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Archives of Physics Research, 2010: 1 (1) 67-74
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Effect of Electron Spin for *d*-orbital in Electro-optical Characteristics of ZnSe

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Abstract

In this paper electro-optic characteristics of ZnSe have been investigated using density functional theory. The Kohn-Sham equations were solved using the full potential linear augmented plane wave approach (FP-LAPW). We used GGA, LDA+U and GGA+U approximations for the exchange correlation potential. The computations were done for energy levels from 0 to 14 eV considering the effect of *d*-orbital and proper choice of U_{eff} =U-J. The width of band gap has been corrected so that it is much closer to experimental result. The theoretical values of band gap and the refractive index have been improved comparing to their experimented values.

Introduction

ZnSe and its related ternary compounds has received much attention over the past years due to several new applications, including fabricating optical devices such as IR widows, various lenses and high power lasers due to its special optical characteristics, low absorption, high refraction index in visible to infrared wavelengths and wide pass band [1]. So far, physical characteristics of this structure have been studied extensively. But, in theoretical analysis, researchers have paid less attention to its optical characteristics rather than the electrical characteristics. Therefore, theoretical investigation of optical characteristics of this compound seems necessary.

First principle calculations, especially density functional theory have become a very useful tool for predicting the electric and optical properties of material. We have used the full potential augmented plane wave method (FP-LAPW) based on the density functional theory implemented in Wien2k code [4].

Because ZnSe compounds are ferroelectric and strongly correlated materials, it seems that it is better to use an orbital dependent potential for the exchange-correlation terms. In order to compare the effect of orbital-dependent potential, we calculated the optical properties using

GGA, GGA+U, LDA and LDA+U for the exchange correlation potential. Our main conclusion is that due to the presence of the localized *d*-orbital of Zn atoms in the compound, adding the Hubbard-U term to the standard local density approximation(LDA) or generalized-gradient approximation (GGA), must improve the calculated results and be in better agreement with experiment data. The LDA+U or GGA+U method include the orbital dependence of the self-energy operators which is absent in the Kohn-Sham potential [6-8].

In this research optical characteristics of ZnSe such as density function, dielectric function, refraction index, extinction index and absorption-induced losses are investigated. This paper is organized as follows. Details of the calculation model which is used are presented in section 2, and results for simulation carried out are interpreted in section 3.

Computational method

All of computations were done by generalized gradient and exact density approximation (GGA, GGA+U, LDA+U) using the full potential linearized augmented plane wave (FP-LAPW) method, in frame of density functional theory (DFT) [8-10], with Wien2k codes. Separation energy between valence and core electrons are considered equal to -6Ryd [3,4]. Computations for ZnSe crystal are done in cubic phase with net constant a=5.6685A^0 and $a=b=c$ in spatial group of $\alpha=\beta=\gamma=90$, $F\bar{4}3m(216)$ [5]. In LDA+U method, total energy is given as

$$E = E_0 + E_{LDA+U} \qquad (1)$$

Where, E_0 is total energy without considering electron spin. In Czyzk and Sawatzky method [7], energy is computed as

$$E_{LDA+U} = -\frac{U+J}{2}\sum_{iat}\sum_{m=-1}\sum_{\delta=\uparrow,\downarrow}(n_{m,\delta}-\overline{n_\delta})^2 \qquad (2)$$

Where, U+J is effective potential that in this research is assumed equal to 1.56eV. Also, $n_{m,\delta}$ is the number of occupied $|l,m,\sigma\rangle$ orbital in atoms and n_δ is the average number of electrons in orbital with σ spin which is calculated according to

$$\overline{n}_\sigma = \frac{1}{2l+1}\sum_{m=-l}^{l} n_{m,\sigma} \qquad (3)$$

Results and Discussion

Density of states in ZnSe compound, for each of ingredient atoms is illustrated in figure 1, by different methods of GGA, GGA+U, LDA+U. Zero energy is indicative of the Fermi level position which is plotted with dotted line perpendicular to energy axis. In low energies, valence band is composed of Zn-3d and Se-4s orbitals. As it can be seen in Fig. 1, considering the potential caused by Zn-3d valence region, the valence band is located at lower energy levels (about -15 eV). Therefore, this compound include atoms that have *d*-orbital. So, effect of the potential caused by electron spin in valence region can not be neglected. In this research, calculations are provided for upward spin. Our computations show that the density of states for upward spin has no difference with that of downward spin.

So, the same as empirical data, it confirms that there is no magnetic moment with spatial preferable direction in this compound. Valence band is near the Fermi level and composed of participation of intensively overlapped of Se-4p and Zn-4s orbital. The first peak, after Fermi level is due to the effect of Zn-4p orbital. As can be seen in Fig. 1, in GGA approximation, Zn-4p orbital has much overlapping with Se-4p and the band gap is also reduced. Band gap increases from 1.5eV in GGA approximation to 2.5eV in LDA+U approximation, according to spin potential assigned to electron. To improve the results, the GGA+U approximation was also used and Eg=2.6eV was obtained that is more consistent to empirical results.

Dielectric function is used to describe crystal response to electromagnetic fields in different directions. In past decade optical spectrometry is developed as the most important empirical tool for determining band structure. In tetragonal phase, optical characteristics are homogenous in only 2 dimensions.

In Fig. 2 real (2.a) and imaginary (2.b) part of dielectric function is illustrated as a function of incident photon energy.

Imaginary part of dielectric function is indicative of real transfers between occupied and unoccupied states. The highest peak in imaginary part of dielectric function (in GGA approximation) is occurred at 5.64 eV that corresponds to transition from valence to conductance band. Indeed, it corresponds to Zn-4p to Se-4p transition. Also in GGA+U and LDA+U methods the highest peaks appear at 4.77 and 4.69 eV respectively. The real part of dielectric function indicates scattering and loss in optical processes. The average of dielectric constant in high frequencies which is called high frequency dielectric constant is given by [6]

$$\varepsilon(\infty) = \frac{1}{3}[\varepsilon^{xx}(\infty) + \varepsilon^{yy}(\infty) + \varepsilon^{zz}(\infty)] \qquad (4)$$

Since displacement of atom centers is negligible, homogeneity in tetragonal structure has no variations and high frequency dielectric constant is the same in 3 directions. So, high frequency dielectric constant is homogenous and has no considerable variation between *x* and *z* directions. Square root of high frequency dielectric constant is the static refraction index, which is

$$n_0 = \sqrt{\mathrm{Re}\,\varepsilon(0)} \qquad (5)$$

Both empirical and computational results for band gap, static refraction index and refraction index in visible wavelength are expressed in table 1. As it can be seen, considering the effect of spin in LDA+U and GGA+U methods, increase band gap to its empirical value. So, the effect of spin can not be neglected. Also, we can conclude that GGA+U method is suitable for such compounds.

Table 1: Comparison of computational and empirical results for static refraction index, visible refraction index, band gap and plasmon resonance energy for ZnSe structure

Structure	ZnSe			
Pass band(um)	0.51-19			
Number or symmetries	48			
Computational method	GGA	GGA+U	LDA+U	Empirical method [7]
Static refraction index	2.56	3.04	3.04	3.02
Refraction index in visible wavelength (665 nm)	2.8	3.34	3.34	2.4
Band gap (eV)	1.5	2.6	2.5	2.58
Energy of plasmon resonance	6.62	5.7	5.8	---

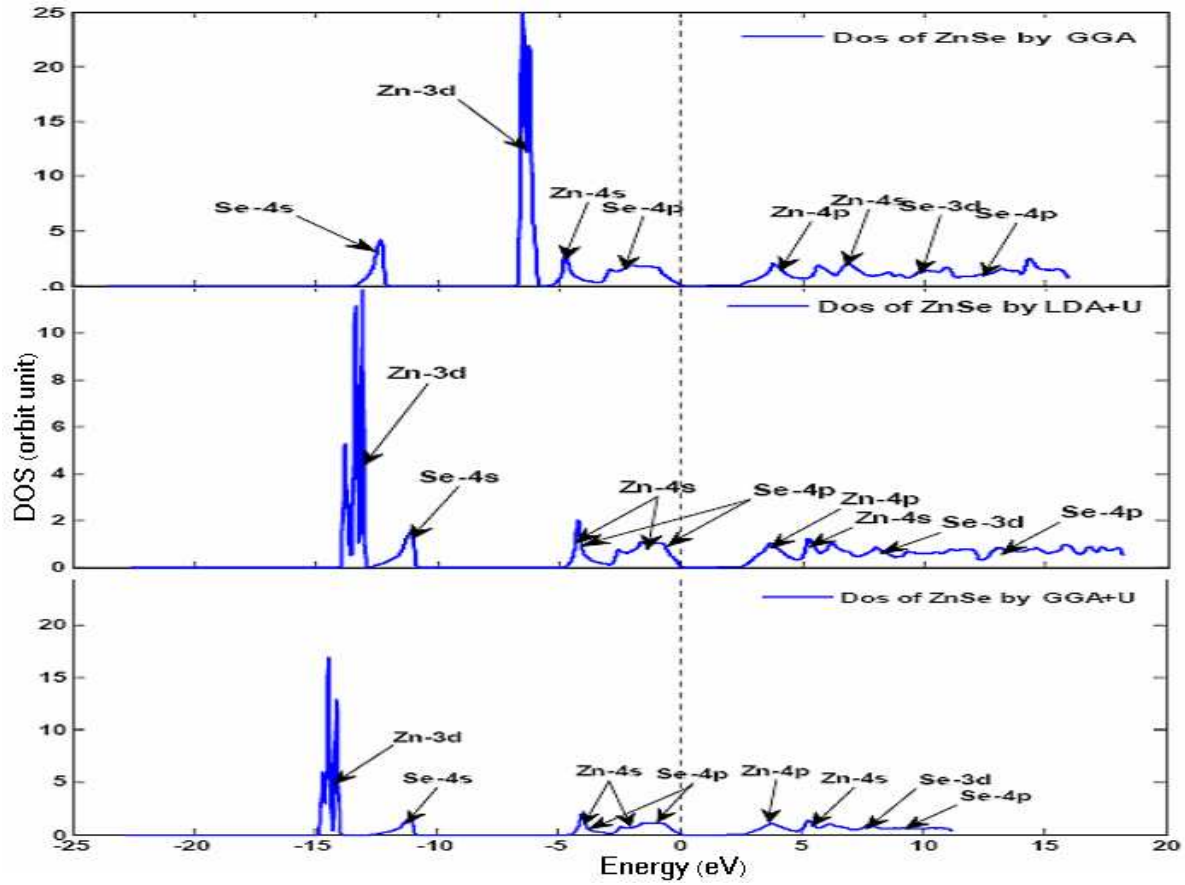

Figure 1: Total density of states for ZnSe structure computed in 3 different methods (GGA, GGA+U, LDA+U)

Diagram of refraction and extinction indexes in tetragonal phase for ZnSe compound are plotted in Fig. 3. As the results show, refraction index increases with increasing of band gap.

As it can be seen in Fig 3.a, first peaks occur at energy of 3.72 eV in GGA method, 3.66 eV in GGA+U method and 3.5 eV in LDA+U method. These peaks are caused by transition of electrons from under Fermi occupied states to unoccupied states in conductance band.

As a result of photon absorption, occupied electron states are exited to ultra Fermi energy levels. This intra-band transition is called optical conductance. In Fig. 4 real and imaginary parts of optical conductance for ZnSe are illustrated. Optical conductance starts from energy of 1.48 eV for GGA method, 1.28 eV for LDA+U method and 1.83 eV for GGA+U method. This value is called optical gap which is different from Kohn-Sham gap. As it can be seen in Fig 4.a peaks in the real part of optical conductance, imaginary parts of dielectric function and extinction index are occurred in the same energies. So, real part of optical conductance is the same as imaginary part of dielectric function. Imaginary part of optical conductance is proportional to loss. Negative slope of the curve in its beginning region shows that there are no losses. The first peak of loss for ZnSe occurs at about 3.68 eV for GGA method and in 4.72 and 5.15 eV for LDA+U and GGA+U, respectively. This peak corresponds to the region with low density of states.

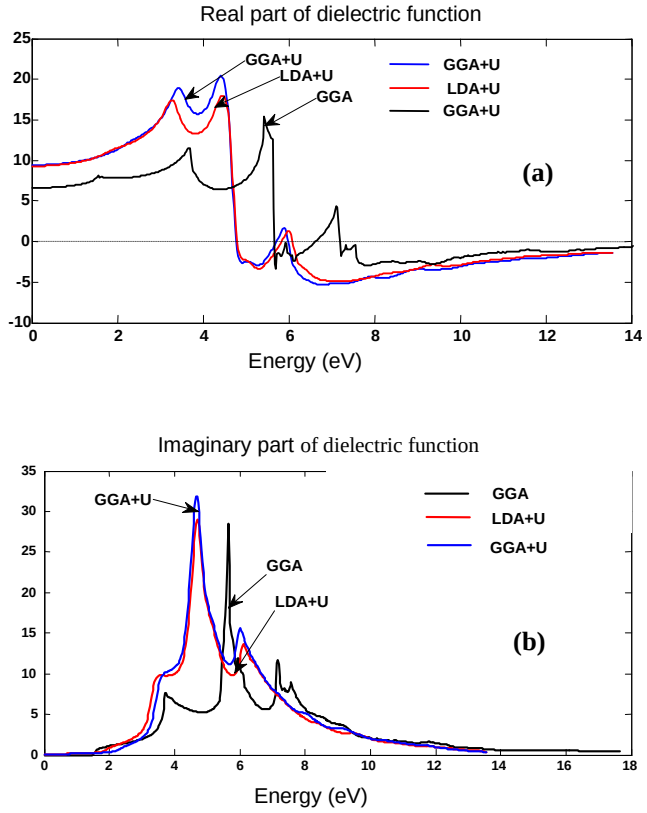

Figure 2: Dielectric function of ZnSe including real (a) and imaginary (b) parts

Electron energy loss spectroscopy is a powerful method for analyzing occupied states over Fermi level with sub-nm resolution. Electron energy loss spectrum is illustrated in Fig. 5. As it can be seen in the figure, energy loss begins at energies above 1.53 eV for GGA and 2 eV for GGA+U and LDA+U, respectively and reaches to its maximum value at about 12 eV. Indeed, the maximum value is related to voluminal plasmons. Comparing dominant peaks of electron loss spectrum (Fig. 5) with roots of real part of dielectric function plasmon resonance energy can be obtained as expressed in table 1.

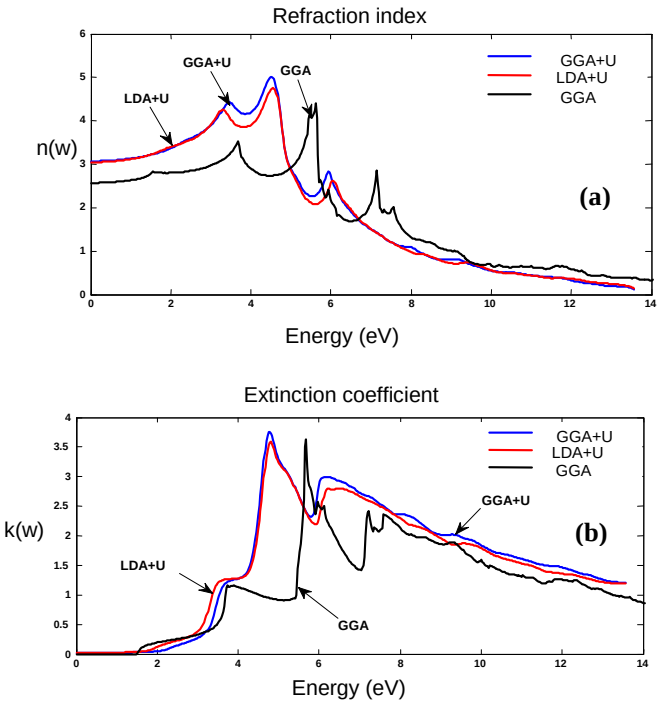

Figure 3: Refraction index (a) and extinction (b) coefficient for ZnSe computed in 3 different methods.

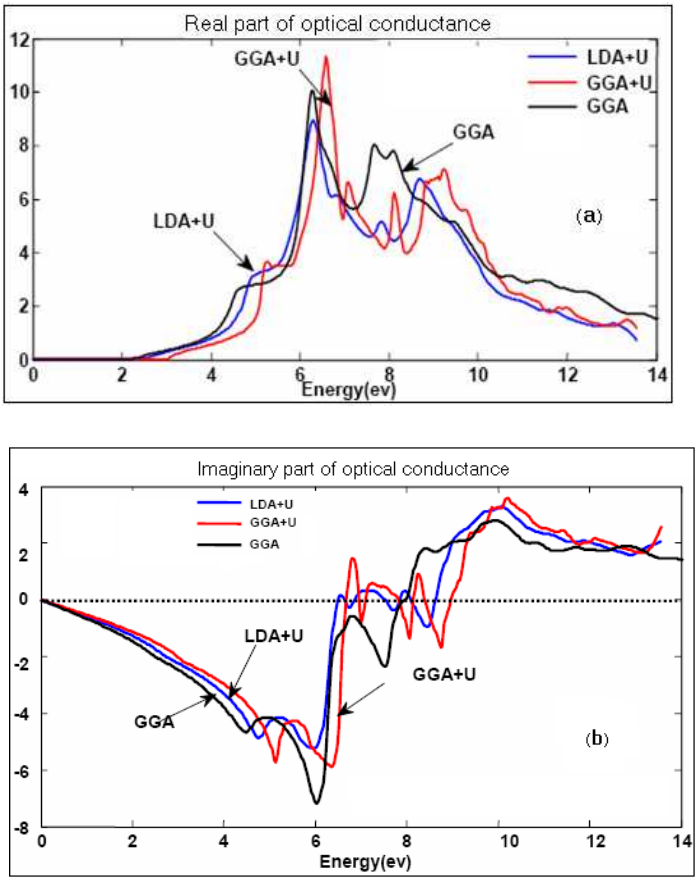

Figure 4: Real (a) and imaginary (b) part of optical conductance

Figure 6 illustrates the joint for energies lower than 1.48 eV (in GGA), 1.82 eV (in LDA+U) and 2.24 eV (in GGA+U). Maximum transition intensity for GGA, GGA+U and LDA+U methods are 5.64 eV, 4.7 eV and 4.69 eV, respectively. Transition intensity in GGA+U and LDA+U methods reduces to near zero values at energies about 14 eV while for GGA method, this take place at energy of about 16 eV.

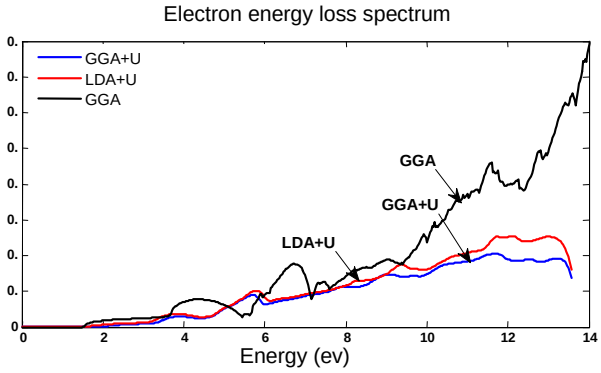

Figure 5: Electron energy loss spectrum for ZnSe

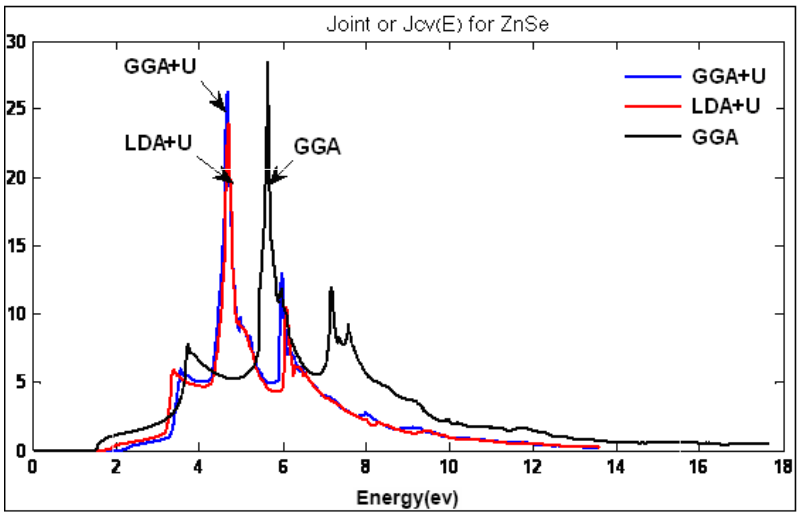

Figure 6: Joint or $J_{cv}(E)$ for ZnSe

Conclusion

In compounds including atoms with *d*-orbital, effect of spin can not be neglected. So, the computational method must be corrected. Using GGA+U and LDA+U methods and setting a wise and proper value for U_{eff} leads to very good results for ZnSe compound that are close to empirical results.

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