Exchange interaction and phonon confinement in CdSe quantum dots

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The fine structure of the lowest $(1S_{3/2}, 1s_e)$ electron-hole pair state has been studied for CdSe quantum dots embedded in glass and with sizes $R<a_B$. Besides the very narrow peaks from the exchange-split lowest pair states (full width at half maximum of 2 meV), two additional structures have been found in luminescence and assigned to confined acoustic phonons. The observation of discrete acoustic phonons in the emission spectra verifies the importance of low-frequency acoustic phonons for energy relaxation in quantum dots. The size dependence of the different peaks has been determined and compared with theoretical models. [S0163-1829(96)07027-0]

Since the observation of discrete optical transitions in quantum dots (QD's), great efforts have been made to study the internal electronic structure of the confined electron-hole pair states. In particular, one is interested in the energies and symmetries of the energetically lowest pair states, as these states essentially determine the band edge absorption and luminescence. To describe CdSe QD's, effective mass models based on zinc blende type semiconductors have been established where the energetically lowest pair state is the eightfold degenerate $(1S_{3/2},1s_e)$ state with the hole arising from the uppermost $J=3/2$ valence band. However, the lifting of this degeneracy is very likely in quantum dots, by, e.g., deviations from spherical shape or wurtzite-type lattice structure. In small QD's with radii R below the bulk excitonic Bohr radius a_B, the pair states split into two states, due to an enhancement of exchange interaction $\sim 1/R^3$.

The problem of an internal structure of the lowest pair states in QD's has been theoretically treated in Refs. 1–5. Experimental evidence for the enhancement of the short-range exchange interaction has been obtained recently in Refs. 6,7, investigating CdSe QD's. Arguments, which support the hypothesis of exchange splitting of the electron-hole pair states are the observation of the time-dependent change of the polarization degree of the luminescence[6] and the tuning of the optical transition probability by applying external magnetic fields.[7]

In this paper, we report on the high-resolution photoluminescence (PL) and the photoluminescence excitation spectroscopy (PLE) of CdSe QD's. The fine structure has been further resolved into four peaks and the size dependence of the single peaks has been studied. The exchange splitting energy has been determined by resolving the ultranarrow peaks of the lowest pair state in both PL and PLE. The additionally observed structures have been explained by confined acoustic phonons created by elastic oscillations of the quantum dot itself. Obviously, these phonons with small but discrete energies can be emitted in phonon-assisted radiative transitions of the electron-hole pairs.

In Fig. 1, we start with a scheme of the supposed level structure for the lowest eightfold degenerate $(1S_{3/2},1s_e)$ electron-hole pair state in CdSe QD's. The electron is only characterized by its spin quantum number $s=1/2$ with the projections $m_s=\pm 1/2$. The hole states are described by the quantum number $F=L+J$, due to valence band mixing. The $1S_{3/2}$ hole state holds $F=3/2$ with the projections $m_F=\pm 3/2,\ \pm 1/2$. To characterize the pair state $(1S_{3/2},1s_e)$, we use the notation of Ref. 7 with $N=F+s$ for the total pair angular momentum and N_m for its projections. The eight single states differ in their quantum numbers according to all possible combinations $|N,N_m\rangle = |F,s,m_F,m_s\rangle$. The crystal field and nonspherical shape both lift the degeneracy and split the state into two groups labeled A and B in Fig. 1. Calculations made in Ref. 7 have shown that the group B energy levels undergo further significant energy splitting in the limit of strong nonsphericity and for the dot radii below 1.5 nm. In the case of nearly spherical nanocrystals, however, with the dot radii between 1.5 and 3 nm, the group A and B levels are well separated in energy by a few tens of meV. In the following, we will concentrate on the group A levels. Due to exchange interaction, the A states split further into two pair states with the projections $N_m=\pm 1$ and ± 2 of the pair total angular momentum $N=2$. The lowest state is labeled A_F and is dipole forbidden because light with angular momentum 1 couples to a state with $N_m=\pm 2$ only in higher orders of perturbation theory. Thus the energetically lowest state in Fig. 1 absorbs only weakly, but can emit after relaxation from higher excited states. The pair state with $N_m=\pm 1$, here labeled A_T, strongly couples to the radiation field.

The experiments have been performed at CdSe QD's em-

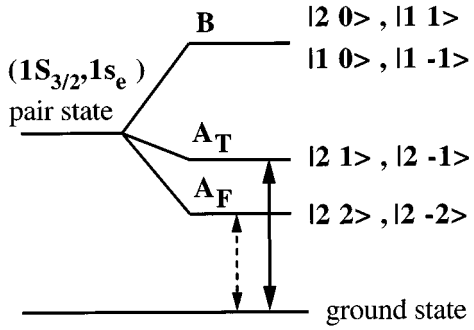

FIG. 1. Lifting of the degeneracy of the $(1S_{3/2},1s_e)$ state, due to nonspherical shape, crystal field splitting, and exchange interaction. The notation of the states is $|N,N_m\rangle$ (see text).

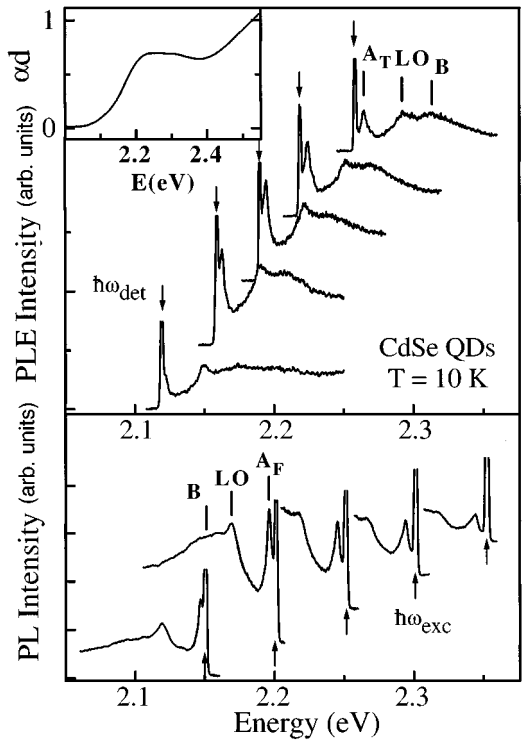

FIG. 2. Linear absorption (αd, inset), photoluminescence (PL), and photoluminescence excitation (PLE) spectra of CdSe quantum dots with $\overline{R}=2.2$ nm. The detection/excitation energies are indicated by arrows.

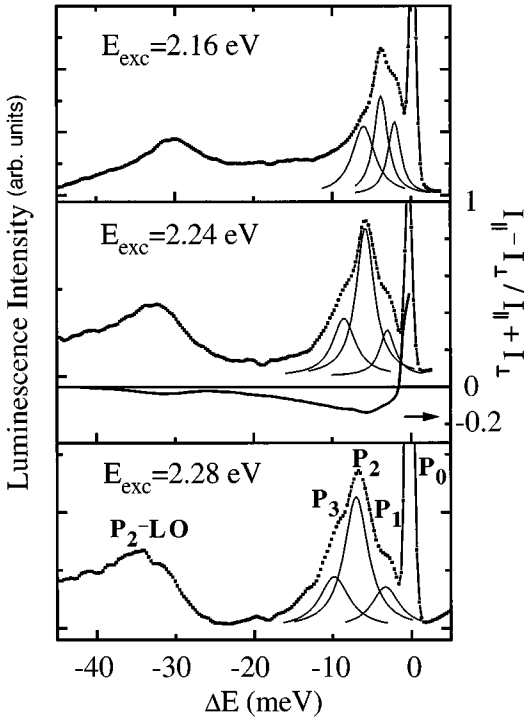

FIG. 3. High-resolution photoluminescence at different excitation energies showing the fine structure with size-dependent energies for the peaks P_1, P_2, and P_3 (P_0 corresponds to the pump laser). Additionally, the degree of linear polarization of the luminescence is plotted for the spectrum pumped at 2.24 eV.

bedded in glass. Great care has been taken to determine size, shape, and structure of the nanocrystals. A calibration curve for the radii has been generated after measuring the average radii of a set of samples by small angle x-ray scattering and transmission electron microscopy (TEM and high-resolution TEM). The investigated nanocrystals are nearly spherical and exhibit a predominantly wurtzite structure. Figure 2 shows the size-selective PL and PLE spectra for CdSe QD's with an average radius of 2.2 nm (for further details of size-selective spectroscopy and determination of pair state energies in dependence on size, see Ref. 8). From both PL and PLE, it can be verified that the group B levels are well separated in their energies from the A_T state and A_F states. By detecting the narrow peak just near the excitation/detection energy in PL and PLE, the energy difference between the A_T and the A_F state of a few meV can be clearly resolved. Its evolution with detuning indicates the exchange splitting as well as its size dependence. Additionally, an LO-phonon replica can be seen.

When investigating the PL with higher spectral resolution, a substructure has been found consisting of three peaks P_1, P_2, and P_3 a few meV below the excitation (P_0), as shown in Fig. 3 for excitation energies of 2.16, 2.24, and 2.28 eV. These peaks lie within the spectral range attributed so far to the A_F state and their individual linewidths amount to only 2 meV full width at half maximum. This value has to be compared to values from 10 to 50 meV found, e.g., in spectral hole burning. To identify the nature of the three transitions, the size dependence of the single peaks will be analyzed below. Additionally the degree of linear polarization (DLP) has been measured for the PL spectrum with the pump at 2.24 eV. Negative DLP means that the emitting dipole is oriented preferentially perpendicular to the absorbing one. Thus, the obtained negative value of the DLP gives evidence that the strong peak P_2 was not directly excited by the laser, but created after relaxation. Therefore, we assign the peak P_2 to the A_F state. The LO-phonon emission starts from the forbidden A_F state, because it has the same negative DLP. This assignment is supported by the constant value of ~ 26 meV for the energy separation between A_F and LO independent of the pump energy. Changes in the linear polarization have been likewise reported in Ref. 6 and explained by a virtual coupling of the group A to the group B states. The 3/2-hole state is lifted to the 1/2-hole state under participation of phonons and, therefore, the luminescence reflects the polarization properties of the B states. Here, we additionally propose the possibility that the electron flips the spin during relaxation, due to the admixture of odd-parity wave functions with 1/2 symmetry or due to interaction with paramagnetic impurities.

The two peaks P_3 and P_1 we attribute for the present to acoustic phonon replica. For the explanation, we consider the two possibilities that either P_1 and P_3 belong to the A_F state and are the result of phonon-assisted absorption and emission (A_F-P_3 and A_F+P_1) or that the two peaks are phonon replica of both the A_F state (A_F-P_3) and the A_T state (A_T-P_1). To examine both hypotheses, we plot in Fig. 4 the size dependences of the energies of the peaks P_1 to P_3. The energetic distance of P_2-P_3, as well as that between P_0 and P_1, can be fitted by a $1/R$ dependence, which is typical for confined acoustic phonons, and is in contrast to the stronger size dependence of the energy separation of P_0 to P_2. The

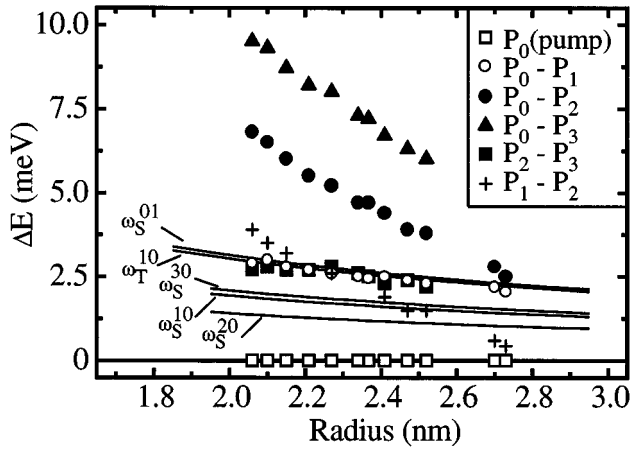

FIG. 4. Size dependence of the energy differences of the peaks P_1, P_2, and P_3 and calculated curves for the lowest eigenfrequencies of the spherical and torsional acoustic phonons ω_S^{ln} and ω_T^{ln}.

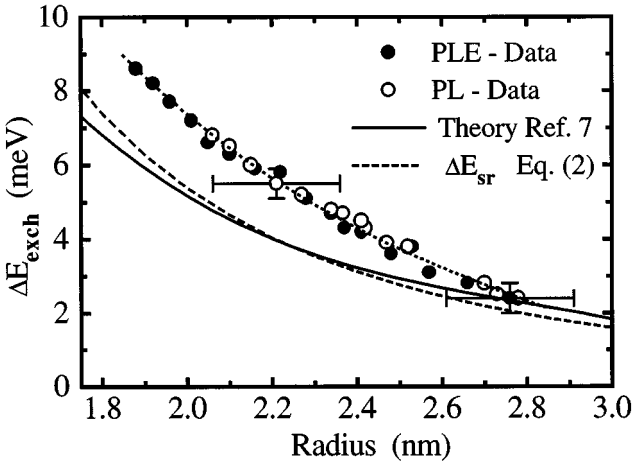

FIG. 5. Experimentally obtained energy splitting ΔE_{exch} between the A_T and A_F state in dependence on radius R. The solid line is the theoretical result of Ref. 7; the dashed line is calculated after Eq. (2) for the short-range exchange interaction. The dotted line fits the experimental data from photoluminescence (PL) and excitation spectra (PLE).

clear deviation from the $1/R$ behavior for the energy distance between P_1 and P_2 makes an interpretation of the peak P_1 in terms of a phonon-assisted *absorption* process starting from A_F rather unlikely. Thus, we classify the substructures into the exchange-split A_T and A_F transitions (P_0 and P_2), accompanied by their acoustic phonon replica P_1 and P_3, respectively. This hypothesis is further confirmed by investigating the temperature dependence of the peak intensities. Supposing that P_1 is caused by phonon-assisted absorption, this peak would be of increasing intensity with rising temperature. We could not find this behavior in the temperature-dependent luminescence.

At higher temperatures corresponding to thermal energies of a few meV ($\approx$ 40 K), a luminescence above the pump energy could be detected. This luminescence arises from quantum dots for which the pump is resonant to the A_F state and the thermal energy allows the population of the higher A_T state, with the help of phonons followed by radiative recombination.

The origin of these low-energy acoustic phonons can be deduced from the model of an oscillating elastic sphere. Solving the differential equation for the vibration of a homogeneous elastic body with spheroidal shape and stress-free boundary conditions, the eigenfrequencies are given by two types of frequencies ω_S^{ln} and ω_T^{ln} for the spheroidal and torsional modes, respectively.[9,10] For CdSe with the ratio of the longitudinal and transversal sound velocities $c_\ell/c_t=2.3$ ($c_\ell=3.63\times10^3$ m/s, $c_t=1.59\times10^3$ m/s), the frequencies of the lowest eigenmodes are

$$\omega_T^{10}=5.8c_t/R,\quad \omega_S^{01}=6.0c_t/R,\quad \omega_S^{10}=3.7c_t/R,$$

$$\omega_S^{20}=2.7c_t/R,\quad \omega_S^{30}=4.0c_t/R,\quad \omega_S^{00}=2.5c_t/R, \qquad (1)$$

where R is the radius of the sphere. For comparison with the experimental data, the calculated frequencies are shown in Fig. 4 for the lowest spheroidal and torsional modes. The modes with $l=1,\ 2,\ 3,\ n=0$ are characterized by large amplitudes at the surface and have energies that are too small to explain the experimental data. Agreement with the experiment exists for the so-called breathing mode with $l=0,\ n=1$, where the whole sphere exhibits dilatation and for the torsional mode with $n=0$ and $l=1$. At least the spheroidal mode with $l=0$ should be able to couple to the pair state. Until now, discrete confined acoustic phonons have been only reported in Raman scattering or spectral hole burning.[10–12] Here, we could resolve a *discrete* confined acoustic mode in photoluminescence, which only occurs in spherical quantum structures. The dominance of this phonon mode strongly indicates the importance of low-frequency acoustic phonons for the energy relaxation process in quantum dots.

In Fig. 5 we analyze the size dependence of the A_F-A_T splitting energy (difference between P_0 and P_2). The data from both PL and PLE are plotted for the range between $R=1.8$ and 3 nm. The experimental data are compared with two curves predicted by theory. First, the size dependence $\Delta E_{\mathrm{sr}}(R)$ has been calculated according to

$$\Delta E_{\mathrm{sr}}=0.67\pi(a_B/R)^3E_{\mathrm{exch}}^{\mathrm{bulk}}, \qquad (2)$$

which has been derived in Refs. 3,5.

The exchange energy ΔE_{sr} is enhanced by a factor of about 30 for dot sizes of $R\approx0.5a_B$ (if one identifies the short-range interaction in the bulk with the singlet-triplet splitting). Second, the result of an extended theoretical approach is shown, which includes the nonspherical shape of the quantum dots (Ref. 7). Our experimental data slightly deviate from these curves. In Ref. 6, acoustic phonons participating at the optical transitions were held responsible for the disagreement, in particular for very small quantum dots. However, knowing now the size dependence of the phonon energy from Fig. 4, this explanation is not very likely. Here, we give two other reasons to explain the discrepancy between the present theory and experiment. First, the exactness of all the data is limited by the unavoidable error in the measurement of the quantum dot sizes illustrated by the error bars for R in Fig. 5. Hence, experimental values even below the theoretical curves are possible. Second, the present

theory only considers the short-range part of the exchange interaction in quantum dots. In bulk material, however, the exchange interaction comprises a long- and a short-range contribution and results in an internal structure of the bulk excitonic states. Whereas only the excitonic wave functions of essentially the same unit cell contribute to the short-range part, the long-range part contains the dipolar interactions between several lattice cells and causes the longitudinal-transversal splitting $\Delta\hbar\omega_{\mathrm{LT}}$ of the exciton energy. For the bulk CdSe, the value for the short-range exchange energy is $\Delta E_{\mathrm{sr}}= 0.13$ meV and the strength of the long-range contribution is given by $\Delta\hbar\omega_{\mathrm{LT}}=0.9$ meV.[13] Thus, in bulk CdSe the long-range interaction dominates the exciton spectrum. In quantum dots, the problem of the so-called nonanalytic exchange is theoretically not considered yet. But the long-range interaction and polariton concept has been theoretically applied to quantum wells and superlattices (Refs. 14–16 and references therein) and an enhancement over the bulk value has been discussed for the longitudinal-transversal splitting energy. First proposals for the contribution of the long-range exchange interaction to the splitting energies in QD's have been made in Ref. 3. A nonvanishing long-range exchange energy has been expected for the case of a nonspherical shape of the QD's and if the envelope function has components with higher l quantum numbers. Using the first estimate for the long-range exchange energy given in Ref. 3, we get the error bars as plotted in Fig. 5 for ΔE_{exch}. Because the effect of radiation coupling between different dots is very sensitive with respect to the dot density and geometry of the single dots, this could lead to even larger differences in the experimental data. In the samples investigated here, the ensemble of QD's is characterized by interdot distances between 10 and 15 nm and the number of dots within the spatial dimension of the wavelength of light is substantial. Additionally, in a single quantum dot, the symmetry of the one-pair wave function is no longer a pure spherical and the A_T-pair state possesses a considerable, finite oscillator strength.

Summarizing, by highly resolved luminescence and excitation spectroscopy, the size dependence of the exchange-splitting energy has been determined for CdSe quantum dots and the present deviations between experiment and theory are discussed. Experimental evidence has been obtained for the appearance of discrete confined acoustic phonons in the photoluminescence of CdSe QD's.

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