High-Resolution Nonlinear Laser Spectroscopy of Heavy-Hole Excitons in GaAs/AlGaAs Quantum-Well Structures: A Direct Measure of the Exciton Line Shape

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We report high-resolution nonlinear laser-spectroscopy studies of the $n=1$ heavy-hole exciton in GaAs multiple quantum wells. Using a new method of cw frequency-domain four-wave mixing, we first show that the excitation relaxation consists of both fast and slow components. We then show that the contribution of well-width fluctuations to inhomogeneous broadening can be eliminated, enabling us to obtain a direct measure of the intrinsic exciton line shape. Under certain conditions, this line shape is non-Lorentzian and cannot be explained on the basis of simple excited-state relaxation dynamics.

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Excitons dominate the linear and nonlinear optical properties of GaAs/AlGaAs multiple quantum wells (MQW) near the fundamental band edge. The coupling of excitons to the applied radiation field is modified by dynamical interactions due to the coupling of the exciton to the surrounding crystal lattice and the vacuum radiation field. These interactions include spontaneous emission, tunneling, diffusion, and scattering from phonons and defects. These processes can result in decay of the excitation as well as decay of the coherence induced between the initial and the excited states. Obtaining a quantitative description of this physics provides insight into the fundamental interactions in the material and aids in understanding the effects of relaxation on optical properties.

If the dynamical interactions are considered to give rise to small random shifts in the resonant frequency, designated $\delta\omega_0(t)$, then the decay of the induced polarization is given by $\langle \exp[-i\int_0^t dt' \delta\omega_0(t')] \rangle$, where $\langle\ \rangle$ denotes the ensemble average.[1] For a Markoff relaxation process, the polarization decays exponentially with a resultant Lorentzian line shape for the absorption profile. In general, however, the homogeneous absorption line shape can be more complex and we designate it by $\mathrm{Im}[f(\omega-\omega_0)]$, where $f(\omega-\omega_0)$ is proportional to the complex optical susceptibility and ω_0 is some characteristic frequency. In a MQW, fluctuations in the well thickness lead to energy-level shifts of the exciton resonance which vary with location. The line shape is then given by the average over these effects: $F(\omega)=\int d\omega_0 \times P(\omega_0)\mathrm{Im}[f(\omega-\omega_0)]$, where $P(\omega_0)$ is a distribution function. If f and P are characterized by widths Γ and $\Delta\omega_{\mathrm{inh}}$, the material is inhomogeneously broadened when $\Delta\omega_{\mathrm{inh}} \gg \Gamma$. In this limit, absorption profiles provide little information on f. In a typical MQW at low temperatures, the excitonic features are inhomogeneously broadened since the absorption linewidth is of order 1 meV, while the intrinsic exciton linewidth may be an order of magnitude smaller.

Making the assumption that the relaxation is exponential, with decay rate $\Gamma/2$ (corresponding to Γ in the FWHM of the line shape), there have been numerous measurements to obtain Γ at low temperature. Early measurements were made by Hegarty,[2] who examined pulse propagation effects and Hegarty and Sturge,[3] who used transient hole burning. This work was followed by an impressive application of resonant Rayleigh scattering where Hegarty *et al.*[4] showed that the linewidth increases dramatically toward the high-frequency side of the heavy-hole absorption maximum. A more direct measurement was obtained with the first demonstration of two-pulse photon echoes in these materials by Schultheis, Sturge, and Hegarty.[5] Assuming an exponential decay, they were able to fit the data by a convolution of the pulse shape and an exponential, providing a measure of the decay rate. In more recent work, Schultheis *et al.*[6] have used transient four-wave mixing (FWM) to study dephasing in a single QW which is homogeneously broadened.

In this paper, we describe the first high-resolution spectroscopy measurements of line shapes related to $f(\omega-\omega_0)$ for the lowest-energy heavy-hole exciton (HH1) in an inhomogeneously broadened MQW. Using a new method of frequency-domain FWM, we demonstrate that there are at least three different states associated with the relaxation of this excitation corresponding to lifetimes of order 100 psec, 30 nsec, and 10 μsec. In addition, the excitation line shape can be highly asymmetric depending on the excitation wavelength and the relative contributions of different states. We discuss the possible physical interpretation of these results and the potential impact on the analysis of earlier work. Moreover, we note that these results cannot be completely described by the existing work on MQW excitons.

Frequency-domain FWM is similar to hole-burning spectroscopy but FWM can often provide more information. In addition, by enabling separate measurements of the homogeneous line shape and the state relaxation rates,[7] FWM eliminates an ambiguity found in ordinary hole-burning measurements[8] where the observed line shape is a complex function of these features. Figure 1 shows the optical configuration with the GaAs/AlGaAs MQW at the intersection of three optical beams. The three beams interact through the nonlinear response of the MQW to produce a *coherent* signal beam, designated $\mathbf{E}_s(\mathbf{k}_s, \omega_s = \omega_f - \omega_p + \omega_b)$.

We briefly summarize the spectroscopic information obtained by FWM.[7] The coupling to the reservoir gives rise to relaxation of the perturbation of the initial state and excited states and induced coherence. The different relaxations can be determined using FWM.[9] In inhomogeneously broadened material for $\mathbf{E}_b \perp \mathbf{E}_f \| \mathbf{E}_p$, measurement of $|E_s|^2$ as a function of $\omega_p - \omega_f = \delta$ (for $\omega_f = \omega_b = \text{const}$), designated the FWMp response, gives a measure of the relaxation rates associated with the optical-field–induced perturbation of the excited states and the ground state, provided there is no orientation signal (i.e., $E_s = 0$ if $\mathbf{E}_b \| \mathbf{E}_f \perp \mathbf{E}_p$, which we have verified experimentally for low-power cw excitation). Moreover, for fixed δ, measurement of $|E_s|^2$ as a function of $\omega_b - \omega_f$ (ω_f constant), designated the FWMb response, gives a line shape related to $f(\omega - \omega_0)$.

More specifically for FWMp in a rate-equation approximation, the equation of motion for ρ_{nn} (the probability per unit volume corresponding to the perturbation of state n) may be solved to give

$$\rho_{nn} = \frac{\zeta_n E_f E_p^*}{i\delta + \gamma_n + D_n |\Delta\mathbf{k}|^2} \exp(i\delta t + i\Delta\mathbf{k}\cdot\mathbf{x}) + \text{c.c.}, \quad (1)$$

where γ_n is the decay rate for state n, D_n is the diffusion coefficient, and $|\Delta\mathbf{k}|^2 = |\mathbf{k}_f - \mathbf{k}_p|^2$ with $k_f \cong k_p = k$. (We have not included the effects of source terms due to reservoir effects and we have assumed the dephasing rate is much larger than state relaxation rates. Corrections to these assumptions lead to a significant modification of the FWM spectral response.[7,9]) The dependence of the FWMp spectral response on γ_n, D_n, and θ gives a way to measure D_n.[10] Hence, for example, in the presence of a mobility edge, we would anticipate that below a critical photon energy the FWMp linewidth would be independent of angle, but above that energy, the linewidth would vary as $\sin^2\theta/2$. A corresponding method in the time domain has been used to study localization effects in these materials.[11]

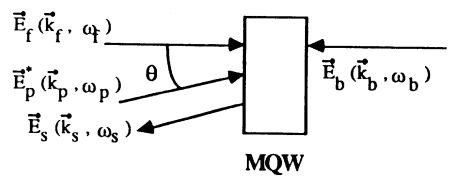

FIG. 1. FWM interaction geometry.

For the FWMb response, we consider the case of only a single state of excitation and $\delta \ll \Gamma$. The forward pump and probe burn a spectral hole in the inhomogeneously broadened absorption profile. The hole is probed by scanning ω_b. The FWMb response measured by the intensity, I, of the signal produced by the nonlinear interaction is then given by $I = |K\int dx\, P(\omega - x) f(\Delta + x) \times \text{Im}[f(x)]|^2$, where $\omega = \omega_f \approx \omega_p$, $x = \omega - \omega_0$, $\Delta = \omega_b - \omega$, and $K = K(\delta)$ contains a denominator like Eq. (1). For ω near the center of P and $\Delta\omega_{\text{inh}} \gg \Gamma$, the line shape is independent of P and is related to the homogeneous line shape. If the FWMp response indicates the existence of different γ_n, the dependence of the FWMb response on δ could indicate there are different states contributing to the total response, each characterized by a different line shape. The additional effects of spectral diffusion on the FWMb response are described below.

The above discussion is *qualitative* and based on detailed understanding of relaxation effects in simpler systems. Even for these systems, the nonlinear response is often more complex because it is the square of the sum of perturbation sequences involving different orderings of the applied fields. However, these problems do not contribute to experiments since no orientation signal is detected and the characteristic width of f is greater than specific state relaxation rates. A more rigorous description and deeper physical insight should be possible based on the recent development of effective optical Bloch equations for semiconductors.[12] Such an analysis would not be expected to change the qualitative understanding.

The experimental arrangement is based on two tunable frequency-stabilized narrow-band dye lasers. For studying excitation relaxation, one laser provides the forward and backward pump beams, and the second laser is used for the probe beam. For measurements of line shapes, one laser is used for the forward pump and probe beams, and the second laser is used for the backward pump beam. The probe frequency can also be adjusted using acousto-optic modulators and phase-locked frequency synthesizers, enabling correlated-field FWM spectroscopy.[13]

The MQW consisted of 65 periods of 96-Å GaAs and 98-Å $Al_{0.3}Ga_{0.7}As$ layers grown by molecular-beam epitaxy. The sample was mounted on a sapphire disk (c axis normal) with the substrate removed and was held at 5 K.

The linear absorption spectrum at 5 K shows the clearly resolved HH1 and LH1 excitons, with each peak having a width of order 2 meV. The degenerate FWM response shows only one peak, shifted 20 cm^{-1} to the red with respect to HH1, and is most likely associated with the exciton localized at island defects.[14] In our measurements, the pump intensity is of order 600

mW/cm^2 corresponding to an exciton density in the well region of order 10^7 cm^{-2}.

The FWM response as a function of δ is shown in Fig. 2. Figure 2(a) shows two resonances with linewidths of 3 GHz and 10 MHz. Figure 2(b) shows a scan of the tip of Fig. 2(a), obtained using the method of correlated optical fields. The linewidth is of the order of 30 kHz. The broad component in Fig. 2(a) corresponds to a lifetime of 100 psec, while the narrow feature corresponds to a lifetime of 30 nsec. In Fig. 2(b), the lifetime is of order 10 μsec. We ascribe the fast time to the intrinsic lifetime of the exciton.[15] A possible explanation for the origin of the 30-nsec state is that local electric fields resulting from surface or bulk localized states may result in a splitting of the electron and hole, an effect which is known to increase the exciton lifetime due to the reduced overlap of the wave functions.[16] The origin of the 10-μsec state is most likely associated with a defect and persists even at room temperature.[10] The line-shape data shown below indicate that these longer-lived states may play an important role in the interpretation of earlier work.

The response in Fig. 2(a) was studied as a function of wavelength and angle to look for the presence of the Mott mobility edge and the effects of diffusion due to delocalization.[11] The nonlinear response was examined over the lower half of the absorption line center. As discussed above, diffusion results in a FWMp response that varies as $\sin^2\theta/2$. Measurements were made between $\theta=2°$ and 30° with no significant changes on the narrow feature in Fig. 2(a). Determination of changes in the broad feature was limited by an error bar of order 100 MHz which prevented a demonstration of the quadratic dependence. However, if the increase in width of this feature with increasing angle is interpreted as diffusion, the change corresponds to an upper limit for D of 1 cm^2/sec, less than that reported earlier at absorption line center,[11] but we observe that our measurement is at a much lower exciton density.

The FWMb response corresponding to the excitation line shape is shown in Fig. 3(a) for $\delta=80$ MHz and was recorded on the low-frequency side of the peak of the nonlinear response. [A portion of the spike at zero detuning may result from stress-induced birefringence in the cryostat windows which leads to polarization leakage and a small contribution of the narrow feature seen in Fig. 2(a) from a grating produced by E_b and E_p^*. We ignore this component for this discussion.] If the spectrum is fitted by a Lorentzian,[17] and we use the relationship $\Gamma^{-1}=2/\pi\Delta\nu$ (note the extra factor of 2 for the FWMb response[7]), then we obtain a decay time of 50 psec. [A comparable time has been measured independently using a three-pulse (stimulated) photon echo (to be discussed elsewhere).] One can also compare the time scales observed in Figs. 2 and 3(a). Namely, for Fig. 3(a), we find $\Gamma\approx 2\times 10^{10}$ sec^{-1}. However, we note that the fastest decay observed in Fig. 2 corresponds to an exciton decay rate, $\gamma_{ex}\approx 10^{10}$ sec^{-1}. In this simple description, the contribution of this decay to Γ is $\gamma_{ex}/2$; that is, 25% of the homogeneous line shape is related to the decay of the exciton, clearly indicating the presence of other contributions to the line shape.

However, the deviation from a Lorentzian and the slight blue shift of the line shape suggests that the line broadening mechanism is more complex than a simple exponential decay of the polarization and the simple relationship above between Γ and $\Delta\nu$ may not be appropriate. More specifically, it can be shown using the expression given above for the FWMb response that the response should be symmetric for $\Delta\rightarrow -\Delta$. In fact, the observed asymmetry becomes more evident if we examine the line shape with $\delta=500$ kHz. On the red side of the degenerate FWM response, the line shape is similar to Fig. 3(a). On the blue side (at the HH1 absorption line center), the line shape, shown in Fig. 3(b), exhibits a high degree of asymmetry and a significant increase in linewidth.

At higher temperatures, such asymmetric line shapes for linear absorption have been predicted,[18] but these line shapes would still lead to a symmetric FWMb response. The observation of asymmetric profiles in FWM, however, is consistent with the possible onset of spectral diffusion in the vicinity of the mobility edge. In particular, variable-range hopping of the exciton[19] is one

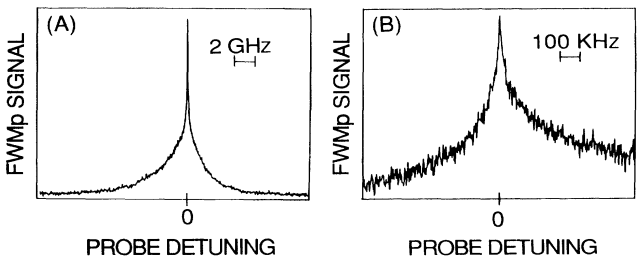

FIG. 2. FWMp response for two different dispersions.

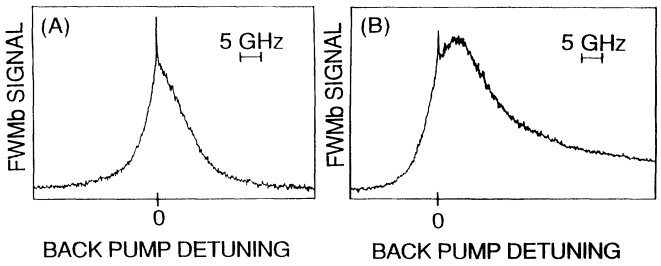

FIG. 3. FWMb response. (a) FWMb spectrum obtained on the low-frequency side of the nonlinear response with $\delta=80$ MHz. (b) FWMb spectrum obtained on the blue side of the nonlinear response at the peak of the HH1 absorption with $\delta=500$ kHz.

example of such an effect, and current analysis suggests that in this temperature range, the rate should be relatively independent of temperature, in agreement with our measurements. In addition, in the presence of spectral diffusion, we note that as δ is decreased from 80 MHz to 500 kHz, it can be shown using modified optical Bloch equations[20] that the degree of asymmetry could increase, in agreement with our experiment, since the reduced value of δ can either increase the contribution of states which have spectrally diffused (in the limit $\delta <$ recombination rate) or increase the contribution of longer-lived states (in the limit $\delta < \gamma_n$) which may be more affected by spectral diffusion. Alternatively, quasistatic line broadening theory (see generalized discussion by Anderson[1]) describes the effects of long-range static or slowly varying interactions which cause shifts in the levels and contribute to the line shape, and can also lead to asymmetric profiles. Finally, we note that the increase in the linewidth which we observed was reported earlier in resonant Raleigh scattering[4] and attributed to increases in the homogeneous linewidth due to the onset of delocalization. The linewidth changes which we observe are consistent with the earlier report; however, as discussed above, the changes which we observe are related to the dynamics of the exciton population.

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