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First-principles study of structural and electronic properties of ZnSe with wurtzite structure

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Abstract

Using Density Functional Theory (DFT) and Local Spin Density Approximation (LSDA) the structural and electronic properties of pure ZnSe wurtzite compound were theoretically investigated. The Hubbard U semiempirical correction has also been used to improve the underestimated DFT calculated band gap. From the DFT+LSDA+U method obtained that the wide of band gap is 2.7 eV and this result is closer to the available experimental results. Current studies reveal that the maximum of valence band and the minimum of conduction band located at the Γ (0, 0, 0) symmetry point on the Brillouin zone. Accurate investigation of the electronic structure of studied material is helpful for the technical applications.

Keywords. ZnSe; LSDA+U; structural; electronic properties.

1. Introduction

II–VI Zn based semiconductor compounds have revealed their potential for technical application according to their wide band gap of 2.70 eV [1]. ZnSe is ideally appropriate for fabrication of photodetectors, CO_2 laser focusing lenses, sensors, solar cells, and other photovoltaic applications [1, 2]. This material can be applied for the production of optoelectronic devices such as light emitters and detectors [3-5].

Investigations show that, numerous research works devoted investigation of structural and electronic properties of defected zinc-blende ZnSe systems [6-14]. However, very few research works reported the structural and electronic of ZnSe hexagonal structure.

In present paper all studies are reported for wurtzite ZnSe material. This work based on the DFT-LSDA and LSDA+U, detailed theoretical studies on the structural and electronic properties for pure ZnSe compound are provided. From LSDA+U method obtained that the calculated energy band gap of ZnSe (2.7 eV) is closer to the known experimental results. Current studies reveal that in ambient conditions both the maximum of valence band and the minimum of conduction band located at the Γ (0, 0, 0) symmetry point on the Brillouin zone.

This paper is organized as follows: in the next section described the detail of the simulation method used for ab initio calculations, and then structural and electronic properties of pure compound are given. At last, the paper is concluded with a summary.

2. Investigation method

The calculations were carried out for the of ZnSe by Density Functional Theory (DFT) [15] within Local Spin Density Approximation (LSDA) [16] and Hubbard U method implemented Atomistix ToolKit code. The Hubbard *U* corrections taken 4.5 *eV* for Zn 4*d*- and 3.5 *eV* for Se 4*p*-states. The interactions between the electrons and ions, and exchange correlation were described by the Fritz-Haber-Institute (FHI) ion pseudopotentials [17] and the Perdew Zunger (PZ) functional [18], respec-

tively. The Kohn-Sham wave functions [19] expanded in a linear combination of atomic orbitals with a kinetic energy cutoff of 75 Ha. The reciprocal space integration was performed with 7×7×7 Monkhorst-Pack [20] *k*-point sampling. The 12 electrons for Zn [Ar] $+3d^{10}4s^2$ and 6 electrons for Se [Ar] $+4s^24p^4$ treated as the valence electrons in current simulations. When calculate structural and electronic properties for pure compound, the primitive cell of ZnSe wurtzite containing 2 Zn and 2 Se atoms and the atomic positions are optimized until the force and stress on each atom converges to less than 0.001 *eV/Å* and 0.001 $eV/Å^3$, respectively.

3. Results and discussions

3.1 Structural properties

The investigated compound ZnSe crystallizes in the wurtzite structure, a hexagonal analog of zinc blende lattice, with a space group $P6_3mc$ with two formula units per unit cell. In this structure each Zn atom is tetrahedrally coordinated with four other Se atoms and the atomic positions for zinc are (0, 0, 0) and (1/3, 2/3, 0.5), for selenium are (0, 0, 0.3408) and (1/3, 2/3, 0.8408) [21]. The Brillouin zone and the crystal structure of ZnSe with wurtzite structure is given in Figure 1.

The first-principles computed Zn-Se and Zn-Zn distances have been found equal to 2.39 and 3.9 Å, respectively. We get a structure with an average Zn-Se bond length of 2.39 Å and this value is in agreement with the reported results (theor.: 2.376 Å [12] and exp.: 2.20 Å [22]).

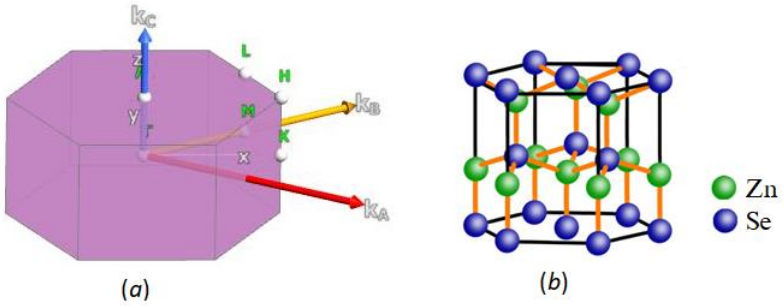

Figure 1. The Brillouin zone (*a*) and the crystal structure (*b*) of ZnSe with wurtzite structure.

In Refs. [23, 24] obtained lattice constants for ZnSe are a = 4.005 *Å*, c = 6.657 *Å* and a = 3.974 *Å*, c = 6.506 *Å* (internal parameter u = 0.375). The reported experimental results are a = 4.003 *Å*, c = 6.540 *Å* [25], and a=3.996 *Å*, c=6.55 *Å* [26].

The values of optimized structural parameters (3.904 *Å*, 6.424 *Å*, u=0.385 (LSDA) and 3.918 *Å*, 6.394 *Å*, u=0.385 (LSDA+U)) for pure ZnSe are presented in Table 1.

Table 1. Ab initio calculated lattice constants and other available values for ZnSe.

a (Å)	*c* (Å)	c/a	Refs.
3.904	6.424	1.645	LSDA
3.918	6.394	1.632	LSDA+U
4.005	6.657	1.66	Theor. [23]
3.974	6.506	1.637	Theor. [24]
4.003	6.540	1.634	Exper. [25]
3.996	6.55	1.639	Exper. [26]

As seen from Table 1, the obtained values of lattice parameters are difference from experimental dates, with 1.7% to 2.47% [25, 26].

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3.2 Electronic properties

Recent successes in Hubbard U correction enabled us to calculate accurate band structures for compounds. Ab initio calculated values of band gaps for ZnSe are given in Table 2. The known experimental measured and other theoretically obtained energy gaps values of ZnSe are included for comparison. The band structures and density of states for pure ZnSe are calculated and shown in Figures 2 and 3, respectively. Firstly, using the LSDA method carried out the band structure calculations and obtained that the values band gap is 1.57 eV, which is underestimated compared with the experimental results of 2.70 eV [27] and 2.763 eV [28].

Table 2. The calculated values electronic energy gaps of bulk ZnSe wurtzite strucure.

Code	Method	k-mesh	Band gap, eV	Refs.
ATK	LSDA, PZ	7×7×7, MP	1.57	This work
ATK,	LSDA+U, PZ	7×7×7, MP	2.7	This work
WIEN 2k	FP-LAPW	2000	2.2	Theor.[29]
VASP	GGA-PBE	1×1×4, MP	1.15	Theor. [23]
WIEN 2k	GGA, PBE	6×6×1, MP	1.85	Theor. [30]
Wavelength-modulated			spectra	Exper.
2.70				[27]
Transmission	Spectroscopy		measurements	Exper.
2.763				[28]

As seen from Table 2, the LSDA+U calculated energy band gap (2.7 eV) value is agree with experimental results (2.70 eV (T=295K) [27] and 2.763 eV (T=273K) [28]).

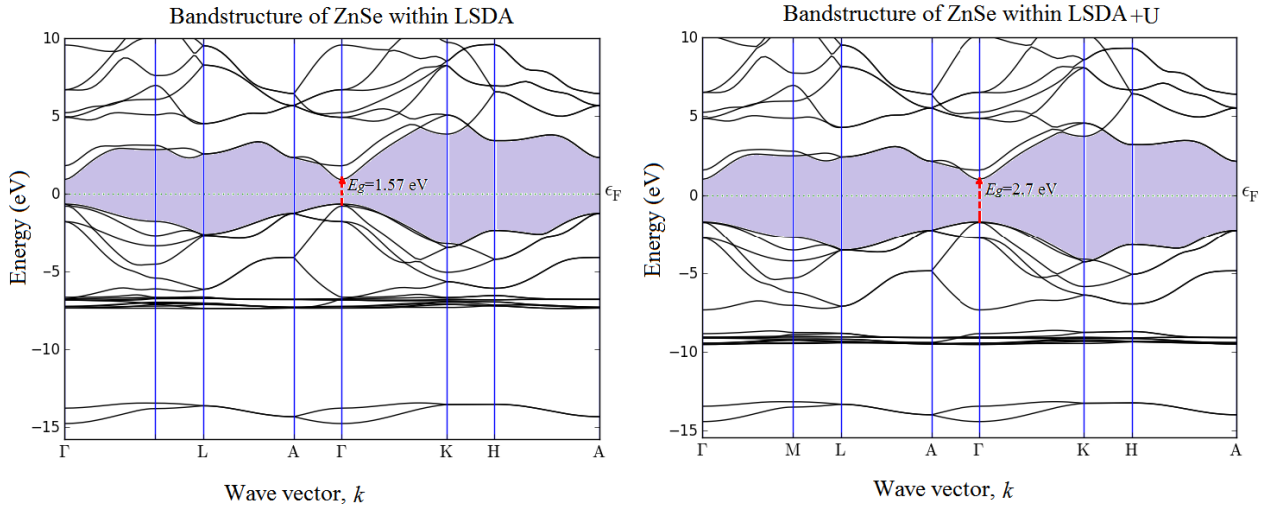

Figure 2. DFT-LSDA (E_g=1.57 eV) and LSDA+U (E_g=2.7 eV) calculated band structures of ZnSe.

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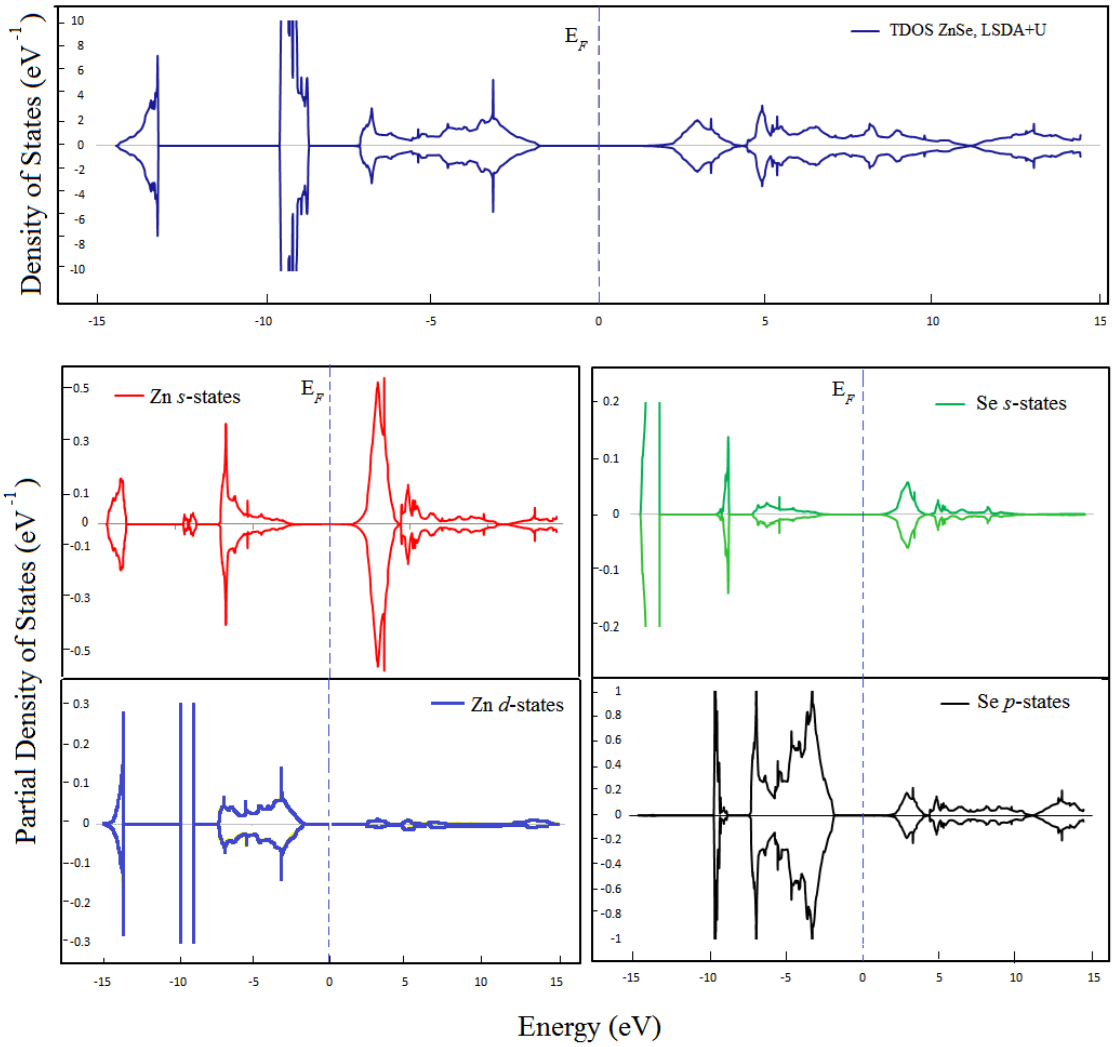

Figure 3. DFT-LSDA+U calculated TDOS and PDOS of pure ZnSe.

In Figures 2 and 3, for band structures and total DOS of pure structure, observed three parts in the valence band. DFT-LSDA calculations for ZnSe shows that the lowest band between -14.4 and -13.4 *eV* is mainly treated from Se-4*s* states. The second part of the valence band from -9.53 to -8.84 *eV*, which is mainly formed by zinc 3d states. The higher energy levels of the valence band with the energy range from -7.3 to -1.7 *eV* is mainly formed by selenium 4*p* states. The conduction band is basically composed of the zinc 4*s* and selenium 4*p* states.

4. Conclusion

In summary, the structural parameters and spin-polarized electronic properties of ZnSe are studied by DFT within the LSDA and LSDA+U method. The calculations revealed that the implementing Hubbard U corrections improved the wide of energy gap. From first-principles calculations the bottom of the conduction band and the top of valence band lies at the Gamma symmetric point, showing that the ZnSe is a direct band gap semiconductor material.

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