Spectroscopy of donor-acceptor pairs in nitrogen-doped ZnSe

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Selective photoluminescence of donor-acceptor pairs (DAP) is used to study the compensating donors in p-type ZnSe layers grown by molecular-beam epitaxy and doped with nitrogen produced by rf plasma. More than 13 lines are identified in the energy range of optical phonons. We demonstrate that the dominant features are associated with local modes of nitrogen bound phonons. The transitions involving a shallow donor with a binding energy of 29.1 ± 0.1 meV are also evidenced. This donor has never been reported before, and, contrary to what it is generally believed, it is not one of the residual impurities usually found in nonintentionally doped layers. Finally, two lines are ascribed to the resonant DAP photoneutralization in the $n=2$ states of a deep donor. The deep-donor ionization energy is then precisely determined as 45.2 ± 0.3 meV. [S0163-1829(96)05432-X]

I. INTRODUCTION

The difficulty of achieving p-type doping of ZnSe has long been a barrier to the fabrication of optoelectronic devices. Indeed, the first ZnSe-based injection blue laser was only demonstrated in 1991.[1] In this laser structure, the successful p-type doping was obtained with nitrogen produced in a plasma discharge.[2,3] Actually, nitrogen still appears as the most convenient dopant, although the hole concentration seems to saturate, in the best case, around 10^{18} cm^{-3}. This upper limit indicates that some compensation mechanisms occur, which is confirmed by a N concentration often several times higher than the effective doping level (N_a-N_d).

Many theoretical models have been proposed in order to explain the carrier compensation[4] such as: bond breaking, solubility limit, native defects, and impurity-associated defects. Although different mechanisms may participate in the compensation process, experimental results agree well with the N-associated defect models. The most evident illustration is provided by the two donor-acceptor pair (DAP) series, usually and reproducibly present in the low-temperature photoluminescence (PL) spectra. As shown by temperature-dependent PL spectroscopy studies, these two series involve the same acceptor level and, thus, two donor species:[5] a shallow donor (D^s) generally ascribed to residual dopants and a deep donor (D^d) attributed to a complex involving N. This assignment is based on the fact that the higher the nitrogen content is, the stronger D^dAP bands are.

However, if the existence of the deep donor is clearly established, there are no available data concerning its electronic structure. For instance, the deep-donor ionization energy is still unsettled, the estimations ranging from 43 to 57 meV.[5–8] Moreover, although attributed to residual dopants, the nature of the shallow donor is also to be specified.

The aim of this paper is to present a thorough investigation on both donors. This work is performed by selective photoluminescence (SPL) on two samples with moderate effective doping levels, but very different N contents. Indeed, whereas the low-temperature PL spectrum of the former is dominated by the nitrogen bound exciton and displays only weak D^dAP bands, the later shows only the D^dAP series.

Before a description of the studied samples and the experimental setup (Sec. III), the principle of SPL applied to the current study will be briefly presented in Sec. II. The selectively excited photoluminescence spectra recorded from 15 to 45 meV below the laser excitation energy appear to be rich in transitions, since up to thirteen lines are detected in this energy range. The excited states of the dominant shallow donor are easily identifiable (Sec. IV A). Quite surprisingly, their associated transition energies correspond to a 29.1-meV donor still unknown in the literature and, moreover, not present in the undoped material. However it is not clear, at this time, whether this donor is related to a residual species introduced with nitrogen or due to the formation of nitrogen-associated complex defects. The other lines necessitate a more detailed examination. Indeed, it appears that the dominant lines, located in the TO to LO range, are the fine structure of acceptor-bound phonons. This assignment is realized, in the Sec. IV B, via the theoretical model of Kanehisa, Petritis, and Balkanski (KPB model).[9] In addition, the influence of the interaction between close DAP's on the acceptor-bound phonon energies is, to the best of our knowledge, observed for the first time. The interaction induced energy shifts are measured and are in agreement with a zero-order approximation of the KPB theory. A donor-bound phonon line is also present, which implies a donor with an ionization energy much higher than the usual substitutional donors in ZnSe. Finally, we identify the transitions between the $n=2$ and the ground states of the deep donor (Sec. IV C 4). The effective-mass model, supported by the measured transition energies, gives a definitive ionization energy of 45.2 meV for the deep donor.

II. GENERAL CONSIDERATIONS

Although SPL and PLE on donor-acceptor pairs have already provided a detailed knowledge of acceptors states in II-VI semiconductors like CdTe,[10] ZnTe,[11,12] and ZnSe,[13–16] the literature is scarce concerning their application to the donor spectroscopy in direct band-gap semiconductors. In-

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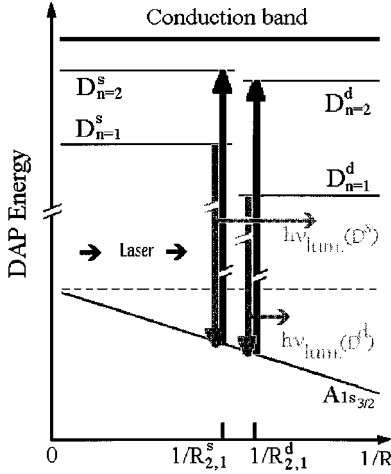

FIG. 1. Schematic diagram showing the resonant excitation of deep- and shallow-donor-acceptor pairs (black arrow), the neutralized donors are in an excited state and the hole in the acceptor ground state. The recombination lines are represented by gray arrows. Ionization energies were taken as 26 (hydrogenlike donor) and 50 meV.

deed, the so-called ''two-electrons transitions'' (TET) spectroscopy seems to have been more appropriate and accurate for bulk ZnSe.[17–20] However, its utilization for impurity studies in ZnSe epilayers grown on GaAs substrates is more problematic. Indeed, the difference in the thermal-expansion coefficients of the two materials gives rise to residual strains, which split impurity bound excitons.[21] In addition, the interest in TET is still reduced further in the case of high impurity content, which strongly broadens the spectral lines.

In contrast, the implementation of SPL and PLE on donor-acceptor pairs appears to be a more suitable technique for the study of donor species introduced during nitrogen p-type doping of heavily compensated ZnSe epilayers. The present study will be principally based on SPL results. Although SPL has already been described in detail in previous papers involving acceptors characterization in bulk ZnSe,[22] its principle will be briefly presented and applied to this work where both shallow and deep donors have to be considered.

As shown on Fig. 1, an incident pump photon with energy $E_{\rm exc}$ creates a neutral excited (shallow or deep) donor-acceptor pair (D_i, A_j), with the electron and the hole in the respective i and j excited states, at a particular pair separation $R_{i,j}$ given by

$$E_{\rm exc}=E_g-E(A_j)-E(D_i)+\frac{e^2}{\varepsilon R_{i,j}}+J_{i,j}(R_{i,j}), \quad (2.1)$$

where E_g is the band gap energy, ε is the static dielectric constant, $E(A_j)$ and $E(D_i)$ are the binding energies of the acceptor and donor excited states, respectively. The interaction term $J_{i,j}(R_{i,j})$ is a correction to the Coulomb effect $e^2/\varepsilon R_{i,j}$, which takes into account the overlap of the excited-donor and acceptor wave functions, which is not more negligible for small R values.

After the D_iA_jP formation, the electron and the hole thermalize quickly into the impurity ground states before recombination giving rise to a sharp resonance line on the SPL spectrum at energy $E_{\rm lum}$:

$$E_{\rm lum}=E_g-E(A_{1S_{3/2}})-E(D_{1S})+\frac{e^2}{\varepsilon R_{i,j}}+J_{1,1}(R_{i,j}). \quad (2.2)$$

Thus, the transition energy between donor and/or acceptor excited and ground states corrected by the amount $J_{i,j}(R)-J_{1,1}(R)$ matches the energy difference $E_{\rm exc}-E_{\rm lum}$:

$$E_{\rm exc}-E_{\rm lum}=E(D_{1S})-E(D_i)+E(A_{1S_{3/2}})-E(A_j)+J_{i,j}(R_{i,j})-J_{1,1}(R_{i,j}). \quad (2.3)$$

Such a mechanism may take place for several R values and, subsequently, each excited level i,j is likely to produce a resonance peak on the background spectrum. Hence, the spectral signature of the impurities can be obtained using this approach. Taking into account that the donor Bohr radii are generally larger than those of acceptors, the interaction energy difference $\Delta J_j(R)=J_{1,j}(R)-J_{1,1}(R)$ are large for acceptors[23] and often imperceptible in the case of donors.

In addition to purely electronic processes, interactions with phonons (or combinations of phonons) may also occur during the neutralization or recombination of donor-acceptor pairs. In this case, the energy difference between excitation and luminescence is exactly the optical-phonon energy $\hbar\omega_{\rm ph}$ without any R dependence:

$$E_{\rm exc}-E_{\rm lum}=\hbar\omega_{\rm ph}. \quad (2.4)$$

Finally, the possible emission of local phonon modes in the vicinity of impurities has also to be taken into account.[24] The binding energies of these quasiparticle states are strictly subjected to the impurity electronic spectra[25] and consequently may be affected by the interimpurity distances, i.e., via $J(R)$.

The preceding considerations indicate that not only donor states but also bound and free optical phonons are expected in the spectral range extending from 18 meV ($1S\rightarrow 2P$ transition energy of the hydrogenic donor) to about 40 meV. This explains why a careful inspection of SPL spectra is needed in order to perform a reliable identification of donor levels.

III. EXPERIMENTAL SETUP AND SAMPLES

The selectively excited PL spectra were carried out at 2 K, the samples being placed in a He-immersion cryostat. The samples were irradiated with a monochromatic light (FWHM $\approx$0.05 meV) from a tunable Stilbene-3 dye laser pumped by the UV lines of a cw Ar-ion laser. PL was dispersed by a 1.0-m focal-length double additive monochromator equipped with 1800 grooves/cm holographic gratings blazed at 400 nm, and detected by a CO_2-cooled photomultiplier. For ordinary PL measurements at 9 K, the excitation light was provided by the 325-nm line of a He-Cd laser and a 64-cm spectrometer was used.

The samples were grown by elemental solid-source

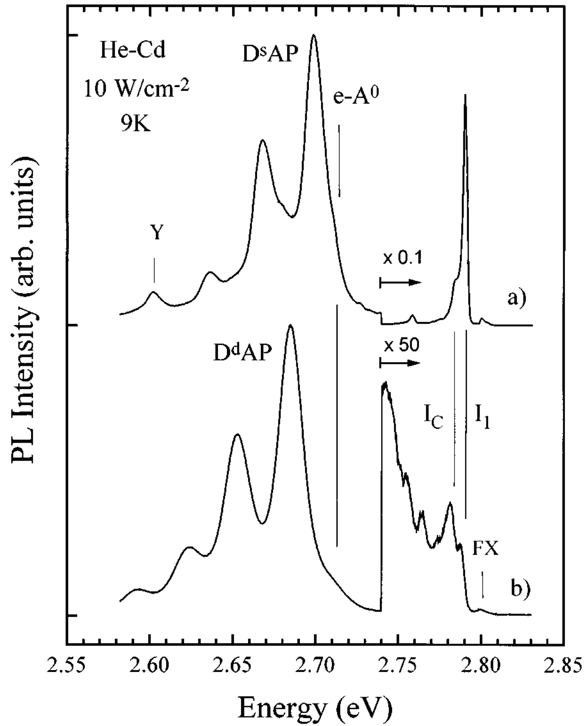

FIG. 2. PL spectra recorded at 9 K for sample 026 (a) and 041 (b). The 325-nm laser excitation intensity is 10 W/cm^2.

molecular-beam epitaxy (MBE) directly on n^+-GaAs (100) substrates without any ZnSe buffer layer. Nitrogen doping was performed using an Oxford Applied Research CARS 25 rf plasma source operating in the high brightness mode. During the growth, the substrate temperature was 280 °C and the Se/Zn flux ratio was ~2–3, i.e., a 2×1 Se-stabilized reconstruction was barely visible by *in situ* reflection high-energy electron diffraction.

Two N-doped samples (Nos. 026 and 041) and one reference-undoped sample (No. 019) were investigated. Their respective thicknesses are 1.5, 3.5, and 2.2 μm. The net carrier concentrations (N_a-N_d) of the doped samples, as determined by capacitance voltage measurements at room temperature, are 1.5×10^{16} cm^{-3} (026) and 7×10^{15} cm^{-3} (041), whereas the residual doping for the 019 epilayer is n type with an effective doping level of 6×10^{14} cm^{-3}. Although the effective doping level of sample 041 is two times lower than that of the lightly doped 026 sample, its PL spectrum [Fig. 2(b)] reveals that its nitrogen content is on the contrary much higher. Indeed, whereas PL spectra of lightly doped ZnSe epilayers are usually dominated by the N-acceptor-bound exciton I_1 and show a weak D^dAP band, the near band edge of overcompensated samples vanishes so that their PL spectra only exhibit the D^dAP band.[26,27] Note also, for sample 041, the increase of the intensity ratio between the I_C and the I_1 peaks. Although the origin of the I_c peak is not yet clearly established, the relative increase of this ratio is generally observed for the highest N concentrations.[5,28]

Concerning the reference-sample 019, its very low impurity background level is also attested by PL. Indeed, the near band edge of its PL spectrum, displayed in Ref. 29, exhibits sharp free exciton, the intensity of which is more than four times stronger than that of the donor-bound exciton I_2. In addition, Y and I_v peaks are clearly visible. Both peaks which are reported to be related to extended defects are expected to be stronger in pure ZnSe material grown on GaAs.[15]

IV. EXPERIMENTAL RESULTS AND DISCUSSIONS

Two SPL spectra of the most compensated sample (No. 041) are shown in Fig. 3. One of them concerns close DAP and displays well-defined transitions in the low-energy range [Fig. 3(i)]. The other, recorded for distant DAP, shows some resonances at higher energies [Fig. 3(ii)]. In fact, the relative intensity of features observed on the SPL spectra can change depending on the nitrogen content and the excitation spectral range. However, as shown on Fig. 4, the spectral position of the lines is sufficiently stable to permit a step-by-step identification.

This figure shows, for both N-doped samples, the resonant transitions displayed on SPL spectra of different experiments with excitation energies tuned from 2.69 eV, in the D^dAP band, to the neutral acceptor bound exciton I_1 at 2.789 eV. Such a presentation is helpful in distinguishing the transitions related to the donor-acceptor distances. The Table I gives a compilation of the different lines with their assignments which will be discussed in the following, starting with those related to the shallow donor.

A. Shallow donor

1. Properties

As expected, the first resonance (a peak on Fig. 3), located at 22.5_8 meV under the excitation energy, is related to the shallow donor D^S mainly present in the samples. Although the first excited state in SPL and PLE spectra of ZnSe or ZnTe bulk material[11,13] was often attributed to a DAP neutralization process in the $2S$ state of donors, more recent magnetoluminescence experiments on nitrogen-doped ZnSe epilayers indicate the actual predominance of D_{2P}-related transitions in SPL spectra,[30] so we attribute the a peak to this transition.

By setting the binding energy $E_D^0=26.0_6+0.15$ meV for the hydrogenic donor,[18,19] a binding energy $E_{D^S}=29.1\pm0.1$ meV is obtained for the considered donor, by simply adding the effective-mass binding energy of the $2P$ level ($E_{2P}^0=6.52\pm0.05$ meV deduced from $E_{nP}^0=E_D^0/n^2$), which is independent on the donor central-cell correction χ (chemical shift), because of the p-state wave-function symmetry. The calculated $1S\rightarrow3P$ transition energy $E_{1S\rightarrow3P}=26.2\pm0.1$ meV is found to be in excellent agreement with the occurrence of the b peak on SPL spectra [Figs. 3(i) and 4]. It should be noted that the $1S\rightarrow4P$ transition, expected at 27.5 meV, is also detected on some spectra of the sample 026 [Fig. 4(b)]. The deduced central-cell correction value ($\chi=3.1\pm$ meV) can be used to estimate the $2S$-$2P$ splitting, which is supposed to be $\chi/8$. The broadening that we often observe on the low-energy side of the $2P$ resonance (a peak) could be satisfactorily explained as induced by the $1S$-$2S$ transition which is not resolved because of the small 0.4-meV $2S$-$2P$ splitting.

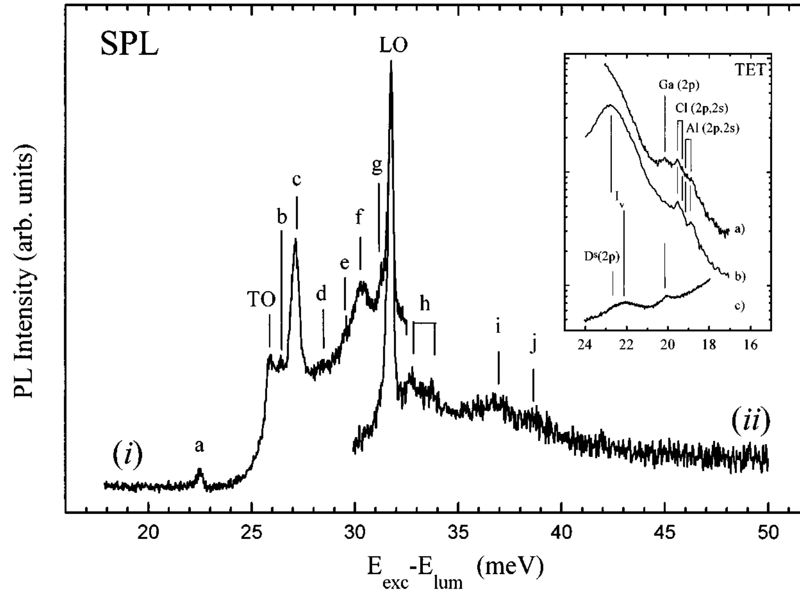

FIG. 3. 2-K selective photoluminescence (SPL) spectra of nitrogen-acceptor related DAP bands of the 041 sample. The laser is tuned at (*i*) 2.775 eV and (*ii*) 2.7065 eV. The inset shows SPL spectra recorded in two-electron transition (TET) spectral range. (a) and (b) display the 019 undoped layer spectra resonantly excited at 2.7967_2 and 2.7970_9 eV, respectively. (c) is the TET spectrum of the 026 N-doped layer excited at 2.7966_8 eV. The measured donor $1S$-$2S$ and $1S$-$2P$ transition energies are, respectively, 18.9_0 and 19.1_6 meV for Al and 19.3_5 and 19.5_6 meV for Cl. The $1S$-$2P$ transition of the Ga donor is found at 20.15 meV. Note that no shift is experimentally detected for the residual impurity transitions in the undoped and the N-doped epilayers compared to that measured in bulk material, which reveals that neither the residual thermal strain nor the nitrogen incorporation affect the binding energies. The horizontal axis gives the energy difference between photoluminescence and excitation.

2. Chemical nature

The existence of a donor with an ionization energy of 29.1 meV being established, the question now arises of its origin and of its chemical nature. In the inset of Fig. 3, TET spectra of undoped and N-doped samples are compared. A resonant excitation of the donor-bound exciton I_2 gives rise to several replica of I_2 shifted by the donor ground to excited states transition energies. In undoped materials, the $1S\rightarrow 2P$ and $1S\rightarrow 2S$ I_2 replica are superimposed on the high-energy side of the I_v line,[31] which are found to be the TET structures of the shallow Ga_{Zn}, Cl_{Se}, and Al_{Zn} donors.[17–19] However, there is no trace, either on SPL or on PLE spectra, of the donor previously characterized in doped samples.

In N-doped ZnSe, the only residual impurity discerned with TET spectroscopy is Ga [Inset of Fig. 3(c)]. It is already known that in thin epilayers deposited on GaAs, interdiffusion effects at the heterointerface boosts the Ga manifestation.[30] As the Ga donor associated signal is always

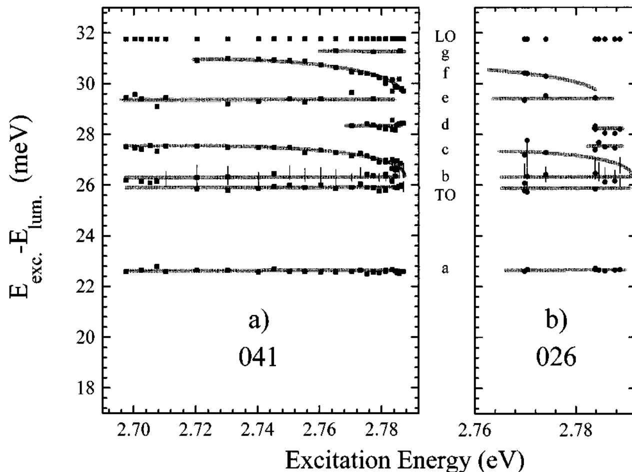

FIG. 4. Plot of the energy difference between the laser excitation light and the resonantly excited DAP recombination lines in samples 041 (a) and 026 (b). The gray lines are guides for the eyes.

TABLE I. Labels, energy separations from the laser line and assignment of the different lines detected in the SPL spectra. The accuracy is better than ±0.1 meV, except when only one digit is given. In this case, the precision is ±0.3 meV. The origin of the *d* line is not yet explained. However, as it is only observed for laser excitation energies in the exciton range, it could arise from exciton-phonon coupling. The asterisk denotes $R_{D,A}$ dependence.

Label	Position energy (meV)	Assignment
a	22.5_8	D^s:$1S\rightarrow 2P$
TO	25.9_3	TO phonon
b	26.3_0	D^s:$1S\rightarrow 3P$
c	27.5*	N-bound phonon (K=3, $2P_{3/2}$)
d	28.2	
e	29.4	D^d-bound phonon ($2P$)
f	31.0*	N-bound phonon (K=3, $2P_{5/2}$)
g	31.3*	N-bound phonon (K=4)
LO	31.7_6	LO phonon
h	33*	close pair splitting of N: $1S_{3/2}$
i	36.7	D^d:$1S\rightarrow 2S$
j	38.7	D^d:$1S\rightarrow 2P$

absent on SPL spectra of DAP, one has to conclude that the Ga residual concentration is low compared to that of the 29.1-meV donor. Among the known donors in ZnSe, few have so a high binding energy. To our knowledge, the only one mentioned in the literature ($E_{1S\rightarrow 2P}$=23.95 meV) was tentatively attributed to iodine, since it has been detected in homoepitaxial samples grown on highly iodine-doped substrates.[20]

In any case, it can be concluded that the 29.1 meV unknown donor is introduced during the N doping of the layers. However, a tentative attribution to a N-associated defect giving rise to a shallow donor is still hazardous. Indeed, it should be mentioned that our results are quite different from those of Albert *et al.*,[30] who recently pointed out the presence, in less doped samples, of an unknown shallow donor, the $1S\rightarrow 2P$ transition energy of which is 20.25 meV, i.e., lower than the value of 22.5_8 obtained with our samples. At this stage, it is impossible to obtain a definitive donor identification. One of the donors ($E_{1S\rightarrow 2P}$=20.25 or 22.5_8 meV), or both could originate from either unidentified impurities carried with N or from N-related defect formed during the doping.

B. Acceptor-bound phonons

Between TO and LO, two lines labeled c and f in Figs. 3(i) and Fig. 4, present a similar behavior and will be discussed together. Not only does the intensity ratio of c and f with respect to that of the optical phonons increase with the nitrogen content, but also their energies are slightly modified for short donor-acceptor distances.

An interpretation of c and f in terms of excited $2P(2S)$ and $3P(3S)$ states of a third residual donor is unconvincing. Indeed, the ionization energy of this donor would be about 34–35 meV and should then give rise to a DAP band in the PL spectra, which is not observed. Moreover, since the shift of D^s_{2P} and D^s_{3P} states is almost indiscernible at high excitation energies, i.e., for the nearest D^sAP, an energy displacement of about 1 meV for both lines is inconceivable for a deeper donor, since a reduction of the donor-acceptor wave function overlap is expected. On the other hand, c and f cannot be attributed to transitions between acceptor states, because such an acceptor would have too small a binding energy. In fact, with transition energies lying between TO and LO, the c and f lines could better agree with a fine structure of an impurity-bound phonon. Indeed, (i) this quasiparticle is known to be easily seen in polar II-VI semiconductors,[10,11,32,33] and (ii) the binding of phonons to impurities is possible as soon as the relevant impurity transition energies are larger than the LO-phonon energy.[24] In our samples, both the neutral N acceptor and the deep donor could bind phonons.

Impurity-bound phonons were first observed and modeled by Dean, Manchon, and Hopfield,[24] who pointed out that neutral donors could provide an effective attractive interaction for the LO phonons in GaP. For a given donor impurity, their approach predicts as many bound phonons as allowed transitions between the levels of the impurity, with binding energies directly depending on the involved impurity excited states.

The impurity-bound phonon theory has recently been reformulated in a more general case for cubic semiconductors by Kanehisa, Petritis, and Balkanski (KPB model),[9] who took into account the valence-band degeneracy, thus allowing one to deal with the acceptor-bound phonons. By considering the total Hamiltonian, sum of the LO phonon, the impurity hole and the Fröhlich-type interaction Hamiltonians, they show that the problem is reduced to solving an algebraic eigenvalue equation:

$$\sum_j S_{ij}\chi_{j\lambda}=E_\lambda \chi_{i\lambda}\,, \tag{3.1}$$

where i and j are the impurity electronic states, E_λ the binding energy of the λth bound phonon, and S_{ij} the scattering matrix elements equal to

$$S_{ij}=\left(\frac{\varepsilon_0}{\varepsilon_\infty}-1\right)D_iD_jX_{ij} \tag{3.2}$$

X_{ij} is the exchange integral among impurity-hole wave functions:

$$X_{ij}=\langle 0i|\frac{e^2}{\varepsilon_0|\mathbf{r}_1-\mathbf{r}_2|}|0j\rangle, \tag{3.3}$$

and D_i the resonance denominator

$$D_i=\left(\frac{(e_i-e_0)\hbar\omega_0}{(e_i-e_0)^2-(\hbar\omega_0)^2}\right)^{1/2}. \tag{3.4}$$

(e_i-e_0) is the transition energy between the i excited state and the ground state of the acceptor, $|i\rangle$ and $|0\rangle$ are the associated-state wave functions. The problem dimension is reduced by considering a spherical model derived from the Lipari and Baldereschi formalism[34] for the acceptor states, and considering that observable bound phonons are mainly associated with $1S_{F_0=3/2}\rightarrow 2P_{F=1/2,3/2,5/2}$ transitions, the matrix elements of which are dominant. Here, $\mathbf{F}=\mathbf{L}+\mathbf{J}$ is the total angular momentum. By introducing the total angular momentum change

$$\mathbf{K}=\mathbf{F}+\mathbf{F}_0, \tag{3.5}$$

the 48×48 scattering matrix can be block diagonalized.

Since F_0 is fixed to be $\frac{3}{2}$, $F=\frac{1}{2}$ gives $K=1$, 2, $F=\frac{3}{2}$ gives $K=0$, 1, 2, 3, and $F=\frac{5}{2}$ gives $K=1$, 2, 3, 4. In fact, only the two-dimensional $K=3$ block and the scalar $K=4$ block can give rise to discernible features in the SPL spectra.

For the numerical results, we kept the Luttinger parameters of Lawaetz.[35] Although this choice could be discussed with regard to the large set of parameters proposed in the literature,[36] these valence-band parameters give, in the spherical model, excited-state energies fairly close to experimental value given in Ref. 37 [$E_{1S_{3/2}}$=110.0 meV, $E_{2P_{3/2}}$=48.5 meV, and $E_{2P_{5/2}}$=28.0 meV to be compared with 111.3, 43.5, and 31.9 (Γ_8) meV, respectively]. Hence, reasonable values for the resonance denominators [Eqs. (3.4)] can be expected. It is the same for the exchange integral elements [Eqs. (3.3)] that depend, as for them, only on the hole spin-orbit coupling parameter μ=0.795,[38] a value consistent with the fit of Ref. 39 (μ=0.75).

In Table II, the calculated energies of the nitrogen acceptor-bound phonons within the KPB model are reported and compared with the results.[40] An excellent agreement be-

TABLE II. Bound phonon transition energies (meV). The chosen dielectric constants for the calculation are $\varepsilon_0=9.14$ (Ref. 18) and $\varepsilon_\infty=5.7$ (Ref. 13). The $K=3$ state has two components. That with the deeper binding energy and located at 27.5 meV is mainly associated with the $1S_{3/2}\rightarrow 2P_{3/2}$ acceptor transition, whereas the other is governed by the $1S_{3/2}\rightarrow 2P_{5/2}$ transition. The $K=4$ bound state is expected to occur at 31.0 meV, i.e., nearby the LO phonon ($\hbar\omega_0=31.7_6$ meV). Not only are the c- and f-peak energies well predicted by the model, but also the nature of the g peak can be explained.

	$\mathbf{K}=\mathbf{F}+\mathbf{F}_0$		
Energy	$K=3$		$K=4$
Theor.	27.5	30.3	31.0
Exp.	27.5_4	30.9_5	31.3
	c line	f line	g line

tween theory and experience is found. Not only are the c and the f line well predicted by the KPB model, but also it explains the presence of a g peak detected on a few SPL spectra where the c and f lines are strong compared to LO.

This identification of c and f lines as due to phonons bound to acceptor states allows one to explain the question of the dependence of their binding energy with the interimpurity distance in the case of close DAP. In fact, as mentioned previously, the closeness of a donor brings a perturbation on the acceptor, the most visible effect of which is a decrease of the ground- to excited-state transition energies by the value $\Delta J_j(R)$, which can reach several meV. By considering a mean pair distance for which the donor-acceptor interaction is still moderate, a zero-order approximation gives the trend. Indeed, the exchange integral elements should be less sensitive to the perturbation than resonance denominators. Only the later have to be recalculated.

For example, by assuming a value of 1 meV for $J_{1S_{3/2}\rightarrow 2P_{3/2}}$ (45 Å) identical to the $J_{1S_{3/2}\rightarrow 2S_{3/2}}$ (45 Å) value measured by Albert *et al.*[6] (this distance corresponds to a laser energy of 2.750 meV), we find for the mainly $1S_{3/2}\rightarrow 2P_{3/2}$ associated bound phonon an energy of 27.3 meV instead of 27.5 meV for distant pairs, in excellent consistency with the experimental results.

Finally, it has to be noted that the principal parameter governing the phonon binding energy is the ionization energy of the impurity which fixes the spectrum of the acceptor excited states. Consequently, since in ZnSe, lithium is an acceptor with almost the same ionization energy [114.2 ± 0.3 meV (Ref. 41)] as nitrogen [111.3 ± 0.5 meV (Ref. 42)], similar results concerning the Li-bound phonons are expected. In fact, Tews, Venghaus, and Dean[13] have reported a value of 27.3 ± 0.2 meV for the Li-bound phonon energy which corroborates our identification.

C. Properties of the deep donor

As previously mentioned, the existence of a coupling between phonons and electronic excitations requires impurity transition energies larger than that of the LO phonon, i.e., $E_{1S\rightarrow 2P}>\hbar\omega_{\mathrm{LO}}$. For a donor, it corresponds to a binding energy of at least 38 meV. Although this energy is much higher than that of usual substitutional donors in ZnSe, deep-donor-bound phonons can be expected since its ionization energy is estimated in the 43–57 meV range. In the assumption of an hydrogenlike behavior for this donor (this hypothesis will be supported later on), a straightforward calculation provides a bound phonon energy of 29.5 meV for the associated $1S\rightarrow 2P$ deep donor transition. Indeed, for a donor, there is no more a splitting of the $2P$ state and the exchange integral matrix is simply the modulus of the $2P$ hydrogenic wave function. This numerical result agrees very well with the e-peak energy (Table I) and allows us thus to identify it.

At this stage, all lines below the free LO in energy are identified either as shallow donor or as bound phonon related transitions. Although it was necessary to assume the existence of a deep donor to explain the e line, up to now there is no direct evidence of D^dAP resonant emission in the SPL spectra.

The h features immediately above the LO can be identified as caused by the acceptor ground-state splitting by the residual strain of the layer[39] plus a Coulomb perturbation induced by the nearest neutral donor. This last phenomenon is well-known in ZnSe,[43] and has also been depicted in several zinc-blende-type semiconductors.[44]

Finally, the two remaining i and j lines are still to be identified. We ascribe them to the recombination of DAP selectively photoneutralized into the $n=2$ split state of the deep donor, i.e., i and j being, respectively, associated with the $1S\rightarrow 2S$ and $1S\rightarrow 2P$ transitions. It is thought that the spectrum of such a deep donor with an electron binding energy evaluated to be 45.2 ± 0.3 meV (i.e., a central-cell correction $\chi=19$ meV) obeys to an effective-mass model. Indeed, in such an approach, the $2S$-$2P$ splitting should be theoretically $\chi/8$, close to the measured ratio of 9.5 (2 meV), which supports the effective mass hypothesis. Note that contrary to the case of D^s, where the $2S$-$2P$ splitting (0.4 meV) is small and prevents the resolution of the $1S\rightarrow 2S$ and $1S\rightarrow 2P$ transitions, the larger chemical shift of D^d allows us to clearly distinguish the two associated lines.

A 45.2-meV ionization energy for the deep donor is moreover in excellent agreement with the previous temperature-dependent PL spectroscopy study,[5] which also estimates a value of 46 meV. On the other hand, it is in disagreement with the 57-meV binding energy determined by Zhu *et al.*,[8] essentially based on the attribution of a peak located at 2.766 eV on PL spectra to the deep-donor–valence-band transition. However, the nature of this peak has been investigated by Hauksson *et al.*[5] who rather conclude to an exciton bound to a deeper donor. In addition, a recent work of Kurtz *et al.*[45] indicates the D^d-h transition at a higher energy, giving 49 ± 3 meV for the D^d binding energy. Finally, Brownlie *et al.* also observe an absorption edge attributed to the corresponding D^d-h threshold around 2.761 eV on PL-excitation spectra detected at 2.680 eV.[8,46] Preliminary results obtained from PL-excitation spectra of D^sAP and D^dAP show that this edge rather appears as the low-energy side of the selective $1S_{3/2}\rightarrow 2S_{3/2}$ and $1S_{3/2}\rightarrow 2P_{3/2}$ (Γ_8) transitions of the nitrogen acceptor.

V. CONCLUSION

The first excited states of nitrogen-related donor-acceptor pairs in ZnSe have been investigated by selectively excited

photoluminescence. The spectra of heavily doped samples are dominated by longitudinal-optical phonons resonantly coupled with the nitrogen neutral-acceptor $1S_{3/2}\rightarrow 2P_F$ states. In addition, a fine structure of impurity-bound phonons is resolved in ZnSe. Also, we evidence the perturbation effect induced by close donors on the phonon binding energies.

Otherwise, it is shown that two donors species are introduced during the growth of p-type-doped epilayers, when a nitrogen rf plasma source is used. One is a deep donor at the origin of the dominant D^dAP band in PL spectra of the highly N-doped samples. Its ionization energy is of 45.2 ± 0.3, meV, within an effective-mass approach supported by the identification of the $2S$ and $2P$ states. The chemical nature of the main shallow donor ($E_{D^s}=29.1\pm 0.1$ meV) in our samples is not yet identified, but, in any case, does not correspond to the residual donors usually seen in undoped material.

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