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MAGNETO-OPTICS OF EXCITONS BOUND TO DISLOCATIONS IN CdS

J. Gutowski and A. Hoffmann
Institut für Festkörperphysik der Technischen Universität Berlin
Hardenbergstr. 36, D-1000 Berlin 12, FRG

ABSTRACT

On the high-energy side of the green edge emission a variety of sharp zero-phonon lines occurs. On the basis of magneto-optic, temperature and uniaxial pressure measurements an interpretation of these lines in terms of a model of excitons bound to dislocations is discussed. Two of these lines are due to excitons bound to a positively charged ionized-donor-like complex.

INTRODUCTION

Optical transitions of excitons bound to shallow defects and impurities [1] have been extensively studied and are well known. The electronic structure of excitons bound to deep centers, complex defects or dislocations are not yet understood from the theoretical point of view [2,3]. The existence of sharp lines in the wavelength region between 505 and 515 nm in CdS was reported by some authors [4,5]. An interpretation in terms of a model of excitons bound to deep impurities [5] or dislocations [6,7] is emphasized due to the observed narrow energy width of the lines. The purpose of this paper is to strongly support the interpretation of several transitions in this wavelength range in terms of dislocation-bound excitons on the basis of magneto-optical measurements.

EXPERIMENTAL RESULTS

A set of sharp emission lines I_I to I_{VII} can be observed in the range just above the green edge luminescence in not intentionally doped CdS samples (fig. 1). Often the occurrence of these zero-phonon lines is connected to a strong blue luminescence in the shallow-bound-exciton range of CdS. All lines are preferably polarized perpendicular to the c-axis. The temperature dependence of the emission lines I_{II} to I_{VII} corresponds to the

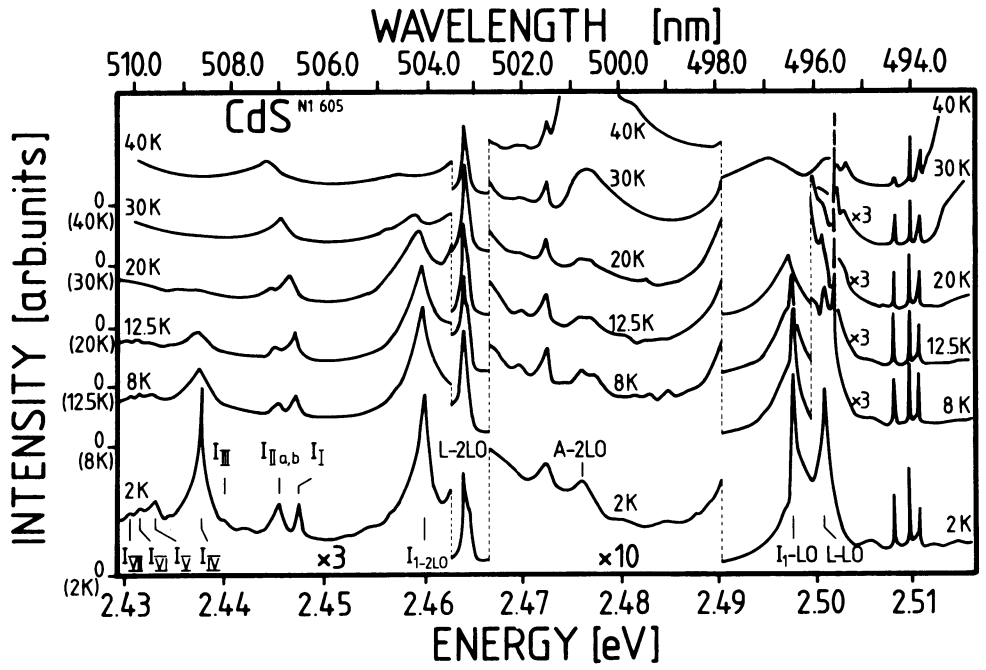

Figure 1 Bound exciton luminescence spectra of CdS in dependence of temperatures. The excitation wavelength is the 488 nm Ar-laser line. In the energy range between 2.43 eV and 2.45 eV a set of sharp emission lines, labelled I_I to I_{VII}, appears which can be attributed to excitons bound to dislocations. The spectral region between 2.455 eV and 2.51 eV shows the 1 phonon and 2 phonon sidebands of the free and shallow-bound excitons. The sharp lines between 2.50 eV and 2.51 eV correspond to the first order Raman lines.

typical behaviour of shallow-bound-exciton transitions in CdS [8]. The lines I_{II} to I_{VII} disappear at about 30 K and do not show an energy shift with rising temperature. Contrary to this, the I_I emission line shifts towards lower energies and broadens with increasing temperature. Up to 40 K, no temperature quenching of I_I is seen. This temperature behaviour is equivalent to that of free excitons in CdS, e.g., the $A_{n=1}$ principal free exciton.

In the excitation spectra of I_I to I_{VII}, resonance maxima are observed at the energies which mark free and shallow-bound exciton transitions. Thus, the build-up of these well-known exciton complexes is seen to be an important mechanism for the formation of deeply bound systems. Under excitation with the 476.5 nm line of an Ar-ion laser, the emission lines I_I to I_{IV} become very weak, while the lines I_V to I_{VII} increase when the spectra are compared with those obtained under excitation with the 488 nm Ar-line.

The dependence of the emission lines I_I to I_{IIb} of a magnetic field up to 15 T is illustrated in fig. 2. The Zeeman patterns show an isotropic behaviour which contrasts to the case of shallow-bound exciton complexes. For the emission lines I_{IIa}-I_{IIb} a zero-field splitting is observed. With increasing magnetic field the intensity of the low-energy Zeeman component becomes stronger, while the intensity of the high energy components decreases. This indicates that an electronic state of a bound exciton complex is responsible for the term splitting. For higher magnetic fields this state splits linearly as a triplet.

The Zeeman behaviour of I_I is also isotropic and shows only a small linear shift towards higher energies. The intensity of the line does not show a dependence on rising magnetic field.

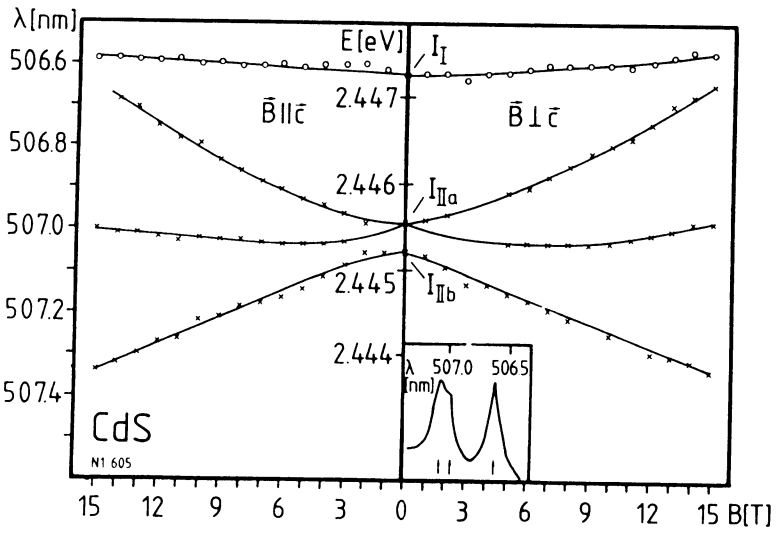

Figure 2 Zeeman patterns of the I_I to I_{IIb} emission lines at T = 1.8 K in Voigt configurations. The I_{IIa} and I_{IIb} lines show a zero field splitting of 0.31 eV.

The Zeeman behaviour of the emission lines I_{III} to I_{IV} is shown in fig. 3. The splitting is again independent of the orientation of the magnetic field. I_{III} shifts with rising magnetic field nearly linearly towards lower energies, while I_{IV} splits into a doublet. For magnetic fields higher than 6 T an additional line appears on the lower-energy side of the doublet. With increasing magnetic field the intensity of this additional line increases, while the doublet of I_{IV} decreases. This indicates for the I_{IV} line also a triplet bound exciton state.

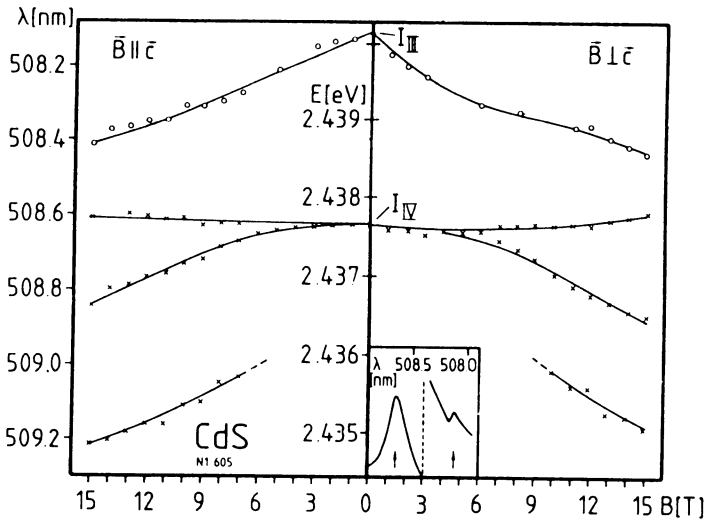

Figure 3 Zeeman patterns of the I_{III} and I_{IV} emission lines at 2 K in Voigt configurations.

The energy positions of the lines I_V to I_{VII} are nearly independent of the external magnetic field (fig. 4).

Under the influence of uniaxial pressure p perpendicular to c ($p \parallel 11\bar{2}0$), the lines I_I to I_{IV} do not show a measurable variation of their emission intensity, while the intensity of the I_V to I_{VII} structures increases with rising pressure. In contrast to that, the intensity of the shallow-bound-exciton luminescence lines (I_2, I_1 lines between 486.9 and 488.9 nm) decreases with increasing uniaxial pressure $p \perp c$. The shift of the I_I to I_{VII} lines is small with rising pressure if the pressure direction is chosen $p \parallel c$, but is much larger than for $p \perp c$.

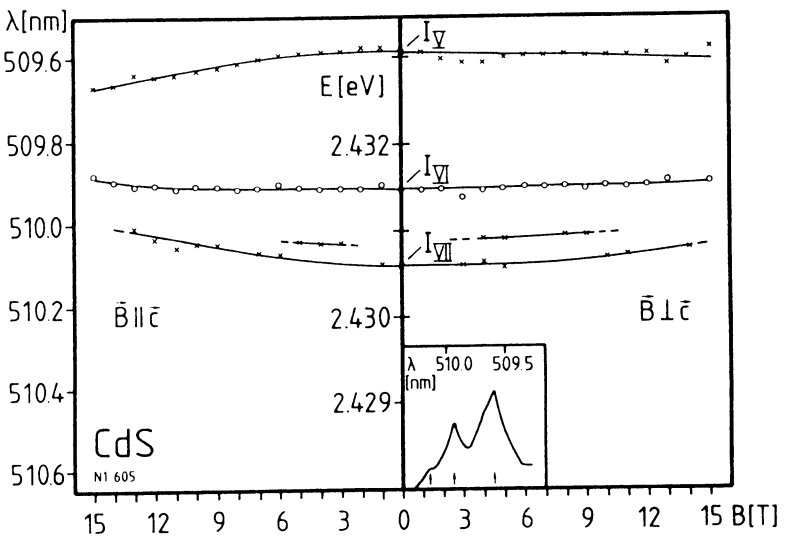

Figure 4 Zeeman patterns of the I_V to I_{VII} lines at T = 2 K in Voigt configurations.

DISCUSSION

As was reported in preceding publications [7,9,10], luminescence light is transferred from the green edge luminescence series of CdS to bands of shorter wavelengths if plastic deformation or an uniaxial pressure $p \perp c$ above a certain threshold value is applied. Therefore, these bands were attributed to dislocation-type bound excitons. The energy positions of these relatively broad bands are in agreement with those reported above. With regard to the small halfwidths of the lines I_I to I_{VII}, we were able to investigate the Zeeman behaviour. Although nearly all lines are polarized $E \perp c$, the Zeeman patterns are rather isotropic. This indicates that no point defect with a localized crystal field screening is involved in these systems but we have to deal with the creation and annihilation of excitons deeply bound to dislocations.

For the lines I_{II} and I_{IV} we can observe a zero-field splitting, which amounts to 0.31 meV for I_{II} and to 0.81 meV for I_{IV}. Due to the isotropic magnetic field behaviour the spin-orbit coupling of these must be weak. Thus, states with large spin quantum number have to be assumed to act as initial levels for the I_{II} and I_{IV} luminescent transitions. From the thermalization of the excited complex transitions within a magnetic field we can further conclude that the Zeeman patterns reflect the splitting of the bound exciton states. This argument is confirmed by the observed diamagnetic shifts towards higher energies, which show that for both line groups the contribution of the ground state to the magnetic field behaviour can be neglected. If one substracts the diamagnetic shifts

in the spectra, the center of gravity for I_{II} is found to be situated at half the distance between the zero-field line pair. For higher magnetic fields, the excited states both split linearly as triplets with a g value of 1.96. This is the typical value of a free electron which has to be expected to be measured for purely large-spin states. For the I_{II}, I_{IV} lines we can thus conclude that an S = 1 excited state is involved. We propose excitons bound to positively charged ionized-donor-like complexes to be the initial systems of these luminescent transitions.

The energy positon of I_I corresponds to a multiphonon sideband of the free A-exciton (A-2 LO-TO). This is in agreement with the temperature behaviour of this line. However, no Zeeman splitting according to $A_n = 1$ is detectable.

The drastic change of the intensity ratio between the I_I to I_{IV} and I_V to I_{VII} lines when exciting with the 476.5 nm instead of the 488.0 nm Ar-laser line can be explained by the fact that the I_{II} to I_{IV} emissions are due to bulk defects, while I_V to I_{VII} are caused by surface defects. The intensity changes under uniaxial pressure measurements support these results.

The magnetic field dependence of the I_V to I_{VII} lines shows that the deeply bound exciton complexes have S = 0 in the initial state. The pressure dependence supports the suggestion that these defects which bind excitons are of dislocation type. The simple polishing of crystals as preparation for the uniaxial pressure experiment is sufficient to cause these bands to appear.

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