Optical Properties of TlGaS₂ Crystals

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Abstract — The anisotropy of transmission spectra was investigated in TlGaS₂ 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 TlGaS₂ 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

TlGaS₂ crystals belong to ternary thallium chalcogenide compounds TlGaX₂ (where X is Te, S, Se) with layered structure. TlGaX₂ 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 TlGaS₂ crystals is important from this point of view. It was shown that dielectric properties of TlGaS₂ 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 TlGaS₂ 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 TlGaS₂ 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 TlGaS₂ 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

TlGaS₂ single crystals were grown in a two stage process using Ti, Ga and S as precursors. The first stage consists of purification of starting materials and synthesis of TlGaS₂. 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 n₁ and nₑ is determined by the tensor of dielectric permittivity $\varepsilon(\omega, k)$, which depends on frequency $\omega$ and wave vector $k$. The spatial dispersion i. e. wave vector $k$ dependence of dielectric constant set conditions for appearance of nondiagonal element $\varepsilon_{zz}$ of dielectric constant tensor.
A strong maximum is observed around 2.515 eV (493 nm) in transmission 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 $\lambda_0$ – 493 nm (300K) and $\lambda_0$ – 482.8 nm (9K). The transparency of crystal in crossed polarizers decreases almost to zero at 300 K when the wavelength is decreased or increased from $\lambda_0$ – 493 nm. The transparency in crossed polarizers diminishes to approximately 50% at 9K if the wavelength is higher then $\lambda_0$ – 482.8 nm (see Fig. 1).

\[
T = \frac{\sin^2\left(\frac{\pi}{\lambda} \sqrt{\left(\Delta n^2 + \Delta n_0^2\right)}\right)}{1 + \left(\Delta n / \Delta n_0\right)^2} \tag{1}
\]

where d is the crystal thickness, $\Delta n = n_0(p_\alpha) - n_0(p_\beta)$ is the difference of refractive index for frequencies higher than $\lambda_0$, where refractive indexes are determined by properties of gyrotropy. In the short wavelength region $\Delta n = n(E\parallel a) - n(E\parallel b)$ 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 $\lambda_0$ at 9K $\Delta n = n_0(p_\alpha) - n_0(p_\beta)$ 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$\parallel a$. Maxima with energy 2.643 eV ($n^a=2$), 2.685 eV ($n^B=2$), 2.810 eV (b1), 2.925 eV (b2), 3.016 eV (b3) were observed in E$\parallel b$ 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 excitonic transitions.

The Rydberg constant of free excitons in E$\parallel a$ polarization calculated according to the energy position of n =1 and 2 lines in TlGaS$_2$ is equal to 35 meV. A band gap $E_g = 2.639$ 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 ($E_g$) equal to 2.699 eV were calculated for E$\parallel b$ polarization on the basis of maxima observed at 2.643 eV ($n^B=1$) and 2.685 eV ($n^B=2$).

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$\parallel a$ and E$\parallel b$ polarizations of the light waves (Fig. 2).
According to theoretical band structure calculations [2], the valence band of TlGaS₂ 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 D₂₅ and D₉₃ factor groups of the crystal [3]. For exciton states it was found that [3]:

\[ \Gamma_{ex}(s) = E + x \cdot E^* = A_0 + B_{2u} + B_{3u} + B_{3g} \]

\[ \Gamma_{ex}(pz) = E + x \cdot E^* \cdot B_{2u} = A_0 + B_{2g} + B_{2u} + B_{2e} \]

\[ \Gamma_{ex}(px) = E + x \cdot E^* = A_0 + B_{2g} + B_{2u} + B_{2e} \]

\[ \Gamma_{ex}(py) = E + x \cdot E^* = A_0 + B_{2g} + B_{2u} + B_{2e} \]

(2)

According to the selection rules [8], the dipole allowed S-exciton transitions with B₃u, B₂u and B₃g 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 B₃u symmetry (marked as A) allowed in E∥a polarization, as well as of excitons with B₃g symmetry (marked as B) allowed in E∥b polarization are observed in TlGaS₂ crystals (Fig. 3). The contours of measured (exp) and calculated (calc) reflection spectra of TlGaS₂ 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 dielectric function near the exciton resonance is written as follows [5]:

\[ \varepsilon(\omega, \mathbf{k}) = \varepsilon_0 + \frac{2\varepsilon_0 \omega_{LT} \omega_0}{\omega_0^2 - \omega^2 + \frac{\hbar^2 \mathbf{k}^2}{2\mathbf{M}} \omega_0 - i\gamma \omega} \]  

(3)

where \( \varepsilon_0 \) is the background dielectric constant with contributions from all the interaction mechanisms except for the oscillator involved, \( \omega_0 \) is the transversal exciton frequency, \( \mathbf{M} = m_e^* + m_v^* \) is the exciton translation mass, \( \mathbf{k} \) is the wave vector, \( \omega_{LT} = \omega_L - \omega_0 \) is the longitudinal-transversal splitting, \( \omega_L \) 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:

\[ R = \left| \frac{1 - n_0 \sqrt{n_1 n_2 + \varepsilon_0 \mathbf{E}_b}}{1 + n_0 \sqrt{n_1 n_2 + \varepsilon_0 \mathbf{E}_b}} \right|^2 \]

\[ \left( \frac{1 - n_0}{1 + n_0} \sqrt{n_0 n_1 + n_0 n_2} \right) e^{2i \lambda \mathbf{E}_b} \]  

(4)

where \( n_0 = \sqrt{\varepsilon_0} \), \( n^* = \frac{n_1 n_2 + \varepsilon_0}{n_1 + n_2} \), \( t \) is the dead layer thickness, \( \mathbf{k} \) is the exciton wave vector, \( n_1, n_2 \) are the refractive indices of transversal waves taking into account dependence on the damping parameter \( \gamma \).

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 B₂₂⁺-exciton was achieved with the following parameters: \( \varepsilon_0 = 6.2 \), \( \omega_0 = 2.604 \text{ eV}, \omega_{LT} = 8 \text{ meV}, \gamma = 13 \text{ meV}, \mathbf{M} = 2.3 m_0 \) and \( L = 15 \text{ Å} \). 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 B₂₂⁺-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 TlGaS₂ 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 B₉₋₂⁺-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: \( \varepsilon_0 = 6.8, \omega_0 = 2.643 \text{ eV}, \omega_{LT} = 3.8 \text{ meV}, \gamma = 6 \text{ meV} \mathbf{M} = 2.0 m_0 \) and \( L = 10 \text{ Å} \). The n=2 excited state of the B₉₋₂⁺-exciton is observed at 2.685 eV, which gives a bandgap of \( \mathbf{E}_g = 2.699 \text{ eV} \). The magnitude of the longitudinal-transversal splitting (\( \omega_{LT} = 3.8 \text{ meV} \)) also confirms that B₃u-excitations are allowed in dipole approximation for the E∥b polarization.
The effective reduced mass of the $B_{3u}$ and $B_{3u}$ excitons was determined from the relation $\mu = e^2 R / \hbar^2$, where $R_0$ is the Rydberg constant of hydrogen atom (13.6 eV) and $R$ is the binding energy of excitons. The reduced mass of the $B_{2e}$-exciton calculated with a background dielectric constant $\varepsilon_0 = 6.2$ 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 $\varepsilon_0 = 6.8$ and a binding energy $R = 56$ meV. The Bohr radius ($a_0$) of the S - state of the $B_{2e}$ and $B_{3u}$ excitons is equal to $0.3x10^{-8}$ cm and $0.2x10^{-8}$ cm, respectively. Taking into account that the exciton mass $m$ is equal to the sum of masses of holes and electrons $m = m_{\psi} + m_e$, and the reduced mass $1/\mu$ is equal to $(1/m_{\psi}) + (1/m_e)$, the effective mass of electrons and holes were estimated as $m_{\psi} = 0.11m_0$, $m_{\psi} = 2.14m_0$, and $m_e = 1.89m_0$.

The investigation of anisotropy of the spectral dependence of refractive indices $n_a$ and $n_b$ for $E||a$ and $E||b$ polarizations in $\text{TlGaS}_2$ 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 reflection 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 $\text{TlGaS}_2$ 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 $\Gamma$-point of the Brillouin zone. $\text{TlGaS}_2$ crystals placed between crossed polarizers have a potential application as narrowband filters.

REFERENCES


[6]