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Size-dependent radiative decay of excitons in CuCl semiconducting quantum spheres embedded in glasses

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We report the radiative-decay behavior of Wannier excitons confined in CuCl semiconducting microcrystallites with radii R of 18–77 Å in glasses. We have observed that the radiative-decay rate is proportional to $R^{2.1}$. This confirms the theoretical prediction for the size dependence of the radiative-decay rate of "zero-dimensional excitons" in quantum spheres. This decay of the exciton is a super-radiant decay in the sense that a coherent polarization is involved.

Recently, quantum size effects of photoexcited carriers and excitons have attracted much attention in low-dimensional semiconductors. In quantum-well structures of GaAs/$Al_xGa_{1-x}As$ thin films, an electron or an exciton is one-dimensionally confined in an ultrathin layer.[1] In tiny semiconducting microcrystallites embedded in glasses,[2–4] a three-dimensional confinement is fulfilled and thus the electronic structure is expected to show zero-dimensional features,[5] since the glass provides a deep confinement potential in all three directions. In particular, linear and nonlinear response to the light can exhibit new and interesting properties compared to the thin films and conventional bulk crystal.[6,7] The recent theoretical studies[7–10] have predicted the enhancement of the oscillator strength and the third-order susceptibility for confined excitonic systems.

In the three-dimensional confinement of Wannier excitons, there appear two limiting situations according to the ratio of the crystallite radius R to the effective Bohr radius a_B.[10,11] For $R/a_B \leq 2$, electrons and holes are individually confined and this confinement is called as the individual particle confinement or the confinement of the relative motion of excitons. For $R/a_B \geq 4$, on the other hand, the character of the exciton as a quasiparticle is well conserved and the translational motion is confined. In this regime, the oscillator strength *per unit volume* f_1 for the exciton in the ground state is almost constant but the oscillator strength *per a quantum sphere* Vf_1 is proportional to the volume V of the microcrystallite.[10] Therefore, if the three-dimensionally confined exciton is coherently excited in a microcrystallite to maintain the coherence of the wave function, such an exciton has the giant oscillator strength. Consequently, the radiative-decay rate is enhanced depending on the volume of a microcrystallite.

In this paper, we report the experimental observation of the size-dependent radiative decay of Wannier excitons in CuCl semiconducting quantum spheres. The study by time-resolved spectroscopy in picosecond region was performed on excitonic systems in CuCl microcrystallites with radii of 18–77 Å which are embedded into silicate glasses. Translational motion of Z_3 excitons is three-dimensionally confined, since the crystal size to effective Bohr radius R/a_B is in the range of 3–10 ($a_B = 6.8$ Å). Lifetime measurements of photoluminescence allowed us to find that the radiative decay times of Z_3 excitons are proportional to $R^{2.1}$, which is in reasonable agreement with the theoretical prediction R^3. These results show that radiative behavior of the "zero-dimensional excitons" is completely different from the bulk excitons whose decay rate is independent of the crystal size.

The CuCl microcrystallites used in the present study were obtained by heat treatments of silicate glasses doped with CuCl. When the glass was annealed at a temperature in the range 520–650 °C and for a duration from 2–60 min, the diffusive decomposition of supersaturated solid solution produces the CuCl microcrystallites with radii in the range 18–77 Å. These microcrystallites are expected to be spherical particles, since the heat-treatment temperature exceeds the melting temperature of CuCl.[2] Ekimov, Efros, and Onushchenko have given the experimental relationship between the particle size and the lowest energy of the confined Z_3 exciton from the measurements of the small-angle x-ray scattering and optical absorption:[12]

$$\hbar\omega_{Z_3} = E_g - E_{ex} + 0.67\frac{\hbar^2\pi^2}{2M_sR^2}, \quad (1)$$

where $E_g - E_{ex}$ is the Z_3 exciton energy of the bulk crystal and M_s is the translational mass equal to $(1.9 \pm 0.2)m_0$ for the CuCl microcrystallites. Therefore, the sizes were determined by adopting this relation to the confinement energies obtained from luminescence peak shifts of Z_3 excitons compared to the bulk exciton energy.

The lifetime measurements were performed using a cw mode-locked Nd:YAG laser (YAG denotes yttrium aluminum garnet), a synchronously mode-locked dye laser, and a time-correlated single-photon counting method. The exciting light with ~375 nm of wavelength and ~5 ps of pulse width was obtained by the optical mixing of a fundamental beam of the Nd:YAG laser and a dye laser beam with ~580 nm by a β-BaB_2O_4 crystal. The time resolution of about 30 ps was obtained for decay curves using a convolution analysis.[13]

Figure 1 represents emission spectra of CuCl microcrystallites with different sizes of 77 K with excitation wavelength of ~375 nm. An emission band is observed at higher energy sides of the Z_3 exciton energy of the bulk

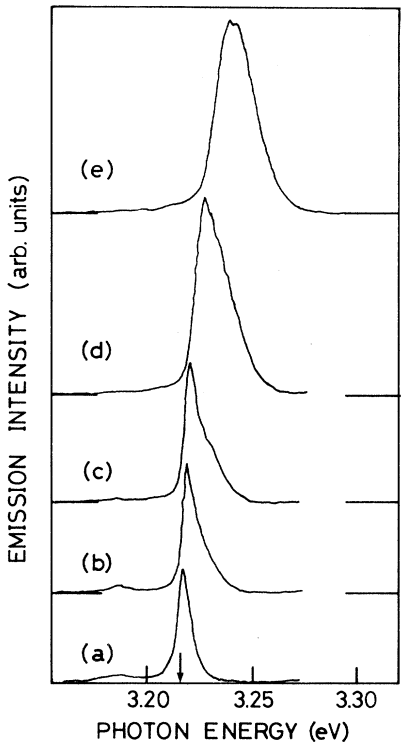

FIG. 1. Emission spectra of CuCl microcrystallites embedded in glasses with different sizes at 77 K. Curve *a*, 650 °C for 15 min ($R=77$ Å); *b*, 600 °C for 15 min ($R=61$ Å); *c*, 575 °C for 15 min ($R=51$ Å); *d*, 550 °C for 15 min ($R=33$ Å); and *e*, 520 °C for 30 min ($R=25$ Å). The arrow indicates the Z_3 exciton energy of the CuCl bulk crystal.

crystal. In the crystal-growth procedures, the higher the heat-treatment temperature and the longer the duration, the larger the crystallite size is produced. When the crystal size is decreased from 77 to 25 Å, the energy shift from the Z_3 exciton energy increases from 2.3 to 23 meV. This behavior of emission bands is consistent with the quantum confinement of Z_3 excitons which was observed for the absorption spectra of CuCl embedded glasses.[2,12] We have also measured absorption spectra and indeed reconfirmed the same results. Therefore, the emission band originates from the Z_3 excitons and the translational motion of these excitons are three-dimensionally confined.

We mention that these emissions are very efficient compared to the bulk CuCl crystal indicating the high quantum efficiency of the confined exciton luminescence. Unfortunately, the relative quantum efficiency of the microcrystallite could not be quantitatively discussed from these spectra, since these samples contained the CuCl microcrystallites with the different concentrations. Thus, the relative intensity of the spectra in Fig. 1 does not mean the change in the quantum efficiency.

To investigate the volume-dependent radiative decay of Z_3 excitons, we have measured decay times of Z_3 exciton luminescence in different samples. Figure 2 shows decay curves of the Z_3 exciton band at 77 K. Since the decay behavior was not changed within the emission band, the decay curves measured at the peak position were shown in this figure. Calculating decay curves by the convolution of a kinetics function with the instrumental response, we have obtained decay times. The convoluted curves giving rise to the best fits to the experimental points are shown by solid curves in Fig. 2. In curves *b*–*e*, the temporal behavior can be fitted by single exponential decay. The decay time of the largest microcrystallites with a radius of 77 Å [curve (*b*)] is 80 ps, while the decay time increases to 400 ps for the smaller microcrystallites with a radius of 33 Å [curve (*e*)]. These results suggest the size-dependent decay of exciton luminescence.

When the crystal size is reduced to less than ~25 Å, decay behavior does not exhibit single exponential decay as shown in curve (*f*) of Fig. 2. Consequently, we have calculated decay curves by the convolution assuming the two exponential functions. The decay times 250 and 750 ps are obtained for curve (*f*). The intensity ratio of the two components is dependent on the samples examined. Since the two-exponential decay behavior is noticed for the samples with smaller microcrystallites, the shorter decay time is presumably attributed to the microcrystallites which are strongly influenced by the matrix glass.[14] Therefore, we regard the longer decay times originating from the more ideal microcrystallites as radiative lifetimes in this range of the crystal size.

The obtained decay times of Z_3 excitons are summarized as a function of radii and confinement energies in

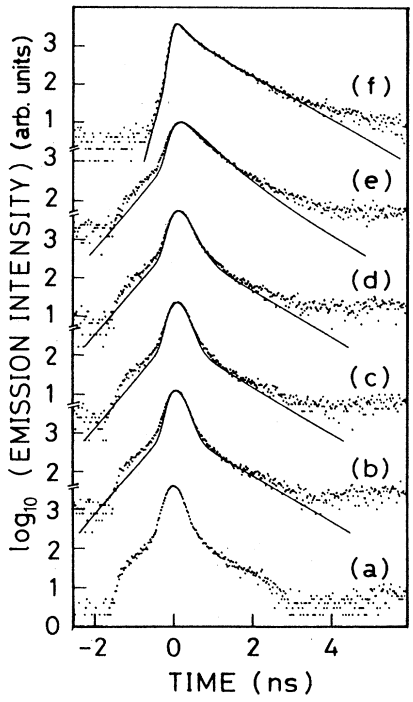

FIG. 2. Decay curves measured at the peak positions of the Z_3 exciton bands of CuCl microcrystallites with different radii. Curve *a*, the instrumental response function for curves *b*–*e*; *b*, $R=77$ Å; *c*, $R=61$ Å; *d*, $R=51$ Å; *e*, $R=33$ Å; *f*, $R=25$ Å. Solid curves represent convoluted ones. The instrumental response function for the curve *f* exhibiting the different response at the negative time is not shown.

Fig. 3. When the radii are decreased from 77 to 21 Å, the decay times (open and closed circles) increase from 80 to 850 ps and they are saturated for $R < 20$ Å. We can find that the measured decay times depend on $R^{-2.1}$.

In a spherical microcrystallite of semiconductors where $R \ll \lambda$, the confined exciton can be a coherent excitation inside the whole microcrystallite and has a macroscopic polarization. The radiative-decay rate of confined excitons in this situation has been calculated. As long as the translational motion of Wannier excitons is confined, the decay rate τ_r^{-1} of the lowest excitons is given by the following expression:[9]

$$\tau_r^{-1} = 64\pi \left(\frac{R}{a_B} \right)^3 \gamma_s, \quad \gamma_s = \frac{4|\mu_{cv}|^2}{3\hbar\lambda^3}, \tag{2}$$

where $|\mu_{cv}|$ is the matrix element of the interband dipole transition. The decay rate is enhanced by the factor $(R/a_B)^3$ compared to the interband transition in the bulk crystal. Accordingly, the radiative lifetimes should depend on R^{-3} if the excitons are three-dimensionally confined in microcrystallites. While the quantum confinement becomes stronger for smaller crystallites, the smaller volume of the crystallite in which a macroscopic or mesoscopic polarization is formed decreases the radiative-decay rate.

We note that this size-dependent lifetime of excitons is analogous to the reduction of lifetime of impurity-bound excitons because of the giant oscillator strength depending on the extent of a bound exciton.[15] The confinement of an exciton in this case results from the Coulomb interaction instead of the externally imposed confinement.

The calculated lifetimes for Z_3 excitons in CuCl microcrystallites are shown by the solid line in Fig. 3. We used the transverse-longitudinal splitting $\Delta_{LT} = 5.7$ meV,[16] dielectric constant $\epsilon = 5.59$ (Ref. 16) and $a_B = 6.8$ Å for the calculation. As shown in Fig. 3, the values of the experimental lifetimes are in good agreement with the calculated ones in the range 21–80 Å without any adjustable parameters. This agreement confirms that the observed lifetimes are mainly determined by the radiative recombination of the confined exciton.

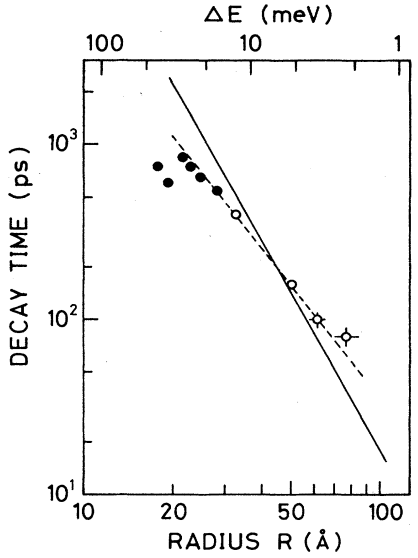

FIG. 3. The decay times of the Z_3 excitons confined three dimensionally as a function of the radius R (the confinement energy ΔE). The open circles represent the decay times determined from the single exponential decay and the closed circles represent the longer decay times of two-component decay. The dashed line and solid line show the dependence of $R^{-2.1}$ and the calculated radiative lifetimes, respectively.

The observed radius dependence of the lifetimes is $R^{-2.1}$, which is smaller than the expected dependence of R^{-3}. In the theoretical model, the infinite barrier potential is assumed outside the quantum sphere consisting of the ideal crystal and the effect of the polarization charge induced at the surface is neglected. In the CuCl microcrystallites embedded in glasses, the confinement potential of the glass is finite and the dielectric constants are different for two materials. Since the finite potential barrier weakens the quantum confinement for the smaller radius, the radius dependence of the decay rate is expected to be reduced. Considering the validity to directly apply this model to our system, this discrepancy of the R dependence is rather acceptable. Therefore, the general agreement of the observed results with the theory allows us to conclude that the radiative-decay rate of the confined Z_3 exciton is nearly volume dependent. Since the microcrystallites with a radius $R \ll \lambda$ are well separated from each other in the glass matrix (volume fraction $\leq 1\%$), the condition that each CuCl microcrystallite interacts independently with the light is fulfilled. Therefore, this size-dependent decay of the confined exciton is the superradiant behavior in the sense that the coherent polarization is involved.[17,18]

The large radiative-decay rate in the small microcrystallite can be also interpreted in terms of the vanishing of the polariton effect. In bulk crystals, the translational motion of the exciton is designated by a wave vector **K** because of the translational symmetry and such an exciton is coupled to the photon with the same wave vector **K** to form a polariton in the crystal. Since the polariton cannot become an external photon unless it is transported to the crystal surfaces, the radiative rate is very small. In the microcrystallite with $R < \lambda$, however, the polariton concept and the translational symmetry break down. Since the exciton is no more trapped in the bulk, it can radiatively decay with a very short lifetime by its macroscopic polarization.

Here, we notice the deviation from the theory for $R < 20$ Å. Since the confinement of the relative motion of excitons appears simultaneously in this range ($R/a_B < 3$), the decrease in the oscillator strength per quantum sphere as a function of R is suppressed as discussed by Kayanuma.[10] Therefore, we can expect the suppression of increase in the lifetimes. However, an alternative explanation is related with the effect of the nonradiative transition on the exciton decay for the smaller microcrystallites in this range. Although we have regarded the longer decay times as the radiative lifetimes, nonradiative processes arising from the surface imperfections of CuCl microcrystallites might affect the exciton decay for the smaller crystal size of $R/a_B < 3$.

It is worth mentioning the possibility of the size-dependent *nonradiative* recombination proposed by Wang *et al.*[19] In CdS microcrystallites with the radii of smaller than 20 Å ($R/a_B < 0.7$), the electron and the hole are trapped by the surface charged defects at different locations. This trapping makes the nonradiative recombination less efficient, which depends on the microcrystallite sizes because of the surface to volume ratio. This may be true for the electron-hole recombination in the regime of the individual particle confinement, since the electron and the hole can be separately trapped. In CuCl microcrystallites studied here, however, the ratio R/a_B is larger than three and the exciton exhibiting the confinement of the translational motion is stably formed. Thus, such suppression of the nonradiative recombination might be observed for the smaller microcrystallites than for those studied here.

In conclusion, we have performed the measurements of the radiative lifetimes of Wannier excitons which are confined in CuCl microcrystallites in glasses. We have demonstrated that the lifetimes depend upon $R^{-2.1}$ which is in reasonable agreement with the theoretical prediction R^{-3}. Such nearly volume-dependent radiative decay can be widely observed in other semiconducting quantum spheres as long as the three-dimensional confinement of the translational motion of excitons is fulfilled. Furthermore, the formation of coherent excitons will give rise to the important result of the large optical nonlinearity due to the deviation from ideal bosons.[9]

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