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Nature of optical transitions in the charge-transfer region of ZnS:Co and ZnSe:Co

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The cobalt center in ZnS:Co and ZnSe:Co has long been considered as a possible candidate for the observation of so-called bound-electron levels. The optical transitions in the vicinity of the charge-transfer transition from the d^6/d^7 charge-transfer level to the conduction band are therefore investigated by their magneto-optical properties. These clearly reveal the identical origin of the observed transitions in the two materials. With the aid of the known charge-transfer energies the transitions are identified as internal $d^7 \rightarrow d^{7*}$ excitations. Possible assignments are discussed within the framework of ligand-field theory, which also delivers an explanation of why similar internal transitions were not yet observed in other II-VI or even III-V compound semiconductors doped with cobalt. A uniform picture of the cobalt center in these semiconductor host materials is thus derived. [S0163-1829(96)04636-X]

I. INTRODUCTION

Transition-metal impurity centers in II-VI and III-V compound semiconductors exhibit optical and electrical properties which are governed by the more or less localized character of the impurity d electrons. This subsystem of highly correlated electrons gives rise to a manifold of levels in the electronic structure of the total system which are still difficult to cope with from a first-principles point of view. Approaching the problem phenomenologically, one distinguishes between the following types of impurity-related levels and transitions:

(a) The centers are locally excited, i.e., the electrons remain localized and their charge densities are only rearranged. These transitions are usually referred to as internal $d^N \rightarrow d^{N*}$ transitions and they represent the solid-state analog to the multiplet excitations of free ions from a ground-state to an excited-state multiplet.

(b) The number of active electrons on the center is changed by either adding an electron from the valence band to the center or removing an electron from the center to the conduction band. The charge-transfer energies of these charge-transfer transitions are strongly reduced compared with free ion ionization energies. The charge-transfer levels are denoted by d^{N-1}/d^N. A transition from a filled d^{N-1}/d^N charge-transfer level to the conduction band changes the charge state from d^N to d^{N-1}, a transition from the valence band into an empty d^{N-1}/d^N charge-transfer level from d^{N-1} to d^N.

(c) In solids a third kind of energy levels exists which has an analog to free ions only in special cases: bound excitons. A charge-transfer level may provide for a local charge distribution which is able to bind an exciton. Dependent on the conditions both charge carriers of the exciton can represent one subsystem and the impurity another subsystem which then couple to produce a total system. In other cases one charge carrier is strongly coupled, i.e., it belongs to the d electron subsystem, whereas the remaining charge carrier is only weakly coupled, i.e., it surrounds the impurity in a hydrogenlike orbit. These levels are denoted by $d^{N+1}h_b$ for bound-hole levels and by $d^{N-1}e_b$ for bound-electron levels.

The bound-electron and -hole levels described in the last part of case (c) were only observed in a few cases. Using optical spectroscopy the nickel d^9h_b complex in ZnS:Ni and CdS:Ni,[1,2] the copper $d^{10}h_b$ complex in ZnS:Cu, ZnO:Cu, and CdS:Cu (Refs. 3,4) and an iron d^6h_b complex in GaP:Fe, InP:Fe, and GaAs:Fe (Refs. 5,6) were found. In GaP:Co a very faint transition was interpreted as being due to the d^7h_b level.[7] A review on the subject was provided by Sokolov and Kikoin.[8]

When one looks closer to the named host-impurity pairs and the involved bound charge-carrier levels three questions emerge: First, for some host lattices (i.e., ZnS, CdS) it is much more probable to observe these energy levels than for others. Second, for some $3d$ centers no evidence on charge-carrier levels exists (i.e., Sc, Ti, V, Cr). And third, the settled evidence focuses on bound-hole and not on bound-electron levels. It is the third question that plays a key role in this publication.

The only candidate system for bound-electron levels mentioned in the past was the cobalt impurity center. There has been some discussion in the literature on the interpretation of some cobalt related transitions observed in ZnSe:Co and ZnS:Co (Refs. 9–13) [cf. Fig. 1(a)]. For the transitions we shall use the nomenclature introduced by Noras, Szawelska, and Allen,[10] which denotes the three zero-phonon lines (zpl's) in ZnSe:Co by L, M, and N and the corresponding absorption lines in ZnS:Co by 1, 11, and 14. To distinguish line splittings due to different polytypes in ZnS:Co, we added a prefix letter ''C'' for labeling the cubic modification.[13]

Robbins *et al.* investigated these transitions in ZnSe:Co and put forward an explanation in terms of d^6e_b bound electron levels since the transition energies are very close to the expected charge-transfer energy from the d^6/d^7 charge-transfer level to the conduction band.[9,11] Since an absorption threshold rises near the N-line transition they interpreted the threshold as charge-transfer transition. They supported their model by magneto-optical transmission spectra of the L and L' line transitions.

This model was rejected by Noras, Szawelska, and Allen, however, who determined a charge-transfer energy much

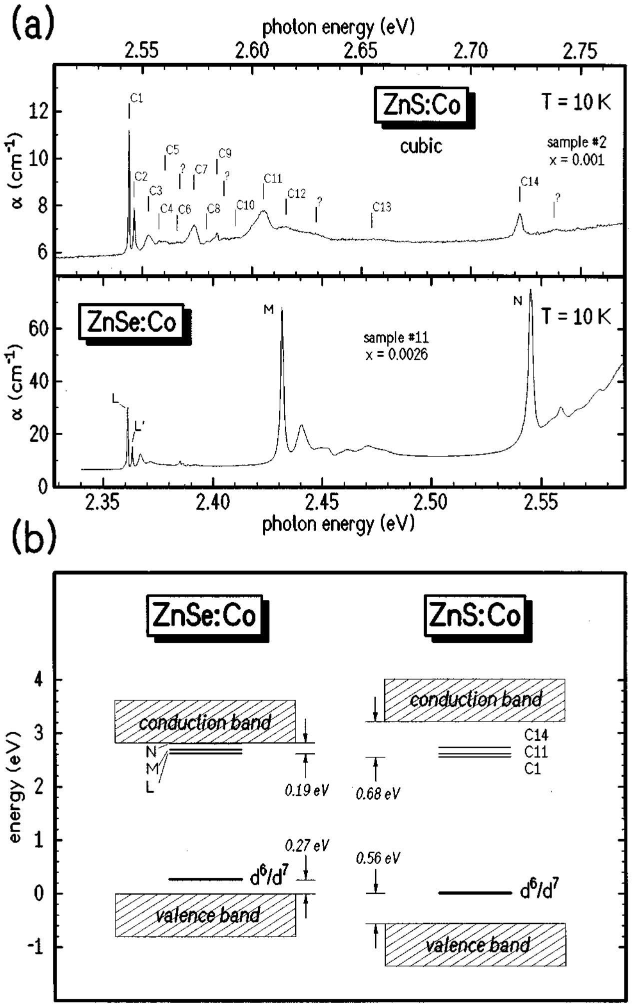

FIG. 1. (a) Weak absorption in the charge-transfer region of ZnS:Co and ZnSe:Co (for the nomenclature see text, ''?'' refers to additional lines). (b) The d^6/d^7 charge-transfer levels of the cobalt center and the binding energies of the L, M, N and $C1$, $C11$, $C14$ transitions in ZnSe:Co and ZnS:Co, respectively.

lower than the excitation energy of the L-, M-, and N-line transitions by photocapacitance measurements [2.2 eV (Ref. 10)]. Sokolov *et al.* added that the fingerprints of bound charge-carrier transitions were missing in their electroabsorption spectra.[12]

The first aim of this paper is to answer the discussion on the nature of the L-, M-, N-line transitions in ZnSe:Co and $C1$-, $C11$-, $C14$-line transitions in ZnS:Co once and for all. The transition lines being narrowest were therefore investigated by their magneto-optical absorption spectra (L, L' in ZnSe:Co and $C1$, $C2$ in ZnS:Co). Though the measurements were a repetition of the experiments of Robbins *et al.* for ZnSe:Co, they were now performed for ZnS:Co, thus enabling a direct comparison of the properties of these transitions. Since the charge-transfer energies from the d^6/d^7 charge-transfer level to the conduction band are different in both host materials[14] [cf. Fig. 1(b)], important conclusions on the participating electronic levels can be drawn. In a second part we present calculations in order to discuss possible level assignments. It is then possible to explain the appearance of the transitions in ZnS:Co and ZnSe:Co and their nonvisibility in other II-VI or even III-V compounds.

II. EXPERIMENT

One sample each of ZnSe:Co (cation substitution index $x=2.5\times10^{-4}$) and ZnS:Co ($x=1.6\times10^{-4}$) were prepared for the Zeeman-absorption measurements. The ZnSe:Co sample has been grown by iodine transport in the material laboratory of our institute, the origin of the ZnS:Co sample was unknown. For the experiments slices of typically 1 mm thickness were produced by cleaving the crystals in [110] planes. The cobalt concentration was determined by integrating the absorption cross section and comparing it with stronger doped samples which had been measured by electron-microprobe measurements.[15] The samples were aligned with the aid of Laue exposures. For the recording of the Zeeman-absorption spectra the samples were mounted in a He-bath cryostat ($T=2 \ldots 6$ K) and set up in both the Faraday and Voigt configuration ($B=0 \ldots 5$ T). The polarized white light provided by a halogen tungsten light source was first shone onto the sample and then dispersed by a grating monochromator.

Absorption spectra covering a larger spectral region and a certain concentration range, which were required for comparison with ligand-field calculations, were taken from Refs. 15 and 16.

III. RESULTS

Figure 2 displays typical Zeeman-absorption spectra of the L, L' and $C1$, $C2$ doublet lines both in Voigt and Faraday configuration for $B=3$ T and for two different temperatures. The optical transitions leading to the observed Zeeman pattern are strongly polarized. The polarization properties are similar to those reported by Robbins *et al.* for ZnSe:Co.[11] Different from the latter work, some split components of the L' line are entangled in Fig. 2. The outstanding result of the present work, however, is the striking similarity of the Zeeman spectra of the $C1$-, $C2$-line doublet in ZnS:Co and the L-, L'-line doublet in ZnSe:Co. This statement holds for the selection rules, for the absolute splitting energies as well as for the intensity ratios. To simplify the comparison of the spectra in the two materials, the Zeeman transition lines were labeled with the same letters, the order of letters being given by the descending photon energy and the primes being introduced to distinguish between the Zeeman components arising from the L, $C1$, and L', $C2$ lines, respectively.

In Voigt configuration the spectra were also recorded for different orientations of the lattice relative to the magnetic field (not shown). As had been found by Robbins *et al.* for ZnSe:Co, we also obtained no indications of anisotropic components in the case of ZnS:Co.

In Fig. 3, all our Zeeman spectra are compiled in a splitting diagram. The optical polarizations of the transitions are indicated. For ZnSe:Co, the labeling according to Robbins *et al.* (lower case letters) is included. The transition line splittings are represented by straight lines as the linear contributions are prevailing. For the L' and $C2$ lines at least four components are clearly resolved. The splitting pattern of the two components being lowest in photon energy (C' and D')

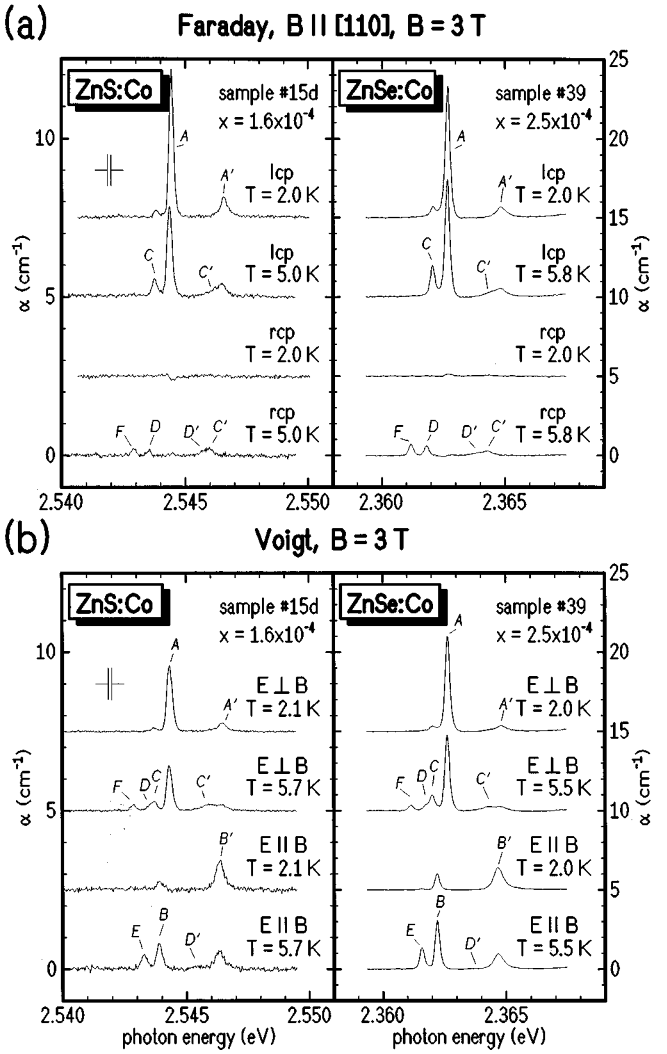

FIG. 2. Polarization of the Zeeman-absorption components of the $C1$, $C2$ and the L, L' absorption line doublets in ZnS:Co and ZnSe:Co for $B=3$ T and two different temperatures. (a) Faraday configuration, (b) Voigt configuration. The spectra are shifted vertically for clarity. ''lcp'' refers to left-circular-polarized and ''rcp'' to right-circular-polarized incident light.

is, however, far from being certain. The tentative character of the corresponding lines is expressed by the dotted lines.

IV. DISCUSSION

Zeeman spectroscopy is a very sensitive tool to probe initial- and final-state wave functions. Even without knowing the exact level assignments yet our results plainly reveal the identical character of the participating Zeeman components of the $^4A_2(F)$ ground state and the excited states of the L, L' and $C1$, $C2$ transitions in ZnSe:Co and ZnS:Co. This is particularly underlined by the fact that the observed optical polarizations cannot be ascribed to solid-state selection rules: for Faraday configuration no distinct circular-polarized transitions are expected according to the C_s point symmetry for $B \| [110]$ orientation.[17] For Voigt configuration the situation is the same: the observed Zeeman splittings and transition probabilities are isotropic within the experimental accuracy. Though in this case solid-state symmetry selection rules cannot be exploited as no anisotropies are noticed in the spectra, the observed polarizations nevertheless reflect the similarity of the involved wave functions.

Using the $^4A_2(F)$ ground-state g factors as known from electron paramagnetic resonance,[18] the splitting pattern of Fig. 3 is transferred into the energy-level diagram shown in Fig. 4. As can be seen directly from Fig. 2 only the A, A', and B' transitions correspond to ''cold'' transitions departing from the $M_s=-3/2$ sublevel of the $^4A_2(F)$ ground state, whereas the other transitions originate from the thermalized sublevels. The observed splittings for the L' and $C2$ lines turn out to be partly due to a splitting of the final states. Two components are certain, at least a third one is very probable. For the L line, Fig. 4 is similar to the level diagram found by Robbins *et al.*[11]

For odd-electron states (here, either d^7 or d^6e_b) the T_d^* double point group yields only Γ_6, Γ_7 (Kramers doublets), and Γ_8 (fourfold degeneracy) symmetric zero-field levels. As was already previously found for the L-line,[11] the $C1$-line's final state turns out to be a Kramers doublet level, too. Since the final states of these two transitions have just been shown to be very similar, they either have both Γ_6 or Γ_7 symmetry. Robbins *et al.* excluded Γ_7 symmetry for the final state's symmetry of the L-line transition. We do not follow their conclusion since this restriction would require the application of solid-state selection rules. As was shown above, such properties cannot be exploited here.

As far as the L' and $C2$ lines are concerned, we found evidence for more than two components for the corresponding final states. Even when the evidence for the third component is weak one has to take into account that the splitting of the two certain components strongly suggests two more components at higher energies. The L'- and $C2$-line's final states therefore have to represent levels with Γ_8 symmetry. This is consistent with the results of Robbins *et al.*, who had performed uniaxial stress measurements which can only produce splittings of Γ_8 levels but not of Γ_6 and Γ_7 levels.

As we already mentioned in the introduction, the charge-transfer energies for a transition from the d^6/d^7 charge-transfer level to the conduction band are much more different than the photon energies of the L, M, N transitions in ZnSe:Co and the $C1$, $C11$, $C14$ transitions in ZnS:Co (Fig. 1). The binding energy of the L-line final-state relative to the conduction-band minimum is 190 meV. Though this is larger than the typical binding energies of 100 meV of bound-hole complexes in ZnS and ZnSe (Refs. 2,4,8) it is not large enough to serve as an argument against the model of a bound-electron system. For ZnS:Co however, the binding energy of 680 meV of the $C1$-line final state is far too large for such an electronic state. We, therefore, conclude that both the $C1$, $C2$ and L, L' absorption line doublets and thus very probably the other transitions shown in Fig. 1(b) have to be attributed to internal $d^7 \rightarrow d^{7*}$ transitions of the cobalt center.

It is worth noting that the isotropic splittings of the investigated transition lines seem to indicate that the final states are pure spin states. Two arguments against this hypothesis exist however. First, the close $C2$ and L' lines are very probably of vibronic origin, i.e., they result from a Jahn-Teller coupling regime. Pure spin states either have A_1 or A_2 orbital symmetry, and these states are not Jahn-Teller active. Sec-

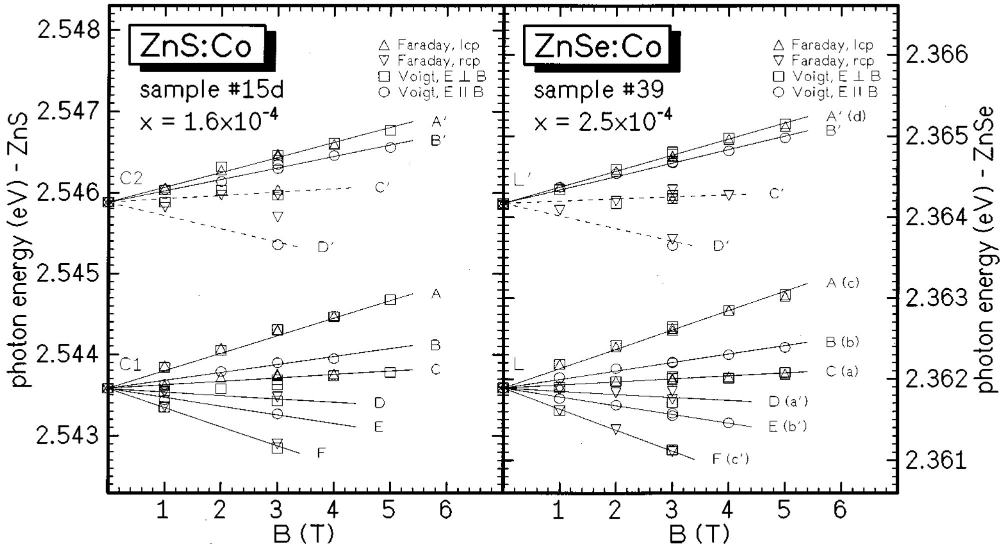

FIG. 3. Zeeman splittings and polarizations of the Zeeman components of the $C1$, $C2$ transitions in ZnS:Co and the L, L' transitions in ZnSe:Co. Dashed lines denote uncertain Zeeman components. The lowercase letters (in brackets) refer to the nomenclature used in Ref. 11. Note that the scale on the photon energy axis is the same for ZnS:Co and ZnSe:Co.

ond, the effective g factors of the L- and $C1$-line final states, $g=-1.4\pm0.4$ and $g=-1.1\pm0.3$, are far from the value expected for a pure spin level, i.e., $g=2$.[19] As a conclusion of this paragraph we can limit the possible final-state orbital symmetries to E, T_1, or T_2 symmetry.

As far as the g value of the L-line final state is concerned Robbins *et al.* obtained $g=-0.7$. We attribute this deviation, which does not affect our arguments, to the different procedure the two values were derived. In the former work only specific Zeeman branches were considered, whereas here an average according to all branches was taken.

Since the L-, M-, N- and $C1$-, $C11$-, $C14$-line transitions are now considered to be due to internal transitions, it is necessary to carry out ligand-field calculations to make more exact level assignments. A complete approach would have to include both electronic and vibronic contributions. For the description of the level fine structure of the ${}^4T_2(F)$ and ${}^4T_1(F)$ excited states, a dynamical Jahn-Teller effect was shown to be necessary in ZnS:Co (Refs. 20,21) and for the ${}^4T_1(F)$ level in ZnSe:Co.[22] Hence it is to be expected that level calculations have to take into account the electron-phonon interaction also for the higher excited states. In the

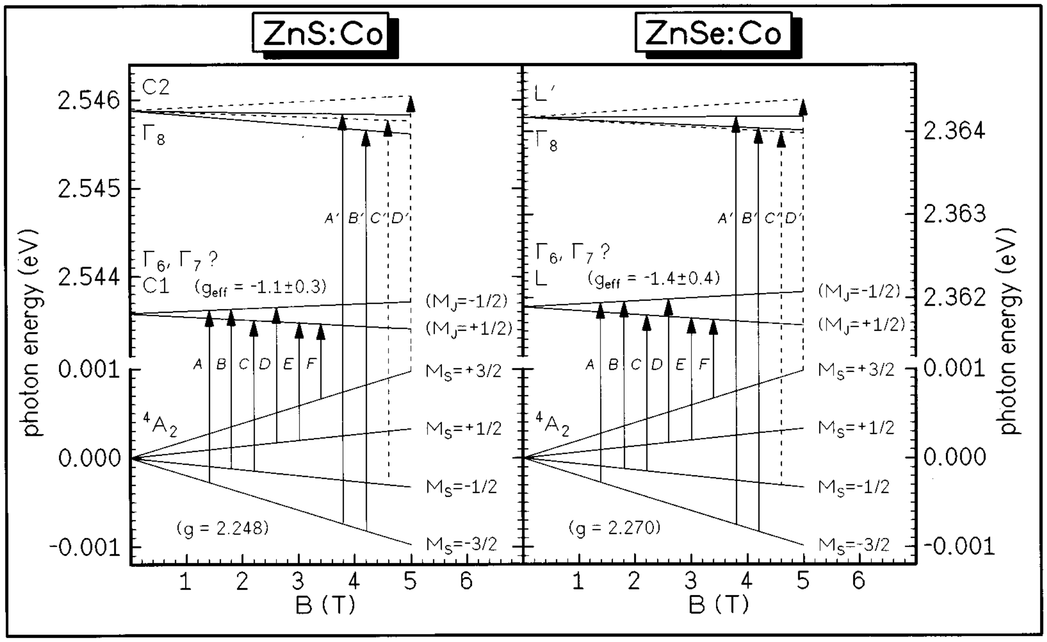

FIG. 4. Final- and initial-state Zeeman level diagram for the $C1$, $C2$ transitions in ZnS:Co and the L, L' transitions in ZnSe:Co. The transitions are labeled according to Fig. 3. The dashed lines refer to uncertain assignments. Note that the scale on the photon energy axis is the same for ZnS:Co and ZnSe:Co. The ground-state g values were taken from Ref. 18.

region of 2.5-eV excitation energy there are a lot of electronic excited states as will become apparent below. The resulting term interaction renders a Jahn-Teller approach almost impossible to carry out, however. We, therefore, focus on the electronic part of the level scheme and try to find arguments in favor of possible level assignments at this level of calculation.

For the electronic part of the total Hamiltonian, several approaches have been proposed to explain the overall multiplet manifold of $3d$ impurity centers. The classical Tanabe-Sugano approach[23] provides for a good empirical description of the multiplet spectra. Yet it lacks a more microscopic insight into the interaction between the impurity and the ligand electrons. All relevant parameters, the Racah parameters B, C and the crystal-field splitting Δ_{cf}, are determined by obtaining a good fit to experimental transition energies. In the past, modifications to this so-called $BC\Delta_{\mathrm{cf}}$ scheme in terms of a molecular-orbital point of view were proposed which have in common the employing of different scaling parameters to consider a different radial expansion of d electrons with e and t_2 orbital symmetry.[24–30] Recently a detailed discussion of semiconductors doped with cobalt has however shown that there is not much justification for the approximations made in these approaches.[16] The Heitler-London analog to the present problem, the so-called configuration interaction approach, represents a totally different way of describing the multiplet problem.[16,31–33] Though it offers a better insight into the hybridization mechanism taking place it yet suffers from a worse quantitative description of the observed transition energies. For the present purpose we therefore consider the utilization of the $BC\Delta_{\mathrm{cf}}$ scheme to be appropriate. To include at least the electronic fine structure the spin-orbit interaction matrices as published by Eisenstein[34] were imposed onto the Coulomb interaction matrices.

We proceeded as follows: In Fig. 5, absorption spectra of ZnS:Co and ZnSe:Co are shown which were obtained from different samples with varying cobalt content. It was therefore possible to cover a large dynamic range of many orders of magnitude. Absorption scaling factors are used to enable a comparison between the various transitions among which the $^4A_2(F)\rightarrow{}^4T_1(P)$ transition has the strongest oscillator strength. The estimated centers-of-gravity energies of the three transitions due to the quartet final states $^4T_2(F)$, $^4T_1(F)$, and $^4T_1(P)$ together with the lowest two transitions due to doublet final levels ($^2E(G)$, $^2T_1(G)$) were fitted to the $BC\Delta_{\mathrm{cf}}$ level scheme (cf. Table I). The latter two doublet level assignments were chosen because of the following reasons:

(i) Absorption measurements even in strongly doped samples ($x\sim0.01$) did not reveal any cobalt correlated transitions between the $^4A_2(F)\rightarrow{}^4T_1(F)$ transition and ~1.4-eV photon energy.

(ii) We performed calculations according to the formalisms described in Refs. 28 and 30, and we derived the configuration interaction perturbation matrices for interaction of $|d^7\rangle$ with single-hole $|d^8\underline{L}\rangle$ configurations. All calculations led to the same two doublet levels being the lowest doublet excited states.[16]

(iii) Though the overall energy of the doublet levels can be adjusted by the Racah parameter C without changing the quartet energies (these do solely depend on B and Δ_{cf}), the energy difference between the two doublet levels is correctly described by the values for B and Δ_{cf}.

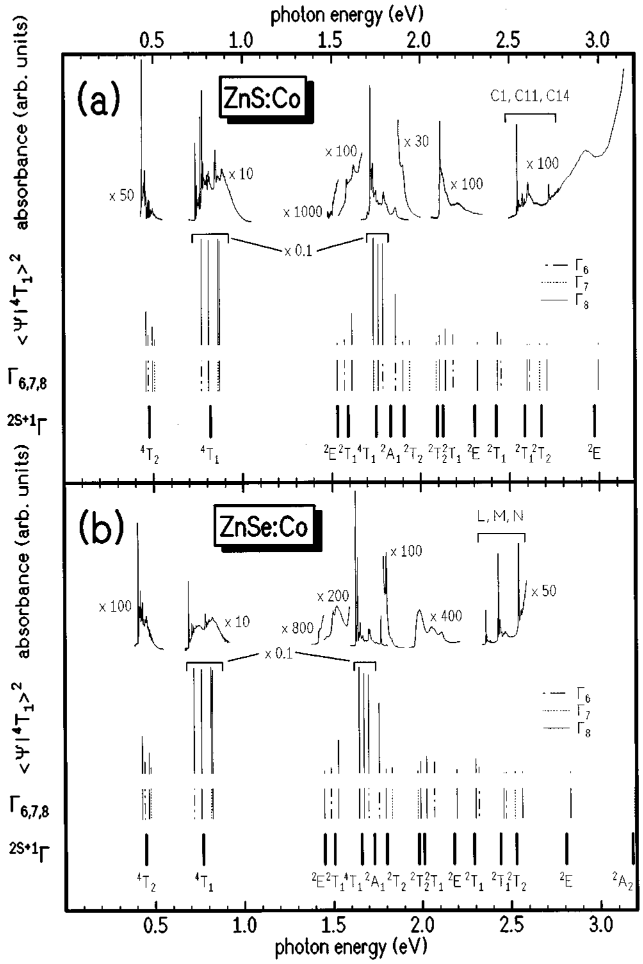

FIG. 5. Collection of internal $d^7\rightarrow d^{7*}$ absorption spectra of cobalt in ZnS:Co and ZnSe:Co and the $BC\Delta_{\mathrm{cf}}$ level scheme including spin-orbit interaction. The individual spectra are scaled relative to the $^4A_2(F)\rightarrow{}^4T_1(P)$ transition. The calculations were performed with the $BC\Delta_{\mathrm{cf}}$ parameters listed in Table II, the spin-orbit coupling parameter was set to $\zeta=50$ meV. The intensities are estimated by the squared $^4T_1$ character of the eigenfunctions.

The results of our calculations for ZnS:Co and ZnSe:Co are shown in Table II and included in Fig. 5 as indicated by the $^{2S+1}\Gamma$ levels. To include spin-orbit interaction we refrained from varying this parameter in the fit procedure. Already for the free ion value of the spin-orbit coupling parameter one notices some scatter in the literature, producing an average of $\zeta=(67\pm3)$ meV.[35] The quenching of ζ is neither very strong in ZnS:Co as was shown by Koidl, Schirmer, and Kaufmann for the first two excited states ($\zeta=46.5$ meV, $\zeta'=56.5$ meV) (Ref. 20) nor in ZnSe:Co as obtained by Uba and Baranowski for the $^4T_1(F)$ level ($\zeta=53.9$ meV). We therefore used an average value of $\zeta=50$ meV. The result is shown in Fig. 5 together with the squared $^4T_1$ character of the spin-orbit levels. The $^4A_2\rightarrow{}^4T_1$ transition is the only allowed electric-dipole transition according to spin- and symmetry-selection rules, and this property already served in some previous works as estimate for the electric-dipole oscillator strength.[29,36]

The four spin-orbit components of the lowest two quartet

TABLE I. Estimated energies of internal $d^7 \rightarrow d^{7}*$ absorption transitions (centers-of-gravity) of cobalt in semiconductors (in eV). The emission energies for the $^4T_2(F) \rightarrow {}^4A_2(F)$ transition are also included to aid as an estimate for the reverse absorption transition in cases where the latter transition is not observed. Values in brackets represent tentative assignments. The # denotes absorption band position estimated from emission band position. The * denotes $^2A_1(G)$.

$^4A_2(F) \rightarrow$	$^4T_2(F)$	$^4T_1(F)$	$^4T_1(P)$	$^2E(G)$	$^2T_1(G)$	$^4T_2(F) \rightarrow {}^4A_2(F)$
ZnO	0.53[a]	0.89[a]	(2.03)[a]	1.91[a]		0.45[b]
ZnS	0.46[c]	0.83[c]	1.75[c]	1.52[c]	1.61[c]	0.43[c]
ZnSe	0.43[c]	0.78[c]	1.66[c]	1.44[c]	1.52[c]	0.40[c]
ZnTe	0.40#	0.73[d]	1.38[d]			0.37[e]
CdS	0.39#	0.68[f]	1.73[f]			0.36[e]
CdSe	0.37[g]	0.71[g]	1.62[g]			0.35[h]
CdTe	0.38[i]	0.66[i]	1.37[i]	(1.16)[i]	(1.29)[i]	0.34[e]
GaP	0.58[j]	1.02[c]	1.54[c]	(1.40)[c]*	(1.19)[c]	0.53[k]
GaAs	0.51[l]	0.95[l]	1.42[l]			0.48[m]
InP	0.49#	0.92[n]	(1.40)[n]			0.46[o]

[a] Reference 40, $T=78$ K.

[b] Reference 41, $T=4.2$ K.

[c] References 15 and 16, $T=10$ K.

[d] Reference 42, $T=4.2$ K.

[e] Reference 43, $T=10$ K.

[f] Reference 44, $T=4.2$ K.

[g] Reference 45, $T=77$ K.

[h] Reference 46, $T=4$ K.

[i] Reference 47, $T=4.5$ K.

[j] Reference 36, $T=4$ K?

[k] Reference 48, $T=5$ K.

[l] Reference 49, $T=6$ K.

[m] Reference 50, $T=1.7$ K.

[n] Reference 51, $T=6$ K.

[o] Reference 51, $T=4.2$ K.

levels correlate well with the observed energy splittings. The spin-orbit components of the $^4T_1(P)$ level are strongly compressed, however. The lowest two spin-orbit components (Γ_8 and Γ_7) are hardly resolved in Fig. 5. Their splitting is entirely due to term-term interaction (sometimes referred to as second-order splitting). In the calculation it amounts to 1 meV, which is not far off the experimental value of 2 meV. In CdTe:Co Babil *et al.* had observed a similar splitting of 1.4 meV, and Zeeman spectroscopy had been used to confirm the Γ_8 and Γ_7 character of the two zero-phonon absorption lines.[37] Hence the observed splitting is satisfactorily explained by electronic parts of the Hamiltonian, i.e., it is not necessary to include vibronic contributions.

We assign the lines at 1.861-eV (ZnS:Co) and 1.772-eV (ZnSe:Co) photon energy, respectively, to the $\Gamma_6({}^2A_1(G))$ final state, which has strong $^4T_1$ character admixed thereto. The level repulsion between this level and the $\Gamma_6({}^4T_1(P))$ component eventually explains the above-mentioned level compression. The weak transitions on the higher-energy side of the $^2A_1$ line are described by the Γ_8 and Γ_7 components of the $^2T_2(G)$ multiplet. On the lower-energy side of the spin-orbit components of the $^4T_1(P)$ level, the $\Gamma_8({}^2E(G))$, $\Gamma_6({}^2T_1(G))$, and $\Gamma_8({}^2T_1(G))$ levels also follow well the intensity pattern.

For higher excitation energies definite assignments are rendered difficult, however. The transitions observed in the spectral region of 2.1 . . . 2.4-eV photon energy in ZnS:Co and 1.9 . . . 2.2-eV photon energy in ZnSe:Co correspond to a mixture of the $\Gamma_7({}^2T_2(H))$, $\Gamma_8({}^2T_2(H))$, $\Gamma_8({}^2T_1(H,P))$, $\Gamma_6({}^2T_1(H,P))$, and maybe the $\Gamma_8({}^2E(H))$ levels. When we further proceed to the range of the L, M, N, transitions in ZnSe:Co and the correspondent transitions in ZnS:Co the situation becomes more sophisticated. Most possibly the lines represent a mixture of the spin-orbit components of two $^2T_1(H,P)$ multiplets and the $^2T_2(D)$ multiplet. Since the L- and $C1$-line final state represent a Kramers doublet, they most possibly represent a final state with Γ_6 symmetry. This is also in agreement with our conclusion made above that the source multiplet has E, T_1, or T_2 orbital symmetry. Yet a close Γ_8 component is predicted by the spin-orbit calculation at lower photon energies which is not observed. Though the L'- and $C2$-lines final state has Γ_8 symmetry, the order of the levels is reversed and much narrower than suggested by the spin-orbit calculation. As was discussed above, it is very probable that a Jahn-Teller regime has to be used here to explain the observed fine structure in detail.

The relative intensities are not very well represented by our calculation for this region of higher excitation energies. This is due to the fact that the $^4T_1$ character of these levels in the framework of the basis states of our calculation is very weak. Instead one would have to take into account additional basis states from the close charge-transfer level continuum.

TABLE II. $BC\Delta_{cf}$ fit parameter sets for the transition energies of Table I and lowest charge-transfer energies E_{ct} (absolute and scaled by B) of the cobalt d^7 charge state in various II-VI and III-V compound semiconductors. A donor charge-transfer (ct) type denotes a transition from the d^6/d^7 charge-transfer level to the conduction band and an acceptor ct-type a transition from the valence band to the d^7/d^8 charge-transfer level. The fundamental band-gap energy E_g is given for comparison (from Ref. 52 for 0 K).

Host	B/meV	C/meV	C/B	Δ_{cf}/meV	E_g/eV	E_{ct} /eV	ct type	E_{ct} /B
ZnO	91.1	446	4.90	520	3.2	<2.88[a]	?	<31.6
ZnS	75.8	351	4.63	477	3.78	3.22[b]	donor	42.5
ZnSe	72.4	331	4.57	448	2.82	2.55[c]	donor	35.2
ZnTe	55.2			423	2.39	1.53[d]	acceptor	27.7
CdS	82.5			391	2.59	<2.48[a]	?	<30.1
CdSe	74.2			400	1.84	1.71[e]	donor	23.0
CdTe	58.5	276	4.72	384	1.61	1.42[f]	acceptor	24.3
GaP	52.7	234	4.43	572	2.35	1.91[g]	donor	36.2
GaAs	43.0			561	1.52	1.36[h]	donor	31.6
InP	43.8			541	1.42	1.12[i]	donor	25.6

[a] cf. text.
[b] Reference 14.
[c] Reference 53.
[d] Reference 54.
[e] Reference 46.
[f] Reference 55.
[g] Reference 56.
[h] Reference 57.
[i] Reference 58.

This is closer in energy in the case of ZnSe:Co than of ZnS:Co [cf. Fig. 1(b)], which might explain the enhanced oscillator strength of the L, M, N transitions in ZnSe:Co compared with the $C1$, $C11$, $C14$ transitions in ZnS:Co. In the latter material, on the other hand, the same kind of mixing could be responsible for an increased oscillator strength of an internal transition observed at about 2.8 . . . 3.0 eV where the $\Gamma_8(^2E(H))$ level is predicted.

Though we have not yet been able to obtain an unambiguous level assignment of the transitions shown in Fig. 1(a) with the aid of the $BC\Delta_{cf}$ approach, we shall now nevertheless try to provide an explanation of why these transitions have not been observed in other II-VI or even III-V compound semiconductors doped with cobalt. The numerical results for the $BC\Delta_{cf}$ parameters using the cobalt internal transition energies for other host semiconductors (cf. Table I) are also compiled in Table II. As an average ratio of the Racah parameters C and B, a value of $C/B=4.6$ is obtained. Figure 6(a) displays a Tanabe-Sugano diagram for the d^7 configuration having this C/B ratio, and Fig. 6(b) shows an enlargement of Fig. 6(a) including the results of Table II. The agreement between the observed and the calculated quartet level energies is excellent for the II-VI compound semiconductors and is still fair for the III-V semiconductors. Similar statements can be made for the $^2E(G)$ and $^2T_1(G)$ doublet levels in those cases where data for the transitions were available.

The position of the vertical bars on the x axis in Fig. 6(b) represents the Δ_{cf}/B ratio for the various host semiconductors. The height of these bars reflects the spectral ''window'' which is available for the observation of internal $d^7 \rightarrow d^{7*}$ transitions. One might suppose that these spectral windows are represented by the fundamental energy-gap energies. This is however not true. Instead the spectral window is much better described by the smallest charge-transfer energy for changing the observed charge state. Though it cannot be generally excluded that internal transitions overlap with charge-transfer continua,[38] these cases have to be considered as being rather exceptional. For cobalt one therefore has to look for the smallest charge-transfer energy E_{ct} among the charge-transfer transitions from the d^6/d^7 charge-transfer level to the conduction band or from the valence band to the d^7/d^8 charge-transfer level. The results of such a survey are also compiled in Table II together with values scaled by the Racah parameter B. Since for ZnO:Co and CdS:Co no firm data on charge-transfer energies exist, we estimated the charge-transfer energy E_{ct} by the photon energy where the rising absorption at higher photon energies reaches the strength of the strongest internal $d^7 \rightarrow d^{7*}$ transition, i.e., the $^4A_2(F) \rightarrow {}^4T_1(P)$ transition. For this purpose spectra of ZnO:Co and CdS:Co from Ref. 39 were analyzed.

The derived spectral windows eventually explain why the L, M, N and $C1$, $C11$, $C14$ transitions have not been observed in other II-VI compound semiconductors than in ZnS:Co and ZnSe:Co. Whereas for the other host semiconductors the charge-transfer energy E_{ct} is lower than the necessary excitation energies, in ZnS:Co and ZnSe:Co the $^2T_2(D)$ multiplet and two $^2T_1(H,P)$ multiplets lie within the accessible spectral window. It is worth noting that in ZnS:Co a $^2E(D)$ multiplet is expected at even higher photon energies, and in fact a further transition was recognized in the spectral region of 2.8 . . . 3.0 eV [cf. Fig. 5(a)].

According to Fig. 6, the lowest of these four multiplet levels should also be expected to be observable in CdS:Co and ZnO:Co. As we just mentioned the charge-transfer ener-

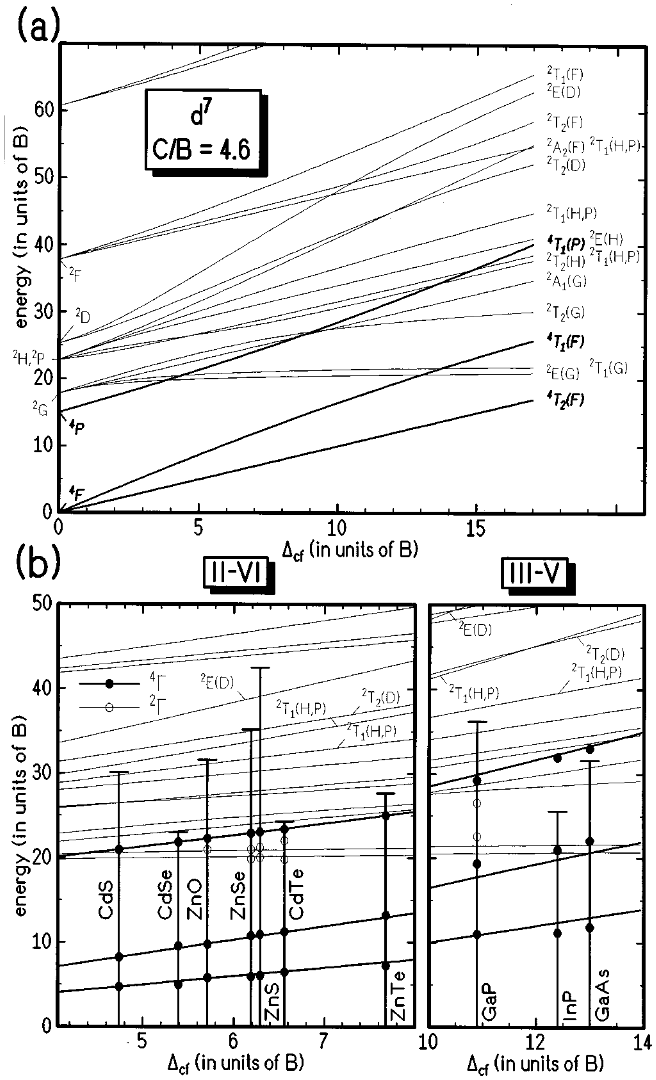

FIG. 6. Tanabe-Sugano diagram for the cobalt d^7 charge state [ground state: $^4A_2(F)$]: (a) complete diagram, (b) enlargement with Δ_{cf}/B values for various host semiconductors (data from Table II). The height of the bars gives the region of the spectral window which is available for the observation of $d^7 \rightarrow d^{7*}$ internal transitions. The full circles denote the quartet level and the hollow circles the doublet level fit energies of Table I.

gies E_{ct} for these semiconductors had to be estimated, however. Due to the estimation procedure the obtained values are likely to be overestimated. Hence the missing of this multiplet level does not represent direct evidence against our interpretation.

In the III-V semiconductors the multiplet pattern is completely different than for the II-VI compound semiconductors. The correspondent multiplet levels are all shifted to higher energies well beyond the observable spectral range, thus explaining why the transitions have not been observed in these semiconductor host materials.

At the end of this section we want to come back to the three questions raised in Sec. I on the nature of bound charge-carrier levels. With the results of this paper we cannot answer the first and the second question, i.e., why the observation of these levels is restricted to certain host semiconductors and to certain $3d$ impurities. Studies on these subjects have to focus on both the electronic structure of the impurity and the host band scheme. Presumably the first question is linked to the host semiconductor band structure, whereas the second problem is obviously connected to the impurity itself. For explaining the occurrence of the levels for a specific impurity, the position of the corresponding charge-transfer level relative to the band edges should play a major role. As far as the third question is concerned, we did not find evidence for an electron-bound level. We therefore attribute the general missing of these levels in optical spectra to the fundamental difference that bound-electron levels will be constructed from perturbed conduction-band states, whereas bound-hole levels will be derived from valence-band states. We conclude that a theoretical approach which claims to describe the bound charge-carrier levels unavoidably has to meet these properties.

V. CONCLUSIONS

The Zeeman-absorption spectra of the $C1$-, $C2$- and L-, L'-line doublet in ZnS:Co and ZnSe:Co were shown to be almost identical. We therefore conclude that the participating initial and final states are also identical. Since the charge-transfer energy from the d^6/d^7 charge-transfer level to the conduction band is far larger in ZnS:Co than the excitation energy of the $C1$, $C2$ lines, these and the correspondent transitions in ZnSe:Co are assigned to $d^7 \rightarrow d^{7*}$ internal transitions of the cobalt impurity and not to a bound-electron final state. Ligand-field theory in the framework of the Tanabe-Sugano approach support this interpretation and explain why similar internal transitions have not been observed in other host semiconductors. In the latter materials the lowest charge-transfer energies turned out to be lower than the necessary excitation energies. The absorption transitions known as the L, M, N and $C1$, $C11$, $C14$ transitions in ZnSe:Co and ZnS:Co, respectively, are tentatively assigned to a mixture of two $^2T_1(H,P)$ multiplets and the $^2T_2(D)$ multiplet. Optical evidence for a $d^N e_b$ bound-electron level for a $3d$ transition-metal impurity in a semiconductor is hence still missing.

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