Spin-flip Raman-scattering studies of compensating donor centers in nitrogen-doped zinc selenide grown by molecular-beam epitaxy

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When ZnSe is doped p type by the incorporation of nitrogen, a compensation process sets in for effective acceptor concentrations between 10^{17} and 10^{18} cm^{-3}. It is generally agreed that this is due to the creation of compensating donors which have been reported to lie at a depth of about 45 meV. It has previously been shown from optically detected magnetic resonance and spin-flip Raman-scattering experiments that these donors have a gyromagnetic ratio (g value) of about 1.4, compared with the g value of 1.1 for the more usual shallow donors (which lie at about 26 meV). We report here a systematic study of a series of ZnSe layers (grown by molecular-beam epitaxy) in which the nitrogen concentration is gradually increased, and we confirm the correlation between the onset of the compensation (at an effective acceptor concentration of about 1.7×10^{17} cm^{-3}) and the appearance of the 45-meV donor. The spin-flip Raman scattering is a resonance process that requires the laser energy to coincide with the excitonic transition associated with the donor, and we have exploited this effect to determine the difference in the localization energies of excitons bound at the two types of donor. The results show that Haynes's rule is obeyed for donor depths E_D extending at least to 45 meV, the exciton localization energy being $0.20E_D$.

I. INTRODUCTION

Recently there have been many attempts to obtain low conductivity p-type ZnSe through the incorporation of nitrogen, both in specimens grown by molecular-beam epitaxy (MBE),[1,2] and in those produced by metal-organic vapor-phase epitaxy (MOVPE).[3] In all cases the effective room-temperature acceptor concentration (N_A-N_D) appears to become saturated at a level between 10^{17} and 10^{18} cm^{-3}, even though the nitrogen itself can be present in the material in amounts of up to two orders of magnitude greater than this.[4] Nevertheless, nitrogen still remains the most promising p-type dopant for ZnSe, and the use of this material in blue/green lasers makes it particularly important to understand the mechanisms that limit the electrically active acceptor concentration. The problem is somewhat complicated, since there is considerable evidence both for the formation of compensating donor centers as the nitrogen doping is increased, and for the formation of deep acceptors that are not ionized at room temperature.[5–7]

The present investigation concerns compensating donors that appear as the nitrogen content exceeds 10^{17} cm^{-3}. Our specimens were grown by MBE and doped with nitrogen from a rf discharge source. In a previous investigation[8] of nitrogen-doped material grown by a similar method but at a different laboratory, we used spin-flip Raman (SFR) scattering by electrons at neutral donors to confirm the existence of two distinct types of donor centers each characterized by its particular value of the gyromagnetic ratio (g value) that describes the splitting of the spin states in a magnetic field. Thus the donors that are usually obtained in ZnSe as a result of impurity incorporation in even the best material are found to have a depth of about 26 meV below the conduction band (values of between 25 and 29 meV have been reported, depending on the nature of the impurity [9–11]), and have a g value of about 1.1,[12,13] which is the value predicted for free electrons in ZnSe:[14] in contrast, those that appear when high levels of nitrogen are incorporated have a depth of about 45 meV [different authors report values in the range 40–57 meV (Refs. 5–7 and 15)] and a g value of about 1.4.[8,15] Both types of donors can be observed directly not only by the SFR (Refs. 8 and 13) experiments but also by optically detected magnetic resonance (ODMR).[12,15,16]

In the present investigation we have used electron SFR to study a series of ZnSe layers in which the nitrogen concentration is gradually increased so as to provide a range of effective acceptor concentrations in the critical region between 1.2×10^{17} and 1.8×10^{17} cm^{-3}. We are thus able to follow the appearance of the compensating donor in more detail than previously. In addition, we have investigated in detail the manner in which different SFR signals are enhanced when the laser energy is adjusted to be in resonance with different excitonic transitions: in this way, we have been able to distinguish between excitons bound to the two types of donors, and to establish the validity of Haynes's rule[17] in this context.

II. EXPERIMENTAL DETAILS

A. Specimen growth

The ZnSe layers were produced at Heriot-Watt by MBE on (001) GaAs substrates. The growth temperature was 280 °C. Solid sources of zinc and selenium were used and the growth rate was about 0.5 μm per hour. The nitrogen was incorporated by using an Oxford Applied Instruments radio-

TABLE I. ZnSe specimens used in the investigation. The figures in parentheses indicate the growth number.

Specimen number	Thickness (μm)	rf power (W)	(N_A-N_D) (cm^{-3})	$g=1.1$ signal	$g=1.4$ signal
1 (490)	0.9	100	1.2×10^{17}	yes	no
2 (492)	1.0	150	1.6×10^{17}	yes	yes (weak)
3 (491)	0.8	200	1.7×10^{17}	yes	yes
4 (493)	1.0	250	1.8×10^{17}	no	yes

frequency plasma source, the dopant level being controlled through adjustment of the radio-frequency power. The doped zinc selenide was grown directly on to the substrate, there being no buffer layer. The ZnSe layer thicknesses and the effective acceptor concentrations (measured by photochemical capacitance-voltage techniques[18]) are given in Table I.

B. Optical experiments

The measurements were made at the University of East Anglia with the specimens in superfluid helium at 1.5 K. Photoluminescence (PL) was excited with 2.88-eV light from a Stilbene 3 dye laser pumped by ultraviolet argon-ion radiation. For the Raman experiments, the dye laser wavelength was set to the region of the excitonic transitions (2.76–2.82 eV). The Raman spectra were obtained in backscattering geometry with the laser incident normally to the layers, and with the magnetic field in the layer plane (in the 110 direction).

1. Photoluminescence spectra

The PL spectra from the four specimens are characterized by excitonic and donor-acceptor pair (DAP) recombination transitions. In Fig. 1 we give the excitonic region of the PL spectrum from specimen 3: A^0X denotes the line due to excitons bound to neutral acceptors,[19] and the band marked C has been attributed to recombination from exciton complexes.[20] The inset to the figure shows the DAP signals with their series of phonon replicas (2.55–2.72 eV) for all three specimens. As the nitrogen level is increased, the series of donor-acceptor lines with its leading signal at 2.700 eV gradually disappears, and is replaced by a series starting at 2.685 eV. This phenomenon has been observed by several groups studying nitrogen-doped ZnSe.[5–7] Care needs to be taken when analyzing these spectra, since the distributions of donor-acceptor separations (and hence the Coulomb contributions to the recombination energies) are not known. However, the first series is usually attributed to recombination involving shallow impurity donors at a depth of about 26 meV, and nitrogen acceptors at about 111 meV (Ref. 21) above the valence band, while the second is generally thought to be due to recombination involving the nitrogen acceptors and a second donor at about 45 meV (the different depths reported by various authors[5–7] probably reflect variations in the spatial distribution of the donor-acceptor pairs and differences in excitation conditions). As can be seen from the PL spectra, the second donor becomes increasingly important as the nitrogen concentration becomes larger, and is generally believed to be responsible for onset of the compensation process at (N_A-N_D) of about 1.7×10^{17} cm^{-3}.[1–4]

2. Spin-flip Raman scattering

The SFR spectra for specimens 1 and 4 are shown in Figs. 2(a) and 2(b). In each case the splitting $2\Delta E$ between the Stokes and anti-Stokes signals is proportional to the applied magnetic field B, and can be written $2\Delta E=2g\mu_B B$, where μ_B is the Bohr magneton. It is found that the values of g for the two specimens differ. Following our previous Raman

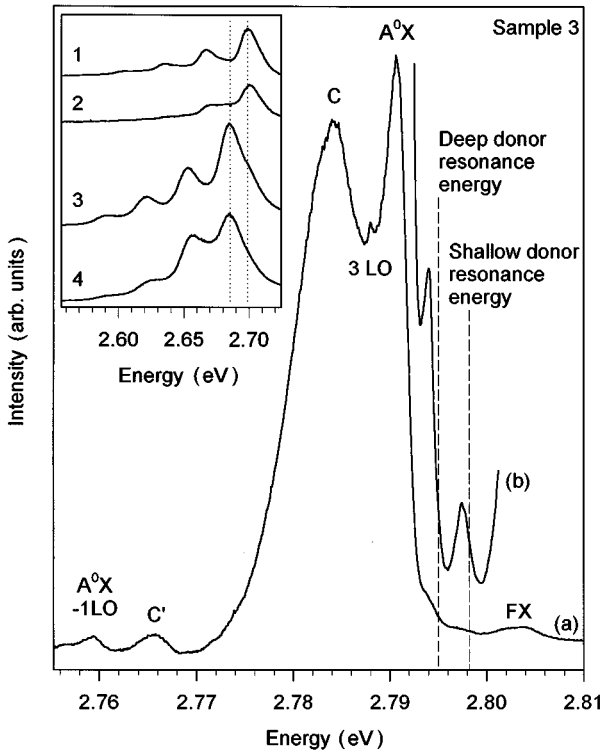

FIG. 1. The excitonic part of the PL spectrum at 1.5 K from the ZnSe specimen number 3. The laser excitation energy for spectrum (a) was 2.88 eV. The inset shows the part of the PL spectrum that contains the donor-acceptor recombination transitions, for all four specimens in the order (downwards) of increasing nitrogen content. Also shown in the main part of the figure are the resonance energies for the two types of spin-flip Raman scattering and (b) part of the PL spectrum from sample number 3 when the laser energy is changed to 2.802 eV [unlike the other spectra in this diagram, which were in zero magnetic field, PL spectrum (b) was taken at 6 T, so as to facilitate comparison with the Raman resonance energies discussed in the text]. Transition FX is due to recombination of free excitons, the signal marked A^0X and its phonon replica A^0X-LO are due to excitonic recombination at neutral acceptors, and the line marked 3LO is a Raman line due to scattering by phonons. Lines C and C' are unidentified but are believed to be associated with the nitrogen doping.

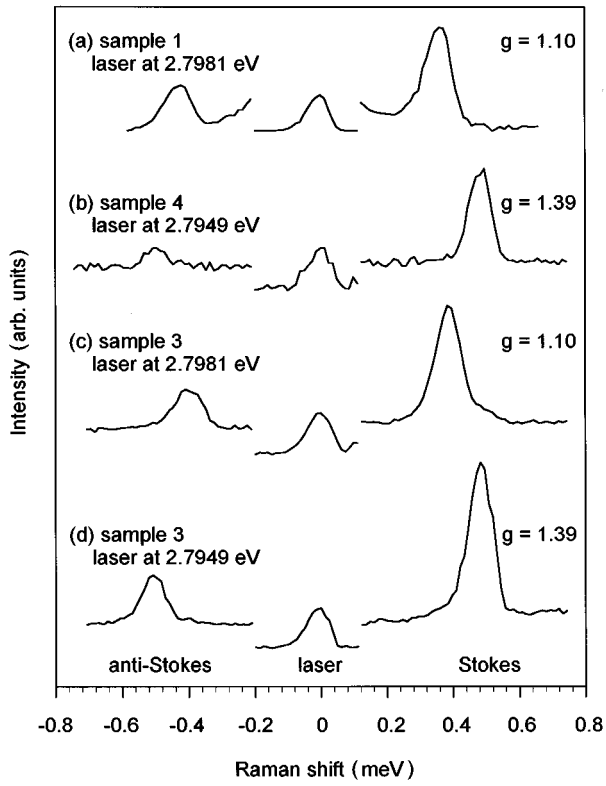

FIG. 2. SFR spectra for (a) specimen 1 and (b) specimen number 4. The laser energies were 2.7981 and 2.7949 eV, respectively, and the laser was attenuated to record the central part of the spectrum, which is due to elastically scattered light. The SFR spectra shown in (c) and (d) are both for the *same* specimen (number 3), but with the laser set respectively to 2.7981 and 2.7949 eV. In all cases, the magnetic field was 6 T and the temperature 1.5 K. For all four specimens, the Raman shifts are proportional to the value of the magnetic field. The diagram demonstrates clearly that different resonance energies are found for the two SFR signals.

study[8] and guided by the ODMR results,[12,15,16] we attribute the g value of 1.10 ± 0.04 to the donor at 26 meV, and the g-value of 1.39 ± 0.04 to the (compensating) donors at 45 meV.

Experimentally, each SFR signal appears only when the laser is set to a certain energy. This is a result of the enhancement of the scattering cross section that occurs when the incoming photon energy coincides with the energy of an appropriate excited state.[22] In the present case, the excited states are those formed by the creation of an exciton bound to a neutral donor. The exciton is therefore formed from two electrons (which are assumed to be spin paired in the exciton state of lowest energy) and a hole, so that the exciton spin states are those of a hole. The ZnSe layers in our specimens are sufficiently thick for us to assume that they are relaxed;[23,24] however, the different thermal expansion coefficients of ZnSe and GaAs substrate are expected to lead to a biaxial tensile strain of the ZnSe layers of up to $+0.1\%$, such that the exciton states formed from the light holes lie lower in energy by about 2 meV.[23–25] A further complication is that, in our experiment, the magnetic field is in the plane of the layer and therefore mixes the light- and heavy-hole states.

The resonance effect for the spin-flip scattering of electrons bound at neutral donors does not appear to have been studied in detail for ZnSe. In the case of ZnTe the selectivity of the resonance process has been demonstrated clearly through the observation of spin-flip scattering by electrons and holes when the laser tuned to the transitions of excitons bound, respectively, at neutral donors and at neutral acceptors.[26] As described below, we make use of a similar selectivity to distinguish between the excitonic transitions associated with the two types of donors in our ZnSe specimens.

A key feature of the SFR spectra is that the laser energy required to obtain resonance in specimen 1 [Fig. 2(a)] is different from that required for specimen 4 [Fig. 2(b)]. This is entirely consistent with the hypothesis that two different kinds of donor are involved, since the binding energy of excitons to neutral donors is expected to depend on the depth beneath the conduction band of the donor itself. That this is not an effect caused by changing from one specimen to another is demonstrated clearly by the SFR spectra in Figs. 2(c) and 2(d), which are both from the *same* specimen (number 3), but were obtained by retuning the laser from 2.7981 eV, for which the signals with $g=1.10$ were observed, to 2.7949 eV, which resulted in the lines with $g=1.39$. In the main part of Fig. 1, we indicate by arrows the laser energies for which each of these SFR signals can be obtained.

By tuning the laser in this way, it was found that signals from the shallow donor could be observed in the specimens with $(N_A\text{-}N_D)$ up to and including 1.7×10^{17} cm^{-3}, whereas the deeper donor is detectable for $(N_A\text{-}N_D)$ greater than 1.6×10^{17} cm^{-3}. In a previous study[8] on material produced by MBE at the Matsushita Laboratories, the shallow donor could be observed in a specimen with an effective acceptor concentrations of 1.0×10^{17} cm^{-3} but not for one with 4.3×10^{17} cm^{-3} in the former of these samples, SFR signals from the deeper donor could just be detected, being much stronger in the latter. The appearance of the deeper donor therefore appears to be correlated with the difficulty of obtaining values of $(N_A\text{-}N_D)$ greater than midway between 10^{17} and 10^{18} cm^{-3}: the behavior of the SFR signals is fully consistent with that of the donor-acceptor PL spectra in this respect. For the SFR signals to be observed, the donors must be in the neutral state, as they must also be in order to recombine with acceptors to produce the characteristic pair emission spectra of the inset to Fig. 1. It therefore appears that, as the concentration of deeper donors increases, electrons that would otherwise become trapped at the shallow impurity donors become localized instead at the deeper ones, resulting in changes that are seen in both the SFR and PL spectra. The lifetime of the electrons photoexcited to the neutral state will not be well defined (since the dynamics of the pair recombination process depend on the distribution of interpair separations), but it is clear from the fact that ODMR signals with linewidths of order 1 μeV (20 mT for $g=1$ at 9 GHz) can be observed[15] from similar specimens that a significant number of electrons must remain at the donors for at least 10^{-8} s.[27] Neither the ODMR technique nor the present SFR experiments yield information on the concentration of donor centers (of either type), but it is clear that if the deeper donor is to provide compensation that limits the effective value of $(N_A\text{-}N_D)$ in the observed manner, it must itself

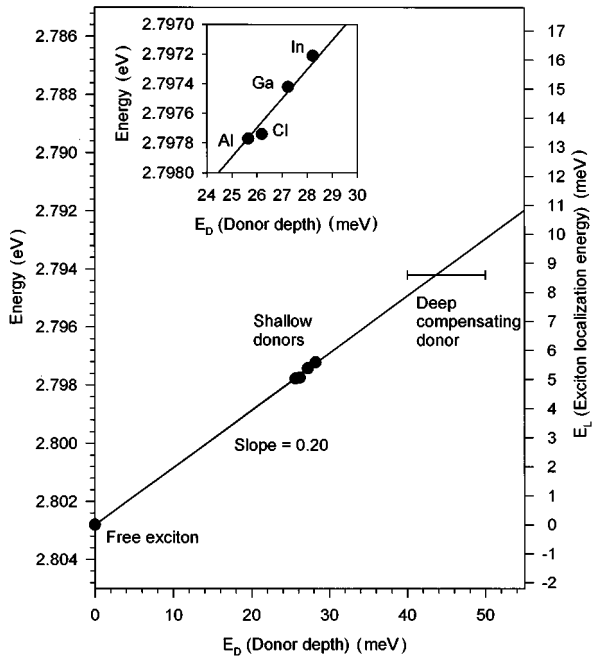

FIG. 3. Transition energies of excitons bound at neutral donors as a function of donor depth. Data for the shallow donors (i.e., those with depths of about 25 meV) are from the PL experiments reported in Ref. 10, as is the free-exciton energy. Taking the free-exciton energy as zero, the localization energy of the exciton is shown on the right-hand vertical axis. The present experiments extend the graph to a donor depth of approximately 45 meV, and establish the validity of Haynes's rule over this range. The inset shows an expanded version of the region that involves the shallow donors.

become present in concentrations in excess of 10^{17} cm^{-3}.

The study of the resonance behavior of the SFR transitions makes it possible to distinguish between the energies of the transitions associated with excitons bound at different neutral donors. If Haynes' rule[17] is obeyed, these energies should be linearly dependent on the donor depth. In Fig. 3 we show the energies of the recombination transitions for excitons trapped at a number of neutral shallow donors,[9–11] together with exciton transition energies obtained from the current study, plotted as a function of the donor depth [the recombination energies of the excitons bound at shallow donors such as gallium are those obtained by PL (Refs. 9–11) for *unstrained* material]. For a given donor impurity, we do not know which of the excitonic states leads to the resonance effect: we therefore cannot necessarily expect the PL recombination energy of the bound exciton to coincide exactly with the energy required for resonance enhancement of the SFR signal. A further complication in comparing our results with those from unstrained material is that the biaxial tensile strain in our epitaxial layers will cause additional small shifts in the excitonic transition energies. Yet another complication arises since our data are obtained in magnetic fields, the line positions being subject to Zeeman and diamagnetic shifts. Rather than attempt to calculate the combined shifts due to all these effects (which would involve several unknown factors), we have adopted the following procedure. To construct Fig. 3 we have shifted the laser energy (2.7981 eV) required to obtain the SFR signals with $g=1.10$ in our layers so that it coincides with the average transition energy (2.7975 eV) observed[10] for the PL transition of excitons bound to shallow donors in *unstrained* material; in other words, we have made our data point for shallow donors coincide with that obtained in the PL studies in unstrained material, We now make the reasonable assumption that the excitonic states that lead to our two observed resonance energies differ only in that they involve excitons bound to donors of differing depths. The strain and diamagnetic effects will be very similar in the two cases, and we can therefore adopt the same procedure (of subtracting 0.7 meV from the resonance energy) in order to plot the point corresponding to the deep donor in Fig. 3 (in which the vertical axis refers to the excitonic transition energies obtained from PL studies[10]). Figure 3 thus represents the situation for notional unstrained ZnSe.

From Fig. 3 we now see that Haynes's rule (a linear dependence of exciton energy on the depth of the donor at which the exciton is localized) is obeyed to within the experimental accuracy, and that the localization energy of an exciton at a neutral donor is 0.20 times the donor binding energy.

Given the energies (Fig. 1) needed to obtain resonance with the exciton transitions, we finally searched for PL signals that could be associated with excitons bound at two types of donor. In the main part of Fig. 1, we show part of the PL spectrum when the laser is set to 2.802 eV (coinciding with the free exciton transitions) and the field is set to 6 T. Two sharp features are observed (at 2.797 and 2.794 eV) which we tentatively attribute, respectively, to the recombination of excitons bound at shallow donors (at about 25 meV) and at the deeper donors (at about 45 meV). Supporting evidence for this attribution is provided by the fact that the 2.794-eV PL is observed only in the specimens that show the SFR signal with a g value of 1.39. If the attribution is correct, there appear to be Stokes shifts between the resonance energies and the PL signals (such shifts would arise, for example, if the resonance transitions involved components of the exciton spin multiplets *other* than the ones that lie lowest in energy).

The present investigation has concerned the SFR scattering by electrons. We note however, that, in a separate specimen (grown by MOVPE), SFR scattering has been observed from holes at the nitrogen acceptors themselves.[28] Here the laser has to be set to resonance with the transition energy of excitons bound at the neutral acceptors (the A^0X line), further illustrating the potential for using resonance SFR spectroscopy as a means of studying selectively the different centers involved in optical processes in these materials.

III. CONCLUSIONS

The present work provides strong confirmation of the model in which the onset of the saturation of the effective acceptor concentration in nitrogen-doped ZnSe is caused by the creation of a compensating donor at a depth of about 45 meV. The electrons bound at these donors have a g value of 1.39 and the appearance of the corresponding SFR signals is strongly correlated with the difficulty of increasing (N_A-N_D) beyond the mid-10^{17}-cm^{-3} range. The result is consistent with that obtained in our previous study[8]of specimens grown at a different source.

The fact that different donors are involved is confirmed

by the different resonance behavior of the two signals. The difference in the resonance energies has enabled us to infer a difference in the corresponding localization energies and hence to establish the validity of Haynes's rule for excitons bound at neutral donors in ZnSe over a range of donor depths considerably greater than previously studied.

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[1] K. Ohkawa, T. Karasawa, and T. Mitsuyu, J. Cryst. Growth **111**, 797 (1991).
[2] R. M. Park, M. B. Troffer, C. M. Rouleau, J. M. Depuydt, and M. A. Haase, Appl. Phys. Lett. **57**, 2127 (1990).
[3] S. Fujita and S. Fujita, J. Electron. Mater. **24**, 137 (1995).
[4] T. Yao, T. Matsumoto, S. Sasaki, C. K. Chung, Z. Zhu, and F. Nishiyama, J. Cryst. Growth **138**, 290 (1994).
[5] I. S. Hauksson, J. Simpson, S. Y. Wang, K. A. Prior, and B. C. Cavenett, Appl. Phys. Lett. **61**, 2208 (1992).
[6] K. Ohkawa, A. Tsujimura, S. Hayashi, S. Yoshii, and T. Mitsuyu, Physica B **185**, 112 (1993).
[7] Z. Zhu, K. Takebayashi, K. Tanaka, T. Ebisutani, J. Kawamata, and T. Yao, Appl. Phys. Lett. **64**, 91 (1994).
[8] P. J. Boyce, J. J. Davies, D. Wolverson, K. Ohkawa, and T. Mitsuyu, Appl. Phys. Lett. **65**, 2063 (1994).
[9] P. J. Dean, D. C. Herbert, C. J. Werkhoven, B. J. Fitzpatrick, and R. N. Bhargava, Phys. Rev. B **23**, 4888 (1981).
[10] M. Isshiki, T. Kyotani, K. Masumoto, W. Uchida, and S. Suto, Phys. Rev. B **36**, 2568 (1987).
[11] P. Blanconnier, J. F. Hogrel, A. M. Jeans-Louis, and B. Sermage, J. Appl. Phys. **52**, 6895 (1981).
[12] D. J. Dunstan, J. E. Nicholls, B. C. Cavenett, and J. J. Davies, J. Phys. C **13**, 6409 (1980).
[13] P. A. Fleury and J. F. Scott, Phys. Rev. B **3**, 1979 (1971).
[14] M. Willatzen, M. Cardona, and N. E. Christensen, Phys. Rev. B **51**, 17 992 (1995).
[15] B. N. Murdin, B. C. Cavenett, C. R. Pidgeon, J. Simpson, I. Hauksson, and K. A. Prior, Appl. Phys. Lett. **65**, 2411 (1993).
[16] T. A. Kennedy, E. R. Glaser, B. N. Murdin, C. R. Pidgeon, K. A. Prior, and B. C. Cavenett, Appl. Phys. Lett. **63**, 1112 (1994).
[17] R. Haynes, Phys. Rev. Lett. **4**, 361 (1960).
[18] S. Y. Wong, J. Simpson, K. A. Prior, and B. C. Cavenett, J. Appl. Phys. **72**, 5311 (1992).
[19] For a review of the optical properties of epitaxial ZnSe, see J. Gutowski, N. Presser, and G. Kudlek, Phys. Status Solidi A **120**, 11 (1990).
[20] E. Kurtz, S. Einfelt, J. Nürnberger, S. Zerlauth, D. Hommel, and G. Landwehr, Phys. Status Solidi B **187**, 393 (1995).
[21] K. Shahzad, B. A. Khan, D. J. Olego, and D. A. Cammack, Phys. Rev. B **42**, 11 240 (1990).
[22] Y. Yafet, Phys. Rev. **152**, 858 (1966).
[23] K Shahzad, Phys. Rev. B **38**, 8309 (1988).
[24] K. Ohkawa, T. Mitsuyu, and O. Yamazaki, Phys. Rev. B **38**, 12 465 (1998).
[25] H. Mayer, U. Rössler, K. Wolf, A. Elstner, H. Stanzl, T. Reisinger, and W. Gebhardt, Phys. Rev. B **52**, 4956 (1995).
[26] Y. Oka and M. Cardona, Phys. Rev. B **23**, 4129 (1980).
[27] J. J. Davies, J. Cryst. Growth **86**, 599 (1988).
[28] C. M. Townsley, B. Schlichtherle, D. Wolverson, J. J. Davies, K. Ogata, and Sg. Fujita, Solid State Commun. **96**, 437 (1995).