Giant-Oscillator-Strength Effect on Excitonic Optical Nonlinearities Due to Localization

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The optical nonlinearity $\chi^{(3)}$ of excitons localized by disorder or impurity has a large value as a consequence of the double multiplication of the giant oscillator strength due to exciton localization because the $\chi^{(3)}$ process involves the double repetition of the excitonic transition. The importance of the exciton correlation in the coherent nonlinear optical process is pointed out for the first time. The sign of $\chi^{(3)}$ relative to $\chi^{(1)}$ gives important information about the character of the exciton correlation.

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The excitonic optical nonlinearities in semiconductor quantum-well heterostructures have attracted much attention in the last few years.[1,2] An enormously large value of the third-order nonlinear optical susceptibility $\chi^{(3)}$ at room temperatures has been reported. It is usually thought that the excitonic optical nonlinearity is enhanced by the two-dimensional confinement effect. However, it is found in this paper for the first time that $\chi^{(3)}$ is really enhanced by the exciton localization effect as well as by the dimensional confinement effect. As is well known, the quantum-well interface is not smooth but has islandlike defects.[3-5] The excitons can be localized at one of these islandlike defects since the exciton energy fluctuates over several millelectronvolts because of the inhomogeneity of the quantum-well thickness in the lateral direction. In addition the excitons are possibly localized at impurities or compositional disorder in the quantum-well layer. In any case, the localization of excitons leads to the enhancement of the oscillator strength as in the case of the bound exciton.[6,7] In the third-order nonlinear optical process, this giant oscillator strength is multiplied twice because the $\chi^{(3)}$ process involves the double repetition of the excitonic transition.

On the other hand, optical bistability due to the I_2-bound exciton in CdS at low temperatures has been observed successfully[8] and holds promise for application to an optical device of very small switching energy. In this case also the excitonic transition gets a giant oscillator strength due to localization at impurity sites (neutral donors). A large value of $\chi^{(3)}$ of about 10^{-4} esu[9] was obtained even for a low impurity concentration of about 10^{15} cm^{-3}.

As noted above, the enhanced excitonic optical nonlinearities are closely related to the giant oscillator strength of the excitonic transition due to exciton localization irrespective of the dimensionality of the system. In this paper the general aspects of this relationship are clarified and it is also found that the correlation between two photogenerated excitons plays a crucial role in the coherent nonlinear optical mixing.

First of all, let us discuss the giant-oscillator-strength effect on the linear susceptibility $\chi_{\rm loc}^{(1)\rm Q2D}$ of the localized quasi-two-dimensional (Q2D) exciton and on $\chi_{\rm loc}^{(1)\rm 3D}$ of the bound exciton in the bulk crystal. By the standard linear response theory,[10] the ratio of $\chi_{\rm loc}^{(1)\rm Q2D}$ to the linear susceptibility $\chi_{\rm bulk}^{(1)\rm 3D}$ of the free exciton in the bulk crystal is calculated as

$$\frac{\chi_{\rm loc}^{(1)\rm Q2D}}{\chi_{\rm bulk}^{(1)\rm 3D}}=\frac{a_B^3}{4L_z\alpha^{-2}I(2\beta L_z)}\frac{32\pi\xi_{\rm loc}^2L_z}{v_0}\frac{v_0}{\sigma_0 L_z}\frac{L_z}{L_z+L_B}, \tag{1}$$

where a_B denotes the exciton Bohr radius in the bulk crystal, L_z the quantum-well thickness, L_B the thickness of the barrier layer, v_0 the volume of the unit cell, σ_0^{-1} the areal number density of the islandlike defects or impurities in the quantum-well layer, $\xi_{\rm loc}$ the localization length of excitons, and I an integral related to the exciton envelope function.[11] The parameters α and β are the variational parameters involved in the exciton envelope function and specify the extent of the electron-hole relative motion in the directions parallel and perpendicular to the quantum-well interface, respectively.[12] Then the first factor on the right-hand side of (1) represents the ratio of the probabilities to find the electron and the hole at the same position, which are inversely proportional to the ratio of the exciton volume. This factor describes the enhancement of the oscillator strength due to the dimensional confinement of excitons. The second factor can be interpreted as the enhancement factor of the oscillator strength due to localization and has a similar expression to that for the bound exciton.[6,7] The third factor is the average number of localized excitons contained in a unit cell, and the fourth factor takes into account the fact that the barrier layer does not contribute to $\chi^{(3)}$ since an infinite potential barrier is as-

sumed for the exciton. The first and second enhancement factors will be denoted by $Q_{\rm dim}$ and $Q_{\rm loc}$, respectively, and are plotted in Fig. 1 as a function of the quantum-well thickness L_z. Curve a for $Q_{\rm loc}$ is calculated for the exciton localized by the interface disorder, choosing the parameter $\xi_{\rm loc}=150$ Å,[4] whereas curve b for $Q_{\rm loc}$ is calculated for the impurity-bound exciton, taking $\xi_{\rm loc}$ equal to the quasi-two-dimensional exciton Bohr radius. The enhancement factor $Q_{\rm loc}$ is enormously large compared to $Q_{\rm dim}$, suggesting the importance of the effect of exciton localization. $Q_{\rm dim}$ increases with decreasing L_z since the exciton confinement becomes stronger. On the other hand, $Q_{\rm loc}$ is larger for more loosely bound excitons and thus the L_z dependence is opposite to that of $Q_{\rm dim}$.

Similarly, for the impurity-bound exciton in the bulk crystal, the ratio $\chi_{\rm loc}^{(1)3D}/\chi_{\rm bulk}^{(1)3D}$ is given by the product of the enhancement factor of the oscillator strength $8\pi\xi_{\rm loc}^3/v_0$ and the average number of bound excitons contained in a unit cell v_0/V_0, where V_0^{-1} is the impurity concentration. The former factor is about 4×10^3 for the I_2-bound exciton in CdS.[8]

The excitonic optical nonlinearities can be measured by the third-order nonlinear susceptibility $\chi^{(3)}$. The latter quantity can be calculated by time-dependent perturbation theory.[13,14] The third-order polarization density induced in a material system by external fields is given by

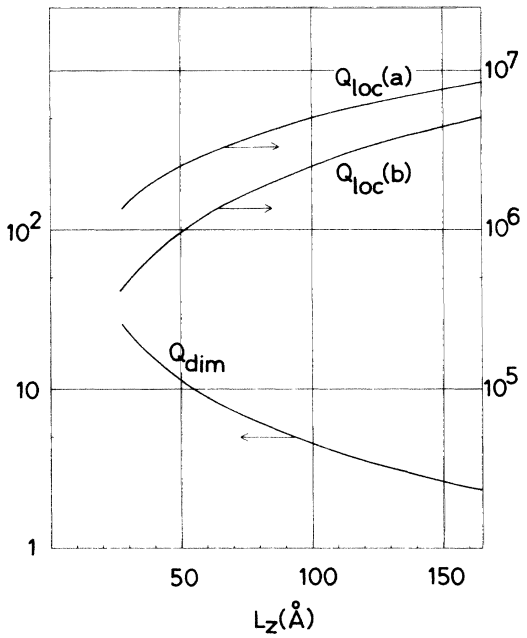

FIG. 1. Enhancement factors $Q_{\rm dim}$ and $Q_{\rm loc}$ plotted as a function of the quantum-well thickness L_z. Curve a, $Q_{\rm loc}$ calculated for the exciton localized by the interface disorder choosing $\xi_{\rm loc}=150$ Å; curve b, $Q_{\rm loc}$ for the impurity-bound exciton taking $\xi_{\rm loc}=a_{\rm B}({\rm Q2D})$.

$$\langle P^{(3)}(r,t)\rangle=(-i/\hbar)^3\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\langle[[[P(r,t),H_i(t_1)],H_i(t_2)],H_i(t_3)]\rangle, \tag{2}$$

with $H_i=-\int d^3r\,P(r)E(r)$, where $P(r)$ is the polarization-density operator and the angular brackets denote a thermal average. The electric field E consists of two external fields with wave vector k_j and frequency ω_j $(j=1,2)$. Hereafter the nonlinear susceptibility $\chi^{(3)}(-2\omega_1+\omega_2;\omega_1,\omega_1,-\omega_2)$ will be denoted simply by $\chi^{(3)}$. In the calculation of the matrix elements in (2), the relevant intermediate states should be inserted between operators. According to the relevant excitonic state, one can classify the susceptibility $\chi^{(3)}$ with suffixes. For example, the susceptibility $\chi^{(3)}$ due to the localized quasi-two-dimensional exciton will be denoted by $\chi_{\rm loc}^{(3)\rm Q2D}$. At low temperatures the excitons are stable against thermal ionization by LO phonons, in contrast to the case at room temperature where they are found to be ionized in less than 1 ps.[15] Thus when one considers $\chi^{(3)}$ at low temperatures or under off-resonant excitation even at room temperature, one can discard the ionized exciton states from the relevant intermediate states in (2).

In the calculation of $\chi^{(3)}$ for the localized exciton, there appear typical terms such as

$$\sum_{R_a,R_b}\langle 0|P(r,t)|R_a\rangle\langle R_a|H_i(t_1)|0\rangle\langle 0|H_i(t_2)|R_b\rangle\langle R_b|H_i(t_3)|0\rangle, \tag{3}$$

$$\sum_{R_a,R_b}\langle 0|P(r,t)|R_a\rangle\langle R_a|H_i(t_1)|R_a,R_b\rangle\langle R_a,R_b|H_i(t_2)|R_b\rangle\langle R_b|H_i(t_3)|0\rangle, \tag{4}$$

where $|0\rangle$, $|R_a\rangle$, and $|R_a,R_b\rangle$ denote, respectively, the crystal ground state, the state having a localized exciton at site R_a, and the state having two localized excitons at sites R_a and R_b. The correlation between the two excitons in $|R_a,R_b\rangle$ plays an important role in the generation of the nonlinear polarization since the coherent nonlinear optical mixing occurs within the coherence lengths of the material excitation and the radiation fields. In fact, it is found that $\chi^{(3)}$ for the localized exciton is proportional to the factor

$$K_\chi=\left|\int dr\int dR\,C(r)G(r+R)|G(R)|^2/\int dr\,G(r)\right|^2-1, \tag{5}$$

where the function C describes the correlation between two localized excitons, G is the normalized localization envelope function, and the integrals are two or three dimensional. The first term on the right-hand side of (5) is the contribution from the terms like (4) in which $R_a = R_b$, while the second term, -1, represents the contribution from the terms like (3) together with that from the terms like (4) in which $R_a \neq R_b$. It is seen that $\chi^{(3)}$ vanishes through the factor K_χ when the two excitons are completely uncorrelated, i.e., $C(r) = 1$.

It is significant to note that the sign of $\chi^{(3)}$ depends on whether the correlation between two excitons is repulsive or attractive. The Pauli exclusion principle and the Coulomb interaction work to induce a repulsive correlation between two bound excitons, i.e., to prohibit formation of two excitons around a single impurity or an interface defect. On the other hand, an attractive correlation works between two free excitons so that an excitonic molecule is formed.[16] The correlation factor K_χ is found to be positive or negative for the case of repulsive or attractive correlation, respectively, by a simple model calculation.[17] Thus the measurement of the sign of $\chi^{(3)}$ relative to $\chi^{(1)}$ gives important information about the character of exciton correlation.

The third-order nonlinear susceptibility $\chi^{(3)3D}_{bulk}$ due to the free exciton in the bulk crystal can be calculated in the same way. Then one finds

$$\frac{\chi^{(3)Q2D}_{loc}}{\chi^{(3)3D}_{bulk}} = \left[\frac{a_B^3}{4L_z\alpha^{-2}I(2\beta L_z)}\right]^2 \left[\frac{32\pi\xi^2_{loc}L_z}{v_0}\right]^2 \frac{v_0}{\sigma_0 L_z}\,\frac{L_z}{L_z+L_B}\,C_\chi, \tag{6}$$

where the correlation factor C_χ will be given later. It is important to note that in the derivation of (6) the energy denominators of $\chi^{(3)}$ are assumed to be the same for both the localized quasi-two-dimensional exciton and the bulk exciton and thus they cancel in the ratio. The interpretation of each of the first four factors on the right-hand side of (6) is the same as given for (1). Both enhancement factors in (1), that due to the dimensional confinement and that due to the exciton localization, appear multiplied twice in (6) since the $\chi^{(3)}$ process involves the double repetition of the excitonic transition. The correlation factor C_χ is absent in (1) because only one excitonic transition is involved in the $\chi^{(1)}$ process. Thus this factor first appears in the nonlinear-response coefficients. For the case of repulsive correlation, C_χ is given explicitly as

$$C_\chi = \left[\frac{6a+1}{8(3a+1)^2}\right]\frac{v_0}{\pi^{3/2}\xi^3_{cor}(3D)}, \tag{7}$$

with $a = \xi^2_{loc}(Q2D)/\xi^2_{cor}(Q2D)$, where the correlation function and localization function are assumed to be Gaussian with characteristic lengths ξ_{cor} and ξ_{loc}, respectively, and the correlation lengths are denoted by $\xi_{cor}(Q2D)$ and $\xi_{cor}(3D)$ for the quasi-two- and three-dimensional cases, respectively.

Now the absolute value of $\chi^{(3)Q2D}_{loc}$ can be estimated theoretically by use of the value of the longitudinal-transverse splitting energy of excitons in GaAs.[18] For the exciton localized by interface disorder, $\chi^{(3)}$ is estimated as 1.2×10^{-5} esu, with the choice of the parameters $L_z = 80$ Å, $\xi_{loc} = 150$ Å,[4] and $\sigma_0 = 10^{-10}$ cm^2,[3] and the assumptions that the correlation length ξ_{cor} is twice the exciton Bohr radius a_B and the off-resonance energy $\Delta\omega$ is 1 meV.[19] For the impurity-bound exciton in the quantum well, $\chi^{(3)Q2D}_{loc}$ is estimated as 2.7×10^{-5} esu, by choice of the impurity concentration to be 10^{17} cm^{-3} [20] and $\xi_{loc} = a_B$. These values are much larger than the $\chi^{(3)}$ values of Si [21] and polydiacetylene.[22]

The discrepancy between the above theoretical value of $\chi^{(3)Q2D}_{loc}$ and the experimental estimate[1] is to be explained. The experiments of Refs. 1 and 15 were carried out under resonant excitation of excitons and at room temperature. In these cases, the exciton dynamics in the presence of bound or free electron-hole pairs plays the key role as clarified by Schmitt-Rink, Chemla, and Miller.[23] On the other hand, when no real electron-hole pairs are created under off-resonant excitation and at low temperatures, the localized treatment of the exciton correlation as given here is relevant to describe the coherent nonlinear optical process, e.g., the dispersive optical bistability. Thus the discrepancy between our theoretical estimate of $\chi^{(3)Q2D}_{loc}$ and the experimental one[1] arises from the difference of the physical situations dealt with. When our theory is extrapolated to the case of resonant excitation, only for a rough order-of-magnitude estimation, the absolute value of $\chi^{(3)}$ is found to be enhanced by a factor of the order of $T_1|\Delta\omega|$, where T_1 is the longitudinal relaxation time and $\Delta\omega$ is the off-resonance frequency. With use of the value $T_1 = 5\times10^{-10}$ s,[24] $\chi^{(3)}$ for the exciton localized by the interface disorder is estimated as 9.1×10^{-3} esu, in fortuitous agreement with the experimental estimate,[1] in order of magnitude.

Similarly for the I_2-bound exciton in CdS,[8] the absolute value of $\chi^{(3)3D}_{loc}$ is estimated to be 2.2×10^{-4} esu on the assumption that the correlation length ξ_{cor} is twice the exciton Bohr radius, and by choice of the off-resonance energy to be 0.3 cm^{-1}.[8] The agreement in order of magnitude with the experimental estimate[9] is satisfactory.

In summary the excitonic optical nonlinearity is

enhanced not only by the dimensional confinement effect but also by the giant-oscillator-strength effect due to exciton localization. For the purpose of obtaining a large value of the excitonic optical nonlinearity, the perfect and clean quantum-well structure is by no means favorable. Instead, by control of the morphology of the quantum-well interface suitably or by utilization of the bound exciton levels effectively, the most effective nonlinear optical devices can be designed.

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