

## Dynamical line broadening in dense exciton systems

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It is shown that a dynamical (i.e., frequency-dependent) collision broadening is necessary to explain the observed spectra of induced absorption in CuCl, which exhibit remarkable exponential absorption wings. The calculated analytical collision broadening allows us to determine the time development of the distribution of optically generated excitonic quasiparticles from transmission spectra, measured in time-resolved pump-and-probe experiments.

In recent time-resolved picosecond experiments on CuCl,<sup>1</sup> an induced exciton absorption has been observed which appeared after a strong two-photon excitation of the excitonic molecules. The observed line shape showed at least over one decade an exponential variation with frequency and was therefore tentatively analyzed in terms of the parameters of an Urbach tail absorption, caused by hot excitons which are generated by the decay of the optically excited cold biexcitons.

In this contribution we will present a microscopic theory of the exciton collision broadening. Within the linear response theory, the optical dielectric function  $\epsilon(\omega)$  around the 1s exciton with an energy  $\omega_x$  is given by the retarded exciton Green's function<sup>2</sup> ( $\hbar=1$ ):

$$\epsilon(\omega) \simeq \epsilon_\infty [1 - \Delta_{LT} G'_x(0, \omega)], \quad (1)$$

where

$$G'_x(\mathbf{k}, \omega) = \frac{1}{\omega - \omega_x(\mathbf{k}) - i \text{Im}\Pi(\mathbf{k}, \omega)}.$$

Spatial dispersion is disregarded for simplicity by setting the exciton momentum equal to zero.  $\epsilon_\infty$  is the high-frequency dielectric constant, and  $\Delta_{LT}$  is the longitudinal-transverse splitting.  $\Pi(\mathbf{k}, \omega)$  is the retarded self-energy of an exciton with momentum  $\mathbf{k}$  and frequency  $\omega$ . Using the empirical fact that the exciton resonance is hardly shifted by high excitation, we limit ourselves to the calculation of the imaginary part due to exciton-exciton intraband scattering, which is the dominant pro-

cess for excitons with such a large binding energy as in CuCl.

The absorption spectrum  $\alpha(\omega)$  is given by  $\alpha(\omega) = \omega \epsilon''(\omega) / n(\omega) c$ , where  $n(\omega)$  is the index of refraction. In the evaluation we consider the following final-state interaction: An exciton which is generated at roughly  $\mathbf{k} \simeq \mathbf{0}$  by a photon with frequency  $\omega$  is scattered to the state  $\mathbf{k} + \mathbf{q}$ , while an already existing exciton is scattered from  $\mathbf{k}'$  to  $\mathbf{k}' - \mathbf{q}$ , thus providing the missing energy under off-resonance excitation. The imaginary part of the self-energy which provides the exciton damping is calculated dynamically, i.e., as a function of the frequency. It is given by (see, e.g., Ref. 2)

$$\begin{aligned} \text{Im}\Pi(\mathbf{k}, \omega) = & - \sum_{\mathbf{k}', \mathbf{q}} | \langle \mathbf{k}, \mathbf{k}' | I | \mathbf{k} + \mathbf{q}, \mathbf{k}' - \mathbf{q} \rangle |^2 \\ & \times \pi \delta(\omega + \omega_{\mathbf{k}'} - \omega_{\mathbf{k} + \mathbf{q}} - \omega_{\mathbf{k}' - \mathbf{q}}) \\ & \times [n_{\mathbf{k}'}(1 + n_{\mathbf{k} + \mathbf{q}})(1 + n_{\mathbf{k}' - \mathbf{q}}) \\ & - (1 + n_{\mathbf{k}'})n_{\mathbf{k} + \mathbf{q}}n_{\mathbf{k}' - \mathbf{q}}], \quad (2) \end{aligned}$$

where  $I$  is the exciton-exciton interaction, and  $n_{\mathbf{k}} = \{\exp[\beta(\omega_{\mathbf{k}} - \mu_x)] - 1\}^{-1}$  is the exciton distribution function, which is assumed to be thermal. The exciton energy is given by  $\omega_{\mathbf{k}} = \omega_x + k^2/2m$ , where  $m$  is the effective mass of the exciton. The chemical potential is also measured relative to the exciton energy  $\mu_x = \omega_x + \mu$ , with  $\mu \leq 0$ . For the thermally distributed excitations, Eq. (2) can be rewritten in the following form:

$$\begin{aligned} \text{Im}\Pi(\mathbf{k}, \omega) = & \{ \exp[-\beta(\hbar\omega - \mu_x)] - 1 \} \sum_{\mathbf{k}', \mathbf{q}} | \langle \mathbf{k}, \mathbf{k}' | I | \mathbf{k} + \mathbf{q}, \mathbf{k}' - \mathbf{q} \rangle |^2 \\ & \times \pi \delta(\omega + \omega_{\mathbf{k}'} - \omega_{\mathbf{k} + \mathbf{q}} - \omega_{\mathbf{k}' - \mathbf{q}}) [n_{\mathbf{k}'}(1 + n_{\mathbf{k} + \mathbf{q}})(1 + n_{\mathbf{k}' - \mathbf{q}})]. \quad (3) \end{aligned}$$

This expression shows immediately that the imaginary part of  $\Pi$  is positive for  $\omega < \mu_x$  and thus gives rise to optical gain (the theory of optical gain due to exciton-exciton collisions is reviewed in Ref. 2). The crossover from gain

to absorption is exactly at  $\omega = \mu_x$ . Because no gain is observed in the experiment of Ref. 1 the chemical potential must have been more than 15 meV below the exciton resonance, thus the assumption  $\mu\beta \gg -1$  is appropriate,

which means that the excitons can be described by a Boltzmann distribution, for which  $\exp(\beta\mu) = Na_0^3(4\pi E_0/kT)^{3/2}$ , where  $a_0$  and  $E_0$  are the exciton Bohr radius and Rydberg energy, respectively, where  $N$  is the number of particles and  $kT$  is the thermal energy of the particles. The exciton interaction matrix element will be taken in the form (see Refs. 3 and 4)

$$|\langle \mathbf{k}, \mathbf{k}' | I | \mathbf{k} + \mathbf{q}, \mathbf{k}', -\mathbf{q} \rangle| = \frac{26}{3} \pi a_0^3 E_0 e^{-(da_0 q)^2} = I_q, \quad (4)$$

where  $d$  is the dimensionless cutoff parameter for the momentum transfer. With these assumptions the imaginary part of  $\Pi$  can be evaluated analytically by elementary integrations. The resulting expression contains the modified Bessel function of first order,  $K_1(z)$ :

$$\begin{aligned} \text{Im}\Pi(0, \omega) = & \frac{kT}{\pi} \left[ \frac{13}{12} \right]^2 (e^{-\beta(\omega - \omega_x - \mu)} - 1) e^{\beta(\omega - \omega_x)} e^{\beta\mu} \\ & \times \left[ \frac{\beta E_0 \Omega^2}{2d^2 + \beta E_0} \right]^{1/2} \\ & \times K_1[\beta E_0 (2d^2 + \beta E_0) \Omega^2]^{1/2}, \end{aligned} \quad (5)$$

where  $\Omega = (\omega - \omega_x)/E_0$ . Equation (5) is the desired dynamical line-broadening formula. An example of the resulting absorption spectrum is shown for CuCl parameters with an exciton temperature  $T = 100$  K and various exciton densities in Fig. 1. The cutoff parameter is here  $d = 1$ . Particularly on the low-energy side there is a large range around  $\alpha \approx 10^3 \text{ cm}^{-1}$ , where the experimental data have been taken, in which  $\alpha(\omega)$  varies exponentially. At low temperatures the decrease on the high-energy side of the exciton resonance is considerably slower than on the low-energy side. This asymmetry is easily understood, because at low temperatures there are no energetic excitons which could provide the necessary energy if the test

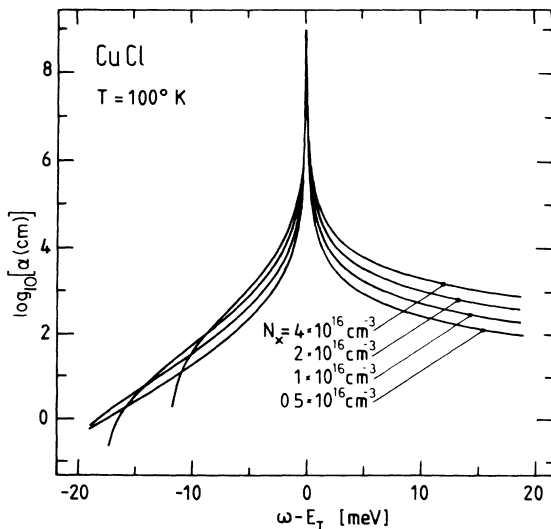


FIG. 1. Calculated exciton absorption spectra induced by exciton-exciton collisions for CuCl with an exciton temperature of 100 K and various exciton densities with  $d = 1$ .

beam is tuned too far below the resonance. On the other hand, for a photon frequency larger than the resonance, the surplus energy can always be transferred to one of the low-energy excitons, so that a certain absorption remains possible on the high-energy side.

The transmission spectra which have been measured for CuCl platelets with a thickness of  $L = 10-30 \mu\text{m}$  can be calculated by inserting the dielectric function (1) into Maxwell's equations. With the boundary conditions for a dielectric medium the transmitted intensity is given by

$$I_t = \left| \frac{4kk_0 e^{ikL} E_i}{(k - k_0)^2 e^{2ikL} - (k + k_0)^2} \right|^2, \quad (6)$$

where  $E_i$  is the amplitude of the incident field.  $k$  is the wave number in the medium  $k = k_0 \sqrt{\epsilon(\omega)}$ , with  $k_0 = \omega/c$ . It contains the polariton aspect. The spatial dispersion which has been neglected gives only minor corrections. The resulting spectrum  $I_t(\omega)$  shows very fine Fabry-Perot modulations in the wings of the exciton resonance due to the rapid variations of  $\exp[ik(\omega)L]$ . The fine structures are smeared out, if one averages the intensity with a Gaussian distribution with a spectral width of 0.2 meV, which corresponds to the finite resolution of the spectrometer.

The changes of the absorption due to a finite concentration of excitons can best be obtained by the induced optical density<sup>5</sup>

$$K(\omega) = -\ln \left[ \frac{\langle I_t(\omega) \rangle}{\langle I_t^0(\omega) \rangle} \right], \quad (7)$$

where  $\langle I_t^0(\omega) \rangle$  is the transmitted intensity of the unexcited crystal with  $N_x = 0$ ,  $N_3$  being the number of excitons.  $\ln K(\omega)$  is asymptotically proportional to the induced absorption as can be shown by a Taylor expansion of this expression. In Fig. 2 we give an example of the calculated  $K(\omega)$  spectra for an exciton temperature of 50 K, an exciton density of  $2 \times 10^{15} \text{ cm}^{-3}$ , and three different

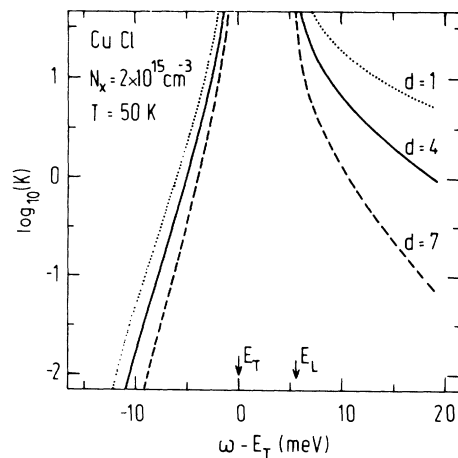


FIG. 2. Calculated induced optical density  $K(\omega)$  for CuCl platelets of  $16 \mu\text{m}$  thickness, in a semilogarithmic scale. The curves are calculated for an exciton density of  $2 \times 10^{15} \text{ cm}^{-3}$ , an exciton temperature of 50 K, and a cutoff parameter  $d$  of 1, 4, and 7, respectively.

values of the cutoff parameter  $d$  for the momentum transfer. A larger momentum cutoff suppresses the broadening on the high-energy side, while the slope on the low-energy side is mainly given by the temperature of the excitons. A comparison with Fig. 1 shows that the  $K(\omega)$  spectrum roughly reproduces the exciton-collision-induced absorption spectrum but shows in addition the stop band due to the longitudinal-transverse splitting.

Figure 3 shows the fits of the calculated  $K(\omega)$  spectra to two experimental spectra, taken at 60 and 200 ps after the pump pulse, respectively, with a CuCl platelet of 16- $\mu\text{m}$  thickness. The pump pulse of 30 ps duration and an intensity of 15 MW/cm<sup>2</sup> excites resonantly biexcitons, which decay into exciton polaritons. The experimental line shapes have been reanalyzed, because an error in the baseline subtraction has introduced a systematic error on the high-energy side of the spectra reported in Ref. 1.

In order to get a good fit, the strength of the scattering matrix element had to be increased by a factor of 20 over the value of Eq. (4), which one obtains from a simple estimate for Wannier excitons.<sup>3</sup> The larger value of the scattering matrix element was also assumed for the calculations to Fig. 2. But even more surprisingly, the best fit on the high-energy side is obtained by choosing the cutoff parameter  $d = 7$ . Thus the momentum transfer is considerably smaller than an inverse exciton Bohr radius.

The large values for the scattering matrix element and for the momentum cutoff may partly be due to the fact that the small excitons in CuCl are not quantitatively described in the Wannier picture.<sup>6</sup> Another possible explanation is that even several hundred picoseconds after the excitation of the biexcitons, the major contribution to the exciton broadening stems from the collisions with biexcitons, rather than excitons. The larger radius of the biexcitons leads to a larger cross section and a larger momentum transfer cutoff. The form of Eq. (3), however, remains valid also for exciton-biexciton scattering. The fits to spectra taken after 20, 60, 100, 200, and 300 ps give

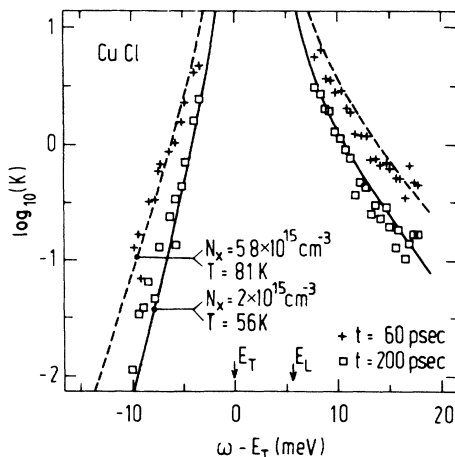


FIG. 3. Calculated (with  $d = 7$ ) and measured induced optical density  $K(\omega)$  for CuCl platelets of 16  $\mu\text{m}$  thickness with delays of 60 and 200 ps after the excitation pulse of an intensity of 15 MW/cm<sup>2</sup>, in a semilogarithmic scale.

the following excitonic temperatures: 121, 81, 60, 56, and 52 K, and the following densities: 6, 5.8, 5.5, 2, and 1.5 in units of  $10^{15} \text{ cm}^{-3}$ . Spectra taken in the early time regime  $t < 20$  ps, where the build-up of the biexciton and exciton concentrations and the heating occurs, are partly distorted due to nonthermal distributions, so that they cannot be fitted with the assumption of a quasiequilibrium distribution.

The relaxation and recombination kinetics, which are obtained from the line-shape analysis are shown in Fig. 4, where the resulting temperature  $T(t)$  and the density  $N(t)$  are plotted for two pump intensities of 15 and 50 MW/cm<sup>2</sup>, respectively. The dashed lines are inserted to guide the eye. For both excitation intensities the temperature variation shows a fast decrease in the period  $20 < t < 100$  ps, probably caused by LO-phonon emission, followed by a slower cooling regime for  $t > 100$  ps. For the high pump intensity, the density decrease is fast up to 100 ps. In this period the recombination is likely to be increased by stimulated biexciton decay. For  $t > 100$  ps the recombination is governed by the slower spontaneous decay, as it is for the lower pump intensity for all times  $t > 20$  ps.

In summary, we have derived an analytical formula for the dynamical excitonic collision broadening. The decrease of the broadening with increasing detuning is responsible for the exponential absorption wings. The theory fits quantitatively the observed induced absorption spectra in CuCl, if a relatively large cutoff of the momentum transfer in the collisions is introduced. The origin of this limited momentum transfer is presently not fully understood. The fits yield an excitonic relaxation and recombination kinetics with two distinctively different regimes.

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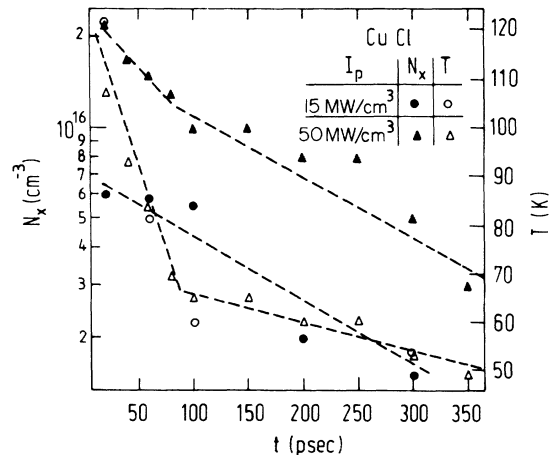


FIG. 4. Resulting excitonic density  $N_x(t)$  and temperature  $T(t)$  plotted vs the delay time  $t$  after the pump pulse for two excitation intensities  $I_p$  of 15 MW/cm<sup>2</sup> ( $\circ$ ) and 50 MW/cm<sup>2</sup> ( $\Delta$ ), respectively.

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