

Chapter 1

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1.1

LATTICE VIBRATIONS AND APPROXIMATIONS

The concept regarding the nature of inter atomic interaction in solids gives to an understanding of their vibrational, thermodynamical, elastic, optical, electrical, dielectric, magnetic, thermal and numerous other physical properties. With the rapid widening of the frontiers of knowledge in this field, there has been a big lead forward in our understanding of crystal dynamics and interaction mechanism.

The III-V and II-VI semiconductor compounds crystallizing in the zinc blends type structure are partially ionic and partially covalent. The dynamical theory of crystal is basically a many body problem of number of electrons interacting with the ions that constitute the lattice and cannot be solved explicitly. It is therefore, imperative to resolve to various approximations in our attempt to solve the problems. These approximation are (i) the adiabatic approximation and (ii) the harmonic approximation.

In the adiabatic approximation, electrons in the metallic crystals are treated to respond so quickly to the motions of the ions, that their state is always just a function of the ionic coordinates. In this way, adiabatic principle allows us to separate the ionic motion from the electronic motion, leaving only a residual interaction between the electrons and the phonons. So we can treat the electrons and lattice waves as nearly independent entities and allot the electrons the same coordinates as that of ions. In this section, we shall set the frame work of Born Von karman^[11] (BVK) formalism analyzing small amplitude vibration of the atoms in the crystal lattice, which is defined as a periodic array in three dimension. The array may be generated by the repetition of a smaller unit called cell. The smallest cell that generates the

crystal is referred to as the unit (primitive) cell, in which some definite number of atoms remains present.

When a thermal wave disturbs the lattice, the ionic displacement in the lattice brings about a change in its total potential energy. If these displacements are small as compared to inter atomic spacing, the potential energy of the lattice can be expanded in powers of ionic displacements by Taylor series. The point at which the series converges is not known with certainty but is expected to converge rapidly. The usual practice is to terminate the series at term containing squares of displacements. This approximation of neglecting the higher order terms than the second in the displacement is known as the harmonic approximation. The harmonic approximation does not offer appreciable error in determining the vibrational properties of the lattice such as dispersion curves and the specific heat. The use of higher order terms than the second (anharmonic terms) becomes important in the study of the properties such as thermal resistivity, thermal expansion and broadening and shift of one phonon peaks in the neutron scattering frequency for the phonon process.

The theory of lattice vibration can be discussed with the help of two approximation mentioned earlier. As a general case, let us consider a three dimensional lattice with a basis comprising N unit cells with basis vectors \vec{a}_1 , \vec{a}_2 and \vec{a}_3 and each unit cell containing n ions (or atoms). The equilibrium position of a k^{th} ion in the cell Γ^{st} cell is given by vector

$$\vec{r}^0(lk) = \vec{r}^0(l) + \vec{r}^0(k) \quad (1.1a)$$

Where

$$\vec{r}^0(l) = l_1\vec{a}_1 + l_2\vec{a}_2 + l_3\vec{a}_3 = a(l_x, l_y, l_z) \quad (1.1b)$$

Where $l_1, l_2,$ and l_3 are the integers, called the cell indices and \vec{a}_1, \vec{a}_2 and \vec{a}_3 are the basis vectors of the crystal lattice a is the semi-lattice parameter and $l_x+l_y+l_z$ is even. The lattice generated by **(1.1b)** is called a Bravais lattice. The triplet (l_1, l_2, l_3) will be denoted by l and named as cell index. An atom (or ion) in a crystal structure with more than one atom of associated with each lattice point will be denoted by a pair of indices (lk) . Atoms in a crystal are capable of executing vibrations about their equilibrium position $\vec{r}^0(lk)$ as result of thermal fluctuations at non zero temperatures. In the vibrating state, the instantaneous position of atom (lk) is denoted by

$$\vec{r}(lk) = \vec{r}^0(lk) + \vec{u}(lk) \quad (1.2)$$

Where $\vec{u}(lk)$ denotes small displacement of $(lk)^{\text{th}}$ atom.

The kinetic energy of the crystal is then given by

$$T = \frac{1}{2} \sum_{lk} m_k u_a^2(lk) \quad (1.3)$$

Where m_k is the mass of the atom in the k^{th} sublattice and $u_a(lk)$ is the component of $\vec{u}(lk)$. The potential energy of the deformed lattice expanded in the Taylor series in power of ionic displacements, can be expressed in harmonic approximation as

$$\phi = \sum_{lk} \phi(\vec{r}^0(lk)) = \sum_{lk} \phi(\vec{r}^0(lk) + \vec{u}(lk))$$

$$\phi = \phi_0 + \sum_{lk a} \phi_a(lk) u_a(lk)$$

$$+ \frac{1}{2} \sum_{lk a} \sum_{l'k' \beta} \phi_{a\beta}(lk, l'k') u_a(lk) u_\beta(l'k') \quad (1.4)$$

where $\phi(\vec{r}^o(lk)) = \phi_o$ is the potential energy of the lattice corresponding to the equilibrium configuration of ions another terms are defined as follows

$$\phi_a(lk) = \left. \frac{\partial \phi}{\partial u_a(lk)} \right|_0 \quad (1.5)$$

$$\phi_{\alpha\beta}(lk, l'k') = \left. \frac{\partial^2 \phi}{\partial u_\alpha(l'k') \partial u_\beta(l'k')} \right|_0 \quad (1.6)$$

'o' signifies that the derivatives is to be evaluated in the equilibrium configuration. It is obvious from the definition, $\phi_\alpha(lk)$ is the negative of force acting on the $(lk)^{\text{th}}$ ion in α - direction in equilibrium configuration. However, in equilibrium configuration the force on any ion must vanish and hence we take $\phi_\alpha(lk) = 0$. Thus the potential energy of the lattice in harmonic approximation is given by

$$\phi = \phi_o + \frac{1}{2} \sum_{lk\alpha} \sum_{l'k'\beta} \phi_{\alpha\beta}(lk, l'k') u_\alpha(lk) u_\beta(l'k') \quad (1.7)$$

and the equation of motion of $(lk)^{\text{th}}$ ion with mass m_k can, be written as

$$m_k u_\alpha(lk) = - \frac{\partial \phi}{\partial u_\alpha(lk)} = - \sum_{l'k'\beta} \phi_{\alpha\beta}(lk, l'k') u_\beta(l'k') \quad (1.8)$$

The coefficient $\phi_{\alpha\beta}(lk, l'k')$ is the force (negative) exerted on $(lk)^{\text{th}}$ ion in α -direction when the $(l'k')^{\text{th}}$ ion is displaced by unit distance in the β -direction ($\alpha, \beta = x, y, z$). From equation (1.6) we see that $\phi_{\alpha\beta}(lk, l'k')$ satisfies the symmetry condition

$$\phi_{\alpha\beta}(lk, l'k') = \phi_{\alpha\beta}(l'k', lk) \quad (1.9)$$

The periodicity of the lattice requires that when the lattice as a whole is translated relative to itself by a lattice vector $\vec{r}(l)$, it coincides with itself.

These force constants satisfy the various symmetry requirements to crystal symmetry and depend only upon the relative positions of the relevant unit cells and not on the cell index particularly. A summary of such symmetry properties has been given by Leibfried and Ludwig^[79].

1.2

SECULAR DETERMINANTS

The solutions of the equation (1.7) are considered only for the normal modes, which represent a system of simultaneous linear differential equations, infinite in number. Owing to the basic property of lattice periodicity, we shall find that an immediate reduction can be effected by using the wave solution-

$$u_{\alpha}(lk) = \frac{1}{\sqrt{m_k}} u_{\alpha}(k/\vec{q}) e^{i(\vec{q}\vec{r}^0(lk) - \omega(\vec{q})t)} \quad (1.10)$$

where $u_{\alpha}(k/\vec{q})$ is independent of l . On substituting this expression in equation (1.7), we find that

$$\omega^2(\vec{q})u_{\alpha}(k/\vec{q}) = \sum_{\beta k'} D_{\alpha\beta}(\vec{q}, kk')u_{\beta}(k') \quad (1.11)$$

The equation can be expressed in matrix notation as

$$\omega^2(\vec{q})U(\vec{q}) = D(\vec{q})U(\vec{q}) \quad (1.12)$$

Here $U(\vec{q})$ is a $3n$ - component column matrix $D_{\alpha\beta}(\vec{q}, kk')$ are the elements of the dynamical matrix, expressed as

$$D_{\alpha\beta}(\vec{q}, kk') = \frac{1}{\sqrt{m_k m_{k'}}} \sum_l \phi_{\alpha\beta}(lk, l'k') e^{i(\vec{q}^0(l'k') - \vec{r}^0(lk))} \quad (1.13)$$

Equation (1.11) represents a set of $3n$ homogeneous linear equations corresponding to $3n$ displacements of n ions of the unit cells. In order to have non trivial solutions of these equations, the determinant of the coefficients must vanish. This gives the secular determinant of order $3n$ for obtaining the phonon frequencies $\omega(\vec{q})$, written as

$$|D(\vec{q}) - \omega^2 I| = 0 \quad (1.14)$$

Where I is a unit matrix of order 3n. $D(\vec{q})$, is 3n dimensional square matrix, called the dynamical matrix, (3nX3n) diagonal mass matrix is given by

$$m_{\alpha\beta} = m_k \delta_{\alpha\beta} \delta_{kk}. \quad (1.15)$$

This determinant (1.14) when expanded, will give a cubic equation in ω^2 . For a given value \vec{q} there will be 3n distinct frequencies, which are usually written as $\omega_j^2(\vec{q})(j=1,2,3,\dots,3n)$. The allowed values of \vec{q} are obtained by imposing the Born's cyclic boundary conditions^[10]. The expansion of the determinant will give an equation of order 3n in ω^2 , if there are n ions or atoms in a unit cell. Hence we will obtain 3n branches; 3 of which would be acoustical and 3n-3 would be optical. The determinant (1.14) is known as the secular determinant. If we confine ourselves to a monatomic lattice (n=1), the determinant equation (1.14) gives only three solutions representing three acoustical braches in which the frequencies are small for small values of q and frequency tends to zero when $q \rightarrow 0$. For n =3 (Fluorite as well as CdI₂ structures), there are three acoustical modes and 6 optical modes.

1.3

THE FLUORITE STRUCTURE

The fluorite lattice comprises three interpenetrating face centered cubic sub lattice with three atoms in the unit cell. One metal atom and two non equivalent fluorine atoms F_1 and F_2 occupy those sub lattices. The lattices of F_1 and F_2 are displaced along the body diagonal of the metal lattice by $(a/4, a/4, a/4)$ and $(3a/4, 3a/4, 3a/4)$ respectively, where 'a' is the lattice constant (Figure 1.1). Each metal is surrounded by four fluorine atoms F_1 and four fluorine atoms F_2 . These eight atoms lie at the corners of a cube with metal atom at the centre. Further, each fluorine atom is surrounded by four metal atoms arranged in the tetrahedral fashion around it. Therefore, metal atom has eight first nearest neighbours lying at a distance of $\sqrt{3} a/4$, six second nearest neighbours at distance $a/\sqrt{2}$. The coordinates at these neighbors are listed in tables 1.1 and 1.2. The unit cell can be chosen as a rhombohedron of volume $a^3/4$ bounded by edges $a_1 = a/2$ (101). The position of atoms in unit cell are specified by the vectors $\vec{r}_m = (0,0,0)$, $r_{F1} = a/4$ (111), $r_{F2} = a/2(111)$. m, F_1 and F_2 refer to metal fluorine F_1 and fluorine F_2 atoms respectively.

It seems desirable to give a brief description of the face centered cubic lattice, its Brillouin Zone and non equivalent points because we shall use these concept in chapter 3 of the thesis, Brillouin zone for f.c.c lattice is shown in figure (1.2) where we have also depicted the critical points. Forty eight non equivalent points for the Brillouin zone are given in the table 1.3

1.3.1 THE FACE CENTERED CUBIC LATTICE

For this structure the unit cell has atoms at the corner and at the center of each face of the cube as shown in figure (1.1). The lattice may be considered as four interpenetrating simple cubic lattices. If \vec{e}_1 , \vec{e}_2 and \vec{e}_3 denote unit vectors along the cube edges, and a is the length of an edge, the lattice may be described as Bravais lattice, with rhombohedral unit cell, having edges

$$\begin{aligned}\vec{a}_1 &= \frac{a}{2} (\vec{e}_1 + \vec{e}_2) \\ \vec{a}_2 &= \frac{a}{2} (\vec{e}_2 + \vec{e}_3) \\ \vec{a}_3 &= \frac{a}{2} (\vec{e}_3 + \vec{e}_1)\end{aligned}\tag{1.16}$$

The volume Ω of the unit cell is $\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \frac{a^3}{4}$. The vectors \vec{a}_i ($i=1, 2, 3$) are known as primitive translation vectors of the face centered cubic lattice. Each atom in a f.c.c. lattice has twelve nearest neighbors at distance $a/\sqrt{2}$ and six next nearest neighbors at distance a .

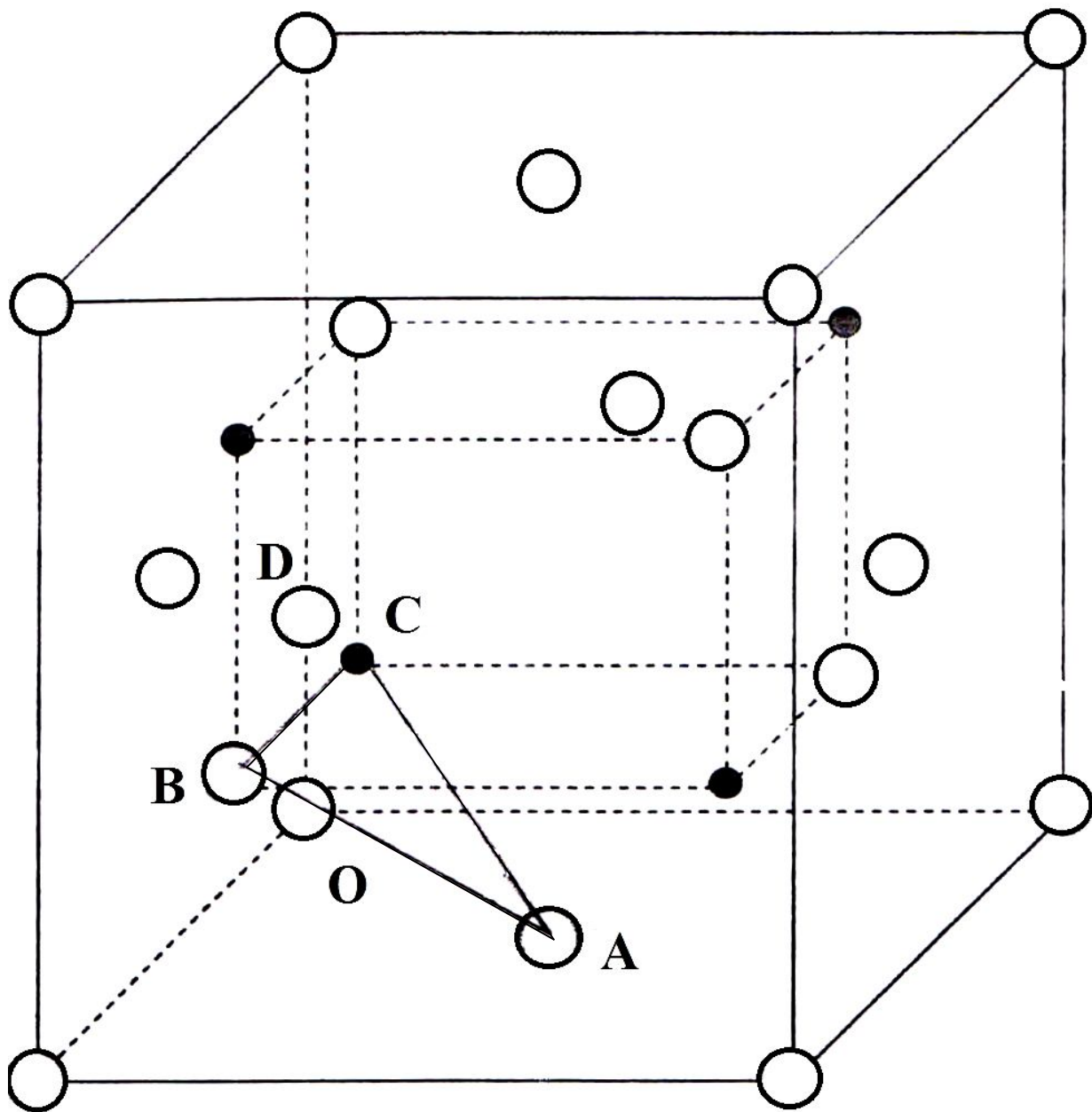


Figure 1.1 The fluorite type lattice structure (RX₂). Open circles denotes metal atoms (R). Double circles denote one type of Fluorine (F₁) atom and solid circles denotes different types of Fluorine (F₂) atoms.

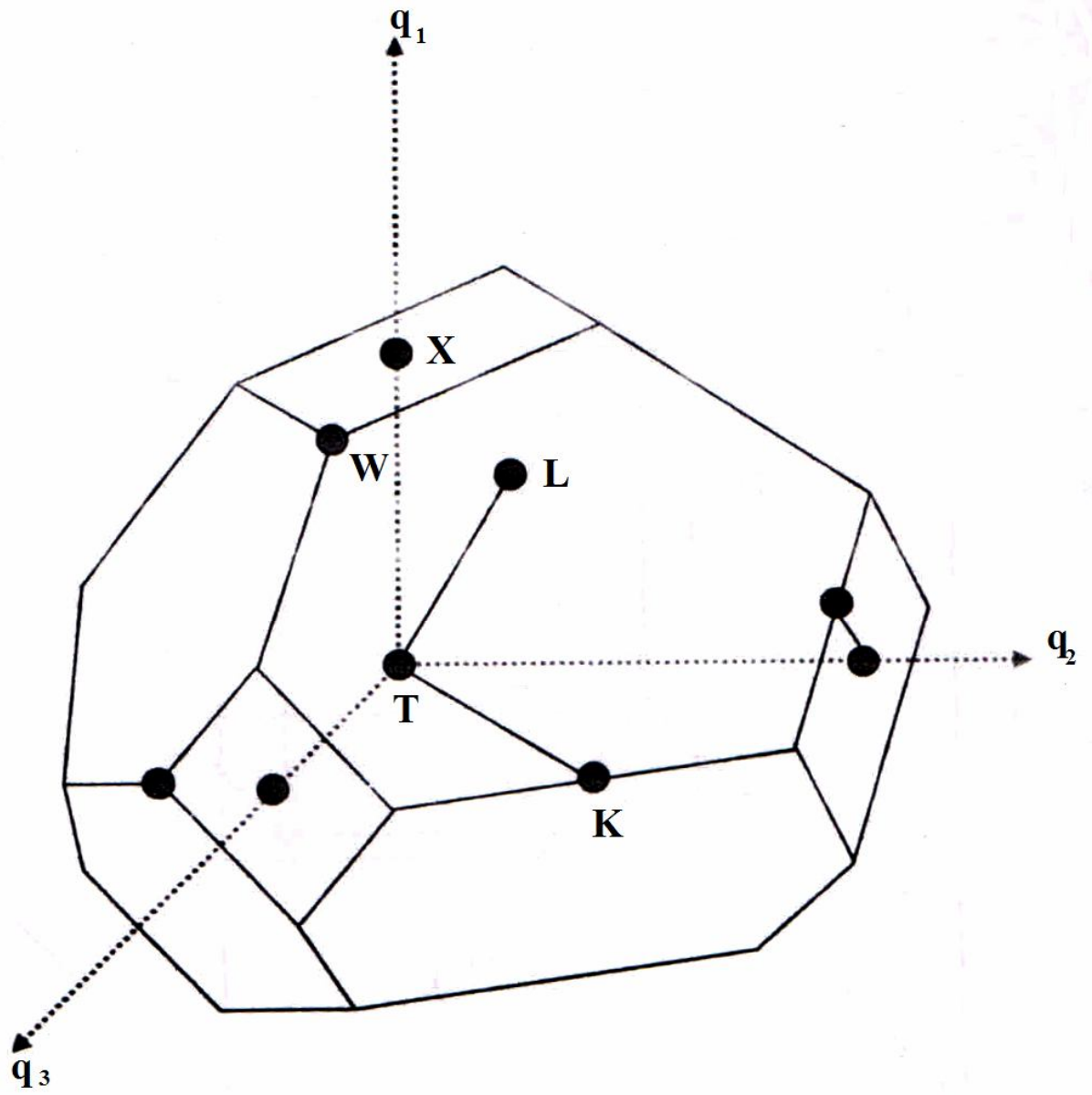


Figure 1.2 The Brillouin zone of face centered cubic structure and critical points.

TABLE 1.1

Direction cosines and coordinates of the various neighbors of fluorite structure:

[i] When metal atom is assumed as origin

Neighbour	Force Constants	Type of atoms	Coordinates			Direction cosine		
			X	Y	Z	Q ₁	Q ₂	Q ₃
First	A₁, B₁	2	a/4	a/4	a/4	1/√3	1/√3	1/√3
		2	-a/4	a/4	-a/4	-1/√3	1/√3	-1/√3
		2	a/4	-a/4	-a/4	1/√3	-1/√3	-1/√3
		2	-a/4	-a/4	a/4	-1/√3	-1/√3	1/√3
		3	a/4	a/4	3a/4	1/√3	1/√3	-1/√3
		3	-a/4	a/4	a/4	-1/√3	1/√3	1/√3
		3	a/4	-a/4	a/4	1/√3	-1/√3	1/√3
		3	-a/4	-a/4	-a/4	-1/√3	-1/√3	-1/√3
Second	A₃	1	a/2	0	a/2	1/√2	0	1/√2
		1	a/2	0	-a/2	1/√2	0	-1/√2
		1	0	a/2	a/2	0	1/√2	1/√2
		1	0	a/2	-a/2	0	1/√2	-1/√2
		1	-a/2	0	a/2	-1/√2	0	1/√2
		1	-a/2	0	-a/2	-1/√2	0	-1/√2
		1	0	-a/2	a/2	0	-1/√2	1/√2
		1	0	-a/2	-a/2	0	-1/√2	-1/√2
		1	a/2	a/2	0	1/√2	1/√2	0
		1	a/2	-a/2	0	1/√2	-1/√2	0
		1	-a/2	a/2	0	-1/√2	1/√2	0
1	-a/2	-a/2	0	-1/√2	-1/√2	0		

TABLE 1.2

[ii] When fluorine atom F_1 or F_2 is assumed as origin

Neighbour	Force Constants	Type of atoms	Coordinates			Direction cosine		
			X	Y	Z	Q_1	Q_2	Q_3
First	A_1, B_1	1	a/4	-a/4	-a/4	$1/\sqrt{3}$	$-1/\sqrt{3}$	$-1/\sqrt{3}$
		1	-a/4	-a/4	a/4	$-1/\sqrt{3}$	$-1/\sqrt{3}$	$1/\sqrt{3}$
		1	-a/4	a/4	-a/4	$-1/\sqrt{3}$	$1/\sqrt{3}$	$-1/\sqrt{3}$
		1	a/4	a/4	a/4	$1/\sqrt{3}$	$1/\sqrt{3}$	$1/\sqrt{3}$
Second	A_2, B_2	3	a/2	0	0	1	0	0
		3	0	a/2	0	0	1	0
		3	0	0	-a/2	0	0	-1
		3	0	0	a/2	0	0	1
		3	0	-a/2	0	0	-1	0
		3	-a/2	0	0	-1	0	0
Third	A_3, B_4	2	a/2	0	a/2	$1/\sqrt{2}$	0	$1/\sqrt{2}$
		2	a/2	a/2	0	$1/\sqrt{2}$	$1/\sqrt{2}$	0
		2	0	a/2	a/2	0	$1/\sqrt{2}$	$1/\sqrt{2}$
		2	a/2	0	-a/2	$1/\sqrt{2}$	0	$-1/\sqrt{2}$
		2	0	a/2	-a/2	0	$1/\sqrt{2}$	$-1/\sqrt{2}$
		2	0	-a/2	-a/2	0	$-1/\sqrt{2}$	$1/\sqrt{2}$
		2	0	-a/2	a/2	0	$-1/\sqrt{2}$	$1/\sqrt{2}$
		2	a/2	-a/2	0	$1/\sqrt{2}$	$-1/\sqrt{2}$	0
		2	-a/2	0	-a/2	$-1/\sqrt{2}$	0	$-1/\sqrt{2}$
		2	-a/2	a/2	0	$-1/\sqrt{2}$	$1/\sqrt{2}$	0
		2	-a/2	0	a/2	$-1/\sqrt{2}$	0	$1/\sqrt{2}$
		2	-a/2	-a/2	0	$-1/\sqrt{2}$	$-1/\sqrt{2}$	0

TABLE 1.3**48 nonequivalent points of the Brillouin zone of f.c.c. lattice**

S.No.	Nonequivalent Points		
	P_x	P_y	P_z
1.	10	4	0
2.	10	2	2
3.	10	2	0
4.	10	0	0
5.	9	5	1
6.	9	3	3
7.	9	3	1
8.	9	1	1
9.	8	6	0
10.	8	4	2
11.	8	4	0
12.	8	2	2
13.	8	2	0
14.	8	0	0
15.	7	7	1
16.	7	5	3
17.	7	5	1
18.	7	3	3
19.	7	3	1
20.	7	1	1
21.	6	6	2
22.	6	6	0
23.	6	4	4
24.	6	4	2

S.No.	Nonequivalent Points		
	P_x	P_y	P_z
25.	6	4	0
26.	6	2	2
27.	6	2	0
28.	6	0	0
29.	5	5	5
30.	5	5	3
31.	5	5	1
32.	5	3	3
33.	5	3	1
34.	5	1	1
35.	4	4	4
36.	4	4	2
37.	4	4	0
38.	4	2	2
39.	4	2	0
40.	4	0	0
41.	3	3	3
42.	3	3	1
43.	3	1	1
44.	2	2	2
45.	2	2	0
46.	2	0	0
47.	1	1	1
48.	0	0	0

1.3.2 THE RECIPROCAL LATTICE AND THE BRILLOUIN ZONE OF F.C.C. LATTICE:

The application of the reciprocal lattice to the crystal physics was first made by Ewald^[44,45]. The primitive translation vectors \vec{b}_1, \vec{b}_2 and \vec{b}_3 of the reciprocal lattice are defined by the relations

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij} \quad (i, j = 1, 2, 3), \quad (1.17)$$

where δ_{ij} is the usual Kronecker delta defined by $\delta_{ij} = 1$ for $i = j$, and 0 for $i \neq j$. The explicit expressions for the reciprocal lattice vectors of f.c.c. lattice are

$$\begin{aligned} \vec{b}_1 &= \frac{2\pi}{\Omega} (\vec{a}_2 \times \vec{a}_3) = 2\frac{\pi}{a} (\vec{e}_1 + \vec{e}_2 - \vec{e}_3) \\ \vec{b}_2 &= \frac{2\pi}{\Omega} (\vec{a}_3 \times \vec{a}_1) = 2\frac{\pi}{a} (-\vec{e}_1 + \vec{e}_2 + \vec{e}_3), \\ \vec{b}_3 &= \frac{2\pi}{\Omega} (\vec{a}_1 \times \vec{a}_2) = 2\frac{\pi}{a} (\vec{e}_1 - \vec{e}_2 + \vec{e}_3) \end{aligned} \quad (1.18)$$

A set of points whose position vectors are given by

$$\vec{g} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3, \quad (1.19)$$

where n_1, n_2, n_3 take on all integral values including zero, constitute the reciprocal lattice for f.c.c. structure. Substitution of values of \vec{b}_j ($j = 1, 2, 3$) in equation (1.19) gives

$$\vec{g} = \frac{2\pi}{a} [(n_1 - n_2 + n_3)\vec{e}_1 + (n_1 + n_2 - n_3)\vec{e}_2 + (-n_1 + n_2 + n_3)\vec{e}_3] \quad (1.20)$$

The shortest eight vectors are given by

$$\frac{2\pi}{a}[\pm\vec{e}_1 \pm \vec{e}_2 \pm \vec{e}_3],$$

And the next shortest are the following six vectors

$$\pm \frac{\pi}{a}\vec{e}_1, \pm \frac{\pi}{a}\vec{e}_2, \pm \frac{\pi}{a}\vec{e}_3,$$

These vectors of the reciprocal lattice may be generated from equation (1.20) by using proper permutation for n_1 , n_2 and n_3 .

A convenient choice of the unit reciprocal lattice cell which displays the full symmetry of the lattice is to choose it in form of the first Brillouin zone. The first Brillouin zone is constructed by drawing vectors to all the lattice points from the origin of the reciprocal space. The planes which are perpendicular bisector of these vectors are the first Brillouin zone. Thus the first Brillouin zone of f.c.c. lattice is the truncated octahedron. The equations of the hexagonal faces, which bisect the shortest \vec{g} vectors, are

$$\pm q_1 \pm q_2 \pm q_3 = \frac{3\pi}{a}$$

And the equations of the square faces, which bisect the next shortest \vec{g} vectors, are

$$q_1 = \pm \frac{2\pi}{a}, q_2 = \pm \frac{2\pi}{a}, q_3 = \pm \frac{2\pi}{a}$$

Where q_1 , q_2 , q_3 , are the component of \vec{q} the position vector of a point on the plane which perpendicularly bisects \vec{g} . The symmetry points and

directions are also shown in figure (1.2). Γ points are the zone centre the coordinates of the symmetry points are as follows;

$$\begin{aligned} \mathbf{X} &= (0, 0, 2\pi/a), & \mathbf{L} &= (\pi/a, \pi/a, \pi/a), \\ \mathbf{W} &= (\pi/a, 0, 2\pi/a), & \mathbf{K} &= (3\pi/2a, 3\pi/2a, 0). \end{aligned}$$

Values of \vec{q} at zone boundaries along symmetry directions are as follows:

- (1) $[\xi 00]$ direction: $|\vec{q}| = 2\frac{\pi}{a}$, with $\xi = 2\frac{\pi}{a}|\vec{q}|$.
- (2) $[\xi\xi 0]$ direction: $|\vec{q}| = \frac{3\pi}{\sqrt{2}a}$, with $\xi = \frac{a}{2\sqrt{2}\pi}|\vec{q}|$.
- (3) $[\xi\xi\xi]$ direction: $|\vec{q}| = \frac{\sqrt{3}\pi}{2a}$, with $\xi = \frac{a}{2\sqrt{3}\pi}|\vec{q}|$.

1.3.3 ALLOWED VALUES OF WAVEVECTORS:

In order to calculate the frequencies of vibration of a lattice one must know the possible values of wave vectors at which the secular determinant (1.14) has to be solved. As mentioned earlier, these values are obtained by imposing the Born's cyclic boundary condition. For a parallelepiped shaped crystal, with its edges parallel to those of a unit cell and having lengths $N_1\vec{a}_1, N_2\vec{a}_2, N_3\vec{a}_3$, the boundary condition gives the relation

$$\exp i[\vec{q} \cdot (N_1\vec{a}_1 + N_2\vec{a}_2 + N_3\vec{a}_3)] = 1$$

$$\text{Or } \vec{q} = \frac{p_1}{N_1}\vec{b}_1 + \frac{p_2}{N_2}\vec{b}_2 + \frac{p_3}{N_3}\vec{b}_3, \quad (1.21)$$

where p_1, p_2, p_3 are integers for $\vec{b}_1, \vec{b}_2, \vec{b}_3$ basis vectors of the reciprocal lattice. In other words if the unit cell of the reciprocal lattice is divided in to

N_1, N_2, N_3 sub cells by dividing the three unit translation vectors into N_1, N_2 and N_3 parts respectively, there can only be one of the wave vector connecting the origin to point of subdivision. The component of \vec{q} must be real and multiple of $2\pi / N_1, 2\pi / N_2$ and $2\pi / N_3$ respectively. In such a case each unit cell of the reciprocal lattice, therefore, contains $N = N_1 N_2 N_3$ distinct values of \vec{q} which for a large N may be regarded as continuous and uniformly distributed in the reciprocal space with density equal to $N / (\vec{b}_1 \cdot \vec{b}_2 \times \vec{b}_3) = V / (2\pi)^3$, where V is the volume of the whole crystal.

As mentioned earlier, the convenient choice of the unit reciprocal lattice cell is the first Brillouin zone which can be divided into a mesh of points using expression (1.21). Assuming $N_1 = N_2 = N_3 = n_s$ and substituting the values of $\vec{b}_1, \vec{b}_2, \vec{b}_3$ from equation (1.21) we get for the f.c.c. lattice.

$$\vec{q} = \frac{2\pi}{n_s a} [p_x \vec{e}_1 + p_y \vec{e}_2 + p_z \vec{e}_3], \quad (1.22)$$

Where $p_x = p_1 - p_2 + p_3, p_y = p_1 + p_2 - p_3$ and $p_z = -p_1 + p_2 + p_3$. It can be shown that p_x, p_y, p_z are integers either all odd or all even. Integers p_x, p_y, p_z are so chosen that the points defining \vec{q} lie in the first Brillouin zone with its centre at the origin of reciprocal space. The boundaries of the Brillouin zone are defined by

$$p_x = \pm n_s, p_y = \pm n_s \text{ and } \pm p_x \pm p_y \pm p_z$$

On account of the cubic symmetry, a number of points will correspond to same values of frequencies. It is sufficient if we consider only those points of the positive octant for which

$$0 \leq p_z \leq p_y \leq p_x \leq n_s$$

and

$$p_x + p_y + p_z \leq 3n_s/2 \quad (1.23)$$

Following Dayal and Singh^[41] we have taken the value of n_s to be 10. In the case of f.c.c. lattice, there are 48 representative (nonequivalent) points defined by equations (1.22) and (1.23) including the origin. The secular determinant (1.14) is solved for a these points except the origin. Each frequency is assigned a statistical weight according to the number of similar points associated with it. The symmetry consideration show that any frequency of the point p_x, p_y, p_z corresponds to 48 frequencies. For points lying on the surface, edges and corners of the Brillouin zone, the above number has to be divided by an appropriate factor, which depends on the number of polyhedral sharing the point if the whole space is filled with zone like polyhedral. When proper weightage is assigned to all the nonequivalent points, we get a total of 1000 points, which give rise to 3000 frequencies, within the whole zone. As mentioned earlier first eight non equivalent points have been given in table 1.1.

1.4

CdI₂ STRUCTURE

The CdI₂ structure is a layered structure of space group D. The individual tightly bounded layer in MX₂ (M=metal atom, X= chalcogenides atom) is an X-M-X sandwich and the adjacent sandwiches are held together along the c-axis by weak Van-der Waals forces (Figure 1.3) because the primary valencies of constituent atoms are almost fully satisfied within the layer. Each metal atom (M) is octahedrally coordinated (Figure 1.3a) to six nearest neighbour X atoms. Each X atom is nested atop a triangle of M atoms. The stacking sequence along the c-axis is thus M-X-X-M, and the relatively weak X-X interaction results in the compound having layer like character (Figure 1.3b). Thus unit cell spans only one layer and contains one molecular unit MX₂ i.e. three atoms. For our convenience, we assigned the lower layer chalcogen atom (X₁) as 1, the metal atom (M) as 2 and upper layer chalcogen atom (B₂) as 3.

The primitive translation vectors of hexagonal close packed lattice are expressed as

$$\begin{aligned}\vec{a}_1 &= a\vec{e}_1 \\ \vec{a}_2 &= \frac{a}{2}\vec{e}_1 + \frac{\sqrt{3}}{2}a\vec{e}_2 \\ \vec{a}_3 &= c\vec{e}_3\end{aligned}\tag{1.24}$$

\vec{e}_1, \vec{e}_2 and \vec{e}_3 , represent the unit vectors along the three Cartesian axes.

In this case equation (1.18) and (1.24) give

$$\begin{aligned}b_1 &= \frac{2\pi}{a}\left(\vec{e}_1 + \frac{1}{\sqrt{3}}\vec{e}_2\right) \\ b_2 &= \frac{4\pi}{a\sqrt{3}}\vec{e}_2\end{aligned}$$

$$b_3 = \frac{2\pi}{c} \bar{e}_3 \quad (1.25)$$

From equations (1.19) and (1.25) we have

$$\begin{aligned} \bar{g} &= n_1 \cdot \frac{2\pi}{a} \left(\bar{e}_1 + \frac{1}{\sqrt{3}} \bar{e}_2 \right) + n_2 = \frac{4\pi}{a\sqrt{3}} \bar{e}_2 + n_3 \frac{2\pi}{c} \bar{e}_3 \\ \bar{g} &= \frac{2\pi}{a} n_1 \bar{e}_1 + \frac{2\pi}{a\sqrt{3}} (n_1 + 2n_2) \bar{e}_2 + \frac{2\pi}{c} \bar{e}_3 \end{aligned} \quad (1.26)$$

The shortest non zero are the following eight vectors,

$$\begin{aligned} &\pm \frac{4\pi}{a\sqrt{3}} \bar{e}_2, \pm \frac{2\pi}{a} \left(\bar{e}_1 - \frac{1}{\sqrt{3}} \bar{e}_2 \right), \pm \frac{2\pi}{a} \left(\bar{e}_1 + \frac{1}{\sqrt{3}} \bar{e}_2 \right) \\ &\pm \frac{2\pi}{c} \bar{e}_3 \end{aligned}$$

In terms of b_1 they are,

$$\pm \bar{b}_1, \pm (\bar{b}_1 - \bar{b}_2), \bar{b}_2, \pm \bar{b}_3 \quad (1.27)$$

If \bar{q} be the phonon wave vector defined by $\bar{q} = 2\pi / \lambda$, then the equations of the planes perpendicular to the vectors given by equation (1.26) is given by

$$2\bar{q} \cdot \bar{g} + |\bar{g}|^2 = 0 \quad (1.28)$$

In order to obtain the first Brillouin zone we draw planes which are perpendicular bisectors of the vectors defined by equation (1.27). Their equations obtained from (1.28) are:

$$\pm \left(|\bar{q}_1| \pm \frac{1}{\sqrt{3}} |\bar{q}_2| \right) = \frac{4\pi}{3a}$$

$$|\bar{q}_2| = \pm \frac{2\pi}{a\sqrt{3}}$$

$$|\bar{q}_3| = \pm \frac{\pi}{c}$$

These boundary planes enclose a hexagonal prism of height $2\pi/c$ and base side $4\pi/3a$. This therefore, the first Brillouin zone of a simple hexagonal lattice. Since the Brillouin zones are a consequence of the translational

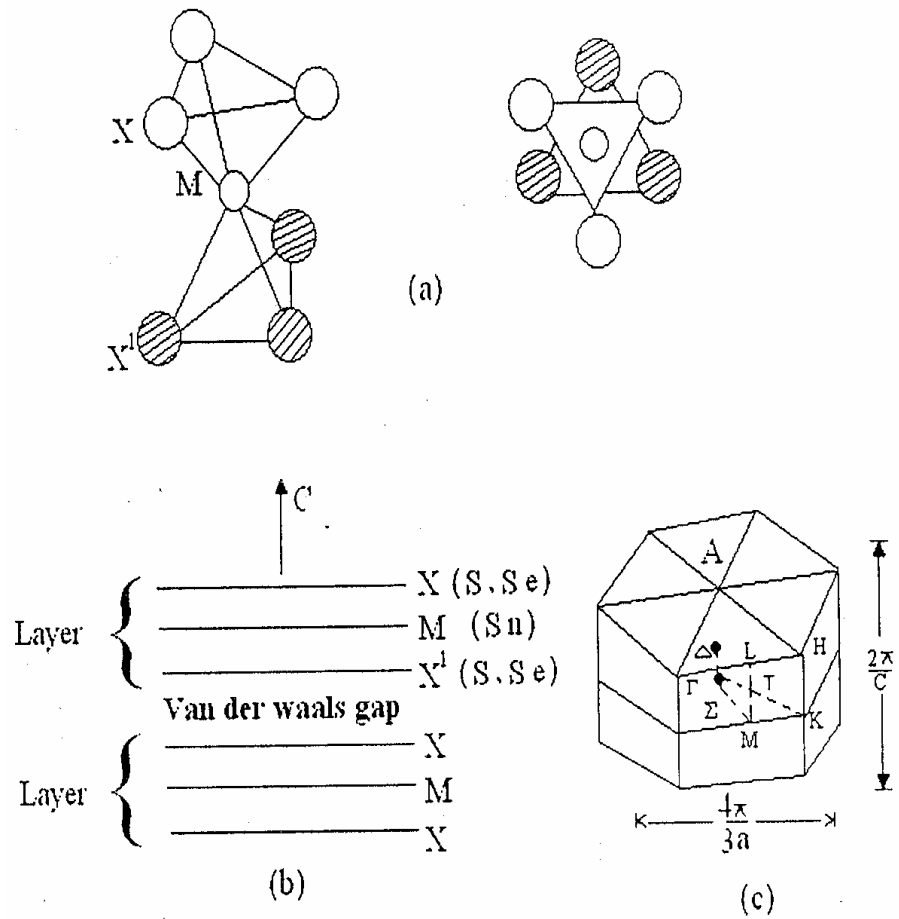


Figure 1.3 MX_2 (CdI_2) crystal structure showing-

- (a) Octahedral coordination within each sandwich,
- (b) The stacking of sandwiches, and
- (c) The hexagonal Brillouin zone.

symmetry of the crystal, the Brillouin zone of hexagonal close packed lattice is the same as that for a simple hexagonal lattice because the translational symmetry is the same in both the cases. The Brillouin zone is shown in (Figure 1.4). The direction cosines and coordinates of the neighbours of CdI₂ structure are listed in tables 1.4, 1.5 and 1.6.

1. Σ represents the symmetry direction $[01\bar{1}0]$.
2. \square represents the symmetry direction $[0001]$.
3. T, T' represents the symmetry direction $[11\bar{2}0]$.
4. Γ stands for the point = 0
5. M stands for the zone boundary along $[0110]$ direction.
6. A stands for the zone boundary along $[0001]$ direction.

In view of equation (1.27) the vector q in the miniature cell of the first Brillouin zone for hexagonal lattice may be written as

$$\vec{g} = p_x \vec{e}_1 + p_y \vec{e}_2 + p_z \vec{e}_3 \quad (1.29)$$

Such that

$$p_x = \frac{2\pi p_1}{an_s}$$

$$p_y = \frac{2\pi(p_1 + 2p_2)}{a\sqrt{3}n_s}$$

$$p_z = \frac{2\pi p_3}{cn_s}$$

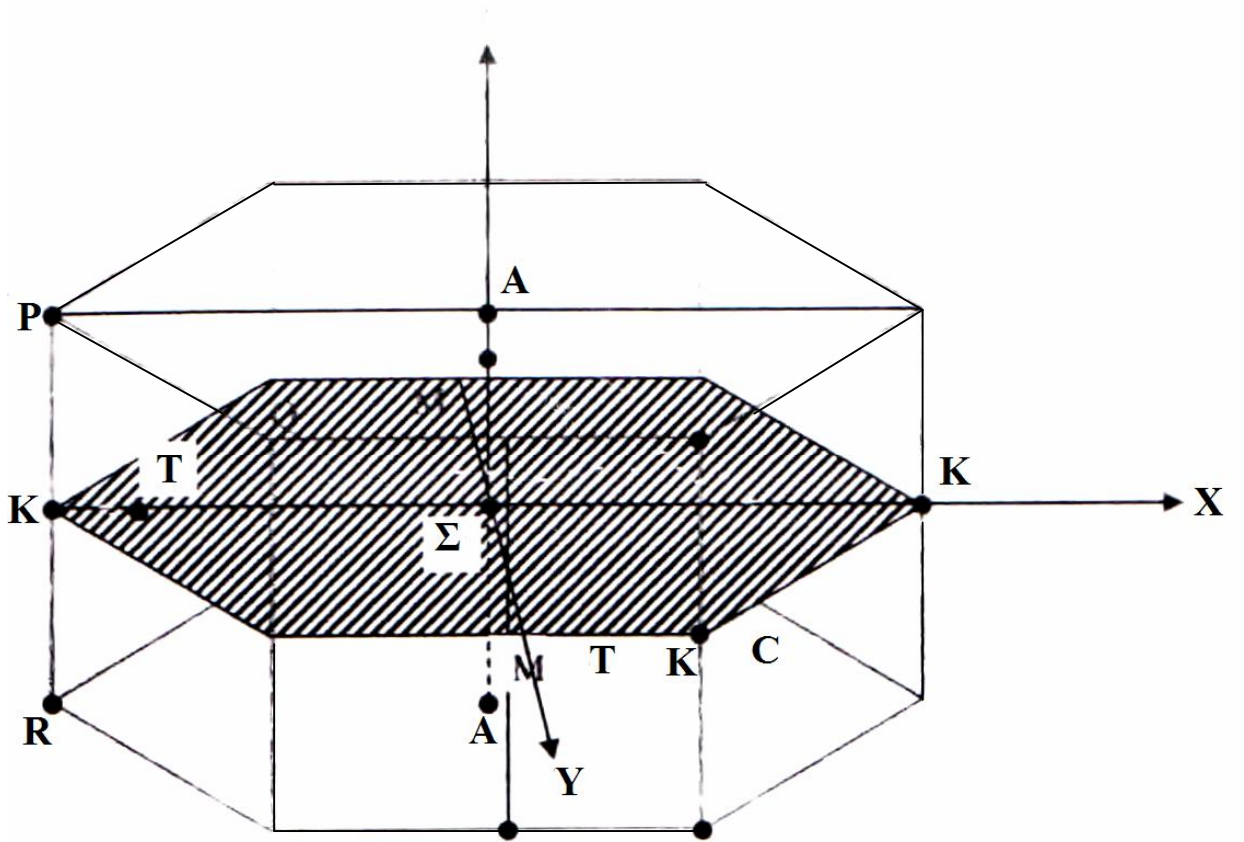


Figure 1.4 Enlarged size of the first Brillouin zone of hexagonal lattice and critical points.

Table 1.4

The Direction cosines and coordinates of the neighbors of CdI₂ structure

[i] When lower layer chalcogen atom (X₁) is assumed as origin

Neigh- bors	Force Constants	Type of atoms	Coordinates			Direction cosine		
			X	Y	Z	Q ₁	Q ₂	Q ₃
First	A₁, B₁	2	a/2	-a/2√3	c/4	a/2A	-a/2√3 A	c/4A
		2	-a/2	-a/2√3	c/4	-a/2A	-a/2√3 A	c/4A
		2	0	a/√3	c/4	0	a/2√3 A	c/4A
Second	A₂, B₂	3	0	-a/√3	c/2	0	-a/√3 B	c/2B
		3	a/2	a/2√3	c/2	a/2B	-a/2√3 B	c/2B
		3	-a/2	a/2√3	c/2	-a/2B	a/2√3 B	c/2B
		3	0	-a/√3	-c/2	0	-a/√3 B	-c/2B
		3	a/2	a/2√3	-c/2	a/2B	a/2√3 B	-c/2B
		3	-a/2	a/2√3	-c/2	-a/2B	a/2√3 B	-c/2B

Where

$$A = \sqrt{\frac{a^2}{3} + \frac{c^2}{16}}$$

$$B = \sqrt{\frac{a^2}{3} + \frac{c^2}{4}}$$

Here a and c are the lattice constants.

Table 1.5

[ii] When upper layer chalcogen atom (X_2) is assumed as origin

Neigh- bors	Force Constants	Type of Atoms	Coordinates			Direction cosine		
			X	Y	Z	Q_1	Q_2	Q_3
First	A_1, B_1	2	$a/2$	$-a/2\sqrt{3}$	$-c/4$	$a/2A$	$-a/2\sqrt{3}A$	$-c/2A$
		2	$-a/2$	$-a/2\sqrt{3}$	$-c/4$	$-a/2A$	$-a/2\sqrt{3}A$	$-c/2A$
		2	0	$a/\sqrt{3}$	$-c/4$	0	$a/\sqrt{3}A$	$-c/2A$
Second	A_2, B_2	3	0	$-a/\sqrt{3}$	$-c/2$	0	$-a/\sqrt{3}B$	$-c/2B$
		3	$a/2$	$a/2\sqrt{3}$	$-c/2$	$a/2B$	$-a/2\sqrt{3}B$	$-c/2B$
		3	$-a/2$	$-a/2\sqrt{3}$	$-c/2$	$-a/2B$	$-a/2\sqrt{3}B$	$-c/2B$
		3	0	$-a/\sqrt{3}$	$c/2$	0	$-a/\sqrt{3}B$	$c/2B$
		3	$a/2$	$a/2\sqrt{3}$	$c/2$	$a/2B$	$a/2\sqrt{3}B$	$c/2B$
		3	$-a/2$	$a/2\sqrt{3}$	$c/2$	$-a/2B$	$a/2\sqrt{3}B$	$c/2B$

Table 1.6

[iii] When metal atom (M) is assumed as origin

Neigh- bors	Force Constants	Type of atoms	Coordinates			Direction cosine		
			X	Y	Z	Q ₁	Q ₂	Q ₃
First	A₁, B₁	1	0	$-a/\sqrt{3}$	$-c/4$	0	$-a/\sqrt{3} A$	$-c/4A$
		1	$a/2$	$a/2\sqrt{3}$	$-c/4$	$a/2A$	$a/2\sqrt{3} A$	$-c/4A$
		1	$-a/2$	$a/2\sqrt{3}$	$-c/4$	$-a/2A$	$a/2\sqrt{3} A$	$-c/4A$
		3	0	$a/\sqrt{3}$	$c/4$	0	$a/\sqrt{3} A$	$c/4A$
		3	$a/2$	$-a/2\sqrt{3}$	$c/4$	$a/2A$	$-a/2\sqrt{3} A$	$c/4A$
		3	$-a/2$	$-a/2\sqrt{3}$	$c/4$	$-a/2A$	$-a/2\sqrt{3} A$	$c/4A$

In actual practice due to symmetry we need to consider only the $1/24^{\text{th}}$ part of the Brillouin zone. The points lying within this irreducible segment are given by the values p_1, p_2, p_3 which are the entire positive subject to the condition,

$$p_1 + 2p_2 < \frac{n_s}{2}, p_3 \leq \frac{n_s}{2}, p_2 < \frac{n_s}{3}, p_1 < p_2$$

We have taken n_s to be 10. This gives a total of 84 points including the origin. However, if an account is taken of all the points in the miniature cell, then the total number of points must come out to be exactly 1000. Non equivalent points their statistical weight are given in table **1.7**.

TABLE 1.7**Representative points of the Brillouin zone at hexagonal lattice**

S.No.	Representative points			No. of similar points	Statistical weight	Remarks
	P ₁	P ₂	P ₃			
1.	5	5	0	3	3/1000	Edge
2.	5	4	0	6	6/1000	Surface
3.	5	4	1	12	12/1000	Surface
4.	5	4	2	6	6/1000	Surface
5.	5	3	0	6	6/1000	Surface
6.	5	3	1	12	12/1000	Surface
7.	5	3	2	12	12/1000	Surface
8.	5	3	3	6	6/1000	Surface
9.	5	2	0	6	6/1000	Surface
10.	5	2	1	12	12/1000	Surface
11.	5	2	2	6	6/1000	Surface
12.	5	1	0	6	6/1000	Surface
13.	5	1	1	6	6/1000	Surface
14.	5	0	0	1	1/1000	Surface
15.	4	5	0	6	6/1000	Surface
16.	4	4	0	12	12/1000	Surface
17.	4	4	1	24	24/1000	Surface
18.	4	4	2	12	12/1000	Surface
19.	4	3	0	12	12/1000	Surface
20.	4	3	1	24	24/1000	Surface
21.	4	3	2	24	24/1000	Surface
22.	4	3	3	12	12/1000	Surface
23.	4	2	0	12	12/1000	Surface
24.	4	2	1	24	24/1000	Surface
25.	4	2	2	12	12/1000	Surface
26.	4	1	0	12	12/1000	Surface
27.	4	1	1	12	12/1000	Surface

S.No.	Representative points			No. of similar points	Statistical weight	Remarks
	P ₁	P ₂	P ₃			
28	4	0	0	2	2/1000	Surface
29	3	5	0	6	6/1000	Surface
30	3	4	0	12	12/1000	Surface
31	3	4	0	24	24/1000	Surface
32	3	4	2	12	12/1000	Surface
33	3	3	0	12	12/1000	Surface
34	3	3	1	24	24/1000	Surface
35	3	3	2	24	24/1000	Surface
36	3	3	3	12	12/1000	Surface
37	3	2	0	12	12/1000	Surface
38	3	2	1	24	24/1000	Surface
39	3	2	2	12	12/1000	Surface
40	3	1	0	12	12/1000	Surface
41	3	1	1	12	12/1000	Surface
42	3	0	0	2	2/1000	Surface
43	2	5	0	6	6/1000	Surface
44	2	4	0	12	12/1000	Surface
45	2	4	1	24	24/1000	Surface
46	2	4	2	12	12/1000	Surface
47	2	3	0	12	12/1000	Surface
48	2	3	1	24	24/1000	Surface
49	2	3	2	24	24/1000	Surface
50	2	3	3	12	12/1000	Surface
51	2	2	0	12	12/1000	Surface
52	2	2	1	24	24/1000	Surface
53	2	2	2	12	12/1000	Surface
54	2	1	0	12	12/1000	Surface
55	2	1	1	12	12/1000	Surface
56	2	0	0	12	2/1000	Surface

S.No.	Representative points			No. of similar points	Statistical weight	Remarks
	P ₁	P ₂	P ₃			
57	1	5	0	6	6/1000	Surface
58	1	4	0	12	12/1000	Surface
59	1	4	1	24	24/1000	Surface
60	1	4	2	12	12/1000	Surface
61	1	3	0	12	12/1000	Surface
62	1	3	1	24	24/1000	Surface
63	1	3	2	24	24/1000	Surface
64	1	3	3	12	12/1000	Surface
65	1	2	0	12	12/1000	Surface
66	1	2	1	24	24/1000	Surface
67	1	2	2	12	12/1000	Surface
68	1	1	0	12	12/1000	Surface
69	1	1	1	12	12/1000	Surface
70	1	0	0	2	2/1000	Surface
71	0	5	0	3	3/1000	Surface
72	0	4	0	6	6/1000	Surface
73	0	4	1	12	12/1000	Surface
74	0	4	2	6	6/1000	Surface
75	0	3	0	6	6/1000	Surface
76	0	3	1	12	12/1000	Surface
77	0	3	2	12	12/1000	Surface
78	0	3	3	6	6/1000	Surface
79	0	2	0	6	6/1000	Surface
80	0	2	2	12	12/1000	Surface
81	0	2	2	6	6/1000	Surface
82	0	1	0	6	6/1000	Surface
83	0	1	1	6	6/1000	Surface
84	0	0	0	1	1/1000	Surface