Picosecond Phase Coherence and Orientational Relaxation of Excitons in GaAs

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(Received 27 January 1986)

The phase coherence and orientational relaxation of excitons resonantly excited in optically thin GaAs layers by a picosecond light pulse is explored by means of time-resolved degenerate-four-wave mixing. At low excitation intensities where contributions due to exciton-exciton scattering can be neglected, a rapid loss of the phase coherence as well as of the optical alignment of the excitonic dipoles within 7 ps is observed. This implies a weak coherent coupling between excitons and photons and raises the question about the range of validity of the commonly employed polariton concept for GaAs.

PACS numbers: 71.35.+z, 42.65.−k, 71.36.+c

Excitons are the lowest intrinsic electronically excited states of a semiconductor and interact strongly with photons via their dipole moment. In direct-band-gap semiconductors the coherent coupling to photons leads to the new eigenstate, polariton, with a modified dispersion relation.[1] The validity of the polariton concept, however, strongly depends on the strength of the interaction between excitons and photons (characterized by the oscillator strength) compared to the strength of the residual interaction between the exciton and the crystal. The latter processes determine the dynamics of the exciton and their strength is characterized by the excitonic phase coherence time T_2. In order to prove the validity of the polariton picture the longitudinal-transverse (L-T) splitting which is a direct measure of the oscillator strength should be compared to the inverse of T_2. Whereas the oscillator strength can be measured easily in the frequency domain and is known for most of the semiconductors, knowledge about the phase-coherence time T_2 of excitons is still lacking. T_2 is usually assumed to be long enough so that the polariton concept can be used.[2]

In principle, the phase-coherence time T_2 of an optical transition can be measured directly in the time domain by means of optical coherent experiments.[3] Unfortunately, the excitonic transition in most of the direct-band-gap semiconductors exhibits a very strong absorption coefficient of about 10^5 cm^{-1} leading to spatially inhomogeneous excitation as well as to extremely weak nonlinear signals due to reabsorption. Thus, in practice high excitation levels are employed which in turn reduce the phase coherence via additional exciton-exciton collisions and prevent insight into the unperturbed dynamics of the exciton.[4] This problem can be overcome by use of *optically thin* GaAs layers with a thickness in the range of 100 to 200 nm. In addition, troublesome phase-matching considerations as well as polariton propagation effects[4] impeding the generation of the nonlinear signal are prevented and in these thin crystals purely excitonic dephasing can be studied by means of time-resolved degenerate-four-wave mixing (DFWM).

We report for the first time on the ultrafast dynamics of Wannier excitons at such *low* exciton densities where exciton-exciton interaction is unimportant. Thus, the observed relaxation times directly measure the residual interaction of excitons with phonons and impurities. The phase coherence is measured by a two-pulse experiment. In a second set of experiments diffraction of a delayed third pulse from an orientational grating formed by two orthogonally polarized pulses is analyzed monitoring the randomization of the excitonic dipoles (loss of optical alignment). The phase-coherence time T_2 as well as the orientational relaxation time T_1 is determined by a line-shape analysis of the time-resolved DFWM signal. We find a surprisingly short phase-coherence time of 7 ps and an orientational relaxation time of 7 ps independent of the excitation intensity provided that the exciton density is below 2×10^{14} cm^{-3}. These results demonstrate that residual scattering of the exciton is much more efficient than the coupling to the photons. Thus, the polariton concept usually employed in GaAs is not the appropriate description for excitons near the resonance.

We used for our experiments high-purity GaAs layers 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 thickness of the unintentionally doped

GaAs layer was 190 nm. The sample was immersed in superfluid helium during the experiments. A synchronously pumped tunable dye laser with Styryl 9 was employed as the excitation source. The autocorrelation width was about 3.7 ps, the width of the power spectrum 0.9 meV. The laser beams were focused onto the sample with a spot size of 5×10^{-4} cm^2. The coherent emission was detected by a cooled photomultiplier with a GaAs cathode.

First, we characterize the exciton transition in the frequency domain. Figure 1 displays typical transmission and photoluminescence spectra of a 190-nm-thick GaAs layer in the vicinity of the $1s$ exciton resonance. The transmission spectrum shows at 1.515008 eV the absorption line of the $1s$ exciton which exhibits a small shoulder on the high-energy side. Additional absorption lines are seen at 1.5158 and 1.5165 eV.

These absorption lines are attributed to exciton transitions belonging to the quantized electronic subbands of index N in the thin GaAs layer. Taking the nominal thickness of $L_z=190$ nm, a heavy-hole mass of $0.45m_0$, and an electron mass of $0.067m_0$, we obtain for the confinement energy E_c of the heavy-hole electron transition in an infinite quantum well a value of $E_c=0.18$ meV. The energy positions of the absorption lines are in reasonable agreement with the corresponding exciton transitions given by $E_N=E_0+E_cN^2$, where $E_0=1.5149$ eV is the band gap of the GaAs minus the exciton binding energy.

In Fig. 1 we also compare the measured transmission spectrum to a theoretical one calculated by using a single oscillator model. If we take into account two exciton-free surface layers, the effective layer thickness is $L_{\text{eff}}=L_z-4a_0=140$ nm, where a_0 is the excitonic Bohr radius.[1] The L-T splitting E_L-E_T is 0.08 meV and the background dielectric constant is 12.6.[5] The background transmission at 1.513 eV is scaled to the experimental one. The good agreement between theoretical and experimental transmission yields the homogeneous linewidth of $\Gamma=0.20$ meV and the transverse eigenenergy $E_T=1.515\,02$ eV which is slightly shifted to lower energies with respect to the absorption peak position.

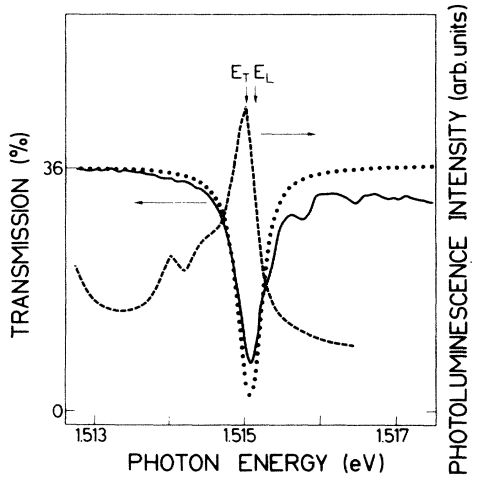

FIG. 1. Experimental (solid line) and theoretical (dotted line) transmission and photoluminescence (dashed line) spectra of a 190-nm-thick GaAs layer in the vicinity of the $1s$ exciton resonance at 2 K. The excitation intensity for the photoluminescence is about 30 mW/cm^2 at an excitation wavelength of 632.8 nm. Spectral resolution is about 0.04 meV.

The small discrepancy of the absolute value of the transmission minimum might be due to our crude single-layer model which does not take into account the smooth change of the excitonic polarizability near the interfaces.[1].

Also shown in Fig. 1 is a photoluminescence spectrum in the near–band-gap region. The energy position of the excitonic emission line at 1.515 eV agrees within spectral resolution with the excitonic eigenenergy as determined from the fit to the absorption line. These results indicate that the absorption as well as the emission of excitons in a thin GaAs layer has to be described by quantized excitonic levels. Optical excitation nearly perpendicular to the layer creates only excitons with a small wave vector $k_{\parallel}$ and therefore close to the resonance frequency. Thus, each exciton can be described by a highly degenerate two-level system.

Next we show in Fig. 2 the results of our degenerate-four-wave mixing experiments where the pulses are tuned to the $N=1$ exciton resonance. The upper inset shows schematically the geometry of the transient-grating experiment. Two incident pulses, overlapping in time and focused onto the sample, are forming a transient grating of excitons which diffracts a third, delayed pulse. The upper gives the intensity of the signal No. 4 for the case that the two incident pulses are polarized parallel to each other. For delays long compared to the pulse length, the diffraction by the population grating directly monitors the decay of an incoherent exciton-*density* grating.

The exciton-density modulation decays by diffusion and by the finite exciton lifetime which is determined by capture by impurities and radiative recombination. The decay time of about 250 ps obtained at low exciton density has to be attributed to a free-exciton lifetime of 500 ps because diffusion can be neglected for the large grating constant of about 20 μm. The exciton lifetime increases up to a few nanoseconds for increasing exciton density indicating the importance of a capture by impurities at low excitation intensities.

The efficient diffraction peak near zero delay arises from a grating formed by the *coherent* macroscopic polarization of excitonic states (orientational grating). Scattering randomizes the orientation of the excitonic

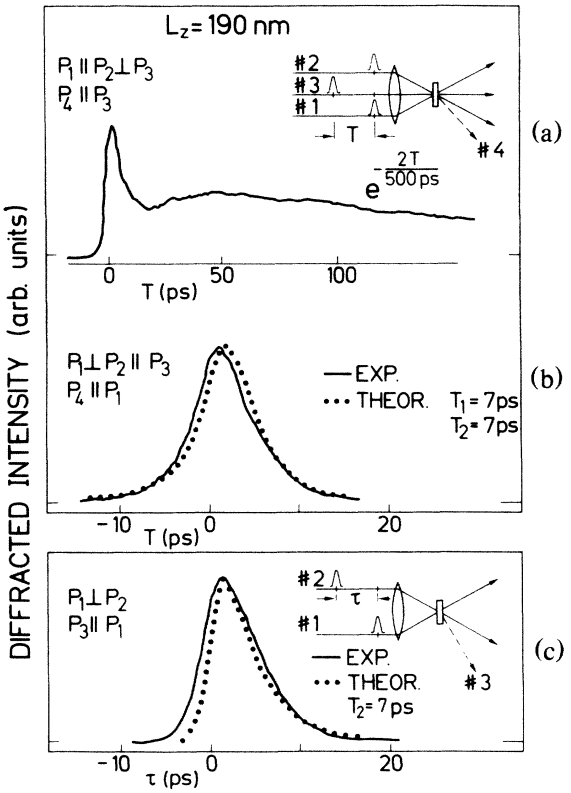

FIG. 2. Experimental (solid line) and theoretical (dotted line) diffracted intensity vs delay of the DFWM experiment for three different configurations. Insets: The schematical arrangements of the three-pulse and two-pulse DFWM. P denotes the polarization of the pulses. The pulses are tuned resonantly to the $1s$ exciton transition. The excitation intensity for the pulses is $I_1 = I_2 = I_3 = 3 \times 10^9$ photons/cm^2 pulse corresponding to 2.4×10^{13} excitons/cm^3 pulse. Comparison with theoretical curves yields the phase coherence time T_2 and the lifetime of an excitonic state T_1.

dipoles as well as the momenta parallel to the layer and gradually transforms the coherent grating into the incoherent exciton-density grating. The orientational relaxation can be observed much more clearly for the case of a grating formed by two *orthogonally* polarized pulses No. 1 and No. 2. In this configuration the exciton distribution is spatially uniform; only the orientation of the excitonic dipoles is periodically modulated. The results are shown in Fig. 2(b). Two mechanisms contribute to the diffraction.

(1) For positive delays the later pulse, No. 3, is diffracted off a grating set up by the first two pulses. Thus, the decay of the orientational grating directly monitors the lifetime of a particular exciton state with a well-defined wave vector $k_\parallel$ and an orientation P as given by the excitation geometry. The corresponding time constant T_1 describes the randomization of the excitonic states.

(2) The rise of the diffraction curve reflects the scattering of a pulse No. 2 off a grating set up by early No. 3 and the later No. 1. This diffraction mechanism probes the phase coherence of the excitons excited by pulse No. 3.[6]

We also show a theoretical diffraction curve calculated for a homogeneously broadened line. In order to incorporate the effect of a finite pulse length, a density-matrix formulation of the optical Bloch equations is used where we treated the $N = 1$ Wannier exciton as a homogeneously broadened two-level system.[7] We assume Gaussian pulse shapes fitted to the autocorrelation trace. The only adjustable parameters are the phase-coherence time T_2 and a population relaxation time T_1. A good agreement between the experimental and theoretical diffraction curves is obtained for a phase-coherence time $T_2 = 7 \pm 0.5$ ps and a lifetime of an excitonic state $T_1 = 7 \pm 0.5$ ps. The fitting procedure also proves that the rise is given by T_2 and the decay by T_1.[8]

The inset in the lower part of Fig. 2 shows the schematic arrangement of the two-pulse DFWM. The first pulse excites excitonic states with a wave vector $k_\parallel = 1.5 \times 10^3$ cm^{-1} and with an orientation given by the excitation geometry. Interference of the macroscopic polarization left from No. 1 with the polarization from the delayed second pulse forms an orientational grating of excitons. The second pulse is self-diffracted, thus probing the phase coherence. In Fig. 2(c) the diffracted intensity of the signal No. 3 versus delay between No. 1 and No. 2 is depicted. Comparison with the theoretical curves yields the phase coherence time $T_2 = 7 \pm 0.5$ ps which is in excellent agreement with the results from the three-pulse experiment.[8]

The phase-coherence time T_2 corresponds to a Lorentzian linewidth Γ given by $\Gamma = (h/e)(2/T_2) = 0.18 \pm 0.01$ meV. This value is in reasonable agreement with the linewidth Γ obtained from the transmission experiment indicating the consistency of the experiments in the frequency and the time domain and confirming the homogeneous broadening of the $N = 1$ exciton transition.

The observed T_1 and T_2 do not depend on the excitation intensity provided that the corresponding exciton density is below 5×10^{14} cm^{-3}. This fact demonstrates that exciton-exciton interaction is neither the origin of the scattering that destroys the phase coherence nor the limitation of the excitonic lifetime, in contrast to the investigations on the excitonic polariton in CuCl.[4] The obtained phase coherence and orientational relaxation times of Wannier excitons are by more than 1 order of magnitude larger than the scattering times of free electron-hole pairs excited above the band gap of GaAs.[9,10] In contrast to free carriers with long-range Coulomb interaction, excitons

are neutral particles with short-range potential. Thus, for sufficiently low exciton density, exciton-exciton interaction can be discarded. This is confirmed by our observation that the phase-coherence time decreases for exciton densities above 5×10^{14} cm^{-3}.

We explain the observed rapid relaxation of the excitonic states by longitudinal acoustic-phonon scattering. For bulk GaAs ($L_z=\infty$) the broadening of the exciton induced by phonon scattering at 2 K is estimated to be $\Gamma=3$ μeV by use of equation 2.27 and the material parameters of Takagahara.[11] However, in a thin GaAs layer ($L_z=3a_0$) the homogeneous linewidth is calculated to be about $\Gamma=1$ meV.[12] This enhancement of the scattering rate is due to the fact that the wave-vector component perpendicular to the layer does not have to be conserved. The linewidth decreases only slowly for increasing layer thickness so that for intermediate thicknesses also an enhanced scattering rate is expected.[12]

This interpretation is confirmed by our observation that the phase-coherence time decreases with increasing temperature ($T_2=5$ ps for $T=5$ K). Acoustic-phonon scattering also explains the fact that the phase coherence is not lifetime limited ($T_1>T_2/2$), i.e., there occur scattering events which change only the phase and not the excitonic state. Scattering by one phonon of wave vectors parallel to the layer, $q_{\parallel}\neq0$, transfers the excitonic state specified by $k_{\parallel}$ into $k_{\parallel}\pm q_{\parallel}$ leading to a randomization of the excitonic states and also of the phase. Scattering with longitudinal phonons of $q_{\parallel}=0$ or with two phonons with $q_{1\parallel}=-q_{2\parallel}$ might leave the state unchanged but destroys the phase.

The surprisingly small value of T_2 found for Wannier excitons in GaAs shows that the coherent coupling between excitons and photons is strongly disturbed. The homogeneous linewidth is two times the L-T split which measures the oscillator strength and corresponds to the time by which excitons switch into photons and vice versa. Thus, the dynamics of Wannier excitons in GaAs is dominated by acoustic-phonon scattering rather than by the coupling to photons. This corresponds to a situation in the bulk crystal where the propagating polaritons excited near resonance are attenuated within the wavelength. The usual description of polariton dynamics by the real part of the dispersion relation has to be extended by inclusion of the nonnegligible imaginary part of the dispersion relation. Consequently, the excitonic resonance is broadened which might obscure detection of spectral features characteristic for spatial dispersion (i.e., the so-called "additional boundary condition" problem).[1]

In conclusion, we have measured for the first time the phase coherence and the orientational relaxation time of Wannier excitons in GaAs by employing a thin layer geometry. The observed short phase-coherence time of 7 ps and orientational relaxation time of 7 ps are due to residual scattering on acoustic phonons and impurities. Comparison of the homogeneous linewidth with the L-T splitting reveals that the coherent interaction between excitons and photons is weak, implying a minor role of the polariton concept for the *dynamics* of excitons in GaAs.

We are grateful to M. D. Sturge for helpful discussions, and H. J. Polland and H. J. Queisser for critical reading of the manuscript. We also thank K. Köhler for helping with the absorption and photoluminescence measurements and R. F. Kopf for assisting with the molecular-beam-epitaxy growth.

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