Effect of photoexcitation intensity on exciton kinetics

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For the first time, it has been found that the intensity of the exciting light affects the kinetics of the relaxation to the steady-state energy distributions of the excitons in the exciton band. The lifetime of the free excitons is shown to increase with increasing excitation intensity. The changes in the lifetime are estimated.

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The intensity of the exciting light (I_{exc}) is frequently varied over high values ($>10^3$ W/cm^2) in experiments on high-density effects, in which the nature and kinetics of the events that occur in the crystal are determined to a significant extent by the collective properties of excitons. As it turns out, even at "ordinary" values of I_{exc}, at which the exciton density is low, the actual value of I_{exc} is a factor which strongly affects the properties of the excitons. It was shown in Ref. 1 that I_{exc} affects the kinetics of the spatial distribution of excitons over the crystal. In the present letter we will demonstrate for the first time that I_{exc} also affects the kinetics of the relaxation to the steady-state energy distribution of excitons along the exciton band.

The test samples were CdS crystals grown from the gas phase. The experiments were carried out at $T = 2$ K. The samples were excited by the 476.5-nm line of an argon laser at an intensity which did not exceed 10^3 W/cm^2.

Figure 1 shows the emission spectra of two of the bulk samples studied in these experiments, for different values of I_{exc}. The events which shape the observed emission spectrum are shown schematically in the inset.[2] The exciting light is scattered by an *LO* phonon and thereby creates excitons at point *i* in the exciton band, $n = 1$A. A subsequent scattering of the excitons by *LA* phonons causes other points of the band to become populated. The spectra shown in this figure correspond to the emission of excitons from various points in the band, accompanied by the transfer to the lattice of the energy of the two *LO* phonons (we will refer to this emission as "two-phonon emission"). The line $3LO$ results from two-phonon emission of excitons from the point *i*. The arrow labeled E_T–$2LO$ gives the long-wave boundary of the two-phonon emission of excitons. The spectral shape of the two-phonon emission is known to reproduce the steady-state energy distribution of the excitons in the band.[3] Figure 1 shows that this distribution is strongly dependent on I_{exc}. The shape of the exciton energy distribution over the band depends on the number of scatterings by *LA* phonons for which the excitons have time during their lifetime in the band, τ. The nature of the change in the distribution of excitons over the band shows that τ increases with increasing I_{exc}. In sample 1, at a low value of I_{exc}, the lifetime is so short that the excitons have time to interact with only a very few *LA* phonons, and the excitons are emitted primarily from the point *i* and its immediate long-wave neighborhood (spectrum 1 in Fig. 1). As I_{exc} is increased, τ increases, and the number of events involving scattering by *LA* phonons increases; at the maximum I_{exc} the excitons populate all points in the band. Most of them lie near the bottom of the band (spectrum 2). For a given excitation intensity, the shape of the distribution and

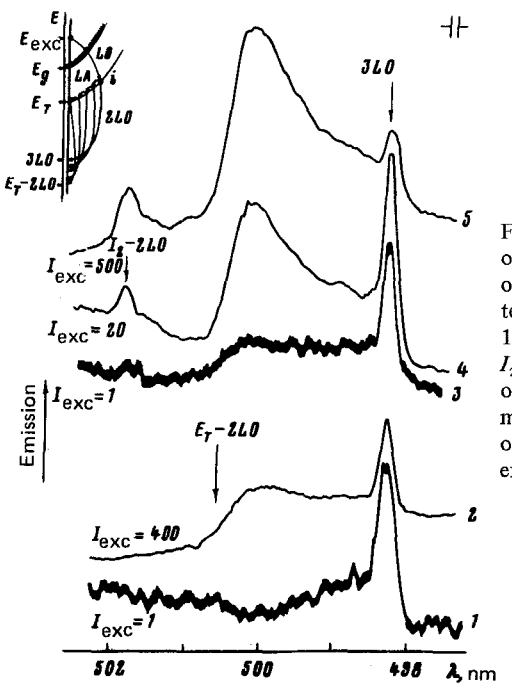

FIG. 1. Spectrum of the two-phonon emission of excitons in bulk CdS samples at various levels of the excitation intensity (at $T = 2$ K). The intensities I_{exc} are given in arbitrary units. Spectra 1, 2–Sample 1; spectra 3-5–sample 2. The line I_2–$2LO$ corresponds to the two-phonon emission of a bound exciton, I_2. In the inset: E_g–Fundamental absorption edge; E_T–bottom of the band of the $n = 1$A exciton state; E_{exc}–energy of the exciting light.

thus the value of τ are in different samples.[2] For example, in sample 2 the "initial" lifetime at the minimum I_{exc} is longer than in sample 1, and the exciton energy distribution (spectrum 3) is approximately the same as that in sample 1 at a high value of I_{exc}.

The total exciton lifetime in the band is determined by the radiative lifetime τ_R and by the radiationless lifetime τ_{nR}:

$$1/\tau = 1/\tau_R + 1/\tau_{nR}. \qquad (1)$$

The radiative lifetime is long, of the order of 10^{-9}-10^{-8} s (Ref. 4). In the bulk samples studied, the probability for the radiationless loss of excitons is high, $\tau_R \gg \tau_{nR}$, so that we have[2] $\tau \approx \tau_{nR}$. The radiationless lifetime is determined by the sum of the probabilities for the capture of excitons by various types of centers:

$$1/\tau_{nR} = \sum_m \bar{v}\sigma_m N_m, \qquad (2)$$

where v is the average exciton velocity, and σ_m and N_m are the capture cross section and the number of centers of type m. As I_{exc} is increased, some of the centers begin to reach saturation, their density decreases, and this decrease evidently leads to an increase in τ. The lifetime may be determined by different types of centers at different values of I_{exc}.

In the least defective (plate-shaped) samples, at all the values of I_{exc} used in these experiments, the two-phonon emission is of an equilibrium nature. In these samples the density of capture centers is far lower than in the bulk samples, and the lifetime is longer than the time required to reach equilibrium. Again in this case there may be a change in τ, as is implied by the increase in the exciton diffusion length with increasing I_{exc}, which is observed in some of these samples at $T = 77$ K (Ref. 1). The reason is that at small values of I_{exc} the lifetime, although longer than the time required for relaxation to equilibrium, is still shorter than τ_R. The time τ_R is evidently an upper limit on the exciton lifetime in the band.

The change in the lifetime in the bulk samples can be estimated by measuring the ratio of the total integrated intensity of the band of two-phonon emission of excitons, I_Σ, to the intensity of the $3LO$ line, I_{3LO} (Ref. 2). The intensity I_Σ is proportional to the total lifetime of an exciton in the band, τ, and I_{3LO} is proportional to the the exciton lifetime at the point i, τ_i ($1/\tau_i = 1/\tau_a + 1/\tau_{nR}$, where τ_a is determined by the time required for an exciton to move from point i to other points of the band as a result of scattering by LA phonons). Consequently,

$$\frac{I_\Sigma}{I_{3LO}} = \frac{\tau}{\tau_i} = 1 + \frac{\tau_{nR}}{\tau_a}, \quad \text{or} \quad \frac{\tau}{\tau_a} = \frac{I_\Sigma}{I_{3LO}} - 1, \qquad (3)$$

Using the value of τ_a found in Ref. 2, we estimated the lifetime in our samples. In sample 1, for example, the lifetime varied from $\sim 4 \times 10^{-12}$ s at the minimum I_{exc} to 1.3×10^{-11} s at the maximum I_{exc}; the range for sample 2 was from $\sim 1 \times 10^{-11}$ s to $\sim 6 \times 10^{-11}$ s.

In summary, these experimental results demonstrate that I_{exc} has an important effect on the kinetic properties of the excitons. When monochromatic exciting light is used, and the samples are chosen appropriately, the excitation intensity I_{exc} can be used as a tool for studying the kinetic phenomena at various stages of the time evolution, down to the picosecond range, under steady-state excitation conditions.

The spectral evidence of the effect of I_{exc} described by us above has also been observed in our experiments on ZnSe crystals, excited by the 441.6-nm line of a cadmium laser. The I_{exc} dependence of the exciton kinetics is evidently a characteristic of all crystals in which radiationless mechanisms for the disappearance of excitons are important. In crystals for which a well-developed technology is available, and for which the defect composition is adjustable, the nature of the radiationless transitions can be studied by studying the I_{exc} dependence of the emission spectrum.

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