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# Band-edge absorption and luminescence of nonspherical nanometer-size crystals

Al. L. Efros
*Technische Universität München, 8046 Garching, Germany*

A. V. Rodina
*State Technical University, St. Petersburg, 198052, Russia*

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The effect of nonspherical shape on the optical properties of semiconductor microcrystals with a degenerate valence band has been theoretically studied. The asymmetry of microcrystals leads to a splitting of the fourfold-degenerate ground hole state into two twofold-degenerate ones. The value of this splitting is proportional to the deviation from sphericity and inversely proportional to the square of the microcrystal size, and is the function of the ratio of light- to heavy-hole effective masses ($\beta$). This splitting could lead to the formation of long-lived electron-hole pairs in the prolate microcrystals of semiconductors with small $\beta$ and in the oblate ones with $\beta > 0.14$.

In the last few years there has been growing interest in the optical properties of semiconductor nanocrystals.[1–10] In microcrystals smaller than the bulk exciton radius, these properties are determined in a first approximation by the transitions between quantum size levels (QSL's) of holes and electrons.[11] In all of these publications, qualitative and quantitative descriptions of QSL's have been done in the approximation of spherically shaped microcrystals.

High-resolution transition electron spectroscopy has shown the deviation from spherical shape of CdSe and $\mathrm{CdSe}_{1-x}\mathrm{S}_x$ microcrystals embedded in silicate glasses.[12,13] The degree of deviation from sphericity has been shown to depend on microcrystal size, heat treatment conditions of growth,[12,13] as well as on the chemical composition of silicate glasses.[14] A nonspherical shape modifies the optical properties of microcrystals, and efforts to describe the luminescence polarization, the Huang-Rhys parameter, and the fine structure of absorption of such microcrystals have been done.[15,16]

The following is a theoretical analysis of band-edge absorption and luminescence of elliptically shaped direct-gap nanometer-size semiconductor crystals. The theory takes into account a valence-band degeneracy and can be applied to microcrystals of most popular semiconductors: GaAs, InAs, InSb, InP, CdTe, as well as widely investigated CdSe with cubic lattice structure.[3,7,8,17]

The conduction band in all these semiconductors can be considered as a simple parabolic one in the region which is close to the band edge. The ground electron state in spherical microcrystals of such semiconductors is well known[11,18] to be the $1S$ state (the first QSL with orbital momentum $l = 0$).

The valence band of these semiconductors is a fourfold-degenerate band $\Gamma_8$, described by a Luttinger Hamiltonian $\hat{H}_L$.[19] It has been theoretically shown that a ground hole state in spherical microcrystals is characterized by the total momentum $F = 3/2$ neglecting cubic-symmetry terms in $\hat{H}_L$ and is fourfold degenerate with respect to momentum projection $M = \pm 3/2, \pm 1/2$.[7,20–22] From now on we will use the notation $1S_{3/2}$ for this level following a paper[7] which demonstrated experimentally an existence of such QSL's in cubic CdSe nanocrystals. Corresponding wave functions of holes in spherical microcrystals with radius $a$ have the form[20]

$$\Psi_M = 2 \sum_{l=0,2} R_l(r) \sum_{m+\mu=M} \begin{pmatrix} 3/2 & l & 3/2 \\ \mu & m & -M \end{pmatrix} Y_{l,m} u_\mu \ , \qquad (1)$$

where $u_\mu$ are the Bloch functions of the $\Gamma_8$ valence subband ($\mu = \pm 3/2, \pm 1/2$ ), $Y_{l,m}$ are the normalized spherical functions, $\left(\begin{smallmatrix} i & k & l \\ m & n & p \end{smallmatrix}\right)$ are the $3j$ Wigner symbols, and radial functions $R_l(r)$ take the form of[10]

$$R_l(r) = \frac{A}{a^{3/2}} \left( j_l(kr/a) - (-1)^{l/2} \frac{j_0(k) j_l(k\sqrt{\beta} r/a)}{j_0(k\sqrt{\beta})} \right) \ , \qquad (2)$$

where $j_l(x)$ are the spherical Bessel functions, $\beta = m_l/m_h$ is the ratio of light- to heavy-hole effective masses, and $k$ is the first root of the following equation:

$$j_0(k) j_2(\sqrt{\beta} k) + j_2(k) j_0(\sqrt{\beta} k) = 0 \ , \qquad (3)$$

connected with the energy of the QSL, $E_h$, by the relation

$$E_h(\beta) = \frac{\hbar^2}{2 m_h a^2} k^2 \ . \qquad (4)$$

The constant $A$ is determined by the normalizing condition $\int [R_0^2(r) + R_2^2(r)]\, dr = 1$. The dependence of the square of the first root of Eq. (3) on parameter $\beta$ is plotted in Fig. 1. The complete energy spectrum of holes described by the Luttinger Hamiltonian $\hat{H}_L$ has been obtained by Ekimov *et al.*[23] and Xia.[21]

Let us consider an elliptically shaped nanocrystal

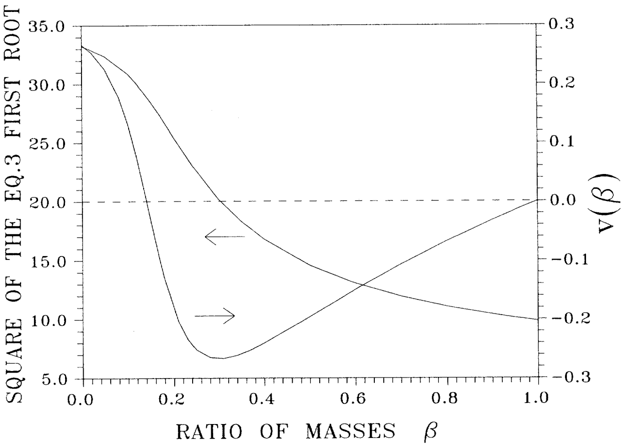

FIG. 1. Dependence of dimensionless splitting of the ground hole state $v(\beta)$ and the square of the first root $(k)$ of Eq. (3) on the ratio of light- to heavy-hole effective masses $(\beta)$.

whose surface is described by the following equation:

$$(x^2+y^2)/b^2+z^2/c^2=1\ . \tag{5}$$

By the following change of variables $x \Rightarrow bx/a$, $y \Rightarrow by/a$, $z \Rightarrow cz/a$, we convert Eq. (5) to the equation for a sphere: $x^2+y^2+z^2=a^2$. The same change of variables modifies the Luttinger Hamiltonian $\hat{H}_L$ which is treated in the spherical approximation to the form

$$\hat{H}=\hat{H}_L+\hat{V}\ , \tag{6}$$

where $\hat{V}$ is an anisotropic perturbation. It means that we reduce the hole movement in the elliptical nanocrystal to the one in a spherical nanocrystal described by the anisotropic Hamiltonian (6).

If the ellipse differs insignificantly from a sphere with radius $a=(b^2c)^{1/3}$, we can write $b$ and $c$ in the form

$$b=a(1-\mu/3)\ ,\quad c=a(1+2\mu/3)\ , \tag{7}$$

where $\mu$ is the degree of ellipticity. $\mu$ is positive in prolate microcrystals and is negative $(\mu<0)$ in oblate ones. If $\mu \ll 1$ we can consider the anisotropic term $\hat{V}$ in Hamiltonian (6) to be a small perturbation. This perturbation can be written as

$$\hat{V}=\mu\left\{\frac{2\hat{H}_L}{3}-\frac{2\hat{p}_z^2}{\beta m_0}+\left(1-\frac{1}{\beta}\right)\left[\frac{\hat{p}_z^2}{4m_0}-\frac{(\hat{p}_z\hat{J}_z)(\hat{\mathbf{p}}\cdot\hat{\mathbf{J}})}{m_0}\right]\right\}, \tag{8}$$

where $\hat{\mathbf{p}}=-i\hbar\nabla$ is the momentum operator, $m_0$ is the mass of the free electron; and $\hat{J}_x$, $\hat{J}_y$, $\hat{J}_z$ are the 4×4 matrices of the projections of the spin momentum $J=3/2$.[19] Using wave functions (1) we can find the shifts of QSL's due to this perturbation. For the QSL's with $M=\pm3/2, \pm1/2$, they have the following forms, respectively:

$$\Delta E_{\pm3/2}=-\Delta E_{\pm1/2}=-\mu v(\beta)E_h(\beta)\ . \tag{9}$$

The ground $1S_{3/2}$ state of holes splits into two twofold-degenerate ones. The splitting is inversely proportional to the square of the microcrystal size $a$ [see Eq. (4)] and depends on the ratio of light- to heavy-hole effective masses $\beta$. The dimensionless function $v(\beta)$ decreases from 4/15 at $\beta=0$, changes its sign at $\beta \approx 0.14$, and goes to zero at $\beta=1$. This dependence is presented in Fig. 1. One can see that a small deviation from sphericity does not change the central position of the $1S_{3/2}$ QSL, i.e., $(\Delta E_{-3/2}+\Delta E_{-1/2}+\Delta E_{1/2}+\Delta E_{3/2})=0$. This statement has been shown to be correct for every QSL of holes:

$$\sum_M \Delta E_M=0\ . \tag{10}$$

The same results have been obtained in Ref. 24 for electrons in the parabolic band: small deviations from sphericity split electron QSL's degenerated with respect to momentum projections, but do not change their central position. The ground electron $1S$ state does not change the energy position in the first order of perturbation theory.

This means that if a fine structure of split QSL's is not seen in absorption of elliptically shaped microcrystals, one can use for its description the spherical approximation. The nonspherical shape of microcrystals leads only to additional broadening of interband transitions. A volume of theoretically considered microcrystals should be equal to the volume of investigated ones $[a=(b^2c)^{1/3}]$.

A microcrystal shape becomes very important for luminescence, because the times of recombination depend on the projection momentum $M$ of photoexcited holes. These times can be significantly different in nanocrystals whose ground state has $M=\pm3/2$, and in those whose ground state has $M=\pm1/2$.

The radiative recombination times $\tau_r(M,\alpha)$ of an electron in the $1S$ state having spin projection $\alpha$ ($\alpha=\uparrow$ or $\downarrow$) with a hole in the $1S_{3/2}$ state having momentum projection $M$ have the following form:[10]

$$\frac{1}{\tau_r(M,\alpha)}=\frac{4e^2\omega n}{3m_0^2c^3\hbar}|\langle M|\hat{p}_\mu|\alpha\rangle|^2\ , \tag{11}$$

where $\omega$ and $c$ are the frequency and velocity of light, and $n$ is the refractive index. Using Eq. (11) one can find[10] that these times are of the order of $\tau_0/K$ for dipole-allowed transitions:

$$\begin{aligned}\tau_r(3/2,\uparrow)&=\tau_r(-3/2,\downarrow)=\tau_0/K\ ,\\ \tau_r(1/2,\uparrow)&=\tau_r(-1/2,\downarrow)=3\tau_0/2K\ ,\\ \tau_r(1/2,\downarrow)&=\tau_r(-1/2,\uparrow)=3\tau_0/K\ ,\end{aligned} \tag{12}$$

where $K$ is the square of the overlap integral between electron and hole wave functions, and

$$\tau_0=\left[\frac{4\omega nP^2}{3\times137m_0^2c^2}\right]^{-1} \tag{13}$$

is the characteristic time of the radiative recombination for bulk semiconductors which is of the order of one nanosecond in most cases ($P$ is the Kane interband matrix element). The overlap integral $K$ is smaller than one.[10] As a result the typical radiative relaxation times should be in the range 1–5 ns.

These times can be observed in microcrystals where the ground hole state has $M = \pm 1/2$ (in oblate microcrystals with $\beta < 0.14$ and prolate ones with $\beta > 0.14$ as can be seen in Fig. 1). In nanocrystals whose ground state has $M = \pm 3/2$ (its condition is opposite to that mentioned above), a thermalization of the holes initially excited into higher states could lead to formation of long-lived $| 3/2, \downarrow\rangle$ and $| -3/2, \uparrow\rangle$ electron-hole pair states. Direct optical recombination of these states is impossible because the matrix elements $\langle 3/2 \mid \hat{\mathbf{p}} \mid \downarrow\rangle$ and $\langle -3/2 \mid \hat{\mathbf{p}} \mid \uparrow\rangle$ in Eq. (11) are equal to zero. The $| 3/2, \downarrow\rangle$ and $| -3/2, \uparrow\rangle$ states could recombine only with the emission or absorption of phonons. At low temperature these processes occur much more slowly than those of direct optical recombination (12).

Existence of such electron-hole pairs in microcrystals with $| \pm 3/2\rangle$ ground hole state is provided through suppression of the usual bulk mechanisms of spin relaxation. Spin-orbital terms mix spin-up (-down) electron states and with the spin-down (-up) electron states whose orbital wave functions have an opposite parity. For the ground electron $1S$ state the closest opposite parity level is the $1P$ state. In small-size microcrystals the distance between these two levels is of the order of several hundred meV,[7] which leads to a very weak mixing of one spin projection to the other. In this case, phonon scattering or hyperfine interaction of the electron spin with the spins of nucleus could start to be the two main mechanisms of the spin relaxation.

The present analysis of luminescence in nonspherical microcrystals, as well as in CdSe microcrystals with hexagonal lattice structure,[10] shows a necessity for the spin relaxation time measurements. The existence of long-lived electron-hole pair states has been already observed by Bawendi *et al.* in CdSe microcrystals.[5] External magnetic fields mix the projections of electron spin and strongly shorten the lifetimes of $| 3/2, \downarrow\rangle$ and $| -3/2, \uparrow\rangle$ states. Investigations of the luminescence in these fields should clarify the physical nature of the observed long-time relaxation. It also makes possible direct measurements of the spin relaxation times (Hanle effect[25]).

In conclusion, investigation of the effect of the nonspherical shape has shown that one can use the spherical approximation for the absorption spectra description. Small deviations of spherical shape lead only to the additional broadening of the interband transition spectra. At the same time, the luminescence in prolate microcrystals differs significantly from those in the oblate ones. Long-lived electron-hole pairs can be formed in microcrystals where the hole first QSL is the $| \pm 3/2\rangle$ state. These pairs have unusual luminescence polarization and temperature-dependent radiative lifetimes. Formation of such pairs should lead to a Stokes shift of luminescence which increases with the size of nanocrystals.

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