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Electro-optic properties of CdS embedded in a polymer

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CdS microcrystals under weak confinement conditions embedded in a polyvinyl alcohol polymer film have been optically characterized by linear absorption and time-resolved luminescence spectroscopy. They are studied in the presence of an external electrical field at low and room temperature and different densities of photoexcited carriers. By applying a voltage of 400 V corresponding to an external electric-field strength of 5×10^4 V/cm, the observed absorption change in this material is $\Delta\alpha/\alpha\approx0.07$. The electrical field produces a redshift of the absorption band which is explained in terms of the quantum-confined Stark effect. In addition, a restoring of the oscillator strength is observed and explained by screening effects of internal fields in the interface region by the photogenerated electron-hole pairs. At high laser excitation an electric-field-induced change of the nonlinear absorption spectrum of $\Delta\alpha/\alpha=0.25$ is achieved, giving a considerable modulation of the absorption edge. The electrical field separates the laser excited carriers and the change in the absorption is attributed to a compensation of the many-particle interaction by the external electrical field.

I. INTRODUCTION

An external electrical field modifies the optical properties in both bulk semiconductors and quantum-confined structures. Most useful for electro-optical devices are semiconducting materials showing large relative changes of the optical density $\Delta\alpha/\alpha$ at comparatively low-field strengths ($\sim10^4$ V/cm). The possibility to use them in integrated devices and to combine electro-optic and nonlinear optical properties makes them interesting for further research and application.

Early studies of excitonic effects and of the electronic band peculiarities in bulk II-VI materials, e.g., in CdS, revealed values of $\Delta\alpha/\alpha$ of some percent in electro-optic experiments at room temperature and at field strengths of 10^4 to 10^5 V/cm.[1-5] The underlying physical mechanism in bulk CdS is to some extent the Stark effect but mainly the field ionization of the discrete exciton states connected with a broadening and a rise of the absorption tail below the band gap with some contributions from Franz-Keldysh oscillations caused by the (partly phonon-assisted) tunneling of electrons.[6-8]

The following arguments suggest carrying out electro-optic experiments at three-dimensionally confined quantum dots, which are mostly available as nanocrystals embedded in a glass matrix.

First, already in two-dimensional quantum wells (QW's) and superlattices (SL's) the field ionization is prevented by the potential formed by the barrier layers. The quantum-confined Stark effect results there in a strong redshift of the exciton resonance if the electrical field is applied in the growth direction.[9,10] The Stark effect is present in the bulk material as well, albeit small, and the field-induced excitonic dissociation hinders its observation. Both the increase of the exciton binding energy with confinement and the large oscillator strength give sharp isolated excitonic resonances at room temperature. Their shift with the electric field results in a good modulation of the absorption coefficient with high values of $\Delta\alpha/\alpha\gg1$. Therefore, it seems reasonable to lock in a next step for quasi-zero-dimensional systems.

Second, some stimulation can be expected from the results for the further development of a unified theory of electro-optic properties in bulk and low-dimensional systems, e.g., for the determination of the ionizing field strengths of the excitons, the relative contributions of the Stark and Franz-Keldysh effect to the absorption changes in dependence on size and dimensionality.

Third, a large electro-optic response is expected for piezoelectrically generated polarization fields in strained-layer superlattices[11,12] modulated by external electrical fields or high densities of laser excited carriers. Therefore, it should be attractive to find zero-dimensional systems exhibiting surface-induced internal fields similar to those produced by the lattice mismatch at the interface in layered, two-dimensional systems.

At present, intensive research work is going on concerning the electro-optic properties of II-VI quantum dots embedded in glass comprising detailed line-shape analysis.[13–18] However, all these investigations show the common result of only small changes in $\Delta\alpha/\alpha$, with values far below 1% and often only visible in modulation spectroscopy and at field strengths of $\geq 10^5$ V/cm. This value is distinctly smaller than in bulk CdS or CdSe. It is also below theoretically predicted and measured values in two-dimensional systems.[9,19,20]

Two problems have turned out to be essential with respect to electro-optic experiments in quantum-confined systems consisting of nanocrystals embedded in glass: (i) the flatness of the absorption edge in the linear spectra caused by the low filling factor ($\leq 10^{-3}$) and the strong inhomogeneous broadening by the size distribution, and (ii) geometrical and technological problems in the realization of electric contacts.

Already in bulk CdS it has been proved that an exact knowledge of the spatial electric-field distribution is the prerequisite for an analysis of the field-induced absorption change.[21] An advantage of confined III-V semiconductor systems is the small total thickness of the layered QW or SL structure of only ~ 1 μm, so that already at low voltages homogeneous field conditions can be ensured.

For the experiments at II-VI quantum dots in glass the capacitor configuration has mostly been used with observations parallel or perpendicular to the electric-field direction. However, high extrinsic voltages of several kV are needed for sample thicknesses up to some millimeters which are necessary due to low-absorption coefficients. From the small changes in α it may be supposed that additional capacities and depolarization occur in the experiment, which prevent the drop of the whole external electrical field across the quantum dots. For instance, only little is known about the interface layer around the quantum dot, the local-field strength, as well as deviations from a spherical shape.

For the above reasons it seems interesting to investigate microcrystals in organic matrices instead of glasses. The promising nonlinear optical properties of CdS in a polymer film environment have already been demonstrated.[22–24] The polymer film acts as a stabilizer resulting in a high uniformity in the size of the nanocrystals. To our knowledge some first results have been published on CdS and CdSe embedded in an acrylonitril-styrene copolymer (AS) and in polymethylmethacrylate (PMMA).[25,26] Electromodulation spectroscopy of absorption and luminescence has been carried out at CdS microcrystals of radii between 1.5 and 3 nm embedded in AS and well-resolved structures are attributed to an excitonic Stark shift in this material.[25] In small CdSe microcrystals of $R=2$ nm in PMMA an electric-field-induced broadening is explained by a change in the dipole moment of the excited state with increasing field strength averaged over a random ensemble of dipoles rigidly held in the polymer.[26] However, again, small values of $\Delta\alpha/\alpha$ inferior to that of the bulk material have been found.

In this paper we present measurements on CdS microcrystals in a film of polyvinyl alcohol (PVA). A mechanically stable film has been obtained with a thickness of some tens of microns and a volume fraction of CdS between 1–3%. The size of the CdS nanocrystals is in the weak confinement range of $R/a_B \geq 5$, where R is the radius of the crystal and a_B the excitonic Bohr radius (in CdS, $a_B = 2.7$ nm). Using planar electrodes and observation in the direction of the electrical field, large values of $\Delta\alpha/\alpha$ up to 7% have been achieved at field strengths of $\sim 5\times 10^4$ V/cm. In addition, the modulation in the absorption coefficient has been investigated combining the external electrical field with high laser excitation intensities. In this case, the observed large changes in the absorption coefficient of about 20% have been tentatively explained by a charge separation of the excited carriers by the electrical field, thus compensating the many-particle interaction causing the optical nonlinearity.

A certain disadvantage of the material in its present form is the strong broadening of the $\Delta\alpha$ spectra attributed to variations in the shapes of the CdS nanocrystals connected with the length and bending of the polymeric chains. Therefore, a detailed analysis of the line shape and of the basic electro-optic properties cannot be obtained at present. The main topic of our contribution consists of the investigation of the electro-optic changes of the absorption spectra in connection with different levels of optical excitation, e.g., at different optically induced charge-carrier concentrations.

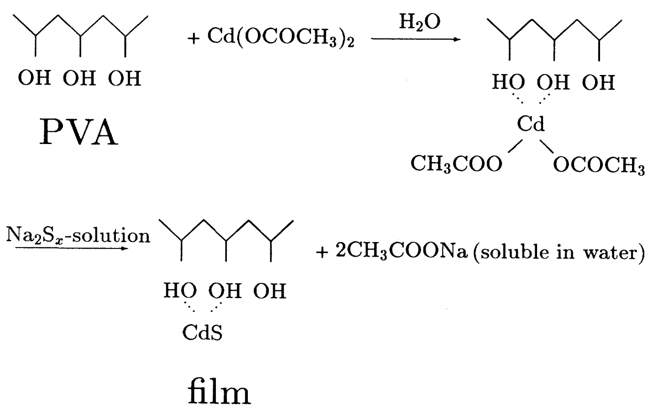
II. SAMPLE PREPARATION

With regard to the electric-field experiments one has to find samples which meet the following requirements: (i) well-defined sizes and thus a good knowledge of the confinement regime, e.g., for the clarification of the influence of Coulomb interaction between electron and hole on the electro-optic properties; (ii) a sharp absorption edge or a narrow absorption peak for optimum modulation contrast; (iii) a volume fraction of the semiconductor quantum dots in the range of 1–10% to decrease the layer thickness down to some tens of microns ensuring a high electrical field at moderate voltages and a reasonable absorption coefficient; and (iv) no (or low) electrical conductivity, realized by an insulating matrix and by keeping an upper limit for the volume fraction of semiconductor dots to prevent a mutual contact or percolation.

Polyvinyl alcohol (PVA) has been proved to be a good stabilizer for quantum dots of the narrow gap semiconductor PbS.[27]

An additional reason for the choice of the wide gap semiconductor CdS and the polymer PVA as the insulating host is the expectation that the combination of Cd^{2+} ions and OH^- groups gives internal polarization fields in the semiconductor-matrix interface region. Besides, it is known already that the bulk semiconductor CdS exhibits large piezoelectric fields in the order of magnitude of ≥ 1 kV/cm.[28]

The films were prepared by the following procedure:



0.4 g polyvinyl alcohol [mass weight (MW) = 14 000; 100% hydrolized] were dissolved in 60-ml distilled water at 70 °C. After addition of 0.16-g (0.6 mmol) $Cd(OAc)_2 \cdot 2H_2O$, the solution was stirred for an hour and then concentrated at 70 °C in a nitrogen stream to a volume of 7 ml. Spreading the solution on a glass substrate and removing residual water under high vacuum gave an elastic transparent colorless film. The film was dipped in 50 ml of a Na_2S_x solution (prepared from 1.5-mol NaOH, 1.5-mol $Na_2S \cdot 9H_2O$, and 1.5-mol sulphur in 1500-ml distilled water at 70 °C) for 40 min, thoroughly washed with distilled water and dried under high vacuum.

After drying, a water-free CdS/PVA film of a dimension of ~ 10 cm^2 and a thickness of 50 to 75 μm was obtained showing a clear yellow color. The film is flexible, has a high tensile strength, and is easy to handle, e.g., for cutting and bending. It shows no photochemical reactions, such as photodarkening, and no long-time changes in the linear absorption spectra under laser illumination.

For the contacts, a symmetric coplanar electrode configuration was used (see Ref. 21) by evaporating metal films at both sides of the sample letting a free slit in the center of about 100 μm for light transmission and detection. In the following, the electric-field strength is given in terms of the *external* electrical field because the knowledge of depolarization factors is rather pure.

The electrical conductivity κ of the CdS/PVA film was measured by means of the two-point method. At room temperature, a value of $\kappa = 6 \times 10^{-8}$ S/cm $= 6 \times 10^{-12}$ m/Ω mm^2 was obtained which is approximately the value of the pure PVA polymer.

III. OPTICAL CHARACTERIZATION

For the characterization of the material, an analysis of the linear and nonlinear optical properties has been carried out. Figure 1 shows the linear absorption and time-resolved luminescence spectra of the CdS microcrystals embedded in a 75-μm-thick PVA film measured at $T = 20$ K. For the luminescence experiments an excimer-laser-pumped quenched dye laser was used providing intense pulses of 70-ps pulse length, a maximum fluence of 60 mJ/cm^2, and an excitation wavelength tunable around 490 nm. For the detection of the luminescence a combination of a spectrometer and a streak camera with a two-dimensional read-out system was applied.[29]

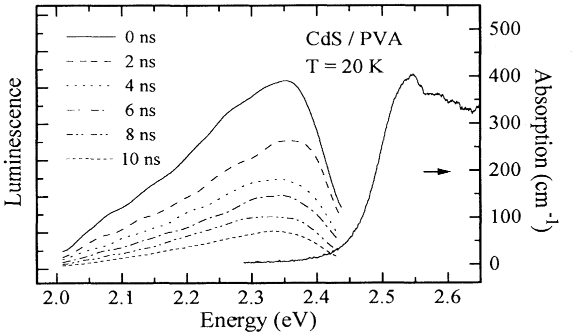


FIG. 1. Linear absorption and luminescence spectra of CdS microcrystals embedded in PVA (thickness of the sample $d = 75$ μm, $T = 20$ K, laser excitation energy at 2.54 eV).

High-resolution electron microscopy gives an estimation of the radii of $\approx 7a_B$. These radii correspond to the weak confinement regime. The confinement-induced high-energy shift expected in the linear absorption spectrum is only in the order of some meV. Accordingly, the linear absorption spectrum in Fig. 1 is still similar to that of bulk CdS. However, a distribution in the shape of the microcrystals has been found which prevents, for the time being, a more detailed theoretical description of the spectra. The polymer host has a finite chain length of some tens of nanometers with bending or coiled structures. Very probably, this results in deviations from a spherical shape of the microcrystals and thus in a broadening of the absorption spectrum.

A steep rise of the absorption can be seen for the CdS/PVA film over 300 cm^{-1} in an energy interval of only 50 meV. Evidently, the sharp onset of the absorption has been achieved which is obligatory for application in electric-field experiments. The steepness of the absorption edge is essentially preserved up to room temperature. Furthermore, a volume fraction of the semiconductor material in the host as large as 1–3 % can be determined from the absorption coefficient. This value is considerably larger as those known from CdS microcrystals embedded in glasses.[30] The sizes of microcrystals realized in the CdS/PVA film are rather large, so that the properties will be close to the bulk properties and a great influence of excitonic effects will be expected.

The linear absorption spectrum shows no shift under long-time laser illumination as it is typically found in colloidal systems and is attributed to long-living photocharged effects.[31]

The spectral behavior of the luminescence is characterized by a broad band with a maximum at 2.34 eV and a long tail towards lower energies which is redshifted by about 200 meV as compared to the absorption. No change in the spectral shape can be seen over a time range of 10 ns. The luminescence decay comprises two components with distinctly different dynamics and decay times of ≈ 200 ps and 7 ns (Fig. 2).

A similar and very efficient redshifted luminescence

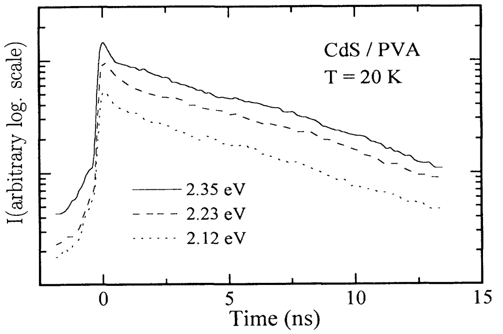


FIG. 2. Luminescence decay measured at three different photon energies within the spectral distribution of luminescence at $T=20$ K and laser excitation energy at 2.54 eV.

has been attributed to Cd^{2+} ion excess in Ref. 27 for CdS nanoclusters in colloidal systems. The maximum of the luminescence has been found to shift depending on the Cd^{2+} concentration in the solvent. From the preparation method used here (see Sec. II), there is a high probability of free Cd^{2+} ions at the polymeric chain without S^{2-} ion counterparts. For that reason, we conclude that a Cd^{2+} or Cd^{+} ion-related recombination mechanism via moderately deep trap states seems to be the dominating recombination channel representing the ns time constant. The short-time constant of 200 ps is then related to the direct electron-hole pair recombination. The lifetime of excited electron-hole pairs, which is also important for application, is therefore determined by these fast trapping processes.

In Fig. 3, the nonlinear optical behavior of the CdS/PVA film is demonstrated. The measurements of the nonlinear absorption were performed using a pump and probe setup consisting of an excimer-laser-pumped dye laser. The pulse duration and the repetition rate were 7 ns and 20 Hz, respectively. The narrow-band pump laser was tuned to an excitation energy of 2.63 eV. For the test beam a broadband dye continuum was used.

The experiment shows a broad absorption bleaching over the whole spectral range of the ground-state absorption peak. From the linear absorption coefficient and the lifetime for a maximum excitation intensity of 1 MW/cm^2 at 2.63 eV an excited carrier density per dot of $n \geq 1\times10^{18}$ cm^{-3} can be estimated.

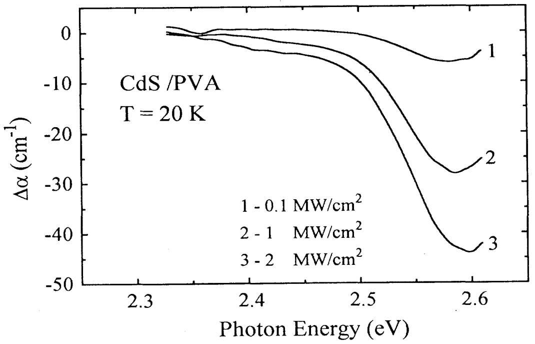


FIG. 3. Absorption bleaching $\Delta\alpha$ of a CdS/PVA film measured in a nanosecond pump-probe experiment under high laser excitation at 2.63 eV, $T=20$ K, and 1, 100 kW/cm^2; 2, 1 MW/cm^2; 3, 2 MW/cm^2.

In bulk CdS the excitonic absorption vanishes with increasing carrier density due to the Mott transition and formation of a dense electron-hole plasma (see, e.g., Refs. 32 and 33). Screening of the Coulomb interaction and gap shrinkage appear combined with band filling effects. In low-temperature measurements of the nonlinear spectra, the peak absorption decreases gradually with rising excitation intensity accompanied by induced absorption besides the exciton state. The stable energy position of the exciton state, which has been found in the experiments (for a review see, e.g., Ref. 34), is explained by a compensation of gap renormalization and the change in binding energy with increasing density.

In contrast to the bulk, in the large CdS microcrystals investigated here, no induced absorption has been found both at low and room temperature. A strong line broadening of the linear absorption of the ground state could mask this feature; however, more important for the explanation of the nonlinear optical-absorption spectra is the change in the interaction mechanisms within the many-particle system occurring due to weak confinement. The higher exciton binding energy in lower-dimensional systems and the minor importance of screening effects due to the restricted mobility of the electron-hole pairs[35] should result in more pronounced exciton-exciton interaction effects.

Exciton population effects in a dense exciton system have been reported for CuBr and CuCl microcrystals with higher exciton binding energy of the corresponding bulk material.[30,36–38] The importance of the Coulomb interaction in small CdS and CdSe quantum dots has been emphasized in Ref. 39 which gives rise to four-particle states. At present, little is known from the experiment about the properties of a high-density electron-hole pair system in large CdS microcrystals showing near bulk properties. This aspect represents an interesting problem for further research.

With respect to CdS microcrystals of comparable sizes embedded in glass, the absorption change obtained at a fixed excited carrier density is considerably larger for a polymer matrix. We explain this difference by the different efficiency of the competitive nonradiative recombination channels via traps in both systems. The attainable large value of the absorption bleaching is the supposition for the experiments presented in Sec. V.

IV. ELECTRIC-FIELD EFFECTS AT LOW LIGHT EXCITATION

The investigations of the optical spectra on the dependence on the strength of an external electrical field have been performed at room and low temperature with some emphasis on the latter case to get a more detailed and comprehensive understanding of the underlying physics.

For CdS quantum dots in the weak confinement range a further strong influence of the excitonic effects can be expected. The case of the action of an electrical field on a

Coulombic bound state connected with a Stark shift of the resonance has been preferred for the investigation because of the promising modulation behavior of a shifting isolated resonance. Therefore, the confinement should be strong enough to suppress the field ionization on the one hand and, on the other hand, to preserve the dominance of the Coulomb potential via the potential of the barrier. Looking at it from this aspect, the weak-confinement range represents an optimum. In the case of strong confinement, i.e., if the size of quantum dots is reduced down to about 1- to 2-nm radius, the Coulomb effects become less important and the action of the electrical field has to be described in terms of the Franz-Keldysh effect. The electron and hole are independently driven by the electric field resulting in an oscillatory behavior of the absorption.

The electro-absorption experiments presented in Fig. 4 were carried out at CdS microcrystals with a certain shape distribution. The experimental result is a spectrally broad absorption change with only positive sign. No significance differences could be detected between the spectral behavior at (spectrum no. 1) low and (spectrum no. 2) room temperature. However, the absolute values of $\Delta\alpha$ are a factor of 10 smaller at room temperature though the electrical field was twice as large. This is attributed to a higher electrical conductivity of the polymer at room temperature reducing the effective-field strength and to a smaller slope of the absorption edge decreasing the modulation contrast. For comparison, the first derivative of the linear absorption spectrum is shown in spectrum no. 3. The difference in the line shape between spectra nos. 1 and 3 is clear evidence that temperature effects due to a simple heating of the sample by light or current cannot explain the results. In this case, the line shape would be that of the derivative somewhat shifted to lower energies.[21]

The spectra obtained in electro-absorption and presented in Fig. 4 distinctly differ from those presented for CdS in glasses.[13–18] First, the change in the absorption coefficient is substantially larger, second, and more unusual, a type of "line shape" has been found characterized by only positive changes of α. While the first fact is easily explained by the higher filling factor and by an optimum contact configuration resulting in a homogeneous field and giving an efficient potential drop over the microcrystal, the second result needs detailed discussion.

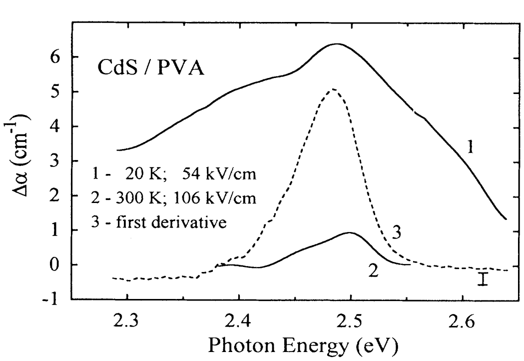


FIG. 4. Electric-field-induced change of the absorption coefficient $\Delta\alpha$ at 1, $T=20$ K and an electric-field strength of $E=54$ kV/cm; 2, room temperature and an electric-field strength of $E=106$ kV/cm. For comparison the first derivative of the linear absorption of Fig. 1 ($T=20$ K) is shown as spectrum no. 3 (not on scale).

If we consider an absorption resonance clearly resolved and sufficiently separated from the neighboring ones, then a broadening in an electro-absorption experiment, due to, e.g., increasing damping, is represented by a so-called three-line structure, i.e., positive values of $\Delta\alpha$ at the low- and high-energy side of the resonance and a negative $\Delta\alpha$ at the position of the absorption maximum. If the increase of the damping is accompanied in addition by an energy shift, e.g., to the redshift, then the three-line structure is asymmetric and the negative peak is shifted, too. In the presence of two or more near neighboring and strongly broadened states, the description by a three-line feature fails. Otherwise, if the absorption is caused by free electron-hole pair states in energy bands, then the carriers driven by an electrical field give an oscillatory absorption characterizing the Franz-Keldysh effect.

Just as well, internal fields can modify the energy levels and the displacement of the carrier wave functions and an applied external field gives then distinct changes in the oscillator strength of the optical transition.

Therefore, we have to consider generally the following relationship where the absorption change $\Delta\alpha$ is considered in a simple way by a functional dependence on the energy $\hbar\omega$, the homogeneous linewidth Γ and the oscillator strength f,

$$\Delta\alpha(\hbar\omega,\Gamma,f)=\frac{\partial\alpha}{\partial\hbar\omega}\Delta\hbar\omega+\frac{\partial\alpha}{\partial\Gamma}\Delta\Gamma+\frac{\partial\alpha}{\partial f}\Delta f+\cdots .$$

The first term is characterized by the quadratic dependence $\Delta\alpha\sim E^2$ if the action of the external electrical field on the exciton state can be discussed in the framework of the Stark effect. The second and the third terms contain changes in line broadening arising, e.g., from field ionization and increasing efficiency of tunneling, modifications in electron-phonon coupling with rising field strength, appearing contributions to the oscillator strength from former forbidden states, or from changes in the transition probability caused by the reduction of potential bending introduced by the interface, etc. Thus, in the case of a superposition of these or further mechanisms, a complex behavior of the spectral shape of $\Delta\alpha$ is expected.

The spectral behavior of $\Delta\alpha$ in Fig. 4 is clear evidence for a simultaneous redshift and broadening of the first absorption peak. It seems that the $\Delta\alpha$ spectrum consists of two parts, i.e., a peak near 2.5 eV and a long tail towards lower energies. The positive part at the high-energy side of the $\Delta\alpha$ maximum implies the increase of the absorption in the whole spectral range investigated.

Figure 5 shows the dependence of the electric-field-induced absorption change on the field strength measured at room temperature. For comparison, the quadratic function is plotted as a straight line in the log-log plot. To some extent an accordance can be achieved at higher field strengths.

The results presented in Figs. 4 and 5 make it convenient to discuss the experiments in terms of the

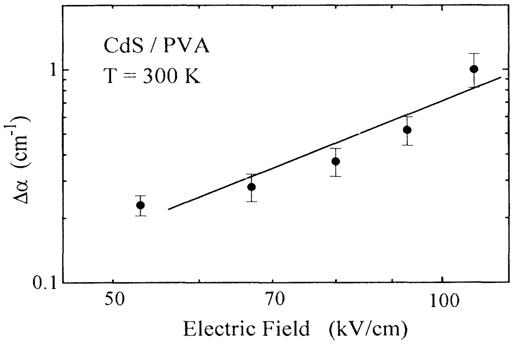


FIG. 5. Dependence of the field-induced absorption change on the strength of the electrical field, measured at room temperature.

quantum-confined Stark effect as already proposed in Refs. 13–17 and 25, however, with a typical behavior more similar to bulk CdS, i.e., more pronounced broadening and a smaller redshift. The excitonic effects are not destroyed by the electrical field even for electric-field strength larger than the ionizing field strength of the bulk semiconductor of $\approx 10^4$ V/cm in CdS.[6] The field ionization is suppressed because the exciton feels the surrounding potential barrier.

The new effect of missing negative parts in the absorption change is a hint to a restoring of the oscillator strength due to screening effects of the internal interface polarization fields. This interpretation will be supported by the experiments presented in Sec. V.

In our opinion the influence of former forbidden states to the high-energy part of the spectrum [which is often discussed in the case of very small crystallites ($\Delta l \neq 0$ due to the external field)], is of minor importance in microcrystals of sizes corresponding to the weak exciton confinement. There are other presumably more important symmetry-breaking mechanisms such as, e.g., the Coulomb potential, the shape of the microcrystal, or the coupling of the valence bands.

Also different depolarization factors have to be kept in mind, possibly leading to new mechanisms of broadening and to a complicated superposition of strongly broadened excited states.

The physical nature of the long tail to lower energies is not yet clear. Several explanations are possible, such as an extension of the excitonic effects down to low energies or surface-related effects.

V. ELECTRIC-FIELD EFFECTS AT HIGH EXCITATION

The experiments carried out at high laser excitation were stimulated by successful applications in the electro-optic devices based on the quantum-confined Stark effect[10] and by the results obtained combining electric fields and high densities of photoexcited carriers in CdS single crystals.[40]

The large value of $\Delta\alpha/\alpha$ obtained allows us to investigate the electro-optic properties of CdS microcrystals under additional pulsed laser excitation. For changes exceeding values of some percent a simple difference method can be applied avoiding modulation spectroscopy.

At high laser excitation we are investigating in reality the action of an electrical field on the excited exciton population. The characteristic change in α in this case is determined both by the change of the absorption spectrum under excitation and the change under the action of the electrical field.

The difference in absorption given by the spectra with and without an electrical field of $E = 50$ kV/cm is shown in Fig. 6 with the excitation intensities as a parameter. $\Delta\alpha$ has been calculated with the *nonlinear absorption* as the reference spectrum at zero electrical field strength. Because of the use of the broadband continuum of a pulsed dye laser to measure the corresponding reference absorption spectra a lower experimental accuracy has to be taken into account.

Starting with an excitation intensity of 100 kW/cm^2 where the absorption is bleached by only some cm^{-1} the action of an external electric field on the nonlinear absorption is within the experimental error (spectrum no. 1). However, a pronounced effect can be detected at excitation intensities of 1 MW/cm^2. The nonlinear spectrum shows absorption bleaching of about 20 cm^{-1} (see Fig. 3). The applied electric field compensates nearly completely the high-density effects induced by the laser excitation (spectrum no. 2). No change in absorption in the low-energy part of the spectrum has been found compared to the spectral behavior shown in Fig. 4 around 2.4 eV. This can be explained by assuming saturation of the states in the slope of the reference absorption spectrum without electrical field. Under high excitation the reference spectrum without field is thus characterized by a steeper rise and shorter absorption tail which is now more tunable by applying an electrical field. Exciting the CdS microcrystals by an intensity of 2 MW/cm^2 the change in absorption obtained is even larger than the bleaching at the same intensity without field (spectrum no. 3).

We explain our results as follows: The electrical field acts on a high-density particle system generated by the laser excitation. The most simple excited state consists of a four-particle system and it is obvious that already this state is more sensitive with respect to the ionizing effect of the external electrical field. For the sizes of microcrys-

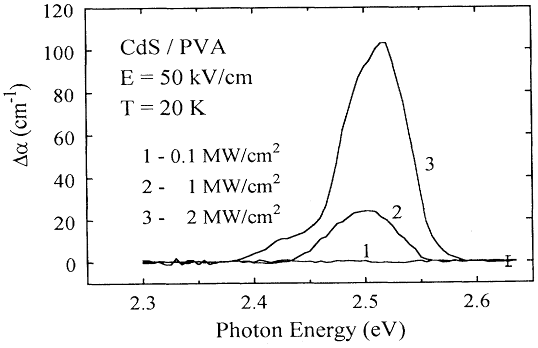


FIG. 6. Change of the absorption coefficient $\Delta\alpha$ of the CdS/PVA film with an applied electric field of 50 kV/cm and increasing excitation at 2.63 eV (measured at $T = 20$ K); 1, 100 kW/cm^2; 2, 1 MW/cm^2; 3, 2, MW/cm^2.

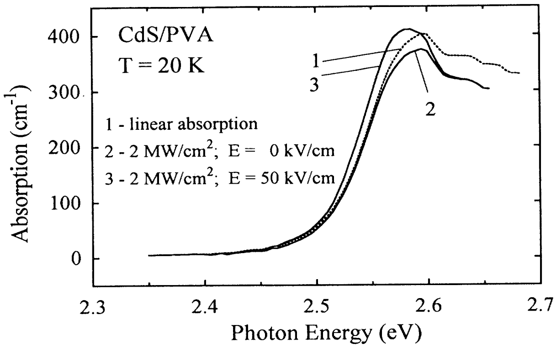


FIG. 7. Absorption spectra of the CdS/PVA film, 1, without electric field and at low excitation densities, 2, without electric field but under laser excitation of 2 $\mathrm{MW/cm^2}$, and 3, with electric field of 50 kV/cm and laser excitation of 2 $\mathrm{MW/cm^2}$.

tals investigated the number of excited electron-hole pairs per dot is even larger than ten. The electrical field separates the excited carriers and cancels the many-particle interaction in the microcrystal, the bleaching is reduced, and a positive change in α is obtained. On the other hand, the optically excited electrons and holes, which are separated and driven by the external field near the interfaces, create a depolarization field. There the charged carrier cloud screens the internal fields and potential fluctuations produced by the interface. Consequently, a restoring of the oscillator strength is evidently connected with the increase of the absorption peak.

To make the situation more clear, in Fig. 7 the absorption spectra are shown at three different conditions: Spectrum no. 1 is the linear spectrum without field and excitation, spectrum no. 2 is for high excitation intensity of 1 $\mathrm{MW/cm^2}$ resulting in a bleaching of the absorption without electrical field. Switching on the electrical field the nonlinear bleaching effect loses in strength for the reasons given above and the linear absorption spectrum is gradually restored. Moreover, at the highest excitation the action of the electrical field results in a larger red-shifted absorption maximum and in a slight decrease of the linewidth (spectrum no. 3).

The experimental data in Figs. 6 and 7 present the influence of the electrical field on the excited- and ground-state absorption in CdS microcrystals populated to various degrees by laser excitation. The modulation in α has been obtained by controlling the efficiency of the many-particle interaction by the external electrical field.

VI. CONCLUSION

The paper deals with the problem of optimization of materials containing semiconductor microcrystals, here CdS, in order to obtain a high-field-induced absorption change. A combination of CdS and the polymer PVA has various advantages: a volume fraction of semiconductor material of some percents and crystallite sizes in the weak confinement range are possible. A thickness of the polymeric film of 75 μm and the choice of symmetric coplanar electrodes ensure a good homogeneous field distribution. The absolute changes obtained for the absorption coefficient are more than an order of magnitude larger than those reported before for microcrystals embedded in glasses and represent a new step towards possible applications.

The spectral behavior can be discussed presently only in a more qualitative way, because only little is known about the shape of the microcrystals and the mechanisms of homogeneous and inhomogeneous broadening for the material investigated.

However, the changes obtained are large enough to investigate the absorption spectrum of a high-density electron-hole pair system in the presence of an external electrical field. In this case the nonlinear optical properties of the microcrystals can be used to engineer the band edge to optimum contrast. Thus, a good modulation can be achieved by only small changes of the electrical field. The method should work for all semiconductors in which the nonlinearities are significantly large before the laser-excited carriers screen the external electrical field. The change in $\Delta\alpha$ can be controlled by tuning the electrical field strength or the excitation intensity and by a suitable choice of the environment determining the interface configuration.

The explanation of the behavior at high laser excitation takes into consideration the action of the electrical field on the excited states. The electrical field decreases the exciton population in the center of the microcrystal by carrier separation and restores the former linear spectrum. This problem is suited to stimulate further theoretical work. In this context it is appropriate to refer to the rapidly developing research on II-VI strained-layer superlattices involving piezofields and its screening to produce optical or electro-optical nonlinearity. It is worthy to transfer these considerations to quantum dots in the near future and look for materials inhibiting internal polarization fields in the interface region. The presented material system of II-VI quantum dots embedded in a polymer could be a promising starting point for these investigations.

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