Collective Effects in Excitonic Free Induction Decay: Do Semiconductors and Atoms Emit Coherent Light in Different Ways?

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(Received 27 May 1992)

We show that the many-body interactions among excitons govern the temporal line shape of the coherent (free induction decay) emission from semiconductor quantum wells. At low exciton densities, they become the dominant contribution to the emission.

PACS numbers: 71.35.+z, 42.65.−k, 71.45.Gm, 78.47.+p

It is well known that a resonantly excited atom acquires a polarization, oscillating at the natural frequency, which radiates and eventually decays away. This basic emission process is known as "free induction decay" (FID) [1]. In solids, however, atoms are densely packed so that absorption and emission are strongly influenced by the long-range Coulomb interaction that couples the charges. This is particularly true in semiconductors, where elementary excitations are delocalized and Coulomb correlation effects dominate [2]. Because the phase relaxation times are very short in such media, direct experimental investigations of the temporal evolution of FID were not possible until the recent development of stable and reliable ultrashort pulse lasers. Femtosecond-time-resolved coherent nonlinear optical experiments, such as four-wave mixing (FWM), have produced results in semiconductors which are qualitatively different from those found in independent systems, such as dilute atomic vapors [3,4]. Theories accounting for Coulomb-mediated many-body effects were able to explain these intrinsic differences [4,5]. The unusual temporal nonlinear optical response of semiconductors originates from the Coulomb renormalization of the coupling of the interband dipole with the electromagnetic (EM) field [6]. This results in interactions of excitonic polarization waves both with the applied EM field and also with other excitonic polarization waves [6,7]. For ultrashort pulse excitations, the temporal profile of the polarization waves is steplike in contrast with the pulselike profile of the applied EM fields. Therefore, polarization-wave interactions have a temporal dependence fundamentally different from that due to EM-field interactions. As we show below, important information on the many-body exciton-exciton interaction is contained in the temporal line shape of the semiconductor optical response under ultrashort pulse excitation. In this Letter, we present results of experiments in which the temporal profile of the FID of quasi-two-dimensional excitons in GaAs quantum wells (QW) has been resolved with a resolution of ≈ 100 fs. This first observation of many-body-mediated polarization-wave scattering demonstrates that, at low excitation, this effect strongly dominates free induction decay in semiconductors.

In our experiment, we use the simplest FWM geometry, where two delayed ultrashort laser pulses with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ interfere in a sample to generate a transient grating, which diffracts photons into the background-free direction $\mathbf{k}_s = 2\mathbf{k}_2 - \mathbf{k}_1$ [4]. For homogeneously broadened lines, the signal is emitted immediately after the second pulse and corresponds to FID. For a strongly inhomogeneously broadened line, however, the signal appears delayed by $\Delta t = t_2 - t_1$ after the second pulse and corresponds to a "photon echo" [1]. Because of the short dephasing time T_2, the emission of semiconductors is conventionally measured as a function of the time delay Δt between the input pulses by using a slow detector that integrates the emitted light. We call the signal obtained in such a measurement the time-integrated diffracted signal (TI-DS). Since we are interested in *time resolving the emission itself*, for a fixed Δt, we cross correlate the light emitted in the direction $\mathbf{k}_s$ with a third laser pulse by sum frequency generation in a highly transparent nonlinear crystal. This cross correlation determines the *temporal profile of the emission versus the absolute time* t [8–12]. We call the signal obtained in such a measurement the time-resolved diffracted signal (TR-DS). It is worth noting that in the latter experimental situation, the sample is in a steady state and the "time-resolved measurement" occurs after and independent of the sample, in contrast with the conventional method.

Homogeneously broadened exciton lines require very high-quality materials, which are often difficult to obtain. A resonance can be homogenized, however, by collisions with phonons at a temperature high enough to produce a large population of thermal phonons. In bulk semiconductors, these collisions broaden excitonic resonances until they disappear at high temperatures. In the case of QW structures, however, electron-hole correlation enhancement by quantum confinement stabilizes the quasi-2D exciton resonances up to room temperature [13]. The disadvantage of such homogenization is, of course, a much shorter dephasing time. We have investigated a sample consisting of 47 periods of 98-Å GaAs QWs and 96-Å $Al_{0.3}Ga_{0.7}As$ barrier layers. The substrate was removed by selective etching to allow for transmission experiments, and the sample was antireflection coated to

avoid Fabry-Pérot interference effects. For the experiments, the output of a mode-locked Ti:sapphire laser, delivering extremely stable ≈ 70–100-fs transform-limited Gaussian pulses at 88 MHz, is tuned to the exciton resonance and split into three beams in order to generate the FWM signal and time resolve its profile, as discussed above. The overall time resolution of the experiment is better than 100 fs. Details about the experimental procedure can be found in Ref. [12].

The experimental data discussed in this Letter are shown in Figs. 1 to 3. In Fig. 1 we display the temporal line shape of the TI-DS versus time delay Δt, and the temporal line shape of the TR-DS (at $\Delta t = 0$) versus the absolute time t. Since we want to compare the profiles, the two curves have been normalized to unity and the unrelated time axes have been shifted to bring the two maxima into coincidence. The difference between the two profiles is evident: The TR-DS, with a slowly rising edge and a significantly nonexponential trailing edge, is clearly broader than the TI-DS, which decays almost exponentially (we have verified this on a semilogarithmic plot). If the TI-DS is analyzed according to the conventional method [1], one obtains $T_2 = 135 \pm 5$ fs. This interpretation is incorrect since (i) it neglects the fact that as Δt varies, the excitation of the sample is not constant, and (ii) it completely ignores the contribution of the polarization-wave scattering. Instead, if one uses the correct analysis of the TR-DS profile, described below, one obtains $T_2 = 190 \pm 5$ fs for a constant excitation of the sample ($\Delta t = 0$ fixed) and a dominant contribution from polarization-wave scattering. In Fig. 2 we present (in thin solid lines) the TR-DS measured for a low exciton density of $N_x \approx 10^{11}$ cm^{-2} at $\Delta t = -40$, 0, 80, and 120 fs. These time traces are all nonexponential and asymmetric in time t, and their peak amplitude is an asymmetric function of Δt as well. For all the Δt series of TR-DS that we have measured, the data show that the DS is emitted immediately after the second pulse (i.e., at $t \approx 0$ after pulse 1 when $\Delta t < 0$, and at $t \approx \Delta t$ after pulse 2 when $\Delta t > 0$). This confirms that the exciton line is predominantly homogeneously broadened at room temperature and, therefore, that the emission corresponds to a FID. Furthermore, the consistency of the data was checked by numerically integrating the TR-DS versus t for each Δt, and comparing the result to the measured TI-DS versus Δt. The agreement is excellent in all cases [12]. Although very surprising, this result is consistent with theory [4,5]: The time integration, performed numerically or experimentally (by the slow detector) hides most of the temporal structure of the FID. (Similar experiments performed at higher excitation display variation of the temporal profile versus t when Δt is varied, due to the fact that the excitation density is very sensitive to the time ordering of the stronger pulse 2 with respect to

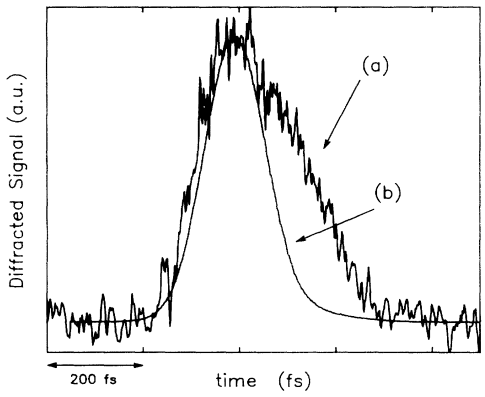

FIG. 1. Comparison of (a) the temporal profile of the time-resolved signal vs absolute time t at $\Delta t = 0$ and (b) the temporal profile of the time-integrated signal vs time delay Δt, for a total exciton density of $N_x = 10^{11}$ cm^{-2}.

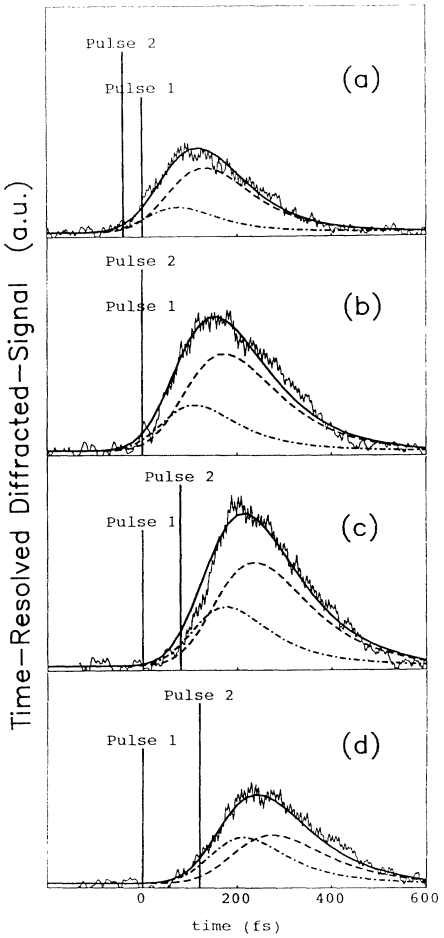

FIG. 2. Temporal profile of the free induction decays (shown by thin solid lines) measured for the low exciton density of Fig. 1, $N_x = 10^{11}$ cm^{-2}, at time delays $\Delta t = -40$, 0, 80, and 120 fs. The thicker lines correspond to the fit discussed in the text: the dash-dotted lines give the phase-space-filling contribution, the dashed ones give that of exciton-exciton interaction, and the solid ones give their sum.

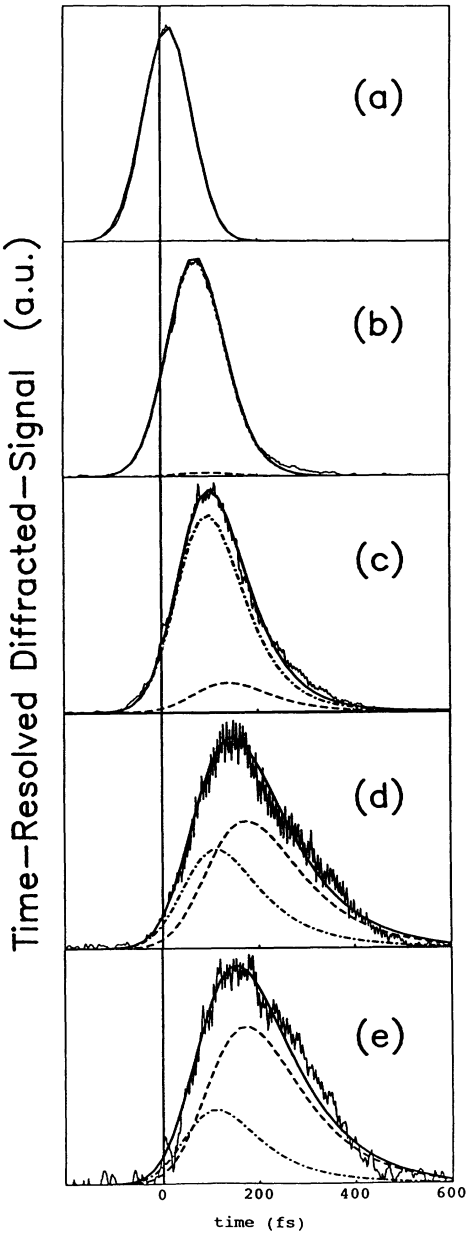

FIG. 3. Temporal profile of a series of time-resolved free induction decays (shown by thin solid lines) measured at $\Delta t = 0$ for total exciton densities of (a) $N_x = 10^{13}$ cm^{-2}, (b) 10^{12} cm^{-2}, (c) 4×10^{11} cm^{-2}, (d) 2×10^{11} cm^{-2}, and (e) 10^{11} cm^{-2}. The thicker lines correspond to the fit discussed in the text: the dash-dotted lines give the phase-space-filling contribution, the dashed ones give that of exciton-exciton interaction, and the solid ones give their sum.

the weaker pulse 1.) In Fig. 3, we show the dependence of the TR-DS line shape, measured at $\Delta t = 0$, on the exciton density for $N_x \approx 10^{13}$ cm^{-2} [3(a)], 10^{12} cm^{-2} [3(b)], 4×10^{11} cm^{-2} [3(c)], 2×10^{11} cm^{-2} [3(d)], and 10^{11} cm^{-2} [3(e)]. At very high density, exceeding the saturation density $N_s \approx 3\times10^{11}$ cm^{-2}, the TR-DS duration is of the order of the laser pulse and its line shape is quite similar to that of the TI-DS. As the density is lowered, the temporal profile is time resolved and evolves toward the nonexponential line shape discussed in Fig. 1.

In order to be more quantitative, we need to compare these experimental results to theory. In a semiconductor excited by an optical field $E(t)$, the exciton amplitude $\psi(t)$ satisfies the nonlinear Schrödinger equation [4,14],

$$\frac{\partial}{\partial t}\psi(t) = -i(\Omega - i\Gamma)\psi(t) + i\mu E(t) - i\mu E(t)\frac{|\psi(t)|^2}{\psi_s^2} - iV|\psi'(t)|^2\psi(t), \quad (1)$$

where only terms up to third order in the field have been retained. In this equation, μ is the interband dipole element (assumed k independent), and Ω and $\Gamma(=T_2^{-1})$ are, respectively, the exciton frequency and half width at half maximum. The first line describes the linear response, while the two terms on the second line describe the nonlinear response. The first term is the Pauli-exclusion reduction of the dipole coupling of the exciton with the field, as measured by the Rabi frequency, $\mu E(t)$. (The saturation parameter, ψ_s, is a material parameter that depends on the exciton characteristics [13].) The second term is specific to dense media and, in semiconductors, it describes the Coulomb-mediated exciton-exciton interaction [14]. Its physical interpretation is that, via the potential V, excitons at one site, $\psi(t)$, interact with excitons at other sites, $\psi'(t)$. It is this last term which describes an interaction between polarization waves within the medium. We will call these two nonlinear terms the phase-space-filling (PSF) and the exciton-exciton interaction (XXI) term, respectively.

We have solved Eq. (1) numerically, in the mean-field approximation, for the nonlinear polarization $P_{k_s}^{(3)}(t) = \mu^* \langle \psi_{k_s}^{(3)}(t) \rangle$ radiating in the direction $\mathbf{k}_s$, using Gaussian laser pulses with a duration corresponding to that of our laser. We use as fitting parameters the exciton relaxation time, T_2, and the ratio of the two nonlinear terms, $V\psi_s^2$. We impose, however, a severe constraint to the fit of our data: All TR-DS curves in a Δt series must have the same origin of the absolute time t and a constant calibration. We find that it is impossible to fit the data with such a constraint if we retain only the PSF term in Eq. (1). An excellent fit is obtained, however, if both the XXI and PSF contributions are considered. This is shown in Fig. 2, where the dash-dotted lines give the PSF contribution, the dashed lines give the XXI, and the thick solid lines give their sum (the data are shown by thin solid lines). The relaxation time for the negative time delay [Fig. 2(a)] is $T_2 = 160 \pm 5$ fs, somewhat shorter than for the positive delays [Figs. 2(b)-2(d)], $T_2 = 190 \pm 5$ fs. This can be explained, as detailed below, by the fact that for Fig. 1(a) pulse 2, the stronger of the two pulses, arrives in the sample first and hence the excitons it creates are ionized by thermal phonons before and during the ar-

rival of the weaker pulse 1 [13]. Collisions with electron-hole pairs generated in this manner then speed up to phase relaxation [15]. In Fig. 2, the ratio of nonlinearities remains essentially constant for all the fits, $V\psi_s^2 = 0.01 \pm 0.001$. More significantly, the contribution of the XXI to the total energy contained in the pulse emitted by the sample (which is proportional to the TR-DS area) is *approximately 2 times larger* than that due to PSF.

When we apply the same fitting procedure to the curves of Fig. 3, we find that the data in Figs. 3(a) and 3(b) do not require XXI and correspond to very short T_2 of 10 and 70 fs, respectively. At these densities, the band gap has renormalized to the point that excitons are unstable, the continuum has shifted below the laser frequency, and the experiment probes exciton scattering states. In this case, the use of Eq. (1) becomes questionable. Beginning with Fig. 3(c), we find that it is impossible to obtain a good fit to the data without including the XXI term. In fact, the XXI term appears to be turned on around $N_x \approx N_s$ and to become predominant at the lower densities of Figs. 3(d) and 3(e). Correspondingly, the relaxation time increases up to $T_2 = 190 \pm 5$ fs and stabilizes. All these observations can be explained by the following sequence of processes based on well established dynamics of excitons in quantum wells at room temperature (see Ref. [13] for details). Consider first the case of an excitation density low enough that photogenerated excitons are in bound states, which interact effectively via the Coulomb force (Fig. 2). When the strongest pulse arrives first in the sample [Fig. 2(a)], it generates excitons in these bound states (binding energy ≈ 10 meV for ≈ 100-Å QW), which ionize by collisions with the energetic thermal phonons (phonon energy ≈ 36 meV for GaAs), generating electron-hole pairs in scattering states (excess energy ≈ 25 meV). Since the phonon-assisted ionization time is ≈ 100–200 fs, the charged carriers shorten the relaxation time owing to their larger effects on the neutral bound states [15]. For the reverse time ordering [Figs. 2(b)–2(d)], when the weaker pulse arrives first, its effects are less pronounced and the sample remains closer to steady state during the FID emission. At very high densities, however, the band gap renormalizes so much during the laser pulses that the excitons are generated in scattering states, giving free electron-hole pairs immediately. They, of course, shorten the relaxation time, but more importantly they screen the XXI efficiently, thus reducing (and eventually eliminating) its contribution to the FID emission [Figs. 3(a) and 3(b)]. Our experimental observations are in agreement with Ref. [16], which showed that exciton collisions with electron-hole pairs are more efficient in shortening the relaxation time than are collisions with other excitons. This description of the exciton dynamics also demonstrates that the conventional experimental technique, TI-DS, does not correspond to a sample in a steady state and therefore provides unreliable data, unless the excitation is extremely weak (which is not the case for most of the published experiments).

In conclusion, we have demonstrated that, because of exciton-exciton interactions, semiconductors emit light in a way fundamentally different from isolated atoms. We have found that the polarization-wave scattering originating from this interaction, is, in fact, dominant at low excitation densities where excitons remain in bound states. The effects of polarization waves in ultrafast optical processes have been recognized only recently [5–7,14,16], and they must be accounted for in a correct description of many phenomena occurring in these materials.

This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

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