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Exciton absorption in InSe crystals at picosecond excitation

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Abstract : The nonlinear light absorption and its time evolution in the exciton resonance region at high optical excitation levels in InSe layered crystals have been investigated experimentally The observed time dependences of the absorption coefficient of InSe crystals and its excitation intensity dependences are determined not only by exciton-exciton interaction and exciton screening by the plasma of nonequilibrium carriers, but also by the phenomena attributed to kinetic and relaxation-recombination processes in the system.

Keywords : Exciton, InSe crystals, nonlinear light absorption

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1. Introduction

In semiconductors, photogenerated electron-hole pairs rapidly thermalize and relax into levels close to the band gap. Direct electron-hole pairs normally have a short recombination lifetime which, at low crystal lattice temperatures T_l, does not allow them to thermalize with the crystal lattice. Thus, the temperature T_e of the electron hole pairs is usually higher than T_l. Therefore, they will not only occupy bound states (excitons) which have the lowest energies but also higher dissociated states (ionized excitons). The electron-hole pair density can be easily raised by increasing the intensity of photoexcitation. A high electron-hole pair density will screen the Coulomb interaction between electrons and holes. For very strong screening no bound electron-hole pair states exist [1,2]. Thus, at low temperatures and with increasing pair density, the electron-hole fluid turns from an insulating gas of mostly bound electron-hole pairs or excitons into a metallic plasma of dissociated pairs. This phase transition is called Mott transition of the excitons [3], even though the carriers are not at zero temperature.

In this paper, we studied the nonlinear absorption in InSe crystals by analyzing the absorption spectrum in the exciton resonance region and its time evolution at high optical excitation levels.

Indium selenide has a layered structure, each layer containing four monatomic sheets in the sequence Se–In–In–Se, with the c axis perpendicular to the layers. The bonding between two adjacent layers is of the Van der Waals type, while within the layer the bonding is predominantly covalent [4]. InSe is of prime interest because it is strongly excitonic [5–11]. But, the behaviour of excitons in InSe at high excitations has not been investigated sufficiently. The behaviour of photoluminescence spectrum in InSe at high excitation intensities is interpreted by the creation of electron-hole plasma (EHP) [12,13].

2. Experimental method

The investigated InSe single crystals were obtained by the Bridgmen method. The ingots were cleaved along the planes of layers, obtaining slices about 10 μm thick. The presence of exciton line in the absorption spectrum is indicative of a good quality material. Mobility and concentration of electrons at T = 80 K were ~1.2 × 10^3 cm^2/V.s and ~7 × 10^{14} cm^{-3}, respectively. The samples were put into a helium cryostat equipped with a temperature controller which allows any temperature between 4.2 and 77 K to be maintained.

As an excitation source, a picosecond YAG : Nd^{3+} laser with a pulse duration of 30 ps were used. In this case, both the single beam and also double beam excitation were used [14]. In the first method, resonant excitation of excitons is performed by a parametric light generator. The second method (double beam method) uses pump-probe spectroscopy. After amplification, the light pulse is divided into two parts and two laser beams are focused on the same spot of a semiconductor sample. The laser labelled 'pump' passes through a KDP crystal and doubles in frequency ($\hbar\omega$ = 2.34 eV). The pump pulse has a relatively large intensity and is usually tuned to an energy within the absorption region of the InSe. The pump beam is absorbed, resulting in the generation of electron-hole pairs. The second light beam, referred to as the 'probe' beam, is used to monitor the changes in the optical properties caused by the pump. The probe intensity is very small, not inducing any changes by itself. The transmission spectrum of the probe beam detected in the presence of the pump beam is compared to the spectrum without pump beam, giving the frequency-dependent absorption of the sample for different intensities of the pump. For this purpose, it is convenient to have a probe beam that is either spectrally broad or easily tunable in wavelength, making it possible to monitor the entire band-edge absorption region. In our case, the probe pulse was formed by passing the second laser beam through deuteroxide, after which it was converted into a pulse having a wavelength in the range 0.75–1.5 μm. The pump-probe technique described above may also be employed to study the time evolution of the absorption spectrum. The time delay Δt between the probe and pump pulses is caused by a change in the path length of the pump pulse. Spectral distribution of probe pulse passing through the sample was investigated by a double-monochromator. All experimental data were processed and analysed by a computer.

3. Results and discussion

Figure 1a illustrates dependence of the magnitude of transmission coefficient on the emission intensity for an InSe single crystal excited by laser light having an energy $\hbar\omega$ = 1.327 eV (resonant excitation of exciton) at 77 K. As it is seen from the figure, a nonlinear absorption

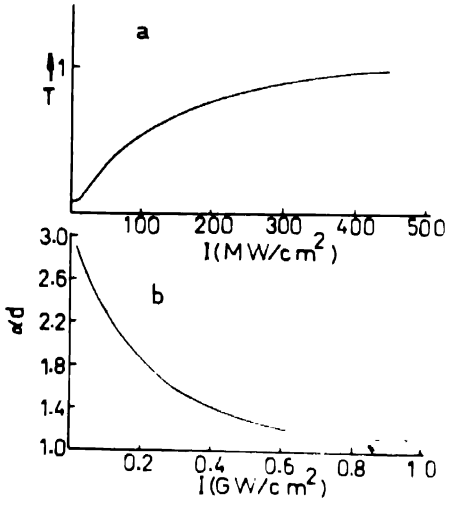

Figure 1. (a) Dependence of the transmission coefficient on the excitation intensity in InSe (in the case of resonant excitation of exciton, $\hbar\omega$ = 1.327 eV) at 77 K
(b) Dependence of the optical density on the excitation intensity ($\hbar\omega_{pump}$ = 2.34 eV, $\hbar\omega_{probe}$ = 1.336 eV, Δt = 0) at 4.2 K

in the exciton resonance region and occurrence of sample bleaching in the indicated light frequency at high excitation levels are observed. The observed bleaching saturates at the incident light intensity of ~ 300 MW/cm^2. Diminishing of the magnitude of exciton absorption may be explained by the process of screening (Mott transition) for a high density exciton system. The density of the electron-hole pairs in our experiment reached ~ 10^{20} cm^{-3} which exceeds the density necessary for the Mott transition in InSe ($n_{Mott} = 2.5 \times 10^{16}$ cm^{-3}) [13].

The detailed investigation of the bleaching and dynamics of nonlinear absorption in the exciton resonance region have been realized by using double beam method at 4.2 K.

Similar to single beam excitation, in this case also a bleaching is observed in the exciton absorption region at T = 4.2. Figure 1b illustrates clearly dependence of optical density on the excitation intensity in a frequency where the exciton absorption is maximum (the time delay between the probe and pump pulses is zero). The observed bleaching saturates at higher excitation levels with respect to the case of resonant excitation of exciton. This can be ascribed to the spatial inhomogenity of the excitation in the sample. Typical absorption length of the excitation power is of the order $1 \sim 1/\alpha \sim 10^4$ cm, $\alpha = 10^4$ cm^{-1} for $\hbar\omega$ = 2.34 eV [5]. Disappearance of the exciton peak in this case may be explained by screening of the

Coulomb interaction by free charge carriers. The screening length can be defined by the following equation [15]

$$L = \frac{\hbar}{2}\left(\frac{\pi}{3}\right)^{1/6} N^{-16}\,\frac{\varepsilon^{1/2}}{em^{*1/2}}$$

where, ε is the dielectric constant of the crystal and m^* is the effective mass. By substituting these values from [16,17] it is found that, $L \sim 10$ Å which is less than the exciton radius (~ 37 Å) [18]. In Figure 2 the absorption spectra of InSe crystals for different time delays

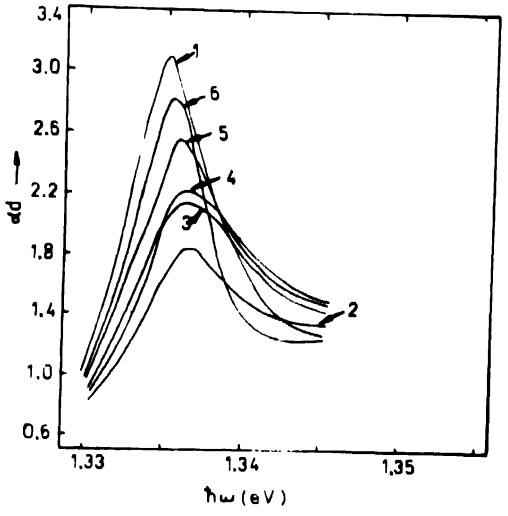

Figure 2. Absorption spectra of InSe for different time delays between the probe and pump pulses 1– $I_{pump} = 0$, 2–$\Delta t = 24$ ps, 3–$\Delta t = 98$ ps, 4–$\Delta t = 297$ ps, 5–$\Delta t = 660$ ps, 6–$\Delta t = 910$ ps, $I_{pump} = 600$ MW/cm^2, $\hbar\omega_{pump} = 2.34$ eV, $T = 4.2$ K.

between the probe and pump pulses are shown. It is clear from the figure that, the exciton absorption peak broadens and shifts towards higher energies with respect to the nonexcitation case. In the energy region between the exciton level and edge of the conduction band, an induced absorption is appeared. It should be noted that at a light intensity $I \sim 600$ MW/cm^2, complete disappearance of the exciton peak is not observed. Thus, a situation is realized experimentally in which both the electron-hole plasma and high-density exciton gas are present in the sample.

Time dynamics of bleaching in both the exciton absorption and induced absorption regions has certain peculiarities (Figures 3a,b). Experiment shows that, bleaching in the exciton absorption region is characterized with a rising front occurring in ~ 60 ps and a falling part consisting with fast and slow components (Figure 3a). Since decreasing of the exciton absorption is due to the screening of the Coulomb interaction by free carriers, so, the increase in probe pulse transmission should be proportional to the integrated pulse intensity, *i.e.* the bleaching rise time should be of the order of the pulse duration. On the other hand, the

retardation of the bleaching front may be due to the diffusion of the nonequilibrium carriers. At first generation of free carriers occurs in a thin layer ~ 10^{-4} cm, afterwards electrons and holes diffuse into the sample causing the exciton absorption to decrease. Since the ambipolar

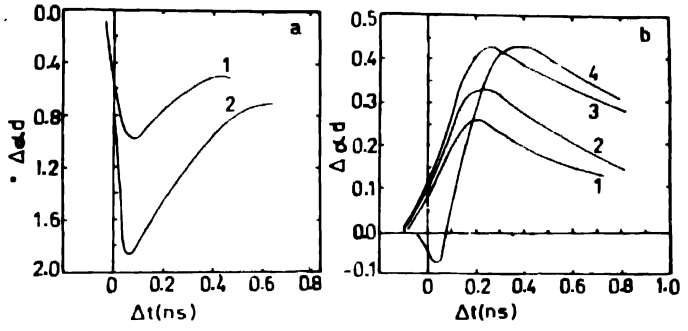

Figure 3. Dependence of the optical density on time delay Δt
(a) at maximum exciton absorption $\hbar\omega_{probe}$ = 1.336 eV, $\hbar\omega_{pump}$ = 2.34 eV, T = 4.2 K, 1–I_{pump} = 100 MW/cm^2, 2–I_{pump} = 200 MW/cm^2;
(b) at absorption continuum, $\hbar\omega_{probe}$ = 1.340 eV, $\hbar\omega_{pump}$ = 2.34 eV, T = 4.2 K, 1–I_{pump} = 100 MW/cm^2, 2–I_{pump} = 200 MW/cm^2, 3–I_{pump} = 300 MW/cm^2, 4–I_{pump} = 600 MW/cm^2

diffusion coefficient in InSe is less than 10 cm^2/s, therefore the time scale of carrier redistribution by diffusion in the sample is greater than 1 ns which indicates, the influence of diffusion process is negligible.

Considering the above exposition, if can be said that the fast falling component of the bleaching (Figure 3a) is basically due to the recombination processes taking place in EHP and high density exciton gas. The slow component may be determined by the process of screening of direct band excitons by the indirect band nonequilibrium carriers (life time of these carriers is of the order 10^{-7} s).

The kinetics of the induced absorption in the energy region between the exciton level and the edge of conduction band is given in Figure 3b. This phenomenon is due to the appearance of continuum states caused by shifting the energy band edges [19]. It is noted that at high excitation levels (I = 600 MW/cm^2), an amplification of the probe pulse is observed which is characterized with a rising front occurring in ~ 60 ps. The induced absorption reaches a maximum at ~ 200-300 ps and shifts towards higher time values by increasing the pumping intensity. This can be qualitatively explained by the following manner. Due to the inhomogenity of the excitation in the vicinity of the front surface of the sample, the density of nonequilibrium carriers is very high and the Fermi level is found to lie inside the renormalized band. This region of the sample causes the probe pulse transmission to rise. In the region of the sample where the Fermi level does not lie inside the band, the probe pulse is absorbed. Then, due to recombination processes taking place in the EHP, the plasma density and respective spacing between the quasi-Fermi levels start to diminish, leading to a rise in the probe pulse absorption. An additional confirmation to this statement is brought about from the

fact that, the rise time of induced absorption is of the same order as the fast fall time of the bleaching in the exciton absorption region (Figure 3a).

Disappearance of the induced absorption is due to the diminishing of the concentration of the nonequilibrium carriers.

4. Conclusions

The exciton-exciton interaction process and screening of excitons by free carriers are the most probable mechanisms responsible for diminishing of exciton absorption in InSe at high excitation intensities. Induced absorption which appeared in the energy region between the exciton level and edge of the conduction band is due to the appearance of continuum states caused by shifting the energy band edges in InSe. Time dynamics of bleaching in both the exciton absorption and induced absorption regions may be explained by the recombination processes taking place in EHP and high density exciton gas.

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