Chapter I

ZINC-BLENDE STRUCTURE

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CHAPTER I

ZINC-BLENDE STRUCTURE

1.1 INTRODUCTION

The study of lattice dynamics forms an important part of any course in solid state physics. The vibration of atoms in a crystal not only determine its thermal properties but also govern phenomena like diffuse scattering of x-rays, neutron scattering, spin-lattice relaxation, etc. In order to understand any of these phenomena it is necessary to develop the theory of vibration of atoms that is the theory of lattice dynamics.

The study of the solid state properties of the semi-conducting ternary mixed crystals is of general scientific and technical interest, as these are widely used in I.R. detectors as sensors of thermal radiations and as wide band detectors in the emerging areas of laser radar and laser communication. The properties of mixed crystals of III-V compounds with different band structure may be used in some areas. Due to their wide applications in various fields of science and technology in recent years many studies of mixed systems have also become a subject of considerable theoretical interest.

As the lattice dynamical studies of solids are a pre-requisite for a proper understanding of various properties of solids, the present work has been devoted
mainly to the theoretical study of III-V and II-VI semiconducting mixed crystals of the type $AB_{1-x}C_x$ having zinc-blende structure.

So far no detailed theoretical studies have been made on mixed semiconductors using a reliable model incorporating interaction interactions in the realistic way. We, therefore, thought it worth while to develop a theoretical model for this purpose.

### 1.2 ZINC-BLENDE STRUCTURE

The Zinc-blende structure is very closely related to the diamond structure. In fact, it is identical to the diamond structure except that the two interpenetrating F.C.C. sublattices are of different atoms: one composed entirely of Zn atoms and the other entirely of 'S' atoms. The theoretical formulation for the lattice dynamics requires the complete understanding of the geometry of the crystal lattice under investigation. It is therefore essential to describe the geometry of the lattice of the zinc-blende crystals for obtaining the theoretical expressions representing the lattice dynamical formulation of such crystals. This structure, named after the compound ZnS, is closely related to the diamond structure, the only difference being that the two atoms forming the basis are of different kind. Each of two types of atoms in the zinc-blende structure occupies the sites of a face centred cubic lattice. When we take the cube side to have a length $2a$. The second such lattice is displaced along the body diagonal of the first lattice by one quarter of the cube diagonal $(\sqrt{3}/2)a$. The three basis vectors that define the rhombohedral parallelepiped unit cell are

$$\vec{a}_i = a(\vec{e}_2 + \vec{e}_3)$$  \hspace{1cm} (1.1a)
\[ \vec{a}_2 = a(\vec{e}_1 + \vec{e}_3) \]  
\[ \vec{a}_3 = a(\vec{e}_1 + \vec{e}_2) \]

where \(\vec{e}_1, \vec{e}_2, \vec{e}_3\) represent the unit vectors along the three Cartesian axes and thus the volume of the unit cell is \(2a^3\).

The Fig. (1.1) illustrates the zinc-blende crystal structure. The filled circles represent 12 atoms situated at a distance \(a/2\) from the reference atom lying at the origin of coordinates. These atoms belong to lattice-I. The open circles represent the four nearest neighbors of filled circles and are in lattice-II. They lie at a distance \(a(\sqrt{3}/2)\) from the reference atom. The positions of the atoms in the unit cell are specified by the vectors \(\vec{r}(k) = a/2(k-1)(\vec{e}_1 + \vec{e}_2 + \vec{e}_3)\), where \(k = 1\) denotes the \(k\) type of atoms and \(k = 2\) denotes \(k'\) type of atoms. The atoms of the lattice-I are located by the vectors

\[
\vec{r}_i(n) = a[(n_1 + n_1)\vec{e}_1 + (n_1 + n_2)\vec{e}_2 + (n_2 + n_3)\vec{e}_3]
\]

\[
= a(l_x\vec{e}_1 + l_y\vec{e}_2 + l_z\vec{e}_3)
\]

\(l_x, l_y\) and \(l_z\) are given by the relation (1.1). The quantities \(n_1, n_2\) and \(n_3\) are integers.

The lattice-II is said to be generated by displacing the first lattice through a displacement \(\vec{r}_{1,2}\) such that

\[
\vec{r}_{1,2} = -\frac{1}{2}a(\vec{e}_1 + \vec{e}_2 + \vec{e}_3) \]  

(-ve sign is chosen in conformity with Cochran and Kellerman). Thus the location of atoms in lattice-II is given by
Fig. 1.1 A diagram of the zinc-blende lattice showing the outlines of the cubic unit cell
\[
\tilde{r}_g(n) = \tilde{r}_i(n) + \tilde{r}_{i_2}(n)
\]
\[
= a \left[ \left( n_x + n_z - \frac{1}{2} \right) \tilde{e}_1 + \left( n_x + n_z - \frac{1}{2} \right) \tilde{e}_2 + \left( n_z - \frac{1}{2} \right) \tilde{e}_3 \right]
\]
\[
= a \left[ \left( l_x - \frac{1}{2} \right) \tilde{e}_1 + \left( l_y - \frac{1}{2} \right) \tilde{e}_2 + \left( l_z - \frac{1}{2} \right) \tilde{e}_3 \right]
\]
\[
= a \left( n_x \tilde{e}_1 + n_y \tilde{e}_2 + n_z \tilde{e}_3 \right)
\]
(1.4)

where
\[
 n_x = l_x - 1/2,
 n_y = l_y - 1/2 \quad \text{and} \quad n_z = l_z - 1/2
\]

The coordinates of the atoms as obtained from (1.3) and (1.4) has been given in Table 1.1

1.3 RECIPROCAL LATTICE

In a crystal there exists many set of planes with different orientations and spacing. These planes can cause deflection. If we draw normal to all set of planes, from a common origin, (the length of normal being proportional to the reciprocal of the interlinear spacing of the corresponding set) then the end points of normal form a lattice which is called as reciprocal lattice. The concept of the reciprocal lattice space was first introduced by Willard Gibbs. The application of this reciprocal lattice to the crystal physics was first made by Ewald. Since then, it has been widely used in x-ray crystallography and in quantum theory of metals and non-metals. The lattice described by the vectors \( \tilde{a}_1, \tilde{a}_2 \) and \( \tilde{a}_3 \) is referred to as the direct lattice. For each direct
Table 1.1  Coordinates of the first and the second neighbours of the reference atom indexed as "0" and the corresponding direction cosines.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Index of Neighbour (Coordination sphere)</th>
<th>Index of atoms</th>
<th>Coordinates</th>
<th>Lattice to which atom belongs</th>
<th>Direction Cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td></td>
<td>0</td>
<td>0 0 0 0</td>
<td>Lattice-I</td>
<td>0 0 0</td>
</tr>
<tr>
<td>2.</td>
<td>1 (nearest neighbour)</td>
<td>1</td>
<td>a/2 a/2 a/2</td>
<td>Lattice-II</td>
<td>1/√3 1/√3 1/√3</td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td>2</td>
<td>-a/2 -a/2 a/2</td>
<td></td>
<td>-1/√3 -1/√3 1/√3</td>
</tr>
<tr>
<td>4.</td>
<td></td>
<td>3</td>
<td>a/2 -a/2 -a/2</td>
<td></td>
<td>1/√3 -1/√3 -1/√3</td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td>4</td>
<td>-a/2 a/2 -a/2</td>
<td></td>
<td>-1/√3 1/√3 -1/√3</td>
</tr>
<tr>
<td>6.</td>
<td>2 (next nearest neighbour)</td>
<td>5</td>
<td>a 0 a</td>
<td>Lattice-I</td>
<td>1/√2 0 1/√2</td>
</tr>
<tr>
<td>7.</td>
<td></td>
<td>6</td>
<td>-a 0 -a</td>
<td></td>
<td>-1/√2 0 -1/√2</td>
</tr>
<tr>
<td>8.</td>
<td></td>
<td>7</td>
<td>-a 0 a</td>
<td></td>
<td>-1/√2 0 1/√2</td>
</tr>
<tr>
<td>9.</td>
<td></td>
<td>8</td>
<td>a 0 -a</td>
<td></td>
<td>1/√2 0 -1/√2</td>
</tr>
<tr>
<td>10.</td>
<td></td>
<td>9</td>
<td>a a 0</td>
<td></td>
<td>1/√2 1/√2 0</td>
</tr>
<tr>
<td>11.</td>
<td></td>
<td>10</td>
<td>-a -a 0</td>
<td></td>
<td>-1/√2 -1/√2 0</td>
</tr>
<tr>
<td>12.</td>
<td></td>
<td>11</td>
<td>a -a 0</td>
<td></td>
<td>1/√2 -1/√2 0</td>
</tr>
<tr>
<td>13.</td>
<td></td>
<td>12</td>
<td>-a a 0</td>
<td></td>
<td>-1/√2 1/√2 0</td>
</tr>
<tr>
<td>14.</td>
<td></td>
<td>13</td>
<td>0 a a</td>
<td></td>
<td>0 1/√2 1/√2</td>
</tr>
<tr>
<td>15.</td>
<td></td>
<td>14</td>
<td>0 -a -a</td>
<td></td>
<td>0 -1/√2 -1/√2</td>
</tr>
<tr>
<td>16.</td>
<td></td>
<td>15</td>
<td>0 -a a</td>
<td></td>
<td>0 -1/√2 1/√2</td>
</tr>
<tr>
<td>17.</td>
<td></td>
<td>16</td>
<td>0 a -a</td>
<td></td>
<td>0 1/√2 -1/√2</td>
</tr>
</tbody>
</table>
lattice we may define a reciprocal lattice by the basis vectors \( \vec{b}_1, \vec{b}_2 \) and \( \vec{b}_3 \) given by the equation.

\[
\vec{a}_i, \vec{b}_j = 2\pi \delta_{ij} (i, j = 1, 2, 3)
\]  

(1.5)

where \( \delta_{ij} \) is the kronecker delta, defined by

\[
\delta_{ij} = 1 \text{ for } i = j
\]

\[
= 0 \text{ for } i \neq j
\]  

(1.6)

The vectors \( \vec{b}_j \) are called the reciprocal vectors and the set of points whose position vectors are given by

\[
\vec{h} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3
\]  

(1.7)

where \( m_1, m_2 \) and \( m_3 \) are integers (positive, negative or zero), are called reciprocal lattice points, is called a reciprocal lattice vector. The explicit expression for the reciprocal lattice vectors are:

\[
\vec{b}_1 = 2\pi / V_a (\vec{a}_1 \times \vec{a}_3)
\]  

(1.8a)

\[
\vec{b}_2 = 2\pi / V_a (\vec{a}_3 \times \vec{a}_1)
\]  

(1.8b)

and

\[
\vec{b}_3 = 2\pi / V_a (\vec{a}_1 \times \vec{a}_2)
\]  

(1.8c)

where \( V_a = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) \) is the volume of the unit cell in the direct space. In the case of the zinc-blende structure crystals the reciprocal lattice basis vectors can be written with the help of equations (1.1a, 1.1b, 1.1c) and (1.8a, 1.8b and 1.8c) as

\[
\vec{b}_1 = \pi / a (-\vec{e}_1 + \vec{e}_2 + \vec{e}_3)
\]  

(1.9a)

\[
\vec{b}_2 = \pi / a (\vec{e}_1 - \vec{e}_2 + \vec{e}_3)
\]  

(1.9b)
and

\[ \tilde{b}_3 = \frac{\pi}{a}(\tilde{e}_1 + \tilde{e}_2 - \tilde{e}_3) \]  

(1.9c)

substituting the values of \( \tilde{b}_1, \tilde{b}_2 \) and \( \tilde{b}_3 \) in (1.7) we get

\[ \tilde{h} = \frac{\pi}{a} \left\{ (-m_1 + m_2 + m_3)\tilde{e}_1 + (m_1 - m_2 + m_3)\tilde{e}_2 + (m_1 + m_2 - m_3)\tilde{e}_3 \right\} \]  

(1.10)

The bounding planes of the first Brillouin zone are set of the eight shortest \( \tilde{h} \) vectors. These vectors are \( \pi/a(\pm \tilde{e}_1 \pm \tilde{e}_2 \pm \tilde{e}_3) \). The next shortest are the six vectors.

\[ \pm \frac{2\pi}{a}\tilde{e}_1, \quad \pm \frac{2\pi}{a}\tilde{e}_2, \quad \pm \frac{2\pi}{a}\tilde{e}_3 \]

The first Brillouin zone is the truncated octahedron shown in the Fig. (1.2) The equations of the hexagonal faces, which bisects the next shortest \( \tilde{h} \) vectors are

\[ \pm q_x \pm q_y \pm q_z = \frac{3\pi}{2a} \]  

(1.11)

and the equation of the square faces, which bisects the next shortest \( \tilde{h} \) vectors are

\[ q_x = \pm \pi/a, \quad q_y = \pm \pi/a, \quad q_z = \pm \pi/a \]  

(1.12)

In the Brillouin zone the symmetry points (critical points) are (see Fig. 1.2).

\[
\begin{array}{ll}
\Gamma & : \quad \text{Centre of the zone} \quad q = (0,0,0) \\
L & : \quad \text{Centre of the face} \quad (1,1,1) \\
X & : \quad \text{Centre of the face} \quad (1,0,0) \\
W & : \quad \text{Summit} \quad (1,1/2,0) \\
K & : \quad \text{Edge of the zone in direction} \quad (1,1,0) \\
\end{array}
\]

In crystals with two atoms per unit cell, such as zinc-blende, there are six branches for the frequency surfaces in Space. Some of them, at certain critical points,
Fig. 1.2 Location of the critical points in the reduced zone of zinc-blende structure
may well be degenerate. In case of zinc-blende, we have the following degeneracies:

i) Longitudinal branches (LO and LA) at critical points X and W

ii) $T_{01}$ and $T_{02}$ at critical points $\Gamma$, X, L and W

iii) $TA_1$ and $TA_2$ at critical points $\Gamma$, X, L and K.

iv) All three acoustical branches are degenerate at $\Gamma$ for $\omega = 0$ and all three optical branches at $\Gamma$.

1.4 ALLOWED WAVE VECTORS

For a parallelepiped shaped crystal, the number of atoms along the three directions of the basis vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ be $n_1, n_2$ and $n_3$ respectively. If $2n$ is the total number of atoms (that is $n$ particles of mass $m$ and same number of particles of mass $M$) then

$$2n = n_1 n_2 n_3$$

(1.13)

The periodic boundary condition in this case would imply

$$\exp[i\vec{q} \cdot \vec{r}(l)] = \exp[i\vec{q} \cdot \vec{r}(l) + n_j \vec{a}_j]$$

$$j = 1, 2, 3$$

(1.14)

and

$$\exp[i\vec{q} \cdot (n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3)] = 1$$

(1.15)

or

$$\vec{q} = \frac{p_1}{n_1} \vec{b}_1 + \frac{p_2}{n_2} \vec{b}_2 + \frac{p_3}{n_3} \vec{b}_3$$

(1.16)

where $p_1, p_2, p_3$ are integers and $\vec{b}_1, \vec{b}_2, \vec{b}_3$ are basis vectors of the reciprocal lattice. In
other words if the unit cell of the reciprocal lattice is divided into \( n_1, n_2, n_3 \) sub-cells by dividing the three unit translation vectors into \( n_1, n_2 \) and \( n_3 \) parts respectively, then \( \vec{q} \) can only be one of the wave vectors connecting the origin to a point of subdivision.

The components 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, constrains \( 2n = n_1n_2n_3 \) distinct values of \( \vec{q} \) which for a large \( 2n \) may be regarded as continuous and uniformly distributed in the reciprocal space.

As mentioned earlier, the convenient choice of the unit reciprocal lattice is the first Brillouin zone which can be divided into a mesh of points using expression (1.16). Assuming \( n_1 = n_2 = n_3 = n \) and substituting the values of \( \vec{b}_1, \vec{b}_2, \vec{b}_3 \) from (1.9a, 1.9b and 1.9c) in (1.16), we get for zinc-blende lattice.

\[
\vec{q} = \frac{\pi}{n_1a} (p_x \vec{e}_1 + p_y \vec{e}_2 + p_z \vec{e}_3) \tag{1.17}
\]

where \( \vec{e}_1, \vec{e}_2, \vec{e}_3 \) are unit vectors and

\[
p_x = -p_1 + p_2 + p_3 \tag{1.18a}
\]
\[
p_y = p_1 - p_2 + p_3 \tag{1.18b}
\]

and

\[
p_z = p_1 + p_2 - p_3 \tag{1.18c}
\]

It can easily 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 center at the origin of reciprocal space. The boundaries of the Brillouin zone are defined by
\[ p_x = \pm n_x, \quad p_y = \pm n_y, \quad p_z = \pm n_z, \]

and

\[ p_x \pm p_y \pm p_z = \frac{3n_z}{2} \quad (1.19) \]

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

\[ 0 \leq p_x \leq p_y \leq p_z \leq n_z \quad (1.20) \]

and

\[ p_x + p_y + p_z \leq \frac{3n_z}{2} \quad (1.21) \]

Following Dayal and Singh\(^5\), we have taken the value of \( n_z \) to be 10. In the case of diamond type of zinc-blende type of crystals, there are 48 representative (non-equivalent) points defined by (1.17), (1.20) and (1.21) including the origin. The secular determinant is solved for all these points except the origin. Each frequency is assigned a statistical weight according to the number of similar points associated with it. The symmetry considerations show that any frequency of the point \( p_x, p_y, p_z \) corresponds to 48 frequencies of \( p_xp_x, p_xp_y, p_xp_y, p_xp_z, 0 \) to 24 frequencies of \( p_xp_z, 0 \) to 12 frequencies: of \( p_x, p_x, p_z \) to 8 frequencies; and of \( p_x, 00 \) to 6 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 polyhedra. When proper weightage is assigned to all the non-equivalent points, we get a total of
1000 points, which give rise to 6000 frequencies within the whole zone.

### 1.5 BINDING IN ZINC BLENDE STRUCTURE

#### 1.5.1 IONICITY

It can be seen from the periodic table that group IIIb atoms have three electrons with an $s^2p^1$-configuration outside a core of closed shells, and that group Vb atoms have five electrons in a $s^2p^3$-configuration. Between them therefore, the III and V atoms have an average of four valence electrons per atom available for binding III-V compounds with the zinc-blende structure do indeed have properties rather like those of the group IV crystals, diamond, silicon, germanium and gray tin in which covalent bonds are formed between tetrahedral $sp^3$-hybrid orbitals.

Though in III-V compound there are the correct number of electrons per atom to form tetrahedral covalent bonds, the two kinds of atom will not, in general, have the same electro- negativity or the same size, and so we might expect a somewhat different bonding scheme from that of the group IV elements.

Let us consider three idealized possibilities "covalent" binding, "ionic" binding and neutral binding.

For covalent bonding each V atom donates an electron to a III atom, so that $V^+$ and $\text{III}^-$ ions are formed, each with four valence electrons. These combine in to $sp^3$-hybrids and tetrahedral bonds are formed, as in diamond. There will, however, be an additional electrostatic attraction between the charged ions. For pure ionic binding we may suppose that the III atoms donate three electrons to the V atoms, forming $\text{III}^{3+}$...
and $V^{3-}$ ions. Each with spherically symmetrical closed shell configuration. These ions would be held together in the crystal by purely electrostatic forces. In the neural bond, proposed by Slater and Koster, the III atoms retain three electrons and V atoms five so that there is no charge difference between the atoms. These three bonding schemes represent simplify ideal cases and actual bonding will not correspond exactly to any one of them. It appears that the bonding in III-V zinc-blende structure crystals is near to the neutral bonding scheme but with a varying degree of charge difference between the III and V atoms in the different compounds.

We may write and approximation to the wave function of the valence electrons in a III-V crystals by means of a combination of idealized states. We can write for the wave function of a III-V bond as

$$\Psi_{III-V} = a_{\text{cov}} \Psi_{\text{cov}} + a_{\text{ion}} \Psi_{\text{ion}}$$

where $\Psi_{\text{cov}}$ and $\Psi_{\text{ion}}$ are the wave functions of idealized covalent and ionic are the wave functions of idealized covalent and ionic structures. As $a_{\text{ion}}$ increases relative to $a_{\text{cov}}$, the bond becomes polarized towards the V atom, and a certain value of $a_{\text{ion}} / a_{\text{cov}}$ will correspond to a neutral bond. Other values of $a_{\text{ion}} / a_{\text{cov}}$ will results in a charge difference between the III and V atoms (some times loosely referred to as the ionicity of the bond). By the variation principle (PI) the best value of $a_{\text{ion}} / a_{\text{cov}}$ is that giving the minimum value of the energy corresponding to III-V Theoretical calculations by Coulson. Redei and Stocker for cubic boron nitride give the result that the covalent BN bond is polarized towards the n atom to such an extent that the contribution form the four bonds gives a net excess charge on each n atom of about one-third of an electron. This corresponds fairly closely to the neutral bonding scheme of Slater and
Koster but with a slight excess of electrons on the V atom. We should at this point consider what we mean when we speak of the charge on an atom in a crystal. Suppose we take the charge to mean the net charge inside a volume which encloses the atom. In an ionic crystal this concept is valid, because the electron density falls to a low value between neighboring nuclei and the volume occupied by each atom is fairly clearly defined. In a covalent crystal, however, the electron density does not fall to a low value between nuclei, so that there is no clear boundary at which one atom ends and the next begins. Consequently, there is no obvious volume surrounding each nucleus within which to consider the net charge and the charge will depend on the size of the volume chosen. A large volume will enclose more electrons and increase the negative part of the charge balance. In III-V compounds we could consider the net charge inside a sphere having the covalent radius of the atom or we might prefer to imagine the crystal divided into equal polyhedral cells centered at each atom. We conclude, therefore, that we cannot attach an absolute value to the charge on the atoms in these crystals, which have a degree of covalent binding, because we do not know the relative volumes of the III and V atoms. On similar arguments in II-VI compounds covalent bonds are formed between tetrahedral $sp^3$ hybrid orbitals.

1.6 PROPERTIES OF ZINC-BLENDE STRUCTURE

As stated above, crystals of III-V compounds usually have the zinc-blende form, and many of their properties relative to the group IV semiconductors depend on
the lower symmetry of the zinc-blende structure compared with that of the diamond structure. In particular, the form of the energy bands is highly dependent on the lattice symmetry.

The unit cell of the zinc-blende structure contains two atoms, one of each kind, but it is usually more convenient to consider a large cubic cell containing eight atoms, four of each kind. The space group is $F\bar{4}3m$ (schoenflies) ($T_d^2$) and the point group is $\bar{4}3m$ ($T_d$). The $T_d$ diamond structure has the higher symmetry of the full cubic point group $m3m$ ($O_h$) or both zinc-blende and diamond crystals the lattice has the twenty four symmetry operations of the tetrahedral point group $T_d$ taken about any lattice site, but the diamond lattice has the additional symmetry of inversion about a point midway between any two adjacent atoms. The absence of a center of symmetry in III-V and II-VI compounds give rise to many of their special properties.

REFERENCES