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CONDENSED MATTER

EXCITONIC SPECTRA of $TlGaSe_2$ CRYSTALS

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Abstract: The indirect transitions in excitonic region with phonons emission in absorption spectra of $TlGaSe_2$ 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.

1. INTRODUCTION

$TaGaSe_2$ 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 $TlGaS_2$ 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 iconicity degree along axes *a* and *b* [12]. There are a lot of references dedicated to investigations of these materials 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 $TlGaSe_2$ crystals were received.

2. EXPERIMENTAL METHODS

Low-temperature spectra of $TlGaSe_2$ 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 $TlGaSe_2$ 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 $TlGaSe_2$ structure is described by C_{2h}^6 space group. The unit cell contains eight formula units. The main motive of structure is formed by tetrahedral polyhedrons Ga_4Se_{10} composite of four $GaSe_4$ tetrahedrons. The structure of $TlGaSe_2$ can be attributed to pseudo tetrahedral, because $a = b = 10.31$ Å, $c = 15.16$ Å and $\beta = 99.7°$ [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].

Absorption spectra of $TlGaSe_2$ crystal of 1.45 mm thickness in polarization E||b at 10 K have a maximum at 2.0435 eV and weak lines γ1–γ7 at 2.0496; 2.0549; 2.0586; 2.0638; 2.0727; 2.089; 2.096 eV (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 γ^1 - γ^7 are due to indirect transitions to excitonic band with phonon emission. The energy distance between E_{gx} (2.0439 eV) and lines γ^1, γ^2… γ^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 [12]. Phonons with minimal energy 4.2 eV (34 cm^{-1}) and symmetry A_g and B_g 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 linens γ^1 - γ^7 (Fig. 1).

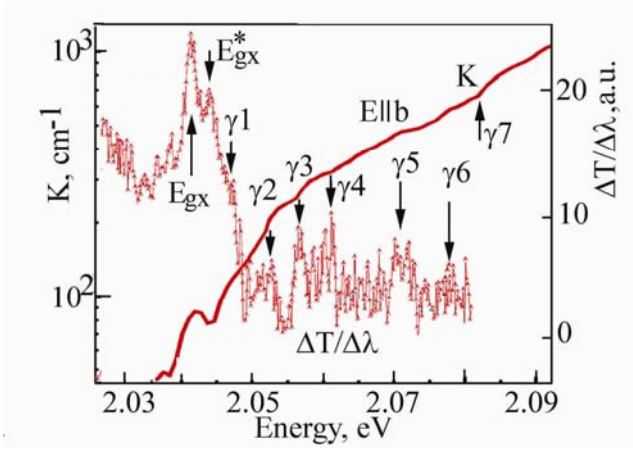

Fig. 1. – Absorption (K) and wavelength modulated transmission ($\Delta T/\Delta\lambda$) spectra of $TlGaSe_2$ crystals of thickness 1.45 μm.

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 λ-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.

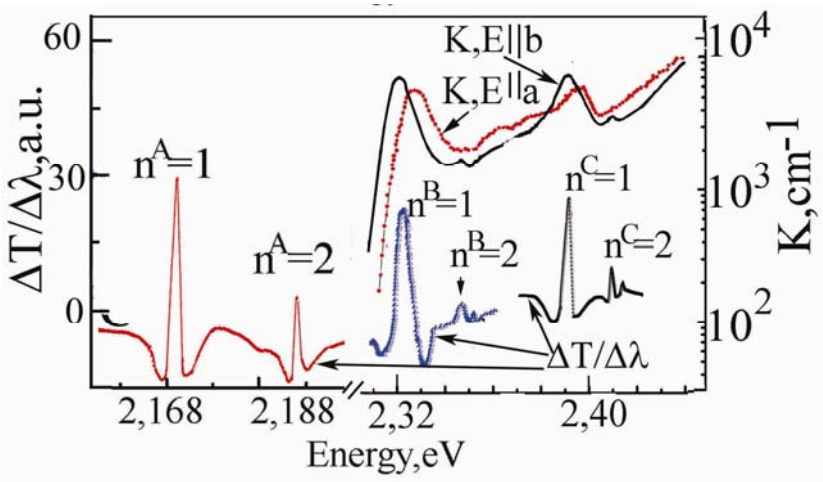

Fig. 2. – Absorption (K) spectra in polarizations $E||a$ and $E||b$ and wavelength modulated transmission ($\Delta T/\Delta\lambda$) spectra of $TlGaSe_2$ crystals of thickness 7 μm.

Absorption spectra (K) of $TlGaSe_2$ crystals at high absorption coefficients were measured for 7 μm crystals in polarizations $E||a$ and $E||b$ (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 a_1–a_5 were observed in wavelength modulated transmission spectra ($\Delta T/\Delta\lambda$) of $TlGaSe_2$ crystals of thickness d = 7 μm at temeperature 10 K in $E||a$ polarization (Fig. 3). Maxima b_1–b_5, which except b_1 shift to higher energies approximately on 5 meV, were discovered in $E||b$ polarization. Almost the same lines except a_1 and b_1 were observed in wavelength modulated reflection ($\Delta R/\Delta\lambda$) at 30 K (Fig. 4). The lines a_6, b_6 and b_7 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 a_1 and b_1 (2.1278 eV)

were not observed in wavelength modulated reflection spectra and thus we suppose that they are due to indirect transitions from Γ point to the excitonic band of second minimum of C_2 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_1 and C_2 are split in point Z–L on 84 meV. Maxima a_3 and b_3 are due to excitonic transitions from valence bands V_1 and V_2 to conduction band C_2 because the splitting of these transitions is equal to 16.0 meV. The splitting of a_2 and b_2 is equal to 12.6 meV. The different value of splitting energy of a_2–b_2 (12.6 meV) and a_3–b_3 (16.0 meV) is caused by the fact that these transitions take place to excitonic bands with a bit different binging energies (with difference around 3.6 meV). High-energy maxima a_4 and $_{b4}$ are attributed to transitions from valence bands V_3 and V_4 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.

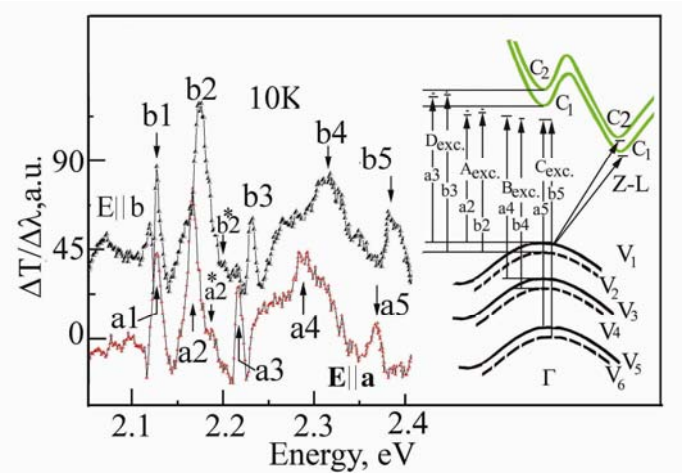

Fig. 3. – Wavelength modulated transmission ($\Delta T/\Delta\lambda$) spectra of $TlGaSe_2$ crystals of 7 μm in polarizations $E||a$ and $E||b$. Insert shows the band structure fragment in Brillouin zone center.

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 $TlGaSe_2$ and $TlGaS_2$ crystals. The reduced effective masses (μ^*) of B_{2u} and B_{3u} were calculated from ratio $\mu^* = \varepsilon_b^2 R/R_H$, where R_H is the Rydberg energy of hydrogen atom (13.6 eV), R is binding energy of corresponding excitons and ε_b is background dielectric constant. The reduced effective mass (μ^*) of A exciton B_{2u}

symmetry is equal to 0.082 m_0, in the case than background dielectric constant ε_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 0.5 m_0 thus effective mass of holes m_{v1}^* = 0.4 m_0 and effective mass of electrons m_{c1}^* = 0.1 m_0. For B exciton B_{3u} symmetry at ε_b = 6.8 and binding energy R = 24 meV the reduced effective mass (μ^*) is equal to 0.08 m_0. On the base of these data effective mass of holes m_{v1}^* = 0.4 m_0 and mass of electron m_{c1}^* = 0.1 m_0. In the case of C excitonic series at ε_b = 6.4 and binding energy R = 28 meV it was calculated the next parameters: reduced effective mass μ^* = 0.08 m_0, effective masses of holes m_{v1}^* = 0.4 m_0 and electrons m_{c1}^* = 0.1m_0. The Bohr radius (α_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.

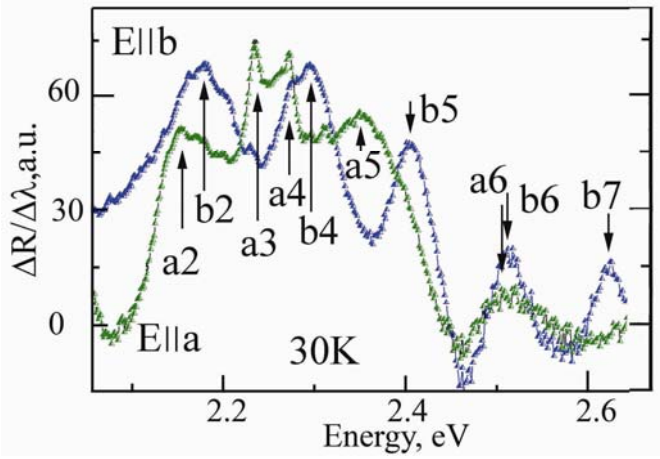

Fig. 4. – Wavelength modulated reflection spectra ($\Delta R/\Delta\lambda$) in $E||a$ and $E||b$ polarizations at temperature 30 K.

The insert of Fig. 3 shows the scheme of electron transitions in Brillouin zone center of $TlGaSe_2$ 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 a_2 and b_2 is equal to 12.6 meV and between maxima a_2 and a_4 corresponds to 73 meV. Top bands V_1, V_2 and V_3 (V_4) are split by crystal field and spin-orbital interaction in Brillouin zone center. According received data about interval between a_2–b_2 and a_2–a_4 one can conclude that valence bands V_1 and V_2 are split on 20 meV by crystal field and bands $V_1(V_2)$–V_3 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 form band C_1 localized in Γ point. Bands C_1 and C_2 have a distance of 50 meV between they in Brillouin zone center and bands C_1 and C_2 in vicinity Z–L are split on 84 meV.

4. CONCLUSION

The indirect transitions in excitonic bands C_1 and C_2 with phonon emission and direct transitions of excitonic series A, B, C and D were observed in absorption spectra of $TlGaSe_2$ 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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