

**Erratum:** The Editorial Board of the journal «Semiconductor Physics, Quantum Electronics and Optoelectronics» apologizes to authors of the paper «Raman scattering of light in biaxial monocline  $\beta$ -ZnP<sub>2</sub> crystals» published in the vol. 4, №3, p. 207-209, and readers of our journal for the error committed when using the uncorrected prn-file of this paper during publication. This mistake is corrected in this issue.

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## Raman scattering of light in biaxial monocline $\beta$ -ZnP<sub>2</sub> crystals

V.O. Gubanov<sup>1</sup>, V.D. Kulakovs'kij<sup>2</sup>, R.A. Poveda<sup>3</sup>, Z.Z. Yanchuk<sup>1</sup>

<sup>1</sup> Taras Shevchenko National University, Kyiv, Ukraine;

<sup>2</sup> Institute for Solid State Physics, Chernogolovka, Russia;

<sup>3</sup> Pedagogical University, Kam'yanets'-Podil's'kiy,

E-mail: poveda@kp.km.ua

**Abstract.** In this paper we represent for the first time observed experimental data on non-resonant Raman scattering in a plate of  $\beta$ -ZnP<sub>2</sub>. The high-frequency part of RS spectra KP  $\beta$ -ZnP<sub>2</sub> is determined by oscillations of sites in *P*-atom spirals considered as building units of the  $\beta$ -ZnP<sub>2</sub> lattice. These spirals, as to their oscillatory properties, are very similar to infinite *P*-atom spirals in  $\alpha$ -ZnP<sub>2</sub>. Thus, the most intensive RS spectral band 433.0 cm<sup>-1</sup> responds to main inphase quasivalence oscillations for all four translations of non-equivalent sites in *P*-spirals while bands 448.4; 458.2; 466.3 cm<sup>-1</sup> to quasivalence out-of-phase excited oscillations orthogonal to the main ones.

**Keywords:**  $\beta$ -ZnP<sub>2</sub>, non-resonant Raman scattering, irreducible representations.

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Biaxial crystals of «black» structural modification of zinc diphosphid,  $\beta$ -ZnP<sub>2</sub>, are widely researched as direct band semiconductors that have very clearly pronounced peculiarities with a disjointed fine structure polyserial ruled absorption spectra and luminescence of Wannier-Mott free excitons [1-3], that, in addition, at rather low levels of energy bind into biexciton molecules [4,5] with the further tendency to their condensation. Unfortunately, up to date, in these chips, the energy spectrum of phonon states is insufficiently researched, although it largely influences exciton processes of light absorption and exciton recombination. Information on these states is possible to be received first of all from spectra of infrared (IR) absorption and spectra of non-resonant or resonant Raman scattering of light. The availability of inversion as an element of a crystal lattice symmetry results in the alternate prohibition, in connection with which phonons, even by their symmetry, can be observed only in Raman spectrum. The technical complication to research, for example, non-resonant Raman scattering of light on phonons in  $\beta$ -ZnP<sub>2</sub> chips is the small value of a forbidden gap that makes only 1.6026 eV at the temperature of 1.6 K. It demands application of an infrared laser for observation non-resonant Raman scattering of light and considerably hampers registration of its spectra.

In this work, for the first time, we show results of experimental investigations of non-resonant Raman scattering spectra in  $\beta$ -ZnP<sub>2</sub> samples. The single crystals of  $\beta$ -ZnP<sub>2</sub> obtained on the technological base of the Experimental Physics Physical Department of the T. Shevchenko Kiev National University were researched. The non-resonant Raman scattering were driven by radiation of the continuous titan-sapphire laser with the wavelength 852.7 nm. As a detector of a scattered radiation, the matrix of charge-coupled devices (CCD) cooled down to 70 K was used. Spectra registered using of a spectrometer Ramanor (Mole 1000) with a half-width of an apparatus function smaller than 0.5 cm<sup>-1</sup>. The direction radiation excitation was always perpendicular to that of registration.

Symmetry of the  $\beta$ -ZnP<sub>2</sub> crystal lattice, which is related to the monocline system and singoniya, is featured by a space group P12<sub>1</sub>/c1 or in abbreviated form P2<sub>1</sub>/c (*C*<sup>5</sup><sub>2h</sub>), and crystalline class 2/m (*C*<sub>2h</sub>). The unit cell contains 24 atoms that belong to 8 formula unit of ZnP<sub>2</sub> composition. As easily seen from Table 1, where the irreducible representations of the point group 2/m are shown, and the selection rules for two orientations of the reference axis *c*<sub>2</sub> (for plates of  $\beta$ -ZnP<sub>2</sub> are accepted for using a crystallographic orientation conventional for monocline chips with *c*<sub>2</sub>||*y*), 72 fundamental vibration

**Table 1.** Irreducible representations of the point group  $2/m$ , selection rule and classification of fundamental oscillations of  $\beta$ -ZnP<sub>2</sub>.

$2/m(C_{2h})$	$e$	$c_2$	$i$	$\sigma_h$	$n_{vib}$	$n_{ac}$	$n_{opt}$	$c_2  z$	$c_2  y$
$\Gamma_1^+$	1	1	1	1	18	0	18	$\alpha_{zz}, \alpha_{xx}, \alpha_{yy}, \alpha_{xy}; ia$	$\alpha_{zz}, \alpha_{xx}, \alpha_{yy}, \alpha_{zy}; ia$
$\Gamma_1^-$	1	1	-1	-1	18	1	17	$\mu_z; v$	$\mu_y; v$
$\Gamma_2^-$	1	-1	1	-1	18	0	18	$\alpha_{zx}, \alpha_{zy}; ia$	$\alpha_{zy}, \alpha_{xy}; ia$
$\Gamma_2^+$	1	-1	-1	1	18	2	16	$\mu_x, \mu_y; v$	$\mu_z, \mu_y; v$
$\chi_{\Gamma_{vib}}$	72	0	0	0					
$\chi_{\Gamma_{ac}}$	3	-1	-3	1					

modes (related to the centre of a Brillouin zone at the point  $\Gamma$ ) are expressed through irreducible representations of the group  $2/m$ :

$$\Gamma_{vib} = 18\Gamma_1^+ + 18\Gamma_1^- + 18\Gamma_2^+ + 18\Gamma_2^-.$$

Among them selected are 3 acoustic:

$$\Gamma_{ac} = \Gamma_1^- + 2\Gamma_2^-$$

and 69 optical modes:

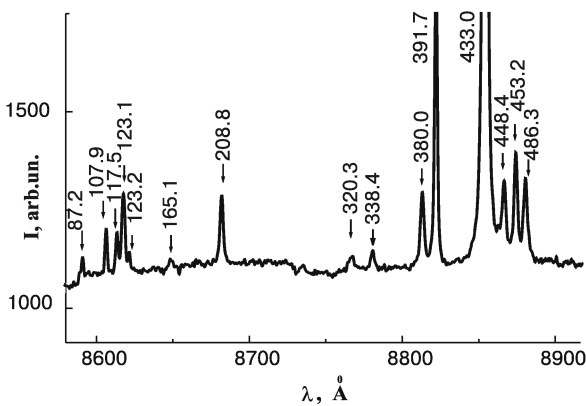
$$\Gamma_{opt} = 18\Gamma_1^+ + 17\Gamma_1^- + 18\Gamma_2^+ + 16\Gamma_2^-.$$

33 odd optical modes are split into modes  $17\Gamma_1^-$  and  $16\Gamma_2^-$  in spectra of infrared absorption, while 36 pair optical modes are split into modes  $18\Gamma_1^+$  and  $18\Gamma_2^+$  in Raman scattering.

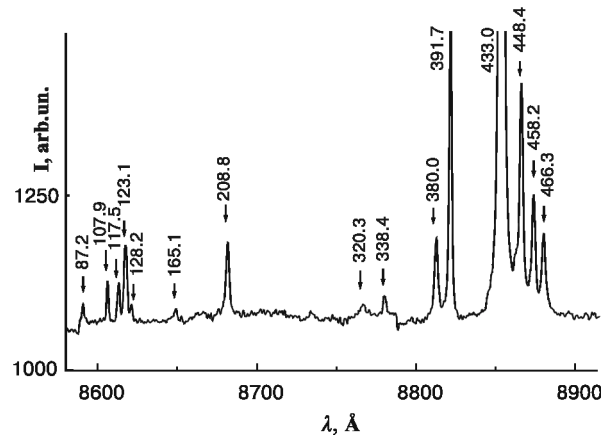
In Figs 1, 2 shown is the experimentally obtained non-resonant Raman scattering spectrum registered at the temperature of the sample  $T_0 = 293$  K in polarizations  $z(xy)x$  and  $z(x(z+y))x$ , accordingly.

It is important to mark that spectral intervals of Raman frequencies in  $\beta$ -ZnP<sub>2</sub> and  $\alpha$ -ZnP<sub>2</sub> coincide. Frequencies of the high-frequency part of spectra practically coincide, too. In  $\alpha$ -ZnP<sub>2</sub> samples these frequencies respond to oscillations of spirals composed of phosphorus ( $P$ ) [6]. The numerical coincidence of high-frequency sites of phonon spectra and modifications of zinc diphosphid testifies that the high-frequency part of the  $\beta$ -ZnP<sub>2</sub> spectrum is determined by oscillations of sites of spirals composed of  $P$  atoms as building blocks of the  $\beta$ -ZnP<sub>2</sub> lattice, which is very similar to infinite spirals consisting of  $P$  atoms in  $\alpha$ -ZnP<sub>2</sub> by their oscillatory properties. Thus, the most intensive spectral band  $433.0$  cm<sup>-1</sup> responds to main inphase quasivalence oscillations of  $P$  atoms for all four translations of non-equivalent sites of  $P$ -spirals and bands  $448.4; 458.2; 466.3$  cm<sup>-1</sup> quasivalence, orthogonal to the main one, out-of-phase excited oscillations.

It is interesting that the polarization dependence in these spectra was detected only for the band  $448.4$  cm<sup>-1</sup>. Beyond any doubts, it is due to dispersion of a phonons with the symmetry  $\Gamma_2^+$ . In  $z(xz)x$  polarization this band remains alone in its Raman spectrum, but scattering for



**Fig. 1.** Spectrum of Raman scattering measured in  $\beta$ -ZnP<sub>2</sub> with polarization  $z(xy)x$ . The digits above bars indicate wave vectors of phonons in cm<sup>-1</sup>.



**Fig. 2.** Spectrum of Raman scattering measured in  $\beta$ -ZnP<sub>2</sub> with polarization  $z(x(z+y))x$ .

this polarization has very weak intensity, which is associated with strong absorption of radiation in the range of 850-890 nm in allowed polarization  $E||Z$  at the expense of band-to-band transitions, which at the temperature 293K become actual because of temperature decrease of width of a forbidden gap.

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