Role of Disorder in Mn:GaAs, Cr:GaAs, and Cr:GaN

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We present calculations of magnetic exchange interactions and critical temperature T_c in $Ga_{1-x}Mn_xAs$, $Ga_{1-x}Cr_xAs$, and $Ga_{1-x}Cr_xN$. The local spin-density approximation is combined with a linear-response technique to map the magnetic energy onto a Heisenberg Hamiltonion, but no significant further approximations are made. We show the following: (i) configurational disorder results in large dispersions in the pairwise exchange interactions; (ii) the disorder strongly reduces T_c; (iii) clustering in the magnetic atoms, whose tendency is predicted from total-energy considerations, further reduces T_c, while ordering the dopants on a lattice increases it. With all the factors taken into account, T_c is reasonably predicted by the local spin-density approximation in Mn:GaAs without the need to invoke compensation by donor impurities.

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Dilute magnetic semiconductors (DMS), i.e., semiconductors doped with low concentrations of magnetic impurities (usually Cr, Mn, or Co), have attracted much interest because of their potential application to spintronics [1,2]. $Ga_{1-x}Mn_xAs$ is the most widely studied DMS, and it continues to attract interest because it is one of the few DMS where it is generally agreed that the magnetism is carrier mediated, where the magnetic state can be manipulated by electrical or optical means.

In recent years Curie temperatures in $Ga_{1-x}Mn_xAs$ have risen steadily, reaching $\sim$170 K for $x \sim 0.08$ when grown in thin films annealed at low temperature [3–5]. It is generally believed defects (probably Mn interstitials) migrate out of the as-deposited films during the anneal, largely eliminating donor defects that hamper ferromagnetism. Since most practical applications of spintronics require room-temperature operation, a crucial question is then, what is the ultimate limit to T_c in the DMS compounds, and in $Ga_{1-x}Mn_xAs$ in particular?

This question was first addressed by Dietl in his now classic paper [6], where he predicted a wide range of T_c in tetrahedrally coordinated alloys. This stimulated a great deal of interest, although there is a growing consensus that most of the claims of that paper were artifacts of the assumptions in his original model. On the other hand, Akai [7] first used the local spin-density approximation (LSDA) to estimate T_c within the coherent potential approximation (CPA) in (In,Mn)As; he argued that a double exchange mechanism was a more appropriate description of the magnetism than the *pd* exchange assumed by Dietl. Since then LSDA calculations of exchange interactions have been performed by a variety of groups [8–13], usually extracting exchange parameters by calculating total energies of a fixed atomic but multiple-spin configurations, or by a linear-response technique within the CPA.

To date, disorder has almost always been neglected or treated within some mean-field (MF) approximation (MFA), either in the computation of the exchange parameters themselves, or in the subsequent analysis of magnetization $M(T)$ at finite temperature, or both (though better treatments within $k \cdot p$ theory has been reported [14]). The LSDA + MF predicts a rather high T_c for $Ga_{1-x}Mn_xAs$ (typically 350–400 K for $x \sim 0.08$). The large discrepancy with experiment (at least in Mn:GaAs) is usually attributed to the very large numbers of compensating defects in real samples, which reduce T_c [3–5]. The situation remains somewhat uncertain because the number of defects still remaining in the best samples to date is not known.

This Letter addresses the issue of the ultimate limit to T_c in some DMS alloys (focusing on Mn:GaAs) by adopting a relatively rigorous approach to the calculation of the magnetic exchange interactions and T_c. Random alloys are approximated by large (128–250 atom) supercells where special quasirandom structures (SQS) [15] are used for the cation sublattice. Using a linear-response technique within the LSDA and the linear-muffin-tin orbitals method [16,17], the magnetic energy is mapped onto a Heisenberg form [18]

$$H = -\sum_{ij} J(R_{ij}) \hat{e}_i \cdot \hat{e}_j \qquad (1)$$

where the sum is over all pairs ij of magnetic atoms. To model $M(T)$ and T_c, Eq. (1) is treated classically and integrated using a spin-dynamics (SD) technique [20]; alternatively $M(T)$ is estimated by the cluster variation method (CVM) [21] adapted [22] to solve Eq. (1). Thus it is evaluated without recourse to empirical parameters or to the MFA. We show that the widely used MFA turns out be a very poor predictor of $M(T)$ in these disordered, dilute alloys, dramatically overestimating T_c.

With SQS we can rather precisely mimic a fully random configuration, but it is also possible to consider configurations that deviate from random. This can be important because LSDA predicts a strong attractive interaction between magnetic elements [8], which implies a tendency towards clustering. In brief, we show that the disorder induces large fluctuations in $J_{ij} \equiv J(R_{ij})$ for every connecting vector R_{ij}; the fluctuations in J_{ij} *reduce* T_c relative to the configurationally averaged $\overline{J}_{ij} = \langle J_{ij} \rangle$; clustering *reduces* T_c, while an ordered arrangement of the magnetic dopants *increases* T_c.

Following the method of Ref. [17], J_{ij} was computed for an ensemble of 108-cation (216-atom) random $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Cr_xN$ alloys at various concentrations; Fig. 1 shows results for $x = 8.3\%$. $3 \times 3 \times 3$ k points were used, enabling the calculation of J to very distant neighbors. We chose these two alloys because they are approximately representative of limiting cases. For Cr:GaN, the GaN host has a wide band gap, and the Cr t_2 level falls near midgap. It broadens into an impurity band with $1/3$ occupancy, and is believed to be responsible for the ferromagnetic exchange. For Mn:GaAs, most of the weight of the Mn t_2-derived state falls below the valence band maximum. A second t_2 impurity band about 0.1 eV above the valence band maximum is mainly responsible for the ferromagnetic exchange coupling in this case; the strength of $J(R)$ depends critically on the amount of Mn character in this band [24].

Comparing Cr:GaN to Mn:GaAs, Cr:GaN shows substantially stronger nearest-neighbor (NN) interactions, owing to its small lattice constant; however, $\overline{J}(R_{ij})$ decays more rapidly with R_{ij}. This is because the wave function overlap between transition metal d states decays more rapidly for midgap states than near band-edge states. Evident also is the large dispersion in J_{ij} for fixed R_{ij}: the root-mean-square fluctuations $\Delta J_{ij} = \sqrt{\langle J_{ij}^2 - \bar{J}_{ij}^2 \rangle}$ are roughly comparable to $\overline{J}$. A similar analysis at other concentrations reveals that ΔJ_{ij} *increases* with x, because the fluctuations in the type of environments increases; also

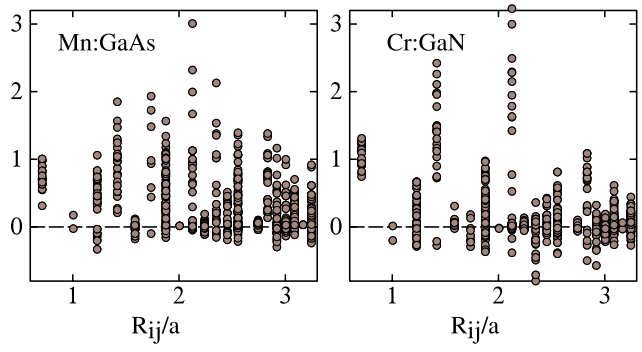

FIG. 1 (color online). Scaled pair exchange interactions $R_{ij}^3 J(R_{ij})$, in a^3 mRy, for Mn:GaAs and Cr:GaN at $x = 8.3\%$. Neighbor distance R_{ij} is in units of the lattice constant a.

ΔJ_{ij} tends to be larger when the Fermi level passes through a midgap state (e.g., Cr:GaN). Note that there is little evidence in either Cr:GaN or Mn:GaAs for oscillatory RKKY-like behavior, which in the simplest approximation predicts $J(R) \sim \cos(2k_F R)/R^3$. Instead, $\overline{J}(R)$ exhibits a rather strong crystallographic dependence, but decays overall somewhat faster than R^3, corresponding to a Fermi surface with imaginary wave number, as would be obtained if the coupling were described by tunneling via a disordered impurity band [25].

We now apply Eq. (1) to compute $M(T)$, focusing on T_c. Mean-field theory, which estimates the effective field at each site from the average field contributed by other sites, predicts T_c well above room temperature both in Mn:GaAs and Cr:GaN [13,26]. In spite of the rather strong differences in the form of $J(R)$ (Fig. 1), mean-field theory predicts that Mn:GaAs and Cr:GaN have roughly similar T_c for $x \sim 0.08$ [26]. This is because the NN interaction in the latter case is strongest, but the J decays faster with R, leading to a comparable mean-field estimate $\overline{T}_c^{\mathrm{MFA}}$. But it should be evident from Fig. 1 that the MFA is of questionable reliability. In addition to the well-known fact that for dilute alloys there is a percolation threshold for the onset of ferromagnetism; the large fluctuations $\Delta J(R)$ may strongly affect T_c, especially since $\Delta J(R)$ itself is a function of the environment [8], and consequently of the local percolation path.

To obtain a precise estimate for $M(T)$ and T_c, we adopt a spin-dynamics approach [20]. A 200 atom SQS structure (250 atom for the 4% alloy) was used to mimic the random alloy. From the TM atoms in the SQS structure, a supercell containing $\sim$2000 Mn or Cr atoms was assembled. Adopting the global-damons method described in Ref. [20], the first-order Landau-Lifshitz (LL) equation was integrated numerically for an initial equilibration time, followed by a simulation for $\sim 2 \times 10^6$ atomic units. The average magnetization $\overline{M}(T)$ was computed as a function of temperature, and T_c was estimated from the inflection point in $\overline{M}(T)$. Owing to finite-size effects and the stochastic character of the simulation, T_c could be determined to a precision of $\sim$5%.

Also we employed a CVM approach recently adapted to the classical Heisenberg Hamiltonion [22]. This relatively simple scheme has been found to be accurate in simple $3d$ magnets, overestimating T_c by $\sim$5% (similar to the usual CVM for the Ising Hamiltonion [23]). We can check the validity of both methods in the DMS case by comparing their predictions of T_c. Figure 2 shows T_c determined by both methods for $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Cr_xAs$: agreement between the two methods is $\sim$10%, which is quite satisfactory considering the complexity of the J_{ij}. $\overline{T}_c^{\mathrm{MFA}}$ is also shown: evidently the MFA rather badly overestimates T_c. $\overline{T}_c^{\mathrm{MFA}} > T_c$ by $\sim$200 K in the Mn:GaAs alloy, and by a somewhat larger amount in Cr:GaAs. The discrepancy is still more dramatic in Cr:GaN (not shown); we find $T_c <$ 50 K for all concentrations studied while $\overline{T}_c^{\mathrm{MFA}} \sim 600$ K

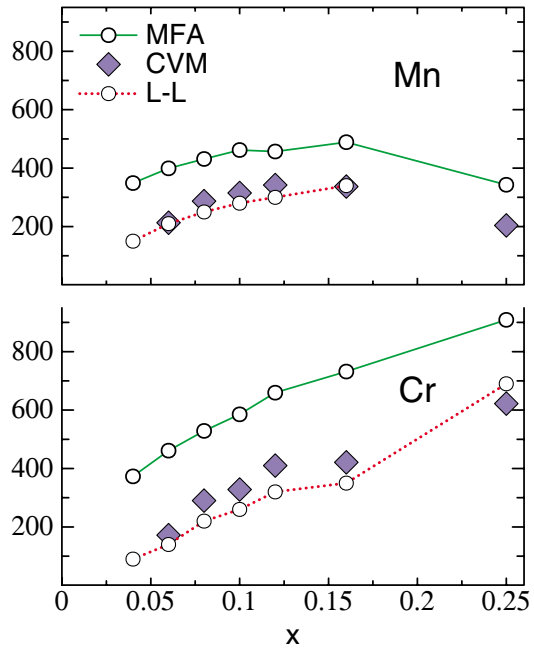

FIG. 2 (color online). Dependence of T_c(K) on x in $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Cr_xAs$. Solid lines: T_c computed from the MF $\overline{T}_c^{\mathrm{MFA}}$. Dotted line: T_c extracted from spin-dynamics simulations of Eq. (1). Diamonds: T_c computed from the Heisenberg cluster variation method.

[26]. Indeed we have found this generally to be the case when $J(R)$ decays rapidly or when $\Delta J(R)/J(R)$ is not small.

These results stand in stark contrast to the ~15% discrepancy between T_c^{MFA} and T_c typically found in simple metals. It is easily understood by considering the effective field a mean-field atom sees, $\vec{H}_i^{\mathrm{eff}} = \sum_j J_{ij}\hat{e}_j$. From the decay of $J(R)$, it is evident that H_i will be dominated by the nearest neighbors. But for dilute alloys, near neighbors are not sufficient to form a percolation path. This is immediately evident in the extreme case of a NN pair of magnetic atoms well separated from any other magnetic atoms: the contribution to T_c^{MFA} from this pair would be high, even though the pair would actually contribute nothing to ferromagnetism. This picture explains naturally why a tight-binding analysis [25], (and also a $k \cdot p$ analysis [27]) using MFA predicted that disorder *increases* T_c, while a Monte Carlo (MC) analysis of the same model suggests that MFA overestimates the effect [28]. A conclusion similar to ours was drawn recently [29], where an LDA magnetic Hamiltonian of averaged $\overline{J}_{ij}$ was computed within the CPA, and mapped onto a large *disordered* simulation cell. They reported a large discrepancy (> 200 K) between T_c^{MFA} and T_c obtained from a Monte Carlo simulation, T_c^{MC}. Using the latter, they found a large decrease in T_c for the disordered cell relative to a virtual-crystal [10] lattice. However, the CPA neglects fluctuations ΔJ, which as we have seen are comparable to $\overline{J}_{ij}$ itself and can have a big effect on T_c.

To assess the effect of fluctuations, we repeated the calculation for T_c within the CVM, replacing the environment-specific J_{ij} with the configurationally averaged $\overline{J}_{ij}$. For $Ga_{1-x}Mn_xAs$ at $x = 0.08$, the effect of disorder ($\overline{J}_{ij} \rightarrow J_{ij}$) was to reduce T_c by 50 K. (It is interesting that the MFA predicts the *opposite* trend. To see this effect, we have calculated two kinds of MFA estimates. In the standard approach sites j is coupled to i by an effective field $\vec{H}_i^{\mathrm{eff}} = \sum_j J_{ij}\hat{e}_j$, and we solve the coupled nonlinear equations in H_i and $\hat{e}_i$. Alternatively, we can replace J_{ij} with its average $\overline{J}_{ij}$ and then calculate $M(T)$ for the $\overline{J}_{ij}$. We call T_c computed by the two approaches, respectively, T_c^{MFA} and $\overline{T}_c^{\mathrm{MFA}}$. The latter can be easily evaluated as $\overline{T}_c^{\mathrm{MFA}} = 2/3\langle\sum_{ij} J_{ij}\rangle$. In the standard approach there is an artificial tendency for $M^{\mathrm{MFA}}(T)$ to track whichever site i has the largest $\vec{H}_i^{\mathrm{eff}}$. Then $T_c^{\mathrm{MFA}} - \overline{T}_c^{\mathrm{MFA}}$ is positive and increases with $\Delta J/J$. This explains why a tight-binding-analysis [25] predicted that disorder *increases* T_c.)

We next consider the effects of nonrandomness. As noted above, real DMS alloys should exhibit some clustering owing to the attractive interaction between magnetic elements [8]. The true situation is complicated by the nonequilibrium growth required to stabilize the alloy in the zinc blende structure. Nevertheless the Mn-Mn or Cr-Cr binding energy is calculated [8] to be an order of magnitude larger than the growth temperature (~250 K), and some pairing or other clustering should be expected, particularly since films must be annealed to obtain good T_c. There is some experimental evidence for a tendency to cluster [30].

The effect of clustering on T_c in $Ga_{0.92}Mn_{0.08}As$ was studied by a simple model. To characterize the configurational disorder we adopt the standard Ising formalism, and assign $\sigma = \pm 1$ to each cation site ($+1$ for Mn and -1 for Ga). The random (SQS) configuration was constructed by searching for configurations which best approximate the ideal random configuration for pair correlation functions $P_{R_{ij}} = \langle\sigma_i\sigma_j\rangle$ (and some higher-order correlation functions) up to some fixed distance. For a random configuration, $P_R = (2x-1)^2$ independent of R. To parameterize the clustering in a simple manner, we adopted the NN pair correlation function P_1 as a measure of clustering. Starting from an initial SQS configuration, a simulated annealing cycle was performed by generating a set of site configurations with increasing P_1, corresponding to longer annealing times (For simplicity, $P_n (n > 1)$ was optimized to be $(2x-1)^2$ for each configuration.) J_{ij} and T_c were computed by the CVM and MFA as a function of P_1; see Fig. 3. T_c is rather strongly *reduced* with increasing P_1. This is perhaps not surprising since increased clustering implies more distant average separation between atoms, which is deleterious to links in the percolation path. Even within the MFA T_c changes slightly, albeit for a different reason. In that case, there is an increase in NN pairs, which would increase T_c, but at the same time there is some increase in the likelihood of *three-* and higher-body neighbors. The

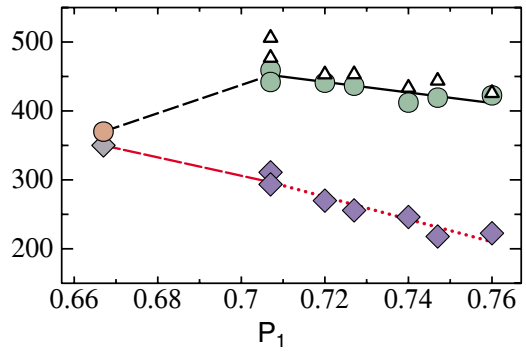

FIG. 3 (color online). Dependence of T_c(K) on the pair correlation function P_1 in $Ga_{0.92}Mn_{0.08}As$. The random (SQS) configuration corresponds to $P_1 = 0.7056$. (Two SQS structures were calculated.) Diamonds show T_c computed with CVM; circles show $\overline{T}_c^{\mathrm{MFA}}$, and triangles show T_c^{MFA}. The point at $P_1 = 2/3$ corresponds to the ordered compound.

presence of a third neighbor has the effect of *reducing* the pairwise J_{ij} [8], and is the origin of the factor-of-three variations in the NN J in Fig. 1.

We also considered the *ordered* limit, by putting 1 Mn in a 24-atom unit cell, corresponding to $x = 0.083$. In this case P_1 decreases to $2/3$, and T_c increases to 350 K (see Fig. 3). Thus we conclude that ordering *increases* T_c, while clustering *decreases* T_c. Perhaps not suprisingly, the MFA T_c approaches the CVM result in the ordered case, since percolation is less critical.

To conclude, we have shown that ferromagnetism is very sensitive to configurational disorder in DMS alloys, and that with proper treatment of disorder T_c is reasonably predicted by the LSDA for $Ga_{1-x}Mn_xAs$, without needing to invoke compensating defects. We briefly consider two important sources of error from elements missing in the theory. First, spin-orbit coupling strongly reduces T_c in $k \cdot p$ models. We estimated its effect by computing the change in $\overline{T}_c^{\mathrm{MFA}}$ when the $L \cdot S$ coupling is added to the LSDA Hamiltonion. For $Ga_{0.92}Mn_{0.08}As$, $\overline{T}_c^{\mathrm{MFA}}$ was reduced by $\sim$10%. Finally, the LSDA itself will overestimate T_c somewhat [24]. In a future work we will present a reliable parameter-free theory that corrects the principal errors in LSDA—most importantly the Mn d character at E_F—and quantify the extent to which the LSDA overestimates T_c. Finally, we conclude that the present calculations represent a rather strict upper bound to T_c, and that for random or clustered $Ga_{1-x}Mn_xAs$ alloys, $T_c > 250$ K is unlikely.

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