CRYSTAL CHEMISTRY AND OPTICAL PROPERTIES
OF MONOCLINIC ZINC DIPHOSPHIDE

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Abstract
This paper reports on the results of investigations into the crystal structure of monoclinic zinc diphosphide. A study of the optical functions of $\beta$-ZnP$_2$ (black modification) in energy range 1.5 to 4.8 eV is presented in case of three polarizations of incident light. Experimental and calculated spectra of absorptivity are compared. Argand diagrams are plotted. Decomposition of imaginary part of dielectric function $\varepsilon_2$ into elementary components is performed. The electronic structures of monoclinic and tetragonal zinc diphosphide are discussed.

Introduction
At present time it is known more than 80 compounds of metals from group II with elements from group VB [1]. Seven compounds with ratio $A^2B^5$ are described in literature. Single crystals CdP$_2$ and $\alpha$- ZnP$_2$ crystallize in tetragonal lattice with space group $P_4_2_1_2$=D$_4$. Single crystals $\beta$-ZnP$_2$ have monoclinic lattice with space group $P_2_1/C=C_2$h and are isomorphic to ZnAs$_2$. The unit cell of all these compounds contains eight formula units [2-4]. Following the classification of [5] red modification $\alpha$- ZnP$_2$ may be concerned to polyanionic compounds in which all anions have the same coordination within the anion sublattice. In this structure all atoms are tetrahedral surrounded, the Zn by 4 P and the P by 2 P and 2 Zn. This coordination suggested that unlike in LiAs bonding in ZnP$_2$ is predominantly covalent. Very interesting configurations are met in the black form $\beta$-ZnP$_2$ [5]. One quarter of the P atoms is bonded to three other P atoms and one Zn atom while the remaining three quarters have two P and two Zn neighbors.

Black zinc diphosphide exhibits exceptional anisotropy of physical property [2]. The methods of growth are described in [2-4,6-8]. The temperature of melting of $\beta$-ZnP$_2$ $\approx$1265 K (for $\alpha$-ZnP$_2$ $\approx$1258 K) [7]. The twinning of elemental cell was detected in the crystals obtained from the vapor phase [9]. The lattice parameters are reported in [3,8,10,11]. Analysis of chemical bonds is carried out in [12,13].

In $\beta$-ZnP$_2$ the Brillouin zone presents itself a prism with bottom in form of hexagon with three pairs of nonequal sides. The specific features of the band symmetry, the dispersion laws and the selection rules are considered in [14,15]. The edge absorption and reflection of $\beta$-ZnP$_2$ were studied in [16]. The electroreflection and cathodoluminescence were investigated in [17,18]. The reflection spectra of $\beta$-ZnP$_2$, obtained in polarized light only at room temperature [19], are characterized by sharp drop of reflectivity at energy $h\nu$$>$3 eV.
most reliable spectra \( R \) at 80 and 293 K for \( E || a, E || b, E || c \) were obtained in [20,21] on samples with natural smooth surfaces. Experimental technique is described briefly in [21,22]. Exciton spectra at 4.2 and 80 K for \( E || c \) were investigated in [23,24]. Optical functions near \( E_g \) were calculated in article [25,26]. Anisotropy of optical functions of \( \beta \)-ZnP\(_2\) in large energy region was investigated in [27,28].

**X-ray structural investigations**

The experimental X-ray diffraction data used in calculations of the crystal structures of \( \beta \)-ZnP\(_2\) were collected on a Siemens P3/PC automatic four-circle diffractometer (\( \lambda \text{MoK}_{\alpha} \), graphite monochromator, \( \theta/20 \) scan mode, \( \theta < 70^\circ \), total sphere of reflections, 293 K). The discrepancy factor was approximately equal to 3.2\% (the number of reflections used in the structure refinement was \( \sim 3560 \)). The unit cell parameters of \( \beta \)-ZnP\(_2\) are as follows: \( a = 8.8630(5) \text{Å}, b = 7.2882(4) \text{Å}, c = 7.5603(4) \text{Å}, \beta = 102.310(5)^\circ \). The data of other authors are represented in Table 1. The sample of spherical form (diameter \( \sim 4 \text{ mm} \)) is maintained in present work. Crystal rhombic prismatic in shape, approximately equidimensional with calculated volume \( \sim 2 \times 10^3 \text{mm}^3 \), selected for data collection in [11]. Enraf-Noins CAD-4F diffractometer is used. X-ray powder diffractometer DRON-3 was used in [10].

<table>
<thead>
<tr>
<th>Parameter a, Å</th>
<th>Parameter b, Å</th>
<th>Parameter c, Å</th>
<th>Parameter ( \beta ), deg</th>
<th>Reference</th>
</tr>
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<td>102.3</td>
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<td>[10]</td>
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<td>8.8752(24)</td>
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<td>7.5590(13)</td>
<td>102.407(20)</td>
<td>[8]</td>
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<td>8.8668(4)</td>
<td>7.2913(5)</td>
<td>7.5615(6)</td>
<td>102.308(5)</td>
<td>[11]</td>
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</table>

Similar to \( \alpha \)-ZnP\(_2\) [13,29] phosphorus atoms in \( \beta \)-ZnP\(_2\) are connected in chains. However, as distinct from red ZnP\(_2\), the P chains in black ZnP\(_2\) are directed only along axis \( c \) and resemble open-ended pentagons as is imaged in Fig.1.

The structure of \( \beta \)-ZnP\(_2\) is characterized by two independent atoms Zn1, Zn2 and four independent atoms P1, P2, P3, P4. The atom Zn1 has a slightly deformed tetrahedral coordination, though its bonds are shorter compared with tetrahedral ones. The atom Zn2 is analog of the atom of zinc in \( \alpha \)-ZnP\(_2\), but its tetrahedral coordination is deformed considerably.

The atom P1 in \( \beta \)-modification bonds one atom Zn2 only and it is the analog of the atom P2 in the \( \alpha \)-ZnP\(_2\) structure. Atom P4 in \( \beta \)-ZnP\(_2\) and atom P1 in \( \alpha \)-ZnP\(_2\) structure have the same deformations of tetrahedral angles. Atoms P3 and P2 in the \( \beta \)-ZnP\(_2\) structure are equivalent to each other and bond atoms Zn1 and Zn2. The values of interatomic distances and bond angles are given in Tables 2, 3. The data, obtained in the present work, specify the results of [11].

Atom Zn1 connects three phosphorus chains by virtue of bonds Zn1-P3 (2.376 Å) and Zn1-P2 (2.396 Å) (with two chains) and by virtue of bonds Zn1-P4 (2.341 Å) and Zn1-P4 (2.342 Å) (with third phosphorus chain). The other independent atom Zn2 connects the phosphorus chains with help of bonds Zn2-P3 (2.431 Å), Zn2-P2 (2.435 Å), Zn2-P1 (2.420 Å). With other chains atom Zn2 is connected by virtue of bond Zn2-P1 (2.361 Å). On the average the distance Zn1-P, equal to 2.363 Å is smaller than Zn2-P (2.412 Å). Moreover, bonds Zn1-P are smaller and bonds Zn2-P are larger than analogous bonds in the structure of tetragonal zinc diphosphide (the average length of bond Zn-P equals 2.389 Å).
Fig. 1. Schematic picture of the structure of $\beta$-ZnP$_2$ with marked phosphorus chains and tetrahedral bonds of every from six independent atoms P1, P2, P3, P4, Zn1, Zn2 (extra bold black and gray lines). Axis $c$ is perpendicular to axis $b$ and forms angle 102.3° with axis $a$.

Every atom P1 has two bonds with atom Zn2, one bond with atom P2 and one bond with atom P3. Both latter bonds are intrachain. Atom P2 connects atoms Zn1 and Zn2 and forms bonds inside chains with P1 and P4. Interatomic distance P2-P4 equals 2.197 Å. Phosphorus P3 forms bonds with P1, P4 inside chains and is connected also with atoms Zn2 and Zn2, which sew together phosphorus chains. Interatomic distance P3-P4 equals 2.184 Å. Independent atom P4 is connected with two atoms Zn1 and with two atoms P2 and P3 (see distance in Table 2). In the structure of $\beta$-ZnP$_2$ the short (2.17 Å) bonds P-P typical for pure phosphorus and for red $\alpha$-ZnP$_2$ are absent [13]. However P-P bonds don't exceed the longest
bonds P-P in these structures. The average length of bond Zn2-P (2.412 Å) is matched in practice with sum of tetrahedral radii of these chemical elements (2.410 Å). At the same time the values of Zn1-P bonds are considerably smaller owing to chemical nonequivalence of atoms in crystal structure.

**Table 2.** Bond lengths (Å) in β-ZnP2 crystals.

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<tbody>
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<td>Zn1 - P2</td>
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<td>P1 - P2</td>
<td>2.2138(8)</td>
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<td>2.3580(7)</td>
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<tr>
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<tr>
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<td>2.4306(6)</td>
<td>P2 - Zn2</td>
<td>2.4344(6)</td>
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Tetrahedral angles are strongly distorted. The maximal angle P-Zn2-P equal 125.4°, and the minimal angle equals 101.3° (See table 3). Thus the atom Zn2 appears to be analogous to Zn in tetragonal modifications of ZnP2 (for comparison P-Zn-P equals 124.2° and 99.4°). However the average interatomic distance in both modifications is somewhat different. The average distance Zn2-P equals 2.411 Å in β–ZnP2 and the average distance Zn-P in α-ZnP2 equals 2.389 Å. We can find and analogs of atoms phosphorus. Such are atom P1 in α-ZnP2 and P1 in β–ZnP2, and also P2 in α-form and P4 in β-form. For searching of analogs is better to use valent angles, but not bond distance.

**Table 3.** Bond angles (deg) in β–ZnP2 crystals.

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<td>P2-P4-Zn1</td>
<td>110.85(3)</td>
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The vapour grown monocrystals of β-ZnP2 represented black mirror-like plates with (100) plane and more seldom (010) plane. At times samples were six-face prism, elongated
along axis c with the top in the form of a wedge, limited by (100) and (110) planes, but the topless ones by the (001) plane. Sometimes small facets (320) arise and the prism becomes octahedron. Some samples were grown by method of oriented crystallization from the melt and represented large mirror-like (100) or (110) cleavage planes. A set of such samples allowed investigating the reflectivity spectra of monoclinic zinc diphosphide for three polarizations of incident light.

Calculations of optical functions

The spectra of optical functions of \( \beta \)-ZnP\(_2\) were obtained in the range 1.5-4.5 eV at 293 K and 80 K in polarized light \((E||a, E||b, E||c)\). The calculations were carried out using the data of [20,21] and Kramers-Kronig relationships [30,31]. The data in the range 4.5-12 eV required for correct calculations were taken from [32].

In this work we examine the following functions: reflection coefficient \( R \), refractive index \( n \), absorption index \( k \), real \( \varepsilon_1 \) and imaginary \( \varepsilon_2 \) parts of permittivity, absorption coefficient \( \mu \), function \( \varepsilon_2*(h\nu)^2 \), effective number of valence electron \( n_{ef} \), effective permittivity \( \varepsilon_{ef} \) and function of bulk plasmons \((-\text{Im} \varepsilon^{-1})\). All these functions are represented in Figs 2-5.

The specific features of \( R \) were described in [20,21]. The spectra of \( n \) and \( \varepsilon_1 \) are similar to those of \( R \) in the range 1.5-3.0 eV and fall off steeply at energy \( h\nu >3.0 \) eV. The spectra of \( k, \mu, \varepsilon_2 \) are also very similar to \( R \) in all energy region, especially for polarizations \( E||a, E||b \). The absorption coefficient \( \mu \) at energy 4.5 eV and 80 K reaches \( 0.45*10^6 \text{cm}^{-1} (E||a) \), \( 0.55*10^6 \text{cm}^{-1} (E||b) \) and \( 1*10^6 \text{cm}^{-1} (E||c) \). The function of bulk plasmons has noticeable structures at \((E||c)\).

![Fig.2](image-url). Experimental spectrum of reflectivity \( R \) (1-solid line) and calculated spectra of refractive index \( n \) (2-solid line) and real part of permittivity \( \varepsilon_1 \) (3- dash) in the range 1.3-4.5 eV at temperature 293 K and light polarizations \( E||a \)-top left, \( E||b \) - top right and \( E||c \)- bottom.
Fig. 3. Optical functions (1) $R$, (2) $n$, (3) $\varepsilon_1$ – [top left]; (1) $\mu$, (2) $k$, (3) $\varepsilon_2$ – [top right] and (1) $n_{\text{ef}}$, (2) $\varepsilon_{\text{ef}}$, (3) $-\text{Im} \varepsilon_1$, (4) $\varepsilon_2^* (h\nu)^2$ - [bottom] in the range 1.7-4.5 eV at 80 K and light polarization $E \parallel a$.

Fig. 4. Optical functions (1) $R$, (2) $n$, (3) $\varepsilon_1$ – [top left]; (1) $\mu$, (2) $k$, (3) $\varepsilon_2$ – [top right] and (1) $n_{\text{ef}}$, (2) $\varepsilon_{\text{ef}}$, (3) $-\text{Im} \varepsilon_1$, (4) $\varepsilon_2^* (h\nu)^2$ - [bottom] in the range 1.7-4.5 eV at 80 K and light polarization $E \parallel b$. 
All these enumerated functions contain the peaks revealed in the reflectivity spectra, except for those observed at the longest wavelengths. The functions $n_{ef}$ and $\varepsilon_{ef}$ are monotone and don’t attain saturation in the region examined.

The strong temperature dependence of all optical functions of $\beta$-ZnP$_2$ is discovered. The main features of optical spectra at 80 K and 293 K coincide with each other. At the same time the majority of the features revealed at room temperature are less pronounced, some of them practically disappear.

It is seen from Figs 2-5 that crystals of black zinc diphosphide possess a clearly pronounced optical anisotropy. Near $E_g$ we see intensive excitonic structure at light polarization $\mathbf{E} \parallel \mathbf{c}$, which is absent at $\mathbf{E} \parallel \mathbf{a}$, $\mathbf{E} \parallel \mathbf{b}$. Optical functions in this region were investigated in detail earlier [25,26]. The weak structures at 2.2 eV ($\mathbf{E} \parallel \mathbf{a}$), 1.8 eV ($\mathbf{E} \parallel \mathbf{b}$) have probably excitonic structure too. Intensities of these structures became smaller after polishing (as in case of $\mathbf{E} \parallel \mathbf{c}$), at the same time the other structures in the region 2.5-4.5 change slightly. The absolute values of all functions examined at $\mathbf{E} \parallel \mathbf{c}$ are larger than those for $\mathbf{E} \parallel \mathbf{a}$ and $\mathbf{E} \parallel \mathbf{b}$.

Argand diagrams

It is known, that the spectral bands, associated with optical transitions, overlap significantly. The separate oscillator with symmetric Lorentzian form of absorption band is a circle at Argand curves $\varepsilon_2 = f(\varepsilon_1)$. One can determine easily three main parameters of elementary oscillator: the energy of position of the maximum of the band associated with the optical transition $E_i$, the half-width of this band $H_i$ and the oscillator strength $f_i$. [31,33]. For analysis the pairs $\varepsilon_2 = f(\varepsilon_1)$, $k = f(n)$ and $\theta = f(R)$ are the most suitable.
The Argand diagram of $\beta$-ZnP$_2$ in the region of exciton ground state ($n=1$) is defined with great precision as an open-ended circle [25,26]. The weak semicircumferences at the outset and the end of curves $\varepsilon_2=f(\varepsilon_1)$ correspond to exciton-impurity complexes and states with $n=2,3$. In case of overlap of optical function of several oscillators Argand diagrams have quite complicated form (Fig.6). Curves have arrangement against of hand. In this article we resolve the spectra $\varepsilon_2(h\nu)$ of $\beta$-ZnP$_2$ in range 1.7-5.2 eV into partial components as well as in case of red tetragonal zinc diphosphide [29].

![Fig.6. Argand diagrams for E || a (left), E || b (middle) and E || c (right).](image)

The exciton parameters are cited in [23-25]. To determine the exciton parameters, we can also use the known formula, which describes the absorption edge taking into account the exciton band and can be written as the Lorentzian:

$$
\mu(h\nu) = \mu_0 \left[ \sum_n \frac{1}{n^2} \left( \frac{\Gamma_n}{2} \right)^2 + \frac{\Gamma_c}{4R_0} \left( \frac{\pi}{2} + \arctan \left( \frac{h\nu - E_g - R_0}{\Gamma_c} \right) \right) \right]
$$

where $E_g$ is the band gap, $R_0$ is the exciton Rydberg, $n$ is the exciton excitation order, $\Gamma_n$ is the oscillator half-width, $\Gamma_c$ is the exciton continuum width, $\mu_0$ is the coefficient proportional to the oscillator intensity $f_{cv}$, and $\Gamma_n^2 = \Gamma_c^2 - (\Gamma_c - \Gamma_1)/n^2$. The parameters $\mu_0$, $\Gamma_1$, $\Gamma_c$, $R_0$ and $E_g$ were selected to achieve the best fit to the experimental data, as in work [34]. Summation was carried out only up to $n = 7$. The experimental data (black squares) and the calculated curve $\mu$ of black ZnP$_2$ are displayed in Fig. 7 together with values of parameters. The results obtained are in good agreement with data of [23-25]. Some deviations take place in the long-wave regime.

![Fig.7. Analysis of the absorptivity (80 K , E || c)](image)
region which are most likely caused by overestimated reflectance because of the effect of the rear surface of the crystal as in case of zinc diarsenide [34].

**Parameters of optical transitions**

We used the Argand diagram technique [31,33] to resolve the spectra $\varepsilon_2(h\nu)$ into partial components attributed to the particular groups of optical transitions with close energies. This process is executed on a computer and repeated as long as the residues of Argand curves contained portions that could be represented by circumferential parts. The results of decomposition of $\varepsilon_2(h\nu)$ are represented in Figs.8-10.

![E2(2eV)](image)

**Fig.8.** Decomposition of dielectric function $\varepsilon_2$ into elementary components ($E||a$, 80 K)

The integral spectra of imaginary part of permittivity of $\beta$-ZnP$_2$ can be reproduced with help of 13-14 Lorentzian oscillators. Thus we discovered new bands, which don’t manifest themselves structurally in reflection spectra (See Figs. 3-5). Only 7-9 peaks are observed distinctly in spectra $R$ at 80 K. The other structure is impossible to find with employment of experimental methods, including differential optical spectra.

It is worth noting that intensive transition with oscillator strength $f_i>1$ is not revealed as in case of tetragonal CdP$_2$ and ZnP$_2$ [29,32]. The $f_i$ values for polarizations $E||a$, $E||b$ are considerably less then those for the polarization $E||c$. All the bands observed can be separated into three groups. The first group contains completely polarized bands (transition is allowed only for one polarization). The other groups involve bands observed at two or three polarizations with close energies, but with different oscillator strengths. The half-width of all
Figs. 9, 10. Decomposition of dielectric function $\varepsilon_2$ into elementary components (E||b, E||c).
oscillators in region 2-4 eV is between 0.2-0.4 eV besides oscillators with $E_i$ equaled 4.33 eV ($E || a$) and 4.34 eV ($E || c$) which are characterized of $H_i$ equaled approximately 0.5-0.6 eV. The values of $f_i$ in region 2-4 eV are very small (for all polarizations) and are equaled to 0.02-0.18. However the values of $f_i$ are equaled 0.32 ($E || a$, 4.33 eV), 0.36 and 0.37 ($E || b$, 4.21 and 4.51 eV), 0.42, 0.66, and 0.35 ($E || c$, 3.80, 4.34, and 4.74 eV). In general Figs 8-9 are rather alike in contrast to Fig.10 (polarization $E || c$).

Conclusions

So, in the present article we described some peculiarities of crystal structure and optical properties of monoclinic black zinc diphosphide and compared them with those of red form of ZnP$_2$. The monoclinic modification of ZnP$_2$ is presumed to be a straight-band semiconductor with the appearance of a free exciton ($E || c$). The value of $E_g$ is equaled to 1.594 eV at 80 K [23]. The absence of edge exciton structures in experimental optical spectra showed the forbidden character of the band gap transitions of tetragonal modification of ZnP$_2$ in accordance with band calculation [21]. The value of $E_g$ is equaled from absorption measurements to $\approx 2.3$ eV.

Both modifications are formed according to the rule of four electrons. There are three crystal chemically independent atoms in the structure of $\alpha$-ZnP$_2$ and six crystal chemically independent atoms in the structure of $\beta$- ZnP$_2$. Tetragonal zinc diphosphide can exist in two enantiomorphic forms. The main structure fragments of both modifications of ZnP$_2$ are composed of phosphorus chains oriented along the [100] and [010] directions in $\alpha$-form and only along axis $c$ in $\beta$-form. Occurrence of Me-X and X-X bonds (Me-metal, X-element of V group) defines the strong anisotropy of optical properties of zinc diphosphide [27,35].

The reflectivity spectra and other optical functions of $\beta$- ZnP$_2$ have very complicated and anisotropic character and exhibit their own specific features in contrast to $\alpha$-ZnP$_2$. The main parameters of optical transitions of black ZnP$_2$ are determined. Analysis of electronic structure of both forms shows the availability of groups of transitions whose energies $E_i$ differ by values of $\Delta E_g$. However it is impossible to determine the nature of transitions in $\beta$- ZnP$_2$ due to absence of quantitative band calculations. We hope that the result of present work will give the reliable basis for precise determination of electronic structure of $\beta$- ZnP$_2$.

References