1 Crystal Structure

1.1 Introduction

Solids consist of atoms, molecules or ions packed very closely together. The forces that hold them in place give rise to distinctive properties of the various kinds of solid. In a broader sense, solids are classified into two categories: Crystalline and non-crystalline or amorphous. A crystal may be defined as a solid in which atoms, molecules or ions are arranged in a periodic pattern in three dimensions. That means crystals have a regular internal structure. An amorphous solid may be defined as a solid in which atoms or molecules are arranged arbitrarily in three dimensions, i.e., amorphous solids have no regular internal structure. A few examples of amorphous substances are glass, plastic, and gel, whereas the list of crystalline solids is very large; most metals are crystalline. Crystals that are composed of two elements are called binary crystals. There are thousands of binary crystals; some examples are sodium chloride (NaCl), alumina (Al₂O₃) and ice (H₂O). A polycrystalline solid is made up of an aggregate of a large number of tiny single crystals called grains oriented in different directions and separated by well-defined boundaries called grain boundaries.

1.2 Geometry of Crystals

For the systematic study of crystals, we should first know the geometry of crystals in which actual atoms or molecules composing the crystal are ignored and their positions in space are taken into consideration. The positions of the atoms or molecules in the crystal define a set of points called point lattice. The point lattice may be regarded as the skeleton on which the actual crystal is built.
1.3 Fundamental Terms

i. **Point lattice**  The point lattice is defined as an array of points in space so arranged that every point has surroundings identical to that of every other point in the array. By identical surroundings we mean that, when we look in a particular direction putting ourselves at a lattice point, the same scenery is visible as that of any other point when we look in the same direction. A two-dimensional point lattice having infinite extension is shown in Fig. 1.1(a) and a three-dimensional point lattice assumed to have infinite extension is shown in Fig. 1.1(b). Point lattice, lattice or space lattice, are synonymously used.

![Two dimensional lattice](image1.png)  
(a) A two-dimensional lattice. 

![Three dimensional lattice](image2.png)  
(b) A three-dimensional lattice. Observe that each point has identical surroundings. ABCD represents a unit cell selected in a two-different ways in a two-dimensional lattice and the heavily outlined one is the unit cell in a three-dimensional lattice.

ii. **Unit cell**  As can be seen in Fig. 1.1(a), the entire two-dimensional lattice can be produced by translating the cell ABCD along the horizontal as well as vertical directions. Hence, ABCD is a unit cell. As has been illustrated in Fig. 1.1(b), the entire three-dimensional lattice can be produced by translating the heavily outlined cell in space in all possible directions. Therefore, the heavily outlined cell of Fig. 1.1(b) is a unit cell. Thus, the unit cell is defined as the smallest cell, translation of which generates the entire lattice. A three-dimensional general unit cell is shown in Fig. 1.1(b) as heavily outlined.

iii. **Crystallographic axes**  The vectors \( \vec{a}_1, \vec{a}_2, \) and \( \vec{a}_3 \) that define the unit cell in Fig. 1.2 are called crystallographic axes of the unit cell. Thus, we can define the crystallographic axes of a unit cell as the three vectors defining the unit cell of a lattice. The crystallographic axes \( \vec{a}_1, \vec{a}_2, \) and \( \vec{a}_3 \) are also called primitive lattice vectors or basis vectors or fundamental translation vectors. Depending upon the magnitudes and directions of the basis vectors \( \vec{a}_1, \vec{a}_2, \) and \( \vec{a}_3, \) different types
Figure 1.2  A generalized unit cell. The vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ defining a unit cell are called crystallographic axes or basis vectors or primitive lattice vectors or fundamental translation vectors (total seven in number) unit cells are formed. The volume of a unit cell $V$ defined by basis vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ is given by

$$V = |\vec{a}_1 \times \vec{a}_2| = |\vec{a}_2 \times \vec{a}_3| = |\vec{a}_3 \times \vec{a}_1|$$  \hspace{1cm} (1.1)$$

iv. **Lattice parameters**  The magnitudes of the crystallographic axes $a_1$, $a_2$, and $a_3$ along with the interfacial angles $\alpha$ (angle between $\vec{a}_2$ and $\vec{a}_3$), $\beta$ (angle between $\vec{a}_3$ and $\vec{a}_1$), and $\gamma$ (angle between $\vec{a}_1$ and $\vec{a}_2$), define the unit cell of Fig. 1.2. The magnitudes of the crystallographic axes $a_1$, $a_2$, and $a_3$ along with the interfacial angles $\alpha$, $\beta$, and $\gamma$ are called lattice constants or lattice parameters of the unit cell.

v. **Lattice translation vector**  Any two lattice points can be connected with each other by a vector of the form

$$\overrightarrow{T} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$  \hspace{1cm} (1.2)$$

The vector defined by Eq. (1.2) is called lattice translation vector $\overrightarrow{T}$ which specifies the position of a lattice point in a lattice. Here, $n_1$, $n_2$, and $n_3$ are integers, may be negative, zero or positive. To be particular, actually, $n_1$, $n_2$, and $n_3$ are the projections of the vector $\overrightarrow{T}$ along $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$, respectively.

vi. **Bravais lattice**  A three-dimensional space lattice is generated by the repeated translation of basis vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$. It turns out that there are only fourteen distinguishable ways of arranging points in three-dimensional space such that each arrangement confirms to the definition of a space lattice. These fourteen space lattices are known as Bravais lattices in honour of their originator, the French crystallographer Auguste Bravais.
vii. **Crystal systems** Depending upon the relative values and orientation of the basis vectors, the fourteen types of Bravais lattices grouped into seven sets are called crystal systems. Along with the Bravais lattices, the seven crystal systems are listed in the following table.

<table>
<thead>
<tr>
<th>Crystal systems</th>
<th>Lattice parameters</th>
<th>Bravais lattice</th>
<th>Examples</th>
<th>No. of lattice points per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$a_1 = a_2 = a_3$, $\alpha = \beta = \gamma = 90^\circ$</td>
<td>Simple</td>
<td>P</td>
<td>Cu, Ag</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Body centered</td>
<td>I</td>
<td>CaCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Face centered</td>
<td>F</td>
<td>NaCl</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a_1 = a_2 \neq a_3$, $\alpha = \beta = \gamma = 90^\circ$</td>
<td>Simple</td>
<td>P</td>
<td>$\beta$-Sn</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Body centered</td>
<td>I</td>
<td>TiO$_2$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a_1 \neq a_2 \neq a_3$, $\alpha = \beta = \gamma = 90^\circ$</td>
<td>Simple</td>
<td>P</td>
<td>Ga</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Body centered</td>
<td>I</td>
<td>Pbco$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Base centered</td>
<td>C</td>
<td>$\alpha$-S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Face centered</td>
<td>F</td>
<td>K$_2$SO$_4$</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>(Also called trigonal)</td>
<td>$a_1 = a_2 = a_3$, $\alpha = \beta = \gamma \neq 90^\circ$</td>
<td>Simple</td>
<td>P</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a_1 = a_2 \neq a_3$, $\alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
<td>Simple</td>
<td>P</td>
<td>Ng, Zn</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a_1 \neq a_2 \neq a_3$, $\alpha = \gamma = 90^\circ \neq \beta$</td>
<td>Simple</td>
<td>P</td>
<td>Gypsum</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Base centered</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>Triclinic</td>
<td>$a_1 \neq a_2 \neq a_3$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$</td>
<td>Simple</td>
<td>P</td>
<td>K$_2$Cr$_2$O$_7$</td>
</tr>
</tbody>
</table>

viii. **Basis** A group of atoms or molecules attached to a lattice point to form the crystal structure is called a basis.

ix. **Crystal structure** A crystal structure is formed when a basis is attached identically to every lattice point. The space lattice is converted into a crystal structure when a basis is attached identically to every lattice point. The logical relation is

Lattice points + basis = crystal structure

x. **Primitive unit cell** The simplest unit cell is the primitive cell of the simple cubic unit cell of simple cubic crystals containing one atom which may be assumed to be at the origin.
Example 1.1

The fundamental lattice translation vectors of a hexagonal lattice may be defined as

\[ \vec{a}_1 = \frac{\sqrt{3}}{2} a \hat{x} + \frac{1}{2} a \hat{y}, \quad \vec{a}_2 = \frac{\sqrt{3}}{2} a \hat{x} + \frac{1}{2} a \hat{y}, \quad \vec{a}_3 = c \hat{z}. \]

Calculate the volume of the hexagonal unit cell.

Solution

\[ \vec{a}_1 \times \vec{a}_3 = \left( \frac{\sqrt{3}}{2} a \hat{x} + \frac{1}{2} a \hat{y} \right) \times \hat{c} = \frac{1}{2} ac \hat{x} + \frac{\sqrt{3}}{2} ac \hat{y} \]

Thus, the volume of the unit cell \( V \) is calculated to be

\[ V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \left( \frac{\sqrt{3}}{2} a \hat{x} + \frac{1}{2} a \hat{y} \right) \cdot \left( \frac{1}{2} ac \hat{x} + \frac{\sqrt{3}}{2} ac \hat{y} \right) \]

\[ = \frac{\sqrt{3}}{4} a^2 c + \frac{\sqrt{3}}{4} a^2 c = \frac{\sqrt{3}}{2} a^2 c \]

1.4 Lattice Directions and Planes

Certain physical properties of a crystal may depend on directions of measurement. The crystals whose certain properties depend on the direction of measurement are called anisotropic crystals and those properties are called anisotropic properties. For this reason, it is necessary to identify specific directions in the crystal. In a crystal, different lattice planes may pass through different lattice points in different orientations. For the study of crystal structure, it is very important to specify various lattice planes in the crystal. The lattice directions and lattice planes are also called crystal directions and crystal planes.

1.4.1 Lattice directions

The direction defined by the lattice translation vector \( \vec{T} \) connecting two points in a lattice is given by

\[ \vec{T} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \] (1.3)
Here, $n_1$, $n_2$ and $n_3$ are the projections of the vector $\mathbf{T}$ along $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ respectively. If one, two or all of $n_1$, $n_2$ and $n_3$ are fractions, they can be converted into smallest integral values by multiplying them by a suitable number (it may be the LCM of the denominators). These smallest integral values are called direction indices of the line represented by the vector $\mathbf{T}$ and are written within square brackets $[]$. The direction indices of a line give the direction of the line in the crystal. It is important to remember that if the direction passes through the origin, to find the direction indices, the origin is first shifted to another lattice point and the direction indices are calculated with respect to this new origin. The following steps are followed in calculating the direction indices of a line.

i. If necessary shift the origin to any other lattice point.

ii. The line whose direction indices are to be found out is represented by a vector of the form $\mathbf{T} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$. If the coordinates of any two points on the line are known, then by using the principles of coordinate geometry we can represent the line by a vector of the form $\mathbf{T} = n_1 \hat{\mathbf{a}}_1 + n_2 \hat{\mathbf{a}}_2 + n_3 \hat{\mathbf{a}}_3$.

iii. The coefficients of $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ i.e., $n_1$, $n_2$, and $n_3$ are written inside a square bracket like $[n_1 \ n_2 \ n_3]$. Commas, dots, are not to be put between the numbers.

iv. If the bracketed terms are fractions, then multiply them with the LCM of their denominators to make them integers.

v. If the bracketed terms are integers having a common multiple, then divide them by that common multiple to reduce them to the smallest integers.

vi. The set of smallest integer written within a square bracket $[]$ is called the direction indices of the line.

vii. If any one or all bracketed terms are negative, a bar is put over the integer(s).

The following example will elucidate the procedures and steps to find the direction indices of a line.

**Case i:** Direction indices of OA: The direction of OA is represented by the vector $\mathbf{T}_{OA} = 1\hat{\mathbf{a}}_1 + 0\hat{\mathbf{a}}_2 + 0\hat{\mathbf{a}}_3$ as seen in Fig. 1.3. Hence, the direction indices of OA will be given by $[1 \ 0 \ 0]$ (read as one zero zero).

**Case ii:** Direction indices of OB: The direction of OB is represented by the vector $\mathbf{T}_{OB} = 1\hat{\mathbf{a}}_1 + 1\hat{\mathbf{a}}_2 + 0\hat{\mathbf{a}}_3$ as seen in Fig. 1.3. Hence, the direction indices of OB will be given by $[1 \ 1 \ 0]$.

**Case iii:** Direction indices of OC: The direction of OC is represented by the vector $\mathbf{T}_{OC} = 1\hat{\mathbf{a}}_1 + 1\hat{\mathbf{a}}_2 + 1\hat{\mathbf{a}}_3$ as seen in Fig. 1.3. Hence, the direction indices of OC will be given by $[1 \ 1 \ 1]$.

**Case iv:** Direction indices of OE: The direction of OE is represented by the vector $\mathbf{T}_{OE} = 0\hat{\mathbf{a}}_1 + 1\hat{\mathbf{a}}_2 + 0\hat{\mathbf{a}}_3$ as seen in Fig. 1.3. Hence, the direction indices of OE will be given by $[0 \ 1 \ 0]$.
Case v: Direction indices of OG: The direction of OG is represented by the vector \( \overrightarrow{T_{og}} = 0 + 0 + 1a_3 \), as seen in Fig. 1.3. Hence, the direction indices of OG will be given by \([0 0 1]\).

Case vi: Direction indices of OH (H is the mid-point of the plane DCFG): The direction of OH is represented by the vector

\[
\overrightarrow{T_{oh}} = \frac{1}{2} \overrightarrow{a_1} + \frac{1}{2} \overrightarrow{a_2} + 1 \overrightarrow{a_3}
\]

as seen in Fig. 1.3. The coefficients of \( \overrightarrow{a_1}, \overrightarrow{a_2}, \) and \( \overrightarrow{a_3} \) are respectively obtained as

\[
\begin{bmatrix}
\frac{1}{2} & 1 & 1 \\
\frac{1}{2} & 2 & 1
\end{bmatrix}
\]

This set of three numbers will be converted into three smallest integers when multiplied by 2. The direction indices of OH will be obtained by multiplying

\[
\begin{bmatrix}
\frac{1}{2} & 1 & 1 \\
\frac{1}{2} & 2 & 1
\end{bmatrix}
\]

by 2. Hence, the direction indices of OH will be given by \([1 1 2]\).

Case vii: Direction indices of OJ (J is the mid-point of the plane ADGO): The direction of OJ is represented by the vector
as seen in Fig. 1.3. The coefficients of $\tilde{a}_1$, $\tilde{a}_2$, and $\tilde{a}_3$ are respectively obtained as

$$
\begin{bmatrix}
\frac{1}{2} & 0 & \frac{1}{2}
\end{bmatrix}
$$

This set of three numbers will be converted into three smallest integers when multiplied by 2. The direction indices of OJ will be obtained by multiplying

$$
\begin{bmatrix}
\frac{1}{2} & 0 & \frac{1}{2}
\end{bmatrix}
$$

by 2. Hence, the direction indices of OJ will be given by [1 0 1].

**Case viii:** Direction indices of BF: The coordinates of B($a_1, a_2, 0$) and F($0, a_2, a_3$) on the line are known, so using the principles of coordinate geometry, the direction of BF is represented by the vector

$$
\mathbf{T}_{BF} = (0-\tilde{a}_1) + (\tilde{a}_2 - \tilde{a}_2) + (\tilde{a}_3 - 0) = -1\tilde{a}_1 + 0 + 1\tilde{a}_3
$$

as seen in Fig. 1.3. The coefficients of and $\tilde{a}_3$ are respectively obtained as $-1$, $0$, and $1$. Hence, the direction indices of BF will be given by [1 0 1] (read as bar one zero one).

From these discussions, it is clear that though

$$
\begin{bmatrix}
\frac{1}{6} & \frac{1}{2} & \frac{2}{3}
\end{bmatrix}, \begin{bmatrix}1 & 3 & 4\end{bmatrix}, \begin{bmatrix}2 & 6 & 8\end{bmatrix}
\begin{bmatrix}1 & 3 & 2\end{bmatrix}
$$

all represent the same direction, $[1 \ 3 \ 4]$ is the preferred form.

**Example 1.2**

If 0.2, 0.4, and 0.3 are the coordinates of a point on a line, determine the direction indices of the line.

**Solution**

The direction indices of the line containing the point (0.2, 0.4, 0.3) are [0.2, 0.4, 0.3]. The most preferred form is obtained by multiplying the indices by 10 as [2 4 3].

**Family of lattice directions**

In the previous discussion, we have represented the direction indices of the body diagonal OC by [111]. As can be checked, the body diagonal ED will be represented by direction indices [111]. The following are the possible combinations including positive and negative values of the three numbers specifying the directions of all the body diagonals: [111], [111],
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\[[\bar{1}T1], [11\bar{1}], [\bar{T} T1], [1T \bar{T}], [\bar{T}1T], [T \bar{T} T]\]. These combinations represent the direction of the body diagonal of the unit cell depicted in Fig. 1.3 and is called the family of lattice directions \([111]\). In symbols, the family of lattice directions \([111]\) is written as

\(<111> = [111], [\bar{T}11], [1\bar{T}1], [11\bar{T}], [\bar{T}\bar{T}1], [1\bar{T}\bar{T}], [\bar{T}1\bar{T}], [\bar{T}\bar{T}\bar{T}]\).

These eight combinations give the direction indices of the body diagonals.

Similarly, the family of lattice directions of edge OA and face diagonal OB, are obtained respectively as \(<100> = [100] [010] [001] [T00] [0T0] [00T] and <110> = [110], [011], [101], [\bar{T}00], [0\bar{T}1], [1 \bar{T}1], [0 \bar{T}1], [10 \bar{T}], [\bar{T}\bar{T}0], [0 \bar{T}\bar{T}], [\bar{T}0\bar{T}]\).

### Linear density of atoms

The linear density of atoms in a lattice is the number of atoms per unit length in a particular direction in the crystal lattice. The number of atoms along the face diagonal of an FCC structure is 3 and the length of the face diagonal of the FCC is \(\sqrt{2}a\) where \(a\) is the lattice parameter of FCC. Hence, the linear density of atoms along the face diagonal in FCC is \(\frac{3}{\sqrt{2}a}\).

#### 1.4.2 Crystal planes

In a crystal, the planes passing through the crystal in different orientations are called lattice planes or crystal planes. Crystal planes are known by their orientations with respect to crystallographic axes. The orientations of the crystal planes are specified by three parameters enclosed in lunar brackets (hk\(\ell\)) called Miller indices. The method of finding Miller indices (hk\(\ell\)) are explained here.

In general, the orientation of a given plane can be specified by knowing the three intercepts made by the plane with the crystallographic axes. These three intercepts will depend on the axial lengths \(a_1\), \(a_2\), and \(a_3\). In order to make these three intercepts independent of the particular axial lengths involved in the given lattice, fractional intercepts are taken instead of intercepts. To avoid the introduction of infinity into the specification of orientation of crystal planes, the reciprocal of fractional intercepts are taken. Thus, we arrive at a workable symbolism for the orientation of a crystal plane called Miller indices. The working definition of Miller indices is given as the reciprocal of the fractional intercepts which the plane makes with the crystallographic axes. It is important to remember that if the crystal plane passes through the origin, the origin is shifted to another lattice point and the Miller indices is calculated with respect to this new origin.

The following steps are involved in the calculation of Miller indices of a crystal plane.

i. If necessary, shift the origin to any other lattice point.

ii. Write down the axial lengths \(a_1\), \(a_2\), and \(a_3\) in order.

iii. Write down the intercepts \(p\), \(q\), \(r\) in order.

iv. Calculate the fractional intercepts, \(\frac{p}{a_1} , \frac{q}{a_2} , \frac{r}{a_3}\).
(A fractional intercept means an intercept is a fraction of the corresponding axial length.)

v. Take the reciprocal of fractional intercepts, i.e., \( \frac{a_1}{p}, \frac{a_2}{q}, \frac{a_3}{r} \).

vi. If \( \frac{a_1}{p}, \frac{a_2}{q}, \frac{a_3}{r} \) are not the smallest integers, then by multiplying or by dividing by a single suitable number, they can be converted into a set of the three smallest integers \( h, k, \ell \) to give the Miller indices.

vii. This set of three smallest integers \( h, k, \ell \) written inside a lunar bracket \( (h, k, \ell) \) gives the Miller indices of the given plane.

viii. If any one or all integers are negative, a bar is put over those integer(s).

The following example will elucidate the procedures and steps to find out the Miller indices of a plane. Let us consider the plane shown in Fig. 1.4.

As shown in Fig. 1.4, the axial length are given as 4Å, 8Å, and 3Å \( (a_1, a_2, a_3) \) respectively and axial intercepts are given as 3Å, 6Å, and 2Å \( (p, q, r) \) respectively. Our aim is to find the Miller indices of the plane shown in Fig. 1.4 by using the steps outlined earlier.

i. Not necessary

ii. Axial lengths 4Å, 8Å, 3Å

iii. Intercept lengths 3Å, 6Å, 2Å

Figure 1.4 The specification of the orientation of crystal planes by Miller indices. Re-draw the figure taking data from the example given here.