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Valence Band Crystal Field Splitting of Hexagonal Diluted Magnetic Semiconductors

By

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The valence band crystal field and spin-orbit splitting in hexagonal diluted magnetic semiconductors based on CdSe and CdS is studied. It is found that the crystal field splitting is practically magnetic ion independent for CdSe based crystals, whereas in the case of CdS based samples a strong influence of magnetic ion substitution on crystal field splitting is observed.

1. Introduction

Diluted magnetic semiconductors (DMS) are materials based on classical semiconductors such as CdZn or ZnS (mostly II-VI compounds) for which a controlled fraction of nonmagnetic cations is substituted by magnetic ions (Mn, Co, Fe, and others) [1]. In the absence of a magnetic field these materials still behave like 'regular' semiconductors but their band sensitivity to magnetic field is strongly enhanced due to s,p-d exchange interaction between delocalized band s,p-type electrons, and localized d-type electrons of magnetic ions [1]. The exchange interaction leads to spectacular magneto-optical effects such as giant Faraday rotation, or strong Zeeman splittings of bands [1]. The interpretation of the experimental results requires input parameters characterizing the actual band structure of the mixed crystal. In many cases the band parameters for pure, nonmagnetic crystals are used, although it is known that at least some of the parameters (e.g. the energy gap) are substantially altered in mixed crystals [2 to 4]. In particular for hexagonal DMS, based on CdSe and CdS, crystal field (CF) and spin-orbit (SO) splittings of the valence band are important parameters for in-field band structure calculations [5 to 7]. It is then a fundamental question to what extent the well-known parameters for pure CdSe or CdS can be adopted for mixed crystals such as CdMnS or CdFeSe. We therefore thought it worthwhile to study this problem in more detail measuring valence band CF and SO splitting for different DMS based on CdSe and CdS. In particular, we focused on CdS-based DMS, which are relatively unexplored until now.

We recall that due to noncubic CF and SO interaction, the valence band of hexagonal crystals is split into three doubly-degenerate subbands of symmetry Γ_9 , Γ_7 , and Γ_7 ,

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respectively. Transition from valence subbands to Γ_6 conduction band lead to the creation of exciton A ($\Gamma_9 \rightarrow \Gamma_6$ transition), exciton B ($\Gamma_7 \rightarrow \Gamma_6$ transition), and exciton C ($\Gamma_7 \rightarrow \Gamma_6$ transition). The energies of these transitions are given by the following formulas [8]:

$$E_A = E_g + \Delta_1 + \Delta_2, \quad (1)$$

$$E_{B,C} = E_g + \frac{1}{2}(\Delta_1 - \Delta_2) \pm \sqrt{\frac{1}{4}(\Delta_1 - \Delta_2)^2 + 2\Delta_3^2}, \quad (2)$$

where $E_{A,B,C}$ is the exciton A, B, C energy, E_g is a constant corresponding to the energy gap (including the exciton binding energy) in the absence of CF and SO, Δ_1 describes noncubic CF, and Δ_2, Δ_3 are SO interaction parameters [8]. In the case of $\Delta_2 \approx \Delta_3$ one can assume $\Delta_2 = \Delta_3$, which constitutes the so-called quasicubic approximation [8]. The energy differences between excitons A, B, and C can be now expressed in a simplified form,

$$E_A - E_{B,C} = \frac{1}{2}[\Delta_{cf} + \Delta_{so} \mp \sqrt{(\Delta_{cf} + \Delta_{so})^2 - \frac{8}{3}\Delta_{cf}\Delta_{so}}], \quad (3)$$

where $\Delta_{cf} = \Delta_1$ and $\Delta_{so} = 3\Delta_2 = 3\Delta_3$. In this case CF (Δ_{cf}) and SO (Δ_{so}) parameters can be evaluated from $E_B - E_A$ and $E_C - E_A$.

We notice that the symmetry of the valence subbands implies selection rules for excitonic transitions for linearly polarized light: both $\Gamma_9 \rightarrow \Gamma_6$ (exciton A) and $\Gamma_7 \rightarrow \Gamma_6$ (exciton B and C) transitions are allowed for light with the electric field vector E perpendicular to the hexagonal axis of the crystal (c -axis), whereas in the case $E \parallel c$ only $\Gamma_7 \rightarrow \Gamma_6$ transitions are possible.

2. Experimental

We studied excitonic transitions of $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$, $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$, $\text{Cd}_{1-x}\text{Co}_x\text{Se}$, $\text{Cd}_{1-x}\text{Cr}_x\text{Se}$, $\text{Cd}_{1-x}\text{Mn}_x\text{S}$, $\text{Cd}_{1-x}\text{Fe}_x\text{S}$, $\text{Cd}_{1-x}\text{Co}_x\text{S}$, and $\text{Cd}_{1-x}\text{Cr}_x\text{S}$ crystals (see Tables 1 and 2). The crystals were grown by the modified Bridgman method and in all cases (except for Cr-based

Table 1
The splitting of excitons A and B for various CdSe-based DMS

material	x	$E_B - E_A$ (meV)	ref.
CdSe	0	26.0	this paper
		24	[4]
		25	[12]
CdMnSe	0.05	22.2	[11]
	0.10	22	[4]
CdFeSe	0.008	25.3	[6]
	0.036	25.2	[6]
	0.037	25.4	[6]
	0.044	25.0	[6]
CdCoSe	0.005	28	this paper
	0.019	26	this paper
	0.022	29	this paper
	0.035	25	[7]
	0.048	26	[7]
CdCrSe	0.001	26	this paper

Table 2

Exciton splittings, crystal field (CF), and spin-orbit (SO) parameters (in meV) of the valence band for various CdS-based DMS (all data this paper)

material	x	$E_A - E_B$	$E_A - E_C$	Δ_{cf}	Δ_{so}
CdS	0	15.1	78.2	26.3	66.9
CdFeS	0.005	21	86	41	66
	0.016	24	92	51	65
	0.016	26	100	52	73
CdCoS	0.016	35			
CdCrS	0.001	16.7	83.5	29.6	70.6

DMS) single-phase monocrystals were obtained. In the case of CdCrSe and CdCrS only low concentration ($x < 0.002$) single-phase crystals could be grown. The attempt to grow samples with higher x resulted in precipitations of chromium selenides or sulfides, respectively. The real Cr concentration of the DMS phase was about $x = 0.001$. Nevertheless, reflectance and luminescence from the DMS phase were observed.

We measured reflectance in the free exciton energy range using a conventional set-up with a halogen lamp as a light source. The samples were mounted on the cold finger of a closed cycle refrigerator, and were typically cooled down to 10 K.

3. CdSe-DMS

The representative spectra for CdSe-based DMS are shown in Fig. 1. For nearly all crystals well pronounced exciton structures are observed. We ascribe the low energy transition to exciton A and the high energy structure to exciton B, according to the situation for pure CdSe (in the case of pure CdSe additionally a bound exciton (BE) is visible below exciton A, Fig. 1). The exciton energy was determined from the inflection point of the reflectance spectra. The resulting exciton splitting for different materials is given in Table 1 together with some previously reported data. First of all we notice that A and B exciton

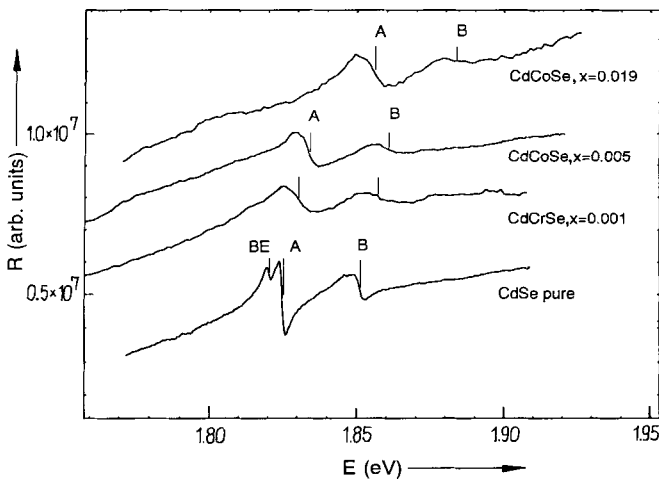


Fig. 1. Reflectance spectra of CdSe-based DMS. The marks indicate the transition energy of excitons A and B, BE denotes bound exciton transition. Pronounced blue shift of exciton structures (CdCoSe) results from an energy gap increase with increasing magnetic ion content [1]

splitting does not depend very much on magnetic ions, at least for DMS with low magnetic ion concentration. The smallest splitting is encountered for CdMnSe (about 20% smaller than for pure CdSe) whereas the largest value of $E_B - E_A$ is found for CdCoSe. For a given magnetic ion and $x < 0.1$ exciton splitting seems to be ion concentration independent (see e.g. CdFeSe, Table 1). We note that only in the case of very high concentrations ($x > 0.3$), which means substantial change of the crystal lattice [9], exciton splitting can change considerably [4].

The CF and SO parameters (Δ_1 , Δ_2 , and Δ_3) cannot be evaluated solely from the energy differences $E_B - E_A$ and $E_C - E_A$. The application of external fields (uniaxial stress or magnetic field) is necessary to accomplish this [11, 12]. An analysis of magnetospectroscopic data of CdMnSe [11] and CdCoSe [7] yielded the following parameters: CdMnSe: $\Delta_1 = 71.7$ meV, $\Delta_2 = 127.4$ meV, and $\Delta_3 = 139.8$ meV, CdCoSe: $\Delta_1 = 80$ meV, $\Delta_2 = 133$ meV, and $\Delta_3 = 150$ meV, whereas for pure CdSe: $\Delta_1 = 68.8$ meV, $\Delta_2 = 138$ meV, and $\Delta_3 = 150.7$ meV [12]. An increase of CF (monitored by Δ_1) is noticeable. On the other hand, the pronounced difference between parameters Δ_2 and Δ_3 makes the quasicubic approximation inadequate. For pure CdS this model leads to $\Delta_{cf} = 38.7$ meV (to be compared with Δ_1) and $\frac{1}{3}\Delta_{so} = 147.8$ meV (to be compared with Δ_2 and Δ_3). Nevertheless if one performs quasicubic analysis the slight variation of CF can be also noticed (for example for Cd_{0.995}Co_{0.005}Se $\Delta_{cf} = 43$ meV and $\frac{1}{3}\Delta_{so} = 146$ meV, while for Cd_{0.999}Cr_{0.001}Se $\Delta_{cf} = 40$ meV and $\frac{1}{3}\Delta_{so} = 139$ meV). Full analysis of exciton splitting is necessary (e.g. piezoreflectance or magnetospectroscopy) to determine the parameters Δ_1 , Δ_2 , and Δ_3 for CdSe-based DMS. However, having in mind the rather small effect of magnetic ion doping on valence subbands one can use pure CdSe parameters as a first approximation, at least for low x values.

4. CdS-DMS

The situation for CdS-based DMS is more complicated from the experimental point of view. Although for pure CdS we observe sharp structures corresponding to free excitons A, B, and C, as well as a bound exciton, for mixed crystals the excitonic structures are much

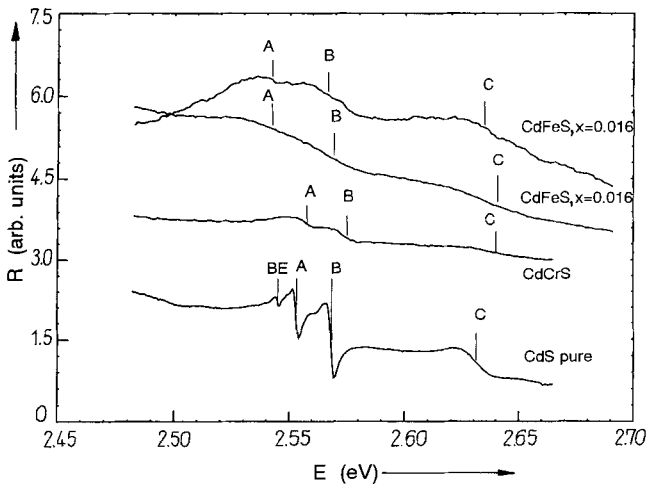


Fig. 2. Reflectance spectra of CdS-based DMS. The marks indicate the transition energy of excitons A, B, and C, BE denotes bound exciton transition

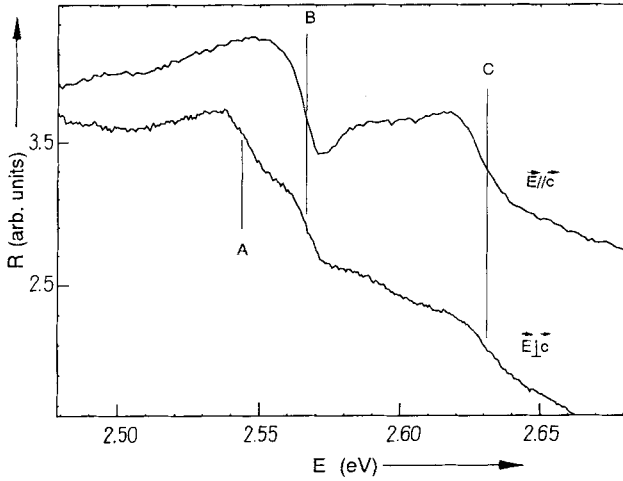


Fig. 3. Reflectance spectra of $\text{Cd}_{0.995}\text{Fe}_{0.005}\text{S}$ for light polarized perpendicular and parallel to the crystal hexagonal axis. The marks indicate the transition energy of excitons A, B, and C

less pronounced and broader (Fig. 2). This fact, together with the smaller exciton splittings in CdS, makes the evaluation of these splittings more difficult. We generally observe three excitonic structures: a weak one at the lowest energies, a strong one at higher energies, and another one at still higher energies. These structures are identified as corresponding to excitons A, B, and C, respectively. In order to check this assignment the reflectance in polarized light is measured. Rotating the polarization plane of the light beam from perpendicular to parallel, with respect to the c -axis, yielded disappearance of the low energy feature, as expected for exciton A. In Fig. 3 we display examples of reflectance spectra of $\text{Cd}_{0.995}\text{Fe}_{0.005}\text{S}$ for $E \parallel C$ and $E \perp c$, where the polarization dependence is clearly visible. Moreover, we also studied photoluminescence (PL) resulting from the recombination of the bound exciton (BE). In Fig. 4 we show the results for pure CdS, CdFeS, and CdCoS. From both reflectance and PL spectra of pure CdS we determined the binding energy of BE as 7.8 meV (relative to exciton A). For CdFeS and CdCoS PL (although much less intense than for pure CdS) is observed *below* the weak, low energy reflectance structure (4 to 9 meV for CdFeS and 4 meV for CdCoS). In this way both polarization and PL results corroborate our identification of excitons A and B. The evaluated exciton splittings are tabulated in Table 2. The exciton splitting is not given for CdMnS since the spectra were too broad and excitons A and B could not be resolved. For CdCoS we were not able to resolve the structure of the exciton C. In the case of CdFeS we included two samples from the same boule with $x = 0.016$. The different splitting values can indicate our actual accuracy of the splitting value or/and possible inhomogeneity of the crystal.

We notice a strong increase of exciton splittings for all mixed crystals (especially for CdCoS) with respect to pure CdS. The analysis of CdS-based DMS data is easier than for CdSe-based materials, since the difference between Δ_2 and Δ_3 is small ($\Delta_2 = 20.9$ meV and $\Delta_3 = 20.7$ meV for pure CdS [12]) and therefore the quasicubic model constitutes a much better approximation in the present case. In Table 2 the CF and SO parameters for different materials resulting from (3) are collected. For pure CdS the quasicubic parameters compare favourably with parameters of the exact model, (1), (2): $\Delta_{\text{cf}} = 26.3$ meV (to be compared with $\Delta_1 = 28.4$ meV [12]) and $\frac{1}{3}\Delta_{\text{so}} = 22.3$ meV (to be compared with Δ_2 and Δ_3). For mixed crystals an increase of both CF and SO parameters with magnetic ion doping can

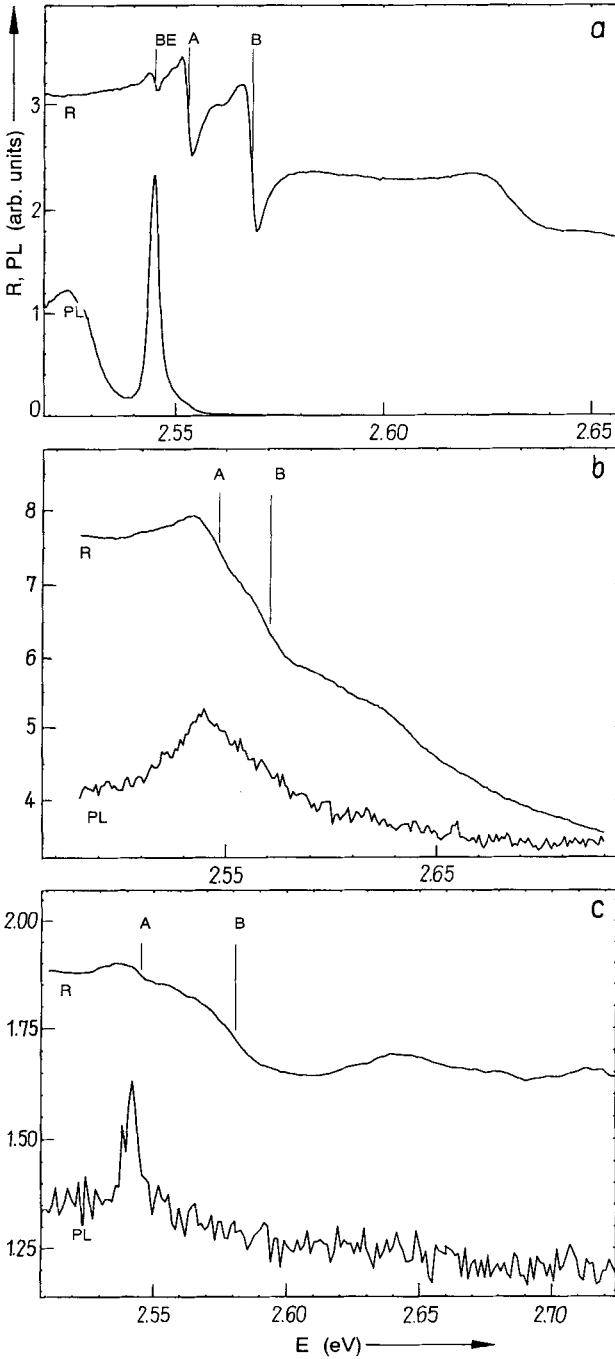


Fig. 4. Reflectance (R) and photoluminescence (PL) spectra of a) pure CdS, b) $\text{Cd}_{0.984}\text{Fe}_{0.016}\text{S}$, and c) $\text{Cd}_{0.984}\text{Co}_{0.016}\text{S}$. The marks indicate the transition energy of excitons A and B, BE denotes bound exciton transition

be noticed. The increase of CF splitting is much stronger in the present case (factor of 2) than it was for CdSe-based DMS. We believe that this cannot result solely from the lattice change induced by magnetic ions, since a similar effect should also be observed for CdSe, which is not the case (cf. CdMnSe case [4]). Pertinent conclusions, however, can only be derived if more precise data are available. We stress that the present data should be considered as preliminary, due to the rather poor experimental resolution. Better crystals (possibly CdS-based epilayers [10]) or/and more advanced techniques should be used. Modulation reflectance methods (e.g. piezomodulation [4]) and magnetorefectance [5 to 7] should be very useful in this task. In particular, we recall that in the presence of a magnetic field parallel to the c -axis, exciton A in DMS should be much more sensitive to the magnetic field than exciton B [5 to 7].

In conclusion we point out that crystal field splitting of the CdSe-based DMS valence band is to a large extent independent of the kind or amount of magnetic ions substituting Cd. For CdS-based DMS this does not seem to be the case, however, further study verifying this conclusion is necessary.

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