CHAPTER 5

Results on Energy Gap for ZnS_xSe_{1-x}: The Effect of Spin-Orbit Interaction

5.1 INTRODUCTION

Solutions to the energy-eigenvalue problem of a semiconductor crystal yields the band structure in the form of "E−k" diagram, or the 'dispersion'-curve of the semiconductor. Electronic, optical, and magnetic phenomena in semiconductors can be understood by looking at a small portion of the band structure. These portions of the band structure are the lowest level in the conduction band and the highest level in the valence band. The highest point of the valence bands are known as the Γ-point, and constitute the (k_x = 0, k_y = 0, k_z = 0) point in the k-space. In most compound semiconductors, the maximum of the valence band and the minimum of the conduction band occur at the same point in the k-space i.e. at the Γ-point. Such semiconductors are called direct band gap semiconductors and form the core of most optical devices.

Spin-orbit splitting occurs in semiconductors in the valence band, because the valence electrons are very close to the nucleus. In quantum-mechanical description, the wave equation depends on the spin of the particles. The usual Schrödinger equation applies to the spin-0 particles in the non-relativistic domain, while the Klein–Gordon equation is the relativistic equation appropriate for spin-0 particles. The spin-1/2 particles are governed by the relativistic Dirac equation which, in the non-relativistic limit, leads to the Schrödinger–Pauli equation [Bjorken and Drell, 1964; Davydov, 1965; Messiah, 1968]. In the case of particles with spin 1 (i.e., bosons), only relativistic equations are considered [Berestetskii, 1989]. A charged particle with non-zero spins couples to an external magnetic field as if, in addition to its electric charge, it had a magnetic dipole moment. In the case of a spin-1/2 charged particle, the relation between the magnitudes of the magnetic dipole moment and of the intrinsic angular momentum given by the Dirac or the Schrödinger–Pauli equation does not coincide with that of a uniformly charged rotating body given by classical physics, but somewhat surprisingly it does coincide with that of a rotating charged black hole in the Einstein–Maxwell theory [Debney *et al.*, 1969; Newman, 2002]. The $\vec{\mathrm{k}}.\vec{\mathrm{p}}$ perturbation method [Nag, 1980; Kane, 1966] is based on the fact that the cell periodic functions for the electrons for any wave number **k** in different bands form a complete set and the expression of the wave functions for electrons are in terms of the functions for the minima and maxima (i.e. HOMO-LUMO bands).

The calculation of *Eg* by solving the Schrödinger-Pauli equation with the effect of spin-orbit interaction will be obtained.

5.2 COUPLING OF SPIN AND ORBITAL ANGULAR MOMENTUM

The energy of an electron due to coupling between its spin (*s*) and orbital angular momentum (*l*) can be derived as follows. The magnetic field *B* generated by an electron travelling with momentum *p* in the electrostatic field Ẽ created by nucleus plus core electrons is given as [Cohen-Tannodji *et al.*, 1977]

$$B = \frac{1}{m_0 c^2} \tilde{\mathrm{E}} \times p \tag{5.1}$$

where m_0 is the free electron mass and *c* is the velocity of light. Since $e\tilde{\mathrm{E}} = -\nabla V$ so

$$B = -\frac{1}{em_0c^2}\nabla V \times p \tag{5.2}$$

where e is the charge of an electron, and V is the effective potential. The intrinsic magnetic moment of the electron

$$M_s = \frac{es}{m_0} = \frac{e\hbar}{2m_0}\sigma \tag{5.3}$$

interacts with *B.* This interaction energy is given by

$$H_{SO} = -M_s.B = \frac{\hbar}{2m_0^2c^2}\sigma.\left(\nabla V \times p\right) \tag{5.4}$$

where σ = *2s/ħ* is the Pauli spin matrices.

Another relativistic correction due to the precession of the spin angular momentum vector relative to the laboratory frame gives an additional factor of 1/2 [McGlynn *et al.,* 1969]. Including this correction factor, the total relativistic contribution to the Hamiltonian due to the spin-orbit coupling is given by [Herman *et al*., 1963]

$$H_{SO} = \frac{\hbar}{4m_0^2c^2}[\vec{\nabla}V \times \vec{p}].\vec{\sigma} \tag{5.5}$$

In a central field potential, $V \equiv V(r)$ and

$$\vec{\nabla}V = \frac{1}{r}\frac{dV}{dr}\vec{r}. \tag{5.6}$$

Consequently, Eqn. (5.5) can be written as

$$\begin{aligned} H_{SO} &= \frac{\hbar}{4m_0^2c^2r}\frac{dV}{dr}\vec{\sigma}.(\vec{r}\times\vec{p}) \\ &= \frac{\hbar}{4m_0^2c^2r}\frac{dV}{dr}\vec{\sigma}.l \\ &= \zeta\, l.s \end{aligned} \tag{5.7}$$

where $\zeta = \frac{1}{2m_0^2c^2r}\frac{dV}{dr}$,and $\vec{s}=\frac{\hbar}{2}\vec{\sigma}$.

H_{SO} is the one-electron spin-orbit coupling operator for one atom. In a solid this operator is summed over all atoms.

5.3 THE $\vec{k}.\vec{p}$ PERTURBATION THEORY WITH THE EFFECT OF SPIN-ORBIT INTERACTION

Let as assume that the conduction band minimum and the valence band maximum are at the zone center and that the valence band is triply degenerate. Define

$$E' = E - \hbar^2k^2/2m_0 \tag{5.8}$$

where E is the energy eigenvalue, $\hbar$ is Plank's constant divided by 2π, and m_0 is the free electron mass. On the basis on this consideration and including the spin vector we may choose iS↑, (X+iY)↓, Z↑, (X-iY)↓, iS↓, Z↓, (X+iY)↑ as the base vectors for ψ. Here X, Y and Z represent the x, y and z axis of the Brillouin zone. The periodic wave function can be written as

$$\psi_{nk\alpha}(\vec{r},\vec{\sigma}) = e^{i\vec{k}.\vec{r}}u_{nk\alpha}(\vec{r},\vec{\sigma}) \tag{5.9}$$

where u is periodic. $\alpha = \pm 1$ is a (pseudo)spin index; σ represents a vector of the Pauli spin matrices $\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$, and $i = \sqrt{-1}$. Using $\psi_{nk\alpha}$ from Eqn. (5.9) in the Schrödinger-Pauli equation gives

$$\left[-\left(\hbar^2/2m_0\right)\nabla^2 + \frac{\hbar}{4m_0^2c^2}[\vec{\nabla}V \times \vec{p}].\vec{\sigma} + V\left(r\right) \right]\psi = E\psi \tag{5.10}$$

Substituting Eqn. (5.9) into Eqn. (5.10) gives

$$\left[-\left(\hbar^2/2m_0\right)\nabla^2 + \frac{\hbar}{4m_0^2c^2}[\vec{\nabla}V \times \vec{p}].\vec{\sigma} + V\left(\vec{r}\right) \right] e^{i\vec{k}.\vec{r}} u_{nk\alpha}\left(\vec{r},\vec{\sigma}\right) = Ee^{i\vec{k}.\vec{r}} u_{nk\alpha}\left(\vec{r},\vec{\sigma}\right) \tag{5.11}$$

that finally leads to

$$\begin{aligned} &-\left(\hbar^2/2m_0\right)\left[e^{i\vec{k}.\vec{r}}\nabla^2 u_{nk\alpha}\left(\vec{r},\vec{\sigma}\right) + 2ike^{i\vec{k}.\vec{r}}\nabla u_{nk\alpha}\left(\vec{r},\vec{\sigma}\right) - k^2 e^{i\vec{k}.\vec{r}} u_{nk\alpha}\left(\vec{r},\vec{\sigma}\right) \right] \\ &+ \left[\frac{\hbar}{4m_0^2c^2}[\vec{\nabla}V \times \vec{p}].\vec{\sigma} + V\left(\vec{r}\right) \right] e^{i\vec{k}.\vec{r}} u_{nk\alpha}\left(\vec{r},\vec{\sigma}\right) \\ &= Ee^{i\vec{k}.\vec{r}} u_{nk\alpha}\left(\vec{r},\vec{\sigma}\right) \end{aligned} \tag{5.12}$$

After factoring the term $e^{i\vec{k}.\vec{r}}$ and replacing $p = \hbar k$ we get

$$\begin{aligned} &\left[-\left(\hbar^2/2m_0\right)\nabla^2 + V\left(r\right) + \frac{\hbar}{m_0}k.p + \left(\frac{\hbar^2 k^2}{2m_0}\right) + \frac{\hbar}{4m_0^2c^2}[\nabla V \times p].\sigma + \frac{\hbar^2}{4m_0^2c^2}[\nabla V \times k].\sigma \right] u_{nk\alpha}\left(\vec{r},\vec{\sigma}\right) \\ &= Eu_{nk\alpha}\left(\vec{r},\vec{\sigma}\right) \end{aligned} \tag{5.13}$$

Note that the total Hamiltonian is given by

$$\begin{aligned} H &= H_0 + H_{SO} \\ &= \frac{-\hbar^2}{2m_0}\nabla^2 + V(\vec{r}) + H_{SO} \end{aligned} \tag{5.14}$$

Taking the *k* vector in the z direction and consider the Hamiltonian corresponding to the terms of Eqn. (5.13), the mutual interaction of the conduction and valence bands leaves the band doubly degenerate. We take as a basis

$$\begin{aligned} &\left| iS\downarrow \right\rangle, \left| (X-iY)\uparrow/\sqrt{2} \right\rangle, \left| Z\downarrow \right\rangle, \left| (X+iY)\uparrow/\sqrt{2} \right\rangle, \left| iS\uparrow \right\rangle \\ &\left| -(X+iY)\downarrow/\sqrt{2} \right\rangle, \left| Z\uparrow \right\rangle, \left| (X-iY)\downarrow/\sqrt{2} \right\rangle \end{aligned} \tag{5.15}$$

The first four functions are respectively degenerate with the last four. The 8 × 8 interaction matrix may be written as $\begin{bmatrix} H & 0 \\ 0 & H \end{bmatrix}$ where

$$H = \begin{bmatrix} E_c & 0 & kP & 0 \\ 0 & E_v - \Delta/3 & \sqrt{2}\,\Delta/3 & 0 \\ kP & \sqrt{2}\,\Delta/3 & E_v & 0 \\ 0 & 0 & 0 & E_v + \Delta/3 \end{bmatrix} \tag{5.16}$$

The positive constant Δ which is the spin-orbit splitting of the valence band, and the real quantity *P* is defined by [Kane, 1957] as

$$P = -i(\hbar/m_0)\left\langle S \left| p_z \right| Z \right\rangle \tag{5.17}$$

and

$$\Delta = \frac{3\hbar i}{4m_0^2c^2}\left\langle X\left|\frac{\partial V}{\partial x}p_y - \frac{\partial V}{\partial y}p_x\right|Y\right\rangle \tag{5.18}$$

E_c and E_v refer to the eigenvalues of the Hamiltonian H_0. E_c corresponds to the conduction band and E_v to the valence band. Symmetry properties have been used. We should note that $H\psi = E\psi$ and H given by Eq. (5.16).

The doubly degenerate wave functions which result from the diagonalization of the Hamiltonian of Eqn. (5.16) may be written as

$$u_1\left(\vec{k},\vec{r}\right) = a_{k+} is \downarrow' + b_{k+}\left(\frac{X'-iY'}{\sqrt{2}}\right)\uparrow' + c_{k+} Z'\downarrow' \tag{5.19}$$

and

$$u_2\left(\vec{k},\vec{r}\right) = a_{k-} is \uparrow' - b_{k-}\left(\frac{X'+iY'}{\sqrt{2}}\right)\downarrow' + c_{k-} Z'\uparrow' \tag{5.20}$$

where the coefficients a_k,, b_k,, c_k are obtained by applying the normalization condition (i.e. $a_k^2 + b_k^2 + c_k^2 = 1$), and are given by [Haga and Kimura, 1964]

$$a_{k\pm} \equiv \beta \sqrt{\frac{Eg_0 - (\gamma_{k\pm})^2 (Eg_0 - \delta')}{Eg_0 + \delta'}}, \quad \beta \equiv \left[\frac{6(Eg_0 + 2\Delta/3)(Eg_0 + \Delta)}{(6Eg_0^2 + 9Eg_0\Delta + 4\Delta^2)} \right]^{1/2},$$

$$\gamma_{k\pm} \equiv \left[\frac{(\zeta_k \mp Eg_0)}{2(\zeta_k + \delta')} \right]^{1/2}, \quad \zeta_k = \hbar^2 k^2 / 2m^*,$$

$$b_{k\pm} = \left(\frac{4\Delta^2}{3(6Eg_0^2 + 9Eg_0\Delta + 4\Delta^2)} \right)^{1/2} \gamma_{k\pm},$$

$$\delta' = (Eg_0^2\Delta)(6Eg_0^2 + 9Eg_0\Delta + 4\Delta^2)^{-1},$$

$$c_{k\pm} \equiv t\gamma_{k\pm}, \quad t \equiv \left[\frac{6(Eg_0 + 2\Delta/3)^2}{(6Eg_0^2 + 9Eg_0\Delta + 4\Delta^2)} \right]^{1/2}$$

s is the s-type atomic orbital (i.e. in conduction band) in both unprimed and primed coordinates (i.e. X, X', Y, Y', and Z, Z') and $\uparrow'$, $\downarrow'$ indicates the spin-up and spin-down function in the primed coordinates, X', Y' and Z' are the p-type atomic orbital's in the primed coordinates.

If the k vector is not in the z direction, the Hamiltonian is more complicated but it can be transformed to the form of Eq. (5.14) by a rotation of the basis function.

$$\begin{bmatrix} \uparrow' \\ \downarrow' \end{bmatrix} = \begin{bmatrix} e^{-i\phi/2}\cos(\theta/2) & e^{i\phi/2}\sin(\theta/2) \\ -e^{-i\phi/2}\sin(\theta/2) & e^{i\phi/2}\cos(\theta/2) \end{bmatrix} \begin{bmatrix} \uparrow \\ \downarrow \end{bmatrix},$$

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\theta & \cos\theta & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix},$$

besides, the spin vector can be written as $\vec{s} = \frac{\hbar}{2}\vec{\sigma}$ [Ghatak *et al*., 2008].

The angles θ and ϕ are the usual polar angles of the *k* vector referred to the crystal symmetry axes x, y, and z: with θ measured from z and ϕ measured from x. This transformation would be obvious if the functions X, Y, Z transformed like the spherical harmonics x, y, z under the full spherical group rather than just under the tetrahedral group.

From the above, it can be written

$$P = -i\left(\hbar/m_0\right)\left\langle s\middle|p_z\middle|Z\right\rangle = -i\left(\hbar/m_0\right)p\left(\vec{k}\right)$$

and

$$\begin{aligned}
p\left(\vec{k}\right) &= \left\langle u_1\left(\vec{k},\vec{r}\right)\middle|\, p\,\middle| u_2\left(\vec{k},\vec{r}\right)\right\rangle \\
&= a_{k+}a_{k-}\left\{\left\langle is\middle|p\middle|is\right\rangle\left\langle\downarrow'\middle|\uparrow'\right\rangle\right\} - \frac{a_{k+}b_{k-}}{\sqrt{2}}\left\{\left\langle is\middle|p\middle|\left(X'+iY'\right)\right\rangle\left\langle\downarrow'\middle|\downarrow'\right\rangle\right\} \\
&+ a_{k+}c_{k-}\left\{\left\langle is\middle|p\middle|Z'\right\rangle\left\langle\downarrow'\middle|\uparrow'\right\rangle\right\} + \frac{b_{k+}a_{k-}}{\sqrt{2}}\left\{\left\langle\left(X'-iY'\right)\middle|p\middle|is\right\rangle\left\langle\uparrow'\middle|\uparrow'\right\rangle\right\} \\
&- \frac{b_{k+}b_{k-}}{2}\left\{\left\langle\left(X'-iY'\right)\middle|p\middle|\left(X'+iY'\right)\right\rangle\left\langle\uparrow'\middle|\downarrow'\right\rangle\right\} + \frac{b_{k+}c_{k-}}{\sqrt{2}}\left\{\left\langle\left(X'-iY'\right)\middle|p\middle|Z'\right\rangle\left\langle\uparrow'\middle|\uparrow'\right\rangle\right\} \\
&+ c_{k+}a_{k-}\left\{\left\langle Z'\middle|p\middle|is\right\rangle\left\langle\downarrow'\middle|\uparrow'\right\rangle\right\} - \frac{c_{k+}b_{k-}}{\sqrt{2}}\left\{\left\langle Z'\middle|p\middle|\left(X'+iY'\right)\right\rangle\left\langle\downarrow'\middle|\downarrow'\right\rangle\right\} \\
&+ c_{k+}c_{k-}\left\{\left\langle Z'\middle|p\middle|Z'\right\rangle\left\langle\downarrow'\middle|\uparrow'\right\rangle\right\}
\end{aligned}$$

Hence, we introduce

$$
\begin{aligned}
p(\vec{k}) &= \langle u_1(\vec{k},\vec{r}) | p | u_2(\vec{k},\vec{r}) \rangle \\
&= \frac{b_{k+}a_{k-}}{\sqrt{2}} \left\{ \langle (X' - iY') | p | is \rangle \langle \uparrow' | \uparrow' \rangle \right\} + c_{k+}a_{k-} \left\{ \langle Z' | p | is \rangle \langle \downarrow' | \uparrow' \rangle \right\} \\
&- \frac{a_{k+}b_{k-}}{\sqrt{2}} \left\{ \langle is | p | (X' + iY') \rangle \langle \downarrow' | \downarrow' \rangle \right\} + a_{k+}c_{k-} \left\{ \langle is | p | Z' \rangle \langle \downarrow' | \uparrow' \rangle \right\} \\
&+ \frac{b_{k+}c_{k-}}{\sqrt{2}} \left\{ \langle (X' - iY') | p | Z' \rangle \langle \uparrow' | \uparrow' \rangle \right\} - \frac{c_{k+}b_{k-}}{\sqrt{2}} \left\{ \langle Z' | p | (X' + iY') \rangle \langle \downarrow' | \downarrow' \rangle \right\}
\end{aligned}
\tag{5.21}
$$

Since we are interested for the effect of spin orbit, the last two terms on Eqn. (5.21) may be neglected since there are no spin term, *is*. Hence from Eqn. (5.21), we can write

$$
\begin{aligned}
\langle (X' - iY') | p | is \rangle &= \langle (X') | p | is \rangle - \langle (-iY') | p | is \rangle \\
&= i \int u_{X'}^{*} ps - \int -iu_{Y'}^{*} piu_X \\
&= i \langle X' | p | s \rangle - \langle Y' | p | s \rangle
\end{aligned}
$$

and for *X'*, *Y'* and *Z'*, we get

$$
\begin{aligned}
|X'\rangle &= \cos\theta\cos\phi |X\rangle + \cos\theta\sin\phi |Y\rangle - \sin\theta |Z\rangle \\
|Y'\rangle &= -\sin\phi |X\rangle + \cos\phi |Y\rangle \\
|Z'\rangle &= \sin\theta\cos\phi |X\rangle + \sin\theta\sin\phi |Y\rangle + \cos\theta |Z\rangle
\end{aligned}
$$

Then

$$
\langle X' | p | s \rangle = \cos\theta\cos\phi \langle X | p | s \rangle + \cos\theta\sin\phi \langle Y | p | s \rangle - \sin\theta \langle Z | p | s \rangle = p\hat{r}
$$

where

$$
\hat{r}_1 = \hat{i}\cos\theta\cos\phi + \hat{j}\cos\theta\sin\phi - \hat{k}\sin\theta_1 ,
$$

and

$$
\langle Y' | p | s \rangle = -\sin\phi \langle X | p | s \rangle + \cos\phi \langle Y | p | s \rangle = p\hat{r}_2 ,
$$

where

$$\hat{r}_2 = -\hat{i}\sin\phi + \hat{j}\cos\phi,$$

so that

$$\left\langle \left(X' - iY'\right) \middle| p \middle| s \right\rangle = p\left(i\hat{r}_1 - \hat{r}_2\right)$$

Thus

$$\frac{a_{k-}b_{+}}{\sqrt{2}}\left\langle \left(X' - iY'\right) p \middle| s\right\rangle \left\langle \uparrow' \middle| \uparrow' \right\rangle = \frac{a_{k-}b_{+}}{\sqrt{2}}\left(i\hat{r}_1 - \hat{r}_2\right)\left\langle \uparrow' \middle| \uparrow' \right\rangle$$

Since

$$\begin{aligned} \left\langle is \middle| p \middle| \left(X' + iY'\right)\right\rangle &= i\left\langle s \middle| p \middle| X'\right\rangle - \left\langle s \middle| p \middle| Y'\right\rangle \\ &= p\left(i\hat{r}_1 - \hat{r}_2\right) \end{aligned}$$

we can write

$$-\frac{a_{k+}b_{k-}}{\sqrt{2}}\left\{\left\langle is \middle| p \middle| \left(X' + iY'\right)\right\rangle \left\langle \downarrow' \middle| \downarrow' \right\rangle\right\} = -\frac{a_{k+}b_{k-}}{\sqrt{2}}\, p\left(i\hat{r}_1 - \hat{r}_2\right)\left\langle \downarrow' \middle| \downarrow' \right\rangle$$

Similarly,

$$\begin{aligned} \left\langle Z' \middle| p \middle| is\right\rangle &= i\left\langle Z' \middle| p \middle| s\right\rangle \\ &= ip\left\{\sin\theta\cos\phi\,\hat{i} + \sin\theta\sin\phi\,\hat{j} + \cos\theta\,\hat{k}\right\} \\ &= ip\hat{r}_3 \end{aligned}$$

where

$$\hat{r}_3 = \hat{i}\sin\theta\cos\phi + \hat{j}\sin\theta\sin\phi + \hat{k}\cos\theta$$

Thus

$$c_{k+}a_{k-}\left\langle Z' \middle| p \middle| is\right\rangle = c_{k+}a_{k-}ip\hat{r}_3\left\langle \downarrow' \middle| \uparrow' \right\rangle$$

and

$$c_{k-}a_{k+}\left\langle is \middle| p \middle| Z'\right\rangle = c_{k-}a_{k+}ip\hat{r}_3\left\langle \downarrow' \middle| \uparrow' \right\rangle$$

Therefore

$$\frac{a_{k-}b_{k+}}{\sqrt{2}}\left\{\left\langle\left(X'-iY'\right)\middle|p\middle|s\right\rangle\left\langle\uparrow'\middle|\uparrow'\right\rangle\right\}-\frac{a_{k+}b_{k-}}{\sqrt{2}}\left\{\left\langle is\middle|p\middle|\left(X'+iY'\right)\right\rangle\left\langle\downarrow'\middle|\downarrow'\right\rangle\right\}$$
$$=\frac{p}{\sqrt{2}}\left(-a_{k+}b_{k-}\left\langle\downarrow'\middle|\downarrow'\right\rangle+a_{k-}b_{k+}\left\langle\uparrow'\middle|\uparrow'\right\rangle\right)\left(i\hat{r}_1-\hat{r}_2\right) \tag{5.22}$$

Similarly

$$c_{k+}a_{k-}\left\langle Z'\middle|p\middle|is\right\rangle\left\langle\downarrow'\middle|\uparrow'\right\rangle+c_{k-}a_{k+}\left\langle is\middle|p\middle|Z'\right\rangle\left\langle\downarrow'\middle|\uparrow'\right\rangle$$
$$=ip\left(c_{k+}a_{k-}+c_{k-}a_{k+}\right)\hat{r}_3\left\langle\downarrow'\middle|\uparrow'\right\rangle \tag{5.23}$$

Combining, Eqn. (5.22) and (5.23), we can write

$$p_{cv}\left(\vec{k}\right)=\frac{p}{\sqrt{2}}\left(i\hat{r}_1-\hat{r}_2\right)\left\{\left(a_{k-}b_{k+}\right)\left\langle\uparrow'\middle|\uparrow'\right\rangle-\left(b_{k-}a_{k+}\right)\left\langle\downarrow'\middle|\downarrow'\right\rangle\right\}+ip\hat{r}_3\left(c_{k+}a_{k-}-c_{k-}a_{k+}\right)\left\langle\downarrow'\middle|\uparrow'\right\rangle \tag{5.24}$$

From the above relations, we can write

$$\uparrow'=e^{-i\phi/2}\cos\left(\theta/2\right)\uparrow+e^{i\phi/2}\sin\left(\theta/2\right)\downarrow$$
$$\downarrow'=-e^{-i\phi/2}\sin\left(\theta/2\right)\uparrow+e^{i\phi/2}\cos\left(\theta/2\right)\downarrow \tag{5.25}$$

Therefore,

$$\left\langle\downarrow'\middle|\uparrow'\right\rangle_x=-\sin\left(\theta/2\right)\cos\left(\theta/2\right)\left\langle\uparrow\middle|\uparrow\right\rangle_x+e^{-i\phi}\cos^2\left(\theta/2\right)\left\langle\downarrow\middle|\uparrow\right\rangle_x$$
$$-e^{i\phi}\sin^2\left(\theta/2\right)\left\langle\uparrow\middle|\downarrow\right\rangle_x+\sin\left(\theta/2\right)\cos\left(\theta/2\right)\left\langle\downarrow\middle|\downarrow\right\rangle_x \tag{5.26}$$

Since $\left\langle\uparrow\middle|\uparrow\right\rangle_x=\left\langle\downarrow\middle|\downarrow\right\rangle_x=0$, and $\left\langle\downarrow\middle|\uparrow\right\rangle_x=\left\langle\uparrow\middle|\downarrow\right\rangle_x=\frac{1}{2}$, so from Eqn. (5.26) we get

$$
\begin{aligned}
\left\langle \downarrow' \middle| \uparrow' \right\rangle_x &= \frac{1}{2}\left[e^{-i\phi}\cos^2(\theta/2) - e^{i\phi}\sin^2(\theta/2) \right] \\
&= \frac{1}{2}\left[(\cos\phi - i\sin\phi)\cos^2(\theta/2) - (\cos\phi + i\sin\phi)\sin^2(\theta/2) \right] \\
&= \frac{1}{2}\left[(\cos\phi - i\sin\phi)\cos^2(\theta/2) - (\cos\phi + i\sin\phi)\left(1 - \cos^2(\theta/2)\right) \right] \\
&= \frac{1}{2}\left[2\cos\phi(\cos\theta + 1) - \cos\phi - i\sin\phi \right] \\
&= \frac{1}{2}\left[\cos\phi\cos\theta - i\sin\phi \right]
\end{aligned}
\tag{5.27}
$$

Similarly

$$
\left\langle \downarrow' \middle| \uparrow' \right\rangle_y = \frac{1}{2}\left[i\cos\phi + \sin\phi\cos\theta \right]
$$

and $\left\langle \downarrow' \middle| \uparrow' \right\rangle_z = -\frac{1}{2}\sin\theta$.

Therefore,

$$
\begin{aligned}
\left\langle \downarrow' \middle| \uparrow' \right\rangle &= \hat{i}\left\langle \downarrow' \middle| \uparrow' \right\rangle_x + \hat{j}\left\langle \downarrow' \middle| \uparrow' \right\rangle_y + \hat{k}\left\langle \downarrow' \middle| \uparrow' \right\rangle_z \\
&= \frac{1}{2}\left\{ (\cos\phi\cos\theta - i\sin\phi)\hat{i} + (i\cos\phi + \sin\phi\cos\theta)\,\hat{j} - \sin\theta\,\hat{k} \right\} \\
&= \frac{1}{2}\left[\left\{ (\cos\phi\cos\theta)\hat{i} + (\sin\phi\cos\theta)\,\hat{j} - \sin\theta\,\hat{k} \right\} + i\left\{ -\hat{i}\sin\phi + \hat{j}\cos\phi \right\} \right]
\end{aligned}
\tag{5.28}
$$

Similarly, we write

$$
\left\langle \uparrow' \middle| \uparrow' \right\rangle = \frac{1}{2}\left[\hat{i}\sin\theta\cos\phi + \hat{j}\sin\theta\sin\phi + \hat{k}\cos\theta \right] = \frac{1}{2}\hat{r}_3
$$

and $\left\langle \downarrow' \middle| \downarrow' \right\rangle = -\frac{1}{2}\hat{r}_3$.

Using the above results and following Eqn. (5.24) we can write

$$p_{cv}\left(\vec{k}\right)=\frac{p}{\sqrt{2}}\left(i\hat{r}_1-\hat{r}_2\right)\left\{\left(a_{k-}b_{k+}\right)\left\langle\uparrow'\middle|\uparrow'\right\rangle-\left(b_{k-}a_{k+}\right)\left\langle\downarrow'\middle|\downarrow'\right\rangle\right\}+ip\hat{r}_3\left(c_{k+}a_{k-}-c_{k-}a_{k+}\right)\left\langle\downarrow'\middle|\uparrow'\right\rangle$$
$$=\frac{p}{2}\hat{r}_3\left(i\hat{r}_1-\hat{r}_2\right)\left\{\left(\frac{\left(a_{k-}b_{k+}\right)+\left(b_{k-}a_{k+}\right)}{\sqrt{2}}\right)+\left(c_{k+}a_{k-}+c_{k-}a_{k+}\right)\right\}$$

(5.29)

Hence,

$$p_{cv}\left(\vec{k}\right)=\frac{p}{2}\hat{r}_3\left(i\hat{r}_1-\hat{r}_2\right)\left\{a_{k-}\left(\frac{b_{k+}}{\sqrt{2}}+c_{k+}\right)+a_{k+}\left(\frac{b_{k-}}{\sqrt{2}}+c_{k-}\right)\right\} \qquad (5.30)$$

We can write $\left|\hat{r}_1\right|=\left|\hat{r}_2\right|=\left|\hat{r}_3\right|=1$, also $p\hat{r}_3=p_x\sin\theta\cos\phi\,\hat{i}+p_y\sin\theta\sin\phi\,\hat{j}+p_z\cos\theta\hat{k}$,

where

$$\begin{aligned}p&=\left\langle s\middle|p\middle|X\right\rangle\\&=\left\langle s\middle|p\middle|Y\right\rangle\\&=\left\langle s\middle|p\middle|Z\right\rangle,\\\left\langle s\middle|p\middle|X\right\rangle&=\int u_c^*\left(0,\vec{r}\right)pu_{vX}\left(0,\vec{r}\right)d^3r\\&=p_{cvX}\left(0\right),\\\left\langle s\middle|p\middle|Y\right\rangle&=p_{cvY}\left(0\right)\end{aligned}$$

and $\left\langle s\middle|p\middle|Z\right\rangle=p_{cvZ}\left(0\right)$.

Then from Eqn. (5.30)

$$\left(\hat{k}.p_{cv}\left(\vec{k}\right)\right)=\hat{k}.\frac{p}{2}\hat{r}_3\left(i\hat{r}_1-\hat{r}_2\right)\left\{a_{k-}\left(\frac{b_{k+}}{\sqrt{2}}+c_{k+}\right)+a_{k+}\left(\frac{b_{k-}}{\sqrt{2}}+c_{k-}\right)\right\} \qquad (5.31)$$

where '.' is the dot product.

Thus

$$\left|\hat{k}.p_{cv}\left(\vec{k}\right)\right|^2=\left|\hat{k}.\frac{p}{2}\hat{r}_3\right|^2.\left|i\hat{r}_1-\hat{r}_2\right|^2\left[a_{k-}\left(\frac{b_{k+}}{\sqrt{2}}+c_{k+}\right)+a_{k+}\left(\frac{b_{k-}}{\sqrt{2}}+c_{k-}\right)\right]^2$$
$$=\frac{1}{4}p_Z^2\cos^2\theta\left[a_{k-}\left(\frac{b_{k+}}{\sqrt{2}}+c_{k+}\right)+a_{k+}\left(\frac{b_{k-}}{\sqrt{2}}+c_{k-}\right)\right]^2. \tag{5.32}$$

So, the average value of $\left|\hat{k}.p_{cv}\left(\vec{k}\right)\right|^2$ over the entire angle θ is

$$\left\langle\left|\hat{k}.p_{cv}\left(\vec{k}\right)\right|^2\right\rangle_{av}=\frac{1}{4}p_Z^2\left[a_{k-}\left(\frac{b_{k+}}{\sqrt{2}}+c_{k+}\right)+a_{k+}\left(\frac{b_{k-}}{\sqrt{2}}+c_{k-}\right)\right]^2\left\{\frac{1}{2}\int_0^\pi d\theta+\frac{1}{2}\int_0^\pi\cos 2\theta d\theta\right\}$$
$$=\frac{\pi}{8}p_Z^2\left[a_{k-}\left(\frac{b_{k+}}{\sqrt{2}}+c_{k+}\right)+a_{k+}\left(\frac{b_{k-}}{\sqrt{2}}+c_{k-}\right)\right]^2. \tag{5.33}$$

Now the equations that gives the energy eigenvalues may be obtained from Eqn. (5.14), keeping only the terms corresponding to conduction band and the degenerate valence bands and neglecting all other terms [Nag, 1980],

$$\begin{aligned}
&a_k(E'-E_c)-c_k pk=0,\\
&b_k(E'-E_v+2\Delta/3)-c_k\sqrt{2}\Delta/3=0,\\
&a_k pk+b_k\sqrt{2}\Delta/3-c_k(E'-E_v+\Delta/3)=0,\\
&d_k(E'-E_v)=0,
\end{aligned} \tag{5.34}$$

The energy eigenvalues are given by equating the determinant of the coefficient of a_k, b_k, c_k to zero i.e.

$$\begin{vmatrix} (E'-E_c) & 0 & -pk \\ 0 & \left(E'-E_v+2\Delta/3\right) & -\sqrt{2}\Delta/3 \\ pk & \sqrt{2}\Delta/3 & -\left(E'-E_v+\Delta/3\right) \end{vmatrix} = 0 \qquad (5.35)$$

and the equation giving the values is

$$(E'-E_c)(E'-E_v)(E'-E_v+\Delta)-p^2k^2(E'-E_v+2\Delta/3)=0 \qquad (5.36)$$

Solving Eqn. (5.36) we get

$$\begin{aligned} E'-E_c &= \frac{p^2k^2\left(E'-E_c+Eg+2\Delta/3\right)}{\left(E'-E_c+Eg\right)\left(E'-E_c+Eg+\Delta\right)} \Rightarrow \\ E_c &= E'-\frac{\left(E'-E_c+Eg+2\Delta/3\right)}{\left(\dfrac{\left(E'-E_c+Eg\right)\left(E'-E_c+Eg+\Delta\right)}{p^2k^2}\right)} \end{aligned} \qquad (5.37)$$

When $E'\rightarrow E_c$, we may neglect $E'-E_c$ in comparison to E_g where $Eg=E_c-E_v$. Egn. (5.37) can be simplified to

$$E_c = E'-\frac{\left(Eg+2\Delta/3\right)}{\left(\dfrac{Eg\left(Eg+\Delta\right)}{p^2k^2}\right)} \qquad (5.38)$$

In a similar way, to get E_v

$$E'-E_v = \frac{p^2k^2\left(E'-E_v+2\Delta/3\right)}{\left(E'-E_v-Eg\right)\left(E'-E_v+\Delta\right)}$$

and hence

$$E_v = E'-\frac{p^2k^2\left(E'-E_v+2\Delta/3\right)}{\left(E'-E_v-Eg\right)\left(E'-E_v+\Delta\right)} \qquad (5.39)$$

When $E' = E_v$, the dispersion relation for two valence band having wave functions (X+iY) and (X-iY) is

$$E = E_v + \frac{\hbar^2 k^2}{2m_0}. \tag{5.40}$$

When $E_c = 0$ this leads as to $E_g = -E_v$, hence we can write Eqn. (5.36) as

$$E' + E_v = \frac{p^2 k^2 \left(E' + Eg + 2\Delta/3\right)}{E'\left(E' + Eg + \Delta\right)}. \tag{5.41}$$

Consequently

$$E_g = E_c - E_v = p^2 k^2 \left[\frac{\left(E' + Eg + 2\Delta/3\right)}{E'\left(E' + Eg + \Delta\right)} - \frac{\left(Eg + 2\Delta/3\right)}{Eg\left(Eg + \Delta\right)} \right]. \tag{5.42}$$

Now if the band edge effective mass is m^*, so from Eqn. (5.38) we get

$$p^2 k^2 = \frac{\left(E' - E_c\right) Eg \left(Eg + \Delta\right)}{\left(Eg + 2\Delta/3\right)}$$

which can be written as

$$\begin{aligned} p^2 &= \frac{Eg\left(E - E_c - \dfrac{\hbar^2 k^2}{2m_0}\right)\left(Eg + \Delta\right)}{\left(Eg + 2\Delta/3\right) k^2} \\ &= \frac{Eg\left(\dfrac{\hbar^2 k^2}{2m^*} - \dfrac{\hbar^2 k^2}{2m_0}\right)\left(Eg + \Delta\right)}{\left(Eg + 2\Delta/3\right) k^2} \\ &= \frac{\left(Eg + \Delta\right)}{\left(Eg + 2\Delta/3\right)} \hbar^2 \left(\frac{1}{m^*} - \frac{1}{m_0}\right) \frac{Eg}{2}. \end{aligned} \tag{5.43}$$

From Eqn. (5.42) we have

$$p^2k^2 = \frac{\left(E'+Eg\right)E'\left(E'+Eg+\Delta\right)}{\left(E'+Eg+2\Delta/3\right)} \tag{5.44}$$

Hence from Eqn. (5.42) and Eqn. (5.43) we have

$$\frac{\hbar^2k^2}{2}\left(\frac{1}{m^*}-\frac{1}{m_0}\right) = E'\frac{\left(E'+Eg\right)\left(E'+Eg+\Delta\right)}{\left(E'+Eg+2\Delta/3\right)}\frac{\left(Eg+2\Delta/3\right)}{Eg\left(Eg+\Delta\right)}. \tag{5.45}$$

If E is small in comparison to Eg, the relation can be simplified to the following

$$\frac{\hbar^2k^2}{2m^*} = E(1+\alpha E) \tag{5.46}$$

where

$$\alpha = \frac{1}{Eg}\left(1-\frac{m^*}{m_0}\right)\times\left(1-\frac{Eg\Delta}{3\left(Eg+2\Delta/3\right)\left(Eg+\Delta\right)}\right) \tag{5.47}$$

as given by Cohen-Tannodji *et al.*, [1977].

Now near a characteristic point $k = 0$ with $n=l$, the energy eigenvalues may be expressed as

$$E_n\left(k\right) = E_n\left(0\right)+\frac{\hbar^2k^2}{2m_0}+\frac{\hbar^2}{m_0^2}\frac{\left|k.P_{cv}\left(0\right)\right|^2}{E_c\left(0\right)-E_v\left(0\right)} \tag{5.48}$$

and near a characteristic point $\boldsymbol{k_0}$ can be expressed as

$$E_n(k) = E_n(k_0) + \frac{\hbar^2(k-k_0)^2}{2m_0} + \frac{\hbar^2}{m_0^2}\frac{\left|(k-k_0).P_{cv}(k_0)\right|^2}{E_c(k_0)-E_v(k_0)} \tag{5.49}$$

Using Eqn. (5.49), the deviations of $E(k)$ near a critical point $\boldsymbol{k_0}$ can be written as

$$E(k-k_0) = -\frac{Eg_0}{2} + \frac{\hbar^2(k-k_0)^2}{2m_0} \pm \frac{1}{2}\sqrt{Eg_0^2 + \frac{4\hbar^2(k-k_0)^2\left|P_{cv}(k_0)\right|^2}{m_0^2}} \tag{5.50}$$

in terms of the band gap Eg_0. The effective mass m^* can be expressed as

$$\frac{1}{m^*} = \frac{1}{m_0} \pm \frac{2\left|p_{cv}(k_0)\right|^2(Eg+2\Delta/3)}{m_0^2 Eg(Eg+\Delta)} \tag{5.51}$$

which is concluded from Eqn. (5.43) and Eqn. (5.45). Note that in case of Δ=0 we can reach the expression for the effective mass in the absence of spin-orbit as in chapter 4. Now following Eqn. (5.50) we can estimate

$$p_Z^2 = \left|\hat{k}.\vec{p}_{cv}(0)\right|^2 = \frac{m_0^2}{4\mu^*}\frac{Eg_0(Eg_0+\Delta)}{\left(Eg_0+\frac{2}{3}\Delta\right)} \tag{5.52}$$

Using Eqn. (5.51) in Eq. (5.49) we obtain

$$E(k-k_0) = -\frac{Eg_0}{2} + \frac{\hbar^2(k-k_0)^2}{2m_0} \pm \frac{1}{2}\sqrt{Eg_0^2 + \frac{\hbar^2(k-k_0)^2}{\mu^*}\frac{Eg_0(Eg_0+\Delta)}{\left(Eg_0+\frac{2}{3}\Delta\right)}}. \tag{5.53}$$

Assuming that the conduction band minimum and the valence band maximum are at the zone center, then we can write

$$E_c(k) = -\frac{Eg_0}{2} + \frac{\hbar^2 k^2}{2m_0} + \frac{Eg_0}{2}\sqrt{1 + \frac{\hbar^2 k^2}{\mu^* Eg_0}\frac{(Eg_0 + \Delta)}{\left(Eg_0 + \frac{2}{3}\Delta\right)}} \tag{5.54}$$

and

$$E_v(k) = -\frac{Eg_0}{2} + \frac{\hbar^2 k^2}{2m_0} - \frac{Eg_0}{2}\sqrt{1 + \frac{\hbar^2 k^2}{\mu^* Eg_0}\frac{(Eg_0 + \Delta)}{\left(Eg_0 + \frac{2}{3}\Delta\right)}}. \tag{5.55}$$

From Eqn. (5.54) and (5.55),

$$\begin{aligned} E_c(k) - E_v(k) &= Eg_0\sqrt{1 + \frac{\hbar^2 k^2}{\mu^* Eg_0}\frac{(Eg_0 + \Delta)}{\left(Eg_0 + \frac{2}{3}\Delta\right)}} \\ &= Eg_0\left(1 + \frac{4\hbar^2 \pi^2}{D^2 \mu^* Eg_0}\frac{(Eg_0 + \Delta)}{\left(Eg_0 + \frac{2}{3}\Delta\right)}\right)^{\frac{1}{2}} \\ &= Eg_0 + \frac{2\hbar^2 \pi^2}{D^2 \mu^*}\frac{(Eg_0 + \Delta)}{\left(Eg_0 + \frac{2}{3}\Delta\right)}. \end{aligned} \tag{5.56}$$

This can be written as

$$\begin{aligned} Eg = E_c(k) - E_v(k) &= Eg_0 + \frac{2\hbar^2 \pi^2}{D^2\left(\frac{\mu^*}{m_c}\right)m_c}\frac{(Eg_0 + \Delta)}{\left(Eg_0 + \frac{2}{3}\Delta\right)} \\ &= Eg_0 + \frac{2\hbar^2 \pi^2}{D^2\left((0.124Eg_0)^{1.76}\right)m_c}\frac{(Eg_0 + \Delta)}{\left(Eg_0 + \frac{2}{3}\Delta\right)} \end{aligned} \tag{5.57}$$

using the assumption

$$\frac{\mu^*}{m_c} = (0.124Eg_0)^{1.76} \tag{5.58}$$

Eqn. (5.57) represents the energy gap for alloys with the effect of spin orbit interaction.

5.4 RESULTS

We exploit Newton interpolation relation to estimate the values of spin orbit constant Δ for the crystal structures in the ZnS_xSe_{1-x} system, which can be expressed by Δ=0.16 x+0.27 for sphalerite crystal structure (Figure 5.1), and Δ=0.328 x+0.092 for wurtzite crystal structure (Figure 5.2). When x=0 we find out that Δ=0.27 eV which gives the spin orbit constant for *ZnS* in case of sphalerite structure and Δ=0.092 eV in case of wurtzite structure which is given in [Nag, 1980]. We find that the values for spin orbit constant increases with x. From these relationships when x=1, the spin orbit constant Δ=0.43 eV for *ZnSe* in case sphalerite structure and Δ=0.42 eV in case of wurtzite structure for *ZnSe*.

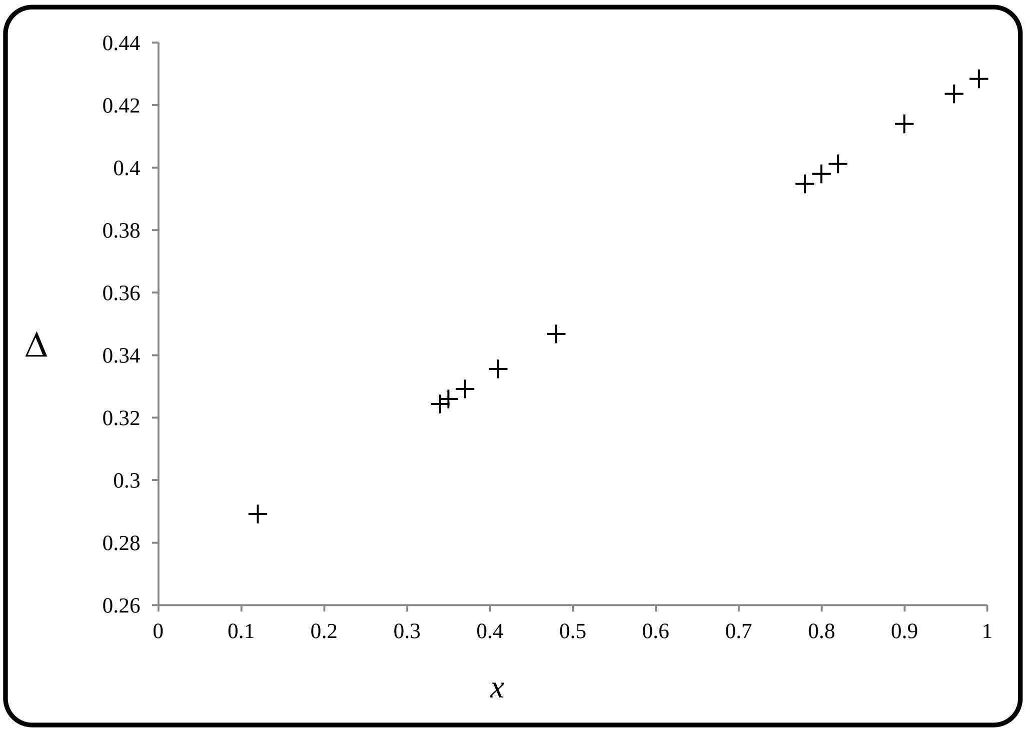

Figure 5.1: Spin orbit splitting constant with various *x* for ZnS_xSe_{1-x} for sphalerite crystal structure.

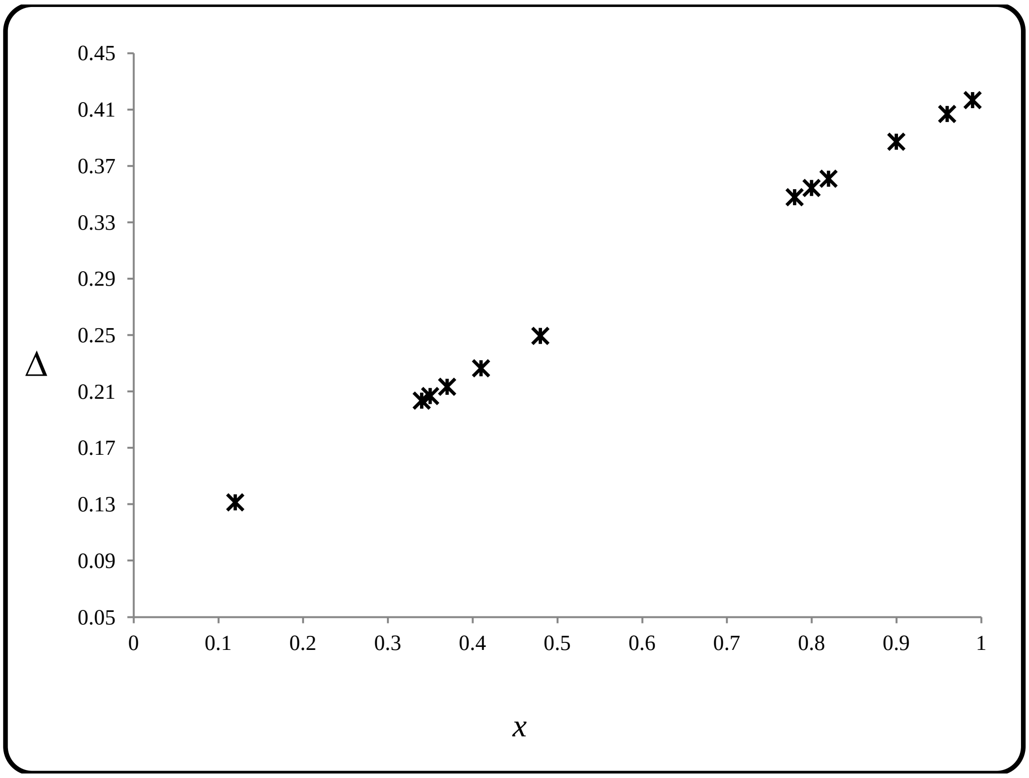

Figure 5.2: Spin orbit splitting constant with various *x* for ZnS_xSe_{1-x} for wurtzite crystal structure.

Figure 5.3, 5.4 shows the effect of spin-orbit splitting constant upon applying the 1.7 and 1.66 correction factors in the case of sphalerite and wurtzite crystal structures comparing with the case of energy gap without spin respectively. The effect of spin-orbit increases the value of energy gap and the values of energy gap upon applying the 1.7 correction factor are greater than the values of energy gap upon applying the 1.66 correction factor.

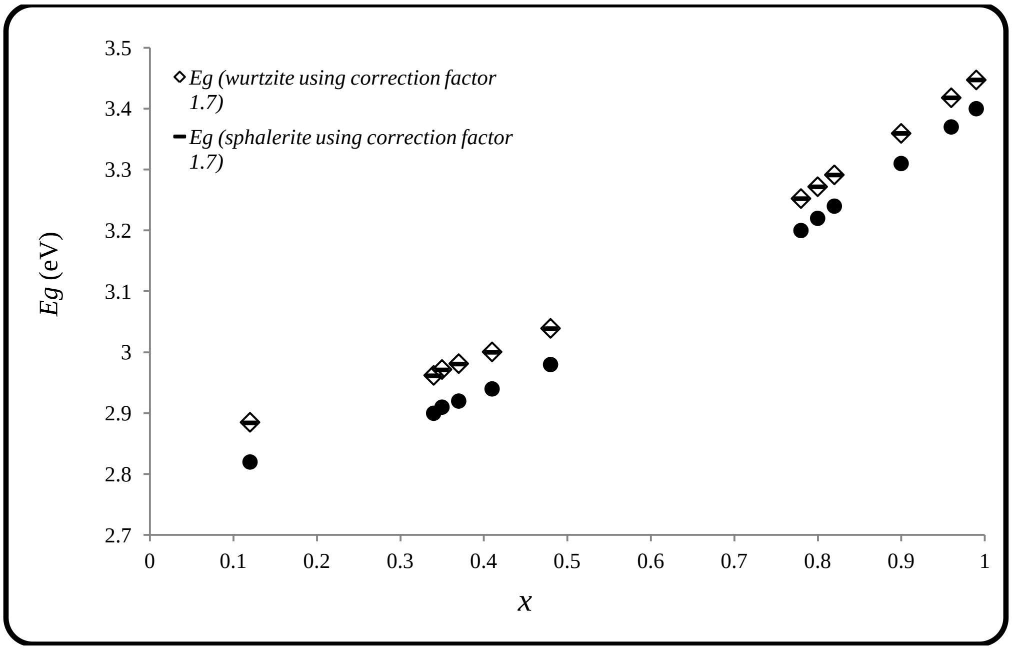

Figure 5.3: ***Eg*** **as a function of a concentration** ***x*** **for** $\boldsymbol{ZnS_xSe_{1-x}}$ **upon applying the 1.7 correction factor in case of wurtzite crystal structure, sphalerite crystal structure, and** ***Eg*** **without spin.**

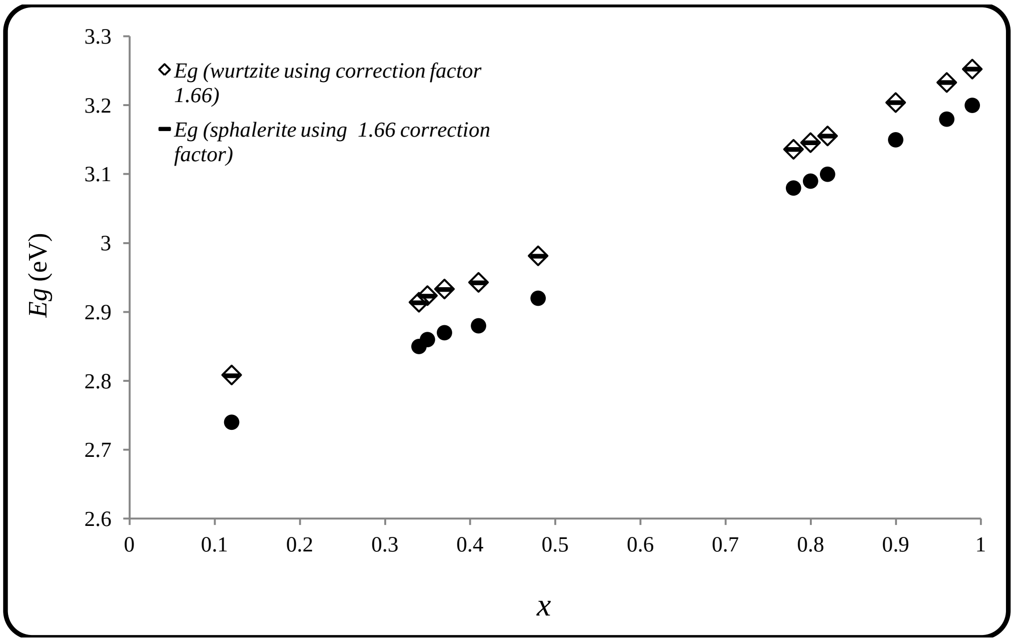

Figure 5.4: ***Eg*** **as a function of a concentration** ***x*** **for** $\boldsymbol{ZnS_xSe_{1-x}}$ **upon applying the 1.66 correction factor in case of wurtzite crystal structure, sphalerite crystal structure, and** ***Eg*** **without spin.**

In Figure 5.5 shows the energy band gap *Eg* with the effect of spin-orbit which is plotted as a function of the concentration *x* upon applying the 1.7 and 1.66 correction factors in the case of sphalerite and wurtzite crystal structures comparing with the experimental results reported by Larach *et al*. [1957] and Abo Hassan *et al*. [2005a].

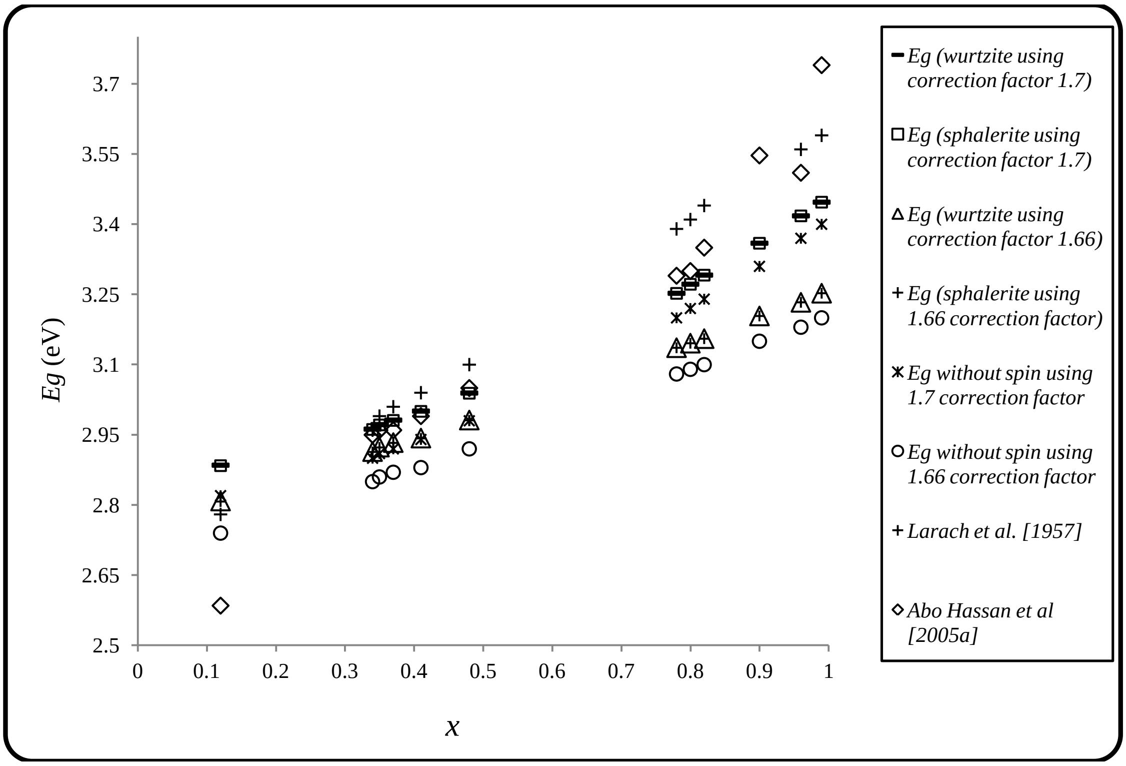

Figure 5.5: ***Eg*** **as a function of a concentration** ***x*** **for** ZnS_xSe_{1-x} **upon applying the 1.7 and 1.66 correction factors in case of wurtzite crystal structure, sphalerite crystal structure,** ***Eg*** **without spin, experimental results reported by** Larach *et al*. [1957] **and** Abo Hassan *et al*. [2005a].

5.5 SUMMARY

The theoretical results for the energy gap for ZnS_xSe_{1-x} alloys with the effect of spin orbit interaction were represented in Eqn. (5.56)

$$
\begin{aligned}
E_c(k) - E_v(k) &= Eg_0 \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* Eg_0} \frac{(Eg_0 + \Delta)}{\left(Eg_0 + \frac{2}{3}\Delta\right)}} \\
&= Eg_0 \left(1 + \frac{2\hbar^2 \pi^2}{D^2 \mu^* Eg_0} \frac{(Eg_0 + \Delta)}{\left(Eg_0 + \frac{2}{3}\Delta\right)} \right)^{\frac{1}{2}} \\
&= Eg_0 + \frac{2\hbar^2 \pi^2}{D^2 \mu^*} \frac{(Eg_0 + \Delta)}{Eg_0 \left(Eg_0 + \frac{2}{3}\Delta\right)} \ .
\end{aligned}
$$

and Eqn. (5.57)

$$Eg = E_c(k) - E_v(k) = Eg_0 + \frac{2\hbar^2\pi^2}{D^2\left(\frac{\mu^*}{m_c}\right)m_c}\frac{\left(Eg_0+\Delta\right)}{\left(Eg_0+\frac{2}{3}\Delta\right)}$$
$$= Eg_0 + \frac{2\hbar^2\pi^2}{D^2\left(\left(0.124Eg_0\right)^{1.76}\right)m_c}\frac{\left(Eg_0+\Delta\right)}{\left(Eg_0+\frac{2}{3}\Delta\right)} \ .$$

by using the empirical relationship given in Eqn. (5.58)

$$\frac{\mu^*}{m_c} = \left(0.124Eg_0\right)^{1.76} .$$