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Effect of an electric field on hydrogen-like states in crystals of monoclinic zinc diphosphide

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The effect of the electric field on hydrogen-like states in β-ZnP$_2$ is investigated. It was found that the exciton states $C_{n=1}$ in the electric field of the Schottky barrier undergo an anomalous Stark shift, and the states that form a reverse hydrogen-like series of absorption lines (IOS) are practically insensitive to the electric field. The laws governing the behavior of the exciton $X_{n=2}$ state „flammable" in an electric field in β-ZnP$_2$ have been determined.

Keywords: Schottky barrier, exciton, hydrogen-like states, anomalous Stark shift.

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1. Introduction

Wannier–Mott excitons have been found in absorption spectra of β-ZnP$_2$ crystals and studied relatively thoroughly; such excitons, due to the low crystal symmetry and withdrawal of degeneration by a crystalline field, are represented by several series of dipole-allowed and dipole-permitted optical transitions [1–3]. β-ZnP$_2$ crystals of the *n*-type of conductivity, moreover, feature a thin structure of hydrogen-like states having a relatively high oscillator strength, located from the long-wave region of the exciton spectrum in the wavelength interval of ~ 20 nm [4–6]. The most intensive lines of this series form a reverse hydrogen-like series (RHS), which in the papers [4–5] is linked with a bielectron-impurity complex (BIC), in the paper [6] with excitons bound on crystalline lattice defects. Experimental detection of a series of RHS lines in BiI$_3$ [7] has initiated the publication of theoretical papers that discuss the possibility of bielectron (bihall) interaction in crystals [8–10], as well as manifestation of photo-induced superconductivity [11]. The possibility of electron excitation to the conductivity band with a negative inert mass was showed in the paper [12]. The pattern of electric field's action on hydrogen-like states in the region of RHS manifestation spectrum is important from the viewpoint of construction of a model of such interactions. The study of exciton singlet and triplet states in an electric field is also of certain interest due to the anomalous behavior of Stark shifts of exciton states, found on $A_{n=1}$ state in CdS [13]. The Stark shift, in compliance with the results of this paper, undergoes significant deviations from the square (by electric field) law and changes its sign in the pre-ionization field. Theoretical bases for this effect for a hydrogen atom in an electric field are given in [14].

Electric field impact on exciton states $C_{n=1}$ — series of hydrogen-like states in β-ZnP$_2$ has been studied in [15]. Long-wave shift of the exciton contour, which acquires the antidispersion form in limit electric fields, is observed in the electric field as it increases. More detailed studies have showed that crystals, where exciton spectra manifest themselves without a thin structure, have the hole type of conductivity, with a thin structure and RHS in spectra, electron [16]. Crystals with the hole type of conductivity in thin layers are characterized by a space-charge-limited mechanism of current passage, in case of which electric field intensity virtually linearly increases from zero on the anode to the maximum values on the cathode. Thereat, electric field magnitude and distribution in the cathode region depend on illumination with probing and background radiation. An electric field of the necessary magnitude for studying the exciton states on „thick" crystals is difficult to create due to the ultimate high values of voltages of traps' full filling. Study of exciton states β-ZnP$_2$ in the electric field of a Schottky barrier according to reflection spectra is also hindered due to partial overlapping of exciton absorption spectra and RHS spectra.

This paper presents the results of studies of hydrogen-like states in the region of the absorption edge β-ZnP$_2$ in the electric field of a Schottky barrier. The studies have been performed on ITO-β-ZnP$_2$ structures according to spectral distribution of photoinduced current at the temperature of 80 K. The main characteristics of such structures, including those at low temperatures, are given in the papers [16,17].

2. Results and discussion

Figure 1 shows the spectral characteristics of the photoinduced current for the ITO-β-ZnP$_2$ structure at reverse shift on the barrier in $\mathbf{E} \parallel \mathbf{c}$ polarization with normal incidence of radiation onto the plane (010).

Value of photoinduced current in Schottky barriers when thickness of the space charge layer (space charge region) W

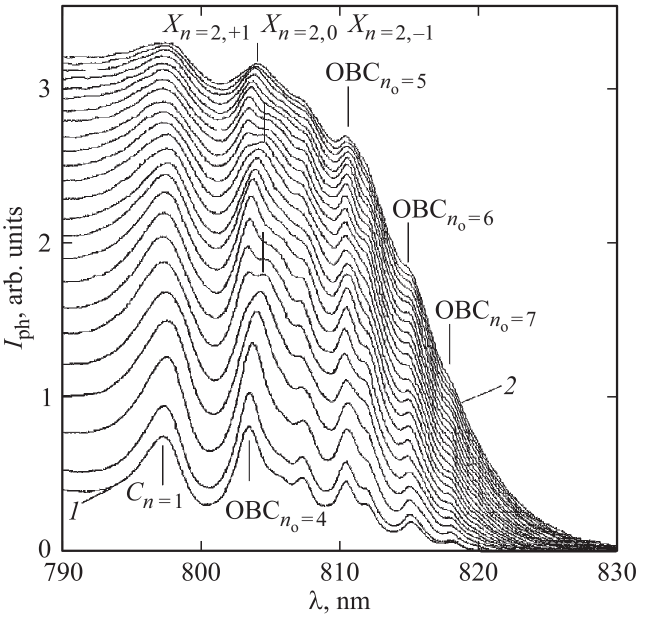

Figure 1. Spectral dependences of photoinduced current at reverse shift of a Schottky barrier, U, V: *1* — 0, *2* — 4.2 (interval between spectral dependences is 0.2 V).

is much lower than the L crystal thickness and the condition $\alpha W \ll 1$ is met, is described by the expression [18]:

$$I_{\mathrm{ph}} \propto (1-R)\,\alpha\,\frac{(L+W)}{(1+\alpha L_p)}, \qquad (1)$$

where R is the light reflection factor, W is the space charge region width, α is the light absorption factor.

Expression (1) for photoinduced current was obtained without taking into account the influence of surface electron states of the contact. Influence on the electric field absorption factor is also neglected here. The contours of the lines of resonance state photoinduced current reflect the spectral distribution of the absorption factor, since photoinduced current is proportional to the absorption factor, while space charge region width and electric field intensity depend on applied voltage. In this case, it is possible to measure the energy characteristics of the absorption lines from the barrier electric field intensity. In zinc diphosphide, in the region of the fundamental absorption edge, light absorption factor α in the maxima for the lines of exciton transitions of the B-series does not exceed $780\,\mathrm{cm}^{-1}$ respectively [2], on the most intensive BIC lines — $75\,\mathrm{cm}^{-1}$ [9] in $\mathbf{E}\parallel\mathbf{c}$ polarization. With SCR width of $\sim 1\,\mu$m, the above-mentioned conditions are met rather well. Barrier electric field intensity from applied voltage is determined by the following dependence [16]:

$$F_m^2 = \varepsilon\varepsilon_0\,\frac{2(\varphi_k-\varphi_d-U)}{qN_d}, \qquad (2)$$

where: N_d is the concentration of ionized donors in the barrier SCR, φ_k is the height of potential barrier, φ_d is the donor occurrence depth, ε is the relative dielectric constant of the semiconductor. It follows from this expression that, if external offset of a barrier is absent, electric field intensity on the SCR boundary with metal reaches considerable values ($\sim 10^4$ V/cm).

The contours of the lines of resonance state photoinduced current reflect a spectral distribution of the absorption factor in β-ZnP$_2$ and significantly widened. The photoinduced current value is smoothed out due to a change in generation depth of nonequilibrium charge carriers upon a change of the absorption factor. This results in a blurred photoinduced current spectrum at relatively small reverse offsets and a weak dependence of photoinduced current value in spectral regions having large absorption factors and at great reverse voltages. The photoinduced current band, corresponding the singlet state $C_{n=1}$ of the exciton in all the studied structures in relatively weak electric fields up to $\sim 2\cdot 10^2$ V/cm, widens and shifts into the long-wave region of the spectrum (Fig. 2). For large fields, the behavior of this band is identical to the behavior of the 1 s state of the exciton in CdS [12], the maximum moves to the short-wave region as the field grows. In our case, upon subsequent voltage increase and growth of the electric field in the barrier, the effect of successive long-wave and short-wave shift of the photoinduced current maximum repeats itself. This effect is predicted in the theoretical paper [14]. Moreover, as field intensity in the barrier increases, the short-wave wing of the photoinduced current band increases due to band overlapping with zone adsorption, the edge of which shifts to the long-wave region due to the Franz–Keldysh zone effect.

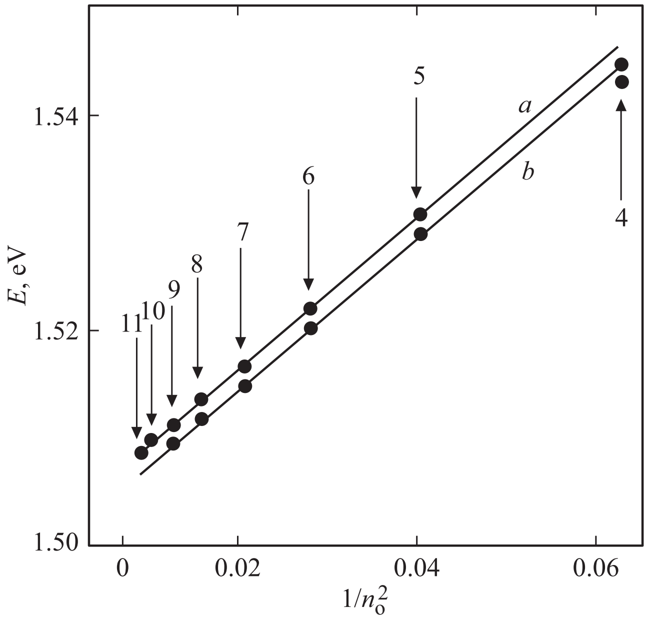

Figure 2. Dependence of RHS transition energies on $1/n_o^2$ for two ITO-ZnP$_2$(C_{2h}^5) structures (plotted according to crystal transmittance spectra). Concentration of free charge carriers in structures № 3 and № 4: *a*) — $10^{20}\,\mathrm{m}^{-3}$, *b*) — $10^{21}\,\mathrm{m}^3$.

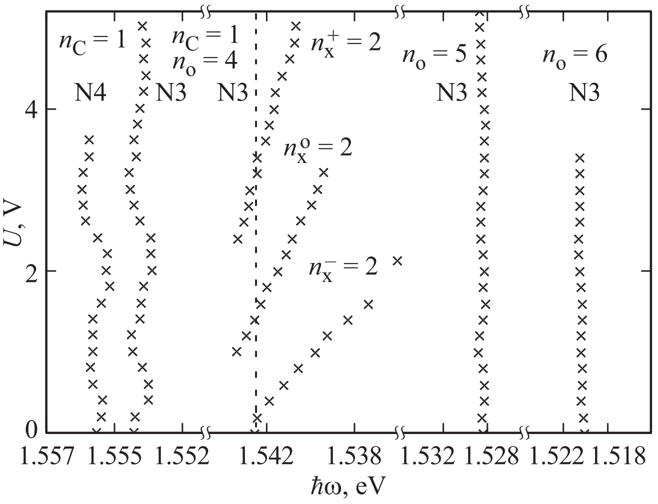

Figure 3. Field dependences of exciton states and extreme values of RHS.

Under the voltages of $|U| \geq -0.6$ V and the corresponding electric field intensities, the spectral region of band RHS$_{n_o=4}$ has bands with different spectral and amplitude shifts dependent on applied voltage with the behavior typical for the quadratic Stark effect (Fig. 3, bands $X^+_{n=2}$, $X^o_{n=2}$, $X^-_{n=2}$). When extrapolated to the zero field, the maxima of these bands converge to the energy of 1.547 eV, which does not match the energy of the band RHS$_{n_o=4}$ (1.544 eV) and energies of exciton states in absorption spectra in the field absence [2,3]. The nearest exciton state corresponds to the energy of $B_{n=1}$. As shown in [2], the B-series is conditioned by nS (states of an ortoexciton, split off by short-range exchange interaction). The state $B_{n=1}$ in photoinduced current spectra is not observed due to a band $C_{n=1}$ of greater intensity in the polarizations $\mathbf{E} \parallel \mathbf{c}$ and $\mathbf{E} \perp \mathbf{c}$. In the $\mathbf{E} \perp \mathbf{c}$ polarization, the prohibition of transitions to the singlet $C_{n=1}$ exciton state in an electric field is apparently partially removed. In photoeffects, the photopleochroism coefficient determined as per the commonly accepted formulas [19] is by many orders lesser than the photopleochroism coefficient determined on the basis of absorption. The energy of observed excitation is apart from $C_{n=1}$ and $B_{n=1}$ by 12 and 10 meV. The coefficients in field dependences of band energies for the states $X^+_{n=2}$, $X^o_{n=2}$, X^-, split in the electric field, are $(0.47, 0.82, 2.19) \cdot 10^{-17}\,\text{meV} \cdot \mu\text{m}^2/\text{V}^2$, respectively. With voltages across the barrier $|U| \leq -0.6$ V, these bands $X_{n=+2}$, $X_{n=0}$, $X_{n=-2}$ do not manifest themselves due to the greater intensity of band RHS$_{n_o=4}$, the position and intensity of which do not change upon a change in electric field intensity. In the spectra given in [2], at the temperatures of 2 K, the X — line in crystals, called „impure" by the article authors, is found on the long-wave side of the $B_{n=1}$ (absorption line). However, the nature of this absorption band is related to crystal defects and is not discussed. It can be supposed that the X bands are related to the excited state of a bound exciton on lattice defects, the ground state of which is in the RHS absorption region.

The bands $n_o = 4-8$, manifesting themselves in these spectra, stay within the reverse hydrogen-like serial dependence noted in [4] (Fig. 2). Field-induced shifts of the maxima of these bands do not exceed the limits of their determination errors. The bends at the bands $n_o = 4$ and 5 should be classified as positive hydrogen-like series of absorption lines (PHS), taking place near each RHS line [1]. Screening results in a shift of the whole spectrum of exciton states for crystals having different charge carrier concentrations, thereat the states $C_{n=1}$ of an exciton series are shifted by 1.4 meV, RHS by 2.2 meV.

X is the exciton line, its split states in the electric field and RHS lines manifest themselves in $\mathbf{E} \parallel \mathbf{c}$ polarizations and in $\mathbf{E} \perp \mathbf{c}$ polarization. Intensity of photoinduced current lines of the whole spectrum in the $\mathbf{E} \perp \mathbf{c}$ polarization is lesser than in the $\mathbf{E} \parallel \mathbf{c}$ polarization. The behavior of exciton states and states of a BIC-complex in the $\mathbf{E} \perp \mathbf{c}$ and $\mathbf{E} \parallel \mathbf{c}$ polarizations have a similar pattern, however, the photoinduced current spectra are shifted in relation to each other by 0.2 meV.

Correlations with the aforesaid dependencies of photoinduced current bands in an electric field are observed in the reflection spectra in the barrier's electric field (Fig. 4).

The peculiarities in the reflection spectra at the wavelengths of $\lambda > 800$ nm are related to RHS resonances, at the wavelengths of $\lambda < 800$ nm they are related to the state $C_{n=1}$ of the exciton. A reflection of the outline of RHS$_{n_o=4}$ is superimposed on the exciton reflection contour $C_{n=1}$. Under positive voltages on the barrier, the spectrum shape

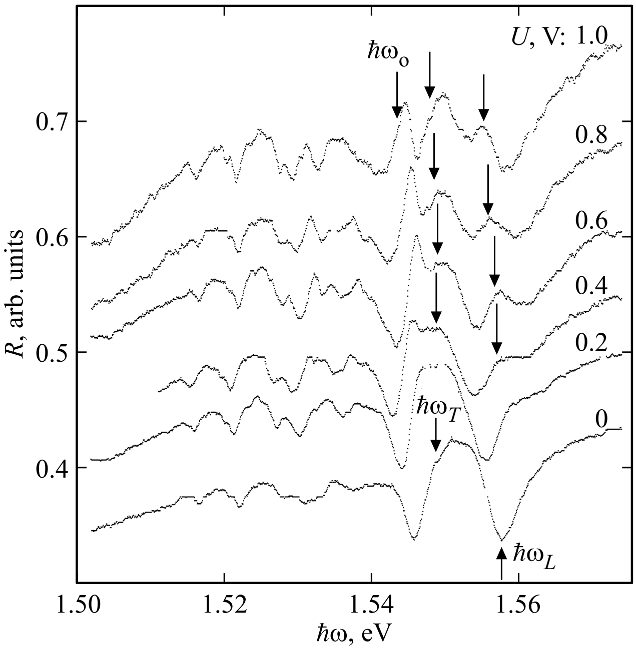

Figure 4. Relative spectra of exciton reflection depending on photon energy at different values of reverse voltage applied to the ITO-ZnP$_2$ structure (80 K).

changes insignificantly, $\hbar\omega_L$ shifts to the short-wave region of the spectrum by 0.2 meV. A spike structure manifests itself under the voltages of $U > 0.4$ V at the energy of $\hbar\omega_L$; the growth of this structure with increase of the voltage and electric field of the barrier converts the reflection contour into an antidispersion form. As barrier field intensity increases, there is a cyclic change in the reflection spectrum shape related to the presence of a „dead“ layer. If reverse voltages are great, the spectrum peculiarities diffuse, which is related to the dissociation of states and superposition of reflections of states having different field coefficients. A mathematical description of spectra in a multi-oscillator model is problematic due to a large number of variables and absence of data on field dissociation of the spectrum components.

The whole spectrum of photoinduced current resonance frequencies and the associated values in the reflection spectra at identical applied barrier shifts are offset by 2.7 meV relative to each other, which can be due to the fact that the reflection spectra were taken at the maximum value of the electric field on the contact boundary, while the photoinduced current spectra were taken at a certain „average“ field.

3. Conclusion

The main peculiarities of light absorption in monocline zinc diphosphide manifest themselves in the photoinduced current spectra for ITO-ZnP$_2$(C^5_{2h}) structures at low temperatures. Singlet states in an electric field undergo an anomalous shift, found for the first time in [11] and typical for atomic spectra of hydrogen in the electric field. The found oscillations in the shift of position $C_{n=1}$ of a singlet exciton in the barrier field agree with the theory for a hydrogen atom in the electric field. The exciton $X_{n=2}$ „ignites“ in the electric field of the Schottky barrier, its intensity increases to the light absorption level of the most intensive line in RHS and is split in compliance with the concepts of hydrogen-like states. The line shift in the fields of (10^4-10^6) V/cm meets the quadratic Stark effect. The nature of this absorption band is unknown and its determination requires additional studies. The states that form RHS behave as an integral unit; the electric field does not considerably affect their energy position in spectra. Hydrogen-like interaction of quasiparticles, which form RHS with ionized donors, is diffused in the electric field due to the low bond energy, which on the whole is in favor of the model suggested in [5]. An important consequence from the presented research is the confirmation of the theoretical analysis and argumentation of the experimentally observed exciton state series in ZnP$_2$ presented in a number of papers [1–5].

Conflict of interest

The authors declare that they have no conflict of interest.

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