Interatomic exchange in Mn-doped III–V semiconductors

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Interatomic exchange in Mn-doped III–V semiconductors

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Abstract
Density-functional calculations are used to determine the electronic structure and magnetic properties of dilute magnetic semiconductors with the composition $X_{1-x}$Mn$_x$N ($X = \text{Al, Ga, In, } x = 6.25\%$ and 12.5\%). Emphasis is on the interatomic exchange as a function of the Mn–Mn distance. Our superlattice calculations show that the Mn dopants are spin-polarized with a half-metallic band gap and a magnetic moment of 4 μ$_B$ per Mn atom at $x = 6.25\%$ and 12.5\%. The Mn (3$d$) bands lie in the band gap but partially hybridize with valence band or N 2$p$ electrons, depending on the group-III element and on the spin direction. To calculate the exchange interaction parameters $J_{ij}$, we have used a Green-function approach. The interaction between Mn atoms extends over several interatomic interactions and is mediated by nitrogen (2$p$) electrons. The exchange is always ferromagnetic and largest for the first nearest neighbors, but substantial ferromagnetic interactions persist over Mn–Mn distances up to sixth nearest neighbors in the considered supercell.

Keywords: magnetic semiconductor, first-principle calculation, exchange interaction

1. Introduction

Dilute magnetic semiconductors, such as III–V semiconductors highly doped with magnetic ions, have recently attracted renewed interest in the context of spintronics, as epitomized by the observation of Curie temperatures of about 110 K in Mn-doped GaAs [1, 2]. These magnetic semiconductors are not only promising for spintronics applications but also pose a number of unique physical challenges, because the compound’s magnetic, optical and electronic effects are all interconnected. A crucial point is the relation between the band structure, doping and magnetism. In particular, the Curie temperature $T_C$ of magnetic semiconductors is very important, because spintronics devices are ideally used at room temperature. For example, room temperature ferromagnetism has recently been reported in Ga$_{0.97}$Mn$_{0.03}$N [3, 4], where $T_C = 400$ K, and in doped AlN, with Curie temperatures $T_C$ of about 300 K for Mn doping [5] and 340 K for Cr doping [6].

The Curie temperature is essentially determined by the interatomic exchange $J_{ij} = J(R_i, R_j)$ between the atomic magnetic moments located at $R_i$ and $R_j$, but the underlying mechanisms are materials-specific and, in general, poorly understood. First-principle calculations indicate that the interactions between the Mn atoms in GaAs are too strong to be explained in terms of the RKKY picture and must be treated non-perturbatively [7]. One reason is the low carrier density, which does not support high Curie temperatures [8]. On the other hand, it is known that hybridizations between iron-series 3$d$ and O (or N) 2$p$ electrons give rise to coupling effects that extend into relatively distant neighborhoods [9, 10]. Simpifying somewhat, this down-folding procedure yields relatively strong interactions between hybridized 2$p$ and 3$d$ orbitals. However, compared to the calculations of the magnetic moment [11–15], little work has been done to actually calculate the interatomic exchange for specific materials, such as Mn-doped GaAs [7] and GaN [16]. A particular question is the quantum-mechanical character of the orbitals that realizes the interatomic exchange. Existing first-principle calculations are complemented by model calculations dealing with various coupling mechanisms, such as RKKY interactions [17, 18] and overlapping localized orbitals [10, 19]. In particular, based on the Zener model, it was suggested that the wide-gap semiconductor GaN doped with 5% Mn should exhibit ferromagnetic behavior up to about 400 K [20], which has sparked intensive research in the field.

From the point of view of basic electronic structure, Mn impurities in GaAs act as shallow acceptors where Mn (3$d$) states hybridize and form a joint band with the nitrogen valence electrons. In Mn-doped GaN, the Mn (3$d$) states form an isolated impurity band inside the wide GaN gap [21–27]. In this work, we examine the nature of Mn impurity states in three nitride compounds namely AlN, GaN and InN. Little work has been done on Mn-doped AlN [28]. This material has a very large band gap of 6.2 eV and may be used as an insulator in GaN based devices or as a magnetic barrier in tunnel junction where it could serve as a spin valve. InN was considered to have a band-gap value of about 2 eV [29], until it was shown recently that the gap is much smaller, about...
Figure 1 shows the \( X_x \text{Mn}_y \text{N}_z \) wurtzite structure investigated in this paper. The lattice constants and some ratios are listed in Table 1. The wurtzite structure is the hexagonal analog of the zinc-blende lattice, characterized by an ABAB-type stacking. The ideal structure, where the nearest-neighbor environments of the atoms are very similar to those in the zinc-blende structure, has \( c/a = \sqrt{8/3} \) and \( u = 3/8 \). In this case, each group-III atom, such as Ga in GaN, has 12 first nearest neighbors of its own type. However, as shown in Table 1, wurtzite GaN, AlN and InN exhibit a compressed \( c/a \) ratio and a slightly different \( u \) value as compared to the ideal case. This leads to two inequivalent Ga positions and the 12 nearest neighbors of any group-III cation split into two types, namely six atoms in the same plane and six atoms in adjacent planes, similar to the locations of the nearest neighbors in the \( a-b \) planes of the hcp crystals. In our calculations, the Mn atoms were placed at the cation (Al, Ga or In) sites, since the 3d impurities are mostly substitutional in III–V semiconductors [31]. Furthermore, we assume that Mn leads to the formation of 2\( \times \)2\( \times \)2 supercells with the chemical compositions \( X_{15} \text{Mn}_1 \text{N}_{16} \) and \( X_7 \text{Mn}_4 \).

Table 1. Lattice parameter used in present calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a [\text{Å}] )</td>
<td>3.112</td>
<td>3.189</td>
<td>3.54</td>
</tr>
<tr>
<td>( c [\text{Å}] )</td>
<td>4.982</td>
<td>5.185</td>
<td>5.705</td>
</tr>
<tr>
<td>( c/a )</td>
<td>1.601</td>
<td>1.626</td>
<td>1.612</td>
</tr>
<tr>
<td>( u )</td>
<td>0.380</td>
<td>0.376</td>
<td>0.377</td>
</tr>
</tbody>
</table>

To perform our electronic-structure calculations, we have used the local-spin-density approximation (LSDA) to the density-functional theory (DFT), within the framework of the linear muffin-tin orbitals method in atomic-sphere-approximation (LMTO-ASA) [32]. The first set of supercell calculations was done with one Mn atom in the 2\( \times \)2\( \times \)2 supercell, corresponding to a composition \( X_{15} \text{Mn}_1 \text{N}_{16} \) (\( X = \text{Al, Ga, In} \)) to and to a Mn concentration of \( x = 6.25 \%). The second set of calculations considers two Mn atoms per supercell, corresponding to \( X_2 \text{Mn}_2 \text{N}_{32} \) (\( X = \text{Al, Ga, In} \)) and \( x = 12.5 \%). Possible local relaxations caused by the substitutional Mn are not considered, because Mn and the group-III atoms have comparable sizes and local relaxations have an insignificant effect on the electronic and magnetic properties, especially in GaN [21]. The calculations employ the exchange-correlation potential of von Barth and Hedin [33], and the Brillouin-zone integrations to achieve a self-consistent use of the tetrahedron method on a mesh of 343 \( k \)-points in the irreducible part of the Brillouin zone.

3. Results and discussions

3.1. Electronic structure

Figure 2(a–c) shows the spin-resolved band structures and partial density of states of Mn-doped III–V nitride semiconductors. The compounds are half-metallic, with the majority being metallic and minority spin being semiconducting. Aside from spin mixing, for example at interfaces and due to thermal activation [34], this corresponds to 100% polarization of conduction carriers, which suggests that these dilute magnetic semiconductors can be used efficiently in injection of the spin-polarized charge carriers.

The \( X \) (or group-III), N and Mn contributions in the majority-spin system (↑) can be divided into three parts. The states in the energy range from \(-8 \) to \(-3 \) eV in the valence band and 3–6 eV in the conduction band primarily arise due to the hybridization between the \( X \) (Al, Ga and In) and N atoms. The states near the Fermi level \( E_F \), in the energy range from \(-2 \) to 2 eV, are of Mn (3\( d \)) and N (2\( p \)) character, and form the lower part of the valence band. This half-metallicity is because the Mn (3\( d \)) states hybridize well with the N (2\( p \)) states. Due to this hybridization with the Mn (3\( d \)) states, the holes are itinerant while keeping their \( d \)-character, meaning that the kinetic energy is lowered so efficiently so as to ensure a ferromagnetic state stabilized by the double-exchange mechanism. In all the three compounds, the bands are spin-polarized with magnetic moments of 4 \( \mu_B \) per Mn atom for both stoichiometries. The moment resides predominantly on Mn. In an ionic picture, as Mn occupies the cation site, it donates 3 electrons to fulfill the bonding and is left with 4 unpaired \( d \) electrons. Therefore, the Mn spin corresponds to a 3\( d^4 \) state with 4↑ electrons per atom.

Going from Al to In, the increasing hybridization between \( X \) (\( p \)) and Mn (\( d \)) causes the Mn impurity band to merge into the valence band. Furthermore, in the two wide-gap compounds AlN and GaN, the Mn 3\( d \) states are split-off in energy from the valence band and positioned as a deep acceptor level inside the gap. Contrary to this, Mn states in InN act like
a shallow acceptor having a large hybridization with N (2p) states, similar to the behavior of Mn-doped GaAs [7]. As in other magnetic semiconductors [35], there is also the question of correlations (Coulomb interaction), which affect parameters such as the width and position of the impurity band and also the Curie temperature itself [16, 24, 36–38]. Judging from the published LSDA+U calculations [24], this effect is likely to somewhat reduce the relative energy of the Mn impurity.

The band structure of the minority spin system also consists of three parts, but with increasing atomic number of the group-III atoms, the band gap decreases. This is mainly due to the large hybridization of the Mn (3d) bands with the N (2p)
bands. The p–d exchange mechanism is also responsible for the ferromagnetic order in Mn-doped XN, because the p orbital energies of N are very close to that of Mn. Clearly, this strong N(p)–Mn(d) exchange interaction plays a role in narrowing the band gap of the Mn-doped XN system with increasing atomic number of the X atom. The spin-resolved partial Mn (3d) DOS, Figure 2(a–c), can be explained by the tetragonal crystal field created by the surrounding N ligands, which splits the five 3d orbitals of the Mn$^{3+}$ ion into three $t_2$ and two $e_g$ levels [27]. The hybridization of $t_2$ and N(p) orbitals further shifts the bonding states $t_2^b$ into the valence band and the antibonding $t_2^a$ states above the two nonbonding $e_g^-$ states.

The Fermi energy is positioned in the middle of the Mn ($t_2$) bands, and therefore the occupied states close to the $E_F$ are of Mn(d)–N(p) antibonding character. This important feature is visible in the charge density contour plots in Figure 3(a–c), where the charge density is significantly reduced at the middle of the Mn–N bond.

3.2. Exchange interaction

The interatomic exchange interactions ($J_{ij}$) are calculated in the Heisenberg approximation, that is, by considering the rotations of spins located at $\mathbf{R}_i$ and $\mathbf{R}_j$. Based on the local approximation to the spin-density functional theory, Lichtenstein et al. [39] have developed a method to calculate the $J_{ij}$. The use of spherical charge and spin densities and of a local force theorem, expression for $J_{ij}$ yields:

$$J_{ij} = \frac{1}{4\pi} \text{Im} \int dz \text{tr} L \left[ \{P_1^\sigma(z) - P_1^\bar{\sigma}(z)\} g_1^\sigma(z) \times \{P_1^\sigma(z) - P_1^\bar{\sigma}(z)\} g_1^\bar{\sigma}(z) \right]$$

Here $\text{tr} L$ is the trace over the angular momentum $L = (lm)$, and the energy integration over $z$ ($z = E + i\delta$, $\delta > 0$) is performed for the upper part of the complex energy plane, over a contour $C$ starting below the bottom of the valence band and ending at the Fermi energy ($E_F$). The diagonal matrices $P_1^\sigma(z)$ are the so-called potential functions for the spin directions $\sigma = \uparrow, \downarrow$, with elements $P_1^\sigma_{iL}(z)$. Finally, $g_1^\sigma(z)$ are the so-called auxiliary Green function matrices with elements $g_1^\sigma_{iL,jL}(z)$ defined as

$$\left[ g_1^\sigma(z) \right]_{iL,jL}^{-1} = P_1^\sigma_{iL}(z) S_1^{\uparrow,\downarrow} \delta_{iL,jL} - S_1^{\uparrow,\downarrow}$$

To calculate the exchange parameters $J_{ij}$ we have substituted two Mn atoms in the supercell at various sets of nearest-neighbor separation between them.

In Figure 4, we have plotted the exchange interaction between two Mn atoms as a function of distance between first-nearest, second-nearest and more distant neighbors, labeled by integer numbers rather than lattice distances, because the
latter vary from compound to compound. In all the three series, exchange is significant only for the first-nearest Mn pairs. The interatomic distances $R_{ij}$ for each pair of Mn atoms in the supercells along with the values of nearest-neighbor and corresponding $J_{ij}$ are listed in Table 2. The magnitude of the exchange is the largest for the Mn–Mn nearest neighbors, and the exchange is ferromagnetic. However, a substantial exchange survives for well-separated Mn atoms up to sixth-nearest neighbors in the considered unit cell. Of course, the supercell periodicity forbids the consideration of much larger Mn–Mn distances.

However, for AlN, third neighbor exchange interaction is also considerable. As discussed above, there are two types of inequivalent Mn–Mn nearest-neighbor pairs, depending on whether the pair is in the basal plane or not. A similar situation is encountered for fourth neighbors. Table 2 indicates that the Mn-doped AlN, GaN and InN are all ferromagnetic, although the smaller exchange values for InN suggest a somewhat reduced Curie temperature for this material.

To see the effect of hole (electron) doping on the exchange parameter, we have studied the exchange interaction parameter as a function of energy, and the result is shown in Figure 5. The doping adds or removes electrons, and this changes the filling of the Mn impurity band. In Figure 5, zero energy refers to the Fermi energy. Above the Fermi energy, the value of exchange interaction decreases and becomes zero within 0.25 eV. This value corresponds to one additional electron per Mn atom in the system. In other words, the exchange interaction between Mn atoms decreases with the decreasing hole concentration. By comparison, at energies lower than the Fermi energy, which corresponds to additional holes in the Mn bands, we observe two maxima at energies near 0.3 eV and 1.2 eV below the Fermi energy. The first maximum is at energy when we have one missing electron (one additional hole) per Mn atom, whereas the second maximum occurs for nearly 3 holes per Mn atom. The exchange interaction is zero again when 4 electrons are removed, because Mn has a configuration close to $3d^4$. Our calculations suggest that although Mn-doped AlN and GaN may have nearly the same transition temperature but the hole doping in AlN might increase its transition temperature considerably.

4. Conclusions

In summary, we have used density-functional calculations to determine the electronic structure of Mn impurities in the wide-band gap bulk semiconductors GaN, AlN and InN. In the supercell calculations, one and two Mn atoms per $2 \times 2 \times 2$ supercell mean that 6.25% and 12.5% of the group-III atoms are replaced by Mn, respectively. All the three systems are half-metallic with a moment of nearly exactly 4 $\mu_B$ per Mn atom. An important point is the calculation of the exchange interaction parameters $J_{ij}$ for the doped semiconductors, varying the Mn–Mn distance of the two Mn atoms in the supercells with 12.5% Mn. The systems are all ferromagnetic and exhibit a strong nearest-neighbor exchange and substantial ferromagnetic interactions over Mn–Mn distances up to the six nearest neighbors. Our explanation of this pronounced interatomic exchange is the involvement of N (2p) electrons.

References


The interatomic distances $R_{ij}$ for each pair of Mn atoms in the supercells along with the values of nearest-neighbor and corresponding $J_{ij}$ are listed in Table 2. The magnitude of the exchange is the largest for the Mn–Mn nearest neighbors, and the exchange is ferromagnetic. However, a substantial exchange survives for well-separated Mn atoms up to sixth-nearest neighbors in the considered unit cell. Of course, the supercell periodicity forbids the consideration of much larger Mn–Mn distances.

Table 2. Exchange parameter (in meV) as a function of $|z|$ of Mn–Mn distance. Two values at first distance are for (i) 6 neighbors in $z = \pm 1/2$ c/a plane (ii) 6 neighbors in the same plane.

| No. | Distance (multiples of ‘a’) | $|z|$ | $J_{ij}$ (meV) |
|-----|-----------------|-----|-------------|
|     | in Al$_x$MnN$_8$ | in Ga$_x$MnN$_8$ | In$_x$MnN$_8$ |
| 1   | 0.99            | 6   | 43.35       | 45.46   | 36.55   |
| 1.00| 6               | 20.24| 30.94      | 23.55   |
| 2   | 1.412           | 6   | 2.63        | 0.62    | 4.13    |
| 3   | 1.626           | 2   | 15.91       | -0.24   | -1.36   |
| 4   | 1.730           | 6   | -2.90       | 1.53    | 1.94    |
| 5   | 1.732           | 6   | -4.66       | 0.06    | 3.21    |
| 6   | 1.909           | 12  | 5.77        | 4.30    | 4.13    |

Figure 5. Pair exchange parameter as a function of energy. Zero value corresponds to the Fermi energy.


