Electronic structure calculations for ZnS_xSe_{1-x}

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Abstract

Energy band gaps and electron effective mass as well as their composition dependence are the most critical parameters for band structure calculations of semiconductor alloys. Therefore, an accurate knowledge of these parameters is very important. Unfortunately, there is a limited experimental and theoretical information in the literature regarding the electronic band parameters for zinc blende ZnS_xSe_{1-x}. This has incited us to carry out such calculations. For this purpose, we have used the empirical pseudo potential method within the Virtual Crystal Approximation and the effect of compositional disorder is treated as an effective potential. The band gap variation versus sulfur concentration x shows two different behaviors: clear diminution of gap energy for low concentrations, and quasi-linear behavior with a small bowing for large values of x. Furthermore, the calculated effective mass shows that the disorder is not only compositional but also structural.
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1. Introduction

During the last decades, II–VI wide gap semiconductors have been extensively investigated since they span a large spectral range that cannot be covered by IV–IV and III–V semiconductors (SC). However, some problems such as doping limits and croissance defects have restrain the use of these compounds in devices. Owing to the progress achieved in crystal growth, a particular attention has been given to II–VI SC due to their great excitonic effects and magnetic aspect [1]. ZnSe and ZnS are especially important for blue light emitting devices [2]. The alloy ZnS_xSe_{1-x} is interesting because several optoelectronic devices that cover a wide spectral region (2.80 eV for ZnSe to 3.67 eV for ZnS) can be designed. For example, ZnS_xSe_{1-x} having $x \geq 0.2$ is used as cladding layer [3] whereas ZnS_xSe_{1-x} with $x = 0.06$ is used as active layer in blue laser diode [1]. To provide some useful information for the design and the application of devices based on wide gap II–VI SC, we have computed the electronic band structure of ZnSSe and some of other electronic properties versus the sulfur composition x.

2. Calculations

To compute the band structure of the zinc blende alloy, we employed the empirical pseudopotential method (EPM) using the virtual crystal approximation (VCA) with and without taking into account the effect of the alloy disorder. The crystal potential in the reciprocal lattice can be written as:

$$V(r) = \sum_G V(G)S(G)e^{iG.r}$$

where $S(G)$ the structure factors. The pseudopotential form factors $V(G)$ are determined by fitting the calculated band structure to experimental data using a non-linear procedure. For zinc blende compounds, only six pseudo-potential form factors are allowed to be non-zero [4,5]. Once the potential is determined, we solve the Schrödinger equation.

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This treatment can be extended to ternary alloys through the use of the VCA. The symmetric and antisymmetric form factors for ZnSSe can be expressed as:

$$V_{ZnSSe}^{S,A}(G) = (1-x)V_{ZnSe}^{S,A} + xV_{ZnS}^{S,A}. \qquad (1)$$

The variation of the lattice constant with composition x is assumed to follow the Vegard's law:

$$a_{ZnSSe} = (1-x)a_{ZnSe} + xa_{ZnS}.$$

It is well known that the VCA does not take into account the effect of the compositional disorder so the bowing factor may deviate from experiments [6]. To reproduce the experience, we have added to the VCA a non-periodic potential. The symmetric and antisymmetric form factors in the so-called improved VCA are expressed as:

$$V_{ZnSSe}^{S,A}(G) = xV_{ZnS}^{S,A} + (1-x)V_{ZnS}^{S,A}$$
$$- p[x(1-x)]^{1/2}\left(V_{ZnS}^{S,A} - V_{ZnSe}^{S,A}\right) \qquad (2)$$

where p is a parameter which simulates the disorder effect. Numerical calculations have been done along the principal directions of symmetry of the Brillouin zone. The matrix dimensions of the eigen value problem are (136×136).

3. Results and discussion

3.1. Band gap energy

We have adjusted the pseudopotential form factors to fit the experimental band gap energies of ZnSe and ZnS. The optimization leads to final adjusted pseudopotential form factors of parent compounds. The values of these parameters (in Ryd) and lattice constants (in nm) are given in Table 1.

Table 2 lists the calculated band gap energies for the zinc blende compounds at the high symmetry points Γ, X and L in the Brillouin zone. Some available results from the literature are also reported in this table. As it can be seen, our results agree well with those of Refs. [1,7–9].

Using Eq. (1), the band gap energies E_g^Γ, E_g^X and E_g^L are calculated for the ternary $ZnS_x Se_{1-x}$ and plotted in Fig. 1 versus the sulfur concentration. The results show that there is a crossover between E_g^X and E_g^L at $x \sim 0.5$. However, is lower than E_g^X and E_g^L over the composition range 0 up to 1. Therefore, the band gap of the studied alloy is direct within the whole range of the x composition. We note a clear decrease of the band gap energy at low sulfur concentration x

Table 2
Band gap energies of ZnSe and ZnS at Γ, X and L points

Material	E_g^Γ (eV)	E_g^X (eV)	E_g^L (eV)	E_X^X (eV)	E_L^L (eV)
ZnSe	2.80[a]	4.49[a]	3.92[a]	5.77[a]	4.50[a]
	2.80[b,c,d]	4.49[b]	3.92[b]	4.73[b]	3.83[b]
ZnS	3.67[a]	5.23[a]	5.22[e]	6.48[a]	5.70[a]
	3.67[b]	5.23[b]	5.22[b]	5.67[b]	5.61[b]

[a] This work.
[b] Ref. [1].
[c] Ref. [7].
[d] Ref. [8].
[e] Ref. [9].

and an increase at high values of x. Polynomial approximations are obtained for the energy gap as a functions of alloy composition at Γ, X and L points. The best fits are:

$$E_g^\Gamma = 2.78 - 2.10x + 7.54x^2 - 4.57x^3$$

$$E_g^X = 4.42 - 3.00x + 3.92x^2$$

$$E_g^L = 3.93 - 3.78x + 10.17x^2 - 5.09x^3$$

This can be written according to the form:

$$E_g(x) = (1-x)E_g(ZnSe) + xE_g(ZnS) - bx(1-x).$$

Since the ZnSSe alloy is a direct gap, our interest will be focused on Γ point. It appears clearly that the bowing parameter of the curve depends of the alloy concentration. To reproduce the experimental bowing at $x = 0.5$ ($b = 0.63$ eV) [10], we introduce the compositional disorder p. Fig. 2 illustrates the band gap energy versus x concentration with disorder ($p = 0.05$) and without disorder. The fit is:

$$E_g^\Gamma = 2.78 - 2.10x + 7.54x^2 - 4.57x^3$$

We note that the bowing parameter b depends strongly on the alloy composition x:

$$b(x) = -4.426x + 1.134.$$

The decrease of energy at low concentrations is useful for laser applications. It can be explained by the fact that at low values of x, the compositional disorder have not yet influenced the ZnSe. But differences in electronegativity and in radius between sulfur and selenium entrain electrostatic forces. Then, a microscopic arrangement of atoms tends to preserve lengths and angles. This arrangement of atoms gives an additional contribution to the atomic potential. Furthermore, the dependence of band energies

Table 1
Pseudopotential form factors and lattice constants for zinc blende ZnSe and ZnS

Compound	V^S (3) (Ryd)	V^S (8) (Ryd)	V^S (11) (Ryd)	V^a (3) (Ryd)	V^a (4) (Ryd)	V^a (11) (Ryd)	Lattice constant (nm)
ZnSe	−0.383536	0.021660	0.094511	−0.140184	0.062	−0.035802	0.56686[a]
ZnS	−0.226152	0.03	0.061513	0.223987	0.14	0.04	0.54093[a]

[a] Ref. [7].