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ZEEMAN SPECTROSCOPY ON THE NITROGEN ACCEPTOR-BOUND EXCITON IN EPITAXIAL ZnSe

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Abstract

We report on the Zeeman splitting of the neutral nitrogen acceptor-bound exciton (I_1^N-line) in free standing ZnSe:N layers. For the isolated nitrogen acceptor N_{Se}, we obtain a g-value of $g = 0.6 \pm 0.02$. The same acceptor is also involved in the donor–acceptor–pair recombination at 2.685 eV which is verified by analysis of the magnetic circular polarization properties.

1. Introduction

The p-type conductivity of ZnSe layers was realized by molecular beam epitaxy (MBE) on GaAs substrate and nitrogen doping from a plasma source [1]. The successful p-type doping resulted in the application of a II-VI compound as a laser emitting diode [2]. At present with this laser diodes, the laser emission with the highest energy available from semiconductors is achieved. However, p-type doping of ZnSe is still a difficult task: In spite of the highly sophisticated growth technique, the free hole concentration ($N_A - N_D$) is limited to approx. 10^{18} cm^{-3} [3]. At higher doping concentrations the layers become highly resistive or even slightly n-type conductive.

The incorporation of isolated nitrogen on a selenium site (N_{Se}) can be judged by photoluminescence (PL) investigations. For low N doping level the nitrogen acceptor-bound exciton is dominating. With increasing nitrogen doping concentration, a new PL band with a zero phonon line (ZPL) at $E = 2.685$ eV appears (see Fig. 1). From temperature dependent PL experiments [4] it is attributed to a recombination between a shallow donor ($E_D = 26$ meV) and the effective mass type acceptor N_{Se} ($E_A = 110$ meV). At still higher doping levels, a second DAP emission appears. PL excitation showed [5] that the recombination is from a deeper donor ($E_D = 53$ meV) to the same acceptor level. The authors of Ref. 4 suggested that the deep donor should be a nitrogen-correlated donor type defect.

In order to identify the atomistic structure of the defects, Murdin *et al.* [6] performed optically detected magnetic resonance (ODMR). They observed three resonance signals with g-values of $g = 1.11$, $g = 1.38$, and $g = 2.00$, respectively. The signal at $g = 1.11$ is the well-known shallow donor resonance [7], probably Ga or Cl. The resonance at $g = 2.00$ was attributed to the isolated nitrogen on selenium site, the $g = 1.38$ defect was proposed to be a V_{Se}–Zn–N_{Se} complex which acts in ZnSe as a donor and can therefore account for the compensation.

In a recent publication [8], Kennedy *et al.* revised their conclusions. The center with $g \approx 2$ was indeed found to have trigonal symmetry. They assigned it to a V_{Se}–X pair with X being most probably copper or silver, a deep donor. The resonance at $g = 1.38$ remained unexplained. To find out whether or not it can be attributed to the N_{Se} acceptor, was the aim of this investigation.

We first report on the magnetic circularly polarized emission (MCPE) measurements of the DAP band (see Fig. 1).

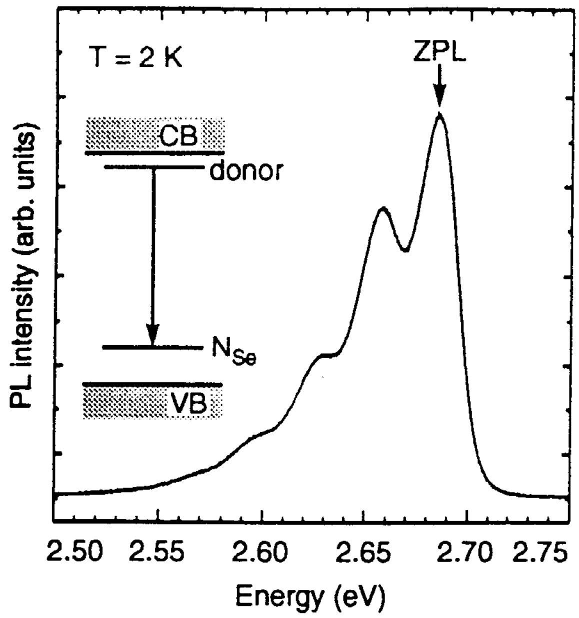

Figure 1:
DAP emission in a ZnSe:N sample for intermediate nitrogen doping levels. The simple recombination scheme between a shallow donor (E_D = 26 meV) and the effective mass type acceptor N_{Se} (E_A = 110 meV) is drawn in the inset.

2. Experimental Results and Discussion

To carry out MCPE experiments, the sample was placed in a Magnex cryomagnetic system achieving magnetic fields up to 4 T in split coil geometry. The sample was directly immersed in liquid helium (T = 4.2 K or T = 1.9 K in pumped helium). The luminescence was excited by the 325 nm line of a HeCd laser, the emission was spectrally dispersed by a single monochromator SPEX 1680 (f 1:4) and detected by a photomultiplier. The circular polarization of the emission was monitored with a combination of a linear polarizer and a stress modulator operating at 50 kHz. Excitation and emission happened along the magnetic field.

In Fig. 2 MCPE measurements are shown for two different temperatures. The photon energy was kept fixed at E = 2.685 eV and the magnetic field was swept from 0 – 2.4 T. To analyze the shape of the MCPE curves, one has to consider the donor to acceptor recombination in a magnetic field. The shallow donor can be described by $J = \frac{1}{2}$, with the occupation numbers of the Zeeman levels n_1 ($m_J = +\frac{1}{2}$) and n_2 ($m_J = -\frac{1}{2}$). For the acceptor, we assume $J = \frac{3}{2}$ with T_d symmetry. With applied magnetic field they split into a quartet with the occupation numbers n_i, (i = 3, 4, 5, 6) with $m_J = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$. The corresponding recombination scheme [9] is shown on the right side of Fig. 2, including the left (σ^+) and right (σ^-) circularly polarized allowed transitions and their respective transition probabilities. Assuming Boltzmann distribution, the $MCPE$ is given by

$$MCPE = n_2 n_6 + \frac{1}{3} n_1 n_5 - (n_1 n_3 + \frac{1}{3} n_2 n_4) \,. \qquad (1)$$

The occupation numbers depend on the temperature T, the magnetic field B and the donor and acceptor g-values, respectively. T and B are known from the experiment, as is g_D = 1.11 [7]. Therefore, the only adjustable parameter is the unknown acceptor g-value g_A. Fitting the experimental data at the two temperatures, we obtain $g_A = 0.68 \pm 0.1$, the fits are drawn in Fig. 2 as dashed lines. Simulations with g_A = 1.38 and larger (Fig. 2) are not in accordance with this experiment.

The properties of the acceptor ground state can also be evaluated when studying the neutral acceptor-bound exciton line (I_1^N) in magnetic field. Zeeman investigations were performed in Voigt- and Faraday configurations in a magnetic field range from 0 – 15 T at 2 K. For

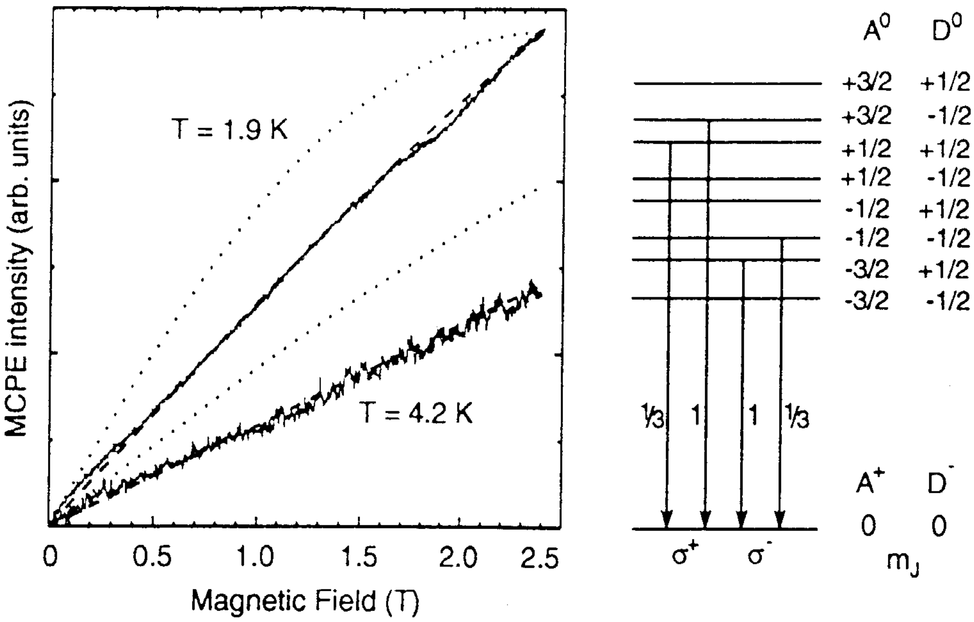

Figure 2: MCPE for two different temperatures on the ZPL of the DAP emission in Fig. (1). The dashed curves correspond to a fit with the parameters $g_A = 0.68$ and $g_D = 1.11$, the dotted one to $g_A = 1.38$ and $g_D = 1.11$. The model for the DAP transition in magnetic field is shown to the right. The allowed optical transitions are right (σ^+) or left (σ^-) circularly polarized and have the relative transition probabilities 1 or $\frac{1}{3}$.

Zeeman spectroscopy a very small linewidth (FWHM) of the exciton is needed. Therefore it was necessary to remove the ZnSe from the GaAs substrate in order to avoid the broadening of the excitonic line due to lattice/thermal mismatch.

In Fig. 3 the luminescence of the I_1^N line is shown at $|\vec{B}| = 14$ T. At such a high field, a well resolved Zeeman splitting can be observed. In the Voigt-configuration with $B||[100]$, the emission is linearly (π) and circularly (σ^+, σ^-) polarized. The polarization properties can be understood within the (A^0,X) recombination model shown in the inset of Fig. 3: The neutral acceptor–exciton complex can be described by three states with $J = \frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$ [10]. In analogy to other II-VI compounds, the $J = \frac{1}{2}$ (Γ_6) state is assumed to be lowest in energy [11] and the recombination ends in the neutral acceptor (ground state). One hence expects six allowed transitions, two with linear and four with circular polarization. However, at very low temperatures and fast spin-lattice relaxation only the $m_j = -\frac{1}{2}$ sublevel of the (A^0,X) complex is populated. Consequently, the number of allowed transitions is reduced to three, as observed in the experiment.

Analyzing the Zeeman splitting, we obtained $g = 0.6 \pm 0.1$ for the isolated nitrogen acceptor, a result which is in nice accordance with the MCPE investigations. A detailed analysis of the MCPE and the Zeeman data, which would exceed the scope of this contribution, will be published elsewhere [12].

The very same g-value are found for the Na and the Li acceptor. Therefore, N shows properties similar to other dopants known to form shallow acceptors in ZnSe. The question remains why only nitrogen doping leads to a sufficient concentration of free carriers. One might speculate that probably the sublattice in which the dopant is located plays an important role. Whether or not the defect with the resonance at $g = 1.38$ plays a paramount role, especially with respect to the compensation, needs further investigation.

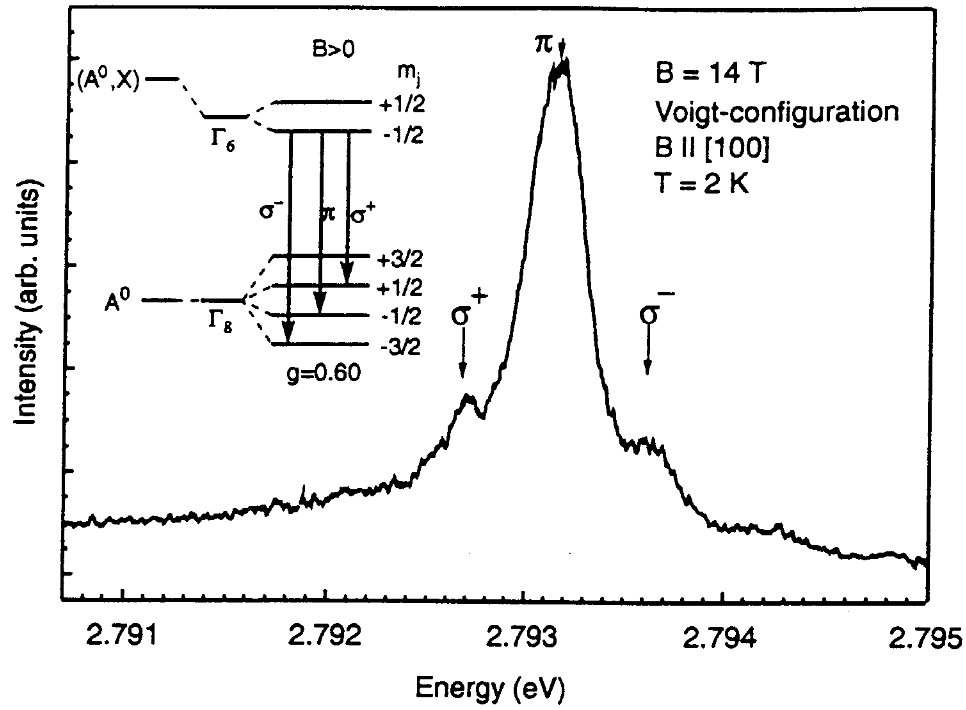

Figure 3: Zeeman splitting of the nitrogen acceptor-bound exciton at $|\vec{B}| = 14$ T. The exciton shows three components with polarization properties as indicated. The model derived from this experiment is shown in the inset.

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References

[1] R.M. Park, M.B. Troffer, C.M. Rouleau, J.M. DePuydt, and M.A. Haase, *Appl. Phys. Lett.* **57**, 2127 (1990)

[2] M.A. Haase, J. Qiu, J.M. DePuydt, and H. Cheng, *Appl. Phys. Lett.* **59**, 1272 (1991)

[3] J. Qiu, J.M. DePuydt, H. Cheng, and M.A. Haase, *Appl. Phys. Lett.* **59**, 2992 (1991)

[4] I.S. Hauksson, J. Simpson, S.Y. Wang, K.A. Prior, and B.C. Cavenett, *Appl. Phys. Lett.* **61**, 2208 (1992)

[5] A. Hofmann, R. Heitz, R. Lummer, V. Kutzer, L. Eckey, I. Broser E. Kurtz, D. Hommel, B. Jobst, J. Nürnberger, and G. Landwehr, *Proc. of the 22nd ICPS*, Vancouver 1994, to be published

[6] B.N. Murdin, B.C. Cavenett, C.R. Pidgeon, J. Simpson, I. Hauksson, and K.A. Prior, *Appl. Phys. Lett.* **63**, 2411 (1993)

[7] D.J. Dunstan, B.C. Cavenett, R.F. Brunwin, and J.E. Nicholls, *J. Phys. C* **10**, L361 (1977)

[8] T.A. Kennedy, E.R. Glaser, B.N. Murdin, C.R. Pidgeon, K.A. Prior, and B.C. Cavenett, *Appl. Phys. Lett.* **65**, 1112 (1994)

[9] D.G. Thomas, J.J. Hopfield, and W.M. Augustyniak, *Phys. Rev.* **101**, A202 (1965)

[10] W. Rühle and D. Bimberg, *Phys. Rev. B* **12**, 2382 (1975)

[11] T. Taguchi, J. Yamamoto, J. Shirafuji, and Y. Inuiski, *Solid State Commun.* **19**, 1037 (1976)

[12] A. Hoffmann, D. Wiesmann, R. Heitz, I. Loa, E. Kurtz, D. Hommel, W. Stadler, D.M. Hofmann, and B.K. Meyer, unpublished