Two-photon four-wave mixing in III-V semiconductors: Evidence for coherent phonons

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We present midgap femtosecond four-wave mixing measurements on single-crystal GaAs and InP that show a surprising nondegenerate emission, shifted to higher energy relative to the laser, by an amount comparable to the energy of an optical phonon. The polarization dependence of the signal rules out ordinary Raman scattering. We discuss the possibility of impulsive excitation of symmetric lattice vibrations, around localized midgap states that may play a significant role in the two-photon transition amplitude.

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Time-resolved spectroscopy has been used extensively in studies of relaxation processes which affect photocarriers out of equilibrium. In particular, the emission of coherent and incoherent optical phonons by photocarriers in semiconductors has received considerable attention.[1] Phonon emission typically expresses itself as sidebands in the energy spectrum of the carrier population, which may be detected by time-dependent differential absorption spectroscopy.[2] The relaxation of coherent phonons has also been investigated, using the time-resolved coherent anti-Stokes Raman scattering (CARS) technique.[3] In other experiments the impulsive excitation of coherent optical phonons was observed as oscillations in the time domain.[4] Although similar in principle to CARS experiments in transparent media, such measurements often show deviations from the selection rules for the optical polarizations which are well known for Raman scattering. In cases where such deviations occur, they are usually explained in terms of a displacive excitation of coherent phonons (DECP).[5]

Time-resolved spectroscopy measures the third-order susceptibility $\chi^{(3)}$. It has been used extensively to characterize the nonlinear response of III-V semiconductors such as GaAs and InP, in particular near the excitonic resonance at the band edge.[6] In that regime the main contributions to $\chi^{(3)}$ result from band filling and Coulomb correlation effects.[7] As the excitation is detuned below the band edge, linear absorption becomes negligible, and with it the contribution of the above effects to $\chi^{(3)}$. In this regime two-photon absorption (2PA) (Refs. 8 and 9) and the nonlinear refractive index n_2 (Kerr effect)[9,10] form the main contributions to $\chi^{(3)}$. The two are related to each other, similarly to the Kramers-Kronig relations in linear response.[11] n_2 is the cause of self-phase modulation (SPM) of short optical pulses as they propagate in a nonlinear medium.[12] $\chi^{(3)}$ processes beyond 2PA and SPM which affect pulse propagation in nonlinear media include self-steepening and stimulated Raman scattering (SRS). SRS is different from other $\chi^{(3)}$ effects in being a delayed scattering process,[13] which occurs on a time scale of $2\pi/\Omega_{ph}$, where Ω_{ph} is the optical-phonon frequency. In materials where the selection rules allow the scattered light to have the same polarization as the input beam, such as glass, SRS is observed in single beam experiments as self-Raman shift of the pulse spectrum towards lower (Stokes) photon energies.[13] The importance of SRS tends to increase for shorter pulses, due to an increased overlap with the Raman gain profile. However, the delayed nature of SRS tends to reduce the efficiency of this process, which is mainly observed under favorable dispersion conditions (anomalous dispersion, where the lower frequency components trail behind the pulse).[14] In contrast, the polarization selection rules for Raman scattering preclude SRS in single beam experiments on single crystals of zinc-blende materials such as GaAs and InP.[15] However, in multiple-pulse experiments SRS may result in a time-delay dependent exchange of energy between the beams, provided that the polarizations of the beams are properly chosen. This effect is a typical feature of CARS experiments,[3] and was also observed in pump-probe (PP) experiments near the middle of the gap in GaAs/AlGaAs waveguides.[16] Another effect which may introduce coupling between different laser pulses that co-propagate in the sample is cross phase modulation (XPM).[13] The combined effects of self-steepening and XPM were demonstrated recently in a PP experiment on GaAs.[17]

In this paper we report four-wave mixing (FWM) and PP measurements on single-crystal GaAs and InP samples, that show a surprising nondegenerate emission. Under strong excitation, near the middle of the gap, the spectrally resolved FWM (SR-FWM) signal has a strong asymmetry in both frequency and time domains. The shift of the nondegenerate emission is to higher energy, and is comparable to the energy of an optical phonon. However, the polarization dependence of the signal indicates that symmetric lattice vibrations are involved, which is in contradiction with the selection rules for Raman scattering in zinc-blende crystals. A possible explanation is the impulsive excitation of symmetric lattice vibrations around localized midgap states—states that may indeed play a significant role as intermediate states in two-photon transition amplitudes.

In the experiment we used high-intensity optical pulses of 50–80 fs duration, at wavelengths between 1200 and 1900 nm, generated by a Spectra Physics OPA-800 optical parametric amplifier. For the PP and FWM measurements the OPA output was split into two beams, which were then focused, by a lens with 45-cm focal length, to 220-μm overlapping spots on the sample. The angle between the beams was 4°, and their power ratio was 2:1. The samples were 500-μm thick wafers of compensated GaAs and InP, polished on both sides, but uncoated. The samples were held on

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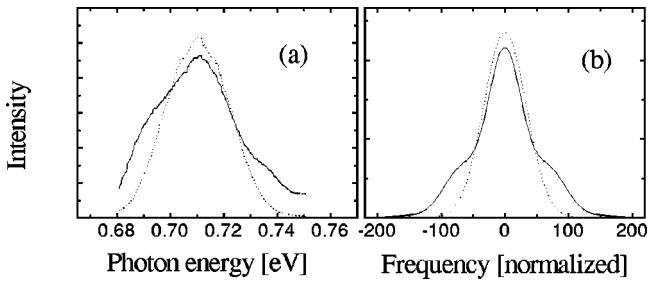

FIG. 1. (a) The spectrum of an input pulse (dotted) compared to the spectrum transmitted through 500 μm of InP (solid), for a typical power density of 100 GW/cm^2 (the two graphs are not to scale); (b) calculated transmitted spectrum (solid) for an input Gaussian pulse (dotted; the two curves are not to scale).

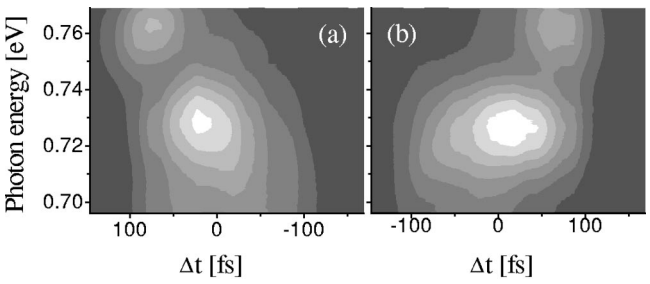

FIG. 2. Time delay–photon energy contour plots of the emitted FWM signal for the two momentum-conserving directions (a) $2k_2-k_1$ and (b) $2k_1-k_2$. The laser is centered at 0.73 eV. The time delays correspond to the normal convention for FWM.

a cold finger of a continuous flow cryostat that allowed measurements from 4.2 K to room temperature. The experimental setup allowed the direction of the FWM emission or the transmitted beams into a spectrometer, where their spectra were measured by an InGaAs detector array.

The maximum pulse energy in the experiment was 8 μJ, corresponding to a peak intensity of 400 GW/cm^2. With a typical power density I of 100 GW/cm^2 at a wavelength $\lambda = 1500$ nm, a propagation length $l = 500$ μm, and a nonlinear refractive index $n_2 = 3.6\times10^{-14}$ cm^2/W,[16,18] the nonlinear phase shift $\Phi = 2\pi n_2 I l/\lambda$ accumulated in our experiment (neglecting 2PA) is $\approx 2.4\pi$, comparable to previous experiments on semiconductor waveguides. At such power levels, and in the absence of 2PA, one usually observes a significant spectral broadening of the pulse, due to SPM.[12] However, in our case 2PA strongly suppresses the broadening, which manifests itself as small spectral wings. These are seen in Fig. 1, which compares the incident and transmitted spectra in a single beam experiment. The figure also shows the results of a calculation of the output spectrum for the above propagation parameters, starting with a Gaussian pulse. The calculation is based on the well-known nonlinear Schrödinger equation,[13] but retains only the effects of 2PA and n_2, while neglecting linear absorption, all dispersion terms, and the self-steepening and Raman terms. The omission of linear dispersion is justified by the fact that the experiment is performed with high laser fluence and a short propagation length, in which case the nonlinear terms dominate.[19] The result is a simple nonlinear propagation equation for the slowly varying amplitude $A(z,t)$: $\partial A/\partial z + (\alpha - i\gamma)|A|^2 A = 0$, where α and γ are the propagation constants related to 2PA and n_2, respectively. The theoretical curve was calculated for parameters which correspond to our experimental conditions. The calculated integrated transmission through the sample ($\approx 10\%$) is also in good agreement with the experiment.

Figure 2 shows two time-energy contour plots of the SR-FWM signal, measured on an InP sample at room temperature, with the laser tuned to a photon energy of 0.73 eV, and with parallel polarizations. Two plots are shown, for the two momentum-conserving directions $2k_2-k_1$ and $2k_1-k_2$ (where k_1 and k_2 are the wave vectors of the two excitation beams). The two are mirror images of each other, as expected. Both show a strong peak at the laser energy and $\Delta t = 0$, as one would expect for an instantaneous process. Surprisingly, a second, weaker peak appears, offset to higher energy and to positive time delay [following the usual convention, positive time delay is defined for emission to $2k_2-k_1(2k_1-k_2)$ as $k_2(k_1)$ lagging behind $k_1(k_2)$]. The higher-energy satellite peak is observed in both InP and GaAs, and its relative intensity increases with laser power. It is most prominent for photon energies slightly above the middle of the gap, where n_2 reaches its maximum value, and follows the shift of the midgap energy as the temperature varies from 4 to 300 K. This proves that the satellite peak is related to material properties rather than laser properties. This point is demonstrated in Fig. 3, which shows data taken on two different samples and at different temperatures, but with similar photon energies. Panel (a) of the figure displays SR-FWM data for an InP sample, at room temperature, with the laser tuned to 0.83 eV (≈ 100 meV above the midgap energy). Panel (b) presents data for a GaAs sample, at 77 K, with the laser tuned to 0.80 eV (≈ 40 meV above the midgap energy, and precisely where n_2 peaks[18]). While in the InP data the satellite peak is rather weak, and the SR-FWM contour plot is quite symmetrical, the GaAs data show a pronounced satellite peak. The above results do not change for perpendicularly polarized excitation beams, with the exception that the FWM intensity is about one order of magnitude lower. Moreover, the signal is independent of sample rotation and tilt, and the polarization of the FWM emitted to $2k_2-k_1(2k_1-k_2)$ is always parallel to the polarization of the $k_1(k_2)$ beam.

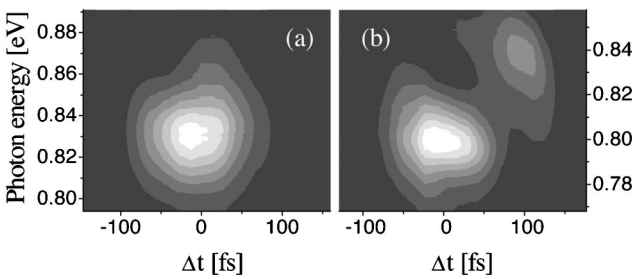

FIG. 3. Time delay–photon energy contour plots of the emitted FWM signal for (a) InP at room temperature, with the laser tuned to 0.83 eV, and (b) GaAs at 77 K, with the laser tuned to 0.80 eV.

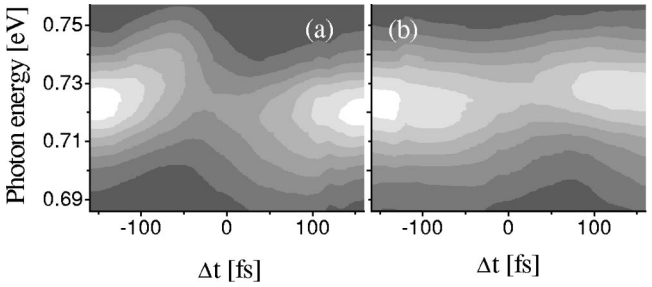

FIG. 4. Time delay–photon energy contour plots of the PP data for directions (a) k_1 and (b) k_2. In both frames $\Delta t>0$ refers to an ordering of the pulses as in Fig. 2(b).

Before we further analyze the data, it is important to note that SR-FWM is sensitive to deviations from a Fourier transform-limited pulse.[20] Linear chirp indeed shows in our low-intensity data, particularly at longer laser wavelengths. However, that chirp is determined mainly by the laser source and not by the sample.[19] Moreover, dispersion (to any order) simply redistributes the spectral components in the time domain, and cannot account for the strong asymmetry of the SR-FWM data, where only a shift to higher energy is observed. We therefore conclude that the satellite peak in our SR-FWM data is due to a nonlinear process.

SPM is a nonlinear process that creates new frequencies. However, the broadening due to SPM alone is symmetric. Furthermore, the broadening of a single beam in our experiment is not sufficient to explain the SR-FWM data. Therefore other $\chi^{(3)}$ processes which affect the pulse as it propagates through the sample, beyond 2PA and SPM, must be considered. Such effects include self-steepening and SRS, both of which are treated on the same level within the framework of the nonlinear Schrödinger equation.[13] Both increase linearly with n_2, in agreement with our finding that the satellite peak is most prominent for photon energies where n_2 reaches its maximum value. However, the polarization dependence of the FWM signal is inconsistent with a Raman process:[15] it implies that the lattice vibration involved in the process is symmetrical, unlike the zone-center phonons in zinc-blende crystals. Therefore self-steepening seems more likely to explain the data. Indeed, a recent PP experiment[17] above the middle of the gap of GaAs demonstrated that self-steepening in combination with XPM results in strong spectral shifts of the probe beam as function of the time delay. Similar shifts are observed in our spectrally resolved PP data, as shown in Fig. 4. The figure shows time-energy contour plots of the transmitted beams for the case of InP at room temperature, with the laser tuned to 0.73 eV, and with parallel polarizations (as for Fig. 2). Figure 4(a) depicts the spectra of the weaker beam as function of time delay, while the spectra of the stronger beam are presented in Fig. 4(b). It is evident that when the two pulses partially overlap their spectra shift in opposite directions, and that the weaker beam is affected more strongly. The size of the shift and its sign are consistent with earlier experiments[17] (note the different signs of n_2). The signs of the spectral shifts are also consistent with the FWM being shifted to higher energy at positive Δt. However, in Fig. 4 the shifts to higher and lower energies are almost symmetrical, which should have resulted in a comparable shift of the FWM, to lower energy, at negative Δt. This is in contradiction with the spectral assymetry which we observe in the SR-FWM data. Moreover, the stronger shift of the weaker beam should have resulted in a strong asymmetry between the SR-FWM signals in the directions $2k_2-k_1$ and $2k_1-k_2$, in contradiction with the data presented in Fig. 2. We therefore conclude that, while the spectral shifts due to the combined effects of self-steepening and XPM may enhance the nonresonant satellite in the SR-FWM emission, it cannot account for its strong spectral and temporal asymmetries.

The above analysis compels us to reconsider the possibility that optical lattice vibrations contribute to the appearance of the satellite peak in the SR-FWM data. Undeniably, its energy shift is in good agreement with the optical-phonon energies in GaAs and InP ($\approx$36 and $\approx$43 meV, respectively, for the longitudinal branch, at the Brillouin-zone center). However, as the polarization dependence of the FWM signal is inconsistent with a Raman process, an alternative coupling mechanism must be considered. We therefore suggest that the lattice vibrations in question are impulsively excited in a DECP process.[5] Such processes are known to exhibit deviations from the selection rules for Raman scattering.[5] As mentioned earlier, the polarization dependence of the signal indicates that symmetric lattice vibrations are involved. Such vibrations are not expected in GaAs under resonant excitation conditions, where only $q=0$ coherent phonons are excited in DECP, and where symmetry breaking by surface charge effects result in a dominant contribution of LO phonons.[21,22] Yet, symmetric lattice vibrations may be important in FWM processes that involve two-photon transitions, in which localized midgap states (such as the LE2 level in GaAs) may play a crucial role as intermediate states, considerably modifying the selection rules. The phonons observed in the FWM experiment are probably launched by the mutual interaction of the two beams. The absorption of a photon from each of the beams results in a carrier density, and thus in phonon amplitude gratings, with grating constants k_2-k_1 and k_1-k_2. Diffraction from these gratings, that oscillate with the phonon frequency, gives rise to the observed spectral shifts. This would explain why the shifts are observed at slightly positive Δt, since for the signal in the direction $2k_2-k_1(2k_1-k_2)$, the grating $k_2-k_1(k_1-k_2)$ must be formed before $k_2(k_1)$ can diffract. In the process, a local vibration is excited at the midgap state, with the result that part of the photon energy goes to excite the vibration. Emission to $k_1(k_2)$ reabsorbs the vibration energy, resulting in conservation of momentum and energy in the coherent process. The energy of the local vibration, and thus the energy shift of the nondegenerate emission, should be comparable to an optical-phonon energy.

The above interpretation leads us to consider other possible manifestations of coherent phonons in the experiment. Coherent phonons are usually observed as oscillations in PP experiments.[4] The impulsive excitation creates real phonons, that have a relatively long lifetime, and can therefore be observed at time delays that are considerably longer than the pulse duration. However, the situation may be quite different

for two-photon DECP processes, where the photocarrier density is proportional to I_{pump}^2 rather than to I_{pump} (as in a resonant experiment). Thus the effect is expected to be of higher order, and consequently we could not find evidence for it in our PP measurements. Nevertheless, the presence of real carriers in our experiment is confirmed by strong photoluminescence from the band edge, even at room temperature.

In conclusion, our midgap SR-FWM and PP measurements on GaAs and InP show evidence for a strong contribution of coherent optical lattice vibrations to the optical nonlinearity. A clear signature of those is observed in the spectral domain, as well as a delayed response in the time domain. The strong deviation from the known selection rules for Raman scattering in zinc-blende crystals suggests that a displacive excitation mechanism of coherent phonons is involved, and that localized midgap states play a crucial role in the two-photon transition amplitudes. A rigorous theoretical analysis of DECP in two-photon processes is required, that will account for the role of intermediate midgap states.

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