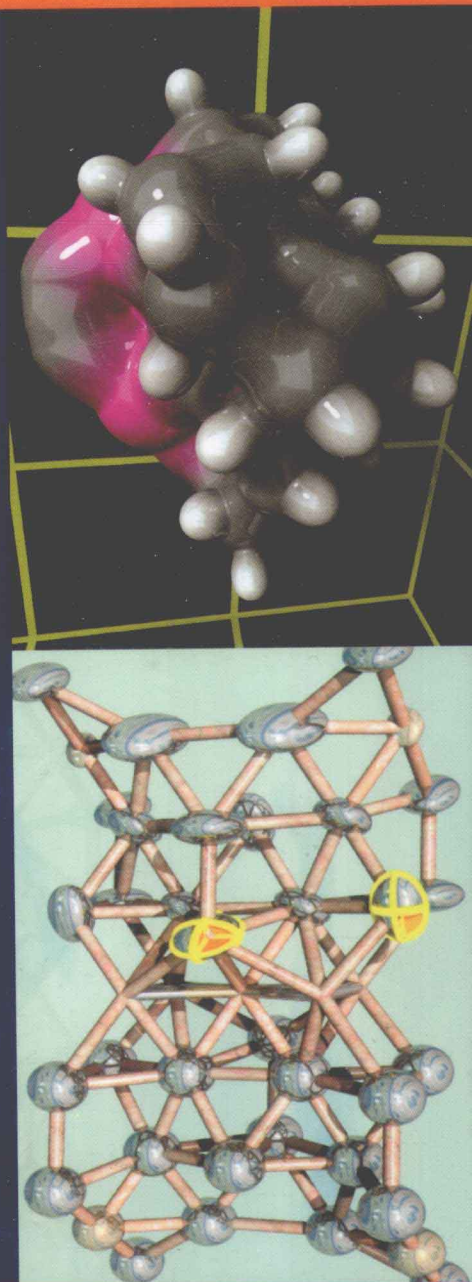


2nd Edition

# Solid State Chemistry

D K CHAKRABARTY



New Age Science

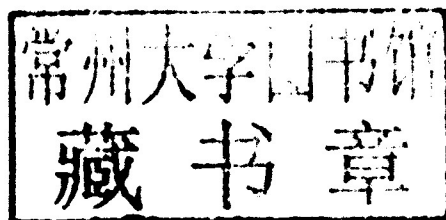
# Solid State Chemistry

Second Edition

**D K CHAKRABARTY**

*Professor Emeritus*

Indian Institute of Technology Bombay  
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**ISBN : 978 1 906574 68 0**

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British Library Cataloguing in Publication Data  
A Catalogue record for this book is available from the British Library

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Printed and bound in India by Replika Press Pvt. Ltd.

# ***Preface to the Second Edition***

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Since its publication in 1996, Solid State Chemistry has gone through several reprints. It was therefore felt that a revision of the book is due. Several chapters have been revised and modified and new materials have been added. The chapters on Reactions of Solids and that on Diffusion in Solids have been merged. A new chapter on Optical and Dielectric Properties has been added.

I thank many of my friends who helped me during this period, particularly Professor B. Viswanathan of the Indian Institute of Technology, Madras and Professor Dipan K. Ghosh of Indian Institute of Technology, Bombay who has kindly revised the chapter on Superconductivity. I shall be rewarded if the students find this useful.

—AUTHOR

# ***Preface to the First Edition***

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Even a few years ago, solid state chemistry did not find a place in the chemistry curricula of our Universities. In fact, the words solid state chemistry used to amuse the physicist, and the chemist was indifferent to it. The situation changed rapidly when new solids started finding their applications in the various areas of technology, from solid catalysts to superconducting magnets. It has been now realised that the chemist has an important role to play in the discovery and preparation of solids with newer properties through cheaper routes. Today, solid state chemistry is an important area. I hope this little book will be able to initiate the student into this interesting subject.

This text is the outcome of a course that I have been teaching at the Indian Institute of Technology, Bombay for many years. The main objective has been to relate some important properties of solids to their structure. It begins with the discussion of simple structures like metals and ionic solids. Point defects have been included as they have a very important role in determining the properties and reactivities of solids. Some pages have been devoted to aspects of nonstoichiometry, solid state reactions and phase transition in solids. Electrical and magnetic properties have been discussed in some details. In order to keep down the bulk of the book that is intended to be an introductory text, some topics such as thermal and optical properties have been left out. Superconductivity has become too important to be ignored and I am grateful to Professor Dipan K. Ghosh of the Department of Physics for writing the chapter on this interesting subject.

The book has many equations. This is bound to be so. If we want to test the ideas and models through experiment, we need to express them in mathematical form. Concepts that cannot be experimentally verified has no meaning in science. Mathematics used in this text is simple.

I thank a large number of my students for raising many questions in the classroom some of which I have tried to answer in these pages. I am particularly thankful to Dr. Ramachandra Bhat and Dr. Debashis Das for correcting the manuscript as well as to Mr. G. Ravichandran and Dr. C.V.V. Satyanarayana for many help. Mr. S.S. Shikare deserves all praises for the neat drawings and Mr. Lalmani Dilgani for technical help.

Financial support from the CDP cell of the Institute is gratefully acknowledged.

I must thank my wife and children for bearing with my irritable mood, which I must admit, was not too infrequent, because of time pressure as this book was written without availing of any form of leave. The shortcomings of the book are the results of my own limitations.

—AUTHOR

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## INDEX

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# The Crystal Structure

1

## 1.1 INTRODUCTION

Intermolecular attraction is minimum in the gaseous state and this disappears completely when the gas is ideal. The interaction is stronger in liquids and is strongest in solids. Thermal motion of the molecules increases or decreases by raising or lowering of temperature. The attractive interaction between the molecules tries to keep them together and the thermal motion is opposed to that. Hence, it is possible to change a substance from one state to another by changing its temperature. If a liquid is allowed to cool slowly, the molecules will arrange themselves in an orderly manner and this will finally result in a *crystalline solid*. If, on the other hand, cooling is rapid, the molecules will not be able to arrange themselves in order. Rapid densification will give a *glass* or an *amorphous solid*. It is not true that the molecules and atoms in a solid have rigidly fixed coordinates. But they move only a small distance about their equilibrium positions. In this book, we are concerned with *crystalline solids* and the word *solid* and *crystalline solid* will be used synonymously.

What is the stable state of a given material will depend on its free energy. The stable state will be the one that has the lowest free energy under the given conditions. Free energy  $A$  is related to internal energy  $U$  and entropy  $S$  of the system as

$$A = U - ST \quad \dots(1.1)$$

Internal energy is lowered by an orderly arrangement of the atoms, molecules or ions as that will lead to maximum energy of interaction. But this will minimise the entropy. Since internal energy and entropy make opposite contribution to free energy, the state of matter will be determined by the relative contributions of  $U$  and  $ST$  to  $A$ . If interaction is strong,  $U$  is highly negative and  $ST$  can overcome the contribution of the former only at high temperatures. Such a substance will remain as a solid even at a relatively high temperature.

The basic feature of a crystalline solid is the regular arrangement of the atoms and molecules. At the macro level, this translates into crystals having sharp boundaries with clear cut shapes. It is these beautiful shapes of natural crystals that attracted human attention for ages. This beautiful shape and colour added to their value as gems.

Early studies of crystals began with the observation of their shapes and this is known as *Geometric Crystallography*. The description of crystal symmetry in terms of point lattice began in the mid-nineteenth century. This was followed by X-ray crystal structure determination following the work of Laue and Bragg on X-ray diffraction by crystals. In the second quarter of the twentieth century, the presence of lattice defects and their role in determining the properties of crystals were recognised. We shall not try to follow the development of the subject in a chronological order as the development of knowledge in an area of science does not take place in the same

logical way as one would like to see it. But only after enough knowledge gets accumulated that a subject is put in a logical perspective. Here we shall follow the rational rather than the chronological course of development of the subject.

### Crystal lattice

It is easy to imagine a crystal as a periodic arrangement of points as shown in figure 1.1. A point may represent an atom or a group of atoms arranged around it in a real crystal. Let us begin with a single point. Repeated translation of this point through a fixed distance  $a$  (a periodic translation) will generate a linear array of points. This movement is denoted by a translation vector  $\hat{t}_1$ . If we add a second translation  $\hat{t}_2$ , it will generate periodically repeating points on a plane and this is known as a *plane lattice*. If a third translation  $\hat{t}_3$  is added, we get a three dimensional arrangement of the points that is called a *space lattice*.

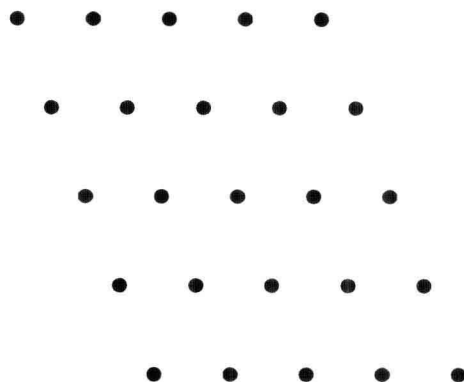


Figure 1.1: A two dimensional plane lattice

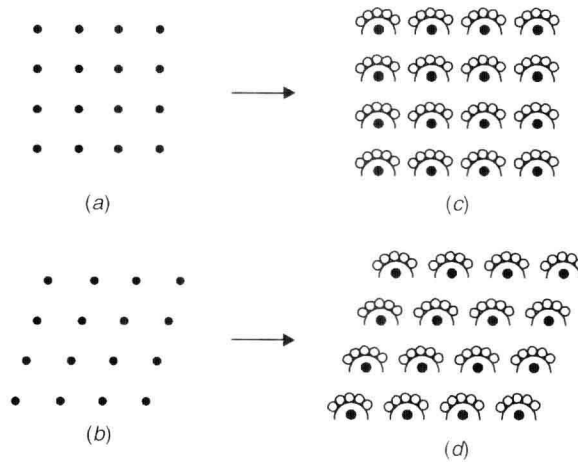
The lattice points are imaginary. In a real crystal, they are occupied by atoms or groups of atoms that are arranged in a regular fashion about the lattice points. This atom or the group of atoms is the *basis* and the arrangement of the imaginary points is the *lattice*. The real crystal is then:

$$\text{basis} + \text{lattice} = \text{crystal}.$$

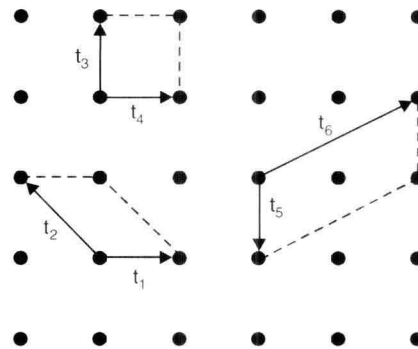
A two dimensional pattern as is usually found on a curtain cloth or a wall paper is analogous to a two dimensional crystal lattice. We can have an array of squarely arranged points (Figure 1.2a) or the points may be arranged along inclined lines (Figure 1.2b). We can select a single motif and place this motif in the same way about each lattice points. This will give two different patterns (Figure. 1.2c and 1.2d). By selecting a different motif, we may get a still different pattern and a large number of patterns can be generated from a limited number of motifs and lattice arrangements.

### Unit cell

We have seen that two noncollinear translations give rise to a plane lattice and introducing a third translation (not on the same plane) generates a space lattice. Since any line joining two lattice points is a translation and there can be wide choice of translation, the question arises as to which two translation should one select to describe a plane lattice. A few such combinations are shown in figure 1.3. It is seen that they generate two dimensional units called *unit cell*. Combination of  $\hat{t}_1, \hat{t}_2$  or  $\hat{t}_3, \hat{t}_4$  leads to cells having only one lattice point per cell. These are known as *primitive unit cell*. The combination  $\hat{t}_5, \hat{t}_6$  generates a *double cell*. There can be many more multiple cells. The unit cell of a lattice can be primitive or multiple. A repetition of the two dimensional unit cell by translation in two directions generates the plane lattice. This may be extended to three dimensional lattice that may be generated by translation of a three dimensional unit cell.



**Figure 1.2:** Two different plain lattices with identical motif leading to two different patterns

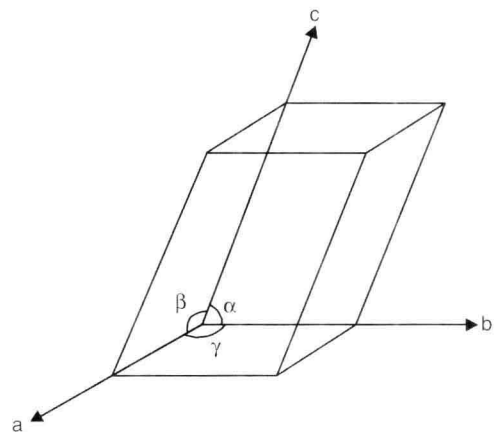


**Figure 1.3:** Different combinations of translation and the unit cell

The three translations are selected along the three edges of the chosen unit cell. The choice of a unit cell for real crystal is done based on the convenience and conventions. It can be a primitive cell or a multiple cell. The three selected axes along the edges of the unit cell are called the *crystallographic axes*  $a$ ,  $b$  and  $c$  and the angles between them  $\alpha$ ,  $\beta$  and  $\gamma$  as shown in figure 1.4.

As has already been said, the early years of study of solids were concerned mostly with crystal geometry. This was followed by the study of crystal symmetry. Bravais in 1848 had shown that all structures can be generated by using only 14 types of space lattice (14 types of unit cell).

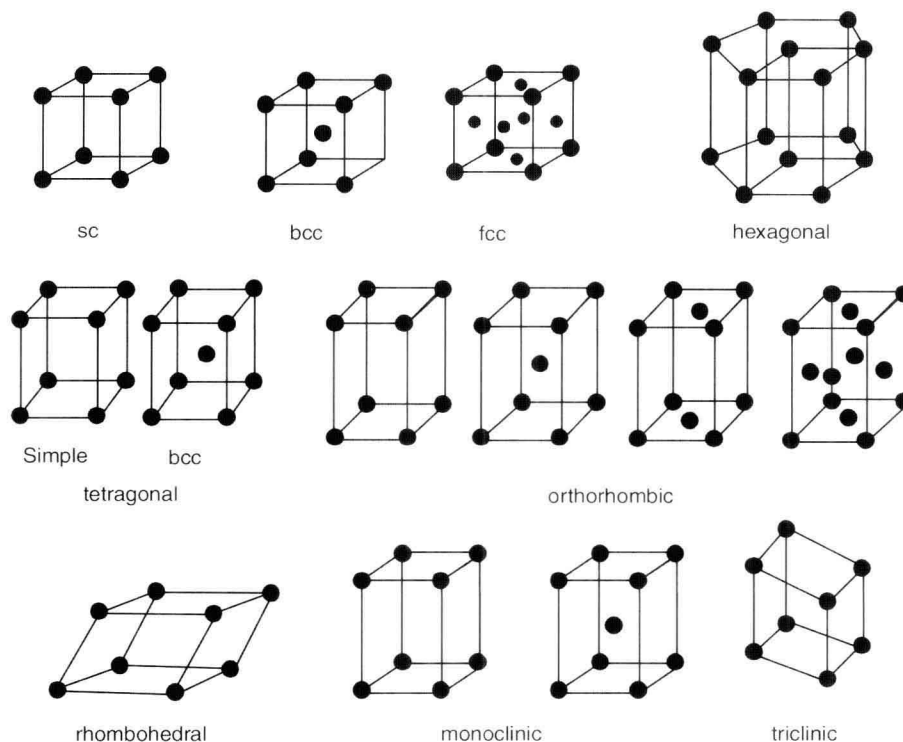
These 14 types of unit cells will give rise to 230 types of lattice structures (space group) by performing such symmetry operations as



**Figure 1.4:** A unit cell showing the edges and the angles

(i) translation, (ii) rotation, (iii) translation + rotation and (iv) reflection. It was shown by Federov and independently by Barlow that it is not possible to have arrangement of lattice points other than these 230 types that can repeat itself infinitely in three dimensions.

The 14 types of Bravais lattices are shown in figure 1.5.



**Figure 1.5:** Fourteen types of Bravais lattice

All real crystals belong to anyone of the 230 space groups. The imaginary lattice points are occupied by atoms or groups of atoms. Table 1.1 shows the classification and the geometric properties of the various Bravais lattices.

**Table 1.1: Classification of the fourteen Bravais lattices**

System	Space Lattice	Condition
<b>Cubic</b>	simple cubic body centered cubic face centered cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$
<b>Hexagonal</b>	hexagonal prism	$a = b \neq c$ $\alpha = \beta = 90^\circ$ ; $\gamma = 120^\circ$
<b>Tetragonal</b>	tetragonal prism tetragonal bcc prism	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$

(Contd.)

<b>Orthorhombic</b>	rectangular prism <i>bc</i> rectangular prism <i>fc</i> rectangular prism base centered prism	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
<b>Rhombohedral</b>	rhombohedron	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$
<b>Monoclinic</b>	parallelopiped <i>bc</i> parallelopiped	$a \neq b \neq c$ $\alpha = \beta = 90^\circ$ ; $\gamma \neq 90^\circ$
<b>Triclinic</b>	triclinic parallelopiped	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$

## 1.2 CRYSTAL PLANES AND MILLER INDICES

In a real crystal, the lattice points are occupied by atoms. One can think of a very large number of lattice planes and one set of parallel planes can be distinguished from another set by their orientation. Miller indices are the labels used to distinguish one set of parallel planes from another. It is a set of three numbers  $h\ k\ l$  that defines a set of parallel planes in a crystal.

The following procedure is generally followed to determine the Miller indices.

1. Choose an origin;
2. Find out the intercept that the first such plane makes with the three crystallographic axes;
3. Obtain their reciprocals;
4. Eliminate fractions.

The set of numbers thus generated in relation with the axes  $a$ ,  $b$  and  $c$  are  $h$ ,  $k$  and  $l$  respectively. A set of parallel planes are labelled by a set of  $hkl$  numbers. Different set of parallel planes have different  $hkl$  or Miller indices. This is illustrated in figure 1.6. Here, the plane nearest to the origin and cutting the  $b$  axis at  $\frac{1}{2b}$ , the  $a$  axis at  $\frac{1}{3a}$  and the  $c$  axis at  $\frac{1}{2c}$  is shown. This makes  $\frac{1}{3}$  intercept along  $a$  axis,  $\frac{1}{2}$  intercept along  $b$  axis and  $\frac{1}{2}$  along  $c$  axis.

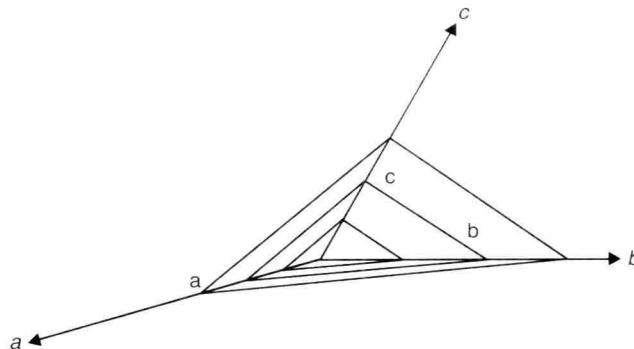


Figure 1.6: (322) set of planes

We can write

	<b>a</b>	<b>b</b>	<b>c</b>
intercept	1/3	1/2	1/2
reciprocal	3	2	2

Hence this plane and a set of parallel planes separated by a distance  $d$  have the Miller indices (322).

It should be noted that a point on a paper actually represents line of points when one considers the three dimensional lattice. Hence on the plane of paper a line of points actually represents a plane.

The major advantage of the Miller indices is that it permits to express interplanar distance  $d_{hkl}$  of a set of  $hkl$  planes in terms of lattice parameters  $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$  and  $\gamma$ .

For a cubic crystal

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

### 1.3 DIFFRACTION OF X-RAYS

In 1912, von Laue first suggested that since the lattice points in a real crystal are occupied by atoms, the crystal lattice should act as a three-dimensional diffraction grating for X-rays. This should happen because X-rays have wavelength of the dimension of interplanar distances in a real crystal. Shortly after this, W.L. Bragg showed that wavelength of the X-ray undergoing diffraction by a crystal is related to the interplanar distances by the famous Bragg's equation.

#### 1.3.1 Bragg's Law of Diffraction

Let there be a set of lattice planes consisting of an array of atoms as shown in figure 1.7. The X-ray beam incident on a plane at angle  $\theta$  will be reflected from the plane such that the angle of

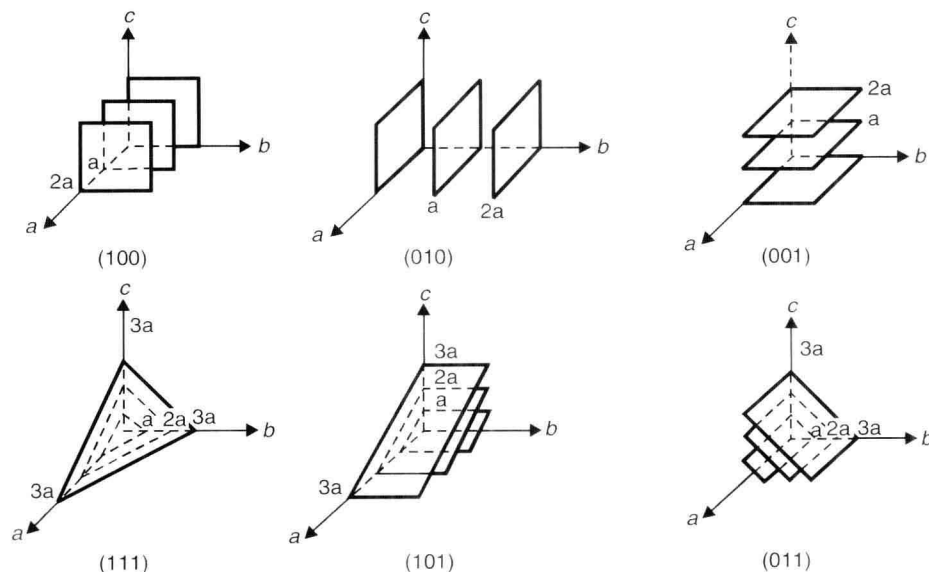


Figure 1.7: Different sets of crystal planes in a cubic crystal



reflection is also  $\theta$  and a part of the intensity will pass through the crystal undeviated from its path. Reflection is caused by the interaction of the electromagnetic radiation with the electrons of the atoms in the lattice. In order that the intensity of the reflection is sufficiently strong, reflected waves from the successive planes separated by  $d_{hkl}$  should be in phase.

From figure 1.8, it is seen that the path difference of the waves from successive planes is  $2d \sin \theta$ . In order that the waves travelling from successive planes are in phase the condition

$$n\lambda = 2d_{hkl} \sin \theta \quad \dots(1.2)$$

should be satisfied. This is Bragg's condition of reflection and is known as Bragg's law.

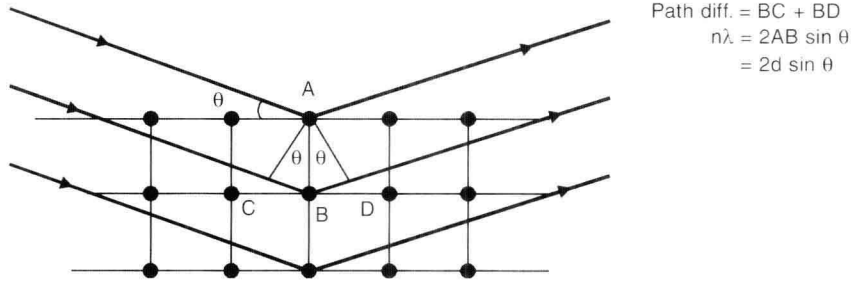


Figure 1.8: Diffraction of X-ray from a set of planes

## 1.4 RECIPROCAL LATTICE

The concept of reciprocal lattice is very useful in X-ray crystallography. It was Ewald who developed the relation between the diffracted X-ray beams. The crystal, instead of being seen as different sets of parallel planes, may be represented by a normal drawn perpendicular to each set of parallel planes from a common point as origin. The length of the normal is proportional to  $1/d_{hkl}$ . This length and direction of the normal is used to represent a set of parallel planes. If a point is placed at the end of each such normal, an array of points is generated. Each point then represents a set of parallel equidistant lattice planes and hence, each point is represented by a set of Miller indices  $(hkl)$  of the crystal. This array of points is known as the reciprocal lattice. The reciprocal lattice vector  $\mathbf{d}_{hkl}$  has a direction same as the normal to the  $d_{hkl}$  planes and its magnitude is  $1/d_{hkl}$ . We see that the arrangements of the points in the reciprocal lattice has the same symmetry as the lattice points of the real crystal.

The concept of reciprocal lattice is particularly helpful in understanding diffraction of X-rays by crystal planes. Let us rewrite the Bragg's equation in reciprocal lattice as

$$\sin \theta_{hkl} = \frac{\lambda/2}{d_{hkl}} = \frac{1/d_{hkl}}{2/\lambda} \quad \dots(1.3)$$

Here, we have tried to relate the magnitude of the reciprocal lattice vector to diffraction angle and the wavelength of the X-ray. In order to see the geometric consequence of this equation, let us imagine a sphere of radius  $1/\lambda = AO$  as shown in figure 1.9.