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Light absorption by excited exciton states in layered InSe crystals

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Abstract. We investigated spectra of light absorption by excitons in InSe crystals of different thicknesses, both pure and doped with iron group impurities, at temperatures from 4.5 up to 100 K. It was shown that, along with the traditional direct optical transition (photon $\rightarrow$ exciton $\rightarrow$ photon) at $k = 0$, exciton production and annihilation (accompanied with photon emission) occurs also via indirect vertical transition (photon $\pm$ phonon $\rightarrow$ exciton $\rightarrow$ photon $\pm$ phonon) at $k \cong 0$. For the $n = 1$ exciton state the direct and indirect vertical transitions were found to be compatible. For excited exciton states these transitions are not compatible; as a result, the integral intensity of absorption bands for excited exciton states, K_n, is over K^0/n^3 (where K^0 is the classic value for the $n = 1$ exciton absorption band) and grows with temperature. For the $n = 1$ exciton state both symmetric and asymmetric (with phonon absorption only) indirect vertical transitions are considered.

Keywords: exciton absorption, layered crystal, InSe.

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1. Introduction

The effect of K_1 (integral intensity of the $n = 1$ exciton absorption band) growth with temperature has been adequately studied for semiconductor crystals [1]. As a rule, such growth is observed starting from some low K_1 values up to K^0. Here K^0 is the classic value of the integral intensity for the $n = 1$ exciton absorption band within the frameworks of the Elliott-Toyozawa theory [2, 3].

The K_1 growth could be explained with several dissipation mechanisms. These are, in particular, the polariton mechanism [4], as well as those of indirect vertical (IV) phototransitions [5] and absorption in the case when exciton states are degenerate (in the momentum space) with those of charge carriers localized in two-dimensional quantum wells (2DQWs) [6].

The first of them, polariton mechanism, results from increase of polariton scattering during its being in the exciton state due to growth of exciton scattering either by defects (when their concentration increases) or by phonons (when temperature grows). In [7, 8] it was shown that K_1 growth in such layered crystals as n-InSe and p-GaSe is due just to this mechanism.

The second (IV transition) mechanism is very similar to the first one. In this case, however, the photon transition into exciton state is proceeding via a virtual state and is accompanied with concurrent emission or absorption of one or two phonons. It is generally accepted [9] that the second mechanism is observed at higher temperatures, when the first (polariton) one has stopped.

The third mechanism comes into action due to redistribution with temperature of charge carriers localized in 2DQWs whose states are degenerate with those of excitons in the momentum space. Such redistribution of 2D charge carriers to states of higher energies lifts off degeneracy of their states with exciton ones. This results in restoration of the oscillator strength for exciton transition. Such an effect has been experimentally observed, in particular, in [8] for p-GaSe crystals. It manifested itself as retardation of K_1 growth with temperature due to degeneracy in the momentum space of the $n = 1$ exciton states with those of holes localized in 2DQWs.

At the same time some distinctions have been found when studying InSe and GaSe crystals [7, 8] between the integral intensities of their absorption bands for the ground and excited exciton states. In particular, the integral intensity of absorption band for excited exciton states, K_n, in these crystals was somewhat over the classic value, K^0/n^3, at any temperature, defect concentration and crystal thickness. In addition, it was observed for InSe and

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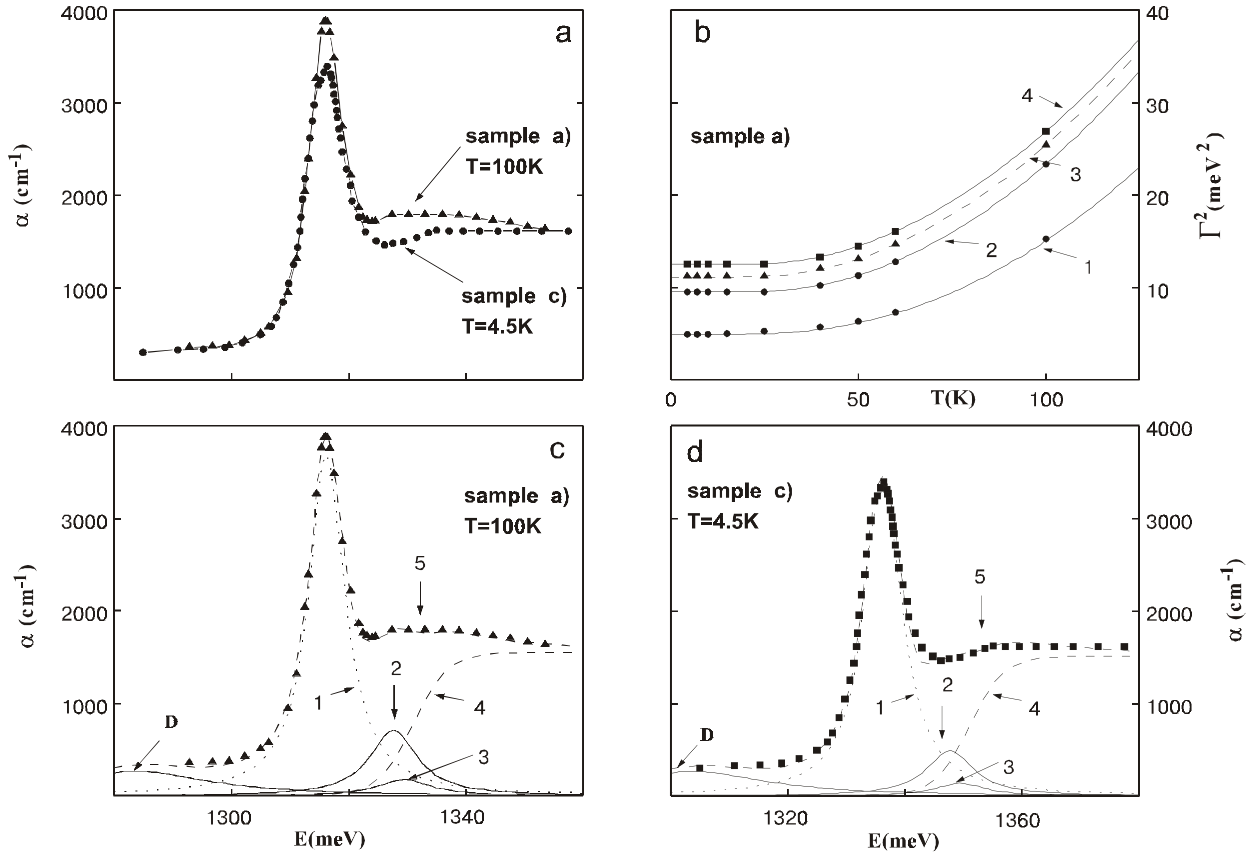

Fig. 1 -a), -c), -d) Experimental absorption spectra of the sample a) at T=100K (triangles) and of sample c) at T=4.5K (square). Curves 1 to 3 represents the absorption bands of n = 1 to 3 exciton states. The dashed curves 4 are the band-to-band absorption coefficient a_0(hw). Curve D is the absorption band of a shallow defect. Curve 5 is the calculated absorption coefficient a($\hbar\omega$) in the region of the fundamental edge. -b) The experimental temperature dependence Γ_1^2(T) for n=1 exciton absorption band of the sample a) (open circles). The curve 1 – according to the Eq. (1a) with Γ_{inh} = 1.3 meV. Solid circles, triangles and open squares - data for Γ_n^2(T) dependence calculated according to the Eq. (1) for n=2,3 and n= ∞ exciton states. Curves 2 to 4 – according to the Eq.(1) with Γ_{inh} = 1.3 meV.

GaSe crystals that this excess of K_n values over the classic one increased with temperature.

This work deals with the effect of the above mechanisms on light absorption by the excited exciton states in InSe crystals. The more complicated situation with *p*-GaSe crystals where degeneracy in the momentum space occurs between states of excitons and holes localized in 2DQWs will be discussed elsewhere.

2. Experimental results

The spectra of light absorption by excitons for InSe crystals were taken with a two-grating monochromator SDL-1 (spectral width of < 0.2 meV). The sample temperature was stabilized (accuracy of 0.1 K) using a cryostat system “UTREKS-1”. Semiconductor temperature-sensitive resistors served as temperature sensors in the 4.2-100 K range; a photomultiplier FEU-62 was used for valid signal detection. For more detailed description of the experimental technique used see [7, 8].

The bulk *n*-InSe single crystals were Bridgman-grown. The controlled impurity concentration was determined in weight percentage of the starting components of material charged. The uncontrolled impurity concentration was below 10^{17} cm^{-3}. For our investigations we have chosen single-crystalline plates of pure and doped InSe crystals. The sample thickness *d* was measured with an optical-mechanical dilatometer (accuracy of 0.05 μm). In this work the samples studied are labeled as in previous discussions (see [7]), namely, sample a) - InSe:0.1 Cr (*d* = 17.2 μm); sample b) - InSe:0.01 Ni (*d* = 11.0 μm); sample c) - InSe:0.01 Mn (*d* = 10.3 μm); sample d) - InSe:0.1 Cr (*d* = 6.9 μm); sample e) - InSe (*d* = 13.8 μm); sample f) - InSe:0.1 Mn (*d* = 9.6 μm); sample j) - InSe:0.01 Mn (*d* = 14.1 μm) and sample h) - InSe (*d* = 8.9 μm). All the exciton absorption spectra for the above InSe crystals at T = 4.5 K are presented in [7].

3. Absorption spectra of InSe crystal and fitting procedure

Shown in Figs 1c and 1d are the absorption spectra for the samples a) at T = 100 K and c) at T = 4.5 K, respectively. The spectra of just these crystals taken at pre-

cisely these temperatures are presented because practically the same K_1, Γ_1 and α'_1 values have been obtained for them in the previous paper [7]. (Here Γ_1 and α'_1 are, respectively, the half-width at half-maximum and peak intensity for the $n = 1$ exciton absorption band.) For the sample a) growth of Γ_1 and K_1 values resulted from increase of temperature of a rather perfect crystal, while for the sample c) it was due to increase of the concentration of crystal imperfections.

Let us denote the half-width, integral intensity and peak intensity for the $n = 1$ exciton band by Γ_1, K_1 and α'_1, respectively, while for the excited ($n > 1$) exciton absorption bands the corresponding quantities will be denoted by Γ_n, K_n and α'_n. The spectra presented in Fig. 1a are shifted on the energy scale and superimposed on one another for convenience of their comparison. One can see that for the sample a), contrary to the sample c), an essential increase of the absorption coefficient $\alpha(\hbar\omega)$ occurs in the region of excited exciton states.

When estimating contribution from the excited exciton states to the fundamental absorption edge for InSe crystal, we made the following assumptions:

1. We supposed that for the excited, as well as ground, exciton states 3D Wannier exciton weakly interacts with the effective crystal lattice vibration W whose energy hW is close to that of a homopolar A'-phonon. The calculations of the absorption spectra for the ground and excited exciton states were performed, with allowance made for broadening, according to the standard convolution procedure for the theoretical value of absorption coefficient $\alpha(\hbar\omega)$ in the Elliott model [2] and Lorentzian $f(\hbar\omega) = \Gamma/[\pi(E^2 + \Gamma^2)]$ in the Toyozawa model [3]. (Here Γ is the exciton absorption band half-width at half-maximum that is related to the lifetime $\hbar/2\Gamma$.)

The contribution from the exciton continuum states to the fundamental absorption edge was obtained by integrating with respect to energy from E_g to $+\infty$ (i.e., over the whole conduction band continuum). Thus the step-function has taken the form of $U = (1/\pi)[\pi/2 + \tan^{-1}(X)]$ where $X = (\hbar\omega - E_g)/G_c$ and G_c is the half-width of the exciton continuum state. (For more details of the fitting procedure see [7, 8].)

2. It was supposed that the character of exciton scattering by phonons and defects, as well as the exciton-phonon interaction constant g, do not change when going from $n = 1$ to $n > 1$ and $n = \infty$ exciton states. The only change occurs in the binding energy value $R_n = R_0/n^2$ for the exciton state (here n = 1, 2, 3,…, ∞). Thus, taking into account scattering by the "effective" phonon W, one obtains for the absorption half-bandwidth of the $n > 1$ exciton state the following expression:

$$\Gamma_n^2(T) = \Gamma_n'^2(T) + \Gamma_{inh}^2 = = [\Gamma_n'(0)\cdot(1 + \beta_n n^*(T))]^2 + \Gamma_{inh}^2, \quad (1)$$

Here $\Gamma'_n(0) = g^2[\hbar\Omega(R_0/n^2 - \hbar\Omega)]^{1/2}$; $\beta_n = 1 + [(R_0/n^2 + \hbar\Omega)/(R_0/n^2 - \hbar\Omega)]^{1/2}$; phonon occupation number $n^*(T) = [\exp(\hbar\Omega/k_BT) - 1]^{-1}$; k_B is the Boltzmann constant. (For the sake of simplicity we took that the Γ_{inh} values of inhomogeneous broadening of the exciton absorption bands for ground and excited exciton states are the same and do not depend on temperature.)

From expression (1) we calculated the Γ_2, Γ_3, Γ_4 and Γ_C values for the samples a) - h) at T = 4.5 K and for the sample a) at T = 4.5-100 K. In doing so we used the parameter values $\Gamma'_1(0) = g^2[\hbar\Omega(R_0 - \hbar\Omega)]^{1/2} = 1.3$ meV, $\hbar\Omega = 13.2 \pm 0.1$ meV and $g = 0.55$ obtained in [7] for the $n = 1$ exciton absorption band, as well as the value R_0 = 14.5 meV. The curves 2, 3 and 4 in Fig. 1b present the dependencies $\Gamma_n^2(T)$ and $\Gamma_c^2(T)$ for the sample a) calculated from expression (1) for the $n = 2, 3$ and $n = \infty$ exciton states with Γ_{inh} = 1.3 meV. The experimental $\Gamma_1^2(T)$ data for the $n = 1$ exciton state and the curve 1 are determined according to either the expression

$$\Gamma_1^2(T) = \Gamma_1'^2(T) + \Gamma_{inh}^2 = = [\Gamma_1'(0)\cdot(\sqrt{2} + \beta_1 n^*(T))]^2 + \Gamma_{inh}^2, \quad (1a)$$

that has been obtained in [6] for $\beta_1 = 1 + [(R_0 + \hbar\Omega)/(R_0 - \hbar\Omega)]^{1/2}$ and Γ_{inh} = 1.3 meV, or the expression

$$\Gamma_1^2(T) = \Gamma_1'^2(T) + \Gamma_{inh}^2 = = [\Gamma_1'(0)\cdot(1 + \beta_1 n^*(T))]^2 + \Gamma_{inh}^2 \quad (1b)$$

obtained for Γ_{inh} = 1.84 meV.

Now, basing on the expressions (1) and (1a), one can easily show that the interrelation between the half-widths of the ground (Γ_1), excited (Γ_n) and continuum (Γ_c) exciton states

$$\Gamma_n = \Gamma_c - \frac{\Gamma_c - \Gamma_1}{n^2} \quad (2)$$

that has been obtained in [10] for rather perfect GaSe crystals at T = 4.2 K should be of the following, more exact, form:

$$\Gamma'_n(0) = \Gamma'_c(0) - \frac{\Gamma'_c(0) - \Gamma'_1(0)}{n^2} \quad (3)$$

Here $\Gamma'_1(0)$, $\Gamma'_n(0)$ and $\Gamma'_c(0)$ are the homogeneous components of the half-widths for the ground, excited and continuum exciton states, respectively, at $T = 0$.

3. The K_n value is proportional to $1/n^3$, so fitting of the calculated spectra to the experimental absorption coefficient was performed with allowance made for the ground ($n = 1$) and three excited (n = 2-4) exciton states. The contribution from the rest ($n > 4$) of the excited states

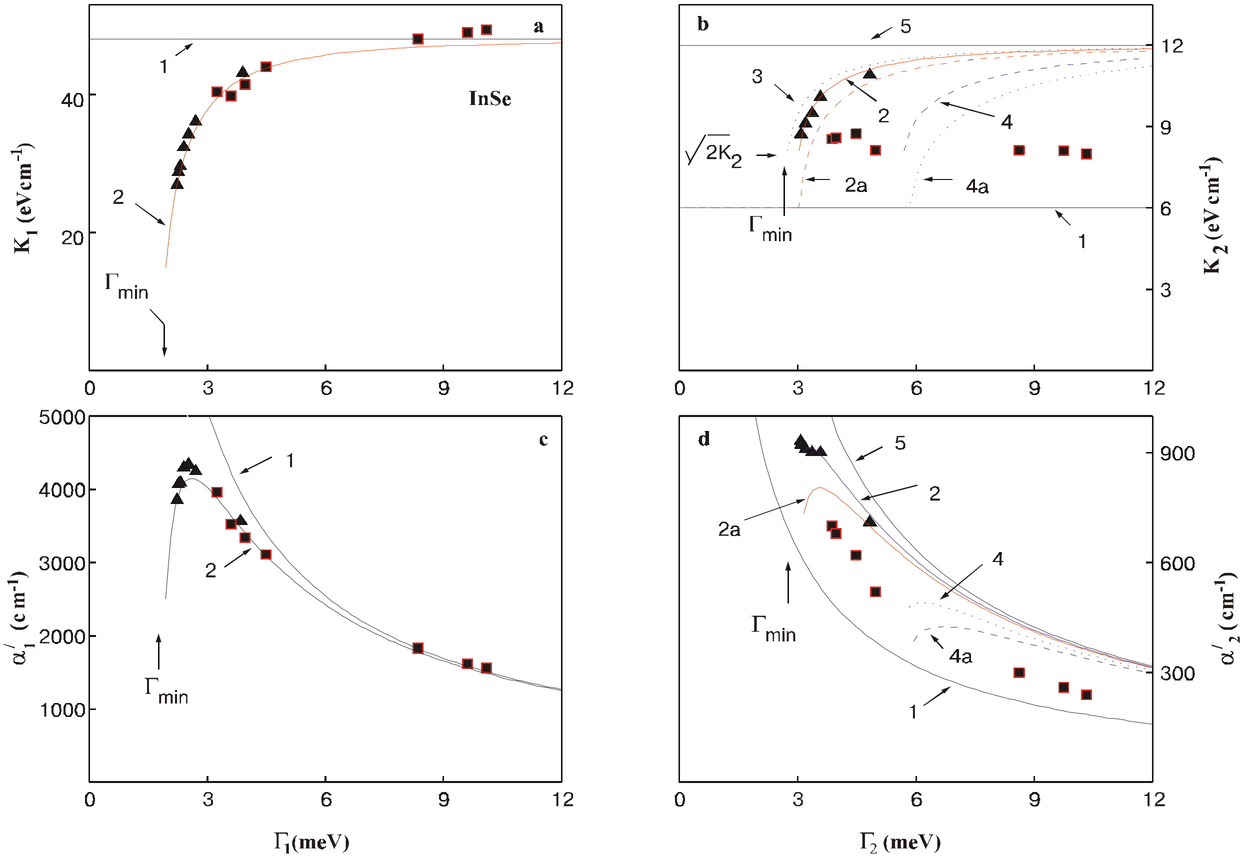

Fig. 2. -a), -c) Values $K_1(\Gamma_1)$ and $\alpha'_1(\Gamma_1)$ for n=1 exciton state of InSe crystal of the samples a) to h) at T=4.5K (solid squares), and of a sample a) T=4.5 to 100K (triangles). The curves $1'$ represent case of a classical absorption when $K_1(\Gamma_1) = K^0$ is *const*. Curves $2'$ in the correspondence with the Eq. (4) and (4a). -b), -d) The values of $K_2(\Gamma_2)$ and $\alpha'_2(\Gamma_2)$ for n=2 exciton state of InSe crystal of the samples a) to h) at T=4.5K (solid squares), and of a sample a) T=4.5 to 100K (triangles). The curves 1 represent the case of a classical absorption when $K_2(\Gamma_2)=K^0/8$. The curves 5 represent the case when $K_2(\Gamma_2)=2K^0/8$. Curves 2a and 4a – in the correspondence with the Eq. (5) and (5a) and with Γ_{inh} = 1.3 meV and Γ_{inh} = 5.2 meV. Curves 2 and 4 – in the correspondence with the Eq. (11) and (11a) and with Γ_{inh} = 1.3 meV and Γ_{inh} = 5.2 meV. Curve 3 - in the correspondence with the Eq. (11) and Γ_{inh} = 0.

to the exciton absorption spectrum was less than 2 %; if one takes interband absorption into account, this contribution becomes less than 1 %.

Finally, the calculated spectra of InSe crystals at the fundamental absorption edge involved the n = 1-4 exciton absorption bands, interband transition and (see [7]) absorption band due to shallow (17 meV) donors of low concentration, shallow (45 meV below the conduction band bottom) defect level (D-band) and trap level (T-band) whose energy was 130 meV over the valence band top.

To illustrate, the results of calculated values fitting to the experimental absorption spectra of InSe crystals for the samples a) at T = 100 K and c) at T = 4.5 K are given in Figs 1c and 1d (dashed curves 5). The curves 1-3 correspond to the n = 1-3 exciton absorption bands, curves 4 correspond to the interband absorption with $\alpha_0(\hbar\omega)$ and curves D correspond to the defect D-band.

In the course of fitting it was found, in particular, that growth of half-width Γ_n due to Γ_{inh} increase does not result in changing the K_n value. The obtained K_n values, however, are somewhat over the classic value K^0/n^3. In addition, growth of the half-width Γ_n with temperature leads to increase of α'_n and K_n. Indeed, one can see from Fig. 1 that the n = 2 and n = 3 exciton absorption bands for the sample a) at T = 100 K are essentially more intense than those for the sample c) at T = 4.5 K.

The dependencies $K_1(\Gamma_1)$, $\alpha'_1(\Gamma_1)$ and $K_2(\Gamma_2)$, $\alpha'_2(\Gamma_2)$ for the absorption bands of the n = 1 and n = 2 exciton states [InSe crystals, samples a) – h)] that were obtained during the fitting procedure are presented in Fig. 2 by squares and triangles. The dependencies $K_1(\Gamma_1)$ and $\alpha'_1(\Gamma_1)$ (see curves 2 in Figs 2a and 2c) correspond to the polariton mechanism. They are described with the following analytical expressions obtained in [7]:

$$K_1(\Gamma_1) = K^0 \times \frac{\sqrt{\Gamma_1^2 - 2\Gamma_1'^2(0)}}{\Gamma_1}, \tag{4}$$

$$\alpha_1^{/}(\Gamma_1) = \frac{K^0}{\pi\Gamma_1} \times \frac{\sqrt{\Gamma_1^2 - 2\Gamma_1^{/2}(0)}}{\Gamma_1}, \qquad (4a)$$

For InSe growth of functions $K_1(\Gamma_1)$ and $\alpha'_1(\Gamma_1)$ begins at $\Gamma_{min} = \sqrt{2}\Gamma_1^{/}(0)$. The curves 1 in Figs 2a and 2c are plotted for the case of classic absorption when $K_1 = K^0$ is *const*. The curves 1 in Figs 2b and 2d are plotted for the case of classic absorption (the $n = 2$ exciton state) when $K_2 = K^0/2^3$ is *const*.

The following distinctions exist between the values obtained for $K_2(\Gamma_2)$ and $\alpha'_2(\Gamma_2)$ (see Figs 2b and 2d) and for $K_1(\Gamma_1)$ and $\alpha'_1(\Gamma_1)$ (see Figs 2a and 2c):

a) the $K_2(\Gamma_2)$ and $\alpha'_2(\Gamma_2)$ values are somewhat over the corresponding classic values $K_2 = K^0/n^3$ and $\alpha'_2 = K^0/\pi n^3\Gamma_2$ where $K^0 = 48$ eV·cm^{-1} and $n = 2$;

b) growth of the half-width Γ_2 with Γ_{inh} (squares) does not change the K_2 value;

c) an additional excess of the K_2 value over the classic one occurs when temperature is increased (triangles); for the excited ($n = 2$) exciton state this growth begins at $\Gamma_{min} = \Gamma'_2(0)$, contrary to the ground state for which $\Gamma_{min} = \sqrt{2}\Gamma_1^{/}(0)$ a) .

The above regularities hold also for the excited $n = 3$ and $n = 4$ exciton states in InSe crystal.

By analogy with expressions (4) and (4a) that were obtained for the $n = 1$ exciton state, one can present the analytical dependencies $K_n(\Gamma_n)$ and $\alpha'_n(\Gamma_n)$ for the excited exciton states in the following form:

$$K_n(\Gamma_n) = \frac{K^0}{n^3} \times \left[1 + \frac{\sqrt{\Gamma_n^2 - \Gamma_n^{/2}(0) - \Gamma_{inh}^2}}{\Gamma_n}\right], \qquad (5)$$

and

$$\alpha_n^{/}(\Gamma_n) = \frac{K^0}{n^3\pi\Gamma_n} \times \left[1 + \frac{\sqrt{\Gamma_n^2 - \Gamma_n^{/2}(0) - \Gamma_{inh}^2}}{\Gamma_n}\right] \qquad (5a)$$

In Figs 2b and 2d the curves 2a present for the sample a) the dependencies for $K_2(\Gamma_2)$ and $\alpha'_2(\Gamma_2)$ that appear as a result of temperature increase. The curves 2a corresponds to expressions (5) and (5a) with $\Gamma_2(T)$ in accordance to expression (1). The curves 4a are plotted for the $n = 2$ exciton absorption band in the case when Γ_2 grows with temperature and Γ_{inh} is four times that for the sample a). The curves 5 are plotted for the case when the $K_2 = 2K^0/2^3$ value is twice as big as the classic ones.

The curves 2a and 4a demonstrate, in particular, that for crystals with any defect concentration, temperature growth leads to increase of the K_n and α'_n values, while growth of the Γ_{inh} value at a constant temperature does not change the K_n values (see squares in Figs 2b and 2d). This is a distinction between the $K_n(\Gamma_n)$, $\alpha'_n(\Gamma_n)$ and $K_1(\Gamma_1)$, $\alpha'_1(\Gamma_1)$ dependencies, since for the ground exciton state an increase of $K_1(\Gamma_1)$ and $\alpha'_1(\Gamma_1)$ always appears when the homogeneous $[\Gamma'_1(T)]$ or inhomogeneous (Γ_{inh}) part of the exciton absorption band grows.

Another fundamental distinction between the $K_n(\Gamma_n)$, $\alpha'_n(\Gamma_n)$ and $K_1(\Gamma_1)$, $\alpha'_1(\Gamma_1)$ dependencies is that growth of the K_1 and α'_1 values with Γ_1 for the $n = 1$ exciton state proceeds according to the scheme “from ‘0’ to ‘1’” (where ‘1’is K^0 or $K^0/\pi\Gamma$), while for the excited exciton states the K_n and α'_n values grow according to the scheme “from ‘1’ to ‘2’” (where ‘1’is now K_n^0/n^3 or $K_n^0/\pi\Gamma_n n^3$).

4. Discussion of results

To explain distinctions in behavior of the dependencies $K_n(\Gamma_n)$, $\alpha'_n(\Gamma_n)$ (for excited states) and $K_1(\Gamma_1)$, $\alpha'_1(\Gamma_1)$ (for the ground state), let us consider the following two types of photon transition to exciton state.

A transition of the first type is an ordinary photon transition immediately to exciton state (photon → exciton → photon) at $k = 0$. This is the so-called direct (D) phototransition. The intensity of photon D transition to exciton state is proportional to the oscillator strength of the exciton (electron) transition, f_{cv}. After D transition photon, being in exciton state, may go back to photon state or be scattered either by a crystal defect (with appearance of inhomogeneous broadening) or by an effective phonon Ω (with its absorption or emission). In the latter case homogeneous broadening $\Gamma'(T)$ increases with temperature.

Thus for D transition both integral intensity of the exciton absorption band, K^D, and probability of photon absorption in exciton state, P(D), grow with temperature and defect concentration from “0” to “1”. In this case half-width of the exciton absorption band begins to increase at $\Gamma_{min} = \Gamma'(0)$.

A transition of the second type (IV transition) may be treated as photon transition to exciton state accompanied with its scattering by an optical phonon (photon ± phonon → exciton → photon ± phonon). In this case $k \cong 0$, and photon comes to exciton state via a virtual state (with absorption or emission of an optical phonon). The intensity of such transition increases with number of phonons, and so it is related to homogeneous broadening $\Gamma'(T)$.

IV transitions may occur according to either symmetric or asymmetric scheme. The symmetric scheme is realized when exciton binding energy, R_0, is over the energy $\hbar\Omega$ of the effective phonon. In this case both virtual states (with phonon Ω emission or absorption) are allowed because they occur in the bandgap. Contrary to this, the asymmetric scheme (that is realized when R_0 is below the energy $\hbar\Omega$ of the effective phonon) allows only those transitions when the phonon Ω is absorbed. The reason is that virtual states for IV transitions with emission of

phonon Ω lie in the conduction band. In this case IV transitions are forbidden because interband electron transitions become allowed.

Thus for IV transitions the K^{IV} and P(IV) values grow with phonon occupation number n^* from “0” to “1”; the minimal half-width for the exciton absorption band, Γ_{min}, is $\Gamma'(0)$ (in the symmetric scheme) or 0 (in the asymmetric scheme).

4.1. Ground (n = 1) exciton state of InSe crystal

For the ground exciton state D and IV transitions depend on each other because they are compatible. This means that, regardless the way in which photon came to exciton state, exciton can come back to photon state via D, as well as IV, transition. Therefore the probability P(D + IV) of two compatible events, D and IV transitions, is

$$P(\mathrm{D+IV}) = P(\mathrm{D}) + P(\mathrm{IV}) - P(\mathrm{D \cdot IV}) \le 1 \quad . \tag{6}$$

The half-width determines dispersion of two compatible events:

$$\Gamma^2_{(\mathrm{D+IV})} = \Gamma^2_{(\mathrm{D})} + \Gamma^2_{(\mathrm{IV})} \, . \tag{7}$$

Thus, according to expression (7), the minimal half-width Γ_{min} of the n =1 exciton absorption band, with allowance made for D and IV transitions, is $\Gamma'_1(0)$ (in the symmetric scheme) or $\Gamma'_1(0)$ (in the asymmetric scheme). In particular, for such III-VI crystals as InSe, GaSe, GaS and GaTe the inequality $R_0 > \hbar\Omega$ is valid. That is why $\Gamma_1(T)$ in InSe and GaSe crystals is given by expression (1a), and the K_1 value becomes to grow at $\Gamma_{min} = \sqrt{2}\,\Gamma'_1(0)$ (see curve 2 in Fig. 2a).

It should be noted that for other crystals (say, II-VI - ZnS, CdS, CdSe and CdTe; III-V - GaP, GaAs, etc.) with $\hbar\Omega > R_0$ IV transitions are asymmetric and the K_1 value becomes to grow at $\Gamma_{min} = \Gamma'_1(0)$. In this case the factor $\sqrt{2}$ in expressions (1a), (4) and (4a) disappears.

4.2. Excited (n > 1) exciton state of InSe crystal

The results of studies show that probability of exciton absorption for excited states in InSe and GaSe crystals is somewhat over ‘1’ ($K_n > K^0/n^3$) even at T = 4.5 K and continues to increase with temperature. Such growth of K_n value may appear when D and IV transitions become independent of one another and incompatible. Then the sum of probabilities is:

$$P_n(\mathrm{D+IV}) = P_n(\mathrm{D}) + P_n(\mathrm{IV}) \le 2. \tag{8}$$

In this case one can present K_n as $K_n = K_n^{D+IV} = K_n^{D} + K_n^{IV} \le 2K^0/n^3$.

When concentration of exciton gas is low, an exciton being in excited state, may be scattered by a phonon or crystal defect before its transition to the ground state (from which photon emission occurs). Thus for D transition $P_n(\mathrm{D}) = 1$, $K_n^D = K^0/n^3$ = const., and the half-width Γ_n^D grows (due to scattering by phonons or defects) from $\Gamma_{min} = \Gamma'_2(0)$ in accordance with expression (1).

For all crystals IV transitions to excited exciton states are asymmetric, i.e., they proceed with optical phonon absorption only. Therefore temperature growth increases the transition probability P_n(IV) from “0” up to “1”, and the contribution from IV transitions to absorption band broadening for excited exciton state is described by scattering processes that involve optical phonon absorption:

$$\Gamma_n^{IV}(T) = g^2 \cdot n^*(T) \cdot \sqrt{\hbar\Omega \cdot (R_0/n^2 + \hbar\Omega)} \equiv$$

$$\equiv \Gamma'_n(0) \cdot (\beta_n - 1) \cdot n^*(T) \, . \tag{9}$$

The total dispersion of D and IV transitions to excited exciton state is determined by expression (7), so the half-width Γ_n (with allowance made for expression (9)) increases from $\Gamma_{min} = \Gamma'_2(0)$ and is of the following form:

$$\Gamma_n^2(T) = \left[\Gamma'_n(0) \cdot \left(1 + \beta'_n \cdot n^*(T)\right)\right]^2 + \Gamma^2_{inh}, \tag{10}$$

where $\beta'_n = \sqrt{2}\,[(\beta_n^2 - 1)/\beta_n]$.

At low temperatures contribution from IV transitions is very small, and expression (10) becomes the same as expression (1). As temperature grows, $n^*(T) > 0$ and expression (10) gives higher values for the temperature broadening Γ_n because $\beta'_n > \beta_n$. (In particular, β'_2/β_2 = 1.15; β'_3/β_3 = 1.1; β'_4/β_4 = 1.08 and β'_c/β_c = 1.06.) However, even slight renormalization of the energy value for the effective phonon Ω results in complete identity of expressions (1) and (10).

Taking into account expressions (10) and (3), as well as fitting Γ_n values that have been fixed for InSe crystal, the final Ω, β'_n and $\Gamma'_n(0)$ values were obtained. At $\hbar\Omega$ = 13.2 meV they are β'_2 = 2.67; β'_3 = 2.348; β'_4 = 2.244; β'_c = 2.121 and $\Gamma_2'(0)$ = 2.81 meV; $\Gamma_3'(0)$ = 3.09 meV; $\Gamma_4'(0)$ = 3.18 meV; $\Gamma_c'(0)$ = 3.3 meV for n = 1, 2, 3, 4 and μ states, respectively.

Let us now consider the α'_n and K_n values that were obtained for InSe crystal during fitting procedure. In particular, for the n = 2 exciton state they are presented in Figs 2b and 2d (squares and triangles). One can see that at T = 4.5 K all of them are over the classic values $K^0/\pi n^3\Gamma_n$ and K^0/n^3 where K^0 = 48 eV·cm^{-1}. The corresponding values (averaged over all the InSe samples) at T = 4.5 K are as follows: $\overline{K}_2$ = 8.4 ± 0.3 eVcm^{-1}; for $K_3S_{T=4.5K} - \overline{K}_3$ = 2.3 ± 0.2 eVcm^{-1}; and for $K_4S_{T=4.5K} - K_4$ = 0.97 ± 0.03 eVcm^{-1}.

Taking into account the average $\overline{K}_n$ values obtained for InSe crystals, as well as the previous results for GaSe crystals (for which the same effects, $\overline{K}_n > K^0/n^3$, were observed), we made an assumption that for excited exciton states one can present the minimal $\underline{K}_n$ values in a more general way, namely, as $K_nS_{T=0} = \sqrt{2}\,K^0/n^3$. This means that the probability of photon absorption in excited

exciton state, with allowance made for the above discussion, begins to grow with temperature from " $\sqrt{2}$ " up to "2", and expressions (5) and (5a) take the following final form:

$$K_n(\Gamma_n) = K_n^D + K_n^{IV} =$$

$$= \frac{2K^0}{n^3} \times \left[\frac{1}{\sqrt{2}} + (1 - \frac{1}{\sqrt{2}}) \frac{\sqrt{\Gamma_n^2 - \Gamma_n'^2(0) - \Gamma_{inh}^2}}{\Gamma_n} \right] \quad (11)$$

and

$$\alpha_n'(\Gamma_n) =$$

$$= \frac{2K^0}{\pi\Gamma_n n^3} \times \left[\frac{1}{\sqrt{2}} + (1 - \frac{1}{\sqrt{2}}) \frac{\sqrt{\Gamma_n^2 - \Gamma_n'^2(0) - \Gamma_{inh}^2}}{\Gamma_n} \right] \quad (11a)$$

Shown by curves 2 in Figs 2b and 2d are K_2 and α'_2 as functions of Γ_2. They were obtained from expressions (11) and (11a) at $K^0 = 48$ eV·cm^{-1}, $\Gamma_{inh} = 1.3$ meV, $\Gamma'_2(0) = 2.81$ meV, $\hbar\Omega = 13.2$ meV and $\beta'_2 = 2.67$. The case with $\Gamma_{inh} = 0$ is given by curve 3 in Fig. 2b, while the case when Γ_{inh} value is four times that for the sample a) is presented by curves 4 in Figs 2b and 2d. One can see that expressions (11) and (11a) give much better description for the experimental $K_2(\Gamma_2)$ and $\alpha'_2(\Gamma_2)$ curves in InSe crystals at low temperatures than expressions (5) and (5a).

Now some words on interband electron transitions. Taking into account the above discussion, it should be noted that interband electron transitions in semiconductor crystals also proceed via compatible D transition and asymmetric IV transition. The interband absorption coefficient is constant: it does not depend on temperature and crystal defect concentration. In this case, however, the "tail" of the density of states is dragged from conduction band into crystal bandgap when temperature and defect concentration are increased.

5. Conclusions

Our investigations on mechanisms for light absorption by excitons near the $n = 1$ and $n > 1$ exciton states in layered InSe crystals have revealed the following:

1. Photon transitions to the ground and excited exciton states proceed via D transitions at $k = 0$, as well as IV transitions (photon transition to exciton state is accompanied by concurrent emission or absorption of optical phonon); in the latter case $k \cong 0$.

2. For the $n = 1$ exciton state D and IV transitions are interdependent and compatible. As a result, according to the polariton mechanism, the integral intensity of the exciton absorption band increases with Γ_1 (due to growth of temperature and defect concentration) up to the classic value K^0. The minimal half-width Γ_{min} of the $n = 1$ exciton absorption band is $\sqrt{2}\,\Gamma'_1(0)$ (in the symmetric scheme of IV transition, when $R_0 > \hbar\Omega$) or $\Gamma'_1(0)$ (in the asymmetric scheme of IV transition, when $R_0 < \hbar\Omega$); here $\Gamma'_1(0)$ is the homogeneous component of the $n = 1$ exciton absorption band at $T = 0$.

3. For excited ($n > 1$) exciton states D and IV transitions become independent of one another and incompatible; IV transition is asymmetric. That is why the integral intensity K_n of the absorption band for excited exciton state, with allowance made for D and IV transitions, becomes over the classic value K^0/n^3, and its growth with temperature from $\sqrt{2}\,K^0/n^3$ up to $2K^0/n^3$ begins at $\Gamma_{min} = \Gamma'_n(0)$.

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