

CHAPTER 7

DISCUSSION

Understanding the properties of matter from first principles is a central problem in condensed matter physics. The properties are, in principle, described by the many-body Hamiltonian [Imada and Miyake, 2010]

$$H = -\sum_i \frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} \quad (7.1)$$

where the first term on the right hand side of the equation represents the kinetic energy of electrons. The second, third and fourth terms are interactions between electrons, electron and nucleus, and nuclei, respectively. Electron positions are noted by real space coordinate r with suffices consisting of lower case i and j . Nuclei positions are denoted by coordinate R with upper case suffices I and J . The electronic bare mass and charge are m and e respectively, while the atomic number is denoted by Z . The spin degrees of freedom, relativistic effects and quantum effects of nuclei are neglected for simplicity. The Hamiltonian is solved exactly only in very limited cases. Developing a practical procedure for the treatment of many-electron systems has long been an important issue. DFT gives an approximate but reasonably accurate and practical method for this problem. Local density function used to determine the exchange correlation energy function ϵ_{XC} appears in Eqn. (2.36) is approximated to be that of a uniform electron gas of the density at a particular position. The explicit formula for ϵ_{XC} has been proposed

based on a perturbation theory. The LDA is by construction exact in the limit of a uniform electron density.

Typically the lattice constant of solids and bond lengths between atoms are computed to be within 2 to 3% experimental error. The accuracy of the ionization energy in molecules and cohesive energy in solids is within 10 to 20% error. The high accuracy is partially rationalized by the fact that the LDA satisfies a sum rule for the exchange-correlation hole.

The solution of the Kohn-Sham equation given in Eqn. (2.37) gives the total energy for the DOS $n(r)$ if the self-consistent method is satisfied. Otherwise, the total energy is again generated and the solving of the equation is repeated. This continues until the value of total energy is consistent. The density of states near the conduction band edge is given as

$$n_c(E) = \frac{(2m_c)^{3/2}}{2\pi^2\hbar^3} (E - E_c)^{1/2}, \quad E \geq E_c \quad (7.2)$$

and the DOS at the HOMO can be given as

$$n_v(E) = \frac{(2m_v)^{3/2}}{2\pi^2\hbar^3} (E_v - E)^{1/2}, \quad E \leq E_v \quad (7.3)$$

It is obvious that from Eqn. (7.2) and (7.3), the energy on the conduction band and the energy on the valence band, can be calculated and hence the energy band gap E_g can be expressed as

$$E_g = (2\pi^2\hbar^3)^2 \left[\frac{[n_c(E)]^2}{(2m_c)^3} - \frac{[n_v(E)]^2}{(2m_v)^3} \right] \quad (7.4)$$

In Chapter 3, *ZnS* and *ZnSe* were modeled following zinc-blend (ZB) structure, *ZnS_{0.125}Se_{0.875}*, *ZnS_{0.25}Se_{0.75}*, *ZnS_{0.375}Se_{0.625}*, *ZnS_{0.75}Se_{0.25}*, *ZnS_{0.875}Se_{0.125}* following Luzonite structure and *ZnS_{0.5}Se_{0.5}* were modeled CuAu-I structure. Numerical calculations were carried out by CASTEP in Material Studio 5.0 based on first principles [Payne *et al.*, 1992].

The energy cutoff of plane wave functions was set at 310 eV. All atomic positions in the *ZnS* [Fischer and Almöf, 1992], and *ZnSe* unit cells, *ZnS_{0.125}Se_{0.875}*, *ZnS_{0.25}Se_{0.75}*, *ZnS_{0.375}Se_{0.625}*, *ZnS_{0.5}Se_{0.5}*, *ZnS_{0.625}Se_{0.375}*, *ZnS_{0.75}Se_{0.25}*, *ZnS_{0.875}Se_{0.125}* supercells have been relaxed according to the total energy. The calculation of total energy is followed by cell optimization with self-consistent field method [Perdew *et al.*, 1996].

The Fermi level of the band structure is at zero energy as shown by the dotted lines in Figures 3.2, 3.5, 3.8, 3.11, 3.14, 3.17, 3.20, 3.23, and 3.26. The bottom of conduction band and top of valence band are both located at the G point (corresponding to the Γ point), for direct transition semiconductors. The energy gap calculated by CASTEP based on LDA is 10 to 20% lower than the experimental value [Xie *et al.*; 2010]. In local density functional theory, the excited states are neglected during solving the Kohn-Sham equation. Due to this, the computed E_g value obtained for each space group is multiplied by the correction factor 1.7, and comparing these results with the results given by multiplication of the 1.66 correction factor reported by Tang *et al.* [1998] and the results reported in the literature.

Figure 3.1 shows the Brillouin zone for ZnS unit cell, given G as a center of crystal which is shown in CASTEP, g_1 , g_2 , and g_3 corresponding to the coordinates x , y , z respectively. The unit cell vectors are $a_1 = (2.7, -2.7, 0)$, $a_2 = (2.7, 2.7, 0)$, $a_3 = (0, 0, 5.4)$ where $a = 5.4 \text{ \AA}$, and $\eta = 1$, and the atomic positions are $\tau_A = (0, 0, 0)$, $\tau_B = (2.7, 0, 2.7)$, $\tau_{C1} = (1.35, 1.35, 1.35)$, $\tau_{C2} = (4.05, 1.35, 4.05)$, $u = 0.25$, and $R_{AC} = R_{BC} = 6.6136 \text{ \AA}$. Lattice constant $a = 5.3 \text{ \AA}$ as reported by Mesri *et al.*, [2007]. For $ZnSe$ the energy gap calculated by CASTEP shown in Figure 3.2 is $E_g = 3.96 \text{ eV}$ whereas 1.26 eV before correction which is close to theoretical results $E_g = 3.85 \text{ eV}$ given by Swarnker *et al.* [2009] with little different from theoretical results $E_g = 3.78 \text{ eV}$ given by Van de Wall [1989] and using LCAO $E_g = 3.68 \text{ eV}$ given by Homann *et al.* [2006].

From Figure 3.3 the total DOS of ZnS is separated to three regions, higher energy region from 2.2 to 11.1 eV , lower energy region from 0 to -6.9 eV and the energy region below -13.5 eV . For the higher energy region, the bonding electrons are mainly contributed by the valence electrons of Zn ($4s$) and S ($3p$) orbitals. The bonding electrons in the lower energy are mainly contributed by the valence electron of Zn ($3d$) and S ($3p$) orbitals. The bonding electrons below -13.5 eV are mainly contributed by valence electron of Zn ($3p$), ($3d$), ($4s$) and S ($3p$) orbitals.

Figure 3.4 shows the Brillouin zone for $ZnSe$, and the notations are the same notations as that given in Figure 3.1. For $ZnSe$ the energy gap calculated by CASTEP shown in Figure 3.5 is $E_g = 2.27 \text{ eV}$ whereas 1.26 eV before correction and also computed at the G -vector on the k -space as shown in Figure 3.6, which is lower than experimental results $E_g = 2.58 \text{ eV}$ [Homann *et al.* 2006], and 2.72 eV [Ebina *et al.*, 1974]. From Figure 3.5 the total DOS is separated to three regions, higher energy region from 1.26 to 11 eV , lower energy region from 0 to -6.9 eV and the energy region

below -13.6 eV. For the higher energy region, the bonding electrons are mainly contributed by the valence electrons of *Zn* (4s) and *Se* (4p) orbitals. The bonding electrons in the lower energy are mainly contributed by the valence electron of *Zn* (3d) and *Se* (4p) orbitals. The bonding electrons below -13.6 eV are mainly contributed of valence electrons of *Zn* (3p), (3d), (4s) and *Se* (4p) orbitals.

Figure 3.7 shows the Brillouin zone for $ZnS_{0.125}Se_{0.875}$ where notations G denotes the center of crystal structure and B, Z and F are centers of faces and Q is the center of an edge.

Figure 3.8 shows the calculated energy band structure for $ZnS_{0.125}Se_{0.875}$ crystal structure. The energy gap calculated using CASTEP shown in Figure 3.9 is $E_g = 2.83$ eV after making correction. Computation over the G-vector in the k-space is lower than the experimental results $E_g = 2.78$ eV given by [Larach *et al.*, 1957] and greater than the experimental results 2.58 eV given by [Abo Hassan *et al.*, 2005a]. From Figure 3.9 the total DOS is separated to three regions, higher energy region from 1.57 to 6 eV, lower energy region from 0 to -7.2 eV and the energy region below -14.2 eV. For the higher energy region, the bonding electrons are mainly contributed by the valence electron of *Zn* (4s) and *Se* (4p) orbitals. The bonding electrons in the lower energy region are mainly contributed by the valence electrons of *Zn* (3d), *S* (3p), and *Se* (4p) orbitals. The bonding electrons below -14.2 eV are mainly contributed of valence electrons of *Zn* (3p) (3d) (4s), *S* (3p) and *Se* (4p) orbitals.

Figure 3.10 shows the Brillouin zone for $ZnS_{0.25}Se_{0.75}$ crystal structure. The energy gap calculated using CASTEP shown in Figure 3.11 is $E_g = 2.81$ eV after using correction factor which is close to experimental results $E_g = 2.85$ eV [Ebina *et al.*, 1974], but is near to the results given by [Homann *et al.*, 2006]. From Figure 3.12 the

total DOS is separated to three regions, higher energy region from 1.64 to 6 eV, lower energy region from 0 to -7.2 eV and the energy region below -14 eV. For the higher energy region, the bonding electrons are mainly contributed by the valence electrons of Zn (4s) and Se (4p) orbitals. The bonding electrons in the lower energy region are mainly contributed by the valence electrons of Zn (3d), S (3p), and Se (4p) orbitals. The bonding electrons below -13.6 eV are mainly contributed of valence electrons of Zn (3p) (3d) (4s), S (3p), and Se (4p) orbitals.

Figure 3.13 shows the Brillouin zone for $ZnS_{0.375}Se_{0.625}$ crystal structure. The energy gap calculated using CASTEP given in Figure 3.14 is $E_g = 3.15$ eV after using the correction factor whereas the energy gap $E_g = 3.01$ eV from [Larach *et al.*, 1957] and $E_g=2.96$ eV from [Abo Hassan *et al.*, 2005a]. From Figure 3.15 the total DOS is separated to three regions, higher energy region from 1.75 to 6 eV, lower energy region from 0 to -7.2 eV, and the energy region below -14 eV. For the higher energy region, the bonding electrons are mainly contributed by the valence electrons of Zn (4s) and Se (4p) orbitals. The bonding electrons in the lower energy region are mainly contributed by the valence electrons of Zn (3d), S (3p), and Se (4p) orbitals. The bonding electrons below -14 eV are mainly contributed by valence electrons of Zn (3p) (3d) (4s), S (3p), and Se (4p) orbitals.

Figure 3.16 shows the Brillouin zone for $ZnS_{0.5}Se_{0.5}$ crystal structure. The energy gap calculated using CASTEP shown in Figure 3.17, and the band gap is $E_g = 3.19$ eV after using correction factor which is near to the experimental results $E_g = 3.08$ eV from [Ebina *et al.*, 1974] and 2.92 eV from [Homann *et al.* 2006]. From Figure 3.18 the total DOS is separated to three regions, higher energy region from 1.78 to 6 eV, lower energy region from 0 to -7eV, and the energy region below -13.9 eV. For the higher energy

region, the bonding electrons are mainly contributed by the valence electrons of *Zn* (4s) and *Se* (4p) orbitals. The bonding electrons in the lower energy are mainly contributed by the valence electrons of *Zn* (3d), S (3p), and *Se* (4p) orbitals. The bonding electrons below -13.9 eV are mainly contributed by valence electron of *Zn* (3p) (3d) (4s), S (3p), and *Se* (4p) orbitals.

Figure 3.19 shows the Brillouin zone for $ZnS_{0.625}Se_{0.375}$ crystal structure. The energy gap calculated by using CASTEP shown in Figure 3.20 is $E_g = 3.29$ eV after using the correction factor 1.8, but there is no experimental data available for comparison upon experimental results given by Larach *et al.* [1957] and Abo Hassan *et al.* [2005a]. As shown in Figure 3.21 the total DOS is separated to three regions, higher energy region from 1.82 to 6 eV, lower energy region from 0 to -7 eV, and the energy region below -13.8 eV. For the higher energy region, the bonding electrons are mainly contributed by the valence electrons of *Zn* (4s) and *Se* (4p) orbitals. The bonding electrons in the lower energy region are mainly contributed by the valence electrons of *Zn* (3d), S (3p), and *Se* (4p) orbitals. The bonding electrons below -13.8 eV are mainly contributed of valence electron of *Zn* (3p) (3d) (4s), S (3p), and *Se* (4p) orbitals.

Figure 3.22 shows the Brillouin zone for $ZnS_{0.75}Se_{0.25}$ crystal structure. The energy gap calculated using CASTEP simulation shown in Figure 3.23 is $E_g = 3.28$ eV after using correction factor, and it is s clear that the value is close to the experimental results $E_g = 3.34$ eV from [Ebina *et al.*, 1974] and 3.17 eV from [Homann *et al.* 2006]. From Figure 3.24 the total DOS is separated to three regions, higher energy region from 1.82 to 6 eV, lower energy region from 0 to -7eV, and the energy region below -13.8 eV. For the higher energy region, the bonding electrons are mainly contributed by the valence electrons of *Zn* (4s) and *Se* (4p) orbitals. The bonding electrons in the lower energy region

are mainly contributed by the valence electrons of Zn (3d), S (3p), and Se (4p) orbitals. The bonding electrons below -13.8 eV are mainly contributed by valence electrons of Zn (3p)(3d)(4s), S (3p), and Se (4p) orbitals.

Figure 3.25 shows the Brillouin zone for $ZnS_{0.875}Se_{0.125}$ crystal structure. The energy gap calculated using CASTEP shown in Figure 3.26 is $E_g = 3.42$ eV after using the correction factor 1.8. No experimental data available, but comparison with the experimental results given by Larach *et al.* [1957] and Abo Hassan *et al.* [2005a] the nearest value for energy gap when $x = 0.9$. Figure 3.27 shows that the total DOS separated into three regions, higher energy region from 1.9 to 6 eV, lower energy region from 0 to -6.8 eV, and the energy region below -13.2 eV. For the higher energy region, the bonding electrons are mainly contributed by the valence electrons of Zn (4s) and Se (4p) orbitals. The bonding electrons in the lower energy are mainly contributed by the valence electrons of Zn (3d), S (3p), and Se (4p) orbitals. The bonding electrons below -13.2 eV are mainly contributed of valence electrons of Zn (3p)(3d)(4s), S (3p), and Se (4p) orbitals.

The energy band gap E_g from CASTEP calculation was plotted as a function of concentration x and shown in Figure 3.28 using two multiplicative correction factor 1.7 that was suggested and 1.66 that was reported by Tang *et al.* [1998]. It is realized that the energy gap increases with x . The value for energy gap when $x = 0.125$ is 2.84 eV upon applying the multiplicative correction factor 1.7 whereas the energy gap is 2.77 eV upon applying the 1.66 multiplicative correction factor which is close to the value for energy gap when $x = 0.25$ (2.82 eV) when apply the 1.7 multiplicative correction factor and 2.74 eV when apply the 1.66 multiplicative correction factor. The value of energy gap when $x = 0.625$ is 3.11 eV when apply the 1.7 multiplicative correction factor

which is close to the value of energy gap when $x = 0.75$ which is 3.1, and the energy band gap value when $x = 0.625$ upon apply the 1.66 multiplicative correction factor is 3.04 eV which is close to the value for the energy gap when $x = 0.75$ as given 3.02 eV.

In Chapter 4, the theoretical technique considered the time independent Schrödinger equation given in Eqn. (4.1), and the wave function given in Eqn. (4.2), it was shown that, at the zone centre, the two expressions for the energy on the conduction band and the valence band can lead to the new expression

$$Eg = Eg_0 + \frac{2\hbar^2\pi^2}{m_c D^2 \left((0.124Eg_0)^{1.76} \right)}$$

for the energy band gap for the materials ZnS_xSe_{1-x} which is written in terms of energy gap Eg_0 of the stress-free crystal depending on the ratio (μ^* / m_c) . This ratio seems to play an important role in the calculations for energy band gap.

In the derivations given in section 4.1, the approximation

$$\frac{1}{\mu^*} \approx 2 \left(\frac{1}{m^*} - \frac{1}{m_0} \right)$$

given in Eqn. (4.18) which is concluded from the experimental results given by Abo Hassan *et al.* [2005a] and the values for the effective mass given in Table 2.2 for ZnS and $ZnSe$ are used in the calculations.

The approximation substituted in the energy equation Eqn. (4.15)

$$E(k-k_0) = -\frac{Eg}{2} + \frac{\hbar^2(k-k_0)^2}{2m_0} \pm \frac{Eg}{2} \sqrt{1 \pm \frac{2\hbar^2(k-k_0)^2}{Eg} \left(\frac{1}{m^*} - \frac{1}{m_0} \right)}$$

formulated the equations for the energies on the conduction band E_c

$$E_c(k) = -\frac{Eg_0}{2} + \frac{\hbar^2 k^2}{2m_0} + \frac{Eg_0}{2} \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* Eg_0}}$$

and on the valence band E_v ,

$$E_v(k) = -\frac{Eg_0}{2} + \frac{\hbar^2 k^2}{2m_0} - \frac{Eg_0}{2} \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* Eg_0}}$$

which leads to the formulation of the energy band equation

$$Eg = Eg_0 + \frac{\hbar^2 k^2}{2\mu^*}$$

shown in Eqn. (4.19). Using the empirical relationship given in Eqn. (4.20) gives the energy gap Eg expression is related to the energy gap Eg_0 for stress free crystal shown in Eqn. (4.22). Eg_0 values are taken from CASTEP computation. Figure 4.1 shows the energy gap using the theory given in this work.

Table 7.1 shows the differences between experimental results given by Larach *et al.* [1957], Abo Hassan *et al.* [2005a], and the results from this work upon applying the 1.7 multiplicative correction factors and upon applying the 1.66 multiplicative correction factors.

Table 7.1: Comparing results for energy band gaps E_g for ZnS_xSe_{1-x} ($0 \leq x \leq 1$).

x	Larach <i>et al.</i> , [1957]	Abo Hassan <i>et al.</i> , [2005a]	This work (applying the 1.7 correction factor)	This work (applying the 1.66 correction factor)
0.12	2.78	2.58	2.82	2.74
0.34	2.96	2.95	2.9	2.85
0.35	2.99	2.96	2.91	2.86
0.37	3.01	2.96	2.92	2.87
0.41	3.04	2.99	2.94	2.88
0.48	3.10	3.05	2.98	2.92
0.78	3.39	3.29	3.2	3.08
0.80	3.41	3.30	3.21	3.09
0.82	3.44	3.35	3.23	3.1
0.96	3.56	3.51	3.37	3.15
0.99	3.59	3.74	3.4	3.2

For comparison, the results given in Table 7.1, most of results that got it upon applying the 1.7 multiplicative correction factor is more accurate than the results that got it upon applying the 1.66 multiplicative correction factor reported by Tang *et al.* [1998].

The effect of spin orbit interaction occurs in the valence band as mentioned in section 5.3, and the wave function given in Eqn. (5.9)

$$\psi_{nk\alpha}(\vec{r}, \vec{\sigma}) = e^{ik \cdot r} u_{nk\alpha}(\vec{r}, \vec{\sigma})$$

depends on the spin particle. The Hamiltonian of the one-electron spin-orbit coupling operator represented in section 5.2 given in Eqn. (5.7)

$$H_{so} = \frac{\hbar}{4m_0^2c^2r} \frac{dV}{dr} \vec{\sigma} \cdot (\vec{r} \times \vec{p})$$

Applying the wave function given in Eqn. (5.9) in the Schrödinger-Pauli equation given in Eqn. (5.10)

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

and using the double degeneracy, leads to the formulation for E_c and E_v which can clearly see the spin orbit splitting constant appearing in the equations of energy in the conduction and valence band.

In Eqn. (5.51)

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

the expression for the effective mass m^* in the conduction or valence band represented by using the spin orbit splitting constant Δ .

In the derivation shown in Chapter 5 the transformations for the coordinates X' , Y' , Z' and for \uparrow , \downarrow were used with the polar angles θ and ϕ [Nag, 1980]. Then polar angles of the k vector refer to the crystal symmetry axes x , y , and z : with θ measured from z and ϕ measured from x . Besides, the expressions for the coefficients a_k , b_k , c_k [Haga and Kimura, 1964] with the transformations leads to useful expression for the doubly degenerate wave function u_1 and u_2 shown in Eqn. (5.17), (5.18), and to the formulations of the energy band gap equation

$$E_g = E_c(k) - E_v(k) = E_{g_0} + \frac{2\hbar^2\pi^2}{D^2 \left(\frac{\mu^*}{m_c}\right) m_c} \frac{(E_{g_0} + \Delta)}{\left(E_{g_0} + \frac{2}{3}\Delta\right)}$$

The energies of the conduction and valence bands shown in Eqn. (5.54), (5.55)

$$E_c(k) = -\frac{E_{g_0}}{2} + \frac{\hbar^2 k^2}{2m_0} + \frac{E_{g_0}}{2} \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* E_{g_0}} \frac{(E_{g_0} + \Delta)}{\left(E_{g_0} + \frac{2}{3}\Delta\right)}}$$

$$E_v(k) = -\frac{E_{g_0}}{2} + \frac{\hbar^2 k^2}{2m_0} - \frac{E_{g_0}}{2} \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* E_{g_0}} \frac{(E_{g_0} + \Delta)}{\left(E_{g_0} + \frac{2}{3}\Delta\right)}}$$

represent the energy of the conduction and valence bands with the effect of spin orbit interaction. It can be recognized that the substitution of the spin orbit splitting constant $\Delta=0$ in these equations results in the equation of the energies of the conduction and valence band that was shown in Chapter 4, Eqn. (4.16), (4.17)

$$E_c(k) = -\frac{E_{g_0}}{2} + \frac{\hbar^2 k^2}{2m_0} + \frac{E_{g_0}}{2} \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* E_{g_0}}}$$

$$E_v(k) = -\frac{E_{g_0}}{2} + \frac{\hbar^2 k^2}{2m_0} - \frac{E_{g_0}}{2} \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* E_{g_0}}}$$

The equation of the energy band gap represented in Eqn. (5.57) can be expressed as the equation given in Chapter 4 i.e. in Eqn. (4.18) if we substitute the value of the spin orbit splitting constant $\Delta = 0$. For the results given in Chapter 5, using the Newton

interpolation technique, the unknown value for spin orbit constant Δ for the materials ZnS_xSe_{1-x} ($0 < x < 1$) was estimated.

According to Eqn. (5.57)

$$Eg = Eg_0 + \frac{2\hbar^2\pi^2}{D^2 \left((0.124Eg_0)^{1.76} \right) m_c} \frac{(Eg_0 + \Delta)}{\left(Eg_0 + \frac{2}{3}\Delta \right)}$$

the spin-orbit splitting constant Δ increase with respect to the energy gap Eg , hence, the increasing of spin-orbit splitting constant Δ based on increasing of x as shown in Figure 5.1, and 5.2, therefore the results from this work are reasonable agreement with Nag [1980].

Table 7.2 shows the values for spin-orbit constants in case of sphalerite and wurtzite crystal structures with the values of density of states for ZnS_xSe_{1-x} ($0 < x < 1$) from this work.

Table 7.2 Spin-orbit splitting constant for sphalerite and wurtzite crystal structures with density of states for ZnS_xSe_{1-x} ($0 < x < 1$)

x	Δ (eV) in case of sphalerite crystal structure	Δ (eV) in case of wurtzite crystal structure	Density of states (electrons/eV)
0.125	0.29	0.133	98
0.25	0.31	0.174	97
0.375	0.33	0.215	93
0.5	0.35	0.256	94
0.625	0.37	0.297	95
0.75	0.39	0.338	95
0.875	0.41	0.379	99

In Figure 5.3, 5.4 the energy band E_g was plotted as a function of a concentration x for ZnS_xSe_{1-x} upon applying the 1.7 and 1.66 correction factors respectively in case of wurtzite and sphalerite crystals structure, and energy gap E_g without spin. It is clear that the values for energy gaps upon applying the 1.7 multiplicative correction factor is more acceptable with the results reported in the literature than the values upon applying the 1.66 multiplicative correction factor.

It is clear that the values for the energy gap for the two cases given (sphalerite and wurtzite), are greater than the value for the energy gap given from this work in case of neglecting the effect of spin-orbit.

In Figure 5.5, the energy gap E_g with the effect of spin-orbit was plotted as a function of 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]. The results given by this work upon using the 1.7 correction factor are reasonably agreement with the results reported By Larach *et al.* and Abo Hassan *et al.*

Theoretical analysis in Chapter 6 focused on the density of states for the II-VI materials in the presence of quantizing magnetic field because number of transport phenomena due to band structure change by the magnetic fields. The formulation of DOS for II-VI materials in the presence of quantizing magnetic field was mutated by considering the form of Schrödinger equation given in Eqn. (6.2)

$$(2m^*)^{-1} (-i\hbar\nabla + eA)^2 \psi - E\psi = 0$$

This equation containing the vector potential A due to the magnetic field B . Using the wave function given in Eqn. (6.6)

$$\psi = \psi_1(x) \exp[i(k_y y + k_z z)]$$

and substituting the magnetic vector potential A in the Schrödinger equation results is Eqn. (6.8)

$$\left(\frac{d\psi_1}{dx} + \frac{i}{\hbar} eBx \right)^2 + \left[\frac{2m^*}{\hbar^2} E - (k_y^2 + k_z^2) \right] \psi_1 = 0$$

From Eqn. (6.7) it can be recognized that the magnetic field introduces dependence only on the x -axis. The energy eigenvalues of quasi-free electrons in the presence of a magnetic field can be expressed as [Nag, 1980] shown in Eqn. (6.11)

$$E_{l,k_z} = \frac{\hbar^2 k_z^2}{2m^*} + (l + 1/2) \left(\frac{\hbar e B}{m^*} \right)$$

which led to derivation of the wave vector k as shown in Eqn. (6.13)

$$\begin{aligned} dk &= \left(\frac{m_c}{\hbar^2} \right) \frac{dE}{k} \\ &= \frac{m_c}{\hbar^2} \frac{dE}{\left(\frac{2m_c}{\hbar^2} \right)^{1/2} \left[E - \left(l + \frac{1}{2} \right) \frac{\hbar e B}{m_c} \right]^{1/2}} \end{aligned}$$

As seen in Eqn. (6.8) that the wave function is not periodic in the x direction; so that the periodic boundary condition cannot be applied, and the boundary condition that may apply for the x -direction is that $\hbar k_x / eB$ should lie within 0 and L_1 , where L_1 is the

dimension of the crystal in the x -direction. The number of states per unit volume of the crystal surface should be represented in terms of k_z which is shown in Eqn. (6.14). Substituting Eqn. (6.13) in Eqn. (6.14) we get the number of states lying between E and $E+dE$ which was given in Eqn. (6.15),

$$g(E)dE = \frac{1}{4\pi^2} \left(\frac{2m_c}{\hbar^2} \right)^{3/2} \frac{\hbar eB}{2m_c} \sum_{l=0}^{l_{\max}} \left(E - \left(l + \frac{1}{2} \right) \frac{\hbar eB}{m_c} \right)^{-1/2} dE.$$

and solving this equation gives expression of DOS for the II-VI materials in the presence of quantizing magnetic field whose unperturbed energy band structures are defined Eqn. (6.17)

$$g(E)dE = \frac{1}{4\pi^2} \left(\frac{2m_c}{\hbar^2} \right)^{3/2} \frac{\hbar eB}{m_c} \left(E - \left(l + \frac{1}{2} \right) \frac{\hbar eB}{m_c} \right)^{1/2}.$$

This can be represented in terms of Eg_0 as a result given in Eqn. (6.22)

$$N(E) = \frac{1}{4\pi^2} \left(\frac{2m_c}{\hbar^2} \right)^{3/2} \frac{\hbar eB}{m_c} \left[E - \left((0.124Eg_0)^{1.76} \right) \frac{(l + (1/2)) \hbar eB}{\mu^*} \right]^{1/2}.$$

The effect of magnetic field on the DOS at different electron energies is shown in Figure 6.1, when $B=0.1$ Tesla at $E=1$ eV the values of DOS is $4.65E+13 \text{ cm}^{-3}$ while for $B=0.5$ DOS is equal $1.4E+14 \text{ cm}^{-3}$ and when $B=0.75$ Tesla DOS equal $2.12E+14 \text{ cm}^{-3}$ and DOS is equal $2.8E+14 \text{ cm}^{-3}$ and so on for various E . The same analysis can apply for Figure 6.2. For $ZnSe$ with the main observation that the DOS for ZnS is greater than the DOS for $ZnSe$ and the DOS when $x=0.9$ which was shown in Figure 6.3.

In Figure 6.4 the DOS was plotted as a function of concentration x for various B and with electron energy $E=1$ eV. Eqn. (6.22) can be written in terms of reduce mass μ^* as

$$N(E) = \frac{1}{4\pi^2} \left(\frac{2\mu^*}{\hbar^2} \right)^{3/2} \left(\frac{\mu^*}{m_c} \right)^{1/2} \frac{\hbar e B}{\mu^*} \left[E - \left((0.124 E g_0)^{1.76} \right) \frac{(l + (1/2)) \hbar e B}{\mu^*} \right]^{1/2}$$

hence using the values of the ratio μ^*/m_c enables the curve to be determined. For details, when $x = 0.12$ the ratio μ^*/m_c is given by Abo Hassan *et al.*, [2005a] as 0.14 and when $x=0.9$ the ratio is 0.23 hence the value of DOS when $x=0.12$ is greater than the value when $x=0.9$.

The increasing of the DOS with x results is in good agreement with the number of electrons in $ZnSe$ orbital which is greater than the number of electrons for ZnS orbital. That is the reason for the differences between the total DOS for these materials, and consequently for the increase of the values of x in the ZnS_xSe_{1-x} material.

In Figure 6.5 the number of electrons are increased with increasing of the amount of $\eta-\phi/2$, the values of $\eta-\phi/2$ were taken from 0.1 to 10 and the values of $F_{-1/2}$ was taken from Cloutman [1989].

CHAPTER 8

CONCLUSIONS AND SUGGESTIONS FOR FUTURE

WORK

The aim of this work is to develop a theory to determine the energy band gap for II-VI materials by choosing ZnS_xSe_{1-x} as an example, and compare the results given by this work with the experimental results given in literature and the results computed using CASTEP.

The CASTEP simulation has been used to calculate the energy band gap and the density of states for ZnS_xSe_{1-x} ($x=0, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875, \text{ and } 1$) and the results corrected by multiplying with the factor 1.66 and 1.7.

The empirical relationship between the reduced mass μ^* and the unperturbed and stress-free crystal energy band gap Eg_0 has been used in deriving the equation for band gap. Using the relationship in the $\vec{k} \cdot \vec{p}$ perturbation theory led to the equations for energy at the conduction band E_c and the energy at the valence band E_v . Finally, expressions for the energy band gap for the case with and without spin-orbit interaction were obtained. Using the values of unperturbed or stress-free crystal energy gap calculated using CASTEP, the energy gap Eg as a function of sulphur content were calculated for the spin and spinless cases.

In this work, the new expression for energy gap in the case of no spin-orbit interaction has been obtained as

$$Eg = Eg_0 + \frac{2\hbar^2\pi^2}{m_c D^2 \left((0.124Eg_0)^{1.76} \right)}$$

where the terms have been defined in Chapter 4. For the case with spin-orbit interaction included, the new equation is

$$Eg = Eg_0 + \frac{2\hbar^2\pi^2}{D^2 \left((0.124Eg_0)^{1.76} \right) m_c \left(\frac{Eg_0 + \Delta}{Eg_0 + \frac{2}{3}\Delta} \right)}$$

Again the terms have been defined in Chapter 5. These equations have been obtained on the terms of the empirical relationship between the reduced mass and the unperturbed or stress-free crystal energy band gap Eg_0

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

Another assumption that has been made is

$$\frac{1}{\mu^*} \approx 2 \left(\frac{1}{m^*} - \frac{1}{m_0} \right).$$

The values of Eg obtained in this work are within the range of experimental results reported in the literature.

The E-k relation has been used to determine the density of states. The study on the density of state (DOS) function for II-VI ZnS_xSe_{1-x} semiconductor materials whose unperturbed energy band structure defined by the parabolic band, in the presence of a quantizing magnetic field, led to a new DOS relation given by

$$N(E) = \frac{1}{4\pi^2} \left(\frac{2m_c}{\hbar^2} \right)^{3/2} \frac{\hbar e B}{m_c} \left[E - \left((0.124 E g_0)^{1.76} \right) \frac{(l + (1/2)) \hbar e B}{\mu^*} \right]^{1/2}$$

Results obtained, showed that the number of electrons in the conduction band increases with electron energy for transport from the valence to the conduction band.

We can suggest the future works as follows:

1. Based on the empirical relationship suggested in this work, the mass of the electron at the conduction band edge and the mass of the electron at the top of the valence band can be studied. This can improve accuracy of the present theory.
2. Using CASTEP the geometric optimization, dynamics, elastic constant, and the optical properties for $\text{ZnS}_x\text{Se}_{1-x}$ can be obtained and compared with the experimental results.
3. Using the theory from this work, the photoemitted current density J for $\text{ZnS}_x\text{Se}_{1-x}$ materials can be calculated for the case in the presence a quantizing magnetic field.