Curie temperature trends in (III,Mn)V ferromagnetic semiconductors

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We present a theoretical survey of ferromagnetic transition temperatures in cubic (III,Mn)V semiconductors based on a model with $S=5/2$ local moments exchange coupled to itinerant holes in the host semiconductor valence band. Starting from the simplest mean-field theory of this model, we estimate the T_c enhancement due to exchange and correlation in the itinerant-hole system and the T_c suppression due to collective fluctuations of the ordered moments. We show that high critical temperatures in these ferromagnetic semiconductors require both the large magnetic susceptibility contribution from the valence-band heavy holes and the large spin stiffness resulting from a complex valence-band structure that includes the more dispersive light holes. Our calculations demonstrate that the model of carrier-induced ferromagnetism of these systems is consistent with high critical temperatures observed experimentally in (III,Mn)V semiconductors.

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The 1992 discovery[1] of hole-mediated ferromagnetic order in (In,Mn)As has motivated research[2] on Mn-doped GaAs and other III-V host materials. Ferromagnetic transition temperatures[3] in excess of 100 K and long spin-coherence times[4] in GaAs have fueled hopes that a new magnetic medium is emerging that could open new pathways for information processing and storage technologies. Recently, reports[5,6] of the room-temperature ferromagnetism predicted[7,8] in (Ga,Mn)N has added to the interest in this class of materials.

When substituted on the cation site of a III-V semiconductor, we assume that Mn acts as an acceptor, leaving a Mn^{2+} half-filled d shell with angular momentum $L=0$ and spin $S=5/2$.[9] There is also experimental evidence[10–13] that ferromagnetism occurs in these materials because of interactions between Mn local moments that are mediated by holes in the semiconductor valence band. The local moments and the itinerant holes are coupled in this approach by an antiferromagnetic exchange interaction. The participation of itinerant holes in the ferromagnetism of these diluted magnetic semiconductors adds to their richness, leading to strong magnetotransport effects that might have important applications and, of particular interest to us here, to transition temperatures that are sensitive to the details of the host band structure.

The description of ordered states in (III,Mn)V systems is greatly simplified by a virtual-crystal-type approximation in which the Mn ion distribution is replaced by a continuum with the same impurity density.[7,14–16] Disorder effects associated with randomness in the Mn ion sites can then be treated perturbatively, when necessary. (For example randomness in the Mn distribution likely limits the conductivity at low temperatures.) This strategy will fail in the limit of dilute Mn ions and also when the exchange interaction between band and Mn spins is too strong.[17] It does, however, seem to be reliable in the limit of principal interest: that of high Mn densities and high critical temperatures, where the holes are metallic and their interaction with Mn acceptors will be effectively screened.

There is at present considerable activity directed toward the growth of many different (III,V) materials containing Mn. In this paper we present and discuss theoretical predictions[18] for their ferromagnetic critical temperatures based on the continuum model. We go beyond the standard mean-field theory of this model by accounting for the role of Coulomb interactions among holes in the valence band, which enhances the critical temperature, and for correlations in Mn ion orientations which reduce the energetic cost of unaligned spin configurations and therefore lower the critical temperature.[19–21]

When disorder and hole correlations are neglected, the mean-field transition temperature of this model is given by[7,15]

$$k_B T_c = \frac{N_{\mathrm{Mn}} S(S+1)}{3} \frac{J_{\mathrm{pd}}^2 \chi_f}{(g\mu_B)^2}, \tag{1}$$

where $N_{\mathrm{Mn}}=4x/a_{\mathrm{lc}}^3$ is the Mn density in $Mn_xIII_{1-x}V$ zinc-blende semiconductors with a lattice constant a_{lc}, J_{pd} is the localized-spin–itinerant-spin exchange coupling constant, and χ_f is the itinerant-hole magnetic susceptibility. To understand the qualitative implications of this T_c equation (1), we first consider the case of a model itinerant-electron system with a single spin-split band and an effective mass m^*. The kinetic energy of the band holes gives a contribution to the susceptibility:

$$\frac{\chi_f^{\mathrm{kin}}}{(g\mu_B)^2} = \frac{m^* k_F}{4\pi^2 \hbar^2}, \tag{2}$$

where k_F is the Fermi wave vector. For weak interactions, the exchange energy of the spin-polarized parabolic-band model adds a contribution

$$\frac{\chi_f^{\mathrm{ex}}}{(g\mu_B)^2} = \frac{e^2 (m^*)^2}{16\pi^4 \varepsilon \hbar^4}, \tag{3}$$

where ε is the dielectric constant of the host semiconductor. At high hole densities p, the kinetic-energy term dominates and the mean-field critical temperature T_c^{MF} is proportional to the Fermi wave vector, i.e., to $p^{1/3}$. Equations (2) and (3) also show that the band contribution to the susceptibility increases linearly with m^* while the exchange correction is proportional to $(m^*)^2$. (Using this simple band model as a guide, hole correlation effects, which will not be discussed in detail here, suppress the critical temperature by several percent for typical experimental hole densities $p \sim 0.1$ nm^{-3}.)

To obtain quantitative predictions for the critical temperature, it is necessary to evaluate the kinetic and exchange contribution to the itinerant-hole susceptibility using a realistic six-band Kohn-Luttinger model,[7,8,22] instead of the parabolic-band model. The band Hamiltonian contains the spin-orbit splitting parameter Δ_{so} and the three Luttinger parameters, γ_1, γ_2, and γ_3, whose values for the specific III-V host can be found, e.g., in Refs. 8 and 23. Only zinc-blende crystals are considered here; in nitrides, which crystallize in both zinc-blende and wurtzite structures, the critical temperature is expected to be only weakly dependent on the lattice configuration.[8] The noninteracting-hole mean-field, T_c^{MF}, and the exchange-enhanced, T_c^{ex}, critical temperatures for GaAs and GaN host semiconductors doped with 5% of Mn are plotted in Fig. 1 as a function of the hole density. Transition temperatures for other III-V hosts and for hole densities $p = 0.1$ and 0.5 nm^{-3} are listed in Table I. We have assumed $J_{\mathrm{pd}} = 55$ meV nm^{-3} for all III-V hosts.[8,13] In the density range considered, only the two heavy-hole and two light-hole bands are occupied in arsenides and antimonides. However, the mixing between these four bands and the two spin-orbit split-off bands is strong and must be accounted for. In nitrides and phosphides, spin-orbit coupling is weaker and all six bands are occupied by holes. The numerical results for the transition temperature are consistent with the qualitative analysis based on the parabolic band model: T_c^{MF} follows roughly the $p^{1/3}$ dependence, the $\sim 10\%-50\%$ exchange enhancement of the critical temperature has a weaker density dependence.

For the thoroughly studied (Ga,Mn)As material[13] doped with 5% of Mn and with $p = 0.35$ nm^{-3}, we find $T_c^{\mathrm{MF}} = 102$ K and $T_c^{\mathrm{ex}} = 112$ K. This result is in remarkably good agreement with the experimental transition temperature of 110 K. Good agreement between experiment[13] and mean-field theory[7,8] is also found in (In,Mn)As compounds that have lower critical temperatures compared to their (Ga,Mn)As counterparts, primarily because they have smaller band masses. An especially important system is (Ga,Mn)N, which appears to exhibit room-temperature ferromagnetism.[5] Our calculations for this III-V semiconductor give $T_c^{\mathrm{MF}} \approx 400-600$ K and $T_c^{\mathrm{ex}} \approx 600-900$ K for Mn content $x = 5\%$ over the range of hole densities studied. Although we cannot compare those numbers directly to the recently measured $T_c = 228-370$ K in Reed *et al.*[5] (Ga,Mn)N samples, since they have inhomogeneous doping profiles, the mean-field theory predictions have the correct order of magnitude but appear to overestimate the transition temperature.

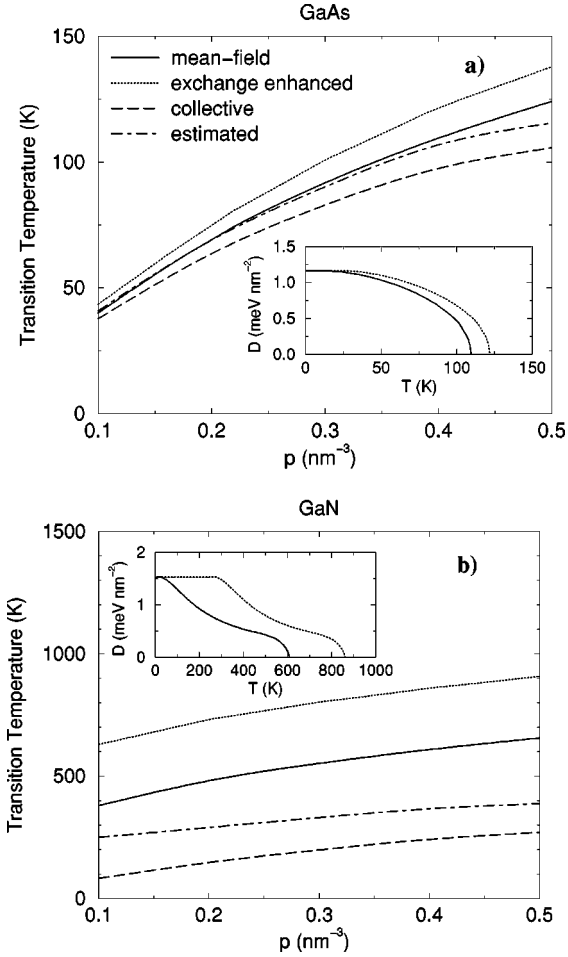

FIG. 1. Main graphs: mean-field (T_c^{MF}), exchange-enhanced (T_c^{ex}), collective (T_c^{coll}), and estimated (T_c^{est}) ferromagnetic transition temperatures in GaAs (a) and GaN (b) host semiconductors doped with 5% of Mn are plotted as a function of itinerant-hole density. Insets: temperature dependence of the spin stiffness (solid lines) calculated from the zero-temperature stiffness and from the mean-field magnetizations. The hole density $p = 0.4$ nm^{-3} and $x = 5\%$ for both GaAs (a) and GaN (b) hosts. Shifted (dotted) curves account for local magnetization enhancement due to exchange interactions in the itinerant-hole system.

We now establish the quantitative reliability of the mean-field theory in arsenides (and also in antimonides and lower-carrier-density phosphides) and explain why mean-field theory overestimates the transition temperature in the heavy-effective-mass nitrides. Our arguments are based on the estimates of the suppression of the transition temperature due to collective spin-wave fluctuations. We emphasize below that mean-field theory would fail badly in any of these materials if the appropriate band model were really a single parabolic band with a mass equal to the material's heavy-hole mass. Strong spin-orbit coupling in the valence band, which yields band states whose orbital and spin character changes completely as the band wave vector varies over the Brillouin zone,[24] enhances the spin stiffness, increases the energy of correlated reduced magnetization configurations, and reduces the importance of corrections to the mean-field-theory result.[21]

TABLE I. Mean-field (T_c^{MF}), exchange-enhanced (T_c^{ex}), collective (T_c^{coll}), and estimated (T_c^{est}) ferromagnetic transition temperatures in III-V host semiconductors doped with 5% of Mn and with itinerant hole densities $p=0.1$ and $p=0.5$ nm^{-3}.

Host	p (nm^{-3})	T_c^{MF}	T_c^{ex}	T_c^{coll}	T_c^{est} (K)
AlAs	0.1	45	53	41	47
	0.5	134	158	105	119
GaAs	0.1	40	43	38	41
	0.5	124	138	106	115
InAs	0.1	14	15	14	15
	0.5	41	44	40	41
AlSb	0.1	19	22	18	20
	0.5	58	64	49	53
GaSb	0.1	18	19	18	19
	0.5	85	88	82	85
InSb	0.1	11	12	11	11
	0.5	37	38	35	36
AlP	0.1	94	127	73	94
	0.5	173	218	105	121
GaP	0.1	57	70	50	60
	0.5	101	115	43	45
InP	0.1	66	80	60	70
	0.5	136	163	103	118
GaN	0.1	379	629	81	250
	0.5	656	907	270	387
InN	0.1	308	549	89	240
	0.5	531	777	303	423

Isotropic ferromagnets have spin-wave Goldstone collective modes whose energies vanish at long wavelengths,

$$\Omega_k = Dk^2 + \mathcal{O}(k^4), \tag{4}$$

where k is the wave vector of the mode. Spin-orbit coupling breaks rotational symmetry and leads to a finite gap. According to our numerical studies,[21] this gap is small, however, much smaller than T_c, for example, and plays a role in magnetic fluctuations only at very low temperatures. Spin-wave excitations reduce the total spin by 1, at an energy cost that is, at least at long wavelengths, much smaller than the mean-field value $J_{\mathrm{pd}}s^{(0)}$, where $s^{(0)}$ is the mean-field band spin density. The importance of these correlated spin excitations, neglected by mean-field theory, can be judged by evaluating an approximate T_c bound based on the following argument which uses a Debye-like model for the magnetic excitation spectrum. When spin-wave interactions are neglected, the magnetization vanishes at the temperature where the number of excited spin waves equals the total spin of the ground state:

$$N_{\mathrm{Mn}}S = \frac{1}{2\pi^2}\int_0^{k_D} dk\, k^2 n(\Omega_k), \tag{5}$$

where $n(\Omega_k)$ is the Bose occupation number and the Debye cutoff, $k_D=(6\pi^2 N_{\mathrm{Mn}})^{1/3}$. It follows that the ferromagnetic transition temperature cannot exceed

$$k_B T_c^{\mathrm{coll}} = \frac{2S+1}{6} k_D^2 D(T_c^{\mathrm{coll}}). \tag{6}$$

In applying this formula to estimate T_c we have approximated the temperature dependence of the spin stiffness by

$$D(T) = D_0 \langle S \rangle (T)/S, \tag{7}$$

as we did in Ref. 25, where D_0 is the zero-temperature stiffness[21] and $\langle S \rangle (T)$ is the mean-field Mn polarization[22] at a temperature T. Here T_c^{coll} is obtained from a solution of Eq. (6) using Eq. (7). If the difference between T_c^{coll} and T_c^{MF} is large, the typical local valence-band carrier polarization will remain finite above the critical temperature and ferromagnetism will disappear only because of the loss of long-range spatial order, the usual circumstance for transition-metal ferromagnetism for example.

In discussing corrections to mean-field-theory T_c estimates, we compare spin-stiffness results obtained with the simple two-band and realistic six-band models. Details on the formalism used to calculate D_0 can be found in Refs. 19 and 21. We find that the zero-temperature spin stiffness is always much larger in the six-band model. For (Ga,Mn)As, for example, the two-band model underestimates D_0 by a factor of $\sim$10–30 over the range of hole densities considered. Furthermore, the trend is different: in the two-band model the stiffness decreases with increasing density, while for the six-band description the initial increase is followed by a saturation. Even in the limit of low carrier concentrations, it is not only the (heavy-hole) mass of the lowest band which is important for the spin stiffness. In the realistic band model, heavy holes have their spin and orbital angular momenta aligned approximately along the direction of the Bloch wave vector and are mixed with more dispersive light holes. Our calculations show that heavy-light mixing is responsible for the relatively large spin stiffnesses which are responsible for the general success of mean-field theory. *Crudely, the large-mass heavy-hole band dominates the spin susceptibility and enables local magnetic order at high temperatures, while the dispersive light-hole band dominates the spin stiffness and enables long-range magnetic order.* The multiband character of the semiconductor valence band plays an essential role in the ferromagnetism of these materials.

In the insets of Figs. 1(a) and 1(b), solid lines show the spin stiffness for GaAs and GaN, doped with 5% of Mn and with $p=0.4$ nm^{-3}, as a function of temperature. The critical temperatures T_c^{coll} were obtained from these curves and from Eqs. (6). Here T_c^{coll}, calculated using a noninteracting hole approximation, and T_c^{ex}, calculated including exchange interactions but neglecting spin-wave excitations, represent our approximate lower and upper bounds for the ferromagnetic transition temperature since T_c^{coll} is always smaller than T_c^{ex}.

With the exception of nitrides and higher-carrier-density phosphides, exchange enhancement and correlated fluctuations change T_c by less than 20%, and these two influences will tend to cancel. This property explains the remarkable success of the mean-field theory in these itinerant ferromagnets. In the heavy-effective-mass nitrides, mean-field theory loses its quantitative accuracy, but still predicts the correct order of magnitude for the ferromagnetic transition temperature.

The dot-dashed lines in Fig. 1 and Table I summarize critical temperature estimates $T_c^{\rm est}$ obtained from Eqs. (6) and (7) with $\langle S\rangle(T)$ curves shifted along the x axis by $T_c^{\rm ex} - T_c^{\rm MF}$. This approach accounts, in an approximate way, for both spin-wave fluctuations and for the fact that the mean-field Mn polarization vanishes at $T_c^{\rm ex}$ rather than $T_c^{\rm MF}$ due to interactions in the itinerant hole system. For arsenides, antimonides, and lower-carrier-density phosphides, $T_c^{\rm est}$ is very close to $T_c^{\rm MF}$, justifying the mean-field description of ferromagnetism in these semiconductor compounds. The estimated critical temperatures for (Ga,Mn)N, $T_c^{\rm est} = 200-400$ K, reflect a more significant suppression of ferromagnetism due to collective excitations. Our theoretical $T_c^{\rm est}$ are in good agreement with available experimental transition temperatures in the studied (III,Mn)V diluted magnetic semiconductors.

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