Superposition of the luminescence spectra of free and bound excitons in ZnP_2-D_4^8

Ion STAMOV, Lucretia NEMERENCO, Iurii IVANENCO, Nicolae SYRBU
Technical University of Moldova
lnemerenco@yahoo.com

***Abstract* – The luminescence spectra of ZnP_2 tetragonal crystals doped Mn, Sn, Cd, Sb at 10 K emission lines of bound excitons is detected. In the spectra non-phonon emission lines of bound and free excitons and their phonon replicas is isolated. The emission lines by the levels of the axial center are described. The composition of the luminescence of free and bound excitons at the axial center is investigated. In the region of phonon replicas of free excitons observed enhancement of lines due to forbidden transitions involving the recombination of excitons. A model of optic recombination transitions of the axial centre is proposed.**

***Index Terms* – luminescence spectra, free and bound exciton, optical phonon, electron transitions, axial center**

I. INTRODUCTION

Compound ZnP_2- D_4^8 indirect-gap semiconductors with band gap 2.21 eV at 10K. ZnP_2- D_4^8 crystals have a pronounced birefringence, bright luminescence and a high photosensitivity [1-3]. On the basis of these crystals active elements p-n structures, Schottky diodes, switches, optical pulses are created and are promising materials for optoelectronic devices polarization.

II. RESULTS AND DISCUSSION.

Optic spectra of absorption and luminescence are measured in cryostat LTS-32C330 Workhorse-type Optical with the help of double Raman spectrometer with the light force 1:5 and dispersion of 5 A/mm. The crystals

ZnP_2 - D_4^8 have the structure described by the space group D_4^8 (D_4^4).The band gap (E_g) is determined by indirect transitions is equal to 2.21 eV. Fig.1 shows photoluminescence spectra of specially nondoped and doped with Mn crystals ZnP_2 at 10 K in the short-wave region, i.e. in the region adjoining the free exciton level. At the energy 2,2085 eV a weak peak of luminescence is found E_{ext}^{L}, according to the edge absorption data it coincides with the radiation energy from the free exciton level. We explain peculiarity x_1 - x_{10} in the luminescence spectra by phonon replicas of the free exciton recombination. The band x_i is behind the free exciton energy E_{gx}^{lib} = 2.2085 by the value of optic phonons. In the luminescence spectra various optic phonons can take part [1]. The luminescence spectra with many narrow lines bound excitons, in which different optical phonons were observed in the crystals ZnP_2 - D_4^8 [1-3] and CdP2 - D_4^8 [4].

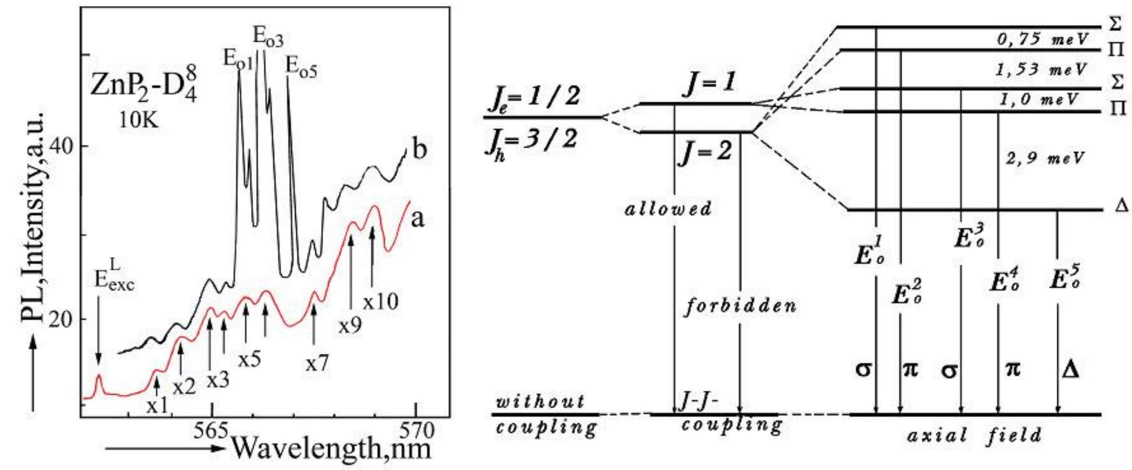

Fig.1. Luminescence spectra of undoped (a) and doped with Mn (b) crystals ZnP_2- D_4^8 at 10K and the energy levels of the electron transitions of bound excitons on axial center of Mn in the crystals ZnP_2- D_4^8.

In the unit cell stacked 8 formula units, i.e. 24 atoms will go into unit cell, in the general case the number of phonon branches is equal to 72. Availability of this quantity of oscillation modes makes it possible to observe radiation of free excitons with emission of many phonons. The luminescence spectra doped with Mn of crystals ZnP2- D_4^8 discovered narrow lines E_{01}-E_{05} and weaker lines x_1-x_{10} (fig.1, curve a). Emission bands of x_i are phonon replicas of free-exciton emission. These bands are observed simultaneously with the narrow emission lines E_{01}-E_{05} bound excitons at the center of the impurity atoms Mn. Non-phonon lines of radiation of bound exciton E_{01}(2,1951 eV),

E_{02} (2,19440 eV), E_{03} (2,1928), E_{04} (2,19277) and E_{05} (2,18987) are seen as narrows lines. The bands x_i are weaker by hundreds times and they have halfwidth being practically by an order larger than the lines. These E_{01}-E_{05} two types of lines x_i and E_{01}-E_{05} of the radiative recombination are observed simultaneously practically in one and the same energy interval (fig.1). As it is known, in the unit cell of the crystal ZnP_2 - D_4^8 there are many atoms (N=24), this determining big quantity of oscillation modes of different symmetry [1-3] in the wide energy range. At the temperature 10 K in the crystals ZnP_2 - D_4^8 the energy distance between the level of free (G_{ext1}) and bound E_0^1 (G_{ext2}) excitons is equal to 13,3 meV, and optic phonons achieve the energy value of 59.5 meV. Hence, exciton levels of bound (E_0) and free exciton (E_{gx}) satisfy the condition $E_{p1}=G_{ext1}-G_{ext2}+E_{p2}$. Thus, the process of recombination radiation may occur simultaneously from two centres. The radiation caused by annihilation of free excitons leads to appearance of a row of bands (x_i) in the longwave region from E_{ext}^{lib} (2,2085 eV) at the energy distance being equal to the energy of optic phonons.

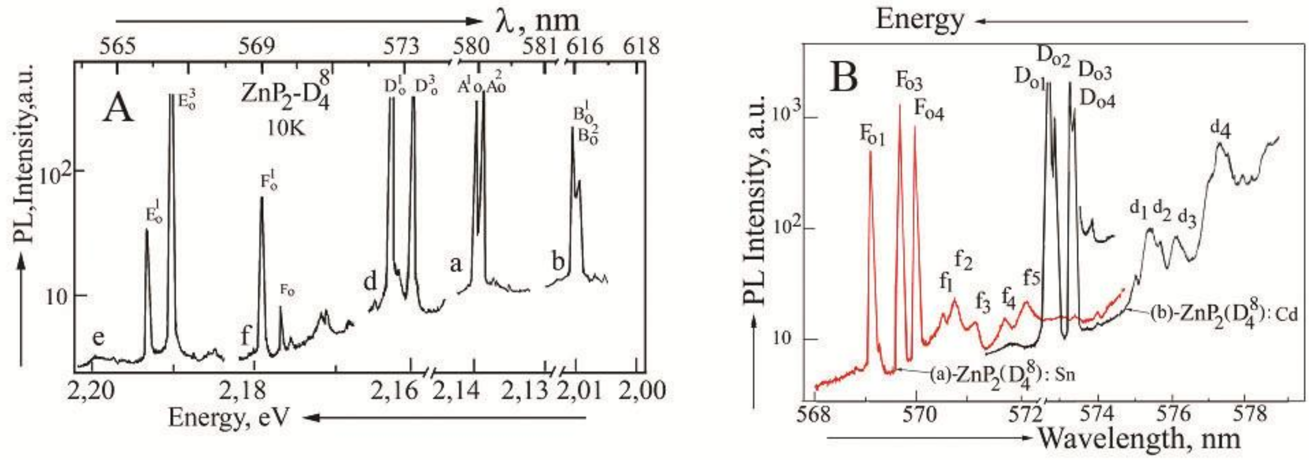

Fig.2. Fragments of the most intense luminescence lines ZnP_2 - D_4^8 crystals at 10 K, doped Mn (curve-e), Sn (curve-f), Cd (curve-a), Sb (curve a and b) and luminescence spectra ZnP_2 - D_4^8 crystals at 10 K doped tin (Sn) and cadmium(Cd).

Electron transitions of the exciton bound on axial centre in the ZnP_2 are shows in the fig.1. We consider that narrow lines $E_0^1 - E_0^5$ are due to phononless lines of exciton bound on axial centre [1-4]. The exciton consisting of the electron with spin 1/2 and hole with spin 3/2 bound on the centre with the axial symmetry forms (from the level J = 1) two levels (Σ and Π). Optic radiative transitions from the levels Σ and Π (J = 1) are allowed and they determine phononless lines E_0^3 and E_0^4. These lines are the most intense and they disappear with the temperature growth (≈40 K). These lines are split by small value (~0,1 meV). The state with J = 2 under the action of the axial field is split into three levels Σ, Π and Δ. Transitions from these levels are forbidden by the selection rules. The phonon energy radiated by the crystal in the result of the free exciton annihilation in the luminescence spectra corresponds to the energy of radiation of the bound exciton forbidden transition. This leads to the resonance excitation of the bound exciton forbidden states and to the removal of the ban and intensification of luminescence from the forbidden levels. The radiation lines E_0^3 and E_0^4 are determined by allowed transitions from the zones of symmetry Σ and Π correspondingly. These levels are split by the crystal axial field of the centre whereon the exciton is bound. The radiation lines E_0^1 and E_0^2 are split by 0,75 meV and they are due to the levels Σ and Π of the forbidden state of the bound exciton. Spin-orbit interaction also leads to the state splitting and appearance of the level Δ. The energy distance between Σ(Π)-Δ determines the value of the level splitting due to spin-orbit interaction (Δ_{SO}). In this model the value of splitting due to the spin-orbit interaction is larger than the value of splitting due to the crystal field. The energy interval between Σ-Σ levels is equal to 2,2 meV. The resulting intensity of the luminescence lines and their energy position shows that the spin-orbit splitting is greater than the splitting due to crystal field (fig. 2). In the transition levels of bound excitons at the axial center should be observed two intense emission lines as a permitted. These lines should be detected in the short wave region. Luminescence lines due to transitions from the levels from which transitions are forbidden by selection rules may occur as weak intensity lines. The situation may change if the phonon energy emitted by the crystal as a result of annihilation of free excitons in the luminescence corresponds to the radiation energy of the forbidden transition of a bound exciton. This can lead to resonant excitation of forbidden states of the bound exciton and to the lifting of the ban and increase the luminescence of prohibited levels. The radiated energy of the phonon may coincide with the energy position of the level of forbidden states of bound exciton. At the free exciton annihilation (E_{gx}^{lib} = 2,2085 eV) the phonon radiative band different from E_{gx}^{lib} at the energy distance 13,3 meV is observed. There is such a phonon of the symmetry E, it is radiated at the energy 2,1951 eV. This radiative band coincides with the energy position of the level of bound exciton E_{0x}^1 (2,19515 eV) and is close to E_{0x}^{2} (2,19440 eV). E_{gx}^{lib} (2,2085 eV) - E_{gx} (13,3 meV) = E_i (2,1952 eV). Such a coincidence of energies of phonon radiation resulting from the free exciton annihilation with the energy levels of bound excitons may remove a ban of optic transitions from the levels of bound exciton, which is put by rules of the bound exciton selection. The ZnP_2 crystals doped with tin (Sn), cadmium (Cd) and antimony (Sb) also exhibit intense luminescence. In these crystals narrow lines of radiation and more gentle luminescence lines are observed. Figure 2A shows fragments of the narrow luminescence lines, which are due non-phonons excitons lines of emission bound these impurities. The luminescence spectra were measured on crystals doped with these impurities under the same experimental conditions. In addition to these luminescence lines are observed their phonon replicas. The luminescence spectra ZnP_2 - D_4^8 crystals at 10K doped with tin (Sn) and cadmium (Cd) are shows in the fig.2B. In these spectra revealed non-phonon excitons lines bound to the tin (Sn) atoms (F_{o1}, F_{o2}, F_{o3}) and their phonon replicas f_1, f_2, f_3, f_4, f_5. In these spectra in the longwave region of the band f_5 has a large number of peaks, which in this figure are not shown. In crystals doped with cadmium discovered a group of intense narrow lines D_{o1}, D_{o2}, D_{o3}, D_{o4} and weaker lines d_1-d_n (fig.2 shows only the four lines).

Narrow and intense luminescence lines D_{o1}, D_{o2}, D_{o3}, D_{o4} crystals ZnP_2 - D_4^8 doped cadmium also caused by excitons bound to the cadmium atom, which, as in previous cases, an axial center. Line D_{o1}, D_{o2}, D_{o3}, D_{o4} are non-phonon luminescence lines and the lines d_1-d_n - their phonon replicas. The experimental results indicate that the considered centers have identical parameters. Energy interval Σ – Σ of the crystals doped with Mn (E_0^1 – E_0^3) equals 2.28 meV, Sn-doped (F_{o1} - F_{o3}) is 2.0 eV and Cd-doped interval D_{o1} –D_{o3} is 2.3 meV. As can be seen, the splitting due to crystal field of the states of electron with spin J_e = 1 / 2 and a hole with spin J_h = 3 / 2 for the three considered centers (impurity atoms) is almost identical.

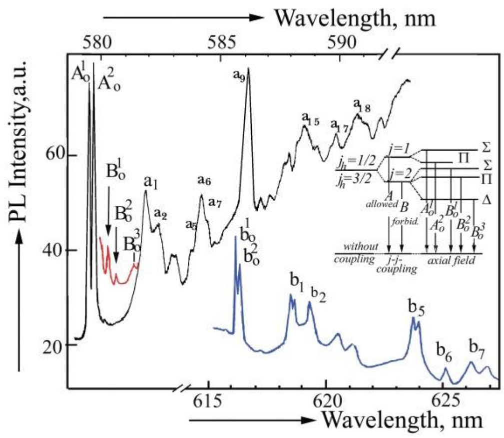

Fig.3. The luminescence spectra ZnP_2 - D_4^8 crystals at 10K doped with tin (Sn)

In the long wave region in the ZnP_2 - D_4^8 crystals Sb-doped there are two groups of lines that were previously found in [1-3]. Narrow intense luminescence line A_0^1 (2.1444 eV) and A_0^2 (2.1442 eV) are non-phonon emission lines of bound excitons to the axial center and are due to transitions from levels Σ, Π (J = 1) in the ground state. These lines are split into 0.22 meV. Weak luminescence line B_0^1 (2.1422 eV), B_0^2 (2.1417 eV) and B_0^3 (2.1400 eV) are due to forbidden transitions from levels Σ, Π and Δ (J = 3 / 2) in the ground state (fig.3). Emission bands a_1, a_2, ..., a_{18} are lines phonon replicas of the non-phonon emission lines A_0^1 and A_0^2. In these spectra, there is no lifting of the ban because of the involvement of phonons, so the luminescence line B_0^1, B_0^2 and B_0^3 are weak. In addition, the luminescence line B_0^1, B_0^2 and B_0^3 located in the long wave region of A_0^1 and A_0^2. Thus, in the band model of the center spin-orbit splitting is less than the splitting due to crystal field. Splitting of the states J = 1 and J = 3 / 2 defined by the energy spacing between levels A_0^1 and B_0^1 is equal to 2.2 meV. Scheme of electronic transitions responsible for the luminescence line (spectra) is shown in fig. 3. In the long wave region observed by us previously in [2, 3] lines B_0^1 (2,0212 eV) and B_0^2 (2,0210 eV) are non-pho luminescence lines of bound excitons to different axial center.

III. CONCLUSION

The luminescence spectra of crystals diphosphide zinc doped tetragonal Mn, Sn, Cd, Sb describes allowed and forbidden recombination transitions in the model levels of the axial center. Superposition of the luminescence of free and bound exciton increase emission lines due to forbidden recombination transitions involving of excitons on the axial center. Amplification with the levels of forbidden transitions of bound excitons occurs at the coincidence of the phonon energy with the energy of the forbidden transition of a bound exciton.

REFERENCES

[1] N.N. Syrbu, Optoelectronic properties compounds A_2B_5, td.Stiinca, Kishinev, 1983
[2] N.N.Syrbu, V.I.Morozova, G.I.Stratan, Phys. and Technics of Semicond., vol. 23 (10), 1771 – 1777, 1989.
[3] N.N.Syrbu, V.I.Morozova, G.I. Stratan, Sov.Phys.Semicond, vol 26 (1), pp. 42-46, Jan 1992, Translated from Phys. and Technics of Semiconductors, vol. 26 (1), pp. 74 – 82, 1992.
[4] R. Bindemann, H.Fisher, K.Kreher, N. N.Syrbu, Phys. St. Sol. (b), vol. 69 (2), pp. K79 – K84, 1975,