Magneto-optics of Ni-bound shallow states in ZnS and CdS

R. Heitz, A. Hoffmann, and I. Broser

Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstrasse 36, D-1000 Berlin 12, Germany

Transition metals in semiconductors give rise to shallow states which cannot be described on the basis of their $3d$ wave functions. In this paper a comparative study of shallow states associated with Ni in ZnS and CdS is presented. By means of high-resolution excitation spectroscopy under the influence of magnetic fields the determination of the electronic origin of the observed fine structure becomes possible. The results give insight into the local binding properties as well as the important role of the exchange interaction. Excitation measurements of the $^3T_1(P)$-$^3T_1(F)$ Ni^{2+} luminescence reveal weak lines on the low-energy onset of the $Ni^{2+/+}$ charge-transfer band due to the formation of shallow states. The high sensitivity of these measurements allows Zeeman investigations of these nonluminescent shallow states. In both ZnS and CdS all lines exhibit a diamagnetic shift towards higher energies, demonstrating the effective-mass-like nature of the excited states. On the other hand, the fine structure as well as the linear Zeeman behavior is quite different in both host materials indicating the formation of different shallow complexes. In ZnS a transient shallow acceptor state (Ni^+, h) is formed. The zero-phonon-line (ZPL) doublet around 2.437 eV with a zero-field splitting of 1.4 meV develops into a singlet and a triplet ($g = 0.50$) in a magnetic field. It is unambiguously explained by the $(Ni^+, h_{n=1})$ ground state, taking into account the exchange interaction. An additional ZPL shifted 25.3 meV towards higher energies is attributed to an excited $(Ni^+, h_{n=2})$ state. From the excited hole state as well as from an observed hole-transfer process between Ni^{2+} and Cu^{2+} centers the binding energy of the (Ni^+, h) complex and the $Ni^{2+/+}$ charge-transfer energy are determined to be 108 meV and 2.545 eV, respectively. In CdS a deeply bound electron-hole pair (Ni^{2+}, e, h) is formed. The ZPL at 2.1904 eV exhibits a zero-field splitting of 50 μeV attributed to the trigonal crystal field and an isotope shift of -37 μeV/nucleon. In a magnetic field it splits into a triplet ($g = 2.26$). The Ni-associated shallow complexes in ZnS and CdS differ in the localization of the electron which depends on the deep $Ni^{2+/+}$ acceptor level. In ZnS this level is deep in the band gap; in CdS it is close to the conduction band.

I. INTRODUCTION

Transition-metal ions act as very efficient recombination centers in semiconductors and strongly influence their electrical and optical properties. Transition-metal doping diminishes the quantum yields in the visible and near-band-gap spectral region[1] and results in short carrier lifetimes useful in fast optoelectronic devices.[2] Cross sections for the trapping of charge carriers up to some 10^{-15} cm^{-2} are found.[3] Even though the carrier-capture processes are not well understood yet, it is very likely that shallow states associated with transition-metal centers are important.[4,5] The cascade capture process across the excited hydrogenlike states of a charged center would explain the large cross sections.[6]

Indeed, optical spectra of transition-metal-doped II-VI (Refs. 7 and 8) and III-V (Refs. 9 and 10) semiconductors exhibit sharp resonances on the low-energy onsets of the charge-transfer bands, corresponding to transitions into states weakly bound to the transition-metal center. The general idea[11] behind this interpretation is that a complex is formed out of an ionized transition-metal ion and a charge carrier bound by the Coulomb interaction. Despite their general occurrence, only in exceptional cases do detailed theoretical considerations exist due to a lack of experimental data: these resonances are extreme-

ly weak, calling for highly sensitive detection methods such as electroabsorption,[8] Fourier transform,[10] or calorimetric absorption[12] spectroscopy, or for high dopant concentrations. This makes it difficult to investigate the influence of external fields, a necessary precondition for the characterization and hence the determination of the involved states. In general, this is manifested in a diverse nomenclature used to describe the shallow states, ranging from deeply bound excitons[7] and charge-transfer states[12] to transient shallow donor or acceptor states.[11]

Rich experimental data exist for the systems ZnO:Cu (Refs. 11 and 13) and ZnSe:Co,[14] the only systems exhibiting sharp emission lines due to the radiative recombination of the shallow states. Theoretical considerations assign the fine structure observed in ZnO to an acceptor-type complex (Cu^+, h) (Ref. 15) and in ZnSe to a donor-type complex (Co^{3+}, e).[14] Nevertheless, recent electroabsorption measurements[16] indicate that at least in the latter case singlet states of the $3d$ shell should be involved, too. In particular, the theoretical work for the system ZnSe:Co (Ref. 14) and recent experimental results concerning Fe centers in III-V semiconductors[10,17] demonstrate the importance of the exchange interaction for the shallow complexes.

Ni centers in all wide band-gap II-VI semiconductors are known to possess shallow states.[18,19] Due to the am-

photeric behavior of the Ni centers both acceptor-type and donor-type states have been observed.[20] Thus, in general, both transitions can coexist in the same system. The present paper is concerned with ZnS:Ni and CdS:Ni. In both materials Ni leads to broad absorption bands in the visible spectral region attributed to the acceptor-type $Ni^{2+/+}$ charge-transfer transition.[21,22] Consequently, sharp absorption resonances observed on the low-energy onset of these bands are interpreted as acceptor-type states.[18,23] Nevertheless, for CdS the donor-type charge-transfer transition is expected in the same spectral region[22] and recent results from electroabsorption measurements indicate a donor-type origin of the observed shallow state.[24]

The shallow states of the incorporated transition-metal ions are, in general, excited states of the center and recombine nonradiatively leading to an excitation of the remaining isoelectronic $3d$ ion.[25,26] Thus, the excitation spectroscopy of the inner center d-d transitions is an extremely sensitive method to investigate shallow states even in weakly doped (≤ 1 ppm) crystals. In ZnS and CdS the $Ni^{2+}(^3T_1(P)$-$^3T_1(F))$ transition gives rise to a structured luminescence band in the near-infrared spectral region,[27] whose excitation behavior is investigated in the present paper. The electronic origin and the fine structure of shallow states associated with Ni centers in ZnS and CdS are investigated by means of magneto-optical spectroscopy. The comparative study of both systems reveals insight into the local binding properties, which are discussed in the framework of jj-coupling schemes.

II. EXPERIMENT

The samples used for the measurements were high-quality platelets of CdS and ZnS with thicknesses between 200 and 800 μm, grown by the group of Dr. R. Broser (Fritz-Haber-Institut of the Max-Planck-Gesellschaft, Berlin) using the Frerichs-Warminsky method.[28] Subsequently, the crystals were doped with nickel (partly with enriched isotopes) in the sub-ppm region by indiffusion. A detailed description of the sample preparation and typical fine-structure spectra have been given elsewhere.[27] The samples were immersed in liquid He at temperatures between 1.8 and 2.0 K. The temperature-dependent measurements were performed in a continuous He flow of variable temperature.

Light from the crystals was decomposed by a 0.75-m double monochromator and recorded with a cooled GaAs photo multiplier. A dye laser pumped by an excimer laser (Lambda Physik) served as a high-resolution tunable light source delivering 20-ns pulses at a repetition rate of 100 Hz. The experiments in a magnetic field were carried out using a 15-T superconducting magnet built in split-coil technique (Intermagnetics and Janis, Inc.), enabling measurements in both Voigt and Faraday configuration.

III. RESULTS

The aim of the present paper is to determine the electronic structure of shallow states associated with Ni

centers in CdS and ZnS. Transitions into these shallow states lead to weak resonances in the excitation spectra of inner center d-d transitions.[25] The excitation spectroscopy of the $Ni^{2+}(^3T_1(P)$-$^3T_1(F))$ luminescence is a highly sensitive method to detect the shallow states and their magneto-optical behavior even at low Ni concentrations. Typical luminescence ad excitation spectra of the investigated CdS:Ni and ZnS:Ni crystals can be found in Refs. 5 and 29.

A. CdS

Figure 1 shows the excitation spectrum of the $Ni^{2+}(^3T_1(P)$-$^3T_1(F))$ luminescence in the spectral region of the low-energy onset of the $Ni^{2+/+}$ charge-transfer band in CdS. The energy position of the weak but extremely sharp zero-phonon line (ZPL) at 2.190 40 eV is in good agreement with results from absorption[23] and electroabsorption[8] measurements on strongly doped samples. The spectrum shown is typical for a crystal containing Ni in the sub-ppm region. Above 1 ppm, the ZPL becomes broader, resulting in an apparently more pronounced phonon side band. This demonstrates the importance of low Ni concentrations for fine-structure investigations as presented in this paper. The ZPL has a side band shifted by 1.3 meV towards higher energies, which corresponds to the typical TA phonon replica observed for acceptor-bound exciton complexes (A^0,X) in CdS.[30] A further line shifted by 8.6 meV is attributed to an acoustical phonon as well. No TO phonon replica is observed, but in the region of the LO(Γ) phonon a strong resonance occurs. The energy shift of 38.5 meV is slightly larger than the energy of the intrinsic LO(Γ) phonon indicating a Ni-associated local mode.

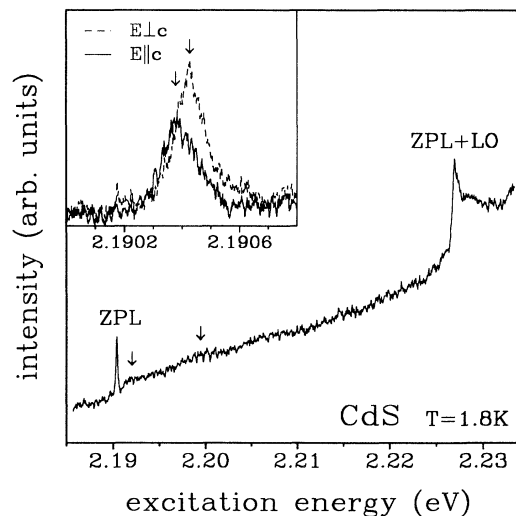Polarized high-resolution spectra obtained for a crystal

FIG. 1. The low-energy onset of the $Ni^{2+/+}$ charge-transfer band in an unpolarized photoluminescence excitation spectrum of the $Ni^{2+}(^3T_1(P)$-$^3T_1(F))$ crystal-field transition in CdS at $T=1.8$ K. The inset shows polarized excitation spectra in the spectral region of the ZPL on an expanded energy scale. The crystal has been doped with enriched Ni^{62}.

doped with enriched Ni[62] show for the first time that the ZPL is a doublet (inset, Fig. 1). The two ZPL's with opposite polarization at 2.190 43 eV ($E \perp c$) and 2.190 38 eV ($E \parallel c$) indicate a trigonal splitting of (50±10) μeV. This splitting has to be attributed to the excited state and represents its trigonal splitting. From the selection rules of the C_{3v} point group follows a term sequence A_1, E in regard to the A_1 ground state of Ni^{2+}. At Ni concentrations well below 1 ppm the ZPLs assume a nearly Lorentzian line shape with a full width at half maximum (FWHM) of 120 μeV.

In order to gather information about the electronic nature of the shallow states formed at Ni centers, we performed magneto-optical investigations of the excitation resonances shown in Fig. 1. The Zeeman behavior of the ZPL doublet at 2.1904 eV observed in Voigt configuration for the magnetic-field orientations $B \parallel c$ and $B \perp c$ is shown by the crosses in Fig. 2. The ZPL doublet splits in an almost isotropic way into a triplet and all components experience a uniform nonlinear shift towards higher energies. The small anisotropy in the splitting results from the trigonal crystal field provided by the hexagonal CdS host crystal, leading to the zero-field splitting already observed without magnetic field (inset, Fig. 1). The whole Zeeman behavior is determined by the excited state, since the $A_1(^3T_1(F))$ spin-orbit ground state of Ni^{2+} neither splits nor shows a nonlinear shift in a magnetic field.[27]

The Zeeman behavior of the ZPL doublet (Fig. 2) can be described with the assumption of a $S = 1$ state taking into account the C_{3v} crystal field (D) and a diamagnetic shift (q),

$$H = g\mu_B B_z S_z + D(S_z^2 + 0.5) + qB_z^2 . \qquad (1)$$

Without magnetic field the triplet splits into a singlet with $S_z = 0$ and a doublet with $S_z = \pm 1$. In the magnetic-field orientation $B \parallel c$ all terms in Eq. (1) permute, making it easy to determine the fit parameters for the system CdS:Ni from the experimental results in Fig. 2. The splitting of the two outer components ($S_z = \pm 1$), Fig. 3(a),

FIG. 3. The Zeeman splitting shown in Fig. 2 in the orientation $B \parallel c$: (a) the energy splitting of the two outer lines as a function of the magnetic induction and (b) the shift of the center of gravity of the whole triplet as a function of the square of the magnetic induction.

yields a g factor of 2.26±0.04. The relative shift of the center of gravity of the threefold splitting behaves linearly with respect to the square of the magnetic induction B, Fig. 3(b), yielding $q = +2.3$ μeV/T^2. The circles in Fig. 2 represent the center of gravity of the two outer $S_z = \pm 1$ components. The systematic shift of (50±5) μeV towards higher energies in comparison to the central $S_z = 0$ component corresponds well to the observed zero-field splitting (inset, Fig. 1), and gives the trigonal constant D.

In the orientation $B \perp c$ the Zeeman behavior is more complex, since the Zeeman and the trigonal term in Eq. (1) no longer permute. Above 11 T the triplet becomes symmetric around the central component. Nevertheless, the Zeeman splitting can again be described with the same parameters as in the orientation $B \parallel c$. This is somewhat surprising because the g factor of free holes in CdS is anisotropic.[31]

Figure 4 presents an excitation spectrum of a CdS crystal doped with natural Ni[58/60] and enriched Ni[64] for the polarization $E \perp c$. The distorted line shape results from
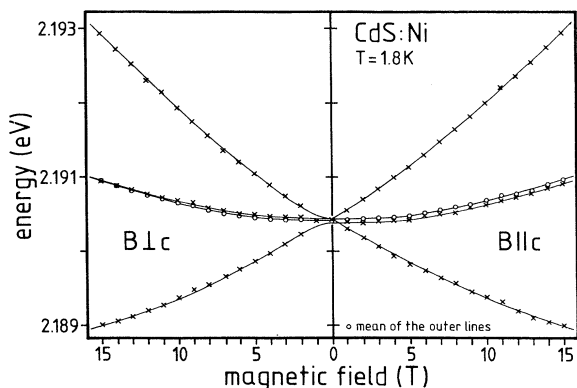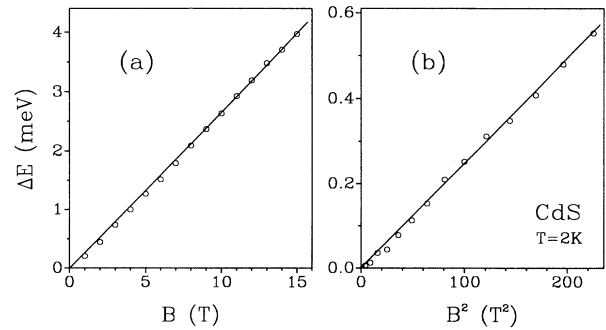

FIG. 2. Zeeman behavior of the ZPL doublet shown in the inset of Fig. 1 for the magnetic-field orientations $B \parallel c$ and $B \perp c$ at $T = 2$ K. The crosses give the experimental line positions and the holes correspond to the center of gravity of the two outer lines.
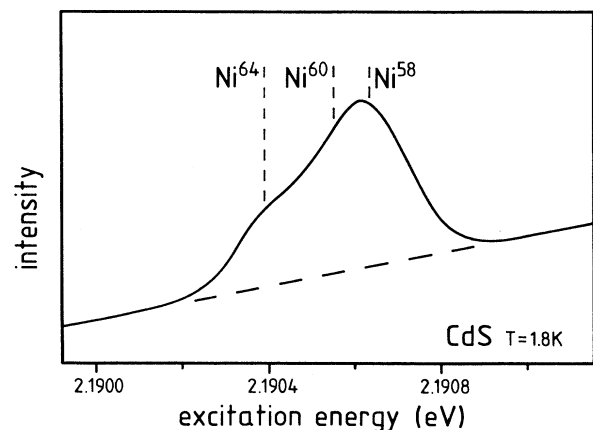

FIG. 4. The ZPL in the excitation spectrum of the $Ni^{2+}(^3T_1(P)-^3T_1(F))$ crystal-field transition at $T = 1.8$ in the polarization $E \perp c$ for a CdS crystal doped with natural Ni[58/60] and enriched Ni[64].

three lines corresponding to the three Ni isotopes. The relative intensities agree well with the relative abundances of the isotopes as obtained from the well-established[27] isotope shifts observed for the $^3T_1(F)$-$^3T_1(P)$ inner center transition. The transition energies observed in crystals doped with natural $Ni^{58/60}$ or the enriched Ni^{62} (inset, Fig. 1) agree as well. A line-shape analysis yields an isotope shift of (-37 ± 6) μeV/nucleon. Thus, the isotope shift of the charge-transfer-type transition into the shallow state is of the same order but has the opposite sign as those of the inner center d-d transitions.[27]

Isotope shifts of optical transitions are the result of *different* mass shifts of the ground and the excited state. The mass dependence of the total energy of each state of the transition-metal center originates from the contribution of mass-sensitive local phonon modes and is altered if these modes are Jahn-Teller active.[32,33] It is interesting to notice that a strong localization of the local phonon mode is a precondition for a strong electron-phonon interaction as well as a large mass sensitivity, which explains the close relation between both effects. In general, the local phonon spectrum as well as the Jahn-Teller interaction depend on the electronic state of the transition metal leading to characteristic mass shifts. Nevertheless, the Jahn-Teller interaction is only of importance for the strongly localized $3d$ states, whereas the rearrangement of the local charge distribution connected with charge-transfer transitions of the transition metal alters the local phonon spectrum. Calculations demonstrate that the isotope shift of the $Ni^{2+}(^3T_1(P)$-$^3T_1(F))$ results from the dynamical Jahn-Teller interaction with a T_2 mode,[32] whereas that of the charge-transfer-type transition in ZnO:Cu results from a mode-softening effect.[34] In order to explain the isotope shift observed for the transition into the shallow state in CdS, Fig. 4, both the Jahn-Teller coupling in the $^3T_1(F)$ ground state and a change in the local phonon spectrum in the formed shallow complex have to be taken into account. The calculated isotope shift of the $^3T_1(F)$ ground state of -86 μeV/nucleon and the observed optical isotope shift of -37 μeV/nucleon result in an isotope shift of the shallow complex of -123 μeV/nucleon, which is larger than those of the $3d$ states of Ni^{2+}. The reason is the lack of a Jahn-Teller interaction in the shallow state leading to a larger mass dependence. In principle, the mass shifts of the local T_2 modes of Ni^{2+} are sufficient to account for the observed isotope shift, but nevertheless, mode-softening effects altering the mass sensitivity of the local phonon modes can contribute as well.

B. ZnS

Figure 5 shows an excitation spectrum of the $Ni^{2+}(^3T_1(P)$-$^3T_1(F))$ luminescence in cubic ZnS doped with 1 ppm Ni. The fine structure observed in the low-energy onset of the $Ni^{2+/+}$ charge-transfer band is in reasonable agreement with less pronounced absorption spectra of strongly doped crystals.[18,19] The dominating ZPL A at 2.437 42 eV is followed by a phonon side band, reflecting mainly the one-phonon density of the undis-
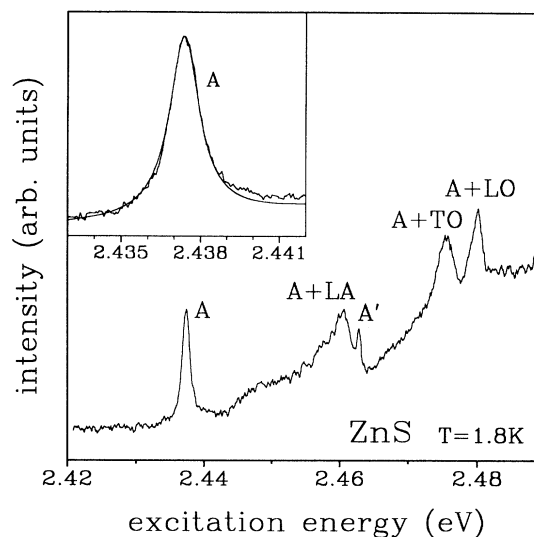

FIG. 5. The low-energy onset of the $Ni^{2+/+}$ charge-transfer band in the photoluminescence excitation spectrum of the $Ni^{2+}(^3T_1(P)$-$^3T_1(F))$ crystal-field transition in ZnS at $T=1.8$ K. The inset shows the ZPL A together with a Lorentz-shaped fit on an expanded energy scale.

turbed ZnS host lattice. The most pronounced peaks are shifted by 23.2, 38.1, and 42.7 meV corresponding to local modes of the Ni center with energies close to the LA, TO, and LO phonons in the center of the Brillouin zone. Recently, the resonance A' at 2.462 75 eV $(\Delta E = +25.33$ meV) has been explained by a corresponding local mode of the Ni center.[19] The high-resolution excitation spectrum, Fig. 5, does not confirm this interpretation. The resonance A' has a FWHM of only 480 μeV, whereas the ZPL A has a FWHM of 1380 μeV. This behavior is not understandable if A' is a phonon replica. Thus, we interpret this absorption line as a further zero-phonon transition A' into an excited electronic state of the shallow complex, a fact which will be confirmed by the magneto-optical results presented in the following. Figure 6 presents the temperature dependence of the excitation spectrum of the $Ni^{2+}(^3T_1(P)$-$^3T_1(F))$ luminescence. Above $T=10$ K the lines become broader due to the interaction with thermally excited phonons and the excitation efficiency decreases. No line shift could be resolved up to $T=34$ K.

The Zeeman behavior of the ZPL's A and A' in cubic ZnS for the magnetic-field orientation $B\|$ [110] is shown in Fig. 7. Additional measurements proved that the Zeeman splitting is isotropic. As in CdS, a threefold splitting of the ZPL A is resolved yielding a g factor of 0.50 ± 0.10. In ZnS the FWHM of the ZPL is much larger and the g factor much smaller than in CdS, making it impossible to establish a uniform quadratic shift for all components, but again the center of gravity of the triplet shifts to higher energies. The assumption of a diamagnetic shift yields the energy shift observed at 15 T, $q=+2.0$ μeV/T^2. Additionally, above 7 T a further component becomes visible on the low-energy side of the ZPL A. An extrapolation shows that this is not a component of the
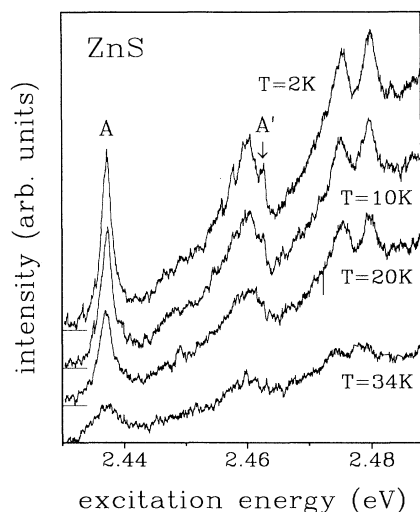
FIG. 6. The low-energy onset of the $Ni^{2+/+}$ charge-transfer band in the photoluminescence excitation spectrum of the Ni^{2+} $^3T_1(P)$-$^3T_1(F)$ crystal-field transition in ZnS at different crystal temperatures.

ZPL A, but has its origin in a further ZPL B not visible in zero magnetic field. The zero-field splitting between the ZPL's A and B amounts to -1.4 meV. For the broad peak attributed to a LA phonon replica of the ZPL A no splitting could be resolved but it shifts parallel to the center of gravity of the components of the ZPL A towards higher energies. In contrast, the Zeeman behavior of the second ZPL A' is not compatible with that of the ZPL A, unequivocally demonstrating its different electronic origin. The measurements revealed a splitting into a quartet, but it is hard to determine an accurate g factor
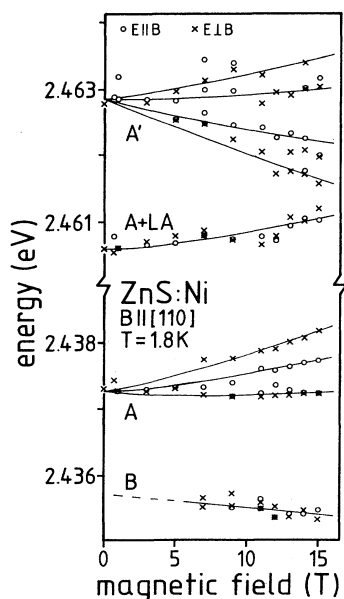
or diamagnetic shift due to the location of the ZPL A' on the high-energy wing of the LA phonon replica of the ZPL A, Fig. 5.

In polymorphic ZnS exist a number of nonequivalent lattice sites resulting in a variety of different point defects which are characterized by their local environment. Thus, in polymorphic ZnS doped with transition metals many different centers are created which can be classified using the notation scheme introduced in Ref. 35. The spectra of transition metals reflect the changes in crystal structure in slightly distorted optical spectra characteristic for each environment. In Fig. 8 the $Ni^{2+}(^3T_1(P)$-$^3T_1(F))$ luminescence spectra of a Ni-doped polymorphic ZnS crystal excited either (a) in the $Ni^{2+/+}$ charge-transfer band at 2.50 eV or (b) below the ZPL A at 2.42 eV are compared. The strong lines in spectrum (b) which are also resolved in spectrum (a) are not due to Ni^{2+} transitions. Recently, the luminescence starting with the doublet at 1.511 eV has been identified as the $^3T_1$-$^1A_1$ transition of the W^{2+} center.[36] The dominating three line groups in spectrum (a) are attributed to Ni^{2+} in the cubic (AN) and the two dominating axial $(PN$ and $AS)$ environments and correspond to the transition into the T_1 spin-orbit component generally labeled[27] with E. The spectra of the different polytypic centers can be separated by means of site-selective spectroscopy as recently demonstrated for the $^3T_1(P)$-$^3T_1(F)$ luminescence exciting via the $^3T_1(F)$-$^1T_2(G)$ absorption.[37] Figure 9 displays site-selective excitation spectra of the E^i lines in Fig. 8 in the spectral region of the low-energy onset of the $Ni^{2+/+}$ charge-transfer band. Besides the cubic ZPL A described above, additional ZPL's shifted towards lower energies are observed at 2.4219 and 2.4266 eV. These lines were observed in electroabsorption spectra,[38] too, but no interpretation has been given yet. The site-selective excitation spectra clearly demonstrate that these lines result from the polymorphic crystal structure of the investigated ZnS crystals and can be attributed to the two axial Ni^{2+}

FIG. 7. Zeeman behavior of the ZPL's A and A' shown in Fig. 5 for the magnetic-field orientation $B\parallel[110]$ at $T=2$ K.
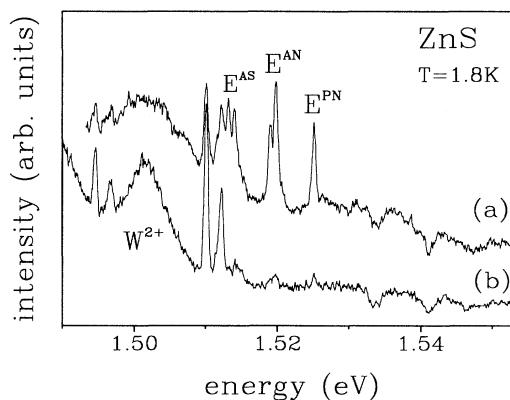

FIG. 8. Luminescence spectra of a Ni-doped polymorphic ZnS crystal excited either (a) in the $Ni^{2+/+}$ charge-transfer band at 2.50 eV, or (b) below the ZPL A at 2.42 eV at 1.8 K. (a) is dominated by the $Ni^{2+}(^3T_1(P)$-$^3T_1(F))$ luminescence of ions with the cubic AN or the axial PN and AS surroundings. (b) shows the ZPL region of the $W^{2+}(^3T_1$-$^1A_1)$ luminescence (Ref. 36).
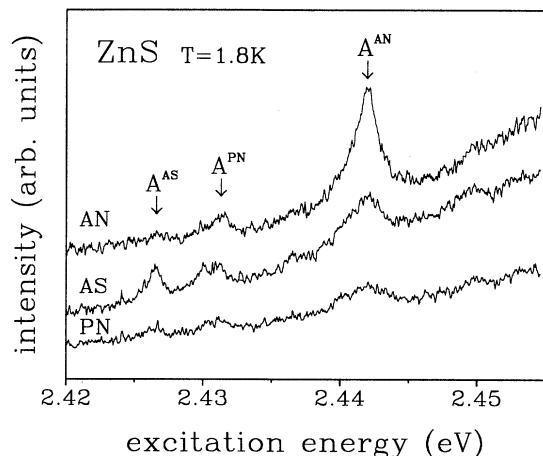
FIG. 9. Site-selective excitation spectra of the $Ni^{2+}(^3T_1(P)$-$^3T_1(F))$ luminescence in polymorphic ZnS at $T=1.8$ K. The E lines of the different polytypic centers as shown in Fig. 8 have been detected.

centers *PN* and *AS*, respectively. The redshifted ZPL's indicate a decreasing $Ni^{2+/+}$ charge-transfer energy for the axial sites, which is rather surprising since the band-gap energy increases in the distorted crystal structure.[39]

IV. DISCUSSION

A. The fine structure

In both ZnS and CdS the broad absorption band in the blue-green spectral region has been associated with the acceptor-type $Ni^{2+/+}$ transition.[21,22] Hence, the shallow states leading to sharp lines on the low-energy onsets of these charge-transfer bands should be associated with the same charge-transfer transition in both materials. Nevertheless, the presented high-resolution excitation spectra as well as the observed Zeeman behavior reveal pronounced differences between the systems ZnS:Ni and CdS:Ni. In contrast to CdS in ZnS a richer fine structure and a stronger coupling to the whole phonon spectrum are observed. Additionally, the rather different g factors indicate a different electronic origin of the triplet states.

The basic idea of shallow states associated with transition-metal centers was introduced to explain the prominent green luminescence in ZnO:Cu.[11] The two oppositely charged particles arising in a charge-transfer process can form bound states via the long-range electrostatic interaction. The generated charge carrier occupies effective-mass-type states localized at the transition-metal center leading to a hydrogenlike energy spectrum. Thus, the created complexes are somewhat similar to main group donors and acceptors. However, in general they form excited states of the isoelectronic transition-metal center. Hence, we call them transient shallow acceptor or donor states. In the case of copper, the situation is relatively simple because Cu^+ has a completely filled $3d$ shell without any spin and orbital momentum.[15,26] Consequently, the fine structure observed can be described with distorted valence-band states, taking into account

the spin-orbit interaction and the C_{3V} crystal field. In general, the open-shell configuration of transition metals provides a spin and orbital momentum leading to an exchange interaction with the bound carrier. In this case the hydrogenlike states formed by valence-band wave functions are just the first approximation. In reality, the states of the shallow complexes have to be described in the product space of the $3d$-like and the hydrogenlike wave functions.

Recently, it has been demonstrated for the system ZnO:Cu that calculations using a cluster approach are able to reproduce the shallow Cu states leading to the prominent green luminescence.[40] Nevertheless, in order to describe the fine structure and the Zeeman behavior of the transient shallow acceptor complex, the exchange interaction has to be taken into account, which can be done in a *jj*-coupling scheme. The problem in the case of the shallow states associated with transition metals lies in the choice of an appropriate subsystem and therefore of the parameters describing the charge carrier and the transition-metal ion. The relative magnitudes of the interactions determining the electronic structures of the central transition-metal ion and of the bound carrier have to be compared with their electrostatic and exchange interaction.

In the case of the Ni systems discussed in this paper the basic transition is the $Ni^{2+/+}$ charge transfer. Thus, a transient shallow acceptor complex (Ni^+,h) should be formed consisting of a central Ni^+ ion and a bound hole from the valence band. In ZnS and CdS the binding energy of an effective-mass-like acceptor[41] is about 170 meV, giving a measure for the electrostatic interaction within the transient shallow acceptor complex. Ni^+ can be represented by its $^2T_2(D)$ ground state as long as the binding energy of the nine electrons in the $3d$ shell is large compared to the binding energy of the hole. In general, the exchange interaction is weaker than the spin-orbit interaction and the Ni^+ ion can be represented by its Γ_7-$^2T_2(D)$ ground state. The g factor of this state is expected to be negative due to the transformation properties of the d orbitals.[42] For ZnS a g factor of -1.40 has been observed.[43] The situation of the bound hole is more complex since the valence band in ZnS and CdS is split by the spin-orbit interaction and in the latter case by an additional C_{6v} crystal field as well. Both interactions are smaller than the electrostatic interaction with the charged transition-metal ion, leading to a strong mixing of the different valence-band states in the bound complex as shown for ZnO:Cu.[15] For the ZPL in CdS:Ni a nearly isotropic Zeeman splitting is observed, Fig. 2. Thus, the bound hole cannot be described by states of the A valence-band alone which possess an anisotropic g factor.[44] On the contrary, magneto-optical investigations of bound exciton complexes[45] indicate that strongly localized holes can be described as spinlike particles with a completely quenched orbital momentum having a g factor around 2. In the transient shallow acceptor complex, the hole occupies hydrogenlike states characterized by the main quantum number n, which can be considered separately, if the exchange interaction is comparatively weak.

In the transient shallow acceptor complex (Ni^+, h), both the Ni^+ and the hole can be represented by an effective orbital momentum of $\frac{1}{2}$ giving rise to a triplet and a singlet state, Fig. 10. The g factor of the triplet state is expected to be

$$g = \tfrac{1}{2}(g_{Ni^+} + g_h) \approx 0.3 , \qquad (2)$$

and from the $^3T_1(F)$ ground state of Ni^{2+} only the transition into the triplet state is spin allowed. This simple model describes very well the experimental observations for the system ZnS:Ni. The ZPL A splits into a triplet with a g factor of 0.5 and is thus attributed to the allowed transition into the triplet state. The Zeeman component originating 1.4 meV below can be attributed to the forbidden transition into the singlet state (see Fig. 10), which becomes allowed in the magnetic field. Thus, the fine structure and the Zeeman behavior in the region of the ZPL A can be explained by the hole in the $n = 1$ ground state of the transient shallow acceptor complex (Ni^+, h). The exchange interaction between the $n = 1$ hole and the $3d$ electrons amounts to 1.4 meV. The higher excited $n = 2$ states are much less localized, which means that the probability of finding the hole in the $3d$ core of the central transition metal decreases, leading to a weaker exchange interaction. This effect is particularly pronounced for the first excited $2P_{3/2}$ state with its p-type orbitals. The ZPL A' is shifted 25.3 meV towards higher energies and develops into a quartet in a magnetic field. Thus, we attribute the ZPL A' to the formation of the (Ni^+, h) complex with the hole in the $2P_{3/2}$ state which is subject to a much weaker exchange interaction. Recently, a $n = 2$ hole state has been postulated for Fe in III-V compounds on the basis of the observed fine structure.[10,17] This interpretation is now supported by the clear results of the Zeeman measurements at the system ZnS:Ni.

Obviously, the model of the transient shallow acceptor complex (Ni^+, h) represented in Fig. 10 fails for the system CdS:Ni. The large g factor of 2.26 observed for the ZPL is not compatible with a hole bound to a Ni^+ center. It has to be noted that recently the ZPL in CdS:Ni has been reinterpreted on the basis of results from electroabsorption measurements.[24] It has been associated with the donor-type charge-transfer transition, which means that a transient shallow donor complex (Ni^{3+}, e) should be formed. The $^4A_2(F)$ ground state of Ni^{3+} can be represented[46] by a spin of $\frac{3}{2}$ and a g factor slightly above 2. Thus, the exchange interaction with the bound elec-

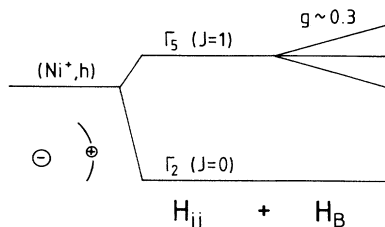tron would result in a triplet and a quintet state with g factors around 2. In principle, the triplet state could explain the Zeeman behavior observed in CdS, Fig. 2. But the exchange interaction in the (Ni^{3+}, e) complex should be in the order of 1 meV as already observed for the (Ni^+, h) complex in ZnS, leading to a strong mixing with the quintet state in magnetic fields. The Zeeman results give no hint for such mixing. In general, the parity-forbidden donor-type transitions are expected to be much weaker than the parity-allowed acceptor-type ones.[47] Additionally, recent time-resolved luminescence measurements yield similar time constants of some 10 ps for the carrier trapping process after excitation in the charge-transfer bands in ZnS and CdS.[4,5] This is in favor of an acceptor-type transition in CdS, especially with regard to the different cross sections[3] for the capture of electrons $(10^{-17} \text{ cm}^{-2})$ and holes $(10^{-15} \text{ cm}^{-2})$ by Ni centers. Thus, the shallow complex observed in CdS:Ni should be associated with the acceptor-type $Ni^{2+/+}$ transition and not with the donor-type $Ni^{2+/3+}$ transition.

The experimental results for the ground state of the shallow complex in CdS:Ni can be explained with a deeply bound electron-hole pair (Ni^{2+}, e, h) with the hole in its $n = 1$ ground state. As will be discussed in Sec. IV C, the excited states $(n \geq 1)$ of the shallow complex have to be described in the model of the transient shallow acceptor (Ni^+, h) again. In principle, the three-particle system (Ni^{2+}, e, h) should be more complicated than the two-particle system (Ni^+, h), but the central Ni^{2+} ion has a diamagnetic A_1 ground state (including spin-orbit interaction) without any effective spin or orbital momentum. Thus, the fine structure is determined by the coupling between the electron $(j_{eff} = \frac{1}{2}, g = 2)$ and the hole, Fig. 11, resulting in a term scheme quite similar to that of the transient shallow acceptor. The most obvious difference is the g factor around 2 now expected for the triplet state which is in good agreement with the Zeeman behavior of the ZPL in CdS:Ni. No transitions terminating in the singlet state have been resolved. In the deeply bound electron-hole complex the increased overlap of the electron and hole wave functions leads to a stronger exchange interaction. Thus, the singlet state becomes well separated from the triplet state. Even in magnetic fields up to 15 T the transition into the singlet remains forbidden since no sufficient singlet-triplet mixing takes place.

FIG. 10. The term scheme of the transient shallow acceptor complex (Ni^+, h) including the exchange interaction between the $3d$ core of Ni^+ and the strongly localized hole.
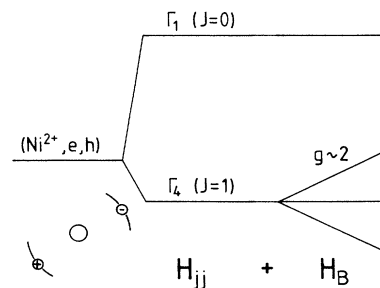

FIG. 11. The term scheme of the deeply bound electron-hole pair (Ni^{2+}, e, h) including the exchange interaction between the electron and the hole localized at the Ni^{2+} ion.

The different nature of the shallow complexes formed in ZnS:Ni and CdS:Ni is also revealed in the phonon coupling. In the optical formation of the transient shallow acceptor state (Ni^+, h) the strongly localized states of the central Ni ion determine the phonon coupling leading to the appearance of the whole phonon spectrum in the side band.[48] In contrast, the formation of the deeply bound electron-hole pairs at the Ni^{2+} center (Ni^{2+}, e, h) does not involve the central ion. Thus, the created electron-hole pair determines the phonon coupling leading to dominating LO modes in the phonon side band as is well known for shallow bound excitons.[44]

B. The relaxation processes

The optical generation of shallow complexes associated with transition-metal centers is extremely unlikely, leading only to weak resonances in optical spectra. In the case of Ni in ZnS and CdS, excitation spectra[5,29] demonstrate that the transition into the shallow complexes is even weaker than the A_1-T_2 ZPL of the spin- and parity-forbidden $^3T_1(F)$-$^1T_2(G)$ transition. In ZnS the transition from the $^3T_1(F)$ ground state of Ni^{2+} into the triplet state of the shallow acceptor complex (Ni^+, h) is parity allowed (due to the dominant p-type character of the bound hole) as well as spin allowed and it is a one-electron transition: the $Ni^{2+}(^3T_1(F))$ state has a $t^4 e^4$ and the $Ni^+(^2T_2(D))$ state has a $t^5 e^4$ configuration. Thus, it is in principle an allowed transition but the poor overlap between the strongly localized $3d$ wave functions describing the $Ni^{2+}(^3T_1(F))$ ground state and the more extended effective-mass-like states describing the (Ni^+, h) complex leads to small transition probabilities. The overlap becomes even smaller for the more extended excited states of the (Ni^+, h) complex. Indeed the ZPL A' attributed to the transition into the $2P_{3/2}$ state has just 7% of the intensity of the ZPL A. In CdS the excitation resonances, Fig. 1, are generally about one order of magnitude weaker than in ZnS. The formation of a deeply bound electron-hole pair (Ni^{2+}, e, h) has a two-particle character and is thus less likely.

No luminescence from shallow states in Ni-activated II-VI semiconductors has yet been reported, indicating dominating nonradiative recombination mechanisms. The excitation spectra demonstrate directly the formation of excited $3d$ states by the recombination of the shallow complexes. The weak oscillator strength of transitions between the $3d$ and the shallow states corresponds to long radiative lifetimes, whereas the rearrangement of the local charge distribution and thus of the equilibrium positions of the atoms leads to a strong electron-phonon interaction, enabling efficient nonradiative recombination channels. For most of the transition metals there exist highly excited $3d$ states which are nearly resonant with the formed shallow complexes. These states, as the $^1T_1(G)$ state of Ni^{2+} in the wide band-gap II-VI semiconductors, are a precondition for the efficient nonradiative recombination. A prominent exception is ZnO:Cu. The energy gap between the transient shallow acceptor state (Cu^+, h) and the excited $Cu^{2+}(^2E(D))$ state of 2.14 eV is much too large for an efficient nonradiative recombina-

tion. Thus, after charge-transfer excitation not the excitation of the $Cu^{2+}(^2E(D)$-$^2T_2(D))$ but the radiative decay of the (Cu^+, h) complex is observed.[11,26]

Recent time-resolved investigations[4,5] demonstrate that the recombination of holes with Ni^+ centers is governed by a cascade relaxation process via the excited states of the transient shallow acceptor complex (Ni^+, h). Time constants of 30 ps in ZnS and 50 ps in CdS have been found for a hole starting in the valence band and ending in the $Ni^{2+}(^3T_1(P))$ state. For the nonradiative recombination of the ground states of the shallow complexes, an upper limit of about 10 ps has been given. The inset of Fig. 4 displays the ZPL A in ZnS together with a Lorentz-shaped fit, giving a FWHM of 1380 μeV. This FWHM is nearly independent of the investigated crystal and the Ni concentration up to some ppm. Thus, we interpret the observed FWHM as a natural linewidth giving a nonradiative recombination time of only 480 fs. These considerations explain the smaller FWHM (480 μeV) of the ZPL A' also. The more extended hole wave function in the $2P_{3/2}$ state diminishes the probability of the nonradiative recombination process. The data are compatible with the assumption of a cascade process, which means that the $2P_{3/2}$ state relaxes first into the (Ni^+, h) $n = 1$ ground state. The ZPL in CdS has just a FWHM of 120 μeV corresponding to a much longer lifetime of about 5 ps. The recombination of the electron-hole pair with the Ni^{2+} has a two-particle character, reducing the nonradiative transition probability. It has to be noted that the observed FWHM's support the simple models—the transient shallow acceptor and the deeply bound electron-hole pair—for the shallow complexes formed at Ni centers in ZnS and CdS, respectively.

C. The binding energies

With regard to the shallow states formed at transition-metal centers at least two energies are important: the energy of the deep donor or acceptor level E_{deep} introduced by the transition metal and the binding energy of the respective shallow state E_{shallow}. The energy of the ZPL E_{ZPL} of the optical transition into the ground state of the shallow acceptor is given by

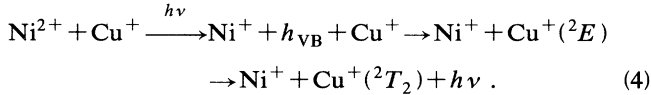$$E_{\text{ZPL}} = E_{\text{deep}} - E_{\text{shallow}} . \tag{3}$$

In general, the shallow complex is an excited state of the transition-metal center and thus of a transient nature. Thus, the direct determination of its binding energy E_{shallow} is difficult. Nevertheless, different indirect methods have been proposed. Recently, for Cu in the wide band-gap II-VI semiconductors the possibility to determine E_{shallow} from the transition between the ionized acceptor Cu^+ and the conduction band has been demonstrated.[26] But as yet, no corresponding optical transition has been observed for other systems.

In principle, E_{shallow} can be determined from E_{deep} and E_{ZPL} using Eq. (3). In most cases E_{deep} is obtained from theoretical fits of the charge-transfer bands observed in absorption, which gives an energy of 2.458 eV for the acceptor-type $Ni^{2+/+}$ transition in ZnS,[19] yielding a very

small binding energy E_{shallow} of 20 meV for the transient shallow acceptor complex (Ni^+,h). However, this method is somewhat problematical because the theoretical fits neglect the transitions leading to the formation of the shallow complex, which superimpose the low-energy onset of the charge-transfer band. Thus, the deduced ionization energies E_{deep} and subsequently the shallow complex binding energies E_{shallow} are systematically too small, depending on the relative intensity of the transitions into the bound states. The importance of this process is obvious for ZnS:W (Ref. 36) where the large binding energy E_{shallow} of the transient shallow acceptor complex (W^+,h) leads to two almost separated absorption bands.

To avoid the troublesome contribution due to the formation of the shallow complexes the generated charge carriers have to be detected directly rather than the absorption. A sensitive method is the investigation of energy-transfer processes between different transition-metal centers as observed in codoped crystals by means of excitation spectroscopy.[18,26] In ZnS crystals codoped with Ni and Cu the $\text{Cu}^{2+}(^2E(D)\text{-}^2T_2(D))$ luminescence can be excited by holes generated in the $\text{Ni}^{2+/+}$ charge-transfer band,[18]

$$\text{Ni}^{2+} + \text{Cu}^+ \xrightarrow{h\nu} \text{Ni}^+ + h_{\text{VB}} + \text{Cu}^+ \rightarrow \text{Ni}^+ + \text{Cu}^+(^2E)$$

$$\rightarrow \text{Ni}^+ + \text{Cu}^+(^2T_2) + h\nu . \qquad (4)$$

The optical formation of the transient shallow acceptor complex (Ni^+,h) does not contribute to this process. With this method the ionization energy E_{deep} of the deep $\text{Ni}^{2+/+}$ acceptor level has been determined[18] to be 2.61 eV, giving a binding energy E_{shallow} of 170 meV, much larger than that obtained from the fit of the charge-transfer absorption. But this investigation has been performed at 77 K with a critical spectral resolution. The results of a repetition at $T = 2$ K with a much better spectral resolution is presented in Fig. 12 showing the contribution of the $\text{Ni}^{2+/+}$ charge-transfer process to the excitation of the $\text{Cu}^{2+}(^2E(D)\text{-}^2T_2(D))$ luminescence in an
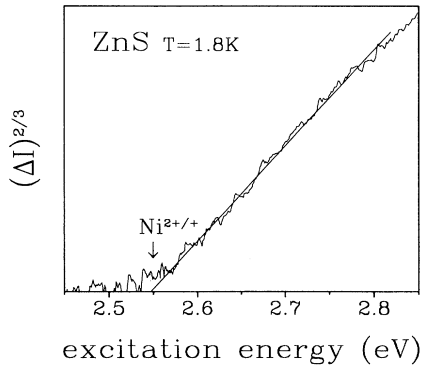

FIG. 12. The low-energy onset of the $\text{Ni}^{2+/+}$ charge-transfer band as observed in the excitation spectrum of the $\text{Cu}^{2+}(^2E(D)\text{-}^2T_2(D))$ luminescence in ZnS in an $I^{2/3}$ plot. The direct excitation via the $\text{Cu}^{2+/+}$ charge-transfer band (Ref. 26) has been subtracted.

$I^{2/3}$ plot. A linear extrapolation yields an ionization energy of the deep Ni acceptor in ZnS at $T = 2$ K of

$$E_{\text{deep}}(\text{N}^{2+/+}) = (2.545 \pm 0.010) \text{ eV} . \qquad (5)$$

Thus, the ionization energy of the transient shallow acceptor complex formed at the Ni center in ZnS amounts to

$$E_{\text{shallow}}((\text{Ni}^+,h)) = (108 \pm 10) \text{ meV} . \qquad (6)$$

The binding energy of the transient shallow acceptor complex in ZnS is smaller than the effective-mass acceptor binding[41] of 176 meV. The same trend has been observed for Cu centers in the wide band-gap II-VI semiconductors.[26] The hybridization of the $3d$ states with the ligand orbitals leads to a smearing of the local charge density, which results in a decrease of the binding energy.[49] The larger extension of the local charge density influences mainly the strongly localized $1S$ hole state but can be neglected for higher excited states of the transient shallow acceptor complex. This means that excited hole states should behave like those of an ideal acceptor as already observed for deep acceptors in Si.[50] The observation of excited states of shallow complexes—which are assumed to behave effective-mass-like—enables an estimation of its binding energy. As discussed in Sec. IV A the ZPL A' in ZnS is attributed to the formation of a (Ni^+,h) complex with the hole in the excited $2P_{3/2}$ state, which has an effective-mass binding energy[41] of 77.6 meV. Thus, the binding energy of the (Ni^+,h) complex in ZnS can be estimated to be $E_{\text{shallow}} = 103$ meV using the energy shift between the ZPL's A and A' of 25.3 meV. This value is in excellent agreement with that determined by the hole transfer process, Fig. 12. The binding energy estimated using a fit of the charge-transfer absorption is too small by a factor of 5 due to the systematic error discussed above.

For Ni centers in CdS, neither hole-transfer processes nor excited states of the formed shallow complex have been observed yet. However, the excitation spectra demonstrate that the oscillator strength for the formation of the (Ni^{2+},e,h) complex in CdS as well as the coupling to phonons are much smaller than for the (Ni^+,h) complex in ZnS. Thus it can be expected that the contribution of transitions into bound states can be neglected in the fitting of the charge-transfer absorption band.[22] An $\text{Ni}^{2+/+}$ ionization energy E_{deep} of 2.333 eV has been determined, yielding a binding energy E_{shallow} of the deeply bound electron-hole pair (Ni^{2+},e,h) of 140 meV, slightly larger than in ZnS.

Even though in both ZnS and CdS the observed shallow complexes are associated with the acceptor-type charge-transfer transition, quite different complexes are realized: the transient shallow acceptor complex (Ni^+,h) and the deeply bound electron-hole pair (Ni^{2+},e,h), respectively. The electron is either localized in the $3d$ shell and takes part in the electron-electron interaction forming the well-known many-electron levels of Ni^+ or it is much less localized and can be neglected by the formation of the many-electron states resulting in the term scheme of Ni^{2+}. Thus, the localization of the last elec-

tron in the $3d$ shell in comparison to that of the bound hole is the parameter governing the electronic structure of the shallow complex.

A measure for the localization of a state is the Bohr radius r_B of the last bound charge carrier with an effective mass m^*,

$$r_B = \frac{\hbar}{\sqrt{2m^*E_1}} \ . \tag{7}$$

E_1 is the localization energy which corresponds to the energy separation of the state from the nearest band. In the case of the Ni centers in ZnS and CdS the last bound electron in the Ni^+ configuration is critical. In ZnS, the Ni^+ ground state lies deep in the band gap 1.303 eV below the conduction band, which corresponds to a Bohr radius r_B of only 0.27 nm. This means that the electron is well localized in the $3d$ shell of Ni^+ and not much influenced by the hole with a binding energy $E_{shallow}$ of about 100 meV. The transient shallow acceptor complex (Ni^+,h) is formed. In CdS the Ni^+ ground state lies just 0.25 eV below the conduction band corresponding to a Bohr radius of 0.48 nm. Thus, the last electron is much less localized than in ZnS and is strongly affected by a hole with a comparable binding energy of about 140 meV. The deeply bound electron-hole pair (Ni^{2+},e,h) is formed, in which the electron-hole interaction dominates the electron-electron interaction in the $3d$ core. On the basis of this consideration it becomes clear that the higher excited states of the shallow complexes formed at Ni centers in CdS should be described in terms of a transient shallow acceptor complex (Ni^+,h) as in ZnS. The interaction between the last bound electron and the hole can be neglected if the hole occupies a weaker bound excited state $(n \geq 2)$, again leading to the formation of Ni^+ states.

V. CONCLUSION

Sharp resonances are found in excitation spectra of the $Ni^{2+}(^3T_1(P)^3T_1(F))$ luminescence on the low-energy onset of the acceptor-type $Ni^{2+/+}$ charge-transfer band in ZnS and CdS. The excited states of these resonances result from the formation of shallow complexes at the Ni ion. The most simple model is a transient shallow acceptor complex (Ni^+,h). Here the Coulomb interaction between the Ni^+ ion and the hole results in hydrogenlike states. Nevertheless, fine structure and Zeeman investigations demonstrate that this model is not sufficient. To explain the experimental data, the exchange interaction between the bound hole and the $3d$ electrons of the Ni ion has to be taken into account. Additionally, the Coulomb interaction between the bound hole and the Ni ion can considerably alter its inner structure, which results in a completely different electronic structure of the shallow complex.

In ZnS the acceptor-type $Ni^{2+/+}$ transition introduces a level deep in the band gap, whereas the binding energy of the shallow complex is determined to be 108 meV. Thus, the binding energy of the hole is much smaller than the localization energy of the electrons and a transient shallow acceptor complex (Ni^+,h) is formed. The zero-field splitting of 1.4 meV observed for the ZPL A at 2.4374 eV as well as the g factor of 0.50 result from the exchange interaction within the (Ni^+,h) complex. The second ZPL A' shifted by 25.3 meV towards higher energies is attributed to the same (Ni^+,h) complex with the hole in its first excited state $2P_{3/2}$. In CdS the acceptor-type $Ni^{2+/+}$ level is found close to the conduction band and a deeply bound electron-hole pair (Ni^{2+},e,h) behaving quite different as the (Ni^+,h) complex is observed. This complex is not a deeply bound exciton. On the contrary with the hole in an excited hydrogenlike state, the best description should be the transient shallow acceptor complex (Ni^+,h) again.

A comparative study of the Zeeman behavior of shallow complexes of transition metals in different host semiconductors has been given. In ZnS and CdS quite different shallow complexes are formed at Ni centers though in both semiconductors the Ni ions are surrounded by four sulfur ligands. This should be a challenge for future theoretical approaches using, e.g., supercell methods.

[1]M. Tabei, S. Shionoya, and H. Ohmatsu, Jpn. J. Appl. Phys. **14**, 240 (1975).

[2]D. H. Auston, in *Ultrashort Laser Pulses and Applications,* edited by W. Kaiser, Topics in Applied Physics Vol. 60 (Springer-Verlag, Berlin, 1988), p. 183.

[3]A. V. Bobyl and M. K. Sheinkman, Fiz. Tekh. Poluprovodn. **13**, 2216 (1979) [Sov. Phys. Semicond. **13**, 1296 (1979)].

[4]R. Heitz, A. Hoffmann, and I. Broser, J. Lumin. **53**, 359 (1992).

[5]R. Heitz, A. Hoffmann, and I. Broser, Opt. Mater. **1**, 75 (1992).

[6]V. N. Abakumov, V. I. Perel, and I. N. Yassievich, in *Nonradiative Recombination in Semiconductors,* Modern Problems in Condensed Matter Science (North-Holland, Amsterdam, 1991), Vol. 33.

[7]D. Robbins, J. Lumin. **24/25**, 137 (1981).

[8]V. I. Sokolov and K. A. Kikoin, Sov. Sci. Rev. A **12**, 149 (1989).

[9]A. Juhl, A. Hoffmann, D. Bimberg, and H.-J. Schulz, Appl. Phys. Lett. **50**, 1292 (1987).

[10]K. Thonke and K. Pressel, Phys. Rev. B **44**, 13 418 (1991).

[11]R. Dingle, Phys. Rev. Lett. **23**, 579 (1969).

[12]T. Wolf, D. Bimberg, and W. Ulrici, Phys. Rev. B **43**, 10 004 (1991).

[13]I. Broser, R. Germer, H.-J. Schulz, and K. Wisznewski, Solid State Electron. **21**, 1597 (1978).

[14]D. J. Robbins, P. J. Dean, C. L. West, and W. Hayes, Philos. Trans. R. Soc. London, Ser. A **304**, 499 (1982).

[15]D. J. Robbins, D. C. Herbert, and P. J. Dean, J. Phys. C **14**, 2859 (1981).

[16]V. I. Sokolov, A. N. Mamedov, T. P. Surkova, M. V. Chukichev, and M. P. Kulakov, Opt. Spektrosk. **62**, 805 (1987) [Opt. Spectrosc. **62**, 480 (1987)].

[17]L. Podlowski, T. Wolf, R. Heitz, A. Hoffmann, D. Bimberg, I. Broser, and W. Ulrici, in *Proceedings of the 27th International Conference on Physics of Semiconductors,* edited by P. Jiang and H.-Z. Zheng (World Scientific, Beijing, 1992), p. 1665.

[18]S. A. Kazanskii and A. I. Ryskin, Opt. Spectrosc. **31**, 325

(1971).

[19] J. M. Noras and J. W. Allen, J. Phys. C **13**, 3511 (1980).

[20] V. I. Sokolov, T. P. Surkova, and V. V. Chernyaev, Phys. Status Solidi B **114**, K195 (1982).

[21] M. Schulz and G. Wepfer, Solid State Commun. **10**, 405 (1972).

[22] Y. I. Vertsimakha, Y. P. Gnatenko, and A. K. Rozko, Fiz. Tverd. Tela (Leningrad) **16**, 3456 (1974) [Sov. Phys. Solid State **16**, 2236 (1975)].

[23] S. A. Permogorov, A. N. Reznitskii, and V. A. Kazenov, Opt. Spectrosc. **32**, 392 (1972).

[24] V. I. Sokolov, A. N. Mamedov, A. N. Reznitskii, G. A. Emel'chenko, and L. G. Kolinova, Fiz. Tverd. Tela (Leningrad) **27**, 3319 (1985) [Sov. Phys. Solid State **27**, 1998 (1985)].

[25] S. G. Bishop, D. J. Robbins, and P. J. Dean, Solid State Commun. **33**, 119 (1980).

[26] R. Heitz, A. Hoffmann, P. Thurian, and I. Broser, J. Phys. Condens. Matter **4**, 157 (1992).

[27] I. Broser, A. Hoffmann, R. Germer, R. Broser, and E. Birkicht, Phys. Rev. B **33**, 8196 (1986).

[28] R. Frerichs, Naturwissenschaften **33**, 281 (1946).

[29] A. Hoffmann, B. Lummer, C. Fricke, R. Heitz, and I. Broser, J. Cryst. Growth **117**, 640 (1992).

[30] E. F. Gross, S. A. Permogorov, and B. S. Razbirin, Dokl. Akad. Nauk SSSR **154**, 1306 (1964) [Sov. Phys. Dokl. **9**, 164 (1964)].

[31] J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).

[32] A. Hoffmann and U. Scherz, J. Cryst. Growth **101**, 385 (1990).

[33] R. Heitz, A. Hoffmann, and I. Broser, Phys. Rev. B **45**, 8977 (1922).

[34] J. A. Van Vechten, Phys. Rev. B **13**, 946 (1976).

[35] T. Buch, B. Clerjaud, B. Lambrt, and P. Kovacs, Phys. Rev. B **7**, 184 (1973).

[36] R. Heitz, P. Thurian, A. Hoffmann, and I. Broser, Mater. Sci. Forum **83–87**, 1247 (1992).

[37] R. Heitz, L. Eckey, A. Hoffmann, and I. Broser, Physica B (to be published).

[38] V. I. Sokolov, T. P. Surkova, M. P. Kulakov, and A. V. Fadeev, Solid State Commun. **44**, 391 (1982).

[39] A. I. Ryskin, L. G. Suslina, G. I. Khil'ko, and E. B. Shadrin, Pis'ma Zh. Eksp. Teor. Fiz. **7**, 335 (1968) [JETP Lett. **7**, 262 (1968)].

[40] K. C. Mishra, P. C. Schmidt, K. H. Johnson, B. G. DeBoer, J. K. Berkowitz, and E. A. Dale, Phys. Rev. B **42**, 1423 (1990).

[41] A. Baldereschi and N. O. Lipari, Phys. Rev. B **9**, 1525 (1974).

[42] C. L. Balehausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1962).

[43] B. Clerjaud, A. Gelineau, F. Gendron, C. Porte, J. M. Baranowski, and Z. Liro, J. Phys. C **17**, 3837 (1984).

[44] D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).

[45] B. Monemar, U. Lindefeld, and W. M. Chen, Physica B **146**, 256 (1987).

[46] W. C. Holton, J. Schneider, and T. L. Estle, Phys. Rev. A **133**, 1638 (1964).

[47] H. Zimmermann, R. Boyn, and N. Nagel, Phys. Status Solidi B **117**, 229 (1983).

[48] V. I. Sokolov and T. P. Surkova, Fiz. Tverd. Tela (Leningrad) **29**, 2938 (1987) [Sov. Phys. Solid State **29**, 1689 (1987)].

[49] V. N. Fleurov and K. A. Kikoin, Solid State Commun. **42**, 353 (1982).

[50] E. Janzén, R. Stedman, and H. G. Grimmeiss, Phys. Rev. B **29**, 1907 (1984).