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MAGNETO-OPTICAL PROPERTIES OF THE I_1^d BOUND EXCITON EMISSION CENTER IN ZNSE

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Zeeman data of the prominent I_1^d emission line in ZnSe bulk crystals are presented. The essentially isotropic pattern is well described by a fourfold ground state splitting with $g=1.0$ and two excited states both exhibiting $g=2.2$ with a common diamagnetic shift of 3.6 μeV/T^2. Magneto-optical properties and dynamic behavior confirm the assignment to an acceptor-bound excitonic recombination. The excited states are interpreted in terms of a quenched angular momentum of the holes within the bound exciton complex.

1. Introduction

In the near band-edge luminescence spectra of ZnSe epitaxial layers and bulk crystals the I_1^d line near 2.783 eV (also denoted I_1^{deep}) is a prominent feature being sensitive to stochiometry and doping. The line exhibits a doublet structure with a splitting of 0.2 meV[1] emerging into four lines at high magnetic fields.[2] The four Zeeman lines were assigned to transitions between a twofold split acceptor-bound exciton state with single electron character and a fourfold split acceptor ground state. The zero-field splitting remained unexplained. The acceptor has been attributed to Cu. In more recent studies, the dominant appearance of the I_1^d emission in samples grown under selenium-rich conditions[3, 4] and in samples annealed in Se atmosphere[3] demonstrated a close relation of the I_1^d emitting center to zinc vacancies V_{Zn} without participation of Cu. The electronic properties and the chemical nature of the center are, however, not well understood. The present magneto-optical study performed with high quality ZnSe bulk crystals revealed a doublet structure of each of the four Zeeman lines reported earlier. The observed additional structure is related to the zero-field splitting and helps to unravel the electronic properties of the I_1^d emitting center.

2. Experimental

The ZnSe samples were single crystals grown by seeded vapour transport in sealed quartz ampoules under hydrogen ambient inducing a slight zinc deficiency. Optical spectra were recorded on cleaved (110) faces properly oriented in the field of a 15 T split coil superconducting magnet equipped with a He immersion cryostat. A continuous flow cryostat was used for temperature-dependent measurements. Luminescence was excited

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by the 325 nm or 441 nm line of a He-Cd laser or, for excitation spectra, by a dye laser and detected by a bialkali PM tube attached to a 0.85 m double-monochromator.

3. I_1^d zero-field spectra

The near band-edge emission of the investigated ZnSe samples show sharp bound exciton lines with dominant emissions I_1 due to lithium acceptor-bound excitons and I_1^d (Fig. 1). In addition, donor-acceptor pair lines of a Q-DAP series with zero phonon transitions Q_0 near 2.695 eV or a R-DAP series with R_0 peaking near 2.71 eV are observed. The LO-phonon coupling strengths of I_1, I_1^d, and DAP are distinctly different. While I_1 shows a weak coupling, phonon replica of I_1^d are much more pronounced and those of the DAP are still stronger. The lattice coupling can be expressed in terms of Huang-Rhys factors S calculated to 0.01, 0.2, and 0.5 for I_1, I_1^d, and DAP, respectively.

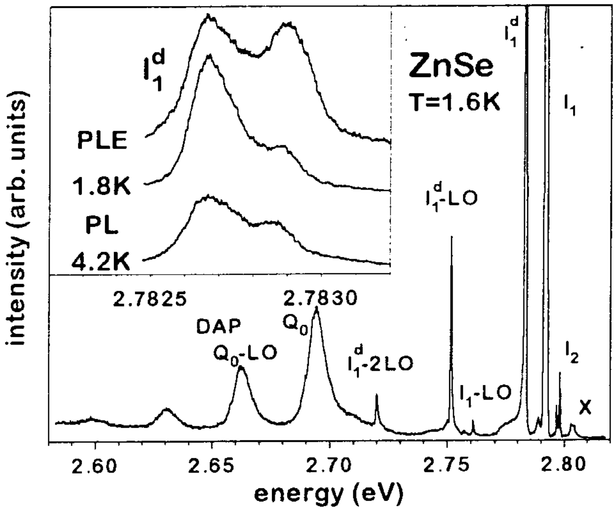

Figure 1: Near band-edge luminescence of an undoped ZnSe crystal. Insert: I_1^d luminescence at 1.8 K and 4.2 K and excitation spectrum detected in the I_1^d-LO line.

The fine structure of the I_1^d line is shown in the insert of Fig. 1. In the emission spectra a thermalized line shifted by 0.23 meV to higher energy is clearly resolved. The excitation spectrum recorded in the I_1^d -LO line demonstrates that both lines have equal oscillator strength. This is also observed in zero-field absorption spectra.[5]

The transient of the I_1^d line is well described by a monoexponential decay after pulse excitation with a lifetime of 1020 ps. The dynamical behavior fits well to the lifetimes of shallow bound excitons in ZnSe showing an increase with increasing binding energy.[6]

4. Zeeman emission spectra

In Voigt configuration **k⊥B**||[001] with **E⊥B**, a fourfold splitting with a pronounced doublet structure of each Zeeman component which has not yet been reported emerges from the zero-field doublet (Fig. 2). The pattern becomes evident at fields above 8 T. In Voigt curve analyses of the corresponding Faraday spectra **k**||**B**||[001] above 7 T, the polarization of the Zeeman transitions with lower energies labeled 1 to 4 show σ^- character and the transitions 5 to 8 with higher energies show σ^- character. In the fan diagram Fig. 2 it can be clearly recognized that each of the two zero field levels leads to two Zeeman lines of σ^- polarization and two lines of σ^- polarization at higher energies.

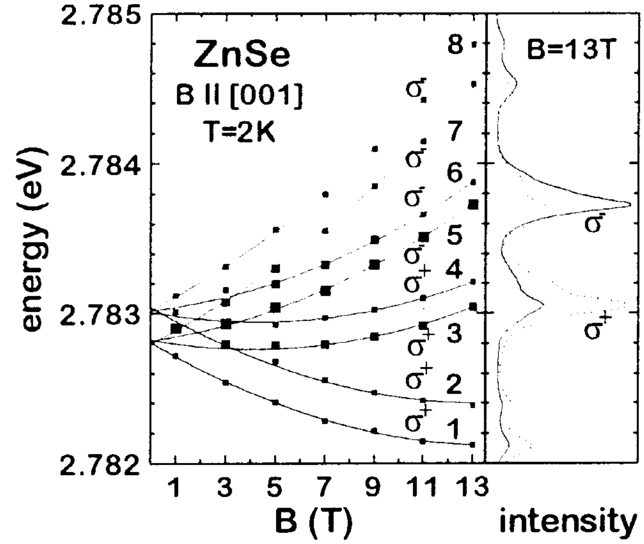

Figure 2: Zeeman effect of the I_1^d line. right hand side: polarized spectra in Faraday configuration.

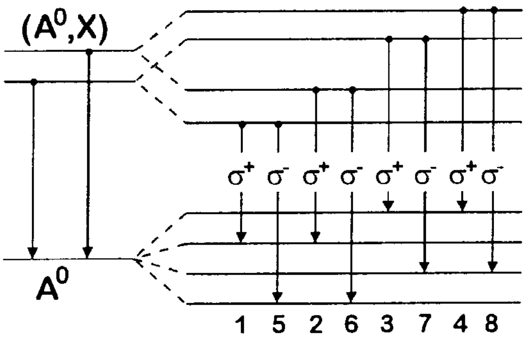

Figure 3: Level diagram of the deep acceptor A^0 and the deep (A^0,X) bound exciton complex.

The evolution of the transition energies with increasing field yields a common diamagnetic shift for all components of 3.6 μeV/T^2.

For a neutral acceptor A^0 a four-fold ground state splitting resulting from the m_j states of the j=3/2 hole is expected. The magnitude of the ground state splitting can be read from the non-thermalized transitions 1 and 5 yielding a g-value of 1.0. This is confirmed by transitions 2 and 6, 3 and 7, and 4 and 8, cf. Fig. 3. As to the states of the (A^0,X) complex ordering of the levels results from the linear term of the parabolic field dependencies drawn as solid lines in Fig. 2. From polarization and level ordering the diagram given in Fig. 3 is derived leading to g-values of 2.2 for both (A^0,X) levels. Rotation of the sample with respect to the magnetic field axis in Voigt configuration yields an essentially isotropic behavior.

5. Discussion

The monoexponential decay of the I_1^d emission demonstrates that the luminescence originates from a single center which previously has been assigned to a deep (A^0,X) complex. The observed lifetime τ=1020 ps is in agreement with a value computed for a deeply bound exciton.[6]

The Zeeman data presented in the previous section yield a ground state splitting as expected for a neutral acceptor A^0. The determined g-value of 1.0 is in agreement with a value reported earlier by Dean.[2] The increase with respect to the more shallow effective-mass like acceptors in ZnSe like lithium with g_{Li}=0.6[7] and nitrogen with g_N=0.7[8] is quite reasonable. The value contradicts, however, more recent data the measurements of which were aggravated by a restricted field strength below 6 T.[5] The energy diagram derived from the low field spectra in ref. 5 cannot explain the structures observed at higher fields and the corresponding g-value thus yields not a suitable description.

The electronic properties of the deep (A^0,X) complex differ significantly from those of the more shallow bound exciton complexes where the interaction between the two holes plays a dominant role.[7] In the *jj* coupling scheme,[9] the hole-hole interaction splits the (A^0,X) states of a shallow acceptor into two levels having total hole momenta $J_h=0$ and $J_h=2$. By the additional coupling of the electron, the $J_h=0$ state results in a $J=1/2$ state with single electron nature. In addition, a twofold splitting of the $J_h=2$ state is induced by electron-hole interaction yielding $J=3/2$ and $J=5/2$. We interpret the magnetic behavior of the bound exciton states as shown in Fig. 3 in terms of two zero-field levels both exhibiting single electron nature. These levels are supposed to originate from the $J_h=0$ and the $J_h=2$ states. The spin-like behavior of the latter is attributed to the strong exciton localization quenching the angular momentum of the two holes.

Localization may also account for a g-value exceeding the value 2.0 of the free electron. An increase of g is known as a common feature of A centers in zinc chalcogenes consisting of a cation vacancy and a donor impurity from either group III or group VII on a neighboring site.[10] In the resulting complex $(h\ V_{Zn}{}^{2-}\ D^+)^0$ the increased g-values originate from localization of the hole h near an anion site due to the repulsion by the charged donor D^+. Such kind of mechanism may also account for the optical properties of the $I_1{}^d$ emission. This would explain the Zeeman behavior as well as the observed intermediate lattice coupling ranging between that of spatially extended donor-acceptor pairs and that of a spatially more localized shallow acceptor complex.

6. Conclusion

Magneto-optical studies confirm the assignment of the $I_1{}^d$ line to the recombination of excitons bound to a deep acceptor. The essentially isotropic Zeeman pattern is well explained by two excited states both exhibiting single electron nature with g=2.2 and a ground state splitting of the neutral acceptor with g=1.0. The (A^0,X) states are interpreted in terms of a quenched angular momentum of the holes.

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