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Comparison study of energy bands and Wannier-Mott excitons in mixed $Zn(P_{1-x}As_x)_2$ 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 $Ry(x)$ 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 Ry 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.

PACS. 71.35.-y Excitons and related phenomena – 74.62.Dh Effects of crystal defects, doping and substitution

1 Introduction

In reference [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 $A^{II}B^{V}$ type, which are poorly investigated.

β-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 $\mathbf{E} \parallel Z(\mathbf{c})$ polarization originating from S-states of C-exciton (this series is observed in reflection spectra as well), forbidden B-series at $\mathbf{E} \perp Z(\mathbf{c})$ polarization originating from S-states of B-exciton, and partially allowed A-series at $\mathbf{E} \parallel X$ polarization originating from S-states of A-exciton (see *e.g.* Refs. [2–4] for ZnP_2 and Refs. [5–7] for $ZnAs_2$). In the photoluminescence (PL) spectra of these crystals at $\mathbf{E} \parallel Z(\mathbf{c})$ 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. [8] for ZnP_2 and Ref. [5] for $ZnAs_2$). Besides this emission series, the so-called B-line is observed in the PL spectra of ZnP_2 at $\mathbf{E} \perp Z(\mathbf{c})$. B-line occurs due to the radiative transitions from the ground state of forbidden B-exciton and corresponds to B_1-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.* [9]), which is characterized by the different symmetry of lattice: symmetry group is D_4^4 for right-rotating and D_4^8 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 reference [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

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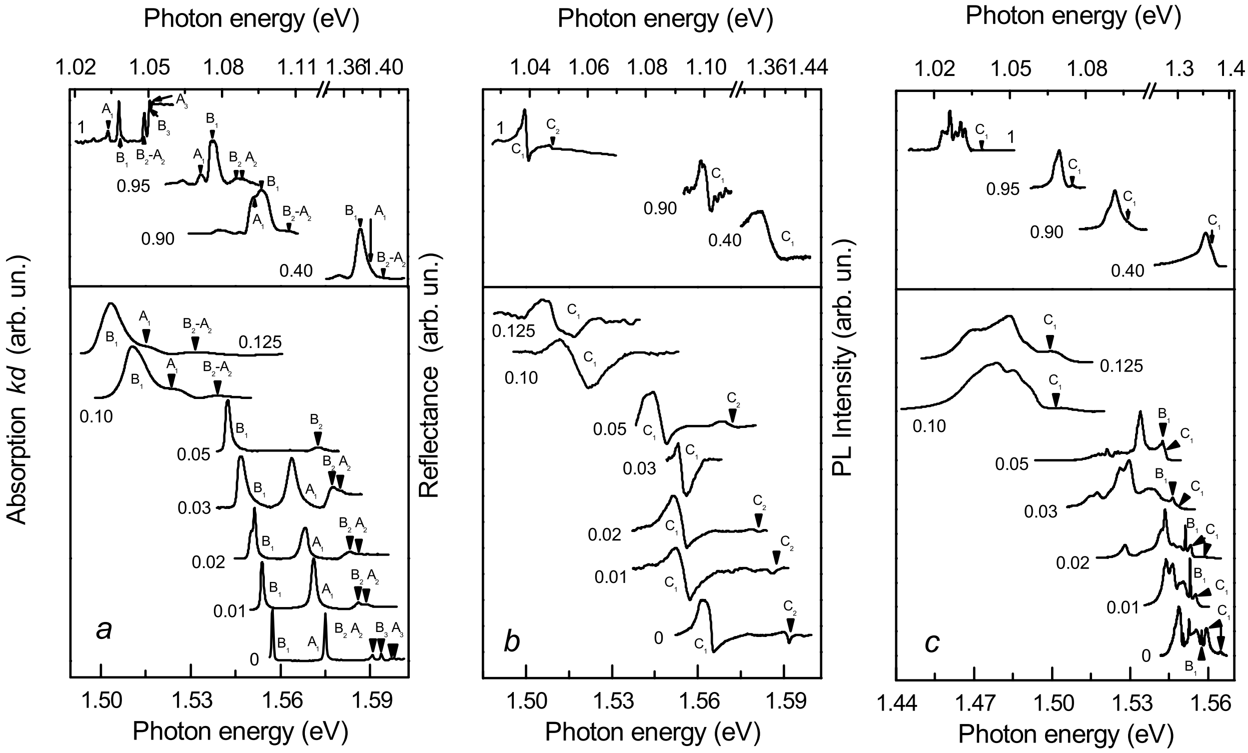

Fig. 1. Optical spectra of $Zn(P_{1-x}As_x)_2$ crystals at temperature 1.8 K. (a) Absorption spectra. Observation conditions: $\mathbf{q} \perp (110)$, $\mathbf{E} \perp Z(\mathbf{c})$ - for crystals with any x except $x = 0.05$; $\mathbf{q} \perp (100)$, $\mathbf{E} \perp Z(\mathbf{c})$ - for crystals with $x = 0.05$. (b) Reflection spectra. Observation conditions: $\mathbf{q} \perp (100)$, $\mathbf{E} \parallel Z(\mathbf{c})$. (c) Photoluminescence spectra. Observation conditions: $\mathbf{q} \perp (100)$.

$Zn(P_{1-x}As_x)_2$ 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 Figure 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)[1] 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 fluctuations of crystal potential) only at rather low substitution levels. At the increase of x the emission lines of both free and localized excitons broaden that is due to the fluctuations of crystal potential and corresponding fluctuations of the parameters of energy bands. It takes an attention on itself the fact of considerable increase of intensity of PL spectra at the increase of x. Most probably, this effect is due to two following causes. First one consists in the partial suppression of the spatial migration of excitons (due to localization of excitons on fluctuations of crystal potential) and the respective decrease of efficiency of non-radiative decay of excitons. Second one consists in the fact that the processes of scattering of excitons on the lattice defects favour to more effective radiative decay of excitons.

With increase in concentration x, spectral lines shift to the low-energy side, which is caused by the decrease of energy gap. This shift could be easily expected, taking into account the fact, that in $ZnAs_2$ energy gap is 0.55 eV smaller than in ZnP_2. The respective dependence $E_g(x)$ is given in Figure 2a. The dependence is slightly nonlinear (sublinear). It has been fitted by the well-known dependence (see, *e.g.* Ref. [10])

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

where E_{g1} and E_{g2} are the energy gaps of ZnP_2 and $ZnAs_2$ respectively, and c is the coefficient of nonlinearity.

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

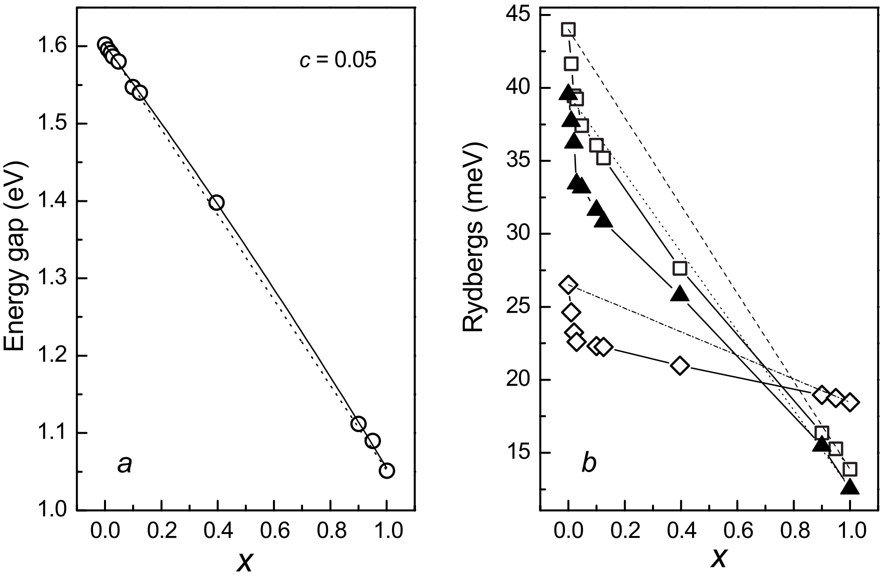

Fig. 2. (a) Dependence of energy gap on x for $Zn(P_{1-x}As_x)_2$ crystals. Solid line represents fitting of the experimental points by expression (1), dotted one is the line connecting points of two extreme cases: ZnP_2 ($x = 0$) and $ZnAs_2$ ($x = 1$). (b) Dependences of excitonic rydbergs on x for $Zn(P_{1-x}As_x)_2$. 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.

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. 2b). 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 $x \to 1$ (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 $\mu_b = 0.56m_0$ [11]) and $ZnAs_2$ ($\mu_{\perp bc} = 0.30m_0$ [5,7]) 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 $\mu_{\perp bc}$ is the component of μ 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 $ZnAs_2$ ϵ is sufficiently higher: average value 15 [5] *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 Figure 3[2]. One can seen, 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 reference [12], 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 the half-width of exciton line), is much larger than exciton Bohr radius: $R_D \gg a_{ex}$. Such situation, as a rule,

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[2] An absence of data on the half-widths of lines for 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.

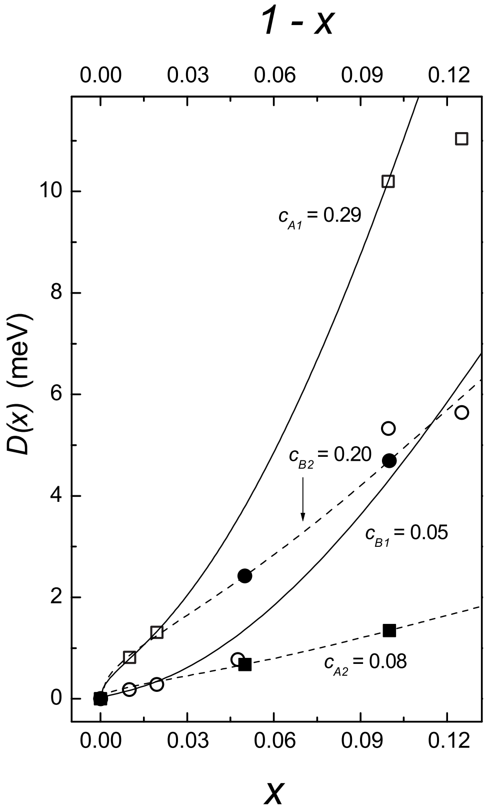

Fig. 3. Dependences of half-widths of excitonic absorption B_1- and A_1-lines in $Zn(P_{1-x}As_x)_2$ crystals on x. Open circles and squares – experimental dependences for B_1- and A_1-lines in crystals close to ZnP_2 ($x \leq 0.125$: bottom x-axis); solid circles and squares – the same for B_1- and 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 $x \geq 0.90$.

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

$$D(x) = 0.08\frac{\alpha^4 M^3 x^2(1-x)^2}{\hbar^6 N^2}, \qquad (2)$$

where $\alpha = \mathrm{d}E_g/\mathrm{d}x$, N is the concentration of sites of lattice, where the substituting atoms can "sit". Such a situation occurs in many semiconductors, in particular in $A^{III}B^{V}$ crystals. The second case takes place at $R_D \ll a_{ex}$. It takes place at $m_h \gg m_e$. In this case, dependence $D(x)$ has such character

$$D(x) = 0.5\alpha\left(\frac{x(1-x)}{Na_{ex}^3}\right)^{1/2}. \qquad (3)$$

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 Figure 3. Likely to data presented in our work [1] the experimental points are badly fitted both by functions (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 Å, a_A = 29.5 Å in ZnP_2, and a_B = 34 Å, a_A = 25.7 Å in $ZnAs_2$, *i.e.* $R_D \sim a_{ex}$. Therefore, the extreme conditions $R_D \gg a_{ex}$ and $R_D \ll a_{ex}$ are not fulfilled, and the intermediate case takes place which is, nevertheless, more close to case of equation (2). Therefore, since the intermediate case takes place, the experimental dependences can be fitted by the function

$$D(x) = (1-c)D_1(x) + cD_2(x), \qquad (4)$$

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 Figure 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 (2) rather well, and the contribution of the function (3) 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 (3) 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 $R_D \gg a_{ex}$ is fulfilled better than in $ZnAs_2$. For the dependence of the half-width of A_1-lines on x we have the quite 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 (3) 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 (3) at $x \to 1$ is smaller than at $x \to 0$,the condition $R_D \gg a_{ex}$ 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 $Zn_{1-x}Cd_xP_2$ 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 $Zn_{1-x}Cd_xP_2$ 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 Figure 1, and the spectra of $Zn_{1-x}Cd_xP_2$ – in Figure 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 $Zn_{1-x}Cd_xP_2$ remain the direct-gap crystals with monoclinic lattice. One can see from the figure, that in the $Zn_{1-x}Cd_xP_2$ 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,

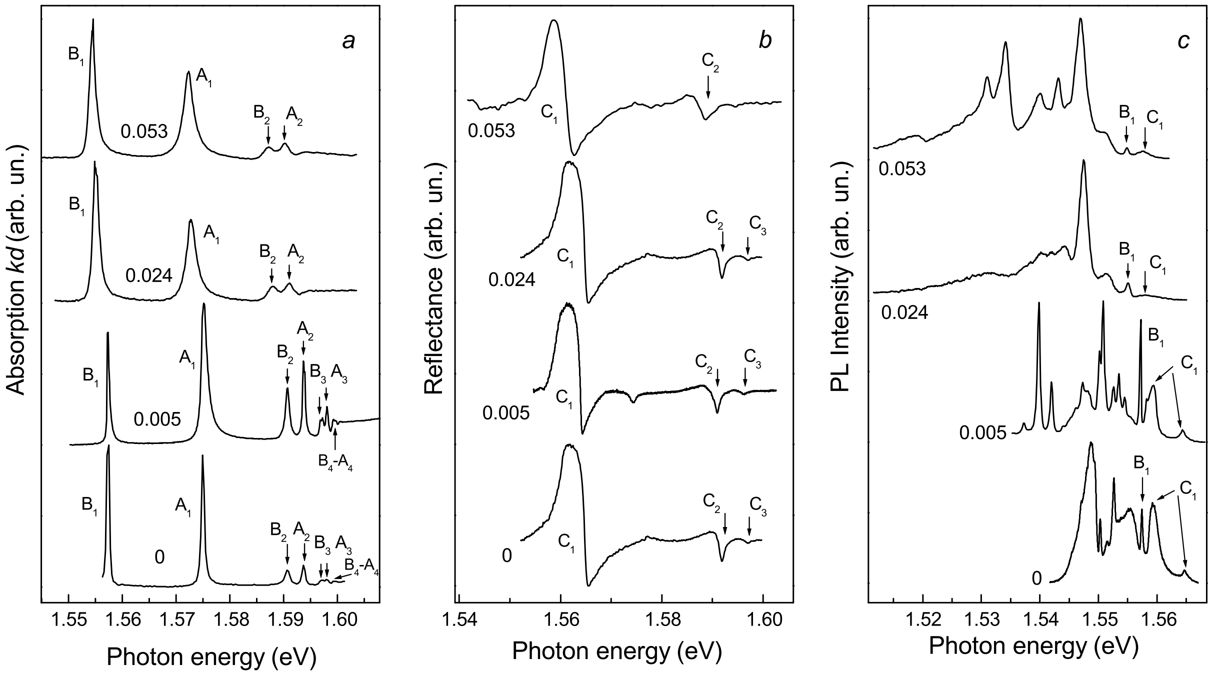

Fig. 4. Optical spectra of $Zn_{1-x}Cd_xP_2$ crystals at temperature 1.8 K. (a) Absorption spectra. Observation conditions: $\mathbf{q} \perp (110)$, $\mathbf{E} \perp Z(\mathbf{c})$. (b) Reflection spectra. Observation conditions: $\mathbf{q} \perp (100)$, $\mathbf{E} \parallel Z(\mathbf{c})$. (c) Photoluminescence spectra. Observation conditions: $\mathbf{q} \perp (100)$.

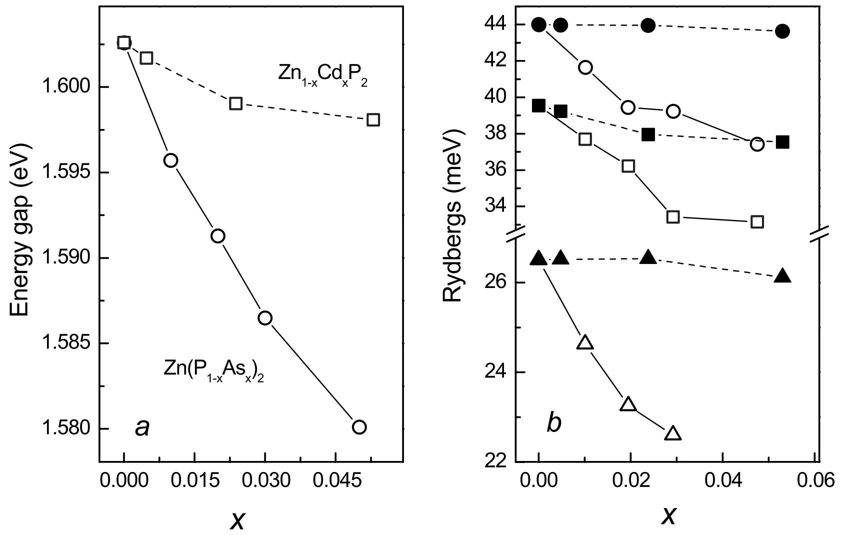

Fig. 5. (a) Dependences of energy gap on x for $Zn(P_{1-x}As_x)_2$ (connected open circles) and $Zn_{1-x}Cd_xP_2$ crystals (connected open squares). (b) Dependences of excitonic rydbergs on x for $Zn(P_{1-x}As_x)_2$ and $Zn_{1-x}Cd_xP_2$. Connected open circles, squares, and up triangles – the dependences $Ry(x)$ 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 $Zn_{1-x}Cd_xP_2$ crystals respectively.

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 $Zn_{1-x}Cd_xP_2$ crystals. 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. 2), 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 $Zn_{1-x}Cd_xP_2$ crystals too. An explanation of such an effect is given as well in Section 2.

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 $Zn_{1-x}Cd_xP_2$ crystals at the increase of x (see Fig. 5a). But the decrease

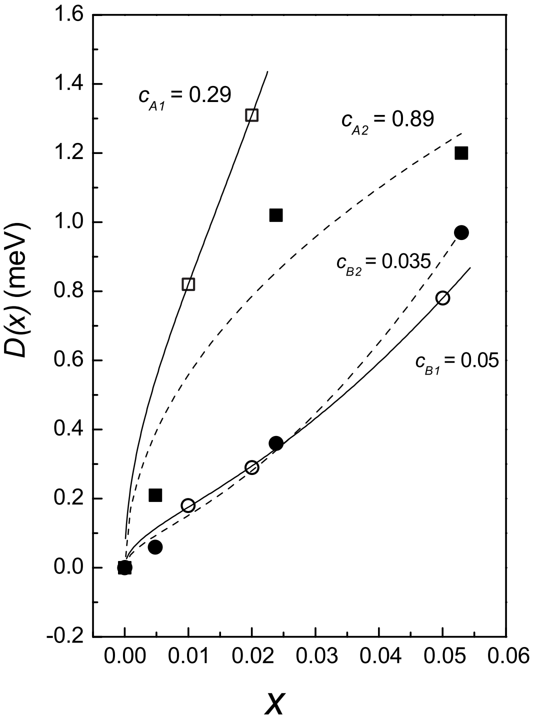

Fig. 6. Dependences of half-widths of excitonic absorption B_1- and A_1-lines on x: open circles and squares respectively – in $\mathrm{Zn(P_{1-x}As_x)_2}$, and solid circles and squares respectively – in $\mathrm{Zn_{1-x}Cd_xP_2}$ crystals. Solid lines represent the fitting of experimental points by expression (4) for $\mathrm{Zn(P_{1-x}As_x)_2}$ crystals; dashed lines – the same for $\mathrm{Zn_{1-x}Cd_xP_2}$ crystals.

of E_g in $\mathrm{Zn_{1-x}Cd_xP_2}$ is much slower. And besides the similarity in dependences of $E_g(x)$, both $\mathrm{Zn(P_{1-x}As_x)_2}$ and $\mathrm{Zn_{1-x}Cd_xP_2}$ crystals have the similarity in the dependences of the rydbergs of excitons on x as well (see Fig. 5b). The rydbergs of all the three A-, B-, and C-series decrease at the increase of x. But, also likely to the dependence $E_g(x)$, the excitonic rydbergs in $\mathrm{Zn_{1-x}Cd_xP_2}$ decrease considerably slower than in $\mathrm{Zn(P_{1-x}As_x)_2}$. Considerably weaker dependences of the energy gap and the rydbergs on x in $\mathrm{Zn_{1-x}Cd_xP_2}$ 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 $\mathrm{CdP_2}$ and $\mathrm{ZnP_2}$ have the different symmetry of lattice, and that $\mathrm{CdP_2}$ is indirect-gap semiconductor.

The dependences of half-widths of absorption B_1- and A_1-lines on x have been also studied in $\mathrm{Zn_{1-x}Cd_xP_2}$ crystals. The results of comparison of such dependences with ones observed for $\mathrm{Zn(P_{1-x}As_x)_2}$ are presented in Figure 6. One can see that $D(x)$ dependences for both types of the mixed crystals are similar for exciton B_1-line. This dependences are described rather well by the function of equation (2) type, contributions of the function (3) are quite small for both type crystals: the weighting factor is $c = 0.05$ for $\mathrm{Zn(P_{1-x}As_x)_2}$ and $c = 0.035$ for $\mathrm{Zn_{1-x}Cd_xP_2}$. It is an evidence that in both cases the effective size of area of the crystal potential fluctuation R_D is rather large comparing to the exciton Bohr radius a_{ex}. Likely to $\mathrm{Zn(P_{1-x}As_x)_2}$, in $\mathrm{Zn_{1-x}Cd_xP_2}$ the dependence of half-width of A_1-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 $R_D \gg a_{ex}$ 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 A_1-line in $\mathrm{Zn_{1-x}Cd_xP_2}$. 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 A_1-line in $\mathrm{Zn(P_{1-x}As_x)_2}$ and for B_1-line in the mixed crystals of both types. Second one is the fact that the contribution of the function (3) is determinative in the fitting function: the weighting factor of the function (3) is $c = 0.89$. For $\mathrm{Zn(P_{1-x}As_x)_2}$ the contribution of the function (3) in the fitting function is considerably smaller: $c = 0.29$. At present moment, both above features of $D(x)$ dependence for A_1-line in $\mathrm{Zn_{1-x}Cd_xP_2}$ 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" $\mathrm{ZnP_2}$ crystal, both in $\mathrm{Zn(P_{1-x}As_x)_2}$ and $\mathrm{Zn_{1-x}Cd_xP_2}$ 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 ($0 \leq x \leq 0.05$) the decrease of the energy gap and exciton rydbergs takes place. The dependences of E_g and Ry on x are considerably stronger in $\mathrm{Zn(P_{1-x}As_x)_2}$ than in $\mathrm{Zn_{1-x}Cd_xP_2}$.

Besides the comparison study of these crystals at small x, the $\mathrm{Zn(P_{1-x}As_x)_2}$ crystals have been studied over the full range of x: $0 \leq x \leq 1$. We have obtained the following results for $\mathrm{Zn(P_{1-x}As_x)_2}$. 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 $\mathrm{ZnP_2}$) and most linear at $x \to 1$ (close to $\mathrm{ZnAs_2}$). At the crossing from $\mathrm{ZnP_2}$ to $\mathrm{ZnAs_2}$, 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 $\mathrm{Zn(P_{1-x}As_x)_2}$ and $\mathrm{Zn_{1-x}Cd_xP_2}$ crystals that is evidence of the increasing role of fluctuations of crystal potential.

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