# Free carrier-induced ferromagnetism in structures of diluted magnetic semiconductors

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Ruderman-Kittel-Kasuya-Yosida interaction between localized spins is considered for various dimensionality structures of doped diluted magnetic semiconductors. The influence of this interaction on the temperature and magnetic-field dependencies of magnetization and spin splitting of the bands are evaluated in the mean-field approximation. The results show that the hole densities that can presently be achieved are sufficiently high to drive a paramagnetic-ferromagnetic phase transition in bulk and modulation-doped structures of II-VI diluted magnetic semiconductors. [S0163-1829(97)51106-4]

It has been known for a long time that the compensation of antiferromagnetic interactions between the localized spins by a ferromagnetic coupling would result in a dramatic enhancement of the sensitivity of diluted magnetic semiconductors (DMS)[1] to the temperature and the magnetic field. Three different approaches have been considered to achieve this goal.

One is to choose a material, in which deviations from stoichiometry would result in the carrier density sufficiently high to produce strong ferromagnetic interactions between the localized spins. This method has successfully been employed by Story *et al.*,[2] who showed that in $Pb_{1-x-y}Sn_yMn_xTe$ with $y \gtrsim 0.6$ the holes concentration is not only very large but can be varied in the range $10^{20}-10^{21}$ cm$^{-3}$ by isothermal annealing. It has been demonstrated that the ferromagnetic phase is observed once the holes start to occupy side bands with a large effective mass.[3]

The second approach, initiated by Munekata *et al.*,[4] is to use III-V matrices, in which divalent magnetic ions act themselves as acceptors, so that a ferromagnetic coupling mediated by the holes may dominate. In order to surpass low solubility of transition metals in III-V compounds, growth by molecular beam epitaxy (MBE) has been employed. Transitions to a ferromagnetic phase at temperatures as high as $\sim$35 K in a heterostructure $In_{1-x}Mn_xAs/(Al,Ga)Sb$ with $x \sim 0.07-0.18$ and $\sim$60 K in an epilayer of $Ga_{1-x}Mn_xAs$, $x \sim 0.035$, have recently been observed.[5,6]

Another method to obtain ferromagnetic compounds is to choose such magnetic ions, for which the net superexchange coupling is ferromagnetic. Indeed, a tight binding model of Blinowski, Kacman, and Majewski[7] suggests that this might be the case of Cr in II-VI semiconductors. Accordingly, an attempt has been undertaken[8] to overcome the well-known small solubility of Cr in II-VI compounds by means of MBE growth of $Cd_{1-x}Cr_xTe$.

Recent years have witnessed a rapid progress in doping of II-VI wide gap semiconductors by *substitutional* impurities. For instance, electron and hole concentrations in the excess of $10^{19}$ cm$^{-3}$ have been reported for ZnSe:I and ZnTe:N,[9,10] respectively. At the same time, modulation doping of II-VI quantum wells by either electrons[11] or holes[12] as well as patterning of conducting quantum wires[13] have successfully been performed. In view of this progress it becomes interesting to analyze the nature and strength of the carrier-mediated spin-spin interactions in bulk, layered, and nanostructured II-VI compounds. Results of this paper suggest that even for the highest available *electron* density no transition to the ferromagnetic phase is expected above 1 K. By contrast, such a transition is predicted for *p*-type materials, either in the bulk or modulation-doped form. Our evaluations indicate, therefore, that the *p*-type doping may constitute an efficient tool to enlarge the magnetic effects in wide gap II-VI DMS. We also point out peculiar features of the carrier-mediated exchange interaction in one-dimensional (1D) systems.

Throughout this paper we consider the influence of delocalized or weakly localized carriers on the interaction between magnetic ions. The dimensionality $d$ of the subsystem of the carriers is determined by the shape of the potential $V(\zeta)$ that leads to their confinement. Accordingly, the case $d=2$ or $d=3$ corresponds to a one- or two-dimensional potential well, respectively. Because of a short magnetic correlation length,[14] the localized magnetic moments $g\mu_B\mathbf{S}_i$ are assumed, to form a macroscopic 3D system. Thus, according to experimental studies,[1,15] their magnetization in the absence of the carriers can be described by a modified Brillouin function, $M(T,H)=g\mu_B\tilde{x}N_oSB_S(T+T_o,H)$, where effective spin concentration $\tilde{x}N_o<xN_o$ and temperature $T+T_o>T$ account for the influence of antiferromagnetic superexchange interactions.[1,7,15]

We begin by considering the Ruderman-Kittel-Kasuya-Yosida (RKKY) model, which provides the energy $J_{ij}$ of the exchange coupling, $H_{ij}=-J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$, between two spins located at $\mathbf{R}_i$ and $\mathbf{R}_j$ as a function of the density of states of the carriers at the Fermi level, $\rho_d(\varepsilon_F)=\pi^{1-d}(2/\pi)^{(d-2)(d-3)/2}m^*k_F^{d-2}/\hbar^2$, and the exchange inte-

 

gral $I$ of their interaction with the spins, $H_i = -I\mathbf{s}\cdot\mathbf{S}_i\delta(\mathbf{R}-\mathbf{R}_i)$. Following the well-known procedure[16] and adopting the one-band effective-mass approximation we obtain to the second order in $I$

$$J_{ij} = \frac{\rho_d(\varepsilon_F)k_F^d I^2}{2\pi}\,\mathcal{F}_d(2k_F|\mathbf{r}_i-\mathbf{r}_j|)|\varphi_o(\boldsymbol{\zeta}_i)|^2|\varphi_o(\boldsymbol{\zeta}_j)|^2. \quad (1)$$

Here $\mathbf{r}$ is the vector in the $d$ dimensional space, $\varphi_o(\boldsymbol{\zeta})$ is the ground-state envelope function of the carriers in the confining potential $V(\boldsymbol{\zeta})$, and

$$\mathcal{F}_1(y) = -\pi\,\mathrm{si}(y)/2, \quad (2a)$$

$$\mathcal{F}_2(y) = \int_1^\infty dt\,\frac{\mathcal{J}_1(yt)}{yt(t^2-1)^{1/2}}, \quad (2b)$$

$$\mathcal{F}_3(y) = [\sin(y) - y\cos(y)]/y^4, \quad (2c)$$

where $\mathrm{si}(y)$ is the sine-integral and $\mathcal{J}_n(y)$ is the Bessel function. The asymptotic behavior of $\mathcal{F}_d(y)$ for large $y$ is $\pi\cos(y)/2y$, $\sin(y)/y^2$, and $-\cos(y)/y^3$, while for $y\to 0$, $\mathcal{F}_d$ tends to $\pi/4$, $[1/2-\gamma+\ln(4/y)]/2$, and $3/y$ for $d=1$, 2, and 3, respectively, where $\gamma = 0.57721\ldots$ is the Euler constant. The formula for $d=3$ reproduces the result first obtained by Ruderman and Kittel,[17] and for $d=1$ that of Yafet,[18] whereas in the case of $d=2$ only the asymptotic form for $y\to\infty$ has so far been considered in the literature.[16]

Knowing the dependence $J_{ij}$ on the distance between the spins $r$ we can calculate the mean-field value of the Curie-Weiss temperature of spins located at $\boldsymbol{\zeta}_i$, $\Theta(\boldsymbol{\zeta}_i) = S(S+1)\Sigma_j J_{ij}/3k_B$. Since in semiconductors, in contrast to metals, the value of $y$ that corresponds to the distance $r$ between the nearest-neighbor spins is much smaller than the period of the oscillatory functions in Eq. (2), $y_{nn} = 2k_F r_{nn} \ll 1$, we replace the summation over the ion positions by an integration extending from $y=0$ to $\infty$. Under the assumption that the distribution of the magnetic ions is random but their effective concentration $\tilde{x}N_o$ is macroscopically uniform over the volume in which the carriers reside, we obtain $\Theta$ in the form,

$$\Theta(\boldsymbol{\zeta}) = S(S+1)\tilde{x}N_o\rho_d(\varepsilon_F)|\varphi_o(\boldsymbol{\zeta})|^2 I^2/12k_B, \quad (3)$$

which shows that the net RKKY interaction is ferromagnetic, $\Theta > 0$. Since $\Theta$ is proportional to the effective mass, to the degree of confinement as well as to the square of the exchange integral $I$ we expect much greater magnitudes of $\Theta$ in the presence of the holes than for the electrons in II-VI DMS.

The above approach neglects intervalley or intersubband virtual transitions. Since those terms in $J_{ij}$, which result from such transitions, contain products of orthogonal envelope functions, $\varphi_\nu^*(\boldsymbol{\zeta}_j)\varphi_{\nu'}(\boldsymbol{\zeta}_j)$, their contribution to $\Theta$ vanishes, provided that the concentration of magnetic ions is uniform. Moreover, in such a case each of the occupied valleys or subbands gives an independent contribution to $\Theta$, described by the relevant $\varphi_\nu(\boldsymbol{\zeta})$ and $k_F^{(\nu)}$

So far we have disregarded the influence of the potential scattering and the Coulomb interactions among the carriers upon the magnitude of $\Theta$. The former is known[20] to introduce a random-phase shift in the oscillatory functions of Eq. (1), which after averaging over the disorder, leads to the dumping $\exp(-r/\ell)$ of the first moment in the distribution of $J_{ij}$,[20,21] where $\ell$ is the mean free path for elastic collisions. The corresponding reduction factor of $\Theta$ to the lowest order in $1/k_F\ell$ is given by $1-1/12(k_F\ell)^2$, $1-\pi/8k_F\ell$, and $1-\pi/4k_F\ell$ for $d=1$, 2, and 3, respectively. Hence the effect of disorder becomes important on approaching the strongly localized regime, $k_F\ell\to 1$. In this range, however, the magnetic susceptibility of the carriers becomes substantially enlarged by the disorder-modified electron-electron interactions.[19] The resulting enhancement factor of $\Theta$ reads[22] $1+FL_s/\ell$, $1+2F\ln(L_s/\ell)/\pi k_F\ell$, and $1+3F(1-\ell/L_s)/(2k_F\ell)^2$, respectively. Here $F$ is the effective Coulomb amplitude, which becomes greater than 1 for $k_F\ell\to 1$; $L_s = \sqrt{(Dt_s)} \gg \ell$ is the spin-diffusion length, where $D = k_F\ell/dm^*$ and $t_s$ is the spin-disorder scattering time,[14,19] considerably shortened at the ferromagnetic transition. We conclude that the disorder enhances the ferromagnetic interaction in low-dimensional semiconductor structures. This enhancement may also be important in pure 1D systems, where the interaction-driven separation of the charge and spin degrees of freedom modifies $J(r)$.[23] In the zero-dimensional case, such as quantum dots, both correlation effects and the fluctuations of magnetization associated with the finite volume visited by the carriers are of paramount importance. A variant of the theory developed for bound magnetic polarons[24] should be applied for those systems.

In addition to $\Theta$, it is interesting to determine the temperature and magnetic-field dependencies of the magnetization of the localized spins, $M(T,H)$ and the spin splitting of the relevant band, $\Delta(T,H) = IM(T,H)/g\mu_B + g^*\mu_B H$, where $g$ and $g^*$ are the Landé factors of the localized spins and the carrier spins, respectively. In the mean-field approximation[25] $M$ is induced by the external field $H$ and the molecular field produced by the carriers, $H^*$ so that $M(T,H) = g\mu_B\tilde{x}N_o S B_S(T+T_o, H+H^*)$, where $H^* = I(n_\downarrow - n_\uparrow)/2g\mu_B$. Here $n_{\downarrow,\uparrow}$ is the density of spin-down and spin-up carriers, respectively, which, at $\varepsilon_F \gg k_B T$, is given by $n_{\uparrow,\downarrow} = \frac{1}{2}|\varphi_o(\boldsymbol{\zeta})|^2\int_{\pm\Delta/2}^{\varepsilon_F} d\varepsilon\,\rho_d(\varepsilon)$, where the dependence of $\varepsilon_F$ on $\Delta$ is to be determined from the condition $n_\uparrow + n_\downarrow = n$, with $n$ being the total carrier density. The effects of disorder and electron-electron interactions can also be incorporated into this formalism by taking into account collision broadening of the density of states as well as by determining $H^*$ from $g\mu_B H^* = I\partial\Omega/\partial\Delta$ with the Gibbs free energy of the carriers, $\Omega$ containing effects of the disorder-modified electron-electron interactions.[19]

The above set of coupled equations makes it possible to determine in a self-consistent way the mean-field values of $M$ and $\Delta$ as functions of temperature and magnetic field. In particular, the total low-field magnetic susceptibility of the coupled system of the carriers and the localized spins assumes the form

$$\chi_{\mathrm{tot}}(T) = \chi_o(T)\,\frac{(1+g^*I\rho_F/4g)^2}{1-\chi_o(T)I^2\rho_F/4g\mu_B} + \frac{1}{4}\,g^{*2}\mu_B^2\rho_F, \quad (4)$$

where $\chi_o = S(S+1)g^2\mu_B^2\tilde{x}N_o/3k_B(T+T_o)$ and $\rho_F = \rho_d(\varepsilon_F)|\varphi(\boldsymbol{\zeta})|^2$.

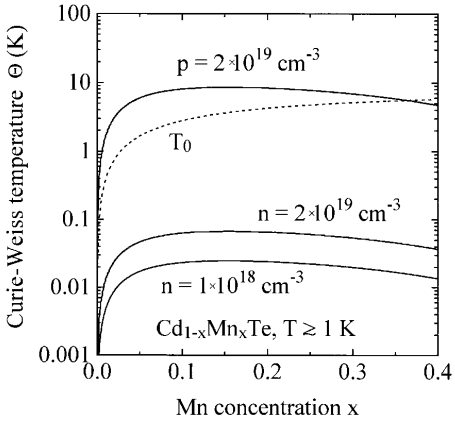


FIG. 1. Mean-field value of the Curie-Weiss temperature $\Theta$ of Eq. (3) for $p$- and $n$-type $Cd_{1-x}Mn_xTe$, compared to antiferromagnetic temperature $T_o(x)$. Ferromagnetic phase transition may occur at $T=\Theta-T_o$. Material parameters as determined at 1.7 K were adopted for the calculation.

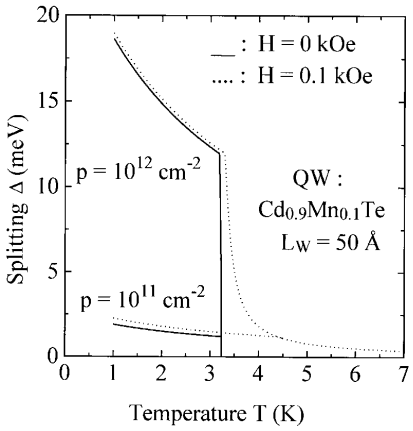


FIG. 2. Temperature dependence of the heavy-hole spin splitting in the 50 Å quantum well of $Cd_{0.9}Mn_{0.1}Te$ for two values of the hole areal densities $p$ and the magnetic fields $H$. Provided that the holes are delocalized, the mean-field value of ferromagnetic critical temperature $T_c\approx 3$ K does not depend on $p$. By contrast, the saturation value of the spin splitting is seen to increase with $p$.

We see that $\chi_{\rm tot}$ diverges at $T=\Theta-T_o$, where $\Theta$ coincides with the Curie-Weiss temperature determined by the RKKY interactions, displayed in Eq. (3). This quantitative agreement between the two approaches in question constitutes the interesting result. It shows, in particular, that for a random distribution of the magnetic ions the effect of the Friedel oscillations upon $\Theta$ averages to zero. However, the spin-glass phase observed in metals points to the importance of the fluctuations in the sign of $J_{ij}$, which are disregarded in our models. These fluctuations, described by higher moments in the distribution of $J_{ij}$,[21] begin to be significant when the concentration of the carriers becomes greater than that of the magnetic ions. In semiconductors, however, where the mean distance between magnetic ions is much smaller than the electron wavelength, $(4\pi\tilde{x}N_o/3)^{-1/3}\ll 2\pi/k_F$, the spin-spin interaction mediated by the carriers is merely ferromagnetic, so that the models discussed here should be qualitatively correct.

Figure 1 shows the magnitude of $\Theta(x)$ for $p$-type and $n$-type bulk $Cd_{1-x}Mn_xTe$, calculated by Eq. (3), with the values of $\tilde{x}(x)$ and $T_o(x)$, as determined by Gaj *et al.*[15] at $T=1.7$ K as well as by taking $m^*=0.8$ and $0.1m_o$ as well as $IN_o=-0.88$ and 0.22 eV for the holes and the electrons, respectively.[15,26] It has been noted that the spin-orbit interaction reduces the spin-splitting of the $\Gamma_8$ heavy holes at the Fermi level according to[29] $\Delta(\mathbf{k})=I|\mathbf{M}\cdot\mathbf{k}|/g\mu_B k$, which results in an effective spin density of states $\tilde{\rho}_F=\frac{1}{2}\rho_F$. We see in Fig. 1 that for sufficiently high hole concentrations so that the holes remain delocalized,[30] $\Theta>T_o$ in a wide range of Mn concentrations. Furthermore, since for the above parameters the Kondo temperature $T_K\approx\varepsilon_F\exp[-1/(3|I|\tilde{\rho}_F)]=1.1$ K, a crossover to the Kondo regime, $T_K>\Theta,T_o$ will take place at relatively low Mn concentrations, $x<1\%$. These considerations suggest, therefore, that a ferromagnetic phase transition can occur above 1 K in $p^+$ II-VI compounds. This is in contrast to the case of $n$-type doping, for which no ferromagnetic phase transition is expected above 1 K, as shown by the two bottom curves in Fig. 1. It is worth noting, however, that on lowering temperature $T_o$ decreases, especially for low Mn concentrations.[27] Indeed, for the highest value of $\chi_o$ ever reported for any DMS,[27] that is $\chi_o=4.8\times10^{-3}$ emu/g for $Cd_{0.99}Mn_{0.01}Se$ at 15 mK, a ferromagnetic phase transition is predicted from Eq. (4) for material parameters of $n$-$Cd_{1-x}Mn_xSe$,[24] provided that $n\geqslant 1.5\times10^{19}$ cm$^{-3}$. Since $I>0$, there is no Kondo effect for the electrons in DMS.

Turning to the case of holes in DMS quantum wells we note that the confinement and possibly the biaxial strain lead to a splitting of the heavy and light hole bands[28] as well as to a strong anisotropy of the spin-splitting.[31] Actually, the coupled system of the 2D holes and the Mn spins is Ising-like as the spin-splitting of the ground-state subband undergoes a maximum for the magnetization parallel to the growth axis. The temperature dependence of $\Delta$ for the uppermost heavy-hole subband in a quantum well of $Cd_{0.9}Mn_{0.1}Te$, computed from the coupled mean-field equations for $m^*=0.4m_o$ and $|\varphi_o(\zeta)|^2=1/L_W$, where $L_W=50$ Å, is depicted in Fig. 2 for the cases of zero and small external magnetic fields. The ferromagnetic transition occurs at about 3 K, independently of the hole areal concentration $p$, since in our model the 2D density of states does not vary with $\varepsilon_F$. At the same time, the saturation values of $\Delta$ and $M$ do depend directly on $p$ according to $\Delta_s(T)=IM(T,H_s^*)/g\mu_B$, where $H_s^*=Ip/2g\mu_B L_W$.

Finally, we note that in the case of 1D structures $\Theta$ increases with *decreasing* the carrier concentration. This, together with the correlation effects discussed above demonstrate the outstanding properties of such systems.

In summary, we have considered effects of the coupling between a macroscopic ensemble of localized spins and electronic systems of various dimensionality $d$. Our results indicate that ferromagnetic DMS can be fabricated by means of $p$-type doping as well as suggest peculiar features of the RKKY interaction in low-dimensionality structures. Additional enhancement of the tendency towards the ferromagnetic ordering is possible by engineering such a microscopic distribution of the magnetic ions, which would reduce $T_o$ and/or increase $\Theta$. Thermodynamic fluctuations of the magnetization as well as quenched magnetic disorder while important quantitatively are not expected to affect our conclu-

sions because of the long range of the spin-spin interaction, Ising symmetry of the coupling in the *p*-type structures as well as the macroscopic size of the Mn spin subsystem involved.

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