Rapid radiative decay and enhanced optical nonlinearity of excitons in a quantum well

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An exciton has a macroscopic transition dipole moment because it is a coherent excitation over the whole crystal. The interaction of this exciton with a radiation field, which results in a polariton in a bulk crystal, brings about the rapid radiative decay of the exciton in low-dimensional systems due to breakdown of the translational symmetry. This large decay constant at the same time makes the excitons deviate from ideal bosons so that we have a large third-order optical susceptibility enhanced by the macroscopic transition dipole moment under near-resonant excitation. The nonlinear optical phenomena are expected to have a fast response time of a picosecond in GaAs quantum wells and a subpicosecond in CdS quantum wells through the short lifetime of excitons.

I. INTRODUCTION

Optical nonlinearity and its dynamical response have been extensively studied[1-4] and have attracted much interest recently.[5] The microscopic mechanism, however, is still not well understood. Many nonlinear optical phenomena are described by the third-order optical susceptibility.[1,2] For example, optical bistability is induced by the combined effect of the optical nonlinearity and feedback of emitted light to the optically nonlinear material.[6] This optical nonlinearity consists of the nonlinear refractive index and/or the optical saturation effect which are described by the real and imaginary parts of $\chi^{(3)}(\omega;-\omega,\omega,-\omega)$, respectively. In order to obtain more effective information processing and storage from optically bistable devices, a nonlinear optical material with larger $\chi^{(3)}$ and faster response is eagerly looked for. In this paper, we propose novel microscopic mechanisms to enhance $\chi^{(3)}$ and to obtain a fast response of the order of subpicoseconds by using excitonic processes in quantum-well systems.

The exciton is a coherent elementary excitation over the whole crystal. As a result, it has a macroscopic transition dipole moment and shows sharp and strong absorption peaks in ideal cases. In the bulk crystal, this exciton can interact with a photon which has the same wave vector due to the translational symmetry of the system. As a result, the polariton, i.e., a hybridized mode of exciton and photon, is formed. The decay of the exciton in the bulk crystal is possible only by a leak of the polariton through the surface of the crystal or by radiative and nonradiative recombination at crystal imperfections. In a two-dimensional quantum-well system, on the other hand, we can show that the exciton can decay superradiantly through its macroscopic transition dipole moment in of the order of a picosecond in GaAs quantum wells and a subpicosecond in CdS quantum wells. This strong radiative decay also makes the excitons in this system deviate from ideal bosons. This results in a finite nonlinear optical susceptibility. Unless the exciton-exciton interaction and the relaxation of the exciton are finite, the exciton behaves as an ideal boson so that it cannot show any nonlinearity. In addition to this, the macroscopic transition dipole moment of the exciton enhances the optical nonlinearity. As a result, we can expect an enhanced optical nonlinearity with subpicosecond response for excitons in quantum-well systems.

First, excitons in a bulk crystal (three-dimensional system) and a quantum sphere (zero-dimensional system) are compared as an introduction to the discussion of the quantum well in Sec. II. Then we will discuss rapid radiative decay of the excitons in a quantum well (two-dimensional system) in Sec. III. Finally combining the macroscopic transition dipole moment and the very rapid radiative decay of excitons in the quantum well, we discuss in Sec. IV the advantage of the quantum-well exciton as a nonlinear optical material and the conditions to make full use of these advantages to obtain large $\chi^{(3)}$ and fast response of the nonlinear optical phenomena, e.g., fast switching between two states of high and low transmission in the optically bistable system under weak pumping power. Section V is devoted to a conclusion and discussion.

II. RADIATIVE DECAY OF EXCITONS IN A QUANTUM SPHERE

Excitons[7] in semiconductors can be described as Wannier excitons in the effective-mass approximation. The envelope function of the $(\nu\mathbf{k})$ exciton is represented as

$$\Psi_{\nu\mathbf{k}}=\frac{1}{\sqrt{V}}\exp(i\mathbf{k}\cdot\mathbf{R})\Phi_{\nu}(\mathbf{r}) , \tag{1}$$

where V is the crystal volume, $\mathbf{R}$ and $\mathbf{k}$ are the coordinate and the corresponding wave vector of the center-of-mass motion, and $\Phi_{\nu}(\mathbf{r})$ denotes the relative motion of the electron and hole in the quantum state ν. Then the exciton-radiation interaction is described by the following Hamiltonian:

$$\mathcal{H}'=-\sum_{\nu}\sum_{\mathbf{k}} i\left[\frac{2\pi\hbar}{ck}\right]^{1/2}\omega_{\nu}(\mathbf{k})\Phi_{\nu}(0)\mu_{cv} \times[(a_{\mathbf{k}}+a^{\dagger}_{-\mathbf{k}})b^{\dagger}_{\nu\mathbf{k}}-(a_{-\mathbf{k}}+a^{\dagger}_{\mathbf{k}})b_{\nu\mathbf{k}}] . \tag{2}$$

Here $\hbar\omega_\nu(\mathbf{k})$ is the energy of exciton $(\nu\mathbf{k})$, μ_{cv} is the transition dipole moment between the relevant conduction and valence bands, and $a_{\mathbf{k}}$ $(a_{\mathbf{k}}^\dagger)$ and $b_{\nu\mathbf{k}}$ $(b_{\nu\mathbf{k}}^\dagger)$ are annihilation (creation) operators of photon $\mathbf{k}$ and exciton $\nu\mathbf{k}$, respectively. Note that only the process in which the wave-number vectors are conserved is present because of the translational symmetry in the bulk [three-dimensional (3D)] crystal. As a result, the hybridized modes of the exciton and the photon, i.e., polaritons,[8] are formed without any radiative decay. Because of the large refractive index inside the crystal, the radiation field is trapped as a polariton inside the crystal. The splitting around $ck=\omega_{1s}(k)$ is as large as $2\sqrt{2}(|\mu_{cv}|^2\hbar\omega_{1s}/a_B^3)^{1/2}$ but the radiative decay of the exciton is very weak, as it occurs as a result of leakage from the surfaces, where a_B is the effective Bohr radius of the $1s$ exciton.

Let us consider such a microcrystallite of a quantum sphere as its radius R_0 is smaller than the wavelength λ of the relevant radiation field but much larger than the exciton Bohr radius a_B. Then the exciton binding energy is much larger than quantization energies of individual electrons and holes, so that the exciton effect is essential.[9] Because of the condition $R_0<\lambda$, however, the polariton effect is negligible and can radiate rapidly due to breakdown of the translational symmetry at surfaces, as shown in the following.

The envelope function of an exciton[9-11] in these quantum spheres is described as

$$\Psi_{nlm}(\mathbf{R},\mathbf{r})=F_{nlm}(R,\theta,\phi)\Phi_0(\mathbf{r}) ,$$

where $\Phi_0(\mathbf{r})$ denotes the relative motion of electron and hole in the lowest exciton state and F_{nlm} the center-of-mass motion:

$$F_{nlm}=Y_{lm}(\theta,\phi)\frac{\sqrt{2}}{R_0\sqrt{R}}\frac{J_{l+1/2}(k_{ln}R)}{J_{l+3/2}(k_{ln}R_0)} .$$

Here Y_{lm} is the spherical function and J_ν the Bessel function of νth order.

The correct boundary condition for $\Psi_{nlm}(\mathbf{R},\mathbf{r})$ should be imposed on at $R=R_0-a_B/2$. However, we are discussing the case $a_B\ll R_0\le\lambda$ so that a_B was neglected in comparison to R_0 here and hereafter. For the optically allowed state of angular momentum $\hbar l=0$ and its component $\hbar m=0$, $k_{0n}R_0=\pi n$ $(n=1,2,\ldots)$ and its eigenenergy is

$$E_n\equiv\hbar\omega_n=E_g-E_{\text{exc}}^b+\frac{\hbar^2\pi^2n^2}{2MR_0^2} .$$

Here E_g is the energy gap between the relevant conduction and valence bands and M is the center-of-mass motion. The transition dipole moment of the optically allowed $(n00)$ exciton[9] is

$$\left\langle\Psi_{n00}\left|\sum_i(-e\mathbf{r}_i)\right|\Psi_g\right\rangle=\boldsymbol{\mu}_{cv}\Phi_0(0)\frac{2}{n}\left[\frac{2}{\pi}\right]^{1/2}R_0^{3/2} , \quad (3)$$

where $|\Psi_g\rangle$ denotes the crystal ground state and $|\Psi_{n00}\rangle$ the excited state with the envelope function Ψ_{n00} in which an electron is excited into the conduction band and a hole is created in the valence band. Because of this, the interband transition dipole moment $\boldsymbol{\mu}_{cv}$ appears in Eq. (3). Then the electron-radiation interaction is described as

$$\mathcal{H}'=-\frac{4i}{\sqrt{V}}\Phi_0(0)R_0^{3/2}\sum_n\sum_{\mathbf{k}}\frac{E_n\hat{\mathbf{e}}_{\mathbf{k}}\cdot\boldsymbol{\mu}_{cv}}{n\sqrt{\hbar ck}}(a_{\mathbf{k}}b_n^\dagger-a_{\mathbf{k}}^\dagger b_n) .$$

Here $\hat{\mathbf{e}}_{\mathbf{k}}$ is a unit polarization vector of the radiation field and the antiresonant terms are neglected. The radiative decay rate 2γ of the lowest-energy exciton (100) is calculated in terms of Fermi's golden rule as follows:

$$2\gamma=\frac{2\pi}{\hbar}\sum_{\mathbf{k}}|\langle\Psi_g|\mathcal{H}'|\Psi_{100}\rangle|^2\delta(E_{100}-\hbar\omega_{\mathbf{k}})$$
$$=64\pi\left[\frac{R_0}{a_B}\right]^3\gamma_s . \quad (4)$$

Here $\hbar\gamma_s\equiv4|\mu_{cv}|^2/3\lambda^3$ is the decay rate from the conduction to valence band for the wavelength $\lambda=2\pi c\hbar/E_{100}$. The summation over $\mathbf{k}$ was replaced by the integral

$$\sum_{\mathbf{k}}=\frac{2V}{(2\pi)^3}\int\frac{\omega^2}{c^3}d\omega\,d\Omega$$

and we assumed the isotropic case:

$$\int|\hat{\mathbf{e}}_{\mathbf{k}}\cdot\boldsymbol{\mu}_{cv}|^2d\Omega=\frac{4\pi}{3}\mu_{cv}^2 .$$

Note the enhancement of the exciton decay rate by the factor $64\pi(R_0/a_B)^3$ in Eq. (4). This comes from the fact that the exciton is a coherent excitation over the quantum sphere and has a macroscopic polarization given by Eq. (3). This decay is a super-radiant decay in the sense that the coherent polarization is involved. Note here again that $R_0<\lambda$. Otherwise multiple interaction between the exciton and the radiation field works in bringing about the polariton effect and Eq. (4) is not justified. Because of $R_0\gg a_B$, however, the exciton effect works so that the coherent excitation as an exciton works over the quantum sphere.

Magnitude of the band-to-band transition dipole moment $\boldsymbol{\mu}_{cv}$ is estimated from the transverse-longitudinal splitting $\hbar\Delta_{\text{LT}}$ of the bulk exciton by the relation

$$\hbar\Delta_{\text{LT}}=\frac{4\pi}{\epsilon_0}|\boldsymbol{\mu}_{cv}\Phi(0)|^2=\frac{4|\boldsymbol{\mu}_{cv}|^2}{\epsilon_0a_B^3} , \quad (5)$$

where ϵ_0 is the static dielectric constant of the bulk crystal. The radiative decay rate $2\gamma_n$ of the higher excitons $(n00)$ in the quantum sphere is reduced by the factor of $1/n^2$, i.e.,

$$2\gamma_n=\frac{2\gamma}{n^2} .$$

This is derived by using Eq. (3). Therefore in order to get the enhanced radiative decay from the lowest exciton state (100), this state should be well separated from the higher excited states $(n00)$ $n\ge2$, i.e.,

$$E_{200}-E_{100}=\frac{3\hbar^2\pi^2}{2MR_0^2}\geq 2\gamma=64\pi\left[\frac{R_0}{a_B}\right]^3\gamma_s\ . \tag{6}$$

When we use the following numerical values corresponding to GaAs and CdS: for GaAs $a_B=100$ Å, $E^b_{\rm exc}=5$ meV, $\hbar\Delta_{\rm LT}=0.1$ meV,[12] $\lambda=8000$ Å, $\epsilon_0=12$, and for CdS $a_B=30$ Å, $E^b_{\rm exc}=30$ meV, $\hbar\Delta_{\rm LT}=1$ meV,[13] $\lambda=5000$ Å, and $\epsilon_0=8$, the condition (6) is satisfied for the spheres with radius $100\ll R_0<1000$ Å (GaAs) and $30\ll R_0\leq 450$ Å (CdS). These lengths are much smaller than the relevant wavelength λ. Then the radiative decay rate $2\gamma=2.5\times10^{11}$ sec^{-1} (GaAs, $R_0=1000$ Å) and 0.8×10^{12} sec^{-1} (CdS, $R_0=450$ Å). These are of the order of picoseconds.

This coherent decay is observable only for such low temperature as the lowest exciton state is dominantly populated, i.e.,

$$\frac{3\hbar^2\pi^2}{2MR_0^2}\geq kT\ .$$

For a CdS sphere with radius $R_0\leq 450$ Å, this radiative decay will be observable below 7 K, and for a GaAs sphere with radius $R_0\leq 1000$ Å, this is below 1.7 K. It is, however, controversial whether this radiative decay was really observed. This will be discussed in Sec. V. The exciton-exciton interaction plays a more important role in making the excitons in microcrystallites deviate from ideal bosons and consequently in bringing about the enhanced nonlinear optical susceptibility, as was discussed in Ref. 9.

III. RAPID RADIATIVE DECAY OF EXCITONS IN A QUANTUM WELL

Rapid radiative decay of excitons in a quantum sphere was restricted to the sphere with the size smaller than the wavelength. As a result, the range of exciton coherency is limited by this size. Excitons in a quantum well are expected to keep dual merits of coherent nature on the two-dimensional plane of the quantum well and superradiant decay in one direction perpendicular to the quantum well. Let us consider such a quantum-well system as the well thickness l satisfies

$$l\sim a_B\ll\lambda\leq L\ , \tag{7}$$

where L^2 is the area of the quantum well. We decompose wave vector $\mathbf{k}$ into $k_z\hat{\mathbf{z}}$ and $\mathbf{q}$ for the components perpendicular and parallel to the surface, respectively. We are now interested in the exciton state with the lowest energy as well as the largest oscillator strength:

$$\Psi_{\mathbf{q}0,1,1}(\mathbf{R},\mathbf{r},z_e,z_h)=\frac{1}{(\sqrt{L^2})^{1/2}}\exp(i\mathbf{q}\cdot\mathbf{R})\times\Phi_0(\mathbf{r})f_1(z_e)f_1(z_h)\ , \tag{8}$$

with

$$f_m(z)=\left[\frac{2}{l}\right]^{1/2}\sin\left[\frac{m\pi z}{l}\right]\ , \tag{8a}$$

$$\Phi_0(\mathbf{r})=\left[\frac{8}{\pi a_B^2}\right]^{1/2}\exp(-2r/a_B)\ . \tag{8b}$$

Here $\mathbf{R}$ and $\mathbf{r}$ describe the exciton coordinates in the plane for the center-of-mass motion and the electron-hole relative motion, respectively. We assumed for simplicity the infinite barrier potential outside the quantum well.[14–17] Then we have the electron and hole quantized state described by Eq. (8a). We took the two-dimensional exciton (8b) for the electron-hole relative motion, and neglected higher states as the interaction with the radiation field is dominated by this lowest state, especially under near-resonant excitation.

The equations of motion for annihilation and creation operators of exciton $b_{\mathbf{q}}$ and $b^\dagger_{-\mathbf{q}}$ and photon $a_{\mathbf{k}}$ and $a^\dagger_{-\mathbf{k}}$ are written as

$$i\frac{d}{dt}b_{\mathbf{q}}=\omega_{\mathbf{q}}b_{\mathbf{q}}+\sum_{k_z}A^*_{\mathbf{q}k_z}(a_{\mathbf{k}}+a^\dagger_{-\mathbf{k}})\ , \tag{9a}$$

$$i\frac{d}{dt}b^\dagger_{-\mathbf{q}}=-\omega_{\mathbf{q}}b^\dagger_{-\mathbf{q}}-\sum_{k_z}A_{\mathbf{q}k_z}(a_{\mathbf{k}}+a^\dagger_{-\mathbf{k}})\ , \tag{9b}$$

$$i\frac{d}{dt}a_{\mathbf{k}}=cka_{\mathbf{k}}+A_{\mathbf{q}k_z}(b_{\mathbf{q}}-b^\dagger_{-\mathbf{q}})\ , \tag{9c}$$

$$i\frac{d}{dt}a^\dagger_{-\mathbf{k}}=-cka^\dagger_{-\mathbf{k}}+A^*_{\mathbf{q}k_z}(b_{\mathbf{q}}-b^\dagger_{-\mathbf{q}})\ . \tag{9d}$$

Note here that the exciton with 2D wave vector $\mathbf{q}$ can couple with the radiation field $\mathbf{k}\equiv(\mathbf{q},k_z\hat{\mathbf{z}})$ because of lack of translational symmetry in the $\hat{\mathbf{z}}$ direction. Therefore we have summations over k_z in Eqs. (9a) and (9b). This gives the radiative decay of excitations. Here $k\equiv(q^2+k_z^2)^{1/2}$ and

$$A^*_{\mathbf{q}k_z}=i\left[\frac{2\pi}{\hbar ckL^2L'}\right]^{1/2}\omega_{\mathbf{q}}\langle\Psi_{\mathbf{q}0,1,1}\,|\,P\,|\,\Psi_q\rangle\ , \tag{10}$$

the exciton transition dipole moment

$$\langle\Psi_{\mathbf{q}0,1,1}\,|\,P\,|\,\Psi_q\rangle=\left[\frac{8}{\pi a_B^2}\right]^{1/2}(L^2)^{1/2}\boldsymbol{\mu}_{cv}\cdot\hat{\mathbf{e}}_{\mathbf{k}} \tag{11}$$

for $qa_B\ll1$. Note here that the macroscopic transition dipole moment of Eq. (11) with the factor $(L^2)^{1/2}$ comes from the 2D coherency of the exciton in the quantum well. The equations of motion (9) are solved as follows:

$$\omega^2-\omega_{\mathbf{q}}^2-2\omega_{\mathbf{q}}\Sigma_{\mathbf{q}}(\omega)=0\ , \tag{12}$$

with the self-energy $\hbar\Sigma_{\mathbf{q}}(\omega)$:

$$\Sigma_{\mathbf{q}}(\omega)=\sum_{k_z}\frac{2ck\,|\,A_{\mathbf{q}k_z}\,|^2}{\omega^2-c^2(q^2+k_z^2)}\ . \tag{13}$$

Here the radiation field is quantized inside the box $L^2\times L'$, where $L'\geq\lambda\gg l$. The factor $|\mu_{cv}\cdot\hat{\mathbf{e}}_{\mathbf{k}}|^2$ is rewritten making use of the fact that the unit polarization vector $\hat{\mathbf{e}}_{\mathbf{k}}$ of the radiation field is perpendicular to $\mathbf{k}\equiv(\mathbf{q},k_z\hat{\mathbf{z}})$ as follows ($\hat{\mathbf{e}}_{\mathbf{k}}$ is abbreviated as $\hat{\mathbf{e}}$ hereafter):

$$|\mu_{cv}\cdot\hat{\mathbf{e}}_{\mathbf{k}}|^2=\mu_{cv}^2\left[\frac{k_z^2}{k^2}|\hat{\mathbf{e}}\times\hat{\mathbf{z}}|^2+\frac{1}{k^2}|\hat{\mathbf{e}}\times\mathbf{q}|^2\right].$$

The real part of self-energy $\hbar\Pi_{\mathbf{q}}(\omega)$ and the radiative-decay rate $\Gamma_{\mathbf{q}}(\omega)$ are evaluated as follows:

$$\begin{aligned}\Pi_{\mathbf{q}}(\omega)&=\mathrm{P}\sum_{k_z}\frac{2ck\,|A_{\mathbf{q}k_z}|^2}{\omega^2-c^2k^2}\\&=2A\,\mathrm{P}\int_0^\infty\frac{dk_z}{\omega^2-c^2(q^2+k_z^2)}\left[\frac{k_z^2}{k^2}|\hat{\mathbf{e}}\times\hat{\mathbf{z}}|^2+\frac{1}{k^2}|\hat{\mathbf{e}}\times\mathbf{q}|^2\right]\\&=\begin{cases}A\left[-q\left[\frac{c}{\omega}\right]^2\pi|\hat{\mathbf{e}}\times\hat{\mathbf{z}}|^2+q\left[\frac{c}{\omega}\right]^2\pi\left|\hat{\mathbf{e}}\times\frac{\mathbf{q}}{q}\right|^2\right] & \text{for } \omega>cq\\ -A\left[\frac{c}{\omega}\right]^2\frac{q^2\pi}{[q^2-(\omega/c)^2]^{1/2}}|\hat{\mathbf{e}}\times\hat{\mathbf{z}}|^2+\cdots & \text{for } \omega<cq\ ,\end{cases}\end{aligned}\tag{14}$$

and

$$\begin{aligned}\Gamma_{\mathbf{q}}(\omega)&=\pi\sum_{k_z}|A_{\mathbf{q}k_z}|^2\delta(\omega-ck)\\&=\pi A\int_0^\infty dk_z\frac{1}{(q^2+k_z^2)^{1/2}}\delta[\omega-c(q^2+k_z^2)^{1/2}]\left[\frac{k_z^2}{k^2}|\hat{\mathbf{e}}\times\hat{\mathbf{z}}|^2+k^{-2}|\hat{\mathbf{e}}\times\mathbf{q}|^2\right]\\&=\begin{cases}\pi A\left[\frac{c}{\omega}\right]^2[(\omega/c)^2-q^2]^{1/2}|\hat{\mathbf{e}}\times\hat{\mathbf{z}}|^2+\pi A\left[\frac{c}{\omega}\right]^2\frac{1}{[(\omega/c)^2-q^2]^{1/2}}|\hat{\mathbf{e}}\times\mathbf{q}|^2 & \text{for } \omega>cq\\ 0 & \text{for } \omega<cq\ .\end{cases}\end{aligned}\tag{15}$$

Here $A\equiv16|\mu_{cv}|^2\omega_{\mathbf{q}}^2/\pi\hbar c^2a_B^2$, and $\hbar\omega_{\mathbf{q}}=E_{\mathbf{q}}$. The summation over k_z was replaced by the integral $(L'/2\pi)\int dk_z$ so that the final result is independent of the quantized volume $L^2\times L'$ for the radiation field as far as $L>\lambda$. A similar result was qualitatively discussed for thin crystal films.[18,19] Under perpendicular incidence of the pump field, the excitons with $\mathbf{q}=\mathbf{0}$ are created. For these excitons, the polariton effect coming from the self-energy $\Pi_{\mathbf{q}}(\omega)$ vanishes and the radiative decay rate $\Gamma_0(\omega)\equiv2\gamma$ is rewritten as follows:

$$\Gamma_0(\omega)=\frac{16|\mu_{cv}|^2\omega_0^2}{\hbar c\,\omega a_B^2}=24\pi\left[\frac{\lambda}{a_B}\right]^2\gamma_s\left[\frac{\omega_0}{\omega}\right]^2,\tag{16}$$

where

$$\gamma_s\equiv\frac{4|\mu_{cv}|^2}{3\hbar\lambda^3}\ .$$

When we confine ourselves to the nearly resonant case $\hbar|\omega_0-\omega|\leq E_{\mathrm{exc}}^b$, the radiative decay rate $\Gamma_0(\omega)$ is almost independent of ω. Then we can define the longitudinal relaxation time $T_1=1/\Gamma_0(\omega_0)=(2\gamma)^{-1}$. The radiative decay rate is enhanced by the factor $24\pi(\lambda/a_B)^2$. This comes from the coherent nature of a 2D exciton with respect to the center-of-mass motion of excitons. The radiative lifetime $T_1\equiv1/\Gamma_0$ of the exciton in the quantum well is estimated using the material parameters for GaAs and CdS given in Sec. II: 2.8 psec ($\Gamma_0=0.36$ meV) for GaAs and 0.6 psec ($\Gamma_0=1.2$ meV) for CdS quantum wells. These values are independent of the well thickness as long as $l\sim a_B\ll\lambda<L$. The values are approximately $a_B=100$ Å and $\lambda=8000$ Å for GaAs and $a_B=30$ Å and $\lambda=5000$ Å for CdS so that the condition $a_B\ll\lambda$ is well satisfied.

This radiative decay process is quenched by thermal ionization of the exciton and thermal relaxation of the center-of-mass motion of the 2D exciton. Here we will discuss these two effects. Once the exciton is scattered into that state of the wave-number vector outside $q_0\equiv\omega_0/c$, the super-radiant decay is prohibited as Eq. (15) shows. A single acoustic-phonon absorption of the 2D exciton is enough to put out the state $\mathbf{q}$ outside $\mathbf{q}_0$. Therefore we evaluate the relaxation rate of the $\mathbf{q}$ exciton by the deformation potential due to the acoustic phonon[20,21] as

$$\Gamma_{\rm ph}(\mathbf{q})=\frac{2\pi}{\hbar}\sum_{q'}\frac{\hbar q'}{2\rho u L^2 l}(D_c-D_v)^2 \times[(n_{q'}+1)\delta(E_{\mathbf{q}-\mathbf{q}'}-E_{\mathbf{q}}+\hbar u q') \times n_{q'}\delta(E_{\mathbf{q}+\mathbf{q}'}-E_{\mathbf{q}}-\hbar u q')] ,$$

where D_c and D_v are the deformation potentials of the conduction and valence bands, respectively, ρ the mass density, u the sound velocity, $n_q=1/[\exp(\hbar u q\beta)-1]$ with $\beta=1/k_BT$, and $E_{\mathbf{q}}=\hbar^2q^2/2M$ with $M=m_e+m_h$. Here we neglected $(q'a_B/4)^2$ in comparison to one. The relaxation rate of the photoexcited exciton $\mathbf{q}=0$ is simplified into the following form:

$$\Gamma_{\rm ph}(0)=\frac{Mq'n_{q'}}{\hbar\rho u l}(D_c-D_v)^2, \quad \text{with } q'=2Mu/\hbar .$$

This is evaluated for the GaAs well with $l=100$ Å as

$$\Gamma_{\rm ph}(0)=1.2\times10^{10}T(\text{in K})\ \text{sec}^{-1} , \tag{17}$$

for $T\gg1.8$ K. Here we used the following material constants of GaAs:[22] $D_v=3.1$ eV, $D_c=-6.5$ eV, $m_e=0.067m$, $m_h=0.45m$, $\rho=5.3$ g/cm^3, $u=4.8\times10^5$ cm/sec. The relaxation rate of the 2D exciton in the CdS well is

$$\Gamma_{\rm ph\parallel}(0)=1.1\times10^{9}T(\text{in K})\,\text{sec}^{-1} \quad (T\gg0.4\ \text{K}) ,$$

$$\Gamma_{\rm ph\perp}(0)=1.2\times10^{10}T(\text{in K})\,\text{sec}^{-1} \quad (T\gg5.6\ \text{K}) ,$$

due to the longitudinal-acoustic phonons propagating along and perpendicular to the c axis, respectively. The following material constants[23] are used for CdS: $D_c-D_v=-1.36$ eV (for the stress e_{zz}), $=-2.28$ (for the stress $e_{xx}+e_{yy}$), $m_e=0.16m$, $m_{h\perp}=0.7m$, $m_{h\parallel}=5m$, $\rho=4.8$ g/cm^3, $u_\perp=4.4\times10^5$ cm/sec, $u_\parallel=1.8\times10^5$ cm/sec. The effect of piezoelectric field on the exciton is estimated to be negligible in comparison to that due to the deformation potential. Thermal ionization time of the optically created exciton was observed to be 0.3 psec at room temperature.[24] If the longitudinal-optical phonons (35 meV) are assumed to ionize the exciton dominantly, the ionization process will be reduced exponentially at low temperature. In conclusion, the superradiant decay overcomes the exciton relaxation and exciton ionization for $T\ll100$ K in both GaAs and CdS quantum wells.

IV. ENHANCED OPTICAL NONLINEARITY

Such elementary excitations as bulk excitons behave as almost ideal bosons, i.e., harmonic oscillators. As long as this approximation is justified, these elementary excitations cannot contribute to nonlinear optical response. Only interactions among excitons, i.e., anharmonic terms and decay and relaxations of excitons, result in finiteness of optical nonlinear response.[9] The third-order optical susceptibility $\chi^{(3)}(\omega;-\omega,\omega,-\omega)$ is obtained by evaluating the contributions of three diagrams in Fig. 1 in the rotating wave approximation. Two lines describe leftward and rightward propagation of the states for the density-matrix operator. Single and double solid lines describe the propagation, respectively, of a single exciton state $|1\rangle$ and of two-exciton state $|2\rangle$, and thin lines that of the electronic ground state. The exciton-exciton interaction works only in the two-exciton state, i.e., for the time interval between t_2 and t_1 in the diagram (1). Then the eigenenergy of this state is obtained as

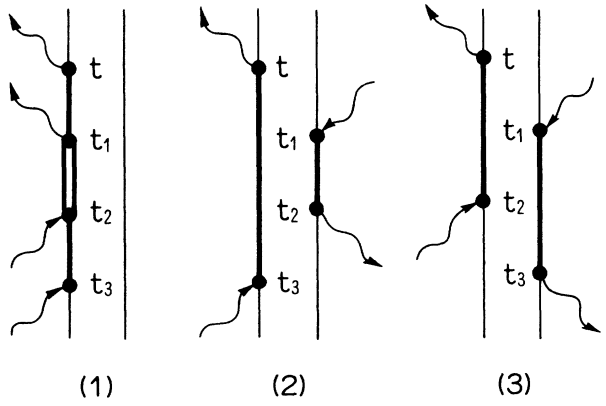

FIG. 1. Feynman diagrams contributing to third-order optical susceptibility in the rotating wave approximation. Two lines on the left- and right-hand sides describe, respectively, leftward and rightward propagation of the states in the density matrix. Single and double solid lines denote a single exciton and a two-exciton state, respectively, and thin line denotes the ground state. The arrows describe the photon absorption or emission.

$$\mathcal{H}|2\rangle\equiv(\hbar\omega_0 b_0^\dagger b_0+\hbar\omega_{\rm int}b_0^\dagger b_0^\dagger b_0 b_0)|2\rangle =2\hbar(\omega_0+\omega_{\rm int})|2\rangle ,$$

while

$$\mathcal{H}|1\rangle=\hbar\omega_0|1\rangle .$$

The exciton is really created for the time interval between t_2 and t_1 in the diagrams (2) and (3). There the longitudinal decay $\Gamma_0=2\gamma\equiv1/T_1$ works while the transverse relaxation $\Gamma=\gamma+\gamma'\equiv1/T_2$ does for the time intervals between t_3 and t_2 and between t_1 and t in the diagrams (1), (2), and (3). Here γ' is the dephasing rate of the exciton. For the interval between t_2 and t_1 in diagram (1), the relaxation rate is 2Γ as two excitons are excited only in the left-hand side. Then the third-order optical susceptibility is calculated according to the methods described in Ref. 9 and Ref. 3 as follows:

$$\chi^{(3)}(\omega;-\omega,\omega,-\omega)=\frac{|P_0|^4}{\hbar^3(\omega-\omega_0+i\Gamma)^2}\frac{1}{(\omega-\omega_0-i\Gamma)} \times\left[\frac{\gamma'}{\gamma}+\frac{2i\Gamma-\omega_{\rm int}}{\omega-\omega_0-\omega_{\rm int}+i\Gamma}\right]\frac{1}{V} . \tag{18}$$

Here P_0 is the transition dipole moment of the lowest exciton and V is the volume of the optically active part of the quantum well L^2l. Let us discuss first the case of

such a low temperature as thermal relaxation of excitons is negligible and the super-radiant decay is dominant, i.e., $\gamma'=0$ and $\Gamma=\gamma$. The exciton is a coherent excitation over the whole optically active region of the quantum well so that the transition dipole moment has the macroscopic enhancement by a factor L/a_B as given by Eq. (11). For such a quantum well of GaAs as $L^2l\sim\lambda^2 a_B$, $\chi^{(3)}$ is estimated to be $|\chi^{(3)}|=0.25$ esu for off-resonance

$$\hbar(\omega_0-\omega)=1 \text{ meV} \gg \hbar\gamma=\hbar\Gamma_0/2=0.18 \text{ meV} ,$$

and for that of CdS, $\chi^{(3)}$ is estimated to be $|\chi^{(3)}|=0.023$ esu for off-resonance

$$\hbar(\omega_0-\omega)=5 \text{ meV} \gg \hbar\gamma=\hbar\Gamma_0/2=0.6 \text{ meV} .$$

Under usual off-resonant conditions $|\omega_0-\omega| \gg \omega_{\text{int}} > \Gamma$, $\chi^{(3)}$ is independent of the well volume because w_{int} in the numerator is proportional to the inverse volume and L^4 coming from $|P_0|^4$ is canceled out by the volume dependence of ω_{int} ($\propto V^{-1}$) and V in the denominator of Eq. (17). On the other hand, the macroscopic enhancement of an order of $(L/a_B)^2$ for $\chi^{(3)}$ under nearly resonant excitation of the 2D exciton comes from the multiple excitation of excitons coherent over the optically pumped region. This is possible as long as spatial coherency both of the pumping light and the exciton in itself is kept. We chose it to be of an order of the light wavelength λ for evaluation of $\chi^{(3)}$.

At room temperature, the lifetime of the exciton in a GaAs quantum well was observed to be 0.3 psec.[24] This is attributed to thermal ionization of the optically created exciton. This fast relaxation results in large deviation of excitons from ideal bosons, but the dissociated electrons and holes persist for a much longer time, of the order of nanoseconds. This process will limit the response time of optical nonlinearity at room temperature. As to the response time of optical nonlinearity, such a low temperature as the present rapid radiative decay dominates over thermal dissociation of excitons is preferable. Because the response time of optical processes is determined by the rapid radiative decay rate 2γ, i.e., $T_1=2.8$ psec for the GaAs well and 0.6 psec for the CdS well. In addition to this fast response, we have the enhancement of $\chi^{(3)}$ due to the macroscopic transition dipole moment of the 2D exciton at those low temperatures and at near-resonant excitation $\hbar|\omega_0-\omega| \leq E_{\text{exc}}^b$.

It is interesting to compare the enhanced $\chi^{(3)}$ and the response time of the optical nonlinearity in the quantum well with those of the microcrystallites.[9] The excitonic enhancement of $\chi^{(3)}$ was not expected for the microcrystallite of GaAs, because the electron mass is very small ($m_e=0.0665m$) and the crystal dielectric constant is very large ($\epsilon_0=12.53$) so that the electron quantization energy becomes much larger than the exciton binding energy. As a result, the exciton effect is reduced. For the close-packed quantum spheres of CdS with the radius 100 Å, $\chi^{(3)}\sim 3.2\times 10^{-6}$ esu under the off-resonance $\hbar|\omega_0-\omega|=5$ meV. For the CdS quantum well $L^2\times l\sim\lambda^2 a_B$, $\chi^{(3)}\sim 2.3\times 10^{-2}$ esu under $\hbar|\omega_0-\omega|=5$ meV. This enhancement in the quantum well mainly comes from the 2D coherent nature of the exciton over the region of λ^2 and the large decay rate Γ_0.

The present $\chi^{(3)}$ consists of a larger imaginary part than real part at the off-resonance energy $|\omega_0-\omega|<\Gamma$ and corresponds to the absorption saturation effect or the state filling effect.[25,26] We have the other merit of this process in addition to the strong resonance enhancement of $\chi^{(3)}$. We are using the real process in contrast to the coherent nonlinear optical process such as the optical Stark effect.[27,28] As a result, we can use the resonant as well as nonresonant excitation and need not prevent the real excitation of excitons, because these excitons can decay and respond in the longitudinal relaxation time of the order of picoseconds or subpicoseconds in these systems as long as other processes do not prevent these excitons from the super-radiant decay.

V. DISCUSSION AND CONCLUSIONS

A few advantages of the semiconductor quantum well as nonlinear optical devices have been pointed out in this paper. Before discussing this point, it is interesting to check whether the rapid decay component of the excitons in microcrystallites is attributed to the rapid radiative process derived in Sec. II. This is because rapid decay of excitons was observed for the quantum sphere of CdS and CdSe,[29–33] but its origin is still controversial. The rapid radiative decay of excitons in GaAs quantum wells is hidden at room temperature by the thermal ionization of excitons in 0.3 psec (Ref. 24) shorter than the radiation decay time of 1.4 psec. This thermal ionization and thermal relaxation are reduced at low lattice temperature as discussed in Sec. III. Schultheis *et al.*[34] observed the transverse relaxation time $T_2=\sim 2-3$ psec for the excitons in the GaAs quantum well at low temperature. The transverse relaxation time T_2 is expressed as

$$\frac{1}{T_2}=\frac{1}{2T_1}+\frac{1}{T_2'}$$

where T_2' is pure dephasing time. The temperature-independent part of $1/T_2$ of an order of a few picoseconds may come from the present radiative decay of excitons $1/2T_1$. The component of $1/T_2$ which increases linearly in the lattice temperature appears to correspond to the thermal relaxation $1/T_2'$, in agreement with Eq. (17) also in the magnitude of the coefficient. We hope that the rapid radiative decay of excitons will be observable at these low temperatures more clearly in a single quantum-well system. Reabsorption in the multi-quantum-well system will partly smear this radiative process.

The large values of third-order optical susceptibility near exciton resonance were observed for the quantum-well system of GaAs.[35,36] This enhancement comes partially from the macroscopic transition dipole moment of the exciton. Under pulse excitation for longer duration than 0.3 psec the excitons are thermally dissociated at room temperature. As a result, Eq. (18) is not applicable in itself to the experimental situation of Refs. 35 and 36.

However, two factors which enhance $\chi^{(3)}$ are at work even in such a situation. First, a large decay constant Γ makes the excitons deviate from ideal bosons, and second, the large transition dipole moment of excitons works also in the excitation process to enhance $\chi^{(3)}$ under near-resonant excitation of excitons. These will be clearly checked at low temperature.

In Sec. IV, we considered the case in which the laser spot was focused on the area with the linear dimension of the optical wavelength. The nonlinear optical susceptibility $\chi^{(3)}$ is dependent on the size of the optically active region as long as the exciton plays the dominant role in $\chi^{(3)}$. Therefore, it is also interesting to check the dependence of $\chi^{(3)}$ on the size of the optically active region. There both the temporal and spatial coherencies of the radiation field as well as the 2D exciton are essential to get the enhancement of $\chi^{(3)}$ through the coherent and macroscopic transition dipole moment of the exciton.

The exciton binding energy in the GaAs quantum well is limited to less than the value $4E^{b}_{\mathrm{exc(3D)}}=20$ meV in the 2D limit. Therefore the excitonic effect may be partially weakened in these systems at room temperature. The one way to make full use of large $\chi^{(3)}$ and its prompt response is to realize the quantum well which has larger binding energy of exciton. This may be realized when we sandwich the quantum well by the barriers with much smaller dielectric constants and larger band gap than the well material.[37] Then the much larger exciton binding energy will bring about simultaneously the femtosecond response and the much larger $\chi^{(3)}$ than the GaAs-GaAlAs quantum-well system.

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