Kinetic Exchange between the Conduction Band Electrons and Magnetic Ions in Quantum-Confined Structures

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We provide an experimental evidence and a theoretical substantiation for a strong reduction of the *s-d* exchange interaction between electrons and Mn-ion spins with increasing degree of the confinement in nanostructures of diluted magnetic semiconductors. By spin-flip Raman scattering a strong (up to 25%) reduction of the exchange parameter is observed in (Cd, Mn)Te/(Cd, Mn, Mg)Te quantum well structures. As a responsible mechanism we suggest switching-on of the kinetic exchange for the conduction electrons with finite **k** vectors. Quantitative agreement between experimental data and calculations is achieved.

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Semimagnetic or diluted magnetic semiconductors (DMS) are known for their giant magneto-optical effects originating in a strong *sp-d* exchange interaction between the band electrons and the magnetic (e.g., Mn) ions. Incorporation of semimagnetic layers in quantum-confined heterostructures opened new possibilities for the "spin splitting engineering" [1]. In this context, in addition to a magnetic field, temperature, and Mn molar fraction dependences, also the confinement energy and the size quantization became means of an effective tuning of the spin splittings. While a precise tuning of the spin splitting is of great significance for future-spin-dependent electronics, it is already now of obvious importance in, e.g., studies of samples with zero g-factor in the fractional quantum Hall regime [2]. Also, exciting physical phenomena have been reported recently for semimagnetic heterostructures: coherent spin excitations [3,4], magnetic polaron formation [5], and ferromagnetic hole alignment in p-type doped structures [6].

For the electrons from the vicinity of the conduction band edge the exchange interaction with the localized d electrons of magnetic ions is described by the Hamiltonian:

$$H_{\mathrm{ex}} = -\alpha \sum_i (\mathbf{s}\mathbf{S}_i)\delta(\mathbf{r} - \mathbf{R}_i), \qquad (1)$$

where the parameter of the *s-d* exchange interaction α is positive. In the case of the holes, the exchange energy has the same form but the parameter of *p-d* exchange interaction $\beta < 0$. In Eq. (1) **s** and **r** are the spin (total angular momentum in the case of the holes) and coordinate operators of a carrier, and $\mathbf{S}_i$ and $\mathbf{R}_i$ are the total spin and coordinate of the ith magnetic ion. A positive sign of α results from the *direct* (or potential) exchange of the conduction band electron with the d electrons of Mn ions. The negative sign of β is due to a dominant role of the *kinetic* exchange [7] which occurs because of possible transitions to virtual states in the d shell [8].

A possibility of a modification of the exchange parameters under quantum-confined conditions has been recognized already with the first semimagnetic semiconductor quantum wells (QWs) studied. However, experimental evidences showing unambiguously such a modification of the exciton Zeeman splitting, i.e., of $(\alpha - \beta)$, have been found only recently [9]. A special design of the QW structures was crucial for the latter studies since one had to rule out effects related to a modification of magnetic properties at the magnetic/nonmagnetic interfaces. A recent theoretical approach to the problem developed by Bhattacharjee [10] shows a qualitative agreement with experiments of Mackh *et al.* [9] but fails to describe quantitatively the large value of $(\alpha - \beta)$ variation amounting to $\sim$15% since it predicts only 2% variation of the exchange parameters. Let us note that the approach of Ref. [10] accounts for the variation only of β.

In this Letter we present new experimental results of direct measurements of the dependence of α on the QW width by means of spin-flip Raman scattering (SFRS). A strong 25% decrease of α is found. We developed also a model accounting for the kinetic exchange for the conduction band electrons in quantum-confinement structures. It shows a good agreement with our experiments and with the data of Ref. [9]. An extension of the model predicts even stronger modifications of the exchange interaction in quantum dot structures made of DMS.

The SFRS spectroscopy has been chosen here since it is the most reliable method of investigating α [11]. We studied a high-quality (Cd, Mn)Te/(Cd, Mn, Mg)Te QW structure grown by molecular-beam epitaxy on (100)-oriented GaAs substrate. It contained a $Cd_{0.98}Mn_{0.02}Te$ single QW sandwiched between $Cd_{0.876}Mn_{0.014}Mg_{0.11}Te$ barriers. Exact Mn contents in the part of the QW and in the barriers were determined from the giant Zeeman effect of the conduction electron states by means of SFRS. A wedgelike shape of the sample (for details see Ref. [12])

allowed us to realize in one single structure an in-plane variation of the well width from 300 Å down to 45 Å and thus to achieve a variation of the electron confinement energy E_e from 5 meV up to 50 meV. The structure was lightly n-type doped in the barriers (about 10^{15} cm^{-3}) in order to enhance the SFRS signal. The spin-flip shift caused by the free electrons in the QW was measured at a temperature of 1.6 K and in magnetic fields up to 7 T applied in the Voigt geometry (for details see Ref. [13]).

Raman shifts corresponding to the giant Zeeman splitting of the conduction band electrons in 45 and 300 Å wide QWs are shown in the inset of Fig. 1. Solid lines trace the fits of the Raman shifts with the use of equation: $\Delta E_{\mathrm{SFRS}} = \alpha(E_e) N_0 x S_{\mathrm{eff}} B_{5/2}[5 g_{\mathrm{Mn}} \mu_B B / 2 k_B (T + T_0)]$. Here N_0 is the number of unit sells per unit volume, $g_{\mathrm{Mn}} = 2$, μ_B is the Bohr magneton, T is the lattice temperature, and S_{eff} and T_0 are effective parameters characterizing magnetic properties of Mn-ion system [9]. The effective parameters were determined from the fit for the widest region (300 Å wide) of the QW done with bulk value of exchange parameter $N_0\alpha = 0.22$ eV. These parameters were kept constant in further determination of $\alpha(E_e)$ in narrow regions of the QW. The dependence

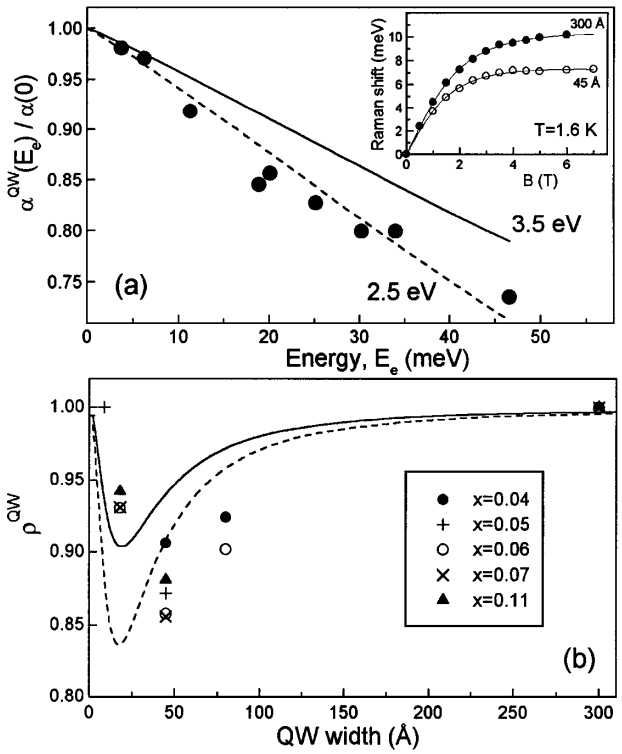

FIG. 1. (a) Exchange parameter α^{QW} as a function of the electron confinement energy in $Cd_{0.98}Mn_{0.02}Te/Cd_{0.876}Mn_{0.014}Mg_{0.11}Te$ single QWs. In the inset magnetic field dependencies for the Raman shift in 300 and 45 Å QWs are presented; (b) reduction factor of exciton Zeeman splitting $\rho^{\mathrm{QW}} = (\alpha^{\mathrm{QW}} - \beta^{\mathrm{QW}})/(\alpha - \beta)$ as a function of QW width in $Cd_{1-x}Mn_xTe/Cd_{0.75-x}Mn_xMg_{0.25}Te$ QWs (experimental data are taken from Ref. [9]). In both panels results of the calculation are shown by the lines: $\varepsilon^- - E_v = 2.5$ eV (dashed) and $\varepsilon^- - E_v = 3.5$ eV (solid).

$\alpha(E_e)$ determined in this way is shown in Fig. 1a. We found a decrease of α by about 25% with QW width being reduced down to 45 Å. On the other hand, the recent theory [10] predicts no confinement energy (i.e., no well width) dependence of α. Because of this conflict between the existing theory and our experimental results we are led to the conclusion that there must be a mechanism, so far not considered, which is responsible for the observed rapid drop of α. Such a mechanism is suggested below involving the *kinetic* exchange also in the case of the conduction band electrons.

Let us recall that the Γ point the kinetic exchange for the electrons is forbidden by their s-like symmetry. In this case the exchange interaction between the band and the localized d electrons has a potential character with $\alpha > 0$. For electronic states away from the Brillouin zone center (i.e., for finite $\mathbf{k}$ vectors), the wave functions of the valence band states with p-like symmetry admix to the Bloch functions of the conduction band. This admixture facilitates the kinetic exchange also for the conduction band electrons, the magnitude of the kinetic exchange being determined by the degree of the admixture. The kinetic mechanism of the exchange leads, in turn, to the negative sign of the contribution to the exchange constant. Therefore, turning on the kinetic exchange causes, at first, a decrease of α and can even induce its sign reversal.

A theoretical approach is developed within the envelope function theory. A calculation in the frame of the Kane model [14] taking into account k^2 terms ($\mathbf{k}$ directed along the z axis) gives the Bloch amplitudes of the electron wave function (for $s = +\frac{1}{2}$) in the following form:

$$u_{c,1/2}(k) \approx \left[1 - \frac{(\hbar p k)^2}{6 m_0^2}\left(\frac{2(E_g + \Delta)^2 + E_g^2}{(E_g + \Delta)^2 E_g^2}\right)\right] S\uparrow + \frac{\hbar p k}{3 m_0}\left[\left(\frac{2}{E_g} + \frac{1}{E_g + \Delta}\right) Z\uparrow - \left(\frac{1}{E_g} - \frac{1}{E_g + \Delta}\right)(X + iY)\downarrow\right]. \quad (2)$$

Here S and X, Y, Z are the orbital components of the Bloch amplitudes at the bottom of the conduction band and at the top of the valence band, respectively, while the arrows $\uparrow, \downarrow$ denote the spin components; E_g and Δ are the energy gap and the spin-orbit splitting at Γ; $p \equiv \langle S | p_x | X \rangle$ is the momentum matrix element between the conduction and the valence band wave functions at Γ; and m_0 is the free electron mass.

The admixture of the p-like wave functions to the conduction band states makes the hybridization of the conduction band states with d orbitals of the magnetic ions possible. Accordingly, the virtual transitions with capture of the electrons from the conduction band by the half-filled d shell (see Fig. 2) become allowed. This means that the mechanism of the kinetic exchange has to be considered also for the conduction band states. In such a case the value of the renormalized parameter of the

exchange interaction for spin components parallel to **k** in Eq. (1) is given by

$$\alpha_{\parallel}(k) = \alpha_{\rm pot}|C_{c,1/2}(k)|^2 + [\beta_{\rm pot} + \gamma(E_e(k))\beta_{\rm kin}] \times [|C_{\nu,0}(k)|^2 - |C_{\nu,1}(k)|^2]. \quad (3)$$

Here $C_{c,1/2}(k)$, $C_{\nu,0}(k)$, and $C_{\nu,1}(k)$ are the coefficients describing the contents of S, Z, and $(X + iY)/\sqrt{2}$ functions in the total Bloch amplitude [in the lowest order of **k** they are given in Eq. (2)]; $\alpha_{\rm pot}$, $\beta_{\rm pot}$, and $\beta_{\rm kin}$ are the potential and the kinetic exchange constants at the conduction band and the valence band edges [i.e., at $k = 0$]. The coefficient $\gamma(E_e)$ describes a possible dependence of the kinetic exchange on the electron kinetic energy E_e.

To calculate the exchange interaction constant for the spin components perpendicular to **k** [i.e., $\alpha_{\perp}(k)$] one can use Eq. (3), with the term $|C_{\nu,1}(k)|^2$ canceled. In (Cd, Mn)Te, where $\Delta < E_g$, the anisotropy of the exchange interaction is very small and will be further neglected.

The dependence $\gamma(E_e)$ is due to the fact that the kinetic exchange is normally calculated in the second order perturbation theory. As a result, $\gamma(E_e)$ depends drastically on the energy difference $E_i - E_n$ between the initial state and a virtual state by which the electron (or the hole) is captured on the d shell of the magnetic ion [15]: $\beta_{\rm kin}(E_i) \propto |V_{pd}|^2 \sum_n (E_i - E_n)^{-1}$. Here V_{pd} is the matrix element of the operator describing the p-d hybridization assumed to be a constant. The virtual states facilitating the kinetic exchange for the conduction electrons are the same as for the valence band holes. Their respective energies are denoted ε^- and ε^+ (see Fig. 2). But the energies of the initial states for the kinetic exchange in the valence and conduction bands differ by E_g. As a result

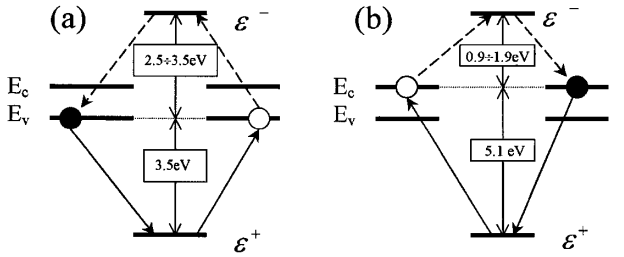

FIG. 2. Scheme of virtual transitions responsible for the kinetic exchange of the carriers in the half-filled d shell of Mn^{2+} ions: (a) for holes in the vicinity of the valence band top E_ν and (b) for electrons in the vicinity of the conduction band edge E_c. ε^+ and ε^- are energy levels for the hole and the electron capture in the d shell, respectively.

$$\gamma(E_e(k)) = \frac{(E_\nu - \varepsilon^+)(\varepsilon^- - E_\nu)}{\{[E_g + E_e(k)] + (E_\nu - \varepsilon^+)\}\{(\varepsilon^- - E_\nu) - [E_g + E_e(k)]\}}. \quad (4)$$

For (Cd, Mn)Te the value of $E_\nu - \varepsilon^+ \approx 3.5$ eV is established fairly accurately from photoemission experiments. For the value of $\varepsilon^- - E_\nu$ no experimental data are available and only estimations in the range from 2.5 to 3.5 eV can be found in literature [16]. Thus, the value of $\varepsilon^- - E_\nu$ is the only parameter of our model that can be adjusted within certain limits.

For small confinement energies, where the linear expansion in terms of E_e is valid we find from Eqs. (2) and (3)

$$\frac{d\alpha(E_e)}{d|E_e|} \approx -\frac{[2(E_g + \Delta)^2 + E_g^2]}{E_g(E_g + \Delta)(3E_g + 2\Delta)} \times \left\{\alpha_{\rm pot} - [\beta_{\rm pot} + \beta_{\rm kin}\gamma(E_e)] \times \left[1 - \frac{4\Delta^2}{3[2(E_g + \Delta)^2 + E_g^2]}\right]\right\}. \quad (5)$$

The dependencies $\alpha(E_e)$ calculated from Eq. (3) for $Cd_{0.98}Mn_{0.02}Te$ for two values of $\varepsilon^- - E_\nu = 2.5$ and 3.5 eV are plotted in Fig. 3. We assume that $\beta_{\rm pot} \ll |\beta_{\rm kin}|$ and $-4\alpha_{\rm pot} \approx (\beta_{\rm pot} + \beta_{\rm kin}) \approx \beta_{\rm kin}$ [10]. Results of the linear approximation by Eq. (5) are shown by dash-dotted lines. Negative values of $E_e(k)$ correspond to states below the band gap, i.e., in the tunneling regime (as appropriate, for example, for the tails of the electron wave functions penetrating into the barriers). One can see that the electron exchange constant decreases with increasing absolute value of $E_e(k)$. For the states with E_e larger than 210 meV and smaller than -260 meV ($\varepsilon^- - E_\nu = 2.5$ eV) the exchange constant α became *negative*.

Using the dependencies of Fig. 3, it is not difficult to calculate an effective modification of the exchange constant in QW well provided that one knows how the carrier wave function is distributed between the QW layer (positive E_e) and the barriers (negative E_e). We performed such calculations to describe experimental results presented in

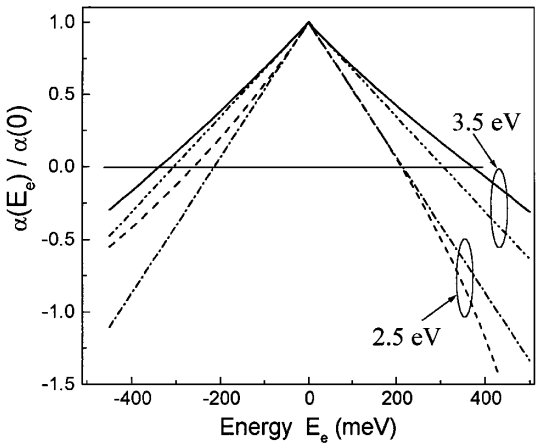

FIG. 3. Dependence of the electron exchange parameter α on the electron kinetic energy in $Cd_{0.98}Mn_{0.02}Te$. Calculations performed according to Eq. (3) and for a linear approximation of Eq. (5) (dash-dotted lines) are shown for two values of $\varepsilon^- - E_\nu$ of 2.5 and 3.5 eV.

Fig. 1. Calculations with $\varepsilon^- - E_\nu = 2.5$ and 3.5 eV are shown by the dashed and solid lines, respectively. Remarkably good quantitative agreement is achieved with our results on SFRS [Fig. 1(a)] with the value of 2.5 eV. The calculated reduction factor of the giant Zeeman splitting $\rho^{\mathrm{QW}} = (\alpha^{\mathrm{QW}} - \beta^{\mathrm{QW}})/(\alpha - \beta)$ is compared with experimental results of Mackh *et al.* in Fig. 1(b). Again $\varepsilon^- - E_\nu = 2.5$ eV corresponds to the best agreement with the experiment. We stress that the variation of the exciton Zeeman splitting is contributed to by both variations of the exchange constants in the conduction and in the valence bands. However, as shown in Ref. [10], only 2% of the effect can be attributed to changes of β^{QW}. Therefore, the dominating contribution to the observed 15% reduction of the Zeeman splitting does come from the decrease of the conduction band exchange constant put forward here.

Note that $\varepsilon^- - E_\nu$ is the only adjustable parameter of our model. The best agreement with experimental data achieved when its value is 2.5 eV makes it possible to estimate the energy ε^- of Mn ion with respect to the valence band edge. To the best of our knowledge this parameter has not been measured experimentally so far.

Let us now turn to zero-dimensional objects, i.e., DMS quantum dots (QDs) embedded in a dielectric matrix. A strong increase of the quantum-confined energy is expected when reducing QD size. Leakage of the carrier wave functions from $Cd_{0.98}Mn_{0.02}Te$ QDs into the dielectric barriers is negligible. The case of a strong carrier quantization, when the confinement energy exceeds the exciton binding energy, allows us to neglect Coulomb corrections to the shape of carrier wave functions in QDs.

The reduction factor for the exciton Zeeman splitting in the QD $\rho^{\mathrm{QD}} = [\alpha^{\mathrm{QD}}(E_e) - \beta^{\mathrm{QD}}]/(\alpha - \beta)$ is plotted in Fig. 4 as a function of the dot radius. For electrons in spherically symmetrical QDs with infinitely high barriers $\alpha^{\mathrm{QD}}(E_e)$ is directly given by Eq. (3) (see also Fig. 3). In the case of (Cd, Mn)Te QDs $\beta^{\mathrm{QD}} \approx 0.8\beta$ [17]. Calculations illustrated in Fig. 4 were performed, again, for two values of the d-level energy, $\varepsilon^- - E_\nu \approx 2.5$ and 3.5 eV. In the first case, the giant Zeeman splitting is much more sensitive to the dot size, which is caused by a relatively small value of the resonant denominator in Eq. (4). It may even approach zero for small size QDs. In this case the value of the effect strongly depends on the broadening of the d level. However, firmly established experimental data for QDs are not available yet.

The calculation of Ref. [10] predicts that the decrease of ρ^{QD} should be noticeable in QDs smaller than 30 Å. In our consideration the remarkable decrease of the Zeeman splitting is predicted already for QDs with radius smaller than 80 Å. In large QDs in external magnetic fields the ground exciton state spin is equal to $+1$ and is optically active (see scheme A in the inset of Fig. 4). In small QDs, with the sign of α^{QD} inverted, the ground exciton state with the spin $+2$ is optically inactive. A strong decrease of the luminescence efficiency and/or remarkable increase of luminescence decay time may be expected to mark a transition to the optically inactive state induced by an external magnetic field.

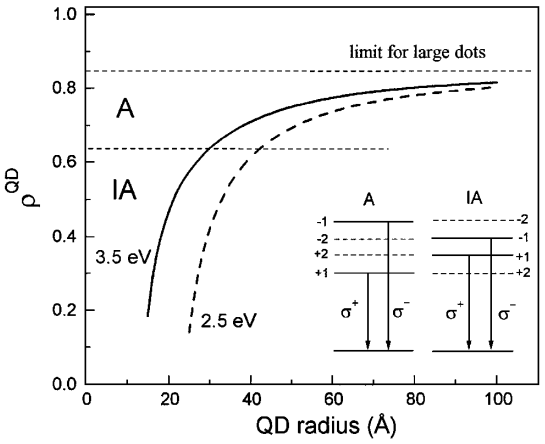

FIG. 4. A giant Zeeman splitting of the exciton state as a function of the radius of a $Cd_{0.98}Mn_{0.02}Te$ quantum dot. Parameters are the same as in Fig. 3. For $\rho^{\mathrm{QD}} < 0.64$, the exchange constant α^{QD} becomes negative leading to an optically inactive exciton ground state in magnetic fields. A scheme for optically active (A) and inactive (IA) exciton ground states is presented in inset ($B \neq 0$).

In conclusion, large modification of the exchange interaction between electrons and magnetic ions has been found experimentally in (Cd, Mn)Te/(Cd, Mn, Mg)Te QWs. The mechanism of a *kinetic exchange* for conduction band electrons, which becomes allowed for the states with finite **k** vector due to admixture of the valence band wave functions to the conduction band ones is suggested.

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