CHAPTER 3

Results for ZnS$_x$Se$_{1-x}$ (0 ≤ x ≤ 1) from CASTEP

3.1 INTRODUCTION

ZnS ($E_g = 3.68$ eV) [Persson and Zunger, 2003] and ZnSe ($E_g = 2.82$ eV) [Huang and Ching, 1993] have received a lot of interest because of their potential applications in optoelectronic devices operating in the visible-light range [Jeon et al., 1992; Kawakamin et al., 1993] and the possibility of having a vanishingly small conduction band offset [Qteish et al., 1995]. Therefore, various research activities have been carried out on the electronic and optical properties of ZnS$_x$Se$_{1-x}$ alloys and their applications in optoelectronic and microelectronic devices [Lai et al., 2003]. The ZnS and ZnSe compounds have zinc blend (F43m) [Wang and Isshiki, 2007] structure at normal conditions. The electronic and optical properties of ZnS and ZnSe have been measured experimentally [Walter and Cohen, 1969; Bir et al., 1970; Freeouf, 1973; Rossetti et al., 1985; Lippens and Lannoos, 1989; Ves et al., 1990; Xue and Raj, 1991; Godlewski and Szczerbakow, 2001; Godlewski et al., 2001]. However, theoretical treatment of the properties is lagging behind the measurements. In the past years several theoretical studies on ZnS and ZnSe have been performed [Bernard and Zunger, 1987; Smelyansky and Tse, 1995; Wei and Zunger, 1999; Milman et al., 2000; Gabrel’yan et al., 2000; Muscat et al., 2001; Luo et al., 2002; Fitzer et al., 2003; Okoye, 2003; Janetzko and Jug, 2004]. In many early attempts to calculate the band structure of ZnS and ZnSe compounds, the local density approximation (LDA) [Perdew and Zunger, 1981] was used. Bernard and Zunger [1987] have determined the band gap of ZnS$_{0.5}$Se$_{0.5}$ and the
corresponding optical bowing parameter using a plane wave method at LDA level, whereas Janetzko and Jug [2004] calculated the band gaps for different compositions of ZnS$_x$Se$_{1-x}$ in a semi-empirical molecular orbital method MSINDO study. Hybrid function formalism was applied for determining band gaps of ZnS and other materials [Muscat et al., 2001].

Mesri et al., [2007] investigated the lattice parameters and band gap energies for ZnS$_x$Se$_{1-x}$. In this investigation the band structure calculations show direct band gaps at Γ point for the whole composition and obtained the downward bowing with the strongest contribution due to the structural relaxation. Bernard and Zunger [1987] calculated electronic structure of zinc blend ZnS and ZnSe using the electron mixed-basis approach to the density-functional formalism. They used a CuAu I-like structure (space group Pbam2), and analyzed the observed optical bowing, and a structural contribution due to the relaxation of the anion-cation bond lengths in the alloy.

In the following sections we are going to calculate the band structure of ZnS$_x$Se$_{1-x}$ ($x$=0, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875, and 1) using CASTEP simulation.

### 3.2 Computational Method

The first-principle calculations applied here used the CASTEP computer code [Payne et al., 1992], which is based on density functional theory using a plane-wave pseudopotential formalism and aided by the Materials Studio graphical front–end interface [Accelrys Inc., 2001]. Computations have been performed via LDA with ultra-soft pseudopotentials. Ceperley–Alders exchange-correlation potential parametrized by Perdew–Zunger [1981] scheme (CA-PZ) is used. The geometries for all systems are
optimized, which uses a conjugated gradient technique in a direct minimization of the Kohn–Sham energy function and employs pseudopotentials to represent core electrons. Plane-wave functions are used as basis sets [Teter, 1989]. A plane-wave cutoff energy of 310 eV has been employed throughout. It has shown that the results are well converged at this cutoff. For the crystal reciprocal-lattices, integrations over the symmetrized Brillouin zone were performed by a sum over special k-points generated from the Monkhorst–Pack scheme [Monkhorst and Pack, 1976]. For calculations, we have sorted the Zn (1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$), S (1s$^2$2s$^2$2p$^6$), and Se (1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$) inner-shell electrons were sorted from the valence electrons of Zn (3d$^{10}$4s$^2$), S (3s$^2$3p$^4$), and Se (3d$^{10}$4s$^2$4p$^4$) shells.

The LDA method underestimates the band gap in both semiconductors and insulators. To adjust the theoretical band gap to experimental result Tang et al., [1998] estimated a multiplicative correction factor of 1.66 applied to the calculated band gaps. In this work the estimation of a multiplicative correction factor of 1.7 will be applied to the calculated band gap and compared with the multiplicative correction factor of 1.66.

The ordered cubic alloys were modelled using Landau–Lifshitz structures [Landau and Lifshitz, 1969; Martins and Zunger, 1986; Mbaye et al., 1988]. Mesri et al., [2007] reported that the binary compounds are modeled using zinc-blend (ZB) structure AB, AC (F-43m), the ternary alloys at 50% are modeled using the CuAu-I structure (P-4m2) and the chalcopyrite structure (I-42d), the alloys at 75% or 25% are modeled using Luzonite structure (P-43m).
Table 3.1: Calculated equilibrium lattice parameters, internal parameter $u$ for ZnS$_x$Se$_{1-x}$ [Mesri et al., 2007]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Space Group [Bernard et al. 1988]</th>
<th>$a$ (nm)</th>
<th>$c/a$</th>
<th>$u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>ZB</td>
<td>F-43m</td>
<td>0.53</td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>ZnS$<em>{0.25}$Se$</em>{0.75}$</td>
<td>LZ</td>
<td>P-43m</td>
<td>0.551</td>
<td></td>
<td>0.247</td>
</tr>
<tr>
<td>ZnS$<em>{0.5}$Se$</em>{0.5}$</td>
<td>CuAu-I</td>
<td>P-4m2</td>
<td>0.54</td>
<td>1</td>
<td>0.247</td>
</tr>
<tr>
<td>ZnS$<em>{0.75}$Se$</em>{0.25}$</td>
<td>CH</td>
<td>I-42d</td>
<td>0.544</td>
<td>1.99</td>
<td>0.267</td>
</tr>
<tr>
<td>ZnSe</td>
<td>ZB</td>
<td>F-43m</td>
<td>0.557</td>
<td></td>
<td>0.25</td>
</tr>
</tbody>
</table>

Hint: ZB zinc-blend structure, LZ Luzonite structure, CuAu-I structure, CH chalcopyrite structure.

The binary compounds have the unit cell vectors given [Bernard and Zunger, 1987] by

$$a_1 = \left( \frac{1}{2}, -\frac{1}{2}, 0 \right) a,$$

$$a_2 = \left( \frac{1}{2}, \frac{1}{2}, 0 \right) a,$$

$$a_3 = (0, 0, 1) \eta a,$$  \hspace{1cm} (3.1)

and the atomic positions

$$\tau_A = (0, 0, 0) a,$$

$$\tau_B = \left( \frac{1}{2}, 0, \eta/2 \right) a,$$

$$\tau_{C1} = \left( \frac{1}{4}, \frac{1}{4}, \eta u \right) a,$$

$$\tau_{C2} = \left( \frac{3}{4}, \frac{1}{4}, \eta(1-u) \right) a.$$  \hspace{1cm} (3.2)

where $\eta = c/a = (1.00 \pm 0.01$ at equilibrium) is the tetragonal ratio and $u$ is the internal structure parameter (cation displacement) expressed as

$$u = (R_{AC}^2 - R_{BC}^2)/a^2 \eta^2 + \frac{1}{4}$$  \hspace{1cm} (3.3)
and $R_{AC}^2$, $R_{BC}^2$ represent the two fundamental bonds lengths in the structure which is expressed as [Bernard and Zunger, 1987]

$$R_{AC}(a,u,\eta) = \left[\frac{1}{8} + \eta^2 u^2\right]^{1/2} a,$$

$$R_{BC}(a,u,\eta) = \left[\frac{1}{8} + \eta^2 \left(u - \frac{1}{2}\right)^2\right]^{1/2} a. \quad (3.4)$$

In the following sections we are going to compute the band gap and density of states for $\text{ZnS}_{x}\text{Se}_{1-x} \ (x=0, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875, \text{and} \ 1)$ by applying given parameters from Eqn.(3.1) to Eqn.(3.4) in the CASTEP program.

### 3.3 COMPUTATIONAL RESULTS

#### 3.3.1 ZnS Band Structure Calculation

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 whereas the other labels were defined in Table 2.1 in chapter 2. The unit cell vectors for ZnS are $a_1 = (2.7, -2.7, 0)$, $a_2 = (2.7, 2.7, 0)$, $a_3 = (0, 0, 5.4)$ where $a = 5.4 \, \text{Å}$, 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 $R_{AC} = R_{BC} = 6.6136 \, \text{Å}$. Lattice constant $a = 5.3 \, \text{Å}$ as reported by Mesri et al., [2007] and from CASTEP gives $a = 5.4 \, \text{Å}$.\,

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With the parameters above the band structure for ZnS is shown in Figure 3.2. The band structure of ZnS has energetically separated low lying bands, positioned around -13 eV, and is derived from S 3s upon comparing with Figure 3.3. These bands are separated from a group of relatively narrow bands arising from the Zn 3d states located around -6.5 eV.

At the symmetry G point, the energy gap is 2.2 eV and upon applying the 1.7 correction factor $E_g$ is 3.74 eV. This is close to the experimental results given by Ebina et al., [1974] which is 3.7 eV, from LCAO [Homann et al., 2006], is 3.68 eV and 3.78 eV as
reported by Van de Walle [1989]. \( E_g \) is 3.65 eV upon applying the 1.66 correction factor which is close to the experimental results given by Ebina et al., [1974] which is 3.7 eV, theoretically results LCAO [Homann et al., 2006], which is 3.68 eV, and theoretically results 3.78 eV as reported by Van de Walle.

![Energy (eV)](image)

**Figure 3.3: Total density of states for ZnS.**

Near the Fermi level \( (E_F) \) in the valence-band region, there is a manifold of several bands, nominally derived from the S 3p states. The valence bands are separated from the conduction bands by an energy band gap of 2.196 eV at the symmetry G point.

### 3.3.2 ZnSe Band Structure Calculation

Figure 3.4 shows the Brillouin zone for ZnSe unit cell. The unit cell vectors, the atomic positions and the internal structure parameter \( u \) for ZnSe are same as ZnS.
Figure 3.4: Brillouin zone for ZnSe crystal structure in simple cubic.

Figure 3.5 shows the band structure for ZnSe. The band structure of ZnSe has energetically separated low lying bands, positioned around -13 eV, are derived from Se 4s comparing with Figure 3.6. These bands are separated from a group of relatively narrow bands arising from the Zn 3d states located around -6.5 eV.

Figure 3.5: The calculated energy band structure for ZnSe.
At the symmetry G point, the energy gap is 1.26 eV and upon applying the 1.7 correction factor $E_g$ is 2.14 eV. This is different from the experimental results given by Homann et al., [2006], which is 2.58 eV and different from experimental results given by Ebina et al. [1974] which is 2.72 eV and theoretical results reported in the literature. $E_g$ is 2.1 upon applying the 1.66 correction factor which is different from the experimental results given by Homann et al. [2006], Ebina et al. [1974], and theoretical results reported in the literature.

Near the Fermi level ($E_F$) in the valence-band region, there is a manifold of several bands, nominally derived from the Se 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.263 eV at the symmetry G point.
3.3.3 ZnS$_{0.125}$Se$_{0.875}$ Band Structure Calculation

Figure 3.7 shows the Brillouin zone for ZnS$_{0.125}$Se$_{0.875}$ supercell, where Z, F, B are centers of faces and Q denote to the center of edge. The unit cell vectors for ZnS$_{0.125}$Se$_{0.875}$ are $a_1 = (2.7, -2.7, 0)$, $a_2 = (2.7, 2.7, 0)$, $a_3 = (0,0,5.4)$ where $a = 5.4 \ \text{Å}$, $c = 10.8186 \ \text{Å}$, 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 $R_{AC} = R_{BC} = 6.6136 \ \text{Å}$ with face centered $(0,0,0)$, $(0,1/2,1)$, $(1/2,0,1)$, $(1/2,1/2,0)$.

Figure 3.7: Brillouin zone for ZnS$_{0.125}$Se$_{0.875}$ crystal structure.

Figure 3.8 shows the band structure for ZnS$_{0.125}$Se$_{0.875}$. The band structure of ZnS$_{0.125}$Se$_{0.875}$ has energetically separated low lying bands, positioned around -14 eV, derived from Se $4s$ and shown in Figure 3.9 at the G point symmetry. These bands are separated from a group of relatively narrow bands arising from the Zn $3d$ states located around -7eV.
Figure 3.8: The calculated energy band structure for ZnS$_{0.125}$Se$_{0.875}$.

At the symmetry G point, the energy gap is 1.67 eV and upon applying the 1.7 correction factor $E_g$ is 2.84 eV. This is close to the experimental results given by Larach et al., [1957] which is 2.78 eV and 2.85 eV as reported by Abo Hassan et al., [2005a]. $E_g$ is 2.77 eV upon applying 1.66 correction factor which is close to the experimental results given by Larach et al. [1975] which is 2.75 eV and 2.85 eV as reported by Abo Hassan et al. [2005a].

Figure 3.9: Total density of states for ZnS$_{0.125}$Se$_{0.875}$.
Near the Fermi level ($E_F$) in the valence-band region, there is a manifold of several bands, nominally derived from the Se 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.656 eV at the G point symmetry. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 2.83 eV.

### 3.3.4 ZnS$_{0.25}$Se$_{0.75}$ Band Structure Calculation

Figure 3.10 shows the Brillouin zone for ZnS$_{0.25}$Se$_{0.75}$ supercell. The atomic vectors for ZnS$_{0.25}$Se$_{0.75}$ are $a_1 = (2.7, -2.7, 0)$, $a_2 = (2.7, 2.7, 0)$, $a_3 = (0, 0, 5.4)$ where $a = 5.4\ \overset{\circ}{\text{Å}}$, $c = 10.8186\ \overset{\circ}{\text{Å}}$, 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 $R_{AC} = R_{BC} = 6.6136\ \overset{\circ}{\text{Å}}$ with face centered (0,0,0), (0,1/2,1), (1/2,0,1), (1/2,1/2,0). The internal structure parameter $u$ from CASTEP computation is 0.25 whereas given $u = 0.247$ as reported by Mesri et al., [2007].

![Figure 3.10: Brillouin zone for ZnS$_{0.25}$Se$_{0.75}$ crystal structure.](image-url)
Figure 3.11 shows the band structure for $\text{ZnS}_{0.25}\text{Se}_{0.75}$. The band structure of $\text{ZnS}_{0.25}\text{Se}_{0.75}$ has energetically separated low lying bands, positioned around -14 eV, are derived from Se 4s comparing with Figure 3.12. These bands are separated from a group of relatively narrow bands arising from the Zn 3d states located around -7eV.

![Figure 3.11: The calculated energy band structure for $\text{ZnS}_{0.25}\text{Se}_{0.75}$.](image)

At the symmetry G point, the energy gap is 1.65 eV and upon applying the 1.7 correction factor $E_g$ is 2.81 eV. This is close to the experimental results given by Larach et al., [1957] which is 2.78 eV and 2.85 eV as reported by Abo Hassan et al., [2005a].
Near the Fermi level ($E_F$) in the valence-band region, there is a manifold of several bands, nominally derived from the Se 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.645 eV at the G point symmetry. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 2.81 eV. We note here that the correction energy gap is less than the energy gap where $x = 0.125$ by 0.034 that is may be because of LDA approximation.

### 3.3.5 $\text{ZnS}_{0.375}\text{Se}_{0.625}$ Band Structure Calculation

Figure 3.13 shows the Brillouin zone for supercell. The atomic vectors for $\text{ZnS}_{0.375}\text{Se}_{0.625}$ are $a_1 = (2.7, -2.7, 0)$, $a_2 = (2.7, 2.7, 0)$, $a_3 = (0, 0, 5.4)$ where $a = 5.4$ Å, $c = 10.8186$ Å, and $\eta = 1$, and the atomic positions are $\tau_A = (0,0,0)$, $\tau_B = (2.7,0,2.7)$, $\tau_{C_1} = (1.35,1.35,1.35)$, $\tau_{C_2} = (4.05,1.35,4.05)$, $u = 0.25$ and $R_{AC} = R_{BC} = 6.6136$ Å.
Figure 3.13: Brillouin zone for ZnS$_{0.375}$Se$_{0.625}$ crystal structure.

Figure 3.14 shows the band structure for ZnS$_{0.375}$Se$_{0.625}$. The band structure of ZnS$_{0.375}$Se$_{0.625}$ has energetically separated low lying bands, positioned around -14 eV, are derived from Se 4s comparing with Figure 3.15. These bands are separated from a group of relatively narrow bands arising from the Zn 3d states located around -7eV.

Figure 3.14: The calculated energy band structure for ZnS$_{0.375}$Se$_{0.625}$. 
At the symmetry G point, the energy gap is 1.75 eV and upon applying the 1.7 correction factor $E_g$ is 2.97 eV. This is close to the experimental results given by Larach et al., [1957] which is 3.01 eV and 2.96 eV as reported by Abo Hassan et al., [2005a].

$E_g$ is 2.9 eV upon applying the 1.66 correction factor which is near to the experimental results given by Larach et al. [1975] and Abo Hassan et al. [2005a].

Near the Fermi level ($E_F$) in the valence-band region, there is a manifold of several bands, nominally derived from the Se 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.75 eV at the G point symmetry. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 3.15 eV.

Figure 3.15: Total density of states for ZnS$_{0.375}$Se$_{0.625}$. 
3.3.6 \textit{ZnS}_{0.5} \textit{Se}_{0.5} Band Structure Calculation

Figure 3.16 shows the Brillouin zone for \textit{ZnS}_{0.5} \textit{Se}_{0.5} supercell. The atomic position are \( a_1 = (2.7, -2.7, 0) \), \( a_2 = (2.7, 2.7, 0) \), \( a_3 = (0, 0, 5.4) \) where \( a = 5.4 \, \text{Å} \), \( c = 10.8186 \, \text{Å} \), 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 \( R_{AC} = R_{BC} = 6.6136 \, \text{Å} \).

![Figure 3.16: Brillouin zone for \textit{ZnS}_{0.5} \textit{Se}_{0.5} crystal structure.](image)

Figure 3.17 and Figure 3.18 shows the band structure and the density of states for \textit{ZnS}_{0.5} \textit{Se}_{0.5} respectively. The band structure of \textit{ZnS}_{0.5} \textit{Se}_{0.5} has energetically separated low lying bands, positioned around \(-14 \, \text{eV}\), and is derived from \textit{Se} 4s comparing the two given figures. These bands are separated from a group of relatively narrow bands arising from the \textit{Zn} 3d states located around \(-6.8 \, \text{eV}\).
At the symmetry G point, the energy gap is 1.77 eV and upon applying the 1.7 correction factor $E_g$ is 3.00 eV. This is close to the experimental results given by Homann et al. [2006] which is 2.92 eV and near to the experimental results which is 3.08 eV as reported by Ebina et al. [1974], and close to theoretical results given by Swarnkar et al. [2009] which is 3.21 eV and using LCAO [Homann et al., 2006] which is 3.29 eV. $E_g$ is 2.94 eV upon applying the 1.66 correction factor which is close to the experimental results given by Homann et al. [2006] which is 2.92 eV and different from experimental results given by Ebina et al. [1974], and theoretical results reported in the literature.
Near the Fermi level ($E_F$) in the valence-band region, there is a manifold of several bands, nominally derived from the Se 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.77 eV at the G point symmetry. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 3.19 eV.

### 3.3.7 ZnS$_{0.625}$Se$_{0.375}$ Band Structure Calculation

Figure 3.19 shows the Brillouin zone for ZnS$_{0.625}$Se$_{0.375}$ supercell. The atomic position are $a_1 = (2.7, -2.7, 0)$, $a_2 = (2.7, 2.7, 0)$, $a_3 = (0, 0, 5.4)$ where $a = 5.4 \text{ Å}$, $c = 10.8186 \text{ Å}$, 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 $R_{AC} = R_{BC} = 6.6136 \text{ Å}$.
Figure 3.19: Brillouin zone for $\text{ZnS}_{0.625}\text{Se}_{0.375}$ crystal structure (with space group CMM2 (C2V-11)).

Figure 3.20 and Figure 3.21 show the band structure and the density of states for $\text{ZnS}_{0.625}\text{Se}_{0.375}$ respectively. The band structure of $\text{ZnS}_{0.625}\text{Se}_{0.375}$ has energetically separated low lying bands, positioned around -13eV, are derived from Se 4s comparing the two given figures. These bands are separated from a group of relatively narrow bands arising from the Zn 3d states located around -6.5eV.

Figure 3.20: The calculated energy band structure for $\text{ZnS}_{0.625}\text{Se}_{0.375}$. 
At the symmetry G point, the energy gap is 1.83 eV and upon applying the 1.7 correction factor $E_g$ is 3.11 eV. There is no theoretical and experimental results reported for this concentration. $E_g$ is 3.04 eV upon applying the 1.66 correction factor.

Near the Fermi level ($E_F$) in the valence-band region, there is a manifold of several bands, nominally derived from the Se 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.83 eV at the G point symmetry. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 3.29 eV.

3.3.8 ZnS$_{0.75}$Se$_{0.25}$ Band Structure Calculation

Figure 3.22 shows the Brillouin zone for ZnS$_{0.75}$Se$_{0.25}$ supercell. The atomic position are $a_1 = (2.7, -2.7, 0)$, $a_2 = (2.7, 2.7, 0)$, $a_3 = (0,0,5.4)$ where $a = 5.4$ Å, $c =$
10.8186 Å\(^0\), 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 \(R_{AC} = R_{BC} = 6.6136\) Å\(^0\).

Figure 3.22: Brillouin zone for Zn\(_{0.75}\)Se\(_{0.25}\) crystal structure.

Figure 3.23 and Figure 3.24 shows the band structure and the density of states for Zn\(_{0.75}\)Se\(_{0.25}\) respectively. The band structure of Zn\(_{0.75}\)Se\(_{0.25}\) has energetically separated low lying bands, positioned around -13 eV, and is derived from Se 4s comparing the two given figures. These bands are separated from a group of relatively narrow bands arising from the Zn 3d states located around -6.5 eV.
At the symmetry G point, the energy gap is 1.82 eV and upon applying the 1.7 correction factor $E_g$ is 3.1 eV. This is close to the experimental results given by Homann et al. [2006] which is 3.17 eV and near to the experimental results which is 3.34 eV as reported by Ebina et al. [1974], and little different from theoretical results given by Swarnkar et al. [2009] which is 3.47 eV and by using LCAO [Homann et al., 2006] which is 3.47 eV. $E_g$ is 3.02 eV upon applying the 1.66 correction factor and this is near to the experimental results 3.17 eV as reported by Homann et al. [2006] and different from the other results reported in the literature.

Figure 3.23: The calculated energy band structure for ZnS$_{0.75}$Se$_{0.25}$. 

At the symmetry G point, the energy gap is 1.82 eV and upon applying the 1.7 correction factor $E_g$ is 3.1 eV. This is close to the experimental results given by Homann et al. [2006] which is 3.17 eV and near to the experimental results which is 3.34 eV as reported by Ebina et al. [1974], and little different from theoretical results given by Swarnkar et al. [2009] which is 3.47 eV and by using LCAO [Homann et al., 2006] which is 3.47 eV. $E_g$ is 3.02 eV upon applying the 1.66 correction factor and this is near to the experimental results 3.17 eV as reported by Homann et al. [2006] and different from the other results reported in the literature.

Figure 3.23: The calculated energy band structure for ZnS$_{0.75}$Se$_{0.25}$. 

At the symmetry G point, the energy gap is 1.82 eV and upon applying the 1.7 correction factor $E_g$ is 3.1 eV. This is close to the experimental results given by Homann et al. [2006] which is 3.17 eV and near to the experimental results which is 3.34 eV as reported by Ebina et al. [1974], and little different from theoretical results given by Swarnkar et al. [2009] which is 3.47 eV and by using LCAO [Homann et al., 2006] which is 3.47 eV. $E_g$ is 3.02 eV upon applying the 1.66 correction factor and this is near to the experimental results 3.17 eV as reported by Homann et al. [2006] and different from the other results reported in the literature.
Near the Fermi level ($E_F$) in the valence-band region, there is a manifold of several bands, nominally derived from the Se 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.82 eV at the symmetry G point. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e. 1.7) which gives 3.28 eV.

### 3.3.9 ZnS$_{0.875}$Se$_{0.125}$ Band Structure Calculation

Figure 3.25 shows the Brillouin zone for ZnS$_{0.875}$Se$_{0.125}$ supercell. The atomic position are $a_1 = (2.7, -2.7, 0)$, $a_2 = (2.7, 2.7, 0)$, $a_3 = (0,0,5.4)$ where $a = 5.4$ Å, $c = 10.8186$ Å, and $\eta = 1$, and the atomic positions are $\tau_A = (0,0,0)$, $\tau_B = (2.7,0,2.7)$, $\tau_{C1} = (1.35,1.35,1.35)$, $\tau_{C2} = (4.05,1.35,4.05)$, $\mu = 0.25$ and $R_{AC} = R_{BC} = 6.6136$ Å.
Figure 3.25: Brillouin zone for ZnS$_{0.875}$Se$_{0.125}$ crystal structure.

Figure 3.26 and Figure 3.27 show the band structure and the density of states for ZnS$_{0.875}$Se$_{0.125}$ respectively. The band structure of ZnS$_{0.875}$Se$_{0.125}$ has energetically separated low lying bands, positioned around -13 eV, and is derived from Se 4s comparing the two given figures. These bands are separated from a group of relatively narrow bands arising from the Zn 3d states located around -6.2 eV.

Figure 3.26: The calculated energy band structure for ZnS$_{0.875}$Se$_{0.125}$.
At the symmetry G point, the energy gap is 1.9 eV and upon applying the 1.7 correction factor \( E_g \) is 3.32 eV. This is no experimental and theoretical results reported. \( E_g \) is 3.15 eV upon applying the 1.66 correction factor.

![Figure 3.27: Total density of states for ZnS\(_{0.875}\)Se\(_{0.125}\).](image)

Near the Fermi level \((E_F)\) in the valence-band region, there is a manifold of several bands, nominally derived from the Se 4p states. The valence bands are separated from the conduction bands by an energy band gap of 1.9 eV at the symmetry G point. It is well known that the LDA in general underestimates energy band gaps. Thus, to get the correct value of the gap one will need to include the multiplicative correction factor (i.e., 1.7) which gives 3.42 eV.

Figure 3.28 describes the relation between the energy gap \( E_g \) and the concentration \( x \) (0<\(x<1\)) from the results of CASTEP applying the 1.66 and 1.7 correction factors, and omitting the values of the energy gap for ZnS and ZnSe. The difference between the
values of energy gap of ZnS, ZnSe and the values given in the literatures are because of applying the LDA.

![Graph showing Eg as a function of x from CASTEP computation upon applying the 1.7 and 1.66 multiplicative correction factors.](image)

**Figure 3.28:** $E_g$ as a function of $x$ from CASTEP computation upon applying the 1.7 and 1.66 multiplicative correction factors.

### 3.4 SUMMARY

The first-principle calculations were applied using the CASTEP computer code based on density functional theory. Computations have been performed via local-density approximation (LDA). Calculations of the band structure and density of states for ZnS$_x$Se$_{1-x}$ alloy based on parameters given in Eqn. (3.1) to Eqn. (3.4) at the Brillouin zone shows that ZnS and ZnSe have unit cell vectors $a_1 = (2.7, -2.7, 0)$, $a_2 = (2.7, 2.7, 0)$, $a_3 = (0,0,5.4)$ with lattice constant $a = 5.4 \AA$ and atomic positions $\tau_A = (0,0,0)$, $\tau_B = (2.7,0,2.7)$, $\tau_{C1} = (1.35,1.35,1.35)$, $\tau_{C2} = (4.05,1.35,4.05)$, with the two fundamental bonds lengths $R_{AC} = R_{BC} = 6.6136 \AA$. The calculations of the band structure for ZnS$_x$Se$_{1-x}$ when (0 < $x$ < 1) at the Brillouin zone gives unit cell vectors $a_1 = (2.7, -2.7, 0)$,
\[ a_2 = (2.7, 2.7, 0), \quad a_3 = (0,0,5.4) \text{ where } a = 5.4 \text{ Å, } c = 10.8186 \text{ Å}, \text{ atomic positions } \tau_A = (0,0,0), \quad \tau_B = (2.7,0,2.7), \quad \tau_{C1} = (1.35,1.35,1.35), \quad \tau_{C2} = (4.05,1.35,4.05), \] and two fundamental bonds lengths \[ R_{AC} = R_{BC} = 6.6136 \text{ Å}. \]

The values of energy gap for \( \text{ZnS}_x\text{Se}_{1-x} (0 \leq x \leq 1) \) were calculated by using a multiplicative correction factor 1.7 to adjust the theoretical band gap to experimental result.