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Optical properties of Ag-related centers in bulk ZnSe

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A detailed optical study of defects induced by Ag diffusion into bulk ZnSe is presented. Two dominating Ag-related centers are found, a deep acceptor $\mathrm{Ag_{Zn}}$ with binding energy $E_A=430\pm2$ meV and a neutral complex with a bound exciton (BE) transition at 2.747 eV. These results are in good agreement with recent data for liquid-phase-epitaxial Ag-doped ZnSe, but differ from previous work on bulk ZnSe, where several additional Ag-related defects were reported from photoluminescence data. From dye-laser-excited selective photoluminescence and excitation spectra both S- and P-like "hydrogenic" excited states of the $\mathrm{Ag_{Zn}}$ acceptor are observed, in a sequence quite similar to more shallow substitutional acceptors in ZnSe. Thus the $\mathrm{Ag_{Zn}}$ acceptor is a conventional acceptor with a $4d^{10}5s^1$ configuration, i.e., no d^9 hole state is observed in the band gap. The temperature dependence of the binding energy of this acceptor level is obtained from a detailed treatment of the phonon coupling in the experimental optical cross sections $\sigma_n^0(h\nu)$. The 2.747-eV BE state is concluded to be a neutral Ag-related complex with an electronic structure compatible with the Hopfield-Thomas-Lynch model, with a hole-attractive central cell, and a shallow donor-like electron state. No splitting of this BE line is observed, and the thermal activation energy for the hole is 52 ± 5 meV, in agreement with this model. The identity for this dominating Ag-related complex is suggested to be the $\mathrm{Ag_{Zn}}$-Ag_i pair (where Ag_i is a silver atom in an interstitial position), probably in the simplest trigonal configuration. The thermal broadening and quenching of the 2.747-eV electronic line is consistent with a linear coupling of low-energy phonon modes (both acoustic lattice modes and quasilocalized modes of energy ~2 meV) with an effective Debye temperature, $\Theta_{D,\mathrm{eff}}\sim60$ K, indicating a strong enhancement of these low-energy modes in the phonon coupling, compared to the lattice phonon density of states in ZnSe.

I. INTRODUCTION

The transition metal Ag introduces acceptor levels in II-VI semiconductors, when introduced substitutionally on the cation site. For CdTe and ZnTe this acceptor acts as a normal shallow acceptor in a d^{10} configuration, while on the other hand the ZnS host makes $\mathrm{Ag_{Zn}}$ an open-shell d^9-type acceptor.[1] The case of Ag-doped ZnSe has recently been investigated for epitaxial layer [liquid-phase-epitaxy material (LPE)] material, where Ag was introduced during the growth. $\mathrm{Ag_{Zn}}$ was concluded to be a conventional d^{10} acceptor in ZnSe, but a deep one ($E_A\sim435$ meV).[1] Additional Ag-related defects causing bound exciton (BE) spectra in the near-band-gap region were also discovered in this recent work, but not identified.

This paper reports on a detailed optical investigation of *bulk* ZnSe, doped with Ag by a diffusion procedure. This is of particular interest, since it is often found for compound semiconductors that doping during LPE growth, as opposed to diffusion of a dopant into bulk material, may result in a rather different picture of defect formation. In a previous work on Ag-doped ZnSe, photoluminescence (PL) spectra revealed defects[2] which were not found in the recent work on LPE Ag-doped ZnSe.[1] It will be demonstrated below that the optical spectra from Ag-diffused bulk ZnSe agree quite well with the recent data for LPE material doped with Ag during the growth. This is encouraging, since it indicates that diffusion-doped bulk ZnSe may be made with a defect quality comparable to good LPE material.

It has been found in this work that Ag doping in bulk ZnSe causes two dominant Ag-related defects; a deep acceptor with binding energy $E_A\sim430$ meV and a shallow (neutral) complex binding an exciton at 2.747 eV at low temperatures. The properties of the deep acceptor are studied in PL spectra via the properties of the corresponding broad donor-acceptor- (DA) pair emission peaking at about 2.23 eV. A detailed analysis of electronic excited states is performed for the first time in both selective PL (SPL) spectra and in PL excitation (PLE) spectra employing a cw tunable dye laser. This study confirms that the center is indeed a normal d^{10}-type acceptor with a strongly enhanced central-cell shift resulting in a binding energy of ~430 meV. Temperature quenching of the PL emission intensity confirms this activation energy. The measurements of the detailed spectral shape of the DA-pair emission allow an evaluation of the phonon-coupling parameters for the $\mathrm{Ag_{Zn}}$ acceptor via a deconvolution procedure.

No new acceptor-related bound exciton (ABE) was found with Ag diffusion in PL spectra; neither was one found after additional Li doping. This is interesting, since it can be concluded that the ABE energy related to $\mathrm{Ag_{Zn}}$ is isoenergetic with other residual shallow ABE's at ~2.793 eV. This is in contrast to the recently demonstrated case[3] of the corresponding ABE for $\mathrm{Cu_{Zn}}$, where a d^9 Cu hole causes a substantial downshift of the ABE en-

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ergy for Cu_{Zn} in ZnSe.

Photoionization cross sections $\sigma_n^0(h\nu)$ for excitations from the acceptor to the conduction band could be measured for the first time for the Ag_{Zn} acceptor via the PLE technique for temperatures between 5 and 273 K. The electronic cross section $\sigma_{n,\mathrm{el}}^0(h\nu)$ was evaluated from experimental data at the lowest temperature via a previously developed deconvolution procedure.[4] The shape of the derived electronic cross section $\sigma_{n,\mathrm{el}}^0(h\nu)$ is consistent with the expected shape for an allowed optical transition. From the temperature-dependent shift of the electronic edge of $\sigma_{n,\mathrm{el}}^0(h\nu)$ evaluated via a convolution procedure, the corresponding shift of the Ag_{Zn} acceptor level in the band gap with temperature could be evaluated.

The shallow BE complex observed at 2.747 eV in both PL and PLE spectra has properties consistent with a neutral complex defect, binding an exciton according to the Hopfield-Thomas-Lynch (HTL) model,[5] with a hole-attractive central cell and a loosely bound electron. A model for the center as a Ag_{Zn}-Ag_i neutral associated (i denotes an interstitial site) is suggested, which is in agreement with recently observed analogous defects in Ag-doped ZnTe (Ref. 6) and CdTe (Ref. 7).

Further, a detailed study is presented on the phonon coupling for the 2.747-eV Ag-related complex. A very strong interaction with low-energy modes in the PL spectrum causes severe broadening of the zero-phonon line, which also disappears rather quickly with increasing temperature due to this phonon coupling. A theoretical model is evaluated, where the contributions to the quenching of the electronic emission by the quasilocalized modes and the continuous, acoustic band could be separated. These calculations confirm that the coupling to low-energy modes is strongly enhanced, compared to an approximately constant coupling strength over the one-phonon band.

In Sec. II below, the sample preparation and the details of optical experiments are described.

Section III contains the experimental results from PL measurements for both the 2.747-eV BE and the Ag-related DA pair at the lowest temperatures as well as at higher temperatures.

In Sec. IV a more detailed discussion is given on the possible identity of the 2.747-eV BE. Also, the electronic structure of the deep Ag_{Zn} acceptor and the photoionization cross section associated with this acceptor are further discussed.

A brief summary is given in Sec. V.

II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

Single crystals of ZnSe were grown by a modified Bridgman technique from the melt (at the Institute of Physics, Nicholas Copernikus University, Torun, Poland) under an overpressure of 11-MPa protective argon atmosphere.[8] Merck ZnSe powder of 99.999% purity was used as starting material in all cases. The crystals were cut into about 1-mm-thick, (111)-oriented wafers. The wafers were then chemically etched in a mixture of K_2CrO_7 and H_2SO_4 (in proportion 3:2) at ~95 °C, followed by a treatment in boiling NaOH solution (~25—30% by weight) for 1—3 min. To create a suitable diffusion source of AgSe at the surface, the samples were dipped in $AgNO_3$ solution. The diffusion was performed in evacuated silica ampoules with excess Zn at 1000 °C for 4—60 h. This treatment normally gave compensated high-Ohmic crystals. For some crystals the diffusion procedure was repeated a second time. Other crystals were doped by heating in molten Zn and 1% (by weight) Ag also at 1000 °C to ensure low-Ohmic n-type behavior. All the samples were rapidly quenched to room temperature after annealing. After diffusion the crystals were etched in concentrated HCl to remove the traces of the Zn metal and then in the same mixture of K_2CrO_7 and H_2SO_4 as mentioned above to remove any surface damage.

The PL measurements were performed employing a Kr^+ laser for intrinsic excitation at 4130 Å and a cw dye laser for selective excitation below the band gap. The temperature could be well regulated in the region 1.8—460 K. PL spectra were obtained with a Jarrel-Ash 0.75-m double-grating monochromator and an $S20$ photomultiplier as a detector. The same detection equipment was used for dye-laser-excited PLE spectra. PLE spectra covering a wider energy range were obtained in the conventional way with a 250-W tungsten lamp as the excitation source.

To get a narrow-band excitation, the light passed through the above mentioned 0.75-m double monochromator. At the detection side the $S20$ photomultiplier was employed. All the spectra were recorded and stored in Nicolet 1174 signal averager and then corrected for the spectral response of the equipment.

III. EXPERIMENTAL RESULTS

A. Bound exciton luminescence

1. *Low-temperature spectra*

In Fig. 1 is shown the near-band-edge luminescence of a bulk ZnSe:Ag sample at 1.8 K. The free-exciton (FE) emission at about 2.804 eV is hardly detectable, while the peak at 2.797 eV is identified as a donor-bound exciton (DBE). The sharp line I_1^{deep} observed at 2.783 eV and the associated LO-phonon replicas are assumed to originate from the neutral Cu ABE,[1,3] which is inadvertently introduced during the diffusion procedure. The remaining peaks below 2.75 eV in Fig. 1 are Ag related, consisting of a BE spectrum with the no-phonon line, Ag_1^0, at 2.747 eV and, in addition, a broad pair band peaking at about 2.23 eV. Ag is expected to occupy a Zn site substitutionally, thus forming a rather deep acceptor (see below). The principal ABE lines for shallow substitutional acceptors in ZnSe all occur around 2.793 eV, and we have to assume that the ABE for Ag_{Zn} is also present around this energy in Fig. 2, although hidden in the broad wing from the DBE spectra. Comparing the Ag-related 2.747-eV BE spectrum in Fig. 2 with shallow ABE spectra in ZnSe, such as excitons bound at the acceptors Li (Refs. 1 and 9), Na (Ref. 9), or the deeper Cu (Fig. 1 and Ref. 10), this Ag-related spectrum shows a stronger and more complex

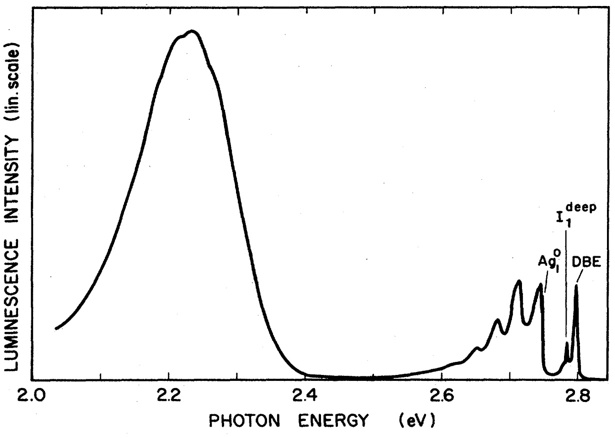

FIG. 1. Low-temperature (1.8 K) PL spectrum of Ag-doped ZnSe, excited with the 4130-Å Kr$^+$-laser line. The two peaks at highest energy, DBE and I_1^{deep}, originate from donor-bound excitons and excitons bound at a neutral Cu-related acceptor, respectively. The remaining structure is Ag-related, consisting of a BE spectrum with the no-phonon line, Ag_I^0, at 2.747 eV and a broad DA-pair emission peaking at ~2.23 eV.

phonon coupling. The Huang-Rhys parameter S, defined as the ratio of the intensity of the one-phonon part to that of the no-phonon part, for the LO-phonon (31.5 meV) coupling, is estimated as $S \sim 0.8$. This is considerably larger than the corresponding S factor for the abovementioned acceptors, where $S=0.1$, 0.03, and 0.3 for Li, Na, and Cu,[9,10] respectively. The structure in the low-energetic, rather broad phonon wing peaking at 2.745 eV (Fig. 2) reveals two different low-energy modes, 2.2 meV $(\mathrm{Ag}_\mathrm{I}^{L_1})$ and 8.7 meV $(\mathrm{Ag}_\mathrm{I}^{L_2})$ with a coupling strength of 1.2 and 0.3, respectively, superimposed on an acoustic-phonon wing. The presence of such low-energy quasilocalized modes points to a center containing a heavy substituent.[11] Furthermore, the presence of *two* such modes strongly indicates that the center consists of more than one atom, i.e., a complex. In fact this argument should be sufficient to rule out the possibility that the 2.747-eV emission is due to the $\mathrm{Ag}_{\mathrm{Zn}}$ ABE. A $\mathrm{Ag}_{\mathrm{Zn}}$-$\mathrm{Ag}_i$ pair is a natural suggestion for the identity of this center, further discussed below. Since the Ag interstitials are abundant during the high-temperature diffusion step, such $\mathrm{Ag}_{\mathrm{Zn}}$-$\mathrm{Ag}_i$ pairs are expected to be formed in a sizable concentration during the cooldown from the diffusion temperature.

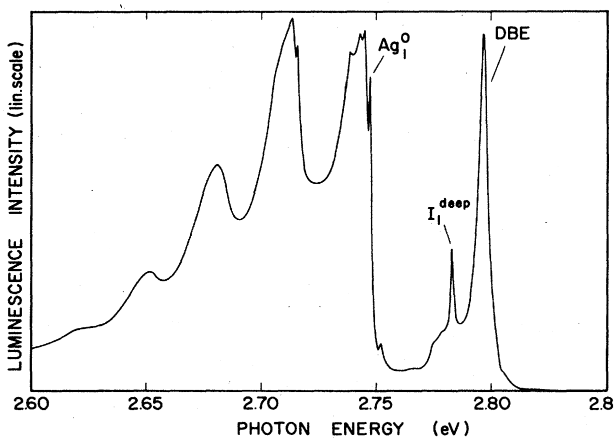

FIG. 2. Selected part of the PL spectrum covering the BE energy region including the Ag_I^0 emission. This BE has a considerably stronger phonon coupling than the more shallow BE's (e.g., DBE and I_1^{deep}). In addition to the LO-phonon replica of Ag_I^0, some discrete low-energy phonons are resolved, superimposed on the continuous acoustic band accompanying the no-phonon line, Ag_I^0.

The same low-energy modes as in PL are observed in the PLE spectrum in Fig. 3. They occur at the same energy but with a weaker coupling than in PL. Further replicas in the neighborhood of the TO and LO phonons can be observed in the PLE spectrum. The TO-phonon replica is not observed in the PL spectrum, but is expected to appear in the same region as the strong, second LO-phonon replica of I_1^{deep}, however. The "LO"-phonon replica of Ag_I^0 observed in PLE is weaker and considerably broader than the corresponding peak in PL. In addition, the "LO"-phonon replica is shifted toward lower energies (~30.6 meV) in comparison with PL emission. This is a rather general feature in similar materials,[12] which is due to impurity localization of LO phonons (bound phonons).[13,14] The 2.747-eV Ag_I^0 line is considerably broadened in both PL and PLE spectra, partly due to the strong coupling to a continuum of low-energy phonons.

In previous work additional, probably Ag-related, lines in PL have been observed.[1,2] Actually, we have only observed one of these lines at ~2.779 eV in our bulk material. It is a very weak feature on the low-energy side of the strong Cu-related I_1^{deep}. The origin of this line was uncer-

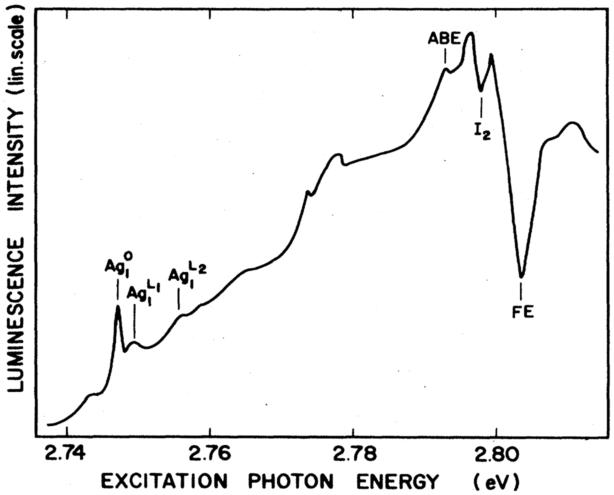

FIG. 3. Excitation spectrum for the Ag_I^0 emission obtained with tunable-dye-laser excitation with the detection at the first LO-phonon replica of Ag_I^0. The same phonon modes as in the PL spectrum are observed (and, in addition, the TO-phonon replica). The peak labeled ABE originates from excitons bound at residual acceptors, e.g., Li or Na. The I_2 dip corresponds to the donor BE, while the most obvious dip, FE, is caused by the free exciton.

tain in earlier reports,[1,2] but a Ag-Na complex has been suggested as the identity for this center.[2] Another line reported in Ref. 2 very close to this (at 2.778 eV) was attributed to the $\mathrm{Ag}_{\mathrm{Zn}}$ acceptor level, which was believed to be shallow in Ref. 2. We conclude that only the 2.747-eV BE spectrum in the near-band-gap energy region is, with certainty, connected with Ag in our bulk samples.

2. Temperature dependence of BE spectra

Already at the lowest temperatures the $\mathrm{Ag}_{\mathrm{I}}^{0}$ electronic line has a finite width as mentioned above due to, e.g., interaction with low-energy phonons in the acoustic band. At higher temperatures the electronic line is further broadened as a result of linear electron-phonon coupling to low-energy phonons,[14] and the integrated intensity of the electronic line decreases gradually. Finally, at a temperature of about 20 K, the electronic line has completely disappeared, while the total emission envelope retains almost the entire strength at this temperature.

The PL spectrum (Fig. 2) shows directly that the coupling to low-energy modes in the acoustic band is very strong. This phonon wing immediately following the no-phonon line consists of discrete quasi-localized modes superimposed on a continuous band. Both types of phonon modes contribute to the quenching of the no-phonon line.

The contribution of discrete modes as well as of the continuous acoustic band to the normalized transition probability for the no-phonon line is given in Ref. 11:

$$\exp[-S_{\mathrm{tot}}(T)]=\exp\left[-\sum_i \lambda_i[2\bar{n}(\omega_i)+1]\exp[-S_0(0)(1+2\pi^2/3)(T/\Theta_D)^2]\right] , \tag{1}$$

where the first part originates from the coupling to discrete modes and the second part from coupling to the continuous band. λ_i denotes the coupling constant for the discrete quasilocalized mode i; S_0 and S_{tot} denote the corresponding coupling strength for the acoustic band and the entire phonon envelope, respectively. Θ_D denotes the Debye temperature and $\bar{n}(\omega)=(e^{\hbar\omega/k_BT}-1)^{-1}$.

If just the discrete modes, $\mathrm{Ag}_{\mathrm{I}}^{L_1}$, $\mathrm{Ag}_{\mathrm{I}}^{L_2}$, and $\mathrm{Ag}_{\mathrm{I}}^{\mathrm{LO}}$, are included in the calculations, the dashed curve in Fig. 4 will result. The higher-energy, discrete phonon modes $\mathrm{Ag}_{\mathrm{I}}^{L_2}$ and particularly $\mathrm{Ag}_{\mathrm{I}}^{\mathrm{LO}}$, give a very small contribution to the quenching of the PL intensity at these low temperatures. The coupling to the $\mathrm{Ag}_{\mathrm{I}}^{L_1}$ mode is thus the dominating quenching mechanism among the discrete modes and is therefore very critical in the computation.

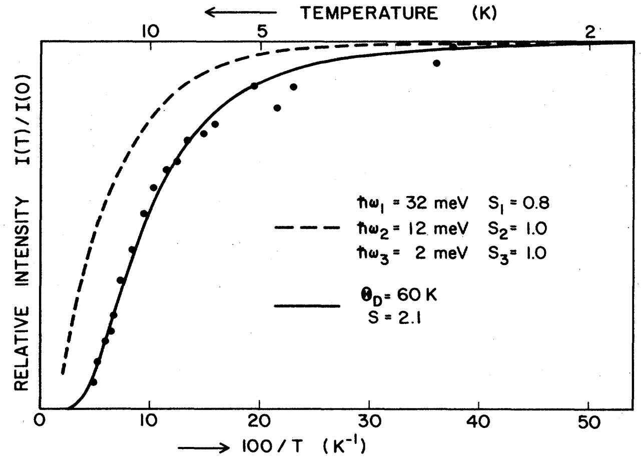

FIG. 4. Illustration of the fit of Eq. (1) to the thermal quenching behavior of the no-phonon line $\mathrm{Ag}_{\mathrm{I}}^{0}$. If just the discrete modes listed in the figure are included in the computation, the upper, dashed curve will result. For a proper calculation it is necessary to take into account also the contribution from the continuous, acoustic band, which can be described by the Debye approximation in this case. The best fit (solid curve) to the experimental values (●) is derived for a Debye temperature Θ_D of 60 K and a coupling strength $S=2.1$ to the continuous band.

Combining the contributions of the discrete modes and the continuous band, the best fit to the experimental points (Fig. 4) is derived when the Debye temperature $\Theta_D=60$ K is used. The value evaluated with Θ_D is low compared with values experimentally determined with different measuring techniques,[15] which in our model can be understood in terms of a much stronger coupling strength to the low-energy part of the continuous phonon spectrum than assumed in the Debye model.

The method employed here to calculate the temperature dependence of the electronic line is admittedly an oversimplification. It shows, however, that the contributions to the quenching of the no-phonon line from the discrete modes and the continuous acoustic band are of about the same magnitude.

In contrast to the case with the no-phonon line, it is possible to fit the thermal quenching data for the total emission intensity to the exponential expression

$$\frac{I(T)}{I(0)}=\frac{1}{1+C_1e^{-E_1/k_BT}+C_2e^{-E_2/k_BT}} . \tag{2}$$

From the fit to this expression shown in Fig. 5, two activation energies are derived, $E_1=21\pm5$ meV and $E_2=52\pm5$ meV, of which E_1 is more uncertain, since the 52-meV slope will dominate the shape of curve already at the temperature of ~ 60 K. In the case of $\mathrm{Ag}_{\mathrm{I}}^{0}$ the hole is expected to be tightly bound, supported by the observed large binding energy of the $\mathrm{Ag}_{\mathrm{Zn}}$ acceptor ($E_A=430$ meV, see below). In the HTL model[5] the electron will be bound by the Coulomb field of the hole with a binding energy approximately equal to the effective-mass value [~ 26 meV in ZnSe (Ref. 16)], or possibly slightly less if the central cell is hole attractive, i.e., electron repulsive.[17] Since the total electron and hole binding energy is 73 meV, a hole binding energy of ~ 47 meV is derived in fair agreement with the provided activation energy from PL

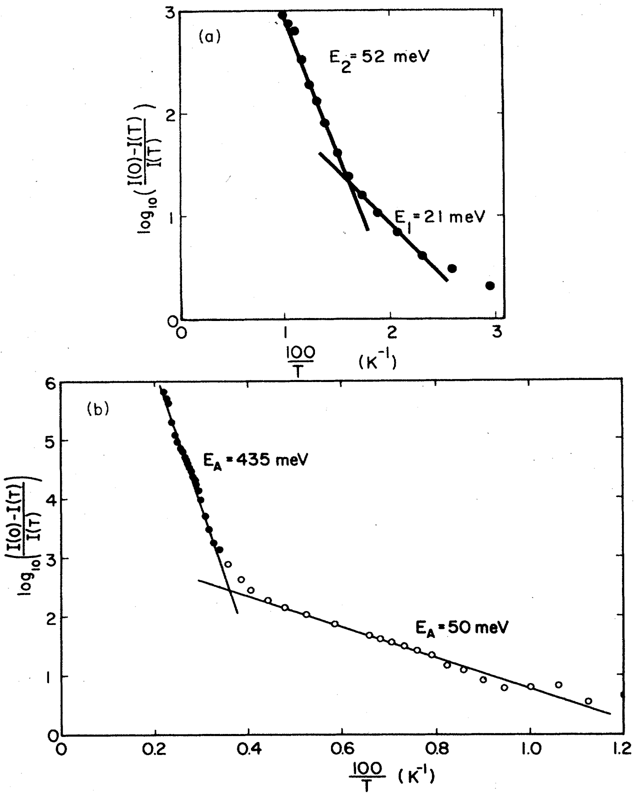

FIG. 5. (a) Thermal quenching data for the Ag_1^0 emission. The experimental points are estimated from the integrated intensity of the total emission. A fit of Eq. (2) to the experimental data is also shown providing the activation energies, $E_1=21$ meV and $E_2=52$ meV, which probably represents the thermal release of the electron and hole, respectively. (b) Illustration of the fit of Eq. (2) to the thermal quenching data for the Ag-related DA-pair spectrum. Two activation energies are provided, $E_A=435$ and 50 meV, which presumably represent the thermal ionization of the involved acceptor and donor, respectively.

quenching (52 meV). The activation energy $E_1 \sim 21$ meV should in such a model correspond to the ionization of the primary particle, the electron. However, if the primary particle is released, the exciton no longer exists. The reason for the appearance of a second activation energy despite this fact is found in the large difference between the prefactors in (2) ($C_1 \ll C_2$). The physical interpretation of this large difference is at present uncertain.[18] Alternatively, the exciton could be released as a whole, but in that case the electron (e) and the hole (h) should be strongly coupled together, causing an enhanced e-h exchange interaction. Such a case is observed for an analogous center in Ag-doped ZnTe.[6] In the case of the Ag_1^0 line in ZnSe we do not, however, see any evidence of such an exchange interaction. Only one electronic state is observed in the environment of the 2.747-eV line in PL and PLE, indicating a small e-h exchange splitting (not resolved spectrally).

B. Donor-acceptor-pair spectra

1. *PL emission spectra*

A broad and bell-shaped emission peaking at ~2.23 eV dominates the PL spectrum at lower photon energies in Ag-doped crystals (see Fig. 1 and, in more detail, Fig. 6). The spectrum is almost structureless, though a barely resolved phonon structure with weak, uniformly spaced peaks superimposed on the emission is observed. The structure is better resolved after a deconvolution procedure[4] (Fig. 6) with a 14-meV phonon mode (a discrete approximation of a high density of states in the acoustic band[15]). The remaining spectrum shows a marked phonon sideband with a periodicity of about 32 meV corresponding to the LO phonon. After a second deconvolution with this LO mode ($S=4.2$), the remaining part will be of mostly electronic origin, though slightly broadened by low-energy modes from the acoustic band. The low-energy limit of ~2.34 eV of this small peak corresponds to large values of R and thus yields the sum of E_D and E_A according to

$$h\nu = E_G - (E_D + E_A) + \frac{e^2}{\epsilon R} . \tag{3}$$

The evaluated value, $E_D+E_A=480$ meV, may be a slight overestimate because of the acoustic broadening mentioned above. Ag is expected to substitute on the Zn site, forming a singly charged acceptor, Ag_{Zn}, while the donor participating in the DA-pair spectrum is not identified. To estimate the binding energy of the dominant donor, which is necessary for the determination of E_A, laser-excited two-electron spectra[19] were utilized. When the dye-laser excitation is resonant with the DBE peak, a novel, rather broad peak is observed about 33 meV from the excitation energy in addition to the LO Raman peak. The

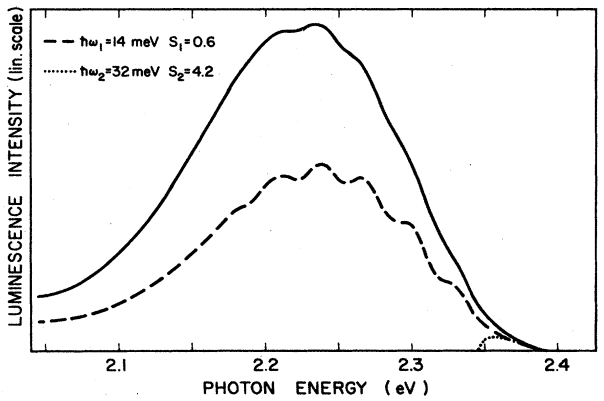

FIG. 6. Photoluminescence spectrum (solid line) for the Ag-related DA-pair emission at 2 K. To provide an "electronic" spectrum a deconvolution procedure is performed. The first phonon mode ($\hbar\omega=14$ meV), which has been "removed," corresponds to a discrete approximation of a high density of states in the acoustic band. In the remaining spectrum (dashed curve) the readily resolved periodicity corresponds to the LO phonon ($\hbar\omega=32$ meV). A second deconvolution with the LO mode provides a spectrum of mainly electronic origin (dotted curve).

peak is assumed to correspond to the first-excited state, $2S$, of the donor, which indicates a donor binding energy of about 45 meV. This is a large value of E_D, since most donors have binding energies in the region 26—30 meV, close to the effective-mass value, 26 meV.[16] We believe, however, that the derived value of E_D is probable, as the peak of our entire pair spectrum is shifted about 20 meV toward lower energies compared with the Ag-Ga DA-pair spectrum,[1] where $(E_D)_{\mathrm{Ga}}=27$ meV. A natural identification of this dominant donor in our material should be as a Ag interstitial, Ag_i. These Ag interstitials are supposed to occur in not insignificant concentrations since Ag is introduced by an interstitial diffusion mechanism, and not all of these interstitials can be expected to form complexes during the rapid cooling procedure employed. Returning to the deconvoluted pair spectrum (Fig. 6), the proposed value on $E_D=45$ meV yields $E_A(\mathrm{Ag})=435$ meV. This value is in good agreement with the thermal quenching measurements (Fig. 5), providing an activation energy equal to the estimated binding energy of $\mathrm{Ag}_{\mathrm{Zn}}$. Further, a second activation energy, ~ 50 meV, is obtained from this temperature-dependence plot, which probably is associated with the donor binding energy.

Selective excitation of DA pairs has turned out to be a powerful technique for investigating excited electronic states of both S- and P-like symmetry for acceptors and donors. The principles of this technique have been presented in previous works[20] and successively utilized for studies of shallow states, where discrete pair lines are resolved. In this work we show that the same procedure can be performed for deep structureless emissions both in PLE or SPL spectra, depending on whether the detection or excitation energy is fixed. In Fig. 7 is shown a SPL spectrum with a peak ~ 394 meV from the excitation energy, together with the LO-phonon replica. This peak is assigned to the transition from the ground state, $1S$, to the first-excited state, $2S$. Additional structure is observed above the $2S$ state, but is hardly resolved because of the increasing intensity from the DA-pair emission. It should be noted that these spectra are very similar to those obtained independently on LPE ZnSe by Dean *et al.*[1]

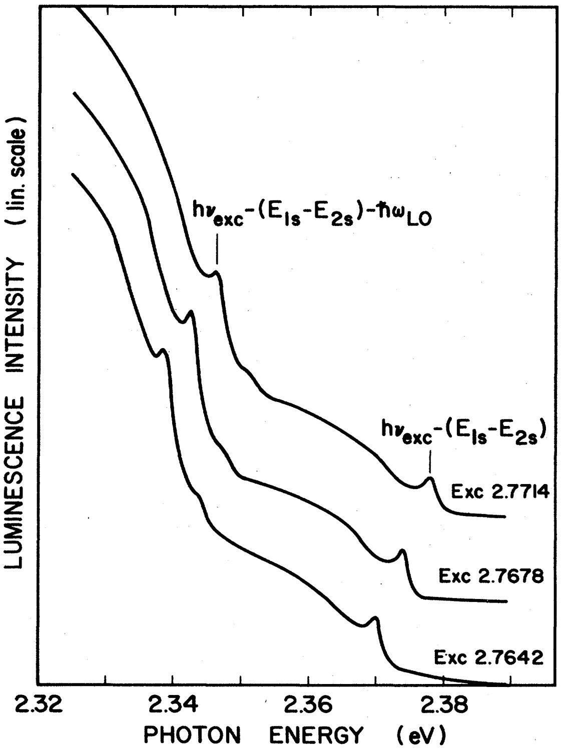

FIG 7. Portion of the PL spectrum for the 2.23-eV DA-pair emission for selective excitation from a tunable dye-laser; EXC is the excitation energy in eV. When the excitation energy is resonant with an excited state of the acceptor (or donor) in a particular DA-pair transition, the recombination rate between the ground states of the same DA pairs is enhanced. Thus the displacement of the detected peaks in the spectrum from the excitation energy corresponds to the energy difference between the ground state and the excited state of the involved Ag acceptor.

However, in the corresponding PLE spectrum (Fig. 8) at least three additional peaks are easily resolved. The next peak at 400 meV is slightly broader than the following two peaks at 410 and 418 meV, respectively. In addition, a broad feature appears in the energy range 419—422 meV depending on the detection energy and thus sometimes overlapping with the 418-meV peak. Figure 8 shows PLE spectra for four different detection energies. The dependence of the peak energies on the detection energy is shown in an inset in Fig. 8. We argue that the first strong peak at about 392 meV corresponds to the $2S_{3/2}$ excited state of the acceptor, while the slightly broader peak at about 400 meV should be the $2P_{5/2}$ state, which usually has a strong oscillator strength.[21] The peaks at 410 and 418 meV are identified as the $3S_{3/2}$ and $4S_{3/2}$ states, respectively. If the empirical formula $E_{nS}=E_0 n^{-1.76}$, which seems to be valid for shallow S states for many acceptors in ZnSe (Ref. 22) and ZnTe (Ref. 23), is applied to the most shallow S states, $3S$ and $4S$, a binding energy of 430 meV is provided. This value is in agreement with the value 431 meV derived from SPL data in the study of Dean *et al.*,[1] as well as with estimates from thermal quenching data and deconvoluted PL spectra as discussed above. It should be noted that the PLE data in Fig. 8 appear to give a more well-defined electronic structure than the SPL data in Fig. 7 and Ref. 1. Utilizing the above-provided formula even for the deeper $2S$ state will yield a binding energy consistent with the dominating $2S$ peak at 392 meV.

The position of the broader $2P_{5/2}$ peak is shifted more with the detection energy (400—403 meV) than are the S states (inset of Fig. 8). The most reliable value, 403 meV, is estimated for distant pairs, where the overlap with the donor wave function is less important. The energy for the $2P_{5/2}$ state is, as distinguished from S states, negligibly affected by central-cell corrections. Thus, if the above estimated $E_A=430$ meV is used, a binding energy of 27 meV for $2P_{5/2}$ can be evaluated, in agreement with theoretical calculations as well as experimental data for more shallow acceptors in ZnSe (Ref. 24), giving support to our identification of the peak. The lowest P state, $2P_{3/2}$, has a too low oscillator strength [$\sim 10\%$ of that of $2S_{3/2}$ (Ref. 24)] to be detectable. The identity of the

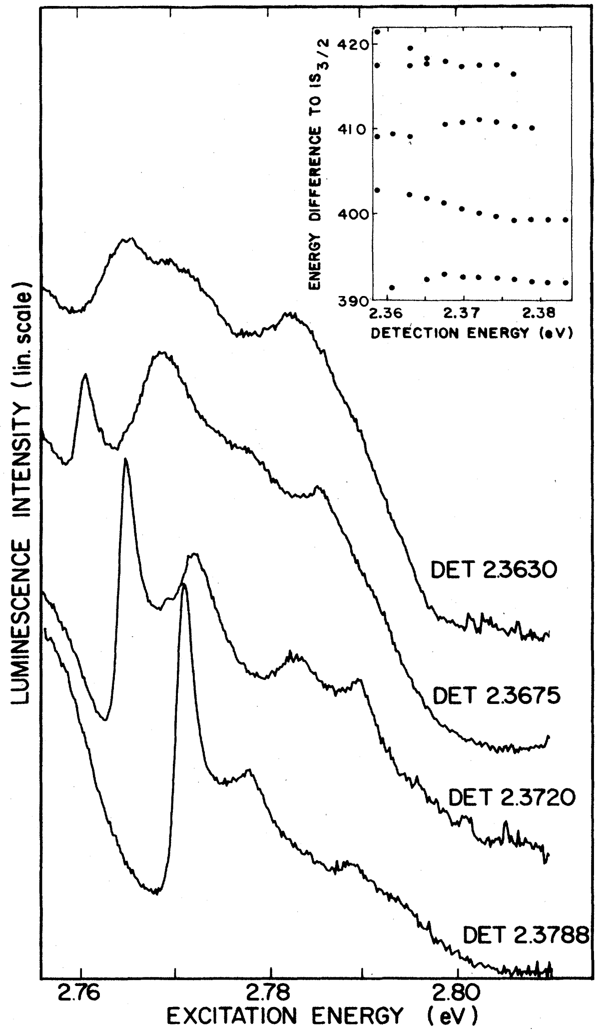

FIG. 8. Portion of the PLE spectrum for the DA-pair emission. This PLE spectrum corresponds to the SPL spectrum shown in Fig. 7. In the case of PLE the detection is fixed at a particular DA pair and the excitation energy is scanned through the excited states; DET is the detection energy in eV. The interpretation of the observed peaks is provided in the text. The dependence of the energy differences between the excited states and the $1S_{3/2}$ ground state (detected in PLE spectra) on the detection energy is shown in the inset. The states at ~400 and ~420 meV are assumed to correspond to transitions to P states, $2P_{5/2}$ and $3P_{5/2}$, respectively. The remaining levels are probably transitions to excited S states, $2S_{3/2}$ (392 meV), $3S_{3/2}$ (410 meV), and $4S_{3/2}$ (418 meV), respectively.

broad peak appearing at ~420 meV is uncertain from the available data. The most plausible suggestion is the $3P_{5/2}$ state. This is based on its broad shape as observed also for $2P_{5/2}$ and its binding energy consistent with the expected value for $3P_{5/2}$.

2. *Photoionization cross sections*

The spectral shape of optical cross sections for excitation of charge carriers from a deep level to a continuum state is often conveniently obtained via PLE spectra.[25] In our case the main radiative emission related to the 0.43-eV Ag acceptor level is a DA-pair emission (Fig. 1).

The PLE spectra shown in Fig. 9 for different temperatures for $\sigma_n^0(h\nu)$ of this acceptor were measured with tungsten lamp excitation via a monochromator and detecting the entire broad green emission. The expected threshold in the optical cross section $\sigma_n^0(h\nu)$ is observed at $E_g - E_A \sim 2.385$ eV at the lowest measuring temperature, 5 K. For comparison, the low-temperature PLE spectrum was also measured with tunable-dye-laser excitation in the photon-energy range 2.35–2.50 eV. The resulting $\sigma_n^0(h\nu)$ was exactly the same as shown in Fig. 9 for all temperatures, as expected from the observed linearity of the PL emission with excitation intensity.

The temperature dependence of an absorption edge for a deep-level defect is governed by two effects: the broadening of the edge due to phonon coupling and the shift of the edge due to the corresponding shift in the electronic level (ground state) for the defect. These two effects occur simultaneously, and therefore the evaluation of phonon coupling and level shift cannot be made directly by inspection of experimental data. In general, the phonon-coupling parameters may be evaluated from the optical cross section at any temperature by a deconvolution procedure.[4] At elevated temperatures this becomes extremely complicated, however, and therefore we adopt the procedure of deconvoluting the low-temperature spectrum under the assumption of a linear phonon coupling. This gives the relevant phonon-coupling parameters for the optical cross section and, in addition, the shape of the electronic cross section $\sigma_{n,\text{el}}^0(h\nu)$. Once these ingredients are available, the expected optical cross section can be computed at any temperature by a convolution of the optical low-temperature electronic spectrum, using the phonon-coupling parameters derived in the low-temperature deconvolution.[4] It is then assumed that the electronic cross section does not appreciably change its shape with temperature, a very good approximation in not

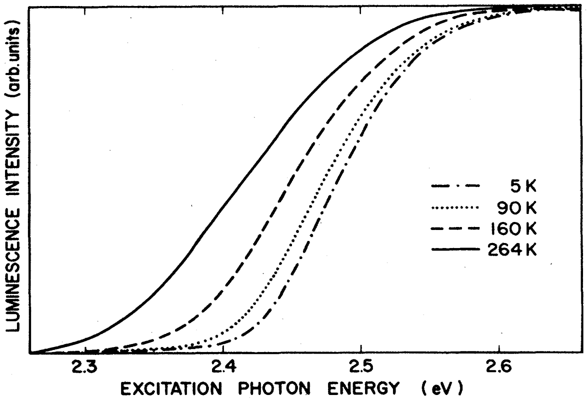

FIG. 9. PLE spectra for Ag-doped ZnSe measured with tungsten-lamp excitation at some different temperatures. The shape of the absorption edge changes with temperature due to phonon coupling and shift of the electronic level. To separate these contributions, a convolution procedure is utilized (as shown in Fig. 10 and described in the text).

too highly doped materials. Further, the linear approximation is adopted for the phonon coupling in the convolution procedure. Therefore we expect to generate by this computing procedure optical spectra that have the same shape as the experimental curves for $\sigma_n^0(h\nu)$ at each temperature chosen. The rigid energy shift of this curve necessary to obtain overlap with the experimental curve is the direct measure of the shift of the electronic deep level with temperature.

The result of the application of such a deconvolution procedure to the experimental low-temperature cross section $\sigma_v^0(h\nu)$ is shown in the inset of Fig. 10. Here the same phonon energies as deduced for the pair emission spectrum has been employed. The general shape of the resulting electronic cross section shows a noticeable peak close to the edge, accompanied by a slowly varying part towards higher energies. This general shape with a peak close to the edge is expected for allowed optical transitions.[4]

As also shown in Fig. 10, this electronic spectrum does reproduce the experimental $\sigma_n^0(h\nu)$ data at low temperatures, upon application of a convolution procedure with the same phonon energies as employed in the analysis of the PL emission spectrum above (Fig. 6). A slight modification in coupling strength for the high-energy 32-meV phonon is necessary (from $S=4.2$ in emission to $S=3.6$ in absorption), however, in order to obtain a good fit. To obtain a smoother shape of the curve, a low-energy mode ($\hbar\omega=2.0$ meV, $S=1.5$) has been added. This mode does not change the principal shape, but just makes the curve smoother, notably at lower temperatures. Figure 10 shows the best fit at low temperatures (14 K) with the stated values of coupling parameters and phonon energies.

In Fig. 10 are also shown two examples of the comparison between an experimental curve for $\sigma_n^0(h\nu)$ at elevated temperatures and the corresponding computed curve obtained from the low-temperature electronic cross section (inset of Fig. 10) with the aid of the convolution procedure at the same temperatures (119 and 264 K, respectively). It is observed that the shape of the curve in the edge region is quite well reproduced by the computed spectrum. These curves give accurate estimates of the energy shift of the electronic cross section and, consequently, the Ag acceptor level in the band gap with temperature, as evaluated from the horizontal distance between the two curves in the region, say between 2.3 and 2.5 eV. The resulting temperature shift of this acceptor level is shown in Fig. 10 (inset). It is observed that up to about 200 K there is an approximately proportional shift of the level in the band gap, i.e., $\Delta E_A^C \approx 0.85 \Delta E_g$ compared to the 0-K reference situation. In other words, the level is approximately pinned to the valence band. This is also what is expected from the simple model of Van Vechten and Thurmond.[26] At higher temperatures a slight deviation from this simple behavior was observed (similar to the case[25] of the deep O donor in GaP). The level tends to shift more from the valence band, which means that ΔE_A^C is a decreasing portion of ΔE_g. For the two highest temperatures we observe $\Delta E_A^C \approx 0.75 \Delta E_g$. No good theory seems to exist at the moment to explain such a temperature dependence.

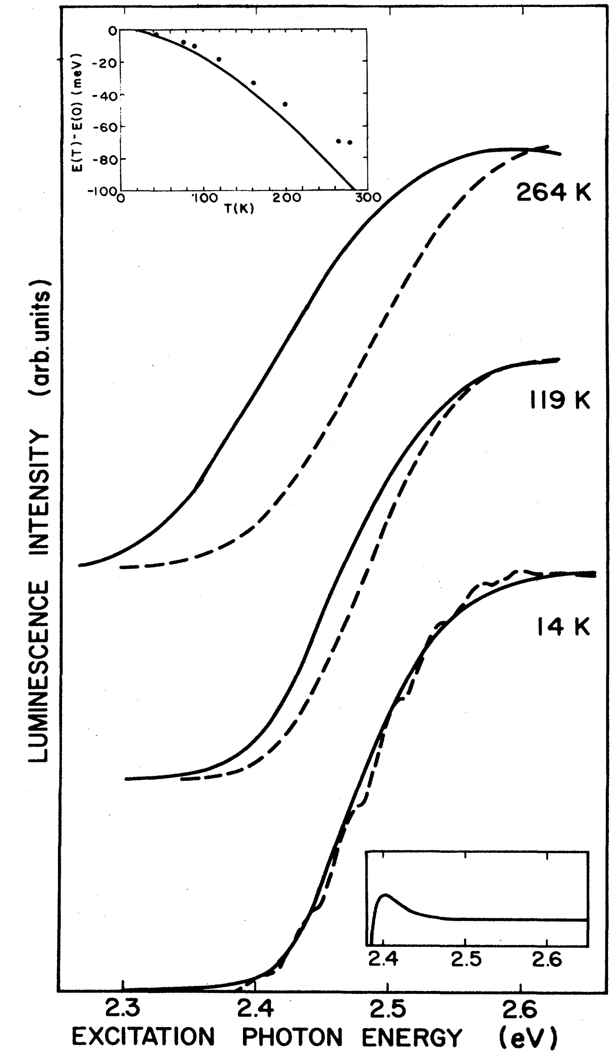

FIG. 10. The shape of the electronic cross section shown in the lower inset is based mainly on deconvolution of an experimental low-temperature excitation spectrum. With a convolution procedure applied to this electronic cross section, it is possible to generate the total phonon-assisted optical cross sections (dashed curves). For comparison, the corresponding experimental spectra are also shown (solid curves). The horizontal displacement between the computed and experimental curves at elevated temperatures corresponds to the shift of the electronic cross section. The resulting temperature dependence of the Ag acceptor level is shown in the upper inset. For comparison, the corresponding shift of the band gap is shown in the same temperature region (solid line).

IV. DISCUSSION

A. The 2.747-eV BE spectrum

The question of the identity of this center, assumed to be a complex mainly from the rather complex spectrum of quasilocalized phonon modes discussed above, remains unclear also from the present study. It is, however, of interest to note that recent detailed optical studies of Ag-doped ZnTe (Ref. 6) and CdTe (Ref. 7) show a rather similar pattern to those of ZnSe, i.e., in both cases we observe a dominant (substitutional) Ag_{Zn} or Ag_{Cd} acceptor and, in addition, a strong BE spectrum. For ZnTe this BE spectrum occurs at 2.3149 eV, i.e., 79 meV below the bandgap, while in CdTe a strong BE no-phonon line is observed at 1.5834 eV, i.e., 23 meV below the band gap. In both ZnTe and CdTe these dominating Ag-related BE spectra have been proven from Zeeman transmission data[6,7] to be of isoelectronic origin. In addition to the arguments discussed in Sec. III A, we therefore infer by analogy to these systems that the Ag_1^0 BE line in ZnSe is probably also an isoelectronic bound exciton (IBE) state, although this has not really been experimentally proved in the absence of Zeeman transmission data. In fact, such experiments in transmission would clarify the question of whether we have a neutral IBE complex or an acceptor-like BE. We argue that the strong emission intensity points to an absence of Auger processes, and therefore we prefer to discuss the Ag_1^0 complex in terms of an IBE state. This statement is also in agreement with the complex phonon coupling. It should be kept in mind that this is not definitely settled, however. Optically detected magnetic resonance (ODMR) measurements in the same way as for the green Cu-related emission in ZnSe (Ref. 27) may reveal the symmetry of the center and are also future experiments of high priority.

The corresponding Ag-related BE in ZnTe is shown to be a trigonal C_{3v} center[6] and therefore most probably a Ag_{Zn}-Ag_i pair. In our discussion of data above we have suggested this possibility as the most probable identity also for the 2.747-eV Ag_1^0 center in ZnSe. Indeed, at high diffusion temperatures the Coulomb forces between charged (ionized) $Ag_{Zn}{}^-$ acceptors and $Ag_i{}^+$ donors would strongly favor the formation of neutral Ag_{Zn}-Ag_i complexes. In addition, since the Ag doping level introduced from diffusion in most of our samples should be higher than any other shallow-donor doping level, it is not likely that residual shallow donors play any roll in the Ag_1^0 complex. Additional doping with Li by a second diffusion step leaves the Ag_1^0 spectrum unchanged (and does not introduce any new BE states in the band gap due to possible complex formation between Ag and Li).

The electronic properties of such a Ag_{Zn}-Ag_i pair are of fundamental interest, since data of the properties for such defects, supposed to be under local compressive axial stress, are scarce in the literature.[28,29] Since only one broadened electronic BE line appears in emission as well as in absorption, the HTL model will probably be applicable for the Ag_1^0 center, where the central-cell potential is attractive for the hole, due to the dominant contribution from the Ag_{Zn} site. The electron is rather weakly bound, mainly by Coulomb forces from the hole, since the rather shallow Ag_i state ($\sim$45 meV) gives a weak central-cell contribution compared to Ag_{Zn}. The electron wave function then does not overlap much with the bound hole and negligible exchange splitting results. This model is also consistent with our results from thermal quenching of the PL intensity shown above.

Interestingly enough, the analogous center in ZnTe behaves differently.[6] A strong exchange coupling occurs between the electron and hole for the Ag-related IBE line at 2.3149 eV in ZnTe. This is understandable, however, since for ZnTe the Ag_{Zn} acceptor is relatively shallow, with a binding energy E_A of only $\sim$125 meV. This is probably comparable to the depth of the Ag_i donor in ZnTe, and therefore it is not obvious whether a hole-attractive or an electron-attractive central cell is expected. In fact, the electron in the ZnTe:Ag case has completely lost its shallow character and its g value is shifted from -0.4 to $+2.0$. This explains why a strong exchange coupling in this case is natural.[6]

A possibility that *a priori* has to be discussed for the 2.747-eV BE state is the charge-transfer (CT) model. Such emissions with similarly rather strong phonon coupling have been identified with CT processes in the cases of ZnSe:Co, ZnSe:Ni, and ZnO:Cu.[30] A CT model applied to our system means that the spectrum should involve a d^9-d^{10} transition of the Ag_{Zn} acceptor. This can be discarded from the simple argument that the Ag_{Zn} shows a normal d^{10}-hole character, which is proven from the appearance of the excited states of the Ag_{Zn} acceptor in our PLE spectra for DA-pair transitions (see below). It is of interest to compare the PL emission properties of Ag in ZnSe with those of Cu. Cu_{Zn} also yields a deep acceptor state (0.65 eV) in ZnSe (Ref. 31), and, in addition, a shallower, green emission arising from a Cu_{Zn}-Cu_i axial center with a binding energy[27] of 0.35 eV. This latter center would then be the analog of our 2.747-eV center in Ag-doped material, but the Cu associate is apparently considerably deeper. We believe the main reason for this difference is that in an associate of two Cu atoms the Cu_{Zn} central-cell potential is still of dominantly d^9 origin, as has recently been found for the isolated Cu_{Zn} bound hole via magneto-optical studies.[3] The Ag_{Zn} state is shown to be of d^{10} character, which should be retained in the associate as well. Indeed, one would expect a hypothetical d^{10} Cu_{Zn} acceptor state in ZnSe to be rather shallow, as for ZnTe. Thus the strong binding energy, $\sim$350 meV, for the Cu_{Zn}-Cu_i associate, compared to the 73 meV found here for the proposed Ag_{Zn}-Ag_i associate, has its origin in a profound difference in the hole-attractive central-cell potential, which is indeed expected to be quite localized when the hole is placed into the d^9 shell.

B. The deep Ag_{Zn} acceptor

The important question, whether the Ag_{Zn} acceptor, here observed via the broad DA-pair band peaking at $\sim$2.23 eV, is to be regarded as a conventional deep acceptor of d^{10} origin, or if we have a d^9 configuration causing a level in the band gap, was discussed by Dean *et al.*[1] They concluded that the normal d^{10} case was the most plausible one for Ag_{Zn} in ZnSe.

Our additional data presented here confirm this point of view. The presence of an open-shell $4d^9$ configuration is expected to give rise to an internal transition within the d^9 configuration, observable both in PL emission and absorption. Sensitive IR detectors were not available for PL emission studies in this work, but Fourier-transform infrared (FTIR) transmission spectra were recorded in the energy region 0.2—0.5 eV, with additional photoexcitation. No sharp lines originating from internal d-line transitions were observed. Unidentified sharp lines did occur around 0.35 eV, but were equally strong in the reference samples (not Ag-doped) and thus these features are not Ag-related.

In addition, the detailed behavior of excited states in PLE spectra for the DA-pair transitions shown above under Sec. III B is consistent with a conventional d^{10} acceptor. Recent work has shown that the behavior of optical transitions from the corresponding charge transfer state for an open d-shell case to excited states of such an acceptor is quite different.[30] Such structures cannot be classified as conventional Coulomb-like excitations of a normal acceptor with a closed d^{10} shell in both charge states, but are strongly influenced by their characteristic of the inter-d-shell transfer. Thus there is no evidence for a d^9 configuration of the $\mathrm{Ag_{Zn}}$ acceptor in ZnSe.

The binding energy of this Ag-related acceptor will probably be too large to allow detection of two-hole spectra via the corresponding ABE state. In addition, the position of the related ABE line is still uncertain. In the absence of information from ABE spectra, the DA-pair transitions measured with tunable-dye-laser excitation seem to be able to supply similar information about the electronic structure of this deep acceptor. Already the SPL spectra give in this bulk material a good value of the $1S$-$2S$ energy separation for the acceptor. An important observation is that the line corresponding to the $1S$-$2S$ transition is unsplit, as expected for a simple substitutional acceptor state of T_d symmetry in contrast to complex acceptors of lower symmetry, where corresponding lines are often split.[32] (FTIR transmission experiments on our Ag-doped material did not reveal any excited states of the Ag acceptor, since the samples were n-type and sufficient hole occupancy of the acceptor could not be obtained even by additional below-band-gap laser excitation.)

The electronic structure of this $\mathrm{Ag_{Zn}}$ acceptor in ZnSe is best resolved from dye-laser-excited PLE spectra in our bulk material. Note that such spectra can only be obtained with good sensitivity and selectivity in bulk material, while rather thin epitaxial layers appear to be unsuitable for this purpose.[1] The energies of the shallow S states observed in PLE spectra allow an accurate determination of the binding energy of the deep $\mathrm{Ag_{Zn}}$ acceptor as $E_A = 430 \pm 2$ meV, in agreement with the value $E_A = 431 \pm 2$ meV deduced by Dean *et al.* from SPL data. The analysis of PLE spectra for identification of excited states of the $\mathrm{Ag_{Zn}}$ acceptor, presented above under Sec. III B, must be regarded as only tentative in the absence of magneto-optical data, where the S and P states can be clearly distinguished from each other. Indeed, in our case the identity of the excited states was mainly based on the assumption that the $2S_{3/2}$ state is the one of strongest intensity in PLE spectra. This has been found to be the case for similar studies of shallower acceptors in ZnSe,[24] and also for ZnTe.[33]

V. SUMMARY

A detailed investigation of the optical properties of the main Ag-related defects in *bulk* ZnSe doped by Ag diffusion was performed. Two dominating centers were found; a rather shallow (BE) state at 2.747 eV and, in addition, a deep acceptor with a binding energy of 430 meV. The phonon-coupling behavior for this BE strongly suggests that it is a complex defect; further, the strong PL intensity points towards the absence of Auger effects, i.e., it is a neutral-complex Ag-related defect. The BE transition consists of a single electronic line in both emission (PL) and absorption (PLE), suggesting negligible jj-coupling between the electron and the hole bound to the center. This is also consistent with the thermal quenching data in PL, where an activation energy of ~52 meV for the hole and about 21 meV for the electron seem to prove that we have a rather conventional situation with a hole bound first (by virtue of the hole-attractive $\mathrm{Ag_{Zn}}$ central-cell potential) and a shallow electron state bound by Coulomb forces. The probable identity as a $\mathrm{Ag_{Zn}}$-Ag_i neutral isoelectronic complex is suggested, in analogy with recent observations in other II-IV compounds such as ZnTe and CdTe doped with Ag.

The phonon coupling to the 2.747-eV BE is studied in detail in PL and PLE spectra, as a function of temperature. Strong quasilocalized modes at ~2.2 meV are found, which appears to be similar to the case of other complex defects involving interstitial species. A second weaker quasilocalized mode occurs at ~8.7 meV. The strong coupling to the low-energy phonons is manifested in a thermal quenching of the electronic line at 2.747 eV already at about 20 K, much faster than the total BE emission envelope, which survives up to about 70 K. A detailed model for the quenching of the no-phonon line within the linear phonon-coupling theory is provided to elucidate these data.

No separate BE line associated with the deep $\mathrm{Ag_{Zn}}$ acceptor was observed, which indicates that it is isoenergetic (within the rather broad linewidth observed) with the other shallow acceptor BE lines at about 2.793 ± 0.002 eV. This means that the Haynes rule is not valid for acceptor BE's in ZnSe, in agreement with the situation for acceptor BE's in other II-VI compounds.[34]

The deep $\mathrm{Ag_{Zn}}$ acceptor at 430 meV is identified as such mainly since it is by far the dominanting Ag-induced acceptor. Further, the $2S$ excited state of this acceptor is unsplit, as expected in cubic symmetry. In addition, this acceptor is not sensitive to doping with other rapid diffusers, such as Li. In fact, no evidence for complexing between Ag and Li was found in this study. Detailed data on excited electronic states for this acceptor were obtained with tunable-dye-laser excitation, both in SPL and PLE spectra. The most detailed electronic spectra was observed in PLE, which is a very useful technique in bulk material. From the observation of both S- and P-like excited states up to $4S$, it is concluded that these states behave quite similarly to those for other shallow cubic acceptors in ZnSe. This confirms that the $\mathrm{Ag_{Zn}}$ acceptor is a normal $4d^{10}$ configuration, in contrast to the case with the similarly deep $\mathrm{Cu_{Zn}}$ acceptor in ZnSe.[3]

Novel data for the optical cross section $\sigma_n^0(h\nu)$ were obtained with the PLE technique for temperatures between 2 and 300 K. A convolution procedure based on the experimentally derived electronic spectrum gives a computed shape of the $\sigma_n^0(h\nu)$ curve at higher temperatures, assuming a fixed binding energy for the acceptor. The rigid shift of such computed curves to achieve overlap with the experimental $\sigma_n^0(h\nu)$ curve at each temperature is the only reasonable way to get reliable values for the temperature dependence of the binding energy of the acceptor. The acceptor was found to be mainly connected to the valence band below 150 K.

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