EXCITON-PHONON LUMINESCENCE SPECTRA WITH EXCITON-POLARITON ANNIHILATION

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Abstract: *Photoluminescence and resonance Raman scattering spectra of $CuGaS_2$ crystals were investigated at low temperature (10 K) under the excitation with the radiation from a spectral interval obtained by passing the radiation of an incandescent or xenon lamp through a monochromator.*

Keywords: *Photoluminescence; excitation; radiation; annihilation; optical phonon*

1. Introductie

The free excitons in semiconductors are characterized by the wave vector **k**, effective translation mass $M = m_e + m_h$, and kinetic energy E. The relations between the exciton energy and the wave vector in the approximation of effective mass is expressed as

$$E_n = E_{0n} + E = E_{0n} + \frac{\hbar^2 \mathrm{k}^2}{2M}$$

were E_{0n} is the energy of the *n* quantum state.

As one can see from the conservation law, excitons with any values of energy and wave vector can participate in the exciton-phonon annihilation processes. The wave vector on exciton is transmitted to the phonons during the optical transition. Particularly, in the case of first-order process schematically illustrated on the energy diagram (Fig. 1), the wave vector of the excited phonon equals to the wave vector of the annihilated exciton (with the precision of the wave vector of the light).

2. Experiment

Photoluminescence and resonance Raman scattering spectra of $CuGaS_2$ crystals were investigated at low temperature (10 K). In the$CuGaS_2$ crystals thermalized luminescence of the Γ_4 and Γ_5 excitons was revealed under the excitation by an interval of photon energies higher than the energy of the ground state of long-wavelength Γ_4 excitons ($\omega_T(\Gamma_4)+1E^1_{LO}$). The energy conversion between the polariton modes in luminescence and resonance Raman scattering spectra was considered. Schematics of the experimental set-up for measuring luminescence and Raman scattering spectra shown in Fig. 2. Therefore, the first monochromator is used for the selection of a narrow spectral interval of the excitation light, while the second monochromator serves for the registration of the secondary emission spectrum. The intensity of the emission from the crystal is rather high near the resonance. This allows one to measure the emission spectra by using a narrow excitation interval of less than 10 cm^{-1}, therefore excluding the employment of an expensive tunable laser in experiments with resonance Raman scattering.

The optical properties and the emission intensity of $CuGaS_2$ crystals are similar to those of CdS crystals. It was shown that the secondary emission spectra due to 2 LO scattering reproduce the stationary energy distribution of the initial polariton states. “Photon-like” polaritons of the low polariton branch are formed under the excitation of the crystal in the region of the exciton resonance [1-3]. The scattering of these polaritons on LO phonons represents the pre-resonance Raman scattering. The scattering intensity on 1 LO phonons in the pre-resonance conditions is lower as compared to the intensity of 2 LO phonon scattering. The lowest frequency (energy) of the optical phonon at T = 10 K in $CuGaS_2$ crystals equals 75 cm^{-1}. $B_2{}^1{}_{LO}$ (89 $см^{-1}$), $B_1{}^1$ (115 $см^{-1}$), E^2_{LO} (141 $см^{-1}$), E^3_{LO} (177 $см^{-1}$) and other high energy phonons are observed at T = 10 K. All the selection rule allowed vibration modes have been observed in $CuGaS_2$ crystals at 300 K and 9 K.

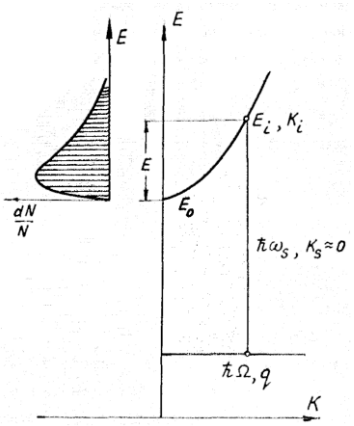

Fig. 1. Schematic presentation of the exciton annihilation process with a concomitant formation of one optical phonon. The quasi-equilibrium distribution of excitons over the kinetic energy *E* is shown in the left part of the figure.

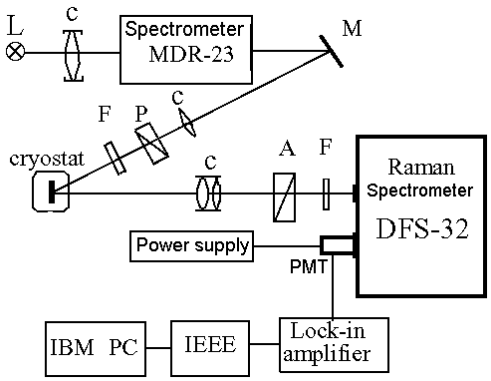

Fig. 2. Schematics of the experimental set-up for measuring luminescence and Raman scattering spectra. Reprinted with permission from [127], N.N. Syrbu, V.E. Tezlevan, I.Galbic, L. Nemerenco, V.V. Ursaki (2009) Exciton–phonon luminescence and Raman scattering in $CuGaS_2$ crystals. Optics Communications **282**, 4562-4566. Copyright (2009), with permission from Elsevier

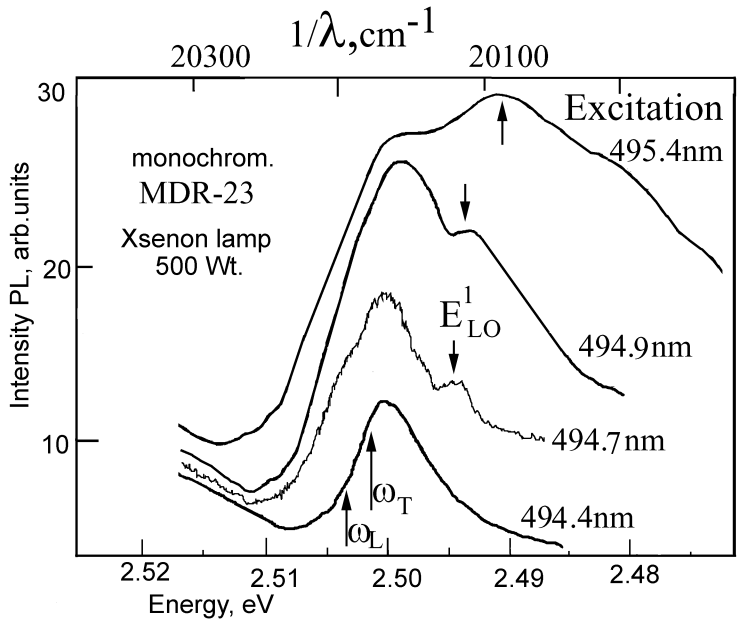

Fig. 3. The emission spectra of $CuGaS_2$ crystals under the excitation with the radiation from a spectral interval of a 500 W xenon lamp. Reprinted with permission from [4], N.N. Syrbu, V.E. Tezlevan, I.Galbic, L. Nemerenco, V.V. Ursaki (2009) Exciton–phonon luminescence and Raman scattering in $CuGaS_2$ crystals. Optics Communications **282**, 4562-4566. Copyright (2009), with permission from Elsevier

The emission spectra in the region of the "bottle neck" are presented in Fig. 2. The spectra were measured with different values of the excitation energy of the light from a xenon lamp passed through a MDR-23 monochromator. An emission maximum at 2.500 eV is observed under the excitation by 2.507 eV (494.4 nm). This value is close to the ω_T energy of the transversal Γ_4 exciton. The reflectivity at the ω_T frequency of the n = 1 band of the Γ_4 exciton reaches the value of 50 %. It could be that the emission band at 2.500 eV which is related to the emission of the thermalized exciton is partially affected by the scattered light. An emission band separated by 75 cm^{-1} from the excitation band emerges in the long wavelength region under the excitation by the 2.506 eV (494.7 nm) which is close the resonance energy of the longitudinal exciton. This value is nearly equal to the energy of the E_{LO}^1 phonon . By changing the excitation energy to 2.502 eV (495.4 nm), the E_{LO}^1 band is shifted to the infrared region by nearly the same energy, i. e. E_{LO}^1 is separated from the E_{exc} by 75 cm^{-1}. This shift is accompanied by the intensification of the long-wavelength luminescence wing (Fig.3). The intensification of the luminescence wing may be due to the increasing probability of the scattering by acoustical phonons as compared to optical phonons for the polariton excited by the light in the region of ω_{LT}. The participation of higher energy LO phonons is not excluded.

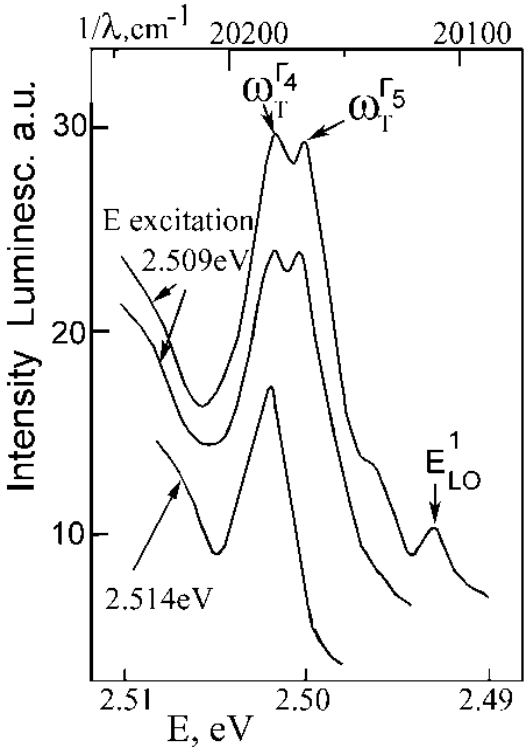

Fig. 4. The emission spectra of $CuGaS_2$ crystals measured in E||c polarization under the excitation with the radiation from a spectral interval of a 100 incandescent lamp. Reprinted with permission from [4], N.N. Syrbu, V.E. Tezlevan, I.Galbic, L. Nemerenco, V.V. Ursaki (2009). Exciton–phonon luminescence and Raman scattering in $CuGaS_2$ crystals. Optics Communications **282**, 4562-4566. Copyright (2009), with permission from Elsevier

As a result, some stationary energy distribution of polaritons is established at the moment of LO-phonon emission. The excitation to the ground state of the upper polatiton branch occurs under the excitation by the light with the energy near ω_L or with higher energy. The luminescence is due to the scattering of these states by acoustical and optical phonons to the states of the lower polariton branch. This is confirmed by the analysis of the character of the luminescence curve presented in Fig. 4. These spectra represent the Raman scattering excited by a tunable monochromatic radiation source, and demonstrate the energy exchange between the lower and upper exciton polariton branches.

Figure 3,4 presents the emission spectra of $CuGaS_2$ crystals excited by the radiation from a spectral interval obtained by passing the radiation of a 100 W incandescent lamp through a MDR-23 monochromator. The spectral slit width is taken small enough in order to minimize the scattered light in the region ω_T. The

sample was replaced by a mirror to control the amount of scattered light in the region ω_T, and the spectral slit width was adjusted to set the scattered light in the region ω_T equal to zero. A luminescence band in the region of 2.501 eV is observed under the excitation by the energy of 2.514 eV (20280 cm^{-1}), i. e. by 75-80 cm^{-1} higher than the energy of the transversal exciton (Fig.4). This emission band is due to the luminescence of the transversal excitons (ω_T ~ 2.5011 эВ). A doublet is observed in the luminescence spectra under the excitation by (E||c) polarized light with the energy of 2.509 eV, i. e. a line in the long wavelength region (2.500 eV) appears in addition to the ω_T line. The energy of this line coincides with the energy of the transversal Γ_5 exciton which is active in the E⊥c polarization [4,5]. Therefore, by adjusting the energy of the (E||c) polarized excitation light equal to $E(\omega_T,\Gamma_5)+E_{phonon}(E^1_{LO})$ = 2.509 eV, one can observe the $\omega_T(\Gamma_4)$ and the $\omega_T(\Gamma_5)$ bands as well as the one-phonon E^1_{LO} (2.495 eV) band. The emergence of the 2.500 eV emission band corresponding to the energy of the transversal Γ_5 exciton indicates on the excitation of the Γ_4 exciton which is active in the (E||c) polarization with a consequent transmission of the energy to the Γ_5 exciton, i. e. the energy conversion between the branches of different excitons occurs. The position of the E^1_{LO} (2.495 eV) band remains practically constant when the energy of excitation changes. The E^1_{LO} (2.495 eV) band is separated by 75 cm^{-1} from the resonant value of the ω_T exciton. One can suggest that this band corresponds to a phonon replica of the luminescence band related to the annihilation of the exciton, and it does not correspond to the resonant Raman scattering.

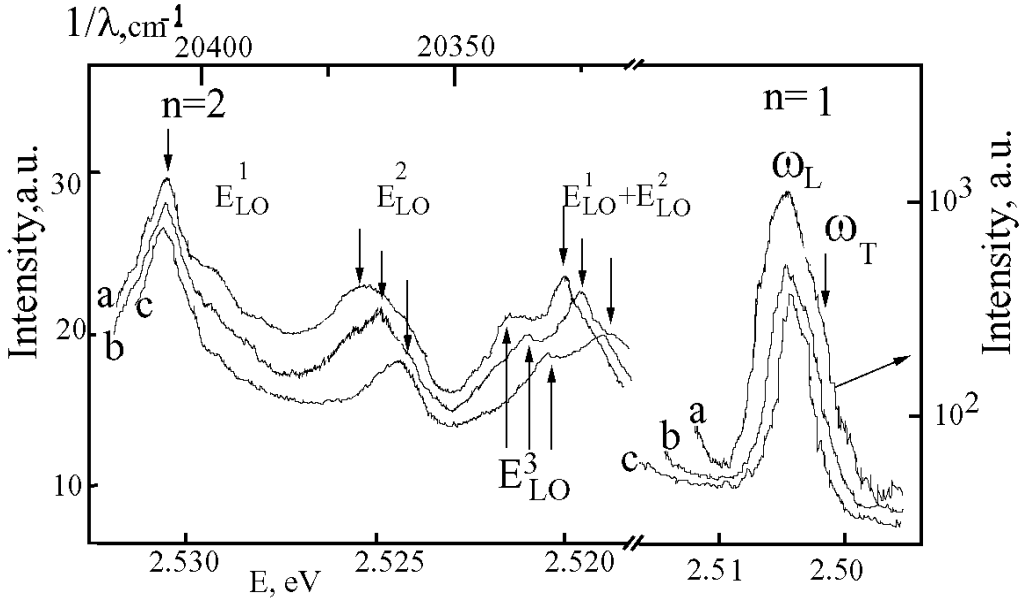

Figure 5. The photoluminescence and Raman scattering spectra of $CuGaS_2$ crystals under the excitation with the radiation from a spectral interval of a 500 W xenon lamp: (a) 487.8 nm (2.541) eV; (b) 488 nm (2.540 eV); (c) 488.3 nm (2.539 eV). Reprinted with permission from [127], N.N. Syrbu, V.E. Tezlevan, I.Galbic, L. Nemerenco, V.V. Ursaki (2009) Exciton–phonon luminescence and Raman scattering in $CuGaS_2$ crystals. Optics Communications **282**, 4562-4566. Copyright (2009), with permission from Elsevier

Two maxima at 2.530 eV and 2.504 eV emerge in the emission spectra of $CuGaS_2$ crystals under the excitation in the region of the continuum with the energy of 2.541 eV (487.8 nm). These maxima are due to the luminescence of the n = 2 and n =1 states of the Γ_4 excitons, respectively (curve (a) in Fig. 5). At the same time, broad bands at 2.525 eV and 2.520 eV are observed. The luminescence peaks related to n = 1 and n = 2 do not change their energy position under the excitation by 2.540 eV (488.0 nm) excitation, while the bands at 2.525 eV and 2.520 eV are shifted to the long wavelength region by the energy equal to the change of the excitation energy (curve (b) in Fig. 5). The same behavior is observed with decreasing the excitation energy to 2.539 eV (488.3 nm). The 2.525 eV and 2.520 eV bands are shifted, while the luminescence peaks related to n = 1 and n = 2 do not change their position (curve (c) in Fig. 5. The shift of the 2.525 eV and 2.520 eV bands indicates that they are Raman scattering lines (Fig. 5). These bands are the most distant bands from the luminescence n = 1 line. The intensity of the emission associated with the ω_T (2.5011 эВ) n =

1 of the Γ_4 excitons is much higher than the intensity of short-wavelength bands. The intensity of the emission at the frequency of the transversal exciton increases from 100 to 1000 arbitrary units with increasing the excitation energy from 2.539 eV to 2.541 eV. This indicates on the resonance character of the process and to the correspondence of the resonance frequency to the frequency of the continuum.In a previous work [1-4], the region of the 2LO scattering has been chosen for the investigation of the secondary emission in CdS, since the probability of this scattering does not depend upon the wave vector of the initial state. A bigger number of phonons emerge in the resonant Raman scattering spectra of $CuGaS_2$ crystals [3, 4], since the unit cell contains a bigger number of atoms. We selected a region of 2LO scattering with the participation of low energy optical phonons (72-75 and 89-90 cm^{-1}) for the investigation of resonant Raman scattering.

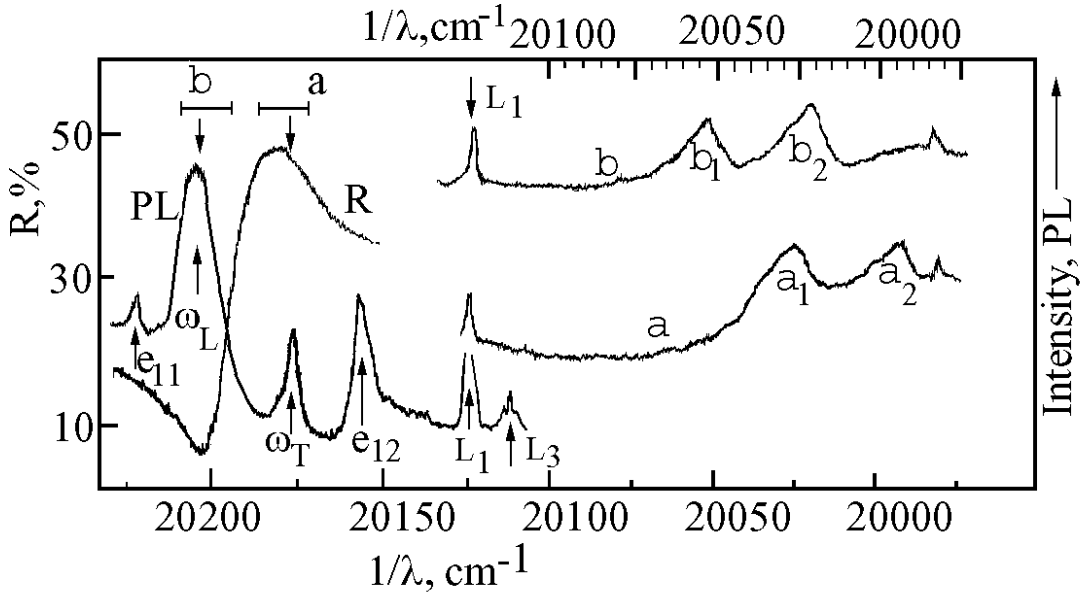

Figure 6. The emission spectra of CuGaS2 crystals under the excitation by the 4765 Å Ar laser line (curve PL), the reflectivity spectrum (curve R), and the emission spectra under the excitation by monochromatic light in the region of the "bottle neck". Reprinted with permission from [127], N.N. Syrbu, V.E. Tezlevan, I.Galbic, L. Nemerenco, V.V. Ursaki (2009) Exciton–phonon luminescence and Raman scattering in $CuGaS_2$ crystals. Optics Communications **282**, 4562-4566. Copyright (2009), with permission from Elsevier

It is known that photon-like polaritons of the lower polariton branch are created under the excitation in the region of the low exciton resonance [1-4]. The scattering of these polaritons on LO phonons represents pre-resonance Raman scattering. The intensity of this scattering is high enough near the resonance. As mentioned above, a spectral interval of the incandescence lamp has been used for the excitation.

The contours of reflectivity (R) and photoluminescence (PL) spectra of the ground state of the Γ_4 exciton under the excitation by the 4765 Å Ar laser line are shown on the left part of the Fig. 6. Narrow e_{10}, e_{11}, ω_L, ω_T lines as well as the lines L_1 (20125 cm^{-1}) and L_3 (20113 cm^{-1}) are observed in the emission spectra of $CuGaS_2$ crystals. The e_{10} and e_{11} lines are related to the resonance Raman scattering. The ω_L, and ω_T lines come from the emission of exciton polaritons, while the L_1 and L_3 lines are due to the emission of bound excitons [3,4]. The L_1 line is the narrowest and the most intensive one among these lines.

The emission spectra measured under the excitation by the radiation passed through a MDR-23 monochromator are shown in the right part of Fig. 6. The excitation has been performed with energies 2.501 eV (20175 cm^{-1}) (a), and 2.504 eV (20203 cm^{-1}) (b). The position of the excitation energies are indicated by the arrows "a" and "b" in the left part of the figure. The width of the excitation band indicated by bars is around 7 cm^{-1}. The L_1 (20125 cm^{-1}) line is observed in these spectra. The form and the position of this line are independent on the frequency of the excitation light, i. e. it is due to the luminescence of bound excitons [3,4]. Apart from that, emission maxima labeled as "a_1, a_2" and "b_1, b_2" are observed in the emission spectra. These lines are separated from the excitation line by $2E^1$ and $2B_1^1$ LO phonon energy, and their position

changes with changing the energy of the excitation photons. Therefore, one can suggest that these lines are due to resonance Raman scattering.

Literature:

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