VACANCY FORMATION ENERGY FOR CHARGED AND NEUTRAL STATES IN $TlInS_2$

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For $TlInS_2$ 64-atom supercell, in LDA approximation of Density Functional Theory taking into account Hubbard+U corrections, from Fermi energy dependence of the Tl, In, S neutral and charged vacancy formation energies the transition levels were defined: for S-rich condition of S vacancies $q=0$ charge state transfers to $q=-2$ charge state, in 1.5 eV; for rich condition of Tl and In vacancies $q=-1$ charge state transfers to $q=-2$ charge state, in 0.5 eV and 1.75eV, respectively.

Considering that the calculated value of the energy gap obtained with LDA and LDA+U schemes (respectively 1.25 eV and 1.47 eV) are lower than experimental one (2.2 eV) and accepting the correction to agree on experimental value it was found that in arbitrary positions of the Fermi level within the band gap no transitions occur from the one charge state to another and as a result S vacancy remains in a neutral $q=0$ state, and Tl and In vacancies in a $q=-1$ charge state.

Keywords: psevdopotential, charged and neutral vacancy, defect, formation energy, valence band maximum.
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INTRODUCTION

The III-III-VI_2 family of crystals exhibit quasi low-dimensionality in the form of layered and chain structures and has become increasingly attractive due to their interesting structural properties and potential optoelectronic applications [1]. Like all layered $TlMeX_2$ (where Me=In or Ga and X=S or Se) $TlInS_2$ has C2/c space group symmetry at room temperature [2]. The fundamental structural unit of a layer is the In_4S_6 (Ga_4S_6) adamantane-like units linked together by bridging S atoms. The Tl atoms are in trigonal prismatic voids resulting from the combination of the In_4S_6 (Ga_4S_6) polyhedra into a layer [3]. The cell structure of $TlInS_2$ shown in fig.1. In the crystal structure of $TlInS_2$, the Van der Waals interaction favors the formation of numerous, both point and extended, defects embedded predominantly in the interlayer space of the crystal. The effect of impurities on the phase transitions in the ferroelectric semiconductors $TlInS_2$ have been studied [4].

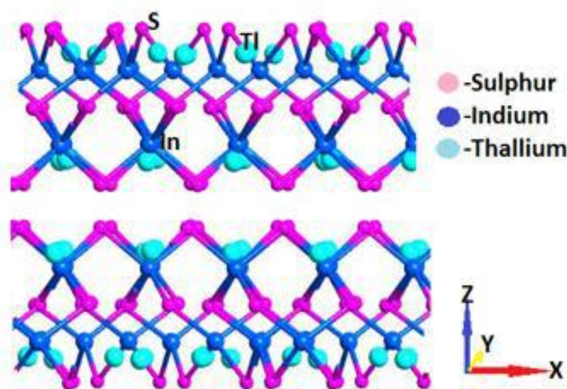

Fig.1. Cell structure of $TlInS_2$.

In this work, we aimed to examine the dependence of the defect formation energies (DFE) on the chemical potentials and Fermi-level position for the various charge states of Tl, In, S vacancy of the $TlInS_2$ segnetoelectric semiconductor supercell containing 64 atoms and to determine corresponds transition levels on this basis. Our calculations were performed for neutral and charged vacancy defect, by Local Density Approximation (LDA) [5] and implementing the LDA+U method using the Atomistix ToolKit software program (ATK, http://quantumwise.com/) [6]. The electron-ion interactions were taken into account through pseudopotentials of the Fritz Haber Institute (FHI). The number of the electrons treated as valence electrons was 3 for Tl ($6s^26p^1$), 3 for In ($5s^25p^1$) and 6 for S ($3s^23p^4$). The Perdew-Burke-Erenzhorf (PBE) exchange-correlation functional and Double Zeta Polarized basis sets were used in our calculations. The kinetic cut-off energy was 150 Ry. To determine the coordinates of the atoms and the lattice parameters of $TlInS_2$ primitive cell structure was relaxed and optimized with force and stress tolerances of 0.0001 eV/Å and 0.0001 eV/Å^3, respectively. The supercells containing vacancies were relaxed with force tolerance of 0.05 eV/Å.

The calculated band structures with LDA using HGH psevdopotential in Quantum Wise Atomistix ToolKit program and SGGA [7] using ultrasoft psevdopotential in Quantum Espresso [8] software programs show that bulk $TlInS_2$ is a direct band gap semiconductor with the valence band top and the conduction band bottom located at the center of the Brullouin zone and E_g=1.25 eV [9]. By LDA+U (the Hubbard parameter U we use for S 3p state U=3eV) scheme we defined that E_g=1.47 eV. The calculated values of the energy gap are lower than experimental one (2.35 eV) [10].

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RESULTS AND DİSCUSSİON

The formation energy of a point defect is not a constant but depends on the growth or annealing conditions [11]. In the case of charged vacancy, the formation energy further depends on the Fermi level (E_F), which is the energy of the electron reservoir, i.e. the electron chemical potential. We calculated formation energy by:

$$E^f\left(V_a^q\right) = E_{tot}\left(V_a^q\right) - E_{tot}(TlInS_2) + \mu_a + q(E_F + E_{VBM}) \qquad (1)$$

where $E_{tot}\left(V_a^q\right)$ is the total energy of a supercell containing the vacancy of atom (*a*=Tl, In, S) in the charge state q, $E_{tot}(TlInS_2)$ is the total energy of $TlInS_2$ perfect crystal in the same supercell and μ_a is the *a*-atoms chemical potential. First we determine the chemical potentials of atoms as E_{tot} energy per one atom. For this purpose we used cell and structure parameters of Tl, In and S taken from the literature [6] and optimized them. Another important physical parameter for the calculation of the defect formation energy is the position of the valence band maximum (VBM), which corresponds to the reference energy level for the electron chemical potential. VBM is determined by adding the perfect supercell VBM with the Fermi level [13].

DFE of charged vacancies calculated in the case of rich atom conditions. Rich conditions of atoms forming the vacancy given by the thermodynamic stability condition:

$$E_{tot}(TlInS_2) - [E_{tot}(Tl) + E_{tot}(In) + 2E_{tot}(S)] = H_f(TlInS_2), \qquad (2)$$

where $H_f(TlInS_2)$ is the enthalpy of formation of bulk $TlInS_2$ negative for a stable compound. The calculated enthalpy of formation of $TlInS_2$ is $H_f(TlInS_2)$=–2.983 eV. Adding the value of enthalpy to chemical potential of atom forming the vacancy we gain the rich condition of this atom respectively [14]. So rich conditions for each of the three atoms can be calculated as follows:

$$\mu_{Tl,In,S}^{min} = E_{tot}(Tl, In, S) + H_f(TlInS_2) \qquad (3)$$

In our calculation transition level $\varepsilon(q/q')$ is defined as the Fermi-level position for which the formation energies of charge states q and q' are equal. $\varepsilon(q/q')$ can be obtained from

$$\varepsilon(q/q') = [E^f(V_q; E_F = 0) - E^f(V_{q'}; E_F = 0)] / (q' - q)\,, \qquad (4)$$

where $E^f(V_q; E_F = 0)$ is the formation energy of the defect V in the charge state q when the Fermi level is at the valence band maximum ($E_F = 0$). -

The experimental significance of this transition level is that for Fermi-level positions below $\varepsilon(q/q')$, charge state q is stable, while for Fermi-level positions above $\varepsilon(q/q')$, charge state q' is stable [12]. In fig. 2 (In-rich limit LDA) the slope of the line changes from -1 to -2 at the intersection of lines with *q=-1* and *q=-2*. For In-rich condition the energy of intersection will be denoted by $\varepsilon(-1/-2)$. The q=-1 state is more stable when $E_F < \varepsilon(-1/-2)$, and the *q=-2* is favorable when $E_F > \varepsilon(-1/-2)$. The calculated transition energy level for In is: E=1.25 eV. In fig.2 (S-rich limit LDA) energy of intersection will be denoted by $\varepsilon(0/-2)$ for S rich condition, where $E_F < \varepsilon(0/-2)$, corresponds to more stable *q=0* state and the *q=-2* is favorable when $E_F > \varepsilon(0/-2)$. Transition energy level for S is: E=1.5 eV. Tl-rich limit LDA (fig.2) describe the line changes from -1 to -2 at the intersection of lines with *q=-1* and *q=-2* for Tl vacancy. In this case the *q=-1* state is more stable when $E_F < \varepsilon(-1/-2)$, and the *q=-2* is favorable when $E_F > \varepsilon(-1/-2)$. Transition energy level for Tl is *E*=1.5 eV.

The band gap obtained from LDA and the LDA + U schemes have been small compared with experimental results. Although the LDA+*U* approach only corrects part of the band-gap error, it provides us with a basis for obtaining a full band-gap correction through a physically justified extrapolation scheme [12]. Our approach takes advantage of the fact that the extent to which transition levels $\varepsilon(q/q')$ change in going from LDA to LDA+*U* reflects their relative valence-band and conduction band character. The procedure is to perform calculations using the LDA, on the one hand, and the LDA+*U*, on the other hand, and then extrapolate to the experimental gap:

$$\varepsilon(q/q') = (\varepsilon(q/q')^{LDA+U} - (\varepsilon\,(q/q')^{LDA})/(E_g{}^{LDA+U} - E_g{}^{LDA}) * (E_g{}^{exp} - E_g{}^{LDA+U}) + \varepsilon\,(q/q')^{LDA+U} \qquad (4)$$

Here, Eg^{LDA} and Eg^{LDA+U} are the band gaps given by the LDA and LDA+*U* approximations and Eg^{exp} is the experimental gap. As a result, Tl(-1/-2)=2.26eV, In(-1/-2)=0.74eV, S(0/-2)=2.26eV from obtaining value it was obvious that in arbitrary positions of the Fermi level within the band gap no transitions occur from the one charge state to another. Thus S vacancy remains in a neutral *q=0* state, and Tl and In vacancies in a *q=-1* charge state.

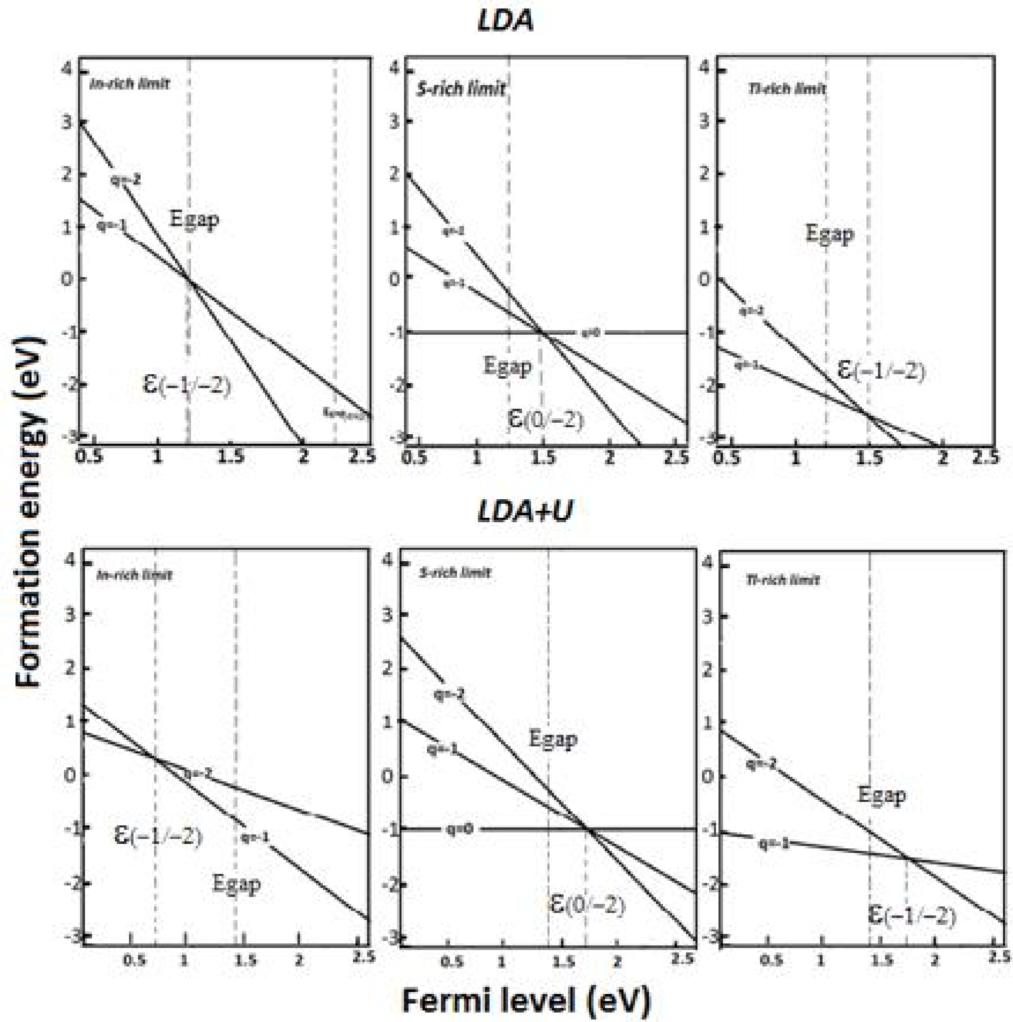

Fig. 2. Formation energies as a function of Fermi-level position for neutral and charged vacancy in $TlInS_2$. Results for In-rich, S-rich and Tl-rich conditions with LDA and LDA+U are shown.

CONCLUSİON

Dependence of formation energy on charged and neutral states as a function of the Fermi level for $TlInS_2$ crystal calculated using the LDA and the LDA + U schemes. Considering that the calculated value of the band gap (1.25 eV with LDA, LDA + U 1.47 eV) are lower than the experimental (2.2 eV), and extrapolating the calculated dependence to experimental value, it was found that in any position of the Fermi level within the band gap S vacancy remains in the neutral charge state $q = 0$, and Tl, In vacancies in the $q = -1$ charge state.

[1] *K.A. Yee, A. Albright, J.Am.Chem*. Soc. 113, 6474 (1991).

[2] *W. Henkel, H.D. Hochheimer, C. Carlone, A. Werner, S. Ves, and H.G. von Shnering*. Phys. Rev., B.26. 3211. (1982).

[3] *N.M. Gasanly and N.S. Yuksek.* Low-Temperature Raman Scattering in $TlGa_xIn_{1-x}S_2$ Layered Mixed Crystals: Compositional Dependence of the Mode Frequencies and Line Shapes Vol. 108 Acta Physica Polonica A No. 6(2005).

[4] *S.S Babaev, E.Basaran, T.G.Mammadov, F.A. Mikailov, F.M. .Salehli, MirHasan Yu. Seyidov and R.A. Suleymanov*. The effect of impurities on the phase transitions in the ferroelectric semiconductors $TlInS_2$ and $TlGaSe_2$ Journal of Physics Vol.27 (2015).

[5] *W. Kohn. and L. Sham*. Self–consistent equations including exchange and corelation Effects, Phys. Rev., 14**0** A1133 – A1138. (1965).

[6] http://quantumwise.com/

[7] *J.Perdew, K.Burk, Y.Wang*. Generalized gradient approximation for the exchange correlation hole of a many-electron system, Phys. Rev. B 54 16533-16539. (1996).

[8] http://quantum-espresso.org

[9] *N.A. Ismayilova, G.S. Orudzhev***.** Electron spectrum and DOS calculations for $TlInS_2$ crystal from first principles**.** ANAS Transaction №5, Vol.35 p.15-19. (2015).

[10] *M.M. El-Nahass and M.M. Sallam* Optical and Photoelectric Properties of TlInS2 Layered Single Crystals. Egypt. J. Solids, Vol. (31), No. (1), (2008).

[11] *C.G. Van de Walle and J.Neugebauer.* J. Appl. Phys. 95, 3851. (2004).

[12] *Anderson Janotti and Chris G.Van de Walle*. Native point defects in ZnO. Phys. Rev., B 76, 165202 (2007)

[13] *M.A. Mehrabova, H.R. Nuriyev, H.S. Orujov*. Defect formation energy for charge states and electrophysical properties of CdMnTe. Photonics, Devices, and Systems VI, edited by Pavel Tománek, Dagmar Senderáková, Petr Páta, Proc. of SPIE Vol. 9450, 94500Q (2015).

[14] *Anderson Janotti and Chris G Van de Walle.* Fundamentals of zinc oxide as a semiconductor. Rep. Prog. Phys. 72 126501 (29pp) (2009).

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