Enhancing $T_c$ in ferromagnetic semiconductors

S. Das Sarma, E. H. Hwang, and D. J. Priour, Jr.
Condensed Matter Theory Center, Department of Physics, University of Maryland, College Park, MD 20742-4111

We theoretically investigate disorder effects on the ferromagnetic transition (“Curie”) temperature $T_c$ in dilute $\text{In}_{1-x}\text{Mn}_x\text{As}$ magnetic semiconductors (e.g., $\text{Ga}_{1-x}\text{Mn}_2\text{As}$) where a small fraction ($x \approx 0.01 - 0.1$) of the cation atoms (e.g., Ga) are randomly replaced by the magnetic dopants (e.g., Mn), leading to long-range ferromagnetic ordering for $T < T_c$. We find that $T_c$ is a complicated function of at least eight different parameters including carrier density, magnetic dopant density, and carrier mean free path; nominally macroscopically similar samples could have substantially different Curie temperatures. We provide simple physically appealing prescriptions for enhancing $T_c$ in diluted magnetic semiconductors, and discuss the magnetic phase diagram in the system parameter space.

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Diluted magnetic semiconductors (DMS), which are ferromagnetic for $T < T_c$, are of great fundamental interest because they provide a unique example of interplay among magnetism, disorder, carrier dynamics, and transport properties. Starting with the early report of carrier-induced global ferromagnetism first in $\text{In}_{1-x}\text{Mn}_x\text{As}$ [1] and later [2] in $\text{Ga}_{1-x}\text{Mn}_2\text{As}$, with the typical magnetic impurity concentration $x \approx 5\%$, there have been many studies reporting ferromagnetism in DMS systems as disparate as $\text{Ge}_{1-x}\text{Mn}_x$ [3], $\text{Ga}_{1-x}\text{Mn}_2\text{N}$ [4], $\text{Ga}_{1-x}\text{Mn}_2\text{P}$ [5], $\text{TiO}_2\text{Co}$ [6], $\text{SnO}_2\text{Co}$ [7], and $\text{ZnCrTe}$ [8] among others. There is a great deal of current research activity in the subject, and new DMS materials with novel magnetic properties are likely to continue appearing in the near future. In spite of this enormous activity, there is no current consensus on the basic magnetic model underlying DMS ferromagnetism. In fact, there is strong disagreement in the literature about the nature of the carrier ground state participating in the ferromagnetism— in particular, whether these carriers are free carriers in the parent-semiconductor bands or are impurity (or defect) band carriers within the fundamental band gap of the semiconductor by the magnetic dopant atoms is a matter of considerable controversy in the literature [9]. Experimentally the situation turns out to be quite complex as the ferromagnetic properties (in particular, the Curie temperature $T_c$) seem to depend very sensitively [10] on the materials growth and processing (e.g., annealing) conditions, and $T_c$ in nominally identical samples could differ substantially depending on the precise details of sample preparation and processing.

In this letter, we develop a theory for the prediction of $T_c$ in DMS systems by focusing on the most-studied DMS system, viz. $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, as a function of various system parameters (to be discussed below). Our work, which includes spatial disorder of the system (by virtue of the random locations of the magnetic Mn atoms), leads naturally to the conclusion that $T_c$ is a complicated (and in general unknown) function of the system parameters; the number of independent variables (at least eight as discussed below) determining $T_c$, even within the minimal zeroth order effective Hamiltonian approach, are sufficiently large that nominally macroscopically identical samples may very well have significant variations in $T_c$, as is indeed observed. Some of the system parameters (e.g. the nature of spatial disorder, various defects present in the real samples, the impurity scattering potential, etc.) are generally unknown as a matter of principle, and therefore a precise quantitative prediction for $T_c$ as a function of the known system parameter (i.e. the Mn concentration $x$ and the carrier density $n_c$), as is often done in the literature, could be quite meaningless because the same values of $x$ and $n_c$ may lead to different $T_c$ values in different samples depending on the details of various defects/impurities/disorder in the system (which can be influenced, for example, by sample annealing). Among the various possible defects, As antisites and Mn interstitials are known to be important. In addition, likely correlated clustering of Mn atoms (instead of uncorrelated random positioning at Ga sites) is also thought to be significant [11]. Experimentally, a strong dependence of $T_c$ on the sample conductivity has been found with $T_c$ typically increasing with conductivity; samples with the highest (lowest) conductivity invariably have the highest (lowest) $T_c$s, but whether this dependence arises entirely from the higher conductivity samples having higher carrier densities (as is commonly assumed in the literature) or longer mean free paths (MFP) (or equivalently, higher mobility) or a combination of the two is presently unknown. We therefore see that $T_c \equiv T_c(n, n_c, l, J_0; N_{AS}, N_I, N_C, J_{AF} \cdots)$ is a function of at least eight different parameters due to the complexity of the problem. The three obvious parameters, which have been discussed widely in the literature, are the active magnetic moment density $n_i$ due to substitutional Mn dopants, the carrier density $n_c$, and the carrier MFP $l$ (as obtained from the dc-conductivity), and in this paper we mostly focus on the dependence of $T_c$ on these three parameters. The other relevant parameters, e.g. $N_{AS}$ (the As antisite defect density), $N_I$ (the Mn interstitial defect density), $N_c$ (a set of parameters defining the clustering of Mn atoms or the correlation in their spatial
positions), and $J_{AF}$ (the direct short-range Mn-Mn antiferromagnetic exchange interaction), are quantitatively important, but essentially unknown (either experimentally or theoretically), and their explicit inclusion in the theory for a quantitative comparison with the experimental results is hence not particularly useful. However, we assume that the influence of these parameters can be included qualitatively in the theory by appropriately adjusting the parameters $n_i$, $n_c$, $l$, and most importantly, the effective ferromagnetic coupling strength $J_0$ which sets the overall energy scale in the problem since we express $T_c$ in the units of $J_0$. We find that even with just three independent parameters ($n_i$, $n_c$, $l$), the problem is quite rich leading to many subtle possibilities.

We use the standard RKKY-Zener effective model [12] for describing the coupled carrier-local moment system since we are interested in the so-called “metallic” DMS regime with itinerant carriers where $T_c$ is maximized. (The insulating strongly localized DMS regime can also be ferromagnetic, but the nature of the insulating DMS ferromagnetism, with typically rather low $T_c$, is fundamentally different [13] from the metallic regime with higher $T_c$ being considered in this Letter.) We note that while it is somewhat crude to characterize the metallic DMS regime by a MFP $l$ extracted from the conductivity $\sigma = n_c e^2 \tau / m_c$ (and $l = v_F \tau$, where $\tau$ is the transport relaxation time, $m_c$ the carrier mass, and $v_F$ the carrier Fermi velocity), the extracted value of the MFP $l$ is rather short (typically around one to a few lattice constants). Following our earlier work [14] we employ an effective magnetic model Hamiltonian for interacting impurity moments where the carrier degrees of freedom have been integrated out:

$$H = \sum_{i,j} J_F(r_{ij}) \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{i,j} J_{AF} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where the subscripts $F$ (AF) denote the ferromagnetic (antiferromagnetic) part of the impurity spin ($\mathbf{S}_i$) interaction and the prime in the second term implies that the sum is restricted to nearest neighbors since the short-range antiferromagnetic interaction only couples nearest-neighbor Mn atoms (if there are any). We do not explicitly include the direct antiferromagnetic exchange term in the results shown in this paper assuming without any loss of generality (within our theoretical scheme) that $J_{AF}$ effectively modifies (in fact, reduces) the carrier-mediated ferromagnetic interaction. Since the interaction strength is the basic energy parameter in our effective magnetic Hamiltonian, it makes little sense to keep two unknown coupling parameters. We write Eq. (1) with the direct antiferromagnetic exchange term for our general qualitative discussion of the DMS phase diagram as described below.

The first term in Eq. (1), the carrier-mediated ferromagnetic inter-impurity interaction, is of the RKKY form in our effective model: $J_F(r) = J_0 [(2k_F r) \cos(2k_F r) - \sin(2k_F r)] / (k_F r)^2$, where $J_0$ is the fundamental ferromagnetic coupling parameter in the problem (which implicitly includes all materials and band structure information about the system) and $k_F$ the carrier Fermi momentum (and $r = |r_{ij}|$ the spatial separation between randomly located substitutional Mn pairs in the GaAs lattice). We note one important feature of $J_F(r)$: for high carrier density, $n_c \geq n_i$, the oscillatory aspects of RKKY interaction come into play, potentially suppressing DMS ferromagnetism — the details of this suppression are an important topic of this work. A straightforward Weiss mean-field treatment of the RKKY interaction, neglecting all spatial disorder effects and assuming a continuum virtual crystal approximation (VCA), was first carried out a long time ago (and has recently been rediscovered in the DMS context) leading to: $T_c^{VCA} \propto n_i n_c^{1/3}$. This $T_c^{VCA}$ (with appropriate quantitative modifications arising from band structure effects) has been extensively (and uncritically in our view) used in the DMS literature for explaining and predicting $T_c$ in DMS systems. In the current work we include in our calculation of $T_c$ spatial disorder (thus relaxing the continuum VCA) and finite MFP, which are both significant in DMS materials.

First we qualitatively discuss the DMS phase diagram as a function of the variable $n_i$, $n_c$, and $l$, noting that the standard VCA implies that the system is a ferromagnet for all values of $n_c$ and $n_i$ with $T_c^{VCA}$ increasing monotonically with increasing impurity ($n_i$) and carrier ($n_c$) density. It is essential to include MFP effects in the theory. The RKKY interaction has been calculated in the presence of resistive scattering earlier in the literature [15], and the modified RKKY interaction in the presence of a finite MFP $l$ has the form $J_F(r;l) = J_F(r)$ for $r \ll l$ and $J_F(r;l) = J_0 \cos(\phi(r))/(2k_F r)^2$ for $r \gg l$, where $J_F(r)$ is the standard RKKY formula and $\phi(r)$ is a completely random function of $r$. The inclusion of short-range direct antiferromagnetic exchange [Eq. (1)], RKKY oscillations, and scattering/transport MFP effects permits us to obtain the qualitative $T = 0$ DMS phase diagram as a function of three length variables $\lambda_c \sim n_c^{1/3}$; $r_o \sim n_i^{-1/3}; l$. The schematic phase diagram depicted in Fig. 1 assumes $\lambda_c, r_o,$ and $l$ to be completely independent variables (which they cannot be in real systems). In each

(a) \begin{tabular}{c|c|c|c|c}
RKKY "SG" & FM I & FM II & \hline
\end{tabular}
\begin{tabular}{c}
$T_c$ increasing \hline
$T_c$ decreasing
\end{tabular}
\Rightarrow \lambda_c

(b) \begin{tabular}{c|c|c|c|c}
"RSO" & FM I & FM II & RKKY "SG" & \hline
\end{tabular}
\begin{tabular}{c}
(with $l_o$) \hline
$T_c$ increasing \hline
$T_c$ decreasing
\end{tabular}
\Rightarrow r_o

(c) \begin{tabular}{c|c|c|c|c}
disordered "RG" & FM I & FM & \hline
\end{tabular}
\begin{tabular}{c}
$T_c$ increasing \hline
$T_c$ saturated
\end{tabular}
\Rightarrow l

FIG. 1. DMS phase diagram. Note that the dashed lines between FM phases are not phase transition.
case shown in Fig. 1 we assume the other variables to be fixed at some reasonable “optimum” values (which may not always be experimentally possible).

In Fig. 1(a) the system is an “RKKY spin-glass (SG)” system at very small values of $\lambda_c$ (equivalently very large values of $n_c$). This arises from the frustration induced by the RKKY oscillations which are dominant in the high $k_F$ ($n_c \gg n_i$) limit (but are essentially absent in the dilute $n_c \ll n_i$ limit). As $\lambda_c$ increases (i.e. $n_c \sim \lambda_c^{-3}$ decreases) the “RKKY SG” phase gives way to a ferromagnetic phase. The Curie temperature of this phase increases with decreasing density until the optimum $T_c$ is reached, after which $T_c$ begins to decrease with decreasing carrier density. In Fig. 1(b) we depict the DMS phase diagram in magnetic impurity density $n_i \sim r_0^{-3}$ assuming $l$ and $\lambda_c$ to be fixed at reasonable optimal values. For small $r_0$ (large $n_i$) the nearest-neighbor direct antiferromagnetic exchange between the Mn moments becomes important and competes with the carrier-induced RKKY interaction, leading to a random spin-ordered (RSO) non-ferromagnetic phase (which may or may not be a SG phase). For larger $r_0$ we enter the ferromagnetic phase with $T_c (r_0)$ similar to the $T_c$ profile in Fig. 1(a); eventually we find a phase transition to the RKKY SG phase for very large $r_0$ where $n_c \gg n_i$. Thus, except for the antiferromagnetic exchange induced “RSO” phase in the high impurity concentration limit in Fig. 1(b), the phase diagrams of Figs. 1(a) and (b) are essentially mirror images of each other as one shifts from $n_c \gg n_i$ ($n_i \gg n_c$) to $n_c \ll n_i$ ($n_c \gg n_c$) in Fig. 1(a) ([b]) respectively. Finally, in Fig. 1(c) we discuss the phase diagram as a function of the MFP for fixed $n_i$ and $n_c$ values. For very small $l$, the carrier-induced ferromagnetic RKKY coupling is suppressed, and the inter-impurity interaction has random sign, leading to a type of (non-RKKY) disordered “random glassy” (RG) non-ferromagnetic ground state which, with increasing $l$, should make a phase transition to the ferromagnetic phase. As one increases $l$ further the ferromagnetic phase should initially be enhanced (i.e. $T_c$ rises with $l$) with an eventual saturation of $T_c$ determined by the precise values of $n_c$ and $n_i$. Thus it is readily evident that the ‘best’ technique to enhance $T_c$ would be to increase the MFP sitting at fixed optimal values of $n_c$ and $n_i$. Although this is perfectly reasonable as a matter of principle, it may be difficult to increase the MFP without affecting $n_c$ and $n_i$.

Following this qualitative introduction to the DMS phase diagram on the basis of the simple effective Hamiltonian approach, we now consider the quantitative dependence of $T_c(n_c, n_i, l)$ in DMS systems focusing on the well-studied Ga$_{1-x}$Mn$_x$As system. To do this we carry out a thermal lattice mean field treatment (treating exactly the spatial disorder of random Mn locations at Ga substitutional sites in the zinc blende GaAs lattice) of the effective Hamiltonian as described in [14]. Such a treatment avoids the physically unrealistic assumptions of the continuum VCA involved in deriving $T_c$, and should be an excellent approximation for obtaining $T_c$ because of the very large coordination number in the fcc zinc blende GaAs lattice structure. As emphasized by us elsewhere, this lattice mean field theory (LMFT) can essentially be carried out for infinite size systems, thus avoiding the finite size complications inherent in direct Monte Carlo simulations which are not particularly well-suited for rapidly determining $T_c$.

In Fig. 2 we present our theoretical results for $T_c(n_c, n_i, l)$. As noted earlier, we have ignored the direct short-range antiferromagnetic exchange interaction in obtaining these results. We also ignore interstitial defects (and antisite As) in this calculation; we assume that $n_i$ and $n_c$ are the effective active local moment and hole density respectively, which already incorporate various defect effects.

In Fig. 2(a) we show the calculated $T_c$ as a function of $n_c/n_i$ for several values of $x$ in a “highly” metallic system ($l/a = 5$, where $a$ is the GaAs lattice constant), whereas in Fig. 2(b) we show $T_c(n_c/n_i)$ for a fixed value of $x = 0.07$ but for several different values of $l/a$. We show the simple continuum VCA result in each case for the sake of comparison. It is obvious that the simple theory of $T_c^{VCA}$ is qualitatively incorrect for large $n_c/n_i$ where $T_c$ actually reaches a maximum and then decreases with increasing carrier density. In Fig. 2(b) we show the calculated $T_c$ as a function of $n_c/n_i$ for several values of $x$ in a “highly” metallic system ($l/a = 5$, where $a$ is the GaAs lattice constant), whereas in Fig. 2(b) we show $T_c(n_c/n_i)$ for a fixed value of $x = 0.07$ but for several different values of $l/a$. We show the simple continuum VCA result in each case for the sake of comparison. It is obvious that the simple theory of $T_c^{VCA}$ is qualitatively incorrect for large $n_c/n_i$ where $T_c$ actually reaches a maximum and then decreases with increasing carrier density. In Fig. 2(b) we show the calculated $T_c$ as a function of $n_c/n_i$ for several values of $x$ in a “highly” metallic system ($l/a = 5$, where $a$ is the GaAs lattice constant), whereas in Fig. 2(b) we show $T_c(n_c/n_i)$ for a fixed value of $x = 0.07$ but for several different values of $l/a$. We show the simple continuum VCA result in each case for the sake of comparison. It is obvious that the simple theory of $T_c^{VCA}$ is qualitatively incorrect for large $n_c/n_i$ where $T_c$ actually reaches a maximum and then decreases with increasing carrier density.
as Mn concentration increases, and this indicates that, for a given value of the effective coupling $J_0$, $T_c$ cannot really be arbitrarily increased just by increasing the carrier density (although increasing carrier density by doping with non-magnetic impurities [16] should enhance $T_c$ somewhat), but typically $T_c$ is optimum for $n_c/n_i \sim 1$. This suggests that the current popular wisdom of trying to enhance $T_c$ for GaMnAs (and other DMS materials) simply by increasing carrier density would not work much beyond $T_c \sim 300$K (since the current maximum $T_c$ is around 170K).

Our results for $T_c(l)$ presented in Fig. 3 indicate one possible strategy for enhancing $T_c$. As can be seen in Fig. 3, $T_c$ increases monotonically with increasing MFP eventually saturating at the maximum possible $T_c$ for a given value of $n_c/n_i$ (which is somewhat below the corresponding $T_c^{VCA}$). Thus a clear strategy to enhance $T_c$ is to optimize $n_c/n_i$ for a given Mn content such that one is at or near the optimum carrier density (i.e. near the maximum in Fig. 2), $n_c/n_i \sim 0.5 - 2$ depending on $x$, and then to enhance the carrier MFP by reducing scattering effects through a systematic improvement of sample quality. Experimentally, it is now established [17] that enhancing conductivity by improving sample quality (e.g. via annealing) can substantially increase $T_c$, but the conductivity $\sigma$ depends both on the carrier density $n_c$ and the MFP $l$, and it has almost universally been assumed that the increase of $T_c$ due to enhanced $\sigma$ arises entirely from the increasing carrier density, whereas we find that $T_c$ improvement arises both from increasing $n_c$ and $l$.

Finally, in Fig. 4 we show a direct comparison between all our theory and recent GaMnAs experimental results from several different groups [10,17–19]. For each set of results in Fig. 4 we have extracted $T_c(n_c, n_i, \sigma(l))$ from the relevant experimental work as described in the figure captions. It is obvious that the experimental results are well-described by the theory: the agreement can be made essentially exact by slightly adjusting $n_i$ and/or by choosing slightly different $J_0$ for different values of $x$, both of which may be reasonable since Mn interstitials (whose density may very well be a function of $x$) are likely to affect the value of effective coupling by modifying the number of active Mn moments participating in global ferromagnetism and by introducing some direct Mn-Mn antiferromagnetic exchange coupling. It is also evident from Fig. 4 that the continuum VCA, while qualitatively reasonable in some regimes of the parameter space, does not provide a good quantitative description for the experimental results.

In conclusion, we have discussed the DMS phase diagram, taking into account effects of carrier-mediated ferromagnetic and antiferromagnetic coupling between the impurity moments as well the frustration arising from the RKKY oscillations, finding that ferromagnetism is only one of four distinct magnetic phases possible in the disordered system. We have also carried out a detailed theoretical $T_c$ calculation as a function of magnetic impurity concentration, carrier density, and conductivity (i.e. MFP) including full effects of spatial disorder and randomness, finding that the maximum $T_c$ is obtained for an optimum carrier density $n_c/n_i \sim 0.5 - 2$ depending on the Mn concentration. We have shown that for $T_c$ to be enhanced at given values of $n_c$ and $n_i$, one needs to increase the MFP as much as possible.

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