First-principles calculations of structural, electronic and thermal properties of Zn$_{1-x}$Mg$_x$S ternary alloys

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Abstract: Structural, electronic and thermal properties of Zn$_{1-x}$Mg$_x$S ternary alloys are studied by using the full potential-linearized augmented plane wave method (FP-LAPW) within the density functional theory (DFT). The Wu-Cohen generalized gradient approximation (WC-GGA) is used in this approach for the exchange-correlation potential. Moreover, the modified Becke-Johnson approximation (mBJ) is adopted for band structure calculations. The dependence of the lattice constant, bulk modulus and band gap on the composition $x$ showed that the first exhibits a small deviation from the Vegard’s law, whereas, a marginal deviation of the second from linear concentration dependence (LCD). The bowing of the fundamental gap versus composition predicted by our calculations agrees well with the available theoretical data. The microscopic origins of the gap bowing are explained by using the approach of Zunger and co-workers. Thermal effects on some macroscopic properties of Zn$_{1-x}$Mg$_x$S alloys are also investigated using the quasi-harmonic Debye model, in which the phononic effects are considered. As, this is the first quantitative theoretical prediction of the thermal properties of Zn$_{1-x}$Mg$_x$S alloys, no other calculated results and furthermore no experimental studies are available for comparison.

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1. Introduction

Binary, ternary and quaternary semiconductor alloys have been lately under increasing investigations both in fundamental studies and for many potential applications such as electronic and electro-optical devices [1]. Since, it is possible to combine two different elements with different
optical and mechanical properties in order to obtain a new compound with intermediate properties, the II–VI semiconductor alloys are used in optoelectronic devices ranging from blue to near-ultraviolet spectral region [2] and are also used to fabricate X-ray and γ-ray detectors [3, 4]. Furthermore, large band gaps of Mg containing II–VI semiconductors make them interesting for opto-electronic devices in the whole visible field [5]. Such materials have also been exploited both for quantum confinement and for achieving waveguides. As a matter of fact Zn$_{1-x}$Mg$_x$S alloys are promising candidates [6] for their energy gaps and lattice constants which can be varied in a wide range of stoichiometry parameter $x$. Although a number of experimental and theoretical studies of Zn$_{1-x}$Mg$_x$S semiconductor alloys have been published [7–12], to the best of our knowledge there are no available data for their thermal properties. Thermodynamic properties for crystalline materials are very important in many applications involving high pressure and high temperature. Although, ab initio calculations have successfully predicted the electronic and structural properties of various materials, these calculations are very often restricted to the 0 K temperatures. In this work, thermal properties are considered by the use of the quasi-harmonic Debye model [13], and in order to provide further works on Zn$_{1-x}$Mg$_x$S alloys, the full-potential linearized augmented plane-wave (FP-LAPW) method combined with the quasi-harmonic Debye model, is used to determine the structural, electronic, and thermal properties of these alloys. The rest of the paper has been divided in three parts. In section 2, we briefly describe the computational techniques used in this study. The most relevant results of Zn$_{1-x}$Mg$_x$S alloys are presented and discussed in section 3. Finally, in section 4 we summarize the main conclusions of our work.

2. Method of calculations

All calculations were performed using the FP-LAPW method [14] within the framework of the density functional theory (DFT) [15, 16] as implemented in the WIEN2K code [17]. For structural properties, the exchange-correlation potential was calculated using the generalized gradient approximation (GGA) in the new form (WC) proposed by Wu and Cohen [18] which is an improved form of the most popular Perdew–Burke–Ernzerhof (PBE) GGA [19]. In addition, and for electronic properties only, we also applied the modified Becke-Johnson (mBJ) exchange potential approximation [20, 21]. In this scheme, crystal unit cell is partitioned into two regions: non-overlapping Muffin-Tin (MT) spheres centred at the atomic sites and the remaining interstitial area. In both regions of unit cell, Kohn-Sham wave functions, charge density and potential were expanded in the different sets of basis functions.

In the interstitial region, the basis sets consist of a plane waves. Inside the MT spheres, the basis sets is described by radial solutions of the one particle Schrödinger equation (at fixed energy) and their energy derivatives multiplied by spherical harmonics. The maximum $l$ quantum number for the wave function expansion inside atomic spheres was confined to $l_{\text{max}} = 10$. The plane wave cutoff parameters were decided by $B_{\text{MT}} K_{\text{max}} = 8.0$ (where $K_{\text{max}}$ is the largest wave vector of the basis set and $B_{\text{MT}}$ is the smallest Muffin-Tin radius in the unit cell) and $B_{\text{MT}} = 14(Ry)^{1/2}$ for Fourier expansion of potential in the interstitial region. The $B_{\text{MT}}$ of Zn, Mg and S atoms have been chosen to be 2.2, 2, and 2, a.u., respectively. Meshes of 47 special k-points for binary compounds and 35 special k-points for alloys were used in the irreducible wedge of the Brillouin zone. To ensure total energy convergence, number of tests has been performed taking different $B_{\text{MT}}$ values and different sets of special k-point.

3. Results and discussions

3.1. Structural properties

The structural properties of the binary compounds ZnS and MgS in the zinc-blende phase using the WC–GGA scheme were calculated, and the alloys are modeled at some selected compositions with ordered structures described in terms of periodically repeated supercells. For the compositions $x = 0.25$, 0.5, and 0.75, the simplest structure is an eight-atom simple cubic lattice. For the structures considered, the structural optimization by minimizing the total energy with respect to the cell parameters and the atomic positions was performed. The idea of constructing an alloy by taking a large unit cell (cubic eight atoms) and repeating it three dimensionally for the calculation of the electronic structure of alloys used by Agrawal et al [22] has been adopted recently by many researchers to investigate properties of alloys [23–25]. For the compositions $x = 0.25$ and 0.75 the simplest structure is an eight-atom simple cubic lattice (luzonite): the anions with the lower concentration form a regular simple cubic lattice, but for the composition $x = 0.5$, the atoms of the same layer are identical. The calculated total energies at many different volumes around equilibrium were fitted by the Murnaghan equation of state [26] in order to determine the ground state properties such as the equilibrium lattice constant $a$, the bulk modulus $B$ and its pressure derivative $B’$. The WC-GGA calculated structural parameters for Zn$_{1-x}$Mg$_x$S at various compositions $x$ are listed in Table 1, where comparison is made with experimental
and previous theoretical values of the lattice constant and bulk modulus. For the lattice constant, the present WC-GGA results agree well with the previous experimental and theoretical reports for the binary compounds, hence, it is reasonable to expect that the lattice constant of the alloys can be described with similar accuracy in these calculations. As it can be seen, the lattice parameter for MgS ($x=1$) is larger than those of ZnS ($x=0$); $a$(ZnS) $<$ $a$(MgS). Since the anion atom is the same in both compounds, this result can be easily explained by considering the atomic radii of Mg and Zn, $R$(Mg)= 1.50 Å, $R$(Zn)= 1.35 Å, i.e. the lattice constant increases with increasing atomic size of the anion element. The bulk modulus value for ZnS is larger than those of MgS, $B$( ZnS) $>$ $B$(MgS); i.e. in inverse sequence to $a$, in agreement with the well-known relationship between $B$ and the lattice constant, $B \propto V_0^{-1}$ [31], where $V_0$ is the unit cell volume. The composition dependence of the calculated lattice constant for Zn$_{1-x}$Mg$_x$S ternary alloys is shown in Fig. 1. The increase of the lattice constant versus concentration $x$ is in good agreement with the available theoretical results. The calculated lattice constant obtained at different compositions was found to vary almost linearly with a marginal upward bowing parameter equal to $-0.008$ Å. The linear behavior of the lattice constant is consistent with the Vegard’s law [32] that is often used for obtaining the lattice constant of zinc-blende semiconductor alloys [33, 34]. This fact suggests that there is a good agreement between the DFT predictions and the linear Vegard’s law. The physical origin of this marginal bowing parameter should be mainly due to the weak mismatches of the lattice constants of ZnS and MgS compounds.

The variation of the bulk modulus versus composition $x$ is displayed in Fig. 2. The dashed lines in this figure represent the variation of the bulk modulus versus composition predicted by a linear concentration dependence method (LCD), where a small deviation from LCD is observed, with downward bowing equal to 8,178 GPa. This deviation is mainly due to the mismatch of the bulk modulus of binary compounds. Furthermore, the bulk modulus decreases with increasing Mg concentration $x$ ($0 \leq x \leq 1$), suggesting that, Zn$_{1-x}$Mg$_x$S becomes more compressible as the concentration $x$ increases from 0 to 1.

### 3.2. Electronic properties

The band structures for the Zn$_{1-x}$Mg$_x$S alloys along the high directions in the first Brillouin zone at the optimized equilibrium lattice constants were calculated giving a direct band gap located at the $\Gamma$ point in the whole range of concentrations. The resulting band structures of Zn$_{0.75}$Mg$_{0.25}$S using the WC-GGA and mBJ schemes are displayed in Figs. 3a and 3b, respectively. The calculated band gaps for all studied compositions are given in Table 2, where the mBJ band gap values of binary compounds are close to the experiment, which is a support for those of the ternary alloys. WC-GGA results for band gaps are underestimated compared to the measured ones as expected (DFT is a ground state theory) [38, 39]. This is mainly due to the fact that the functionals within this approximation have simple forms that are not sufficiently flexible to reproduce accurately both exchange-correlation energy and its charge derivative. According to current calculations, mBJ performed better than other conventional DFT functionals to calculate band structure. For this reason, mBJ is a very effective method for electronic properties and it

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**Figure 1.** Composition dependence of the calculated lattice constant (filled squares) of Zn$_{1-x}$Mg$_x$S alloys compared with Vegard’s prediction (dashed line).

**Figure 2.** Composition dependence of the calculated bulk modulus (filled squares) of Zn$_{1-x}$Mg$_x$S alloys compared with the linear composition dependence prediction (dashed line).
can be used for a wide range of semiconductors.

Fig. 4 shows the composition dependence of the calculated band gaps using WC-GGA and mBJ schemes, where, the band gap varies non-linearly with the composition \( x \) providing a band gap bowing which is calculated by fitting the non-linear variation of the calculated band gap versus concentration with quadratic function. The results obey the following variations:

\[
E_y^{WG-GGA} = 2.062 + 0.738 + 0.434x^2, \tag{1}
\]

\[
E_y^{mBJ} = 3.762 + 0.85x + 1.46x^2, \tag{2}
\]

where the quadratic terms express the band gap bowing parameters.

The main influence of the band gap energy is due to the lattice constant and the electronegativity mismatch of the parent atoms.

The physical origins of the band gap bowing in these alloys are better understood by following the procedure of Bernard and Zunger [40], in which the bowing parameter \( b \) is decomposed into three physically distinct contributions. In fact the overall band gap bowing coefficient at \( x = 0.50 \) measures the change in the band gap according to the reaction:

\[
AB(a_{AB}) + AC(a_{AC}) \rightarrow AB_{0.5}C_{0.5}(a_{eq}), \tag{3}
\]

which can be decomposed into the following three steps:

\[
AB(a_{AB}) + AC(a_{AC}) \xrightarrow{VD} AB(a) + AC(a), \tag{4}
\]

\[
AB(a) + AC(a) \xrightarrow{CE} AB_{0.5}C_{0.5}(a), \tag{5}
\]

\[
AB_{0.5}C_{0.5}(a) \xrightarrow{SR} AB_{0.5}C_{0.5}(a_{eq}), \tag{6}
\]

where \( a_{AB} \) and \( a_{AC} \) are the equilibrium lattice constants of the binary compounds \( AB \) and \( AC \), respectively; \( a_{eq} \) is the alloy equilibrium lattice constant.

The first step measures the volume deformation (VD) effect on the bowing. The corresponding contribution to the total gap bowing parameter \( b_{VD} \) represents the relative response of the band structure of the binary compounds \( AB \) and \( AC \) to hydrostatic pressure, which arises from the change of their individual equilibrium lattice constants to the alloy equilibrium lattice constant value \( a(x) \) (Vegard’s rule). The second contribution, the charge exchange (CE) contribution \( b_{CE} \), reflects a charge transfer effect which is due to the different (averaged) bonding behavior at the lattice constant \( a \). The final step measures change due to structural relaxation (SR) in passing from unrelaxed to the relaxed alloy. Consequently, the total gap bowing parameter is defined as:

\[
b = b_{VD} + b_{CE} + b_{SR}. \tag{7}
\]

where

\[
b_{VD} = 2[\epsilon_{AB}(a_{AB}) - \epsilon_{AB}(a) + \epsilon_{AC}(a_{AC}) - \epsilon_{AC}(a)], \tag{8}
\]

\[
b_{CE} = 2[\epsilon_{AB}(a) + \epsilon_{AC}(a) - 2\epsilon_{ABC}(a)], \tag{9}
\]

\[
b_{SR} = 2[\epsilon_{ABC}(a) - \epsilon_{ABC}(a_{eq})], \tag{10}
\]

where \( \epsilon \) is the energy gap calculated for the indicated atomic structures and lattice constants. We calculated the bowing contributions at composition \( x = 0.5 \) based on Eqs. (8)–(10) with self-consistent band structure FP-LAPW within both WC-GGA and mBJ approaches. The results are given in Table 3 together with the bowing obtained using a quadratic variation of the band gap energy versus composition \( x \) and compared with available theoretical results.

The calculated quadratic parameters (gap bowing) are in reasonable agreement with the values found from Bernard and Zunger’s approach. The charge transfer contribution \( b_{CE} \) dominates the total band gap bowing parameter.

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**Table 1.** Calculated equilibrium lattice constant and bulk modulus of zinc-blende ZnS and MgS compounds and their ternary alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Lattice constant a (Å)</th>
<th>Bulk Modulus B (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Exp</td>
</tr>
<tr>
<td></td>
<td>WC-GGA</td>
<td></td>
</tr>
<tr>
<td>Zn&lt;sub&gt;1−x&lt;/sub&gt;Mg&lt;sub&gt;x&lt;/sub&gt;S</td>
<td>0.5</td>
<td>5.519</td>
</tr>
<tr>
<td>Zn&lt;sub&gt;1−x&lt;/sub&gt;Mg&lt;sub&gt;x&lt;/sub&gt;S</td>
<td>0.75</td>
<td>5.589</td>
</tr>
<tr>
<td>Zn&lt;sub&gt;1−x&lt;/sub&gt;Mg&lt;sub&gt;x&lt;/sub&gt;S</td>
<td>1</td>
<td>5.658</td>
</tr>
</tbody>
</table>

<sup>a</sup>Ref. [23], <sup>b</sup>Ref. [24], <sup>c</sup>Ref. [25], <sup>d</sup>Ref. [6], <sup>e</sup>Ref. [12], <sup>f</sup>Ref. [11], <sup>g</sup>Ref. [26]
in the studied alloys; this is related to electronegativity mismatch between the constituting atoms: Zn (1.65), Mg (1.31) and S (2.58). Furthermore, the contribution of \( b_{V} \) to \( b \) is negative, i.e. it decreases the value of \( b \). The contribution of the structural relaxation \( b_{SR} \) is small in these alloys. Finally, the mBJ values for bowing parameters are larger than the corresponding values within WC-GGA.

3.3. Thermal properties

The study of Zn\(_{1-x}\)Mg\(_{x}\)S alloy thermal properties, was done within the quasi-harmonic Debye model [13] and combined with ab-initio calculations of the static total energy, in which the non-equilibrium Gibbs function \( G^*(V; P, T) \) can be written in the form:

\[
G^*(V; P, T) = E(V) + PV + A_{Vib}[\theta(V); T],
\]

where \( E(V) \) is the total energy per unit cell, \( PV \) corresponds to the constant hydrostatic pressure condition, \( \theta(V) \) is the Debye temperature, and \( A_{Vib} \) is the vibrational term, which can be written using the Debye model of the phonon density of states as [41, 42]:

\[
A_{Vib} = n k_B T \left[ \frac{9 \theta}{8 T} + 3 \ln \left( 1 - e^{-\theta/T} \right) - D(\theta/T) \right],
\]

where \( D(\theta/T) \) represents the Debye integral, \( n \) is the number of atoms per unit cell.

For an isotropic solid, \( \theta \) is expressed as [41]:

\[
\theta_D = \frac{\hbar}{k_B} \left[ 6 \pi^2 V^{1/3} n \right]^{1/3} f(\alpha) \sqrt{\frac{B_S}{M}}.
\]

\( M \) being the molecular mass per unit cell and \( B_S \) the adiabatic bulk modulus, approximated by the static compressibility [13]

\[
B_s \approx B(V) = V \left\{ \frac{d^2 E(V)}{dV^2} \right\}.
\]

\( f(\alpha) \) is given by:

\[
f(\alpha) = \left\{ \left[ 3 \left( \frac{21}{31} + \frac{\alpha}{2} \right) \right]^{3/2} + \left( \frac{11}{31} - \frac{\alpha}{2} \right) \right\}^{1/3}.
\]

The Poisson ratio \( \sigma \) is taken as 0.25 [43]. Therefore, the non-equilibrium Gibbs function \( G^*(V; P, T) \) as a function of \( (V; P, T) \) can be minimized with respect to volume \( V \):

\[
\left[ \frac{\partial G^*(V; P, T)}{\partial V} \right]_{P, T} = 0.
\]

By solving Eq. (16), one can get the thermal equation of state (EOS) \( V(P, T) \). The isothermal bulk modulus \( B_T \), the heat capacity \( C_V \) and the thermal expansion coefficient \( \alpha \) are given by [43]:

\[
B_T(P, V) = V \left\{ \frac{\delta^2 G^*(V; P, T)}{\delta V^2} \right\},
\]

\[
C_V = 3 n k_B \left[ 4 D(\theta/T) - \frac{3 \theta/T}{e^{\theta/T} - 1} \right],
\]

\[
\alpha = \gamma C_V \frac{B_T}{V}.
\]

Where \( \gamma \) is the Grüneisen parameter, which is defined as:

\[
\gamma = -\frac{d \ln \theta(V)}{d \ln V}.
\]

Through the quasi-harmonic Debye model, one could calculate the thermodynamic quantities of any temperatures and pressures of compounds from the calculated \( E - V \) data at \( T = 0 \) and \( P = 0 \). The thermal properties are determined in the temperature and pressure ranges 0–900 K and 0–6 GPa, respectively. Since, to the best of knowledge no experimental nor theoretical data are available for comparison, this work is the first theoretical prediction for these thermal quantities. A similar behaviour is obtained for all concentrations, therefore, only the results related to the concentration 0.75, are presented.

The variation of the lattice constant \( \alpha \) of Zn\(_{0.25}\)Mg\(_{0.75}\)S alloy versus temperature at several pressures is shown in Fig. 5. When \( T \) is smaller than 100 K, \( \alpha \) is nearly constant for all applied pressures, but, when \( T > 100 \) K, the lattice constant increases with increasing temperature at a given pressure. On the other side, as the pressure increases, the lattice constant decreases at a given temperature. The rate of increase of the lattice constant with temperature decreases with increasing pressure. This effect of increasing pressure on Zn\(_{0.25}\)Mg\(_{0.75}\)S is just the same as that of decreasing temperature on this material.

The bulk modulus \( B \) is related to interatomic potentials and can be obtained by the second derivative of the internal energy with respect to strain. The temperature dependence of \( B \) partially reflects the anharmonic interactions since for a purely harmonic crystal, the bulk modulus would be independent of temperature. The bulk modulus \( B \) of Zn\(_{0.25}\)Mg\(_{0.75}\)S alloy as a function of temperature up to 900 K at several pressures is plotted in Fig. 6. \( B \) remains constant for \( T < 100 \) K, but for \( T > 100 \) K, \( B \) decreases dramatically as \( T \) increases. This indicates that the volume of Zn\(_{0.25}\)Mg\(_{0.75}\)S alloy varies significantly as the temperature increases when \( T > 100 \) K. However, the...
The heat capacity of a substance not only provides essential insight into its vibrational properties but is also mandatory for many applications. Two famous limiting cases are correctly predicted by the standard elastic continuum theory [44]. At high temperature, the constant volume heat capacity \( C_v \) does not depend much on temperature and tends to the Dulong-Petit limit, \( C_v \approx 3R \) for monoatomic solids [45], which is true to all solids at high temperatures. At sufficiently low temperature, \( C_v \) is proportional to \( T^1 \) [44]. At intermediate temperatures, however, the temperature dependence of \( C_v \) is governed by the details of vibrations of the atoms and for a long time could only be determined from experiments. Fig. 7. displays the dependence of \( C_v \) on temperature and pressure for the Zn_{0.25}Mg_{0.75}S alloy. It is shown that for \( T < 500\) K, the heat capacity depends on both temperature and pressure. At high temperatures, \( (T > 500 \) K) \( C_v \) tends to the Dulong-Petit limit, \( C_v \) tends to \( 48.97 \) J mol\(^{-1}\)K\(^{-1}\) at high temperatures. The variation of \( C_v \) with respect to temperature under low pressure is great than those under higher pressure. The variation of the heat capacity at constant pressure \( C_p \) versus temperature at 0, 2, 4 and 6 GPa pressures for the Zn_{0.25}Mg_{0.75}S alloy is shown in Fig. 8. The variation features of \( C_p \) at low temperature are similar to the behavior of \( C_v \). However, for high temperatures, \( C_p \) exhibits apparently different features. \( C_p \) values decrease with increasing pressures and do not converge to a constant value. At room temperature and zero pressure, the value of \( C_p \) is about 42.07 J mol\(^{-1}\)K\(^{-1}\). Fig. 9. shows the variation of the thermal expansion coefficient \( \alpha \) with respect to the temperature at several pressures for the Zn_{0.25}Mg_{0.75}S alloy. As the thermal expansion coefficients have anharmonic behaviors, no linear variation with temperature \( T \) is expected. \( \alpha \) increases with \( T^1 \) at low temperatures and gradually approaches a linear increase with enhanced temperature and the propensity of increment becomes moderate, which means that the temperature dependence of \( \alpha \) is very small at high temperature. For a given temperature, \( \alpha \) decreases dramatically with increasing pressure. With increasing pressure, the increase in \( \alpha \) is weakened. The calculated properties at different temperatures are very sensitive to the vibrational effects. In the quasi-harmonic Debye model, the Debye temperature is a key parameter. The temperature dependence of the Debye temperature \( \theta_D \) at several pressures for the Zn_{0.25}Mg_{0.75}S alloy is plotted in Fig. 10. \( \theta_D \) is nearly constant from 0 to 100 K and decreases almost linearly with increasing temperature for \( T > 100 \) K. It is also shown that \( \theta_D \) increases with applied pressure at a

### Table 2. Direct band gap energy \( E_g \) (eV) of Zn_{1-x}Mg_{x}S alloys at various \( x \) compositions.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>This work</th>
<th>Exp</th>
<th>Other calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>WC-GGA</td>
<td>mbJ</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.993</td>
<td>3.722, 3.68, 3.80, 2.37, 1.953, 2.792, 1.97, 2.823</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>2.429</td>
<td>3.950</td>
<td>2.263, 3, 1.144</td>
</tr>
<tr>
<td>Zn_{1-x}Mg_{x}S</td>
<td>0.5</td>
<td>2.491</td>
<td>4.167</td>
</tr>
<tr>
<td>0.75</td>
<td>2.771</td>
<td>4.441</td>
<td>2.817, 3.715</td>
</tr>
<tr>
<td>1</td>
<td>3.288</td>
<td>5.141, 4.45, 4.50</td>
<td>4.48, 3.42, 3.327, 4.385, 3.333, 4.418</td>
</tr>
</tbody>
</table>

\( ^a \)Ref. [6], \(^b \)Ref. [24], \(^c \)Ref. [25], \(^d \)Ref. [12], \(^e \)Ref. [11], \(^f \)Ref. [31], \(^g \)Ref. [32]

### Table 3. Decomposition of bowing parameter into volume deformation (VD), Charge exchange (CE), and structural relaxation (SR) contributions compared with that obtained by a quadratic fit and other predictions (all values are in eV).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>This work</th>
<th>Zunger approach</th>
<th>Quadratic fits</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WC-GGA</td>
<td>mbJ</td>
<td>WC-GGA</td>
</tr>
<tr>
<td>b_{VD}</td>
<td>-0.226</td>
<td>-0.103</td>
<td>-0.099, -0.657</td>
</tr>
<tr>
<td>b_{CE}</td>
<td>1.181</td>
<td>0.689</td>
<td>0.502, 1.509</td>
</tr>
<tr>
<td>Zn_{1-x}Mg_{x}S</td>
<td>b_{SR}</td>
<td>0.103</td>
<td>0.013</td>
</tr>
<tr>
<td>b</td>
<td>1.058</td>
<td>0.599</td>
<td>1.146, 0.434</td>
</tr>
</tbody>
</table>

\( ^a \)Ref. [12] using PBE-GGA approximation
\( ^b \)Ref. [12] using Engel-Vosko EV-GGA approximation.
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Figure 3. (a) Calculated band structure of Zn$_{0.25}$Mg$_{0.75}$S alloy using WC-GGA scheme. (b) Calculated band structure of Zn$_{0.25}$Mg$_{0.75}$S alloy using mBJ scheme.

Figure 4. Composition dependence of calculated band gap using WC-GGA (solid squares) and mBJ (solid circles) for Zn$_{1-x}$Mg$_x$S alloys.

Figure 5. Variation of the lattice constant of Zn$_{0.25}$Mg$_{0.75}$S alloy as a function of temperature at several pressures.

given temperature and decreases with increasing pressure. Our calculated $\theta_D$ at zero pressure and 300 K is equal to 622.12 K. Compared with Fig. 5, one can see that the compressibility increase leads to Debye temperature decrease. This result is in accordance with the fact that Debye temperature is proportional to the bulk modulus and that a hard material exhibits a high Debye temperature. The dispersal of energy and matter is described by the entropy, denoted by the symbol $S$. On a microscopic scale, the entropy can be defined as a measure of disorder of a system. The variation of the entropy $S$ versus temperature and pressure for the Zn$_{0.25}$Mg$_{0.75}$S alloys is displayed in Fig. 11. It is found that $S$ increases sharply with increasing temperature and decreases with the increase of pressure. As the temperature increases, the vibrational contribution to the entropy increases and therefore the entropy increases with temperature.

4. Conclusions

Structural, electronic, and thermal properties of Zn$_{1-x}$Mg$_x$S mixed crystals in the zinc blende phase have been studied using the FP-LAPW method within the DFT in the framework of WC-GGA and mBJ. The main results can be summarized as follows:

1. The calculated lattice constants and bulk modulus
of the binary compounds are in good agreement with available experimental and other theoretical data, however, a negligible deviation from Vegard’s law for the lattice constant regarding the normal substitution for $\text{Zn}_{1-x}\text{Mg}_x\text{S}$ alloys is observed.

2. A non-linear behavior of the bulk modulus and band gap dependence on $x$ has been observed.

3. The investigation of the origin of the band gap bowing shows that it is mainly dominated by the charge transfer effect, while the volume deformation and the structural relaxation contribute at smaller magnitude.

4. Finally, the quasi-harmonic Debye model is successfully applied to determine the thermal prop-
First-principles calculations of structural, electronic and thermal properties of Zn\textsubscript{1-x}Mg\textsubscript{x}S ternary alloys

Figure 11. Variation of the Entropy of Zn\textsubscript{0.25}Mg\textsubscript{0.75}S alloy versus temperature at several pressures.

Properties at different temperatures and pressures. It is our ambition that these calculations will inspire further experimental research on these systems.

References
