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The Band Structure of $TlGaSe_2$ Crystals

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Abstract

Energies of electron transitions for the energy diapason 2 - 6 eV were identified from the analysis of reflection and wavelength modulated reflection spectra measured at temperature 30 K. Bands parameters were determined in framework of theoretically calculated band structure. The spectral dependencies of optical functions were calculated and the interpretation of observed electron transitions was suggested.

Keywords

Semiconductor Compound, Optical Absorption and Reflection Spectra, Kramers-Kronig Relations, Optical Constants, Band Structure

1. Introduction

$TlGaSe_2$ crystals are a group of triple thallium chalcogenide compounds with a well pronounced layered structure. $TaGaSe_2$, $TlGaS_2$ and $TlInS_2$ semiconductors crystallize as a layered structure and have monoclinic lattice at room temperature and atmosphere pressure according literature data [1, 2]. These crystals have a strong anisotropy of physical characteristics due to the specificity of the crystal structure [1 -3].

The temperature and pressure influence on the optical spectra near the absorption edge in $TlGaS_2$ crystals was studied [4 - 11]. The Raman scattering at different geometries and temperatures (from 77 to 400 K) was investigated [12]. Polar vibrational LO and TO modes and their main parameters were extracted from reflection vibrational spectra measured for 4000 - 50 cm^{-1}. Calculations of anions and cations relative effective charges for E||a and E||b polarizations show the difference in iconicity degree of cations and anions along axes a and b [12]. The switching phenomenon in current-voltage and optoacoustic characteristics was discovered in these crystals [13 - 15]. There are a lot of references dedicated to investigations of these materials (see Ref. [4 - 16]).

Spectra of wavelength modulated reflection and transmission for energies 2 - 6 eV were investigated in present work. The new data of excitonic states and electron transitions in intrinsic region for $TlGaSe_2$ crystals were received. The spectral dependencies of optical functions for investigated energies were calculated.

2. Experimental Methods

Low-temperature spectra of $TlGaSe_2$ crystals were measured by high-aperture spectrometer MDR-2 with linear dispersion 7Å/mm and aperture ratio 1:2. Photoelectric multiplier PMP-136 was used as detector. The optical systems are computerized. Wavelength modulated spectrawere registered at frequencies 89 Hz. The optical system allows registering data with bandwidth 0.2Å (±0.1 meV). Transmission and reflection interference spectra were registered with accuracy ±0.2 meV. The cleaved crystals of $TlGaSe_2$ with different thicknesses were mounted into the LTS-22 C 330 optical helium cryogenic system.

3. Experimental Results and Discussion

3.1. Electron Transitions and Optical Functions of $TlGaSe_2$ Crystals in the Absorption Band Depth

Figure 1 shows the spectral dependence of reflectivity of

$TlGaSe_2$ in E||a polarization measured at temperature 300 K. Downstairs one can see the spectral dependence of wavelength modulated reflectivity measured at energies 2 - 6 eV. Maxima A1 - A11 and B1 - B11 were observed in intrinsic region of reflection spectra in E||a and E||b polarizations, respectively (see Fig. 1). Maxima of reflection spectra are grouped into the four groups. The most long-wavelength group is formed in the region of exitonic transitions (A, B, C and D). The second group is situated at energies 2.9 - 3.6 eV, the next group at 4 eV and the most high-energy group at 5 - 6.5 eV.

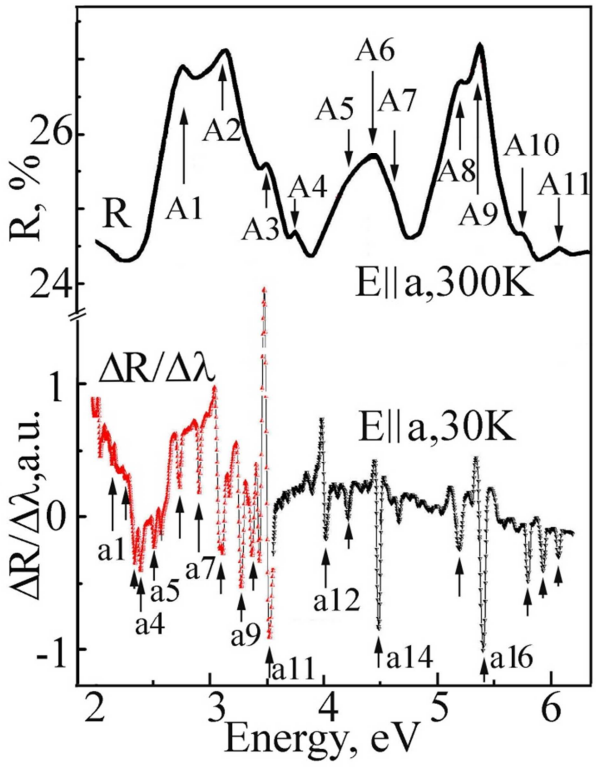

Fig. 1. *Reflection (R) and wavelength modulated reflection (ΔR/Δλ) spectra of $TlGaSe_2$ crystals measured at temperatures 300 K and 30 K in E||a polarization.*

The wavelength-modulated spectra have more well pronounced peaks at temperature 30 K in both polarizations (E||a and E||b). It was recognized a1 - a19 and b1 - b19 peaks in E||a and E||b polarizations, respectively (see Fig. 1 and 2). These data are evidence of the big amount of direct electron transitions which take place between maxima of valence bands and minima of conduction bands.

The theoretical calculations of $TlGaTe_2$ [17, 18], $TlInTe_2$ [19], $T1GaSe_2$ [20 - 22], $TlInSe_2$ [23], TlSe [24], TlS [25], $TlGaS_2$ [26, 27] crystals band structure were carried out in wide energy diapason of interband transitions and for a lot of points of Brilloin zone. The common features of band structure and the family likeness of optical spectra were discovered in the crystals of thallium base. The same behavior is observed in all well-investigated crystals (Si, Ge, $A^{III}B^{V}$ and $A^{II}B^{VI}$ compounds). For all investigated crystals the direct electronic transitions discovered in reflection spectra at energies $E \geq E_g$ take place in the points of Brullouin zone where maxima of valence bands and minima of conduction bands have the same wave-vector value.

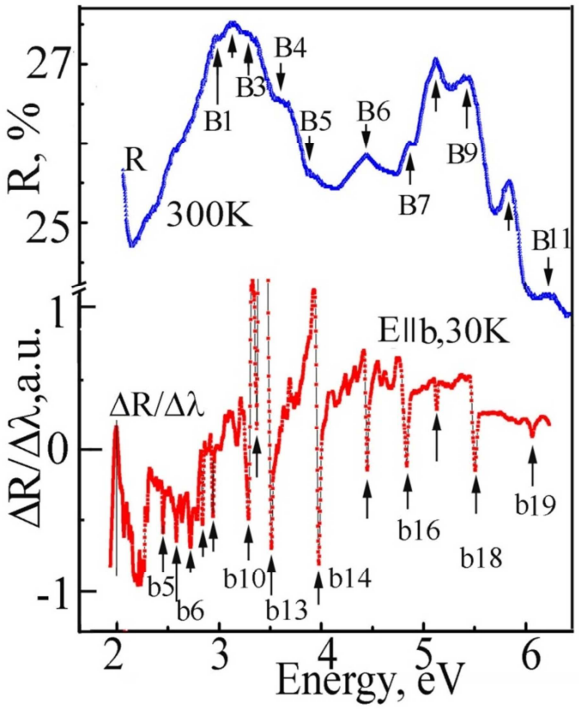

Fig. 2. *Reflection (R) and wavelength modulated reflection (ΔR/Δλ) spectra of $TlGaSe_2$ crystals measured at temperatures 300 K and 30 K in E||b polarization.*

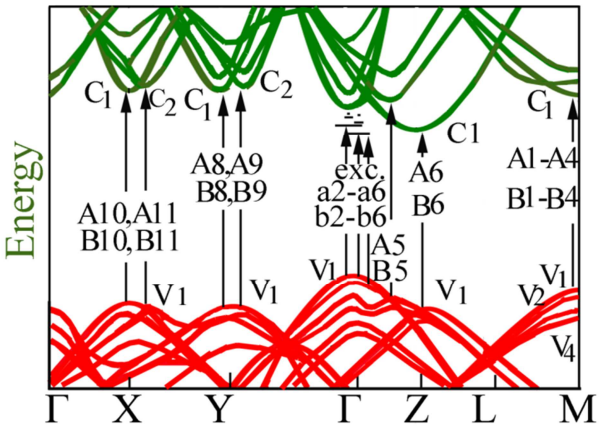

Fig. 3. *The fragment of band structure of $TlGaSe_2$ crystal according theoretical calculations of Ref. [22].*

According the theoretical calculations of band structure the top valence band maximum in$TlGaSe_2$crystals are localized in $\Gamma(2A_2)$ point [20 - 22]. The lowest level of conduction band according Ref. [20, 21] is localized in Z - Y point. According the later calculations of authors Ref. [22] the lowest minimum of conduction band is localized in Γ - L direction (See Fig. 3).Additional minima of conduction band situate in points Y, X and M. The indirect transitions at energy 2.054 eV (T = 5 K) [3, 5] and direct transitions at 2.128 eV (T = 5 K) [4, 16] were observed in $TlGaSe_2$ crystals.

The theoretical calculations were carried out without a spin-orbital interaction and possible splitting due to crystal field. This means that bands are degenerated in all points of Brillouin zone for theoretically calculated band structure. In real band diagrams the bands are split and the amount of valence and conduction bands extrema is more than expected according theory.

According theoretical calculations of band structure [21-23] the valence band in crystal $TlGaSe_2$ is formed by single-electron states 6s of selenium ions and 4s states of gallium ions. The conduction band is formed by single-electron 6s states of gallium, 6p states of thallium and 4p states of selenium ions. The formula of $TlGaSe_2$ compound according data of Ref. [9, 10] could be written as $T1^{+}(Ga^{3+}Se_2^{2-})^{1-}$. Taking into account configuration of Se^{2-} and Ga^{3+}ions at loss or capture of electron it have been concluded that the top of valence band is due to 4pstates of selenium ions $3p^5$ (term $^2P_{1/2}$) and the conduction band is caused by sstates of gallium ions $3d^{10}4s$ (term $^2S_{1/2}$).

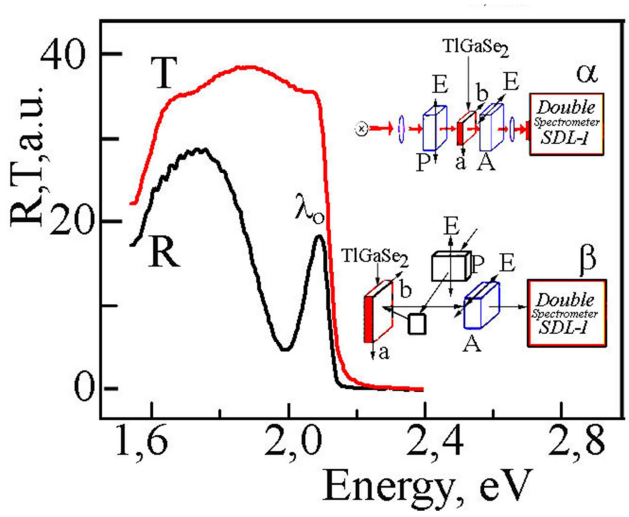

Fig. 4. *Transmission (T) and reflection (R) spectra of $TlGaSe_2$ crystals in crossed polarizers measured at temperature 10 K. Inserts show the schemes of transmission (α) and reflection (β) spectra measurement in crossed polarizers.*

3.2. Optical Functions for E >E_g

$TlGaSe_2$ are layered birefringence crystals with anisotropy of interatomic interaction forces. The birefringent crystals are used in different devices as polarizers, interferometers, dispersion compensators, deflectors and etc.). The different expansion velocities of light waves for different directions of birefringent crystals allow developing devices with interesting properties. Polarizations states (i.e. ordinary and extraordinary waves existing) making difference of effective length way for these polarization states determines the main using of such materials. The ordinary and extraordinary light beams passing through crystal have different degree of refractivity and thus consume propagation difference. These beams interfere in crystal.The above-mentionedgives big possibilities and wide application areas of these properties as band-pass and band-elimination filters. These properties are most interesting in layered crystals on the base which the different nanoelectronic devices were developed. The spectral dependence of refractive index in birefractive crystalsdistinguishes for different light wave polarizations. This differ is significant as for intrinsic and extrinsic areas of crystals. This fact is very important for nanoelectornic.

Figure 4 shows the transmission and reflection spectra of $TlGaSe_2$ crystal deposed between two crossed polarizers. One can see on inserts of Fig. 4 schemes for measurementsof these spectra. The crystal was deposed in cryostat and cooled down to temperature 10 K. The transmission spectrum does not show some well pronounced features (see curve T on Fig. 4). The reflection spectrum has a broad line near 1.7 - 1.8 eV and a sharp line $\lambda_0$at 2.0933 eV (curve R on Fig. 4). The energy of λ_0 line is less than energy of indirect excitonic transitions $\Gamma(V_1)\rightarrow Z\text{-}L(C_2)$ (2.1278 eV) and high than energy of direct excitonic transitions $\Gamma(V_1)\rightarrow Z\text{-}L(C_1)$ (2.045 eV).

Refractive indexes for polarizations E||a and E||b are equal and the crystal is isotropic at λ_0 wavelength that leads to the increasing of transmission at this wavelength. At $\lambda > \lambda_0$ and $\lambda < \lambda_0$ light waves are propagate like in birefringence crystal outside the isotropic wavelength. This phenomenon is observed in transmission spectra at corresponding crystal thicknesses. The isotropic wavelength can be observed and at another wavelength i.e. in the depth of absorption band. For this it is necessary to determine the spectral dependencies of refractive indexes for corresponding polarizations into the depth of absorption band. These dependencies of refractive indexes in intrinsic region for $TlGaSe_2$ crystals in polarizations E||a and E||b were calculated from measured reflection spectra by Kramers-Kronig analysis.

It is well known that the amplitude of reflectivity R relates with phase φ of reflected beam by the following equation:

$$r = \sqrt{R}e^{-i\phi} \tag{1}$$

The spectral dependence of reflection coefficient R and optical constants n, k, φ, ε_1, ε_2 bind to each other via following relations:

$$\begin{cases} r = \dfrac{N-1}{N+1} = \dfrac{n+ik-1}{n+ik+1} \\ r = \sqrt{R}\,e^{-i\phi} = \sqrt{R}(\cos\phi - i\sin\phi) \end{cases} \Rightarrow \begin{cases} n = \dfrac{1-R}{1-2\sqrt{R}\cos\phi + R} \\ k = \dfrac{2\sqrt{R}\sin\phi}{1-2\sqrt{R}\cos\phi + R} \end{cases} \tag{2}$$

The amplitude of reflectivity simultaneously with its phase should be determined for each wavelength i.e. $R \approx R(\omega)$ and $\varphi \approx \varphi(\omega)$. The phase of reflected beam correlates with reflection coefficient by Kramers-Kronig integral:

$$\phi(\omega_0) = \frac{\omega_0}{\pi}\int_0^{\infty} \frac{\ln R(\omega)}{\omega_0^2 - \omega^2}\,d\omega \tag{3}$$

To determine the phase of reflected beam from experimentally measured reflectivity, it is necessary to make measurements for an infinite diapason of frequencies. The

measurements of reflection spectra are possible for a limited energy interval ($\omega_a - \omega_b$) and in our case are made for energies from 2 to 6 eV. For calculation of phase φ we used a well known approach [6, 7] based on the assumption that in the high-energy part of the spectrum, where the measurements have not been executed, thereflectivity spectral dependence can be extrapolated by help of decay function. The function $R(\omega) = c\omega^{-p}$ (where c and p are constants) for the spectral diapason $b \le \omega \le \infty$ was used [6, 7]. The approach $R(\omega) = R(a)$ was applied for frequencies $0 \le \omega \le a$. The calculated phase φ and the measured reflectivity R allow to determine optical functions n, k, ε_1, ε_2.

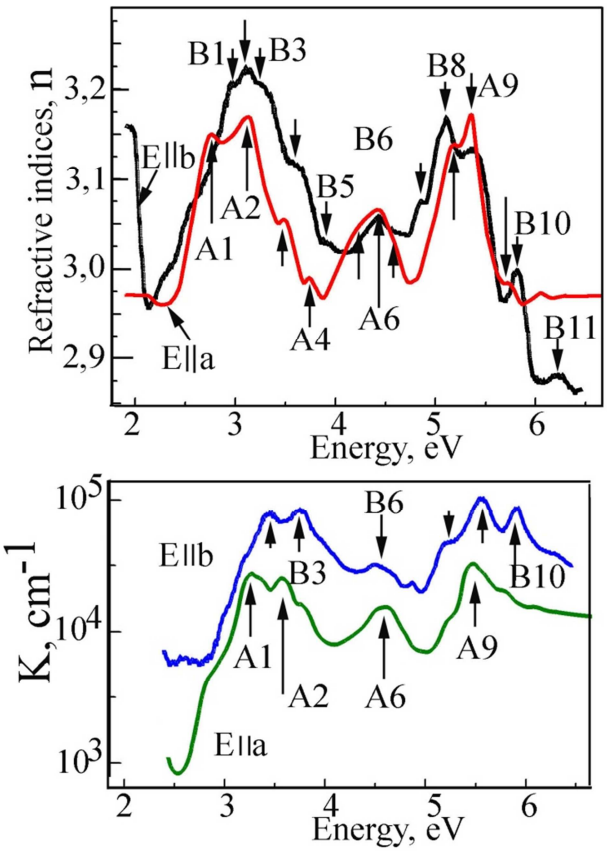

Fig. 5. *The spectral dependence of refractive index (n) and absorption coefficient (K) of $TlGaSe_2$ crystals calculated from reflection spectra by Kramers-Kronig relations.*

Figure 5 shows the spectral dependencies of refractive index (n) and absorption coefficient (K) of $TlGaSe_2$ crystals. The same features and at almost the same energies like in reflection spectra were observed and in refractive index spectra (see Fig. 5). The absorption coefficients for both polarizations have values more than 10^4 cm^{-1}. The spectral dependencies of complex dielectric constant real ε_1 and imaginary ε_2 parts were calculated by Kramers-Kronig analysis (see Fig. 6). The features of both functions have a good correlation with ones A1 - A1 and B1 - B11 from reflection spectra.

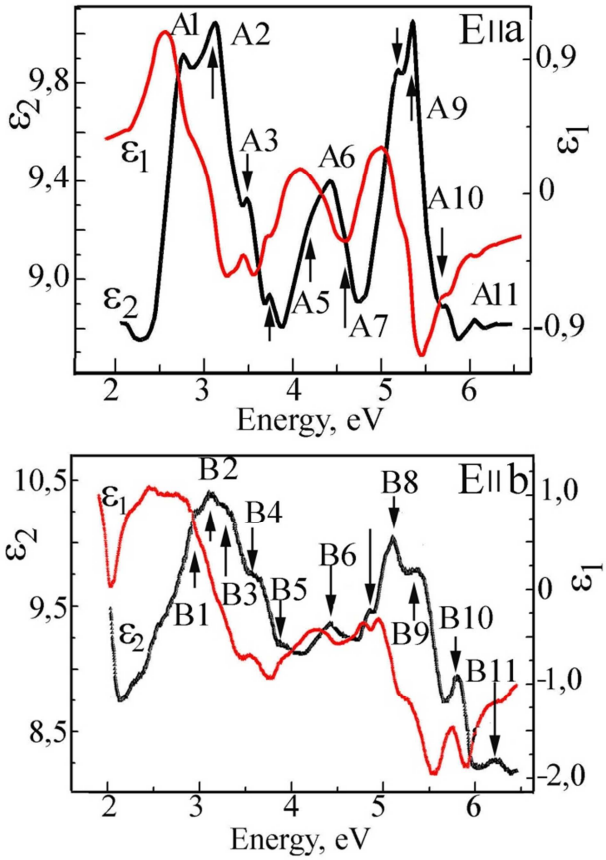

Fig. 6. *The spectral dependence of permittivity real (ε_1) and imaginary (ε_2) parts for $TlGaSe_2$ crystals received form calculations of reflection spectra measured in E||a and E||b polarizations at temperature 300 K.*

4. Conclusion

Investigated reflection spectra at 300 K and wavelength modulated reflection spectra at 30 K of $TlGaSe_2$ crystals in E||a and E||b polarizations show features caused by direct electron transitions in actual points of Brillouin zone. The results of reflection spectra calculations by Kramers-Kronig method prove the anisotropy of optical functions and electron transitions for energy diapason 2 - 6 eV. The isotropic wavelength at 2.0933 eV was discovered for samples deposed in crossed polarizers.

References

[1] D. Muller, E. Poltmann, H. Hahn, *Zur structur ternarer Chalkogenide des Thalliums mit Aluminium and Indium*, Zeitschrift für Naturforschung,29(1) (1974) 117-118.

[2] D. Muller, H. Hahn, *Untersuchungen über ternäre Chalkogenide. XXIV. Zur Struktur des $TlGaSe_2$*, Zeitschrift für anorganische und allgemeine Chemie , 438(1) (1978) 258-272.

[3] Klaus-Jürgen Range, Günther Mahlberg, Sigrid Obenland, K.J. Range, G. Mahleberd, S. Obenland, *Notizen: Hochdruckphasen von $TlAlSe_2$ und TlGaSe, mit TlSe-Struktur / High Pressure Phases of $TlAlSe_2$ and $TlGaSe_2$ with TlSe-type Structure*, Zeitschrift für Naturforschung B, 32(11) (1977) 1354-1355.

[4] S. N. Mustafaeva, E.M. Kerimova, N.Z. Gasanov, *Exciton characteristics of intercalated $TlGaSe_2$ single crystal,* Semiconductors, 32(2) (1998) 145-147.

[5] A. V. Sheleg, O.B. Plusch, V.A. Aliev, *X-ray investigation of incommensurate phase in β-$TlInS_2$ crystals*, Solid State Physics, 36(1) (1994) 226-230.

[6] E. M. Kerimova, S. N. Mustafaeva, R. N. Kerimov, G. A. Gadzhieva, *Photo- and roentgenoconductivity of $(TlGaS_2)_{1-x}(TlInSe_2)_x$crystals*, Inorganic Materials, 35(11) (1999) 1123.

[7] S.B. Vakhrushev, V. V. Zhdanova, B.E. Kvyatkovskii, N.M. Okuneva, K.R. Allakhverdiev, R.A. Aliev, R.M. Sardarly, *Incommensurate phase transition in a $TlInS_2$ crystal*, JETP Letters, 39(6) (1984) 291-293.

[8] S.G. Guseinov, G.D. Guseinov, N.Z. Gszanov, S.B. Kiazimov, *Special features of exciton absorption spectra of $A^{III}B^{III}X_2^{VI}$-type layer-semiconductor crystals*, Physica Status Solidi (b), 133(1) (1986) K25-K30.

[9] S.G. Abdulaeva, S.S. Abdinbekov, G.G. Guseinov, *Electroabsorption in monocrystals $TlGaSe_2$ and $TlGaS_2$*, DAN AzSSR, 36(8) (1980) 34. (in Russian)

[10] N.M. Gasanli, B.N. Mavrin, Kh. E. Sterin, V.I. Tagirov, Z.D. Khalafov, *Raman study of layer $TlGaS_2$, β-$TlInS_2$, and $TlGaSe_2$ crystals*, Physica Status Solidi (b), 86 (1978) K49-K53.

[11] N.M. Gasanli, N.N. Mel'nik, A.S. Ragimov, V.I. Tagirov, Solid State Physics, 26(2) (1984) 558.

[12] N.N. Syrbu, V.E. L'vin, I.B. Zadnipru, H. Neumann, H. Sobotta, V. Riede, *Raman and infrared vibration spectra in $TlGaS_2$ crystals*, Semiconductors, 26(2) (1992) 232-245.

[13] K.R. Allakhverdiev, T.G. Mamedov, R.A. Suleymanov, N.Z. Gasanov, *Pressure and temperature effects on electronic spectra of $TlGaSe_2$ type crystals*, Fizika, 8 (2002) 44-47.

[14] S.A. Husein, G. Attia, S.R. Alharbi, A.A. AlGhamdi, F.S. AlHaxmi, S.E. AlGarni, *Investigation of the switching phenomena in $TlGaSe_2$ single crystal*, JKAU: Sci., 21(2009A.D./1430A.H.) 27-29.

[15] V. Grivickas, V. Bigbajevas, V. Gavriusinas, J. Linnros, *Photoacoustic pulse generation in $TlGaSe_2$ layered crystals*, Materials Science (Medziagotyra), 12(2006)4-8.

[16] S.G. Abdulaeva, N.T. Mamedov, G.S. Orudznev, *Near-band-edge optical properties of $TlGaS_{2x}Se_{2(1-x)}$mixed crystals*, Physica Status Solidi (b), 102 (1980) K19-K22.

[17] K. Okazaki, T. Tanaka, J. Matsuno, A. Fujimori, L.F. Mattheiss, S. lida, E. Kcrimova, N. Mamcdov, *Angle-resolved photoemission and band-structure results for linear chain $TlGaTe_2$*, Physical Review B, 64, (2001) 045210.

[18] E.M. Godjaev, G. Orudzhev, D.M. Kafarova, Solid State Physics, 46(5) (2004) 811.

[19] G. Orudzhev, E.M. Godjaev, R.A. Kerimova, E.A. Allahiarov, *Band structure and optical properties of chain compound $TlInTe_2$*, Solid State Physics, 48 (2006) 40-43.

[20] S.G. Abdulaeva, N.T. Mamedov, G.S. Orudznev, *Band structure of $TlGaSe_2$*, Physica Status Solidi (b), 119 (1983) 41-48.

[21] S.G. Abdulaeva, N.T. Mamedov, *Band structure of $TlGaSe_2$ ternary layered crystals*, Physica Status Solidi (b), 133 (1986) 171-177.

[22] S. Kashida, Y. Yanadori, Y. Otaki, Y. Seki, A.M. Panich, *Electronic structure of ternary thallium chalcogenide compounds*, Physica Status Solidi (a), 203(11)(2006) 2666-2669.

[23] G. Orudzhev, N. Mamedov, H.Uchiki, N. Yamamoto, S. lida, H. Toyota, E. Gojacv, F. Hashimzade, *Band structure and optical functions of ternary chain $TlInSe_2$*, Journal of Physics and Chemistry of Solids, 64 (2003) 1703-1706.

[24] S. Ellialtioglu, E. Mete, R. Shaltaf, K. Allakhverdiev, F. Gashimzade, M. Nizametdinova, G. Orudzhcv, *Electronic structure of the chainlike compound TlSe*, Physical Review B, 70(19)(2004) 195118.

[25] M P Hanias, A N Anagnostopoulos, K Kambas and J Spyridelis, *Electrical and optical properties of as-grown $TlInS_2$, $TlGaSe_2$ and $TlGaS_2$ single crystals*, Materials Research Bulletin, 27(1) (1992) 25-38.

[26] I.S. Gorban`, O.B. Ohrimenko, *Parameters of excitonic absorption in $TlGaS_2$ crystal*, Solid State Physics, 43 (2011)1963-1965.

[27] I.G. Stamov, N.N. Syrbu, V.V. Ursaki, V.V. Zalamai, *Birefringence and excitonic spectra of $TlGaS_2$ crystals*, Optics Communications, 298-299 (2013) 145-149.