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Perturbation of the magneto-optical properties of nanocrystalline CdSSe

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The excited state dynamics of CdSe and CdSSe nanocrystals is complex, involving exciton-polaron formation and state mixing. Evidence of symmetry breaking in a 3.0 nm CdSSe sample shows evidence of exciton-polaron excited state character, in addition to lowering of the exciton symmetry. The lowered symmetry results in new exciton levels that can mix as evidenced in the field dependent polarization ratio, spinor intensities, and energy shifts of the circular polarized magnetophotoluminescence experiment. Coupling of the individual spinor levels results in loss of spin polarization for the CdSSe alloy.

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I. INTRODUCTION

The ground state and excited state properties for wurtzite nanocrystals of CdSSe and CdSe, whether chemically prepared as colloidal materials or embedded in optical glass, have been extensively studied.[1–13] The result of steady state, time-resolved, temperature dependent, and magnetic field dependent spectroscopic measurements has yielded a model where the observed absorption and emissive behaviors can be described as an eightfold degenerate exciton model, which is derived from the band splitting in the C_{6v} symmetry of the wurtzite lattice (Fig. 1).[1,2,6,14,15] Ground state optical absorption measurements are readily fit to the exciton model; however, excited state transitions are influenced by the exciton trapping events following photoexcitation.[16,17] It is generally accepted that relaxation of the initially formed exciton occurs within 150 ps with the formation of an emissive self-trapped exciton or exciton-polaron delocalized over the nanocrystal.[16] Consistent with this, the photoluminescence quantum yield is independent of excitation at low power, the transient absorption identifies separate trapping events for the e^- and h^+, and a recent four-wave mixing experiment identifies a two-step trapping event leading to an exciton-polaron emissive state.[14] The *two-step* trapping event will lead to a lowering of the measured polarization for the individual exciton spin levels in excited state Zeeman experiments due to loss of spin coherence.[14] At high laser fluence or above 3 eV, it has been suggested that the exciton can split and form electron and hole polarons, which can recombine in a multi-impact ionization event, but at powers less than 120 μW or below 3 eV, the exciton-polaron formation is the dominant process.[18] The observed photoluminescence behavior may be further perturbed by the presence of structural ansiotropy as suggested in recent magneto-photoluminescence (MPL) measurements, or lowering of symmetry in alloyed samples.[7]

MPL allows perturbation of the exciton state splitting behavior to be directly interrogated by analyzing the individual spin polarization. Using magnetophotoluminescence, the energy of the exciton states are split into their individual spinor levels, which will emit with right (σ^+) or left (σ^-) circularly polarized light in accord with the selection rules. The intensity and overall polarization are strongly influenced by state coupling, the existence of the exciton-polaron, and symmetry lowering. The general magnitude of splitting should follow $E = g\mu_\beta H$, while the intensity will track the population of the two spinor states as described by Fermi-Dirac statistics. The MPL behavior for nanocrystalline CdSe has been confirmed to qualitatively track the first order Zeeman predictions at low field, although state mixing was invoked to explain the loss of spin polarization. At higher fields in the presence of an exciton-polaron, a better fit to the data is achieved using a second order Zeeman to account for formation of a self-trapped exciton, or exciton-polaron, due to electron-phonon coupling. Perturbations to the exciton model were accounted for in the earlier work by inclusion of structural anisotropy lifting of exciton degeneracy and subsequent enhanced mixing (Δ_{bd}) between the lowest energy dark ($J=2$) and higher energy bright ($J=1$) states.[6,7] Alternatively, symmetry breaking may account for the observations, since the lowering of symmetry from C_{6v} to C_{3v} along the *c* axis leads to loss of the dark character for the lowest energy state (Fig. 2). The loss of the $J=2$ character can be described by considering that lowered symmetry would occur along the $\langle 002 \rangle$ face due to loss of the 6_3 (S_6 in Schoenfliss notation) improper rota-

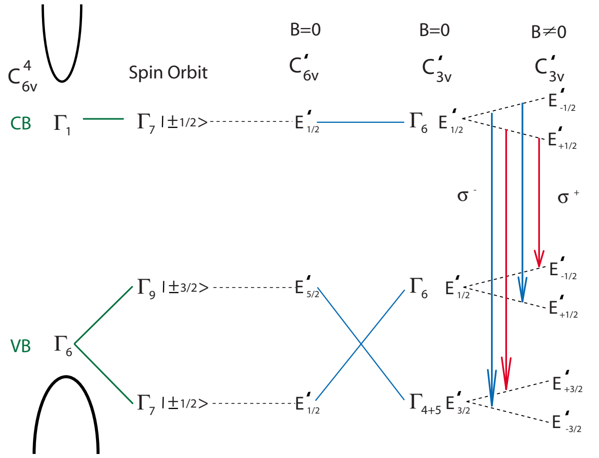

FIG. 1. (Color online) Band diagram for a wurtzite structure with the spin designations. The double symmetry state character for the C_{6v}'s wurtzite structure symmetry is shown. Reduction of symmetry from a C'_{6v} to a C'_{3v} using double groups probes an inversion of the $E_{5/2}$ and $E_{1/2}$ levels. The crystal field Γ_7 is not shown.

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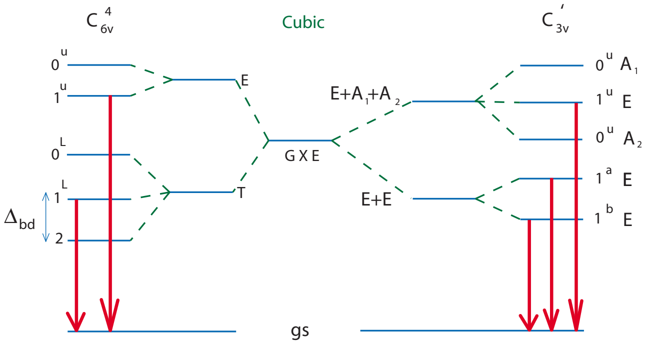


FIG. 2. (Color online) The correlation diagram for the exciton model for a cubic (T_d) to hexagonal (C_{6v}^4) and to a C_{3v}' is shown.

tion axis. This is the axis involved in exciton recombination in CdSe nanocrystals and makes distinguishing between structural anisotropy and symmetry breaking difficult in a pure system. Loss of the 6_3 axis results in two significant perturbations. Namely, an energy reversal of the 3/2 and 1/2 exciton states with identical symmetry (E') and, more importantly, the $E'_{3/2}$ level has a component along the c axis, allowing mixing with the $E'_{1/2}$ state that is polarized along the c axis.[19–21] The impact on the MPL results will be similar to structural anisotropy agreement, but the magnitude of mixing will be stronger.

The rather complex excited state dynamics in nanocrystals can be probed by MPL accurately if a second order Zeeman expression is utilized to fit high field data in order to fully allow the polarization to asymptote. By analyzing the change in energy and intensity of the individual spinor levels, a model can be developed that accurately fits the observed Zeeman data. This paper aims to analyze a wurtzite lattice, spherical morphology CdSSe alloy to allow the distinction between structural anisotropy and broken symmetry to be analyzed. The CdSSe is a known statistical system, where symmetry can be reduced by alloy formation. The alloy is advantageous as it allows direct comparison to studies that have been performed in doped optical glasses on CdSSe. The CdSSe alloy is an example of a solid solution, with the sulfur distributed statistically throughout the lattice. This results in changes of band gap (E_g) with minimal perturbation of the Brillouin zone.[5,15] The observed MPL data for the CdSSe alloy are expected to reflect the lowered symmetry, and are analyzed by a second order Zeeman perturbation to account for the experimentally observed exciton-polaron in nanocrystals. The observed asymmetry in the Zeeman behavior is analyzed as a loss of the $J=\pm 2$ state character and formation of $J=\pm 1^a, \pm 1^b$ states of the same symmetry (E') and polarization axis.[2] This gives rise to spin depolarization of the excitons in CdSSe, requiring the inclusion of two discrete levels to quantitatively fit the field dependent intensity and energy data, since the states compete for intensity but have opposite spin polarity.[22]

II. EXPERIMENT

MPL studies were carried out on chemically prepared nanocrystalline (NC) CdSSe embedded in an organic amorphous silane glass. The glass samples were prepared by dissolving the NC-CdSSe in pyridine, adding *N*-(3-(trimethoxisilyl)-propyl)ethylenediamine, and allowing the sample to condense for 12 h. The experiments are conducted on $0.5 \times 200 \times 200$ mm^3 rectangular samples that are ~10 μM in the nanocrystal. The chemically prepared NC-CdSSe are prepared as hexadecylamine passivated materials using a modification of the method used by Cumberland *et al.*[23] This yields NC-CdSSe samples with $4 \pm 1\%$ S (3.0 nm diameter CdSSe) and $8 \pm 1\%$ S (3.2 nm diameter CdSSe) based on x-ray fluorescence spectroscopy. The lower sulfur concentration was achieved by allowing partial decomposition of thiophenol during the reaction, while the higher concentration requires elemental sulfur addition.[24,25] The CdSSe nanocrystals are spherical and exhibit wurtzite symmetry based on x-ray diffraction and transmission electron microscopy (TEM) measurements (Fig. 3). TEM analysis shows a 5% size distribution, which is confirmed by the narrow photoluminescence (PL) full width at half maximum (70 meV).

MPL experiments were performed at the National High Magnetic Field Laboratory (NHFML-FSU) using an Ar$^+$ ion laser (70 μW at 458 nm) coupled through UV fiber optic into a Janis cryostat (4.2–300 K). The cryostat was placed into the 31 T resistive magnet (0–31 T) in backscattering geometry to allow Faraday geometry for the experiment (magnetic field parallel to the incident light direction). Right and left circularly polarized spectra were collected with a fixed circular polarizer by measuring −31 to 31 T for simplicity in data collection. Circular polarized photoluminescence was collected in backscattering geometry on a separate fiber coupled to a 1 m monochromator (600 g/mm) using a Princeton Instruments liquid N$_2$ cooled charge coupled device, (512×1024 pixels).

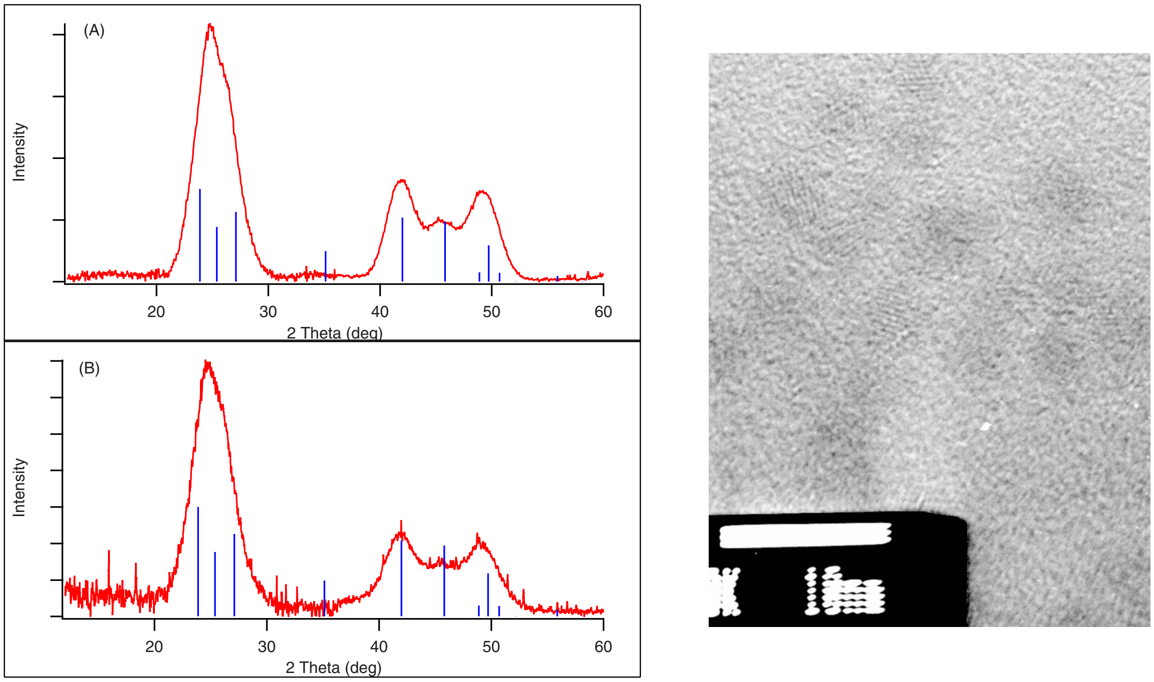
III. RESULTS

A. Exciton polarization

In a nanocrystalline semiconductor, the electronic properties are quantum confined by particle size, but are expected to be periodic and, therefore, exhibit classical Brillouin behavior as a function of magnetic field. Therefore, the Zeeman splitting can be fitted to a Langevin function by taking into account the random orientation of the nanocrystals relative to the orientation of the applied field.[22] In Fig. 4(a), we plot the observed spectral shift in PL for σ^+ and σ^- polarized spectra between 0 and 31 T for the two sulfur doping levels in CdSSe. While the Zeeman energy shift requires a second order Zeeman expression, the intensity can be fitted by considering that the intensity traces can be analyzed individually for I$_+$ and I$_-$ as

$$\begin{aligned} I_{\mp}(\cos\theta) = {} & [(1 \pm \cos\theta)^2 e^{g\mu_B H \cos\theta/2k_BT} \\ & + (1 \mp \cos\theta)^2 e^{-g\mu_B H \cos\theta/2k_BT}]/(e^{g\mu_B H \cos\theta/2k_BT} \\ & + e^{-g\mu_B H \cos\theta/2k_BT}). \end{aligned} \tag{1}$$

The g value is the exciton polarization dependent g value, H is the field, and $\cos\theta$ is the dipole angle with respect to the



(a)

(b)

FIG. 3. (Color online) (a) Powder x-ray diffraction (XRD) (Cu $K\alpha$) of (A) 4% and (B) 8% CdSSe alloy exhibiting a wurtzite structure. The lines represent XRD of CdSe (PDF No. 00-008-0459). (b) TEM of the 3.0 nm 4% CdSSe on amorphous carbon on a Holey carbon 400 mesh ramped at 210 KeV.

field direction (θ will be averaged over all possible directions with respect to the dipole-magnetic field direction). Attempts to fit the intensity data to a single emitting state, as previously described in CdSe for a system in which a dark and a bright state are mixed by structural anisotropy, fails to fit the experimental data. If we assume that a symmetry breaking occurs for the NC-CdSSe lattice, the data can be fitted to the combination of two $|1/2\rangle$ symmetry allowed states, which arose from the loss of the 6_3, thus generating four states $(|+1^a\rangle,|+1^b\rangle,|-1^a\rangle,|-1^b\rangle)$ (Fig. 2). The fit to the data by expanding Eq. (1) for the four total states is shown in Fig. 4(b) and fits the data quantitatively. The presence of two states will have a dramatic impact on the polarization, intensity, and energy levels of the states as a function of field. The four polarized transitions will have independent g values, which can be extracted from the polarization data as an average g value for σ^+ and σ^-. The g values will not be equivalent when coupling arises between the $|1^a\rangle$ and $|1^b\rangle$ states, and will depend on the magnitude of coupling and the spin value. A plot of the polarization data

$$\rho = I_- - I_+/I_- + I_+ \tag{2}$$

yields a ρ value of 60% for CdSSe ($x=4\%$) and a ρ value of 17% for $x=8\%$ [Fig. 5(b)]. The expected value for ρ in the absence of state mixing (using a bulk value for $g=0.6$ and 4.2 K) for CdSe is 54% at 31 T, which is the same value as observed for the lower doped sample, but far higher than observed for the 8% sample. The lowered ρ value is believed to reflect loss of spin coherence due to depopulation of the $|-1^a\rangle$ by $|+1^b\rangle$ state. The dramatic difference in the values for ρ between the two samples is believed to be due to changes in the energy splitting between the states.

Since the polarization ratio does not allow the individual spinor levels to be distinguished, an average g value for the samples can be analyzed by integrating over all angles of the exciton dipole relative to the magnetic field using Eq. (2),

$$\rho = \int_0^1 \frac{I_-(\cos\theta) - I_+(\cos\theta)}{I_-(\cos\theta) + I_+(\cos\theta)} d\cos\theta, \tag{3}$$

where Θ is the angle between the magnetic field and dipole moment. Fitting ρ yields an average g value of 1.74 for the NC-CdSSe samples. The calculated g value data are large compared to bulk CdSe values ($g=0.6$) and earlier reports on pure NC-CdSe, where values of 1.2 and 0.75 have been reported.[6,7]

By considering the expression for the intensity trajectories, the g values for each spinor level can be analyzed separately by assuming a spin value of 1/2. The experimentally measured individual σ^+ and σ^- polarizations correspond to I_+^a/I_-^b (σ^-) and I_-^a/I_+^b (σ^+). Fitting the data to a two component problem yields for the 4% sulfur sample a σ^+ $g=+1.40$ $(|+1^a\rangle)$ and -1.40 $(|+1^b\rangle)$, and for σ^- a $g=-0.76$ $(|+1^a\rangle)$ and $+0.24$ $(|+1^b\rangle)$. The 8% sample gives σ^+ values of $g=+0.52$ $(|+1^a\rangle)$ and -0.64 $(|+1^b\rangle)$, and σ^- is composed of $g=-1.01$ $(|+1^a\rangle)$ and $+1.31(|+1^b\rangle)$. The asymmetries of the g values are indicative of a strong coupling existing between the lowest energy excitons in the alloy material.[1]

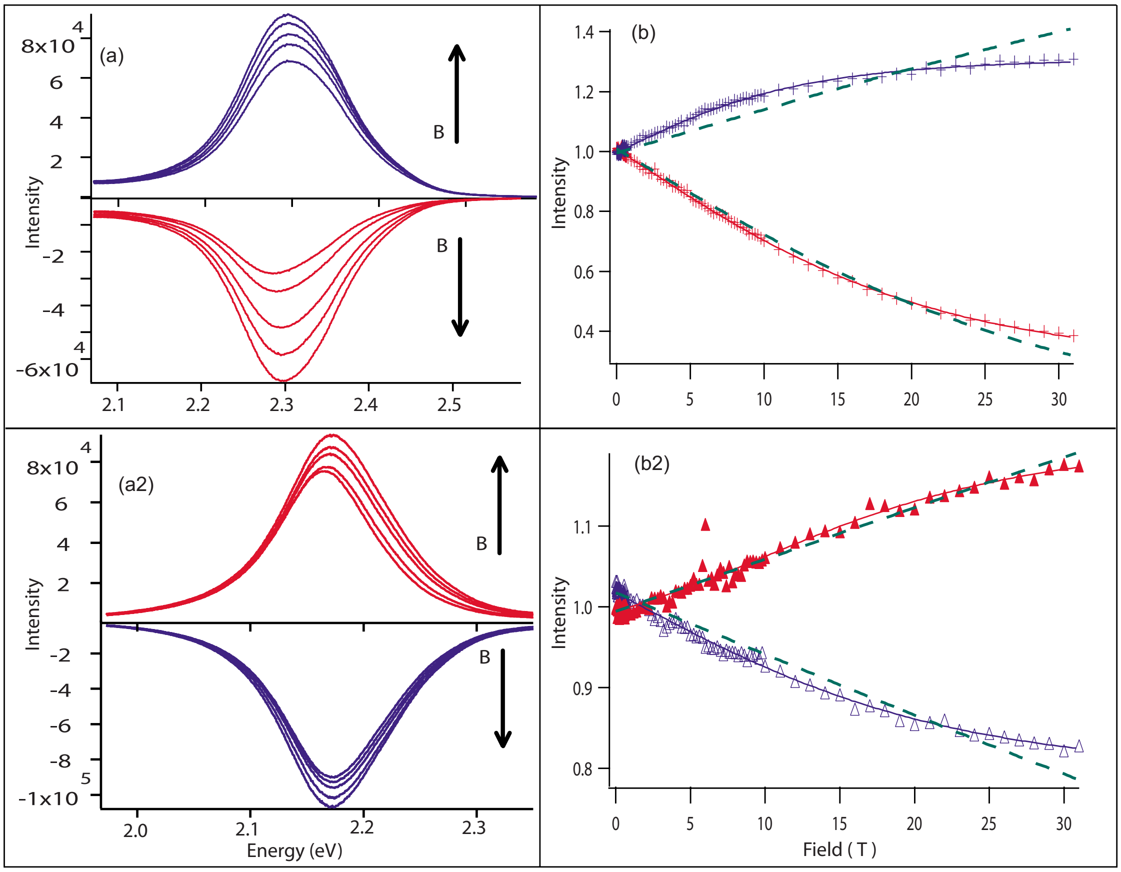


FIG. 4. (Color online) (a) [(1) CdSe 4% S and (2) CdSSe 8% S] Circularly polarized photoluminescence [σ^- (positive), σ^+ (negative)] taken at 4.2 K for 0.01, 5, 10, 20, and 31 T. (b) [(1) CdSe and (2) CdSSe] Circularly polarized photoluminescence intensity data and two state contribution fit [σ^- (solid), σ^+ (open)] taken at 4.2 K. For both samples, a fit to a single state is added to the data as a dashed line for both polarizations.

B. Zeeman energy splitting

In Fig. 5, the fit to the energy trajectories for σ^+ and σ^- are shown. If the symmetry breaking argument and subsequent creation of two $|1/2\rangle$ exciton states are to be believed, then the energy plots [Figure 5(a)] should exhibit a bowing of the trajectory at high field due to state coupling. The bowing will be more extreme in the higher sulfur content sample, presumably due to the higher degree of perturbation from a simple wurtzite exciton model as observed in the intensity and polarization ratio plots. Consistent with this prediction, inspection of Fig. 5 shows significant bowing at high field.

The experimental field dependent energy plots are fitted to a second order perturbation expression for the Zeeman splitting. The second order Zeeman splitting includes a Landé splitting term, a diamagnetic contribution, and an electron-phonon (el-ph) coupling term, where

$$E(H) = E_o + g\mu_B SH + DH^2 + \alpha[\coth(g\mu_B SH/k_B T) - 1/(g\mu_B SH/k_B T)], \quad (4)$$

E_o is the zero Kelvin band gap, g is the exciton Landé term, S is the exciton spin, H is the magnetic field, D is the diamagnetic contribution due to electron cyclotron resonance,[26] α is the el-ph coupling constant, and T is the temperature. The fit to the field dependent energy of the photoluminescence, $E(H)$ does not incorporate separate contributions from the different states $J=1^a$ and 1^b due to lack of resolution in the spectral profile. Since the contribution from the $J=1^a$ is dominant, it will reflect a weighted value and, therefore, we report only the g^{σ^+} and g^{σ^-} values without state deconvolution.

In the low sulfur concentration sample, fitting the energy profiles yields a g value of 1.2 for the σ^- state. The experimentally extracted g value is consistent with previously reported average g values for pure NC-CdSe.[27,28] The g value for the σ^- photoluminescence in 4% CdSSe is 3.2, providing the strongest evidence of mixing between the $|-1\rangle$ and $|+1\rangle$ states at high fields. Mixing of the states depolarizes the $|-1\rangle$ state, where one predicts that the g value for the $|-1\rangle$ state should approach the value for the $|+1^b\rangle$ level if state coupling occurs, which has been theoretically predicted to be 4.0 if we assume that the $J=2$ state calculation still applies.[27,29]

In the 8% CdSSe, the g value for the $|+1\rangle$ photoluminescence state is 3.5, and for the $|-1\rangle$ state, a value of 0.98 is extracted. The inversion of the g value for the 8% sample is surprising, but suggests that an inversion of the $|1^a\rangle$ and $|1^b\rangle$ levels must occur, resulting in mixing of the $|+1^b\rangle$ with the

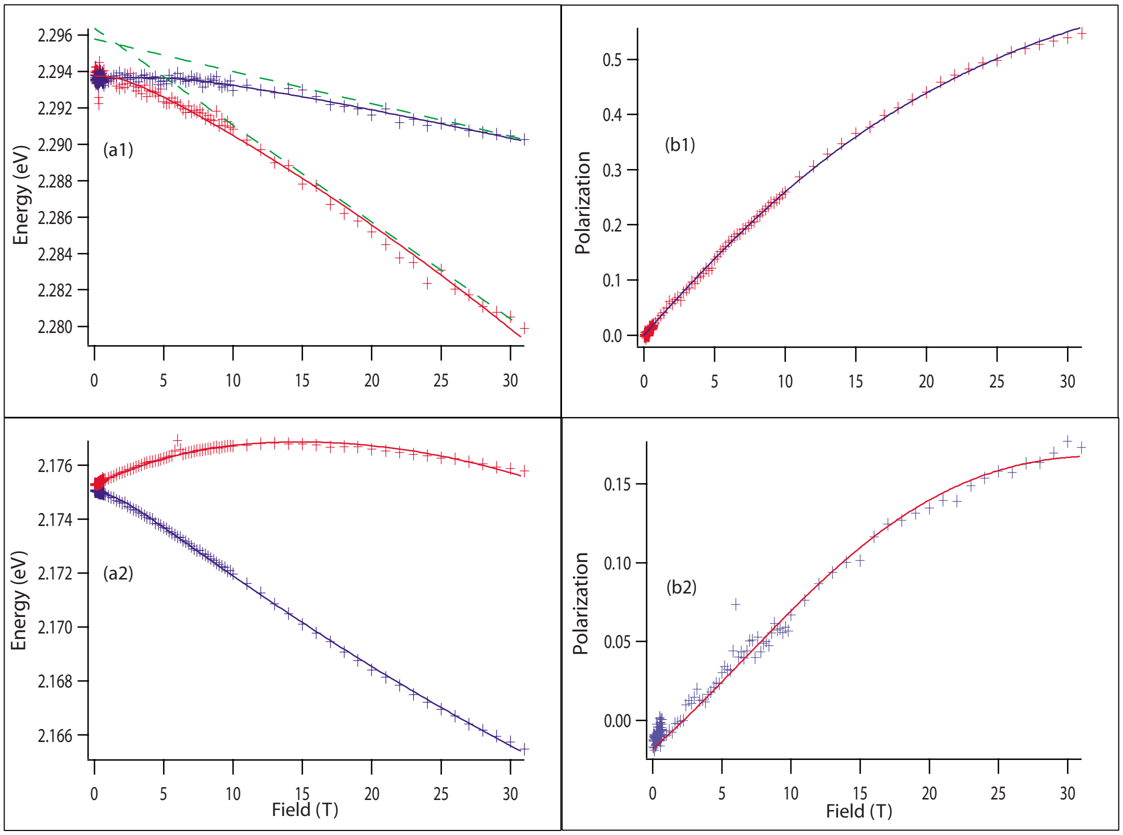


FIG. 5. (Color online) (a) Photoluminescence energy as a function of polarization and field. This includes the energy fit for (1) 4% and (2) 8% CdSSe samples. The 4% sample shows the extrapolation of the high field splitting (—) to extract Δ_{bd}. (b) Polarization dependence of the intensity and fit for (1) 4% and (2) 8% CdSSe samples.

$|-1^a\rangle$ level and, therefore, the unexpected large value of g for the σ^- state. This observation supports the results observed for the intensity data behavior, which indicate a loss of the initial spin value for the lower state, as has been predicted by Ivinchenko[30] for a symmetry broken system.

Assuming that the bowing in the E plot reflects the separation between the $|1^a\rangle$ and $|1^b\rangle$ exciton levels, the energy separation between the E' levels at zero field (Fig. 5) can be extracted by projecting the value to zero field (Fig. 5) This yields a value of 3 meV for the state separation in the 4% CdSSe sample. This value is close to the theoretical value in 3.0 nm CdSe nanocrystals of 6 meV for the separation of the dark and bright excitons.[7,22] As the concentration of S is increased, the energy splitting is convoluted by strong mixing and the inversion of the exciton levels.

As the magnitude of the perturbation increases with sulfur incorporation, we also expect changes in the electron-phonon coupling matrix element (α). In Eq. (5), the el-ph term (α) is size dependent:[11,31–35]

$$\alpha = \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\frac{e^2}{2r_p^2}\frac{1}{\hbar\omega_L}, \tag{5}$$

where ϵ_∞ and ϵ_0 are the high and low frequency dielectric constants, e is the charge of an electron, r_p is the polaron radii, and ω_L is the LO phonon frequency. A large polaron will typically exhibit a large α. In the two samples, the value of α is 0.31 for 4% S and 0.22 for 8% S, consistent with values for NC-CdSe.[31] From the value of α, the size of the emissive exciton can be extracted using Eq. (2). This predicts a diameter of 3.9–4.5 nm for the CdSSe alloy samples, which correlates with the NC diameter. While the result is not surprising, the observation is important as it confirms that the photoluminescence arises from a self-trapped excitonic polaron of the size of the nanocrystal rather than a localized emissive state, as described by Klimov *et al.*[17,36–38]

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