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Exciton Scattering by Dislocations in the CdSe Crystal

YU. A. OSIP'YAN, V. B. TIMOFEEV, AND É. A. SHTEĬNMAN

Institute of Solid State Physics, USSR Academy of Sciences

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Relaxation properties of excitons in CdSe crystals are studied in the presence of dislocations introduced by plastic deformation. The exciton lifetimes in the band are measured by the technique of absorption saturation in the exciton-phonon spectrum. It is found that scattering of excitons by dislocations in CdSe crystals is of an inelastic nature. Estimates are made of the cross section for inelastic interaction between the exciton and structure defects.

INVESTIGATIONS of the relaxation properties of quasiparticles (electrons, excitons, etc.) in crystals containing defects are very important for the understanding of the nature of the interaction between a mobile nonlocalized excitation with a static local defect. The purpose of the present investigation was to study the dynamic properties of excitons as functions of the content of structural defects in the crystal. It seems to us that a qualitative manifestation of the exciton-dislocation interaction consists in the following. If the scattering of an exciton by a static defect is elastic[1)], then such an interaction can greatly influence the transverse relaxation time of the excitons, change the mean free path of the exciton, and also change the width of the exciton line, provided the effective collision frequency in the exciton-dislocation interaction channel exceeds the damping in the exciton-phonon interaction channel. However, elastic interactions can hardly change the exciton lifetimes in the band and hence the quantum yield of the luminescence connected with the radiative annihilation of the excitons. If the collisions of the excitons with the dislocations are inelastic, then such an interaction, in contrast to the elastic one, should change the exciton lifetimes, and consequently influence the distribution of the excitons in the band and the exciton-luminescence yield. We have previously established[2] that the quantum yield of the exciton luminescence decreases in crystals with high dislocation density, and the distribution of the intensity in the spectrum corresponds to a strong violation of the equilibrium distribution of the excitons in the band.

Thus, information concerning the character of the interaction of the excitons with the dislocations can be obtained by investigating the relaxation properties of the excitons in the crystal in the presence and in the absence of dislocations. To this end, we investigated experimentally the behavior of the exciton lifetimes in the band as functions of the dislocation content in CdSe crystals.

1. The method of experimentally determining the exciton lifetime is based on an investigation of the dependence of the absorption coefficient in the exciton-phonon region of the spectrum on the incident-radiation power density (the previously-investigated so-called saturation absorption in the exciton-phonon spectrum of a semiconductor[3]). The absorption takes place in the anti-Stokes region of the exciton-phonon spectrum and is characterized by the conservation laws

$$\hbar\omega = E_g - G + \hbar^2\mathbf{k}^2/2m_{\text{э}} - \hbar\Omega(-\mathbf{k}), \tag{1}$$

where $\hbar\omega$ is the photon energy, E_g is the width of the forbidden band, $\hbar\Omega$ is the energy of the optical phonon, and G and $\hbar^2\mathbf{k}^2/2m$ are respectively the exciton dissociation and motion energies (see Fig. 1a).

In the region of transitions accompanied by phonon absorption, the exciton-phonon absorption coefficient α is determined by the difference between the occupation numbers $n(\mathbf{k})$ and $\nu(-\mathbf{k})$ of the excitons and phonons; this difference, in turn, depends on the radiation power density

$$\alpha = \hbar\omega \sum_{\mathbf{k}} W(\mathbf{k}, \omega)(\nu - n), \tag{2}$$

where $W(\mathbf{k}, \omega)$ is a function characterizing the probability of the optical transition under the influence of the radiation. Only in a weak field, when the number of the excited excitons is negligibly small, is the absorption coefficient independent of P and its value is

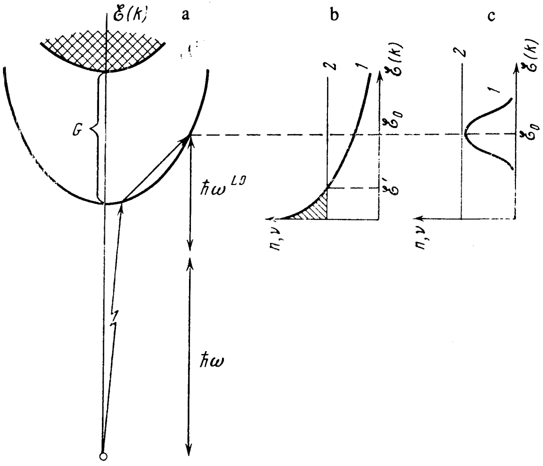


FIG. 1. Energy diagram of exciton-phonon transition with absorption of L0 phonon (a). Illustration of the equilibrium (b) and nonequilibrium (c) distributions of the excitons in the band when the excitons are monochromatically excited. Curves 1 and 2 are the distributions of the occupation numbers of the excitons and phonons, respectively.

[1)] The process of elastic interaction of an exciton with a dislocation is analogous to the elastic scattering of an exciton by a deformation potential, particularly by deformation acoustic phonons[1].

$$\alpha_0 = \hbar\omega \sum_{\mathbf{k}} W(\mathbf{k}, \nu)\,\nu. \tag{2'}$$

It is understandable that the dependence of the absorption coefficient on P will be determined by the relaxation properties of the excitons. Thus, it is shown in[3] that if the intraband exciton relaxation along the energy axis is faster than the departure (annihilation) of the exciton from the band, then the behavior of the exciton-phonon absorption coefficient with changing power density is as follows:

$$\alpha = \alpha_0 / (1 + f_1 P), \tag{3}$$

and the saturation parameter f_1 is equal to

$$f_1 = \frac{\alpha_0 \exp(-\mathscr{E}_0/kT)}{\nu\hbar\omega \sum_{\mathbf{k}} \exp(-\mathscr{E}(\mathbf{k})/kT)} \overline{\Delta t}_{exc}, \tag{4}$$

where $\mathscr{E}_0$ is the exciton-motion energy and $\Delta\overline{t}_{\mathrm{exc}}$ is the integral lifetime of the excitons with equilibrium distribution in the band.

If the intraband longitudinal relaxation is a slower process than the annihilation of the exciton at each point of the band (the condition $\tilde{\tau}(\mathscr{E}) > \Delta t_{\mathrm{exc}}$), then the excitons generated by the light have a nonequilibrium distribution, and the absorption coefficient has the following dependence on the power density:

$$\alpha = \alpha_0 / \sqrt{1 + f_2 P}. \tag{5}$$

The saturation parameter f_2 is equal to

$$f_2 = \frac{\pi\hbar\alpha_0\sqrt{2}}{m_e^{3/2}\,\omega\nu\sqrt{\mathscr{E}}} \tau_{ph}\,\Delta t_{exc}(\mathscr{E}), \tag{6}$$

where τ_{ph} is the lifetime of the L0 phonon, and $\Delta t_{\mathrm{exc}}(\mathscr{E})$ is the lifetime of an exciton with motion energy $\mathscr{E}$.

2. The investigations were performed on CdSe single crystals grown from the gas phase. We chose for the measurements the most perfect samples in the sense of the stoichiometric composition and minimum content of impurities or structure defects. Thus, for example, the initial dislocation density was $N_D \lesssim 10^2$ cm^{-2}. The dislocations were introduced into the crystal by plastically deforming the crystals at a temperature 150° C by the method described in[3]. By varying the degree of plastic deformation ϵ up to $\epsilon = 7\%$, we could obtain a set of samples with dislocation densities in the range 10^2–10^9 cm^{-2}.

The saturation of the exciton-phonon absorption was measured as a function of the power density by using a Q-switched ruby laser (radiation power density ~20 MW/cm^2, pulse duration ~4×10^{-8} sec. The absorption coefficient was measured by comparing the powers P_0 and P of the signals entering and leaving the crystal, which were registered by photodetectors with the aid of a high-speed broadband (100 MHz) oscilloscope. The absorption coefficients were measured in a dynamic range of power from 10 to 10^6 W/cm^2. The exciton-phonon absorption coefficient was measured at temperatures T = 80–100°K. With the temperature varied in this range, a ruby laser of stable frequency could excite excitons with wave vectors in the interval from 2×10^6 to 4×10^6 cm^{-1} (the corresponding energy interval in the exciton band is 7 MeV). We note that the choice of the lower value of the temperature is connected with the red boundary of the exciton-phonon spectrum (at $\hbar\omega < E_g - G + \mathscr{E}(\mathbf{k}) - \hbar\Omega$, the laser radiation lies in the transparency region of the CdSe crystal). At high temperatures, the ruby-laser radiation is close to the region of the direct interband transitions.

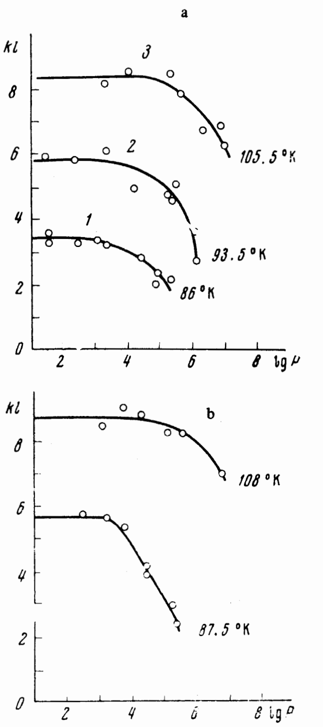


FIG. 2. Saturation of absorption in the exciton-phonon spectrum of CdSe with increasing radiation power density: a) undeformed crystals, $\epsilon = 0$; b) degree of plastic deformation $\epsilon = 3\%$.

3. Figure 2 shows the dependence of the optical density of the CdSe crystals on the radiation power density in coordinates $\ln P_0/P$ and $\log P_0$. The curves of Fig. 2a correspond to undeformed crystals (dislocation density $\lesssim 10^2$ cm^{-2}) with respective temperatures 86, 93, and 105°K. The curves of Fig. 2b illustrate, at the same temperatures, the saturation of the absorption in plastically deformed crystals for which the degree of deformation was $\epsilon = 3\%$ and the resultant density of the edge dislocations was ~10^7 cm^{-2}. Each curve corresponds to optical transitions to different parts of the exciton band (the energy $\mathscr{E}(\mathbf{k})$ of the excitons generated by the light increases with increasing number of the curve). The intercepts of the curves with the ordinate axis correspond to the limiting values of the optical densities of the crystals, corresponding in turn to zero power $P_0 = 0$.

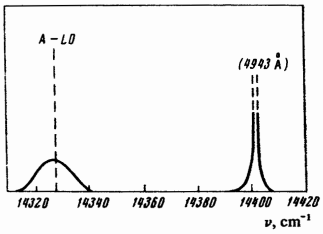
The first question to arise is: what is the mechanism of absorption saturation in deformed CdSe crystals? To answer this question, we have investigated the exciton luminescence spectrum excited by a ruby laser directly in the exciton-phonon region of the absorption spectrum. At strong absorption saturation in that place of the exciton band to which the optical transition takes place (for example $\mathscr{E}_0$ in Fig. 1), the occupation numbers of the excitons and the phonons remain close $n(\mathbf{k}_0) \to \nu(\mathbf{k}_0)$. If the relaxation of the excitons along the energy axis is faster than the departure of the excitons from the band (i.e., the saturation mechanism is differential), then the excitons have a nonequilibrium distribution in the band and consequently the exciton-photon luminescence certainly has a spontaneous and nonequilibrium character (see Fig. 1c).

If the longitudinal relaxation of the excitons is a faster process than their damping in the band, then the spontaneous exciton-photon luminescence corresponds to an equilibrium distribution of the excitons in the band. The excitons may acquire an inverse distribution relative to the L0-phonon band under conditions of strong absorption saturation in the exciton-band region near $\mathbf{k} = 0$, i.e., $n(\mathbf{k}) > \nu(\mathbf{k})$ at $|\mathbf{k}| < |\mathbf{k}'|$ (see the shaded region in Fig. 1b). As a result, induced luminescence can arise near the red boundary of the exciton-spectrum under the condition $\alpha l \gtrsim 1$ (α is the negative absorption coefficient and l is the sample thickness).

Induced exciton-phonon luminescence is observed in nondeformed CdSe crystals at exciting-laser powers starting with 5×10^5 W/cm^{-2} and above. Figure 3 shows the distribution of the intensity in the spectrum of the induced luminescence of undeformed single crystals excited by a ruby laser at T = 100°K. The figure indicates the red boundary of the exciton-phonon spectrum, calculated with allowance for the local heating of the crystal. There is no induced luminescence in deformed crystals at the same excitation powers. This indicates that in deformed crystals the exciton lifetime is at most shorter than the energy relaxation time, in contrast to crystals that are practically free from dislocations. The saturation-absorption phenomenon itself has a differential character in deformed crystals.

It is useful to note that the character of the intraband relaxation of the excitons and the ratio of their lifetime in the band to the time of their longitudinal relaxation can be judged qualitatively from the spectrum of the spontaneous exciton-phonon luminescence produced when the excitons are monochromatically excited (for example, in accordance with the conservation law (1)). To illustrate this, we show in Fig. 4 two distributions in the spectrum of the spontaneous exciton-photon luminescence of CdS crystals, where curve a corresponds to the spectrum of dislocation-free crystals and curve b to crystals in which the concentration of the edge dislocations was $\sim 10^7$ cm^{-2}. The luminescence at T = 77°K was excited with an argon laser, and this light generated "monochromatic" excitons with motion energy ~26 meV and wave vectors $\sim 10^7$ cm^{-1}. In the former case, the distribution in the spectrum of the spontaneous luminescence corresponds to excitons uniformly distributed in the band[4], and in the latter case to an essentially nonequilibrium distribution.

FIG. 3. Spectral distribution of the induced exciton phonon luminescence excited at T = 100°K in undeformed crystals by a ruby laser. The figure shows the position of the red boundary of the exciton-phonon spectrum (A–L0) and of the laser line.



ε = 0			ε = 3%		
(T, °K) E$_0$, eV	f_1	t$_1$, sec	(T, °K) E$_0$, eV	f_2	t$_2$, sec
86° $1.24 \cdot 10^{-3}$	$1.2 \cdot 10^{-1}$	$2 \cdot 10^{-5}$	84° $1.24 \cdot 10^{-3}$	$2.2 \cdot 10^{-2}$	$8.8 \cdot 10^{-11}$
93° $3.7 \cdot 10^{-3}$	$2.24 \cdot 10^{-2}$	$3.5 \cdot 10^{-9}$	108° $9.6 \cdot 10^{-3}$	$1.72 \cdot 10^{-3}$	$2.7 \cdot 10^{-11}$

The procedure for determining the lifetime of the excitons consisted in the following. We first determined the saturation parameters f_1 and f_2 from the curves of Fig. 2, using a formula valid for the region of weak nonlinearity (when $\alpha l - \ln(P_0/P) < 1$[3]

$$f_1 = \frac{\alpha_0 - \alpha_1}{\alpha_0 (P_0 - P)} \left(\alpha l - \ln \frac{P_0}{P} \right) = \frac{1}{2} f_2,$$

where α_0 and α_1 are the exciton-phonon and phonon absorption coefficients. Then expressions (4) and (6) were used to calculate the lifetimes for the cases of excitons with equilibrium and nonequilibrium distributions in the band. The table lists the obtained values of the parameters f_1 and f_2, and also the calculated lifetimes t_1 and t_2 for undeformed ($N_D \sim 10^2$ cm^{-2}) and deformed crystals ($N_D \sim 10^7$ cm^{-2}), respectively.

From the results in the table we see that the lifetime t of the uniformly-distributed excitons decreases with increasing temperature. This agrees with an earlier result[3] and is apparently connected with the decay of the excitons on the phonons[5]. The lifetimes of the excitons in deformed crystals turn out to be much shorter (by almost two orders of magnitude) than those in crystals that are practically free of dislocations. This result correlates with the facts that the quantum yield of the exciton-phonon luminescence decreases sharply and that the equilibrium distribution of the excitons in the band is disturbed, judging from the spectra of the spontaneous luminescence following monochromatic excitation, in crystals with high edge-dislocation density. Indeed, the average relaxation time of the exciton energy over an interval on the order of kT is

$$\bar{\tau}(\mathscr{E}) = kT\tau(\mathscr{E})/2mS^2,$$

where $\tau(\mathscr{E})$ is the average lifetime of the exciton in a state with wave vector $\mathbf{k}(\mathscr{E})$ (transverse-relaxation time),

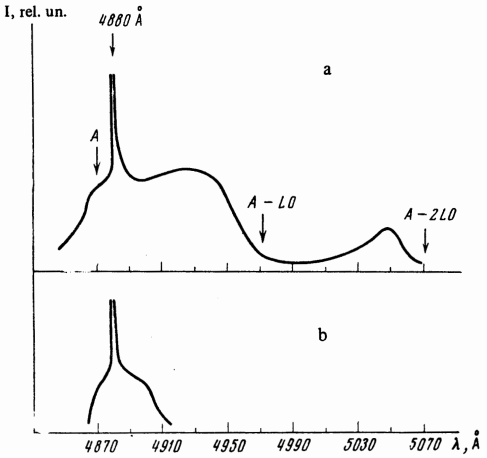


FIG. 4. Distribution, in the spectrum, of the spontaneous exciton-phonon luminescence of CdS crystals under monochromatic excitation (λ = 4880Å) in the case of equilibrium (a) and nonequilibrium (b) distribution of the excitons in the band.

and S is the speed of sound in the crystal[2]. Estimates show that $T \sim 10^{2}$°K and $\tilde{\tau}(\mathscr{E}) \sim 10^{-10}$ sec. This time is shorter by one order of magnitude than the exciton lifetime in undeformed crystals and is larger by approximately one order of magnitude than the exciton lifetime in deformed crystals.

The strong decrease (by almost two orders of magnitude) of the exciton lifetime in crystals with large dislocation density is apparently to be attributed to inelastic interaction of the exciton (a moving quasiparticle) with the dislocation (a local spatially-extended defect). Knowing the velocity and lifetime of the exciton, and also the concentration of the structure defects corresponding to a specified dislocation density (in our case $n \sim 10^{15}$ cm^{-3} at $\epsilon = 3\%$), we can estimate the cross section σ for inelastic exciton-dislocation collisions using the formula $\sigma = 1/nv\tau$, where v and τ are the velocity and lifetime of the exciton. At T = 97°K the value of σ turned out to be $\approx 10^{-10}$ cm^{2}.

Let us discuss the question of the mechanism of inelastic interaction between the exciton and the dislocation. The dislocation, being a static lattice defect, cannot be a direct cause of dissociation (decay) of an exciton whose energy lies below the bottom of the conduction band, as follows from the energy-conservation law. An energy sufficient for the decay of the exciton could be obtained from its kinetic energy, but in our experiments the motion energy of the light-generated excitons is always smaller than the binding energy, and in addition $G < kT$. An inelastic dissociation of the exciton by interaction with a static defect is even less likely, since the realization of such a process calls for the exciton to collide with an excited defect whose excitation energy is transferred to the exciton and is sufficient for its ionization.

It seems to us that a more probable mechanism of inelastic interaction is the ionization, by excitons, of local defects connected with the dislocations. This causes the exciton to annihilate and give up its excitation energy to the release of an electron or a hole connected with the dislocation. We note that a mechanism of this type is analogous to the photo-ionization of color centers in alkali-halide crystals by excitons, a mechanism previously established in[6-7]. If the notion that the exciton ionizes a structure defect is correct, then such an inelastic interaction should be accompanied by an additional increase of the photoconductivity following optical excitation in the exciton-phonon part of the spectrum, since the exciton itself is a neutral "non-current-conducting" formation.

We are continuing research on the details of the mechanism of inelastic interaction between excitons and dislocations.

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[2] Account is taken here of relaxation processes in the interaction with acoustic phonons. Optical phonons do not take part in the relaxation processes in our case, since the motion energy of the excitons excited by light is smaller than the energy of the optical LO phonon.