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First-Principles Calculation of Electronic Structure and Effective Mass of a $TlInS_2$ Crystal

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Electronic structure, DOS effective mass, conductivity effective mass, reduced effective mass are calculated for a $TlInS_2$ crystal from first principles within the framework of the density functional theory. The electronic structure of $TlInS_2$ is investigated by the Quantum Wise and Quantum Espresso software program packages within the LDA and SGGA corrections, respectively. The band structures calculated with use of the FHI exchange-correlation and relativistic pseudopotentials show that both the valence band maximum and the conduction band minimum located at the Γ point of the Brillouin zone. The top of the valence band and the bottom of the conduction band originate generally from 6*s*-states of Tl atoms and 5*s*-states of In atoms. Influence of the spin–orbit interaction on the electronic structure is investigated. As found, inclusion of the spin–orbit interaction is not essential for the energy states near the gap and removes the band degeneracy along the T–*Z* symmetry line, but does not remove the degeneracy at the T, *Z*, and Γ, *Y* points. The maximum value of the spin–orbit splitting is ≅ 0.3 eV. The effective masses along [001], [010], and [100] directions are calculated taking into account non-parabolicity of the bands. In this paper, DOS effective mass, conductivity effective mass, and reduced effective mass are calculated theoretically for the first time.

Key words: LDA, GGA, spin–orbit interaction, DOS effective mass, conductivity effective mass.

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Для кристалу $TlInS_2$ з перших принципів в рамках теорії функціоналу густини було розраховано: електронну структуру, DOS-ефективну масу, ефективну масу провідности, наведену ефективну масу. Електронну структуру кристалу було вивчено з використанням пакетів програм Quantum Wise та Quantum Espresso, відповідно, в LDA- та SGGA-наближеннях. Зонні структури, розраховані з використанням обмінно-кореляційного потенціялу FHI та релятивістського псевдопотенціялу, показують, що стеля валентної зони і дно зони провідности розташовані в центрі Бріллюенової зони. Стеля валентної зони і дно зони провідности в основному походять з 6*s*-станів атомів Tl та 5*s*-станів атомів In. Також досліджувався вплив спін-орбітальної взаємодії на енергетичний спектер. Було встановлено, що врахування спін-орбітальної взаємодії не є істотним для енергетичних станів поблизу забороненої зони, знімає виродження зон по лінії симетрії T–*Z*, але не знімає виродження в самих точках T, *Z*, а також Г, *Y*. Максимальне спін-орбітальне розщеплення зон становить $\cong 0{,}3$ еВ. З огляду на непараболічність зон було розраховано ефективні маси в напрямках [001], [010], [100]. У цій роботі було вперше теоретично розраховано DOS-ефективну масу, ефективну масу провідности, наведену ефективну масу, що досі не зустрічалися в літературі.

Ключові слова: LDA, GGA, спін-орбітальна взаємодія, DOS-ефективна маса, ефективна маса провідности.

Для кристалла $TlInS_2$ из первых принципов в рамках теории функционала плотности были рассчитаны: электронная структура, DOS-эффективная масса, эффективная масса проводимости, приведённая эффективная масса. Электронная структура кристалла была изучена с использованием пакетов программ Quantum Wise и Quantum Espresso, соответственно, в LDA- и SGGA-приближениях. Зонные структуры, рассчитанные с использованием обменно-корреляционного потенциала FHI и релятивистского псевдопотенциала, показывают, что потолок валентной зоны и дно зоны проводимости расположены в центре зоны Бриллюэна. Потолок валентной зоны и дно зоны проводимости в основном происходят из 6*s*-состояний атомов Tl и 5*s*-состояний атомов In. Также исследовалось влияние спин-орбитального взаимодействия на энергетический спектр. Было установлено, что учёт спин-орбитального взаимодействия не существен для энергетических состояний вблизи запрещённой зоны, снимает вырождения зон по линии симметрии T–*Z*, но не снимает вырождения в самих точках T, *Z*, а также Г, *Y*. Максимальное спин-орбитальное расщепление зон составляет $\cong 0{,}3$ эВ. С учётом непараболичности зон были рассчитаны эффективные массы в направлениях [001], [010], [100]. В этой работе впервые теоретически рассчитаны DOS-эффективная масса, эффективная масса проводимости, приведённая эффективная масса, которые до сих пор не встречались в литературе.

Ключевые слова: LDA, GGA, спин орбитальное взаимодействие, DOS-эффективная масса, эффективная масса проводимости.

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1. INTRODUCTION

The III–III–VI_2 type 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] (see also references therein). As well as layered $Tl{Me}X_2$ (where Me = In or Ga and X = S or Se) crystals, $TlInS_2$ has $C2/c$ space group symmetry at room temperature [2]. The fundamental structural unit of the layer is the In_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 polyhedra into a layer [3]. Absorption spectra of thin films of the $TlInS_2$ crystals are used to study the energy gap and the interband transitions in the energy region of 2–2.4 eV. The direct band gap was determined to be 2.34 eV [4]. Hole, electron, hole–electron pair effective masses of $0.24m_0$, $0.14m_0$ and $0.09m_0$ are obtained from the Hall effect measurements [5]. Obtained from the excitonic and interband transitions' studies of the $TlInS_2$ crystals, reduced masses are $0.15m_0$ [6], $0.17m_0$ [7]. In some studies, we came across some information about effective mass of the crystal; however, this information is not sufficient and in this work made a detailed investigation of the hole electron DOS effective mass, reduced and conductivity effective mass.

2. COMPUTATIONAL METHOD

In this article, we present the results of electronic structure for $TlInS_2$ crystal from the first principles in the framework of the DFT (Density Functional Theory) [8] by the Quantum Wise and Quantum Espresso software program packages, within the Local Density Approximation (LDA) [9] and the Spin Generalized Density Approximation (SGGA) [10], respectively.

The lattice parameters and the equilibrium atomic positions in a unit cell were determined by the minimization of the Hellmann–Feynman forces until forces and stresses were less than 0.0001 eV/Å and 0.0001 eV/Å^3, respectively. The Perdew–Burke–Erenzhorf (PBE) exchange–correlation functional and Double Zeta Polarized basis sets were used in our calculations. The wave function was expanded taking into account plane waves with energies of up to 150 Ry, which provide a good convergence of the total energy. Lattice parameters of the optimized structure in good agreement with experimental result [11] and differ from them only $\cong 1\%$. The electron configuration of atoms in HGH pseudopotentials were chosen as (core + electron) $Tl[Xe]4f^{14} + 5d^{10}6s^26p^1$, $In[Kr] + 4d^{10}5s^25p^1$ and $S[Ne] + 3s^23p^4$, and in FHI pseudopotentials were chosen as $Tl[Xe]4f^{14}5d^{10} + 6s^26p^1$, $In[Kr]4d^{10} + 5s^25p^1$, $S[Ne] + 3s^23p^4$.

3. RESULTS AND DISCUSSION

Let us examine the band structures calculated by different methods separately. The band structure calculated by using FHI pseudopotential show that the valence band maximum and minimum of the conduction band located at the Γ point of the Brillouin zone (Fig. 1). Therefore, $TlInS_2$ is a direct band gap semiconductor as obtained in the spectroscopic measurements [4]. The band gap obtained by HGH and FHI pseudopotentials are 1.43 eV and 1.25 eV, respectively, and are smaller than experimental one (2–2.3 eV) [4]. It is well known that the LDA and GGA usually underestimate the band gaps of the Kohn–Sham electronic band structure. The electronic structure calculated by HGH pseudopotential has been widely discussed in our work [12].

The spin–orbit splitting has been investigated by using full-relativistic pseudopotential in Quantum Espresso.

In electronic structure calculated by the SGGA, fundamental absorption edge of crystal is formed with direct transition. The values of band gap and lattice parameters are given in Table 1. According to the calculated structures by the SGGA in Quantum Espresso and Quantum Wise, the spin–orbit interaction influences along the symmetry line of T–*Z* (Fig. 2).

Thus, excluding T and *Z* symmetry points, along this line, double degeneracy of the bands is removed by taking into account the spin–orbit interaction.

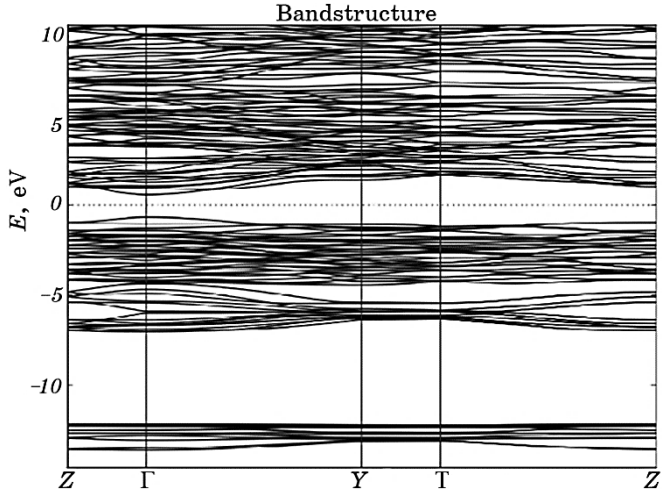

Fig. 1. Electronic structure calculated within the LDA by means of the FHI pseudopotential.

It is not observed degeneracy in the other symmetry points and symmetry lines. In spite of band gap gets smaller to 0.2 eV, in general,

TABLE 1. Lattice parameters and band gap calculated within the LDA using the FHI and HGH pseudopotentials and within the SGGA using the full relativistic pseudopotential.

	Quantum wise	Quantum espresso	Exp. [11]
	LDA (FHI, HGH)	SGGA (full-relativistic)	
a (Å)	10.800	11.0146	10.90
b (Å)	10.845	11.0132	10.90
c (Å)	15.054	15.3488	15.19
β (°)	100.375	100.27	100.55
E_g (eV)	1.25 (FHI),1.43 (HGH)	1.25	2.35

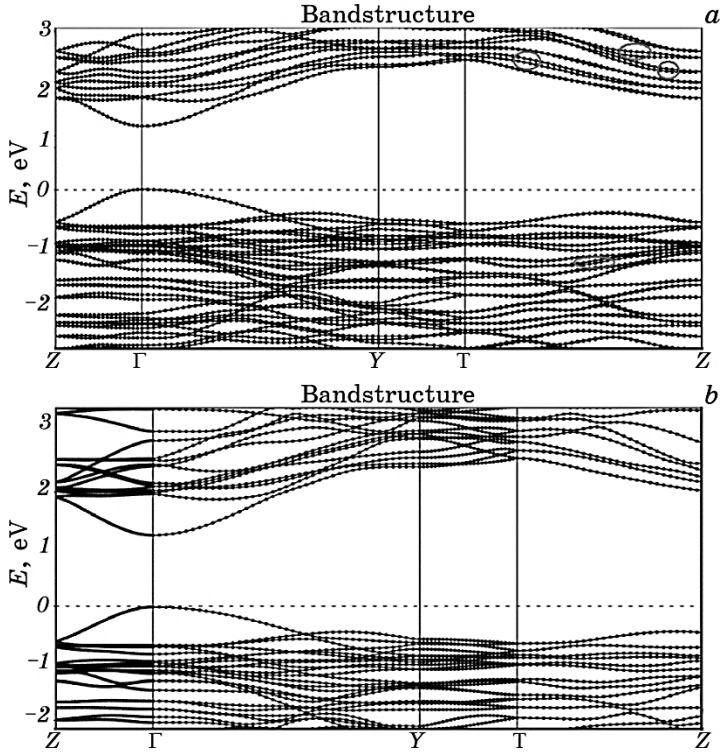

Fig. 2. Electronic structure calculated by Quantum Espresso program excluding the spin–orbit interaction (used pseudopotential is relativistic) (*a*) and electron spectrum calculated with taking into account the spin–orbital interaction (used pseudopotential is full relativistic) (*b*).

spin–orbit interaction does not influence seriously on surrounding state of band gap. The splitting observed in lower parts of conductivity bands, which are formed from 5*s*-electron states of In atoms.

It is also calculated DOS effective mass, conductivity effective mass, reduced effective masses of electrons and holes within the LDA by the FHI pseudopotential using 11×11×11 **k**-point sets. Taking into account non-parabolicity of maximum of the valence band and minimum of the conduction band at the Γ point, effective mass is calculated by $E(1+\alpha E)=\frac{h^2k^2}{2m^*}$. Here, the quantity of parabolic characterize is α. In our software calculations, **k**-points were expressed with basis translations of the reciprocal lattice, and directions were taken as O*X*— $\mathbf{g}_1-\mathbf{g}_2$, O*Y*— $\mathbf{g}_1+\mathbf{g}_2$, and O*Z*— $\mathbf{g}_3$.

Note that direction $\mathbf{g}_1-\mathbf{g}_2$ in fact is different from direction O*X* by $\cong 10°$. Nevertheless, this difference in direction does not affect the results, and the relative error is not more than 2%. Here, basis translations of the reciprocal lattice are as follow:

$$\mathbf{g}_1 = 2\pi\left(\frac{1}{a},\frac{1}{b},\frac{1}{a}\tan\left(\beta-\frac{\pi}{2}\right)\right),$$

$$\mathbf{g}_2 = 2\pi\left(-\frac{1}{a},\frac{1}{b},-\frac{1}{a}\tan\left(\beta-\frac{\pi}{2}\right)\right),$$

$$\mathbf{g}_3 = 2\pi\left(0,0,\frac{1}{c\cos\left(\beta-\pi/2\right)}\right).$$

Calculated effective masses for each of the three directions of electron (hole) were given in Table 2. Calculated value for electron (hole) effective mass, $0.14m_e$ ($0.24m_e$), in the $\mathbf{g}_3$ direction is in a good agreement with experimental effective mass for electron (hole) $0.14m_e$ ($0.19m_e$) in this direction [5].

TABLE 2. The electron and hole effective masses in directions O*Z*, O*Y*, O*X* calculated within the LDA. All the masses are given in units of free electron mass.

Directions	LDA (FHI)		Exp. [3]	
	m_e^*	m_h^*	m_e^*	m_h^*
$\mathbf{g}_3 \uparrow\uparrow OZ$	0.14	0.19	0.14	0.24
$\mathbf{g}_1+\mathbf{g}_2 \uparrow\uparrow OY$	0.33	0.71		
$\mathbf{g}_1-\mathbf{g}_2 \uparrow\uparrow OX$	0.28	0.59		

TABLE 3. Calculated electron (hole) DOS, conductivity and reduced effective masses. All the masses are given in units of free electron mass.

$m^*_{e\,\mathrm{DOS}}$	$m^*_{h\,\mathrm{DOS}}$	$m^*_{e\mathrm{con}}$	$m^*_{h\mathrm{con}}$	m^*_{red}	$m^*_{\mathrm{red}}(111)$	$m^*_{\mathrm{red}}(001)$	$m^*_{\mathrm{red}}(001)$ Exp. [6], [7]
0.24	0.41	0,22	0.35	0.15	0.20	0.17	0.15

For calculation DOS effective mass, we used

$$m^*_{e(h)\mathrm{DOS}} = M^{\frac{2}{3}}_{e,(h)}(m^*_{e(h)x}m^*_{e(h)\mathrm{y}}m^*_{e(h)z})^{\frac{1}{3}}. \qquad (1)$$

Here, $M_{e,(h)}$ is number of equivalent valleys for electrons and holes. The conduction (valence) band minimum (maximum) is located in the centre of the Brillouin zone. For this reason, numbers of equivalent values in both cases were equal to unit. Here, $m^*_{e,(h)x}$, $m^*_{e,(h)y}$ and $m^*_{e,(h)z}$ are electron (hole) effective masses in the direction of a coordinate axis. Similarly, for calculation of conductivity effective mass, we used

$$m^*_{e(h)\mathrm{con}} = \frac{3}{(m^*_{e,(h)x})^{-1} + (m^*_{e,(h)y})^{-1} + (m^*_{e,(h)z})^{-1}}, \qquad (2)$$

$$m^*_{e\,\mathrm{con}} = 0.221\,m_e,\ \ m^*_{h\,\mathrm{con}} = 0.355\,m_e.$$

Reduced effective mass $m^*_{\mathrm{red}} = 0.15\,m_e$ (Table 3) was calculated using values of the three mutually perpendicular directions electron and hole effective masses. Note that obtained reduced effective mass in [6] and [7] experimental works was carried out only by the (001) plane. For calculated reduced effective mass in this plane, we have found geometric mean effective masses of hole and electron, which are calculated parallel to the axis O*Y* and O*X*. Obtained result, $0.20m_e$, is in a good agreement with experimental results: $0.17m_e$ [6] and $0.15m_e$ [7].

4. CONCLUSION

Calculated electronic structure by the Quantum Wise and Quantum Espresso software within the LDA, SGGA in different pseudopotential show that valence band maximum and conductivity band minimum are located at the Γ point of the Brillouin zone. Spin–orbit interaction removes double degeneracy along the symmetry T–*Z* line, excluding symmetry T and *Z* points. Maximum spin–orbit splitting is of 0.3 eV.

Calculated DOS effective masses of electron and hole are $m^*_{e\,\mathrm{DOS}} = 0.24\,m_e$ and $m^*_{h\,\mathrm{DOS}} = 0.41\,m_e$, respectively. Conductivity effective masses of electron and hole are $m^*_{e\,\mathrm{con}} = 0.221\,m_e$ and $m^*_{h\,\mathrm{con}} = 0.355\,m_e$, respectively. Reduced effective mass is $m^*_{\mathrm{red}} = 0.15\,m_e$,

and in-plane (001) reduced effective mass is $m^*_{\mathrm{red}(001)} = 0.20\, m_e$.

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