Wannier–Mott excitons in GaSe single crystals

V V Zalamai$^{1,2}$, N N Syrbu$^{1}$, I G Stamov$^3$ and S I Beril$^3$

$^1$ Technical University of Moldova, 168 Stefan cel Mare Avenue 2004, Chisinau, Moldova
$^2$ National Center for Materials Study and Testing, Technical University of Moldova, Bv. Stefan cel Mare 168, Chisinau 2004, Moldova
$^3$ T.G. Shevchenko State University of Pridnestrovie, 25 Oktyabrya street 107 3300, Tiraspol, Moldova

E-mail: victor.zalamai@cnstm.utm.md

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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

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 converters, 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 this 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...
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 $\beta = \Delta E/\Delta T = 2.7 \times 10^{-4}$ 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 $n = 1$ of excitons (transversal mode $\omega_T$). A very weak peak $E^\ast$ 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 $n = 1$ of Wannier–Mott excitons. The excited states $n = 2$ and $n = 3$ 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 $R$ of the exciton is equal to 20.6 meV.

The fitting of the contour of the reflection spectrum calculated by dispersion relations ($R_{\text{cal.}}$) [12] experimentally measured in the non-polarized light reflection spectrum ($R_{\text{exp.}}$) 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 (Ella and Ellb) light. The obtained reflection spectra
provide evidence that excitonic spectra in Ella and Ellb 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 $\Gamma_1$ symmetry to the conduction band $C_1$ with $\Gamma_6$ symmetry is equal to 2.1325 eV. These transitions are allowed in polarization $E \perp c$.

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

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
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 $C_1(Γ_6)$ and holes of the valence band $V_1 (Γ_1)$ [9].

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.
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 \( C(\Gamma_4) \) 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 \( V_2(\Gamma_5) \) 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// and El// with 45° angle to axis \( a \) and \( b \), are practically identical. The broad band is observed in the range \( E < E_g (2.1 \text{ eV}) \) 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 (\( PL^I \)) 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

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**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 \( \Gamma \) 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 \( \beta = \Delta E/\Delta T = 0.38 \cdot 10^{-2} \text{ eV K}^{-1} \). 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 \( \beta \) of \( E_F \) line is \( 0.82 \cdot 10^{-3} \text{ eV K}^{-1} \) (see figure 6(B)).
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 (\( e_B = 5.0 \), \( \omega_T = 2.1121 \) eV, \( \omega_{LT} = 3 \) eV, \( \gamma = 1.4 \) meV and \( M = 2.5 \) \( m_0 \)) were obtained by calculations of excitonic spectra contours. At an energy of 2.127 eV, the excited state \( n = 2 \) of the excition was observed. The excited states up to \( n = 5 \) were observed in the photoluminescence spectra. Taking into account these parameters, the minimal band gap \( E_g \) for direct transitions from the valence band \( V_1 \) with \( \Gamma_1 \) symmetry to the conduction band \( C_1 \) with \( \Gamma_6 \) symmetry is equal to 2.1325 eV. These transitions are allowed in polarization E.I.C. The reduced effective mass \( \mu \) of this exciton is estimated as 0.038\( m_0 \). The effective mass of electrons in the conduction band \( C_1 \) is 0.37\( m_0 \). 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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### ORCID iDs

V V Zalamai [https://orcid.org/0000-0002-1882-2622](https://orcid.org/0000-0002-1882-2622)

N N Syrbu [https://orcid.org/0000-0001-9368-6096](https://orcid.org/0000-0001-9368-6096)

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