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Behaviour of manganese impurity in β -ZnP₂

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Abstract. Behavior of manganese impurity in black zinc diphosphide was investigated for the first time by the EPR method at room temperature. The nature of basic singularities of an EPR spectrum was determined. The defect structure evolution of irradiated and annealed ZnP₂ was studied by the method of the paramagnetic probe (Mn²⁺).

Keywords: singularity, paramagnetic center, spin - Hamiltonian, defect, interstitial, vacancy, tetrahedron.

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1. Introduction

Black zinc diphosphide – a direct-zone semiconductor with an energy gap $E_g = 1.33$ eV at 300 K that has high photoconductivity in near infra-red (IR) region ($\lambda_{\max} = 1.06$ μm) [1], – is promising material for designing fast IR detectors [2,3] and displays a number of unique biexciton [4,5] and gyrotropic [6] effects.

On the other hand, these devices are sensitive to electron irradiation. The linear dose dependence of the resistivity in the wide fluency region up to 10^{18} cm^{-2} [7] makes it possible to use ZnP₂ diodes as sensors of electron irradiation. High-energy particle irradiation promotes purposeful control of their properties. However, defect structure of β -ZnP₂ is not clear so far and needs further study.

The possibility to use paramagnetic centers as indicators of a local electrical field for study of radiation defects in semiconductors is well known. In the given work the method of a paramagnetic probe (Mn) was applied for an evaluation of changes of a defect structure of β -ZnP₂ crystals under irradiation and thermal annealing.

According to the theory of the self-consistent method of the electron structure calculation of iron group transi-

tional elements in binary phosphide, the minimal level depth E_a of these metals from the valence zone can be described [8] by the formula:

$$E_a \cong 0.5E_g(1-f), \quad (1)$$

where f is the magnitude of an ion degree. For β -ZnP₂, where $f = 0.42$ [9]), $E_a \cong 0.40$ eV. In order to compare this value with the position of impurity levels appearing in the forbidden gap during irradiation and annealing, optical absorption and Hall effect measurements were carried out.

Experimental results are presented and main features of ZnP₂ defect structure are discussed.

2. Experiment

Black ZnP₂ crystals grown from a vapor phase were studied. The doping was carried out during synthesis of the composition. Manganese was incorporated in the form of phosphide. In order to receive the homogeneous distribu-

tion of impurities in the volume of the crystals, the method proposed in [10] was used. The impurity concentration was controlled by the method of mass-spectrometry of secondary ions, using LAS-600 [11]. Roentgen-structural analysis was carried out using roentgenmeter TUR-62.

Crystals were irradiated by high-energy electrons ($E = 14$ MeV) up to the fluence $\Phi = 10^{17}$ cm⁻² at room temperature. The isochronous annealing with the period of 15 minutes was carried out in special vacuum ampoule using a method proposed in [12].

Optical characteristics of crystals were measured at $T = 77$ K using a spectrometer of the Pye Unicam corporation, and electrical – by a five-probe method using highly sensitive amplifiers [13].

EPR spectra in the X-range were studied in powder samples by a radiospectrometer RE 1301 at room temperature and calculated by the technique given in [14–17].

3. Results and discussion

As one can see from the experiment, optical absorption of samples doped by manganese displays the shift of the edge of a fundamental absorption and a lack of selective bands in a spectral region from 0.1 up to 1.4 eV, comparing with initial spectra (Fig. 1).

Hall effect measurements have shown the drop of the hole concentration by 4 orders of value when Mn is incorporated into β -ZnP₂ (Table 1).

In doped crystals, as one can see in the Table 1, the activation energy of the dominating acceptor level does not vary, the magnitude of mobility increases a bit, but its temperature dependence has remained without change (Fig. 2). All this indicates that in zinc diphosphide as well as in crystals A³B⁵ [8] impurities of transitional metals with unfilled 3d- shell form deep local levels with the

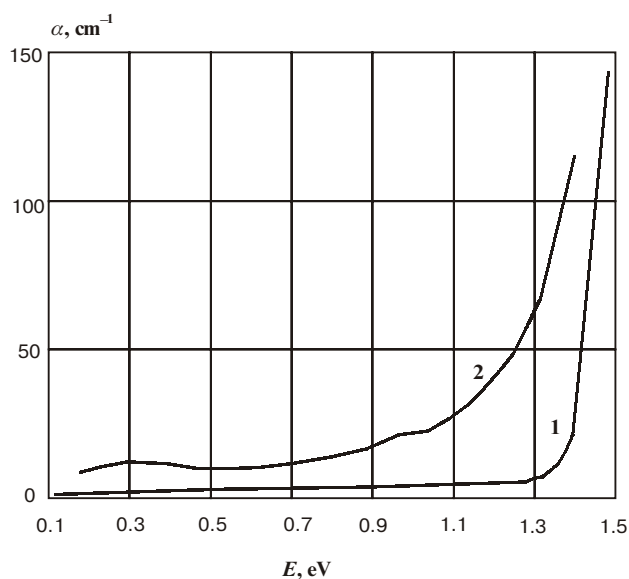


Fig. 1. Absorption spectra for initial (a) and manganese doped (b) black zinc diphosphide crystals

Table 1. Electrical parameters of black zinc diphosphide crystals

Crystal \ Parameter	p, m^{-3}	$\mu \cdot 10^4, \text{m}^2/\text{V} \cdot \text{s}$	E_a, eV
Initial	$6.8 \cdot 10^{14}$	48	0.36
ZnP ₂ : Mn	$3.1 \cdot 10^{10}$	50	0.36
Anneal $T = 800$ °C	$7 \cdot 10^{10}$	50	0.36
Anneal $T = 850$ °C	$3 \cdot 10^{11}$	52	0.30

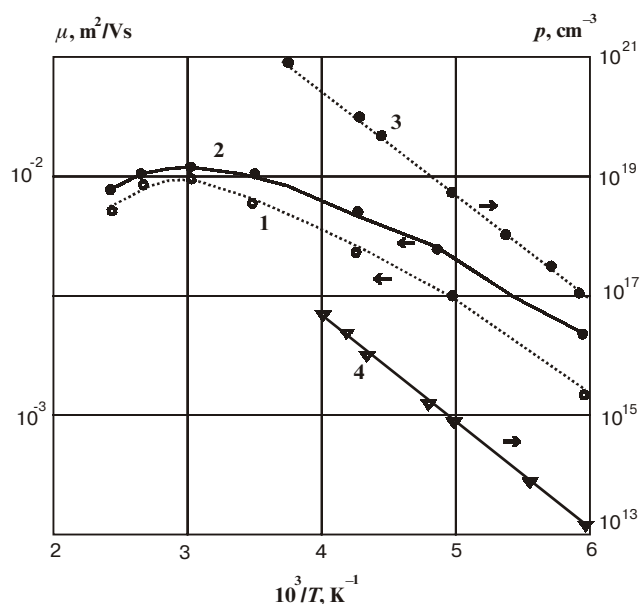


Fig. 2. Temperature dependences of the mobility and carrier concentrations for initial (dotted lines) and manganese doped (solid lines) black zinc diphosphide crystals

small capture cross section of charge carriers in a forbidden zone.

As was established earlier in [18], initial crystals possess low thermal stability of main electrical parameters: at $T = 760$ °C electroconductivity already increases by four orders, and varies ambiguously during farther heating. From the Table 1, it is clear that electrical parameters of manganese doped crystals are much more thermostable. Such property is characteristic for materials, in which doping impurities are in a substitution solution [19,20]. As it was shown in majority of works concerning EPR radiospectroscopy of wide-zone semiconductors [21–26], atoms of transitional metals can occupy interstitial positions (for example, in SiC [21]) or substitute metal (for example, in GaN [24]). For the definition of a manganese position in a lattice of β -ZnP₂ crystals the spectra of an electron paramagnetic resonance were studied. To the beginning of our researches, the EPR spectra in complex phosphides A²B⁵₂ have not been studied yet, except of triple germanium diphosphide ZnGeP₂ [27–29]. Our experiments are the first of this kind.

According to the concentration of manganese in synthesized substance, spectra of two types were obtained.

The first type (Mn content did not exceed 0.01 weight %). EPR spectrum consists of four groups of lines nearly the same intensity (Fig. 3). Every group possesses six equidistant lines (Fig. 3, curve *a*), which responds to central transitions (CT) of Mn²⁺ ions in zinc diphosphide : $|1/2, m < \leftrightarrow -1/2, m >$. The complicated picture of weak lines was observed near this intensive CT, which makes it unable to observe hyperfine forbidden transitions (HFT): $|1/2, m < \leftrightarrow -1/2, m + 1 >$. In this case, parameters of a fine structure (*D* and *E*) have a broad distribution, contrary to parameters *g* and *A*, presented in Table 2.

Table 2. EPR parameters of singularities of spectra of p-type doped crystals

g_{ef}	A, mT
20	5.4
2.55	4.4
2.17	6.2
1.94	6.2

One can see that the magnitude of the parameter lies within limits 4.4-6.2 mT, which is characteristic of compounds with the significant part of covalent bonds [15]. It is necessary to notice that the behavior of spectra is explained within the framework of the common analysis of unordering structures [14, 27].

In the second type EPR spectrum (with the Mn content up to 0,1 weight of%) compared with the spectrum of the first type, the intensity of singularities with $g_{ef} = 20$ is increased, the singularities with $g_{ef} = 4.3$ and the broad band of Lorentz form in the region 270-370 mT appear (Fig. 3, curve *b*).

EPR spectra of manganese ions in the field of 270–370 mT

As one can see in Fig. 3, the band of Lorentz form has not a hyperfine structure (HFS) or bands are strongly superimposed. In order to define its basic characteristics the method of simultaneous observation of EPR spectrum in two substances was used: the unknown crystal and measured standard (MgO). The resulting spectrum is shown in Fig. 4. Using data of the measured standard spectrum, calculations of the *g*-factor and the width of a researched band were made:

$$g_{ef} = (B_1/B_2) g_1 = (3200/3165) 1.9880 = 2.0099$$

$$\Delta B = (65 \text{ mm}) \cdot 2.18 (\text{Oe/mm}) = 141.7 \text{ Oe} = 14 \text{ mT}.$$

If the width of individual lines caused by relaxation processes exceeds a distance between adjacent lines of the FS

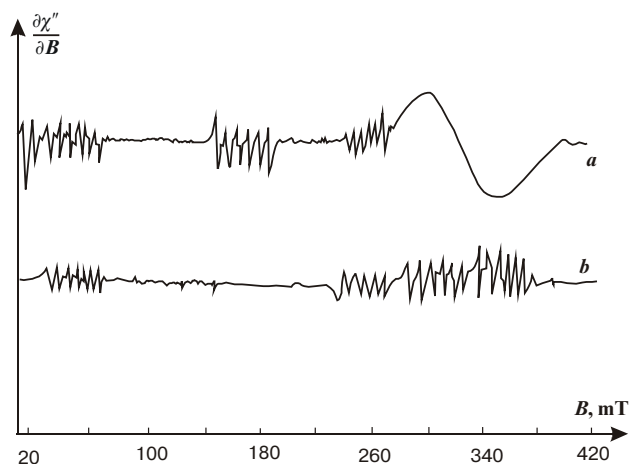


Fig. 3. EPR spectra for β -ZnP₂: Mn crystals with the different doping content: a) 0,01 weight %, b) 0,1 weight %.

and HFS, the structureless spectrum is observed [15]. For its separation, temperature researches were carried out. EPR spectra with $g_{ef} = 2.0099$ at different temperatures (77–500 K) are given in Fig. 5. One can see that the width and the intensity of the band vary weakly with temperature. The magnitude of an activation energy of the band, determined from a temperature dependence of a line width ($\Delta B = \Delta B_0 \exp(-E_a/kT)$) [22], is equal 0.03 eV. The obtained low value of an activation energy indicates an asymmetrical paramagnetic center (PC) configuration [15]. In this case, a relaxation process in an external field does not require large energy expenses. As it is known, if the form of a EPR line depends poorly on temperature, the spin number is determined precisely enough as a square under the curve of the intensity derivative magnitude I_0^* dependence on magnetic field induction [14]:

$$S = (\pi / \sqrt{3} \mu_0) I_0^* \Delta B^2 \quad (2)$$

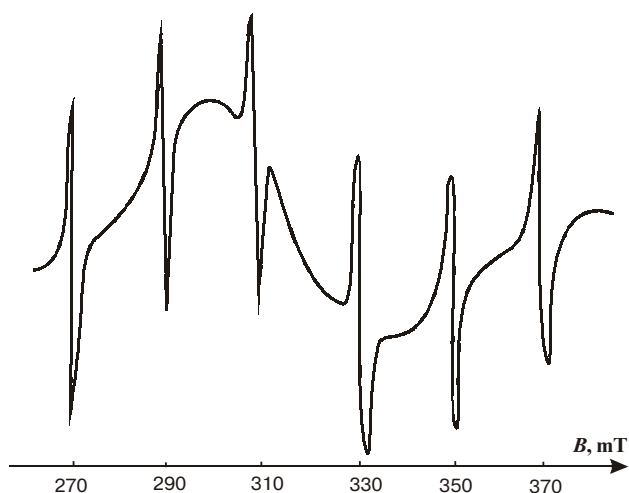


Fig. 4. EPR spectra in the $B = 270$ – 370 mT region for β -ZnP₂: Mn and MgO measured standard

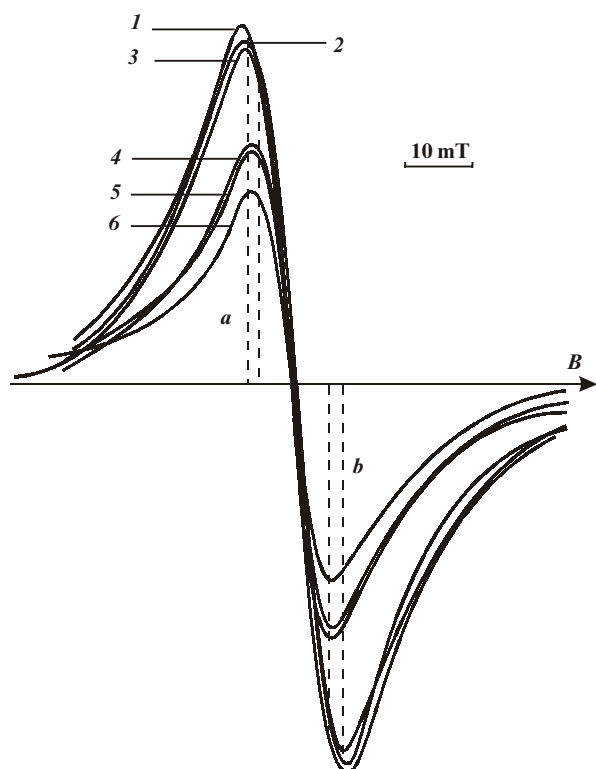


Fig. 5. EPR spectra with $g_{ef} = 2.0099$ for initial β -ZnP₂: Mn at different observed temperatures: $T = 77$ K (1), $T = 200$ K (2), $T = 500$ K (3), irradiated by electrons with the energy $E = 14$ MeV (4) and annealed at $T = 100$ °C (5), $T = 300$ °C (6). Asymmetry parameters (a, b) are shown as dotted lines

Using the known value of uncoupled spins in the measured standard (MgO) and data obtained from Fig. 4, the concentration of paramagnetic centers in zinc diphosphide responsible for a band with $g_{ef} = 2.0099$ was found to be $N = 1.5 \cdot 10^{17} \text{cm}^{-3}$.

In majorities of semiconductors doped by Mn, the wide line (with a width > 10 mT) without HFS is ascribed to the manganese existence as unisolated centers [24, 25]. To determine a charge state of PC, to which EPR spectrum with $g_{ef} = 2.0099$ responds, doped samples were annealed at three temperatures: 800 °C (I mode), 1000 °C (II mode) and 1100 °C (III mode). In the first mode the pressure of a phosphorus vapor was lower than the equilibrium one, in the second was equal to equilibrium, and in the third was higher than the equilibrium one, according to the P - T - V diagram for a system β -ZnP₂ [30]. Samples were annealed in evacuated silica ampoules during 12 hours which enabled to provide equilibrium of a vapor-solid system in a layer of 300-micron width. It is known that high-temperature treatment causes appearance of imperfections, the pressure of vapor component determines the type of which in binary compounds. So, when the phosphorus vapor pressure is lower than the equilibrium one, the concentration of phosphorus vacancies – deep donors with $E_a = 0.24$ eV (in β -ZnP₂, $E_g = 1.4$ eV [31]) – increases; when the pressure is more than equi-

librium – the concentration of zinc vacancies, that are deep acceptors $E_a = 0.3$ eV [32], increases. Values of concentrations of paramagnetic centers (PC) and holes after different heat treatments are given in Table 3.

Table 3. Concentrations of PC and charge carriers after different annealing modes

Sample	Initial	1 mode	2 mode	3 mode
PC concentration, cm^{-3}	$1.5 \cdot 10^{17}$	$7 \cdot 10^{16}$	$2 \cdot 10^{17}$	$6 \cdot 10^{17}$
Hole concentration, cm^{-3}	$6.5 \cdot 10^{20}$	$2 \cdot 10^{18}$	$4 \cdot 10^{20}$	$8 \cdot 10^{21}$

From the Table 3, it is visible that the heat treatment at the first mode caused an additional compensation of PC due to appearance of donor electrons of phosphorous vacancies, and at the third mode – to PC recompensation. The second mode is intermediate. Such character of a modification of the PC and hole concentrations during annealing indicates the recharge of deep centers of manganese at a displacement of the Fermi level. So, the charge state of studied PC in initial crystals is close to neutral.

In order to find out its structure and position in a lattice β -ZnP₂, let us analyze parameters of spin-Hamiltonian: D (tensor of the FS), A (tensor HFS) and g -factor.

One can see from Fig. 3 that the relative intensity of a band with $g_{ef} = 2.0099$ is much higher than the intensity of a background created by non-central transitions of a fine structure (FS) in lines with others g_{ef} -factors. A similar background is presented in majority of Mn^{2+} experimental spectra with $g_{ef} = 2.00$ in oxide polycrystals and glasses [33]. For the evaluation of the width of distribution of the thin structure parameter D for Mn^{2+} in zinc diphosphide one can use the half-quantity analysis of a EPR Mn^{2+} structureless line with the close g -factor received for $\text{ZnCl}_2:\text{Mn}$ [33] – the structural analog of crystals studied. The comparative analysis has shown that the parameter D distribution at the half-height of a band in β -ZnP₂ must be $\Delta D > 10$ mT. In binary compounds the spectrum with broad distribution of a parameter D ($0.07 < D < 0.25$) in Tesla can be explained by effects of composite disorder of the Mn^{2+} second coordination sphere and is caused by the existence of manganese ion clusters as separate phases, which are not mixed up with a basic matrix of a lattice [15]. So, the data obtained in measurements of the Mössbauer effect [34] and EXAFS [35] in polycrystals showed that ions with the d^5 configuration in interstate positions cause a broad background absorption.

Comparing EPR spectra in Fig. 3 (a) and (b) one can see that in the magnetic field region of $B = 290$ – 370 mT, where there is a broad band in highly doped samples, in crystals of β -ZnP₂ with small Mn (0.01 %) content there are singularities with $g_{ef} = 2.17$ i $g_{ef} = 1.92$ and with an identical parameter $A = 6.2$ mT. From the EPR spectrum modeling in polycrystals [16] it is clear that the presence of separate singularities responds to the existence of isolated Mn^{2+} in a lattice. For Mn^{2+} ions an additional information about

possible number of the close neighbours can be received by the HFS constant (A) that determines PC coordination and rises, when the coordination number increases [15]. PC with $g_{ef} = 2.17$ i $g_{ef} = 1.92$ have the greatest value of the A parameter, therefore, their first coordination sphere should have the greatest amount of ligands, comparing with other centers in zinc diphosphide. Such position in a lattice can belong to Mn_i interstitial.

Obviously, two different structural positions of manganese in a lattice with the identical coordination of centers in a weak ligand field respond to ascertained singularities. Then, the formation of a broad band with $g_{ef} = 2.0099$, when the manganese concentration increases, can be caused by two factors – displacement of the g -factor of singularities with $g_{ef} = 2.17$ and 1.92 as well as the extension of FS lines. It is known [14] that the displacement of the magnitude of the g -factor is a result of modification of spin-orbit bonds in PC, arising in the course of restructurization, and lowering of a local PC symmetry causes extension of FS lines. Such reorganization can be performed by defect clusters that have an asymmetrical configuration, as it was stated above. It is also necessary to mention that the formation of interstitial clusters is peculiar to atoms that diffuse easily [36].

So, studied properties of spin-Hamiltonian parameters of a band with $g_{ef} = 2.0099$ indicate that the band is caused by clusters of manganese atoms, which are embedded impurities in β -ZnP₂.

EPR spectra of manganese ions in the region B = 150-180 mT

EPR spectrum in the region $B = 150\text{--}180$ mT (Fig. 6) is characteristic to manganese ions in an axial crystalline field [15] and is satisfactory described by spin-Hamiltonian :

$$\mathfrak{H} = g\beta(HS) + D[S_z^2 - 1/3\{S(S+1)\}] + A(SI) \quad (3)$$

The magnitude D can be evaluated by measuring the relative intensity I of hyperfine forbidden transitions (HFT) $\{-1/2, m \leftrightarrow +1/2, m = \pm 1\}$. For polycrystals the intensity can be expressed by the spin-Hamiltonian constants [37]:

$$I_{\text{HFT}} = (512D^2/15H_0^2)(35/4 - m(m+1)) \quad (4)$$

Ratio of amplitudes of low field HFT transition $(-1/2, -5/2 \leftrightarrow +1/2, -3/2)$ to appropriate hyperfine CT components $(-1/2, -5/2 \leftrightarrow +1/2, -5/2)$ (at $A < 0$) is equal 0.10 and, accordingly, $D = 7$ mT. For the more precise definition of spin-Hamiltonian constants let us use the expression for an angular dependence of a spectral position of thin structure lines [37]:

$$H = H_0 - D(M_s - 1/2)(3\cos^2\Theta - 1) + (D^2\cos^2\Theta \times \sin^2\Theta/2H_0)[4S(S+1) - 24M_s(M_s+1) - 9] - (D^2 \times \sin^4\Theta/8H_0)[2S(S+1) - 6M_s(M_s-1) - 3] - Am - (A^2/2H_0) \times$$

$$\times [I(I+1) - m^2 + (2M_s - 1)m] - (D^2 A \sin^2\Theta \cos^2\Theta/2H_0^2) \{ [(M_s^2 - S(S+1))^2 - M_s^2]/M_s - [(M_s - 1)^2 - S(S+1)^2 - (M_s - 1)^2]/(M_s - 1) \} m - (D^2 \sin^4\Theta/8H_0) \{ (M_s[2M_s^2 + 1 - 2S(S+1) - (M_s - 1)[2(M_s - 1)^2 + 1 - 2S(S+1)]) \} m \quad (5)$$

In polycrystals, the PC number of the spectrum in an interval of fields H i $H + \Delta H$, is proportional to magnitude Δn , depending on signal intensity $I(\Theta)$ by the formula:

$$\Delta n = \sin\Theta I(\Theta)\Delta H/(dH/d\Theta), \quad (6)$$

where Θ is an angle between a crystalline axes and magnetic field. The maximum of the intensity in a background EPR signal occurs under condition $(\Delta n/\Delta H) \rightarrow \infty$. By the differentiating the expression (5) on an angle and putting an obtained value $(dH/d\Theta)$ into the equation (6), one can receive values of angles of the particle orientation, at which there should be maximal EPR signal in an absorption curve for different transitions:

for $(-1/2, m) \leftrightarrow (+1/2, m)$ – angles $\Theta_1 = 90^\circ$, $\Theta_2 = \arctg\{(4 - 36Am/H)/(5 - 37Am/H)\}^{-1/2}$

for $(\pm 1/2, m) \leftrightarrow (\pm 3/2, m)$ and $(\pm 3/2, m) \leftrightarrow (\pm 5/2, m)$ – angle $\Theta = 90^\circ$.

So, using calculated values Θ_1 and Θ_2 for transitions $(-1/2, m) \leftrightarrow (+1/2, m)$ and experimentally obtained magnitudes of the strength of a magnetic field, which respond to maximum of signals – responses of FS transitions (Fig. 6), using the formula (5), the interval of modifying the A parameter was defined as $A = (6.4 \pm 0.1)$ mT.

In low field ($a-e$) and high field ($a'-e'$) parts of the spectrum (Fig. 6) observed are weak lines caused by signals-responses of FS transitions: $(\pm 1/2, \pm 5/2) \leftrightarrow (\pm 3/2, \pm 5/2)$ and $(\pm 3/2, \pm 5/2) \leftrightarrow (\pm 5/2, \pm 5/2)$. By determining their positions concerning the nearest central transitions and by comparing them with the values eveluted by the formula (5), there were found the interval of a modification of a parameter $D = 6.5 \pm 0.2$ mT and (using the equation of the work [15]) – parameter $E = 0.5 \pm 0.1$.

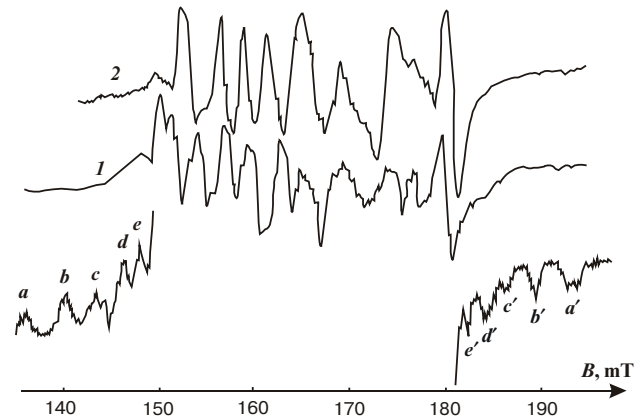


Fig. 6. EPR spectra with $g_{ef} = 4.3$ for initial (1) and irradiated (2) b -ZnP₂: Mn crystals

Thus, relation between obtained spin-Hamiltonian constants D and E ($D/E \neq 3$), the magnitude of g -factor ($g_{ef} = 30/7 \approx 4.3$), and also dependence of the absorption intensity of a EPR signal on the manganese concentration (Fig. 3, a and θ) indicate its connection with Mn^{2+} ions in strong crystalline field of four -multiple coordination with weak rhombic distortion [15]. The computer study of the Roentgen-structural analysis data of β -ZnP₂ crystals (space group $P2_1/c = C_{2h}^5$) (Table 4) has shown that all structural positions of zinc atoms are tetrahedrally coordinated. So, the ions of manganese, replacing zinc atoms in spots of a crystalline lattice are responsible for the EPR spectrum with $g_{ef} = 4.3$.

As it is clear from the Table 4, the zinc atom has two nonequivalent positions in the first coordination sphere: the atom of zinc is surrounded by four atoms of phosphorous – the 1st state, and, if atom of zinc is surrounded by two atoms of zinc and two atoms of phosphorous, – the 2nd state. In opposition to the tetrahedral α -ZnP₂ modification there are bonds metal–metal Zn2–Zn2, available in β -ZnP₂. So, when zinc atoms are substituted by manganese atoms, three possible tetrahedrons can be received in the structure β -ZnP₂, which differ by the first coordination sphere of an Mn ion environment 1) Mn (Zn1) and four P; 2) Mn (Zn2), Zn2 and three P; 3) Mn (Zn1), Mn (Zn2) and two P. For each tetrahedron it is possible to count an ion degree of four bonds as a sum of electroconductivity differences of bound atoms. The calculation shows, that there is the greatest ion degree of bonds for the tetrahedron of the first type, at which manganese ion substitutes the zinc atom in a state Zn₁; and the least ionization degree is for the third type of tetrahedron, in which two manganese atoms substitute the two zinc atoms in a state Zn₂.

Calculations of EPR spectra in all researched region have shown that singularities with $g_{ef} = 4.3$, have the greatest value of an HFS parameter ($A = 6.4$ mT). It is known [15] that the magnitude of a parameter A for Mn^{2+} increases with a diminution of a bond covalent degree and magnification of their length. That is, the tetrahedron with the greatest ion degree in binary composition responds to the singularity with the greatest parameter A . By comparing values of bond ion degrees in tetrahedrons mentioned and the distance between ligand in them (Table 4), it is possible to state, that PC of tetrahedral kind, in which Mn^{2+} substitutes atom of zinc in a Zn1 position, respond to the singularity with $g_{ef} = 4.3$.

The presence of singularities with $g_{ef} = 2.55$, $g_{ef} = 4.3$ and $g_{ef} = 20$ in highly doped crystals indicates the existence of three types of centers in a strong ligand field; Mn^{2+} has a different environment in these centers. One can explain it as the presence of structural nonequivalent positions of atoms in a lattice of β -ZnP₂ crystals. The existence of singularities with $g_{ef} > 20$ in an EPR spectrum (Fig. 3) indicates a high degree of continual violations of the near order in highly doped crystals.

Thus, the manganese atoms can occupy a series of structural – nonequivalent positions in a zinc diphosphide lattice, forming some types of paramagnetic centers (penetration and substitution), which can be indicators of a local electrical field at defect creation processes .

Table 4. Interatomic distances and angles (according to the direction of atom bond with first ligand) in black β -ZnP₂.

Atom	Ligands	Distances, Å	Angle, °
Zn1	P ₂	2.306	–
	P ₃	2.424	110.2
	P ₄	2.335	108.2
	P ₄	2.341	113.2
Zn2	Zn2	2.433	–
	P ₁	2.343	119.5
	P ₂	2.375	109.6
	P ₃	2.324	108.5
P ₁	Zn2	2.343	–
	P ₁	2.255	128.3
	P ₂	2.388	101.2
	P ₃	2.332	102.0
P ₂	Zn1	2.306	–
	Zn2	2.375	118.0
	P ₁	2.388	122.8
	P ₄	2.221	107.5
P ₃	Zn1	2.424	–
	Zn2	2.324	118.9
	P ₁	2.332	120.7
	P ₄	2.168	104.6
P ₄	Zn1	2.335	–
	Zn1	2.341	107.9
	P ₂	2.221	110.1
	P ₃	2.168	113.5

EPR of manganese ions in irradiated zinc diphosphide crystals

In Fig. 5 EPR spectra of ions of manganese with $g_{ef} = 2.0099$ are shown after irradiation by electrons with $E = 14$ MeV and annealing at temperatures, which respond to the stage ends of isochronous electroconductivity annealing [7]. One can see that the magnitude of amplitude of the first derivative and a line width ΔB are decreased on irradiation, which indicates a falling of PC concentration (equation 2). Besides, the amplitude of a high-field part of the band (b) is 10 % larger then the low-field part (a). After irradiation the parameter of asymmetry (a/b) is nearly equal to one. Such character of a band asymmetry change indicates a lowering of spin-orbit bonds of initial PC after irradiation [14]. It is obviously that Mn_i PC interstitial clusters are rebuilt due to the interaction with radiation defects. The character of change can be judged by estimating average distances between PC as the band spin-packet width ΔB using Eq. (3), in the case of the dipole–dipole interaction between PC parts [38]:

$$r \approx (a \Delta B / c \mu_0)^{-1/3} \quad (3)$$

Factors a and c in the equation (3) are special compound constants. The ratio of average distances $r_o/r_f \approx 50$ one can receive by measuring the spin-packet width of the band studied in initial (ΔB_o) and irradiated (ΔB_f) crystals (Fig. 5). That is, distances between PC increase after irradiation.

To understand the nature of radiation defects, which influence on EPR spectrum parameters of irradiated samples, let us analyze the spectrum in the interval $B = 250\text{--}277$ mT. The Mn²⁺ EPR spectra in this interval for initial and irradiated crystals are shown in Fig. 7. It is obvious that the introduction of radiation defects reduces singularity intensities and the magnitude of the g -factor. The displacement of the g -factor of the spectrum is observed in a case of continual violations of long-distance sphere of PC [17]. The EPR line inhomogeneous extension of impurity PC, observed as the change of ratios of amplitudes of allowed and forbidden FS transitions (in particular, in the high-field part) (Fig. 7), has shown the presence of fields of electrically active imperfections in irradiated samples [37]. Such imperfections in zinc diphosphide are complexes of vacancies of zinc and phosphorous in different coordinate positions of phosphorous sublattice, which are main conductivity compensators in irradiated crystals [7].

Modifications of A parameter and PC concentration of two singularities with $g_{ef} = 4.3$ and $g_{ef} = 2.0099$ after irradiation and annealing are shown in Fig. 8. One can see from this figure that the PC concentration with $g_{ef} = 4.3$ increases and with $g_{ef} = 2.0099$ decreases. The opposite radiation influence on the concentration of these centers confirms a different nature of centers. An isochronous annealing has shown (Fig. 8) that at $T = 300$ °C, when the centers are disintegrated on separate mobile vacancies [18], the PC concentration with $g_{ef} = 2.0099$ continues to drop, and $g_{ef} = 4.3$ – to increase. Thus, changes observed in EPR spectra of irradiated crystals are connected with the Mn_i capture by radiation induced vacancies and the transition of atoms of manganese from the state of penetration impurity to the substitution state.

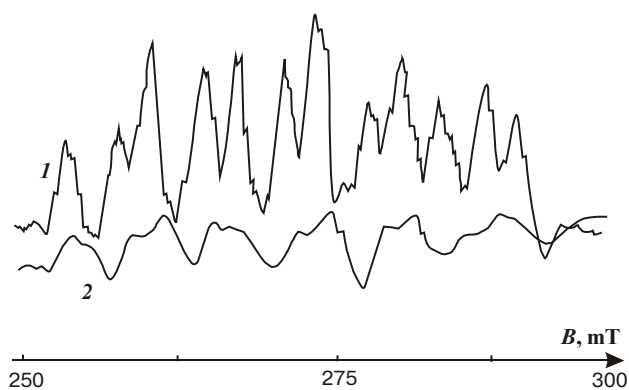


Fig. 7. Manganese ion EPR spectra in the $B = 250\text{--}300$ mT region for initial (1) and irradiated (2) β -ZnP₂: Mn crystals

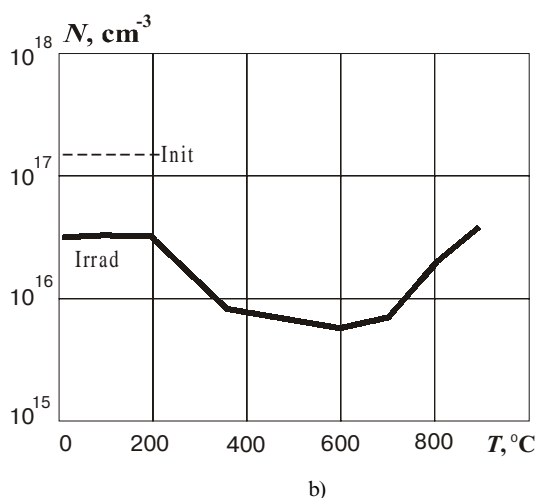
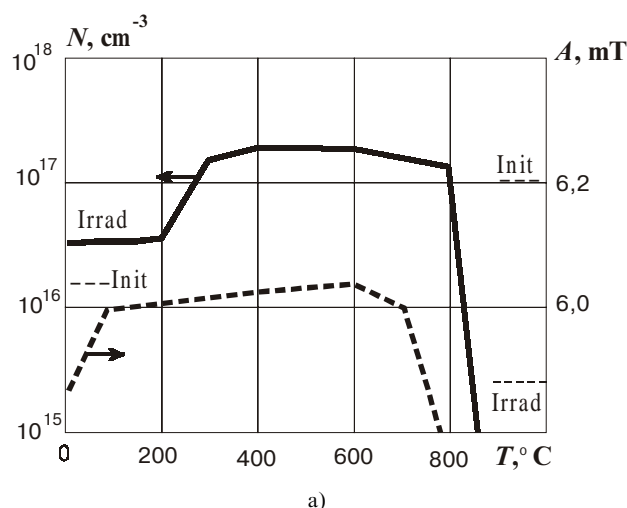


Fig. 8. Changes of A parameter of EPR and PC concentrations with $g_{ef} = 4.3$ (A) and $g_{ef} = 2.0099$ (B) for irradiated and isochronically annealed crystals

One can see from Fig. 6 that the low-field group of spectrum peaks with $g_{ef} = 4.3$ (a, b) is displaced into the large field region, thus the position of high-field singularities (c, d) remains constant. The A parameter decreases as well. The anomaly of local widths of Mn²⁺ singular lines in binary compositions one can explain (in the framework of one-harmonic model) as the amplitude fluctuations of lattice atom displacements [39]. Besides the lack of the splitting of resonance lines can testify the preservation of a PC local symmetry [40]. The parameter A diminution after irradiation is, as it has been already mentioned, the direct evidence of the increase of the covalent degree in the first coordination sphere in the environment of manganese, which substitute zinc in the position Zn1. All this indicates the rebuilding of the PC structure with $g_{ef} = 4.3$ after irradiation with involvement of imperfections of a substitution type.

An isochronous annealing has shown (Fig. 8) that the parameter A is almost completely restored at temperatures considerably lower than annealing temperature of vacancy complexes – main electrically active radiation defects of

zinc diphosphide crystals [18]. That is, EPR spectrum study has shown that at $T = 80$ °C radiation defects are annealed, which do not influence on electroconductivity [18] but act in exciton IR reflection spectra [41]. Obviously, these defects are simpler than vacancy complexes. Taking into account the high mobility of primary defects in zinc diphosphide at $T < 300$ K [42], antistructural imperfections could be such substitute defects. Our proposition is confirmed by the calculation of bond ion degrees. The replacement by zinc atom of one phosphorous atom from the manganese environment, to which the spectrum with $g_{ef} = 4.3$ (tetrahedron of a first type) responds, reduces a bond ion degree from the value 1.84 up to 1.78. Thus, the A parameter changes in this temperature interval are caused by antistructural imperfections of a type ZnP appearing in irradiated zinc diphosphide crystals.

Beginning from temperature $T = 600$ °C the A parameter of the spectrum with $g_{ef} = 4.3$ begins to drop, and at $T > 850$ °C the EPR spectrum in this g-factor region is absent. As one can see from Fig. 8, at these temperatures the concentration of singularities with $g_{ef} = 2.0099$ increases. That is, ions of manganese in the temperature interval of 850–900 °C, diffusing from crystalline lattice spots, create interstate PC complexes. Such character of the PS rebuilding reduces the thermo-hardness of crystal electrical parameters (Table 1).

Conclusions

Thus, from results received by EPR, Hall effect, optical and Roentgen-structural analysis of black zinc diphosphide crystals doped by manganese it is possible to conclude:

1. The existence of singularities with $g_{ef} = 20$, $g_{ef} = 4.3$, $g_{ef} = 2.55$ and $g_{ef} = 2.0099$ in the EPR spectrum are connected with spatially - nonequivalent positions of manganese atoms in a crystalline lattice of β -ZnP₂.

2. The broad unstructured band with $g_{ef} = 2.0099$ and the width $\Delta B = 14$ mT in initial crystals is caused by of manganese interstate clusters (penetration impurity) with charge state close to neutral.

3. EPR spectra with $g_{ef} = 4.3$ belongs to Mn²⁺ ions, which substitute atoms of zinc in the state Zn1.

4. Interstitial atoms of manganese in crystals irradiated by electrons with $E = 14$ MeV while interacting with of vacancies of zinc have become impurities of substitution.

5. Mn(Zn1) centers of substitution cause high thermal stability of electrical characteristics of β -ZnP₂:Mn crystals.

6. The antistructural defects of a ZnP type arising after irradiation by electrons with $E = 14$ MeV, can be annealed at temperature $T = 80$ °C

Abbreviations

CT – central transitions
HFS – hyperfine forbidden transitions
PC – paramagnetic centers
FS – fine structure
HFS – hyperfine structure

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