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Electronic structure and effective masses of $TlInSe_2$ under pressure

G.S. ORUDZHEV[1,2], N.A. ISMAYILOVA[1,*], V.N. JAFAROVA[1]

[1]Institute of Physics ANAS, Baku, AZ-1143, Azerbaijan
[2]Azerbaijan Technical University, Baku, AZ-1073, Azerbaijan

We have studied the band structure and the band gap closure of $TlInSe_2$ under pressure in the range of 0 GPa to 21 GPa, by employing the first-principles method based on the density functional theory. We discuss the possible metallic transition in the tetragonal phase of $TlInSe_2$ crystal. Our calculation results show that the value of the pressure at the crossover from the direct to the indirect gap is found to be 8 GPa. The "semiconductor-metal" transition is determined to occur at 14 GPa. The study of the pressure effect on the effective masses for semiconductor state shows that with increasing pressure, the effective masses of holes and electrons decrease and the anisotropy of effective masses of holes is weakening.

Keywords: *Density Functional Theory; metallic transition; General Gradient Approximation; band structure.*

1. Introduction

$TlInSe_2$ compound belongs to a class of semiconductors with TlSe-type structure [1]. $TlInSe_2$, with the quasi-one-dimensional chain structure has attracted much interest because of the negative differential resistance [2] and interesting thermoelectric properties [3, 4]. $TlInSe_2$ crystallizes in a tetragonal system with a body-centered lattice and space group symmetry D_{4h}^{18} (I4/mcm) at ambient conditions. $TlInSe_2$ has a rather complex tetragonal layer-chain structure, which can be described as a set of InSe4 chains extended along the c-axis and connected with each other through one-dimensional chains of Tl atoms.

Some of the physical properties of $TlInSe_2$ crystal have been investigated. The first electronic structure calculations of $TlInSe_2$ based on pseudopotential model reported in the literature [5] revealed an indirect energy gap for $TlInSe_2$. Calculations using non-local ionic pseudopotentials, where screening and exchange-correlation effects were treated within Hubbard-Sham model with selected parameters of the charge distribution around each particular ion, showed that $TlInSe_2$ is a direct gap semiconductor (both the valence band maximum and conduction band minimum are located at the T point on the surface of the Brillouin zone) [6]. Our previous theoretical study by DFT method [8] also confirmed this result [6]. Density of states (DOS) calculations carried out in this work show that valence band maximum at the T point and the surrounding parts originate mainly from 6s states of univalent Tl and 3p states of Se atoms. Bottom of the conduction band is caused by the contribution of 6p-states of Tl and 5s states of In atoms.

In the literature [7], the effective masses were calculated for the electron dispersion, which was fitted to the electronic structure calculated in the literature [6].

The electrical properties of the $TlInSe_2$ compound were studied in the literature [9, 10]. The band gap obtained from the experiment was found to be equal to 1.1 eV [9] and 1.2 eV [10].

The effect of hydrostatic pressure on the electrical conductivity of p-$TlInSe_2$ single crystals measured along the tetragonal axis [0 0 1] in the range from 0 to 3 GPa was studied in the literature [11]. According to those results if gap narrowing under the law:

*E-mail: ismayilova_narmin_84@mail.ru

$$E(P) = E(0) - |G|P \quad (1)$$

where $|G| = 1.75 \cdot 10^{-10}$ eV/Pa proceeds also at hydrostatic pressure P > 3 GPa, then at a certain critical value of pressure P ≈ 6 GPa, overlapping of bands E(P) = 0 takes place, i.e. a phase transition "semiconductor-metal" occurs.

Jabarov et al. [12] reported the results of the first high pressure neutron scattering study of $TlInSe_2$, supported by ab initio calculations. According to the calculations, the observed pressure dependence of the lattice parameters allows us to assume that a structural phase transition from tetragonal to cubic phase, similar to the one observed earlier in the analogous structure of $TlInSe_2$, takes place at P > 20 GPa.

In the present work, the transition pressure at which $TlInSe_2$ transforms from direct band gap to indirect one is reported for the first time by first principle calculations. Furthermore, effective masses have been studied as dependent on pressure for semiconductor state. We have also compared our results with previous experimental and theoretical studies on $TlInSe_2$ compound.

2. Method of calculation

The first-principles calculations were performed by the pseudopotential method, using the Atomistic ToolKit program ATK [13] based on density functional theory (DFT) [14], which had been shown to yield reliable results for the electronic and structural properties of various solids. For structural property calculations, the exchange correlation potential was described in the generalized gradient approximation (GGA) [15] using the Becke-Lee-Yang-Parr (BLYP) functional [16]. The electron-ion interactions were taken into account through the norm conserving SG15 pseudopotentials. The number of electrons treated as valence electrons was 13 for Tl [Xe] $4f^{14} + 5d^{10}6s^26p^1$, 13 for In [Kr] + $4d^{10}5s^25p^1$ and 6 for Se [Ne] + $3s^23p^4$. 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) was carried out using the Monkhorst-Pack method [17] with a 5 × 5 × 5 special k-point mesh. The primitive cell of $TlInSe_2$ was optimized with force and stress tolerances of 0.001 eV/Å and 0.001 eV/Å^3 respectively.

3. Results and discussion

At normal pressure, band gap of $TlInSe_2$ is direct (Fig. 1a) with the top of the valence band and the bottom of the conduction band located at the symmetry point T. The Fermi level is shown by the dashed line in the figures. Calculated energy band gap $E_g = 1.02$ eV is in a good agreement with experimental values of 1.1 eV [9] and 1.12 eV [10]. With an increase of pressure, the band gap decreases and at ∼8 GPa the fundamental absorption edge changes from direct to indirect gap where $E_{g,d} = 0.55$ eV; $E_{g,I} = 0.41$ eV (Fig. 1b), since the bottom of the conduction band changes its position from symmetry point T to midpoint of the symmetry line P-N. In the whole investigated region, the top of valence band does not change its position and remains at the symmetry point T.

The increase of pressure leads to overlapping of bands and reaching zero of the band gap at metallization pressure P ∼ 14 GPa, (where $E_{g,d} = 0.3$ eV; $E_{g,I} = 0$ eV) (Fig. 1c). Metallization takes place by indirect closure of band gap between valence band (at T point) and conduction band (on the P-N symmetry line). The curve pressure versus band gap of $TlInSe_2$ is given in Fig. 2.

Ab initio calculated DOS coincide with our previous results [8] for ambient case (we used there HGH pseudopotential and BLYP functional) where we have reported that valence states, from −4 eV up to the Fermi energy, are dominated by the Se-3p states and surrounding parts at the T point originate mainly from 6s states of univalent Tl ions.With increasing pressure, the metallic properties in the crystal manifest themselves by 3p states of Se and 6s states of Tl atoms. At 15 GPa (Fig. 3c) it seems that the zone which crosses the Fermi level comes from 3p and 6s states of Se and Tl atoms, respectively.

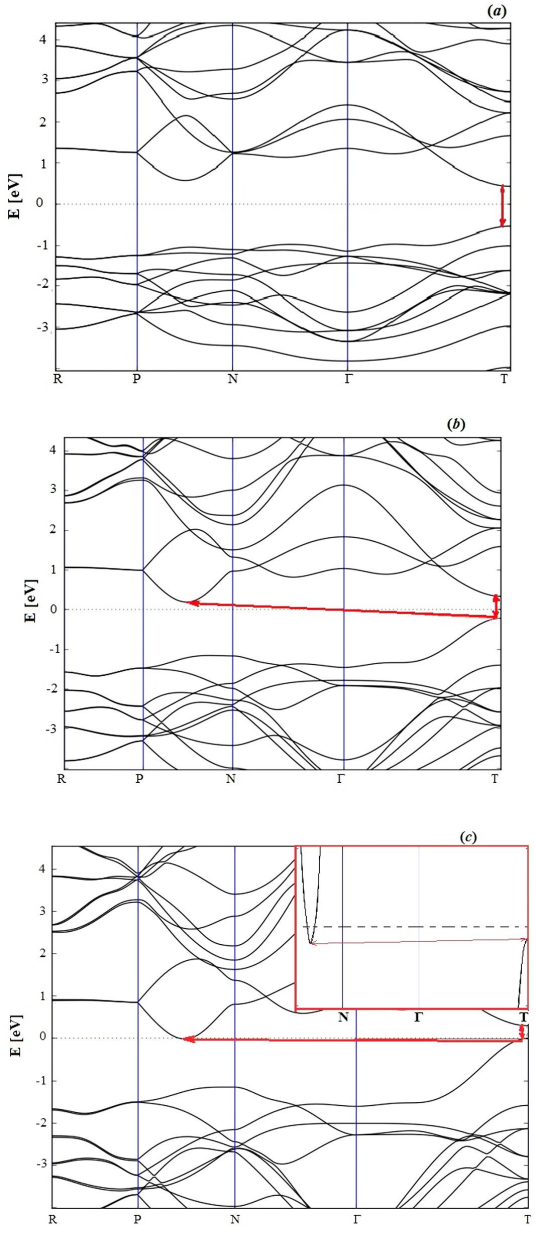

Fig. 1. GGA band structures of $TlInSe_2$ in the tetragonal structure at ambient conditions (a), the fundamental absorption edge change from direct to indirect gap at 8 GPa (b) and a transition from semiconductor to metal structure at 14 GPa (c). The ordinates are in units of eV.

Taking into account the fact that in the neutron diffraction experiments [12] it was observed that the phase transition in the crystal occurs at a pressure above 20 GPa, it can be concluded that the metallic properties of the crystal manifest themselves before phase transition. This means

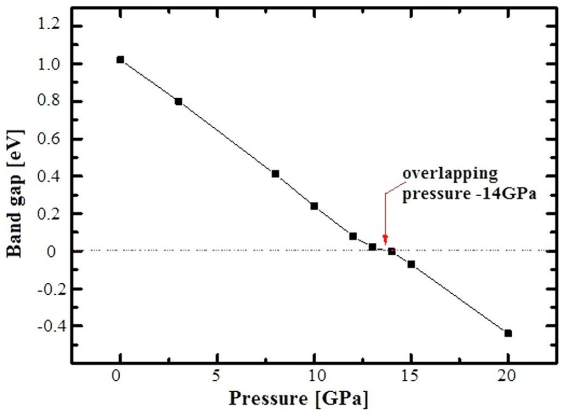

Fig. 2. Ab initio calculated band gap as a function of pressure for $TlInSe_2$. Fermi level is indicated by the dotted horizontal line.

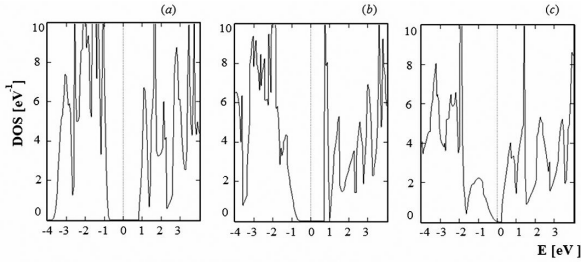

Fig. 3. Calculated DOS of $TlInSe_2$ compound at zero (a), 8 GPa (b) and 15 GPa (c) pressures.

that the metallic properties are not related to phase transition.

Influence of pressure on the effective masses of $TlInSe_2$ compound is considered for the semiconductor state of the crystal in the pressure range 0 GPa to 14 GPa. The valence and conduction band effective masses for tetragonal $TlInSe_2$ at relevant symmetry points of the BZ are presented in Table 1. Results of calculations show that effective masses of holes in the parallel and perpendicular directions to the tetragonal axis reveal strong anisotropy: $m_{h,|}/m_{h,\perp} = 5.1$. It is in good agreement with our previous result (4.7) [8]. As shown in the Table 1, with increasing pressure the ratio of hole effective masses $m_{h,|}/m_{h,\perp}$ in parallel and perpendicular directions to the tetragonal axes are decreased. This, in turn, leads to a decrease in the anisotropy of the crystal. By analyzing the DOS, it can be found that in the metal phase of $TlInSe_2$, the 3p states of Se

Table 1. Ab initio calculated effective masses in parallel and perpendicular directions to the tetragonal c-axes for electrons and holes under pressure. All the masses are given in units of electron free mass m_e.

Pressure [GPa]	Transitions	$m_{h,\perp}$	$m_{h,\vert}$	$m_{e,\perp}$	$m_{h,\vert}$	$m_{h,\vert}/m_{h,\perp}$	$m_{h,DOS}$	$m_{e,DOS}$
0	T→ T	0.504	2.619	0.476	0.478	5.196	0.872	0.476
3	T→ T	0.466	2.201	0.446	0.481	4.723	0.781	0.457
8	(P-N)→ T	0.267	1.147	0.287	0.174	4.293	0.434	0.242
10	(P-N)→ T	0.239	0.992	0.286	0.168	4.150	0.384	0.239
12	(P-N)→ T	0.221	0.877	0.286	0.164	3.986	0.348	0.237
13	(P-N)→ T	0.212	0.834	0.286	0.162	3.933	0.334	0.236
14	(P-N)→ T	0.239	0.936	0.286	0.161	3.916	0.376	0.235

and 6s states of Tl atoms play a key role in the band structure. Therefore, the zone which crosses the Fermi level comes from 3p states of Se and 6s states of Tl atoms.

4. Conclusion

We studied the band structure and effective masses of $TlInSe_2$ under pressure in the range of 0 GPa to 21 GPa. According to the present calculations, with increase of pressure, the band gap decreases and at ∼8 GPa, the fundamental absorption edge changes from direct to indirect gap. The increase of pressure leads to overlapping of bands and reaching zero of the band gap at metallization pressure P ∼ 14 GPa. From DOS calculations it was found that the metallic properties in the crystal manifest themselves due to the 3p states of Se and 6s states of Tl atoms. Phase transition takes place at higher pressure than the "semiconductor-metallic" transition and it means that metallic properties are not related to phase transition.

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References

[1] MULLER D., EULENBERGER G., HAHN H., *Z. Anorg. Allg. Chem.*, 398, (1973) 207.

[2] HANIAS M., ANAGNOSTOPOULOS A.N., KAMBAS K., SPYRIDELIS J., *Phys. Rev. B*, 43, (1991), 4135.

[3] GUSEINOV G.D., MOOSER E., KERIMOVA E.M., GAMIDOV R.S., ALEKSEEV I.V., ISMAILOV M.Z., *Phys. Status Solidi B*, 34, (1969), 33.

[4] MAMEDOV N., WAKITA K., ASHIDA A., MATSUI T., MORI K., *Thin Solid Films*, 499, (2006), 275.

[5] GASHIMZADE F.M., ORUDZHEV G.S., *Dokl. Akad. Nauk Azerb. SSR*, 36, (1980), 18.

[6] ORUDZHEV G.S., MAMEDOV N.T., UCHIKID H., YAMAMOTOC N., IIDAD S., TOYOTAD H., GOJAYEV E., HASHIMZADE F., *J. Phys. Chem. Solids*, 64, (2003), 1703.

[7] YILDIRIM O., *Thesis for the degree of Master of Science in Physics*, Turkish (2005), 47.

[8] ISMAYILOVA N.A., ORUDZHEV G.S., JABAROV S.H., *Mod. Phys. Lett. B*, 31, (2017), 14.

[9] GUSEINOV G., RAMAZANZADE A., KERIMOVA E., ISMAILOV M.Z., *Phys. Status Solidi B*., 22, (1967), K117.

[10] KARPOVICH I.A., CHERNOVA A.A., DEMIDOVA A.I., Izv. Akad. Nauk SSSR, *Neorg. Mater.*, 10, 12, (1974), 2216.

[11] MATIYEV A. KH., GEORGOBIANI A.N., KODIN V.V., MATIYEV M.A., *Ferroelectrics*, 397, (2010), 198.

[12] JABAROV S.H., ORUDZHEV G.S., MAMMADOV T.G., SHIM Y., WAKITA K., MAMEDOV N., KICHANOV S.E., NADJAFOV A.I., ISMAYILOVA N.A., DANG N.T., *ICTMC-20*, 05-09 September, Leopoldina, Halle Germany (2016).

[13] `http://quantumwise.com/`

[14] HOHENBERG P., KOHN W., *Phys. Rev. B,* 136, (1964), 864.

[15] PERDEW J., BURK K., WANG Y., *Phys. Rev. B,* 54, (1996), 16533.

[16] LEE C., YANG W., PARR R.G., *Phys. Rev. B,* 37, (1988), 785.

[17] MONKHORST H.J., PACK J.D., *Phys. Rev. B,* 13, (1976), 5188.

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