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Electronic structure and magnetism of diluted magnetic semiconductors

O Eriksson[1], L Bergqvist[1], B Sanyal[1], J Kudrnovský[2], V Drchal[2], P Korzhavyi[3] and I Turek[4]

[1] Department of Physics, Uppsala University, Box 530, 751 21 Uppsala, Sweden
[2] Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, CZ-182 21 Prague 8, Czech Republic
[3] Department of Materials Science, Royal Institute of Technology, SE-10044, Stockholm, Sweden
[4] Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Zizkova 22, CZ-616 62 Brno, Czech Republic

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Abstract

The electronic structure and magnetism of selected diluted magnetic semiconductors (DMS) is reviewed. It is argued that the effect of antisite defects plays an important role in the magnetism of DMS materials and that these defects lower the saturation moment and ordering temperature. We also show that the interatomic exchange of these materials is short ranged. By combining first principles calculations of interatomic exchange interactions with a classical Heisenberg model and Monte Carlo simulations, we show that the observed critical temperatures of a broad range of diluted magnetic semiconductors, involving Mn-doped GaAs and GaN as well as Cr-doped ZnTe, are reproduced with good accuracy. We show that agreement between theory and experiment is obtained only when the magnetic atoms are randomly positioned on the Ga (or Zn) sites. This suggests that the ordering of DMS materials 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.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The suggestion of magnetic ordering in semiconducting devices [1] has spurred a tremendous interest in diluted magnetic semiconductors (DMS), i.e. semiconducting materials that have been doped with magnetic elements. One of the most frequently studied systems is Mn doped GaAs [2–6], 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

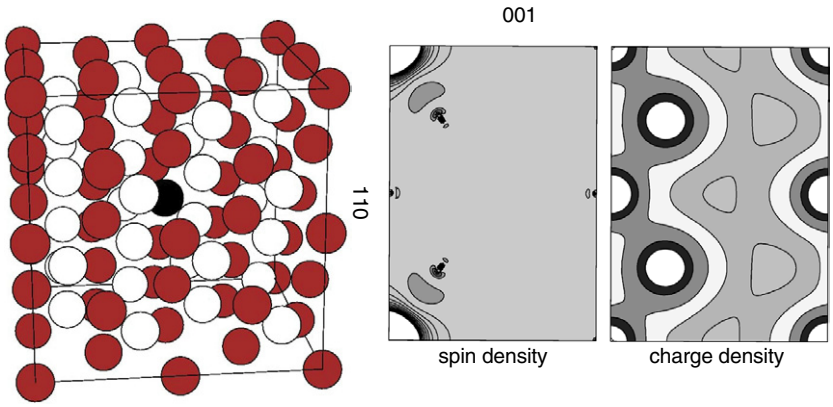

Figure 1. Calculated spin and charge density of Mn doped GaAs. The Mn atom is located in the lower left and upper left corner of the plot. A symbolic figure of the doped lattice is given in the left-hand part of the figure.

of, e.g. Cr doped ZnTe [9]. 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 of the sample preparation: the Mn-concentration, possible clustering effects as well as the concentration of non-magnetic defects. Hence, the critical temperature can vary over a large range, sometimes reaching room temperature [9].

In this paper we review some of our efforts in this field [4, 10, 11], and we make comparison to experimental observations as well as other theoretical works. The theoretical methods used here rely on a full potential linear muffin-tin orbital method [12], a non-collinear linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA) [13] as well as an LMTO-ASA Green function method combined with the coherent potential approximation to treat alloy disorder [5]. In addition to first principles calculations of magnetic moments and exchange interactions we report on calculations of critical temperatures, using a classical Heisenberg Hamiltonian and Monte Carlo simulations. For these calculations we first calculated the self-consistent electronic structure of a system for a collinear spin structure at zero temperature and the interatomic exchange parameters of an effective classical Heisenberg Hamiltonian are determined, using the magnetic force theorem and the one-electron Green functions [14]. In the second step the calculated exchange interactions are used in a simulation cell, where the statistical mechanics part of the problem is solved by means of Monte Carlo simulations [15].

2. Results

2.1. Magnetism of Mn doped GaAs

The calculated (FP-LMTO) spin and charge density of Mn doped GaAs is shown in figure 1. As is seen from the figure, the charge density around a Mn atom is very similar to that around a Ga atom, which means that the covalent charge distribution (which is the result of sp^3 hybrids) is maintained around the Mn atom. This is somewhat surprising since there is no formation of sp^3 hybrids in Mn. The spin density is seen to be almost entirely located on the Mn atom and the calculated total magnetic moment/fu corresponds to 4 μ_B per doped Mn atom (this is obtained for a large range of Mn concentrations). The integer number of the magnetic moment is due to the half metallic character of the electronic structure [2, 4, 6]. The calculated

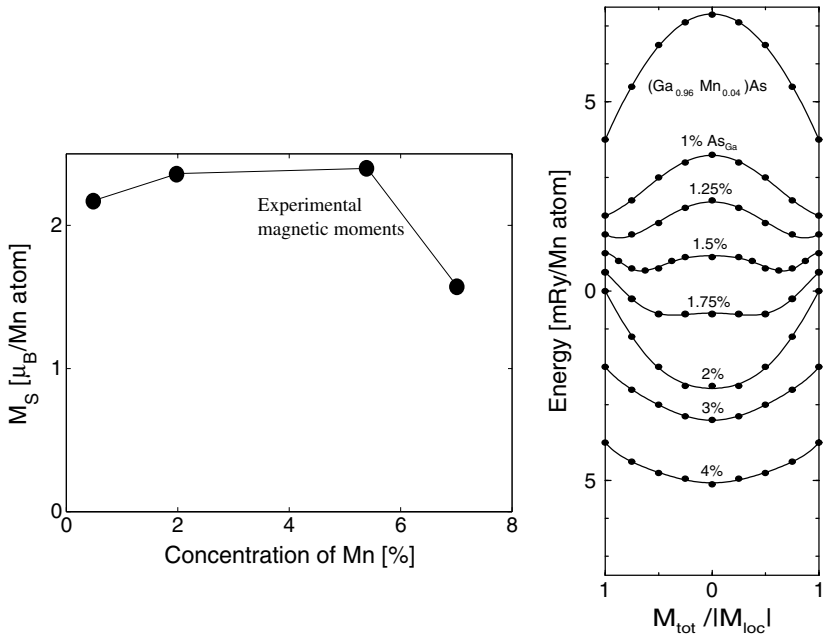

Figure 2. Measured saturation magnetization of 5.5% Mn doped GaAs (left figure, redrawn after [4]). In the right part of the figure we display the calculated total energies of the DLM state of Mn–GaAs as a function of As antisite concentration. $M_{\rm tot}/M_{\rm loc}$ is a measure of the fraction of 'Mn up' and 'Mn down' atoms.

magnetic moment may be compared to experimental values (figure 2) [4]. It is clear that the theoretical moment does not compare particularly well with experiment, since, depending on concentration, the measured moments range from 1.5 to 2.4 $\mu_{\rm B}$ per doped Mn atom. Typically, first principles based methods reproduce the spin and orbital moments with an error not larger than some 10% [16], if the correct magnetic structure is considered, and the poor agreement between calculated and measured spin moments of Mn doped GaAs has led us to consider other magnetic configurations.

Since the presently studied systems are characterized by having magnetic atoms distributed randomly on the Ga (or Zn) sublattice of the zincblende structure it becomes natural to explore the so-called disordered local moment configuration (DLM) [17]. This configuration represents a random distribution of Mn atoms where some atoms have a magnetic moment aligned parallel with the global magnetization of the crystal whereas the rest of the Mn atoms are aligned anti-parallel with the global magnetization direction. We will refer to these atoms as 'Mn up' and 'Mn down', respectively. In the right-hand side of figure 2 we show the total energy as a function of the distribution of 'Mn up' and 'Mn down' atoms ($M_{\rm tot}/M_{\rm loc} = 1$ corresponds to a ferromagnetic state and $M_{\rm tot}/M_{\rm loc} = 0$ an even but random distribution of 'Mn up' and 'Mn down' atoms). It is seen from the figure that if no As anti-site defects [18] are considered the ferromagnetic state is stable, whereas if As anti-site defects are taken into account one finds a minimum in the total energy for values of $M_{\rm tot}/M_{\rm loc}$ intermediate between 0 and 1. This means that there is a random distribution of 'Mn up' and 'Mn down' atoms and figure 2 shows that the fraction between these atoms depends on the As antisite concentration. Obviously the DLM state lowers the total magnetic moment of the sample, and in figure 3 we display the calculated total magnetic moment as a function of As anti-site concentration. Each point

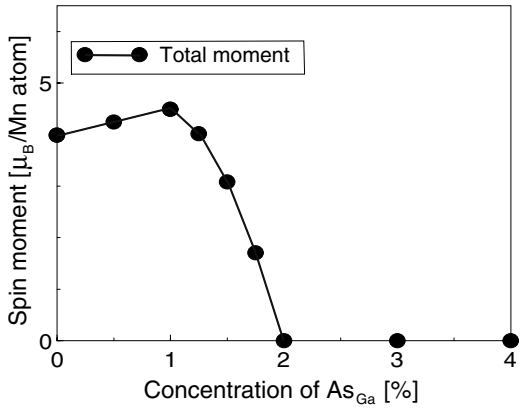

Figure 3. Calculated total moment of 5.5% Mn doped GaAs as a function of As antisite concentration.

in figure 3 corresponds to an energy minimum in figure 2. We observe that a concentration of As antisites of approximately 1.2–1.5% yields a total magnetic moment that is consistent with the experimental data of figure 2. It should be noted here that interstitial Mn atoms most likely are also present in the samples and since the exchange interaction between the interstitial and substitutional Mn atoms is calculated to be anti-ferromagnetic [11], one expects a further reduction of the total magnetization due to these interstitial Mn atoms.

2.2. Electronic structure of Mn doped GaAs

In figure 4 we show the calculated density of states (DOS) of a DLM state of Mn doped GaAs. The plot corresponds to 3.75% 'Mn up' atoms and 0.25% 'Mn down' atoms, and we show the DOS for a system with and without As antisite defects. It is clear that when no As defects are present the Fermi level (E_F) cuts through a sharp peak of the DOS of the 'Mn down' projected states. This is an energetically unfavourable situation and the system can lower its total energy by reducing the amount of 'Mn down' atoms, so that the ferromagnetic state is stable (see also figure 2). However, the presence of As defects changes the situation such that E_F is moved up in energy and there is no longer a sharp peak at E_F. In the right-hand side of figure 4 we show a model DOS that applies to Mn doped GaAs as well as to dilute magnetic semiconductors in general. From the figure it is clear that the two electrons that accompany the As defect level can lower their energy by recombining with Mn induced hole states in the DLM configuration. However, for the ferromagnetic situation only one of these electrons finds a hole to recombine with, which suggests that the DLM state becomes stabilized due to the As antisite defects (in accordance with the results of figure 2).

2.3. Mixing energies of Mn doped GaAs

In figure 5 we show the calculated mixing energy for Mn doped GaAs, i.e. we show $E[(Ga_{1-x}Mn_x)As]$–$xE[MnAs]$–$(1-x)E[GaAs]$, where all compounds are in the zincblende structure. Figure 5 shows that in the absence of As antisites the mixing energy is positive for all Mn concentrations, which suggests that Mn atoms would like to phase separate to a MnAs phase. In the presence of As antisites the mixing energy is negative for certain Mn concentrations. In this case we find that the lowest energy is always found for Mn and As antisite concentrations which corresponds to complete compensation, i.e. when the holes

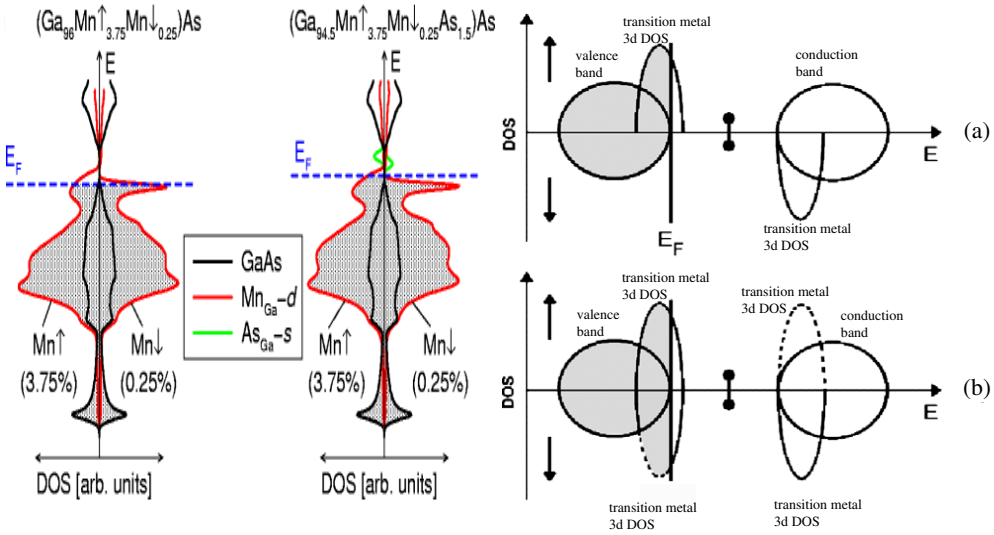

Figure 4. Electronic structure of Mn doped GaAs (left part of the figure) with and without As antisites. The energy scale is on the vertical axis in this part of the figure. In the right part of the figure we show a model DOS of transition metal doped semiconductors with As antisite defects. In this part of the figure the energy axis is the horizontal axis. The DOS of transition metals with a magnetization along the global magnetization axis is given by full lines, whereas the DOS of atoms with a magnetization opposite to the global magnetization is given by dashed lines. The upper plots (a) corresponds to a ferromagnetic state, whereas the lower plot (b) corresponds to a DLM state. The two dots correspond to two electrons of the As defect level.

introduced by the Mn atom are filled with electrons of the As antisites. This means that for a Mn concentration of, e.g. 5%, complete compensation occurs for a 2.5% As antisite concentration. This situation is however not very desired since such a compensation results in an zero total moment, due to the formation of a DLM state with equal amounts of 'Mn up' and 'Mn down' atoms (as is clear from figures 2 and 3).

2.4. Critical temperatures

In the past there have been several attempts to calculate the critical temperatures of DMS materials, using model Hamiltonians [19, 20]. 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, materials specific capability, it would clearly be advantageous to avoid any such assumptions, something a first principles approach provides. Several attempts to estimate the critical temperatures of magnetic materials in general have been made by calculating interatomic exchange interactions from first principles and then using mean field theories, e.g. the virtual crystal approximation or averaged lattice approach, for the evaluation of the critical temperature [5, 21]. The results of these calculations always seem to be too large as compared to experiment. One step further can be taken by considering first principles calculations of the interatomic exchange interaction that are then used in a classical Heisenberg Hamiltonian where the statistical physics part of the problem is solved by Monte Carlo simulations. This was for instance done for Mn doped GaAs in [10], but also in this approach was it found that theory gave too large values of the critical temperature. For instance,

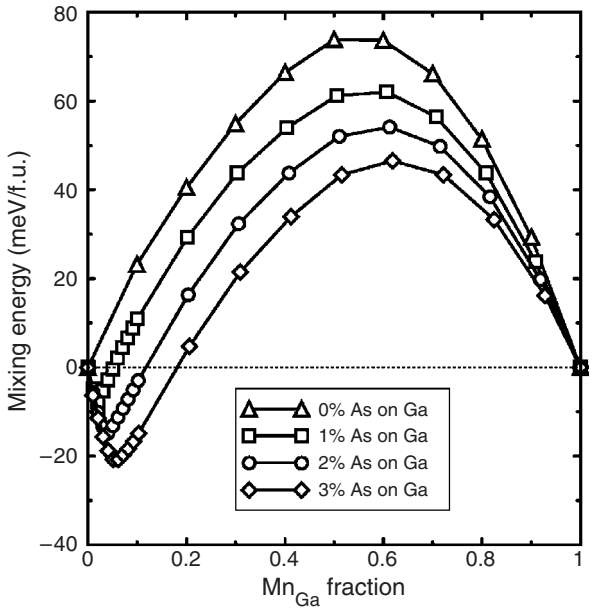

Figure 5. Calculated mixing energy of Mn doped GaAs as a function of As antisite concentration.

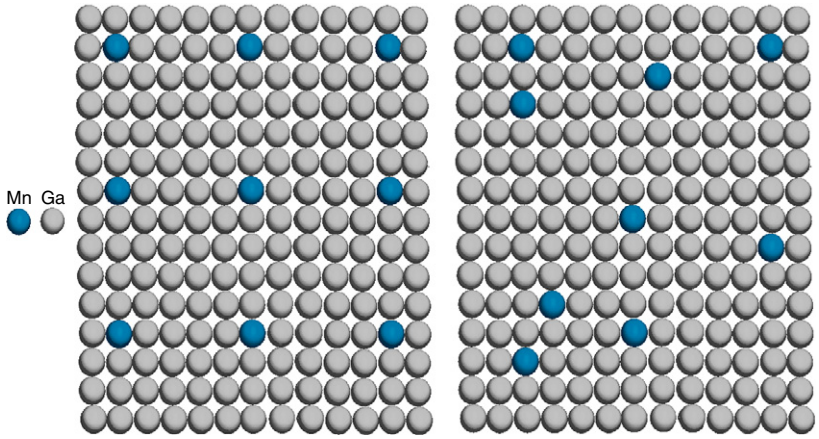

Figure 6. Symbolic structure of the simulation cell of the Heisenberg Hamiltonian. The light spheres correspond to Ga (or Zn atoms), whereas the darker spheres correspond to Mn (or Cr) atoms.

using an ordered structure as shown in the left part of figure 6, exchange interactions were evaluated from self-consistently calculated spin-wave curves. These interactions were then used in a Heisenberg Hamiltonian and a simulation cell with ordered Mn atoms (figure 6, left part) and the evaluated critical temperatures (from Monte Carlo simulations) were ∼160 K for 3% Mn, ∼270 K for 6% Mn, ∼300 K for 12.5% Mn and ∼250 K for 25% Mn [10]. These values are too large compared to experimental data and we come to the conclusion that the previous studies are unrealistic since the Mn-atoms were assumed to be situated in an ordered way. We have tried to improve on the above mentioned shortcomings and treated the

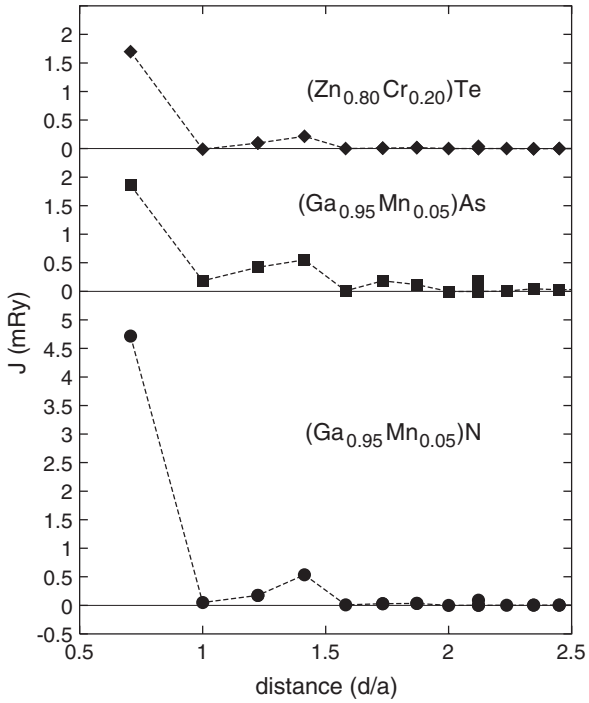

Figure 7. Exchange interactions for Mn in GaAs (square) and GaN (circle) and Cr in ZnTe (diamond), plotted as a function of the distance d/a, between magnetic impurities (a is the lattice constant). The calculations were made for a Mn concentration of 5% and a Cr concentration of 20%.

effect of disorder exactly by considering a random distribution of Mn (or Cr) atoms on the semiconducting lattice (as is the case in the right part of figure 6) together with a classical Heisenberg Hamiltonian and first principles calculations of the exchange parameters. In this part of our study we have chosen to compare our theoretical results to experimental data for Mn doped GaAs [3] 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.

Before we come to the results of the critical temperatures we show in figure 7 the calculated values of the interatomic exchange interaction for Mn in GaAs and GaN as well as for Cr in ZnTe. It may be seen that for all three systems there is an exponential damping with respect to distance due to disorder effects and the half metallic nature of these systems [5]. From figure 7 we observe that the exchange interactions are very different for the three studied materials: the behaviour of Mn in GaAs is quite different from that of Mn in GaN or Cr in ZnTe. The exchange interactions are of shortest range for Mn in GaN and longest range for Mn in GaAs. Our calculations also show that Cr in ZnTe lies between these limits. Another important feature is a strong angular component in the coupling, as shown in [5]. These results demonstrate that one needs to employ material-dependent exchange interactions rather than ad hoc chosen functional forms or empirical parameterizations [19, 20] in order to calculate critical temperatures in DMS materials.

With the exchange parameters shown in figure 7 we then set up a Heisenberg Hamiltonian and evaluated the critical temperature by means of Monte Carlo simulations. In these

calculations several simulation cells with random distribution of Mn (or Cr) atoms were considered and the final result was obtained as an average of these different simulations. For Mn doped GaAs we also investigated the effect of As antisites. In the calculations we considered concentrations of Mn and Cr atoms that are similar to those reported in the experimental studies. The calculated value of the critical temperature for (20%) Cr doped ZnTe is 301 K which is in excellent agreement with the observed value of 300 K. The excellent agreement is obviously fortuitous; in general one can not expect an error smaller than some 10% with this approach. For (5%) Mn in GaAs we obtain results ranging from 26 to 137 K, depending on As antisite concentration, which should be compared to experimental data ranging from 45 to 140 K. Finally, our calculations for (5%) Mn doped GaN give low ordering temperatures, which suggests that samples of Mn doped GaN that exhibit high ordering temperatures are heavily influenced by clustering effects or phase separation.

Compared to our previous calculations [10] we observe that only Monte Carlo simulations that assume a realistic, random distribution of magnetic atoms give ordering temperatures of Mn-doped GaAs and GaN that are satisfactory, i.e. that either are in good agreement with experiment or that lie within the range of experimentally observed ordering temperatures. That the calculated critical temperature depends heavily on the distribution of the magnetic atoms, is simply a reflection of the short ranged nature of the exchange interactions and our results are reminiscent of percolation phenomena in general.

3. Conclusion

In conclusion, we have reproduced the magnetic moments and ordering temperatures of several representative groups III–V and II–VI diluted magnetic semiconductors, demonstrating that defects and a random distribution of magnetic atoms is important to consider. We have also argued that the presence of As antisite defects stabilizes a DLM state and that (as usual) the magnetic coupling can be intimately connected to the electronic structure of the material. Further, by combining first principles theory with a classical Heisenberg Hamiltonian and Monte Carlo simulations, we find that a random distribution of magnetic atoms on the host lattice plays a crucial role for obtaining an accurate critical temperature. When combined with the short ranged, anisotropic behaviour of the exchange interactions in these materials, the magnetic ordering displays features that are analogous to percolation phenomena in general. The present results also 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.

Finally we remark that the present formalism has also been pursued in [22] and represents a general scheme that can be applied to a number of relevant problems not addressed in this paper. Examples of these are the effect of clustering of the magnetic atoms, as well as the occurrence of magnetic atoms and defects on several sublattices (e.g. Mn-doped GaAs with native Mn-interstitial defects).

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