

# EXCITONIC SPECTRA of TlGaSe<sub>2</sub> CRYSTALS

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**Abstract:** The indirect transitions in excitonic region with phonons emission in absorption spectra of TlGaSe<sub>2</sub> crystals and ground and excited states of four excitonic series A, B, C and D were observed. The parameters of excitons and bands were determined by analysis of discovered excitonic series.

**Index Terms:** reflection and transmission spectra, wavelength-modulated spectra, excitons.

## 1. Introduction

TaGaSe<sub>2</sub> semiconductors crystallize as a lamellar structure and have monoclinic lattice [1, 2]. One of the features of these crystals is a strong anisotropy of physical characteristics due to the specificity of the crystal structure [1 -3]. The influence of temperature and pressure on the optical spectra near the absorption edge in TlGaSe<sub>2</sub> crystals were studied [4 - 11]. It was investigated the Raman scattering at different geometries and temperatures (from 77 to 400 K) [12]. The calculations of anions and cations relative effective charges for E||a and E||b polarizations show the difference in its ionicity degree along axes a and b [12]. There are a lot of references dedicated to investigations of these materials (see Ref. [4 - 15]). Spectra of wavelength modulated reflection and transmission were investigated in present work. The new data of excitonic states and electron transitions in intrinsic region for TlGaSe<sub>2</sub> crystals were received.

## 2. Experimental methods

Low-temperature spectra of TlGaSe<sub>2</sub> crystals were measured by high-aperture double spectrometers DFS-32 and SDL-1 with linear dispersion 7 Å/mm and aperture ratio 1:2. The optical system allows registering data with bandwidth 0.2Å (±0.1 meV). The cleft crystals of TlGaSe<sub>2</sub> with different thicknesses were mounted into the LTS-22 C 330 optical helium cryogenic system.

## 3. Experimental results and discussion

According to crystallographic data the TlGaSe<sub>2</sub> structure is described by C<sub>2h</sub><sup>6</sup> space group. The unit cell contains eight formula units. The main motive of structure is formed by tetrahedral polyhedrons Ga<sub>4</sub>Se<sub>10</sub> composite of four GaSe<sub>4</sub> tetrahedrons. The structure of TlGaSe<sub>2</sub> can be attributed to pseudo tetrahedral, because a = b = 10.31 Å, c = 15.16 Å and β = 99.7° [1 - 3]. According Ref. [4, 16] the beginning of absorption edge for these crystals are formed by indirect excitonic transitions with energy 2.160 eV (5 K). The minima direct transitions are due to excitonic states 2.128 eV and 2.160 eV (5 K) for E||b polarization and 2.154 eV in E||a polarization [4, 16].

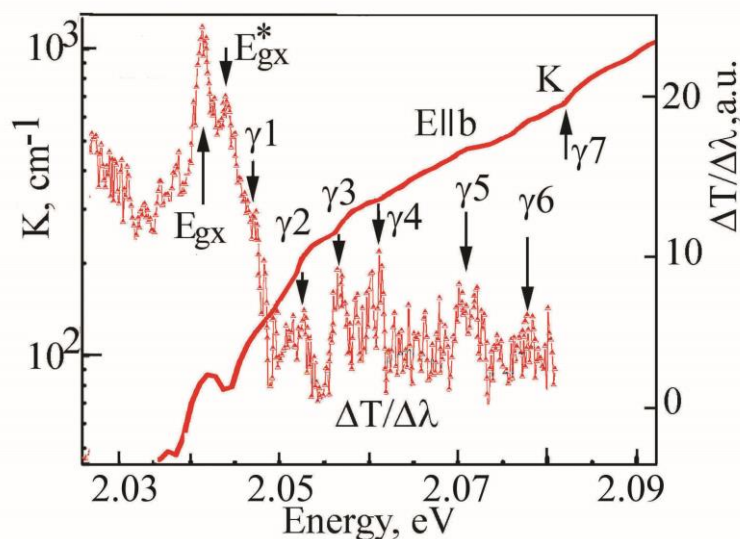


Figura 1. Absorption (K) and wavelength modulated transmission ( $\Delta T/\Delta\lambda$ ) spectra of TlGaSe<sub>2</sub> crystals of thickness 1.45 μm.

Absorption spectra of TlGaSe<sub>2</sub> crystal of 1.45 mm thickness in polarization E||b at 10 K have a maximum at 2.0435 eV and weak lines  $\gamma_1 - \gamma_7$  at 2.0496; 2.0549; 2.0586; 2.0638; 2.0727; 2.089; 2.096 eV (see Fig. 1). The most long-wavelength (2.0435 eV) line in wavelength-modulated transmission spectra is split on two maxima  $E_{gx}$  (2.0439 eV) and  $E_{gx}^*$  (2.0466 eV). These maxima are caused by indirect transitions to excitonic band [16]. Line  $\gamma_1 - \gamma_7$  are due to indirect transitions to excitonic band with phonon emission. The energy distance between  $E_{gx}$  (2.0439 eV) and lines  $\gamma_1, \gamma_2 \dots \gamma_5$  are equal to 5.7, 11.0, 14.7, 19.9 and 29.2 meV, respectively. These values almost coincide with values of optical phonons from IR reflection spectra (see Ref. [12]). Phonons with minimal energy 4.2 eV (34 cm<sup>-1</sup>) and symmetry A<sub>g</sub> and B<sub>g</sub> were observed in Raman spectra [12]. The splitting energy of maxima  $E_{gx}$  (2.0439 eV) and  $E_{gx}^*$  (2.0466 eV) is 2.7 meV i.e. it is smaller than minimal phonon energy. It is possible, that this splitting reflects the change interaction or connects with interference effects. The interference lines bend almost all lines  $\gamma_1 - \gamma_7$  (see Fig. 1).

Two maxima at 2.168 eV and 2.189 eV due to the ground ( $n^A = 1$ ) and excited ( $n^A = 2$ ) states of long-wavelength excitons (marked as A excitons) is observed in  $\lambda$ -modulated transmission spectra (Fig. 2). For A excitonic series the binding energy (R) of excitons is equal to 28 meV and band gap equals to 2.196 eV.

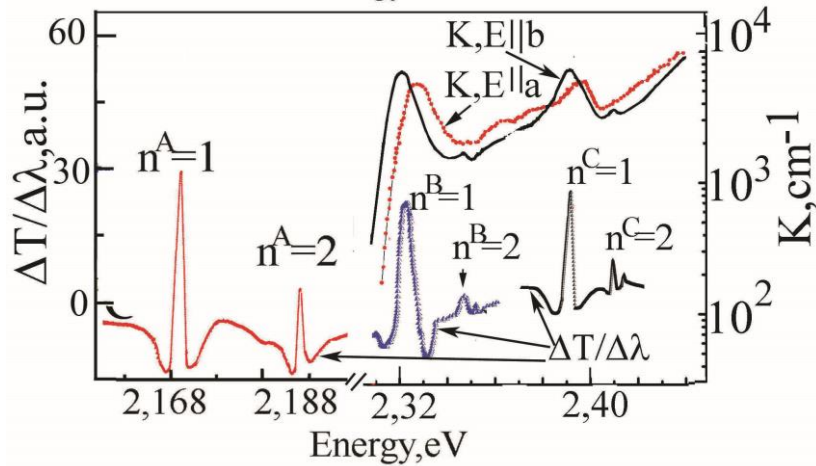


Figure 2. Absorption (K) spectra in polarizations E||a and E||b and wavelength modulated transmission ( $\Delta T/\Delta\lambda$ ) spectra of TlGaSe<sub>2</sub> crystals of thickness 7  $\mu\text{m}$ .

Absorption spectra (K) of TlGaSe<sub>2</sub> crystals at high absorption coefficients were measured for 7  $\mu\text{m}$  crystals in polarizations E||a and E||b (see Fig. 2). The ground and excited states of B and C excitons were discovered in wavelength modulated transmission ( $\Delta T/\Delta\lambda$ ) spectra at temperature 10 K (Fig. 2). The observed absorption band at 2.3273 eV is due to  $n^B = 1$  and line at 2.3450 eV to  $n^B = 2$  states of B excitonic series. The binding energy (R) of this series excitons is equal to 23.6 meV and band gap equals to 2.3509 eV. Maxima of absorption and wavelength modulated transmission were observed at energies 2.390 eV and 2.4103 eV and can be attributed to the states  $n^C = 1$  and  $n^C = 2$  of excitonic series C, respectively. Authors of Ref. [4] reported about the observing in absorption spectra a maximum at 2.39 eV attributed to direct excitonic transitions. According our data the binding energy is corresponding to 28.4 meV and the continuum energy is equal to 2.4174 eV.

Maxima a1 - a5 were observed in wavelength modulated transmission spectra ( $\Delta T/\Delta\lambda$ ) of TlGaSe<sub>2</sub> crystals of thickness  $d = 7 \mu\text{m}$  at temperature 10 K in E||a polarization (Fig. 3). Maxima b1 - b5, which except b1 shift to higher energies approximately on 5 meV, were discovered in E||b polarization. Almost the same lines except a1 and b1 were observed in wavelength modulated reflection ( $\Delta R/\Delta\lambda$ ) at 30 K (Fig. 4). The lines a6, b6 and b7 were revealed at higher energies. The insert of Fig. 3 shows a fragment of band structure for explaining observed electron transitions. The sharp lines of modulated transmission spectra a1 and b1 (2.1278 eV) were not observed in wavelength modulated reflection spectra and thus we suppose that they are due to indirect transitions from  $\Gamma$  point to the excitonic band of second minimum of C<sub>2</sub> conduction band nearby points Z - L (see insert of Fig. 3). Authors of Ref. [16] have discovered maxima at 2.128 eV which is attributed to the direct excitons transitions. Bands C<sub>1</sub> and C<sub>2</sub> are split in point Z - L on 84 meV. Maxima a3 and b3 are due to excitonic transitions from valence bands V<sub>1</sub> and V<sub>2</sub> to conduction band C<sub>2</sub> because the splitting of these transitions is equal to 16.0 meV. The splitting of a2 and b2 is equal to 12.6 meV. The different value of splitting energy of a2 - b2 (12.6 meV) and a3 - b3 (16.0 meV) is caused by the fact that these transitions take place to excitonic bands with a bit different binding energies (with difference around 3.6 meV). High-energy maxima a4 and b4 are attributed to transitions from valence bands V<sub>3</sub> and V<sub>4</sub> to

conduction band  $C_1$  and the band splitting is equal to 26 meV. Maxima  $a_5$  and  $b_5$  observed at short-wavelengths are probably caused by transitions from valence bands  $V_5$  and  $V_6$  to conduction band  $C_1$  or transitions from bands  $V_3$  and  $V_4$  to conduction band  $C_2$ .

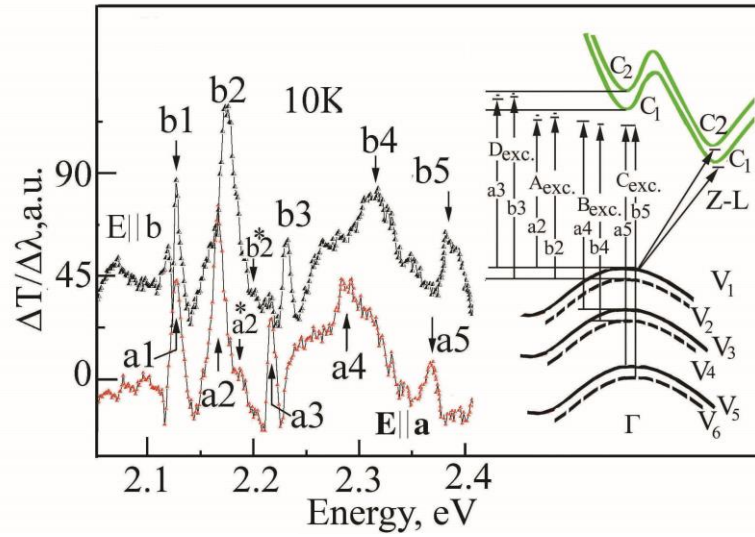


Figure 3. Wavelength modulated transmission ( $\Delta T/\Delta\lambda$ ) spectra of TlGaSe<sub>2</sub> crystals of 7  $\mu\text{m}$  in polarizations E||a and E||b. Insert shows the band structure fragment in Brillouin zone center.

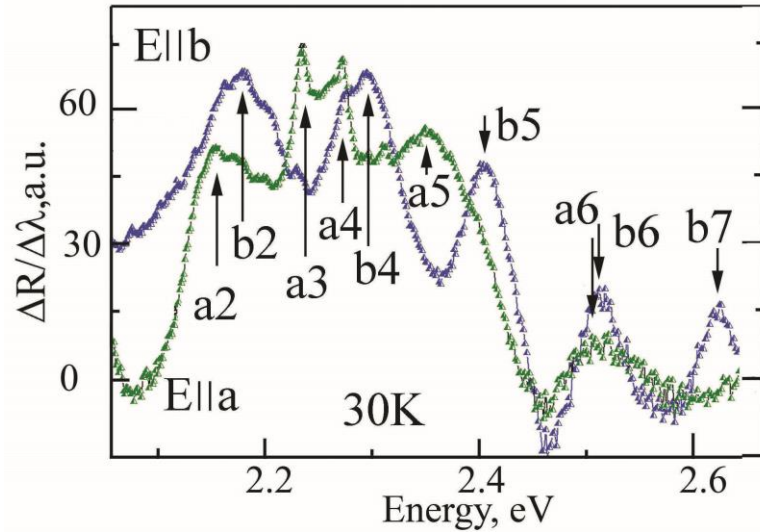


Figure 4. Wavelength modulated reflection spectra ( $\Delta R/\Delta\lambda$ ) in E||a and E||b polarizations at temperature 30 K.

According data of Ref. [17] was determined by selection rules that dipole-allowed S excitonic transitions with  $B_{1u}$ ,  $B_{2u}$  and  $B_{3u}$  symmetry are allowed in polarizations E||c, E||a and E||b, respectively. P excitonic transitions in dipole approaching are forbidden by selection rules. Thus the lines of excitons  $B_{2u}$  and  $B_{3u}$  symmetry allowed in polarizations E||a and E||b, respectively were observed in TlGaSe<sub>2</sub> and TlGaS<sub>2</sub> crystals. The reduced effective masses ( $\mu^*$ ) of  $B_{2u}$  and  $B_{3u}$  were calculated from ratio  $\mu^* = \epsilon_b^2 R/R_H$ , where  $R_H$  is the Rydberg energy of hydrogen atom (13.6 eV),  $R$  is binding energy of corresponding excitons and  $\epsilon_b$  is background dielectric constant. The reduced effective mass ( $\mu^*$ ) of A exciton  $B_{2u}$  symmetry is equal to  $0.082m_0$ , in the case than background dielectric constant  $\epsilon_b = 6.2$  and binding energy  $R = 28$  meV. Assumed that translation mass  $M = m_c^* + m_v^*$  is less than one and approximate equal to  $0.5m_0$  thus effective mass of holes  $m_{v1}^* = 0.4m_0$  and effective mass of electrons  $m_{c1}^* = 0.1m_0$ . For B exciton  $B_{3u}$  symmetry at  $\epsilon_b = 6.8$  and binding energy  $R = 24$  meV the reduced effective mass ( $\mu^*$ ) is equal to  $0.08m_0$ . On the base of these data effective mass of holes  $m_{v1}^* = 0.4m_0$  and mass of electron  $m_{c1}^* = 0.1m_0$ . In the case of C excitonic series at  $\epsilon_b = 6.4$  and binding energy  $R = 28$  meV it was calculated the next parameters: reduced effective mass  $\mu^* = 0.08m_0$ , effective masses of holes  $m_{v1}^* = 0.4m_0$  and electrons  $m_{c1}^* = 0.1m_0$ . The Bohr radius ( $\alpha_B$ ) of S state of A, B and C excitonic series with  $B_{3u}$  and  $B_{2u}$  symmetries is equal to  $0.3 \cdot 10^{-5}$  cm.

The insert of Fig. 3 shows the scheme of electron transitions in Brillouin zone center of TlGaSe<sub>2</sub> crystals. The fragment of band diagram with taking into account band dispersion was taken from theoretical calculations from Ref. [18 - 22]. The amount of bands and its energy splitting were built on the base of experimental results (excitonic spectra measured in E||a and E||b polarizations). The energy gap between maxima a2 and b2 is equal to 12.6 meV and between maxima a2 and a4 corresponds to 73 meV. Top bands V<sub>1</sub>, V<sub>2</sub> and V<sub>3</sub> (V<sub>4</sub>) are split by crystal field and spin-orbital interaction in Brillouin zone center. According received data about interval between a2 - b2 and a2 - a4 one can conclude that valence bands V<sub>1</sub> and V<sub>2</sub> are split on 20 meV by crystal field and bands V<sub>1</sub>(V<sub>2</sub>) - V<sub>3</sub> are split by spin-orbital interaction on 65 meV. The bottom conduction band is localized in direction Z - L and is positioned on 122 meV from band C<sub>1</sub> localized in  $\Gamma$  point. Bands C<sub>1</sub> and C<sub>2</sub> have a distance of 50 meV between they in Brillouin zone center and bands C<sub>1</sub> and C<sub>2</sub> in vicinity Z - L are split on 84 meV.

#### 4. Conclusion

The indirect transitions in excitonic bands C<sub>1</sub> and C<sub>2</sub> with phonon emission and direct transitions of excitonic series A, B, C and D were observed in absorption spectra of TlGaSe<sub>2</sub> crystals. The ground and excited states of excitons were discovered in wavelength modulated transmission spectra for E||a and E||b polarizations. The main parameters of excitons and bands for all excitonic series as binding energy of excitons, reduced effective mass, masses of electrons and holes were determined.

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