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Exciton dynamics in Ni-activated CdS

R. Heitz, A. Hoffmann, and I. Broser
Institut fuer Festkoerperphysik, Technische Universitaet Berlin, Hardenbergstrasse 36, 10623 Berlin, Germany

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The recombination processes of excitonic complexes in undoped and Ni-activated CdS crystals are investigated by means of time-resolved photoluminescence spectroscopy at liquid-He temperatures. The free-exciton recombination is found to be dominated by trapping at impurities, making the free-exciton lifetime a sensitive measure of crystal purity. Bound-exciton lifetimes in the ps region are observed which increase with increasing binding energy of the complex and are altered by the Ni doping. Calculations on the basis of the model of Rashba and Gurgenishvili show that competing nonradiative Auger-recombination processes can be neglected in undoped CdS. In Ni-doped samples a pronounced reduction of the excitonic lifetimes is found and attributed to energy-transfer processes. The deep Ni center offers an additional nonradiative recombination channel for bound-exciton complexes, which is assigned to "deep-center Auger processes" exciting charge-transfer transitions of Ni. Additionally, a bound-exciton complex with a binding energy of 13 meV is found to be related to the Ni doping. This complex is attributed to an exciton bound to a Ni-related neutral acceptor formed by the deep substitutional Ni acceptor paired with a shallow donor. The results demonstrate the possibility of the formation of shallow bound-exciton complexes at transition-metal centers.

I. INTRODUCTION

The wide-band-gap II–VI semiconductors retain considerable interest due to their potential for all-optical and electro-optical devices operating in the visible spectral region.[1] In general, the relevant optical processes are connected with the generation and recombination of excitons calling for a detailed understanding of exciton dynamics in the presence of deep defects or at high doping levels. However, most time-resolved studies of exciton dynamics at low excitation densities have been restricted to ultrapure or lightly doped samples in order to investigate inelastic phonon scattering of free excitons[2,3] as well as the properties of isolated bound-exciton complexes.[4–6] Recent results show that high concentrations of shallow defects can result in enhanced radiative recombination rates due to Coulomb screening of the exciton binding.[7,8] On the contrary, deep defects are expected to offer nonradiative recombination channels reducing the luminescence efficiency in the near-band-gap region.[9] However, no time-resolved investigation of energy-transfer processes between bound excitons and deep centers is available to date.

The dissipation and relaxation of excitonic polaritons in CdS has been studied both time integrated[10] and time resolved.[2] Free-exciton lifetimes up to 3 ns were found in high-purity samples. For bound-exciton complexes, lifetimes in the ps region were reported.[5,11] Nevertheless, only recently interaction between different bound-exciton complexes has been investigated using time-resolved spectroscopy. Even in undoped CdS the dephasing times of bound-exciton complexes can be limited by interactions with other defects[12,13] and a reduction of the bound-exciton lifetimes in strongly In-doped CdS has been attributed to Coulomb screening.[7,8] The influence of doping with deep impurities on excitonic recombination processes has not been studied, yet. Ni is a thoroughly investigated recombination center in CdS and, thus, an ideal model system to study the interaction between excitonic states and deep centers. The electronic structure as well as the deep-center properties of isolated Ni^{2+} are well known.[14–16] Additionally, ps-relaxation and recombination processes at Ni centers have been established using time-resolved luminescence and excitation spectroscopy.[17,18]

In the present paper, the influence of deep centers formed by the transition metal Ni on free and bound excitons in CdS is studied by means of time-integrated and time-resolved photoluminescence spectroscopy. We compare excitonic processes in undoped and Ni-activated CdS crystals in order to gain information on nonradiative recombination channels for bound-exciton complexes connected with deep defects. Here, we show that Ni in CdS offers an efficient nonradiative recombination channel for bound-exciton complexes. The energy transfer results from "deep defect Auger processes" exciting charge-transfer transitions of the Ni center. A Ni-related emission in the near-band-gap region is attributed to the radiative decay of an exciton bound to a defect pair out of substitutional Ni and a donor.

II. EXPERIMENT

The investigated samples are high-quality platelets of CdS with thicknesses between 150–800 μm, grown by the group of Dr. R. Broser (Fritz-Haber-Institut of the Max-Planck-Gesellschaft, Berlin) using the Frerichs-Warminsky method.[19] The Ni-activated crystals were doped in the ppm region by subsequent indiffusion. A detailed description of the sample preparation is given elsewhere.[15] Recently, these samples have been used to investigate the vibronic fine structure of intracenter *d-d*

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transitions,[15,20] the electronic structure of shallow bound states,[16] as well as the dynamics of the relaxation processes of the Ni^{2+} center.[17,18]

For the photoluminescence measurements the samples were immersed in superfluid He and excited with laser pluses of 3 ps duration and wavelengths between 460–510 nm of a dye laser synchronously pumped by an actively mode-locked and frequency-tripled Nd:YAG (neodymium-doped yttrium-aluminum-garnet) laser. The photoluminescence signal was spectrally decomposed by a 0.35 m subtractive double monochromator and detected with a micro-channel-plate photomultiplier using time-correlated single-photon counting. An overall time resolution of about 10 ps is achieved employing deconvolution techniques.

III. EXPERIMENTAL RESULTS

A. Time-integrated luminescence

The lower trace in Fig. 1 gives the near-band-gap luminescence spectrum of a typical undoped sample upon band-to-band excitation as recorded with the experimental setup for the time-resolved measurements. The observed linewidths correspond to the limited spectral resolution of this ps setup. High-resolution spectra show much narrower lines and, in general, yield additional fine structure due to chemically different donors and acceptors. Nevertheless, the spectrum resembles structures typical for high-quality CdS crystals.[21] The radiative recombination of excitons bound to neutral donors around 2.547 eV (I_2) and to neutral acceptors around 2.536 eV (I_1) dominates. Weak emissions on the high-energy side of the I_2 line correspond to the free A exciton and excitons bound to ionized donors (I_3). On the low-energy side weak LO-phonon replica are observed.

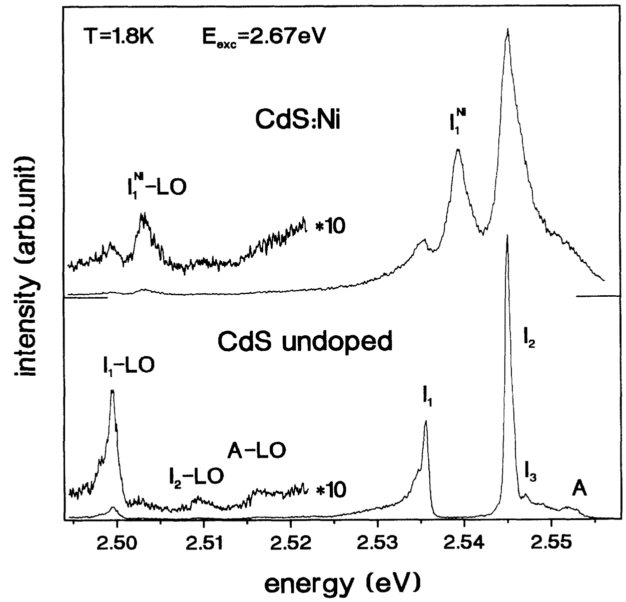

FIG. 1. Luminescence spectra of an undoped and a Ni-activated ($[Ni] \approx 0.5$ ppm) CdS crystal at $T = 1.8$ K excited at 2.67 eV. The integrated luminescence intensity of the Ni-activated sample is about two orders of magnitude smaller than that of the undoped sample.

The upper trace in Fig. 1 gives the luminescence of a CdS crystal doped with Ni. Ni in concentrations around 0.5 ppm strongly influences excitonic processes in CdS. Comparing different samples, three main changes in the near-band-gap luminescence can be related to the Ni doping: The integrated intensity decreases by orders of magnitude, the linewidth of the emission increases drastically, and a new bound-exciton emission (labeled I_1^{Ni} in Fig. 1) occurs at 2.540 eV in between the I_1 and the I_2.

At Ni concentrations around 1 ppm the bound-exciton emissions exhibit full widths at half maximum (FWHM's) far above 1 meV. High-resolution spectra of the intracenter d-d transitions of Ni^{2+} prove that the crystal structure does not suffer from Ni doping in the ppm range. Nevertheless, the deep Ni center is a very local probe due to its strongly localized wave functions, whereas bound-exciton complexes have comparably extended wave functions. Thus, the bound-exciton complexes are more sensitive than Ni centers to local lattice distortions and electronegativity changes caused by defects (e.g., Ni centers) in their spatial surrounding. The intensity of the I_1^{Ni} is correlated with the Ni doping and the LO-phonon sideband has an intensity typical for an I_1 complex. The origin of this bound-exciton complex will be discussed in detail in Sec. IV C.

B. Time-resolved luminescence

The dynamical behavior of a system of free and bound excitons in a semiconductor is quite complex, especially after band-to-band excitation. Nevertheless, under certain conditions a three-level system, Fig. 2, is a reasonable approximation. The generation and thermalization of free excitons after band-to-band excitation[3] takes place in a few ps and, thus, can be neglected in time-resolved luminescence experiments with a temporal resolution of about 10 ps. The upper excited state (FE) in Fig. 2 represents free A excitons, which recombine either radiatively generating LO-phonons (τ_{sc}) (or leaving the crystal at the surface) or are trapped at defects (τ_{cap}) forming bound-exciton complexes (BE). As obvious from Fig. 1,

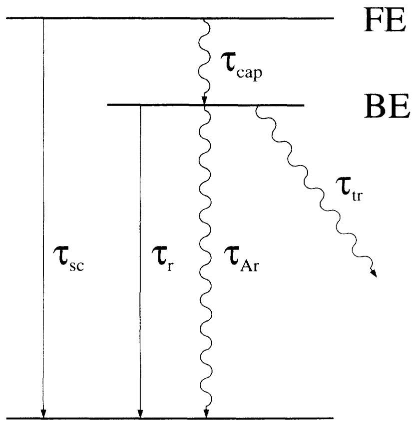

FIG. 2. Three-level scheme describing the recombination dynamics of free and bound excitons. The different recombination processes are discussed in the text.

even in undoped samples the bound-exciton emission dominates proving the importance of these capture processes. The free-exciton lifetime is given by $\tau_{\mathrm{FE}}^{-1}=\tau_{\mathrm{cap}}^{-1}+\tau_{\mathrm{sc}}^{-1}$. Bound-exciton complexes can be treated as isolated two-level systems and decay either radiatively (τ_r) or nonradiatively by Auger processes exciting the charge carrier of the neutral donor or acceptor (τ_{Ar}). The aim of the present paper is to discuss energy-transfer processes observed at high background concentrations of deep defects and represented by τ_{tr} in Fig. 2. The lifetime of a bound-exciton complex is given by $\tau_{\mathrm{BE}}^{-1}=\tau_r^{-1}+\tau_{Ar}^{-1}+\tau_{\mathrm{tr}}^{-1}$.

The solution of the rate equations describing a three-level system is given in Ref. 22. Exciting resonantly the luminescent state a monoexponential decay is expected, whereas after generation of free excitons the luminescence dynamics of bound-exciton complexes are more complicated:

$$I_{\mathrm{BE}}(t)\propto\frac{\tau_{\mathrm{BE}}\tau_{\mathrm{FE}}}{\tau_{\mathrm{BE}}-\tau_{\mathrm{FE}}}n_0\left[\exp\left[-\frac{t}{\tau_{\mathrm{BE}}}\right]-\exp\left[-\frac{t}{\tau_{\mathrm{FE}}}\right]\right]. \tag{1}$$

The generation of bound-exciton complexes as a result of the capture of free excitons leads to luminescence rise processes and both the free- (τ_{FE}) and the bound- (τ_{BE}) exciton lifetimes are accessible in the time evolution of the bound-exciton emissions. The luminescence rise is governed by the shorter time constant and its decay by the longer one. Thus, employing nonresonant excitation bound-exciton transients have to be analyzed very carefully. It should be noted that Eq. (1) does not take into account the finite number of shallow defects. At high excitation densities or in high-purity samples, saturation effects can considerably alter the luminescence dynamics.

1. Undoped CdS

Figure 3 gives transients of different excitonic emissions for a typical undoped CdS sample after band-to-band excitation. (The corresponding time-integrated luminescence spectrum is given by the lower trace in Fig. 1.) The *A* exciton is found to decay monoexponentially with 100 ps, whereas for the different bound-exciton transitions both rise and decay processes are resolved. Excellent fits of the transients are obtained using Eq. (1). The luminescence of the I_3 rises with a time constant of 50 ps and decays with 100 ps, following the decreasing concentration of free excitons. Obviously, the lifetime τ_{BE} of the (D^+,X) complex amounts to 50 ps, which is astonishingly short compared to recent results.[12] Both, the I_2 and the I_1 show a slower luminescence rise with 100 ps corresponding to the free-exciton lifetime τ_{FE} and decay with 300 and 980 ps, respectively. These decay times are in reasonable agreement with those observed elsewhere[11] and confirm a general trend stated for other wide-band-gap II–VI semiconductors.[4–6] The lifetime τ_{BE} of the bound-exciton complexes increases with increasing binding energy.

The capture of free excitons by shallow impurities should be a complex multistep process involving the rich spectrum of excited states of bound-exciton complexes. Nevertheless, the good experimental agreement between the free-exciton decay times and the bound-exciton rise times demonstrates that this cascade capture process proceeds too fast to be resolved in our experiments. This is in good agreement with similar observations in various broad band II–VI bulk semiconductors.[5,6,23] However, a recent investigation on ZnSe indicates a different behavior in strained epilayers.[24]

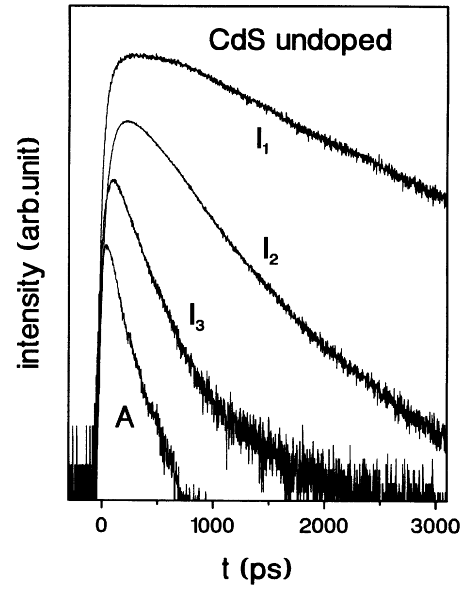

FIG. 3. Luminescence transients of free and bound excitons in an undoped CdS crystal after band-to-band excitation. The corresponding luminescence spectrum is shown in Fig. 1.

The bound-exciton transients are found to differ considerably after band-to-band excitation depending on the investigated CdS sample. A detailed analysis shows that the free *A* exciton lifetime τ_{BE} ranges between 100–600 ps, whereas the bound-exciton lifetimes τ_{BE} remain unchanged. Figure 4 compares the transients of the (D^0,X) recombination for two undoped CdS samples with free-exciton lifetimes of 600 ps (a) and of 100 ps (b) following band-to-band excitation. The longer free-exciton lifetime in sample (a) indicates a lower impurity concentration and results in a quite different I_2 transient, which cannot be fitted using Eq. (1) due to saturation effects. Nevertheless, the exponential decay at times longer than 1 ns follows the decay of the free *A* exciton density. After resonant excitation of the I_2 [curve (c) in Fig. 4] a monoexponential decay with 300±20 ps is observed for both crystals. Assuming that the free-exciton lifetime of 3000 ps in high-purity CdS observed by Wiesner and Heim[2] results from LO-phonon scattering only (τ_{SC}), the mean time τ_{cap} for the capture of free excitons by shallow defects in our undoped samples ranges between 100–750 ps. The free-exciton decay time is a sensitive measure of the crystal purity.

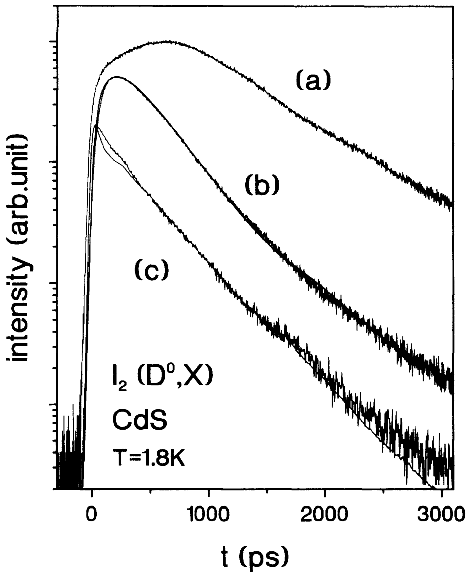

FIG. 4. Transients of the I_2 of an undoped ($\tau_{\mathrm{BE}}=100$ ps) (b) and a high-purity ($\tau_{\mathrm{Fe}}=600$ ps) (a and c) CdS sample after band-to-band excitation of 2.67 eV (a and b) and after resonant excitation (c).

2. *Ni-activated CdS*

The luminescence as well as its dynamics in the near-band-gap region of CdS are strongly altered in Ni-activated samples. Figure 5 gives transients of the excitonic emissions after band-to-band excitation in a CdS crystal containing 0.5 ppm Ni. (The corresponding luminescence spectrum is given in the upper part of Fig. 1.) All transients have a fast component, whose intensity decreases with decreasing energy of detection. Its time behavior matches that of the free A-exciton. Thus, we attribute this fast component to a weak luminescence underground due to a broad A exciton resonance. For the crystal shown an A-exciton lifetime of 15 ps is observed. Nevertheless, this short lifetime is not directly correlated with the Ni concentration, other Ni-activated samples with comparable Ni concentrations exhibit lifetimes up to 60 ps. All bound-exciton transients show a second slower exponential component, which is attributed to the decay of the complexes. The lifetimes τ_{BE} are found to be reduced in comparison to those in undoped samples. The (A^0,X) complex has a lifetime of 750 instead of 980 ps and the lifetime of the (D^0,X) complex is reduced from 300 to 30 ps. The I_3 could not be resolved in the Ni-activated samples due to the large FWHM's of the excitonic emissions. Neither the radiative (τ_r) nor the Auger (τ_{Ar}) recombination rates of bound-exciton complexes should be altered in the presence of Ni. Thus, the experimental data indicate fast energy-transfer processes between bound-exciton complexes and deep centers introduced by the Ni doping.

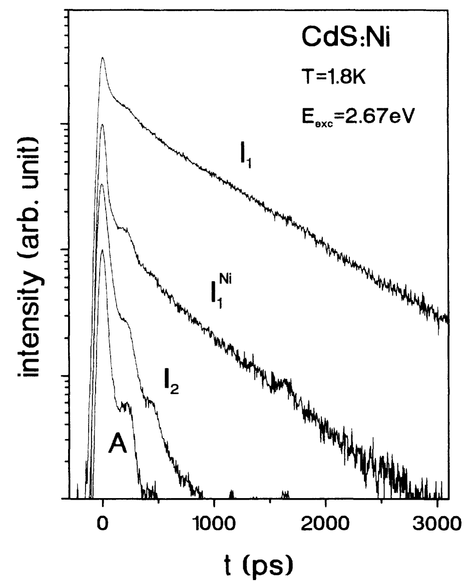

FIG. 5. Luminescence transients of free and bound excitons in a Ni-activated ([Ni]≈0.5 ppm) CdS crystal after band-to-band excitation. The corresponding luminescence spectrum is shown in Fig. 1.

In the sample shown in Fig. 5, the I_1^{Ni} decays with a time constant of 620 ps. Investigating different CdS samples doped with Ni in the ppm region, lifetimes between 580–650 ps are observed. The lifetimes of the (A^0,X) and the (D^0,X) complexes are found to vary in a similar way.

IV. DISCUSSION

The experimental results presented provide clear evidence for a pronounced interaction between bound-exciton complexes and deep centers. Efficient energy-transfer processes reduce the bound-exciton lifetimes in Ni-doped CdS crystals and a new Ni-correlated bound-exciton complex is observed. In order to understand these processes, at first, the radiative and nonradiative recombination of bound excitons in undoped samples will be discussed. Here, the bound-exciton complexes can be treated as isolated centers ($\tau_{\mathrm{tr}}^{-1}=0$).

A. The radiative lifetimes

Isolated bound-exciton complexes can recombine either radiatively by the emission of electric dipole radiation or nonradiatively by Auger processes exciting the bound charge carrier of the neutral donor or acceptor. In general, the recombination mechanisms of excitons depend critically on their localization. For excitons bound at shallow defects, it can be expected that the radiative recombination rate decreases[25] whereas the Auger-recombination rate increases with increasing localization. Thus, the experimental results for undoped CdS (Table I) indicate a dominating radiative decay in good agreement with similar results for other wide-band-gap II–VI semiconductors.[4–6]

Rashba and Gurgenishvili (RG) introduced a model explaining the enhanced oscillator strength of bound excitons compared to that of the free exciton.[25] The basic idea is that all free-exciton oscillators within the space occupied by the bound exciton contribute to the bound-

TABLE I. The lifetimes of free and bound excitons observed for undoped and Ni-activated ([Ni]$\approx$0.5 ppm) CdS at $T=1.8$ K. The third column (RG) gives lifetimes calculated for radiative recombination using Eq. (2).

			τ (ps)		
CdS		E_b (meV)	Undoped	[Ni]$\approx$0.5 ppm	RG
Free exciton	A		100–600	15–60	
(D^+,X)	I_3	5.4	50±20		220
(D^0,X)	I_2	7.6	300±20	30	360
(A^0,X)?	I_1^{Ni}	13		620	810
(A^0,X)	I_1	17.2	980±30	750	1230

exciton oscillator strength. Thus, the bound-exciton oscillator strength is expected to decrease with increasing localization. The interaction potential is attractive for one charge carrier of the exciton but repels the other reducing the overlap of the wave functions of the electron and the hole. In the model of RG the radiative lifetime τ_r of a bound-exciton complex is a function of material parameters like the free-exciton oscillator strength f_{ex} and the binding energy E_b of the bound-exciton complex:

$$\tau_r(s)=0.51\frac{V_E m_{ex}^{3/2}[\lambda(cm)]^2}{n f_{ex}\hbar^3}E_b^{3/2} . \qquad (2)$$

Equation (2) predicts a decrease of the radiative transition probability with increasing binding energy, which is in agreement with the experimental data, Table I. Lifetimes calculated using Eq. (2) and an effective mass[26] m_{ex} of 1.30, a volume of the primitive elementary cell V_E of 0.0494 nm^3, a refractive index n of 3.05 and a free-exciton oscillator strength[27] f_{ex} of 0.002 56 per molecule are given in the last column of Table I. The observed (undoped samples) and the calculated lifetimes agree within 20% for the (D^0,X) and the (A^0,X) complex. This is an excellent agreement in view of the uncertainty of the effective exciton mass and the comparably simple theoretical concept.[28] Nevertheless, the theory of RG is known to give reasonable quantitative agreement for the other wide-band-gap II–VI semiconductors, too.[4–6] On the contrary, the lifetime of the (D^+,X) complex is not reproduced by Eq. (2). This is not surprising since charged impurity centers can not be represented by a δ-function potential as done in the theory of RG. Obviously, Auger recombination can be neglected ($\tau_{A_r} \gg \tau_r$) for shallow bound excitons in CdS and the observed lifetimes of 300±20 and 980±30 ps for the (D^0,X) and the (A^0,X) complex, respectively, represent the radiative lifetimes τ_r.

B. Energy-transfer processes in Ni-activated samples

A decrease of bound-exciton lifetimes in doped semiconductors can result either from distortions of the bound-exciton complexes altering the radiative decay rates or from the introduction of competing recombination channels. Recently, a reduction of the bound-exciton lifetimes observed in highly In-doped CdS has been attributed to increasing radiative decay rates.[7,8] Indium forms a shallow donor in CdS and at concentrations above 10^{17} cm^{-3} the Coulomb interaction between different In donors becomes important, leading to a screening of the interaction between the exciton and the shallow defect. The decreasing effective binding energy of the complex results in a shorter radiative lifetime τ_r corresponding to the theory of RG discussed in the previous section. The situation is completely different for deep centers like Ni. No Coulomb screening is expected from the isoelectronic Ni^{2+} center. Obviously, Ni doping introduces competing nonradiative recombination channels represented by the energy-transfer process τ_{tr} in Fig. 2. The rate τ_{tr}^{-1} describing the energy transfer between bound excitons and the deep Ni center critically depends on the overlap of the respective wave functions and, therefore, on the bound-exciton localization. Assuming an energy-transfer process the larger lifetime reduction of 90% of the (D^0,X) complex, Table I, compared to that of only 25% of the (A^0,X) complex can be understood. The larger binding energy of the (A^0,X) complex corresponds to a stronger localization and, thus, a lower mean energy-transfer rate for a given Ni concentration. Comparing the data of the undoped and the 0.5 ppm Ni containing sample given in Table I the mean energy-transfer times τ_{tr} are calculated to 30 and 3200 ps for the (D^0,X) and the (A^0,X) complex, respectively.

Ni^{2+} has an electronic d^8 configuration leading to a rich spectrum of electronic states.[14,15] In principle, it can be expected that energy-transfer processes excite intracenter luminescence transitions of the Ni center. Figure 6 shows polarized excitation spectra of the Ni^{2+} $[{}^3T_1(P)-{}^3T_1(F)]$ luminescence in the near-band-gap region. The free as well as the bound-exciton resonances occur as minima of the excitation efficiency, which seems to be in contradiction to the proposed efficient energy-transfer processes between bound-exciton complexes and the Ni center. For photon energies above about 2.3 eV the intracenter transitions of Ni^{2+} in CdS are excited by the acceptor type Ni$^{2+/+}$ charge-transfer process and the recapture of the generated hole.[16] In good agreement Fig. 6 shows high excitation efficiency below the excitonic band gap, which decreases at higher energies due to the generation of free A- ($E\perp c$) and B- ($E\parallel c$) excitons. Exciting free or bound excitons, their radiative recombination acts as a competing recombination channel lowering the excitation efficiency of the intracenter Ni^{2+} luminescences. Only part of the excitation is transferred to the Ni center by the discussed energy-transfer processes counteracting this effect. Thus, the efficient Ni$^{2+/+}$ charge-transfer excitation hampers the detection of energy-transfer processes originating at excitonic states by means of excitation spectroscopy. Nevertheless, the time-resolved measurements presented unambiguously prove such energy-transfer process. The experimental situation could be improved using extremely thin samples. In such samples volume-dependent processes would be suppressed in favor of strongly absorbing excitonic processes.

This situation is different for rare-earth elements with only one stable charge state in most semiconductors. The excitation of intracenter transitions of these rare-earth centers after band-to-band excitation is explained[29] by

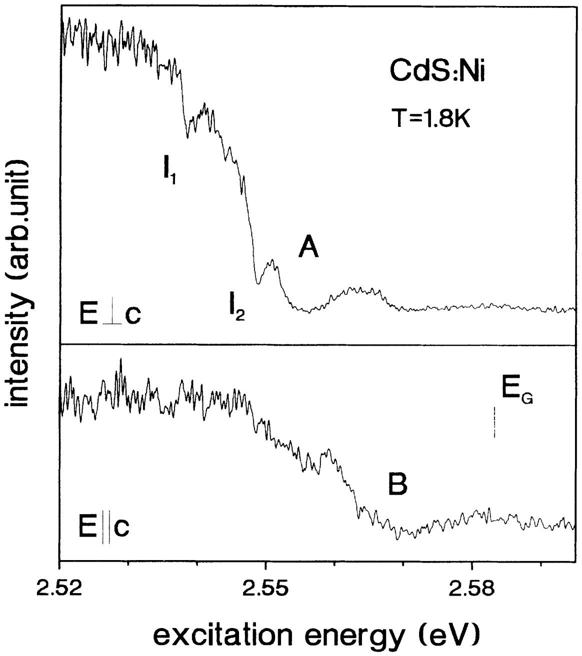

FIG. 6. Polarized excitation spectra of the Ni^{2+}[$^3T_1(P)-{}^3T_1(F)$] luminescence in CdS doped with about 0.5-ppm Ni.

energy-transfer processes originating either at donor-acceptor pairs or at excitonic states. The basic mechanisms are the so called "three-center Auger recombination"[30] or "defect Auger recombination,"[31] respectively. These processes are efficient if the recombination energies of the donor-acceptor pair or the exciton are nearly degenerate with an intracenter transition.[32] In the case of Ni in CdS no intracenter transition is nearly resonant with the bound-exciton recombination, but both the acceptor-type Ni$^{2+/+}$ and the donor type Ni$^{2+/3+}$ transition are resonant.[33] Thus, the energy-transfer processes between bound-exciton complexes and the deep Ni center in CdS can result from Auger-type processes, exciting charge-transfer transitions of the Ni center.

As stated in Sec. III A 1 the luminescence efficiency in the near-band-gap region after band-to-band excitation is reduced by some orders of magnitude in the Ni-doped samples. A similar effect is known for other transition metals, too.[34] The competing nonradiative relaxation channels due to the Auger-type excitation of the deep Ni center lowers the efficiency of excitonic luminescence processes but cannot account for a decrease by more than about one order of magnitude. The dominating contribution is given by the suppression of exciton formation after band-to-band excitation. Ni is an efficient hole trap.[18] After generation of free carriers the recombination of holes with Ni centers suppresses the formation of excitons and, thus, decreases drastically the near-band-gap luminescence efficiency.

C. The I_1^{Ni}

The origin of the I_1^{Ni} at 2.540 eV in Ni-activated CdS samples is not clear, yet, although it is related with the Ni doping. The emission can be attributed to a bound-exciton recombination and the presented spectroscopic characteristics indicate a neutral acceptor as the relevant defect. Both the LO-phonon coupling and the lifetime are very similar to those of the I_1, see Fig. 1 and Table I.

The simplest defect would be Ni^{2+} on cation site forming a deep acceptor level 2.333 eV above the valence band.[33] Local lattice distortions as well as the electronegativity difference between the Ni^{2+} ion and the replaced Cd^{2+} ion could result in a local potential able to bind an exciton. Obviously, Haynes rule fails for this complex, which could be attributed to the transition-metal nature of the defect. Similar bound-exciton complexes have been suggested for rare-earth centers,[32,35] recently. Nevertheless, there are some severe problems in proposing a shallow bound (Ni^{2+},X) complex. The relevant $4f$ ions are stable in their isoelectronic charge state. Thus, no direct recombination of a hole or an electron with the center is possible. This situation is different for transition-metal centers, such as isolated Ni, with up to three stable charge states. In this case, one charge carrier of the bound exciton tends to be localized in the $3d$ shell participating in the electron-electron interaction of the core electrons. The formed many-particle system has to be described in terms of a transient shallow donor or acceptor complex[36] rather than as a bound-exciton complex and would have a considerably larger binding energy. Such shallow states have been observed for different transition-metal centers in the wide-band-gap II–VI semiconductors indicating a general phenomenon.[37]

Recently, for Ni in CdS a weak excitation resonance observed on the low-energy onset of the acceptor-type charge-transfer band has been attributed to the formation of an electron hole pair (Ni^{2+},e,h) deeply bound to the isoelectronic Ni^{2+} center.[16] This complex is associated with the Ni$^{2+/+}$ charge-transfer process and, thus, rather a transient shallow acceptor state than a bound-exciton complex. The (Ni^{2+},e,h) complex has a large binding energy of 362 meV (from an excitonic point of view) and recombines completely nonradiatively exciting the Ni^{2+} center in contrast to the findings for the I_1^{Ni}. It is unlikely that a shallow bound-exciton complex (Ni^{2+},X) can coexist with the deeply bound electron hole pair (Ni^{2+},e,h). Additionally, efficient defect Auger processes should lead to a nonradiative recombination of excitons located directly at the Ni center as indeed observed for the (Ni^{2+},e,h) complex.[18] In contrast, the lifetime of 650 ps observed for the new complex fits well to that observed for the I_1 and that calculated with the theory of RG, Table I. Obviously, the I_1^{Ni} recombines predominantly radiatively and experiences nonradiative energy transfer to statistically distributed Ni centers just like the other bound-exciton complexes. Thus, the I_1^{Ni} cannot result from an exciton weakly bound to an isolated Ni ion.

Recently, emission in the spectral region between the I_2 and the I_1 has been reported[38,39] for distorted CdS crystals and attributed to the recombination of excitons bound at defect complexes. On the basis of excitation and Zeeman measurements[39] pairs formed by a deep double acceptor on a Cd site and an interstitial donor, probably Li or Na, have been proposed. Thus, the I_1^{Ni} can be assigned to a complex defect either created by the Ni-doping procedure or, more likely, containing Ni. We propose an exciton bound at a Ni-related pair $(\mathrm{Ni}_{\mathrm{Cd}}^{-}, D^{+})$ consisting of the deep Ni acceptor on Cd site and a donor. The direct involvement of Ni is supported by results of resonant Raman-scattering experiments on Ni-doped CdS crystals.[40] Exciting near the I_1^{Ni} resonance a relation between the scattered LO-intensity and the Ni concentration is observed. In principle, the formation of shallow bound-exciton complexes at complex transition-metal defects is possible as has been demonstrated for Cu-related defects in ZnTe.[41,42] Although no hints of Ni-related pairs have been found in CdS to date, they were observed in III–V semiconductors by means of optical spectroscopy[43] and electron spin resonance investigations[44,45] show a general tendency of transition metals to form pairs with shallow impurities in the wide-band-gap II–VI compounds. The fine-structure spectra of isolated Ni^{2+} are not altered by this pairing, since the energy shifts of the intracenter transitions caused by the neighboring donor are large compared to the fine-structure splittings.

V. CONCLUSION

The dynamics of free and bound excitons in high-purity and Ni-activated CdS samples are investigated by means of time-resolved photoluminescence spectroscopy. Even in high-purity samples a strong interaction of free excitons with impurities is found. Trapping at shallow impurities is demonstrated as a dominating recombination channel of free excitons. Thus, the free-exciton lifetime is a sensitive measure for the crystal purity. In contrast, at low-impurity concentrations the lifetimes of bound-exciton complexes are not affected. A comparison with lifetimes calculated under the assumption of radiative decay using the model of Rashba and Gurgenishvili shows that Auger-recombination processes can be neglected in CdS. A pronounced alteration of the excitonic luminescence and recombination dynamics is found in Ni-activated samples. A new Ni-related excitonic emission line is observed and attributed to the recombination of an (A^0, X) complex formed at a neutral Ni-related pair consisting of the deep substitutional Ni acceptor and a donor. This complex is found to decay predominantly radiative and proves the possibility of forming shallow bound-exciton complexes at deep transition-metal defects. Additionally, the bound-exciton lifetimes are reduced in the presence of Ni. Ni offers a competing recombination channel due to "deep-center Auger recombination" exciting charge-transfer transitions of the Ni center. This energy-transfer process is especially efficient for weakly localized complexes like the (D^0, X) complex. The strong reduction of the near-band-gap luminescence efficiency after band-to-band excitation in Ni-activated samples is caused by the suppression of exciton formation due to hole capture at Ni^{+} centers as well as the nonradiative energy-transfer processes.

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