Anomalous polarization of the photoluminescence from anisotropic colloidal CdSe nanocrystals subject to external magnetic fields

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We explain anomalous polarization of magnetophotoluminescence from CdSe nanocrystals with built-in anisotropy observed by Htoon *et al.*, [Phys. Rev. Lett. **102**, 017402 (2009)] in external magnetic fields up to 5 T. While there are two radiative doublets associated with the exciton ground state, it is the lower component of the upper doublet which demonstrates a truly anomalous behavior. We further describe complex behavior of the doublets components polarization in high-magnetic fields. The polarization degree of the upper component of each doublet varies with the applied magnetic field slower than that of the lower component. However, for the upper doublet this behavior is more pronounced and becomes apparent at much lower fields.

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Since the pioneering works by Dzhioev *et al.*[1] magnetophotoluminescence spectroscopy has become a standard tool to measure zero-field splittings of exciton radiative doublets in semiconductor quantum dots. The splittings of exciton radiative doublets into orthogonally linearly polarized components occur in epitaxially grown quantum dot structures with built-in anisotropy. They are caused by the long-range electron-hole exchange interaction[2] (also known as nonanalytical exchange or annihilation interaction). Very recently application of magnetophotoluminescence spectroscopy has revealed fine structure of radiative exciton doublets in colloidal CdSe nanocrystals[3] provoking a number of subsequent studies.[4–6] In Ref. 4 it was pointed out that the origin of the exciton radiative doublet splitting in colloidal nanocrystals is quite different from that for epitaxially grown quantum dots. This difference stems from the fact that the exciton envelope wave function for epitaxial quantum dots is highly anisotropic and must be treated as such even in the zeroth order of the perturbation theory. Then the electron-hole long-range exchange interaction, which is very sensitive to the shape of the exciton envelope function, can be treated as a perturbation and yields a splitting of the radiative doublet in the first order.[2] In colloidal quantum dots, whose shapes are close to spherical, the states of confined electron, hole or exciton in the zeroth order of the perturbation theory can all be characterized by the corresponding angular momentum[7] and wave functions forming bases for representations of the rotation-inversion group. In this case both long-range (nonanalytical) and short-range (analytical) parts of the electron-hole exchange interaction treated in the first order of the perturbation theory add up to produce a splitting between exciton sublevels characterized by different values of the total exciton angular momentum.[8] On the other hand, the anisotropy of the nanocrystal shape must be treated in the same first order of the perturbation theory as the electron-hole exchange interaction, along with the crystal field accounting for the underlying wurtzite structure of CdSe. Thus, the splittings of exciton radiative doublets in colloidal CdSe nanocrystals are results of combined action of all these perturbations. While being exchange induced and vanishing if the exchange interaction is set to zero, the splittings are equally contributed by the short-range and long-range parts of the exchange interaction.[4] Another specifics of CdSe nanocrystals is that there are two radiative doublets associated with the exciton ground state and polarized in the plane perpendicular to the wurtzite axis.

In a recent experiment,[6] evolution of photoluminescence peaks with well-resolved zero-field fine structure under application of magnetic field up to 5 T directed along the wurtzite axis was studied in individual CdSe nanocrystals subject to nonpolarized excitation. It was expected that at magnetic fields corresponding to Zeeman energies exceeding the zero-field splitting one would observe circularly polarized luminescence from both components of the doublet seen in the photoluminescence. Such picture was indeed observed for quantum dots with relatively small zero-field splittings of the radiative doublet, $\Delta_{xy}<0.5$ meV. However, for relatively large splittings, $\Delta_{xy}\gtrsim 1$ meV, it occurred that while the lower component of the doublet was circularly polarized, the upper component preserved its linear polarization.

In this Brief Report we theoretically study evolution of polarization with applied magnetic field for the components of both radiative doublets associated with the ground exciton state of CdSe nanocrystals with built-in anisotropy. We find that, for large zero-field splittings, one of the components exhibits a rather anomalous behavior. Our analysis enables us to conclude that photoluminescence signal observed in the experiment[6] is associated with the upper rather than lower-lying exciton radiative doublet.

In the zeroth order of the perturbation theory the states of a valence-band hole confined within a CdSe nanocrystal are characterized by the hole total angular momentum $\mathbf{F}=\mathbf{L}+\mathbf{J}$ [which is the sum of the hole orbital angular momentum, $\mathbf{L}$, and the hole pseudo-spin, $\mathbf{J}(J=3/2)$], the total angular momentum projection, F_z, and parity. The lowest hole level of size quantization corresponds to the fourfold degenerate even state with $F=3/2$. The lowest state of the confined electron is an s state with the spin $S=1/2$, twofold degenerate over the spin projection, S_z. The exciton states can be characterized by the total angular momentum $\boldsymbol{\mathcal{F}}=\mathbf{F}+\mathbf{S}$ (assuming the values $\mathcal{F}=1,2$) and its projection, $\mathcal{F}_z$.

The eightfold degeneracy of the exciton ground state is lifted in the first order of the perturbation theory. The perturbation can be written in the form of the effective Hamiltonian[4]

$$\hat{H} = -\frac{\Delta}{2}\left(J_z^2 - \frac{5}{4}\right) - \bar{\eta}(\boldsymbol{\sigma}\boldsymbol{J}) + \frac{C}{\sqrt{3}}(J_x^2 - J_y^2) + \frac{1}{2}g_e\mu_B\sigma_z H - g_h\mu_B J_z H. \quad (1)$$

Here $\sigma_\alpha(\alpha = x,y,z)$ are the Pauli matrices, J_α are the matrices of projections of the $J=3/2$ angular momentum operator (which in the present context refers to the total hole angular momentum $F=3/2$), z axis is along the C_6 axis of wurtzite, the magnetic field, $\mathbf{H}$, is directed along z, μ_B is the Bohr magneton, g_e and g_h are the electron and the hole g factors. The first term in Eq. (1) describes the crystal-field induced splitting due to the wurtzite structure of CdSe. The second one accounts for the electron-hole exchange interaction and is contributed by both the long-range (nonanalytic) and short-range (analytic) components.[8] The parameter Δ is size independent while $\bar{\eta}$ scales as R^{-3} with the nanocrystal radius, R. The third term in Eq. (1) accounts for the minimal built-in anisotropy required to produce a finite zero-field splitting.[4] Its appearance can be thought of as arising from the two linear deformations, one squeezing the spherical nanocrystal in the x direction and the other stretching it in the y direction in such a way that the nanocrystal size in the z direction remains unchanged. The last two terms in Eq. (1) account for the effect of the magnetic field.

When written in the basis of the states $|F_z, S_z\rangle$ arranged in the following order:

$$\left|\frac{1}{2},\uparrow\right\rangle, \left|\frac{3}{2},\downarrow\right\rangle, \left|-\frac{3}{2},\uparrow\right\rangle, \left|-\frac{1}{2},\downarrow\right\rangle, \left|-\frac{1}{2},\uparrow\right\rangle, \left|\frac{1}{2},\downarrow\right\rangle, \left|\frac{3}{2},\uparrow\right\rangle, \left|-\frac{3}{2},\downarrow\right\rangle, \quad (2)$$

the 8×8 matrix (1) is reduced to two 4×4 blocks. It is the upper block which being diagonalized produces the four eigenstates corresponding to the components of the two radiative doublets. When the functions $|F_z\rangle$ are chosen to represent a canonical basis of eigenfunctions of the $F=3/2$ angular momentum operator,[7] the upper block assumes the form

$$\hat{H} = \begin{bmatrix} \frac{-\bar{\eta}+\Delta+(g_e-g_h)\mu_B H}{2} & -\sqrt{3}\bar{\eta} & C & 0 \\ -\sqrt{3}\bar{\eta} & \frac{3\bar{\eta}-\Delta-(g_e+3g_h)\mu_B H}{2} & 0 & C \\ C & 0 & \frac{3\bar{\eta}-\Delta+(g_e+3g_h)\mu_B H}{2} & -\sqrt{3}\bar{\eta} \\ 0 & C & -\sqrt{3}\bar{\eta} & \frac{-\bar{\eta}+\Delta-(g_e-g_h)\mu_B H}{2} \end{bmatrix}. \quad (3)$$

If $C=0$ and the nanocrystal has a spherical shape then the overall symmetry is cylindrical and the exciton total angular momentum projection onto the wurtzite axis, $\mathcal{F}_z$, is a good quantum number. In this limit the four eigenstates of matrix (3) are labeled as $\pm 1^U$ and $\pm 1^L$, where the indices U and L refer to the upper- and lower-energy states, respectively. The term in Eq. (1) proportional to C destroys the cylindrical symmetry and leads to mixture of all the four states. Even though the exciton total angular momentum projection, $\mathcal{F}_z$, is no longer a good quantum number, we keep the notations $\pm 1^U$ and $\pm 1^L$ beyond the limit $C=0$. The zero-field splittings of the two radiative doublets are of the same magnitude but of the opposite signs.[4] We choose the direction of the axes x and y in such a way that the uppermost energy state is x polarized. This corresponds to the negative value of C.

Out of the basis functions (2) one can form eigenfunctions of the exciton total angular momentum, $\mathcal{F}$, and its projection, $\mathcal{F}_z$. We have

$$|+1\rangle \equiv |\mathcal{F}=1, \mathcal{F}_z=+1\rangle = \frac{1}{2}\left|\frac{1}{2},\uparrow\right\rangle - \frac{\sqrt{3}}{2}\left|\frac{3}{2},\downarrow\right\rangle,$$

$$|-1\rangle \equiv |\mathcal{F}=1, \mathcal{F}_z=-1\rangle = -\frac{1}{2}\left|-\frac{1}{2},\downarrow\right\rangle + \frac{\sqrt{3}}{2}\left|-\frac{3}{2},\uparrow\right\rangle. \quad (4)$$

One can further define

$$|x\rangle = \frac{1}{\sqrt{2}}(|-1\rangle - |+1\rangle), \quad |y\rangle = \frac{i}{\sqrt{2}}(|-1\rangle + |+1\rangle). \quad (5)$$

Then, for arbitrary eigenvector, $|\lambda\rangle$, of matrix (3), one can define the degrees of circular, ρ_c, and linear, ρ_l, polarization as follows:

$$\rho_c = \frac{|\langle +1|\lambda\rangle|^2 - |\langle -1|\lambda\rangle|^2}{|\langle +1|\lambda\rangle|^2 + |\langle -1|\lambda\rangle|^2}, \quad \rho_l = \frac{|\langle x|\lambda\rangle|^2 - |\langle y|\lambda\rangle|^2}{|\langle x|\lambda\rangle|^2 + |\langle y|\lambda\rangle|^2}. \quad (6)$$

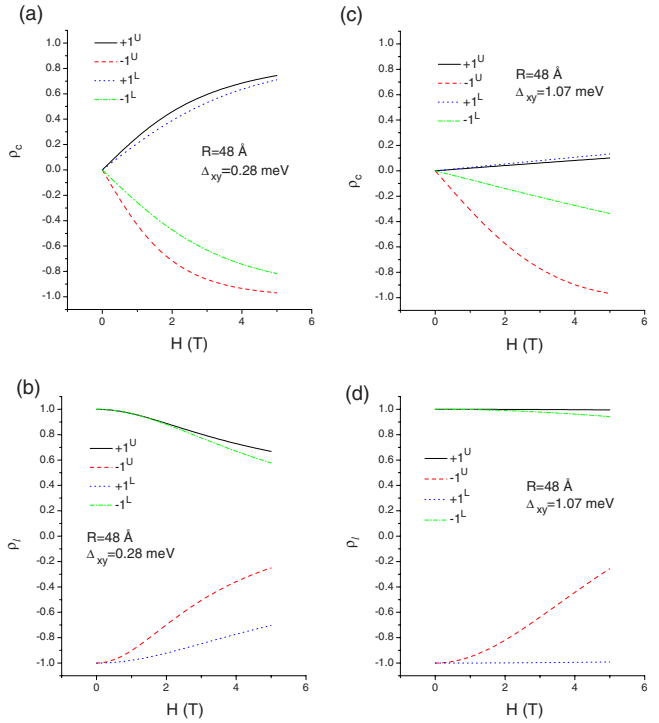

FIG. 1. (Color online) Magnetic-field dependences of circular (a,c) and linear (b,d) polarization degrees for exciton radiative doublets in CdSe nanocrystals of radius $R=48$ Å and zero-field splitting (a,b) $\Delta_{xy}=0.28$ meV and (c,d) $\Delta_{xy}=1.07$ meV.

In Fig. 1 are presented the calculated degrees of circular and linear polarizations for all the four components of the radiative doublets for nanocrystals of the radius $R=48$ Å with different values of the zero-field splitting as a function of magnetic field up to 5 T. All the material parameters as well as the values of Δ and $\bar{\eta}$ are taken from Ref. 8 except for the electron and hole g factors, $g_e=1.014$ and $g_h=-0.73$ (Ref. 9). For simplicity we neglect the difference in the background dielectric constants of the nanocrystal and its environment. Figures 1(a) and 1(b) correspond to the zero-field splitting $\Delta_{xy}=0.28$ meV. At zero field all the components of the two doublets are hundred percent linearly polarized. As magnetic field increases, they gradually acquire circular polarization. A different situation occurs when the zero-field splitting is relatively large, $\Delta_{xy}=1.07$ meV [Figs. 1(c) and 1(d)]. Here the states $+1^U$, $+1^L$, and -1^L remain linearly polarized up to the field of 5 T while the state -1^U gradually acquires circular polarization with increasing magnetic field. Such well-pronounced behavior enables us to suggest that it is photoluminescence from the upper doublet which was detected in the experiment of Ref. 6.

In order to better understand the observed behavior we plotted the dependences of the levels energy positions [Figs. 2(a) and 2(c)] as well as the degrees of circular polarization [Figs. 2(b) and 2(d)] for magnetic fields up to 60 T. The corresponding degrees of linear polarization are shown in Figs. 3(a) and 3(b). From Fig. 2(c) one can see that at the field $H=5$ T the Zeeman energy is still less than the zero-field splitting. Therefore, it is natural to expect the components of the radiative doublets to remain linearly polarized

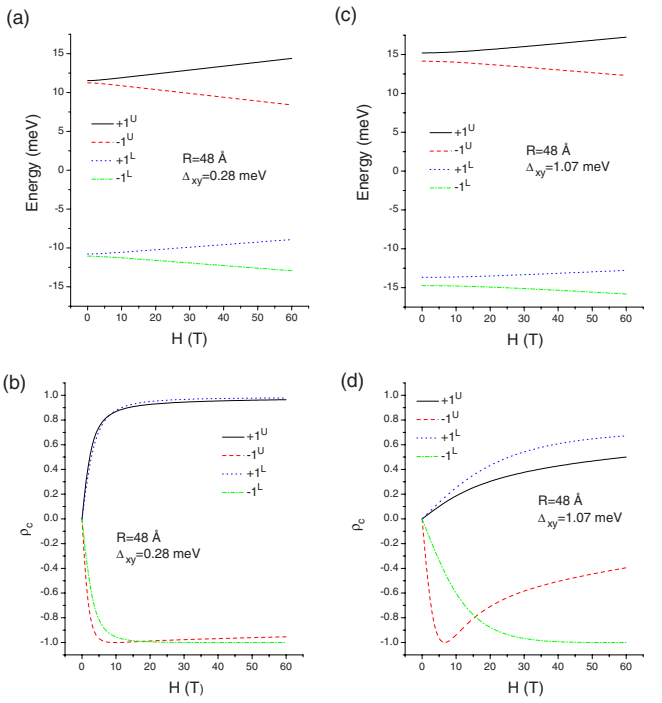

FIG. 2. (Color online) Magnetic-field dependences of level energy positions (a,c) and circular polarization degrees (b,d) for exciton radiative doublets in CdSe nanocrystals of radius $R=48$ Å and zero-field splitting (a,b) $\Delta_{xy}=0.28$ meV and (c,d) $\Delta_{xy}=1.07$ meV.

up to this field [cf. Fig. 1(d)]. However, the -1^U component exhibits a rather anomalous behavior as it first rapidly acquires circular polarization [Fig. 2(d)] and then gradually switches to linear polarization orthogonal to the zero-field polarization [Fig. 3(b)]. At the same time, the polarization degrees for the states $+1^U$ and $+1^L$ change considerably slower than those for the states -1^U and -1^L. But for the upper doublet the difference in behavior of the doublet components becomes apparent at much lower magnetic fields than for the lower doublet. The same trend as for the nanocrystals with relatively large zero-field splittings, but much less pronounced, can be noticed for the nanocrystals with small zero-field splittings [Figs. 2(b) and 3(a)]. As might be expected, an anomalous polarization of photoluminescence

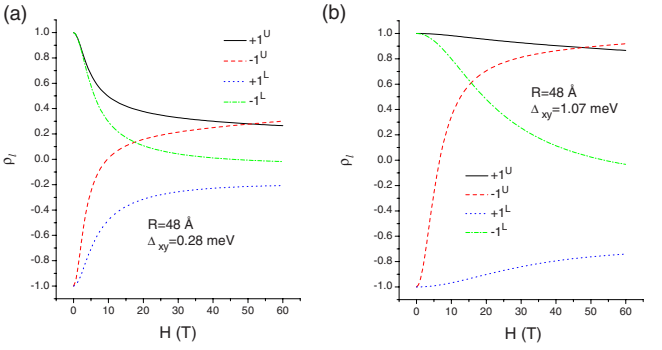

FIG. 3. (Color online) Magnetic-field dependences of linear polarization degrees for exciton radiative doublets in CdSe nanocrystals of radius $R=48$ Å and zero-field splitting (a) $\Delta_{xy}=0.28$ meV and (b) $\Delta_{xy}=1.07$ meV.

occurs when all of the off-diagonal matrix elements in Eq. (3) are of the same order of magnitude with the Zeeman energy. This circumstance limits one's ability to perform a qualitative analysis of this situation.

In summary, we have studied the polarization evolution of the components of exciton radiative doublets in colloidal CdSe nanocrystals with built-in anisotropy with magnetic field applied along the wurtzite axis of CdSe. We have shown that, even in magnetic fields lower than 5 T, at least one of the four components can exhibit a truly anomalous behavior if the anisotropy is large enough. We believe that this behavior was detected in recent magnetophotoluminescence measurements of Ref. 6. We further described a complex behavior of the doublets components polarization in high magnetic fields. The polarization degree of the upper component of each doublet varies with the applied magnetic field slower than that of the lower component. But for the upper doublet this behavior is more pronounced and becomes apparent at much lower fields.

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