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Vacancy Formation Energy for the Charged and Neutral States of $TlGaSe_2$ Crystal

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Electronic band structure and defect formation energy of $TlGaSe_2$ are studied using density functional method within the Local Density Approximation. Calculated band structure shows that the top of valence band and the bottom of conduction band locate at the symmetry point Γ and along the symmetry line Γ–*Y*, respectively. The defect formation energy is calculated as the difference between the total energy of a stable structure and the relaxed defect structure at constant volume. Calculation is done for the five charge states: +2, +1, 0, –1, –2. Energies of vacancies' (V_{Tl}, V_{Ga}, V_{Se}) formation are determined for the $TlGaSe_2$ crystal consisting of 63 atoms for the various charge states as a function of Fermi energy. The calculated optical properties indicate that the optical energy gap is increased due to the Se and Tl vacancies.

Key words: density functional theory, local density approximation, charged vacancy, defect formation energy, Fermi level.

Електронна структура зон та енергія утворення дефектів кристалу $TlGaSe_2$ вивчалися з використанням методи функціонала густини в наближенні локальної густини. Одержані з розрахунків електронного спектра кристалу у LDA-наближені результати показали, що дно зони провідности та стеля валентної зони розташовані в центрі Бріллюенової зони (у симетрійній точці Γ) та вздовж симетрійної лінії Γ–*Y* відповідно. Енергія утворення дефекту обчислюється як ріжниця між повними енергіями

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стабільної й оптимізованої дефектної структур при постійному об'ємі. Розрахунки було виконано для п'ятьох зарядових станів: +2, +1, 0, –1, –2. Було встановлено енергії формування вакансій V_{Tl}, V_{Ga}, V_{Se} у кристалі $TlGaSe_2$, який складається з 63 атомів, для різних зарядових станів, залежно від рівня енергії Фермі. Обчислені оптичні властивості показують, що оптична енергетична щілина збільшується через вакансії Se та Tl.

Ключові слова: теорія функціонала густини, наближення локальної густини, заряджені вакансії, енергія утворення дефекту, рівень Фермі.

Электронная структура зон и энергия образования дефектов кристалла $TlGaSe_2$ изучались с использованием метода функционала плотности в приближении локальной плотности. Полученные из расчётов электронного спектра кристалла в LDA-приближении результаты показали, что дно зоны проводимости и потолок валентной зоны расположены в центре зоны Бриллюэна (в симметрийной точке Γ) и вдоль симметрийной линии Γ–Y соответственно. Энергия образования дефекта вычисляется как разность между полными энергиями стабильной и оптимизированной дефектной структур при постоянном объёме. Расчёты были выполнены для пяти зарядовых состояний: +2, +1, 0, –1, –2. Были установлены энергии формирования вакансий V_{Tl}, V_{Ga}, V_{Se} в кристалле $TlGaSe_2$, состоящем из 63 атомов, для различных зарядовых состояний в зависимости от уровня энергии Ферми. Вычисленные оптические свойства показывают, что оптическая энергетическая щель увеличивается из-за вакансий Se и Tl.

Ключевые слова: теория функционала плотности, приближение локальной плотности, заряженные вакансии, энергия образования дефекта, уровень Ферми.

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1. INTRODUCTION

The compound $TlGaSe_2$ is a representative of the class of triple chalcogenide semiconductors with the general formula $A^{III}B^{III}C_2^{VI}$ (A = Tl; B = Ga, In, Fe; C = S, Se). In recent years, the semiconductor compound $TlGaSe_2$, as well as its structural analogue $TlInS_2$, is studied rather intensively. They attract interest because of structural phase transitions found in these crystals. According to the data of [1–5], at room temperature and atmospheric pressure, $TlGaSe_2$ has a layered monoclinic structure (space group $C2/c$) with the parameters $a = 10.772$ Å, $b = 10.771$ Å, $c = 15.636$ Å, $\beta = 100.06°$. The layers are formed by Ga_4Se_{10} tetrahedra connected to each other by selenium atoms and in turn consisting of four small $GaSe_4$ tetrahedra. The optical properties of the $TlGaS_2$, $TlGaSe_2$, and $TlInS_2$ crystals have been investigated through transmission and reflection measurements in the wavelength range of 400–1100 nm. Optical indirect and direct band gap energies are 1.97 and 2.26 eV [6]. Formation of defect states in the $TlGaSe_2$

band-gap due to different chemical elements is, however, unclear as $TlGaSe_2$ retains the *p*-type conductivity under any doping conditions [7–11]. It is speculated that impurity atoms tend to segregate and self-compensate at the abundant stacking faults occurring at an every fourth layer [5]. The most comprehensive studies were done regarding Fe impurities in $TlGaSe_2$. X-ray diffraction revealed that few percent of Fe impurities have a weak effect on the crystalline structure and orientation [11]. The result of the work [12] revealed that Fe impurities form the distinct deep band-gap levels but have a weak effect on the formation of the fundamental absorption edge.

The electronic and magnetic properties of ternary $TlGaS_2$ crystal with alone vacancy or their clusters were studied by means of first-principle (*ab initio*) approximation. It was shown that presence of S-vacancy clusters narrows the band gap of $TlGaS_2$ crystal significantly, while Tl-vacancy clusters increase it slightly [13]. In the listed papers, the electronic spectrum of crystal doped with impurity and consisting with cluster vacancies were studied. In our opinion, it will be interesting to study the electronic spectrum of crystal consisting of neutral and charged vacancies and compare our result with previous investigation.

2. METHOD OF CALCULATION

Our calculations were performed for the primitive cell of $TlGaSe_2$, and for the supercell consisting from 64 atoms. Calculation has been done by Atomistix Tool Kit program software [14] using Local Density Approximation (LDA) [15]. The electron–ion interactions were taken into account through the HGH (Hartwigsen–Goedekker–Hutter) pseudopotentials. The numbers of the electrons treated as valence electrons were as follow: 13 for Tl $[Xe]4f^4+5d^{10}6s^26p^1$, 13 for Ga $[Ar]+3d^{10}4s^24p^1$ and 6 for Se $[Ar]3d^{10}+4s^24p^4$.

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. The primitive cell of $TlGaSe_2$ was relaxed and optimized with force and stress tolerances of 0.003 eV/Å and 0.003 eV/Å^3, respectively. Defects in the supercell were allowed to relax in constant volume until the forces were below 0.05 eV/Å.

3. RESULTS AND DISCUSSION

The primitive cell contains 8 formula units. Unit cell parameters and reduced coordinates of atoms inside the unit cell (in units of the corresponding parameters of monoclinic unit cell) taken from [16, 17], and

TABLE 1. Experimental and optimized unit cell parameters of $TlGaSe_2$.

Cell parameters	a, Å	b, Å	c, Å	β, °
Experimental [16]	10.772	10.771	15.636	100.06
Experimental [17]	10.879	10.797	15.707	100.47
Optimizations	10.552	10.557	15.289	99.97

TABLE 2. Experimental and optimized atomic coordinates of $TlGaSe_2$.

Atom	x^{opt}	y^{opt}	z^{opt}	x^{exp}	y^{exp}	z^{exp}
Tl1	0.6591	0.7580	0.1069	0.6517	0.7253	0.1078
Tl2	0.3049	0.8424	0.6180	0.2776	0.845	0.6158
Ga1	0.5830	0.7857	0.8380	0.5861	0.7899	0.8378
Ga2	0.2141	0.4169	0.3310	0.21	0.9178	0.3391
Se1	0.9280	0.9280	0.2499	0.9295	0.9295	0.25
Se2	0.4619	0.4619	0.25	0.4468	0.4468	0.25
Se3	0.6410	0.2103	0.0620	0.6417	0.2323	0.0695
Se4	0.4543	0.9224	0.2498	0.447	0.9294	0.2508
Se5	0.7317	0.8563	0.5623	0.7665	0.8583	0.5732

our optimized data are given in Tables 1 and 2.

From calculated band structure with LDA approximation, the top of valence band and the bottom of conduction band were shown to be localized at different points on the surface of the Brillouin zone. At the symmetry point Γ, there is located top of valence band and, along symmetry Γ–Y line; there is located bottom of conduction band (Fig. 1). This, in their turn, indicates that $TlGaSe_2$ is an indirect gap semiconductor with the indirect gap from Γ to Γ–Y line of 0.87 eV, while the direct gap at the Γ-point is 0.99 eV. Indirect scenario of bands at the energy gap is favoured by other works, *e.g.*, [18–21] too. However, the particular indirect schemes vary from work to work according to the earlier works [18, 19]: the additional valence band maximum on Y line might be responsible for the indirect scenario. Nevertheless, the later works [20, 21] and the present calculations, which used more advanced computation techniques, commonly advocate the conduction band bottom that is not in Γ-point. At the same time, the just mentioned works specify different positions of this bottom in the BZ. Nevertheless, the indirect scenario is hardly doubtful and the off-zone-centre conduction band bottom likewise.

In this work, we aimed to examine the formation energy of $TlGaSe_2$ semiconductors with supercell of 64 atoms for the various charge

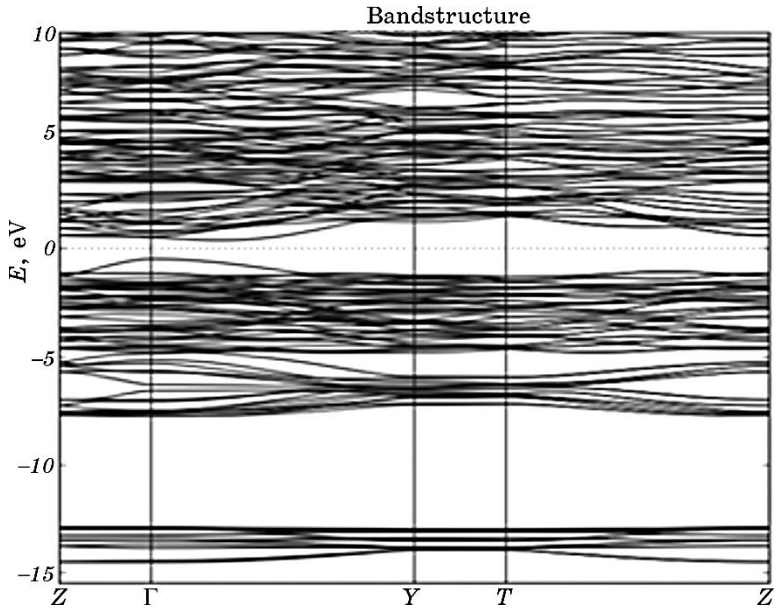

Fig. 1. Calculated electronic structure within the LDA by the HGH pseudopotential.

states for the Tl, Ga and Se vacancies.

If the vacancy is charged, 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 [22]. In the case of charge vacancy, the formation energy is given by:

$$\begin{aligned} E^F(V_a^q) &= E_{\text{tot}}(V_a^q) - E_{\text{tot}}\left(\text{TlGaSe}_2\right) + \mu_a + q(E_F + E_{\text{VBM}}), \\ \varepsilon(q/q^{\text{I}}) &= [E^F(V_q; E_F = 0) - E^F(V_{q^I}; E_F = 0)]/(q^I - q), \end{aligned} \tag{1}$$

where $E^F(V_a^q)$ is the total energy of a supercell containing the vacancy in the charge state q, $E_{\text{tot}}\left(\text{TlGaSe}_2\right)$ is the total energy of a $TlGaSe_2$ perfect crystal in the same supercell, and μ_a is a-atoms chemical potential corresponding to the defect-free supercell energy per atom. Expressions similar to equation (2) apply to all the native point defects. The Fermi level E_F is taken with respect to the valence-band maximum and can vary from 0 to E_g, where E_g is the fundamental band gap. We calculated $E^F(V_a^q)$ for five charge states of the vacancy defects: +2, +1, 0, –1, –2. In our calculation, transition level $\varepsilon(q/q^{\text{I}})$ is defined as the Fermi-level position, for which the formation energies of charge states q and q^{I} are equal [22]; $\varepsilon(q/q^{\text{I}})$ can be obtained from:

$$\varepsilon(q/q^{\text{I}}) = [E^F(V_q; E_F = 0) - E^F(V_{q^{\text{I}}}; E_F = 0)]/(q^{\text{I}} - q), \tag{2}$$

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

The experimental significance of this transition level is that for the Fermi-level positions below $\varepsilon(q/q^I)$, charge state q is stable, while for the Fermi-level positions above $\varepsilon(q/q^I)$, charge state q^I is stable [12]. In Figure 2 (Ga-rich limit), the slope of the line changes from –1 to –2 at the intersection of lines with $q = -1$ and $q = -2$. For the Ga-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 favourable when $E_F > \varepsilon(-1/-2)$. The calculated transition energy level for Ga is $E = 0.15$ eV. In Figure 2 (Se-rich limit), energy of intersection will be denoted by $\varepsilon(0/-2)$ for the Se rich condition, where $E_F < \varepsilon(0/-2)$, corresponds to more stable $q = 0$ state and the $q = -2$ is favourable when $E_F > \varepsilon(0/-2)$. Transition energy level for Se is $E = 1.1$ eV. Tl-rich limit (Fig. 2) describes the line changes from –1 to –2 at the intersection of lines with $q = -1$ and $q = -2$ for the Tl vacancy. In this case, the $q = -1$ state is more stable when $E_F < \varepsilon(-1/-2)$, and the $q = -2$ is favourable when $E_F > \varepsilon(-1/-2)$. Transition energy level for Tl is $E = 1.1$ eV.

As a result, $\mathrm{Tl}(-1/-2) = 1.1$ eV, $\mathrm{Ga}(-1/-2) = 0.15$ eV, $\mathrm{Se}(0/-2) = 1.1$ eV; from obtaining values, it was obvious that, in arbitrary positions of the Fermi level within the band gap, in Tl and Se vacancies, no transitions occur from the one charge state to another. Thus, Se vacancy remains in a neutral $q = 0$ state; Tl vacancies remain in a $q = -1$ charge state. In Ga vacancy, 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 the neutral and charged defect cases, width of forbidden gap increases for the neutral Tl vacancies (direct

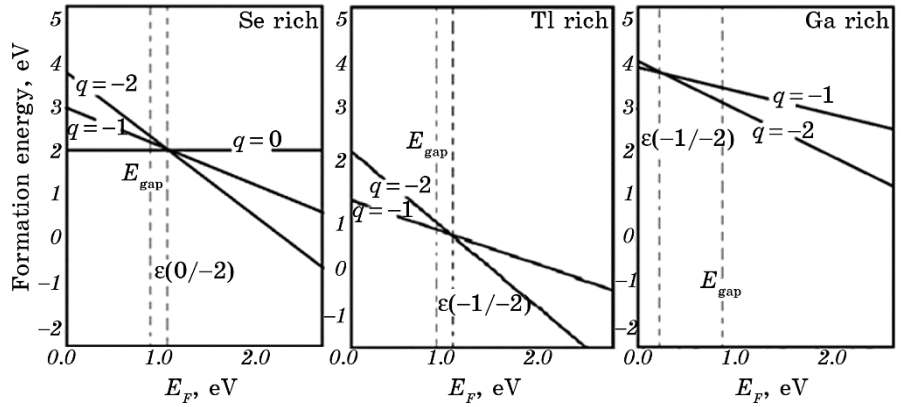

Fig. 2. Dependence of DFE of the V_{Tl}, V_{Ga} and V_{Se} vacancy on charge states as a function of Fermi energy for the crystal consisting of 63 atoms.

gap from 0.99 eV to 1.42 eV, indirect gap from 0.87 to 1.13 eV) and for the neutral Se vacancies (direct gap from 0.99 eV to 1.68 eV, indirect gap from 0.87 to 1.34 eV). While in the case of neutral In vacancy, the width of forbidden gap decreases (direct gap from 0.99 eV to 0.86 eV, indirect gap from 0.87 to 0.78 eV). This result contradicts the results of Ref. [13], since in their case presence of S-vacancy clusters narrows the band gap of $TlGaS_2$ crystal significantly while Tl-vacancy clusters increase it slightly. In addition, it should be noted that, with positively charged vacancies, in all cases, the width of forbidden gap increases and, for the negative charged vacancies, the width of forbidden band is decreased.

4. CONCLUSION

In this article, we present the results of electron spectrum and DFE calculations for the $TlGaSe_2$ crystal from the first principle in the framework of density functional theory. Investigation showed that $TlGaSe_2$ is an indirect gap semiconductor with the indirect gap from Γ to Γ–Y line of 0.87 eV and the direct gap at the Γ-point is 0.99 eV. Electronic spectra for the neutral and charged defect were cased; width of forbidden gap increases for the neutral Tl and neutral Se vacancies, while, in the case of neutral In vacancy, the width of forbidden gap decreases. It was found that the greatest defect formation energy is revealed in the case of the Ga vacancy. By increasing the degree of positive charged defect, it is possible to achieve an increase in the band gap.

REFERENCES

1. D. Muller, F. E. Poltman, and H. Z. Hahn, *Z. Natuforsch.*, **29**: 117 (1974).
2. D. Muller and H. Z. Hahn, *Anorg. Allg. Chem.*, **438**: 258 (1978).
3. K. R. Allakhverdiyev, T. G. Mamedov, B. G. Akinoglu, and Sh. S. Ellialtioglu, *Turk. J. Phys.*, **18**, No. 1: 1 (1994).
4. W. Henkel, H. D. Hochheimer, C. L. Carlone, A. Werner, S. Ves, and H. G. V. Schnering, *Phys. Rev. B*, **26**: 3211 (1982).
5. K. A. Yee and T. A. Albright, *J. Am. Chem. Soc.*, **113**: 6474 (1991).
6. N. M. Gasanly, *J. Korean Physical Society*, **57**, No. 1: 164 (2010).
7. E. Senturk, L. Tumbek, and F. A. Mikailov, *Cryst. Res. Technol.*, **40**: 901 (2005).
8. M-H. Yu. Seyidov, E. Coskun, Y. Sahin, R. Khamoev, and R. A. Suleymanov, *Semicond. Sci. Technol.*, **21**: 171 (2006).
9. N. S. Yuksek, H. Kavas, N. M. Gasanly, and H. Ozkan, *Physica B*, **344**: 249 (2004).
10. A. F. Qasrawi and N. M. Gasanly, *Mater. Res. Bull.*, **39**: 1353 (2004).
11. F. A. Mikailov, B. Z. Rameev, S. Kazan, F. Yildiz, T. G. Mammadov, and B. Aktas, *Solid State Commun.*, **133**: 389 (2005).
12. V. Grivickas, V. Gavryushin, P. Grivickas, A. Galeckas, V. Bikbajevas, and

K. Gulbinas, *phys. status solidi (a)*, **208**, No. 9: 2186 (2011).
13. O. A. Kozlova, V. V. Lyskouski, and V. V. Nelayev, *Mater. Phys. Mechanics*, **13**: 124 (2012).
14. http://quantumwise.com
15. W. Kohn and L. Sham, *Phys. Rev.*, **140**: A1133 (1965).
16. M. A. Nizametdinova, F. M. Hashimzade, D. A. Huseinova, G. S. Orudzhev, and K. R. Allakhverdiyev, *Moldavian J. Physical Sciences*, **9**: 350 (2010).
17. S. H. Jabarov, T. G. Mammadov, A. I. Mammadov, S. E. Kichanov, V. B. Alieva, and E. V. Lukin, *J. Synch. Investig.*, **9**, No. 1: 35 (2015).
18. G. Abdullaeva, N. T. Mamedov, and G. S. Orudzhev, *phys. status solidi (b)*, **119**: 41 (1983).
19. S. G. Abdullaeva and N. T. Mamedov, *phys. status solidi (b)*, **133**: 171 (1986).
20. K. A. Yee and T. A. Albright, *J. Am. Chem. Soc.*, **113**: 6474 (1991).
21. S. Kashida, Y. Yanadori, Y. Otaki, Y. Seki, and A. M. Panich, *phys. status solidi (a)*, **203**: 2666 (2006).
22. A. Janotti and C. G Van de Walle, *Rep. Prog. Phys.*, **72**: 126501 (2009).