"Acceptor" and "donor" excitons bound to transition-metal impurities in II–VI semiconductors

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The electroabsorption method is used to investigate narrow lines on the edge and in the interior of the photoabsorption band of nickel-doped ZnSe. These lines are interpreted as the first experimental proof of the amorphous character of exciton capture by a transition-metal impurity: the lines on the photoabsorption edge correspond to capture of an electron by a *d*-shell and of a hole by a hydrogenlike orbit ("acceptor" exciton), while capture of a line in the interior of the photoabsorption band corresponds to formation of a "donor" exciton with a hole in the *d* shell. A theory for amphoteric bound excitons is developed and the effect of giant enhancement of the oscillator strength following optical excitation of a donor exciton is explained.

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INTRODUCTION

It is known that the optical spectra of excitons bound to nickel impurities in the compounds ZnSe, ZnS, and CdS do not fit the usual "neutral donor plus hole" or "neutral acceptor plus electron" picture that dates back to Lampert's paper.[1] The impurity atom of the transition metal $\mathrm{Me}(3d^n4s^2)$, replaces as a rule the atom A in the $\mathrm{A_2B_6}$ isoelectronically, i.e., it turns out to be the neutral center $\mathrm{Me}^2 + (3d^n)$ in the ground state. The optical spectra of excitons bound to the impurity $\mathrm{Ni}(3d^8)$ in the aforementioned compounds[2–6] can be explained with the aid of the following mechanism for the formation of a bound exciton:

$$d^8+\hbar\omega=[d^9h]. \tag{1}$$

This means that the light causes one of the valence electrons to be captured in the *d*-shell of the impurity, while the hole produced in the valence band is bound on a hydrogenlike large-radius orbit via the Kohn-Luttinger mechanism (the square brackets in (1) symbolize this bond). The free-exciton capture corresponding to this mechanism is described as follows:

$$d^8+[eh]=[d^9h]+\hbar\omega. \tag{2}$$

The energies of the optical transitions corresponding to the reactions (1) ad (2) are respectively

$$E_{(1)}=E(d^9)-E(d^8)-\varepsilon_v-\varepsilon_h=\varepsilon_{i-}-\varepsilon_h,$$
$$E_{(2)}=\varepsilon_c-[E(d^9)-E(d^8)]+\varepsilon_h-\varepsilon_{ex}=\varepsilon_c-\varepsilon_{i-}+\varepsilon_h-\varepsilon_{ex}.$$

Here ε_{i-} is the energy of the level corresponding to the singly charged state of the center Me^+, reckoned from the edge of the valence band, ε_h is the binding energy of the hole on the hydrogenlike orbit, $\varepsilon_{\mathrm{ex}}$ is the binding energy of the free exciton. Thus, a bound exciton should produce in the optical spectra a narrow line in front of the edge of the impurity absorption band corresponding to photoionization of the holes in the valence band $d^8+\hbar\omega=d^9+h$. According to the experimental data, the energy of the absorption edge is 1.849 eV.[5]

In this paper we investigate theoretically and experimentally an alternate mechanism of formation of a bound exciton, namely capture of the hole by the *d* shell and of the electron by a hydrogenlike orbit, and discuss the differences between the optical spectra of the two types of excited states of 3*d* impurities. The analog of the reaction (1) takes in this case the form

$$d^8+\hbar\omega=[d^7e],\ E_{(3)}=\varepsilon_c-[E(d^8)-E(d^7)]-\varepsilon_e=\varepsilon_c-\varepsilon_{i0}-\varepsilon_e \tag{3}$$

(ε_e is the binding energy of the electron on the hydrogenlike level, ε_{i0} is the energy of the neutral impurity center in the forbidden band); the exciton constitutes so to speak an excited state of an impurity ion one of whose 3*d* electrons of the shell is taken out to an "outer orbit" of large radius. Accordingly, the capture of the free exciton via this mechanism is described by the reaction

$$d^8+[eh]=[d^7e]+\hbar\omega,\quad E_{(4)}=\varepsilon_{i0}+\varepsilon_e-\varepsilon_{ex}. \tag{4}$$

This process is accompanied by emission of a photon.

The two types of bound excitons can be called "acceptor" [reactions (1) and (2)] and "donor" [reactions (3) and (4)], in accord with the manner in which the carriers are trapped on the hydrogenlike levels. It can be seen from (1) and (2) that an exciton can be bound via the acceptor mechanism only by impurities that form charged states of Me^+ with energy ε_{i-} in the forbidden band. The existence of such levels is by far not a general rule. At the same time, for a donor exciton to be produced, there are no restrictions of this type, inasmuch as any impurity center can certainly be photoionized ($d^n\rightarrow d^{n-1}+e$).

Donor acceptors are close in their nature to x-ray core excitons (see, e.g., Ref. 7). These types of excitations of *d* atoms in crystals differ to the extent that the wave functions of the atomic shell are distorted by the crystalline surrounding. These distortions play practically no role in the case of x-ray excitation of a hole in the inner shell, but can exert a rather substantial effect on optical transitions, which affect the last shell of the 3*d* atoms placed in a semiconductor matrix and, as will be shown below, influence decisively its properties.

In the next section we report the results of experimental investigations of electroabsorption spectra in ZnSe⟨Ni⟩.Th-

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ese results, in our opinion, can be interpreted as evidence in favor of the existence of donor excitons in this system.

ELECTROABSORPTION SPECTRA IN ZnSe⟨Ni⟩

Very narrow peaks at an optical photon energy ~ 2.64 eV were observed[8] by the electroabsorption method in ZnSe doped with nickel. The general structure of the levels of the charged state of the impurity $\mathrm{Ni}^+(d^9)$, as determined by optical measurements,[2,5] is shown in Fig. 1. It can be seen that the newly observed lines cannot be regarded as transitions from states near the top of the valence band into the only excited state d^9 possessed by the ion. To assess the possibility of an alternate explanation, it was necessary to carry out a more detailed comparison of the electroabsorption spectra on the edge of the photoionization band with $\hbar\omega \sim 1.82$ eV and in its depth ($\hbar\omega \sim 2.64$ eV).

The electroabsorption spectra were measured on ZnSe⟨Ni⟩ crystals with density $5.4\cdot10^{16} - 5.4\cdot10^{17}\ \mathrm{cm}^{-3}$ at $T = 4.2$ K. For measurements near the edge of the photoionization band, samples were prepared with thickness 2–8 mm, and for the measurements in the interior of the photoionization band the thickness was 150–200 μm. An electric field in the form $F = F_M \cos \Omega t$ was varied in the range 5–40 kV/cm, and the alternating signal was registered at the frequency 2Ω.

Figures 2 and 3 show the spectra of the amplitude of the second harmonic of the electroabsorption, α_2, for ZnSe⟨Ni⟩ in the region of the photoionization band (1.82 eV) and in the interior of this band (2.64 eV). Together with the α_2 spectrum in the 1.82 eV region, the figures show also the absorption spectrum from Ref. 5, while the arrows indicate the positions of the absorption lines observed in Ref. 2. The no-phonon line appears in the absorption spectrum at 1.822 eV (Ref. 5), and the corresponding singularity in the electroabsorption spectrum consists of approximately equal positive and negative peaks, which is evidence, in accordance with the phenomenological approach,[9] of a shift of the absorption line by the electric field. In this case the position of the absorption line should coincide with the null point in the spectral dependence of α_2, something definitely observed in our experiment.

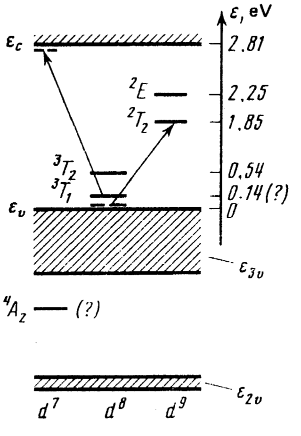

FIG. 1. Energy levels for ZnSe⟨Ni⟩. The experimentally known[2,4,5] energy intervals are indicated; the arrows mark single-electron transitions corresponding to reactions (1) and (3). Also shown are the multielectron terms corresponding to the initial and final states for these reactions.

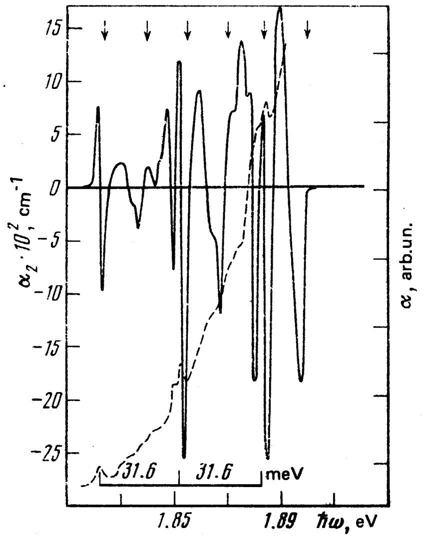

FIG. 2. Spectral dependence of the amplitude of the second harmonic of the electroabsorption, α_2, in the region of the photoabsorption edge of ZnSe⟨Ni⟩. $F_M = 25$ kV/cm, $c_{Ni} = 5.4\times10^{17}$ cm^{-3}, $T = 4.2$ K. The dashed line shows the absorption spectrum obtained in Ref. 5, the arrows indicate the absorption lines observed in Ref. 2.

At shorter wavelengths, at energies separated from the energy position of the no-phonon line by a value equal to the LO oscillation (31.6 meV), the electroabsorption spectrum α_2 has singularities that duplicate exactly in shape the peaks near 1.822 eV. Similar singularities appear also at an energy that is located at a distance of two LO oscillations and are the second phonon replica of the leading line. In addition to these replicas, the spectral dependence of α_2 has also other peaks with a period 31.6 meV. The absorption spectrum given in Ref. 5 does not show the singularities corresponding to them, although in Ref. 2 one of these peaks was apparently registered. In addition, in the electroabsorption spectra obtained by us there are two distinct and two weak negative peaks, as well as a very intense peak just barely to the left of the first LO replica. This peak is separated from the leading line by an energy 26 meV, and is probably its TO replica (the

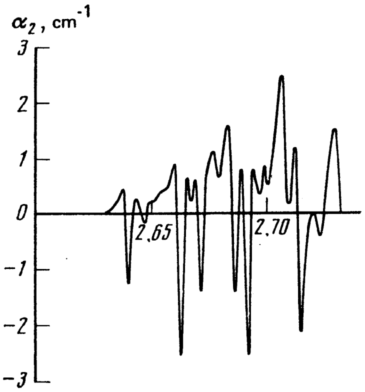

FIG. 3. Spectral dependence of the amplitude of the second harmonic of the electroabsorption, α_2, in the interior of the photoabsorption band of ZnSe⟨Ni⟩ kV/cm, $c_{Ni} = 5.4\times10^{17}$ cm^{-3}, $T = 4.2$ K.

TO-phonon energy is 25.6 meV). The other negative peaks are separated from the leading line by the following energies: the strong ones by 14.4 meV and 21 meV, and the weak ones by 12 and 23 meV. These energy intervals are in principle comparable with the energies of the acoustic oscillations measured from the absorptions and luminescence spectra in Refs. 10–12 and calculated in Ref. 13. One cannot exclude, however, the possibility that these peaks are due to other energy states of the bound exciton itself.

In the 2.64 eV region, the α_2 spectrum has a different structure. The leading line consists of two positive peaks and of a deep negative peak between them. Such a shape of the electroabsorption spectrum is evidence of broadening of the absorption line in the electric field,[9] and its position is determined by the energy of the central minimum (it should be noted here that no lines were observed in the absorption spectrum in this region). The subsequent weak negative peak and two weak positive peaks are shifted by 7.5, 12, and 17.5 meV towards higher energies and are apparently acoustic replicas of the leading line. The intense negative peak with shift by 23.5 meV in energy is close to the *TA* phonon.[12,13] The negative peak 33 meV away from the leading line, judging from all the foregoing, is its first *TO*-phonon replica. The structure of all the succeeding intense peaks duplicates physically the structure of the leading line. This demonstrates indirectly that they all are phonon replicas of the first line. Nonetheless, the situation in this region of the electroabsorption spectrum is less clear than at the photoabsorption edge.

The most reliable facts obtained as a result of measurements of the α_2 spectra in ZnSe⟨Ni⟩ are the following:

1) The amplitudes of the α_2 peaks in the interior of the photoabsorption band exceed the amplitudes of the peaks at the edge of this band by approximately 1–1.5 orders of magnitude.

2) The distinctive form of the leading line in the electroabsorption spectrum indicates that it is shifted by the electric field on the edge of the photoabsorption band and broadens in the interior of the photoabsorption band.

3) The structure of the peaks of high energies duplicates the structure of the leading line in all regions of the spectrum.

4) The amplitudes of the peaks of the *LO* phonon replicas is larger by 2.5 times than the amplitude of the peaks of the leading line on the edge of the photoabsorption band and are approximately equal to it in the interior of the this band.

5) The widths of the electroabsorption peaks in the interior of the photoabsorption bands are somewhat smaller than on its edge.

We assume that the different character of the spectra on the edge and in the interior of the photoabsorption band is due to the fact that in our experiment we observed two different types of exciton acceptor in the former case and donor in the latter case. To determine the nature of those differences it is necessary to consider the selection rules and calculate the oscillator strengths for two types of optical transitions. This, in turn, calls for knowledge of the wave functions of the initial and final states in reactions (1)–(4), which we now proceed to calculate.

WAVE FUNCTIONS OF DONOR AND ACCEPTOR EXCITONS

From the statements made in the introduction it is clear that excitons bound to transition-metal impurities differ from ordinary bound excitons primarily in that the packet made up of the Bloch waves of the conduction band or the valence band (electron or hole on a hydrogenlike orbit) is bound with a charged center having its own structure—an unfilled *d* shell with nonzero spin and orbital momenta. Therefore the problem of constructing the wave functions of such excitons cells for unification of the premises of the Kohn-Luttinger effective mass theory (EMT) and the multielectron theory of impurity 3*d* centers.

It must first be recalled how the multielectron wave function is constructed for the 3*d* shell of a transition-metal atom in a semiconductor matrix. It is shown in Ref. 14 that such a wave function can be constructed in accordance with the usual prescriptions of the crystal-field theory, but the initial single-electron Hartree basis must be chosen to be the functions

$$\begin{aligned}\psi_{\gamma\mu}(\mathbf{r})&=\psi_{d,\gamma\mu}(\mathbf{r})+\psi_{b,\gamma\mu}(\mathbf{r})\\&=A_\gamma^{-1/2}\left[\varphi_{\gamma\mu}(\mathbf{r})+\sum_{\mathbf{k}a}\frac{(\gamma\mu|U'|\mathbf{k}a)}{\varepsilon_{\mathbf{k}a}-\varepsilon_{i\gamma}}\varphi_{\mathbf{k}a}(\mathbf{r})\right],\\A_\gamma&=1+\sum_a M_a'(\varepsilon_{i\gamma}),\quad M_a'(\varepsilon_{i\gamma})=\sum_{\mathbf{k}}\frac{|(\gamma\mu|U'|\mathbf{k}a)|^2}{(\varepsilon_{\mathbf{k}a}-\varepsilon_{i\gamma})^2}.\end{aligned}\tag{5}$$

Here $\varphi_{\gamma\mu}$ are linear combinations of atomic 3*d* functions that transform in accordance with the line μ of the representation γ of the point group of the crystal, and are contained in the usual crystal-field theory ($\gamma = t_2, e$). The second term in the square bracket describes the distortion of the initial wave function, due to the admixture of bloch states φ_{ka} from different bands *a* of the superconductor. The hybridization matrix element contains the crystal field

$$U'(\mathbf{r})=\sum_{n\neq 0}V(\mathbf{r}-\mathbf{R}_n)$$

(substitutional impurities are considered). Hybridization with the band states renormalizes also the energy level ε_γ of the electron in the crystal field: the true single-electron level $\varepsilon_{i\gamma}$ is obtained from the equation

$$\varepsilon_{i\gamma}=\varepsilon_\gamma+\sum_{\mathbf{k}a}\frac{|(\gamma\mu|U'|\mathbf{k}a)|^2}{\varepsilon_{\mathbf{k}a}-\varepsilon_{i\gamma}}.\tag{6}$$

In the situation of interest to us the forbidden band contains single-electron Hartree levels $\varepsilon_{i\gamma}$ both for the ion $\tilde{d}^n$ and for the ion $\tilde{d}^{n+1}$ (the tilde indicates that the "pseudoion" states are constructed out of "swelling" wave functions of the type (5)). As to the level $\varepsilon_{i\gamma}$ for the ion $\tilde{d}^{n-1}$, it can be assumed that in the semiconductor ZnSe with rather narrow upper valence band ε_{3v} it turns out to be located in the broad gap betwen the bands ε_{3v} and ε_{2v}, being pushed out there by the hybridization interaction (see (6)) and lands thus in the region of the discrete spectrum of the crystal (Fig. 1). Its energy splitting is determined in this case mainly by the usual crystal field U', and the contribution of the hybridization to $\psi_{\gamma\mu}$ and $\varepsilon_{i\gamma}$ will be small compared with the configurations $\tilde{d}^{\,n}$ and $\tilde{d}^{\,n+1}$.

Multielectron wave functions for the configuration $\tilde{d}^{\,n}$ and $\tilde{d}^{\,n\pm1}$ are constructed in accordance with the usual scheme of the strong crystal field out of the cubic harmonics of $\tilde{d}^{\,n}$ and $\tilde{d}^{\,n\pm1}$ (5) with the aid of Clebsch-Gordan coefficients for point groups and the Racah fractional-parentage coefficients:

$$\Psi_{\Gamma M,SM_S}\{\tilde{d}^n\} = \sum_{\Gamma'M'S'M_S'} \sum_{\gamma\mu\sigma} G^{\Gamma S}_{\Gamma'S'} C^{\Gamma M}_{\Gamma'M'\gamma\mu} C^{SM_S}_{S'M'^1\!/_2\sigma} \Psi_{\Gamma'M'S'M_S'}\{\tilde{d}^{n-1}\}\psi_{\gamma\mu} \qquad (7)$$

(we disregard for the time being the spin-orbit interaction). Accordingly, the multielectron energies for the ions $\tilde{d}^{\,n}$ and $\tilde{d}^{\,n\pm1}$ are obtained from the Hartree energies $E(\tilde{t}_2{}^m\tilde{e}^{n-m})$ and $E(\tilde{t}_2{}^{m'}\tilde{e}^{n\pm1-m'})$ with allowance for the nonspherical part of the Coulomb interaction and exchange (which are described by the known Racah parameters A, B, and C).[15] In this case the crystal-field parameter $10\tilde{D}q$ contains besides the usual contribution also the hybridization renormalization[16] defined by Eq. (6).

The bound exciton is in essence an excited state of the ion $\tilde{d}^{\,n}$, in which either an electron was transferred to an outer hydrogenlike orbit (donor exciton $[\tilde{d}^{\,n}e]$), or a Coulomb hole of Bloch waves of the valence band is produced near the charged ions (acceptor exciton $[\tilde{d}^{\,n+1}h]$). To find its eigenfunctions and eigenenergies it is therefore necessary to go through a procedure similar to that described above. We shall demonstrate how this is done using the simpler example of a donor exciton. In contrast to the ground state (7), in this case there are $n-1$ equivalent electrons making up a $\tilde{d}^{\,n-1}$, configuration, to which is added one weakly localized electron on an outer orbit. To construct the correct n-electron wave function one can therefore use the fractional-parentage scheme

$$\Psi_\Lambda\{\tilde{d}^{n-1}e\} = \hat{A}\sum_\lambda C^{\Lambda}_{\Lambda'\lambda}\Psi_{\Lambda'}(r_1\ldots r_{n-1})\psi_\lambda^{(e)}(\mathbf{r}_n). \qquad (8)$$

The indices Λ and Λ' denote here the aggregate of the quantum numbers for the configurations $\tilde{d}^{\,n-1}e$ and $\tilde{d}^{\,n-1}$ respectively, ψ^e_λ is the wave function of the "hydrogenlike" electron, $C^{\Lambda}_{\Lambda'\lambda}$ are Clebsch-Gordan coefficients that reduce the direct product of the representations of the point group Λ' and λ and add up their spin vectors, and $\hat{A}$ is the antisymmetrization operator of the electron coordinates. The fractional-parentage scheme is constructed for a fixed state Λ' of the $\tilde{d}^{\,n-1}$ ion (as a rule, the ground state shown in Fig. 1 if there are no physical reasons for assuming that the creation or decay of the exciton is accompanied by excitation of inner electrons).

The wave function ψ^e_λ is calculated in the central-field approximation, the Hartree potential of which has the usual form of the effective-mass theory:

$$V_H(\mathbf{r}) = -e^2/\varepsilon r + V_{cc}(\mathbf{r}), \qquad (9)$$

i.e., it consists of the Coulomb substitution potential of the $\tilde{d}_{n-1}$ ion and corrections for the fact that the charge is not pointlike. These corrections are substantial only if the ion radius r_d is comparable with the radius of the orbit r_e of the donor electron. In the case of the ion $\tilde{d}^{\,n-1}$, as already mentioned, they can apparently be neglected. The solution of the problem is then well known and is of the form

$$\psi_\lambda(\mathbf{r}) = u_{c0}(\mathbf{r})A_{nlm}(\mathbf{r}); \qquad (10)$$

$u_{c0}(\mathbf{r})$ is the Bloch amplitude at the bottom of the conduction band, and A_{nlm} is the hydrogenlike envelope. The energy of the exciton in the Hartree approximation is

$$E^{(ex)}_\Lambda = E_{\Lambda'}(\tilde{d}^{n-1}) + \varepsilon_c - \varepsilon_n^{(e)}, \qquad (11)$$

where $\varepsilon_n^{(e)}$ is the Coulomb level of a shallow donor. Allowance for the noncentral Coulomb field and for the exchange interaction reduces the wave function to the form (8) and splits the terms $E^{(ex)}_\Lambda$ in accordance with the expansion of the direct product $\Lambda = \Lambda' \times \lambda$ into irreducible representations. In the concrete case of the Ni^{3+}(d^7) ion we have for the ground state of the electron on a hydrogenlike orbit $\Lambda' = {}^4A_2$, $\lambda = {}^2A_1$. If the spin-orbit interaction in the d shell is less than the Coulomb and exchange interactions between $\tilde{d}^{\,n-1}$ and e, the angular momenta add up in accordance with the LS scheme:

$$C^{\Lambda}_{\lambda'\lambda} = (2S+1)^{1/2}\left\langle\begin{matrix}0&1&1\\0&0&0\end{matrix}\right\rangle\begin{pmatrix}{}^3\!/_2&{}^1\!/_2&S\\M_S'&\sigma&-M_S\end{pmatrix}$$

(the notation in the 3Γ symbol for the point group T_d is taken in accordance with Ref. 17). As a result, the quantum numbers $\Lambda = \Gamma MSM_s$ correspond to two exciton levels ${}^{4\pm1}A_2$. Allowance for spin-orbit interaction leads to splitting of the quintet and to a shift of the triplet:

$${}^5A_2 \to E + T_1, \quad {}^3A_2 \to T_2.$$

The wave function of the acceptor exciton is sought in the form

$$\Psi_\Lambda\{\tilde{d}^{n+1}h\} = \hat{A}\sum_\lambda C^{\Lambda}_{\Lambda'\lambda}\Psi_{\Lambda'}(\mathbf{r}_1\ldots\mathbf{r}_{n+1})\psi_\lambda{}^h(\mathbf{r}_{n+2}). \qquad (12)$$

The indices Λ' and Λ correspond here respectively to the configurations $\tilde{d}^{\,n+1}$, $\tilde{d}^{\,n+1}\tilde{h}$; ψ^h_λ is the wave function of the hole, i.e., a superposition of Slater determinants for the valence band without one column that corresponds to the coordinate $\mathbf{r}_{n+2}$. In the case of nickel it is convenient to go over to hole notation and in the d shell we have ($\tilde{d}^{\,9} \to \tilde{d}^{\,*}$):

$$\Psi_\Lambda\{\tilde{d}^*h\} = \hat{A}\sum C^{\Lambda}_{\gamma\mu,\lambda}\psi_{\gamma\mu}{}^*(\mathbf{r}_1)\psi_\lambda{}^h(\mathbf{r}_2). \qquad (13)$$

In the case of an acceptor exciton allowance for the spin-orbit interaction becomes already of fundamental importance, at least as applied to ψ^h_λ, since the hole binding energy is $\varepsilon_n^{(h)} \ll \Delta$, where Δ is the Kane parameter of the spin-orbit interaction at the center of the Brillouin zone. Changing over to the effective-mass theory for holes, we have (see, e.g., Refs. 18 and 19)

$$\psi_\lambda{}^h(\mathbf{r}) = \sum_\mu u_{\gamma\mu,0}(\mathbf{r})A_{\gamma\mu}{}^\lambda(\mathbf{r}). \qquad (14)$$

Here $u_{\gamma\nu},{}_0$ are the components of the Bloch amplitude at the top of the valence band ($\gamma = \Gamma_s$), $A^{\lambda}_{\gamma\mu}$ are envelopes. The wave function of the ground state of the acceptor takes in the spherical approximation[18,19] the form

$$\begin{aligned}&\psi^{h}_{S^{3/2}}(\mathbf{r})=u_p(\mathbf{r})\,A_{S^{3/2}}(r),\\&A_{S^{3/2}}(r)=R_0(r)\,|0\,{}^3/_2\,{}^3/_2\,F_z)+R_2(r)\,|2\,{}^3/_2\,{}^3/_2\,F_z),\\&|l\,{}^3/_2\,F\,F_z)\\&=(2F+1)^{1/2}(-1)^{l-3/2+F_z}\sum_{m\sigma}\begin{pmatrix} l & {}^3/_2 & F\\ m & \sigma & -F_z\end{pmatrix}Y_{lm}(\Omega_{\mathbf{r}})\chi_\sigma.\end{aligned}\tag{15}$$

The $3j$ symbols correspond here to vector addition of the angular momentum l and of the effective spin $j=3/2$ to form the total angular momentum $F=3/2$ and $u_p(r)$ is the radial component of the Bloch amplitude. The functions $R_l(r)$ are determined by a system of two differential equations and can be obtained by a variational[19] or by a numerical[20] method. Allowance for the cubic terms in the EMT transforms the representation FF_z into $\Gamma_8 M$.

The influence of the spin-orbit interaction on the state of the "core" is much weaker, although it manifests itself in several places: in particular, in the single-electron function (5) it changes all the components of both terms in the square bracket. This question will be considered in greater detail separately, but for our present purposes it suffices to note that the ground-state term $d^*(t_2)$ splits, when account of V_{S_0} is taken, into $\Gamma_7+\Gamma_8$, so that among the states (13) that transform in accordance with the irreducible representations contained in $\Gamma_8\times\Gamma_7$ and $\Gamma_8\times\Gamma_8$, there are terms with arbitrary symmetry from A_1 to T_2.

SELECTION RULES AND PROBABILITIES OF OPTICAL TRANSITIONS

The selection rules for optical transitions with participation of bound excitons are dictated by the configurational quantum numbers $A\,(\tilde{d}^{\,n})$, $A'(\tilde{d}^{\,n-1}e)$ and $A'(\tilde{d}^{\,n+1}h)$, but the oscillator strengths are determined by the single-electron matrix elements, so the usual spectroscopic treatment is insufficient, and to obtain complete information it is necessary to calculate in explicit form the reduced matrix elements of the dipole operator.

We begin with calculation of the probability of the transition (3) with excitation of a donor exciton. If we disregard the fine structure of the spectrum, which is due to V_{S_0}, we have only one allowed transition ${}^3T_1(\tilde{d}^{\,8})\mapsto{}^3A_2(\tilde{d}^{\,7}e)$ for the excitation of the lower Lyman state of the bound exciton. We note that the fractional-parentage coefficients that connect the configuration ${}^4A_2(t_2^3e^4)$ with the states $A\,(t_2^m e^{8-m})$ impose very stringent restrictions on the possible reaction channels: e.g., transition with excitation of a ${}^3A_2$ exciton is possible only from the ground state of the ion $\tilde{d}^{\,8}$.

We reduce the matrix element of the dipole transition operator $\hat{D}$ to a single-particle reduced matrix element, using the fact that for the exciton wave function $\Psi(\tilde{d}^{\,n-1}e)$ the fractional-parentage scheme (8) is valid. Leaving out the spin quantum numbers with respect to which the transition is diagonal, we have

$$\begin{aligned}(\tilde{d}^n,\Gamma M\,|\,\hat{D}\,|\,\tilde{d}^{n-1}e,\Gamma'M')&=\sum_{M''\mu\mu_S}\left\langle\begin{matrix}\Gamma'' & \gamma\,\Gamma\\ M'' & \mu\,M\end{matrix}\right\rangle\left\langle\begin{matrix}\Gamma''' & \gamma_s & \Gamma'\\ M'' & \mu_s & M'\end{matrix}\right\rangle\\&\times[\Gamma]\,[\Gamma']\,G^{\Gamma S\,(\tilde{d}^n)}_{\Gamma'S'\,(\tilde{d}^{n-1})}(\gamma\mu\,|\,\hat{D}\,|\,\gamma_s\mu_s).\end{aligned}\tag{16}$$

Here $\Gamma''M''$ is the representation with respect to which the term of the configuration $\tilde{d}^{\,n-1}$ is transformed (in this case this is ${}^4A_2(t_2^3e^4)$), $\gamma_s\mu_s$ are the indices of the representation λ for the donor exciton ($\gamma_s=A_1$), $[\Gamma]$ is the dimensionality of the representation Γ. The fractional-parentage coefficient $G^{3T_1(d^8)}_{4A_2(d^7)}=1$ (see Ref. 17, Appendix 5). Using the Wigner–Eckart theorem and summing over the intermediate indices $M''\mu\mu_s$, we obtain

$$\begin{aligned}(\tilde{d}^n,\Gamma M|\hat{D}|\tilde{d}^{n-1}e,\Gamma'M')&=[\Gamma]\,[\Gamma']\,(-1)^{T_2+\Gamma+\Gamma'}\\&\times\sum_q\left\langle\begin{matrix}\Gamma'T_2\Gamma\\ M'qM\end{matrix}\right\rangle\left\{\begin{matrix}\Gamma'T_2\Gamma\\ \gamma\Gamma''\gamma_s\end{matrix}\right\}\ \langle\gamma_s\|D\|\gamma\rangle,\end{aligned}\tag{17}$$

where the curly brackets denote the 6Γ-coefficient.

It is known that the state ${}^3T_1(\tilde{d}^{\,8})$ in the field of a crystal of a Coulomb potential corresponds to the mixed configuration $5^{-1/2}(2t_2^4e^4-t^5e^3)$, but after the integration in (16) only the first term survives, so that $\gamma=T_2$. Although formally the selection rules for the symmetry allow the dipole transition $T_2\rightarrow A_1$, it is important in our case that the actually corresponding matrix element differs from zero only by virtue of the admixture, to the d states with $l=2$, of Bloch p-waves of different parity (cf. Ref. 16), i.e., owing to the presence of the "tail" ψ_b in (5). To calculate the reduced matrix it is convenient to expand the functions $\psi_b(\mathbf{r})$ and $\gamma_{\gamma s}(\mathbf{r})$ in the Kohn-Luttinger basis χ_{ka}:

$$\begin{aligned}&\psi_{b,\gamma\mu}(\mathbf{r})=\sum_{ka}F^{\gamma\mu}_{ka}\chi_{ka}(\mathbf{r}),\qquad\psi_{\gamma_s\mu_s}(\mathbf{r})=\sum_k A^{\gamma_s\mu_s}_{kc}\,\chi_{kc}(\mathbf{r}),\\&\chi_{ka}(\mathbf{r})=N^{-1/2}u_{0a}(\mathbf{r})\exp(-i\mathbf{kr}).\end{aligned}\tag{18}$$

The matrix element of the gradient operator then takes the form

$$(A_1|\nabla|T_2M)=\sum_{ka}F_{ka}A_{kc}(0c|\nabla-i\mathbf{k}|0a).\tag{19}$$

The wave function of the donor electron is well localized in k-space and is "tied" to the point Γ_c. For wave functions of a deep level, the one-band approximation is generally speaking incorrect but, as already noted by Keldysh,[21] their localization in j-space is preserved to a considerable degree (if there are no special reasons connected with symmetry.[22]), and in convolutions of the type (18) the use of the approximations of the $\mathbf{k{\cdot}p}$ theory is perfectly permissible. Then

$$(A_1\|\nabla\|T_2)\approx\sum_a\{(F_a|A_c)\,(0a|\boldsymbol{\nabla}_z|0c)+(F_a|\nabla_z|A_c)\,(0a|0c)\}.\tag{20}$$

$F_a(\mathbf{r})$ and $A_c(\mathbf{r})$ are the envelopes for the functions $\psi_{b},{}_{\tau\mu}$ and $\psi_{\gamma_s\mu_s}$. As shown in Ref. 23, the radial part of the envelope for the function ψ_b can be approximately written in the form

$$\begin{aligned}&F_a(r)=\left\{\frac{M_a'}{1+\sum_a M_a'}\right\}^{1/2}\varkappa_a^{1/2}\frac{\exp(-\varkappa_a r)}{r},\\&\varkappa_a=\frac{1}{\hbar}(2m_a^*|\varepsilon_{i,8}-\varepsilon_a|)^{1/2}.\end{aligned}\tag{21}$$

Here $\varepsilon_{i,8}$ is the energy of the deep level for the initial state $\tilde{d}^{\,8}$ of the reaction (3).

Assuming that the spectrum in the interior of the photoabsorption band is connected with a donor exciton, we must regard the level $\varepsilon_{i,8}$ as quite shallow ($\varepsilon_{i,8} - \varepsilon_v \approx 0.14$ eV). In the sum over a in (20) we can then leave only the valence bands. As a result

$$(A_1\| \nabla_z \| T_2) \approx \sum_v (F_v | A_c) \frac{m_0 P}{\hbar^2}. \qquad (22)$$

Here $P = m_0{}^{-1}\hbar^2(S\,|\,\nabla_z\,|Z\,)$ is a known matrix element that determines the Kane spectrum of the semiconductors.

Finally, for the transition probability we have

$$W\{{}^3T_1(d^8) \rightarrow {}^3A_2[\tilde{d}^7 e]\}$$
$$= \frac{(eE)^2 \hbar}{(m\omega)^2} [T_2]^{-1} |\langle A_1 \| \nabla \| T_2 \rangle|^2 \delta(\hbar\omega - E_{if}). \qquad (23)$$

The transition frequency is determined by the energy difference (4).

The procedure for calculating the probability of the optical transitions with excitation of an acceptor exciton with wave function (13), (15) is somewhat more cumbersome because of the spinor character of the basis functions and the abundant fine structure of the final state, due to the spin-orbit interaction and exchange in the $\tilde{d}\,{}^*h$ pair. Recognizing that in the experimental electroabsorption spectrum (Fig. 2) this structure is apparently not resolved, we estimate, for a qualitative comparison of the spectra of the two types, the transition probability in "integral" fashion, taking the wave functions of the initial and final states simply in the Hartree approximation. In this case in the state $\tilde{d}\,{}^{*2}(\tilde{d}\,{}^8)$, which as already mentioned is a superposition of functions of the type t_2^2 and t_2e, it is necessary to retain only the configuration t_2^2, just as in the case of a donor exciton, since in the final state the d-hole has the symmetry t_2.

To estimate the reduced matrix element we use the same approximation as in the case of the donor exciton [see Eqs. (20)–(22)]. It must be remembered here, however, that in this case the kernel ψ_d of the function (5) also contributes to the optical matrix element, and furthermore, the singly charged level $\varepsilon_{i,9}$ lies much deeper in the forbidden band than the neutral $\varepsilon_{i,8}$, therefore the wave function of the tail ψ_b is formed both by the valence bands and by the conduction band.

As a result we obtain

$$(\lambda_h \| \nabla \| T_2) = (\lambda_h \| \boldsymbol{\nabla} \| d) + (\lambda_h \| \nabla \| b),$$
$$(\lambda_h \| \nabla \| b) = \frac{m}{\hbar^2} \sum_v [(F_c | A_v) P + P_v], \qquad (24)$$
$$P_v = \frac{\hbar^2}{m_0} (F_v | \nabla_z | A_v).$$

The matrix element P_v was determined in analogy with the Kane parameter P, but its brackets contain in place of the Bloch amplitudes $u_{v,c}$ the envelopes of the impurity wave functions. For the transition probability we have an expression similar to (23), in which the irreducible matrix element and the frequency of the light are determined by Eqs. (24) and (1′), respectively.

DISCUSSION OF RESULTS

The theory constructed in the preceding section for donor and acceptor excitons enables us to analyze the electroabsorption spectra shown in Figs. 2 and 3, and argue that the second of them corresponds to optical transitions with excitation of donor excitons. It was already stated above that the position of the leading electroabsorption line in the interior of the photoabsorption spectrum ($\hbar\omega = 2.64$ eV) cannot be ascribed to a transition into an excited state of an exciton $[d^9 h]$, since this assumption does not fit the well known structure of the energy levels of the ion d^9 (see Fig. 1). Furthermore, a transition into the excited state should give braoder lines in the spectrum than a transition to the ground state, whereas in experiment the picture observed is reversed. If, however, we assume that the 2.64-eV line corresponds to the transition $\tilde{d}\,{}^8 \rightarrow [d^7 e]$, then the level $\varepsilon_{i,8}$ turns out to be much shallower than the level $\varepsilon_{i,9}$: $\varepsilon_{i,8} - \varepsilon_v \approx 0.14$ eV, $\varepsilon_{i,9} - \varepsilon_v = 1.85$ eV. This circumstance explains the most striking difference between the electroabsorption spectra on the edge and in the interior of the photoabsorption band—giant increase of the amplitude of the peaks in second case compared with the first.

It is known that this enhancement is observed in the case of transitions with participation of bound excitons compared with free ones. Rashba and Gurgenishvili[4] attributed this fact to the greater smearing of the envelope for the bound exciton, which increases the amplitude of the interaction of the exciton with the light field (the "antenna effect"). A peculiar antenna effect acts also in our case, but the interaction with the electromagnetic field involves not only weakly localized wave functions of donor and acceptor electrons on the outer shells, but also the swelling shells of the impurity core. Indeed, the values of the reduced matrix elements in (23) for the transition probability are determined principally by the degree of overlap of the wave function of the electrons in the d shell and on the hydrogenlike orbit, but it is precisely with respect to this degree of overlap that the donor and acceptor excitons in ZnSe:Ni differ.

In the case of a donor exciton we have for the envelopes (21) and (10)

$$(F_v | A_c) = \left[\frac{M_v'(\varepsilon_{i,8})}{1 + \sum_a M_a'(\varepsilon_{i,8})} \right]^{1/2} \left(\frac{r_v}{r_d} \right)^{3/2}, \qquad (25)$$

where r_d is the radius of the orbit of the donor electron, $r_v = \varkappa_v^{-1}$ is the radius of the Bloch component of the tail, a component connected with the band v, and the factor $M'(1 + \Sigma M')^{-1}$ determines the contribution of this component to the wave function. In the calculation of the corresponding factor for the acceptor exciton one must bear in mind a circumstance noted in Ref. 22: the vicinity of the point Γ_c makes practically no contribution to the envelope F_c, since the density of states at the bottom of the conduction band is low and hybridization at the center of the Briollouin zone is symmetry-forbidden so that for the Bloch component of the wave function of the impurity electron the effective forbidden band is in fact the distance between the points Γ_v

and L_c in the Brillouin zone. Thus, the level $\varepsilon_{i,9}$ reckoned from the bottom of the conduction band turns out to be quite deep, and to estimate the wave-function radius we can use $r_c = \hbar[2m_0(\varepsilon_{L_c} - \varepsilon_{i,9}]^{1/2}$, where m_0 is the free mass. For the acceptor envelope (15) there are unfortunately no analytic expressions, but in the calculation of the overlap integral with a strongly localized function $F_c(r)$ we can use for the radial function $R_0(r)$ the expression[20]

$$R_0(r)=2\varkappa_{hh}{}^{3/2}J^{-1/2}\exp(-\varkappa_{hh}r), \quad J=\int(|R_0|^2+|R_2|^2)r^2\,dr, \tag{26}$$

where $r_{hh} = \hbar^2\varepsilon/m_{hh}{}^*e^2$ is the radius of its central part and is determined by the effective mass of the heavy hole. The contribution to the integral from R_2 can at any rate be neglected, inasmuch as in the localization region of $F_c(r)$ we have $R_2 \sim r$, so that $R_2(r) \ll R_0(r)$ at $r < r_c$. Then

$$(F_c|A_v)\approx[M_c'(\varepsilon_{i,9})/J\{1+M_c'(\varepsilon_{i,9})\}]^{1/2}(r_c/r_{hh})^{3/2}. \tag{27}$$

The function $M_a'(\varepsilon_i)$ in the approximation $(\gamma\mu|U'|ka) = \text{const}$ is the derivative of the Hilbert transform of the state density taken with opposite sign. For arguments its behavior is known:

$$M_a'(\varepsilon_i)\sim m_a{}^{*3/2}\varepsilon_i{}^{-1/2} \quad \text{at} \quad \varepsilon_i/\varepsilon_B\ll 1, \tag{28}$$

where ε_B is the width of the allowed band.

The matrix elements $(\lambda_h\|\nabla\|b)$ in (24) can be estimated as $\sim m_0P\hbar^{-2}(r_d/r_{hh})^{3/2}$, i.e., as the "atomic" matrix element multiplied by the degree of overlap of the atomic and acceptor wave functions. It can be seen that they can be neglected compared with (27). Finally, the matrix element P_v can be estimated at $P(r_a/r_{hh})$, where r_a is of the order of the radius of the Wannier functions for semiconductor bands and is discarded under the condition $r_a \ll r_c$.

With account taken of all these relations, we obtain the following estimate for the ratio of the probabilities for the excitation of the donor and acceptor excitons:

$$\alpha=\frac{W\{\tilde{d}^8\to[d^7e]\}}{W\{\tilde{d}^9\to[\tilde{d}^9h]\}}\sim\left(\frac{\varepsilon_{L_c}-\varepsilon_{i,9}}{\varepsilon_{i,8}-\varepsilon_v}\right)^2\left(\frac{m_c^*}{m_{hh}^*}\right)^3. \tag{29}$$

With respect to the values of the parameters ε_{L_c} and m_{hh} the published data are contradictory but, using the latest experimental estimates[25] for the parameters $m_c^* = 0.16m_0$, $m_{hh}{}^* = 0.29m_0$) of the band structure of ZnSe and choosing for the positions of the levels $\varepsilon_{i,8}$ and $\varepsilon_{i,9}$ the values 0.14 and 3 eV respectively, we find that the gain is $\alpha \approx 80$. Taking into consideration the roughness of the approximations made when describing the acceptor exciton, this estimate can be regarded only as qualitative. Nonetheless we assume that in principle it explains the mechanism whereby the intensity of the optical transitions is increased in the case of donor excitons.

The fact that the absorption lines in the interior of the photoexcitation band in a strong electric field broaden, and the lines on the edge of the photoexcitation band only shift, can also be explained by assuming that there are different types of excitons corresponding to these lines, but this difference is due not to the "inner" d shells, for which these fields are too weak, but the outer hydrogenlike electrons (holes). Since the donor level in ZnSe is much shallower than the acceptor level (30 and 100–120 meV, respectively), in a field $F \approx 40$ kV/cm the second of them undergoes only a Stark shift, whereas for the first there can take place a noticeable tunnel ionization. Indeed, if we use for the estimate of the probability of such an ionization the elementary quasiclassical formula

$$W_{ion}\sim\hbar^{-1}\lambda\,\mathrm{Ry}^*\exp(-2\lambda/3),$$

where $\lambda = Ry^*/eFr_a$, Ry^* is the effective Rydberg, r_a is the radius of the wave function, and F is the intensity of the electric field, we obtain for a donor exciton $\lambda \cong 2$ at $F = 40$ kV/cm, so that the level acquires an appreciable width. No quantitative theory of ionization in strong electric fields has yet been developed for acceptor levels, but an estimate can be obtained with the aid of the same quasiclassical formula. If it is recalled that Ry* for an acceptor is determined principally by the heavy mass m_{hh}, and the wave-function asymptotic value that governs the tunnel integral is determined by the light mass $m_{eh}{}^* \approx m_c^*$ (Refs. 18–20), it can be seen that in one and the same field F the ionization probability of the acceptor exciton is smaller by a factor $\exp(-m_{hh}/m_{eh})$ than the probability of ionization of the donor exciton, although allowance for the corrections for the central cell can decrease this estimate somewhat.

Thus, on the basis of the arguments presented in this section it can be stated that the line width $\hbar\omega = 2.64$ eV in the interior of the photoabsorption band corresponds to a spin-allowed transition $\tilde{d}^8(^3T_1)\to\tilde{d}^7e(^3A_2)$ with formation of a donor exciton. The absence of noticeable electroabsorption lines that are not phonon replicas of the leading line points to weakness of the spin-orbit interaction in this case.

As for the phonon replicas of the electroabsorption lines, for their unambiguous interpretation it is necessary to know what part of the exciton wave function contributes mainly to the exciton-lattice interaction—the "swelling" $\tilde{d}$ core or the hydrogenlike envelope. To answer this question, a microscopic theory must be developed for multiphonon optical transitions from deep d levels, in addition to the already existing symmetry premises that use effective phenomenological Hamiltonians. The development of such a theory is a task for the nearest future.

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