

# Resonance Raman Scattering and Excitons Optical Orientation in CuGaSe<sub>2</sub> Crystals

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**Abstract** — Resonance Raman and luminescence spectra of CuGaSe<sub>2</sub> crystals measured at 9 K and excited by He-Ne (632.8 nm) and Ar<sup>+</sup> (514.5 nm) lasers were investigated. Excitons parameters in the region of A, B and C excitonic series where a multiphonon LO Raman scattering observed were determined. Magnitudes of splitting due to crystal field and spin-orbital interaction were estimated. Effective masses of electrons ( $m_{C_1}^*$ ) and holes ( $m_{V_1}^*$ ,  $m_{V_2}^*$  and  $m_{V_3}^*$ ) were calculated and values of energy intervals  $V_1(\Gamma_7)$ - $C_1(\Gamma_6)$ ,  $V_2(\Gamma_6)$ - $C_1(\Gamma_6)$  and  $V_3(\Gamma_7)$ - $C_1(\Gamma_6)$  were determined.

**Index Terms** — CuGaSe<sub>2</sub> compound, effective masses of electrons and holes, excitonic-polariton branches, luminescence, Resonance Raman scattering

## I. INTRODUCTION

CuGaSe<sub>2</sub> compounds belongs to I-III-VI<sub>2</sub> group and crystallizes in chalcopyrite structure with I42D ( $D_{12d}^{12}$ ) space group. There is an interest to the crystals of this group due to possible using in optoelectronic devices. Solar energy convertors have been developed on the base of CuGaSe<sub>2</sub> and CuInSe<sub>2</sub>. A stimulated emission, a second harmonic generation at 10.6  $\mu$ m and infrared emission in the range 4.6 and 12  $\mu$ m were observed in some materials of this group [1]. Biexcitons [2], an interference of additional excitonic waves [3], resonance Raman scattering [4] and an intensive emission of exciton-polaritons and bound excitons [5] were discovered. Nine polar vibrational modes are allowed in these crystals by selection rules.

## II. EXPERIMENTAL METHODS

CuGaSe<sub>2</sub> crystals investigated in present work were grown from the gas phase and are prisms or thin plates limited by growth surfaces. The faces parallel and perpendicular with a optical axis have mirrored non-polished surfaces. The spectra were recorded by a setup based on a DFS-32 double Raman spectrometer. The width of the spectrometer slit was 0.015  $\text{\AA}$  when measuring the absorption and about 0.05 - 0.1  $\text{\AA}$  when recording the luminescence and Raman spectra. Reflection spectra and wavelength modulated reflection spectra were measured by help of MDR-2 spectrometer.

## III. EXPERIMENTAL RESULTS AND DISCUSSIONS

According theoretical calculation of band structure [6] of CuGaSe<sub>2</sub> crystals the minimum of band gap is formed by direct electron transitions in Brillouin zone center. The lower conduction band has  $\Gamma_6$  symmetry and top valence bands  $V_1$ ,  $V_2$  and  $V_3$  possess  $\Gamma_7$ ,  $\Gamma_6$  and  $\Gamma_7$  symmetries, respectively. An interaction of electrons of  $\Gamma_6$  conduction

band and holes of  $\Gamma_7$  band are described by nonanalyzable representation  $\Gamma_1 \times \Gamma_6 \times \Gamma_7 = \Gamma_3 + \Gamma_4 + \Gamma_5$ . As a result of this interaction an exciton  $\Gamma_4$  allowed in E||c polarization,  $\Gamma_5$  allowed in E $\perp$ c polarization and  $\Gamma_3$  forbidden in both polarizations are formed in long-wavelength region. The interaction of electrons of conduction band  $C_1$  of  $\Gamma_6$  symmetry and holes of valence band  $V_2$  with  $\Gamma_6$  symmetry is due to an appearance of three excitonic series  $\Gamma_1$ ,  $\Gamma_2$  and  $\Gamma_5$ . According selection rules in E $\perp$ c polarization  $\Gamma_5$  excitons are allowed and  $\Gamma_1$  and  $\Gamma_2$  excitons are forbidden.

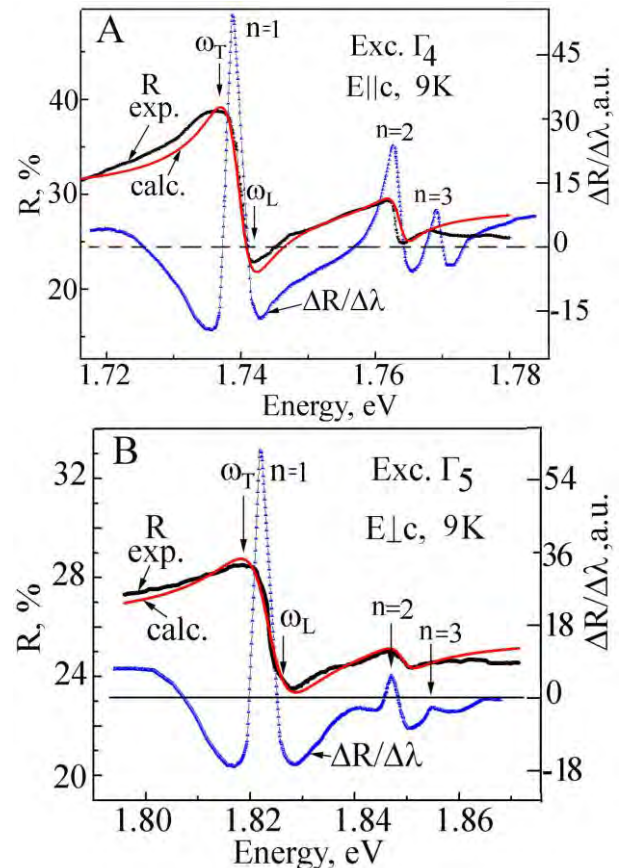


Fig. 1 Reflection (R) and wavelength modulated reflection ( $\Delta R/\Delta\lambda$ ) spectra of CuGaSe<sub>2</sub> crystals in E||c (A) and E $\perp$ c (B) polarizations measured at temperature 9 K.

Lines  $n = 1$  ( $\omega_T = 1.7377$  eV,  $\omega_L = 1.7423$  eV),  $n = 2$  (1.7619 eV) and  $n = 3$  (1.768 eV) of hydrogen like series of  $\Gamma_4$  exciton are observed in  $E_{||c}$ ,  $k_{\perp c}$  polarization in reflection spectra of CuGaSe<sub>2</sub> crystals measured at temperature 9 K (see Fig. 1, A). The reflection spectra in the region of  $n = 1$  line have a traditional fro excitons view with maximum and minimum. These features are due to a presence of longitudinal and transversal excitons. Based on these data a longitudinal-transversal splitting energy for  $\Gamma_4$  exciton is estimated as equal to 4.6 meV. States  $n = 1$ , 2 and 3 are observed in wavelength modulated reflection spectra ( $\Delta R/\Delta\lambda$ ) of CuGaSe<sub>2</sub> crystal measured at temperature 9 K in  $E_{||c}$  polarization (Fig. 1, A). The features observed in  $R$  and  $\Delta R/\Delta\lambda$  spectra are in the experimental error agreed with results of Ref. [7]. Authors of Ref. [7] reported that an excitonic maximum in reflection spectra was observed at energy 1.7368 eV (transversal exciton) and minimum at energy 1.7385 eV (longitudinal exciton). The longitudinal-transversal splitting is equal to 2.3 meV for these crystals. Rydberg constant for excitonic series  $\Gamma_4$  is equal to 0.036 eV and it is determined from energy positions of lines  $n = 1$  and  $n = 2$  (Fig. 1, A). Continuum energy ( $E_g$ ) is equal to 1.7745 eV. According data of reflection spectra shown in Fig. 1, B a binding energy of exciton is equal to 0.0356 eV and a convergence limit ( $E_g$ ) is equal to 1.7724 eV.

Lines  $n = 1$  ( $\omega_T = 1.8226$  eV and  $\omega_L = 1.8266$  eV),  $n = 2$  (1.8476 eV) and  $n = 3$  (1.8528 eV) of hydrogen like series of  $\Gamma_5$  exciton are discovered in reflection spectra of CuGaSe<sub>2</sub> crystals measured at temperature 9 K in  $E_{\perp c}$  polarization (see Fig. 1, B). Lines of excitons  $\Gamma_5$  (C excitonic series) are revealed at high-energies of reflection ( $R$ ) and wavelength modulated reflection spectra ( $\Delta R/\Delta\lambda$ ) in CuGaSe<sub>2</sub> crystals at temperature 10 K in  $E_{\perp c}$  polarizations. The ground state  $n = 1$  is observed at energies  $\omega_T = 2.0279$  eV,  $\omega_L = 2.0308$  eV,  $n = 2$  at 2.0503 eV and  $n - 3$  at 2.0611 eV (Fig. 3 A and B). Two luminescence maxima from lower (2.0226 eV) and upper (2.0280 eV) branches of exciton-polaritons are discovered in region of line  $n = 1$  in luminescence spectra excited by 514.5 nm Ar<sup>+</sup> laser line (see Fig. 3). An excited state  $n = 3$  of excitons is very weak in reflection spectra but it is revealed clearly in wavelength modulated reflection spectra, Fig. 3, A.

Contours of reflection spectra are calculated in framework of classical optic with taking into account spatial dispersion and presence of dead layer [9] for a determination of excitonic parameters. The calculated contours are marked in figures as “calc”. A reduced mass  $\mu$  is equal to  $0.136m_0$  ( $\mu = \epsilon_d^2 R/R_H$ , where  $R = 0.0336$  eV is Rydberg constant and  $R_H = 13.6$  eV is Rydberg energy of hydrogen atom) for long-wavelength  $\Gamma_4$  exciton at background permittivity  $\epsilon_b = 7.4$ . Bohr radius (aB) of s-state of  $\Gamma_4$  exciton is equal to  $0.3 \times 10^{-6}$  cm.

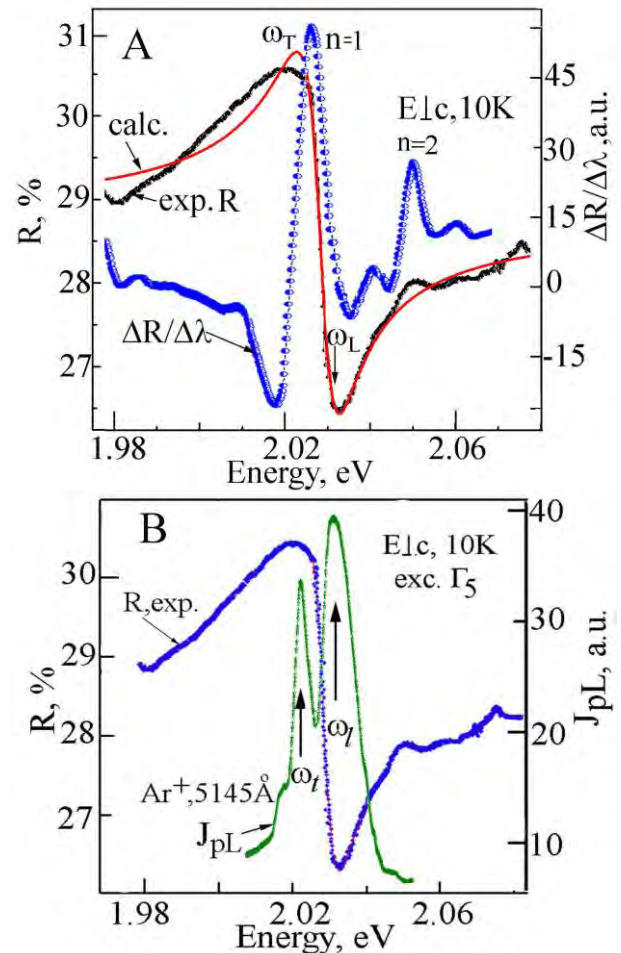


Fig. 3. Reflection ( $R$ ), wavelength modulated reflection ( $\Delta R/\Delta\lambda$ ) and luminescence ( $J_{pL}$ ) spectra of CuGaSe<sub>2</sub> crystals measured at temperature 10 K in  $E_{\perp c}$  polarization.

A conformity of calculated and measured contours of reflection spectra are shown in Fig. 1, A and B and Fig. 3, A. A translation mass for three excitonic series A, B and C of  $\Gamma_4$  and  $\Gamma_5$  symmetry varies in the range 1.4 - 1.45 $m_0$ . The background permittivity is equal to 7.4 for A, B and C excitons.

Taking into account that  $M = m_v^* + m_c^*$  and  $1/\mu = 1/m_v^* + 1/m_c^*$  where  $m_c^*$  and  $m_{v1-3}$  are effective masses of conduction band and three valence bands  $\Gamma_7(V_1)$ ,  $\Gamma_6(V_2)$  and  $\Gamma_7(V_3)$  these effective masses are calculated. The effective mass of electrons  $m_c^*$  is equal to  $0.15m_0$  and the effective mass of holes  $m_{v1}^*$  is equal to  $1.29m_0$  at  $M = 1.45m_0$  and  $\mu = 0.136m_0$ . The calculated value  $m_{v1}^* = 1.29m_0$  is insignificantly differ from data of  $1.24m_0$  [7] and  $1.2m_0$  from Ref. [8]. Taking into account fact that parameters of  $\Gamma_5$  excitons is practically little differ from parameters of  $\Gamma_4$  excitons, for example the effective mass  $m_{v2}^*$  equal to  $1.28m_0$  i.e. practically coincide with mass  $m_{v2}^*$ . The electron mass  $m_c^*$  is equal to  $0.15m_0$  and the effective mass of holes  $m_{v3}^*$  is equal to  $0.84m_0$  for C exciton at  $\epsilon_b = 7.4$ ,  $R = 32$  meV,  $M = 1m_0$  and  $\mu = 0.129m_0$ .

Vibrational modes are characterized the next nonanalyzable representation ( $\Gamma = A_1(\Gamma_1) + 2A_2(\Gamma_2) + 3B_1(\Gamma_3) + 3B_2(\Gamma_4) + 6E(\Gamma_5)$ ) in crystals of  $D_{2d}^{12}$  symmetry in Brillouin zone center. The modes  $A_2$  are forbidden both in Raman scattering and in IR spectra. The mode  $A_1$  and three polar modes  $B_2$  and 6 polar modes  $E$  are optically active in

analyzed CuGaSe<sub>2</sub> crystals. Lines a1 - a12 are found out in resonance Raman scattering spectra measured at temperature 9 K and excited by 632.8 nm He-Ne laser line (see Fig. 4, A). A figure 4, B shows resonance Raman spectra at 300 K discussed in Refs. [9]. Resonance Raman scattering lines a1 - a7 are practically coincide with LO frequencies of single-phonon scattering. According theory the lines of 1LO scattering are forbidden in spectra. Appearing of these lines is connected with presence of microdefects in crystals or other mechanisms which breaks the selection rules on wave vector. Scattering lines a8 - a13 are due to the Raman resonance of excitonic-polaritons with two LO phonon aided. In case of an excitation of CuGaSe<sub>2</sub> crystals by energy ( $\lambda = 632.8$  nm) more than exciton B( $\Gamma_3$ ) ground state energy an effective mechanism of this energy relaxation with participation of LO-phonons exists. Such excitation leads to formation of free excitons with different internal or kinetic energy.

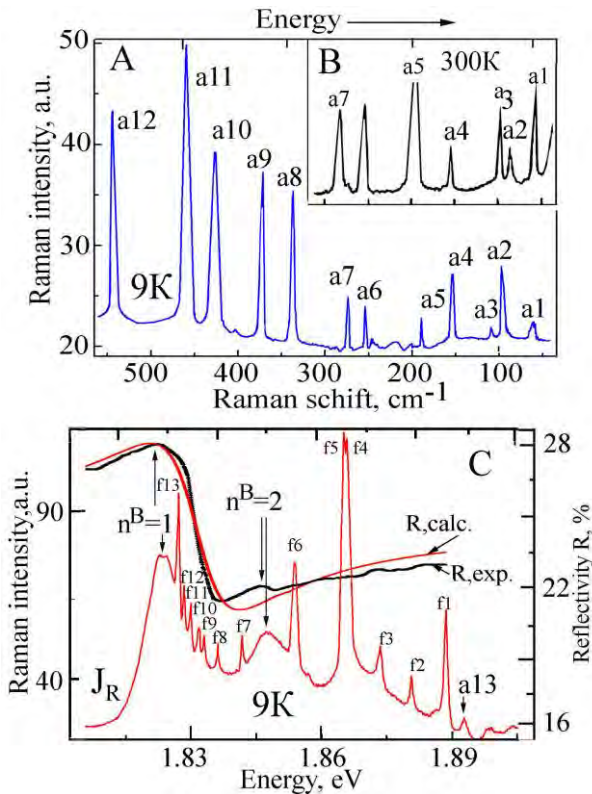


Fig. 4. Resonance Raman scattering spectra (A, C) excited by 632.8 nm line of He-Ne laser and reflection spectra (C) of CuGaSe<sub>2</sub> crystals measured at 9 K. Insert shows the results of Ref. [17].

Lines (band) f1 - f6 are revealed in resonance Raman scattering at proximity to the excited state  $n = 2$  of B excitons (see Fig. 4, C). The intensity of these lines are in few time more than one of lines a8 - a12 shown in Fig. 4, A. The scattering lines f1 - f6 are due to a dispersion of excitonic-polaritons energies with three LO phonons aided. Lines f5 and f4 are more intensive and possess a small enough half-width and close positions. A scattering line f6 is situated on a background of band of thermalized luminescence of B exciton  $n = 2$  state. Luminescence spectra ( $J_R$ ) are put over the experimentally measured ( $R, \text{exp.}$ ) and calculated ( $R, \text{calc.}$ ) contours of

reflection, where states  $n = 1$  and  $n = 2$  of B exciton are observed. The broad band of luminescence with sharp lines f7 - f13 in long-wavelength part are appeared in the region of  $n = 2$  of B exciton. These sharp lines overlaps the broad luminescence band of thermalized B excitons from  $n = 1$  state. Table 2 shows the energy positions of these sharp emission lines (f7 - f13) and the energy difference from band bottom of longitudinal excitonic-polaritons ( $\omega_L - f7, \omega_L - f8$ ). Received differences practically coincide with phonon energies reported in Refs. [10]. The values of phonon energies are presented in brackets in Table 2.

The different phonons (1LO, 2LO and etc.) are participated in the processes of relaxation of excitons energy in CuGaSe<sub>2</sub> crystals. As shown in Fig. 4, A the a8 - a12 lines are more intensive than a1 - a7 lines. The intensity of lines due to scattering on 2, 3 and etc. phonons is more than in case of single-phonon scattering. The phonons of different symmetry appear at LO-phonons scattering process.

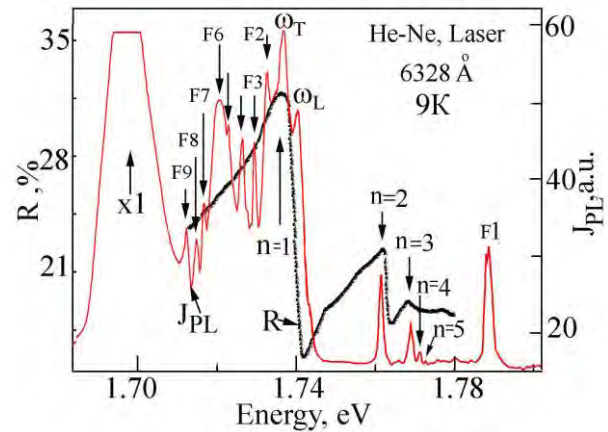


Fig. 5. Resonance Raman scattering ( $J_{PL}$ ) and reflection (R) spectra of CuGaSe<sub>2</sub> crystals nearby A excitonic series measured at temperature 9 K and excited by 6328 Å line of He-Ne laser.

The character of the excitonic-polariton relaxation energy mechanism in CdS crystals and other  $A^{II}B^{VI}$  compounds is considerably changed close by a band bottom. The intensification of Raman scattering line intensity at approaching to an excitonic resonance takes place. It works practically for all investigated  $A^{II}B^{VI}$  compounds. This regularity is retraced and for CuGaSe<sub>2</sub> crystals (see Fig. 4, C) but some features exist. At energies higher than the  $n = 2$  B exciton energy the sharp lines f7 - f13 are superimposed on the contour of excitonic luminescence from the ground state  $n = 1$  of B exciton. At approaching to the energy of  $n = 2$  state of B excitons the relaxation of these states on phonons, demanding longer time, takes place. This leads to an establishment of the thermal equilibrium in excitonic band  $n = 2$  with further transition in  $n = 1$  state with phonon emission that is apparent in exciton-phonon luminescence spectra (line f7 - f13).

Figure 5 shows resonance Raman scattering spectra excited by 6328 Å He-Ne laser line measured in backscattering geometry [x(zz)x]. The intensive emission maxima from upper ( $\omega_L$ ) and lower ( $\omega_T$ )  $\Gamma_4$  excitonic-polariton branches are discovered in the energy interval 1.7368 - 1.7405 eV. The lines F2 - F9 and X1 are observed in long-wavelength part from  $\omega_T$ . The band X1 is due to the luminescence from local center

(defects or impurity states). In some crystals the X1 band has a less intensity and on it contours the narrow lines as F2 - F9 are also presented. The narrow lines (F2 - F9) are energy of LO and 2LO phonons distant from the bottom of excitonic band ( $\omega_L$ ) of A exciton on. This lines are due to the LO and 2LO phonon emission at excitonic-polariton A series relaxation. Table 2 shows the energy position of scattering lines and the combination of LO and 2LO phonons by means of which the scattering of excitonic-polaritons takes place. The intensity of luminescence lines from states of  $\Gamma_5(B)$  excitons in a order less than it from states of  $\Gamma_4(A)$  excitons. The luminescence of states of  $\Gamma_5(B)$  excitons is almost undistinguishable on the background of intensive luminescence lines of  $n = 1, 2, 3, 4$  and 5 states of  $\Gamma_4(A)$  excitons.

#### IV. CONCLUSION

The series of equidistant lines shifted in long-wavelength part from excitation line on energy equal to energies of one, two, three etc. is observed at CuGaSe<sub>2</sub> crystals excitation of He-Ne laser line at temperature 9 K. The lines are due to a resonance Raman scattering and overlapped on luminescence spectra from ground and excited excitonic states. An enhancement of intensity is observed for lines situated near the excitonic resonance. A width of multiphonon lines does not increase considerable with its order growth.

A relaxation on phonons of  $\Gamma_5(B)$  exciton  $n = 2$  state occurs with approaching to the energy of these states. An establishment of thermal equilibrium in the  $n = 2$  excitonic band leads to transitions in  $n = 1$  state with phonons emission. It becomes apparent in exciton-phonon luminescence spectra (lines f7 - f13). The intensity of  $\Gamma_5(B)$  excitonic states luminescence is in a order less than it for states of  $\Gamma_4(A)$  excitons. Because of intensive luminescence from  $\Gamma_4(A)$  excitons  $n = 1, 2, 3, 4$  and 5 states it failed to

find the emission from  $\Gamma_5(B)$  exciton states. The energy distance from maxima of thermalized luminescence (F2 - F9) from band bottom of longitudinal excitonic-polariton  $\Gamma_4(A)$  is equal to the energy of LO phonons.

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