Diluted Magnetic $Ga_{1-x}Mn_xN$ Alloys: A First-Principles Study

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The utilization of the quantum properties of the electron spin wave function will allow the development of a new class of devices. The problem is still controversial and unsettled, even qualitatively, especially for concentrated spin systems such as 3d metals and their alloys. The variety of crystal structures of 3d metals makes difficult the direct comparison between the experimental results and the theoretical conclusions. On the account of this difficulty, substitutional alloys with the same crystal structure, especially face-centered cubic alloys, have been investigated extensively. In this work the properties of diluted $Ga_{1-x}Mn_xN$ (x = 0.0630; 0.0315) alloys are calculated in the zinc-blende phase, within the framework of the density functional theory, using the full-potential linearized augmented plane wave (FLAPW) method and the local density approximation (LDA). The alloys are simulated using 32-atom and 64-atom large unit cells, containing one substitutional Mn atom for a Ga atom. The calculations are spin-polarized and we analyze band structures, density of states and total magnetizations. A half-metallic state is predicted at $a_0 \sim 4.45$Å. The majority-spin band has a rather sharp peak, characteristic of a narrow band, while the minority-spin has a gap. The total magnetization of the cell is $4.00\mu_B$ which does not change with the Mn concentration. The valence band is ferromagnetically coupled with the Mn atoms, and the spin splitting is not linearly dependent on the Mn concentration.

1 Introduction

Half-metals are defined as magnetic materials showing a band gap at the Fermi energy for one spin direction [1]. As a consequence, the electric conduction has contribution only from charge carriers of one spin direction. The possibility of the combined use of both properties, charge and spin, of the electrons suggests many semiconductor devices such as spin qubits [2], spin valves [3], spin-field-effect transistors [4], among others, having applications in quantum computing or spintronics. The aim nowadays in experimental and theoretical research in this area is to find materials that can be high-efficient sources of charge carriers with well defined spin [5]. A candidate material would be ferromagnetic zinc-blende MnAs [6,7] which suffers from some experimental and theoretical drawbacks [5,8]. Other candidates, the diluted magnetic semiconductor alloys $Ga_{1-x}Mn_xN$ have been under debate in connection with the detailed mechanism which originate their ferromagnetism, and their half-metallic character [9-15]. The injection of spin-polarized charge carriers into semiconductors was achieved successfully for electrons, employing magnetic semiconductors based on $Be_xMn_yZn_{1-x-y}Se$ [16]. On the other hand the hole injection in conventional semiconductors like GaAs is much less favorable because of the spin-orbit splitting of the top of the valence band. These spin-orbit effects are, in principle, reduced in lighter semiconductors like GaN or AlN. Accordingly, there are starting searches for half-metallic nitrides nowadays [1,17]. Another aspect to be taken into account is that spin electronics requires control over the spin direction of the charge carriers injected into devices, what may be facilitated by the ability of the nitrides to change easily from a low spin state to a high spin state under the action of an applied magnetic field. In the present paper we present *ab initio* total-energy-all-electron spin-polarized-density-functional calculations for the electronic structure of the diluted magnetic semiconductor alloys $Ga_{1-x}Mn_xN$, with realistic x=0.063 and x=0.031, in the ordered zinc-blende ferromagnetic phase. We find that the majority-spin system is half-metallic and the minority-spin system is isolating, the alloys being, therefore, candidates for application in *spintronics*.

2 Theoretical Framework

We carry out first-principles band structure and total-energy calculations within the framework of the density functional theory [18] in the approach of the local density approximation (LDA). We use the full-potential linearized augmented plane wave method (FP-LAPW) as implemented in the Wien2k code [19], and applied to large unit cells containing 32 and 64 atoms in order to simulate x=0.063 and x=0.031, respectively, by the substitution of one Ga atom by one Mn atom in the cation fcc sublattice of the zinc-blende structure of GaN. The calculations involve all electrons and the Ga-3d and Mn-3d electrons are included explicitly in the valence band. We adopt the Ceperley-Alder data [20] for the electron gas exchange term. The muffin-tin radii adopted were 2.0 a. u. (Ga), 1.64 a. u. (N) and 2.0 a.u

(Mn). The Rkmax parameter, which defines the basis set size in the FP-LAPW method, was taken as 7.0 and the angular momentum l=10 for the expansions inside the spheres. The total energy and eigenvalues were converged to 10^{-5}eV, and 10^{-4}eV, respectively. The calculations were performed with spin-polarized potentials in order to analyze the ferromagnetic phases of the alloys. The lattice parameter used were determined by using the Vègard's law, a_o = 4.45 Å (x=0.063), a_o= 4.46 Å (0.031) as applied to the binary components GaN (a_o=4.47 Å) and MnN (a_o=4.19 Å), whose lattice parameters were obtained by total-energy minimization using the same theoretical approach. We analyze the band structures, density of states, the Fermi level and the magnetic moments.

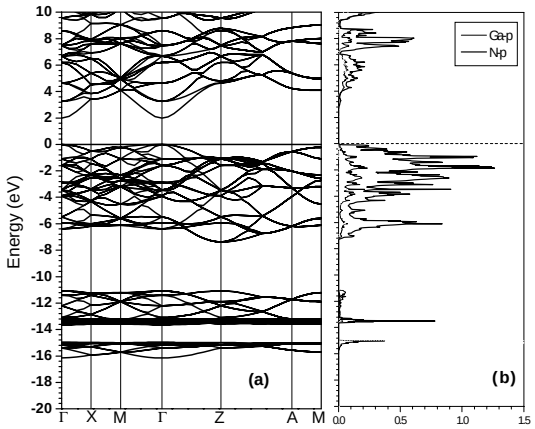

Figure 1. (a) Band structure for zinc-blende GaN at the LDA energy minimum (a_o=4.47Å); (b) Partial density of states showing the contributions of Ga-p and N-p states.

3 Results and Discussion

In Fig. 1 we show, for comparison, the band structure and density of states for bulk GaN using a 32-atom unit cell, the LDA approach and the equilibrium lattice parameter $a = 4.47$ Å. One first notes the folding of the bands due to the large unit cell we used. The Ga-3d states are low-lying around –13.5 eV, below the top of the valence band. The direct band gap at Γ is E_g=1.98 eV. As shown by the partial density of states curves, the top of the valence band is dominated by Ga-4p and N-2p states. In Fig. 2 we show the spin-polarized band structure diagram for $Ga_{0.94}Mn_{0.06}N$ calculated in the LDA approach at the lattice parameter a_o=4.45Å. In Fig. 3 we display the density of states for both alloys, $x = 0.063$ and $x = 0.031$. Except for the presence of the Mn-3d bands, the band structures look like those of the non-magnetic GaN shown in Fig. 1. The introduction of Mn atoms do not polarize the valence band appreciably. The majority-spin system exhibit a gap of energy inside which two bands appear, corresponding to the Mn-3d states, both about 0.6 eV wide, one close to the top of the valence band ∼0.33 eV and the other located around 1.4eV above the top of the valence band. The important feature is that the Fermi level falls inside this last band. It is apparent from Fig. 3 that the Mn-3d and N-2p states interact and dominate the spin-polarization effects. By its side, the minority-spin system exhibit an empty gap of about 2.3 eV, being isolating, with the Fermi level falling at mid-gap. The Mn atoms introduce a noticeable polarization of the bottom of the conduction band, due to the presence of the Mn-3d related states.

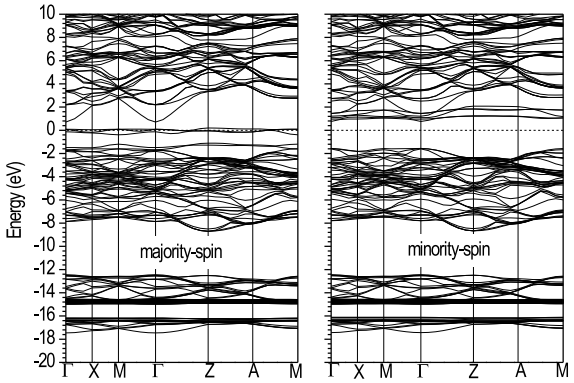

Figure 2. Spin-polarized band structure of $Ga_{0.94}Mn_{0.06}N$ at a_o=4.45Å. The horizontal line correspond to the Fermi level.

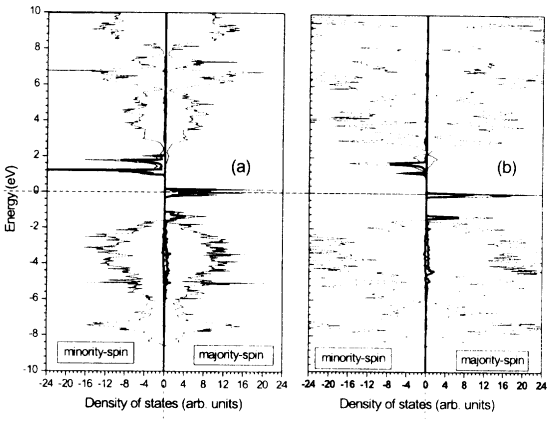

Figure 3. Spin-polarized density of states for (a) $Ga_{0.94}Mn_{0.06}N$ and (b) $Ga_{0.97}Mn_{0.03}N$. The thick lines correspond to the Mn-3d states. The horizontal line refers to the Fermi level.

As expected, one can see in Fig. 3 that the Mn-3d bands get thinner when the concentration x is diminished. The overall effect of introducing the Mn atom into the GaN semiconductor is the presence of a spin-polarization with the appearance of a partially occupied band in the gap of the majority-spin system. This band has some dispersion along some directions of the Brillouin zone and this is an important detail for the alloys to behave properly as half-metallic, as the Fermi level runs across the band.

This majority-spin band is actually a band of spin-polarized holes which must have sufficient mobility. Different effective masses around the Γ-point are expected from

the majority-spin diagram. Their calculations and analysis are underway. With respect to the magnetization, by the very way we made the calculations, having only one Mn atom per unit cell, the phase calculated is ferromagnetic. The magnetic moment found was 4.00μ_B for both x=0.063 and x=0.031, showing that the magnetization of the cell does not change with the Mn concentration. On the other hand we found the local magnetic moments as 3.16μ_B (Mn), 0.11μ_B (Ga) and 0.186μ_B (N). These results show that the interaction of the Mn atoms with the valence band is ferromagnetic. The coupling tends to be independent of x.

4 Conclusion

We performed spin-polarized calculations and analyzed the band structures, density of states and magnetizations of zinc-blende, ferromagnetic $Ga_{0.94}Mn_{0.06}N$ and $Ga_{0.97}Mn_{0.03}N$. A half-metallic state is predicted at a_o=4.45Å. The majority-spin band has a rather sharp peak, characteristic of a narrow band, while the minority-spin has a gap. The total magnetization of the cell is 4.00 μ_B which does not change with the concentration. Both the valence and conduction bands are ferromagnetically coupled to the Mn atoms and the spin splittings are not linearly dependent on the Mn concentration.

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References

[1] C. M. Fang, G. A. de Wijs, and R. A. de Groot, J. of Appl. Phys. **91**, 8340 (2002).

[2] G. Burkard, D. Loss, and D. P. Di Vincenzo Phys. Rev. B **59**, 2070 (1999)

[3] G. Prinz, Science **282**, 1660 (1998).

[4] S. Datta and B. Das, Appl. Phys. Lett. **56** (7), 665(1990).

[5] M. Jain, L. Kronik, and J. R. Chelikowsky. V. V. Godlevsky, Phys. Rev. B **64**, 245205 (2001).

[6] M. Shirai, T. Ogwa, I. Kitagawa, and N. Suzuki, J. Magn. Magn. Mater. **177-181**, 1383 (1998).

[7] See our other paper in this issue and references there in.

[8] S. Sanvito and N. A. Hill, Phys. Rev. B **62**, 15553 (2000).

[9] Y. Ohno, D. K. Young, B. Beschoten, F. Matsukura, H. Ohno, and D. D. Awschalom, Nature **402**, 790 (1999).

[10] G. Schmidt, D. Ferrand, L. W. Molenkamp, A. T. Filip, and B. J. van Wees, Phys. Rev. B **62**, R4790 (2000)

[11] D. P. Di Vincenzo, Science **270**, 255 (1995).

[12] T. Dietl, H. Ohno, F. Matsukura, J. Cibèrt, and D. Ferrand, Science **287**, 1019 (2000).

[13] H. Akai, Phys. Rev. Lett. **81**, 3002 (1998).

[14] S. Sanvito, P. Ordejón, and N. A. Hill, Phys. Rev. B **63**, 165206 (2001)

[15] M. Jain, L. Kronik, and J. R. Chelikowsky, Phys. Rev. B **64**, 245205 (2001).

[16] R. Fiederling, M. Keim, G. Reuscher, W. Ossau, G. Schmidt, A. Waag, and L. W. Molenkamp, Nature **402**, 787 (1999).

[17] L. Kronik, M. Jain, and J. R. Chelikowsky , Phys. Rev. B **66**, 041203 (R) (2002).

[18] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, ibid. **140**, A 1133 (1965).

[19] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, Techn. Universität Wien, Austria, 2001. ISBN 3-9501031-1-2.

[20] D. M. Cerperly and B. I. Alder, Phys. Rev. Lett. **45**, 566 (1980).