Wavelength Modulated Optical Spectra of $TlGaS_2$ Crystals

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***Abstract* – Wavelength modulated reflection spectra measured at temperatures 14 K and 300 K in E||a and E||b polarizations for $TlGaS_2$ crystals were investigated. The ground and excited states of excitons B_{2u} in E||a polarization and B_{3u} in E||b polarization were observed and the main parameters of exitons and bands were determined. The optical functions for wide energies (2 - 6 eV) were calculated by Kramers-Kronig analysis of reflection spectra. The wavelengths of isotropic points in $TlGaS_2$ crystals were defined.**

***Keywords* – semiconductor compound; optical absorption and reflection spectra; wavelength modulated spectra; Kramers-Kronig relations; optical constants; band structure.**

I. Introductions

$TlGaS_2$ crystals belong to triple thallium chalcogenides with well-pronounced lamellar structure. Due to specificity of crystal structure these crystals have a strong anisotropy of physical properties [1 - 8]. The authors of Ref. [3] report about a high sensitivity of $TlGaS_2$ monocrystals in x-ray diapason at energies 25 - 50 keV. The dependence of the crystal conductivity on intensity of x-ray radiation dose has a power-law character. Raman scattering spectra for different geometries and they temperature dependences for temperatures 77 - 400 K were investigated in $TlGaS_2$ crystals [9]. The vibrational reflection spectra in the region 50 - 4000 cm^{-1} were investigated and the main parameters of polar vibrational LO and TO modes were distinguished. The calculations of relative effective charges of anions and cations in E||a and E||b polarizations show a difference of its ionicity degree along axes a and b [9]. These materials were intensively investigated (see Ref. [9 - 13, 15]). The birefringence effects and reflection spectra of excitons were investigated for these crystals by our research group [14].

This work is dedicated to the investigation of excitonic states and electron transitions in $TlGaS_2$ crystals. Wavelength modulated reflection spectra for energies 2 - 6 eV at temperatures 300 K and 14 K in E||a and E||b polarizations were investigated. The ground and excited states of excitons B_{2u} in E||a and B_{3u} in E||b polarizations were observed and the main parameters of excitons and bands in k = 0 were determined. Optical functions for wide energy diapason (2 - 6 eV) in E||a and E||b polarizations were calculated. The isotropic points (where crystal is isotropic) of $TlGaS_2$ crystal was identified.

II. Experimental Methods

The crystals grown by Bridgman method have 2×1×1 cm size and easy can be cleaved. The optical measurements were carried out on computerized spectrometers MDR-2, SPECORD M40 and JASCO-670. The low-temperature spectra were measured on samples mounted on cold-finger of Helium optical cryogenic system LTS-22 C 330.

III. Experimental Results and Discussions

Excitonic spectra in $TlGaS_2$ crystals

The structure of $TlGaS_2$ is described by C_{2h}^6 space group according crystallographic data. The unit cell has eight formula units. The main motive of structure is formed by tetrahedral polyhedrons Ga_4S_{10} consist of four tetrahedrons of GaS_4. The structure $TlGaS_2$ is pseudo-tetragonal since a = b = 10.31 Å, c = 15.16 Å and β = 99.7° [6]. The narrow peak at 2.605 eV due to forming of direct exciton in Brillouin zone center is observed in region of edge absorption at temperature 1.8 K in E||c polarization [7, 8]. The value of absorption in the maximum of excitonic peak is larger than 2000 cm^{-1}. Since crystals $TlGaS_2$ are cleft perpendicular to crystallographic axis c so absorption spectra are measured for two polarizations of light waves E||a and E||b. Figure 1, A shows absorption spectra of crystals $TlGaS_2$ measured in E||a and E||b polarizations at temperatures 9 - 300 K. The excitonic peaks are observed in both polarizations and shift to higher energies. The temperature shift coefficient of exciton maxima β is equal to 2.4×10^{-4} eV/K and 3.5×10^{-4} eV/K in E||a and E||b polarizations, respectively. The value of absorption coefficient in excitonic peaks maxima corresponds to 4000 cm^{-1}. These results confirm the results of Ref. [8, 14] that excitonic transitions are allowed for these polarizations. Figure 1, C shows wavelength modulated transmission spectra measured at temperature 14 K in E||a and E||b polarizations. The indirect transitions [5, 12] considerably situated at energies 2.3 - 2.5 eV are not observed by us in both absorption spectra and wavelength modulated transmission spectra. The interference was observed in wavelength modulated transmission spectra measured at temperature 14 K at energies E < 2.55 eV.

The well-pronounced interference right up to 3 eV was discovered in wavelength modulated reflection spectra of 7.5 μm thickness crystals in E||a and E||b polarizations (see Fig. 2). Figure 2, A shows the wavelength modulated reflection spectra only for one polarization inasmuch as for another

polarization the spectrum has a similar shape. The refractive indices for corresponding polarizations were calculated from interference spectra. The spectral dependences of refractive indices (n_a(E||a) and n_b(E||b)) at temperature 300 K intersect at energies 2.505 eV (495 nm) and 3.01 eV (412 nm). The interference spectra of thick crystals (d ≈ 970 μm) were observed at energies E < 2.5 eV (see Fig. 2, B).

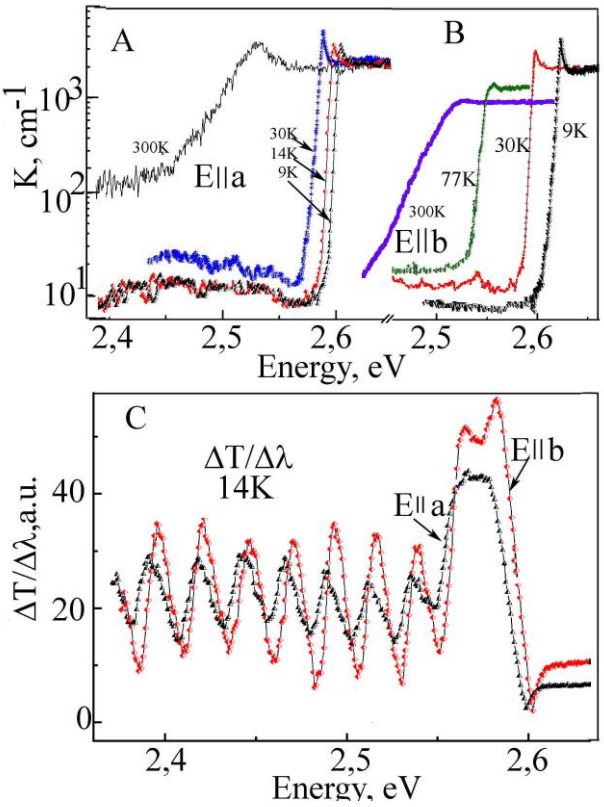

Fig. 1. A, B - Absorption spectra of $TlGaS_2$ crystals of 17.5 μm thickness in polarizations E||a (A) and E||b (B) measured at different temperatures. C - Wavelength modulated transmission spectra measured at temperature 14 K.

The optical absorption spectra of these crystals at temperature 1.8 eV were considered and the symmetry of excitonic bands was calculated and oscillator strengths of transitions in excitonic band were calculated in Ref. [8]. The authors of Ref. [8] note that exciton-phonon interaction is less than exciton-photon at 1.8 K and so the line shapes of excitonic absorption have small distortions. According the data of Ref. [8] the shape of excitonic absorption curve in $TlGaS_2$ crystals is described by the antiresonance Fano contour. The experimentally observed excitonic peak corresponds to the modified state, which appears as a result of the configuration interaction of discrete state (exciton) with the quasi-infinite continuum of conduction band states. One can conclude that the ecxtionic transitions allowed according the calculations of oscillator strength ($F_n = 1.22\times10^{-2}$) for transition into the discrete ("pure") excitonic state. These conclusions were confirmed by the results of this work and data of Ref. [14].

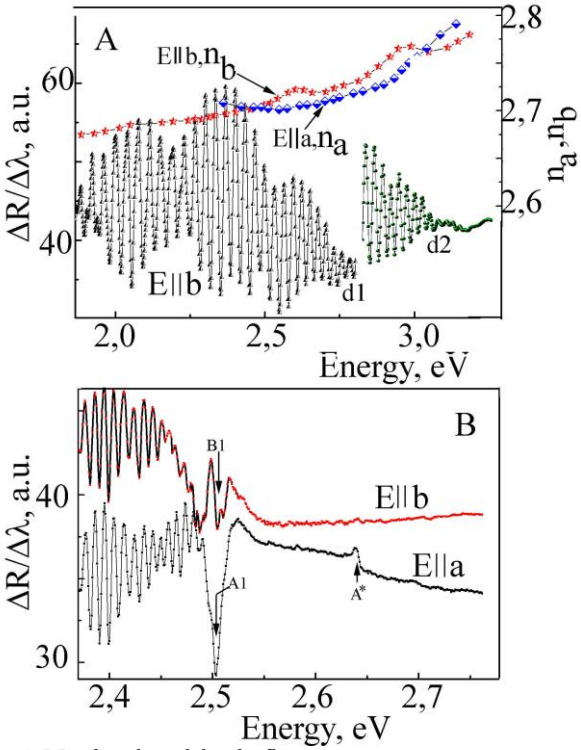

Fig. 2. Wavelength modulated reflection spectra in excitonic region in polarizations E||a and E||b of $TlGaS_2$ crystals with thicknesses d1 = 350 μm and d2 = 7.5 μm (A) and d = 950 nm (B) and refractive indices n_a(E||a) and n_b(E||b) measured at temperature 300 K.

The maxima at energies 2.643 eV (n^B = 1), 2.685 eV (n^B = 2), 2.81 eV (b1), 2.929 eV (b2) and 3.016 eV (b3) were observed in reflection spectra of E||b polarizations (see Ref. [14]). The maximum of reflection at 2.604 eV (n^A = 1) and weak feature at 2.620 eV were discovered in E||a polarization at long-wavelengths. The ascertained maxima (2.604 eV (n^A = 1), 2.643 eV (n^B = 1) and 2.691 eV (n^B = 2)) are due to the ground and excited states of excitonic transitions. These transitions are formed by electrons and holes of bands V1 - C1 and V2 - C1 [14]. The excitonic states in such crystals at room temperature in reflection spectra were not observed. The features A1 and B1 at 2.5041 eV in both polarizations of wavelength modulated reflection spectra measured at temperature 300 K were discovered in the minimum of interband gap (see Fig. 2, B). These features are caused by electron transitions V1 - C1 and V2 - C1. A weak peak A^* at 2.6397 eV were observed in E||a polarization.

The features at energies 2.6098 eV, 2.6448 eV and 2.6518 eV were recognized in wavelength modulated reflection spectra at 14 K in E||b polarization. These features are corresponded to ground (n^B = 1) and excited (n^B = 2, n^B = 3) states of B_{3u} symmetry excitons. According the data of Ref. [8] the dipole-allowed S- excitonic transitions of B_{1u}, B_{2u} and B_{3u} symmetries are allowed in E||c, E||a and E||b polarizations according selection rules. On the other hand P- excitonic transitions in dipole approximation are forbidden by selection rules.

Taking into account the energy positions of $n^B = 1$ and $n^B = 2$ was calculated the binding energy R = 48 meV. In the case of using energies of n = 2 and n = 3 the binding energy is equal to 50 meV. According the data [14] of reflection spectra measured at 9 K in E||b polarization were determined the exciton binding energy R (56 meV) and band gap E_g (2.699 eV) based on the observed maxima: 2.643 eV ($n^B = 1$) and 2.685 eV ($n^B = 2$). The features at energies 2.5655 eV, 2.5923 eV and 2.5973 eV due to n =1, n = 2 and n = 3 states of B_{2u} excitons were found out in wavelength modulated reflection spectra measured at 14 K in E||a polarization. Using these data one can estimate the binding energy (35 meV) and band gap (2.6012 eV) for these excitons at 14 K. At temperature 9 K and in E||a polarization the binding energy is equal to 35 eV too and band gap E_g = 2.639 eV [14].

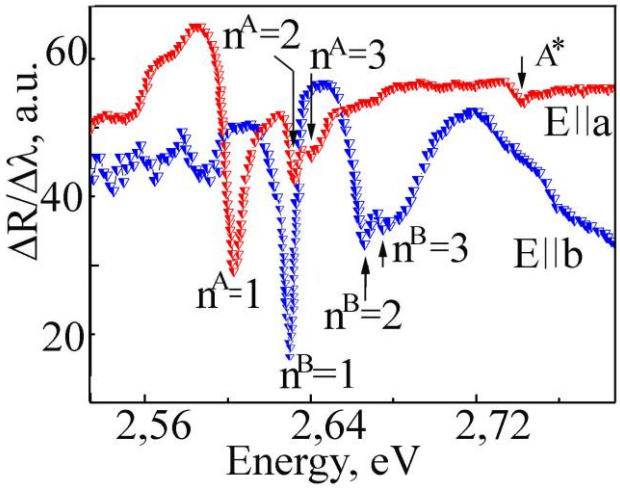

Fig. 3. Wavelength modulated reflection spectra of $TlGaS_2$ crystals with 970 μm thickness measured in excitonic region in E||a and E||b polarizations at temperature 14 K.

Thus the excitons of B_{2u} and B_{3u} symmetries (marked as A and B) allowed in E||a and E||b polarizations, respectively were observed in $TlGaS_2$ crystal (see Fig. 3). The contours of measured (exp.) and calculated (calc.) reflection spectra of $TlGaS_2$ crystals in E||a and E||b polarizations at 9 K were discussed in Ref. [14]. The calculations of reflection spectrum contour for ground state of S exciton of B_{3u} symmetry were carried out on the base of formulas for two-oscillator modes [14, 15]. These calculations give good agreement between experiment and theory with the next parameters $\varepsilon_b = 6.8$, ω_0 = 2.643 eV, ω_{LT} = 3.8 meV, γ = 6 meV, M = 2.0m_0 and L = 10 Å. The value of longitudinal-transversal splitting (ω_{LT} = 3.8 meV) confirms that the excitons of B_{3u} symmetry allowed in dipole approximation in E||b polarization.

The reduced effective mass of B_{2u} and B_{3u} excitons were determined by help of a relation $\mu^* = \varepsilon_b^2 R/R_H$ where R_H is Rydberg energy of hydrogen atom (13.6 eV) and R is binding energy for corresponding excitons. The reduced effective mass μ^* is equal to 0.099m_0 for B_{2u} excitons at background dielectric constant ε_b = 6.2 and binding energy R = 35 meV. In the case of B_{3u} symmetry at ε_b = 6.8 and R = 50 - 56 meV the reduced exciton mass μ^* = 0.19m_0. Bohr radius (α_B) of S - state B_{2u} exciton is equal to 0.3×10^{-5} cm and for B_{3u} - α_B = 0.2×10^{-6} cm. Taking into account the fact that exciton mass M = $m_v^* + m_c^*$ and reduced mass $1/\mu^* = (1/m_v^*) + (1/m_c^*)$ the effective masses of electrons in conduction band (m_c^* = 0.11m_0) and holes in valence bands (m_{v1}^* = 2.14m_0 and m_{v2}^* = 1.89m_0) were estimated from experimentally determined values of M and μ^* in Ref. [14].

Electron transition and optical functions in the depth of absorption band of $TlGaS_2$ crystals

Spectral dependences of wavelength modulated reflection spectra at energies 2 - 6 eV measured at temperatures 30 and 300 K are shown in figure 4. Maxima A1 - A12 in intrinsic region of reflection spectra in polarization E||a were discovered (see Fig. 4). The large amount of pronounced maxima (a1 - a19) was observed in wavelength modulated reflection spectra in E||a polarization at temperatures 30 K and 300 K. These data are evidence of large quantity of direct electron transitions happened between maxima of valence bands and minima of conduction bands. The maxima of reflection spectra and especially maxima of modulated ΔR/Δλ are grouped into few groups. The most long-wavelength group (a1 - a6) is formed in excitonic region and situated at energies 2.5 - 3.5 eV. The second group of maxima (a7 - a10) has energies 3.5 -4.1 eV. The next group (a11 - a13) is situated in energy interval 4.1 - 4.7 eV and the most high-energy groups (a13 - a16 and a17-a19) have energies 5 - 6.5 eV.

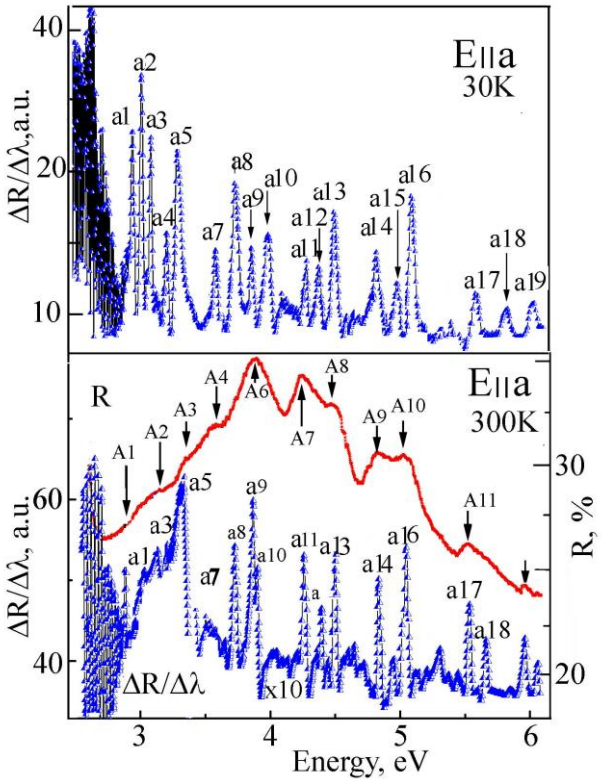

Fig. 4. Reflection (R) and wavelength modulated reflection (ΔR/Δλ) spectra of $TlGaS_2$ crystals measured at temperatures 30 K and 300 K in E||a polarization.

Maxima (B1 - B11) in reflection spectra of $TlGaS_2$ crystals in E||b polarization were also observed in intrinsic region (Fig. 5). A lot of well pronounced maxima (b0, b1 - b19) were

recognized in wavelength modulated reflection spectra in E||b polarization at temperatures 30 K and 300 K. These results are also indicated on huge amount of electron transitions in E||b polarization between maxima of valence bands and minima of conduction bands. The maxima of $\Delta R/\Delta\lambda$ spectra are also grouped to few groups. These groups are next: the first group (b0, b1 - b6) at energies 2.5 - 3.1 eV, the second group (b7 - b10) at energies 3.1 - 3.6 eV, the third group (b11 - b13) at energies 3.7 - 4.1 eV and the fourth group at energies 4.8 - 6 eV.

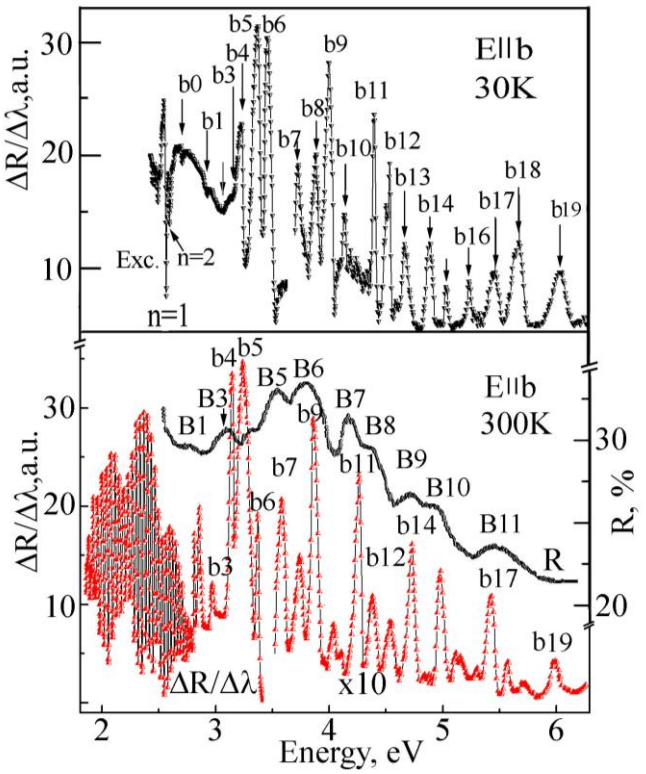

Fig. 5. Reflection (R) and wavelength modulated reflection ($\Delta R/\Delta\lambda$) spectra of $TlGaS_2$ crystals in E||b polarization measured at temperatures 30 K and 300K.

The theoretical calculations of band structure in wide energy diapasons of interband transitions for many points of Brillouin zone were carried out for a lot of crystals $TlGaS_2$ [16, 17], $TlGaTe_2$ [18, 19], $TlInTe_2$ [20], $TlGaSe_2$ [16, 17, 21], $TlInSe_2$ [22], TlSe [16, 23] and TlS [16, 23]. The generalities of band structure and ancestral likenesses of optical spectra and functions in the group of crystals based on thallium were revealed. The similar situation takes place in well-studied crystals (Si, Ga, $A^{III}B^{V}$ and $A^{II}B^{VI}$ compounds). The results of band structure calculations for series of crystals $TlMX_2$ (M = Ga, In; X = S, Se, Te) have a general character and reflect only the main features of energy bands. According the theoretical calculations of band structure the energy spectrum near the fundamental absorption edge $TlGaS_2$ is characterized by the presence of the main maximum of valence band in $\Gamma(2A_2)$ point [16, 20 - 23]. The bands are formed by 4s states of Ga atoms, 6s states of Tl atoms and 3s states of S atoms in energy interval 3 - 5 eV [16]. The highest density of states of lowest conduction band in Γ point is determined by 4s states of Ga atoms. The density of states of top valence band is determined by 6s states of Tl atoms.

The direct electron transitions which observed in reflection spectra at energies $E > E_g$ take place in the vicinity of those points of Brillouin zone where maxima of valence bands and minima of conduction bands have the same values of wave-vector. This rule is true for all studied crystals. And of course the same regularity is characterized $TlGaS_2$ crystals. The huge amount of bands is contained in the narrow energy diapason of the $TlGaSe_2$ crystal band structure according the theoretical calculations. However these theoretical calculations were carried out without taking into account the possible splitting due to spin-orbital interaction and crystal field. This means that the bands in theoretically calculated bands structure are degenerated in all points of Brillouin zone. In the case of real band diagrams the bands will be split and the band amounts in extrema of conduction and valence bands will increase.

The large amount of features (a1 - a19 and b1 - b19) due to direct electron transitions were revealed in measured wavelength modulated reflection spectra. It was mentioned above that the received maxima could be separated on a few groups. We conjecture that each group of peaks is caused by electron transitions in nearby of Brillouin zone points where maxima of valence band and minima of conduction band are situated. Such points in Brillouin zone of $TlGaS_2$ crystals are Γ, Z and L points and X - Y and Γ - X directions. The discovered electron transitions happen in the surroundings of these abovementioned points (see Fig. 6 and Table 1). Figure 6 shows the enlarged fragment of band structure according the theoretical calculation represented in Ref. [16]. The band structures of $TlGaS_2$ and $TlGaSe_2$ crystals virtually are identical according the data of Ref. [16]. The results of band structure calculations show that dispersion of the valence band top state along Γ - Z line is relatively strong due to high hybridization between 6s states of Tl atoms and 4p states of Se atoms or 2p states of S atoms. According the theoretical calculations $TlGaSe_2$ crystal is not direct-gap semiconductor. The indirect energy gap is formed by transitions from Γ point to direction Z - L and equal to 1.24 eV. The value of this energy gap determined experimentally is a bit higher. According the calculations of Ref. [16] $TlGaS_2$ crystal is indirect semiconductor too. The direct (1.70 eV) and the indirect (1.58 eV) gaps are formed by transitions in Γ point and from Γ to Γ- Y, respectively [16]. These results have good agreement with the previous [11, 12] empirical calculations by pseudo-potential method where $TlGaSe_2$ and $TlGaS_2$ are attributed indirect semiconductors. The experimentally determined by Hanias et al [17] energy gaps for $TlGaSe_2$ correspond to $E_g^d = 2.11$ eV and $E_g^i = 1.83$ eV where E_g^d and E_g^i are direct and indirect gaps, respectively. According the data subsequent Ref. [4, 17] the indirect excitonic transitions at energy 2.054 eV (5 K) and direct exciton transitions at

TABLE 1. LINES OBSERVED IN REFLECTION, WAVELENGTH MODULATED REFLECTION, REAL (E1) AND IMAGINARY (E2) PARTS OF DIELECTRIC CONSTANT SPECTRA OF $TlGaS_2$ CRYSTALS AND ELECTRON TRANSITIONS RESPONSIBLE FOR THESE FEATURES.

E‖a, 300K					E‖b, 300K					Transitions
№		R, eV	ε_2, eV	ΔR/Δλ, eV, 10K	№		R, eV	ε_2, eV	ΔR/Δλ, eV, 10K	
						b1			2.8063	Γ(V1) → Γ(C1)
A1				2.8843						Γ(V2) → Γ(C1)
					B1,	b2	2,785		2,8578	Γ(V1) → Γ(C2)
A1,	a2	2.884		3.1117						Γ(V2) → Γ(C2)
					B2,	b3	3.014		2.9723	Γ(V3) → Γ(C1)
A2,	a3	3.345		3.3323						Γ(V4) → Γ(C1)
					B2,	b4	3.098		3,1498	Γ(V5) → Γ(C1)
A3,	a4	3.567		3.4310						Γ(V6) → Γ(C1)
						b5			3.2433	Γ(V3) → Γ(C2)
	a5			3.5207						Γ(V4) → Γ(C2)
A4,	a6				B3,	b6	3.318		3.3788	Γ(V5) → Γ(C2)
		3,.876								Γ(V6) → Γ(C2)
	a7			3.6685	B4,	b7	3.548		3.5868	Z(V1) → Z(C1)
	a8			3.7297		b8	3.798		3.7433	Z(V2) → Z(C1)
A1,	a9	2.950		3.8685				3.118	3.8673	Z(V1) → Z(C2)
A2,	a10	3.157		3.9111	B6,	b9		3.494	4.0448	Z(V2) → Z(C2)
A3,	a11	3.289		4.2645		b10				
	a12			4.4033						
A4,	a13	3.613	3.581	4.5074	B7,	b11	4.183	3.750	4.2623	L(V1) → L(C1)
A5,	a14		3.919	4.8434	B8,	b12	4.378		4.3883	L(V2) → L(C1)
						b13			4.5448	L(V3) → L(C1)
A6,	a15	3.876	4.436	4.9474	B9,	b14	4.738	4.425	4.7413	Y-X(V1) → Y-X(C1)
A7,	a16	4.244	4.870	5.0500		b15			4.9818	Y-X(V2) → Y-X(C1)
A8,	a17	4.481	5.089	5.5343	B10,	b16				Y-X(V3) → Y-X(C1)
							4.979		5.1382	
A9,	a18	4.826	5.362	5.6714		b17			5.4283	X-Γ(V1) → X-Γ(C1)
A10,	a19	5.042	5.797	6.053	A11,	b18	5.467	5.713	5.7107	X-Γ(V2) → X-Γ(C1)
A11		5.507	6.217		A12,	b19	6.050	6.050	6.0359	X-Γ(V3) → X-Γ(C1)
A12		5.970								

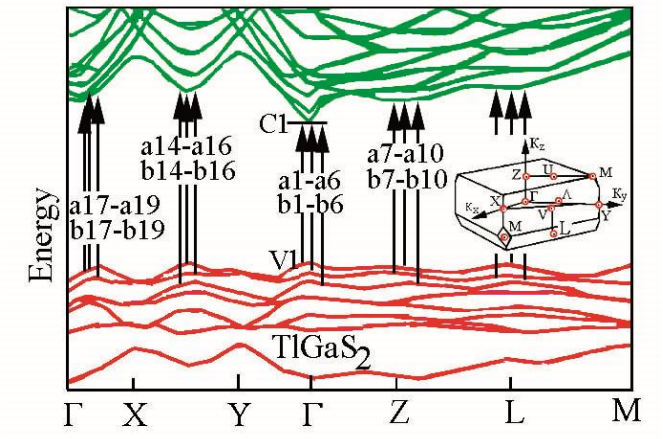

Fig. 6. The enlarged fragment of band structure and Brillouin zone of $TlGaS_2$ crystal according Ref. [16].

energy 2.128 eV (5 K) were observed in $TlGaSe_2$ crystals. For $TlGaS_2$ crystals authors of Ref. [17] give the next values: E_g^i = 2.38 eV and E_g^d = 2.53 eV. These values are larger than calculated in Ref. [16]. The ground and excited states of excitons were observed in measured at 9 K in E||a and E||b polarizations reflectivity spectra according Ref. [14]. According these data the direct band gap is equal to 2.639 eV and 2.699 eV for E||a and E||b polarizations, respectively. The indirect transitions were not found out.

Optical functions at energies $E > E_g$

$TlGaS_2$ are birefringence lamellar crystals with different degree of interatomic interaction forces anisotropy. Birefringent crystals use in different devices for example: polarizers, interferometers, dispersion compensators, deflectors etc. The difference in velocities of light waves

propagations along different directions of such crystals allows to develop optical devices with amazing properties. The polarization states (sc. ability of ordinary and extraordinary beams) creating a difference of effective path lengths determine the main application of such materials. Ordinary and extraordinary light beams passed through the crystal feel a different refractivity and consequently acquire the path difference. These beams are also interfered in crystal. Such peculiarity allows using this crystal in narrow-band and combing filters. These properties are interesting especially in layered crystals on those base different nano-electronic devices are developed and have been created. Spectral dependence of refractive index in birefractive crystals differ for diverse polarizations. This difference is significant both in intrinsic and extrinsic absorption regions of crystal, this is very important for nanoelectronics.

As mentioned in Ref. [14] the maximum at 2.515 eV (λ_0 = 493 nm) was found out in reflection spectra of $TlGaS_2$ crystal deposed between crossed polarizers at temperature 300 K. This maximum is shifted to short-wavelengths with temperature decreasing and it is observed at energy 2.568 eV (λ_0 = 482.8 nm) at temperature 9 K. These maxima positions are correspond to wavelengths where refractive indices for different polarizations intersect. These wavelengths are named as well the isotropic points [14].

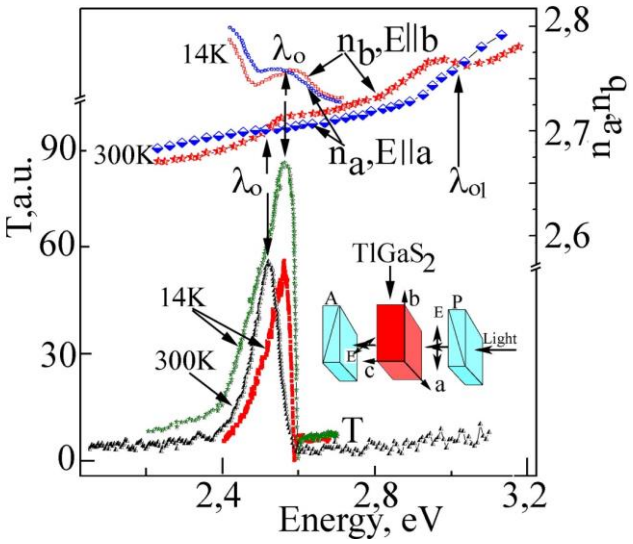

Fig. 7. Transmaiison (T) spectra of $TlGaS_2$ crystals deposed in crossed polarizers, and spectral dependences of refractive indices (n_a and n_b) calculated from interference spectra mesured at temeperarutes 14 K and 300 K. Insert shows the scheme of tramsmission spectra measurement for samples deposed between crossed polarizers.

Figure 7 shows transmission (T) spectra of $TlGaS_2$ crystals deposed between crossed polarizers at temeperatures 300 K and 14 K. Spectral dependences of refractive indices for E||a and E||b polarizations calculated from interference spectra are presented in top part of figure 7. On the contrary spectra of refractive indices analysed in Ref. [14] were calculated from reflection spectra using Kramers-Kronig equations. The intensive line at 2.5236 eV (λ_0 = 493 nm) is observed in transmission spectra at room temperature. At temperature 14 K this transmission line is shifted to short-wavelengths and it is observed at 483 nm (2.5660 eV). The refractive indices for E||a and E||b polarizations are equal at λ_0 wavelength. That is to say the crystal does not recognize the light polarization. The intense transmission line is observed at this wavelength for crystal in crossed polarizers (see Fig. 7). At wavelengths $\lambda > \lambda_0$ and $\lambda < \lambda_0$ the light waves propagate like in birefractive crystal [14]. One can see from Fig. 7, that at $\lambda < \lambda_0$ the refractive index $n_b(E||b) < n_a(E||a)$ and for $\lambda > \lambda_0$ is $n_b(E||b) > n_a(E||a)$. The isotropic wavelengths can be observed and at another wavelengths (energies). The intersection of refractive indices at wavelength λ_{01} = 427.6 nm (2.9 eV) was received from transmission interference spectra of thin crystals (7.5 μm). This isotropic point is situated in the intrinsic absorption. The similar intersection of refractive indices can take pace and at higher energies. For clearness spectral dependences of refractive indices in respective polarization in depth of absorption band of $TlGaS_2$ crystals were investigated. The polarization dependences of refractive indices in the depth of absorption band of $TlGaS_2$ crystals in polarizations E||a and E||b were determined from the calculations of reflection spectra using Kramesr-Kronig relations [14].

It is well know that the amplitude of reflectivity R is connected with phase φ of reflected beam by the next equation:

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

$$t = \frac{I_t}{I_0} = \frac{(1-R)^2\left(1+\frac{k^2}{n^2}\right)\ell^{-Kd}}{\left(1-R\ell^{-Kd}\right)^2 + 4R\ell^{-Kd}\sin^2(\alpha+\varphi)}. \tag{2}$$

The spectral dependences of reflection coefficient R and optical functions n, k, φ, ε_1 and ε_2 relate to each other by next relation:

$$\begin{cases} r = \dfrac{N-1}{N+1} = \dfrac{n+ik-1}{n+ik+1} \\ r = \sqrt{R}e^{-i\varphi} = \sqrt{R}(\cos\varphi - i\sin\varphi) \end{cases} \Rightarrow \begin{cases} n = \dfrac{1-R}{1-2\sqrt{R}\cos\varphi + R} \\ k = \dfrac{2\sqrt{R}\sin\varphi}{1-2\sqrt{R}\cos\varphi + R} \end{cases}. \tag{3}$$

The peak value of reflection with its phase ($R \approx R(\omega)$ and $\varphi \approx \varphi(\omega)$) for every value of wavelength should be determined simultaneously. The phase of reflected beam is bound with amplitude of reflection coefficient by Kramers-Kronig integral:

$$\varphi(\omega_0) = \frac{\omega_0}{\pi}\int_0^\infty \frac{\ln R(\omega)}{\omega^2 - \omega_0^2} d\omega; \tag{4}$$

For determining of reflected beam phase from experimentally measured reflectivity is necessary to make measurements for infinite frequency range (see formula 4). But the experimental measurements of reflection spectra is possible for the limited energy interval (ω_a - ω_b), in our case measurements have been carried out for energies 2 - 6 eV. The amplitude of reflected beam changes sharply and strongly only in nearby of ω_0. It was used the integration by parts method for phase calculation in measured diapason. However we need

introduce some correction data which take into account the influence of high-energy and low-energy parts of integral (4). It was used the functions $R(\omega) = C\omega^{-p}$ (where C and p is constants) and $R(\omega) = R(a)$ for frequencies $b < \omega < \infty$ and $0 < \omega < a$, respectively. The calculated value of φ and experimentally determined value of R allow determining the optical functions (n, k, ε_1 and ε_2).

Figure 8 shows the refractive index (n), real (ε_1) and imaginary (ε_2) parts of complex dielectric constant and absorption coefficient (K) spectral dependences of $TlGaS_2$ crystal. The same spectral features like in abovementioned spectra at the same energies were observed in refractive indices spectra (see Fig. 8). The absorption coefficient for both polarizations reaches the values of 10^4 cm^{-1}. Spectral dependences of optical functions (real (ε_1) and imaginary (ε_2) parts of complex dielectric constant) were calculated (see Fig. 8). These features correlate fully with features A1 - A11 and B1 - B11 determined form reflection spectra (Table 1).

The minimum of interband gap in $TlGaS_2$ crystals is formed by direct excitonic transitions in Brillouin zone center [5, 6]. The scheme of electron transitions in Brillouin zone center for $TlGaS_2$ crystals is presented in Ref. [14]. The amount of bands and its splitting were determined based on excitonic reflection spectra measured in E||a and E||b polarizations. Valence bands Γ(V1) and Γ(V2) have a energy gap around 60 meV, since E_g in E||a polarization equal to 2.639 eV and in the case of E||b polarization it equal to 2.699 eV. Maxima a1 and b1 are spaced by the distance of ~70 meV. These maxima more probably were attributed to electron transitions from Γ(V1) to Γ(C2) bands and from Γ(V2) to Γ(C2) bands, respectively. If the maximum b2 is associated with transitions from Γ(V3) to Γ(C1) bands than energy distance between bands Γ(V2) and Γ(V3) is equal approximately to 119 eV. The estimated values of effective masses of electrons and holes and the symmetry of excitons responsible for these transitions were shown in bans diagram. The fragment of theoretically calculated band structure [16] for these group crystals was used for interpretation of experimentally observed electron transitions (see Fig. 6). The band structure fragment is stretched in all direction of wave vector **k** proportionally. The minimal energy intervals are observed in Brillouin zone center as one can see from figure 6. At energy increasing the energy intervals take place in Z and L points and X - Y and X - Γ directions of **k** - space. Loads of bands are observed in all above-mentioned points of Brillouin zone and huge amount of electron transitions have been observed experimentally too. We suppose that maxima a1 - a6 and b1 - b6 are due to transitions in Brillouin zone center. The next transitions a7 - a10 and b7 - b10 are associated with transitions in Z point of Brillouin zone. The features observed in reflection and wavelength modulated reflection spectra at higher energies are connected with electron transitions in points L, X - Y and X - Γ (see Fig. 6 and Table 1).

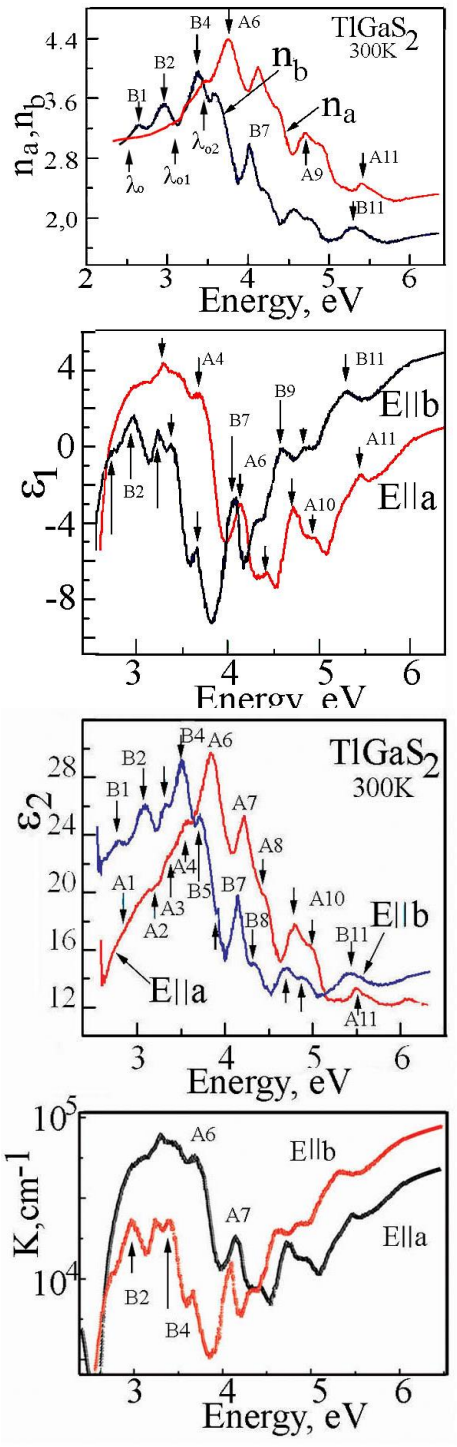

Fig. 8. Spectral dependences of refractive indices (n_a and n_b), dielectric constant real (ε_1) and imaginary (ε_2) parts and absorption coefficient (K) calculated from measured reflection spectra of $TlGaS_2$ crystals by Kramers-Kronig analysis.

IV. CONCLUSION

Ground and excited states of excitons were found out in reflection (R) and wavelength modulated reflection ($\Delta R/\Delta\lambda$) spectra of E||a and E||b polarizations. The main parameters of B_{2u} (series A) and B_{3u} (series B) excitons and bands in $\mathbf{k} = 0$ were determined. The optical reflection and wavelength modulated reflection spectra of $TlGaS_2$ crystals in E||a and E||b polarizations at temperatures 14 K and 300 K were investigated. The features associated with direct electron transitions in actual points of Brillouin zone were revealed. The optical functions (n, k, ε_1 and ε_2) indicating about anisotropy of optical parameters and electron transitions for wide energy diapason (2 - 6 eV) were calculated by Kramers-Kronig method from measured optical reflection spectra. Crystals $TlGaS_2$ deposed between crossed polarizers are isotropic near wavelengths 493 nm (300 K) and 483 nm (14 K). Refractive indices for E||a and E||b polarizations intersect at these wavelengths. The refractive indices intersection was observed and for intrinsic absorption region.

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