Thermodynamics of Carrier-Mediated Magnetism in Semiconductors

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(Received 21 May 2007; published 21 December 2007)

We propose a model of carrier-mediated ferromagnetism in semiconductors that accounts for the temperature dependence of the carriers. The model permits analysis of the thermodynamic stability of competing magnetic states, opening the door to the construction of magnetic phase diagrams. As an example, we analyze the stability of a possible *reentrant* ferromagnetic semiconductor, in which increasing temperature leads to an increased carrier density such that the enhanced exchange coupling between magnetic impurities results in the onset of ferromagnetism as temperature is raised.

DOI: 10.1103/PhysRevLett.99.257202 PACS numbers: 75.50.Pp, 75.10.Lp, 75.30.Hx

Ferromagnetic semiconductors (FS) show important and potentially useful differences from their metallic counterparts. For example, if the magnetism in a magnetically doped semiconductor is mediated by carriers, then changes in the carrier density induced by light or applied bias may significantly alter the exchange interaction between the carriers and magnetic impurities. When this effect is sufficient to turn the ferromagnetism on or off, there arise intriguing possibilities for light- or bias-controlled ferromagnetism [1–4] not possible in conventional ferromagnetic metals.

Another approach to controlling ferromagnetism in FS materials is to exploit the strong temperature dependence of carrier density that is the hallmark of semiconductors. Despite this dependence, most analysis of FS has assumed a metallic picture [5,6] in which carrier density is treated as independent of temperature. Consequently, a number of experimental features observed in certain FS materials remain incompletely explained. Examples include the metal-insulator transition [7] in Mn-doped GaAs, the impurity band in oxide FS [8,9], and the resistivity peak in Mn-doped GaAs observed near the Curie temperature, T_C, which is usually attributed to temperature-dependent scattering [10] as in metals [11].

In this Letter we show that each of these features may originate from the temperature dependence of the carrier density. We first develop a model of ferromagnetism in semiconductors that includes the temperature dependence of the carriers. By providing a way to analyze the stability of competing magnetic states, this model allows a self-consistent calculation of the magnetic phase diagram of a FS. Here we use the model to calculate the temperature-dependent magnetization of a simple generic FS. In contrast to the standard monotonic decay of magnetization with increasing temperature found in metals, we demonstrate the possibility of stable ''reentrant'' ferromagnetism: as the temperature is increased the higher density of thermally excited carriers can enhance the exchange coupling between magnetic impurities—and thereby *increase* the magnetization over some range of temperatures. Of course, whether such a possibility can be realized depends on the stability of the reentrant phase relative to other magnetic states. Our model provides a theoretical framework for computing the free energy of each possible magnetic state.

We begin by considering a FS doped with donors of density N_d and magnetic impurities of density N_i. For simplicity we assume that no acceptors are present, that electrons are the only carriers, and that the magnetic impurities are electrically neutral. The interaction between electron spins $\vec{s}_i$ and localized impurity spins $\vec{J}_j$ is

$$H_{\mathrm{ex}} = -\Gamma_{\mathrm{ex}} \sum_{i,j} \delta(\vec{r}_i - \vec{R}_j)\vec{s}_i \cdot \vec{J}_j, \tag{1}$$

where Γ_{ex} is the exchange coupling and $\vec{r}_i$ ($\vec{R}_j$) is the position of the carrier (impurity). We assume a nondegenerate semiconductor in which the conduction band is separated from the donor level (or impurity band) by ε_d in the absence of magnetic order, as in Fig. 1(a). When magnetic order is present the conduction band and donor level experience spin splittings of Δ [12] and Δ_d [13], respectively, as in Fig. 1(b). For simplicity we assume that the ratio $\Delta_d/\Delta \equiv \gamma$ has a fixed, material-specific value.

These spin splittings can arise from either an applied magnetic field or from the carrier-impurity interaction, and in general will modify the temperature dependence of the electron density [14]. We can obtain an expression for the density n of conduction electrons as follows. Electroneutrality requires that $n + N_d^0 = N_d$, where N_d^0 is the density of neutral (nonionized) donors. If we take the effective density of states in the conduction band as $N_c = (1/4) \times (2m^* k_B T/\pi\hbar^2)^{3/2}$ [15], then the electroneutrality condition can be satisfied by introducing the chemical potential μ that satisfies $N_c \exp(\mu/k_B T)\cosh(\Delta/2k_B T) = N_d/[1 + 2\exp[(\mu + \varepsilon_d)/k_B T]\cosh(\Delta_d/2k_B T)]$. This is equivalent to a quadratic equation in the electron density, and has the solution

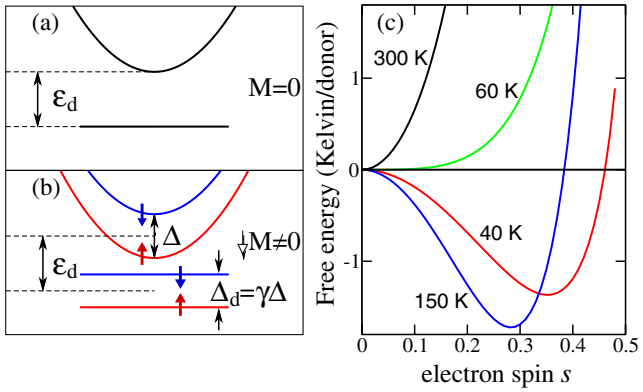

FIG. 1 (color online). Schematic energy-band structure and temperature evolution of free energy. (a) In the absence of magnetization ($M = 0$) both the conduction band and the donor level (at $-\varepsilon_d$ relative to the band edge) are unsplit. (b) The onset of magnetic order ($M \neq 0$) leads to spin splitting Δ of the conduction band and Δ_d of the donor level . Thick arrows represent two spin projections. (c) Free energy $\mathcal{F}$ vs average electron spin s. Materials parameters were chosen based on Gd-doped EuO [21]: $\Gamma_{ex} = 40$ eV $\cdot$ Å^3, $|\varepsilon_d| = 20$ meV, $N_d = 3.5 \times 10^{19}$ cm^{-3}, $m^* = 2$, lattice constant $a_0 = 5.15$ Å, $N_i = 4/a_0^3$, $\gamma = 1$, $a_B = 8$ Å, and $J = 7/2$. Behavior at 40 and 150 K reveals ferromagnetic states.

$$n(s,T) = \tfrac{1}{2}N_d\kappa(s,T)[\sqrt{1 + 4/\kappa(s,T)} - 1]. \quad (2)$$

Here we have expressed the dependence of n on the splitting Δ equivalently as a dependence on the average spin of the conduction electrons, $s = (1/2)\tanh(\Delta/2k_BT)$. We have also defined the auxiliary function $\kappa(s,T) = (N_c/N_d)\exp(-\varepsilon_d/k_BT)(1-4s^2)^{(\gamma-1)/2}/[(1+2s)^\gamma + (1-2s)^\gamma]$. In addition, for later use it is here convenient to introduce the *relative* density of conduction electrons $\nu(s,T) = n(s,T)/N_d$, so that $0 < \nu(s,T) < 1$.

In the magnetically ordered state, both the conduction electrons and the electrons bound to donors experience the field from the ordered impurity spins. The impurity spins in turn experience both a long-ranged uniform field from the delocalized conduction electrons and a short-ranged field from the bound donor electrons. This situation can be described using two coupled order parameters: the average spin s of the conduction electrons and the average spin $m = M/N_i g_i \mu_B$ of the impurities (here M is the magnetization due to the impurities and g_i is the electron g factor).

Using these two order parameters, we can write the free-energy density of the system in the form

$$\mathcal{F} = \mathcal{F}_i + \mathcal{F}_e - \Gamma_{ex}N_iN_d[\nu(s,T)s + \nu_d(s,T)s_d]m. \quad (3)$$

Here $\mathcal{F}_i = \mathcal{F}_i(m)$ is the contribution from the entropy of the impurity spins, and $\mathcal{F}_e = \mathcal{F}_e(s)$ is the contribution from the entropy of the conduction electrons. The former can be obtained by expressing the free energy of the impurity spins as a function of an external magnetic field and then applying a Legendre transformation [16]:

$$\mathcal{F}_i(m) = N_ik_BT\left[2m\alpha(m) - \ln\frac{\sinh[(2J+1)\alpha(m)]}{\sinh[\alpha(m)]}\right], \quad (4)$$

where $\alpha(m) = B_J^{-1}(m/J)/2J$, and $B_J^{-1}(x)$ denotes the inverse of the Brillouin function [15].

The electron contribution $\mathcal{F}_e(s)$ can be derived using a similar approach. We first define the density-weighted average spin of conduction and donor electrons,

$$\tau(s,T) = \nu(s,T)s + [1 - \nu(s,T)]s_d, \quad (5)$$

where the average spin of donor electrons is given by $s_d = (1/2)[(1+2s)^\gamma - (1-2s)^\gamma]/[(1+2s)^\gamma + (1-2s)^\gamma]$. We next invert the function $\tau(s,T)$ by solving Eq. (5) for $s = s(\tau,T)$. This function can then be used to obtain the free energy of the conduction and donor electrons:

$$\mathcal{F}_e(s) = k_BTN_d\int_0^{\tau(s,T)}\ln\frac{1+2s(\tau',T)}{1-2s(\tau',T)}d\tau'. \quad (6)$$

The third term in Eq. (3) is the mean-field approximation for the internal energy described by the Hamiltonian of Eq. (1) and represents the coupling of the order parameters s and m. The expression in square brackets makes explicit the separate contributions from conduction and donor electrons. Since the conduction electrons are delocalized, they mediate a long-ranged interaction between impurity spins. In contrast, the interaction between donor electrons and impurity spins is short ranged and is controlled by a contact term given by the value of the donor wave function at the impurity site. We turn now to evaluating this interaction by deriving an explicit expression for the term $\nu_d(s,T)$ appearing in Eq. (3).

We use a "two-color" percolation model to represent the short-ranged interaction between the randomly distributed donor electrons and impurity spins [17,18]. This is a generalization of an approach originally proposed for dilute ferromagnets [19] and recently applied to magnetic semiconductors [20]. Within the two-color model, an interaction is counted for each pair of sites whose separation is less than $R_c = [B_c/(4\pi/3)]^{1/3}(N_iN_d^0)^{-1/6}$, where $B_c \approx 2.7$ is the average coordination number [17]. The density of pairs within the infinite percolation network is $N_{cl}B_c/2$, where $N_{cl} = 2/(4\pi R_c/3)^3$ is the average density of donor and impurity sites in the network.

Within the mean-field approximation, the contribution of these pairs to the internal energy can be shown to be $U_{cl} = -\Gamma_{ex}|\psi(0)|^2\exp(-2R_c/a_B)(1/2)N_{cl}B_cms_d$, where $\psi(0)$ is the value of the donor wave function at the origin [$|\psi(0)|^2 = 1/\pi a_B^3$ for hydrogenic donors]. Comparing this result to Eq. (3) implies that

$$\nu_d = |\psi(0)|^2(N_iN_d)^{-1/2}(1-\nu)^{1/2}\exp(-2R_c/a_B). \quad (7)$$

Having now obtained explicit expressions for all the terms in Eq. (3), we can directly obtain $s(T)$ and $m(T)$ by minimizing the free energy $\mathcal{F}$. This results in

$$s = \frac{1}{2}\tanh\left[\frac{\Gamma_{\rm ex} N_i m}{2k_B T}\frac{\partial[\tilde{\nu}(s,T)s]}{\partial\tau(s,T)}\right], \quad (8)$$

$$m = JB_J\left[\frac{J\Gamma_{\rm ex} N_d \tilde{\nu}(s,T)s}{k_B T}\right], \quad (9)$$

where $\tilde{\nu}(s,T) = \nu(s,T) + \nu_d(s,T)s_d/s$. By expanding Eqs. (8) and (9) for small s and m we obtain an implicit expression for the critical temperature:

$$T_C = T_C^0 \tilde{\nu}(0,T_C)/[\gamma + (1-\gamma)\nu(0,T_C)]^{1/2}, \quad (10)$$

where $T_C^0 = (\Gamma_{\rm ex}/k_B)[N_i N_d J(J+1)/12]^{1/2}$ is the Curie temperature in the limit of completely ionized donors [9].

We now turn to exploring the predictions of our model for a realistic example. We choose materials parameters approximately corresponding to Gd-doped EuO [21], a magnetic material known to exhibit strong temperature dependence of n. Figure 1(c) shows the resulting free energy $\mathcal{F}$ as a function of conduction-electron spin s, at $T = 40$, 60, 150, and 300 K. A ferromagnetic state (at 150 K) appears at *higher* temperature than a paramagnetic state (at 60 K), and is thus a reentrant ferromagnetic state. This phenomenon is a direct consequence of the increased number of thermally excited carriers which sufficiently increase the exchange coupling between magnetic impurities to overcome the additional entropic cost of a magnetically ordered state.

Figure 2 shows the temperature dependence of $s(T)$ and $m(T)$ for these parameters. There are three different solutions of Eq. (10) for T_C, as shown. The reentrant ferromagnetic state exists in the range $T_{C2} \le T \le T_{C3}$. The inset shows the temperature dependence of the combined average spin from all electrons (conduction, donor, and impurity), revealing behavior very different from the conventional monotonic decay [15].

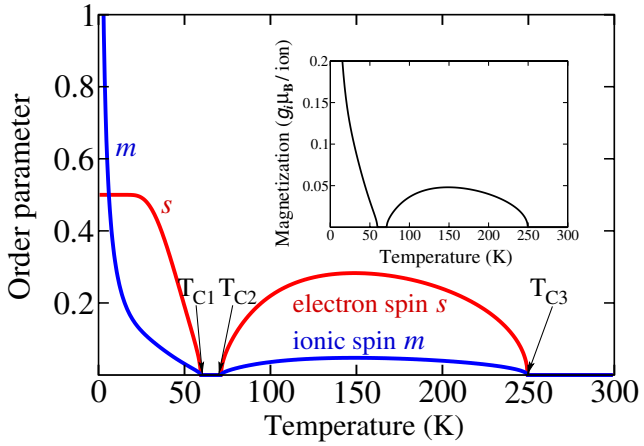

FIG. 2 (color online). Temperature dependence of order parameters s and m, showing reentrant behavior at $T = T_{C2}$ as temperature is raised. Curie temperatures $T_{C1,2,3}$, at which m and s both vanish, define phase boundaries between two ferromagnetic and two paramagnetic states. Inset: temperature dependence of the combined average spin from all electrons. Materials parameters are the same as in Fig. 1.

In the standard theoretical description of FS the ferromagnetism is mediated entirely by "free" carriers (usually holes in the valence band) [5,6]. An important check of our theory is that it reproduces earlier results obtained in this limit. We thus consider the case with all donors ionized, $n = N_d$. In this regime the entropy contribution $\mathcal{F}_e(s)$ must be replaced with its degenerate counterpart for the internal energy, $\mathcal{F}_e^{\rm deg}(s) = (3nE_F/10)[(1+2s)^{5/3} + (1-2s)^{5/3}]$, where $E_F = (\hbar^2/2m^*)(3\pi^2 n)^{2/3}$ is the Fermi energy. Substituting this expression into Eq. (3) and expanding $\mathcal{F}$ in s and m near the Curie temperature, we obtain $T_C = (\Gamma_{\rm ex}^2/k_B)N_i N_0 J(J+1)/12$, where $N_0 = 3n/2E_F$ is the electronic density of states at E_F. This is the standard expression for T_C given as Eq. (7) of Ref. [6].

The possibility of reentrant ferromagnetism in semiconductors was first discussed over 40 years ago [22], and again recently [23]. In neither case was the thermodynamic stability of the magnetism discussed. Moreover, the role of the donor electrons was not included, an omission that can lead to contradictions. For example, in Ref. [23] it was assumed that the conduction-electron density has no explicit dependence on the magnetization. This assumption is justified only if the spin splitting of the donor level (Δ_d) and conduction band (Δ) are equal, i.e., $\gamma = 1$. However, the self-consistency equation given in Ref. [23] for the magnetization of the impurity spins is only correct for the case $\gamma = 0$. This can be seen by substituting our Eq. (8) into Eq. (9) and comparing to the corresponding equation in Ref. [23]. This internal inconsistency has substantial consequences. Specifically, for the case $\gamma = 1$, expanding the self-consistency equation for small magnetization in the vicinity of the critical temperature yields $T_C = T_C^0 \nu(0,T_C)$. But for the case $\gamma = 0$, a similar expansion yields the qualitatively different dependence $T_C = T_C^0\sqrt{\nu(0,T_C)}$.

Our theory predicts an unconventional nonmonotonic $M(T)$, caused by a strong temperature dependence of n. Such behavior has already been observed in various FS materials, such as $ZnGeP_2$: Mn chalcopyrites [24], layered III-VI:Mn compounds [25,26], and in (Fe,Mn)S [27]. These observations have been reported with little, if any, recognition of their significance. Our work provides a plausible theoretical explanation for these observations.

In its present form, our model does not include several physical effects which could alter the magnetic ordering at low temperature. (1) Hopping and Coulomb fluctuations will broaden the donor levels into an impurity band [28]. (2) The neutral donors may form bound magnetic polarons [29] by aligning nearby impurity spins, thereby increasing ε_d (the donor level moves down). (3) There could be a large antiferromagnetic interaction between nearest-neighbor impurity spins. This would have two consequences: $\mathcal{F}$ in Eq. (3) would acquire a contribution $\propto m^2$, while

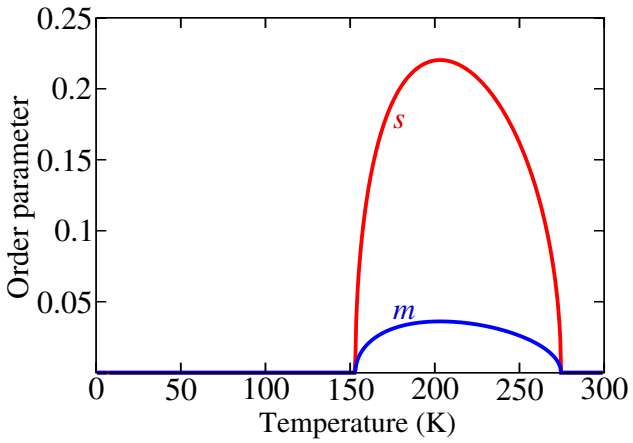

FIG. 3 (color online). Temperature dependence of order parameters s and m when percolation is omitted (see text). Materials parameters are the same as in Fig. 1, except for $m^* = 2.5$.

the argument in the mean-field expression for m in Eq. (9) would be reduced by a term $\propto m$.

All three of these effects would suppress ferromagnetism at low temperatures. While the situation is fairly complex, we can describe it qualitatively by omitting the percolation term in Eq. (3), i.e., by setting $\nu_d(s, T) = 0$ or, equivalently, by taking $a_B \to 0$ in Eq. (7). Figure 3 shows the resulting behavior for $s(T)$ and $m(T)$. The striking feature is that the ferromagnetism is absent at both low and high temperatures, corresponding to spin-glass and paramagnetic states, respectively. A similar interpretation of reentrant ferromagnetism was proposed in Ref. [22] to explain experimental data on (Li,Mn)Se [30]. Furthermore, both of the scenarios for reentrant ferromagnetism shown in Figs. 2 and 3 are consistent with the recent experiments in (In,Mn)Se [25]. With the change in Mn density there is a change in the number of peaks in the temperature dependence of dynamic magnetic susceptibility, supporting the existence of either two or three distinct critical temperatures (see Figs. 2 and 3). While, for simplicity, we have focused on the parameters for Eu-based semiconductors, there is a need to explore other FS for possible reentrant ferromagnetism.

Predictions of reentrant ferromagnetism could also be directly tested in transport experiments. By using a reentrant FS as the spin injector, a nonmonotonic temperature dependence of the electroluminescence in a spin light-emitting diode [4], similar to that for $s(T)$ in Figs. 2 or 3, would be expected. Reentrant behavior could also be detected electrically, without a spin light-emitting diode, by demonstrating nonmonotonic $M(T)$ in a semiconductor heterojunction [14,31] that includes a reentrant FS.

Finally, our model affords study of the interplay between electronic phenomena—such as the metal-insulator transition (MIT)—and magnetism in FS. Indeed, at the high-temperature onset of the ferromagnetism ($T \gtrsim T_C$) one would expect a surge in $n(T)$ as the system is cooled below T_C. This happens because the spontaneous spin splitting of the band makes the donor level shallower [Fig. 1(b)], or even merge with the band (MIT). We believe this behavior to be quite universal for FS materials. The surge of $n(T)$ manifests itself in a resistivity peak and a dip that have been observed in a number of experiments [5]. With a straightforward generalization for the free-electron part of the free energy to account for finite-temperature Fermi statistics, our model can provide a self-consistent description of this phenomenon as well.

We thank H. Munekata for valuable discussions. This work was supported by the US ONR, NSF-ECCS, CAREER, CNMS at ORNL, and the CCR at SUNY UB.

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