Clustering in disordered ferromagnets: The Curie temperature in diluted magnetic semiconductors

D. J. Priour, Jr. and S. Das Sarma
Condensed Matter Theory Center, Department of Physics, University of Maryland, College Park, MD 20742-4111
(September 8, 2018)

We theoretically investigate impurity correlation and magnetic clustering effects on the long-range ferromagnetic ordering in diluted magnetic semiconductors, such as Ga$_{1-x}$Mn$_x$As, using analytical arguments and direct Monte Carlo simulations. We obtain an analytic formula for the ferromagnetic transition temperature $T_c$ which becomes asymptotically exact in the strongly disordered, highly dilute (i.e. small $x$) regime. We establish that impurity correlations have only small effects on $T_c$ with the neutrally correlated random disorder producing the nominally highest $T_c$. We find that the ferromagnetic order is approached from the high temperature paramagnetic side through a random magnetic clustering phenomenon consistent with the percolation transition scenario.

PACS numbers: 75.50.Pp,75.10.-b,75.10.Nr,75.30.Hx

MOTIVATION AND INTRODUCTION

The effect of disorder on magnetism is an old and important problem in condensed matter physics and materials science. Worldwide current activity in diluted magnetic semiconductors (DMS) where cationic substitutional doping (by a few percent) of a semiconductor with magnetic impurities (e.g. Ga$_{1-x}$Mn$_x$As with $x \approx 0.01 - 0.1$) seemingly leads to an intrinsic ferromagnetic material with a relatively high Curie temperature ($T_c \approx 100K - 200K$), has renewed vigorous recent interest in this important subject. In particular, the intrinsic mechanism of ferromagnetism (i.e. the physics underlying the long-range ordering of the randomly distributed magnetic impurity moments) as well as the precise role of disorder (e.g. arising from the random distribution of magnetic Mn ions at the cation sites in the GaAs lattice) are substantial questions, both from the fundamental perspective of understanding the competition between disorder and magnetic interactions as well as the technological perspective of the fledgling subject of ‘spintronics’ (or spin electronics) where the projected seamless integration of magnetics and electronics on a single ferromagnetic semiconductor chip could lead to a new paradigm in microelectronics.

In this article, we study theoretically the competition between quenched disorder (i.e. the random spatial distribution of the magnetic impurities) and magnetic correlations in DMS materials using analytical arguments supported by extensive large-scale Monte Carlo simulations on a disordered Heisenberg model. Our main findings are that (1) site disorder by itself has a relatively small effect on the magnitude of the DMS ferromagnetic transition temperature $T_c$, and (2) global ferromagnetic ordering in DMS is approached from the high-temperature (i.e. $T > T_c$) paramagnetic phase through the formation of random disconnected magnetic clusters of increasing size as $T$ approaches $T_c$ from above, which coalesce at $T = T_c$ leading to a magnetic percolation transition, similar to what was postulated in ref.5. We believe that our theoretical findings are quite general, and should apply to all diluted site disordered ferromagnetic materials including doped magnetic oxides, which are insulators or poor metals (with short mean free paths comparable to lattice spacings). In particular, we speculate that the results presented herein are sufficiently general to be valid for all site disordered ferromagnets (with localized impurities providing the underlying magnetic moments) in the dilute (or, equivalently, strongly disordered) regime, though we discuss our work entirely in the context of Ga$_{1-x}$Mn$_x$As since this is by far the most extensively studied DMS material experimentally and theoretically.

A key feature of DMS materials is that the ferromagnetic interaction between the impurity magnetic moments is an indirect exchange interaction mediated by the semiconductor carriers (which are holes in Ga$_{1-x}$Mn$_x$As). The ‘standard’ model for DMS ferromagnetism was developed more than forty years ago, and has recently been rediscovered. This model, which we refer to as the VCA model, is a simple mean-field model in both the spatial disorder (i.e. a continuum virtual crystal approximation, VCA) and the thermal fluctuations (i.e. a Curie-Weiss mean field theory for the ferromagnetic ordering of the impurity moments) with the magnetic interaction between the impurity moments being mediated by the indirect exchange interaction arising from the carrier-induced RKKY-Zener mechanism. Although the extreme simplicity of the VCA model, for example its analytic prediction of $T_c \propto m J_{pd}^3 n_h c^3 x$ (where $J_{pd}$ is the effective p-d exchange interaction strength between the p-type holes in GaAs and the Mn d-level, and $m$, $n_h$, $c$ are the effective hole mass and density, respectively), has led to its widespread application in the DMS literature, we emphasize here that the model is conceptually wrong since it predicts a monotonically increasing ferromagnetic transition temperature with increasing carrier density, impurity density, and magnetic coupling strength - in fact, all three trends are conceptually incorrect (and the simple VCA model provides no mechanism for estimating its regime of validity in the $J_{pd}$, $n_h$, $x$, $T$, and...
where \( S \) is the range of the RKKY function. The large value (the Mn spins as classical Heisenberg spins. Hence, our dimensions by \( J \) approaches magnets can also be viewed in terms of a limiting the-

important refinement in addressing the discrete crystal neglect of site disorder and thermal fluctuations. We also find that in the strong disorder limit (i.e. highly diluted case of \( x \ll 1 \)), where the VCA fails most miserably, \( T_c(J_{pd}, x, n_c) \) has a qualitatively different behavior than that predicted by the standard DMS VCA mean field theory.

**ASPECTS OF THE CALCULATION**

We assume Mn ions randomly occupy only Ga sites in the GaAs zinc-blende lattice (fcc) with a lattice constant \( a \). We operate in the (weakly) metallic limit and assume the carrier-mediated effective Mn-Mn indirect exchange interaction to be of the RKKY form. However, with DMS systems being at best poor or bad metals with a mean free path typically of the order of 1-2\( \AA \) which is less than \( a \), it is important to include the effects of a finite carrier mean free path; we do this by introducing a cutoff \( l \lesssim a \) in the range of the RKKY function. The large value (\( S = 5/2 \)) of the impurity moment spins allows a treatment of the Mn spins as classical Heisenberg spins. Hence, our Hamiltonian is given by

\[
\mathcal{H} = \sum_{ij} J(r_{ij}) \mathbf{S}_i \cdot \mathbf{S}_j, \tag{1}
\]

where \( r_{ij} \) is the separation between moments \( i \) and \( j \), and \( J(r) \) is the damped RKKY range function given in three dimensions by

\[
J(r) = J_0 e^{-r/l} r^{-4} |\sin(2k_F r) - 2k_F r \cos(2k_F r)|; \tag{2}
\]

\( k_F = (\frac{2\pi^2 n_c}{l})^{1/3} \) is the Fermi wave number and \( n_c \) is the hole density. \( J_0(> 0) \) is related to the local Zener coupling \( J_{pd} \) between the Mn local moments and hole spins, \( J_0 \propto m J_{pd}^2 \) where \( m \) is the hole effective mass (for convenience, spin units are used with the factor \( S^2 = (5/2)^2 \) absorbed into \( J_0 \)). While \( l \) sets the range of interaction between moments, \( l_s = n_i^{-1/d} \) (where \( n_i \) is the volume Mn density) gives the mean inter-impurity separation and provides a measure of the disorder strength with \( l_s \approx a \) for weak disorder and \( l_s \gg a \) for strong disorder. Note that by definition the strong disorder limit is equivalent to the dilute limit, which is the situation appropriate for DMS materials. For weak disorder with a long range interaction (i.e for \( l \gg \{l_s, a\} \)), Curie Wiess Mean Field Theory (MFT) fares well (though lattice MFT\(^{11} \) is an important refinement in addressing the discrete crystal structure); we show here that strongly disordered ferromagnets can also be viewed in terms of a limiting theory in which the Curie temperature asymptotically approaches

\[
T_c = \frac{\eta}{k_B} J(2r_c n_i^{-1/d}), \tag{3}
\]

where \( \eta \) is a constant of order unity and \( r_c \) is the dimensionless critical radius for random sphere percolation with \( r_c = 0.4436^{12} \). We concentrate entirely on the currently experimentally relevant three-dimensional (\( d = 3 \)) DMS systems in this paper). It is clear that this \( T_c \) expression, \( T_c \approx J(n_i^{-1/d}) \), bears little resemblance to the VCA result \( T_c \propto n_i \int J(r) d^d r \).

To calculate quantities such as \( T_c \) and the spontaneous magnetization \( \mathbf{M} \), we use a hybrid Monte Carlo technique combining Wolff Cluster\(^{13} \) and Heat Bath\(^{14} \) moves. The Wolff moves overcome critical slowing down near \( T_c \), and Heat Bath moves ensure that ergodicity is attained efficiently by thermalizing spins weakly coupled to their neighbors. We calculate \( T_c \) by locating the crossing temperature of Binder cumulants \( U^{15} \) for two different system sizes; in our case, \( U = 1 - (1/3)\langle |\mathbf{M}|^4 \rangle/\langle |\mathbf{M}|^2 \rangle^2 \), where angular and square brackets denote thermal and disorder averaging, respectively. Since we invariably have \( \langle N_{imp} \rangle = n_s L^d \geq 2 \times 10^4 \), we have found it useful to exploit our large system sizes; calculating magnetization moments \( |\mathbf{M}|^i \) by simply raising the total magnetization \( \mathbf{M} \) to the \( i \)th power disposes of information that can be gleaned by dividing the system into \( n_s \) subsystems and averaging \( |\mathbf{M}|^i \) evaluated for each of these. \( (n_s = \langle N_{imp}\rangle^{1/2} \) has proven to be a reasonable choice). Operating in this manner, we use as few as 50 total Monte Carlo sweeps \( (n_{eq} = 25 \) for equilibration and \( n_{eq} = 25 \) for statistical sampling) with no compromise in accuracy. We have checked for each calculation the adequacy of the equilibration stage by comparing “cold starts” (systems prepared with perfect ferromagnetic order) and “hot starts” (systems with initially randomized spins), finding in each case agreement to within random statistical error (confined to less than 1% for all results reported here).

**CORRELATED MAGNETIC MOMENTS**

Relaxing the requirement that magnetic impurities reside on the discrete fcc lattice in favor of continuously distributed Mn is a simple way to examine the sensitivity of the ferromagnetic state to how the Mn ions are distributed. In principle, the discrete and continuum cases represent very different situations. Even so, it its evident in Figure 1 that Curie temperatures for the discrete \( (T_c^{\text{lat}}) \) and continuum \( (T_c^{\text{cont}}) \) cases (shown for more than a decade of \( x \) values) are in close agreement. The main graph shows critical temperatures directly for \( l/a = 0.5 \), inset (a) depicts the ratio of continuum and lattice \( T_c \)'s for \( l/a = 0.5 \), and inset (b) displays the same result for the even smaller cutoff \( l/a = 0.25 \). In the continuum model, it is possible for magnetic impurities to cluster more tightly than in the discrete case, and the spins in such clusters are therefore more strongly aligned. However, the enhanced intra-cluster coupling of the compact clusters tends to be offset by a weaker coupling to neigh-
boring spins (since the overall constancy of \( x \) requires that compact structures be more isolated, on average, than more diffuse Mn assemblies). The close agreement of \( T_{c}^{\text{cont}} \) and \( T_{c}^{\text{lat}} \) in Figure 1 suggests that these two effects nearly precisely cancel. It is important to note that the close similarity of continuum and discrete \( T_{c} \)'s does not justify the VCA result. The latter, given by

\[
T_{c}^{\text{VCA}} = 4\pi \frac{J_{0}}{3} x \int r^{2} J(r) dr
\]

does not take into account thermal and disorder fluctuations (important in the dilute DMS regime). The disparity between the VCA and Monte Carlo results is nearly precisely cancel. It is important to note that the close agreement in panel (c) of Figure 1, and is even greater if the damping factor \( e^{-r/l} \) is not taken into account.

![Graph](image)

**FIG. 1.** In the main graph, \( T_{c}^{\text{cont}} \) (continuum) and \( T_{c}^{\text{lat}} \) (discrete) are graphed with continuum \( T_{c} \)'s shown as closed circles and discrete \( T_{c} \)'s plotted as open circles; \( n_{c}/n_{i} = 0.1 \) and \( l/a = 0.5 \). In inset (a), ratios \( T_{c}^{\text{cont}} / T_{c}^{\text{lat}} \) are shown; again, \( n_{c}/n_{i} = 0.1 \) and \( l/a = 0.5 \). The graph in inset (b) shows \( T_{c}^{\text{cont}} / T_{c}^{\text{lat}} \) for \( n_{c}/n_{i} = 0.1 \) and \( l/a = 0.25 \) with the horizontal dark reference line indicating unity. Panel (c) shows VCA (solid and broken lines for damped and undamped cases, respectively) and Monte Carlo \( T_{c} \)'s on the same graph with \( n_{c}/n_{i} = 0.1 \) and \( l/a = 1.0 \) (the damping refers to the inclusion of mean free path effects).

**impurity clustering**

To examine impurity correlations in a way that is continuously tunable, we introduce a local attractive interaction between impurity moments yielding the configurational energy \( E_{\text{conf}} = -E_{0} \sum_{n_{n}}(\text{bonds}) \) where \( \sum_{n_{n}}(\text{bonds}) \) is the total number of bonds shared by neighboring Mn ions. We prevent the formation of a single large cluster by limiting the lateral dimension of clusters, requiring in this case that the size along any axis be smaller than \( a \). We vary the extent of impurity clustering via an annealing temperature \( T_{A} \); large \( T_{A} \) values lead to weaker clustering, while in the low \( T_{A} \) limit, impurities tend to be more exclusively bound in the complexes mentioned above. Configurations are prepared by subjecting initially neutrally correlated samples to an equilibration stage at \( T_{A} \) (consisting of 500 Metropolis sweeps), and the extent of clustering in the resulting sample is characterized by \( \langle n_{\text{size}} \rangle \), the mean cluster size. Impurity moments locked in clusters tend to align due to their proximity, but the large inter-cluster spacings makes the alignment of cluster moments with each other more readily disrupted by thermal fluctuations. In fact as \( x \) is decreased, one ultimately obtains an essentially paramagnetic state composed of large but very weakly coupled cluster moments. In Fig. 2(a) and Fig. 2(b) the impact of clustering on \( T_{c} \) is shown for two different Mn concentrations \( x \) for clustering ranging from very weak to quite strong. For \( x = 0.03 \) (the case depicted in Fig. 2(a)), the overall Mn density is sufficiently low that one does see a slight diminution of \( T_{c} \) for increasing clustering. However, when \( x \) is doubled to \( x = 0.06 \) (shown in Fig. 2(b)), the \( T_{c} \) curve is essentially flat. Hence, even for fairly small Mn densities, the effects of enhanced intra-cluster alignment and diminished inter-cluster coupling are roughly the same in magnitude, leading to a weak net effect. Thus impurity correlation or clustering does not seem to have much effect on \( T_{c} \). We mention as an important caveat that in Ga\(_{1-x}\)Mn\(_{x}\)As, two closely placed Mn ions (e.g. a substitutional and interstitial Mn atom in the same unit cell) experience very strong nearest-neighbor short-range direct antiferromagnetic exchange coupling. This would lead to a strong suppression of ferromagnetic \( T_{c} \) at large values of \( x \) if there is substantial Mn clustering. This effect is not included in our model.
impurity superlattices

In a sense opposite to inducing impurity clustering is arranging Mn ions in superlattices, which tends to break up impurity clumps to form a homogeneous lattice. Again, we begin with perfect superlattices and introduce deviations by annealing at the “disordering temperature” $T_{\text{dis}}$; the mean displacement of impurities $\langle r_d \rangle$ from their sites on the superlattice characterizes the resulting configuration (very small values of $\langle r_d \rangle$ correspond to nearly perfect superlattices while $\langle r_d \rangle \sim a$ indicates an essentially “melted” state with randomized impurities). Curie temperatures for a broad range of $\langle r_d \rangle$ are shown in panel (c) of Fig. 2 (our superlattice is simple cubic with lattice constant 2$a$, which corresponds to $x = 0.031$). While the calculated $T_c$ in (c) slightly increases as the superlattice is disrupted, the effect is relatively modest, consistent with previous work comparing random disorder and pure superlattice configurations.\textsuperscript{17,18} The results suggest that while an excessive degree of clustering can lower $T_c$, the absence of any inhomogeneities in the impurity configurations is also deleterious to the ferromagnetic state. As the transition is made from a perfect superlattice to more disordered configurations, more and more impurities are displaced and can act as a bridge between neighboring superlattice sites, thereby increasing the effective coupling between neighboring Mn ions still occupying superlattice sites. Ultimately, the $T_c$ curve saturates for large $\langle r_d \rangle$ where superlattice modulations vanish. It thus appears that the uncorrelated impurity distributions occupy a “happy” medium with a critical temperature higher than that of either strongly clustered configurations or states with superlattice structure. Thus random disorder modestly enhances DMS $T_c$.

THE STRONG DISORDER LIMIT

Finally, we examine the regime of very strong disorder (i.e., $l_s \gg \{l, a\}$), finding that the Curie temperature exhibits well-defined asymptotic behavior in the large $l_s$ limit corresponding to the percolation of randomly placed spheres. We first exploit the strong similarity of the behavior of discrete and continuum systems shown in Figure 1 by relaxing the discrete occupancy requirement, although this condition is still imposed in the numerical calculations. For convenience, we rescale the linear dimensions in such a way that $l_s$ is equal to unity, thereby mapping our problem to a new ferromagnetic system where the range of $J(r')$ is shortened to $l = l/l_s$. Hence, for large $l_s$, $J(r')$ varies quite rapidly and as a result the coupling between pairs of spins tends either to be very large or very small. The strong disorder limit thus can be viewed as the regime in which spins even slightly closer than the “correlation radius” $r_{\text{corr}}$ are strongly correlated whereas for separations greater than $r_{\text{corr}}$, the coupling rapidly becomes small relative to $k_B T$. This is essentially a real space renormalization group (RG) argument for the scaling of the spin coupling. This observation motivates a comparison with the problem of randomly placed spheres (distributed with unit density $n = 1$), which form percolating networks when their radii exceed $r_c$; it is natural to identify the critical value of $r_{\text{corr}}$ with $2r_c$ and to write $k_B T^* = J(r_{\text{corr}})$ for the ferromagnetic transition temperature.\textsuperscript{19} However, a constant $\eta$ of order unity is needed to take thermal fluctuations into account and one actually has $T_c = \frac{\eta}{l_s} J(2r_c l_s)$, where the final form is expressed in terms of the original, unmodified units. Our MC simulations give essentially exact (within $1-2\%$) quantitative agreement (shown in Fig. 3 for the $x = 0 - 0.1$ range we checked) between the numerical MC $T_c$ results and the theoretical $T^*$ with both showing essentially singular $x^{4/3} \exp(-\alpha x^{-1/3})$ behavior for small $x$.

![Monte Carlo: ○ Theory: —](image)

FIG. 3. The graph shows together the numerical MC $T_c$ results (open circles) and the theoretical $T^*$ (solid line) for $n_c/n_s = 0.1$ and $l/a = 0.5$.

We show explicitly in Fig. 4 that the approach to $T_c$ from above is marked by the formation of magnetic clusters of correlated spins by visualizing these clusters using the Swendsen-Wang algorithm\textsuperscript{21} (which partitions the entire system into spin clusters). To facilitate view-

![Graph](image)
ing, we examine a 2D system, a dilute site-disordered Ising model, where \((x = 0.05\) and \(l/a = 1.0\)). In Fig. 4, Swendson-Wang snapshots are depicted for four temperatures. One can see the merging of disconnected clusters to form a spanning cluster at \(T_c\), though substantial clustering occurs even well above \(T_c\). This is very similar to the magnetic polaron percolation picture of DMS ferromagnetism theoretically envisioned in Ref.\(^5\) and the qualitative discussion in Refs.\(^{17,18}\). We point out, however, that the \(T_c\) formula in our RG argument (validated by our MC simulations) differs somewhat from the corresponding percolation theory result\(^5\). We emphasize that although our discussion has been in the DMS context, our arguments are not dependent on particular traits of the RKKY range function.

![Swendson-Wang snapshots](image)

FIG. 4. The four panels (a,b,c, and d) display clusters of correlated spins for \(x = 0.05\), \(J(r) = J_{0}e^{-r/l}\) where \(l/a = 1.0\). Each panel corresponds to a different temperature with \(T/T_c = \{4.0, 2.0, 1.0, 0.5\}\) for (a), (b), (c), and (d) respectively. Dark/open circles represent “up”/“down” spins.

**CONCLUSIONS**

In conclusion, we have examined the effect of impurity correlation in diluted magnetic semiconductors. We find that the presence of correlations among impurity positions affects the critical temperature \(T_c\) only mildly, with the calculated \(T_c\) being optimal for neutral impurity correlations (i.e. random disorder). In addition, we have verified via explicit numerical calculation that just as ferromagnetic behavior in the weak disorder mean field limit is amenable to mean field approaches, the strong disorder regime also can be understood in terms of a limiting theory, random sphere percolation. We develop a new theory for the dependence of \(T_c\) on the magnetic impurity density by mapping the discrete random problem to a continuum problem using real space RG arguments, and validate the theory by Monte Carlo simulations. This work is supported by US-ONR.

1. S. Das Sarma, E. H. Hwang, and A. Kaminski, Solid State Comm. 127, 99 (2003).
2. C. Timm, J. Phys. Condens. Matter 15, R1865 (2003).
3. A.H. MacDonald, P. Schiffer, and N. Samarth, Nature Materials 4, 195 (2005).
4. I. Zutic, J. Fabian, and S. Das Sarma, Rev. Mod. Phys. 76, 323 (2004).
5. A. Kaminski and S. Das Sarma, Phys. Rev. Lett. 88, 247202 (2002).
6. S. B. Ogale, R. J. Choudhary, J. P. Buban, S. E. Løfland, S. R. Shinde, S. N. Kale, V. N. Kulkarni, J. Higgins, C. Lanci, J. R. Simpson, N. D. Browning, S. Das Sarma, H. D. Drew, R. L. Greene, and T. Venkatesan, Phys. Rev. Lett. 91, 077205 (2003).
7. J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, Nature Materials 4, 233 (2005).
8. A. Abrikosov and L.P. Gorkov, Zh. Eksp. Teor. Fiz. 43, 2230 (1962) [Sov. Phys. JETP 16, 1575 (1963)].
9. T. Dietl, H. Ohno, and F. Matsukura, Phys. Rev. B 63, 195205 (2001).
10. A. Chattopadhyay, S. Das Sarma, and A. J. Millis, Phys. Rev. Lett. 87, 227202 (2001).
11. D. J. Priour, Jr., E. H. Hwang, and S. Das Sarma, Phys. Rev. Lett. 92, 117201 (2004).
12. C. D. Lorenz and R. M. Ziff, J. Chem. Phys. 114, 3659 (2001).
13. U. Wolff, Phys. Rev. Lett. 62 361 (1989).
14. Y. Miyatake, M. Yamamoto, J. J. Kim, M. Yoyonaga, and O. Nagai, J. Phys. C 19 2539 (1986).
15. K. Binder, Z. Phys. B 43, 119 (1981).
16. S. Das Sarma, E. H. Hwang, and D. J. Priour, Jr., Phys. Rev. B 70, 161203(R) (2004).
17. M. Mayr, G. Alvarez, and E. Dagotto, Phys. Rev. B 65, 241202(R) (2002).
18. G. Alvarez and E. Dagotto, J. Magn. Magn. Mater 272, 15 (2004).
19. I. Y. Korenblit et al., E. F. Shender, and B. I. Shklovskii, Phys. Rev. Lett. 46A, 275 (1972).
20. A. Kaminski, V. M. Galitski, and S. Das Sarma, Phys. Rev. B 70, 115216 (2004).
21. R.H. Swendsen and J. S. Wang, Phys. Rev. Lett 58, 86 (1987).