Optical Dephasing of Excitonic Polaritons in CuCl Studied by Time-Resolved, Nondegenerate Four-Wave Mixing

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Optical dephasing of excitonic polaritons in CuCl is directly measured for the first time in the picosecond time domain by means of time-resolved, nondegenerate four-wave mixing. Dephasing of the ω_1 polariton pulse is probed by an interrogation ω_2 polariton pulse whose group velocity is faster than that of the ω_1 polariton pulse. It is found that the dephasing damping constant $\Gamma/2$ of excitonic polaritons is of order of 0.01 meV and increases as $\hbar\omega_1$ approaches the exciton resonance energy from below.

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Recent studies in the picosecond time domain have revealed dynamical aspects of excitonic polaritons. By studying the transient induced absorption from the excitonic polariton state to the excitonic molecule state, energy relaxation processes of excitonic polaritons have been clarified.[1] In solids, it is considered that the phase relaxation is generally much faster than the energy relaxation. However, there has been no direct experimental information in the time domain about the phase relaxation of excitonic polaritons. In addition, the concept of the optical dephasing of excitonic polaritons has not been made clear yet.

Dephasing of localized excitation can be directly measured in the ultrashort time domain by means of time-resolved, degenerate four-wave mixing which is a generalized modification of the photon echo.[2] Under irradiation by two light pulses, $(\vec{k}_1,\omega_1)$ and $(\vec{k}_2,\omega_1)$, which are resonant with some material excitation, the output of the $(2\vec{k}_2-\vec{k}_1,\omega_1)$ pulse is measured as a function of the time separation between the two pulses. This measurement is based on the principle that the third-order nonlinear polarization which generates the $(2\vec{k}_2-\vec{k}_1,\omega_1)$ pulse depends on the nondephased part of excitation generated by the first $(\vec{k}_1,\omega_1)$ pulse at the time when the second, delayed $(\vec{k}_2,\omega_1)$ pulse reaches the excitation. In the study of the phase relaxation of excitonic polaritons, on the other hand, it is important to note that excitonic polaritons are composite particles of excitons and photons. Incident photons $(\vec{k}_1,\omega_1)$ and $(\vec{k}_2,\omega_1)$ are converted to polaritons (k_1,ω_1) and (k_2,ω_1) inside the crystal. As they propagate at the same group velocity $v_g(\omega_1)$, the excitonic polariton pulse (k_1,ω_1) cannot be caught up with by the second, delayed pulse (k_2,ω_1). Therefore, it is necessary to modify this technique. If the delayed interrogation pulse (k_2,ω_2) is suitably chosen so that its group velocity is faster than that of the first pulse (k_1,ω_1), this (k_2,ω_2) pulse catches up with the (k_1,ω_1) pulse, and the third-order nonlinear polarization which now emits a $(2k_2-k_1,\ 2\omega_2-\omega_1)$ pulse is generated in proportion to the nondephased part of the (k_1,ω_1) pulse. Therefore, we can obtain information about the optical dephasing of the (k_1,ω_1) polariton pulse by measuring the $2\omega_2-\omega_1$ output as a function of the relative time delay between the two pulses. To confirm the above mentioned ideas, we have tried an experiment for excitonic polaritons in CuCl. As mentioned below, it is demonstrated for the first time that the optical dephasing of excitonic polaritons can be directly measured in the picosecond time domain by use of this time-resolved, nondegenerate four-wave mixing.

Tunable picosecond light pulses ω_1 and ω_2 were generated in the following way. Two temperature-controlled $LiNbO_3$ parametric oscillators were pumped by the second-harmonic radiation of a repetitively mode-locked Nd^{+3}-doped yttrium aluminum garnet laser,[3] and ω_1 and ω_2 pulses were obtained by taking the second harmonics of parametric signals. The temporal widths of the ω_1 and ω_2 pulses were about 20 ps. The peak powers of the ω_1 and ω_2 pulses were kept at 130 kW and 85 kW, respectively. Flakes of CuCl single crystals having {111} faces were grown from the vapor phase. They were directly immersed in superfluid helium. Two beams, $(\vec{k}_1,\omega_1)$ and $(\vec{k}_2,\omega_2)$,

were focused on a CuCl crystal with a spot size of 140 μm in diameter. One of them, the ω_1 beam, was variably delayed by use of an optical delay. When the temporal coincidence as well as the spatial overlap were optimum, a signal of $2\omega_2-\omega_1$ was clearly observed in the direction of $2\tilde{k}_2-\tilde{k}_1$. The $2\omega_2-\omega_1$ signal can always be kept in the transparent region of the crystal, in contrast to the $2\omega_1-\omega_2$ signal, since $2\omega_2-\omega_1=\omega_2-(\omega_1-\omega_2)<\omega_2$. Thus the measurement of the $2\omega_2-\omega_1$ signal is quite feasible. The angle between the ω_1 and ω_2 beams was 15°. The $2\omega_2-\omega_1$ signal was highly directional (solid angle $\simeq 1.1\times 10^{-4}$ sr), so that it was spatially separated from the background scattering by use of a diaphragm. It was detected by a photomultiplier and a boxcar integrator through a monochromator. The spectral width [full width at half maximum (FWHM)] of ω_1 and ω_2 was 1.8 meV while that of $2\omega_2-\omega_1$ was about 4.6 meV. The central spectral part of the $2\omega_2-\omega_1$ signal with a spectral width (FWHM) of 0.5 meV was selected.

In Fig. 1, the output intensity of $2\omega_2-\omega_1$ pulses is shown as a function of the relative time delay t_2-t_1. The positive direction of t_2-t_1 means that the slower ω_1 pulse is ahead of the faster ω_2 pulse. Here ω_2 was kept almost constant at ~3.178 eV. It is very helpful to note the group velocity and the transit time of the excitonic polaritons ω_1 and ω_2 in order to interpret the results of Fig. 1. In Fig. 2, the experimentally confirmed dispersion relation and the group velocity of excitonic polaritons in CuCl are illustrated together with the calculated transit time of the excitonic polariton pulse through the sample of 14.15 μm thickness.[4] The transit time of the ω_2 pulse through the sample is 1.4–1.5 ps, while that of the ω_1 pulse varies from 3.88 ps to several hundred picoseconds. The correlation traces 1 to 6 show asymmetry tailed toward $t_2-t_1>0$. This asymmetry grows as we go from 1 to 3, and then decreases from 3 to 8. Then, the correlation traces 8 to 10 are sharp and almost symmetric. The asymmetric tail toward $t_2-t_1>0$ suggests that the phase of the ω_1 polariton pulse survives for a while and then it is probed by the ω_2 polariton pulse when the latter catches up with the ω_1 polariton pulse. The reason why the asymmetry grows in going from 1 to 3 is that the transit time of the ω_1 polariton pulse increases. Because the dephasing damping of the ω_1 polariton pulse increases, the asymmetry decreases in going from 3 to 8.

Dispersion of excitonic polaritons including the damping term Γ is written as[5]

$$\left(\frac{ck}{\omega}\right)^2=\epsilon(k,\omega)=\epsilon_\infty\left(1+\frac{\omega_l^{\,2}-\omega_t^{\,2}}{\omega_t^{\,2}+(\hbar\omega_t/M)k^2-\omega^2+i\omega\Gamma}\right). \quad (1)$$

This damping term Γ has always been introduced phenomenologically. However, we can give a physical meaning to Γ. Equation (1) is derived from the coupled equations described below:

$$\begin{aligned} &P+\Gamma\dot{P}+[\omega_t-(\hbar/2M)\nabla^2]^2P=\beta\omega_t^{\,2}E,\\ &\epsilon_\infty\ddot{E}-c^2\nabla^2E=-4\pi\ddot{P},\\ &\epsilon(k,\omega)E=\epsilon_\infty E+4\pi P, \end{aligned} \quad (2)$$

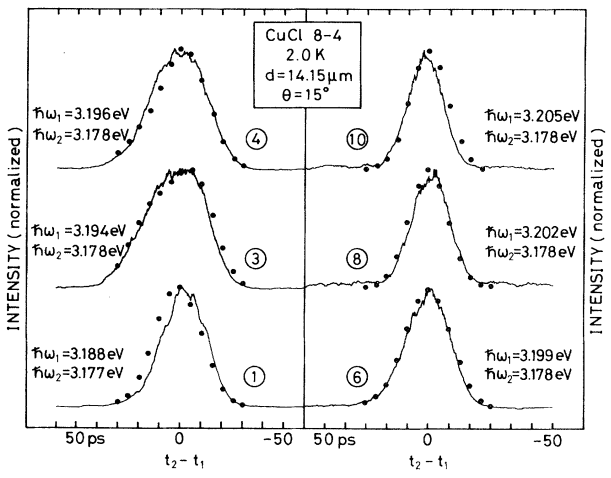

FIG. 1. Intensity of the $2\omega_2-\omega_1$ beam emitted from a CuCl crystal as a function of the relative time delay between the ω_2 and ω_1 pulses, t_2-t_1.

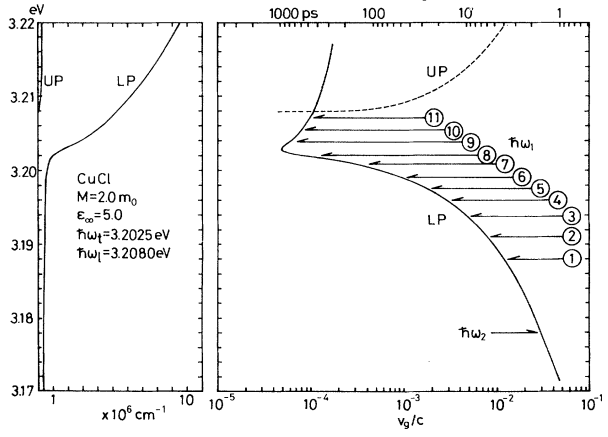

FIG. 2. Left: Dispersion relation of excitonic polaritons in CuCl. Right: Corresponding group velocity of excitonic polariton pulses normalized by c (light velocity in vacuum) and the calculated transit time of the pulses through a CuCl crystal of 14.15 μm thickness.

where β is defined by $4\pi\beta\omega_t^2/\epsilon_\infty=\omega_l^2-\omega_t^2$. The first equation, that is, the equation of motion of macroscopic polarization P due to excitonic polaritons, is the same as a familiar equation of polarization in a semiclassical laser theory[6] except for the spatially dispersive term. In the laser theory the equation of motion of macroscopic polarization is derived from the density matrix formalism for the two-level system. In the density matrix formalism, $\Gamma/2$ is defined as the dephasing damping (transverse relaxation) constant.[7] Therefore, it is reasonable to identify $\Gamma/2$ as the dephasing damping constant of excitonic polaritons.

In CuCl the third-order nonlinear polarization $P_{NL}^{(3)}$ is generated through a four-polariton parametric process around the exciton resonance or a two-photon resonance of excitonic molecules.[8] As a result, $P_{NL}^{(3)}(2\omega_2-\omega_1)$ is proportional to the product of macroscopic polarizations due to excitonic polaritons, $[P(z,t|k_2,\omega_2)]^2P^*(z,t|k_1,\omega_1)$, where the macroscopic polarization in the crystal is given by

$$P(z,t|k,\omega)=(\tfrac{1}{4}\pi)[\epsilon(k,\omega)-\epsilon_\infty]\{p(\omega)\exp[-ik(\omega)z]E(t-z/v_g(\omega))+q(\omega)\exp[ik(\omega)z]E(t+z/v_g(\omega))\}. \quad (3)$$

Here, z is the coordinate perpendicular to the sample surface, $k(\omega)$ is the complex wave vector determined by Eq. (1), $v_g(\omega)$ is the group velocity of polaritons ω, E is the envelope of the electric field of the incident pulse, and pE and qE are the envelopes of the electric field associated with polaritons propagated forward and backward in the crystal, respectively. The electric field outside the crystal $E(r,t)$ generated by $P_{NL}^{(3)}(2\omega_2-\omega_1)$ is proportional to[9]

$$\int_0^d dz\,\exp[i(2\omega_2-\omega_1)(z-d)/v_p][P(z,t-t_2+t_1+(z-d)/v_p|k(\omega_2),\omega_2)]^2P^*(z,t+(z-d)/v_p|k(\omega_1),\omega_1), \quad (4)$$

where d is the thickness of the crystal and v_p is the phase velocity at $2\omega_2-\omega_1$. The correlation trace is calculated by the time integral of the absolute square of $E(r,t)$. A numerical calculation was done based on the dispersion relation of excitonic polaritons in CuCl shown in Fig. 2. The results are plotted by the closed circles in Fig. 1. Here, adjustable parameters are limited to $k(\omega_1)$ and $k(\omega_2)$ which are implicitly determined by $\Gamma(\omega)$. As a result, $k(\omega_1)$ and $\Gamma(\omega_1)$ can be almost uniquely determined, because ω_2 is fixed as is shown in Fig. 1. Obtained values of Γ are plotted as a function of $\hbar\omega_1$ in Fig. 3. The right vertical axis indicates the dephasing time $\hbar/(\Gamma/2)$ of the macroscopic polarization P due to the ω_1 polariton. As is seen in Fig. 3, $\Gamma/2$ is of the order of 0.01 meV and increases as $\hbar\omega_1$ approaches the resonance energy of the exciton, $\hbar\omega_t$. In the energy region above 3.200 eV, $\Gamma(\omega)$ could not be definitely determined, because the correlation trace was insensitive to the value of $\Gamma(\omega)$.

The order of $\Gamma/2$ cannot be explained by the LA phonon interaction, because the scattering rate of excitonic polaritons due to LA phonons is by far slower than the observed $\hbar/(\Gamma/2)$.[1,10] The most probable mechanism of dephasing is polariton-polariton collision. It is known that four-polariton parametric scattering occurs efficiently in CuCl and even the superbroadened distribution of excitonic polaritons was observed.[11] A model calculation of the rate of polariton-polariton scattering was performed with neglect of the wave-vector dependence of the collision matrix element. The absolute value of Γ was fitted to the experimental value at 3.188 eV. The calculated result is shown by a dashed line in Fig. 3. The increasing trend of experimental Γ with polariton energy is interpreted by the calculation. This model suggests that correlation traces should depend on the intensity of the incident light. In fact, experimental data were found to depend on the intensity of the incident light. The details will be described in a forthcoming paper.

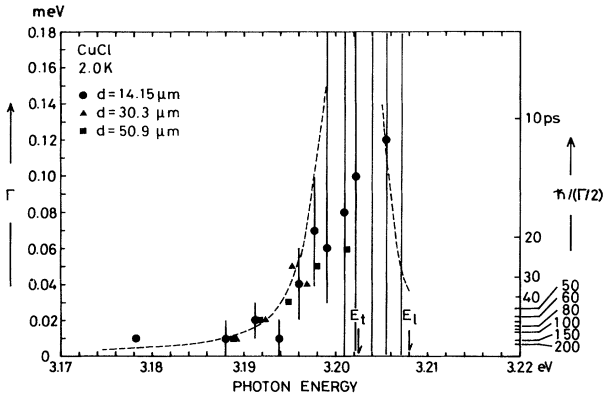

FIG. 3. Dephasing damping constant Γ as a function of the energy of excitonic polaritons. The three data symbols correspond to samples of different thicknesses. Very long error bars above 3.200 eV mean that Γ cannot be definitely determined. The dashed line is the calculated energy dependence of the dephasing damping constant based on a model of polariton-polariton scattering.

It is instructive to compare the population decay with the phase decay of excitonic polaritons and to clarify the difference. The population decay was measured by the time-resolved induced absorption (IA) from the excitonic polariton state to the excitonic molecule state.[1,11,12] It was found that the ω_1 (= 3.199 eV) polaritons survive in the crystal of 51.9 μm thickness as long as 200 ps after the injection of the ω_1 pulse.[11] However, the signal of $2\omega_2 - \omega_1$ is exactly zero at 50 ps in the same sample, since the correlation trace shows almost the same temporal profile as is seen in 6 of Fig. 1. In the IA case, all the polaritons which are scattered in various directions but almost elastically can contribute to the signal. The decay time constant of the IA reflects the energy relaxation of the ensemble of injected polaritons. In the case of four-wave mixing, on the other hand, even the elastically scattered polaritons do not contribute to the signal, because the signal arises from the coherent mixing of polariton waves and the detection is spatially well collimated. Thus the momentum relaxation due to the polariton-polariton scattering which is much faster than the energy relaxation contributes dominantly to the dephasing damping of excitonic polaritons.

In summary, we have demonstrated that the optical dephasing of excitonic polaritons in CuCl is directly measurable in the picosecond time domain by time-resolved, nondegenerate four-wave mixing at 2.0 K. The observed dephasing damping constant $\Gamma/2$ is of the order of 0.01 meV and increases as the energy approaches the resonance energy of the transverse exciton from below. This energy dependence suggests that the optical dephasing of excitonic polaritons is attributable to the process of polariton-polariton scattering.

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