SPATIAL DIFFUSION OF HIGHLY CREATED EXCITONS IN CdS

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ABSTRACT

The exciton density is determined in CdS from the magnetic field dependence of the triplet-exciton emission intensity. The result shows that the exciton density is saturated markedly for very intense excitations by a nitrogen laser. This behavior is analyzed in terms of the diffusion process of optically created particles from the generated surface to the interior of the crystal. The diffusion length is found to be enhanced by two orders of magnitude for high excitations. This fast diffusion is ascribed to the high-density electron-hole plasma created at the crystal surface.

In the study of highly excited states of materials, one of the fundamental parameters is the density or the number of the optically created particles. This has been investigated extensively, for instance, in the case of the electron-hole drops in Ge. However, for the particles such as excitons and excitonic molecules in semiconductors, there exist only relatively poor estimations of their densities. In this paper we present a new method to determine the density and distribution of optically created excitons in CdS from the magnetic field dependence of the triplet-exciton emission intensity. The result of an analysis suggests the existence of electron-hole plasma state, which plays an important role in the spatial diffusion of excited particles.

High-purity platelets of CdS were excited by a pulsed nitrogen laser (λ = 337.1 nm, duration 10 nsec) and a cw argon laser (λ = 476.5 nm). Excitation power densities were 1 MW/cm^2 at the maximum in the case of the nitrogen laser and 10 W/cm^2 in the case of the argon laser. Fluorescence spectrum in the region of the free exciton line and its LO phonon sideband was measured at various excitation levels under the

magnetic field H perpendicular to the crystal c-axis. Figure 1 shows the emission spectrum under the excitation power of 10 kW/cm^2 obtained in the configuration of the polarization vector of the emitted light parallel to the c-axis. In this configuration, the longitudinal

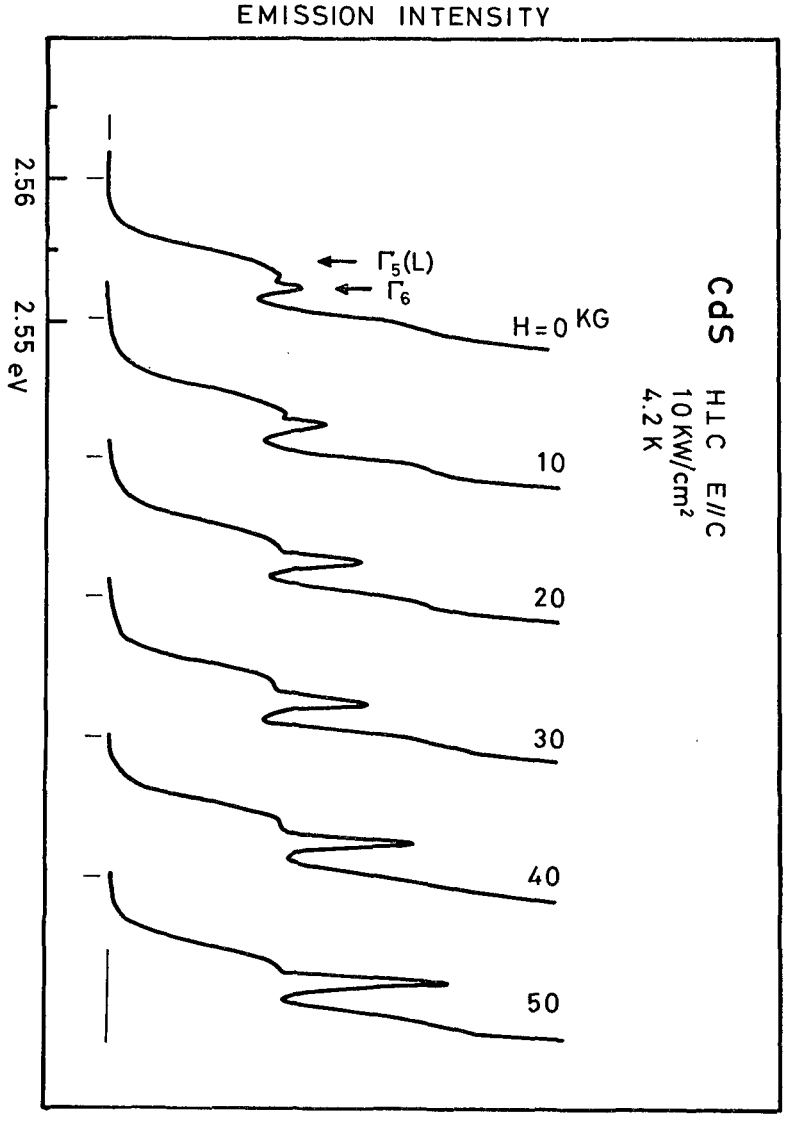

Fig.1. Emission spectra of CdS around the free exciton energy under the excitation of 10 kW/cm^2 with various magnetic fields perpendicular to the c-axis.

component of the singlet exciton emission (Γ_5) and the triplet line (Γ_6) are observed. In Fig.1, we notice that the intensity of the triplet

exciton line is dependent on the magnetic field. This H-dependence was found to vary with excitation power. In the case of weak excitation by an argon laser, the triplet line varies as H^2. On the other hand, the dependence is more gradual for intense excitations by a nitrogen laser and the triplet emission intensity remains almost unchanged with H at the maximum excitation intensity (1 MW/cm^2).

The above result is explained well by the mixing of the triplet state with the singlet due to the interaction between the excitons.[1] The triplet state under the influence of the interaction among excitons and the magnetic field ($H \perp c$) may be expressed as

$$| T > = | \Gamma_6 > + (\gamma + \beta H) | \Gamma_5 > \qquad (1)$$

with $\beta = g_\perp \mu_B / \Delta E$,

where γ is the mixing coefficient due to the high density effect, and $g_\perp$, μ_B, and ΔE are g-value of the triplet state for $H \perp c$, the Bohr magneton, and the exchange splitting energy between the Γ_5 and Γ_6 states, respectively ($g_\perp$ = 1.72 and ΔE = 1.3 meV in CdS). The evaluation of the mixing coefficient γ is made by using Hanamura's theory on high density excitons.[2] For the interaction between the lowest state excitons, the main contribution comes from the exclusion and exchange effects among excitons. Then the mixing coefficient γ is expressed as

$$\gamma = \frac{\rho}{2} \frac{26}{3} \pi a_0^3 E_{ex}^b / \Delta E \ , \qquad (2)$$

where ρ is the density of created excitons, a_0 and E_{ex}^b are the Bohr radius and the binding energy of the exciton, respectively.

The strength of the electric dipole transition from the triplet state f_T is expressed by renormalizing the wave function of eq.(1) as

$$f_T \propto \frac{(\gamma + \beta H)^2}{1 + (\gamma + \beta H)^2} \ . \qquad (3)$$

In Fig.2, H-dependence of f_T is shown for several values of γ (or ρ).

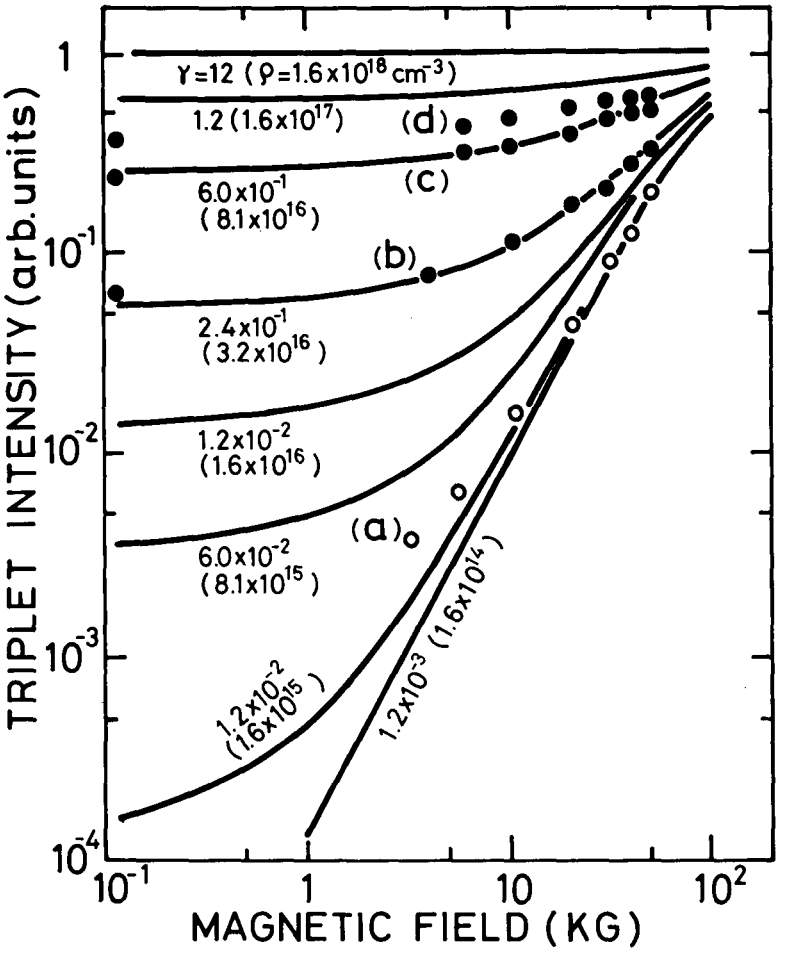

Fig.2. Theoretically derived magnetic field dependence of the electric dipole transition strength of the triplet exciton line (solid line) and the experimentally obtained dependence of the triplet emission intensity (circles). Here, (a), (b), (c) and (d) correspond to the excitation densities of 10 W/cm^2, 10 kW/cm^2, 100 kW/cm^2, and 1 MW/cm^2, respectively.

It is noted that f_T increases in proportion to H^2 for the small values of γ, namely for low density of excitons, while it is independent of magnetic field in large γ limit. Experimental points are also plotted in this figure. We see that the experimental result is explained well by the theoretical dependence. By fitting the experimental H-dependence of the triplet emission intensity with the theoretical curve, we can

determine the exciton density ρ for each excitation level. The exciton density ρ thus obtained is shown in Fig.3 by a solid line. The exciton density is considered to increase linearly for the excitations below 10 kW/cm^2. In the region of higher excitations, however, the density ρ is saturated markedly and tends to a value of 10^{17} cm^{-3}. The critical density ρ_c of the transition from the insulating phase of the exciton to the metallic phase is about 6×10^{17} cm^{-3} in CdS. It is noted that the saturated value of the exciton density is of the same order as ρ_c.

Now let us study another aspect of the exciton emission. The intensity of the phonon-assisted emission line of exciton is considered to represent the total number of the excitons created in the crystal. Excitation power dependence of the intensity of the 2LO phonon sideband of the exciton line was measured simultaneously with the measurement of the zero phonon line of exciton described above. The intensity of the 2LO sideband was found to increase almost linearly with the excitation intensity. This result agrees with the observation reported by Leheny *et al.*[3] The total number of created excitons can be estimated from the photon flux density of excitation under the assumption that the quantum efficiency for exciton generation is unity. An experiment under pico-second pulse excitation revealed that the intensity of the phonon-assisted exciton emission decays in a time of $1 \sim 5 \times 10^{-10}$ sec. We employ the value of 10^{-10} sec for the lifetime of the exciton. Then we obtain the total number of excitons per unit area of the crystal ρ^{tot} as shown in Fig.3 by a dashed curve.

In spite of the strong saturation of the exciton density, ρ^{tot} increases almost in proportion to the excitation power. This result clearly indicates that the diffusion of optically created particles is significant in the case of very intense excitations. Even in the weak excitation case, excitons are concluded to diffuse from the generated surface region into the interior because the diffusion length of exciton of 3.3×10^{-5}cm, which is determined from the experimental value of

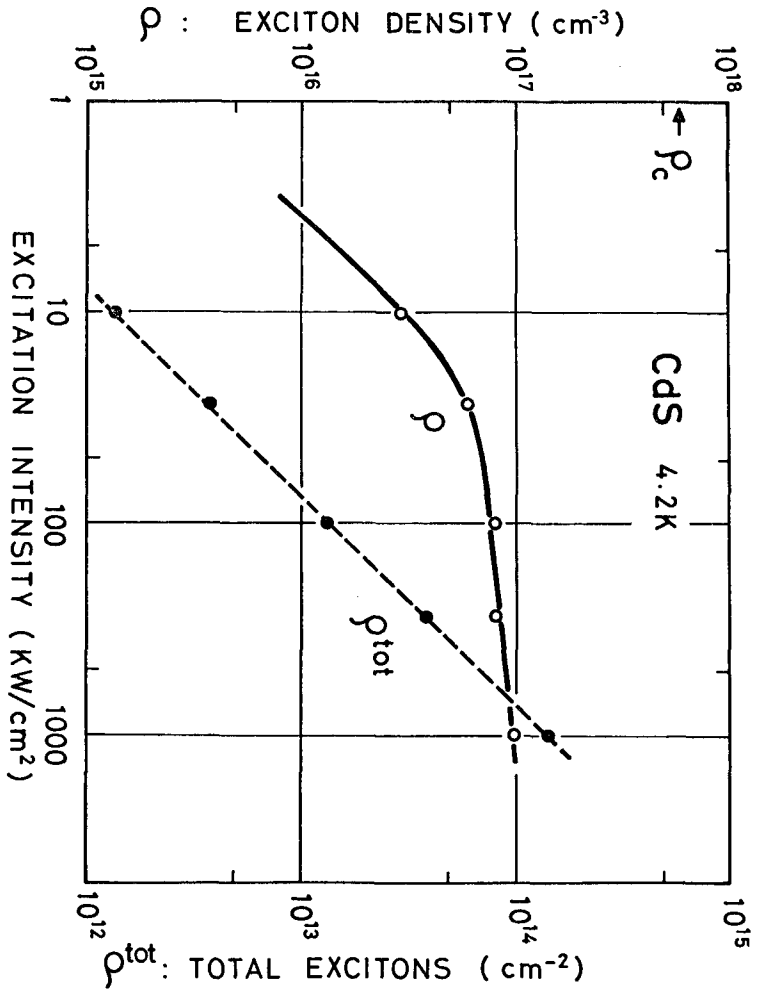

Fig.3. Excitation intensity dependence of the exciton density ρ and the total number of the created exciton per unit area ρ^{tot}.

ρ tot/ρ, is much larger than the reciprocal of the optical absorption coefficient. In the high excitation case, because the diffusion occurs much strongly, we conjecture that some new mechanism becomes dominant above the excitation density of 10 kW/cm^2. Since the saturated value of the exciton density is lower but close to the critical density ρ_c, the metallic electron-hole plasma state is considered to play an important role in this fast diffusion. In fact, if we use the absorption

coefficient of incident photons of 5×10^5 cm^{-1} and the lifetime of the optically created particles of 10^{-10} - 10^{-11} sec, the density of created particles is estimated to be much higher than the critical density of exciton ρ_c under the intense optical excitations above 100 kW/cm^2 (10^{23} photons/$cm^2 \cdot$sec). Thus the state realized just after the excitation is probably the metallic phase of the exciton, *i.e.*, the electron-hole plasma (EHP) state. However, we mainly observe emissions due to excitons such as phonon sidebands of exiton line and also the exciton-exciton collision emission. Thus we consider in the following way. The EHP diffuses very rapidly into the crystal and the plasma density is decreased. Then the excitons are formed from the EHP and luminescence related to the exciton is emitted. We shall calculate the distributions of EHP and excitons on the basis of this consideration. Since the duration of the excitation laser-pulse is 10^{-8} sec and the lifetimes of the excitons and EHP are of the order of 10^{-10} sec or less, the steady state analysis is considered to be a good approximation.

The density of the electron-hole pairs in the plasma in the steady state N(X) is assumed to decrease exponentially with the depth from the surface X as

$$N(X) = Ae^{-X/L} + Be^{-\alpha X} \quad , \tag{4}$$

where L and α are the diffusion length of EHP and the absorption coefficient for the incident photons. This dependence is of the same form as that of the solution of the diffusion equation for the particles optically created within the penetration depth. The coefficients A and B determined from the boundary condition are given by

$$A = N(0) - B$$

$$B = \frac{1}{1 - \alpha^2 L^2} \eta (1 - R) F \alpha \quad ,$$

where N(0) is the density of EHP at the surface and η, R and F are the lifetime of EHP, the reflectivity and the flux density of incident

photons, respectively.

Distribution of the exciton $\rho(X)$ in a steady state can be expressed by the following diffusion equation.

$$D \frac{d^2\rho}{dX^2} - \frac{\rho}{\tau} + \frac{N}{\eta} = 0 \quad , \tag{5}$$

where τ and D are the lifetime and the diffusion coefficient of the exciton. By substituting eq.(4) into eq.(5), $\rho(X)$ is solved as

$$\rho(X) = \left[\rho(0) - A' + B'\right] e^{-\frac{X}{\sqrt{D\tau}}} + A'e^{-X/L} - B'e^{-\alpha X} \quad , \tag{6}$$

in which $A'/A = A'/B = -\tau L^2/\eta(D\tau - L^2)$. The integration of eq.(6) gives the total number of exciton per unit area:

$$\rho^{tot} = \int_0^\infty \rho(X)\, dX \quad . \tag{7}$$

If we use the values of ρ and ρ^{tot} in Fig.3 as $\rho(0)$ and the total number of exciton, the diffusion length L can be determined from the above relations for various excitation levels. We shall use the parameter values of $\tau = 10^{-10}$ sec and $\alpha = 5 \times 10^5$ cm^{-1}. Further, the diffusion coefficient D is calculated as 10 cm^2/sec from τ and the diffusion length of the exciton $(= \sqrt{D\tau})$ in the low excitation case. Under the excitation by intense pico-second pulses the formation time of exciton has been measured to be 10^{-11} sec in CdSe.[4] Since the lifetime of EHP is considered to be the same as the exciton formation time, we employ the value of $\eta = 10^{-11}$ sec.

Figure 4 shows the spatial distributions of the exciton and EHP determined from eqs.(6) and (4) by using the obtained value of L for each excitation level. The result may be summarized as follows. In the case of the excitation of 10 kW/cm^2, excitons remain within the range of about 3×10^{-5} cm, which is determined by the usual diffusion of

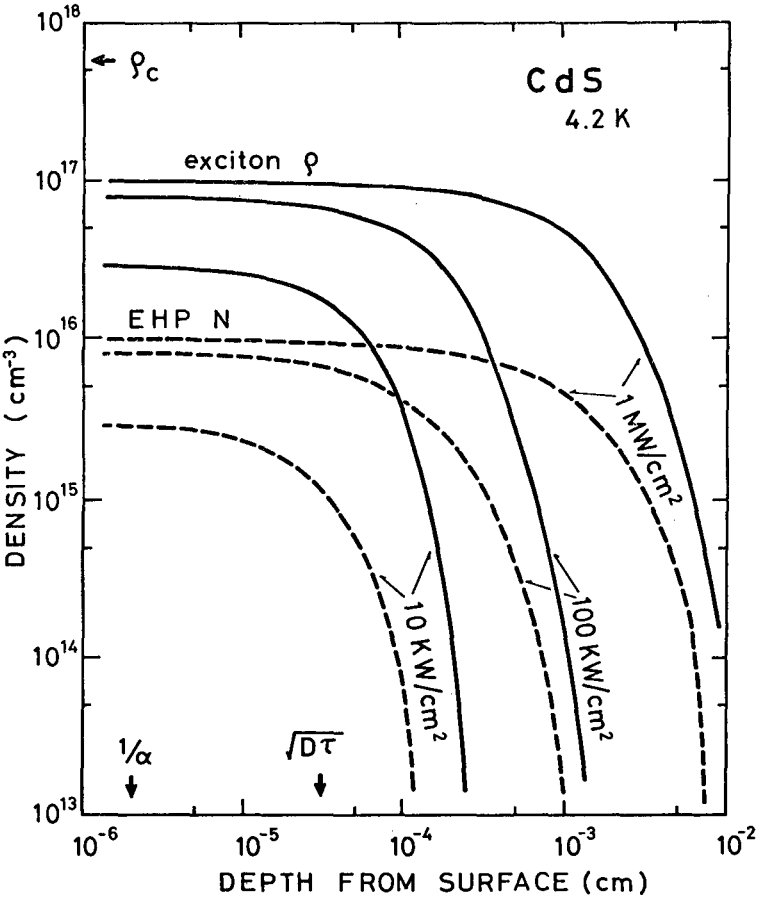

Fig.4. Spatial distribution of the density of the exciton and of the electron-hole plasma N for three excitation intensities.

exciton in low density. When the excitation power is raised, the diffusion length of optically generated EHP increases considerably. The distributed region of EHP reaches the depth of 10^{-3} cm from the surface at the maximum excitation density of 1 MW/cm^2. Since the excitons are formed from the EHP, the distribution of exciton follows that of EHP. On account of the fast diffusion of EHP into the crystal, the density of the exciton is suppressed within 10^{17} cm^{-3} even at the crystal surface. In the steady state, the density of EHP is always one order of magnitude smaller than that of exciton. This is because the EHP has a lifetime much shorter than the exciton.

In conclusion, the spatial distribution and diffusion of excited particles under the intense optical excitation were studied. An analysis suggests that the high density electron-hole plasma state is actually realized in highly excited crystals and plays an important role in the rapid diffusion. However, the emissions due to EHP has not been identified yet. The broad band nature of the EHP emission and also the existence of various intense emission lines near the band edge may cause the difficulty to observe this emission.

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