BANDGAP RENORMALIZATION OF THE InSe BY LASER RADIATION

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Nonlinear absorption of light and its time evolution in InSe under the influence of picoseconds laser excitation have been investigated experimentally. It was shown that the decrease in exciton absorption in InSe at high levels of optical excitation due to the exciton – exciton interaction and screening of the Coulomb potential by free carriers, generated by laser light. Observations of induced absorption in the energy region between the exciton level and the edge of the conduction band are associated with the appearance of a continuum of states due to a shift in the edge of the energy band.

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1. INTRODUCTION

As you know, the interaction of light waves of high power and high monochromaticity with matter, lead to the emergence of a new field of physics - nonlinear optics. In turn out that under sufficiently strong excitation the optical properties of basically all semiconductors exhibit nonlinear characteristics. They may give rise to effects such as excitation-dependent absorption and refraction, nonlinear wave mixing, optical bistability, harmonic generation, parametric light generation, multiphoton absorption, band filling, band renormalization, thermal nonlinearities, or other optical instabilities. Some of these effects have attracted considerable attention, since the may be useful for applications in optical switching devices, optical logic gates, or even optical computing. A variety of experimental methods have been employed to study mechanisms responsible for optical nonlinearities in the absorption spectra and to measure the nonlinear refractive indices in semiconductors. Pump-probe spectroscopy, nonlinear interferometry, beam-distortion measurements, four-wave mixing and phase conjugation are among these techniques [1–4].

InSe crystals belonging to III-VI compounds semiconductors have received considerable attention recently as an interesting class of nonlinear optical materials. Due to the layered structure, crystal structure features, high polarizability, optical uniformity, the presence of natural mirror surfaces, strong and broadband light absorption in a wide frequency range, the presence of exciton absorption with a fairly high binding energy (~ 25 meV), the possession of the band gap areas of generation of modern lasers, a variety of nonlinearity mechanisms and the existence of developed technology for producing perfect crystals makes InSe crystals popular in quantum electronics. This article is an experimental study of the renormalization of bands in InSe crystals at high levels of optical excitation.

2. EXPERIMENTAL METHODS

Indium selenide has a layered structure, where each layer contains two indium and two selenium close-packed sublayers in the stacking sequence Se-In-In-Se [5]. The bonding between two adjacent layers is of the Van der Waals type, while within the layer the bonding is predominantly covalent. The investigated InSe crystals were obtained by the Bridgman method. The ingot were cleaved along the planes of layers ($\perp$ to the c-axis), obtaining slices about 10-50 μm thick. Mobility and concentration of charge carriers measured by conventional methods at room temperature were μ_n ~$1{,}2\times10^3$ $sm^2/V\cdot s$ and $n=7\times10^{14}$ sm^{-3}, respectively.

In our experiments, we used a picosecond YAG: ND^3 laser, generating light pulses of 25 ps duration, operating in the mode synchronization mode, as a light source. After amplification, the light pulse was split into two: the first, converted in the KDP crystal into a light pulse with a double frequency $\hbar\omega_H = 2{,}34эВ)$, served as an excitation source, the second was converted into a light pulse with a wide spectral distribution when passing through a cell with heavy water (0.75 ÷1.5) μm. The time delay between the probe light pulse and the pump pulse was carried out by changing the path length of the pump pulse. The zero delay was determined by measuring the correlation function of the pump pulse and the probe pulse by m of up-conversion in a KDP crystal The spectral distribution of the probe pulse transmitted through the InSe sample was studied using an M833 automatic double-dispersion monochromator (spectral resolution ~0.024 nm at a wavelength of 600 nm), with a detector detecting radiation in the length range waves of 350 - 2000 nm, a storage oscilloscope ((Le Croy 9400) and a computer system (board Master 800 ABI 8). The exciton absorption spectra and the dynamics of nonlinear absorption of light were studied at T = 4.2 K using the pump-probe spectroscopy method. In this case, the crystal was excited by an intense light pulse $\hbar\omega$ = 2.34 eV and the absorption spectra were recorded using a probe pulse at different instants of time. The experimental setup is shown in Figure 1.

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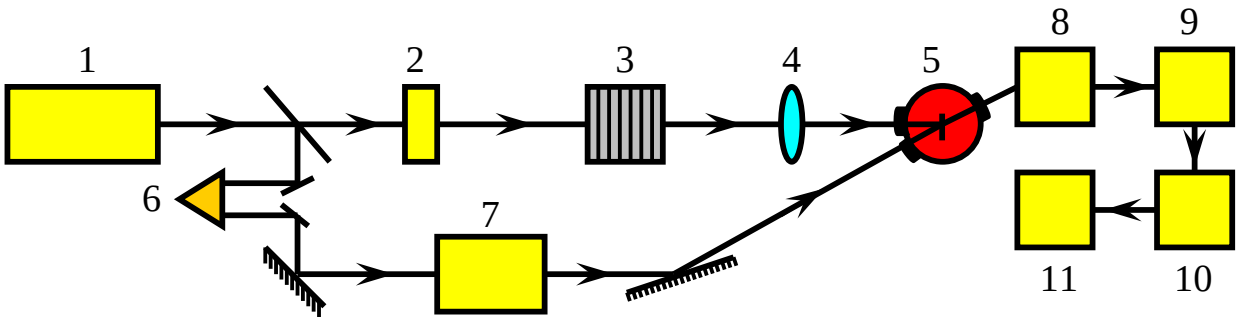

Fig. 1. Schematic of an experimental setup for measuring the transmission spectra of InSe crystals: 1-YAG: Nd^3 laser, 2-crystal KDR, 3-optical filters, 4-lens, 5-sample, 6- delay time, 7-cell with heavy water (deuteroxide), 8-monochromator, 9-detector, 10-oscilloscope, 11-computer system.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2a shows the spectral dependence of the optical density of InSe crystals at various excitation intensities (there is a zero time delay between the pump pulse and the probe pulse). As can be seen from the figure, nonlinear absorption is observed in the exciton absorption region ($\hbar\omega = 1{,}336$ eV) and the sample is bleached at the indicated radiation frequency at high excitation levels. The observed bleaching is saturated at an incident light intensity of ~ 600 MW/sm^2. The characteristic absorption length of the pump radiation is $\ell = 1/\alpha = 10^{-4}$ sm, $\alpha = 10^4$ sm^{-1} for $\hbar\omega = 2{,}34$ eV.

Figure 2b shows the absorption spectra of InSe crystals for various time delays between the probe pulse and the pump pulse. A broadening of the spectral line and a shift in the maximum of exciton absorption to the region of high energies relative to the unexcited state are observed. In the energy region between the exciton level and the edge of the conduction band, induced absorption appears.

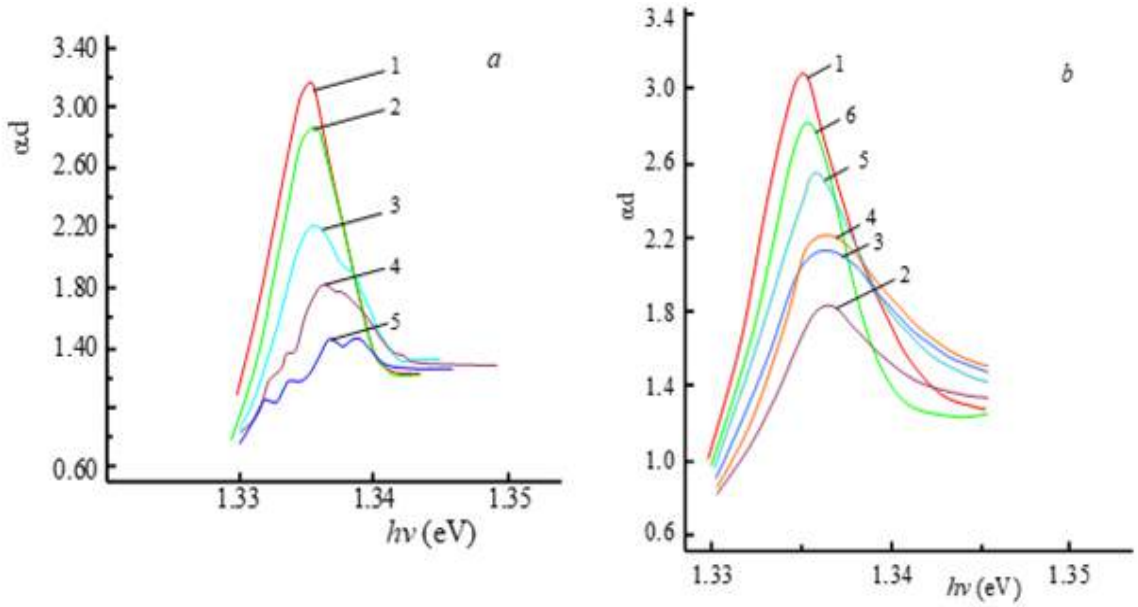

Fig. 2. a) absorption spectra of InSe at various excitation intensities I_{pump} (MW/ sm^2): 1 - 0, 2-12, 3-60, 4-250, 5-600 (there is zero time delay between the pump pulse and the probe pulse, $\Delta t = 0$) at T = 4.2K, b) absorption spectra of InSe for various time delays between the pump pulse and the probe pulse: 1 - I_{pump} = 0, 2 - Δt = 24 ps, 3 - Δt = 98 ps, 4 - Δt = 297ps, 5- Δt = 660ps, 6- Δt = 910ps, I_{pump} = 600 MW/sm^2, $\hbar\omega_{pump}$ = 2.34 eV, T = 4.2 K.

The time dynamics of bleaching in the region of exciton absorption and induced absorption has its own characteristic features (Fig. 3, a, b). It was experimentally established that the bleaching in the exciton absorption region is characterized by a rise front in time of ~ 60 ps, and the decay has a fast and slow kinetics (Fig. 3, a). The kinetics of induced absorption in the energy region between the exciton level and the edge of the conduction band is shown in Fig. 3, b. Note that at high excitation levels (I~600MW/sm^2), a probe pulse is amplified and the rise front is characterized by a time of ~ 60 ps. The maximum of the induced absorption is reached over the time of ~200÷300ps and with an increase in the pump intensity, shifts toward longer times.

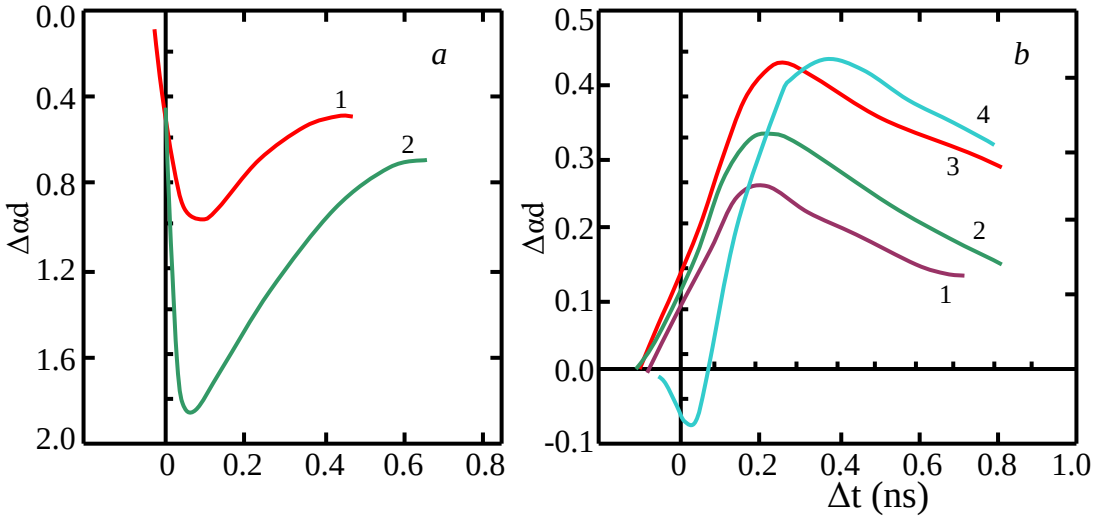

Fig. 3. Dependence of the optical density InSe on the delay time between the pump pulse and the probe pulse (Δt). a) at the maximum of the exciton absorption, $\hbar\omega_{probe}$ = 1.336 eV, $\hbar\omega_{pump}$= 2.34 eV, T = 4.2 K; 1- I_{pump}= 100 MW/sm^2, 2- I_{pump}= 200 MW/sm^2; b) in the absorption continuum, $\hbar\omega_{probe}$ = 1.340 eV, $\hbar\omega_{pump}$ = 2.34 eV, T = 4.2 K; 1- I_{pump} = 100 MW/sm^2, 2- I_{pump} = 200 MW/sm^2, 3- I_{pump} = 300 MW/sm^2, 4- I_{pump} = 400 MW/sm^2.

In our opinion, nonlinear absorption is observed in InSe crystals at high levels of optical excitation in the exciton absorption region. The observed features in the InSe absorption spectra can be explained by the interaction of excitons and the screening of the Coulomb potential by free carriers generated by laser radiation. Indeed, when InSe crystals are excited by laser light, electrons and holes bind to excitons. Subsequently, with an increase in the excitation intensity, the density of excitons increases, and when it reaches a certain critical value, an interaction between excitons occurs, which leads to the decay of excitons and the formation of free electron-hole pairs. This phase transition is called the Mott criterion for excitons [6]

$$n_{Momm} = \frac{\pi}{3}\left(\frac{1{,}46}{4a_{экс.}}\frac{m_0}{m_e + m_h}\right)^3 \qquad (1)$$

Knowing the effective masses of electrons and holes (m_e=0.7m_0, m_h =0.5 m_0), as well as the Bohr radius of the exciton $a_{ex.}$= 3.7 nm in InSe, we can calculate the exciton concentration, which turned out to be equal to $n_{Mott} \sim 2{,}5\times10^{16}\,см^{-3}$. Experiments show that in InSe the density of pairs generated by laser light with an intensity of I_0=1,5x10^{26} photon/sm^2 ·s, α ~10^4 sm^{-1} and duration of Δt=2,5x10^{-11} s is

$$\Delta n = \alpha\, I_0 \Delta t = 3{,}8\text{x}10^{19}\,\text{sm}^{-3} \qquad (2)$$

As can be seen from a comparison of formulas (1) and (2), the values of the concentration of nonequilibrium carriers obtained by us are three orders of magnitude higher than the exciton density required for the Mott transition.

We also determined the screening length of the Coulomb interaction by free carriers. The shielding length can be determined using the following formula [7]

$$L = \hbar/2(\pi/3)^{1/6} N^{-1/6} \frac{\varepsilon^{1/2}}{em^{*1/2}} \qquad (3)$$

where ε is the dielectric constant of the crystal, m∗ is the effective mass, and N is the concentration of the generated carriers.

Substituting the values of the corresponding parameters of InSe crystals, we find that the screening length L ~ 10A° is much smaller than the radius of the exciton. The Bohr radius of the exciton in InSe is ~ 37A°.

As can be seen from Fig. 2b, at a light intensity of I_{pump}~600MW/sm^2, the complete disappearance of the exciton absorption line was not detected. This, apparently, is associated with inhomogeneous excitation of the sample at $\hbar\omega_{pump}$=2.34eV. Thus, a situation is experimentally realized when both the electron-hole plasma (EHP) and the dense exciton gas are present in the sample.

Since the decrease in exciton absorption is due to the interaction of excitons and the screening of the Coulomb potential by free carriers, the increase in the transmission of the probe pulse should be proportional to the integrated pulse intensity, i.e. the rise time of enlightenment should be of the order of the pulse duration (see Fig. 3, a, b). On the other hand, the tightening of the leading front of enlightenment may be due to the diffusion of nonequilibrium carriers. Initially, the generation of free carriers occurs in a thin layer of ~10^{-4} sm, subsequently, electrons and holes diffuse deep into the sample, thereby reducing exciton absorption. The ambipolar diffusion coefficient in InSe is <10 sm^2/s; therefore, the time scale of carrier redistribution due to diffusion over the sample is more than 1 ns, which indicates an insignificant effect of the diffusion process.

It seems that a rapid decrease in the bleaching (see Fig. 3, a) is mainly associated with recombination processes in the electron – hole pair and dense exciton

gas. Slow kinetics is possibly determined by the screening process of excitons of the direct zone by nonequilibrium carriers of the indirect zone (the lifetime of these carriers is ~10^{-7} s).

Another consequence that exciton interaction and screening of the Coulomb potential by free carriers generated by laser radiation can lead to is a decrease in the bandgap or renormalization of bands in InSe at high levels of optical absorption. In our opinion, our observation of induced absorption in the energy region between the exciton level and the edge of the InSe conduction band is associated precisely with the appearance of a continuum of states due to a shift in the edge of the energy band (see Fig. 2, b)[8]. As a result of the renormalization of the forbidden zone the energies of the electrons and holes in their respective bands are reduced. This energy reduction is a consequence of the exchange effect for particles with equal spin and Coulomb correlation effect for all particles. The exchange effect is caused by the Pauli exclusion principle. The probability that two Fermions with identical quantum numbers are at the same point in real space is zero. For increasing separation between the particles, the probability slowly approaches unity. Hence, the Pauli exclusion leads to a reduction of the probability that equally charged particles come close to each other and this in turn reduces the repulsive (i.e., positive Coulomb energy) contribution. This situation for particles with equal spins is often described by the presence of an "exchange hole", where each Fermion is surrounded by a region where the probability for the existence of another identical Fermion is very small. Correspondingly, equally charged Fermions with different quantum numbers (e.g., electrons with different spins) avoid each other because of the Coulomb repulsion. As in the case of the exchange hole, this "Coulomb hole" also leads to a decrease of the overall energy.

A good approximation for the bandgap reduction is

$$\delta E_g = \sum_{q\neq 0}\left[V_s(q) - V(q)\right] - \sum_{q\neq 0} V_s(q)\left[f_e(q) + f_h(q)\right] \quad (4)$$

where the first and second terms are called the "Coulomb-hole" and "screened-exchange" contributions, respectively. Here $V(q)$ and $V_s(q)$ are the Fourier transform of the unscreened and screened Coulomb potentials, respectively. The renormalized bandgap is then

$$E_g^{/} = E_g + \delta E_g \quad (5)$$

with $\delta E_g < 0$ [the first term in Eq. (4) has a negative sign since the screened Coulomb potential is smaller than the bare Coulomb potential, $V_s(q) < V(q)$].

The bandgap shift when the concentration of excitons is high enough and their collective properties must be taken into account. More specifically, we are talking about such concentrations $n_{ex.}$, at which the value $(n_{эк.} \cdot a_{эк.}^3)^{1/3}$ begins to approach unity, i.e. the average distance between excitons becomes comparable with their radius. The bandgap shift depends on the distance r_s between two excitons

$$r_s \equiv \left(\frac{1}{n_{эк.} a_{эк.}^3}\frac{3}{4\pi}\right)^{1/3} \quad (6)$$

With decreasing r_s renormalization of zones increases.

We see that the screened exchange and the Coulomb-hole contributions both increase with increasing carrier density (decreasing particle separation). For low carrier densities, the dominating contribution comes from the Coulomb-hole term, whereas at elevated densities, both terms are equally important. An often useful approximation for the bandgap reduction has been derived in [9]

$$\frac{\delta E_g}{E_B} = E_{xc} + n\frac{\partial E_{xc}}{\partial n} \quad (7)$$

where E_B is the exciton Rydberg energy and

$$E_{xc} = \frac{4.8316 + 5.0879 r_s}{0.0152 + 3.0426 r_s + r_s^2} \quad (8)$$

Bandgap reduction leads to a monotonous red shift of the onset of the continuum absorption in semiconductors. At the Mott density the bandgap has shifted one exciton Rydberg energy below the zero-density bandgap E_g. For even higher densities, bandgap renormalization may cause increasing absorption in the spectral region below the exciton resonance. Whether such an increasing absorption is visible in an experimental spectrum depends on the magnitude of the bandgap renormalization versus the increasing chemical potential due to the bandfilling effect.

Qualitatively, the renormalization of zones can be explained as follows. Due to inhomogeneous excitation near the front surface, the density of nonequilibrium carriers is high and the Fermi level is in the renormalized zone. The contribution of this region of the sample to the transmission of the probe pulse leads to its increase. In the same part of the sample where the Fermi level does not lie in the zone, the probe pulse is absorbed. Subsequently, due to recombination processes in the electron – hole pair, the plasma density and the corresponding interval between the Fermi quasilevels decrease, which leads to an increase in the absorption of the probe pulse. An additional confirmation of this is the fact that the rise time of the induced absorption is of the order of the time of a rapid decay of the bleaching in the exciton absorption region (Fig. 3, a). The disappearance of induced absorption is associated with a further decrease in the concentration of nonequilibrium carriers.

CONCLUSION

In InSe layered crystals, the absorption spectra and its time evolution at various laser intensities were studied by the method of pump-probe spectroscopy. It is shown that the bleaching in the region of exciton absorption is due to the screening of the Coulomb potential by free carriers and the exciton-exciton interaction. Experiments show that the density of pairs generated by laser light (~ $4.5x10^{19}cm^{-3}$) in InSe is three orders of magnitude higher than the exciton density required for the Mott transition in these crystals ($n_{Мотт} \sim 2{,}5 \times 10^{16}\ см^{-3}$). An estimate shows that the screening length of the Coulomb potential by free carriers (L~10Aº) is much shorter than the Bohr radius of the exciton (~ 37Aº) in InSe. In the energy region between the exciton level and the edge of the conduction band, induced absorption is detected. The reason for this absorption is the renormalization of bands in InSe at high levels of optical excitation.

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