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# MAGNETIC IONS IN STUDIES OF SEMICONDUCTOR QUANTUM WELL STRUCTURES

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A few aspects of a relation between magnetic properties of Mn ion system and electronic states confined in CdTe based quantum wells are discussed. It is shown that the influence of the magnetic fluctuations on the states confined in the quantum well results in the reduction of the relative valence band offset with temperature. Also the decrease in the effective Zeeman splitting is observed by a modulation technique at high temperatures and is explained in terms of the modification of the selection rules for an exciton localised in thermal fluctuations. For the *p*-doped samples the giant Zeeman splitting is used to tune the polarization of a hole gas by a small magnetic field. The "competition-like" relation between the oscillator strength of exciton ($X$) and positive trion ($X^+$) is proved experimentally.

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## 1. Introduction

The introduction of semimagnetic (diluted magnetic) semiconductors (DMS) in the growth of low-dimensional structures opened a wealth of new interesting phenomena related to giant magnetic shifts of energy bands in these compounds. One of the best known materials in this family is cadmium manganese telluride [1, 2]. The use of this material in the growth of semiconductor structures has added a new dimension to band gap engineering, allowing us to tailor these structures not only by controlling the growth processes but also by varying the energies using an external magnetic field. In consequence, such phenomena as the field-induced type I to type II transition can be observed [3]. The introduction of magnetic ions has also introduced a variety of effects related to the ion–carrier interactions specific for heterostructures with DMS, such as the self-trapped magnetic polaron formation [4]. Studies of excitonic Zeeman effect in CdTe/$Cd_{1-x}Mn_x$Te quantum wells and superlattices have also helped to understand the role of interface mixing and allowed us to create a magneto-optical method of interface characterization [5, 6].

This paper contains a discussion of a few aspects of a relation between magnetic properties of Mn ion system and electronic states confined in CdTe based quantum wells. In particular, precise magnetooptic measurements of the exciton states confined in the quantum wells allow us to go beyond the simplest static mean field and virtual crystal approximations and study the influence of the magnetic fluctuations on the states confined in the quantum well. In the absence of magnetic field this effect leads to a temperature variation of the relative valence band offset. This variation can be detected by measurements of the exciton energies and exceeds 20% between 2 K and 100 K in typical quantum wells.

Thermal fluctuations may also result in localization of quantum well excitons and, as a consequence, in the modification of the selection rules. The relaxation of the selection rules can be observed as a reduction of the effective Zeeman splitting measured by a modulation technique at higher temperatures. This effect represents a new tool for studies of exciton localization in thermal fluctuations.

The use of diluted magnetic semiconductors in modulation doped heterostructures added also a new possibility of tuning the polarization of carrier gas by a small external magnetic field. The giant band splittings in magnetic field give us a tool for investigation of the influence of the carrier gas on the exciton states in the low-field range, where the exciton wave function is perturbed negligibly. Therefore, the pure information about population effects can be obtained. Such a possibility is especially valuable in the investigation of the competition between the neutral and charged exciton transitions.

## 2. Band offsets in CdTe/$Cd_{1-x}Mn_xTe$ structures

In the first part of this paper the contribution to the energy gap due to magnetic fluctuations is considered. This contribution was shown [7, 8] to be negative and proportional to a product of the temperature and magnetic susceptibility. The band gap narrowing is distributed between the conduction and the valence bands, proportionally to the product of square of a corresponding Mn-carrier exchange constant and the appropriate effective mass. This product has a much higher value in the case of the valence band. In this way, magnetic fluctuations influence the relative valence band offset [9]. At low temperatures the magnetic contribution is negligibly small, therefore, the conclusions from previous works (see for example [10] and [11]) concerning relative insensitivity of the offsets to the temperature and the Mn mole fraction, based on low-temperature data, remain valid. However, already at 10 K the magnetic contribution becomes significant and up to 100 K may exceed the usual (nonmagnetic) temperature variation of the gap.

The variation of the relative valence band offset with temperature, predicted by the magnetic fluctuation model, was experimentally verified by the precise measurements of energies of excitons confined in CdTe/(Cd,Mn)Te heterostructures [9]. The experiment was done with the use of the structures grown by molecular beam epitaxy (MBE). The manganese mole fraction of the barrier material was chosen above 37% to obtain a significant contribution of magnetic fluctuations to the temperature variation of energy gap. The well width (40–66 Å) was determined as a result of compromise between the sharpness of the reflectivity structures (better for thick quantum wells) and sufficient sensitivity of the exciton energy to the valence band offset. The precise parameters of all quantum wells (well width and CdTe–$Cd_{1-x}Mn_xTe$ interface mixing) were obtained by the Zeeman effect measurements performed at 1.9 K and in magnetic fields up to 5 T. The low-temperature data was described in terms of the model proposed in Ref. [5]. The precise control of the strain of the sample during experiment was done by a measurement of the energy of the exciton confined in a very thick (134 Å) reference quantum well grown in the same heterostructure. In order to reduce the influence of strain there were analysed only the differences between the energy of an exciton in thin quantum wells and an exciton in the reference one. The zero-field reflectivity spectra were measured up to 100 K. The exciton energy decreases with the temperature due to the variation of the energy gap of both CdTe and $Cd_{1-x}Mn_xTe$ materials. The results are shown in Fig. 1. The calculations were performed in two

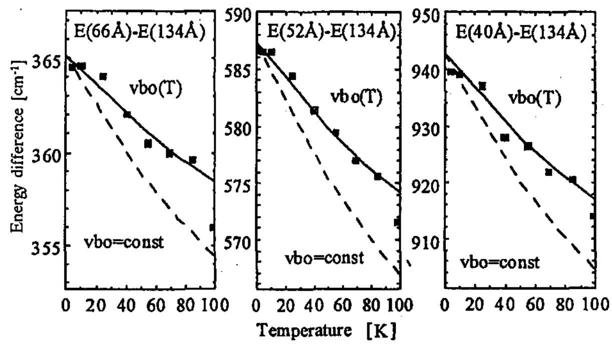


Fig. 1. Energy differences between excitons confined in quantum wells of different widths vs. temperature. The points represent the experimental data. Various types of the lines correspond to model simulations. The solid line shows the results for valence band offset including its temperature dependence. The dashed line shows the calculation with constant valence band offset.

cases: assuming the constant relative valence band offset equal to 0.3 or assuming that the difference of energy gap temperature variation between $Cd_{1-x}Mn_xTe$ and CdTe, which is due to magnetic fluctuations, originates from the valence band only. The second case means the decrease in the relative valence band offset from 0.3 at 1.9 K to 0.24 at 100 K for Mn mole fraction in the barrier $x = 0.375$. The experimental results clearly favour the second case. A similar analysis was done for samples containing CdTe/MnTe superlattices. Also for those samples experimental data are much better described by the calculations performed with the assumption of the variation of the valence band offset with temperature.

## 3. Zeeman effect at high temperatures

Features in excitonic reflectivity in superlattices often remain clearly visible at temperatures higher than those at which similar structures in the bulk became impossible to resolve. The advantage of this property was taken to measure the evolution of the Zeeman effect of excitons in CdTe/MnTe superlattices up to room temperature [12]. A range of high temperatures gives opportunity to simplify the description of the magnetic properties of heterostructure by the use of high-temperature expansion. This approach may be applied for the temperature range above 100 K, for which the susceptibility of $Cd_{1-x}Mn_xTe$ obeys the Curie–Weiss law [13]. It is correct even in the interface region and its accuracy was verified by direct magnetization measurements ([12, 14]).

The experimental study of the high-temperature Zeeman effect was done by reflectivity measurements of thick superlattices (containing 200 periods of CdTe wells separated by MnTe barriers) in a magnetic field equal to 5 T. Since at high temperatures the difference between the spectra measured for different circular polarizations is small, the polarization modulation technique was applied, and the Zeeman splitting was determined by comparing a given reflectivity spectrum with a corresponding reflectivity polarization spectrum (cf. [15]).

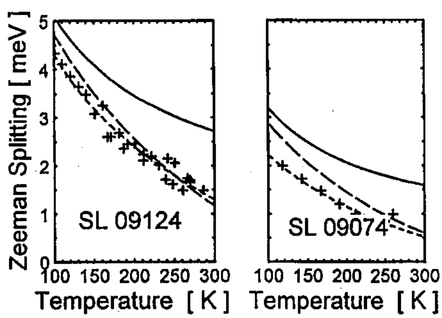


Fig. 2. The Zeeman splitting versus the temperature. The points represent the experimental data. The solid line is calculated using the values of the superlattice parameters obtained by fitting the low-temperature Zeeman effect. The dashed line is obtained taking the decrease in the effective Zeeman effect due to thermal fluctuations into account. The dotted line is to guide the eye.

The Zeeman splitting obtained in this way is presented as a function of temperature in Fig. 2. The results of the numerical calculation are plotted in the same figure. The Zeeman splittings were calculated as differences between the energies of the heavy-hole and electron states with different spins, where the ground states of electrons and heavy holes were found by numerical integration of the Schrödinger equation. The potentials for electrons and heavy holes were calculated with subband splittings obtained from the local magnetization in the particular positions in the structure.

The values of superlattice parameters used in these simulations (well width and interface mixing) were obtained in terms of the model described in Ref. [5] by the Zeeman effect measurements performed at 1.9 K and in magnetic fields up to 5 T.

The experimental data show almost twice smaller high-temperature Zeeman splittings than the values obtained in the simulation.

As an explanation of the observed discrepancy, it is proposed to consider the exciton interaction with thermal fluctuations. Such interaction leads to a mixing of the wave functions of different in-plane wave vectors [7]. Because of the complex structure of the valence band, the functions with non-zero in-plane wave vectors ($k_{\parallel} \neq 0$), are composed of different spin components. Therefore, the influence of fluctuations leads to a relaxation of the optical selection rules, and thus to changes of the effective Zeeman effect.

Particularly in Faraday configuration the transitions involving both Zeeman-split hole subbands (originated from pure $|+3/2\rangle$ and $|-3/2\rangle$ states in $k_{\parallel} = 0$) are allowed in each circular polarization. For narrow lines one can expect occurrence of two lines in each circular polarization. If the line width is larger than their splitting (as is the case of high temperatures), the two lines could not be distinguished and a broad line is observed. The modulation technique measures the splitting between the centres of mass of the broad lines in two polarizations. Therefore, the relaxation of the selection rules results in a decrease in the observed Zeeman effect.

The influence of the fluctuations on the exciton may be estimated from the temperature broadening of the exciton line. Such estimation together with the true valence band calculations (cf. [16]) gives quantitative agreement with experiment.

## 4. Observation of positively charged trions

In the fourth part of this paper it is shown that diluted magnetic semiconductors can be used as a tool for tuning the spin polarization of carrier gas by applying a small external magnetic field. Such opportunity is especially interesting in the investigation of the population effects of trion and exciton transitions. Due to a giant Zeeman effect, the complete polarization of hole gas can be achieved at a field which does not affect exciton wave function significantly.

The positively charged trions were observed in the modulation doped structure containing a single 80 Å quantum well (QW) of $Cd_{1-x}Mn_xTe$ embedded between $Cd_{0.66}Mg_{0.27Z}Zn_{0.07}Te$ barriers grown pseudomorphically on a (100) $Cd_{0.88}Zn_{0.12}Te$ substrate. Such a layout assures a large confinement energy for the holes in the quantum well, minimising at the same time the effects of lattice mismatch. The low Mn concentration in QW ($x = 0.0018$) assured a very small line broadening. On the other hand, it was high enough to lead to a significant Zeeman splitting of the exciton levels. The sample was *p*-type modulation doped, with the nitrogen-doped region located at the distance of 200 Å from the QW. The nominal hole concentration in the structure, evaluated from a self-consistent solution of the Poisson and Schrödinger equation is $2 \times 10^{11}$ cm$^{-2}$. In order to observe the trion creation, the hole gas population was reduced by an additional white light illumination.

Figure 3 shows an example of the transmission spectra versus magnetic field. The intensity of the lower ($X^+$) line changes dramatically when the hole gas is spin polarised. Such behaviour is explained by the fact that the $X^+$ state is built from a photoexcited electron–hole pair and an extra hole present already in the initial state [17, 18]. Since the ground state of the trion is a singlet, the two holes forming the trion correspond to opposite spins. Therefore, the intensity of $X^+$ line should be roughly proportional to the population of holes already present in the appropriate spin subband. We use a simple thermodynamic distribution between Zeeman split subbands to describe the area of the $X^+$ line

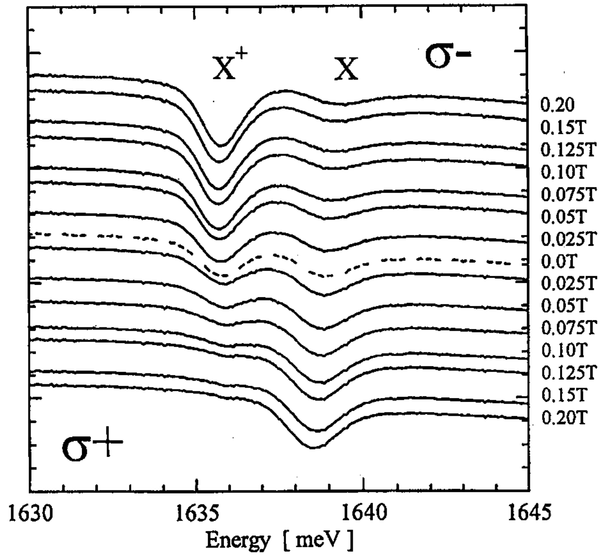


Fig. 3. Transmission spectra measured in magnetic field. Two absorption lines are related to the exciton and positively charged trion transitions. The population of hole gas in QW was reduced by an additional white light illumination.

$$I_{\sigma^+,\sigma^-} = I_0 \frac{1}{1+\exp[\pm\Delta/(2k_{\mathrm{B}}T)]}, \tag{1}$$

where $\Delta$ denotes the Zeeman splitting of the valence band edge, $T$ is the hole gas temperature, and $k_{\mathrm{B}}$ is the Boltzmann constant. The Zeeman splitting $\Delta$ is obtained directly from the shift of the exciton line in a magnetic field and has the same value as that obtained with the use of the phenomenological expressions given in Ref. [5] for the bulk material. Such an approach to the integrated intensity

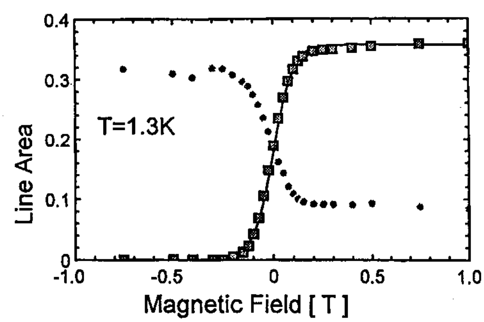


Fig. 4. The area of the absorption lines versus magnetic field, obtained from the transmission spectra by fitting of two Gaussian functions. Squares represents $X^+$, circles $X$ and solid line a fit of Eq. (1).

of the $X^+$ line describes satisfactorily the experimental data obtained for different temperatures (in the range of 1.3–4.2 K) and different illuminations (hole gas concentrations). The temperature of the hole gas obtained from the fit of Eq. (1) is slightly higher than the temperature of the system of magnetic moments, determined from a high-field Zeeman analysis (by less than 0.4 K). This difference may be related to the fact that the sample remains under stationary conditions with a continuous diffusion of photoexcited electrons which neutralise the hole gas, but may also heat the carrier gas in the quantum well.

The change of the $X^+$ trion oscillator strength is always accompanied by a significant change of the neutral exciton line strength. Variations of both intensities are proportional to each other, which is clearly visible in Fig. 4.

This effect cannot be explained as being due to the $X$ line width variation, because the exciton line width can be easily determined from the experimental spectra, and remains almost constant in the experimental range of the magnetic fields. The experiment gives a direct proof of the "competition-like" relation between the oscillator strength of exciton ($X$) and positive trion ($X^+$).

## 5. Conclusions

The presented above personal selection of the phenomena related to the influence of magnetic ions on exciton states confined in CdTe-based quantum structures demonstrates that the physics of diluted magnetic semiconductors continues to supply challenging problems. I am convinced that the progress of low-dimensional semiconductor physics will create many new opportunities to show the value of magnetic ions as one of its tools.

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