Transition Temperature of Ferromagnetic Semiconductors: A Dynamical Mean Field Study

A. Chattopadhyay,[1,3] S. Das Sarma,[2] and A. J. Millis[3]

[1]*IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120*

[2]*Department of Physics, University of Maryland, College Park, Maryland 20742*

[3]*Center for Materials Theory, Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854*

(Received 22 June 2001; published 8 November 2001)

We formulate a theory of doped magnetic semiconductors such as $Ga_{1-x}Mn_xAs$ which have attracted recent attention for their possible use in spintronic applications. We solve the theory in the dynamical mean field approximation to find the magnetic transition temperature T_c as a function of magnetic coupling strength J, carrier density n, and Mn density x. We find that T_c is determined by a subtle interplay between carrier density and magnetic coupling.

DOI: 10.1103/PhysRevLett.87.227202 PACS numbers: 75.30.Mb, 71.27.+a, 75.20.Hr

Diluted magnetic semiconductors have attracted much recent attention [1] for their potential use in spintronic devices. The prospect of carrying out both information processing and storage on the same chip is an exciting possibility. For applications it is desirable to find materials which are ferromagnetic at as high a temperature as possible, so the discovery [2] of a ferromagnetic transition with T_c as high as 110 K in molecular beam epitaxy grown $Ga_{1-x}Mn_xAs$ has inspired a great deal of interest. In addition to its potential technological significance, the ferromagnetism of $Ga_{1-x}Mn_xAs$ is an important fundamental condensed matter problem. The cause of ferromagnetism in $Ga_{1-x}Mn_xAs$ (and similar materials, e.g., $In_{1-x}Mn_xAs$ where $T_c \approx 25-30$ K [2]) is controversial: the different proposed mechanisms [3–9] do not qualitatively agree with each other. In this paper we present a new theoretical approach which allows calculation of magnetic transition temperatures (and other properties) over a much wider temperature range than had previously been possible and provides new insights into the factors controlling T_c.

It is well established that in III-V systems such as $Ga_{1-x}Mn_xAs$, the Mn ions go in substitutionally at the cation (Ga) sites and contribute itinerant holes to the GaAs valence band. The experimental hole density n is typically a small fraction (10% or so) of the Mn concentration perhaps due to strong localization at As antisite defects [2] so the $Ga_{1-x}Mn_xAs$ system could be considered partially compensated. The Mn ion has a half-filled d-shell and acts as a $S = 5/2$ local moment; the itinerant carriers are locally magnetically coupled to the Mn spins via an exchange coupling J. Band theory [10] suggests that in GaAs:Mn $J > 0$ (antiferromagnetic) for electrons and $J < 0$ for holes (relevant case). Our results are independent of the sign of J.

It is generally accepted [1–10] that the magnetic semiconductors are described by the model:

$$H_{\mathrm{KL}} = \sum_{i,j} J_{\mathrm{AF}}(R_i - R_j)\mathbf{S}_i \cdot \mathbf{S}_j + \sum_{u\alpha} \int d^3x\, \psi^+_{pu\sigma}(x)\left(\frac{-\nabla^2}{2m_u} + V_r(x)\right)\psi_{pu\sigma}(x) + \int d^3x \sum_{iu\alpha\beta} W(x - R_i)\psi^+_{u\alpha}(x)\psi_{u\alpha}(x) + J\mathbf{S}_i \cdot \psi^+_{u\alpha}(x)\sigma_{\alpha\beta}\psi_{u\beta}(x)b^3\delta^3(x - R_i), \quad (1)$$

where u labels the relevant bands of the semiconductor (the two hole bands in hole-doped GaAs, for example), V_r is a potential arising from randomness in the host lattice (e.g., As antisite defects), R_i are the positions of the Mn dopants, W is the (presumably Coulombic) potential arising from the Mn dopant, J_{AF} is a direct antiferromagnetic exchange between Mn spins arising from other orbitals unrelated to the doped holes, J is the local exchange coupling between the spin of the Mn and the spins of the semiconductor carriers, and σ is the Pauli matrix. We normalize the δ function in the J term to the volume $b^3 = (3.56\ \text{Å})^3$ per GaAs unit. The large ($\mathbf{S} = 5/2$) value of the Mn spin justifies treating the spins classically, so the partition function Z may be determined by finding the free energy $F(\{\mathbf{S}_i\})$ of holes in a fixed spin configuration and then averaging over spin configurations, i.e.,

$$Z = \int \{d\mathbf{S}_i\} e^{-[\sum_{i,j} J_{\mathrm{AF}}(R_i - R_j)\mathbf{S}_i \cdot \mathbf{S}_j + F(\{\mathbf{S}_i\})]/k_BT}. \quad (2)$$

The key issue is therefore the evaluation of $F(\{\mathbf{S}_i\})$. From Eq. (1), we see that F is the free energy of noninteracting carriers in a spin dependent potential, which may have randomness both from the distribution of Mn positions and from spin disorder. Further, as will be shown explicitly below, the relevant temperatures are small compared to the hole Fermi energy (E_F), so that F is to a good approximation simply the carrier ground state energy in the given spin configuration. The crucial quantity governing T_c is the *change* in F as the spin configuration goes from disordered to ordered. As we will show below, the change in F

involves several competing effects not evident in previous calculations of T_c such as the static mean field theory [5].

In this paper we study in detail the idealized Kondo lattice model, in which $J_{\rm AF}$, V_r, and W in Eq. (1) are neglected. These may easily be included in our formalism, and will be discussed in a future paper. We absorb the magnitude of the spin into the definition of J and study first the $T \to 0$ limit of the fully polarized ferromagnetic state, $\mathbf{S}_i \parallel \hat{z}$ at $T = 0$. In this state the carriers feel a spatially varying spin dependent potential with mean strength $\propto xJ$ per GaAs unit cell, for a Mn concentration x. It leads to a shift in the band offset (upwards for one species and downwards for the other) proportional to xJ. For values of J less than a critical value J_c, the spin dependent potential does not lead to any bound states. The wave functions are scattering states and the band offset is of order $\pm xJ$. The energy is given simply by filling the up and down bands to the appropriate chemical potential. The critical value J_c corresponds to a magnetic coupling strong enough to bind a hole of the appropriate spin to a Mn site, causing a "parallel-spin" impurity band to split off from the main band. Sanvito *et al.* [10] used the local spin density approximation (LSDA) and supercell methods to study $Ga_{1-x}Mn_xAs$ with a dilute but spatially ordered Mn lattice. The LSDA prediction for J was stated to be very close to the critical value needed for impurity band formation.

We now consider energetics of arbitrary spin configurations. In the small J limit, perturbation theory shows that

$$\delta F = \frac{1}{2}\sum_{ij} J^2 \chi(R_i, R_j)\mathbf{S}_i \cdot \mathbf{S}_j \qquad (3)$$

with $\chi(R_i, R_j)$ the static spin susceptibility computed from Eq. (1) with $J = 0$. This is often referred to [3–5] as the "RKKY" limit although strictly speaking the term RKKY refers to the behavior of χ at distances long compared to the spacing between carriers and Eq. (3) applies even for spins closer together than this distance. When Eq. (3) applies, the ordering wave vector is the one that maximizes χ and $T_c \sim J^2$, which is also the static mean field result [5]. Note that for n greater than a (numerically small but band-structure dependent) critical value n_c, the maximum in χ is at a nonzero wave vector, leading to a nonferromagnetic ordered state.

In the $J \to \infty$ limit, at all times each carrier is bound to an Mn site with a binding energy proportional to J and spin parallel to the Mn spin on that site. The dependence of energy on spin configurations arises because in the paramagnetic state some hopping processes are blocked [11] and are therefore set by the impurity bandwidth which is never large (because the Mn are dilute) and vanishes as $J \to \infty$ due to the contraction of the Bohr radius of the bound state. In this limit T_c depends crucially on the impurity band filling. For a full impurity band (one carrier per Mn) no low energy hopping processes are possible in a fully polarized ferromagnetic state; the ground state for a filled or nearly filled impurity band is antiferromagnetic or phase separated. The static mean field theory [5,6] does not capture this physics at all, predicting instead a $T_c \sim J^2$ for all J.

We now present a dynamical mean field theory which gives a reasonable account of the small and intermediate J regime as well as the crossover to the "impurity band" regime. It, however, does not adequately treat the band narrowing arising from extreme wave function localization so breaks down at some $J \gg J_c$. We model the GaAs:Mn system as a lattice of sites, which are randomly nonmagnetic (with probability $1 - x$) or magnetic (with probability x). Standard arguments [12] show that the relevant physics may then be determined from the local (momentum-integrated) Green function $\mathbf{G}^{a,b}_{\rm loc}(\omega) = b^3 \int \frac{d^3p}{(2\pi)^3}[\omega - \Sigma^{a,b}_{\alpha\beta}(\omega) - \varepsilon_{pa}]^{-1}$. $G_{\rm loc}$ is in general a matrix in spin and band (not shown) indices and depends on whether one is considering a magnetic (a) or nonmagnetic (b) site. Being a local function, it is the solution of a local problem specified by the partition function $Z_{\rm loc} = \int d\mathbf{S} e^{-S_{\rm loc}}$ with action $S_{\rm loc} = g^a_{0\alpha\beta}(\tau - \tau')c^+_{a\alpha}(\tau)c_{a\beta}(\tau') + J\mathbf{S}\cdot\sum_{a\alpha\beta} c^+_{a\alpha}(x)\boldsymbol{\sigma}_{\alpha\beta}c_{a\beta}(x)$ on the a (magnetic) site and $S_{\rm loc} = g^b_{0\alpha\beta}(\tau - \tau')c^+_{a\alpha}(\tau)c_{a\beta}(\tau')$ on the nonmagnetic (b) site. The a-site mean field function g^a_0 can be written as $g^a_{0\alpha\beta} = a_0 + a_1\hat{m}\cdot\boldsymbol{\sigma}_{\alpha\beta}$ with $\hat{m}$ the magnetization direction and a_1 vanishing in the paramagnetic state. It is specified by the condition that the local Green function computed from $Z_{\rm loc}$, namely $\delta \ln Z_{\rm loc}/\delta g^a_0 = (g^a_0 - \Sigma)^{-1}$ is identical to the local Green function computed by performing the momentum integral using the same self-energy. The momentum integral requires an upper cutoff because the $p^2/2m$ dispersion given in Eq. (1) applies only near the band edges. We take the density of states as a semicircle, $N(\varepsilon) = b^3 \int \frac{d^3p}{(2\pi)^3}\delta(\varepsilon - \varepsilon_p) = \sqrt{4t^2 - \varepsilon^2}/2\pi t^2$ with parameter t chosen to give a bandwidth of order the full GaAs bandwidth ($\sim$10 eV) implying $t \sim 2.5$ eV. This choice of cutoff corresponds to a Bethe lattice in infinite dimensions; the crucial point is that it has the correct qualitative behavior and correct order of magnitude of the density of states in the region of order J of the band edge. Then g_0 obeys the equation $\mathbf{g}^a_0(\omega) = \mathbf{g}^b_0(\omega) = \omega + \mu - xt^2\langle[\mathbf{g}^a_0(\omega) + J\mathbf{S}\cdot\boldsymbol{\sigma}_{\alpha\beta}]^{-1}\rangle - (1 - x)t^2\mathbf{g}^b_0(\omega)^{-1}$ where the angular brackets denote averages performed in the ensemble defined by the appropriate $Z_{\rm loc}$.

The solution of the equation depends crucially on J/t, x, and T. The inset of Fig. 1 shows the majority-spin density of states corresponding to the $T = 0$ ferromagnetic state. For small J we see the expected shift proportional to xJ. For $J > J_c = t$ an impurity band centered at $\sim -J$ and containing x states is seen to split off from the main band. The dynamical mean field theory J_c is in good numerical agreement with the results of [10]; this and the obviously correct qualitative behavior confirms its reliability in the experimentally relevant regime.

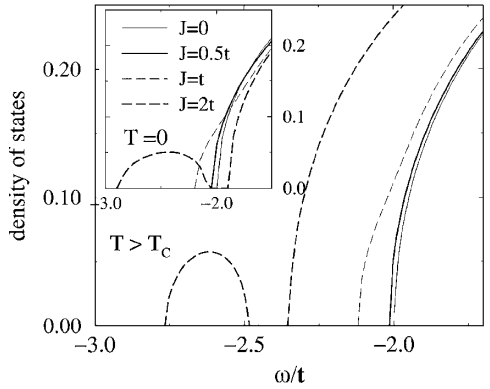

FIG. 1. Main panel: Density of states at $T > T_c$ for $J = 0$, $0.5t$, t, and $2t$. Inset: Majority-spin density of states at $T = 0$ for the same parameter values.

As the temperature is increased, the spins disorder and eventually the magnetic transition temperature is reached. Above this temperature, g_0 is spin independent. The main panel of Fig. 1 shows the density of states for $T > T_c$. For $xJ^2/(t^2 - J^2) \ll 1$ there is a small spin independent band offset of size $xJ^2/(t^2 - J^2)$. For $J > t$ an impurity band forms, corresponding to carriers locally parallel to Mn spins.

The ferromagnetic transition temperature T_c may be obtained by linearizing the equation in the magnetic part of g_0, leading to an implicit equation for T_c.

$$1 = \sum_n \frac{-2t^2(xJ)^2/3}{(g_0^2 - x^2J^2)^2(1 - t^2/g_0^2) - xJ^2t^2(5/3 - J^2/g_0^2)}, \tag{4}$$

where temperature is contained in the Matsubara sum over the frequency ω_n on which g_0 depends.

Figure 2 shows the electron density dependence of the magnetic transition temperature for $J = 0.5t$ (less than the critical value for impurity band formation), $J = t$ (the critical value for impurity band formation), and $J = 1.5t$ and $2t$ (where the impurity band is well formed). The striking feature, evident in all three curves, is the nonmonotonic behavior of the transition temperature.

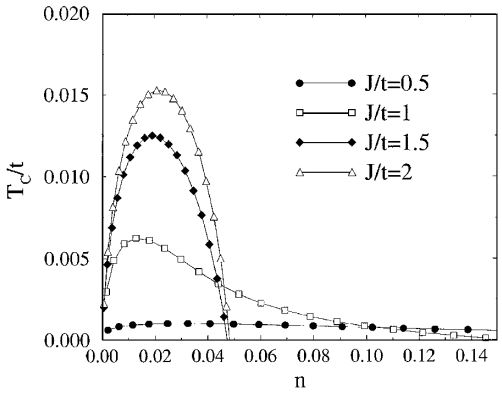

FIG. 2. Calculated transition temperature vs carrier concentration for $x = 0.05$ and various J values as shown.

This has different origins in different regimes. For $xJ^2/(t^2 - J^2) < 1$ an analytic solution for T_c may be obtained. The details will be presented elsewhere; one result is that the density $n^{\max}$ at which T_c is maximized is $n^{\max} = \frac{1}{\pi}(2 - \sqrt{3 + 2J^2/t^2 - J^4/t^4})^{3/2} + \mathcal{O}(xJ^2/(t^2 - J^2)) \approx 0.04 - \mathcal{O}(J/t)$. Thus, in this limit the T_c maximum is a consequence of structure in the underlying electronic susceptibility. The precise position depends on the cutoff, but is very low. For $J > t$ the physics is dominated by the spin-polarized impurity band. In this limit T_c is controlled by the delocalization energy in the impurity band, and is therefore maximized when the band is half filled. In a filled impurity band ($n = x$) no low energy hopping processes are allowed in a ferromagnetic state, whereas in an antiferromagnetic state hopping is allowed with amplitude $x^{1/2}t/\Delta$ where $\Delta \sim J$ is the gap between the impurity and conduction band. This physics implies that very near the filled impurity band limit, the ground state is antiferromagnetic. As Δ increases the window of antiferromagnetism decreases.

Figure 3 shows the magnetic transition temperature as a function of magnetic coupling J for different hole densities ranging from $n_h = 0.1/\mathrm{Mn}$ to $1/\mathrm{Mn}$ (in our conventions, $n = xn_h$). The collapse in T_c for the filled band is evident. The physically evident decrease of T_c at very large J due to the decrease of impurity state Bohr radius is not captured by our model, so we expect that for $J > 2t$ our calculation overestimates T_c.

Figure 4 shows the dependence of T_c on Mn concentration x for $J = t$, a value of the order of the LSDA estimate. We see that simultaneous increases in the Mn concentration (by, say, a factor of 2) and the density (by, say, a factor of 4) should increase T_c by more than a factor of 2.

We compare our results to the predictions of other means of calculation. The "Weiss mean field theory" [5] applied to our model predicts $T_c = xn^{1/3}J^2/t$ at all n, J. In the limit $xJ^2/(t^2 - J^2) < 1$ and $n^{\min} < n < n^{\max}$

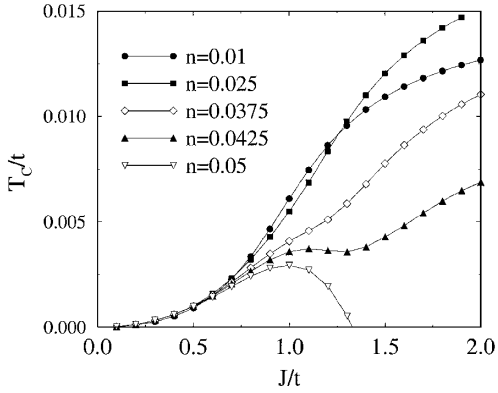

FIG. 3. Calculated T_c as a function of the local exchange coupling J for a fixed value ($x = 0.05$) of the Mn concentration and for different values of the hole density per Mn ion, n_h. T_c saturates as $J \to \infty$, but as explained in the text, at large J the T_c value is overestimated.

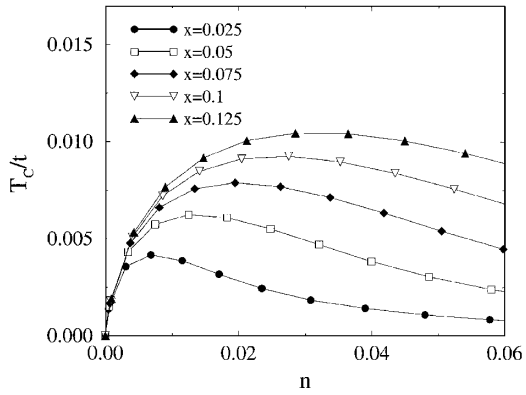

FIG. 4. Variation of T_c with n at various Mn concentration x and $J = 1$.

our analytic solution of the equations yields the mean field result, but we find deviations as J approaches t or when n exceeds $n^{\max}$ or in the extremely low density limit $n < (xJ^2/t)^{3/2}$ (not visible in the plots shown here) where $T_c \sim xn$. An alternative approach to T_c involves spin-wave excitations [6,9]. In classical high-spin magnets at $T \sim T_c$ spin waves are excited throughout the Brillouin zone and T_c occurs when the number of excitations (set by T divided by a typical magnon energy) is large enough. The present theory may be thought of as a calculation of a typical (i.e., averaged over the zone) magnon energy (which is itself determined by the changes in electronic energy due to spin disorder) on the assumption that the spin wave excitations have no particular spatial structure. In $d = 3$ for T near T_c this is correct except for small amplitude critical fluctuations of no particular energetic significance. More importantly, our calculation provides detailed access to the experimentally relevant intermediate J, n, x regimes and demonstrates the crucial importance of impurity band formation.

We now briefly discuss numerical estimates of T_c for GaAs:Mn. We first note that the value of J relevant to the actual systems is unclear. In a recent band theory calculation [10], J was defined in terms of the ratio of the $T = 0$ band splitting to the Mn concentration x. We find that this ratio strongly depends on the value of J: at $J = 0.5t$ and $x = 0.05$, the splitting is about $3.6x$, while at $J = 0.75t$ and $x = 0.05$, it is almost $6x$. For a rough estimate we rely instead on the observation [10] that in band theory, J is close to the critical value needed for impurity band formation, i.e., $J \leq t$, along with our estimate $t \approx 2.5$ eV. Then from Fig. 2 we see that for $n_h = 0.1/\text{Mn}$ ($n = 0.005$) we obtain a single-band $T_c \approx 70$ K. In the multiband models previously studied [11] the contribution from different bands add, suggesting a physical system $T_c \approx 150$ K. Although our theoretical estimates agree well with the experimental T_c [1,2], this agreement should not be taken too seriously in view of the simplifying approximations of our model. Increase of n by about 50% will increase T_c by a similar amount. Increases in J (if it can be managed) will also increase T_c (although much less rapidly than the quadratic dependence predicted by the mean field theory). The most promising route to a higher temperature ferromagnet is predicted to be a simultaneous increase in x to a value of order 0.1 and n to about 0.02 or about $0.2/\text{Mn}$.

In summary, we have presented a theory of the magnetic semiconductors which can handle both the weak coupling limit (xJ less than Fermi energy E_F) and the intermediate coupling regime ($J > t$ but not too large). This method correctly treats the physically relevant situation in which the carriers are constrained to be locally parallel to the Mn spins and allows, for example, calculation of the resistivity and optical conductivity. Discussion of these quantities will be given elsewhere. Also, the method can be extended to include the realistic density of states and spin-orbit coupling; work in this direction is in progress.

We thank T. Dietl for helpful correspondence. This work is supported by NSF-DMR-MRSEC-0080008 (A. C., A. J. M.), US-ONR, and DARPA (S. D. S.).

[1] H. Ohno, Science **281**, 951 (1998); J. Magn. Magn. Mater. **200**, 110 (1999); T. Dietl and H. Ohno, Physica (Amsterdam) **9E**, 185 (2001); H. Ohno and F. Matsukura, Solid State Commun. **117**, 179 (2001).

[2] H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and Y. Iye, Appl. Phys. Lett. **69**, 363 (1996). See also H. Ohno *et al.,* Phys. Rev. Lett. **68**, 2664 (1992); H. Munekata *et al.,* Phys. Rev. Lett. **63**, 1849 (1989); A. Van Esch *et al.,* Phys. Rev. B **56**, 13 103 (1997).

[3] F. Matsukura, H. Ohno, A. Shen, and Y. Sugawara, Phys. Rev. B **57**, R2037 (1998).

[4] H. Akai, Phys. Rev. Lett. **81**, 3002 (1998).

[5] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000); T. Dietl, H. Ohno, and F. Matsukura, cond-mat/0007190.

[6] J. König, H. H. Lin, and A. H. MacDonald, Phys. Rev. Lett. **84**, 5628 (2000); J. Schliemann *et al.,* cond-mat/0010036.

[7] X. Wan and R. N. Bhatt, cond-mat/0009161; R. N. Bhatt and M. Berciu, cond-mat/0011319.

[8] V. I. Litvinov and V. K. Dugaev, Phys. Rev. Lett. **86**, 5593 (2001).

[9] E. L. Nagaev, Sov. Phys. Usp. **39**, 781 (1996).

[10] S. Sanvito, P. Ordejón, and N. A. Hill, Phys. Rev. B **63**, 165206 (2001).

[11] A. Chattopadhyay, A. J. Millis, and S. Das Sarma, Phys. Rev. B **61**, 10 738 (2000).

[12] A. Georges, G. Kotliar, W. Krauth, and M. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).