Interferometric four-wave-mixing spectroscopy on bulk GaAs

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A phenomenon in interferometric four-wave mixing is reported which can be used to quantify effects beyond the third-order perturbational limit in a sensitive and intuitive fashion. The experiments on bulk GaAs at $T=77$ K on a time scale of 10 fs and at excited carrier densities as low as 2.3×10^{14} cm^{-3} show that the third-order perturbational limit can hardly be reached experimentally. [S0163-1829(97)10307-1]

Interferometric transient four-wave-mixing techniques have the potential of being extremely sensitive with respect to the dynamics of elementary excitations[1] and might be the key to studying non-Markovian relaxation on an ultrafast time scale. While the first studies on semiconductors have employed interferometric sensitivity only after the sample,[2] more recent experiments on semiconductors[3] and on the non-Markovian dynamics of molecular systems[4,5] use phase-locked pulses to excite the system, thus delivering coherent control[6] over the system. This has enabled the observation of subtle interference phenomena.[5] In this paper we report the observation of a novel interference phenomenon in four-wave mixing.

In a four-wave-mixing experiment, with incoming beams having wave vectors $\vec{q}_1$ and $\vec{q}_2$, respectively, the beam in direction $\vec{q}_1$ clearly enters linearly into the diffracted signal with wave vector $2\vec{q}_2-\vec{q}_1$ in the third order perturbational regime. Consequently, a phase-locked pair of optical pulses $\mathcal{E}(t-t_1)$ and $\mathcal{E}(t-t_{1'})$ on the same axis $\vec{q}_1$ and degenerate in frequency leads to a simple interference as a function of their time delay $t_1-t_{1'}$ with the frequency of the laser for resonant excitation. Beyond the third-order perturbation limit, contributions wich propagate in the same diffracted direction, as, e.g., $2\vec{q}_2+\vec{q}_1-2\vec{q}_{1'}$, $2\vec{q}_2+\vec{q}_{1'}-2\vec{q}_1$, interfere among themselves and with the above contribution and consequently lead to components oscillating with twice and three times the laser frequency. Similar, yet higher order contributions show up as yet higher harmonics in the time-delay domain. In this paper we apply such interferometric four-wave-mixing technique to a very simple situation, namely resonant excitation of the band edge of high-quality bulk GaAs at low temperatures on a 10 fs time scale. The excitation density is varied systematically in the range from 2.3×10^{14} cm^{-3} to 2.0×10^{17} cm^{-3}.

The experimental setup is similar to the one previously employed[7,8] except for the extension to three collinearly polarized beams of comparable intensity, two of which propagate in the same direction $\vec{q}_1=\vec{q}_{1'}$ (Fig. 1). Their time delay $t_{11'}\equiv t_1-t_{1'}$ is controlled by means of a piezoelectric actuator. The corresponding resolution is limited by the number of bits of the driving digital to analog converter (12 bits) and corresponds to 0.05 fs for the full travel of the stage of about 220 fs. The wave vector $\vec{q}_2$ of the third pulse $\mathcal{E}(t-t_2)$ includes a small angle ($\approx1°$ in the medium) with the wave vector $\vec{q}_1$. The corresponding time delay $t_{21'}\equiv t_2-t_{1'}$ is also controlled by a piezoelectric stage. The center frequency of the closely transform-limited optical pulses of 15 fs duration is tuned to the 1*s*-exciton resonance of bulk GaAs at $T=77$ K and the diffracted signal in direction $2\vec{q}_2-\vec{q}_1$ is detected with a photomultiplier. All carrier densities quoted refer to the incoherent superposition of the three beams. They are determined in a fashion consistent with previous, noninterferometric experiments.[7,8] A density of, e.g., 10^{15} cm^{-3} corresponds to a peak intensity of 1.3×10^{6} W cm^{-2} and an energy of 0.3 pJ per pulse.

Figure 2 shows a typical set of FWM traces as a function of $t_{11'}$ for three different $t_{21'}$. Beside the simple interference with roughly the band gap frequency, additional fine structure is observed around $t_{11'}\approx0$. From the inset in Fig. 2 it already becomes evident that this fine structure is related to higher frequency components. The origin of these fast oscillations becomes yet more clear when inspecting the Fourier transforms of the data with respect to $t_{11'}$. The absolute value of the Fourier transforms for four different total carrier densities, separated by one order of magnitude, plotted as a function of the energy, is depicted in Fig. 3. It is obvious that only integer harmonics of the basic frequency occur. For a density of, e.g., 2.9×10^{15} cm^{-3}, the second harmonic is merely a factor of 3 weaker than the fundamental. Somewhat surprisingly, the relative weight of the harmonics shows a rather small influence on carrier density. It is only at the lowest carrier densities that the strength of the higher harmonics decreases somewhat. Interestingly, the higher harmonics also decrease slightly in strength for densities above several 10^{15} cm^{-3}.

Intuitively, one might expect that the occurrence of these higher harmonics in the time-delay domain could be related to higher harmonics in the real-time domain. The latter effect is well known and stems from the nonlinear optical contributions beyond the rotating wave approximation.[9] A straightforward estimate for the present conditions, however, clearly shows that these nonresonant contributions are many orders

TABLE I. Time dependence of components of the polarization with wave vector $2\vec{q}_2-\vec{q}_1$ within the rotating wave approximation from a pertubational analysis.

Third order	$e^{-i\omega(t-[2t_2-t_1])}, e^{-i\omega(t-[2t_2-t_{1'}])}$
Fifth order	$e^{-i\omega(t-[2t_2-t_1])}, e^{-i\omega(t-[2t_2-t_{1'}])}$
	$e^{-i\omega(t-[2t_2+t_{1'}-2t_1])}, e^{-i\omega(t-[2t_2+t_1-2t_{1'}])}$

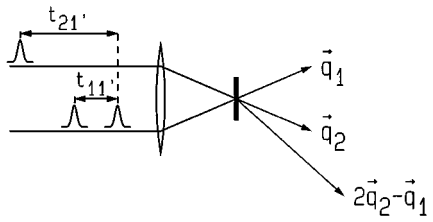

FIG. 1. Schematic of the experimental setup.

of magnitude smaller than the resonant contributions. As argued earlier in this paper, we interpret the higher harmonics in the time-delay domain as being due to resonant nonlinear optical contributions beyond the third order. Table I lists the phase factors of all third- and fifth-order contributions to the FWM signal with wave vector $2\vec{q}_2-\vec{q}_1$. In third order, the only occurring beat oscillation is $\omega(t_1-t_{1'})=\omega t_{11'}$ while up to fifth order terms like $2\omega t_{11'}$ come into play also. The following analysis confirms this general reasoning. Here we exclusively account for the dominant nonlinear optical contribution to the coherent response at excitation densities lower than 5×10^{15} cm^{-3} in bulk GaAs, which has recently been shown to originate from exciton-continuum scattering.[8] A similar coupling of exciton and continuum has also been found in quantum wells.[10] Within the model for exciton-continuum scattering[8] the polarization of the 1*s*-exciton P_{1s} obeys the following equation of motion:

$$\left(\frac{\partial}{\partial t}+i\Omega_{1s}+\gamma_2\right)P_{1s}(t)=\frac{i}{\hbar}d_{1s}E(t), \tag{1}$$

where phase space filling and the exchange interaction among excitons have already been neglected. $\hbar\Omega_{1s}$ is the 1*s*-exciton transition energy, d_{1s} is the corresponding dipole matrix element, and $E(t)$ is the total incident electric field. Scattering enters through a Taylor expansion of the dephasing rate γ_2 in powers of the occupation of (exciton) continuum states f_n labeled by the exciton quantum number n:

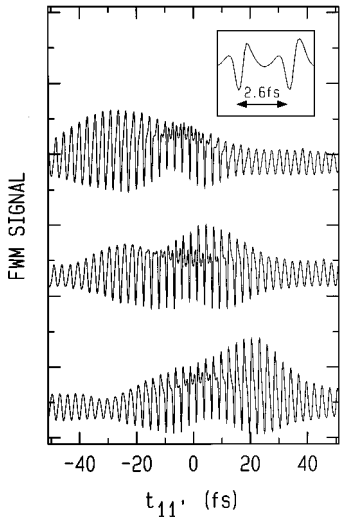

FIG. 2. Experiment: interferometric four-wave-mixing signal, GaAs at 77 K and a total carrier density of 2.9×10^{15} cm^{-3}, as a function of $t_{11'}$ for three fixed $t_{21'}$ (from top to the bottom $t_{21'}=-10$,0,10 fs). Inset: Signal for $t_{21'}=0$ and $t_{11'}\approx0$.

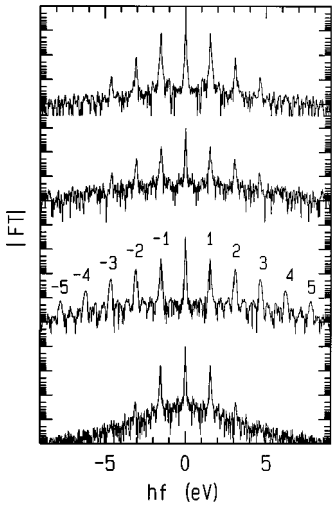

FIG. 3. Experiment: absolute value of the Fourier-transform (FT) with respect to $t_{11'}$ of traces similar to those of Fig. 2 for $t_{21'}\approx0$. The total carrier density from top to bottom; 2.0×10^{17}, 2.0×10^{16}, 2.9×10^{15}, and 2.3×10^{14} cm^{-3}.

$$\gamma_2=\gamma_2^0+\sum_n \gamma_2'(n)f_n(t), \tag{2}$$

γ_2' is assumed to be constant. The perturbational approach used in the above general discussion is not appropriate for a quantitative analysis of Eqs. (1) and (2) as contributions from increasing orders become comparable. Hence our modeling is based on the alternative and well-known wave vector selection procedure, e.g., described in Ref. 11, which is also meaningful beyond the third-order perturbational regime. For the electric field as well as for the polarization and the occupations a discrete spatial Fourier expansion with respect to the wave vectors $\vec{q}_1$ and $\vec{q}_2$ is performed.

$$E(t)=E^{10}(t)e^{i(\vec{q}_1\vec{r}-\omega t)}+E^{01}(t)e^{i(\vec{q}_2\vec{r}-\omega t)}, \tag{3}$$

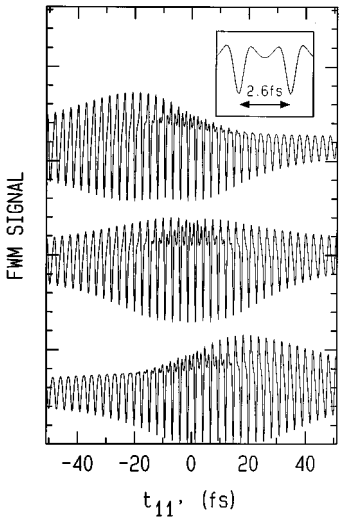

FIG. 4. Model: interferometric four-wave-mixing signal as a function of $t_{11'}$ for three fixed $t_{21'}$ (from top to the bottom $t_{21'}=-10$,0,10 fs). Inset: signal for $t_{21'}=0$ and $t_{11'}\approx0$. This behavior has to be compared with the experiment (Fig. 2).

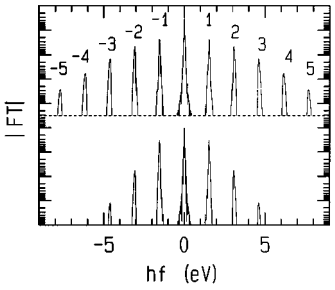

FIG. 5. Model: absolute value of the Fourier transform with respect to $t_{11'}$, at $t_{21'}=0$. The excited density of the upper curve corresponds to Fig. 4, the density of the lower curve is one order of magnitude lower.

$$f_n(t)=\sum_{n_1,n_2;n_1+n_2=0} f_n^{n_1n_2}(t)e^{i(n_1\vec{q}_1+n_2\vec{q}_2)\vec{r}}, \tag{4}$$

$$P_{1s}(t)=\sum_{n_1,n_2;n_1+n_2=1} P_{1s}^{n_1n_2}(t)e^{i[(n_1\vec{q}_1+n_2\vec{q}_2)\vec{r}-\omega t]}. \tag{5}$$

The restrictions in the summations result from the rotating wave approximation. In order to obtain a closed set of equations, the Fourier series is truncated in the usual fashion ($|n_1|+|n_2|\leqslant 3$).[11] Introducing Eqs. (3)–(5) in Eqs. (1) and (2) leads to the following set of equations for resonant excitation ($\omega=\Omega_{1s}$):

$$\left(\frac{\partial}{\partial t}+\gamma_2^0\right)P_{1s}^{10}=\frac{i}{\hbar}d_{1s}E^{10}-P_{1s}^{10}\sum_n \gamma_2' f_n^{00}-P_{1s}^{01}\sum_n \gamma_2' f_n^{1-1} - P_{1s}^{2-1}\sum_n \gamma_2' f_n^{-11}, \tag{6}$$

$$\left(\frac{\partial}{\partial t}+\gamma_2^0\right)P_{1s}^{01}=\frac{i}{\hbar}d_{1s}E^{01}-P_{1s}^{10}\sum_n \gamma_2' f_n^{-11}-P_{1s}^{01}\sum_n \gamma_2' f_n^{00} - P_{1s}^{-12}\sum_n \gamma_2' f_n^{1-1}, \tag{7}$$

$$\left(\frac{\partial}{\partial t}+\gamma_2^0\right)P_{1s}^{2-1}=-P_{1s}^{10}\sum_n \gamma_2' f_n^{1-1}-P_{1s}^{2-1}\sum_n \gamma_2' f_n^{00}, \tag{8}$$

$$\left(\frac{\partial}{\partial t}+\gamma_2^0\right)P_{1s}^{-12}=-P_{1s}^{01}\sum_n \gamma_2' f_n^{-11}-P_{1s}^{-12}\sum_n \gamma_2' f_n^{00}. \tag{9}$$

Because of the free polarization decay of the continuum states, a similar treatment of their dephasing has no effect on the calculation. Furthermore their occupations are still small. Therefore a perturbational treatment of the continuum states is still justified. If the Coulomb correlations are neglected for the continuum, the occupations can be evaluated by the optical Bloch equations and the summations Σ_n can be replaced by an integral with the joint density of states.

It is the coupling of the different Fourier components in Eqs. (6)–(9) that leads to the higher harmonics in the time delay domain. Using the parameters of the experiment ($\hbar\gamma_2^0=1$ meV, $\hbar\Omega_{1s}=1500$ meV, the individual pulses are sech^2-shaped with a full width at half maximum of 15 fs) the numerical solutions shown in Figs. 4 and 5 are obtained. In Fig. 4 again fast oscillations of the four-wave-mixing signal in direction $2\vec{q}_2-\vec{q}_1$ $[\sim\int_{-\infty}^{+\infty}|P_{1s}^{-12}(t)|^2dt]$ are observed which show up as integer harmonics of the fundamental frequency when performing a Fourier transform with respect to $t_{11'}$ (Fig. 5). The overall qualitative agreement with the experiment is satisfactory (compare Figs. 2 and 4 and Figs. 3 and 5). The strength of the higher harmonics scales with the factor $\Sigma_n\gamma_2' f_n/\gamma_2^0$ which is obviously proportional to the excited carrier density. This behavior can be seen in Fig. 5, where the carrier density has been varied by a factor of 10. It is interesting to note that for lower temperatures or yet higher quality samples (leading to smaller γ_2^0) an even more pronounced influence of contributions beyond third order would result.

In conclusion transient four-wave mixing employing phase-locked pairs of ultrashort pulses is a sensitive tool to quantify the influence of resonant nonlinear optical contributions beyond third order. At total carrier densities of 2.3×10^{14} cm^{-3} which are among the lowest ever reported for semiconductors, these contributions still have considerable strength. At first this poses limits to the applicability of an interesting approach to solve the Hamiltonian of interacting fermions of the semiconductor beyond the Hartree-Fock approximation,[9] which has been discussed quite recently.[12] In their appealing approach, the dynamics-controlled-truncation (DCT) of the hierarchy of density matrices of the semiconductor, in principle no approximations have to be made concerning the Coulomb interaction but rather an ordering with respect to powers of the electric field is performed only. From our experiments it is evident that such approach can only be expected to deliver quantitative results for densities in the range of $\leqslant 10^{14}$ cm^{-3} under the above conditions. Second, coherent control experiments on semiconductors in general not only have to control the phase much better than one wavelength of the fundamental but much better than one wavelength of the relevant harmonics.

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