On the nature of ferromagnetism in diluted magnetic semiconductors: GaAs:Mn, GaP:Mn.

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A microscopic Hamiltonian for interacting manganese impurities in diluted magnetic semiconductors (DMS) is derived. It is shown that in p-type III-V DMS the indirect exchange between Mn impurities has similarities with the Zener mechanism in transition metal oxides. Here the mobile holes and localized states near the top of the valence band play the role of unoccupied oxygen orbitals which induce ferromagnetism. The Curie temperature estimated from the proposed kinematic exchange agrees with recent experiments on GaAs:Mn. The model is also applicable to the GaP:Mn system.

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The discovery of ferromagnetism (FM) with $T_C=110\text{K}$ in Ga$_{0.947}$Mn$_{0.053}$As [1] stimulated the systematic study of the III-V dilute magnetic semiconductors (DMS). Recently, above room temperature FM order was found in p-type GaP and GaN doped with Mn [2].

Most of the existing theories of FM in III-V DMS are based on semi-phenomenological models, which postulate the existence of local magnetic moments on the Mn sites, indirect exchange between these moments and holes in the valence band of the host crystals (see, e.g. [3]) and sometimes emphasizes the role of shallow acceptor levels [4]. In this paper we present a microscopic model, which takes into account the origin of localized magnetic moments and shallow acceptor levels induced by the Mn impurity and derive the effective
kinematic exchange from the generic two-impurity Hamiltonian. This mechanism cannot be reduced to any previously proposed models, but it is based on Zener’s idea of double exchange via unoccupied p-orbitals.

In the present paper the basis for a microscopic description of an isolated magnetic impurity is the Anderson Hamiltonian which was modified in Refs. to the case of a semiconductor host. A two-impurity generalization of the Anderson model for metals was proposed in Ref. (hereafter referred as AA). An indirect exchange between magnetic moments arises as a result of virtual electron transitions into unoccupied states shared by two impurities.

It is known (see Refs. ) that 3d impurities create both deep localized states in the energy gap and resonance states in the valence and conduction bands. Three types of states are generated by the 3d impurities in zinc blende semiconductors: non-bonding states retaining the angular e-symmetry of the states in a cubic crystal field and two types of t2 states (bonding and antibonding). The latter arise due to a strong hybridization between the atomic t2 orbitals and the p-states of the same symmetry belonging mainly to the heavy hole (hh) band. They are called crystal field resonance (CFR, predominantly d-type) and dangling bond hybrid (DBH, predominantly p-type). One of these states, as a rule, gives an impurity level in the energy gap and another manifests itself as a resonance within the valence band. According to its position in a series of transition metal elements, the Mn-impurity in the Ga-site should have the configuration 3d4. However, the Mn ion retains its fifth electron in the 3d shell because of a specific stability of a high-spin half-filled state d5 and the impurity state is Mn(3d5p), p is the bound hole state. Actually, in GaAs:Mn the mobile hole concentration is about 30% of the nominal Mn concentration.

The pd-hybridization together with the Anderson-Hubbard repulsion U is eventually the source of the magnetic interaction in DMS. To describe the indirect exchange, we start with the single impurity resonance scattering model for t2 electrons and generalize it to the case of two impurities along the lines of the AA approach. The 'passive' non-bonding e-states contribute to the localized moment, but do not participate in the indirect exchange. Therefore, the minimal two-impurity Hamiltonian involves t2-electrons:

\[
H = \sum_{p,\sigma} \varepsilon_p^h c_{p\sigma}^{h\dagger} c_{p\sigma} + \sum_{p,\sigma,i} \left( V_{pd} c_{p\sigma}^{d\dagger} d_{i\sigma} e^{i\mathbf{R}_i} + h.c. \right) + \sum_{\sigma,i} \left( E_d \hat{n}_i^\sigma + \frac{U}{2} \hat{n}_i^\sigma \hat{n}_i^\bar{\sigma} \right),
\]

where only hh states are retained in the band Hamiltonian. Here \( c_{p\sigma}^{\dagger} (c_{p\sigma}) \) is the creation
(annihilation) operator of a $hh$ with the momentum $p$ and spin $\sigma$. The second term describes the resonant impurity scattering induced by the $pd$-hybridization $V_{pd}$. The last term contains the atomic energy levels of the localized $d$ electrons with the $t_2$-electron occupation operator $\hat{n}_i^\sigma = \hat{d}_i^\dagger \hat{d}_i^\sigma$ of the Mn impurity in the Ga sites labelled by $i = 1, 2$.

The system of Dyson equations for the d-electron Green’s functions $G_{\sigma i'j}^\sigma (i,i' = 1,2)$ has the following form:

$$G_{\sigma i'j}^\sigma (\varepsilon) = g_{\sigma i}(\varepsilon) \left( \delta_{i'j} + V^2 \sum_j L_{ij}(\varepsilon) G_{\sigma ji'}^\sigma (\varepsilon) \right),$$

where $g_{\sigma}(\varepsilon) = (i\varepsilon - E_d - Un_i^{-\sigma})^{-1}$ is the single site Green’s function for a $t_2$ electron, $L_{ij}(\varepsilon) = \sum_p e^{-i\frac{\pi}{2}(R_i - R_j)}(i\varepsilon - \varepsilon_p)^{-1}$ is the lattice Green’s function for $hh$. The momentum dependence of the hybridization matrix elements is neglected, i.e. $V_{pd} \approx V$. The solution of the system of Eqs (2) is

$$G_{\sigma i'j}^\sigma = \left[ g_{\sigma i}^{-1}(\varepsilon) - V^2 L_{ij}^\sigma(\varepsilon) \right] / R^\sigma(\varepsilon), \quad G_{\sigma ij}^\sigma = V^2 L_{ij}^\sigma(\varepsilon) / R^\sigma(\varepsilon),$$

$(i = 1, 2; j = 2, 1)$ and the two-impurity levels are found from

$$R^\sigma(\varepsilon) = \prod_{i=1,2} \left[ g_{\sigma i}^{-1}(\varepsilon) - V^2 L_{ii}^\sigma(\varepsilon) \right] - V^4 L_{12}^\sigma(\varepsilon) L_{21}^\sigma(\varepsilon) = 0.$$

The zeros of the expression in the square brackets describe the impurity $d$-level renormalized by their hybridization with the $hh$ band. For sufficiently large hybridization (or narrow valence band) the DBH states arise above the top of the valence band, whereas the CFR levels appear deep in the valence band below the bottom of the $hh$ subband (the left panel of Fig. 1). The inter-site interaction $V^4|L_{12}^\sigma|^2$ results in mixing of the CFR and the DBH states belonging to the two impurities (right panel of Fig. 1).

The occupied CFR levels $E_i^\sigma$ correspond to the states $d^5/d^4$ of the Mn ions, whereas the empty $d^6/d^5$ CFR levels ($E_{i\sigma}$) are shifted to the conduction band by the Anderson-Hubbard repulsion $U$ (Fig. 1) responsible for the spin-dependent inter-impurity interaction and eventually for the FM order.

Both in GaAs:Mn and GaP:Mn the deep CFR states are completely occupied, and the DBH states in the energy gap are empty (see, e.g., Refs. [11, 14]). Two competing mechanisms of the magnetic interaction arise, since the indirect exchange between neighboring impurities involves either the empty states near the top of the valence band and the empty $(d^6/d^5)$ CFR levels. To determine the type of magnetic ordering, we consider the indirect exchange between two neighboring magnetic ions and calculate its sign and magnitude.
FIG. 1: Left panel: graphic solution of equation (3) for the bonding CFR and antibonding DBH levels. Right panel: energy levels in GaAs:Mn. The CFR d-levels \( d^{5}/d^{4} \) (denoted by \( R_{1,2} \)) of each impurity, lie below the \( hh \) band. The DBH levels (energies \( \varepsilon_{1\sigma}, \varepsilon_{2\sigma} \)) are split from the \( hh \) band and form localized (acceptor) levels in the energy gap. The CFR levels \( d^{6}/d^{5} \) \( R_{-1,-2} \) lie high in the conduction band.

The impurity related correction to the energy of the system is given by the standard formula

\[
E_{\text{magn}} = \frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} \varepsilon \Delta \text{Tr} G[\varepsilon - i\delta \text{sign}(\varepsilon - \varepsilon_{F})]d\varepsilon - \frac{1}{2} \sum U \bar{n}_{di\uparrow} \bar{n}_{di\downarrow},
\]

(4)

where \( G(E) = (E - H)^{-1} \) is the full Green’s function. We estimate first the contribution of the CFR levels. In this case the two-site lattice Green’s function \( L_{12}(\varepsilon) \approx L_{12}(E_{ba}) \equiv L \) is approximated by its value for the CFR \( d \)-level position

\[
E_{i\sigma} = E_{d} + V^{2}L_{ii}(E_{i\sigma}).
\]

(5)

The quantity \( L \) depends exponentially on the intersite distance \( R_{12} \): \( L \sim \)
exp\left(-\kappa_b R_{12}\right)/\left(\kappa_b R_{12}w\right)\) where \(\kappa_b = \sqrt{2m \left(\varepsilon_{b\text{h}} - E_{i\sigma}\right)/\hbar}\), with \(\varepsilon_{b\text{h}}\) standing for the bottom of the \(hh\) band, \(w\) is the \(hh\) bandwidth, \(E_{i\sigma}\) is the energy of the CFR level below the bottom of the \(hh\) band.

Due to the on-site repulsion \(U\), the structures of discrete CFR levels differ for FM and antiferromagnetic (AFM) orientations of neighboring impurity spins. For the AFM alignment the occupation numbers are \(\bar{n}_{1\uparrow} = \bar{n}_{2\downarrow} = 1\), \(\bar{n}_{1\downarrow} = \bar{n}_{2\uparrow} = 0\). As a result, the tunneling processes which influence energy positions of the occupied states involve large \(U\), and the secular equation (3) yields the following expressions for the occupied impurity levels (see Fig. 1):

\[
E_{b\uparrow} \approx E_{1\uparrow} - J_A, \quad E_{b\downarrow} \approx E_{2\downarrow} - J_A,
\]

where the indirect exchange parameter

\[
J_A = V^4 L^2 / U.
\]

is the Anderson superexchange, which favors AFM order in transition metal oxides.

In the FM case: \(\bar{n}_{1\uparrow} = \bar{n}_{2\uparrow} = 1\), \(\bar{n}_{1\downarrow} = \bar{n}_{2\downarrow} = 0\). Then the states, which mediate exchange between the impurity spins, are the mobile hole states below the top of the valence band and the localized DBH states above its top. The role of these states in the DMS is the similar to the that of the empty atomic states in the conventional Zener double exchange mechanism for \((\text{La, } A^{2+})\text{MnO}_3\) [5]. An important difference is that in Zener’s case the Mn ions are in different valence states (Mn\(^{3+}\) and Mn\(^{4+}\)). In other words, one of the two levels \(E_{b\uparrow}\) is empty. Since in our case both of these states are occupied, the Zener mechanism in its original form does not work. Formally, one gets a pair of bonding/antibonding CFR states \(E_{(b,a)\uparrow} = E_{i\uparrow} \pm J_Z\) from (3) without any energy gain, since both levels are occupied. It will be shown below that FM order arises only at a finite hole concentration in the valence band.

Impurity related corrections to the band energy are obtained from the integrations in Eq. (4). (cf. Ref. [8] where a similar procedure was carried out for a single impurity). Then, the variation of the total band energy due to the two-impurity scattering is

\[
\Delta E_b = -\frac{1}{\pi} \text{Im} \int_{-\hbar}^{\varepsilon_f} d\varepsilon \ln \{[g_{d^{-1}}(i\varepsilon) - V^2 L_{11}(i\varepsilon)]^2 - V^4 L_{12}^2(i\varepsilon)\}.
\]

Here \(L_{ij}(i\varepsilon) = P_{ij}(\varepsilon) + \frac{i}{2} \Gamma_{ij}(\varepsilon)\) and

\[
\begin{align*}
P_{11}(\varepsilon) &= P_{22}(\varepsilon) = \int d\omega \frac{\rho(\omega)}{\varepsilon - \omega}, \quad P_{12}(\varepsilon) = \int d\omega \frac{\sin k R_{12} \rho(\omega)}{k R_{12}}, \\
\Gamma_{12}(\varepsilon) &\approx 2\pi \rho(\varepsilon) \sin k R_{12} / k R_{12}, \quad \Gamma_{11}(\varepsilon) \approx \pi \rho(\varepsilon) = \Gamma_{22}(\varepsilon).
\end{align*}
\]

Only the spin-up (majority spin) band contributes to \(\Delta E_b\). Here and below the spin index is omitted for the sake of brevity. The value of the wave-vector \(k\) is found from the
equation $\varepsilon = \varepsilon_{hh}(k)$, where $\varepsilon_{hh}(k)$ is the $hh$ energy dispersion. Since $V/\left(g_d^{-1} - V^2P_{11}\right) = V/\left(\varepsilon - E_d - V^2P_{11}(\varepsilon)\right) \ll 1$ one can extract from Eq. (4) the spin-dependent $hh$ band contribution to the exchange energy, which reads

$$E_{ex} = \frac{-V^4}{4\pi}(\vec{\sigma}_1 \cdot \vec{\sigma}_2 + 3) \left\{ \int_{\varepsilon_F}^{0} d\varepsilon \frac{\Gamma_{12}(\varepsilon)P_{12}(\varepsilon)}{[\varepsilon - E_d - V^2P_{11}(\varepsilon)]^2 + \frac{V^4}{4}\Gamma_{11}^2} + 3x \frac{P_{12}(\varepsilon_i)P_{12}^*(\varepsilon_i)}{1 - V^2P_{11}(\varepsilon_i)^2} \right\}$$

(9)

where $\vec{\sigma}_{1,2}$ are the vectors of Pauli matrices. The terms in curly brackets correspond to the contribution of mobile and localized holes. The factor 3 appeared due to the degeneracy of the localized acceptor $p$-levels $\varepsilon_i$. The function $P_{ij}'(\varepsilon) = dP_{ij}(\varepsilon)/d\varepsilon$ is negative at $\varepsilon = \varepsilon_i$; (see left panel of Fig. 1).

Eq. (9) is the main result of our theory from which we obtain $T_C$. In the evaluations of Anderson-type and Zener-type coupling constants we use the estimates: $P_{ij} \sim w^{-1}$, $\Gamma_{ij} \sim \varepsilon_{F}^{1/2}w^{-3/2}$, $\varepsilon_{F} - E_d - V^2P_{11}(\varepsilon_F) = 4\alpha V^2/w$ with $\alpha < 1$ (see left panel of Fig. 1). Then one finds from Eqs. (4) and (1) that $J_A \sim V^4[\exp(-\kappa_b R_{12}) / (\kappa_b R_{12})]^2 / (Uw^2)$, with $\kappa_b = \sqrt{2m(\varepsilon_{bh} - E_{dr})}/h$, $J_F \sim 2\varepsilon_{F}(\varepsilon_{F}/w)^{1/2} / [(4\alpha)^2 + \varepsilon_{F}/(4w)]$ and FM pairing is realized provided $J_F > J_A$.

To calculate the exchange energy Eq.(4), one needs the dependence of the Fermi level on the Mn concentration $\varepsilon_F(x)$. It is governed by the equation $x_s = 2\int_{\varepsilon_F}^{0} \rho_v(\varepsilon)d\varepsilon$, where $x_s$ is the hole concentration per site. We assume a semi-elliptical density of states, $\rho_v(\varepsilon) = 2[\pi w^2]^{-1}\sqrt{-\varepsilon(\varepsilon + w)\theta(-\varepsilon)}$, where $w = 2.9$ eV [17]. The hole concentration per site, $x_s$, is proportional to the hole density per volume $p_h$: $x_s = 1/8a^3p_h$, as there are four III-V pairs in a unit cell volume $a^3$ in zinc-blende structures. Based on the experimental data $p_h(x)$ of Ref.[16] we used a polynomial fit for the hole density dependence on the Mn concentration in GaAs:Mn.

To compare the values of $J_A$ and $J_F$ we use the calculated $\varepsilon_F(x = 5.3\%) = -50$ meV, $U \approx 4.5$ eV, the hybridization parameter $V = 1.27$ eV obtained from [3] for the acceptor level $\varepsilon_i = 85$ meV ($\varepsilon_i^{exp} = 110$ meV [10]) and the CFR level $E_i = -3.0$ eV ($E_i^{exp} = -3.4$ eV [18]). At these values $\alpha = w[\varepsilon_F - E_d - V^2P_{11}(\varepsilon_F)] / (4V^2) = -0.32$ and the ratio $r = 2.13$ justifies the dominance of FM coupling in GaAs:Mn: $J_F > J_A$.

Eq. (1) allows one to compute the Curie temperature $T_C(x) = E_{ex}(x)/k_B$. The results are presented in Fig. 2. The calculated dependence $T_C(p_h)$ is given in Fig. 3 for different values of the Mn concentration.
FIG. 2: The dependence of the kinematic exchange (left axis) and the $T_C$ (right axis) on the impurity concentration. Experimental results (filled circles with error bars) are taken from Ref. [16]. The solid and dashed curve are obtained using the experimental obtained central and upper values of the error bars for the hole density, respectively of Ref. [16].

Although we neglected in this paper formation of an impurity band around $x \approx 5\%$ our results for $T_C(x)$ and $T_C(p_h)$ are in good agreement both with available experimental data, and the theoretical phenomenological estimates. The dielectric structure parameters such as DBH, lower CFR energies and $V$ are calculated self-consistently (Eq. (5) and see the left panel of Fig.1) for the graphical solution). Even our estimated value of $V = 1.27$ eV is in a reasonable agreement with the hybridization parameter $\sim 1.4$ eV which can be extracted from the data of Ref.[19]. This implies that the present theory, in fact, has no real fitting parameters. Note that in Ref. [20] the authors took into account the magnetic correlation mediated by holes originating from shallow acceptors without a proper regard of the role of the impurity levels, which we consider to be important, and later calculated $T_C$ by minimizing the Landau free energy.
FIG. 3: The predicted dependence $T_C (p_h)$, at the fixed manganese concentration $x = 5.3\%$ and $7\%$. (solid lines). The dashed line are the theoretical result of Ref. [20], derived from the phenomenological Landau free-energy functional within the framework of the Zener model. The dash-dot line is the recent result [24] obtained by using the exchange-enhanced mean-field theory. The point at $x = 5.3\%$ corresponds to the experimentally found [16] maximal value of $T_C$ for GaAs:Mn.

In conclusion, we proposed a microscopic model for a double exchange in $p$-type III-V:Mn DMS based on the known mechanism of interaction between substitutional transition metal impurities and the host semiconductor [10], [11]. A presence of holes is crucial for the FM double exchange between neighboring Mn ions. Our model there does not require an introduction a adhoc phenomenological $pd$- or RKKY-type exchanges. The source of the magnetic coupling is the energy gain in the kinetic energy of holes in case when neighboring ion spins are parallel. Among existing approaches the closest one to ours is the LSDA+U method[21], in which the system of $t_2\sigma$- and $e\sigma$- levels and the hole pocket for majority spin density of states correlates with our spectrum presented in Fig. [13]. However, instead of
extracting the \textit{pd}-exchange from this band structure we calculated the genuine Zener-like exchange which emerges since the band energy is lower in the FM case then in the AFM case \cite{23}. In our model this exchange is defined by Eq. (9). Similar ideas were applied to DMS CdGeP$_2$:Mn \cite{23}, where the interplay between CFR and DBH states turned out to be crucial for the onset of FM order. The theory may be applied to GaP:Mn which has a similar structure of chemical bonds around the Mn ion \cite{14}; however, experimental data on the CFR and DBH states as well as the dependencies $p_h(x)$ and $T_C(x)$ are not available. The proposed \textit{kinematic exchange} can also be applied to other DMS including GaN:Mn and A$^{2+}$GeP$_2$:Mn, which is left for future work.

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