THE FERROMAGNETIC p–d EXCHANGE IN DILUTED MAGNETIC SEMICONDUCTORS*

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The antiferromagnetic type of the interaction between the Γ_8-band electrons and the Mn^{2+} ions in $A^{II}B^{IV}$ diluted magnetic semiconductors has been explained by invoking the p–d hybridization mechanism. In this paper it is shown that for particular electronic configurations of the magnetic ions in diluted magnetic semiconductors the p–d hybridization can lead to a ferromagnetic interaction between the valence-band electrons and the localized spins. This happens when all the one-electron d-orbitals which hybridize with p-band states are empty (e.g., as in Sc^{2+} and Ti^{2+} ions). The appropriate p–d Hamiltonian is derived and the ferromagnetic exchange constants are evaluated.

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The spin-dependent interactions of the band carriers with the localized magnetic moments of transition metal ions in diluted magnetic semiconductors (DMS) result from either the direct Coulomb exchange or from the hybridization mediated kinetic exchange [1]. The hybridization allows for transitions in which the electron hops out of the band into a given ionic d-orbital and vice versa. The resulting states of $N+1$ d-electrons or $N-1$ d-electrons and 2 band electrons differ in energy from the initial states of N d-electrons and 1 electron in the band. Thus, they can serve only as intermediate states for series of consecutive virtual transitions. The kinetic exchange is a second-order process involving two such transitions.

Despite the fact that in each transition the electron spin is conserved the effective scattering of band electrons on magnetic ions can be spin-dependent, due to two reasons. Firstly, by the Pauli principle, the possibility of the virtual transitions depends on the relative alignment of the ionic and band electron spins (if, for example, all d-orbitals are occupied by spin-up electrons only the spin-down band electron can hop onto the ion). Secondly, depending on the spin of the band

electron, the transition can either increase or decrease the total spin of the ion giving (by Hund's rule) different energies of the intermediate states [2].

In zinc-blende-type $A^{II}B^{VI}$ DMS with Mn^{2+} ions both the Coulomb and the kinetic exchange lead to the Kondo-like interaction Hamiltonian but with two different signs of the exchange constant. The Coulomb exchange favoring the parallel, or ferromagnetic, alignment of the interacting spins explains well the spin properties of the Γ_6-conduction band electrons. In contrast, the experimental results for Γ_8 bands can be well accounted for by the antiferromagnetic kinetic exchange mechanism [3–7], the direct exchange being very small for holes localized mostly on anions. Within the mean field approximation, the effective kinetic exchange Hamiltonian has the form [7, 8]:

$$H_{ex} = -(1/3)\beta x N_0 \langle S_z \rangle J_z, \tag{1}$$

where $\langle S_z \rangle$ is the thermodynamical average of the z-component of the total spin of an Mn^{2+} ion and xN_0 is the concentration of these ions. J_z represents the z-component of the fictitious angular momentum (with $j = 3/2$) of the Γ_8 band electron. The negative exchange constant β is given by the formula [6]:

$$\beta = 3(V^2/S) \left[\left(E_5^{5/2} - E_4^{3/2} - \varepsilon_p \right)^{-1} + \left(E_5^{5/2} + \varepsilon_p - E_6^{3/2} \right)^{-1} \right], \tag{2}$$

where E_N^S denotes the unperturbed energy of the d-shell with N electrons and the total spin S. ε_p is the energy of the Γ_8 bands at $k = 0$ and V is the hybridization parameter which can be simply related to Slater–Koster interatomic matrix elements. For all zinc-blende-type $A^{II}B^{VI}$ DMS the experimentally obtained values of $N_0\beta$ are close to -1 eV [8].

In a Mn^{2+} ion all three t_{2g} d-orbitals hybridizing with the Γ_8 valence band states are singly occupied, so that both types of virtual transitions, the annihilation and the creation of an electron in the d-shell are possible and contribute to the exchange constant β giving the two appropriate energy denominators. We note here that the annihilation as well as the creation of an electron in an initially singly occupied orbital leads always to the decrease by one half of the total spin of the d-shell, so that the contribution to the kinetic exchange induced by the Hund's rule is absent in this case.

We have a completely different situation if we consider zinc-blende-type $A^{II}B^{VI}$ DMS doped with Sc^{2+} ($N = 1$) or Ti^{2+} ($N = 2$) ions instead of Mn^{2+}. In the ground orbital states of $N = 1$ and $N = 2$ ions e_g orbitals are occupied whereas all t_{2g} orbitals are empty. Thus, in this case the Pauli principle does not exclude virtual transitions for any direction of the band electron spin. Moreover, the virtual transitions of electrons from these orbitals to the band are non-existent, so that the contribution to the kinetic exchange due to the annihilation of the d-electron has to be absent. On the other hand, the creation of an electron in an empty orbital can produce virtual states with two values of the total spin, $S + 1/2$ and $S - 1/2$, having different energies.

We have examined the spin-dependent part of the p–d interactions in DMS doped with these ions. The obtained effective kinetic exchange Hamiltonian has the form:

$$H_{ex} = -(1/3)\gamma x N_0 \langle S_z \rangle J_z, \tag{3}$$

where the exchange constant is given by

$$\gamma = \frac{6V^2}{2S+1}\left[\left(E_N^S + \varepsilon_p - E_{N+1}^{S-1/2}\right)^{-1} - \left(E_N^S + \varepsilon_p - E_{N+1}^{S+1/2}\right)^{-1}\right]. \qquad (4)$$

According to Hund's rule, for a given number of d-electrons the energy of the state with a higher total spin is lower, thus the exchange constant γ in (4) is positive, if only the state of N d-electrons and one band electron is energetically stable. Consequently, for these materials, in contrast to the situation in DMS doped with Mn^{2+} ions, the effective p–d interaction induced by the kinetic exchange should have a ferromagnetic character.

To estimate the value of the exchange constant γ given by Eq. (4) one has to know the appropriate energy differences between the ionic and band states as well as the hybridization parameter V. The latter should not depend very strongly on the type of the magnetic ion within the $3d$ series, so that we take $V = 1.2$ eV, a value obtained from the exchange constant β of DMS with Mn^{2+} ions. The energy denominators can be estimated by following the chemical trends in $A^{II}B^{VI}$ semiconductors, discussed in a row of papers (e.g. [9]). This gives a similar estimate for the kinetic exchange constant for both Sc^{2+} and Ti^{2+} ions:

$$N_0\gamma = 0.2 \text{ eV} \pm 0.1 \text{ eV},$$

i.e., the value close to that of the direct Coulomb exchange constant for the conduction band electrons in DMS.

In conclusion, in diluted magnetic semiconductors doped with Sc or Ti ions we expect similar ferromagnetic splittings for both conduction and valence bands. We expect therefore, the pattern of exciton magnetooptical transitions to be completely different from that observed in DMS with Mn ions. In Faraday configuration the strong components in σ_+ and σ_- polarization should not depend on magnetic field (so that, the Faraday effect should be small). Still, the magnetic field induced splittings between the weak components in σ_+ and σ_- polarization as well as the splittings for the π polarization (in Voight configuration) should be much larger than in the $A^{II}B^{VI}$ nonmagnetic semiconductors.

Since in Cd-compounds Sc, and perhaps also Ti, donate their d-electrons to the conduction band [10], the materials to observe these effects should be probably the Zn-compounds.

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