INTERFERENCE OF RESONANCE LUMINESCENCE OF EXCITON POLARITONS IN CuGaS$_2$ CRYSTALS

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Abstract

The nonmodulated and wavelength-modulated reflection spectra of CuGaS$_2$ crystals for the polarization $E||c$ of 10 K are studied. The states $n = 1$, 2 and 3 of the excitons $\Gamma_4$ (A-excitons) and $n = 1$, $n = 2$ of B- and C-excitons are found. The nonmodulated absorption spectra for the polarization $E\perp c$ at 10 K have been studied. The states $n=1$, 2 and 3 of $\Gamma_5$ excitons are found. The main parameters of the A ($\Gamma_4$, $\Gamma_5$) and B, C exciton series at the energies of the longitudinal and transverse excitons $\Gamma_4$ for the states $n = 1$ and $n = 2$, the effective masses of electrons ($m^*_1$) and holes ($m^*_1$, $m^*_2$, $m^*_3$) are determined.

Introduction

Up to the present moment polariton spectra, problems of space dispersion and many other extremely important peculiarities of behaviour of exciton polaritons have been studied mainly for A$^{II}$B$^{VI}$ crystals (e.g., [1-3] and references there). In order to confirm universality of the polariton luminescence phenomenon, elastic scattering of polaritons, optic orientation of exciton spins, it is important to study these effects in crystals of multicomponent materials, CuGaS$_2$ compound belongs to them. In these crystals polariton luminescence [4] and resonance Raman scattering of exciton polaritons [5-7] are found.

In the present work new information on parameters of long-wave exciton polaritons is obtained. Reflection spectra in the polarization $E||c$ are studied, the states $n = 1$, 2 and 3 are found and parameters of the excitons $\Gamma_4$ are determined. In the polarization $E\perp c$ the transmission spectra are studied, where ground and excited states ($n = 1$, 2 and 3) of the excitons $\Gamma_5$ are found. Resonance luminescence and its interference in the region of excited states of the excitons $\Gamma_4$ and $\Gamma_5$ are found. Polariton branches of the exciton polaritons $\Gamma_5$ are restored.

Experiment methods

The investigations were carried out in CuGaS$_2$ samples obtained by the method of gas transport reactions. The optic spectra of reflection and luminescence were registered with the help of an installation mounted on the basis of double Raman spectrometer $\Delta$ФС-32. The samples were fixed to the cold conduit of the cryostat LTS-22C330 of the Workhorse type and were kept at the temperature of 9±0.5 K. The luminescence spectra were excited by the radiation lines $\lambda = 4880$ and 4765 Å of Ar$^+$-laser.
Experimental results and discussion

The minimum direct-gap transition at $\Gamma$ point is only related to the free exciton luminescence in CuGaS$_2$ because the uppermost valence band is sufficiently separated from the next lower valence band due to the large crystal field splitting (~120 meV). The relevant free excitons $\Gamma$ for $D_{2d}$ symmetry are composed of an electron from the $\Gamma_6$ conduction band and a hole from the $\Gamma_7$ valence band. Symmetry of the s-like states of this A exciton is given by the product

$$\Gamma_1 \otimes \Gamma_6 \otimes \Gamma_7 = \Gamma_3 + \Gamma_4 + \Gamma_5$$

(1)

![Reflection spectra of the CuGaS$_2$ crystals at 8 K for the polarization $E||c$, $k \perp c$ and luminescence spectra excited by the line 488 nm of Ar$^+$ laser.](image)

Fig. 1. Reflection spectra of the CuGaS$_2$ crystals at 8 K for the polarization $E||c$, $k \perp c$ and luminescence spectra excited by the line 488 nm of Ar$^+$ laser.

Selection rules show that the exciton $\Gamma_4$ is allowed for the polarization vector $E$ parallel to the axis $z$ ($E||z$), $\Gamma_5$ is allowed for $E$ perpendicular to the axis $z$ ($E \perp z$), and $\Gamma_3$ is forbidden. From analyses of the polarized reflection and absorption spectra, Tell and Kasper [10] have found that the oscillator strength for the exciton $\Gamma_4$ is much larger (by ~2500 times) than that for the exciton $\Gamma_5$. Thus, the allowed strong transitions of the exciton A in CuGaS$_2$ are readily observed for the $\Gamma_4$ state polarized with $E||z$.

In the reflection spectra in CuGaS$_2$ crystals in the polarization $E||c$, $k \perp c$ the lines $n = 1$ ($\omega_r = 2.50109$ eV, $\omega_L = 2.50454$ eV), $n = 2$ (2.5303 eV) and $n = 3$ (2.5357 eV) of the hydrogen-like series of the exciton $\Gamma_4$ are found (Fig. 1).

The reflection spectra in the region of the line $n = 1$ have the form with maximum and minimum being traditional for excitons. These peculiarities are determined by availability of transverse and longitudinal excitons. On the basis of these data the energy of longitudinal-transverse splitting of the excitons $\Gamma_4$ is estimated, being equal to 3.9-4.4 meV. In the luminescence spectra (Fig. 1) at excitation by the radiation line with $\lambda = 4880$ Å of Ar$^+$ laser at the frequencies corresponding to $\omega_{n_1}^L$ and $\omega_{n_1}^T$, the luminescence peaks are found, being caused by radiation from the upper ($\omega_{n_1}^L$) and the lower ($\omega_{n_1}^T$) branches of the exciton polaritons. These results are in agreement with the ones presented in works [5, 6]. The radiation intensity maxima in our spectra are shifted by 1.8 Å into the short-wave region relative to $R_{\text{min}}$ and $R_{\text{max}}$ in the reflection spectra. In the high-energy region in the reflection spectra there are also found the lines $n = 2$ with the maximum at 2.5303 eV ($\omega_{n_2}^L$) and the minimum at 2.5310 eV...
(ω₂₃) and the line n = 3 at the energy of 2.5357 eV (maximum). In the luminescence spectra in the region of n = 2 there appear peaks denoted as ω₂ and ω₃, being most probably caused by the transverse-longitudinal splitting ωₐT of the state n=2 of the exciton series Γ. Splitting ωₐT for n = 2 is 1.1-1.3 meV. We do not attribute the radiation maxima at 2.53373 and 2.53473 eV to the lines of the resonance combination scattering because in the energy scale they are apart the radiation laser line of 4880 Å by the value being less than the optic phonon energy in CuGaS₂ crystals. Taking into account the energy position of the lines n = 2 and n = 3, one can determine the Rydberg constant for the A-exciton series, being is equal to 0.0384 eV. The energy of the continuum (Eₓ, n = ∞) is equal to 2.54135 eV. At ε₉ = 7 [11, 12] the reduced effective mass of A(Γ) excitons is μ = e²R/ε₉H₂ = 0.117m₀, where R (0.03247 eV) is the Rydberg constant of A-exciton and R₂ is the Rydberg energy of a hydrogen atom (13.6 eV). The Bohr radius (a₀) of the S-state of Γ-exciton is equal to 0.32×10⁻⁶ cm.

For calculation of the reflection spectra contours near the resonance it is necessary to take into account space dispersion (finiteness of the exciton mass M) and boundary conditions on the crystal surface [2]. The finiteness of M leads to appearance of the normal waves in the region of transverse-longitudinal splitting between the frequencies ω₀ and ω[L] [1-3]. The calculations of contours of reflection spectra in CuGaS₂ crystals were carried out taking into consideration the theory of supplementary exciton waves [2], which takes into account the excitonless “dead” layer on the crystal surface [3].

![Fig. 2. Wavelength-modulated reflection spectra of CuGaS₂ crystals at 10 K for the polarization E∥c.](image)

![Fig. 3. The absorption spectra of CuGaS₂ crystals in the polarization E⊥c (E∥a, E∥b, k∥c).](image)

Taking into account the relations M = m⁺⁺⁺⁺ and 1/μ = 1/m⁺⁺⁺⁺ + 1/m⁺⁺⁺⁺⁺⁺, the effective masses of electrons, the masses of light and heavy holes were determined. For the exciton mass...
$M = 2m_0$, $m^*_c = 0.124m_0$; at $M = 2.5m_0$, $m^*_c = 0.122m_0$, at $M = 3.5m_0$, $m^*_c = 0.121m_0$. It is seen from these data that even at big errors of determination of $M$ the mass $m^*_c$ changes weakly. The translational mass $M$ for the excitons $\Gamma_4$ (the $A$ series) was determined from the calculation of contours of the reflection spectra with the accuracy of $\pm 0.2m_0$. Thus, if $M = 2m_0$, the electron mass value is equal to $m^*_c = 0.12m_0$, and the mass $m^*_c = 1.87m_0$.

In the region of the absorption edge, in the $\lambda$-modulated reflection spectra (Fig. 2) of CuGaS$_2$ crystals (10 K) in the polarization $E||c$, $k\perp c$ the peak structure at the energies of 2.5016, 2.5331, and 2.5375 eV is found, its form and energy position corresponding to $n=1$, 2 and 3 of the A-exciton series ($\Gamma_4$-exciton). In the short-wave region at 2.6217 and 2.6536 eV there are found lines being the lines $n = 1$ and 2 of the B-exciton series, and the lines at 2.6323 and 2.6611 eV correspond to $n = 1$ and 2 of the C-exciton series. Positions of the absorption lines corresponding to the ground states of the excitons $A$, $B$, and $C$ are in agreement with the known literature data [5-12].

Calculations of contours of the $\lambda$-modulated reflection spectra were carried out for $A$-, $B$- and $C$-exciton lines $n = 1$ measured at 10K. For the line $n = 1$ of $A$-excitons, the best agreement of the experimental curve with the calculated one is observed at the following parameters: $\varepsilon_b = 7$, $\gamma = 0.5$ meV, $\omega_b = 2.5016$ eV, $\omega_{LT} = 4$ meV, $l = 15$ Å, and $M = 2m_0$. For the B-exciton line the following parameters are obtained: $\varepsilon_b = 7$, $\gamma = 0.5$ meV, $\omega_b = 2.6217$ eV, $\omega_{LT} = 3.5$ meV, $M = 2m_0$, $l = 15$ Å. For the C-exciton line: $\varepsilon_b = 7$, $\gamma = 0.7$ meV, $\omega_b = 2.6323$ eV, $\omega_{LT} = 2.5$ meV, $l = 15$ Å, and $M = 2m_0$.

At the same time it should be noted that for the $B$ series with $\mu = 0.148m_0$ $m^*_c = 0.74m_0$, from the data for the $C$ series it follows that at $\mu = 0.144m_0$ $m^*_c = 0.89m_0$. For determination of the effective masses $m_{v1}$, $m_{v2}$, and $m_{v3}$, the effective mass $M$ calculated for $A$ ($\Gamma_4$)-exciton and the $\mu$ value for the $B$ and $C$ series were taken into account.

In the absorption spectra in polarization $E\perp c$ $k\parallel y$ there are found a maximum at 2.50175 eV and a peak at 2.4998 eV, which are caused by the transverse mode of the exciton $\Gamma_4$ (Fig. 3). The reflectivity between the minimum and the maximum in this polarization $E\perp c$ begins at larger wavelengths than the reflectivity increase in polarization $E||c$. In the polarization $E||c$ at the wavelength of 4948 Å the reflectivity begins to increase sharply, and in the polarization $E\perp c$ the reflectivity decreases.

This confirms that the reflection peak found in the polarization $E\perp c$ is not a manifestation of the residual reflection of the exciton $\Gamma_4$ and it is caused by the exciton $\Gamma_5$ allowed in this polarization. The absorption spectra measured by us and the results of published works [6, 7, 8] testify to the fact that the oscillator strength of the exciton $\Gamma_4$ is many times higher than that of the exciton $\Gamma_5$. This determines high absorption coefficient in the polarization $E||c$ of the $\Gamma_4$ exciton wave, and therefore even crystals of small thickness ($d = 1 - 2$ μm) are opaque in the region $\omega_t$ of the exciton $\Gamma_4$. In the polarization $E\perp c$ the crystals of the thickness less than 10 μm are transparent. The absorption spectra of the crystals of the thickness 3 μm in the polarization $E\perp c$ are shown in Fig. 3. In the spectra the intense maxima at 2.50109 and 2.4998 eV are found. The same doublet structure practically at the same energies is found in work [12]. The short-wave maximum corresponds to the transverse frequency $\omega_t$ of the exciton $\Gamma_5$, and the long-wave maximum 2.4998 eV is determined by the forbidden exciton $\Gamma_3$. 

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From the side of lower energies from the band of 2.4998 eV the bands of absorption of bound excitons are found. In the short-wave region (~4900 Å) in the absorption spectra a doublet band is observed, being caused by the state \( n = 2 \) of the exciton \( \Gamma_5 \). The doublet observed at the energies of 2.5254 eV and 2.5245 eV may be considered as a result of removal of the orbit degeneration of the \( \Gamma_5 \) higher exciton states under the crystal field action. At the energy of 2.5307 eV a weak peak of absorption is found, it is caused by the state \( n = 3 \) of the exciton \( \Gamma_5 \). Thus, the exciton \( \Gamma_5 \) has the following parameters:

\[
\begin{align*}
\omega_t &= 2.50109 \text{ eV}, \quad \omega_L = 2.50175 \text{ eV}, \\
n &= 2 (2.52524 \text{ and } 2.52425 \text{ eV}), \\
n &= 3 (2.5307 \text{ eV}),
\end{align*}
\]

the Rydberg constant 30.5-32.4 meV, \( E_g = 2.5336 \text{ eV} \), the exciton mass \( M = 0.6 m_0 \).

In the polarization \( \text{E} \parallel c \) the allowed exciton \( \Gamma_4 \) with large oscillator strength is observed. The absorption coefficient of this exciton at the frequency \( \omega_t \) exceeds \( 10^5 \text{ cm}^{-1} \). The crystals of the thickness ~1.5 \( \mu \text{m} \) are opaque for the \( \Gamma_4 \) exciton waves. This was reported by the authors of works [5-7, 12]. In the polarization \( \text{E} \perp c \) the allowed exciton \( \Gamma_5 \) has considerably less oscillator strength, the absorption coefficient at the frequency \( \omega_t (\Gamma_5) \) does not exceed 600 cm\(^{-1}\) (Fig. 3). The results of our investigations are in agreement with the results of works [12-15].

In the polarization \( \text{E} \perp c \) the crystals of the thickness ~1.5 \( \mu \text{m} \) are transparent. In these crystals we have successfully measured the absorption coefficient of the excitons \( \Gamma_4 \) and \( \Gamma_5 \) up to the continuum, i.e. we have found the lines \( n = 1, 2 \) and \( 3 \) lines of the exciton \( \Gamma_5 \) (Fig. 3).

Thus, in the short-wave region the excited states of the excitons \( \Gamma_4 \) and \( \Gamma_5 \) are determined unambiguously. This is due to the fact that in reflection the exciton \( \Gamma_4 \) is shown, and in absorption - \( \Gamma_5 \).

In the samples of small thickness in the radiation spectra in the region of \( n = 3 \) and \( n = 4 \) of the exciton \( \Gamma_5 \) fine structure is found (Fig. 4). The distance between the bands is much less than the energy of the \( \Gamma \) phonons or the difference between the energies of \( \Gamma \) phonons. This structure of the bands is explained by the luminescence interference in thin plate CuGaS\(_2\). Earlier in work [7] we have reported on interference in the spectra of absorption of the \( \Gamma_5 \) exciton wave observed up to the states \( n = 3 \) and \( n = 4 \) of the exciton \( \Gamma_5 \). Interference in the luminescence spectra is observed in the samples of the thickness 0.5-1.5 \( \mu \text{m} \) (Fig. 4). At excitation by the line 4765 Å of the Ar\(^+\) laser the radiation bands are not practically found, i.e. their intensity is very weak. We consider that the observed radiation possesses a resonance character, because the excitation energy of 2.5402 eV is close to the lines \( n = 2 \) of the exciton \( \Gamma_4 \). In these luminescence spectra another peculiarity is observed too. The intensity of the interference bands (bands 3, 2, 1) decreases as the wavelength increases relative to the central band of radiation of 2.5307 eV. From the short-wave side the intensity of the interference bands (bands 19, 20) also decreases as the wavelength decreases relative to the band 2.5332 eV. Interference takes place at three frequencies where the energies \( n = 4 \) of the exciton \( \Gamma_5 \) and the energies \( n = 2 \) of the exciton \( \Gamma_4 \) coincide. We consider that at excitation of these states there occurs an exchange between two polariton branches, i.e. the exchange between \( \omega_t \) of the state \( n = 2 \) of the exciton \( \Gamma_4 \) and \( \omega_L \) (or \( \omega_t \)) \( n = 4 \) of the exciton \( \Gamma_5 \). Taking into account the absorption coefficient for excitons \( \Gamma_4 \) and \( \Gamma_5 \) it may be surely considered that the Fabry-Perot interference at the thickness \( d \sim 0.5-1.5 \mu \text{m} \) takes place only for the exciton \( \Gamma_5 \) wave. For the waves of the excitons \( \Gamma_4 \) these thicknesses are opaque. These waves appearing in the surface region attenuate before reaching the second face of the crystal.
Fig. 4. The interference in the luminescence spectra of thin ($d \sim 0.6 \mu m$) CuGaS$_2$ crystals excited by the lines 488 nm of Ar$^+$ laser.

Fig. 5. The dispersion curves for the upper and lower branches of the $\Gamma_5$ exciton polariton calculated from the absorption spectra of $n=1$ line with $\varepsilon_0=6$, $M=0.7m_0$ [10], and from the interference in the luminescence spectra (square symbol).

It should be noted that the oscillator strength of the exciton $\Gamma_4$ is much larger than that of the exciton $\Gamma_5$. Therefore, the state $n = 2 \Gamma_4$ of the exciton polariton is excited, it causes an excited polariton wave of the exciton $\Gamma_5$ (in the region $n = 3$ and $n = 4$) by the energy exchange. The Fabry-Perot interference characterizes polariton branches (the refractive index) of the exciton $\Gamma_5$. In CuGaS$_2$ crystals polariton branches are restored in the region of “bottle neck” for the states $n = 1$ of the exciton polaritons $\Gamma_4$ and $\Gamma_5$. For the upper polariton branch $\omega_L (n = 1)$ of the exciton $\Gamma_5$ the refractive index is equal to 3.45 at the wavelength 4840 Å. We suppose that the refractive index value will be equal to 4 in the region of the polariton branch $\omega_L (n = 2)$ of the polariton $\Gamma_5$, and it will be equal to 4.5 in the region $\omega_L (n = 3)$ of the polariton $\Gamma_5$. Proceeding from these approximations, we estimate the order of the interference bands and dispersion of the polariton branch $\omega_L (n = 3)$ of the exciton $\Gamma_5$ (Fig. 5). The upper polariton branch $\omega_L (n = 1)$ transits into the transverse (lower) polariton branch $\omega_L$ of the state $n = 2$ (Fig. 5). The upper polariton branch $\omega_L$ of the state $n = 2$ transits into the transverse polariton branch $\omega_L$ of the state $n = 3$. Considering that in the region of “bottle neck” of the states $n = 3$ the refractive index is equal to 4, the samples thickness is equal to 0.8 μm, from the Fabry-Perot interference condition $2nd = \lambda N$ the order of the interference bands (N) for each found band (m) is determined. Proceeding from these data, i.e. taking into account these suppositions the change of the refractive index of the polariton branch $\omega_L$ for the state $n = 3$ of the exciton $\Gamma_5$ is calculated (Fig. 5). At higher frequencies the interference bands
(m = 9-20) are caused by the change of the refractive index of the polariton branches of the states n = 4 of the exciton polaritons Γ₅.

Thus, the results obtained in the work confirm that the crystals CuGaS₂ are interesting objects for investigation of exciton polaritons. Strong difference of the oscillator strength of exciton transitions for the excitons Γ₄ and Γ₅ allowed in the polarizations EIlc and E⊥c, correspondingly, gives a possibility to reliably interpret experimental results on the luminescence interference. The radiation found in the region of higher excited states of the exciton polaritons (n = 3, n = 4) is of resonance character and testifies to excitation (initiation) of the exciton wave Γ₅ by the exciton waves Γ₄.

References