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Modeling of Chlorine Related Defects and Complexes in ZnMgSe

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ABSTRACT

We have used the *ab-initio* full potential LMTO method to model native defects and chlorine-impurity-related defects in ZnSe and $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$. Our results show that there is a strong tendency for formation of a defect complex between a chlorine impurity at the Se site and a vacancy at the neighboring Zn site. The formation energies of this complex and other chlorine related defects decrease in the presence of magnesium. However, the maximum achievable electron concentration in the presence of magnesium is lower because of the increase in the band gap.

INTRODUCTION

The wide-band-gap semiconductors ZnSe and its alloy $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$ are of great interest because of their application to blue-green light emitting diodes and laser devices. Several calculations¹⁻⁹ have been developed on the role of defects and defects complexes in ZnSe with n-type and p-type doping. Compared to ZnSe, $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$ has a higher band gap, which may give an improved optical and electrical confinement. By increasing the Mg content, the band gap of $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$ can be modified from 2.7eV for pure ZnSe to approximately 3.7eV for MgSe. Chlorine is the most successful n-type dopant to ZnSe, it is certainly considered as a candidate for n-type doping in ZnMgSe. Therefore, we modeled chlorine-related defects in ZnSe and $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$ alloy, and focused on the changes in the electronic properties with increase of Mg content.

COMPUTATIONAL APPROACH

FP-LMTO Method

For this calculation, we used an *ab-initio* full-potential linear muffin-tin-orbital method (FP-LMTO) including a force routine¹⁰ with the electron exchange-correlation treated in the local-density approximation (LDA). Detailed information about this method can be found in reference 13. Zinc 3d-electrons were treated as valence electrons, while Se 3d-electrons were included in the core. For the charged defects, a neutralizing uniform background charge was used to avoid long-range Coulomb interactions. Different concentrations of Mg were achieved by substituting one, two, or three Zn atoms with Mg atoms in a 32-atom supercell. Therefore, three ZnMgSe

alloys: $\text{Zn}_{0.94}\text{Mg}_{0.06}\text{Se}$, $\text{Zn}_{0.87}\text{Mg}_{0.13}\text{Se}$, $\text{Zn}_{0.81}\text{Mg}_{0.19}\text{Se}$ were considered. Lattice relaxation around the defects has been shown to be significant for ZnSe in previous works^{3,7,8,13}. It is even more important for the present calculation since the differences on the formation energies of the same defect in $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$ with different Mg content is very small. In our calculation, lattice relaxation around defects was calculated using Hellman-Feynman¹¹ forces.

In order to minimize numerical discrepancy, all calculations for a material have been performed using supercells with identical symmetry and the same k-points in the Brillouin zone. In this approach, most of the numerical errors associated with limited sampling of the Brillouin zone cancel each other. Tests were performed to insure that the size of the supercell and number of k-points do not affect final results.

Formation Energy of Defects

In the calculation of the formation energy, we compare the total energy for a supercell with a defect and the total energy for a corresponding perfect supercell. Formation energy E^f of the defect of type D^n with charge n is calculated as:

$$E^f = \text{TE}_{\text{Defect}} + \mu_{\text{defect}} + n\mu_e - \text{TE}_{\text{Perfect}} \quad (1)$$

Where $\text{TE}_{\text{Defect}}$ is the total energy of a supercell with defect, $\text{TE}_{\text{Perfect}}$ is the total energy of a corresponding perfect supercell, μ_e is the electron chemical potential (Fermi level) measured with respect to the valence-band maximum. μ_{defect} is the change in chemical potential due to removing or substituting atoms necessary to form a defect; it can be expressed as:

$$\mu_{\text{defect}} = \begin{cases} \mu_{\text{Se}} - \mu_{\text{Cl}} & \text{for Cl substituted for Se} \\ \mu_{\text{ZnSe}} - \mu_{\text{Cl}} & \text{for Cl substituted for Se with Zn vacancy as neighbor} \\ \mu_{\text{Zn}} & \text{for Zinc vacancy} \end{cases}$$

Where μ_{se} , μ_{zn} , μ_{cl} and μ_{znse} are the chemical potentials of Se atom, Zn atom, Cl atom and ZnSe pair in ZnSe. In turn, μ_{se} , μ_{zn} and μ_{znse} can be obtained as:

$$\mu_{\text{se}} = \mu_{\text{se}}^{\text{bulk}} - \lambda \Delta H, \quad \mu_{\text{zn}} = \mu_{\text{zn}}^{\text{bulk}} - (1-\lambda) \Delta H, \quad \mu_{\text{se}} + \mu_{\text{zn}} = \mu_{\text{znse}} = \mu_{\text{se}}^{\text{bulk}} + \mu_{\text{zn}}^{\text{bulk}} - \Delta H$$

Where ΔH is the heat of formation of ZnSe, λ varies from 0 to 1, $\lambda = 0$ for Zn-rich and $\lambda = 1$ for Se-rich. For the chemical potential of chlorine atom (μ_{cl}), we used a total energy of a single chlorine atom. This calculation uses a different symmetry, and in addition the LDA with the Ceperly-Alder¹⁴ exchange-correlation function parameterized by Perdew and Zunger¹⁵ (as used for the rest of the calculation) is not very accurate for isolated atoms; therefore there might be a significant computational error associated with μ_{cl} . However, this error can only affect absolute values, while the differences between formation energies as presented in Table 1 are still reliable.

RESULTS AND DISCUSSION

For this paper, we calculated formation energies for chlorine substituting for selenium (neutral Cl_{se}^0 and single positive charge $\text{Cl}_{\text{se}}^{1+}$ states), zinc vacancy (double negative charge V_{zn}^{2-} state) and $(\text{Cl}_{\text{se}}-V_{\text{zn}})^{1-}$ complex in pure ZnSe and in $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$ with three different Mg contents.

First the equilibrium lattice constants for ZnSe and ZnMgSe alloys with different Mg content were calculated. We obtained the following lattice constants: 5.636, 5.646, 5.662, 5.683 Å

for pure ZnSe, $Zn_{0.94}Mg_{0.06}Se$, $Zn_{0.87}Mg_{0.13}Se$ and $Zn_{0.81}Mg_{0.19}Se$ respectively. These numbers are in good agreement with experiment values when they are available and/or with values obtained by using Vegard's law.

We found that without chlorine additives, magnesium atoms do not have preferential positions in ZnMgSe alloy. However, in the presence of chlorine dopant, magnesium atoms tend to be located as chlorine's nearest neighbors. For $Zn_{0.81}Mg_{0.19}Se$, when the three Mg atoms are located as chlorine's nearest neighbors, the total energy of the 32-atom supercell is 0.57eV lower than when the three Mg atoms are the third nearest neighbors (still in Zn site). Therefore, for the results in Table 1, Mg atoms are all in the positions as the nearest neighbors of chlorine atoms.

Defect Formation Energies in ZnSe and ZnMgSe

The calculated formation energies are showed in Table 1, and the formation energy of defects vs. μ_e are showed in Fig1-4.

Our result shows that the formation energies for $(Cl_{se})^0$, $(Cl_{se})^{1+}$ and $(Cl_{se}-V_{zn})^{1-}$ defects decrease with Mg's presence if we fix μ_e . The formation energy of the doping defect $(Cl_{se})^{1+}$ is 0.61eV lower for $Zn_{0.81}Mg_{0.19}Se$ than for pure ZnSe, which is favorable for n-type doping. However, the formation energy of the main compensating complex is also 0.41eV lower, and that would lead to stronger compensation. From Fig. 1-4, we can see that the Fermi level will be pinned at 1.31eV, 1.36eV, 1.39eV, 1.41eV for chlorine doping in ZnSe, $Zn_{0.94}Mg_{0.06}Se$, $Zn_{0.87}Mg_{0.13}Se$ and $Zn_{0.81}Mg_{0.19}Se$ respectively due to the compensation of $(Cl_{se}-V_{zn})^{1-}$. The maximum achievable μ_e increases 0.10eV from 1.31eV for pure ZnSe to 1.41eV for $Zn_{0.81}Mg_{0.19}Se$, which makes it favorable for the n-doping, providing that the band gap is the same for the two materials.

Table 1 Defect formation energy in ZnSe and ZnMgSe, All the energies given are in eV.

| | Defect | Formation Energy |
|--|-------------------------|--------------------------------------|
| pure ZnSe (32 atom supercell) | $(Cl_{se})^0$ | $1.36 + \lambda * \Delta H$ |
| | $(Cl_{se})^{1+}$ | $-0.86 + \lambda * \Delta H + \mu_e$ |
| | $(Cl_{se}-V_{zn})^{1-}$ | $1.76 - \mu_e$ |
| | $(V_{zn})^{2-}$ | $4.09 - 2\mu_e$ |
| $Zn_{0.94}Mg_{0.06}Se$ (one Mg atom in 32 atom supercell) | $(Cl_{se})^0$ | $1.22 + \lambda * \Delta H$ |
| | $(Cl_{se})^{1+}$ | $-1.09 + \lambda * \Delta H + \mu_e$ |
| | $(Cl_{se}-V_{zn})^{1-}$ | $1.63 - \mu_e$ |
| | $(V_{zn})^{2-}$ | $4.18 - 2\mu_e$ |
| $Zn_{0.87}Mg_{0.13}Se$ (two Mg atoms in 32 atom supercell) | $(Cl_{se})^0$ | $1.02 + \lambda * \Delta H$ |
| | $(Cl_{se})^{1+}$ | $-1.30 + \lambda * \Delta H + \mu_e$ |
| | $(Cl_{se}-V_{zn})^{1-}$ | $1.48 - \mu_e$ |
| | $(V_{zn})^{2-}$ | $4.28 - 2\mu_e$ |
| $Zn_{0.81}Mg_{0.19}Se$ (three Mg atoms in 32 atom supercell) | $(Cl_{se})^0$ | $0.91 + \lambda * \Delta H$ |
| | $(Cl_{se})^{1+}$ | $-1.47 + \lambda * \Delta H + \mu_e$ |
| | $(Cl_{se}-V_{zn})^{1-}$ | $1.35 - \mu_e$ |
| | $(V_{zn})^{2-}$ | $4.37 - 2\mu_e$ |

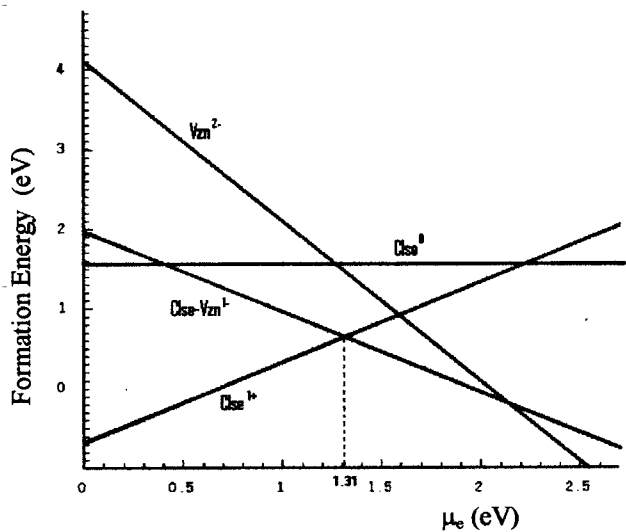


Fig. 1. Formation Energies of defects in pure ZnSe under Zn-rich conditions.

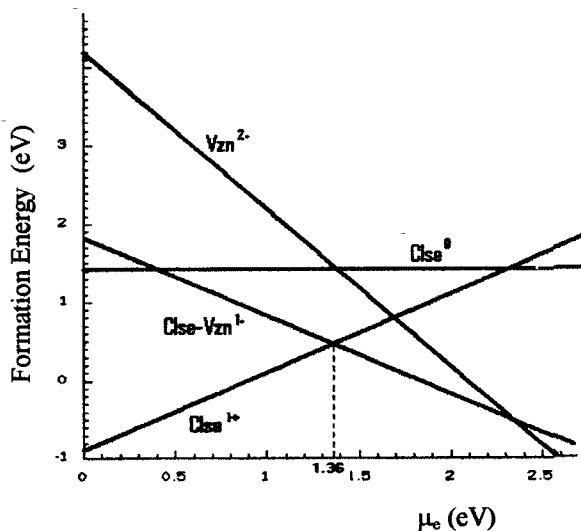


Fig. 2. Formation Energies of defects in $Zn_{0.94}Mg_{0.06}Se$ under Zn-rich conditions.

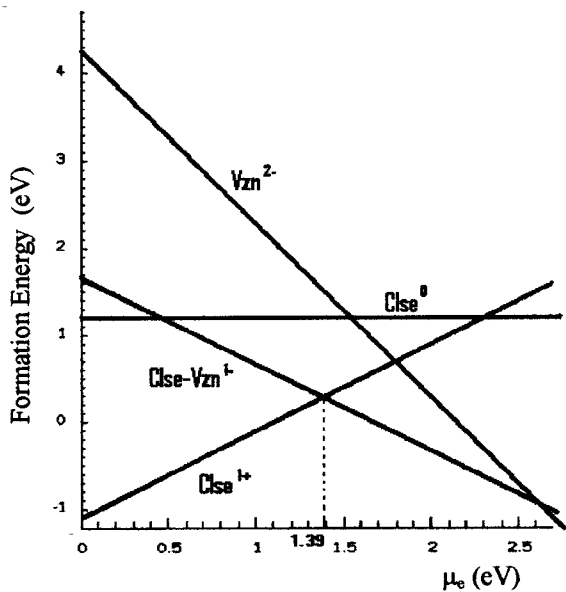


Fig. 3. Formation Energies of defects in $Zn_{0.87}Mg_{0.13}Se$ under Zn-rich conditions.

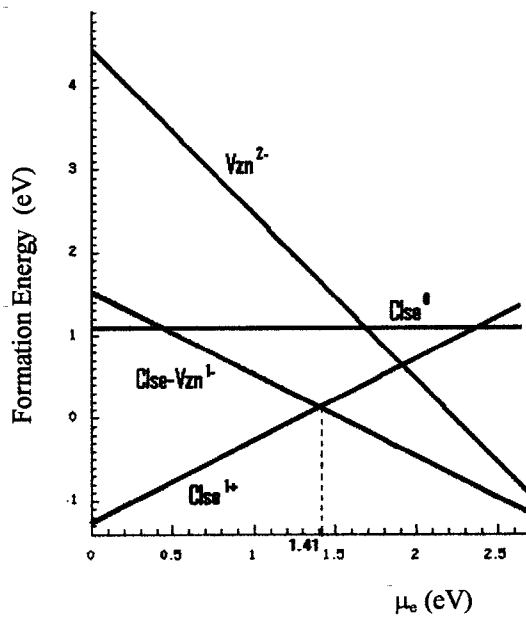


Fig. 4. Formation Energies of defects in $Zn_{0.81}Mg_{0.19}Se$ under Zn-rich conditions.

Discussion

In order to estimate the maximum electron concentration, one can find the electron concentration as:

$$n = N_c \exp[-(E_{\text{gap}} - \mu_e)/k_B T] \quad (2)$$

For $\text{Zn}_x\text{Mg}_{1-x}\text{Se}$ with different Mg content, we can assume the N_c are the same, and E_{gap} has linear dependence with x .

$$E_{\text{gap}} = x E_{\text{gap}}^{\text{ZnSe}} + (1-x) E_{\text{gap}}^{\text{MgSe}} \quad (3)$$

Denoting maximum electron concentrations in pure ZnSe, $\text{Zn}_{0.94}\text{Mg}_{0.06}\text{Se}$, $\text{Zn}_{0.87}\text{Mg}_{0.13}\text{Se}$, and $\text{Zn}_{0.81}\text{Mg}_{0.19}\text{Se}$ as n_0 , n_1 , n_2 , and n_3 respectively, one can calculate the ratios between them by substituting the pinned μ_e from Fig. 1-4 into equation (2), this gives:

$$n_0 / n_1 = 1.3 \quad n_0 / n_2 = 4.1 \quad n_0 / n_3 = 18$$

on choosing $T=300\text{K}$, $E_{\text{gap}}^{\text{ZnSe}} = 2.67\text{eV}$, $E_{\text{gap}}^{\text{MgSe}} = 3.60\text{eV}$

Comparisons with the experimental result by S. O. Ferreira *et al*¹² are shown on Fig. 5. (assuming the n_0 are the same for both cases). It can be seen that, our prediction at the maximum electron concentration is lower than the experiment value, but reproduce the tendency for the change of electron concentration in ZnMgSe with Mg content. The reason why the calculated concentration is lower than the experiment value can be easily understood: In our model, the content ratio between chlorine and magnesium is 1:1 to 1:3, however, in reality, that ratio is much smaller (on the order of 1:1000 for chlorine concentration around $10^{18}/\text{cm}^{-3}$ and Mg content around 10%). As our result showed, magnesium atoms and chlorine atoms tend to be neighbors to each other. Therefore in reality, chlorine atoms tend to stay in a mg-rich region, and should have more magnesium atoms as its neighbors, which is in favor to lower the formation energy of $(\text{Cl}_{\text{Se}})^{1+}$ and correspondingly increasing the electron concentration.

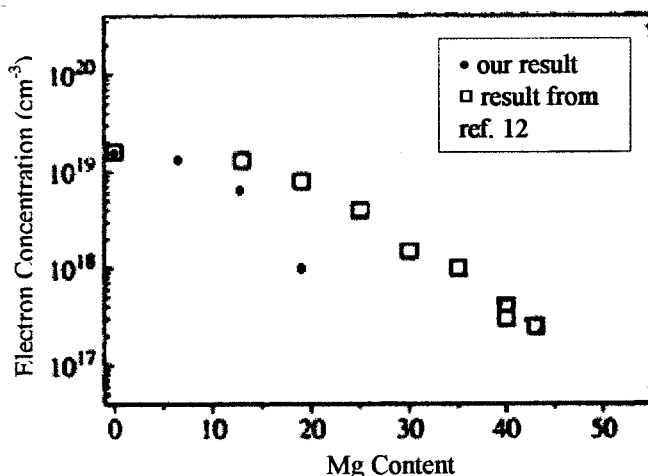


Fig. 5. Maximum achievable electron concentration as a function of Mg content in the ZnMgSe alloy.

CONCLUSION

Formation energies for the chlorine-substituting-for-selenium defect and the chlorine-substituting-for-selenium with neighboring zinc-vacancy defect complex decrease with increase of Mg content for the same μ_e . The maximum achievable μ_e goes up with the increase of Mg concentration in ZnMgSe; however, the increase in band gap is larger, and this explains the experimental result that maximum electron concentration decreases with higher concentration of Mg.

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