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## Shallow impurity- and defect-related complexes in undoped ZnSe crystals

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### Abstract

The electronic structure of bound excitons involving native- as well as point-defects is investigated by optical spectroscopy using highly crystalline ZnSe samples grown by the Markov method. We demonstrate that the interactions of attendant single particles is responsible for the splitting of the ( $D^0$ , X) and ( $A^0$ , X) states. From these splittings the hole–hole interaction parameter  $\gamma$  and the cubic crystal-field parameter  $\beta$  for the Li bound exciton complex has been determined unambiguously for the first time. The  $I_1^d$  emission line shows a fine structure which is similar to the  $I_1^{Li}$  exciton line.  $I_1^d$  is therefore assigned to an acceptor–bound exciton recombination with an associate formed by a zinc vacancy and an impurity donor combined acting as an acceptor.

### 1. Introduction

The increasing interest in growing high-quality ZnSe samples for opto-electronic device applications in the blue range of the visible spectrum raised a series of open questions about the responsible excitation channels [1] and the nature and behaviour of shallow impurities. In this context, a major problem is the strong self-compensation mechanism, avoiding effective p-type low-resistance conductivity. Up to now, only nitrogen seems to be a suitable candidate.

For the investigations of shallow donor and acceptor bound excitons and the interaction with point defects, we used ZnSe single crystals grown by the Markov vapour phase transport method [2]

at 1190°C with a thermal gradient of 10°C to the source material. Near-band-edge photoluminescence measurements at different temperatures, as well as excitation and reflection spectroscopy lead to detailed information on the electronic structure of the exciton complexes involved.

The emission spectrum obtained by band-to-band excitation, recorded in the exciton energy range, is shown in Fig. 1. Due to the high crystallinity of the used samples, pronounced donor-bound exciton lines  $I_2$  and a predominant acceptor–bound exciton recombination  $I_1^{Li}$  could be resolved. The main interest is focussed on the nature of the  $I_1^d$  line (also denoted as  $I_1^{deep}$  or  $I_1^C$  by other authors) which up to now is controversially discussed in terms of either involved native acceptors or point-defect related centres. Due to the close relation of  $I_1^d$  to zinc vacancies and its appearance in doping studies of ZnSe epilayers,

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the understanding of its origin is of great importance. From the LO coupling strength, a localization of the corresponding centre between that of donor–acceptor pairs (Q series) and that of shallow bound excitons ( $I_1$  and  $I_2$  lines) must be concluded (see Fig. 1). Since the  $I_1^d$  recombination centre interacts strongly with the weaker bound excitons, the precise understanding of the electronic structure of the involved shallow bound excitons is indispensable. Thus the shallow ( $D^0, X$ ) and ( $A^0, X$ ) complexes will be considered in more detail before referring to the nature of the  $I_1^d$  line.

### 2. Donor bound exciton complexes

The luminescence of ( $D^0, X$ ) complexes shown in the insert of Fig. 1 is dominated by a strong  $I_{20}^{Al}$  line near 2.7977 eV exhibiting additional structures at the low energy side due to Ga and In donors. At the high energy side, several  $I_{2\alpha}$  lines ( $\alpha = a$  to  $e$ ) and a resonance at the free exciton transition can be recognized. The exact value of the free exciton transition at 2.8028 eV is obtained from reflection spectra. The  $I_{2\alpha}$  lines which have already been reported by Merz et al. [3], Dean et al. [4] and Isshiki et al. [5] have recently been explained by Kudlek et al. [6] in terms of radiating relaxation from excited states of the

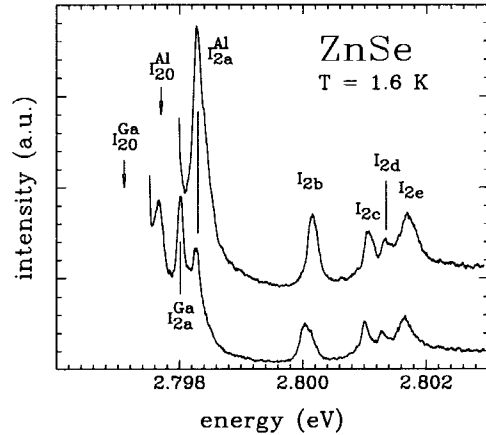


Fig. 2. Comparative photoluminescence excitation spectra of ( $D^0, X$ ) complexes. Arrows indicate registration energies.

( $D^0, X$ ) complexes. The  $I_{2\alpha}$  lines depicted in the insert of Fig. 1 are found to consist essentially of two superimposed series, one of which is connected to an Al donor and the other to Ga.

Narrow band registration of the  $I_{20}$  line due to a specific donor reveals the corresponding transitions in the excitation spectra (see Fig. 2). The observed energy differences  $E(I_{2\alpha}) - E(I_{20})$  can be described by a four-particle model regarding  $D^+$ ,  $e_D$  and the exciton particles  $e$  and  $h$  [7]. According to this model, the  $I_{2\alpha}$  resonances originate from excited states of the exciton hole classified by radial and angular quantum numbers  $n$  and  $l$ , respectively. The energy differences of the excited states  $E|n, l\rangle$  given in ref. [6] and the ( $D^0, X$ ) ground state can be written

$$E|n, l\rangle - E|0, 0\rangle \sim -s^2 t^2 \frac{E_D}{\sigma} \times \left[ n + \frac{1}{2} + \left( \left( l + \frac{1}{2} \right)^2 + st^2 \frac{a_e}{\sigma a_D} \right)^{1/2} \right]^{-2}, \quad (1)$$

with the specific donor Rydberg  $E_D$ , parameters  $s = 1.0136$  and  $t = 1.3370$  describing the Kratzer model potential of the hole,  $\sigma = m_e/m_h$  the ratio of the effective masses of electron and hole, and  $a_D/a_e$  the ratio of the donor electron radius and the Bohr radius, respectively. Using donor energies of  $E_D = 26$  meV and  $E_D = 27.7$  meV corre-

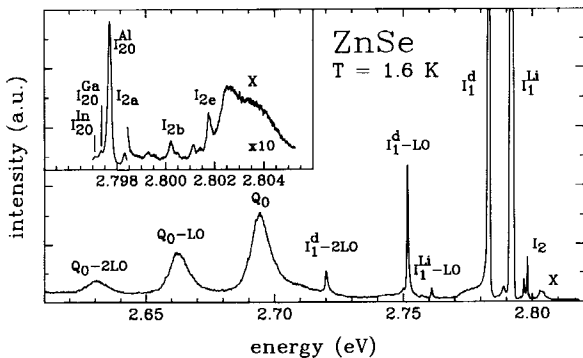


Fig. 1. Photoluminescence spectrum of a nominally undoped ZnSe bulk crystal in the near-band-edge region under band-to-band excitation. Insert: donor bound exciton luminescence and the free exciton recombination denoted X.

sponding to the Al and Ga donor ionization energies, the series  $E(I_{2\alpha}) - E(I_{20})$  of both donors matches well the series  $E|n, l\rangle - E|0, 0\rangle$  computed without changing the other free parameters of  $\sigma = 0.26$  and  $a_D/a_c = 0.36$ . Lines  $I_{2a}$  to  $I_{2c}$  are thus assigned to the  $|n, l\rangle$  series of the states  $|0, 1\rangle$ ,  $|1, 0\rangle$ ,  $|1, 1\rangle$ ,  $|2, 0\rangle$  and  $|2, 1\rangle$ , respectively.

### 3. Acceptor bound exciton complexes

On the lower energy side of the donor bound excitons a dominant emission of an  $(A^0, X)$  complex is observed in samples of this kind (see Fig. 1). With the energy position of the donor–acceptor pairs  $Q_0$ , and the Al-donor Rydberg of 26 meV, an acceptor ionization energy of 114 meV was calculated. This value corresponds well with the reported Li Rydberg energy in ZnSe. In addition, the obtained transition energy matches the values reported from Li-doped samples [8]. The appearance of Li is quite reasonable due to the well-known incorporation of Li and Na in not intentionally doped ZnSe crystals, leading to dominant  $I_1^{\text{Li}}$  and  $I_1^{\text{Na}}$  lines.

While the term structure of Na-bound excitons is known [9], the structure of the  $(A^0_{\text{Li}}, X)$  complex is not yet clear. Bhargava [10] found a manifold structure in the  $I_1^{\text{Li}}$  energy regime. Exact energy positions, however, have not been given. In strained MBE-grown ZnSe/GaAs epilayers a double structure has been observed [11]. Taking into account the simultaneously acting influence of strain and the  $jj$  interaction, the authors discussed several possible parameter values for the hole–hole interaction and the cubic crystal field. To achieve a clear assignment, we used bulk ZnSe samples with highly resolved  $I_1$  lines. In this case the influence of strain can be neglected.

Fig. 3 shows the comparative luminescence spectra in the  $I_1^{\text{Li}}$  energy range for two different temperatures. The lower spectrum recorded at  $T = 1.6$  K contains three highly resolved transitions  $I_1$ ,  $I_{1a}$  and  $I_{1b}$  with 0.13 meV FWHM each.  $I_{1a}$  is shifted by 0.22 meV and  $I_{1b}$  by 0.37 meV to higher energy with respect to line  $I_1$ . The intensity ratio of the lines  $I_1$ ,  $I_{1a}$  and  $I_{1b}$  as determined

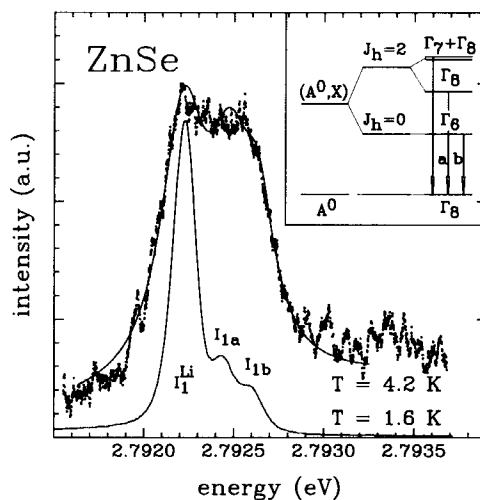


Fig. 3. Temperature-dependent emission of the  $(A^0_{\text{Li}}, X)$  exciton complex, showing three resolved subcomponents  $I_1$ ,  $I_{1a}$  and  $I_{1b}$ . The related term structure is given in the insert.

from a Lorentz profile analysis is 1:0.15:0.11. At a temperature of 4.2 K, a strong thermalization is observed, leading to a changed intensity ratio of roughly 1:0.93:0.82. Due to the strong correlation between these three lines, it is evident that all transitions belong to the same  $(A^0_{\text{Li}}, X)$  complex.

An explanation of  $I_1$ ,  $I_{1a}$  and  $I_{1b}$  can be given in terms of a fine-structure splitting of the  $(A^0, X)$  electronic ground state. The  $jj$  coupling of the two  $j = 3/2$  holes in this complex, one originating from the neutral acceptor  $A^0$  and the other from the free exciton, yields a total hole momentum of  $J_h = 0$  and  $J_h = 2$  (see insert of Fig. 3). These two states are separated by the hole–hole interaction  $\gamma$ . The additional coupling of the single electron leads to  $J = 1/2, 3/2$  and  $5/2$  states with  $\Gamma_6, \Gamma_8$  and  $\Gamma_7 + \Gamma_8$  symmetry, respectively [12]. The  $\Gamma_8$  and  $\Gamma_7 + \Gamma_8$  degeneracy is lifted by the cubic crystal-field interaction  $\beta$ . Both the relative strength of the hole–hole interaction and the influence of the crystal field strongly depend on the used zincblende-structured host material, the incorporated chemical acceptor and the corresponding Rydberg energy [13–15].

The observed strong thermalization suggests a level sequence of increasing degeneracy  $\Gamma_6, \Gamma_8$  and  $\Gamma_7 + \Gamma_8$  with increasing energy (see insert of

Fig. 3). From this ordering,  $\beta$  and  $\gamma$  can be determined according to

$$\beta = E(I_{1b}) - E(I_{1a}) = 0.14 \text{ meV}, \quad (2)$$

$$\gamma = E(I_{1a}) - E(I_1) + \frac{3}{5}\beta = 0.30 \text{ meV}. \quad (3)$$

Taking into account the intensity ratio and the separation energies at  $T = 4.2 \text{ K}$ , we calculate a oscillator strength ratio of 1:1.8:2.3 corresponding reasonably well to the theoretical ratio of 1:2:3.

In comparison with the  $(A_{\text{Na}}^0, X)$  complex [9], we observe an equal term sequence of the Li and Na acceptor exciton complexes in ZnSe. The influence of the cubic crystal-field  $\beta$  in both kinds of complexes is also comparable. Although in the Na-doped samples the splitting induced by  $\beta$  could not be resolved, it leads to a  $I_1^d$  line being four times broader than the  $I_1$  line originating from the lowest state  $I_6$ . The  $jj$  coupling in the  $(A_{\text{Li}}^0, X)$  complex, however, is found to be much smaller.

#### 4. The $I_1^d$ emission centre

In contrast to the bound excitons described above, the nature of the  $I_1^d$  recombination centre has not been clarified up to now, due to reported different energy positions and various chemical impurities involved. The first interpretations in terms of an acceptor-bound exciton with copper acting as an acceptor are not in agreement with our investigations and magneto-optical results [16]. The authors observed a  $g$  value of 2 in accordance with a zinc vacancy with a free hole. The close correlation of the  $I_1^d$  centre to zinc vacancies  $V_{\text{Zn}}$  has been demonstrated by differently annealed ZnSe samples. In samples annealed in Zn atmosphere, a suppression of the  $I_1^d$  is observed, whereas on the other side the luminescence of ZnSe samples annealed in Se atmosphere is dominated by the strongly increasing  $I_1^d$  emission. These findings are supported by studies of the influence of the Zn-to-Se flux ratio in MBE-grown ZnSe epilayers [17] and CVD-grown polycrystalline ZnSe on the optical spectra [18]. Summarizing, the participation of  $V_{\text{Zn}}$  in the

$I_1^d$  centre without any connection to Cu must be concluded.

Zinc vacancies, however, are known to act as very deep and strongly localized defects with a double acceptor behaviour. The appearance as a more shallow single acceptor in the near-band-edge luminescence could be explained by the formation of an associate including a neighbored donor leading to an effective neutral acceptor. The participation of the donor induces a delocalization which can be clearly observed in the phonon coupling (see Fig. 1). The LO-phonon coupling of the  $I_1^d$  centre is significantly more pronounced than for the spatially localized shallow bound exciton complexes like  $(A_{\text{Li}}^0, X)$ , but still weaker than for the spatially extended donor–acceptor pairs. This intermediate localization can be expressed in terms of a Huang–Rhys factor which is calculated to be 0.2 for  $I_1^d$  compared to 0.01 for  $I_1^{\text{Li}}$  and 0.5 for  $Q_0$ .

To get additional information on the electronic structure of the  $I_1^d$  complex, we performed excitation spectroscopy in the energy range of the  $I_1^d$  transition recorded in the  $I_1^d$ -LO line (see

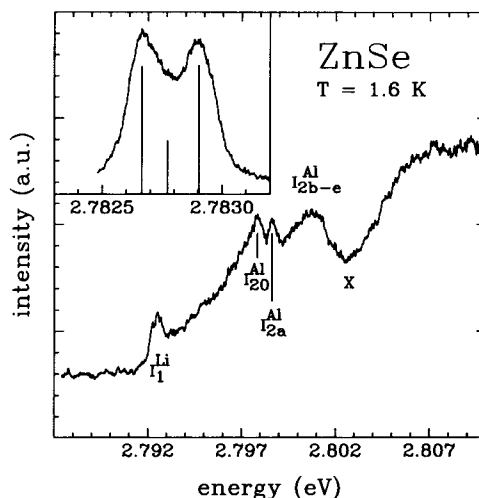


Fig. 4. Excitation spectrum of the  $I_1^d$  line in the excitonic energy range. To resolve the  $I_1^d$  fine structure the excitation spectrum recorded in the  $I_1^d$ -LO line is depicted in the insert; the bars denote energy positions and intensities of fitted Lorentz profiles.

insert of Fig. 4). In highly resolved spectra, a triplet line structure becomes evident, with energy positions at 2.78267, 2.78277 and 2.78290 eV. The intensity ratio fitted by three Lorentz profiles of 0.125 meV FWHM each is found to be 5:2:5, respectively. The energy distance between the two intensive components of 0.23 meV corresponds well to the value reported in ref. [19].

The triplet structure resembles the structure observed for the shallow ( $A^0, X$ ) complexes, as described in the previous section. The oscillator strength ratio of the  $I_1^d$  subcomponents should be expected from an ( $A^0, X$ ) complex under dominating crystal-field influence and weak  $jj$  coupling leading to a term sequence with the  $F_6$  state lying between the two levels of higher degeneracy. Similar to the ( $A_{Li}^0, X$ ) and ( $A_{Na}^0, X$ ) recombination lines, the oscillator strength ratio of the sum of the stronger subcomponents to the weaker one is 5:1.

As to the chemical nature of the  $I_1^d$  centre, the combination of a donor and a zinc vacancy  $V_{Zn}$  seems to be evident. The connection with shallow impurities can be seen in the excitation spectrum of the  $I_1^d$  line given in Fig. 4. The appearance of  $Li_{Zn}$  acceptors and  $Al_{Zn}$  donors is supposed to result from the spatial extension expressed by the intermediate localization of the  $I_1^d$  centre, as discussed above. While the connection of Al donors to  $V_{Zn}$  seems to be straightforward, an associate formed by  $V_{Zn}$  and  $Li_i$  ( $i$  = interstitial) is assumed to be more likely. The amphoteric behaviour of Li acting as a substitutional acceptor or an interstitial donor is well known [20]. Due to the strong tendency of Li to leave its substitutional Zn site and the considerably higher abundance of Li in the studied Markov samples, we assign the  $I_1^d$  centre to an ( $A^0, X$ ) complex with a ( $V_{Zn}, Li_i$ ) acceptor in these samples. The assignment should not exclude other donors to form a similar acting complex. As a consequence of the given assignment, the formation of an  $I_1^d$  centre in the Markov samples can be induced by a single  $Li_{Zn}$  leaving its substitutional site and thus creating a neighbored  $V_{Zn}$ . The participation of the amphoteric Li is of special interest due to a possible enhancement of the intrinsic self-compensation effect of ZnSe.

## 5. Conclusion

Due to the high crystalline quality of the studied ZnSe Markov-grown samples, sharp emission and excitation lines of Al, Ga, In and Li related shallow bound exciton complexes are observed. The electronic structure of the donor bound excitons is described by excited single hole states with quantum numbers  $n$  and  $l$ , changing only the donor Rydberg. The highly resolved fine structure of the ( $A_{Li}^0, X$ ) complex is found to result from the  $jj$  splitting ( $\gamma = 0.3$  meV) and the influence of the cubic crystal field ( $\beta = 0.14$  meV).

Strong evidence is found for the  $I_1^d$ -related centre which exhibits an electronic fine structure comparable to the ( $A^0, X$ ) complexes to be built by a ( $V_{Zn}, Li_i$ ) associate acting as an acceptor. The instability of the Li acceptor against dissociation into a zinc vacancy ( $V_{Zn}$ ) and interstitial Li ( $Li_i$ ) leads to a self-compensation effect aggravating effective p-type doping.

## 6. References

- [1] N. Presser, Ch. Fricke, G. Kudlek, R. Heitz and I. Broser, *J. Crystal Growth* 138 (1994) 820.
- [2] E.V. Markov and A.A. Davydov, *Neorg. Mater.* 11 (1975) 1755.
- [3] J.L. Merz, H. Kukimoto, K. Nassau and J.W. Shiever, *Phys. Rev. B* 6 (1972) 545.
- [4] P.J. Dean, D.C. Herbert, C.J. Werkhoven, B.J. Fitzpatrick and R.N. Bhargava, *Phys. Rev. B* 23 (1981) 4888.
- [5] M. Isshiki, T. Kyotani, K. Masumoto, W. Uchida and S. Suto, *Phys. Rev. B* 36 (1987) 2568.
- [6] G.H. Kudlek, U.W. Pohl, Ch. Fricke, R. Heitz, A. Hoffmann, J. Gutowski and I. Broser, *Physica B* 185 (1993) 325. In this and in previous work,  $\sigma^{-1}$  has erroneously been replaced by  $\sigma$ .
- [7] J. Puls, F. Henneberger and J. Voigt, *Phys. Status Solidi* (b) 119 (1983) 291.
- [8] P.J. Dean, W. Stutius, G.F. Neumark, B.J. Fitzpatrick and R.N. Bhargava, *Phys. Rev. B* 27 (1983) 2419.
- [9] G.H. Kudlek, A. Hoffmann, R. Heitz, C. Fricke, J. Gutowski, G.F. Neumark and R.N. Bhargava, *J. Luminescence* 48&49 (1991) 138.
- [10] R.N. Bhargava, *J. Crystal Growth* 50 (1982) 15.
- [11] Y. Zhang, B.J. Skromme and H. Cheng, *Phys. Rev. B* 47 (1993) 2107.
- [12] B. Stebe and G. Munsch, *Solid State Commun.* 40 (1981) 663.
- [13] E. Molva and Le Si Dang, *Phys. Rev. B* 32 (1985) 1156.

- [14] W. Schairer, D. Bimberg, W. Kottler, K. Cho and M. Schmidt, *Phys. Rev. B* 13 (1976) 3452.
- [15] K.R. Elliot, G.C. Osbourn, D.L. Smith and T.C. McGill, *Phys. Rev. B* 17 (1978) 1808.
- [16] X.J. Jiang, T. Hisamune, Y. Nozue and T. Goto, *J. Phys. Soc. Japan* 52 (1983) 4008.
- [17] T. Taguchi and T. Yao, *J. Appl. Phys.* 56 (1984) 3002.
- [18] E. Krause, H. Hartmann, J. Menninger, A. Hoffmann, Ch. Fricke, R. Heitz, B. Lummer, V. Kutzer and I. Broser, *J. Crystal Growth* 138 (1994) 75.
- [19] P.J. Dean and J.L. Merz, *Phys. Rev.* 178 (1969) 1310.
- [20] T. Sasaki, T. Oguchi and H. Katayama-Yoshida, *Phys. Rev. B* 43 (1991) 9362.