On Wannier exciton 2D localization in hydrogen intercalated InSe and GaSe layered semiconductor crystals

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Abstract. Exciton absorption spectra of layered InSe and GaSe crystals electrochemically intercalated by hydrogen were investigated. It was found that the observed at $T = 80$ K non-monotonic shift of the exciton absorption peak $n = 1$ with growing hydrogen concentration x (here x is the amount of hydrogen atoms per a formula unit of a crystal matrix) stems from the increasing dielectric permittivity of the crystal ε_0 due to availability of hydrogen in the van der Waals gap. Growth of $\varepsilon_0(x)$ results in decrease of the exciton binding energy but, at larger x concentrations (when the anisotropy parameter $\varepsilon^*(x)$ grows), 2D localization of exciton motion in the crystal layer plane takes place, which causes reduction and then, at $x > 1$, stabilization of sizes both for the exciton and quantum well.

Keywords: exciton absorption, layered crystal, InSe, GaSe, quantum well.

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1. Introduction

A^3B^6 semiconductor compounds including layered γ-InSe and ε-GaSe crystals attract investigator's interest due to the fact that heterostructures of these crystals possess a good photosensitivity and find their application in solar cells [1-4]. By convention, the great attention of researchers is paid to intercalation, that is to insertion of atoms and molecules into the interlayer space of a layered crystal (the so-called van der Waals gap) where weak molecular bonds act between crystal layers. Appearance of great impurity amounts in the gap can essentially change the intrinsic electrical resistance of the crystal from semiconductor to metallic values in the direction perpendicular to the layer, can cause a growth of the crystal dielectric permeability [5], appearance of supplementary (local) interlayer vibrations in its phonon spectrum [6] and even crystal exfoliation when intercalation reaches a sufficient level [7].

Layered γ-InSe and ε-GaSe crystals are rather promising for hydrogen energetics as operating elements in systems for hydrogen accumulation [8-10]. The concentration of hydrogen in them can reach values $x = 3...5$, where x is the amount of introduced atoms per one formula unit of the crystal bulk.

In this work, we report on the investigations of the hydrogen intercalation influence on optical properties of γ-InSe and ε-GaSe crystals in the region of $n = 1$ exciton resonance.

2. Experimental part

Layered InSe and GaSe crystals belong to A^3B^6 binary compounds. The layers in them consist of four Se-In(Ga)-In(Ga)-Se sheets with three Se atoms coordinated to one In(Ga) atom that corresponds to spatial group D_{3h}^1 (see Fig. 1). The covalent In(Ga)-In(Ga) bonds are oriented perpendicular to the layers. Bridgman grown InSe and GaSe crystals have four (β-, δ-, ε-, and γ-) polytypes [11, 12], which differ by sequence of layers stacking. Thus, bulk InSe single crystals are related to the γ-polytype with the rhombohedral (trigonal) crystal structure (space group C_{3v}^5, one In_2Se_2 molecule in the primitive unit cell). The conventional hexagonal unit cell extends over three layers and consists of three In_2Se_2 molecules. GaSe single crystal has the ε-polytype structure. It belongs to the hexagonal crystal structure (space group D_{3h}^1) primitive unit cell of which consists of two Ga_2Se_2 molecules (eight atoms) located within two crystal layers [12].

Lattice parameters of γ-InSe and ε-GaSe crystals are well known. For ε-GaSe they are: $C_0 = 15.95$ Å and $a_0 = 3.755$ Å [13]. For γ-InSe they are: $C_0 = 25.32$ Å and
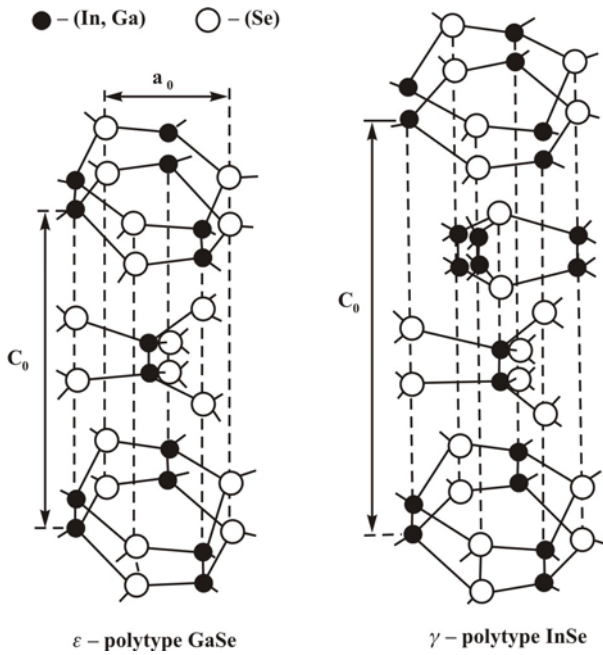
Fig. 1. The crystal structure and stacking of a crystal layers in γ-InSe and ε-GaSe.
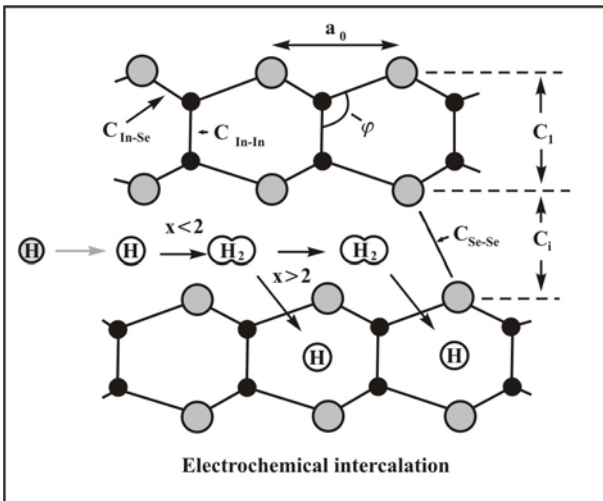
Fig. 2. Scheme demonstrates processes of hydrogen intercalation in layered crystals.

$a_0 = 4.001$ Å. Interlayer nearest-neighbour distances in layers (see Fig. 2) are $C_{\text{In-In}} = 2.79$ Å and $C_{\text{In-Se}} = 2.65$ Å, respectively; the angle $\varphi = 119.3°$, the layer thickness $C_1 = 5.36$ Å, the distance between layers $C_i = 3.08$ Å and their interlayer distance $C_{\text{Se-Se}} = 3.80$ Å [14, 15].

2.1. Intercalation

Hydrogen intercalation of single crystal γ-InSe and ε-GaSe samples of 10 to 20 μm thickness was carried out (like as in [10]) using the electrochemical method from 0.1 normal solution of hydrochloric acid with sweeping electric field in the galvanostatic regime. A special choice of the optimal current density enabled to obtain homogeneous in their composition intercalated with hydrogen H_xInSe and H_xGaSe samples within the range of concentrations $0 < x \le 2$. The hydrogen concentration in H_xInSe was determined via the quantity of electrical charge transported through the sample placed into the special cell. We assume that atomic hydrogen enters into the van der Waals gap where H_2 molecules creates that occupy positions schematically shown in Fig. 2.

In the present work, there was carried out the X-ray diffraction study of H_xGaSe crystals at 300 K. It was shown that the parameter C_0 grows with x and increases by 0.031 Å at $x = 1.0$. The same data about the growing C_0 parameter were observed also in [5] when GaSe crystals were intercalated with fluorine.

X-ray diffraction data are in a good agreement with our calculations for InSe, which, according to Clapeyron's equation $P = Nk_BT$ for the ideal gas pressure, shown that, at $x = 2$, in the interlayer space (equal to 9.4 MPa at $T = 80$ K and 35.4 MPa at $T = 300$ K) and in accordance to [15] pressure of H_2 caused an increase of the interlayer distance and the parameter C_0 growth by 0.024 ± 0.001 Å at $T = 300$ K and by 0.009 ± 0.001 Å at $T = 80$ K. Moreover, when $x = 2$ and $T = 80$ K the rotation of H_2 molecules in translationally ordered cites of the gap is practically absent (for H_2 $T_r = h^2/8\pi^2Jk_B = 90$ K, where J is the rotational moment of inertia) and this state may be treated as the state of a "quasi-liquid monolayer".

It was also shown that geometrical sizes of H_2 molecules and van der Waals gap have such values that causes the quantum-size effect. This effect together with a Pauli principle (for Fermi particles such as molecular para- and ortohydrogen in discrete states) caused a strong repulsion of more than one H_2 molecule in translationally ordered cites, shown in Fig. 2. This repulsion leads to the condition that, at $x > 2$, the only one molecule of H_2 remains in this van der Waals gap cites, while abundant atomic hydrogen should penetrate into interstices of crystal layers.

2.2. Absorption

Investigations of H_xInSe and H_xGaSe crystals absorption spectra were carried out at $T = 80$ K using the ½ m spectrometer with 600 grooves/mm diffraction grating and resolution not worse than 0.5 meV. As a light source, we used the incandesent filament lamp supplied from the stabilized direct current unit.

InSe and GaSe crystals are characterized with a weak interaction of 3D Wannier excitons with homopolar optical A′-phonons [16, 17]. Therefore, when calculating the exciton absorption spectra (see Fig. 3), we took into consideration effects of broadening the exciton states using the standard convolution procedure (see in [16]) for theoretical values of $\alpha(\hbar\omega)$ the absorption coefficient in the Elliott model [18] with $f(\hbar\omega) = \Gamma/[\pi(E^2+\Gamma^2)]$ the Lorentzian function in the
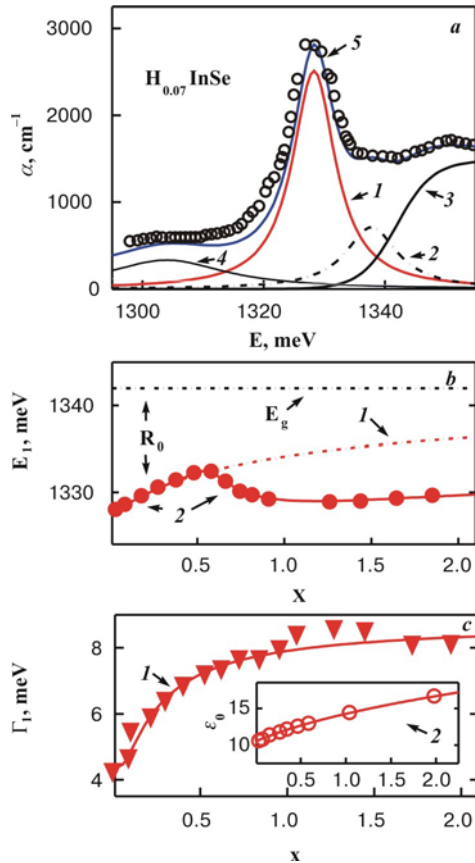
Fig. 3. Exciton absorption spectra of H_xInSe at $T = 80$ K.

a – experimental (open circles) and calculated (curve 5) exciton absorption spectra of $H_{0.07}InSe$ crystal at $T = 80$ K. Curves $1 – 4$ are the bands of $n = 1, 2$ exciton states, band-to-band transition and shallow donor states;

b – circles show experimental shift of $n = 1$ exciton absorption band maximum E_1 on x for H_xInSe. The line denoted as E_g shows the stable energy position of E_g on x. Curve 1 is plotted in accordance with the assumption of increase of the dielectric permeability ε_0. Curve 2 – with account of exciton localization in the layer plane. R_0 show a decrease of the exciton binding energy with x when exciton localization is ignored;

c – solid triangles show the experimental Γ_1 dependence on x. Curve 1 is plotted in accordance with Eq. (1) . In insert, open circles show the experimental ε_0 dependence on x. Curve 2 is plotted in accord to Eq. (5).

Toyozawa model [19], where Γ is the half-width at half-maximum which is usually associated with the lifetime $\hbar/2\Gamma$.

Basing on the performed calculations, it was shown that polaritonic effects associated with the growth of the integral intensity of $n = 1$ exciton absorption band K does not take place in our crystals at $T = 80$ K. Therefore, we suppose that $K \cong K^0$, where K^0 is the classical value. Thus, in Fig. 3, it was shown the experimental (open circles) and calculated (curve 5)

exciton absorption spectra of $H_{0.07}InSe$ crystal at $T = 80$ K.

At the same time, when introducing hydrogen into the interlayer space, one can observe the following peculiarities:

1. In Fig. 3b, depicted by circles is the experimental dependence of the maximum position for $n = 1$ exciton absorption bands E_1 on x for H_xInSe crystals. Within the range $0 < x \leq 0.5$, the peak energy position shifts upward by $\Delta E_1 = 4.5$ meV from $E_1 = 1327.5$ meV up to $E_1 = 1332.0$ meV; at $0.5 < x \leq 1$, it goes downward to the energy $E_1 = 1329.5$ meV; the further increase of hydrogen amount in the interlayer space does not result in changing $E_1(x)$ values.

2. In Fig. 3c, the curve of solid triangles means the change of the halfwidth Γ_1 of the $n = 1$ excitonic absorption band on x for H_xInSe crystals. It can be seen that Γ_1 increases with x within the range $0 < x \leq 1$ and becomes practically constant at $x > 1$. The experimental $\Gamma_1(x)$ dependence can be expressed by the following function:

$$\Gamma_1(x)\ [\text{meV}] = \Gamma_1\{1+1/\exp[1/(\Gamma_1 x)]\}, \qquad (1)$$

where $\Gamma_1 = 4.4$ meV.

The marked peculiarities of the nonlinear shift inherent to the $n = 1$ exciton absorption band maximum at $T = 80$ K with hydrogen concentration are also observed in H_xGaSe crystals. However, in H_xGaSe these phenomena are less pronounced. Thus, within the range $0 < x \leq 0.8$, the peak energy position shifts upward by $\Delta E_1 = 3.0$ meV from $E_1 = 2099.0$ meV up to $E_1 = 2102.0$ meV; at $0.8 < x \leq 1.5$, one can observe its shift down to the energy $E_1 = 2100.5$ meV; the further increase of hydrogen amount in the interlayer space does not result to changing $E_1(x)$ values. Simultaneously with $E_1(x)$ nonlinear shift experimental dependence Γ_1 also increases with x within the range $0 < x \leq 1.5$ and becomes practically constant at $x > 1.5$. For H_xGaSe, the experimental dependence $\Gamma_1(x)$ is in accordance with Eq. (1) for $\Gamma_1 = 3.6$ meV.

3. Discussion

At first, we shall carry out a discussion taking into account the experimental data obtained for InSe crystals and then generalize them to InSe and GaSe crystals.

The observed in InSe crystals shortwave shift of E_1 with x growth could be explained in a most simple way by a change of the forbidden gap E_g with the pressure growth, this pressure being caused by hydrogen in the interlayer space. Moreover, as shown in [14, 20], the $E_g(P)$ dependence in γ-InSe crystals is non-monotonic. For example, at the hydrostatic pressures of 10^5 up to

$4.2 \cdot 10^8$ Pa in γ-InSe crystals, E_g decreases by 3.3 meV, but with the following pressure increase it grows, too.

As shown in the previous part, the hydrogen concentration increase up to $x = 2$ gives rise to the pressure between layers up to $P = 9.4$ MPa at $T = 80$ K, which stimulates an increase of the van der Waals gap. Making extrapolation in accord with the analytical dependences [14, 20], we obtained E_g growth by 0.2 meV at $P = 9.4$ MPa. At $x = 0.5$ and $T = 80$ K, this increase is $\Delta E_g = 0.05$ meV. The shift $\Delta E_g = 4.5$ meV could take place at the pressure of molecular hydrogen on layer packages $P = 205$ MPa. Indeed, hydrogen can provide this pressure at $x = 12$ and $T = 300$ K but under the only condition that, for $x > 2$, it does not penetrate into interstices of InSe layer packages and contains six H_2 molecules in the cavity. Hence, we made the conclusion that the observed shortwave shift of E_1 by 4.5 meV cannot be caused by a baric shift of E_g.

It is also known [21] that an increase of the hydrostatic pressure in A^3B^6 crystals, contrary to A^2B^6 and A^3B^5 ones, results in increasing $\varepsilon_0^{\parallel}$ component of the crystal dielectric permeability. As it was shown by direct measurements of the capacitance [21], $\varepsilon_0^{\parallel}$ of InSe grows almost linearly by 15% within the range 10^5 to 10^9 Pa. Thereof, in accord with the mean ε_0 value that is defined as $\varepsilon_0 = [\varepsilon_0^{\parallel} \varepsilon_0^{\perp 2}]^{1/3}$ in anisotropic layered crystals (when, accordingly to [16], $\varepsilon_0^{\perp} = 10.9$, $\varepsilon_0^{\parallel} = 9.9$, and indexes $\parallel$, $\perp$ correspond to parallel and perpendicular orientations relatively to the optical axis C), ε_0 grows by 5%. This ε_0 increase should result in decreasing the exciton binding energy R_0. Indeed, the decrease of R_0 from 14.2 meV down to 12.9 ± 0.4 meV at $P = 1$ GPa was reported in [14]. The R_0 value obtained in [14] and ε_0 observed in [21] increase by 5% which are in a good agreement with the well-known dependence

$$R_0 \text{ [meV]} = 13605\mu / \varepsilon_0^2 \qquad (2)$$

combining R_0 with ε_0 and μ – reduced exciton mass (in InSe $\mu = [m_e^{-1} + m_h^{-1}]^{-1} = 0.12 m_0$ [16], where m_0 is the mass of the free electron).

Extrapolating data [14, 21] onto our case of the van der Waals gap growth, one can say that, at $x = 2$ ($P = 9.4$ MPa), ε_0 should decrease by 0.7 % and R_0 increase by 0.2 meV, which at $x = 0.5$ and $\Delta\varepsilon_0(P) = 0.2$% results in $\Delta R_0(P) = 0.06$ meV and the respective longwave shift of E_1.

The performed analysis of obtained by various authors data upon the pressure influence on the energy structure of InSe crystal enables one to draw the conclusion that the shortwave shift of E_1 by 4.5 meV cannot be reasonably explained by $R_0(P)$, $\varepsilon_0(P)$ and $E_g(P)$ dependences, as $R_0(P)$ and $E_g(P)$ contributions into this shift are opposite at $x = 0.5$ ($P = 2.4$ MPa) and their total contribution is only 0.01 meV, which is considerably lower than the observed one.

At the same time, this behaviour of exciton parameters $E_1(x)$ and $\Gamma_1(x)$ gives grounds to deem that the shortwave shift of the exciton absorption band is caused by the ε_0 increase stemming from the hydrogen presence in the interlayer space, which results in R_0 decrease in accord with Eq. (2).

To make our discussion convenient, we shall describe the ε_0 increase caused by molecular hydrogen in the interlayer space introducing an additive to $\varepsilon_0^{\parallel}$ parameter $\varepsilon^*(x)$ increasing with x and characterizing the degree of dielectric permeability anisotropy for the medium comprised by the exciton in the following form:

$$\varepsilon_0(x) = [\varepsilon_0^{\perp 2} \varepsilon_0^{\parallel} \varepsilon^*(x)]^{1/3} \equiv \varepsilon_0[\varepsilon^*(x)]^{1/3}, \qquad (3)$$

where parameter

$$\varepsilon^*(x) = \prod_{j=1}^{w} \varepsilon_i(x) \equiv \varepsilon_i(x)^w. \qquad (4)$$

w is the degree index characterizing the quantity of interlayer space comprised by the exciton diameter d_{exc}, and $\varepsilon_i(x)$ is the dependent on x dielectric permeability of the van der Waals gap, which is equal to that of vacuum $\varepsilon_i(0) = \varepsilon_v = 1$ in the case of pure InSe.

To simplify our estimation procedure, we shall consider that hydrogen introduction into the interlayer space changes neither E_g nor μ. Then, the shortwave shift of $E_1(x)$ in the range $0 < x \leq 0.5$ (see Fig. 3b) is caused by R_0 decrease from 14.5 down to 10.0 meV, which results in practically linear growth of the obtained experimental $\varepsilon_0(x)$ values from 10.5 to 12.6 in accord with Eq. (2) (see insert of Fig. 3c) and is described rather well by the following dependence:

$$\varepsilon_0(x) = 10.5 \, (1 + 1.5x)^{1/3} \qquad (5)$$

shown by the curve 2. The curve 1 in Fig. 3b represents the dependence $R_0(x)$ for $0 < x \leq 2$ obtained according to Eq. (2) in the case when $\varepsilon_0(x)$ corresponds to Eq. (5). As it can be seen, the curve 1 well describes the experimental dependences $R_0(x)$ within the range $0 < x \leq 0.5$. In accord with Eq. (3), $\varepsilon_0^{\parallel}(x)$ increases from 9.9 up to 16.9 due to the growth of parameter $\varepsilon^*(x)$ from $\varepsilon_v = 1$ up to 1.7. In accordance with the expression

$$a_{exc} \text{ [nm]} = 0.053\varepsilon_0(x)/\mu, \qquad (6)$$

where a_{exc} is the exciton radius, the exciton diameter grows linearly with changing $\varepsilon_0(x)$ from 9.51 up to 11.43 nm, which is equivalent to the increase of the exciton diameter from $d_{exc} = 11.3$ up to 13.5 crystal layers (layer thickness of InSe $d_{layer} = 8.44$ Å). Thereof, for $w = 13$ in accord to Eq. (4) at $x = 0.5$ ($P = 2.3$ MPa) and $T = 80$ K, one can deduce $\varepsilon_i = 1.04$.
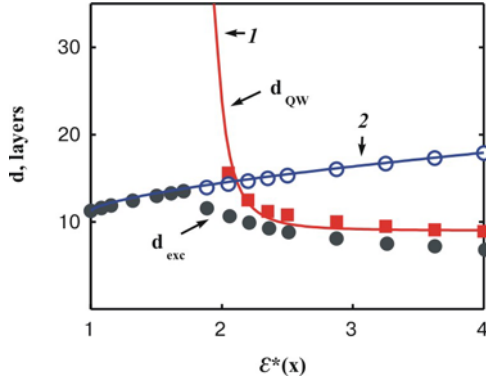
Fig. 4. Solid squares are the experimental values for the quantum well thickness d_{QW} on the $\varepsilon^*(x)$ parameter for $H_x InSe$ at $T = 80$ K. Circles and solid circles are experimental dependences for the exciton diameter d_{exc} on the $\varepsilon^*(x)$ parameter without and with the account of exciton localization. Curve 1 and 2 are plotted in accord to Eqs (10) and (6).

Considering Eq. (5) defining the dependence of ε_0 on x, which is associated with hydrogen introduction into interlayer space, we may perform extrapolation of $\varepsilon_0(x)$ to $x = 1$. Obtained data will be as follows: $\varepsilon_0 = 14.25$ and parameter $\varepsilon^* = 2.5$. R_0 should decrease down to 6.45 meV, while the exciton diameter should increase to $d_{exc} = 12.9$ nm ($d_{exc} = 15.3$ crystal layers). For $w = 15$ at $x = 1$ ($P = 4.7$ MPa) and $T = 80$ K, one can determine $\varepsilon_i = 1.062$.

In the similar way, for $x = 2$ we can obtain $\varepsilon_0 = 16.67$ and $\varepsilon^* = 4.0$, $R_0 = 5.73$ meV, $d_{exc} = 15.1$ nm ($d_{exc} = 17.9$ crystal layers). For $w = 18$ at $x = 2$ ($P = 9.4$ MPa) and $T = 80$ K, one can determine $\varepsilon_i = 1.081$. It is evident that ε_i value also grows with x and begins to approach to experimental data inherent to the dielectric permeability of condensed hydrogen [22], which is 1.253 and 1.230 at the temperatures 14 and 20.5 K, respectively.

The obtained numeric values for dependences of parameter ε^* and ε_i on x are well described by the following analytical expressions:

$$\varepsilon^*(x) = \varepsilon_v + 1.5x \qquad (7)$$

and

$$\varepsilon_i(x) = \varepsilon_v + 0.06x^{1/2}, \qquad (8)$$

where $\varepsilon_v = 1$. It is seen that ε_i growth as a whole causes increasing the crystal dielectric permeability that leads to the experimentally observed R_0 decrease in complete agreement with Eqs (2) and (5), as shown by the curve 1 in Fig. 3b.

However, at $0.5 < x < 1$, $E_1(x)$ shift changes its sign by the opposite one, and at $1 < x < 2$ E_1 position is stabilized. This behaviour of $E_1(x)$ allows us to posit that $\varepsilon_i(x)$ increase causes a growth of a_{exc}. As a consequence, parameter $\varepsilon^*(x)$ characterizing the degree of anisotropy

inherent to medium comprised by the exciton grows so much that at $\varepsilon^* = 1.7$ ($x = 0.5$) the exciton motion is localized in the plane of layers. Further increase of $\varepsilon_i(x)$ causes reducing the exciton radius and quantum well (QW) width d_{QW}.

In Fig. 4, squares shown the dependence of the localized exciton QW width on the parameter $\varepsilon^*(x)$ obtained in accordance with

$$E = \frac{\pi^2 \hbar^2}{2d^2 M} \qquad (9)$$

and experimental $\Delta E_1(x)$ data. For convenience, we chose the thickness of the crystal layer as a unit of the d_{QW}. Open circles show the dependence of the exciton diameter d_{exc} on parameter $\varepsilon^*(x)$ without taking into account exciton localization, while solid circles do that considering the localization in the QW.

As seen from this figure, within the range of parameter values $1 < \varepsilon^*(x) < 1.7$ the QW does not appear ($d_{QW} = \infty$), and we deal with the ordinary growth of d_{exc} (open circles) bound by $\varepsilon_i(x)$ increase. At $1.7 < \varepsilon^*(x) < 2.5$, strong localization of the exciton takes place in the layer plane, and the QW narrows from 107 down to 12.8 layers. At the same time, d_{exc} decreases from 13.5 down to 8.8 layers.

Further x increase, in accord with Eq. (7), causes $\varepsilon^*(x)$ parameter growth from 2.5 up to 4.0 and decrease the QW and exciton diameter down to $d_{QW} = 12.8$ layers and $d_{exc} = 10.55$ layers. R_0 and d_{exc} are stabilized at the final level, and the exciton is localized in the crystal layer plane. Experimental data of $d_{QW}(\varepsilon^*)$, where [see Eq. (7)] $\varepsilon^* = f(x)$, is well approximated by the following expression:

$$d_{QW}(\varepsilon^*) \text{ [layers]} = 9 + 0.4/(\varepsilon^*(x) - 1.7)^3 \qquad (10)$$

represented by the curve 1 in Fig. 4.

Note that, at $\varepsilon^*(x) > 1.7$, numeric d_{exc} values were obtained in approximation that increasing the parameter up to $\varepsilon^*(x) > 1.7$ should be followed by the condition $\varepsilon_i(x)^w \leq 1.7$. As $\varepsilon_i(x)$ value grows with x, the quantity of layers comprised by the exciton w should be decreased.

This statement is confirmed by the experimental dependence of the $n = 1$ exciton absorption band halfwidth Γ_1 on x depicted in Fig. 3c. Indeed, the experimentally observed d_{exc} growth in the range $x < 0.5$ results in increasing the probability of exciton scattering by point defects and increasing the initial value of homogeneous broadening the ground as well as excited exciton states $\Gamma_i'(0) = g^2[\hbar\Omega(R_0/i^2 - \hbar\Omega)]^{1/2}$. Despite the more smooth $\Gamma_i^2(T)$ dependence, the total exciton scattering rises at the low temperature ($T = 80$ K), which results in experimentally observed Γ_1 growth. In the range $x > 0.5$, the exciton localization causes $\varepsilon_i(x)$ growth and d_{exc} decrease, which results in stabilization of exciton and QW sizes and reaching a stationary value of the probability for excitons to be scattered by defects.

The experimental $\Gamma_1(x)$ dependence is in accordance with Eq. (1) depicted by the curve 1. Here $\Gamma_1 = 4.4$ meV.

Comparing InSe with GaSe crystals shows that, in GaSe crystals, described above phenomena of E_1 nonlinear behaviour with x are less expressed and more delayed at the large hydrogen concentration. The main reason of these differences is that, in GaSe crystal, exciton diameter ($d_{exc} = 9$ crystal layers) is less than that in InSe crystal, where exciton diameter d_{exc} envelop 11.3 crystal layers. It is clear that, at a smaller exciton diameter, the described phenomena require larger hydrogen concentrations. That is why, in H$_x$GaSe crystals, the effects of reduction of the exciton binding energy and subsequent exciton localization with an increase of hydrogen in van der Waals gap are more delayed and much less expressed.

Oneself paid attention that, for $T = 80$ K and $x = 0$, the experimental halfwidth of the $n = 1$ exciton absorption band Γ_1 in InSe crystals is greater than that in GaSe crystals. First of all, it is connected with the fact that, in GaSe crystals, the energy of homopolar phonon is essentially higher than that in InSe crystals and hence its contribution to Γ_1 broadening as well as to growth of the integral intensity of $n = 1$ exciton absorption band up to classical values is manifested at higher temperatures.

4. Conclusions

The performed investigations of hydrogen intercalation in layered InSe and GaSe crystals have shown that hydrogen in the atomic state enters into the van der Waals gap and forms H$_2$ molecules that, with the growth of hydrogen concentrations up to $x = 2$, has a tendency to occupy translation ordered states in the gap and causes there a pressure resulting in experimentally observed and predicted by our calculations growth of the interlayer lattice parameter C_0.

At $x = 2$ and $T < 80$ K, this state of H$_2$ in the gap can be treated as a "quasi-liquid monolayer". At $x > 2$, atomic hydrogen begins to incorporate into interstices of the crystal lattice due to quantum-size effects arising in the gap and strong repulsion between H$_2$ molecules.

It was found that the observed at $T = 80$ K non-monotonic shift of the $n = 1$ exciton absorption band peak with x stems from the increasing dielectric permeability ε_0 of the crystal due to presence of H$_2$ molecules in the gap. A growth of the exciton anisotropy parameter $\varepsilon^*(x)$ results in decrease of the exciton binding energy R_0. When $\varepsilon^*(x)$ exceeds the critical value $\varepsilon^* \le 2$, 2D localization of exciton motion in the crystal layer plane followed by the growth of R_0 takes place, which causes reduction and then stabilization of sizes both for the exciton and quantum well. Due to the difference in exciton diameters ($d_{exc}^{GaSe} < d_{exc}^{InSe}$), this phenomena in GaSe crystals are more delayed and much less pronounced.

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