# Non-Markovian Dynamics of Spectral Narrowing for Excitons in the Layered Semiconductor GaSe Observed Using Optical Four-Wave Mixing Spectroscopy

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We have investigated non-Markovian dephasing by using time-resolved and spectrally resolved four-wave mixing measurements in a layered semiconductor GaSe. When the time interval between the first and second excitation pulses is increased, photon echo spectra exhibit narrowing only in a regime of a few picoseconds. In the initial dephasing of these signals, fast damping is observed. The narrowing of the spectrally resolved signal is consistent with the Fourier transformation of the time-resolved signals. Spectral narrowing is crucial evidence of the transition from non-Markovian to Markovian dynamics. By comparing experimental data with calculation results based on the non-Markovian theory, we have found that the correlation time of the exciton-phonon interaction is 1.1 ps.

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A coherent light pulse induces polarization in a medium through light-matter interaction. Since the coherence of polarization is lost by electron-electron and electron-phonon interactions, the investigation of the decoherence process is important for achieving a fundamental understanding of these interactions. Dephasing is introduced phenomenologically by the exponential decay term in the optical Bloch equations [1]. This treatment is valid only in the Markovian regime, where the time scale of observation is longer than the correlation time of the system-reservoir interaction. Within the correlation time, the frequency fluctuations due to the interaction exhibit complicated dynamics, which is referred to as non-Markovian dynamics [2,3]. Because a large number of environmental modes, e.g., acoustic phonons, are involved in the reservoir, the dephasing is discussed in terms of the correlations with all coupled modes. This approach is different from that used for a system with a few discrete levels, e.g., excitons coupled to optical phonons [1,4–6]. The non-Markovian process is directly characterized by the correlation function of the system describing frequency fluctuations; therefore the analysis of non-Markovian dynamics is necessary to understand the microscopic behavior of electrons. Recently, correlation functions for non-Markovian dynamics have been investigated by using four-wave mixing (FWM) measurements in an atomic vapor, liquid water, and some semiconductors [7–11]. The correlation of system-reservoir interaction, i.e., the reservoir memory effect, is the problem to be solved for quantum dynamical systems. In addition, the understanding of the decoherence mechanism is important for quantum information applications. The suppression of decoherence has been investigated theoretically [12,13]. It has also been studied experimentally for some materials [14–16].

In this Letter, we report the observation of non-Markovian dephasing by using time-resolved (TR) and spectrally resolved (SR) FWM measurements in a layered semiconductor GaSe. Spectral narrowing was observed in the transition from non-Markovian to Markovian dynamics. We find that this spectral narrowing means the memory loss of the reservoir due to frequency fluctuation of the exciton-phonon interaction.

The investigated sample was a layered semiconductor GaSe, and it was set at 3.4 K in a closed-cycle refrigerator. The excitons in GaSe are confined to about 10 layers due to a stacking disorder [17,18]. Further, because of this anisotropic crystal structure, the exciton-phonon interaction along the $c$-axis direction is stronger than that in the perpendicular plane [19]. Optical pulses were generated by a frequency-doubled optical parametric oscillator pumped by a mode-locked Ti:sapphire laser tuned to the exciton resonant energy of 2.109 eV. The pulse duration and repetition rate were 200 fs and 76 MHz, respectively. The first and second excitation pulses were sent into the sample with wave vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$, respectively. The diffracted signal in the direction of $2\boldsymbol{k}_2 - \boldsymbol{k}_1$ was measured at various delay times $\tau$, which are the time intervals between the first and second excitation pulses. In order to exclude the biexciton contribution, the polarizations of the two excitation pulses were adjusted such that they became cocircular. For the TR-FWM measurements, the FWM signals were detected by employing the heterodyne technique. In this technique, acousto-optic modulators were used to shift the frequency of the reference pulse and that of the second excitation pulse by $\nu_1$ and $\nu_2$, respectively. Then, interference of the reference pulse and the FWM signals whose frequencies were shifted by $2\nu_2$ in the direction of $2\boldsymbol{k}_2 - \boldsymbol{k}_1$ was carried out. This interference was detected by a photodetector to which a spectrum analyzer was connected. The FWM signals were detected by tuning the spectrum analyzer to frequencies of $2\nu_2 - \nu_1$. The TR-FWM signals were measured by changing the delay time of the reference pulse relative to the FWM signal. For the SR-FWM measurements, the FWM signals

 

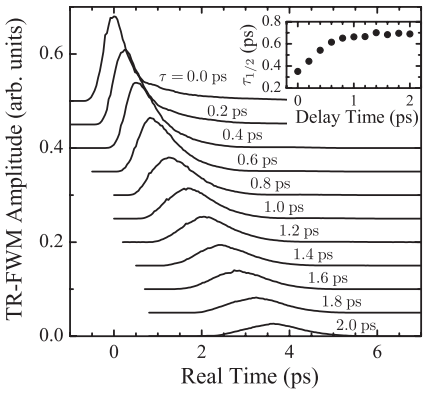


FIG. 1. Time-resolved four-wave mixing amplitude as a function of the real time for various delay times $\tau$. The delay time varies from 0.0 to 2.0 ps in 0.2 ps steps, as indicated. The origin of the real time axis is equal to the arrival time of the first excitation pulse. The inset shows the half-decay time $\tau_{1/2}$ as a function of the delay time.

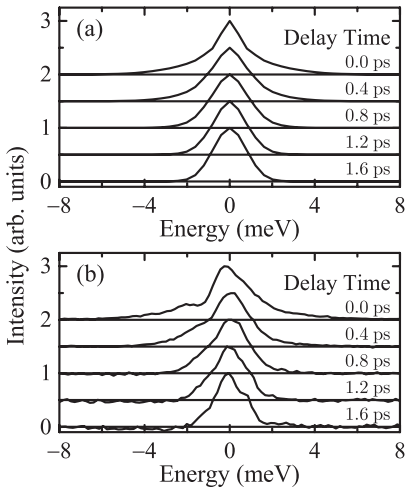


FIG. 2. (a) Power spectrum for the indicated delay times. The power spectrum is obtained from the Fourier transformation of the time-resolved four-wave mixing signal. (b) Spectrally resolved four-wave mixing intensities for the indicated delay times. The centers of the peaks are at an energy of 0 meV.

in the direction of $2\boldsymbol{k}_2 - \boldsymbol{k}_1$ were spectrally resolved by a monochromator and detected by a photomultiplier tube.

The measured TR-FWM amplitudes are shown in Fig. 1. Fast damping is observed only in the initial dephasing at delay times of 0.0, 0.2, and 0.4 ps. After the delay time of 0.4 ps, fast damping gradually disappears and then only the Gaussian signal is observed. The half-decay times $\tau_{1/2}$, which are determined on the basis of the corresponding signal peak, are plotted in the inset of Fig. 1. Initially, as the delay times increased, the half-decay time also increased (half-decay times are 0.35, 0.44, and 0.54 ps for delay times of 0.0, 0.2, and 0.4 ps, respectively). Subsequently, for longer delay times ($\tau > 0.8$ ps), the half-decay times remained almost independent of the delay time at a constant value $\tau_{1/2} = 0.68$ ps. In the optical Bloch equations theory, the TR-FWM signals for any delay times have a Gaussian shape with a constant linewidth, which is defined by a distribution of the resonant energies, i.e., the so-called inhomogeneous broadening [20]. The increase in the half-decay time with an increase in the delay time cannot be explained by the phenomenological introduction of the inhomogeneous broadening.

In order to clarify the development of the damping shape with increasing delay time, the Fourier transformation of the TR-FWM signal is performed for each delay time, as shown in Fig. 2(a). For the delay time of 0.0 ps, a broadband that extends up to 5 meV is observed in the spectrum. However, for a longer delay time of more than 1.6 ps, the broadband extends only up to 2 meV. This shows that the FWM spectra become narrower with increasing delay time and that the spectral narrowing in the initial dephasing is caused by the non-Markovian effect. Spectral narrowing is observed not only in the Fourier transformation of the TR-FWM signals but also in the SR-FWM measurements, as shown in Fig. 2(b). The power spectra of the TR-FWM signals do not exactly correspond to the SR-FWM signals, because the time evolution of the phase factor cannot be determined from the TR-FWM measurements. Both spectra, however, are adequately consistent with each other in terms of the spectral narrowing. In a layered semiconductor GaSe, the exciton-phonon interaction along the $c$-axis direction is particularly important in the dephasing process because of the acoustic deformation potential coupling. This interaction has been investigated by studying the wave-packet motion, which causes the FWM spectrum to be asymmetric, as reported in our previous study [21]. However, this asymmetry is not critical for the spectral narrowing of the symmetric tails.

The spectral narrowing can be explained by the non-Markovian dynamics caused by the exciton-phonon interaction. In order to understand theoretically the initial dephasing, the theory of non-Markovian dephasing is employed: the dephasing process is not introduced phenomenologically but is treated microscopically in terms of frequency fluctuation related to the phonon dynamics [2]. The total Hamiltonian of the electron-phonon system, $H_0$, is expressed as

$$H_0 = H_{gg}|g\rangle\langle g| + H_{ee}|e\rangle\langle e| \tag{1}$$

with

$$H_{gg} = \sum_k \hbar\omega_k \left( b_k^\dagger b_k + \frac{1}{2} \right), \tag{2}$$

$$H_{ee} = \hbar\omega_{eg} + H_{gg} - V, \tag{3}$$

$$V = \sum_k g_k (b_k + b_k^\dagger), \tag{4}$$

where $|g\rangle$ ($|e\rangle$) is the eigenstate of ground (exciton) state, whose Hermitian conjugate is represented as $\langle g|$ ($\langle e|$), and

$H_{gg}$ ($H_{ee}$) is the eigenvalue of the ground (exciton) state. These eigenvalues are operators for the reservoir variables of the phonon system, and they can be expressed by Eqs. (2) and (3), where $\hbar = h/2\pi$ and $h$ is the Planck constant, $\omega_k$ is the frequency of the phonon mode for a wave number $k$, and $\omega_{eg}$ is the exciton resonance frequency. The annihilation and creation operators of the phonon mode for the wave number $k$ are denoted by $b_k$ and $b_k^\dagger$, respectively. The Hamiltonian $V$ of the exciton-phonon interaction is expressed as in Eq. (4), where $g_k$ is the coupling constant corresponding to the wave number $k$.

The equation of motion for the density matrix $\rho(t)$ is as follows:

$$\frac{d}{dt}\rho(t) = -\frac{i}{\hbar}[H_0 + H_1, \rho(t)]. \tag{5}$$

Before the excitation of the first pulse ($t < 0$), the initial density matrix is assumed to be $\rho(t) = \rho_R|g\rangle\langle g|$ with $\rho_R = \exp(-\beta H_{gg})/\mathrm{Tr}_R[\exp(-\beta H_{gg})]$. Here $\beta = 1/k_B T$ at the temperature $T$, $k_B$ is the Boltzmann constant, and $\mathrm{Tr}_R[A]$ is the trace of all phonon modes for the arbitrary element $A$. Within the electric dipole approximation, the Hamiltonian of the radiation-matter interaction, $H_1$, is expressed as follows: $H_1 = -\mu_{eg}E(\boldsymbol{r}, t)|e\rangle\langle g| - \mu_{ge}E^*(\boldsymbol{r}, t)|g\rangle\langle e|$, where $\mu_{eg}$ is the electric dipole moment and the second term is the Hermitian conjugate of the first term. For simplicity, we assume that $\mu_{eg}$ is independent of the operators in the reservoir variables and that $\mu_{eg}$ is a real number, i.e., $\mu_{eg} = \mu_{ge}$. Here, $E(\boldsymbol{r}, t)$ is the electric field with the frequency $\omega$. In the two-pulse electric field $E(\boldsymbol{r}, t)$, the first (second) excitation pulse is assumed to be the delta function pulse whose arrival time is $t = 0$ ($t = \tau$) with the wave vector $\boldsymbol{k}_1$ ($\boldsymbol{k}_2$) and the pulse area $\theta_1$ ($\theta_2$).

The FWM signal in the direction of $2\boldsymbol{k}_2 - \boldsymbol{k}_1$ is expressed as $P^{(2\boldsymbol{k}_2-\boldsymbol{k}_1)}(\boldsymbol{r}, t) = \mu_{ge}\mathrm{Tr}_R[\rho_{eg}^{(3)}]$, where the third-order off-diagonal density matrix element $\rho_{eg}^{(3)}$ is proportional to the third power of the electric field. The trace of all phonon modes is calculated into the simple representation by using the cumulant expansion method up to the second order of $V$ [2,3]. As a result of the cumulant expansion, the FWM signal after the two-pulse excitation ($t > \tau$) can be expressed as follows:

$$\begin{aligned} P^{(2\boldsymbol{k}_2-\boldsymbol{k}_1)}(\boldsymbol{r}, t) = & -i\mu_{ge}\theta_2^2\theta_1 \exp[i(2\boldsymbol{k}_2 - \boldsymbol{k}_1)\cdot\boldsymbol{r}] \\ & \times \exp[-i\omega t]\exp[i(\omega - \omega_{eg})(t - 2\tau)] \\ & \times \exp\{-[2S(t-\tau) + 2S(\tau) - S(t)]\} \\ & \times \exp\{i[S'(t-\tau) + S'(\tau) - S'(t)]\}, \end{aligned} \tag{6}$$

where $S(t)$ and $S'(t)$ are defined as

$$S(t) = \frac{1}{\hbar^2}\int_0^t ds(t-s)\mathrm{Re}[\langle V(s)V(0)\rangle], \tag{7}$$

$$S'(t) = \frac{1}{\hbar^2}\int_0^t ds(t-s)\mathrm{Im}[\langle V(s)V(0)\rangle] \tag{8}$$

with $V(t) = \exp[iH_{gg}t/\hbar]V\exp[-iH_{gg}t/\hbar]$. For the arbitrary element $A$, the thermal expectation value $\langle A\rangle$ is defined as $\langle A\rangle = \mathrm{Tr}_R[A\rho_R]$, and the real (imaginary) part is expressed as $\mathrm{Re}[A]$ ($\mathrm{Im}[A]$). The actual exciton system has the inhomogeneous broadening of the exciton resonances. We assume that the inhomogeneous broadening can be expressed by the Gaussian distribution function as follows: $g_{\mathrm{eg}}(\omega) = \exp[-(\omega - \omega_0)^2/\sigma_i^2]/\sqrt{\pi}\sigma_i$, where $\omega_0$ and $\sigma_i$ are the center frequency and the width of the distribution, respectively. The macroscopic polarization with the inhomogeneous broadening, $P_i^{(2\boldsymbol{k}_2-\boldsymbol{k}_1)}(\boldsymbol{r}, t)$, is determined by using the following equation: $P_i^{(2\boldsymbol{k}_2-\boldsymbol{k}_1)}(\boldsymbol{r}, t) = \int_{-\infty}^{\infty} d\omega_{eg} g_{\mathrm{eg}}(\omega_{eg})P^{(2\boldsymbol{k}_2-\boldsymbol{k}_1)}(\boldsymbol{r}, t)$, where $P^{(2\boldsymbol{k}_2-\boldsymbol{k}_1)}(\boldsymbol{r}, t)$ is a function of $\omega_{eg}$, as expressed by Eq. (6).

The FWM signal shows different behavior between before and after the correlation time $\tau_c$, which is defined as the damping constant of the correlation function $\langle V(t)V(0)\rangle$. The dephasing behavior is approximately expressed by using the Taylor expansion. For the non-Markovian dynamics ($t \ll \tau_c$), the dephasing is approximately expressed as follows:

$$|P_i^{(2\boldsymbol{k}_2-\boldsymbol{k}_1)}(\boldsymbol{r}, t)| = \mu_{ge}\theta_2^2\theta_1 \exp[-\tfrac{1}{4}(\sigma_i^2 + D^2)(t - 2\tau)^2], \tag{9}$$

where $D^2 = 2\mathrm{Re}[\langle V(0)V(0)\rangle]/\hbar^2$. The interaction $V$ can be treated as the inhomogeneous broadening characterized by $D$. Irrespective of whether or not an exciton system has inhomogeneous broadening, the correlation function indicates the generation of a photon echo at twice the delay time $2\tau$. The Markovian dynamics ($\tau_c \ll t$) can be approximately expressed as follows:

$$\begin{aligned} |P_i^{(2\boldsymbol{k}_2-\boldsymbol{k}_1)}(\boldsymbol{r}, t)| = & \mu_{ge}\theta_2^2\theta_1 \exp\left[-\frac{1}{4}\sigma_i^2(t - 2\tau)^2\right] \\ & \times \exp\left[-\frac{1}{T_2}t\right], \end{aligned} \tag{10}$$

where $1/T_2 = \int_0^\infty ds\mathrm{Re}[\langle V(s)V(0)\rangle]/\hbar^2$. The correlation function indicates the exponential decay, which is expressed as a function of the dephasing time $T_2$. The decay shape corresponds to the phenomenological introduction of the dephasing term: $\exp[-t/T_2]$. Using Eqs. (9) and (10), spectral narrowing can be explained on the basis of the narrowing of the inhomogeneous broadening from $\sqrt{\sigma_i^2 + D^2}$ to $\sigma_i$ with increasing delay time. The exciton-phonon interaction behaves as inhomogeneous broadening only for non-Markovian dynamics.

This non-Markovian feature can be explained qualitatively by assuming a phenomenological stochastic correlation function [7,8]. However, in order to analyze quantitatively the spectral narrowing, the microscopic

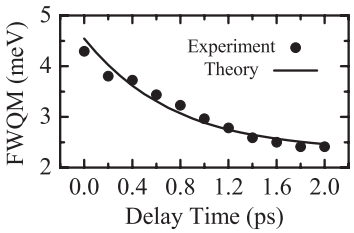


FIG. 3. Full width at quarter maximum of the four-wave mixing spectrum as a function of the delay time. The solid line represents the calculation results based on the non-Markovian theory.

treatment of the correlation function is necessary, just like the case of the wave-packet motion [21]. The correlation function $\langle V(t)V(0)\rangle$ is expressed as

$$\langle V(t)V(0)\rangle = \int_0^\infty d\omega I_{\text{ex-ph}}(\omega)\{[n(\omega)+1]e^{-i\omega t} + n(\omega)e^{i\omega t}\}, \quad (11)$$

where $n(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ is the Bose-Einstein distribution function of the phonon mode with the frequency $\omega$ at the temperature $T$. The spectral density of the exciton-phonon interaction $I_{\text{ex-ph}}(\omega)$ is defined as $\sum_k g_k^2 \delta(\omega - \omega_k)$. By taking into account the acoustic deformation potential coupling with longitudinal acoustic phonons, the spectral density can be expressed as $I_{\text{ex-ph}}(\omega) = \alpha^2\hbar^2\omega \exp[-l^2\omega^2/2u_s^2]$, according to the analysis results for a layered semiconductor GaSe [21]. Here $\alpha$ is the dimensionless coupling constant, $l$ is the confinement length of excitons in the $c$-axis direction, and $u_s$ is the sound velocity of the longitudinal acoustic phonons which is reported as $u_s = 2.482 \times 10^5$ cm/s [22].

In order to fit the calculation to the narrowing of the FWM spectrum, the full width at quarter maximum (FWQM) of the FWM spectrum is measured, as shown in Fig. 3. The experimental data, which are obtained from the FWM spectra, are consistent with the calculation results based on the non-Markovian theory. The restriction on the fitting parameters is given by the dephasing time $T_2 = 1.7$ ps, which is obtained from the TR-FWM signals for the Markovian dynamics. The inhomogeneous broadening of the excitons $\sigma_i$ is measured to be 1.4 meV. The parameters are determined to be $l = 2.8$ nm and $\alpha = 0.7$ after fitting. These values indicate that the excitons are localized in 7 layers and that the coupling constant is approximately 1. These results are consistent with the results of previous investigations [17,18,21].

The correlation time $\tau_c$ can be estimated from the spectral density $I_{\text{ex-ph}}(\omega)$. More specifically, the relationship between narrow (broad) linewidth corresponding to $I_{\text{ex-ph}}(\omega)$ and the long (short) correlation time is expressed as follows: $\tau_c = l/u_s$.

The correlation time $\tau_c$ is calculated to be 1.1 ps by substituting the parameters. This result indicates that the time evolution of the correlation function can be reversed if the second excitation pulse arrives within a few picoseconds, as shown in Eq. (9). In fact, the decoherence suppression of the excitons in GaSe has been reported within the non-Markovian regime ($t \ll \tau_c$) [16].

In summary, we have observed the spectral narrowing in the non-Markovian regime by using time-resolved and spectrally resolved four-wave mixing measurements on a layered semiconductor GaSe. This narrowing is conclusive evidence of the transition from non-Markovian to Markovian dynamics. We have demonstrated that the correlation time, which defines the non-Markovian regime, can be determined from the spectral narrowing by using the theory of non-Markovian dephasing. The calculation based on the non-Markovian theory reveals that the correlation time of the exciton-phonon interaction is 1.1 ps in GaSe.

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[1] H. Haug and S. W. Koch, *Quantum Theory of the Optical and Electronic Properties of Semiconductors* (World Scientific, Singapore, 2009), 5th ed.
[2] M. Aihara, Phys. Rev. B**25**, 53 (1982).
[3] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).
[4] L. Bányai *et al.*, Phys. Rev. Lett. **75**, 2188 (1995).
[5] D. Steinbach *et al.*, Phys. Rev. B **60**, 12079 (1999).
[6] S. Cronenberger *et al.*, Phys. Rev. B **77**, 195311 (2008).
[7] V. O. Lorenz and S. T. Cundiff, Phys. Rev. Lett. **95**, 163601 (2005).
[8] V. O. Lorenz *et al.*, Phys. Rev. Lett. **100**, 013603 (2008).
[9] M. L. Cowan *et al.*, Nature (London) **434**, 199 (2005).
[10] V. M. Axt *et al.*, Phys. Rev. Lett. **93**, 127402 (2004).
[11] S. G. Carter, Z. Chen, and S. T. Cundiff, Phys. Rev. B **76**, 121303(R) (2007).
[12] L. Viola and S. Lloyd, Phys. Rev. A **58**, 2733 (1998).
[13] C. Uchiyama and M. Aihara, Phys. Rev. A **66**, 032313 (2002).
[14] M. F. Andersen *et al.*, Phys. Rev. A **70**, 013405 (2004).
[15] T. D. Ladd *et al.*, Phys. Rev. B **71**, 014401 (2005).
[16] T. Kishimoto *et al.*, Phys. Rev. B **74**, 073202 (2006).
[17] J. J. Forney *et al.*, J. Phys. C **10**, 1887 (1977).
[18] V. Capozzi and K. Maschke, Phys. Rev. B **34**, 3924 (1986).
[19] M. Schlüter, Nuovo Cimento B **13**, 313 (1973).
[20] T. Yajima and Y. Taira, J. Phys. Soc. Jpn. **47**, 1620 (1979).
[21] H. Tahara, Y. Ogawa, and F. Minami, Phys. Rev. B **82**, 113201 (2010).
[22] Kh. M. Khalilov and K. I. Rzaev, Kristallografiya **11**, 929 (1966).[Sov. Phys. Crystallogr. **11**, 786 (1967)].