Disorder effects in diluted ferromagnetic semiconductors

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Carrier induced ferromagnetism in diluted III-V semiconductor (DMS) is analyzed within a two-step approach. First, within a single site coherent-potential approximation formalism, we calculate the element resolved averaged Green's function of the itinerant carrier. Then using a generalized RKKY formula we evaluate the Mn-Mn long-range exchange integrals and the Curie temperature as a function of the exchange parameter, magnetic impurity concentration, and carrier density. The effect of a proper treatment of the disorder which includes all single-site multiple scattering appears to play a crucial role. The standard RKKY calculation which neglects disorder, strongly underestimates the Curie temperature and is inappropriate to describe magnetism in DMS. It is also shown that an antiferromagnetic exchange favors higher Curie temperature.

After the recent discovery by Ohno *et al.* that by doping GaAs (Ref. 1) with only 5% of magnetic impurities Mn^{2+}, the Curie temperature T_C could already exceed 100 K and because of all the possible technological applications, the interest for the III-V DMS has increased considerably. In spite of the apparent success of different methods [mean field, first principle, random-phase approximation (RPA)] where disorder is either neglected or treated at the lowest order to reproduce the Curie temperature,[2–8] there is still some shadow region concerning the effect of disorder on magnetism. Indeed only few works, mainly based on numerical simulations, are including the effect of positional disorder.[9] Recently, in order to provide a simultaneous and self-consistent treatment of the itinerant carrier and magnetic impurity, an approach based on the equation of motion method was proposed.[8] However, as a consequence of the RPA decoupling the self-energy of the itinerant carriers Green's function (GF) is reduced to the lowest-order term $\Sigma_\sigma = (z_\sigma/2)J_{pd}c\langle\hat{S}^z\rangle$ (where $z_\sigma = \pm 1$ and c is Mn^{2+} concentration). Because of the difficulty to include higher-order scattering terms within this formalism, we follow in this paper a slightly different approach and focus first on the effect of the disorder on the itinerant carriers. First, we calculate the itinerant carrier GF by treating the effect of disorder in the full coherent-potential approximation (CPA), which means that all single-site multiple-scattering processes are properly included. In the second step we calculate the exchange integrals between spin impurities using the projected GF on the Mn sites. The difficulty is to perform properly the averaged T-matrix calculation since the holes/electrons scattering depends on the impurity spin operator. For that purpose we follow the procedure described in Ref. 10. It should be added that in this work, spin impurities are treated fully quantum mechanically. The purpose of this work is to study the effect of multiple scatterings on a magnetic impurity treated in the framework of CPA, on magnetic properties. We neglect other possible sources of disorder: As antisites defects, Mn interstitials, and other impurities. In this work, the effect of compensation of carrier density due to Mn intersti-

tials and As antisites defects is taken into account in a simplified manner common in current theories.[2,3]

We consider the following minimal Hamiltonian which is the good starting point to study dilated ferromagnetic semiconductors (DMS),

$$H = \sum_{ij,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i J_i \mathbf{S}_i \cdot \mathbf{s}_i, \tag{1}$$

where $t_{ij} = t$ for i and j nearest neighbors and zero otherwise. The exchange between localized impurities spin and itinerant electron gas J_i is a random variable: $J_i = J$ ($J \geq 0$ means antiferromagnetic coupling) if the site i is occupied by a magnetic impurity, and zero otherwise. $\mathbf{S}_i$ is the magnetic impurity spin operator at site i and $\mathbf{s}_i = c_{i\alpha}^\dagger (1/2\boldsymbol{\sigma}_{\alpha\beta}) c_{i\beta}$ is the spin operator at site i of the itinerant electron gas.

The T matrix associated to the multiscattering of a single magnetic impurity (at site m) embedded in the effective medium is

$$\hat{\mathbf{t}}_m = \hat{\mathbf{V}}_m (\mathbf{1} - \bar{\hat{\mathbf{G}}} \hat{\mathbf{V}}_m)^{-1}, \tag{2}$$

where

$$\hat{\mathbf{V}}_m^{Mn} = \begin{pmatrix} \frac{1}{2} J\mathbf{S}_m^z - \Sigma_\uparrow & \frac{1}{2} J\mathbf{S}_m^- \\ \frac{1}{2} J\mathbf{S}_m^+ & -\frac{1}{2} J\mathbf{S}_m^z - \Sigma_\downarrow \end{pmatrix}. \tag{3}$$

On the other hand, for Ga at site m, $\hat{\mathbf{V}}_m^{Ga}$ is obtained by taking $J = 0$ in the previous equation.

The 2×2 averaged Green's function matrix $\bar{\hat{\mathbf{G}}}$ is

$$\bar{\hat{\mathbf{G}}} = \begin{pmatrix} \bar{\hat{\mathbf{G}}}_\uparrow & 0 \\ 0 & \bar{\hat{\mathbf{G}}}_\downarrow \end{pmatrix} \tag{4}$$

with $\bar{\hat{\mathbf{G}}}_\sigma = (\omega\mathbf{I} - \bar{\hat{\mathbf{K}}}_\sigma)^{-1}$, where $\bar{\hat{\mathbf{K}}}_\sigma = \Sigma_\mathbf{k}(\epsilon_\mathbf{k} - \Sigma_\sigma) c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}$.

In the following, we omit the site index m. The self-energy Σ_σ is obtained by solving the coupled self-consistent equations:

$$\langle t_{\sigma\sigma} \rangle_{\mathrm{dis},T} = (1-c)\langle t_{\sigma\sigma}^{\mathrm{Ga}} \rangle_T + c\langle t_{\sigma\sigma}^{\mathrm{Mn}} \rangle_T = 0. \tag{5}$$

Here $\sigma = \pm 1$ and $\langle \cdots \rangle_{\mathrm{dis},T}$ denote configuration average and thermal average at temperature T for the spin operator, c is the concentration of Mn impurities. Note that since impurity spins are treated *quantum mechanically*, the thermal averaged quantities are evaluated using the following decomposition, $\langle \hat{\mathbf{O}}(\hat{\mathbf{S}}^z) \rangle_T = \Sigma_{i=0}^{2S} a_i \langle (\hat{\mathbf{S}}^z)^i \rangle_T$, where $\hat{\mathbf{O}}$ denotes a general operator which depends in a non trivial manner on $(\hat{\mathbf{S}}^z)^i$. Additionally, as it was shown by Callen-Shtrikman, $\langle (\hat{\mathbf{S}}^z)^i \rangle_T$, and hence $\langle \hat{\mathbf{O}}(\hat{\mathbf{S}}^z) \rangle_T$, are universal functions of $\langle \hat{\mathbf{S}}^z \rangle_T$ only.[11] After solving the coupled set of equations [Eq. (5) with $\sigma = \pm 1$] one gets the total averaged GF of the itinerant carriers.

The following step consists in calculating the long-range exchange integrals J_{ij}^{eff} between magnetic impurities for the effective Heisenberg Hamiltonian

$$H^{\mathrm{Heis}} = \frac{1}{2} \sum_{i \neq j} J_{ij}^{\mathrm{eff}} \mathbf{S}_i \cdot \mathbf{S}_j . \tag{6}$$

The exchange integrals between two impurities separated by a distance $\mathbf{R}$ is given by the generalized RKKY formula

$$J^{\mathrm{eff}}(\mathbf{R}) = -\frac{1}{2} J^2 \left[-\frac{1}{\pi} \mathrm{Im}\chi(\mathbf{R}) \right], \tag{7}$$

where the susceptibility is

$$\chi(\mathbf{R}) = \sum_{\mathbf{k},\mathbf{q}} \int d\omega f(\omega) \bar{G}_{\uparrow}^{\mathrm{Mn}}(\mathbf{k},\omega) \bar{G}_{\downarrow}^{\mathrm{Mn}}(\mathbf{k}+\mathbf{q},\omega) e^{i\mathbf{q}\cdot\mathbf{R}}. \tag{8}$$

The chemical potential μ entering the Fermi-Dirac function $f(\omega)$ is determined at each temperature by fixing the itinerant carrier density. Note that the exchange integrals are T dependent through the averaged GF. When replacing $\bar{G}_{\sigma}$ by the free particle GF the exchange integrals reduce to the standard RKKY. Additionally, it is important to stress that to calculate J_{ij}^{eff}, one has to take into account that both sites i and j should be occupied by Mn atom. Thus the nonlocal GF in Eq. (8) should be the Mn-projected GF but not the full averaged one.

To derive the projected GF on Mn sites, we essentially follow the procedure described in Ref. 12, which gives

$$\bar{G}_{\sigma}^{\mathrm{Mn}}(\mathbf{k},\omega) = F_{\sigma}(\omega)(1-F_{\sigma}(\omega))\bar{G}_{\sigma}(\omega) + F_{\sigma}^2(\omega)\bar{G}_{\sigma}(\mathbf{k},\omega), \tag{9}$$

where

$$\bar{G}_{\sigma}(\omega) = \frac{1}{N} \sum_{\mathbf{k}} \bar{G}_{\sigma}(\mathbf{k},\omega)$$

and

$$F_{\sigma}(\omega) = [1 - \bar{G}_{\sigma}(\omega)(V_{\mathrm{eff},\sigma}^{\mathrm{Mn}} - \Sigma_{\sigma})]^{-1}.$$

The determination of the effective potential $V_{\mathrm{eff},\sigma}^{\mathrm{Mn}}$ leads to

$$V_{eff,\sigma}^{Mn} = \Sigma_{\sigma} \frac{1 + \Sigma_{\sigma}\bar{G}_{\sigma}}{c + \Sigma_{\sigma}\bar{G}_{\sigma}}. \tag{10}$$

We can now evaluate the Curie temperature by using mean-field theory for the effective Heisenberg model:

$$k_B T_C = \frac{2}{3} S(S+1)c \frac{1}{N} \sum_{\mathbf{q}} E(\mathbf{q}) \tag{11}$$

$E(\mathbf{q})$ is the T-dependent magnon spectrum: $E(\mathbf{q}) = \tilde{J}^{\mathrm{eff}}(\mathbf{0}) - \tilde{J}^{\mathrm{eff}}(\mathbf{q})$, where $\tilde{J}^{\mathrm{eff}}(\mathbf{q})$ denotes the Fourier transform of the exchange integrals.

Let us discuss the numerical results. In Fig. 1, the total density of states (DOS) and the projected one on Mn site are shown as a function of energy for different values of J/t. In the weak coupling regime ($J/t = 0.86$) the spin-resolved DOS is almost identical to the unperturbed one although the Mn-projected DOS is already strongly affected by the inclusion of multiscattering. By further increase of J/t, an impurity band appears at low energy. Note that the impurity band splits first at $E \leq 0$, and the position of the peaks in the Mn-DOS are not symmetric with respect to zero. This can be understood by analyzing the atomic limit ($J/t \to \infty$) which is properly described. In the paramagnetic phase, we get a peak at $E_{\mathrm{h}} = +\frac{1}{2}JS$ and another at $E_{\mathrm{l}} = -\frac{1}{2}J(S+1)$ with respective weights $(S+1)/(2S+1)c$ and $S/(2S+1)c$.[14]

Due to the presence of compensation defects As antisites or Mn interstitials the hole concentration is much smaller than c.[15] In order to take into account these effects we introduce a free parameter $\gamma = n_h/c$ (n_h is the hole concentration).

In Fig. 2, the dependence of T_C on γ is discussed. At fixed γ, the Curie temperature increases significantly with J/t and large values are reached when approaching the split-band regime. In the intermediate regime ($J/t \gtrsim 2$), T_c appears to be *very sensitive* to J/t, a maximum at $\gamma \approx 0.10$ is observed before T_C decreases and eventually vanishes at γ_c which is J/t dependent. These results are qualitatively comparable to those of Ref. 13, although we obtain Curie temperature significantly larger. Additionally, in comparable regime the maximum of T_c in Ref. 13 corresponds to half-filled impurity band ($\gamma \approx 0.50$) and T_c is symmetric with respect to this point (it vanishes at $\gamma = 1$). Later it will be shown that the sign of J which is irrelevant in most of the model calculations plays in fact an important role. As it will be discussed in the following section, the value of γ_c for which T_C vanishes depends on both the sign and amplitude of J/t.

In Fig. 3, T_C as a function of J/t is shown for both anti-ferromagnetic and ferromagnetic couplings for different carrier density. First, the sign of J/t appears to be relevant. Indeed, T_C is strongly asymmetric with respect to $J/t = 0$. In the case of ferromagnetic coupling the maximum of T_C is *much smaller* than that for antiferromagnetic coupling. However, as expected, for $|J|/t \lesssim 1$ they are comparable and reduce to the standard RKKY result ($T_C \propto J^2$). For both, ferromagnetic and antiferromagnetic couplings, the position of the maximum depends on the hole concentration. However,
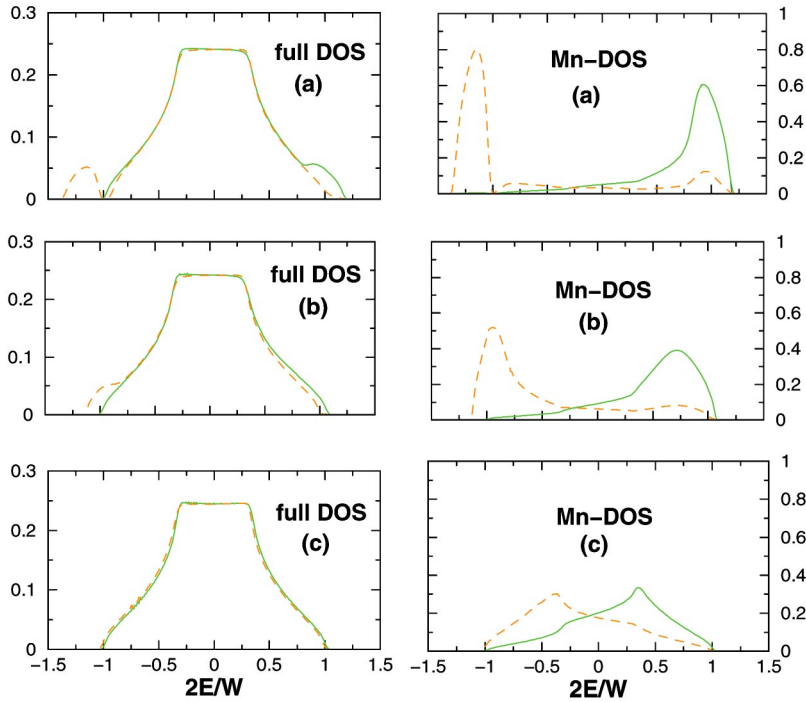
FIG. 1. (Color online) Total DOS (left panels) and Mn projected DOS (right) as a function of $2E/W$ (bandwidth $W=12t$), for majority spin (dashed curve) and minority spin (full curve) at $T=0$ K. The value of J/t are $J/t=3.45$ (a), $J/t=2.33$ (b), and $J/t=0.86$ (c). The concentration of impurity is $c=5\%$.

the maximum occurs earlier in the ferromagnetic case. Note that in the *intermediate regime* $1 \leqslant J/t \leqslant 3$, T_C^{RKKY} is *much smaller* than T_C^{CPA}: for $J/t=2$, $T_C^{\mathrm{CPA}} \approx 3\, T_C^{\mathrm{RKKY}}$ for $n_h =0.015$. Additionally, after the maximum is reached, T_C drops rapidly, and vanishes at a n_h-dependent value of J/t. These results can be understood in the following way: In the weak and intermediate regimes due to multiscattering the probability of finding a carrier at the impurity site is larger than when the scatterings are neglected (RKKY). Thus the coupling with the impurity is stronger in the former than in the latter case and as a consequence T_C gets larger. On the other hand, when the scattering strength increases further the carriers get more localized and thus the exchange integrals

between impurities start to decrease. This explains why T_C reaches a maximum before it decreases. We observe that in the split-band regime $J/t \geqslant 3.5$ *no ferromagnetic ordering* is possible. In contrast to other approaches, our theory appears to be more suitable in the large coupling regime.

Let us now discuss briefly the relevance of our results with respect to experimental data of $\mathrm{Ga}_c\mathrm{Mn}_{1-c}\mathrm{As}$. Our model is based on a one-band model, similar to Ref. 8, we fix t by assuming a hole effective mass $m^*=0.5\, m_e$. This leads to a value $t=0.58$ eV.[16] We assume that the 5.3%-doped sample (highest $T_C=110$ K) contains $n_h \approx (0.3 \pm 0.1)c$. Using Fig. 4, we obtain $J=-1.12 \pm 0.12$ eV to get the same Curie temperature.[17] Surprisingly, although our calculations
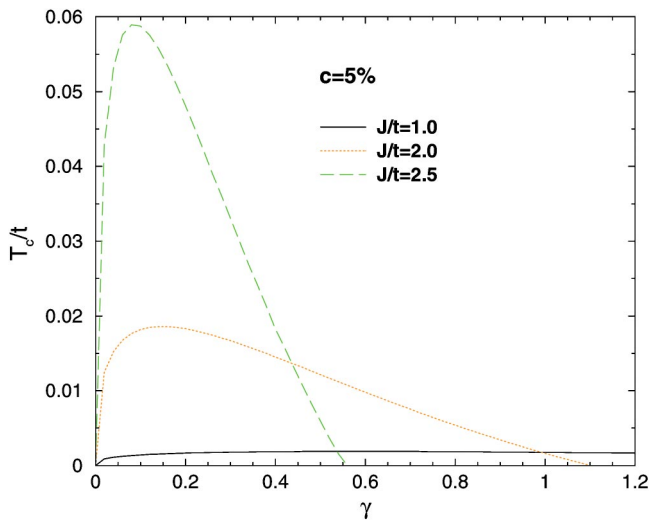

FIG. 2. (Color online) T_C/t as a function of $\gamma=n_h/c$ for different values of J/t. The concentration of impurity is fixed to $c=5\%$.
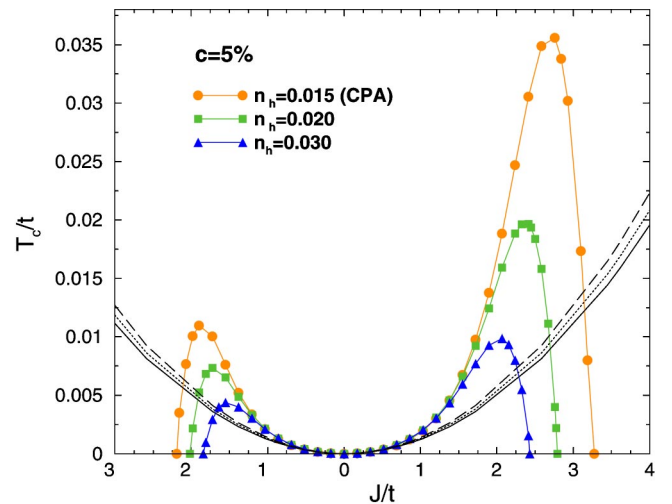

FIG. 3. (Color online) T_C/t as a function of J/t for different carrier density. The impurity concentration is $c=5\%$. The RKKY calculation corresponds to the continuous, dashed, and dotted curves and the full CPA treatment to symbols.
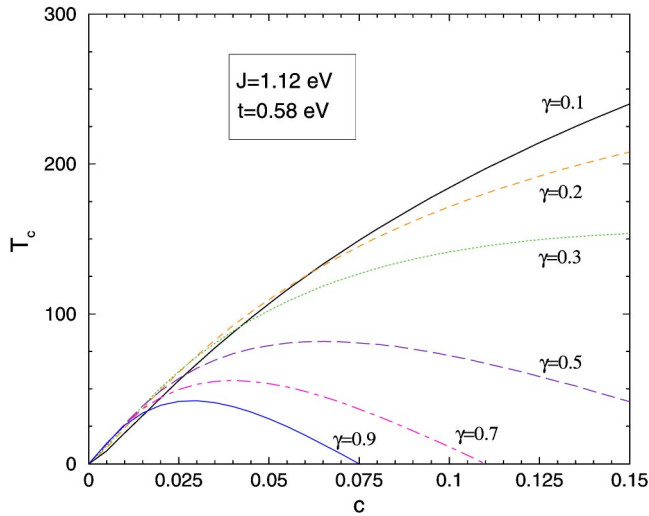
FIG. 4. (Color online) T_C (in K) as a function of c for different values of γ (see figure). The parameters are $t = 0.58$ eV and $J = 1.12$ eV (see text).

are done within a one-band model, this value agrees well with the estimate $J = -1.1 \pm 0.2$ eV based on photoemission experiment.[18] However, from magnetotransport measurements Matsukura *et al.*[1] have suggested $|J| = 3.3$ eV (i.e., $J/t = 5.68$). According to Fig. 3, no ferromagnetism is possible for $|J| \gtrsim 2.1$ eV ($T_c = 0$).

In Fig. 4 we analyze the dependence of T_C on the impurity concentration c, for different values of γ. For a given c, we observe that T_C is nonmonotonic with respect to γ. How-

ever, it is clear that even at large concentration the low hole density is more favorable to get a high Curie temperature. More precisely T_C is larger when $\gamma \approx 0.1$. For instance, when $c = 0.15$ we get $T_C \approx 240$ K. Additionally, for sufficiently large γ, we see that when increasing c, T_C shows a maximum and decreases until it vanishes. It is expected that T_C will first vanish for larger itinerant carrier density. Indeed, the localization effect is stronger at higher carrier density.

In conclusion, we have presented a theory to study ferromagnetism in DMS, which consists (i) in treating the itinerant carriers within the best single-site approximation (CPA) and (ii) performing the susceptibility calculation using the disordered Green's functions to get the Curie temperature. It is shown that a better treatment of the disorder beyond virtual crystal approximation, which means that the theory includes properly all single-site multiscatterings, leads to significantly higher values of the Curie temperature with respect to a standard RKKY calculation. We also show that in the strong disorder regime, for sufficiently large J_{pd} coupling, the ferromagnetism becomes unstable and T_c vanishes. Additionally, it is shown that an antiferromagnetic coupling favors a higher T_C in the hole doped materials as compared to the local ferromagnetic coupling. The reason of this difference can be attributed to both (i) quantum-mechanical treatment of the magnetic impurities and (ii) to the fact that AF local coupling favors the spin-flip processes. A detailed study of this aspect will be the subject of another publication.

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[14] In the case of $S = 1/2$, this corresponds to a singlet state $E_S = -\frac{3}{4}J$ with degeneracy 1 and a triplet state $E_T = +\frac{1}{4}J$ with degeneracy 3.

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[16] In GaAs the unit cell volume is $v = a_0^3/4$ ($a_0 = 0.565$ nm). For simplicity, our calculations are performed on a simple cubic lattice, thus the lattice spacing we take is $a_1 = (a_0^3/4)^{1/3}$.

[17] Assuming a larger n_h of the order of 0.3–0.4 leads to a value of J weakly affected (only within 10%).

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