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Measurements of exciton diffusion by degenerate four-wave mixing in $CdS_{1-x}Se_x$

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We performed transient-grating experiments to study the diffusion of excitons in $CdS_{1-x}Se_x$ mixed crystals. The decay of the initially created exciton density grating is well described for $t \leq 1$ ns by a stretched-exponential function. For later times this decay changes over to a behavior that is well fitted by a simple exponential function. During resonant excitation of the localized states, we find the diffusion coefficient (D) to be considerably smaller than in the binary compounds CdSe and CdS. At 4.2 K, D is below our experimental resolution which is about 0.025 cm^2/s. With increasing lattice temperature (T_{lattice}) the diffusion coefficient increases. It was therefore possible to prove, in a diffusion experiment, that at $T_{\text{lattice}} \leq 5$ K the excitons are localized, while the exciton-phonon interaction leads to a delocalization and thus to the onset of diffusion. It was possible to deduce the diffusion coefficient of the extended excitons as well as the energetic position of the mobility edge.

I. INTRODUCTION

The relaxation of optically excited excitons in semiconductors is a fundamental physical process of the light-matter interaction. The methods of degenerate four-wave mixing (DFWM) are particularly powerful tools to study the possible relaxation processes. After the excitation with a light field, the phase of the excitation decouples from the driving field due to the interaction with defects, phonons, and other excitons. This process and the characteristic time, the so-called dephasing time T_2, have been studied extensively in recent years.[1–6] After these initial relaxation processes the excitons are decoupled from the exciting light field, and relax energetically due to phonon and photon emission and migrate within the crystal lattice.

In the alloy semiconductor $CdS_{1-x}Se_x$ the statistical substitution of sulphur by selenium on the corresponding lattice sites gives rise to a fluctuating band gap which localizes the holes and consequently the excitons as a whole.[1,2,7–9] The square-root dependence of the density of states is modified on the low-energy side due to localization, leading to an exponential tail of localized states reaching into the band gap.[7] The luminescence of this kind of mixed crystals can be attributed to the radiative recombination of localized states.[8,9] The transition region between localized and extended states is energetically located at the high-energy side of the luminescence band. The dynamic behavior of localized states is drastically changed compared to excitons in the binary constituents. Recent experiments have shown that, at low temperatures, the phase relaxation is governed by the inter- and intraband relaxation leading to dephasing times of the order of several hundred picoseconds.[1,2,10] The intraband relaxation itself leads to nonexponential decays of the time-resolved luminescence well described by a hopping model.[11]

II. EXPERIMENTAL PROCEDURE

A direct proof of the existence of localization is the measurement of the ambipolar diffusion coefficient D which can be evaluated in a transient-grating experiment. Two light pulses $\mathbf{E}_1(\mathbf{k}_1,\omega)$ and $\mathbf{E}_2(\mathbf{k}_2,\omega)$ are focused onto the sample where they overlap temporally and spatially. The photon energy is chosen to fit with an electronic resonance of the material. The interference of the two beams sets up a real population grating from which a probe beam $\mathbf{E}_3(\mathbf{k}_3,\omega)$ will be diffracted into the directions $\mathbf{k}_3 \pm (\mathbf{k}_2 - \mathbf{k}_1)$. Due to energy relaxation and diffusion the grating will decay with a time constant T_G. The intensity of the diffracted signal beam I_S, proportional to the square of the grating amplitude, decays with a time constant T_S given by[12]

$$\frac{1}{T_S} = \frac{2}{T_L} + \frac{8\pi^2 D}{\Lambda^2} , \tag{1}$$

where T_L and Λ denote the spectral lifetime and grating constant, respectively. In a DFWM experiment, I_S is evaluated by measuring the signal intensity $I_S[\mathbf{k}_3 + (\mathbf{k}_2 - \mathbf{k}_1)]$ as a function of the time delay τ between the pump beams and the probe beam. The recombination rate and the diffusion coefficient can be extracted when the grating constant is varied by changing the angle θ between the incident beams

$$\Lambda = \frac{\lambda}{2\sin(\theta/2)} . \tag{2}$$

λ is the wavelength of the exciting laser. In a plot of T_S^{-1} versus $8\pi^2/\Lambda^2$ the diffusion coefficient denotes the slope of the straight line, while T_L is deduced from the intersection with the T_S^{-1} axis.

In the DFWM experiments we used a mode-locked argon-ion laser synchronously pumping a dye laser. The repetition rate of this system is 82 MHz providing pulses of 8 ps full width at half maximum (FWHM) and 1.5 meV spectral FWHM. We split the laser beam into three beams. The probe beam passed a computer-controlled variable delay line. All beams were focused on a 50-μm spot onto the sample, the polarization being perpendicular to the optical c axis of the crystals. The high-quality thin samples were mounted in a variable-temperature He cryostat. The diffracted signal was passed through a spectrometer and monitored by an optical multichannel analyzer (OMA) system.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1, the signal intensity is plotted versus the time delay τ. The temperature and spectral position were 20 K and 2.1982 eV, respectively. The solid line represents a stretched-exponential fit with the formula

$$I_S \propto e^{-(\tau/T_S)^n} . \tag{3}$$

The exponent n was found to be 0.865 at 5 K, while the lifetime T_L depends on the experimental conditions. T_S varies between 1 and 1.5 ns with energy and temperature and is of the same order of magnitude as interband and intraband relaxation times.[1,2,10,11] The exponent is slightly decreasing with increasing temperature, and we find n to be 0.83 at $T_{\text{lattice}}=20$ K.

This kind of nonexponential decays are typical for energy relaxation within localized states.[13,14] At $\tau=0$, a spectrally very narrow exciton distribution is created within the localized states. These excitons will relax further down in energy by multiple trapping or hopping[11,15] leading to a broadening of the exciton distribution. The interband relaxation times[11] involved in this process are comparable with the intraband relaxation times leading to the observed stretched-exponential decay of I_S. A power-law dependence of the signal decay, often used to describe energy relaxation within localized states, cannot fit our measurements. The best power-law fit is plotted as a dashed-dotted line in Fig. 1, having strong deviations from the measured points.

The initially created excitons will predominantly relax down in energy into sites within the same potential well and neighboring ones. These processes do not lead to a significant change of the grating structure. At higher lattice temperatures this relaxation is influenced by the larger number of acoustical phonons resulting in the observed change of the exponent n. After these initial relaxation processes, the dynamic behavior of the excitons changes. In Fig. 2 the signal intensity is plotted for four different grating constants on a logarithmic scale versus the time delay for $\tau \geq 0.8$ ns. As can be seen the decays are exponential and it is therefore possible to apply Eq. (1) for these times.

In Fig. 3, the inverse signal decay time is plotted versus $8\pi^2/\Lambda^2$. At $T_{\text{lattice}}=20$ K and $E=2.1982$ eV, T_S^{-1} increases with Λ^{-2} indicating that the grating decay is faster due to diffusion for small grating constants. The diffusion coefficient is represented by the slope of the straight line in Fig. 3 and is 0.09±0.04 cm^2/s, while the

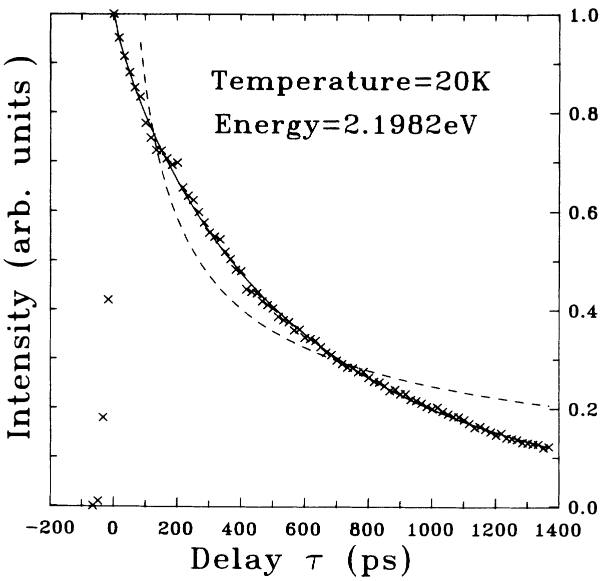

FIG. 1. Signal intensity of the first diffracted order I_S vs the time delay τ of the probe. The stars indicate the measured intensities in arbitrary units and the full line is a fit with Eq. (3), while the dashed line represents a power-law decay.

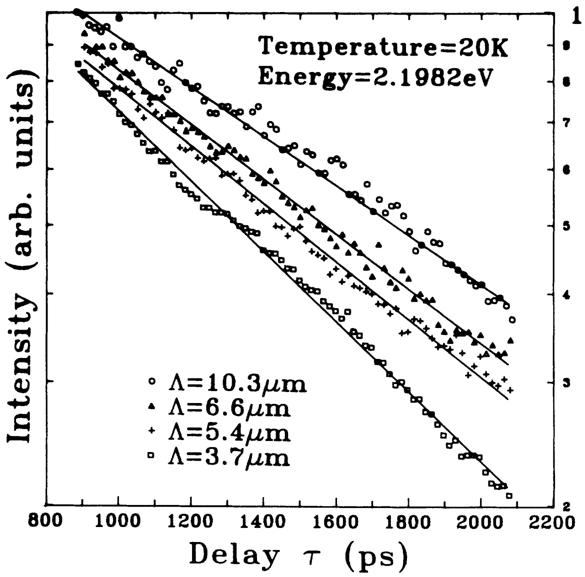

FIG. 2. Signal intensity of the first diffracted order I_S on a logarithmic scale vs τ for four different angles of the pump beams. The grating constants and decay times are 10.3 μm and 1.3 ns (○), 6.6 μm and 1.15 nm (△), 5.4 μm and 1.08 ns (+), 3.7 μm and 0.9 ns (□). The lattice temperature and detection energy are 20 K and 2.1982 eV, respectively.

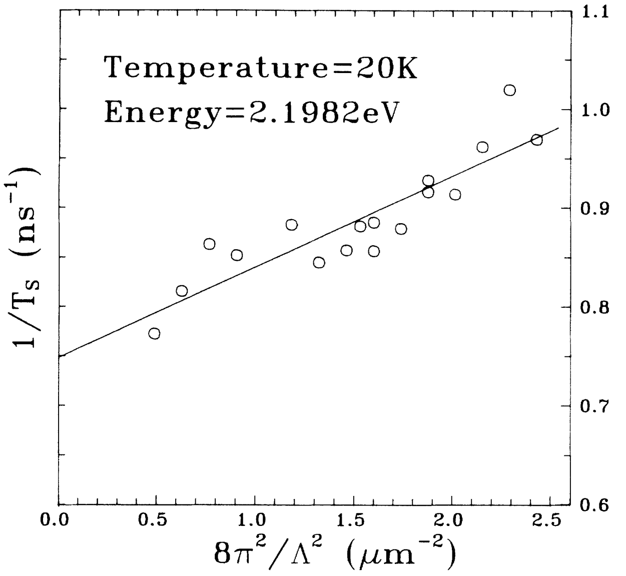

FIG. 3. Inverse signal decay times T_S^{-1} as a function of $8\pi^2/\Lambda^2$ measured at 20 K and 2.1982 eV. The straight line is a fit using the parameters $D=0.09$ cm²/s and $T_L=2.66$ ns.

spectral lifetime is in this case about 2.66 ns. The uncertainty of the diffusion coefficient is estimated from the reproducibility of the measurements which was mainly limited by the frequency stability of the laser system used and general noise. The large values found for T_L indicate that we are indeed measuring the radiative lifetime of the resonantly excited excitons. This is only possible if the intraband relaxation is decreased significantly due to the saturation of the deep localized states. From these experiments it is possible to deduce diffusion coefficients at certain energies even if the created carrier distribution is broadened due to the energy relaxation of the excitons. The reason for this behavior is based in the nonlinearities responsible for the creation of the diffracted orders. The main contribution to the signal intensity stems from an amplitude grating where only a bleaching of the states at the energetic position of the probe beam is important. A small fraction of I_S results from a phase grating where one has to take into account also states at other energies. Their influence on the diffracted order decreases very drastically with the energetic distance to the signal beam as well as with the decreasing occupation number of these states. In the experiment we will therefore average over an energetic range that is considerably smaller than the energetic width of the exciton distribution.

The values of D are more than one decade smaller than the ones reported for the binary constituent CdSe (Ref. 16) and CdS.[17] In CdSe the diffusion coefficient was found to be 3.0±0.3 cm²/s at 30 K. In CdS quasistationary DFWM experiments were reported leading to diffusion coefficients of the same order of magnitude. In addition preliminary experiments in the $CdS_{1-x}Se_x$ system did also show larger values of D.[8] The reason for this latter finding was based in the bad signal-to-noise ratio in these experiments. Thus it was not possible to measure with long delays and therefore only the grating decay up to $\tau=600$ ps was detected. The signal decay was then fitted with an exponential function leading to wrong values for T_S and thereby D.

In principle it would be interesting to map the dependence of D on the two independent variables T_L and $\hbar\omega$. Since, however, every experimental point for $D(T_L,\hbar\omega)$ results already from a rather time-consuming measurement in which Δ and τ have to be varied independently, it is hardly feasible to measure the whole two-dimensional dependence. Instead we measured along two orthogonal cuts in the $T_L,\hbar\omega$ plain, i.e., $D(T_L)$ for constant $\hbar\omega$ and vice versa. For the measurement at constant T_L we choose a relatively high value of 20 K since the expected variations of D are there more pronounced than at lower T_L.

The evaluated diffusion coefficients are plotted in Fig. 4 as a function of the lattice temperature. The excitation and measuring energy coincide with the high-energy wing of the luminescence band at low temperatures. We are thus creating localized states that are very close to the mobility edge. At 4.2 K no diffusion is found within the uncertainty of the measurements. Due to the large residual phase coherence of the excitons at 4.2 K the evaluation on the diffusion coefficient has a large uncertainty at this lattice temperature. With increasing T_{lattice} we also find increasing values of D up to $D=0.15\pm0.04$ cm²/s at 15 K. To prove that the localization depth of the carriers created at this energy does not change with temperature due to the band shift, the luminescence was measured in the covered range of T_{lattice}. It was found that the shift is below 1 meV and therefore the localization energy does

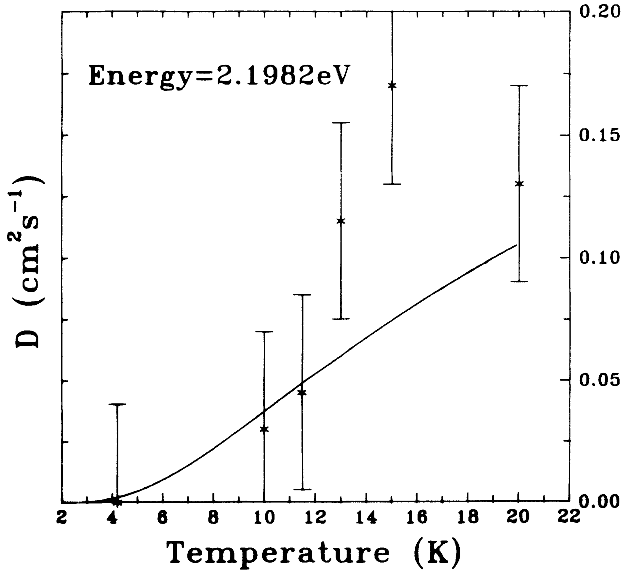

FIG. 4. Diffusion coefficient as a function of the lattice temperature. The excitation and detection energy is 2.1982 eV. The solid line is a fit using Eq. (4).

not change significantly. In Fig. 5 the measured diffusion coefficient is plotted versus the photon energy at $T_{\text{lattice}} = 20$ K. D increases from 0 ± 0.04 cm^2/s at 2.194 eV to $D \approx 0.16 \pm 0.04$ cm^2/s at 2.198 eV. No systematic dependence of the measured lifetime on the photon energy is found in the experiment. This also indicates that T_L is indeed the radiative recombination time. If there was a contribution to the decay from the intraband relaxation one would expect an increase of T_L with decreasing photon energy.

There are two main mechanisms for the spatial diffusion of localized excitons. The first one is tunneling between neighboring sites. This effect decreases very drastically with increasing localization depths due to the larger mean distance between the sites and increasing barrier heights. The diffusion coefficient connected with this process is very small and cannot be resoved with our setup. The second mechanism for the spatial motion of localized excitons is thermally activated hopping or multiple trapping. In this process a phonon is absorbed by the exciton bringing it up to a state above the mobility edge. Within this state it can migrate until the exciton is trapped again at another site or recombines. Due to the small number of phonons this process has a very small probability at low temperatures proven by photon echo experiments in this material. It was found that at 4.2 K the dephasing time is given by the lifetime of the excitons, indicating that exciton-phonon interaction is very small.[1,2,10]

With increasing lattice temperature the phonon density increases, leading to nonzero diffusion coefficients. At 15 K the diffusion coefficient $D = 0.15 \pm 0.04$ cm^2/s, which is the highest value measured at this excitation energy. While raising the temperature to 20 K no significant increase of D is observed. At even higher temperatures the signal intensity drastically drops and therefore limits the covered range of T_{lattice} in which we can measure.

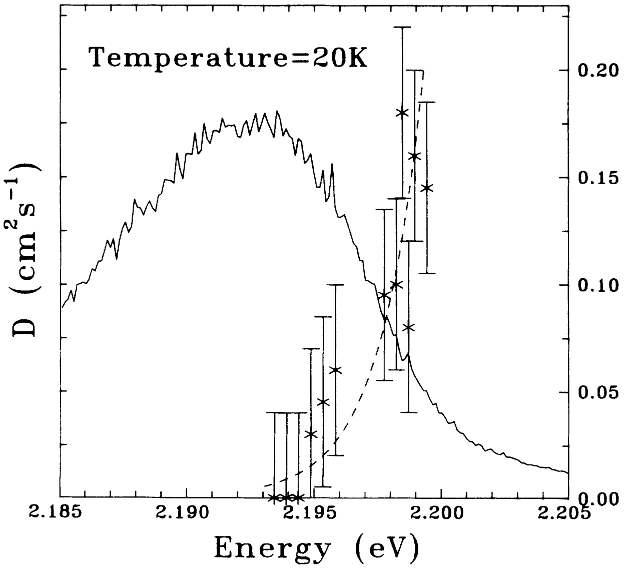

FIG. 5. Diffusion coefficient as a function of energy at $T_{\text{lattice}} = 20$ K. The stars are the experimental values for D while the dashed line is a fit using Eq. (4).

Thermally activated multiple trapping leads to an exponential dependence of the diffusion coefficient on the energetic distance of the carriers (E_{exc}) from the mobility edge (E_{mob}) as well as on the temperature:

$$D = D_0 \exp\left[\frac{E_{\text{exc}} - E_{\text{mob}}}{k_B T}\right] . \tag{4}$$

D_0 and k_B denote the diffusion coefficient of the extended excitons and the Boltzmann constant, respectively. This equation is used to fit the temperature dependence of D, represented by a solid line in Fig. 4. The parameters used are $D_0 = 0.3$ cm^2/s and $E_{\text{mob}} = 2.2$ eV. With the same equation, using a D_0 of 0.3 cm^2/s and the same energy for the mobility edge, we have also been able to represent the energy dependence of D for constant T_{lattice}, as shown by the dashed curve in Fig. 5. In Eq. (4) the diffusion coefficient of the extended excitons was assumed to be independent of the temperature. From diffusion measurements it is known that D decreases with increasing T_{lattice} leading to stronger changes of D_0 with temperature and by that to the observed deviations of the measured values from the calculated curve in Fig. 4. It was possible to deduce an activation energy in these experiments because D was measured after a time delay of 800 ps. During this time the initially sharp energy distribution of the excitons is thermalized leading to a broad distribution with, at low temperatures, a well-defined high-energy threshold. The diffusion coefficient was evaluated at this high-energy onset and the activation energy is given by the energetic distance to the extended (mobile) exciton states.

The diffusion coefficient of the extended excitons is smaller than in the binary compounds. The reason for this finding is the high probability for exciton-potential fluctuation scattering which hinders the exciton migration. This process is the main scattering mechanism for extended excitons at low temperatures in this material leading to dephasing times in the 100-fs range.[18] The energetic position of the mobility edge coincides with the high-energy onset of the luminescence band. This finding is in agreement with previous measurements on this material.[2,8,11,19]

IV. SUMMARY

The diffusion of excitons in CdS$_{1-x}$Se$_x$ was investigated by degenerate four-wave mixing. It was possible to prove directly the influence of localization on the exciton mobility as a function of temperature and localization depth. We have found that the decay of the population grating is for $\tau \leq 1$ ns described by a stretched-exponential function. Such a behavior is expected when the energy relaxation within a band is governed by hopping processes as it was found before in this material.[11] After this initial relaxation the grating decay is nearly exponential and makes the determination of a decay time T_G possible. In order to extract the diffusion coefficient, the grating decay was measured for different grating constants. D increases at 20 K from 0 ± 0.04 cm^2/s at 2.194 eV up to 0.19 ± 0.04 cm^2/s at 2.198 eV. This diffusion is governed by thermally activated hopping processes. The probability for such a process is determined by the energetic distance of the excited state to the mobility edge and therefore decreases with decreasing energy. In a temperature-dependent experiment we found that D decreases at 2.1982 eV from 0.14 ± 0.04 cm^2/s at 20 K to 0 ± 0.04 cm^2/s at 4.2 K in agreement with the decreasing number of acoustical phonons necessary for multiple trapping processes.

The temperature and energy dependence of the diffusion coefficient was found to be well fitted with an exponential function, indicating that the spatial mobility of the excitons is indeed due to thermal activation. The diffusion coefficient of the extended excitons is 0.3 cm^2/s in this material. This number is much smaller than the values found for the free excitons in the binary compounds due to the large probability for exciton-alloy disorder scattering. The mobility edge of the investigated sample is situated at 2.2 eV, which coincides with the high-energy onset of the luminescence band.

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