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Enhancement of interactions between magnetic ions in semiconductors due to declustering

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It is often assumed that the exchange interaction between two magnetic ions in a semiconductor host depends only on the distance and orientation of the magnetic ions. Using first-principles electronic structure calculations of Mn impurities in GaAs, we show that the exchange interaction between two magnetic ions depends also on the concentration and spatial arrangement of the other, "spectator" magnetic ions. Thus, such systems cannot be described by a Heisenberg Hamiltonian with fixed exchange interactions. Specifically, we find that at fixed Mn concentration, association ("clustering") of Mn impurities leads to a decrease of the Curie temperature, while dissociation ("declustering") leads to higher Curie temperatures. We conclude that clustering is the major impediment to achieve high Curie temperatures in Mn-doped GaAs.

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One of the peculiar phenomena surrounding dilute magnetic semiconductors is the persistence of ferromagnetism even for high dilution of the magnetic ions.[1] Here we point out, via first-principles electronic structure calculations of the exchange interactions J_{ij} in various configurations of Mn ions in GaAs, that such interactions exhibit an "elasticity effect," whereby the interaction between two fixed Mn ions is enhanced upon dilution or dissociation ("declustering") of the other, "spectator" Mn ions. Thus, although the Curie temperature T_C generally decreases with reduced concentration of magnetic ions, this decrease is slower than expected from fixed exchange interactions.

In ferromagnetic systems, the exchange interactions J_{ij} between pairs of magnetic ions i and j determine the Curie temperature T_C, a relationship that is often described by solving the Heisenberg Hamiltonian $\hat{H}=-\Sigma_{i,j}J_{ij}\,\boldsymbol{s}_i\cdot\boldsymbol{s}_j$ for magnetic moments $\boldsymbol{s}_i$ and $\boldsymbol{s}_j$. The standard approach to T_C calculations is to obtain the exchange interactions $J_{ij}(x^0,\sigma^0)$ from some reference system with a given concentration x^0 and spatial configuration σ^0 of the magnetic ions (e.g., isolated Mn-Mn pairs), and then apply such $J_{ij}(x^0,\sigma^0)$ to the calculation of $T_C(x,\sigma)$ for the physically interesting compositions x and ionic configurations σ (e.g., random alloys or ordered compounds). This is done in the RKKY approximation[2] or other model Hamiltonians,[3] as well as in the supercell approach[4] (where the pair of Mn atoms is embedded in a real lattice) and in the coherent potential approximation[5,6] (where the pair is embedded in a fictitious, high-symmetry lattice). This "superposition approximation," assuming that the rigid J_{ij}'s can be transferred to different environments, was recently shown to be invalid in dilute magnetic semiconductors, where the J_{ij}'s depend strongly on the environment (x^0,σ^0) from which they are drawn.[7–10] For example, the interaction J_{ij} between two Mn substitutional impurities in GaAs depends on the presence/absence of spectator Mn ions in the vicinity of i and j. As a result, $T_C(x,\sigma)$ depends on the composition x and chemical configuration σ not only through the sum over the magnetic moments $\boldsymbol{s}_i$ and $\boldsymbol{s}_j$ in the Heisenberg Hamiltonian, but also through the dependence of the coefficients J_{ij} on x and σ. The fact that even at fixed composition and carrier density different ion configurations have different T_C was recently exploited[10] to identify high-T_C configurations of MnAs/GaAs systems.

What we show here is that in dilute magnetic semiconductors such as (Ga, Mn)As there is a special dependence of the exchange interactions J_{ij} on the Mn concentration x and configuration σ, such that when x is reduced, both the range and the amplitude of the ferromagnetic exchange interactions between Mn ions increase. This explains, in part, the paradox[1] of strong ferromagnetism in dilute ($\sim$1%) alloys where a rigid-J picture would predict absence of site-to-site percolation and hence, no magnetism. The dependence of J on x and σ also implies that association (clustering) of Mn atoms at fixed x leads to weaker exchange interactions between Mn ions and to reduced T_C, relative to the system with the same x but with dispersed Mn atoms. Conversely, dissociation ("declustering") of Mn ions at fixed x leads to stronger exchange interactions and thus, increased T_C. We explain this dependence via a level-repulsion model,[11] showing that association (dissociation) of Mn atoms leads to stronger (weaker) coupling between the hole-carrying electronic levels of different Mn sites, and hence, to more localized (delocalized) orbitals. Our results indicate that contrary to a widely accepted prejudice, dilute magnetic semiconductors cannot be treated by using a Heisenberg Hamiltonian with fixed exchange interactions, and that each configuration of magnetic ions is described by a different Hamiltonian.[12]

For each composition x and configuration σ of Mn ions in GaAs, we first calculate the electronic structure self-consistently using the local-density approximation (LDA) to density-functional theory. We then obtain the exchange interactions $\{J_{ij}(x,\sigma)\}$ using the linear response theory (LRT) approach described in Ref. 13. The approximations inherent to this approach are the following: (i) The use of the linear muffin-tin orbital (LMTO) method in the atomic-sphere approximation (ASA). The introduction of empty spheres at interstitial lattice positions, which renders the system closed packed, makes the LMTO-ASA approximation quite reason-

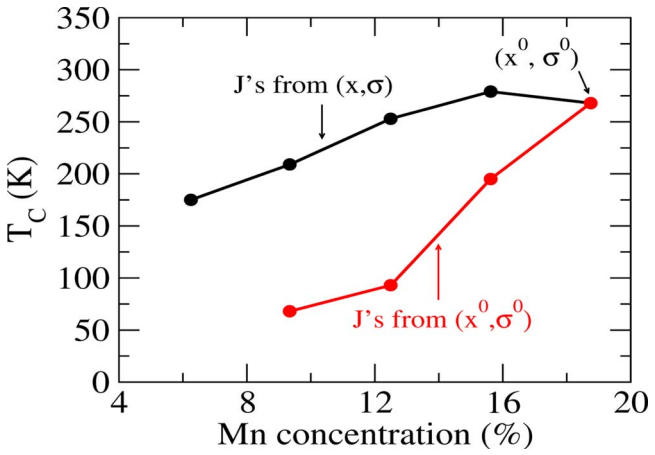

FIG. 1. (Color online) Curie temperature T_C as a function of Mn concentration, obtained using the directly calculated $J_{ij}(x,\sigma)$ (black), and the fixed-configuration $J_{ij}(x^0,\sigma^0)$ (red or gray).

able for the systems considered here.[14] (ii) The discretization of the interactions between rigid spins centered at atomic sites (rigid spin approximation). (iii) The use of the magnetic susceptibility rather than its inverse. (iv) The classical treatment of spin excitations. Approximations (ii)–(iv) are justified if there are large magnetic moments associated with the magnetic ions,[13] as is the case for Mn impurities in GaAs ($\mu \sim 4\mu_B$).

The main advantages of the approach used here, compared to other approaches discussed in the literature,[2–6] are the following: (i) The $J_{i,j}$'s are obtained from *small-angle* rotations, as appropriate for the Heisenberg Hamiltonian, rather than from *large-angle* ferromagnetic/anti-ferromagnetic total-energy differences.[4] (ii) The magnetic ions are embedded in a real lattice, not in a fictitious CPA medium,[5,6] so the $J_{i,j}$'s are explicitly dependent not only on x, but also on σ. (iii) In contrast to RKKY,[2] the exchange interactions exhibit a strong dependence on the lattice orientation of the pair of magnetic ions,[11] i.e., Mn-Mn pairs at the same distance but different lattice orientations have different J's. (iv) Even Mn-Mn pairs at the same distance and lattice orientation may have different J's ("plurality effect"), reflecting different configurations of the spectator Mn ions. This effect was shown to be quite dramatic in disordered alloys.[15]

Once the $\{J_{ij}(x,\sigma)\}$ have been obtained for a given Mn concentration x and configuration σ, we calculate $T_C(x,\sigma)$ from Monte Carlo simulations of the Heisenberg Hamiltonian. We use Monte Carlo simulation cells up to $8\times8\times8$ or $10\times10\times10$ times the unit cell used to calculate $J_{ij}(x,\sigma)$. The number of Monte Carlo steps ($\sim 10^4-10^5$) and the number of independent Monte Carlo runs are systematically increased until the statistical error bars of the cumulants allow us to determine $T_C(x,\sigma)$ to within ~ 3 K.

Figure 1 shows $T_C(x,\sigma)$ as a function of the Mn concentration x, calculated from Monte Carlo simulations with two different sets of magnetic interactions J's: (i) A fixed set $\{J_{ij}(x^0,\sigma^0)\}$, calculated for a reference structure (x^0,σ^0), namely, a $Ga_{26}Mn_6As_{32}$ supercell with $x^0=18.7\%$ and Mn atoms randomly distributed. This set is then applied to calculate T_C of other random structures (x,σ), with $x<x^0$. (ii)

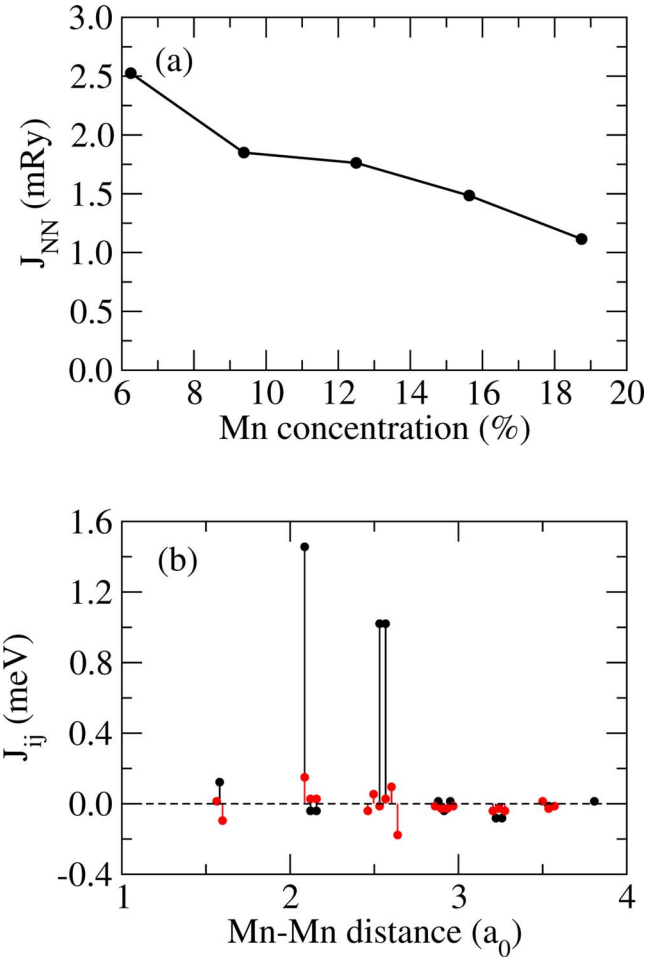

FIG. 2. (Color online) (a) Nearest-neighbor Mn-Mn exchange interactions $J_{NN}(x,\sigma)$ as a function of the Mn concentration, as "spectator" Mn ions are added to the system. (b) Mn-Mn exchange interactions calculated without spectator Mn ions (black circles) and with spectator Mn ions (red or gray circles) as a function of the Mn-Mn separation R_{ij} (in units of the GaAs lattice constant a_0). Points corresponding to the same R_{ij} have been slightly shifted on the x axis for clarity purposes.

The set $\{J_{ij}(x,\sigma)\}$ calculated directly via LRT for the structures of interest (x,σ), and applied to calculate their Curie temperature $T_C(x,\sigma)$. We use a 64-atom cubic supercell where the Mn impurities substitute for randomly chosen Ga atoms in the fcc cation sublattice. We see from Fig. 1 that (i) at any given Mn concentration x, T_C is significantly higher when obtained directly from $J_{ij}(x,\sigma)$ than when calculated from the reference configuration $J_{ij}(x^0,\sigma^0)$. (ii) While $T_C[J_{ij}(x^0,\sigma^0)]$ increases monotonically in the range $9.3\%<x<18.7\%$, $T_C[J_{ij}(x,\sigma)]$ has a maximum ($T_C\sim 275$ K) for $x\sim 16\%$. This result indicates that the use of fixed exchange interactions $J_{ij}(x^0,\sigma^0)$ to calculate T_C may introduce qualitative as well as quantitative errors, leading in some cases to predict incorrectly the dependence of T_C on Mn concentration. The RKKY approximation,[2] which uses fixed exchange interactions J_{ij}, predicts a *monotonic increase* of T_C with increasing Mn concentration, because adding Mn ions raises the Fermi energy of the holes. Instead, as shown by Xu and van Schilfgaarde,[16] T_C reaches a maximum when

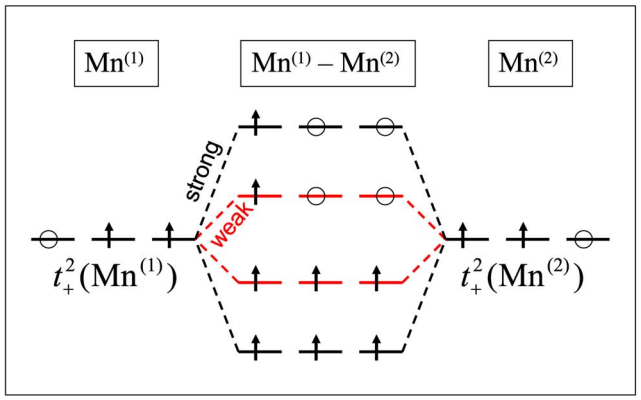

FIG. 3. (Color online) Schematic energy-level diagram of two interacting t_+^2 orbitals, located on different Mn ions.

the hole density corresponds to a half-filled Mn t_2 band. This is so because ferromagnetism in this system is due to the interaction between partially occupied orbitals localized on different Mn sites, not to RKKY-type interactions.[11]

To understand the dependence of T_C on the presence of spectator Mn ions (Fig. 1), we show in Fig. 2(a) the LRT-calculated exchange interactions J_{NN} between two specific nearest-neighbor Mn ions [denoted in the following as $\mathrm{Mn}^{(1)}$ and $\mathrm{Mn}^{(2)}$] as a function of Mn concentration. We see that as the Mn concentration increases (i.e., more spectator Mn ions are added to the system), the exchange interaction between $\mathrm{Mn}^{(1)}$ and $\mathrm{Mn}^{(2)}$ decreases from ~2.5 mRy (for $x=6.2\%$) to ~1 mRy (for $x=18.8\%$). Qualitatively similar results were obtained by Kudrnovsky *et al.*[5] and by Sandratskii and Bruno.[17]

Figure 2(b) shows the exchange energies $J_{ij}(x,\sigma)$ between periodic replicas of $\mathrm{Mn}^{(1)}$ and $\mathrm{Mn}^{(2)}$, calculated with spectator Mn ions ($Ga_{26}Mn_6As_{32}$ supercell, red symbols) and without spectator Mn ions ($Ga_{30}Mn_2As_{32}$ supercell, black symbols), as a function of the Mn-Mn distance R_{ij}. We see that the $J_{ij}(x,\sigma)$ have both larger amplitude and longer range when no spectator Mn ions are present, compared to the case where spectator Mn ions are present. Due the finite range of the Mn-Mn exchange interactions, there is a minimum Mn concentration (x_{perc}) below which magnetic percolation does not occur, and therefore $T_C=0$. We find that $x_{\mathrm{perc}}\sim 0.5\%$ if the $\{J_{ij}(x,\sigma)\}$ are obtained from a $Ga_{30}Mn_2As_{32}$ supercell calculation, compared to $x_{\mathrm{perc}}\sim 0.9\%$ when the $\{J_{ij}(x,\sigma)\}$ are drawn from a $Ga_{26}Mn_6As_{32}$ supercell. This result suggests that the "elasticity" effect, whereby the range of magnetic interactions increases upon dilution of the magnetic ions, explains in part the persistence of strong ferromagnetism in very dilute systems.

The dependence of the exchange interactions J_{ij} on x and σ can be understood considering the level interacting model,[11] leading to ferromagnetism (Fig. 3). Each substitutional Mn impurity on a Ga site leads to fully occupied t_+^3 and e_+^2 spin-up orbitals inside the valence band (not shown), as well as partially occupied (hole-carrying) t_+^2 spin-up orbitals (shown in Fig. 3) that represent Mn d-As p "dangling-bond hybrids" located in the band gap of the GaAs host crystal. When two such orbitals, centered on two different Mn sites ($\mathrm{Mn}^{(1)}$ and $\mathrm{Mn}^{(2)}$), interact in a ferromagnetic fashion (Fig. 3), they form a bonding state occupied by three electrons, and an antibonding state at lower hole energy (higher electron energy) occupied by one electron and two holes. The stronger the Mn-Mn interaction, the lower the energy of the hole-carrying states, and the more localized the hole orbital. In turn, this leads to shorter-ranged and weaker exchange interactions (Fig. 2) and ultimately to lower T_C's (Fig. 1).

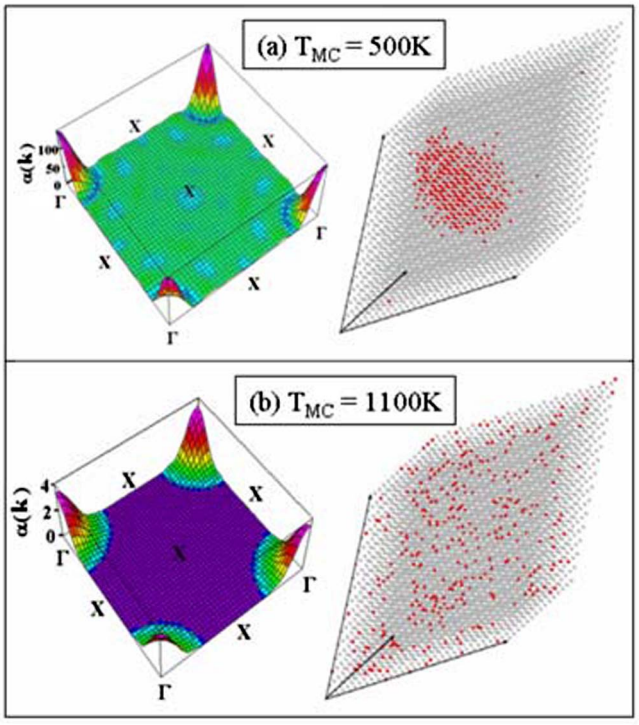

FIG. 4. (Color online) The reciprocal-space SRO parameter $\alpha(\boldsymbol{k})$ of a $Ga_{0.92}Mn_{0.08}As$ disordered alloy, calculated for Monte Carlo simulation temperatures of 500 K (a) and 1100 K (b), is shown on the left-hand side. The real-space configurations of the alloy, obtained from Monte Carlo simulations, are shown on the right-hand side. Red circles denote Mn atoms, gray circles denote Ga atoms.

Having established the dependence of the exchange interactions J's on the Mn concentration, we examine next the extent to which T_C of a disordered alloy changes upon clustering or declustering of the Mn impurities at fixed Mn concentration. As observed by Raebiger *et al.*,[9] dissociation (association) of Mn atoms leads to a more delocalized (localized) hole density and hence, longer-range (shorter-range) interactions (Fig. 2) and higher (lower) T_C (Fig. 1). To accurately determine the effects of clustering or declustering on the Curie temperature, we need (i) a large supercell realization of the alloy and (ii) a physically guided generation of disordered configurations. Both goals can be achieved through statistical-mechanics simulations of a cluster expansion of the (Ga, Mn)As alloy Hamiltonian.[18] In this approach, we expand the formation energy of any arbitrary configuration σ as

$$\Delta H_{CE}(\sigma) = h_0 + \sum_i h_i S_i + \sum_{i,j} h_{ij} S_i S_j + \sum_{i,j,k} h_{ijk} S_i S_j S_k + \ldots, \quad (1)$$

where we denote the occupation of an fcc lattice site by Ga as $S_i=1$ and by Mn as $S_i=-1$. The coefficients

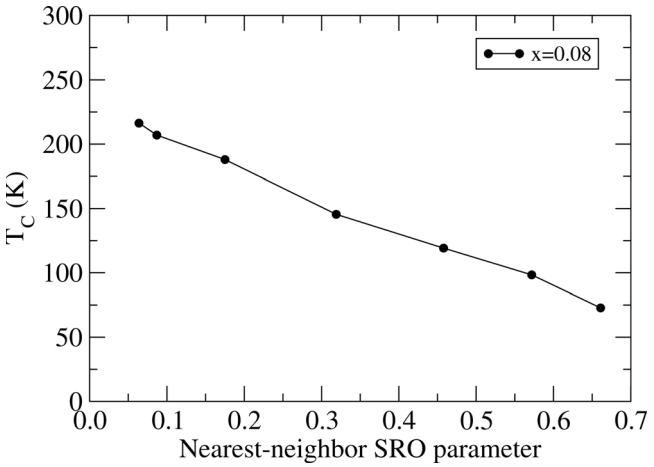

FIG. 5. Calculated Curie temperature of a $Ga_{0.92}Mn_{0.08}As$ disordered alloy as a function of the nearest-neighbor SRO parameter $\alpha_{1,1,0}$. A similar trend is observed when T_C is plotted vs other (e.g., second-nearest-neighbor) SRO parameters.

$\{h_i, h_{ij}, h_{ijk}, \ldots\}$ were determined[18] by fitting Eq. (1) to a large number of first-principles total-energy calculations of $\Delta H_{CE}(\sigma)$ of different chemical arrangements σ of Mn and Ga atoms in (Ga, Mn)As. Once established, the cluster expansion can be subjected to a Monte Carlo simulation to produce configurations with arbitrary degree of short-range order (SRO). The Monte Carlo simulation cell includes 8192 atoms (4096 cations). The SRO parameter of shell (h,k,l) is defined as $\alpha_{h,k,l}=1-P_{h,k,l}(x)/x$, where $P_{h,k,l}(x)$ is the probability, given a Mn atom located at the origin, of finding a Mn atom in the (h,k,l) shell.[19] Figure 4 shows the Fourier transform of the SRO parameter $\alpha_{h,k,l}$ of a $Ga_{0.92}Mn_{0.08}As$ disordered alloy for two different Monte Carlo simulation temperatures. We see that at low temperature [$T_{MC}=500$ K, Fig. 4(a)] the SRO parameter is almost a delta function centered at the Γ point of the Brillouin zone, indicating phase separation. At high temperature [$T_{MC}=1100$ K, Fig. 4(b)] the SRO parameter varies smoothly between ~ 0.7 and ~ 4.5, reflecting the nearly random character of the Mn distribution at such temperature. Also shown in Fig. 4 are real-space visualizations of the Mn ion configurations. At low temperature [Fig. 4(a)] Mn clustering is clearly seen, while at high temperature [Fig. 4(b)] the configuration of the Mn atoms is nearly random.

To evaluate T_C for such different configurations, we cannot use directly the LRT method as done for smaller supercells (Figs. 1 and 2), because the Monte Carlo cell contains over 8000 atoms. Instead, we cluster expand T_C itself[10] in a way formally analogous to the cluster expansion of $\Delta H_{CE}(\sigma)$,

$$T_{CE}(\sigma) = \tau_0 + \sum_i \tau_i S_i + \sum_{i,j} \tau_{ij} S_i S_j + \ldots , \qquad (2)$$

where the coefficients $\{\tau_i, \tau_{ij}, \tau_{ijk}, \ldots\}$ are determined by fitting Eq. (2) to the directly calculated Curie temperature $T_{CE}(\sigma)$ of ~ 50 small-cell configurations obtained via LRT+Monte Carlo simulations.[10]

The calculated T_{CE} of disordered configurations at fixed Mn concentration ($x=0.08$) is shown in Fig. 5 as a function of the SRO parameter $\alpha_{1,1,0}$, which provides a measure of the degree of Mn clustering. We see that T_{CE} decreases sharply (by a factor of two or more) as $\alpha_{1,1,0}$ increases. This result indicates that the presence of SRO (or clustering) in diluted magnetic semiconductors strongly decreases the attainable T_C, and that careful annealing procedures, which can potentially reduce SRO, are necessary to achieve high T_C.

In conclusion, we have shown that the exchange interaction between pairs of Mn ions in Mn-doped GaAs depends sensitively on the concentration and spatial arrangement of "spectator" Mn impurities. At fixed Mn concentration, clustering of Mn impurities leads to reduced exchange interactions and lower Curie temperatures, while "declustering" leads to enhanced exchange interactions and higher Curie temperatures. This "elasticity effect" explains strong magnetism in dilute systems.

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