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 Γ_4 (A-excitons) and n = 1, n = 2 of B- and C-excitons are found. The nonmodulated absorption spectra for the polarization E⊥c at 10 K have been studied. The states n=1, 2 and 3 of Γ_5 excitons are found. The main parameters of the A (Γ_4, Γ_5) and B, C exciton series at the energies of the longitudinal and transverse excitons Γ_4 for the states n = 1 and n = 2, the effective masses of electrons (m^*_{e1}) and holes ($m^*_{v1}, m^*_{v2}, m^*_{v3}$) 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 Γ_4 are determined. In the polarization E⊥c the transmission spectra are studied, where ground and excited states (n = 1, 2 and 3) of the excitons Γ_5 are found. Resonance luminescence and its interference in the region of excited states of the excitons Γ_4 and Γ_5 are found. Polariton branches of the exciton polaritons Γ_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 ДФС-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 λ = 4880 and 4765 Å of Ar^+-laser.

Experimental results and discussion

The minimum direct-gap transition at Γ 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 A for D_{2d} symmetry are composed of an electron from the Γ_6 conduction band and a hole from the Γ_7 valence band. Symmetry of the s-like states of this A exciton is given by the product

$$\Gamma_1 \otimes \Gamma_6 \otimes \Gamma_7 = \Gamma_3 + \Gamma_4 + \Gamma_5 \quad (1)$$

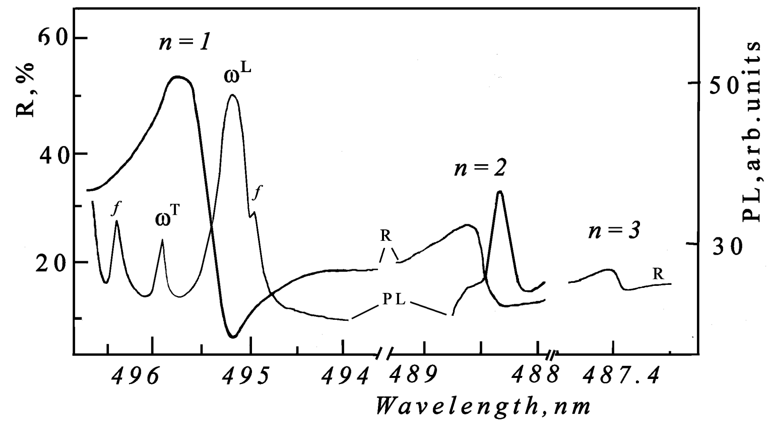

Fig. 1. Reflection spectra of the $CuGaS_2$ crystals at 8 K for the polarization E||c, k⊥c and luminescence spectra excited by the line 488 nm of Ar^+ laser.

Selection rules show that the exciton Γ_4 is allowed for the polarization vector E parallel to the axis z (E||z), Γ_5 is allowed for E perpendicular to the axis z (E⊥z), and Γ_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 Γ_4 is much larger (by ~2500 times) than that for the exciton Γ_5. Thus, the allowed strong transitions of the exciton A in $CuGaS_2$ are readily observed for the Γ_4 state polarized with E||z.

In the reflection spectra in $CuGaS_2$ crystals in the polarization E||c, *k*⊥c the lines $n = 1$ (ω_t = 2.50109 eV, ω_L = 2.50454 eV), $n = 2$ (2.5303 eV) and $n = 3$ (2.5357 eV) of the hydrogen-like series of the exciton Γ_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 Γ_4 is estimated, being equal to 3.9-4.4 meV. In the luminescence spectra (Fig. 1) at excitation by the radiation line with λ = 4880 Å of Ar^+ laser at the frequencies corresponding to ω_{n1}^L and ω_{n1}^T, the luminescence peaks are found, being caused by radiation from the upper (ω_{n1}^L) and the lower (ω_{n1}^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_{min} and R_{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 (ω_{n2}^L) and the minimum at 2.5310 eV

(ω_{n2}^{L}) 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 ω_{n2}^{L} and ω_{n2}^{L}, being most probably caused by the transverse-longitudinal splitting ω_{LT} of the state n=2 of the exciton series Γ_4. Splitting ω_{LT} 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 $CuGaS_2$ 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 (E_g, $n = \infty$) is equal to 2.54135 eV. At $\varepsilon_b = 7$ [11, 12] the reduced effective mass of $A(\Gamma_4)$ excitons is $\mu = \varepsilon_b^2 R / R_{H_2} = 0.117 m_0$, where R (0.03247 eV) is the Rydberg constant of A-exciton and R_{H_2} is the Rydberg energy of a hydrogen atom (13.6 eV). The Bohr radius (a_B) of the S-state of Γ_4-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 ω_0 and ω^L [1-3]. The calculations of contours of reflection spectra in $CuGaS_2$ 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].

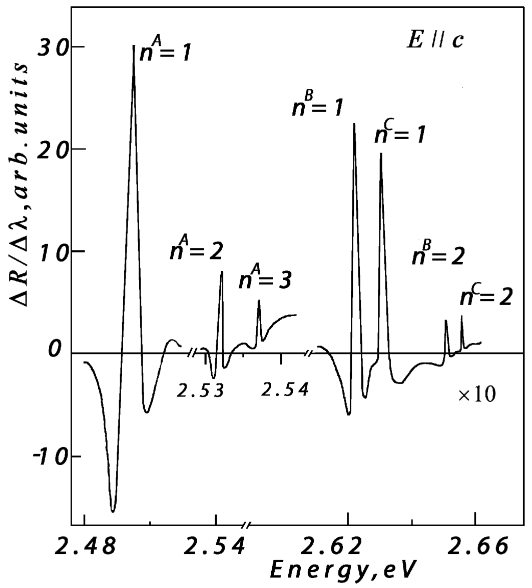

Fig. 2. Wavelength-modulated reflection spectra of $CuGaS_2$ crystals at 10 K for the polarization E||c.

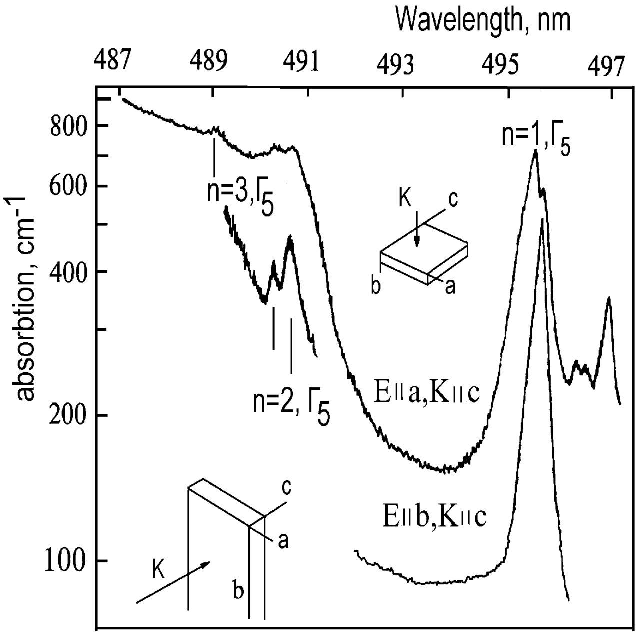

Fig. 3. The absorption spectra of $CuGaS_2$ crystals in the polarization E⊥c (E||a, E||b, k||c).

Taking into account the relations $M = m_v^* + m_c^*$ and $\frac{1}{\mu} = \frac{1}{m_v^*} + \frac{1}{m_c^*}$, 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 Γ_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 $m_v^* = 1.87m_0$.

In the region of the absorption edge, in the λ-modulated reflection spectra (Fig. 2) of $CuGaS_2$ crystals (10 K) in the polarization E||c, k⊥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 (Γ_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 λ-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, $\omega_0 = 2.5016$ 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, $\omega_0 = 2.6217$ eV, $\omega_{LT} = 3.5$ meV, $M = 2m_0$, $l = 15$ Å. For the C-exciton line: $\varepsilon_b = 7$, $\gamma = 0.7$ meV, $\omega_0 =$ 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 $\mu = 0.148m_0$ $m_{v2}^* = 0.74m_0$, from the data for the C series it follows that at $\mu = 0.144m_0$ $m_{v3}^* = 0.89m_0$. For determination of the effective masses m_{v1}, m_{v2}, and m_{v3}, the effective mass M calculated for A (Γ_4)-exciton and the μ value for the B and C series were taken into account.

In the absorption spectra in polarization E⊥c k||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 Γ_5 (Fig. 3). The reflectivity between the minimum and the maximum in this polarization changed within the limits of 1-2%. The reflectivity increase in E⊥c begins at lager 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⊥c the reflectivity decreases.

This confirms that the reflection peak found in the polarization E⊥c is not a manifestation of the residual reflection of the exciton Γ_4 and it is caused by the exciton Γ_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 Γ_4 is many times higher than that of the exciton Γ_5. This determines high absorption coefficient in the polarization E||c of the Γ_4 exciton wave, and therefore even crystals of small thickness (d =1-2 μm) are opaque in the region ω_t of the exciton Γ_4. In the polarization E⊥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⊥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 ω_t of the exciton Γ_5, and the long-wave maximum 2.4998 eV is determined by the forbidden exciton Γ_3.

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 Γ_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 Γ_5 higher exciton states under the crystal field action. At the energy of 2.53072 eV a weak peak of absorption is found, it is caused by the state n = 3 of the exciton Γ_5. Thus, the exciton Γ_5 has the following parameters: n = 1 (ω_t = 2.50109 eV, ω_L = 2.50175 eV), n = 2 (2.52524 and 2.52425 eV), n = 3 (2.5307 eV), the Rydberg constant 30.5-32.4 meV, E_g = 2.5336 eV, the exciton mass $M = 0.6m_0$.

In the polarization E||c the allowed exciton Γ_4 with large oscillator strength is observed. The absorption coefficient of this exciton at the frequency ω_t exceeds 10^5 cm^{-1}. The crystals of the thickness ~1.5 μm are opaque for the Γ_4 exciton waves. This was reported by the authors of works [5 - 7, 12]. In the polarization E⊥c the allowed exciton Γ_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 E⊥c the crystals of the thickness ~1.5 μm are transparent. In these crystals we have successfully measured the absorption coefficient of the excitons Γ_5 up to the continuum, i.e. we have found the lines n = 1, 2 and 3 lines of the exciton Γ_5 (Fig. 3).

Thus, in the short-wave region the excited states of the excitons Γ_4 and Γ_5 are determined unambiguously. This is due to the fact that in reflection the exciton Γ_4 is shown, and in absorption - Γ_5.

In the samples of small thickness in the radiation spectra in the region of n = 3 and n = 4 of the exciton Γ_5 fine structure is found (Fig. 4). The distance between the bands is much less than the energy of the Γ phonons or the difference between the energies of Γ 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 Γ_5 exciton wave observed up to the states n = 3 and n = 4 of the exciton Γ_5. Interference in the luminescence spectra is observed in the samples of the thickness 0,5-1,5 μm (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 Γ_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 Γ_5 and the energies n = 2 of the exciton Γ_4 coincide. We consider that at excitation of these states there occurs an exchange between two polariton branches, i.e. the exchange between ω_t of the state n = 2 of the exciton Γ_4 and ω_t (or ω_L) n = 4 of the exciton Γ_5. Taking into account the absorption coefficient for excitons Γ_4 and Γ_5 it may be surely considered that the Fabry-Perot interference at the thickness d ~ 0,5-1,5 μm takes place only for the exciton Γ_5 wave. For the waves of the excitons Γ_4 these thicknesses are opaque. These waves appearing in the surface region attenuate before reaching the second face of the crystal.

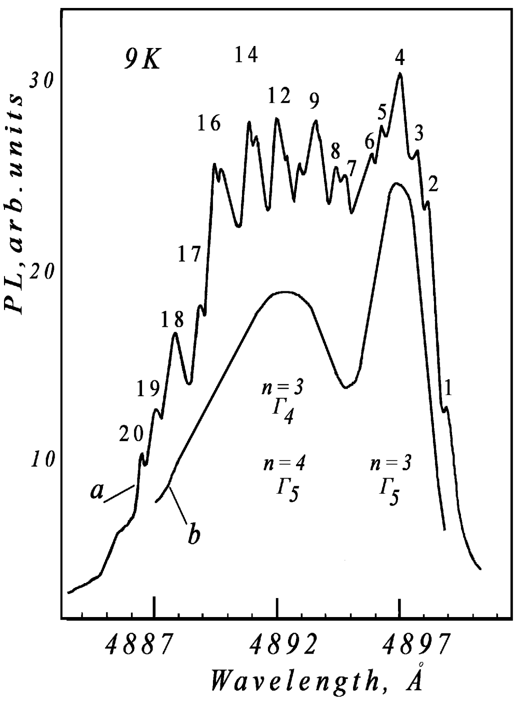

Fig. 4. The interference in the luminescence spectra of thin (d ~0.6 μm) $CuGaS_2$ crystals excited by the lines 488 nm of Ar^+ laser.

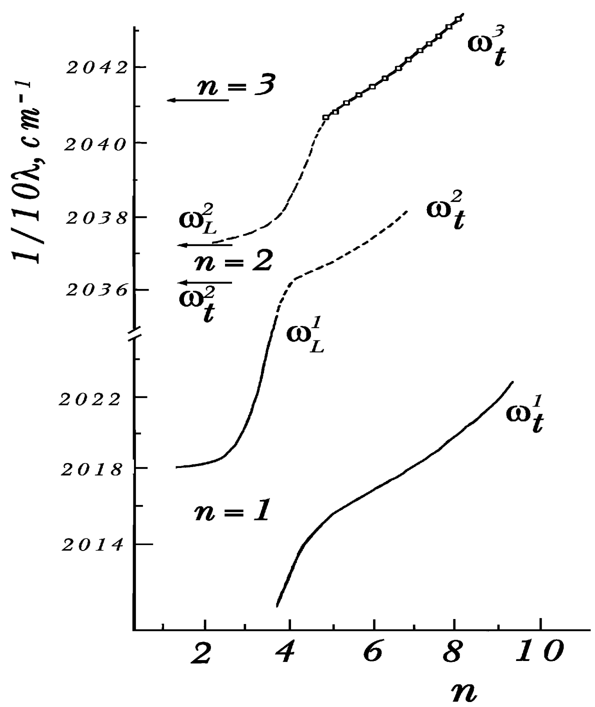

Fig. 5. The dispersion curves for the upper and lower branches of the Γ_5 exciton polariton calculated from the absorption spectra of n=1 line with ε_0 =6, M=0.7m_0 [10], and from the interference in the luminescence spectra (square symbol).

It should be noted that the oscillator strength of the exciton Γ_4 is much larger than that of the exciton Γ_5. Therefore, the state n = 2 Γ_4 of the exciton polariton is excited, it causes an excited polariton wave of the exciton Γ_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 Γ_5. In $CuGaS_2$ crystals polariton branches are restored in the region of "bottle neck" for the states n = 1 of the exciton polaritons Γ_4 and Γ_5. For the upper polariton branch ω_L (n = 1) of the exciton Γ_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 ω_t (n = 2) of the polariton Γ_5, and it will be equal to 4,5 in the region ω_L (n = 3) of the polariton Γ_5. Proceeding from these approximations, we estimate the order of the interference bands and dispersion of the polariton branch ω_L (n = 3) of the exciton Γ_5 (Fig. 5). The upper polariton branch ω_L (n = 1) transits into the transverse (lower) polariton branch ω_t of the state n = 2 (Fig. 5). The upper polariton branch ω_L of the state n = 2 transits into the transverse polariton branch ω_t 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 ω_t for the state n = 3 of the exciton Γ_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 Γ_5.

Thus, the results obtained in the work confirm that the crystals $CuGaS_2$ are interesting objects for investigation of exciton polaritons. Strong difference of the oscillator strength of exciton transitions for the excitons Γ_4 and Γ_5 allowed in the polarizations E||c 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 Γ_5 by the exciton waves Γ_4.

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