrated the diffraction of x-rays from a thin single crystal of zinc blende (ZnS). The diffraction pattern obtained on a photographic film consisted of a series of dark spots arranged in a definite order. Such a pattern is called the *Laue's pattern* and reflects the symmetry of the crystal. Apart from this, the phenomenon of x-ray diffraction has become an invaluable tool to determine the structures of single crystals and polycrystalline materials. It is also extensively used to determine the wavelength of x-rays.

2.2 X-RAY DIFFRACTION

When an atomic electron is irradiated by a beam of monochromatic x-rays, it starts vibrating with a frequency equal to that of the incident beam. Since an accelerating charge emits radiations, the vibrating electrons present inside a crystal become sources of secondary radiations having the same frequency as the incident x-rays. These secondary x-rays spread out in all possible directions. The phenomenon may also be regarded as scattering of x-rays by atomic electrons. If the wavelength of incident radiations is quite large compared with the atomic dimensions, all the radiations emitted by electrons shall be in phase with one another. The incident x-rays, however, have the same order of wavelength as that of the atomic dimensions; hence the radiations emitted by electrons are, in general, out of phase with one another. These radiations may, therefore, undergo constructive or destructive interference producing maxima or minima in certain directions.

Consider a one-dimensional row of similar atoms having interatomic spacing equal to a . Let a wave front of x-rays of wavelength λ be incident on the row of atoms such that the wave crests are parallel to the row. The atoms emit secondary wavelets which travel in all possible directions. As shown in Fig. 2.1, the reinforcement of secondary wavelets takes place not only in a direction perpendicular to the row of atoms but also in other directions. These directions correspond to different orders of x-ray diffraction. The zeroth, first and second order diffraction directions are shown in Fig. 2.1. It may be noted that reinforcement takes place in some particular directions only, whereas in other directions the wave fronts interfere destructively and the intensity is minimum. Such reinforcements produce Laue's pattern.

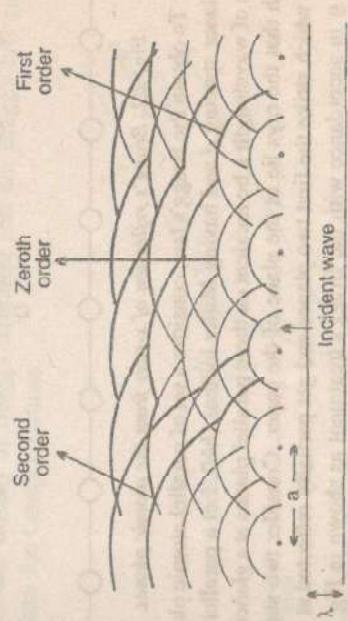


Fig. 2.1. Reinforcement of scattered waves resulting in diffracted beams of different orders.

In actual crystals, the problem is more complicated because of the presence of three-dimensional arrangement of atoms. The conditions for a crystal to diffract x-rays can be determined by using either Bragg's treatment or Von Laue's treatment.

2.2.1 The Bragg's Treatment : Bragg's Law

In 1912, W.H. Bragg and W.L. Bragg put forward a model which generates the conditions for diffraction in a very simple way. They pointed that a crystal may be divided into various sets of parallel planes. The directions of diffraction lines can then be accounted for if x-rays are considered to be reflected by such a set of parallel atomic planes followed by the constructive interference of the resulting reflected rays. Thus the problem of diffraction of x-rays by the atoms was converted into the problem of reflection of x-rays by the parallel atomic planes. Hence the words 'diffraction' and 'reflection' are mutually interchangeable in Bragg's treatment. Based on these considerations, Braggs derived a simple mathematical

relationship which serves as a condition for the Bragg reflection to occur. This condition is known as the Bragg's law.

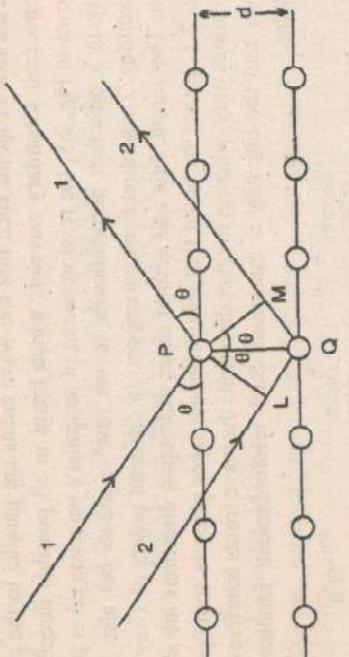


Fig. 2.2. Bragg's reflection of x-rays from the atomic planes.

To obtain the Bragg's law, consider a set of parallel atomic planes with interplanar spacing d and having Miller indices (hkl) . Let a parallel beam of x-rays of wavelength λ be incident on these parallel planes at a glancing angle θ such that the rays lie in the plane of the paper. Consider two such rays 1 and 2 which strike the first two planes and get partially reflected at the same angle θ in accordance with the Bragg's treatment as shown in Fig. 2.2. The diffraction is the consequence of constructive interference of these reflected rays. Let PL and PM be the perpendiculars drawn from the point P on the incident and reflected portions of ray 2 respectively. The path difference between rays 1 and 2 is, therefore, given by $(LQ + QM)$. Since $LQ = QM = d \sin\theta$, we get

$$\text{Path difference} = 2d \sin\theta$$

For constructive interference of rays 1 and 2, the path difference must be an integral multiple of wavelength λ , i.e.,

$$2d \sin\theta = n\lambda \quad (2.1)$$

where n is an integer. This equation is called the Bragg's law. The diffraction takes place for those values of d , θ , λ and n which satisfy the Bragg's condition. In Eq. (2.1), n represents the order of reflection. For $n = 0$, we get the zeroth order reflection which occurs for θ equal to zero, i.e., in the direction of the incident beam and hence it cannot be observed experimentally. For the given values of d and λ , the higher order reflections appear for larger values of θ . The diffraction lines appearing for $n = 1, 2$ and 3 are called first, second and third order diffraction lines respectively and so

on. The intensity of the reflected lines decreases with increase in the value of n or θ . The highest possible order is determined by the condition that $\sin\theta$ cannot exceed unity. Also, since $\sin\theta \leq 1$, λ must be $\leq d$ for Bragg reflection to occur. Taking $d \approx 10^{-10}$ m, we obtain $\lambda \leq 10^{-10}$ m or 1\AA . X-rays having wavelength in this range are, therefore, preferred for analysis of crystal structures.

2.2.2 The Von Laue Treatment : Laue's Equations

Von Laue treated the phenomenon of diffraction in a more general way by considering the scattering of x-rays from individual atoms in the crystal followed by their recombination to obtain the directions of diffraction maxima. It will be shown below that diffraction maxima appear in some specific directions which obey certain conditions known as the Laue's equations. It also proves the validity of Bragg's treatment and the Bragg's law can be derived from the Laue's equations.



Fig. 2.3. Scattering of x-rays from two identical scattering centres separated by a distance r .

Consider the scattering of an incident beam from two identical scattering centres A and B placed at a distance r from each other in a crystal as shown in Fig. 2.3. Let \hat{n}_1 and \hat{n}_2 be the unit vectors in the directions of the incident and scattered beams respectively and let the angle between \hat{n}_1 and \hat{n}_2 be 2θ . Draw BM and AL perpendiculars to the directions of the incident and scattered beams respectively. Then the path difference between the rays scattered from A and B is given by

$$\text{Path difference} = AM - BL = \mathbf{r} \cdot \hat{n}_1 - \mathbf{r} \cdot \hat{n}_2 = \mathbf{r} \cdot (\hat{n}_1 - \hat{n}_2) = \mathbf{r} \cdot \mathbf{N}$$

where $\mathbf{N} = \hat{n}_1 - \hat{n}_2$. As will be seen later, the vector \mathbf{N} happens to be a normal to the reflecting plane. It is a plane which may be assumed to be reflecting the incident ray into the direction of the scattered ray following the ordinary laws of reflection. This is one of the planes which forms the basis of Bragg's treatment. From Fig. 2.4, we find

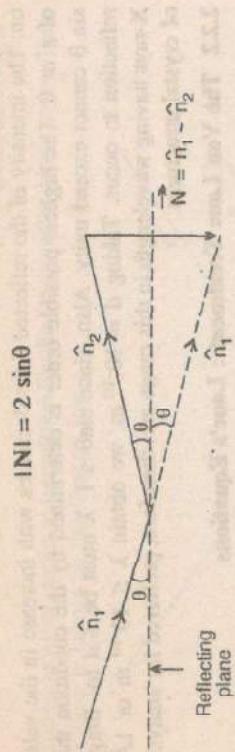


Fig. 2.4. Geometrical relationship of incident beam, scattered beam, reflecting plane and the normal.

The phase difference between the rays scattered from A and B is

$$\frac{2\pi}{\lambda} (\mathbf{r}_B - \mathbf{r}_A) \quad (2.2)$$

The radiations scattered by atoms A and B will interfere constructively only if the phase difference becomes an integral multiple of 2π . Due to periodicity of the crystal, the other atoms placed in the same direction would also scatter the radiations exactly in phase with those scattered from A and B. In a three-dimensional crystal, \mathbf{r} may coincide with any of the three crystallographic axes a , b and c . Thus for the occurrence of a diffraction maximum, the following three conditions must be satisfied simultaneously :

$$\begin{aligned} \frac{2\pi}{\lambda} (\mathbf{a} \cdot \mathbf{N}) &= 2\pi h' = 2\pi nh \\ \frac{2\pi}{\lambda} (\mathbf{b} \cdot \mathbf{N}) &= 2\pi k' = 2\pi nk \\ \frac{2\pi}{\lambda} (\mathbf{c} \cdot \mathbf{N}) &= 2\pi l' = 2\pi nl \end{aligned} \quad (2.3)$$

where h' , k' and l' represent any three integers. While obtaining Eqs. (2.3), it is assumed that atoms A and B are the nearest neighbours and, so, the magnitudes a , b and c represent the interatomic distances along their respective crystallographic directions. The integers h' , k' and l' and h , k , l differ only by a common factor n which may be equal to or greater than unity. Thus the integers h , k and l cannot have a common factor other than unity and resemble the Miller indices of a plane which happens to be the reflecting plane. Let α , β and γ be the angles between the scattering normal N and the crystallographic axes a , b and c respectively. Then,

$$a \cdot N \cos \alpha = 2 \sin \theta \cos \alpha, \text{ and so on.}$$

Therefore, Eqs. (2.3) become

$$\begin{aligned} a \cdot N &= 2a \sin \theta \cos \alpha = h'\lambda = nh\lambda \\ b \cdot N &= 2b \sin \theta \cos \beta = k'\lambda = nk\lambda \\ c \cdot N &= 2c \sin \theta \cos \gamma = l'\lambda = nl\lambda \end{aligned} \quad (2.4)$$

Equations (2.4) are known as *Lau's equations* and represent the conditions for diffraction to occur. In an orthogonal coordinate system, α , β and γ also satisfy the condition

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \quad (2.5)$$

where $\cos \alpha$, $\cos \beta$ and $\cos \gamma$ represent the direction cosines of the scattering normal. The Eqs. (2.4) and (2.5) yield the values of α , β , γ and θ for which diffraction takes place provided h , k , l and n are known. Thus, for a given reflecting plane, Eqs. (2.4) serve to determine unique values of θ and N which define a scattering direction.

From Eqs. (2.4), we also find that, for fixed θ , the direction cosines $\cos \alpha$, $\cos \beta$ and $\cos \gamma$ of the scattering normal are proportional to h/a , k/b and l/c . Also, as described in Sec. 1.9, the direction cosines of the normal to any arbitrary plane $(hk\ell)$ are proportional to h/a , k/b and l/c . This leads to the conclusion that the scattering normal N is the same as the normal to the plane $(hk\ell)$ and hence the arbitrary plane $(hk\ell)$ happens to be the reflecting plane.

To obtain the Bragg's law, consider the expressions for interplanar spacing for the $(hk\ell)$ planes as given by Eq. (1.7), i.e.,

$$d = \frac{a}{h} \cos \alpha = \frac{b}{k} \cos \beta = \frac{c}{l} \cos \gamma$$

In combination with Eqs. (2.4), these yield

$$2d \sin \theta = n\lambda$$

which is the Bragg's law. Here n represents the order of reflection and, as described above, is the greatest common factor among the integers h' , k' and l' in Eqs. (2.4). Thus one may have the planes $(hk\ell)$ and consider different orders of reflection from these; alternatively, one may have the planes $(nh nk nl)$ or $(h'k'l')$ and always consider the first order reflection. The latter practice is normally adopted during the process of structure determination by X-ray diffraction. It is obvious that the n th order reflection from the planes $(hk\ell)$ would overlap with the first order reflection from the planes $(nh nk nl)$ or $(h'k'l')$. Thus, putting n equal to 1, one can get rid of the factor n in the Bragg's equation provided the reflections from all the planes, real or imaginary, having Miller indices with or without a common factor be considered.

2.3 X-RAY DIFFRACTION METHODS

The phenomenon of x-ray diffraction is employed to determine the structure of solids as well as for the study of x-ray spectroscopy. The underlying principle in both the cases is the Bragg's law as given by Eq. (2.1). Considering only the first order reflections from all the possible atomic planes, real or fictitious, the Bragg's law may be written as

$$(2.6) \quad 2d \sin \theta = \lambda$$

The reflections take place for those values of d , θ and λ which satisfy the above equation. For structural analysis, x-rays of known wavelength are employed and the angles for which reflections take place are determined experimentally. The d values corresponding to these reflections are then obtained from Eq. (2.6). Using this information, one can proceed to determine the size of the unit cell and the distribution of atoms within the unit cell. In the x-ray spectroscopy, x-rays are incident on a particular cleavage surface of a single crystal so that the interplanar spacing d is known. The angle for which reflections take place are determined experimentally. The wavelength λ of the incident x-rays is then obtained from Eq. (2.6).

It may be noted that the x-rays used for diffraction purposes should have wavelength which is the most appropriate for producing diffraction effects. Since $\sin \theta$ should be less than unity, Eq. (2.6) yields

$$\lambda < 2d$$

Normally,

$$\begin{aligned} d &\sim 3 \text{ \AA} \\ \lambda &< 6 \text{ \AA} \end{aligned}$$

Longer wavelength x-rays are unable to resolve the details of the structure on the atomic scale whereas shorter wavelength x-rays are diffracted through angles which are too small to be measured experimentally.

In x-ray diffraction studies, the probability that the atomic planes with right orientations are exposed to x-rays is increased by adopting one of the following methods:

- (i) A single crystal is held stationary and a beam of white radiations is inclined on it at a fixed glancing angle θ , i.e., θ is fixed while λ varies. Different wavelengths present in the white radiations select the appropriate reflecting planes out of the numerous present in the crystal such that the Bragg's condition is satisfied. This technique is called the *Lau's technique*.
- (ii) A single crystal is held in the path of monochromatic radiations

and is rotated about an axis, i.e., λ is fixed while θ varies. Different sets of parallel atomic planes are exposed to incident radiations for different values of θ and reflections take place from those atomic planes for which d and θ satisfy the Bragg's law. This method is known as the *rotating crystal method*.

- (iii) The sample in the powdered form is placed in the path of monochromatic x-rays, i.e., λ is fixed while both θ and d vary. Thus a number of small crystallites with different orientations are exposed to x-rays. The reflections take place for those values of d , θ and λ which satisfy the Bragg's law. This method is called the *powder method*.

2.3.1 The Lau's Method

An experimental arrangement used to produce *Lau's pattern* is shown in Fig. 2.5. It consists of a flat plate camera which contains a collimator with a fine hole to obtain a very fine beam of x-rays. The sample is placed on a goniometer which can be rotated to change the orientation of the single crystal. Two flat photographic films are used, one for receiving the transmitted diffracted beam and the other for receiving the reflected diffracted beam for back reflection experiments. Such experiments are performed particularly when there is excessive absorption of x-rays in the crystal.

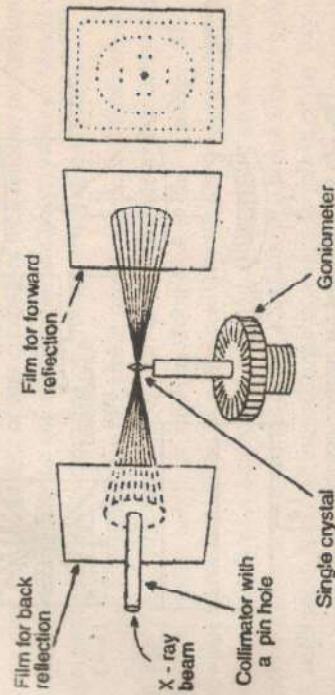


Fig. 2.5. A flat plate camera used in Lau's diffraction method.

Initially, a single crystal specimen having dimensions of the order of $1\text{mm} \times 1\text{mm} \times 1\text{mm}$ is held stationary in the path of white x-rays having wavelengths ranging from 0.2 to 2 \AA . Since the crystal contains a number of sets of parallel atomic planes with different interplanar spacings, diffraction is possible for certain values of λ and d which satisfy the Bragg's condition. Thus diffraction spots are produced on the photographic films as shown in Fig. 2.5. The crystal can be rotated with the help of goniometer to change its orientation with respect to the incident beam. By doing so, the

diffraction condition may be satisfied for a new set of atomic planes and hence a different type of pattern may be obtained on the photographic film. The symmetry of the crystal is, however, reflected in each pattern.

The Laue's method is mostly used to determine the crystal symmetry. For example, if a crystal having four-fold axial symmetry is oriented so that its axis is parallel to the beam, the resulting Laue's pattern also exhibits the four-fold symmetry. The symmetry of the pattern helps to determine the shape of the unit cell. It is, however, not practicable to determine the structure of the crystal by this method. It is because a number of wavelengths may be reflected from a single plane in different orders and may superpose at a single point resulting in the loss of a number of reflections. The symmetry of the Laue's pattern also helps to orient the crystals for various solid state experiments. Another application of the Laue's method is the determination of imperfections or strains in the crystal. An imperfect or strained crystal has atomic planes which are not exactly plane but are slightly curved. Thus instead of sharp diffraction spots one gets streaks in the Laue's pattern. This type of streaking on Laue's photographs is called *astigmatism*.

2.3.2 Rotating Crystal Method

The diffraction takes place from those planes which satisfy the Bragg's law for a particular angle of rotation. The planes parallel to the axis of rotation do not diffract the incident rays in a horizontal plane. However, reflections cannot be observed for those planes which always contain the incident beam. The planes inclined to the rotation axis produce reflections above or below the horizontal plane depending upon the angle of inclination. The horizontal lines produced by diffraction spots on the photographic film are called *layer lines*. If the crystal is positioned such that its c-axis coincides with the axis of rotation, all the planes with Miller indices of the type $(hk0)$ will produce the central layer line. Likewise, the planes having Miller indices of the type (hkl) and $(hk\bar{l})$ will produce the layer lines above and below the central line respectively, and so on. These layer lines are shown in Fig. 2.6c. The vertical spacing between the layer lines depends on the distance between the lattice points along the c-axis. Hence the distance c can be measured from the photographic film. Similarly, one can determine the translation vectors a and b on mounting the crystal along a and b axes respectively. Thus the dimensions of the unit cell can be easily determined.

2.3.3 Powder Method

This is the most widely used diffraction method to determine the structure of crystalline solids. The sample used is in the form of a fine powder containing a large number of tiny crystallites with random orientations. It is prepared by crushing the commonly available polycrystalline material, thus eliminating the tedious process of growing the single crystals.

The experimental arrangement used to produce diffraction is shown in Fig. 2.7. It consists of a cylindrical camera, called the Debye-Scherrer camera, whose length is small as compared to the diameter. The finely powdered sample is filled in a thin capillary tube or is simply pasted on a wire by means of a binder and mounted at the centre of the camera. The capillary tube or wire and the binder should be of a non-diffracting material. A collimated beam of monochromatic x-rays is produced by passing the x-rays through a filter and a collimator. The x-rays enter the camera through the collimator and strike the powdered sample. Since the specimen contains a large number of small crystallites ($\sim 10^{12}$ in 1mm^3 of powder sample) with random orientations, almost all the possible θ and d values are available. The diffraction takes place for those values of d and θ which satisfy the Bragg's condition, i.e., $2d \sin\theta = n\lambda$, λ being a constant in this case. Also, since for a particular value of the angle of incidence θ , numerous orientations of a particular set of planes are possible, the diffracted rays corresponding to fixed values of θ and d lie on the surface of a cone with its apex at the sample and the semivertical angle equal to 2θ . Different cones are observed for different sets of d and θ for a particular value of n , and also for different combinations

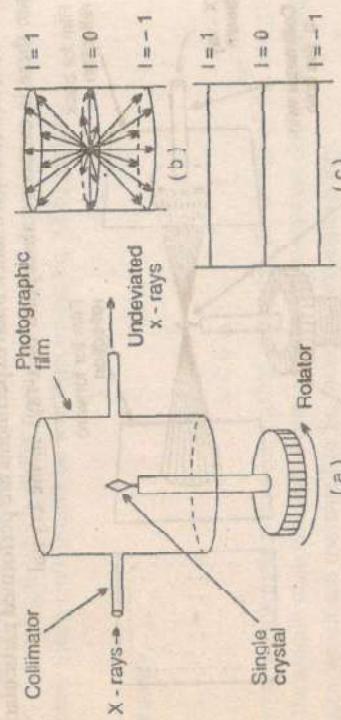


Fig. 2.6. (a) Apparatus for rotating crystal method.
(b) Cones of scattered x-rays corresponding to reflections from (hkl) planes.
(c) Layer lines produced after flattening the photographic film.

In this method, a monochromatic beam of x-rays is incident on a single crystal mounted on a rotating spindle such that one of its crystallographic axes coincides with the axis of rotation which is kept perpendicular to the direction of the incident beam. The single crystal having dimensions of the order of 1mm is positioned at the centre of a cylindrical holder concentric with the rotating spindle as shown in Fig. 2.6. A photographic film is attached at the inner circular surface of the cylinder.

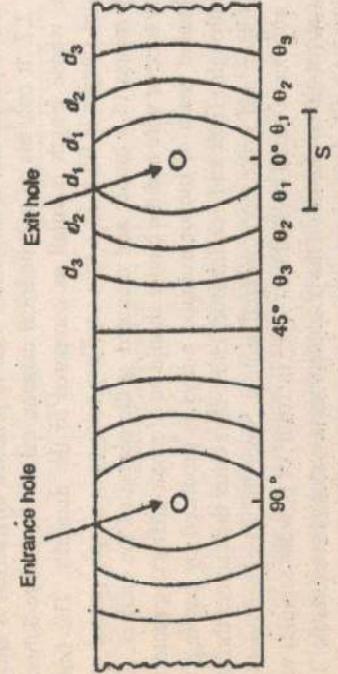
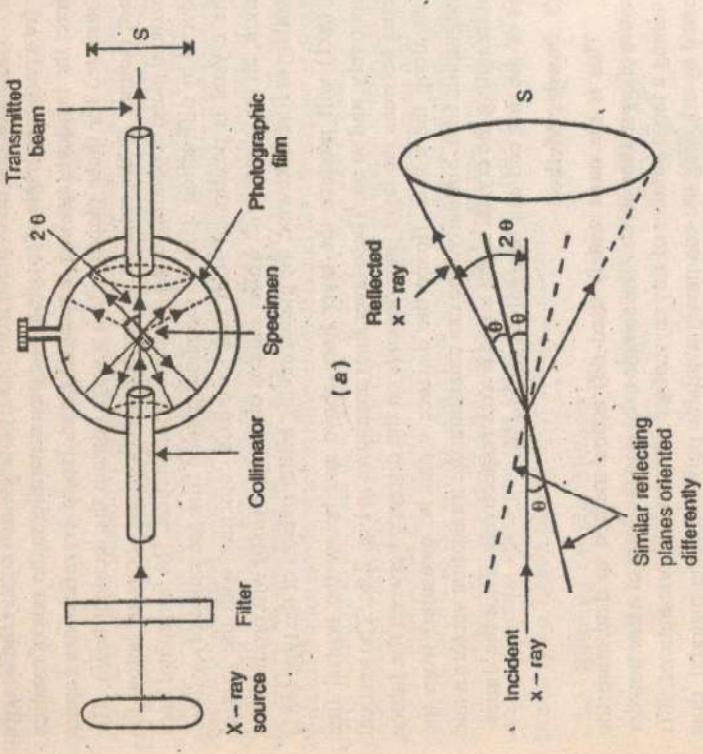


Fig. 2.7. (a) Front view of the Debye-Scherrer Camera.
 (b) A cone produced by reflection of x-rays from identical planes having different orientations.

(c) Flattened photographic film after developing and indexing of diffraction lines.

of θ and n for a particular value of d . The transmitted x-rays move out of the camera through an exit hole located diametrically opposite to the entrance hole. A photographic film is attached to the inner side of the curved surface of the camera. Each cone of the reflected beam leaves two impressions on the film which are in the form of arcs on either side of the exit hole, with their centres coinciding with the hole. Similarly, cones produced by back-reflected x-rays produce arcs on either side of the entrance hole. If the sample consists of coarse grains rather than fine particles, a spotty diffraction pattern may be obtained. This is because a sufficient number of crystallites with all possible orientations may not be available in a coarse-grained sample. In such a case, the sample has to be rotated to obtain almost continuous diffraction arcs. The film is exposed for a long time (- a few hours) in order to obtain reflected lines of sufficiently high intensity. It is then removed from the camera and developed. The arcs produced by reflected rays appear dark on the developed film. The angle θ corresponding to a particular pair of arcs is related to the distance S between the arcs as

$$4\theta \text{ (radians)} = \frac{S/R}{R} \quad (2.7)$$

where R is the radius of the camera. If θ is measured in degrees, the above equation is modified as

$$4\theta \text{ (degrees)} = \frac{57.296S}{R} \quad (2.8)$$

The calculations can be made simpler by taking the radius of the camera in multiples of 57.296. For example, taking $R = 57.296$ mm, we get

$$\theta \text{ (degrees)} = S \text{ (mm)} / 4 \quad (2.9)$$

Thus one-fourth of the distance between the corresponding arcs of a particular pair in mm is a measure of the angle θ in degrees. Knowing all the possible θ 's and considering only the first order reflections from all the possible planes, Eq. (2.6) is used to calculate the interplanar spacing for various sets of parallel planes which contribute to these reflections. Thus, we have

$$d = \lambda / (2 \sin \theta) \quad (2.10)$$

These d values are used to determine the space lattice of the crystal structure.

In modern x-ray diffractometers, the photographic film is replaced by a radiation detector, such as ionization chamber or scintillation detector, which records the positions and relative intensities of the various reflected lines as a function of the angle 2θ . The detector is mounted on a goniometer and is capable of rotation about the sample at different speeds. The whole system is computerised. The availability of a lot of software makes the system versatile.

2.4 RECIPROCAL LATTICE

As described earlier, the diffraction of x-rays occurs from various sets of parallel planes having different orientations (slopes) and interplanar spacings. In certain situations involving the presence of a number of sets of parallel planes with different orientations, it becomes difficult to visualize all such planes because of their two-dimensional nature. The problem was simplified by P.P. Ewald by developing a new type of lattice known as the *reciprocal lattice*. The idea underlying the development was that each set of parallel planes could be represented by a normal to these planes having length equal to the reciprocal of the interplanar spacing. Thus the direction of each normal represents the orientation of the corresponding set of parallel planes and its length is proportional to the reciprocal of the interplanar spacing.

The normals are drawn with reference to an arbitrary origin and points are marked at their ends. These points form a regular arrangement which is called a reciprocal lattice. Obviously, each point in a reciprocal lattice is a representative point of a particular parallel set of planes and it becomes easier to deal with such points than with sets of planes.

A reciprocal lattice to a direct lattice is constructed using the following procedure :

- Take origin at some arbitrary point and draw normals to every set of parallel planes of the direct lattice.
- Take length of each normal equal to the reciprocal of the interplanar spacing for the corresponding set of planes. The terminal points of these normals form the reciprocal lattice.

Consider, for example, a unit cell of monoclinic crystal in which $a \neq b \neq c$, $\alpha = \gamma = 90^\circ$ and $\beta > 90^\circ$ as shown in Fig. 2.8. For simplicity, we orient the unit cell in such a way that the b-axis is perpendicular to the plane of the paper, hence a and c-axes lie in the plane of the paper as shown in Fig. 2.9.

Consider planes of the type $(h\bar{0}l)$ which are parallel to b-axis, i.e., perpendicular to the plane of the paper. Hence normal to these planes lie in the plane of the paper. The planes $(h\bar{0}l)$, being perpendicular to the plane of the paper, are represented by lines. Thus the line (101) in fact means the plane (101), and so on. Taking the point of intersection of the three axes as the origin, normals are drawn to the

planes $(h\bar{0}l)$ and their lengths are taken to be $1/d_{h\bar{0}l}$, where $d_{h\bar{0}l}$ is the interplanar spacing for the planes $(h\bar{0}l)$. For example, since the planes (200) have half the interplanar spacing as compared to the plane (100), the reciprocal lattice point (200) is twice as far away as point (100) from the origin. If normals to all the $(h\bar{k}l)$ planes are drawn, a three-dimensional reciprocal lattice is obtained.

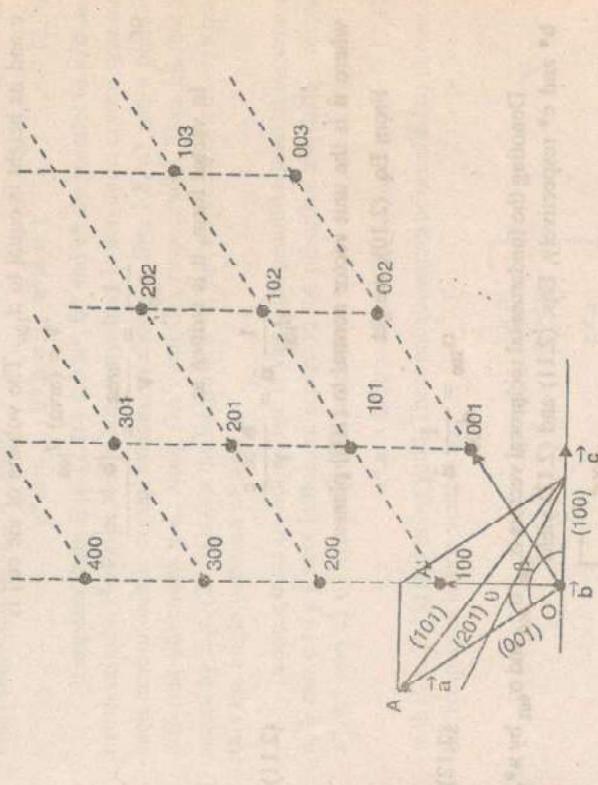


Fig. 2.9. Two-dimensional reciprocal lattice to a monoclinic lattice.
The b-axis is perpendicular to the plane of the paper.

2.4.1 Reciprocal Lattice Vectors

A reciprocal lattice vector, $\sigma_{h\bar{k}l}$, is defined as a vector having magnitude equal to the reciprocal of the interplanar spacing $d_{h\bar{k}l}$ and direction coinciding with normal to the $(h\bar{k}l)$ planes. Thus, we have

$$\sigma_{h\bar{k}l} = \frac{1}{d_{h\bar{k}l}} \hat{n} \quad (2.10)$$

where \hat{n} is the unit vector normal to the $(h\bar{k}l)$ planes. In fact, a vector drawn from the origin to any point in the reciprocal lattice is a reciprocal lattice vector.

Like a direct lattice, a reciprocal lattice also has a unit cell which is of the form of a parallelopiped. The unit cell is formed by the shortest

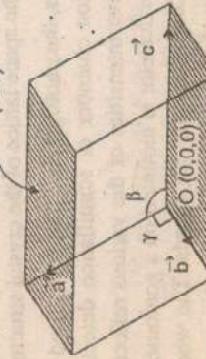


Fig. 2.8. Unit cell of a monoclinic crystal.

normals along the three directions, i.e., along the normals to the planes (100), (010) and (001). These normals produce reciprocal lattice vectors designated as σ_{100} , σ_{010} and σ_{001} which represent the fundamental reciprocal lattice vectors.

Let \mathbf{a} , \mathbf{b} and \mathbf{c} be the primitive translation vectors of the direct lattice as shown in Fig. 2.8. The base of the unit cell is formed by the vectors \mathbf{b} and \mathbf{c} and its height is equal to d_{100} . The volume of the cell is

$$V = (\text{area}) d_{100} \quad (2.11)$$

or

$$\frac{1}{d_{100}} = \frac{\text{area}}{V} = \frac{|\mathbf{b} \times \mathbf{c}|}{V}$$

In vector form, it is written as

$$\frac{1}{d_{100}} \hat{\mathbf{n}} = \frac{\mathbf{b} \times \mathbf{c}}{V} \quad (2.11)$$

where $\hat{\mathbf{n}}$ is the unit vector normal to (100) planes.

From Eq. (2.10), we get

$$\sigma_{100} = \frac{1}{d_{100}} \hat{\mathbf{n}} \quad (2.12)$$

Denoting the fundamental reciprocal vectors σ_{100} , σ_{010} and σ_{001} by \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* respectively, Eqs. (2.11) and (2.12) yield

$$\mathbf{a}^* = \sigma_{100} = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad (2.13)$$

Similarly,

$$\mathbf{b}^* = \sigma_{010} = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad (2.13)$$

and

$$\mathbf{c}^* = \sigma_{001} = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad (2.14)$$

where $\mathbf{a} \cdot \mathbf{b} \times \mathbf{c} = \mathbf{b} \cdot \mathbf{c} \times \mathbf{a} = \mathbf{c} \cdot \mathbf{a} \times \mathbf{b}$ is the volume of the direct cell. Thus the reciprocal translation vectors bear a simple relationship to the crystal translation vectors as

- \mathbf{a}^* is normal to \mathbf{b} and \mathbf{c}
- \mathbf{b}^* is normal to \mathbf{c} and \mathbf{a}
- \mathbf{c}^* is normal to \mathbf{a} and \mathbf{b}

In vector notation, it means

$$\begin{bmatrix} \mathbf{a}^* \cdot \mathbf{b} = 0 & \mathbf{a}^* \cdot \mathbf{c} = 0 \\ \mathbf{b}^* \cdot \mathbf{c} = 0 & \mathbf{b}^* \cdot \mathbf{a} = 0 \\ \mathbf{c}^* \cdot \mathbf{a} = 0 & \mathbf{c}^* \cdot \mathbf{b} = 0 \end{bmatrix} \quad (2.15)$$

Taking scalar product of \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* with \mathbf{a} , \mathbf{b} and \mathbf{c} respectively and using Eqs. (2.13), we find

$$\mathbf{a}^* \cdot \mathbf{a} = 1, \quad \mathbf{b}^* \cdot \mathbf{b} = 1, \quad \mathbf{c}^* \cdot \mathbf{c} = 1 \quad (2.16)$$

It appears from Eqs. (2.16) that \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* are parallel to \mathbf{a} , \mathbf{b} and \mathbf{c} respectively. However, this is not always true. In non-cubic crystal systems, such as monoclinic crystal system, as shown in Fig. 2.8, \mathbf{a}^* and a point in different directions, i.e., along OA' , and OA respectively. Thus all that is meant by Eqs. (2.16) is that the length of \mathbf{a}^* is the reciprocal of $a \cos \theta$, where θ is the angle between \mathbf{a}^* and \mathbf{a} .

In some texts on Solid State Physics, the primitive translation vectors \mathbf{a} , \mathbf{b} and \mathbf{c} of a direct lattice are related to the primitive translation vectors \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* of the reciprocal lattice as

$$\mathbf{a}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{b} = \mathbf{c}^* \cdot \mathbf{c} = 2\pi \quad (2.17)$$

with Eqs. (2.15) still being valid. These equations can be satisfied by choosing the reciprocal lattice vectors as

$$\begin{bmatrix} \mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \\ \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \\ \mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \end{bmatrix} \quad (2.18)$$

It is now obvious that every crystal structure is associated with two important lattices — the direct lattice and the reciprocal lattice. The two lattices are related to each other by Eqs. (2.13). The fundamental translation vectors of the crystal lattice and the reciprocal lattice have dimensions of [length] and [length]⁻¹ respectively. This is why the latter is called the reciprocal lattice. Also, the volume of the unit cell of a reciprocal lattice is inversely proportional to the volume of the unit cell of its direct lattice.

A crystal lattice is a lattice in real or ordinary space, i.e., the space defined by the coordinates; whereas a reciprocal lattice is a lattice in the reciprocal space, associated k-space or Fourier space. A wave vector \mathbf{k} is always drawn in the k-space. The points of the crystal lattice are given by

$$\mathbf{T} = m\mathbf{a} + n\mathbf{b} + p\mathbf{c} \quad (2.19)$$

where m, n and p are integers. Similarly, the reciprocal lattice points or reciprocal lattice vectors may be defined as

$$\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (2.20)$$

where h, k and l are integers. Every point in the Fourier space has a meaning, but the reciprocal lattice points defined by Eq. (2.20) carry a special importance. In order to find the significance of $\mathbf{G}'s$, we take the dot product of \mathbf{G} and \mathbf{T} :

$$\begin{aligned} \mathbf{G} \cdot \mathbf{T} &= (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (m\mathbf{a} + n\mathbf{b} + p\mathbf{c}) \\ &= 2\pi (hm + kn + lp) = 2\pi \text{ (an integer)} \end{aligned}$$

or

$$\exp(i\mathbf{G} \cdot \mathbf{T}) = 1$$

where we have used Eq. (2.17). Thus it is clear from Eq. (2.20) that h, k and l define the coordinates of the points of reciprocal lattice space. In other words, it means that a point (h, k, l) in the reciprocal space corresponds to the set of parallel planes having the Miller indices (hkl) . The concept of reciprocal lattice is useful for redefining the Bragg's condition and introducing the concept of Brillouin zones.

2.4.2 Reciprocal Lattice to SC Lattice

The primitive translation vectors of a simple cubic lattice may be written as

$$\mathbf{a} = a\hat{\mathbf{i}}, \mathbf{b} = a\hat{\mathbf{j}}, \mathbf{c} = a\hat{\mathbf{k}}$$

$$\text{Volume of the simple cubic unit cell} = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$$

$$= a^3 (\hat{\mathbf{i}} \cdot \hat{\mathbf{j}} \times \hat{\mathbf{k}}) = a^3$$

Using Eqs. (2.18), the reciprocal lattice vectors to the sc lattice are obtained as

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} = 2\pi \frac{a\hat{\mathbf{j}} \times a\hat{\mathbf{k}}}{a^3} = \frac{2\pi}{a} \hat{\mathbf{i}} \quad (2.21)$$

Similarly,

$$\mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} = \frac{2\pi}{a} \hat{\mathbf{j}} \quad (2.21)$$

and

$$\mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} = \frac{2\pi}{a} \hat{\mathbf{k}} \quad (2.21)$$

The Eqs. (2.21) indicate that all the three reciprocal lattice vectors are equal in magnitude which means that the reciprocal lattice to sc lattice is also simple

cubic but with lattice constant equal to $2\pi/a$.

2.4.3 Reciprocal Lattice to BCC Lattice

The primitive translation vectors of a body-centred cubic lattice, as shown in Fig. 2.10, are

$$\begin{aligned} \mathbf{a}' &= \frac{a}{2} (\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}}) \\ \mathbf{b}' &= \frac{a}{2} (-\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}}) \\ \mathbf{c}' &= \frac{a}{2} (\hat{\mathbf{i}} - \hat{\mathbf{j}} + \hat{\mathbf{k}}) \end{aligned} \quad (2.22)$$

Fig. 2.10. Primitive translation vectors of a bcc lattice.
where a is the length of the cube edge
and $\hat{\mathbf{i}}, \hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$ are the orthogonal unit vectors along the cube edges. The volume of the primitive cell is given by

$$\begin{aligned} V &= \mathbf{a}' \cdot \mathbf{b}' \times \mathbf{c}' = \frac{a}{2} (\hat{\mathbf{i}} + \hat{\mathbf{j}} - \hat{\mathbf{k}}) \cdot \left[\frac{a^2}{4} (-\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}}) \times (\hat{\mathbf{i}} - \hat{\mathbf{j}} + \hat{\mathbf{k}}) \right] \\ &= \frac{a}{2} (\hat{\mathbf{i}} + \hat{\mathbf{j}} - \hat{\mathbf{k}}) \cdot \frac{a^2}{2} (\hat{\mathbf{i}} + \hat{\mathbf{j}}) \\ &= a^3/2 \end{aligned}$$

Using Eqs. (2.18), the reciprocal lattice vectors are obtained as

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b}' \times \mathbf{c}'}{\mathbf{a}' \cdot \mathbf{b}' \times \mathbf{c}'} = \frac{2\pi(a^2/2)}{a^3/2} (\hat{\mathbf{i}} + \hat{\mathbf{j}}) = \frac{2\pi}{a} (\hat{\mathbf{i}} + \hat{\mathbf{j}}) \quad (2.23)$$

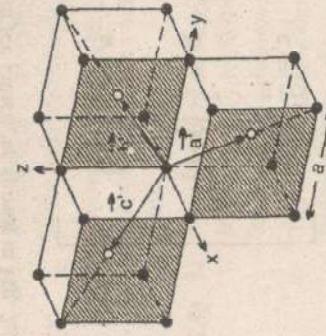
Similarly,

$$\mathbf{b}^* = 2\pi \frac{\mathbf{c}' \times \mathbf{a}'}{\mathbf{a}' \cdot \mathbf{b}' \times \mathbf{c}'} = \frac{2\pi}{a} (\hat{\mathbf{j}} + \hat{\mathbf{k}}) \quad (2.23)$$

and

$$\mathbf{c}^* = 2\pi \frac{\mathbf{a}' \times \mathbf{b}'}{\mathbf{a}' \cdot \mathbf{b}' \times \mathbf{c}'} = \frac{2\pi}{a} (\hat{\mathbf{k}} + \hat{\mathbf{i}}) \quad (2.23)$$

As will be seen later, these are the primitive translation vectors of an fcc lattice. Thus the reciprocal lattice to a bcc lattice is fcc lattice.



Solid State Physics

2.5 PROPERTIES OF RECIPROCAL LATTICE

1. Each point in a reciprocal lattice corresponds to particular set of parallel planes of the direct lattice.
2. The distance of a reciprocal lattice point from an arbitrarily fixed origin is inversely proportional to the interplanar spacing of the corresponding parallel planes of the direct lattice.
3. The volume of a unit cell of the reciprocal lattice is inversely proportional to the volume of the corresponding unit cell of the direct lattice.
4. The unit cell of the reciprocal lattice need not be a parallelepiped. It is customary to deal with Wigner-Seitz cell of the reciprocal lattice which constitutes the Brillouin zone.
5. The direct lattice is the reciprocal lattice to its own reciprocal lattice. Simple cubic lattice is self-reciprocal whereas bcc and fcc lattices are reciprocal to each other.

2.6. BRAGG'S LAW IN RECIPROCAL LATTICE

- The Bragg's diffraction condition obtained earlier by considering reflection from parallel lattice planes can be used to express geometrical relationship between the vectors in the reciprocal lattice. Consider a reciprocal lattice as shown in Fig. 2.12. Starting from the point A (not necessarily a reciprocal lattice point), draw a vector \vec{AO} of length $1/\lambda$ in the direction of the incident x-ray beam which terminates at the origin O of the reciprocal lattice. Taking A as the centre, draw a sphere of radius \vec{AO} which may intersect some point B of the reciprocal lattice.

Using Eqs. (2.18), the primitive translation vectors of the reciprocal lattice are obtained as

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b}' \times \mathbf{c}'}{\mathbf{a}' \cdot \mathbf{b}' \times \mathbf{c}'} = 2\pi \frac{(\mathbf{a}^2/4)(\hat{\mathbf{i}} + \hat{\mathbf{j}} - \hat{\mathbf{k}})}{\mathbf{a}^3/4} = \frac{2\pi}{\mathbf{a}^3/4} (\hat{\mathbf{i}} + \hat{\mathbf{j}} - \hat{\mathbf{k}}) \quad (2.25)$$

Similarly,

$$\mathbf{b}^* = 2\pi \frac{\mathbf{c}' \times \mathbf{a}'}{\mathbf{a}' \cdot \mathbf{b}' \times \mathbf{c}'} = \frac{2\pi}{\mathbf{a}^3/4} (-\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}})$$

and

$$\mathbf{c}^* = 2\pi \frac{\mathbf{a}' \times \mathbf{b}'}{\mathbf{a}' \cdot \mathbf{b}' \times \mathbf{c}'} = \frac{2\pi}{\mathbf{a}^3/4} (\hat{\mathbf{i}} - \hat{\mathbf{j}} + \hat{\mathbf{k}})$$

Comparing Eqs. (2.25) with Eqs. (2.22), we find that these are the primitive translation vectors of a bcc lattice having length of the cube edge as $2\pi/a$. Thus the reciprocal lattice to an fcc lattice is a bcc lattice.

2.4.4 Reciprocal Lattice to FCC Lattice

The primitive translation vectors of an fcc lattice, as shown in Fig. 2.11, are

$$\left[\begin{aligned} \mathbf{a}' &= \frac{\mathbf{a}}{2} (\hat{\mathbf{i}} + \hat{\mathbf{j}}) \\ \mathbf{b}' &= \frac{\mathbf{a}}{2} (\hat{\mathbf{j}} + \hat{\mathbf{k}}) \\ \mathbf{c}' &= \frac{\mathbf{a}}{2} (\hat{\mathbf{k}} + \hat{\mathbf{i}}) \end{aligned} \right] \quad (2.24)$$

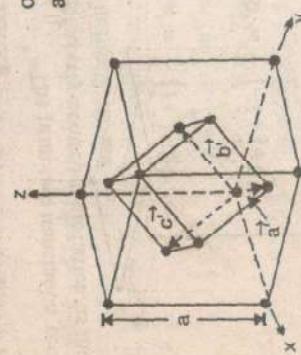


Fig. 2.11: Primitive translation vectors of an fcc lattice.

given by

$$\begin{aligned} V &= \mathbf{a}' \cdot \mathbf{b}' \times \mathbf{c}' \\ &= \frac{\mathbf{a}}{2} (\hat{\mathbf{i}} + \hat{\mathbf{j}}) \cdot \frac{\mathbf{a}^2}{4} [(\hat{\mathbf{j}} + \hat{\mathbf{k}}) \times (\hat{\mathbf{k}} + \hat{\mathbf{i}})] \\ &= \frac{\mathbf{a}}{2} (\hat{\mathbf{i}} + \hat{\mathbf{j}}) \cdot \frac{\mathbf{a}^2}{4} (\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}}) \\ &= \mathbf{a}^3/4 \end{aligned}$$

Using Eqs. (2.18), the primitive translation vectors of the reciprocal lattice are obtained as

$$|\vec{OB}| = nld_{hk\ell} \quad (2.26)$$

It follows from the geometry of Fig. 2.12, that one such plane is the plane AE. If $\angle EAO = \theta$ is the angle between the incident ray and the normal, then from ΔAOB , we have

$$OB = 2 OE = 2 OA \sin\theta = (2 \sin\theta)/\lambda \quad (2.27)$$

From Eqs. (2.26) and (2.27), we get

$$(2 \sin\theta)/\lambda = n/d_{hk\ell}$$

These four lines, i.e., $k_x = \pm\pi/a$ and $k_y = \pm\pi/a$, are plotted in Fig. 2.14. Taking origin as shown, all the \mathbf{k} -vectors originating from it and terminating on these lines will produce Bragg reflection. The square bounded by these four lines is called the *first Brillouin zone*. Thus the first zone of a square lattice of side a is a square of side $2\pi/a$. In addition to this set of lines, some other sets of lines are also possible which satisfy (2.31). For example, for $h = \pm 1$ and $k = \pm 1$, the condition (2.31) gives the following set of four lines.

$$\pm k_x \pm k_y = 2\pi/a$$

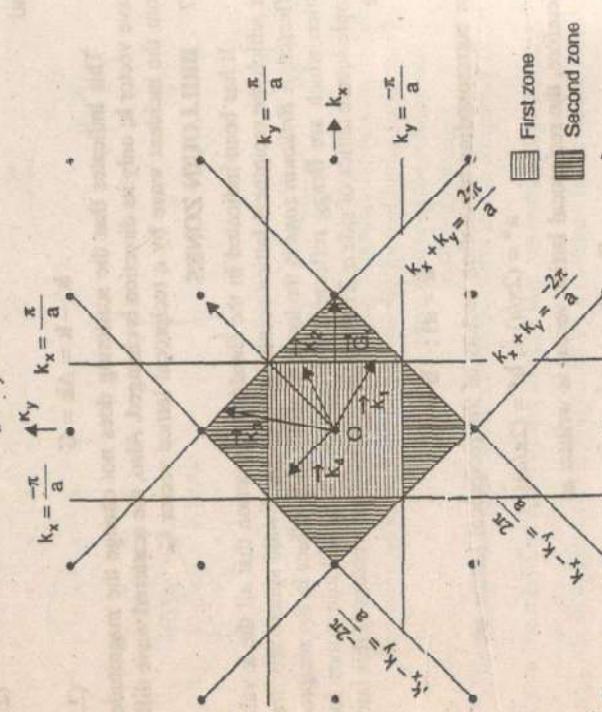


Fig. 2.14. Brillouin zones of a square lattice in its reciprocal lattice. The vectors \mathbf{k}_x , \mathbf{k}_y , and \mathbf{k}_z are Bragg reflected whereas \mathbf{k}_4 is not. The vectors \mathbf{k}_1 and \mathbf{k}_2 have the same reciprocal lattice vector \mathbf{G}_1 , while \mathbf{G}_2 is the reciprocal vector of \mathbf{k}_3 . These lines are also plotted in Fig. 2.14. The additional area bounded by these four lines is the *second Brillouin zone*. Similarly the other zones can be constructed. The boundaries of the Brillouin zones represent the loci of \mathbf{k} -values that are Bragg reflected and hence may be considered as the reflecting planes. The boundaries of the first zone represent the reflecting planes for the first order reflection, those of the second zone represent the reflecting planes for the second order reflection, and so on. A \mathbf{k} -vector that does not terminate at a zone boundary cannot produce Bragg reflection. Thus the Brillouin zone pattern can be employed to determine the x-ray diffraction pattern of a crystal and vice versa.

The Brillouin zones for a three-dimensional cubical lattice are constructed using the generalized equation

$$hk_x + hk_y + hk_z = -(xa)(h^2 + k^2 + l^2) \quad (2.32)$$

where a is the length of the cube edge. It is clear from Eq. (2.32) that the first zone is a cube having side equal to $2\pi/a$. The second zone is formed by adding pyramids to each face of the cube (first zone) as triangles are added to the square in two dimensions, and so on.

There is another simple method to determine Brillouin zones. We note from Fig. 2.14 that the reciprocal lattice vector \mathbf{G} which satisfies Eq. (2.28) is a perpendicular bisector of the zone boundary and all the \mathbf{k} -vectors lying on this boundary have the same \mathbf{G} for reflection. Thus it is sufficient to consider only the allowed \mathbf{G} -values and their normal bisectors to construct the Brillouin zones. The first Brillouin zone is the region bounded by the normal bisectors of the shortest possible \mathbf{G} -vectors, the second zone is the region bounded by the normal bisectors of the next larger \mathbf{G} -vectors, and so on. This method will be used to determine the Brillouin zones of the *bcc* and *fcc* lattices as given below.

2.7.1 Brillouin Zone of BCC Lattice

The primitive translation vectors of a *bcc* lattice are

$$\begin{aligned} \mathbf{a} &= (\alpha/2)(\hat{i} + \hat{j} - \hat{k}) \\ \mathbf{b} &= (\alpha/2)(-\hat{i} + \hat{j} + \hat{k}) \\ \mathbf{c} &= (\alpha/2)(\hat{i} - \hat{j} + \hat{k}) \end{aligned}$$

The primitive translation vectors of its reciprocal lattice are (Sec. 2.4.3)

$$\begin{aligned} \mathbf{a}^* &= (2\pi/a)(\hat{i} + \hat{j}) \\ \mathbf{b}^* &= (2\pi/a)(\hat{j} + \hat{k}) \\ \mathbf{c}^* &= (2\pi/a)(\hat{k} + \hat{i}) \end{aligned}$$

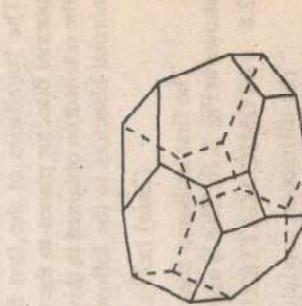


Fig. 2.15. First Brillouin zone of a bcc lattice.

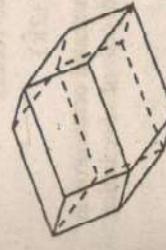


Fig. 2.16. First Brillouin zone of an fcc lattice.

The G-type reciprocal lattice vector is

$$\begin{aligned} \mathbf{G} &= h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \\ &= (2\pi/a) [(h+k)\hat{\mathbf{i}} + (h+k+l)\hat{\mathbf{k}}] \end{aligned} \quad (2.33)$$

The shortest non-zero G's are the following twelve vectors

$$(2\pi/a)(\pm\hat{\mathbf{i}} \pm \hat{\mathbf{j}}); (2\pi/a)(\pm\hat{\mathbf{j}} \pm \hat{\mathbf{k}}); (2\pi/a)(\pm\hat{\mathbf{k}} \pm \hat{\mathbf{i}})$$

The first Brillouin zone is the region enclosed by the normal bisector planes to these twelve vectors. This zone has the shape of a regular twelve-faced solid as shown in Fig. 2.15 and is called rhombic dodecahedron.

2.7.2 Brillouin Zone of FCC Lattice

The primitive translation vectors of an fcc lattice are

$$\begin{aligned} \mathbf{a} &= (a/2)(\hat{\mathbf{i}} + \hat{\mathbf{j}}) \\ \mathbf{b} &= (a/2)(\hat{\mathbf{j}} + \hat{\mathbf{k}}) \\ \mathbf{c} &= (a/2)(\hat{\mathbf{k}} + \hat{\mathbf{i}}) \end{aligned}$$

The primitive translation vectors of its reciprocal lattice are (Sec. 2.4.4)

$$\begin{aligned} \mathbf{a}^* &= (2\pi/a)(\hat{\mathbf{i}} + \hat{\mathbf{j}} - \hat{\mathbf{k}}) \\ \mathbf{b}^* &= (2\pi/a)(-\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}}) \\ \mathbf{c}^* &= (2\pi/a)(\hat{\mathbf{i}} - \hat{\mathbf{j}} + \hat{\mathbf{k}}) \end{aligned}$$

The G-type vector is

$$\begin{aligned} \mathbf{G} &= h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \\ &= (2\pi/a)[(h-k+l)\hat{\mathbf{i}} + (h+k-l)\hat{\mathbf{j}} + (-h+k+l)\hat{\mathbf{k}}] \end{aligned} \quad (2.34)$$

The shortest non-zero G's are the following eight vectors

$$(2\pi/a)(\pm\hat{\mathbf{i}} \pm \hat{\mathbf{j}} \pm \hat{\mathbf{k}})$$

The boundaries of the first Brillouin zone are determined mostly by the normal bisector planes to the above eight vectors. However, the corners of the octahedron obtained in this manner are truncated by the planes which are normal bisectors to the following six reciprocal lattice vectors

$$(2\pi/a)(\pm 2\hat{\mathbf{i}}); (2\pi/a)(\pm 2\hat{\mathbf{j}}); (2\pi/a)(\pm 2\hat{\mathbf{k}})$$

The first Brillouin zone has the shape of the truncated octahedron as shown in Fig. 2.16. This is also one of the primitive unit cells of a bcc lattice.

2.8 ATOMIC SCATTERING FACTOR

The diffraction conditions given by Bragg and Laue are concerned with scattering of x-rays from point scattering centres arranged on a space lattice. Since an electron is the smallest scattering centre, the diffraction conditions would ideally be applicable to a lattice in which every lattice point is occupied by an electron. This is, however, not a realistic situation. Lattice

points are always occupied by atoms which may contain a number of electrons. Also, since the wavelength of x-rays used for diffraction purposes is of the order of atomic dimensions, the x-rays scattered from different portions of an atom are, in general, not in phase. Thus the amplitude of radiation scattered by a single atom is not necessarily equal to the product of the amplitude of radiation scattered by a single electron and the number of electrons (atomic number, Z) present in the atom. It is generally less than this value. The atomic scattering factor or form factor, f , describes the scattering power of a single atom in relation to the scattering power of a single electron and is given by

$$f = \frac{\text{amplitude of radiation scattered from an atom}}{\text{amplitude of radiation scattered from an electron}}$$

In general, $f < Z$. It approaches Z in the limiting case.

Another type of scattering centres in the atoms may be nuclei, but due to their weak interaction with x-rays, the scattering due to nuclei is neglected compared with that due to electrons.

To calculate f , consider an atom containing electrons arranged in a spherically symmetric configuration around its centre which is taken as origin. Let r be the radius of the atom and $\rho(r)$ the charge density at a point r . Considering a small volume element dV at r , the charge located at r is $\rho(r)dV$. We first consider the scattering from the charge $\rho(r)dV$ and an electron located at the origin. If

Fig. 2.17. Geometry of x-ray scattering for the calculation of the atomic scattering factor.

as shown in Fig. 2.17, the phase difference between the wave scattered from the charge $\rho(r)dV$ and that scattered from the electron, in accordance with Eq. (2.2), is given by

$$\phi_r = (2\pi/\lambda) \mathbf{r} \cdot \mathbf{N} \quad (2.35)$$

where \mathbf{N} is the scattering normal. Let the scattering amplitude from the point electron in the direction $\hat{\mathbf{n}}_2$ be written as $Ae^{i(kx-\phi)} e^{i\theta}$ where x is the distance covered along $\hat{\mathbf{n}}_2$ and k is the wave number. Then the scattering amplitude from the charge $\rho(r)dV$ in the same direction will be proportional to the magnitude of the charge and will contain the phase factor $e^{i\phi_r}$, i.e., it is of the form

$$Ae^{i(kr-\omega t)+i\theta} \rho(r)dV$$

Therefore, the ratio of the amplitude of the radiation scattered by the charge element to that scattered by a point electron at the origin is

$$\frac{df}{dV} = \frac{Ae^{i(kx - \omega t) + i\phi_r} p(r) dr}{Ae^{i(kx - \omega t)}}$$

$$= e^{i\mu r} \cdot p(r) dr$$

Thus the ratio of the amplitude from the whole atom to that from an electron is

$$f = \int_V p(r) e^{i\mu r} dr \quad (2.36)$$

where V is the volume of the atom. Since electrons in the atom have spherically symmetric charge distribution, $p(r)$ is a function of r only. Using spherical polar coordinates, we obtain

$$dr = 2\pi r^2 \sin\theta d\phi dr \quad (2.37)$$

Also, from Sec. 2.2.2, we have

$$|N| = 2 \sin\theta$$

Therefore, the Eq. (2.35) becomes

$$\phi_r = (2\pi/\lambda) r N \cos\phi = (4\pi/\lambda) r \sin\theta \cos\phi = \mu r \cos\phi \quad (2.38)$$

where

$$\mu = (4\pi/\lambda) \sin\theta$$

From Eqs. (2.36), (2.37) and (2.38), we get

$$f = \int_{r=0}^{\infty} \int_{\phi=0}^{\pi} p(r) e^{i\mu r \cos\phi} 2\pi r^2 \sin\theta d\phi dr$$

$$\int e^{i\mu r \cos\phi} \sin\theta d\phi = \frac{2(\sin\mu r)}{\mu r} \quad (2.40)$$

$$f = \int_0^{\infty} 4\pi r^2 p(r) \frac{\sin\mu r}{\mu r} dr$$

This is the general expression for atomic scattering factor. A further evaluation needs information about the charge distribution. This type of information may be obtained from a Hartree approximation, or from the statistical model of Thomas and Fermi if atoms contain a large number of electrons (beyond rubidium). These models, however, are strictly applicable to free atoms only. Nevertheless, the results obtained by the application of

these models are fairly accurate and match with the experimental values of x-ray intensities. For example, the variation of f with $(\sin\theta)/\lambda$ for magnesium ($Z = 12$) is shown in Fig. 2.18. It is clear that $f \rightarrow Z$ as $\theta \rightarrow 0$. The same result can also be obtained from Eq. (2.40), since for $\theta \rightarrow 0$, $\mu \rightarrow 0$ and $(\sin\mu)/\mu r \rightarrow 1$, and we get

$$f = \int_0^{\infty} 4\pi r^2 p(r) dr \quad (2.36)$$

The integrand represents the charge inside a spherical shell of radius r and thickness dr . Hence the integral gives the total electronic charge stored inside the atom, i.e., Z .

2.9 GEOMETRICAL STRUCTURE FACTOR

The intensity of an x-ray beam diffracted from a crystal not only depends upon the atomic scattering factors of the various atoms involved but also on the contents of the unit cell, i.e., on the number, type and distribution of atoms within the cell. The x-rays scattered from different atoms of the unit cell may or may not be in phase with each other. It is, therefore, important to know the effect of various atoms present in the unit cell on the total scattering amplitude in a given direction. The total scattering amplitude $F(hk\ell)$ for the reflection $(hk\ell)$ is defined as the ratio of the amplitude of radiation scattered by the entire unit cell to the amplitude of radiation scattered by a single point electron placed at the origin for the same wavelength. It is given by

$$F(hk\ell) = \sum_j f_j e^{i(2\pi/\lambda)(r_j \cdot N)} \quad (2.41)$$

where f_j is the atomic scattering factor for the j th atom, ϕ_j is the phase difference between the radiation scattered from the j th atom of the unit cell and that scattered from the electron placed at the origin. The expression for ϕ_j follows from Eq. (2.2), r_j is the position of j th atom and N is the scattering normal. Also, the summation in Fig. (2.41) extends over all the atoms present

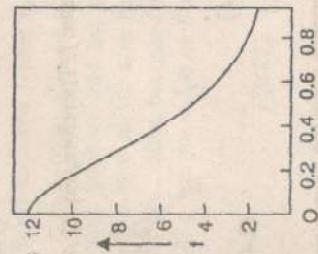


Fig. 2.18. Atomic scattering factor versus $\frac{\sin\theta}{\lambda(\text{\AA})}$ for magnesium.

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62 in the unit cell. If (u_j, v_j, w_j) represent the coordinates of j th atom, we can write

$$\mathbf{r}_j = u_j \mathbf{a} + v_j \mathbf{b} + w_j \mathbf{c} \quad (2.42)$$

From Eqs. (2.3), $a.N = h'\lambda$, etc.

$$\mathbf{r}_j \cdot \mathbf{N} = \lambda (u_j h' + v_j k' + w_j l') \quad (2.43)$$

and Eq. (2.41) becomes

$$F(h'k'l') = \sum_j f_j e^{i2\pi(u_j h' + v_j k' + w_j l')} \quad (2.44)$$

For identical atoms, all the f_j 's have the same value f . Therefore, Eq. (2.43) takes a simple form

$$F(h'k'l') = f S \quad (2.44)$$

where

$$S = \sum_j e^{i2\pi(u_j h' + v_j k' + w_j l')} \quad (2.45)$$

is called the *geometrical structure factor* as it depends upon the geometrical arrangement of atoms within the unit cell. Equation (2.44) defines the structure factor as the ratio of the total scattering amplitude to the atomic scattering factor. For dissimilar atoms, Eq. (2.43) should be used instead of Eq. (2.44). Now since the intensity of a radiation is proportional to the square of its amplitude, the intensity of diffracted beam may be written, by using Eq. (2.43), as

$$I = |F|^2 = F^* F = \left[\sum_j f_j \cos 2\pi(u_j h' + v_j k' + w_j l') \right]^2 + \left[\sum_j f_j \sin 2\pi(u_j h' + v_j k' + w_j l') \right]^2 \quad (2.46)$$

where F^* is the complex conjugate of F . It to be noted that, whereas the space lattice of a crystal structure may be defined from the position of basis diffraction lines in the x-ray diffraction pattern, the determination of basis diffraction lines. Thus the concept of structure factor carries a special importance in the context of structure determination. The structure factors for some simple crystals are calculated below and the intensity of various orders of reflections associated with these structures is discussed.

(i) Simple Cubic Crystals

The effective number of atoms in a unit cell of simple cubic structure is one. Assuming that it lies at the origin, the structure factor given by Eq. (2.45) comes out to be unity. The diffraction amplitude, from Eq. (2.44), becomes

$$F(h'k'l') = f$$

Thus all the diffraction lines predicted by the Bragg's law would appear in the diffraction pattern provided the value of f is large enough to produce peaks of observable intensity.

(ii) Body-Centred Cubic Crystals

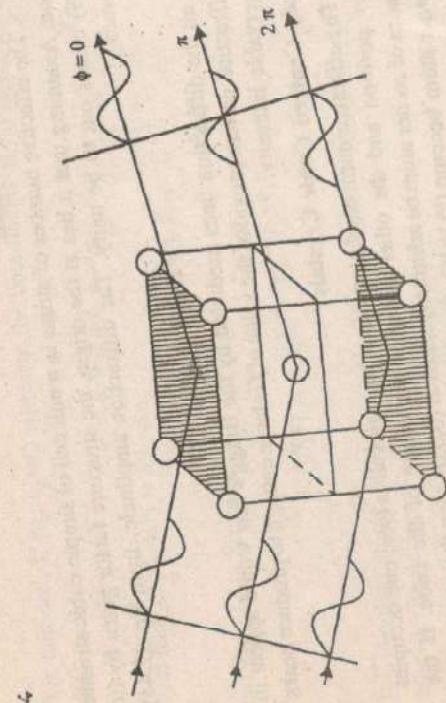
The effective number of atoms in a bcc unit cell is two; one occupies a corner position and the other occupies the centre of the cube. If the coordinates of corner atom be arbitrarily taken as $(0,0,0)$, then the coordinates of other atom become $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Since both the atoms are identical, Eq. (2.44) gives the value of F as

$$F(h'k'l') = f \sum_j e^{2\pi(i(u_j h' + v_j k' + w_j l'))} \\ = f [1 + e^{i2\pi(h' + k' + l')}] \quad (2.47)$$

The expression within the square brackets represents the structure factor for bcc crystal. Here it has been assumed that only one of the eight corners of the cube is occupied and has the coordinates $(0,0,0)$. The validity of this assumption can be verified by considering all the corner positions and using the fact that the contribution of each corner atom is $1/8$. This yields the same structure factor as included in Eq. (2.47).

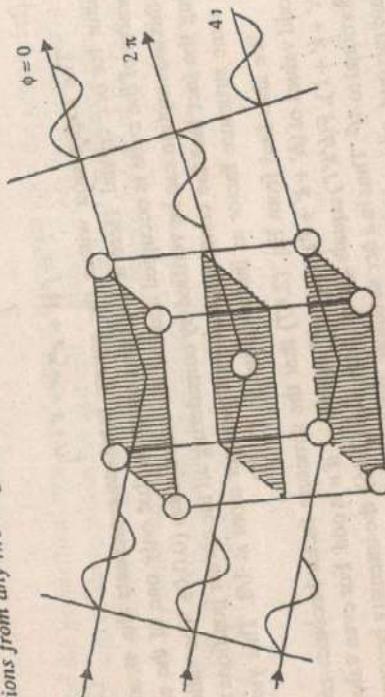
We also find from Eq. (2.47) that the structure factor becomes zero for odd values of $(h' + k' + l')$, since $e^{i\pi(n)}$ equals -1 if n is odd. For even values of $(h' + k' + l')$, $F(h'k'l')$ equals $2f$ and, from Eq. (2.46), the intensity becomes proportional to $4f^2$. Thus in a bcc structure, reflections like $(100), (111), (210)$, etc. are missing, whereas the diffraction lines corresponding to $(110), (200), (222)$, etc. reflections are present. It is to be noted that the presence or absence of a reflection is considered only in terms of the first order reflection. This is because the Miller indices of the planes $(h'k'l')$ used in Eq. (2.43) may have a common factor n ; thus we determine reflections from the planes $(nh nk nl)$. As described earlier, the appropriate Bragg's law applicable to such a case is

$$2d_{hkl} \sin \theta = \lambda. \quad (2.48)$$



(a)

Fig. 2.19. (a) First order reflections from (100) planes (shaded) in a bcc crystal. The reflections from any two neighbouring planes exactly cancel each other.



(b)

Fig. 2.19. (b) Second order reflections from (100) planes or first order reflections from (200) planes (shaded). The path difference between the rays reflected from any two neighbouring planes is λ , which means constructive superposition of waves. We have noted that the first order reflection from (100) planes is absent, whereas a similar reflection from (200) planes is present. It is also easy to find that the second order reflection from (100) bcc crystal is absent, whereas a similar reflection from (200) planes is present and it is this reflection which appears at the position of the first order reflection from (200) planes. This can be understood from Fig. 2.19a. The Eq. (2.48) indicates that the reflections from two neighbouring

$h'k'l'$) planes have a path difference of λ or the phase difference of 2π . Thus considering reflections from (100) planes as shown in Fig. 2.19a, we find that the waves reflected from the top and bottom surfaces of the cube differ in phase by 2π . Since in bcc crystals, there exists a central plane which is exactly identical to the (100) planes, a wave reflected from this plane must have a phase difference of π relative to its neighbouring (100) planes. Thus the diffracted beams from a regular (100) plane and a body centre plane interfere destructively in pairs causing absence of (100) reflection. Similarly, by using Eq. (2.48), it can be shown that the first order reflections from any two neighbouring (200) planes must differ in phase by 2π radians and hence undergo constructive interference causing the occurrence of these reflections in bcc crystals. The presence of second order reflections from (100) planes can be shown by using Eq. (2.1). The second order reflection from two neighbouring (100) planes has a phase difference of 4π radians, which means that the reflection from the middle plane would differ from the reflections from top and bottom planes by a phase difference of 2π . The situation is exactly identical to that shown in Fig. 2.19b, thus indicating that the second order reflection from (100) planes is present. As described earlier, it overlaps with the first order reflection from (200) planes.

(iii) Face-Centred Cubic Crystal

An fcc unit cell has four identical atoms. One of these atoms is contributed by corners and may arbitrarily be assigned coordinates (0,0,0), whereas the other three are contributed by face centres and have the coordinates $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(0, \frac{1}{2}, \frac{1}{2})$. From Eq. (2.39), the diffraction amplitude becomes

$$F(h'k'l') = f [1 + e^{i\vec{k}(h+k)} + e^{i\vec{k}(h+k+l)} + e^{i\vec{k}(k+l)}]$$

where the expression within the square brackets is the structure factor for fcc crystals. It is obvious that the structure factor is non-zero only if h, k and l are all even or all odd and has a value equal to 4. Thus the diffraction amplitude becomes 4f and the intensity becomes proportional to $16f^2$. The structure factor vanishes for all other odd-even combinations of h, k and l . Hence reflections of the type (111), (200), (220), etc. are present, whereas those of the type (100), (110), (211), etc. are absent for an fcc crystal.

The conclusions drawn above regarding allowed reflections for sc, bcc and fcc crystals are summarized in Table 2.1 and are called extinction rules. The extinction rules for dc structure are also included.

TABLE 2.1 Extinction rules for cubic crystals.

Crystal	Reflections allowed for
SC	all possible values of h , k and l
BCC	even values of $(h+k+l)$
FCC	all odd or all even values of h , k and l
DC	all odd h , k and l , or all even h , k and l with $(h+k+l)$ divisible by 4

The ratios of $(h^2 + k^2 + l^2)$ values for allowed reflections from cubic crystals as obtained from the extinction rules are given as follows :

$$\text{SC} : 1 : 2 : 3 : 4 : 5 : 6 : 8 \dots$$

$$\text{BCC} : 2 : 4 : 6 : 8 : 10 : 12 : 14 \dots$$

$$\text{or } 1 : 2 : 3 : 4 : 5 : 6 : 7 \dots$$

$$\text{FCC} : 3 : 4 : 8 : 11 : 12 : 16 : 19 \dots$$

$$\text{DC} : 3 : 8 : 11 : 16 : 19 \dots$$

A comparison of these ratios with the observed ratios of $\sin^2\theta$ values is made to identify the cubic crystal structures.

SOLVED EXAMPLES

Example 2.1. An x-ray beam of wavelength 0.71\AA is diffracted by a cubic KCl crystal of density $1.99 \times 10^3 \text{ kgm}^{-3}$. Calculate the interplanar spacing for (200) planes and the glancing angle for the second order reflection from these planes. The molecular weight of KCl is 74.6 amu and the Avogadro's number is $6.023 \times 10^{26} \text{ kg}^{-1} \text{ mole}^{-1}$.

Solution. For cubic crystals, we have

$$a^3 = \frac{n' M}{N \rho}$$

where a is the lattice constant, n' is the number of molecules in a unit cell, M is the molecular weight, N is the Avogadro's number and ρ is the density. KCl has the same structure as NaCl

$$n' = 4$$

$$\therefore a^3 = \frac{4 \times 74.6}{6.023 \times 10^{26} \times 1.99 \times 10^3} = 0.249 \times 10^{-27} \text{ m}^3$$

or

$$a = 6.29 \times 10^{-10} \text{ m}$$

The interplanar spacing for (200) planes is

$$d_{200} = \frac{a}{(4+0+0)^{\frac{1}{2}}} = \frac{6.29 \times 10^{-10}}{2} = 3.145\text{\AA}$$

From Bragg's law, we have

$$(2d \sin\theta = n\lambda)$$

For second order reflection, $n = 2$

$$\sin\theta = \lambda d = 0.71/3.145 = 0.4610$$

or

Example 2.2. A powder camera of radius 57.3 mm is used to obtain diffraction pattern of gold (fcc) having a lattice parameter of 4.08\AA . The monochromatic Mo- K_α radiation of wavelength 0.71\AA is used. Determine the first four S -values.

Solution. We have,

$$R = 57.3 \text{ mm}$$

$$\lambda = 0.71 \text{ \AA}$$

$$a = 4.08 \text{ \AA}$$

The $(h^2 + k^2 + l^2)$ values for the first four reflections from an fcc crystal are 3, 4, 8 and 11.

The Bragg's law for first order reflection is

$$2d \sin\theta = \lambda \quad (2.49)$$

Also, for cubic crystals, we have

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{\frac{1}{2}}} \quad (2.50)$$

From Eqs. (2.49) and (2.50), we obtain

$$\sin^2\theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2) \quad (2.51)$$

For $h^2 + k^2 + l^2 = 3$, it gives

$$\sin^2\theta_1 = \frac{3(0.71)^2}{4(4.08)^2} = 0.0227$$

$$\theta_1 = 8.67^\circ$$

or
Similarly, for $h^2 + k^2 + l^2 = 4, 8$ and 11 , the angles θ_2, θ_3 and θ_4 are obtained as $10.02^\circ, 14.25^\circ$ and 16.78° respectively.

Since radius of the camera is 57.3 mm, Eq. (2.9) gives

$$S_1 = 40_1 = 34.68^\circ$$

$$\text{Likewise, } S_2 = 40.08^\circ, S_3 = 57.0^\circ \text{ and } S_4 = 67.12^\circ$$

Example 2.3. In a powder diffraction experiment using Cu- K_α radiation of wavelength 1.54\AA , the first five lines are observed from a monoatomic cubic crystal when the angle 2θ is $38.0, 44.2, 64.4, 77.2$ and 81.4 degrees. Determine the crystal structure and the lattice parameter.

Solution. From Eq. (2.51), we have

$$\sin^2\theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

or
The $\sin^2\theta$ values calculated from the given data are tabulated below :

Line	2θ (degrees)	θ (degrees)	$\sin^2\theta$	Ratio (approx.)
1	38.0	19.0	0.1060	3
2	44.2	22.1	0.1415	4
3	64.4	32.2	0.2840	8
4	77.2	38.6	0.3892	11
5	81.4	40.7	0.4252	12

Since, within experimental errors, $\sin^2\theta$ values for the first five lines are in the ratio $3 : 4 : 8 : 11 : 12$, the structure is fcc.
From Eq. (2.51), we have

$$a^2 = \frac{\lambda^2}{4 \sin^2 \theta} (h^2 + k^2 + l^2)$$

For $\sin^2\theta = 0.1060$, $h^2+k^2+l^2 = 3$

$$a = \left[\frac{3(1.54)^2}{4(0.1060)} \right]^{1/4} = 4.10 \text{ \AA}$$

∴

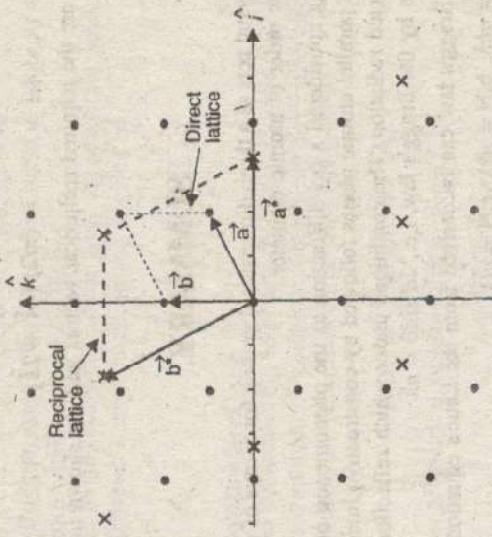


Fig. 2.20. Two-dimensional direct and reciprocal lattices.
Example 2.4. The primitive translation vectors of a two-dimensional lattice are

$$\mathbf{a} = 2\hat{i} + \hat{j}, \mathbf{b} = 2\hat{j}$$

Determine the primitive translation vectors of its reciprocal lattice.

Solution. We assume that the third translation vector \mathbf{c} of the given lattice lies along the z-axis and is of unit magnitude, i.e.,

$$\mathbf{c} = \hat{k}$$

From Eqs. (2.18), the reciprocal lattice vectors are given by

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}, \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$

It is obvious that vectors \mathbf{a}^* and \mathbf{b}^* lie in the plane of \mathbf{a} and \mathbf{b} .

$$\begin{aligned} \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) &= (2\hat{i} + \hat{j}) \cdot (2\hat{j} \times \hat{k}) \\ &= 2(2\hat{i} \times \hat{j}) \cdot \hat{k} \\ &= 2(2+0) = 4 \\ &\therefore = (2\pi/4)(2\hat{j} \times \hat{k}) = \hat{k} \end{aligned}$$

$$\mathbf{b}^* = (2\pi/4) [\hat{\mathbf{k}} \times (2\hat{\mathbf{i}} + \hat{\mathbf{j}})]$$

$$= (\pi/2) [-\hat{\mathbf{i}} + 2\hat{\mathbf{j}}]$$

\mathbf{a}^* and \mathbf{b}^* are the required reciprocal vectors and are shown in Fig. 2.20.

SUMMARY

- A crystal acts as a three-dimensional grating for x-rays of wavelength of the order of atomic diameter.
- Bragg considered x-ray diffraction as the phenomenon of reflection from parallel atomic planes followed by constructive interference of reflected radiation. The conditions under which reflection occurs is given by the Bragg's law, i.e., $2d \sin\theta = n\lambda$
- The Bragg's law can be derived from the Laue's equations given as $a.N = nh\lambda$, $b.N = nk\lambda$, $c.N = nl\lambda$.
- X-ray diffraction is utilized to determine the structure of solids and for the study of x-ray spectroscopy. The position of diffraction lines determines the space lattice and their intensity determines the basis.
- Every direct lattice in real space is associated with a reciprocal lattice in k-space or Fourier space. A reciprocal lattice point corresponds to a particular set of parallel planes of the direct lattice. The distance of a reciprocal lattice point from an arbitrary origin is inversely proportional to the interplanar spacing of the corresponding parallel planes of the normal lattice.
- The fundamental translation vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} of direct lattice and \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* of reciprocal lattice are mutually related as

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}, \quad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}, \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$

$$\text{or } \mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}, \quad \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}, \quad \mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$

- A reciprocal lattice vector is expressed as

$$\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

where h , k and l are integers or zero. A reciprocal lattice point (nh, nk, nl) for which Bragg reflection occurs corresponds to n th order reflection from (hk) planes.

- The Bragg's law is also expressed as $2\mathbf{k} \cdot \mathbf{G} + \mathbf{G}^2 = 0$; $\Delta\mathbf{k} = \mathbf{G}$
- A Brillouin zone is the locus of all those \mathbf{k} -values in the reciprocal lattice which are Bragg reflected.
- The atomic scattering factor gives the scattering power of an atom relative to a single electron and is given by

$$f = \int 4\pi r^2 p(r) \frac{\sin \mu r}{\mu r} dr$$

where $\mu = (4\pi/\lambda) \sin t$

- The total scattering amplitude for a particular direction is the ratio of the amplitude of radiation scattered by the entire unit cell to that scattered by a single electron. It is expressed as

$$F(hkl) = \sum f_j e^{2\pi i (u_j h + v_j k + w_j l)}$$

- The geometrical structure factor is given by

$$S = \sum e^{2\pi i (u_j h + v_j k + w_j l)}$$

- It indicates the presence or absence of a particular reflection in the diffraction pattern.

VERY SHORT QUESTIONS

- What are x-rays?
- What is Bragg's law?
- Why zeroth order diffraction is not considered in x-ray diffraction?
- Write the Laue's equations for x-ray diffraction.
- Define a reciprocal lattice.
- Give the dimensions of translation vectors of a direct lattice and its reciprocal lattice.
- Write the Bragg's law in vector form and give the meaning of each term.
- What is Brillouin zone?
- Define atomic form factor.
- Define the geometrical structure factor.
- What types of diffraction patterns are obtained for crystalline and amorphous solids?
- Give extinction rules for allowed reflections for bcc crystals.
- For some crystals the Bragg's diffraction condition is satisfied but x-ray diffraction line is not observed. Explain.
- Give the first four values of $(h^2 + k^2 + l^2)$ for which reflections are allowed for fcc crystals.

15. What is the structure factor for simple cubic crystal?
 16. For what values of h , k and l reflections are allowed in simple cubic lattice crystals?

SHORT QUESTIONS

1. Why cannot ordinary optical grating diffract x-rays?
2. What is the optimum order of x-ray wavelength used to observe the diffraction effects? What happens if the wavelength deviates too much from this value?
3. Why are imaginary planes also taken into account while using Bragg's law for determination of crystal structure?
4. Prove that the m th order reflection from $(hk\ell)$ planes overlap with the first order reflection from $(nh nk nl)$ planes.
5. Obtain the Bragg's law from the Laue's equations.
6. Why only first order diffraction is usually considered while applying the Bragg's law for the crystal structure determination.
7. What are the basic principles of the Laue's method, the rotating crystal method and the powder method of x-ray diffraction?
8. How can the Laue's method be employed to determine the symmetry of a crystal?
9. Describe the rotating crystal method to observe x-ray diffraction of any material. What additional information do you get as compared to the Laue method?
10. What are layer lines? How are they produced in the rotating crystal method?
11. Describe the procedure for finding the d -values of reflecting planes in a powder's diffraction method.
12. State the properties of a reciprocal lattice. How is a reciprocal lattice constructed from a direct lattice?
13. Distinguish between reciprocal lattice and direct lattice. How can you observe reciprocal lattice of a crystal experimentally?
14. Prove that fcc lattice is reciprocal to bcc lattice.
15. Show that a simple cubic lattice is self-reciprocal but with different cell dimensions.
16. Find the reciprocal lattice to a fcc lattice.
17. Obtain the vector form of Bragg's law using the concept of reciprocal lattices to compare with the Miller indices.
18. Discuss how the concept of reciprocal lattice helps in the Ewald construction and determination of crystal structure.
19. What is Ewald construction? How does it help to interpret x-ray diffraction photographs? (Reciprocal lattice method)
20. To easily find the Miller indices of a reflection, we use the Ewald construction. Explain this method.

21. Obtain the structure factor for a square lattice.
22. Derive an expression for the scattering amplitude in terms of geometrical structure factor for fcc crystals. Find the values of h , k and l for allowed reflections.
23. Calculate the geometrical structure factor for the bcc structure and explain the fact that the (100) reflection line vanishes for metallic sodium but not for CsCl, both having the bcc structure.
24. Calculate the geometrical structure factor for NaCl structure. Will you get the same diffraction pattern for KCl? Explain.
25. The first order reflections from (100) planes for a bcc crystal are absent while reflections of the same order from (200) planes are present. Explain.

LONG QUESTIONS

1. Obtain Laue's equations for x-ray diffraction by crystals. Show that these are consistent with the Bragg's law.
2. Describe the principle of Laue's diffraction method. Explain the origin of Laue's spots. What is the utility of Laue's diffraction pattern?
3. Describe the rotating crystal method for diffraction of x-rays. How do layer lines form?
4. Describe the powder method for x-ray diffraction. Discuss the formation of diffraction pattern on the photographic film.
5. What is the reciprocal lattice and why is it named so? Derive the relationships for the primitive translation vectors of the reciprocal lattice in terms of those of the direct lattice.
6. What are Brillouin zones? Determine the reciprocal lattice vectors, which define the Brillouin zones of bcc and fcc lattices.
7. What is atomic scattering factor? Derive the general expression for the atomic scattering factor using spherical polar coordinates.
8. Define the geometrical structure factor. How is it related to the atomic scattering factor? Write the structure factor for bcc crystal and account for the missing reflections for this crystal.
9. Define a Brillouin zone. If the ratio of the length and the width of a two dimensional rectangular lattice is 3, what kind of first Brillouin zone will you expect? Explain your answer with the help of diagrams.

PROBLEMS

1. The Bragg's angle for (220) reflection from nickel(fcc) is 38.2° when x-rays of wavelength 1.54\AA are employed in a diffraction experiment. Determine the lattice parameter of nickel. (3.52 Å)