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Evidence of exchange interaction of localized carriers and transition metals in diluted II-VI nanostructures: ODMR study

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Optically detected magnetic resonance study of (CdMn)Te/(CdMg)Te quantum wells allowed to reveal the formation of exchange-coupled complexes consisting of Mn ions and localized holes in quantum wells with excess hole concentration and the directional electron tunneling towards wider wells in multiple quantum well structures. The existence of a distribution of Mn-hole complexes that differ in a number of Mn ions interacting with a localized hole is justified.

In colloidal cobalt doped ZnO nanocrystals, several nm in diameter, the interaction between the magnetic ions and the shallow donor electron in the confined system of ZnO quantum dots has been revealed. Direct evidence of interaction of Co ions with the interstitial Li shallow donor in the ZnO nanocrystal core and hyperfine coupling with ^{1}H in the quantum dot shell have been demonstrated.

1 Introduction In diluted magnetic semiconductors (DMS), the strong interaction between the two spin subsystems - free carriers and localized spins of impurity transition ions is known to give rise to the giant Zeeman splitting of both the conduction and valence bands [1]. It was shown that manipulating the density of the two-dimensional hole gas (2DHG) affects the ferromagnetic properties of magnetic quantum wells (QWs) and drives the system between the ferromagnetic and paramagnetic phases due to free carriers mediated exchange coupling [2], in a direction which can be selected by an appropriate design of the structure [3]. Spin-flip Raman studies of such QWs have demonstrated a reduction of the Mn paramagnetic resonance frequency with an increase of the hole concentration [4]. New optically detected magnetic resonance (ODMR) spectra have been found in these QWs [5].

Colloidal ZnO nanocrystals, or quantum dots (QDs) are widely studied with magnetic resonance techniques [6]. ZnO QDs doped with cobalt present a promising class of DMS for spintronics applications.

In this paper, we present an ODMR study of (CdMn)Te quantum wells (QWs) with excess hole concentration and ZnO:Co nanocrystals.

2 Results and discussion

2.1 ODMR of (CdMn)Te quantum wells with 2D hole gas (CdMn)Te QWs were grown by molecular-beam epitaxy on (001)-oriented GaAs substrates. A multple QW structure had a thick (100 nm) $Cd_{0.8}Mg_{0.2}Te$ buffer layer and contained three 4, 6, and 10 nm wide $Cd_{1-x}Mn_xTe$ QWs (x=1%) QWs. The QWs were separated by rather large (30 nm) $Cd_{0.8}Mg_{0.2}Te$ barriers and covered with a 100 nm $Cd_{0.8}Mg_{0.2}Te$ cap layer. A schematic of the sample is shown in the inset of Fig. 1(a). For comparison, ODMR was measured in 10 nm wide single $Cd_{1-x}Mn_xTe$ QWs (x= 0.02) described in [4, 5], in which the excess hole concentration was created under optical excitation owing to the surface states and in QWs without excess holes and in QWs without excess holes.

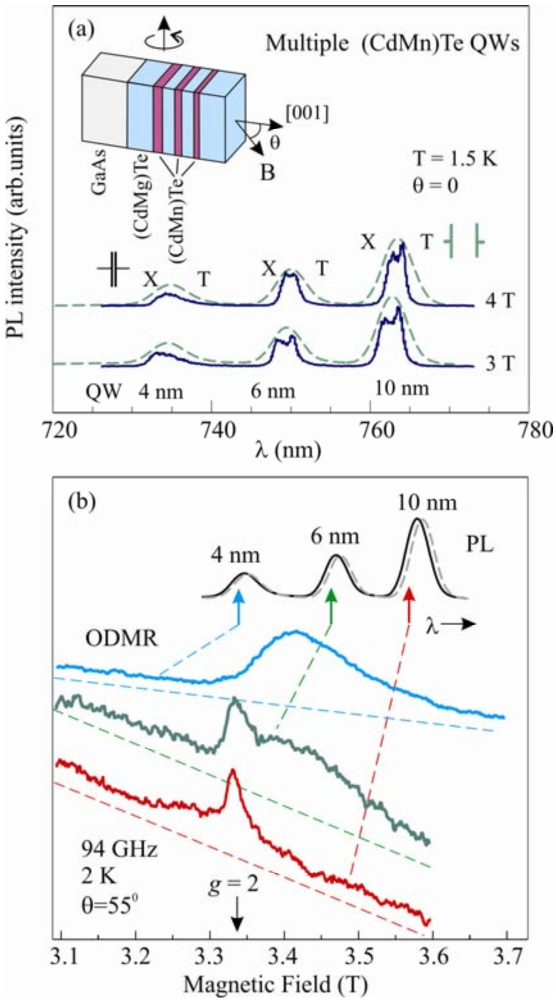

Figure 1 (a) A schematic of a triple (CdMn)Te QW structure (inset) and PL spectra recorded at 1.5 K in magnetic fields of 3 T and 4 T. Dashed lines show PL spectra measured with a reduced spectral resolution that was used in the ODMR measurements. X and T denote the emission lines of excitons and charged excitons (trions). (b) PL intensity dependences on magnetic field recorded at the wavelengths marked by arrows without microwave field (dashed lines) and in the presence of 94 GHz microwaves (solid lines). Solid and dashed lines in the inset show PL spectra measured at 3 T and 4 T, respectively. The angle θ between the magnetic field direction and the [001] growth axis is 55°. T = 2 K.

ODMR was measured at 94 GHz and 35 GHz via photoluminescence. Comparing the spectra recorded in two microwave bands is important for their identification and for a reliable determination of the spin Hamiltonian parameters that must be the same for any microwave frequency. In the case of anisotropic spectra this allows to distinguish between the *g*-factor anisotropy and the zero-field splitting such as fine-structure or exchange splitting. In 94 GHz experiments, a 100 mW generator and a quasi-optical microwave circuit were used [7]. The 35 GHz ODMR spectrometer was the same as in Ref. [8].

High-resolution photoluminescence (PL) spectra of the multiple (CdMn)Te QW structure recorded at 3 T and 4 T are shown in Fig. 1(a). For each QW the spectrum consists of two emission lines, excitons (X) and charged excitons (trions, T). They manifest similar shifts to lower energy (larger wavelength) with increasing magnetic field due to the giant Zeeman splitting of both the conduction and valence bands [1, 9]. The shift is determined by the spin polarization of Mn paramagnetic centers involved in the exchange interaction with the carriers, which is influenced by EPR transitions. This allows EPR optical detection of Mn-related paramagnetic centers.

We used a reduced spectral resolution in our ODMR experiments. The corresponding PL spectra measured at B = 3 T and 4 T are shown in Fig. 1(a) and in the inset in Fig. 1(b). PL was excited with a semiconductor laser (650 nm, ca. 1 W/cm^2). By an appropriate choice of the detection wavelength at a slope of the PL line it was possible to monitor the shift of the PL lines by detecting the PL intensity at a fixed wavelength. Figure 1(b) shows that the magnetic-field dependencies of the PL intensity measured at the wavelength marked by arrows are close to linear when no microwave field is applied. Application of 94 GHz microwaves results in a non-resonant shift of these dependencies and to the appearance of the EPR signals. The ODMR spectra recorded at both slopes of the PL lines have been found to be identical, which proves reasonableness of such an approach.

The ODMR spectra shown in Fig. 1(b) are anisotropic. They are similar to those observed in (CdMn)Te QW with 2DHG [5] and consist of two lines. With the increasing angle θ between the magnetic field direction and the [001] growth axis the narrow line slightly shifts from high fields corresponding to $g<2$ for θ=0 to lower fields ($g>2$) while the anisotropy of the broad line is much larger and shows the opposite behavior. In (CdMn)Te QWs without 2DHG no such broad line was found [5, 9]. The observed anisotropy suggests that localized holes may be involved in the paramagnetic center.

The narrow ODMR line can be ascribed to Mn ions [5, 9]. A spin Hamiltonian for isolated Mn^{2+} is given by

$$\hat{H}_{Mn} = g\mu_B \vec{B}\cdot\vec{S} + D\left[S_Z^2 - \frac{1}{3}S(S+1)\right] \quad (1)$$

where μ_B is Bohr magneton, g = 2.0032 and is isotropic, S = 5/2, and D describes the stress-induced fine structure splitting. Because of the large Boltzmann factor at low temperatures and high magnetic fields the lowest levels are mostly populated and the transition $M_S = -5/2 \leftrightarrow M_S = -3/2$ dominates the spectrum. This is the reason of the observed anisotropy [8].

Localized heavy holes in QWs can be described by an effective spin S* = ½ and a spin Hamiltonian with a strongly anisotropic g-factor [5]:

$$\hat{H}_h = \mu_B \left[g_{h\|} B_z S_z^* + g_{h\perp} (B_x S_x + B_y S_y) \right] \quad (2)$$

The broad ODMR lines in (CdMn)Te QW with 2DHG and in the narrowest QWs of the triple QW structure can be attributed to exchange-coupled complexes formed by localized holes and Mn ions. The spin Hamiltonian of a complex can be written as:

$$\hat{H}_{exc} = \hat{H}_{Mn} + \hat{H}_h + \hat{S}_h^* \cdot \sum c_i \hat{S}_{Mn_i} \ , \quad (3)$$

where the first two terms are the spin Hamiltonians (1) and (2) and the last one describes the exchange interaction of a localized hole and Mn ions. It should be noted that this exchange interaction is surely not the same as the strong exchange interactions of free electrons or holes and localized transition element impurity spins that give rise to the giant Zeeman spitting of both conduction and valence band.

The ODMR spectra in 4 nm, 6 nm and 10 nm QWs can be decomposed into two lines which are similar to those in the QW with 2DHG but their relative amplitudes are different for different QWs (see Fig. 2(a)). The broad line ascribed to the exchange-coupled complexes dominates the ODMR spectrum of the narrowest 4 nm QW while the ODMR signal of isolated Mn ions is the strongest in the widest 10 nm QW. In 6 nm QW both signals are present.

Observation of the ODMR signals of Mn-hole complexes seems to indicate the presence of 2DHG in the narrowest and intermediate-width QWs. It is obviously created as a result of directional electron tunneling from narrower to wider QWs. In spite of large barriers and very low tunneling probability there is an accumulation of excess holes in the narrowest QWs.

The shape of the ODMR lines of the exchange-coupled complexes is asymmetrical and depends on the microwave power. Figure 2(b) shows that the center of mass of the line shifts in the direction of magnetic fields corresponding to g=2 with increasing microwave power. Such a behavior can be explained assuming a distribution of complexes that are formed by a localized hole with the strongly anisotropic g-factor and several Mn ions with g=2. The observed ODMR signal is a superposition of the ODMR signals of such complexes. In the case of a sufficiently large exchange interaction g–factor of an exchange-coupled system approaches an average of the partner's g-factors, i.e. becomes closer to 2, in our case. It is known that the spin-lattice relaxation time of an exchange-coupled complex decreases with an increase of the number of particles in the complex [10]. To observe ODMR signals it is necessary that the rate of microwave-induced transitions between the spin sublevels be higher than the relaxation rate. This means that the contribution of faster relaxing complexes to the overall ODMR signal increases with increasing microwave power.

Calculations have been performed with EasySpin [11] to simulate the ODMR spectra using a simplified model of exchange-coupled complexes in which a localized hole interacts with 1, 2, 3, and 4 Mn ions. The Boltzmann distribution of the level populations and different contributions of complexes with different numbers of Mn ions to ODMR spectra recorded at various microwave power were taken into account. The following parameters have been used in calculations: g=2 and D=15×10^{-4} cm^{-1} for Mn, $g_{\|}$=2.4 and $g_{\perp}$=1.1 for a localized hole, and c_i= –1 cm^{-1}. A 160 mT wide Lorentzian line was used to account for spreading of the exchange interactions.

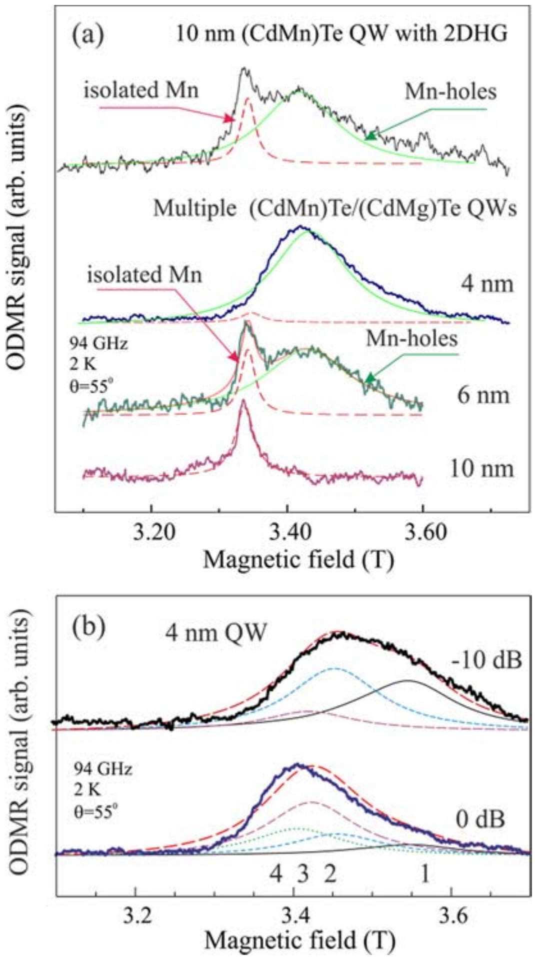

Figure 2 (a) 94 GHz ODMR spectra measured at 2 K and 94 GHz in 10 nm QW with 2DHG and in 4, 6, and 10 nm wide QWs of the triple QW structure. (b) Experimental (full lines) and simulated (dashed lines) ODMR spectra of 4 nm QW recorded with the maximum microwave power (0 dB) and with 10 dB attenuation. The numbers on the bottom denote the number of Mn ions in a complex localized hole – Mn. In the simulated spectra, different contributions of complexes including 1, 2, 3, and 4 Mn ions at different levels of microwave power were taken into account.

Similar spectra simulations have been performed for ODMR spectra recorded at both 94 GHz and 35 GHz for different sample orientations. The simulated and experimental spectra are in good agreement, which seems to justify the proposed model.

2.2 Magnetic resonance in ZnO colloidal nanocrystals doped with Co ZnO quantum dots, which consist of a ZnO nanocrystal core and $Zn(OH)_2$ shell can be effectively studies by magnetic resonance techniques [6]. Cobalt doped ZnO quantum dots were prepared by chemical wet method and had a diameter of 2 to 6 nm. They contained 0.01 to 1% of Co.

ODMR techniques based on EPR detection via photoluminescence (PL) or tunneling afterglow that can be observed for a long time after preliminary X-ray or UV irradiation proved to be very useful for a study of colloidal ZnO nanocrystals. ODMR of shallow donors and deep acceptors were recorded in ZnO:Co nanocrystals via the intensity of PL and tunneling afterglow. High sensitivity of ODMR allowed its application for characterization of ZnO QDs dispersed in transparent media, which cannot be studied by conventional EPR.

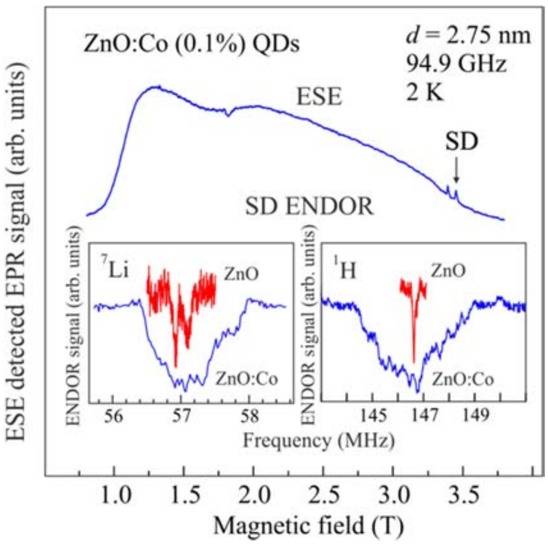

Figure 3 High frequency ESE-detected EPR and ENDOR (insets) spectra in ZnO:Co (0.1%) quantum dots. ENDOR spectra were recorded at the magnetic field value corresponding to the shallow donor (SD) EPR line (arrow). The ENDOR lines in Co-free ZnO nanocrystals are shown for comparison.

Figure 3 shows the high-frequency electron spin echo (ESE) detected EPR and electron-nuclear double resonance (ENDOR) spectra, measured in ZnO:Co quantum dots using the techniques described in Ref. [6]. The shallow donor (SD) signals appeared only after UV excitation. The ENDOR signals (insets) were recorded at the magnetic field value, which corresponds to SD EPR and is marked in Fig. 3 by arrow. For comparison ENDOR signals measured on EPR of SD in Co-free ZnO QDs are shown. They correspond to hyperfine interaction of the SD unpaired electron with ^{7}Li nuclei, which are Coulombic centers of shallow donors localized in the ZnO nanocrystal core, and ^{1}H nuclei in the QD $Zn(OH)_2$ shell. The line width of the ENOR signals is strongly enlarged in Co-doped ZnO QDs as compared to that in the undoped QDs due to the interaction with the local magnetic fields induced by Co ions.

3 Conclusions In conclusion, two systems in which localized carriers, i.e., localized holes in (Cd,Mn)Te quantum wells and shallow donors localized in the central part of the ZnO quantum dots, interact with transition metal impurity ions. Exchange-coupled complexes formed by a localized hole and Mn ions have been revealed by ODMR in (CdMn)Te QWs containing 2DHG in the narrowest QWs of a triple QW structure. It was concluded that the optically induced p-type doping of (CdMn)Te QWs can be achieved in the narrowest QWs of the multiple QW structures. The existence of a distribution of complexes formed by a localized hole and several Mn ions has been justified. Direct evidence of interaction between the localized electron in the confined system of ZnO:Co QDs and Co ions has been presented.

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