Transient Phase-Space Filling by Resonantly Excited Exciton Interactions in CuCl

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We report time-resolved induced-absorption measurements near the Z_3-exciton resonance in CuCl platelets which were excited at the biexciton resonance by laser pulses of 30-ps duration. We find that the excitons created through biexciton decay induce exponential tails on their absorption line. This effect can be explained in terms of exciton phase-space filling if quantum fluctuations in the local exciton density are taken into account.

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The nonlinear optical properties of direct-band-gap semiconductors excited near excitonic resonances have attracted increasing attention these recent years because of potential applications in the field of optoelectronics.[1] In particular, excitonic absorption changes in the high-excitation-density regime have been shown to be of crucial importance. It was often thought that the main mechanisms governing excitonic nonlinearities consisted in screening of the long-range Coulomb interaction by charged free carriers[2] and scattering by phonons. However, it has been realized recently that exciton-exciton interactions in GaAs play an important role and can result in a saturation of the exciton absorption similar in magnitude to the one induced by free electron-hole pairs.[3] The exciton-exciton interactions stem from the fact that excitons are not pure bosons so that, at high exciton density, phase-space-filling effects take place.[4] In first order, these effects result in an efficient scattering mechanism, and the excitonic absorption is broadened and shifted towards the high energies.[4,5]

In this paper, we report picosecond time-resolved induced-absorption measurements performed near the Z_3-exciton resonance in CuCl samples in which high densities of biexcitons are resonantly created by two-photon absorption. Given the high binding energy of the excitons and biexcitons in CuCl,[6] the density of free carriers remains negligibly small under the experimental conditions described below. The observed nonlinearities can therefore be considered as resulting from the presence of neutral excitations. We find that the exciton population generated by the rapid decay of the originally created biexcitons induces an exponential absorption tail on both the low- and high-energy sides of the Z_3-exciton resonance. This behavior can tentatively be explained by our taking into account quantum fluctuations in the expectation value of the exciton density operator.

We studied in our experiments thin CuCl platelets (thicknesses of about 30 μm), grown by vapor-phase deposition. The samples were cooled down to 4.2 K in a continuous-flow cryostat. They were excited by spectrally narrow laser pump pulses of 30-ps duration (full width at half maximum), generated from a tunable BiBuQ [4,4‴-*bis*-(2-butyloctyloxy)-*p*-quaterphenyl] dye laser synchronously pumped by the third harmonics of a mode-locked Nd-doped yttrium aluminum garnet laser. The pump beam was sent in an optical delay line and focused onto the sample at an angle of 12°. The energy density on the sample was maintained at 0.5 mJ cm^{-2} ($\pm 10\%$). The pump photon energy was set at 3.186 eV; that is half the biexciton energy. Under such conditions, small-wave-vector biexcitons are created by two-photon absorption.[7,8] These biexcitons eventually decay, giving rise to well-defined exciton populations.[9] The time evolution of these populations and their effects on the exciton absorption peak were followed by our recording the transmission of spectrally broad test pulses of 30-ps duration obtained from the superradiant emission of a BiBuQ dye also excited by the third harmonics of the Nd-doped garnet laser. The test beam was normally incident on the sample. Its transmitted intensity was analyzed through a Huet spectrometer (focal length 65 cm) and detected by a PAR optical multichannel analyzer.[10]

The optical density induced in the crystal at a photon energy $\hbar\omega$ by the pump beam is given by

$$K(\hbar\omega,t) = -\log\left[\frac{I_T(\hbar\omega,t)}{I_T(\hbar\omega,t=-\infty)}\right], \quad (1)$$

where I_T is the transmitted test intensity and t denotes the time delay between the maxima of the test and pump pulses.[11] Figure 1 shows $K(\hbar\omega,t)-K_0$, where K_0 is a constant determined independently in the regions below and above the Z_3-exciton resonance. It is meant to take into account processes like induced absorption towards the biexciton level, increased absorption from the $Z_{1,2}$-exciton resonance, and small changes in the exciton reflectivity. Because of the limited dynamic range of the detection apparatus, induced optical density higher than 1.5 could not be reliably measured. Nevertheless, in the range where the data are significant, $K(\hbar\omega)$ at a given time t can very well be reproduced by the expression

$$K(\hbar\omega) = K_0 + K_1 \exp[-(\hbar\omega - E_0)/\gamma]. \quad (2)$$

It is to be noted that the intrinsic exciton absorption in

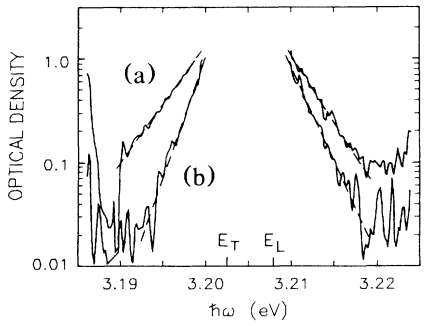

FIG. 1. Induced optical density as a function of photon energy for a delay between test and pump pulses of (a) 30 ps and (b) 250 ps. The dashed lines indicate the best fit of the data with Eq. (2).

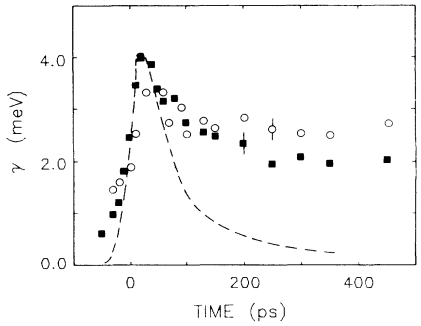

FIG. 2. γ as a function of time. Squares, $\hbar\omega < E_T$; circles, $\hbar\omega > E_L$. The dashed line represents the normalized intensity of the A_N induced-absorption line (from Ref. 9).

the same spectral range is less than 500 cm^{-1}, which is several orders of magnitude lower than the Z_3-exciton absorption at its peak. The parameters K_0, K_1, and γ have been determined separately in the two regions $\hbar\omega < E_T$ and $\hbar\omega > E_L$, where $E_T = 3.2025$ eV and $E_L = 3.2080$ eV are respectively the transverse and longitudinal Z_3-exciton energies. For computational convenience, the redundant parameter E_0 has been fixed at 3.1980 eV for $\hbar\omega < E_T$ and at 3.2120 eV for $\hbar\omega > E_L$.

The time evolution of γ and K_1 is shown in Figs. 2 and 3. It has already been reported in Ref. 9 that, under the same excitation conditions as the ones detailed above, the resonantly created small-wave-vector biexcitons decay into a narrowly distributed population of polaritons at an energy $\hbar\omega = 3.201$ eV, slightly below the polariton bottleneck located around 3.2025 eV.[12] Test-beam-induced transitions from the occupied polariton states to the biexciton level give rise to a narrow absorption line, labeled A_N in Ref. 9, whose normalized intensity is also shown in Figs. 2 and 3. It can be seen that there is a good temporal correlation between the growth of the exponential tail on the low-energy side of the exciton resonance and the creation of the narrow distribution of excitons.

The observed induced optical density at the pump photon energy is 0.95. This corresponds to an average small-wave-vector biexciton density of 2×10^{17} cm^{-3}. Even if allowance is made for a density gradient in the sample, the above-mentioned density remains much smaller than the Mott critical density n_c which is approximately given by[13]

$$n_c^{1/3} a_0 \simeq 0.38, \tag{3}$$

where a_0 is the Bohr radius. In CuCl, Eq. (3) gives $n_c \approx 2\times10^{20}$ cm^{-3}. Moreover, time-resolved luminescence experiments[14] do not reveal any electron-hole plasma emission at carrier density lower than 10^{19} cm^{-3}. It is therefore justified to neglect the influence of the free carriers in the system considered here.

The exciton-exciton interactions can in first approximation be described by elastic collisions between hard spheres with a cross section at low kinetic energy $\sigma = 12\pi a_0^2$ (Ref. 5). The mean free path of a polariton can then be written as

$$l = (\sigma N)^{-1}. \tag{4}$$

If one assumes that all created biexcitons have decayed into excitons, the mean free path is $l \approx 0.3$ μm for polaritons with energy $\hbar\omega < E_T$. This value is about one hundredth of the sample thickness. It follows that exciton-exciton scattering is a microscopic process which involves a limited number of excitons, so that fluctuations in their local density have to be considered.

The fluctuations probably have no influence near the center of the exciton resonance, where the theory developed in Ref. 4 applies. It is worth noting here that the predictions of this theory, i.e., a broadened exciton absorption peak shifted towards the high energies, have been observed in CuCl thin films excited by intense subpicosecond laser pulses.[14] On the other hand, the fluctuations can give rise to important modifications of the line shape in the tails of the absorption, as can be seen

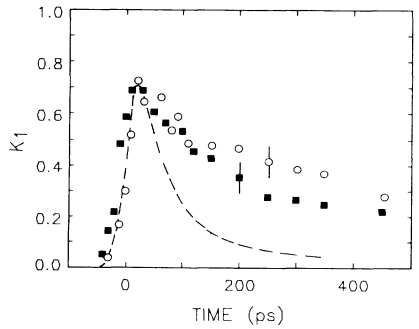

FIG. 3. K_1 as a function of time. Squares, $\hbar\omega < E_T$ and $E_0 = 3.1980$ eV; circles, $\hbar\omega > E_L$ and $E_0 = 3.2120$ eV. The dashed line represents the normalized intensity of the A_N induced-absorption line (from Ref. 9).

from the following. The Hamiltonian of the system can be written within the Hartree-Fock approximation as[13]

$$H=\sum_{\mathbf{k}}\hbar\omega_{\mathbf{k}}n_{\mathbf{k}}-\sum_{\mathbf{k}\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}n_{\mathbf{k}'}n_{\mathbf{k}}, \tag{5}$$

where $n_{\mathbf{k}}=c_{\mathbf{k}}^{\dagger}c_{\mathbf{k}}$, $c_{\mathbf{k}}^{\dagger}$ is an exciton creation operator, and $V_{\mathbf{k}\mathbf{k}'}$ is an interaction potential. In first approximation, a uniform density of excitons on a macroscopic scale can be assumed. The optical density is then proportional to the imaginary part of the optical dielectric function

$$\mathrm{Im}\varepsilon(\hbar\omega)\approx-\mathrm{Im}\Sigma(\hbar\omega)/\{[\hbar\omega-E_T-\mathrm{Re}\Sigma(\hbar\omega)]^2+[\mathrm{Im}\Sigma(\hbar\omega)]^2\}, \tag{6}$$

where $\Sigma(\hbar\omega)$ is the exciton self-energy due to exciton-exciton interactions. If the k dependence of $V_{\mathbf{k}\mathbf{k}'}$ is neglected, the self-energy is given by

$$\Sigma(\hbar\omega)=G^0(\hbar\omega)^{-1}-G(\hbar\omega)^{-1}, \tag{7}$$

where

$$G(\hbar\omega)=\int_0^{\infty}dn\,P(n)[G^0(\hbar\omega)^{-1}+V_0n]^{-1} \tag{8}$$

and

$$n=\sum_{\mathbf{k}}n_{\mathbf{k}}. \tag{9}$$

If $P(n)$ is assumed to be Gaussian,

$$P(n)=\frac{1}{(\langle n^2\rangle-\langle n\rangle^2)^{1/2}}\frac{1}{(2\pi)^{1/2}}\exp\left[-\frac{1}{2}\frac{(n-\langle n\rangle)^2}{\langle n^2\rangle-\langle n\rangle^2}\right], \tag{10}$$

the propagator $G(\hbar\omega)$ reduces to the one introduced by Sumi and Toyozawa[15] in the description of the Urbach tail induced by phonon scattering in wide-gap semiconductors. Using a simple analytical form for the free exciton propagator G^0, they have performed numerical calculations which show that Eqs. (6)–(10) result in an exponential tail below the exciton resonance, with a parameter γ proportional to

$$\gamma\propto V_0[\langle n^2\rangle-\langle n\rangle^2]^{1/2}. \tag{11}$$

It is, however, expected that this result can be extended to both sides of the resonance if the propagator G^0 relevant to the Z_3 exciton is inserted in Eq. (8). Indeed, the presence of an exponential tail does not depend on the details of the interaction. It rather appears to be the rule in systems where fluctuations described by a Gaussian distribution exist.

It can be seen in Fig. 2 that for times smaller than 100 ps, γ reaches a higher value for $\hbar\omega<E_T$ than for $\hbar\omega>E_L$, indicating some k dependence of the interaction potential $V_{\mathbf{k}\mathbf{k}'}$. This is hardly surprising since the scattered polaritons involved are on different branches of their dispersion curve. The initially created narrow distribution of excitons is eventually replaced by important populations of hot biexcitons, and of transverse excitons distributed above their bottleneck.[9] These longer-lived excitations are probably responsible for the stabilization of the parameter γ which is observed at times longer than 100 ps. The phonon bath generated by the creation and relaxation of the hot biexcitons could have a role to play as well on this longer time scale by giving rise to another scattering mechanism.[16]

In conclusion, our measurements indicate that phase-space filling can be observed in CuCl at exciton densities several orders of magnitude below the Mott critical density. It induces a broadening of the Z_3-exciton resonance which manifests itself as strong exponential absorption tails. This result can be understood in terms of exciton-exciton elastic scattering if quantum fluctuations in the density of excitons on a microscopic scale are taken into account.

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