

## Magnetic Percolation in Diluted Magnetic Semiconductors

L. Bergqvist,<sup>1</sup> O. Eriksson,<sup>1</sup> J. Kudrnovský,<sup>2</sup> V. Drchal,<sup>2</sup> P. Korzhavyi,<sup>3</sup> and I. Turek<sup>4</sup>

<sup>1</sup>*Department of Physics, Uppsala University, Box 530, 751 21 Uppsala, Sweden*

<sup>2</sup>*Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, CZ-182 21 Prague 8, Czech Republic*

<sup>3</sup>*Department of Materials Science, Royal Institute of Technology, SE-10044, Stockholm, Sweden*

<sup>4</sup>*Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žitkova 22, CZ-616 62 Brno, Czech Republic*

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We demonstrate that the magnetic properties of diluted magnetic semiconductors are dominated by short ranged interatomic exchange interactions that have a strong directional dependence. By combining first principles calculations of interatomic exchange interactions with a classical Heisenberg model and Monte Carlo simulations, we reproduce the observed critical temperatures of a broad range of diluted magnetic semiconductors. We also show that agreement between theory and experiment is obtained only when the magnetic atoms are randomly positioned. This suggests that the ordering of diluted magnetic semiconductors is heavily influenced by magnetic percolation, and that the measured critical temperatures should be very sensitive to details in the sample preparation, in agreement with observations.

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The suggestion of magnetic ordering in semiconducting devices [1,2] has spurred a tremendous interest in the so-called diluted magnetic semiconductors (DMS), i.e., semiconductors that have been doped with magnetic elements. One of the most frequently studied systems is Mn-doped GaAs [3–6] but other III-V semiconductors have also been investigated, e.g., Mn-doped GaP [7] and GaN [8]. Among the II-VI semiconductors there have been experimental reports of Cr-doped ZnTe [9] and Mn-doped ZnO [10], whereas for more complex semiconducting or insulating materials one may note Mn-doped ZnGeP<sub>2</sub> [11] and Co doped SnO<sub>2</sub> [12] and TiO<sub>2</sub> [13]. In all these studies one comes to the conclusion that the magnetic properties, in particular, the ordering temperature and the magnetic moment, depend critically on the details in the sample preparation: the Mn concentration, possible clustering of Mn atoms as well as the concentration of nonmagnetic defects. Hence, the critical temperature can vary over a large range, sometimes reaching room temperature [9]. This is a very important finding since for applications one needs ordering temperatures above room temperature [1,2]. Several DMS materials with a critical temperature close to, or above, room temperature have been reported [7–13], but it is likely that some of these reports represent magnetic properties of impurity phases and/or clusters.

Theoretically there have been several attempts to calculate the magnetic properties of these materials, especially the critical temperatures, using model Hamiltonians [14] even for random distribution of magnetic atoms [15]. Unfortunately these works rely on assumed forms of the exchange interactions between the magnetic atoms in the semiconducting host. Typically one assumes either an RKKY or a double exchange interaction to be relevant. In order to have predictive capability, it would

clearly be advantageous to avoid any such assumptions, something a first principles approach provides.

Some attempts to estimate the critical temperature of DMS materials have been made by calculating interatomic exchange interactions from first principles and then using mean field theories for the evaluation of the critical temperature [6,16]. These calculations seem always to overestimate the critical temperature. In addition there have been attempts using the random-phase approximation (RPA-VCA) [17] or Monte Carlo simulations (MC-VCA) [5] in the framework of the virtual-crystal treatment (VCA) of a random Heisenberg Hamiltonian (the average lattice) providing similar results. In the present report we have attempted to make realistic calculations of the critical temperature of DMS systems in which we have abandoned the approximation of an ordered lattice and treated the effect of randomness properly. We have chosen to compare our theoretical results to experimental data for Mn-doped GaAs [3–6] and GaN [8] as well as Cr-doped ZnTe [9], since in these systems the reported magnetic properties seem to reflect the true nature of DMS systems, and not clustering or impurity effects which can be avoided by a proper synthesis yielding a more or less random distribution of magnetic atoms.

We have calculated interatomic exchange interactions using a first principles theory, and then simulated the critical temperature using a Heisenberg Hamiltonian with magnetic atoms distributed randomly. The critical temperature was calculated by means of Monte Carlo simulations. For materials with large atomic spins a classical Heisenberg Hamiltonian has good accuracy as was recently demonstrated for the case of transition metal ferromagnets [18].

In principle, exchange interactions between atoms  $i$  and  $j$ ,  $J_{ij}$ , have to be determined for each geometry of the

Monte Carlo simulation cell (typically 50 000 atoms) using *ab initio* electronic structure calculations. Since this is computationally impossible we have made the approximation to calculate them using the coherent-potential approximation (CPA) and using the local spin density approximation (LSDA), as implemented in the framework of the tight-binding linear muffin-tin orbital (TB-LMTO) method [6].

This approach neglects possible local environment effects in the system, but it is nevertheless a good approximation since: (i) the CPA properly describes concentration variations of alloy properties, in particular, the carrier concentration and electronic properties of various defects that are of key importance for properties of exchange interactions (the size and topology of the Fermi surface); (ii) exchange splittings are robust with respect to local environment effects for atoms with large local magnetic moments, like, e.g., Mn- or Cr-atoms; and (iii) the local environment effects can influence the electronic structure of the system, but numerical studies indicate that the CPA gives an accurate description of disordered states if the Fermi energy is located inside the valence band, i.e., in the metallic regime which is of interest here. The local environment effects can be important for the case of compensated alloys with the Fermi level in quasilocalized states at band edges and, in particular, for the transport properties in this regime [19].

We employ here a two-step approach: in the first step, the self-consistent electronic structure of a system is calculated for a collinear spin structure at zero temperature in the framework of the LSDA-CPA and the parameters of an effective classical Heisenberg Hamiltonian are determined, using the magnetic force theorem and the one-electron Green functions [20]. The carrier concentration is determined self-consistently for a given system and alloy composition, including the effect of finite carrier lifetime due to disorder. In the second step the calculated exchange interactions are used in a simulation cell, where the statistical mechanics is solved by means of the Monte Carlo approach [21]. The main advantage of the two-step approach is the separation of the electronic and statistical degrees of freedom which allows a sophisticated treatment of spin fluctuations as well as the effect of disorder which are both needed for evaluation of the Curie temperature.

If we neglect for simplicity small induced moments on nonmagnetic atoms, the nonvanishing pair exchange interactions are only among substitutional magnetic atoms on the cation sublattice, namely

$$\bar{J}_{ij} = \frac{\text{Im}}{4\pi} \int_{-\infty}^{E_F} \text{tr}_L [\delta_i^M(\varepsilon) \bar{g}_{ij}^{M,M1}(\varepsilon) \delta_j^M(\varepsilon) \bar{g}_{ji}^{M,M1}(\varepsilon)] d\varepsilon. \quad (1)$$

Here  $\text{tr}_L$  denotes the trace over the angular momentum  $L = (\ell m)$ ,  $\delta_i^M(\varepsilon)$  is related to the exchange splitting corresponding to the magnetic atom  $M$ ,  $\bar{g}_{ij}^{M,M1}(\varepsilon)$  and

$\bar{g}_{ji}^{M,M1}(\varepsilon)$  refer to site off-diagonal blocks of the conditionally averaged Green function, namely, the average over all configurations with a pair of magnetic atoms fixed at the sites  $i$  and  $j$ , and  $E_F$  denotes the Fermi energy. Positive (negative) values of  $J_{ij}$  correspond to the ferromagnetic (antiferromagnetic) coupling, respectively, while the values of magnetic moments are included in the definition of  $J_{ij}$ 's by construction. We also mention a strong directional character of  $J_{ij}$ 's due to real lattice and the nonspherical shape of the Fermi surface and its possible smearing out due to disorder. For further details we refer to Ref. [6]. There are two important differences from the conventional RKKY expression: (i) The presence of the conditionally averaged Green functions in (1) which properly includes strong multiple-scattering effects on magnetic impurities and other defects as compared with the ideal, unperturbed semiconductor host, and (ii) the exponential damping of  $J_{ij}$  with the distance between magnetic atoms which is due to randomness (the finite carrier lifetime) and the half-metallic character of the studied alloys.

The Monte Carlo (MC) treatment of the Heisenberg Hamiltonian,  $H = -\sum_{ij} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j$ , employed the Metropolis algorithm. Magnetic atoms were distributed completely randomly on the Ga (Zn) positions of the zinc blende lattice and the number of Mn (Cr) atoms was varied between 8000–30 000, in order to use finite size scaling. All thermodynamic observables were averaged

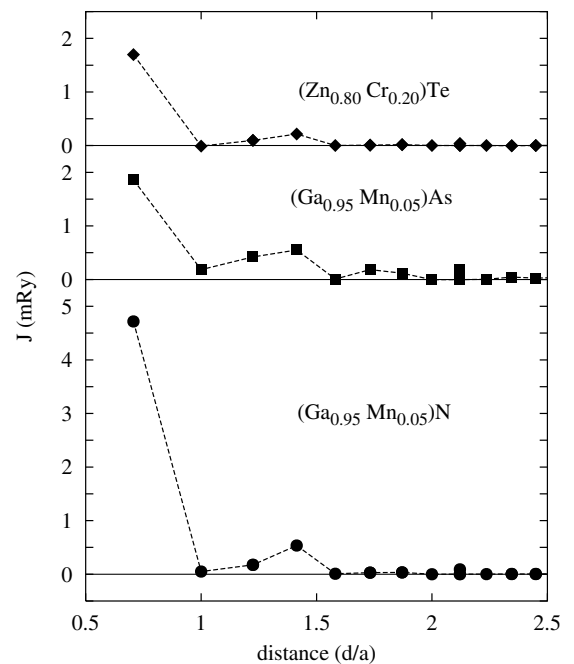


FIG. 1. Exchange integrals for 5% Mn in GaAs (square) and GaN (circle) and 20% Cr in ZnTe (diamond), plotted as a function of the distance  $d/a$ , between magnetic impurities ( $a$  is the lattice constant).

over five different disorder configurations and the critical temperature was determined using the cumulant crossing method [5,21]. Exchange interactions up to 16 shells of neighboring spins in the Heisenberg model were used to achieve convergence with respect to the shell number.

In Fig. 1 we show the calculated values [22] of the interatomic exchange interaction for Mn in GaAs and GaN as well as for Cr in ZnTe, which all are ferromagnetic essentially over all distances, which explains the ferromagnetism in these alloys. They also exhibit exponential damping with respect to distance due to disorder effects and the half-metallic nature of these systems [6]. From Fig. 1 we observe that the exchange interactions are strongly material dependent: the behavior of Mn in GaAs is quite different from that of Mn in GaN or Cr in ZnTe. Another important feature is a strong directional dependence in the coupling, as shown in Ref. [6]. All these results demonstrate that one needs to employ material-dependent exchange interactions rather than *ad hoc* chosen functional forms or empirical parametrizations [14,15] in order to calculate critical temperatures in DMS materials.

In Table I we compare the critical temperatures calculated in different approximations for Mn-doped GaAs and GaN, as well as for Cr-doped ZnTe, with experimental data. In the calculations we have employed concentrations of Mn and Cr atoms that are similar to those reported in the experimental studies. The effect of As antisites in Mn-doped GaAs is also considered as a prototype of native defects [3]. The self-consistently determined carrier concentration  $n$  in this case is  $n = x - 2y$ , where  $x$  and  $y$  are, respectively, concentrations of Mn atoms and As antisites. The most important finding from Table I is that only Monte Carlo simulations that assume a realistic, random distribution of magnetic atoms give ordering temperatures of Cr-doped ZnTe and Mn-doped GaAs and GaN that are satisfactory, i.e., either are in good agreement with experiment or that lie within the range of experimentally observed ordering temperatures. For example, for 5% Mn in GaAs we obtain results ranging from 26 to 137 K, depending on carrier concen-

tration, which should be compared to experimental data ranging from 45 to 118 K. The large spread in the experimental values reflects the fact that the samples produced early had a higher concentration of compensating defects whereas the most recently fabricated samples are essentially defect free [4]. It is important that the theory captures this behavior on a quantitative level. Finally, our calculations for (5%) Mn-doped GaN give low ordering temperatures, which suggests that those samples of Mn-doped GaN that exhibit high ordering temperatures are heavily influenced by clustering effects or phase separation.

One may also note that the MFA values overestimate the critical temperatures somewhat, as compared to MC-VCA and RPA-VCA calculations. In addition we note that MC-VCA and RPA-VCA results agree well with each other [17]. The calculations on an averaged lattice (VCA) in general strongly overestimate the critical temperatures, since the large nearest-neighbor interactions (NN) included in the VCA-like approaches are effectively missing in the MC model which has real distances among impurities. If we omit the first NN interaction in the MFA expression, the critical temperatures for 5% Mn-doped GaAs (GaN) are reduced to 163 K (77 K), which is rather close to the MC (random) results. One can also compare the most realistic results in Table I with data obtained from Monte Carlo simulations on an ordered lattice by Bergqvist *et al.* [5]. From such a comparison it becomes clear that the random distribution of the magnetic atoms lowers the calculated critical temperature with on average 50%. Finally, we remark that the large value of the critical temperature for  $\text{Zn}_{0.8}\text{Cr}_{0.2}\text{Te}$  is due to the fact that first NN interactions become important for these large Cr concentrations, since one approaches the percolation limit.

In conclusion, we have reproduced the ordering temperatures of several archetypical group III-V and II-VI diluted magnetic semiconductors. We have demonstrated, by combining first principles theory with Monte Carlo simulations, that a proper theoretical treatment of the magnetic atoms in a diluted magnetic semiconductor, is

TABLE I. Critical temperatures of Mn-doped GaAs without and with As antisites, Mn-doped GaN, and Cr-doped ZnTe in K. MFA denotes the mean field result, MC-VCA the result from MC simulations on an average ordered network of magnetic atoms, and MC (random) the main result from MC simulations on a disordered network of magnetic atoms. We also include the RPA-VCA [17] values for all systems. In all calculations the same number of shells (16) was included. Expts. denotes experimental values from Refs. [3,8,9].

	$(\text{Ga}_{0.95-y}\text{As}_y\text{Mn}_{0.05})\text{As}$				$(\text{Ga}_{1-x}\text{Mn}_x)\text{N}$				$(\text{Zn}_{1-z}\text{Cr}_z)\text{Te}$
	$y = 0.0$	$y = 0.005$	$y = 0.01$	$y = 0.0125$	$y = 0.015$	$x = 0.03$	$x = 0.05$	$x = 0.08$	$z = 0.20$
Expts.	45–118	45–118	45–118	45–118	45–118	0–370	0–370	0–370	$300 \pm 10$
MFA	281	222	131	72	3	342	376	376	557
MC-VCA	272	215	130	70	0	305	330	334	491
RPA-VCA	266	212	128	70	0	293	327	323	477
MC (random)	137	124	92	55	26	35	55	90	301

essential in order to reproduce observed ordering temperatures. In particular, it is the random distribution of magnetic atoms on the host lattice that plays a crucial role: models employing the average lattice strongly overestimate calculated critical temperatures. The reason for this is the short ranged, anisotropic behavior of the exchange interactions in these materials. Hence, the magnetic ordering in these systems displays features that are analogous to percolation phenomena in general. In fact a geometrical percolation that assumes nearest-neighbor interactions only and the presently investigated crystal structure, predicts an absence of magnetic ordering for a concentration of magnetic atoms lower than 20%. Hence the fact that magnetic ordering is observed (and calculated by us) for lower concentrations of magnetic atoms shows that the exchange interactions are somewhat more extended in space, which is consistent with the results shown in Fig. 1.

Another scenario that is not considered in the present work is the formation of isolated ferromagnetic clusters with an absent or weak long-range ferromagnetic order, expected at a temperature  $T = T^*$  [23,24] that is higher than the critical temperature,  $T_c$ . Although for certain samples this is an interesting and expected scenario we have not pursued this possibility here.

The present results demonstrate that percolation becomes more important for lower concentrations of magnetic impurities and for systems where the exchange interactions are strongly localized in a real space. Our analysis most likely explains the large range of experimentally reported ordering temperatures, since the distribution of magnetic atoms on the semiconducting lattice is critically dependent on how the samples are prepared, resulting in a large range of ordering temperatures.

We also note that we have evaluated the interatomic exchange parameters using an LDA + U approach [6], that takes electron-electron correlations into account in a more explicit way. From the simulations we obtained critical temperatures that are quite close to the LDA values given in Table I. Finally, we remark that the present formalism represents a general scheme that can be applied to a number of relevant problems, not addressed in this Letter. Examples of these are the effect of clustering of the magnetic atoms, the effect of electron correlations beyond LSDA, the occurrence of magnetic atoms and defects on several sublattices (e.g., Mn-doped GaAs with native Mn-interstitial defects) and finally doped group-IV diluted magnetic semiconductors.

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