

Excitons and energetic bands structure of ZnP₂-C_{2h}⁵ crystals

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Abstract

Reflectivity and transmittance spectra of $ZnP_2-C_{2h}^{5}$ crystals in the region of A, B and C excitons and $E>E_g$ had been researched. The spectra had been calculated using dispersion correlations and the Kramers-Kronig correlations. The exciton parameters and optical functions *n*, *k*, ε_1 and ε_2 had been determined for all excitons. The changes of the damping factor γ , the transversal-longitudinal Δ_{LT} exciton splitting $\Gamma_2^{-}(z)$, and the exciton mass M in dependence on temperature had been revealed. The effective electron mass $m_c^*=0,23m_0$ had been determined. It was shown that the holes mass $m_{V1}^*=4,27m_0$ for $E \parallel c$, k \parallel a and E \parallel b, k \parallel a polarizations and $m_{V1}^*=0,55m_0$ for E $\parallel a$, k $\parallel B$ polarizations. The energies of electronic transitions from V₁, V₂ and V₃ zones into C₁ zone and the symmetry of zones in the Γ point had been determined. The splitting value of V₁-V₂ zones had been determined as being equal 92meV and V₂ - V₃ equals 143.6meV. The singularity of optical functions n, k, ε_1 , ε_2 , $d^2\varepsilon_1/dE^2$ and $d^2\varepsilon_2/dE^2$ had been determined inside the energy interval 1 – 10eV and were interpreted basing on the theoretical zone calculations.

Keywords

 $ZnP_2-C_{2h}^5$ Crystals, Excitons, Reflectivity and Transmittance Spectra, Optical Functions, Kramers-Kronig Analysis, Band Structure

1. Introduction

 ZnP_2 crystals of a monoclinic modification belong to the compounds group A^2B^5 , which are crystallizing into a lattice with spatial group C_{2h}^{5} . The monoclinic $ZnP_2-C_{2h}^{5}$ is a direct band of low symmetry, in which several hydrogen-like excitonic series are exciting conditioned as by the electric [1 - 4] as by dipole-forbidden transitions [1, 3 – 5].

Excited states lines up to n=9 are revealed in polarized spectra of excitonic series [1 - 6]. The excitonic spectra in ZnP₂ - (C_{2h}⁵) crystals are characterized by a strong exciton polaritonic effect [3 - 8]. A different Raman scattering of excitonic polaritons in the region of transversal-longitudinal exciton splitting is observed in crystals [9 - 12]. A bigger amount of lines are manifesting in transmittance spectra, which are conditioned by opto-excitonic states [13 - 16]. In

papers [17 - 20] it was mentioned that an inverse hydrogenlike series (IHS) was present in these crystals in the long wavelength part of excitonic states. In papers [21 - 23] had been studied different influences on optical exciton spectra. A big interest on β -ZnP₂ is, also, the inside condensation phenomena of biexcitonic gas [9] into electron-hole quantum liquid [10]. That is why the monoclinic ZnP₂ represents a model material for studying the Wannier-Mott excitons and their linked phenomena in low symmetry crystals. Active elements and different device structures are developed basing on this crystals, which parameters are researched basing on the anisotropy of optical parameters [23 – 30].

New information on electronic transitions in β -ZnP₂ crystals is obtained in this paper. The optical spectra of β -ZnP₂ crystals are studied in a wide region of energies and temperature values. The absorption and reflectivity spectra

are researched for different temperatures in the region of A, B and C – excitonic series. Theoretical spectra calculations had been carried out as in the excitonic region as in the depth of the absorption line and the electronic transitions had been analyzed.

2. Experimental Method

The $ZnP_2-C_{2h}^5$ single crystals grown from gas phase in closed quartz ampoules represent thin plates with parallel plan surfaces. The plates contained the axis C along the plate boundary. Single crystals grown from melt, had measures of 1mm thickness, 1cm width and 3-5cm in length, sharing above the weld's plane easily. The optical spectra had been measured inside the excitonic region using a double Raman spectrometer $\mathcal{A}\Phi C-24$ and $C\mathcal{A}JI-1$ (5-7 Å/mm dispersion, aperture ratio 1:5 and 1:2). The spectra had been measured using a double ray spectrometer Specord-M40 in the short wavelength region. The results had been digitally recorded. The measurements at 2K had been carried out in liquid helium. The samples were fixed on the cryostat cold conductor "LTS-22 C 330 Work Horse-Type Optical" for 10 – 300K measurements.

3. Experimental Data and Discussions

Figure 1 shows the spectral dependence of the refractive index for E c polarization (solid curve) and luminescence spectra (point curve) measured at 2K. The lines of ground n=1 and excited n=2, 3 and 4 excitonic states are revealed in these spectra. This excitonic series was revealed for the first time in paper [3] at E||c polarization for $k\perp c$. The excitonic series possesses a big oscillatory force of excitonic transition, which is conditioned by the electric-dipole transitions of the singlet exciton (C-series). The data obtained in papers [1 - 6] are later confirmed in a row of researches of crystals with different quality obtained in different laboratories [7 - 12]. The singlet excitons of $\Gamma_2(z)$ symmetry are allowed in crystals of C_{2h}^{5} symmetry at E||c polarization [13 – 16]. A series of thin lines are revealed at E⊥c polarization in case of 1.2mm layer thickness, which are converging towards short wavelength part. It is possible to observe up to 7 lines, from which the lines 3, 4 and 5 are appearing as doublets (fig. 1, B). This series was studied for the first time in paper [3], and it was confirmed that the long wavelength line 1^* at E \perp c polarization is thinner in transmittance spectra than the corresponding line in the reflectivity spectra at Ellc polarization and is shifted in reference towards lower energies. This line is linked with the dipole-forbidden state of n=1 exciton, which is split from the dipole-active state because of the influence of exchange interaction, which takes off the degeneracy between singlet and triplet excitonic states. The n=3, 4 and 5 states are split on 0.5meV, 0.3meV and 0.3meV, respectively. The doublet structures of 3, 4 and 5 lines can be interpreted as the results of orbital degeneracy

cancellation of the highest excitonic states influenced by the crystal field. The absorption lines series n=1 - 27 at E⊥c polarization is fitting well into the hydrogen-like dependence with excitonic binding energy R=46.2meV and the band gap of E_∞=1.6028eV [3 - 6]. The revealed series at E⊥c polarization was, also, studied in papers [13 - 16] for crystals of different quality and was confirmed in papers [3 - 6]. A dipole-forbidden series B of optoexciton was observed at light polarization E||b (E⊥c) in absorption spectra for light wave vector k||a and k||c [3, 5, and 6]. Figure 1, A shows luminescence spectra in the region of excitonic spectra of β-ZnP₂ crystals. Pronounced maxima are revealed in luminescence spectra for the frequencies of transversal and longitudinal excitons of $\Gamma_2^-(z)$ symmetry.



Fig. 1. A – spectral dependence of reflection coefficient for E||c polarization (solid curve) and luminescence spectra (dashed curve) measured at 2K; B – transmittance spectrum at $E\perp c$, E||b polarizations of $ZnP_2-C_{2h}^{5}$ crystals at 2K.

Due to low symmetry of ZnP_2 crystal lattice of $2/m(C_{2h})$ class the orbital degenerations of excitonic states was canceled by the anisotropic crystal field, and the lines series of excitonic absorption are revealed at different directions of wave vector k and radiation polarization states [3 - 6, 13]. Table 1 shows experimentally observed lines of B-spectrum and the energies calculated using the hydrogen-like approximation by the series' components n=2 and 3 as for low energetic as for high energetic doublet components, and also its difference. In paper [15] it was mentioned that the absorption coefficient *a* at the maximum of $B_{n=1}$ -line and also its integral absorption (IA) are changing at helium temperatures from crystal to crystal, the absorption coefficient K is increasing at thinner samples. At crystals with a thickness of d = 0.038mm the K coefficient was reaching 685 cm^{-1} in the excitons line's maximum $B_{n=1}$, basing on which the authors [31 - 33] made the conclusions,

that the excitonic B-series occurred because of faint allowed dipole transitions. In papers [3, 31, 32] it is mentioned that the B-excitonic series is conditioned by nS-states of the triplet exciton, split by a short acting interchange influence. It is considered that the doublet lines for the components of this

series with n>3 are appearing due to the mix of wave vectors of opto-exciton in nS-states of the Γ_1^+ series with a full symmetric function from the functions $3\Gamma_1^+ + 2\Gamma_2^+$ into nD-states. The low energetic components into doublet lines are attributed to D-states [31 – 33].

Table 1. The experimentally observed and calculated energies of A, B, and C lines using the hydrogen-like approximation and the C-excitonic series of ZnP_2 -C2h5 crystals measured at 2K.

	n	Results of our work		E [2 6 9]	F [2 6 9]	E [14.16]
		ω _T (ω _L)	calculated	$E_{n.eV}$ [3-0,0] exp.	$E_{n.eV}$ [3-0,0] calc.	L _{n. eV} [14-10]
E∥ck∥a	1	1,5602(1,5650)		1,5663	1,5591	
	2	1,5905(1,5920)		1,5919	1,5919	
	3	1,5960(1,5972)		1,5980	1,5980	
	4	1,5980(1,5987)		1,6002	1,6001	
	R	0,0399(0,0359)			0,0439	
	E_{∞}	1,6011(1,6009)			1,6030	
	1	1,5578	1,5588	1,5581	1,5578	1,55775
	2	1,5918	1,5918	1,5919	1,5918	1,59108
	3	1,5980	1,5980	1,5980	1,5981	1,59721
	3	1,5987		1,5982		1,59768
	4	1,6006	1,6006	1,6004	1,6003	1,59958
	4	1,6009				1,59987
Ellokla	5	1,6018	1,6016	1,6009	1,6007	1,60070
	5	1,6020				1,60090
	6	1,6023	1,6022			1,60137
	7	1,6026	1,6025			
	R		0,0446		0,0454	0,04505
	E_{∞}		1,6034		1,6030	1,60269
E∥ak∥c	1	1,57440	1,5645	1,5744	1,5625	1,57553
	2	1,59348	1,59348	1,5939	1,5937	1,59410
	3	1,59774	1,59774	1,5997	1,5997	1,59848
	4	1,60067	1,59994	1,6011	1,6011	1,60020
	5	1,60074	1,60078			1,60097
	R		0,0378			0,0354
	E∞		1,6023		1,6043	1,60240

As it was approved by the authors [14] the lines of high energy doublet components are better corresponding to hydrogen-like rule than the series of low energy components. The authors explained that for the state with $n \ge 3$ at (s - d)splitting low energetic are the nS-states, and high energetic are the nD-states.

In order to determine the excitonic state a calculation of excitonic reflectivity spectra shape was made in the region 1.550 - 1.570eV using the single oscillator and multi oscillator model. The calculations of the shapes of reflectivity spectra was made in the theory limits, that takes into consideration the spatial dispersion (SD), with the condition of Thomas-Hopfield "dead" layer presence at the crystal's boundary, which inside boundary have true Pekar boundary conditions. The dielectric constant of the medium in the region of excitonic resonance has the form [3, 34]:

$$\varepsilon(\omega, \vec{k}) = \varepsilon_F + \frac{2\varepsilon_0 \omega_{LT} \omega_0}{\omega_0^2 - \omega^2 + \frac{\hbar^2 k^2}{2M} \omega_0 - i\gamma\omega}$$
(1)

where ϵ_b - background dielectric constant, conditioned with the contribution of all interaction mechanisms except the

studied oscillator; ω_0 - transversal exciton frequency; $M = m_C^* + m_V^*$ - translational exciton mass; k – wave vector; $\omega_{LT} = \omega_L - \omega_0$ - transversal-longitudinal splitting value; ω_L longitudinal exciton frequency. The reflection coefficient of the crystal in case of normal light flow on the boundary crystal – LL (Low Layer) – vaccum is determined by the following expression:

$$R = \left| \left(\frac{1 - n_0}{1 + n_0} + \left(\frac{n_0 - n^*}{n_0 + n^*} \right) e^{i2kn_0 t} \right) / \left(1 + \left(\frac{1 - n_0}{1 + n_0} \right) \left(\frac{n_0 - n^*}{n_0 + n^*} \right) e^{i2kn_0 t} \right) \right|^2$$
(2)

where $n_0 = \sqrt{\varepsilon_b}$, $n^* = \frac{n_1 n_2 + \varepsilon_b}{n_1 + n_2}$, t – depth of "dead" layer, k –

exciton's wave vector, $n_1 n_2$ – refractive indexes of transversal waves taking into consideration the dependence of the damping factor γ . The value of the background dielectric constant near excitonic resonance was used in calculations.

Figure 2, A shows the comparison of experimentally measured reflectivity spectra (exper.) and the calculated ones (calc.) using the dispersion correlations. The curves a* correspond to the calculations using the single oscillator model and the b* curves to the multi oscillator model. The

calculations of the excitons' parameters were made using the method of parameters' changing up to the whole, possible correspondence of the calculated curves with the experimental ones. In case of low values of the background dielectric constant $\varepsilon_{\rm B}$ in the region of the beginning of excitonic reflection it was observed a shape of low reflection values (region α). IN case of high oscillator force of the n=2 state the calculated reflection shape corresponds to the β curve. A good correspondence of the theory with the experiment was reached in the frame of the model of excitonic reflection Hopfield -Thomas as in the region of background state n=1 as in the region of the excited state n=2 of the $\Gamma_2(z)$ excitons. The following values of the main parameters of excitonic resonance n=1 at 2Kwere obtained form calculations of β -ZnP₂ crystals: resonance energy $\hbar\omega_0$ =1.56018eV, longitudinal-transversal splitting value $\Delta \omega_{LT}$ =5.0 meV, translational excitonic mass $M=4.89m_0$ (m₀ – mass of free electron), the background dielectric constant 10.64 and the damping factor γ =0.55meV. The resonance energy $\hbar\omega_0=1.59091 \text{eV}$ for the n=2 state at 2K temperature value, the longitudinal-transversal splitting value $\Delta \omega_{LT}$ =0.75meV, the background dielectric constant is 8.64 and the damping factor $\gamma = 0.35$ meV.



Fig. 2. Transmittance spectrum of $ZnP_2-C_{2h}^{5}$ crystal at E || a, k || c polarization measured at 2K.

Figure 2, B shows the reflectivity spectra in the region of $\Gamma_2^{-}(z)$ excitonic excited states at 2K, 32K and 77K temperature values.

Figure 3, A shows the experimentally measured (exper.) and calculated (calc.) shapes of reflectivity spectra of $\Gamma_2^-(z)$ excitons for different temperature values in β -ZnP₂ crystals. The excitonic parameters γ , ω_T , ϵ_B , M and Δ_{LT} obtained from theoretic calculations at different temperatures are shown in table 2. As the temperature increases the excitonic shape of reflectivity spectra is shifting towards long wavelength region. The oscillation amplitude (R_{max}-R_{min}) decreases as the temperature increases, analogical to the observations made by the authors [12].



Fig. 3. A- Reflectivity spectra experimentally measured (exper.) and calculated (calc.) using the dispersion correlations. The a^* curves correspond to the calculations using the single oscillator model and the curves b^* - the multi oscillator model; B – reflectivity spectra in the region of the excitonic excited states at 2K, 32K and 77K. Calculated curves received at fitting by step-by-step method are demonstrated as thin red lines in the top figure.



Fig. 4. A- Experimentally measured (exper.) and calculated (calc.) shapes of reflectivity spectra $\Gamma_2^{-}(z)$ excitons at different temperatures in β -ZnP₂ crystals and temperature dependences of γ , ω_T ,M and Δ_{LT} parameters obtained from theoretical calculations

It was obtained from the calculation of reflectivity spectra shapes that the energy of transversal exciton (ω_T) is decreasing from 1.56018eV to 1.5421eV as the temperature changes from 2K up to 120K. The values of the longitudinal-transversal splitting at these temperatures is also decreasing from 5.0 down to 3.4meV, and the damping factor is increasing from 0.55meV up to 3.076meV (table 2). The same value ε_B =7.04 is obtained at 2K for the samples measured in liquid helium. The rest of the results are obtained for crystals attached to the cold head of the helium

cryostat "LTS-22 C 330 Work Horse-Type Optical". It is evident from the obtained results, that the amplitude of the reflectivity spectra coefficient, i.e. the changing of ($R_{max.}$) down to R, is essentially decreasing (\approx 30%) in the long wavelength part, the region determined by $\epsilon_{\rm B}$. This change is conditioned by the change of the excitonic translational mass Γ_2 (z). The M mass is changing from 4.5m₀ down to 2.5m₀ as the temperature changes form 2K up to 120K (table 2).

Table 2. Excitonic parameters obtained from the calculations of reflectivity spectra shapes of 1S state of the $\Gamma_2(z)$ singlet exciton of $ZnP_2-C_{2h}^5$ crystals for different temperature values.

Temperature, K	ω _T , eV	Δ_{LT} , meV	$M = (m_v^* + m_c^*)m_o$	ε _b	γ, meV
2	1,56018	5,0	4,5	7,0	0,5
10	1,5599	4,6	4,4	7,0	1,2
32	1,5587	4,2	3,6	7,0	1,2
52	1,5574	3,9	3,2	7,0	1,9
95	1,5500	3,6	2,9	7,0	2,0
110	1,5449	3,4	2,5	7,0	3,0

The below presented experimental data talk about the fact that B-spectrum represents a single optoexcitonic series, split by the exchange interaction. The value of the exchange splitting of the degenerated excitonic state equals to the doubled exchange integral, which can be evaluated using the value $A\approx (e^2/d)(d/a_{ex})3$ for nS-states, where d – the distance between atoms, a_{ex} – Bhor ecitonic radius. The distance between neighbor phosphor and zinc atoms in β -ZnP₂ crystals equals d=0.239nm [35], and the Bhor radius of the 1S singlet exciton $a_{ex} \sim 1.8$ nm, respectively 2A $\sim 2.8 \cdot 10^{-3}$ eV.



Fig. 5. A- Reflectivity spectra (R) and spectral dependencies of the absorption coefficient (K) and the phases of the reflected ray (Φ) calculated from the reflectivity spectra using the Kramers-Kronig correlations. B – Comparison of absorption spectra (K) measured at $E \parallel b$, (E \perp c) polarizations and absorption spectra (K) calculated from reflectivity spectra at $E \parallel c$ polarization.

As it was mentioned earlier, the measurement of absorption spectra at Ellc polarization were not able to be carried out because a high absorption value. In order to determine a fixed energetic position of the absorption maximum for n=1 of the C-excitonic series there had been made calculations of the absorption coefficient from reflective spectra R using the Kramers-Kronig correlations. Figure 4, B show the comparison of absorption spectra measured for E||b (E \perp c) for n=1 of the B-excitonic series with the reflective spectra maximum calculated from the reflective coefficient R (E||c). The difference between energetic positions of the $B_{n=1}$ (1,5578eV) exciton on the energy of transversal exciton $C_{n=1}$ (1.5602eV) equals 2.4meV. This distance equals 2.6meV if considering the data from [15, 35], which is, practically, corresponding to our data and to the theoretical estimation. Although, a short acting exchange interaction does not lead to the dependence of the exciton energy on the wave vector direction, which is observed for the B-series [15].

It is evident from calculations that the absorption coefficient at E||c polarization reaches 10^6 cm⁻¹ at a resonance value $\omega_T = 1,5602$ eV. The Bouguer law is violated if measuring absorption spectra at E⊥c polarization in the excitonic resonance n=1 at low temperatures: as the crystal's thickness decreases lower than the estimated value *d* the absorption coefficient increases [13, 36]. An analogical image is observed at E||c polarization for crystals with several microns thickness, which are opaque. This is conditiones by γ increase due to the increase of scattering of excitonic polaritons for surface layers *l* in comparison with the crystal's inside region *d* in which, the damping is determined only by the energy dissipation of light excitons on the defects of the crystal lattice [14].

The excitonic polaritons are absorbed in crystals if the scattering occurs from mechanical energy, characterized by the damping parameter. The part of electromagnetic energy of excitonic polariton, or the force of the exciton-photoic interaction, is linked with the "delay" effect and is characterized by the value of the transversal-longitudinal splitting, which is determined by the oscillator force of excitonic transition. If increasing the crystal's temperature, the damping factor γ is smoothly changing, table 2. At a certain temperature T_c it reaches the critical value $\gamma \geq \gamma_c$, when the interaction of excitons and photons is negligibly small and the crystal looses the spatial dispersion. This is confirmed by the transparency losses for n=1 of excitonic resonances. The surface under the curve becomes proportional to the oscillator force of the excitonic transitions F and do not depend on the temperature and sample's thickness according to the semi classical theory of excitonic absorption [37].

The attenuation of excitonic polaritons is considerably depending on the surface's state. The *l* thickness is determined by polaritonic effects, i.e by the conversion frequency of the electromagnetic part of the light exciton's energy into mechanical one, which is determines by the oscillator force of the excitonic transition or by the transversal-longitudinal splitting Δ_{LT} [37]. Tehn calculations of the absorption coefficient and the reflected ray phase at Ellc polarization possess particularities at frequencies of longitudinal exciton. The phase has minimal value and the absorption coefficient has a fraction. These calculations show, that the Kramers-Kronig method as, also, the calculations using the dispersion correlations present information about the fix value as of the transversal as of the longitudinal excitons. The spectral dependencies of optical functions n, k, ε_1 and ε_2 obtained from the calculation of reflectivity spectra R at E||c polarization are shown in figure 5. The fraction at energies of the transversal exciton is, also, observed in spectral dependence of the extinction -k and the refractive index has a pronounced broad minimum.



Fig. 6. Spectral dependencies of optical functions n, k, ε_1 and ε_2 obtained from calculations of reflectivity spectra R at $E \parallel c$ polarization.



Fig. 7. A- Spectral dependencies of the refractive indexes n^{\parallel} and n^{\perp} , respectively for the E||c and $E \perp c$ polarizations obtained from calculations of reflectivity spectra at 300 and 2K. B – energetic position of the maximum of transversal exciton ω_T at different temperature values.



Fig. 8. Transmittance spectra T and $d^2T/dE^2 ZnP_2$ crystals with 4.5µm thickness at 300K and 77K at $E \parallel c$ and $E \perp c$ polarizations, differential spectrum at $E \parallel c$ polarization is shifted from the 0 point by coordinate axis.

Figure 6 shows the spectral dependence of the refractive indexes n^{\parallel} and n^{\perp} at $E \parallel c$ and $E \perp c$ polarizations, respectively. The refractive indexes are calculated from reflective spectra using the Kramers-Kronig correlations. As it is evident, the refractive indexes n^{\parallel} and n^{\perp} are intersecting at 2K at wavelength value λ_0 =798nm and at 300K at wavelength value λ_0 =906nm. These wavelengths are isotropic for ZnP₂ crystals at respective temperatures. In the short wavelength part of the spectral dependence of the refractive index n^{\parallel} at

300K there are revealed two maxima $e1^*$ and $e2^*$ at wavelength values 855nm and 734nm. At E⊥c polarization, i.e. in the spectral dependence n^{\perp} the short wavelength maximum e2* corresponds to the 734nm wavelength. The e1* maximum is pronounced at Ellc polarization, which is positioned near the energy of the transversal exciton ω_T The anisotropy of the boundary absorption in these crystals is observed, because in crystals of C_{2h}^{5} symmetry the optical transitions are occurring according to the selection rules at different polarizations. Figure 8 shows the transmittance spectra (T) and the second derivate by the energy of transmittance spectra (d^2T/dE^2) of ZnP₂ crystals with 4.5µm thickness at 300K and Ellc and Ec polarizations. The singularity e1^{*} at 1.450eV is observed in transmittance spectra and, also, in differential transmittance spectra at Ellc polarization. The e2* maximum is pronounced at 1.6919eV in high energy region at tis polarization and in differential spectra. A doublet maximum e3*-e4* at 1.8355eV and 1.8801eV energy values, respectively, are observed at Ec polarization in differential spectra. The revealed particularities e1^{*}, e2^{*} and e3^{*}-e4^{*} are conditioned by direct electronic transitions in the center of Brillouin zone. The maxima $e1^*$ and $e2^*$ at 77 – 2K are shifted one from another on an energetic interval of 92meV, e2^{*} and e3^{*} are distanced on an energetic interval 143.6meV. The doublet maxima e3^{*} $e4^*$ are revealed in one polarization (E \perp c) are, most possibly split on 44.6meV because of the spin-orbital interaction, and the e2^{*} and e3^{*} maxima are split by the crystal field. In this case the valence bands V2 and V3 in the center of Brillouin zone possess the same symmetry and their splitting equals 143.6meV. The symmetry of V1 zone differs from V2 symmetry, the transitions V1 - C1 are allowed at Ellc polarization and the V2-C1 transitions are observed at E1c polarization.

According to the theoretical-group calculations of the selection rules [38, 39] in the center of Brillouin zone into dipole approximation and E||c polarization the transitions between zones of the symmetry $\Gamma_1 \rightarrow \Gamma_2$, $\Gamma_2 \rightarrow \Gamma_1$, $\Gamma_3 \rightarrow \Gamma_4$ and $\Gamma_4 \rightarrow \Gamma_3$ are allowed. The minimum of conduction band in the theoretic calculations of energetic zones is determines by the Γ_1 symmetry. Therefore, the electronic transitions e1^{*}, E_{∞} from valence band V_1 with Γ_2 symmetry occur into the conduction band C_1 with Γ_1 symmetry. The valence bands V_2 , V_3 and V_4 possess the Γ_4 , Γ_4 and Γ_2 symmetries, respectively. The fragment of zonal model in the center of Brillouin zone is presented in the insertion of figure 9.

The below presented experimental data on reflective and transmittance spectra talk about the fact that the revealed excitonic reflective spectra at E||c polarization (C-exciton) and the transmittance spectra at E⊥c polarization (B-exciton) represent an unique optoexciton series, split by the exchange interaction. This way, the excitonic spectra revealed in reflective and transmittance spectra occur from the same pair of electronic and holes zone, which represent nS-states of the singlet Γ_2 (z) and triplet $2\Gamma_1$ (y) + Γ_2 (x) excitons, respectively [3, 13]. This is confirmed by the measurements of transmittance spectra at 300K (fig. 7), in which is present

only one transition e1^{*} in the long wavelength part from V1 zone into C1 band. Three hydrogen-like series A, B and C of the singlet electric-dipole exciton and its mixed mode are present in optical spectra of monoclinic ZnP₂ crystals, near the fundamental absorption line. Basing on the results of this paper and the results published in [11 - 13, 15] the excitonic Rydberg constant (R_v) from each series of absorption lines is different (table 1); all the series are converging to one limit Eg= (1.6026 ± 0.0002) eV as the main quantum number n increases. This allows admitting that the C, B and A series are excitonic states, formed from wave functions of the same pair of electronic zones. Due to low symmetry of crystal lattice of $2/m(C_{2h})$ class the orbital degeneration of excitonic states is canceled by the anisotropic crystal field, and the series of excitonic absorption lines are pronounced at different directions of wave vector k and polarization states of radiation. This was mentioned, practically, in all scientific papers [3 - 6, 11 - 14]. The derivated effective mass $\mu^* =$ $(\epsilon_b)^2 R_{exc}/R_{H2}$ is linked with the effective electron masses m_c^* and holes masses m_V^* according to the expression:

$$\frac{1}{\mu^*} = \frac{1}{\mu_c} + \frac{1}{\mu_V}$$
(3)

and the translational exciton mass $M = m_c^* + m_V^*$.

The Rydberg constant R=0.0359eV for the excitonic series C, for the B-series R=0.0446eV and for A-series R=0.0378eV. The values of the background dielectric constant $\varepsilon_{\rm b}$ differ for these series. The background dielectric constant ε_b =9.0 at E||c, k||a polarizations. The background dielectric constant $\varepsilon_b=8.16$ and $\varepsilon_b=7.6$, respectively, at E b, k a and E a, k c polarizations, i.e it is lower than that for E c, k a polarizations. Such correlation is observed as at 300K as at 2K (fig. 7). The measured refractive indexes n^{\parallel} , n^{\perp} (fig. 7) at Ellc and E \perp c polarization showed that as nearer is the resonant excitonic frequency as higher is the difference between n^{\parallel} and n^{\perp} . The derived effective masses had been calculated using these values of $\varepsilon_{\rm h}$ and the magnitudes of the Rydberg constant (R). $\mu^*=0,21m_0$ for the excitonic series C at $E \parallel c, k \parallel a$ polarizations, $\mu^* = 0.397 m_0$ for $E \parallel b, k \parallel a$ polarizations (B-exciton) at $\varepsilon_b=8.16$ and $\mu^*=0.16m_0$ at E a, k c polarizations (A-exciton) at $\varepsilon_b=7.6$. Taking into consideration the value of derived effective mass ($\mu^*=0.21m_0$) and considering the value of the translational exciton mass M=4.5m₀ at E $\|$ c, k $\|$ a polarizations the effective electron mass $m_c^* = 0,2\ddot{3}m0$ was estimated, and the effective holes mass $m_{V1}^* = 4.27 m_0$. The M mass tends to the $2m_0$ value at 300K (fig. 4), respectively, the effective holes' mass $m_{V1}^*=1.77 m_0$. As it was earlier mentioned, all excitonic series (C, B and A) are formed in the neighborhood of one pair of zones $V_1 - C_1$. The anisotropy of effective mass is faint or absent, i.e. different binding exciton energies (R_{exc.}) for excitonic series C, B and A are conditioned by different effective mass of holes. $m_{V1}^* = (4.27 - 4.25)m_0$ at E || c, k || a and $E \| c, k \|$ a polarizations. $m_{V1}^* = 0.55 m_0$ at $E \bot c, k \| b$ polarizations. As it is evident, the effective masses are differing on one order, depending on the direction of the

wave vector k. The same anisotropy of effective masses is observed at InP crystals (m^{||}=3.71m₀, m^{\perp} =0.255m₀ and GaSb m^{||}=3.51m₀, m^{\perp} =0.24m₀) [37].

Reflective spectra are measured at Ellc polarization in the depth of fundamental absorption of ZnP₂-C_{2h}⁵ crystals in the energy interval 1 - 6eV and 80K, and in the region 6 - 10eVat 300K temperature value (fig. 7). The reflective spectra are measured at E \perp c polarization in the energy interval 1 - 6.5 eV. The absorption coefficient K for both polarizations was calculated from reflective spectra using the Kramers-Kronig correlations. a1-a12 maxima are revealed in the own region $(E \sim 1.5-10 \text{eV})$ and in reflective spectra at E||c polarization and e_2-e_8 maxima at E \perp c polarization. The absorption coefficient at Ellc polarization for all measured region possesses a high value and changes in the limits $10^5 - 10^7$ cm⁻ . The absorption coefficient is rather lower at $E \perp c$ polarization and changes from $5 \cdot 10^4$ up to $8 \cdot 10^5$ cm⁻¹. In the own region the absorption is one order higher at Ellc polarization than at ELc polarization, as, also, for the excitonic region.

The optical functions n, k, ε_1 , ε_2 , $d^2\varepsilon_1/dE^2$ and $d^2\varepsilon_2/dE^2$ in all measured region for both polarizations are calculated using the Kramers-Kronig correlations (fig. 8, 9). The maxima of reflective spectra are, also, pronounced in optical functions n, k, ε_1 , ε_2 and $d^2\varepsilon_2/dE^2$. The particularities in reflective spectra and optical functions are conditioned by direct optical transitions in actual points of Brillouin zone.



Fig. 9. The spectral dependence of refractive index R and absorption coefficient K for ZnP_2 crystals.

The Brillouin zone represents a rectangular prism with 14 special points [39, 40]. The theoretical-grouping calculations of dispersion law in actual points of Brillouin zone and, also, the calculations of selection rules for ZnP_2 are made for all points of Brillouin zone considering and not considering the spin-orbital interaction [39, 40]. The actual points of Brillouin zone (point of null energy slope), dispersion laws and selection rules had been estimated. The null energy slope in Γ , *Z*, M, R, Σ , Λ , N, *X*, R, A points is realized by two from three directions K_x, K_y, K_z. The null energy slope is realized along all three directions in the Γ , M, R points without considering the spin-orbital interaction. The null energy slope is realized along all directions in the point Γ if considering the spin.

The dispersion correlation analysis shows that those have the most simple view in the Γ , X, P, N, Z points. According to the selection rules the transitions in the R, X, Y, T, S, and Σ points are polarized. The selection rules in the center of Brillouin zone confirm that the transitions possess different energetic interval at each polarization, i.e. are polarized.

The theoretic calculations of the zonal structure using the pseudo-potential method are made for Zn₃P₂ crystals with D_{2h}^{20} symmetry in a wide energy region for different points of Brillouin zone [41, 42]. The crystal lattice of Zn_3P_2 was studied in theoretic calculations as an analog of fluorite crystal lattice. Zn atoms are doped as vacancies, periodically positioned along the crystal lattice. The maximum of the valence zone and the minimum of conduction band are positioned in the center of the Brillouin zone, in the Γ point. The spin-orbital interaction and other relativity effects were not considered in calculations. The maximum of valence zone in Γ point is three times degenerated. The calculated value Eg =1.886eV. The consideration of crystal field potential and spin-orbital interaction in real crystals will lead to the splitting of valence bands. The maximum of valence zone Γ_{15} will split into three zones due to degeneration cancellation. Valence zones posess maxima and the conduction bands posess minima for the same values of wave vector k in the Γ , X and L points. The theoretic calculations of zonal structure of ZnP₂ crystals using the pseudo-potential method was made and, also, realized in papers [43 - 45]. The calculations are made in the points of Γ , Z, V, U, R, A, P, M, and Λ symmetry in a wide energy region (25eV). Lots of zones that possess a plain character are obtained. The low conduction band is single, as it is, also, in calculations [41, 42], which minimum is positioned in the Γ point. The valence zones are, also, plain. In the obtained structure of energetic zones [43 - 45] is rather complicated to be estimate at which values of wave vector the maxima of valence band are corresponding with the minima of conduction band. The calculations of zonal structure of ordered chalcopyrite ZnSnP₂ and disordered structure of Zn(Sn)P₂ in Γ , X, P, N and Z points of the Brillouin zone are made in paper [46]. The low conduction band is formed by the S-states of Zn atoms, the upper valence band by the P-states of phosphor atoms. The obtained zonal diagrams for Zn(Sn)P₂ [46] and Zn_3P_2 [41, 42] crystals have a lot in common and are not in contradiction with the results of ZnP_2 calculations[43-45], although, the comparison of experimental results can be made basing on the zones' calculations [41, 42]. The maxima of valence band and minima of conduction band are positioned in the center of Brillouin zone. The Γ , X, L points can be distinguished from the results of zones' calculation, in which neighborhood the maxima of valence band and minima of conduction band are revealed at the same values of wave vector. It is at these points of Brillouin zone, where the selection rules are performed for the wave vector and the electronic transitions occur.

3.4 0.6 A 3 ZnP₂ 3. a_{10} 2.8 0.0 2.6 0.22.4-0.4 $\frac{8 - 10}{\text{Energy, eV}}$ 12 4 3.2 В 3. q 2.8 0.02.6 -0.2 2. 4 3 Energy, eV

Fig. 10. Spectral dependence of optical functions n, k for $E \parallel c$ (*A*) and $E \perp c$ (*B*) polarizations.

The maxima e_3^* , e_4^* are shifted one in comparison to another on an energetic distance of 143.5meV. Perhaps, this magnitude corresponds to the spin-orbital zones' splitting into the Γ point. The value of spin-orbital splitting of valence band is estimated in the approximation of covalent linkages to be $\Delta_{so} = 0.06$ eV. In the approximation of one and double order ionized Zn ions $\Delta_{so} = 0.15$ eV and 0.30eV. It is evident from experimental data that the splitting of valence band cause by the crystal field V₂-V₃ equals 44.5meV and that by the spin-orbital interaction V₁-V₂ equals 143.6meV.



Fig. 11. Spectral dependence of optical functions ε_1 , ε_2 and $d^2\varepsilon_2/dE^2$.

Table 3. Energies of electronic transitions obtained from calculations of reflective spectra using Kramers-Kronig correlations in ZnP₂.C_{2h}⁵ crystals

	-					
No	Max.R,	$d^2 \varepsilon_2/dE^2$, $d^2 T/dE^2$,	N⁰	Max.R,	$d^2 \varepsilon_2 / dE^2$, $d^2 T / dE^2$	Transition
0.12	E c, eV	E c, eV		E⊥c, eV	E ⊥c, eV	
e1*	1,450					$\Gamma_{15}(V_1) - \Gamma_1(C_1)$
e2*				1,6919		$\Gamma_{15}(V_2) - \Gamma_1(C_1)$
			e1	1,836	1,839	
			e3*	1,8355	1,8355	$\Gamma_{15}(\mathbf{V}_3) - \Gamma_1(\mathbf{C}_1)$
			e4*	1,8801	1,8801	$\Gamma_{15}(V_4) - \Gamma_1(C_1)$
a2	2,301	2,298	e2	2,264	2,260	$L_3(V_1) - L_1(C_1)$
a3	2,761	2,745	e3	2,788	2,768	$L_3(V_2) - L_1(C_1)$
a4	3,451	3,439	e4	3,447	3,447	$L_3(V_3) - L_1(C_1)$
a5	4,236	4,223	e5	3,814	3,865	$X_{5}(V_{1}) - X_{1}(C_{1})$
a6	4,570	4,567	e6	4,252	4,256	$X_{5}(V_{2}) - X_{1}(C_{1})$
a7	4,842	4,877	e7	4,470	4,467	$X_{5}(V_{1}) - X_{3}(C_{2})$
a8	5,710	5,762	e8	5,230	5,237	$X_{5}(V_{2}) - X_{3}(C_{2})$
a9	6,73	6,73	e9	5,768	5,771	$\Gamma_{15}(\mathbf{V}_1) - \Gamma_{25}(\mathbf{C}_1),$
a10	7,27	7,30				$\Gamma_{15}(V_2) - \Gamma_{25}(C_1)$
a11	8,06	8,06				$\Gamma_{15}(V_3) - \Gamma_{25}(C_1)$
a12	10,1	10,1				$\Gamma_{15}(V_2) - \Gamma_{25}(C_2) \Gamma_{15}(V_1) - \Gamma_{25}(C_2)$

Minima e1^{*} at 1.4500eV energy are revealed in the region of band gap minimum in transmittance and d^2T/dE^2 spectra at E||c polarization for ZnP₂ crystals. This transition responds for the minimum of band gap (V1 – C1) at the given polarization and 300K. The e2^{*} maximum is revealed in transmittance and d^2T/dE^2 spectra at 1.6919eV energy value, at 77K and E⊥c polarization. This particularity, also, occurs in the center of Brillouin zone from V2 zone into C1 zone. A doublet maximum e₃^{*}, e₄^{*} is present at 1.8355eV and 1.8801eV energy values, respectively, in the short wavelength part in T and d^2T/dE^2 spectra. The e1 maximum is, also, revealed in reflective spectra at 1.836eV energy values. These maxima appear from the zones split because of the crystal field V3 and V4 to the conduction zone C1. The value of this splitting equals 44.6meV.

The following energetic intervals are positioned in the L point of Brillouin zone as the energy increases. The e2 (2.260eV) and a2 (2.298eV) maximum determined from experimental data are conditioned by the electronic transitions $L_3(V_1)-L_1(C_1)$. The a2 (2.745eV) and e₃ (2.768eV) maxima are conditioned by the transitions $L_3(V_2)-L_1(C_1)$, and *c* is conditioned by the transitions $L_3(V_3)-L_1(C_1)$. Therefore, the valence zones splitting in the L point of Brillouin zone caused by the crystal field $\Delta_{CR}=0,508eV$. The splitting value of valence band caused by the crystal field Δ_{CR} is lower in L point and, also, in the Γ point of Brillouin zone than the one caused by the spin-orbital interaction Δ_{SO} .



Fig. 12. Electronic transitions and a model of energetic band structure of $ZnP_2-C_{2h}^{5}$ crystals [41, 42].

The energetic interval revealed experimentally a5 (4.223eV) and e5 (4.265eV) is conditioned by the transitions $X_5(V_1)-X_1(C_1)$ and the energetic interval a6 (4.567eV) and e₆ (4.256eV) is conditioned by the transitions $X_5(V_2)-X_1(C_1)$. The energetic interval a7 (4.877eV) and e7 (4.67eV) is caused by the transitions $X_5(V_1) - X_3(C_2)$. The electronic transitions $X_5(V_2) - X_3(C_2)$ are responsible for the energetic interval a8 (5.762eV) and e8 (5.230eV). Higher energetic transitions a9, a10, a11 and a12 are, probably, appearing in the center of Brillouin zone and are conditioned by the

transitions $\Gamma_{15}(V_1) - \Gamma_{25}(C_1)$, $\Gamma_{15}(V_2) - \Gamma_{25}(C_1)$, $\Gamma_{15}(V_3) - \Gamma_{25}(C_1)$ and $\Gamma_{15}(V_2) - \Gamma_{25}(C_2)$, respectively (table 2).

The experimentally obtained energetic intervals are studied as their energy increases. Those are interpreted (positioned) into the zonal model, also, in increasing order of the distance of interband intervals. The quantity of zones in each point of Brillouin zone, in the studied model of zonal structure, has to be twice greater than it is presented in the zonal diagram. The difference of energies of same name maxima a(e) shows this fact. The order of the revealed transitions in the Brillouin zone could change as more precise calculation methods of zones appear for these crystals, but the values of electronic transitions and their splitting will, practically, remain the same.

4. Conclusions

The experimentally measured reflective exciton spectra had been calculated at $E \| c, k \|$ a polarizations in $ZnP_2(C_{2h})$ crystals by single oscillator and multi oscillator model of dispersion correlations at different temperature. The background dielectric constant $\varepsilon_{\scriptscriptstyle B}$, the damping factor $\hbar\Gamma$, the energy of transversal exciton $\omega_{\rm T}$, the value of transversallongitudinal exciton Δ_{LT} , derived mass μ^* and the translational mass M for $\Gamma_2(z)$ C-excitons had been determined from calculations. The spectral dependencies of optical functions n, k, ε_1 and ε_2 for the C-excitonic series had been determined by calculating the excitonic reflective spectra basing on Kramers-Kronig correlations. The calculations of reflective spectra at $E \parallel c, k \parallel a$ and $E \perp c, k \parallel a$ polarizations had revealed the anisotropy of dielectric constant and showed that ε_{e} is higher at E c, k a polarization than it is at $E\perp c$, k || a polarizations as at 300K as at 2K. The temperature increase leads to the increase of damping factor γ and to the decrease of the transversallongitudinal splitting Δ_{LT} of $\Gamma_2(z)$ exciton, ω_T and exciton mass M. Derived effective masses had been calculated using the ε_b values at different polarizations and values of Rydberg constant R. $\mu^*=0.21m_0$ for $\Gamma_2(z)$ exciton of the C-series at $E \| c, k \| a$ polarizations. The effective electrons' mass m_c $=0.23m_0$ was estimated considering the value of derived effective mass ($\mu^*=0.21m_0$) and the value of translational exciton mass M=4.5m₀ for C-excitons, and the holes' effective mass $m_{V1}^*=4.27 \text{ m}_0$. The parameters $\mu^*=0.218m_0$ at $\varepsilon_{\rm B} = 8.16$ had been determines from measured transmittance spectra at E b, k a polarizations. The holes' effective mass for the given orientation of wave vector mV1=4.25m0, i.e. is, practically, matching the mass at $E \parallel c, k \parallel a$ polarizations. The holes' mass $m_{V1}^*=0.55m_0$ in case of wave vector orientation along the b axis (k||b) for A-excitonic series and $\mu^*=0.162m_0$ at $\varepsilon_{\rm B}$ =7.6. The results of this paper and the results of the published papers show that all excitonic series (C, B and A) are formed in the neighborhood of one pair of zones V_1 - C_1 . Therefore, different binding energies (Rexc.) of excitons, for excitonic series C, B and A, are conditioned by different effective holes' mass for different orientations of wave vector. The effective masses are differing on one order in

dependence on the orientation of the wave vector k. The energies of interband intervals conditioned by electronic direct transitions into Γ point from V₁, V₂ and V₃ zone towards C1 zone had been determined by studying the transmittance spectra T and d^2T/dE^2 of thin ZnP₂ crystals at 300K and 77K and E \parallel c and E \perp c polarizations, in the short wavelength region of excitonic series. The energetic intervals between the zones V₁-V₂ =92meV and V₂-V₃=143.6meV, which are split because of the crystal field and spin-orbital interaction, had been determined. Polarized reflective spectra measured in the region 6 - 10eV had been calculated using the Kramers-Kronig correlations and the optical functions n, k, ε_1 , ε_2 d² ε_1/dE^2 and d² ε_2/dE^2 had been determined for the whole measures region. The particularities of optical functions are interpreted by direct optical transitions into actual points of Brillouin zone basing on the present theoretic calculations of the zonal structure.

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