Density Dependence of the Exciton Energy in Semiconductors

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We investigate both experimentally and theoretically the excitonic absorption in ZnSe in a temperature range between 2 and 60 K with increasing densities of carriers. For higher temperatures a weak redshift of the exciton resonance is found which turns into a blueshift for lower temperatures. While the widely used simplified treatment of the scattering processes within a static screening approximation fails completely to describe this thermally induced crossover, it can be explained by the interplay between Coulomb-Hartree-Fock renormalizations and carrier-carrier and carrier-polarization scattering including the dynamical screening. [S0031-9007(98)06251-6]

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The nonlinear behavior of the excitonic absorption is one of the most investigated manifestations of many-particle effects in a highly excited narrow-gap semiconductor. For instance the Mott transition observed for increasing excitation densities is well understood as a consequence of screening of the Coulomb interaction between charge carriers. While the absolute energy of the $1s$ exciton stays nearly unchanged in bulk samples over a wide range of carrier densities its oscillator strength disappears due to band gap shrinkage. This was proved in many experiments [1–3] and explained qualitatively by strong compensation of gap shrinkage and weakening of the Coulomb interaction due to screening inspecting the effective Wannier equation of an exciton embedded in a thermal plasma [4–7]. The situation is rather different in quantum wells, where a blueshift of the exciton with increasing density was observed [8,9]. Qualitatively, this behavior is caused by the reduced dimensionality, which leads to a reduction of the Coulomb interaction between carriers [10] as was confirmed by more elaborated calculations for a dense exciton gas model [11]. In $GaAs/Ga_{1-x}Al_xAs$ quantum wells the transition from quasi-2D to 3D behavior was found to occur at well widths of 19 nm, i.e., already at less than two exciton Bohr radii [9,12].

The present situation is characterized by two aspects. At first, recent experimental results shed new light on the commonly accepted view that the excitonic resonance stays nearly constant in a large density region. In $GaAs/Ga_{1-x}Al_xAs$ quantum wells of 21 nm width the exciton shift was found to change from a weak blueshift under resonant excitation to a weak redshift under nonresonant excitation [13]. Also in bulk ZnSe, where the influence of many-particle effects on the exciton can be observed much more pronounced than in the III-V semiconductors (GaAs) due to the larger exciton binding energy, a weak blueshift of the exciton [14] at resonant excitation and low temperatures has been found recently. Second, substantial progress has been achieved during the last few years to find out which many-particle effects have to be included into the semiconductor-Bloch equations (SBE) in order to describe the nonlinear absorption features of laser pulses. In particular, inclusion of carrier-polarization scattering processes was shown to be necessary for a correct description of different phenomena in excited semiconductors. The so-called off-diagonal dephasing [15], which is related to the imaginary part of the corresponding scattering integral, was used to describe the shape of phonon replica after pulsed excitation [16], the low-energy tail of gain spectra [17], and the exciton broadening [18]. The real part was demonstrated in [19] to reproduce the correct switch from absorption to gain in II-VI quantum wells. Both these aspects indicate a need to revisit the problem of nonlinear absorption properties of the exciton, which is a fundamental topic in semiconductor optics.

In the following we will present a careful experimental analysis of the exciton energy in bulk ZnSe in dependence on carrier density and temperature. ZnSe serves here as a model semiconductor providing both small exciton broadening (0.3 meV) and a large exciton binding energy (19 meV). Subsequently, it will be demonstrated that the complex experimental behavior is consistently explained by solving the SBE including both carrier-carrier (c-c) and carrier-polarization (c-p) scattering and the dynamical screening of the Coulomb interaction.

Our samples consist each of a binary ZnSe epilayer embedded in ternary ZnS_xSe_{1-x} barriers grown on subsequently removed GaAs substrates by molecular-beam epitaxy. The ternary barriers are lattice matched to the GaAs substrate, and the thickness of the ZnSe layers ($\leq$100 nm) is kept well below the critical value for dislocation formation, thus resulting in homogeneous compressive strain. For excitation the transform limited 100 fs pulses of a frequency-doubled Ti:sapphire laser were used. The full width at half maximum of the laser spectrum amounted to 15 meV. Pump and probe beams

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were chosen to be linearly cross polarized. The probe-beam intensity was detected via a grating monochromator by a photomultiplier tube using the lock-in technique. Chopping of the pump beam leads to a signal proportional to the pump-induced change of the transmitted intensity. In earlier investigations the optical response of these heterostructures was carefully analyzed in the spectral and temporal domain [14,20]. There, nearly quantitative agreement was found between experimental data and calculations based on polariton theory. Thus, the sample optics is well understood including the complicated fine structure of the spectra caused by polariton interferences.

Figure 1(a) shows differential transmission spectra $\Delta T/T_0$ (being the pump-induced change of transmission normalized to the linear transmission) in the excitonic energy region of a 22 nm ZnSe layer (approximately five Bohr radii) taken at a delay of 20 ps for different lattice temperatures. Since this delay is several times larger than the exciton dephasing time ($\approx$2 ps) no coherent interaction between pump and probe pulses occurs. Main features of spectra are the first three Fabry-Pérot modes of the heavy-hole polariton ($hh^{m=1,2,3}$) and the first mode of the light-hole polariton ($lh^{m=1}$). The pump is absorbed mainly by the lowest strong $hh^{m=1}$ mode. As a consequence, the initial exciton distribution has an effective temperature determined by the absorption linewidth Γ^{hh}. The latter quantity scales monotonously with the lattice temperature T_L and amounts in this sample to $\Gamma^{hh}/k_B = 4$ K (k_B: Boltzmann constant) at $T_L = 2$ K. Therefore, even the initial effective temperature of the excitons is comparable with the lattice temperature. This is supported by the fact that an increase of the delay from 20 to 100 ps does virtually not change the shape of the nonlinear spectra except from a small reduction of the amplitude. The nonlinear response most clearly seen for the strongest hh resonance exhibits a dispersive shape indicating a blueshift at 2 and 30 K and a shift toward lower energies at 60 K. In Fig. 1(b) the corresponding linear (solid lines) and nonlinear transmission spectra ($T' = T_0 + \Delta T$, dotted lines) are shown in the vicinity of the $hh^{m=1}$ mode. Here, a clear blueshift is seen at 2 K, almost no shift occurs at 30 K, and the resonance shifts distinctly to lower energies at 60 K. Interestingly, the dispersive shape of the differential transmission spectrum at 30 K corresponds to almost no shift of the resonance. In this case it is caused solely by a simple broadening of the resonance which has an asymmetric shape due to the polariton effect.

Figure 2 shows the absolute energy of the $hh^{m=1}$ mode in dependence on the temperature and the photon flux as extracted by fits to the line shape of T'. The dotted lines mark the respective resonance energies in the low-density limit which show the reduction of the band-gap energy with increasing temperature. Concerning the density dependence, a monotonous shift is observed at any temperature; however, slightly above 30 K a crossover occurs from a blueshift to a redshift. The above shifts have been confirmed for a sample containing a thicker ZnSe layer (35 nm). Because of the superior signal-to-noise ratio of the $\Delta T/T$ spectra the change of sign is observable in Fig. 1(a) even for the $hh^{m=3}$ mode (compare spectra for 2 and 60 K). This behavior clearly shows that the lower polariton dispersion branch shifts in energy as a whole as it corresponds to a variation of the exciton energy. In conclusion of the experimental part, exciton shifts as reported for GaAs samples in the transition region between 2D and 3D [13] are observed here in thicker bulklike ZnSe layers. Moreover, the effect is found to exhibit a distinct temperature dependence.

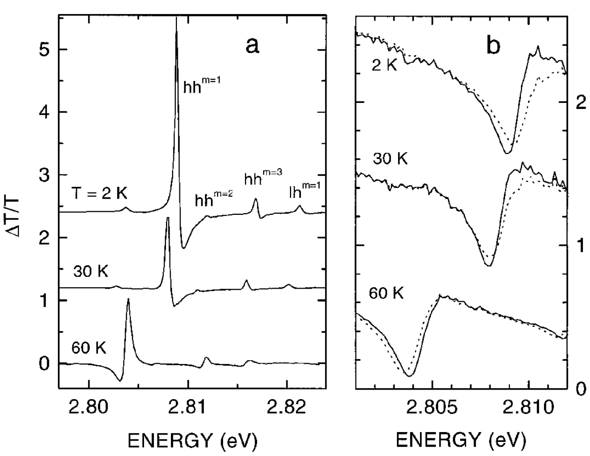

FIG. 1. (a) Differential transmission spectra $\Delta T/T$ of a sample containing a ZnSe layer of 22 nm thickness at a pump photon flux of 3.4×10^{13} photons/pulse/cm^2 for different sample temperatures. The central laser energy was tuned 10 meV below the $hh^{m=1}$ mode at any temperature. (b) Linear (solid lines) and nonlinear (dotted) transmission spectra of the first hh-polariton mode corresponding to the data in (a).

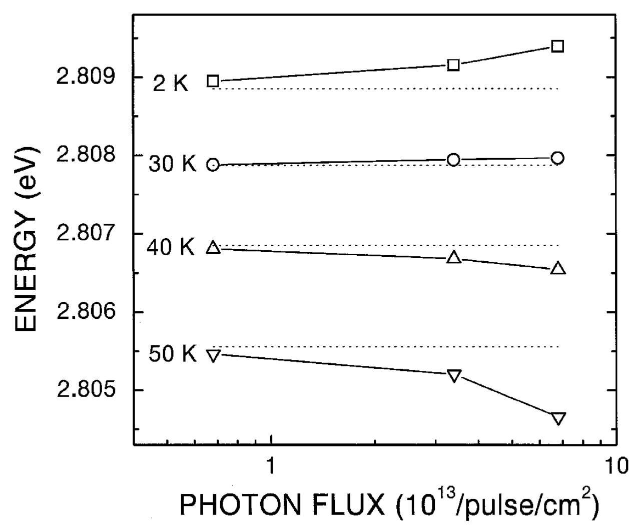

FIG. 2. Absolute energy of the first hh-polariton mode in dependence on pump photon flux at different lattice temperatures (open symbols). The size of the symbols corresponds to the estimated error of the shift of the resonance energy relative to its low-density limit indicated by dotted lines.

The absorption of a weak probe pulse in a highly excited semiconductor can be described by a linear susceptibility $\chi(\omega)$ defined via $p(\omega) = \chi(\omega)E(\omega)$, where the coherent polarization $p(\omega) = \sum_k p_k(\omega)$ induced by the light field $E(\omega)$ follows from the SBE

$$[\omega - \epsilon_k^e - \epsilon_k^h]p_k(\omega) + [1 - f_k^e - f_k^h]\Omega_k(\omega) = I_k^{\mathrm{sc}}. \tag{1}$$

Here, f_k^e (f_k^h) are the carrier distributions for electrons (holes) characterizing the e-h plasma in thermal equilibrium. $\Omega_k(\omega) = dE(\omega) + \sum_q v_{k-q}p_q(\omega)$ is the Coulomb-Hartree-Fock (CHF) renormalized Rabi energy of the pulse and $\epsilon_k^a = e_k^a - \sum_q v_{k-q}f_q^a$ the CHF-renormalized carrier energy ($a = e, h$), both calculated with the bare Coulomb potential v_k. Without the scattering integral I_k^{sc} and the driving electric field $E(\omega)$, Eq. (1) would correspond to the Wannier equation of an exciton where the influence of Pauli's exclusion principle due to the factor $[1 - f_k^e - f_k^h]$ and the CHF-renormalized carrier energies describing band-gap shrinkage are added. A fundamental property of both is to compensate each other widely. Even if the occupation of carriers is increased leading to a strong shrinkage of the band gap, the energy of the exciton stays nearly unchanged.

The effect of screening as a basic many-body effect in a Coulomb system beyond the CHF (mean-field) renormalizations is contained in the scattering integral on the right-hand side of (1). Using Green's function (GF) techniques [21] it can be arranged as

$$I_k^{\mathrm{sc}} = \sum_q [\Theta_{q,k}p_k - \Theta_{k,q}p_q]. \tag{2}$$

While the diagonal contribution (first term) is generated by collisions between carriers only, the off-diagonal contribution with respect to the wave number k describes collisions between carriers and the laser-induced polarization. The complex interaction matrix

$$\Theta_{k,q} = -\sum_{a\neq b}\int \frac{d\omega}{2\pi}\,\frac{[1 - f_k^a]V_{k-q}^{>}(\omega) - f_k^a V_{k-q}^{<}(\omega)}{\omega - \epsilon_k^a - \epsilon_q^b - \omega + i\varepsilon} \tag{3}$$

includes the dynamical screening via plasmon GF's $V^{\gtrless}$, which are related to the retarded dynamical screened potential and the dielectric function, respectively. For a more detailed analysis we refer to [22], where dynamical screening was shown to reduce the dephasing rates nearly by a factor of 2 in comparison to a static approximation. Additionally to the CHF renormalizations in (1) the first (diagonal) term in (2) represents the scattering induced renormalization of the interband energy $\Delta e_k^{\mathrm{sc}} = \mathrm{Re}\sum_q \Theta_{q,k}$ and the (diagonal) dephasing rate $\Gamma_k = -\mathrm{Im}\sum_q \Theta_{q,k}$, whereas the second term contains the effective interaction $\Delta V_{k,q}^{\mathrm{eff}} = -\mathrm{Re}\,\Theta_{k,q}$ modifying the Coulomb interaction in the Rabi energy and the off-diagonal dephasing $\Gamma_{k,q} = -\mathrm{Im}\,\Theta_{k,q}$. Both real and imaginary parts compensate each other widely, as the CHF renormalizations contained on the left-hand side of (1) do, and finally, the shift of the exciton results form the interplay of all this many-body effects as will be demonstrated below.

In contrast to former approaches [16–19,22] we have evaluated the scattering integrals with the Free Generalized Kadanoff Baym (FGKB) ansatz [23,24], which explicitly considers the laser-induced coherent polarization to be peaked at the laser frequency ω. This is reflected explicitly in the energy conserving relation in the denominator of (3). Collision terms with a similar kernel as (2) and (3) were derived on a completely different way investigating the optical response of an e-h plasma in thermal equilibrium via an equation of Bethe-Salpeter type including a dynamically screened potential. In [4,7] the Bethe-Salpeter equation for the e-h (two-particle) GF was reduced to an effective Schrödinger equation describing an electron-hole pair embedded in an e-h plasma. However, the imaginary part of the complex kernel (3) was neglected and the broadening of the exciton was calculated perturbatively with effective wave functions. In [5,6] an equation for the incoherent polarization was considered including both dephasing and energy renormalization.

In both the above approaches the Shindo approximation was used to solve the reconstruction problem, where the GF's in the scattering integrals depending on two times or two frequencies have to be replaced by the one depending on one time or frequency. However, the Shindo approximation fails for higher excitation and particularly for lower temperatures and in the vicinity of the Mott transition, if $f_k^e + f_k^h \approx 1$ [21]. In order to avoid this problem we apply in our coherent approach the FGKB ansatz [23,24] instead of the Shindo approximation. For weak occupations $f_k^e + f_k^h \ll 1$ of carriers the scattering integrals of both approaches coincide. In this limit $\Theta_{k,q}$ is symmetric and both scattering contributions in (2) compensate widely, because both the effective interaction and the off-diagonal dephasing are strongly localized for $k \approx q$.

Results of our theoretical approach for the shift of the exciton resonance in dependence on the temperature and density of the carriers, including the scattering integral (2), are presented in Figs. 3(a) and 3(b). First of all one should notice that in contrast to earlier approximative treatments of the scattering contributions [25,26] only weak shifts are found with increasing excitation. This arises due to the strong compensation not only of CHF but also of scattering (screening) effects. As in the experiments (Fig. 2) a crossover from a weak redshift at higher temperatures (60 K) to a blueshift at lower temperatures (2 K) is found. Moreover, the absolute shift of the exciton amounts up to 2 meV in the displayed range of densities in accordance with the experimental data. The origin of the thermally induced crossover becomes clear if only the CHF contributions [left-hand side of (1)] to the shift are considered, whereas the scattering contributions on the right-hand side

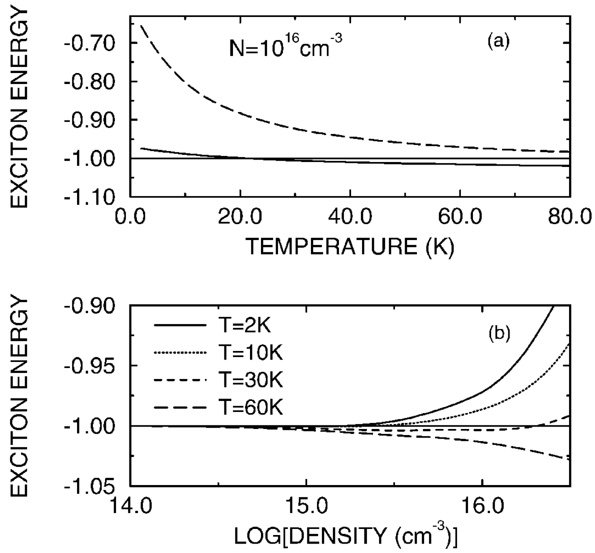

FIG. 3. Shift of the exciton energy with respect to the unrenormalized gap in dependence on the temperature (a) and the carrier density (b). In (a) the total shift of the exciton (solid line) is compared with the pure CHF contribution (dashed). Excitonic units are used, binding energy of the exciton $E_{\mathrm{ex}}^{b} =$ 19 meV.

are neglected. According to [10] the CHF contributions correspond to the excitonic Hartree-Fock contribution derived from exciton-gas theory, when thermal exciton distributions are present. As shown in Fig. 3(a) this CHF or excitonic contributions (dashed) strongly increase and dominate over the scattering contributions for the lower temperatures. The theoretically predicted crossover occurs at lower temperatures (slightly below 30 K) than in the experiments (slightly above 30 K). This deviation might be caused by the influence of the occupation of bound electron-hole pairs which should modify our thermal carrier distributions.

We have consciously avoided putting our theoretical results of Fig. 3(b) directly into Fig. 2 with those from the experiments, because one is not able to determine the carrier densities generated by the photon fluxes of the pump as accurate as it would be necessary to present a serious quantitative comparison. However, as can be seen from the figures, the absolute values of theoretical and experimental shifts are in good agreement, and the point we want to address is the explanation of the thermal crossover of the shifts, which is independent of the strength of the pump and carrier density, respectively.

In conclusion, in contrast to widely held opinions, our careful experimental analysis of the absolute energy of excitons in bulk ZnSe yields a weak but distinct shift for increasing excitation densities which changes its sign in dependence on temperature. A comprehensive theoretical explanation can be obtained through the interplay between Coulomb-Hartree-Fock and scattering contributions in the SBE taking into account carrier-carrier, carrier-polarization scattering, and dynamical screening.

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