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Wannier–Mott excitons in GaSe single crystals

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Abstract
The absorption, reflection and photoluminescence spectra of GaSe crystals with different thicknesses (100 nm–1 mm) were investigated in a wide temperature interval (300 K–10 K). Features due to excitonic states in the spectra were recognized. The contours of the excitonic reflection spectra measured at 10 K were calculated by dispersion equations. On the basis of these calculations, the parameters of the observed excitons were determined. Photoluminescence spectra from the cleaved surface and from the uncleaved facet of a sample were measured at low temperatures.

Keywords: gallium monoselenide, excitonic states, optical spectroscopy, absorption, reflection and photoluminescence spectra

(Some figures may appear in colour only in the online journal)

1. Introduction

Gallium selenide (GaSe) compound is a layered crystal with unique properties. It is easily cleaved along the cleavage plane perpendicular to the optical axis *c*. In the layers plane, this crystal has covalent chemical bonds and Van der Waals forces acting between the layers [1, 2]. The existence of weak bonds between the layers and the absence of dangling bonds exclude the possibility of surface level formation. The concentration of these bonds is two orders lower than in usual semiconductors. This allows us to obtain very thin optically homogeneous samples with thicknesses down to 100 nm with a natural mirror surface. Due to the relatively low absorption coefficient ($\alpha \approx 10^3$ cm^{-1}) in the beginning of the intrinsic absorption region, deep penetration of the incident radiation into the sample is possible [1–6].

Detectors of visible and near infrared optical emission were developed on the basis of this material [5–7]. It is predicted that this material will be used in quantum electronics and for the development of highly effective photovoltaic convertors, gas sensors, thermoelectric converters and effective sources of terahertz laser emission [6, 8, 9].

Two-dimensional mono-chalcogenides (GaSe) belong to a unique and promising class of layered crystals. Different optical and optoelectronic properties have been investigated many times [5–11]. The possibilities of device development on thists basis have been studied too [10, 11].

The progress achieved in growing GaSe crystal technology, and the prospects for their technical use, have led to numerous studies of optical properties of GaSe-type semiconductors, and they have stimulated the band structure calculations of these crystals. The valence band of single layer GaSe, as predicted by theory, is inverted into a bow-shaped (often referred to as an inverted sombrero) and relatively flat dispersion, which is expected to give rise to strongly correlated effects [9, 10].

Using theoretical calculations and experimental investigations of multilayered GaSe, the authors of [1, 5, 7, 9, 10] have demonstrated that the top valence bands in the center of the Brillouin zone consist of five bands. These bands are split by spin orbital interaction and crystal fields. Electron density distribution levels in a layered semiconductor were built by the
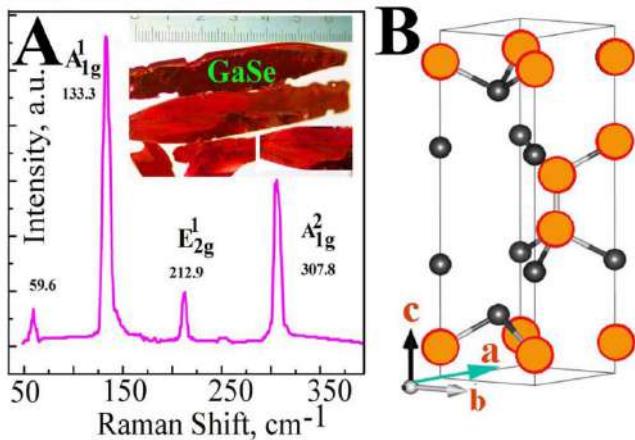
Figure 1. The typical Raman spectrum (A) and crystal structure of GaSe single crystals (B).

authors and experimental evidence of the validity of such calculations has been obtained. It transpired that energy states, whose electron density formed from atomic orbitals overlapping between separate layers, situate on the border of the conduction band and valence band. This predetermines the presence of several bands and a very weak anisotropy of excitons in $\overrightarrow{k} = 0$ in GaSe crystals.

In this work, absorption, reflection and photoluminescence spectra in the near edge region were investigated in GaSe single crystals in the temperature range 10 K–300 K. The excitonic states of Wannier—Mott with low binding energy (21.8 meV) were determined. For the first time, contours of excitonic reflection spectra were calculated and exciton and band parameters were determined.

2. Experimental methods

GaSe single crystals were grown in ampoules by the zone melting method in the form of ingots with a size of $1 \times 1.2 \times 6.5$ cm. These ingots were easy cleaved and this allowed us to obtain mirror surfaces of plates with different thicknesses from 100 nm 5 mm. Very thin samples were obtained by exfoliation with the help of scotch tape. Raman and x-ray spectroscopy were used for crystal quality control. The Raman spectra and images of the grown crystals are shown in figure 1(A). The presence of other structural phases in the volume of GaSe single crystals was controlled by SEM images and Raman spectra measured in different places in the samples. The typical Raman spectrum of a single crystal is shown in figure 1(A). Figure 1(B) demonstrates the positions of gallium (Ga) and selenium (Se) atoms in the GaSe unit cell (Ga is the small balls and Se is the large balls) and the crystallographic axes directions.

Most of the optical transmission and reflection spectra were measured on a double high-aperture spectrometer SDL-1 with aperture 1:2 and a linear dispersion of 7 Å mm^{-1}. The low temperature spectra of the investigated crystals deposited in a closed-circuit helium optical cryogenic system LTS-22 C 330

were measured when the entrance and exit slits of the spectrometer did not exceed 70 μm, i.e. with a resolution of ~0.7 Å. The obtained plate surfaces were perpendicular to the *c* axis and had a high reflection coefficient similar to the reflectivity of a polished aluminum mirror. Raman spectra were measured with the help of a double grating spectrometer DFS-32 (figure 1(C)). Wavelength modulation reflection and transmission spectra were measured by a single-grating spectrometer MDR-2 with aperture 1:2 and a linear dispersion of 7 Å mm^{-1}. PL spectra were excited in back scattering mode by a He-Ne gas laser (325 nm) and a semiconductor blue laser (448 nm) and were measured on a double grating spectrometer SDL-1.

3. Experimental results and discussions

Figure 2(A) illustrates the edge absorption spectra of a GaSe single crystal measured in the temperature range of 300 K–10 K. The edge absorption shifts to higher energies as the temperature decreases. A temperature shift coefficient $\beta = \Delta E/\Delta T = 2.7 \ 10^{-4}$eV/K. Figure 2(B) illustrates the comparison of the photoluminescence from the cleavage surface with the absorption spectra of GaSe crystals measured at room temperature. The sample thicknesses were chosen to avoid interference in the measured absorption spectra. The intensive maximum at 2.0335 eV is determined in the photoluminescence spectrum. The same maximum appears in the absorption spectra. This line is due to the ground state $\boldsymbol{n} = 1$ of excitons (transversal mode ω_T). A very weak peak E^* at 2.153 eV is recognized in the spectra of some crystals and it can be associated with excitonic states.

The absorption spectra shown in figure 3 were measured for crystals with thicknesses of 100 and 300 nm. For the crystals with these thicknesses, the interference fringes are insignificant. An intensive maximum at 2.1120 eV is observed at 10 K. This maximum can be attributed to the ground state $\boldsymbol{n} = 1$ of Wannier—Mott excitons. The excited states $\boldsymbol{n} = 2$ and $\boldsymbol{n} = 3$ of the exciton are observed at energies of 2.1275 and 2.1305 eV, respectively. Taking into account the positions of the ground and excited states of the exciton, the binding energy $\boldsymbol{R}$ of the exciton is equal to 20.6 meV.

The fitting of the contour of the reflection spectrum calculated by dispersion relations ($\boldsymbol{R_{calc.}}$) [12] experimentally measured in the non-polarized light reflection spectrum ($\boldsymbol{R_{exp.}}$) is shown in figure 4(B). The calculations of the reflection spectrum contour were effectuated by both single-oscillator and multi-oscillator models. The theory of these models is sufficiently detailed in [12] (see source references in this work). The influence of interference fringes on the reflection spectra takes place. Thus, besides the maxima associated with excitonic states, the maxima due to interference appear (see figure 4). Those maxima whose positions do not vary with thickness are selected as excitonic features. In the case of interference fringes, their positions change with thickness; namely, the maxima whose position is not dependent on thickness.

Figure 4(A) illustrates the measurements at 10 K reflection spectra of a bulk GaSe crystal in non-polarized (n/p) and polarized (E∥a and E∥b) light. The obtained reflection spectra
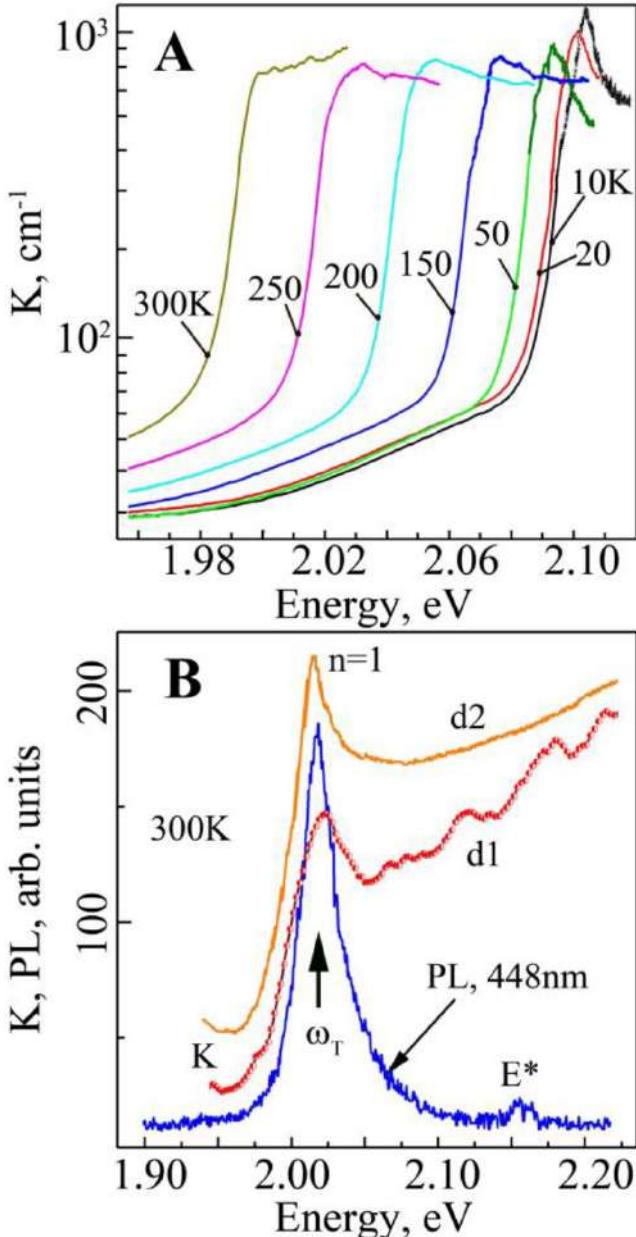
Figure 2. (A) Temperature dependence of the edge absorption spectra of GaSe crystals. (B) The photoluminescence spectrum excited by a 448 nm laser line and the absorption spectra of two crystals with thicknesses of 12 μm (d1) and 7.2 μm (d2) measured at room temperature.

Figure 3. Absorption spectra of GaSe crystals with thicknesses of 100 and 300 nm measured at temperature 10 K.

provide evidence that excitonic spectra in E∥a and E∥b polarizations are practically identical to the spectra in non-polarized light. The intensive maximum at 2.1121 eV caused by the ground state $n = 1$ of Wannier—Mott excitons is determined in the spectra. The lines $n = 2$, $n = 3$ and $n = 4$ at energies of 2.1267, 2.1304 and 2.1318 eV, respectively, are discovered in the high-energy part of the spectra.

The calculation of the reflection spectra for Wannier—Mott excitons (figure 4) gives a good agreement between theory and experiment at the next parameters: $\varepsilon_b = 5.0$ (background permittivity), $\omega_T = 2.1121$ eV (energy of transversal exciton),
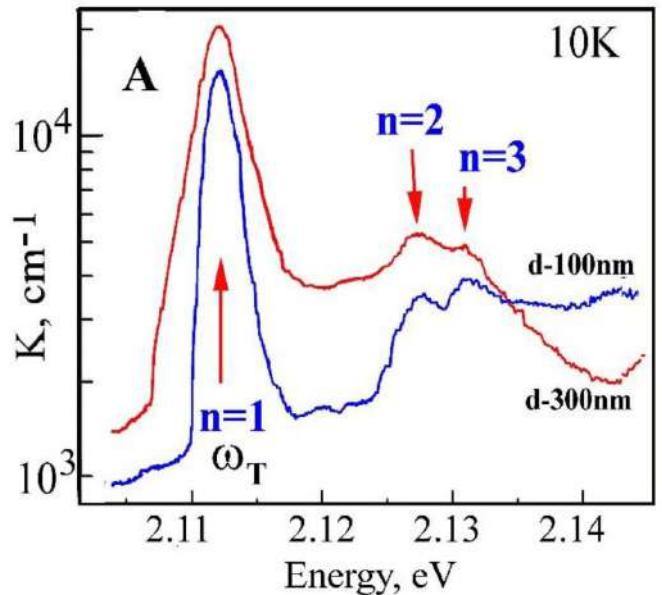
$\omega_{LT} = 3$ meV (longitudinal transversal splitting), $\gamma = 1.4$ meV (damping constant), and $M = 2.5m_0$ (exciton mass). The excited state $n = 2$ of this exciton is observed at 2.127 eV. The longitudinal transversal splitting is $\omega_{LT} = 3$ meV and the binding energy of Wannier—Mott excitons is equal to 20.4 meV. Taking into account these parameters, the minimal band gap E_g for direct transitions from the valence band V_1 of Γ_1 symmetry to the conduction band C_1 with Γ_6 symmetry is equal to 2.1325 eV. These transitions are allowed in polarization E⊥c. The reduced effective mass (μ) of this exciton is 0.038m_0 ($\mu = \frac{\varepsilon_b^2 R}{13.6}$ where R is the binding energy of the exciton and ε_b is the background permittivity). In this case, the effective mass of the electrons in the conduction band C_1 (Γ_6) takes the value of 0.37m_0.

Photoluminescence spectra from the cleavage face excited by different lasers (448 and 325 nm) measured at 10 K are shown in figure 5. An intensive maximum at 2.1145 eV is observed in the spectra excited by the He-Cd laser (325 nm). This maximum is due to the ground state $n = 1$ of Wannier—Mott excitons. The inset of figure 5 illustrates the photoluminescence spectra in the region of excited states of Wannier—Mott excitons. The excited states $n = 2$ (2.1299 eV), $n = 3$ (2.1332 eV), $n = 4$ and $n = 5$ are observed in the inset of figure 5. The binding energy of the exciton according to the above-mentioned data is equal to 20.5 meV. The weak maximum E_b at an energy of 2.0881 eV is determined at long-wavelengths. This maximum was observed at similar energies by Dey *et al* [13] and attributed to biexciton states. The intensive maximum E_F at an energy of 2.0510 eV is observed in the region of lower energies in the photoluminescence spectra at excitation by the semiconductor laser with line 448 nm. In [13], the luminescence spectra are investigated at energies less than the energy of the exciton ground state, where a maximum at a similar energy is determined. The authors of this
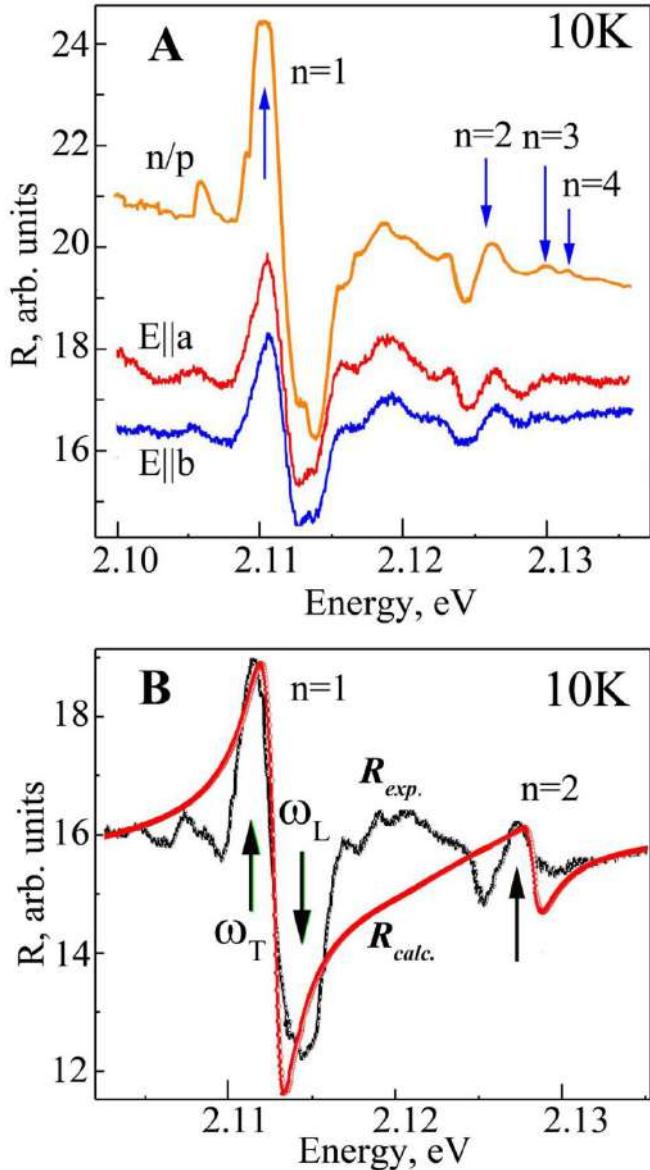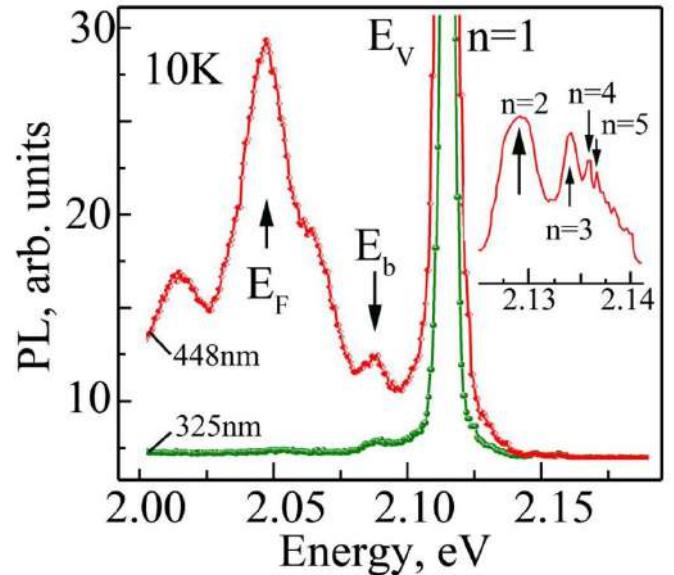
Figure 5. Photoluminescence spectra obtained from the cleavage surface at excitation by different lasers (352 and 448 nm) measured at a temperature of 10 K. The inset illustrates the excited states of the exciton.

Figure 4. (A) Reflection spectra of bulk GaSe single crystal measured at 10 K in non-polarized light (n/p, raised vertically by five units) and in E∥a (raised by two units) and E∥b polarizations. (B) Reflection spectra contours measured in non-polarized light ($R_{exp.}$) and calculated by dispersion equations [12] ($R_{calc.}$).

The weak maximum E_B is possibly caused by biexcitons, as mentioned by Dey *et al* [13]. In the photoluminescence spectra excited by a 448 nm laser, the same intensive maxima E_F, E_V and the weak maximum E_B are observed at the above-mentioned energies. In the photoluminescence spectra excited by a 325 nm laser, the one intensive long-wavelength maximum E_F (2.0462 eV) is determined. At excitation by a short-wavelength line of 325 nm, the intensity of this maximum is one and a half orders of magnitude less. This can be associated with the fact that the long-wavelength laser of 448 nm penetrates deeper into the crystal and the light emission originates from the crystal volume. When a short-wavelength laser of 325 nm excites the crystal, the excitation energy penetrates into a narrower region of the crystal layers and excitons with a low binding energy, Wannier—Mott excitons, appear in the luminescence. These excitonic transitions are possible and have a good agreement with the model of the band structure shown in the insets of figure 6.

Figure 6(A) illustrates the photoluminescence spectra from the cleavage surface measured at 10 K with excitation by 325 and 448 nm lasers. Intensive maxima E_F (2.0462 eV) and E_V (2.1145 eV) in the photoluminescence spectra excited by a 448 nm laser are observed. A weak peak E_B at 2.0881 eV between these intensive maxima is determined.

The temperature dependence of the photoluminescence spectra excited by a 448 nm laser is shown in figure 6(B). The intensive maximum at 2.000 eV is discovered in the photoluminescence spectrum measured at room temperature. Photoluminescence lines observed at room temperature at 2.0335 eV (figure 2(B)) and 2.000 eV (figure 6(B)) can be associated with longitudinal and transversal branches of exciton polaritons. As the temperature decreases, the photoluminescence maximum E_V is shifted toward higher energies at the absorption edge.

work associate this photoluminescence maximum with bound excitons. The presence of bound excitons in this region is not excluded and is even possible. In the above-mentioned spectra, the line E_F is possible due to bound excitons or ground states of excitons with a large binding energy (Frenkel excitons). A very weak peak E^* is also observed in some crystals at 2.153 eV and can be associated with excitonic states (see figure 2(B)).

The short-wavelength maximum E_V (2.1145 eV) is undoubtedly caused by the ground states of Wannier—Mott excitons. These Wannier—Mott excitons are formed by electrons of the conduction band $C_1(\Gamma_6)$ and holes of the valence band V_1 (Γ_1) [9].
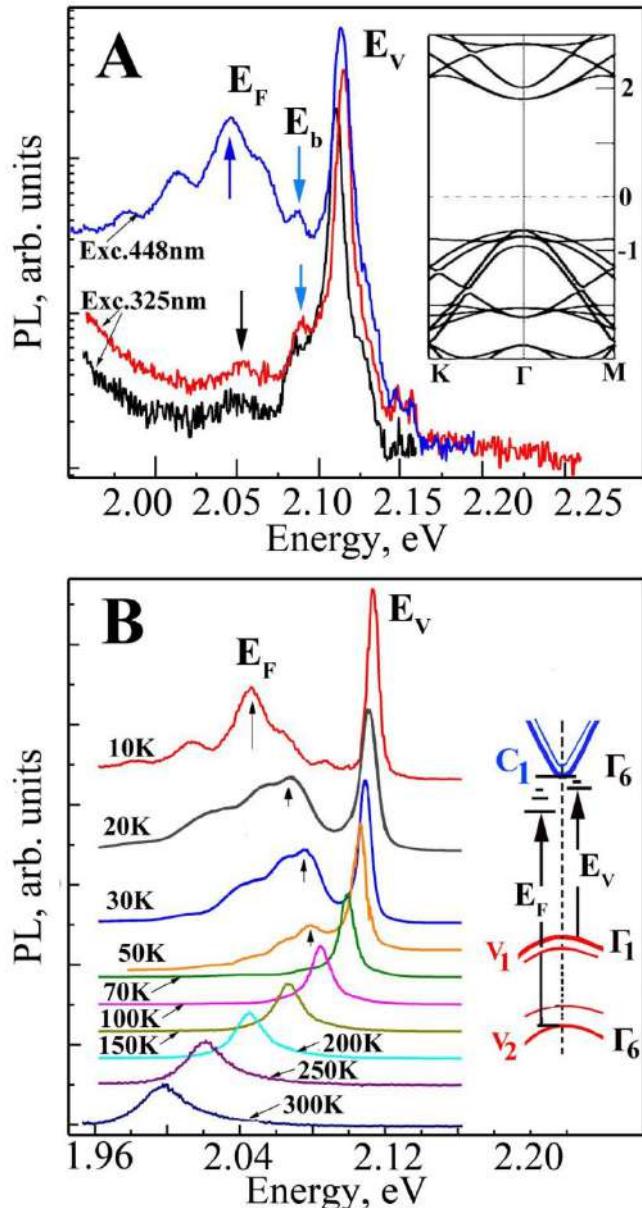
Figure 6. (A) Photoluminescence spectra from the cleavage plane of the sample excited by different lasers measured at a temperature of 10 K. The inset illustrates the band structure fragment from [9]. (B) Temperature dependence of the photoluminescence spectra measured in back scattering mode from the cleavage plane excited by a 448 nm laser. The band structure in Γ point is shown in the inset.

An additional maximum E_F appeared in the long-wavelength part from the maximum E_F at a temperature of 70 K and the intensity of this maximum grows as the temperature decreases. The main characteristic of these intensive maxima is the fact that the maximum E_V shifts to higher energies with coefficient $\beta = \Delta E/\Delta T = 0.38 \cdot 10^{-2}$ eV K^{-1}. However, the intensive photoluminescence maximum E_F undergo another characteristic temperature shift. This maximum appears at temperatures of 50 K and as the temperature decreases, it shifts toward lower energies. The temperature shift coefficient β of E_F line is $0.82 \cdot 10^{-3}$ eV K^{-1} (see figure 6(B)).

A similar dependence is also observed in the experimental results reported in [13] and is associated with free and binding excitons. In the results of the above-mentioned work, two maxima are also observed. The maximum appearing at 300 K shifts toward the higher energies as the temperature decreases down to 50 K as if with a saturation effect. At temperatures 70 K–100 K, an additional long-wavelength maximum appears and it shifts to long-wavelengths as the temperature decreases. Dey *et al* [13] ascribe the luminescence maxima in this region as due to impurity states (bound excitons). Such a situation is possible but the changing energy positions of levels responsible for the maxima E_F and E_V as the temperature decreases (different sign of shift coefficients $\beta = \Delta E/\Delta T$ for maxima E_F and E_V) requires an additional explanation. For these data, it follows that the level of bound excitons shifts toward the long-wavelength side with decreasing temperature, and the bands V_1 and C_1 shift to the short wavelength side.

It is possible that this effect is associated with the saturation of the impurity donor or acceptor level. In the temperature range 300 K–50 K, this saturation effect does not appear and at temperatures lower than 50 K the concentration of charge carriers on the impurity level changes. Moreover, this fact leads to the emission maximum position changing. In the same energy interval, certainly at an energy of 2.062 eV at 4.2 K in [14], the maximum attributed to indirect transitions was discovered. The intensities of the PL spectra in this region of our spectra and spectra measured in [14] are relatively high. In addition, several maxima and the most intense E_F line at energies of 2.0462 eV are observed in this region. Some authors affirm that as the temperature decreases, the band structure of GaSe transforms from indirect to direct [14].

It is possible that in this region, in addition to bound excitons, ground states of excitons with a higher binding energy (Frenkel excitons) appear. These excitons are due to electrons and holes from the conduction band $C_1(\Gamma_6)$ and valence band $V_2(\Gamma_6)$, respectively. The valence bands in $k = 0$ are degenerated. Perhaps as the temperature decreases, the band $V_1(\Gamma_1)$ shifts down in energy and band $V_2(\Gamma_6)$ moves up in energy. It leads to different signs of temperature band shifts (luminescence maxima). These transitions appear at temperatures lower than 50 K since, at these temperatures, the layered structure of the crystal shrinks and volume properties of the crystal are manifested. It should be mentioned that in this crystal, the Frenkel excitons are determined at 77 K in [15] at an energy of 3.378 eV with a binding energy of 318 meV. The authors attribute these exciton formations to C_1—V_1 bands.

The contours of the reflection spectra of the bulk GaSe crystals at 10 K measured in non-polarized light (n/p), in polarizations E∥a and E∥b and with 45° angle to axis *a* and *b*, are practically identical. The broad band is observed in the range $E < E_g$ (2.1 eV) and this band corresponds completely to the excitonic contour of the reflection spectrum. In a narrow energy region near 2.1 eV, a fairly well-studied series of Wannier—Mott excitations with a low binding energy is determined. The photoluminescence spectra from the cleavage face (**PL^c**) and from the surface perpendicular to the cleavage face (**PL^b**) at excitation by a laser line 325 nm are shown in figure 7(B). In the spectra, two regions of intensive
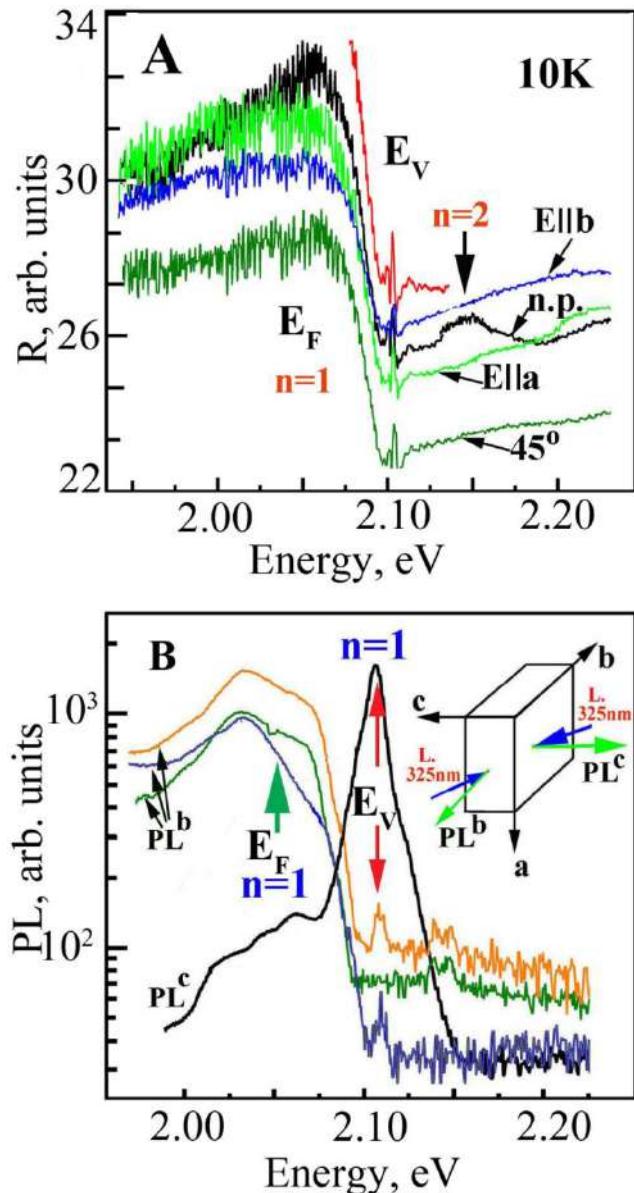
Figure 7. (A) Reflection spectra of bulk GaSe crystal at 10 K measured in non-polarized light (n/p), in polarizations E‖a and E‖b and at an angle of 45° to the axes *a* and *b*. (B) Photoluminescence spectra measured from cleavage plane (*PL*^{C}) and from the edge of the perpendicular cleavage plane (*PL*^{b}) at excitation by laser line 325 nm.

photoluminescence at energies 2.05 and 2.1 eV are observed. At excitation of the cleaved surface and registration from the same surface, the photoluminescence maximum E_V at 2.1072 eV is observed. In the case where excitation comes to the surface perpendicular to the cleavage face, the intensive doublet maximum E_F at 2.05 eV is determined.

4. Conclusions

Investigations of edge absorption, reflection and photoluminescence spectra of bulk GaSe crystals at temperatures 10 K–300 K show a presence of excitonic states with a low

binding energy (21.8 meV) of Wannier—Mott excitons. The main parameters of the excitons ($\varepsilon_b = 5.0$, $\omega_T = 2.1121$ eV, $\omega_{LT} = 3$ eV, $\gamma = 1.4$ meV and $M = 2.5$ m$_0$) were obtained by calculations of exitonic spectra contours. At an energy of 2.127 eV, the excited state $n = 2$ of the exciton was observed. The excited states up to $n = 5$ were observed in the photoluminiscence spectra. Taking into account these parameters, the minimal band gap E_g for direct transitions from the valence band V_1 with Γ_1 symmetry to the conduction band C_1 with Γ_6 symmetry is equal to 2.1325 eV. These transitions are allowed in polarization E⊥c. The reduced effective mass μ of this exciton is estimated as 0.038m$_0$. The effective mass of electrons in the conduction band C$_1$(Γ_6) is 0.37m$_0$. It has been suggested that an exciton with a high binding energy (120 meV) exists. The observed excitonic series have a good agreement with the theoretical calculations of the band structure, and the model of bands in the Brillouin zone center is suggested.

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References

[1] Yagmurcukardes M, Senger R T, Peeters F M and Sahin H 2016 Mechanical properties of monolayer GaS and GaSe crystal *Phys. Rev.* B **94** 245407
[2] Belen'kii G L and Stopachinskii V B 1983 Electronic and vibrational spectra of III-VI layered semiconductors *Phys.-Uspekhi* **140** 234
[3] Guo J *et al* 2015 Doped GaSe crystals for laser frequency conversion *Light Sci. Appl.* **4** e362
[4] Hsu Y-K, Chen C G-W, Huang J Y and Pan C-L 2006 Erbium doped GaSe crystal for mid-IR applications *Opt. Express* **14** 5484
[5] Allakhverdiev K R, Yetis M Ö, Özbek S, Baykara T K and Salaev E Y 2009 Effective nonlinear GaSe crystal. Optical properties and applications *Laser Phys.* **19** 1092
[6] Tonndorf P *et al* 2017 Single-photon emitters in GaSe *2D Mater.* **4** 021010
[7] Pham K D, Phuc H V, Hieu N N, Hoi B D and Nguyen C V 2018 Electronic properties of GaSe/MoS$_2$ and GaS/MoSe$_2$ heterojunctions from first principles calculation *AIP Adv.* **8** 075207
[8] Asensio M C, Lhuillier E, Eddrief M, Fal'ko V I and Ouerghi A 2018 Valence band inversion and spin - orbit effects in the electronic structure of monolayer GaSe *Phys. Rev.* B **98** 115405
[9] Wei C, Chen X, Li D, Su H, He H and Dai J-F 2016 Bound exciton and free exciton states in GaSe thin slab *Sci. Rep.* 33890

[10] Kodolbas A O and Mamedov G M 2004 Exciton photoconductivity in layered semiconductor GaSe *Mater. Sci. Eng.* B **110** 52

[11] Errandonea D, Segura A, Manjón F J, Chevy A, Machado E, Tobias G, Ordejón P and Canadell E 2005 Crystal symmetry and pressure effects on the valence band structure of γ-InSe and ε-GaSe: transport measurements and electronic structure calculations *Phys. Rev.* B **71** 125206

[12] Syrbu N N and Ursaki V V 2010 Exciton polariton dispersion in multinary compounds *Exciton Quasiparticles: Theory, Dynamics and Applications*, ed R M Bergin (New York: Nova Science Publishers Inc) pp 1–30

[13] Dey P *et al* 2015 Biexciton formation and exciton coherent coupling in layered GaSe *J. Chem. Phys.* **142** 212422

[14] Abdullaev G B, Belenkii G L, Balaev E Y U and Suletmanov R A 1977 Interlayer interaction and exciton spectrum of GaSe at low temperatures *IL Nuovo Cimento* **38** 469

[15] Subashiev V K and Chertcova L S 1971 Hyperbolic excitons in GaSe *Solid State Commun.* **9** 369