# Picosecond Stimulated Photon Echo Due to Intrinsic Excitations in Semiconductor Mixed Crystals

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Time-resolved demonstration of picosecond photon echoes due to intrinsic optical excitations of a semiconductor is presented. Phase relaxation times up to several hundred picoseconds are found for excitons localized by chemical disorder in $CdS_xSe_{1-x}$ mixed crystals. These long dephasing times are attributed to reduced scattering of the localized excitons as compared to free excitons. Dephasing is identified as due to energy relaxation of the excitons.

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Laser excitation of electronic resonances in condensed media initially creates a coherent macroscopic polarization. The decay of this coherent polarization reflects the very first interaction of an excited state with its environment and thus is considered as one of the most fundamental steps in light-matter interaction.

The detailed characteristics of the decay of the macroscopic polarization, however, are fundamentally different for homogeneously and inhomogeneously broadened optical transitions, respectively. The decay is exponential for homogeneous transitions with the phase relaxation time $T_2$ as the characteristic time constant, describing the rate of decay due to scattering events. In the case of an inhomogeneous transition the macroscopic polarization decays faster due to the interference of the contributions from the different resonance frequencies within the inhomogeneous line (free-induction decay). As a consequence, the dephasing time $T_2$ cannot be measured using a single excitation pulse. However, if a second laser pulse is applied the different oscillators will rephase, generating again a macroscopic polarization at a time which is twice the time delay $t_{21}$ between the two excitation pulses.[1-3] The macroscopic polarization acts as a source of a photon-echo pulse, which can be detected experimentally. As a function of the pulse separation $t_{21}$ the echo amplitude decays according to the dephasing time $T_2$.

The occurrence of photon echoes was first demonstrated for optical excitations involving impurity centers in ruby.[4] In semiconductors photon echoes have been demonstrated for bound-exciton-related transitions.[5] Rather long dephasing times in the nanosecond to microsecond regime have been reported as a direct consequence of the fact that the respective optical transitions involve isolated extrinsic centers.[6] For intrinsic electronic states in semiconductors the dephasing times are expected to be much faster due to the very fast quasiparticle interaction involving the continuum band states. In fact, dephasing times of a few femtoseconds have been reported recently for continuum-state excitation of GaAs.[7] Dephasing times of free excitons are of the order of a few picoseconds as determined experimentally for GaAs bulk material,[8,9] and quantum wells,[10,11] as well as for bulk CdSe.[12] The free-exciton transitions in bulk crystals, however, are predominantly homogeneously broadened[8,9] and a photon echo thus cannot occur. In quantum-well structures these transitions may contain a considerable inhomogeneous broadening due to fluctuations of the layer thickness.[13] However, due to the short times involved a photon echo has not been clearly resolved in time.[10]

In this paper we report the first time-resolved observation of spontaneous and stimulated photon echoes due to intrinsic excitations of a semiconductor. The optical transitions involve excitons localized by disorder-induced fluctuations of the crystal potential in a mixed crystal of $CdS_xSe_{1-x}$. Optical dephasing times of the order of several hundred picoseconds are demonstrated at low crystal temperatures. Our results clearly reveal the important consequences of disorder and Anderson localization on the nonlinear optical response of a solid in accordance with recent theoretical predictions.[6]

The experiments are performed at a temperature of 10 K in the standard four-wave-mixing configuration. The sample is excited by three successive pulses (No. 1 at $t=0$, No. 2 at $t=t_{21}$, and No. 3 at $t=T$) with wave vectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$, respectively. A stimulated photon echo is expected in this configuration to be emitted in the momentum-matching direction corresponding to $\mathbf{k}_3+\mathbf{k}_2-\mathbf{k}_1$ at a time $t=T+t_{21}$ for inhomogeneous broadening of the respective electronic transition. The peak intensity of the emitted photon echo decays as $\exp(-4t_{21}/T_2)$.[2] The more commonly used two-beam configuration (spontaneous-photon-echo configuration) can be considered as a degenerate case with $\mathbf{k}_3=\mathbf{k}_2$ and $t_{21}=T$.

Experiments were performed with a synchronously mode-locked and cavity-dumped dye laser, generating pulses of 7-ps duration at a repetition rate of 500 kHz. The time delays $t_{21}$ and $T$ are obtained by using optical delay lines. A synchroscan streak camera providing time resolution of 20 ps is employed for time-resolved detection of the photon-echo pulse emitted from the sample as

 

well as of the three incoming excitation pulses. The signals from the excitation pulses result from light scattered at the sample surface into the momentum-matching direction. We have studied a high-quality platelet of a mixed $CdS_xSe_{1-x}$ ($x \simeq 0.40$) single crystal with a thickness of about 50 $\mu$m. In this sample the luminescence peak is at 2.054 eV (FWHM 10 meV), which is within the exponential tail of the absorption spectrum thus corresponding to localized exciton transitions.[14]

The results of a time-resolved stimulated-photon-echo experiment are shown in Fig. 1 for resonant excitation of localized excitons (excitation photon energy 2.0505 eV). Original streak-camera traces are depicted for different spacings $t_{21}$ of the excitation pulses 1 and 2 and a fixed delay $T = 400$ ps of pulse 3. The curves from the bottom to the top correspond to increasing time delay $t_{21}$. The plots are normalized to the maximum amplitude in each sequence. These data clearly show the emission of the stimulated-photon-echo pulse at $t = t_{21} + T$ for $t_{21} > 0$. No photon echo is observed in the direction $\mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1$ if pulse 2 precedes pulse 1 ($t_{21} < 0$). To the best of our knowledge, this is the first unambiguous—because time resolved—demonstration of a photon echo from intrinsic excitations of a semiconductor.

A dephasing time of 400 ps, corresponding to a homogeneous width of the exciton transition of 0.02 meV, is obtained from the data in Fig. 1. The dephasing time $T_2$ increases with decreasing excitation photon energy. In Fig. 2 the dephasing time $T_2$ is plotted versus the excitation photon energy $E_{exc}$ for a fixed excitation intensity of 0.1 mW, which corresponds to exciton densities from about $2\times10^{14}$ to about $5\times10^{15}$ cm$^{-3}$ depending on the respective photon energy. The spectral dependence of the stimulated-photon-echo intensity measured at fixed time delays $t_{21} = 100$ ps and $T = 400$ ps and at an excitation intensity of 0.05 mW is also shown for comparison. The spectral characteristic of the photon-echo intensity exhibits a pronounced resonance behavior with its peak corresponding to about the position of the luminescence maximum. The dephasing time varies from 260 ps at the high-energy side of the spectral response curve to 500 ps at the low-energy side.

Two definite and fundamental conclusions can be drawn immediately: (i) The excitonic transitions in this semiconductor mixed crystal are predominantly inhomogeneously broadened, and (ii) the dephasing times of the excitons are longer by at least 1 order of magnitude than in the binary compound semiconductors[8,9,12] where chemical disorder and intrinsic exciton localization are absent. Thus, the long dephasing times are a consequence of the localization of the electronic states. Exciton-exciton and exciton-phonon scattering have to be considerably reduced compared to the binary compounds without disorder. In particular, the contribution of exciton-exciton scattering to the dephasing is negligible as the dephasing times do not depend on the excitation density in the density regime investigated here.[15] Consequently, the increase of the dephasing times with

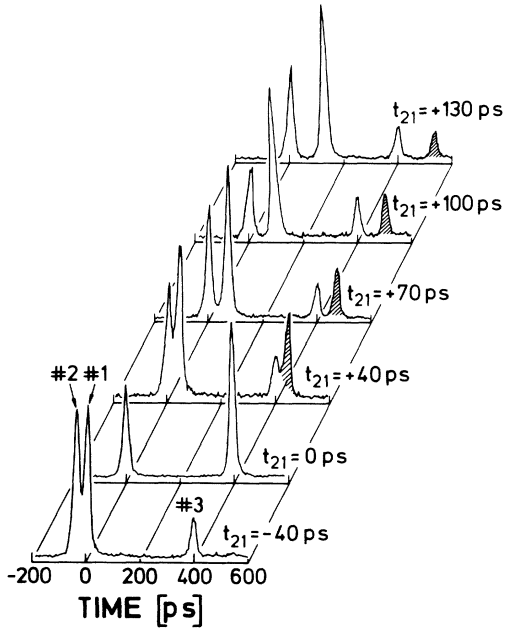


FIG. 1. Time-resolved streak-camera traces of the stimulated photon echo from a $CdS_xSe_{1-x}$ mixed crystal (temperature 10 K) for resonant excitation of localized excitons ($E_{exc} = 2.0505$ eV). The time separation $t_{21}$ between pulse 1 and pulse 2 increases from the bottom to the top. In all traces pulse 3 is delayed by $T = 400$ ps. Each plot is normalized to the highest amplitude in the sequence. The echo pulses are shaded.

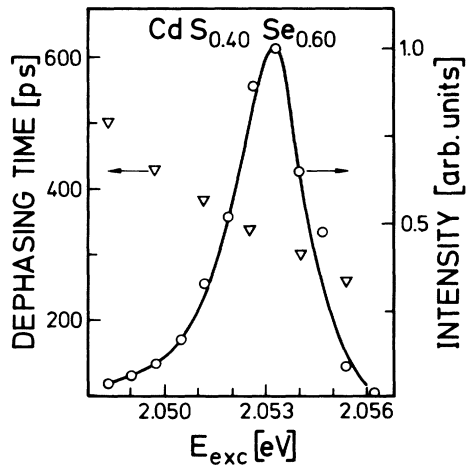


FIG. 2. Dephasing times $T_2$ of localized excitons vs excitation photon energy $E_{exc}$ (triangles, left scale) for an excitation intensity of 0.1 mW corresponding to exciton densities from about $2\times10^{14}$ to $5\times10^{15}$ cm$^{-3}$. The dependence of the stimulated-photon-echo intensity on excitation energy for fixed time delays $t_{21} = 100$ ps and $T = 400$ ps and a constant excitation intensity of 0.05 mW is also shown (circles, right scale). The solid line is a guide to the eye. All data are obtained at 10 K.

decreasing excitation energy is due to the stronger localization at lower photon energies.

Saturation of the photon-echo intensity is observed at relatively low excitation intensities (typically of the order of 0.1 mW).[16] The saturation is most pronounced at the low-energy side of the spectral response curve, where the saturation intensity is lowest ($<0.05$ mW). As an example of the saturation behavior we have plotted the photon-echo intensity versus the excitation intensity $I_{exc}$ in Fig. 3 (circles). The results are taken in the spontaneous-echo configuration for a fixed delay $t_{21}$ $=100$ ps at a photon energy of 2.0526 eV. The respective curve for the stimulated photon echo shows the same feature. The echo intensity depends much more weakly on excitation intensity than the expected third-order power law and clearly saturates at higher excitation intensities. The transmitted intensity of the excitation pulse 2 (Fig. 3, triangles) increases about linearly with excitation intensity at low excitation but increases superlinearly at higher excitation intensities, where the echo signal saturates. This superlinear increase is a clear indication of absorption bleaching.

This pronounced absorption bleaching as well as the saturation of the echo signal are a direct consequence of the long dephasing times. Actually, the experimentally determined dephasing times also set a lower limit for the intraband-energy-relaxation time constant $T_{rel}$ ($T_{rel} \geq T_2/2$), which characterizes the inelastic scattering to sites at lower energies, i.e., hopping within the distribution of the localized excitons. From our results we obtain this lower limit for $T_{rel}$ to be in the range of 130 to 250 ps, increasing with decreasing energy of the exciton within the localized-exciton distribution. These values are in good agreement with the energy relaxation time constants determined independently by means of time-resolved luminescence.[17] Nonequilibrium state filling of the optically coupled states is easily accomplished due to this slow inelastic scattering of the localized excitons resulting in the efficient bleaching of the second excitation beam and the saturation of the echo signal. Thus, we finally conclude that the phase relaxation of the localized excitons in the semiconductor mixed crystal $CdS_xSe_{1-x}$ is determined by inelastic scattering due to hopping of the excitons to different sites at lower energies.

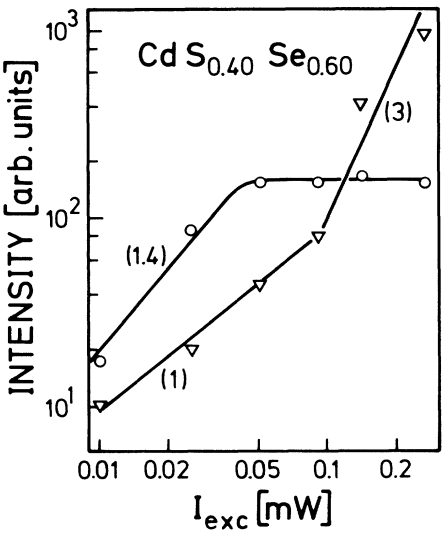


FIG. 3. Double-logarithmic plot of the spontaneous-photon-echo intensity (circles) and the transmitted intensity of pulse 2 (triangles) vs the input excitation intensity $I_{exc}$ for a photon energy of 2.0526 eV and a fixed time delay $t_{21}=100$ ps (temperature 10 K). The appropriate values of the slopes are indicated in brackets.

In conclusion, we have demonstrated in real time the delayed emission of a coherent photon-echo pulse due to intrinsic continuum excitations of a semiconductor involving excitons localized by disorder. The phase relaxation times of the excitons are of the order of several hundred picoseconds, which is longer by orders of magnitude as compared to excitons in binary semiconductors, where localization effects are absent. The long phase relaxation times are explained by reduced quasiparticle scattering of localized excitons, which demonstrates the fundamental effect of localization on dynamical and nonlinear optical properties of semiconductors. Since localization of electronic states is a quite general phenomenon in solid-state physics our findings are of significance not only for semiconductor mixed crystals but many other systems and structures with localization, including in particular low-dimensional semiconductor heterostructures and superlattices.

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[16]The characteristic time constants for dephasing, intraband energy relaxation, recombination, and diffusion, which determined the absolute amplitude of the echo signal, do not depend on excitation intensity for the intensity range under consideration and the large grating constant used [see Ref. 15, S. Shevel, R. Fischer, E. O. Göbel, G. Noll, P. Thomas, and C. Klingshirn, J. Lumin. **37**, 45 (1987), and G. Noll, Ph.D. thesis, Philipps-Universität, Marburg (unpublished)]. Thus, saturation of the photon-echo intensity due to changes of these time constants can be excluded.

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