The influence of electrostatic potentials on the apparent $s$-$d$ exchange energy in III-V diluted magnetic semiconductors

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The muffin-tin model of an effective-mass electron interacting with magnetic ions in semiconductors is extended to incorporate electrostatic potentials that are present in the case of Mn-based III-V compounds (Ga$_{1-x}$Mn$_x$N, Ga$_{1-x}$Mn$_x$As). Since the conduction band electron is repelled from negatively charged magnetic ions and attracted by compensating donors, the apparent value of the $s$-$d$ exchange coupling $N_0\alpha$ is reduced. It is shown that the magnitude of this effect increases when $x$ diminishes. Our model may explain an unusual behavior of electron spin splitting observed recently in those two materials in the Mn concentration range $x \leq 0.2\%$.

Owing to the possibility of a gradual incorporation of magnetism to the well-known semiconductor matrices, diluted magnetic semiconductors (DMS) offer unprecedented opportunity for examining energies characterizing spin dependent couplings between the band carriers and electrons localized in the open magnetic shells. Surprisingly, however, a series of recent experiments on (III,Mn)V DMS points to our limited understanding of the $s$-$d$ exchange interaction in this important material family. The determined $s$-$d$ exchange integral appears to have much smaller magnitude and even opposite sign to that expected according to the present knowledge on the origin of the $s$-$d$ coupling in tetrahedrally coordinated DMS.

In this paper, we list first a number of obstacles making a quantitative determination of the exchange integrals in III-V DMS difficult. We then analyze an additional ingredient of these systems, namely the presence of Coulomb potentials centered on the magnetic ions as well as on compensating donors. We evaluate electron wave function in the field of negatively charge magnetic impurities and show that the Coulomb repulsion reduces the apparent magnitude of the $s$-$d$ exchange integral. Importantly, the effect increases with lowering magnetic ion concentration $x$, and becomes particularly significant in the experimentally relevant range, $x \leq 0.2\%$.

In the case of archetypical II-VI DMS such as (Cd,Mn)Te, the ferromagnetic exchange interaction between the conduction band electrons and Mn spins is described by $N_0\alpha$ ≈ 0.2 eV, where $N_0$ is the cation concentration and $\alpha$ is the $s$-$d$ exchange integral. This value of $N_0\alpha$ is about two times smaller than that describing the ferromagnetic exchange interaction between the $4s$ and $3d$ electrons in the free Mn$^{+1}$ ion. This reduction is caused by matrix polarizability and the fact that not only cation but also anion $s$-type wave functions contribute to the Bloch amplitude of the conduction band electrons. In the case of the valence band holes, the exchange energy results from the symmetry-allowed $p$-$d$ hybridization, the typical value of the exchange energy being $|N_0\beta| \approx 1$ eV. Within the molecular-field (MFA) and virtual crystal approximations (VCA), the exchange spin-splitting of the two-fold degenerate conduction and four-fold degenerate valence band is then, $s_\alpha M/g_{\mu B}$ and $j_z\beta M/g_{\mu B}$, where $s_\alpha = \pm 1/2$ and $j_z = \pm 1/2; \pm 3/2$, respectively, $M = M(T,H)$ is spin magnetization of the substitutional magnetic ions characterized by the Landé factor $g$.

The proportionality between exchange splittings and independently measured magnetization has been demonstrated by a variety of magneto-optical and magnetotransport experiments, and has made it possible to determine accurately the values of $N_0\alpha$ and $N_0\beta$ for a number of systems.

However, the above simple scenario has been called into question in several important cases. First, the orbital and carrier contribution to the measured $M$ has to be taken into account. Second, when the exchange energy $|N_0\beta|$ becomes comparable to the valence band width, the MFA and VCA break down, particularly in the range of small magnetic ion concentrations. Third, the magnitude and sign of $\beta$ depend on the relative position of the $p$ and $d$ states. If, therefore, the charge state and thus the energy of the relevant $d$ levels can be altered by the position of the Fermi energy, the character of $p$-$d$ exchange will cease to be universal in a given material but instead will depend on the doping type and magnitude. Fourth, the intensity, and even the sign of the magnetic circular dichroism is strongly affected by the Moss-Burstein effect. Accordingly, a simple relation between positions of the absorption edge for two circular light polarizations and the splitting of the bands breaks down in the presence of the delocalized or weakly localized carrier liquid. This may account for the sign reversal of the apparent $\beta$ on going from $n$-type to $p$-type (Ga,Mn)As. Finally, spin-orbit interactions and $k$-$p$ mixing between bands make spin-splitting away from band extrema to be a complex non-linear function of $\alpha M$ and $\beta M$ as well as of relevant $k$-$p$ parameters. This, in

\[\alpha M \approx \beta M \approx 1 \text{eV} \text{.} \]
particular, has precluded a conclusive determination of the values of the sp-d exchange integrals for narrow-gap DMS of mercury and lead chalcogenides. Such multi-band effects are especially important in quantum structures, where dimensional quantization enhances the kinetic energy of the carriers and, thus, the effects of the k · p coupling. Indeed, an anomalous behavior of electron spin-splitting in quantum wells of (Cd,Mn)Te and (Ga,Mn)As has been assigned to the k · p admixture of the valence band states to the electron wave function.

Despite the difficulties in the precise determination of the exchange integrals, particularly in quantum structures and systems containing carriers, a series of recent experiments suggesting anomalous magnitude and sign of α in (III,Mn)V DMS call for a detail consideration. In particular, Heinbrodt et al. detected spin-flip Raman scattering of conduction band electrons in Ga1−xMnxAs, and evaluated N0α = 23 meV for x = 0.1%. Even a lower value |N0α = 14 ± 4| meV was found by Wołos et al., who analyzed the broadening by the electrons of the Mn spin resonance line in n-Ga1−xMnxN with 0.01% ≤ x ≤ 0.2%. More recently, Myers et al. examined spin precession of the electrons in Ga1−xMnxAs quantum wells of the thickness between 3 and 10 nm, and Mn content x up to 0.03%. As a result of aforementioned admixture of the valence band states, the observed sign of the exchange splitting is negative. The value N0α = −90 ± 30 meV was determined under a simplified assumption that the spin-splitting is proportional to magnetization, and by extrapolating the resulting apparent exchange energy N0α to the infinite quantum well width. In contrast to the striking finding listed above, a large positive value N0α ≈ 0.5 eV is consistent with intraband magnetoabsorption in n-In1−xMnxAs with a relatively high Mn content, x ≥ 2.5%.

We point here to an additional mechanism that may contribute to the anomalous behavior of electron-spin splitting in III-V DMS. We note that the electric charge of the Mn2+ ion replacing e.g. a Ga3+ ion in the lattice of a III-V compound (like GaN and GaAs) is a source of a repulsive electrostatic potential. Furthermore, the studied samples are either n-type or at least highly compensated, as evidenced by the presence of electron spin-flip Raman scattering and donor-related luminescence. This indicates the existence of attractive potentials associated with ionized non-magnetic donors. Thus, the probability of finding a conduction band electron at the core of the magnetic ion is reduced, and hence the apparent value of the exchange energy (the observed spin splitting) is diminished. It worth noting that a possibility that the Coulomb potentials could affect the apparent value of the exchange integrals has already been mentioned in the context of divalent Mn in GaN and trivalent Fe in HgSe.

To evaluate a lower limit of the effect we neglect the presence of compensating donors and calculate the apparent sp-d exchange integral αsp for an electron subject to the repulsive potential generated by the Mn acceptors.

We follow a Wigner-Seitz-type approach put forward by one of us and co-workers to describe the interaction of the carrier spin with the Mn ions in the case of the strong coupling limit, that is when the depth of the local Mn potential is comparable to the carrier band width. It has been found in the subsequent works that the corrections to the Wigner-Seitz approach caused by a random distribution of Mn ions are quantitatively unimportant.

We consider a Mn ion with the 5/2 spin $\vec{S}_i$ located at $\vec{R}_i$, which interacts with the carrier via the Heisenberg term $I(\vec{r} - \vec{R}_i)\vec{s} \cdot \vec{S}_i$. The form of the function $I(\vec{r} - \vec{R}_i)$ makes the interaction local: it vanishes outside the core of the Mn ion. For simplicity, $I(\vec{r} - \vec{R}_i) = a \theta (|\vec{r} - \vec{R}_i| - b^3)$. The exchange energy is then $\alpha = \int d^3r I(\vec{r}) = a \cdot \frac{4}{3} \pi b^3$. Moreover, in case of III-V compounds considered here, the impurity generates an electrostatic potential. If screening by the electrons is present, as in case of n-Ga1−xMnxN, this po-
tential is $e^2 \exp(-\lambda r)/(4\pi \varepsilon_0 \varepsilon r)$, where $\varepsilon$ is the static dielectric constant, and the screening parameter $\lambda$ is given by $\lambda^2 = e^2 \mathcal{N}(\varepsilon_F)/(\varepsilon_0 \varepsilon)$, where $\mathcal{N}(\varepsilon_F) = \frac{3}{2} n/kT_F$.\[^{[17]}\]

For the Ga$_{1-x}$Mn$_x$N samples, $n \approx 10^{19}$ cm$^{-3}$ corresponds to $T_F \approx 890$ K ($\varepsilon_F \approx 0.12$ eV), and therefore $1/\lambda \approx 1.6$ nm.

In the spirit of the Wigner-Seitz approach we assume that the carrier energy $E$ and the envelope function $\psi(r)$ are given by the ground state solution of the one-band effective mass equation which contains the potential $U(r)$ created by the magnetic ion located at $r = 0$. The standard one-impurity boundary condition $\psi(r) \to 0$ for $r \to \infty$ is replaced by the matching condition $\psi(r) = 0$ at $r = R$ to take into account the presence of other magnetic ions. The value $R$ is determined by the concentration of the magnetic ions $x$ according to the equation $(4\pi R^3/3)^{-1} = N_0 x$. The exchange interaction is modelled by a square well potential $U(b - r)$ superimposed on the electrostatic potential of an elementary charge located at $r = 0$. The potential $U = \pm \frac{\tilde{a}}{r}$ is, of course, different for spin-down and spin-up carriers.

We first ignore free carrier screening, $\lambda \to 0$. The solution of the time-independent Schrödinger equation for the conduction band electron is then

$$\psi(r) = c_0 \exp(-\beta r) \Phi(1 + \frac{A}{\beta r}; 2; 2\beta r) \equiv c_0 f$$  \hspace{1cm} (1)

for $0 < r < b$, and the following linear combination for $b < r < R$

$$\psi(r) = c_1 \exp(-\beta' r) \Phi(1 + \frac{A}{\beta' r}; 2; 2\beta' r) +$$

$$+ c_2 \exp(\beta' r) \Phi(1 - \frac{A}{\beta' r}; 2; -2\beta' r)$$

$$\equiv c_1 g + c_2 h,$$  \hspace{1cm} (2)

where $A = e^2 m^*/(4\pi \varepsilon_0 \varepsilon_0 \hbar^2)$, $\beta = [2m^*(U - E)]^{1/2}/\hbar$, $\beta' = [2m^*(-E)]^{1/2}/\hbar$ (notice that changing the sign of $\beta$ leaves $\psi$ invariant, while changing the sign of $\beta'$ interchanges $c_1$ with $c_2$; also, $\Phi$ and $\Psi$ are not in general linearly independent). We used the symbols $\Phi$, $\Psi$ for the confluent hypergeometric functions $F_1(a; b; z)$, $U(a; b; z)$\[^{[22]}\].

The constants $c_0$, $c_1$, $c_2$ are determined by the continuity conditions $\psi(-b) = \psi^*(b)$, $\psi'(-b) = \psi'(b^+)$. Solving those two equations we obtain an equation for $E$,

$$\frac{w_{f,g}(b)g'(R) - w_{f,g}(b)h'(R)}{w_{g,h}(b)} = 0,$$  \hspace{1cm} (3)

where by $w_{f,g}$ we denoted the Wronskian $fg' - f'g$. In the following, $\psi(r)$ is normalized as $\psi(0) = c_0 = 1$.

We assume the following parameters for Ga$_{1-x}$Mn$_x$N: $m^* = 0.22 m_e$, $N_0 = 4.38 \cdot 10^{22}$ cm$^{-3}$ = 0.006495 a.u., $\varepsilon = 8.9$; and the following for Ga$_{1-x}$Mn$_x$As: $m^* = 0.067 m_e$, $N_0 = 2.21 \cdot 10^{22}$ cm$^{-3}$ = 0.003281 a.u., $\varepsilon = 12.9$. In the experiments, samples were used with $0.01 \% \leq x < 0.2 \%$ of Mn in GaN\[^{[22]}\] and with $0.0006 \% \leq x \leq 0.03 \%$ of Mn in GaAs\[^{[22]}\]. Those concentrations correspond to $R$ up to about 75 a.u. for GaN and up to about 250 a.u. for GaAs.

To visualize the effect of the Coulomb term in the Mn potential, we have calculated the energies and wave functions including and disregarding the additional Coulomb term for both GaN ($b = 2$ a.u. $\approx 0.1$ nm, $a = 0.0371$ a.u. = 1.0 eV) and GaAs ($b = 2$ a.u. $\approx 0.1$ nm, $a = 0.0735$ a.u. = 2.0 eV). These parameters correspond to $N_0 \alpha = 0.22$ eV, a value for CdS\[^{[22]}\]. We have found that when calculating $\alpha_{sp}/\alpha$, the details of the exchange potential (like the values of $b$ and $\alpha$ within the expected range) are not quantitatively important.

In order to take into account the fact that the core and lattice polarizability decrease at small distances, $\varepsilon \to 1$ for $r \to 0$, we interpolate $\varepsilon(r)$ between $\varepsilon(0) = 1$ and the macroscopic value attained at a distance of the bond length. The assumed dependence, presented in Fig. 3, is given by $\varepsilon(r)$, and for Ga$_{1-x}$Mn$_x$N and various models of screening.
valid for the Coulomb potential. Then, the spin splitting for a given value of \( x \) (or for the corresponding \( R \)) is evaluated as the difference of the energy \( E \) calculated for the spin-up and spin-down carriers from the equation \( \psi'(R) = 0 \). Here, \( \psi(r) \) is the numerical solution of the Schrödinger equation with the potential that is different for spin-up and spin-down carriers.

The results of our calculations of \( \alpha_{ap}/\alpha \) as a function of the Mn ion concentration \( x \) are presented in Fig. 5 for Ga\(_{1-x}\)Mn\(_x\)As. Independently of assumptions concerning screening, in both materials \( \alpha_{ap}/\alpha \) diminishes significantly when \( x \) decreases, up to factor of three in the experimentally relevant range of \( x \). However, this reduction of \( \alpha_{ap}/\alpha \) is still smaller than that seen experimentally, presumably because of an additional effect coming from the presence of attractive potentials brought about by compensating non-magnetic donors.

In summary, we have enlisted a number of effects that renders an accurate experimental determination of the \( sp-d \) exchange integrals difficult, particularly in cases when both \( p \)-like and \( s \)-like states contribute to the carrier wave function. The interaction of conduction band electrons with the magnetic ions in (Ga\(_{1-x}\)Mn\(_x\)N, Ga\(_{1-x}\)Mn\(_x\)As) has been considered quantitatively taking into account the electrostatic potential created by the magnetic ion. A substantial reduction in the magnitude of the apparent exchange energy has been found at low Mn concentrations, and interpreted as coming from the decrease of the carrier probability density at the core of the magnetic ion caused by the electrostatic repulsion. It has been suggested that this effect, enhanced by an attractive potential of compensating donors, accounts for abnormally small values of the exchange spin splitting observed experimentally in III-V DMS containing a minute amount of Mn\(_{0.05}\). In view of our findings, the presence of electrostatic potentials associated with magnetic ions makes that the apparent exchange energies should not be viewed as universal but rather dependent on the content of the magnetic constituent and compensating donors.

FIG. 5: The dependence of the ratio of the apparent and bare exchange energies \( \alpha \) on \( x \) for Ga\(_{1-x}\)Mn\(_x\)As.

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1 J.K. Furdyna and J. Kossut, eds. Diluted Magnetic Semiconductors, in Semiconductors and Semimetals vol. 25, edited by R. K. Willardson and A. C. Beer (Academic Press, New York, 1988).
2 T. Dietl, in: Handbook on Semiconductors, vol. 3B edited by T.S. Moss (Elsevier, Amsterdam, 1994) p. 1251.
3 F. Matsukura, H. Ohno, T. Dietl, III-V Ferromagnetic Semiconductors, in: Handbook of Magnetic Materials, vol.14, edited by K.H.J. Buschow (Elsevier, Amsterdam, 2002) p. 1.
4 W. Heimbrodt, Th. Hartmann, P. J. Klar, M. Lampalzer, W. Stolz, K. Volz, A. Schaper, W. Treutmann, H.-A. Krug von Nidda, A. Loidl, T. Ruf, and V.F. Sapega, Physica E 10, 175 (2001).
5 A. Wołoś, M. Palczewska, Z. Wilamowski, M. Kamińska, A. Twardowski, M. Bockowski, I. Grzegory, and S. Porowski, Appl. Phys. Lett. 83, 5428 (2003).
6 R. C. Myers, M. Poggio, N. P. Stern, A. C. Gossard, and D. D. Awschalom, preprint arXiv:cond-mat/0502115.
7 T. Dietl, C. Śliwa, G. Bauer, and H. Pascher, Phys. Rev. B 49, 2230 (1994).
8 See, e. g., P. Kacman, Semicond. Sci. Technol. 16, R25 (2001).
9 T. Dietl, H. Ohno, and F. Matsukura, Phys. Rev. B 63, 195205 (2001).
10 C. Benoit à la Guillaume, D. Scalbert, and T. Dietl, Phys. Rev. B 46, 9853 (1992).
11 J. Tworzydło, Phys. Rev. B 50, 14591 (1994); Solid State Commun. 94, 821 (1995).
12 Th. Hartmann, S. Ye, P. J. Klar, W. Heimbrodt, M. Lampalzer, W. Stolz, T. Kurz, A. Loidl, H.-A. Krug von Nidda, D. Woverson, J. J. Davies, and H. Overhof, Phys. Rev. B 70, 233201 (2004).
13 J. Szczytko, W. Mac, A. Twardowski, F. Matsukura, and H. Ohno, Phys. Rev. B 59, 12935 (1999).
14 I. A. Merkulov, D. R. Yakovlev, A. Keller, W. Ossau, J. Heurts, A. Waag, G. Landwehr, G. Karczewski, T. Wojtowicz, and J. Kossut, Phys. Rev. B 83, 1431 (1999).
15 M. A. Zudov, J. Kono, Y. H. Matsuda, T. Ikaida, N. Miura, H. Munekata, G. D. Sanders, Y. Sun, and C. J. Stanton, Phys. Rev. B 66, 161307(R) (2002).
16 Z. Wilamowski, A. Mycielski, W. Jantsch, and G. Hendzior, Phys. Rev. B 38, 3621 (1988).
17 See, J. M. Ziman, Principles of the theory of solids, (Cambridge University Press, London, 1972), §5.2.
18 L. J. Slater, Confluent hypergeometric functions (Cambridge University Press, Cambridge, 1960).
19 R. Resta, Phys. Rev. B 16, 2717 (1977).