Energy bands and Wannier-Mott excitons in Zn(P_{1-x}As_x)\_2 and Zn_{1-x}Cd_xP_2 crystals

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Abstract

Excitonic absorption, reflection and photoluminescence spectra of mixed Zn(P_{1-x}As_x)\_2 crystals over the full range of \( x \) (0 \( \leq x \leq 1 \)) and Zn_{1-x}Cd_xP_2 crystals at 0 \( \leq x \leq 0.05 \) have been studied at low temperatures (1.8 K). The decrease of the energy gap in Zn(P_{1-x}As_x)\_2 at the increase of \( x \) occurs slightly sublinearly. The rydbergs of excitonic series in this crystals decrease as well, and the dependences \( R_g(x) \) for all series are strongly superlinear at small \( x \). In Zn_{1-x}Cd_xP_2 crystals the energy gap and rydbergs decrease at the increase of \( x \) (at 0 \( \leq x \leq 0.05 \)) as well. The dependences of \( E_g \) and \( R_g \) on \( x \) are considerably stronger in Zn(P_{1-x}As_x)\_2 than in Zn_{1-x}Cd_xP_2. At the increase of \( x \) the half-width of excitonic absorption lines increases monotonically in both type crystals that is evidence of the increasing role of fluctuations of crystal potential.

1 Introduction

In Ref. \[1\] we performed the spectroscopic studies of an influence of substitution of phosphorus by arsenic on the structure of valence and conduction bands, and on the parameters of Wannier-Mott excitons in mixed crystals (solid solutions) of isovalent substitution Zn(P_{1-x}As_x)\_2 at low levels of substitution \( x \leq 0.05 \). In present work we have proceeded with these studies at 0 \( \leq x \leq 1 \). By the other hand we have performed here the similar study (in comparison to Zn(P_{1-x}As_x)\_2) of another type mixed crystals of isovalent substitution Zn_{1-x}Cd_xP_2 at small substitution levels \( x \leq 0.05 \). As we know, the Zn_{1-x}Cd_xP_2 crystals were not studied earlier. Both Zn(P_{1-x}As_x)\_2 and Zn_{1-x}Cd_xP_2 belong to the mixed crystals of \( A^IIB^VI \) type, which are poorly investigated.

\( \beta \)-ZnP_2 (further ZnP_2) and ZnAs_2 crystals are strongly anisotropic direct-gap semiconductors (energy gap: 1.6026 eV for ZnP_2 and 1.052 eV for ZnAs_2), which are characterized by the same symmetry group \( C_{2h}^5 \) (monoclinic syngony). Besides the symmetry of the lattice, the similarity of ZnP_2 and ZnAs_2 exists in the structure of energy bands and exciton states, namely, three excitonic series are observed in the absorption spectra of these crystals: dipole allowed C-series at \( \textbf{E} \parallel Z(c) \) polarization originating from S-states of C-exciton (this series is observed in reflection spectra as well), forbidden B-series at \( \textbf{E} \perp Z(c) \) polarization originating from S-states of B-exciton, and partially allowed A-series at \( \textbf{E} \parallel X \) polarization originating from S-states of A-exciton (see e.g. Refs. \[2, 3, 4\] for ZnP_2 and Refs. \[1, 2, 3\] for ZnAs_2). In the photoluminescence (PL) spectra of these crystals at \( \textbf{E} \parallel Z(c) \) polarization, a series of lines caused by the radiative transitions from the ground and excited states of allowed C-exciton is observed (see e.g. Ref. \[5\] for ZnP_2 and Ref. \[6\] for ZnAs_2). Besides this emission series, the so-called B-line is observed in the PL spectra of ZnP_2 at \( \textbf{E} \perp Z(c) \). B-line occurs due to the radiative transitions from the ground state of forbidden B-exciton and corresponds to B1-line of absorption B-series.

In contrast to ZnP_2 and ZnAs_2 crystals, CdP_2 is indirect-gap semiconductor (energy gap: 2.155 eV; see, e.g. \[4\]), which is characterized by the different symmetry of lattice: symmetry group is \( D_4^h \) for right-rotating and \( D_4^a \) for left-rotating modification (tetragonal syngony). Therefore, the comparison study of an influence of substitution of \( P \) by As in Zn(P_{1-x}As_x)\_2 and of \( Zn \) by \( Cd \) in Zn_{1-x}Cd_xP_2 on parameters of energy bands and excitonic states seems to be rather interesting.

The technological operations of growing of Zn(P_{1-x}As_x)\_2 and Zn_{1-x}Cd_xP_2 crystals were carried out according to described in Ref. \[1\].

2 Zn(P_{1-x}As_x)\_2 crystals over the full range of \( x \)

In the present work the low-temperature (1.8 K) absorption, reflection and photoluminescence spectra of Zn(P_{1-x}As_x)\_2 crystals have been studied at the following levels of substitution of \( P \) by As: \( x = 0.01, 0.02, 0.03, 0.05, 0.10, 0.125, 0.40, 0.90, 0.95 \). Respective spectra as well as spectra of pure ZnP_2 (\( x = 0 \)) and ZnAs_2 (\( x = 1 \)) are presented in Fig. \[1\]. As one can expect, the Zn(P_{1-x}As_x)\_2 crystals are direct-gap semiconductors as well as ZnP_2 and ZnAs_2. One can see from the figure, that in the mixed crystals the same excitonic C-,
B- and A-series are observed, as in pure crystals. Let us note the doublet structure of an absorption $n = 1$ line of B-series in crystals with $x = 0.02$. Proceeding from intensities and half-widths of the components of this doublet, we have made a conclusion, that narrow high-energy component is $n = 1$ line of B-series. An origin of low-energy component, which is missing for crystals with $x \neq 0.02$, is not clear. One can see from absorption and reflection spectra of Zn($P_{1-x}As_x$)$_2$ crystals that at the increase of $x$ (or at the increase of $1 - x$ if to go from the ZnAs$_2$ side) the lines corresponding to exciton states with higher $n$ disappear, and the lines with $n = 1, 2$ broaden. Probably, this fact is a result of "blurring" of the band edges, which takes place owing to fluctuations of crystal potential, caused by chaotic distribution of As ($P$) atoms in sites of lattice at substitution of $P$ ($As$) atoms. In PL spectra the emission lines of free excitons can be easily separated from the lines of localized excitons (including, most likely, emission of excitons autholocalized on half-widths of these lines. As we have pointed out above, half-width of the B- and A-series are observed, as in pure crystals. Let us note the doublet structure of an absorption $P_x$ line of B-series in crystals with $x = 0.02$. The respective dependence $E_g(x)$ is given in Fig. 2(a). The dependence is slightly nonlinear (sublinear). It has been fitted by the well-known dependence (see, e.g. Ref. [4])

$$E_g(x) = E_{g1} - (E_{g1} - E_{g2})x + cx(1 - x), \tag{1}$$

where $E_{g1}$ and $E_{g2}$ are the energy gaps of ZnP$_2$ and ZnAs$_2$ respectively, and $c$ is the coefficient of nonlinearity. The coefficient $c$ was obtained to be 0.05. But besides the trivial decrease of $E_g$ with the increase of $x$, there is also decrease of the excitonic series rydbergs (see Fig. 2(b)). Values of $E_g$ and rydbergs were obtained from fitting of excitonic series by simple hydrogenlike dependence: $E(n) = E_g - Ry/n^2$. One can see from the figure that the dependences of excitonic rydbergs on $x$ are rather remarkable. These dependences are strongly superlinear at small $x$ (close to ZnP$_2$) and most linear at $x \rightarrow 1$ (close to ZnAs$_2$). Strongest superlinearity takes place at $x \leq 0.05$. Let us note that the rydbergs of B- and A-series decrease considerably: at crossing from ZnP$_2$ to ZnAs$_2$ the rydbergs decrease more than in 3 times. Meanwhile, the rydberg of A-series decreases sufficiently less: it decreases in 1.4 times. Let us note that in ZnP$_2$ the $n = 1$ state of A-exciton is energy highest, and the $n = 1$ state of B-exciton is energy lowest. But, due to the slower decrease of $Ry_a(x)$ than ones observed for B- and A-series, at substitution levels $x \sim 0.70$ the $n = 1$ state of A-exciton leaves off to be the energy highest. And in extreme case of ZnAs$_2$ an opposite situation takes place: $A_1$-state is energy lowest. The $n = 1$ state of allowed C-exciton is energy highest in ZnAs$_2$ crystal. There are exist two possible causes of such a fast decrease of excitonic rydbergs at small $x$. First one is the decrease of exciton reduced mass at the increase of $x$. This our assumption is based on the data of the exciton reduced masses in ZnP$_2$ ($\mu_a = 0.45m_0$, $\mu_c = 0.10m_0$ and $\mu_b = 0.56m_0$ [1]) and ZnAs$_2$ ($\mu_{ab,c} = 0.30m_0$ [2, 3]) as well as on our previous evaluation of the dependences of $m_e(x)$ and $m_h(x)$ at small $x$ [1]. Here, $\mu_{a,b,c}$ is the components of the reduced mass of exciton in ZnP$_2$ in different crystallographic directions, and $\mu_{ab,c}$ is the component of $\mu$ in the direction perpendicular to plane (100) (this direction almost coincides with a axis of crystal). Second cause of the fast decrease of rydbergs at small $x$ is the possible fast increase of dielectric constant, as in ZnAs$_2$ $\epsilon$ is sufficiently higher: average value 15 [2] versus $\epsilon_a = 9.1$, $\epsilon_c = 9.3$ and $\epsilon_b = 10.1$ in ZnP$_2$. Slower decrease of excitonic rydbergs at higher $x$ can be most likely explained by possible slower decrease of the reduced exciton mass and increase of the dielectric constant at higher $x$.

There were also studied dependences on $x$ of the half-widths of absorption $n = 1$ lines of B- and A-series. These dependences are given in Fig. 3. One can see, that half-widths of $B_1$- and $A_1$-lines increase monotonously with the increase of $x$. As known, the increase of half-width of exciton lines is the result of fluctuations of crystal potential and respective fluctuations of energy gap. The theory of influence of fluctuations of composition $x$ on half-width of exciton absorption lines was developed in Ref. [3], where two extreme cases were considered. First one takes place, if the effective size of area of the crystal potential fluctuation $R_D = \hbar/(2MD)^{1/2}$, where $M$ is the total mass of exciton and $D(x) = W(x) - W(0)$ ($W(x)$ is

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1Further, writing "the increase of $x$" we mean the increase of $x$ at $x \leq 0.50$ and the increase of $1 - x$ at $x > 0.50$.

2An absence of data on the half-width of lines of crystal with $x = 0.03$ is due to the fact that the respective sample was rather thick, therefore, full absorption occurred in $B_1$- and $A_1$-lines. So, it was not possible to determine correctly the half-widths of these lines. As we have pointed out above, half-width of $B_1$-line for crystal with $x = 0.02$ was determined for the high-energy component of doublet.
the half-width of exciton line), is much larger than exciton Bohr radius: $R_D >> a_{ex}$. Such situation, as a rule, takes place, if the effective masses of electron and hole are small and differ slightly: $m_e \sim m_h$. In this case $D$ should depend on $x$ as

$$D(x) = 0.08 \alpha^4 M^3 x^2 (1 - x)^2 / R^6 N^2,$$

(2)

where $\alpha = dE_g/dx$, $N$ is the concentration of sites of lattice, where the substituting atoms can ”sit”. Such a situation occurs in many semiconductors, in particular in $A_II\!I\!I$ $B_V$ crystals. The second case takes place at $R_D << a_{ex}$. It takes place at $m_h >> m_e$. In this case, dependence $D(x)$ has such character

$$D(x) = 0.5 \alpha (x(1 - x) / N a_{ex}^2)^{1/2}.$$

(3)

The experimental dependences $D(x)$ for absorption $B_1$- and $A_1$-lines of Zn(P$_{1-x}$As$_x$)$_2$ crystals are presented in Fig. 3. Likely to data presented in our work [1] the experimental points are badly fitted both by function (2) and (3). In ZnP$_2$ and ZnAs$_2$ crystals the effective size of area of crystal potential fluctuation is about some tens of angstrom, and the Bohr radii of B- and A-excitons in these crystals are the following: $a_B = 16 \AA$, $a_A = 29.5 \AA$ in ZnP$_2$, and $a_B = 34 \AA$, $a_A = 25.7 \AA$ in ZnAs$_2$, i.e. $R_D \sim a_{ex}$. Therefore, the extreme conditions $R_D >> a_{ex}$ and $R_D << a_{ex}$ are not fulfilled, and the intermediate case takes place which is, nevertheless, more close to case of Eq. (2). Therefore, since the intermediate case takes place, the experimental dependences can be fitted by the function

$$D(x) = (1 - c)D_1(x) + c D_2(x),$$

(4)

which is the superposition of function $D_1(x)$ of type (2) and $D_2(x)$ of type (3), $c$ is the weighting factor. One can see from Fig. 3 that for the mixed crystals close to ZnP$_2$, i.e. at $x \to 0$, the experimental dependence of the half-width of $B_1$-line on $x$ is fitted by function (3) rather well, and the contribution of the function (2) is rather small ($c = 0.05$). The situation is quite different for the mixed crystals close to ZnAs$_2$, i.e. at $x \to 1$, as the contribution of the function (2) is considerably larger ($c = 0.20$). It is rather simple to understand, as the Bohr radius of B-exciton in ZnAs$_2$ is about two times larger than in ZnP$_2$. So, in ZnP$_2$ the condition $R_D >> a_{ex}$ is fulfilled better than in ZnAs$_2$. For the dependence of the half-width of $A_1$-lines on $x$ we have the opposite situation. For the mixed crystals close to ZnP$_2$, the experimental dependence of the half-width of $A_1$-line on $x$ deviates considerably from function (2), and the contribution of the function (3) is rather large ($c = 0.29$). For the mixed crystals close to ZnAs$_2$, the contribution of the function (2) to the fitting function is quite small ($c = 0.08$). The Bohr radius of A-exciton, as we have noted above, almost does not differ in ZnP$_2$ and ZnAs$_2$. So, as the contribution of function (2) at $x \to 1$ is smaller than at $x \to 0$, the condition $R_D >> a_{ex}$ is fulfilled better for A-exciton in the crystals close to ZnAs$_2$. Thus, we can make a conclusion of larger effective size of area of the crystal potential fluctuation in crystals close to ZnAs$_2$, than in ones close to ZnP$_2$.

3 Zn(P$_{1-x}$As$_x$)$_2$ and Zn$_{1-x}$Cd$_x$P$_2$ at small $x$: comparison

The comparison studies of the low-temperature absorption, reflection and photoluminescence spectra of Zn(P$_{1-x}$As$_x$)$_2$ and Zn$_{1-x}$Cd$_x$P$_2$ crystals have been performed at small levels of substitution of Zn by Cd: $x \leq 0.05$. Respective spectra of Zn(P$_{1-x}$As$_x$)$_2$ are presented in Fig. 3 and the spectra of Zn$_{1-x}$Cd$_x$P$_2$ – in Fig. 4. In spite of the difference of the symmetries of lattice and structure of energy bands of ZnP$_2$ and CdP$_2$ crystals (monoclinic and tetragonal, direct- and indirect-gap respectively: see Sect. 1), at small $x$ Zn$_{1-x}$Cd$_x$P$_2$ remain the direct-gap crystals with monoclinic lattice. One can see from the figure, that in the Zn$_{1-x}$Cd$_x$P$_2$ crystals the same excitonic C-, B- and A-series are observed, as well as in pure ZnP$_2$ and mixed Zn(P$_{1-x}$As$_x$)$_2$ crystals. One can see from absorption and reflection spectra that, likely to Zn(P$_{1-x}$As$_x$)$_2$, already at rather small $x$ only the excitonic states with $n = 1, 2$ are observed clearly in the spectra of Zn$_{1-x}$Cd$_x$P$_2$. The higher components of exciton spectra disappear, and the lines with $n = 1, 2$ broaden. In PL spectra, at the increase of $x$ the emission lines of both free and localized excitons broaden. As noted above (see Sect. 3), all these effects are due to the fluctuations of crystal potential and corresponding fluctuations of the parameters of energy bands. Likely to Zn(P$_{1-x}$As$_x$)$_2$, an effect of considerable increase of intensity of PL spectra at the increase of $x$ takes place in Zn$_{1-x}$Cd$_x$P$_2$ crystals too. An explanation of such an effect is given as well in Sect. 3.

In spite of the fact that the CdP$_2$ crystal has larger energy gap than the ZnP$_2$, likely to Zn(P$_{1-x}$As$_x$)$_2$ there is a decrease of the energy gap of Zn$_{1-x}$Cd$_x$P$_2$ crystals at the increase of $x$ (see Fig. 4(a)). But the decrease of $E_g$ in Zn$_{1-x}$Cd$_x$P$_2$ is much slower. And, besides the similarity in dependences of $E_g(x)$, both
Zn(P1−xAsx)2 and Zn1−xCdxP2 crystals have the similarity in the dependences of the rydbergs of excitons on x as well (see Fig. 3(b)). The rydbergs of all the three A-, B-, and C-series decrease at the increase of x. But, also likely to the dependence E0(x), the excitonic rydbergs in Zn1−xCdxP2 decrease considerably slower than in Zn(P1−xAsx)2. Considerably weaker dependences of the energy gap and the rydbergs on x in Zn1−xCdxP2 are, most probably, the results of the weaker changes in parameters of the energy bands, in particular in effective masses of electrons and holes, and in dielectric constant. But, at higher x one can expect the more interesting and stronger changes in the parameters of energy bands and excitonic states with regard to the fact that CdP2 and ZnP2 have the different symmetry of lattice, and that CdP2 is indirect-gap semiconductor.

The dependences of half-widths of absorption B1- and A1-lines on x have been also studied in Zn1−xCdxP2 crystals. The results of comparison of such dependences with ones observed for Zn(P1−xAsx)2 are presented in Fig. 3. One can see that D(x) dependences for both types of the mixed crystals are similar for exciton B1-line. This dependences are described rather well by the function of Eq. (2) type, contributions of the function (3) are quite small for both type crystals: the weighting factor is c = 0.05 for Zn(P1−xAsx)2 and c = 0.035 for Zn1−xCdxP2. It is an evidence that in both cases the effective size of area of the crystal potential fluctuation RD is rather large comparing to the exciton Bohr radius ac. Likely to Zn(P1−xAsx)2, in Zn1−xCdxP2 the dependence of half-width of A1-line on x deviates strongly from the function (2), the contribution of the function (3) is large. As we assumed above, it is the result of the fact that A-exciton has considerably lower binding energy comparing to B-exciton, and larger Bohr radius correspondingly. So, the condition RD >> ac is not fulfilled, and the dependence D(x) is not described by the function (2). At the same time, there are two remarkable features of D(x) dependence for A1-line in Zn1−xCdxP2. First one is the considerable deviations of the experimental points from the fitting function. It is quite remarkable as such deviations are very small for the D(x) dependences for A1-line in Zn(P1−xAsx)2 and for B1-line in the mixed crystals of both types. Second one is the fact that the contribution of the function (2) is determinant in the fitting function: the weighting factor of the function (3) is c = 0.89. For Zn(P1−xAsx)2 the contribution of the function (3) is considerably smaller: c = 0.29. At present moment, both above features of D(x) dependence for A1-line in Zn1−xCdxP2 are obscure. Thus, a comparison of the energy bands and exciton parameters behaviour versus x reveals as similar tendencies and different ones.

4 Conclusions

In conclusion, we have obtained the following results. We have found that, likely to "pure" ZnP2 crystal, both in Zn(P1−xAsx)2 and Zn1−xCdxP2 mixed crystals the same three excitonic hydrogenlike series (C, B, and A) are observed. At the increase of x in the range of small x (0 ≤ x ≤ 0.05) the decrease of the energy gap and exciton rydbergs takes place. The dependences of Eg and Ry on x are considerably stronger in Zn(P1−xAsx)2 than in Zn1−xCdxP2.

Besides the comparison study of these crystals at small x, the Zn(P1−xAsx)2 crystals have been studied over the full range of x: 0 ≤ x ≤ 1. We have obtained the following results for Zn(P1−xAsx)2. At the increase of x the energy gap decreases slightly sublinearly. The exciton rydbergs decrease as well. The dependences Ry(x) are strongly superlinear at small x (close to ZnP2) and most linear at x → 1 (close to ZnAs2). At the crossing from ZnP2 to ZnAs2, the rydbergs of B- and C-series decrease more than in 3 times. Meanwhile, the rydberg of A-series decreases sufficiently less: in 1.4 times.

At the increase of x the half-width of excitonic absorption lines increases monotonically both in Zn(P1−xAsx)2 and Zn1−xCdxP2 crystals that is evidence of the increasing role of fluctuations of crystal potential.

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Figure 1: Optical spectra of Zn(P$_{1-x}$As$_x$)$_2$ crystals at temperature 1.8 K. (a) Absorption spectra. Observation conditions: $\mathbf{q} \perp (110)$, $\mathbf{E} \perp Z(\mathbf{c})$ - for crystals with any $x$ except $x = 0.05$; $\mathbf{q} \perp (100)$, $\mathbf{E} \perp Z(\mathbf{c})$ - for crystals with $x = 0.05$. (b) Reflection spectra. Observation conditions: $\mathbf{q} \perp (100)$, $\mathbf{E} \parallel Z(\mathbf{c})$. (c) Photoluminescence spectra. Observation conditions: $\mathbf{q} \perp (100)$. 
Figure 2: (a) Dependence of energy gap on $x$ for Zn(P$_{1-x}$As$_x$)$_2$ crystals. Solid line represents fitting of the experimental points by expression (1), dotted one is the line connecting points of two extreme cases: ZnP$_2$ ($x = 0$) and ZnAs$_2$ ($x = 1$). (b) Dependences of excitonic rydbergs on $x$ for Zn(P$_{1-x}$As$_x$)$_2$. Connected open squares - experimental dependence for B-series, connected solid up triangles - the same for C-series, connected open diamonds - the same for A-series. Dashed line connects two extreme cases (mentioned above in this caption) for B-series, dotted one - for C-series, dashed-dotted one - for A-series.
Figure 3: Dependences of half-widths of excitonic absorption $B_1$- and $A_1$-lines in Zn(P$_{1-x}$As$_x$)$_2$ crystals on $x$. Open circles and squares - experimental dependences for $B_1$- and $A_1$-lines in crystals close to ZnP$_2$ ($x \leq 0.125$: bottom x-axis); solid circles and squares - the same for $B_1$- and $A_1$-lines in crystals close to ZnAs$_2$ ($x \geq 0.90$: top x-axis). Solid lines represent the fitting of experimental points by expression (4) for crystals with $x \leq 0.125$; dashed lines - the same for crystals with $x \geq 0.90$. 

$c_{A1} = 0.08$
$c_{B1} = 0.05$
$c_{A0} = 0.29$
$c_{B0} = 0.20$
Figure 4: Optical spectra of Zn$_{1-x}$Cd$_x$P$_2$ crystals at temperature 1.8 K. (a) Absorption spectra. Observation conditions: $\mathbf{q} \perp (110), \mathbf{E} \perp Z(c)$. (b) Reflection spectra. Observation conditions: $\mathbf{q} \perp (100), \mathbf{E} \parallel Z(c)$. (c) Photoluminescence spectra. Observation conditions: $\mathbf{q} \perp (100)$. 
Figure 5: (a) Dependences of energy gap on $x$ for Zn(P$_{1-x}$As$_x$)$_2$ (connected open circles) and Zn$_{1-x}$Cd$_x$P$_2$ crystals (connected open squares). (b) Dependences of excitonic rydbergs on $x$ for Zn(P$_{1-x}$As$_x$)$_2$ and Zn$_{1-x}$Cd$_x$P$_2$. Connected open circles, squares, and up triangles - the dependences $Ry(x)$ for B-, C-, and A-series of Zn(P$_{1-x}$As$_x$)$_2$ crystals respectively; connected solid circles, squares, and up triangles - the dependences $Ry(x)$ for B-, C-, and A-series of Zn$_{1-x}$Cd$_x$P$_2$ crystals respectively.
Figure 6: Dependences of half-widths of excitonic absorption $B_1$- and $A_1$-lines on $x$: open circles and squares respectively – in Zn$(P_{1-x}As_x)_2$, and solid circles and squares respectively – in Zn$_{1-x}$Cd$_x$P$_2$ crystals. Solid lines represent the fitting of experimental points by expression (4) for Zn$(P_{1-x}As_x)_2$ crystals; dashed lines - the same for Zn$_{1-x}$Cd$_x$P$_2$ crystals.