

Homogeneous width of exciton absorption spectra in CuCl microcrystals

Yasuaki Masumoto, Tetsuro Wamura, and Atsushi Iwaki
Institute of Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

(Received 27 March 1989; accepted for publication 6 October 1989)

The homogeneous width of Z_3 exciton absorption spectra in CuCl microcrystals was measured for the first time. It was determined to be $0.18 \pm_{-0.05}^{+0.01}$ meV at 77 K by laser saturation spectroscopy. The temperature dependence of the Z_3 exciton absorption linewidth also supported the result. The measurements of the saturation power density, the homogeneous linewidth, and the lifetime of Z_3 excitons informed us of the transition dipole moment for a CuCl microcrystal. The obtained transition dipole moment for a CuCl microcrystal is about 13 times that for a unit cell in bulk CuCl.

Recently, nonlinear optical properties of semiconductor microcrystals have attracted much interest. CuCl microcrystals, especially, which give the typical example of the exciton quantization,¹ are expected to show the large optical nonlinearity.^{2,3} In our previous letter, we demonstrated the optical nonlinearity of Z_3 excitons in CuCl microcrystals in NaCl host crystals by laser saturation spectroscopy.⁴ However, the basic optical characteristics of CuCl microcrystals, such as the homogeneous width of Z_3 excitons, their transition dipole moment, and so on, are not yet known. The homogeneous width is masked by the inhomogeneous broadening due to the size distribution of CuCl microcrystals. Homogeneous width is one of the most important parameters characterizing the linear and nonlinear optical properties of excitons because it determines the coherent length which dominates the exciton lifetime and the transition dipole moment for a microcrystal. This is because the transition dipole moment of excitons in the coherent volume are superposed and thus enhanced.⁵⁻⁷ In this work, we investigated the homogeneous width of the Z_3 exciton absorption spectra in CuCl microcrystals by the laser saturation spectroscopy. Simultaneously, we observed the temperature dependence of the absorption linewidth of Z_3 excitons to clarify the mechanism of the homogeneous broadening as well as to ascertain the homogeneous width obtained by laser saturation spectroscopy. We also measured the lifetime of Z_3 excitons. The saturation density, the homogeneous linewidth, and the lifetime of excitons informed us of the transition dipole moment of excitons for a CuCl microcrystal, referred to by the current theory.^{2,3}

Samples of CuCl microcrystals in NaCl host crystals were grown by the transverse Bridgman method followed by heat treatment.⁴ The size of the CuCl microcrystals was determined by the absorption peak energy of Z_3 excitons at 77 K following the method established by Itoh *et al.*⁸ In this study, we used a typical sample of 0.035 cm thickness containing CuCl microcrystals with a mean radius of 6.1 nm. The CuCl molar fraction in the sample is determined to be 0.16% by plasma emission spectroscopy.⁴

To obtain the temperature dependence of the absorption spectra, we used a temperature variable cryostat. We also used an incandescent lamp, a monochromator, a photomultiplier, and a lock-in amplifier. For the laser saturation spectroscopy, we used a dye laser pumped by a nitrogen laser. The sample was directly immersed in liquid nitrogen. The

dye laser is composed of an output mirror, a dye cell filled with BBQ in dioxane, a beam expander made of two prisms, and an echelle grating (316 grooves/mm). Selecting the order of the grating and adjusting the beam expander, we could easily change the linewidth of the laser output quasi-continuously. The peak photon energy of the laser light was set to be 3.223 eV (3.84.58 nm), which corresponds to the Z_3 exciton absorption peak of the sample at 77 K. The pulse duration was 3.6 ns and the pulse power was measured by using a pyroelectric energy detector. The size of the excitation spot was measured under a microscope. The transmitted laser light was detected directly by a photomultiplier with a calibrated set of neutral density filters. The signal was averaged by using a Boxcar integrator.

In Fig. 1 the temperature dependence of the absorption spectra of CuCl microcrystals is shown. At low temperatures, spectra are composed of sharp Z_3 and $Z_{1,2}$ exciton

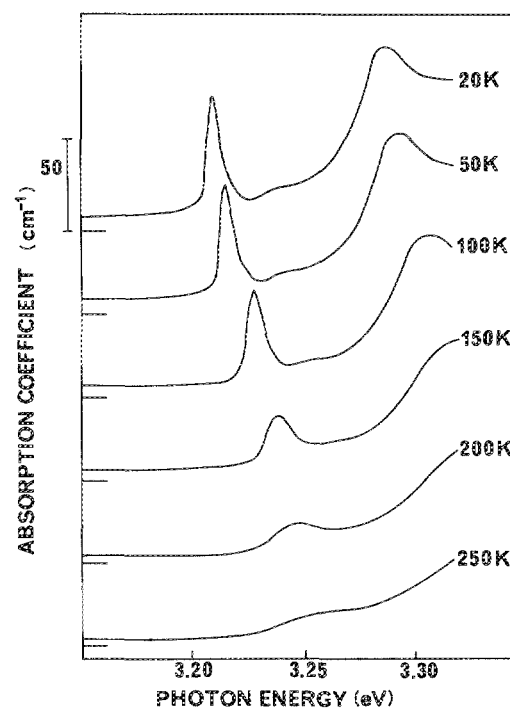


FIG. 1. Absorption spectra of CuCl microcrystals in NaCl at various temperatures. The mean radius of the CuCl microcrystals is 6.1 nm.

absorption lines. With the rise of temperature, the exciton structure broadens together with the blue shift. At elevated temperatures, exciton absorption spectra have the Lorentzian shape. The linewidth of the Z_3 exciton absorption is plotted as a function of temperature in Fig. 2.

As is shown, the linewidth changes little below 70 K. The size distribution of CuCl microcrystals causes the inhomogeneous broadening of the exciton absorption. The linewidth below 70 K almost comes from the inhomogeneous linewidth. The temperature dependence of the linewidth of the Z_3 exciton absorption $\Gamma(T)$ is well expressed by⁹

$$\Gamma(T) = \Gamma_{\text{inh}} + \frac{A}{\exp(B/k_B T) - 1}, \quad (1)$$

where $\Gamma_{\text{inh}} = 8.0$ meV is the inhomogeneous broadening. The best fitting is obtained with parameters $A = 474$ meV and $B = 55.7$ meV, as shown in Fig. 2. Fitting is satisfactory. Fitting is not good if we use the fitting function $\Gamma(T) = \Gamma_{\text{inh}} + CT^2$, where C is a fitting parameter. So far, the expression has been used to explain the temperature dependence of the Z_3 exciton linewidth in CuCl.¹⁰ In this case the line broadening is due to interactions of excitons with long-wavelength acoustic phonons.¹¹

Instead, the validity of Eq. (1) implies that the line broadening is due to interactions of Z_3 excitons with optical phonons. Energies of longitudinal optical (LO) phonon and transverse optical (TO) phonon at the Γ point in CuCl are 25.6 and 20.0 meV, respectively.¹² The absorption of one optical phonon cannot explain Eq. (1), because the value of B is about twice of the LO phonon energy. Successive absorption of two LO phonons can explain Eq. (1), because $nn' = [\exp(\hbar\omega_{\text{LO}}/k_B T) - 1]^{-1} [\exp(\hbar\omega'_{\text{LO}}/k_B T) - 1]^{-1} \approx \{\exp[(\hbar\omega_{\text{LO}} + \hbar\omega'_{\text{LO}})/k_B T] - 1\}^{-1}$ holds when $\hbar\omega_{\text{LO}}, \hbar\omega'_{\text{LO}} \gg k_B T$. Here $n(n')$ and $\hbar\omega_{\text{LO}}(\hbar\omega'_{\text{LO}})$ are the phonon occupation number and the LO phonon energy, respectively. Therefore, a possible broadening mechanism for the Z_3 excitons at elevated temperatures is the scattering of the Z_3 excitons to the $Z_{1,2}$ excitons as a result of the successive absorption of two LO phonons, because the $Z_{1,2}$ exciton state is higher than the Z_3 exciton state by 70 meV. Exciton thermal ionization cannot be taken into account in contrast to the case of GaAs quantum wells,⁹ because the binding

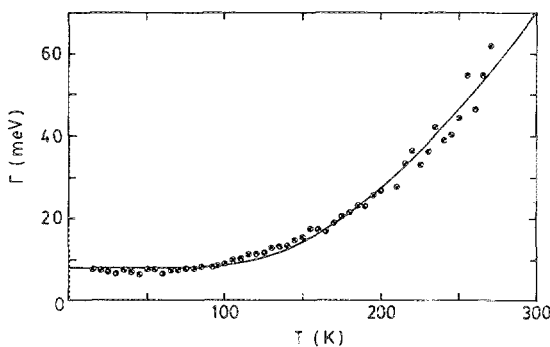


FIG. 2. Temperature dependence of the linewidth of the Z_3 exciton absorption. The fitting is shown by the solid line described by the equation $\Gamma(T) = \Gamma_{\text{inh}} + A/[\exp(B/k_B T) - 1]$, where $\Gamma_{\text{inh}} = 8.0$ meV, $A = 474$ meV, and $B = 55.7$ meV.

energy of the Z_3 excitons is 213 meV, which is much larger than the value of B . The large binding energy and the 70 meV energy splitting of Z_3 and $Z_{1,2}$ excitons may cause the peculiar thermal broadening mechanism of Z_3 excitons. Our experimental observation about the phonon broadening of the Z_3 exciton absorption is limited to the elevated temperatures, because the inhomogeneous broadening dominates the broadening at low temperatures. Therefore, we cannot infer the phonon broadening mechanism at low temperatures.

Next, the homogeneous width of the Z_3 exciton absorption was studied by laser saturation spectroscopy.¹³ On the basis of the laser saturation spectroscopy, the saturation power density I_s is expressed by

$$I_s = \epsilon_0 c \hbar^2 / (2|\mu|^2 T_1 T_2), \quad (2)$$

where ϵ_0 is the dielectric constant in vacuum, c is the light velocity in vacuum, μ is the transition dipole moment, T_1 is the longitudinal relaxation time, and T_2 is the transverse relaxation time. This equation holds when the laser linewidth is sufficiently narrower than the homogeneous width $\Gamma_h = \hbar/T_2$. When the laser linewidth Γ_l is comparable to or larger than the homogeneous width Γ_h , Eq. (2) is rewritten as¹⁴

$$I_s = \epsilon_0 c \hbar \Gamma_{\text{eff}} / (2|\mu|^2 T_1), \quad (3)$$

$$\Gamma_{\text{eff}} = \Gamma_h + \Gamma_l.$$

Here Γ_{eff} is the effective linewidth which is the convoluted result of the homogeneous linewidth and the laser linewidth. We assumed the laser spectra to be Lorentzian for simplicity. The homogeneous width Γ_h is obtained if I_s is investigated as a function of Γ_l . Figure 3 shows the fitting of the experimental result of the intensity-dependent absorption coefficient by the expression $\alpha = \alpha_1 / (1 + I/I_s) + \alpha_2$, where α is the absorption coefficient, I is the laser power density, and α_1 and α_2 are fitting parameters. The obtained saturation power density I_s is shown by arrows in Fig. 3. The saturation power densities thus obtained are plotted as a function of the laser

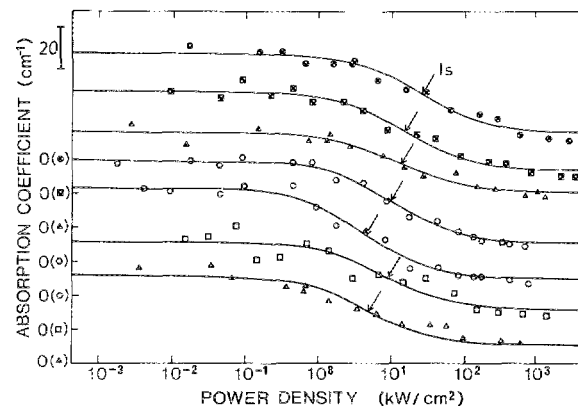


FIG. 3. Laser power density dependence of the absorption coefficient at the Z_3 exciton resonance at 77 K. Experimental points are shown by various symbols corresponding to the laser linewidth Γ_l (meV). The least-squares-fitted results are shown by solid lines. Open circles, open hexagons, solid triangles, and solid squares represent experimental points in cases where the laser linewidth is 0.10, 0.32, 0.51, 0.74, 0.96, 1.23, or 1.70 meV, respectively.

linewidth Γ_l in Fig. 4. The saturation power density increases with the increase of the laser linewidth, as expected. By fitting Eq. (3) to the experimental results, we obtained the homogeneous linewidth of the Z_3 exciton in CuCl at 77 K. It is $0.18 \pm_{0.05}^{0.03}$ meV.

We can easily obtain the homogeneous broadening at elevated temperatures because the phonon broadening is dominant. Reversely, we must estimate the homogeneous broadening at low temperatures by extrapolating the phonon broadening contribution. The calculation based on Eq. (1) gives 0.1 meV to the homogeneous width of the Z_3 excitons at 77 K in fairly good agreement with the result of the laser saturation spectroscopy. Therefore, the experiments on the temperature dependence of the linewidth support our decision on the homogeneous width. At low temperatures, the homogeneous width is expected to decrease much more, because the phonon broadening is reduced. Experimental demonstration that the saturation power density depends on Eq. (3) suggests that it decreases much more at low temperatures.

Equation (2) informs us that the transition dipole moment $|\mu|$ is determined, if we obtain I_s , T_2 , and T_1 . The luminescence lifetime of Z_3 excitons was measured to be 610 ps at 77 K under band-to-band excitation by using ultraviolet picosecond pulses (3.42 eV) and a synchroscan streak camera. Using the values of $I_s = 2.3 \pm 1.0$ kW/cm², $\hbar/T_2 = 0.18 \pm_{0.05}^{0.03}$ meV, and $T_1 = 610$ ps, we can obtain the value of $|\mu|$ to be $5.1 \pm_{0.5}^{0.7} \times 10^{-18}$ esu cm ($5.1 \pm_{0.5}^{0.7}$ debye) for a CuCl microcrystal. The oscillator strength f for a unit cell in bulk CuCl is 5.8×10^{-3} . This corresponds to the dipole moment of 0.40×10^{-18} esu cm (0.40 debye), because the transition dipole moment $|\mu|$ and the oscillator strength f are related to each other by the equation $f = 2m_0\hbar\omega(|\mu|/e\hbar)^2$, where m_0 is the electron mass and e is the electron charge. Therefore, the transition dipole moment for a CuCl microcrystal is enhanced by about 13. The coherent volume in a CuCl microcrystal is about 160 times that of the unit cell but is not extended for the whole microcrystal volume as theory expected.^{2,3} In fact, the whole microcrystal is considered to be coherent, because the energy split between the first and second quantum levels in a CuCl microcrystal whose radius is 6.1 nm is 15 meV and is larger than $\Gamma_h = 0.18 \pm_{0.05}^{0.03}$ meV. We cannot explain this discrepancy. We may have to measure T_1 under the resonant excitation of the Z_3 excitons.

In summary, the homogeneous width of Z_3 exciton absorption spectra in CuCl microcrystals was measured by using laser saturation spectroscopy for the first time. It was $0.18 \pm_{0.05}^{0.03}$ meV at 77 K for CuCl microcrystals whose mean radius is 6.1 nm. The extrapolation of the temperature broadening of the Z_3 exciton absorption linewidth to 77 K also supported the result. The laser saturation spectroscopy also suggests that the transition dipole moment for a CuCl

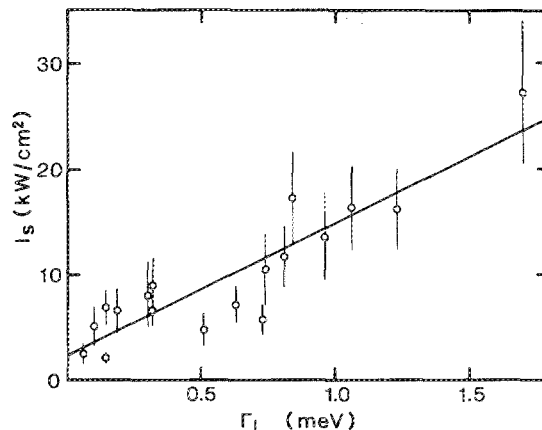


FIG. 4. Saturation power density as a function of the laser linewidth. The solid line is the fitted result based on the equation $I_s = \epsilon_0 c \hbar (\Gamma_h + \Gamma_l) / (2|\mu|^2 T_1)$. The experimental uncertainties mainly come from the uncertainty in the measurement of the excited area.

microcrystal is about 13 times that for a unit cell in bulk CuCl.

The authors would like to express their sincere thanks to Professor E. Hanamura at the University of Tokyo for the critical reading of the manuscript and enlightening discussions. They are indebted to H. Tanaka and Y. Yamada for the sample preparation and the lifetime measurement. This work was supported in part by Grant-in-Aid No. 01604515 for Scientific Research on Priority Areas, New Functionality Materials—Design, Preparation and Control—by the Ministry of Education, Science and Culture of Japan.

¹A. I. Ekimov, A. I. Efros, and A. A. Onushchenko, *Solid State Commun.* **56**, 921 (1985).

²E. Hanamura, *Solid State Commun.* **62**, 465 (1987).

³E. Hanamura, *Phys. Rev. B* **37**, 1273 (1988).

⁴Y. Masumoto, M. Yamazaki, and H. Sugawara, *Appl. Phys. Lett.* **53**, 1527 (1988).

⁵J. Feldmann, G. Peter, E. O. Göbel, P. Dawson, K. Moore, C. Foxon, and R. J. Elliott, *Phys. Rev. Lett.* **59**, 2337 (1987).

⁶E. Hanamura, *Phys. Rev. B* **38**, 1228 (1988).

⁷E. Hanamura, in *Optical Switching in Low-Dimensional Systems*, edited by H. Haug and L. Bányai (Plenum, New York, London, 1989), p. 203.

⁸T. Itoh, Y. Iwabuchi, and M. Kataoka, *Phys. Status Solidi B* **145**, 567 (1988).

⁹D. A. B. Miller, D. S. Chemla, D. J. Eilenberger, P. W. Smith, A. C. Gosard, and W. T. Tsang, *Appl. Phys. Lett.* **41**, 679 (1982).

¹⁰Y. Kaifu and T. Komatsu, *Phys. Status Solidi B* **48**, K125 (1971).

¹¹Y. Toyozawa, *Progr. Theor. Phys.* **27**, 89 (1962).

¹²In *Landolt-Börnstein—Numerical Data and Functional Relationships in Science and Technology, Vol. 17b Semiconductors—Physics of II-VI and I-VII Compounds, Semimagnetic Semiconductors*, edited by O. Madelung (Springer, Berlin, 1982), p. 255.

¹³K. Shimoda, *Introduction to Laser Physics* (Springer, Berlin, 1986), Chap. 8.

¹⁴J. Hegarty and M. D. Sturge, *J. Opt. Soc. Am. B* **2**, 1143 (1985).