LASER MODULATION SPECTROSCOPY STUDIES OF THE ENERGY STATE STRUCTURE OF α-ZnP_2:Ge SINGLE CRYSTALS

I.I. PATSKUN, N.YU. PAVLOVA

M.P. Dragomanov National Pedagogical University
(9, Pirogov Str., Kyiv 01030, Ukraine; e-mail: shev@ipms.kiev.ua)

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The results of researches of the impurity and band states of current carriers in α-ZnP_2:Ge are reported. Using the laser modulation spectroscopy, 14 critical points of the second kind have been found in the Brillouin zone. Their energy positions have been determined.

Zinc diphosphide is a perspective material for nonlinear optics and semiconducting optoelectronics. An opportunity to obtain the inversion of the conductivity type, a rather large energy gap, and anisotropy of optical properties with a high birefringence allow this substance to be used for creating the elements of microelectronics, diode structures with switching elements, photodetectors of laser emission, frequency converters, extenders of ruby laser pulses, shape-preserving extenders of laser pulses, fast-response photoresistors, and so on. At the same time, the actual energy structure of ZnP_2 has not been studied yet sufficiently well.

The investigated crystals were grown using the sublimation in a two-zone oven. Doping Ge was inserted into the initial stoichiometric batch. In this work, the variation of the absorption coefficient of the probing radiation induced by a laser pulse is studied. To generate the probing radiation, a xenon flash tube with a duration of glowing equal to 200 μs was used. As a source of the modulating radiation, we also used an Nd:YAG laser with Q-switching possessing the following characteristics: a 31-ns pulse duration and a 1.17-eV energy of quanta. The orientational characteristics of the radiation and the crystal satisfied the condition $\vec{q}_1 \parallel \vec{q}_2 \parallel \vec{c} \perp \vec{e}_1 \parallel \vec{e}_2$, where c is the ort directed along the optical axis of the crystal, and $\vec{q}_i$ and $\vec{e}_i$ are the wave vector and the polarization ort of the radiation of the i-th kind, respectively (hereafter, the subscript $i = 1$ denotes the laser modulation radiation, while $i = 2$ the probing one emitted by the xenon tube). The details of the installation used for laser modulation spectroscopy of semiconductors were described in work [1]. The variation of the absorption coefficient $\Delta K(\omega_2, t)$ of the probing radiation ($\hbar\omega_2$) stimulated by the laser radiation ($\hbar\omega_1$) was determined by the formula [2]

$$\Delta K(\omega_2, t) = -\frac{1}{z} \ln\left\{1 - \frac{\Delta H(\omega_2, t)}{H_0(\omega_2)}\right\},$$

where $H_0(\omega_2)$ is the probing-radiation-induced deviation of the electron beam (on the oscillograph screen) from the zero-level position at the initial moment of the laser pulse emission ($t_0 = 0$), $\Delta H(\omega_2, t)$ is the laser-emission-induced deviation of the electron beam from the $H_0(\omega_2)$ level at $t > t_0$, and $z = 2.1$ mm is the thickness of the specimen.

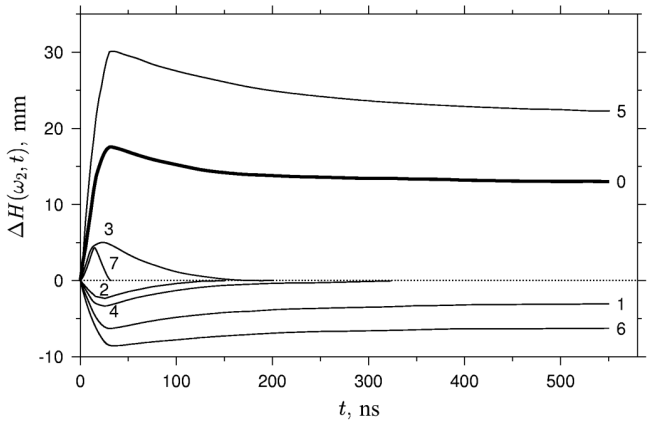

Fig. 1. Oscillogram $\Delta H(\omega_2, t)$ at $\hbar\omega_2 = 1.72$ eV and $I_1 = 10.9$ MW/cm^2 (curve *0*). Curves *1* to *7* are the components of curve *0*

In Fig. 1, the oscillogram $\Delta H(\omega_2, t)$, obtained at $\hbar\omega_2 = 1,72$ eV and provided the maximal intensity of the laser pulse $I_1 = 10$ MW/cm^2, is depicted (curve *0*). The same figure also exhibits the components of this dependence; the method, which allowed us to determine those components, is described below.

We studied the dependence of the variation of the absorption coefficient of probing radiation $\Delta K(\omega_2, t)$ on the intensity of the laser emission radiation I_1 (the intensity dependence) with a step of 0.01−0.05 eV within the $\hbar\omega_2$ interval between 1.2 and 2.1 eV. Measurements were carried out at a moment t that was 35 ns distant

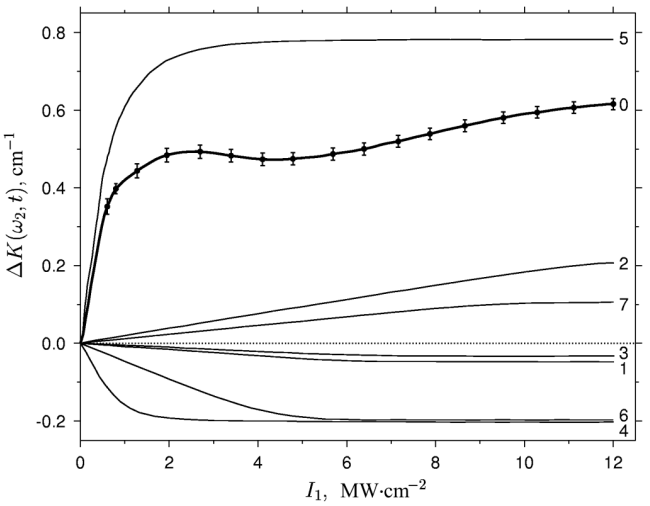

Fig. 2. Dependence of the variation of the absorption coefficient of probing radiation $\Delta K(\omega_2, t)$ on the intensity of laser radiation I_1 at the moment $t = 35$ ns (curve *0*). Curve *0* was obtained at $\hbar\omega_2 = 1.88$ eV. Curves *1* to *7* are the components of curve *0*

from the start of a laser pulse. In Fig. 2, the intensity dependence obtained at $\hbar\omega_2 = 1.88$ eV is shown (curve *0*), as well as the components of this dependence.

In order to obtain the dependence of the variation of the absorption coefficient of probing radiation $\Delta K(\omega_2, t)$ that was caused by a laser pulse on the energy of quanta of this radiation (the spectral dependence), measurement were carried on with a step of 0.005—0.02 eV within the $\hbar\omega_2$ interval between 1.2 and 2.1 eV. The spectral dependence, obtained at the moment $t = 35$ ns and provided the intensity $I_1 = 10$ MW/cm^2, is shown in Fig. 3 (curve *0*). The intensity and spectral dependences were plotted point by point, each of the points being a result of the averaging over tens of records. The confidence intervals shown in Figs. 2 and 3 correspond to the confidence probability of 0.8.

The intensity dependence were decomposed into exponential-like components of the form $A[1 - \exp(-BI_1)]$, where $B > 0$. The analysis of all the intensity dependences obtained testifies to that they consist of six to eight exponential-like components (except for the spectral bands with the maxima at $\hbar\omega_2 = 1.40$, 1.49, 1.54, 1.63, and 1.93 eV).

Using the intensity components *1—8*, we plotted the components of the spectral dependence (Fig. 3). The dotted curve corresponds to the sum of these components, and the additional absorption bands (a difference between curve *0* and the dotted curve) are exposed in the top margin of the figure. Curve *0* form Fig. 1 was decomposed making use of the components

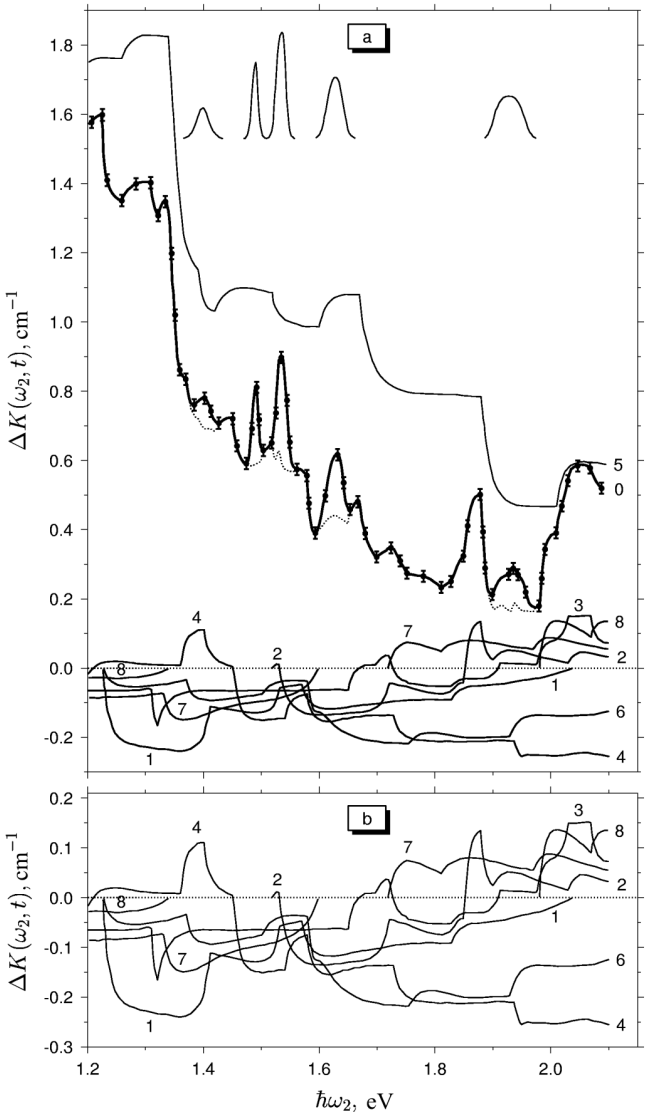

Fig. 3. Dependence of the variation of the absorption coefficient of probing radiation $\Delta K(\omega_2, t)$ on the energy of quanta of this radiation (curve *0*) at $t = 35$ ns and $I_1 = 10$ MW/cm^2. Curves *1* to *8* are the components of curve *0*. The dashed curve corresponds to curve *0* with all singularities removed. In the top margin of panel *a*, the profiles of these singularities are shown. Panel *b* exposes components *1* to *4* and *6* to *8* scaled up

of the intensity dependences measured at $t = 10$, 15, 20, 25, 30, 35, 40, 50, 65, 80, 100, 150, 220, 300, 400, and 575 ns.

The fact that components *1—8* of the intensity dependences are revealed in a wide spectral range of measurements evidences for the relation of those

components to the electron transitions between the deep energy levels of defects (the impurity centers) and the energy levels in the valence and conduction bands.

The coherent two-photon absorption is absent at $t = 31$ ns, because $\Delta K(\omega_2, t) = \Delta K^{(1)}(\omega_2, t)$ after the action of a laser pulse, belongs to a single-photon resonance only, and is caused only by the population redistribution.

The complicated structure of the spectral components $f = 1 \div 8$ (Fig. 3) is a result of their proportionality to the electron density of states in the bands. The influence of the transition matrix elements on the peculiarities of this structure is not important [3]. According to work [1], the variation of the coefficient of single-photon absorption $\Delta K^{(1)}(\omega_2, t)$, taking the transitions "the valence band—f-centers ($f = 1 \div 8$)"and "f-centers—the conduction band"into account, is determined by the expression

$$\Delta K_f^{(1)}(\omega_2, t, I_1) = A(\omega_2, t)(1 - e^{-\frac{\sigma'_{Vf}+\sigma'_{fC}}{2\hbar\omega_1} I_1 \cdot t_f^3}), \qquad (1)$$

where

$$A(\omega_2, t) = N_f(\sigma''_{Vf} + \sigma''_{fC})\Big[\rho_f(0) - \frac{\sigma'_{vf}}{\sigma'_{Vf} + \sigma'_{fC}}\Big]\eta_f, \quad (2)$$

N_f is the concentration of f-centers; σ'_{Vf} and σ'_{fC} are the cross-sections of laser radiation absorption at the transitions "the valence band—f-centers"and "f-centers–the conduction band", respectively; σ''_{Vf} and σ''_{fC} are the cross-sections of probing radiation absorption at these transitions; $\rho_f(0)$ is the population of f-centers at the moment $t_0 = 0$, $t_f^{\rm sb}$ is the time coordinate of a point, where the f-component of the $\Delta H(\omega_2, t)$ oscillogram start to deviate from the linear section, and $\eta_f = \Delta H_f(\omega_2, t)/\Delta H_f(\omega_2, t_f^{\rm sb})$. The superscript of ΔK denotes the single-photon nature of the corresponding absorption. From Eq. (1), taking into account that

$$\frac{\Delta K_f^{(1)}(\omega_2, t, I_1^{\rm mb})}{A(\omega_2, t)} = 0.865,$$

at the point of the maximal bend of the f-component, we obtain the following relationship:

$$\sigma'_{Vf} + \sigma'_{fC} = \frac{7.49 \cdot 10^{-19}\,\text{Дж}}{I_{1f}^{\text{м·эг}} \cdot t_f^3}. \qquad (3)$$

Van Hove singular points of the M_0-type will manifest themselves in the $\Delta K_f^{(1)}(\omega_2, t)$ spectra as a step up or a step down towards the short-wave range, while the singular points of the M_3-type also as a step up or a step down but towards long waves [4]. The position of the initial edge of such a step in the plot of the spectral f-component corresponds to the energy distance between the corresponding singular point in the band and the impurity energy level in the energy gap. In order to determine the energy positions of van Hove singularities in the bands, one should know the energy depth of an arbitrary impurity level located deeply in the gap. In works [6, 7], an impurity level e has been revealed at a depth of $E_C - 1.17$ eV. This level is located $V_2 - 1.36$ eV from the top of the second valence subband. Component *5* of the spectral dependences revealed the step edge at 1.35 eV which corresponds to the depopulation of the corresponding centers by a laser pulse. Therefore, component *5* is caused by the population change of the centers which possess energy levels in the energy gap at a depth of $E_C - 1.17$ eV.

Knowing the energy depth of e-centers and analyzing the structure of component *5*, we can determine the energy locations of van Hove singularities in the bands as well as their types. The initial edges of the steps at $\hbar\omega_2 = 1.34$, 1.39, 1.52, 1.67, and 1.88 eV in component *5* correspond to critical points of the M_0-type located in the valence band at distances of 1.34, 1.39, 1.52, 1.67, and 1.88 eV, respectively, from level *5;* and the initial edges of the steps at $\hbar\omega_2 = 1.26$, 1.42, 1.60, and 2.01 eV correspond to critical points of the M_0-type located in the conduction band. Having compared the structures of the spectral components *1–8* with the energy depths of critical points of the first kind in the bands, which had been determined by us, we found the positions of the energy levels of centers *1–8* in the energy gap. This allowed us to reveal additional critical points in the electron density of states in the bands. The results of the analysis carried out for the spectral components are quoted in Tables 1, 2, and 3.

T a b l e 1. Energy levels of impurity centers in the energy gap

Level	$E - E_V$, eV	$E_C - E$, eV
1	0.38	1.82
2	0.69	1.52
3	0.88	1.32
4	1.11	1.07
5	1.17	1.01
6	1.50	0.71
7	1.72	0.46
8	1.98	0.21

N o t a t i o n s: E is the level energy, E_V the energy of the top of the valence band, and E_C the energy of the bottom of the conduction band.

T a b l e 2. Singular points in the conduction band

$E - E_C$, eV	Singularity type	SPBZ
1.19	M_0	Z
1.15	M_3	Γ
1.03	M_3	R
0.84	M_0	M
0.43	M_0	Z
0.25	M_0	Γ
0.09	M_0	Z
0.00	M_0	Γ

N o t a t i o n s: E is the singularity point energy, E_C the energy of the bottom of the conduction band, and SPBZ stands for the singular point in the Brillouin zone.

T a b l e 3. Singular points in the valence band

$E_V - E$, eV	Singularity type	SPBZ
0.00	M_0	Γ
0.33	M_0	Γ
0.38	M_0	Γ
0.51	M_0	
0.66	M_0	
0.87	M_0	

N o t a t i o n s: E is the singularity point energy, E_V the energy of the top of the valence band, and SPBZ stands for the singularity point in the Brillouin zone.

The energy levels of impurity centers in the energy gap are listed in Table 1. The data concerning the energy levels, which correspond to van Hove singularities and were revealed in the conduction or the valence band, are presented in Table 2 or 3, respectively. The same tables also contain information concerning the symmetry points in the Brillouin zone, which may include the van Hove singularities. The symmetry points in the Brillouin zone, which correspond to critical points of the first kind, agree with the band structure calculated in work [8].

In accordance with Fig. 1, $t_f^{\rm sb} = 22$ ns. The maximal bends of the exponential-like components correspond to $I_1^{\rm mb} = 6.2$, 12.3, 6.7, 1.4, 1.5, 4.8, 9.6, and 3.4 MW/cm^2 (curves *1* to *8*, respectively). (The ordinate of the point of the maximal component bend was taken as approximately 0.865 times the asymptotic value of the relevant curve.) Using formula (3), we obtain (in units of 10^{-18} cm^2):

$$\sigma'_{V8} = 5.0, \quad \sigma'_{V7} = 1.8, \quad \sigma'_{V6} = 3.6,$$

$$\sigma'_{V5} + \sigma'_{5C} = 8.3, \quad \sigma'_{V4} + \sigma'_{4C} = 1.25,$$

$$\sigma'_{3C} = 2.5, \quad \sigma'_{2C} = 1.4, \quad \sigma'_{1C} = 2.8.$$

Thus, in this work, we have demonstrated an opportunity to use effectively the method of laser modulation spectroscopy of semiconductors to study the features of the band structure of α-ZnP_2:Ge. The researches carried out have allowed us to determine the energy positions of critical points of the M_0 and M_3 types located in the valence and conduction bands, as well as to calculate the absorption cross-section of laser radiation at transitions between the impurity centers and the bands.

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ДОСЛІДЖЕННЯ СТРУКТУРИ ЕНЕРГЕТИЧНИХ СТАНІВ МОНОКРИСТАЛІВ α-ZnP_2:Ge МЕТОДАМИ ЛАЗЕРНО-МОДУЛЯЦІЙНОЇ СПЕКТРОСКОПІЇ

І.І. Пацкун, *Н.Ю. Павлова*

Р е з ю м е

Представлено результати дослідження домішкових та зонних станів носіїв в α-ZnP_2:Ge. Методом лазерно-модуляційної спектроскопії в зоні Бріллюена виявлено 14 критичних точок другого роду. Визначено їх енергетичне положення.