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Theory of transient excitonic optical nonlinearities in semiconductor quantum-well structures

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We present theoretical results for the effects of an exciton gas and an electron-hole plasma on the excitonic optical absorption in a two-dimensional semiconductor and compare these with recent experimental results on absorption saturation in single- and multiple-quantum-well structures. A simple theoretical description of the nonlinear optical properties of these microstructures is developed for the case of low-density optical excitation near and above the band edge. We argue that the effects of Coulomb screening of excitons by the plasma are relatively weak in these structures but that the consequences of phase-space filling and exchange are significant in each case. We are able to explain the recent unexpected experimental result that "cold" excitons are more effective than "hot" carriers in saturating the excitonic absorption. Good agreement with the experimental data is obtained without adjustable parameters.

I. INTRODUCTION

Recent investigations have shown that semiconductor quantum-well structures exhibit unusually large optical nonlinearities[1] and electroabsorption.[2] Both effects are due to the persistence of strong and well-resolved excitonic resonances up to high temperatures (e.g., room temperature). These have been observed in the absorption spectra of GaAs-AlGaAs and GaInAs-AlInAs multiple- and single-quantum-well structures (MQWS's and SQWS's).[3–5] In these structures the carrier confinement in ultrathin layers increases the exciton binding energy and enhances the contrast between the exciton peak and the unbound-pair continuum. This explains why exciton resonances are observed even at room temperature, despite the large density of thermal phonons.

In polar semiconductors, LO-phonon scattering is the major source of the temperature broadening of excitonic resonances. Studies of the temperature dependence of the broadening of the exciton peak in MQWS's have shown that the linewidth is the sum of a constant inhomogeneous term that is due to the fluctuations of the layer thickness and a temperature-dependent term proportional to the density of LO phonons. From this dependence it is possible to deduce a mean time for exciton ionization by thermal phonons at room temperature; $t_i = 0.4$ ps and $t_i = 0.25$ ps for GaAs and GaInAs MQWS's, respectively.[4,6] Thus, when a photon whose energy is resonant with that of the exciton is absorbed, it creates a bound electron-hole (e-h) pair that is ionized in a fraction of a picosecond by thermal phonons. Models based on the bleaching of the excitonic resonance by the e-h plasma (released via thermal-phonon ionization of optically created excitons) have explained the nonlinear optical properties of MQWS's excited with optical pulses long compared to t_i;[7,8] the saturation densities are well explained by these models, although some aspects of the form of the nonlinear spectra remain to be quantitatively explained (e.g., the "broadening" in the experimental spectra).

Recent experiments using femtosecond spectroscopic techniques have time resolved the ionization of excitons in GaAs MQWS's.[9] At room temperature, t_i was measured directly and was found to be $t_i = 300 \pm 100$ fs, in excellent agreement with the estimate based on the linewidth studies. More surprisingly, it was also found that the selective generation of excitons produces, before they ionize, a saturation of the exciton absorption *2 times* larger than that induced by free e-h pairs created either directly or via exciton ionization.[9]

It is often thought that screening governs the excitonic nonlinear optical effects near the band gap of semiconductors and that charged plasmas are much more effective in screening the Coulomb interaction than neutral exciton gases.[10] Thus, the observation that the effects of excitons on the absorption spectra can be larger than those of free carriers seems to be in contradiction with the present descriptions of semiconductor nonlinearities.[11–13] The purpose of the present article is to explain this unexpected experimental result and, more generally, to develop a comprehensive description of the excitonic nonlinearities in these important microstructures.

The paper is organized as follows. In Sec. II we summarize the experimental results on room-temperature excitonic absorption saturation obtained by Chemla, Miller, and co-workers.[1,3–7,9] In particular, we examine the experimental conditions under which excitonic effects were found to be larger than those due to an e-h plasma. We identify two important aspects: one is related to the transient "temperatures" of the exciton gas and of the e-h plasma; the other is related to the reduced dimensionality of the system. We then discuss complementary experiments designed to investigate the dimensionality and importance of Coulomb screening in MQWS's. In Sec. III we present a model of the excitonic nonlinearities for

two-dimensional systems that deals with both of these aspects and that gives simple analytical results for the contributions to exciton bleaching of phase-space filling and exchange for both the exciton gas and the *e-h* plasma. In Sec. IV we discuss the application of the model to actual MQWS's and SQWS's and we compare the theory to the experimental data. Good qualitative and quantitative agreements are obtained *without* adjustable parameters. Our conclusions are summarized in Sec. V.

II. SATURATION OF EXCITONIC ABSORPTION IN QUANTUM-WELL STRUCTURES: EXPERIMENTAL RESULTS

A. Continuous and picosecond excitation

Large changes in the excitonic absorption are observed under cw or ps optical excitation at or above the exciton absorption resonances[1,6,7] at room temperature. The magnitudes of the exciton peaks are found to decrease strongly and the peaks broaden but no noticeable shifts of the resonances are observed. In the case of these long-duration excitations, the variations of the absorption spectra are essentially the same when the laser frequency is resonant or nonresonant with the exciton peak. The effects depend only on the density of free-carrier pairs generated indirectly (by resonant creation of excitons followed by their thermal phonon ionization) or directly (by nonresonant absorption above the resonances). These results have been interpreted as follows.[7,8] As *e-h* pairs are created they change the single-particle states of the system, resulting in the renormalization of the band gap, whereas the excitonic resonances do not shift significantly owing to the neutrality of a bound state. The binding energy of the excitons measured from the renormalized band gap decreases so that the size of the bound-state orbitals increases and the absorption diminishes.

At large enough densities the excitonic resonances have all but disappeared and are replaced by the shifted renormalized continuum. The point at which the resonances disappear from the optical-absorption spectrum corresponds empirically to carrier densities such that there is a large probability of finding a carrier within any given exciton volume in the crystal. The effect of free carriers on the excitonic absorption spectrum has been referred to in general terms as "screening";[7] in what follows we will adopt stricter definitions that will change the terminology somewhat. In particular, we will argue that classical screening due to the long-range Coulomb interaction is comparatively weak in its effect on the exciton, and "screening" is dominated by short-range exchange effects.

B. Ultrashort-pulse excitation

In the experiments where excitation by ultrashort pulses ($\sim$150 fs) is studied, the changes of absorption of a MQWS under two excitation conditions are compared.[9] In one set of experiments ultrashort excitation resonant with the heavy-hole exciton is used to generate primarily heavy-hole excitons; in the other set, the MQWS is excited well above the exciton peaks to produce free *e-h* pairs directly. The intensity is adjusted so that the density of *e-h* pairs, bound or free, is the same in both cases (i.e., $N \sim 7 \times 10^{10}$ cm^{-2}). The absorption spectrum is probed at varying delays with very weak continuum pulses covering the whole absorption edge. The duration of the continuum pulses is the same as that of the pump pulses.

In the case of nonresonant pumping, it is found that the changes in the absorption spectrum vary very smoothly in time, following rather well the density of carriers generated (i.e., the changes appear to be proportional to the integral of the excitation pulse). By the end of the pump pulse, the changes in the absorption spectrum are identical to those observed using excitations long compared to t_i. These changes then last for long periods of the order of 20 ns, i.e., of the order of the recombination time of the free *e-h* pairs.

In the case of resonant excitation, qualitatively different effects are observed. First, a strong bleaching of the heavy-hole absorption lasting less than 0.5 ps occurs; then the absorption at the heavy-hole exciton peak partly recovers to settle at the same level as for nonresonant excitation after about 1 ps (see Fig. 2 of Ref. 9). The dynamics of the heavy-hole exciton-peak absorption can be described by a simple semiempirical rate-equation model assuming the instantaneous generation of a first species (excitons) that transforms with a (300$\pm$100)-fs time constant into another species (free electron-hole pairs) which then live for very long times (e.g., the free-carrier lifetime of approximately 20 ns). A good fit is obtained for the bleaching of the absorption at the heavy-hole exciton peak if the change in absorption per excited exciton (first species) is about twice as large as the change in absorption per free-carrier pair (second species). Because the optical pulse width (150 fs full width at half maximum) is comparable to the 300-fs time constant, there is some conversion of the first species into the second species during the pulse, and consequently the fitted bleaching is only 1.4 times larger at its peak than the bleaching observed in the quasi-steady-state at times greater than 1 ps. However, for both excitations the changes in absorption at the light-hole exciton peak are the same within the experimental accuracy, even when observed on the very sensitive differential spectra. In addition, the spectral distribution of the changes in absorption close to the heavy-hole exciton peak is not the same for the two excitation cases. Under resonant excitation the low-energy part of the exciton peak saturates the most. In fact, when the spectra for resonant excitation are subtracted from those obtained under nonresonant pumping, the increased bleaching of the exciton peak, which last only 300 fs, is very clearly displayed and shows a spectral distribution that resembles that of the absorbed pump beam. During the transient strong bleaching, no broadening of the heavy-hole exciton peak is observed [see Figs. 1(a) and 1(b) of Ref. 9], but some broadening is seen at long times [see Fig. 1(c) of Ref. 9], as in the nonresonant case.

In the case of resonant pumping the excitons are selectively generated by optical pulses whose duration is purposely chosen to be shorter than the mean time for scattering by thermal LO phonons. Between the absorption event and the first collision with a thermal LO phonon the excitons have not yet had time to interact with

the thermal reservoir. Their "temperature" (insofar as their temperature is defined) is determined by the distribution of absorbed photons, which in this case is centered on the low-energy side of the exciton resonance [see Fig. 1(d) of Ref. 9]. Therefore, for a very short time, the gas of excitons is essentially at a very low temperature close to absolute zero. Then, because the energy of the LO phonon (37 meV in GaAs) is much larger than the exciton binding energy ($\sim$9 meV in a 100-Å GaAs QW), the first collision with a LO phonon ionizes the excitons and produces e-h pairs of rather large thermal energy (>28 meV). Just as for the free e-h pairs generated in the nonresonant case (where the average excess energy per pair is $\sim$43 meV), these initially form a nonequilibrium distribution. It may take a few carrier-phonon collision times (e.g., a time of the order of a picosecond) for these to equilibrate fully with the lattice,[14] but in both the resonant and nonresonant cases the free e-h pairs are never "cold" because they are created with such large excess energies.

The simple rate-equation model discussed above for the exciton-absorption dynamics does not attempt to include any changes in absorption which might result from the thermalization of the free-carrier plasma after it is created. A more simple model is comparison of the absorption change at long times (after the plasma has thermalized) to the peak absorption change at short times (when a large fraction of excitons exists); this ratio (1.4) sets a lower limit for the effects of "cold" excitons compared to "hot" thermalized free-carrier pairs. Thus, because of the ultrashort resonant excitation used, the experiment of Ref. 9 compares a cold exciton gas to a hot e-h plasma, and we may conclude that the "cold" excitons are 1.4—2 times more effective in bleaching the heavy-hole exciton-peak absorption than the "hot" free-carrier pairs.

C. Single-quantum-well experiment

The second important aspect of all the experiments is related to the reduced dimensionality of the semiconductor system investigated. In the MQWS samples used, the $\sim$100-Å GaAs quantum well were separated by AlGaAs barrier layers thick enough ($\sim$100 Å) to prevent significant overlap of the carrier wave functions in adjacent quantum wells (at least for the lowest confined state). As we shall discuss in more detail later, the saturation of excitonic resonances is governed by two mechanisms, the exclusion principle and screening. The effects of the exclusion principle can be divided into the phase-space-(band-) filling effects (blocking of transitions) and the usual fermion-exchange effects. The latter effects are very short ranged compared to the long-range (direct) Coulomb correlations that give rise to the screening. In an e-h plasma, the long-ranged many-body effects can be identified approximately with the electrostatic screening in the classical sense, and in an exciton gas they correspond to the van der Waals attraction of excitons.[13]

In the experiments reported so far by Chemla, Miller, and co-workers, the barriers between adjacent quantum wells are chosen sufficiently thick that there is very little wave-function overlap between adjacent wells. Consequently, the exchange effects are effective only within the same layer. However, with regard to the long-range Coulomb interaction, layered structures may exhibit a behavior intermediate between two dimensions (2D) and three dimensions (3D), depending on the magnitude of the screening length relative to the layer spacing.[15] Long-range electrostatic screening is known to be much weaker in 2D than in 3D (Refs. 15 and 16) (one simple physical reason for this is that the carriers are not able to move in one of the dimensions). Therefore, in order to investigate the importance of long-range Coulomb correlations, experiments have been performed with waveguide structures containing a single quantum well.[5] In this work, saturation of the excitonic absorption under picosecond excitation is studied for light propagating along the plane of the QW using the same apparatus as was used previously for MQWS's.[6,7] This configuration also shows interesting selection rules not accessible for light propagating perpendicular to the layers because it is now possible to propagate light with polarization perpendicular to the layers (e.g., the heavy-hole to conduction-band transitions become forbidden at the zone center), although this will not concern us further here. What is relevant for the present discussion is that, for light propagating with polarization parallel to the layers (the same polarization as used for all the MQWS experiments), the saturation behavior seen with these single-well samples is very similar to that seen with the multiple-well samples. In particular, within the overall experimental error (of the order of a factor of 2 in absolute saturation intensity), the saturation intensity is essentially the same for both systems. Since only effects associated with the long-range nature of the Coulomb interaction can be different in SQWS's and MQWS's the results of Ref. 5 strongly suggest that, at least up to densities corresponding to the saturation intensity, long-range Coulomb correlation effects are only due to Coulomb interactions within the same layer, or that they are not very important with regard to the bleaching of the exciton both in SQWS's and in MQWS's. In the next section we will show that this interpretation does indeed agree with our theory.

III. THEORY OF (TRANSIENT) EXCITONIC OPTICAL NONLINEARITIES IN TWO-DIMENSIONAL STRUCTURES

The linear optical properties of two-dimensional excitons have been investigated theoretically in Ref. 17. As in three dimensions, the linear susceptibility χ is determined by the expression

$$\chi=\sum_n \frac{f_n}{\omega-\omega_n+i\gamma_n}\ , \tag{1}$$

where the index n runs over all exciton states (discrete and continuous), ω_n and γ_n are the energy and width of each state, and f_n is the oscillator strength of the transition.

The oscillator strength is proportional to the square of the valence-band to conduction-band dipole matrix element r_{cv}, and to the probability of finding the electron and the hole in the same unit cell, i.e., the square of the exciton relative-motion orbital wave function $U_n(r)$ for $r=0$,

$$f_n \propto |r_{cv}|^2 |U_n(r=0)|^2 . \quad (2)$$

For frequencies in the vicinity of the $1S$-exciton peak it is legitimate to retain only the resonant term in (1),

$$\chi \sim \frac{f_{1S}}{\omega-\omega_{1S}+i\gamma_{1S}} . \quad (3)$$

The nonlinearity arises when one or more of the three quantities f_{1S}, ω_{1S}, or γ_{1S} is changed by the optical excitation. In this paper we will be concerned only with the dominant effects, and we shall consider only terms which are linear in N, the density of e-h pairs (bound or unbound). Consequently, we expect that our description will break down at large N (e.g., for densities greater than or of the order of the saturation density N_s defined below).

In the work reported in Ref. 9 no appreciable shift of the exciton peak is observed, at least for the pair densities explored in these studies. This remarkable constancy of the exciton energy was observed with excitations long compared to t_i as well.[7] This result is in agreement with theory in 2D as well as in 3D.[8,11] It simply reflects the charge neutrality of the exciton, i.e., the fact that the effects of the other e-h pairs on the electron of a bound pair are strongly compensated for by their effects on the companion hole. Thus, we can neglect the variation of the exciton energy in (3).

Let us now consider the change of the linear susceptibility due to the renormalization of the exciton oscillator strength. We use the notation

$$\frac{\delta f_{1S}}{f_{1S}} = -\frac{N}{N_s} , \quad (4)$$

where N_s is the saturation parameter or saturation density which will be evaluated for the case of e-h—plasma generation and for the case of selective creation of excitons.

Two processes contribute to the change of f_{1S}: the blocking mechanism due to the exclusion principle, and the changes in the exciton orbital wave function due to the modification of the e-h interaction induced by the presence of other e-h pairs. This latter process includes both exchange effects, another consequence of the exclusion principle, and long-range Coulomb effects.

Because of the exclusion principle, only transitions into unoccupied final states are allowed. This is a blocking mechanism in the sense that transitions are forbidden but the states are not modified. For generation of free carriers it corresponds to the well-known band-filling effects. In the dilute limit, and for a nondegenerate plasma in equilibrium, the carrier distributions are given by the Boltzmann distributions

$$f_i(k) = \frac{N\hbar^2\pi}{m_i k_B T} e^{-\hbar^2 k^2/2m_i k_B T} , \quad (5)$$

where m_i, $i=e$ or h, are the electron and hole effective masses, and T is the temperature.

The effects due to the exclusion principle in the case of generation of excitons are less well known. To be correctly described they require a multiexciton Wannier formalism.[11,13] Although the theory is quite elaborate, the results are very simple and have a direct intuitive interpretation. The resonant generation of excitons yields a distribution of electrons and holes given by

$$f_e(k) = f_h(k) = \frac{N}{2} |U_{1S}(k)|^2 , \quad (6)$$

where $U_{1S}(k)$ is the Fourier transform of the relative-motion orbital wave function $U_{1S}(r)$. The physical meaning of this expression is that since an exciton is built up from a linear combination of single-particle fermion states distributed according to $U_{1S}(k)$, the creation of one exciton corresponds to an occupation probability in the fermion phase space $|U_{1S}(k)|^2$ that is equally shared between the spin-up and- down states, hence the factor $\frac{1}{2}$.

In the case of two-dimensional excitons the wave function is

$$U_{1S}(r) = \left[\frac{2}{\pi}\right]^{1/2} \frac{2}{a_0} e^{-2r/a_0} , \quad (7a)$$

$$U_{1S}(k) = \sqrt{2\pi} \frac{a_0}{[1+(a_0 k/2)^2]^{3/2}} . \quad (7b)$$

In the present paper, in order to avoid confusion, we will use as natural units of length and energy the usual 3D Bohr radius $a_0 = \epsilon_0\hbar^2/e^2\mu$ and the 3D Rydberg constant $R = e^4\mu/2\epsilon_0^2\hbar^2$, where μ is the e-h reduced mass ($\mu^{-1} = m_e^{-1} + m_h^{-1}$) and ϵ_0 is the dielectric constant. With these notations the maximum of the radial probability in real space for the 2D exciton occurs at $a_{2D} = a_0/4$ and the binding energy of the $1S$ state is $E_{1S} = 4R$.

The relative change in the exciton oscillator strength due to the exclusion principle through "phase-space filling" is

$$\left.\frac{\delta f_{1S}}{f_{1S}}\right|_{\text{PSF}} = -\sum_{\mathbf{k}} [f_e(k)+f_h(k)] \frac{U_{1S}(k)}{U_{1S}(r=0)} , \quad (8)$$

where $f_{e,h}(k)$ are the electron and hole distribution functions given by (5) and (6) for the e-h plasma and the exciton gas, respectively. States in phase space which are already occupied by electrons or holes (bound or free) are no longer available for the formation of excitons. Correspondingly, (8) can be interpreted as describing a correction due to the proper normalization of the exciton wave function in the presence of other e-h pairs. For an exciton gas (e.g., as obtained initially by resonant creation of excitons), one obtains

$$\left.\frac{1}{N_S}\right|_{\text{PSF,ex}} = \frac{32}{7}\pi a_{2D}^2 . \quad (9)$$

This result has the following intuitive interpretation: when an exciton is created, a small area of the semiconductor layer around the bound e-h pair cannot sustain more excitons; this area is $\frac{32}{7} \sim 4$ times larger than the area defined by the 2D Bohr radius of the exciton, a_{2D}. The factor $\frac{32}{7}$ simply accounts for the fact that a large fraction of the charge density is located outside the disk of radius a_{2D}.

For the case of an e-h plasma (e.g., as obtained by nonresonant excitation of carrier pairs or by ionization of previously created excitons), (8) is not simple to evaluate

analytically for an arbitrary temperature. The two limits of interest, corresponding to high and low temperatures, are

$$\left.\frac{1}{N_S}\right|_{\mathrm{PSF,pl}} = 8\pi a_{\mathrm{2D}}^2, \quad k_B T/E_{1S} \ll 1 \tag{10a}$$

$$\left.\frac{1}{N_S}\right|_{\mathrm{PSF,pl}} = 8\pi a_{\mathrm{2D}}^2 \frac{E_{1S}}{k_B T}, \quad k_B T/E_{1S} \ll 1 \; . \tag{10b}$$

This shows that at low temperatures phase-space filling effects due to free e-h pairs are larger than those due to excitons ($\sim\frac{7}{4}$ times larger), but as the temperature increases free e-h—pair effects become weaker and eventually tend to zero. Above a temperature of about $k_B T = 7E_{1S}/4$, free e-h—pair effects are smaller than exciton effects.

Let us now consider the reduction of the oscillator strength due to the renormalization of the exciton orbital wave function. In the presence of other e-h pairs, the bound-state binding energy is weakened and the bound-state orbital wave function is blown up in real space. This reduces the probability of finding the electron near the hole and yields a second negative contribution to $\delta f_{1S}/f_{1S}$. Strictly speaking, one has to account for both short-range exchange effects and long-range direct Coulomb correlations. As discussed above, the experimental results on excitonic saturation in SQWS's[5] strongly suggest that the latter effects are only important within a given layer or that they are not very important at all. Long-range direct Coulomb correlations of a given exciton with other neutral bound pairs correspond to the usual van der Waals attraction in an exciton gas. In a complete theory they should be contained in an *ab initio* exciton-exciton interaction. They are very small effects that even in three dimensions are dominated by the short-range exchange effects.[13] We will neglect these in the present study. Long-range Coulomb correlations with free e-h pairs correspond to the direct Coulomb screening of the e-h attraction by the charged plasma.

In 2D, direct screening is strongly reduced compared to 3D and saturates.[16] For example, in the static limit the screening of a point charge by a charged plasma in 2D has a power-law decay at long distances significantly slower than the 3D exponential decay. The screening parameter q_s is independent of the carrier density at low temperatures (due to the constant density of states),

$$q_s = 2(m_e + m_h)/\mu a_0 \; ,$$

and decreases rapidly at high temperatures,

$$q_s = 4\pi N e^2/\epsilon_0 k_B T \; .$$

It is worth noting that in 2D an attractive potential, no matter how weak it is, always supports at least one bound state.[16] Thus, even an ultimately statically screened Coulomb potential would always have a bound state with a significant (i.e., *not* exponentially small) binding energy because of the saturation of screening in 2D. Furthermore, the dynamic screening that enters the renormalization of the exciton wave function is even weaker,[8] so that under nonresonant excitation the exciton is only weakly polarized.

The relative unimportance of screening in quasi-two-dimensional e-h systems has been experimentally demonstrated by the observation of excitonic resonances in modulation-doped samples with doping densities as large as $\sim 10^{17}$ cm^{-3}.[18] In these experiments the $n=1$ exciton, which is affected both by the exclusion principle and the screening, is completely bleached, whereas the $n=2$ exciton, which is only affected by the screening, shows up as in undoped samples. Consequently, we expect that screening of excitons by an e-h plasma is a relatively weak effect in SQWS's and MQWS's and therefore we will neglect it in the following and consider only the effects of the exclusion principle.

In this context, it is worth mentioning a related two-dimensional system, a photoexcited thin semiconductor film of very high permittivity. Due to the strong dielectric confinement (image forces) the Coulomb interaction in this system will vary like a logarithmic interaction.[19] In the nondegenerate limit, the problem reduces then to the classical two-dimensional Coulomb-gas problem, which can be solved exactly.[20,21] The e-h system will undergo a Kosterlitz-Thouless transition[22] from an *ideal* exciton gas to a charged e-h plasma, the critical temperature being *independent* of the pair density. Although this is an elementary consequence of the logarithmic interaction (which is the true long-range Coulomb interaction in 2D), the Coulomb gas provides an example of a dilute two-dimensional e-h system in which classical Coulomb correlations of pairs are *rigorously* negligible. Anisotropic systems, such as QWS's, are intermediate between this genuine two-dimensional limit and three-dimensional systems in the sense that there is spatial but (practically) no dielectric confinement, so that the Coulomb interaction is still three dimensional. The relative enhancement of two-body e-h correlations is, however, already present in these systems, as should be clear from the enhanced exciton binding energy. This holds even in the high-density plasma state, where they show up as strong e-h—pair fluctuations preceding the "pseudotransition" to the excitonic insulator state.[23] Clearly, screening has to be included in the weak-coupling plasma limit. Here, however, we are interested in the *dominant* effects in the opposite strong-coupling exciton limit, in which bound states are well defined. We argue that the effects of screening are weak and that the bleaching of excitonic resonances mainly occurs because the particles overlap and the exclusion principle becomes important.

Describing the unperturbed and the perturbed e-h relative motion by the Hamiltonians H_0 and H, respectively, one obtains in first order in the perturbation $H-H_0$,

$$\left.\frac{\delta f_{1S}}{f_{1S}}\right|_{\mathrm{EXCH}} = \sum_{n\,(\neq 1S)} \left[\frac{\langle 1S \,|\, H-H_0 \,|\, n\rangle}{\omega_{1S}-\omega_n} \frac{U_n^*(r=0)}{U_{1S}^*(r=0)} + \frac{\langle n \,|\, H-H_0 \,|\, 1S\rangle}{\omega_{1S}-\omega_n} \frac{U_n(r=0)}{U_{1S}(r=0)} \right] , \tag{11}$$

where

$$\langle \mathbf{k} \mid H-H_0 \mid \mathbf{k}' \rangle = -\delta_{\mathbf{k},\mathbf{k}'} \left[\sum_{\mathbf{k}''} V(\mathbf{k}-\mathbf{k}'')[f_e(k'')+f_h(k'')] \right] + V(\mathbf{k}-\mathbf{k}')[f_e(k)+f_h(k)] \tag{12}$$

is the contribution of fermion exchange to $H-H_0$ and $V(q)=2\pi e^2/\epsilon_0 q$ is the two-dimensional Coulomb interaction (note that H is non-Hermitian). The first term on the right-hand side (rhs) of (12) is a self-energy correction that comprises the electron and hole exchange self-energies, i.e., the energies that parallel spin particles gain by avoiding each other. The second term on the rhs of (12) is a vertex correction. It describes the weakening of the attractive e-h interaction due to the exclusion principle.

Equation (12) is the mean-field correction to the effective e-h Hamiltonian. When only excitons are present, its expectation value is the exciton self-energy in the Hartree approximation. At zero temperature, it gives rise to a small blue shift of the exciton resonance,

$$\delta E_{1S} = 16\pi N a_{2D}^2 (1-315\pi^2/2^{12}) E_{1S}$$

(i.e., $\sim 3.86\pi a_{2D}^2 N E_{1S}$); in a composite-particle picture this shifts results from the short-range hard-core repulsion of the excitons (treated in first order and in a Heitler-London—type approximation). In three dimensions it is partly compensated by a red shift due to the screening.[13] In two dimensions, however, because of the relative unimportance of the screening, this compensation does not occur, and hence a small shift is expected at low temperatures. This may explain the blue shift observed in recent low-temperature experiments on MQWS's.[24] Furthermore, this implies that a dilute two-dimensional exciton gas is thermodynamically stable (apart from possible collapse into biexcitons), in disagreement with the results of Ref. 25.

To evaluate Eq. (11) we need to perform the summation over all the excited states of the exciton. In 2D the bound-state binding energies are given by $E_n = R/(n-\frac{1}{2})^2$, where n is the principal quantum number; the $n>1$ states are thus very close to the continuum and can be approximately neglected (giving a slight underestimate of $1/N_s$). When the summation is carried out over a *complete set* of uncorrelated pair (plane-wave) states, the following results are obtained:

$$\left.\frac{1}{N_s}\right|_{\text{EXCH,ex}} = \frac{4832}{1225}\pi a_{2D}^2 \tag{13}$$

for the selective generation of excitons. In the case of generation of free e-h pairs the results of the two interesting limits are

$$\left.\frac{1}{N_s}\right|_{\text{EXCH,pl}} = 4(\pi-\tfrac{2}{3})\pi a_{2D}^2, \quad k_BT/E_{1S} \ll 1 \tag{14a}$$

$$\left.\frac{1}{N_s}\right|_{\text{EXCH,pl}} = 16\pi a_{2D}^2 \frac{E_{1S}}{k_BT}, \quad k_BT/E_{1S} \gg 1\ . \tag{14b}$$

Contrary to (13) and (14a), (14b) is exact and not accompanied by uncertainties due to the replacement of the excited exciton states by uncorrelated pair states. Note that for $E_{1S}/k_BT \ll 1$ the self-energies in (12) reduce to constants proportional to $nT^{-1/2}$, which do *not* contribute to (11), because of the orthogonality of the exciton states.

In Table I we summarize the results for the various mechanisms [as given by expressions (9), (10), (13), and (14)] for saturation of the exciton oscillator strength due to phase-space filling and exchange by other excitons and by free e-h pairs [the sum of (10b) and (14b) agrees well with the high-temperature results of Ref. 8, where additionally various approximate forms of screening have been studied].

TABLE I. Inverse of saturation densities for excitonic absorption (oscillator) strength, in units of πa_{2D}^2 ($1/N_s\pi a_{2D}^2$), i.e., these numbers are the (low-density) fractional change in total $1S$ exciton absorption for each carrier pair per unit exciton "area," with exciton area defined as πa_{2D}^2. E_{1S} is taken as ~ 9 meV.

Saturating particles	Mechanism: Phase-space filling	Mechanism: Exchange
Excitons	$\frac{32}{7}\sim 4.57$	$\frac{4832}{1225}\sim 3.94$
Free e-h pairs		
"Cold"	8	$4(\pi-\frac{2}{3})\sim 9.90$
"Hot"	$8(E_{1S}/k_BT)$	$16(E_{1S}/k_BT)$
300 K	~ 2.8	~ 5.5

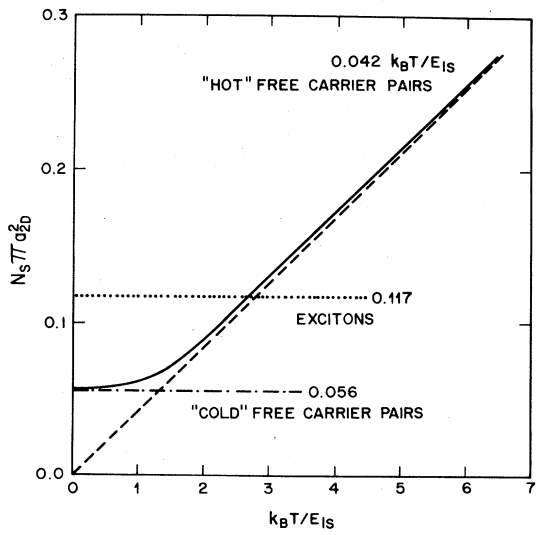

FIG. 1. Saturation densities N_s (in units of $1/\pi a_{2D}^2$) for the combined effects of phase-space filling and exchange for each of three cases: (i) exciton gas (· · · ·); (ii) limit of "cold" free-electron-hole pairs (— · — · —); (iii) limit of "hot" free-electron-hole pairs (——). The solid line is a sketch of the transition from one temperature limit to the other and is not calculated.

To lowest order, we may add the reciprocal saturation densities from the two effects of phase-space filling and exchange to obtain the combined saturation density, i.e.,

$$1/N_s=(1/N_s)_{\mathrm{EXCH}}+(1/N_s)_{\mathrm{PSF}} .$$

The resulting dependence of $N_s\pi a_{2\mathrm{D}}^2$ versus k_BT/E_{1S} is sketched in Fig. 1. For saturation by bound pairs (excitons), the "saturation" of the resonance (at $N\sim 0.5N_s$) occurs when the distance between particles is about twice the two-dimensional Bohr diameter. Considering the charge distribution of the orbital, Eq. (7a), this result is intuitively appealing. At low temperatures, the free e-h pairs are about twice as efficient as the bound pairs in bleaching the exciton resonances. This results from the large overlap of the plane-wave states occupied at low temperatures with a given bound state, compared with the overlap of a given bound state with the other bound states. However, as the temperature increases, the thermal wavelength decreases and the free e-h—pair overlap effects disappear. At high temperatures the free e-h—pair contribution to saturation tends towards zero linearly with E_{1S}/k_BT.

IV. COMPARISON OF THEORY WITH QUANTUM-WELL EXPERIMENTS

The theory presented above relates strictly to the two-dimensional limit, whereas all the experiments are performed in samples where the thickness of the exciton (i.e., the total extent of the wave function perpendicular to the layers) is not negligible compared to the lateral extent of the wave function in the plane. The first comment on this is that the numbers are rather deceptive in this regard; a scale drawing shows the exciton to be much larger in the plane of the layer than perpendicular to it, even although the layer thickness is ~ 100 Å and the Bohr diameter is ~ 120 Å. However, it is true that the exciton binding energy (~ 9 meV) is only about halfway between the two- and three-dimensional limits.

There are, however, two rigorous reasons for applying the two-dimensional theory to the quasi-two-dimensional case. The first argument relates to the form of the density of states in the real samples. The second argument is a scaling argument that enables us to use effective Bohr radii in place of the two-dimensional Bohr radius $a_{2\mathrm{D}}$.

An important fact in assessing the effective dimensionality of the structures is that the higher confined states of the electrons and the holes in the well are separated from the lowest confined states by energies larger than the relevant energies in our problem, and so we are justified in considering only the lowest confined electron and hole states. This approach works well for the exciton binding energy, where the wave function perpendicular to the layers can be taken as the unperturbed electron and hole (lowest) confined wave functions[2] at these thicknesses. When only the lowest subbands need to be considered, the density of states takes on the same form as in the two-dimensional case (i.e., proportional to the effective mass and independent of energy above the bottom of the subband). Therefore, as far as the density of states is concerned, the derivations of the appropriate formulas are identical.

It would be possible to rederive all the formulas with a different radius a_{eff} for the exciton, provided that we retain the same form for the wave function in the plane. Variational calculations of the exciton that retain a two-dimensional Bohr orbital form in the plane[2] (with adjustable radius) give binding energies in reasonable agreement with experiment. For $E_{1S}a_{\mathrm{eff}}\sim$const (this relation is exact in comparing the two- and three-dimensional limiting cases and we find that it holds approximately for the variational wave functions as well), the results will scale in that we may replace $a_{2\mathrm{D}}$ by a_{eff}. Hence we may use expressions (9), (10a), (13), and (14a) by substituting the variational radius a_{eff} for $a_{2\mathrm{D}}$. This holds for (10b) and (14b) as well, which additionally contain the fraction of thermalized particles within the phase space sampled by the exciton, E_{1S}/k_BT (as determined by the square of the ratio of the thermal wavelength and the exciton Bohr radius).

Because it is difficult to perturb the wave functions perpendicular to the layers, motion in this direction is impeded, so we should expect weakening of screening as in the two-dimensional limit (where such motion is totally prevented). If we presume that the exciton orbit in the plane of the layers is also of the same form as the two-dimensional limit wave function, but with a variationally adjusted radius,[2] then we can scale our results from the two-dimensional-limit cases derived above.

A simplification that we will use throughout the subsequent discussion is that we will neglect any conversion of heavy holes into light holes. As far as exciton-exciton interactions are concerned, this is valid because there is no mechanism with enough energy to perform this conversion in less than the phonon-induced ionization time. As for the plasma, the light-hole mass is much less than the heavy-hole mass so that in thermal equilibrium there are many fewer light holes than heavy holes, and we simply neglect the light-hole density.

The first experimental feature that we wish to compare is the ratio of the heavy-hole (HH) exciton saturation with equal numbers of excitons or free e-h pairs. For large temperatures the ratio of the changes of the oscillator strength at the heavy-hole exciton peak under the two excitation conditions is

$$R_{\mathrm{HH}}=\frac{\delta\chi\,|_{\mathrm{ex}}}{\delta\chi\,|_{\mathrm{pl}}}\sim\frac{\frac{32}{7}+\frac{4832}{1225}}{8+16}\frac{k_BT}{E_{1S}}\simeq 0.35\left[\frac{k_BT}{E_{1S}}\right], \tag{15}$$

which at room temperature ($k_BT/E_{1S}\sim 2.9$) gives

$$R_{\mathrm{HH}}\sim 1 . \tag{16}$$

Most importantly, the theory therefore predicts that "cold" excitons can be of comparable efficiency in bleaching the absorption as the same density of "hot" free-carrier pairs. This is also in good quantitative agreement with the room-temperature experiment, which suggests a value of $R_{\mathrm{HH}}\sim 1.4$ in the case of thermalized free carriers [most likely, the exact evaluation of (11) in the case of excitons will yield a room temperature value for R_{HH} somewhat larger than 1].

The second comparison concerns the light-hole (LH) exciton. As we have already mentioned, the bleaching of the absorption in the vicinity of the light-hole exciton peak was essentially the same in the two excitation configurations and about half the magnitude of that at the heavy-hole exciton peak. This observation is also well explained by our model.

For the case of saturation by excitons, assuming light-hole and heavy-hole valence bands decoupled near $k=0$, the reduction of the oscillator strength at the light-hole exciton peak should be exactly one-half of that at the heavy-hole exciton peak if the exciton parameters were identical, i.e.,

$$\delta f_{1S}^{\mathrm{ex}}(\mathrm{LH})=\tfrac{1}{2}\delta f_{1S}^{\mathrm{ex}}(\mathrm{HH}) . \tag{17}$$

This is because the light-hole exciton is only influenced by the effects of the exclusion principle due to the photoexcited electrons and not the heavy holes.

For the same reason, in the case of the free e-h plasma, the reduction of oscillator strength has to be corrected by the mass ratio, i.e.,

$$\delta f_{1S}^{\mathrm{pl}}(\mathrm{HH})=\left[1+\frac{m_e}{m_h}\right]\delta f_{1S}^{\mathrm{pl}}(\mathrm{LH}) , \tag{18}$$

which gives ($m_e/m_h\sim\frac{1}{3}$)

$$R_{\mathrm{LH}}/R_{\mathrm{HH}}=\left[1+\frac{m_e}{m_h}\right]\Big/2\sim\tfrac{2}{3} . \tag{19}$$

This is in good agreement with the experimental result $R_{\mathrm{LH}}/R_{\mathrm{HH}}\sim 1/1.4\sim 0.7$.

Finally, let us consider the absolute magnitude of the effects. The change in absorption coefficient at the heavy-hole exciton peak measured in Ref. 9 was expressed in terms of the nonlinear cross section σ defined by

$$\alpha\simeq\alpha_0-\sigma\overline{N} , \tag{20}$$

where $\overline{N}$ is the average pair density per unit volume. As a function of N and of the quantum-well and barrier-layer thicknesses L_z and L_b, $\overline{N}$ is given by $\overline{N}=N/(L_z+L_b)$, so that

$$\sigma=\alpha_0\frac{L_z+L_b}{N_s} . \tag{21}$$

The quasi-two-dimensional heavy-hole exciton Bohr radius calculated using a variational procedure[2] in 96-Å GaAs quantum wells is $a_{2\mathrm{D}}\sim 63$ Å. Assuming that all the changes of the absorption coefficient result from loss of oscillator strength, we find, by adding the contributions of phase-space filling (9) and exchange (13), for the effect of an exciton gas on the excitonic absorption that $\sigma_{\mathrm{theor}}=2.5\times 10^{-13}$ cm^2; this is to be compared to the experimental value $\sigma_{\mathrm{expt}}=10^{-13}$ cm^2. Considering the possible errors in our theoretical model (which corresponds to the first Born approximation) and the difficulty of making very accurate measurements of the excited-carrier pair density in a femtosecond pump-and-probe experiment, the agreement is very satisfactory.

The last point we wish to discuss is the question of the line broadening. Some broadening of the exciton lines is observed in the experiments in the case of the e-h plasma. If there are broadening mechanisms, they will make a contribution to the loss of absorption at the exciton peak, and therefore ideally should be included in our theoretical comparisons. Unfortunately, broadening is a complex problem for several reasons, and we will not attempt to fit the experimental broadening in this paper. However, some comments on the problem are relevant. Let us first remark that the origin of the exciton line profile in MQWS's is a subject of intense research and is not yet fully understood. It is presently believed that fluctuations of the order of one monolayer in the layer thickness produce an inhomogeneous broadening[26,27] that is superimposed on a homogeneous broadening that varies across the width of the line.[28] Despite this complex structure, the temperature dependence of the full linewidth is well described by the sum of a constant term, representing the effect of layer fluctuations, and a term proportional to the density of LO phonons.[6,7] The exciton—LO-phonon interaction thus seems to govern the temperature broadening as in other polar semiconductors. However, the nature of the line in the presence of the two broadening mechanisms is not yet understood.

The situation where e-h pairs are also present in the system is even more complex to describe so we will limit ourselves to a qualitative discussion. A major effect of e-h pairs on the line shape is collisional broadening, which is governed by the scattering cross section, density, and kinetic energy of the colliding species. For selective generation of excitons, the kinetic energy of the particles (before ionization) is very small, corresponding at most to a photon wave vector. Therefore, one should not expect much broadening from such exciton-exciton collisions; indeed, the spectra at short times under resonant excitation show no increase in the exciton peak width. In the case of free e-h pairs, the broadening should increase with temperature, which is in qualitative agreement with experiment since broadening is observed in the presence of the "hot" e-h plasma. To go beyond this crude picture would require the development of a good theoretical model of exciton profiles in QWS's, which is beyond the scope of this paper.

V. CONCLUSIONS

We have derived theoretical saturation densities for the effects of both an e-h plasma and an exciton gas on the exciton absorption strength in a two-dimensional semiconductor. In the limit of low density, we calculate the effects of both phase-space filling and exchange. Interestingly, we find that the effects of phase-space filling and of exchange are comparable to each other for each of the three cases we have calculated explicitly (i.e., "cold" exciton gas, "cold" e-h plasma and "hot" e-h plasma). We have argued that these results can be extended to the case of a quasi-two-dimensional semiconductor, and that they are valid in cases of experimental interest. We have also argued that the effects of the long-range Coulomb screening of excitons are relatively weak in 2D and for many

practical quasi-two-dimensional systems; this argument is based both on theoretical considerations and on interpretation of experimental results in modulation-doped samples[18] and in SQWS saturation.[5]

Although the theory that underlies our model is relatively sophisticated, all of our results can be understood in a simple manner. Both phase-space filling and exchange are consequences of the Pauli exclusion principle. If we assign to the exciton an effective radius, we find first of all that in the case of "cold" excitons our model corresponds to requiring that two disks of this effective radius cannot share the same space. The effective radii are very similar for the phase-space filling and exchange effects, and are about twice the Bohr radius. In the case of "cold' e-h pairs in a plasma, the model corresponds to requiring that a single carrier cannot occupy the space occupied by a hard disk also with an effective radius of about two Bohr radii for both phase-space filling and exchange (note that the numbers in Table I correspond to carrier pairs). In the case of a "hot" plasma, the same notion can be retained, only now we must note that only a fraction of the order of E_{1S}/k_BT occupy the phase space sampled by the exciton; i.e., a carrier with thermal energy greater than E_{1S} can occupy the same space as an exciton without violating Pauli exclusion. This intuitive picture gives a good *"a posteriori"* justification to the "hard-disk" model of Ref. 7.

One major result of this work is that we predict theoretically that a "cold" exciton gas can be more effective than a "hot" e-h plasma in saturating the exciton absorption; this therefore agrees with the surprising experimental result of Knox *et al.*,[9] where a decrease in saturation was observed as created excitons were ionized to create a room-temperature plasma. Furthermore, we find good quantitative agreement between our calculated saturation cross sections and those measured experimentally.

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