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Determination of diffusion coefficients of an exciton and excitonic molecule in CuCl by picosecond transient grating spectroscopy

Yoshinobu Aoyagi, Yusaburo Segawa, and Susumu Namba
The Institute of Physical and Chemical Research, Wako-shi, Saitama, 351, Japan
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We have made the first successful direct observation of the diffusion coefficients of an exciton and excitonic molecule in CuCl by tunable picosecond transient grating spectroscopy under the resonant two-photon excitation of the excitonic molecule. The diffusion coefficients of the exciton and the excitonic molecule are 330 ± 200 and 45 ± 10 $\mathrm{cm^2/sec}$ at 1.8 K, respectively. The main part of this difference between the diffusion coefficients of the exciton and excitonic molecule is explained by the difference of the size of the exciton and excitonic molecule.

Scattering processes of excited particles in solids like exciton and excitonic molecule strongly influences optical properties such as line shapes of the related absorption and luminescence. One of the useful approaches to clarify the scattering processes is to examine the diffusion coefficients of those excited particles. However, diffusion coefficients of the exciton and excitonic molecule in crystals have not been observed directly, to our knowledge, because electronic methods widely used to determine the diffusion coefficients of an electron and hole are not applicable to uncharged particles.

We made the first successful observation of the diffusion coefficients of the exciton and excitonic molecule by a picosecond transient grating spectroscopy (PTGS).

In this Communication we present the diffusion coefficients of the exciton and excitonic molecule in CuCl and discuss the difference between the diffusion coefficients of both particles.

Transient grating methods have already been reported by several authors.[1-6] However, in their methods the excitation was not the resonant excitation, and the spectrum of the diffracted light was not observed. In our spectroscopy (PTGS) the excitonic molecule was directly excited by resonant two-photon absorption,[7] and the spectra of the diffracted light of the probe light from the transient density grating of the exciton and excitonic molecule were observed as a function of time. From these spectra the diffusion coefficients and the relaxation times of the exciton and excitonic molecule were independently determined.

Figure 1 shows a schematic diagram of this spectroscopy. The excitation laser at a wavelength of the resonant two-photon absorption of the excitonic molecule in CuCl (389.13 nm) was split into two beams and they crossed each other in the sample with an angle θ to produce selectively a transient density grating of the excitonic molecule in the crystal. The probe light with a broad band (2 nm) was passed through an optical delay line and was diffracted by this transient grating. The spectra of the diffracted light at different delay times were observed by an optical multichannel analyzer (OMA). The tunable excitation and the probe lasers consisted of two dye oscillators[8] and two dye amplifiers pumped by the third harmonics of pulse trains from a mode-locked Nd–(YAG) yttrium aluminum garnet laser. The pulse width and bandwidth of the excitation laser were 40 psec and 0.02 nm, respectively. This narrow bandwidth of the excitation laser was necessary to excite selectively the excitonic molecule in CuCl.[9]

Figure 2 shows the spectra of the diffracted light at different delay times. The narrow and intense diffracted spectra A and A' are assigned to be the parametric coupling signals between the weak probe light and the strong excitation light in the sample due to large nonlinear susceptibility[10] at the wavelength of the two-photon absorption. These signals built up and decreased rapidly. This time behavior was the same as that of the excitation laser. The broad spec-

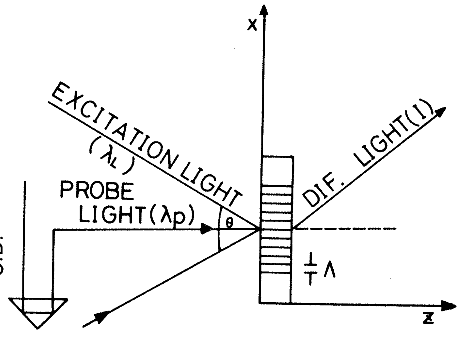

FIG. 1. The schematic diagram of the transient grating spectroscopy (PTGS).

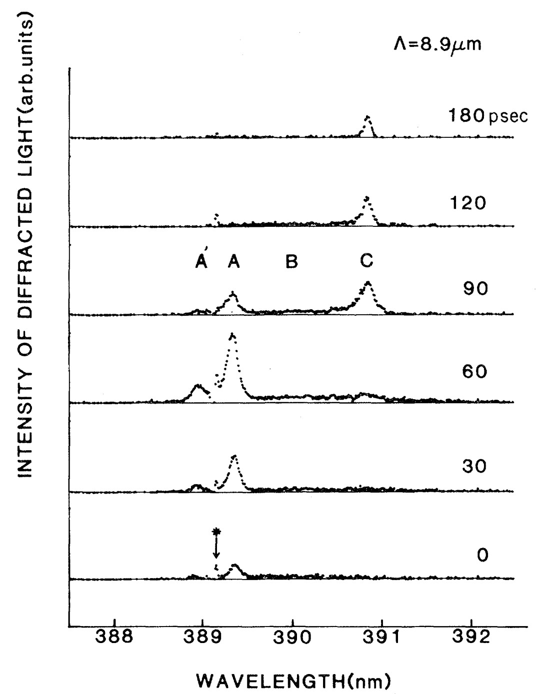

FIG. 2. The spectra of the diffracted light at different delay times. The asterisk indicates the excitation light scattered at the sample. As for the nomenclature *A*, *A'*, *B*, and *C*, see the text.

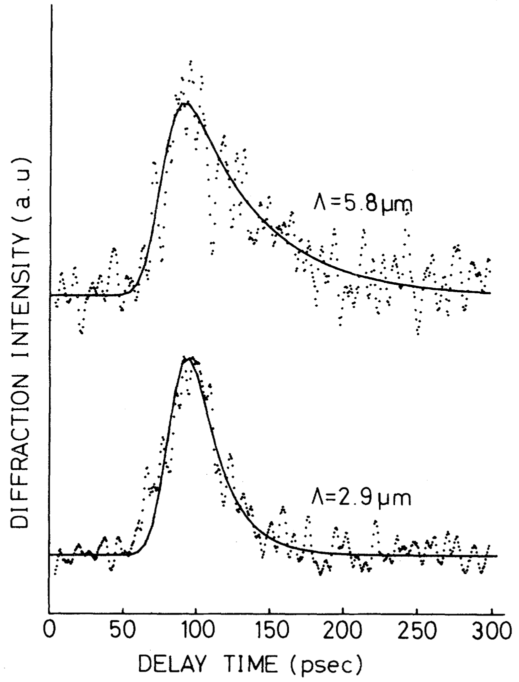

FIG. 3. The typical behavior of the diffracted light for the spectrum *B* at the different grating pitches. Solid lines: theoretical results. Dotted lines: experimental results.

trum *B* is due to the diffraction of the probe light by the index grating of the periodically induced density modulation of the excitonic molecule in the crystal. The band *B* built up together with the excitation pulse and decayed with a time constant depending on the grating pitch as shown typically in Fig. 3. The diffracted light *C* built up after the excitation of the excitonic molecule with some delay time and decayed with some decay constant as shown in Fig. 2. This band is assigned to be the diffraction from the grating of the exciton which is generated after some delay time due to the radiative relaxation of the excitonic molecule.[11] The large susceptibility charge due to the resonant reabsorption from the exciton level to the excitonic molecule was expected at this wavelength and the strong diffracted light was observed. This wavelength is coincident with the wavelength of the luminescence corresponding to the transition from the excitonic molecule to the transverse exciton. The spectrum *C* is sharper than the spectrum *B*. This is due to the sharp resonant characteristics of spectrum *C* related to the absorption transition from the exciton level to the excitonic molecule level and the off-resonant characteristics of spectrum *B* related to the change of the refractive index due to the density modulation of the excitonic molecule.

The decay time of spectrum *C* also depended on the grating period. From the dynamic behavior of the diffracted light for each spectrum, we can estimate the generation and relaxation times of the excitonic molecule and exciton in addition to the diffusion coefficients of each particles.

The rate equations of the density of the excitonic molecule and exciton under the resonant two-photon excitation of the excitonic molecule are given by

$$\frac{\partial N}{\partial t} - D_m\frac{\partial^2 N}{\partial X^2} + \frac{N}{\tau} = g\left[1+\cos\left(\frac{2\pi X}{\Lambda}\right)\right]^2 \exp\left(\frac{-2t^2}{\sigma^2}\right) , \tag{1}$$

$$\frac{\partial n}{\partial t} - D_{\mathrm{ex}}\frac{\partial^2 n}{\partial X^2} + \frac{n}{\tau_{\mathrm{ex}}} = \frac{N}{\tau_m} , \tag{2}$$

where D_m, D_{ex}, τ_m, τ_{ex}, are the diffusion coefficients and the lifetimes of the excitonic molecule and exciton, N and n are the densities of the excitonic molecule and exciton, g and Λ are the proportionality constants, respectively. σ is a half-width of the excitation laser pulse. In these equations it is assumed for simplicity that the sample is illuminated uniformly across the incident excitation beam and the generation of the excitonic molecule by the absorption of the probe light and by the exciton-exciton interaction is negligible. These assumptions are valid in our experimental absorption coefficient of the excitation light, much weaker probe light than the excitation light, and relatively low probability of the generation of the excitonic molecule through the exciton-exciton interaction in comparison with the direct generation of the excitonic molecule by the two-photon absorption of the excitation light. The diffraction intensity due to the excitonic molecule is analytically given from Eq. (1) to be

$$I_m(t)=K_m^2\exp\left(\frac{-2t}{\tau_m}\right)\left[\mathrm{erf}\left(\frac{c_1}{\sigma}\right)-\mathrm{erf}\left(\frac{c_1}{\sigma}-\frac{c_1-t}{\sigma}\right)\right]^2 , \tag{3}$$

where K_m is a proportional constant and

$$\frac{1}{T_m}=\frac{1}{\tau_m}+\left(\frac{4\pi^2}{\Lambda^2}\right)D_m , \tag{4}$$

$$C_1=\frac{\sigma^2}{2T_m} . \tag{5}$$

The diffraction intensity due to the excitation is given from Eqs. (1) and (2) to be

$$I_{\mathrm{ex}}=K_{\mathrm{ex}}^2\exp\left(\frac{-2t}{T_{\mathrm{ex}}}\right)\left\{\int_0^t\exp\left[-\left(\frac{1}{T_m}-\frac{1}{T_{\mathrm{ex}}}\right)t\right]\left[\mathrm{erf}\left(\frac{C_1}{\sigma}\right)-\mathrm{erf}\left(\frac{C_1-t}{\sigma}\right)\right]dt\right\}^2 , \tag{6}$$

where K_{ex} is a proportional constant and

$$\frac{1}{T_{\mathrm{ex}}}=\frac{1}{\tau_{\mathrm{ex}}}+\frac{4\pi^2}{\Lambda^2}D_{\mathrm{ex}} . \tag{7}$$

The observed dynamic behaviors of the spectra *B* and *C* for each grating periods were analyzed by Eqs. (3) and (6), respectively. The typical experimental and analytical results of the excitonic molecule are shown in Fig. 3 for two grating periods. The solid lines are the calculated curves according to the Eq. (3). The calculated results are in good agreement with the observed results for each grating period. From this analysis we determined the decay time T_m.

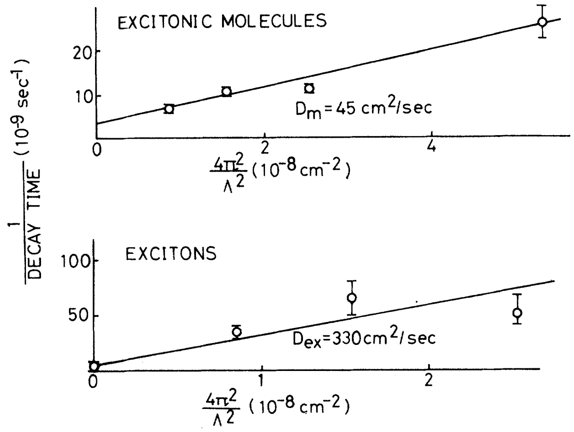

FIG. 4. The inverse decay time ($1/T$) vs the inverse square of the grating pitch ($4\pi^2/\Lambda^2$) for the excitonic molecule and exciton.

The diffusion coefficient D_m and the lifetime τ_m are estimated from the day time T_m for the various grating pitches according to Eq. (4) as shown in Fig. 4(a). The slope and the crosspoint to the *y* axis in the $1/T_m$ vs $4\tau^2/\Lambda^2$ plot give the diffusion coefficient and the lifetime of the excitonic molecule, respectively. From Fig. 4(a), the diffusion coefficient and the lifetime of the excitonic molecule at 1.8 K are estimated to be 45 ± 10 cm^2/sec and 280 psec, respectively. The lifetime observed in this method is in good agreement with the value observed by the decay of the luminescence of the excitonic molecule.[12]

We also determined the diffusion coefficient of the exciton to be 330 ± 200 cm^2/sec by the same method as shown in Fig. 4(b). In this case we used the exciton lifetime[13] of 300 psec to determine the diffusion coefficient. These diffusion coefficients observed for the exciton and excitonic molecule are the first presentation.

There are many scattering processes for exciton and excitonic molecule, such as exciton-exciton, excitonic molecule-excitonic molecule, exciton-impurity, exciton-phonon collision, and so on. In any scattering mechanism the size of the particles are strongly related to the diffusion coefficients. The main part of the difference of the diffusion coefficients of the exciton and excitonic molecule are explained by the difference of the size of the both particles, that is, the ratio of the cross section of the both particles is about 4.[14]

In conclusion, we made the first successful direct observation of the diffusion coefficients of the exciton and excitonic molecule to the 330 ± 200 and 45 ± 10 cm^2/sec, respectively, by the picosecond transient grating spectroscopy. In this spectroscopy, the diffusion coefficients of the uncharged particles can be obtained clearly.

[1] D. W. Phillion, D. J. Kuizenga, and A. E. Siegman, Appl. Phys. Lett. 27, 85 (1975).

[2] R. Baltrameyunas, Yu. Vaitkus, and K. Yarashyunas, Fiz. Tekh. Poluprovodn. 10, 969 (1976) [Sov. Phys. Semicond. 10, 572 (1976)].

[3] K. Jarasiunas and J. Vaitkus, Phys. Status Solidi A 44, 793 (1977).

[4] C. A. Hoffman, K. Jarasiunas, H. J. Gerritsen, and A. V. Nurmikko, Appl. Phys. Lett. 33, 536 (1978).

[5] J. R. Saludo, A. E. Siegman, D. D. Dlott, and M. D. Fayer, Phys. Rev. Lett. 41, 131 (1978).

[6] K. Jarasiunas and H. J. Gerritsen, Appl. Phys. Lett. 33, 190 (1980).

[7] G. M. Gale and A. Mysyrowicz, Phys. Rev. Lett. 32, 727 (1974).

[8] K. Azuma, O. Nakagawa, Y. Segawa, Y. Aoyagi, and S. Namba, Jpn. J. Appl. Phys. 18, 209 (1979).

[9] R. W. Suorec and L. L. Chase, Solid State Commun. 20, 353 (1976).

[10] A. Maruani, J. L. Ouder, E. Batifol, and D. S. Chemla, Phys. Rev. Lett. 41, 1372 (1978).

[11] N. Nagasawa, N. Nakata, Y. Doi, and M. Ueta, J. Phys. Soc. Jpn. 39, 987 (1975).

[12] Y. Segawa, Y. Aoyagi, O. Nakagawa, K. Azuma, and S. Namba, Solid State Commun. 27, 785 (1978).

[13] Y. Segawa, Y. Aoyagi, and S. Namba, Solid State Commun. 39, 535 (1981).

[14] M. Ojima, T. Kushida, Y. Tanaka, and S. Shionoya, J. Phys. Soc. Jpn. 44, 1294 (1978).