Excited states of shallow acceptors in ZnSe

H. Tews, H. Venghaus, and P. J. Dean* Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Germany (Received 15 December 1978)

Excitation spectra of different donor-acceptor pair emission bands and selective pair luminescence spectra were measured on cubic ZnSe crystals with different impurity contents. For the Na and Li acceptor we found the excited states with s symmetry up to 4S, as well as the four 2P excited states. These experiments further demonstrate that the acceptor involved in the R pair band reported in the literature is substitutional Li. The observed excited acceptor states are compared to results of the effective-mass theory of Baldereschi and Lipari, after the theoretical state energies have been scaled by the experimentally determined Rydberg energy of the respective acceptor.

I. INTRODUCTION

Cubic ZnSe exhibits near-bandgap photoluminescence spectra governed by bound exciton (BE) and donor-acceptor pair (DAP) emission which is characteristic for direct-band-gap semiconductors. ZnSe is usually n type, and accordingly donor states and donor-related phenomena have been investigated in considerable detail.¹ Similar information on acceptors is still very limited. However, even in n-type material acceptor states can be analyzed, provided the samples are sufficiently compensated to exhibit DAP emission bands. Three different DAP bands (labeled P, Q, and R) have been reported in the literature²⁻⁷; the former (P and Q) are assigned to some shallow donor with an ionization energy of $\simeq 25$ meV, and to Na and Li acceptors on Zn sites, respectively.³⁻⁵ The interpretation of the R band is controversial. It is alternatively attributed to: (a) the DAP band of the Na acceptor, however modified by electron-phonon interaction,⁵ (b) Li acceptors on Zn sites with interstitial Li acting as shallow donor, 7 (c) unidentified donors and acceptors of approximately equal binding energy,² or finally (d) to complexes of Na plus a vacancy acting as acceptor and interstitial Zn as donor.⁴

The purpose of the present paper is to present a detailed investigation of the acceptors involved in the P, Q, and R DAP bands. In particular, we want (a) to obtain as many excited-state energies as possible for each acceptor to provide a basis for theoretical models and for impurity state calculations, and (b) to investigate the nature of the constituents forming the R band. Comparison of the energy levels of the acceptor involved in the R band with the energies of the Na and Li acceptor will permit a definite conclusion, whether the former is identical either to Na, to Li, or to another impurity. The experimental techniques applied are excitation spectroscopy (ES) and selective pair luminescence (SPL). As will be demonstrated below, SPL is closely related to ES; however, it is significantly more sensitive. A larger number of higher excited states is observed with greater accuracy with SPL than with ES.

The paper is organized as follows: After a description of the experimental arrangement in Sec. II, the physics of ES and SPL is discussed in Sec. III. Section IV gives the results of ES and SPL for the Li, Na, and the R acceptor. In Sec. V the results are discussed and compared with theoretical calculations. Section VI finally summarizes the results.

II. EXPERIMENTAL

The experiments were performed on not intentionally doped crystals, grown from solution or by vapor transport. Some were covered with a liquid phase epitaxial layer. The samples generally showed both the Q and P pair band in photoluminescence, with no sign of the R band. A large number of crystals with different ratios Q/P was examined so that a correlation between the observed excitation structures and involved impurities could be established. These correlations were confirmed on samples which showed only one DAP band Q or P in luminescence.

The samples were immersed in liquid He pumped below the λ point. The excitation was done with a dye laser using Stilbene 3. The half-width of the exciting laser linewas less than 0.3 meV. The luminescence light was analyzed with a 1-m singlegrating spectrometer and a photon counting setup.

III. GENERAL CONSIDERATIONS

Excitation spectroscopy of donor-acceptor pair emission and selective pair luminescence are powerful methods to measure excited impurity levels in semiconductors.⁸⁻¹⁰ Both *s*- and *p*-symmetric

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states of majority and minority carriers can be investigated in a single experiment.

The principle of SPL is illustrated in Fig. 1 with emphasis on excited acceptor states. Solid bent lines indicate the excited acceptor state energies with respect to the donor 1S level as a function of D-A separation R_{DA} . The R_{DA} dependence is due to the Coulomb interaction $e^2/\epsilon R_{DA}$ between the donor and the acceptor, and to the correlation interaction $J(R_{DA})$ of the overlapping impurity wave functions. In Fig. 1 it is assumed that J(R) is the same for all acceptor states. The energy of the incoming pump photon is chosen such that a donor-excitedacceptor pair (D^0, A^{0*}) is created at a particular pair separation R'_{DA} . Since the relaxation time of the hole is much shorter than the DAP lifetime, the excited acceptor A^{0*} is rapidly deexcited to its ground state A^{0} before the initially created DAP decays radiatively, emitting a luminescence photon with energy

$$\hbar\omega_{I} = \hbar\omega_{P} - (E_{A0} - E_{A0}) + \Delta J(R'_{DA}), \qquad (1)$$

where $\Delta J(R_{DA})$ represents the difference in the correlation energies between a (D^0, A^{0*}) and a (D^0, A^0) pair. A sharp luminescence line at $\hbar \omega_1$



FIG. 1. Principle of SPL. Pump photon (1) creates electron in 1S state at donor plus (2) excited hole (e.g., in 3S state) at acceptor separated by R'_{DA} from the donor. (3) Acceptor hole relaxes to 1S ground state. (4) Pair decays radiatively, giving sharp luminescence peak (inset). Coulomb energy was added to acceptor levels to get horizontal lines for fixed pump energy. Indicated edges for conduction (CB) and valence (VB) bands apply for $R \rightarrow \infty$. Numerical values hold for n-ZnSe with Li acceptors.

is observed, if the following sequence of processes prevails compared to competing decay channels: (1) pumping, (2) pair formation, (3) deexcitation, and (4) luminescence. This condition is fulfilled for luminescence on the high-energy side of the pair band as shown in the inset of Fig. 1, where a sharp line is riding on the broad pair recombination background. This luminescence background has several origins: (a) Since $\hbar \omega_{p} >$ $E_{gap} - E_A - E_D$, donor-acceptor pairs (D^0, A^0) can be created in competition with the excitation of (D^{0}, A^{0*}) . (b) The probability for a pair to recombine with the original partner is a function of the pair separation R_{DA} . For small R_{DA} the probability for radiative recombination is high, and the number of alternative partners in a sphere of radius R_{DA} is small. For $large R_{DA}$, the donor and the acceptor of the pair created at R_{DA} will find many other A^0 and D^{0} , respectively, at shorter distances, and might recombine with one of these. Thus the luminescence at $\hbar \omega_i$ of Eq. (1) will not be observable as a sharp peak. This broadening becomes even stronger if the pump intensity is high, and therefore many impurities become excited. (c) At large R_{DA} the pair lifetime is of the order of microseconds. Thus migration of the excitation is likely to occur.

These effects, (a)-(c), which produce the broad luminescence background, limit the observability of the luminescence line at $\hbar\omega_1$ for large R_{DA} . At small separations the restricted number of available lattice sites (which is proportional to R_{DA}^2) limits the creation of pairs (D^0, A^{0*}) and thus the luminescence at $\hbar\omega_1$.

In SPL the excitation is confined to DAP's with optimal R_{DA} , assuring a large number of excited pairs and a high radiative recombination probability, thus discriminating against competing processes. When the emission is placed on the steepest part of the pair band, highly excited states with small oscillator strengths can clearly be seen.

For ES the detector is kept at a fixed energy $\hbar\omega'_i$, corresponding to emission from DAP's separated by R'_{DA} , and the excitation energy is scanned. Whenever DAP's with one partner in an excited state (A^{0*} or D^{0*}) and separated by R'_{DA} are created, the detector signal is enhanced, since photons emitted after deexcitation of D^{0*} or A^{0*} to D^0 or A^0 , respectively, have energy $\hbar\omega'_i$ and correspond exactly to the detector setting. In analogy to Eq. (1), the energy separation between the detector energy $\hbar\omega'_i$ and maxima in the ES spectra directly yield the energy separation between ground and excited donor or acceptor states.

So far, it appears that ES and SPL would give the same information. However, additional maxima or minima (depending on the actual experimen-

tal parameters) appear in ES, when the pump energy coincides with bound or free exciton states, and these features heavily mask and distort excited impurity state structures occurring in the same energy range. In SPL, on the other hand, excited impurity state lines are transferred from the near-band-gap spectral region governed by alternative processes and disturbing structures to an energy range, where exciton related maxima usually are very weak. Further, no minima due to absorption in exciton states exist. Thus even weak peaks are easily discriminated against the smoothly varying luminescence background. In SPL the excitation can be placed close to BE lines where the absorption coefficient is sufficiently large such that epitaxial layers can be examined without problems from substrate excitation. These considerations show that SPL has significant advantages compared to ES.

IV. EXPERIMENTAL RESULTS

A. Na and Li acceptors

A typical DAP excitation spectrum is shown in Fig. 2. The detector setting corresponds to the high-energy side of the Li-related DAP band. We interpret the lowest-energy structure in Fig. 2 as a shallow donor 1S-2S transition in accordance with the fact that in direct gap semiconductors the electron mass is smaller than the hole mass. An energy separation $E_D^{1S} - E_D^{2S} = 19.4$ ± 0.5 meV is obtained. This energy can be compared with values derived by Merz et al. for various donors.¹ These authors report values of 18.9 meV for Al and 19.3 meV for Cl, with an error of approximately 0.1 meV. Consequently our results indicate the predominant shallow donor to be Cl. although the presence of Al cannot be completely excluded due to experimental precision. The



FIG. 2. Example of an excitation spectrum. The luminescence is detected at the high-energy side of the Li-related DAP band.

energy separations to the next higher structures and their interpretation are $TO(\Gamma) = 26.0 \pm 0.5 \text{ meV}$ and $LO(\Gamma) = 31.6 \pm 0.5$ meV. The peak between the TO and the LO phonon at 27.3 ± 0.5 meV coincides in energy with the LO(X).¹¹ Phonons from points in the Brillouin zone other than the Γ point have been observed in other semiconductors as well.¹² They are not strictly forbidden since the phonon selection rules for pair bands are determined by the axial symmetry of the donor-acceptor pair. (See Note added in proof.) The energy region between 45 and 65 meV is dominated by twophonon lines in agreement with theoretical calculations and experimental results of Irwin and LaCombe.¹¹ The dips labeled I_{1}^{deep} I_1^x , and I_1^y occur at fixed energies. They are attributed to a deep-acceptor, the Li-, and the Naacceptor bound exciton, respectively. The negative features I_2 and FE behave in a similar way and correspond to a shallow-donor BE and to the free exciton, respectively. The peaks observed at 72.4 and 82.0 meV in Fig. 2 are attributed to excited acceptor states. Further acceptor levels are observed for different detector settings, and the results are summarized in Fig. 3. In addition to the energies of the various states, Fig. 3 also demonstrates (a) that groups of excited states (a-e orf, g, i, and j, for example) are apparently related to the same acceptor, and (b) that excited acceptor states are observed only if the detector is on the high-energy side of the corresponding DAP band. The interpretation of the lines is given in Table I and is discussed in Sec. V. Line b at $76.6 \pm 1 \text{ meV}$ was found only in samples cut from one crystal. Line b occurred in addition to the other lines and cannot be interpreted definitely at present. It might represent the $2S_{3/2}$ state of an unidentified additional acceptor.

The attempt to determine the energy of excited acceptor states by DAP excitation spectroscopy as close as possible to the respective acceptor ionization energy is restricted by the following limitations (see also Sec. III): If the detector is on the high-energy side of the DAP band under investigation, excited acceptor states significantly higher than $2S_{3/2}$ are masked by BE structures. If the detector is set to very distant DAP's, excited acceptor states are no longer observed at all, since the initial excitation process becomes less significant as the radiative lifetime increases for large DAP distances.

In order to overcome these limitations we performed SPL measurements. Corresponding results are shown in Fig. 4 for a sample having the Li- and the Na-related DAP band of comparable intensity. Excitation is in the energy region of the acceptor BE I_1^x , I_1^y , and I_1^{deep} . The main results



FIG. 3. Summary of the results of the excitation spectroscopy. In the left part of the picture a typical luminescence spectrum for above-band-gap excitation is shown. Q and P are the pair bands of the Li and Na acceptor, respectively. FE indicates the free exciton. Lines h, k, l, and m are LO-phonon replicas of a, c, e, and f.

obtained by SPL on samples with different Li to Na ratio are the following: In general the same lines are observed in SPL as in ES, and the SPL measurements support the association of groups of lines with excitation of the same acceptor as already inferred from ES. However, SPL reveals additional excitation structures, marked with an asterisk in Table I.

The SPL lines are always found on the high-energy side of the DAP band and disappear, if they fall either above the energy region of efficient DAP emission or into the energy range corresponding to emission from more distant DAP's (cf. Sec. III). This can be seen in Fig. 4. At $\hbar \omega_p = 2.769$ eV the lines \overline{f} and j are strongest. At 2.790 eV, these two lines have reached the top of the corresponding DAP bands and disappeared. At even lower pump energy, lines c and f predominate. Line f and \overline{f} have approximately the same energy in Fig. 4. In Fig. 5 it is shown that f and \overline{f} are really two different lines resulting from the P and the Q acceptor, respectively. Several samples are examined which show the P and the Q band in luminescence (full circles), or the Q band only

TABLE I. Experimental and theoretical results for the energy separation between excited states and the ground state of the Li and Na acceptor in ZnSe. The asterisks (*) indicate lines that could only be detected by selective pair luminescence, but not by excitation spectroscopy. The letter symbols refer to Fig. 3.

	Line	Energy-level sep Experimental	aration (meV) Theoretical	Identification
		Li acceptor :	$E_A = 114 \text{ meV}$	
	a	72.9 ± 1	71.9	$1S_{3/2} - 2P_{3/2}$
	с	82.6 ± 1	82.7	$1S_{3/2} - 2S_{3/2}$
•	d	85.8 ± 2	84.0	$1S_{3/2} - 2P_{5/2}(\Gamma 8)$
	e	93.0 ± 1	91.3	$1S_{3/2} - 2P_{5/2}(\Gamma 7)$
	*	97.8 ± 1	97.5	$1S_{3/2} - 3S_{3/2}$
	*	100.0 ± 1	98.9	$1S_{3/2} - 2P_{1/2}$
	*	102.5 ± 1	104.1	$1S_{3/2} - 4S_{3/2}$
				0,1 0,1
		Na acceptor :	$E_A = 128 \text{ meV}$	
	*	83.1 ± 1	80.7	$1S_{3/2} - 2P_{3/2}$
	f	97.6 ± 1	92.9	$1S_{3/2} - 2S_{3/2}$
	g	100.4 ± 2	94.4	$1S_{3/2} - 2P_{5/2}(\Gamma 8)$
	ī	106.8 ± 1	102.5	$1S_{3/2} - 2P_{5/2}(\Gamma 7)$
	j	110.5 ± 1	109.5	$1S_{3/2} - 3S_{3/2}$
	*	113.0 ± 1	111.1	$1S_{3/2} - 2P_{1/2}$
	*	114.7 ± 1	116.8	$1S_{3/2} - 4S_{3/2}$



FIG. 4. SPL spectra taken at five different excitation energies. The notation of the lines refers to Fig. 3 and to Table I.

(crosses). In Fig. 5 the energy of f and \overline{f} is drawn as a function of $\hbar \omega_l$, i.e., pair separation. The P and Q pair bands are indicated in the lower part of the picture. One finds: (i) Line \overline{f} is correlated with the Q band, and f belongs to the P band. The lines \overline{f} and f can only be seen if the Q or the Ppair band, respectively, appears in the luminescence spectrum. (ii) The energy separation between the ground state and the respective excited state, giving rise to the f and the \overline{f} line, is a function of pair separation R_{DA} [cf. Eq. (1)].



FIG. 5. $\hbar\omega_p - \hbar\omega_1 \operatorname{vs} \hbar\omega_1$ for lines f and \overline{f} from SPL experiments. The samples contained either the Q acceptor plus the P acceptor (full circles), or the Q acceptor alone (crosses). The solid lines are intended as a help for the eye.



FIG. 6. Energy differences between $1S_{3/2}$ and $2S_{3/2}$ state of the Li acceptor in ZnSe as a function of pair separation R_{DA} . Crosses: results from excitation spectroscopy; circles: results from SPL technique.

This effect is further investigated in Fig. 6 for line c (corresponding to the Li $2S_{3/2}$ state, cf. Table I and Sec. V). Figure 6 also shows that the detectibility of excited states extends to much closer pairs in SPL compared to ES. This explains the apparent inconsistency between Fig. 3 and Figs. 5 and 6; since $\Delta J(R_{DA})$ [cf. Eq. (1)] increases with decreasing R_{DA} , as can be seen in Fig. 6, the shift in the line positions is greatest for small separations. In ES, however, only peaks in a small energy range can be discriminated against the heavily structured near-band-gap luminescence background. Further, the strengths of the absorption dips in the ES spectra differ from sample to sample, thus producing a large experimental error in the peak positions.

B. R band

We analyzed the R acceptor by SPL experiments. Peaks corresponding to excited acceptor states are found on the high-energy side of the R band if the pump energy $\hbar \omega_p \ge 2.780$ eV. In Fig. 7 four spectra obtained for different pump energies are shown, measured on a sample that has neither the Q nor the P band in luminescence. Excited-state structures occur at the same energies with respect to the exciting light as in the case of the Li acceptor. From the coincidence of the excited-state energies of the R and the Li acceptor we conclude that Li is the acceptor involved in the R band. This conclusion is supported by atomic absorption experiments, showing ~30 times greater Li contents in samples with an R band compared to samples with the Q band, but without R band.

There is no evidence from our experiments that the different energies of the Q and the R DAP emission bands are donor induced. We find a



FIG. 7. SPL spectra for the investigation of the R acceptor, taken at four different pump energies. The shifting sharp line in the spectra is probably an exciton bound to an unknown deep impurity.

1S-2S energy separation of 19.6 ± 1 meV for the donor in samples that show the *R* band compared to 19.4 ± 0.5 meV for the donor of the *P* and *Q* band. Thus donors with nearly the same binding energy seem to be involved in all three DAP bands. A possible explanation for the existence of two DAP bands from the same donor and the Li acceptor could be the preferential incorporation of Li acceptors at small distances. The donors require further investigation.

V. DISCUSSION

Excited acceptor states in semiconductors were calculated in the effective-mass approximation by Baldereschi and Lipari.¹³ This theory, however, does not predict a dependence of acceptor energies on the chemical nature of the different impurities, although the experimental results demonstrate the presence of such effects. Recent calculations including q-dependent electronic screening, the detailed structure of the Bloch functions, and umklapp contributions to the potential matrix elements indicate how the effective-mass theory can be improved.¹⁴ Such a detailed calculation, however, is beyond the scope of the present paper. We calculated the acceptor state spectrum in units of the effective Rydberg R_0 within the effective-mass approach of Baldereschi and Lipari,¹³ taking R_0 from the experimentally determined ionization energies, thus scaling the whole acceptor state spectrum. From the luminescence spectra for low-intensity above-band-gap excitation, we obtained $E_A = 114 \pm 2$ meV for Li and 128 ± 2 meV for Na.³⁻⁶ The valence-band parameters used in the present calculation are taken from recent work on free excitation magnetoreflectance: γ_1 = 4.3, $\gamma_2 = 0.59$, $\gamma_3 = 1.34$.¹⁵ The 3S and 4S states were calculated according to the relation

$$E_{nS} = E_A n^{-1.76}$$
 (2)

derived for acceptor states in GaP (Ref. 16) and also shown to give a good description of acceptor states in ZnTe.¹⁷

The theoretical energy separations are listed in Table I together with the experimental results. For the Li acceptor, the agreement is good and allows an immediate identification of the observed lines. In the case of Na, the effective-mass calculation reveals energies which are ~4 meV too large. As for the Li acceptor, Eq. (2) is found to give a good description of the 3S and 4S levels. The discrepancies between theoretical and experimental results can be reduced if an ionization energy of $E_A \sim 134 \text{ meV}$ is assumed. However, such a large value is not supported by our aboveband-gap luminescence spectra. The energy separation between the $2P_{_{3/2}}$ and $2P_{_{5/2}}$ states we obtain for the Na acceptor is ~4 meV larger than for the Li acceptor. However, approximately the same energy separation between corresponding Pstates is expected for different acceptors having comparable ionization energy. Thus it cannot be excluded that the 83.1 meV structure does not represent the Na- $2P_{3/2}$ state. The large experimental errors are due to the uncertainty in determining the excited states at donor-acceptor pairs in the limit of infinite pair separation R_{DA} , as can be seen in Fig. 6. For small R_{DA} excited acceptor state energies are changed by the interaction with nearby donors, as already observed by Street and Senske.⁸ The examination of this effect by ES failed in the case on ZnSe, since the related peaks already moved into the energy region dominated by absorption structures, while the corresponding pair separation was still too large to give observable acceptor state changes.

As stated above, we did not try to develop refined theories for the calculation of acceptor states. The aim of the calculations was to get estimates of the energy splittings between ground and excited states, and to compare these results with the experimental data for the purpose of identification. The deviations in Table I between theory and experiment might be due to several reasons: (i) We scaled the whole theoretical spectrum with the experimentally determined Rydberg energy. However, there is no justification for the assumption that both s- and p-symmetric states can be shifted with the same factor. (ii) Since $R_0 \propto \epsilon_0^{-2}$ (Ref. 13), the dielectric constant can be deduced from the experimentally determined R_{0} . We get $\epsilon = 5.950$ for Li and 5.615 for Na. These values of ϵ agree with published values for ϵ_{m} , which range from 5.4 to 6.3.¹⁸ While it seems reasonable to take ϵ_{m} for the calculation of excited acceptor levels which have an energy separation from the valence band of more than the LO phonon energy, deviations should be expected for shallow states with energy below the LO energy, e.g., the $2P_{1/2}$ states. For these shallow states, calculations with ϵ_0 seem more appropriate. However, no excited acceptor levels are observed at energies calculated with ϵ_0 , while the agreement between the theory using ϵ_{∞} and the experiment is fairly good, as can be seen in Table I.

SPL experiments in magnetic fields are currently under way in this laboratory to check the assignments given above.

VI. SUMMARY

Excitation spectroscopy and selective pair luminescence were used to examine the excited states of the shallow acceptors in ZnSe. For the Li and the Na acceptor, states up to 4S could be detected. The excited states are compared with theoretical calculations, and good agreement is obtained. The

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R acceptor is also found to be caused by Li. In the R band, donors of the same binding energy are involved as in the P and Q band.

Comparing ES and SPL, we show that SPL generally reveals a significantly higher accuracy and reproducibility in crystals of different impurity composition and doping concentration, since in ES exciton-related absorption mask the spectra. As a consequence, much higher excited states can be detected in SPL than in ES, and the regime of detection is extended.

Note added in proof. Recent excitation spectra on the DAP band in ZnTe doped with different shallow acceptors (Li, P, As) demonstrate, that phonons other than $TO(\Gamma)$ and $LO(\Gamma)$ are apparently dependent on doping. [H. Venghaus and P. J. Dean, Phys. Rev. B (to be published)]. Thus the 27.3 meV peak may coincide only accidentally with the expected LO(X) position, but may actually be due to acceptor-related lattice vibrations. A definite conclusion cannot be drawn at present, but requires additional experiments on ZnSe samples doped with different shallow acceptors.

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