First-principles study of the electronic structure and DOS spectrum of $TlGaSe_2$

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The electronic band structure, density of states (DOS) of $TlGaSe_2$ are calculated by the using Quantum Wise Atomistix Tool Kit program on the basis of density functional theory. The calculated band structure shows direct and indirect band gap of 0.87 and 0.99 eV. Top of valence band located at the Γ point, bottom of conduction band located along the Γ-Y line. From the DOS analysis, have been established that top of valence band mainly originated from 6p state electrons of Se atoms. Bottom of conduction band originated from 4s state of Ga atoms.

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1. Introduction

The ternary compounds $TlGaS_2$, $TlGaSe_2$ and $TlInS_2$ belong to the class of layered semiconducting chalcogenides $TlBX_2$ (where B = Ga or In, X = S or Se). Stacking of the atoms in the crystals is in the form of two twisted anionic layers with weakly bonded Tl^{1+} cations located in the trigonal cavities between them. Therefore, the crystals consist of separate layers with strong bonding between atoms within the layer and weak bonding between the layers [1-5].

$TlGaSe_2$ compound has a monoclinic crystal structure with space group C2/c, with lattice parameters a = 10.8797(4) Å, b = 10.7975(1) Å, c = 15.7070(4) Å and β = 100.47°, respectively [6]. The ions of univalent thallium are situated in the trigonal voids between the Ga_4Se_{10} complexes. The unit cell consists of two layers rotated with respect to each other by 90° and shifted with respect to each other along the (010) direction by the value of a side of the small $GaSe_4$ tetrahedron. The deviation from tetragonal symmetry appears as a result of this shift. Each layer consists of seven atomic planes located in the sequence Se–Tl–Ga–Se–Ga–Tl–Se.

In the past, a large number of studies on the fundamental optical absorption in $TlGaSe_2$ crystal were done. Namely, the fundamental absorption edge was reported to be formed by the indirect and the direct transitions with room-temperature energies varying over large ranges: E_g^i = 1.83 - 2.13 eV, E_g^d = 2.08 - 2.23 eV [7] and E_g^i = 1.83 eV and E_g^d = 2.11 eV [8].

In some studies, we came across some information on the DOS spectrum of the crystal, however, this information is not sufficient and in this work made a detailed investigation of the electronic structure, band structure and DOS of $TlGaSe_2$.

2. Computational method

Our calculations were performed for the primitive cell of $TlGaSe_2$ by Local Density Approximation (LDA) [9] using the Atomistix ToolKit software program (ATK) [10]. The electron-ion interactions were taken into account through pseudopotentials of the Hartwigsen-Goedekker-Hutter (HGH). 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 $TlGaSe_2$ consisting from 32 atoms calculating structure was optimized with force and stress tolerances of 0.003 eV/Å and 0.003 eV/Å^3, respectively. Note that for HGH pseudo-potential electron configuration of atoms as (core + electron) were chosen; for Tl $[Xe]4f^{14}+5d^{10}6s^26p^1$, for Ga $[Ar]+3d^{10}4s^24p^1$ and for Se $[Ar]3d^{10}+4s^24p^4$.

3. Results and discussion

Ternary $TlGaSe_2$ compound crystallizes in a monoclinic system with base-centered lattice and space group symmetry C2/c at room temperature [6, 11]. The primitive cell contains 8 formula units. Optimized coordinates of atoms which settled in non-equivalent positions given in $\vec{t}_1$, $\vec{t}_2$, $\vec{t}_3$ basis. Here $\vec{t}_1$, $\vec{t}_2$, $\vec{t}_3$ is basis vectors of base centered monoclinic cell (Table 1).

$$\vec{t}_1 = \left(\frac{a}{2}, \frac{b}{2}, 0\right); \quad \vec{t}_2 = \left(-\frac{a}{2}, \frac{b}{2}, 0\right); \quad \vec{t}_3 = (c\cos\beta, 0, c\sin\beta) \quad (1)$$

Table 1. Experimental [6, 11] and optimized atomic coordinates of $TlGaSe_2$

Atom	x^{exp}	y^{exp}	z^{exp}	x^{opt}	y^{opt}	z^{opt}
Tl1	0.6481	0.7263	0.0958	0.6591	0.7580	0.1069
Tl2	0.2748	0.8496	0.5994	0.3049	0.8424	0.6180
Ga1	0.584	0.794	0.8241	0.583	0.785	0.838
Ga2	0.2061	0.416	0.3248	0.2141	0.4169	0.3380
Se1	0.9329	0.9329	0.25	0.9280	0.9281	0.2499
Se2	0.4424	0.4424	0.25	0.4619	0.4620	0.25
Se3	0.6483	0.2261	0.0946	0.6410	0.2103	0.0620
Se4	0.4425	0.9329	0.2502	0.4543	0.9224	0.2498
Se5	0.7731	0.8617	0.5910	0.7317	0.8563	0.5623

From calculated structure (Fig. 1) we can see that the crystal structure consists of layers composed of tetrahedral complexes Ga_4Se_{10} linked together by the common atoms of selenium. Univalent thallium ions are in trigonal-prismatic voids between these complexes. Two layers within the unit cell are rotated relative to each other at 99.97°. Optimized lattice parameters of crystal in good agreement with experimental [6, 11] (Table 2).

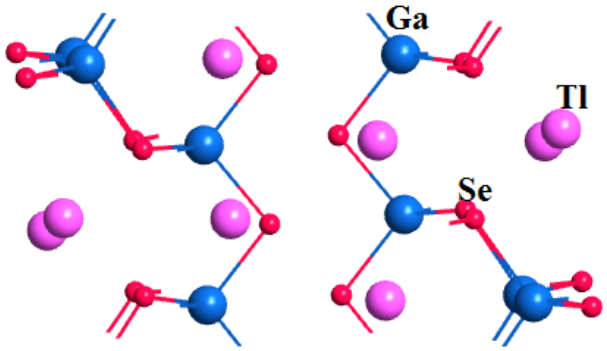

Fig. 1. The primitive cell of $TlGaSe_2$

Table 2. Experimental [6, 11] and optimized unit cell parameters of $TlGaSe_2$

Cell parameters	*a* (Å)	*b* (Å)	*c* (Å)	*β* (˚)
Experimental [11]	10.772	10.771	15.636	100.06˚
Experimental [12]	10.879	10.797	15.707	100.47°
Optimizations	10.552	10.557	15.289	99.97˚

From calculated band structure 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 of the monoclinic base-centered lattice, namely at the symmetry point Γ located top of valence band and along symmetry line Γ-Y located bottom of conduction band (Fig. 2). 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. In (Fig. 2) zero of the energy scale shows the position of the Fermi level. The calculated valence bands below the Fermi energy agree well with other first principle studies [12, 13].

The band gap is smaller than the experimental result [7] of 0.96 and 1.09 eV, probably due to a discrepancy in the GGA method. If we add a correction factor to this band gap, the results are found to be in excellent agreement with the experimental data.

The partial density of states (PDOS) of the Tl, Ga, and Se atoms are shown in Fig. 3. The low-energy peak around -16 to -14 eV is a contribution mainly from the Ga-3d states, with a small component from the Se-4s and Ga-4s orbitals. The DOS peak at around -8 to -5 eV mainly represents the contribution of the Tl- 6s and Ga- 4s states. The Tl-5d state give contribution to originate low-energy peak around -11 eV. Top of valence band mainly take their origin from 4p state of Se atoms and partially from 4p and 6p state of Ga, Tl atoms respectively. The Tl-6p state contribution to originate bottom of conduction band around energy range 0.5 to 5 eV. As well as this energy range partly take their origin from 4s and 4p state of Ga and 4p state of Se atoms. It should be pointed out that the PDOS spectrum in Fig. 3 includes eight Tl atom, eight Ga atom, and sixteen Se atoms.

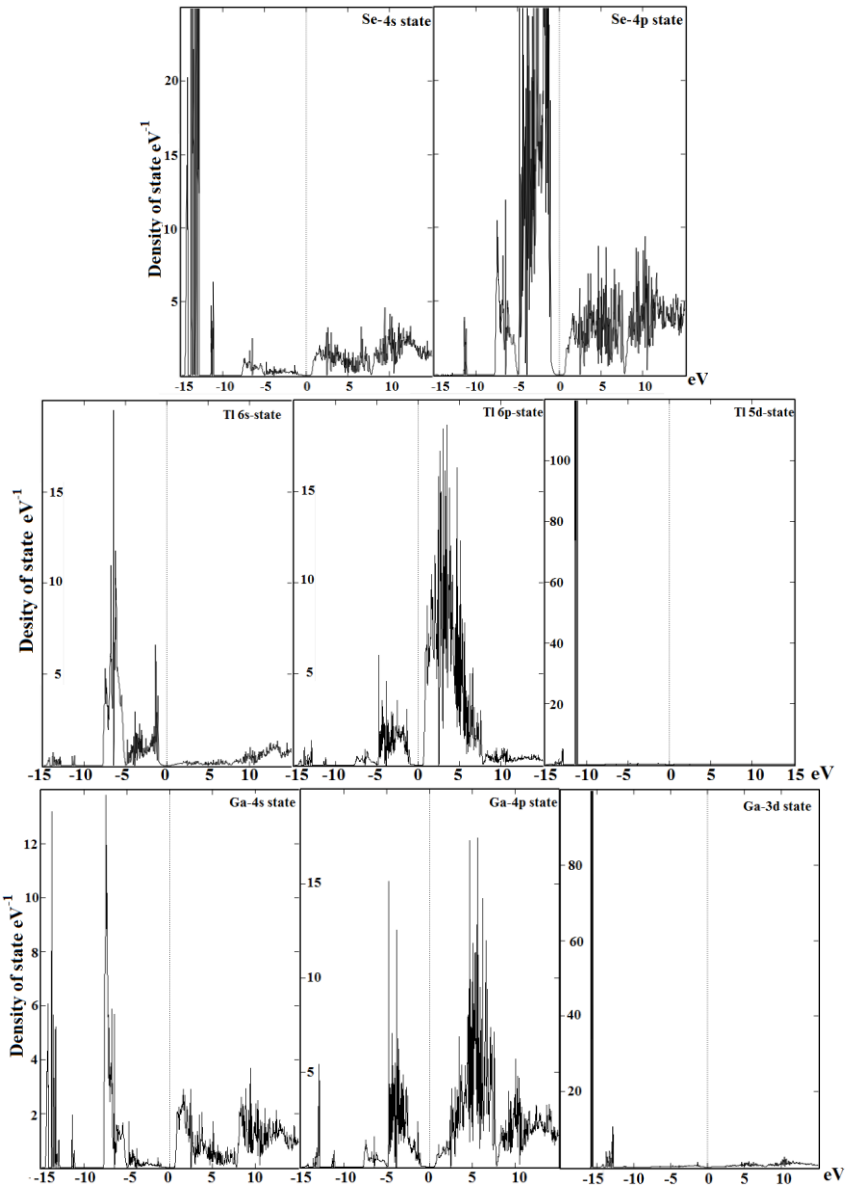

Fig. 2. The calculated with HGH pseudo-potential electronic band structure for monoclinic $TlGaSe_2$

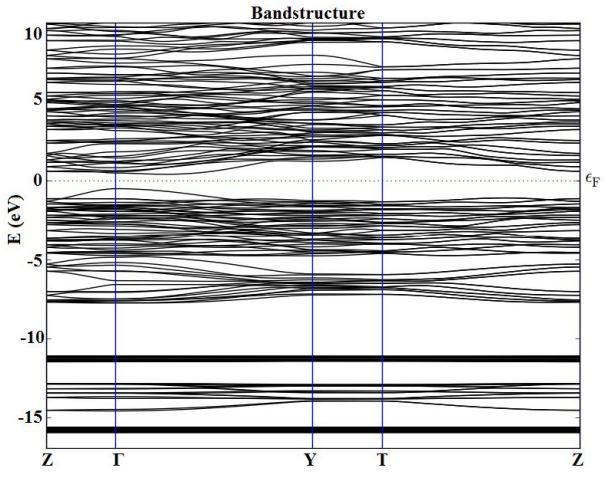

Fig. 3. The density of states (DOS) for $TlGaSe_2$

4. Conclusions

In this work have made a detailed investigation of the electronic structure, band structure and DOS of $TlGaSe_2$ crystal from first principle using LDA approximation. It has been concluded that the top of the valence band is mainly composed of the 4p state of Se atoms and the bottom of conduction band mainly consists of 6p states of Tl atoms. The calculations show that the fundamental gap of $TlGaSe_2$ is indirect. Our calculated fundamental indirect gap is E_g^i=0.87 eV.

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