

## Luminescence polarization of CdSe microcrystals

Al. L. Efros

*Technische Universität München, 8046 Garching, Germany*

(Received 13 December 1991)

We have considered theoretically the polarization of the luminescence of small CdSe microcrystals due to the hexagonal structure of the lattice. We derive the energy spectrum and wave functions of holes in spherical microcrystals. It is shown that the value of the splitting between the *A* and *B* hole states in microcrystals could be five times smaller than the corresponding value of crystal-field splitting  $\Delta$  in bulk hexagonal semiconductors. The times of radiative recombination and the polarization of light connected with transitions between the electron and hole quantum size levels (QSL's) were calculated. The time dependence of the luminescence polarization has been found. At the first instant after short impulse excitation the degree of polarization should be equal to 13/51. It is shown that nonequilibrium electron-hole pairs, with long lifetimes, are formed in microcrystals as a result of the hole thermalization to the *A* state after excitation into the *B* state. The recombination of these states requires the participation of phonons, resulting in a strong dependence of the recombination rate on the temperature. The degree of luminescence polarization of these states depends on the type of phonons involved in optical transitions.

### I. INTRODUCTION

The optical properties of microcrystals have attracted considerable attention in the past years.<sup>1-11</sup> In microcrystals smaller in size than the bulk exciton radius these properties are determined at a first approximation by transitions between quantum size levels (QSL's) of holes and electrons. The quantitative descriptions of absorption and luminescence have to take into account the real band structure of microcrystals because it leads to the shift of optical transition energies and/or to the changing of the optical selection rules.<sup>4,5,11</sup>

The optical properties of small-size CdSe microcrystals with hexagonal lattice structure have recently been investigated.<sup>1</sup> The high quality of these microcrystals makes it possible to reveal the fine structure of the absorption and excitation spectrum due to the structure of the valence band. The existence of intrinsic asymmetry in such microcrystals caused by the hexagonal axis of the lattice leads to asymmetry of their optical properties. It should lead and does lead<sup>12</sup> in particular to the polarization of luminescence. The observed value of this polarization is certainly reduced by the accidental distribution of the hexagonal axis directions in different microcrystals. The polarization of luminescence has been observed also in large-size CdSe microcrystals.<sup>13</sup>

Investigation of the luminescence polarization could provide information on the processes of thermal and spin relaxation of electrons and holes in microcrystals. The nature of their interactions with phonons has not yet been established, and the degree of polarization, depending strongly on the type of this interaction, might reveal it.

The following is a theoretical analysis of the linear polarization of luminescence of small-size CdSe microcrystals with hexagonal lattice structure. The paper comprises the following. First of all we will consider the energy spectrum and wave functions of the hole's QSL's.

After that, the times of radiative recombination and dependencies of the light absorption and emission on the angle between the hexagonal axis of the microcrystal and the polarization vector of light will be found. After considering the recombination kinetic of nonequilibrium electron-hole pairs (Sec. IV) the time dependence of luminescence polarization will be obtained (Sec. V). Finally, we will discuss received results.

### II. ENERGY SPECTRUM AND WAVE FUNCTIONS OF HOLES

Let us assume that the microcrystal is a semiconductor sphere with radius *a* surrounded by an infinitely high potential barrier.<sup>14</sup> The energy and wave functions of QSL's of holes and electrons will be treated in the framework of the effective-mass approximation.

The hole Hamiltonian in hexagonal crystals  $\hat{H}_h$  has a rather complicated form.<sup>15</sup> It could be obtained from the Luttinger Hamiltonian  $\hat{H}_L$  (Ref. 16) by adding an anisotropic term  $\hat{V}$ :<sup>15</sup>

$$\hat{H} = \hat{H}_L + \hat{V}, \quad (1)$$

where  $\hat{H}_L$  could be treated in the spherical approximation:

$$\hat{H}_L = (\gamma_1 + \frac{5}{2}\gamma) \frac{\hat{p}^2}{2m_0} - \frac{\gamma}{m_0} (\hat{\mathbf{p}}\mathbf{J})^2, \quad (2)$$

where  $\hat{\mathbf{p}} = -i\hbar\nabla$  is the momentum operator,  $m_0$  is the mass of the free electron;  $\gamma_1$  and  $\gamma$  are Luttinger parameters, and  $J_x, J_y, J_z$  are the  $4 \times 4$  matrices of the projections of the spin momentum  $J = \frac{3}{2}$ .<sup>16</sup> The simplest term  $\hat{V}$  expressing the main feature of the valence band of hexagonal semiconductor structures is

$$\hat{V} = -\Delta(J_z^2 - \frac{1}{4})/2 = - \begin{pmatrix} \Delta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \Delta \end{pmatrix}, \quad (3)$$

where  $\Delta$  is the value of crystal-field splitting of the valence band, the distance between  $A$  and  $B$  valence subbands.

The effective-mass tensors in subbands  $A$  and  $B$  are anisotropic. Effective masses of holes along the hexagonal axis  $m_{\parallel A}$  and perpendicular to this axis  $m_{\perp A}$  in the  $A$  subband are connected with  $\gamma$  parameters by the relationship

$$m_{\parallel A} = m_0 / (\gamma_1 - 2\gamma), \quad m_{\perp A} = m_0 / (\gamma_1 + \gamma). \quad (4)$$

Corresponding values for the  $B$  subband are

$$m_{\parallel B} = m_0 / (\gamma_1 + 2\gamma), \quad m_{\perp B} = m_0 / (\gamma_1 - \gamma). \quad (5)$$

In sufficiently small microcrystals, i.e., when the size quantization energy of holes is larger than the value of crystal-field splitting  $\Delta$ , we can find the energy spectrum of Hamiltonian (1) within the framework of perturbation theory.

Every state of the Hamiltonian (2) describing free holes in a spherical potential well is characterized by the total momentum  $F$  ( $F = \frac{1}{2}, \frac{3}{2}, \dots$ ).<sup>17,18</sup> The Hamiltonian (2) also commutes with the parity operator  $\hat{I}$ . As a result, the common solution of (2) has the following form:

$$\Psi_{F,M,I} = \sqrt{2F+1} \sum_{l_I} R_{l_I}(r) (-1)^{M+1_I-3/2} \times \sum_{m+\mu=M} \begin{pmatrix} \frac{3}{2} & l_I & \frac{3}{2} \\ \mu & m & -M \end{pmatrix} Y_{l,m} u_{\mu}, \quad (6)$$

where  $l_I$  have the value  $F - \frac{3}{2}, F + \frac{1}{2}$  for odd solutions and  $F - \frac{1}{2}, F + \frac{3}{2}$  for the even ones. Radial functions  $R_{l_I}(r)$  for every parity satisfy the set of second-order differential equations.<sup>18</sup> Linear combinations of the spherical Bessel functions  $j_1(x)$  (Ref. 5) are the solutions of this set in the case of free holes.  $Y_{l,m}(\theta, \varphi)$  are the normalized spherical functions,

$$\begin{pmatrix} i & k & l \\ m & n & p \end{pmatrix}$$

are the  $3j$  Wigner symbols, and  $u_{\mu}$  ( $\mu = \pm\frac{1}{2}, \pm\frac{3}{2}$ ) are the Bloch functions of the fourfold degenerate valence band  $\Gamma_8$ :

$$A^2 = 1 / \int dx x^2 \left[ \left( j_2(kx) + \frac{j_0(k)}{j_0(k\beta^{1/2})} j_2(k\beta^{1/2}x) \right)^2 + \left( j_0(kx) - \frac{j_0(k)}{j_0(k\beta^{1/2})} j_0(k\beta^{1/2}x) \right)^2 \right]. \quad (12)$$

When the effective mass of the light holes is much smaller than the one for heavy holes ( $\beta \ll 1$ ), Eq. (2) reduces to  $j_2(k) = 0$ . The energy of the ground QSL of holes  $E_h$  is<sup>5,11</sup>

$$E_h = \hbar^2 \varphi_2^2 / (2m_{\parallel A} a^2), \quad (13)$$

$$\begin{aligned} u_{3/2} &= \frac{1}{\sqrt{2}} (X + iY) \uparrow, \\ u_{-3/2} &= \frac{i}{\sqrt{2}} (X - iY) \downarrow, \\ u_{1/2} &= \frac{1}{\sqrt{6}} [(X + iY) \downarrow - 2Z \uparrow], \\ u_{-1/2} &= \frac{i}{\sqrt{6}} [-(X - iY) \uparrow + 2Z \downarrow]. \end{aligned} \quad (7)$$

The positions of QSL's for the boundary condition  $\Psi_{F,M,I}(a) = 0$  corresponding to an infinitely high potential barrier surrounding the microcrystal have been found in Ref. 5. In this paper we will only be interested in the odd states with  $F = \frac{3}{2}$ , because, as will be shown further on, they are the only states that participate in the optical transitions to the lowest QSL of electrons.

The equation determining the energy of these QSL's,  $E_h$  can be written down as

$$j_0(k) j_2(\sqrt{\beta} k) + j_2(k) j_0(\sqrt{\beta} k) = 0, \quad (8)$$

where  $k = a \sqrt{2m_{\parallel A} E_h} / \hbar$ ,  $\beta = m_{\parallel B} / m_{\parallel A}$  is the ratio of light- (5) to heavy- (4) hole effective masses in the fourfold degenerate valence band.<sup>16</sup> Wave functions of the odd states with  $F = \frac{3}{2}$  have the form

$$\Psi_M = 2 \sum_{l=0,2} R_l(r) \sum_{m+\mu=M} \begin{pmatrix} \frac{3}{2} & l & \frac{3}{2} \\ \mu & m & -M \end{pmatrix} Y_{l,m} u_{\mu}, \quad (9)$$

where  $M = \pm\frac{3}{2}, \pm\frac{1}{2}$ , and radial functions  $R_l(r)$  take the form

$$\begin{aligned} R_2(r) &= \frac{A}{a^{3/2}} \left[ j_2(kr/a) + \frac{j_0(k)}{j_0(k\beta^{1/2})} j_2(k\beta^{1/2}r/a) \right], \\ R_0(r) &= \frac{A}{a^{3/2}} \left[ j_0(kr/a) - \frac{j_0(k)}{j_0(k\beta^{1/2})} j_0(k\beta^{1/2}r/a) \right], \end{aligned} \quad (10)$$

$k$  is one of the roots of Eq. (8) connected with the energy of QSL's by the relation

$$E_h = \frac{\hbar^2}{2m_{\parallel A} a^2} (k)^2. \quad (11)$$

The constant  $A$  is determined by the normalizing condition

$$\int dr r^2 [R_0^2(r) + R_2^2(r)] = 1$$

and is equal to

where  $\varphi_2 \approx 5.76$  is the first root of  $j_2(x)$ . The normalized radial wave functions  $R_0$  and  $R_2$  of this state have the following analytical form:

$$\begin{aligned} R_0 &= C [j_0(\varphi_2 r/a) - j_0(\varphi_2)], \\ R_2 &= C j_2(\varphi_2 r/a), \end{aligned} \quad (14)$$

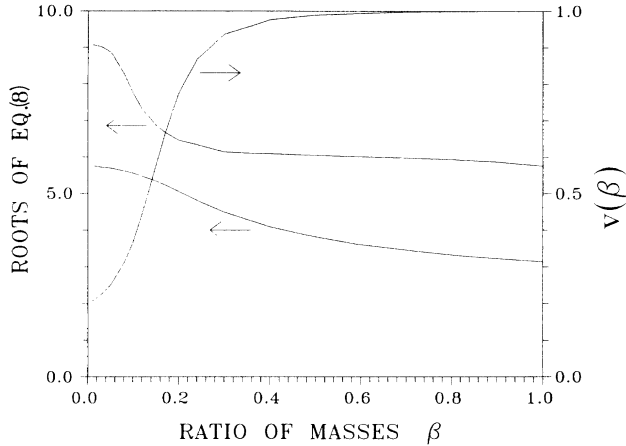


FIG. 1. Dependences of the dimensionless ground-hole state splitting  $v(\beta)$  and the two smallest roots of Eq. (8) on the ratio of the light- to heavy-hole effective masses  $\beta$ .

where  $C \approx 6.044/a^{3/2}$ . The dependences of the first two roots of Eq. (8) are plotted in Fig. 1.

We can consider the influence of term (3) on the energy spectrum in the perturbation theory framework if the energy of the hole size quantization is larger than  $\Delta$ . The first-order perturbation theory gives the shift of the state with  $M = \mp \frac{3}{2}$ :

$$\begin{aligned} \delta_{3/2} &= -4\Delta \int dr r^2 \left[ R_0^2 \begin{pmatrix} 0 & \frac{3}{2} & \frac{3}{2} \\ 0 & \frac{3}{2} & \frac{3}{2} \end{pmatrix}^2 + R_2^2 \begin{pmatrix} 2 & \frac{3}{2} & \frac{3}{2} \\ 0 & \frac{3}{2} & \frac{3}{2} \end{pmatrix}^2 \right] \\ &= -\Delta \int dr r^2 \left[ R_0^2 + \frac{1}{3} R_2^2 \right]. \end{aligned} \quad (15)$$

For the states with  $M = \mp \frac{1}{2}$  the shift is

$$\begin{aligned} \delta_{1/2} &= -4\Delta \int dr r^2 R_2^2 \left[ \begin{pmatrix} 2 & \frac{3}{2} & \frac{3}{2} \\ -1 & \frac{3}{2} & -\frac{1}{2} \end{pmatrix}^2 \right. \\ &\quad \left. + \begin{pmatrix} 2 & \frac{3}{2} & \frac{3}{2} \\ 2 & -\frac{3}{2} & -\frac{1}{2} \end{pmatrix}^2 \right] \\ &= -\frac{4}{3}\Delta \int dr r^2 R_2^2. \end{aligned} \quad (16)$$

By substituting Eq. (10) into Eqs. (15) and (16) we can define the splitting between states with  $|M| = \frac{1}{2}$  and  $|M| = \frac{3}{2}$ :

$$\begin{aligned} \delta_{3/2} - \delta_{1/2} &= -\Delta \int dr r^2 \left[ R_0^2(r) - \frac{3}{5} R_2^2(r) \right] \\ &= -v(\beta)\Delta. \end{aligned} \quad (17)$$

The dimensionless splitting function  $v(\beta)$  depends only on the ratio  $\beta$  between the light- and heavy-hole effective masses—it does not depend on the size of microcrystals. The function  $v(\beta)$  is plotted in Fig. 1. If  $\beta = 0$  for the ground QSL,  $v(0) \approx 0.2$ . The splitting between the  $A$  and  $B$  hole states is five times smaller than in the bulk semiconductor. As Fig. 1 shows, the splitting is very sensitive to the value of  $\beta$  in the interval  $0 < \beta < 0.3$ .

### III. POLARIZATION OF LUMINESCENCE AND RADIATIVE RECOMBINATION OF THE SYSTEM OF SELECTIVE EXCITED ANISOTROPIC MICROCRYSTALS

Let us consider the interband transitions to and from the lowest QSL of electrons caused by the absorption and emission of the linear polarized light. The wave function of ground QSL of electrons has the form<sup>13</sup>

$$\begin{aligned} \Psi_{e\alpha}(\mathbf{r}) &= \left[ \frac{2}{a} \right]^{1/2} \frac{\sin(\pi r/a)}{r} Y_{00} |S\alpha\rangle \\ &= f(r) Y_{00} |S\alpha\rangle, \end{aligned} \quad (18)$$

where  $|S\alpha\rangle$  are the Bloch functions of the conduction band and  $\alpha$  is the projection of the electron spin:  $\alpha = \downarrow$  or  $\uparrow$ . The probability  $P$  of optical transitions is proportional to the squared matrix element of the operator  $\mathbf{e}\hat{\mathbf{p}}$  between the electrons (18) and the holes (6) wave functions:

$$\begin{aligned} P_M &= \sum_{\alpha, \mu} |\langle u_\mu | \mathbf{e}\hat{\mathbf{p}} | S\alpha \rangle|^2 (2F+1) \\ &\quad \times \left| \int dr^3 f(r) Y_{00} \right. \\ &\quad \left. \times \sum_{l_I} R_{l_I}(r) \begin{pmatrix} \frac{3}{2} & l_I & \frac{3}{2} \\ \mu & M-\mu & -M \end{pmatrix} Y_{l_I, M-\mu} \right|^2, \end{aligned} \quad (19)$$

where  $\mathbf{e}$  is the vector of light polarization. This matrix element is nonzero only for odd states of holes with  $F = \frac{3}{2}$  because only these wave functions have components with the spherical function  $Y_{00}$  giving nonzero contribution in Eq. (19):  $\int d\Omega Y_{lm} Y_{00} = \delta_{l0}$ . Substituting Eq. (9) into Eq. (19) we obtain

$$\begin{aligned} P_{M,\alpha} &= |\langle \Psi_M | \mathbf{e}\hat{\mathbf{p}} | \Psi_{e\alpha} \rangle|^2 \\ &= \left| \int dr r^2 f(r) R_0(r) \right|^2 |\langle u_{\mu=M} | \mathbf{e}\hat{\mathbf{p}} | S\alpha \rangle|^2 \\ &= K |\langle u_M | \mathbf{e}\hat{\mathbf{p}} | S\alpha \rangle|^2; \end{aligned} \quad (20)$$

here  $K$  is the overlap integral squared:

$$K = \left| \int dr r^2 f(r) R_0(r) \right|^2. \quad (21)$$

Its value is independent of microcrystal size  $a$  and depends only on  $\beta$ . The dependences of  $K$  on  $\beta$  for two lowest QSL's of holes are presented in Fig. 2.

We can expand the scalar product  $\mathbf{e}\hat{\mathbf{p}}$  for linearly polarized light in Eq. (20):

$$\mathbf{e}\hat{\mathbf{p}} = e_z \hat{p}_z + e_- \hat{p}_+ + e_+ \hat{p}_-, \quad (22)$$

where  $z$  is the direction of hexagonal axis of microcrystal,

$$e_\pm = (e_x \mp i e_y) / \sqrt{2}, \quad \hat{p}_\pm = (\hat{p}_x \mp i \hat{p}_y) / \sqrt{2}.$$

The light with polarization  $\mathbf{e}$  excites the transitions be-

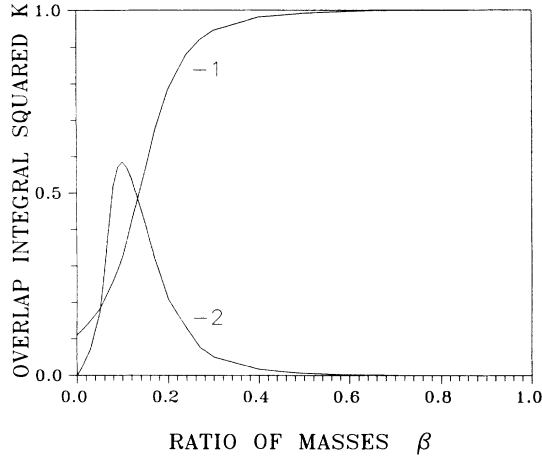


FIG. 2. Dependences of the overlap integral squared  $K$  for the first (curve 1) and second (curve 2) QSL on the ratio of the light- to heavy-hole effective masses  $\beta$ .

tween the hole states with  $M = \frac{3}{2}$  and the electron state with spin up (marked as  $|\frac{3}{2}\rangle$  and  $|\uparrow\rangle$ ) with the relative probability

$$\begin{aligned} |\langle \uparrow | e_+ \hat{p}_- | \frac{3}{2} \rangle|^2 &= K \left| \left\langle S \uparrow \left| e_+ \hat{p}_- - \frac{1}{\sqrt{2}}(X + iY) \uparrow \right. \right\rangle \right|^2 \\ &= K |e_+ \langle S \uparrow | \hat{p}_x X + \hat{p}_y Y | \uparrow \rangle|^2 \\ &= (e_x^2 + e_y^2) K P^2 / 2 \\ &= e_1^2 K P^2 / 2 = (K P^2 / 2) \sin^2(\theta), \end{aligned} \quad (23)$$

where  $P = \langle S | \hat{p}_y | Y \rangle$  is the Kane interband matrix element and  $\theta$  is the angle between the light polarization and the hexagonal axis of the microcrystal. The same expression describes the transition probability between the hole state  $M = -\frac{3}{2}$  ( $|\frac{3}{2}\rangle$ ) and the electron state with spin down ( $|\downarrow\rangle$ ):

$$|\langle \downarrow | e_- \hat{p}_+ | -\frac{3}{2} \rangle|^2 = (K P^2 / 2) \sin^2(\theta). \quad (24)$$

Corresponding calculations for the hole state with  $M = \frac{1}{2}$  ( $|\frac{1}{2}\rangle$ ) give

$$\begin{aligned} |\langle \uparrow | e_z \hat{p}_z | \frac{1}{2} \rangle|^2 &= K |\langle S \uparrow | e_z \hat{p}_z | \sqrt{2/3} Z \uparrow \rangle|^2 \\ &= \frac{2}{3} e_z^2 K P^2 = \frac{2}{3} K P^2 \cos^2(\theta), \\ |\langle \downarrow | e_+ \hat{p}_- | \frac{1}{2} \rangle|^2 &= K \left| \left\langle S \downarrow \left| e_+ \hat{p}_- - \frac{1}{\sqrt{6}}(X + iY) \downarrow \right. \right\rangle \right|^2 \\ &= (K P^2 / 6) \sin^2(\theta). \end{aligned} \quad (25)$$

The same calculations for the  $M = -\frac{1}{2}$  state ( $|\frac{1}{2}\rangle$ ) give

$$\begin{aligned} |\langle \downarrow | e_z \hat{p}_z | -\frac{1}{2} \rangle|^2 &= \frac{2}{3} K P^2 \cos^2(\theta), \\ |\langle \uparrow | e_- \hat{p}_+ | -\frac{1}{2} \rangle|^2 &= (K P^2 / 6) \sin^2(\theta). \end{aligned} \quad (26)$$

The total probability of the excitation of the twofold degenerate state of holes with  $|M| = \frac{1}{2}$  is proportional to

$$\begin{aligned} \bar{P}_{1/2} &= 2K P^2 \left[ \frac{2}{3} \cos^2 \theta + \frac{1}{6} \sin^2 \theta \right] \\ &= \frac{2}{3} K P^2 [1 + P_2(\cos \theta)], \end{aligned} \quad (27)$$

where  $P_2(x)$  is the Legendre polynomial. For the twofold degenerate hole state with  $|M| = \frac{3}{2}$  this probability is proportional to

$$\bar{P}_{3/2} = 2K P^2 \sin^2 \theta = \frac{2}{3} K P^2 [1 - P_2(\cos \theta)]. \quad (28)$$

It means that the excitation probabilities of these two states differ from each other and depend on the angle between light polarization  $\mathbf{e}$  and the hexagonal axis  $C$  of the microcrystal. For one orientation of microcrystals light excites the states with  $|M| = \frac{3}{2}$ , for the others  $|M| = \frac{1}{2}$  states. This also causes the polarization of luminescence because the selection rules of radiative recombination are the same as those of absorption.

The relative probabilities of the radiative recombination of the electron-hole pair (EHP) are described by the same matrix elements (24)–(26). For the  $|M, \alpha\rangle$  EHP states the intensities  $I_e(M, \alpha)$  of the light emission with the polarization vector  $\mathbf{e}'$  are proportional to

$$\begin{aligned} I_e(-\frac{3}{2}, \downarrow) &= I_e(\frac{3}{2}, \uparrow) \sim (K P^2 / 2) \sin^2(\theta'), \\ I_e(-\frac{1}{2}, \uparrow) &= I_e(\frac{1}{2}, \downarrow) \sim (K P^2 / 6) \sin^2(\theta'), \\ I_e(-\frac{1}{2}, \downarrow) &= I_e(\frac{1}{2}, \uparrow) \sim (2K P^2 / 3) \cos^2(\theta'), \end{aligned} \quad (29)$$

where  $\theta'$  is the angle between  $\mathbf{e}'$  and the hexagonal axis of the microcrystal.

The total times of the radiative recombination of the  $|M, \alpha\rangle$  states  $\tau_r(M, \alpha)$  can be obtained by summing up probabilities (20) over all light polarizations. They have the following form:<sup>19</sup>

$$\frac{1}{\tau_r(M, \alpha)} = \frac{4e^2 \omega n}{3m_0^3 c^3 \hbar} |\langle M | \hat{p}_\mu | \alpha \rangle|^2, \quad (30)$$

where  $\omega$  and  $c$  are the frequency and velocity of light,  $n$  is the refractive index. Using Eqs. (20) one can find

$$\begin{aligned} \frac{1}{\tau_r(\frac{3}{2}, \uparrow)} &= \frac{1}{\tau_r(-\frac{3}{2}, \downarrow)} = \frac{1}{\tau_0} K, \\ \frac{1}{\tau_r(\frac{1}{2}, \uparrow)} &= \frac{1}{\tau_r(-\frac{1}{2}, \downarrow)} = \frac{2}{3\tau_0} K, \\ \frac{1}{\tau_r(\frac{1}{2}, \downarrow)} &= \frac{1}{\tau_r(-\frac{1}{2}, \uparrow)} = \frac{1}{3\tau_0} K, \end{aligned} \quad (31)$$

where

$$\tau_0 = \left[ \frac{4\omega n P^2}{3 \times 137 m_0 c^2 m_0} \right]^{-1} \quad (32)$$

is the characteristic time of the radiative recombination for bulk semiconductors. We can estimate  $\tau_0 \approx 1.0$  ns for CdSe using  $P^2 / 2m_0 \approx 20$  eV.

The radiative recombination times in microcrystals for different states (31) satisfy the rule 1:2:3 and are of  $\tau_0 / K$  order. The value of the overlap integral squared  $K$  (21) is very sensitive to the ratio of light- to heavy-hole effective masses  $\beta$  (see Fig. 2). In most of the semiconductors  $\beta$  is

of the order of 0.1. At such  $\beta$  the value of  $K$  considerably reduces the oscillator strength of the interband optical transitions between the ground hole and the ground electron state and makes the radiative recombination times in the semiconductor microcrystals one order of magnitude larger than  $\tau_0$ .

At the same time direct optical recombination of the  $|\frac{3}{2}, \downarrow\rangle$  and  $|\frac{3}{2}, \uparrow\rangle$  EHP states are impossible because the matrix elements  $\langle \frac{3}{2}, \downarrow | \mathbf{e} \hat{\mathbf{p}} | \downarrow \rangle$  and  $\langle \frac{3}{2}, \uparrow | \mathbf{e} \hat{\mathbf{p}} | \uparrow \rangle$  are equal to zero. Such states could be formed as a result of the thermalization of the holes initially excited into the states with  $M = \mp \frac{1}{2}$ . The  $|\frac{3}{2}, \downarrow\rangle$  and  $|\frac{3}{2}, \uparrow\rangle$  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 (31). This leads to the formation of the long-living EHP states in microcrystals with hexagonal lattice structure.

#### IV. KINETIC OF ELECTRON-HOLE PAIR RECOMBINATION

In Sec. III we obtained Eq. (29) for the dependence of luminescence intensity  $I_e(M, \alpha)$  on the angle  $\theta$  between the vector of light polarization  $\mathbf{e}'$  and the microcrystal hexagonal axis  $\mathbf{C}$  due to the annihilation of the  $|M, \alpha\rangle$  EHP state. The total intensity of luminescence  $\mathcal{J}_e$  should be a product of  $I_e(M, \alpha)$  and the number of microcrystals containing such  $e$ - $h$   $N_{M, \alpha}(\mathbf{C})$  integrated over all directions of microcrystal axis  $\mathbf{C}$  and summed up over all possible EHP states:

$$\mathcal{J}_e = \sum_{M, \alpha} \int I_e(M, \alpha) N_{M, \alpha}(\mathbf{C}) d\Omega. \quad (33)$$

The numbers of microcrystals  $N_{M, \alpha}(\mathbf{C})$  are determined by the probabilities of the EHP excitation described Eqs. (23)–(26) and by the kinetic of the radiative and thermal relaxation of excited EHP's. For the holes excited in the upper  $|\mp \frac{1}{2}\rangle$  states this kinetic can be described by the following system of equations:

$$\begin{aligned} \frac{dN_{1/2, \uparrow}}{dt} &= -\frac{N_{1/2, \uparrow}}{\tau_r(\frac{1}{2}, \uparrow)} - N_{1/2, \uparrow} \left[ \frac{1}{\tau_{3/2}} + \frac{1}{\tau_{-3/2}} \right] \\ &\quad + W_{1/2} \frac{2}{3} \cos^2(\theta), \\ \frac{dN_{-1/2, \uparrow}}{dt} &= -\frac{N_{-1/2, \uparrow}}{\tau_r(-\frac{1}{2}, \uparrow)} - N_{-1/2, \uparrow} \left[ \frac{1}{\tau_{-3/2}} + \frac{1}{\tau_{3/2}} \right] \\ &\quad + W_{1/2} \frac{1}{6} \sin^2(\theta), \\ \frac{dN_{3/2, \uparrow}^T}{dt} &= -\frac{N_{3/2, \uparrow}^T}{\tau_r(\frac{3}{2}, \uparrow)} + \frac{N_{1/2, \uparrow}}{\tau_{3/2}} + \frac{N_{-1/2, \uparrow}}{\tau_{-3/2}}, \\ \frac{dN_{-3/2, \uparrow}^T}{dt} &= -\frac{N_{-3/2, \uparrow}^T}{\tau_{ir}} + \frac{N_{1/2, \uparrow}}{\tau_{-3/2}} + \frac{N_{-1/2, \uparrow}}{\tau_{3/2}}, \end{aligned} \quad (34)$$

where  $\tau_r(M, \alpha)$  are the times of radiative recombination (31),  $\tau_{3/2}$  is the time of the hole thermalization from the states  $|\mp \frac{1}{2}\rangle$  to the states  $|\mp \frac{3}{2}\rangle$  and  $\tau_{-3/2}$  is the time of the thermalization from the states  $|\mp \frac{1}{2}\rangle$  to the states  $|\pm \frac{3}{2}\rangle$ ,  $\tau_{ir}$  is the long time of the indirect optical recombination of the  $|\frac{3}{2}, \uparrow\rangle$  EHP state. The nonhomogeneous terms in the right side of Eq. (34), which are propor-

tional to  $W_M$ , take into account the angle dependence of the probability of the EHP excitation by the light with the polarization vector  $\mathbf{e}$  (23)–(27).

For the holes excited directly in the  $|\mp \frac{3}{2}\rangle$  state, thermalization is impossible and the kinetic equations have a much more simple form:

$$\frac{dN_{3/2, \uparrow}}{dt} = -\frac{N_{3/2, \uparrow}}{\tau_r(\frac{3}{2}, \uparrow)} + W_{3/2} \frac{1}{2} \sin^2(\theta). \quad (35)$$

The systems (34) and (35) concern only the EHP states with an electron in the  $|\uparrow\rangle$  state. A similar system could be written for the  $|\downarrow\rangle$  electron state but it is not necessary. The second electron state only leads to the factor 2 in Eq. (33).

The probabilities  $W_{1/2}$  and  $W_{3/2}$  are proportional to the light intensity and the number of microcrystals  $n_{|M|}$  taking part in the absorption at the frequency  $\omega$ . The numbers of microcrystals  $n_{1/2}$  and  $n_{3/2}$  can differ from each other because the levels of holes with  $M = \mp \frac{1}{2}$  and  $\mp \frac{3}{2}$  are split by the amount  $\delta_{3/2} - \delta_{1/2}$  (17). As a result the photons with energy  $\hbar\omega$  excite the  $|\mp \frac{3}{2}\rangle$  and  $|\mp \frac{1}{2}\rangle$  states in microcrystals with different sizes. Its relative numbers are determined by the size distribution of microcrystals.  $W_{3/2} \approx W_{1/2} = W$  if this distribution does not change too rapidly  $((\partial n / \partial a) / (n/a) [(\delta_{3/2} - \delta_{1/2}) / (\hbar^2 \pi^2 / m_e a^2)] \ll 1)$ .

Using Eqs. (31) we write the times of the radiative recombination in the form

$$\begin{aligned} \frac{1}{\tau_r(-\frac{1}{2}, \uparrow)} &= \frac{1}{3\tau_0} K = \frac{1}{\tau_{dr}}, \\ \frac{1}{\tau_r(\frac{1}{2}, \uparrow)} &= \frac{2}{\tau_{dr}}, \quad \frac{1}{\tau_r(\frac{3}{2}, \uparrow)} = \frac{3}{\tau_{dr}}. \end{aligned} \quad (36)$$

The times of the thermalization  $\tau_{\mp 3/2}$  in Eq. (34) are determined by the hole interaction with the phonons. The spectrum and wave functions of the phonons in the spherical microcrystals differ from the ones in bulk semiconductors. Each phonon state should be characterized by the orbital momentum  $l$  and it is  $2l+1$ -fold degenerate with respect to the projection momentum  $m$ . The wave functions of these states were found by Englman and Ruppin<sup>20</sup> and Ruppin.<sup>21</sup>

The Hamiltonian of the electron interaction with such spherical phonons in the second quantization representation can be written in the form

$$\hat{U}_{e-p} = \sum_{\substack{l=0,1,\dots \\ l \leq m \leq l,n}} \xi_{l,n}(r) [b_{lmn} Y_{lm}(\theta, \varphi) + b_{lmn}^\dagger Y_{lm}^*(\theta, \varphi)], \quad (37)$$

where  $b_{lmn}$  and  $b_{lmn}^\dagger$  are the creation and annihilation operators of the  $n$ th type of the spherical phonons with the orbital momentum  $l$  and the momentum projection  $m$ . The radial functions  $\xi_{l,n}$  depend on the type of phonons. For the longitudinal optical and surface phonons these functions have been found in Refs. 22 and 2.

The thermalization of holes from the upper  $|\mp \frac{1}{2}\rangle$  states is followed by phonon emission. The probability of the transition from the  $|\frac{1}{2}\rangle$  to the  $|\frac{3}{2}\rangle$  holes states is determined by the squared matrix element:

$$\begin{aligned}
\frac{1}{\tau_{3/2}} &\sim |\langle \frac{3}{2}, b_{lmn}^\dagger | \hat{U}_{e-p} | \frac{1}{2} \rangle|^2 \\
&= \frac{4}{\pi} \delta_{l,2} \delta_{m,(-1)} \left[ \begin{array}{ccc} 2 & \frac{3}{2} & \frac{3}{2} \\ -1 & \frac{3}{2} & -\frac{1}{2} \end{array} \right]^2 J_{ln}^2 \\
&= \frac{2}{5\pi} \delta_{l,2} \delta_{m,(-1)} J_{ln}^2, \tag{38}
\end{aligned}$$

$$\int d\Omega \Psi_M Y_{l,m}(\theta, \varphi) \Psi_M = \frac{\delta_{l,0} \delta_{M,M'}}{\sqrt{4\pi}} [R_0^2(r) + R_2^2(r)] + \frac{2}{\sqrt{\pi}} (-1)^{M'+1/2} \delta_{l,2} \left[ \begin{array}{ccc} 2 & \frac{3}{2} & \frac{3}{2} \\ m & M & -M' \end{array} \right] R_0(r) R_2(r), \tag{39}$$

where the wave functions  $\Psi_M$  are determined in Eq. (9). The same calculation for the transitions from the  $|\frac{1}{2}\rangle$  to the  $|\frac{3}{2}\rangle$  hole states gives

$$\begin{aligned}
\frac{1}{\tau_{-3/2}} &\sim \frac{4}{\pi} \delta_{l,2} \delta_{m,2} \left[ \begin{array}{ccc} 2 & \frac{3}{2} & \frac{3}{2} \\ 2 & -\frac{3}{2} & -\frac{1}{2} \end{array} \right]^2 J_{ln}^2 \\
&= \frac{2}{5\pi} \delta_{l,2} \delta_{m,2} J_{ln}^2. \tag{40}
\end{aligned}$$

Only phonons with  $l=2$  and  $m=2$  take part in these transitions, but the times of the thermalization in both cases are equal to each other:

$$\tau_{3/2} = \tau_{-3/2} \equiv \tau_T. \tag{41}$$

Finally, let us discuss the recombination time  $\tau_{ir}$  of the  $|\frac{3}{2}, \downarrow\rangle$  EHP states and the polarization properties of these transitions. Direct optical recombination of the  $|\frac{3}{2}, \downarrow\rangle$  EHP state is impossible because a photon cannot have the projection of momentum equal to 2. Nevertheless, this process could occur with the absorption or the emission of the phonons taking up a part of this projection.

This recombination proceeds through several virtual intermediate states and two channels and these processes can be considered. The electrons from the  $|\downarrow\rangle$  state transfer to the  $|\uparrow\rangle$  state emitting or absorbing spherical phonons with  $m = \mp 1$ . Energy conservation is not necessary for the transition to the virtual intermediate state. The intermediate  $|\frac{3}{2}, \uparrow\rangle$  EHP state formed by the phonons can recombine radiatively. Polarization properties of this recombination are determined by the second state of this process and are described by the  $I_{e,(\frac{3}{2}, \uparrow)}$  dependence [Eq. (29)].

The other channel can be described as the lifting of holes from the state  $|\frac{3}{2}\rangle$  to the  $|\frac{1}{2}\rangle$  or to the  $|\frac{1}{2}, \downarrow\rangle$  states by emitting or absorbing phonons. These  $|\frac{1}{2}, \downarrow\rangle$  and  $|\frac{1}{2}, \uparrow\rangle$  EHP states emit light with polarizations correspondingly determined by the  $I_{e,(\frac{1}{2}, \downarrow)}$  and  $I_{e,(\frac{1}{2}, \uparrow)}$  dependences [Eq. (29)].

The time of such two-step recombination can be written down in the form<sup>24</sup>

$$\begin{aligned}
\frac{1}{\tau_{ir}} &= \frac{2\pi}{\hbar} \sum_q \sum_j \frac{|M_{i,j}^{\text{phon}}|^2 |M_{j,f}^{\text{phot}}|^2}{(\varepsilon_i - \varepsilon_j - \hbar\omega)^2} \\
&\quad \times \delta(\varepsilon_f - \varepsilon_i - \hbar\omega \mp \hbar\omega_q), \tag{42}
\end{aligned}$$

where a radial integral

$$J_{ln} = \int dr r^2 R_0(r) R_2(r) \xi_{ln}(r).$$

It is seen that only phonons with  $l=2$  and  $m=-1$  can take part in such transitions. We obtained Eq. (38) by using the identity<sup>23</sup>

where the indices  $i, f$ , and  $j$  mark the initial, final, and all intermediate EHP states with energies  $\varepsilon_i, \varepsilon_f$ , and  $\varepsilon_j$  correspondingly, the index  $q$  marks all phonon states with the energy  $\hbar\omega_q$ . The matrix elements of EHP-photon transitions  $M_{j,f}^{\text{phot}}$  have been considered in Sec. III. We will now consider the matrix elements of EHP phonon transitions  $M_{i,j}^{\text{phon}}$ .

The phonon-induced spin-flip transitions of electrons are allowed by a spin-orbit term

$$\hat{H}_{s.o.} = \lambda [\sigma, \hat{p}]_z, \tag{43}$$

where  $\sigma$  is the Pauli matrix, and  $\lambda$  is the coupling parameter. This term, contained by the electron Hamiltonian of semiconductors with hexagonal lattice,<sup>15</sup> mixes the  $|\uparrow\rangle$  and the  $|\downarrow\rangle$  electron states. Due to this term the wave function of the lowest QSL of electrons in second-order perturbation theory has the form

$$\Psi_{e\uparrow}(\mathbf{r}) = f(r) Y_{0,0} |S\uparrow\rangle + \lambda Y_{l,+1} \sum_v f_v(r) \xi_v |S\downarrow\rangle, \tag{44}$$

where  $f(r)$  is the unperturbed wave function, Eq. (18),

$$\xi_v = \left(\frac{2}{3}\right)^{1/2} \left| \int dr r^2 f_v(r) \frac{\partial f(r)}{\partial r} \right| / (\varepsilon - \varepsilon_v),$$

$\varepsilon_v$  and  $f_v$  are the energies and wave functions of the  $v$ th QSL of electrons with orbital momentum  $l=1$ ,  $\varepsilon$  is the energy of the lowest electron QSL. Using Eq. (44) one can show that the matrix element of electron-phonon interaction (37),  $\langle \Psi_{e\uparrow} | \hat{U}_{e-p} | \Psi_{e\downarrow} \rangle$ , is nonzero only for the transitions occurring with emission or absorption of phonons with  $l=1$  and  $m = \mp 1$ .

Interaction of the spherical phonons with  $|\mp \frac{3}{2}\rangle, |\mp \frac{1}{2}\rangle$  hole states have been considered above in Eqs. (38)–(41). The transitions from the  $|\frac{3}{2}\rangle$  to the  $|\frac{1}{2}\rangle$  state and from the  $|\frac{3}{2}\rangle$  to the  $|\frac{1}{2}, \downarrow\rangle$  state have been shown to have the same probability and to be caused by the phonons with orbital momentum  $l=2$ .

Using Eqs. (41) and (36) we can rewrite system of Eqs. (34) and (35) as

$$\begin{aligned}
\frac{dN_{1/2,\uparrow}}{dt} &= -N_{1/2,\uparrow} \left[ \frac{2}{\tau_{dr}} + \frac{2}{\tau_T} \right] + W_{1/2} \frac{2}{3} \cos^2(\theta), \\
\frac{dN_{-1/2,\uparrow}}{dt} &= -N_{-1/2,\uparrow} \left[ \frac{1}{\tau_{dr}} + \frac{2}{\tau_T} \right] + W_{1/2} \frac{1}{6} \sin^2(\theta), \\
\frac{dN_{3/2,\uparrow}^T}{dt} &= -\frac{3N_{3/2,\uparrow}^T}{\tau_{dr}} + \frac{N_{1/2,\uparrow}}{\tau_T} + \frac{N_{-1/2,\uparrow}}{\tau_T}, \\
\frac{dN_{-3/2,\uparrow}^T}{dt} &= -\frac{N_{-3/2,\uparrow}^T}{\tau_{ir}} + \frac{N_{1/2,\uparrow}}{\tau_T} + \frac{N_{-1/2,\uparrow}}{\tau_T}.
\end{aligned} \tag{45}$$

For microcrystals directly excited in the  $|\frac{3}{2}, \uparrow\rangle$  state, Eq. (35) reduces to

$$\frac{dN_{3/2,\uparrow}}{dt} = -\frac{3N_{3/2,\uparrow}}{\tau_{dr}} + W_{3/2} \frac{1}{2} \sin^2(\theta). \tag{46}$$

Solution of Eq. (45) gives the time decay of the number of microcrystals containing EHP with an electron in the  $|\uparrow\rangle$  state:

$$\begin{aligned}
N_{1/2}(t) &= \exp[-t(2/\tau_{dr} + 2/\tau_T)] N_{1/2}(0), \\
N_{-1/2}(t) &= \exp[-t(1/\tau_{dr} + 2/\tau_T)] N_{-1/2}(0), \\
N_{3/2}^T(t) &= \exp(-3t/\tau_{dr}) \left[ N_{3/2}^T(0) - \frac{\exp[-t(2/\tau_T - 1/\tau_{dr})] - 1}{2 - \tau_T/\tau_{dr}} N_{1/2}(0) - \frac{\exp[-t(2/\tau_T - 2/\tau_{dr})] - 1}{2 - 2\tau_T/\tau_{dr}} N_{-1/2}(0) \right], \\
N_{-3/2}^T(t) &= \exp(-t/\tau_{ir}) \left[ N_{-3/2}^T(0) - \frac{\exp[-t(2/\tau_T + 2/\tau_{dr} - 1/\tau_{ir})] - 1}{2 + 2\tau_T/\tau_{dr} - \tau_T/\tau_{ir}} N_{1/2}(0) - \frac{\exp[-t(2/\tau_T + 1/\tau_{dr} - 1/\tau_{ir})] - 1}{2 + \tau_T/\tau_{dr} - \tau_T/\tau_{ir}} N_{-1/2}(0) \right].
\end{aligned} \tag{47}$$

The system of Eqs. (47) describes the time dependence of the number of microcrystals  $N_{\mp 3/2}^T$  appearing as a result of thermalization. The decay kinetic of the microcrystal number directly excited in the  $|\frac{3}{2}, \uparrow\rangle$  state has the form

$$N_{3/2}(t) = \exp(-3t/\tau_{dr}) N_{3/2}(0). \tag{48}$$

Initial concentrations  $N_M(0)$  in Eqs. (47) and (48) depend on the angle  $\theta$  between the **C** axis of microcrystals and vector polarization **e** of the exciting light and the condition of the initial excitation.

It is reasonable to consider two types of these processes: luminescence decay after steady-state excitation and decay after short impulse excitation. In the first case, the numbers of microcrystal  $N_M(0)$  are

$$\begin{aligned}
N_{1/2}(0) &= W_{1/2} \frac{\frac{2}{3} \cos^2(\theta)}{2/\tau_{dr} + 2/\tau_T}, \\
N_{-1/2}(0) &= W_{1/2} \frac{\frac{1}{6} \sin^2(\theta)}{1/\tau_{dr} + 2/\tau_T}, \\
N_{3/2}^T(0) &= (\tau_{dr}/3\tau_T) [N_{1/2}(0) + N_{-1/2}(0)], \\
N_{-3/2}^T(0) &= (\tau_{ir}/\tau_T) [N_{1/2}(0) + N_{-1/2}(0)], \\
N_{3/2}(0) &= W_{3/2} (\tau_{dr}/3) \sin^2(\theta)/2.
\end{aligned} \tag{49}$$

In the second case, if the excited impulse is shorter than the times of thermalization  $\tau_T$  and recombination  $\tau_{dr}$  these numbers  $N_M(0)$  can be written down in the form

$$\begin{aligned}
N_{1/2}(0) &\sim W_{1/2} \frac{2}{3} \cos^2(\theta), \\
N_{-1/2}(0) &\sim W_{1/2} \frac{1}{6} \sin^2(\theta), \\
N_{3/2}^T(0) &= 0, \quad N_{-3/2}^T(0) = 0, \\
N_{3/2}(0) &\sim W_{3/2} \frac{1}{2} \sin^2(\theta).
\end{aligned} \tag{50}$$

## V. TIME DEPENDENCE OF LUMINESCENCE POLARIZATION

We can completely describe the luminescence polarization properties of these structures by substituting solutions (47) and (48) together with initial conditions (49) and (50) in Eq. (33). We only need the angular dependence of the intensity of the phonon-assisted luminescence. As was mentioned in Sec. IV its properties are determined by the channel through which the recombination goes on. If the main channel is connected with the flip of the electron spin  $I_{e'}(\frac{3}{2}, \downarrow)$  has the form

$$\begin{aligned}
I_{e'}(\frac{3}{2}, \downarrow) &\sim KP^2 \frac{\tau_{dr}}{\tau_{ir}} \sin^2(\theta')/2 \\
&= KP^2 \frac{\tau_{dr}}{\tau_{ir}} \{1 - P_2[\cos(\theta')]\}/3.
\end{aligned} \tag{51}$$

If the mechanism of the holes lifting to the  $|\frac{1}{2}\rangle$  and  $|\frac{1}{2}\rangle$  states dominates, the dependence of the luminescence intensity is described by the following expression:

$$I_{e'(\frac{3}{2}, \downarrow)} \sim KP^2 \frac{\tau_{dr}}{\tau_{ir}} \left[ \frac{2 \cos^2(\theta')}{3} + \frac{\sin^2(\theta')}{6} \right] = KP^2 \frac{\tau_{dr}}{\tau_{ir}} \frac{1 + P_2[\cos(\theta')]}{3}. \quad (52)$$

As a result Eq. (33) for the total intensity of luminescence can be written down as

$$\mathcal{J}_{e'} \sim KP^2 \int \frac{d\Omega}{4\pi} \left[ [N_{3/2}(t) + N_{3/2}^T(t)] \frac{\sin^2(\theta')}{2} + N_{1/2}(t) \frac{2 \cos^2(\theta')}{3} + N_{-1/2}(t) \frac{\sin^2(\theta')}{6} + N_{-3/2}^T(t) \frac{\tau_{dr}}{\tau_{ir}} \frac{1 \mp P_2[\cos(\theta')]}{3} \right], \quad (53)$$

where the  $-$  or  $+$  signs correspond to the one of the two indirect channels of recombination and  $N_M(t)$  depends on the angle  $\theta$  between microcrystal axis and polarization vector of exciting light through initial conditions described by Eqs. (49) and (50). Substituting Eqs. (50) into Eqs. (47) we found for the case of the short-impulse excitation:

$$\begin{aligned} \mathcal{J}_{e'} \sim KP^2 W \int \frac{d\Omega}{4\pi} & \left[ \frac{1}{4} \sin^2(\theta) \sin^2(\theta') \exp(-3t/\tau_{dr}) + \frac{4}{9} \cos^2(\theta) \cos^2(\theta') \exp[-t(2/\tau_{dr} + 2/\tau_T)] \right. \\ & + \frac{1}{36} \sin^2(\theta) \sin^2(\theta') \exp[-t(1/\tau_{dr} + 2/\tau_T)] \\ & + \frac{1}{3} \cos^2(\theta) \sin^2(\theta') \exp(-3t/\tau_{dr}) \frac{1 - \exp[-t(2/\tau_T - 1/\tau_{dr})]}{2 - \tau_T/\tau_{dr}} \\ & + \frac{1}{12} \sin^2(\theta) \sin^2(\theta') \exp(-3t/\tau_{dr}) \frac{1 - \exp[-t(2/\tau_T - 2/\tau_{dr})]}{2 - 2\tau_T/\tau_{dr}} \\ & + \frac{\tau_{dr}}{\tau_{ir}} \frac{2}{9} \cos^2(\theta) [1 \mp P_2\{\cos(\theta')\}] \exp\left[-\frac{t}{\tau_{ir}}\right] \frac{1 - \exp[-t(2/\tau_T + 2/\tau_{dr} - 1/\tau_{ir})]}{2 + 2\tau_T/\tau_{dr} - \tau_T/\tau_{ir}} \\ & \left. + \frac{\tau_{dr}}{\tau_{ir}} \frac{1}{18} \sin^2(\theta) [1 \mp P_2\{\cos(\theta')\}] \exp\left[-\frac{t}{\tau_{ir}}\right] \frac{1 - \exp[-t(2/\tau_T + 1/\tau_{dr} - 1/\tau_{ir})]}{2 + \tau_T/\tau_{dr} - \tau_T/\tau_{ir}} \right]. \quad (54) \end{aligned}$$

Here we assumed that  $W_{3/2} = W_{1/2} = W$ . Using the relationship  $\sin^2(\theta) = 2[1 - P_2(\cos\theta)]/3$  and the following identity:

$$\int \frac{d\Omega}{4\pi} [1 + \eta' P_2(\cos\theta')] [1 + \eta P_2(\cos\theta)] = 1 + \frac{\eta'\eta}{5} P_2(\cos\chi), \quad (55)$$

where  $\chi$  is the angle between the polarization of exciting light  $e$  and the polarization of luminescence  $e'$ , we found from Eq. (54)

$$\begin{aligned} \mathcal{J}_{e'} \sim KP^2 W / 81 & \left[ 9[1 + \frac{1}{5} P_2(\cos\chi)] \exp(-3t/\tau_{dr}) + 4[1 + \frac{4}{5} P_2(\cos\chi)] \exp[-t(2/\tau_{dr} + 2/\tau_T)] \right. \\ & + [1 + \frac{1}{5} P_2(\cos\chi)] \exp[-t(1/\tau_{dr} + 2/\tau_T)] \\ & + 6[1 - \frac{2}{5} P_2(\cos\chi)] \exp(-3t/\tau_{dr}) \frac{1 - \exp[-t(2/\tau_T - 1/\tau_{dr})]}{2 - \tau_T/\tau_{dr}} \\ & + 3[1 + \frac{1}{5} P_2(\cos\chi)] \exp(-3t/\tau_{dr}) \frac{1 - \exp[-t(2/\tau_T - 2/\tau_{dr})]}{2 - 2\tau_T/\tau_{dr}} \\ & + \frac{\tau_{dr}}{\tau_{ir}} 6[1 \mp \frac{1}{5} P_2(\cos\chi)] \exp\left[-\frac{t}{\tau_{ir}}\right] \frac{1 - \exp[-5(2/\tau_T + 2/\tau_{dr} - 1/\tau_{ir})]}{2 + 2\tau_T/\tau_{dr} - \tau_T/\tau_{ir}} \\ & \left. + \frac{\tau_{dr}}{\tau_{ir}} 3[1 \pm \frac{1}{5} P_2(\cos\chi)] \exp\left[-\frac{t}{\tau_{ir}}\right] \frac{1 - \exp[-t(2/\tau_T + 1/\tau_{dr} - 1/\tau_{ir})]}{2 + \tau_T/\tau_{dr} - \tau_T/\tau_{ir}} \right]. \quad (56) \end{aligned}$$

Using Eq. (56) we can find the time dependence of the linear luminescence polarization degree (DLP)  $\rho(t)$  for the light propagating parallel to the direction of the excitation:



$$\begin{aligned}
\rho(t) &= \frac{\mathcal{J}_{\parallel} - \mathcal{J}_{\perp}}{\mathcal{J}_{\parallel} + \mathcal{J}_{\perp}} \\
&= \left[ 9 \exp(-3t/\tau_{dr}) + 16 \exp[-t(2/\tau_{dr} + 2/\tau_T)] + \exp[-t(1/\tau_{dr} + 2/\tau_T)] \right. \\
&\quad + 3 \exp(-3t/\tau_{dr}) \left[ -4 \frac{1 - \exp[-t(2/\tau_T - 1/\tau_{dr})]}{2 - \tau_T/\tau_{dr}} + \frac{1 - \exp[-t(2/\tau_T - 2/\tau_{dr})]}{2 - 2\tau_T/\tau_{dr}} \right] \\
&\quad \left. \pm 3 \frac{\tau_{dr}}{\tau_{ir}} \exp(-t/\tau_{ir}) \left[ \frac{1 - \exp[-t(2/\tau_T + 1/\tau_{dr} - 1/\tau_{ir})]}{2 + \tau_T/\tau_{dr} - \tau_T/\tau_{ir}} - 4 \frac{1 - \exp[-t(2/\tau_T + 2/\tau_{dr} - 1/\tau_{ir})]}{2 + 2\tau_T/\tau_{dr} - \tau_T/\tau_{ir}} \right] \right] \\
&\times \left[ 63 \exp(-3t/\tau_{dr}) + 32 \exp[-t(2/\tau_{dr} + 2/\tau_T)] + 7 \exp[-t(1/\tau_{dr} + 2/\tau_T)] \right. \\
&\quad + 3 \exp(-3t/\tau_{dr}) \left[ 12 \frac{1 - \exp[-t(2/\tau_T - 1/\tau_{dr})]}{2 - \tau_T/\tau_{dr}} + 7 \frac{1 - \exp[-t(2/\tau_T - 2/\tau_{dr})]}{2 - 2\tau_T/\tau_{dr}} \right] \\
&\quad + \frac{\tau_{dr}}{\tau_{ir}} \exp(-t/\tau_{ir}) \left[ (40 \mp 4) \frac{1 - \exp[-t(2/\tau_T + 1/\tau_{dr} - 1/\tau_{ir})]}{2 - \tau_T/\tau_{dr} - \tau_T/\tau_{ir}} \right. \\
&\quad \left. \left. + (20 \pm 1) \frac{1 - \exp[-t(2/\tau_T + 2/\tau_{dr} - 1/\tau_{ir})]}{2 + 2\tau_T/\tau_{dr} - \tau_T/\tau_{ir}} \right] \right]^{-1}, \tag{57}
\end{aligned}$$

where  $\mathcal{J}_{\parallel}$  is the intensity of luminescence polarized like the exciting light  $\mathbf{e}$  [ $\chi=0, P_2(\cos\chi)=1$ ], and  $\mathcal{J}_{\perp}$  is the intensity of luminescence with a polarization perpendicular to the  $\mathbf{e}$  [ $\chi=\pi/2, P_2(\cos\chi)=-\frac{1}{2}$ ]. The DLP depends strongly on the relationship between the radiative recombination time  $\tau_{dr}$  and the time of the hole thermalization  $\tau_T$ . A general result exists only for the initial luminescence after short impulse excitation. From Eq. (54) one can obtain  $\rho(0)=\frac{13}{31}$ . After that it decreased down monotonically. If  $\tau_T \ll \tau_{dr} \ll \tau_{ir}$ ,  $\rho(t)=\frac{3}{61}$  for the time range  $\tau_T \ll t < \tau_{dr}$ . In the longest times ( $t \gg \tau_{dr}$ ), DLP is due

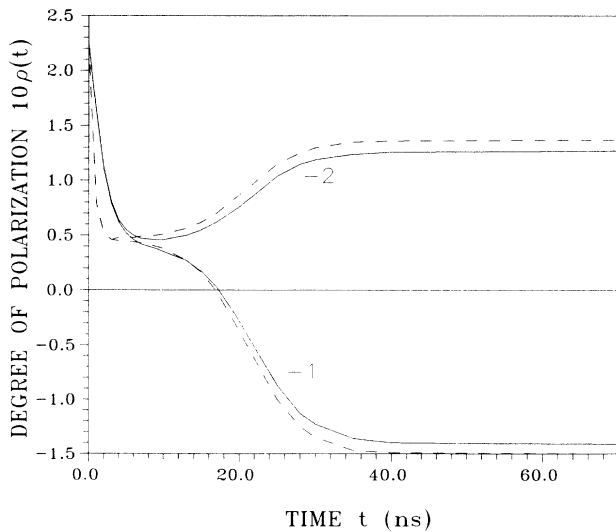


FIG. 3. Time dependences of the degree of linear polarization. 1, recombination assisted by flip of the electron spin. 2, recombination assisted by the virtual hole lifting into the  $|\mp \frac{1}{2}\rangle$  states. Solid lines were calculated for  $\tau_{dr}=9.4$  ns,  $\tau_{ir}=1000$  ns,  $\tau_T=3$  ns and dashed lines with  $\tau_T=1$  ns.

to the recombination of long-living states  $|\frac{3}{2}, \downarrow\rangle$  and  $|\frac{3}{2}, \uparrow\rangle$ . If the main channel of the phonon-assisted recombination is determined by the lifting of holes to the  $|\mp \frac{1}{2}\rangle$  states, then  $\rho(\infty)=\frac{1}{7}$  and the DLP as a function of time has a minimum. In the other case when the main channel is connected with the flip of electron spin, Eq. (54) gives  $\rho(\infty)=-\frac{3}{19}$  and DLP becomes negative. The dependence of DLP on time corresponding to this case is shown in Fig. 3.

Time dependence of DLP after steady-state excitation can be obtained in a similar way by using Eq. (49) instead of Eq. (50) as initial conditions. In this case the main difference is due to the accumulation of the EHP's by the long-living states [see Eq. (49)]. The initial DLP depends strongly on the main channel of the phonon-assisted recombination and it can significantly reduce the initial DLP  $\rho(0)$  for the case of spin-flip recombination.

## VI. RESULTS AND DISCUSSION

We have found the energy spectrum of holes in the small-size CdSe microcrystals with the hexagonal lattice structure. At first approximation this spectrum is similar to those of the microcrystals with the cubic lattice structure. The ground state of the holes is practically fourfold degenerate with respect to the momentum projection  $M = \mp \frac{3}{2}, \mp \frac{1}{2}$ . In microcrystals with a hexagonal lattice structure the crystal field splits this state into two twofold degenerate states with  $M = \mp \frac{1}{2}$  and with  $M = \mp \frac{3}{2}$ . The value of the splitting  $\delta_{3/2} - \delta_{1/2}$  does not depend on the microcrystal radius  $a$ . It depends only on the relationship between the light- and heavy-hole effective masses  $\beta$  and could be five times smaller than its bulk value  $\Delta$ . In CdSe,  $\Delta \approx 25$  meV.<sup>25</sup>

This fine structure is difficult to observe in the absorp-

tion because the broadening of the transition between electron and hole ground states is of the order 200–300 meV due to the microcrystal size distribution. Nevertheless, it is possible that this splitting was observed in Refs. 1 and 2. The Stokes shift of the luminescence from the resonant excitation was found in CdSe microcrystals with average radius 16 Å. This shift does not depend on the frequency of excitation and was equal to 9.3 meV. If we connect this shift with thermalization of holes from the  $|\mp\frac{1}{2}\rangle$  states on the  $|\mp\frac{3}{2}\rangle$  states the independence of the Stokes shift of the frequency agrees with the independence of  $\delta_{3/2}-\delta_{1/2}$  of the radius. For  $\Delta=25$  meV one can find that  $\delta_{3/2}-\delta_{1/2}=9.3$  meV at  $\beta=0.10$  (see Fig. 2). This looks very reasonable because for most cubic semiconductors the value of  $\beta$  is close to 0.1.

The above considerations showed that the hexagonal axis of the microcrystal gives the possibility to form eight well-defined  $|M, \alpha\rangle$  EHP states where  $M = \mp\frac{3}{2}, \mp\frac{1}{2}$  and  $\alpha = \downarrow$  or  $\alpha = \uparrow$ . The wave functions of holes corresponding to these states have the mixed  $s$ - $d$  type of symmetry and they differ significantly from the wave function of the lowest electron QSL. As a result the squared overlap integral  $K$  is significantly smaller than 1 and it reduces the oscillator strength of the interband optical transitions. The times of the radiative recombination of the EHP states  $\tau_r(\frac{3}{2}, \uparrow) = \tau_r(-\frac{3}{2}, \downarrow)$ ,  $\tau_r(\frac{1}{2}, \uparrow) = \tau_r(-\frac{1}{2}, \downarrow)$ ,  $\tau_r(\frac{3}{2}, \downarrow) = \tau_r(-\frac{1}{2}, \uparrow)$  are of the order of 10 ns and satisfy the rule 1:2:3 [see Eq. (31)].

Direct optical excitation and recombination of the  $|\mp\frac{3}{2}, \uparrow\rangle$  and  $|\frac{3}{2}, \downarrow\rangle$  EHP states are forbidden by the selection rules. These states can be formed as a result of the hole thermalization from the  $|\mp\frac{1}{2}\rangle$  states. The radiative recombination of the long-living  $|\mp\frac{3}{2}, \uparrow\rangle$  and  $|\frac{3}{2}, \downarrow\rangle$  EHP states is governed by phonon-assisted optical transitions. The recombination times decrease exponentially with the temperature since they are proportional to the number of phonons [ $\sim \exp(-\hbar\omega_{ph}/kT)$ ].

At low temperatures the acoustic phonons will give the main contribution to the recombination because they have minimal energy and their number is maximal. By considering the quantization of the phonon spectra within the microcrystals one can estimate this energy for

the phonons with orbital momentum  $l=1$  as  $\hbar\omega_{ph,1} = s\hbar(4.49/a)$  and for those with  $l=2$  as  $\hbar\omega_{ph,2} = s\hbar(5.76/a)$ , where  $s$  is the sound velocity.

The anisotropy of the microcrystals leads to the selective excitation of the EHP states by the linear polarized light. The holes with  $M = \mp\frac{3}{2}$  are mainly excited in the microcrystals where the hexagonal axis  $\mathbf{C}$  is parallel to the light direction  $\mathbf{n}$ . The excitation of holes with  $M = \mp\frac{1}{2}$  mainly takes place in the microcrystals where  $\mathbf{C} \perp \mathbf{n}$ . The luminescence of such a system of anisotropic microcrystals will be polarized because the polarization of emitted light has the same angle dependence. The DLP depends strongly on the processes of recombination and thermalization of the nonequilibrium EHP's and on the time dependence of the pumping light. In the first moment after the short impulse excitation the DLP could be  $\frac{15}{51}$  and it falls afterwards due to the thermalization of holes on the lowest  $|\mp\frac{3}{2}\rangle$  states.

The DLP of the long-living states is determined by the type of the phonons assisting the process of recombination. The DLP may be different for the recombination assisted by acoustic phonons and with optical ones. If the main contribution to the recombination is given by the phonons with orbital momentum  $l=1$ , which flip the electron spin, the DLP in the long times will be negative:  $\rho(\infty) = -\frac{3}{19}$ . In the case when the recombination occurs with the phonons with  $l=2$ ,  $\rho(\infty) = \frac{1}{7}$  and the DLP as a function of time has a minimum. The above consideration has shown that the experimental investigation of the luminescence polarization degree gives important information on EHP phonon interaction.

#### ACKNOWLEDGMENTS

I would like to express my gratitude to L. E. Brus and M. G. Bawendi whose challenging discussion stimulated this investigation. I am also grateful to I. N. Uralt'sev and D. R. Yakovlev for useful comments on this paper and J. Worlock for a critical reading of the manuscript. The author wishes to acknowledge the support of the Deutsche Forschungsgemeinschaft.

<sup>1</sup>M. G. Bawendi, W. L. Wilson, L. Rothberg, P. J. Carroll, T. M. Jedju, M. L. Steigerwald, and L. E. Brus, *Phys. Rev. Lett.* **65**, 1623 (1990).

<sup>2</sup>Al. L. Efros, Al. L. Ekimov, F. Kozlowski, V. Petrova-Koch, H. Schmidbauer, and S. Schumilov, *Solid State Commun.* **78**, 853 (1991).

<sup>3</sup>M. A. Olshavsky, A. N. Goldstein, and A. P. Alivisatos, *J. Am. Chem. Soc.* **112**, 9438 (1990).

<sup>4</sup>J. B. Xia, *Phys. Rev. B* **40**, 8500 (1989).

<sup>5</sup>G. B. Grigoryan, E. M. Kazaryan, Al. L. Efros, and T. V. Yazeva, *Fiz. Tverd. Tela Leningrad* **32**, 1772 (1990) [*Sov. Phys. Solid State* **32**, 1031 (1990)].

<sup>6</sup>A. P. Alivisatos, T. D. Harris, P. J. Carrell, M. L. Steigerwald, and L. E. Brus, *J. Chem. Phys.* **90**, 3463 (1989).

<sup>7</sup>L. Katsikas, A. Eyshmüller, M. Giersig, and H. Weller, *Chem. Phys. Lett.* **172**, 201 (1990).

<sup>8</sup>A. Henglein, *Chem. Rev.* **89**, 1861 (1989).

<sup>9</sup>A. Uhrig, L. Banyai, Y. Z. Hu, S. W. Koch, C. Klingshirn, and N. Neuroth, *Z. Phys. B* **81**, 385 (1990).

<sup>10</sup>U. Woggon, I. Rucekmann, J. Kornack, M. Mueller, J. Cesnulevicius, J. Kolenda, and M. Petruskas, *Proc. SPIE* **1362**, 885 (1990).

<sup>11</sup>Al. L. Efros and A. V. Rodina, *Solid State Commun.* **72**, 645 (1989).

<sup>12</sup>M. G. Bawendi, P. J. Carroll, William L. Wilson, and L. E. Brus, *J. Chem. Phys.* **96**, 946 (1992).

<sup>13</sup>M. A. Chamarro, C. Gourdon, and P. Lavallard (unpublished).

<sup>14</sup>Al. L. Efros and A. L. Efros, *Fiz. Tekh. Poluprovodn.* **16**, 1209 (1982) [*Sov. Phys. Semicond.* **16**, 772 (1982)].

<sup>15</sup>G. L. Bir and G. E. Pikus, *Symmetry and Strain-Induced Effects in Semiconductors* (Wiley, New York, 1975).

- <sup>16</sup>J. M. Luttinger, *Phys. Rev.* **102**, 1030 (1956).
- <sup>17</sup>N. O. Lipari and A. Baldereschi, *Phys. Rev. Lett.* **42**, 1660 (1970).
- <sup>18</sup>B. L. Gel'mont and M. I. D'yakonov, *Fiz. Tekh. Poluprovodn.* **5**, 2191 (1971) [*Sov. Phys. Semicond.* **5**, 1905 (1972)].
- <sup>19</sup>L. D. Landau and E. M. Lifshitz, *Relativistic Quantum Theory*, 2nd ed. (Pergamon Press, Oxford, 1965).
- <sup>20</sup>R. Englman and R. Ruppin, *J. Phys. C* **1**, 614 (1968).
- <sup>21</sup>R. Ruppin, *J. Phys. C* **8**, 1969 (1975).
- <sup>22</sup>M. C. Klein, F. Hache, D. Ricard, and C. Flytzaniss, *Phys. Rev. B* **42**, 11 123 (1990).
- <sup>23</sup>B. L. Gel'mont, A. V. Rodina, and Al. L. Efros, *Fiz. Tekh. Poluprovodn.* **24**, 198 (1990) [*Sov. Phys. Semicond.* **24**, 120 (1990)].
- <sup>24</sup>A. I. Ansel'm, *Introduction in the Theory of Semiconductor* (Nauka, Moscow, 1978).
- <sup>25</sup>*Semiconductors*, edited by O. Madelung, M. Schultz, and H. Weiss, *Landolt-Börnstein, New Series, Group III, Vol. 17a* (Springer, Berlin, 1982).