On the Kinetic Exchange in $A^{III}B^V$ Diluted Magnetic Semiconductors

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In the case of II–VI diluted magnetic compounds it was shown that the kinetic exchange mechanism depends crucially on the electronic configuration of the magnetic ions and the charge transfer energies for the transitions from the band onto the magnetic ion and vice versa. In the present paper we analyze these effects in the family of III–V diluted magnetic semiconductors, showing that they affect considerably the predictions of the values of the Curie temperature and should be taken into account in the search for room temperature ferromagnetism in diluted magnetic semiconductors.

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The hope for finding diluted magnetic semiconductors (DMS) exhibiting ferromagnetism at room temperatures was awoken when Matsukura et al. [1] reported the Curie temperatures reaching 110 K in GaMnAs alloys. The pursuit for room-temperature ferromagnetism in semiconductors was recently additionally boosted by the theoretical predictions of the Curie temperature for various *p*-type DMS [2]. In [2] Dietl et al. used the Zener model to explain the origin of the ferromagnetism in DMS, as well as to predict the values of the Curie temperatures. These predictions were made under the assumptions that all Mn ions have the same d^5 electronic configuration in all materials considered and that the kinetic exchange constants in $A^{III}B^V$ type DMS with Mn obey the simple scaling rule observed in $A^{II}B^{VI}$ materials. In the mean field Zener model the ordering of spins results from the *p*–*d* kinetic exchange interaction between the magnetic ions and the free, delocalized or weakly localized, holes in the *p*-type crystal. The large kinetic exchange constant, $N_0\beta$, is thus (together with the high concentrations of holes and Mn ions) a crucial condition for high temperature ferromagnetism. For many of the II–VI DMS, which have been extensively studied in the last two

decades, the values of $N_0\beta$ are well known, see, e.g., [3]. In contrast, the available information on this constant in III–V DMS concerns primarily GaAs with Mn^{2+} ions — for this material several values, ranging from -0.9 eV [4] and -1 eV [5] to -4.5 eV [6] have been suggested. At present, the most reliable seems to be the value $N_0\beta = -1.2$ eV inferred from the photoemission data [7]. The latter value, scaled by the inverse volume of the elementary cell, was used in [2] to estimate the p – d exchange constant for other III–V DMS.

The kinetic exchange coupling in DMS results from the hybridization of the d -orbitals of the transition metal ions with the Bloch functions of the p -type valence band. Within the second-order perturbation theory the kinetic exchange can be described in terms of virtual transitions of electrons between the band and the ionic d -shell. For the p -band in the vicinity of the Γ point, the transitions only to/from the ionic t_{2g} orbitals are allowed. In the case of II–VI DMS it was shown in [8] that the kinetic exchange mechanism depends crucially on the electronic configuration of the magnetic ions, i.e., on the occupation of the ionic t_{2g} orbitals. The virtual transitions involving singly occupied orbitals lead to the exchange constant (see [3]):

$$N_0\beta_N = -\frac{V_{pd}^2}{S} \left(\frac{1}{E_{N-1}^{S-1/2} + \epsilon_p - E_N^S} + \frac{1}{E_{N+1}^{S-1/2} - \epsilon_p - E_N^S} \right), \quad (1)$$

whereas the transitions involving only empty t_{2g} orbitals to the constant

$$N_0\gamma_N = \frac{V_{pd}^2}{S + 1/2} \left(\frac{1}{E_{N+1}^{S+1/2} - \epsilon_p - E_N^S} + \frac{1}{E_{N+1}^{S-1/2} - \epsilon_p - E_N^S} \right), \quad (2)$$

where V_{pd} is the hybridization matrix element, E_N^S is the energy of the ion with N d -electrons and the total spin S and ϵ_p is the energy of the electron at the top of the p -band. In [8] it was also shown that for the ions with all t_{2g} orbitals occupied by the same number of electrons, the kinetic exchange leads to the Kondo-like Hamiltonian, with the exchange constant $N_0\beta_N$ for ions with d^5 , d^6 , or d^7 electronic configurations and with $N_0\gamma_N$ for the d^1 and d^2 ions. For other electronic configurations the kinetic exchange Hamiltonian is more complex and depends on the ionic orbital degrees of freedom — still, for the d^3 and d^4 ions the Kondo-like form of the Hamiltonian can be restored by the static Jahn–Teller effect, provided the cubic symmetry is in average conserved.

The values and even the signs of the exchange constants depend on the charge transfer energies in the denominators in Eqs. (1) and (2), which are related to the distances between the donor or acceptor levels and the edge of the valence band [9]. To study the chemical trends of the kinetic exchange in the III–V DMS we determine these distances by exploiting the internal reference rule proposed by Langer and Heinrich [10]. For this purpose we collected in Fig. 1 the literature data concerning valence band offsets and energy gaps for the III–V semiconductors. As a reference for the positions of magnetic impurity levels in these compounds we

have used the distance 0.4 eV from the valence band edge of GaP to the Mn acceptor ground state level, $A(0/-)$, determined in [11]. For this compound also the position of the excited acceptor level, $A^*(0/-)$, for which the ionized acceptor in the final state has lower spin than the initial neutral acceptor, is taken from [11]. The positions of the other transition metal impurity levels in III-V compounds relative to the Mn acceptor were taken after [12]. We note that in the III-V hosts the donor (denoted by $D(0/+)$) and acceptor ($A(0/-)$) ground state levels, correspond to the transformation of the triply ionized magnetic ions M^{3+} into M^{4+} and into M^{2+} ions, respectively. It should be also stressed that the energy distances obtained in this way are approximate and appropriate primarily for low concentrations of magnetic ions.

Fig. 1. Approximate energy level positions of transition metals donor $3+/4+$ (circles) and acceptor $3+/2+$ (squares) states with respect to the valence and conduction band edges of III-V compounds. By open square the excited acceptor $A^*(3+/2+)$ for Mn ion is denoted (after [20, 12, 23–26, 11]).

We start with the Mn based III-V DMS. We recall that the Zener model proposed in [2] requires the free carriers in the valence band and assumes that all magnetic ions are Mn^{2+} with five electrons in the d -shell. Such a situation is realized only when all the Mn^{3+} ions act as acceptors, i.e., when the acceptor $A(0/-)$ level is situated in the valence band, well below the Fermi level. The position of the Mn acceptor level $A(0/-)$ as shown in Fig. 1 suggests that simultaneous existence of the d^5 configuration of manganese ion and the holes in the valence band is possible only for Ga- and In-arsenides and all the antimonides. If one considers the positions inferred from the internal reference rule as reliable, the situation required in the Zener model seems to be obviously realizable only in GaSb and InSb, whereas in GaAs, InAs, and AlSb the acceptor level lies too close to the valence band edge. For the latter compounds, one can imagine that the Fermi level reaches the acceptor level position and remains pinned to it. Thus, only a part of the manganese ions acquires the d^5 configuration and the Mn^{2+} and Mn^{3+} ions coexist in

the crystal. Such mixed valence would open an additional channel of the exchange interaction, namely, the ferromagnetic double exchange, which can be thought in terms of the hopping of the extra electron between the Mn^{2+} and the Mn^{3+} ions via the anion p -orbitals. In Ref. [13] it was shown, however, that the double exchange mechanism is very sensitive to the local potential energy fluctuations in the random system of ionized impurities. Moreover, the good agreement between the predictions of the Zener model and the observed value of the Curie temperature in GaMnAs seems to indicate that in this compound, the dominant part of the Mn ions is in the d^5 configuration. This might be related to the compensation of the manganese acceptors by the arsenic antisites of donor character [14].

One can ask the question whether similar situations can be expected in III–V DMS with other transition metal ions. The positions of the $A(0/-)$ level for the Co and Mn ions as shown in Fig. 1 are almost identical. As the occupations of the t_{2g} orbitals for the d^5 and d^7 electronic configurations are also identical, one can expect similar properties for those Mn- and Co-based III–V DMS, for which the acceptor level lies in the valence band. We note, however, that for a given host material and identical concentrations of holes and magnetic ions the Curie temperature for Co-based material should be lower than for Mn-based one, despite the fact that one expects a bigger value of the p – d exchange constant for DMS with Co ions. First of all, the increase in $N_0\beta$ resulting from the smaller value S of the Co ionic spin in the denominator of Eq. (1) is apparent as it is compensated by the decrease in the magnetization in the same proportion. At the same time, the hybridization matrix element is smaller for Co than for Mn due to the smaller ionic radius of the former [15]. The acceptor level of Fe also enters the valence bands, but only in the GaSb and InSb, which are less promising for high temperature ferromagnetism, because of their relatively large lattice constants and, consequently, weak p – d hybridization.

According to the predictions made within the Zener model [2], the most promising III–V DMS material for the room temperature ferromagnetism is GaMnN. Recently, the first samples of GaMnN are reported in the literature [16–18]. As deduced from Fig. 1, in GaN, as well as in other phosphides and nitrides for which the hybridization is particularly strong, the acceptor levels of all transition metal ions are situated above the valence band and, in consequence, the magnetic ions do not act as acceptors. The gap positions of the acceptor Mn level in GaN and GaP were confirmed by optical measurements [17, 18, 11]. The possibility of obtaining p -type materials by co-doping depends on the position of the donor level relative to the valence band. For Ti and Cr ions, for which these positions are presented in the figure, the p -type samples are not possible at all. The positions of donor levels for the other transition metal ions are not known, but being guided by their positions relative to the acceptor levels in II–VI compounds we expect the Mn, Fe, and Co $D(0/+)$ levels deep in valence band. Thus, in principle, the p -type co-doping of the phosphides and nitrides with these magnetic ions should

be effective. In such *p*-type materials the charge state of Mn, Fe, and Co should remain the same as for the host cations, i.e., these ions should have the electronic configurations d^4 , d^5 , and d^6 , respectively. In [16], the d^5 configuration of Mn in GaN was observed in the EPR measurements, but contrary to what was concluded by the authors the situation in GaMnN is by far not similar to the situation in GaMnAs — the fact that in GaN the Mn acceptor is ionized and has five electrons in the *d*-shell can result solely from the *n*-type character of the studied samples.

The very fact that the Mn acceptor level is situated in the energy gap of GaN, i.e., that in the *p*-type material the Mn should be in the d^4 electron configuration has important consequences for the predictions of the high temperature ferromagnetism in GaMnN. For impurities with d^4 configurations in zinc-blende type structures, e.g. GaP:Mn [11] or different II–VI semiconductors with Cr ions [19], the tetragonal static Jahn–Teller effect was observed. In such case, if the cubic symmetry is in average preserved, the exchange constant in the Kondo Hamiltonian can be written [3] in the form: $N_0(\frac{2}{3}\beta_4 + \frac{1}{3}\gamma_4)$. Since the two constants $N_0\beta_4$ and $N_0\gamma_4$, given by Eq. (1) and Eq. (2), respectively, have opposite signs and comparable absolute values, the resulting *p*–*d* kinetic exchange constant in GaN with Mn^{3+} ions would be strongly reduced. Moreover, the magnetization related to the ions with the total spin $S = 2$ is considerably smaller than that for d^5 ions with $S = 5/2$. One can expect that much more promising should be GaN with iron or cobalt ions, for which the electron configurations are d^5 and d^6 , respectively, and the exchange constants are simply $N_0\beta$.

To calculate the *p*–*d* exchange constant from Eqs. (1) and (2) one has to know the appropriate charge transfer energies and the values of the hybridization matrix elements in the compound. Figure 1 does not provide the exact values of the charge transfer energies and the positions of donor level for Mn, Fe, and Co are not known at all. We choose an arbitrary value 2 eV for the distances of donor levels of all the three ions to the top of the GaN valence band and we take the other charge transfer energies from Fig. 1. Moreover, we use the hybridization matrix element V_{pd} in the form related to the Harrison interatomic matrix elements: $V_{pd} = \frac{4}{3}(V_{pd\sigma} - 2V_{pd\pi}/\sqrt{3})$ [3]. The Harrison parameters $V_{pd\sigma}$ and $V_{pd\pi}$ depend on $1/d^7/2$, where d is the bond length between the anion and the magnetic ion [15]. This bond length is different from the anion–cation distance in the host material — it should be rather close to the anion–cation distance in the transition metal nitrides [21]. Thus, to estimate the hybridization matrix elements for GaN with Mn, Fe, and Co we use the value $d = 2.11$ Å, typical of transition metal nitrides [22]. The obtained values of the kinetic exchange constants for the Mn^{3+} , Fe^{3+} , and Co^{3+} in GaN are –1.5 eV, –2.8 eV, and –3.1 eV, respectively.

In conclusion, we have discussed the dependence of the *p*–*d* kinetic exchange of the III–V DMS on the electronic configuration of magnetic ions and on the position of their charge transfer states relative to the valence band edges. From this analysis it follows that the most promising III–V material for high temperature

ferromagnetism seems to be GaFeN, co-doped for the p -type, despite the larger exchange constant for GaCoN. This is due to the fact that, for a given magnetic ion content, the magnetization in GaCoN is smaller than in GaFeN, as the spin of Co^{3+} is 2 while that of Fe^{3+} is $5/2$. Still, the expected Curie temperature in p -type GaCoN seems to be higher than in the p -type GaMnN, where the spin of Mn^{3+} ions is also equal to 2 but the kinetic exchange constant is reduced, due to the d^4 electronic configuration of the ion.

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