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FIRST-PRINCIPLES CALCULATION OF DEFECT FORMATION ENERGY IN $TlInSe_2$

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Abstract. In the paper defect formation energies for a $TlInSe_2$ have been investigated using the first-principles total energy calculations. Calculation has been done for the five charge states +2, +1, 0, -1, -2. We defined formation energies of vacancy V_{Tl}, V_{In}, V_{Se} in $TlInSe_2$ consisting of 48 atoms as a function of the Fermi energy. The results of the calculations show that with the transition from a negative charged defect states to a positive defect states, the width of the forbidden gap increases for each vacancy. The Se vacancy defect has the lowest formation energy, as compared with that of other defects.

Keywords: *Defect formation energies, vacancy, defect, forbidden gap*.

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1. Introduction

The ternary compound $TlInSe_2$ belongs to the group of semiconductors with chain crystal structure and is a structural analog of TlSe in which thallium trivalent ions $T1^{3+}$ are replaced by indium trivalent ions In^{3+}. The lattice of $TlInSe_2$ by analogy with TlSe has the space symmetry group D_{4h}^{18} (Miller *et al*., 1972; Guseinov *et al*., 1969). Indium trivalent ions In^{3+} are surrounded by four selenium ions and form negatively charged chains $(In^{+3}\ Se^{-2})^{-}$ along the tetragonal *z* axis. These chains are connected by thallium univalent ions $T1^{+}$. Forces between atoms inside chains are strongly covalent and weaker forces of ionic type are realized between chains (Allakhverdiyev *et al*., 1982). Electronic structure of crystal was studied in reference (Ismayilova *et al*., 2017). In ref. (Abasova *et al*., 2011) reported result of the effect J-irradiation on the current transport mechanism in the p-$TlInSe_2$ heterostructures. They investigation revealed that the interaction of radiation defects with the initial defects of crystals brings in the reconstruction and redistribution of defects at the edge of heterojunction separation. These results led to an insignificant change of hetero-recombination processes in the current transport mechanism. Abnormal dose dependence of the heterojunction characteristics is explained by a level compensation rate at the edge of separation and in the structure base. Despite the fact that the some properties of crystal was investigated, but there is not any data about defect formation energies in the literature. In our previous work (Orudzhev & Ismayilova, 2017) where we investigated defect formation energy for $TlInS_2$ and $TlGaSe_2$ we have been found out that for both crystal in any position of the Fermi level within the band gap S (Se) vacancy remains in the neutral charge state q = 0, Tl, In vacancies in the q = -1 charge states. For vacancy Ga atom was observed transitions from -1 charge state to -2 charge state in the position Fermi energy 0.15 eV. Since $TlInSe_2$ is from one family with crystals of $TlInS_2$ and $TlGaSe_2$, in our opinion it will be interesting to study the electronic

spectrum and defect formation energy is calculated of crystal consisting of neutral and charged vacancies and compare our result with previous investigation.

2. Method of calculation

In this work, first-principles total energy calculations within density functional theory DFT are carried out using the Atomistic ToolKit program (ATK, http://quantumwise.com/) (http://quantumwise.com/). For structural property calculations, the exchange correlation potential is described in the generalized gradient approximation (GGA) (Perdew *et al*., 1996) using the functional Becke-Lee-Yang-Parr (BLYP) (Lee *et al*., 1988). The electron-ion interactions were taken into account through norm conserving SG15 pseudopotentials. The Kohn-Sham wave functions were expanded in a linear combination of numerical real-space atomic orbitals as basis set with a kinetic energy cutoff of 300 Ry. The special points sampling integration over the Brillouin zone (BZ) are carried out using the Monkhorst-Pack method with a 5×5×5 special *k*-point mesh. The relaxation procedures were truncated when all the residual forces for the relaxed atoms were less than 0.001 eV/Å.

The formation energy of point defects was calculated from the difference of total energy between perfect crystal and imperfect crystal. The formation energy of a neutral vacancy in a compound depends on the atomic chemical potentials in the system. The formation energies of Tl, In and Se vacancies can be, respectively, presented by:

$$E_f = E_f^v[Tl_{n-1}In_nSe_{2n}] - E_f[Tl_nIn_nSe_{2n}] + \mu_{Tl}$$

$$E_f = E_f^v[Tl_nIn_{n-1}Se_{2n}] - E_f[Tl_nIn_nSe_{2n}] + \mu_{In}$$

$$E_f = E_f^v[Tl_nIn_nSe_{2n-1}] - E_f[Tl_nIn_nSe_{2n}] + \mu_{Se}$$

where E_f^v is the total energy of the supercell with a defect and E_f is the total energy of the perfect crystal (Janotti & Van de Walle, 2009). The symbol μ is the chemical potential of the constituent elements (Tl, In and Se) and n = 12. The chemical potential, μ should be correlated with each other to satisfy the following equation:

$$\mu_{Tl} + \mu_{In} + 2\mu_{Se} = \mu_{TlInSe2}(bulk)$$

If the vacancy is charged, the formation energy further depends on the Fermi level (E_F). In the case of charge vacancy the formation energy is given by:

$$E_f = \left(V_a^q\right) = E_f^v\left(V_a^q\right) - E_f(TlInSe_2) + \mu_a + q(E_F + E_{VBM})$$

The Fermi level E_F is taken with respect to the valence-band maximum (E_{VBM}), and can vary from 0 to Eg, where Eg is the fundamental band gap. We calculated $E_f\left(V_a^q\right)$ for the five charge states +2, +1, 0, −1, −2, for the vacancy defects. 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 (Lee *et al*., 1988). $\varepsilon(q/q')$ can be obtained from;

$$\varepsilon(q/q') = [E_f(V^q; E_F = 0) - E_f(V^{q'}; E_F = 0)] / (q' - q)$$

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 ($E_F = 0$).

Fig. 1a, 1b, 1c schematically presents vacancy formation energies of Tl, In and Se atoms for different charge states respectively. Fig.1a shows that, the thermodynamically stable electronic charge state -2 ((-2/-1) = 1.37 eV) of a Tl vacancy does not changes its position and until the end remain stable in -2 charge state. The same situation is observed for the In (fig. 1b) and Se (fig.1c) vacancy too. So that in arbitrary positions of the Fermi level within the band gap in In ((-2/-1) = 1.35 eV) and Se ((0/-2) = 1.17 eV) vacancy does not occur transitions from the one charge state to another. Thus Se vacancy remains in a neutral q=0 state, In vacancies in a q=-2 charge state. Also it was found that the greatest defect formation energy is revealed in the case of the In vacancy.

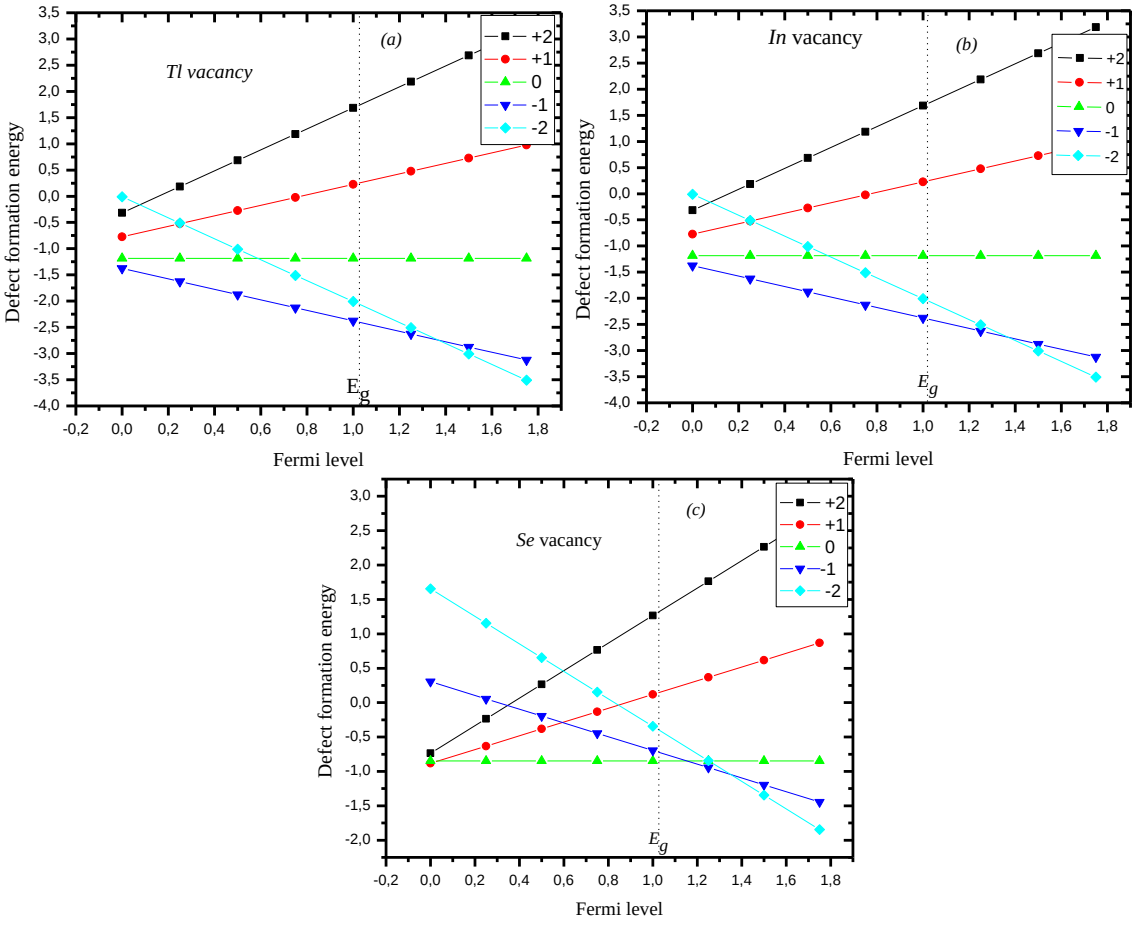

Fig. 1. Dependence of DFE of vacancy V_{Tl} (a), V_{In} (b), V_{Se} (c) on charge states as a function Fermi energy for crystal consisting of 47 atoms

The result we get in this study are approximately identical with the results which we obtained for crystals from this family in our previous calculations. Thus, the deffect formation energy estimations in $TlInS_2$ and $TlGaSe_2$ crystals have also shown that in any transition from one charge state to another for vacancy Tl, In, S, Se (besides Ga vacancy) in this crystal does not occur. In crystal $TlGaSe_2$, for Ga vacancy unlike them transitions

occur from -1 charge state to -2 charge state in the position Fermi energy 0.15 eV. According to the results by electronic spectrum for $TlInSe_2$ forbidden gap was decreases for negative states of vacancy while for positive states the gap was increased. It means that, by increasing the degree of positive charged defect, it is possible to achieve an increase in the band gap.

3. Conclusion

We have studied the dependence of defect formation energies on supercell size for charged vacancy defects in $TlInSe_2$. A detailed analysis of the defect formation energy showed that, greatest defect formation energy is revealed in the case of the in vacancy. From obtaining value Tl(-1/-2)=1.37eV, In(-1/-2) = 1.35 eV, Se(0/-2) = 1.17eV it was obvious that in arbitrary positions of the Fermi level within the band gap in Tl, In and Se vacancy does not occur transitions from the one charge state to another. It was found that the greatest defect formation energy is revealed in the case of the in vacancy.

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