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Magneto-optical investigation of the shallow lithium acceptor in zinc selenide

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Abstract

In ZnSe crystals Li acceptors were investigated as a model system to determine the general fine-structure of shallow acceptor-bound exciton complexes. Magneto-optical measurements yielded an evident sequence of the $J = 1/2$, $J = 3/2$, and $J = 5/2$ states, splitted by hole–hole, electron–hole and crystal-field interaction. A common diamagnetic shift of 4.5 $\mu eV/T^2$ and g values of 1, -0.8, and 1.1 were found, respectively. The A^0_{Li} ground state was found to be described by $g = 0.6$.

1. Introduction

Recent progress in growing ZnSe-based laser structures are based on reasonable conductivity control [1,2]. Effective p-type doping remains, however, a difficult task [3]. Compensation mechanisms are not well understood up to now [4,5]. They are connected to the insertion of the acceptors into the crystal and their resulting electronic structure. An optical analysis of the term structure of acceptors in ZnSe epilayers [6] is aggravated by the simultaneous acting influences of strain, crystal-field and interactions of particles within the exciton complex. To avoid the strain influence we therefore studied unstrained ZnSe bulk crystals. The shallow lithium acceptor (the bound exciton complex (A^0_{Li},X) of which gives rise to sharp luminescence lines) was taken as a model system.

At zero field the known I_1^{Li} bound exciton line (2.7919 eV) [7] shows a threefold fine structure with thermalized emission lines I_{1a}^{Li} and I_{1b}^{Li} shifted by 0.22 and 0.37 meV to higher energy, respectively (cf. Fig. 1). The origin of the fine structure has been attributed to the interaction of the bound particles, i. e. the two holes with $j_h = 3/2$ and the electron with $j_e = 1/2$ [8]. From thermalization studies [9] the initial states of the lines I_{1a}^{Li} and I_{1b}^{Li} were assigned to the states $J = 3/2$ and $J = 5/2$, respectively, of the bound exciton complex (A^0_{Li},X).

2. Experimental procedure

Nominally undoped ZnSe crystals were grown by seeded vapour transport in a sealed quartz ampoule using a method first applied by Markov and coworkers [11]. Growth occurred in a hydrogen ambient at 1470°C with a thermal gradient of 10°C to the source material. The resulting single crystals were twin-free and bounded by (110) and (111) faces. From photoluminescence studies a presence of residual Al donors and Li acceptors can be concluded [9].

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For magneto-optical experiments a 15 T superconducting magnet equipped with a He immersion cryostat was used. The luminescence was excited by the 325 nm line of a He–Cd Laser and detected by a bialkali PM tube after spectral selection using a double monochromator with 2 · 0.85 m focal length.

3. Zeeman emission spectra

At high magnetic fields distinct lines can be clearly recognized in Voigt configuration $k \perp B \| [001]$, see Fig. 1. From the evolution of the transition energies with increasing field as shown in Fig. 2 a nearly equal diamagnetic shift for all components described by 4.5 $\mu eV/T^2$ can be deduced (dotted lines in Fig. 2). All lines observed above 5 T at low temperature are found to originate from the lines I_{1a} and I_{1b} which are connected to the excited (A^0_{Li},X) states $J = 3/2$ and $J = 5/2$. This finding which will be discussed in more detail below is consistent with a weaker splitting of a (A^0_{Li},X) ground state $J = 1/2$ exhibiting predominantly single electron nature. I_{1a} is the origin of the Zeeman components 1, 2 and 5, I_{1b} is the origin of the lines 3, 4 and 6. The following assignments of the individual lines to initial and final states are based on selection rules, the pronounced polarization and thermalization behaviour and the linear components of the energy shifts with increasing field. These components increase with the given line numbers. In the following the transitions are described assuming isotropic hole-g values. The underlying assumption of negligible cubic terms in the Hamiltonian (resulting in $g_{1/2} = g_{3/2}$ for A^0) appears reasonable especially in the strain free case which is an important simplification with respect to the strained problem described in Ref. [10]. In the investigated ZnSe bulk crystal the absence of strain is evidenced by sharp bound exciton lines with 130 μeV FWHM.

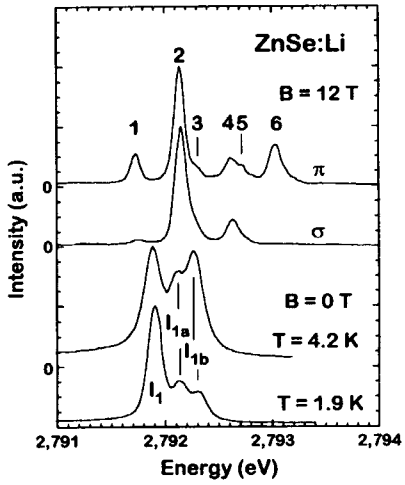

Fig. 1. Luminescence spectra of the (A^0_{Li},X) exciton complex at $B = 0$ T, $T = 1.9$ K and $T = 4.2$ K, and at $B = 12$ T, $T = 1.9$ K in Voigt configuration $B \| [001]$.

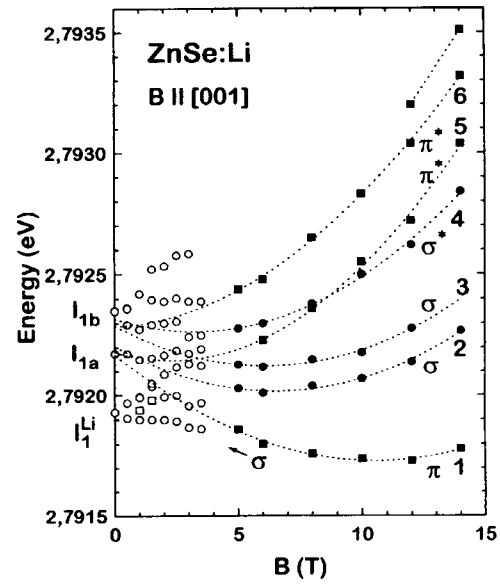

Fig. 2. Zeeman splitting of the I_1^{Li} bound exciton line. Squares and circles denote π and σ polarization, respectively, stars at polarization labels indicate thermalized transition lines. Open symbols at fields below 5 T denote transition energies obtained from Lorentz curve analysis, see text.

The ground state splitting of A^0 can be read from the not thermalized transitions 1 and 2 yielding $g(A^0) = 0.6$, see Fig. 3. This value is confirmed by the thermalized transitions 4 and 6 which stem from the separate state $J = 5/2$. Thermalized line 5 which has the same origin as line 2 reflects the splitting of the $J = 3/2$ state. From polarization and energy ordering a negative g value of $g = -0.8$ must be concluded. For the state $J = 5/2$ the splitting is derived from line 3 and the thermalized line 6 giving $g = 1.1$.

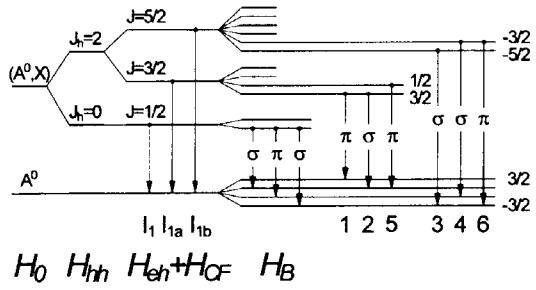

Fig. 3. Level diagram of the lithium acceptor A^0 and of the (A^0_{Li},X) bound exciton complex as a function of hole–hole interaction H_{hh}, electron–hole interaction and cubic field interaction $H_{eh}+H_{CF}$ and Zeeman level splitting H_B.

The assignments give a coherent description of all observed transitions. It should be noted that the centre of gravity of the level splitting in this simple picture is found to shift with increasing field. Shifts can be roughly approximated linearly by -0.04 meV/T of the lower ling state $J=3/2$ and $+0.06$ meV/T for the state $J=5/2$ and indicate term interactions occurring at low fields not taken into account.

In the low field range up to 4 T the Zeeman effect of the Li-bound exciton emission shows a rich structured pattern induced by thermalized lines. Superposition of lines is already indicated at fields near 6 T where the polarization of line 1 changes from π to σ with decreasing field, see arrow in Fig. 2. To separate different Zeeman components in the low field range we performed Lorentz curve analysis. In the analysis the FWHM of all transitions was kept constant because no line broadening is observed in the high field spectra. The results seem reasonable though they appear less evident than those obtained from distinguished lines at higher fields. Derived transition energies are denoted with unfilled symbols in Fig. 2. Obviously the line shifts in the low field range cannot be described by a simple parabolic dependence. This is attributed to strong term interactions. At fields near 1 T two lines with σ polarization and one line with π originating from the state $J=1/2$ can be recognized. The threefold structure represents the splitting of the (A^0) ground state. A broadening of the lines due to superimposing thermalized transitions are observed at higher temperatures. The broadening can be explained by a larger splitting of the state $J=1/2$ and consequently by a larger g value as compared to the A^0 ground state. This value is assumed to be approximately $|g|=1$. Within this frame a crossing of the lowest Zeeman level of the state $J=1/2$ and of the state $J=3/2$ between 3 T and 4 T and consequently a change of the polarization of the emission line with lowest energy can be understood.

4. Discussion

The Zeeman spectra presented in the previous section lead to a term scheme of the (A^0_{Li},X) complex with three resolved states $J=1/2$, $J=3/2$ and $J=5/2$ in the order of increasing energy. The measurements thus confirm the formerly given assignments [9] which were essentially based on thermalization studies. The ordering implies a low lying $J_h=0$ level, i.e. a negative hole–hole interaction γ. This is also observed in ZnS [12] and for deep acceptors in CdTe [13] where the ordering to the state $J_h=2$ is reversed for shallow acceptors.

The value $g_{Li}=0.6$ of the neutral acceptor A^0_{Li} agrees well with the value $g_N=0.7$ recently obtained for the shallow nitrogen acceptor in unstrained free standing ZnSe:N epilayers [6]. The agreement is quite meaningful since both Li and N have similar binding depths resulting in a comparable degree of spin–orbit coupling.

As to the three states of the (A^0_{Li},X) complex a common diamagnetic shift near 4.5 $\mu eV/T^2$ and g values near $|g|=1$ are found. The sign reversal of g in the state $J=3/2$ is not yet understood. Compared to the (A^0_N,X) complex in strain-free ZnSe:N epilayers [6] the zero field spectrum of (A^0_{Li},X) shows a nearly equal hole–hole-interaction. The crystal-field interaction, however, appears significantly reduced for nitrogen leading to only two resolved emission lines I_1^N and $I_1^{N'}$ at $B=0$. It should be noted that both acceptor bound exciton complexes show the same ordering of the states $J=0$ and $J=2$.

In a magnetic field the Zeeman components of nitrogen- and lithium-bound exciton complexes show a comparable diamagnetic shift, that of N being a factor 1.2 larger. Also well coinciding values of $|g|$ are observed in the (A^0,X) states of both acceptors.

While the same value is found for the state $J = 5/2$ of Li and the two (unresolved) states $5/2$ and $3/2$ of N (strain-free case) some differences are found for the state $J = 3/2$.

From the apparent similar magneto-optical properties of the shallow acceptors Li and N in ZnSe we conclude that both can be regarded as effective mass acceptors. This gives a reasonable evidence for the substitutional incorporation of nitrogen in ZnSe epilayers.

5. Conclusion

Magneto-optical investigations of the lithium-bound exciton complex (A^0_{Li},X) confirmed formerly given assignments of the level ordering $J = 1/2$, $3/2$ and $5/2$ with increasing energy. For these zero-field states g values of 1, -0.8 and 1.1 were found, respectively. A common diamagnetic shift of 4.5 $\mu eV/T^2$ was observed. For the A^0 ground state $g = 0.6$ was obtained. Apparent similarities were found comparing the optical properties of the shallow lithium and nitrogen acceptors in ZnSe. As a consequence evidence for the substitutional incorporation of nitrogen into ZnSe epilayers is concluded.

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