Density functional theory study on the origins of the gap bowing in Zn$_{1-x}$Mg$_x$Se

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Abstract

Self-consistent density functional theory based on a direct supercell approach is reported for Zn$_{1-x}$Mg$_x$Se pseudobinary alloy. The calculation includes, in a natural way, atomic relaxation and self-consistent charge transfer, hence providing a link between the electronic structure and the interaction energies which decide phase stability. We model the alloys at some selected compositions with ordered structures described in terms of periodically repeated supercells. Results include structural, electronic, and bonding properties as well as the density of occupied states and their variations upon alloying. Using the approach of Zunger and co-workers, the microscopic origins of compositional disorder have been detailed and explained. The disorder parameter (bowing) is found to be small and is mainly caused by the volume deformation effect. The chemical charge transfer also contributes to the bowing parameter at a smaller magnitude, while the relaxation contribution is even smaller.

1. Introduction

Wide-gap semiconductors have recently aroused enormous technological interest [1] both because of their potential use in devices capable of operating at high power levels and high temperatures, and because of the need for optical materials active in the blue–green spectral range. For technological applications, ZnSe can be used for operation in this spectral range provided that current device lifetime problems are overcome. One major goal in materials engineering for opto-electronic applications is the ability to tune the band gap independently in order to obtain the desired optical properties, and the lattice parameter of the material in order to be able to grow it on a given substrate.

Recent theoretical works have addressed these systems of alloys [2, 3]. Benkabou *et al* [4] have calculated the band-gap bowing of this alloy by using the empirical pseudopotential method and the virtual-crystal approximation (VCA). Another theoretical work reported a first-principles study of the structural properties of ZnSe–MgSe superlattices [5]. In addition,

extensive theoretical studies of the quaternary alloy $Zn_{1-x}Mg_xS_{1-y}Se_y$ addressed the structural and thermodynamic properties [7] and the optical gap [6] in detail. The latter works include the main preliminary steps of our present work regarding the properties of the pure materials that form the binary alloy studied, i.e. ZnSe and MgSe. This eliminates the need to conduct another exhaustive study of the bulk materials; we note that we use the same method of calculation.

In this work we focus our efforts on the study of the variation of the optical band gap within the alloy fraction. The alloy is modelled at some selected compositions by ordered structures described in terms of periodically repeated supercells. This can be done with little effort (i.e. with few atoms per unit cell) for the compositions $x = 0.25, 0.5, 0.75$. The main focus in the present study is on the determination of the disorder present in this alloy. We deduce the bowing value first from a simple quadratic fit of the band-gap variation versus the alloy concentration. Secondly, the bowing is calculated following the approach of Zunger and co-workers [8]. The latter method allows us to analyse the physical origins of bowing. The chemical disorder is analysed in terms of charge-density transfer and is explained by the estimated ionicity variation.

The remainder of this paper is organized as follows. The computational details are given in section 2. Results are presented in section 3. Section 4 contains the conclusions.

2. Computational details

The ground-state properties of our system are computed by using the plane-wave (PW) pseudopotential scheme. The frozen-core approximation holds when the energies of the core electrons are much lower than the valence electron energies. In such a case, the overlap between the core and the valence charges is negligible and it is possible to separate the non-linear exchange–correlation term as follows: $\varepsilon_{xc}(n_c(r) + n_v(r)) \approx \varepsilon_{xc}(n_c(r)) + \varepsilon_{xc}(n_v(r))$, including the core part in the pseudopotential.

The case of zinc atoms is however more difficult to deal with, because the energy of the closed shell of 3d orbitals is quite close to the 4s and 4p electron energy and higher than the anion s band energy in the compounds considered here. This fact suggests the possibility of a failure of the frozen-core approximation: in the solid there is a core relaxation which is completely neglected in the pseudopotential picture. Furthermore, there is a large overlap between the core and the valence charges. In principle, one may consider also d electrons as valence electrons, but this would require the use of a very large PW basis set with the standard norm-conserving pseudopotential technique or of the more cumbersome ultrasoft-pseudopotential scheme [9]. The error associated with the core relaxation is almost unavoidable with PW, but it is possible to improve the transferability of the potential by following the von Barth and Car (VBC) recipe [10], in which they use the following analytical form:

$$v^{loc}(r) = \frac{-Z_v}{r}\,\mathrm{erf}(r\sqrt{\alpha_c}), \qquad v_l = (a_l + b_l r^2)\exp(-\alpha_l r^2), \tag{1}$$

and by minimizing the squared differences of pseudo-electron and all-electron wavefunctions for a number of electronic configurations [11].

It is possible to correct the large error due to the charge overlap by adopting the non-linear core-corrections (NLCC) scheme [11, 12]. The NLCC solution consists in including the total charge rather than just the valence in the dependence of the exchange–correlation term:

$$E_{xc} = \int \epsilon_{xc}(n_c(r) + n_v(r))(n_c(r) + n_v(r))\,\mathrm{d}r, \tag{2}$$

where n_c is the core charge calculated 'once for all' for the atomic configuration, and then added to the valence charge when needed. In our calculations, the core charge is parametrized as

$$n_c(r) = (a_{cc} + b_{cc}r^2)\mathrm{e}^{-\alpha_{cc}r^2} \tag{3}$$

which is easily computed both in direct and reciprocal space. This correction improves the results also for the magnesium pseudopotential; we describe the Se atoms in the VBC scheme.

We have calculated the structural properties of the two pure materials in the zinc-blende structure. The electron-gas exchange–correlation energy and potential used in our local density approximation (LDA) scheme are those determined by Ceperley–Alder quantum Monte Carlo simulations [13], in the Perdew–Zunger [14] parametrization. Our results are well converged using a kinetic energy cut-off of 15 Ryd and BZ sampling of ten special k-points [15] for the structures used.

3. Results and discussion

It is well known that energy gaps are systematically underestimated in *ab initio* calculations and that this is an intrinsic feature of density functional theory (DFT) with the DFT-LDA [16], DFT being a ground-state theory not suitable for describing excited-state properties, such as the energy gap. Other approaches based on quasi-particle description of electronic excitations in the quasi-particle approach, based on the Green function method, and in the GW approximation (G is the Green function, W is the screened Coulomb interaction) [18] have been developed in the last decade, and applied also to the case of II–VI semiconductors [17]. However, it is widely accepted that LDA electronic band structures are qualitatively in good agreement with experiments as regards the ordering of the energy levels and the shape of the bands.

ZnSe and MgSe are the basic constituents, corresponding to $x = 0, 1$ in the ternary $Zn_{1-x}Mg_xSe$ alloy. The calculation of the structural properties of such materials is straightforward within DFT. The comparison of our theoretical predictions with the experimental structural parameters and phase stability obtained in these simpler cases is a necessary step in determining the degree of accuracy that we can expect for the alloy. However, since calculations of the properties of pure materials have already been reported in the previous works of Saitta *et al* [6] using the same method and also the same code, there is no need to present an exhaustive study for the pure materials. Nevertheless, we refer the reader to the above-mentioned works for additional evidence regarding the electronic and structural properties of ZnSe and MgSe. Thus, our main goal remains that of investigating the electronic structure of the binary alloy $Zn_{1-x}Mg_xSe$ and identifying the origins of the bowing in the optical band gap.

3.1. Theoretical approaches to the alloy problem

Through density functional theory, it is possible to calculate the ground-state energy of a given microscopic configuration in a disordered system. This choice is however not of practical use: in the theoretical study of disordered alloys, one should consider several supercells containing thousands of atoms, in order to cope with disorder, and to take into account different configurations. For this reason, such a 'direct' approach has always been considered well beyond the achievable numerical power. The typical approaches to the study of alloys are based on approximations in which all the possible, inequivalent, microscopical configurations are averaged into an effective medium having the same crystal structure as the underlying lattice, in order to recover the translational symmetry.

The simplest of these historical approaches is the so-called VCA [19], in which the real, disordered, alloy is modelled with a crystalline solid of 'virtual' atoms which are given by an average, weighted by the composition, of the 'real' atoms, and whose chemical properties are intermediate between those of the pure constituents. A refinement of this method is the coherent potential approximation (CPA) [20], where the potential is modified with respect to VCA only at lattice sites; hence all the like atoms are separately considered equivalent and each is embedded in a uniform medium. These theories are all non-structural in the sense that they consider only the average occupations of lattice sites, retaining the topology, but removing all the information associated with the geometrical arrangements of atoms around such sites.

The range of validity of such approximations is limited to those properties that are associated with symmetry-preserving, uniform-volume changes, and that for typical semiconductors are simple functions of the composition, and depend only weakly on the local environment of the atoms. These theories are therefore inadequate for the study of properties, such as the vibrational or electronic properties, that in many cases strongly depend on the substitutional disorder; for these it is necessary to consider different approaches, more recently developed.

The condition of lattice matching, assumed up to now, is very well satisfied in some III–V semiconductor alloys such as $Ga_x Al_{1-x} As$. In the general case, however, the system at equilibrium does not have the ideal geometry of the lattice, but must be locally distorted from the ideal positions, in order to account for the different bond lengths of its constituents. In the case of a binary or pseudobinary alloy, the molar fractions of the pure constituents needed for the formation of the alloy with a given composition, x, are uniquely determined by it.

3.2. Projected density of states and chemical bonds

In the present work, we model the alloys at some selected compositions with ordered structures described in terms of periodically repeated supercells. This can be done with little effort (i.e. with few atoms per unit cell) for the compositions $x = 0.25, 0.5, 0.75$. For the structures considered, we perform a structural optimization minimizing the total energy with respect to the cell parameters and to the atomic positions. For the compositions $x = 0.25$ and 0.75 the simplest structure is an eight-atom simple cubic cell (luzonite): the cations with the lower concentration form a regular simple cubic lattice. For the composition $x = 0.5$, the smallest ordered structure is a four-atom tetragonal cell, corresponding to the (ZnSe)(MgSe) (001) or—equivalently—(110) superlattice. This structure is strongly anisotropic, and thus not very suitable for simulating random alloys which are macroscopically isotropic. We consider therefore also the chalcopyrite structure, which has a 16-atom tetragonal cell. The corresponding structures are presented in figure 1.

Using the optimized structures, we perform density-of-states (DOS) calculations. With the various technical parameters used in the calculations (kinetic energy cut-off, ten special points for self-consistency, points for the band-structure non-self-consistent calculations), we have obtained a DOS with a numerical resolution of 0.1 eV. The uncertainty being much larger than the numerical one arises from the use of the DFT-LDA, and from the non-relativistic approach. We report in figure 2, the DOS for the average concentration (50% Mg). The figure corresponds to relaxed chalcopyrite structure. In the same plot, we report the projected DOS calculated with a factor of proportionality corresponding to the concentrations of the species considered. The high peaks at low and high energies corresponds mainly to s-like Se states; the contributions arising from the Zn and Mg species are rather weaker and more or less the same.
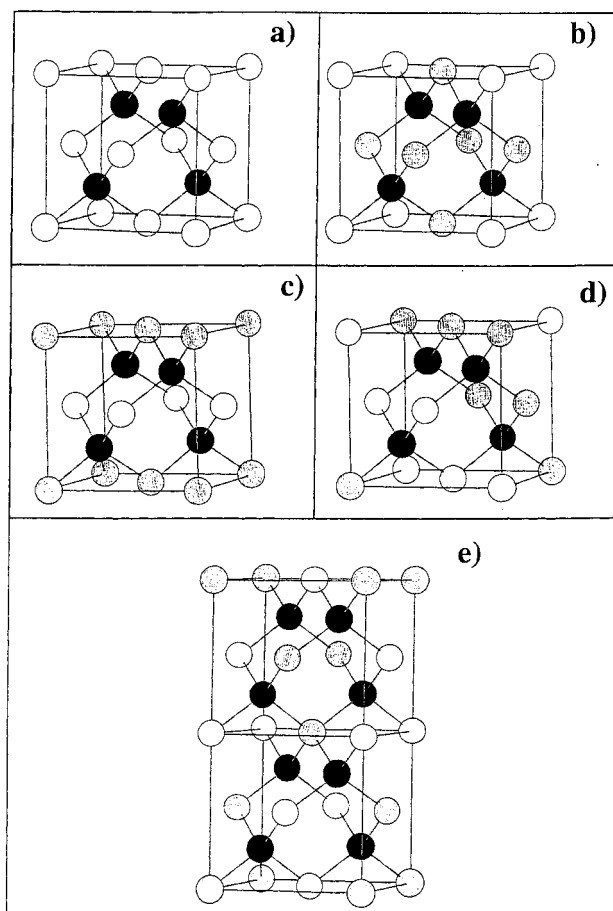
Figure 1. Selected ordered pseudobinary structures with cationic disorder: the zinc-blende structure (*a*) for $x = 0, 1$; luzonite (*b*) for $x = 0.25, 0.75$; the (001) SL (*c*), (111) SL (*d*), and chalcopyrite structure (*e*) for $x = 0.5$.

In figure 3, we display the valence electronic charge-density differences between the pure compounds and the chemical bond for the selected compositions. In this figure, we can see the negative values of the difference of the charges of ZnSe (bulk) and Zn–Se bonds at the intermediate concentrations ($x = 0.25, 0.50$, and 0.75). The situation is obviously the inverse when we consider the difference in charge between the pure MgSe and the Mg–Se bonds at the same intermediate concentrations, due to the supposed higher ionicity of MgSe. Moreover, we underline the presence of a pronounced positive part for the first case (Zn–Se differences) and the negative charges for the second one (Mg–Se differences), especially at $x = 0.50$. At this concentration the compensation of charges is most important, as is confirmed from the ionicity calculations presented in figure 4. The calculations of the ionicity parameter have been carried out on the basis of our ionicity model [21] which gives values of the same order of magnitude as those of Garcia and Cohen [22] for the pure compounds (ZnSe and MgSe). These values are roughly 0.63 and 0.79 respectively for ZnSe and MgSe, although the reported ones for the bonds upon alloying are arbitrarily higher. This essentially shows that for the intermediate concentration the alloy exhibits somewhat more ionic character than the pure compounds.
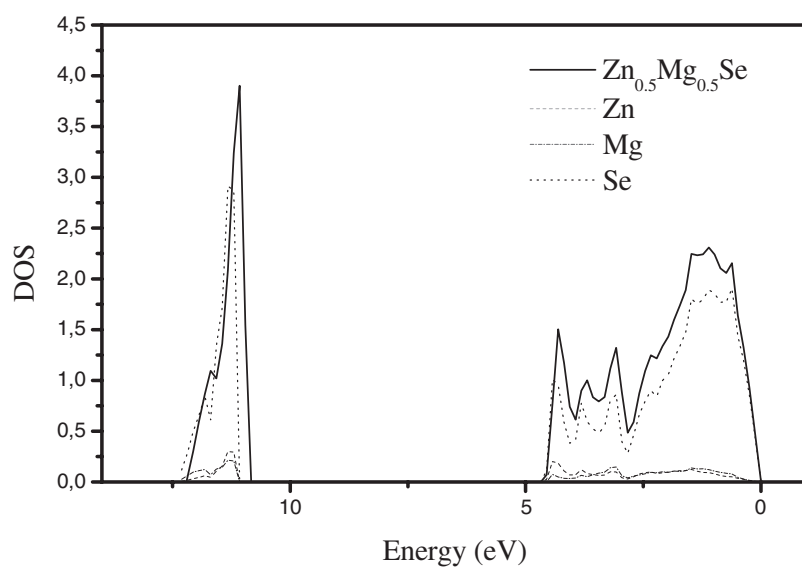
Figure 2. Projected and total DOS for (Zn, Mg)$_{0.5}$Se. The DOS are given in states per unit cell.
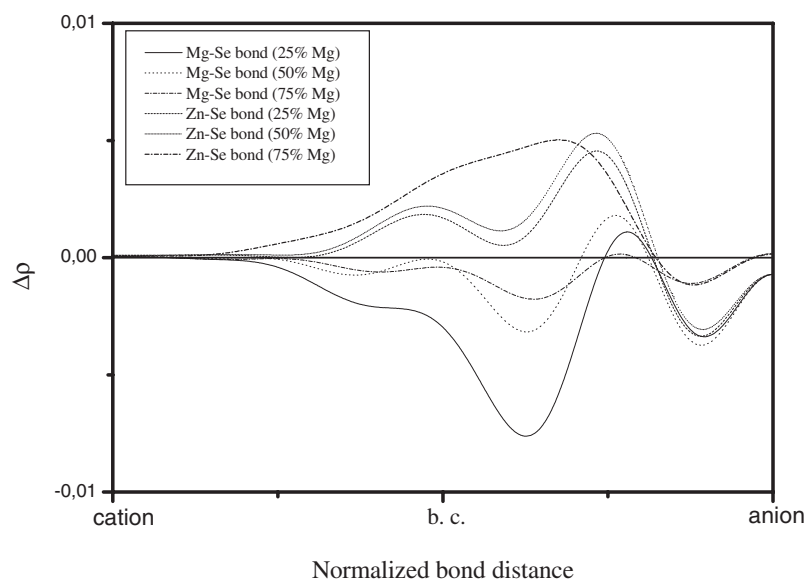

Figure 3. The valence charge-density difference between the pure compound and its bonds at an intermediate concentration of the alloy.

3.3. Optical bowing and its origins

In this work, we follow the approach of special quasi-random structures (SQS) [8], which are rather small supercells containing up to a few atoms, and yet are still representative of the alloy (figure 1). They are in fact constructed in such a way as to have short-range correlations as similar to those of the 'real' alloy as possible. This approach allows application of first-principles methods to the calculation of the optical properties of solid solutions.
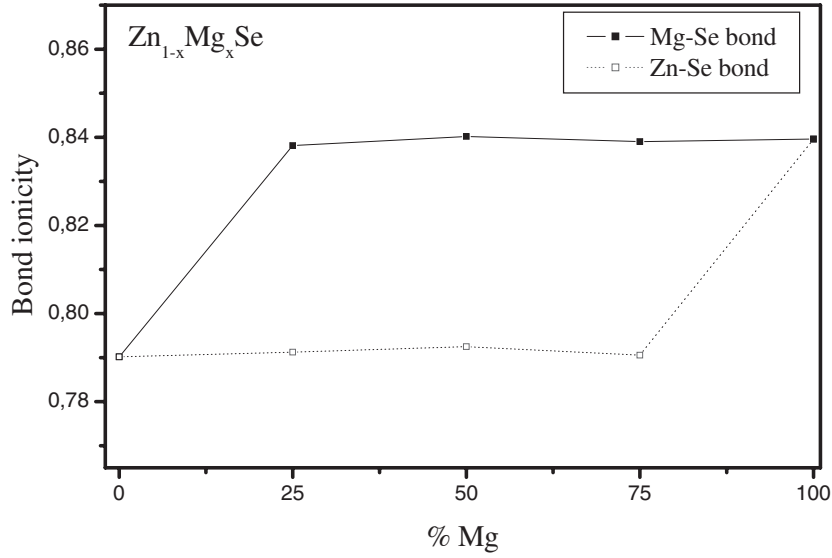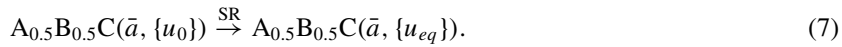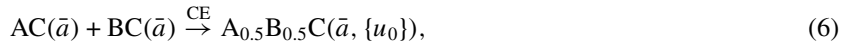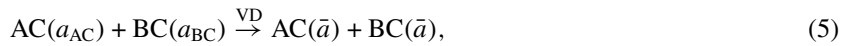
Figure 4. The ionicity of the bonds at different concentrations.

Describing alloys in terms of short-period supercells clearly introduces spurious correlations beyond a certain distance. However, for many physical properties, interactions between distant neighbours are generally much less important than those between close neighbours, and it will be shown that this condition is satisfactorily fulfilled for the electronic properties of $Zn_{1-x}Mg_xSe$.

To analyse the physical origins of bowing, we follow Bernard and Zunger [8] and decompose b into three components. The overall bowing value at $x = 0.5$ measures the change in band gap in the formal reaction

$$AC(a_{AC}) + BC(a_{BC}) \rightarrow A_{0.5}B_{0.5}C(\bar{a}, \{u_{eq}\}) \qquad (4)$$
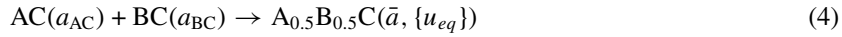
where a_{AC} and a_{BC} are the equilibrium lattice constants of the binary constituents AC and BC, respectively; $\bar{a}$ is the alloy equilibrium lattice constant, and $\{u_{eq}\}$ denotes the equilibrium values of the cell internal structural parameters of the alloy. We now decompose reaction (4) into three steps:

$$AC(a_{AC}) + BC(a_{BC}) \overset{VD}{\rightarrow} AC(\bar{a}) + BC(\bar{a}), \qquad (5)$$

$$AC(\bar{a}) + BC(\bar{a}) \overset{CE}{\rightarrow} A_{0.5}B_{0.5}C(\bar{a}, \{u_0\}), \qquad (6)$$

$$A_{0.5}B_{0.5}C(\bar{a}, \{u_0\}) \overset{SR}{\rightarrow} A_{0.5}B_{0.5}C(\bar{a}, \{u_{eq}\}). \qquad (7)$$

The first step measures the 'volume deformation' (VD) contribution b_{VD}, the second the 'charge-exchange' (CE) contribution b_{CE} due to formation of the unrelaxed ($u = u_0$) alloy from AC + BC already prepared at the final lattice constant $\bar{a}$, and the final step measures changes due to 'structural relaxation' (SR), i.e., $u_0 \rightarrow u_{eq}$. The total bowing b is

$$b = b_{VD} + b_{CE} + b_{SR}. \qquad (8)$$

We decompose the optical bowing value (after crystal-field averaging) of $Zn_{1-x}Mg_xSe$ into VD, CE, and SR pieces. The calculated average lattice parameter is very close to Vegard's prediction. The bowing components are reported in table 1 together with the bowing found
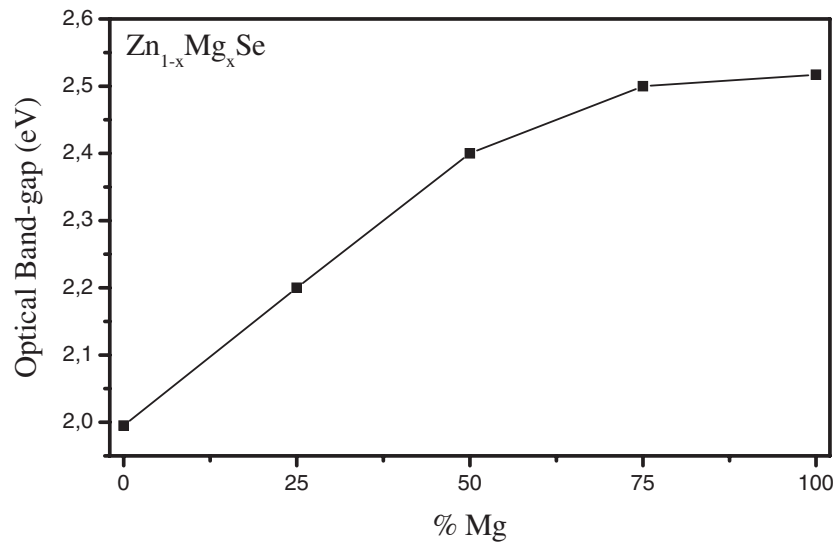
Figure 5. The energy gap of (Zn, Mg) Se pseudobinary alloy as function of the composition.

Table 1. Decomposition of the optical bowing into VD, CE, and SR contributions (all values are in eV).

	b_{VD}	b_{CE}	b_{SR}	b
Present work	2.0702	−1.4594	−1.1768	−0.56
Present work from equation (9)				−0.544
VCA				1.711 [4]
Experiment				0.47 [23]

from the non-linear variation of the band gap versus concentration. The latter is plotted in figure 5 and shows the following variation:

$$E_g(x) = 1.9856 + 1.081x - 0.544x^2. \tag{9}$$

The quadratic parameter reflects the disorder effects, i.e. the bowing, which is in excellent agreement with the value found from the approach of Zunger and co-workers. The comparison with the previous VCA calculation and/or with experiment [23] gives however less agreement; nevertheless, the order of magnitude is small, which confirms a weak general bowing. From the method of Zunger and co-workers, we can extract the different contributions to the disorder. Table 1 shows a strong bowing contribution from the volume deformation effects with a value of 2.07 and a second contribution which comes from the charge-transfer effects (−1.46), which is more important than the disorder due to the relaxation effects. The lattice difference between the two pure compounds (5.59 Å for ZnSe and 5.99 Å for MgSe) contributes fundamentally to the deformation effects and the relaxation ones. The ionicity differences between the constituents, as shown in the previous paragraph, mainly cause charge-transfer effects.

4. Conclusions

Self-consistent density functional calculations based on a direct supercell approach are reported for $Zn_{1-x}Mg_xSe$ pseudobinary alloy. We have shown that a disordered solution can be

mimicked by using rather small supercells that reproduce the alloy as well as is possible. Our calculations provide the equilibrium structural properties of the alloy, the projected DOS, as well as the bonding behaviour for the alloy compositions. The bowing is found to be small and mainly caused by the volume deformation effects, followed by the chemical charge-transfer contribution, and then by the relaxation contribution as well. It is worth noting that even if the total bowing is found to be small, there may be a range of concentrations where a larger band gap can be exhibited when the lattice constant takes an intermediate value.

Acknowledgment

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