A new route to enhance the ferromagnetic transition temperature in diluted magnetic semiconductors

Kalpataru Pradhan¹, Subrat K Das²

¹CMP Division, Saha Institute of Nuclear Physics, HBNI, Kolkata 700064, India
²SKCG Autonomous College, Paralakhemundi, Odisha 761200, India

We investigate the magnetic and the transport properties of diluted magnetic semiconductors using a spin-fermion Monte-Carlo method on a 3D lattice in the intermediate coupling regime. The ferromagnetic transition temperature \(T_c\) shows an optimization behavior, first increases and then decreases, with respect to the absolute carrier density \(p_{abs}\) for a given magnetic impurity concentration \(x\), as seen in the experiment. Our calculations also show an insulator-metal-insulator transition across the optimum \(p_{abs}\) where the \(T_c\) is maximum. Remarkably, the optimum \(p_{abs}\) values lie in a narrow range around 0.11 for all \(x\) values and the ferromagnetic \(T_c\) increases with \(x\). We explain our results using the polaron percolation mechanism and outline a new route to enhance the ferromagnetic transition temperature in experiments.

Diluted magnetic semiconductors (DMSs) are materials of strong interest due to both, their novel ferromagnetism and potentiality for future spintronics. In particular, Ga\(_{1-x}\)Mn\(_x\)As\(_{1-y}\)As with ferromagnetic transition temperature \(T_c\approx 173\text{ K}\) in bulk\(^2\), \(≈ 191\text{ K}\) in films\(^3\), and even more (\(≈ 200\text{ K}\))\(^4\) in nano wires has led intensive efforts to increase \(T_c\) in view of possible technological applications.

It is widely accepted that Mn\(^{2+}\) ion (\(Mn_{Ga}\)) replace Ga\(^{3+}\) ion in Ga\(_{1-x}\)Mn\(_x\)As and thereby contributes a hole to the semiconductor valence band, which mediates the magnetic interaction between the localized spins. However, point defects like \(Mn\) interstitials (\(Mn_I\)) and As anti-sites\(^1\) significantly act as impurities that limit the hole density. In addition, \(Mn_I\) are highly mobile and preferentially choose the interstitial positions adjacent to Ga substituted \(Mn\) ions (\(Mn_{Ga}\)), thus forming anti-ferromagnetic \(Mn_{Ga-Mn_I}\) pairs\(^1\) and consequently increases the \(Mn\) inactive sites. So overall \(Mn_I\) reduces the hole density and the effective \(Mn\) concentration \((x_{eff})\) to \(Mn_{Ga-2Mn_I}\) and \(Mn_{Ga-Mn_I}\), respectively, hindering the higher ferromagnetic \(T_c\) in DMSs. We define the carrier density \(p=p_{abs}/x\), where \(x\) is the \(Mn\) concentration and \(p_{abs}\) is the absolute carrier density. The \(p_{abs}\) in our language is similar to the hole density (holes per cm\(^3\)), generally reported in the experiments.

Most of the experimental studies have been devoted in search of room-temperature ferromagnetism using different methods. Post-growth annealing is one of the most extensively used technique which enhances the \(T_c\) by reducing the \(Mn_I\) concentration and in turn increasing the carrier concentration\(^5\). It is important to note that all \(Mn_I\) can not be removed from the sample\(^6\). Even after annealing the fraction of \(Mn_I\) increases beyond 0.2 for \(x \sim 0.1\), putting a limit to the \(T_c\) which either saturates or decreases at larger \(x\). Consequently, the system goes from insulating to metallic and then again to insulating phase with \(x\)\(^7\).

Another route to enhance the \(T_c\) is by p-type and n-type co-doping method that can tune the hole density. It is shown that with Be co-doping both p and \(T_c\) increase for low \(x\) (=0.03), where as for \(x \geq 0.05\) p saturates and \(T_c\) decreases due to the increase in \(Mn_I\) concentration\(^8\). In contrast, in Si co-doped samples \(T_c\) systematically increases with \(x\) even for \(x \geq 0.07\) [Ref. \(^9\)]. It is found that p has lower values in the Si co-doped samples for all values of \(x\). For low \(x\) (\(\leq 0.08\)) samples the \(T_c\) is lower compared to the un-co-doped ones\(^10\) and for higher \(x\) the co-doped sample shows higher \(T_c\). This enhancement in \(T_c\) is attributed to the increase in the hole mobility in the impurity band. In addition, for lower \(x\) (\(\leq 0.08\)) and higher Si co-doped samples both p and \(T_c\) increase as Si start to replace \(Mn_I\) sites.

It is believed that it is necessary to increase \(Mn\) concentration to enhance the \(T_c\), but \(T_c\) decreases beyond \(x_{eff}=0.07\) [Ref. \(^11\)]. So it is important to search a route in which both the \(Mn\) concentration and the hole density can be altered using growth and post-growth technique. In this letter, we investigate this scenario and outline a procedure to enhance \(T_c\) with \(x\). We calculate the ferromagnetic transition temperature within a diluted Kondo lattice model in the intermediate coupling regime using a Monte-Carlo technique based on travelling cluster approximation\(^12\) on large size systems. The ferromagnetic \(T_c\) shows an optimization behavior with \(x\) and \(p_{abs}\), and in the process system undergoes an insulator-metal-insulator transition. Our results qualitatively agree with the recent experiments. We find that optimum \(p_{abs}\), where \(T_c\) is maximum, lies around 0.11 for a wide range of \(x\) (\(=0.1-0.35\)). For a fixed \(p_{abs}\) ferromagnetic \(T_c\) increases with \(x\), which suggests a new pathway to achieve high temperature DMSs.

We consider a particle-hole symmetric diluted Kondo lattice Hamiltonian\(^13\) in 3D. The model is given by

\[
H = - \sum_{\langle ij \rangle \sigma} t_{ij} c_{i \sigma}^\dagger c_{j \sigma} - \frac{J}{2} \sum_k \mathbf{S}_k \cdot \hat{\sigma}_k - \mu \sum_i n_i,
\]

where \(t\) is the nearest neighbor hopping parameter, \(\mu\) is the chemical potential, and \(J > 0\) is the Hund’s coupling between the localized impurity spins \(\mathbf{S}_k\) and the itinerant electrons \(\langle \hat{\sigma}_k \rangle\) at random impurity sites \(k\).
We assume that the \( S_k \) to be classical unit vectors. We have considered simple cubic lattice with one atom per unit cell, where as GaAs is face centered cubic with four atoms per unit cell. So, roughly 25% of \( x \) in our case corresponds to 6.25% that in real experiments. Magnetic moment clustering and hence the direct exchange interaction between the spins are neglected.

In random systems like DMSs the theoretical calculations must adequately a large system size and also able to capture the effects of spatial fluctuations for a better estimation of any physical quantity such as \( T_c \). Spin-ferron Monte-Carlo is an effective approach to take spatial fluctuations into account. An exact diagonalization scheme is applied to the itinerant carriers in the background of randomly located classical spins \( S_k \). In order to avoid size limitation we employ a Monte-Carlo technique based on travelling cluster approximation to handle system size as large as \( N = L^3 = 10^3 \). All physical quantities are averaged over ten different such random configurations. In our particle-hole symmetric model the magnetic and transport properties are presented in terms of the hole density. We set \( t = 1 \) and all other parameters like \( J \), temperature \( T \) are scaled with \( t \).

Magnetic properties in DMSs are consequence of the competition between the carrier mediated ferromagnetic spin-spin interaction and the carrier localization. We start our calculation with a specific choice of \( x = 0.25 \) and \( p = 0.5 \) which is a good starting point for simple cubic lattice. For \( J \sim 0 \) there is no Mn-Mn interaction and for very large \( J \) the carriers are trapped in Mn sites. So ferromagnetism is suppressed in these two extreme limits and the optimal \( T_c \) lies in the intermediate range of \( J \) as shown in Fig.1(a). Carrier localization for higher \( J \) leads to the developments of an impurity like band in the density of states, \( N(\omega) = \langle \sum_j \delta(\omega - \epsilon_j) \rangle \) at relatively high temperature \( T=0.05 \), as shown in Fig.1(b). We estimate \( T_c \) from the ferromagnetic structure factor \( S(0) \), where \( S(q) = \frac{1}{2} \sum_{ij} S_i S_j e^{iq \cdot (r_i - r_j)} \). The ferromagnetic structure factor for \( J=5, x=0.25 \), and \( p=0.5 \) is plotted in Fig.1(c) and the inset shows that \( S(0) \) for \( L=8 \) and \( L=10 \) are barely distinguishable at \( T_c \). So we have considered \( L=8 \) for rest of our calculations.

We obtain the resistivity for different \( J \) values by calculating the dc limit of the conductivity as determined by the Kubo-Greenwood formula as shown in Fig.1(d). At low temperature the system shows metallic behavior for small and intermediate \( J \) values. As \( J \) increases (\( J = 7 \)) the system remains insulating in the whole temperature range due to carrier localization at impurity sites. Hereafter, we concentrate in the intermediate coupling regime (\( J = 5 \)) where \( T_c \) is found to be maximum and relevant to DMSs. Temperature dependence of the resistivity and the ferromagnetic structure factor in Fig.1(c) show one-to-one correspondence between the onset of the ferromagnetism and the metalicity at \( T_c = 0.037 \).

In carrier-mediated magnetic systems a minimum amount of carrier is essential to initiate the coupling between the magnetic spins, which depends on \( J \) and \( x \). On the other hand, for higher carrier density the magnetism is suppressed due to decrease in carrier mobility. The overall behavior of \( T_c \) with \( p \) is shown in Fig.2(a) for \( J=5 \) and \( x=0.25 \). The mobility picture is confirmed from the conductivity calculation, where \( T_c \) and the conductivity (at the low temperature) are maximum at \( p=0.45 \) (see inset). In order to compare our result with the experiment we plot data from Ref. [17] in Fig. 2(b) such that the impurity concentration \( x \) lies in a narrow range from 0.025 – 0.035 which we assume to be constant. Now if we match, the \( T_c \) vs \( p \) behavior in the experiment is very similar to our results. A metal-insulator transition with \( p \) is also observed in the same experiment (not shown here) which we already illustrated the inset of Fig.2(a).

The carrier mobility and hence the ferromagnetism can be tuned with \( J \), \( p \) or \( x \) independently. The carrier-spin interaction \( J \) is only operative at the impurity sites i.e., for fixed \( J \) value the effective coupling strength of the system increases with impurity concentration \( x \). This is similar to the case of increasing \( J \) with keeping \( x \) fixed. So the variation of \( T_c \) with \( x \) for fixed \( p \) values [Fig. 2(c)] can be understood from the \( T_c \) dependence of \( J \) as in Fig. 1(a). We plot the experimental data from Ref. [17] in Fig. 2(d) such that the carrier density \( p \) lies in a narrow range from 0.86 – 0.93. We have neglected this small variation of \( p \) for qualitative comparison with our calculations and...
found that the $T_c$ shows an optimization behavior with $x$, quite similar to our results. It is important to note that if we increase both $x$ and $p$ along the arrow shown in Fig. 2(c) the $T_C$ increases, which-mimics the effect of post-growth annealing on $T_C$.

Fig.3(a) shows the ferromagnetic windows for various values of $x$ in a wide range starting from as small as 10%. We find that the optimal $p$ value where the $T_c$ is maximum decreases with $x$, which is in contrast to the earlier claim where $p=0.5$ is suggested to be the optimum value irrespective of $x$ values. In experiment, both $x$ and $p$ can be changed simultaneously by co-doping method. It is found that $p$ decreases in the Si co-doped samples for all values of $x$. Consequently, for low $x$ ($\leq 0.08$) the $T_c$ decreases as compared to the un-codoped ones and for higher $x$ the co-doped sample has larger $T_c$. To compare our results with the experiment we focus around $p=0.4$ in Fig.3(a) (the dotted line). Now, if we decrease $p$ the transition temperature decreases for lower values of $x$ ($=0.25$ and 0.20) but increases for higher values like $x=0.30$ and 0.35, which captures the experimental results discussed above. Our calculations clearly demonstrate that the $T_c$ can be increased with $x$ provided the $p$ value is tuned properly but not arbitrarily. For $t=0.5$ eV the estimated $T_c$ is 120 K for $x=0.1$ which qualitatively matches with with the experimentally observed $T_c$ range.

It is generally believed that the $p$ value must be maximized to obtain a higher ferromagnetic $T_c$ in DMSs. In Fig.3(a) our calculations show otherwise, that the optimum $p$ value decreases with increasing $x$. To interpret our finding, in Fig.3(b), we re-plot the ferromagnetic windows in terms of the absolute carrier density $p_{abs}$ as defined earlier. Interestingly, we find that the ferromagnetic windows lie on top of each other with optimum $p_{abs}$ around 0.11 for $x=0.35$, which decreases slightly for smaller $x$ values. To understand this we start our discussion from the double exchange (large $J$) limit where carrier spins are aligned in the direction of the core spin. For $x=1$ (spins at each site) carriers get delocalized and the electronic kinetic energy is minimized for the ferromagnetic ground state in the range $0 < p_{abs} < 1$, where the optimum ferromagnetic $T_c$ is found to be at $p_{abs}=0.5$ [Ref. 31]. This we call the optimum $p_{abs}$. The range of ferromagnetic ground state is confined to $0 < p_{abs} < 0.3$ in the intermediate coupling regime and the optimum $p_{abs}$ decreases to $\sim 0.15$ [Ref. 32]. In the diluted limit ($x=0.1-0.35$) we find [see Fig.3(b)] that the optimum $p_{abs}$ value is $\sim 0.11$ which is in the right ball park as compared to the $x=1$ limit. This can be understood within a polaron picture discussed below.

In the double exchange limit for one spin and one carrier problem the carrier remains localized to the core spin. A single site localized polaron is shown schematically as the shaded region in Fig.4(a). In the intermediate coupling regime the carrier localization extends over many lattice sites as shown in Fig.4(b). For a given $x$ a minimum concentration of polarons is required for ferromag-
note that co-doping not only tunes the hole density but also increases the effective $g_{abs}$ and will be helpful to enhance the $T_c$ further. We believe that a systematic combination of experimental processes e.g. doping, annealing, hydrogenation, and co-doping can be designed to prepare DMSs with higher $T_c$.

In conclusion, our model calculations provide a new framework to increase the ferromagnetic $T_c$ in diluted magnetic semiconductors. The optimum $p_{abs}$ (absolute carrier density), where $T_c$ is maximum, lies around $0.11$ and $T_c$ increases with $x$ for fixed $p_{abs}$ in a broad range of $x$ studied in this letter. To replicate such a scenario in the experiment, $p_{abs}$ has to be determined for small $x$ and then effort should be made to increase $x$ without altering the $p_{abs}$ value. This procedure, viable in experiments, would enhance the ferromagnetic $T_c$. We hope that our finding will motivate new experiments by combining the growth and the post-growth process outlined here to achieve high $T_c$ DMSs for spintronics applications.

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