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Ferromagnetism in diluted magnetic semiconductors: A comparison between *ab initio* mean-field, RPA, and Monte Carlo treatments

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We have determined from first principles the Curie temperature in the diluted magnetic semiconductor ($Ga_{1-x-y}Mn_xAs_y$) As alloys, where the compensation effect by As antisites is taken into account. The disorder due to random positions of Mn impurities and As antisites is taken into account in the framework of the coherent potential approximation. We demonstrate that a simple mean-field approximation (MFA) already gets T_c accurately. In particular, it is shown that the calculated T_c in the random-phase approximation and Monte Carlo simulations differ only weakly from the MFA values. The reason is that a proper treatment of the disorder beyond the virtual-crystal approximation leads, in this doped material, to a flat magnon dispersion in a large part of the Brillouin zone.

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I. INTRODUCTION

The discovery of carrier induced ferromagnetism in diluted III-V semiconductors (DMS) has stimulated an interest from both theoreticians[1–7] and experimentalists[8–10] in these materials. The main reason for such interest in these materials is their possible technological applications. There is a clear effort to find materials with Curie temperatures above room temperature. Present experiments show Curie temperatures of the order of 110 K for GaAs doped with about 5% of Mn impurities.[11,12] A similar magnitude of T_c was also reported recently for Ge doped with about 3.5% of Mn atoms.[13] The doping of a III-V semiconductor compound with Mn impurities introduces simultaneously local magnetic moments and itinerant valence-band carriers. Note that due to compensation effects, the hole concentration n_h is generally lower as compared to the Mn-impurity concentration x, but its actual value is not known precisely yet.

It is rather surprising that models which neglect the disorder and treat the p-d exchange term in a mean-field approximation (MFA) provide a Curie temperature in a good agreement with the experiment. For instance, using six-band Kohn-Luttinger Hamiltonian to describe the band structure and assuming reasonable values for two adjustable parameters, namely, the p-d exchange integral $J_{pd}=1.3$ eV and the effective hole concentration $n_h \approx 0.3x$, gives the correct value of T_c as compared to the experiment.[14] In order to avoid possible uncertainties due to the choice of adjustable parameters, we adopt the first-principles approach to determine the Curie temperature of GaMnAs alloys, assuming that the compensation is due to As antisites only. It should be noted that As antisites represent only one of the possible compensating defects, the self-compensating Mn interstitials are the other possible candidates, as demonstrated recently.[15] Based on first-principles calculations, we construct an effective Heisenberg model whose long-range exchange integrals are computed by including the effect of disorder on the electronic structure generally neglected in model studies. The Curie temperature corresponding to the Heisenberg model will be determined in the framework of the MFA, the random-phase approximation (RPA), and Monte Carlo (MC) treatment. MC simulations will provide an exact numerical value for T_c and thus allow us to test the validity of the analytical approaches (RPA and MFA). RPA treatment will allow us to make a conclusion about the validity of the MFA: RPA goes beyond MFA since it provides a better treatment of magnons excitations, relevant for the determination of T_c.

II. ELECTRONIC STRUCTURE

We have determined the electronic structure of DMS by *ab initio* Green function method implemented in the framework of all-electron tight-binding linear muffin-tin orbital (TB-LMTO) method within the atomic-sphere approximation.[16] The valence basis consists of s, p, and d orbitals and we include scalar-relativistic corrections but neglect the spin-orbit effects. We used equal Wigner-Seitz radii for all atoms and empty spheres and introduce empty spheres into the interstitial positions of the zinc-blende GaAs semiconductor for a better space filling.[17] The lattice constant of the pure GaAs ($a=5.653$ Å) was used in all calculations. Charge self-consistency is achieved within the framework of the local spin-density approximation using the Vosko-Wilk-Nusair parametrization for the exchange-correlation potential.[18] The effect of substitutional disorder due to impurities in the GaAs host can be included straightforwardly in the framework of the Green function method by performing the configurational averaging within the coherent-potential approximation (CPA).[19] CPA is a single-site approximation which consists in replacing the disordered system by an effective medium characterized by a complex self-energy determined self-consistently from the condition that $\langle t_i \rangle_{dis} = 0$, where t_i denotes the t matrix of a single impurity embedded in this effective medium. The average is done over all alloy components. CPA neglects local environment effects

and possible lattice relaxations, but it correctly reproduces concentration trends and can also treat systems with small but finite concentrations of defects typical for DMS. This is an advantage in comparison with the supercell method[6,15,20] which requires *large supercells* to simulate semiconductor crystals with low impurity concentrations. More details of the method can be found in Ref. 21. In the following, we denote, respectively, by x and y the Mn-atoms and As-antisites concentration. Note that the carrier concentration is $n_h = x - 2y$.

III. EFFECTIVE PAIR EXCHANGE PARAMETERS

The evaluation of T_c requires the knowledge of pair exchange interactions.[7,22] In the present paper they are obtained by evaluating the change of energy associated with a constrained rotation of the spin-polarization axes at the sites i and j, and comparing it with the corresponding energy obtained from the effective classical Heisenberg Hamiltonian.[22,23] This approach is based on the adiabatic treatment of atomic moments, in which noncollinear configurations of magnetic moments are taken into account, and it is justified for magnetic atoms with large exchange splitting such as, e.g., Mn atoms. The spins are treated classically, which is reasonable for Mn atoms with spin $S=5/2$. The mapping is further simplified by using the magnetic force theorem[23] which allows one to use the band energy of the calculated ground state as a good estimate also for total-energy differences of the perturbed ground state. Finally, we employ the vertex-cancellation theorem (VCT) (Ref. 24) which justifies the neglect of disorder-induced vertex corrections in Eq. (1). The VCT was derived under rather general conditions and can be applied to the efficient evaluation of exchange interactions, exchange stiffnesses, spin-wave energies, etc. We refer the reader to Refs. 22–24 for more details. It should be noted that a similar approach, based on the mapping of total energies obtained from the supercell electronic structure calculations onto the classical Heisenberg model was developed recently.[13,20]

If we neglect, for simplicity, small induced moments on non-Mn atoms, the nonvanishing pair exchange interactions are only among substitutional Mn atoms on the Ga sublattice, namely,

$$\overline{J}_{ij}^{\mathrm{Mn,Mn}} = \frac{1}{4\pi}\mathrm{Im}\int_C \mathrm{tr}_L[\,\delta_i^{\mathrm{Mn}}(z)\,\overline{g}_{ij}^{\mathrm{Mn,Mn}\uparrow}(z)\,\delta_j^{\mathrm{Mn}}(z)\,\overline{g}_{ji}^{\mathrm{Mn,Mn}\downarrow}(z)]\,dz. \tag{1}$$

Here, tr_L denotes the trace over the angular momentum $L=(\ell m)$, $\delta_i^{\mathrm{Mn}}(z)=P_i^{\mathrm{Mn},\uparrow}(z)-P_i^{\mathrm{Mn},\downarrow}(z)$, $P_i^{\mathrm{Mn},\sigma}(z)$ are L-diagonal matrices of the Mn-potential functions of the TB-LMTO method corresponding to the spin $\sigma=\uparrow,\downarrow$, $\overline{g}_{ij}^{\mathrm{Mn,Mn}\uparrow}(z)$ and $\overline{g}_{ji}^{\mathrm{Mn,Mn}\downarrow}(z)$ refer to site off-diagonal blocks of the conditionally averaged Green function, namely, the average of the Green function over all configurations with a pair of Mn-atoms fixed at the sites i and j,[21] and the energy integration is done over the contour C in the complex energy plane starting at the bottom of the band and ending at the Fermi energy. Positive (negative) values of $J_{ij}^{\mathrm{Mn,Mn}}$ correspond to ferromagnetic (antiferromagnetic) coupling, respectively. The presence of the conditionally averaged Green functions in Eq. (1), which properly include strong multiple-scattering effects on Mn impurities and As antisites, is the main difference from the conventional RKKY expression where the Green functions of the ideal, unperturbed GaAs host appear.

We now discuss the statistical treatment of the Heisenberg model. The MFA and RPA values of the Curie temperature (T_c) (Refs. 7 and 22) are

$$(k_{\mathrm{B}}T_c^{\mathrm{MFA}}) = \frac{2x}{3}\sum_{i\neq 0}\overline{J}_{0i}^{\mathrm{Mn,Mn}} = \frac{2x}{3}\frac{1}{N}\sum_{\mathbf{q}}\overline{J}(\mathbf{q}) \tag{2}$$

and

$$(k_{\mathrm{B}}T_c^{\mathrm{RPA}})^{-1} = \frac{3}{2x}\frac{1}{N}\sum_{\mathbf{q}}\frac{1}{\overline{J}(\mathbf{q})}, \tag{3}$$

respectively. In Eqs. (2) and (3), we have denoted

$$\overline{J}(\mathbf{q}) = \sum_i \overline{J}_{0i}^{\mathrm{Mn,Mn}}(1-e^{i\mathbf{q}\cdot\mathbf{R}_{0i}}), \tag{4}$$

where $\mathbf{R}_{0i}=\mathbf{R}_0-\mathbf{R}_i$ are lattice vectors. It should be noted that up to a constant factor, $\overline{J}(\mathbf{q})$ is proportional to the magnon dispersion law.[22] Due to the divergence at $\mathbf{q}=0$, the evaluation of T_c^{RPA} is done as in Ref. 22. Note that Eqs. (2) and (3) imply a virtual-crystal treatment of the effective Heisenberg model while a more sophisticated treatment in the framework of RPA-CPA is also possible.[25]

Additionally, we also provide a Monte Carlo treatment of the effective Heisenberg model. The single-flip Metropolis algorithm was used and the critical temperature was determined using the cumulant crossing method.[26] A lattice of size $L\times L\times L$ in fcc crystal structure with periodic boundary conditions was employed. The linear lattice size L was varied from $16\,a$ to $48\,a$ (a is lattice constant) and the total number of MC steps/spin were around 15 000. The averages of the thermodynamic observables were measured in the last 12 500 steps. Interactions up to 12 shells of neighboring spins in the effective Heisenberg model were included to achieve convergence with respect to the shell number. This has been possible by rewriting the algorithm into an efficient parallel program and using parallel computers.

IV. RESULTS FOR T_c

Calculated temperatures T_c^{MFA}, T_c^{RPA}, and T_c^{MC} for $(Ga_{0.95-y}Mn_{0.05}As_y)$ As alloys with varying As concentration y are presented in Table I. We find that with increasing y the Curie temperature quickly decreases in all cases. The presence of As antisites reduces the number of carriers which mediate the indirect exchange coupling between the magnetic impurities and as a consequence T_c decreases, a result known also from model studies.[14] We observe that the general relation $T_c^{\mathrm{RPA}} < T_c^{\mathrm{MFA}}$ (Ref. 22) is obeyed. The most re-

TABLE I. Calculated Curie temperatures (T_c) in [K] for ($Ga_{0.95-y}Mn_{0.05}As_y$) As and three different values of As-antisite concentrations y. The values of T_c for the mean-field approximation (T_c^{MFA}), random-phase approximation (T_c^{RPA}), and Monte Carlo simulations (T_c^{MC}) up to 12 nearest-neighbor shells of $\overline{J}_{ij}^{\mathrm{Mn,Mn}}$ are shown. The MFA results for 12 nearest-neighbor shells, $T_c^{\mathrm{MFA}}(12)$, are given for a comparison.

y	T_c^{MFA}	T_c^{RPA}	$T_c^{\mathrm{MFA}}(12)$	$T_c^{\mathrm{MC}}(12)$
0.0	289	275	271	257
0.005	221	212	212	202
0.01	126	122	122	117

markable result is, however, the smallness of the difference between T_c^{MC} and T_c^{RPA} and a simple mean-field value T_c^{MFA}, in particular for alloys with larger concentration of As antisites. This situation is very different from that found for elemental ferromagnets such as bcc Fe or fcc Co, where T_c^{RPA} is smaller than T_c^{MFA} by factors 0.67 and 0.8, respectively.[22]

T_c^{RPA} was recently determined also in the framework of the supercell LMTO approach[20] for the case without As antisites. The estimated difference between T_c^{MFA} and T_c^{RPA} for ($Ga_{0.95}Mn_{0.05}$) As is about 50 K as compared to about 15 K in the present case. Also, the calculated value of T_c^{MFA} is smaller, being 225 K as compared to 289 K in the present case. It should be noted, however, that the effect of disorder is neglected in the supercell approach and Mn atoms form an ordered simple cubic lattice, in contrast with random positions of Mn atoms on fcc Ga sublattice in the present case. Spin waves in DMS were studied in Ref. 27. The authors found that for six-band model, the spin-wave energies for realistic carrier concentrations are much closer to the mean-field value than for a single-band model, and conclude that this explains the success of the mean-field theory to reproduce T_c. The effect of disorder was also neglected in this study. In model calculations, including disorder effects at the lowest order in a single-band model,[7] it was shown that the relation $T_c^{RPA} \approx T_c^{MFA}$ is valid only in the regime of very low carrier concentration but not for the regime relevant for experiments. For example, for $n_h = 0.3x$, $(T_c^{MFA} - T_c^{RPA})/T_c^{MFA} \approx 0.60$ is in contradiction with results presented in Table I. The reason for such disagreement was already mentioned: a qualitatively different behavior of the spin waves relevant for determination of T_c for a single-band model and for realistic bands at large carrier concentrations (see Figs. 2 and 3 of Ref. 27). This demonstrates the relevance of a proper description of the electronic structure of the system, both the realistic band structure and the inclusion of disorder for a quantitative description of T_c.

In Fig. 1, we show $\overline{J}_{\mathbf{R}}^{\mathrm{Mn,Mn}}$ as a function of the distance $|\mathbf{R}|$ between Mn impurities for (a) uncompensated and (b) compensated cases. In both the cases, in contrast to the standard RKKY results, we find that the oscillations of the long-range exchange interactions are suppressed. The coupling thus remains ferromagnetic up to large number of shells. We also observe a strong reduction of the nearest-neighbor interaction when only 1% of As antisite is present: the corresponding exchange interaction is reduced by one order of magnitude as compared to the uncompensated case. On the other hand, the fact that the corresponding T_c (see Table I) is only two times smaller indicates that next-neighbor exchange couplings also contribute significantly to the magnitude of T_c [see Eq. (2)]. Suppression of RKKY-type oscillation of exchange integrals can be attributed to damping effects. There are two mechanisms which contribute to it.

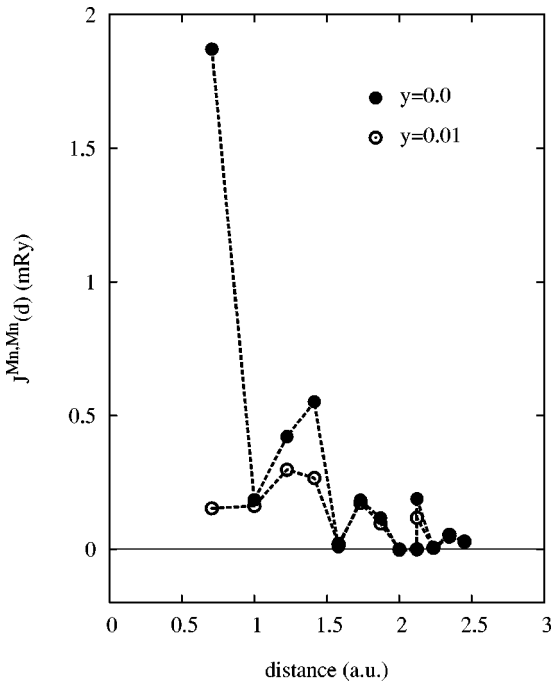

FIG. 1. Pair exchange interactions $\overline{J}_{ij}^{\mathrm{Mn,Mn}}$ for ($Ga_{0.95-y}Mn_{0.05}As_y$) As in the ferromagnetic state as a function of the interatomic distance $d = \mathbf{R}_i - \mathbf{R}_j$ for two different concentrations of As antisites.

(i) The effect of alloying, which introduces an exponential damping in $\overline{g}_{ij}^{\mathrm{Mn,Mn}\sigma}(z)$, Eq. (1), for both the majority and the minority channels. This effect was first discussed qualitatively by de Gennes.[28] (ii) An additional damping due to a half metallic character of the system, i.e., the Fermi energy, lies in the energy gap of the minority band.[22]

Note that the latter mechanism is also effective for the case of metallic fcc Ni although for this case the mechanism is masked by the strong sp-d hybridization.[22]

In Fig. 2 we present the magnon dispersion [Eq. (4)] for both uncompensated and compensated cases. In the first case, except for a small region around the Γ point, where the dispersion drops to zero in agreement with Goldstone theorem, the dispersion is rather flat in the rest of the Brillouin zone. This flatness is a consequence of the exponential damping of exchange interactions mentioned above: exchange interactions are ferromagnetic and not oscillating. Mathematically, the lattice Fourier transform $\overline{J}(\mathbf{q})$ of localized exchange interactions [Eq. (4)] is delocalized and flat in the reciprocal space: the larger the localization of exchange interactions in real space, the stronger the can be effect observed. As antisites in GaMnAs represent an additional strong disorder and the flatness of the magnon dispersion law

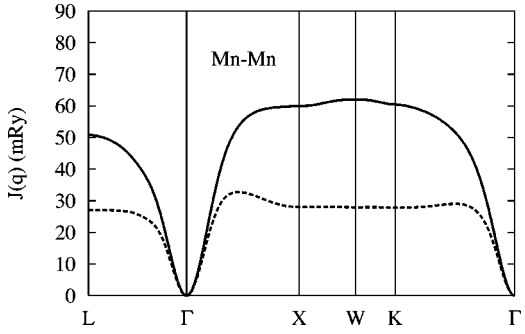

FIG. 2. The lattice Fourier transform, Eq. (4), for ($Ga_{0.95}Mn_{0.05}$)As (continuous line) and ($Ga_{0.94}Mn_{0.05}As_{0.01}$) (dashed line) along the lines of high symmetry in the fcc Brillouin zone of the Ga sublattice. Only Mn-Mn pair exchange interactions are taken into account.

becomes even more pronounced and T_c^{MFA} is thus closer to T_c^{RPA}/T_c^{MC}. The localization of exchange interactions in real space due to their exponential damping which leads to rather flat magnon dispersion thus explains why the RPA/MC and MFA Curie temperatures shown in Table I differ from each other only weakly.

V. CONCLUSION

Curie temperatures are calculated for III-V diluted ferromagnetic semiconductors in presence of As antisites by combining first-principle approach and CPA to treat the disorder. It has been shown that the mean-field treatment of the effective Heisenberg model gives Curie temperatures which are close to both the RPA values and results of Monte Carlo simulations. It is also shown that in contrast to a standard RKKY calculation which neglects the disorder, the Mn-Mn exchange integrals are strongly damped and remain ferromagnetic up to a large number of shells. As a consequence, the magnon dispersion is found to be flat in the whole Brillouin zone except a small region around the Γ point.

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