

PACS: 78.30.-j, 31.30.Gs

Raman scattering of light in biaxial monocline β -ZnP₂ crystals

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Abstract. In this paper we represent for the first time observed experimental data on non-resonant Raman scattering in a plate of β -ZnP₂. The high-frequency part of RS spectra KP β -ZnP₂ is determined by oscillations of sites in *P*-atom spirals considered as building units of the β -ZnP₂ lattice. These spirals, as to their oscillatory properties, are very similar to infinite *P*-atom spirals in α -ZnP₂. Thus, the most intensive RS spectral band 433.0 cm⁻¹ 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⁻¹ to quasivalence out-of-phase excited oscillations orthogonal to the main ones.

Keywords: β -ZnP₂, non-resonant Raman scattering, irreducible representations.

Paper received 27.03.01; revised manuscript received 23.06.01; accepted for publication 13.07.01.

Biaxial crystals of «black» structural modification of zincdiphosphid, β -ZnP₂, 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 free excitons Van'y-Mott [1-3], which in addition, communicate at rather low levels of energization in biexcitons of a molecule [4,5] with the further tendency to their condensation. Up to date, unfortunately, in these chips the power spectrum of phonon states is insufficiently researched, which one largely influence processes excitons a light absorption and excitons of recombination. The information on these states are possible to be received first of all from spectra of infrared (IR) absorption and spectra of nonresonance or resonance Raman scattering of light. The availability of inversion as an element of a crystal lattice symmetry is reduced in the alternate prohibition, in connection with which one pair behind a symmetry the phonons can be observed only in Raman spectrum. The technical complication for research, for example, non-resonant Raman scattering of light on phonons in chips β -ZnP₂ is the small value of a forbidden region, which one at the temperature of 1.6 K to makes only 1.60263 eV. 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 β -ZnP₂ samples. The single crystals β -ZnP₂ the stands, obtained on technological base, of experimental physics of physical faculty of the T. Shevchenko Kiev National University were researched. The non-resonance Raman scattering were driven by radiation of the continuous titan-sapphire laser with a 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⁻¹. The direction radiation excitation was always perpendicular to that of registration.

Symmetry of crystal lattice of chips β -ZnP₂, which one fall into to the monocline system and singoniya, is featured by a space group P12₁/c1 or in abbreviated form P2₁/c (*C*⁵_{2h}), and crystalline class 2/m (*C*_{2h}). The unit cell contains 24 atoms, that belong to 8 formula unit of ZnP₂ composition. As easily seen from Table 1, where the irreducible representations of the point group 2/m are reduced and the selection rules for two orientations of the reference axis *c*₂ (for plates of β -ZnP₂ are accepted for using a crystallographic orientation conventional for monocline chips with *c*₂||*y*), 72 fundamental vibration

Table 1. Irreducible representations of the point group $2/m$, selection rule and classification of fundamental oscillations of β -ZnP₂.

$2/m(C_{2h})$	e	c_2	i	σ_h	n_{vib}	n_{ac}	n_{opt}	$c_2 z$	$c_2 y$
Γ_1^+	1	1	1	1	18	0	18	$\alpha_{zz}, \alpha_{xx}, \alpha_{yy}, \alpha_{xy}; \text{ia}$	$\alpha_{zz}, \alpha_{xx}, \alpha_{yy}, \alpha_{zy}; \text{ia}$
Γ_1^-	1	1	-1	-1	18	1	17	$\mu_z; \nu$	$\mu_y; \nu$
Γ_2^-	1	-1	1	-1	18	0	18	$\alpha_{zx}, \alpha_{zy}; \text{ia}$	$\alpha_{zy}, \alpha_{xy}; \text{ia}$
Γ_2^+	1	-1	-1	1	18	2	16	$\mu_x, \mu_y; \nu$	$\mu_z, \mu_y; \nu$
$\chi_{\Gamma_{\text{vib}}}$	72	0	0	0					
$\chi_{\Gamma_{\text{ac}}}$	3	-1	-3	1					

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

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

Among them selected are 3 acoustic:

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

and 69 optical modes:

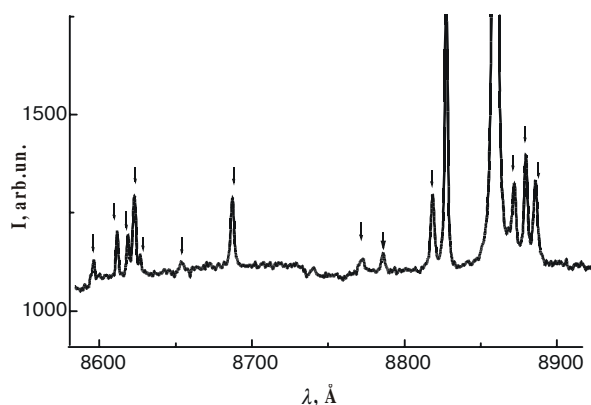
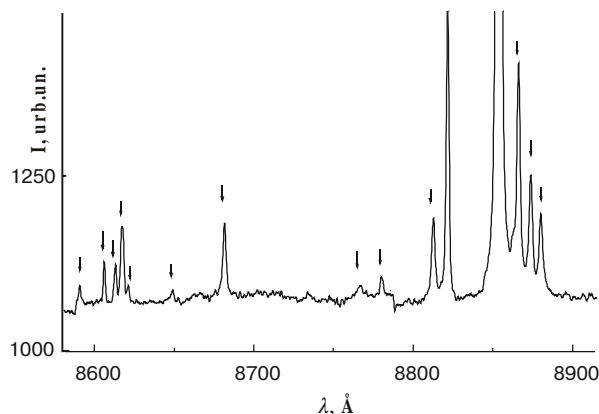
$$\Gamma_{\text{opt}} = 18\Gamma_1^+ + 17\Gamma_1^- + 18\Gamma_2^+ + 16\Gamma_2^-.$$

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

In Figs 1, 2 the reduced experimentally obtained non-resonant Raman scattering spectrum, that registered at the temperature of 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 β -ZnP₂ and α -ZnP₂ coincide. Frequencies of high-frequency part of spectra practically coincide, too. In α -ZnP₂ 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 zincum diphosphid testifies that the high-frequency part β -ZnP₂ spectrum is determined by oscillations of sites of spirals composed of P atoms as building blocks of the β -ZnP₂ lattice, which are very similar by their oscillatory properties to infinite spirals consisting of P atoms in α -ZnP₂. Thus, the most intensive spectral band 433.0 cm^{-1} responds to main inphase quasivalence oscillations of P atoms for all four translations of non-equivalent sites of P -spirals and bands $448.4; 458.2; 466.3 \text{ cm}^{-1}$ 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 $448,4 \text{ cm}^{-1}$. Beyond any doubts it is due to dispersion of a phonons with the symmetry Γ_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 β -ZnP₂ with polarization $z(xy)x$. The digits above bars indicate wave vectors of phonons in cm^{-1} .

Fig. 2. Spectrum of Raman scattering measured in β -ZnP₂ with polarization $z(x(z+y))x$.

this polarization has very weak intensity, which is bound 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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