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 were determined.*

Keywords: *semiconductor compound; optical absorption and reflection spectra; wavelength modulated spectra; band structure.*

1. Introduction

$TlGaS_2$ 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].

2. Experimental methods

The crystals grown by Bridgmann 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.

3. Experimental results and discussions

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. The 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. The 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.

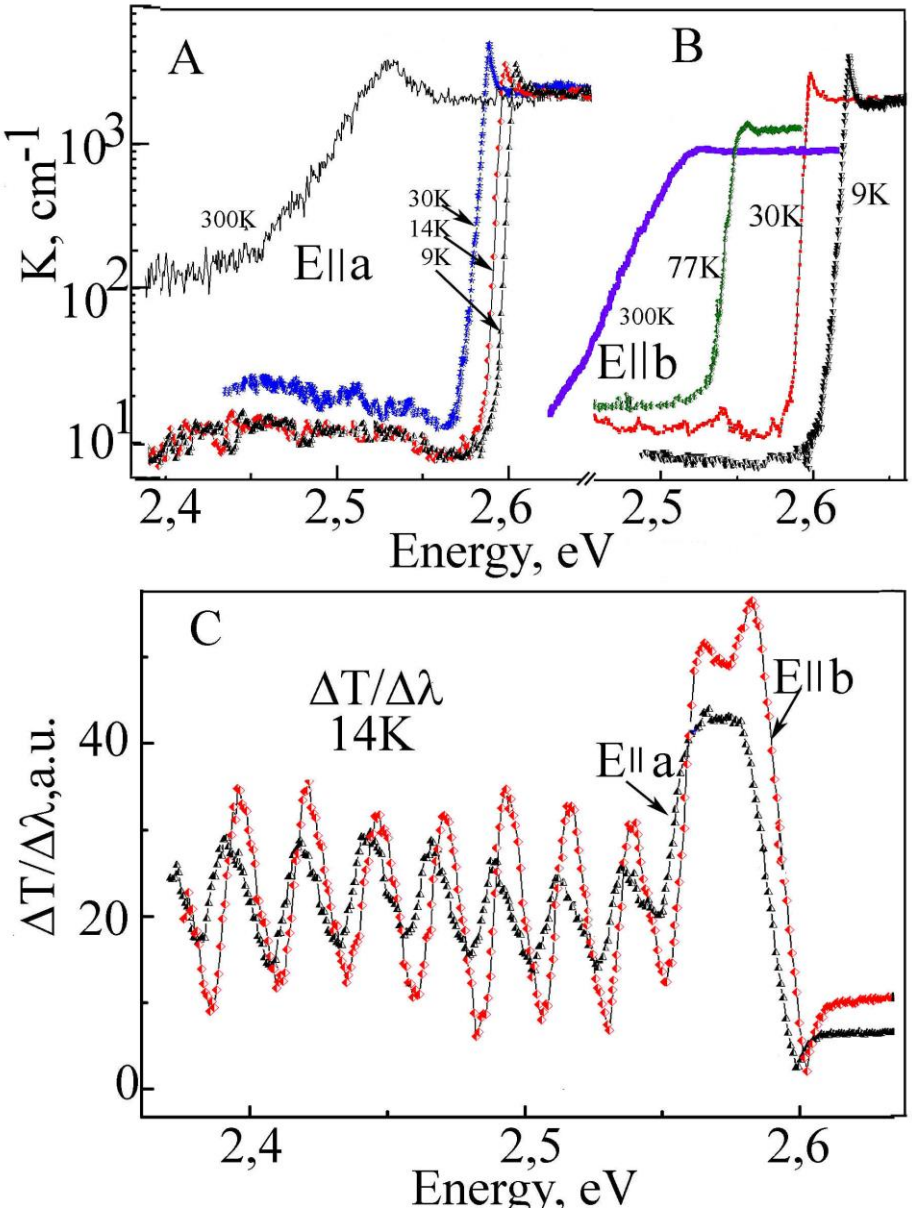

Figura 1. A, B - Absorption spectra of $TlGaS_2$ crystals of 17.5 μm thickness in polarizations E||a (A) and E||b (B) measured at different temperatures. C - Wavelength modulated transmission spectra measured at temperature 14 K.

The 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 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.

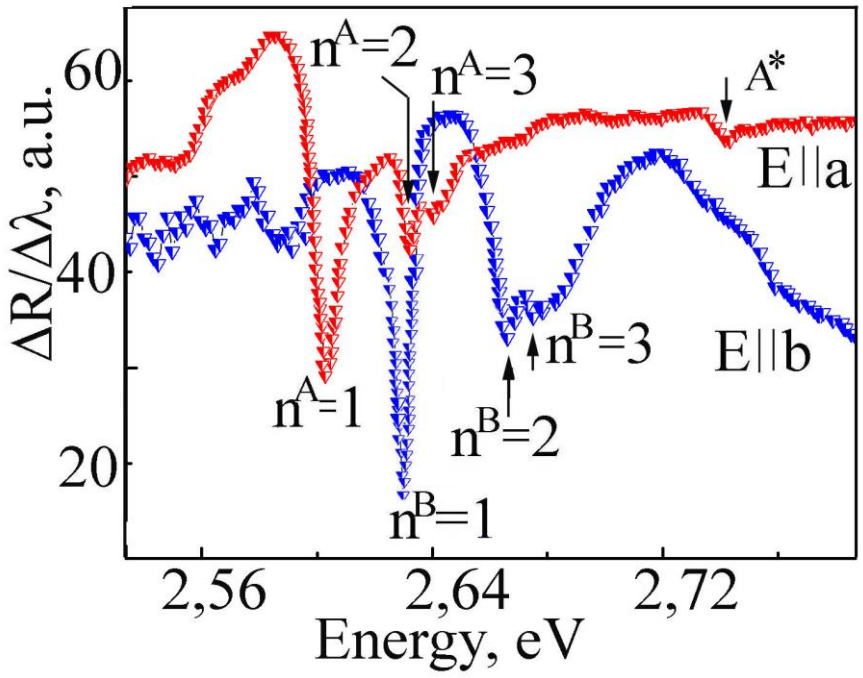

Figura 2. Wavelength modulated reflection spectra of $TlGaS_2$ crystals with 970 μm thickness measured in excitonic region in E||a and E||b polarizations at temperature 14 K.

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].

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. 2). 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 $\varepsilon_b = 6.8$, $\omega_0 = 2.643$ eV, $\omega_{LT} = 3.8$ meV, $\gamma = 6$ 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 $\varepsilon_b = 6.2$ and binding energy R = 35 meV. In the case of B_{3u} symmetry at $\varepsilon_b = 6.8$ and R = 50 - 56 meV the reduced exciton mass $\mu^* = 0.19m_0$. Bohr radius (α_B) of S - state B_{2u} exciton is equal to 0.3×10^{-5} cm and for B_{3u} - $\alpha_B = 0.2\times10^{-6}$ 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].

4. 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 **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.

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