Phase Diagram of a Model for Diluted Magnetic Semiconductors Beyond Mean-Field Approximations

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A lattice spin-fermion model for diluted magnetic semiconductors (DMS) is investigated numerically, improving on previously used mean-field approximations. Curie temperatures are obtained varying the Mn spin x and hole n densities, and the impurity-hole exchange J in units of the hopping t. Optimal values are found in the subtle intermediate regime between itinerant and localized carriers. At intermediate and large J/t, a "clustered" state is observed above the Curie temperature and ferromagnetism is suppressed. Formal analogies between DMS and manganites are discussed.

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Diluted magnetic semiconductors (DMS) based on III-V compounds are attracting considerable attention due to their combination of magnetic and semiconducting properties, which may lead to spintronic applications [1,2]. $Ga_{1-x}Mn_xAs$ is the most studied of these compounds with a maximum Curie temperature $T_C \approx 110$ K at low doping x, and with a carrier concentration $p = (n/x) < 1$ due to the presence of As antisite defects [1] or Mn interstitials [3]. It is widely believed that this ferromagnetism is carrier induced, with holes introduced by doping mediating the interaction between $S = 5/2$ Mn spins. This Zener mechanism operates in other materials as well [4].

In spite of the excitement around 110 K DMS, room temperature ferromagnetism should be achieved for potential applications. For this reason, a goal of the present effort is to analyze the dependence of T_C on the parameters x, p, and J/t, helping in setting realistic expectations for DMS potential technological applications. This goal can be achieved only with good control over the many-body aspects of the problem, and for this purpose lattice Monte Carlo (MC) techniques are crucial, improving on previously employed mean-field (MF) approximations. Our results lead to an optimistic view, since T_C is found to increase linearly with x up to $x \sim 0.25$.

Our effort builds upon previous important DMS theoretical studies [2,5–10]. However, to analyze whether T_C can be substantially increased from current values, techniques as generic as possible are necessary. In particular, both the strong interactions and disorder must be considered accurately, with computational studies currently providing the best available tools. For these reasons, our work differs from previous approaches in important qualitative aspects: (i) some groups use a continuum six-band description of DMS [5]. (ii) Other theories assume carriers strongly bounded to impurity sites [6] and employ Hartree-Fock approximations. (iii) Dynamical MF theory (DMFT) [7] may not capture the percolative character of DMS, with a random impurity distribution and cluster picture [8,9]. (iv) Other approaches use MF uniform states [2] or introduce a reduced basis in simulations [10]. While the previous work is important in describing current DMS materials, our goal is to establish the phase diagram of a DMS model avoiding MF approximations.

For the above mentioned reasons, here a generic MC study of a lattice spin-fermion model for DMS is reported. The Hamiltonian is

$$\hat{H} = -t \sum_{\langle ij \rangle, \sigma} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma} + J \sum_{I} \vec{S}_I \cdot \vec{\sigma}_I, \qquad (1)$$

where $\hat{c}^{\dagger}_{i\sigma}$ creates a hole at site i with spin σ, and the hole spin operator interacting antiferromagnetically with the localized Mn spin $\vec{S}_I$ is $\vec{\sigma}_I = \hat{c}^{\dagger}_{I\alpha} \vec{\sigma}_{\alpha,\beta} \hat{c}_{I\beta}$. The carrier can visit *any* site of the lattice (assumed cubic [11]). The interaction term is restricted to randomly selected sites, I, with an $S = 5/2$ Mn moment. These spins are here considered classical with $|\vec{S}_I| = 1$, as widely assumed, allowing for a MC simulation similarly as in other contexts [12]. Photoemission and band calculations locate J/t near 2 [7,10,13,14]. Rather than fixing parameters to current DMS values, here J/t is unrestricted, while x and p mainly vary in the range [0,1]. Approximations include the neglect of on-site Coulomb repulsion, valid at small x and p where double occupancy is unlikely. In addition, Mn-oxide investigations [4] show that an intermediate or large J/t plays a role analogous to a Hubbard U/t at *any* x [4,15]. At low x, the probability of nearest-neighbors (NN) Mn spins is also low (0.0625 at $x = 0.25$), justifying the neglect of an antiferromagnetic (AF) Mn-Mn coupling. The hole motion is described by a one-band tight-binding model, while a more realistic model should include many bands as well as spin-orbit interaction [5]. Despite this simplification, our study considers the underlying lattice, absolutely necessary for a qualitative understanding of the DMS phase diagram.

The MC technique used here is as in Mn-oxide investigations [4]: it includes the full exact diagonalization (ED) of the hole sector for each MC spin configuration, and density-of-states expansion calculations [16].

The latter allows us to reach clusters with up to $8^3 = 512$ sites if up to 40 terms are included, reaching an accuracy comparable to ED for smaller clusters. Both methods are nearly exact, and the error bars of our results mainly arise from intrinsic thermal fluctuations and averages over several random Mn-disorder configurations. Comparing estimations of different clusters and based on previous experience with similar models [4], T_C can be calculated within a $\sim$25% accuracy, sufficient for our purposes [17]. The order parameter for the ferromagnetic-paramagnetic transition was taken to be the absolute value of the magnetization of the spins normalized to 1, namely, $|M| = \frac{1}{xN}\sqrt{\sum_{I,R}\langle \vec{S}_I \cdot \vec{S}_R\rangle}$. Size effects are better visualized in the zero-momentum spin structure factor $S(q=0) = \frac{1}{xN}\sum_{I,R}\langle \vec{S}_I \cdot \vec{S}_R\rangle$. Another useful quantity is the spin-spin correlation at distance d, $C(d) = \frac{1}{N(d)}\sum_{|I-R|=d}\langle \vec{S}_I \cdot \vec{S}_R\rangle$, where $N(d)$ is the number of pairs of Mn moments separated by a distance d.

Typical results for small and intermediate J/t of our large-scale computational effort are in Fig. 1(a). There $S(q=0)$ and $|M|$ vs temperature T are shown for three cluster sizes, $x = 0.1$, and $p = 0.4$. Note the small size dependence of the magnetization (inset) and the volume growth of $S(q=0)$ at fixed $T < T_C$. The estimated T_C/t is $\sim$0.04, with an uncertainty 0.01 sufficiently small for our purposes. Even with just the 4^3 cluster, T_C could be estimated fairly well, as shown in Fig. 1(b). This is important to simplify our computational search for optimal T_C's varying many parameters. In Fig. 1(b), the temperature where a deviation from the high-T limit is found is slightly larger than the $T_C/t = 0.04$ obtained from larger clusters (indicated). Studying the spin-spin correlation at the largest available distance, a nonzero value characteristic of an ordered ferromagnetic (FM) state was obtained at T just below 0.04. Figure 1(c) provides another example of our comprehensive T_C study, using just two cluster sizes at the x-p location of our most optimal T_C, at fixed $J/t = 2$. Using only 4^3 and 6^3 clusters provides a fairly accurate value $T_C \sim 0.08t$.

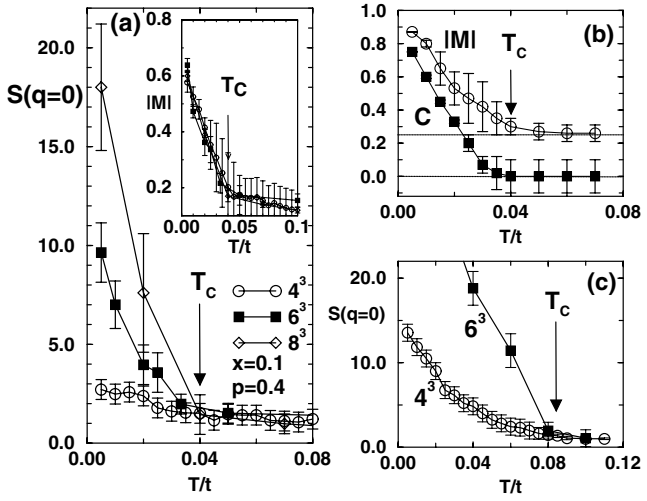

FIG. 1. (a) $S(q=0)$ vs temperature, T, for 4^3 (circles), 6^3 (squares), and 8^3 (diamonds) clusters at $J/t = 2.0$, $x = 0.1$, and $p = 0.4$, using the MC technique. The inset shows the magnetization $|M|$ for the same clusters, with a vertical scale referred to the asymptotic 8^3 $T = \infty$ value. (b) $|M|$ (circles) and spin-spin correlation C at maximum distance (squares) vs T, on a 4^3 cluster, at $J/t = 1.0$, $x = 0.25$, and $p = 0.4$. The 0.25 horizontal line indicates $|M|$ value at $T = \infty$. (c) $S(q=0)$ vs T, at $J/t = 2.0$, $x = 0.25$, and $p = 0.4$ using 4^3 (circles) and 6^3 (squares) clusters. In all cases T_C is indicated.

To understand the qualitative T_C trends, first consider the simplest case: the p dependence at fixed J and x. Using the results in Fig. 2(a) contrasted against Fig. 1(b) (same cluster size) T_C is found to change by a factor of $\sim$2, when p varies from 0.1 to 0.4. However, this tendency does not continue with increasing p, since at $p = 1$ or beyond, a FM state is not formed: the Pauli principle reduces drastically the carrier kinetic energy, leading instead to an AF state. An example at $p = 3$ and on an 8×8 cluster (results are qualitatively similar in two and three dimensions) is in Fig. 2(b), where the oscillations in the spin correlations indicate staggered order. In general, the optimal p is $\sim$0.5, between the hole empty $p = 0$ and saturated $p = 1$ limits [7]. A similar result occurs in Mn-oxide models, recovered from Eq. (1) at $x = 1$. In that

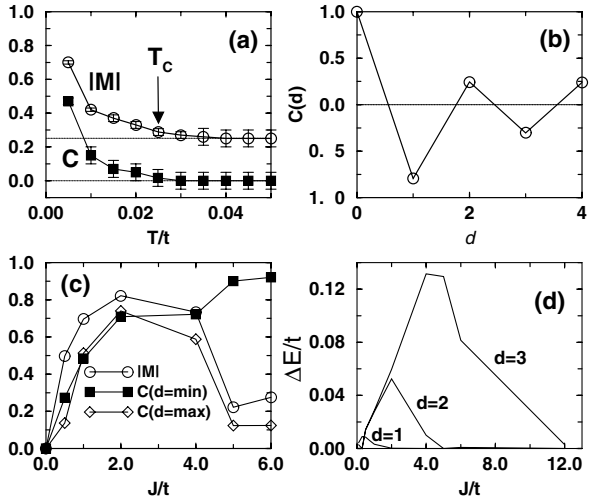

FIG. 2. (a) Magnetization $|M|$ (circles) and spin-spin correlation at maximum distance C (squares) vs T, at $J/t = 1.0$, $x = 0.25$, and $p = 0.1$, using a 6^3 cluster. (b) $C(d)$ vs d at $p \sim 3.0$, $x = 0.25$, $J/t = 1.0$, and $T/t = 0.005$, using an 8^2 cluster. The oscillations indicate an AF state. (c) $|M|$ (circles), spin-spin correlation at minimum distance $C(d_{\min})$ (squares), and at maximum distance $C(d_{\max})$ (diamonds) vs J/t, for a 4^3 cluster at $x = 0.25$, $p = 0.4$, and $T/t = 0.005$. (d) $\Delta E = E(\theta = \pi) - E(\theta = 0)$ vs J/t calculated exactly on finite but large clusters at $T = 0$ for a system of two Mn spins and one electron, θ being the relative angle between the Mn spins. Results in one, two, and three dimensions are indicated. The spin distance is such that the associated effective $x \sim 0.1$ is the same in all cases.

context, investigations at large Hund coupling, the analog of J for DMS, have shown that $p = 0.5$ optimizes T_C to a number $\sim 0.11t$–$0.13t$ [4,18], likely an *upper bound* on the T_C for Eq. (1).

Consider now the J/t dependence of T_C. The MF approximation suggests $T_C^{\mathrm{MF}} \propto J^2$. However, this does not hold when more accurate methods are used in the calculations. In fact, for $J/t \to \infty$ and a Mn dilute system, the holes are trapped in Mn sites, reducing drastically the conductance and T_C. Small FM clusters of spins are formed at a temperature scale T^*, but there is no correlation between them, leading to a global vanishing magnetization [9]. These results *cannot* be obtained within a mean-field approximation. The large-J/t ideas can be tested in our MC simulation by monitoring the short- and long-distance behavior of the spin-spin correlations $C(d)$. In a clustered state (large J/t), $C(d)$ at the shortest distance can be robust at $T < T^*$, but $C(d)$ at the largest distance vanishes due to the uncorrelated magnetism between independent clusters [see Fig. 2(c)]. This subtle effect explains the incorrect MF prediction, since $T_C^{\mathrm{MF}} \sim T^*$, which grows with J/t, rather than the true T_C [see also Fig. 4(a)]. Since both in the $J/t \sim 0$ and $J/t = \infty$ limits T_C is suppressed, an *optimal* $J/t|_{\mathrm{opt}}$ must exist where T_C is maximized. Simulation results as in Fig. 2(c) indicate that the optimal J/t value is close to 2. This phenomenon is not captured by other methods.

The existence of a $J/t|_{\mathrm{opt}}$ can be illustrated just using *two* spins and *one* carrier in a finite cluster at $T = 0$. For any fixed angle θ between the Mn spins, assumed coplanar, the energy is found exactly. The ground state of this $p = 0.5$ system is always at $\theta = 0$ (FM configuration), while the energetically worse state is $\theta = \pi$ (AF configuration). Their energy difference ΔE is a crude estimation of the FM state stability [Fig. 2(d)]. An optimal J/t is found in all dimensions, with stability increasing with the coordination number [19]. The result [Fig. 2(d)] is understood measuring the electronic density $n(i)$ of the same problem on a chain [Fig. 3(a)]. At small J/t, the delocalization manifests in the nearly uniform density, leading to weak FM. At large J/t, strong localization decouples the Mn spins, producing again weak FM. However, there is an optimal value where the system takes advantage of J/t but also allows for a nonzero effective coupling among separated classical spins, leading to a stronger FM.

Consider now the x dependence of T_C. For simplicity, $J/t = 2$ is mainly studied, which is both close to optimal and experimentally realistic [21]. Figure 3(b) shows T_C vs x at $p \sim 0.4$, and for two reasonable values of t. Experiments [1] indicate a linear growth of T_C up to 5% (shown), as in the numerical results. The slope of T_C vs x is in remarkable agreement with MC predictions, in a reasonable range of t. Regarding $x > 0.05$, a reduction of T_C was originally reported in experiments [1]. However, recent data gathered with an optimized annealing treatment [22] indicate a T_C "plateau," suggesting that even more refined thin films may continue increasing T_C with

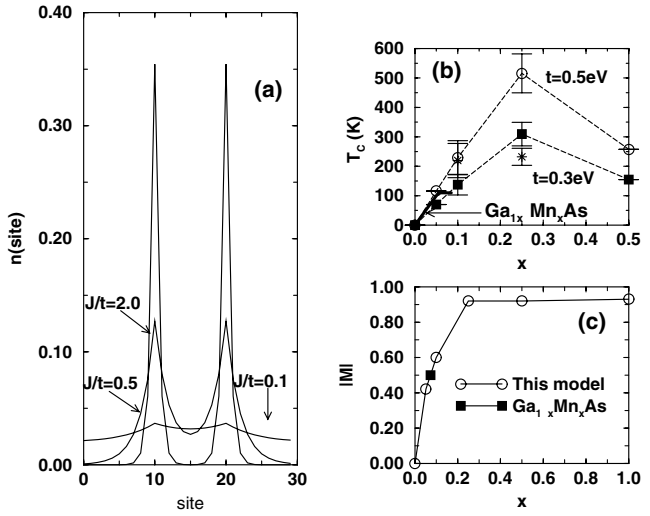

FIG. 3. (a) Exact $T = 0$ local carrier density, for one carrier and two parallel spins at sites 10 and 20, of a 30-site chain, varying J/t. (b) T_C vs x for $Ga_{1-x}Mn_xAs$ [20] (thick line), and for Eq. (1) using $t = 0.3$ eV (squares) and $t = 0.5$ eV (circles). In both cases, $p \sim 0.4$ and $J/t = 2.0$. Typical error bars are shown. Stars are for $p \sim 0.5$, $J/t = 1$, and $t = 0.5$ eV. (c) Magnetization $|M|$ vs x for model Eq. (1) (circles) at $T/t = 0.005$, $J/t = 2$, $p = 0.4$, compared with the experimental value [1] for $Ga_{1-x}Mn_xAs$ at $x \sim 0.07$ and $T = 2$ K (squares).

increasing x. The MC results clearly indicate linear behavior up to $x \sim 0.25$ [Fig. 3(b)]. To the extent Eq. (1) describes DMS quantitatively, higher values of T_C could be expected experimentally. Regarding the presence of a T_C maximum at $x = 0.25$: the origin of this effect is the growing probability with x of having both holes and Mn spins at NN sites. In this case, AF links are formed since $J/t = 2$ is not so strong to keep the link FM, reducing T_C at large x even at $p = 0.5$. As J/t grows, the effect diminishes and the maximum in T_C moves toward $x = 1$, as naively expected. Reciprocally, as J/t decreases from 2 [$J/t = 1$ shown in Fig. 3(b)], the maximum in T_C moves toward smaller x's, and only $t > 0.5$ can provide high-T ferromagnetism. This illustrates the key role that the optimization of J/t plays in these models.

$|M|$ at $T \sim 0$ is in Fig. 3(c). In agreement with experiments, the $x \sim 0.1$ result indicates a magnetization $\sim 50\%$ of its maximum value. This nonsaturated behavior originates in the random distribution of Mn spins, since Mn clusters trap holes. Nonclustered spins are not much visited by those holes, and their spins are not polarized. With growing x, holes are more itinerant, polarizing the entire sample [Fig. 3(c)] [23].

In summary, MC investigations of a spin-fermion model for DMS unveils substantial differences with previously reported results employing MF techniques. The subtle regime of intermediate J/t appears the most relevant in these compounds. $T_C \sim 0.08t$ is an upper limit for the FM critical temperature, a result close to those

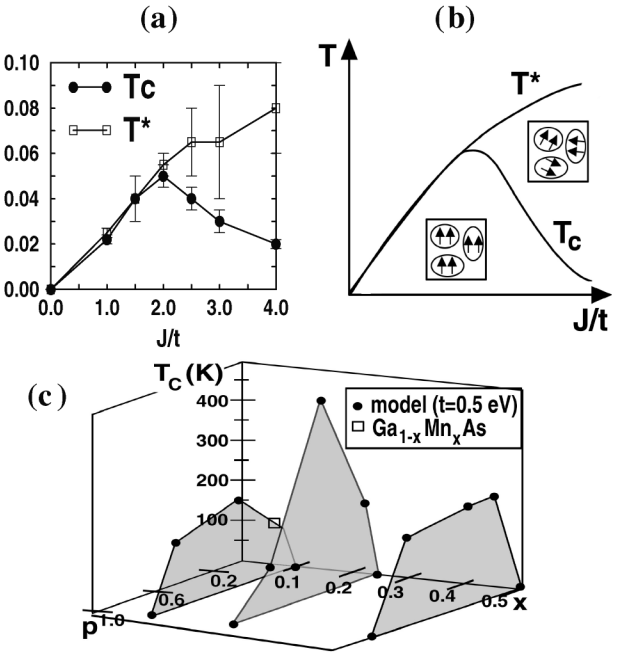

FIG. 4. (a) MC phase diagram in 2D varying J/t, at fixed x and p. At large J/t, a broad scale T^* corresponds to the formation of uncorrelated clusters. T_C is the "true" transition temperature, defined as the T where FM correlations develop at the largest distance in the clusters used. At small J/t, those temperatures are similar. The optimal J/t is intermediate between itinerant and localized regimes. (b) Schematic phase diagram believed to be valid both in 2D and 3D, with the clustered and FM states indicated. (c) Numerically obtained T_C vs x and p, at $J/t = 2.0$. Filled circles are from model Eq. (1) with $t = 0.5$ eV. The open square corresponds to the experimental value for $Ga_{1-x}Mn_xAs$ at $x \sim 0.1$.

accepted for $x = 1$ [4,24]. Our main results are summarized in Fig. 4, which contains (a),(b) the nontrivial J/t dependence of T_C and T^* and (c) T_C with varying x and p, at optimal J/t. To the extent that the present model is applicable to DMS materials, broad guidelines to improve T_C can be established: (i) the optimal $J/t|_{\text{opt}} \sim 2$ must be intermediate between the itinerant and localized limits [Figs. 4(a) and 4(b)]. This J/t, or larger, is expected to keep the semiconducting nature of the state at $T > T_C$. Only band calculations beyond our model can predict which particular material will have such an optimal J/t. (ii) x should be increased beyond 0.1. At $J/t|_{\text{opt}}$, the best value is $x \sim 0.25$. Currently, $x = 0.14$ is the experimental limit [25]. (iii) The number of antisite defects must be controlled such that $p \sim 0.5$ ($p \sim 1$ would be detrimental due to competing antiferromagnetism). (iv) As the coordination number grows, T_C grows. (v) Finally, the simplest procedure to increase T_C relies on increasing the scale t. In fact, (Ga,Mn)As and (In,Mn)As have different hybridization strengths [26], and this should be an important consideration in studying new materials. Our work also suggests formal analogies between DMS and manganite models, with similar T_C's, and a related clustered state above ordering temperature [27].

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[1] H. Ohno, Science **281**, 951 (1998).
[2] T. Dietl, cond-mat/0201282.
[3] K. Yu *et al.*, Phys. Rev. B **65**, 201303 (2002).
[4] E. Dagotto *et al.*, Phys. Rep. **344**, 1 (2001).
[5] J. Schliemann and A. H. MacDonald, Phys. Rev. Lett. **88**, 137201 (2002); J. Schliemann *et al.*, Phys. Rev. B **64**, 165201 (2001); Appl. Phys. Lett. **78**, 1550 (2001).
[6] M. Berciu and R. N. Bhatt, Phys. Rev. Lett. **87**, 107203 (2001); M. P. Kennett *et al.*, cond-mat/0203173; see also C. Timm *et al.*, cond-mat/0111504.
[7] A. Chattopadhyay *et al.*, Phys. Rev. Lett. **87**, 227202 (2001).
[8] A. Kaminski and S. Das Sarma, Phys. Rev. Lett. **88**, 247202 (2002).
[9] M. Mayr *et al.*, Phys. Rev. B **65**, 241202(R) (2002).
[10] M. J. Calderón *et al.*, cond-mat/0203404.
[11] Our study shows the standard T_C increase with coordination number. If a large T_C is reached with cubic, even larger values are expected with realistic FCC lattices.
[12] This assumption is much used in manganites [4].
[13] J. Okabayashi *et al.*, Phys. Rev. B **58**, R4211 (1998).
[14] S. Sanvito *et al.*, Phys. Rev. B **63**, 165206 (2001).
[15] Potential disorder is neglected [8,10].
[16] N. Furukawa *et al.*, Comput. Phys. Commun. **142**, 410 (2001).
[17] Our results for $x = 0.1$, $p = 0.1$, $J/t = 2$, with a $T_C/t \sim 0.02$ for an 8^3 cluster, are comparable with results of Ref. [10] at $x = 0.1$, $p = 0.07$, $J/t = 3$, using a 14^3 cluster, that report $T_C/t \sim 0.03$. This reasonable agreement in the difficult regime of small x and p suggests that size effects are under reasonable control in these studies.
[18] J. L. Alonso *et al.*, Nucl. Phys. **B596**, 587 (2001).
[19] The optimal J/t of this "toy" example is larger only by a factor of 2, compared with the realistic value [Fig. 2(c)].
[20] S. J. Potashnik *et al.*, Appl. Phys. Lett. **79**, 1495 (2001).
[21] For $J/t \gg 1$ values, the optimal density for T_C would be $x = 1$, as in manganites.
[22] S. J. Potashnik *et al.*, cond-mat/0204250.
[23] Note also that the nonsaturated low-T state can be fully polarized with relatively small magnetic fields: in our studies, fields of just 10 T are sufficient to raise $|M|$ from 0.5 to nearly 1.0, at $x = 0.1$.
[24] $La_{0.6}Sr_{0.4}MnO_3$ has a $T_C \sim 340$ K, and our simulations suggest that similar values could be reached for DMS.
[25] A. J. Blattner and B. W. Wessels, cond-mat/0205602.
[26] J. Okabayashi *et al.*, cond-mat/0203056.
[27] The existence of a T^* is of much interest in manganites, where the state between T_C and T^* is believed to cause the colossal magnetoresistance [see J. Burgy *et al.*, Phys. Rev. Lett. **87**, 277202 (2001)]. Other doped magnetic systems, such as $Eu_{1-x}Gd_xO$, have a similar phenomenology [H. Rho *et al.*, Phys. Rev. Lett. **88**, 127401 (2002)].