Ultrafast Phase Relaxation of Excitons via Exciton-Exciton and Exciton-Electron Collisions

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The ultrafast relaxation of excitons in GaAs, coherently excited by a short optical pulse and subjected to collisions with free carriers and noncoherent excitons which are independently created by a second synchronized light pulse, is studied directly in the time domain by a probing of the excitonic phase coherence. The relaxation rates reveal strong exciton-exciton scattering with a collision efficiency of 1.6×10^{-4} cm^3 s^{-1} and even 10 times more efficient exciton–free-carrier scattering.

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The optical properties of a semiconductor depend strongly on the density of the photoexcited electron-hole pairs.[1] At high densities, the Coulomb interaction of the photocreated electrons and holes leads to a collective plasma excitation with its characteristic metal-like features.[1] At low and intermediate densities, however, the optical spectra near the band gap are dominated by the two-particle excitation which is the lowest intrinsic electronically excited state of a semiconductor. Whereas a wealth of knowledge on the high-density phenomena[1] exists for direct–band-gap semiconductors, little is known about the transition from the low- to the high-density regime where exciton-exciton as well as exciton–free-carrier interaction start to modify the exciton dynamics.

Early photoluminescence studies[2] have revealed a broadening of the excitonic line with increasing free-carrier density, due to exciton-electron interaction. Quasi-cw transmission experiments[3] have indicated a bleaching and broadening of the excitonic line at free-carrier densities in the 10^{14}-cm^{-3} range and a complete bleaching at still higher densities.[3] In contrast, recent time-resolved transmission experiments could not find any broadening of the absorption line up to exciton densities of 10^{16} cm^{-3} and up to free-carrier densities of 10^{15} cm^{-3},[4,5] implying negligible exciton-exciton as well as exciton-electron interaction below these relatively high densities.

We report in this Letter on the dynamics of excitons coherently excited by a short optical pulse and colliding with either free carriers or with noncoherent excitons. The excitonic phase coherence of a low-density, coherent ensemble of excitons in GaAs is measured by time-resolved degenerate four-wave mixing (DFWM) while free carriers or excitons are additionally injected. The dependence of the phase coherence on the density of the scatterers directly yields the dephasing efficiency of each collision process. Exciton-exciton scattering is surprisingly efficient even below 5×10^{14} cm^{-3}, which corresponds to a mean exciton separation of more than 100 nm. Scattering by free carrriers is even 10 times more efficient. Our DFWM results obtained in the time domain agree well with the increase in collision broadening of the excitonic absorption line with increasing densities, confirming the homogeneous line broadening at low and intermediate densities. A consistent picture thus arises for exciton-exciton (X-X) as well as exciton–free-carrier (X-eh) interactions. A blue shift of the excitonic absorption line further indicates the repulsive character of X-X collisions, as predicted theoretically.

We used for our experiments high-purity GaAs layers (thicknesses between 100 and 190 nm) clad by $Al_{0.3}Ga_{0.7}As$ and grown on n^+-GaAs substrates by molecular-beam epitaxy. The substrates were polished down to wedges of about 30-μm average thickness. The samples were immersed in superfluid He. Two synchronously pumped tunable dye lasers with Styryl 9 were employed as the excitation sources. The autocorrelation width was 3.7 ps, the width of the power spectrum 0.9 meV, and the cross-correlation width 6.4 ps.

Figure 1 depicts the excitation geometry of our pump and probe configuration employing time-resolved DFWM. Two weak probe laser pulses, No. 1 and No. 2, with identical frequencies are tuned into the excitonic resonance and are focused on the sample. The first pulse sets up a macroscopic polarization of excitons. The electric field of the second and delayed pulse interacts with the polarization left from the first pulse, giving rise to self-diffraction. The dependence of the self-diffracted signal No. 4 on the delay τ_{12} is a direct measure of the excitonic phase coherence.[6] This coherent emission is detected by a cooled pho-

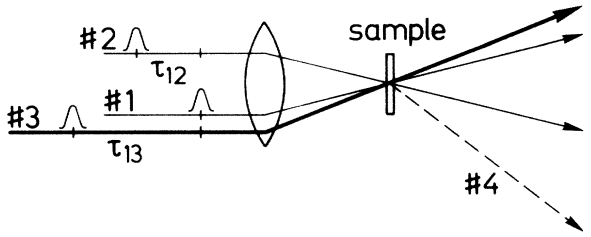

FIG. 1. Schematic excitation arrangement of the DFWM pump and probe experiment. The self-diffracted signal No. 4 from an orientational grating formed by pulses No. 1 and No. 2 (delayed by τ_{12}) monitors the phase coherence of the excitons in the presence of additional incoherent excitons or free carriers created by the stronger pulse No. 3 (advanced by τ_{13}).

tomultiplier with a GaAs cathode. The intensity of the pulses is adjusted to a level where the phase coherence is independent of the exciton density. A third, much stronger laser pulse, No. 3, with a frequency which can be tuned *independently,* creates additional noncoherent excitons at a time $\tau_{13}=20$ ps before pulse No. 1 arrives, or free carriers in temporal overlap ($\tau_{13}=0$ ps) with No. 1. Thus, the DFWM experiment on the probe ensemble of excitons directly measures the collisions with a background carrier or exciton distribution.

Figure 2 shows the diffracted intensity versus delay τ_{12} for three exciton densities at 2 K of a sample with a thickness of the central GaAs layer of 190 nm. The decay rate of the diffraction signal monitoring the excitonic phase coherence increases dramatically with increasing exciton density N_X. We analyze the experimental diffraction curves by performing a line-shape analysis based on an iterative solution of the optical Bloch equations in the small-signal limit.[7] The comparison with theory, also shown in Fig. 2, yields the excitonic phase coherence time T_2.

Figure 3 depicts T_2 versus the density of excitons (N_X) as well as versus the pair density of free carriers (N_{eh}). Below $N_X=2\times10^{14}$ cm^{-3} T_2 remains constant but drops rapidly above this level. For excitation of free carriers the functional dependence of T_2 is qualitatively the same as for excitons, but the same reduction of T_2 is observed at 10 times smaller densities than in the case of excitons. Thus, free carriers destroy the excitonic phase coherence by a factor of 10 more efficiently than excitons.

We analyze the density dependence of the measured phase coherence time T_2 by assuming a linear relationship between the inverse phase-coherence time T_2^{-1} which is proportional to the homogeneous linewidth, and the density $N_{(X,eh)}$ of the scatterers. Such a linear relation is appropriate in the low-density regime:

$$T_2^{-1}=T_2'^{-1}+(\gamma/2)N. \quad (1)$$

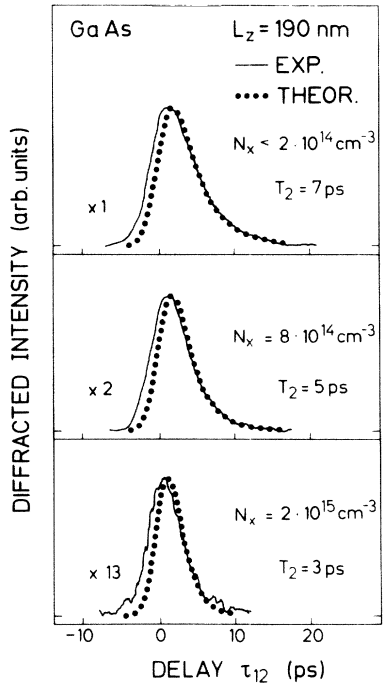

FIG. 2. Experimental (full line) and theoretical (dotted line) diffraction curves for additional exciton densities N_X. The comparison with the theory yields the phase-coherence time T_2.

Here T_2' is the residual phase-coherence time lumping together all dephasing processes except exciton-exciton and exciton–free-carrier interaction and γ is the collision-rate parameter, called here collision efficiency. A fit to the experimental data yields a residual phase coherence of $T_2'=7.5$ ps and collision efficiencies of $\gamma_{XX}=1.6\times10^{-4}$ cm^3 s^{-1} for free excitons and

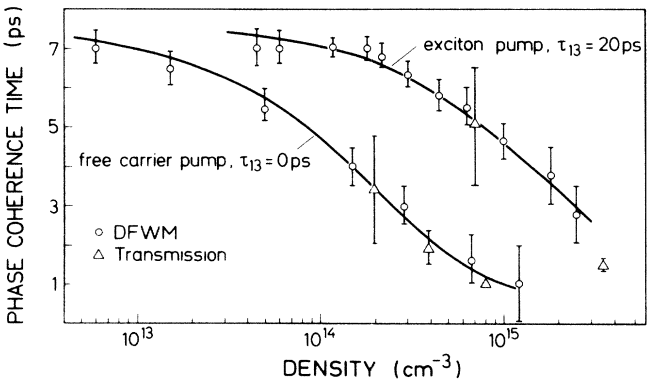

FIG. 3. The phase-coherence time T_2 of a small exciton ensemble subjected to collision with additional free carriers or excitons. The presented data are from DFWM experiment (circles) and time-resolved transmission (triangles). The collision rates are derived from the theoretical fit (full curve).

$\gamma_{Xeh} = 1.6\times10^{-3}$ cm^3 s^{-1} for free carriers.

Also shown in Fig. 3 are the results of additional time-resolved transmission experiments performed at the same excitation conditions as the DFWM experiments. The experimental spectra are analyzed by deconvolution of the spectral laser profile from the transmission spectra. From the linewidth Γ of the excitonic resonance a phase-coherence time $T_2 = 2/\Gamma$ is then determined. As shown in Fig. 3, the results of the frequency-domain experiments agree well with the time-domain DFWM results, which confirms homogeneous line broadening. Our results demonstrate that even for mean distances as large as 100 nm for excitons, or about 250 nm for free carriers, dephasing collisions with an exciton occur within 10 ps. Such surprisingly high sensitivity of the exciton to collisions can be explained by its large Bohr radius a_0 of about 13 nm. For still higher densities for which the average separation is of the order of the Bohr radius, a description of the dense exciton or electron-hole gas in terms of colliding particles is not appropriate. Rather, many-body effects such as the screening of the electron-hole Coulomb attraction, as well as exchange and correlation effects, have to be taken into account.[1,8]

Next we try to estimate the experimental collision efficiencies. A comprehensive comparison is impossible because the presently applied theoretical approaches[9,10] involve approximations of the complicated three- or four-particle scattering problem which have not been proven for the carrier interaction in semiconductors. For the most effective elastic *X-X* scattering[9] the two colliding excitons in the $1s$ state only change their wave vectors without any exchange of energy. The collision efficiency γ depends on the total cross section σ according to

$$\gamma = \sigma v, \tag{2}$$

where v is the relative velocity of the two colliding excitons.

At low kinetic energy the elastic *X-X* scattering cross section has been calculated to be $\sigma = 12\pi a_0^2$.[9] Assuming $v = 1.5\times10^6$ cm/s for the highly randomized exciton distribution after 20 ps (corresponding to a mean kinetic energy of 0.3 meV) we obtain $\gamma_{XX}^{\text{th}} = 10^{-4}$ cm^3 s^{-1} in reasonable agreement with experiment. Similar theoretical approaches have been applied to calculate the scattering cross sections of *X-eh* collisions.[10] They show strong enhancement of the cross section for low velocities. A total elastic cross section for $24\pi a_0^2$ is calculated in the low-velocity limit.[10] Taking an electron mass of $m = 0.66 m_0$ and an average, quasithermal electron velocity of 4×10^6 cm/s (corresponding to 0.3 meV kinetic energy) we obtain $\gamma_{Xeh}^{\text{th}} = 5.2\times10^{-4}$ cm^3 s^{-1} which agrees within a factor of 3 with our experiment.

A somewhat more illustrative, very early approach applied to the analogous hydrogen-electron scattering yields a scattering cross section diverging like v^{-1}.[11] This functional dependence is typical for the classical r^{-4} interaction potential of a charge with a neutral particle separated by a distance r ("Stark broadening"). Hence, the collision efficiency in the low-velocity limit becomes $\gamma_{Xeh}^{\text{th}} = 20 a_0 h/m$ (cf. Erginsoy[12]) giving a value of $\gamma_{Xeh}^{\text{th}} = 4.5\times10^{-4}$ cm^3 s^{-1}, also in reasonable agreement with our experiment. Furthermore this simple formula demonstrates that (i) the particle velocity is not important for *X-eh* collisions, and (ii) exciton–heavy-hole scattering is of minor importance because of the large hole mass. Scattering with the light holes may be as efficient as with electrons but the density of states is too low for a significant contribution.

Collisions usually not only produce a line broadening but may also shift the line. In the low-density regime the *X-X* interaction can be considered as being composed of the attractive van der Waals forces and repulsive hard-core forces having their origin in the Pauli exclusion principle. Separately performed time-resolved transmission experiments reveal a blue shift of the excitonic absorption line of 0.4 meV for an exciton density of 3×10^{15} cm^{-3} which is about 10% of the binding energy. Such a blue shift, which has not been reported for 3D excitons so far, indicates that the repulsive forces dominate over the attractive ones.[13]

The interaction of a neutral particle with an electron consists of (i) the attractive electrostatic interaction (polarization) which presumably leads to a red shift for the $1s$ exciton energy level, and (ii) the repulsive exchange interaction of electrons with parallel spins. Experimentally, the time-resolved transmission spectra at $\tau = 0$ ps do not exhibit any shift of the absorption line, which suggests that the attractive and repulsive forces cancel approximately. We conjecture that the blue shift originates from the formation of excitons because it can be observed in the case of free-carrier injection only at later times ($\tau \geq 10$ ps) and higher densities.

Our observed line shift is consistent with similar, time-resolved transmission experiments on 2D excitons in quantum wells,[14] but in contradiction to previous studies of Fehrenbach *et al.*[4,5]

The observed exciton-exciton scattering rates imply that for exciton densities below 10^{13} cm^{-3} exciton-exciton scattering is not effective in forming an exciton equilibrium distribution within the exciton lifetime of about 1 ns. However, randomization *via* scattering with phonons and impurities destroys the nonthermal exciton distribution on a 10- to 100-ps time scale. The quasiequilibrium distribution is then determined by the wave-vector dependence of the exciton-phonon and exciton-impurity interactions.

In addition, our results unambiguously demonstrate

that collisions dominate the bleaching of the excitonic resonance at low and intermediate densities. The bleaching (spectral hole burning) of the excitonic absorption in GaAs has been addressed in recent investigations.[3-5] Previous quasi-cw transmission as well as time-resolved transmission experiments have used the bleaching of the excitonic resonance as a measure of the exciton screening due to many-body effects (loss of oscillator strength). In contradiction to our observations, it was found by Fehrenbach *et al.*[4,5] that the excitonic line does not broaden below $N_X = 10^{16}$ cm^{-3} and $N_{eh} = 10^{15}$ cm^{-3}.

However, we believe that the reason for these discrepancies is the sample geometry used in these early experiments. First, the commonly employed optically thick semiconductor layers ($L_z \geq 1/\alpha = 100$ nm) prevent an accurate interpretation of transmission experiments because of the spatially inhomogeneous excitation conditions. The total change of the excitonic transmission depends nonlinearly on the local bleaching, which in turn is given by the local, but spatially inhomogeneous, exciton density. Thus, the densities necessary to produce a certain total bleaching might be overestimated by orders of magnitude depending on the thickness. Second, difficulties in the interpretation of transmission spectra arise if optically thin but self-supported and unclad GaAs platelets are used. These samples are strained and typically exhibit large inhomogeneous broadening of the excitonic resonance with typical linewidths of about 0.8 meV.[4,5] In addition, the unclad GaAs surfaces permit highly efficient and fast surface recombination which reduce strongly the electron-hole densities.[5]

In conclusion, we have reported the ultrafast dynamics of excitons in GaAs in the presence of additional free carriers as well as of excitons. We applied a new optical coherent technique employing excitonic phase coherence as a probe of phase-destroying collisions with free carriers or with incoherent excitons injected by a second, independent optical pulse. Our experiments demonstrate that X-X scattering is highly efficient even for low exciton densities, and allow us to determine collision efficiencies. Collisions with free carriers are found to be more effective by a factor of 10 because of the long-range nature of the Coulomb interaction. Time-resolved transmission experiments confirm the collisional origin of the line broadening. Thus, a consistent picture of X-X as well as X-eh interaction is obtained. In addition, we find that X-X collisions lead to a blue shift of the excitonic absorption line, which indicates the repulsive nature of X-X interaction. We hope that this work will stimulate further theoretical efforts to gain a comprehensive understanding of interaction of excitons and free carriers.

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