Optical Properties of $TlGaS_2$ Crystals

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***Abstract* — The anisotropy of transmission spectra was investigated in $TlGaS_2$ crystals. An intensive transmission line was found in samples placed between two crossed polarizers. Ground and excited states of excitons were detected in reflectivity spectra of $TlGaS_2$ crystals measured in E ‖ a and E ‖ b polarizations. The reflection spectra of excitons were calculated according to dispersion equations, and the main parameters of excitons and energy bands were determined in the center of the Brillouin zone.**

***Index Terms* - semiconductor compound; optical constants; excitons; band structure.**

I. INTRODUCTION

$TlGaS_2$ crystals belong to ternary thallium chalcogenide compounds $T1GaX_2$ (where X is Te, S, Se) with layered structure. $TlGaX_2$ semiconductor compounds crystallize as structures with strong anisotropy of optical properties. They have some features which make them different from other classical semiconductors and make them prospective from the practical point of view. Visible and infrared light detectors as well as high-sensitive detectors of laser beam radiation were proposed on the basis of these compounds. Several phenomena such as induced emission, photoresistive, photoacoustical, and electrooptical effects were discovered in these compounds [1 - 4]. N or S type current-voltage characteristics and switching effects were observed in Me - crystal - Me structures. The investigation of $TlGaS_2$ crystals is important from this point of view. It was shown that dielectric properties of $TlGaS_2$ can be controlled by chromium doping.

These crystals exhibit a strong anisotropy of physical characteristics due to peculiarities of their crystal structure [3]. A high x-ray sensitivity of $TlGaS_2$ single crystals was reported at fixed values of the accelerating potential in energy diapason from 25 to 50 keV [2]. The dependence of crystal conductivity on the x-ray dose has a power-law character. The temperature dependence of Raman scattering spectra of $TlGaS_2$ crystals were investigated in the temperature range of 77-400K [4]. Vibration reflectivity spectra were analyzed in the range of 50 – 4000 cm^{-1}. Polar LO and TO modes have been revealed and their main parameters were determined. The calculations of anion and cation effective charges in E ‖ a and E||b polarizations suggest that the degree of ionicity of cations and anions in the directions of a- and b-axes is different [4]. Other properties of these materials were widely investigated (see [2 - 4] and references therein). Little attention has been paid to birefringence and reflectivity spectra in the excitonic region for these crystals. Although detected ground and excited states of excitonic spectra allow a more precise determination of the main bands parameters of crystal in a band gap region.

In this work new data concerning exciton states for $TlGaS_2$ crystals are presented. Ground and excited exciton states were detected in E ‖ a and E ‖ b polarizations. The contours of exciton spectra were calculated and the main parameters of bands and excitons for k = 0 were determined on the basis of these spectra. New experimental dependences were revealed by these investigations, which provide opportunity for a deeper understanding of physical processes occurring in these crystals.

II. EXPERIMENTAL DETAILS

$TlGaS_2$ single crystals were grown in a two stage process using Tl, Ga and S as precursors. The first stage consists of purification of starting materials and synthesis of $TlGaS_2$. The synthesis was carried out in quartz ampoules placed in a high pressure chamber (≈40 atm.). In the second stage, the synthesized compound was introduced into an installation for the crystal growth by Bridgman method. Single crystals with a length of 2 cm and a diameter around 1 cm were produced. The crystals can be cleaved easily for obtaining mirror-like faces. All optical measurements were carried out for crystals with mirror-like untreated faces with computer controlled MDR-2, SPECORD M40 and JASCO-670 spectrometers. The samples were mounted on the cold station of a LTS-22 C 330 optical cryogenic system for low temperature measurements.

III. RESULTS AND DISCUTIONS

In the region of crystal transparency, absorption is low and it is determined by several mechanisms as native optical activity and polarized local absorption lines of impurities, defects etc. The existence of two types of waves in crystal (ordinary and extraordinary) with differ refractive index n_o and n_e is determined by the tensor of dielectric permittivity $\varepsilon(\omega, k)$, which depends on frequency ω and wave vector k. The spatial dispersion i. e. wave vector k dependence of dielectric constant set conditions for appearance of nondiagonal element ε_{zz} of dielectric constant tensor.

A strong maximum is observed around 2.515 eV (493 nm) in transmision spectra of $TlGaS_2$ crystals placed between two crossed polarizers at 300K. The maximum shifts to short wavelength and it is observed at 2.568 eV (482.8 nm) if the temperature goes down to 9 K. The wavelengths of these maxima correspond to wavelengths at which refractive indexes intersect (Fig. 1). Refractive indexes were calculated from reflection spectra by means of Kramers-Kronig relations. Thus the crystal is isotropic at λ_o – 493 nm (300K) and λ_o – 482.8 nm (9K). The transparence of crystal in crossed polarizers decreases almost to zero at 300 K when the wavelength is decreased or increased from λ_o – 493 nm. The trancparence in crossed polarizers diminishes to aproximately 50% at 9K if the wavelength is higher then λ_o - 482.8 nm (see Fig. 1).

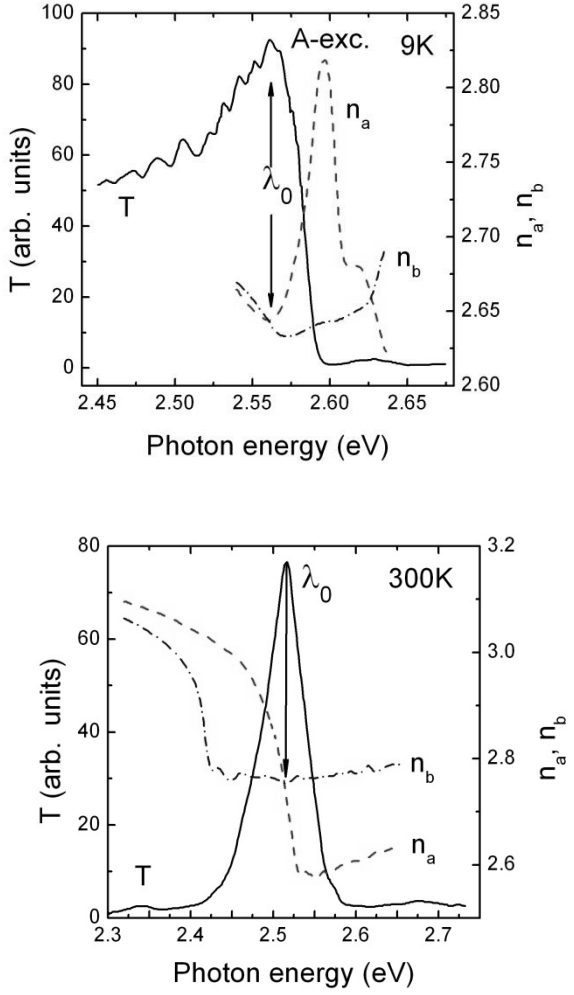

Fig. 1. Transmission spectra (T) of $TlGaS_2$ crystals placed in crossed polarizers and refractive indexes for E || a and E || b polarization measured at temperatures 300K and 9K.

The radiation transmitted througth crystal remains linearly polarized in the izotropic point of a crystal. Every linearly polarized emission can be represented as a sum of two circularly polarized in opposite direction waves. Therefore, the transmission of a system polarizer – crystal – analyzer (in crossed polarizers) in the izotropic point is due to interaction of ordinary and extraordinary waves, which aquire a phase difference determined by the value of the crystal specific rotation ρ. The magnitude of crystal transmission T with crossed polarizers is described by the expression:

$$T = \frac{\sin^2(\pi/\lambda)\left[\left(\delta n^2 + \Delta n^2\right)^{1/2} d\right]}{1+\left(\Delta n/\delta n\right)^2} \qquad (1)$$

where d is the crystal thickness, $\delta n = n(\rho_d) - n(\rho_s)$ is the difference of refractive index for frequencies higher than λo, where refractive indexes are determined by properties of gyrotropy. In the short wavelength region $\Delta n = n(E \| a) - n(E \| b)$ is determined by the oscillator strength of electronic transitions in corresponding polarizations [4]. One can see from fig. 1 that in long wavelength region of λ_o at 9K $\delta n = n(\rho_d) - n(\rho_s)$ differs from that at 300K.

Spectra shown in Fig. 2 have maxima at 2.604 eV (n^A=1) and 2.880 eV (a1) in polarization E||a. Maxima with energy 2.643 eV (n^B=1), 2.685 eV (n^B=2), 2.810 eV (b1), 2.929 eV (b2), 3.016 eV (b3) were observed in E||b polarization. The long wavelength reflectivity maxima at 2.604 eV (n^A=1), 2.643 eV (n^B=1), and 2.691 eV (n^B=2) are due to exitonic transitions.

The Rydberg constant of free excitons in E||a polarization calculated according to the energy position of n =1 and 2 lines in $TlGaS_2$ is equal to 35 meV. A band gap Eg = 2.639 eV was determined taking into account a binding energy of excitons of 35 meV. A binding energy of excitons (R) equal to 56 meV and a band gap (Eg) equal to 2.699 eV were calculated for E||b polarization on the basis of maxima observed at 2.643 eV (n^B=1) and 2.685 eV (n^B=2).

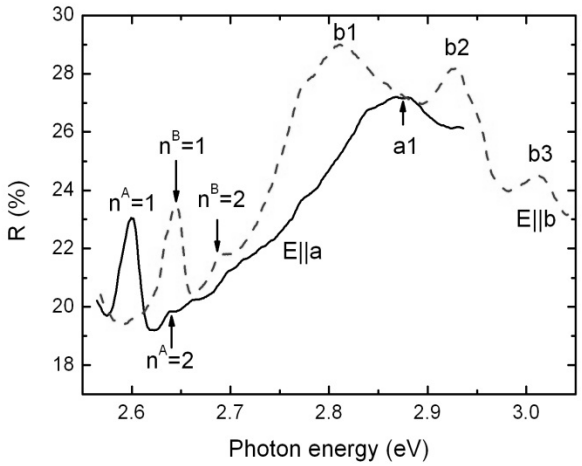

Fig. 2. Reflection spectra of $TlGaS_2$ crystals measured in E||a and E||b at 9K.

The analysis of polarized Raman and IR reflection spectra of $TlGaS_2$ crystals for two potential D_{2h} and D_{4h} symmetry groups [3, 4] also shown that the crystals are described by the D_{2h} symmetry group. Since $TlGaS_2$ crystals are cleft perpendicularly to the c-axis, the reflection spectra from the cleaved surfaces were measured for two E ‖ a and E ‖ b polarizations of the light waves (Fig. 2)

According to theoretical band structure calculations [2], the valence band of $TlGaS_2$ crystals is formed from one-electron states of sulfur ions, and the conduction band is formed from one-electron states of gallium ions. The analysis of selection rules for exciton transitions was carried out on the basis of correlation diagrams for two possible D_{2h} and D_{4h} factor groups of the crystal [3]. For exciton states it was found that [3]:

$$\begin{aligned} \Gamma exc(s) &= E+ \times E^{-} = A_u + B_{1u} + B_{2u} + B_{3u}, \\ \Gamma exc(pz) &= E+ \times E^{-} \times B_{1u} = A_g + B_{1g} + B_{2g} + B_{3g}, \\ \Gamma exc(px) &= E+ \times E^{-} \times B_{2u} = A_g + B_{1g} + B_{2g} + B_{3g}, \\ \Gamma exc(py) &= E+ \times E^{-} \times B_{3u} = A_g + B_{1g} + B_{2g} + B_{3g}. \end{aligned} \quad (2)$$

According to the selection rules [8], the dipole allowed S-exciton transitions with B_{1u}, B_{2u} and B_{3u} symmetry are allowed in E‖c, E‖a and E‖b polarizations, respectively. The P-exciton transitions are forbidden by the selection rules in the dipole approximation. Therefore, the lines of excitons with B_{2u} symmetry (marked as A) allowed in E‖a polarization, as well as of excitons with B_{3u} symmetry (marked as B) allowed in E‖b polarization are observed in $TlGaS_2$ crystals (Fig. 3). The contours of measured (exp) and calculated (calc) reflection spectra of $TlGaS_2$ crystals for E‖a and E‖b at 9K are presented in Fig. 3.

The calculations of reflection spectra were carried out in the frame of the Thomas-Hopfield model taking into account the spatial dispersion (SD), the presence of a "dead" layer (DL) with additional boundary conditions of Pekar. The dialectic function near the excitonic resonance is written as follows [5]:

$$\varepsilon\left(\omega,\vec{k}\right) = \varepsilon_b + \frac{2\varepsilon_b\omega_{LT}\omega_0}{\omega_0^2 - \omega^2 + \frac{\hbar^2k^2}{2M}\omega_0 - i\gamma\omega} \quad (3)$$

where ε_b is the background dielectric constant with contributions from all the interaction mechanisms except for the oscillator involved, ω_0 is the transversal exciton frequency, $M = m_C^* + m_V^*$ is the exciton translation mass, $\boldsymbol{k}$ is the wave vector, $\omega_{LT} = \omega_L - \omega_0$ is the longitudinal-transversal splitting, ω_L is the longitudinal exciton frequency. The reflection coefficient for a normal incidence of the light on the crystal-DL-vacuum boundary is described by the following expression:

$$R = \left| \frac{\left(\frac{1-n_0}{1+n_0} + \left(\frac{n_0-n^*}{n_0+n^*}\right)e^{i2kn_0t}\right)}{\left(1+\left(\frac{1-n_0}{1+n_0}\right)\left(\frac{n_0-n^*}{n_0+n^*}\right)e^{i2kn_0t}\right)} \right|^2 \quad (4)$$

where $n_0 = \sqrt{\varepsilon_b}$, $n^* = \frac{n_1n_2 + \varepsilon_b}{n_1 + n_2}$, t is the dead layer thickness, k is the exciton wave vector, n_1, n_2 are the refractive indices of transversal waves taking into account dependence on the damping parameter γ.

A value of the background dielectric constant near the exciton resonance was used in calculations. A good agreement of theoretical calculations with experimental contours of reflection spectra for the n=1 state of the B_{2u}-exciton was achieved with the following parameters: ε_b = 6.2, ω_0 = 2.604 eV, ω_{LT} = 8 meV, γ = 13 meV, M = 2.3m_0 and L = 15 Å. A large longitudinal-transversal splitting (8 meV) and a high value of the damping parameter (13 meV) were obtained from calculations for the S-state of the B_{2u}-exciton. These data confirm that excitons with this symmetry are allowed in the dipole approximation for the E‖a polarization.

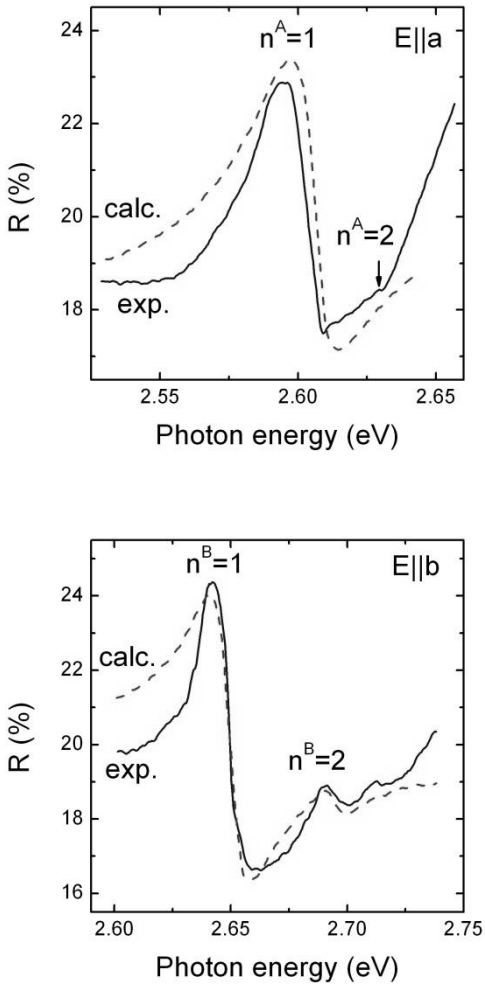

Fig. 3. Experimental (exp.) and calculated (calc.) reflection spectra of $TlGaS_2$ crystals measured at 9K in E‖a (top) and E‖b (bottom) polarizations.

Calculations of the reflection line contour for the ground state of the B_{3u}-exciton were also carried out with a two-oscillator model by means of the above presented formulation. A satisfactory concordance of calculated and experimental spectra is achieved with the following parameters: ε_b = 6.8, ω_0 = 2.643 eV, ω_{LT} = 3.8 meV, γ = 6 meV M = 2.0 m_0, and L = 10 Å. The n=2 excited state of the B_{3u}-exciton is observed at 2.685 eV, which gives a bandgap of Eg = 2.699 eV. The magnitude of the longitudinal-transversal splitting (ω_{LT} = 3.8 meV) also confirms that B3u-excitons are allowed in dipole approximation for the E‖b polarization.

The effective reduced mass of the B_{2u} and B_{3u} excitons was determined from the relation $\mu=\varepsilon_b^2 R/R_H$, where R_H is the Rydberg constant of hydrogen atom (13.6 eV) and R is the binding energy of excitons. The reduced mass of the B_{2u}-exciton calculated with a background dielectric constant ε_b = 6.2 and a binding energy R = 35 meV is equal to $\mu = 0.099m_0$. For the B_{3u} - exciton, a reduced mass of $\mu = 0.190m_0$ is obtained with a background dielectric constant ε_b = 6.8 and a binding energy R = 56 meV. The Bohr radius (α_B) of the S - state of the B_{2u} and B_{3u} excitons is equal to $0.3x10^{-5}$ cm and $0.2x10^{-6}$ cm, respectively. Taking into account that the exciton mass M is equal to the sum of masses of holes and electrons $m^*_V + m^*_C$, and the reduced mass $1/\mu$ is equal to $(1/m^*_V)+(1/m^*_C)$, the effective mass of electrons and holes were estimated as $m^*_C=0.11m_0$, $m^*_{V1}=2.14m_0$, and $m^*_{V2}=1.89m_0$.

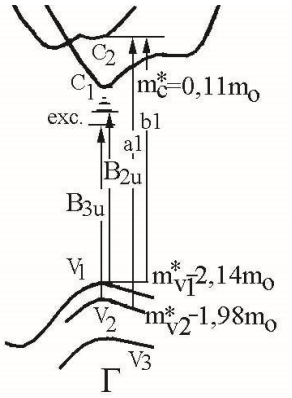

Fig. 4. The energy band structure of $TlGaS_2$ crystals in the region of the bandgap.

The bandgap of $TlGaS_2$ crystals is formed by direct excitonic transitions in the center of the Brillouin zone [2, 3]. Figure 4 presents the scheme of electronic transitions in the center of the Brillouin zone of $TlGaS_2$. This segment of the band diagram is obtained as a result of theoretical calculations [2, 3]. The number of bands and their splitting is determined on the basis of experimental exciton reflection spectra measured in E||a and E||b polarizations. The splitting between the $\Gamma(V_1)$ and $\Gamma(V_2)$ valence bands is 60 meV, since the bandgap E_g equals 2.639 eV and 2.699 eV for E||a and E||b polarizations, respectively. The maxima a1 and b1 are separated by an interval of ~70 meV. These maxima are related probably to electronic transitions from $\Gamma(V_1)$ to $\Gamma(C_2)$ bands, and from $\Gamma(V_2)$ to $\Gamma(C_2)$ bands, respectively. If maxima b1 correspond to transitions $\Gamma(V_3)$ - $\Gamma(C_1)$ then the distance between the bands $\Gamma(V_1)$ and $\Gamma(V_2)$ split by crystal field and $\Gamma(V_2)$ and $\Gamma(V_3)$ split by spin-orbital interaction equal to 68 meV and 119 meV, respectively. The estimated values of effective masses of electrons and holes, as well as the symmetry of excitons responsible for electronic transitions are also presented in the band diagram (Fig. 4).

CONCLUSION

The investigation of anisotropy of the spectral dependence of refractive indices n_a and n_b for E||a and E||b polarizations in $TlGaS_2$ crystals revealed their intersection at 493 nm (300K) and 482.8 nm (9K) wavelengths near the absorption edge. An intensive transmission band was observed at 493 nm (300K) and 482.8 nm (9K) for crystals placed between two crossed polarizers. The refraction indices n_a and n_b for E||a and E||b polarizations were determined from Kramers-Kronig analysis. The ground and excited states of excitons were observed in reflection spectra of $TlGaS_2$ crystals measured in E||a and E||b polarizations. The contours of exciton reflection spectra were calculated according to dispersion relations, and the main parameters of excitons and bands were determined in the center of the Brillouin zone. The values of the crystal field V_1-V_2 and the spin orbital interaction V_2-V_3 splitting were estimated to be equal to 68 meV and 177 meV, respectively. A model of the energy band structure is proposed for the Γ-point of the Brillouin zone. $TlGaS_2$ crystals placed between crossed polarizers have a potential application as narrowband filters.

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